Electronic Supplementary Information (ESI)

Understanding the role played by a PIL and the substituent effect for enhancing the generation of *Z*-Cinnamic Acid derivatives

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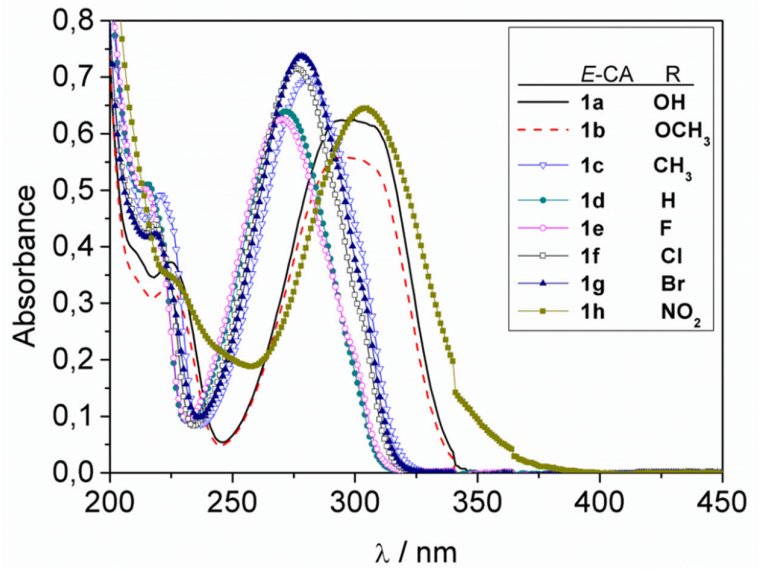


Figure S1. UV-visible absorption spectra of *E*-4-substituted cinnamic acids as PILs recorded in acetonitrile at 25 ºC. All *E*-cinnamic acids solutions were at the same concentration of 3.3 10^{-5} M. Concentration of *n*-butylamine 3.3 10^{-5} M.

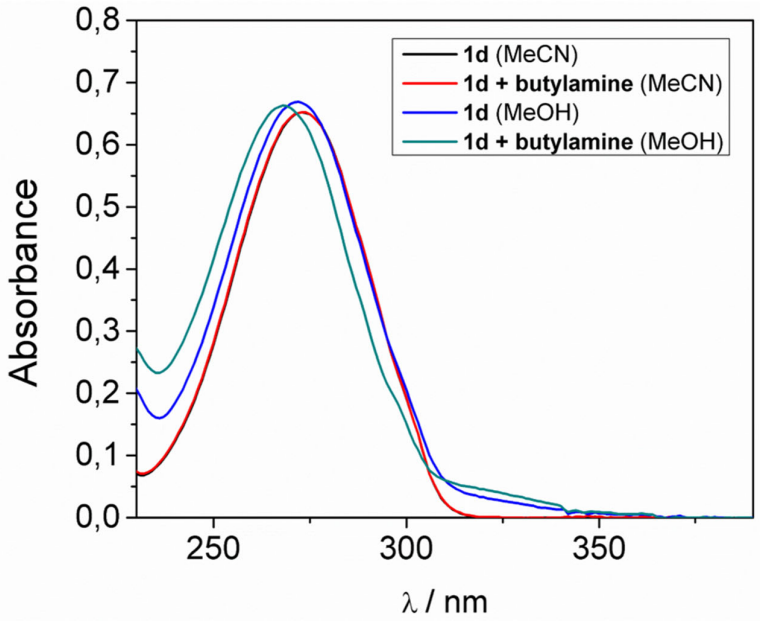


Figure S2. Effect of solvent on the UV absorption spectra of *E*-cinnamic acid in their acid forms and as PILs recorded in acetonitrile and methanol at 25 ºC. Concentration of *E*-cinnamic acids (**1d**) 3.3 10^{-5} M. Concentration of *n*-butylamine 3.3 10^{-5} M.

