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Microwave-assisted, montmorillonite K-10 catalyzed three-component synthesis of *2H*-indazolo[2,1-*b*]phthalazine-triones under solvent-free conditions

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ABSTRACT

An efficient, rapid, and green synthesis of *2H*-indazolo[2,1-*b*]phthalazine-triones has been accomplished under solvent-free conditions by the reaction of phthalhydrazide, aldehydes and 5,5-dimethylcyclohexane-1,3-dione. This approach exploits the synthetic potential of microwave irradiation and Montmorillonite K-10 combination and offers many advantages, such as excellent product yields, shorter reaction time, reusable catalyst, easy isolation of products, and environmentally benign reaction conditions.

1. Introduction

Green chemistry approaches are significant due to the reduction in by-products, reaction waste, and reduction of energy cost. Organic reactions under solvent-free conditions have attracted much interest from chemists particularly from the viewpoint of green chemistry.[1–3] In recent times, exploration of solvent-free reactions has gained importance due to several advantages, such as experimental simplicity, less energy requirement, and almost quantitative reactivity of the substrates due to intimacy of the reagents. Improving the substrates reactivity and product formation efficiency by energising the reactions with microwave irradiation is another development in organic green chemical synthesis. Microwave-assisted organic synthesis is characterized by spectacular accelerations in many reactions as a consequence of three dimensional heating of the reaction mass, which cannot be produced by classical heating. Simple workup, high yields, improved selectivity and clean reaction pathways are additional advantages with microwave-assisted preparation of organic compounds. Indeed, even reactions that do not occur by conventional heating can be effectively performed using microwaves. In particular, microwave heating when coupled with solvent-free strategy, presents a powerful and green alternative to conventional synthesis. Theoretical calculations have also suggested that reactions with high activation energies can be performed under microwave irradiation without the use of harsh reaction conditions.

Recently, numerous important heterocycles have been synthesized under solvent-free conditions accelerated by microwave irradiation.[4–9]

Nitrogen-containing heterocyclic compounds are widespread in nature, and their applications to pharmaceuticals, agrochemicals, and functional materials are becoming more and more important.[10] Among a large variety of *N*-containing heterocyclic compounds, those containing hydrazine moiety as 'fusion site' have received considerable attention because of their pharmacological properties and clinical applications.[11] Moreover, fused phthalazines were found to possess multiple biological activities, such as antimicrobial,[12] anticonvulsant,[13] antifungal,[14] anticancer,[15] and anti-inflammatory activities.[16] Nevertheless the development of new synthetic methods for the efficient preparation of heterocycles containing phthalazine ring fragment is an interesting challenge. Recently, several elegant multicomponent strategies for the synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones by the cyclocondensation of phthalhydrazide, aldehydes, and 1,3-diketones utilizing different types of catalysts have been reported.[17–25] The reported methods show varying degrees of successes as well as limitations, such as harsh reaction conditions, expensive catalyst/reagent, toxic organic solvents, low product yields, long reaction times, and co-occurrence of several side products. Thus, a simple, rapid and efficient procedure is still

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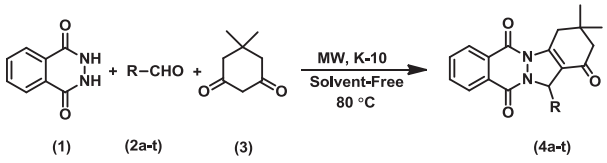
strongly desired for the synthesis of these important fused heterocyclic compounds.

Solid acids catalysts have gained much importance in recent years due to economic by reusability and environmental benefits by non-toxic.[26–29] Recently, the use of environmentally friendly and economically viable solid acids is increasing continuously owing to their ease of handling and high catalytic activities. Among them, montmorillonite K-10 is a well-known and widely used solid acid catalyst in synthetic organic chemistry. It has received considerable attention due to its non-toxicity, cost effectiveness, air and water compatibility, ease of handling, good reactivity, recyclability, experimental simplicity, commercially availability, green catalyst remarkable ability to suppress side reactions in acid sensitive substrates and supports for a wide variety of reactions. Microwave-promoted solvent-free solid acid reactions are well known as environmentally benign methods that also usually provide improved selectively, enhanced reaction rates, cleaner products and manipulative simplicity.[26–29] It is also an excellent catalyst for microwave-assisted organic synthesis.[30–33] This area has also attracted considerable attention in recent years.

Our literature survey at this stage revealed that there are no reports on the synthesis of *2H*-indazolo[2,1-*b*]phthalazine-triones under microwave-assisted in solvent-free at 80 °C mediated by K-10. Our main target is to develop a green organic reaction methodology, which is relatively faster and cleaner than conventional reactions. As part of our ongoing research program on the development of clean protocols[34,35] herein, we report a facile one-pot synthesis of *2H*-indazolo[2,1-*b*]phthalazine-triones via three-component coupling of phthalhydrazide, aldehydes and 5,5-dimethylcyclohexane-1,3-dione in the presence of catalytic amount (5 mol %) of K-10 under solvent-free microwave irradiation at 80 °C (Scheme 1).



Scheme 1. Synthesis of 2*H*-Indazolo[2,1-*b*]phthalazine-triones catalyzed by K-10 under microwave irradiation in solvent-free condition.

2. Results and discussion

Initially we have synthesiszed*2H*-indazolo[2,1-*b*]phthalazine-triones by the one-pot condensation of phthalhydrazide, aldehydes and 5,5-dimethylcyclohexane-1,3-dione in the presence of K-10 as catalyst by microwave irradiation under solvent-free conditions at 80 °C (Scheme 1). The reactions were carried out in a CEM Discover Benchmate microwave reactor using an open vessel technique.

