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Electron-deficient naphthalene diimides as efficient planar π-acid organocatalysts for selective oxidative C–C coupling of 2,6-di-*tert*-butylphenol: A temperature effect

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ABSTRACT

An efficient planar π-acid electron transfer organocatalyst based on electron-deficient substituted naphthalene diimide has been developed for oxidative C–C coupling of 2,6-di-*tert*-butylphenol to its dimeric derivative or unexpected ring-rearranged trimeric quinone methide by controlling the reaction temperatures.

1. Introduction

The formation of carbon–carbon (C–C) bond is arguably one of the most important reactions in synthetic chemistry [1], because it allows the transformations of small, readily accessible reactants into larger, value-added products with useful physical and chemical properties. Generally, the C–C bond formation reactions, in particular the C–C coupling reactions of aromatic molecules, are kinetic unfavourable, but it can be promoted in the presence of suitable catalysts. Transition-metal based catalysts, such as Pd, Rh, Cu and Ni complexes, have already been demonstrated to be the most important class of catalysts for the C–C bond formations [2]. However, they also suffer from some intrinsic drawbacks, *e.g.* the high cost, high toxicity and air-sensitivity, which somewhat limit their scope for applications.

To overcome the aforementioned disadvantages of transition-metal based catalysts, an emerging class of catalysts based on purely organic molecules (called organocatalysts) has been successfully developed in the past decade [3]. Among the reported organocatalysts, organic π-acid catalysts are most distinctive [4]. Different from the common Lewis acid organocatalysts that generally use only single atom containing empty orbits to accept electrons from reaction substrates, such unique π-acid organocatalysts based on electron-deficient π-conjugated systems could abstract the additional electrons through a linear or planar π system, which undoubtedly increase their reaction cross sections towards the substrates. In spite of foreseeable advantages, so far only three electron-deficient π-conjugated molecules, *i.e.* tetracyanoethylene (TCNE, Fig. 1) [5], dicyanoketene acetal (DCKA) [6] and dichlorodicyanobenzoquione (DDQ) [7], have found catalytic activities for organic synthesis, wherein few examples deal with the C–C bond formation reactions [8].

Naphthalene diimides (NDIs) [9] are an attractive class of electron-deficient π-conjugated molecules since their parent core possesses a high quadrupole moment (QZZ) up to +55.5 B, which is around three times that of the explosive trinitrotoluene [10]. This makes them a strong tendency to compactly interact with and therefore possibly abstract electrons from the surrounding electron-rich atoms, groups or molecules. For example, due to a remarkable anion–π interaction with electron-rich anions, such unique class of π-acids has already been applied in the fields of anion sensors [11] and anion transports [12]. More recently, Matile and co-workers have indeed demonstrated the applications of the anion–π interactions could be extended to the catalysis field [13]. Herein, we reported a new oxidative C–C coupling of 2,6-di-*tert*-butylphenol (**2**, Scheme 1) by molecular oxygen in present of electron-deficient NDI **1** (Fig. 1), which serves as an organocatalyst through totally electron transfer but not pure anion–π interactions. The reason why NDI **1** was chosen is mainly in view of

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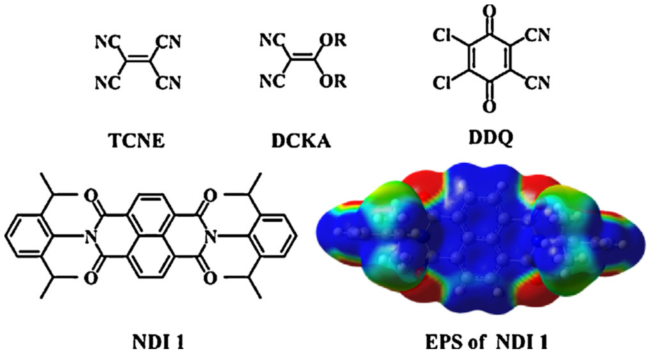


Fig. 1. Molecular structures of the available π-acid organocatalysts TCNE, DCKA, DDQ and the title compound NDI **1**, as well as its electrostatic potential surface (EPS, blue positive, red negative, ±0.01 Hartree, B3LYP/6-311G**). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

its simple structure but high solubility in most organic solvents. With regards to the reaction substrate, the phenol **2** was chosen as a proof-of-concept example since the exceptional electron donation of its anion, which is expected to offer an electron to the electron-deficient NDI **1**. Although the oxidative transformation of phenol **2** to coupling product **3** by the inorganic catalysts is very common [14], its organocatalytic reaction and particularly further ring-rearranged product quinone methide derivative **4** is first observed.

