Organic & Biomolecular Chemistry

PAPER

Cite this: *Org. Biomol. Chem.*, 2021, **19**, 2725

Ruthenium(II)-catalyzed decarbonylative and decarboxylative coupling of isatoic anhydrides with salicylaldehydes: access to aryl 2-aminobenzoates†

Bidisha R. Bora, Rashmi Prakash, Sabera Sultana and Sanjib Gogoi *

Received 6th January 2021,
Accepted 23rd February 2021

DOI: 10.1039/d1ob00027f

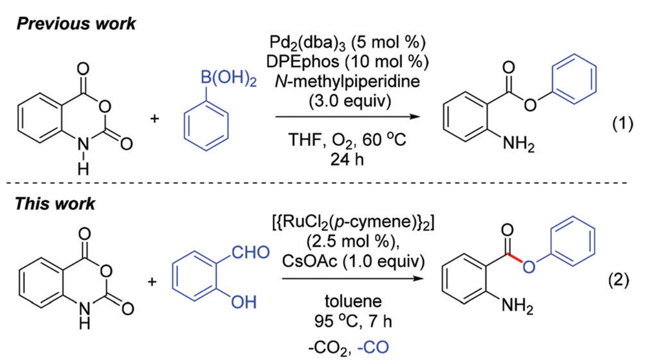
rsc.li/obc

A ruthenium(II)-catalyzed coupling reaction of isatoic anhydrides and salicylaldehydes has been developed for the synthesis of 2-aminobenzoates. This reaction proceeds through metal-catalyzed decarbonylation and decarboxylation to afford good yields of aryl 2-aminobenzoates.

The aryl esters of benzoic acids are very important synthons for the synthesis of various pharmaceutically active compounds as well as natural products.[1] In photochemistry, aryl benzoates are used as chemiluminescent indicators.[2] Among the aryl benzoates, particularly, the aryl 2-aminobenzoates have received significant attention because of their utility in the synthesis of bioactive nitrogen containing heterocycles.[3] Some of these 2-aminobenzoates have application in fragrance and flavor industries owing to their pleasant scent.[4] Furthermore, some of the aminobenzoate derivatives exhibit anti-bacterial, anti-fungal and anti-inflammatory activities.[5] The drug glafenine is a nonsteroidal anti-inflammatory drug that possesses 2-aminobenzoate as the key skeleton.

These aryl benzoates are traditionally synthesized by esterification, transesterification and Baeyer–Villiger oxidation reactions.[6] However, the highly acidic and basic conditions used in esterification and transesterification reactions might not be suitable for some compounds possessing sensitive functional groups in the molecule. Again, acid-catalyzed esterification of anthranilic acid to get the ester is a tough reaction owing to the presence of *ortho* amino group. This amino group consumes large amount of the acid before esterification with the alcohol. To overcome these problems, designing of new method for the synthesis of these esters are very essential. In recent years, various metal-catalyzed coupling reactions have been developed for the synthesis of benzoic esters.[7] However, metal-catalyzed reactions for the synthesis of aryl 2-aminobenzoates are rare. Wu and co-workers reported a $Pd_2(dba)_3$-catalyzed reaction of isatoic anhydrides with arylboronic acids in the presence of the ligand DPEphos for the synthesis of aryl *o*-aminobenzoates (Scheme 1, eqn (1)).[8] In continuation of our work on metal-catalyzed C–H, C–C functionalization reactions,[9] herein, we disclose an unprecedented decarbonylative and decarboxylative coupling reaction of isatoic anhydrides and salicylaldehydes for the synthesis of aryl 2-aminobenzoates (Scheme 1, eqn (2)).

Initially, the Ru(II)-catalyzed coupling reaction between isatoic anhydride (**1a**) and salicyldehyde (**2a**) was selected as a model reaction to find out the optimized reaction conditions for the synthesis of the ester **3aa**. As shown in Table 1, among all the metal complexes studied for this esterification reaction, only the [{$RuCl_2$(*p*-cymene)}$_2$] catalyst provided the ester **3aa** in 43% yield using $Cu(OAc)_2$ and ^{t}AmOH as the additive and solvent, respectively. To improve the yield of **3aa**, some other commonly used additives such as CsOAc, AgOAc and KOAc were tested which revealed CsOAc to be the best additive which afforded 58% yield of **3aa** (entry 5). Then, further screening of some common solvents proved the aprotic solvent

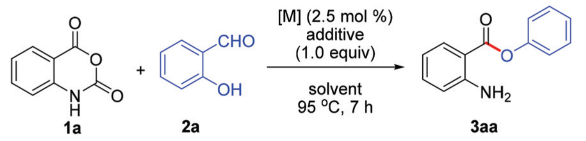


Scheme 1 Metal-catalyzed synthesis of aryl 2-aminobenzoates.

