# **Supporting Information**

## Four-Component Regio-divergent Carbonylative Condensations in

### the Sustainable Syntheses of Acylhydrazones

Wenjun Jiang, Yan Cai, Mengdi Pang, Guohui Zhang, Yaru Liu\* and Guoying Zhang\*

# **Table of contents**

1	General
2	Screening of reaction parametersS4
	2.1 Screening of reaction parameters for branched acylhydrazoneS4
	2.2 Screening of reaction parameters for line acylhydrazoneS13
3	Experimental characterization data for acylhydrazonesS19
	3.1 Substrate scope of branched acylhydrazones
	3.2 Substrate scope of line acylhydrazones
4	Characterization dataS21
5	Mechanism investigationsS110
	5.1 Control experiments for branched acylhydrazonesS110
	5.2 Time conversion plot experiments of branched acylhydrazonesS115
	5.3 Labelled investigations of branched acylhydrazonesS117
	5.4 Control experiments of branched acylhydrazonesS123
	5.5 Labelled investigations of branched acylhydrazonesS127
6	Further Transformations
7	Gram-scale experimentsS134
8	Synthesis of the intermediates
9	References
10	NMR Spectra

#### 1. General

**Experimental**: Deuterated solvents were bought from Cambridge Isotope Laboratories, distilled accordingly, and stored over molecular sieves (3 Å). Other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were collected on a Varian INOVA 400 MHz spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm relative to residual solvent signal. Coupling constants (*J*) are given in Hz (coupling patterns: s: singlet, s\_br: broad singlet, d: doublet, t: triplet, q: quartet, m: multiplet). GC analyses were carried out using an Agilent Technologies 6890N system equipped with a Machinery-Nagel (MN) Optima 5 HT column (30 m, 320 µm, 0.25 µm) or an Agilent Technologies 6850 system equipped with a MN Optima 17 column (30 m, 320 µm, 0.25 µm). GC-MS analyses were carried out on an Agilent 7890A/MSD 5975C system equipped with a HP-5MS column (30 m, 320 µm, 0.25 µm). High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass (ESI). MN silica gel 60 (0.040 – 0.063 mm particle size) was used for flash column chromatography.

#### 2. Screening of reaction parameters

#### 2.1 Screening of reaction parameters for the branched acylhydrazone

Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, alkene (A1), hydrazine (B1), aldehyde (C1), [Pd], ligand, and solvent. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D1**.

Entry	Parameter
Table S1	The difference of ligand screening
Table S2	The difference of catalyst screening
Table S3	The loading catalyst screening
Table S4	The loading of solvent screening
Table S5	The difference of solvent screening
Table S6	The loading of A1 screening
Table S7	The loading of <b>B1</b> screening
Table S8	The loading of C1 screening
Table S9	Reaction pressure screening
Table S10	Reaction temperature screening
Table S11	Reaction time screening

~	N.	[Pd]	Ph No	
Ph + 41	CO + H <sub>2</sub> N <sup>·</sup> ·Ph + B1	O <sup>F</sup> <sup>Ph</sup> C1	D1 <sup>Ph</sup>	D75 Ph
Entry	Ligand (mmol)	D1 (%)	D75 (%)	D1+D75 (%)
1	L1	2	1	3
2	L2	1	1	2
3	L3	2	1	3
4	L4	6	1	7
5	L5	36	7	43
6	L6	44	22	66
7	L7	26	29	55
8	L8	26	30	56
9	L9	36	17	53
10	L10	28	13	41
11	L11	31	33	64
12	L12	69	1	70
13	L13	45	1	46
14	L14	94	1	95
15	L15	80	1	81
16	L16	62	1	63
17	L17	61	1	62
18	L18	0	0	0
19	L19	0	1	1
20	L20	0	1	1
21	L21	1	2	3
22	L22	20	22	42
23	L23	39	42	81
24	L24	1	2	3
25	L25	2	3	5
26	L26	10	78	88

 Table S1: The difference of ligand screening <sup>a</sup>

Entry	Ligand (mmol)	<b>D1</b> (%)	<b>D75</b> (%)	<b>D1+D75</b> (%)
27	L27	11	56	67
28	L28	12	57	69
29	L29	8	70	78
30	L30	7	65	72
31	L31	1	3	4
32	L32	1	2	3
33	L33	14	41	55
34	L34	1	3	4
35	L35	3	9	12
36	L36	1	2	3
37	-	0	0	0

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), B1 (1.0 mmol), C1 (1.5 mmol), DCM (2.0 mL), PdCI<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (0.02 mmol), CO (2.5 MPa), 120 °C, 6 h. Yield of D1 and D75 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.



Table S2: The difference of catalyst screening <sup>a</sup>

Ph + CO +	$H_2 N \xrightarrow{H} Ph + 0 \xrightarrow{Ph} Ph \xrightarrow{Ph} Ph$	Ph	+ Ph
Entry	Catalyst (0.02 mmol)	D1 (%)	D1:D75
1	PdCl <sub>2</sub>	20	>99:1
2	PdBr <sub>2</sub>	23	96:4
3	PdI <sub>2</sub>	<5	-
4	Pd(OAc) <sub>2</sub>	<5	-
5	Pd(TFA) <sub>2</sub>	<5	-
6	PdCl <sub>2</sub> (CH <sub>3</sub> CN) <sub>2</sub>	94	>99:1
7	PdBr <sub>2</sub> (CH <sub>3</sub> CN) <sub>2</sub>	42	>99:1
8	PdCl <sub>2</sub> (COD)	31	92:8
9	PdBr <sub>2</sub> (COD)	26	90:10
10	PdCl <sub>2</sub> (PhCN) <sub>2</sub>	68	96:4
$11^{b}$	[PdCl(CH <sub>2</sub> =CHCH <sub>2</sub> )] <sub>2</sub>	12	92:8
$12^{b}$	[PdCl(PhCH <sub>2</sub> =CHCH <sub>2</sub> )] <sub>2</sub>	16	90:10
13 <sup>c</sup>	PdCl <sub>2</sub> (Ph <sub>3</sub> P) <sub>2</sub>	42	96:4
$14^c$	Pd(Ph <sub>3</sub> P) <sub>4</sub>	<5	-
15 <sup>c</sup>	$Pd(^{t}Bu_{3}P)_{2}$	<5	-
16	Pd/C	<5	-
<b>17</b> °	PdCl2[P(3,5-F2Ph)3]2	96	>99:1
18 <sup>c</sup>	-	<5	-

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), B1 (1.0 mmol), C1 (1.5 mmol), DCM (2.0 mL), P(3,5-F<sub>2</sub>Ph)<sub>3</sub> (0.05 mmol), CO (2.5 MPa), 120 °C, 6 h. Yield of D1 and the ratio of D1:D75 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard. <sup>*b*</sup> [Pd] (0.01 mmol). <sup>*c*</sup> P(3,5-F<sub>2</sub>Ph)<sub>3</sub> omitted.

Ph + CO	+ H <sub>2</sub> N <sup>N</sup> Ph + OPh [Pd]	Ph N Ph	+ Ph
A1	B1 C1	D1 <sup>Ph</sup>	<b>D75</b> Ph
Entry	Cat. (mmol)	<b>D1</b> (%)	D1:D75
1	0	0	-
2	0.005	46	>99:1
3	0.01	89	>99:1
4	0.02	96	>99:1
6	0.03	95	>99:1
7	0.05	96	>99:1

**Table S3**: The loading catalyst screening <sup>*a*</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), B1 (1.0 mmol), C1 (1.5 mmol), DCM (2.0 mL), CO (2.5 MPa), 120 °C, 6 h. Yield of D1 and the ratio of D1:D75 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

Ph + CO	+ $H_{2N}^{N}$ Ph + $O^{Ph}$ $\stackrel{[Pd]}{\longrightarrow}$	Ph	∧_N≈ <sup>Ph</sup>
A1	B1 C1	D1 <sup>Ph</sup>	D75 <sup>Ph</sup>
Entry	DCM (ml)	D1 (%)	D1:D75
1	-	16	80:20
2	0.5	43	90:10
3	1.0	72	95:5
4	1.5	84	>99:1
5	2.0	96	>99:1
6	2.5	90	>99:1
7	3.0	89	>99:1

**Table S4**: The loading of solvent screening<sup>*a*</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), B1 (1.0 mmol), C1 (1.5 mmol), PdCl<sub>2</sub>[P(3,5- $F_2Ph$ )<sub>3</sub>]<sub>2</sub> (0.02 mmol), CO (2.5 MPa), 120 °C, 6 h. Yield of D1 and the ratio of D1:D75 determined by GC-analysis using *n*-dodecane (100 µL) as internal standard.

 Table S5: The difference of solvent screening<sup>a</sup>

		Pd] Ph ↓ N ↓ Ph + F	Ph ∧ N ∼ Ph
Pn	B1 C1	D1 <sup>Ph</sup>	D75 Ph
Entry	Solvent (2 mL)	<b>D1</b> (%)	D1:D75
1	DMAc	<5	-
2	DMF	<5	-
3	DMSO	<5	-
4	THF	61	>99:1
5	PE	34	>99:1
6	1,4-dioxane	72	>99:1
7	anisole	95	>99:1
8	1,2-dimethoxyethane	83	>99:1
9	mesitylene	34	>99:1
10	nitrobenzene	<5	-
11	toluene	22	>99:1
12	Et <sub>3</sub> N	<5	-
13	Ру	<5	-
14	EtOH	<5	-
15	IPA	21	>99:1
16	2-Methyl-2-propanol	41	>99:1
17	2-Methyl-2-butanol	43	>99:1
18	EA	52	>99:1
19	hexane	38	>99:1
20	acetonitrile	90	>99:1
21	DCM	96	>99:1
22	DCE	13	>99:1
23	CHCI3	38	>99:1
24	CH <sub>3</sub> NO <sub>2</sub>	<5	-

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), B1 (1.0 mmol), C1 (1.5 mmol), solvent (2.0 mL), PdCl<sub>2</sub>[P(3,5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.02 mmol), CO (2.5 MPa), 120 °C, 6 h. Yield of D1 and the ratio of D1:D75 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

Table S6: The loading of A1 screening<sup>*a*</sup>

Ph + CO	+ $H_{2N}^{N}$ Ph + $O^{Ph}$ $\xrightarrow{[Pd]}$	Ph <mark>, N</mark> → Ph +	Ph N Ph
A1	B1 C1	D1 <sup>Ph</sup>	<b>D75</b> Ph
Entry	A1 (mmol)	D1 (%)	D1:D75
1	0.5	81	>99:1
2	1.0	90	>99:1
3	1.25	91	>99:1
4	1.4	95	>99:1
5	1.5	96	>99:1
6	1.6	96	>99:1
7	1.75	95	>99:1
8	2.0	96	>99:1

<sup>*a*</sup> Reaction conditions: A1, B1 (1.0 mmol), C1 (1.5 mmol), DCM (2.0 mL), PdCl<sub>2</sub>[P(3,5- $F_2Ph)_3$ ]<sub>2</sub> (0.02 mmol), CO (2.5 MPa), 120 °C, 6 h. Yield of D1 and the ratio of D1:D75 determined by GC-analysis using *n*-dodecane (100 µL) as internal standard.

Table S7: The	loading of <b>B1</b>	screening <sup><i>a</i></sup>
---------------	----------------------	-------------------------------

Dh + CO	+ $H_{AN}$ Ph + $O$ Ph = [Pd]	Ph N +	Ph N Ph
A1	B1 C1	D1 <sup>Ph</sup>	D75 Ph
Entry	<b>B1</b> (mmol)	<b>D1</b> (%)	D1:D75
1	0.5	54	>99:1
2	0.8	79	>99:1
3	0.9	92	>99:1
4	1.0	96	>99:1
5	1.1	95	>99:1
6	1.2	94	>99:1
7	1.4	91	>99:1
8	1.5	88	>99:1

<sup>*a*</sup> Reaction conditions: A1 (1.4 mmol), C1 (1.5 mmol), DCM (2.0 mL), PdCl<sub>2</sub>[P(3,5- $F_2Ph$ )<sub>3</sub>]<sub>2</sub> (0.02 mmol), CO (2.5 MPa), 120 °C, 6 h. Yield of D1 and the ratio of D1:D75 determined by GC-analysis using *n*-dodecane (100 µL) as internal standard.

Dh + CO	+ $H_{n}N$ Ph + $O$ Ph $(Pd)$	Ph↓ <mark>Ph</mark> ↓	Ph N Ph
A1	B1 C1	D1 Ph	D75 Ph
Entry	C1 (mmol)	<b>D1</b> (%)	D1:D75
1	1.0	74	>99:1
2	1.1	79	>99:1
3	1.2	80	>99:1
4	1.3	84	>99:1
5	1.4	92	>99:1
6	1.5	96	>99:1
7	1.75	95	>99:1
8	2.0	94	>99:1

Table S8: The loading of C1 screening<sup>*a*</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.4 mmol), B1 (1.0 mmol), DCM (2.0 mL), PdCl<sub>2</sub>[P(3,5- $F_2Ph$ )<sub>3</sub>]<sub>2</sub> (0.02 mmol), CO (2.5 MPa), 120 °C, 6 h. Yield of D1 and the ratio of D1:D75 determined by GC-analysis using *n*-dodecane (100 µL) as internal standard.

Ph + CO	H + H₂ <b>N´<sup>N</sup>`</b> Ph +		+ Ph
A1	B1	C1 D1 <sup>Ph</sup>	<b>D75</b> Ph
Entry	P [MPa]	<b>D1</b> (%)	D1:D75
1	0	0	-
2	0.1	<5	-
3	1.0	79	>99:1
4	2.0	91	>99:1
5	2.5	96	>99:1
6	3.0	95	>99:1
7	4.0	96	>99:1

 Table S9: Reaction pressure screening<sup>a</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.4 mmol), B1 (1.0 mmol), C1 (1.5 mmol), DCM (2.0 mL), PdCl<sub>2</sub>[P(3,5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.02 mmol), 120 °C, 6 h. Yield of D1 and the ratio of D1:D75 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

Ph + CO +	$H_{2N} \rightarrow H_{2N} \rightarrow H$		Ph + Ph PT5 Ph
Entry	t [h]	D1 (%)	D1:D75
1	2	51	>99:1
2	4	73	>99:1
3	6	96	>99:1
4	8	96	>99:1
5	10	95	>99:1
6	12	96	>99:1

**Table S10:** Reaction time screening <sup>*a*</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.4 mmol), B1 (1.0 mmol), C1 (1.5 mmol), DCM (2.0 mL), PdCl<sub>2</sub>[P(3,5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.02 mmol), CO (2.5 MPa), 120 °C, Yield of D1 and the ratio of D1:D75 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

~

Ph + C	O + H₂N <sup>∽N</sup> ∑Ph + ∩ <sup>3</sup>		<sup>h</sup> + Ph → N → Ph
A1	B1	C1 D1 <sup>Ph</sup>	D75 <sup>Ph</sup>
Entry	T [° C]	<b>D1</b> (%)	D1:D75
1	RT	0	-
2	40	<5	-
3	60	24	>99:1
4	80	36	>99:1
5	100	81	>99:1
6	120	96	>99:1
7	130	93	>99:1
8	140	90	>99:1

 Table S11: Reaction temperature screening<sup>a</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.4 mmol), B1 (1.0 mmol), C1 (1.5 mmol), DCM (2.0 mL), PdCl<sub>2</sub>[P(3,5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.02 mmol), CO (2.5 MPa), 6 h. Yield of D1 and the ratio of D1:D75 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

#### 2.2 Screening of reaction parameters for the line acylhydrazone

Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, alkene (A1), hydrazine (B1), aldehyde (C1), [Pd], ligand, and solvent. Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D75**.

