Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2014

Supporting Information

Conjugated Mesoporous poly-benzobisthiadiazole network for visible light-driven photoredox reaction

Zi Jun Wang, Saman Ghasimi, Katharina Landfester and Kai A. I. Zhang*

Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany, E-mail: kai.zhang@mpip-mainz.mpg.de

Table of contents:

1. Materials and methods

Materials

Di-hexyl-dibromofluorene (99%), tetrakis(triphenylphosphine) palladium(0) (99%), copper (I) iodide (CuI), potassium carbonate (K_2CO_3), Span® 80 nonionic surfactant, 1,3,5-triethynylbenzene (97%), Hantzsch ester, diisopropyethylamine (DIPEA), 2-bromoacetophenone, 2-bromo-4'-fluoroacetophenone, 2-bromo-4'-bromoacetophenone, 2-bromo-4'-

cyanoacetophenone, 2-bromo-4'-methylacetophenone, 2-bromo-4'-methoxyacetophenone, 2-bromo-4'-nitroacetophenone and all other solvents were purchased from Aldrich. Bibromo-benzo-bis-thiodiazole (99%) was purchased from Solarmer Materials, Inc. All chemicals and solvents were used as received unless otherwise specified.

Methods

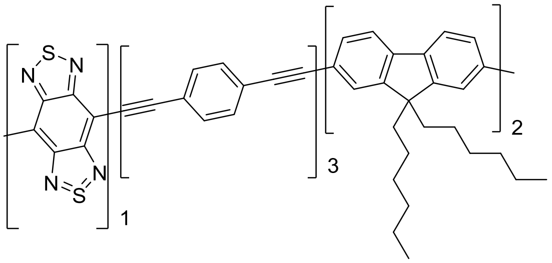
UV-vis absorption and emission spectra were recorded at room temperature on a Perkin Elmer Lambda 100 spectrophotometer and J&M TIDAS spectrofluorometer, respectively. NMR measurements were recorded on Bruker AVANCE 250, Bruker AVANCE 300 systmes. FT-IR sepctra were recorded on a Varian 1000 FT-IR spectrometer. Solid State NMR measurements were carried out using Bruker Avance II solid state NMR spectrometer operating at 300 MHz Larmor frequency equipped with a standard 4mm magic angle spinning (MAS) double resonance probe head. Scanning electron microscope (SEM) images were acquired on a LEO Gemini 1530 (Carl Zeiss AG, Germany) using an in lens SE detector. Inductively coupled plasma analysis (ICP) was performed on a Jobin-Yvon Activa M spectrometer. The TGA measurement was conducted under nitrogen with temperature increasing from 25 ^{o}C to 1000 ^{o}C at a rate of 10 ^{o}C/min. Polymer surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using Autosorb 1 (Quantachrome Instruments). Data was evaluated using QuadraWin software from Quantachrome Instruments. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using Quenched Solid Density Functional Theory (QSDFT, N_2, assuming carbon adsorbent with slit pores). Samples were degassed at 100 ^{o}C for 24 h under high vacuum before analysis. The BET surface area calculation was based on data points obtained from $0<P/P_0<0.25$ and the nonlinear density functional theory (NLDFT) equilibrium model was used for the BET model fitting. : Electron paramagnetic resonance (EPR) was measured on a Magnettech Miniscope MS200 spectrometer.

Procedure for the Sonogashira cross-coupling reaction via high internal phase emulsion (HIPE) polymerization

B_2-FL_2-BBT. To 0.5 mmol (75 mg) of triethynylbenzene, 0.5 mmol (246 mg) di-hexyl-dibromofluorene, 0.25 mmol (88 mg) dibromo-benzo-bis-thiodiazole, 0.025 mmol (29 mg) of tetrakis(triphenylphosphine) palladium(0), 0.02 mmol (5 mg) of CuI and 100 mg of Span® 80 were dissolved in 1 mL of toluene. 414 mg of K_2CO_3 was dissolved in 9 mL of Milli-Q water. Then, the aqueous phase was slowly added to the organic phase under vigorous stirring using an Ultra Turrax® IKA T18 mechanical stirrer at 14000 RPM. After 30 min, the homogeneous mixture became viscous and was heated to 80 ^{o}C for 12 h. The resulted monolithic polymer was then washed with Milli-Q water several times and extracted with 50/50 dichloromethane and methanol solution in soxhlet for 24 h. Drying of the polymer was then performed using supercritical CO_2 on a CPD 300 critical point dryer. Elemental analysis: Calculated (based on two repeating units). C, 79.53; H, 6.13; N, 6.68; S, 7.65. Found: C, 66.14; H, 5,24; N, 3,91; S, 5.04. IPC: Cu: 20 ppm, Pd: 15 ppm.

B_2-FL_3. To 0.5 mmol (75 mg) of triethynylbenzene, 0.75 mmol (369 mg) di-hexyl-dibromofluorene, 0.025 mmol (29 mg) of tetrakis(triphenylphosphine) palladium(0), 0.02 mmol (5 mg) of CuI and 100 mg of Span® 80 were dissolved in 1 mL of toluene. 414 mg of K_2CO_3 was dissolved in 9 mL of Milli-Q water. Purification of B-FL3 was carried out in the same procedure as for B-FL2-BBT as described above. Elemental analysis: Calculated: C, 91.45; H, 8.55. Found: C, 89.90; H, 8.13; N, 0.11; S, 0.19. IPC: Cu: 25 ppm, Pd: 20 ppm.

