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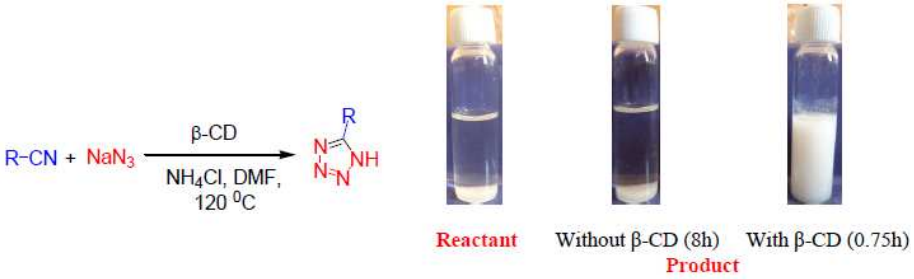
Graphical Abstract:

β-CD has been reported as an effective supramolecular catalyst for [2+3] cycloaddition reaction.



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β-Cyclodextrin mediated highly efficient [2+3] cycloaddition reaction for synthesis of 5-substituted 1*H*- tetrazoles

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Abstract β-Cyclodextrin promoted [2+3] cycloaddition reaction between nitriles and sodium azide in presence of ammonium chloride in DMF at 120 ^{0}C is reported affording various 5-substituted 1*H*-tetrazoles in good to excellent yields in short reaction times. The presence of β-CD renders the formation of precipitate-like gel in reaction media under the thermal effect. No precipitation occurs in absence of NaN_3 as well as NH_4Cl. The precipitation responses with other salts such as LiCl, $NiCl_2$ were weaker than with NH_4Cl. In present paper the application of supramolecular aggregates reported for the [2+3] cycloaddition reaction. The β-cyclodextrin can be recovered and reused without significance loss of activity.

Keywords β-Cyclodextrin (β-CD), [2+3]-Cycloaddition, 5-Substituted 1*H*-tetrazoles.

Introduction

Tetrazoles are the class of heterocyclic compounds which has wide range of applications like in coordination chemistry as ligands,[1] in medicinal chemistry as isosteric replacement for carboxylic acid in drug design,[2] as precursors of different nitrogen containing heterocycles,[3] in material science as explosive [4] and in information recording system.[5] Tetrazoles have similar acidities to those of carboxylic acids; they have been used in drugs as replacement for the COOH unit when the carboxylic acid has unsatisfactory properties for human medicine. A

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simple example is the anti-arthritis drug indomethacin whose carboxylic acid group may be replaced by tetrazole with no loss of activity.[6] Tetrazole moieties has also been incorporated into angiotensin II antagonist structures sartans[7] (Losartan, Valsartan and BMS-183920) (Fig. 1).

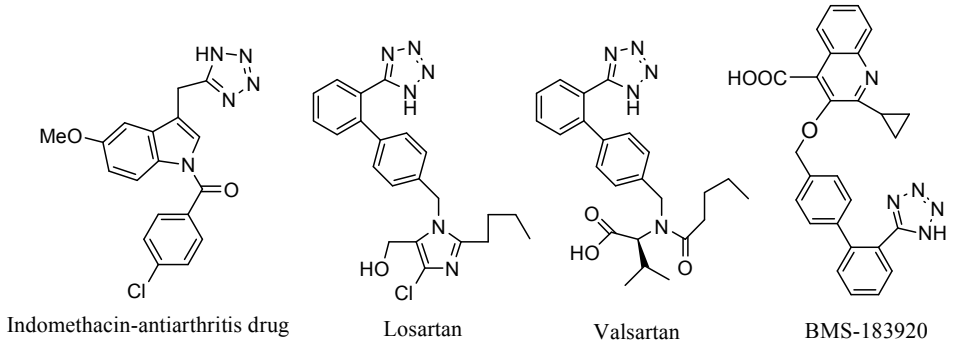

Fig. 1 Bioactive tetrazole moieties.

