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Synthesis of Bis-1,3,4-Oxadiazoles Utilizing Monomers Derived from the Degradation of PET (Polyethylene Terephthalate) in an Eco-Friendly Manner †

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Abstract

The chemical recycling process of polyethylene terephthalate (PET) was executed through aminolysis employing N, N-Diisopropylethylamine (DIPEA) as the catalytic agent, commencing with the systematic collection and comprehensive purification of discarded PET bottles to remove contaminants and additives. The depolymerization reaction utilized hydrazine as the primary amine source, facilitating the cleavage of ester bonds within the polymer matrix under controlled temperature and pressure conditions. The synthesis of the diamine compound, terephthalohydrazide, was successfully achieved through this catalytic aminolysis pathway, demonstrating high conversion efficiency and product selectivity. The resulting terephthalohydrazide served as a crucial intermediate and was subsequently utilized for the further synthesis of BIS-1,3,4-Oxadiazole derivatives through a comprehensive methodology rigorously aligned with the fundamental principles of green chemistry, including atom economy, reduced waste generation, and environmentally benign reaction conditions. A diverse series of six distinct products derived from various carboxylic acids employed in the cyclization synthesis of BIS-1,3,4-Oxadiazoles were systematically produced under optimized reaction parameters. These products were meticulously characterized using advanced nuclear magnetic resonance (NMR) spectroscopy techniques, including both ^{1}H and ^{13}C NMR analyses, confirming their structural integrity and chemical composition. This sequential approach represents a significant advancement in heterocyclic synthesis methodology, using sustainable pathway to find structural diversity.

Keywords: polyethylene terephthalate (PET); BIS-1,3,4-oxadiazoles; chemical recycling process; terephthalohydrazide

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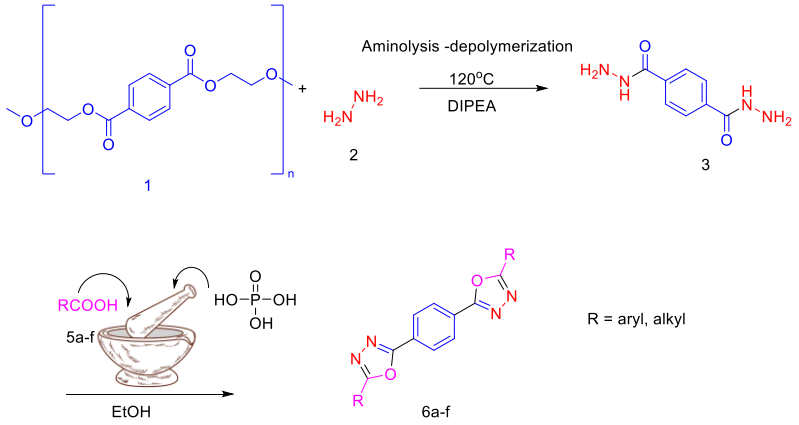
1. Introduction

Plastic waste, particularly that which arises from post-consumer packaging, presently encounters considerable obstacles in terms of recycling efficacy. conventional mechanical recycling techniques frequently prove inadequate for managing such waste because of elevated contamination levels, costly sorting and purification procedures, and the nascent state of relevant technologies. Consequently, chemical recycling [1–3] has surfaced as an essential strategy to tackle the challenges associated with plastic waste. In this study, we delineate the process of depolymerization utilizing the aminolysis approach, employing a diverse array of amines such as ethanolamine, ethylene diamine, and hydrazine [3–6]. In the current study, we elucidate the synthesis of bis-1,3,4-oxadiazoles that are derived from the chemical recycling of polyethylene terephthalate (PET).

1,3,4-oxadiazoles are five membered heterocycles which contain one oxygen and two nitrogen atoms [7–9]. These molecular entities demonstrate an extensive array of biological activities, encompassing anti-inflammatory [10], analgesic [11], antiviral [12] antifungal [13], and antitumor [12], antimicrobial properties [14]. Considering their biological efficacy, the synthesis of these compounds is of paramount importance; consequently, we have formulated a green chemical methodology for the synthesis of these 1,3,4-oxadiazoles utilizing monomers derived from plastic materials (Scheme 1).



