molecules

Supporting information

Mechanochemistry and Eco-bases for Sustainable Michael Addition Reactions

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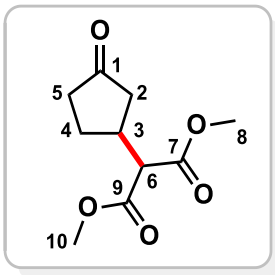
1. Spectral data

1.1. Dimethyl 2-(3-oxocyclopentyl)malonate

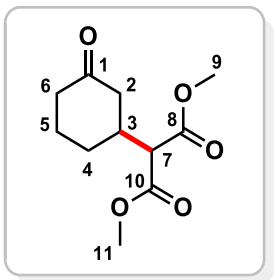


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.75 (1 H, s, **H-8**), 3.73 (1H, s, **H-10**), 3.37 (1H, d, *J* = 9.4 Hz, **H-6**), 2.88-2.80 (1 H, m, **H-3**), 2.49 (1H, dd, *J* = 18.4, 7.6 Hz, **H-2a**), 2.38-2.2 (1 H, m, **H-6a**), 2.27-2.22 (1H, m, **H-2b**), 2.22-2.15 (1H, m, **H-6b**) 1.99 (1H, ddd, *J* = 18.4, 11.0, 1.2 Hz, **H-4a**), 1.71-1.57 (1H, m, **H4-b**)

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 217.0 (**C-1**), 168.64 (**C-7**), 168.5 (**C-9**), 56.2, (**C-6**), 52.8 (x2) (**C-8, C-10**), 43.0 (**C-3**), 38.3 (**C-2**), 36.5 (**C-6**), 27.6 (**C-4**).

IR (neat, cm^{-1}) : 2959, 2921, 2852, 1729,1436, 1147.

1.2.Dimethyl 2-(3-oxocyclohexyl)malonate

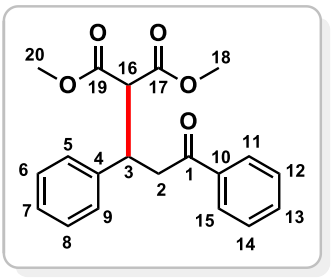


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.72 (3H, s, **H-9**), 3.71 (3H, s, **H-11**), 3.32 (1H, d, *J* = 8 Hz, **H-7**), 2.51 (1H, dddd, *J* = 19.4, 15.7, 11.8, 7.7, 3.8 Hz, **H-3**), 2.39-2.45 (2H, m, **H-6a**, **H-2b**), 2.23-2.29 (2H, m, **H-6b**, **H-2b**), 2.04 (1H, dddd, *J* = 14.6, 10.4, 6.9, 3.6, **H-5a**), 1.93-1.96 (m, 1H, **H-4a**), 1.64-1.73 (1H, m, **H-5b**), 1.46-1.55 (1H, m, **H-4b**).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 209.6 (**C-1**), 168.3 (**C-8**, **C-10**), 56.7 (**C-7**), 52.7 (x2) (**C-9**, **C-11**), 45.1 (**C-2**), 41.1 (**C-6**), 38.2 (**C-3**), 28.9 (**C-5**), 24.6 (**C-4**).

IR (neat, cm^{-1}) : 2955, 2868, 1732, 1710, 1435, 1150.

1.3. Dimethyl 2-(3-oxo-1,3-diphenylpropyl)malonate



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.90 (2H, ddd, *J* = 8.1, 2.9, 1.8, **H-11, H-15**), 7.53 (1H, dddd, *J* = 8.6, 6.9,1.3, 1.3, **H-13**), 7.46-7.42 (2H, m, **H-12, H-14**), 7.28-7.26 (4H, m, **H-5, H-9, H-6, H-8**), 7.23-7.17 (1H, m, **H-7**), 4.20 (1H, ddd, *J* = 14.1, 8.9, 5.0, **H-3**), 3.87 (1H, d, *J* = 9.4 Hz, **H-2**), 3.73 (3H, s, **H-18**), 3.57 (1H, dd, *J* = 16.9, 4.9 Hz, **H-16a**), 3.50 (3H, s, **H-20**), 3.48 (1 H, dd, *J* = 16.9, 8.7 Hz, **H-16b**).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 197.6 (**C-1**), 168.9 (**C-17**), 168.3 (**C-19**), 140.6 (**C-4**), 136.9 (**C-10**), 133.2 (**C-11**), 128.6 (x2) (**C-5**,**C-9**), 128.2 (x2) (**C-6**,**C-8**), 127.3 (**C-15**), 57.4 (**C-16**), 52.8 (**C-18**), 52.5 (**C-20**), 42.4 (**C-2**), 40.9 (**C-3**).

IR (neat, cm^{-1}): 3667, 2989, 2958, 2901, 1728, 1681, 1234, 1159.