First, the optimisation of temperature required for the reaction of phthalhydrazide(**1**, 1 mmol), 3-fluorobenzaldehyde (**2b**, 1 mmol) and 5,5-dimethylcyclohexane-1,3-dione (**3**, 1 mmol) in the presence of K-10 was standardised by carrying out the reaction at different temperatures ranging from 40 to 120 °C for 30 min by conventional heating (Table 1). It was found that above and below 80 °C and 30 min of time, the yield of the product was low. Only at 80 °C and with 30 min of reaction time, the highest product yield of 75% was observed (Table 1, entry 3). Thus it was proved that 80 °C is the optimised temperature required for effecting this reaction by conventional heating. However, when the same reaction was carried out by microwave irradiation at 80 °C, the reaction was complete in 5 min with 96% yield (Table 1, entry 6).

Table 1
Effect of temperature on the synthesis of 13-(3-fluorophenyl)-3,4-dihydro-3,3-dimethyl-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione(**4b**)

Entry	Temperature (°C)	Time (min)	Yield[a] (%)
1	40	30	30
2	60	30	50
3	80	30	75
4	100	30	70
5	120	30	60
6[b]	80	5	96

[a] Isolated yield.
[b] Reaction was carried out by microwave irradiation.

Next the effect of catalyst plays an important role in the formation of *2H*-indazolo[2,1-*b*]phthalazine-triones derivatives. 3-Fluorobenzaldehyde (**2b**, 1 mmol), phthalhydrazide (**1**, 1 mmol), and 5,5-dimethylcyclohexane-1,3-dione (**3**, 1 mmol) at 80 °C, under microwave irradiation in solvent-free conditions were selected as representative substrates to investigate the reaction conditions. In the absence of the catalyst, the reaction could be carried out but the product was obtained in very low yield after prolonged reaction time. Therefore, our efforts focused on the search for a suitable catalyst. Initially, TiO_2 was chosen as the catalyst to carry out this reaction. As a result, long reaction times were needed and low transformation rates were observed. Attempts with different catalysts at 80 °C, under microwave irradiation in solvent-free conditions, and the results are listed in Table 2. It was found that K-10 showed better catalytic activity among these catalysts. Most excitingly, when K-10 was used, the reaction proceeded very smoothly and gave the product **4b** in 96% yield (Table 2, entry 9). Moreover, we found that the yields were obviously affected by the amount of K-10 loaded. When 1 mol %, 3 mol %, 5 mol %, and 10 mol % of K-10 were used, the yields were 30, 75, 96, and 96%, respectively (Table 2, entries 9–12). Therefore, 5 mol % of K-10 was sufficient and excessive amount of catalyst did not increase the yields significantly (Table 2, entries 9). The catalytic activity of the recycled K-10 was also examined. K-10 could be reused three times for the reaction without noticeable loss of activity (Table 2, entry 9).

Table 2
Influence of the catalyst on the synthesis of 13-(3-fluorophenyl)-3,4-dihydro-3,3-dimethyl-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (**4b**)[a]

Entry	Catalyst	Catalyst (mol %)	Time (min)	Yield[b] (%)
1	NO	—	100	25
2	TiO_2	5	60	40
3	BF_3–SiO_2	5	30	75
4	InF_3	5	40	70
5	$GaBr_3$	5	30	60
6	TiO_2–SiO_2	5	100	40
7	Amberlyst 15	5	55	40
8	$Y(OAc)_3 7 \cdot H_2O$	5	100	35
9[c]	K-10	5	5	96, 93, 90
10	K-10	1	20	30
11	K-10	3	10	75
12	K-10	10	5	96

[a] Reaction of 3-fluorobenzaldehyde (1 mmol), phthalhydrazide(1 mmol) and 5,5-dimethylcyclohexane-1,3-dione (1 mmol) under microwave irradiation in solvent-free conditions at 80 °C.
[b] Isolated yield.
[c] Catalyst was reused three times.

Then, we examined the effect of solvents over the above reaction. The results of Table 3 indicate that solvents affected the efficiency of the reaction. Yields were poor in acetonitrile, dichloromethane, and tetrahydrofuran (Table 3, entries 1–3). Better

Table 3
Influence of the solvent on the synthesis of 13-(3-fluorophenyl)-3,4-dihydro-3,3-dimethyl-*2H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (**4b**)[a]

Entry	Solvent (2 mL)	Time (min)	Yield[b] (%)
1	Acetonitrile	30	30
2	Dichloromethane	30	40
3	Tetrahydrofuran	30	35
4	Methanol	30	60
5	Ethanol	30	65
6	Neat	5	96

[a] Reaction of 3-fluorobenzaldehyde (1 mmol), phthalhydrazide(1 mmol) and 5,5-dimethylcyclohexane-1,3-dione (1 mmol) catalysed by K-10 under microwave irradiation at 80 °C.
[b] Isolated yield.

yields were obtained in more polar solvents like methanol and ethanol (Table 3, entries 4 and 5). However, the best results were obtained under solvent free conditions. Recently, organic synthesis involving multicomponent reactions under solvent-free conditions has attracted much attention, therefore we explored the possibility of obtaining the target compounds under solvent-free conditions. We found that the reaction proceeded smoothly in much shorter time at mild temperature and resulted in the formation of products in higher yield. It is desirable to minimize the amount of waste for each organic transformation.

In order to extend the above reaction (Scheme 1) to a library system, various kinds of arylaldehydes**2** (Table 4) were subjected to react with **1** and **3** to give the corresponding 2*H*-indazolo[2,1-*b*] phthalazine-triones **4**, and representative examples are shown in Table 4. All of **2** gave the expected products at high yields, either bearing electron-withdrawing groups or electron-donating groups under the same reaction condition. The acid-sensitive heterocyclic/alphatic aldehydes were also obtained in good yields. Various functional groups were found to be compatible under the reaction conditions. In general, the reactions were clean and no side products were detected. In all cases, the reactions proceeded efficiently at 80 °C under microwave irradiation in solvent-free and K-10 (5 mol %) conditions. All of the structures were characterized by ^{1}H NMR, ^{13}C NMR, IR and HRMS.

