---------- *Supplemental Information* ----------

Crystal Engineering Construction of Caffeic Acid Derivatives with Potential Applications in Pharmaceuticals and Degradable Polymeric Materials

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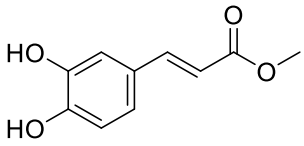
1. Spectra of NMR, FT-IR and UV-Vis.

1.1. NMR spectra of MC, CBDE-10, and CBDA-10.



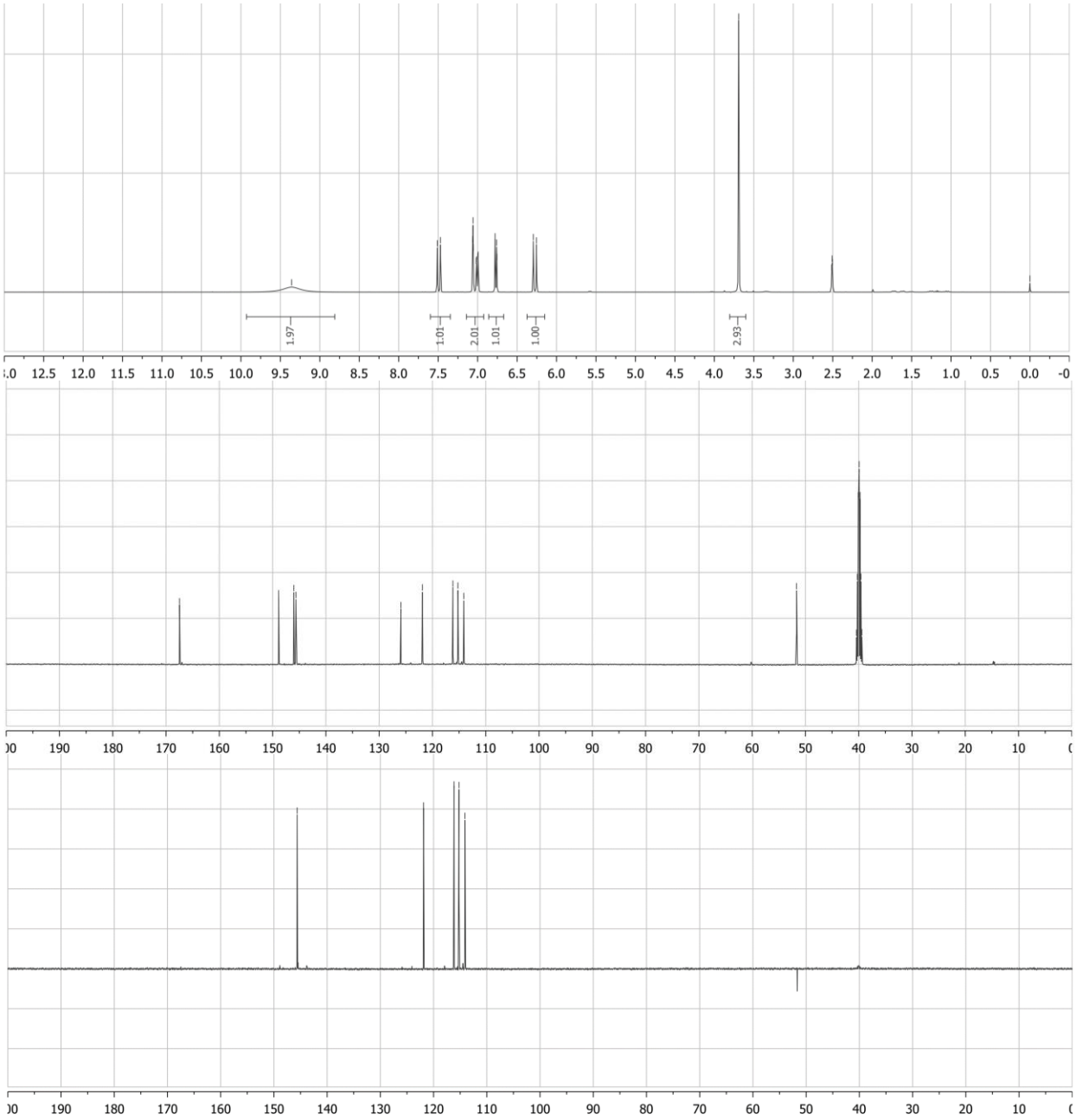


Figure S1. ^{1}H- (top), ^{13}C- (middle), and DEPT90- (bottom) NMR spectra of MC in DMSO-d_6.