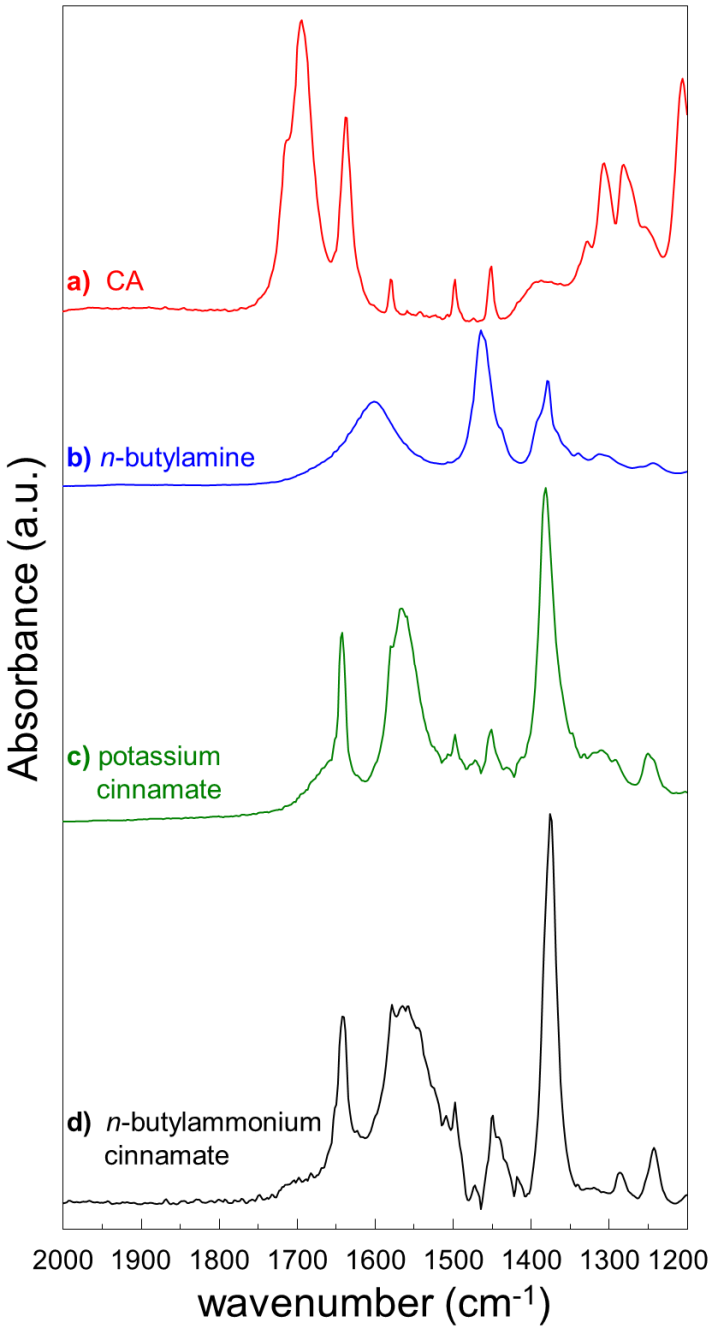


Figure S3. FT-IR spectra in the region between 2000 and 1200 cm^{-1} of pure cinnamic acid (a), *n*-butylamine (b), potassium cinnamate (c), and *n*-butylammonium *E*-cinnamate as PIL (d). Samples were measured in solution at the concentration of 0.075 M in MeCN:MeOH (95:5 v/v).