The proposed mechanism for the synthesis of 2*H*-indazolo [2,1-*b*]phthalazine-triones is illustrated in Scheme 2. The reaction is thought to proceed in a stepwise manner. Firstly, we assumed that the reaction occurs via a Knoevenagel condensation between 1,3-dicarbonyl compounds **3** and aromatic aldehydes **2** to form the intermediate **5** on the acidic active surface of K-10, which suffers immediate Michael addition of phthalhydrazide **1** to the C=C bond of **5**. Intramolecular concerted cyclocondensation of amino and carbonyl of the Michael adduct **6** was performed to afford the corresponding products (**4a**–**t**). During the reaction process, the hydrogen ion transfers through the surface of K-10. The hydrogen ion helps in the enolization of 1,3-dicarbonyl compounds to form the enolate intermediate.

3. Conclusion

In conclusion, we have successfully developed a simple, green, and efficient microwave assisted one-pot multicomponent

Table 4
Microwave-assisted synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones[a]

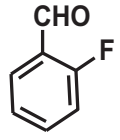
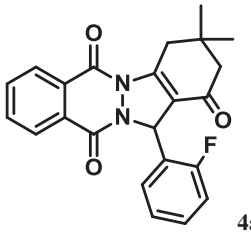
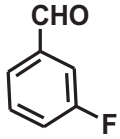
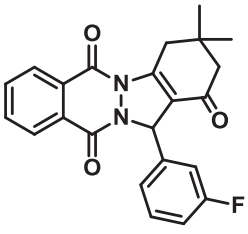
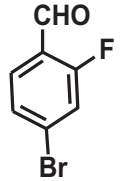
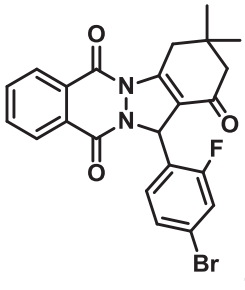
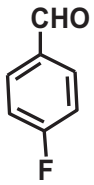
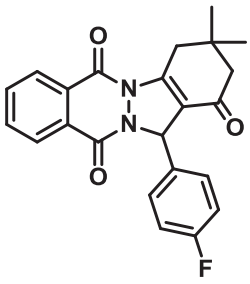
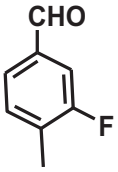
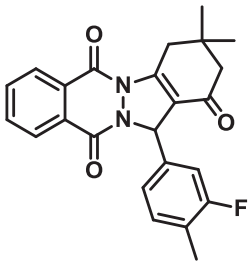
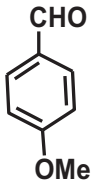
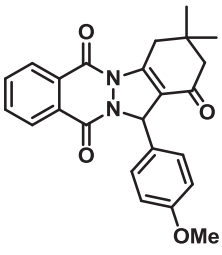
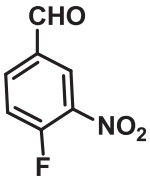
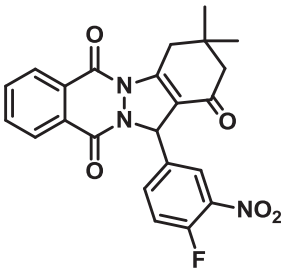
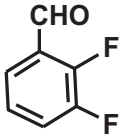
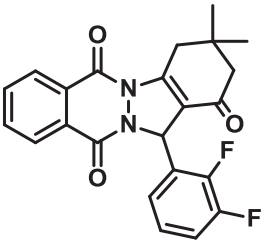
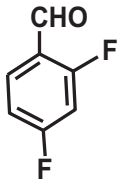
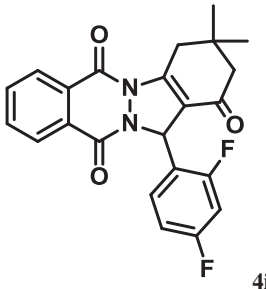
Entry	Aldehyde	Product	Time (min)	Yield[b] (%)	Mp (°C)	
					Found	Reported
1		 **4a**	5	92	270–272	—
2		 **4b**	5	96	228–230	—
3		 **4c**	8	90	280–282	—

Table 4 (*continued*)

Entry	Aldehyde	Product	Time (min)	Yield[b] (%)	Mp (°C)	
					Found	Reported
4		 **4d**	5	96	217–219	(217–219)[17]
5		 **4e**	5	96	228–230	—
6		 **4f**	6	94	220–222	(218–220)[24]
7		 **4g**	12	90	225–227	—
8		 **4h**	7	90	265–267	—
9		 **4i**	8	90	266–268	—

(*continued on next page*)

Table 4 (*continued*)