Scheme 1. Synthesis of 2,5-diaryl-Bis-1,3,4-oxadizaoles.

2. Results and Discussion

Initially, we procured post-consumer PET bottles (**1**) and subsequently subjected them to rigorous cleansing with a neutral soap solution, followed by a drying process and subsequent reduction into flakes for the ensuing reaction. The PET flakes were then exposed to a reaction with hydrazine (**2**) and DIPEA (Di-isopropyl ethylamine) serving as a base at a temperature of 120 degrees Celsius to facilitate the synthesis of terephthalohydrazide (**3**).

The terephthalohydrazide was thoroughly characterized by utilizing Infrared Spectroscopy (IR) FIT-IR (ATR, cm^{-1}): 3313.7, 1604, 1539, 1489, 1338, 1099, 925.8, 883, 736, 713.in conjunction with both Proton Nuclear Magnetic Resonance (^{1}H NMR) and Carbon-13 Nuclear Magnetic Resonance (^{13}C NMR) (Refer to Figures 1 and 2). Upon examination of the ^{1}H NMR spectrum, notable peaks indicative of the terminal amine functional group (-NH_2) are observed at 4.57 ppm, whereas the Amide NH resonance appears at 9.87 ppm; finally, the aromatic -CH signals are detected within the chemical shift range of δ 7.88–7.86 ppm. Following the validation of the depolymerization phase, we advanced to the mechanochemical cyclo-condensation stage; in contrast to the established methodology reported by Agarwal et al. (2017) [15], which utilized phosphorus oxychloride, a significantly harsh condition for the synthesis of bis-1,3,4-oxadiazole.

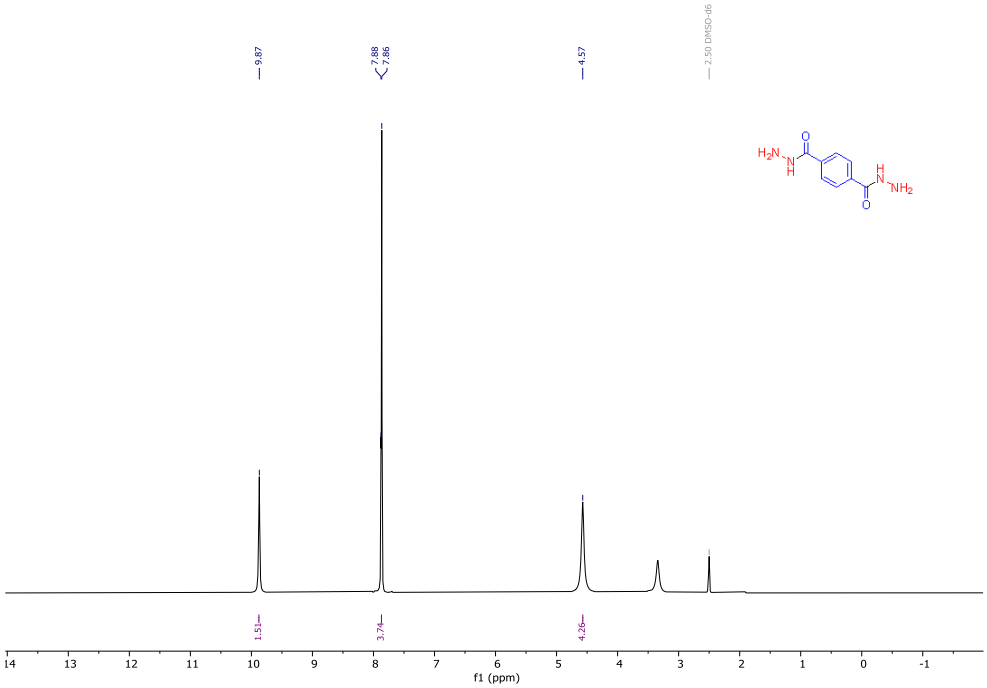


Figure 1. ^{1}H NMR of terephthalohydrazide **3**.

