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Novel one-pot synthesis of nitrogen-containing derivatives via C-N bond formation and C-O bond cleavage

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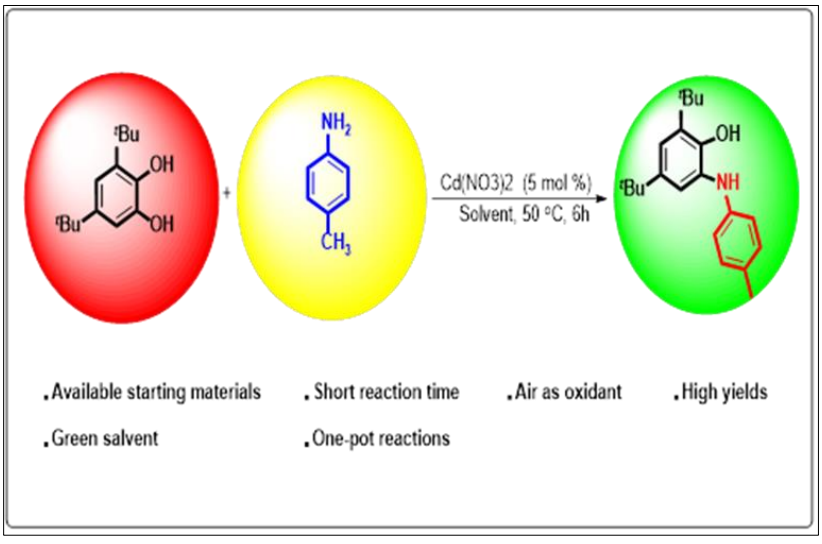
Abstract

Ortho-aminophenols are significant organic compounds known for their versatility and wide-ranging applications in materials science, synthesis, pharmaceuticals, agriculture, and industry. In this work, we present novel synthetic methods that utilize readily available and cost-effective materials, namely catechol, Cd(NO3)2 as a catalyst, and H2O/EtOH solvent. These proposed synthesis methods involve mild, one-pot reactions that facilitate the formation of both C-N and cleavage of C-O bond. This approach leads to the production of various nitrogen-containing derivatives with remarkably high yields and efficiency.

Keywords: Heterocyclic compounds; Benzoxazole; catechol; Manganese catalysis; C-O bond cleavage; oxidative condensation.

Graphical Abstract



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1. Introduction

The C-N bonds bond formation and breaking of C-O bonds are two key processes of the synthesis of organic compounds which enable the creation of various compounds utilized in materials science, pharmaceuticals, and other industries[1, 2]. Transition metal catalysts facilitate the coupling of carbon-based substrates with nitrogen-containing reagents, leading to the formation of C-N bonds and breaking of C-O bond[3]. Palladium, nickel, iron, and copper are commonly employed as catalysts due to their ability to activate substrates and reagents under mild conditions[4, 5]. Important techniques in this process include reductive elimination, transmetalation, and oxidative addition[6]. Cadmium catalysts have become invaluable in hydrogen transfer reactions, demonstrating significant effectiveness in various organic synthesis transformations[7, 8]. A key application of these catalysts is in carbon-nitrogen (C-N) coupling reactions, where they offer a sustainable method for creating essential C-N bonds[9, 10, 11]. By using cadmium complexes with bidentate ligands that have hemilabile functionalities, researchers have been able to catalyze C-N coupling reactions under mild conditions, producing a wide range of aromatic amines[4, 12, 13]. The ability of cadmium to simultaneously activate carbon and nitrogen substrates highlights its versatility in C-N bond formation and C-O bond-breaking processes, leading to the efficient and selective synthesis of nitrogen-containing compounds[14]. Cadmium catalysts have become invaluable in hydrogen transfer reactions, demonstrating significant effectiveness in various organic synthesis transformations[15]. A key application of these catalysts is in carbon-nitrogen (C-N) coupling reactions, where they offer a sustainable method for creating essential C-N bonds[13]. By using cadmium complexes with bidentate ligands that have hemilabile functionalities, researchers have been able to catalyze C-N coupling reactions under mild conditions, producing a wide range of aromatic amines[16]. The ability of cadmium to simultaneously activate carbon and nitrogen substrates highlights its versatility in C-N bond formation and C-O bond-breaking processes, leading to the efficient and selective synthesis of nitrogen-containing compounds[14, 17, 18].

2. Material and methods

By taking advantage of C-N bond-forming and C-O band-breaking steps, we present an effective strategy for creating various derivatives of 2,4-di-*tert*-butyl-6-(phenylamino)phenol (3) using by reaction between 3,5-di-*tert*-butylbenzene-1,2-diol (**1**, 1 mmol) (1) and anilines (**2**, l mmol) compounds in the presence of $Cd(NO_3)_2$ catalyst (2 mol%) and H_2O/EtOH (2:1) (5ml) as solvent at temperatures of 50 °C in ambient air for 6 h (Scheme 1). Ultimately, spectroscopic data like ^{1}H-NMR and ^{13}C-NMR and MS obtained from these derivatives were analyzed to confirm their structures align with the predicted ones.

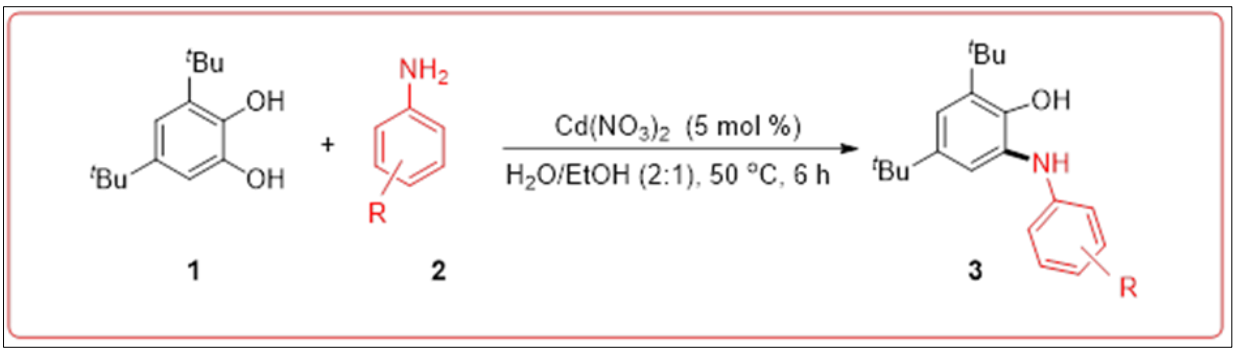


Figure 1 Synthesis of *O*-aminophenols (3) through Condensation of Catechol Derivatives (1) with anilines (2) using cadmium as a Catalyst under Aerobic Oxidation in H2O/EtOH at 50 °C

