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Synthesis of 2,3-dihydro-1*H*-indazoles by Rh(III)-catalyzed C–H cleavage of arylhydrazines†

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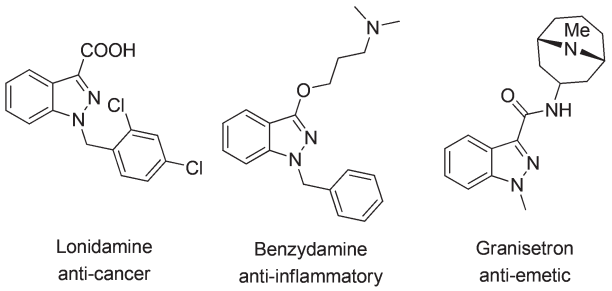
A rhodium-catalyzed efficient method for the synthesis of 2,3-dihydro-1*H*-indazoles is described. The reaction of arylhydrazines with olefins results in the corresponding 2,3-dihydro 1*H*-indazoles with exclusive regioselectivity *via* C–H bond activation. The utility of the methodology is illustrated by a rapid synthesis of 1*H*-indazoles under mild reaction conditions in half an hour.

Introduction

Heterocycles are frequently found in bioactive natural products and have been intensively studied as drug candidates. Accordingly, development of efficient and economic ways to construct heterocycles has been a subject of considerable interest in organic synthesis.[1] In particular, the domino C–H activation/cyclization method has emerged as a powerful tool for the synthesis of heterocycles.[2–4]

The indazole is an important heterocycle and the key motif of anti-cancer, anti-inflammatory, anti-HIV, and anti-emetic drugs (Scheme 1).[5] Consequently, the diverse approach to indazoles has attracted much attention over the past few decades.[6] Besides the traditional methods of condensation and transition metal-catalyzed intramolecular amination of *o*-halo arylhydrazones,[7] synthesis of indazoles *via* transition metal-catalyzed C–H functionalization has aroused much attention recently. Starting from arylhydrazones, three examples of Pd-, Fe-, and Cu-catalytic systems were reported to synthesize 1*H*-indazoles through intramolecular C–H amination by Hiroya, Bao and Jiang, respectively.[8] Glorius reported a synthesis of 1*H*-indazoles from easily available arylimidates and organo azides *via* the Rh-catalyzed C–H activation/C–N bond formation and Cu-catalyzed N–N bond formation.[9] Recently, the preparation of *N*-aryl-2*H*-indazoles initiated by Rh(III)-catalyzed direct addition of an azobenzene C–H bond to an aldehyde with subsequent cyclization and aromatization is demonstrated by Lavis and Ellman.[10]

Arylhydrazine is a widely used chemical reagent and its derivatives can be readily prepared. However, the utilization of arylhydrazines in the direct functionalization of the C–H bond is rarely studied.[11] Herein, we wish to report a highly efficient method for the synthesis of 2,3-dihydro-1*H*-indazoles *via* the rhodium-catalyzed C–H activation process. The corresponding 1*H*-indazoles could be readily prepared by the treatment of 2,3-dihydro-1*H*-indazoles with 2 N HCl in ethanol in half an hour.



Scheme 1 Some examples of biologically active 1*H*-indazoles.

Results and discussion

In the preliminary investigation, we examined the reaction of *N*′-methyl-*N*′-phenyl-acetylhydrazide with ethyl acrylate in the presence of $[Cp^*RhCl_2]_2$ (5 mol%), $Cu(OAc)_2$ (2.0 equiv.), and DCE at 110 °C under nitrogen (Table 1, entry 1). To our delight, the desired product **3aa** was obtained in 61% yield. Further studies showed that the addition of 1.0 equiv. AcOH improved the yield to 73% (Table 1, entry 2). Other additives, such as PivOH, CsOAc, and LiOAc, were found less effective (Table 1, entries 3–5). No reaction was observed in the absence of an oxidant or a catalyst (Table 1, entries 6–7). The desired product was not observed when $[Rh(COD)Cl_2]_2$ and $[RuCl_2(p\text{-cymene})]_2$ were used as catalysts (Table 1, entries 8–9). Among the solvents investigated, dichloroethane was the best. Other solvents, such as *t*-AmOH, toluene, DME, and acetone, were ineffective (Table 1, entries 10–13). In the case of decreasing

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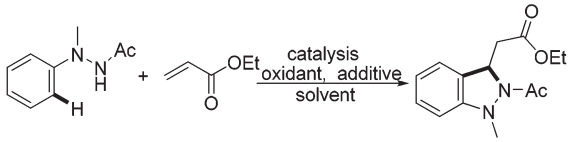
†Electronic supplementary information (ESI) available: Experimental details. Spectral data and other ESI. See DOI: 10.1039/c4ob00921e

Table 1 Optimization of reaction conditions[a]



1a 2a 3aa

Entry	Catalyst	Additive	Solvent	Yield[b] (%)
1	$[Cp^*RhCl_2]_2$	—	DCE	61
2	$[Cp^*RhCl_2]_2$	AcOH	DCE	73
3	$[Cp^*RhCl_2]_2$	PivOH	DCE	68
4	$[Cp^*RhCl_2]_2$	CsOAc	DCE	57
5	$[Cp^*RhCl_2]_2$	LiOAc	DCE	55
6	$[Cp^*RhCl_2]_2$	AcOH	DCE	N.D.[c]
7	—	AcOH	DCE	N.D.
8	$[Rh(COD)Cl_2]_2$	AcOH	DCE	N.D.
9	$[RuCl_2(p\text{-cymene})]_2$	AcOH	DCE	N.D.
10	$[Cp^*RhCl_2]_2$	AcOH	*t*-AmOH	Trace
11	$[Cp^*RhCl_2]_2$	AcOH	Toluene	36
12	$[Cp^*RhCl_2]_2$	AcOH	DME	50
13	$[Cp^*RhCl_2]_2$	AcOH	Acetone	58
14	$[Cp^*RhCl_2]_2$	AcOH	DCE	41[d]
15	$[Cp^*RhCl_2]_2$	AcOH	DCE	50[e]
16	$[Cp^*RhCl_2]_2$	AcOH	DCE	49[f]

