

Supporting Information

Preparation of acifluorfen-based ionic liquids with fluorescent properties for enhancing biological activities and reducing the risk to the aquatic environment

Gang Tang, Junfan Niu, Wenbing Zhang, Jiale Yang, Jingyue Tang, Rong Tang, Zhiyuan Zhou, Jianqiang Li, Yongsong Cao*

College of Plant Protection, China Agricultural University, Beijing, China

*Corresponding author: NO.2 Yuanmingyuan West Road, China Agricultural University, Beijing, China, 100193

Telephone: 86-10-62734302. Fax: 86-10-62734302.

Email: caoysong@126.com, caoys@cau.edu.cn

Number of pages: 23

Number of figures: 46

Number of tables: 1

Fig. S1 ^1H NMR (300.13 MHz; CDCl_3) of **Est1** (Methyl 2-hydroxybenzoate)

Fig. S2 ^1C NMR (75.47 MHz; CDCl_3) of **Est1** (Methyl 2-hydroxybenzoate)

Fig. S3 ^1H NMR (300.13 MHz; CDCl_3) of **Est2** (Methyl 3-hydroxy-2-naphthoate)

Fig. S4 ^1C NMR (75.47 MHz; CDCl_3) of **Est2** (Methyl 3-hydroxy-2-naphthoate)

Fig. S5 ^1H NMR (300.13 MHz; CDCl_3) of **Est3** (Ethyl 2-oxo-2H-chromene-6-carboxylate)

Fig. S6 ^1C NMR (75.47 MHz; CDCl_3) of **Est3** (Ethyl 2-oxo-2H-chromene-6-carboxylate)

Fig. S7 ^1H NMR (300.13 MHz; CDCl_3) of **Frc1** (2-Hydroxybenzohydrazide)

Fig. S8 ^1C NMR (75.47 MHz; DMSO) of **Frc1** (2-Hydroxybenzohydrazide)

Fig. S9 ^1H NMR (300.13 MHz; DMSO) of **Frc2** (3-Hydroxy-2-naphthohydrazide)

Fig. S10 ^1C NMR (75.47 MHz; DMSO) of **Frc2** (3-Hydroxy-2-naphthohydrazide)

Fig. S11 ^1H NMR (300.13 MHz; CDCl_3) of **Frc3** (2-Oxo-2H-chromene-6-carbohydrazide)

Fig. S12 ^1C NMR (75.47 MHz; DMSO) of **Frc3** (2-Oxo-2H-chromene-6-carbohydrazide)

Fig. S13 ^1H NMR (300.13 MHz; CDCl_3) of **HIL1**

Fig. S14 ^1C NMR (75.47 MHz; DMSO) of **HIL1**

Fig. S15 ^1H NMR (300.13 MHz; CDCl_3) of **HIL2**

Fig. S16 ^1C NMR (75.47 MHz; DMSO) of **HIL2**

Fig. S17 ^1H NMR (300.13 MHz; CDCl_3) of **HIL3**

Fig. S18 ^1C NMR (75.47 MHz; DMSO) of **HIL3**

Fig. S19 ^1H NMR (300.13 MHz; CDCl_3) of **HIL4**

Fig. S20 ^1C NMR (75.47 MHz; DMSO) of **HIL4**

Fig. S21 ^1H NMR (300.13 MHz; CDCl_3) of **HIL5**

Fig. S22 ^1C NMR (75.47 MHz; CDCl_3) of **HIL5**

Fig. S23 ^1H NMR (300.13 MHz; CDCl_3) of **HIL6**

Fig. S24 ^1C NMR (75.47 MHz; CDCl_3) of **HIL6**

Fig. S25 ^1H NMR (300.13 MHz; CDCl_3) of **HIL7**

Fig. S26 ^1C NMR (75.47 MHz; CDCl_3) of **HIL7**

Fig. S27 ^1H NMR (300.13 MHz; CDCl_3) of **HIL8**

Fig. S28 ^1H NMR (300.13 MHz; CDCl_3) of **HIL9**

Fig. S29 ^1H NMR (300.13 MHz; CDCl_3) of **HIL10**

Fig. S30 ^1H NMR (300.13 MHz; CDCl_3) of **HIL11**

Fig. S31 ^1H NMR (300.13 MHz; CDCl_3) of **HIL12**

Fig. S32 The surface tension curves (γ -lg C curves) for HIL1-12

Table S1 The values of critical micelle concentration (CMC) of HIL1-12

Methyl 2-hydroxybenzoate (Est1). ^1H NMR (300.13 MHz; CDCl_3 ; Me_4Si) δ ppm = 10.79 (s, 1H, OH), 7.85 (m, 1H, CH), 7.48 (m, 1H, CH), 7.01 (m, 1H, CH), 6.90 (m, 1H, CH), 3.97 (s, 3H, CH_3); ^{13}C NMR (75.47 MHz; CDCl_3 ; Me_4Si) δ ppm = 51.99, 112.22, 117.36, 117.40, 118.93, 129.69, 129.73, 135.46

Methyl 3-hydroxy-2-naphthoate (Est2). ^1H NMR (300.13 MHz; CDCl_3 ; Me_4Si) δ ppm = 10.43 (s, 1H, OH), 8.49 (s, 1H, CH), 7.80 (m, 1H, CH), 7.68 (m, 1H, CH), 7.49 (m, 1H, CH), 7.32 (m, 2H, CH), 4.02 (s, 3H, CH_3); ^{13}C NMR (75.47 MHz; CDCl_3 ; Me_4Si) δ ppm = 52.22, 113.37, 113.89, 123.61, 126.00, 126.75, 128.82, 128.89, 132.12, 137.63, 155.99, 169.96

Ethyl 2-oxo-2H-chromene-6-carboxylate (Est3). ^1H NMR (300.13 MHz; CDCl_3 ; Me_4Si) δ ppm = 8.54 (s, 1H, CH), 7.65 (m, 2H, CH), 7.35 (m, 2H, CH), 4.42 (q, J = 7.15 Hz, 2H, CH_2), 1.42 (t, J = 7.13 Hz, 3H, CH_3); ^{13}C NMR (75.47 MHz; CDCl_3 ; Me_4Si) δ ppm = 14.00, 61.67, 116.46, 117.65, 118.07, 124.66, 129.35, 134.12, 148.28, 154.89, 156.42, 162.73

2-Hydroxybenzohydrazide (Frc1). ^1H NMR (300.13 MHz; CDCl_3 ; Me_4Si) δ ppm = 7.56 (br, 1H, CH), 7.43 (m, 1H, CH), 7.32 (m, 1H, CH), 7.00 (m, 1H, CH), 6.87 (m, 1H, CH), 4.08 (br, 2H, NH_2); ^{13}C NMR (75.47 MHz; DMSO ; Me_4Si) δ ppm = 114.60, 117.43, 118.76, 127.72, 133.49, 159.73, 168.07

3-Hydroxy-2-naphthohydrazide (Frc2). ^1H NMR (300.13 MHz; CDCl_3 ; DMSO) δ ppm = 10.20 (br, 1H, OH), 8.44 (s, 1H, CH), 7.82 (m, 1H, CH), 7.72 (m, 1H, CH), 7.48 (m, 1H, CH), 7.32 (m, 1H, CH), 7.26 (s, 1H, CH), 4.75 (br, 2H, NH_2); ^{13}C NMR (75.47 MHz; DMSO ; Me_4Si) δ ppm = 110.76, 118.21, 123.75, 125.92, 126.80, 128.21, 128.79, 129.14, 135.98, 155.19, 167.17

2-Oxo-2H-chromene-6-carbohydrazide (Frc3). ^1H NMR (300.13 MHz; CDCl_3 ; Me_4Si) δ ppm = 11.39 (s, 1H, NH), 8.72 (s, 1H, CH), 7.38 (m, 2H, CH), 6.98 (m, 2H, CH); ^{13}C NMR (75.47 MHz; DMSO ; Me_4Si) δ ppm = 116.49, 118.57, 119.38, 125.39, 130.09, 134.52, 148.08, 149.95, 154.08, 158.47

HIL1. ^1H NMR (300.13 MHz; CDCl_3 ; Me_4Si) δ ppm = 8.02 (d, J = 8.98 Hz, 1H, CH), 7.83 (m, 1H, CH), 7.63 (m, 1H, CH), 7.51 (m, 1H, CH), 7.48 (m, 1H, CH), 7.30 (m, 1H, CH), 7.25 (m, 1H, CH), 7.09 (m, 1H, CH), 7.01 (m, 1H, CH), 6.90 (m, 1H, CH); ^{13}C NMR (75.47 MHz; DMSO ; Me_4Si) δ ppm = 114.65, 117.34, 117.67, 118.74, 119.33, 121.47, 122.90, 125.08, 126.59, 127.18, 127.55, 128.45, 132.16, 132.27, 143.01, 153.20, 159.07, 159.51, 165.86, 167.79

HIL2. ^1H NMR (300.13 MHz; CDCl_3 ; Me_4Si) δ ppm = 8.43 (s, 1H, CH), 8.12 (m, 1H, CH), 8.06 (d, J =

8.94 Hz, 1H, CH), 7.80 (m, 1H, 2H), 7.70 (m, 1H, CH), 7.49 (m, 2H, CH), 7.36 (m, 1H, CH), 7.29 (m, 3H, CH); ^{13}C NMR (75.47 MHz; DMSO; Me₄Si) δ ppm = 110.71, 117.72, 118.20, 119.47, 122.96, 123.71, 125.87, 126.62, 126.97, 127.60, 128.19, 128.77, 129.27, 131.91, 135.97, 142.99, 153.21, 155.05, 159.11, 165.76, 166.99

HIL3. ^1H NMR (300.13 MHz; CDCl₃; Me₄Si) δ ppm = 9.11 (s, 1H, CH), 7.99 (d, J = 8.97 Hz, 1H, CH), 7.78 (m, 1H, CH), 7.62 (m, 1H, CH), 7.40 (m, 2H, CH), 7.25 (m, 1H, CH), 7.10 (m, 1H, CH), 7.00 (m, 2H, CH); ^{13}C NMR (75.47 MHz; DMSO; Me₄Si) δ ppm = 117.76, 119.61, 121.51, 123.01, 125.12, 126.27, 126.25, 126.70, 127.05, 127.19, 127.63, 128.50, 128.54, 131.49, 142.95, 153.19, 159.16, 165.65

HIL4. ^1H NMR (300.13 MHz; CDCl₃; Me₄Si) δ ppm = 8.06 (d, J = 8.92 Hz, 1H, CH), 7.95 (m, 1H, CH), 7.72 (m, 1H, CH), 7.37 (m, 1H, CH), 7.31 (m, 1H, CH), 7.07 (m, 1H, CH), 3.64 (s, 12H, CH₃); ^{13}C NMR (75.47 MHz; DMSO; Me₄Si) δ ppm = 54.47, 116.43, 117.07, 121.57, 122.47, 125.20, 126.53, 126.93, 127.37, 128.35, 141.58, 144.17, 153.99, 157.87, 155.02

HIL5. ^1H NMR (300.13 MHz; CDCl₃; Me₄Si) δ ppm = 7.82 (d, J = 8.94 Hz, 1H, CH), 7.73 (m, 1H, CH), 7.50 (m, 1H, CH), 7.18 (m, 2H, CH), 6.84 (m, 1H, CH), 3.36 (m, 8H, CH₂), 1.69 (m, 8H, CH₂), 1.35 (m, 8H, CH₂), 0.94 (t, J = 7.30 Hz, 12H, CH₃); ^{13}C NMR (75.47 MHz; CDCl₃; Me₄Si) δ ppm = 13.21, 19.29, 23.69, 58.53, 115.63, 117.58, 121.02, 124.54, 125.05, 126.06, 126.98, 127.61, 140.08, 141.36, 153.54, 159.03, 170.04

HIL6. ^1H NMR (300.13 MHz; CDCl₃; Me₄Si) δ ppm = 7.65 (m, 2H, CH), 7.41 (m, 1H, CH), 7.22 (m, 1H, CH), 7.10 (m, 1H, CH), 6.67 (m, 1H, CH), 3.46 (m, 2H, CH₂), 3.35 (s, 9H, CH₃), 1.69 (m, 2H, CH₂), 1.23 (m, 18H, CH₂), 0.87 (t, J = 6.68 Hz, 3H, CH₃); ^{13}C NMR (75.47 MHz; CDCl₃; Me₄Si) δ ppm = 13.52, 22.12, 22.58, 25.67, 28.83, 31.36, 52.78, 48.99, 66.29, 115.54, 119.44, 120.99, 124.41, 125.09, 126.04, 127.14, 127.65, 139.50, 141.77, 153.30, 158.88, 169.62