Applied Organic Chemistry, Chemical Sciences & Technology Division, CSIR-North East Institute of Science and Technology, Jorhat-785006, AcSIR, Ghaziabad-201002, India. E-mail: skgogoi1@gmail.com, sanjibgogoi@neist.res.in

†Electronic supplementary information (ESI) available: Copies of ^{1}H NMR, ^{13}C NMR spectra of the synthesized compounds. See DOI: 10.1039/d1ob00027f

Table 1 Reaction conditions optimization for **3aa**[a]

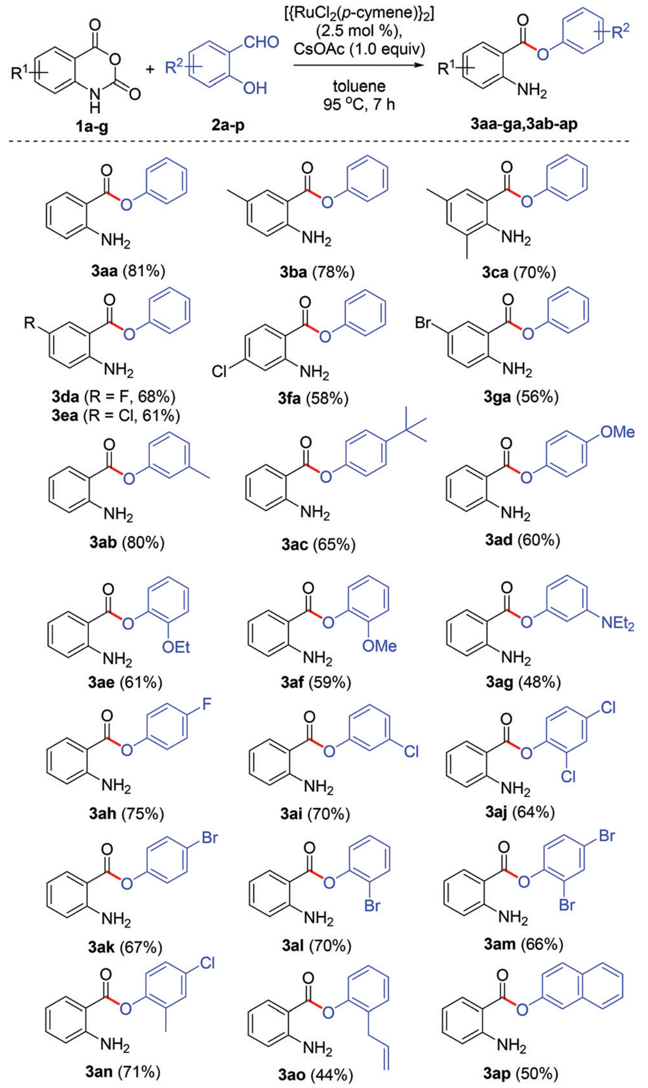


Entry	Catalyst	Additive	Solvent	**3aa**[b] (%)
1	$Pd(OAc)_2$	$Cu(OAc)_2 \cdot H_2O$	^{t}AmOH	0
2	$RuCl_3 \cdot xH_2O$	$Cu(OAc)_2 \cdot H_2O$	^{t}AmOH	0
3	$[RuCl_2(PPh_3)_3]$	$Cu(OAc)_2 \cdot H_2O$	^{t}AmOH	0
4	$[\{RuCl_2(p\text{-cymene})\}_2]$	$Cu(OAc)_2 \cdot H_2O$	^{t}AmOH	43
5	$[\{RuCl_2(p\text{-cymene})\}_2]$	CsOAc	^{t}AmOH	58
6	$[\{RuCl_2(p\text{-cymene})\}_2]$	AgOAc	^{t}AmOH	27
7	$[\{RuCl_2(p\text{-cymene})\}_2]$	KOAc	^{t}AmOH	38
8	$[\{RuCl_2(p\text{-cymene})\}_2]$	CsOAc	MeCN	25
9	$[\{RuCl_2(p\text{-cymene})\}_2]$	CsOAc	DCE	42
10	$[\{RuCl_2(p\text{-cymene})\}_2]$	CsOAc	Toluene	81
11	$[\{RuCl_2(p\text{-cymene})\}_2]$	CsOAc	Dioxane	54

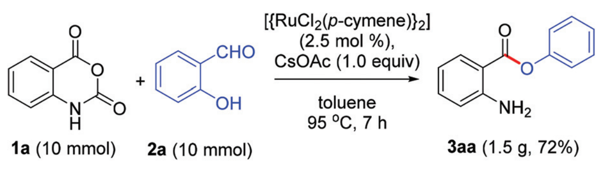
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), catalyst (2.5 mol%), additive (0.5 mmol) and solvent (4.0 mL) heated at 95 °C for 7 h under air. [b] Isolated yields.

toluene to be the best solvent for the synthesis of the ester **3aa** (81%, entry 10).

