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ORIGINAL PAPER

An efficient and convenient protocol for the synthesis of diaminotriarylmethanes

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Abstract A novel and efficient procedure was developed for the preparation of diaminotriarylmethanes through the Baeyer condensation of aromatic aldehydes and *N*,*N*-dimethylaniline or *N*,*N*-diethylaniline in the presence of niobium chloride under solvent-free conditions. This approach offers several advantages, such as short reaction time, high yields, low cost, and mild reaction conditions.

Keywords Diaminotriarylmethanes · Aldehyde · Baeyer condensation · Niobium chloride · Solvent-free

Introduction

The synthesis of triarylmethanes is an old but still active research area in organic synthesis. The continuing interest in this topic stems from the fact that these compounds play an important role in many fields. Triarylmethanes and their analogues are an important class of synthetic dyes used to colour silk, wool, jute, leather, cotton, and paper. These dyes are renowned for their outstanding intensity of colour, their brilliant shades of red, blue, and green, and low light fastness on many substrates [1]. They have been reported to possess diverse biological properties such as antifungal, antiproliferative, antiviral and cytotoxic, anti-HIV, CNS activity, and phototoxicity toward tumour cells [2–4]. In addition, they have been widely used in analytical fields, for example, detection of hydrogen peroxide in medical diagnostic kits, biotechnology process control, analysis of biological fluids, and waste water treatment [5]. Furthermore, these compounds have also been employed as precursors in high-performance polymer synthesis, copper corrosion inhibitors, and are used for the preparation of heat-, light-, and pressure-sensitive recording materials for high speed photoduplicating and photoimaging devices [6, 7]. Consequently, great efforts have been made to find efficient synthetic methodologies to gain access to such compounds [8–14]. Among the existing methods, the acid-catalysed Baeyer condensation of aromatic aldehydes and *N*,*N*-dimethylaniline is one of the most simple and straightforward approaches for the synthesis of diaminotriarylmethanes. A variety of reagents such as *p*-toluenesulfonic acid [15, 16], aniline hydrochloride [6], polymer-supported sulfonic acid [17], montmorillonite K-10 [18, 19], $ZrOCl_2 \cdot 8H_2O$ [5], and 1-*n*-butylpyridinium chloroaluminate [20] have been employed to accomplish this transformation. However, some of the reported methods have some disadvantages such as a relatively long reaction time [17], low yield [5], a corrosive catalyst [15], and the use of harmful volatile organic solvents [17, 19]. Thus, it is desirable to develop an efficient and convenient method to construct this type of compound.

$NbCl_5$ was recently discovered to be a useful mild Lewis acid catalyst in a variety of organic transformations, such as Mannich reactions [21], synthesis of bisindolylalkanes [22], 1,1-diacetates [23], 1,5-benzodiazepine derivatives [24], α-aminonitriles [25], and trisubstituted alkenes [26]. In our previous work, this catalyst was developed to promote some organic reactions and exhibited high catalytic activity [27, 28]. As part of our continuing interest in the development of new synthetic methodologies [29–36], we report herein an efficient and simple procedure for the synthesis of diaminotriarylmethanes by Baeyer condensation of aromatic aldehydes and *N*,*N*-dimethylaniline or *N*,*N*-diethylaniline catalysed by $NbCl_5$ under solvent-free conditions (Scheme 1).

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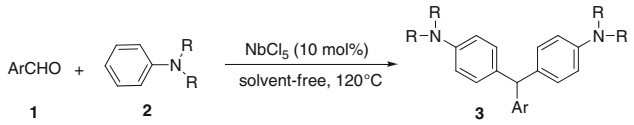

