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# Solubility of cyclohexyl-phosphoramidic acid diphenyl ester in selected solvents



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## A R T I C L E I N F O

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# ABSTRACT

Cyclohexyl-phosphoramidic acid diphenyl ester (CPADE) was synthesized and characterized by elemental analysis (EA), mass spectrum (MS), infrared spectroscopy (IR) and nuclear magnetic resonance (NMR). The thermostability of CPADE was measured by thermogravimetric analysis (TGA) and the melting temperature and the fusion enthalpy of CPADE were evaluated by using differential scanning calorimeter (DSC). The solubilities of CPADE in selected solvents were obtained by a gravimetric method. The experimental data were well correlated by the Wilson, nonrandom two liquid (NRTL), and universal quasichemical (UNIQUAC) equations. And the dissolution enthalpy, entropy, and the molar Gibbs energy of CPADE in the selected solvents are also calculated by the van't Hoff equation.

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#### 1. Introduction

Organic polymer materials that greatly improve the quality of modern life are used in many fields because of their good heat endurance, chemical corrosion resistance, desired mechanical properties and so on. Unfortunately, most of the polymers are flammable, which limited their applications [1]. So the polymer materials with high heat-resistant and flame-retardant properties are urgently required. The well-known method to enhance the flame retardancy is to blend the flame retardant additives into the polymer materials. The flame retardants mainly work as two modes of actions, condensed phase and/or gas phase activities [2]. The condensed phase effects of flame retardants are relevant to a char layer which can obstruct the polymer surface from heat and air [3–5], while the gas phase effects are related to the mechanism of hydrogen and hydroxyl radical scavengers [6,7].

In general, the halogenated compounds with the antimonous oxide are often applied to give the polymers flame retardancy because of their good flame-resistant characteristics. However, this material causes environmental problems as toxic combustion products are released during combustion [8]. Hence, non-halogenated based flame retardants become increasingly popular alternatives in replacing the halogenated flame retardants. Among the available non-halogenated based flame retardants, phosphorus containing compounds are often regarded as

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http://dx.doi.org/10.1016/j.molliq.2015.05.024 0167-7322/© 2015 Elsevier B.V. All rights reserved. potential candidates, because these materials, working as the modes of condensed phase action and gas phase action during the flame retardancy process, typically do not generate any toxic gas [9]. In recent years, nitrogen–phosphorus flame-retardant synergism is recognized by the researchers [10]. The compounds containing phosphorus and nitrogen are usually named intumescent flame retardants owing to a foam char layer in the condensed phase [11]. The incombustible gases without toxic smoke and fog generated from these materials can dilute the concentration of the oxygen near the flame and foam superior protective barriers to the main materials against flame and heat while heating [12,13]. Now, most of the literatures on the halogen-free retardants are deeply relevant to the phosphorus–nitrogen-based products. Furthermore, they are believed to be the biggest growing share of the flame retardant market in the future [8].

Cyclohexyl-phosphoramidic acid diphenyl ester (CPADE) ( $C_{18}H_{22}O_3PN$ , CAS Registry No. 6372-21-0) is one of versatile intumescent flame retardants; its chemical structure is shown in Fig. 1.

This compound has a bright future, owing to its powerful flame retardancy to the polymers. It was widely used in Ethylene-Propylene-Diene Monomer (EPDM) [14], thermoplastic polyolefin [15], poly(styrene–ethylene/butene–styrene) (SEBS) [16], polyethylene [17,18], epoxy resins [19], polycarbonate (PC) [20] etc. However, some impurities have greatly affected its thermal property and applications. Thus, the purification process employed to obtain CPADE with high purity is very significant.

In the industry, the pure production of CPADE is always obtained by crystallization which is an important separation and purification process [21]. The (solid + liquid) equilibrium (SLE) measurements of CPADE in



Fig. 1. Structures of the cyclohexyl-phosphoramidic acid diphenyl ester (CPADE).

organic solvents are helpful to determine and estimate some crystallization parameters and reaction kinetics or thermodynamics study. However, there has no report as to the solubilities of CPADE in selected solvents. In this work, CPADE was synthesized and characterized. To achieve more thermodynamic data on the crystallization of CPADE from some organic solvents, the solubilities of CPADE in the ten selected organic solvents were measured. The Wilson [22], nonrandom two-liquid (NRTL) [23], and UNIQUAC [24] models were employed to fit the solubility data based on the pure component thermophysical properties. Comparison and discussion of the solubility were also presented in this study. And the dissolution behaviors of CPADE in the selected solvents were also estimated by van't Hoff equation [25].

## 2. Experimental

## 2.1. Materials

Diphenyl chlorophosphate was purchased from Zhangjiagang Xinyi Chemical Co., Ltd. and purified by distillation before used. Triethylamine and cyclohexylamine were kindly supplied by Weisi Chemical Reagents Co., Ltd. All of the organic solvents used for the experiments were analytical grade reagents, which were purchased from Beijing Chemical Factory. Purities and sources of all the materials used in this study are shown in Table 1.

#### Table 1

The source, mass purity and purification method o	of the sample used in	this paper.
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Chemical name	Source	Mass purity	Purification method
Diphenyl chlorophosphate	Zhangjiagang Xinyi Chemical Co., Ltd	> 0.990	Distillation
Triethylamine	Weisi Chemical Reagents Co., Ltd	>0.990	None
Chloroform	Beijing Chemical Factory	>0.995	None
Cyclohexylamine	Weisi Chemical Reagents Co., Ltd	>0.990	None
Ethyl acetate	Beijing Chemical Reagents Co., Ltd	>0.995	None
Acetone	Beijing Chemical Factory	>0.995	None
Ethanol	Beijing Chemical Factory	>0.995	None
Methanol	Beijing Chemical Factory	>0.995	None
Tetrahydrofuran	Beijing Chemical Factory	>0.998	None
Dichloromethane	Beijing Chemical Factory	>0.995	None
Benzene	Beijing Chemical Factory	>0.995	None
Adipic acid	Sigma-Aldrich	>0.990	None
Toluene	Beijing Chemical Factory	>0.995	None
Acetonitrile	Beijing Chemical Factory	>0.995	None
CPADE	As prepared	>0.990	Recrystallization



**Fig. 2.** Schematic diagram of the experimental apparatus: 1, thermostatic water-circulator bath; 2, sample gauge; 3, jacketed glass vessel; 4, magnetic stirrer; 5, magnetic agitator drive; 6, thermometer; 7, condenser.

#### 2.2. Apparatus and procedure

The experimental apparatus for the solubility measurements was the same as it was described in our previous work [26]. The diagrammatic sketch of the experimental apparatus was shown in Fig. 2.

A jacketed equilibrium cell was applied for the solubility measurements with a working volume of 120 mL and a magnetic stirrer, and a circulating water bath was used with a thermostat (type 50 L, made from Shanghai Laboratory Instrument Works Co., Ltd.) with an uncertainty of  $\pm$  0.01 K so that the system could reach and keep the required temperature. To prevent the evaporation of the solvent, a condenser was introduced. An analytical balance (type TG328B, Shanghai Balance Instrument Works Co., Ltd.) with an uncertainty of  $\pm$  0.1 mg was used during the mass measurements.

Fourier transform infrared (FTIR) spectrum was performed on a Perkin Elmer 400 spectrometer (Connecticut, USA). The melting point and enthalpy of fusion were measured with a DSC Q100 (TA Instruments) differential scanning calorimeter (DSC) in flowing nitrogen at a heating rate of 10 K  $\cdot$  min<sup>-1</sup>. The uncertainty of DSC measurement was the same as it was described in the literature [26]. The elemental



**Fig. 3.** Comparison of the literature and experimental mole fraction of adipic acid solubility (x) against temperature in water:  $\blacksquare$ , literature;  $\triangle$ , this work.

analysis was performed on an Elementar Vario EL element analyzer, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained with a Bruker ARX-400. Thermogravimetric analysis (TGA) was obtained with an SDT Q600 (TA Instruments) thermogravimetric analyzer at a heating rate of 10 K  $\cdot$  min<sup>-1</sup> under nitrogen atmosphere.

#### 2.3. Synthesis and characterization of CPADE

CPADE was prepared by the method similar to our previous work [27]. To a dry chloroformic solution of  $(C_6H_5O)_2P(O)Cl$ , a dry chloroformic solution of cyclohexylamine and triethylamine (1:1:1.1 molar ratio) was added dropwise over a period of 1 h at 273 K. After 6 h of stirring, the solvent was removed at reduced pressure and recrystallization of the residual material after being washed with cold distilled water from acetone afforded CPADE as a white crystalline solid. The mass fraction purity of PAETE was about 0.99.