Initially the optimized reaction conditions were applied to study the substrate scope of the isatoic anhydrides (**1a–g**). As shown in Scheme 2, isatoic anhydrides substituted with mono-methyl and di-methyl substituents **1b–c** provided 70–78% yields of the products **3ba–ca**. Similarly, isatoic anhydrides substituted with electron-withdrawing substituents such as fluoro, chloro and bromo **1d–g**, provided good yields (56–68%) of the products **3da–ga**, irrespective of the position of the substituents on the aromatic ring. Next, the scope of the salicylaldehydes **2b–p** were studied with **1a** for this esterification reaction. As shown in Scheme 2, various salicylaldehydes possessing electron-rich substituents such as methyl, *tert*-butyl, methoxy, ethoxy and diethylamino on the phenyl ring of salicylaldehyde **2b–g** provided 48–80% yields of the esters **3ab–ag**. Similarly, some of the salicylaldehydes substituted with one or two electron-withdrawing substituents such as fluoro, chloro and bromo on the phenyl ring of salicylaldehyde **2h–m** provided 64–75% yields of the products **3ah–am**. For the products **3ag** and **3ai**, 4-(diethylamino)-2-hydroxybenzaldehyde (**2g**) and 4-chloro-2-hydroxybenzaldehyde (**2i**) were used. The methyl and chloro group substituted salicylaldehyde **1n** also turned out to be a good substrate for this reaction which provided 71% yield of product **3an**. The sensitive allyl group containing salicylaldehyde **2o** provided 44% yield of **3ao**. Finally, 2-hydroxy-1-naphthaldehyde **2p** was tested to afford 50% yield of ester **3ap**. The reaction of **1a** and 3-hydroxy-2-naphthaldehyde also provided the same ester **3ap** in 53% yield under the standard reaction conditions. A gram-scale esterification reaction between **1a** and **2a** provided 72% yield of **3aa**, which suggest the practical applicability of this reaction (Scheme 3). The phosphomolybdic acid test and lime water test indicated



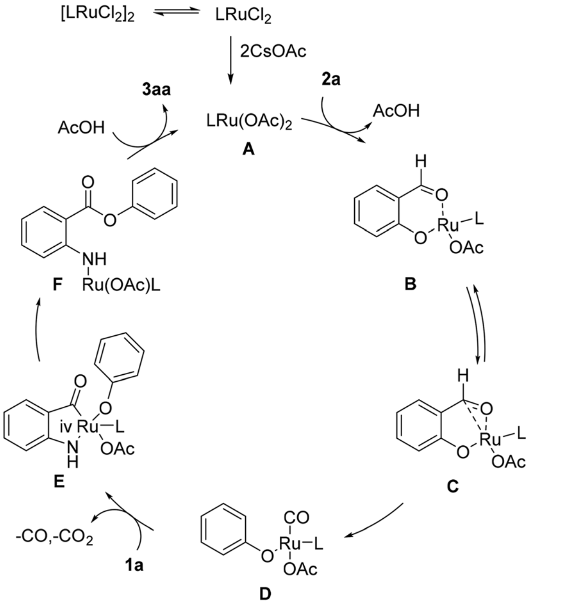
Scheme 2 Scope with isatoic anhydrides and salicylaldehydes. Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), Ru(II) catalyst (2.5 mol%), CsOAc (0.5 mmol) and toluene (4.0 mL) heated at 95 °C for 7 h under air.



Scheme 3 Gram-scale synthesis of ester **3aa**.

the evaluation of carbon monoxide and carbon dioxide, respectively, from the reaction mixture.[9b]

A plausible mechanism for the formation of **3aa** is proposed in Scheme 4, based on literature reports.[10] As the reaction of **1a**, **2a** and $[\{RuCl_2(p\text{-cymene})\}_2]$ in the absence of the additive CsOAc could not provide **3aa** in toluene at 95 °C, probably $[Ru(OAc)_2(p\text{-cymene})]$ (**A**) might be the active catalyst.[10e]



Scheme 4 Possible mechanism.

First, the active catalyst **A** forms Ru(II)-complex **B** by elimination of one molecule of acetic acid. This complex **B** might exist as tautomer with π-bonded Ru-complex **C**, which on decarbonylation generates a Ru–CO complex **D**.[10a] Then, oxidative addition of this Ru complex in the C–O bond of **1a** followed by decarboxylation and decarbonylation affords Ru-complex **E**. Reductive elimination of the metal initially generates Ru complex **F**, which in the presence of acetic acid affords the active catalyst **A** and the ester **3aa**.

In conclusion, a novel Ru(II)-catalyzed coupling reaction of isatoic anhydride and salicylaldehyde was developed. This reaction proceeds through decarboxylation and decarbonylation to afford good yields of important aryl 2-aminobenzoates.

Experimentalsections

General information

Melting points were measured with a Buchi B-540 melting point apparatus. The NMR spectra were recorded on Bruker Avance III 500 MHz FTNMR spectrometer using tetramethylsilane (TMS) as an internal standard. All the commercially available regents were used as received. All experiments were monitored by thin layer chromatography (TLC). TLC was performed on Merck TLC Silica gel 60 F254 precoated plates. Column chromatography was performed on silica gel (100–200 mesh, Merck). The starting isatoic anhydrides were synthesized using isatins by following a known procedure.[11]

General procedure A (GPA)

A mixture of isatoic anhydride (**1**, 0.5 mmol), salicyaldehyde (**2**, 0.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), CsOAc (0.5 mmol) in toluene (4.0 mL) was stirred at 95 °C under open air for 7 hours. The solvent was removed under vacuum and the crude reaction mixture was poured into water and extracted with dichloromethane (25 mL × 2). The dichloromethane layer was then washed with brine. Finally, it was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product thus obtained was purified by silica gel (100–200 mesh) column chromatography using EtOAc/Hexane as the eluant to afford **3**.