Scheme 1

Results and discussion

Initially, the reaction of *p*-methylbenzaldehyde and *N*,*N*-dimethylaniline under solvent-free conditions was considered as a model reaction. A number of catalysts were evaluated using the model reaction. When the reaction was carried out in the presence of solid acid such as Amberlyst-15, heteropoly acids such as tungstophosphoric acid and tungstosilicic acid, Lewis acids such as I_2, $(NH_4)_2Ce(NO_3)_4$, $(NH_4)_2Ce(SO_4)_3{\cdot}4H_2O$, $InBr_3$, $In(OTf)_3$, $Zr(SO_4)_2$, $FeCl_3{\cdot}6H_2O$, and $LaNO_3{\cdot}6H_2O$ at 120 °C under solvent-free conditions, the isolated yields were only 23–61%. To our delight, under the same conditions the reaction proceeded steadily to provide the target product **3c** in high yield using $NbCl_5$ as a catalyst (Table 1, entry 12). The effect of the amount of catalyst on the yield was investigated. As there was no obvious difference between using 10 and 15 mol% catalyst loading, we inferred that 10 mol% of $NbCl_5$ was sufficient for this reaction. We also investigated the effect of temperature on this reaction. When the reaction was carried out at 120 °C, the maximum yield was obtained. Control experiments revealed that no reaction occurred in the absence of the catalyst (Table 1, entry 13).

Using the optimized reaction conditions, we studied the efficiency of this protocol for the synthesis of various diaminotriarylmethanes, and the results are summarized in Table 2. In most cases, the reaction proceeded with high efficiency and broad functional group tolerance. The substituents on the aromatic rings of aldehydes played a significant role in the reaction. The presence of an electron-withdrawing group enhanced the product formation as indicated by a shorter reaction time and higher yield. On the contrary, with an electron-donating group on the aromatic rings of aldehydes, the desired product was obtained in lower yield and a longer reaction time was required. *ortho*-Substituted aromatic aldehydes with steric hindrance suffered from a slower reaction. It is noteworthy that heteroaryl aldehydes, such as thiophene-2-carbaldehyde, picolinaldehyde, and nicotinaldehyde were also cleanly converted to the corresponding diaminotriarylmethanes in high yields (Table 2, entries x–z). The use of *N*,*N*-diethylaniline in place of *N*,*N*-dimethylaniline also gave similar results as shown in Table 2. However, when an unactivated ketone such as acetophenone was used in this protocol under the optimized conditions, the corresponding product could not be obtained.

To show the merit of this work in comparison with results reported in the literature, we compared our results with $ZrOCl_2{\cdot}8H_2O$, polymer-supported sulfonic acid, montmorillonite K-10, and 1-*n*-butylpyridinium chloroaluminate in the synthesis of **3c**. As demonstrated in Table 3, $NbCl_5$ is an equally or more efficient catalyst for this reaction in terms of yield and reaction rate.

Table 1 Optimization of the reaction conditions for the Baeyer condensation between *p*-methylbenzaldehyde and *N*,*N*-dimethylaniline

Entry	Catalyst	Catalyst loading (mol%)	Temp (°C)	Time (h)	Yield (%)
1	Amberlyst-15	10	120	2.0	40
2	$H_3PO_4{\cdot}12MoO_3{\cdot}24H_2O$	10	120	2.0	47
3	$H_3PO_4{\cdot}12WO_3{\cdot}xH_2O$	10	120	2.0	49
4	I_2	10	120	2.0	50
5	$(NH_4)_2Ce(NO_3)_4$	10	120	2.0	42
6	$(NH_4)_2Ce(SO_4)_3{\cdot}4H_2O$	10	120	2.0	47
7	$InBr_3$	10	120	2.0	56
8	$In(OTf)_3$	10	120	2.0	61
9	$Zr(SO_4)_2$	10	120	2.0	23
10	$FeCl_3{\cdot}6H_2O$	10	120	2.0	45
11	$LaNO_3{\cdot}6H_2O$	10	120	2.0	52
12	$NbCl_5$	10	120	2.0	88
13	$NbCl_5$	0	120	5.0	0
14	$NbCl_5$	5	120	2.0	70
15	$NbCl_5$	15	120	2.0	89
16	$NbCl_5$	10	100	2.0	72
17	$NbCl_5$	10	110	2.0	87
18	$NbCl_5$	10	130	2.0	85