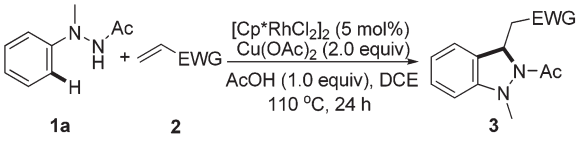
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), catalyst (5 mol%), $Cu(OAc)_2$ (2.0 equiv.), additive (1.0 equiv.), solvent (2 mL), 110 °C, 24 h, under N_2. [b] Isolated yield. [c] Without $Cu(OAc)_2$. [d] 2.5 mol% $[RhCp^*Cl_2]_2$ was used. [e] The reaction time was 12 h. [f] The reaction was conducted at 90 °C.

the catalyst amount by half, the yield dropped to 41% (Table 1, entry 14). The reaction time and temperature influenced the reaction. The yield dropped to 50% when the reaction time was decreased to 12 h (Table 1, entry 15). Lower temperature was unsuitable for the reaction (Table 1, entry 16). Thus, the optimal reaction conditions were $[RhCp^*Cl_2]_2$ (5.0 mol%), $Cu(OAc)_2$ (2.0 equiv.), and HOAc (1.0 equiv.) under nitrogen in DCE (2.0 mL) at 110 °C for 24 h.

With the optimized reaction conditions in hand, the scope and limitation of olefins were examined as shown in Table 2. A series of acrylates, ethyl acrylate, methyl acrylate, *n*-butyl acrylate, *t*-butyl acrylate, phenyl acrylate, and benzyl acrylate (**2a–f**) participated in the reaction smoothly to give the products in good yields (Table 2, entries 1–6). It is noteworthy that acrylonitrile and 1-arylprop-2-en-1-ones were also effective in this reaction, providing the desired products in moderate yields (Table 2, entries 7–11).

Next, we evaluated the scope of the reaction with regard to a range of the *N*′-alkyl-*N*′-arylacetohydrazides as shown in Table 3. In general, the reaction occurred smoothly to give the N^1,N^2-disubstituted-2,3-dihydro-1*H*-indazoles in moderate to good yields. A variety of functional groups, including methyl, methoxy, fluoro, chloro and bromo on the aryl ring, were compatible under the optimal reaction conditions (Table 3, entries 1–9). Notably, the reaction presented regioselectivity at the *ortho*-position of the less steric side of the arenes furnishing the corresponding products in good yields (Table 3, entries 2, 9). *N*′-Methyl-*N*′-arylacetohydrazide with *ortho*-substituents

Table 2 Scope of olefines[a]



1a 2 3

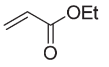
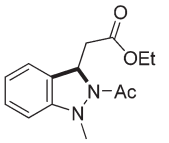
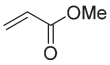
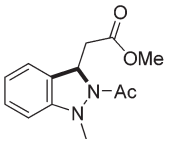
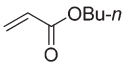
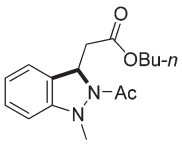
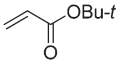
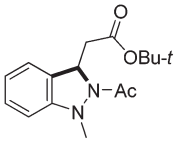
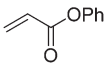
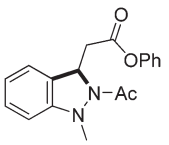
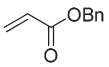
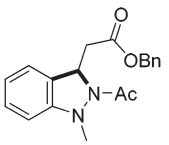
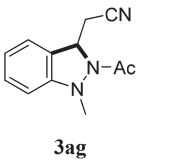
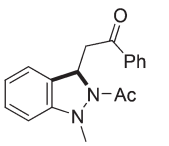
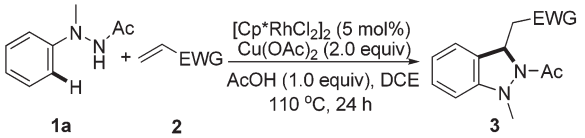
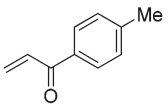
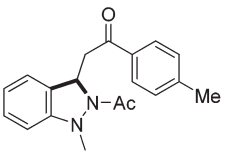
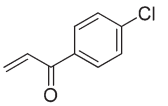
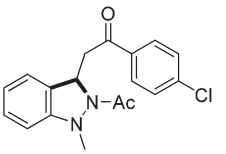
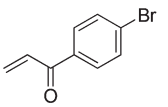
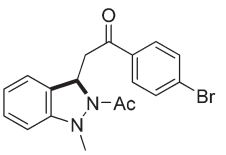
Entry	Substrate (2)	Product (3)	Yield[b] (%)
1	 **2a**	 **3aa**	73
2	 **2b**	 **3ab**	69
3	 **2c**	 **3ac**	71
4	 **2d**	 **3ad**	59
5	 **2e**	 **3ae**	57
6	 **2f**	 **3af**	66
7	 **2g**	 **3ag**	45
8	 **2h**	 **3ah**	55

Table 2 *(Contd.)*



Entry	Substrate (2)	Product (3)	Yield[b] (%)
9	 2i	 3ai	49
10	 2j	 3aj	52
11	 2k	 3ak	54

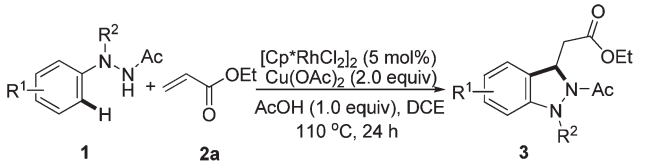
[a] Reaction conditions: **1a** (0.2 mmol), olefin (0.4 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $Cu(OAc)_2$ (2.0 equiv.), AcOH (1.0 equiv.), DCE (2.0 mL), 110 °C, 24 h, under N_2. [b] Isolated yield.

gave a 32% yield, illustrating that the steric hindrance played a role in the reaction (Table 3, entry 3). Various halogen substituents showed good compatibility, which added flexibility to further elaborate the indazole derivatives (Table 3, entries 7–9). The protective group other than methyl in the N-atom was also investigated. Ethyl and *n*-butyl substituted 2-phenylacetohydrazides were compatible with the reaction conditions and provided the products in moderate yields (Table 3, entries 10–11).