HIL7. ^1H NMR (300.13 MHz; CDCl₃; Me₄Si) δ ppm = 7.88 (d, J = 8.94 Hz, 1H, CH), 7.75 (m, 1H, CH), 7.52 (m, 1H, CH), 7.18 (m, 1H, CH), 7.10 (m, 1H, CH), 6.90 (m, 1H, CH), 3.37 (s, 9H, CH₃), 1.74 (m, 2H, CH₂), 1.25 (m, 28H, CH₂), 0.88 (t, J = 6.65 Hz, 3H, CH₃); ^{13}C NMR (75.47 MHz; CDCl₃; Me₄Si) δ ppm = 13.63, 22.25, 22.58, 25.79, 29.12, 31.50, 52.77, 66.30, 115.35, 117.50, 120.90, 121.36, 124.51, 125.24, 126.32, 127.63, 128.22, 140.49, 141.97, 153.42, 159.03, 169.08

HIL8. ^1H NMR (300.13 MHz; CDCl_3 ; Me_4Si) δ ppm = 8.75 (s, 1H, CH), 7.99 (d, J = 8.95 Hz, 1.1H, CH), 7.82 (m, 1.1H, CH), 7.62 (m, 1.1H, CH), 7.41 (m, 2H, CH), 7.22 (m, 1.1H, CH), 7.07 (m, 2H, CH), 6.99 (m, 1.1H, CH), 3.30 (s, 1H, CH_3), 1.74 (m, 0.2H, CH_2), 1.26 (m, 3.1H, CH_2), 0.90 (t, 0.3H, CH_3)

HIL9. ^1H NMR (300.13 MHz; CDCl_3 ; Me_4Si) δ ppm = 8.72 (s, 0.7H, CH), 7.92 (d, J = 8.97 Hz, 1H, CH), 7.77 (m, 1H, CH), 7.54 (m, 1H, CH), 7.38 (m, 1.4H, CH), 7.24 (m, 1H, CH), 7.14 (m, 1H, CH), 7.03 (m, 1.4H, CH), 6.99 (m, 1H, CH), 3.29 (s, 2.7H, CH_3), 1.78 (m, 0.6H, CH_2), 1.23 (m, 8.4 H, CH_2), 0.87 (t, J = 6.68 Hz, 0.9 H, CH_3)

HIL10. ^1H NMR (300.13 MHz; CDCl_3 ; Me_4Si) δ ppm = 8.73 (s, 1H, CH), 7.91 (d, J = 8.88 Hz, 2H, CH), 7.77 (m, 2H, CH), 7.55 (m, 2H, CH), 7.39 (m, 2H, CH), 7.20 (m, 2H, CH), 7.12 (m, 2H, CH), 7.03 (m, 2H, CH), 6.97 (m, 2H, CH), 3.32 (s, 9H, CH_3), 1.78 (m, 2H, CH_2), 1.24 (m, 28H, CH_2), 0.88 (t, J = 6.45 Hz, 3H, CH_3)

HIL11. ^1H NMR (300.13 MHz; CDCl_3 ; Me_4Si) δ ppm = 8.73 (s, 0.3H, CH), 7.88 (d, J = 8.95 Hz, 1H, CH), 7.76 (m, 1H, CH), 7.54 (m, 1H, CH), 7.36 (m, 0.7H, CH), 7.10 (m, 1H, CH), 7.04 (m, 1H, CH), 6.96 (m, 0.7H, CH), 6.92 (m, 1H, CH), 3.33 (s, 6.3H, CH_3), 1.75 (m, 0.6H, CH_2), 1.24 (m, 19.6 H, CH_2), 0.88 (t, J = 6.52 Hz, 2.1H, CH_3)

HIL12. ^1H NMR (300.13 MHz; CDCl_3 ; Me_4Si) δ ppm = 8.73 (s, 0.1H, CH), 7.89 (d, J = 8.94 Hz, 1H, CH), 7.75 (m, 1H, CH), 7.50 (m, 1H, CH), 7.36 (m, 0.2H, CH), 7.17 (m, 1H, CH), 7.09 (m, 1H, CH), 6.96 (m, 0.2H, CH), 6.88 (m, 1H, CH), 3.37 (s, 8.1H, CH_3), 1.75 (m, 1.8H, CH_2), 1.25 (m, 25 H, CH_2), 0.88 (t, J = 6.68 Hz, 2.7H, CH_3)

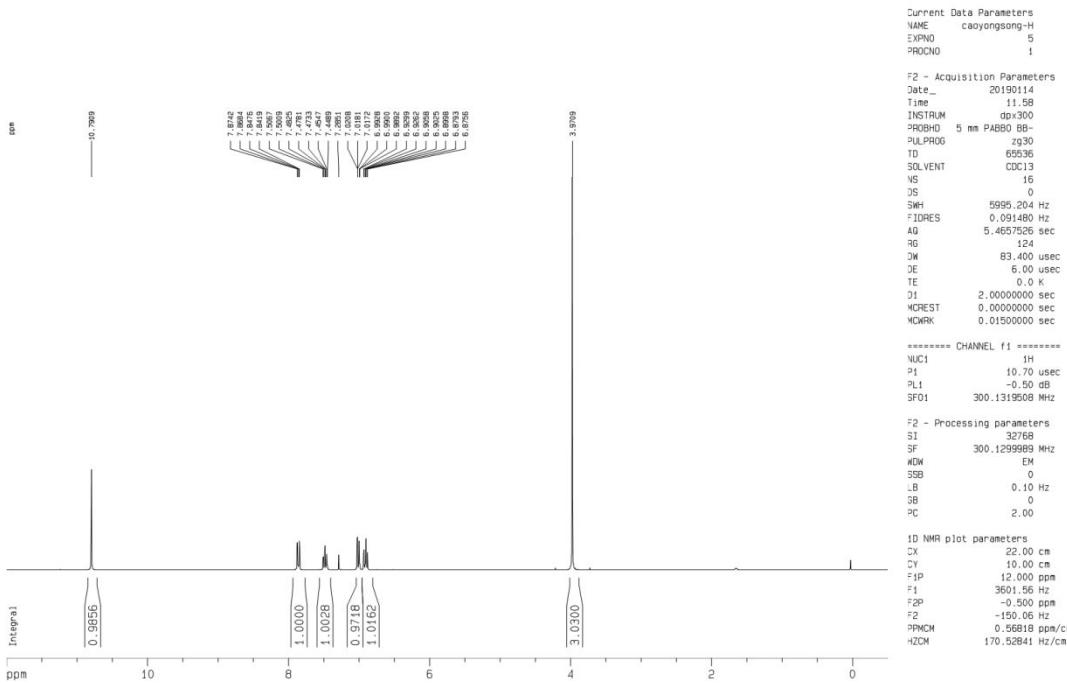


Fig. S1 ^1H NMR (300.13 MHz; CDCl_3) of **Est1** (Methyl 2-hydroxybenzoate)

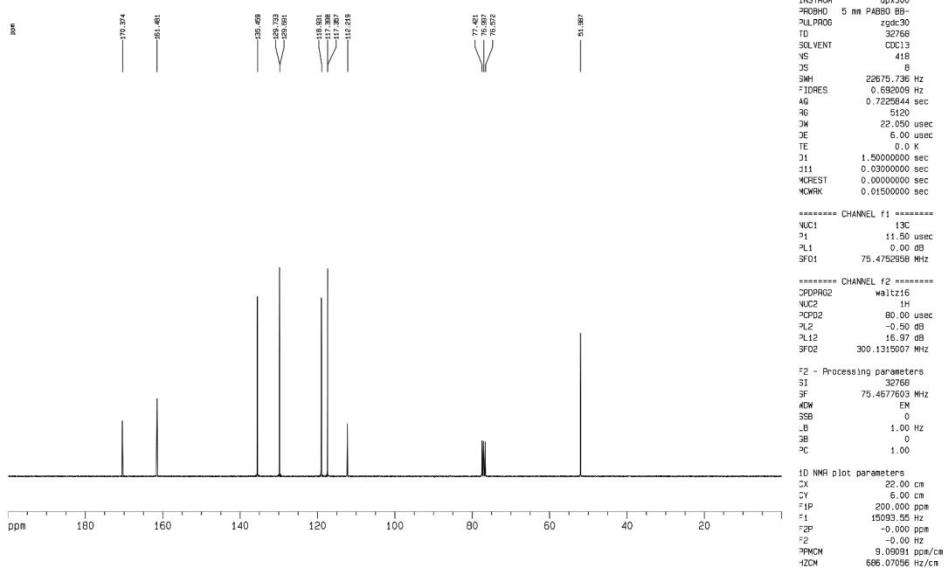


Fig. S2 ^{13}C NMR (75.47 MHz; CDCl_3) of **Est1** (Methyl 2-hydroxybenzoate)

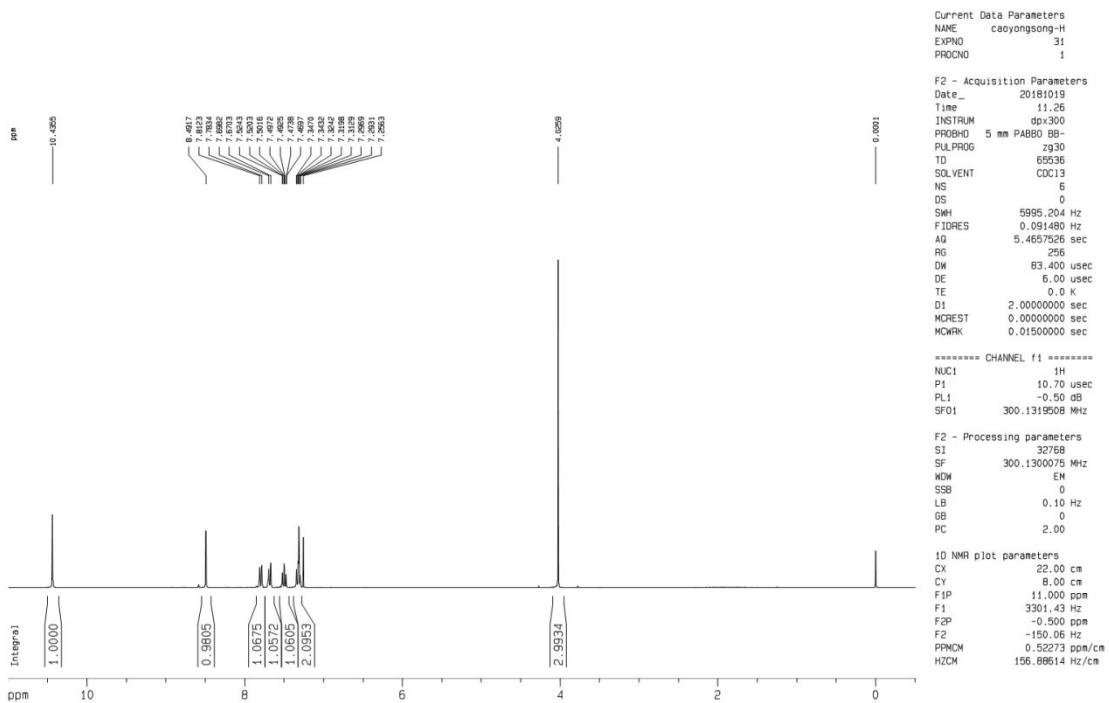


Fig. S3 ^1H NMR (300.13 MHz; CDCl_3) of **Est2** (Methyl 3-hydroxy-2-naphthoate)