Yields refer to isolated pure product

Table 2 Synthesis of diaminotriarylmethane derivatives

Entry	Aldehydes	R	Time (min)	Yield (%)[a]	R_f	m.p. (°C)	
						Found	Reported
a	C_6H_5CHO	Me	100	90	0.40	93–94	95–96 [19]
b	2-Me-C_6H_4CHO	Me	150	86	0.42	96–97	98–100 [37]
c	4-Me-C_6H_4CHO	Me	120	88	0.41	97–98	99–100 [19]
d	2-MeO-C_6H_4CHO	Me	150	78	0.36	150–151	151–153 [37]
e	4-MeO-C_6H_4CHO	Me	120	80	0.30	100–101	102–103 [19]
f	2-HO-4-MeO-C_6H_3CHO	Me	180	62	0.08	137–139	
g	3-PhO-C_6H_4CHO	Me	120	85	0.36	139–140	
h	3,4-(OCH_2O)-C_6H_3CHO	Me	120	88	0.29	164–165	162–164 [38]
i	4-F-C_6H_4CHO	Me	60	92	0.48	100–101	99–100 [17]
j	2-HO-4-F-C_6H_3CHO	Me	60	84	0.12	121–122	
k	2-Cl-C_6H_4CHO	Me	70	86	0.43	143–144	142–144 [20]
l	3-Cl-C_6H_4CHO	Me	60	91	0.45	108–109	110–111 [19]
m	4-Cl-C_6H_4CHO	Me	60	90	0.44	98–100	97–98 [19]
n	2,4-Cl_2-C_6H_3CHO	Me	70	89	0.46	105–106	104–105 [37]
o	2,6-Cl_2-C_6H_3CHO	Me	70	85	0.41	135–136	134–136 [37]
p	2-HO-5-Cl-C_6H_3CHO	Me	60	83	0.11	153–154	
q	2-Br-C_6H_4CHO	Me	70	90	0.40	151–152	152–153 [37]
r	3-Br-C_6H_4CHO	Me	60	92	0.38	113–114	111–112 [17]
s	4-Br-C_6H_4CHO	Me	60	92	0.40	119–120	117–118 [17]
t	2-NO_2-C_6H_4CHO	Me	60	87	0.24	158–159	159–160 [19]
u	3-NO_2-C_6H_4CHO	Me	50	93	0.26	150–152	152–153 [19]
v	4-NO_2-C_6H_4CHO	Me	50	92	0.26	181–182	184–185 [19]
w	3-CF_3-C_6H_4CHO	Me	45	95	0.42	122–124	
x	Thiophene-2-carbaldehyde	Me	90	75	0.40	84–85	83–84 [5]
y	Picolinaldehyde	Me	90	76	0.02	171–172	170–172 [38]
z	Nicotinaldehyde	Me	90	79	0.24	100–101	99–100 [5]
aa	C_6H_5CHO	Et	120	84	0.66	63–64	64 [39]
ab	4-Me-C_6H_4CHO	Et	120	82	0.68	Oil	
ac	3-MeO-4-HO-C_6H_3CHO	Et	200	67	0.24	Oil	
ad	2,4-Cl_2-C_6H_3CHO	Et	60	89	0.77	85–87	
ae	3,4-Cl_2-C_6H_3CHO	Et	75	83	0.64	78–80	
af	2-NO_2-C_6H_4CHO	Et	60	90	0.51	105–106	106–107 [39]
ag	3-NO_2-C_6H_4CHO	Et	50	91	0.52	93–94	95 [39]
ah	4-NO_2-C_6H_4CHO	Et	50	92	0.53	114–115	113–114 [39]
ai	4-CHO-C_6H_4CHO	Et	180	65	0.01	Oil	

R_f values were determined by thin-layer chromatography (TLC) using ethyl acetate/*n*-hexane (1:6)

[a] Isolated yields

Table 3 Comparison of our results with previously reported data for synthesis of **3c**

