Supporting Information

Boosting Organic Solar Cell Efficiency via Tailored End-Group Modifications of Novel Non-Fused Ring Electron Acceptors

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1. Fabrication and Characterization of OSCs

The pre-patterned ITO-coated glass substrates were cleaned with detergent and sonicated in deionized water, acetone and isopropyl alcohol for 20 minutes each, followed by drying in an oven overnight.For binary and ternary cells, Device was fabricated with conventional device structure of ITO/2PACz/Active layer/PDINN/Ag. Ethanol solution of 2PACz (Purchased from Tokyo Chemical Industry) was spin-cast onto the ITO surface at 5000 rpm for 30 s (the thickness is about 40 nm), and baked at 60 °C for 1 min in air. A mixture of D18 and acceptors (weight ratio of 1:1.2) in CF solution was stirring at 60 °C for 1 hour to make sure the solid was fully. Ternary blends based on D18:2BTh-C2:2BTh-CN (1:1:0.1) were solubilized under the same conditions. The concentration of D18 was set to 4 mg/mL. And the molecular weight of D18 is 12.8 kDa. After the film was completely dried, it was thermally annealed at 100 °C for 1 min. Afterwards, a methanolic solution of PDINN (1.5 mg mL^{-1}) was poured on top of the active layer by rotating it at 3000 rpm. Finally, a 100 nm Ag layer was thermally deposited under vacuum pressure below 10^{-7} Torr. The effective area of each cell is 0.04 cm^{2}.

The J-V curves for photocurrent are recorded in a glove box at about 25 °C using an instrument from Enli Technology Ltd.,Taiwan(SS-F53A) under AM 1.5G illumination (AAA solar simulator with an intensity of 100 mW cm^{-2} calibrated with a standard monocrystalline PV cell). The external quantum efficiency (EQE) measurements are performed in unencapsulated air. EQE data are obtained using a solar cell spectral response measurement system (QER3011, Enli Tech-nology Co. Ltd), and the intensity is calibrated with a standard single crystal Si photovoltaic cell.

2. Fabrication and characterization of the hole/electron-only devices

Devices with the architecture of ITO/PEDOT:PSS/active layer/MoO3/Ag and ITO/ZnO/active layer/PDINO/Ag were applied to construct the hole and electron-only device, respectively. The active layers were prepared under the optimal conditions.

According to the Mott-Gurney equation: $J = 9\varepsilon\varepsilon_0\mu/(8L^3)V^2$, the mobility can be described as $\mu = \frac{8JL^3}{9\varepsilon\varepsilon_0V^2}$. Herein, ε denotes the dielectric constant of the blended film based on organic materials, and it was assumed to be constant (3.0); ε_0= 8.85419×10-12 F m^{-1}, which meant the permittivity of the vacuum; μ represented the zero-field mobility; J was the current density; L was the thickness of the films; and $V = V_{appl} - V_{bi}$; V_{appl} and V_{bi} are the applied voltage to the device and the build-in voltage, respectively.

3. Calculation of Flory-Huggins interaction parameters

The surface energy γ values could be calculated according to the Wu model on the neat films by the Equation:

$$\gamma = \gamma^d + \gamma^p$$

$$\gamma_{LV}(1 + cos\theta) = \frac{4\gamma_S^d\gamma_L^d}{\gamma_S^d + \gamma_L^d} + \frac{4\gamma_S^p\gamma_L^p}{\gamma_S^p + \gamma_L^p}$$

And the two different contact angles of water and glycerol are measured to achieve the γ of acceptor and polymer donor. And the γ is the sum of dispersion (d) and polar (p) components.

As $\delta \propto \sqrt{\gamma}$, we could calculate all the solubility parameter (δ) of acceptor and polymer. Further, the Flory-Huggins interaction parameter χ could be calculated according to the Equation:

$$\chi_{ij} = \frac{V_1}{RT}(\delta_i - \delta_j)^2 + 0.34$$

Since we adopt the chloroform as the solvent, the V_1 is 119.38 cm^{3}mol^{-1}. We calculate the χ of the blend of different components, and the results are shown in Table S5.