2. Experimental

2.1. Materials and measurements

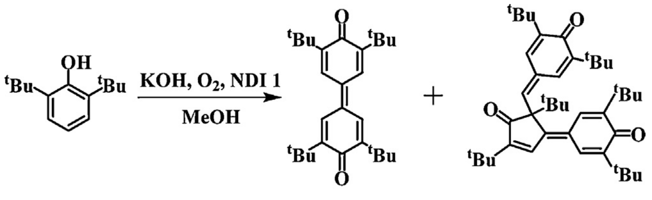
2.1.1. Materials and methods

1,4,5,8-Naphthalenetetracarboxylic (95%), 2,6-diisopropylbenzenamine (95%), 2,6-di-*tert*-butylphenol (97%), potassium hydroxide (≥99%), methanol (99.5%), dichloromethane (DCM, 99.5%) and petroleum ether (PE, 60–90 °C) were obtained from commercial suppliers. All chemicals and reagents were used as received unless otherwise stated. Column chromatography was performed using silica gel (Si60, mesh size 150 μm from Sinopharm Chemical Reagent Co., Ltd.). NMR spectra were recorded with a Bruker Avance 400 MHz NMR spectrometer. Chemical shifts are given in parts per million (ppm) and referred to TMS as internal standard. ^{1}H coupling constants J are given in Hertz (Hz). ESI mass spectra were recorded on a LCQ Fleet from Thermo Fisher Scientific. High-resolution mass spectra (HRMS) were acquired on the Thermo Scientific Exactive Plus Mass spectrometer equipped with an electrospray ionization (ESI) source.

2.2. Synthesis and catalytic experiments

2.2.1. Synthesis of organocatalyst NDI **1**

The synthesis of NDI **1** is similar to the procedure reported in the literature [15]. Under the argon, a mixture of naphthalene tetracarboxylic anhydrides (3 g, 11.2 mmol), imidazole (15 g, 220.1 mmol), 2,6-diisopropylaniline (10 g, 56 mmol) were added to a three-necked flask and then heated in 160 °C for 12 h. After being cooled to room temperature, the solid was poured into 1 mol L^{-1} aqueous HCl (500 mL) and extracted using dichloromethane (DCM) (100 mL) twice. The obtained organic solution was washed with aqueous $NaHCO_3$ and water twice, and further dried by anhydrous Na_2SO_4 for 2 h. Filtration and removal the organic solvents afford a gray solid, which was purified by column chromatography (SiO_2, DCM:PE = 1:1) resulting in **N**DI **1** as a white solid (2.2 g, 40%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.92 (s, 1*H*), 7.55 (t, J = 7.2 Hz, 2*H*), 7.40 (d, J = 6.9 Hz, 4*H*), 2.84–2.61 (m, 4*H*), 1.20 (d, J = 5.9 Hz, 24*H*); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): 162.94, 145.54, 131.60, 130.01, 130.00, 127.68, 126.92, 124.25, 29.33, 23.97. MS (ESI): calculated for $[M+H]^+$ of **3**, 587.72, found, 587.19; HRMS (ESI): calculated for $[M+H]^+$, 587.2832, found, 587.2889.



2 3 4

Scheme 1. Selective oxidative C–C coupling of **2** to its dimer **3** or ring-rearranged trimeric **4** in the presence of organocatalyst NDI **1**.