Synthesis of the short linear polymer B-FL_2-BBT-L



A 25 ml Schlenck tube was filled under nitrogen atmosphere with 70 mg (0.2 mmol, 1eq) dibromobenzothiadiazole, 196 mg(0.4 mmol, 2 eq) 9,9-di-n-hexyl-2,7-dibromofluorene, 76 mg (0.6 mg, 3 eq) 1,4-diethynylbenzene. The starting material was dissolved in a mixture of 2.5 ml dimethylformamid and 2.5 ml triethylamine. Additionally 12 mg (0.01 mmol, 5 mol%) tetrakistriphenylphosphinepalladium(0) and 9 mg (0.05 mmol, 24 mol%) CuI were added. The mixture was heated for 24 h at 85 °C under constantly stirring. The crude product was dissolved in dichlormethane and washed several times with brine and water. The organic phase was filtered through cellite. The product was concentrated in a rotatory evaporator and precipitated in methanol. Overall the yield for the polymer was 36 mg (15 %). Mn: 2600 Da, PDI: 1.27. ^{1}H

NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.66-7.43 (aromatic-H), 1.94-0.78(alkyl-H). Elemental analysis: Cal. C, 84.00; H, 6.23; N, 4.56; S, 5.21. Found: C, 67.14; H, 6.66; N, 0.67; S, 1.53. ICP: Cu: 0.4 ppm, Pd: 0.13 ppm.

General procedure for the photodehalogenation reaction of α-bromo acetopheone derivatives

10 mg of B_2-FL_2-BBT, 0.2 mmol of substrate, 0.22 mmol (56 mg) of Hantzsch ester and 0.4 mmol (70 μL) of DIPEA and 0.4 mmol (36 μL) of trichloroethylene (internal standard) were added to 1 mL of deuterated DMF, which was degassed with nitrogen for 5 min. The reaction vial was placed in front of a 23 W household energy saving fluorescent light bulb. Samples were taken and conversions were determined by ^{1}H NMR using the calibrated internal standard.

Dehalogenation reaction of α-bromo-acetophenone using the linear polymer as photocatalyst

5 mg of conjugated linear polymer B-FL_2-BBT-L, 0.1 mmol (20 mg) of α-bromo-acetophenone, 0.11 mmol (28 mg) of Hantzsch ester and 0.2 mmol (35 μL) of DIPEA and 0.2 mmol (18 μL) of trichloroethylene (internal standard) were added to 0.5 mL of deuterated DMF and then degassed with nitrogen for 2 min. The reaction vial was placed 5 cm in front of a 23 W household energy saving fluorescent light bulb overnight. Samples were taken before and after the reaction for ^{1}H NMR and UV/Vis measurements.

Table S1: Surface area and pore size distribution data of the polymers.

Polymer	**S_{BET} [m^2/g]**	**Pore diameter [nm]**	**Pore volume [cm^3/g]**
B_2-FL_2-BBT	23	3.6	0.06
[a] B_2-FL_2-BBT	21	3.9	0.06
B_2-FL_3	17	3.2	0.03

[a]: Measured after the reductive photodehalogenation.

