Article

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Trityl Chloride (TrCl): Efficient and Homogeneous Organocatalyst for the Solvent-Free Synthesis of 14-Aryl-14*H*-dibenzo[*a*,*j*]xanthenes by *in situ* Formation of Carbocationic System

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Trityl chloride (triphenylmethyl chloride, TrCl, Ph_3CCl) is utilized as an efficient and homogeneous organocatalyst for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes from β-naphthol and arylaldehydes under solvent-free conditions. Moreover, a plausible mechanism is suggested based on the literature and on *in situ* formation of trityl carbocation with inherent instability during the reaction.

Keywords: Trityl chloride (triphenylmethyl chloride, TrCl, Ph_3CCl); Trityl carbocation; Organocatalyst; 14-Aryl-14*H*-dibenzo[*a*,*j*]xanthenes; β-Naphthol; Solvent-free.

INTRODUCTION

Xanthene derivatives, especially benzoxanthenes are of importance since they have various biological activities including antibacterial,[1] antiviral[2] and anti-inflammatory[3] properties.[4] They have also been used in photodynamic theraphy.[5] Furthermore, some other benzoxanthenes have found application in industries such as dyes in laser technology[6] and fluorescent materials for visualization of biomolecules.[7] The most useful protocol for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes, as a class of benzoxanthenes, is the condensation of β-naphthol with aldehydes using Brønsted or Lewis acidic catalysts, e.g. selectfluor™,[4] sulfamic acid,[8] SiO_2-Pr-SO_3H,[9] HBF_4-SiO_2,[10] heteropolyacids,[11] $Al(HSO_4)_3$,[12] nano-TiO_2,[13] silica-bonded *N*-propyl sulfamic acid,[14] $KAl(SO_4)_2.12H_2O$,[15] $InCl_3$,[16] $Yb(OTf)_3$[17] and ceric ammonium nitrate.[18] Although some catalysts for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes are known, newer catalysts continue to attract attention for their difference with the others, high novelty and efficacy. In addition, most of the reported methods for the preparation of these compounds are associated with some limitations such as long reaction times, high catalyst loadings, the use of toxic solvents or special apparatuses, the use of expensive, non-available or toxic catalysts and poor agreement with the green chemistry protocols.

Development of organocatalytic processes, in which the reactions are catalyzed by organic molecules in homogeneous media, has attracted much attention in current organic synthesis, particularly from the green chemistry point of view.[19-22] Unlike the conventional catalysis, organocatalysts are advantageous in many ways like high stability, availability of the catalyst, metal-free nature, reduced toxicity and simple reaction conditions, and can promote a chemical reaction through different activation modes.[23] Along this line, we have recently introduced triarylmethyl chlorides (Ar_3CCl) as novel organocatalysts for the synthesis of bis(indolyl)methanes,[24] *N*-sulfonyl imines[25] and 1-amidoalkyl-2-naphtols,[26] in which triarylmethyl carbocation has acted as catalyst. In fact, the inherent instability of carbocations has precluded up to now their use in catalysis with decent turnover numbers.[26] It should be mentioned that triarylmethyl chlorides are inexpensive and can be obtained commercially. These compounds have been extensively applied as bulky protective groups for amino and primary hydroxyl functional groups in multi-step organic synthesis.[27] Furthermore, triarylmethyl chlorides in combination with metal salts particularly $SnCl_2$ have been used in a few organic transformations.[28] Nevertheless, the use of these compounds to promote organic reactions in the absence of co-catalysts is really attractive.

In this work, we have introduced a high novelty in the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes from β-

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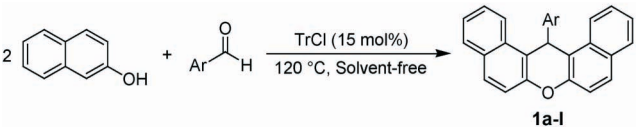
naphthol and aromatic aldehydes, and used trityl chloride (TrCl, Ph_3CCl) as an efficient, attractive, inexpensive, commercially available, homogeneous and green organocatalyst to promote the reaction at 120 °C in the absence of solvent (Scheme I).

Scheme I The solvent-free synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes by the condensation of β-naphthol with arylaldehydes using TrCl



RESULTS AND DISCUSSION

To optimize the reaction conditions, the condensation of β-naphthol (2 mmol) with 3-nitrobenzaldehyde (1 mmol) was selected as a model reaction to provide 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene **1c**, and its behavior was studied in the presence of 15 mol% of trityl chloride (TrCl), monomethoxytrityl chloride [$Ph_2(p\text{-}MeOC_6H_4)CCl$, MMTCl], dimethoxytrityl chloride [$Ph(p\text{-}MeOC_6H_4)_2CCl$, DMTCl] and also trityl alcohol (TrOH) at 120 ºC under solvent-free conditions. The results are summarized in Table 1. As it is shown in Table 1, higher yield, TOF (turn over frequency) and TON (turn over number) as well as shorter reaction time were obtained when trityl chloride was utilized.