Entry	Catalyst	Reaction conditions	Time (h)	Yield (%)	Ref.
1	$ZrOCl_2 \cdot 8H_2O$	Solvent-free, 120 °C	4.0	65	[5]
2	Polymer-supported sulfonic acid	Solvent-free, 120 °C	8.0	71	[17]
3	Montmorillonite K-10	Solvent-free, 100 °C	18.0	81	[19]
4	1-*n*-Butylpyridinium chloroaluminate	Solvent-free, 90 °C	2.5	80	[20]
5	$NbCl_5$	Solvent-free, 120 °C	2.0	88	This work

Experimental

Melting points were determined on an X-4 apparatus. Analytical TLC was performed on glass plates of silica gel GF_{254} of 0.2-mm thickness. IR spectra were measured on a Shimadzu FTIR-8900 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker DRX-500 spectrometer using TMS as internal standard. Elemental analysis was carried out on a Vario EL III CHNOS elemental analyser. Their values (C, H, and N) were in good agreement with the calculated ones. Commercially available reagents were used without further purification.

Representative procedure for the preparation of diaminotriarylmethane derivatives

A mixture of aldehyde (5 mmol), *N*,*N*-dimethylaniline or *N*,*N*-diethylaniline (15 mmol), and $NbCl_5$ (0.5 mmol) was heated in an oil bath at 120 °C for the indicated time. The progress of the reaction was monitored by TLC using an ethyl acetate/*n*-hexane (1:5) mixture as eluent. After completion, the reaction mixture was cooled to room temperature and treated with 20 cm^3 water. The resulting mixture was extracted with 3 × 10 cm^3 ethyl acetate. The combined organic layer was dried with anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave a residue that was purified by chromatography on silica gel (hexane/ethyl acetate) to the give the pure product.

Except for compounds **3f**, **3g**, **3j**, **3p**, **3w**, **3ab–3ae**, and **3ai**, all products are known compounds. The physical and spectroscopic data for all known compounds were found to be identical to those described in the literature.

2-[Bis[4-(dimethylamino)phenyl]methyl]-5-methoxyphenol (**3f**, $C_{24}H_{28}N_2O_2$)
IR (KBr): $\overline{\nu}$ = 3,412, 2,924, 2,853, 1,616, 1,567, 1,518, 1,504, 1,086, 1,304, 984, 866 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.92 (s, 12H), 3.75 (s, 3H), 4.86 (br s, 1H), 5.35 (s, 1H), 6.39 (d, J = 8.5 Hz, 1H), 6.43 (s, 1H), 6.64–6.73 (m, 5H), 7.01 (d, J = 8.5 Hz, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.6, 49.4, 55.3, 102.3, 106.0, 112.9, 123.6, 129.8, 130.8, 149.3, 154.7, 159.5 ppm.

4,4′-[(3-Phenoxyphenyl)methylene]bis-(N,N-dimethylaniline) (**3g**, $C_{29}H_{30}N_2O$)
IR (KBr): $\overline{\nu}$ = 3,412, 2,887, 2,802, 1,616, 1,589, 1,578, 1,518, 1,481, 1,444, 1,348, 1,225, 1,124, 1,096, 1,066, 983, 949, 874, 809 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.90 (s, 12H), 5.34 (s, 1H), 6.66 (d, J = 8.0 Hz, 4H), 6.78 (d, J = 8.0 Hz, 1H), 6.87 (s, 1H), 6.89 (d, J = 7.5 Hz, 1H), 6.95–6.99 (m, 6H), 7.05 (t, J = 7.5 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.7, 54.9, 112.6, 116.2, 118.5, 120.4, 122.5, 124.5, 129.2, 129.4, 129.6, 129.9, 147.7, 148.9, 156.8, 157.4 ppm.