Entry	Parameter
Table S12	The loading catalyst screening
Table S13	The loading of solvent screening
Table S14	The difference of solvent screening
Table S15	The loading of A1 screening
Table S16	The loading of <b>B1</b> screening
Table S17	The loading of C1 screening
Table S18	Reaction pressure screening
Table S19	Reaction temperature screening
Table S20	Reaction time screening

Ph +	$H_{2N} + H_{2N} + O$	$\sim_{\text{Ph}} \xrightarrow{[\text{Pd}]} \text{Ph}$	N N Ph
Entry	Cat. (mmol)	D75 (%)	D75 '''
1	0	0	-
2	0.005	31	89:11
3	0.01	82	90:10
4	0.02	93	89:11
6	0.03	92	90:10
7	0.05	93	89:11

Table S12: The loading catalyst screening <sup>a</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), B1 (1.0 mmol), C1 (1.5 mmol), PdCl<sub>2</sub>(Xantphos)<sub>2</sub>, anisole (2.0 mL), CO (3.0 MPa), 120 °C, 16 h. Yield of D75 and the ratio of D75:D1 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

Ph	+ $CO$ + $H_2N^{N}$ Ph + $O^{Ph}$ -	[Pd] Ph Ph Ph Ph
A1	B1 C1	<b>D75</b> <sup>Ph</sup>
Entry	anisole (ml)	D75 (%) D75:D1
1	-	26 70:30
2	0.5	63 89:11
3	1.0	82 90:10
4	1.5	90 89:11
5	2.0	93 89:11
6	2.5	92 89:11
7	3.0	90 90:10

**Table S13**: The loading of solvent screening<sup>*a*</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), B1 (1.0 mmol), C1 (1.5 mmol), PdCl<sub>2</sub>(Xantphos)<sub>2</sub> (0.02 mmol), CO (3.0 MPa), 120 °C, 16 h. Yield of D75 and the ratio of D75:D1 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

Ph + 41	$\frac{H}{Ph} + \frac{H}{Ph} + \frac{H}{Ph}$ B1 C1	rh ────────────────────────────────────	O V N D75 Ph Ph
Entry	Solvent (2 mL)	<b>D75</b> (%)	D75:D1
1	DMAc	<5	-
2	DMF	<5	-
3	DMSO	<5	-
4	THF	23	80:20
5	PE	26	81:19
6	1,4-dioxane	56	90:10
7	anisole	93	89:11
8	1,2-dimethoxyethane	81	90:10
9	mesitylene	43	80:20
10	nitrobenzene	32	92:8
11	toluene	68	80:20
12	Et <sub>3</sub> N	20	80:20
13	Ру	12	91:9
14	EtOH	<5	-
15	IPA	<5	-
16	2-Methyl-2-propanol	36	85:15
17	2-Methyl-2-butanol	43	80:20
18	EA	32	87:13
19	hexane	12	80:20
20	acetonitrile	42	85:15
21	DCM	39	80:20
22	DCE	48	85:15
23	CHCl <sub>3</sub>	<5	-
24	CH <sub>3</sub> NO <sub>2</sub>	<5	-

 Table S14: The difference of solvent screening<sup>a</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), B1 (1.0 mmol), C1 (1.5 mmol), PdCl<sub>2</sub>(Xantphos)<sub>2</sub> (0.02 mmol), CO (3.0 MPa), 120 °C, 16 h. Yield of D75 and the ratio of D75:D1 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

Ph + A1	$\frac{H}{B1} + \frac{H}{C1}$	[Pd] → Ph	O N N Ph Ph
Entry	A1 (mmol)	<b>D75</b> (%)	D75:D1
1	0.5	41	62:38
2	1.0	71	81:19
3	1.25	82	85:15
4	1.4	90	85:15
5	1.5	93	89:11
6	1.6	92	89:11
7	1.75	93	89:11
8	2.0	92	89:11

 Table S15: The loading of A1 screening<sup>a</sup>

<sup>*a*</sup> Reaction conditions: **B1** (1.0 mmol), **C1** (1.5 mmol),  $PdCl_2(Xantphos)_2$  (0.02 mmol), anisole (2.0 mL), CO (3.0 MPa), 120 °C, 16 h. Yield of **D75** and the ratio of **D75:D1** determined by GC-analysis using *n*-dodecane (100 µL) as internal standard.

Ph +	$H_{2N} + H_{2N} + O_{Ph}$	[Pd] Ph	O N N Ph
Entry	B1 C1	<b>D75</b> (%)	D75 · ···
1	0.5	81	88:12
2	0.8	90	89:11
3	0.9	92	88:12
4	1.0	93	89:11
5	1.1	92	89:11
6	1.2	90	90:10
7	1.4	86	89:11
8	1.5	81	88:12

Table S16: The loading of B1 screening<sup>*a*</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), C1 (1.5 mmol), PdCl<sub>2</sub>(Xantphos)<sub>2</sub> (0.02 mmol), anisole (2.0 mL), CO (3.0 MPa), 120 °C, 16 h. Yield of D75 and the ratio of D75:D1 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

Ph + 41	$\begin{array}{c} H \\ CO + H_2 N N Ph + O Ph \\ B1 C1 \end{array}$	[Pd] → Ph	OT5 Ph
Entry	C1 (mmol)	<b>D75</b> (%)	D75:D1
1	1.0	66	88:12
2	1.1	70	89:11
3	1.2	76	89:11
4	1.3	83	90:10
5	1.4	90	89:11
6	1.5	93	89:11
7	1.75	92	89:11
8	2.0	93	90:10

 Table S17: The loading of C1 screening<sup>a</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), B1 (1.0 mmol), PdCl<sub>2</sub>(Xantphos)<sub>2</sub> (0.02 mmol), anisole (2.0 mL), CO (3.0 MPa), 120 °C, 16 h. Yield of D75 and the ratio of D75:D1 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

Ph ·	+ <b>CO</b> + H <sub>2</sub> N <sup>N</sup> Ph	+ OMPH	Ph
A1	B1	C1	D75 <sup>Ph</sup>
Entry	P [MPa]	<b>D75</b> (%)	D75:D1
1	0	0	-
2	0.1	<5	-
3	1.0	44	80:20
4	2.0	75	89:11
5	2.5	84	90:10
6	3.0	93	89:11
7	3.5	93	90:10

 Table S18: Reaction pressure screening<sup>a</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), B1 (1.0 mmol), C1(1.5 mmol), PdCl<sub>2</sub>(Xantphos)<sub>2</sub> (0.02 mmol), anisole (2.0 mL), 120 °C, 16 h. Yield of D75 and the ratio of D75:D1 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

Ph + CO A1	H + H <sub>2</sub> N <sup>N</sup> Ph + B1	$O^{\frown}Ph \xrightarrow{[Pd]}$	Ph D75 Ph
Entry	t [h]	<b>D75</b> (%)	D75:D1
1	2	11	89:11
2	4	42	90:10
3	8	81	89:11
4	16	93	89:11
5	24	93	90:10
6	36	93	90:10

 Table S19: Reaction time screening <sup>a</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), B1 (1.0 mmol), C1(1.5 mmol), PdCl<sub>2</sub>(Xantphos)<sub>2</sub> (0.02 mmol), anisole (2.0 mL), CO (3.0 MPa), 120 °C. Yield of D75 and the ratio of D75:D1 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

Ph +	CO + H <sub>2</sub> N <sup>N</sup> Ph	+ OMPh	Ph N → Ph
A1	B1	C1	<b>D75</b> <sup>Ph</sup>
Entry	T [° C]	<b>D75</b> (%)	D75:D1
1	RT	0	-
2	40	<5	-
3	60	<5	-
4	80	<5	-
5	100	81	89:11
6	120	93	89:11
7	130	92	90:10
8	140	90	86:14

**Table S20**: Reaction temperature screening<sup>*a*</sup>

<sup>*a*</sup> Reaction conditions: A1 (1.5 mmol), B1 (1.0 mmol), C1(1.5 mmol), PdCl<sub>2</sub>(Xantphos)<sub>2</sub> (0.02 mmol), anisole (2.0 mL), CO (3.0 MPa), 16 h. Yield of D75 and the ratio of D75:D1 determined by GC-analysis using *n*-dodecane (100  $\mu$ L) as internal standard.

#### 3. Experimental characterization data for products

#### 3.1 Substrate scope of branched acylhydrazones



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, alkenes (A 1.4 mmol), hydrazines (B 1.0 mmol), aldehydes (C 1.5 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.02 mmol, 2 mol%), and DCM (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 5:1) on silica gel to give the corresponding products D1-D60.

#### 3.2 Substrate scope of line acylhydrazones



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, alkenes (A 1.5 mmol), hydrazines (B 1.0 mmol), aldehydes (C 1.5 mmol), PdCl<sub>2</sub>(Xantphos) (0.02 mmol, 2 mol%), and anisole (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (3.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 16 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 5:1) on silica gel to give the corresponding products **D75-D91**.

#### 4. Characterization data



N'-benzylidene-N,2-diphenylpropanehydrazide (D1)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 285.4 mg, 87% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.46 (m, 6H), 7.45 – 7.40 (m, 1H), 7.36 – 7.28 (m, 5H), 7.23 – 7.17 (m, 1H), 7.14 (s, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 5.09 (d, *J* = 7.2 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 142.5, 141.5, 136.3, 134.4, 130.2, 129.8, 129.2, 128.7, 128.6, 127.8, 127.3, 126.7, 42.9, 19.5 ppm.

**MS** (70 eV): m/z (%) = 328 [M]<sup>+</sup>, 225, 196, 105.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O [M+H]: 329.1648, found: 329.1645.





#### *N'*-benzylidene-*N*-phenyl-2-(*p*-tolyl)propanehydrazide (D2)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 311.2 mg, 91% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 6.4 Hz, 2H), 7.47 – 7.43 (m, 2H), 7.42 – 7.33 (m, 3H), 7.32 – 7.27 (m, 3H), 7.16 – 7.08 (m, 3H), 7.05 (d, *J* = 7.6 Hz, 2H), 5.07 (d, *J* = 7.2 Hz, 1H), 2.25 (s, 3H), 1.58 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.0, 141.5, 139.6, 136.4, 136.2, 134.6, 130.2, 129.9, 129.5, 129.3, 128.8, 127.8, 127.3, 42.6, 21.2, 19.7 ppm.

**MS** (70 eV): m/z (%) = 342 [M]<sup>+</sup>(100), 223, 196, 119.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 343.1805, found: 343.1806.





#### N'-benzylidene-N-phenyl-2-(m-tolyl)propanehydrazide (D3)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 287.3 mg, 84% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.54 – 7.44 (m, 4H), 7.43 – 7.37 (m, 1H), 7.36 – 7.24 (m, 5H), 7.22 – 7.16 (m, 1H), 7.13 (s, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.2 Hz, 1H), 5.03 (d, *J* = 7.2 Hz, 1H), 2.31 (s, 3H), 1.58 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.9, 142.5, 141.5, 138.2, 136.4, 134.5, 130.2, 129.9, 129.3, 128.7, 127.5, 127.3, 124.9, 43.1, 21.6, 19.6 ppm.

**MS** (70 eV): m/z (%) = 342 [M]<sup>+</sup>(100), 196, 119, 91.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 343.1805, found: 343.1805.





#### N'-benzylidene-N-phenyl-2-(o-tolyl)propanehydrazide (D4)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 249.7 mg, 73% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.53 – 7.45 (m, 2H), 7.43 – 7.33 (m, 4H), 7.29 – 7.24 (m, 3H), 7.21 – 7.15 (m, 2H), 7.14 – 7.07 (m, 4H), 5.12 (d, *J* = 6.8 Hz, 1H), 2.56 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.3, 142.0, 141.4, 136.5, 135.1, 134.4, 130.5, 130.3, 129.8, 129.3, 128.6, 127.4, 126.6, 126.2, 39.7, 19.8, 18.5 ppm.

**MS** (70 eV): m/z (%) = 342 [M]<sup>+</sup>(100), 196, 119, 91.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 343.1805, found: 343.1807.





*N'*-benzylidene-2-(4-(*tert*-butyl)phenyl)-*N*-phenylpropanehydrazide (D5) The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 345.6 mg, 90% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 (d, *J* = 6.8 Hz, 2H), 7.47 – 7.41 (m, 4H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.35 – 7.26 (m, 5H), 7.14 (s, 1H), 7.05 (d, *J* = 7.6 Hz, 2H), 5.12 (d, *J* = 6.8 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H), 1.27 (s, 9H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.1, 149.44, 141.5, 139.3, 136.4, 134.6, 130.2, 129.9, 129.3, 128.8, 127.5, 127.4, 125.6, 42.2, 34.5, 31.6, 19.6 ppm.

**MS** (70 eV): m/z (%) = 384 [M]<sup>+</sup>(100), 252, 196, 105.

HRMS (ESI) calcd. for C<sub>26</sub>H<sub>29</sub>N<sub>2</sub>O [M+H]: 385.2274, found: 385.2272.





#### N'-benzylidene-2-(2-methoxyphenyl)-N-phenylpropanehydrazide (D6)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 250.6 mg, 70% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.50 – 7.32 (m, 6H), 7.26 – 7.21 (m, 3H), 7.17 – 7.05 (m, 4H), 6.93 – 6.82 (m, 2H), 5.43 (d, *J* = 6.8 Hz, 1H), 3.90 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.7, 156.2, 140.8, 136.5, 134.8, 131.7, 130.2, 129.7, 129.3, 128.6, 127.7, 127.4, 127.2, 120.9, 110.4, 55.4, 36.6, 18.3 ppm.

**MS** (70 eV): m/z (%) = 358 [M]<sup>+</sup>(100), 196, 135, 105.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> [M+H]: 359.1754, found: 359.1753.





2-([1,1'-biphenyl]-4-yl)-1-(2-benzylidene-1-phenyl-114,214-diazenyl)propan-1-one (D7)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 331.3 mg, 82% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.85 – 7.70 (m, 8H), 7.69 – 7.62 (m, 2H), 7.60 – 7.47 (m, 6H), 7.47 – 7.42 (m, 1H), 7.37 (s, 1H), 7.27 (d, *J* = 7.2 Hz, 2H), 5.38 (d, *J* = 6.8 Hz, 1H), 1.87 (d, *J* = 6.8 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 141.8, 141.1, 139.7, 136.4, 134.6, 130.4, 130.1, 129.4, 128.9, 128.5, 127.5, 127.4, 127.2, 42.7, 19.7 ppm.

**MS** (70 eV): m/z (%) = 404 [M]<sup>+</sup>(100), 384, 196, 161.

HRMS (ESI) calcd. for C<sub>28</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]: 405.1961, found: 405.1959.





#### N'-benzylidene-2-(4-fluorophenyl)-N-phenylpropanehydrazide (D8)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 283.7 mg, 82% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.68 – 7.55 (m, 6H), 7.54 – 7.49 (m, 1H), 7.46 – 7.42 (m, 3H), 7.32 –7.28 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 8.4 Hz, 2H), 5.23 (d, *J* = 5.2 Hz, 1H), 1.79 – 1.65 (m, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.6, 163.0, 160.6, 141.8, 138.2, 136.2, 134.4, 130.3, 130.0, 129.5, 129.4, 129.2, 128.9, 127.3, 115.6, 115.4, 42.1, 19.6 ppm.

<sup>19</sup>**F** NMR (376 MHz, CDCl<sub>3</sub>) δ -116.1.

**MS** (70 eV): m/z (%) = 346 [M]<sup>+</sup>(100), 243, 196, 123.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>FN<sub>2</sub>O [M+H]: 347.1554, found: 347.1555.





#### N'-benzylidene-2-(3-fluorophenyl)-N-phenylpropanehydrazide (D9)

The title compound was prepared according to the general procedure and purified by column chromatography to give the light-yellow oil, 252.6 mg, 73% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.52 – 7.44 (m, 4H), 7.42 – 7.36 (m, 1H), 7.34 – 7.20 (m, 6H), 7.17 (s, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 7.89 – 7.83 (m, 1H), 5.10 (d, *J* = 7.2 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.2, 164.3, 161.9, 145.1, 141.9, 136.2, 134.3, 130.3, 130.2, 130.1, 129.4, 129.2, 128.9, 127.3, 123.6, 114.9, 114.7, 113.8, 113.6, 42.8, 19.5 ppm.

<sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>) δ -112.8.

**MS** (70 eV): m/z (%) = 346 [M]<sup>+</sup> (100), 243, 196, 123.

**HRMS** (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>FN<sub>2</sub>O [M+H]: 347.1554, found: 347.1552.





#### N'-benzylidene-2-(2-fluorophenyl)-N-phenylpropanehydrazide (D10)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 231.8 mg, 67% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.50 – 7.37 (m, 6H), 7.28 – 7.24 (m, 3H), 7.16 – 7.01 (m, 6H), 5.36 (d, *J* = 6.8 Hz, 1H), 1.65 – 1.49 (m, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.3, 161.3, 158.9, 141.9, 136.2, 134.3, 130.3, 129.9, 129.4, 129.3, 128.7, 128.4, 128.3, 128.2, 127.4, 124.6, 124.5, 115.6, 115.4, 36.0, 18.5 ppm.

<sup>19</sup>**F** NMR (376 MHz, CDCl<sub>3</sub>) δ -118.6.