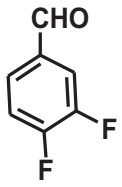
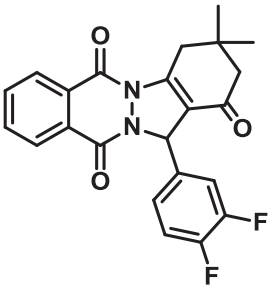
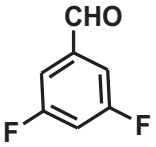
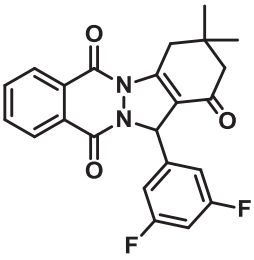
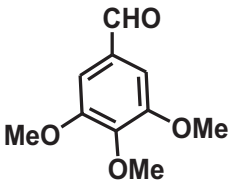
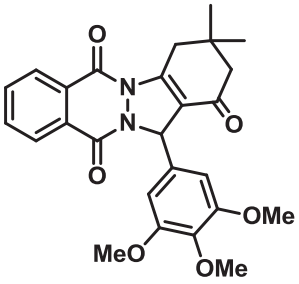
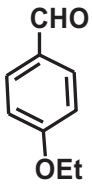
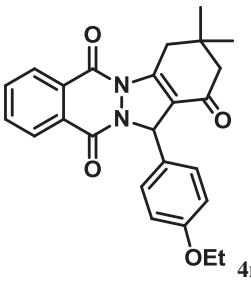
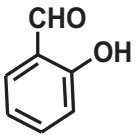
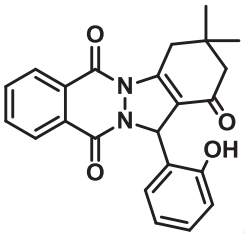
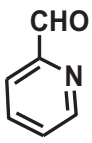
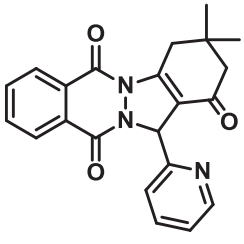
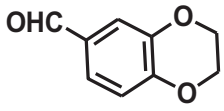
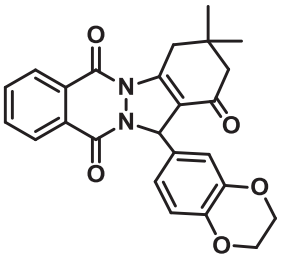
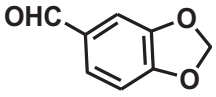
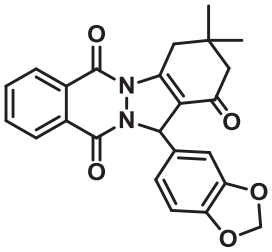
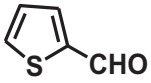
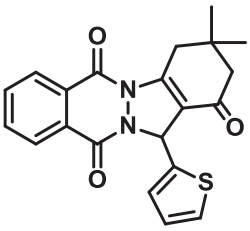
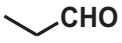
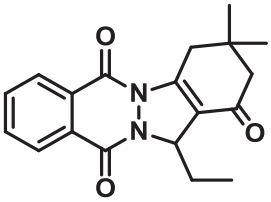
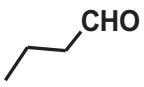
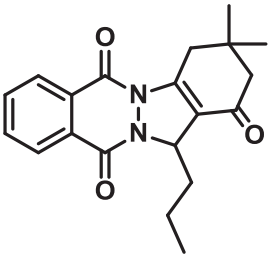
Entry	Aldehyde	Product	Time (min)	Yield[b] (%)	Mp (°C)	
					Found	Reported
10		 **4j**	7	91	206–208	—
11		 **4k**	6	92	230–232	—
12		 **4l**	12	90	233–235	(233–235)[23]
13		 **4m**	7	93	178–180	—
14		 **4n**	13	92	188–190	—
15		 **4o**	10	90	229–231	(230–232)[24]

Table 4 (*continued*)

Entry	Aldehyde	Product	Time (min)	Yield[b] (%)	Mp (°C)	
					Found	Reported
16		 **4p**	8	90	254–256	—
17		 **4q**	8	91	258–260	—
18		 **4r**	8	90	218–220	(217–219)[24]
19		 **4s**	15	80	146–148	(145–147)[23]
20		 **4t**	15	81	136–138	(136–138)[23]

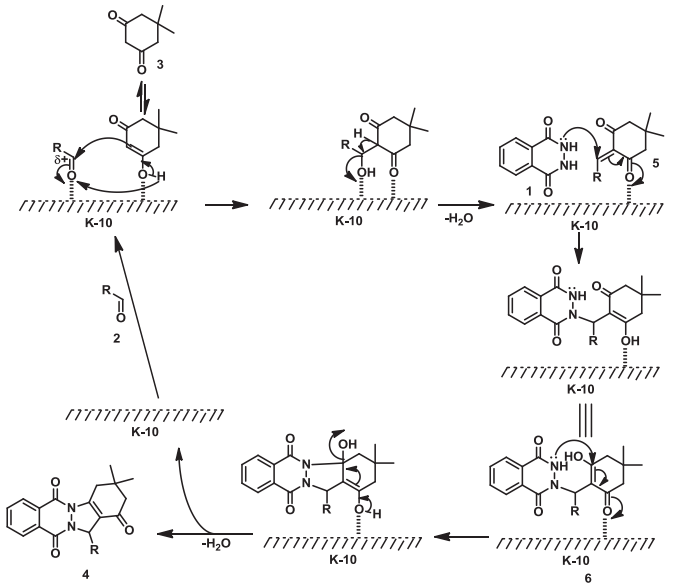
[a] Reaction of aldehydes (1 mmol), phthalhydrazide(1 mmol) and 5,5-dimethylcyclohexane-1,3-dione (1 mmol) catalysed by K-10 under solvent-free microwave irradiation at 80 °C.
[b] Isolated yield.

synthesis of *2H*-indazolo[2,1-*b*]phthalazine-triones derivatives from easily available starting materials using K-10 as a catalyst under solvent-free conditions. This protocol is attractive in terms of, atom economy, shortened reaction time, simple and clean reaction profiles, tolerance of various functional groups, and reusability of the catalyst.