3. Results and discussion

In order to scrutiny the optimal reaction conditions in terms of catalyst, solvent and temperature, the reaction of 4-methylaniline and 5,3-di-*t*-butyl catechol was used as the model reaction. Initially, the reaction without catalyst was investigated at 50 °C in H_2O/EtOH (2:1) and no product was synthesized as observed (Table 3-1, entry 1). The catalyst $Cd(NO_3)_2$ was employed to proceed with the reaction, resulting in the highest synthesis yield (Table 1, entry 2). Despite similar conditions, other catalysts with different core metals (Cr, K, Mg, Bi, Ag, Cu, Ce, Zn, La) did not produce high yields (Table 1, entries 3-11). Therefore, the catalyst with a cadmium core was selected as the optimal choice due to its superior yield and faster reaction time. Various solvents, including H_2O/EtOH, EtOH, THF, CH3CN, DCE, MeOH, Dioxane, isopropanol, and H_2O were tested to determine the best reaction conditions (Table 1, entries 2 and 12-18). The findings indicated that H_2O/ EtOH provided the highest yield among the solvents. Consequently, H_2O/ EtOH, being widely

available, cost-effective, and environmentally friendly, was used for the reaction. It was found that using 5 and 10 mol% of the catalyst resulted in favorable yields (Table 1, entries 2 and 20), while reducing the catalyst amount to 2 mol% led to a decrease in reaction efficiency (Table 1, entry 21). Although performing the reaction at temperatures higher than 50 does not make a difference in the reaction efficiency, but reducing the temperature to less than 50 degrees Celsius has a significant decrease in the reaction efficiency (Table 1, entries 22 and 23).

Table 1 Optimizing the reaction conditions for synthesizing *O*-aminophenols derivatives

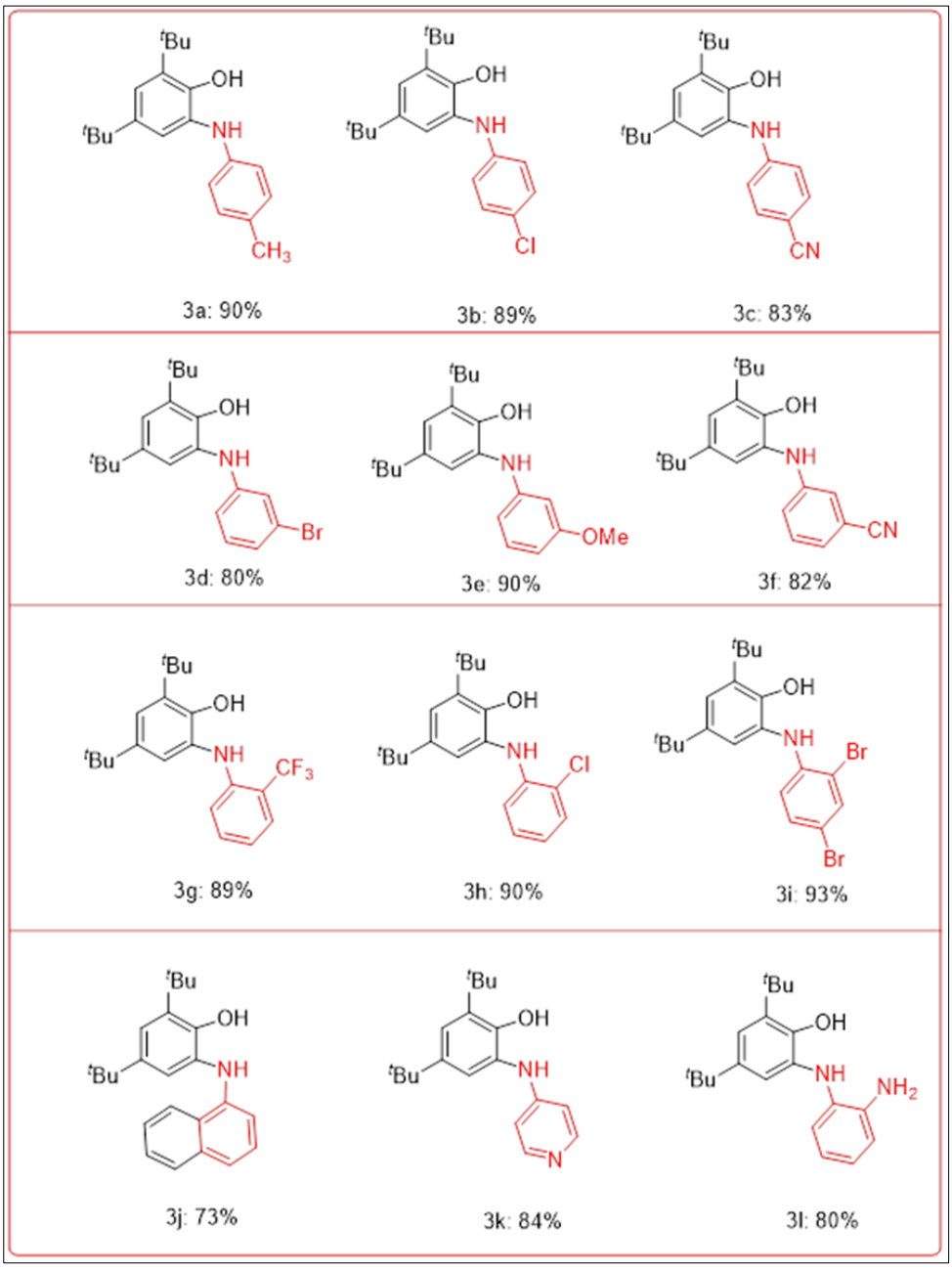
Entry	Cat (mol %)	Solvent	Temp (°C)	Yield (%)[b]
1	-	EtOH/ H_2O	50	-
2	$Cd(NO_3)_2$ (5 mol%)	EtOH/ H_2O	50	93
3	$Cr(NO_3)_3$ (5 mol%)	EtOH/ H_2O	50	15
4	KNO_3 (5 mol%)	EtOH/ H_2O	50	30
5	$Mg(NO_3)_2$ (5 mol%)	EtOH/ H_2O	50	5
6	$Bi(NO_3)_3$ (5 mol%)	EtOH/ H_2O	50	10
7	$AgNO_3$ (5 mol%)	EtOH/ H_2O	50	20
8	$Cu(NO_3)_2$ (5 mol%)	EtOH/ H_2O	50	40
9	$Ce(NO_3)_3$ (5 mol%)	EtOH/ H_2O	50	45
10	$Zn(NO_3)_2$ (5 mol%)	EtOH/ H_2O	50	50
11	$La(NO_3)_2$ (5 mol%)	EtOH/ H_2O	50	62
12	$Cd(NO_3)_3$ (5 mol%)	EtOH	50	85
13	$Cd(NO_3)_2$ (5 mol%)	THF	50	30
14	$Cd(NO_3)_2$ (5 mol%)	CH_3CN	50	25
15	$Cd(NO_3)_2$ (5 mol%)	DCE	50	40
16	$Cd(NO_3)_2$ (5 mol%)	MeOH	50	55
17	$Cd(NO_3)_2$ (5 mol%)	Dioxane	50	30
18	$Cd(NO_3)_2$ (5 mol%)	Isopropanol	50	80
19	$Cd(NO_3)_2$ (5 mol%)	H_2O	50	45
20	$Cd(NO_3)_2$ (10 mol%)	EtOH/ H_2O	50	85
21	$Cd(NO_3)_2$ (2 mol%)	EtOH/ H_2O	50	80
22	$Cd(NO_3)_2$ (5 mol%)	EtOH/ H_2O	25	10
23	$Cd(NO_3)_2$ (5 mol%)	EtOH/ H_2O	70	93