Conventional method for synthesis of 5-substituted 1*H*-tetrazole is via [2+3] cycloaddition between an azide and nitrile.[8,9] Recently Sharpless and co-workers reported a "click" chemistry approach for synthesis of tetrazoles by [2+3] cycloaddition of nitriles and NaN_3 using stoicheometric amounts or 50 mol % of Zn(II) salts[10,11,12] but still requires tedious time consuming steps such as removal of zinc salts from acidic products. Earlier reported methods for synthesis of 5-sustituted 1*H*- tetrazole suffer from drawback such as the use of strong lewis acids or expensive and toxic metals. In order to overcome these difficulties several new pathways have been developed such as use of metal complexes[13,14] as a catalyst, use of $TMSN_3$-TBAF,[15] $FeCl_3$-SiO_2,[16] Zn/Al-hydrocalcite,[17] Fe_2O_3,[18] Zn Hydroxyapatite,[19] Sb_2O_3,[20] $NaHSO_4.SiO_2$ or I_2,[21] Mesoporous ZnS nanospheres,[22] Tungstates as novel heterogeneous catalyst[23] and $CuFe_2O_4$.[24] The catalytic role of β-CD for the synthesis of 5-phenyl 1*H*-tetrazole has been compared with various reported catalyst (Table 1). However some of these methods still require long reaction times to achieve reasonable yields, environmentally hazardous catalysts and tedious purification of products.

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Table 1 Comparison for preparation of 5-phenyl 1*H* tetrazole with various reported catalyst.

Entry	Catalyst	Time (h)	Yield (%)	Ref.
1	$ZnBr_2$ (in H_2O)	24	76	[10]
2	$TMSN_3$-TBAF.$3H_2O$	18	86	[15]
3	$FeCl_3$-SiO_2	12	79	[16]
4	Zn/Al hydrocalcite	12	84	[17]
5	Fe_2O_3	36	81	[18]
6	Zn Hydroxyapatite	12	78	[19]
7	Sb_2O_3	08	86	[20]
8	$CuFe_2O_4$	12	82	[24]

Cyclodextrins are cyclic oligomers of D-glucose and are named α, β and γ- cyclodextrin for hexamer, heptamer and octamer respectively.[25] They have toroidal cyclic structure (Fig. 2) with secondary hydroxyl glucose C-2 and C-3 on their more open face and the primary C-6 hydroxyl group on primary face.[26] They catalyze reaction by supramolecular catalysis involving the formation of host-guest complexes by non covalent bonding interactions.[27] The internal cavity of cyclodextrin molecule is strongly hydrophobic in nature and this particular characteristic of cyclodextrin molecule enables them to bind with wide range of guest molecules.[28] Cyclodextrin binds with substrate in its hydrophobic cavity and catalyze reactions in selective manner. Supramolecular catalysis is the discipline chemistry which involves all intermolecular interactions where covalent bonds are not established between interacting species that is molecules, ions or radicals.[29] Among various cyclodextrins, β-CD as a catalyst is attractive since it is useful both from economic and environment point of view, apart from being non toxic, metabolically safe[30] and can also be readily recovered and reused.

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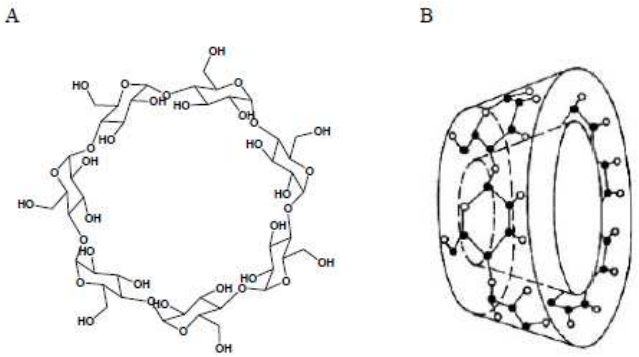

Fig. 2 The chemical structure (A) and the toroidal shape (B) of β-cyclodextrin molecule.

Literature survey shows that some of the organic molecules bind with cyclodextrins by supramolecular interactions in the non-aqueous solvent like dimethyl sulfoxides (DMSO), DMF, acetonitrile, etc.[31] Host-guest interactions of cyclodextrin with guest were efficiently employed in constructing the supramolecular gel.[32, 33] The earlier expertise in the field of biomimetic modeling of organic chemical reaction involving cyclodextrins,[34-37] continuation of our work in the field of β-CD[38] and the complex forming ability of β-CD by supramolecular interaction in non-aqueous solvent like DMF studied by Guang Yan Du et al.[39] prompted us to attempt the synthesis of 5-substituted 1*H*-tetrazoles.