The acid-mediated deprotection protocol can be successfully applied for the synthesis of 1*H*-indazoles. For example, the above prepared **3aa** and **3ah** products could be easily transformed to **4a** and **4b** 1*H*-indazoles in 2 N HCl in ethanol in half hour in good yields (Scheme 2).

Based on previous studies of rhodium catalysis, a plausible mechanism is proposed as illustrated in Scheme 3. First, the rhodacycle intermediate **A** was formed through the reaction of *N*′-methyl-*N*′-phenyl-acetohydrazide with the acetohydrazide-assisted C–H activation process. The subsequent coordination of the intermediate **A** with the olefin afforded the intermediate **B**, which was transformed into **C** by 1,2-migratory insertion. The β-hydride elimination of the intermediate **C** gives the intermediate **D** followed by reductive elimination to yield the Rh(I) species. An intramolecular aza-Michael addition of the

Table 3 Scope of *N*′-alkyl-*N*′-arylacetohydrazides[a]



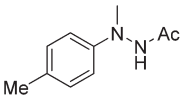
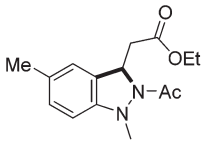
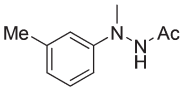
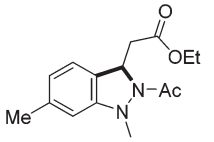
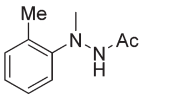
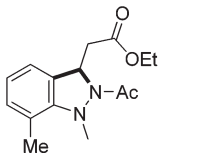
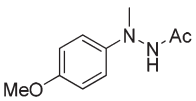
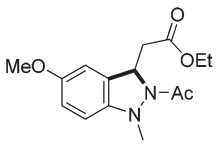
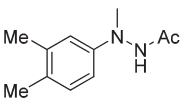
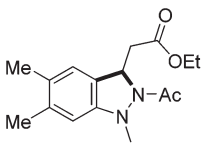
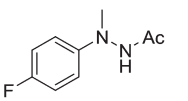
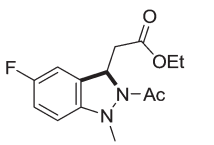
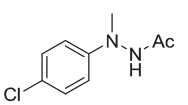
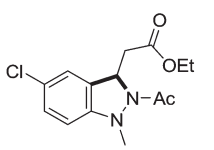
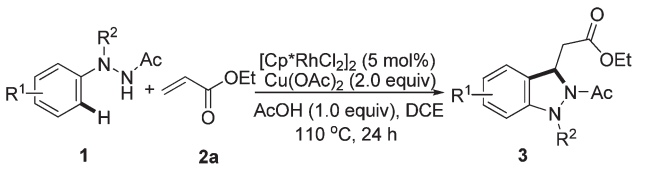
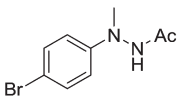
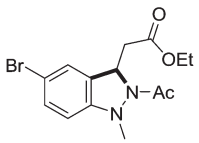
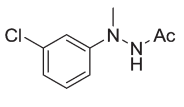
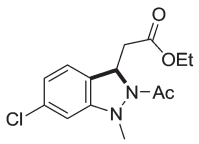
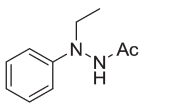
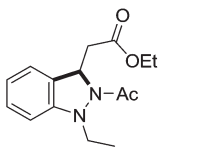
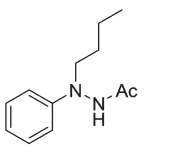
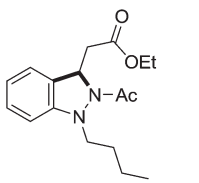
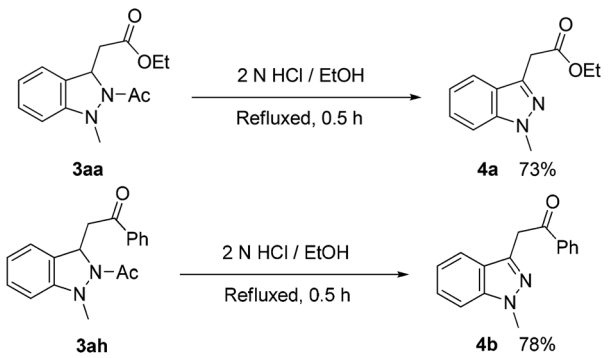
Entry	Substrate (1)	Product (3)	Yield[b] (%)
1	 1b	 3ba	70
2	 1c	 3ca	75
3	 1d	 3da	32
4	 1e	 3ea	61
5	 1f	 3fa	71
6	 1g	 3ga	63
7	 1h	 3ha	72

Table 3 *(Contd.)*

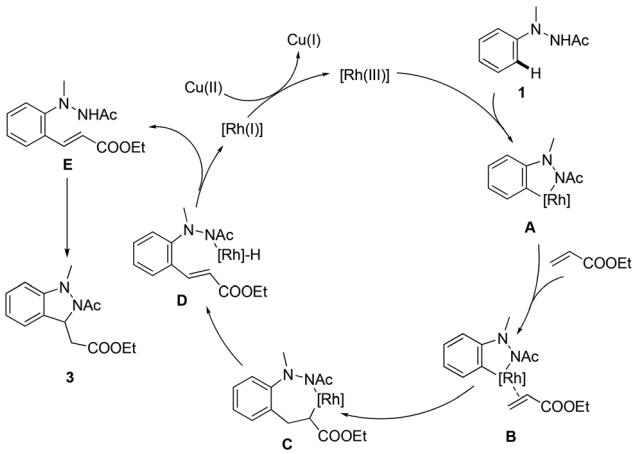


Entry	Substrate (1)	Product (3)	Yield[b] (%)
8	 1i	 3ia	64
9	 1j	 3ja	67
10	 1k	 3ka	62
11	 1l	 3la	46

[a] Reaction conditions: *N*′-alkyl-*N*′-arylacetohydrazide (0.2 mmol), **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $Cu(OAc)_2$ (2.0 equiv.), AcOH (1.0 equiv.), DCE (2.0 mL), 110 °C, 24 h, under N_2. [b] Isolated yield.