After determining the optimal reaction conditions, various derivatives of *ortho*-aminophenols were synthesized from 5,3-di-*t*-butyl catechol and different anilines catalyzed by $Cd(NO_3)_2$ in H_2O/EtOH (2:1) under a mild conditions.

In order to develop the synthesis of *ortho*-aminophenols, the relevant reaction was tested with different derivatives of anilines containing electron-donating groups and electron-accepting groups in the *ortho*, *meta*, and *para* positions were investigated, which according to the investigations of the resulting products From the reaction with anilines containing electron-donating substituents (methyl, and methoxy), they had an excellent yield, this efficiency was significantly high in the electron-donating groups at the para position (3a). Also, electron-withdrawing substituents (nitrile and trifluoromethyl) were also tested, and the products were synthesized with a high yields of 80% (3c, 3f, 3g). In this project, halogenated derivatives including (bromine and chlorine) had very good efficiency (3b,3d,3h). Also, the reaction of aniline with bromine substitution in two *ortho* and *para* positions with respect to the amine group also showed a

good yield of 93% (5i), which indicates the good performance of halogens in this reaction. Notably, naphthalen-1-amine, as part of a fused ring system, proved effective in synthesizing the corresponding ortho-aminophenol derivatives (3j). This reaction was conducted with both a benzene-1,2-diamine derivative and a pyridin-4-amine heterocyclic derivative, and in both cases, the product was synthesized with significant efficiency (3k,3l)(Table 2).

Table 2 Synthesized derivatives of *ortho*-aminophenols in this project



According to the proposed mechanism for the synthesis of ortho-aminophenol derivatives, the starting material 3,5-di-*tert*-butylcatechol, in the presence of a cadmium nitrate catalyst, undergoes enol-keto tautomerism to form the intermediate 3,5-di-*tert*-butyl-6-hydroxycyclohexa-2,4-dien-1-one (II). When aniline is added to the reaction mixture, during the condensation process, the corresponding nucleophile attaches to the carbonyl group. This results in the formation of an imine (III) through dehydration, which ultimately leads to the synthesis of *ortho*-aminophenol (IV) during the cyclization step.

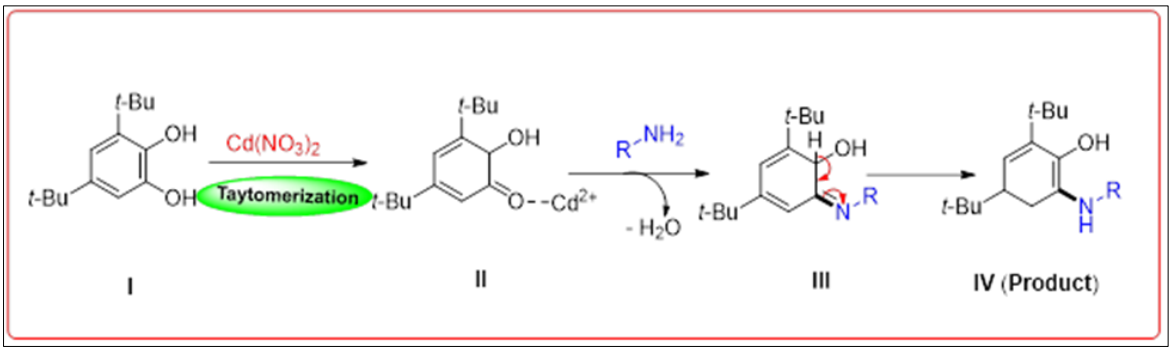


Figure 2 Suggested Reaction Pathway for Benzoxazole Synthesis

3.1. Spectroscopic data obtained from synthesized derivatives

- 5,7-di-*tert*-butyl-2,2-dimethyl-3-(*p*-tolyl)-2,3-dihydrobenzo[*d*]oxazole (3a).