Results and Discussion

In order to optimized the reaction condition and performance of β-CD as a catalyst for [2+3] cycloaddition, the reaction between benzonitrile, NaN_3 and NH_4Cl has been selected as a model reaction for synthesis of 5- phenyl 1*H*-tetrazole using different reaction parameters (Table 2). The NH_4Cl has been choose as it helps in situ formation of ammonium azide by its reaction with NaN_3 in DMF.[40] The reaction does not proceed in absence of NH_4Cl. The best result was obtained for 2 mmol of β-CD (Table 2, entry 4) affording 89% of 5-phenyl 1*H*-tetrazole in 0.75 h. Further increase in amount of catalyst has no significant effect on the yield as well as reaction time (Table 2, entry 5-8). The reaction in water (Table 2, entry 9)

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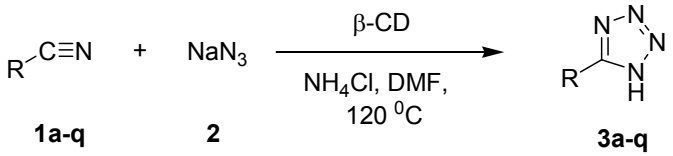
does not give the product because no formation of gel like precipitate occurs in presence of water. Where as in DMF-H_2O (7:3) and DMSO, only partial formation of gel like precipitate occurs affording only 47% (Table 2, entry 10) and 61% (Table 2, entry 11) of product respectively. The increase in amount of NaN_3 and NH_4Cl from 13 to 15 mmol was found to be no effect on the yield (89%). The role of β-CD as a catalyst has been confirmed when similar reaction was carried out in absence of catalyst (Table 2, entry 1) giving only 86% of yield with longer reaction time of 8 h. It indicates that β-CD not only improves the yield of product but also accelerate the rate of [2+3] cycloaddition reaction.



Scheme 1 A general scheme for synthesis of 5-substituted 1*H*-tetrazole

Table 2 Formation of 5-phenyltetrazole using various reaction conditions.[a]

Entry	Solvent	β-CD (mmol)	Time (h.)	Yield [b](%)
1	DMF	-	8	86
2	DMF	0.5	2.5	80
3	DMF	1	2	88
4	DMF	2	0.75	89
5	DMF	3	0.75	89
6	DMF	4	1	88
7	DMF	5	1	87
8	DMF	10	1.25	89
9	Water	2	15	-
10	DMF-H_2O (7:3)	2	12	47
11	DMSO	2	6	61

[a] Reaction was carried out with benzonitrile (10 mmol), NaN_3 (13 mmol), ammonium chloride (13 mmol), solvent (25 mL) and catalytic amount of Beta-cyclodextrin , [b] Isolated yield.

The significant presence of β-CD has great influence on reaction time as well as yield (Table 3, entry 1). The reaction was also carried out in presence of salts like Li and Ni salts in order to check their azide ion releasing capacity and its influence on precipitate-like gel

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formation but affording only 67% and 46% of product respectively. The comparative study for synthesis of 5-phenyl 1*H*-tetrazole with and without catalyst is shown in Fig. 3. The novelty of reaction is that, the presence of β-CD leads to the formation of precipitation like gel that makes the clear visible difference between active role of presence and absence of catalyst for these reactions. Temperature plays an important role as surprisingly there were no precipitations occurs at lower temperature and reaction does not proceed. The system is multicomponent solution in which each of components is required for formation of precipitation.