Scheme 2 Transformation of products.



Scheme 3 Proposed reaction mechanism.

intermediate **E** affords the product **3**. The oxidation of Rh(I) by $Cu(OAc)_2$ generates Rh(III) species to fulfill the catalytic cycle.

Conclusions

In summary, we have developed a facile and efficient strategy for the construction of 2,3-dihydro-1*H*-indazoles *via* rhodium(III)-catalyzed C–H activation of arylhydrazines.[12] The reaction exhibits a good tolerance for a broad range of functional groups. Starting from simple hydrazine substrates, this method provides an easy alternative to the synthesis of 1*H*-indazoles.

Experimental

General

Unless stated otherwise, all reactions were performed under air atmosphere. All solvents were used without further purification. Spectra were recorded for ^1H NMR at 400 MHz, and ^{13}C NMR at 100 MHz using TMS as an internal standard. The following abbreviations were used to describe peak patterns where appropriate: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), multiplet (m), broad resonances (br). Mass spectroscopy data of the products were collected on an HRMS-APCI instrument or a low-resolution MS instrument using EI or ESI ionization.

General procedure for the starting materials

N′-*Alkyl-N*′-*arylacetohydrazide were prepared according to published procedures.*[11,13] To a solution of arylhydrazine hydrochloride salt (20 mmol) in 1 N NaOH (40 mL) and THF (10 mL) was added acetic anhydride (2.0 g, 20 mmol) dropwise. After stirring for 30 min the mixture was extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4 and filtered through the pad of silica gel. The filtrate was concentrated to afford a solid residue. Recrystallization from a mixture of petroleum ether–ethyl acetate (5 : 1) gave 2-acetyl-1-arylhydrazine.

Freshly cut Na (0.23 g, 10 mmol) was added to absolute ethanol (6 mL) in a sealed tube to obtain a clear solution. 2-Acetyl-1-arylhydrazine (10 mmol) was added to the resulting solution, and then halogenated alkane (iodomethane for **1a–1j**, bromoethane for **1k** and *n*-butyl chloride for **1l**) was added. The resulting solution was sealed and kept at 100 °C in the dark for 20 h. The solution was concentrated and the residue was dissolved in ethyl acetate (20 mL), and then washed with water, dried over Na_2SO_4 and filtered through the pad of silica gel. The filtrate was concentrated and the resulting residue was purified by flash column chromatography (silica gel, ethyl acetate–petroleum ether = 1 : 2, v/v) to obtain the desired products.

Characterization data of the starting materials

*N′-Methyl-N′-phenylacetohydrazide (**1a**).*[13] White solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.34–7.24 (m, 2H), 6.89–6.83 (m, 3H), 3.20 and 3.18 (2 × s, 3H), 2.09 and 2.07 (2 × s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 168.9, 149.3, 149.0, 129.4, 129.1, 120.7, 120.0, 113.2, 113.0, 42.1, 40.9, 21.1, 19.1; HRMS (EI) Calcd for $C_9H_{12}N_2O$ $(M)^+$ 164.0950; Found, 164.0948.

*N′-Methyl-N′-p-tolylacetohydrazide (**1b**).*[13] White solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.93 (br s, 1H), 7.09 and 7.01 (2 × d, J = 8.4, 8.0, 2H), 6.75–6.70 (m, 2H), 3.08 (s, 3H), 3.28 and 3.22 (2 × s, 3H), 2.04 and 1.98 (2 × s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 169.0, 147.2, 147.1, 130.0, 129.8, 129.5, 129.1, 113.5, 113.3, 42.3, 40.9, 20.9, 20.2, 19.0; HRMS (EI) Calcd for $C_{10}H_{14}N_2O$ $(M)^+$ 178.1106; Found, 178.1106.

*N′-Methyl-N′-m-tolylacetohydrazide (**1c**).* White solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.20–7.04 (m, 2H), 6.75–6.70 (m, 3H), 3.13 and 3.12 (2 × s, 3H), 2.33 and 2.29 (2 × s, 3H), 2.06 and 2.02 (2 × s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 169.0, 149.4, 149.2, 139.3, 138.8, 129.2, 128.9, 121.5, 120.7, 114.0, 113.7, 110.4, 110.2, 42.1, 40.8, 21.7, 21.7, 21.0, 19.1; HRMS (EI) Calcd for $C_{10}H_{14}N_2O$ $(M)^+$ 178.1106; Found, 178.1107.

*N′-Methyl-N′-o-tolylacetohydrazide (**1d**).* White solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.26–7.15 (m, 4H), 3.10 and 2.91 (2 × s, 3H), 2.36 and 2.28 (2 × s, 3H), 2.13 and 1.94 (2 × s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 167.8, 149.8, 148.0, 132.0, 131.3, 131.1, 130.7, 126.8, 126.0, 124.8, 123.8, 118.8, 117.4, 46.4, 41.9, 20.9, 19.7, 18.4, 17.9; HRMS (EI) Calcd for $C_{10}H_{14}N_2O$ $(M)^+$ 178.1106; Found, 178.1110.

*N′-(4-Methoxyphenyl)-N′-methylacetohydrazide (**1f**).*[13] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 6.83–6.75 (m, 4H), 3.74 and 3.70 (2 × s, 3H), 3.04 and 3.03 (2 × s, 3H), 2.05 and 1.94 (2 × s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 169.1, 154.2, 153.6, 143.5, 115.1, 114.9, 114.5, 114.3, 55.5, 55.4, 42.8, 41.2, 20.9, 19.0; HRMS (EI) Calcd for $C_{10}H_{14}N_2O_2$ $(M)^+$ 194.1055; Found, 194.1057.