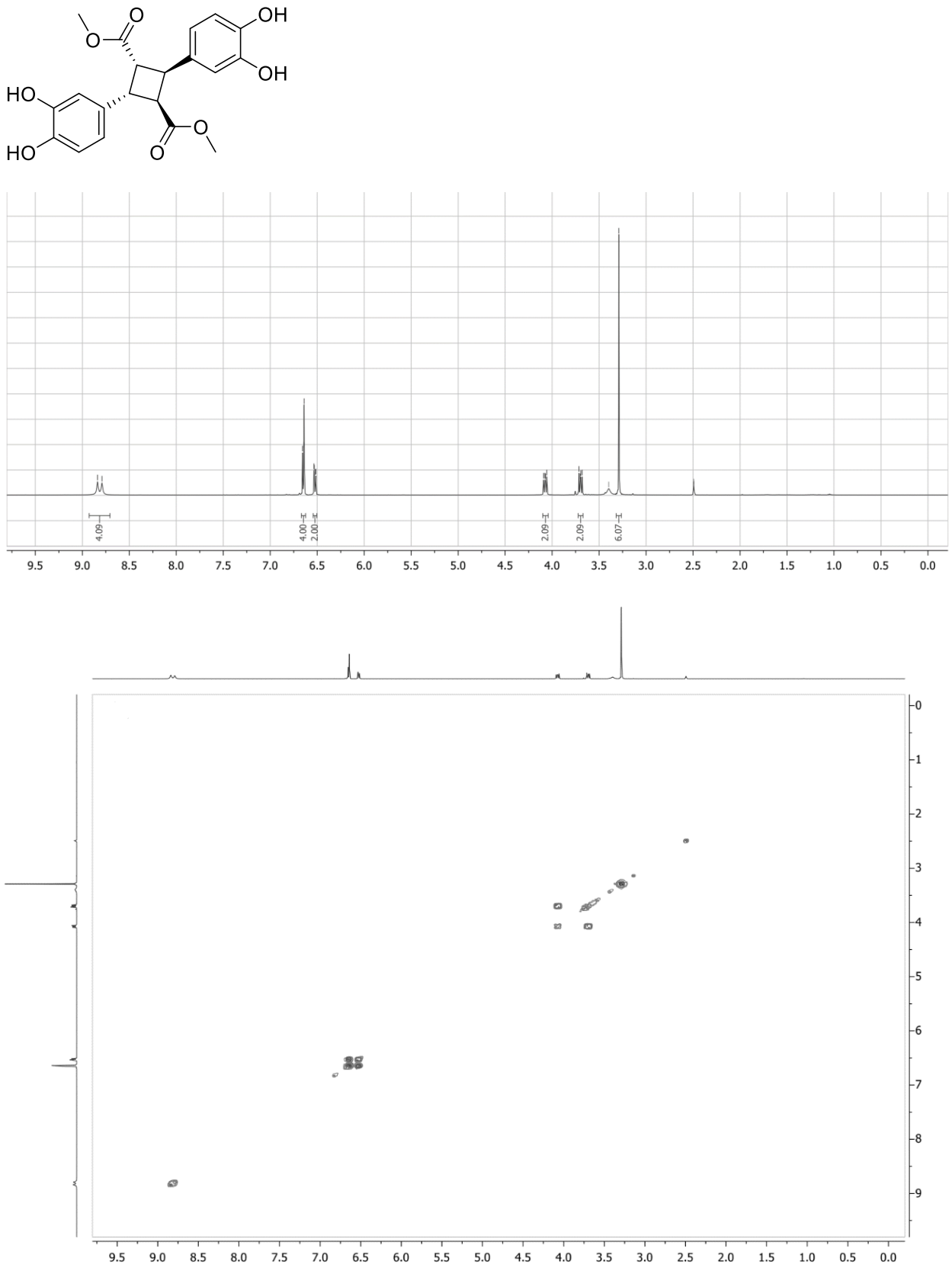


Figure S2. ^{1}H- (top) and COSY- (bottom) NMR spectra of CBDE-10 in DMSO-d_6.

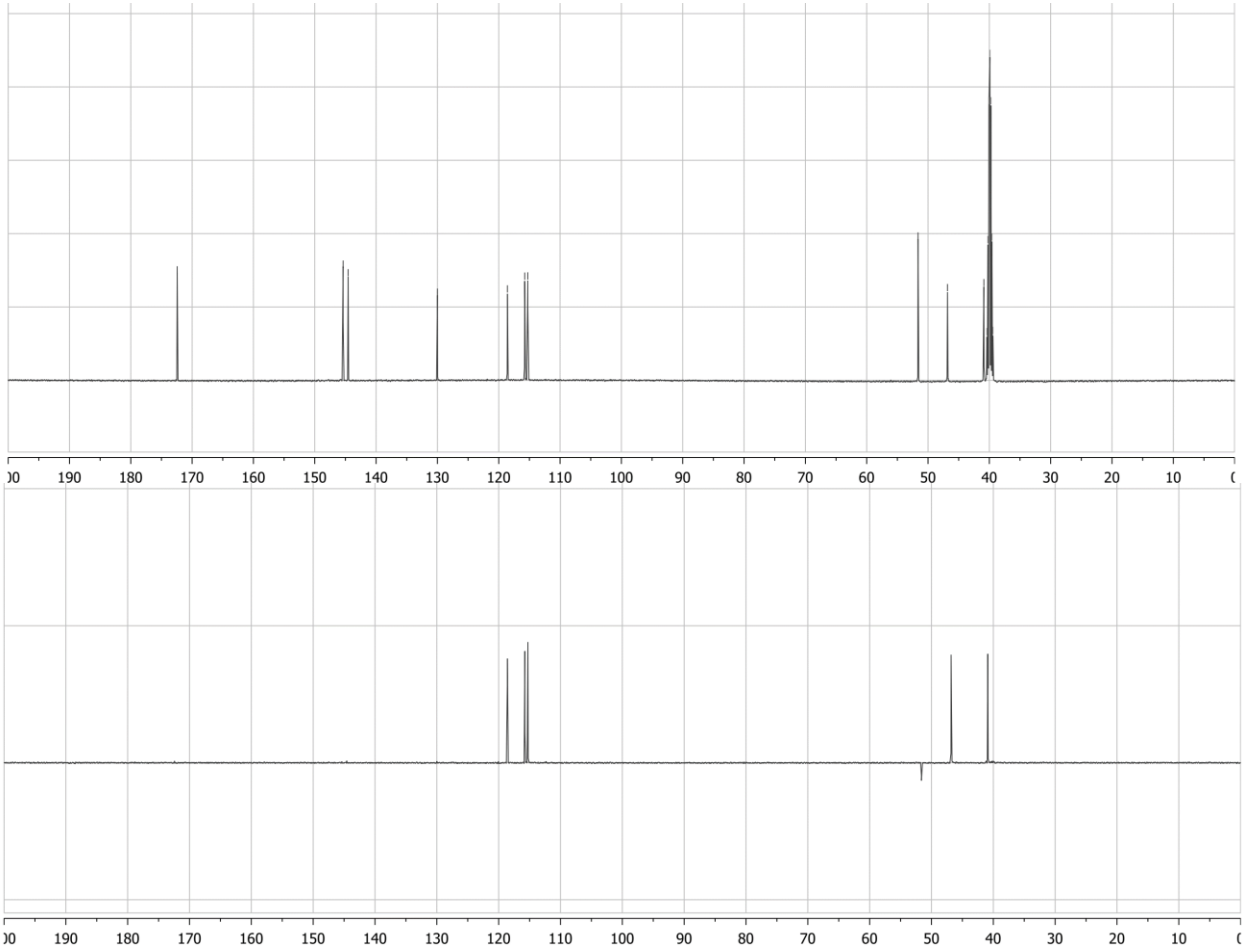


Figure S2 continued. ^{13}C- (top) and DEPT90- (bottom) NMR spectra of CBDE-10 in DMSO-d_6.