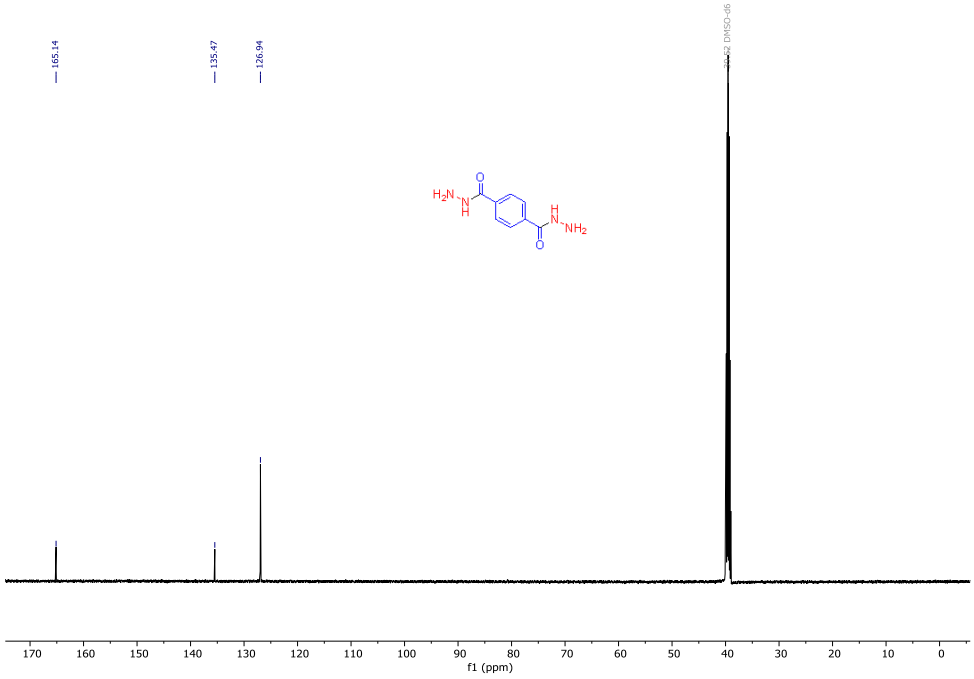
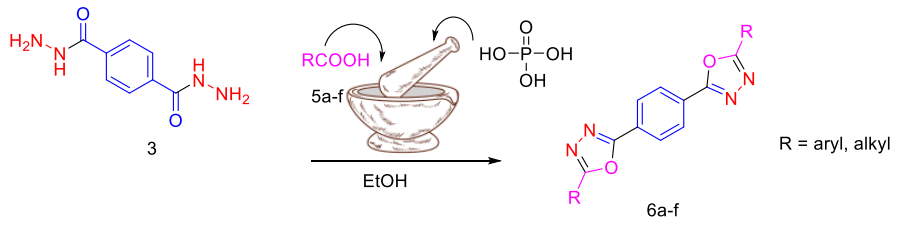


Figure 2. ^{13}C NMR of terephthalohydrazide **3**.

Herein, we present an effective and environmentally benign reagent, phosphoric acid, as a substitute for phosphorus oxychloride (Scheme 2).



Scheme 2. Synthesis of 2,5-diaryl-bis-1,3,4-oxadiazoles (**6a–f**).

The reaction was executed through the amalgamation of terephthalohydrazide 3 with the corresponding five equivalents of phosphoric acid and carboxylic acid derivatives 5a–f, resulting in the formation of bis-1,3,4-oxadiazole derivatives with yields ranging from good to excellent (72–94%), which are substantiated by ^{1}H, and ^{13}C NMR spectroscopy. (Refer to Figures 3 and 4).