Compound characterizations

Phenyl 2-aminobenzoate (3aa).[8] Synthesized using GPA from **1a** (81 mg,0.5 mmol) and **2a** (61 mg, 0.5 mmol). The crude product was purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3aa** (86 mg, 81%). M.p.: 70–72 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, J = 7.9 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.36–7.33 (m, 1H), 7.29–7.26 (m, 1H), 7.20–7.18 (m, 2H), 6.74–6.70 (m, 2H), 5.78 (bs, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 151.1, 150.7, 134.8, 131.5, 129.4, 125.7, 122.6, 121.9, 116.7, 116.3, 114.4, 109.5. Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.68; H, 5.01; N, 6.81.

Phenyl 2-amino-5-methylbenzoate (3ba).[8] Synthesized using GPA from **1b** (88 mg, 0.5 mmol) and **2a** (61 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid (88 mg, 78%). M.p.: 60–62 °C. ^{1}H NMR (500 MHz, CDCl3) δ 7.89 (s, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.29–7.25 (m, 1H), 7.15–7.20 (m, 3H), 6.64 (d, J = 8.4 Hz, 1H), 5.62 (bs, 2H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 150.7, 149.1, 136.0, 131.0, 129.4, 125.7, 125.4, 121.9, 116.8, 109.3, 20.2. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.20; H, 5.83; N, 5.93.

Phenyl 2-amino-3,5-dimethylbenzoate(3ca). Synthesized using GPA from **1c** (95 mg, 0.5 mmol) and **2a** (61 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid (84 mg, 70%). M.p.: 101–103 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.29–7.25 (m, 1H), 7.18 (d, J = 8.3 Hz, 2H), 7.12 (s, 1H), 5.73 (bs, 2H), 2.27 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 150.8, 147.6, 136.9, 129.4, 128.8, 125.6, 124.7, 123.2, 122.0, 108.9, 20.2, 17.3. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.51; H, 6.45; N, 6.09.

Phenyl 2-amino-5-fluorobenzoate(3da).[8] Synthesized using GPA from **1d** (90 mg, 0.5 mmol) and **2a** (61 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford yellow solid of **3da** (78 mg, 68%). M.p.: 110–112 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, J = 9.6, 3.0 Hz, 1H), 7.47–7.42 (m, 2H), 7.31–7.25 (m, 1H), 7.20–7.16 (m, 2H), 7.09–7.14 (m, 1H), 6.68 (dd, J = 9.1, 4.5 Hz, 1H), 5.65 (bs, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 153.7 (d, J = 234 Hz), 150.4, 147.7, 129.4, 125.9, 122.9 (d, J = 23.8 Hz), 121.8, 117.9 (d, J = 7.5 Hz), 116.2 (d, J = 23.8 Hz), 116.14, 109.3 (d, J = 7.5 Hz). Anal. Calcd for $C_{13}H_{10}FNO_2$: C, 67.53; H, 4.36; N, 6.06. Found: C, 67.79; H, 4.30; N, 5.87.

Phenyl 2-amino-5-chlorobenzoate (3ea).[8] Synthesized using GPA from **1e** (98 mg, 0.5 mmol) and **2a** (61 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford yellow solid of **3ea** (75 mg) with 61% yield. M.p.: 100–102 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.06 (s, 1H), 7.44 (t, J = 8.1 Hz, 2H), 7.30–7.26 (m, 2H), 7.18 (d, J = 7.6 Hz, 2H), 6.66 (d, J = 8.8 Hz, 1H), 5.79 (bs, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 165.8, 150.4, 149.6, 134.8, 130.6, 129.4, 125.9, 121.7, 120.7, 118.1, 110.3. Anal. Calcd for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07; N, 5.66. Found: C, 63.27; H, 4.30; N, 5.82.

Phenyl 2-amino-4-chlorobenzoate (3fa).[12] Synthesized using GPA from **1f** (98 mg, 0.5 mmol) and **2a** (61 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3fa** (71 mg, 58%). M.p.: 95–97 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.01 (d, J = 8.6 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.29–7.25 (m, 1H), 7.19–7.16 (m, 2H), 6.73–6.66 (m, 2H), 5.86 (bs, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.2, 151.8, 150.5, 140.8, 132.9, 129.4, 125.8, 121.8, 116.8, 116.0, 108.1. Anal. Calcd for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07; N, 5.66. Found: C, 62.86; H, 4.08; N, 5.93.

Phenyl 2-amino-5-bromobenzoate (3ga). Synthesizedusing GPA from **1g** (121 mg, 0.5 mmol) and **2a** (61 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3ga** (82 mg, 56%). M.p.: 111–113 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.19 (s, 1H), 7.45–7.37 (m, 3H), 7.29–7.24 (m, 1H), 7.17 (d, J = 7.5 Hz, 2H), 6.59 (d, J = 8.8 Hz, 1H), 5.80 (bs, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 165.7, 150.4, 150.0, 137.4, 133.6, 129.4, 125.9, 121.8, 118.4, 110.8, 107.3. Anal. Calcd for $C_{13}H_{10}BrNO_2$: C, 53.45; H, 3.45; N, 4.79. Found: C, 53.46; H, 3.32; N, 4.97.