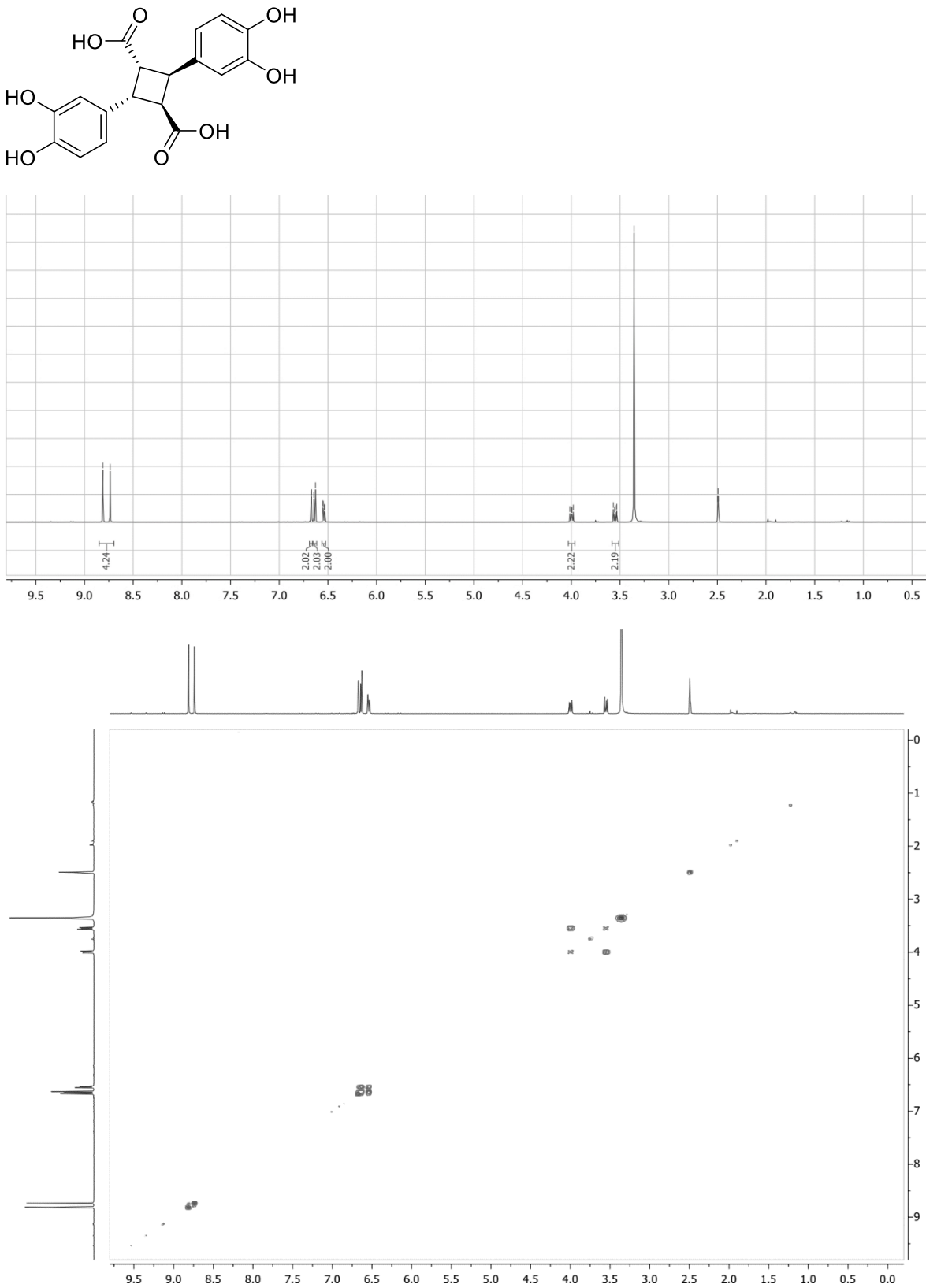


Figure S3. ^{1}H- (top) and COSY- (bottom) NMR spectra of CBDA-10 in DMSO-d_6.

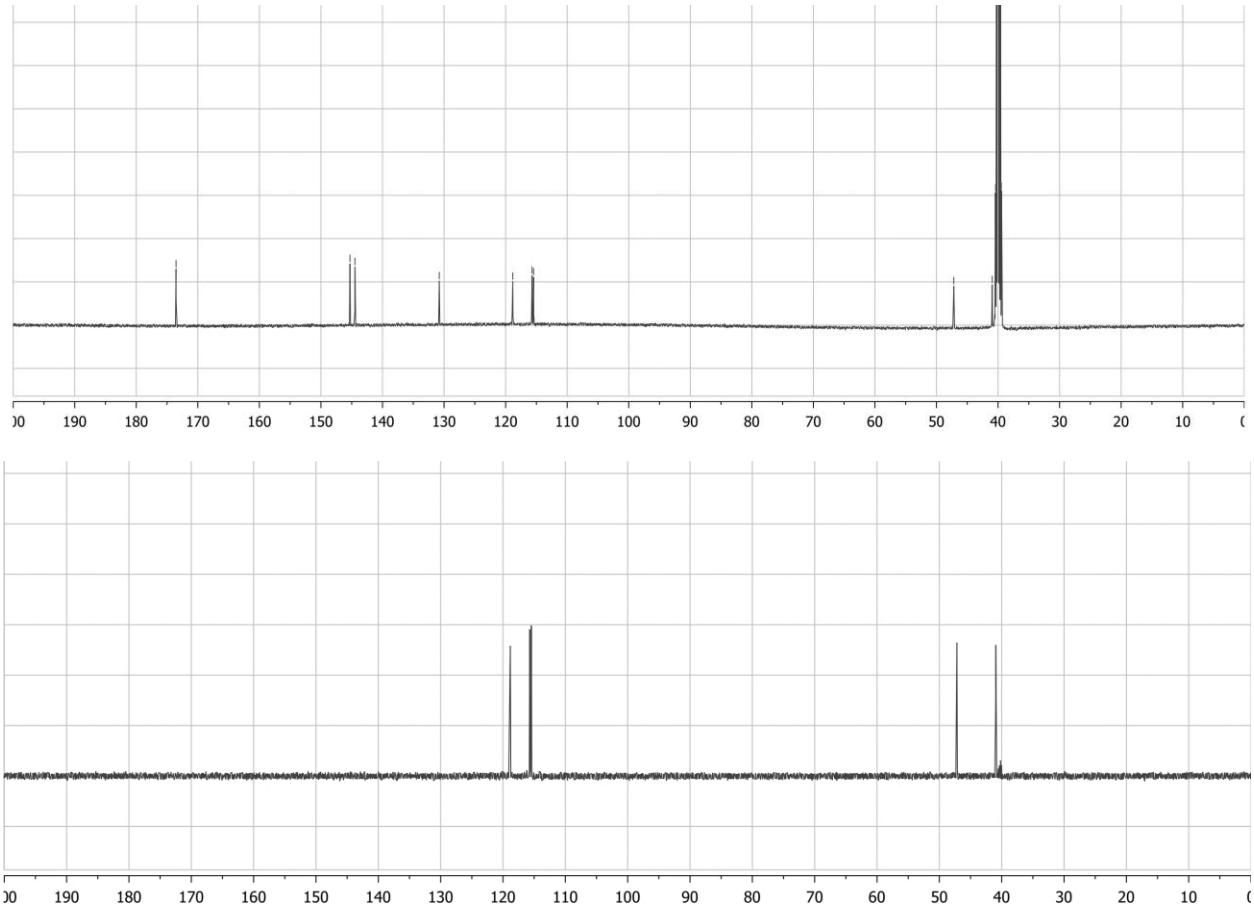


Figure S3 continued. ^{13}C- (top) and DEPT90- (bottom) NMR spectra of CBDA-10 in DMSO-d_6.