In another study, the reaction of β-naphthol (2 mmol) with 3-nitrobenzaldehyde (1 mmol) was tested using different amounts of TrCl at range of 100-130 ºC in the absence solvent (Table 2). As Table 2 indicates, only 37% yield of the product was obtained in catalyst-free conditions at 120 ºC; and 15 mol% of the organocatalyst was sufficient to promote the reaction efficiently at 120 ºC (Table 2, entry 3). Higher amount of TrCl and higher temperature did not improve the reaction results (Table 2, entries 4 and 7).

Next, to investigate the efficacy and the generality of the organocatalyst, we examined the condensation of β-naphthol with various arylaldehydes under the optimized reaction conditions. The results are displayed in Table 3. As it can be seen in Table 3, all aromatic aldehydes, including benzaldehyde as well as aldehydes containing electron-withdrawing substituents, halogens or electron-releasing substituents on the aromatic ring, afforded the corresponding 14-aryl-14*H*-dibenzo[*a,j*]xanthenes in high to excellent yields (83-95%) in relatively short reaction times (60-130 min). Thus, TrCl was efficient and general.

Table 1. The solvent-free reaction of β-naphthol with 3-nitrobenzaldehyde in the presence of different triarylmethyl chlorides and trityl alcohol at 120 ºC

Catalyst	Time (min)	Yield[a] (%)	TOF (min^{-1})	TON
TrCl	60	95	0.106	6.33
MMTCl	60	91	0.101	6.06
DMTCl	60	87	0.097	5.80
TrOH	240	41	0.011	2.73

[a] Isolated yield.

Table 2. Effect of amounts of the catalyst and temperature on the condensation of β-naphthol with 3-nitrobenzaldehyde

Entry	Mol% of TrCl	Temp. (°C)	Time (min)	Yield[a] (%)
1	-	120	240	37
2	10	120	80	89
3	15	120	60	95
4	20	120	60	95
5	15	100	150	71
6	15	110	100	84
7	15	130	60	95

[a] Isolated yield.

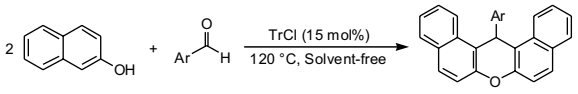
Based on the literature reports related to the presented reaction shown in Scheme II, our mechanistic proposal is that from the interaction of aldehyde and trityl chloride, complexes of intermediates **I** and **II** could be generated via a reversible reaction pathway.[24-26]

In order to validate our proposal, benzaldehyde was reacted with trityl chloride, and then IR, ^1H and ^{13}C NMR spectra of the resulting interacted aldehyde functional group of proposed intermediates **I** and **II** in the reaction mixture were compared with those in benzaldehyde as follows:[26]

According to the obtained FT-IR spectrum of the resulting reaction mixture, stretching vibration of the carbonyl of the aldehyde functional group slighlty shifts to lower frequency because of increased dipole moment character of carbonyl funcionality: IR (nujol): ν_{max} (cm^{-1}) of C=O in benzaldehyde (1705) decreased to (1700) in the reaction mixture.

Accordingly, in the ^1H and ^{13}C NMR spectra, the aldehyde hydrogen as well as carbonyl carbon were deshielded which is in agreement with the increased single bond charachter of carbonyl functional group observed in