4. Experimental

4.1. General

Chemicals were purchased from Aldrich and Alfaaesar Chemical Companies. NMR spectra were recorded in parts per million in $CDCl_3$



Scheme 2. Schematic presentation of the possible mechanism of products **4a**–**t** formation.

on a Jeol JNM ECP 400 NMR instrument using TMS as internal standard. Mass spectra were recorded on a Jeol JMS-700 mass spectrometer. All melting points were determined using open capillaries on an Electrothermal-9100 (Japan) instrument. Infrared (IR) spectra were obtained using a ShimadzuIR Prestige-21 FTIR Spectrophotometry.

4.2. Synthesis of 13-(3-fluorophenyl)-3,4-dihydro-3, 3-dimethyl-*2H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione (4b)

A mixture of phthalhydrazide (**1**, 162 mg, 1 mmol), 3-fluorobenzaldehyde (**2b**, 105 mg, 1 mmol), 5,5-dimethyl-cyclohexane-1,3-dione (**3**, 140 mg, 1 mmol) and K-10 (5 mol %, 50 mg) was taken in an open vessel and irradiated at 80 °C in solvent-free condition for 5 min. The reactions were followed by thin layer chromatography (TLC) using hexane/ethyl acetate (3:1) as an eluent (R_f=0.70). After completion of the reaction, the mixture was washed with ethyl acetate and filtered to recover the catalyst. The filtrate was evaporated, and the crude product was recrystallized from ethanol to afford pure 13-(3-fluorophenyl)-3,4-dihydro-3,3-dimethyl-*2H*-indazolo-[2,1-*b*] phthalazine-1,6,11(13*H*)-trione (**4b**) in excellent yield (380 mg).

*4.2.1. 13-(2-Fluorophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo [2,1-b]phthalazine-1,6,11(13H)-trione (**4a**).* R_f value=0.56 (hexane/ethyl acetate (3:1)); Yield 92%; yellow powder; mp 270–272 °C. IR (KBr): ν=2956, 2865, 1660, 1357, 1312 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35–8.33 (m, 1H), 8.21–8.19 (m, 1H), 7.89–7.87 (m, 2H), 7.44 (t, *J*=7.3 Hz, 1H), 7.31–7.26 (q, 1H), 7.14 (t, *J*=7.6 Hz, 1H), 7.01 (t, *J*=10.2 Hz, 1H), 6.54 (s, 1H), 3.41 and 3.22 (AB System, *J*=19.1 Hz, 2H), 2.31 (s. 2H), 1.22 (s, 3H), 1.18 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 159.2, 155.0, 153.3, 150.8, 133.7, 132.8, 129.5, 1294.5, 128.2, 127.9, 127.2, 126.5, 123.5, 115.9, 114.9, 59.7, 50.0, 37.1, 33.8, 28.0, 27.2 ppm. HRMS (ESI, *m*/*z*): calcd for $C_{23}H_{19}FN_2O_3$ ($M+H^+$) 390.1380; found: 390.1378.

*4.2.2. 13-(3-Fluorophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo [2,1-b]phthalazine-1,6,11(13H)-trione (**4b**).* R_f value=0.70 (hexane/ethyl acetate (3:1)); Yield 96%; yellow powder; mp 228–230 °C. IR (KBr): ν=2971, 2865, 1660, 1365, 1304 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36–8.34 (m, 1H), 8.27–8.25 (m, 1H), 7.86–7.84 (m, 2H), 7.33–7.23 (m, 2H), 7.08 (d, *J*=9.5 Hz, 1H), 6.97 (t, *J*=8.4 Hz, 1H), 6.42 (s, 1H), 3.40 and 3.23 (AB System, *J*=19.0 Hz, 2H), 2.33 (s, 2H), 1.20 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 161.5, 155.9, 154.3, 151.0, 138.8, 134.5, 133.6, 130.2, 128.9, 128.0, 127.6, 122.9, 117.9, 115.7, 114.0, 113.8, 64.2, 50.8, 37.9, 34.6, 28.5, 28.4 ppm. HRMS (ESI, *m*/*z*): calcd for $C_{23}H_{19}FN_2O_3$ ($M+H^+$) 390.1380; found: 390.1377.

*4.2.3. 13-(4-Bromo-2-fluorophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4c**).* R_f value=0.56 (hexane/ethyl acetate (3:1)); Yield 90%; yellow powder; mp 280–282 °C. IR (KBr): ν=2956, 2882, 1652, 1349, 1289 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37–8.34 (m, 1H), 8.26–8.23 (m, 1H), 7.87–7.85 (m, 2H), 7.38 (t, *J*=8.0 Hz, 1H), 7.29 (d, *J*=8.4 Hz, 1H), 7.18 (dd, *J*=11.7, 1.4 Hz, 1H), 6.48 (s, 1H), 3.40 and 3.21 (AB System, *J*=19.0 Hz, 2H), 2.32 (s, 2H), 1.21 (s, 3H), 1.18 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 156.0, 154.4, 151.9, 134.5, 133.6, 131.3, 129.2, 128.6, 128.0, 127.8, 123.2, 122.8, 120.1, 119.6, 116.2, 60.8, 50.2, 37.9, 34.6, 28.8, 28.0 ppm. HRMS (ESI, *m*/*z*): calcd for $C_{23}H_{18}BrFN_2O_3$ ($M+H^+$) 468.0485; found: 468.0480.

*4.2.4. 13-(4-Fluorophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo [2,1-b]phthalazine-1,6,11(13H)-trione (**4d**).* R_f value=0.62 (hexane/ethyl acetate (3:1)); Yield 96%; yellow powder; mp 217–219 °C (217–219 °C).[17] IR (KBr): ν=2971, 2850, 1659, 1350, 1312 cm^{-1} ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30–8.28 (m, 1H), 8.24–8.22 (m, 1H), 7.87–7.84 (m, 2H), 7.42–7.39 (m, 2H), 7.03 (t, *J*=8.8 Hz, 2H), 6.43 (s, 1H), 3.42 and 3.25 (AB System, *J*=19.1 Hz, 2H), 2.35 (s, 2H), 1.24 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.8, 156.4, 154.4, 151.5, 134.6, 133.3, 131.9, 129.2, 128.7, 128.0, 127.5, 117.9, 115.5, 115.0, 60.3, 51.9, 38.2, 34.3, 28.7, 28.4 ppm.