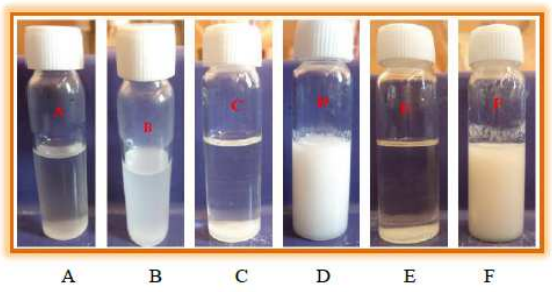

Fig. 3 Comparisons of reaction without and with β-CD

Where, A: Reaction without β-CD at zero time, B: Reaction with β-CD at zero time, C: Reaction without β-CD after 0.25h, D: Reaction with β-CD after 0.25h, E: Reaction without β-CD after 0.75h, F: Reaction with β-CD after 0.75h

A variety of structurally divergent nitriles possessing a wide range of functional groups (Scheme 1) selected to understand the scope and generality of the β-CD promoted [2+3] cycloaddition reaction to form 5-substituted 1*H*-tetrazoles. The results obtained are summarized in Table 3. For all nitriles, DMF used as a solvent and the reaction was conducted at 120 ^{0}C. In all cases the conversion was completed within 0.5 - 8 h with good to excellent yields (Except Table 3, Entry 6). Further increase in reaction time has no significant effect on yields. Aromatic nitriles containing both electron donating and electron withdrawing groups underwent the conversion smoothly. The nitriles having electron donating substituents require longer reaction time (Table 3, entry 6, 8, 10) as donating substituent on aromatic ring decreases the electrophilic character of nitrile. The benzyl

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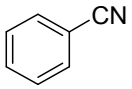
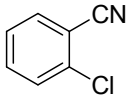
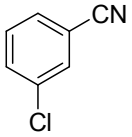
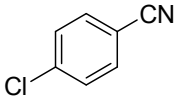
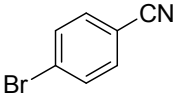
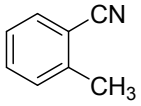
nitriles (Table 3, entry 11, 12, 13) require longer reaction times than benzonitriles because of absence of conjugated electron withdrawing aromatic ring in benzyl nitrile. The ortho substituted nitriles render lower yields (Table 3, entry 2, 6) due to the steric hindrance. The longer reaction time of 8 h was required with 76% yield for 2, 2-diphenylacetonitrile (Table 3, entry 14), this might be steric hindrance of two phenyl rings. The 93% of yield was obtained for ethylcyano acetate (Table 3, entry 17) within very short reaction time of 0.5 h without affecting ester functionality. The β-CD was chosen as catalyst since it is inexpensive, biodegradable and easily accessible. All synthesized compounds have been characterized by its physical constant, FTIR, ^{1}H NMR, ^{13}C NMR and mass spectroscopy and compared with literature data.

Table 3 β-CD catalyzed synthesis of 5-substituted 1*H* tetrazoles.[a]

Entry	Substrate	Product	Time (h.)	Yield[b] (%)
1		3a	0.75	89, 87[c]
2		3b	2	76
3		3c	1	93
4		3d	1.25	92
5		3e	1.75	95
6		3f	16, 48	43[d], 45[d]

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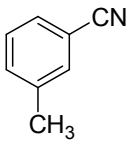
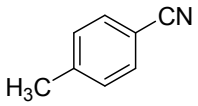
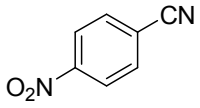
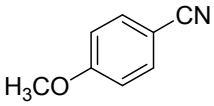
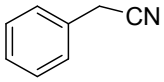
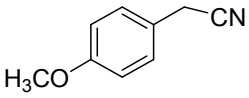
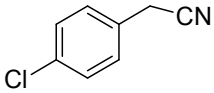
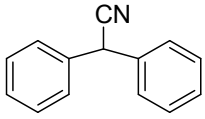
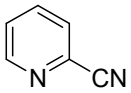
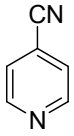
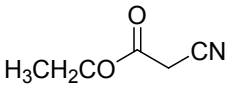
7		3g	2	90
8		3h	4	88
9		3i	1	83
10		3j	7	85
11		3k	6	93
12		3l	1.5	92
13		3m	3.5	84
14		3n	8	76
15		3o	1.25	80
16		3p	1.25	84
17		3q	0.5	93

[a] Reaction was carried out with nitrile (10 mmol), NaN_3 (13 mmol), ammonium chloride (13 mmol) and Beta cyclodextrin (2 mmol) in 25 mL of DMF at 120 ^{0}C , [b] Isolated yield, [c] Yield after third recycle of catalyst, [d] Reaction not proceed to completion.