Polymer Characterization

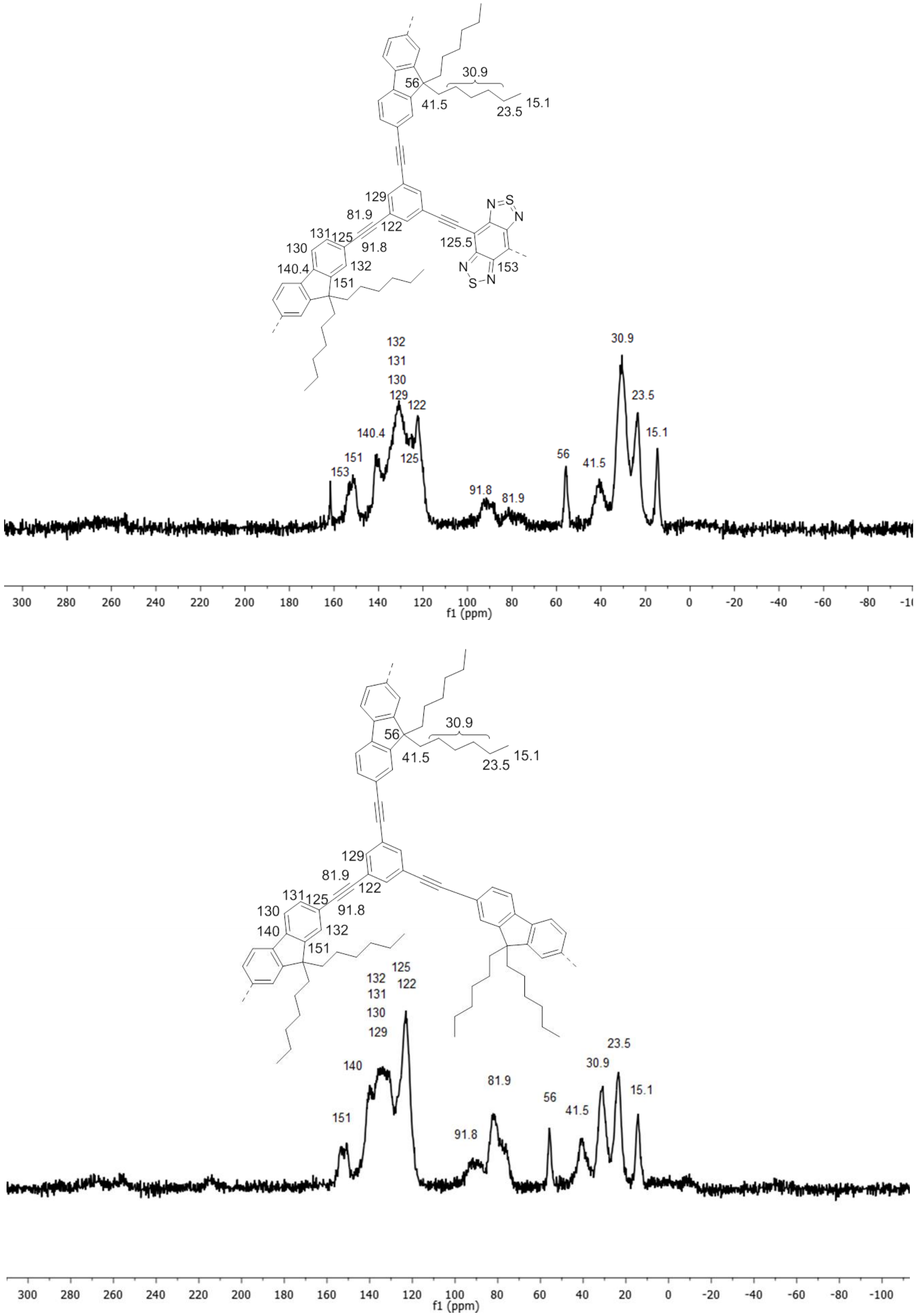


Fig S1: Solid state ^{13}C/MAS NMR spectrum of B_2-FL_2-BBT and B_2-FL_3.

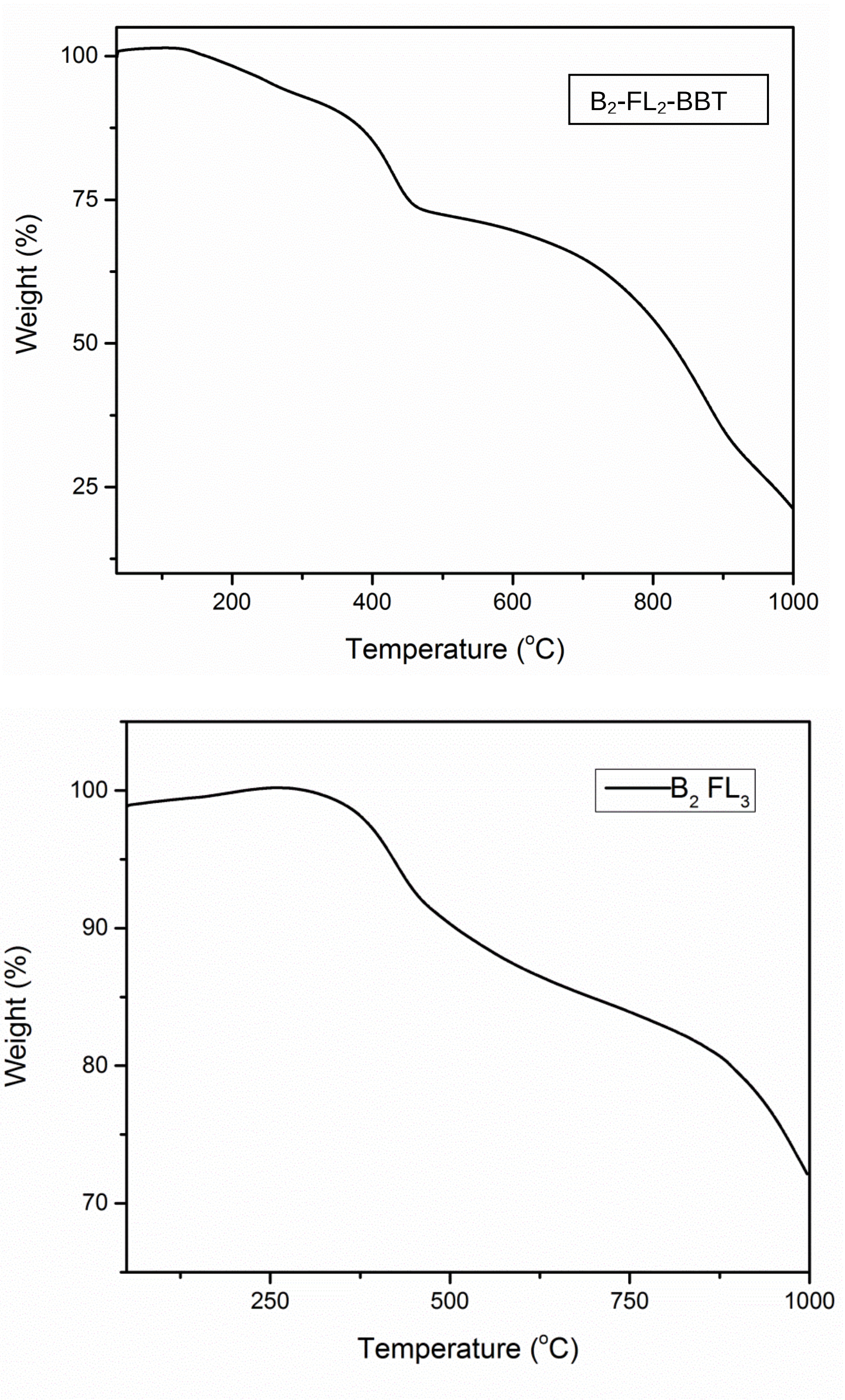
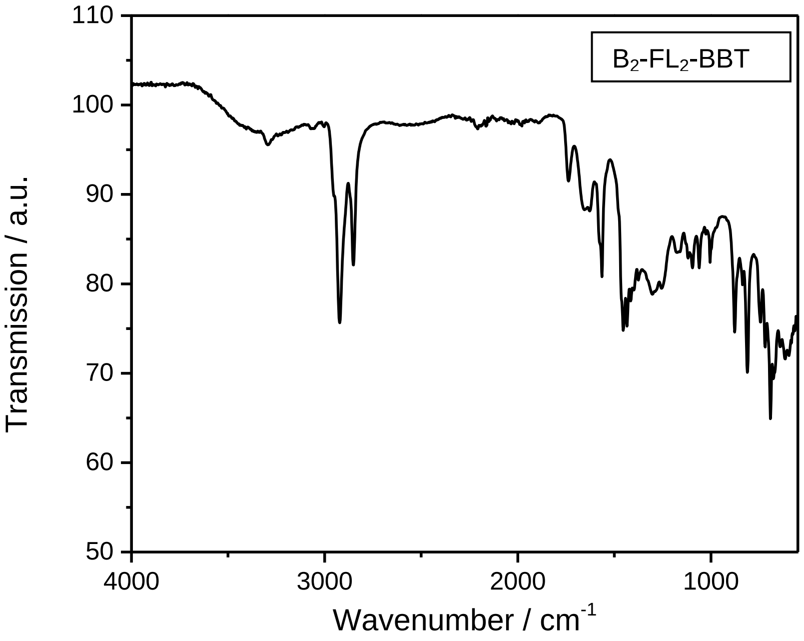