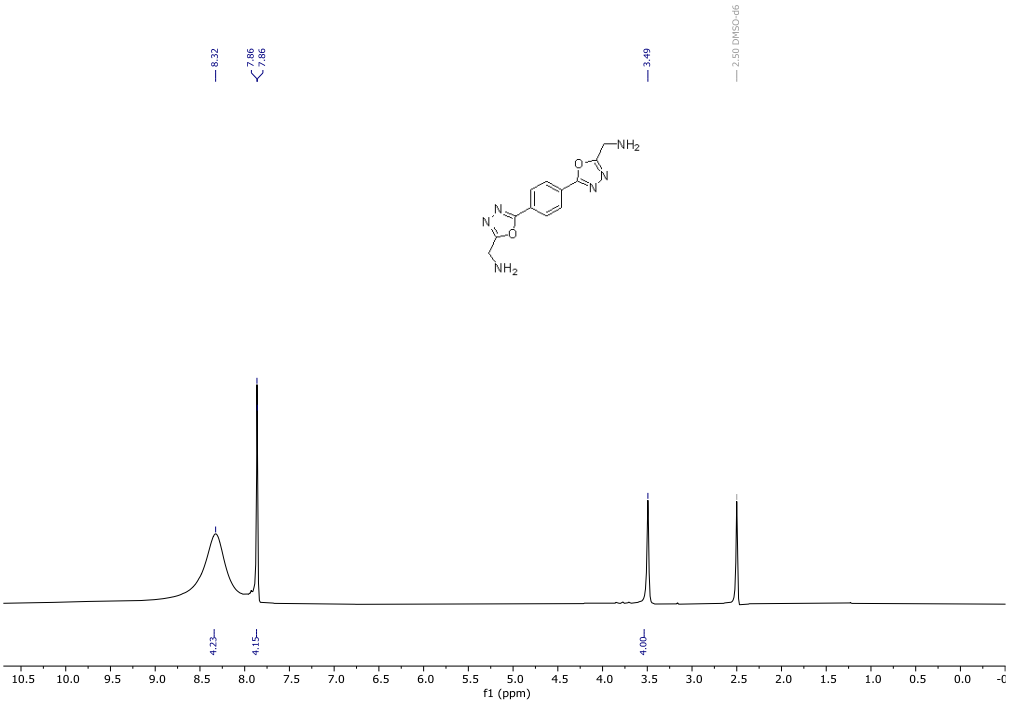


Figure 3. ^{1}H NMR of (1,4-phenylenebis(1,3,4-oxadiazole-5,2-diyl))dimethanamine **5a**.