**MS** (70 eV): m/z (%) = 346 [M]<sup>+</sup>(100), 243, 196, 123.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>FN<sub>2</sub>O [M+H]: 347.1554, found: 347.1555.





N'-benzylidene-2-(4-chlorophenyl)-N-phenylpropanehydrazide (D11)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 300.5 mg, 83% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 – 7.45 (m, 4H), 7.42 (d, *J* = 8.0 Hz, 3H), 7.37 – 7.30 (m, 3H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.16 (s, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 5.08 (d, *J* = 7.2 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.3, 141.9, 141.0, 136.1, 134.3, 132.5, 130.3, 130.0, 129.4, 129.3, 129.2, 128.8, 127.3, 42.3, 19.5 ppm.

**MS** (70 eV): m/z (%) = 362 [M]<sup>+</sup>(100), 230, 105, 77.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>ClN<sub>2</sub>O [M+H]: 363.1258, found: 363.1259.







#### N'-benzylidene-2-(3-chlorophenyl)-N-phenylpropanehydrazide (D12)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 267.9 mg, 74% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.54 – 7.43 (m, 5H), 7.43 – 7.28 (m, 5H), 7.22 – 7.13 (m, 3H), 7.06 (d, *J* = 7.6 Hz, 2H), 5.03 (d, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.0, 144.6, 142.0, 136.1, 134.4, 134.3, 130.3, 130.1, 130.0, 129.4, 129.2, 128.9, 128.3, 127.4, 127.0, 126.0, 42.9, 19.5 ppm.

**MS** (70 eV): m/z (%) = 362 [M]<sup>+</sup>(100), 259, 196, 139.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>ClN<sub>2</sub>O [M+H]: 363.1258, found: 363.1258.





#### *N'*-benzylidene-2-(2-chlorophenyl)-*N*-phenylpropanehydrazide (D13)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 246.2 mg, 68% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 – 7.47 (m, 4H), 7.45 – 7.37 (m, 3H), 7.26 (s, 3H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.15 – 7.07 (m, 4H), 5.42 (d, *J* = 6.8 Hz, 1H), 1.55 (d, *J* = 6.8 Hz, 3H) ppm.

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.4, 142.0, 140.8, 136.2, 134.2, 133.3, 130.3, 129.9, 129.7, 129.4, 129.2, 128.6, 127.9, 127.8, 127.5, 127.4, 40.6, 17.9 ppm.

**MS** (70 eV): m/z (%) = 362 [M]<sup>+</sup>(100), 224, 196, 139.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>ClN<sub>2</sub>O [M+H]: 363.1259, found: 363.1256.





N'-benzylidene-2-(4-bromophenyl)-N-phenylpropanehydrazide (D14)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 324.8 mg, 80% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.51 (m, 4H), 7.48 – 7.40 (m, 3H), 7.40 – 7.32 (m, 5H), 7.18 (s, 1H), 7.09 (d, *J* = 7.6 Hz, 2H), 5.08 (d, *J* = 7.2 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.2, 141.9, 141.4, 136.0, 134.2, 131.7, 130.2, 130.0, 129.6, 129.3, 129.1, 128.8, 127.2 120.5, 42.4, 19.3 ppm.

**MS** (70 eV): m/z (%) = 406 [M]<sup>+</sup>(100), 196, 104, 77.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>BrN<sub>2</sub>O [M+H]: 407.0754, found: 407.0754.





#### N'-benzylidene-2-(3-bromophenyl)-N-phenylpropanehydrazide (D15)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 284.2 mg, 70% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.68 (s, 1H), 7.52 – 7.44 (m, 4H), 7.43 – 7.36 (m, 2H), 7.35 – 7.27 m, 4H), 7.17 – 7.10 (m, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 5.00 (d, *J* = 7.2 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.0, 144.9, 142.0, 136.1, 134.3, 131.3, 130.3, 130.1, 129.9, 129.4, 129.2, 128.9, 127.4, 126.4, 122.7, 43.0, 19.5 ppm.

**MS** (70 eV): m/z (%) = 406 [M]<sup>+</sup>(100), 196, 167, 104.

**HRMS** (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>BrN<sub>2</sub>O [M+H]: 407.0753, found: 407.0750.




# N'-benzylidene-N-phenyl-2-(4-(trifluoromethyl)phenyl)propanehydrazide (D16)

The title compound was prepared according to the general procedure and purified by column chromatography to give a light-yellow solid, 293.0 mg, 74% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.63 – 7.55 (m, 4H), 7.53 – 7.47 (m, 4H), 7.45 – 7.40 (m, 1H), 7.37 – 7.29 (m, 3H), 7.19 (s, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 5.17 (d, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.0, 146.5, 142.2, 136.0, 134.2, 130.3, 130.1, 129.4, 129.1, 128.8, 128.3, 127.3, 125.6, 42.9, 19.4 ppm.

<sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.2.

**MS** (70 eV): m/z (%) = 396 [M]<sup>+</sup>(100), 293, 196, 173.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O [M+H]: 397.1522, found: 397.1523.





### N'-benzylidene-2-(4-nitrophenyl)-N-phenylpropanehydrazide (D17)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 160.4 mg, 43% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.57 – 7.44 (m, 5H), 7.39 – 7.33 (m, 3H), 7.26 – 7.16 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 5.19 (d, *J* = 7.2 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.3, 150.0, 146.8, 142.5, 135.7, 134.0, 130.3, 130.2, 129.5, 129.0, 128.8, 128.7, 127.2, 123.9, 43.0, 19.2 ppm.

**MS** (70 eV): m/z (%) = 373 [M]<sup>+</sup>(100), 270, 196, 120.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>N<sub>3</sub>O<sub>3</sub> [M+H]: 374.1499, found: 374.1497.





methyl-4-(1-(2-benzylidene-1-phenylhydrazineyl)-1-oxopropan-2-yl)benzoate (D18)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 312.7 mg, 81% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.51 – 7.44 (m, 4H), 7.42 – 7.37 (m, 1H), 7.34 – 7.27 (m, 3H), 7.17 (s, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 5.14 (d, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 1.61 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.9, 166.9, 147.9, 141.9, 136.1, 134.2, 130.3, 130.0, 129.4, 129.1, 128.8, 128.7, 127.8, 127.3, 52.0, 43.3, 19.3 ppm.

**MS** (70 eV): m/z (%) = 386 [M]<sup>+</sup>(100), 283, 196, 163.

HRMS (ESI) calcd. for C<sub>24</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> [M+H]: 387.1703, found: 387.1702.





# 4-(1-(2-benzylidene-1-phenylhydrazineyl)-1-oxopropan-2-yl)phenyl acetate (D19)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 293.4 mg, 76% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.57 – 7.43 (m, 6H), 7.43 – 7.37 (m, 1H), 7.36 – 7.28 (m, 3H), 7.17 (s, 1H), 7.11 – 7.02 (m, 4H), 5.13 (d, *J* = 7.2 Hz, 1H), 2.20 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.5, 169.5, 149.5, 141.8, 139.8, 136.2, 134.4, 130.2, 129.9, 129.3, 129.2, 128.9, 128.8, 127.3, 121.6, 42.1, 21.2, 19.5 ppm.

**MS** (70 eV): m/z (%) = 386 [M]<sup>+</sup>(100), 196, 121, 77.

HRMS (ESI) calcd. for C<sub>24</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> [M+H]: 387.1703, found: 387.1703.





#### N'-benzylidene-2-(naphthalen-2-yl)-N-phenylpropanehydrazide (D20)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 332.6 mg, 88% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.00 (s, 1H), 7.89 – 7.81 (m, 3H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.65 – 7.51 (m, 4H), 7.51 – 7.43 (m, 3H), 7.42 – 7.34 (m, 3H), 7.18 (s, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 5.30 (d, *J* = 7.2 Hz, 1H), 1.74 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.7, 141.6, 140.0, 136.3, 134.4, 133.8, 132.5, 130.2, 129.8, 129.3, 129.2, 128.7, 128.3, 127.8, 127.7, 127.3, 126.5, 126.3, 126.0, 125.5, 43.2, 19.5 ppm.

**MS** (70 eV): m/z (%) = 378 [M]<sup>+</sup>(100), 258, 196, 155.

HRMS (ESI) calcd. for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 379.1805, found: 379.1801.





#### N'-benzylidene-2-(naphthalen-1-yl)-N-phenylpropanehydrazide (D21)

The title compound was prepared according to the general procedure and purified by column chromatography to give the light-yellow oil, 272.2 mg, 72% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.40 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.55 (m, 3H), 7.49 – 7.30 (m, 5H), 7.11 – 7.03 (m, 3H), 7.00 (s, 1H), 6.99 – 6.87 (m, 4H), 5.72 (d, *J* = 7.2 Hz, 1H), 1.69 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.4, 141.5, 140.0, 136.4, 134.4, 134.2, 131.4, 130.4, 129.7, 129.4, 129.3, 128.5, 127.3, 126.4, 126.1, 125.8, 123.8, 123.6, 39.4, 19.1 ppm.

**MS** (70 eV): m/z (%) = 378 [M]<sup>+</sup>(100), 196, 155, 77.

HRMS (ESI) calcd. for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 379.1805, found: 379.1802.





# $N'\mbox{-benzylidene-$N$-phenyl-2-(thiophen-2-yl)propanehydrazide (D22)}$

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 113.6 mg, 34% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.59 (m, 2H), 7.55 – 7.49 (m, 2H), 7.47 – 7.43 (m, 1H), 7.39 – 7.36 (d, *J* = 5.0 Hz, 3H), 7.25 (d, *J* = 2.8 Hz, 2H), 7.18 – 7.06 (m, 4H), 6.96 – 6.93 (m, 1H), 5.46 (d, *J* = 6.8 Hz, 1H), 1.70 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ 174.8, 144.5, 141.8, 136.0, 134.2, 130.2, 130.0, 129.3, 129.1, 128.8, 127.4, 126.6, 124.5, 124.1, 37.6, 19.5 ppm.

**MS** (70 eV): m/z (%) = 334 [M]<sup>+</sup>(100), 196, 111, 77.

**HRMS** (ESI) calcd. for C<sub>20</sub>H<sub>19</sub>N<sub>2</sub>OS [M+H]: 335.1212, found: 335.1209.





N'-benzylidene-2-cyclohexyl-N-phenylpropanehydrazide (D23)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 267.2 mg, 80% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.52 (m, 4H), 7.47 – 7.43 (m, 1H), 7.37 – 7.34 (m, 3H), 7.22 (s, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 3.87 – 3.63 (m, 1H), 1.93 (d, *J* = 12.4 Hz, 1H), 1.88 – 1.56 (m, 6H), 1.30 – 1.22 (m, 7H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.6, 140.9, 136.6, 134.6, 130.2, 129.7, 129.3, 129.1, 128.8, 127.1, 41.3, 41.1, 31.8, 29.9, 26.6, 26.5, 14.4 ppm.

**MS** (70 eV): m/z (%) = 334 [M]<sup>+</sup>(100), 196, 111, 69.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>27</sub>N<sub>2</sub>O [M+H]: 335.2117, found: 335.2116.





# N'-(benzylidene)-2-(cyclohex-3-en-1-yl)-N-phenylpropanehydrazide (D24)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 249.0 mg, 75% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.51 (m, 4H), 7.49 – 7.43 (m, 1H), 7.40 – 7.32 (m, 3H), 7.26 – 7.22 (m, 1H), 7.21 – 7.11 (m, 2H), 5.68 (d, *J* = 14.4 Hz, 2H), 3.87 (d, *J* = 17.6 Hz, 1H), 2.44 – 1.63 (m, 7H), 1.35 – 1.20 (m, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.3, 178.2, 141.2, 141.2, 136.5, 134.6, 130.2, 129.8, 129.3, 129.2, 128.8, 127.2, 126.9, 126.6, 126.4, 41.2, 40.2, 37.1, 36.8, 30.0, 28.8, 27.8, 25.8, 25.5, 25.4, 14.3 ppm.

**MS** (70 eV): m/z (%) = 332 [M]<sup>+</sup> (100), 252, 196, 109.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]: 333.1961, found: 333.1959.





### N'-benzylidene-3-cyano-2-methyl-N-phenylpropanehydrazide (D25)

The title compound was prepared according to the general procedure and purified by column chromatography to give the light-yellow oil, 186.2 mg, 64% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.51 (m, 4H), 7.50 – 7.44 (m, 1H), 7.40 – 7.33 (m, 3H), 7.31 (s, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 4.17 – 4.09 (m, 1H), 2.83 – 2.75 (m, 1H), 2.67 – 2.59 (m, 1H), 1.52 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.7, 142.8, 135.5, 133.9, 130.4, 130.3, 129.6, 129.1, 128.9, 127.4, 118.9, 34.5, 21.1, 17.3 ppm.

**MS** (70 eV): m/z (%) = 291 [M]<sup>+</sup>(100), 196, 167, 77.

HRMS (ESI) calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>3</sub>O [M+H]: 292.1444, found: 292.1443.





#### N'-benzylidene-2-methyl-N-phenylhexanehydrazide (D26)

The title compound was prepared according to the general procedure and purified by column chromatography to give the light-yellow oil, 194.0 mg, 63% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.50 (m, 4H), 7.47 – 7.42 (m, 1H), 7.39 – 7.30 (m, 3H), 7.25 – 7.22 (m, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 3.86 (d, *J* = 6.8 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.58 – 1.23 (m, 8H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.7, 141.1, 136.5, 134.6, 130.2, 129.8, 129.3, 129.1, 128.7, 127.2, 36.3, 33.7, 29.8, 22.9, 17.3, 14.2, 12.2 ppm.

**MS** (70 eV): m/z (%) = 308 [M]<sup>+</sup> (100), 196, 85, 43.

HRMS (ESI) calcd. for C<sub>20</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]: 309.1961, found: 309.1961.





*N'*-benzylidene-2-methyl-*N*-phenyloctanehydrazide (D27)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 225.1 mg, 67% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.51 (m, 4H), 7.47 – 7.42 (m, 1H), 7.36 – 7.33 (m, 3H), 7.24 (s, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 3.86 (d, *J* = 6.6 Hz, 1H), 1.93 – 1.85 (m, 1H), 1.42 – 1.21 (m, 12H), 0.87 (t, *J* = 6.6 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.7, 141.1, 136.5, 134.6, 130.2, 129.7, 129.3, 129.1, 128.7, 127.2, 36.2, 34.1, 31.9, 29.5, 27.5, 22.7, 17.3, 14.1 ppm.

**MS** (70 eV): m/z (%) = 336 [M]<sup>+</sup>(100), 196, 149, 57.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>29</sub>N<sub>2</sub>O [M+H]: 337.2274, found: 337.2272.





N'-benzylidene-2-methyl-N-phenyldecanehydrazide--methane (1/1) (D28)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 254.8 mg, 70% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.50 (m, 4H), 7.46 – 7.41 (m, 1H), 7.36 – 7.32 (m, 3H), 7.24 (s, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 3.87 (d, *J* = 6.6 Hz, 1H), 1.52 – 1.09 (m, 17H), 0.86 (t, *J* = 6.8 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.7, 141.1, 136.5, 134.6, 130.2, 129.8, 129.3, 129.1, 128.7, 127.2, 36.2, 34.1, 31.9, 29.9, 29.7, 29.4, 27.6, 22.8, 17.3, 14.2 ppm.

**MS** (70 eV): m/z (%) = 364 [M]<sup>+</sup>(100), 196, 149, 85.

HRMS (ESI) calcd. for C<sub>24</sub>H<sub>33</sub>N<sub>2</sub>O [M+H]: 365.2587, found: 365.2582.





#### N'-(4-methylbenzylidene)-N,2-diphenylpropanehydrazide (D29)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 314.6 mg, 92% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 – 7.46 (m, 4H), 7.45 – 7.39 (m, 3H), 7.31 (t, J = 7.6 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.19 – 7.14 (m, 2H), 7.12 (s, 1H), 7.08 (d, J = 7.6 Hz, 2H), 5.09 (d, J = 7.2 Hz, 1H), 2.35 (s, 3H), 1.59 (d, J = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.7, 142.5, 141.6, 140.0, 136.3, 131.7, 130.1, 129.5, 129.2, 129.1, 128.6, 127.8, 127.2, 126.6, 42.9, 21.5, 19.4 ppm.