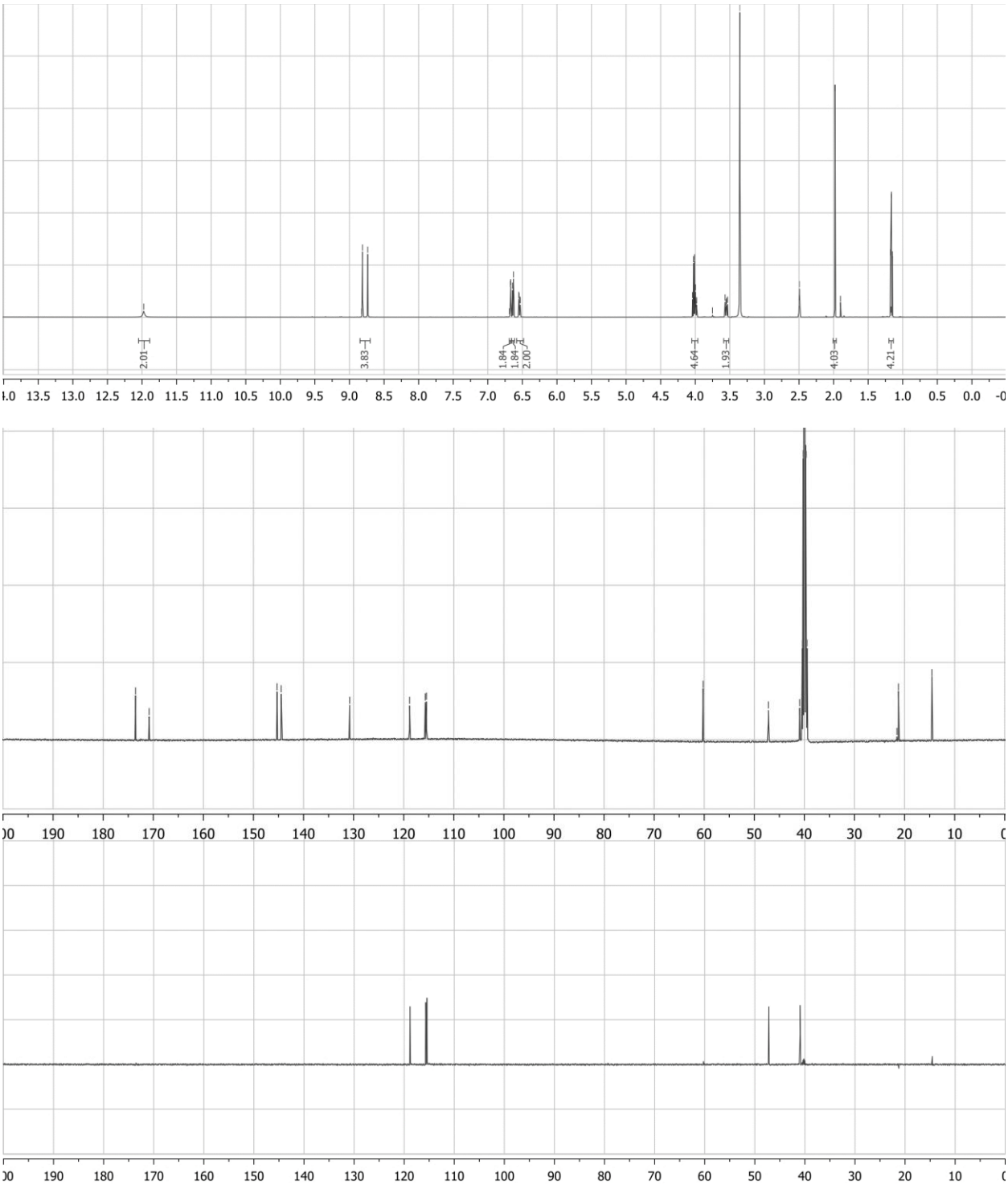


Figure S4. ^{1}H- (top), ^{13}C- (middle), and DEPT90- (bottom) NMR spectra of CBDA10-co-EA crystals in DMSO-d_6.