Fig S2: TGA of of B_2-FL_2-BBT and B_2-FL_3.



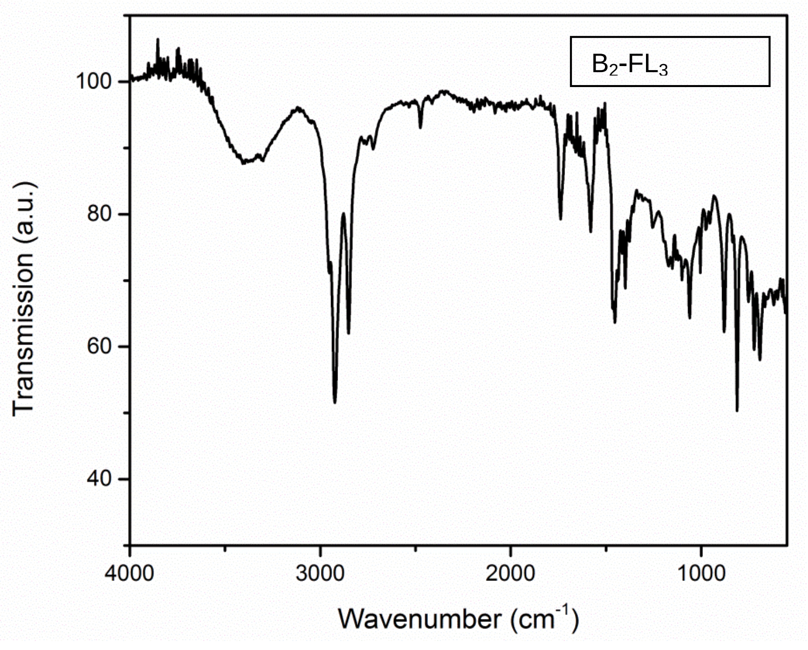


Fig S3: FT-IR spectra of B$_2$-FL$_2$-BBT and B$_2$-FL$_3$.