**MS** (70 eV): m/z (%) = 342 [M]<sup>+</sup>(100), 225, 210, 105.

**HRMS** (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 343.1805, found: 343.1803.





*N'*-(3-methylbenzylidene)-*N*,2-diphenylpropanehydrazide (D30)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 283.9 mg, 83% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.52 – 7.42 (m, 4H), 7.39 – 7.34 (m, 1H), 7.32 – 7.27 (m, 4H), 7.21 – 7.14 (m, 2H), 7.12 – 7.08 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 5.08 (d, *J* = 7.2 Hz, 1H), 2.30 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 142.7, 141.8, 138.4, 136.4, 134.5, 130.7, 130.3, 129.3, 128.7, 128.1, 127.9, 126.8, 124.5, 43.1, 21.5, 19.7 ppm.

**MS** (70 eV): m/z (%) = 342 [M]<sup>+</sup>(100), 210, 105, 77.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 343.1805, found: 343.1804.





#### N'-(2-methylbenzylidene)-N,2-diphenylpropanehydrazide (D31)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 273.6 mg, 80% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 – 7.64 (m, 1H), 7.57 – 7.38 (m, 6H), 7.32 (t, J = 7.6 Hz, 2H), 7.26 – 7.19 (m, 3H), 7.13 – 7.07 (m, 3H), 5.09 (d, J = 6.8 Hz, 1H), 2.14 (s, 3H), 1.59 (d, J = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 142.4, 140.5, 136.9, 136.4, 132.3, 130.8, 130.2, 129.5, 129.2, 129.1, 128.6, 127.8, 126.6, 126.5, 126.2, 42.8, 19.6, 19.4 ppm.

**MS** (70 eV): m/z (%) = 342 [M]<sup>+</sup>(100), 225, 210, 105.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 343.1805, found: 343.1803.





*N*,2-diphenyl-*N'*-(2,4,6-trimethylbenzylidene)propanehydrazide (D32) The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 299.7 mg, 81% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.76 (s, 1H), 7.70 – 7.63 (m, 4H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.32 (m, 3H), 6.99 (s, 2H), 5.29 (d, *J* = 6.8 Hz, 1H), 2.40 (d, *J* = 6.8 Hz, 9H), 1.81 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.9, 143.1, 142.4, 138.8, 137.5, 136.8, 130.4, 129.7, 129.5, 129.3, 128.7, 128.5, 128.0, 126.8, 42.4, 21.3, 20.1 ppm.

**MS** (70 eV): m/z (%) = 370 [M]<sup>+</sup>(100), 225, 105, 93.

HRMS (ESI) calcd. for C<sub>25</sub>H<sub>27</sub>N<sub>2</sub>O [M+H]: 371.2118, found: 371.2117.





#### *N'*-(4-(*tert*-butyl)benzylidene)-*N*,2-diphenylpropanehydrazide (D33)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 334.1 mg, 87% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 – 7.41 (m, 7H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.18 (m, 1H), 7.14 (s, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 5.09 (d, *J* = 7.2 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H), 1.32 (s, 9H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.7, 153.2, 142.5, 141.5, 136.4, 131.7, 130.1, 129.2, 129.1, 128.6, 127.8, 127.0, 126.6, 125.7, 42.8, 34.9, 31.2, 19.4 ppm.

**MS** (70 eV): m/z (%) = 384 [M]<sup>+</sup>(100), 252, 195, 105.

HRMS (ESI) calcd. for C<sub>26</sub>H<sub>29</sub>N<sub>2</sub>O [M+H]: 385.2274, found: 385.2272.





### N'-([1,1'-biphenyl]-4-ylmethylene)-N,2-diphenylpropanehydrazide (D34)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 335.3 mg, 83% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.47 (m, 8H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.32 – 7.24 (m, 3H), 7.19 – 7.13 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 5.11 (d, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 142.7, 142.6, 141.2, 140.4, 136.4, 133.6, 130.3, 129.4, 129.3, 129.1, 128.8, 128.0, 127.9, 127.5, 127.2, 126.9, 43.2, 19.8 ppm.

**MS** (70 eV): m/z (%) = 404 [M]<sup>+</sup>(100), 281, 207, 105.

HRMS (ESI) calcd. for C<sub>28</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]: 405.1961, found: 405.1958.





# N'-(4-methoxybenzylidene)-N,2-diphenylpropanehydrazide (D35)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 322.2 mg, 90% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 – 7.41 (m, 6H), 7.39 – 7.33 (m, 1H), 7.29 (t, J = 7.6 Hz, 2H), 7.19 – 7.14 (m, 1H), 7.10 (s, 1H), 7.05 (d, J = 7.6 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.09 (d, J = 7.2 Hz, 1H), 3.72 (s, 3H), 1.58 (d, J = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.6, 161.1, 142.7, 141.5, 136.5, 130.2, 129.3, 129.2, 128.8, 128.7, 127.9, 127.2, 126.7, 114.3, 55.4, 43.0, 19.6 ppm.

**MS** (70 eV): m/z (%) = 358 [M]<sup>+</sup>(100), 226, 182, 105.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> [M+H]: 359.1754, found: 359.1750.





N'-(3-methoxybenzylidene)-N,2-diphenylpropanehydrazide (D36)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 290.0 mg, 81% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 (t, *J* = 7.6 Hz, 4H), 7.42 – 7.37 (m, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.17 (m, 2H), 7.15 – 7.10 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.89 – 6.83 (m, 1H), 5.07 (d, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.7, 160.0, 142.6, 141.4, 136.3, 135.8, 130.2, 129.8, 129.3, 129.2, 128.7, 127.7, 126.7, 120.5, 116.3, 111.2, 55.4, 43.2, 19.7 ppm.

**MS** (70 eV): m/z (%) = 358 [M]<sup>+</sup> (100), 226, 105, 77.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> [M+H]: 359.1754, found: 359.1751.





N'-(2-methoxybenzylidene)-N,2-diphenylpropanehydrazide (D37)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 261.3 mg, 73% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.79 (d, *J* = 7.6 Hz, 1H), 7.49 (s, 1H), 7.39 – 7.32 (m, 4H), 7.28 – 7.23 (m, 1H), 7.21 – 7.13 (m, 3H), 7.08 – 7.04 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 4.99 (d, *J* = 7.2 Hz, 1H), 3.44 (s, 3H), 1.48 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.6, 156.9, 141.5, 136.7, 135.4, 130.0, 128.9, 128.0, 127.9, 127.5, 126.7, 125.5, 125.0, 121.8, 119.7, 109.9, 54.2, 41.8, 18.4 ppm.

**MS** (70 eV): m/z (%) = 358 [M]<sup>+</sup>(100), 226, 210, 105.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> [M+H]: 359.1754, found: 359.1753.





#### N'-(4-fluorobenzylidene)-N,2-diphenylpropanehydrazide (D38)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 304.5 mg, 88% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.39 (m, 7H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.17 (m, 4.3 Hz, 1H), 7.13 – 6.97 (m, 5H), 5.04 (d, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.6, 164.9, 162.4, 142.5, 140.2, 136.2, 130.7, 130.2, 129.3, 19.1, 129.0, 128.9, 128.6, 127.7, 126.7, 115.9, 115.7, 43.0, 19.5 ppm.

<sup>19</sup>**F** NMR (376 MHz, CDCl<sub>3</sub>) δ -110.4.

**MS** (70 eV): m/z (%) = 346 [M]<sup>+</sup>(100), 214, 105, 77.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>FN<sub>2</sub>O [M+H]: 347.1554, found: 347.1551.





*N'*-(3-fluorobenzylidene)-*N*,2-diphenylpropanehydrazide (D39)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 245.7 mg, 71% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.51 – 7.45 (m, 4H), 7.43 – 7.37 (m, 1H), 7.34 – 7.23 (m, 4H), 7.23 – 7.15 (m, 2H), 7.11 – 7.02 (m, 3H), 7.01 – 6.95 (m, 1H), 5.03 (d, *J* = 6.8 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.8, 164.3, 161.9, 142.5, 140.1, 136.9, 136.8, 136.1, 130.3, 129.4, 129.1, 128.7, 127.7, 126.8, 123.6, 123.5, 116.9, 116.6, 113.3, 113.1, 43.2, 19.6 ppm.

<sup>19</sup>**F** NMR (376 MHz, CDCl<sub>3</sub>) δ -112.4.

**MS** (70 eV): m/z (%) = 346 [M]<sup>+</sup>(100), 214, 105, 77.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>FN<sub>2</sub>O [M+H]: 347.1554, found: 347.1549.





N'-(2-fluorobenzylidene)-N,2-diphenylpropanehydrazide (D40)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 214.5 mg, 62% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.87 (s, 1H), 7.53 – 7.39 (m, 5H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.26 – 7.11 (m, 3H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.95 – 6.88 (m, 1H), 5.09 (s, 1H), 1.69 – 1.53 (m, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 162.7, 160.2, 142.5, 136.1, 134.8, 131.4, 131.3, 130.3, 129.4, 129.1, 128.7, 127.8, 126.8, 124.5, 122.4, 122.3, 116.0, 115.8, 43.1, 19.7 ppm.

<sup>19</sup>**F** NMR (376 MHz, CDCl<sub>3</sub>) δ -120.5.

**MS** (70 eV): m/z (%) = 346 [M]<sup>+</sup>(100), 214, 105, 77.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>FN<sub>2</sub>O [M+H]: 347.1554, found: 347.1550.





N'-(4-chlorobenzylidene)-N,2-diphenylpropanehydrazide (D41)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 311.3 mg, 86% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 – 7.37 (m, 7H), 7.52 – 7.40 (m, 4H), 7.22 – 7.17 (m, 1H), 7.09 – 7.04 (m, 3H), 5.08 (d, *J* = 6.8 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.7, 142.4, 140.1, 136.1, 135.6, 133.0, 130.2, 129.4, 129.1, 129.0, 128.7, 128.4, 127.7, 126.7, 43.1, 19.6 ppm.

**MS** (70 eV): m/z (%) = 362 [M]<sup>+</sup>(100), 230, 105, 77.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>ClN<sub>2</sub>O [M+H]: 363.1258, found: 363.1254.





N'-(2-chlorobenzylidene)-N,2-diphenylpropanehydrazide (D42)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 224.4 mg, 62% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (d, *J* = 7.6 Hz, 1H), 7.59 (s, 1H), 7.51 – 7.45 (m, 4H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.27 – 7.23 (m, 1H), 7.23 – 7.16 (m, 3H), 7.09 (d, *J* = 7.6 Hz, 2H), 5.05 (d, *J* = 6.8 Hz, 1H), 1.60 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 142.5, 138.3, 136.2, 134.4, 131.9, 130.7, 130.3, 129.9, 129.5, 129.0, 128.8, 127.8, 127.1, 126.8, 43.2, 19.7 ppm.

**MS** (70 eV): m/z (%) = 362 [M]<sup>+</sup>(100), 224, 105, 77.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>ClN<sub>2</sub>O [M+H]: 363.1258, found: 363.1256.







N'-(4-bromobenzylidene)-N,2-diphenylpropanehydrazide (D43)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 332.9 mg, 82% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 – 7.35 (m, 7H), 7.34 – 7.25 (m, 4H), 7.16 (t, J = 7.6 Hz, 1H), 7.06 – 7.01 (m, 3H), 5.03 (d, J = 7.2 Hz, 1H), 1.58 (d, J = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.7, 142.6, 140.1, 136.2, 133.5, 132.0, 130.3, 129.4, 129.2, 128.8, 128.7, 127.7, 126.8, 124.0, 43.2, 19.7 ppm.

**MS** (70 eV): m/z (%) = 406 [M]<sup>+</sup>(100), 274, 194, 105.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>BrN<sub>2</sub>O [M+H]: 407.0753, found: 407.0751.





#### N'-(2-bromobenzylidene)-N,2-diphenylpropanehydrazide (D44)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 296.4 mg, 73% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.48 – 7.40 (m, 4H), 7.33 (t, *J* = 7.6 Hz, 3H), 7.24 – 7.19 (m, 1H), 7.18 – 7.13 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 5.03 (d, *J* = 6.8 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.7, 142.4, 140.8, 136.1, 133.3, 133.1, 130.9, 130.3, 129.4, 128.9, 128.7, 127.7, 127.6, 127.4, 126.7, 124.5, 43.1, 19.6 ppm.

**MS** (70 eV): m/z (%) = 406 [M]<sup>+</sup>(100), 274, 225, 195.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>BrN<sub>2</sub>O [M+H]: 407.0753, found: 407.0750.





*N'*-(3-hydroxy-4-methoxybenzylidene)-*N*,2-diphenylpropanehydrazide (D45) The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 299.2 mg, 80% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.47 (t, *J* = 7.6 Hz, 4H), 7.41 – 7.37 (m, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.15 (m, 2H), 7.10 – 7.05 (m, 3H), 6.82 – 6.75 (m, 2H), 6.36 (s, 1H), 5.04 (d, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 1.58 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.6, 147.9, 147.2, 142.9, 142.1, 136.4, 130.2, 129.2, 128.7, 127.6, 126.8, 126.7, 122.5, 114.6, 108.1, 56.0, 43.3, 19.7 ppm.

**MS** (70 eV): m/z (%) = 374 [M]<sup>+</sup>(100), 281, 242, 207.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> [M+H]: 375.1703, found: 375.1701.





# *N'*-(2-hydroxybenzylidene)-*N*,2-diphenylpropanehydrazide (D46) The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 251.1 mg, 73% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 11.86 – 10.26 (m, 1H), 7.55 – 7.40 (m, 5H), 7.35 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 7.13 (s, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.74 (t, *J* = 7.2 Hz, 1H), 4.67 – 3.58 (m, 1H), 1.57 (s, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.2, 157.4, 146.2, 141.0, 135.3, 131.6, 130.5, 129.7, 129.4, 129.0, 127.5, 127.1, 127.1, 119.6, 117.6, 116.8, 112.5, 43.5, 20.5 ppm.

**MS** (70 eV): m/z (%) = 344 [M]<sup>+</sup>(100), 281, 212, 105.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> [M+H]: 345.1597, found: 345.1595.





*N*,2-diphenyl-*N'*-(4-(trifluoromethoxy)benzylidene)propanehydrazide (D47) The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 358.4 mg, 87% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.52 (t, *J* = 8.8 Hz, 4H), 7.46 (d, *J* = 7.2 Hz, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.14 – 7.05 (m, 3H), 5.03 (d, *J* = 6.8 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.7, 150.0, 142.4, 139.7, 136.1, 133.1, 130.2, 129.3, 129.1, 128.7, 128.6, 127.6, 126.7, 121.7, 121.0, 119.1, 43.1, 19.5 ppm.

<sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>) δ -57.7.

**MS** (70 eV): m/z (%) = 412 [M]<sup>+</sup> (100), 280, 105, 77.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub> [M+H]: 413.1471, found: 413.1467.





*N*,2-diphenyl-*N'*-(4-(trifluoromethyl)benzylidene)propanehydrazide (D48) The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 328.7 mg, 83% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.60 (s, 4H), 7.56 – 7.51 (m, 2H), 7.49 – 7.44 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.15 (s, 1H), 7.09 (d, *J* = 7.6 Hz, 2H), 5.03 (d, *J* = 6.8 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 142.3, 139.5, 137.8, 136.0, 131.4, 131.0, 130.3, 129.5, 129.0, 128.7, 127.6, 127.3, 126.7, 125.6, 125.3, 122.6, 43.2, 19.5 ppm.

<sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.7.

**MS** (70 eV): m/z (%) = 396 [M]<sup>+</sup> (100), 264, 105, 77.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O [M+H]: 397.1522, found: 397.1518.





# N'-(4-cyanobenzylidene)-N,2-diphenylpropanehydrazide (D49)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 289.5 mg, 82% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.55 (m, 4H), 7.52 – 7.40 (m, 5H), 7.34 – 7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 7.11 (s, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 5.03 (d, *J* = 6.8 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 142.3, 139.1, 138.7, 135.8, 132.5, 130.4, 129.6, 129.0, 128.8, 127.6, 126.9, 118.7, 112.7, 43.3, 19.7 ppm.

**MS** (70 eV): m/z (%) = 353 [M]<sup>+</sup>(100), 221, 105, 77.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>20</sub>N<sub>3</sub>O [M+H]: 354.1600, found: 354.1595.





methyl-4-((2-phenyl-2-(2-phenylpropanoyl)hydrazineylidene)methyl)benzoate (D50)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 347.4 mg, 90% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.43 (m, 4H), 7.40 – 7.35 (m, 1H), 7.31 – 7.26 (m, 2H), 7.18 – 7.14 (m, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 5.06 (d, *J* = 6.8 Hz, 1H), 3.82 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 177.6, 175.8, 166.5, 142.4, 140.5, 140.1, 138.7, 136.0, 130.9, 130.3, 130.0, 129.5, 129.1, 128.8, 128.7, 127.7, 127.1, 126.8, 52.2, 45.3, 43.2, 19.7, 18.5 ppm.