***m*-Tolyl 2-aminobenzoate (3ab).**[8] Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2b** (68 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford colorless oily product of **3ab** (91 mg, 80%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.08 (d, J = 7.7 Hz, 1H), 7.36–7.30 (m, 2H), 7.09 (d, J = 7.6 Hz, 1H), 7.00–6.98 (m, 2H), 6.73–6.70 (m, 2H), 5.78 (bs, 2H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.9, 151.1, 150.6, 139.6, 134.7, 131.5, 129.1, 126.5, 122.5, 118.8, 116.6, 116.3, 109.6, 21.3. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.37; H, 5.91; N, 6.39.

4-(*tert*-Butyl)phenyl 2-aminobenzoate (3ac). Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2c** (89 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford yellow solid of **3ac** (87 mg, 65%). M.p.: 119–121 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.09 (d, J = 7.1 Hz, 1H), 7.44 (d, J = 8.6 Hz, 2H), 7.36–7.32 (m, 1H), 7.11 (d, J = 8.6 Hz, 2H), 6.73–6.70 (m, 2H), 5.78 (bs, 2H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 167.2, 151.1, 148.5, 148.2, 134.7, 131.5, 126.3, 121.2, 116.6, 116.3, 109.6, 34.5, 31.6. Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.89; H, 7.34; N, 5.52.

4-Methoxyphenyl 2-aminobenzoate (3ad).[8] Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2d** (76 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3ad** (72 mg, 60%). M.p.: 102–105 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.08 (d, J = 8.6 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 6.71 (t, J = 8.1 Hz, 2H), 5.77 (bs, 2H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 167.1, 157.1, 151.1, 144.1, 134.7, 131.5, 122.6, 116.6, 116.3, 114.4, 109.6, 55.5. Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.80; H, 5.27; N, 5.30.

2-Ethoxyphenyl 2-aminobenzoate (3ae). Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2e** (83 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3ae** (78 mg, 61%). M.p.: 67–70 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.12 (dd, J = 8.3, 1.6 Hz, 1H), 7.35–7.32 (m, 1H), 7.23–7.19 (m, 1H), 7.15 (dd, J = 7.8, 1.6 Hz, 1H), 7.02–6.97 (m, 2H), 6.74–6.70 (m, 2H), 5.73 (bs, 2H), 4.07 (q, J = 6.9 Hz, 2H), 1.31 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.7, 150.9, 150.7, 140.2, 134.5, 131.8, 126.6, 123.1, 120.7, 116.5, 116.3, 113.7, 109.8, 64.4, 14.7. Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.31; H, 5.94; N, 5.37.

2-Methoxyphenyl 2-aminobenzoate (3af).[8] Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2f** (76 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3af** (71 mg, 59%). M.p.: 111–112 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.37–7.29 (m, 2H), 6.84–6.77 (m, 2H), 6.75–6.69 (m, 3H), 5.77 (bs, 2H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.6, 160.5, 151.7, 151.1, 134.8, 131.5, 129.7, 116.7, 116.3, 114.1, 111.6, 109.5, 107.8, 55.3. Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.26; H, 5.10; N, 5.83.

3-(Diethylamino)phenyl 2-aminobenzoate (3ag). Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2g** (96 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford yellow solid of **3ag** (68 mg, 48%). M.p.: 43–45 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.10–8.07 (d, J = 8.0 Hz, 1H), 7.35–7.31 (m, 1H), 7.22 (t, J = 8.1 Hz, 1H), 6.73–6.70 (m, 2H), 6.57–6.55 (m, 1H), 6.45–6.42 (m, 2H), 5.78 (bs, 2H), 3.34 (q, J = 7.0 Hz, 4H), 1.16 (t, J = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 166.9, 152.0, 151.0, 134.5, 131.5, 129.7, 116.6, 116.2, 109.9, 109.0, 108.3, 104.8, 44.3, 12.4. Anal. Calcd for $C_{17}H_{20}N_2O_2$: C, 71.81; H, 7.09; N, 9.85. Found: C, 71.59; H, 6.90; N, 9.52.

4-Fluorophenyl 2-aminobenzoate (3ah).[8] Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2h** (70 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3ah** (86 mg, 75%). M.p.: 91–93 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.06 (d, J = 7.3 Hz, 1H), 7.36–7.33 (m, 1H), 7.16–7.09 (m, 4H), 6.73–6.70 (m, 2H), 5.76 (bs, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.7, 160.1 (d, J = 242.5 Hz), 151.2, 146.5 (d, J = 2.5 Hz), 134.9, 131.4, 123.3 (d, J = 8.8 Hz), 116.7, 116.3, 116.1 (d, J = 22.5 Hz), 115.9, 109.2. Anal. Calcd for $C_{13}H_{10}FNO_2$: C, 67.53; H, 4.36; N, 6.06. Found: C, 67.69; H, 4.67; N, 5.85.