*N′-(3,4-Dimethylphenyl)-N′-methylacetohydrazide (**1g**).* White solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.06 and 7.01 (2 × d, J = 8.4, 8.0, 1H), 6.72 (br s, 1H), 6.68–6.60 (m, 2H), 3.16 and 3.12 (2 × s, 3H), 2.25 and 2.22 (2 × s, 3H), 2.20 and 2.17 (2 × s, 3H), 2.09 and 2.06 (2 × s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 168.9, 147.6, 147.5, 137.5, 137.0, 130.3, 130.0, 128.8, 127.9, 114.9, 114.9, 110.8, 110.8, 42.3, 41.0, 21.0, 20.1, 19.0, 18.6; HRMS (EI) Calcd for $C_{11}H_{16}N_2O$ $(M)^+$ 192.1263; Found, 192.1267.

*N′-(4-Fluorophenyl)-N′-methylacetohydrazide (**1h**).*[13] White solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.36 (br s, 1H), 7.00–6.88 (m, 2H), 6.80–6.68 (m, 2H), 3.09 and 3.05 (2 × s, 3H), 2.04 and 1.96 (2 × s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 169.3, 158.4 ($J_{C–F}$ = 53.6 Hz), 156.1 ($J_{C–F}$ = 53.1 Hz), 145.8 ($J_{C–F}$ = 1.6 Hz), 145.7 ($J_{C–F}$ = 2.2 Hz), 115.7 ($J_{C–F}$ = 22.4 Hz), 115.4 ($J_{C–F}$ = 22.0 Hz), 114.7 ($J_{C–F}$ = 53.6 Hz), 114.3 ($J_{C–F}$ = 53.6 Hz), 42.6, 41.0, 20.9, 19.0; HRMS (EI) Calcd for $C_9H_{11}FN_2O$ $(M)^+$ 182.0855; Found, 182.0857.

*N′-(4-Chlorophenyl)-N′-methylacetohydrazide (**1i**).*[13] White solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.26–7.18 (m, 2H), 6.90 (br s, 1H), 6.80–6.75 (m, 2H), 3.18 and 3.16 (2 × s, 3H), 2.06 and 2.06 (2 × s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 169.2, 147.9, 147.8, 129.2, 128.9, 125.7, 124.6, 114.5, 114.1, 42.1, 40.7, 20.9, 19.1; HRMS (EI) Calcd for $C_9H_{11}ClN_2O$ $(M)^+$ 198.0560; Found, 198.0564.

*N′-(4-Bromophenyl)-N′-methylacetohydrazide (**1j**).*[2] White solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.91 (br s, 1H), 7.38–7.26 (m, 2H), 6.71–6.62 (m, 2H), 3.12 and 3.10 (2 × s, 3H), 2.03 and 2.00 (2 × s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 169.2, 148.3, 148.2, 132.1, 131.7, 114.8, 114.5, 112.9, 111.7, 42.0, 40.6, 20.9, 19.0; HRMS (EI) Calcd for $C_9H_{11}BrN_2O$ $(M)^+$ 242.0055; Found, 242.0057.

*N′-(3-Chlorophenyl)-N′-methylacetohydrazide (**1k**).* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.94 (br s, 1H), 7.19–7.08 (m, 1H), 6.90–6.61 (m, 3H), 3.13 and 3.11 (2 × s, 3H), 2.03 and 2.00 (2 × s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 169.4, 150.5, 150.3, 135.3, 135.0, 130.5, 130.2, 120.5, 119.4, 113.3, 112.8, 111.3, 110.9, 42.0, 40.6, 21.0, 19.1; HRMS (EI) Calcd for $C_9H_{11}ClN_2O$ $(M)^+$ 198.0560; Found, 198.0560.

*N′-Ethyl-N′-phenylacetohydrazide (**1k**).* White solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.31–7.27 (m, 1H), 7.22–7.21 (m, 1H), 6.94–6.82 (m, 3H), 3.54–3.49 (m, 2H), 2.06 and 2.04 (2 × s, 3H), 1.20 (2 × t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 169.4, 148.6, 148.2, 129.4, 129.1, 120.6, 119.7, 113.9, 113.3, 48.6, 46.4, 20.9, 19.2, 11.2, 10.5; HRMS (EI) Calcd for $C_{10}H_{14}N_2O$ $(M)^+$ 178.1106; Found, 178.1104.

*N′-Butyl-N′-phenylacetohydrazide (**1l**).* White solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.31–7.22 (m, 2H), 6.94–6.82 (m, 3H), 3.51–3.42 (m, 2H), 2.08–2.03 (2 × s, 3H), 1.63–1.59 (m, 2H), 1.42–1.36 (m, 2H), 0.97 (t, J = 7.2, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 169.1, 148.9, 148.3, 129.4, 129.2, 120.5, 119.8, 113.7, 113.1, 54.6, 52.3, 28.5, 27.7, 21.0, 20.9, 20.2, 19.2, 13.9, 13.9; HRMS (EI) Calcd for $CH_{18}N_2O$ $(M)^+$ 206.1419; Found, 206.1418.

General procedure for the reaction of *N′*-methyl-*N′*-arylacetohydrazide 1 with olefine. To a 25 mL sealed tube containing a magnetic stir bar, were added **1** (0.2 mmol), olefine **2** (0.4 mmol), $[Cp^*RhCl_2]_2$ (6 mg, 5 mol%), $Cu(OAc)_2$ (72 mg, 0.4 mmol), AcOH (12 mg, 0.2 mmol), and DCE (2 mL). The tube was sealed under nitrogen and heated to 110 °C with stirring for 24 h. Then the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The reaction mixture was filtered through a plug of Celite and the residue

was washed with ethyl acetate (2 × 5 mL). The combined organic layer was concentrated under vacuum and the residue was purified by flash column chromatography (silica gel, ethyl acetate–petroleum ether = 1 : 2, v/v) to afford the corresponding products.

Characterization data of the products

*Ethyl 2-(2-acetyl-1-methyl-2,3-dihydro-1H-indazol-3-yl)acetate (**3aa**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.30–7.26 (m, 2H), 7.08–7.04 (m, 1H), 6.92 (d, J = 7.6 Hz, 1H), 5.72 (t, J = 6.0 Hz, 1H), 4.21–4.17 (m, 2H), 3.07 (s, 3H), 2.95 (dd, J = 15.2, 5.2 Hz, 1H), 2.68 (dd, J = 15.2, 8.4 Hz, 1H), 2.26 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 170.0, 150.0, 130.8, 128.6, 123.9, 123.3, 113.7, 60.7, 57.8, 48.7, 43.2, 21.0, 14.1; HRMS (EI) Calcd for $C_{14}H_{18}N_2O_3$ $(M)^+$ 262.1317; Found, 262.1320.