**MS** (70 eV): m/z (%) = 386 [M]<sup>+</sup>(100), 254, 105, 77.



**HRMS** (ESI) calcd. for C<sub>24</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> [M+H]: 387.1703, found: 387.1700.


# N'-(naphthalen-2-ylmethylene)-N,2-diphenylpropanehydrazide (D51)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 347.8 mg, 92% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.75 – 7.71 (m, 1H), 7.66 (s, 1H), 7.55 – 7.50 (m, 4H), 7.49 – 7.40 (m, 3H), 7.36 – 7.29 (m, 3H), 7.22 – 7.18 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 5.14 (d, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 142.5, 141.6, 136.3, 134.1, 133.2, 132.2, 130.2, 129.2, 129.1, 128.7, 128.6, 128.2, 127.9, 127.8, 127.0, 126.7, 126.6, 122.8, 43.0, 19.5 ppm.

**MS** (70 eV): m/z (%) = 378 [M]<sup>+</sup>(100), 246, 207, 153.

HRMS (ESI) calcd. for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 379.1805, found: 379.1802.





N'-(naphthalen-1-ylmethylene)-N,2-diphenylpropanehydrazide (D52)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 306.2 mg, 81% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 7.2 Hz, 1H), 7.84 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.34 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.12 (m, 3H), 5.15 (d, *J* = 6.8 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.9, 142.6, 141.3, 136.5, 134.0, 130.9, 130.6, 130.5, 130.0, 129.5, 129.0, 128.9, 128.0, 127.2, 127.1, 126.9, 126.3, 125.5, 123.8, 43.2, 20.1 ppm.

**MS** (70 eV): m/z (%) = 378 [M]<sup>+</sup>(100), 246, 153, 105.

HRMS (ESI) calcd. for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 379.1805, found: 379.1802.





# N'-(anthracen-9-ylmethylene)-N,2-diphenylpropanehydrazide (D53)

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 329.6 mg, 77% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 8.36 (s, 1H), 8.25 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.40 (m, 5H), 7.39 – 7.31 (m, 5H), 7.27 (d, *J* = 7.2 Hz, 1H), 5.08 (d, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.1, 142.4, 141.2, 136.6, 131.3, 130.6, 130.0, 129.6, 129.4, 129.2, 129.1, 129.0, 128.9, 128.8, 128.0, 127.8, 126.8, 126.0, 125.4, 124.8, 119.8, 47.9, 42.6, 20.1, 18.7 ppm.

**MS** (70 eV): m/z (%) = 428 [M]<sup>+</sup>(100), 378, 246, 105.



**HRMS** (ESI) calcd. for C<sub>30</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]: 429.1961, found: 429.1966.



*N*,2-diphenyl-*N'*-(thiophen-2-ylmethylene)propanehydrazide (D54) The title compound was prepared according to the general procedure and purified

by column chromatography to give the yellow oil, 136.9 mg, 41% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.57 – 7.46 (m, 4H), 7.45 – 7.40 (m, 1H), 7.34 – 7.28 (m, 3H), 7.27 – 7.18 (m, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 3.4 Hz, 2H), 4.99 (d, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.4, 142.3, 139.8, 136.1, 135.9, 130.2, 129.6, 129.3, 129.1, 128.6, 128.0, 127.7, 127.4, 126.6, 42.8, 19.3 ppm.

**MS** (70 eV): m/z (%) = 334 [M]<sup>+</sup>(100), 202, 105, 77.

HRMS (ESI) calcd. for C<sub>20</sub>H<sub>19</sub>N<sub>2</sub>OS [M+H]: 335.1212, found: 335.1212.





# N'-benzylidene-2-phenyl-N-(p-tolyl)propanehydrazide (D55)

The title compound was prepared according to the general procedure and purified by column chromatography to give the light-yellow oil, 311.2 mg, 91% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (d, *J* = 7.2 Hz, 4H), 7.31 – 7.22 (m, 7H), 7.17 – 7.11 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 5.09 (d, *J* = 7.2 Hz, 1H), 2.33 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 142.7, 141.5, 139.3, 134.6, 133.6, 131.0, 129.9, 129.0, 128.8, 128.7, 127.9, 127.3, 126.8, 43.1, 21.5, 19.7 ppm.

**MS** (70 eV): m/z (%) = 342 [M]<sup>+</sup>(100), 210, 105, 77.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 343.1805, found: 343.1806.





# N'-benzylidene-2-phenyl-N-(m-tolyl)propanehydrazide (D56)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 273.6 mg, 80% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 6.8 Hz, 4H), 7.37 – 7.25 (m, 6H), 7.21 – 7.13 (m, 3H), 6.87 – 6.83 (m, 2H), 5.09 (d, *J* = 6.8 Hz, 1H), 2.32 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 142.6, 141.6, 140.3, 136.2, 134.6, 130.2, 130.2, 129.9, 129.7, 128.8, 128.7, 127.9, 127.3, 126.7, 126.1, 43.0, 21.5, 19.6 ppm.

**MS** (70 eV): m/z (%) = 342 [M]<sup>+</sup>(100), 210, 105, 77.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 343.1805, found: 343.1805.





# N'-benzylidene-2-phenyl-N-(o-tolyl)propanehydrazide (D57)

The title compound was prepared according to the general procedure and purified by column chromatography to give the light-yellow oil, 174.4 mg, 51% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 – 7.34 (m, 4H), 7.28 – 7.10 (m, 8H), 7.10 – 7.03 (m, 1H), 7.01 – 6.97 (m, 1H), 6.89 (s, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.02 (d, *J* = 7.2 Hz, 1H), 2.00 (s, 1H), 1.54 (s, 2H), 1.53 – 1.47 (m, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.5, 175.2, 142.5, 142.2, 140.8, 137.3, 136.8, 135.2, 134.9, 134.6, 131.6, 131.5, 129.9, 129.7, 129.4, 129.2, 128.8, 128.7, 128.6, 128.1, 127.9, 127.8, 127.7, 127.3, 126.8, 42.8, 19.5, 19.2, 17.6, 16.9 ppm.

**MS** (70 eV): m/z (%) = 342 [M]<sup>+</sup> (100), 239, 210, 105.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 343.1805, found: 343.1804.





#### *N'*-benzylidene-*N*-(4-ethylphenyl)-2-phenylpropanehydrazide (D58)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 327.5 mg, 92% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 7.2 Hz, 4H), 7.32 – 7.23 (m, 7H), 7.18 – 7.12 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.09 (d, *J* = 7.2 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.59 (d, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.9, 145.4, 142.7, 141.5, 134.6, 133.7, 129.8, 129.7, 129.0, 128.8, 128.7, 127.9, 127.3, 126.7, 43.0, 28.8, 19.7, 15.5 ppm.

**MS** (70 eV): m/z (%) = 356 [M]<sup>+</sup>(100), 253, 224, 105.

HRMS (ESI) calcd. for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]: 357.1961, found: 357.1962.





# N'-benzylidene-N-(3-fluorophenyl)-2-phenylpropanehydrazide (D59)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 269.9 mg, 78% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.43 – 7.38 (m, 2H), 7.37 – 7.28 (m, 3H), 7.25 – 7.15 (m, 5H), 7.10 – 6.97 (m, 3H), 6.76 – 6.67 (m, 2H), 4.94 (d, *J* = 4.8 Hz, 1H), 1.48 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.7, 164.8, 162.3, 142.2, 141.9, 137.8, 137.7, 134.2, 131.5, 131.4, 130.1, 128.8, 127.8, 127.4, 126.8, 125.2, 125.1, 116.9, 116.7, 116.5, 43.0, 19.5 ppm.

<sup>19</sup>**F** NMR (376 MHz, CDCl<sub>3</sub>) δ -110.0.

**MS** (70 eV): m/z (%) = 346 [M]<sup>+</sup>(100), 214, 105, 77.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>FN<sub>2</sub>O [M+H]: 347.1554, found: 347.1552.





#### N'-benzylidene-N-(2,6-difluorophenyl)-2-phenylpropanehydrazide (D60)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 152.9 mg, 42% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.52 (m, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.44 – 7.25 (m, 6H), 7.23 – 7.14 (m, 2H), 7.11 – 6.97 (m, 2H), 5.06 (d, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ 175.4, 160.5, 160.3, 160.2, 158.0, 157.9, 157.8, 157.7, 141.9, 141.0, 133.9, 131.6, 131.5, 131.4, 130.1, 128.7, 128.5, 127.8, 127.5, 126.7, 112.7, 112.6, 112.5, 112.4, 112.3, 43.2, 19.4 ppm.

<sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>) δ -115.5, -115.9.

**MS** (70 eV): m/z (%) = 364 [M]<sup>+</sup>(100), 232, 209, 105.

**HRMS** (ESI) calcd. for C<sub>22</sub>H<sub>19</sub>F<sub>2</sub>N<sub>2</sub>O [M+H]: 365.1459, found: 365.1459.







# N'-benzylidene-N-(3-bromophenyl)-2-phenylpropanehydrazide (D61)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 337.0 mg, 83% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 – 7.48 (m, 3H), 7.44 (d, *J* = 6.8 Hz, 2H), 7.34 – 7.27 (m, 6H), 7.23 (s, 1H), 7.19 – 7.14 (t, *J* = 7.4 Hz, 1H), 7.11 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 5.02 (d, *J* = 5.6 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.7, 142.2, 142.0, 138.2, 137.6, 134.2, 132.6, 132.4, 131.4, 130.5, 130.1, 128.8, 128.1, 127.8, 127.4, 126.8, 126.4, 123.6, 122.3, 115.5, 111.4, 43.0, 19.5 ppm.

**MS** (70 eV): m/z (%) = 406 [M]<sup>+</sup>(100), 274, 105, 77.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>BrN<sub>2</sub>O [M+H]: 407.0753, found: 407.0753.





#### N'-benzylidene-N-(2-bromophenyl)-2-phenylpropanehydrazide (D62)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 162.4 mg, 40% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (dd, J = 8.0, 1.6 Hz, 1H), 7.68 (dd, J = 8.0, 1.2 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.53 – 7.47 (m, 2H), 7.48 – 7.39 (m, 1H), 7.40 – 7.28 (m, 5H), 7.27 – 7.16 (m, 2H), 7.05 (dd, J = 7.6, 1.6 Hz, 1H), 6.99 (d, J = 3.2 Hz, 1H), 5.30 – 4.94 (m, 1H), 1.62 (d, J = 7.2, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.3, 175.1, 142.1, 141.4, 141.0, 135.7, 135.4, 134.3, 134.1, 133.9, 131.4, 131.3, 130.9, 129.9, 129.2, 129.1, 128.7, 128.6, 128.3, 127.9, 127.3, 126.7, 123.9, 123.7, 42.7, 19.4, 19.1 ppm.

**MS** (70 eV): m/z (%) = 406 [M]<sup>+</sup>(100), 274, 194, 105.



**HRMS** (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>BrN<sub>2</sub>O [M+H]: 407.0753, found: 407.0751.



# *N'*-benzylidene-2-phenyl-*N*-(4-(trifluoromethoxy)phenyl)propanehydrazide (D63)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 346.1 mg, 84% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.52 (m, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.25 (m, 7H), 7.20 – 7.13 (m, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 5.07 (d, *J* = 6.4 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.9, 149.4, 142.3, 141.8, 134.7, 134.2, 131.0, 130.1, 128.8, 127.8, 127.4, 126.8, 122.6, 43.0, 19.5 ppm.

<sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>) δ -57.7.

**MS** (70 eV): m/z (%) = 412 [M]<sup>+</sup>(100), 280, 105, 77.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub> [M+H]: 413.1471, found: 413.1470.





# N'-benzylidene-2-phenyl-N-(4-(trifluoromethyl)phenyl)propanehydrazide (D64)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 316.8 mg, 80% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.52 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.25 (m, 5H), 7.23 – 7.16 (m, 3H), 7.13 (s, 1H), 5.06 (d, *J* = 5.6 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.7, 142.1, 139.8, 134.1, 131.5, 131.1, 130.2, 130.0, 128.9, 128.8, 127.8, 127.4, 126.9, 125.2, 122.5, 43.1, 19.5 ppm.

<sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.6.

**MS** (70 eV): m/z (%) = 396 [M]<sup>+</sup>(100), 264, 105, 77.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O [M+H]: 397.1522, found: 397.1518.





# N'-benzylidene-N-(naphthalen-1-yl)-2-phenylpropanehydrazide (D65)

The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 162.5 mg, 43% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.88 (dd, *J* = 26.0, 8.0 Hz, 2H), 7.60 – 7.54 (m, 3H), 7.52 – 7.43 (m, 3H), 7.42 – 7.34 (m, 3H), 7.33 – 7.24 (m, 4H), 7.19 – 7.12 (m, 1H), 6.94 (s, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 5.32 – 5.21 (m, 1H), 1.66 (t, *J* = 8.0 Hz, 3H) ppm.

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ 176.1, 175.9, 142.5, 142.3, 141.8, 134.8, 134.5, 134.4, 133.1, 132.8, 130.0, 129.9, 129.8, 128.8, 128.7, 128.6, 128.2, 128.0, 127.8, 127.7, 127.5, 127.3, 127.0, 126.8, 126.7, 126.0, 125.9, 122.6, 122.3, 43.2, 43.1, 19.6, 19.3 ppm.

**MS** (70 eV): m/z (%) = 378 [M]<sup>+</sup>(100), 246, 142, 105.

HRMS (ESI) calcd. for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 379.1805, found: 379.1805.





#### N'-benzylidene-N-(naphthalen-2-yl)-2-phenylpropanehydrazide (D66)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 310.0 mg, 82% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.62 (s, 1H), 7.60 – 7.41 (m, 6H), 7.41 – 7.25 (m, 5H), 7.24 – 7.17 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 5.15 (d, *J* = 6.8 Hz, 1H), 1.63 (d, *J* = 6.8 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.0, 142.5, 141.8, 134.4, 133.9, 133.6, 133.3, 130.3, 129.8, 128.7, 128.3, 127.9, 127.3, 127.2, 126.7, 126.2, 43.0, 19.5 ppm.

**MS** (70 eV): m/z (%) = 378 [M]<sup>+</sup>(100), 246, 105, 77.



**HRMS** (ESI) calcd. for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 379.1805, found: 379.1804.





The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 249.7 mg, 73% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 – 7.51 (m, 3H), 7.49 – 7.43 (m, 2H), 7.36 – 7.26 (m, 5H), 7.24 – 7.13 (m, 4H), 7.00 (d, *J* = 6.8 Hz, 2H), 5.30 (d, *J* = 16.4 Hz, 1H), 5.17 – 5.06 (m, 2H), 1.61 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.2, 142.3, 139.9, 135.2, 134.8, 129.7, 128.9, 128.7, 128.6, 127.9, 127.3, 127.2, 126.8, 126.3, 44.8, 42.4, 19.5 ppm.

**MS** (70 eV): m/z (%) = 342 [M]<sup>+</sup>(100), 238, 196, 182.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 343.1805, found: 343.1805.





# N'-benzylidene-N-(4-methoxybenzyl)-2-phenylpropanehydrazide (D68)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 264.1 mg, 71% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 – 7.53 (m, 3H), 7.50 – 7.41 (m, 3H), 7.36 – 7.27 (m, 5H), 7.22 – 7.16 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.24 (d, *J* = 16.4 Hz, 1H), 5.13 – 5.04 (m, 2H), 3.71 (s, 3H), 1.60 (d, *J* = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.2, 158.8, 142.3, 139.8, 134.8, 129.6, 128.9, 128.7, 128.6, 127.9, 127.6, 127.1, 126.7, 126.3, 114.3, 114.1, 55.3, 44.2, 42.3, 19.4 ppm.

**MS** (70 eV): m/z (%) = 372 [M]<sup>+</sup>(100), 268, 136, 121.

HRMS (ESI) calcd. for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub> [M+H]: 373.1911, found: 373.1912.





N'-benzylidene-N,3-diphenylpropanehydrazide (D75)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 262.4 mg, 80% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.51 (m, 4H), 7.50 – 7.44 (m, 1H), 7.37 – 7.28 (m, 7H), 7.24 – 7.17 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.36 (s, 2H), 3.23 – 2.99 (m, 2H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.3, 141.6, 136.1, 134.3, 130.2, 129.9, 129.3, 128.7, 128.5, 127.2, 126.1, 36.0, 31.3 ppm.