El mass spectrum of CPADE can be seen in Fig. S1. The intensity (%) m/z of CPADE is 332.3 (M<sup>+</sup>). Elemental analysis (%, calcd): C, 65.25% (65.37%); H, 6.69% (6.72%); N, 4.23% (4.28%). In Fig. S2, the infrared spectrum of CPADE contains characteristic absorptions at 3216 cm<sup>-1</sup> for N–H stretching, 3072 cm<sup>-1</sup> for aromatic –C==C–H stretching, 2933 and 2854  $\text{cm}^{-1}$  for -HC-H stretching, ring carbon-carbon stretching vibrations occur in 1589, 1489 and 1455  $\text{cm}^{-1}$ , 1194  $\text{cm}^{-1}$  for the P=0 stretching, 1024 cm<sup>-1</sup> for the P-N stretching, 1236 cm<sup>-1</sup> for the C–N stretching and 904–955 cm<sup>-1</sup> for the P–O–Aryl stretching. The <sup>1</sup>H NMR spectrum of CPADE is shown in Fig. S3 of the Supporting information. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92–7.00 (m, 10H), 3.35 (d, J = 11.9 Hz, 1H), 2.03 (d, J = 13.2 Hz, 1H), 1.80-1.22 (m, 10H). Fig. S4 presents <sup>13</sup>C NMR (400 Hz, CDCl<sub>3</sub>) spectrum of CPADE. The chemical shifts of carbons with different chemical environments in CPADE structure are 25.03, 25.35, 35.50, 51.30, 120.25, 124.83, 129.67, and 151.06, respectively.

#### 2.4. Solubility measurement

A gravimetric method [26] was used to measure the solubilities of the CPADE in methanol, acetone, acetonitrile, tetrahydrofuran, ethyl acetate, chloroform, ethanol, benzene, toluene and dichloromethane. For each measurement, an excess mass of CPADE was introduced into a known mass of solvent. Then the equilibrium cell was heated and stirred at a constant temperature. After at least 3 h (different dissolution times were tested to determine the suitable equilibrium time. It was found that 3 h was enough to reach equilibrium), the stirring was stopped, and the solution was kept still until it was clear. Then, samples of the clear saturated solution were withdrawn by a preheated injector with a cotton filter. The mass of the saturated clear solution sample was determined with the analytical balance. Each solution sample was dried in a vacuum oven for at least 3 days to evaporate all solvents. The mass of the samples was weighed repeatedly throughout the drying process to make sure that no solvent remained. The weights were recorded after the solvents have been completely evaporated. During our experiments, three parallel measurements were performed at the same composition of solvent for each temperature, and an average value is given. FTIR was used to analyze the sample to ensure that no thermal decomposition effect had occurred on PNBE and no solvate material was generated during the experiments. Finally the sample was characterized by DSC to ensure that the solute maintained the crystalline form under all the experimental conditions. Based on error analysis and repeated observations, the estimated relative uncertainty of the solubility values was  $u_{\rm r}(x) = 0.02.$ 

The solubility of adipic acid in water was obtained by using experimental apparatus and illustrated in Fig. 3. Fig. 3 showed that the experimental data agreed well with the data in the literature<sup>28</sup>, thus the reliability of our experimental setup was verified.



Fig. 4. Experimental heat Q flow from DSC measurement of CPADE.

#### 3. Results and discussion

#### 3.1. Evaluation of pure component properties

From the results achieved by DSC and TGA analysis, as shown in Fig. 4 and Fig. 5, the melting point was 381.69 K  $\pm$  0.05 K; the enthalpy of fusion of CPADE was 27.57 kJ·mol<sup>-1</sup>. TGA results illustrate that there is one single step decomposition, and about 1% char residue for CPADE which shows that the CPADE should be used as intumescent flame retardant together with the char-forming agent. The entropy of fusion of CPADE  $\Delta_{fus}S$  was 72.24 J/(mol·K), which was calculated by Eq. (1).

$$\Delta_{fus}S = \frac{\Delta_{fus}H}{T_m}.$$
(1)

#### 3.2. Solubility data and correlation

The measured solubility data of CPADE in acetonitrile, methanol, acetone, tetrahydrofuran, chloroform, ethyl acetate, toluene, ethanol, benzene and dichloromethane are shown in Table 2. The mole-fraction solubility data of CPADE in the selected solvents are plotted in Fig. 6.



Fig. 5. TGA thermograms of CPADE under N<sub>2</sub>.

Table 2 (continued)

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# Table 2

Mole fraction solubilities (x) and activity coefficients ( $\gamma$ ) of CPADE in the selected solvents at temperature *T* and pressure p = 0.1 MPa.<sup>a</sup>