1.2. FT-IR spectra of CA, MC, CBDE-10, and CBDA-10.

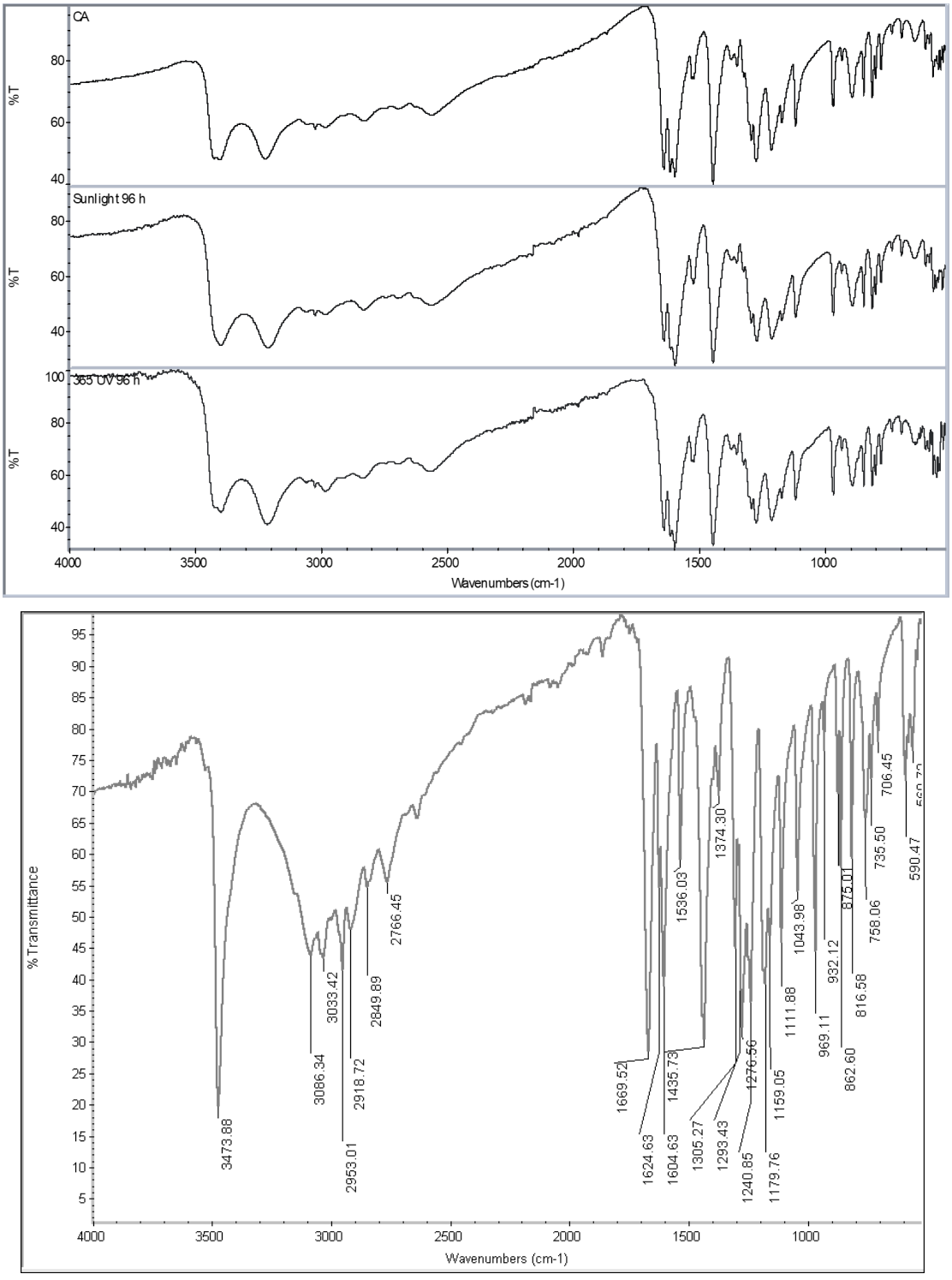


Figure S5. IR spectra of CA (top) and MC (bottom).

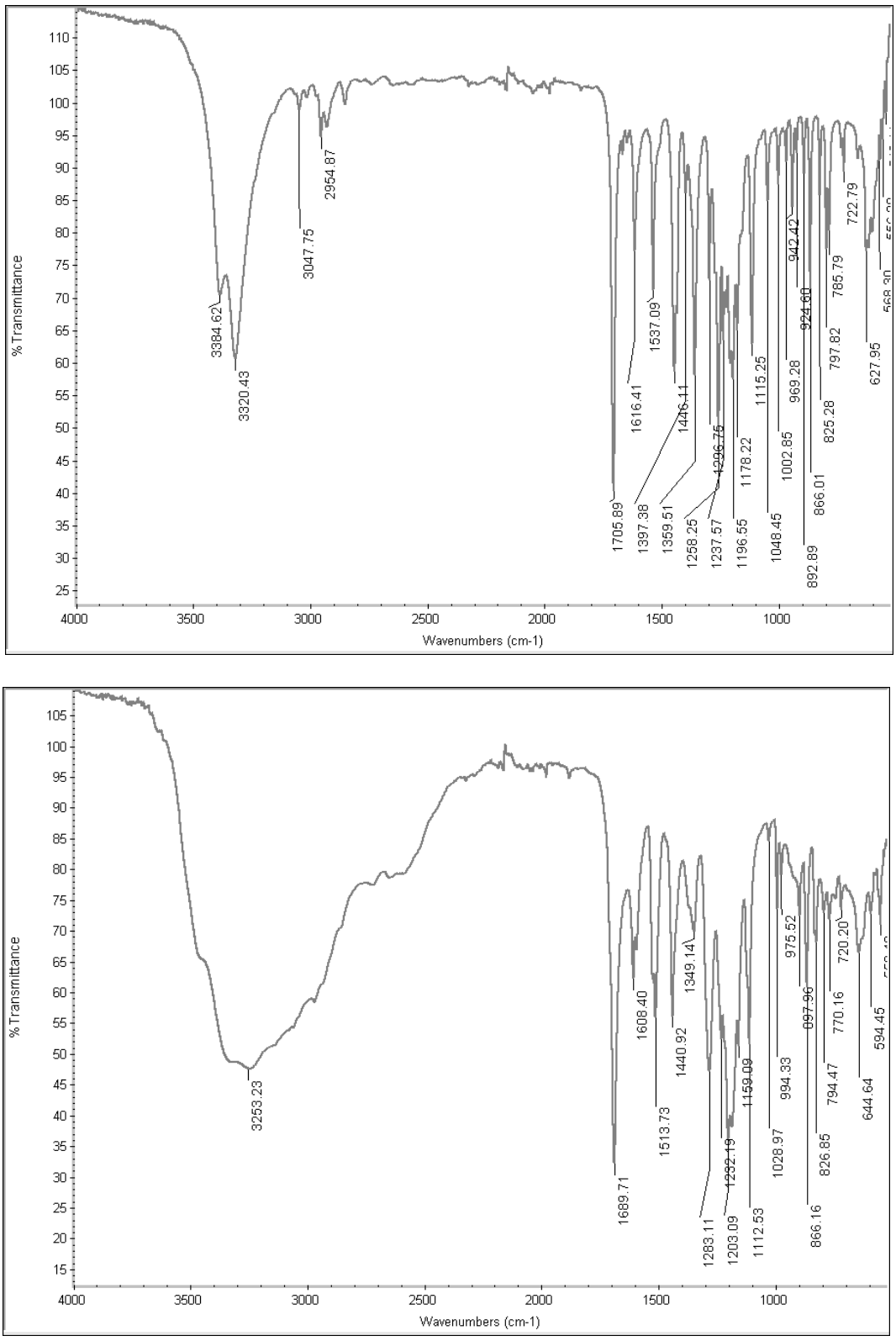


Figure S5 continued. IR spectra of CBDE-10 (top) and CBDA-10 (bottom).