2. NMR Spectra

2.1. dimethyl 2-(3-oxocyclopentyl)malonate

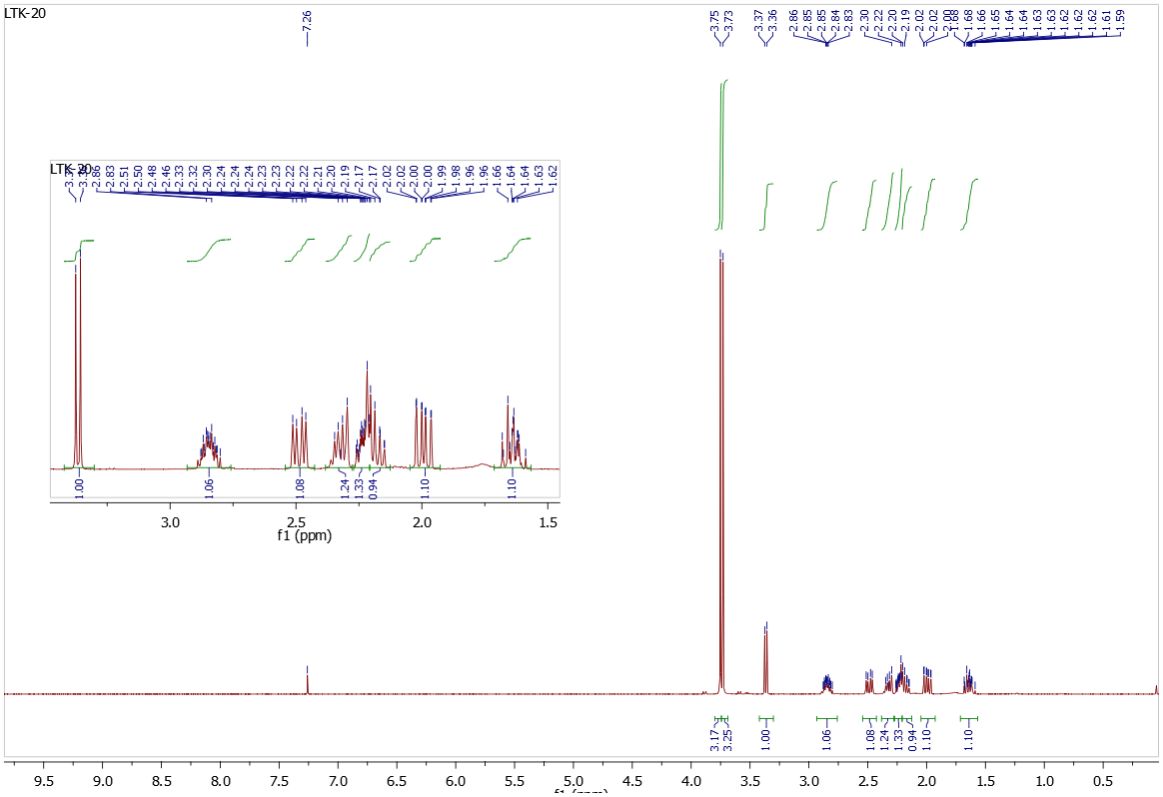


Figure S1. ^{1}H NMR (400 MHz) spectrum of dimethyl 2-(3-oxocyclopentyl)malonate

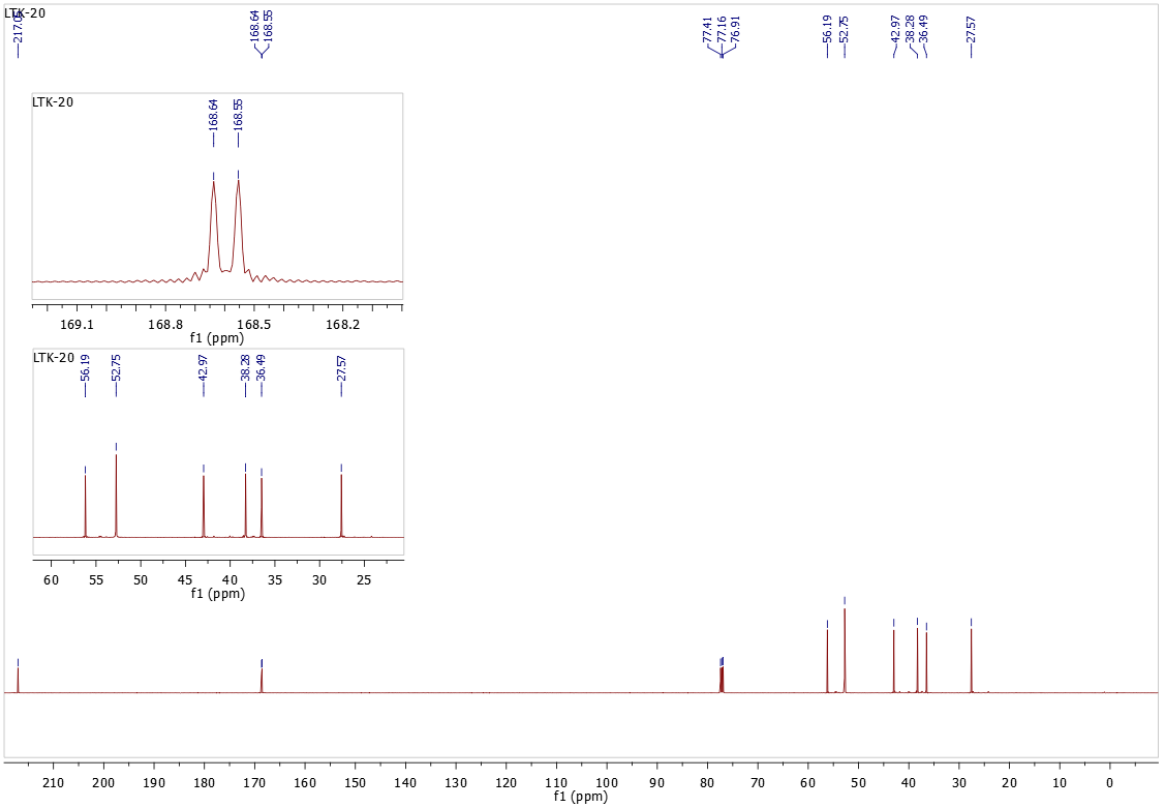


Figure S2. ^{13}C NMR (100 MHz) of dimethyl 2-(3-oxocyclopentyl)malonate

2.2. dimethyl 2-(3-oxocyclohexyl)malonate

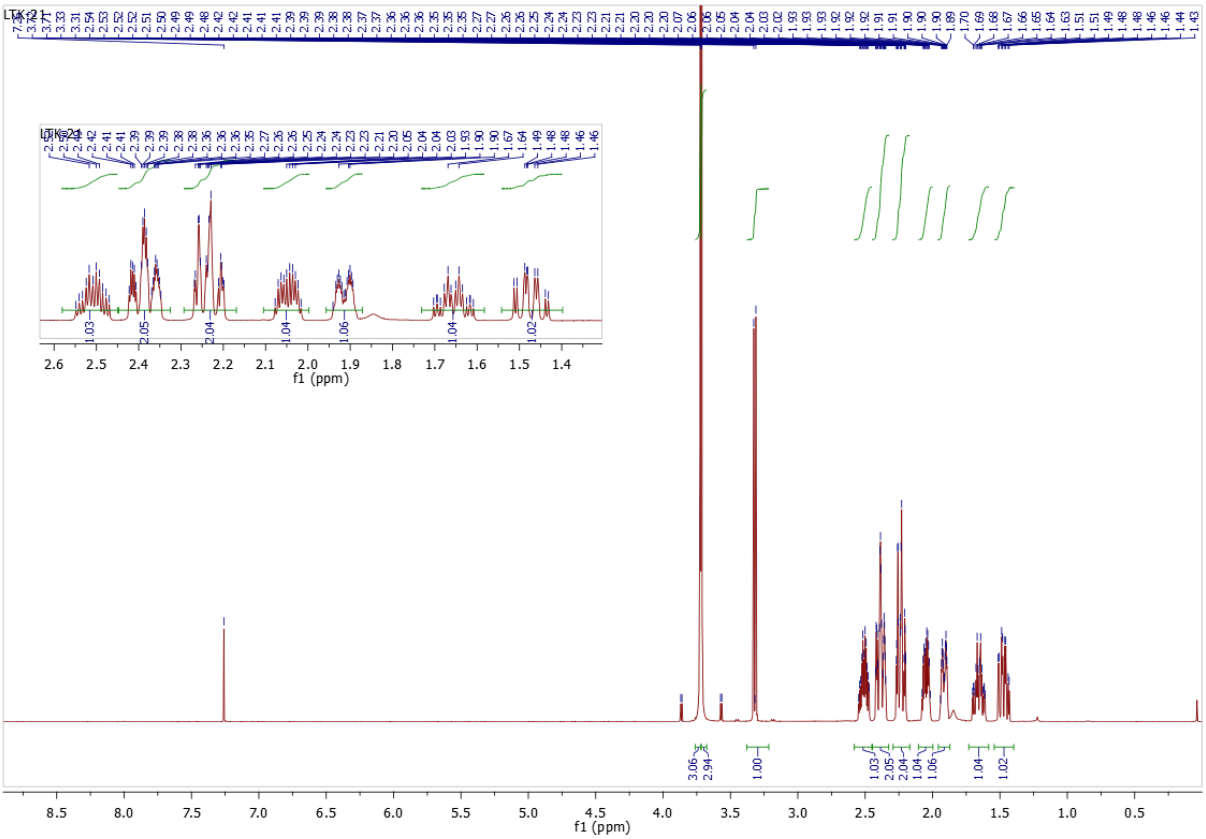