Methanol293.151.95184.110286.151.82035.328303.151.66067.017306.151.45669.553313.151.21216.10323.150.954542200323.150.8275135.56Acetone233.150.8275135.56308.151.20810.82730.315303.151.42697.965308.151.20810.827303.151.01322.90303.151.01322.90303.151.01322.90303.151.01322.90303.151.01322.90303.151.01322.90303.151.01322.90303.151.01322.90303.151.01322.90303.151.01322.90303.151.5743.76303.151.5743.76303.151.5743.76303.151.5743.76303.151.3752.623313.151.3752.623313.151.3752.623333.151.3762.623333.151.3762.623233.150.50795.666333.151.3743.649333.151.3743.649333.151.3743.649333.151.3813.649333.151.3813.649333.151.3813.649333.151.3813.649<	Solvent	T/K	γ	10 <sup>2</sup> x
28815         1.8203         5.33           30315         1.4566         7.017           31315         1.4566         7.017           31315         1.2122         16.10           32315         0.8354         28.09           328.15         0.95544         28.09           33315         0.87751         3556           0.83315         1.8259         4.394           293.15         1.8882         6.107           303.15         1.2369         33.35           308.15         1.2369         33.35           308.15         1.2369         33.35           308.15         0.3085         3.7544           303.15         4.060         2.201           328.15         0.98926         2.711           288.15         5.6787         1.708           303.15         4.0700         2.476           303.15         3.7544         3.706           303.15         1.6757         1.684           303.15         2.770         7.588           303.15         1.6752         2.689           313.15         0.5374         3.681           303.15         0.51964 <td< td=""><td>Methanol</td><td>293.15</td><td>1.9518</td><td>4.110</td></td<>	Methanol	293.15	1.9518	4.110
303.15         1.6606         7.017           308.15         1.4566         9.553           313.15         1.3676         12.08           318.15         1.2122         16.10           323.15         0.95454         28.09           Acetone         293.15         1.8259         4.34           298.15         1.5882         6.107           303.15         1.4629         7.965           308.15         1.2808         10.86           303.15         1.4629         7.965           308.15         1.2808         1.36           313.15         1.2808         1.36           313.15         1.2808         1.36           313.15         1.65757         1.708           303.15         4.7060         2.476           303.15         3.1731         5.208           313.15         3.1731         5.208           313.15         3.1731         5.208           313.15         1.6532         19.09           313.15         1.5754         2.683           313.15         5.5757         1.708           303.15         0.50761         16.84           293.15		298.15	1.8203	5.328
308.15         1.4566         9.553           313.15         1.2767         1.208           313.15         1.2122         16.10           323.15         0.95454         28.09           333.15         0.87751         35.56           323.15         1.8229         4.394           293.15         1.5882         6.107           303.15         1.6269         7.965           308.15         1.208         10.86           313.15         1.2399         13.36           303.15         0.80256         7.11           Acetonitrile         293.15         6.9513         1.154           293.15         5.6787         1.708           303.15         3.7544         3.706           303.15         3.754         3.706           313.15         3.754         3.706           313.15         3.754         3.754           313.15         1.6352         19.09           313.15         1.6352         19.09           313.15         1.6352         19.09           313.15         0.50780         22.90           313.15         0.50880         22.90           313.15		303.15	1.6606	7.017
313.15         1.2672         16.10           318.15         1.2162         16.10           328.15         0.95454         28.09           333.15         0.87751         3556           298.15         1.5882         6.107           303.15         1.4629         7.965           308.15         1.2369         1336           318.15         1.0438         1870           303.15         6.5513         1.154           298.15         5.6787         1.708           303.15         4.7060         2.476           298.15         5.6787         1.708           303.15         4.7060         2.476           303.15         4.7060         2.476           303.15         5.6787         1.708           303.15         5.6787         1.708           303.15         3.754         3.766           323.15         1.650         35.81           333.15         1.650         35.81           333.15         0.50460         19.22           303.15         0.51764         26.89           303.15         0.51764         3.80           313.15         0.5379         <		308.15	1.4566	9.553
Acetone         333.15         1.212         16.10           323.15         1.0838         2.1.16           323.15         0.8751         35.56           Acetone         293.15         1.8259         4.394           298.15         1.5882         6.107           303.15         1.4269         7.965           308.15         1.2308         10.86           313.15         1.0438         18.70           323.15         0.98926         27.11           Acetonitrile         293.15         6.9513         1.154           293.15         5.6787         1.708           303.15         3.7544         3706           313.15         3.1731         5.208           313.15         3.1731         5.208           313.15         1.6352         19.09           313.15         1.6352         19.09           313.15         1.6352         19.09           313.15         1.6352         19.09           313.15         1.6352         19.09           313.15         1.6352         19.09           313.15         1.6352         19.02           313.15         0.5415         3.724		313.15	1.3676	12.08
Acetone         328.15         0.95454         28.09           328.15         0.87751         35.56           293.15         1.8259         4.33           303.15         1.4629         7.965           303.15         1.2808         10.86           313.15         1.2369         13.36           318.15         1.0438         18.70           323.15         0.98926         27.11           Acetonitrile         293.15         6.5513         1.154           288.15         5.6787         1.708           308.15         3.7544         3.706           313.15         2.1602         10.62           323.15         1.8069         14.84           333.15         1.652         19.09           388.15         1.3736         26.32           333.15         1.650         35.81           1.650         33.815         1.650           333.15         0.50460         19.22           303.15         0.51754         26.89           313.15         0.52415         37.24           323.15         0.52419         50.39           313.15         0.52419         50.39      <		318.15	1.2122	16.10
Acetone         233.15         0.37751         355.55           Acetone         293.15         1.8259         4.394           298.15         1.5882         6.107           303.15         1.4629         7.965           308.15         1.2808         10.86           313.15         1.2808         10.86           313.15         1.2809         7.965           308.15         1.2808         10.86           313.15         1.2808         10.86           323.15         1.0013         22.90           303.15         4.7060         2.476           303.15         3.7544         3.766           313.15         3.7544         3.766           313.15         3.7544         3.766           323.15         1.6652         10.62           323.15         1.6652         10.62           333.15         0.57640         19.22           303.15         0.51754         26.89           333.15         0.51754         26.89           333.15         0.51754         26.89           333.15         0.51754         26.89           333.15         0.51754         26.89 <t< td=""><td></td><td>323.15</td><td>1.0838</td><td>21.16</td></t<>		323.15	1.0838	21.16
Acetone         233.15         1.8259         4.334           283.15         1.8259         4.334           283.15         1.5882         6.107           303.15         1.4629         7.965           308.15         1.2808         10.86           313.15         1.0013         22.90           323.15         0.989266         27.11           Acetonitrile         293.15         6.9513         1.154           298.15         5.6787         1.708           303.15         4.7060         2.476           303.15         3.7544         3.706           318.15         2.5720         7.588           323.15         1.8069         14.84           333.15         1.6352         19.09           338.15         1.3736         26.32           333.15         0.50460         12.22           303.15         0.50460         2.220           303.15         0.51964         31.80           232.15         0.5341         16.84           233.15         0.53219         50.39           313.15         0.51964         31.80           313.15         0.5415         37.24		320.15	0.95454	26.09
298.15         1.5882         6.107           303.15         1.4629         7.965           308.15         1.2808         10.86           313.15         1.2369         13.36           313.15         1.0438         18.70           323.15         1.0013         229.00           328.15         0.58926         27.11           Acetonitrile         293.15         5.6513         1.154           281.5         5.6787         1.708           308.15         3.7544         3.706           303.15         4.7060         2.476           303.15         1.6352         10.62           328.15         1.6352         10.62           328.15         1.6352         10.62           328.15         1.650         3581           Tetrahydrofuran         293.15         0.47651         16.84           298.15         0.50460         12.22           303.15         0.51754         26.89           313.15         0.52415         37.24           323.15         0.55079         56.66           293.15         0.26308         3.049           328.15         0.55079         56.66     <	Acetone	293.15	1 8259	4 394
303.15         1.4629         7.965           308.15         1.2808         10.86           313.15         1.2369         13.36           318.15         1.0438         18.70           328.15         0.98926         27.11           235         5.6787         1.708           303.15         4.7060         2.476           303.15         4.7060         2.476           303.15         3.7544         3.706           313.15         3.1731         5.208           313.15         2.1602         10.62           328.15         2.1602         10.62           333.15         1.135         2.1602           333.15         1.1650         35.81           333.15         1.1650         35.81           233.15         0.50460         19.22           303.15         0.51754         26.89           313.15         0.51754         26.89           313.15         0.51754         26.89           313.15         0.51754         34.80           323.15         0.53219         50.39           333.15         0.5479         34.946           333.15         0.5479	Theorem .	298.15	1.5882	6.107
308.15         1.2808         10.86           313.15         1.2369         13.36           318.15         1.0438         18.70           223.15         0.98926         27.11           228.15         5.6787         1.708           308.15         3.7060         2.476           308.15         3.7544         3.706           313.15         3.7541         3.706           313.15         2.710         6.623           313.15         2.1602         10.62           328.15         1.6352         19.09           333.15         1.6553         3.81           333.15         1.650         3.581           283.15         0.50460         19.22           303.15         0.50480         2.290           308.15         0.51754         26.89           313.15         0.52415         37.24           328.15         0.53219         50.30           303.15         2.1216         5.44579           303.15         1.2394         7.212           313.15         0.53219         50.66           283.15         0.53219         50.66           283.15         1.24579		303.15	1.4629	7.965
313.15         1.2369         13.36           313.15         1.0438         18.70           323.15         1.0013         22.90           323.15         0.98926         27.11           298.15         5.6787         1.708           303.15         4.7060         2.476           308.15         3.7544         3.7064           313.15         3.1731         5.208           313.15         3.1731         5.208           323.15         1.6052         10.62           323.15         1.6052         10.62           333.15         1.6352         19.09           338.15         1.3736         26.32           333.15         0.50460         19.22           303.15         0.51754         26.89           313.15         0.51754         26.89           313.15         0.51754         26.89           313.15         0.55079         56.66           Ethyl acetate         293.15         0.5415         37.24           293.15         0.52179         34.66         30.815           293.15         0.52415         37.24         34.315           293.15         0.55079		308.15	1.2808	10.86
318.15         1.0438         18.70           323.15         1.0013         22.90           Acetonitrile         293.15         6.9513         1.154           298.15         5.6787         1.708           303.15         4.7060         2.476           303.15         3.7544         3.702           313.15         3.1731         5.208           313.15         2.1602         10.62           328.15         1.8069         14.84           333.15         1.6352         19.09           338.15         1.3736         26.32           343.15         1.1650         35.81           7etrahydrofuran         293.15         0.47651         16.84           293.15         0.50460         19.22         303.15         0.51754         26.89           313.15         0.51754         26.89         30.49         31.315         37.24           323.15         0.52415         37.24         323.15         0.5307         56.66           Ethyl acetate         298.15         2.4579         3.946         30.315         2.1216         5.492           333.15         1.5249         1.280         33.45         1.023		313.15	1.2369	13.36
323,15         1.0013         22.90           328,15         0.98926         27.11           Acetonitrile         293,15         6.9513         1.154           298,15         5.6787         1.708           303,15         4.7060         2.476           303,15         3.7544         3.706           318,15         2.5720         7.588           323,15         1.6052         10.62           328,15         1.8069         14.84           333,15         1.6352         19.09           338,15         1.3736         26.32           343,15         1.650         35.81           1.650         35.81         1.909           338,15         0.50460         19.22           303,15         0.51754         26.89           313,15         0.50460         19.22           303,15         0.51754         26.89           313,15         0.52415         37.24           323,15         0.52415         37.24           323,15         0.52419         50.39           333,15         0.52419         50.39           333,15         0.52419         50.39           333,15		318.15	1.0438	18.70
328.15         0.9992b         27.11           Acetonitrile         298.15         5.6787         1.708           308.15         3.7544         3.706         2.476           308.15         3.7544         3.706         2.476           313.15         3.1731         5.208         313.15         3.1731         5.208           313.15         3.1731         5.208         313.15         1.652         10.68           323.15         1.1609         14.84         333.15         1.6552         19.09           338.15         1.3736         2.63.2         343.15         1.1650         5.81           298.15         0.50460         19.22         303.15         0.51754         2.68.9           313.15         0.51754         2.68.9         313.15         0.51754         2.68.9           313.15         0.51754         2.68.9         313.15         0.51764         4.18.9           328.15         0.53219         5.039         333.15         0.53219         5.039           298.15         2.4579         3.946         303.15         1.24579         3.946           323.15         1.3814         1.660         328.15         1.2710         2.110		323.15	1.0013	22.90
Accountine 295.15 0.5913 1.134 298.15 5.6787 1.708 303.15 4.7060 2.476 308.15 3.7544 3.706 313.15 3.1731 5.208 318.15 2.5720 7.588 323.15 1.8069 14.84 333.15 1.6352 19.09 338.15 1.3736 26.32 343.15 1.1650 35.81 Tetrahydrofuran 293.15 0.47651 16.84 298.15 0.50460 19.22 303.15 0.50880 22.90 308.15 0.51754 26.89 313.15 0.51964 31.80 338.15 0.52415 37.24 323.15 0.504749 41.89 328.15 0.53219 50.39 333.15 0.55079 56.66 Ethyl acetate 293.15 2.6308 3.049 298.15 2.4579 3.946 303.15 1.9294 7.212 313.15 1.7473 9.457 318.15 1.5249 12.80 323.15 0.47651 1.642 308.15 1.9294 7.212 313.15 1.7473 9.457 318.15 1.5249 12.80 323.15 0.48890 3.2457 333.15 0.48890 3.2457 333.15 0.48890 3.2457 333.15 0.48890 3.2457 333.15 0.48873 26.56 Chloroform 293.15 0.43873 26.56 298.15 0.44199 31.27 313.15 0.44899 31.27 313.15 0.44890 3.524 303.15 0.43873 26.56 308.15 0.44499 31.27 313.15 0.44899 31.27 313.15 0.4589 3.24 303.15 0.43873 26.56 303.15 0.44899 31.27 313.15 0.43873 26.56 303.15 0.44499 31.27 313.15 0.48890 3.524 303.15 0.43873 26.56 303.15 0.44499 31.27 313.15 0.48890 3.524 303.15 0.43873 26.56 303.15 0.44499 31.27 313.15 0.48890 3.524 303.15 0.4585 3.585 Ethanol 298.15 0.5011 4.585 328.15 0.5011 4.585 328.15 0.5011 4.585 328.15 0.5011 4.585 328.15 0.9811 4.585 338.15 0.9811 4.585 338.15 0.9811 4.585 338.15 0.9811 4.585 338.15 0.9811 4.585 338.15 0.98490 1.5015 338.15 0.98490 1.5015 338.15 0.98490 1.5015 338.15 0.98490 1.5015 338.15 0.98490 1.5015 338.15 0.98490 333.15 0.98490 333.15 0.98490 333.15 0.98490 333.15 0.98490	Acotonitrilo	328.15	0.98926	27.11