1.3. UV-Vis spectrum of CA, MC, and CBDE-10.

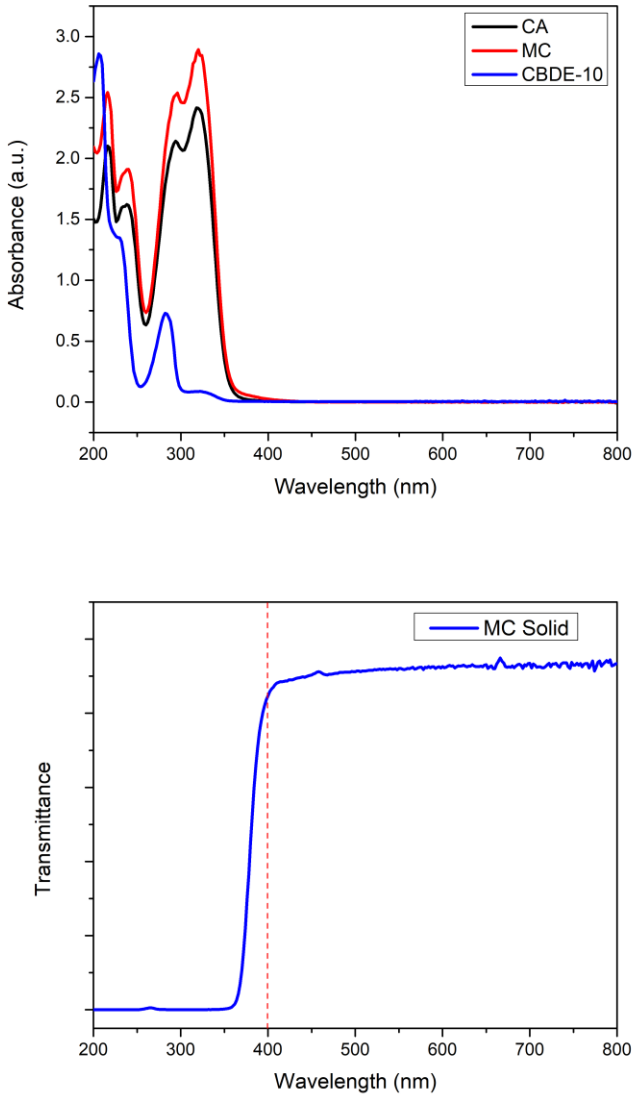


Figure S6. UV-vis absorbance of CA, MC, and CBDE-10 in acetonitrile (top) and MC transparency in the solid-state.

3. Single crystal data of CA, MC, CBDE-10, and CBDA-10.

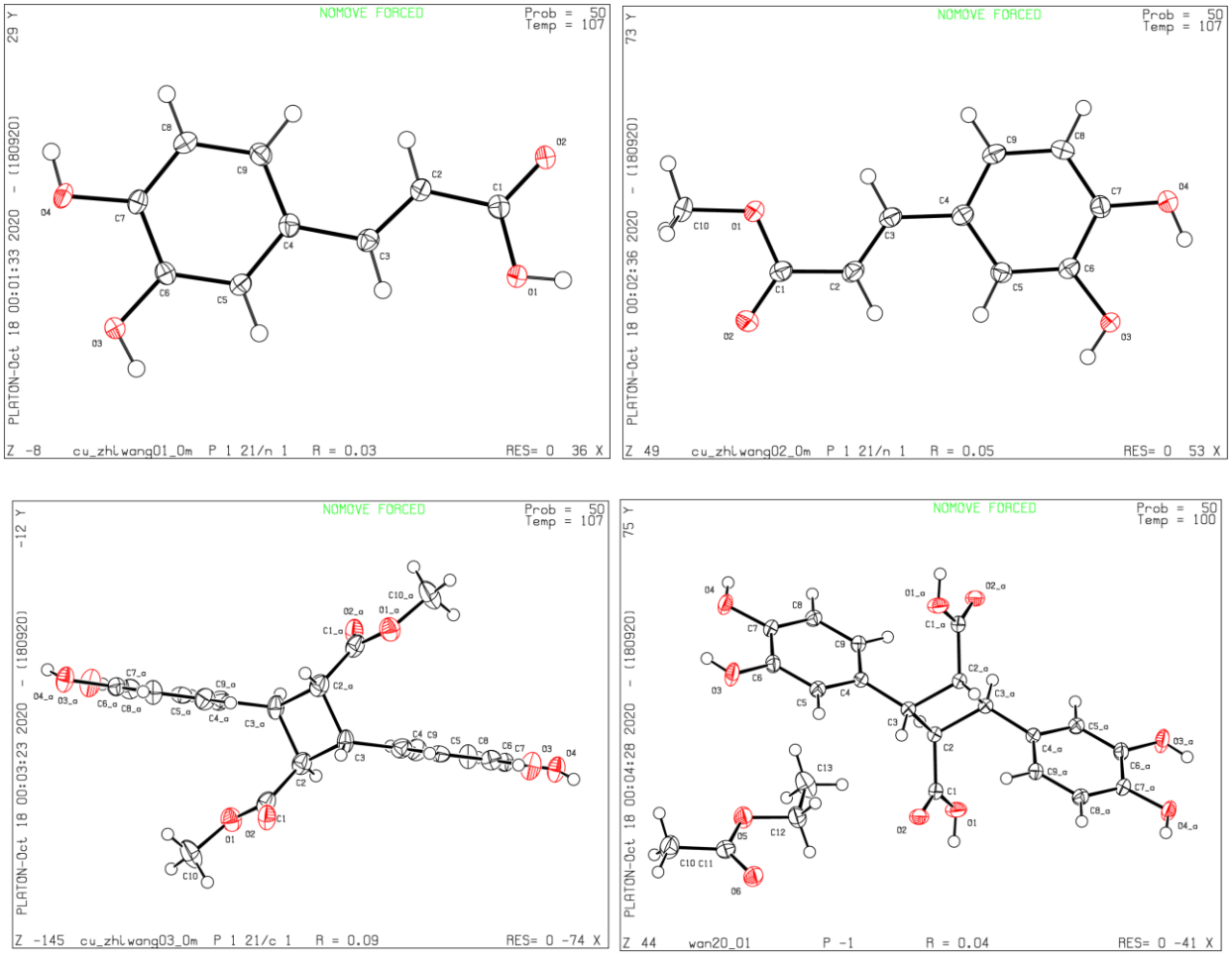


Figure S7. Single crystal X-ray diffraction ellipsoid structures of CA, MC, CBDE-10, and CBDA-10.