*Methyl 2-(2-acetyl-1-methyl-2,3-dihydro-1H-indazol-3-yl)acetate (**3ab**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.30–7.26 (m, 2H), 7.06 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 5.70 (s, 1H), 3.72 (s, 3H), 3.07 (s, 3H), 2.95 (dd, J = 15.2, 5.2 Hz, 1H), 2.70 (dd, J = 15.2, 8.0 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 170.4, 150.0, 130.7, 128.7, 123.9, 123.3, 113.7, 57.9, 51.8, 48.7, 43.1, 21.0; HRMS (EI) Calcd for $C_{13}H_{16}N_2O_3$ $(M)^+$ 248.1161; Found, 248.1162.

*n-Butyl 2-(2-acetyl-1-methyl-2,3-dihydro-1H-indazol-3-yl)acetate (**3ac**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.30–7.26 (m, 2H), 7.06 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 5.71 (s, 1H), 4.13–4.10 (m, 2H), 3.06 (s, 3H), 2.96 (dd, J = 15.2, 5.2 Hz, 1H), 2.68 (dd, J = 15.2, 8.0 Hz, 1H), 2.26 (s, 3H), 1.64–1.57 (m, 2H), 1.39–1.33 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 170.0, 150.0, 130.9, 128.6, 123.9, 123.3, 113.7, 64.6, 57.9, 48.7, 43.2, 30.45, 21.0, 19.1, 13.6; HRMS (EI) Calcd for $C_{16}H_{22}N_2O_3$ $(M)^+$ 290.1630; Found, 290.1627.

*tert-Butyl 2-(2-acetyl-1-methyl-2,3-dihydro-1H-indazol-3-yl)-acetate (**3ad**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.33–7.25 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 5.70 (s, 1H), 3.06 (s, 3H), 2.93 (dd, J = 15.2, 4.8 Hz, 1H), 2.56 (dd, J = 15.2, 8.8 Hz, 1H), 2.25 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 179.3, 150.0, 131.2, 128.5, 123.8, 123.6, 113.7, 81.1, 57.9, 48.6, 44.2, 28.1, 21.0; HRMS (EI) Calcd for $C_{16}H_{22}N_2O_3$ $(M)^+$ 290.1630; Found, 290.1629.

*Phenyl 2-(2-acetyl-1-methyl-2,3-dihydro-1H-indazol-3-yl)acetate (**3ae**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.40–7.36 (m, 3H), 7.31 (t, J = 7.6 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.11–7.07 (m, 3H), 6.95 (d, J = 8.0 Hz, 1H), 5.84 (s, 1H), 3.14 (dd, J = 15.2, 6.0 Hz, 1H), 3.11 (s, 3H), 2.98 (dd, J = 15.2, 7.2 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 168.5, 150.5, 150.1, 130.4, 129.4, 128.8, 125.9, 124.0, 123.4, 121.6, 113.8, 58.0, 48.7, 43.4, 21.1; HRMS (EI) Calcd for $C_{18}H_{18}N_2O_3$ $(M)^+$ 310.1317; Found, 310.1316.

*Benzyl 2-(2-acetyl-1-methyl-2,3-dihydro-1H-indazol-3-yl)acetate (**3af**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35–7.32 (m, 5H), 7.28–7.24 (m, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 5.73 (s, 1H), 5.15 (dd, J = 17.2, 12 Hz, 2H), 3.03 (s, 3H), 2.98 (dd, J = 15.2, 5.6 Hz, 1H), 2.74 (dd, J = 14.8, 8.0 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 169.8, 150.0, 135.6, 130.6, 128.7, 128.5, 128.5, 128.3, 123.9, 123.3, 113.7, 66.7, 57.9, 48.7, 43.2, 21.0; HRMS (EI) Calcd for $C_{19}H_{20}N_2O_3$ $(M)^+$ 324.1474; Found, 324.1472.

*2-(2-Acetyl-1-methyl-2,3-dihydro-1H-indazol-3-yl)acetonitrile (**3ag**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35–7.30 (m, 2H), 7.15–7.11 (m, 1H), 6.95 (d, J = 8.0 Hz, 1H), 5.56 (t, J = 4.8 Hz, 1H), 3.16 (s, 3H), 2.98–2.95 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 150.0, 129.6, 127.1, 124.1, 122.7, 117.2, 113.7, 58.0, 48.7, 26.0, 21.1; HRMS (EI) Calcd for $C_{12}H_{13}N_3O$ $(M)^+$ 215.1059; Found, 215.1055.

*2-(2-Acetyl-1-methyl-2,3-dihydro-1H-indazol-3-yl)-1-phenylethanone (**3ah**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.01 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.49–7.45 (m, 2H), 7.32 (d, J = 7.6 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 5.93–5.90 (m, 1H), 3.77–3.73 (m, 1H), 3.30 (dd, J = 15.6, 9.6 Hz, 1H), 3.08 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 172.6, 149.9, 136.5, 133.3, 131.3, 128.6, 128.5, 128.2, 124.1, 124.0, 113.6, 57.8, 48.9, 47.3, 21.0; HRMS (EI) Calcd for $C_{18}H_{18}N_2O_2$ $(M)^+$ 294.1368; Found, 294.1373.

*2-(2-Acetyl-1-methyl-2,3-dihydro-1H-indazol-3-yl)-1-p-tolylethanone (**3ai**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.91 (d, J = 7.6 Hz, 2H), 7.32–7.23 (m, 4H), 7.02 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 5.91–5.89 (m, 1H), 3.74–3.70 (m, 1H), 3.27 (dd, J = 15.2, 10.0 Hz, 1H), 3.07 (s, 3H), 2.40 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 172.7, 149.9, 144.2, 134.1, 131.4, 129.3, 128.5, 128.3, 124.2, 124.0, 113.6, 58.0, 48.9, 47.3, 21.6, 21.0; HRMS (EI) Calcd for $C_{19}H_{20}N_2O_2$ $(M)^+$ 308.1525; Found, 308.1523.