203.15         2.0705         1.705           303.15         3.7544         3.706           313.15         3.1731         5.208           313.15         3.1731         5.208           313.15         3.1731         5.208           313.15         2.1602         10.62           323.15         2.1602         10.62           323.15         1.0535         19.09           333.15         1.3736         2632           333.15         1.6535         19.09           333.15         1.650         35.81           333.15         0.50460         19.22           303.15         0.50460         19.22           303.15         0.504751         16.84           298.15         0.50460         19.22           303.15         0.51754         26.89           313.15         0.51664         31.80           318.15         0.52415         37.24           323.15         0.53219         50.39           333.15         0.55079         56.66           293.15         2.4579         3.946           303.15         1.2457         3.049           303.15         1.2457	AcetoIIItIIIe	293.15	5 6787	1.134
308.15         3.7544         3.706           313.15         3.1731         5.200           318.15         2.5720         7.588           323.15         1.8069         14.84           333.15         1.6352         19.09           338.15         1.3736         26.32           343.15         1.1650         35.81           1.815         0.50460         19.22           303.15         0.50460         19.22           303.15         0.50460         19.22           303.15         0.50460         19.22           303.15         0.50460         19.22           303.15         0.51754         26.89           313.15         0.54749         41.89           328.15         0.53719         50.39           328.15         0.53719         50.39           328.15         1.5249         12.80           333.15         1.5249         12.80           333.15         1.5249         12.80           333.15         1.3814         16.60           328.15         1.2710         21.10           333.15         1.3814         16.60           328.15         0.38010 <td></td> <td>303.15</td> <td>4,7060</td> <td>2.476</td>		303.15	4,7060	2.476
313.15         3.1731         5.208           313.15         2.5720         7.588           323.15         2.1602         10.62           328.15         1.8069         14.84           333.15         1.6352         19.09           343.15         1.3736         26.32           343.15         1.1650         35.81           7etrahydrofuran         293.15         0.47651         16.84           298.15         0.50460         19.22           303.15         0.51754         26.89           313.15         0.51754         26.89           313.15         0.51754         26.89           313.15         0.52415         37.24           323.15         0.53219         50.39           333.15         0.54749         41.89           323.15         0.54749         41.89           333.15         0.52415         37.24           303.15         1.26308         3.049           298.15         2.4579         3.946           293.15         2.4579         3.946           323.15         1.9294         7.212           313.15         1.4547         26.35 <td< td=""><td></td><td>308.15</td><td>3.7544</td><td>3.706</td></td<>		308.15	3.7544	3.706
318.15         2.5720         7.588           323.15         2.1602         10.62           328.15         1.8069         1.434           333.15         1.6352         19.09           338.15         1.3736         26.32           433.15         1.1650         35.81           Tetrahydrofuran         293.15         0.47651         16.84           203.15         0.50460         19.22           303.15         0.51754         26.89           313.15         0.51754         26.89           313.15         0.52415         37.24           323.15         0.55079         56.66           293.15         2.6308         3.049           308.15         1.9294         7.212           313.15         1.5249         12.80           308.15         1.9294         7.212           313.15         1.5249         12.80           323.15         1.3814         16.60           323.15         1.3814         16.60           323.15         1.3814         16.60           323.15         1.3814         16.60           323.15         0.38015         0.4548         23.34		313.15	3.1731	5.208
323.15         2.1602         10.62           328.15         1.8069         14.84           333.15         1.6352         19.09           338.15         1.3736         26.32           343.15         1.1650         35.81           1.993.15         0.47651         16.84           298.15         0.50460         19.22           303.15         0.51754         26.89           313.15         0.51764         31.80           313.15         0.52415         37.24           323.15         0.53219         50.39           328.15         0.53219         50.39           328.15         0.52415         3.744           323.15         0.55079         56.66           298.15         2.4579         3.946           303.15         1.1216         5.492           303.15         1.2216         5.492           303.15         1.249         12.80           323.15         1.3814         16.60           303.15         1.2710         21.10           333.15         1.182         2.635           338.15         0.38795         20.68           233.15         0.38795 </td <td></td> <td>318.15</td> <td>2.5720</td> <td>7.588</td>		318.15	2.5720	7.588
328.15         1.8069         14.84           333.15         1.6352         19.09           343.15         1.13736         26.32           343.15         1.1650         35.81           Tetrahydrofuran         293.15         0.47651         16.84           298.15         0.50460         19.22           308.15         0.51754         26.89           313.15         0.52415         37.24           323.15         0.54749         41.89           323.15         0.55779         56.66           Ethyl acetate         293.15         2.6308         3.049           298.15         2.4579         3.946           303.15         1.1294         7.212           313.15         1.5249         7.212           313.15         1.7473         9.457           318.15         1.5249         7.212           313.15         1.814         16.60           323.15         1.3814         16.60           323.15         1.3814         16.60           323.15         0.38795         20.68           293.15         0.4473         26.56           308.15         0.44899         31.27		323.15	2.1602	10.62
333.15         1.6352         19.09           338.15         1.3736         26.32           343.15         1.1650         35.81           293.15         0.47651         16.84           298.15         0.50460         19.22           303.15         0.51754         26.89           313.15         0.51964         31.80           318.15         0.52415         37.24           322.15         0.54749         41.89           328.15         0.53219         50.39           333.15         0.55079         56.64           293.15         2.4579         3.946           303.15         1.2924         7.212           313.15         1.7473         9.457           313.15         1.7473         9.457           313.15         1.7473         9.457           313.15         1.7473         9.457           313.15         1.7473         9.457           313.15         1.7473         9.457           313.15         1.7473         9.457           323.15         0.38795         20.68           232.15         0.5079         56.66           24449         3.2315		328.15	1.8069	14.84
338.15         1.3736         20.32           343.15         1.1650         35.81           Tetrahydrofuran         293.15         0.47651         16.84           298.15         0.50460         19.22           303.15         0.50880         22.90           308.15         0.51754         26.89           313.15         0.51964         31.80           318.15         0.52415         37.24           323.15         0.53219         50.39           328.15         0.53219         50.39           333.15         0.55079         56.66           Ethyl acetate         293.15         2.4579         3.946           303.15         1.1216         5.492           303.15         1.1224         7.212           313.15         1.7473         9.457           318.15         1.5249         12.80           323.15         1.3814         16.60           328.15         1.0599         34.11           333.15         1.3814         16.60           328.15         0.41548         23.34           303.15         0.4877         40.05           293.15         0.41548         2.34		333.15	1.6352	19.09
343.13         1.1030         5.34           Tetrahydrofuran         293.15         0.47651         16.84           298.15         0.50460         19.22           303.15         0.50880         22.90           308.15         0.51754         26.89           313.15         0.52415         37.24           323.15         0.54749         41.89           328.15         0.53219         50.39           333.15         0.55079         56.66           Ethyl acetate         293.15         2.4579         3.946           303.15         2.1216         5.492           303.15         1.2924         7.212           313.15         1.7473         9.457           318.15         1.5249         12.80           323.15         1.3814         16.60           323.15         1.3814         16.60           323.15         1.710         21.10           333.15         0.48901         42.56           Chloroform         293.15         0.38795         20.68           298.15         0.41548         23.4           303.15         0.43873         26.56           308.15         0.46890<		338.15	1.3/36	26.32
Iterative         253.15         0.47051         10.24           303.15         0.50460         19.22           303.15         0.50880         22.90           308.15         0.51754         26.89           313.15         0.51964         31.80           313.15         0.52415         37.24           323.15         0.54749         41.89           323.15         0.55079         56.66           Ethyl acetate         293.15         2.6308         3.049           298.15         2.4579         3.946           303.15         1.9294         7.212           313.15         1.7473         9.457           318.15         1.5249         12.80           323.15         1.3814         16.60           323.15         1.3814         16.60           323.15         1.7473         9.457           318.15         0.98010         42.56           Chloroform         293.15         0.38795         20.68           298.15         0.41548         23.34           303.15         0.44899         31.27           313.15         0.46890         32.24           303.15         0.46890 <td>Tetrahydrofuran</td> <td>293.15</td> <td>0.47651</td> <td>16.84</td>	Tetrahydrofuran	293.15	0.47651	16.84
303.15         0.50880         22.90           308.15         0.51754         26.89           313.15         0.51754         26.89           313.15         0.52415         37.24           323.15         0.54749         41.89           328.15         0.53219         50.39           333.15         0.55079         56.66           293.15         2.6308         3.049           308.15         1.9294         7.212           303.15         2.1216         5.492           303.15         1.9294         7.212           313.15         1.7473         9.457           313.15         1.7473         9.457           313.15         1.7473         9.457           313.15         1.7473         9.457           313.15         1.7473         9.457           313.15         1.710         21.10           333.15         1.1842         26.35           338.15         1.0599         34.11           333.15         0.41548         23.34           303.15         0.48727         40.05           323.15         0.50015         45.85           328.15         0.50015 <td>retranytrortitan</td> <td>298.15</td> <td>0.50460</td> <td>19.22</td>	retranytrortitan	298.15	0.50460	19.22
308.15         0.51754         26.89           313.15         0.51964         31.80           318.15         0.52415         37.24           323.15         0.55079         56.66           293.15         2.6308         3.049           298.15         2.4579         3.949           298.15         2.4579         3.9457           303.15         2.1216         5.492           308.15         1.9294         7.212           313.15         1.5249         12.80           323.15         1.3814         16.60           328.15         1.2710         21.10           333.15         1.1842         26.35           338.15         1.0599         34.11           343.15         0.98010         42.56           Chloroform         293.15         0.38795         20.68           298.15         0.41548         23.34           303.15         0.48890         35.24           318.15         0.50715         58.85           323.15         0.50715         58.85           323.15         0.50715         58.85           323.15         0.50715         58.85           32		303.15	0.50880	22.90
313.15         0.51964         31.80           318.15         0.52415         37.24           323.15         0.55749         41.89           328.15         0.553219         50.39           333.15         0.55079         56.66           293.15         2.6308         3.049           298.15         2.4579         3.946           303.15         1.9294         7.212           313.15         1.7473         9.457           318.15         1.5249         12.80           323.15         1.3814         16.60           323.15         1.3814         16.60           323.15         1.3814         16.60           323.15         1.3814         16.60           323.15         1.3814         16.60           323.15         0.98010         42.56           333.15         0.98010         42.56           Chloroform         293.15         0.48737         26.56           308.15         0.48890         35.24           303.15         0.48890         35.24           303.15         0.48890         35.24           303.15         0.868         6378           308.1		308.15	0.51754	26.89
318.15         0.52415         37.24           323.15         0.54749         41.89           328.15         0.53219         50.39           333.15         0.55079         56.66           Ethyl acetate         293.15         2.6308         3.049           298.15         2.4579         3.946           303.15         2.1216         5.492           318.15         1.7473         9.457           318.15         1.5249         12.80           323.15         1.3814         16.60           328.15         1.2710         21.10           333.15         1.8812         26.35           338.15         1.0599         34.11           343.15         0.98010         42.56           Chloroform         293.15         0.38795         20.68           298.15         0.41548         23.34           303.15         0.48873         26.56           308.15         0.44499         31.27           313.15         0.448727         40.05           323.15         0.51719         51.85           298.15         0.51719         51.85           298.15         1.6053         8.669		313.15	0.51964	31.80
323.15         0.54749         41.89           328.15         0.53219         50.39           333.15         0.55079         56.66           293.15         2.6308         3.049           298.15         2.4579         3.946           303.15         2.1216         5.492           308.15         1.9294         7.212           313.15         1.7473         9.457           318.15         1.5249         12.80           323.15         1.3814         16.60           328.15         1.2710         21.10           333.15         1.1842         26.35           338.15         1.0599         34.11           343.15         0.98010         42.56           Chloroform         293.15         0.38795         20.68           298.15         0.41548         23.34           303.15         0.43873         26.56           308.15         0.44499         31.27           313.15         0.43873         26.56           308.15         0.50715         45.85           328.15         0.50719         51.85           328.15         0.50719         51.85           303		318.15	0.52415	37.24
328.15         0.53219         50.39           333.15         0.55079         56.66           293.15         2.6308         3.049           288.15         2.4579         3.946           303.15         2.1216         5.492           308.15         1.9294         7.212           313.15         1.7473         9.457           318.15         1.5249         12.80           323.15         1.3814         16.60           328.15         1.2710         21.10           333.15         1.842         26.35           338.15         1.0599         34.11           343.15         0.98010         42.56           308.15         0.41548         23.34           303.15         0.43873         26.56           308.15         0.44499         31.27           313.15         0.48800         35.24           313.15         0.48803         35.24           313.15         0.48803         35.24           313.15         0.48803         35.24           313.15         0.48803         35.24           303.15         0.5015         45.85           328.15         0.501719<		323.15	0.54749	41.89
333.15         0.50/9         56.66           293.15         2.6308         3.049           298.15         2.4579         3.946           303.15         2.1216         5.492           308.15         1.9294         7.212           313.15         1.7473         9.457           318.15         1.5249         12.80           323.15         1.3814         16.60           228.15         1.2710         21.10           333.15         1.1842         26.35           338.15         1.0599         34.11           343.15         0.98010         42.56           293.15         0.38795         20.68           293.15         0.41548         23.34           303.15         0.48737         26.56           308.15         0.44499         31.27           313.15         0.46890         35.24           303.15         0.50719         51.85           293.15         0.50015         45.85           303.15         1.8063         6.378           303.15         1.8268         6.378           303.15         1.8268         6.378           303.15         1.8268		328.15	0.53219	50.39