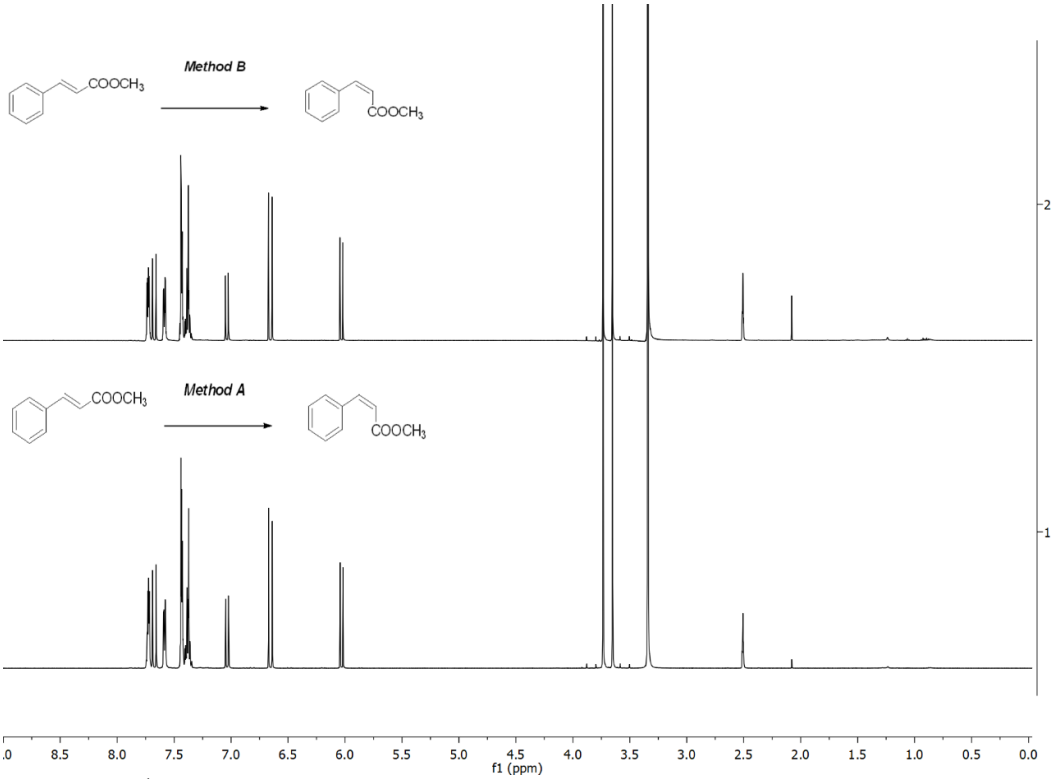


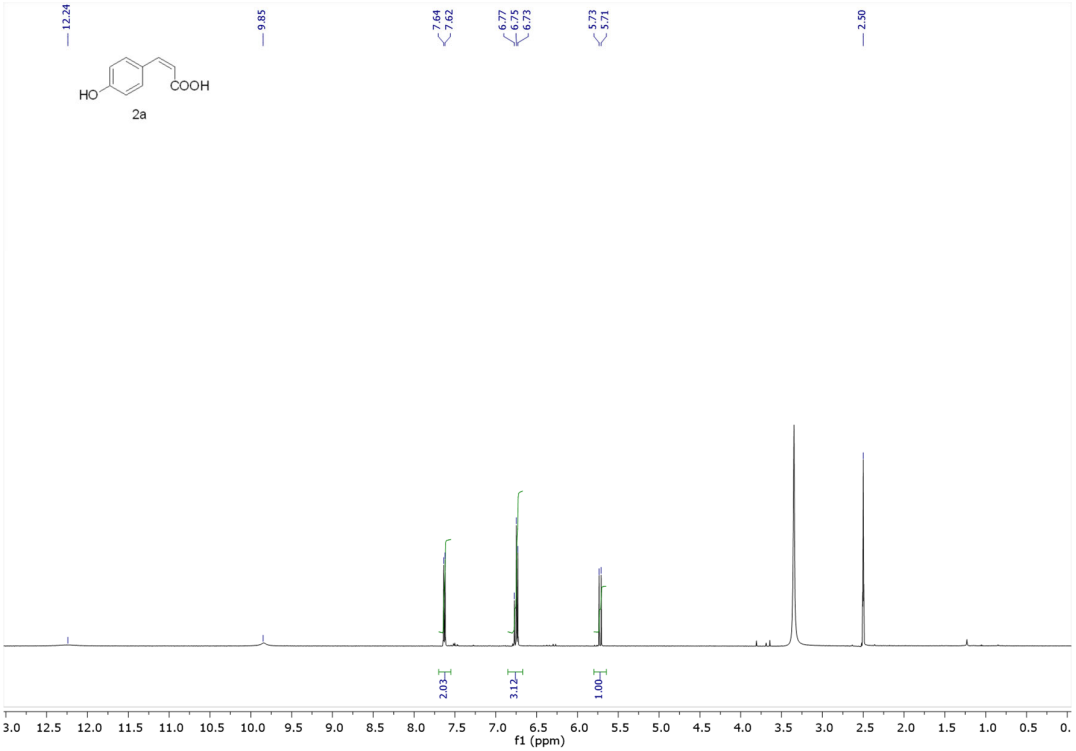
Figure S4. ^{1}H-NMR spectra in DMSO-*d*$_6$ of *E*-methyl cinnamate after irradiation by method A (bottom) and method B (top).

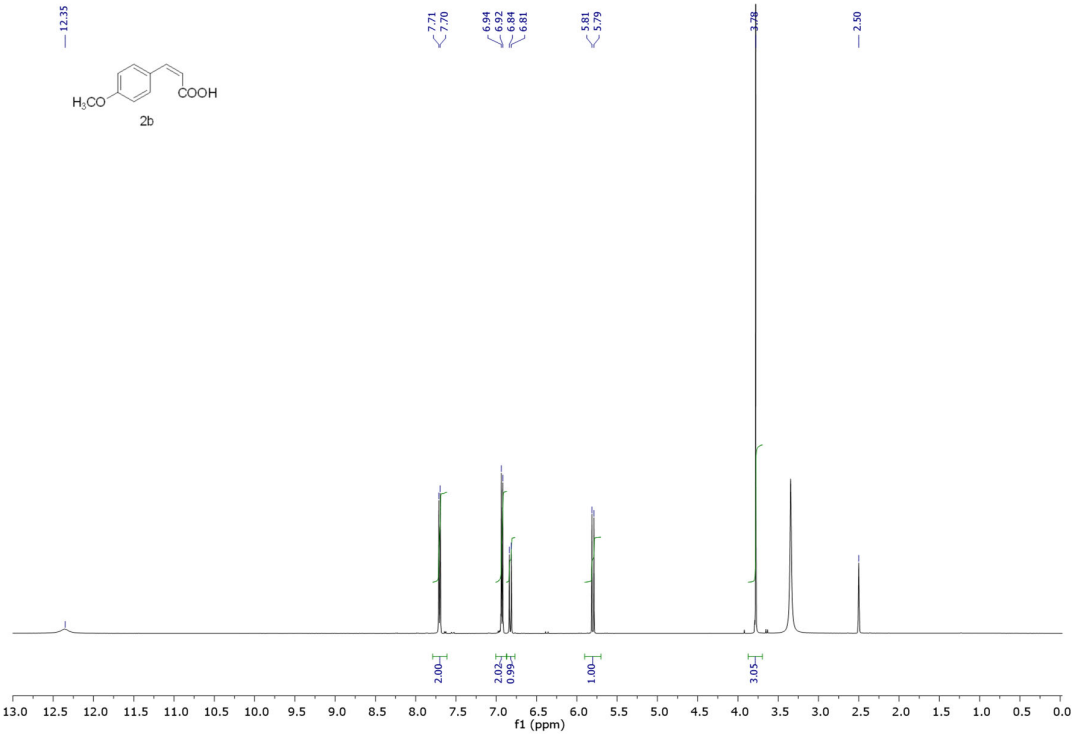
Table S1. Logarithm of molecular extinction coefficients at 300 nm of 4-substituted-CA isomers in their acid forms and as PILs in MeCN:MeOH (98:2 v/v).