2.2.2. Catalytic experiments of organocatalyst NDI **1** towards oxidative C–C coupling of **2**

To a three-necked flask, a MeOH solution of NDI **1** (for entry 2, **2** is absent), starting material **2** and KOH (for entry 3, KOH is absent) was added and then reacted at 20 °C (entry 5), 40 °C (entry 1) or 90 °C (entry 6) for 24 h or 200 h (the reaction progress is monitored by thin layer chromatography). After being cooled to room temperature, the cooled mixture was poured into 1 mol L^{-1} aqueous HCl (100 mL) and extracted with DCM (50 mL) twice. The obtained organic solution was washed with a saturated solution of $NaHCO_3$ (50 mL) and water for two times, and further dried by anhydrous Na_2SO_4. Filtration and removal the organic solvents afford a brown solid, which was purified by column chromatography (SiO_2, DCM:PE = 1:1) affording compound **3** as a yellow solid (815 mg, 80%) and Compound **4** is a light yellow solid (70 mg, 5%) for entry 1, but **3** of 60 mg (*ca.* 5%) and **4** of 817 mg (85%) for entry 6. For other trials (entry 2–5), almost no oxidative products was obtained.

Compound **3**: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ = 7.73 (s, 4H), 1.38 (s, 36H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): 186.44, 150.43, 136.13, 126.00, 36.03, 29.60. MS (ESI): calculated for $[M+H]^+$ of **3**, 409.62, found, 409.20; HRMS (ESI): calculated for $[M+H]^+$, 409.3028, found, 409.3089.

Compound **4**: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.20 (s, 1*H*), 7.43 (d, J = 2.5 Hz, 1*H*), 7.02 (d, J = 2.5 Hz, 1*H*), 6.88 (d, J = 2.4 Hz, 1*H*), 6.75 (s, 1*H*), 6.27 (d, J = 2.3 Hz, 1*H*), 1.35 (s, 9*H*), 1.31 (s, 9*H*), 1.24 (s, 9*H*), 1.12 (s, 9*H*), 1.08 (s, 9*H*), 0.97(s, 9*H*). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): 204.51, 185.58, 185.51, 156.56, 154.19, 149.08, 148.83, 148.06, 147.51, 146.48, 143.30, 134.56, 131.88, 126.39, 126.13, 125.97, 65.01, 38.96, 35.58, 35.55, 35.52, 29.58, 29.41, 29.32, 29.26, 28.49, 27.72. MS (ESI): calculated for $[M-H]^-$ of **4**, 611.92, found, 612.25; HRMS (ESI): calculated for $[M+H]^+$, 613.4542, found, 613.4593.

3. Results and discussions

The organocatalyst NDI **1** was prepared according to the procedure reported in the literature [15], and its molecular structure was assigned by NMR spectroscopy as well as by single-crystal X-ray analysis (for details, see Supporting information). Electrostatic potential surfaces (EPS) of NDI **1** was calculated at the B3LYP/6-311G** level, which provided a visual indication of the potential reaction cross section of organocatalyst NDI **1** towards the electron-rich substrates (Fig. 1). Due to the introduction of two di-iso-propyl phenyl substituents at two imide positions perpendicularly, the positive electrostatic surface (blue) of the NDI plane was extended in a continuous way to the equatorial region of the phenyl plane, which remarkably expanded the potential reaction cross section of

Table 1
Reaction condition optimizations for the selective C–C coupling of **2** to dimeric **3** or rearranged trimeric **4**.

Entry	Molar ratio[a]	Under argon[b]	Temp. (°C)	Time (h)	Yield of **3** (%)[c]	Yield of **4** (%)[c]
1	1:1:0.05	Not	40	24	80	5.0
2	1:1:0	Not	40	24	0	0
3	1:0:0.05	Not	40	24	0	0
4	1:1:0.05	Yes	40	24	Trace	Trace
5	1:1:0.05	Not	20	200	0	0
6	1:1:0.05	Not	90	24	5.0	85

[a] Molar ratio meant **2**:KOH:NDI **1**.
[b] Not under argon meant the reaction was exposed to the air.
[c] The yield is referred to the starting material **2**.