Table 4 500 MHz ^{1}H chemical shift of β-CD protons in free and complex state in DMF-d6.[a]

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	OH-2	OH-3	OH-6	H-1	H-2	H-3	H-4	H-5	H-6ab
β-CD	5.906	5.816	4.683	4.955	3.464	3.819	3.491	3.764	3.834
Complex	5.871	5.792	4.634	4.957	3.459	b	3.486	3.771	3.841

[a] Chemical shifts expressed in ppm, [b] Reading not occurs due to spectral overlap.

Evidence for the association of nitrile and cyclodextrin in DMF is provided by ^{1}H NMR spectroscopy. As the reaction medium is DMF, the ^{1}H NMR of pure β-CD and β-CD: p-chlorobenzonitrile complex were undertaken in DMF-d6 and the results obtained shown in Table 4. Protons involved in hydrogen bonds are much more deshielded than "free" protons. In pure β-CD the OH-2, OH-3 and OH-6 show downfield shift because of solvent-cyclodextrin association due to hydrogen bonding as DMF itself act as hydrogen acceptor. However on addition of nitrile guest, the upfield shift in hydroxyl OH-2, OH-3 and OH-6 protons occurs. This indicates that the association of cyclodextrin with solvent decreases and on the other hand its association with guest molecule may occurs. Though our expectation for the H-3 and H-5 proton of cyclodextrin in complex was upfield shift but actually in our results we got upfield shift in H-2 and H-4 protons of cyclodextrin. Some loss of resolution in the spectral lines of the NMR spectra can be observed, due to the complexation effects with the β-CD molecule.

The catalytic activity of β-CD for these [2+3] cycloaddition reaction is established by the fact that a long reaction time and comparatively lower yield of product was observed (Table 2, entry 1) when similar reaction was carried out in absence of β-CD which do not afford formation of precipitation. The presence of cyclodextrin in reaction medium may prevent sublimation of ammonium azide that prepared in situ by reaction of sodium azide and ammonium chloride[40] and thus overall increasing the rate of reaction. The formation of precipitation occurs due to the supramolecular aggregates by cyclodextrin.[41] It is tough to design the actual mechanism for reaction under the influence of such supramolecular

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aggregates. The high performance has been shown by beta cyclodextrin due to supramolecular interactions with guest molecule (Prove by ^{1}H NMR). The nitriles get activated by hydrogen bonding with cyclodextrin and thus facilitate the attack of azide ion. The presence of cyclodextrin and formation of precipitate like gel under the thermal effect may allow the intimate contact of nitrile and azide in cavity for [2+3] cycloaddition. When similar reaction was performed in open carbohydrate moiety like glucose or dextrose, reaction does not complete even up to longer reaction time leading to blackish material indicating the essential role of cyclodextrin.

The catalyst reusability was studied three times including use of fresh catalyst for synthesis of 5-phenyl 1*H*-tetrazole. The catalyst was almost quantitatively recovered and no significant loss in yields was observed (Fig. 4). The mass of recovered cyclodextrin has taken which shows characteristics peak of $(M+H)^{+}$ ion indicates that no reaction occurs on cyclodextrin itself. The FTIR of fresh β-CD and recovered from reaction also studied (Fig. 5) and no change found in functional group as well as fingerprint region indicating no reaction occurs with β-CD.

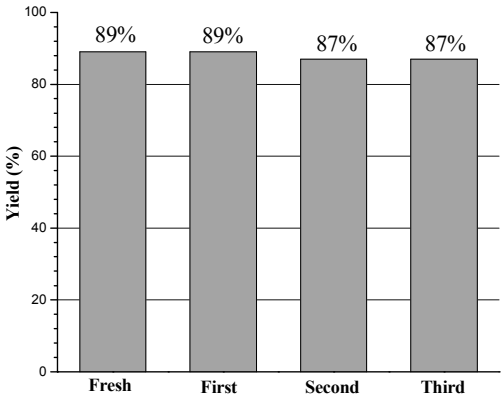

Fig. 4 Catalyst (β-cyclodextrin) recyclability data.