*4.2.5. 13-(3-Fluoro-4-methylphenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4e**).* R_f value=0.60 (hexane/ethyl acetate (3:1)); Yield 96%; yellow powder; mp 228–230 °C. IR (KBr): ν=2956, 2865, 1660, 1350, 1312 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35–8.33 (m, 1H), 8.26–8.24 (m, 1H), 7.85–7.83 (m, 2H), 7.15 (dd, *J*=12.6, 2.2 Hz, 2H), 7.02, (d, *J*=9.2 Hz, 1H), 6.38 (s, 1H), 3.40 and 3.23 (AB System, *J*=19.3 Hz, 2H), 2.33 (s, 2H), 2.20 (s, 3H), 1.20 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 159.9, 155.8, 154.2, 150.9, 136.0, 134.4, 133.5, 131.6, 128.8, 127.9, 127.6, 125.4, 122.7, 118.0, 113.6, 64.2, 50.8, 37.9, 34.5, 28.5, 28.3, 14.3 ppm. HRMS (ESI, *m*/*z*): calcd for $C_{24}H_{21}FN_2O_3$ ($M+H^+$) 404.1536; found: 404.1534.

*4.2.6. 3,4-Dihydro-13-(4-methoxyphenyl)-3,3-dimethyl-2H-indazolo [2,1-b]phthalazine-1,6,11(13H)-trione (**4f**).* R_f value=0.58 (hexane/ethyl acetate (3:1)); Yield 94%; yellow powder; mp 220–222 °C (218–220 °C).[24] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36–8.33 (m, 1H), 8.26–8.23 (m, 1H), 7.86–7.83 (m, 2H), 7.30 (d, *J*=8.8 Hz, 2H), 6.86 (d, *J*=8.4 Hz, 2H), 6.42 (s, 1H), 3.78 (s, 3H), 3.40 and 3.24 (AB System, *J*=19.1 Hz, 2H), 2.35 (s, 2H), 1.22 (s, 6H) ppm. ^{13}C NMR (CDC_{l3}, 100 MHz) δ 192.2, 159.9, 156.0, 154.6, 150.1, 134.4, 133.3, 129.1, 128.8, 128.5, 128.3, 127.9, 127.7, 118.5, 114.1, 60.6, 55.2, 51.0, 38.5, 34.0, 28.7, 28.1 ppm.

*4.2.7. 13-(4-Fluoro-3-nitrophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4g**).* R_f value=0.60 (hexane/ethyl acetate (3:1)); Yield 90%; yellow powder; mp 225–227 °C. IR (KBr): ν=2958, 2874, 1652, 1319, 1274 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38–8.36 (m, 1H), 8.26–8.23 (m, 1H), 8.02 (dd, *J*=9.2, 2.0 Hz, 1H), 7.90–7.87 (m, 3H), 7.30 (d, *J*=8.5 Hz, 1H), 6.46 (s, 1H), 3.42 and 3.26 (AB System, *J*=19.2 Hz, 2H), 2.35 (s, 2H), 1.22 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 155.9, 154.7, 151.9, 135.2, 134.8, 133.9, 133.6, 128.9, 128.5, 127.6, 124.3, 118.8, 118.6, 116.7, 63.5, 50.7, 37.9, 34.7, 28.7, 28.4 ppm. HRMS (ESI, *m*/*z*): calcd for $C_{23}H_{18}FN_3O_5$ ($M+H^+$) 435.1230; found: 435.1230.

*4.2.8. 13-(2,3-Difluorophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4h**).* R_f value=0.56

(hexane/ethyl acetate (3:1)); Yield 90%; yellow powder; mp 265–267 °C. IR (KBr): ν=2956, 2863, 1652, 1350, 1312 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$): δ 8.37–8.34 (m, 1H), 8.26–8.20 (m, 1H), 7.80–7.88 (m, 2H), 7.22–7.19 (m, 1H), 7.13–7.10 (m, 2H), 6.57 (s, 1H), 3.41 and 3.23 (AB System, J=19.4 Hz, 2H), 2.34 (s, 2H), 1.22 (s, 3H), 1.19 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 155.4, 153.8, 134.0, 133.2, 131.9, 128.4, 128.0, 127.5, 126.8, 125.8, 125.2, 123.8, 116.9, 116.4, 115.7, 59.3, 50.1, 37.3, 34.0, 28.2, 27.5. HRMS (ESI, m/z): calcd for $C_{23}H_{18}F_2N_2O_3$ ($M+H^+$) 408.1285; found: 408.1282.

*4.2.9. 13-(2,4-Difluorophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4i**).* R_f value=0.59 (hexane/ethyl acetate (3:1)); Yield 90%; yellow powder; mp 266–268 °C. IR (KBr): ν=2956, 2865, 1660, 1357, 1304 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$): δ 8.37–8.34 (m, 1H), 8.26–8.24 (m, 1H), 7.87–7.84 (m, 2H), 7.50–7.45 (m, 1H), 6.91–6.88 (m, 1H), 6.77–6.74 (m, 1H), 6.50 (s, 1H), 3.41 and 3.21 (AB System, J=19.0 Hz, 2H), 2.33 (s, 2H), 1.21 (s, 3H), 1.19 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.3, 156.1, 154.4, 151.7, 134.5, 133.6, 131.7, 130.2, 129.1, 128.9, 128.0, 127.6, 121.0, 116.6, 112.1, 111.8, 104.7, 60.8, 50.8, 37.9, 34.6, 28.8, 28.0 ppm. HRMS (ESI, m/z): calcd for $C_{23}H_{18}F_2N_2O_3$ ($M+H^+$) 408.1285; found: 408.1285.