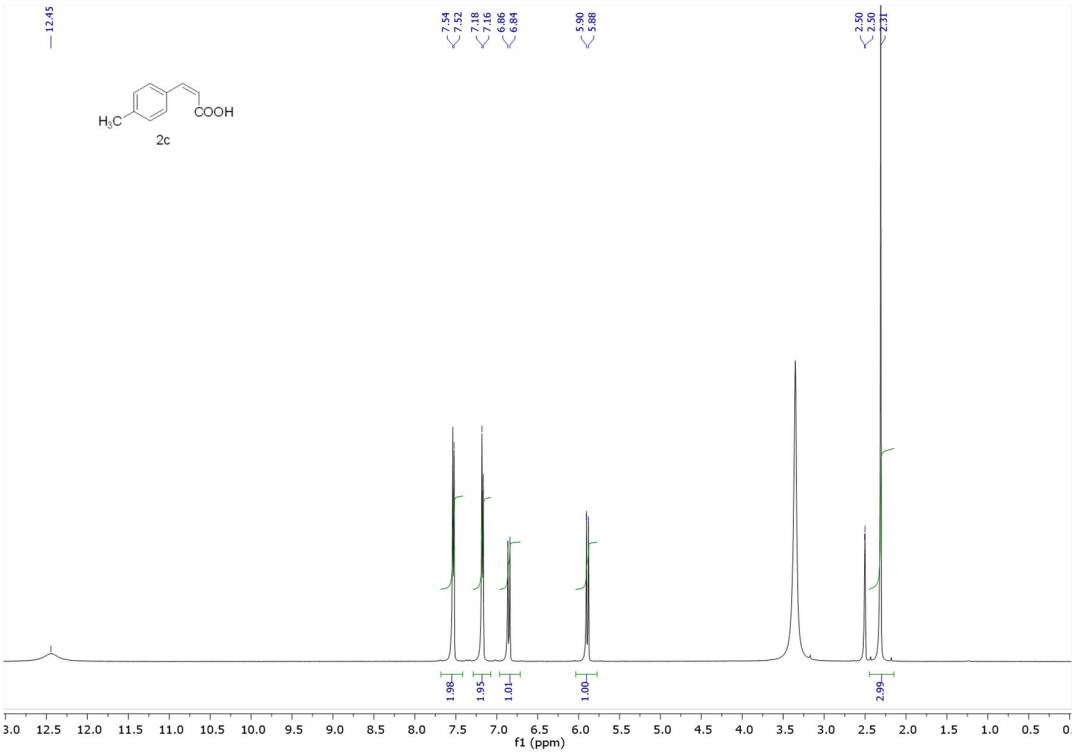
	R	Log ε *E*-CA	Log ε *Z*-CA	Log ε *E*-CA+butylamine[a]	Log ε *Z*-CA+butylamine[a]
1	OH	4.32	4.10	4.28	4.04
2	OCH_3	4.30	4.11	4.27	4.05
3	CH_3	4.15	3.83	4.12	3.71
4	H	3.78	3.39	3.73	3.30
5	F	3.84	3.48	3.80	3.39
6	Cl	4.02	3.70	3.99	3.61
7	Br	4.11	3.80	4.06	3.71
8	NO_2	4.31	4.10	4.26	4.02

[a]Equimolar amount of cinnamic acid and *n*-butylamine

Figure S5. ^{1}H RMN spectra in DMSO-*d*$_{6}$.