3-Chlorophenyl 2-aminobenzoate (3ai). Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2i** (78 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3ai** (86 mg, 70%). M.p.: 85–87 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (dd, J = 8.8, 1.6 Hz, 1H), 7.41–7.32 (m, 3H), 7.13 (d, J = 8.8 Hz, 2H), 6.74–6.70 (m, 2H), 5.76 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 151.3, 149.2, 135.0, 131.5, 131.1, 129.4, 123.3, 116.7, 116.4, 109.1. Anal. Calcd for $C_{13}H_{10}ClNO_2$: C, 63.04; H, 4.07; N, 5.66. Found: C, 63.31; H, 3.88; N, 5.28.

2,4-Dichlorophenyl 2-aminobenzoate (3aj). Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2j** (95 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3aj** (89 mg, 64%). M.p.: 90–93 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.43 (s, 1H), 7.29 (t, *J* = 8.1 Hz, 1H), 7.23–7.18 (m, 1H), 7.12 (d, *J* = 8.6 Hz, 1H), 6.65 (t, *J* = 8.9 Hz, 2H), 5.67 (bs, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 151.4, 145.8, 135.3, 131.7, 131.6, 130.0, 128.2, 127.8, 124.9, 116.7, 116.5, 108.6. Anal. Calcd for $C_{13}H_9Cl_2NO_2$: C, 55.35; H, 3.22; N, 4.96. Found: C, 55.01; H, 3.07; N, 5.30.

4-Bromophenyl 2-aminobenzoate (3ak).[8] Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2k** (100 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3ak** (97 mg, 67%). M.p.: 77–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.4 Hz, 1H), 7.56–7.52 (m, 2H), 7.37–7.32 (m, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.73–6.69 (m, 2H), 5.77 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 151.3, 149.7, 135.0, 132.4, 131.4, 130.8, 123.8, 118.8, 116.7, 116.4, 109.1. Anal. Calcd for $C_{13}H_{10}BrNO_2$: C, 53.45; H, 3.45; N, 4.79. Found: C, 53.81; H, 3.62; N, 4.70.

2-Bromophenyl 2-aminobenzoate (3al).[8] Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2l** (100 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford colorless oily product of **3al** (101 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.43–7.36 (m, 2H), 7.32–7.29 (m, 1H), 7.20–7.16 (m, 1H), 6.71 (d, *J* = 8.4 Hz, 2H), 5.83 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 151.2, 148.0, 134.9, 133.0, 131.5, 128.2, 127.0, 123.9, 116.5, 116.3, 116.1, 108.5. Anal. Calcd for $C_{13}H_{10}BrNO_2$: C, 53.45; H, 3.45; N, 4.79. Found: C, 53.75; H, 3.36; N, 4.98.

2,4-Dibromophenyl 2-aminobenzoate (3am). Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2m** (139 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3am** (122 mg, 66%). M.p.: 99–101 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–8.11 (m, 1H), 7.81–7.79 (m, 1H), 7.50–7.48 (m, 1H), 7.37–7.34 (m, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 6.74–6.70 (m, 2H), 5.74 (bs, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 151.4, 147.6, 135.6, 135.2, 131.7, 131.4, 125.3, 119.3, 117.5, 116.7, 116.5, 108.6. Anal. Calcd for $C_{13}H_9Br_2NO_2$: C, 42.08; H, 2.45; N, 3.78. Found: C, 42.30; H, 2.60; N, 4.06.

4-Chloro-2-methylphenyl 2-aminobenzoate (3an). Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2n** (85 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3an** (92 mg, 71%). M.p.: 61–64 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10–8.07 (m, 1H), 7.37–7.33 (m, 1H), 7.27–7.25 (m, 1H), 7.23–7.20 (m, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.72 (m, 2H), 5.76 (bs, 2H), 2.21 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 151.2, 147.8, 135.0, 132.4, 131.4, 131.0, 130.8, 126.8, 123.5, 116.7, 116.4, 109.1, 16.1. Anal. Calcd for $C_{14}H_{12}ClNO_2$: C, 64.25; H, 4.62; N, 5.35. Found: C, 64.13; H, 4.60; N, 5.09.

2-Allylphenyl 2-aminobenzoate (3ao). Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2o** (81 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford white solid of **3ao** (55 mg, 44%). M.p.: 45–48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.37–7.21 (m, 4H), 7.15 (d, *J* = 8.1 Hz, 1H), 6.75–6.71 (m, 2H), 5.98–5.88 (m, 1H), 5.78 (bs, 2H), 5.06–5.01 (m, 2H), 3.36 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 151.2, 148.9, 135.8, 134.8, 132.3, 131.5, 130.3, 127.4, 126.1, 122.6, 116.7, 116.4, 116.3, 109.9, 34.6. Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.60; H, 6.05; N, 5.77.