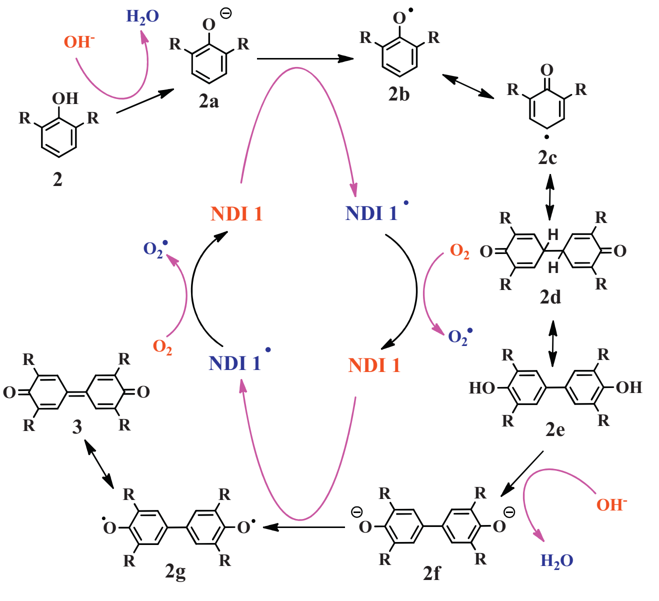
NDI **1**. Accordingly, NDI **1** should be a high performance electron acceptor for the additional electrons.

The catalytic activities of NDI **1** towards the selective C–C coupling of **2** to its dimer **3** or trimeric **4** (Scheme 1) were attempted by dissolving a mixture of **2**, NDI **1** and KOH in methanol (MeOH) and then monitoring the reactions under varying conditions (molar ratio of the reactant, catalyst and base, reaction atmosphere, temperature and time) *via* thin layer chromatography (TLC) (for the detailed experiments and characterizations of the oxidative products, see Supporting information). The results for several trials are shown in Table 1.

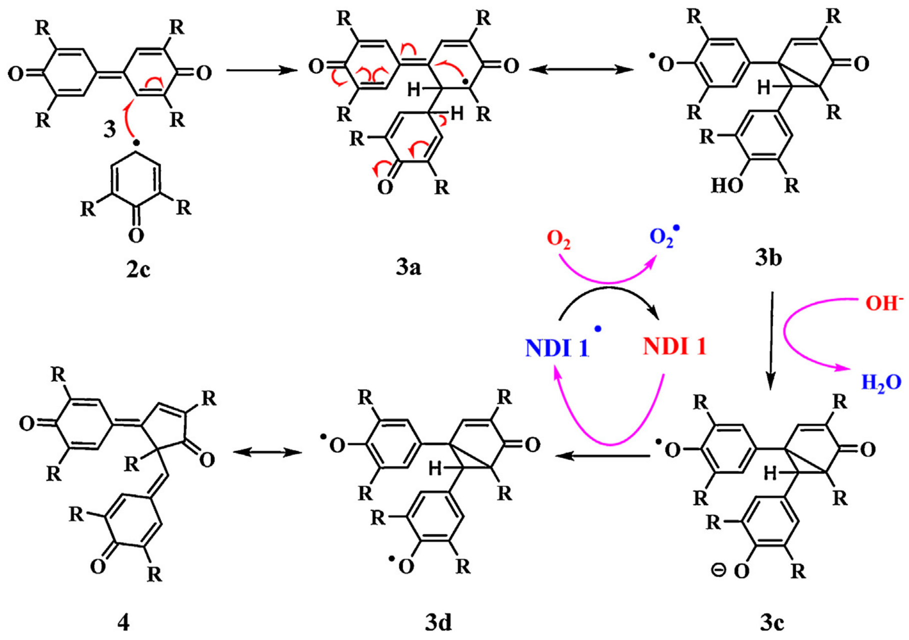
As expected, under a base condition and an exposed atmosphere, the oxidative C–C coupling reaction of **2** could indeed be promoted in the presence of a trace amount of electron-deficient NDI **1**. In more specific terms, the highest conversion to **3** was obtained in a yield of 80% when the molar ratio of **2**, KOH and NDI **1** is 1:1:0.05 and reaction temperature is at 40 °C (entry 1). The absence of NDI **1** and KOH resulted in almost no dimeric products **3** (entry 2 and 3), which confirmed the indispensability of organocatalyst NDI **1** and deprotonated **2** in this C–C coupling reaction. Last but not less important, the oxidant is supposed to be molecular oxygen because only trace product could be detected if the reaction was performed under argon (entry 4).