Figure S3. [1]H NMR (400 MHz) spectrum of dimethyl 2-(3-oxocyclohexyl)malonate

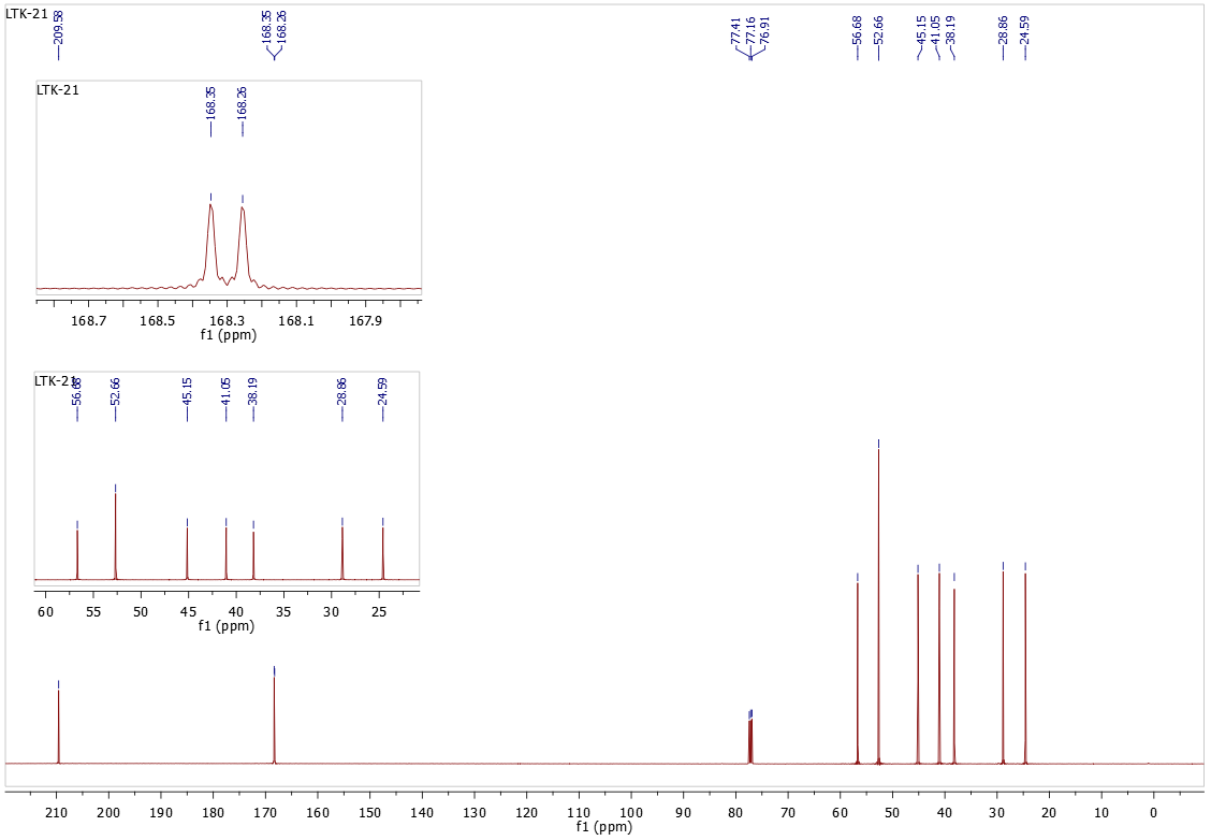


Figure S4. [13]C NMR (100 MHz) spectrum of dimethyl 2-(3-oxocyclohexyl)malonate

2.3. dimethyl 2-(3-oxo-1,3-diphenylpropyl)malonate

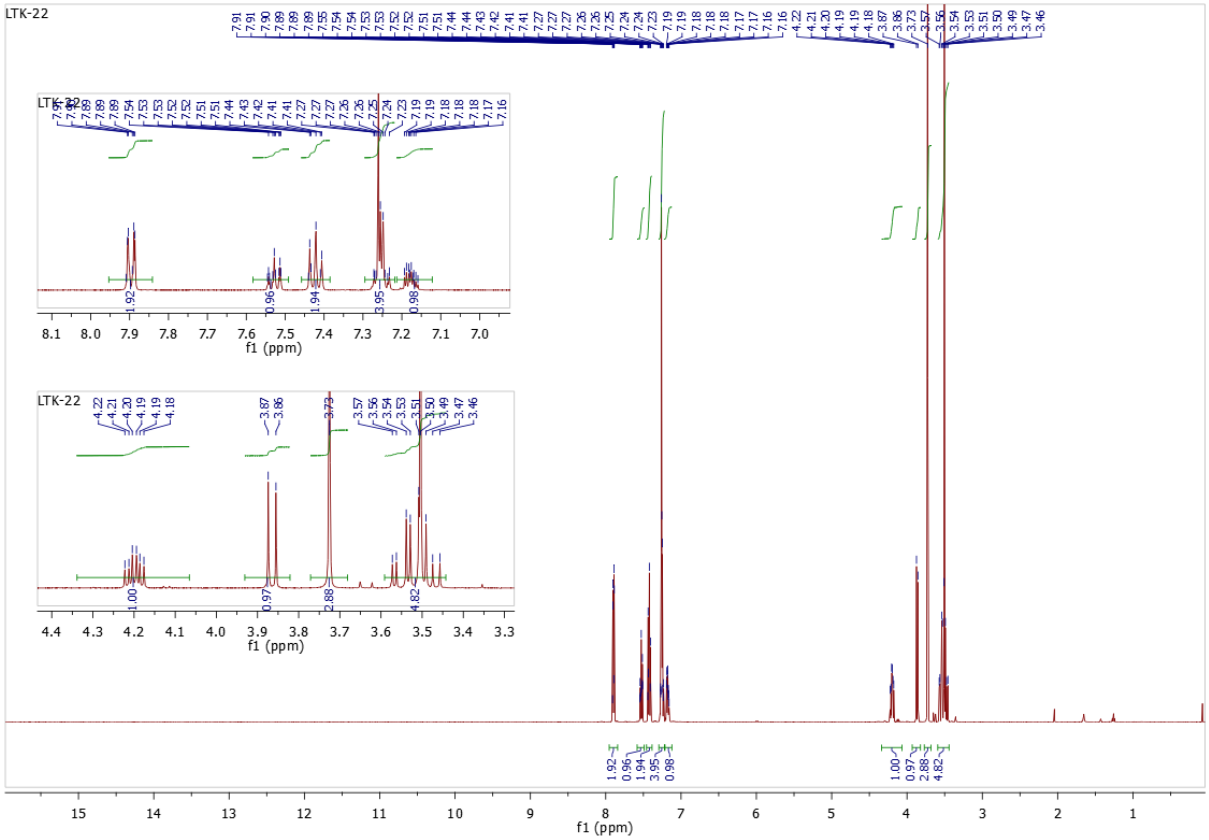


Figure S5. ^{1}H NMR (400 MHz) spectrum of dimethyl 2-(3-oxo-1,3-diphenylpropyl)malonate