Linyr acture         253,15         2,4579         3,946           298,15         2,4579         3,946           303,15         2,1216         5,492           308,15         1,9294         7,212           313,15         1,7473         9,457           318,15         1,5249         12,80           323,15         1,3814         16,60           328,15         1,2710         21,10           333,15         1,1842         26,35           338,15         1,0599         34,11           343,15         0,98010         42,56           293,15         0,41548         23,34           303,15         0,43873         26,56           308,15         0,44499         31,27           313,15         0,46890         35,24           313,15         0,46890         35,24           313,15         0,50015         45,85           323,15         0,50015         45,85           323,15         0,50015         45,85           303,15         1,8268         6,378           303,15         1,8202         4,898           303,15         1,8202         4,898           303,	Ethyl acetate	333.15 293.15	2 6308	3 049
addits         addits         addits           303.15         2.1216         5.492           308.15         1.9294         7.212           313.15         1.7473         9.457           318.15         1.5249         12.80           323.15         1.3814         16.60           328.15         1.2710         21.10           333.15         1.1842         26.35           338.15         1.0599         34.11           343.15         0.98010         42.56           298.15         0.41548         23.34           303.15         0.43873         26.56           308.15         0.44499         31.27           313.15         0.46890         35.24           318.15         0.48727         40.05           323.15         0.50015         45.85           328.15         0.51719         51.85           Ethanol         293.15         2.2387         3.585           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         0.2387         3.585           328.15         1.0600         25.30           333.15 <td>Luiyi acciate</td> <td>298.15</td> <td>2.0508</td> <td>3 946</td>	Luiyi acciate	298.15	2.0508	3 946
308.15         1.9294         7.212           313.15         1.7473         9.457           318.15         1.5249         12.80           323.15         1.3814         16.60           328.15         1.2710         21.10           333.15         1.1842         26.35           338.15         1.0599         34.11           343.15         0.98010         42.56           298.15         0.41548         23.34           303.15         0.43873         26.56           308.15         0.43873         26.56           308.15         0.44499         31.27           313.15         0.46890         35.24           313.15         0.46890         35.24           313.15         0.48727         40.05           323.15         0.51719         51.85           Ethanol         293.15         2.2387         3.585           303.15         1.8208         6.378           303.15         1.8208         6.378           303.15         1.6053         8.669           313.15         1.4303         11.55           318.15         0.298.15         0.600         25.30      <		303.15	2.1216	5.492
313.15         1.7473         9.457           318.15         1.5249         12.80           323.15         1.3814         16.60           328.15         1.2710         21.10           333.15         1.1842         26.35           338.15         1.0599         34.11           343.15         0.98010         42.56           Chloroform         293.15         0.38795         20.68           298.15         0.41548         23.34           303.15         0.43873         26.56           308.15         0.44499         31.27           313.15         0.44890         35.24           303.15         0.48727         40.05           323.15         0.5015         45.85           328.15         0.51719         51.85           Ethanol         293.15         1.2387         3.585           313.15         1.4303         11.55           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         0.8911         40.58           323.15         0.9856         31.67           338.15         0.8911         40.58		308.15	1.9294	7.212
318.15         1.5249         12.80           323.15         1.3814         16.60           328.15         1.2710         21.10           333.15         1.1842         26.35           338.15         1.0599         34.11           343.15         0.98010         42.56           Chloroform         293.15         0.38795         20.68           298.15         0.41548         23.34           303.15         0.43873         26.56           308.15         0.43873         26.56           308.15         0.44499         31.27           313.15         0.48800         35.24           318.15         0.48727         40.05           323.15         0.50015         45.85           328.15         0.51719         51.85           Ethanol         293.15         1.2387         3.585           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         0.9856         31.67           333.15         0.9856         31.67           333.15         0.9856         31.67		313.15	1.7473	9.457
323.15         1.3814         16.60           328.15         1.2710         21.10           333.15         1.1842         26.35           338.15         1.0599         34.11           343.15         0.98010         42.56           Chloroform         293.15         0.38795         20.68           298.15         0.41548         23.34           303.15         0.43873         26.56           308.15         0.44899         31.27           313.15         0.46890         35.24           313.15         0.46890         35.24           318.15         0.4727         40.05           323.15         0.5015         45.85           328.15         0.51719         51.85           293.15         1.8062         4.898           303.15         1.8268         6.378           303.15         1.8268         6.378           303.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         0.9856         31.67           338.15         0.97824         9.915           303.15		318.15	1.5249	12.80
328.15         1.2710         21.10           333.15         1.1842         26.35           338.15         1.0599         34.11           343.15         0.98010         42.56           Chloroform         293.15         0.38795         20.68           298.15         0.41548         23.34           303.15         0.43873         26.56           308.15         0.443873         26.56           308.15         0.44899         31.27           313.15         0.46890         35.24           318.15         0.48727         40.05           323.15         0.50015         45.85           328.15         0.51719         51.85           Ethanol         293.15         1.2387         3.585           298.15         1.9802         4.898           303.15         1.8268         6.378           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         0.600         25.30           333.15         0.8911         40.58           Benzene         293.15         1.0420         <		323.15	1.3814	16.60
333.15         1.1642         20.33           338.15         1.0599         34.11           343.15         0.98010         42.56           Chloroform         293.15         0.38795         20.68           298.15         0.41548         23.34           303.15         0.43873         26.56           308.15         0.44899         31.27           313.15         0.46820         35.24           318.15         0.46827         40.05           323.15         0.50015         45.85           328.15         0.51719         51.85           293.15         2.2387         3.585           293.15         1.8062         4.898           303.15         1.8268         6.378           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         0.8911         40.58           323.15         0.9856         31.67           338.15         0.8911         40.58           303.15         0.97824         9.915           303.15         0.97824         9.915           303.		328.15	1.2710	21.10
Jobsits         Jossits         Jossits <t< td=""><td></td><td>338.15</td><td>1,1842</td><td>20.33</td></t<>		338.15	1,1842	20.33
Chloroform         293.15         0.38795         20.68           298.15         0.41548         23.34           303.15         0.43873         26.56           308.15         0.44499         31.27           313.15         0.46890         35.24           318.15         0.48727         40.05           323.15         0.50015         45.85           328.15         0.51719         51.85           293.15         2.2387         3.585           298.15         1.9802         4.898           303.15         1.8268         6.378           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         0.6000         25.30           333.15         0.8956         31.67           338.15         0.8911         40.58           Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915           303.15         0.92121         12.65           308.15         0.87495         15.90           313.15         0.87495         15.90		343.15	0.98010	42.56
298.15         0.41548         23.34           303.15         0.43873         26.56           308.15         0.44499         31.27           313.15         0.46890         35.24           318.15         0.48727         40.05           323.15         0.50015         45.85           328.15         0.51719         51.85           293.15         2.2387         3.585           298.15         1.9802         4.898           303.15         1.8268         6.378           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         0.6000         25.30           333.15         0.8911         40.58           381.5         0.8911         40.58           Benzene         293.15         0.97824         9.915           303.15         0.92121         12.65           308.15         0.87495         15.90           313.15         0.87495         15.90           315         0.97824         9.915           303.15         0.92121         12.65           303.15 <td>Chloroform</td> <td>293.15</td> <td>0.38795</td> <td>20.68</td>	Chloroform	293.15	0.38795	20.68
303.15         0.43873         26.56           308.15         0.44499         31.27           313.15         0.46890         35.24           318.15         0.48727         40.05           323.15         0.50015         45.85           328.15         0.51719         51.85           293.15         2.2387         3.585           298.15         1.9802         4.898           303.15         1.8268         6.378           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         0.6000         25.30           333.15         0.9856         31.67           338.15         0.8911         40.58           Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915         303.15         0.92121         12.65           308.15         0.87495         15.90         313.15         0.87495         15.90           313.15         0.87495         15.90         313.15         0.7844         9.915		298.15	0.41548	23.34
308.15         0.44499         31.27           313.15         0.46890         35.24           318.15         0.48727         40.05           323.15         0.50015         45.85           328.15         0.51719         51.85           293.15         2.2387         3.585           298.15         1.9802         4.898           303.15         1.8268         6.378           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         1.1678         19.64           328.15         0.8911         40.58           Benzene         293.15         0.4200         7.699           298.15         0.97824         9.915           303.15         0.92121         12.65           308.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           315         0.97824         9.915           303.15         0.87495         15.90           315		303.15	0.43873	26.56
313.15         0.46890         35.24           318.15         0.48727         40.05           323.15         0.50015         45.85           328.15         0.51719         51.85           293.15         2.2387         3.585           298.15         1.9802         4.898           303.15         1.8268         6.378           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         1.1678         19.64           328.15         0.9856         31.67           333.15         0.8911         40.58           Benzene         293.15         0.97824         9.915           303.15         0.97824         9.915         303.15         0.87495         15.90           313.15         0.87495         15.90         313.15         0.87495         15.90		308.15	0.44499	31.27
318.15         0.48/27         40.05           323.15         0.50015         45.85           328.15         0.51719         51.85           293.15         2.2387         3.585           298.15         1.9802         4.898           303.15         1.8268         6.378           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         1.1678         19.64           328.15         1.0600         25.30           333.15         0.9856         31.67           38.15         0.8911         40.58           Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915         303.15         0.87495         15.90           303.15         0.87495         15.90         313.15         0.87495         15.90           315         0.87495         15.90         313.15         0.87495         15.90		313.15	0.46890	35.24
328.15         0.50015         43.83           328.15         0.51719         51.85           293.15         2.2387         3.585           298.15         1.9802         4.898           303.15         1.8268         6.378           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         1.1678         19.64           328.15         0.9856         31.67           338.15         0.8911         40.58           Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915           303.15         0.87495         15.90           313.15         0.87495         15.90           315         0.78048         25.01		318.15	0.48727	40.05
Ethanol 293.15 2.2387 3.585 298.15 1.9802 4.898 303.15 1.8268 6.378 308.15 1.6053 8.669 313.15 1.4303 11.55 318.15 1.2748 15.31 323.15 1.1678 19.64 328.15 1.0600 25.30 333.15 0.9856 31.67 338.15 0.8911 40.58 Benzene 293.15 1.0420 7.699 298.15 0.97824 9.915 303.15 0.97824 9.915 303.15 0.87495 15.90 313.15 0.84909 19.46		328.15	0.50015	51.85
298.15         1.9802         4.898           303.15         1.8268         6.378           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         1.1678         19.64           328.15         1.0600         25.30           333.15         0.9856         31.67           338.15         0.8911         40.58           Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915           303.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.78048         25.01	Ethanol	293.15	2.2387	3.585
303.15         1.8268         6.378           308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         1.1678         19.64           328.15         1.0600         25.30           333.15         0.9856         31.67           338.15         0.8911         40.58           Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915           303.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.78048         25.01		298.15	1.9802	4.898
308.15         1.6053         8.669           313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         1.1678         19.64           328.15         1.0600         25.30           333.15         0.9856         31.67           338.15         0.8911         40.58           Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915           303.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.78048         25.01		303.15	1.8268	6.378
313.15         1.4303         11.55           318.15         1.2748         15.31           323.15         1.1678         19.64           328.15         1.0600         25.30           333.15         0.9856         31.67           338.15         0.89511         40.58           Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915           303.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.87495         15.90           313.15         0.78048         25.01		308.15	1.6053	8.669
318.15         1.2/48         15.31           323.15         1.1678         19.64           328.15         1.0600         25.30           333.15         0.9856         31.67           338.15         0.8951         40.58           Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915           303.15         0.82121         12.65           308.15         0.87495         15.90           313.15         0.87495         15.90           318.15         0.78048         25.01		313.15	1.4303	11.55
323.13         1.1078         19.04           328.15         1.0600         25.30           333.15         0.9856         31.67           338.15         0.88911         40.58           Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915           303.15         0.82121         12.65           308.15         0.87495         15.90           313.15         0.84909         19.46           318.15         0.78048         25.01		318.15	1.2748	15.31
333.15         0.9856         31.67           333.15         0.9856         31.67           338.15         0.8911         40.58           Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915           303.15         0.92121         12.65           308.15         0.87495         15.90           313.15         0.884909         19.46           318.15         0.78048         25.01		323.13	1.1076	19.04 25.30
338.15         0.8911         40.58           Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915           303.15         0.92121         12.65           308.15         0.84909         19.46           318.15         0.78048         25.01		333.15	0.9856	31.67
Benzene         293.15         1.0420         7.699           298.15         0.97824         9.915           303.15         0.92121         12.65           308.15         0.87495         15.90           313.15         0.87499         19.46           318.15         0.78048         25.01		338.15	0.8911	40.58
298.15         0.97824         9.915           303.15         0.92121         12.65           308.15         0.87495         15.90           313.15         0.84909         19.46           318.15         0.78048         25.01	Benzene	293.15	1.0420	7.699
303.15         0.92121         12.65           308.15         0.87495         15.90           313.15         0.84909         19.46           318.15         0.78048         25.01		298.15	0.97824	9.915
308.15         0.87495         15.90           313.15         0.84909         19.46           318.15         0.78048         25.01		303.15	0.92121	12.65
313.15 0.84909 19.46 318.15 0.78048 25.01		308.15	0.87495	15.90
51815 11/81/48 /5(1)		313.15	0.84909	19.46
323 15 0.78423 23.01		218.12 272.15	0.78048	25.01 29.24
328.15 0.71749 37.37		328 15	0.71749	37 37
333.15 0.68310 45.69		333.15	0.68310	45.69