Taking all the above observations into consideration, a radical reaction sequence was the most plausible scenario for the oxidative C–C coupling reaction of **2** to its dimeric **3**. As shown in Scheme 1, the electron-deficient NDI **1** is supposed to serve as a single electron transfer catalyst, which can accept an electron from the deprotonated phenolate ion **2a**, making the latter to a 2,6-di-*tert*-butyl-phenoxide radical **2b**. This intermediate immediately transforms into a carbon radical **2c** and subsequently generates a new diphenol derivative **2e** by a homocoupling reaction. The latter species may undergo another deprotonation and electron transfer steps to afford the final product **3**. Owing to the reaction exposed to the air, the organocatalyst NDI **1** could be reactivated from the generated radical anion NDI **1**$^{\bullet}$ by transferring the additional electron to the molecular oxygen in the air [16]. Evidence for the formation of NDI radical anions is given by a colour change of the solution from light yellow to orange during the reaction, which is in accordance with the spectral characteristics of spectroelectrochemically generated NDI radical anions [17]. This proposed radical reaction mechanism is strongly supported by the high yield of **3** obtained under the base condition. Analysis of Hammett coefficients suggests that a more pronounced intermolecular electron transfer from the substrates to NDI **1** could >be achieved upon deprotonation of hydrogen group ($\sigma_p{}^+ = -0.92$ for –OH) of phenol **2** to its oxide anion ($\sigma_p{}^+ = -2.30$ for $-O^-$) [18]. Indeed, a similar phenomenon about the intramolecular electron transfer enhancement has already been observed in perylene diimides covalently functionalized by one or two 4-hydroxyphenyl substituents upon addition of base [19]. Moreover, almost no dimeric product **3** generated at low temperature (20 °C, entry 5) but further chain propagation to form a trimeric **4** in a yield of *ca.* 85% under reflux (90 °C, entry 6, the details will be described in the following), corroborates such a radical mechanism (Scheme 2).

Interestingly, as mentioned above, an increased temperature of the reaction resulted in the further chain propagation of the formed dimeric **3**, affording a ring-rearranged trimeric **4** in a high yield (85%, entry 6). The molecular structure of **4** was firstly assigned by single-crystal X-ray analysis (for details and crystal data, see Supporting information), which unequivocally confirm its ring-rearranged structure with two *p*-quinone methide moieties (bond lengths of 1.34–1.37 Å for C=C, 1.45–1.49 Å for C–C, and *ca.* 1.23 Å for C=O bonds, Fig. 2c) interconnected by a cyclopentenone unit (bond lengths of *ca.* 1.35 Å for C=C, 1.45–1.48 Å for C–C, and *ca.* 1.21 Å for C=O bonds) through a shared C atom and a C–C bond (*ca.* 1.50 Å), respectively (Fig. 2). Each quinone and cyclopentenone moiety was functionalized by two *tert*-butyl substituents leading to a high soluble **4**. This structural feature was also supported by ^{1}H and HH-COSY NMR spectra of **4** (see Figs. S8–S10 in Supporting information), which showed six sets of single signals with same integrated ratios between 6.0 and 8.5 ppm, corresponding to the six protons in the core of **4**. Owing to one *p*-quinone methide moiety bonded to cyclopentenone on a sp^3 C atom, **4** may be a mixture of two equimolar enantiomers, which is indeed observed in its single-crystal structure (Fig. 2a). Although the dimerization of **2** to **3** has already been reported to be promoted by several oxidative catalysts, such as Cu, Mn, Fe and Co complexes [20], no one exhibited such temperature-dependent selective oxidative catalysis, particularly for synthesis of complex molecules beyond dimeric **3**. Considering the possible applications of the quinone methide



Scheme 2. Possible mechanistic pathways for the oxidative C–C coupling reaction of **2** to its dimer **3** from under an organocatalysis of NDI **1** (*R* = *tert*-butyl).