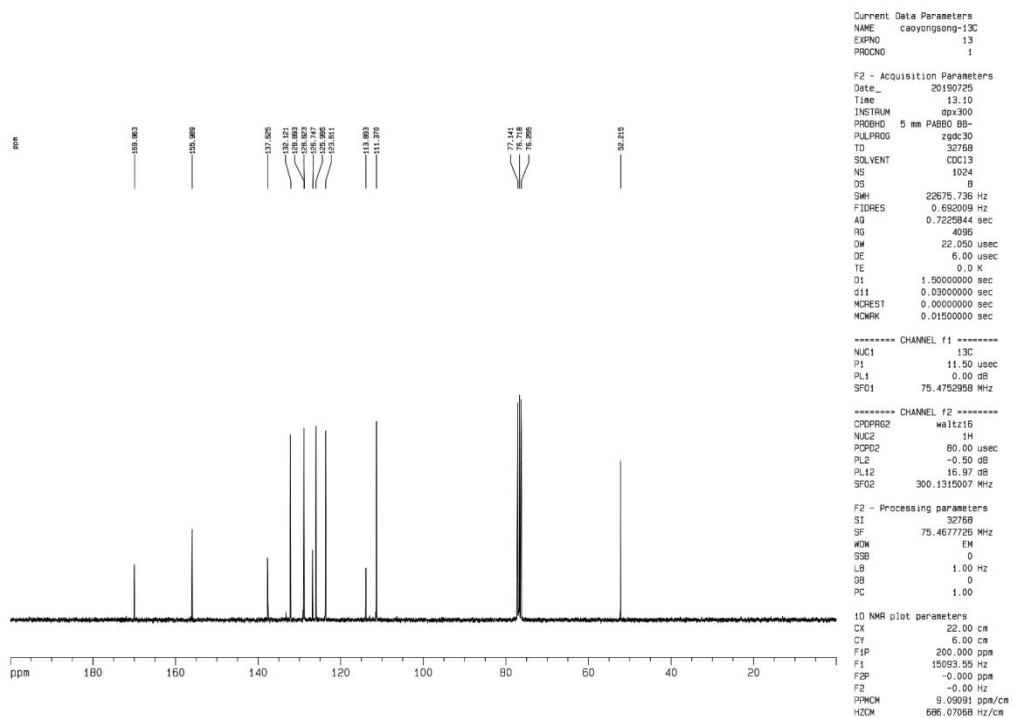


Fig. S4 ^{13}C NMR (75.47 MHz; CDCl_3) of **Est2** (Methyl 3-hydroxy-2-naphthoate)

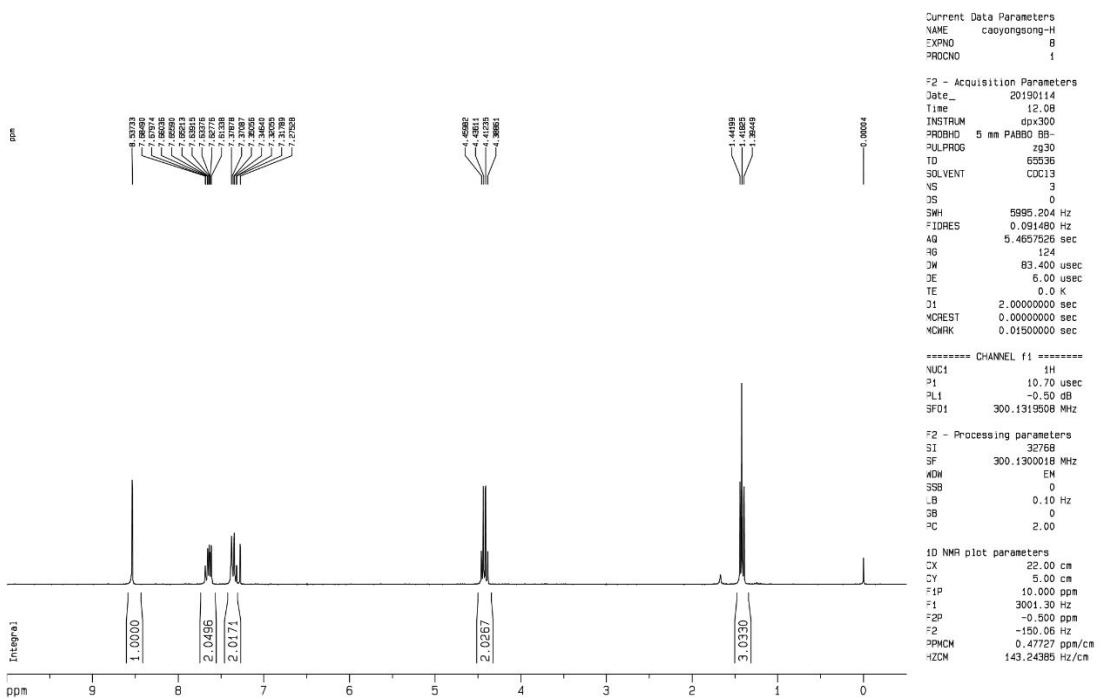


Fig. S5 ^1H NMR (300.13 MHz; CDCl_3) of **Est3** (Ethyl 2-oxo-2H-chromene-6-carboxylate)

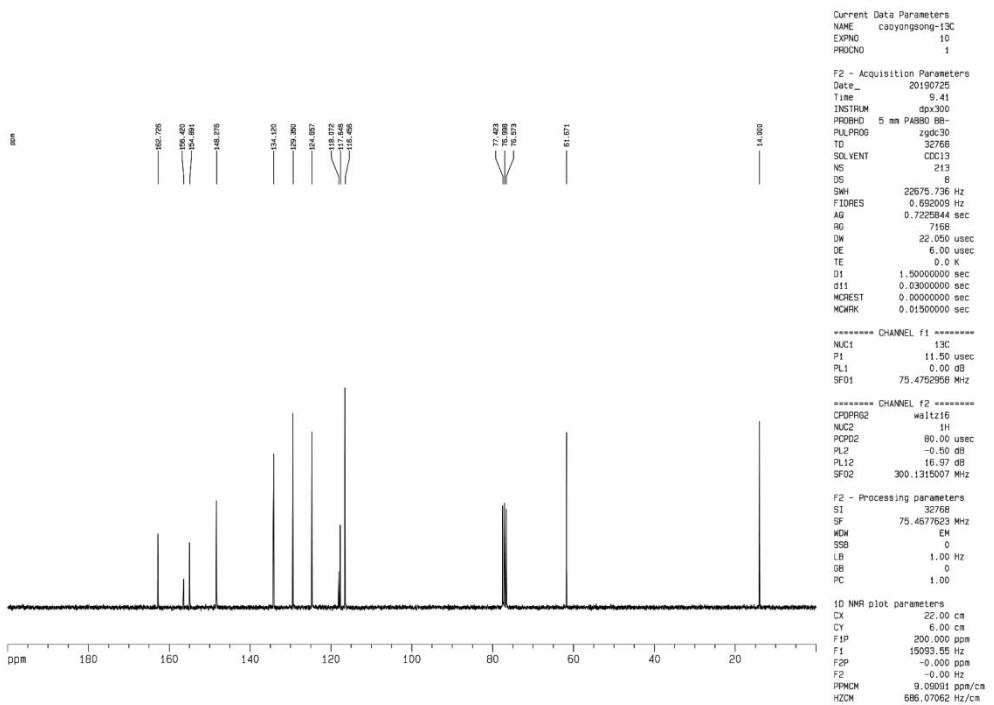


Fig. S6 ^{13}C NMR (75.47 MHz; CDCl_3) of **Est3** (Ethyl 2-oxo-2H-chromene-6-carboxylate)

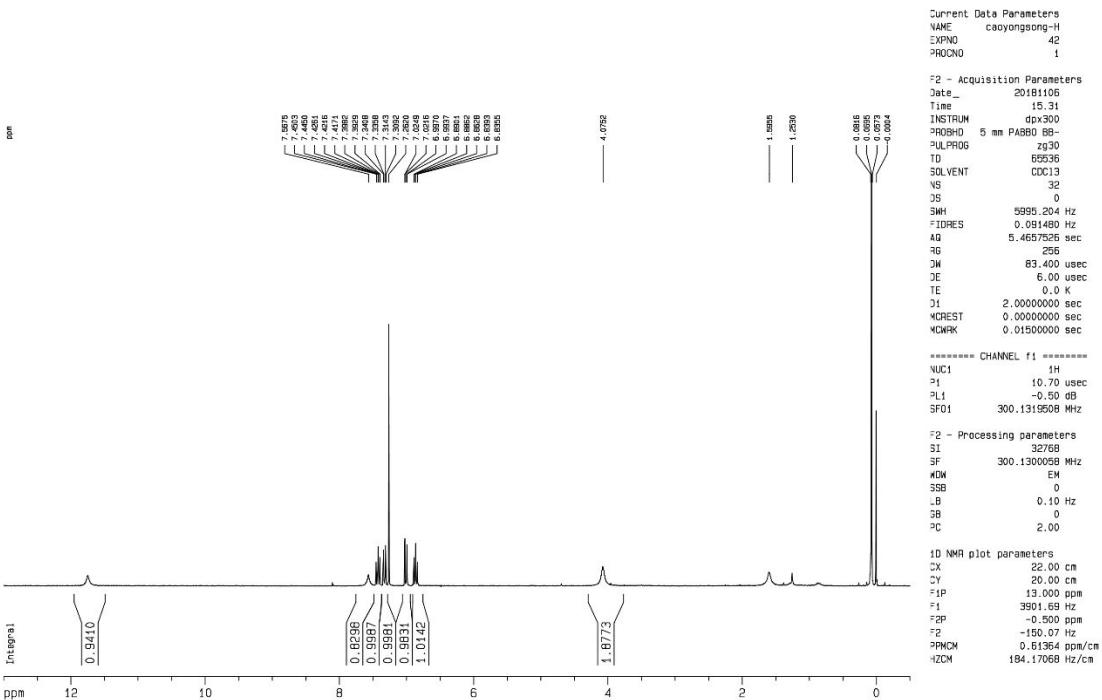


Fig. S7 ^1H NMR (300.13 MHz; CDCl_3) of **Frcl** (2-Hydroxybenzohydrazide)

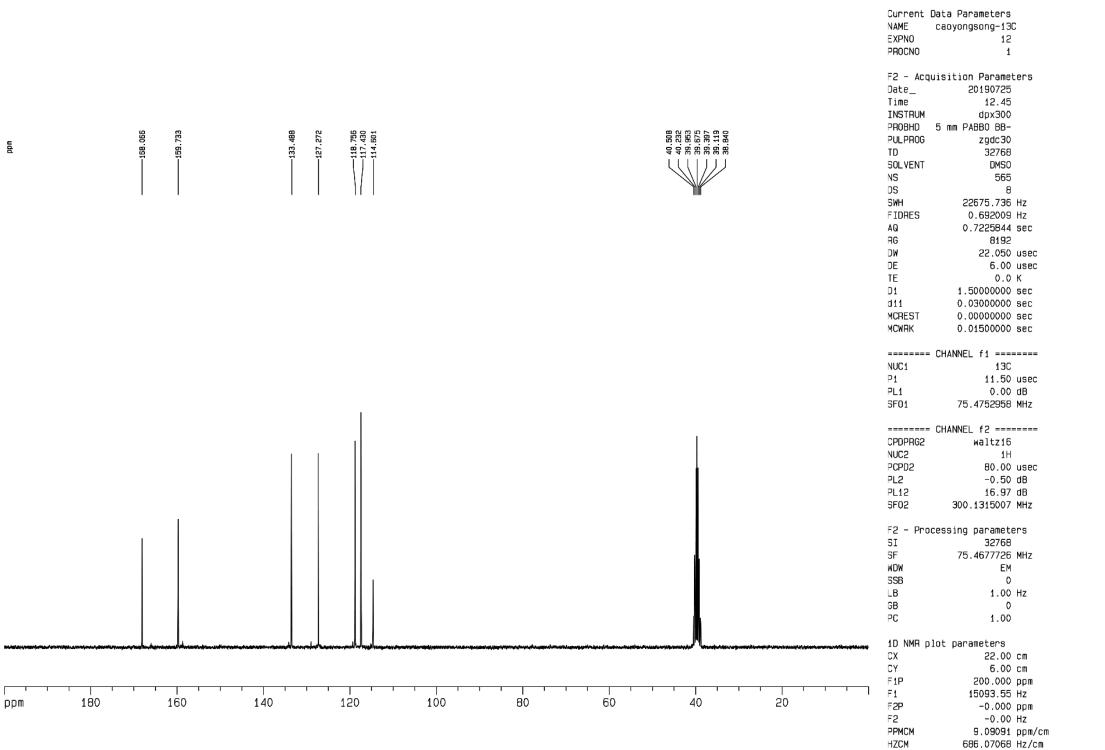


Fig. S8 ^{13}C NMR (75.47 MHz; DMSO) of **Frcl** (2-Hydroxybenzohydrazide)