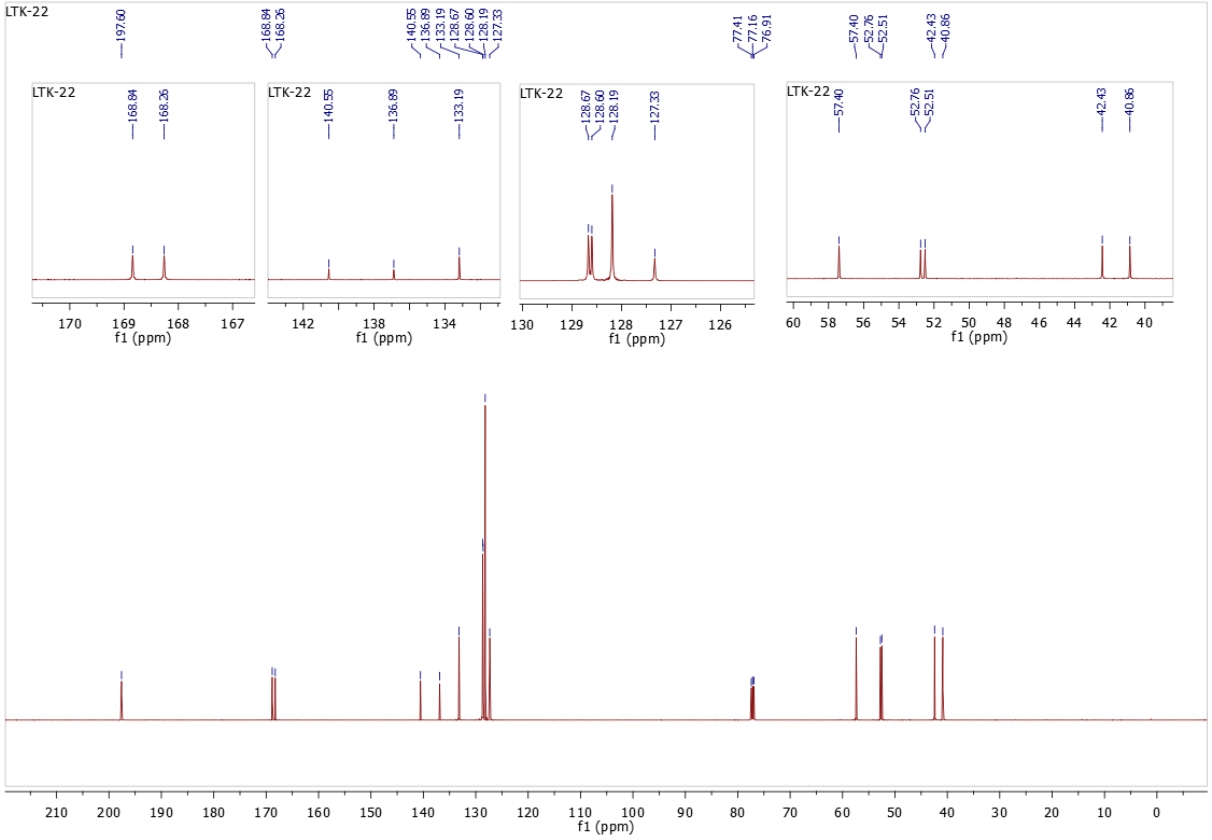


Figure S6. ^{13}C NMR (100 MHz) spectrum of dimethyl 2-(3-oxocyclopentyl)malonate