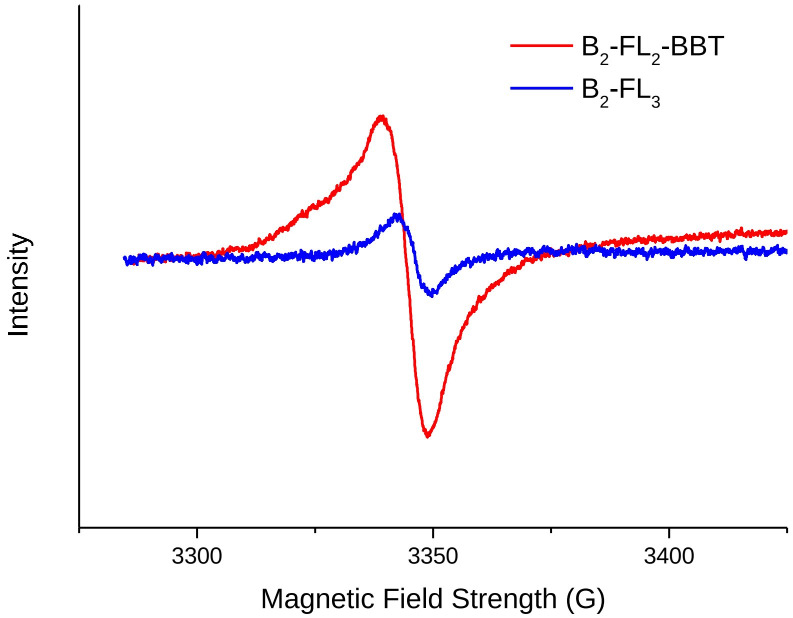
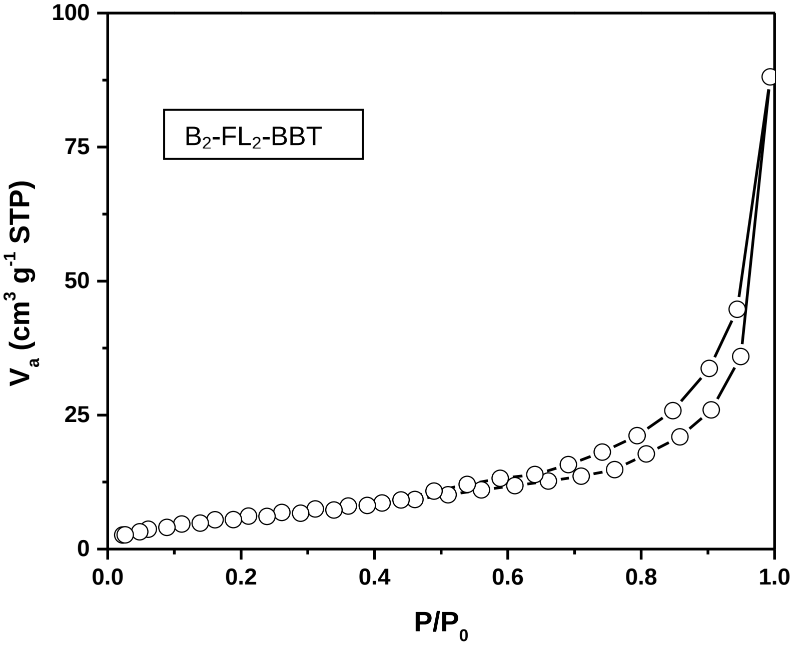


Fig S4: Electron paramagnetic resonance (EPR) spectra of B_2-FL_2-BBT and B_2-FL_3 under light irradiation.



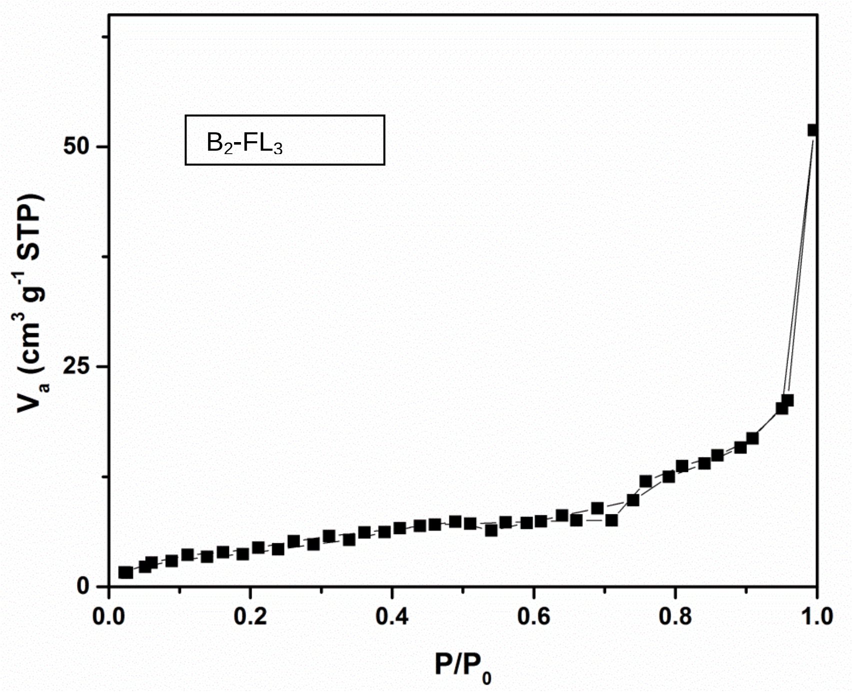
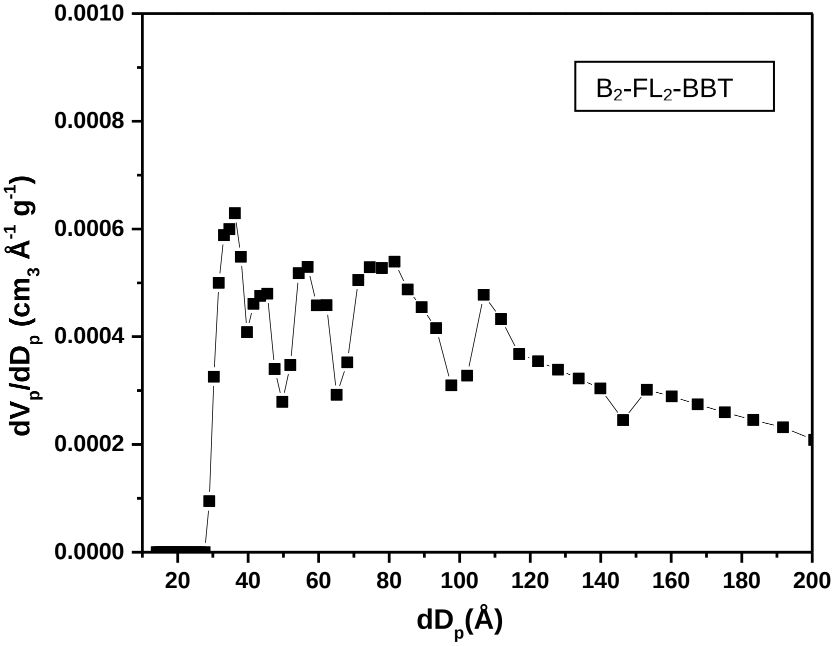