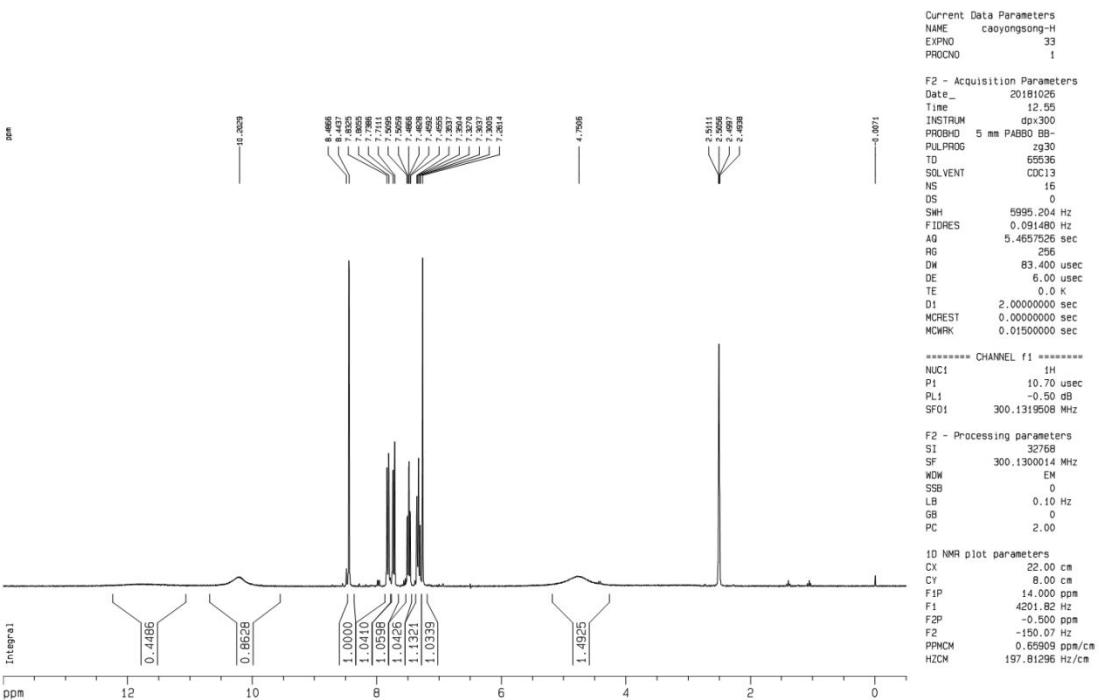


Fig. S9 ^1H NMR (300.13 MHz; DMSO) of **Frc2** (3-Hydroxy-2-naphthohydrazide)

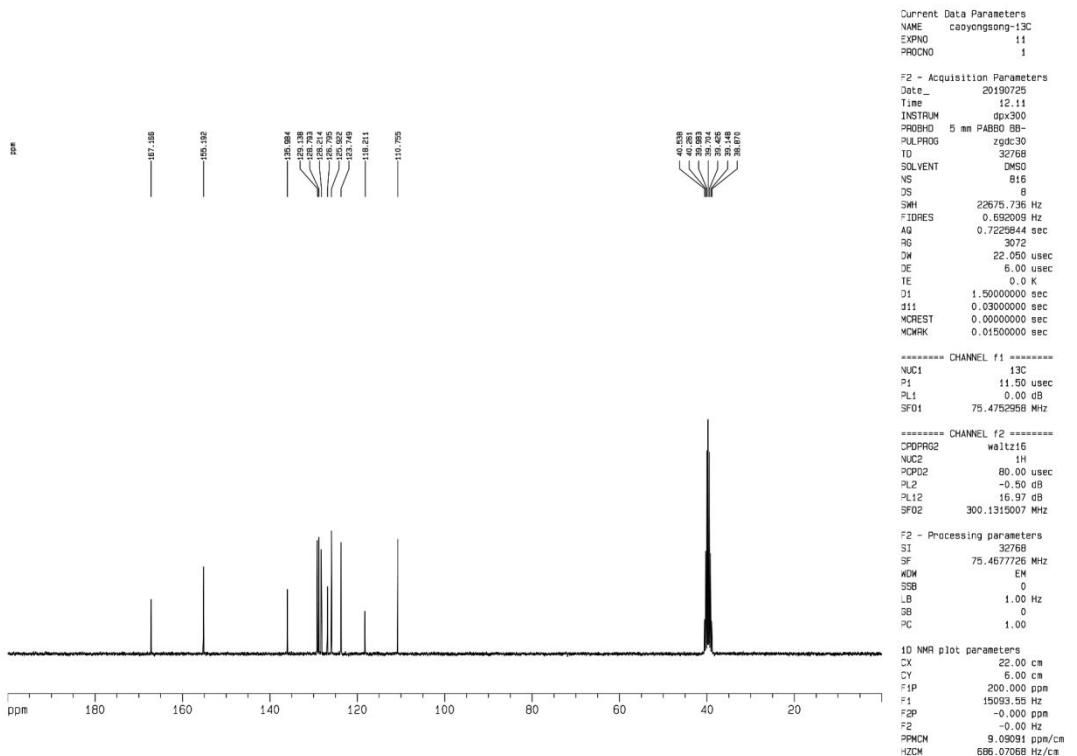


Fig. S10 ^{13}C NMR (75.47 MHz; DMSO) of **Frc2** (3-Hydroxy-2-naphthohydrazide)

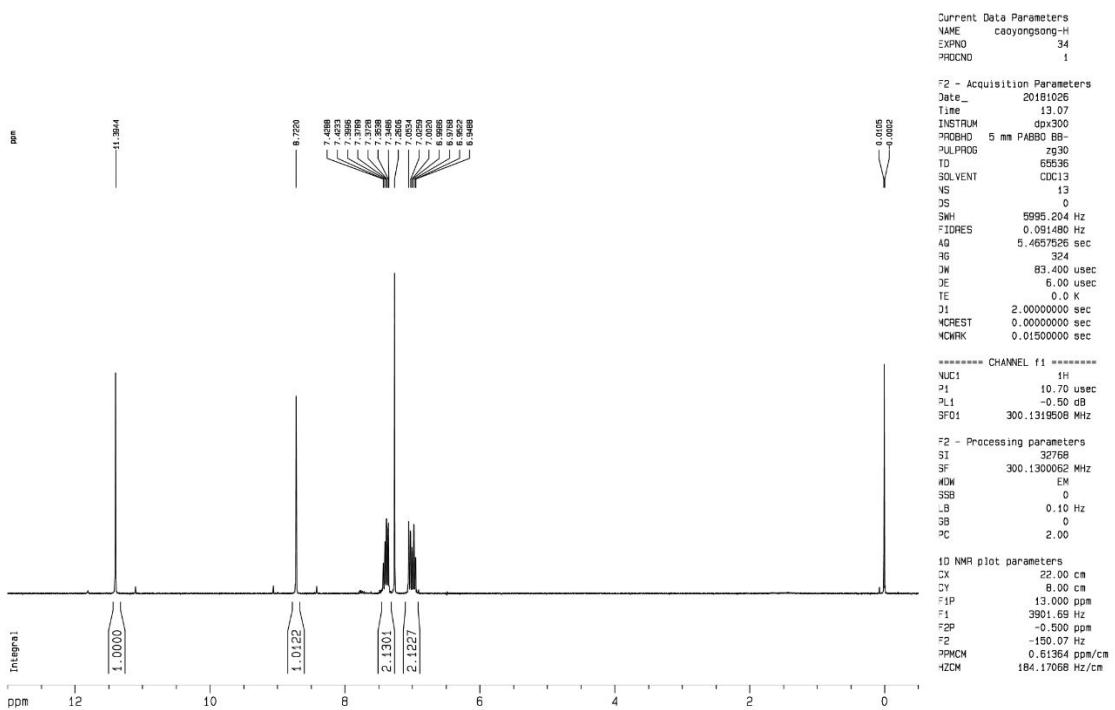


Fig. S11 ^1H NMR (300.13 MHz; CDCl_3) of FrC3 (2-Oxo-2H-chromene-6-carbohydrazide)

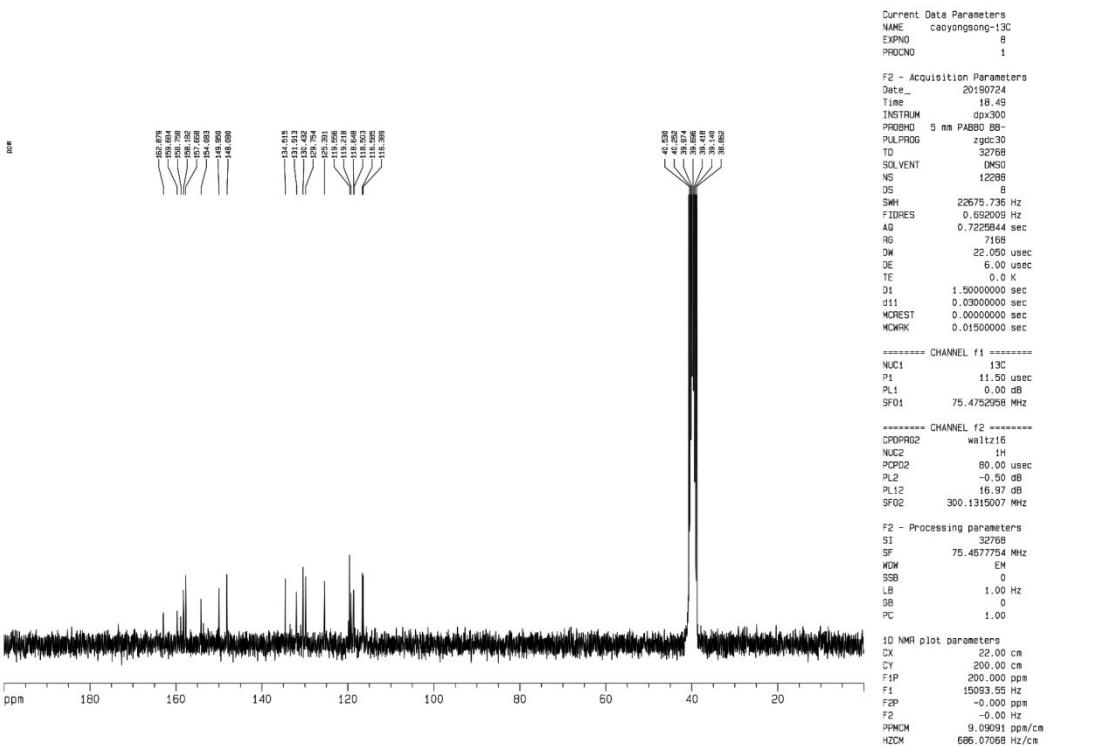


Fig. S12 ^{13}C NMR (75.47 MHz; DMSO) of FrC3 (2-Oxo-2H-chromene-6-carbohydrazide)