Naphthalen-2-yl 2-aminobenzoate (3ap).[8] Synthesized using GPA from **1a** (81 mg, 0.5 mmol) and **2p** (86 mg, 0.5 mmol) which was then purified by column chromatography using EtOAc/Hexane (1 : 9) to afford yellow solid of **3ap** (65 mg, 50%). M.p.: 121–122 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.93–7.82 (m, 3H), 7.65 (s, 1H), 7.54–7.47 (m, 2H), 7.39–7.32 (m, 2H), 6.77–6.71 (m, 2H), 5.80 (bs, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 151.2, 148.3, 134.8, 133.7, 131.5, 131.4, 129.3, 127.7, 127.6, 126.4, 125.6, 121.5, 118.8, 116.7, 116.3, 109.5. Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.84; H, 5.22; N, 5.49.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank SERB and CSIR New Delhi for the financial support *via* the GPP-0367 (CRG/2019/001898) and OLP 2038 projects. We thank the Director of CSIR-NEIST for his constant support. B. R. Bora thanks DST for the INSPIRE-SRF fellowship.

References

1 (*a*) A. Moretto, A. Nicolli and M. Lotti, The search of the target of promotion: Phenylbenzoate esterase activities in hen peripheral nerve, *Toxicol. Appl. Pharmacol.*, 2007, **219**, 196–201; (*b*) C. James and V. Snieckus, Combined directed remote metalation-transition metal catalyzed cross coupling strategies: the total synthesis of the aglycones of the gilvocarcins V, M, and E and arnottin I, *J. Org. Chem.*, 2009, **74**, 4080–4093; (*c*) J. J. Child, T. Oka, F. J. Simpson and H. G. Krishnamurty, Purification and properties of a phenol carboxylic acid acyl esterase from Aspergillus flavus, *Can. J. Microbiol.*, 1971, **17**, 1455–1463; (*d*) M. C. Berndt, M. R. Bowles, G. J. King and B. Zerner, Inhibition of chicken liver carboxylesterase by activated carbonyls and carbonyl hydrates, *Biochim. Biophys. Acta*, 1996,

1298, 159–166; (*e*) A. Dhar, S. Liu, J. Klucik, K. D. Berlin, M. M. Madler, S. Lu, R. T. Ivey, D. Zacheis, C. W. Brown, E. C. Nelson, P. J. Birckbichler and D. M. Benbrook, Synthesis, Structure–Activity Relationships, and RARγ-Ligand Interactions of Nitrogen Heteroarotinoids, *J. Med. Chem.*, 1999, **42**, 3602–3614.

2 K. Krzymiński, A. Ozóg, P. Malecha, A. D. Roshal, A. Wróblewska, B. Zadykowicz and J. Bzazejowski, Chemiluminogenic Features of 10-Methyl-9 (phenoxycarbonyl)acridinium Trifluoromethanesulfonates Alkyl Substituted at the Benzene Ring in Aqueous Media, *J. Org. Chem.*, 2011, **76**, 1072–1085.

3 (*a*) M. Soural, J. Hlavác, P. Hradil and M. Hajdúch, Efficient Synthesis and Cytotoxic Activity of Some Symmetrical Disulfides Derived from the Quinolin-4(1*H*)-one Skeleton, *Eur. J. Org. Chem.*, 2009, 3867–3870; (*b*) C. Mitsos, A. Zografos and O. Igglessi-Markopoulou, Reactions of *N*-Hydroxysuccinimide Esters of Antranilic Acids with Anions of *β*-Keto Esters. A New Route to 4-Oxo-3-quinolinecarboxylic Acid Derivatives, *Chem. Pharm. Bull.*, 2000, **48**, 211–214.

4 G. D. Yadav and M. S. Krishnan, An Ecofriendly Catalytic Route for the Preparation of Perfumery Grade Methyl Anthranilate from Anthranilic Acid and Methanol, *Org. Process Res. Dev.*, 1998, **2**, 86–95.

5 (*a*) K. Mahiwal, P. Kumar and B. Narasimhan, Synthesis, antimicrobial evaluation, ot-QSAR and mt-QSAR studies of 2-amino benzoic acid derivatives, *Med. Chem. Res.*, 2012, **21**, 293–307; (*b*) L. Clark, J. Cummings, S. Bird and E. Aronov, Acute toxicity of the bird repellent, methyl anthranilate, to fry of Salmo salar, Oncorhynus mykiss, Ictalurus punctatus and Lepomis macrochirus, *Pestic. Sci.*, 1993, **39**, 313–317.