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:9). Isolated yield: 316 mg, 90%. Yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.14 (s, 9H), 1.28 (s, 9H), 1.48 (s, 6H), 2.30 (s, 3H), 6.40 (d, *J* = 2.8 Hz, 1H), 6.59 (d, *J* = 3.1 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 22.0, 25.7, 28.4, 32.8, 35.0, 38.7, 103.7, 105.2, 1136.1, 128.8, 130.6, 130.9, 135.4, 139.3, 140.9, 141.1, 147.7. Anal. Calcd for $C_{24}H_{33}NO$: C, 82.00; H, 9.46; N, 3.98; Found: C, 82.56; H, 9.85; N, 4.44.

- 2,4-di-*tert*-butyl-6-((4-chlorophenyl)amino)phenol (3b).

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:9). Isolated yield: 309 mg, 89%. Colorless liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.27 (s, 9H), 1.41 (s, 9H), 5.01 (br, 1H), 6.30 (br, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 28.93, 30.92, 33.79, 34.42, 111.76, 118.07, 121.38, 122.36, 129.00, 132.13, 135.52, 142.44, 146.35, 150.21. Anal. Calcd for $C_{20}H_{26}ClNO$: C, 72.38; H, 7.90; N, 4.22; Found: C, 72.26; H, 7.95; N, 4.28.

- 4-((3,5-di-*tert*-butyl-2-hydroxyphenyl)amino)benzonitrile (3c).

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:9). Isolated yield: 268 mg, 83%. Yellow liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.27 (s, 9H), 1.43 (s, 9H), 5.55 (br, 1H), 5.99 (br, 1H), 6.67 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 3.1 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 29.5, 31.6, 34.4, 35.1, 101.6, 114.7, 119.9, 121.7, 123.1, 125.6, 133.8, 136.1, 142.9, 149.1, 150.6. Anal. Calcd for $C_{21}H_{26}N_2O$: C, 78.22; H, 8.13; N, 8.69; Found: C, 78.16; H, 8.17; N, 8.76.

- 2-((3-bromophenyl)amino)-4,6-di-*tert*-butylphenol (3d).

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:9). Isolated yield: 295 mg, 80%. White liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.25 (s, 9H), 1.41 (s, 9H), 4.94 (br, 1H), 6.53 (br, 1H), 6.55 (dd, *J* = 8.0, 3.4 Hz, 1H), 6.67 (t, *J* = 2.4 Hz, 1H), 6.81 (dd, *J* = 7.9, 2.9 Hz, 1H), 6.99 (d, *J* = 2.8 Hz, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 2.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 28.52, 32.92, 35.04, 37.22, 113.26, 116.58, 120.41, 121.56, 122.53, 126.84, 130.37, 134.21, 141.24, 144.96, 148.12, 149.29.Anal. Calcd for $C_{20}H_{26}BrNO$: C, 63.83; H, 6.96; N, 3.72; Found: C, 63.50; H, 6.59; N, 3.33.

- 2,4-di-*tert*-butyl-6-((3-methoxyphenyl)amino)phenol (3e).

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:9). Isolated yield: 295 mg, 90%. White liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.28 (s, 9H), 1.38 (s, 9H), 3.41 (s, 3H), 5.30 (br, 1H), 6.28 (br, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 6.60 (s, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.31 (t, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 22.5, 32.9, 31.7, 35.9, 55.8, 104.1, 109.0, 111.9, 122.6, 124.1, 130.4, 134.4, 135.6, 142.9, 148.1, 149.1, 160.7. Anal. Calcd for $C_{21}H_{29}NO_2$: C, 77.02; H, 8.93; N, 4.28; Found: C, 76.15; H, 8.73; N, 4.12.

- 3-((3,5-di-*tert*-butyl-2-hydroxyphenyl)amino)benzonitrile (3f).

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:9). Isolated yield: 264 mg, 82%. Colorless liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.28 (s, 9H), 1.42 (s, 9H), 5.71 (br, 1H), 5.99 (br, 1H), 6.49 (d, *J* = 7.5 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 3.2 Hz, 1H), 7.21(d, *J* = 2.4 Hz, 1H), 7.27 – 7.35 (m, 1H), 7.50 (d, *J* = 6.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 28.40, 31.57, 34.44, 35.12, 97.83, 112.35, 117.48, 119.27, 121.46, 123.31, 127.59, 132.63, 134.40, 137.07, 143.15, 146.31, 149.25. Anal. Calcd for $C_{21}H_{26}N_2O$: C, 78.22; H, 8.13; N, 8.69; Found: C,78.10; H, 8.20; N, 8.77.

- 2,4-di-*tert*-butyl-6-((2-(trifluoromethyl)phenyl)amino)phenol (3g).

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:9). Isolated yield: 325 mg, 89%. white liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.34 (s, 9H), 1.50 (s, 9H), 5.69 (br, 1H), 6.27 (br, 1H), 6.61 (d, *J* = 8.3 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 2.3 Hz, 1H), 7.32-7.37 (m, 2H), 7.59 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 29.25, 31.37, 34.44, 34.81, 115.03, 118.39, 122.15, 122.93, 123.68, 125.04 (q, *J* = 5.5 Hz), 132.09, 135.25, 141.34, 144.56, 148.97. Anal. Calcd for $C_{21}H_{26}F_3NO$: C, 69.02; H, 7.17; N, 3.83; Found: C, 68.24; H, 7.28; N, 3.75.

- 2,4-di-*tert*-butyl-6-((2,4-dibromophenyl)amino)phenol (3i).

Purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:9). Isolated yield: 421 mg, 93%. Colorless liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.29 (s, 9H), 1.46 (s, 9H), 5.59 (br, 1H), 6.24 (br, 1H), 6.43 (d, *J* = 8.7 Hz, 1H), 6.69 (d, *J* = 2.9 Hz, 1H), 7.05 (dd, *J* = 8.5, 2.6 Hz, 1H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.38 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 29.72, 31.58, 34.43, 36.00, 115.44, 118.72, 120.75, 122.88, 125.13, 126.12, 127.95, 128.87, 135.84, 141.93, 142.70, 149.42. Anal. Calcd for $C_{20}H_{25}Br_2NO$: C, 52.77; H, 5.54; N, 3.08; Found: C, 54.74; H, 5.41; N, 3.02.

4. Conclusion

In this project, various derivatives of *ortho*-aminophenols were synthesized using a cadmium catalyst. The synthesis methods were designed to adhere to the principles of green chemistry. Ethanol and water were employed as green solvents, and catechol was used as an environmentally friendly raw material. The project introduces new and straightforward methods that result in the synthesis of nitrogen and oxygen-containing products with easy separation, high efficiency, and suitable for large-scale production.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

The authors state that they have no known financial conflicts of interest or personal relationships that could have influenced the work reported in this paper.

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Appendix

Supporting Information

General Information. All chemicals materials were acquired from commercial sources and used without additional purification. The NMR spectra were recorded for ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) in CDCl3 as solvent and tetramethylsilane (TMS) as internal standard.