Solvent	T/K	γ	$10^{2}x$
	338.15	0.65709	55.03
	343.15	0.65599	63.59
Toluene	293.15	1.4871	5.395
	298.15	1.4091	6.883
	303.15	1.2787	9.112
	313.15	1.0708	15.43
	323.15	0.88656	25.87
	333.15	0.76373	40.86
	343.15	0.68232	61.13
Dichloromethane	278.15	0.49305	8.840
	283.15	0.52642	10.22
	288.15	0.51063	12.91
	293.15	0.51669	15.53
	298.15	0.53811	18.02
	303.15	0.54057	21.56
	308.15	0.53439	26.04

<sup>a</sup> The standard uncertainties u is u(x) = 0.0002.

For each solvent researched, the solubility of CPADE increases as the temperature rises, but the systems behave differently. At a given temperature, the order of solubility of CPADE is as follows: chloroform > tetrahydrofuran > dichloromethane > benzene > toluene > acetone > methanol > ethanol > ethyl acetate > acetonitrile. The solubility of CPADE in acetonitrile shows the lowest value, and in chloroform gives the highest value. The higher solubility value in chloroform and dichloromethane than other solvents but tetrahydrofuran might be owing to the strong electronegativity of elemental chlorine. As there coexist both NH group and P=O group in CPADE, it can be the proton donor or acceptor. The fact that the solubility value in tetrahydrofuran is higher than that in the alcohols shows the property of the proton donor of NH group in CPADE. Accordingly, it might be the hydrogen bond between tetrahydrofuran and CPADE molecules that play an important role in contributing to the higher solubility of CPADE in tetrahydrofuran in the ten solvents. From the solubility data, tetrahydrofuran, chloroform and dichloromethane appear to be more appropriate solvents for the crystallization of CPADE. The three solvents are also suggested as the appropriate reaction solvents.