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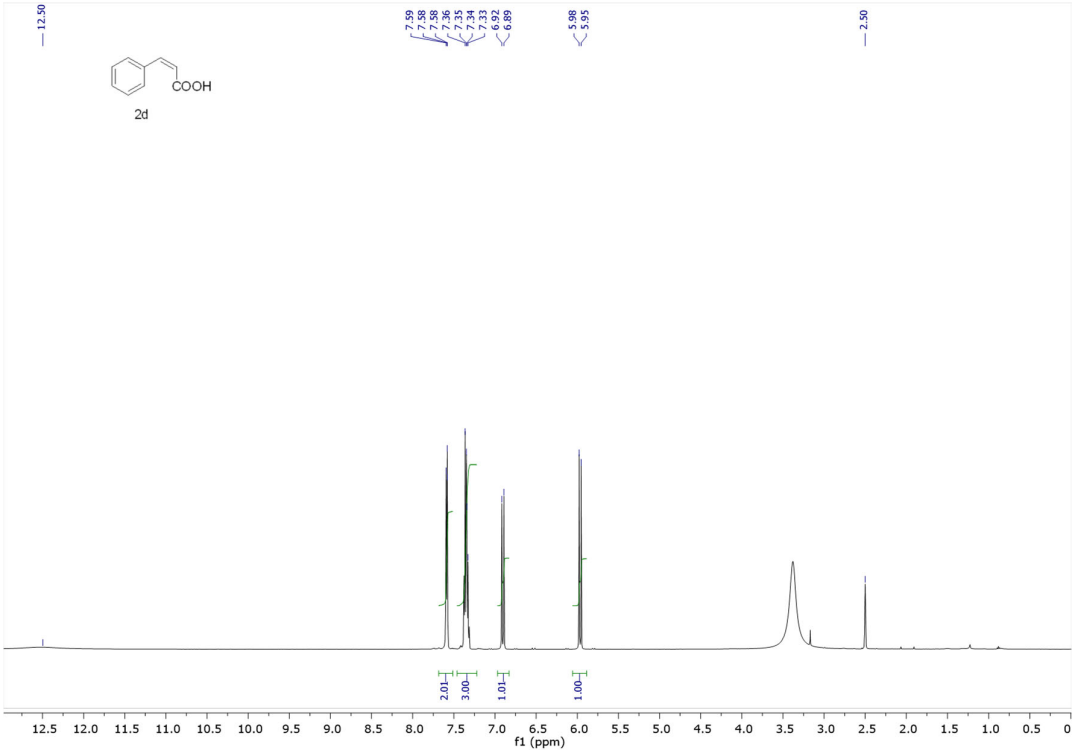
7.54
7.52
7.18
7.16
6.86
6.84
5.90
5.88
2.50
2.50
2.31
H3C
COOH
2c
1.98
1.95
1.01
1.00
2.99
f1 (ppm)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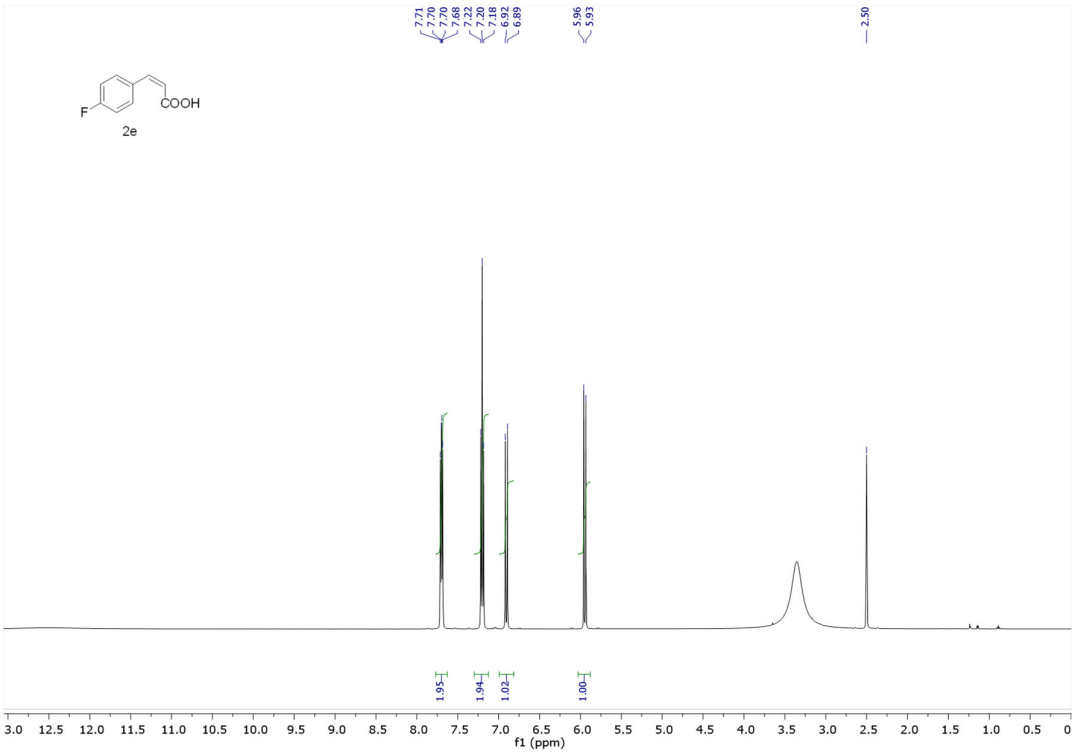
7.58
7.38
7.36
7.35
7.34
7.33
6.92
6.89
5.98
5.95
2.50
COOH
2d
2.01
3.00
1.01
1.00
f1 (ppm)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7.70
7.70
7.68
7.22
7.20
7.18
6.92
6.89
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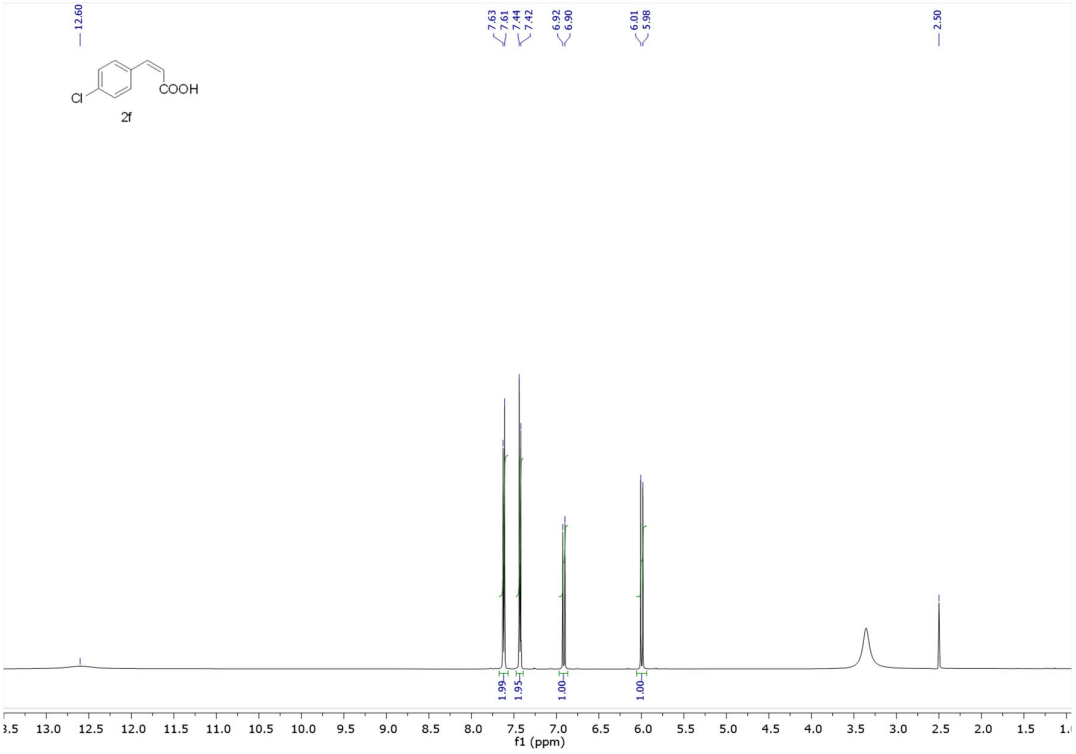
5.93
2.50
F
COOH
2e
1.95
1.94
1.02
1.00
f1 (ppm)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7.44
7.42
6.92
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2.50
Cl
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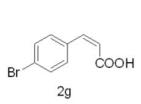
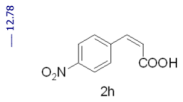
1.95
1.00
1.00
f1 (ppm)