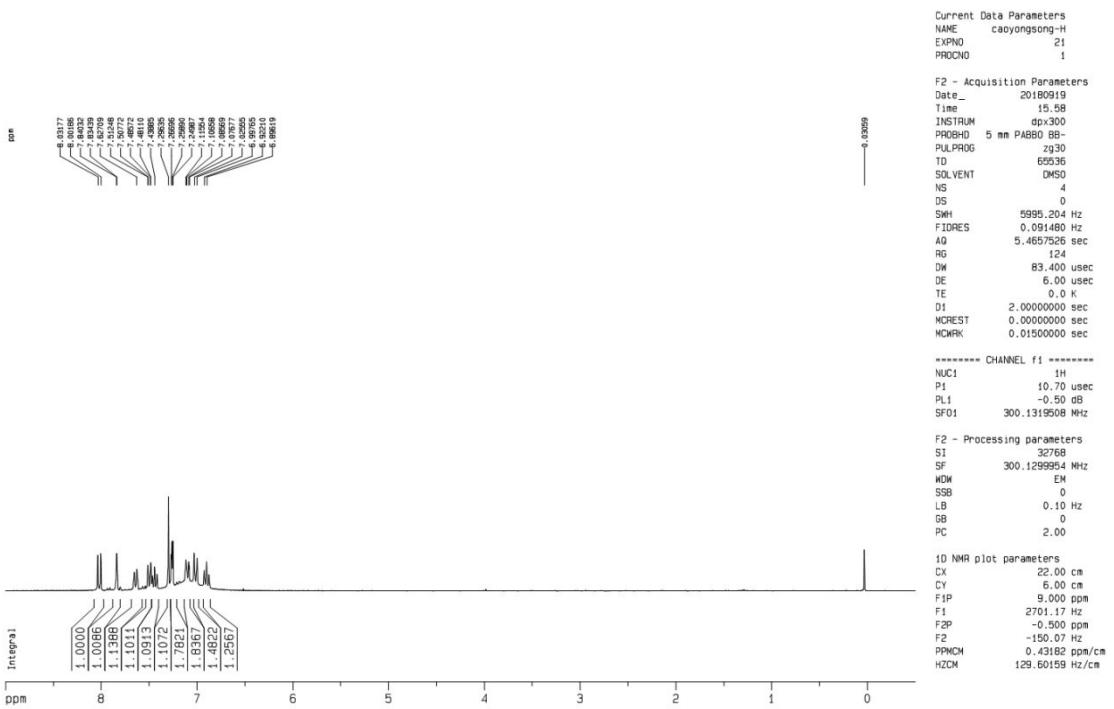


Fig. S13 ^1H NMR (300.13 MHz; CDCl_3) of **HIL1**

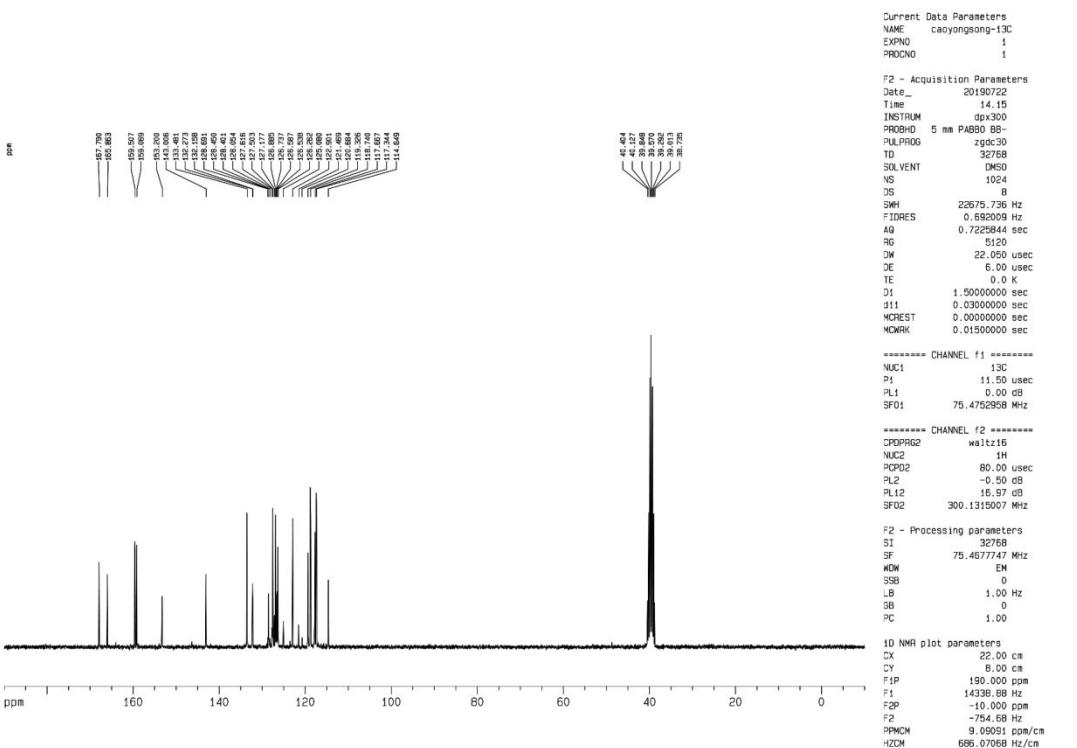


Fig. S14 ^{13}C NMR (75.47 MHz; DMSO) of **HIL1**

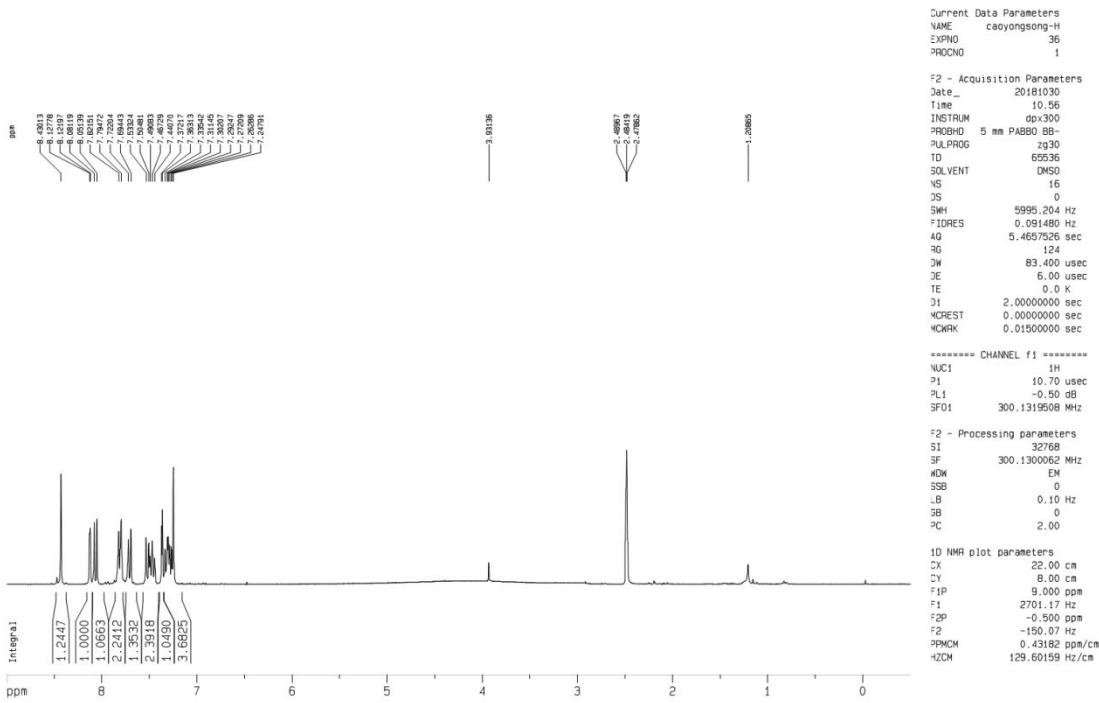


Fig. S15 ^1H NMR (300.13 MHz; CDCl_3) of **HIL2**

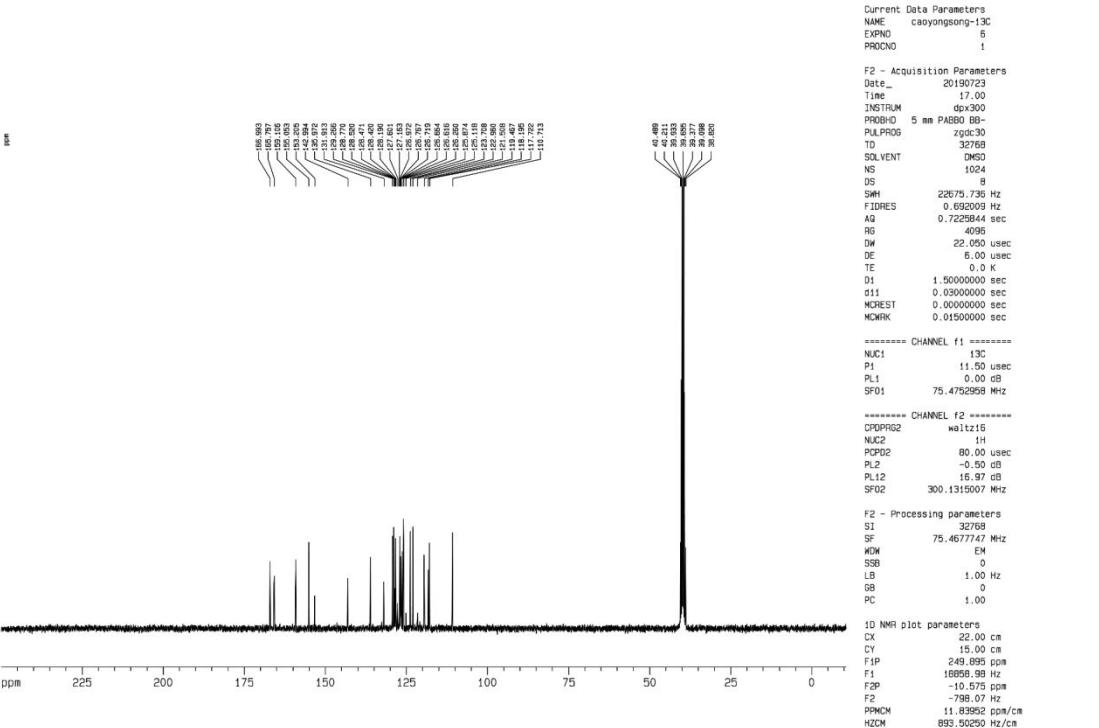


Fig. S16 ^{13}C NMR (75.47 MHz; DMSO) of **HIL2**

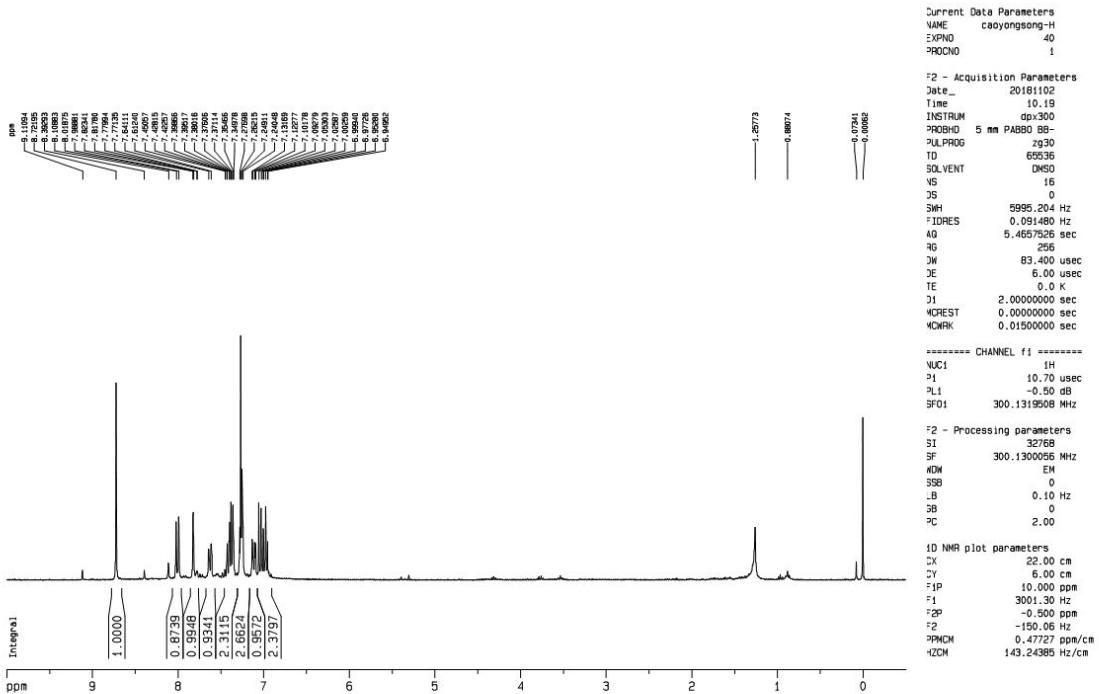


Fig. S17 ^1H NMR (300.13 MHz; CDCl_3) of HIL3

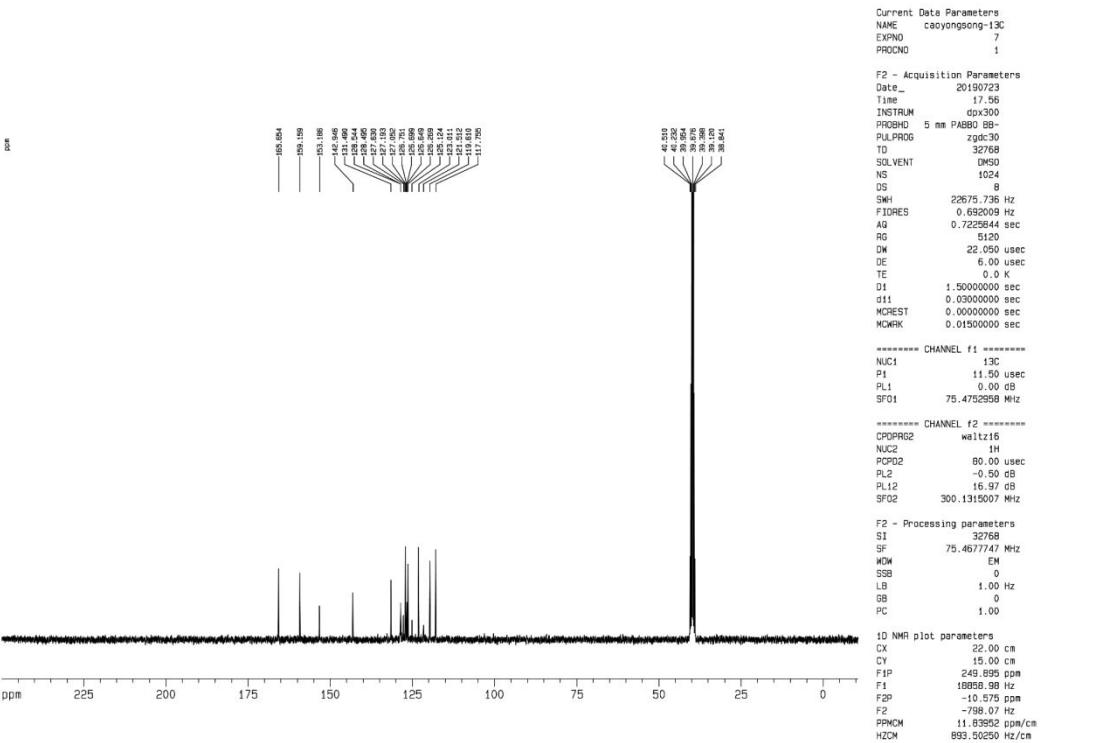


Fig. S18 ^{13}C NMR (75.47 MHz; DMSO) of HIL3