From the thermodynamic principles, solid–liquid phase equilibrium can be described as follows [29]:

$$\ln\frac{1}{x_1\gamma_1} = \frac{\Delta_{fus}H}{RT_m} \left(\frac{T_m}{T} - 1\right) + \frac{\Delta_{tr}H}{RT_{tr}} \left(\frac{T_{tr}}{T} - 1\right) - \frac{\Delta C_p}{R} \left(\ln\frac{T}{T_m} + \frac{T_m}{T} - 1\right)$$
(1)

where,  $T_m$  is the melting temperature of the solute, respectively;  $\Delta_{fus}H$ , and  $\Delta H_{tr}$  stand for enthalpy of fusion of the solute at melting temperature and enthalpy of solid–solid phase transition of the solute, respectively;  $T_{tr}$  denotes temperature of phase transition and  $\Delta C_p$  denotes heat capacity of the solute at melting temperature. Here,  $\Delta H_{tr}$  and  $\Delta C_p$ can be neglected because no transition in CPADE solid phase occurs, which is determined by the DSC throughout the whole experiments [30]. And thus a simplified form of the solid–liquid phase equilibrium equation can be written in the following form [31]:

$$\ln \frac{1}{x_1 \gamma_1} = \frac{\Delta_{fus} H}{RT_m} \left( \frac{T_m}{T} - 1 \right). \tag{2}$$

Based on the values of  $x_1$ , Tm and  $\Delta_{fus}H$ , the activity coefficients of CPADE in solid–liquid equilibrium can be calculated via Eq. (2) and are also presented in Table 2.

The solubility of CPADE varying with temperature can be correlated by the Wilson equation. In the binary system, Wilson model can be shown in the following form:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$$
(3)

$$\Lambda_{12} = \frac{\nu_2}{\nu_1} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) = \frac{\nu_2}{\nu_1} \exp\left(-\frac{\Delta\lambda_{12}}{RT}\right) \tag{4}$$

$$\Lambda_{21} = \frac{\nu_1}{\nu_2} \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right) = \frac{\nu_1}{\nu_2} \exp\left(-\frac{\Delta\lambda_{21}}{RT}\right).$$
(5)

Here,  $v_1$  and  $v_2$  denote the molar volumes of solute and solvent respectively.  $\Delta \lambda_{11}$ , and  $\Delta \lambda_{12}$  represent the cross interaction energy parameters, (J·mol<sup>-1</sup>), which can be regressed from the experimental data.

The NRTL activity coefficient model is used in this work to correlate the experimental solubility data, which has been successfully used to correlate the solid–liquid equilibrium for many nonideal solutions in wide temperature ranges [32–34]. The NRTL model which is applied to determine the activity coefficient of a solute in pure solvents can be expressed as following:

$$\ln \gamma_1 = x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{\left( x_2 + x_1 G_{12} \right)^2} \right]$$
(6)

where  $G_{12}$ ,  $G_{21}$ ,  $\tau_{12}$  and  $\tau_{21}$  represent NRTL model parameters that demand to be experimentally determined by

$$G_{ij} = \exp(-a_{ij}\tau_{ij}) \tag{7}$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = \frac{\Delta g_{ij}}{RT}.$$
(8)

In which,  $\Delta g_{12}$  and  $\Delta g_{21}$  refer to the two cross interaction energy parameters (J·mol<sup>-1</sup>); *a* reflects the parameter related to the nonrandomness in the mixture. *a* is chosen to be 0.3 as usual.

The mole fraction solubility data in the selected solvents were also described by the UNIQUAC model in the following form:

$$\ln\gamma_1 = \ln\gamma_1^C + \ln\gamma_1^R \tag{9}$$



**Fig. 6.** Mole fraction solubility (*x*) data of CPADE in selected solvents:  $\Box$ , methanol;  $\bigcirc$ , acetone;  $\triangle$ , acetonitrile;  $\bigtriangledown$ , tetrahydrofuran;  $\Rightarrow$ , ethyl acetate;  $\blacktriangledown$ , chloroform;  $\blacksquare$ , ethanol;  $\triangle$ , benzene;  $\bigstar$ , toluene;  $\diamondsuit$ , dichloromethane.