2-[Bis[4-(dimethylamino)phenyl]methyl]-5-fluorophenol (**3j**, $C_{23}H_{25}FN_2O$)
IR (KBr): $\overline{\nu}$ = 3,420, 2,922, 2,852, 1,616, 1,558, 1,522, 1,437, 1,416, 1,356, 1,304, 1,269, 1,082, 984, 932, 866, 814, 810 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.92 (s, 12H), 4.68 (br s, 1H), 5.39 (s, 1H), 6.53 (d, J = 9.0 Hz, 1H), 6.68 (d, J = 8.0 Hz, 4H), 6.74–6.82 (m, 2H), 6.99 (d, J = 8.0 Hz, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.6, 49.8, 112.9, 113.7 (d, $^2J_{FC}$ = 22.9 Hz), 116.7 (d, $^2J_{FC}$ = 23.9 Hz), 117.1 (d, $^3J_{FC}$ = 8.0 Hz), 129.5, 129.8, 133.3 (d, $^3J_{FC}$ = 6.5 Hz), 149.5, 149.7, 157.2 (d, $^1J_{FC}$ = 235.9 Hz) ppm.

2-[Bis[4-(dimethylamino)phenyl]methyl]-4-chlorophenol (**3p**, $C_{23}H_{25}ClN_2O$)
IR (KBr): $\overline{\nu}$ = 3,414, 2,923, 2,808, 1,612, 1,558, 1,522, 1,481, 1,445, 1,416, 1,356, 1,304, 1,269, 1,195, 1,114, 1,047, 984, 949, 929, 866, 851, 812, 793 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.93 (s, 12H), 4.91 (br s, 1H), 5.37 (s, 1H), 6.69 (d, J = 7.5 Hz, 4H), 6.74 (d, J = 8.0 Hz, 1H), 6.80 (s, 1H), 6.99 (d, J = 7.5 Hz, 4H), 7.08 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.6, 49.8, 112.9, 117.7, 125.4, 127.5, 129.8, 129.9, 133.3, 149.4, 152.5 ppm.

4,4′-[[3-(Trifluoromethyl)phenyl]methylene]bis-(N,N-diethylaniline) (**3w**, $C_{24}H_{25}F_3N_2$)
IR (KBr): $\overline{\nu}$ = 3,412, 2,887, 2,810, 1,616, 1,522, 1,485, 1,437, 1,360, 1,327, 1,308, 1,256, 1,231, 1,165, 1,122, 1,074, 984, 949, 910, 897, 816, 793 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.91 (s, 12H), 5.41 (s, 1H), 6.66 (d, J = 8.0 Hz, 4H), 6.95 (d, J = 8.0 Hz, 4H), 7.30 (d, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.40–7.44 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.6, 54.8, 112.6, 122.7 (q, $^3J_{FC}$ = 3.6 Hz), 124.3 (q, $^1J_{FC}$ = 270.1 Hz), 125.9 (q, $^3J_{FC}$ = 3.7 Hz), 128.4, 129.8, 130.3 (q, $^2J_{FC}$ = 31.7 Hz), 131.8, 132.7, 146.5, 149.1 ppm.

4,4′-[(4-Methylphenyl)methylene]bis(N,N-diethylaniline) (**3ab**, $C_{28}H_{36}N_2$)
IR (KBr): $\overline{\nu}$ = 3,407, 2,970, 2,868, 2,928, 2,868, 1,682, 1,612, 1,558, 1,514, 1,464, 1,448, 1,396, 1,373, 1,356, 1,265, 1,198, 1,151, 1,094, 1,076, 1,013, 928, 839, 808 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 (t, J = 7.0 Hz, 12H), 2.30 (s, 3H), 3.30 (q, J = 7.0 Hz, 8H), 5.28 (s, 1H), 6.58 (d, J = 8.5 Hz, 4H), 6.94 (d, J = 8.5 Hz, 4H), 7.03 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.7, 20.9, 44.3, 54.5, 111.6, 128.6, 129.2, 130.0, 131.9, 135.0, 142.7, 146.0 ppm.