Table S1. Crystal data of CA, MC, CBDE-10, and CBDA-10

Crystal	CA	MC	CBDE-10	CBDA10coEA
CCDC #	2021369	2021371	2021372	2021374
Formula	$C_9H_8O_4$	$C_{10}H_{10}O_4$	$C_{20}H_{20}O_8$	$C_{26}H_{32}O_{12}$
Formula weight	180.15	194.18	388.36	536.51
Temp. (K)	107.0	107.24	107.02	100.00(13)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	P-1
a (Å)	6.6967(2)	7.2043(3)	8.841(3)	5.38820(10)
b (Å)	5.7405(2)	11.5780(4)	10.807(3)	8.4135(2)
c (Å)	20.7844(7)	11.3815(4)	9.978(3)	14.8002(4)
α (°)	90	90	90	77.600(2)
β (°)	94.953(3)	105.771(3)	112.64(2)	80.086(2)
γ (°)	90	90	90	88.273(2)
V ($Å^3$)	796.02(5)	913.61(6)	879.9(5)	645.49(3)
Z	4	4	2	1
ρ_{calc} (g/cm^3)	1.503	1.412	1.466	1.380
μ (mm^{-1})	1.020	0.929	0.964	0.931
F(000)	376.0	408.0	408.0	284.0
Crystal size (mm^3)	0.11 × 0.081 × 0.057	0.16 × 0.102 × 0.088	0.151 × 0.134 × 0.077	0.23 × 0.137 × 0.131
Radiation type	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	Cu Kα (λ = 1.54184)
Reflections collected	8004	8341	6758	11740
Independent reflections	1408 [Rint = 0.0354, Rsigma = 0.0231]	1597 [R_{int} = 0.0495, R_{sigma} = 0.0333]	1519 [R_{int} = 0.1206, R_{sigma} = 0.0941]	2628 [R_{int} = 0.0404, R_{sigma} = 0.0261]
R1/wR2 ($I \geq 2\sigma$) (%)	R_1 = 0.0331, wR_2 = 0.0866	R_1 = 0.0459, wR_2 = 0.1251	R_1 = 0.0919, wR_2 = 0.2104	R_1 = 0.0358, wR_2 = 0.0958
R1/wR2 (all data) (%)	R_1 = 0.0394, wR_2 = 0.0906	R_1 = 0.0564, wR_2 = 0.1311	R_1 = 0.1418, wR_2 = 0.2312	R_1 = 0.0383, wR_2 = 0.0985

4. DPPH free radical scavenging assay

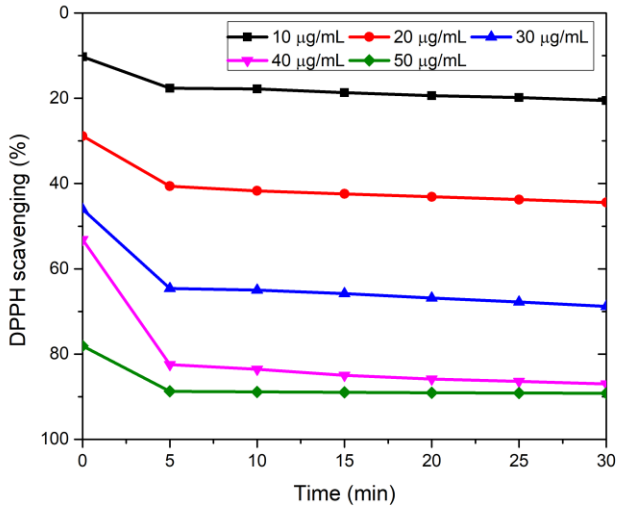


Figure S8. Kinetic study of DPPH scavenging of CBDE-10.

Table S2. DPPH radical-scavenging activities

	CA	MC	CBDE-10
10 μg/mL	2.175 ± 0.052	2.341 ± 0.028	2.397 ± 0.055
20 μg/mL	1.496 ± 0.091	1.555 ± 0.010	1.759 ± 0.020
30 μg/mL	0.788 ± 0.079	0.968 ± 0.024	1.132 ± 0.020
40 μg/mL	0.345 ± 0.034	0.424 ± 0.003	0.582 ± 0.040
50 μg/mL	0.256 ± 0.011	0.338 ± 0.007	0.296 ± 0.005

Table S3. DPPH radical-scavenging efficiency

Scavenging (%) / Concentration	CA	MC	CBDE-10
10 μg/mL	25.5 ± 1.8	21.1 ± 0.9	17.3 ± 1.9
20 μg/mL	48.8 ± 3.1	47.5 ± 0.3	39.3 ± 0.7
30 μg/mL	73.0 ± 2.7	67.3 ± 0.8	60.9 ± 0.7
40 μg/mL	88.1 ± 1.2	85.7 ± 0.1	79.9 ± 1.4
50 μg/mL	91.2 ± 0.4	88.6 ± 0.2	89.8 ± 1.8

5. Lipid peroxidation assay

Table S4. Antioxidation activity

Absorbance / Time (h)	Control	CA	MC	CBDE-10
1	0.712 ± 0.016	0.332 ± 0.009	0.323 ± 0.013	0.348 ± 0.011
2	0.919 ± 0.037	0.399 ± 0.031	0.351 ± 0.016	0.422 ± 0.030
3	1.138 ± 0.043	0.466 ± 0.008	0.408 ± 0.011	0.507 ± 0.027
4	1.290 ± 0.060	0.546 ± 0.019	0.469 ± 0.022	0.612 ± 0.032
5	1.461 ± 0.084	0.649 ± 0.006	0.517 ± 0.018	0.708 ± 0.013
6	1.610 ± 0.066	0.717 ± 0.031	0.564 ± 0.013	0.807 ± 0.060
7	1.754 ± 0.036	0.815 ± 0.020	0.602 ± 0.030	0.868 ± 0.028
8	1.876 ± 0.140	0.889 ± 0.032	0.643 ± 0.043	0.969 ± 0.048
9	1.873 ± 0.081	0.998 ± 0.026	0.685 ± 0.028	1.084 ± 0.078
10	2.142 ± 0.106	1.087 ± 0.018	0.754 ± 0.043	1.156 ± 0.074