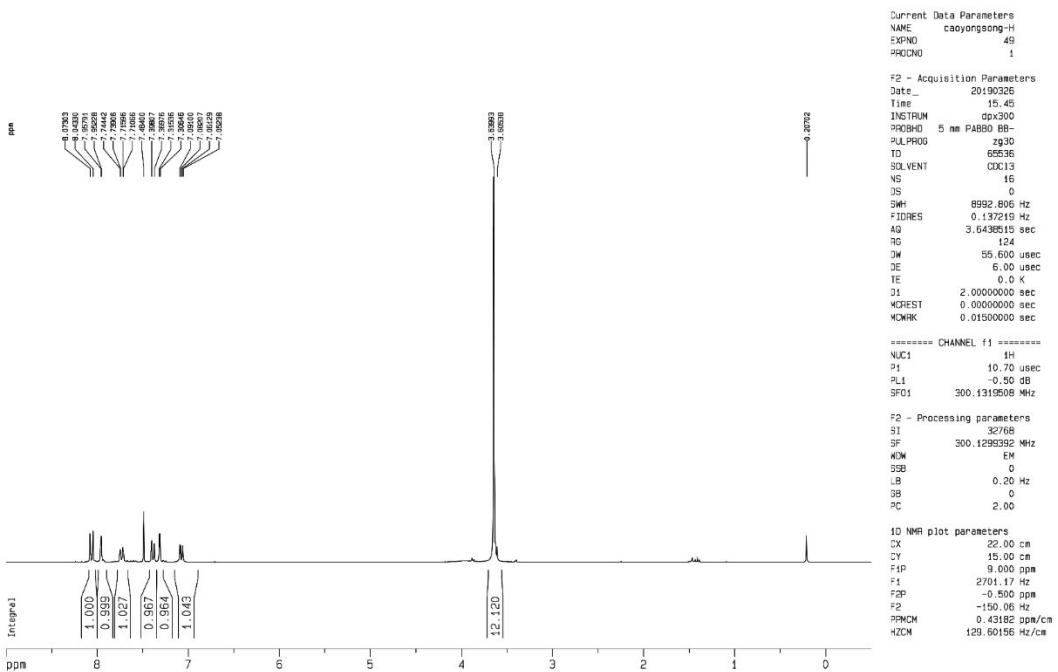


Fig. S19 ¹H NMR (300.13 MHz; CDCl₃) of HIL4

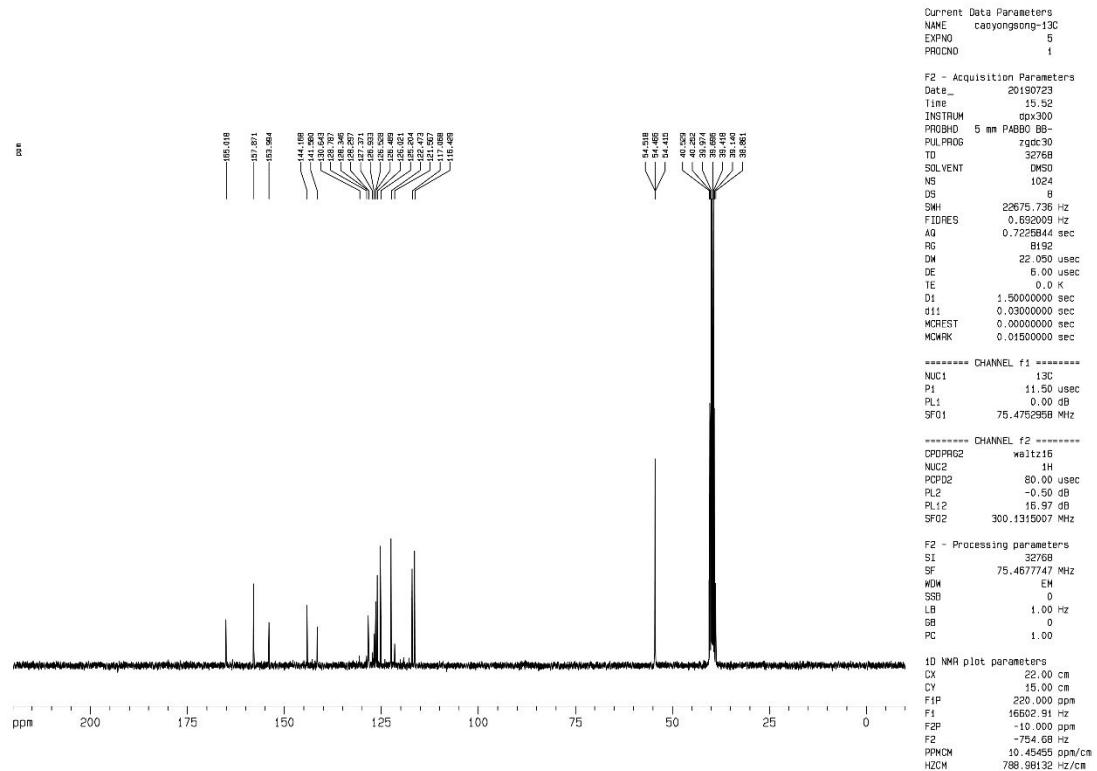


Fig. S20 ¹³C NMR (75.47 MHz; DMSO) of HIL4

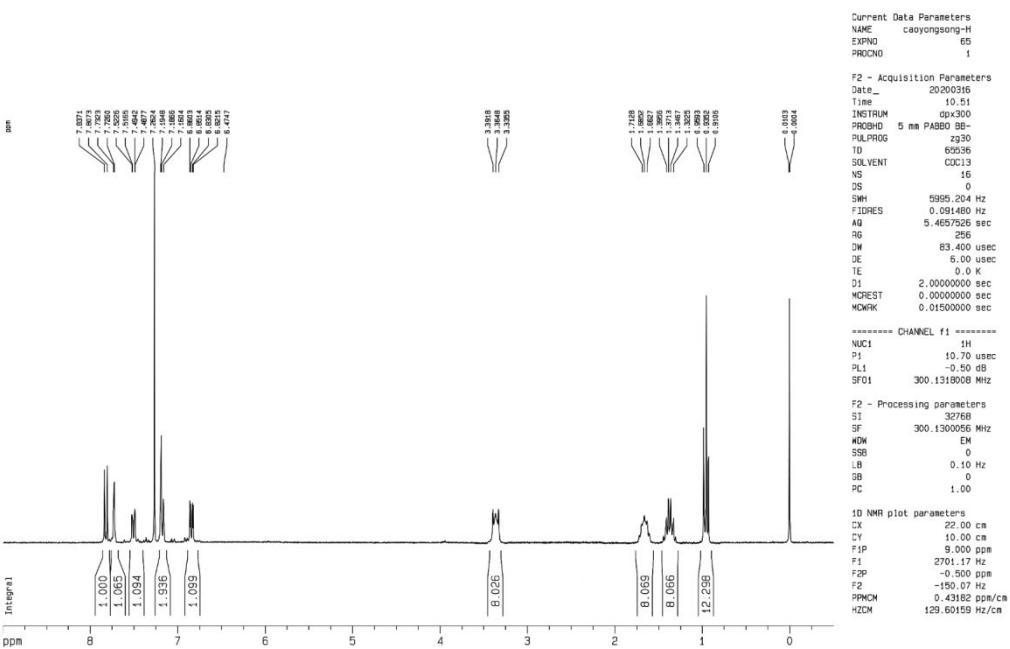


Fig. S21 ^1H NMR (300.13 MHz; CDCl_3) of **HIL5**

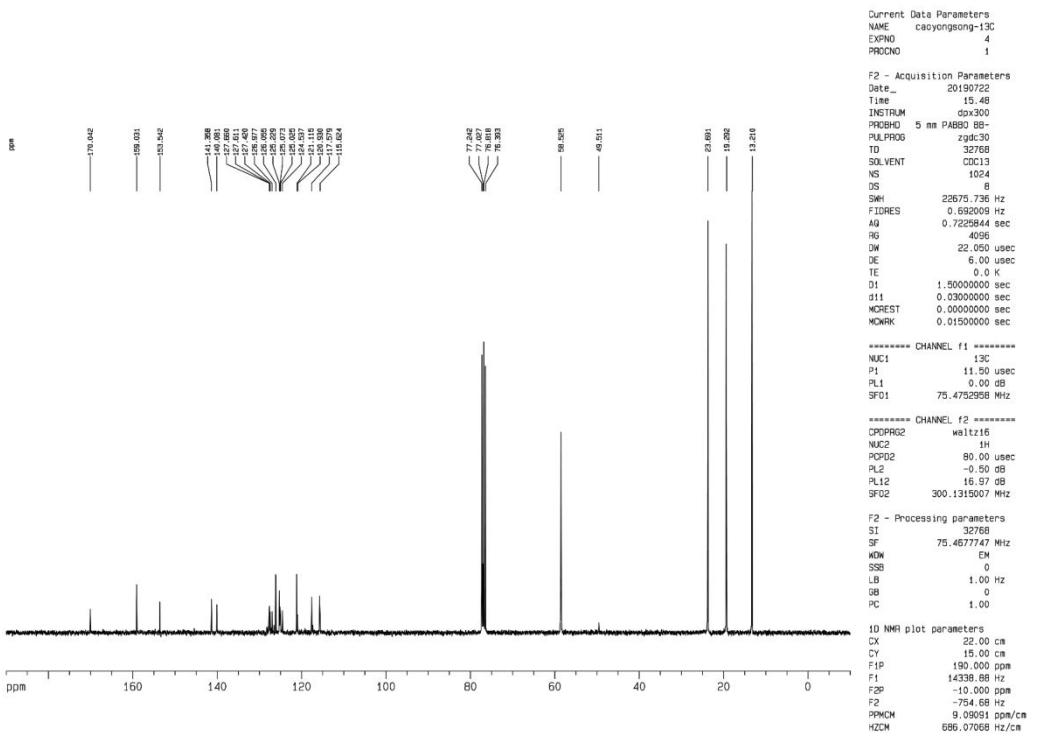


Fig. S22 ^{13}C NMR (75.47 MHz; CDCl_3) of **HIL5**

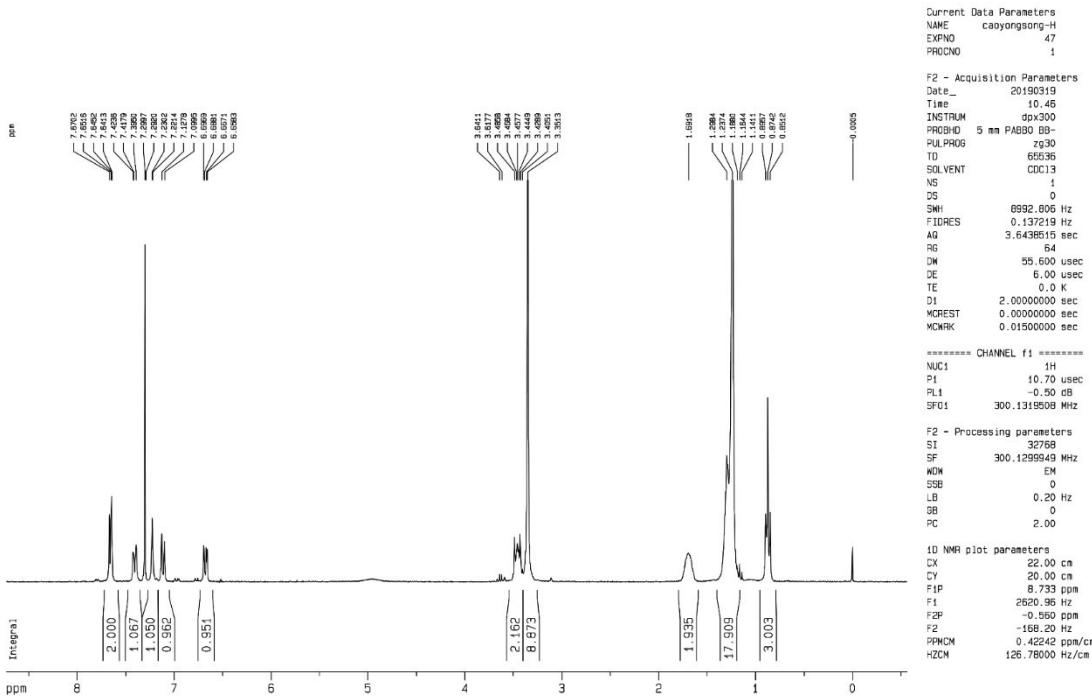


Fig. S23 ^1H NMR (300.13 MHz; CDCl_3) of **HIL6**

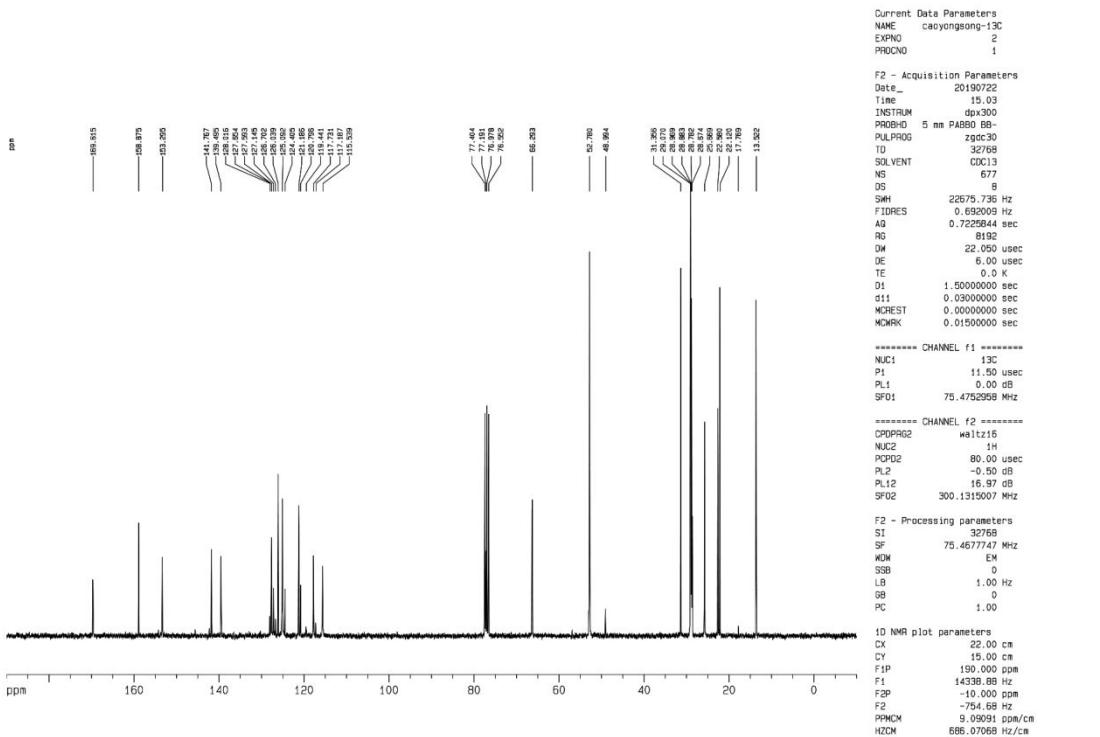


Fig. S24 ^{13}C NMR (75.47 MHz; CDCl_3) of **HIL6**