Scheme 3. Plausible mechanistic pathways for the oxidative C–C coupling reaction of **2** to its ring-rearranged trimeric **4** from under an organocatalysis of NDI **1** (*R* = *tert*-butyl).

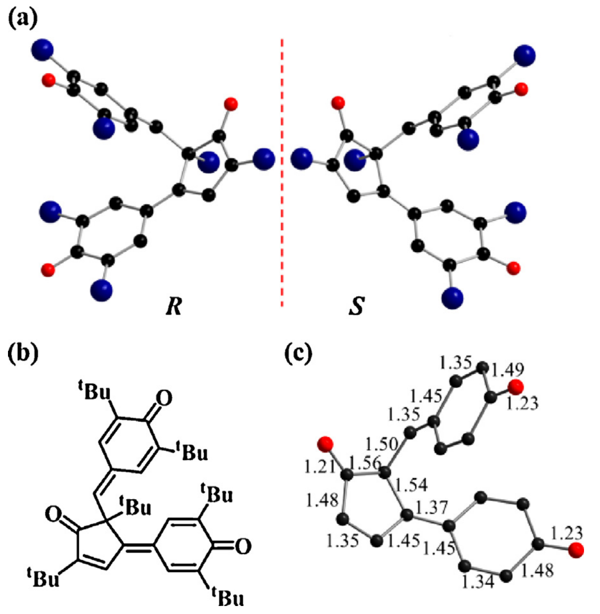


Fig. 2. The molecular structures of two enantiomers of **4** in the crystal ((a), black C, red O) and a proposed chemical structure of **4** (b) according to its bond length of its backbone (c). For clarity, the *tert*-butyl groups were represented by blue balls and all hydrogen atoms were omitted in (a), however, all the *tert*-butyl groups and hydrogen atoms were omitted in (c)[1]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

derivatives in the pharmaceuticals [21], the organocatalysts NDI **1** is anticipated to open up a facial synthetic approach for such reactive intermediates.

Mechanistically, a radical ring-rearranged sequence (Scheme 3) may account for the formation of **4**. Due to the high activity of radical **2c** at high temperature, it could attack the C=C bond of the generated **3** at the position with a low steric hindrance leading to a trimeric radical **3a**, which could be further chain propagated and resonated to its phenol **3b**. The obtained species may also undergo a similar deprotonation and electron transfer steps to those in the formation of dimeric **3** affording an unstable diradical **3d**, which is easy to be transformed to the final product **4** after a key electron rearrangement and ring-open reaction caused by a steric hindrance.

4. Conclusions

In conclusion, we have demonstrated an efficient planar π-acid electron transfer organocatalyst for the selective oxidative C–C coupling of 2, 6-di-*tert*-butylphenol. To the best of our knowledge, although the electron-deficient naphthalene diimides have been extendedly studied, this is first-time observation of the C–C coupling catalytic function for such versatile compounds. More importantly, the reaction products of 2,6-di-*tert*-butylphenol (dimeric **3** or ring-rearranged trimeric **4**) could be controlled by the reaction temperatures in the presence of single electron transfer catalyst NDI **1**. Owing to the ring-rearranged trimeric **4** belonging to the important intermediates quinone methide derivatives, the synthetic method developed in this work will open up a facial approach for the synthesis of the relative bioactive natural products.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.01.014.

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[1] Crystallographic data for **4**: $C_{42}H_{60}O_3$, $M = 612.90$, monoclinic, $a = 12.349(3)$ Å, $b = 17.039(3)$ Å, $c = 18.483(4)$ Å, $\alpha = 90.00^\circ$, $\beta = 96.09(3)^\circ$, $\gamma = 90.00^\circ$, $V = 3867.0(13)$ Å^3, $T = 293(2)$ K, space group *Pc*, $Z = 4$, 37,069 reflections measured, 16,242 independent reflections. The final R_1 values were 0.0487 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1169 ($I > 2\sigma(I)$). The final R_1 values were 0.0787 (all data). The final $wR(F^2)$ values were 0.1304 (all data). The goodness of fit on F^2 was 1.024. Flack parameter = 0.0.(3).

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