3. IR Spectra

3.1. dimethyl 2-(3-oxocyclopentyl)malonate

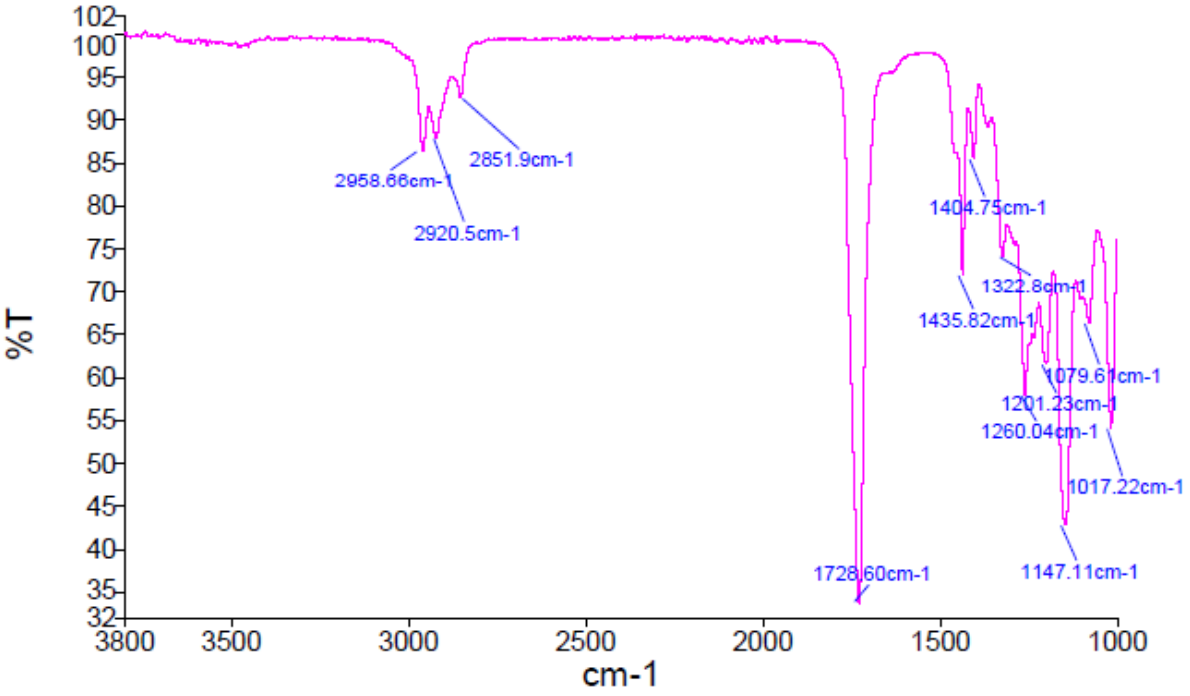


Figure S7. IR spectrum of dimethyl 2-(3-oxocyclopentyl)malonate

3.2. dimethyl 2-(3-oxocyclohexyl)malonate

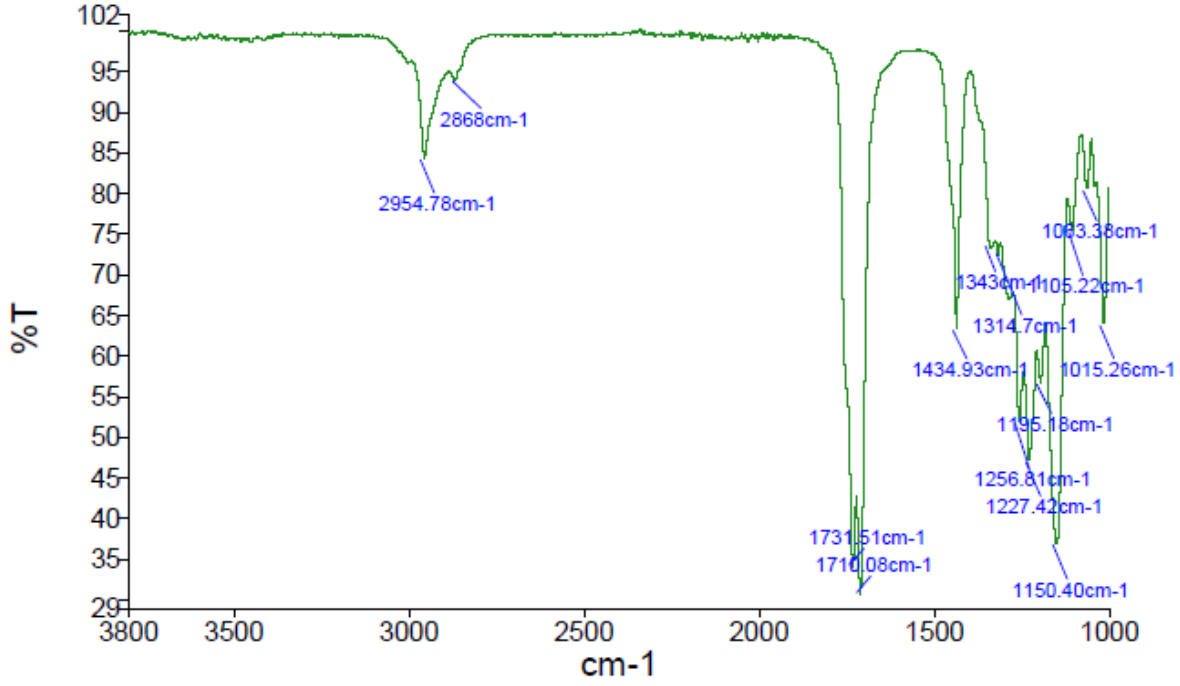


Figure S8. IR spectrum of dimethyl 2-(3-oxocyclohexyl)malonate

3.3. dimethyl 2-(3-oxo-1,3-diphenylpropyl)malonate

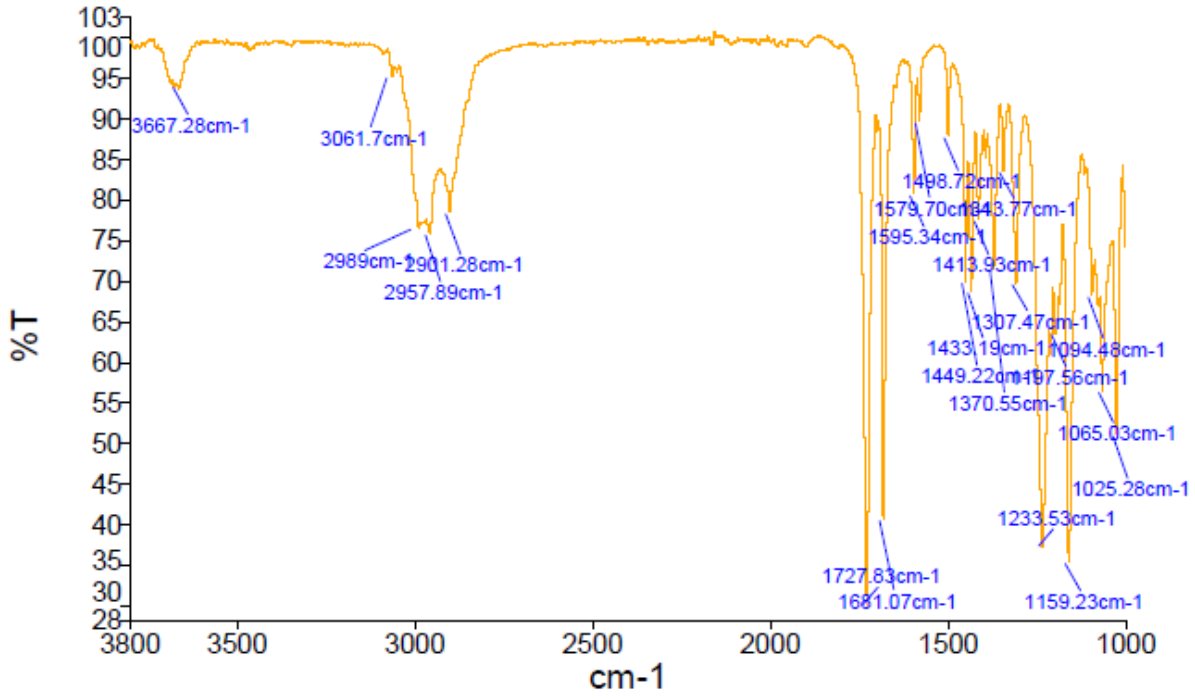


Figure S9. IR spectrum of dimethyl 2-(3-oxo-1,3-diphenylpropyl)malonate

4. ESBD Images

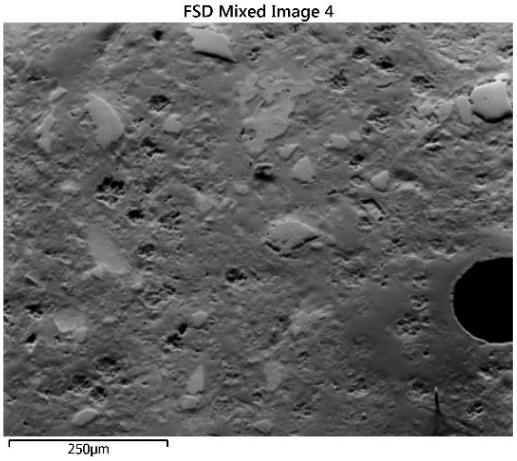


Table S1. ESBD Map Settings Table

Accelerating Voltage	20.00 kV
Specimen Tilt (degrees)	70.00 °
Hit Rate	14.87 %
Speed of Acquisition	39.46 Hz

Table S2. Phase for acquisition

Phase	a	b	c	Alpha	Beta	Gamma	Space Group	Database
Calcite	4.99 Å	4.99 Å	17.06 Å	90.00 °	90.00 °	120.00 °	0	HKL
Quartz	4.91 Å	4.91 Å	5.50 Å	90.00 °	90.00 °	120.00 °	0	CHANNELPhaseDatabase
K_Feldspar	8.57 Å	12.96 Å	7.22 Å	90.66 °	115.93 °	87.62 °	0	CHANNELPhaseDatabase
Dolomite	4.78 Å	4.78 Å	15.73 Å	90.00 °	90.00 °	120.00 °	148	ICSD
Calcite	4.99 Å	4.99 Å	17.06 Å	90.00 °	90.00 °	120.00 °	167	ICSD
Oxyapatite	9.43 Å	9.43 Å	6.88 Å	90.00 °	90.00 °	120.00 °	174	ICSD
Tremolite	9.86 Å	18.12 Å	5.29 Å	90.00 °	104.57 °	90.00 °	12	ICSD
Low albite	8.14 Å	12.78 Å	7.16 Å	94.19 °	116.61 °	87.68 °	0	CHANNELPhaseDatabase