*2-(2-Acetyl-1-methyl-2,3-dihydro-1H-indazol-3-yl)-1-(4-chlorophenyl)-ethanone (**3aj**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96 (d, J = 8.4 Hz, 2H), 7.46–7.43 (m, 2H), 7.31–7.25 (m, 2H), 7.04 (t, J = 7.2 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 5.87 (dd, J = 9.6, 3.6 Hz, 1H), 3.70 (dd, J = 16.0, 2.8 Hz, 1H), 3.28 (dd, J = 15.6, 9.6 Hz, 1H), 3.07 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 172.8, 149.9, 139.8, 134.9, 131.0, 129.7, 129.0, 129.0, 128.6, 124.0, 113.7, 57.9, 48.9, 47.3, 21.0; HRMS (EI) Calcd for $C_{18}H_{17}ClN_2O_2$ $(M)^+$ 328.0979; Found, 328.0970.

*Ethyl 2-(2-acetyl-1,5-dimethyl-2,3-dihydro-1H-indazol-3-yl)-acetate (**3ba**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.09–7.07 (m, 2H), 6.81 (d, J = 8.0 Hz, 1H), 5.67 (s, 1H), 4.21–4.16 (m, 2H), 3.02 (s, 3H), 2.94 (dd, J = 15.2, 5.6 Hz, 1H), 2.67 (dd, J = 15.2, 8.4 Hz, 1H), 2.32 (s, 3H), 2.25 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 170.1, 147.7, 133.6, 131.0, 129.3, 123.8, 113.5, 60.7, 57.8, 48.9, 43.2, 21.0 (2 C), 14.1; HRMS (EI) Calcd for $C_{15}H_{20}N_2O_3$ $(M)^+$ 276.1474; Found, 276.1475.

*Ethyl 2-(2-acetyl-1,6-dimethyl-2,3-dihydro-1H-indazol-3-yl)-acetate (**3ca**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.15 (d, J = 7.6 Hz, 1H), 6.87 (d, J = 7.2 Hz, 1H), 6.74 (s, 1H), 5.67 (s, 1H), 4.20–4.14 (m, 2H), 3.00 (s, 3H), 2.94 (dd, J = 15.2, 5.2 Hz, 1H), 2.64 (dd, J = 15.2, 8.4 Hz, 1H), 2.35 (s, 3H), 2.24 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 170.0, 150.2, 138.8, 128.0, 124.8, 123.0, 114.3, 60.7, 57.8, 48.7, 43.3, 21.5, 21.0, 14.1; HRMS (EI) Calcd for $C_{15}H_{20}N_2O_3$ $(M)^+$ 276.1474; Found, 276.1473.

*Ethyl 2-(2-acetyl-1,7-dimethyl-2,3-dihydro-1H-indazol-3-yl)-acetate (**3da**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.16 (d, J = 7.6 Hz, 1H), 7.09–7.07 (m, 1H), 7.04–7.00 (m, 1H), 5.70–5.67 (m, 1H), 4.23–4.17 (m, 2H), 3.00 (s, 3H), 2.97 (dd, J = 15.2, 5.6 Hz, 1H), 2.70 (dd, J = 15.2, 8.4 Hz, 1H), 2.32 (s, 3H), 2.27 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 170.0, 148.6, 130.4, 127.8, 124.7, 124.1, 120.9, 60.8, 57.4, 46.9, 43.3, 20.9, 17.4, 14.1; HRMS (EI) Calcd for $C_{15}H_{20}N_2O_3$ $(M)^+$ 276.1474; Found, 276.1471.

*Ethyl 2-(2-acetyl-5-methoxy-1-methyl-2,3-dihydro-1H-indazol-3-yl)acetate (**3ea**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 6.79–6.76 (m, 3H), 5.61 (s, 1H), 4.13–4.10 (m, 2H), 3.70 (s, 3H), 2.93 (s, 3H), 2.90 (dd, J = 15.2, 5.2 Hz, 1H), 2.60 (dd, J = 15.2, 8.4 Hz, 1H), 2.17 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 170.1, 156.8, 143.5, 132.3, 114.8, 114.6, 108.6, 60.8, 58.0, 55.7, 49.3, 43.2, 21.0, 14.2; HRMS (EI) Calcd for $C_{15}H_{20}N_2O_4$ $(M)^+$ 292.1423; Found, 292.1421.

*Ethyl 2-(2-acetyl-1,5,6-trimethyl-2,3-dihydro-1H-indazol-3-yl)-acetate (**3fa**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.04 (s, 1H), 6.72 (s, 1H), 5.64 (s, 1H), 4.21–4.16 (m, 2H), 3.02 (s, 3H), 2.93 (dd, J = 15.2, 5.6 Hz, 1H), 2.64 (dd, J = 15.2, 8.4 Hz, 1H), 2.25 (s, 3H), 2.24 (s, 3H), 2.22 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 170.1, 148.1, 137.2, 132.3, 128.4, 124.1, 114.8, 60.7, 57.8, 48.9, 43.4, 21.0, 20.1, 19.5, 14.1; HRMS (EI) Calcd for $C_{16}H_{22}N_2O_3$ $(M)^+$ 290.1630; Found, 290.1626.

*Ethyl 2-(2-acetyl-5-fluoro-1-methyl-2,3-dihydro-1H-indazol-3-yl)-acetate (**3ga**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.04–6.96 (m, 2H), 6.87–6.84 (m, 1H), 5.69 (s, 1H), 4.22–4.16 (m, 2H), 3.03 (s, 3H), 2.98 (dd, J = 15.6, 4.8 Hz, 1H), 2.67 (dd, J = 15.6, 8.4 Hz, 1H), 2.25 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 169.8, 159.6 (d, J_{C-F} = 239.8 Hz), 146.1, 132.7 (d, J_{C-F} = 7.4 Hz), 115.6 (d, J_{C-F} = 22.9 Hz), 114.7 (d, J_{C-F} = 8.1 Hz), 110.8 (d, J_{C-F} = 24.1 Hz), 60.9, 57.7, 49.1, 42.9, 21.0, 14.1; HRMS (EI) Calcd for $C_{14}H_{17}FN_2O_3$ $(M)^+$ 280.1223; Found, 280.1222.