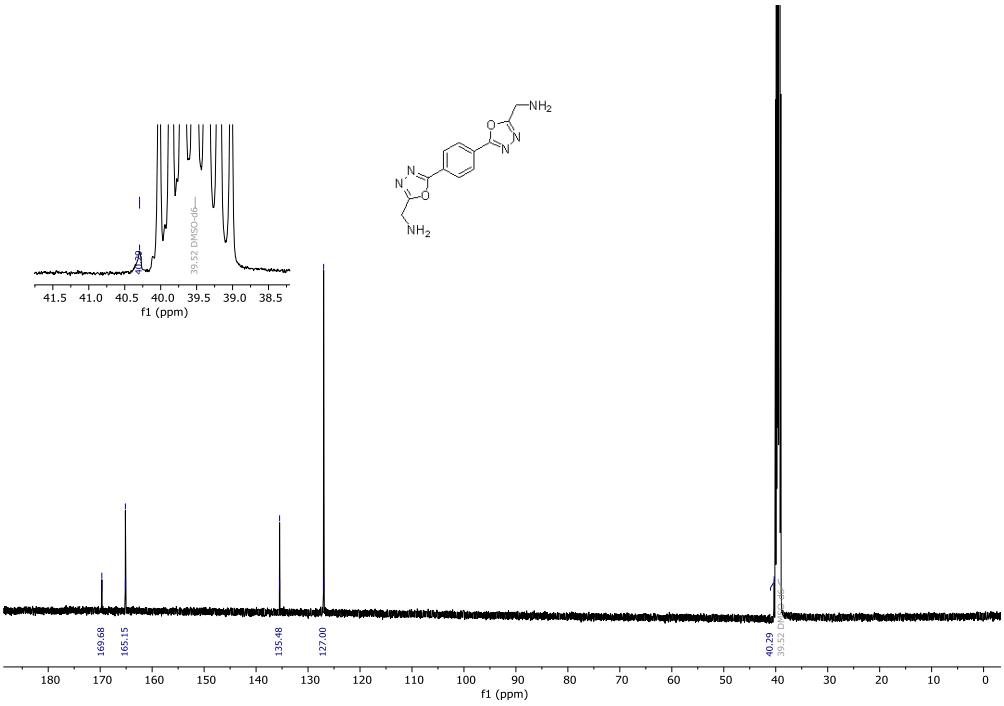


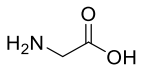
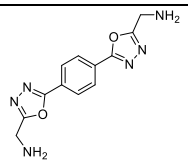
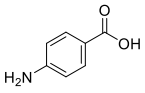
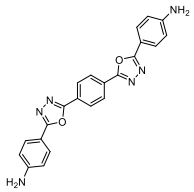
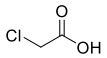
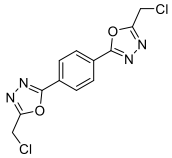
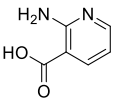
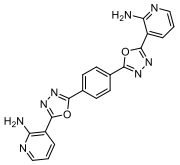
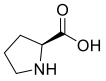
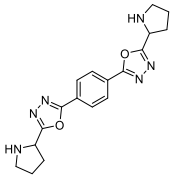
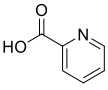
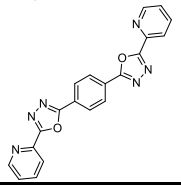
Figure 4. ^{13}C NMR of **(**1,4-phenylenebis(1,3,4-oxadiazole-5,2-diyl)) dimethanamine **5a**.

Upon a thorough analysis of the NMR spectroscopy pertaining to compound **5a**, which is synthesized through the reaction with glycine as a carboxylic acid derivative, we ascertain via proton NMR the existence of terminal amine functionalities at δ 8.35 ppm,

while the signal at δ 3.49 ppm corresponds to the -CH2 group. In contrast, the ^{13}C NMR delineates significant peaks at 169.68 ppm and 165.15 ppm, which are indicative of the ipso carbon within the oxadiazole ring, whereas the peak at 135.48 ppm is representative of the aromatic benzene ring.

Following the verification of oxadiazole synthesis, we subsequently established a modest repository of compounds as delineated in Table 1, along with the corresponding yields of each compound.

Table 1. synthesis of 2,5-diaryl-bis-1,3,4-oxadiazole derivatives.

RCOOH	Oxadiazole	%Yield
		88
		72
		50
		85
		93
		94

[1] Tables may have a footer.

3. Experimental Section

3.1. General Information, Software Instrumentation and Chemicals

^{1}H and ^{13}C NMR were acquired on Varian 500 MHz the solvent for NMR DMSO-d6, Chemical shift was reported in ppm (δ/ppm), Coupling constants are reported in Hertz (J/Hz).) Multiplicities of signals are reported using the standard abbreviations: singlet (s), doublet (d), triplet (t), the quartet (q) and multiplet (m). NMR spectra were analyzed using the MestreNova software. IR spectroscopy was recorded on Shimadzu-IR tracer-100 spectrometer by ATR method using neat compounds. The wavelengths are reported in reciprocal centimeters (max/cm^{-1}). Melting points were determined on a Fisher-Johns apparatus and were uncorrected. The solvents were distilled and dried according to standard procedures. Commercially available reagents were purchased to Sigma-Aldrich and were

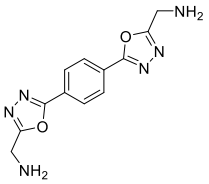
used without further purification. Structure names and drawings were done using the ChemBioDraw Ultra software.