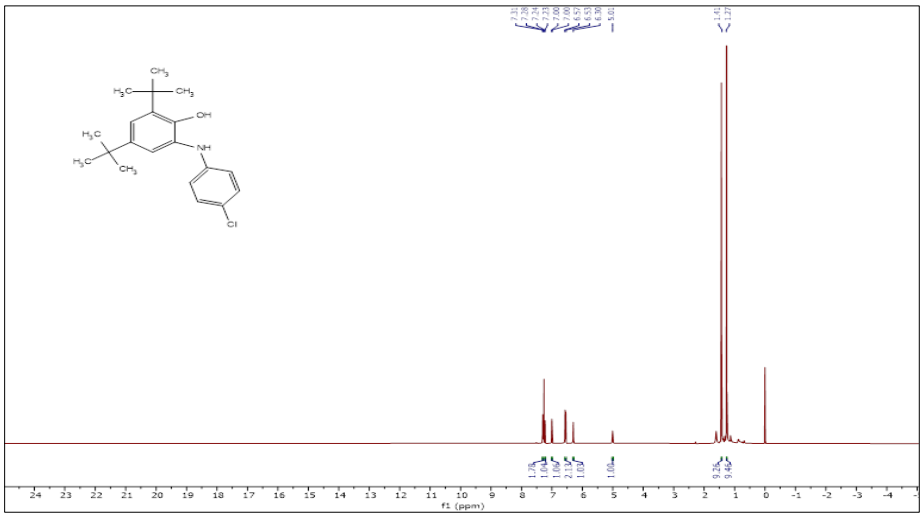

Figure 1 ^{1}H NMR compound 3b, $CDCl_3$, 400 MHz

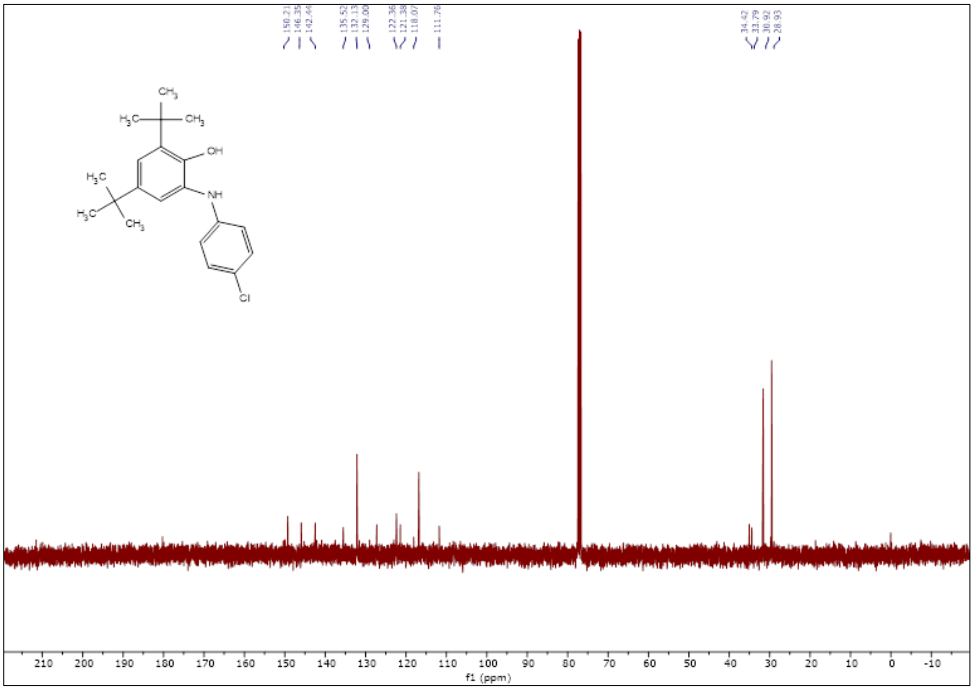

Figure 2 ^{13}C NMR compound 3b, $CDCl_3$, 101 MHz

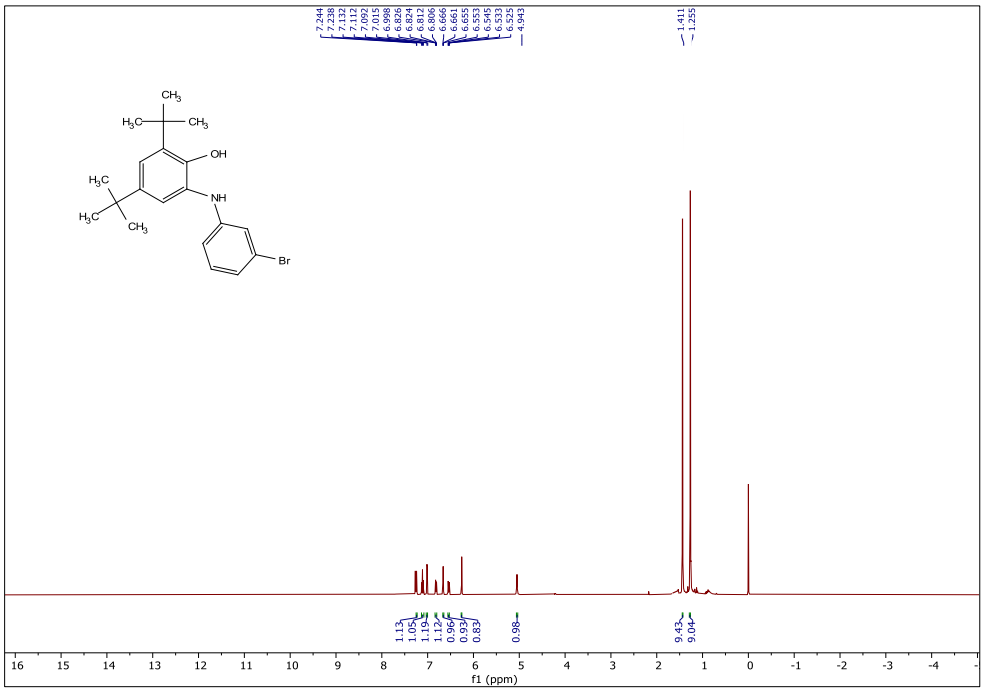

Figure 3 ^{1}H NMR compound 3d, $CDCl_3$, 400 MHz

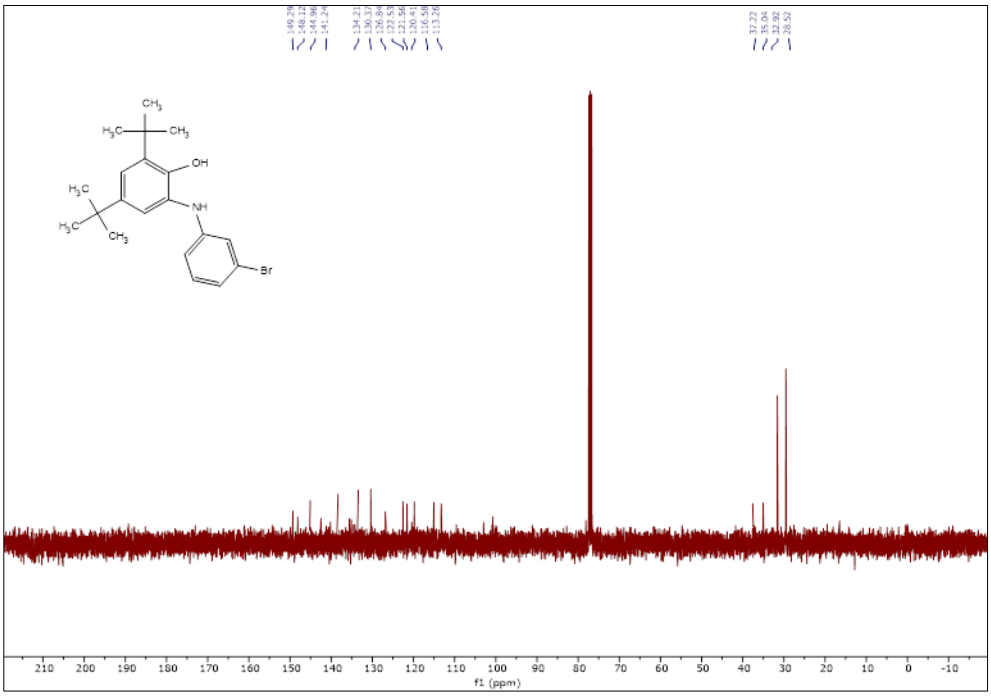