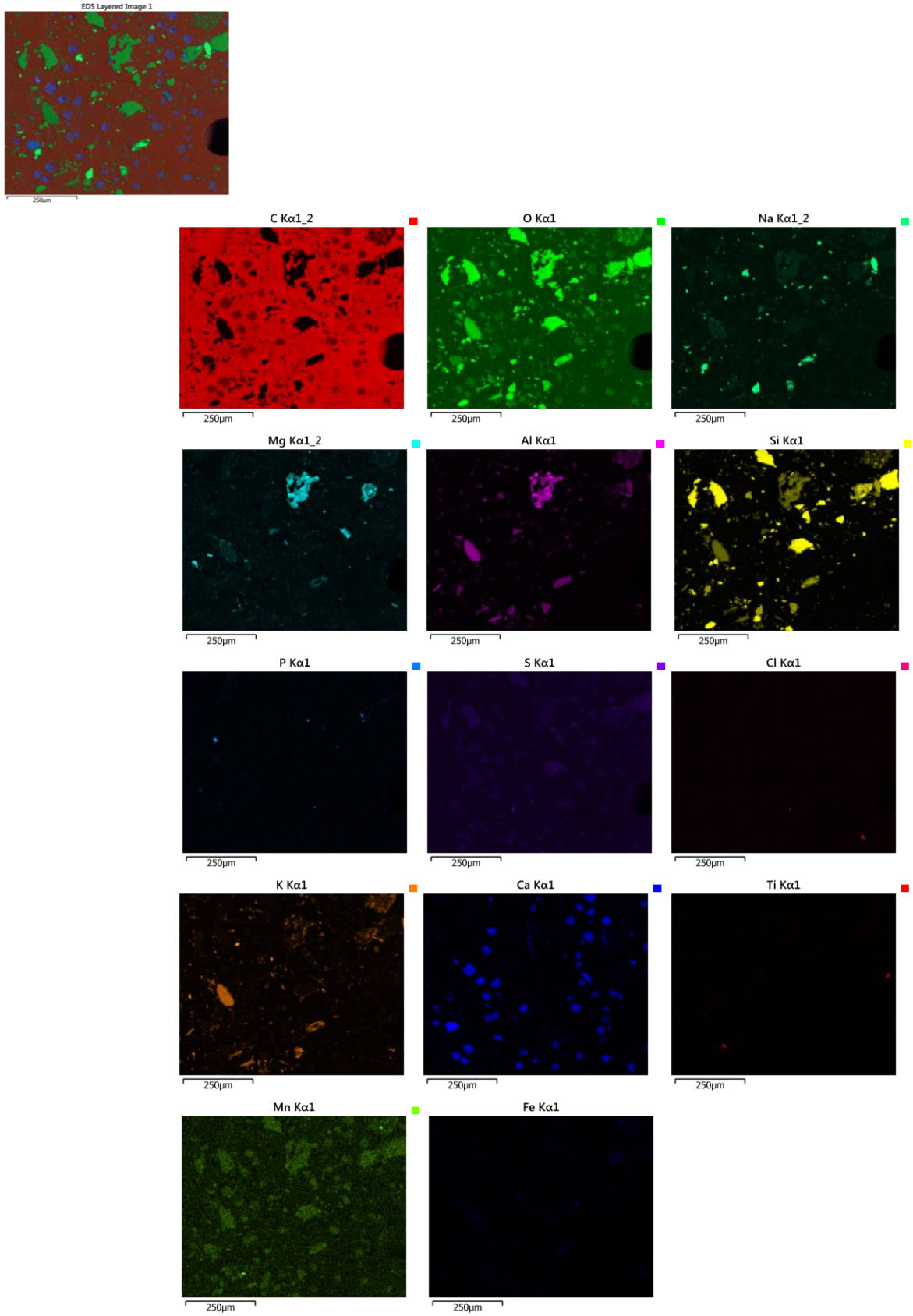


Figure S10. EDS Layered Images

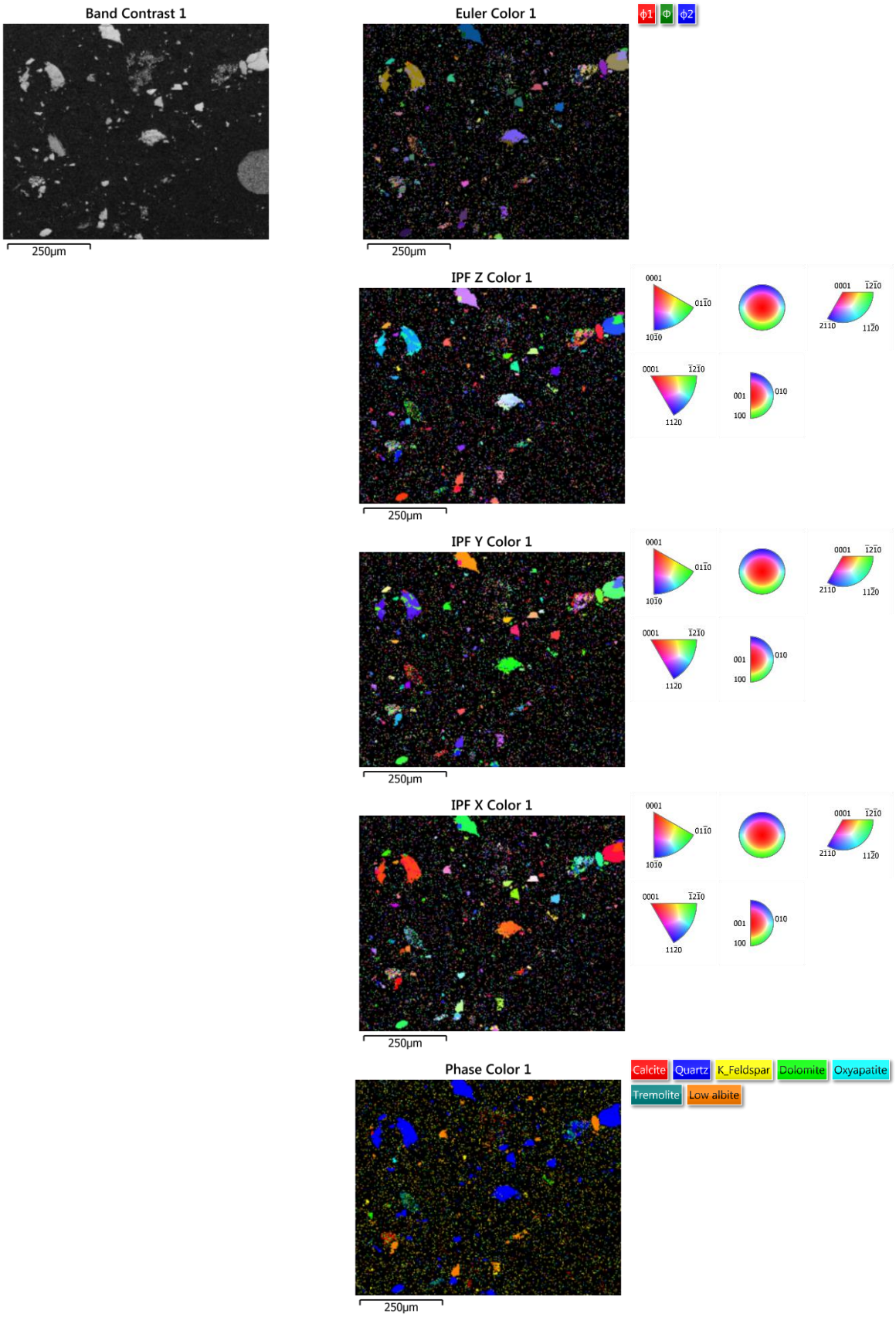


Figure S11. Phase coloration

Table S3 : Phase fraction

Phase Name	Phase Fraction (%)	Phase Count	Mean Band Contrast	Standard Deviation Band Contrast	Min Band Contrast	Max Band Contrast	Mean MAD	Standard Deviation MAD	Min MAD	Max MAD
Calcite	0.56	475	101.03	41.35	25.00	211.00	0.93	0.22	0.39	1.99
Quartz	4.73	3991	131.43	41.37	23.00	200.00	0.74	0.28	0.21	1.98
K_Feldspar	4.01	3384	45.25	18.08	23.00	154.00	1.26	0.28	0.34	2.00
Dolomite	0.91	769	64.40	39.51	24.00	196.00	1.18	0.34	0.31	1.99
Oxyapatite	0.35	299	54.99	31.69	25.00	193.00	1.23	0.31	0.39	2.00
Tremolite	1.65	1393	55.07	28.35	23.00	174.00	1.18	0.31	0.41	1.99