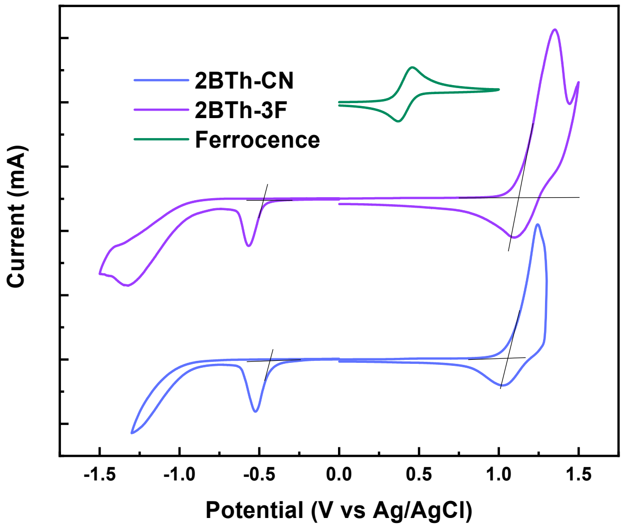


Figure S1. CV curves of LJ1 using ferrocene (Fc) as an internal standard.

Table S1. J-V data of 2BTh-CN and 2BTh-3F.

Acceptor	Ratio	V_{oc} (V)	J_{sc} (mAcm^{-2})	FF (%)	PCE (%)
2BTh-CN	1:1	0.87	23.15	74.42	14.97
	1:1.2	0.86	23.30	75.38	15.11
	1:1.5	0.86	22.88	71.22	14.00
2BTh-3F	1.2:1	0.95	17.67	59.63	10.05
	1:1	0.95	17.46	60.96	10.12
	1:1.2	0.94	17.18	57.83	9.34

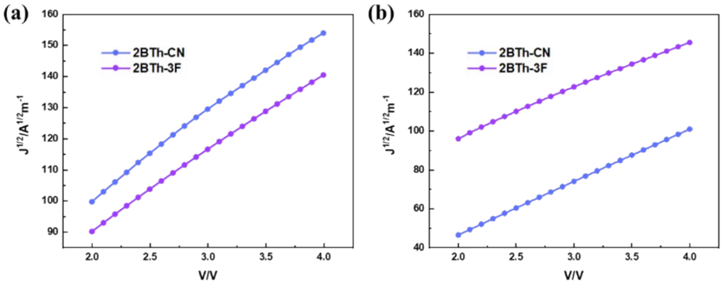


Figure S2. $J^{1/2}$–V characteristics of electron and hole-only devices of **2BTh-3F** and **2BTh-CN** -based blends by the space-charge-limited current (SCLC) method.

Table S2. Electron and hole mobilities of devices based on **2BTh-3F** and **2BTh-CN**.

Active layer	μ_e (cm^2 V^{-1} s^{-1})	μ_h (cm^2 V^{-1} s^{-1})	μ_h/μ_e
D18:2BTh-CN	2.13 x 10^{-4}	2.45 x 10^{-4}	1.15
D18:2BTh-3F	1.65 x 10^{-4}	2.12 x 10^{-4}	1.28

Table S3. Lattice parameters of the pure films of 2BTh-3F and 2BTh-CN, and blend films of D18: acceptors.

Film	***π*-Stacking**		
	***π*-*π* distance (Å)**	**FWHM ($Å^{-1}$)**	**CCL (Å)**
2BTh-3F	3.65	0.55	10.16
2BTh-CN	3.60	0.45	12.42
D18: 2BTh-3F	3.65	0.26	21.50
D18: 2BTh-CN	3.65	0.24	23.28