Br
COOH

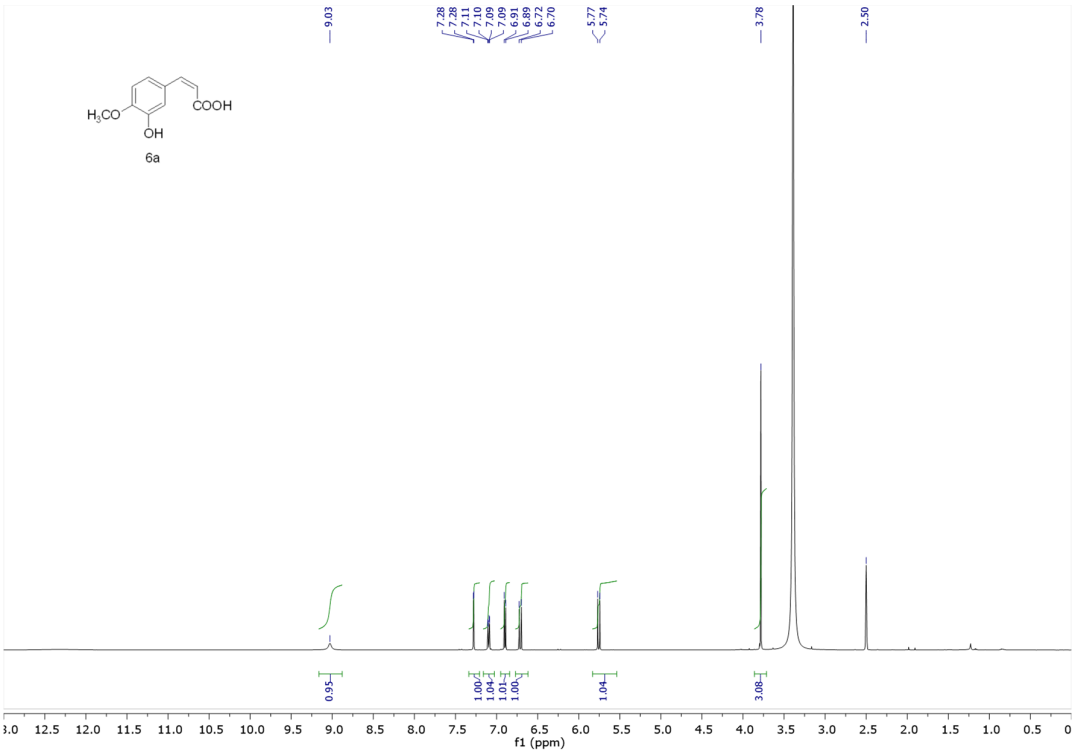
2g

7.58
7.56
7.54
7.53
6.91
6.88
6.01
5.99
2.50
3.95
1.00
1.00
f1 (ppm)