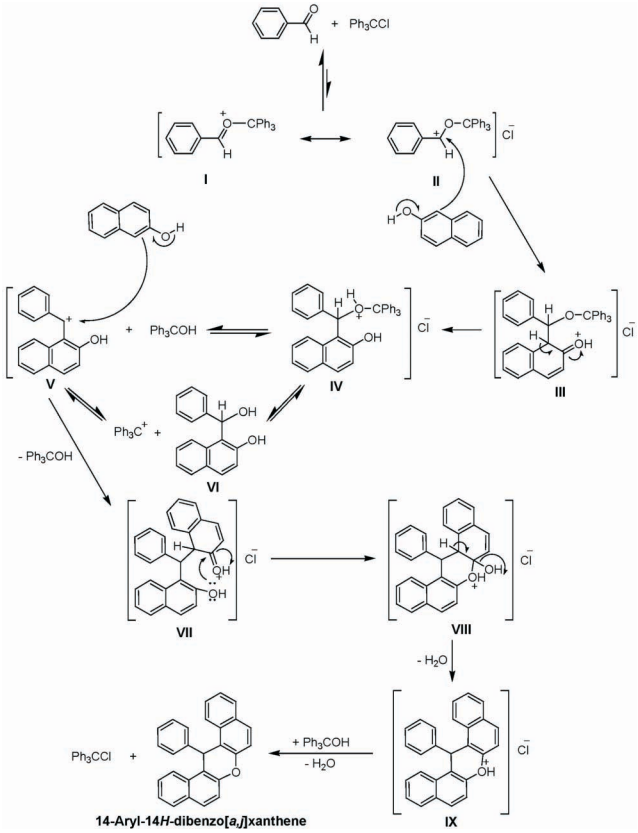
Table 3. The solvent-free preparation of 14-aryl-14*H*-dibenzo-[*a*,*j*]xanthenes from β-naphthol and arylaldehydes using TrCl



Compound number	Ar	Time (min)	Yield[a] (%)	M.p. °C (lit.)
1a	C_6H_5	70	89	185-187 (182)[12]
1b	4-$O_2NC_6H_4$	60	92	313-315 (310-311)[16]
1c	3-$O_2NC_6H_4$	60	95	214-216 (214)[12]
1d	2-$O_2NC_6H_4$	60	93	212-214 (214-215)[13]
1e	4-ClC_6H_4	60	91	285-287 (289-290)[15]
1f	3-ClC_6H_4	90	96	207-209 (209-211)[13]
1g	2-ClC_6H_4	60	94	210-212 (214-216)[13]
1h	3-BrC_6H_4	90	91	187-189 (190-191)[13]
1i	3-HOC_6H_4	90	83	239-241 (242-243)[16]
1j	4-MeC_6H_4	90	96	226-228 (227)[17]
1k	4-$MeOC_6H_4$	80	95	200-202 (203-205)[15]
1l	4-($PhCH_2O$)C_6H_4	130	86	163-165

[a] Isolated yield.

Scheme II The proposed mechanism for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes from β-naphthol and arylaldehydes catalyzed by TrCl (Ph_3Cl)



the FT-IR spectra: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) of the aldehydic hydrogen (9.78) increased to (10.04) in the reaction mixture. ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) of the carbonyl carbon (191.8) increased to (195.2) in the reaction mixture.

These results confirm that intermediates **I** and **II** are present in the reversible reaction media.[26] Moreover, the cationic intermediates of type **I** and **II** are known and have been reported by Oikawa et al. for the first time.[29] These complexes, in which the carbonyl group has been activated to accept nucleophilic attack, react with β-naphthol to provide intermediate **III**. This intermediate is converted into intermediate **IV** by aromatization of the β-naphthol ring followed by proton transfer. In the next step, either Ph_3COH or Ph_3C^+ leaves the system from intermediate **IV** to provide **V** or **VI** respectively, via the reversible reactions (intermediate **IV**, **V** and **VI** are in equilibrium). Then, intermediate **V** reacts with β-naphthol to produce **VII** which undergoes an intramolecular ring closure between the hydroxyl group and the activated carbonyl to form intermediate **VIII** which followed by elimination of one molecule H_2O affords **IX**. Subsequently, the reaction of **IX** with Ph_3COH, produced previously during the reaction process, gives the main product and Ph_3CCl. This proposed mechanism is in accordance with the literature reports,[9,12,18,24-26,29] and also by the fact that the catalyst was completely recovered unchanged and also triphenylmethanol couldn't be detected after completion of the reaction as it could be observed on TLC by comparison with the pure authentic samples. In another study, to demonstrate that TrCl can not be converted into TrOH and HCl by the water generated during the reaction progress, and consequently to prove that HCl is not the actual catalyst of the process, the reaction of β-naphthol with 3-nitrobenzaldehyde was examined in the presence of the expected amount of HCl produced by the reversible reaction of TrOH with H_2O which yielded the purified product in 67% within 100 min. The reaction was also tested using

pyridine as base in which the reaction yield was 37% after 240 min. Moreover, the reaction was checked in the presence of TrCl (15 mol%) and pyridine (15 mol%) as acid scavenger wherein the reaction well proceeded and the desired product was obtained in 94% yield within 65 min (the base didn't affect the reaction results significantly). It is clear that in these conditions, pyridine can abstract one proton from intermediate **VII** and produce pyridinium chloride; however, pyridinium chloride reacts with TrOH, produced from intermediate **V** to **VII** conversion, and forms TrCl. To prove this, in a separate reaction, pyridinium chloride was reacted with TrOH which resulted in formation of TrCl while also the reaction was not complete and amount of starting materials were left unreacted. Finally, the reaction was studied in the presence of pyridinium chloride (15 mol%) wherein the reaction yield was 58% after 240 min. These evidences demonstrated that HCl is not produced from TrCl in these conditions, and clarifies that TrCl acts as the actual catalyst.