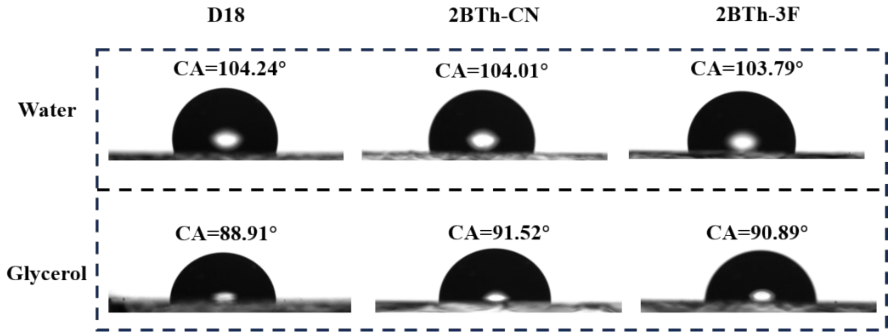
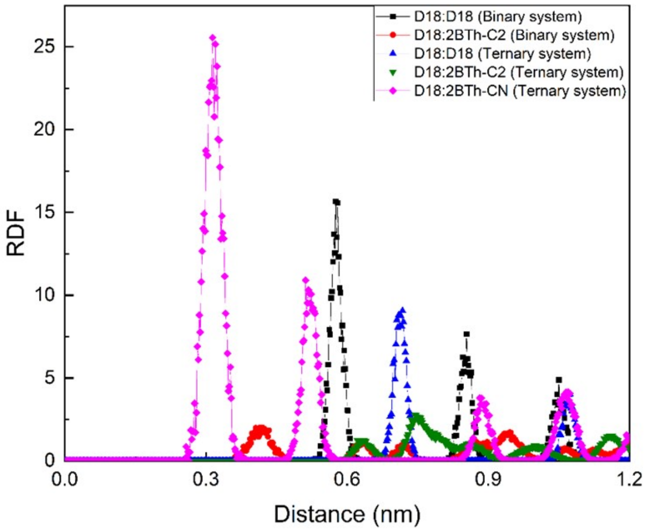


Figure S3. The contact angle images of D18, 2BTh-CN and 2BTh-3F films tested by water and glycerol.

Table S4. Surface tension (γ) and Flory-Huggins interaction parameter (χ) obtained from water and glycerol contact angle measurement of D18, 2BTh-CN and 2BTh-3F films.

Sample	θ_{water} [°]	θ_{GL} [°]	γ [mN m^{-1}]	χ with 2BTh-CN [$\times k \text{ mN m}^{-1}$]	χ with 2BTh-3F [$\times k \text{ mN m}^{-1}$]
D18	104.24	88.91	19.50	0.40	0.38
2BTh-CN	104.01	91.52	16.45	-	0.34
2BTh-3F	103.79	90.89	16.98	0.34	-



FigureS4. Radial distribution functions (RDFs) of center-of-mass (COM) for dondor-dondor and dondor-acceptor pairs in simulated systems.

In comparison, the radial distribution functions (RDFs) based on center-of-mass (COM) between selected pairs (donor-donor and donor-acceptor) are calculated and shown in Figure S1. The increased first peak location of RDFs between D18 and D18 COMs indicates that adding **2BTh-CN** results in the looser arrangement among donor molecules. For donor-acceptor pairs, the first RDF peak between D18 and **2BTh-CN** is located at the closest distance of ca. 0.31 nm. Moreover, the second RDF peak between D18 and **2BTh-CN** is also closer than the first peak for D18:2BTh-C2 pair. This means there exist strong interactions between D18 and **2BTh-CN** molecules. For the first peak of RDFs between D18 and 2BTh-C2 COMs, the first peak is located at farther distance in comparison with no **2BTh-CN** added system. Since simulated one D18 polymer chain was composed of four D18 monomers (labeled as D18-M1, D18-M2, D18-M3 and D18-M4), we further calculated the (RDFs) of center-of-mass (COM) between each donor monomer unit and acceptor as shown in Figure S2. The **2BTh-CN** molecules mainly interact with the intermediate units (D18-M3) on D18 polymer chain. Obviously, the first RDF peak between D18-M2 and 2BTh-C2 (Figure S2b) shifts to closer distance that can be comparable to the one between D18-M3 and **2BTh-CN** (Figure S2c), which indicates that the third component **2BTh-CN** can cause denser distribution of 2BTh-C2 around D18 polymer. In the D18: 2BTh-C2:**2BTh-CN** system, looser distribution of D18 molecules can facilitate the intercalations of **2BTh-CN** and 2BTh-C2 molecules around donor molecules (as shown in Figure 7), which may lead to the improvement in *π–π* interactions for donor-acceptor pairs.