6. Hirshfeld Surface Analysis

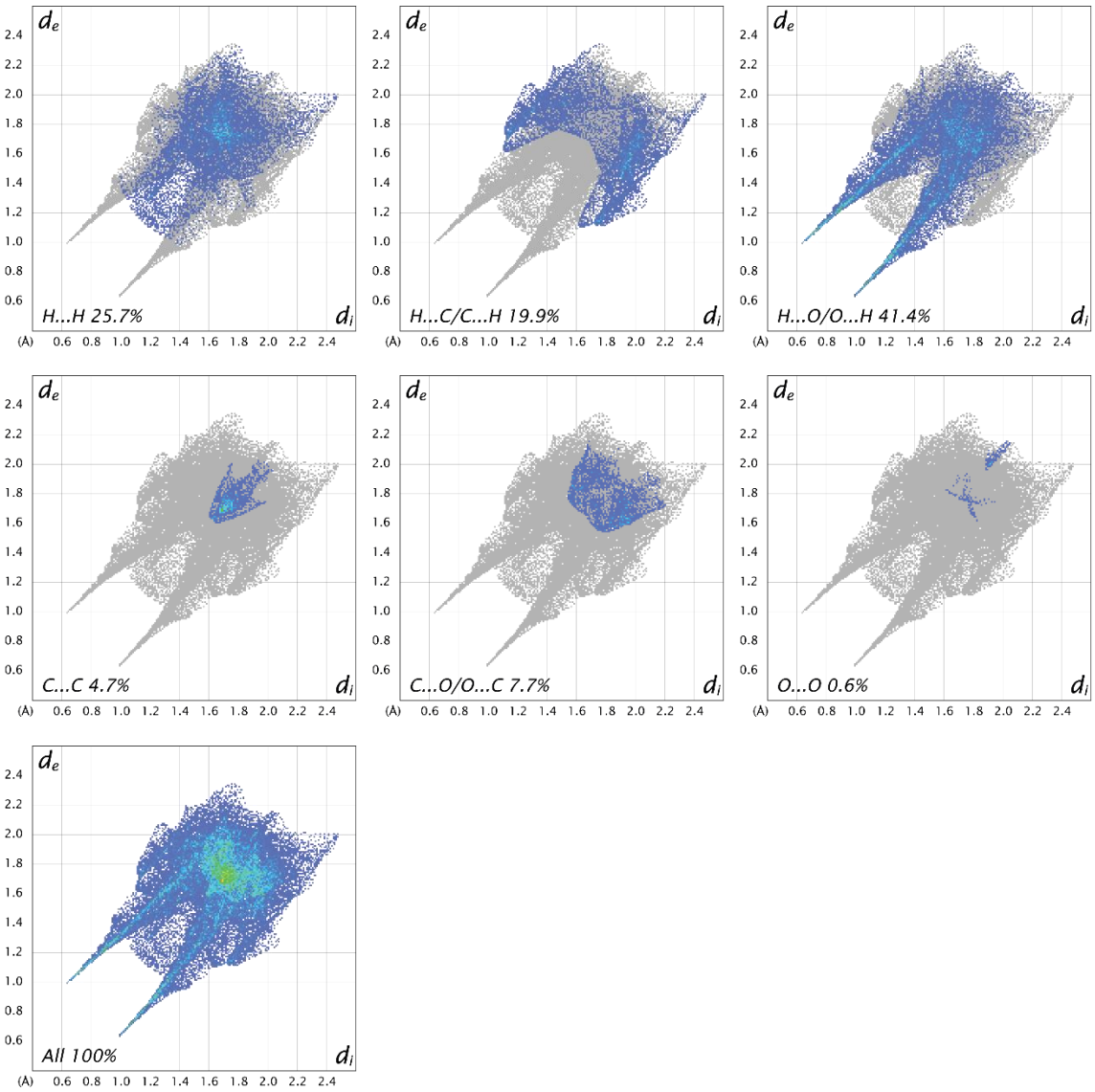


Figure S9. The full two-dimensional fingerprint plots for the CA, showing (a) all interactions and delineated into (b) H···H, (c) H···C/C···H, (d) H···O/O···H, (e) C···C, (f) C···O/O···C, and (g) O···O interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

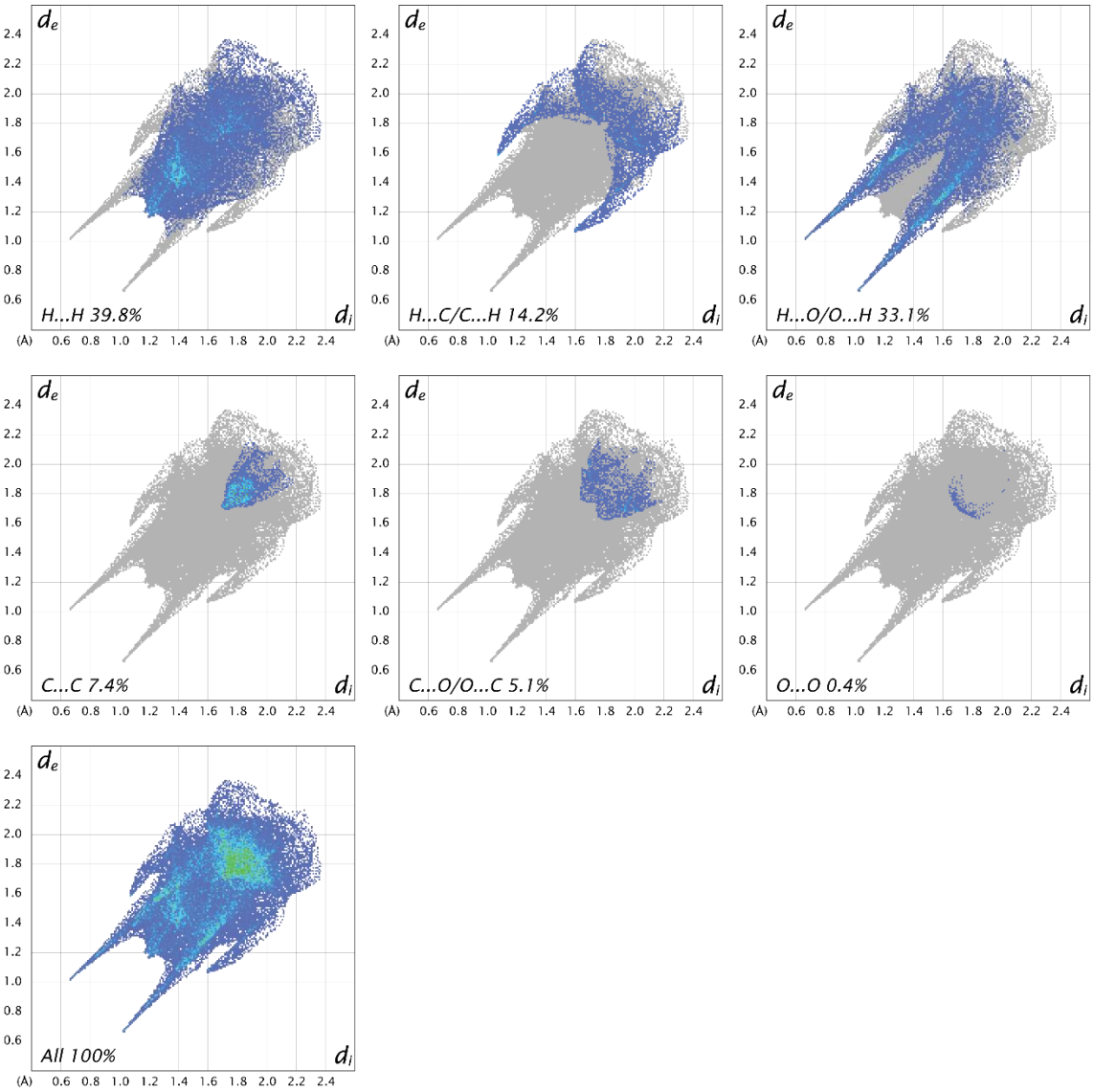


Figure S10. The full two-dimensional fingerprint plots for the MC, showing (a) all interactions and delineated into (b) H···H, (c) H···C/C···H, (d) H···O/O···H, (e) C···C, (f) C···O/O···C, and (g) O···O interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.