In conclusion, we have developed a new method with high novelty for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]-xanthenes using TrCl as a green, efficient and homogenous organocatalyst. Clean reaction, simple purification, short reaction time, high yield, and economic availability of the catalyst are some advantages of in this work.

EXPERIMENTAL

All chemicals were purchased from Merck or Fluka Chemical Companies. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by thin layer chromatography (TLC) using silica gel SIL G/UV 254 plates. The melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. The ^{1}H NMR (300 or 400 MHz) and ^{13}C NMR (75 or 100) were run on a Bruker Avance DPX, FT-NMR spectrometers, δ in ppm. Mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model.

General procedure for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes

A mixture of β-naphthol (0.289 g, 2 mmol) and aryl-aldehyde (1 mmol) in a test tube was heated and stirred at 120 °C, and then TrCl (0.042 g, 0.15 mmol) was added to it. The resulting mixture was firstly stirred magnetically, and after solidification of the reaction mixture with a small rod, at 120 ºC. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature, petroleum ether (10 mL) was added to it, refluxed and stirred for 3 min, and filtered to separate the catalyst. The resulting precipitate was recrystallized from EtOH (95%) to give the pure product.

Spectral data of the products

Note: All compounds are known except **1l**.

14-Phenyl-14*H*-dibenzo[*a,j*]xanthene 1a

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 6.74 (s, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.62-7.66 (m, 4H), 7.91-7.93 (m, 4H), 8.70 (d, *J* = 8.8, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 37.0, 117.9, 118.2, 123.9, 124.9, 126.7, 127.4, 128.4, 128.8, 129.1, 129.5, 131.1, 131.4, 146.0, 148.5.

14-(4-Nitrophenyl)-14*H*-dibenzo[*a,j*]xanthene 1b

^{1}H NMR (300 MHz, DMSO-d$_6$): δ 6.95 (s, 1H), 7.43 (t, *J* = 7.2 Hz, 3H), 7.58-7.65 (m, 4H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.90-7.95 (m, 4H), 8.14 (d, *J* = 7.8, 1H), 8.45 (s, 1H), 8.72 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 36.4, 116.9, 118.2, 122.0, 123.6, 125.2, 127.7, 129.1, 130.0, 130.4, 131.11, 134.7, 147.9, 148.3, 148.6.

14-(3-Nitrophenyl)-14*H*-dibenzo[*a,j*]xanthene 1c

^{1}H NMR (300 MHz, DMSO-d$_6$): δ 6.91 (s, 1H), 7.11-7.25 (m, 1H), 7.43-7.48 (m, 2H), 7.55-7.71 (m, 4H), 7.88-8.03 (m, 7H), 8.66 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 36.7, 116.6, 118.2, 120.1, 123.6, 124.2, 125.2, 127.6, 129.1, 129.5, 130.0, 131.1, 131.2, 134.2, 146.3, 148.4, 153.1.

14-(2-Nitrophenyl)-14*H*-dibenzo[*a,j*]xanthene 1d

^{1}H NMR (300 MHz, DMSO-d$_6$): δ 6.94 (s, 1H), 7.41-7.46 (m, 3H), 7.56-7.65 (m, 4H), 7.79 (d, *J* = 2.1, 1H), 7.89-7.94 (m, 4H), 8.13 (d, *J* = 7.8, 1H), 8.45 (s, 1H), 8.70 (d, *J* = 6, 2H); ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 36.4, 116.9, 118.1, 122.0, 122.5, 123.6, 125.2, 127.7, 129.1, 130.0, 130.4, 131.1, 134.7, 138.2, 147.9, 148.3, 148.6.

14-(4-Chlorophenyl)-14*H*-dibenzo[*a,j*]xanthene 1e

^{1}H NMR (300 MHz, DMSO-d$_6$): δ 6.76 (s, 1H), 7.18 (d, *J* = 6.8 Hz, 2H), 7.46-7.64 (m, 10H), 8.92 (d, *J* = 7.79 Hz, 2H), 8.66 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 36.3, 117.4, 118.1, 123.4, 123.7, 125.0, 127.4, 128.8, 129.1, 129.6, 130.1, 131.1, 131.2, 144.8, 148.4.