**MS** (70 eV): m/z (%) = 328 [M]<sup>+</sup>(100), 225, 196, 105.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O [M+H]: 329.1648, found: 329.1645.





# N'-benzylidene-N-phenyl-3-(o-tolyl)propanehydrazide (D76)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 277.0 mg, 81% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.47 (m, 4H), 7.46 – 7.41 (m, 1H), 7.33 – 7.26 (m, 4H), 7.21 (s, 1H), 7.16 – 7.08 (m, 5H), 3.32 (s, 2H), 3.16 – 3.08 (m, 2H), 2.39 (s, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.5, 141.8, 139.7, 136.3, 134.4, 130.4, 130.3, 130.0, 129.4, 129.2, 128.8, 127.3, 126.4, 126.2, 34.6, 28.9, 19.6 ppm.

**MS** (70 eV): m/z (%) = 342 [M]<sup>+</sup>(100), 196, 105, 93.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 343.1805, found: 343.1806.





# N'-benzylidene-3-(2-methoxyphenyl)-N-phenylpropanehydrazide (D77)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 275.7 mg, 77% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.51 (m, 4H), 7.49 – 7.43 (m, 1H), 7.35 – 7.31 (m, 3H), 7.28 – 7.24 (m, 1H), 7.23 – 7.18 (m, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.33 (s, 2H), 3.15 – 3.10 (m, 2H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.9, 157.7, 141.2, 136.3, 134.5, 130.4, 130.2, 129.8, 129.7, 129.3, 129.2, 128.6, 127.4, 127.2, 120.4, 110.3, 55.3, 34.3, 26.5 ppm.

**MS** (70 eV): m/z (%) = 358 [M]<sup>+</sup>(100), 255, 196, 121.

HRMS (ESI) calcd. for C23H23N2O2 [M+H]: 359.1754, found: 359.1754.





N'-benzylidene-3-(2-fluorophenyl)-N-phenylpropanehydrazide (D78)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 245.7 mg, 71% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.36 (m, 4H), 7.33 – 7.28 (m, 1H), 7.23 – 7.16 (m, 4H), 7.07 (s, 1H), 7.04 – 6.97 (m, 3H), 6.95 – 6.91 (m, 1H), 6.90 – 6.82 (m, 1H), 3.25 (s, 2H), 3.04 (t, *J* = 7.6 Hz, 2H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.2, 162.7, 160.3, 141.7, 136.1, 134.3, 131.2, 130.3, 130.0, 129.4, 129.3, 128.8, 128.4, 128.2, 128.0, 127.3, 124.1, 115.5, 115.2, 34.5, 25.2, 25.1 ppm.

<sup>19</sup>**F** NMR (376 MHz, CDCl<sub>3</sub>) δ -118.0.

**MS** (70 eV): m/z (%) = 346 [M]<sup>+</sup>(100), 243, 196, 109.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>FN<sub>2</sub>O [M+H]: 347.1554, found: 347.1553.





# N'-benzylidene-3-(2-chlorophenyl)-N-phenylpropanehydrazide (D79)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 253.4 mg, 70% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.49 (m, 4H), 7.46 – 7.41 (m, 1H), 7.38 – 7.29 (m, 5H), 7.20 – 7.16 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 3H), 3.39 (s, 2H), 3.27 – 3.21 (m, 2H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.2, 141.8, 139.1, 136.1, 134.3, 134.2, 131.0, 130.3, 130.0, 129.6, 129.4, 129.3, 128.7, 127.7, 127.3, 126.9, 33.9, 29.4 ppm.

**MS** (70 eV): m/z (%) = 362 [M]<sup>+</sup>(100), 224, 196, 125.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>ClN<sub>2</sub>O [M+H]: 363.1259, found: 363.1255.





# N'-benzylidene-3-(naphthalen-1-yl)-N-phenylpropanehydrazide (D80)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 275.9 mg, 73% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.20 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.44 (m, 5H), 7.43 – 7.35 (m, 5H), 7.25 – 7.21 (m, 3H), 7.17 (s, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 3.61 – 3.56 (m, 2H), 3.55 – 3.44 (m, 2H) ppm.

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ 174.6, 142.0, 137.7, 136.3, 134.3, 134.1, 132.1, 130.4, 130.0, 129.5, 129.4, 129.1, 128.8, 127.4, 127.2, 126.6, 126.2, 125.8, 125.7, 124.1, 35.5, 29.0 ppm.

**MS** (70 eV): m/z (%) = 378 [M]<sup>+</sup>(100), 251, 155, 77.

HRMS (ESI) calcd. for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 379.1805, found: 379.1803.







# N'-benzylidene-3-cyclohexyl-N-phenylpropanehydrazide (D81)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 257.2 mg, 77% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.51 – 7.41 (m, 4H), 7.38 – 7.33 (m, 1H), 7.29 – 7.22 (m, 3H), 7.13 (s, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 2.94 (s, 2H), 1.74 (d, *J* = 12.8 Hz, 2H), 1.66 – 1.55 (m, 5H), 1.21 – 1.09 (m, 4H), 0.95 – 0.87 (m, 2H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.8, 141.3, 136.3, 134.5, 130.2, 129.8, 129.3, 129.2, 128.7, 127.2, 37.7, 33.3, 32.8, 31.9, 26.7, 26.4, 25.3, 22.7, 14.2 ppm.

**MS** (70 eV): m/z (%) = 334 [M]<sup>+</sup> (100), 196, 93, 55.

HRMS (ESI) calcd. for C<sub>22</sub>H<sub>27</sub>N<sub>2</sub>O [M+H]: 335.2118, found: 335.2121.





# N'-benzylidene-N-phenylheptanehydrazide (D82)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 246.4 mg, 80% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.51 (m, 4H), 7.49 – 7.43 (m, 1H), 7.38 – 7.32 (m, 3H), 7.25 – 7.21 (m, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 3.02 (s, 2H), 1.85 – 1.79 (m, 2H), 1.78 – 1.69 (m, 1H), 1.47 – 1.23 (m, 5H), 0.91 (t, *J* = 6.8 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.4, 141.2, 136.3, 134.5, 130.2, 129.8, 129.3, 129.2, 128.7, 127.1, 37.7, 34.2, 33.3, 32.8, 31.8, 29.3, 26.7, 26.4, 25.2, 22.6, 14.2 ppm.
MS (70 eV): m/z (%) = 308 [M]<sup>+</sup>(100), 196, 193, 43.

HRMS (ESI) calcd. for C<sub>20</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]: 309.1961, found: 309.1960.





N'-benzylidene-N-phenylundecanehydrazide--methane (1/1) (D83)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 262.1 mg, 72% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.53 (m, 4H), 7.50 – 7.45 (m, 1H), 7.39 – 7.35 (m, 3H), 7.24 (s, 1H), 7.18 (d, *J* = 7.2 Hz, 2H), 3.04 (s, 2H), 1.87 – 1.78 (m, 2H), 1.47 – 1.26 (m, 14H), 0.89 (t, *J* = 6.8 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.4, 141.2, 136.3, 134.5, 130.2, 129.8, 129.3, 129.2, 128.7, 127.1, 120.4, 119.8, 34.2, 32.0, 29.7, 29.6, 29.5, 29.4, 27.6, 25.3, 22.7, 18.1, 14.2 ppm.

**MS** (70 eV): m/z (%) = 364 [M]<sup>+</sup>(100), 281, 196, 93.

HRMS (ESI) calcd. for C<sub>24</sub>H<sub>33</sub>N<sub>2</sub>O [M+H]: 365.2587, found: 365.2582.





N'-benzylidene-N-(m-tolyl)-3-(o-tolyl)propanehydrazide (D84)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 288.4 mg, 81% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.51 (m, 2H), 7.44 – 7.37 (m, 1H), 7.32 – 7.23 (m, 5H), 7.22 (s, 1H), 7.16 – 7.11 (m, 3H), 6.96 – 6.92 (m, 2H), 3.32 (s, 2H), 3.14 – 3.09 (m, 2H), 2.39 (s, 6H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.5, 141.8, 140.4, 139.8, 136.3, 136.1, 134.4, 130.4, 130.2, 130.1, 129.9, 129.8, 129.2, 128.8, 127.3, 126.4, 126.2, 34.6, 28.9, 21.5, 19.6 ppm.

**MS** (70 eV): m/z (%) = 356 [M]<sup>+</sup>(100), 210, 105, 91.

HRMS (ESI) calcd. for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]: 357.1961, found: 357.1960.





# N'-benzylidene-3-(o-tolyl)-N-(4-(trifluoromethyl)phenyl)propanehydrazide (D85)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 270.6 mg, 66% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.49 (m, 2H), 7.38 – 7.32 (m, 3H), 7.28 (d, *J* = 8.4 Hz, 3H), 7.20 (s, 1H), 7.17 – 7.12 (m, 3H), 3.38 – 3.23 (m, 2H), 3.21 – 3.04 (m, 2H), 2.40 (s, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.4, 142.3, 139.6, 139.4, 136.3, 133.9, 131.5, 131.2, 130.4, 130.3, 130.0, 129.2, 128.8, 127.4, 126.4, 126.2, 125.1, 122.4, 34.4, 28.7, 19.5 ppm.

<sup>19</sup>**F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.6.

**MS** (70 eV): m/z (%) = 410 [M]<sup>+</sup>(100), 264, 161, 105.

HRMS (ESI) calcd. for C<sub>24</sub>H<sub>22</sub>F<sub>3</sub>N<sub>2</sub>O [M+H]: 411.1679, found: 411.1679.





#### N'-benzylidene-N-(3-bromophenyl)-3-(o-tolyl)propanehydrazide (D86)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 264.6 mg, 63% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.51 (m, 3H), 7.42 – 7.31 (m, 5H), 7.26 (d, *J* = 6.8 Hz, 1H), 7.21 (s, 1H), 7.19 – 7.11 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 3.37 – 3.20 (m, 2H), 3.17 – 3.05 (m, 2H), 2.39 (s, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.4, 142.2, 139.5, 137.6, 136.3, 134.0, 132.6, 131.5, 130.4, 130.2, 129.2, 128.8, 128.2, 127.4, 126.5, 126.2, 123.7, 34.5, 28.8, 19.6 ppm.

**MS** (70 eV): m/z (%) = 420 [M]<sup>+</sup>(100), 273, 105, 91.



**HRMS** (ESI) calcd. for C<sub>23</sub>H<sub>22</sub>BrN<sub>2</sub>O [M+H]: 421.0910, found: 421.0898.

S104



#### N'-benzylidene-N-(4-methoxybenzyl)-3-(o-tolyl)propanehydrazide (D87)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 289.5 mg, 75% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 (s, 1H), 7.56 – 7.52 (m, 2H), 7.33 – 7.29 (m, 3H), 7.28 – 7.24 (m, 1H), 7.18 – 7.13 (m, 3H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.19 (s, 2H), 3.74 (s, 3H), 3.32 – 3.25 (m, 2H), 3.14 – 3.07 (m, 2H), 2.39 (s, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.9, 158.9, 140.0, 139.7, 136.3, 134.7, 130.3, 129.7, 129.0, 128.7, 127.8, 127.2, 127.1, 126.3, 126.2, 114.4, 55.3, 44.2, 34.1, 29.0, 19.5 ppm.

**MS** (70 eV): m/z (%) = 386 [M]<sup>+</sup>(100), 282, 136, 121.

HRMS (ESI) calcd. for C<sub>25</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub> [M+H]: 387.2067, found: 387.2066.





# N'-(4-methylbenzylidene)-N-phenyl-3-(o-tolyl)propanehydrazide (D88)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 288.4 mg, 81% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.68 – 7.63 (m, 2H), 7.56 (d, *J* = 7.2 Hz, 3H), 7.45 – 7.41 (m, 1H), 7.34 (s, 1H), 7.31 – 7.23 (m, 7H), 3.46 (s, 2H), 3.29 – 3.25 (m, 2H), 2.54 (s, 3H), 2.46 (s, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.5, 142.0, 140.2, 139.8, 136.3, 131.7, 130.4, 130.3, 129.5, 129.4, 129.3, 129.2, 127.3, 126.4, 126.2, 34.6, 29.0, 21.6, 19.6 ppm.

**MS** (70 eV): m/z (%) = 356 [M]<sup>+</sup>(100), 210, 105, 93.

HRMS (ESI) calcd. for C<sub>24</sub>H<sub>25</sub>N<sub>2</sub>O [M+H]: 357.1961, found: 357.1964.





# *N*-phenyl-3-(*o*-tolyl)-*N*'-(2,4,6-trimethylbenzylidene)propanehydrazide (D89)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 203.5 mg, 53% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.50 (m, 3H), 7.45 – 7.40 (m, 1H), 7.23 (d, *J* = 6.4 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.14 – 7.08 (m, 3H), 6.81 (s, 2H), 3.25 (s, 2H), 3.13 – 3.05 (m, 2H), 2.33 (s, 3H), 2.23 (s, 9H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.5, 142.5, 139.7, 138.8, 137.4, 136.4, 136.3, 130.3, 129.7, 129.4, 129.3, 128.8, 128.4, 126.2, 126.1, 34.3, 28.5, 21.3, 21.2, 19.5 ppm.
MS (70 eV): m/z (%) = 384 [M]<sup>+</sup> (100), 238, 222, 146.

HRMS (ESI) calcd. for C<sub>26</sub>H<sub>29</sub>N<sub>2</sub>O [M+H]: 385.2274, found: 385.2277.





# N'-(4-bromobenzylidene)-N-phenyl-3-(o-tolyl)propanehydrazide (D90)

The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 298.2 mg, 71% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (t, *J* = 7.6 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.37 – 7.33 (m, 2H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.22 – 7.04 (m, 6H), 3.30 (s, 2H), 3.15 – 3.05 (m, 2H), 2.38 (s, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.5, 140.4, 139.6, 136.3, 136.1, 133.3, 132.0, 130.4, 129.5, 129.3, 129.2, 128.7, 126.5, 126.2, 124.1, 34.5, 28.9, 19.6 ppm.

**MS** (70 eV): m/z (%) = 420 [M]<sup>+</sup>(100), 273, 105, 91.

HRMS (ESI) calcd. for C<sub>23</sub>H<sub>22</sub>BrN<sub>2</sub>O [M+H]: 421.0910, found: 421.0907.




methyl-4-((2-phenyl-2-(3-(o-tolyl)propanoyl)hydrazineylidene)methyl)benzoate (D91)

The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 332.0 mg, 83% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.49 (m, 4H), 7.47 – 7.43 (m, 1H), 7.27 (d, *J* = 6.8 Hz, 1H), 7.23 (s, 1H), 7.16 – 7.10 (m, 5H), 3.86 (s, 3H), 3.33 (s, 2H), 3.18 – 3.04 (m, 2H), 2.39 (s, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.6, 166.6, 140.3, 139.5, 138.5, 136.2, 136.0, 131.0, 130.4, 130.0, 129.6, 129.2, 127.1, 126.4, 126.2, 52.3, 34.5, 28.9, 19.5 ppm.

**MS** (70 eV): m/z (%) = 400 [M]<sup>+</sup>(100), 207, 193, 44.

HRMS (ESI) calcd. for C<sub>25</sub>H<sub>25</sub>N<sub>2</sub>O<sub>3</sub> [M+H]: 401.1859 found: 401.1860.



# 5. Mechanism investigations

## 5.1 Control experiments for branched acylhydrazones

# 5.1.1 Control experiments with D69



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, **D69** (1.4 mmol), **B1** (1.0 mmol), **C1** (1.5 mmol),  $PdCl_2[P(3, 5-F_2Ph)_3]_2$  (0.02 mmol, 2 mol%), and DCM (2.0 mL). Then the glass tube was closed tightly and removed from the glove box. Then the tube immersed into a preheated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D1** in 90% yield.

### 5.1.2 Control experiments with D69 in the absence of [Pd]



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, **D69** (1.4 mmol), **B1** (1.0 mmol), **C1** (1.5 mmol), and DCM (2.0 mL). Then the glass tube was closed tightly and removed from the glove box. Then the tube immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography

(petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D1** in 91% yield.

# 5.1.3 Control experiments with D70



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, A1 (1.4 mmol), D70 (1.0 mmol), PdCl<sub>2</sub>[P(3, 5- $F_2Ph$ )<sub>3</sub>]<sub>2</sub> (0.02 mmol, 2 mol%), and DCM (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 10:1) on silica gel to give the corresponding product D1 in 56% yield.