Table S5 Molecule numbers in simulated D18:2BTh-C2 and D18:2BTh-C2: 2BTh-CN systems

System	D18	2BTh-C2	2BTh-CN	$CHCl_3$
D18:2BTh-C2	18	72	0	23666
D18:2BTh-CN	18	60	12	23666

Theoretical Calculation and Simulation

All MD simulations were performed with GROMACS 2021.3 software [1]. The Generalized Amber Force Field (GAFF2) parameters [2] were used to describe the bonded and non-bonded interactions of all studied molecules and the solvent chloroform. For D18 donor, the degree of polymerization of 4 was used. The LINCS algorithm [3] was used to constrain all bonds. For non-bonded interactions, the Particle-Mesh-Ewald (PME) summation method [4] was used to calculate electrostatic interactions with the cutoff at 10 Å. For van der Waals, a 10 Å cutoff was also set.

The number of molecules for MD simulations was determined from the experimental feed composition. Detailed information of simulated systems was listed in Table Sxx. Initial structures were constructed in the 15×15×15 nm^3 box with embedded program in the GROMACS. For each system, simulation protocol consisted of a 100 ns NPT ensemble equilibrium MD simulation under solvation conditions, a quasi-equilibrium MD approach to model the solvent evaporation process, and a 100 ns NPT MD production simulation. All simulations proceeded under 298 K and 1 bar in agreement with experimental environments. To model the solvent evaporation process, 100 random solvent molecules was evaporated in the time interval of 1 ns and 10 ns equilibrium was carried out after the completion. Representative snapshots of binary and ternary systems with and without $CHCl_3$ solvents were shown in Fig. S1. Then, it was annealed to 600 K and quenched back to 298 K to perform 100 ns NPT MD production process. The V-rescale thermostat [5] and Berendsen barostat [6] under the NPT ensemble were applied to control the temperature and pressure. In the final MD production, the Parrinello-Rahman method was applied. The VMD software [7] was used for the visualization. The Multiwfn software [8] was used to carry out weak interaction analyses, which were visualized by the VMD.

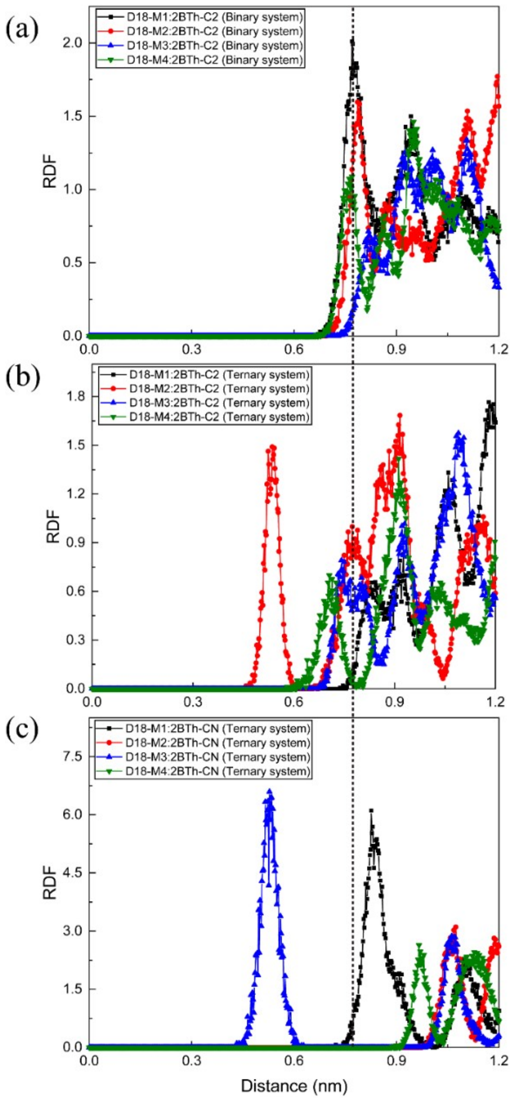
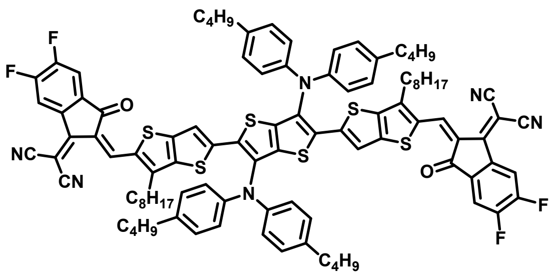