14-(3-Chlorophenyl)-14*H*-dibenzo[*a,j*]xanthene 1f

^{1}H NMR (300 MHz, DMSO-d$_6$): δ 6.74 (s, 1H), 7.01 (d, *J* = 8.1, 1H), 7.13 (t, *J* = 7.8, 1H), 7.42 (t, *J* = 7.2, 2H), 7.52-7.66 (m, 6H), 7.91 (d, *J* = 8.7, 4H), 8.67 (d, *J* = 8.7,

2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 36.5, 117.2, 118.1, 123.7, 125.1, 126.8, 127.0, 127.5, 127.9, 129.1, 129.7, 130.7, 131.1, 131.2, 133.5, 148.2, 148.5.

14-(2-Chlorophenyl)-14*H*-dibenzo[*a,j*]xanthene 1g

^{1}H NMR (300 MHz, DMSO-d_6): δ 6.64 (s, 1H), 6.91-7.03 (m, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.38-7.50 (m, 5H), 7.57-7.70 (m, 2H), 7.76-7.90 (m, 4H), 8.54 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 34.8, 116.9, 118.2, 123.3, 124.9, 127.4, 128.5, 128.8, 129.2, 129.8, 130.2, 130.3, 130.9, 131.4, 132.0, 143.2, 148.7.

14-(3-Bromophenyl)-14*H*-dibenzo[*a,j*]xanthene 1h

^{1}H NMR (300 MHz, DMSO-d_6): δ 6.63 (s, 1H), 6.90-7.02 (m, 2H), 7.26 (d, *J* = 7.7 Hz, 2H), 7.37-7.49 (m, 5H), 7.58 (t, *J* = 7.9 Hz, 2H), 7.85-7.89 (m, 4H), 8.53 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 34.8, 116.9, 118.2, 123.3, 124.9, 127.4, 128.5, 128.8, 129.1, 129.8, 130.2, 130.3, 130.9, 131.4, 132.0, 143.2, 148.6.

14-(3-Hydroxyphenyl)-14*H*-dibenzo[*a,j*]xanthene 1i

^{1}H NMR (DMSO-d_6, 300 MHz): δ 6.37 (s, 1H), 6.61 (s, 1H), 6.83 (s, 1H), 6.92 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.41-7.63 (m, 6H), 7.89 (t, *J* = 3.0 Hz, 4H), 8.64 (d, *J* = 8.4 Hz, 2H), 9.20 (s, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 36.8, 113.8, 115.4, 117.9, 118.1, 119.3, 123.9, 124.9, 127.3, 129.0, 129.5, 129.7, 131.0, 131.4, 147.3, 148.4, 157.8.

14-(4-Methylphenyl)-14*H*-dibenzo[*a,j*]xanthene 1j

^{1}H NMR (300 MHz, DMSO-d_6): δ 2.01 (s, 3H), 6.63 (s, 1H), 6.90 (d, *J* = 7.2, 2H), 7.40-7.61 (m, 8H), 7.88 (t, *J* = 2.7, 4H), 8.61 (d, *J* = 8.7, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 20.8, 37.4, 117.9, 118.1, 123.8, 124.9, 127.3, 128.2, 129.0, 129.3, 129.3, 131.1, 131.3, 135.8, 143.0, 148.3.

14-(4-Methoxyphenyl)-14*H*-dibenzo[*a,j*]xanthene 1k

^{1}H NMR (300 MHz, DMSO-d_6): δ 3.52 (s, 3H), 6.63-6.67 (m, 3H), 7.19-7.62 (m, 8H), 7.87-7.92 (m, 4H), 8.64 (d, *J* = 8.7, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 36.0, 55.3, 114.1, 118.1, 123.9, 124.9, 127.9, 124.9, 127.3, 129.2, 131.1, 135.7, 138.1, 147.0, 149.4, 157.9.

14-(4-Benzyloxyphenyl)-14*H*-dibenzo[*a,j*]xanthene 1l

^{1}H NMR (300 MHz, DMSO-d_6): δ 4.42 (s, 2H), 4.82 (s, 1H), 6.65 (s, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 7.27 (s, 5H), 7.41-7.78 (m, 8H), 7.88 (t, *J* = 6.4, 4H) 8.66 (d, *J* = 8.3, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 36.2, 62.5, 114.9, 118.0, 123.8, 124.8, 127.2, 127.9, 128.1, 128.7, 129.0, 129.2, 129.3, 131.1, 131.3, 137.3, 138.3, 148.3, 157.1; MS (*m/z*): 465 (M^++1), 464 (M^+), 373 (M^+-C_7H_7), 281 (M^+-$C_{13}H_{11}O$).

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