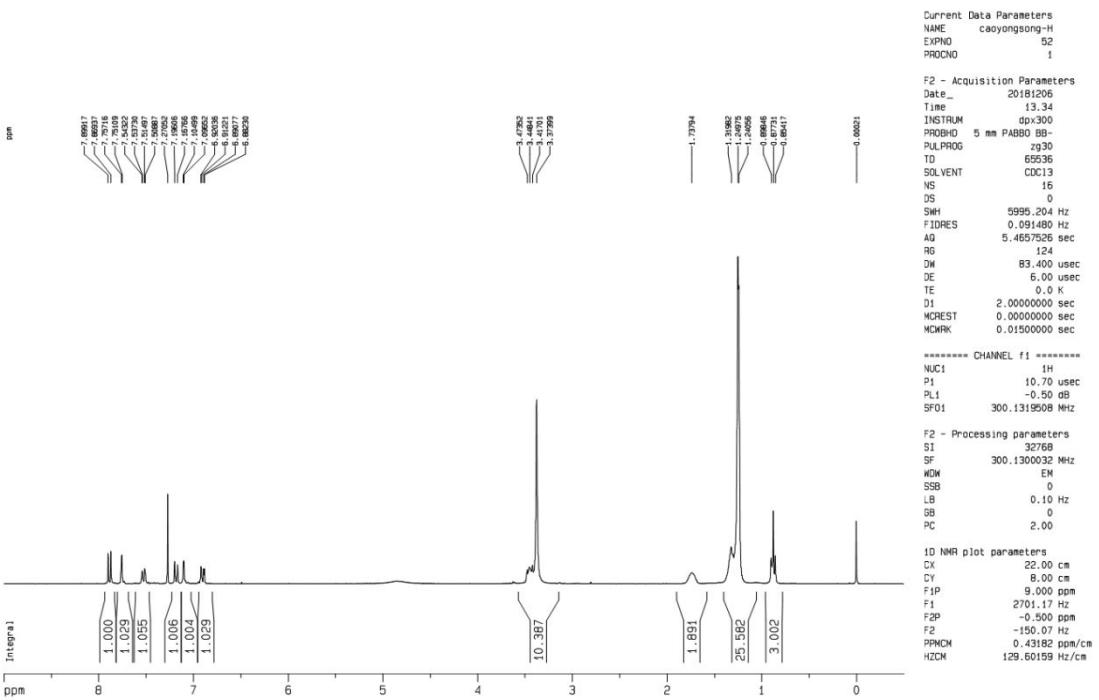


Fig. S25 ^1H NMR (300.13 MHz; CDCl_3) of **HIL7**

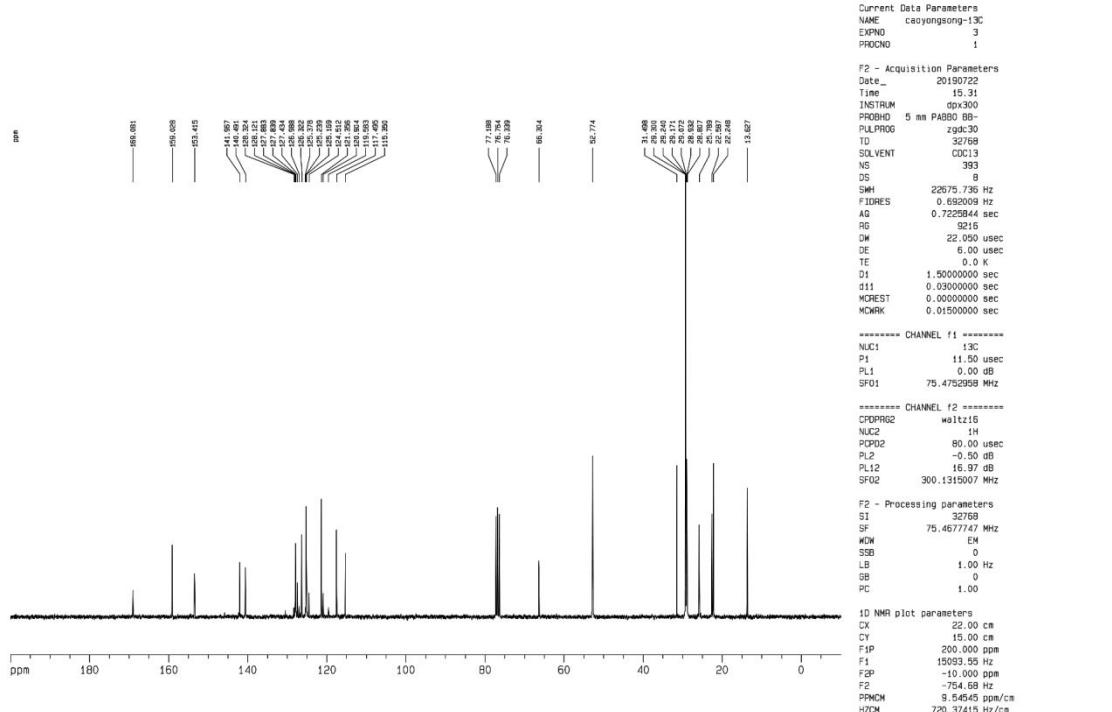


Fig. S26 ^1C NMR (75.47 MHz; CDCl_3) of **HIL7**

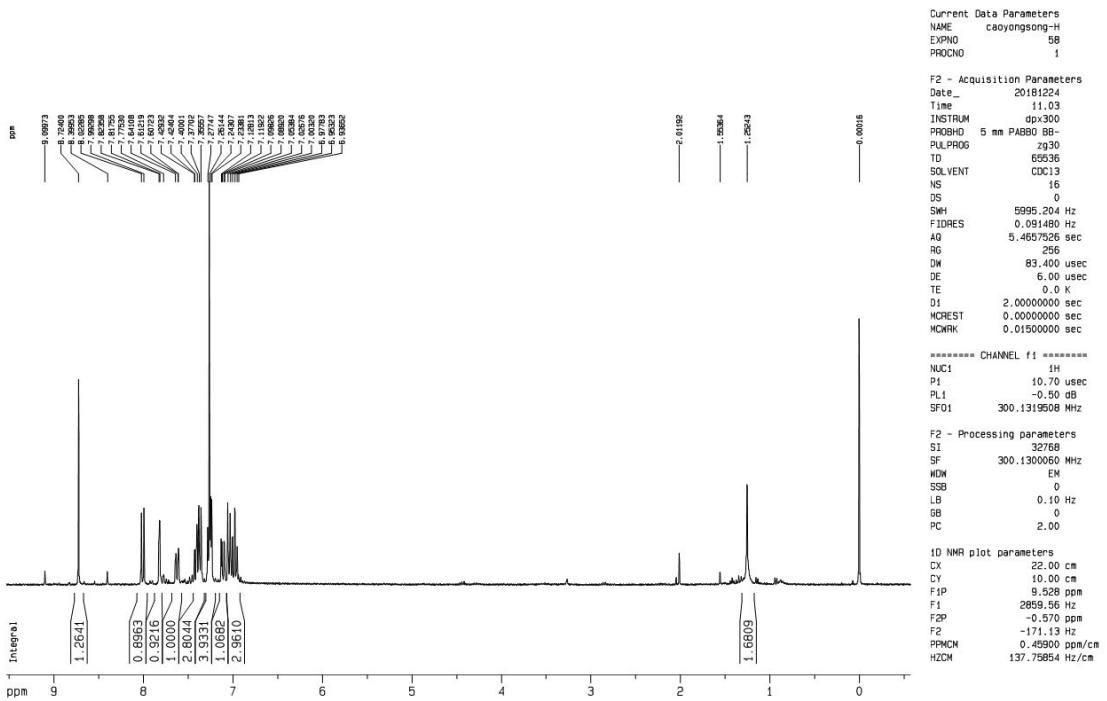


Fig. S27 ^1H NMR (300.13 MHz; CDCl_3) of **HIL8**

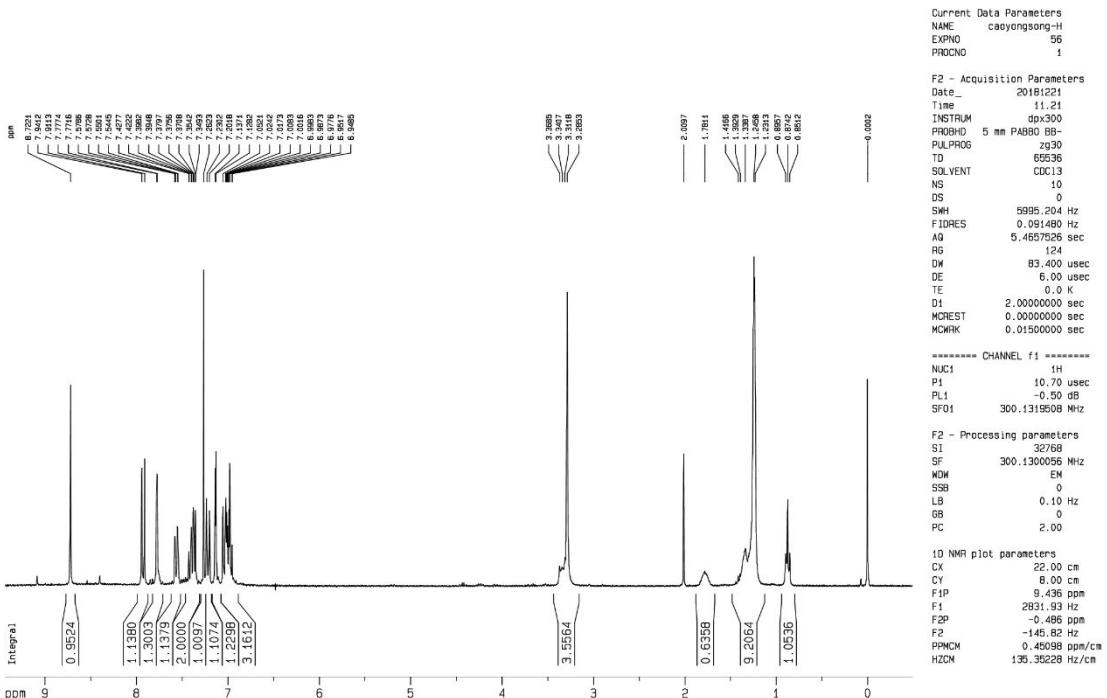


Fig. S28 ^1H NMR (300.13 MHz; CDCl_3) of **HIL9**

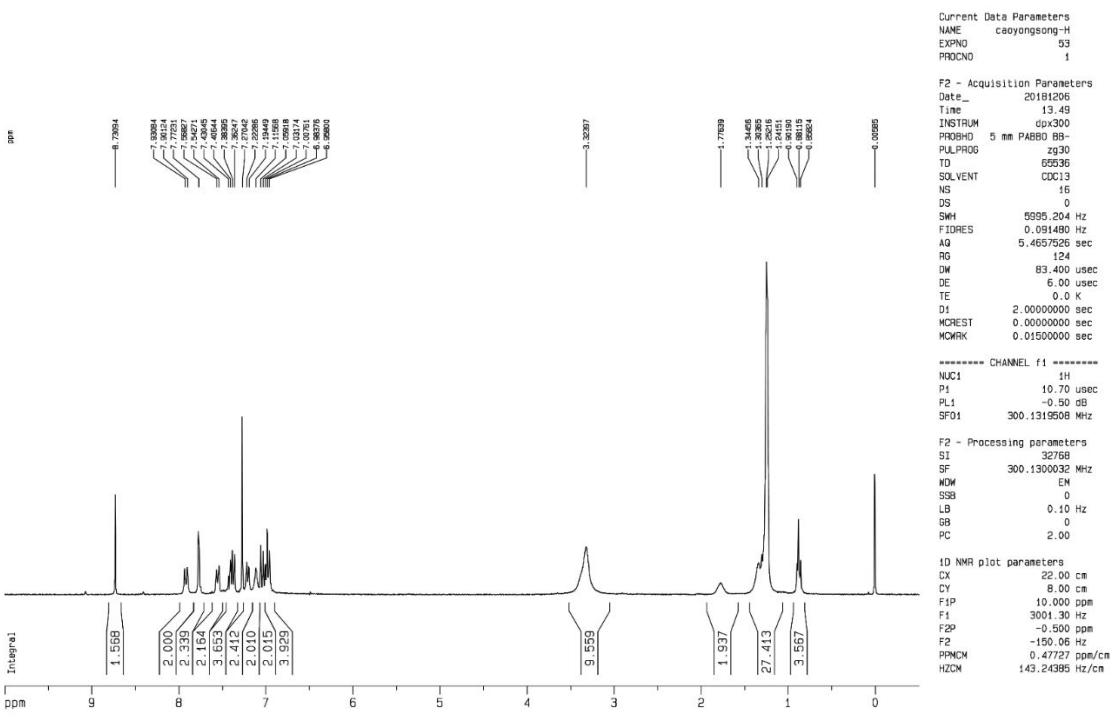


Fig. S29 ^1H NMR (300.13 MHz; CDCl_3) of **HIL10**

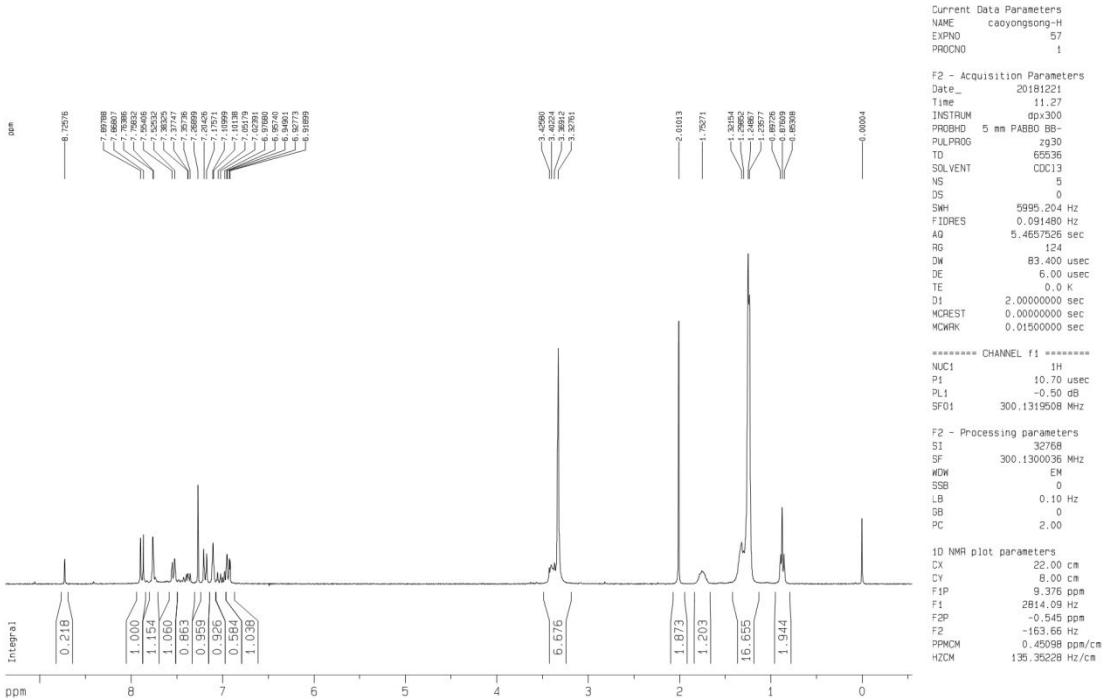


Fig. S30 ^1H NMR (300.13 MHz; CDCl_3) of HIL11