12.78
O2N
COOH

2h

8.23
8.22
8.21
7.77
7.75
7.10
7.07
6.19
6.17
2.50
1.98
1.96
1.01
1.00
f1 (ppm)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7.28
7.11
7.10
7.09
7.09
6.91
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6.72
6.70
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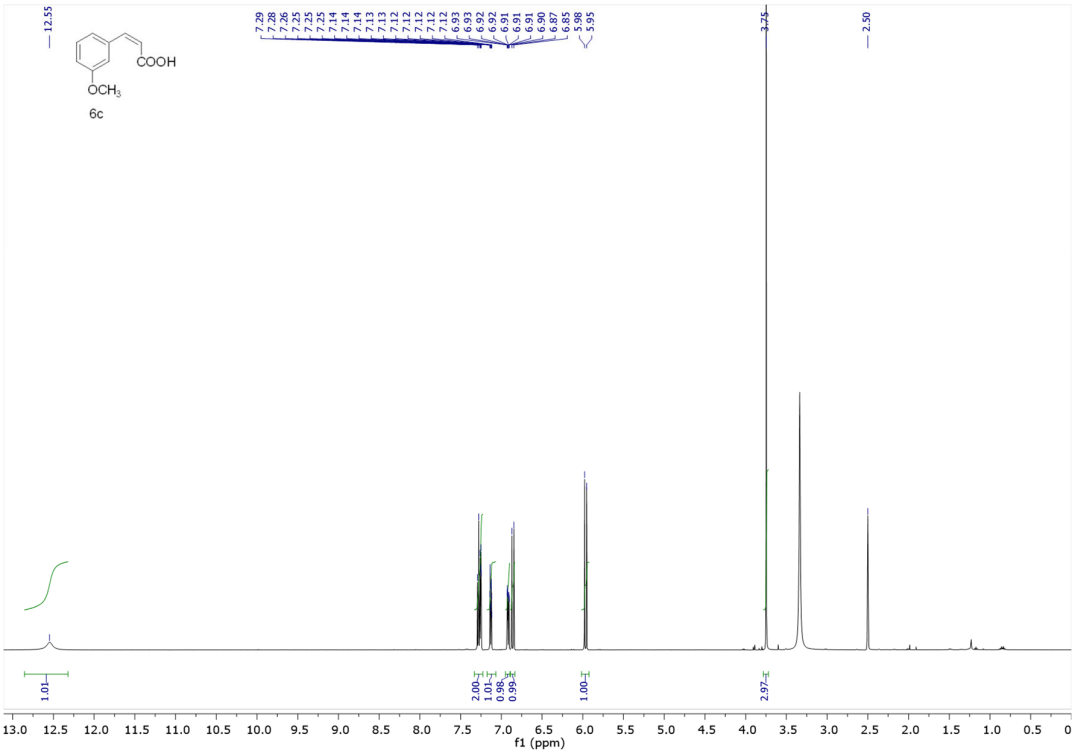
5.74
3.78
2.50
H3CO
COOH
OH
6a
0.95
1.00
1.04
1.01
1.00
1.04
3.08
f1 (ppm)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7.28
7.26
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7.25
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7.14
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7.12
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7.12