6 For examples, see: (*a*) A. K. Chakraborti, B. Singh, S. V. Chankeshwara and A. R. J. Patel, Protic Acid Immobilized on Solid Support as an Extremely Efficient Recyclable Catalyst System for a Direct and Atom Economical Esterification of Carboxylic Acids with Alcohols, *J. Org. Chem.*, 2009, **74**, 5967–5974; (*b*) K. Krzyminski, A. D. Roshal, B. Zadykowicz, A. Bialk-Bielinska and A. Sieradzan, Chemiluminogenic Properties of 10-Methyl-9-(phenoxycarbonyl)acridinium Cations in Organic Environments, *J. Phys. Chem. A*, 2010, **114**, 10550–10562; (*c*) M. A. K. Zarchi, B. F. Mirjalili and A. K. J. Acal, Convenient synthesis of benzoate esters mediated by polymer supported benzoyl chloride, *Appl. Polym. Sci.*, 2010, **115**, 237–241; (*d*) S. Murahashi, S. Ono and Y. Imada, Asymmetric baeyer-villiger reaction with hydrogen peroxide catalyzed by a novel planar-chiralbisflavin, *Angew. Chem., Int. Ed.*, 2002, **41**, 2366–2368; (*e*) Y. Yoshida, K. Murakami, H. Yorimitsu and K. Oshima, Hypervalent λ^3-Bromane Strategy for Baeyer–Villiger Oxidation: Selective Transformation of Primary Aliphatic and Aromatic Aldehydes to Formates, Which is Missing in the Classical Baeyer–Villiger Oxidation, *J. Am. Chem. Soc.*, 2010, **132**, 9236–9239.

7 For examples, see: (*a*) C. M. Qin, H. Y. Wu, J. X. Chen, M. C. Liu, J. Cheng, W. K. Su and J. C. Ding, Palladium-Catalyzed Aromatic Esterification of Aldehydes with Organoboronic Acids and Molecular Oxygen, *Org. Lett.*, 2008, **10**, 1537–1540; (*b*) Z. Xin, T. M. Gøgsig, A. T. Lindhardt and T. Skrydstrup, Rapid Syntheses of Heteroaryl-Substituted Imidazo[1,5-*a*]indole and Pyrrolo [1,2-*c*]imidazole *via* Aerobic C2–H Functionalizations, *Org. Lett.*, 2012, **14**, 284–287; (*c*) R. Lerebours and C. Wolf, Chemoselective Nucleophilic Arylation and Single-Step Oxidative Esterification of Aldehydes Using Siloxanes and a Palladium–Phosphinous Acid as a Reaction Switch, *J. Am. Chem. Soc.*, 2006, **128**, 13052–13053.

8 W. Lu, J. Chen, M. Liu, J. Ding, W. Gao and H. Wu, Palladium-Catalyzed Decarboxylative Coupling of Isatoic Anhydrides with Arylboronic Acids, *Org. Lett.*, 2011, **13**, 6114–6117.

9 (*a*) J. Phukon and S. Gogoi, Palladium(II)-catalyzed vinylic geminal double C–H activation and alkyne annulation reaction: synthesis of pentafulvenes, *Chem. Commun.*, 2020, **56**, 1133–1136; (*b*) P. P. Kaishap, G. Duarah, B. Sarma, D. Chetia and S. Gogoi, Ru(II)-Catalyzed Synthesis of Spiro Benzofuranones via Decarbonylative Annulation Reaction, *Angew. Chem., Int. Ed.*, 2018, **57**, 456–460, and references cited therein.

10 (*a*) S. Modem, S. Kankala, R. Balaboina, N. S. Thirukovela, S. B. Jonnalagadda, R. Vadde and C. S. Vasam, Decarbonylation of Salicylaldehyde Activated by *p*-Cymene Ruthenium(II) Dimer: Implication for Catalytic Alkyne Hydrothiolation, *Eur. J. Org. Chem.*, 2016, 4635–4642; (*b*) T. Shiraim, K. Sugimoto, M. Iwasaki, R. Sumida, H. Fujita and Y. Yamamoto, Decarbonylation through Aldehydic C-H Bond Cleavage by a Cationic Iridium Catalyst, *Synlett*, 2019, **30**, 972–976; (*c*) A. Modak, A. Deb, T. Patra, S. Rana, S. Maity and D. Maiti, A general and efficient aldehyde decarbonylation reaction by using a palladium catalyst, *Chem. Commun.*, 2012, **48**, 4253–4255; (*d*) T. Morimoto, K. Fuji, K. Tsutsumi and K. Kakiuchi, CO-Transfer, Carbonylation Reactions. A Catalytic Pauson-Khand-Type Reaction of Enynes with Aldehydes as a Source of Carbon Monoxide, *J. Am. Chem. Soc.*, 2002, **124**, 3806–3807; (*e*) X. Wu and H. Ji, Ruthenium-Catalyzed C–H Allylation of Alkenes with Allyl Alcohols via C–H Bond Activation in Aqueous Solution, *J. Org. Chem.*, 2018, **83**, 12094–12102.

11 D. Yang, S. Zhang, X. Fang, L. Guo, N. Hu, Z. Guo, X. Li, S. Yang, J. C. He, C. Kuang and Q. Yang, *N*-Benzyl/Aryl Substituted Tryptanthrin as Dual Inhibitors of Indoleamine 2,3-Dioxygenase and Tryptophan 2,3-Dioxygenase, *J. Med. Chem.*, 2019, **62**, 9161–9174.

12 L.-Z. Huang, R.-Y. Ma, L.-N. Zhou, Z.-T. Du and T. Zhang, Syntheses of Benzo[*c*]Chromen-6-ones by Palladium Catalyzed C–H Bond Activation using Diazonium Salts, *Nat. Prod. Commun.*, 2017, **12**, 537–540.