Fig S5: N_2 sorption isotherms of B_2-FL_2-BBT and B_2-FL_3.



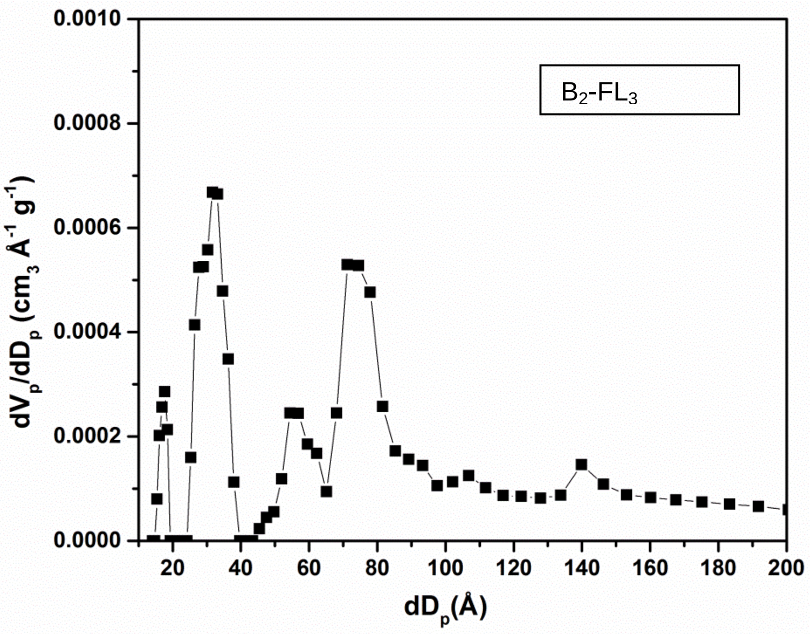
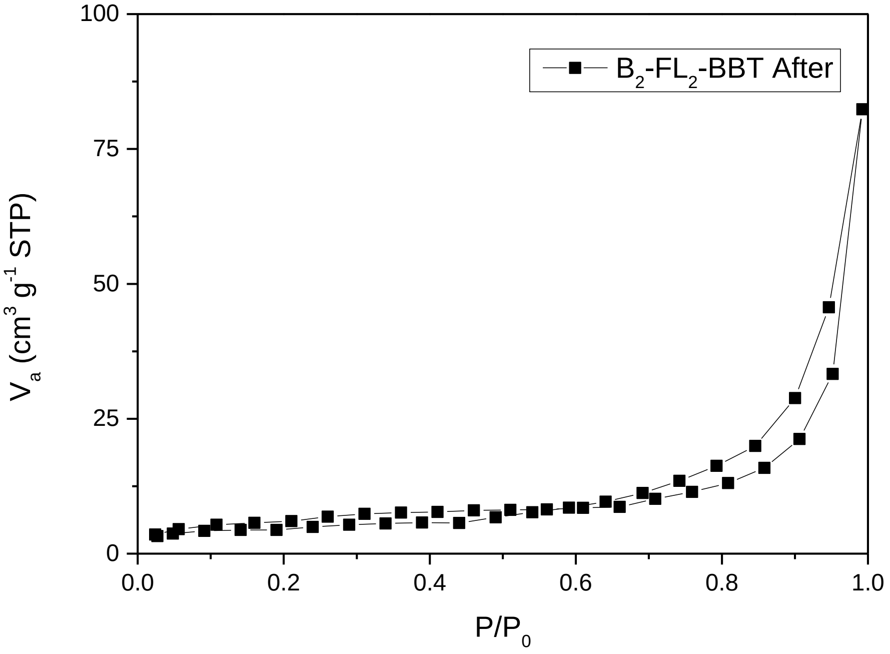


Fig S6: Pore size Distributions of B_2-FL_2-BBT and B_2-FL_3.