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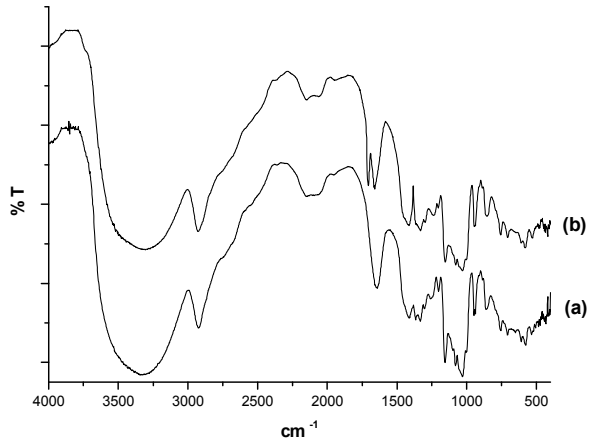

Fig. 5 FTIR of (a) Fresh β-CD (b) Recovered β-CD

Conclusions

In conclusion, we herein report β-CD as an efficient and environmentally benign catalyst for [2+3] cycloaddition of azide with wide varieties of nitriles in DMF to form 5-substituted 1*H*-tetrazoles. We have investigated the advantages of β-CD to form precipitation with multicomponent system in DMF for the enhancement of [2+3] cycloaddition reaction. The benefits of this catalytic system are: good yields of product, short reaction time, inexpensive and nontoxicity of catalyst, simple and clean workup of desire product without column chromatography, easy recovery and reuse of catalyst.

Experimental

General Remarks

All nitriles, NaN_3 and NH_4Cl were purchased from S. D. Fine and Spectrochem. β-CD was purchased from Aldrich. Infrared (IR) spectra were obtained with IR Affinity Model-I spectroscopy (Shimadzu) using KBr pelleting. Both ^1H NMR and ^{13}C NMR were recorded on a Bruker Avance- II spectrophotometer operating at 200 MHz and 500 MHz. The mass spectra were recorded under ESI mode on Waters Micromass equipment (model Q-TOF micro).

General process for preparation of 5-substituted 1*H*- tetrazole

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β-Cyclodextrin (2.26 g, 2 mmol) was dissolved in DMF (25 mL) at room temperature by stirring until a clear solution was formed. Then benzonitrile (Table 3, entry 1, 1.03 g, 10 mmol) added and allows stirring at room temperature for 0.25 h followed by the addition of NaN_3 (0.845 g, 13 mmol) and NH_4Cl (0.695 g, 13 mmol). The reaction mixture was constantly stirred at 120 ^{0}C for 0.75 h. Then reaction mixture was allowed to cool at room temperature, acidify carefully to pH 5 with 5M HCl. The organic material was extracted twice with ethyl acetate; the combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting product, although evident as single compound by TLC was purified by simple recrystalization in aqueous ethanol giving pure 5-phenyl 1*H*-tetrazole (1.30 g, 89%),

Catalyst Recovery and Reuse

To the aqueous layer, acetone (5 mL) added dropwise with stirring at room temperature giving white turbid solution of precipitated β-CD which was cooled to 5 ^{0}C to recover cyclodextrin by filtration, dried and reused.

Spectral data of selected compounds

3a. M. P. 218 ^{0}C[42], IR (KBr) cm^{-1} = 2459-3213, 1564, 1608, 727, ^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.62 - 7.65 (m, 3H, aromatic), 8.07 – 8.09 (m, 2H, aromatic), ^{13}C NMR (500 MHz, DMSO-d_6): δ = 155.62, 131.31, 129.45, 126.96, 124.05, m/z = 147 (M+1).

3c. M. P. 139-140 ^{0}C[24], IR (KBr) cm^{-1} = 3226-3460, 1577, 1556, 775, ^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.65 – 8.08 (m, 4H, aromatic), ^{13}C NMR (500 MHz, DMSO-d_6): δ = 154.87, 134.03, 131.48, 131.05, 126.55, 126.28, 125.63, m/z = 181 $(M+1)^+$.

3e. M. P. 267-268 ^{0}C[42], IR (KBr) cm^{-1} = 2482-3118, 1604, 829, 744, ^{1}H NMR (200 MHz, DMSO-d_6): δ = 8.00 (d, 2H, J = 8.6 Hz, aromatic), 7.84 (d, 2H, J = 8.6 Hz, aromatic), ^{13}C NMR (500 MHz, DMSO-d_6): δ = 155.67, 132.51, 128.90, 124.76, 123.48, m/z = 224 $(M+1)^+$.