Figure 4 ^{13}C NMR compound 3d, $CDCl_3$, 101 MHz

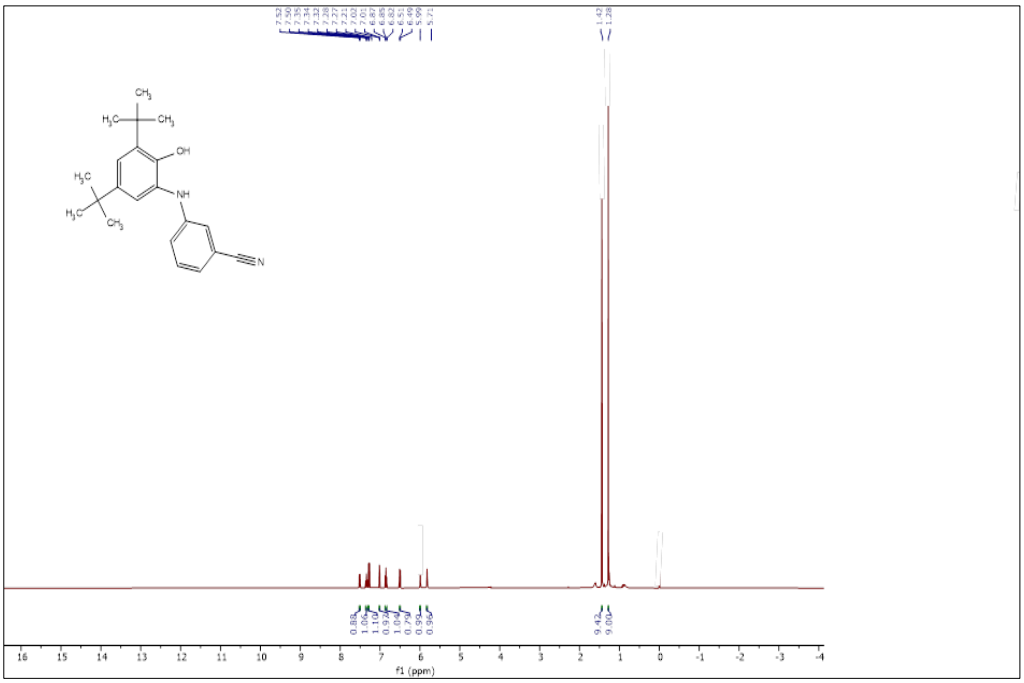

Figure 5 ^{1}H NMR compound 3f, $CDCl_3$, 400 MHz

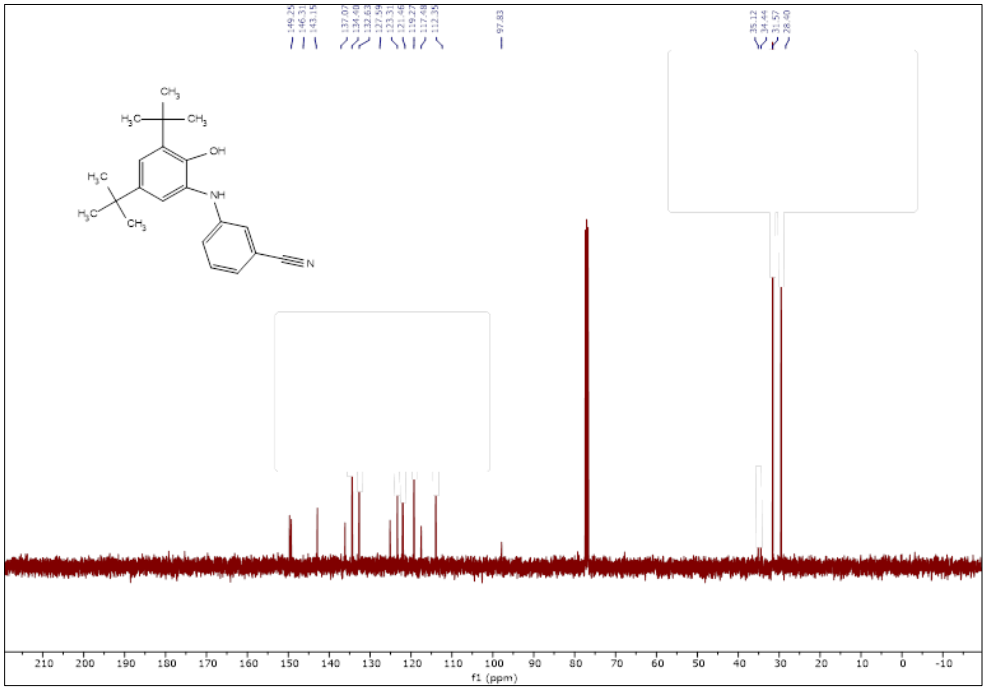

Figure 6 ^{13}C NMR compound 3d, $CDCl_3$, 101 MHz

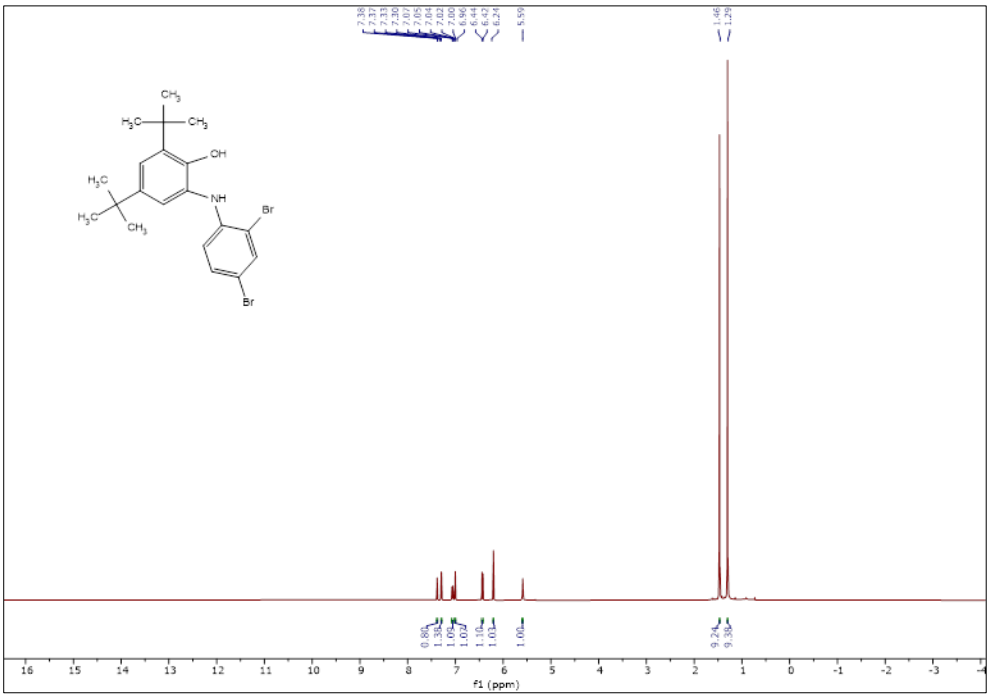