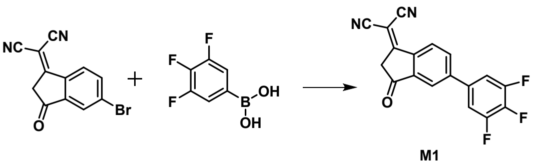
Figure S5. Radial distribution functions (RDFs) of center-of-mass (COM) between each donor monomer unit and acceptor in simulated systems. The D18-M1, D18-M2, D18-M3, and D18-M4 represents four monomer units from one end to another end of the D18 polymer chain, respectively. The (a), (b) and (c) denote the D18-M1/2/3/4:2BTh-C2 pairs in binary stem, D18-M1/2/3/4:2BTh-C2 pairs in ternary system, and D18-M1/2/3/4:2BTh-CN pairs in ternary system.

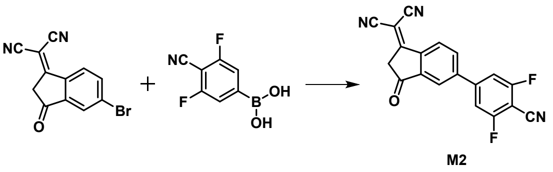


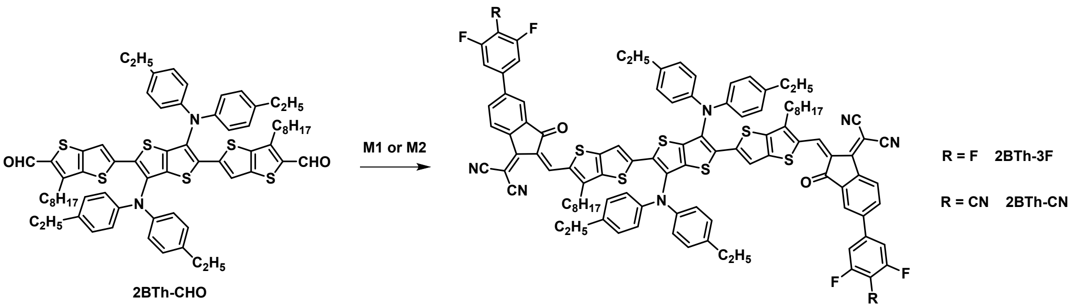
2BTh-2F

Figure S6. The molecular formula of 2BTh-2F.

4. Materials and Synthesis.







Compound 2BTh-CHO was synthesized according to previous report (10.1002/aenm.202102591).

Synthesis of compound **M1**

Compound **M1** can be synthesized by Suzuki coupling reaction. 2-(5-bromo-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (300 mg, 1.1 mmol), (3,4,5-trifluorophenyl)boronic acid (232 mg, 1.3 mmol), $Pd(PPh_3)_4$ (30 mg) and Na_2CO_3 (233 mg, 2.2 mmol) were added to a degassed mixture of THF (20 mL) and water (6 mL) under nitrogen. The mixture was reacted at 80 °C for 1 day. After cooling to room temperature, saturated sodium bicarbonate solution was added and stirred for 3 hours. The mixture was extracted with dichloromethane for three times; and the combined organic phases were washed with saturated salt solution, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was chromatographically purified on silica gel column eluting with dichloromethane/petroleum ether (3:1, v/v) to give compound **M1** (313 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72-8.74 (d, *J*=8Hz, 1H), 8.09 (s, 1H), 8.01-8.03 (d, *J*=8Hz, 2H), 7.30-7.33 (m, 2H), 3.79 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 199.43, 165.21, 145.42, 141.95, 141.46, 134.36, 126.89, 122.50, 112.19, 112.00, 111.95, 111.92, 111.84, 111.81, 43.59.

Synthesis of compound **M2**

Compound **M2** can be synthesized by Suzuki coupling reaction. 2-(5-bromo-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (300 mg, 1.1 mmol), (4-cyano-3,5-difluorophenyl)boronic acid (238 mg, 1.3 mmol), $Pd(PPh_3)_4$ (30 mg) and Na_2CO_3 (233 mg, 2.2 mmol) were added to a degassed mixture of THF (20 mL) and water (6 mL) under nitrogen. The mixture was reacted at 80 °C for 1 day. After cooling to room temperature, saturated sodium bicarbonate solution was added and stirred for 3 hours. The mixture was extracted with dichloromethane for three times; and the combined organic phases were washed with saturated salt solution, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was chromatographically purified on silica gel column eluting with dichloromethane/petroleum ether (3:1, v/v) to give compound **M2** (301 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78-8.79 (d, *J*=4Hz, 1H), 8.14 (s, 1H), 8.06-8.08 (d, *J*=8Hz, 2H), 7.37-7.39 (d, *J*=8Hz, 2H), 3.81 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 194.12, 164.89, 145.80, 143.00, 141.51, 134.54, 132.16, 128.81, 127.13, 123.00, 112.04, 111.41, 112.27, 111.25, 43.56.