3.2. Synthesis and Characterization of 2,5-diaryl-bis-1,3,4-oxadiazoles

General Procedure (GP): In a meticulously cleaned and thoroughly dried 30 mL porcelain mortar, 5.15 mmol (1 equivalent) of product **3** (1 g) was introduced, followed by the addition of 1 mL of ethanol, which was subsequently triturated using the pestle until a uniform white amalgamation was achieved; thereafter, 25.75 mmol (5 equivalents) of 85% phosphoric acid (1.76 mL) was incorporated and subjected to grinding for an approximate duration of 10 min. To prevent desiccation of the mixture, ethanol was continuously introduced in incremental volumes. Upon achieving a homogenous blend, 10.30 mmol (2 equivalents) of respective carboxylic acid was further ground for around 45 min, resulting in a uniform mixture and an observable transition in color. The resultant mixture underwent vacuum filtration, with the addition of a small quantity of ethanol and 10 mL of water to eliminate any unreacted excess of phosphoric acid and respective carboxylic acid. The mixture was allowed to dry for a period of 24 h, yielding a 2,5-diaryl-bis-1,3,4-oxadiazoles (**6a–f**).

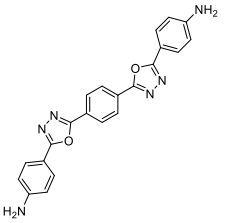
3.3. Spectral Data

*(1,4-phenylenebis(1,3,4-oxadiazole-5,2-diyl))dimethanamine (**6a**)*



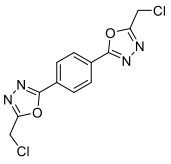
According to GP, terphthalohydrazide **3** (1 g, 5.15 mmol), 85% phosphoric acid (1.76 mL, 25.5 mmol) and Glycine **5a** (773.1 mg, 10.30 mmol) in EtOH to obtain white creamy powder 1,24 g 88%. ^{1}H NMR (500 MHz, DMSO -d6) δ 8.32 (s, 4H), 7.86 (q, J = 3.5 Hz, 4H), 3.49 (s, 4H).^{13}C NMR (126 MHz, DMSO -d6) δ 169.69, 165.15, 135.48, 127.00, 40.29. Mp: >300 °C.

*4,4′-(1,4-phenylenebis(1,3,4-oxadiazole-5,2-diyl))dianiline (**6b**)*



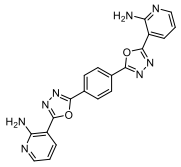
According to GP, terphthalohydrazide **3** (1 g, 5.15 mmol), 85% phosphoric acid (1.76 mL, 25.5 mmol) and p-aminobenzoic acid **5b** (1.41 g 10.30 mmol) in EtOH to obtain white creamy powder after filtration gives 6b 1.45 g of 72% ^{1}H NMR (500 MHz, DMSO-d6) δ 7.87 (s, 4H), 7.78 (s, 4H), 7.60 (d, J = 8.4 Hz, 4H), 6.54 (d, J = 8.3 Hz, 4H).^{13}C NMR (126 MHz, DMSO-d6) δ 167.57, 165.19, 153.20, 135.43, 131.27, 127.08, 116.93, 112.62. Mp: >300 °C.

*1,4-bis(5-(chloromethyl)-1,3,4-oxadiazol-2-yl) benzene (**6c**)*



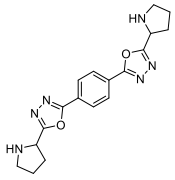
According to GP, terphthalohydrazide **3** (1 g, 5.15 mmol), 85% phosphoric acid (1.76 mL, 25.5 mmol) and 2-chloroacetic acid **5c** (0.973 g 10.30 mmol) in EtOH to obtain white solid with 50% (0.8 g) ^{1}H NMR (500 MHz,DMSO-d6) δ 7.85 (s, 4H), 5.94 (s, 4H). ^{13}C NMR (126 MHz, DMSO-d6) δ 164.36, 163.85, 127.35, 125.85, 35.08. Mp: >300 °C.