Figure 7 ^{1}H NMR compound 3i, $CDCl_3$, 400 MHz

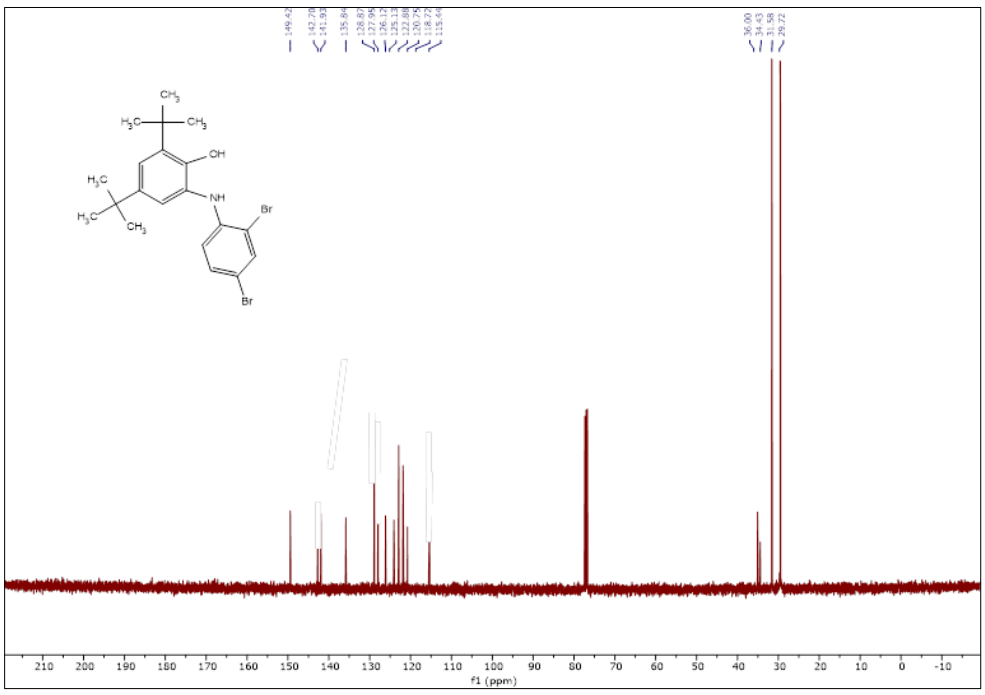

Figure 8 ^{13}C NMR compound 3i, $CDCl_3$, 101 MHz

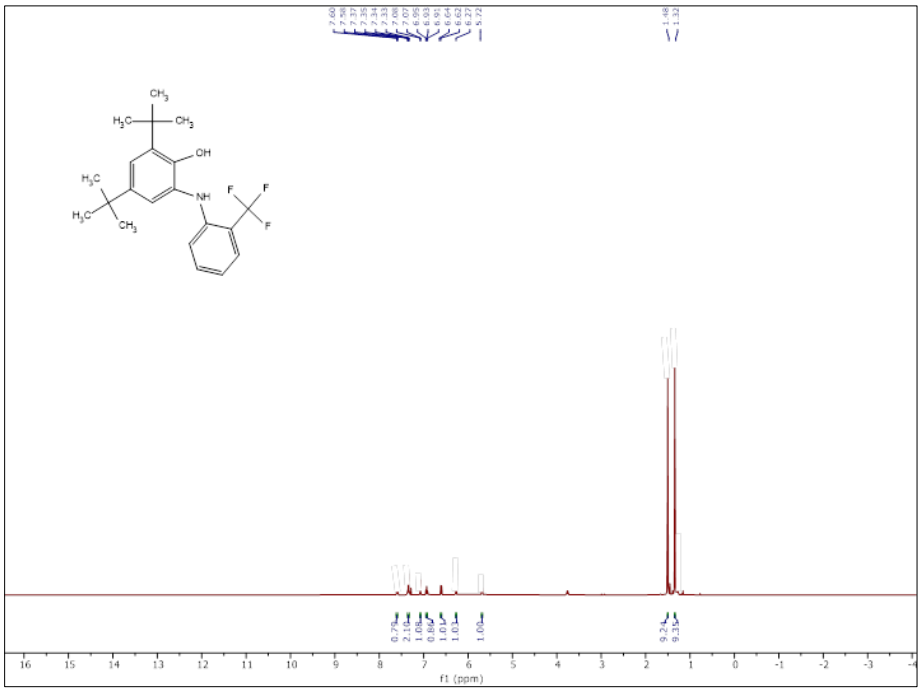

Figure 9 ^{1}H NMR compound 3g, $CDCl_3$, 400 MHz

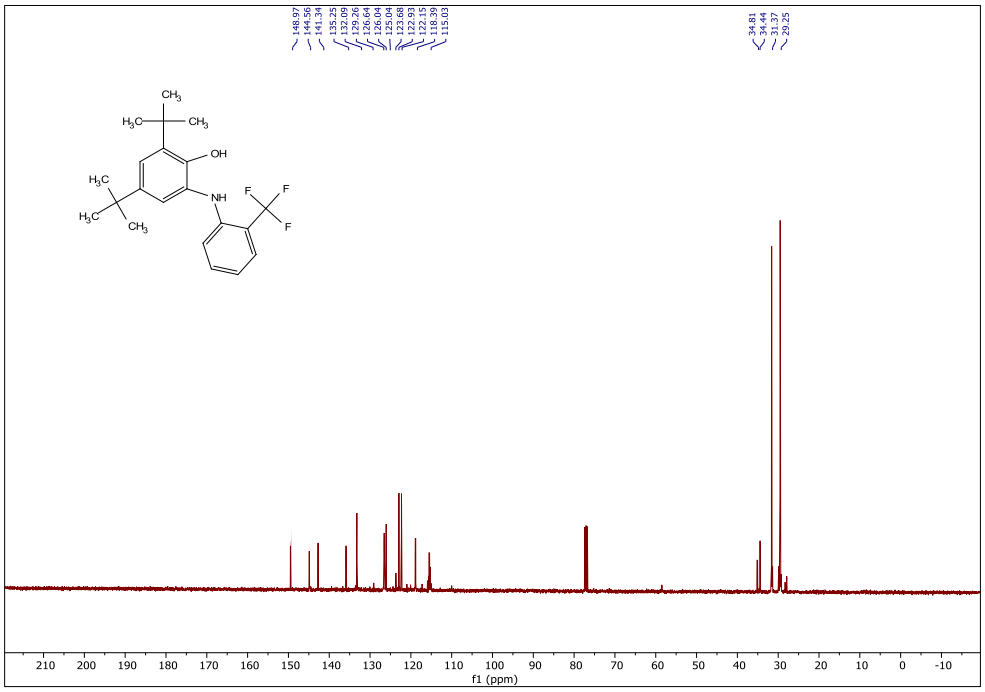

Figure 10 ^{13}C NMR compound 3g, $CDCl_3$, 101 MHz