*4.2.10. 13-(3,4-Difluorophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4j**).* R_f value=0.65 (hexane/ethyl acetate (3:1)); Yield 91%; yellow powder; mp 206–208 °C. IR (KBr): ν=2956, 2855, 1667, 1357, 1266 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$): δ 8.36–8.34 (m, 1H), 8.27–8.25 (m, 1H), 7.87–7.85 (m, 2H), 7.23–7.11 (m, 3H), 6.39 (s, 1H), 3.39 and 3.23 (AB System, J=19.1 Hz, 2H), 2.34 (s, 2H), 1.20 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 155.9, 154.5, 151.2, 134.7, 133.7, 133.4, 128.9, 128.8, 128.1, 127.7, 123.8, 117.6, 117.4, 116.3, 63.9, 50.8, 38.0, 34.6, 28.6, 28.4 ppm. HRMS (ESI, m/z): calcd for $C_{23}H_{18}F_2N_2O_3$ ($M+H^+$) 408.1285; found: 408.1285.

*4.2.11. 13-(3,5-Difluorophenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4k**).* R_f value=0.58 (hexane/ethyl acetate (3:1)); Yield 92%; yellow powder; mp 230–232 °C. IR (KBr): ν=2971, 2865, 1652, 1357, 1305 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$): δ 8.37–8.35 (m, 1H), 8.28–8.26 (m, 1H), 7.88–7.86 (m, 2H), 6.95 (d, J=7.2 Hz, 2H), 6.74–6.69 (m, 1H), 6.39 (s, 1H), 3.38 and 3.23 (AB System, J=19.1 Hz, 2H), 2.34 (s, 2H), 1.20 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 164.2, 155.9, 154.5, 151.4, 140.3, 134.7, 133.8, 128.9, 128.1, 127.7, 117.4, 110.4, 104.4, 103.9, 63.9, 50.8, 38.0, 34.6, 28.6, 28.4 ppm. HRMS (ESI, m/z): calcd for $C_{23}H_{18}F_2N_2O_3$ ($M+H^+$) 408.1285; found: 408.1284.

*4.2.12. 3,4-Dihydro-13-(3,4,5-trimethoxyphenyl)-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4l**).* R_f value=0.60 (hexane/ethyl acetate (3:1)); Yield 90%; yellow powder; mp 235–237 °C (233–235 °C).[23] ^1H NMR ($CDCl_3$, 400 MHz) δ 8.30–8.22 (m, 2H), 7.89–7.87 (m, 2H), 6.60 (s, 2H), 6.45 (s, 1H), 3.83 (s, 9H), 3.42 and 3.21 (AB System, J=19.1 Hz, 2H), 2.33 (s, 2H), 1.24 (s, 6H) ppm. ^{13}C NMR(CDCl3, 100 MHz) δ 192.0, 156.3, 154.6, 153.0, 150.8, 138.6, 134.3, 133.3, 131.3, 129.0, 128.4, 128.0, 127.5, 118.3, 104.3, 65.6, 60.3, 56.9, 50.9, 38.0, 34.6, 28.9, 28.1 ppm.

*4.2.13. 13-(4-Ethoxyphenyl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4m**).* R_f value=0.60 (hexane/ethyl acetate (3:1)); Yield 93%; yellow powder; mp 178–180 °C. IR (KBr): ν=2971, 2850, 1652, 1349, 1312 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$): δ 8.24–8.22 (m, 1H), 8.09–8.09 (m, 1H), 7.95–7.92 (m, 2H), 7.32 (d, J=8.8 Hz, 2H), 6.83 (d, J=8.5 Hz, 2H), 6.22 (s, 1H), 4.00–3.94 (m, 2H), 3.32 and 3.15 (AB System, J=19.2 Hz, 2H), 2.25 (s, 2H), 1.28 (t, J=6.8 Hz, 3H), 1.19 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 158.2, 155.3, 154.0, 151.0, 134.4, 133.6, 129.2, 128.9, 128.7, 127.4, 126.6, 117.3, 113.9, 63.8, 62.9, 50.2, 37.2, 34.2, 28.0, 27.8, 14.6 ppm. HRMS (ESI, m/z): calcd for $C_{25}H_{24}F_2N_2O_4$ ($M+H^+$) 416.1736; found: 416.1730.

*4.2.14. 3,4-Dihydro-13-(2-hydroxyphenyl)-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4n**).* R_f value=0.56 (hexane/ethyl acetate (3:1)); Yield 92%; yellow powder; mp 188–190 °C. IR (KBr): ν=2971, 2865, 1644, 1365, 1229 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$): δ 11.5 (s, 1H), 8.03–8.01 (m, 2H), 7.85–7.81 (m, 2H), 7.06–7.02 (m, 1H), 6.95–6.89 (m, 3H), 3.42 and 3.22 (AB System, J=19.1 Hz, 2H), 2.30 (s, 2H), 1.28 (t, J=6.8 Hz, 3H), 1.17 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 155.1, 154.0, 149.6, 132.5, 128.3, 126.8, 125.6, 125.1, 124.1, 120.3, 115.2, 111.2, 62.3, 50.4, 38.8, 31.5, 28.1, 27.5 ppm. HRMS (ESI, m/z): calcd for $C_{23}H_{20}F_2N_2O_4$ ($M+H^+$) 388.1423; found: 388.1420.