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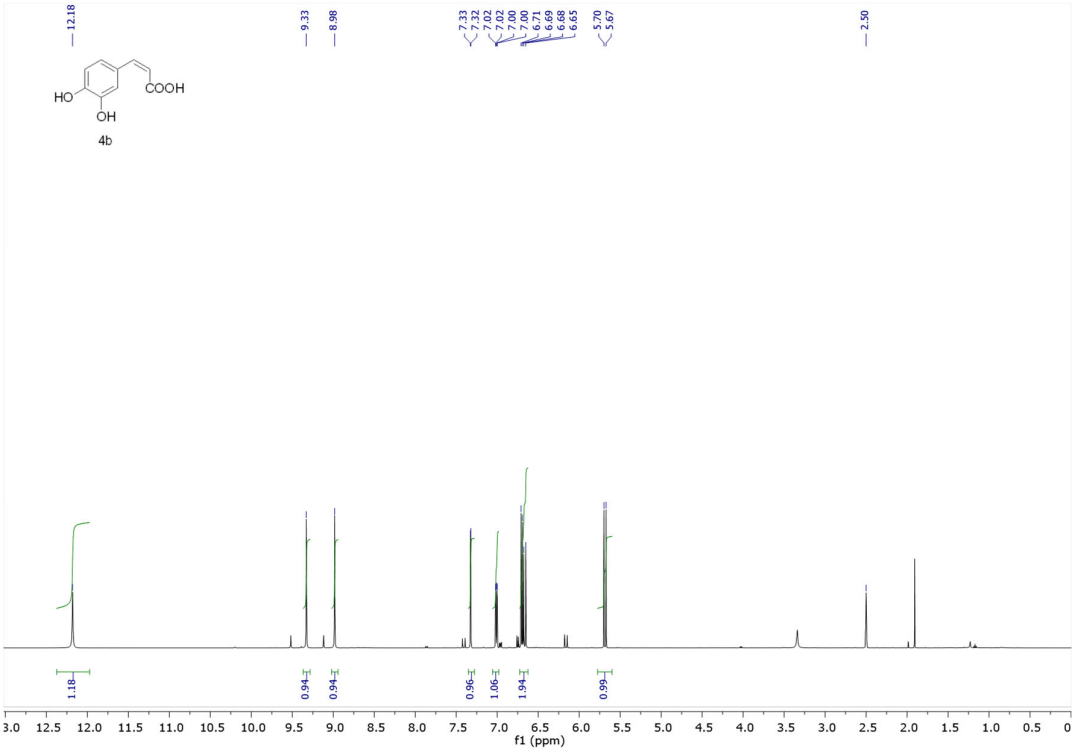
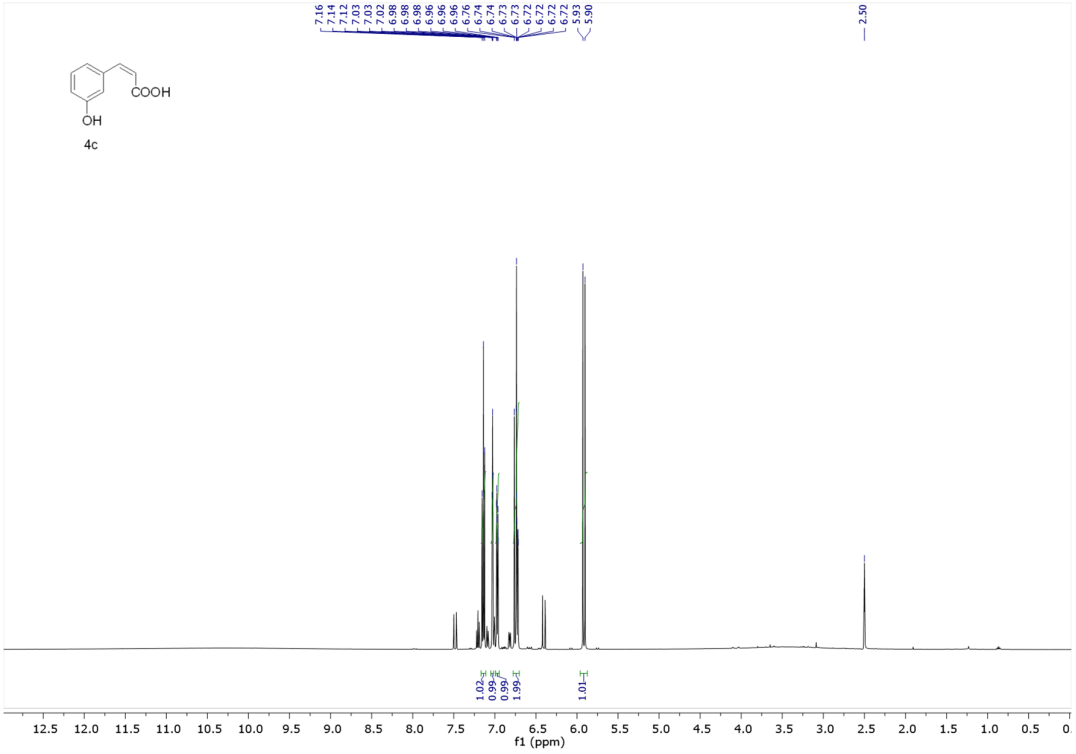
6.93
6.92
6.92
6.91
6.91
6.91
6.90
6.87
6.85
5.98
5.95
3.75
2.50
COOH
OCH3
6c
1.01
2.00
1.01
0.98
0.99
1.00
2.97
f1 (ppm)


12.18
9.33
8.98
7.33
7.32
7.02
7.02
7.00
7.00
6.71
6.69
6.68
6.65
5.70
5.67
2.50
HO
OH
COOH
4b
1.18
0.94
0.94
0.96
1.06
1.94
0.99
f1 (ppm)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7.14
7.12
7.03
7.03
7.02
6.98
6.98
6.98
6.96
6.96
6.96
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6.74
6.74
6.73
6.73
6.72
6.72
6.72
6.72
5.93
5.90
2.50
OH
COOH
4c
1.02
0.99
0.98
1.99
1.01
f1 (ppm)