### 5.1.4 Control experiments with D70 in the absence of [Pd]



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, A1 (1.4 mmol), D70 (1.0 mmol), and DCM (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction

was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D1** in <5% yield and **D70** was recovered in 97% yield.

#### 5.1.5 Control experiments with D70 and D92 in the presence of H2O



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, A1 (1.4 mmol), D70 (1.0 mmol), H<sub>2</sub>O (1.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.02 mmol, 2 mol%), and DCM (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product D1 in 91% yield.

# 5.1.6 Control experiments with D70 and D69 in the absence of [Pd]



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, **D69** (1.4 mmol), **D70** (1.0 mmol), and DCM (2.0

mL). Then the glass tube was closed tightly and removed from the glove box. Then the tube immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D1** in 92% yield.

#### 5.1.7 Control experiments with D71



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, C1 (1.5 mmol), D71 (1.0 mmol), PdCl<sub>2</sub>[P(3, 5- $F_2Ph$ )<sub>3</sub>]<sub>2</sub> (0.02 mmol, 2 mol%), and DCM (2.0 mL). Then the glass tube was closed tightly and removed from the glove box. Then the tube immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 10:1) on silica gel to give the corresponding product **D1** in 81% yield.

### **5.1.8** Control experiments with D71 in the absence of [Pd]



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, C1 (1.5 mmol), D71 (1.0 mmol), and DCM (2.0  $_{S113}$ 

mL). Then the glass tube was closed tightly and removed from the glove box. Then the tube immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D1** in 73% yield.

#### 5.1.9 Control experiments with D72



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, C1 (1.5 mmol), D72 (1.0 mmol), PdCl<sub>2</sub>[P(3, 5- $F_2Ph$ )<sub>3</sub>]<sub>2</sub> (0.02 mmol, 2 mol%), and DCM (2.0 mL). Then the glass tube was closed tightly and removed from the glove box. Then the tube immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 10:1) on silica gel to give the corresponding product D1 in <5% yield and D72 was recovered in 95% yield.

## 5.2 Time conversion plot experiments for branched acylhydrazones



Using a nitrogen-filled glove box, an oven-dried pressure tube (50.0 mL) was charged with a magnetic stirring bar, A1 (14.0 mmol), B1 (10.0 mmol), C1 (15.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.2 mmol, 2 mol%), and DCM (20.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 0 – 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D1**.



S115

Entry	Time/h	<b>D70</b> (M)	<b>D1</b> (M)
1	0	0	0
2	0.1	0.325	0.03
3	0.2	0.38	0.06
4	0.4	0.355	0.14
5	0.6	0.29	0.205
6	0.8	0.235	0.26
7	1	0.175	0.315
8	1.2	0.15	0.345
9	1.6	0.11	0.375
10	2	0.1	0.39
11	2.4	0.09	0.4
12	2.8	0.085	0.405
13	3.2	0.08	0.415
14	3.6	0.07	0.43
15	4	0.06	0.445
16	4.4	0.05	0.45
17	4.8	0.035	0.465
18	5.2	0.025	0.47
19	5.6	0.025	0.475
20	6	0.02	0.48

Table S21 Time conversion plot experiments

Reaction conditions A: A1 (14 mmol), B (10 mmol), C1 (15 mmol), PdCl<sub>2</sub>[P(3,5- $F_2Ph$ )<sub>3</sub>]<sub>2</sub> (0.2 mmol, 2 mol%), DCM (20 mL), CO (2.5 MPa), 120 °C, 0 – 6 h.

## 5.3 Labelled investigations for branched acylhydrazones

5.3.1 Labelled investigations with CCl<sub>2</sub>D<sub>2</sub>



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, A1 (1.4 mmol), B1 (1.0 mmol), C1 (1.5 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.02 mmol, 2 mol%), and CCl<sub>2</sub>D<sub>2</sub> (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D73-d** in 83% yield.

$$H^{\alpha} = \frac{1-0.97}{1} \times 100\% = 3\%$$
  $H^{\beta} = \frac{3-2.97}{3} \times 100\% = 1\%$ 



5.3.2 Labelled investigations with D<sub>2</sub>O



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, A1 (1.4 mmol), B1 (1.0 mmol), C1 (1.5 mmol), D<sub>2</sub>O (1.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.02 mmol, 2 mol%), and DCM (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D73-d** in 86% yield.

$$H^{\alpha} = \frac{1-0.96}{1} \times 100\% = 4\%$$
  $H^{\beta} = \frac{3-2.76}{3} \times 100\% = 8\%$ 



#### 5.3.3 Labelled investigations with D74



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, **D74** (1.4 mmol), **B1** (1.0 mmol), **C1** (1.5 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.02 mmol, 2 mol%), and DCM (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D20-d** in 81% yield.

$$H^{\alpha} = \frac{1-0.92}{1} \times 100\% = 8\%$$
  $H^{\beta} = \frac{3-2.14}{3} \times 100\% = 28\%$ 





#### 5.3.4 Labelled investigations with D74 in the presence of D<sub>2</sub>O



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, **D74** (1.4 mmol), **B1** (1.0 mmol), **C1** (1.5 mmol),  $D_2O$  (1.0 mmol),  $PdCl_2[P(3, 5-F_2Ph)_3]_2$  (0.02 mmol, 2 mol%), and DCM (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 10:1) on silica gel to give the corresponding product **D20-d** in 82% yield.

 $H^{\alpha} = \frac{1-0.96}{1} \times 100\% = 4\%$   $H^{\beta} = \frac{3-1.48}{3} \times 100\% = 51\%$ 





#### 5.3.5 Labelled investigations with D74 in the presence of CCl<sub>2</sub>D<sub>2</sub>



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, **D74** (1.4 mmol), **B1** (1.0 mmol), **C1** (1.5 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.02 mmol, 2 mol%), and CCl<sub>2</sub>D<sub>2</sub> (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D20-d** in 80% yield.

$$H^{\alpha} = \frac{1-0.93}{1} \times 100\% = 7\%$$
  $H^{\beta} = \frac{3-1.83}{3} \times 100\% = 39\%$ 







Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, **D74** (1.4 mmol), **B1** (1.0 mmol), **C1** (1.5 mmol), D<sub>2</sub>O (1.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.02 mmol, 2 mol%), and CCl<sub>2</sub>D<sub>2</sub> (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 6 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D20-d** in 80% yield.

$$H^{\alpha} = \frac{1-0.87}{1} \times 100\% = 13\%$$
  $H^{\beta} = \frac{3-1.10}{3} \times 100\% = 63\%$ 





# 5.4 Control experiments for branched acylhydrazones

### 5.4.1 Control experiments with D70



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, A1 (1.4 mmol), D70 (1.0 mmol), PdCl<sub>2</sub>(Xantphos) (0.02 mmol, 2 mol%), and anisole (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (3.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 16 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product D75 in 52% yield.

### 5.4.2 Control experiments with D70 in the presence of H<sub>2</sub>O



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, A1 (1.4 mmol), D70 (1.0 mmol), H<sub>2</sub>O (1.0 mmol), PdCl<sub>2</sub>(Xantphos) (0.02 mmol, 2 mol%), and anisole (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (3.0 MPa) and immersed into a preheated metal bath (120 °C) for 16 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot

of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D75** in 83% yield.

#### 5.4.3 Control experiments with D70 in the absence of [Pd]



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, A1 (1.4 mmol), D70 (1.0 mmol), and anisole (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (3.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 16 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product D75 in 0% yield and D70 was recovered in 97% yield.





Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, **D92** (1.4 mmol), **B1** (1.0 mmol), **C1** (1.5 mmol), and anisole (2.0 mL). Then the glass tube was closed tightly and removed from the glove box. Then the tube immersed into a pre-heated metal bath (120  $^{\circ}$ C) for 16 hours.

After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product D75 in 63% yield.



D92

Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, D92 (1.4 mmol), D70 (1.0 mmol), and anisole (2.0 mL). Then the glass tube was closed tightly and removed from the glove box. Then the tube immersed into a pre-heated metal bath (120 °C) for 16 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D75** in 74% yield.

### 5.4.6 Control experiments with D93 in the absence of [Pd]



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, D93 (1.0 mmol), C1 (1.5 mmol), and anisole (2.0 mL). Then the glass tube was closed tightly and removed from the glove box. Then the tube immersed into a pre-heated metal bath (120 °C) for 16 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D75** in 90% yield.

#### 5.4.7 Control experiments with D94 in the absence of [Pd]



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, **D94** (1.0 mmol), **C1** (1.5 mmol), and anisole (2.0 mL). Then the glass tube was closed tightly and removed from the glove box. Then the tube immersed into a pre-heated metal bath (120 °C) for 16 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D75** in 0% yield and **D94** was recovered in 96% yield.

## 5.5 Labelled investigations for branched acylhydrazones

5.5.1 Labelled investigations in the presence of D<sub>2</sub>O



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, A1 (1.4 mmol), B1 (1.0 mmol), C1 (1.5 mmol), D<sub>2</sub>O (1.0 mmol), PdCl<sub>2</sub>(Xantphos) (0.02 mmol, 2 mol%), and anisole (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (3.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 16 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product D95-*d* in 86% yield.





### 5.5.2 Labelled investigations with D96



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, D96 (1.4 mmol), B1 (1.0 mmol), C1 (1.5 mmol), PdCl<sub>2</sub>(Xantphos) (0.02 mmol, 2 mol%), and anisole (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (3.0 MPa) and immersed into a preheated metal bath (120 °C) for 16 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D97-***d* in 81% yield.



 $H^{\alpha} = \frac{2-1.56}{2} \times 100\% = 22\%$   $H^{\beta} = \frac{2-1.50}{2} \times 100\% = 25\%$ 

#### 5.5.3 Labelled investigations with D96 in the presence of D2O



Using a nitrogen-filled glove box, an oven-dried pressure tube (10.0 mL) was charged with a magnetic stirring bar, **D96** (1.4 mmol), **B1** (1.0 mmol), **C1** (1.5 mmol), D<sub>2</sub>O (1.0 mmol), PdCl<sub>2</sub>(Xantphos) (0.02 mmol, 2 mol%), and anisole (2.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (3.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 16 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D97-d** in 80% yield.

$$H^{\alpha} = \frac{2-1.44}{2} \times 100\% = 28\%$$
  $H^{\beta} = \frac{2-1.22}{2} \times 100\% = 39\%$ 



# 6. Further Transformation

## 6.1 Synthesis of N,2-diphenylpropanamide



Using a nitrogen-filled glove box, add a magnetic stir bar, **D1** (328 mg, 1.0 mmol),  $SmI_2$  (219 µL, 0.5 mmol), and THF (5.0 mL) to the dried pressure tube (38 mL volume). Then the sealing tube was closed tightly with teflon cover and immersed in a preheated metal bath (65 °C) for 5 hours. A small fraction of the organic phase was analyzed by gas chromatography and gas chromatography-mass spectrometry to monitor product formation. Then the solvent was evaporated under reduced pressure, and the residue was purified on silica gel by flash column chromatography to obtain products **D98** (180.0 mg, 80%) and **D99** (86.6 mg, 71%).

## N,2-diphenylpropanamide<sup>1</sup>

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.34 (m, 6H), 7.33 – 7.24 (m, 3H), 7.10 – 7.03 (m, 2H), 3.71 (q, *J* = 7.2 Hz, 1H), 1.64 – 1.57 (m, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.3, 140.9, 137.9, 129.2, 128.9, 127.7, 127.6, 124.3, 119.7, 48.2, 18.6 ppm.

**MS** (70 eV): m/z (%) = 225 [M]<sup>+</sup>(100), 132, 105, 93.

**HRMS** (ESI) calcd. for C<sub>15</sub>H<sub>16</sub>NO [M+H]: 226.1227, found: 226.1227.



### 6.2 Synthesis of 1-benzylidene-2-phenylhydrazine



Using a nitrogen-filled glove box, add a magnetic stir bar, **D1** (328 mg, 1.0 mmol), NaOH (160 mg, 4.0 mmol), and EtOH (5.0 mL) to the dried pressure tube (38 mL volume). Then the sealing tube was closed tightly with teflon cover and immersed in a preheated metal bath (65 °C) for 4 hours. A small fraction of the organic phase was analyzed by gas chromatography and gas chromatography-mass spectrometry to monitor product formation. Then the solvent was evaporated under reduced pressure, and the residue was purified on silica gel by flash column chromatography to obtain products **D70** (180.3mg, 92%) and **D100** (128.8 mg, 71%).

### 1-benzylidene-2-phenylhydrazine<sup>2</sup>

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 – 7.62 (m, 3H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.87 (t, *J* = 7.2 Hz, 1H) ppm.

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ 144.7, 137.3, 135.3, 129.3, 128.6, 128.5, 126.2, 120.1, 112.8 ppm.

**MS** (70 eV): m/z (%) = 196 [M]<sup>+</sup> (100), 92, 65, 39.

HRMS (ESI) calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>2</sub> [M+H]: 197.1073, found: 197.1070.



### 6.3 Synthesis of N'-benzyl-N,2-diphenylpropanehydrazide



Using a nitrogen-filled glove box, add a magnetic stir bar, **D1** (328 mg, 1.0 mmol), Pd/C (21.2 mg, 0.2 mmol), and IPA (5.0 mL) to the dried pressure tube (38 mL volume). HCOONH<sub>4</sub> (315 mg, 5.0 mmol) and H<sub>2</sub>O (480  $\mu$ L, 30 mmol) were added while stirring, then the tubes were tightly sealed with teflon caps and immersed in a preheated metal bath (60 °C) for 4 hours. A small fraction of the organic phase was analyzed by gas chromatography and gas chromatography-mass spectrometry to monitor product formation. Then the solvent was evaporated under reduced pressure, and the residue was purified on silica gel by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 5:1) to obtain product **D101** (313.5 mg, 95%).

### N'-benzyl-N,2-diphenylpropanehydrazide

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.29 – 7.22 (m, 4H), 7.22 – 7.18 (m, 2H), 7.15 (s, 4H), 6.97 – 6.94 (m, 3H), 6.76 – 6.72 (m, 2H), 6.33 (s, 1H), 5.40 (s, 1H), 5.20 (s, 1H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.7, 136.2, 134.0, 131.9, 128.8, 127.9, 127.7, 127.5, 127.2, 126.9, 126.1, 125.6, 110.2, 60.3 ppm.

**MS** (70 eV): m/z (%) = 330 [M]<sup>+</sup>(100), 225, 105, 91.

**HRMS** (ESI) calcd. for C<sub>22</sub>H<sub>23</sub>N<sub>2</sub>O [M+H]: 331.1805, found: 331.1803.



### 6.4 Synthesis of N'-(cyano(phenyl)methyl)-N,2-diphenylpropanehydrazide



Using a nitrogen-filled glove box, add a magnetic stir bar, **D1** (328 mg, 1.0 mmol), TMSCN (252  $\mu$ L, 2.0 mmol), BF<sub>3</sub>Et<sub>2</sub>O (24  $\mu$ L, 0.2 mmol) and CH<sub>3</sub>CN (5.0 mL) to the dried pressure tube (38 mL volume). Then close the teflon cover of the sealing tube and react for 6 hours at room temperature. A small fraction of the organic phase was analyzed by gas chromatography and gas chromatography-mass spectrometry to monitor product formation. Then the solvent was evaporated under reduced pressure, and the residue was purified on silica gel by flash column chromatography (petroleum ether/ethyl acetate = 100:1 – 5:1) to obtain product **D102** (294.7 mg, 83%).

#### N'-(cyano(phenyl)methyl)-N,2-diphenylpropanehydrazide

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.53 – 7.46 (m, 2H), 7.40 – 7.33 (m, 6H), 7.24 – 7.14 (m, 4H), 7.11 – 7.06 (m, 1H), 7.06 – 7.01 (m, 1H), 7.01 – 6.96 (m, 1H), 6.21 (dd, *J* = 46.4, 6.8 Hz, 1H), 5.00 (dd, *J* = 45.6, 6.8 Hz, 1H), 3.78 – 3.66 (m, 1H), 1.54 – 1.39 (m, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.1, 173.8, 140.7, 140.6, 140.3, 139.9, 131.8, 131.6, 129.8, 129.5, 129.3, 129.1, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.5, 127.4, 127.1, 118.0, 117.9, 54.8, 54.7, 43.1, 42.8, 20.2, 19.9 ppm.