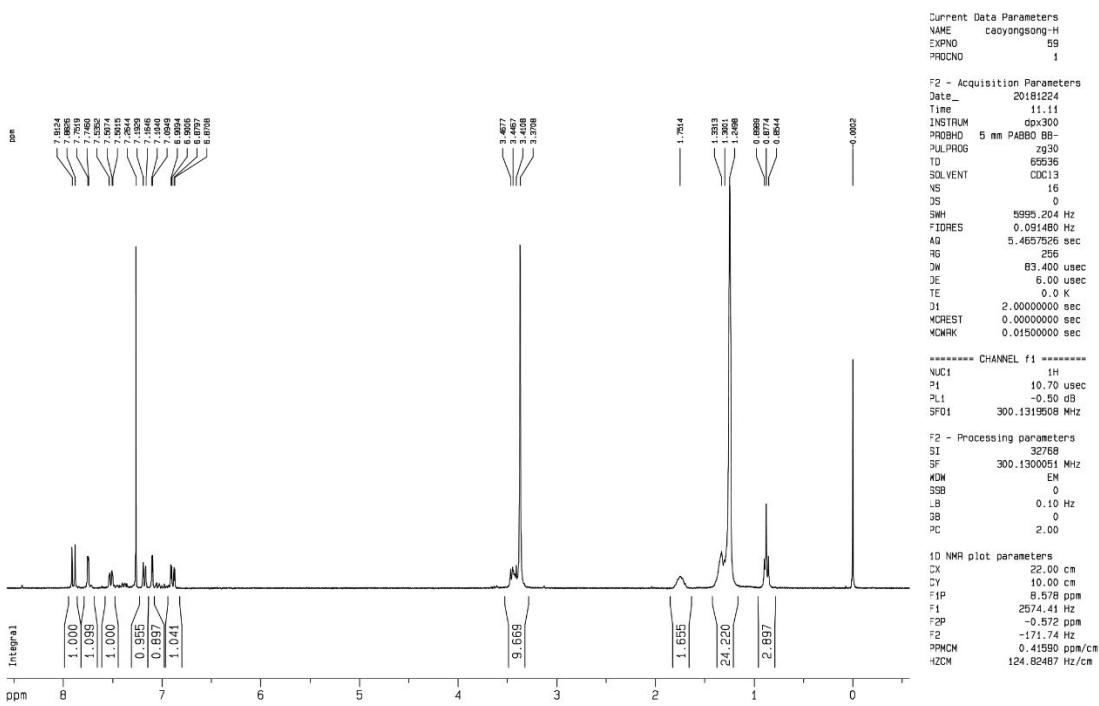


Fig. S31 ¹H NMR (300.13 MHz; CDCl₃) of **HIL12**

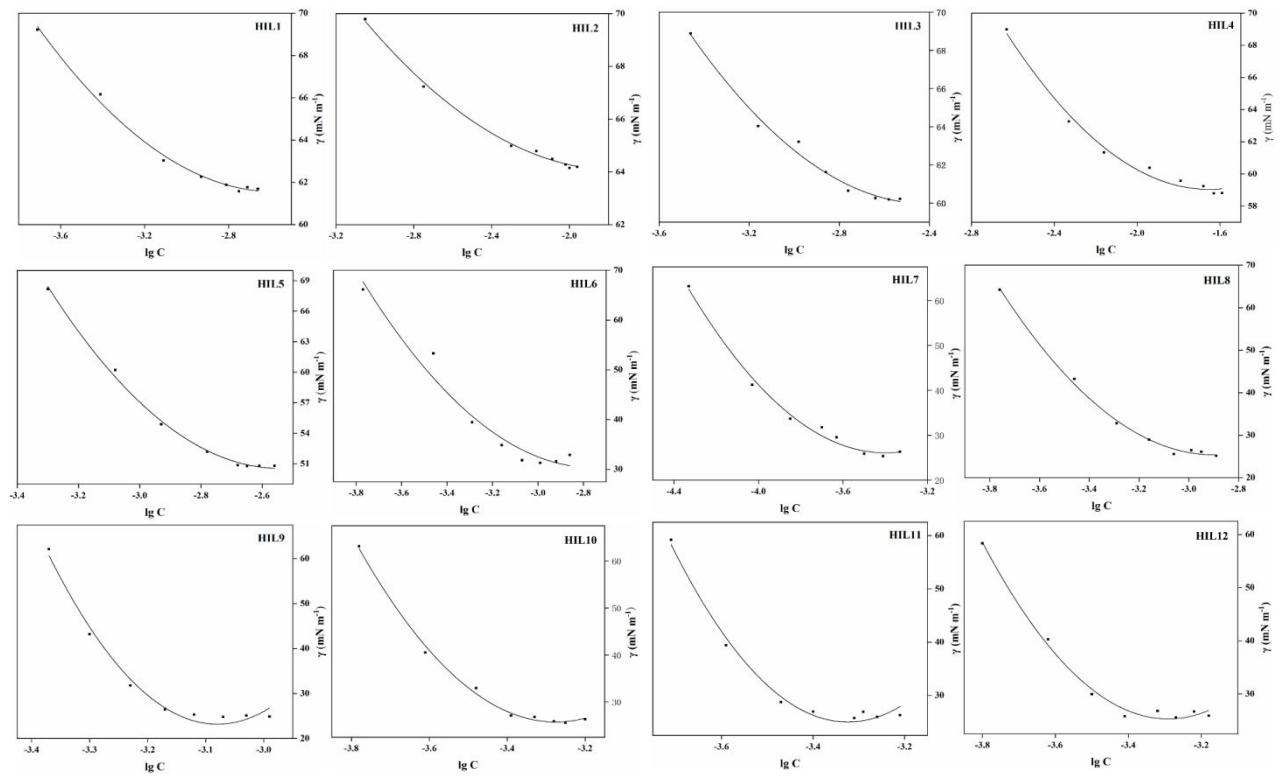


Fig. S32 The surface tension curves (γ - $\lg C$ curves) for HIL1-12.

TableS1 The values of critical micelle concentration (CMC) of HIL1-12

#	Abbreviation	CMC (mol/L)
1	HIL1	1.291×10^{-3}
2	HIL2	7.079×10^{-3}
3	HIL3	1.738×10^{-3}
4	HIL4	0.015
5	HIL5	1.950×10^{-3}
6	HIL6	7.856×10^{-3}
7	HIL7	3.548×10^{-4}
8	HIL8	7.586×10^{-4}
9	HIL9	7.244×10^{-4}
10	HIL10	4.677×10^{-4}
11	HIL11	3.802×10^{-4}
12	HIL12	4.074×10^{-4}