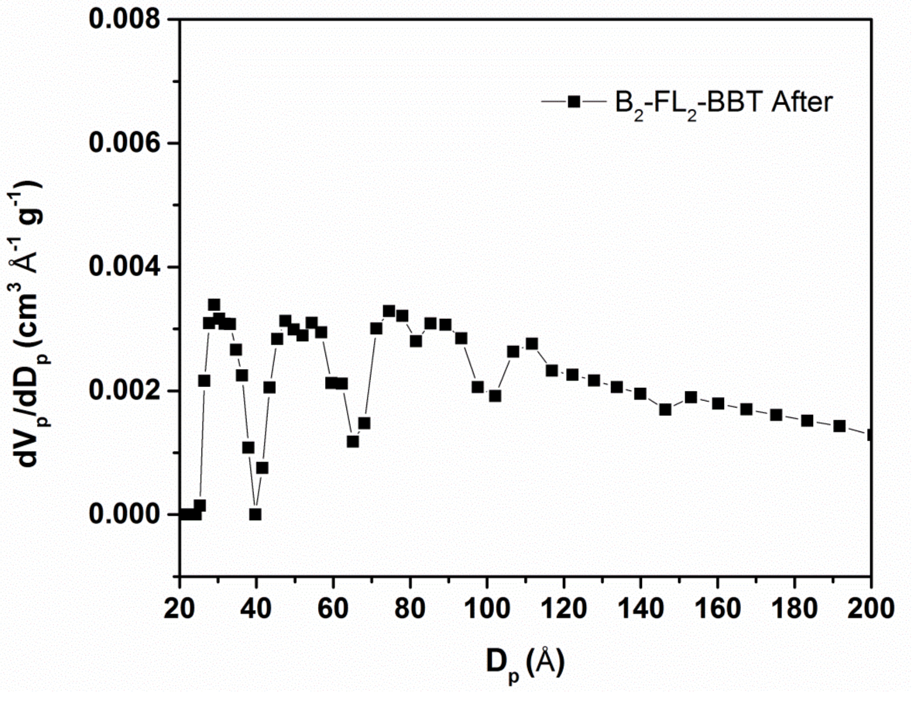
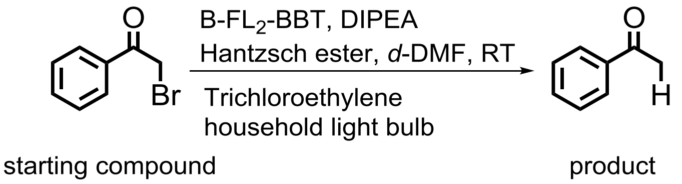


Fig S7. N_2 sorption isotherms and pore size distribution of B_2-FL_2-BBT after the reductive dehalogenation reaction.

3. Determination of conversion of the dehalogenation reaction

Determination of the conversion of photo dehalogenation reaction of haloketones using an internal standard.