**MS** (70 eV): m/z (%) = 355 [M]<sup>+</sup>(100), 250, 105, 91.

**HRMS** (ESI) calcd. for C<sub>23</sub>H<sub>22</sub>N<sub>3</sub>O [M+H]: 356.2121, found: 356.2121.



## 7. Gram-scale experiment

# 7.1 10 mmol scale for A1



Using a nitrogen-filled glove box, an oven-dried pressure tube (100.0 mL) was charged with a magnetic stirring bar, A1 (14.0 mmol), B1 (10.0 mmol), C1 (15.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.2 mmol, 2 mol%), and DCM (20.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 24 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D1** in 86% yield (2.8 g).

### 7.2 10 mmol scale for A5



Using a nitrogen-filled glove box, an oven-dried pressure tube (100.0 mL) was charged with a magnetic stirring bar, A5 (14.0 mmol), B1 (10.0 mmol), C1 (15.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.2 mmol, 2 mol%), and DCM (20.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 24 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A

small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D5** in 87% yield (3.4 g).

### 7.3 10 mmol scale for A8



Using a nitrogen-filled glove box, an oven-dried pressure tube (100.0 mL) was charged with a magnetic stirring bar, A8 (14.0 mmol), B1 (10.0 mmol), C1 (15.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.2 mmol, 2 mol%), and DCM (20.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 24 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D8** in 80% yield (2.9 g).

# 7.4 10 mmol scale for A20



Using a nitrogen-filled glove box, an oven-dried pressure tube (100.0 mL) was charged with a magnetic stirring bar, A20 (14.0 mmol), B1 (10.0 mmol), C1 (15.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.2 mmol, 2 mol%), and DCM (20.0 mL). Then the glass S135

tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 24 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D20** in 84% yield (3.2 g).

### 7.5 10 mmol scale for C35



Using a nitrogen-filled glove box, an oven-dried pressure tube (100.0 mL) was charged with a magnetic stirring bar, A1 (14.0 mmol), B1 (10.0 mmol), C35 (15.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.2 mmol, 2 mol%), and DCM (20.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 24 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product D35 in 87% yield (3.1 g).

# 7.6 10 mmol scale for C51



Using a nitrogen-filled glove box, an oven-dried pressure tube (100.0 mL) was charged with a magnetic stirring bar, A1 (14.0 mmol), B1 (10.0 mmol), C51 (15.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.2 mmol, 2 mol%), and DCM (20.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 24 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product D51 in 90% yield (3.4 g).

## 7.7 10 mmol scale for B55



Using a nitrogen-filled glove box, an oven-dried pressure tube (100.0 mL) was charged with a magnetic stirring bar, A1 (14.0 mmol), B55 (10.0 mmol), C1 (15.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.2 mmol, 2 mol%), and DCM (20.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 24 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A S137

small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D55** in 88% yield (3.0 g).

### 7.8 10 mmol scale for B61



Using a nitrogen-filled glove box, an oven-dried pressure tube (100.0 mL) was charged with a magnetic stirring bar, A1 (14.0 mmol), B61 (10.0 mmol), C1 (15.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.2 mmol, 2 mol%), and DCM (20.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 24 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product D61 in 81% yield (3.3 g).

### 7.9 10 mmol scale for B67



Using a nitrogen-filled glove box, an oven-dried pressure tube (100.0 mL) was charged with a magnetic stirring bar, A1 (14.0 mmol), B67•HCl (10.0 mmol), C1 (15.0

mmol), KOH (10.0 mmol), PdCl<sub>2</sub>[P(3, 5-F<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (0.2 mmol, 2 mol%), and DCM (20.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 24 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D67** in 70% yield (2.4 g).





Using a nitrogen-filled glove box, an oven-dried pressure tube (100.0 mL) was charged with a magnetic stirring bar, A76 (15.0 mmol), B1 (10.0 mmol), C1 (15.0 mmol), PdCl<sub>2</sub>(Xantphos) (0.2 mmol, 2 mol%), and anisole (20.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (3.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 48 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D76** in 76% yield (2.6 g).

## 7.11 10 mmol scale for A83



Using a nitrogen-filled glove box, an oven-dried pressure tube (100.0 mL) was charged with a magnetic stirring bar, **A83** (15.0 mmol), **B1** (10.0 mmol), **C1** (15.0 mmol), PdCl<sub>2</sub>(Xantphos) (0.2 mmol, 2 mol%), and anisole (20.0 mL). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (3.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 48 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D83** in 76% yield (2.9 g).

# 7.12 1.0 mol scale for A1



An oven-dried pressure tube (2.5 L) was charged with a magnetic stirring bar, A1 (1.4 mol), B1 (1.0 mol), C1 (1.5 mol),  $PdCl_2[P(3, 5-F_2Ph)_3]_2$  (0.01 mol, 1 mol%), and DCM (1.0 L). Then the glass tube was placed in an autoclave which was closed tightly. Then the autoclave was purged and charged with CO (2.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 72 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the

residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D1** in 78% yield (255.8 g).

### 7.13 1.0 mol scale for A103



An oven-dried pressure tube (2.5 L) was charged with a magnetic stirring bar, A104 (0.5 MPa), B1 (1.0 mol), C1 (1.5 mol), PdCl<sub>2</sub>(Xantphos) (0.001 mol, 1 mol‰), and anisole (1.0 L). Then the glass tube was placed in an autoclave which was closed tightly. Then the autoclave was purged and charged with CO (0.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 60 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product D103 in 61% yield (153.7 g).

### N'-benzylidene-N-phenylpropionohydrazide

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.57 – 7.46 (m, 4H), 7.44 – 7.37 (m, 1H), 7.30 (s, 3H), 7.22 (s, 1H), 7.13 (d, J = 7.6 Hz, 2H), 3.03 (s, 2H), 1.29 (t, J = 7.2 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.9, 141.2, 136.3, 134.5, 130.3, 129.9, 129.4, 129.3, 128.8, 127.2, 27.7, 9.4 ppm.

**MS** (70 eV): m/z (%) = 252 [M]<sup>+</sup>(100), 196, 149, 92.

## 7.14 1.0 mol scale for A103



An oven-dried pressure tube (2.5 L) was charged with a magnetic stirring bar, A104 (0.5 MPa), B1 (1.0 mol), C1 (1.5 mol), PdCl<sub>2</sub>(Xantphos) (0.005 mol, 5 mol‰), and anisole (1.0 L). Then the glass tube was placed in an autoclave which was closed tightly. Then the autoclave was purged and charged with CO (0.5 MPa) and immersed into a pre-heated metal bath (120 °C) for 60 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. A small aliquot of the reaction mixture was analyzed by GC and GC-MS to monitor product formation. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product D103 in 91% yield (229.3 g).

# 8. The synthesis of the intermediates

# 8.1 Synthesis of D70



Using a nitrogen-filled glove box, add C1 (106  $\mu$ L, 1.0 mmol) in DCM (5.0 mL) to a 50.0 mL oven-dried round-bottomed flask containing a magnetic stirring bar and B1 (98  $\mu$ L, 1.0 mmol). Stir the reaction mixture for 1 hour at room temperature. After complete consumption of aldehyde, monitor the reaction by thin layer chromatography. If a precipitate forms, pour the reaction mixture over a Buchner funnel. Wash the solid with a minimum of cold methanol to give the corresponding product D70 in 96% yield (216.0 mg).

## 1-benzylidene-2-phenylhydrazine<sup>2</sup>

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 – 7.62 (m, 3H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.87 (t, *J* = 7.2 Hz, 1H) ppm.

# 8.2 Synthesis of D71



Under the nitrogen, a mixture of **B1** (980  $\mu$ L, 10.0 mmol) and DCM (10.0 mL) was placed in a round-bottomed flask equipped with a magnetic stir bar and the temperature was kept at 0 °C by adding ice. Over the course of 20 minutes, (Boc)<sub>2</sub>O (2.8 mL, 12.0 mmol) was added to this mixture and the reaction was allowed to proceed for at least an hour, during which time a constant check was performed by TLC. Once the reaction had progressed to the desired extent, **D69** (1.8 mL, 12.0 mmol) was added drop by drop to the reaction mixture. Under vigorous agitation, triethylamine (3.5 mL, 25.0 mmol) was added through a constant-pressure funnel within 30 minutes. After

completion of the TLC-monitored reaction, the solution was stirred for an additional 4 hours. Filter all sediment, then place the remaining mixture in a round-bottomed flask fitted with a magnetic stir bar. Stir the mixture vigorously, keeping the temperature at 0 °C by adding additional ice. Trifluoroacetic acid (1.0 mL, 13.0 mmol) was added drop by drop to the reaction mixture. The reaction was allowed to run for at least 30 minutes, during which time the TLC was checked for constancy. Once the reaction has progressed to the desired extent, a saturated aqueous NaOH solution is added to the reaction mixture drop by drop until pH > 7. After the TLC-monitored reaction was complete, all precipitates were filtered and then the remaining mixture was extracted with DCM. The organic phase was washed with saturated salt solution and filtered and dried with MgSO<sub>4</sub>. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 - 3:1) on silica gel to give the corresponding product **D71** in 63% yield (1.5 g).

# N,2-diphenylpropanehydrazide

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.27 (m, 4H), 7.26 – 7.17 (m, 3H), 7.14 –

7.04 (m, 3H), 4.37 (br, 2H), 3.73 (d, J = 5.6 Hz, 1H), 1.44 (d, J = 6.8 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.2, 142.2, 141.3, 129.3, 128.5, 128.3, 127.5, 126.9, 42.8, 20.1 ppm.

**MS** (70 eV): m/z (%) = 240 [M]<sup>+</sup> (100), 108, 77, 51.

### 8.3 Synthesis of D72



The acid (5.4 mL, 40.0 mmol) was dissolved or suspended in CH<sub>3</sub>CN (80.0 mL) at room temperature. HOBt (6.5 g, 48.0 mmol) was added in one portion followed by EDC (3.8 mL, 48.0 mmol). The mixture was stirred at room temperature, and the reaction progress was monitored by HPLC until all of the acid was converted to the activated ester/amide mixture. The resulting mixture was then slowly added to a solution of **B1** (7.8 mL, 80.0 mmol) and cyclohexene (1.0 mL, 10.0 mmol) in CH<sub>3</sub>CN
(40.0 mL) while the temperature was maintained at 0-10 °C. The reaction was usually complete upon the completion of addition. Water (40.0 mL) was added. The aqueous CH<sub>3</sub>CN mixture was extracted with ethyl acetate followed by a carbonate wash of the organic layer to remove HOBt. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 - 3:1) on silica gel to give the corresponding product **D72** in 50% yield (4.8 g).<sup>3</sup>

#### 8.4 Synthesis of D74



To a stirred round bottomed flask which charged with PPh<sub>3</sub> (524.0 mg, 2.0 mmol), THF (10.0 ml) was dropwise added CD<sub>3</sub>I (435.0 mg, 3.0 mmol) at room temperature. After completed the reaction (about 6 hours), the mixture was filtered by a Buchner funnel and washed by THF. The methyl-D<sub>3</sub>-triphenylphosphonium iodide was obtained in 91% yield (740.7 mg).

To a 25 ml flask were added methyl-D<sub>3</sub>-triphenylphosphonium iodide (488.4 mg, 1.2 mmol), 'BuOK (134.4 mg, 1.2 mmol) and THF (5.0 mL). The mixture was stirred at room temperature for 1 hour. Then, a solution of 2-naphthaldehyde (156.0 mg, 1.0 mmol) in THF (1.0 ml) was added to the flask. The reaction was stirred at room temperature for overnight. After completion of the reaction, the mixture was diluted with DCM (5.0 ml x 3) and washed with brine (5.0 mL). The organic phase was washed with saturated salt solution and filtered and dried with MgSO<sub>4</sub>. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1 - 10:1) on silica gel to give the corresponding product **D74** in 79% yield (123.0 mg).

2-(vinyl-2,2-d<sub>2</sub>) naphthalene<sup>4</sup>

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 – 7.76 (m, 4H), 7.67 (dd, J = 8.8, 1.2 Hz, 1H), 7.52 – 7.45 (m, 2H), 6.91 (s, 1H), 5.90 (d, J = 17.6 Hz, 0.05H), 5.36 (d, J = 10.8 Hz, 0.05H) ppm.



# 8.5 Synthesis of D93



Under the nitrogen, a mixture of **B1** (980  $\mu$ L, 10.0 mmol) and DCM (10.0 mL) was placed in a round-bottomed flask equipped with a magnetic stir bar and the temperature was kept at 0 °C by adding ice. Over the course of 15 to 20 minutes, (Boc)<sub>2</sub>O (2.8 mL, 12.0 mmol) was added to this mixture and the reaction was allowed to proceed for at least 1 hour, during which time a constant check was performed by TLC. Once the reaction had progressed to the desired extent, **D92** (1.8 mL, 12.0 mmol) was added drop by drop to the reaction mixture. Under vigorous agitation, triethylamine (3.5 mL, 25.0 mmol) was added through a constant-pressure funnel within 30 minutes.

After completion of the TLC-monitored reaction, the solution was stirred for an additional 4 hours. Filter all sediment, then place the remaining mixture in a round-bottomed flask fitted with a magnetic stir bar. Stir the mixture vigorously, keeping the temperature at 0 °C by adding additional ice. Trifluoroacetic acid (1.0 mL, 13.0 mmol) was added drop by drop to the reaction mixture. The reaction was allowed to run for at least 30 minutes, during which time the TLC was checked for constancy. Once the reaction has progressed to the desired extent, a saturated aqueous NaOH solution is added to the reaction mixture drop by drop until PH > 7. After the TLC-monitored reaction was complete, all precipitates were filtered and then the remaining mixture was extracted with DCM. The organic phase was washed with saturated salt solution and filtered and dried with MgSO<sub>4</sub>. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 - 3:1) on silica gel to give the corresponding product **D93** in 69% yield (1.7 g).

#### N,3-diphenylpropanehydrazide

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.03 (m, 10H), 4.78 (s, 2H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.2, 142.3, 140.8, 129.4, 128.5, 128.4, 128.0, 126.9, 126.2, 35.4, 31.7 ppm.

**MS** (70 eV): m/z (%) = 240 [M]<sup>+</sup>(100), 108, 91, 65.

## 8.6 Synthesis of D94



Under the nitrogen, a mixture of **B1** (980  $\mu$ L, 10.0 mmol) and DCM (10.0 ml) was placed in a round-bottomed flask equipped with a magnetic stir bar. **D92** (1.8 mL, 12.0 mmol) was added to the mixture and the reaction was allowed to proceed for at least 1 hour at room temperature, during which time a constant check was performed by TLC. Once the reaction had progressed to the desired extent, the organic phase was washed

with saturated salt solution and filtered and dried with MgSO<sub>4</sub>. Then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 - 3:1) on silica gel to give the corresponding product **D94** in 85% yield (2.0 g).

## N',3-diphenylpropanehydrazide

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.91 (s, 1H), 8.51 (s, 1H), 7.51 – 6.79 (m, 10H),

2.92 – 2.76 (m, 2H), 2.53 – 2.32 (m, 2H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.7, 141.5, 140.6, 140.3, 129.6, 128.5, 128.4, 127.8, 126.3, 124.8, 35.6, 31.1 ppm.

**MS** (70 eV): m/z (%) = 240 [M]<sup>+</sup> (100), 108, 91, 65.

## 9. References

[1] Métro, T. X.; Bonnamour, J.; Reidon, T.; Duprez, A.; Sarpoulet, J.; Martinez, J.; Lamaty, F. Comprehensive study of the organic-solventfree CDI-mediated acylation of various nucleophiles by mechanochemistry. *Chem.-Eur. J.* **2015**, *21*, 12787–12796.

[2] Vantomme, G.; Jiang, S.; Lehn, J.-M. Adaptation in constitutional dynamic libraries and networks, switching between orthogonal metalloselection and photoselection processes. *J. Am. Chem. Soc.* **2014**, *136*, 9509–9518.

[3] Zhang, X. N.; Breslav, M.; Grimm, J.; Guan, K. L.; Huang, A. H.; Liu, F. Q.; Maryanoff, C. A.; Palmer, D.; Patel, M.; Qian, Y.; Shaw, C.; Sorgi, K.; Stefanick, S.; Xu, D. W. A new procedure for preparation of carboxylic acid hydrazides. *J. Org. Chem.* 2002, *67*, 9471–9474.

[4] Lu, W.; Zhu, X.; Yang, L.; Wu, X.; Xie, X.; Zhang, Z. Distinct catalytic performance of dirhodium(II) complexes with ortho metalated DPPP in dehydrosilylation of styrene derivatives with alkoxysilanes. *ACS Catal.* **2021**, *11*, 10190–10197.

#### **10. NMR Spectra**







































































































































































S233






























































































S280
























S292






















































