4-[Bis[4-(diethylamino)phenyl]methyl]-2-methoxyphenol (**3ac**, $C_{28}H_{36}N_2O_2$)
IR (KBr): $\bar{\nu}$ = 3,392, 2,970, 2,932, 2,870, 1,612, 1,558, 1,514, 1,464, 1,448, 1,396, 1,375, 1,356, 1,265, 1,198, 1,151, 1,124, 1,094, 1,078, 1,034, 1,013, 881, 808 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.11 (t, J = 7.5 Hz, 12H), 3.28 (q, J = 7.5 Hz, 8H), 3.73 (s, 3H), 5.25 (s, 1H), 5.56 (br s, 1H), 6.58 (d, J = 8.5 Hz, 4H), 6.58 (d, J = 8.5 Hz, 4H), 6.61 (dd, J = 8.5, 1.5 Hz, 1H), 6.69 (d, J = 1.5 Hz, 1H), 6.79 (d, J = 8.5 Hz, 1H), 6.94 (d, J = 8.5 Hz, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.5, 44.2, 54.5, 55.6, 111.7, 112.0, 113.7, 121.9, 129.8, 131.9, 137.5, 143.5, 145.9, 146.1 ppm.

4,4′-[(2,4-Dichlorophenyl)methylene]bis-(N,N-diethylaniline) (**3ad**, $C_{27}H_{32}Cl_2N_2$)
IR (KBr): $\bar{\nu}$ = 3,419, 3,092, 2,968, 2,870, 1,611, 1,585, 1,560, 1,518, 1,466, 1,396, 1,354, 1,267, 1,199, 1,126, 1,078, 1,028, 1,013, 953, 862, 843, 814, 800 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.12 (t, J = 7.0 Hz, 12H), 3.32 (q, J = 7.0 Hz, 8H), 5.66 (s, 1H), 6.58 (d, J = 8.5 Hz, 4H), 6.88 (d, J = 8.5 Hz, 4H), 6.97 (d, J = 8.0 Hz, 1H), 7.10 (dd, J = 8.0, 2.0 Hz, 1H), 7.34 (d, J = 2.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.8, 44.4, 51.2, 111.8, 126.7, 129.2, 129.7, 129.8, 130.3, 132.1, 135.1, 142.3, 146.5 ppm.

4,4′-[(3,4-Dichlorophenyl)methylene]bis-(N,N-diethylaniline) (**3ae**, $C_{27}H_{32}Cl_2N_2$)
IR (KBr): $\bar{\nu}$ = 3,420, 2,966, 2,928, 2,868, 1,611, 1,564, 1,518, 1,466, 1,396, 1,375, 1,267, 1,199, 1,154, 1,126, 1,028, 1,013, 953, 908, 862, 843, 814 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.13 (t, J = 7.0 Hz, 12H), 3.31 (q, J = 7.0 Hz, 8H), 5.25 (s, 1H), 6.59 (d, J = 8.5 Hz, 4H), 6.90 (d, J = 8.5 Hz, 4H), 6.98 (dd, J = 8.5, 2.0 Hz, 1H), 7.24 (d, J = 2.0 Hz, 1H), 7.29 (d, J = 8.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.7, 44.4, 54.3, 111.8, 128.9, 129.6, 129.9, 130.1, 130.3, 131.3, 132.1, 146.4 ppm.

4-[Bis[4-(diethylamino)phenyl]methyl]benzaldehyde (**3ai**, $C_{28}H_{34}N_2O$)
IR (KBr): $\bar{\nu}$ = 3,412, 2,970, 2,929, 1,701, 1,605, 1,589, 1,543, 1,518, 1,464, 1,447, 1,373, 1,356, 1,198, 1,142, 1,067, 1,015, 951, 929, 907, 863, 808 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.13 (t, J = 7.0 Hz, 12H), 3.31 (q, J = 7.0 Hz, 8H), 5.38 (s, 1H), 6.59 (d, J = 9.0 Hz, 4H), 6.92 (d, J = 9.0 Hz, 4H), 7.33 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 9.96 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.7, 44.3, 55.3, 111.7, 129.7, 130.1, 130.2, 130.4, 134.4, 146.4, 153.4, 192.1 ppm.

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