*3,3'-(1,4-phenylenebis(1,3,4-oxadiazole-5,2-diyl))bis(pyridin-2-amine) (**6d**)*



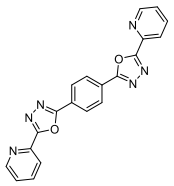
According to GP, terphthalohydrazide **3** (1 g, 5.15 mmol), 85% phosphoric acid (1.76 mL, 25.5 mmol) and 2-aminonicotinic acid **5d** (1.42 g 10.30 mmol) EtOH to obtain white solid with 85% yield (1.75 g) ^{1}H NMR (300 MHz, DMSO) δ 8.16 (s, 2H), 8.03 (d, J = 7.7 Hz, 2H), 7.87 (s, 4H), 6.60 (t, J = 6.3 Hz, 6H). ^{13}C NMR (75 MHz, DMSO) δ 168.69, 165.29, 159.74, 153.35, 140.30, 135.55, 127.11, 111.99, 105.83. Mp: >300 °C.

*1,4-bis(5-(pyrrolidin-2-yl)-1,3,4-oxadiazol-2-yl)benzene (**6e**)*



According to GP, terphthalohydrazide **3** (1 g, 5.15 mmol), 85% phosphoric acid (1.76 mL, 25.5 mmol) and L-proline 5e (1.19 g, 10.30 mmol) in EtOH to obtain white solid with 93% yield (1.7 g) ^{1}H NMR (300 MHz, DMSO) δ 7.86 (s, 4H), 5.80 (s, 2H), 3.81 (t, *J* = 7.7 Hz, 2H), 3.21 (dt, *J* = 12.9, 6.6 Hz, 2H), 3.05 (dt, *J* = 11.3, 7.3 Hz, 2H), 2.09 (dd, *J* = 12.2, 8.4 Hz, 2H), 1.91 (dt, *J* = 12.2, 6.1 Hz, 2H), 1.76 (tq, *J* = 12.9, 6.8 Hz, 4H). ^{13}C NMR (75 MHz, DMSO) δ 170.57, 165.12, 135.47, 126.95, 60.35, 45.19, 28.77, 23.71. Mp: >300 °C.

1,4-bis(5-(pyridin-2-yl)-1,3,4-oxadiazol-2-yl)benzene (**6f**)



According to GP, terphthalohydrazide **3** (1 g, 5.15 mmol), 85% phosphoric acid (1.76 mL, 25.5 mmol) and picolinic acid in EtOH to obtain white solid with 94% yield (1.79 g) (1.27 g 10.30 mmol) ^{1}H NMR (300 MHz, DMSO) δ 8.70 (ddd, J = 4.8, 1.7, 1.0 Hz, 2H), 8.00 (dtd, J = 17.0, 7.7, 1.5 Hz, 2H), 7.87 (s, 4H), 7.62 (ddd, J = 7.4, 4.7, 1.5 Hz, 2H), 6.14 (s, 2H).

^{13}C NMR (75 MHz, DMSO) δ 166.25, 165.19, 149.48, 148.42, 137.58, 135.46, 127.14, 127.05, 124.71. Mp: >300 °C.

4. Conclusions

We have formulated an efficient and cost-effective methodology for synthesizing 2,5-diaryl-bis-1,3,4-oxadiazole, which encompasses a range of variations and diversity by employing various carboxylic acids along with the monomer derived from the chemical recycling of polyethylene terephthalate (PET), achieving yields that range from good to excellent. The primary benefit of this approach is that it facilitates the generation of value-added compounds from waste plastic materials through the application of mechanochemical reactions.

Author Contributions: All authors contributed equally to this work. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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