*4.2.15. 3,4-Dihydro-3,3-dimethyl-13-(pyridin-2-yl)-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4o**).* R_f value=0.56 (hexane/ethyl acetate (3:1)); Yield 90%; yellow powder; mp 229–231 °C (230–232 °C).[24] ^1H NMR (400 MHz, $CDCl_3$): δ 8.36–8.30 (m, 2H), 8.04 (d, J=8.4 Hz, 1H), 7.87–7.84 (m, 2H), 7.66–7.50 (m, 3H), 6.40 (s, 1H), 3.40 and 3.21 (AB System, J=19.1 Hz, 2H), 2.30 (s, 2H), 1.19 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 156.2, 154.3, 151.6, 148.6, 138.6, 134.4, 133.4, 129.3, 128.2, 127.8, 123.8, 119.4, 115.4, 60.0, 50.9, 38.4, 31.2, 28.8, 28.4 ppm.

*4.2.16. 3,4-Dihydro-13-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4p**).* R_f value=0.62 (hexane/ethyl acetate (3:1)); Yield 90%; yellow powder; mp 254–256 °C. IR (KBr): ν=2956, 2880, 1660, 1349, 1289 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$): δ 8.34–8.32 (m, 1H), 8.28–8.26 (m, 1H), 7.84–7.82 (m, 2H), 6.95 (d, J=8.2 Hz, 1H), 6.82 (d, J=9.2 Hz, 2H), 6.34 (s, 1H), 4.19 (s, 4H), 3.39 and 3.22 (AB System, J=19.1 Hz, 2H), 2.33 (s, 2H), 1.22 (s, 3H), 1.19 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 155.9, 154.2, 150.6, 143.8, 134.4, 133.4, 129.5, 129.1, 128.9, 127.9, 127.6, 120.7, 118.4, 117.4, 115.7, 64.4, 64.1, 50.9, 37.9, 34.6, 28.5 ppm. HRMS (ESI, m/z): calcd for $C_{25}H_{22}N_2O_5$ ($M+H^+$) 430.1529; found: 430.1528.

*4.2.17. 13-(Benzo[d][1,3]dioxol-5-yl)-3,4-dihydro-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4q**).* R_f value=0.61 (hexane/ethyl acetate (3:1)); Yield 91%; yellow powder; mp 258–260 °C. IR (KBr): ν=2956, 2880, 1660, 1364, 1312 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$): δ 8.36–8.33 (m, 1H), 8.26–8.23 (m, 1H), 7.88–7.84 (m, 2H), 6.88–6.75 (m, 3H), 6.32 (s, 1H), 5.93 (s, 2H), 3.40 and 3.22 (AB System, J=19.2 Hz, 2H), 2.32 (s, 2H), 1.21 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.0, 156.9, 152.0, 148.4, 145.3, 137.5, 135.6, 133.5, 129.6, 128.9, 128.1, 121.6, 115.6, 114.5, 106.7, 102.3, 65.0, 51.3, 35.4, 33.9, 28.0, 27.8 ppm. HRMS (ESI, m/z): calcd for $C_{24}H_{20}N_2O_5$ ($M+H^+$) 416.1372; found: 416.1374.

*4.2.18. 3,4-Dihydro-3,3-dimethyl-13-(thiophen-3-yl)-2H-indazolo [2,1-b]phthalazine-1,6,11(13H)-trione (**4r**).* R_f value=0.59 (hexane/ethyl acetate (3:1)); Yield 90%; yellow powder; mp 218–220 °C (217–219 °C).[24] ^1H NMR ($CDCl_3$, 400 MHz): δ 8.30–8.25 (m, 2H), 7.85–7.82 (m, 2H), 7.30 (s, 1H), 7.23–7.22 (m, 1H), 6.95–6.93 (m, 1H), 6.52 (s, 1H), 3.41 and 3.22 (AB System, J=19.1 Hz, 2H), 2.31 (s, 2H), 1.22 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl3): δ 192.0, 154.2, 150.5, 138.6, 134.3, 133.5, 129.0, 128.8, 128.1, 127.9, 127.2, 125.8, 117.3, 60.2, 50.2, 37.8, 34.3, 28.9, 28.0 ppm.

*4.2.19. 13-Ethyl-3,4-dihydro-3,3-dimethyl-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (**4s**).* R_f value=0.61 (hexane/ethyl acetate (3:1)); Yield 80%; yellow powder; mp 146–148 °C (145–147 °C).[23] ^1H NMR (400 MHz, $CDCl_3$): δ 8.30–8.33 (m, 1H), 8.26–8.23 (m, 1H), 7.88–7.84 (m, 2H), 5.70–5.68 (m, 1H), 3.40 and 3.22 (AB

System, J=19.2 Hz, 2H), 2.32 (s, 2H), 1.65–1.61 (m, 2H), 1.21 (s, 6H), 0.96 (t, J=7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 155.3, 151.6, 134.5, 133.2, 129.3, 128.6, 127.8, 117.6, 62.0, 51.3, 38.4, 33.9, 28.0, 27.8, 22.3, 8.2 ppm.

*4.2.20. 3,4-Dihydro-3,3-dimethyl-13-propyl-2H-indazolo[2,1-b] phthalazine-1,6,11(13H)-trione (**4t**).* R_f value=0.65 (hexane/ethyl acetate (3:1)s); Yield 81%; yellow powder; mp 136–138 °C (136–138 °C).[23] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30–8.22 (m, 2H), 7.88–7.85 (m, 2H), 5.72–5.69 (m, 1H), 3.40 and 3.21 (AB System, J=19.1 Hz, 2H), 2.32 (s, 2H), 2.20–1.68 (m, 4H), 1.21 (s, 6H), 0.92 (t, J=7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 154.3, 151.6, 134.4, 133.4, 129.3, 128.2, 127.8, 119.4, 60.0, 50.9, 38.0, 33.2, 31.5, 28.8, 28.4, 20.3, 14.6 ppm.

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