Low albite	2.65	2238	68.95	40.70	24.00	169.00	1.12	0.36	0.35	2.00
Zero Solutions	85.13	71815	42.37	12.46	0.00	177.00				

5. XRPD analysis

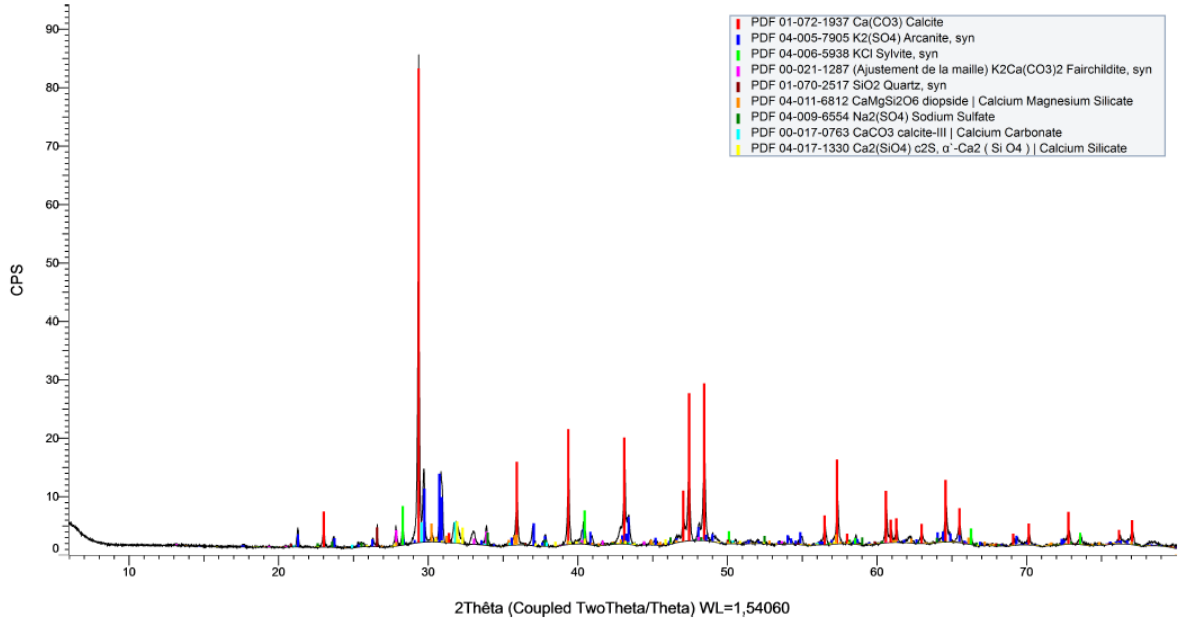


Figure S12 : XRPD analysis of Eco-base-Fj

6. Ionic chromatography

1.0018 g of Eco-base-Fj and water (10 mL) was stirred during 2 h. The solid state of Eco-base-Fj was centrifugated and the liquid state was analyzed.

Table S4. Ionic chromatography of Eco-base-Fj

$[X^{n-}]$	tr (min)	$[X^{n-}]$ (g/L)	$[X^{n-}]$ (mg/g of Eco-base-Fj)	$[X^{n-}]$ (mmol/g of Eco-base-Fj)	$[K_nX]$ (mg/g of Eco-base-Fj)
$[Cl^-]$	8.9	7.967	79.5	2.24	163
$[SO_4^{2-}]$	22.6	6.838	68.3	0.71	124
$[CO_3^{2-}]$	18.1	4.377	37.8	0.63	87