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3h. M. P. 250 $^{0}C^{42}$, IR (KBr) cm^{-1} = 2476-3082, 1614, 823, ^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.93 (d, 2H, J = 8 Hz, aromatic), 7.42 (d, 2H, J = 8 Hz, aromatic), 3.60 (brs, 1H), 2.39 (s, 3H), ^{13}C NMR (500 MHz, DMSO-d_6): δ = 155.17, 141.32, 129.96, 126.87, 121.15, 21.02, m/z = 161 $(M+1)^{+}$.

3i. M. P. 218-220 $^{0}C^{43}$, IR (KBr) cm^{-1} = 3236-3444, 1533, 1340, 854, ^{1}H NMR (200 MHz, DMSO-d_6): δ = 8.45 (d, 2H, aromatic), 8.31 (d, 2H, aromatic), ^{13}C NMR (500 MHz, DMSO-d_6): δ = 155.53, 148.74, 130.62, 128.24, 124.62, m/z = 192 $(M+1)^{+}$.

3j. M. P. 232-233 $^{0}C^{43}$, IR (KBr) cm^{-1} = 2414-3145, 1614, 1502, 1182, 1056, 835, ^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.99 (d, 2H, J = 8.8 Hz, aromatic), 7.17 (d, 2H, J = 8.8 Hz, aromatic), 3.85 (s, 3H), ^{13}C NMR (500 MHz, DMSO-d_6): δ = 161.44, 154.88, 128.65, 116.31, 114.86, 55.46, m/z = 176 (M^{+}).

3k. M. P. 121-123 $^{0}C^{42}$**,** IR (KBr) cm^{-1} = 2601-3101, 1548, 1531, 734, ^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.28 - 7.34 (m, 5H, aromatic), 4.29 (s, 2H), 3.76 (brs, 1H), ^{13}C NMR (500 MHz, DMSO-d_6): δ = 155.31, 135.90, 128.75, 128.65, 127.05, 28.86, m/z = 161 $(M+1)^{+}$.

3l. M. P. 162-164 ^{0}C, IR (KBr) cm^{-1} = 2468-3107, 1612, 1514, 1247, 1178, 825, ^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.22 (d, 2H, J = 8.6 Hz, aromatic), 6.92 (d, 2H, J = 8.6 Hz, aromatic), 4.24 (s, 2H), 3.74 (s, 3H), ^{13}C NMR (500 MHz, DMSO-d_6): δ = 158.28, 155.60, 129.76, 127.71, 114.13, 55.08, 28.01, m/z = 190 (M^{+}).

3n. M. P. 165-166 $^{0}C^{42}$, IR (KBr) cm^{-1} = 2455-3103, 1566, 1496, 725, ^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.20 – 7.40 (m, 10H, aromatic), 5.98 (s, 1H), ^{13}C NMR (500 MHz, DMSO-d_6): δ = 158.10, 140.00, 128.75, 128.40, 127.27, 45.73, m/z = 236 (M^{+}).

3p. M. P. 256-258 $^{0}C^{44}$, IR (KBr) cm^{-1} = 2970-3267, 1633, 1531, ^{1}H NMR (200 MHz, DMSO-d_6): δ = 8.84 (d, 2H, aromatic), 8.04 (d, 2H, aromatic), 6.09 (bs, 1H), ^{13}C NMR (500 MHz, DMSO-d_6): δ = 155.33, 150.24, 133.19, 120.97, m/z = 148 $(M+1)^{+}$.

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3q. M. P. 130 $^{0}C^{43}$, IR (KBr) cm^{-1} = 2461-3471, 1747, 1568, ^{1}H NMR (200 MHz, DMSO-d_6): δ = 4.17 (s, 2H), 4.14 (q, 2H, J = 2 Hz), 1.20 (t, 3H, J = 2 Hz), ^{13}C NMR (200 MHz, DMSO-d_6): δ = 167.78, 150.55, 61.29, 29.53, 13.99, m/z = 157 $(M+1)^{+}$.

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