#### Table 3

Molar volume (*V*), UNIQUAC volume parameter (*r*), and surface parameter (*q*) values for selected solvents.<sup>a</sup>

Solvent	$10^{6}V_{i}/m^{3}\cdot mol^{-1}$	r	q
Methanol	40.70	1.4311	1.432
Ethanol	58.52	2.1055	1.972
Dichloromethane	64.43	2.2564	1.988
Acetonitrile	52.68	1.8701	1.724
Ethyl acetate	98.59	3.4786	3.116
Tetrahydrofuran	81.94	2.9415	2.720
Chloroform	80.66	2.8700	2.410
Benzene	89.48	3.1878	2.400
Toluene	106.6	3.9228	2.968
Acetone	73.93	2.5735	2.336
CPADE	275.9	12.326	13.09

<sup>a</sup> Data from Prausnitz.<sup>26</sup>

$$\ln \gamma_1^{\ C} = \ln \left(\frac{\phi_1}{x_1}\right) + \frac{z}{2} q_1 \ln \left(\frac{\theta}{\phi_1}\right) + \phi_2 \left(l_1 - \frac{r_1}{r_2} l_2\right)$$
(10)

$$\ln \gamma_1{}^R = -q_1 \ln (\theta_1 + \theta_2 \tau_{21}) + \theta_2 q_1 \left( \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right)$$
(11)

$$l_{1} = \frac{z}{2}(r_{1}-q_{1})-(r_{1}-1)$$

$$l_{2} = \frac{z}{2}(r_{2}-q_{2})-(r_{2}-1)$$
(12)

$$\tau_{12} = \exp\left(-\frac{u_{12} - u_{22}}{RT}\right) = \exp\left(-\frac{\Delta u_{12}}{RT}\right) \tag{13}$$

$$\tau_{21} = \exp\left(-\frac{u_{21} - u_{11}}{RT}\right) = \exp\left(-\frac{\Delta u_{21}}{RT}\right).$$
(14)

In which,  $\Delta u_{12}(\Delta u_{21})$ , z,  $\Phi$  and  $\theta$  denote two adjustable energy parameters; the coordination number usually taken as 10; the volume fraction and molecular surface fraction of solute or solvent, respectively. Parameters r and q refer to the UNIQUAC volume parameter and surface parameter of solvent and solute, which are listed in Table 3. The values of r and q of solute can be obtained from the group volume parameters (R) and surface parameters (Q) of the UNIFAC model, which are listed in Table 4.

The cross-interaction parameters of the Wilson equation ( $\Delta\lambda_{12}$  and  $\Delta\lambda_{21}$ ), the NRTL equation ( $\Delta g_{12}$  and  $\Delta g_{21}$ ), and the UNIQUAC equation ( $\Delta u_{12}$  and  $\Delta u_{21}$ ) are written as the following Eq. (15):

$$k_{ij} = \alpha_{ij} + \beta_{ij}T \tag{15}$$

where *k* stands for any interaction parameter mentioned above.  $\alpha$  and  $\beta$  denote the parameters to be fitting the solubility data.

The parameters of the Wilson, nonrandom two-liquid (NRTL), and UNIQUAC model which were obtained by fitting the experimental solubility data and the relative standard deviations (RSDs) defined by

Van der Waals group volume and surface area parameters for the UNIQUAC model.

Table 4

Group	R	Q
(0-)(-0)P(=0)-a	1.9312	1.762
-CHNH-	0.97950	0.6240
ACH	0.53130	0.4000
AC	0.36520	0.1200
-CH <sub>2</sub> -	0.67440	0.5400

<sup>a</sup> is taken from literature.<sup>27</sup> The other values in this table are from literature.<sup>26</sup>

<b>Table 5</b> Parameters of t <sub>i</sub>	the models and	1 RSD% of different c	orrelation models in ten	pure solvents.							
		Methanol	Tetrahydrofuran	Ethyl acetate	Chloroform	Ethanol	Benzene	Toluene	Dichloromethane	Acetone	Acetonitrile
Wilson	$\alpha_{12}$	43802	-32071	32882	-36098	43649	95370	88233	258917	2254.4	5725.9
model	$\beta_{12}$	-111.24	119.74	-76.752	136.84	-101.4	-264.39	-245.3	-804.65	-3.7491	1.5994
	$\alpha_{21}$	8408.5	19681	14206	11396	15431	9696.7	13810	133.97	-12654	24918
	$\beta_{21}$	-46.539	-85.271	-56.548	-61.606	-69.862	-50.596	-59.773	-27.107	52.024	-86.848
	RSD %	1.15	1.73	1.45	0.99	1.02	1.44	1.43	1.78	1.91	1.61
NRTL	$\alpha_{12}$	-19155	7414.6	-319.16	-1365.8	-11232	164401	26065	14435	22412	32491
model		79.802	-43.075	17.134	-16.062	52.198	-489.10	-93.798	-62.414	-32.097	-95.200
	$\alpha_{21}$	13415	63075	5742.5	53686	12414	4065.8	74819	- 25688	-15179	-6491.1
	$\beta_{21}$	-52.058	-173.12	-25.182	-148.44	-47.57	-26.682	-203.78	97.151	35.714	23.318
	RSD %	1.93	1.98	1.81	1.19	2.01	1.89	1.55	1.92	0.949	1.64
UNIQUAC	$\alpha_{12}$	2559.8	54879	-436.10	40751	1007.7	81903	80135	69621	2503.7	1958.8
model	$\beta_{12}$	-13.509	-171.20	-4.7816	-130.40	-9.1657	-247.44	-239.16	-220.49	-6.2505	-9.5509
	$\alpha_{21}$	30121	-3125.1	12467	-5525.5	20136	-1913.9	-3900.9	-3714.0	-4156.7	-240.30
	$\beta_{21}$	-77.537	3.7098	-26.755	10.439	-48.467	-1.8949	4.3439	6.9123	13.815	11.993
	RSD %	2.22	3.02	1.89	1.96	1.91	2.12	1.97	1.43	1.55	1.45

Table 6	
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The overall RSD% of different correlation models.

	Wilson model	NRTL model	UNIQUAC model
Overall RSD%	1.45	1.69	1.95

Eq. (16) were used to compare the experiment data and the calculated data by the models mentioned above.

$$RSD = \left[\frac{1}{N}\sum_{i=1}^{N} \left(\frac{x_i - x_i^{cacld}}{x_i}\right)^2\right]^{\frac{1}{2}}$$
(16)

Herein, N,  $x_i$  and  $x_i^{cacld}$  denote the number of experimental points; the experimental solubility data and the calculated solubility data by the models, respectively.

The calculated parameters of all the models mentioned above are listed in Table 5 together with the RSDs. The overall relative standard deviations are displayed in Table 6. The results show that all the models can describe the experimental data well with the optimized parameters. The overall RSDs of the models are 1.45% (Wilson), 1.69% (NRTL) and 1.95% (UNIQUAC). For the CPADE systems, the Wilson model is better than the other models in reproducing the temperature dependence of solubility.

3.3. Calculation of dissolution enthalpy, entropy, and the molar gibbs energy

The values of standard molar dissolution enthalpy and entropy at saturation can be determined by the van't Hoff equation. The Gibbs energy of solution at saturation can be calculated by Gibbs–Helmoholtz equation,[35]

$$\ln x_1 = -\frac{\Delta H_d^0}{RT} + \frac{\Delta S_d^0}{R} \tag{17}$$

$$\Delta G_d^0 = \Delta H_d^0 - T \Delta S_d^0. \tag{18}$$

The achieved dissolution enthalpy and entropy are listed in Table 7 and the Gibbs energy is plotted in Fig. S5. From the data in Table 7, the  $\Delta H_d^0$  of CPADE in each solvent is endothermic ( $\Delta H_d^0 > 0$ ), which explains the increasing solubility of CPADE with increasing temperature [36].

#### 4. Conclusions

The CPADE was synthesized in this work. The solubility data of CPADE in methanol, chloroform, acetone, ethyl acetate, acetonitrile, tetrahydrofuran, ethanol, benzene, toluene and dichloromethane were obtained at different temperatures. The melting temperature and the enthalpy of fusion were measured by DSC. The order of the solubility of CPADE is: chloroform > tetrahydrofuran > dichloromethane > benzene > toluene > acetone > methanol > ethanol > ethyl acetate > acetonitrile. The experimental data were correlated with the Wilson, nonrandom two-liquid (NRTL), and UNIQUAC model. The results show that the Wilson model is more suitable in determining the solubility of CPADE compared with the other models. Based on the van't Hoff equation, the dissolution enthalpy, entropy, and molar Gibbs free energy of CPADE are calculated in different solvents.

#### Notes

The authors declare no competing financial interest.

#### Table 7

Caculated values for dissolution enthalpy and dissolution entropy of CPADE in different pure solvents

Solvent	$\Delta H_{\rm d}$ (K J/mol)	$\Delta S_{\rm d} \left( J/({\rm mol} \times {\rm K}) \right)$
Methanol	44.2	124.1
Acetone	42.2	118.2
Acetonitrile	57.5	159.1
Tetrahydrofuran	25.1	70.7
Ethyl acetate	44.5	122.7
Chloroform	21.3	59.3
Ethanol	44.6	124.3
Methyl acetate	35.6	100.3
Toluene	41.2	116.2
Dichloromethane	25.8	72.4

#### Appendix A. Supplementary data

Supplementary data of MS spectra of CPADE, IR spectra of CPADE, <sup>1</sup>H NMR spectra of CPADE, <sup>13</sup>C NMR spectra of CPADE associated with this article can be found, in the online version, at

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