*Ethyl 2-(2-acetyl-5-chloro-1-methyl-2,3-dihydro-1H-indazol-3-yl)-acetate (**3ha**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.21–7.15 (m, 2H), 6.76 (d, J = 8.4 Hz, 1H), 5.61 (s, 1H), 4.11 (q, J = 7.2 Hz, 2H), 2.97 (s, 3H), 2.88 (dd, J = 15.6, 5.2 Hz, 1H), 2.60 (dd, J = 15.6, 8.4 Hz, 1H), 2.17 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 169.8, 148.7, 132.7, 129.1, 128.8, 123.7, 114.7, 60.8, 57.7, 48.6, 42.8, 21.0, 14.1; HRMS (EI) Calcd for $C_{14}H_{17}ClN_2O_3$ $(M)^+$ 296.0928; Found, 296.0931.

*Ethyl 2-(2-acetyl-5-bromo-1-methyl-2,3-dihydro-1H-indazol-3-yl)-acetate (**3ia**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.43 (s, 1H), 7.40–7.37 (m, 1H), 6.79 (d, J = 8.4 Hz, 1H), 5.69 (s, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.07 (s, 3H), 2.95 (dd, J = 15.6, 5.2 Hz, 1H), 2.67 (dd, J = 15.6, 8.4 Hz, 1H), 2.24 (s, 3H), 1.27 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 169.7, 149.2, 133.0, 131.6, 126.6, 116.4, 115.1, 60.8, 57.6, 48.5, 42.9, 21.0, 14.1; HRMS (EI) Calcd for $C_{14}H_{17}BrN_2O_3$ $(M)^+$ 296.0928; Found, 340.0419.

*Ethyl 2-(2-acetyl-6-chloro-1-methyl-2,3-dihydro-1H-indazol-3-yl)-acetate (**3ja**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.21 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.91 (s, 1H), 5.67 (s, 1H), 4.19–4.14 (m, 2H), 3.07 (s, 3H), 2.94 (dd, J = 15.2, 4.8 Hz, 1H), 2.66 (dd, J = 15.2, 8.4 Hz, 1H), 2.24 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 169.8, 151.2, 134.3, 129.3, 124.3, 124.0, 114.0, 60.8, 57.6, 48.4, 42.9, 21.0, 14.1; HRMS (EI) Calcd for $C_{14}H_{17}ClN_2O_3$ $(M)^+$ 296.0928; Found, 296.0932.

*Ethyl 2-(2-acetyl-1-ethyl-2,3-dihydro-1H-indazol-3-yl)acetate (**3ka**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.29–7.24 (m, 2H), 7.04 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 5.74 (s, 1H), 4.25–4.18 (m, 2H), 3.34 (d, J = 6.8 Hz, 2H), 2.91 (dd, J = 15.2, 5.2 Hz, 1H), 2.66 (dd, J = 15.2, 8.8 Hz, 1H), 2.25 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.16 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 170.1, 148.2, 131.6, 128.5, 123.7, 123.2, 113.8, 60.8, 58.1, 54.3, 42.4, 21.3, 14.1, 11.7; HRMS (EI) Calcd for $C_{15}H_{20}N_2O_3$ $(M)^+$ 276.1474; Found, 276.1472.

*Ethyl 2-(2-acetyl-1-ethyl-2,3-dihydro-1H-indazol-3-yl)acetate (**3la**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.29–7.24 (m, 2H), 7.04 (t, J = 7.2 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 5.73 (s, 1H), 4.24–4.19 (m, 2H), 3.23 (d, J = 8.8 Hz, 2H), 2.91 (dd, J = 15.2, 6.0 Hz, 1H), 2.66 (dd, J = 15.2, 8.8 Hz, 1H), 2.25 (s, 3H), 1.69–1.48 (m, 2H), 1.36 (t, J = 7.2 Hz, 2H), 1.30 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 170.1, 148.7, 129.5, 128.4, 123.7, 123.3, 113.9, 60.8, 60.5, 58.0, 42.5, 28.8, 21.3, 20.1, 14.1, 13.8; HRMS (EI) Calcd for $C_{17}H_{24}N_2O_3$ $(M)^+$ 304.1787; Found, 304.1791.

Transformation of products. To a solution of compound **3** (0.2 mmol) in ethanol (1.0 mL) was added 2 N HCl (0.3 mL). The mixture was refluxed for 0.5 h. Then the reaction mixture was allowed to cool to room temperature. Water (10 mL) was added, and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over Na_2SO_4 and filtered through the pad of silica gel. The filtrate was concentrated and the resulting residue was purified by flash column chromatography (silica gel, ethyl acetate–petroleum ether = 1 : 3, v/v) to obtain the desired product.

*Ethyl 2-(1-methyl-1H-indazol-3-yl)acetate (**4a**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71 (d, J = 8.4 Hz, 1H), 7.38–7.34 (m, 2H), 7.16–7.12 (m, 1H), 4.18 (q, J = 7.2 Hz, 2H), 4.03 (s, 3H), 4.00 (s, 2H), 1.25 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 140.9, 137.7, 126.3, 122.8, 120.4, 120.2, 109.0, 61.1, 35.3, 33.5, 14.1; HRMS (EI) Calcd for $C_{12}H_{14}N_2O_2$ $(M)^+$ 218.1055; Found, 218.1052.

*2-(1-Methyl-1H-indazol-3-yl)-1-phenylethanone (**4b**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.13–8.11 (m, 2H), 7.69–7.67 (m, 1H), 7.54–7.52 (m, 1H), 7.46–7.43 (m, 2H), 7.36–7.33 (m, 2H), 7.13–7.09 (m, 1H), 4.64 (s, 2H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 140.9, 138.2, 136.3, 133.2, 128.8, 128.5, 126.3, 123.1, 120.7, 120.3, 108.9, 38.2, 35.3; HRMS (EI) Calcd for $C_{16}H_{14}N_2O$ $(M)^+$ 250.1106; Found, 250.1102.

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