Synthesis of compound **2BTh-3F**

A mixture of **2BTh-CHO** (150 mg, 0.13 mmol) and **M1** (169 mg, 0.52 mmol) in chloroform (20 mL) was carefully degassed and pyridine (0.5 mL) was added. The mixture was stirred and refluxed under nitrogen overnight, and the solvent was removed under reduced pressure. The crude product was purified on silica gel chromatography using dichloromethane/petroleum ether (2:1, v/v) as an eluent to obtain the target compound **2BTh-3F** (200 mg, 87%) as a black solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99 (s, 2H), 8.68-8.69 (d, *J*=4Hz, 2H), 7.97 (s, 2H), 7.75-

7.77 (d, J=8Hz, 2H), 7.28-7.29 (d, J=8Hz, 4H), 7.20 (s, 2H), 7.13-7.15 (d, J=8Hz, 8H), 7.08-7.10 (d, J=8Hz, 8H), 2.96-2.99 (m, 4H), 2.60-2.64 (m, 8H), 1.62-1.65 (m, 4H), 1.21-1.24 (m, 32H), 0.86-0.88 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 187.68, 160.37, 157.72, 151.98, 151.17, 150.77, 145.09, 144.29, 143.91, 143.00, 142.21, 141.42,141.24, 139.90, 139.57, 137.90, 136.39, 134.98, 132.19, 128.91, 125.90, 122.18, 121.36, 117.03, 115.33, 111.61, 111.47, 100.00, 68.37, 31.95, 30.66, 29.93, 29.61, 29.45, 29.19, 28.30, 22.71, 15.55, 14.19.

Synthesis of compound **2BTh-CN**

A mixture of **2BTh-CHO** (150 mg, 0.13 mmol) and **M2** (172 mg, 0.52 mmol) in chloroform (20 mL) was carefully degassed and pyridine (0.5 mL) was added. The mixture was stirred and refluxed under nitrogen overnight, and the solvent was removed under reduced pressure. The crude product was purified on silica gel chromatography using dichloromethane/petroleum ether (2:1, v/v) as an eluent to obtain the target compound **2BTh-CN** (193 mg, 83%) as a black solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.01 (s, 2H), 8.74-8.76 (d, J=8Hz, 2H), 8.02 (s, 2H), 7.83-7.84 (d, J=4Hz, 2H), 7.34-7.35 (d, J=4Hz, 4H), 7.22 (s, 2H), 7.13-7.15 (d, J=8Hz, 8H), 7.08-7.10 (d, J=8Hz, 8H), 2.97-2.99 (m, 4H), 2.60-2.64 (m, 8H), 1.61-1.65 (m, 4H), 1.21-1.25 (m, 32H), 0.86-0.88 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 187.32, 164.50, 163.22, 162.79, 159.98, 152.43, 151.61, 145.52, 142.96, 142.34, 142.27, 139.98, 137.97, 136.52, 135.83, 135.79, 135.12, 133.12, 132.16, 128.93, 126.08, 122.20, 121.71, 120.80, 117.03, 111.05, 110.89, 108.88, 68.81, 31.94, 30.69, 29.98, 29.63, 29.45, 29.18, 28.31, 22.71, 15.55, 14.19.

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[2] GAFF and GAFF2 are public domain force fields and are part of the AmberTools16 distribution, available for download at http://amber.org Internet address (accessed March 2018). According to the AMBER development team, the improved version of GAFF, GAFF2, is an ongoing poject aimed at ”reproducing both the high quality interaction energies and key liquid properties such as density, heat of vaporization and hydration free energy”. GAFF2 is expected ”to be an even more successful general purpose force field and that GAFF2-based scoring functions will significantly improve the successful rate of virtual screenings.”.

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