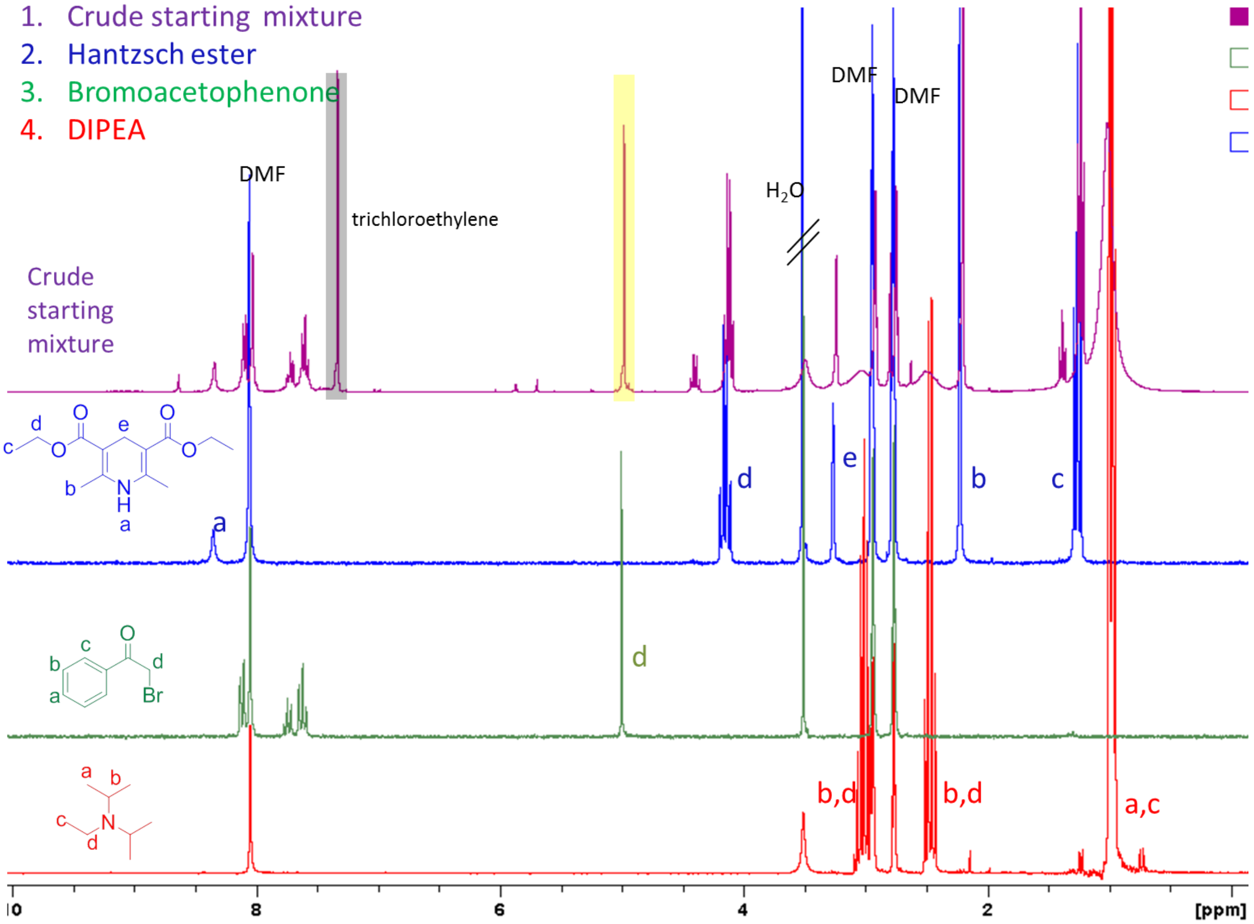


Fig S8. ^{1}H NMR spectra of the reaction mixture **before** light irradiation and the reaction components taken separately in DMF-*d*. δ = 7.35 ppm (s, 1H, trichloroethylene), 4.98 ppm (s, 2H, C(O)-C**H**$_2$-Br, starting material).

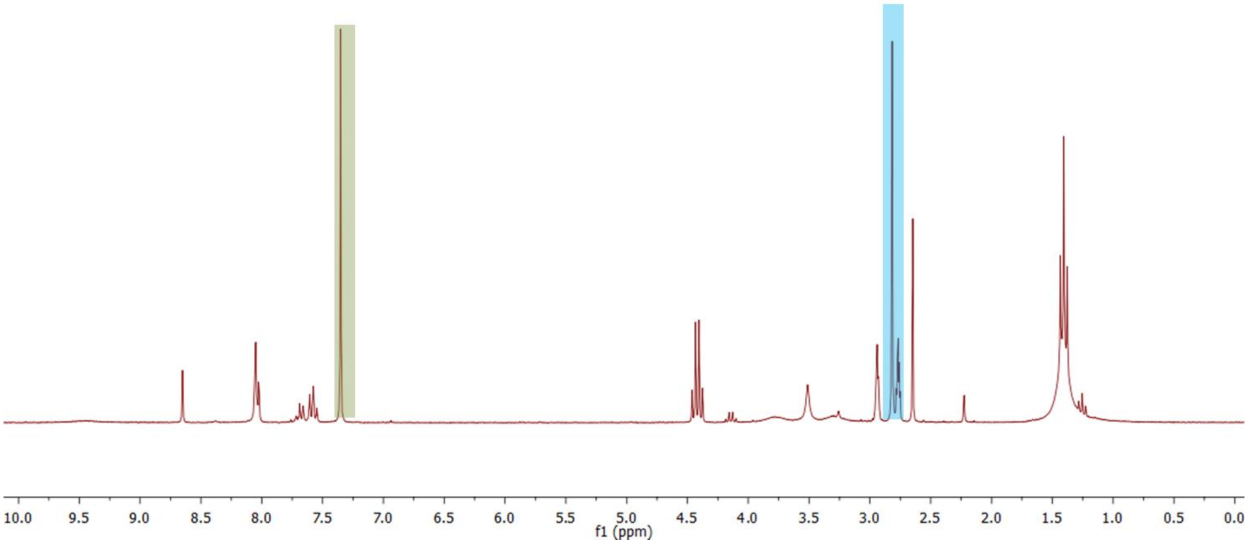
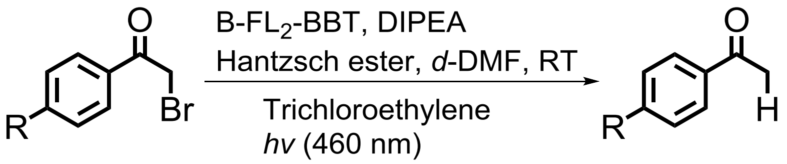


Fig S9. ^{1}H NMR spectrum of the reaction mixture **after** light irradiation δ = 7.35 ppm (s, 1H, trichloroethylene), 2.80 ppm (s, 3H, C(O)-C**H**$_3$, product).

4. Apparent Quantum Yield (AQY) Estimation



The apparent quantum yield (AQY) for the dehalogenation of 2-bromoacetopheone was measured using a single wavelength blue LED light source (4.5 W/cm^2, 460 nm) (OSA Opto Lights). 0.2 mmol of 2-bromoacetophenone, 0.22 mmol of Hantzsche ester, 0.2 mmol of DIPEA and 0.4 mmol of trichloroethylene dissolved in 1 mL of *d*-DMF were added to a glass vial and the irradiation area was controlled at 5.63 cm^2. After 3 hours, ^{1}H NMR analysis was conducted (Fig S6) and the conversion was calculated by comparing the signal intensity of protons of starting compound (5.0 ppm, 2H, s) and the protons of product (2.82 ppm, 3H, s). A conversion of the dehalogenation reaction of 60% was obtained, which corresponds to an apparent quantum yield (AQY) of 1.2 %.

The apparent quantum yield (AQY) was estimated according to the so-called “tried-and-trusted methodology” as the following:[1]

$$\text{AQY (\%)} = \frac{\text{number of moles of product obtained}}{\text{number of moles of incident photons}} \times 100$$

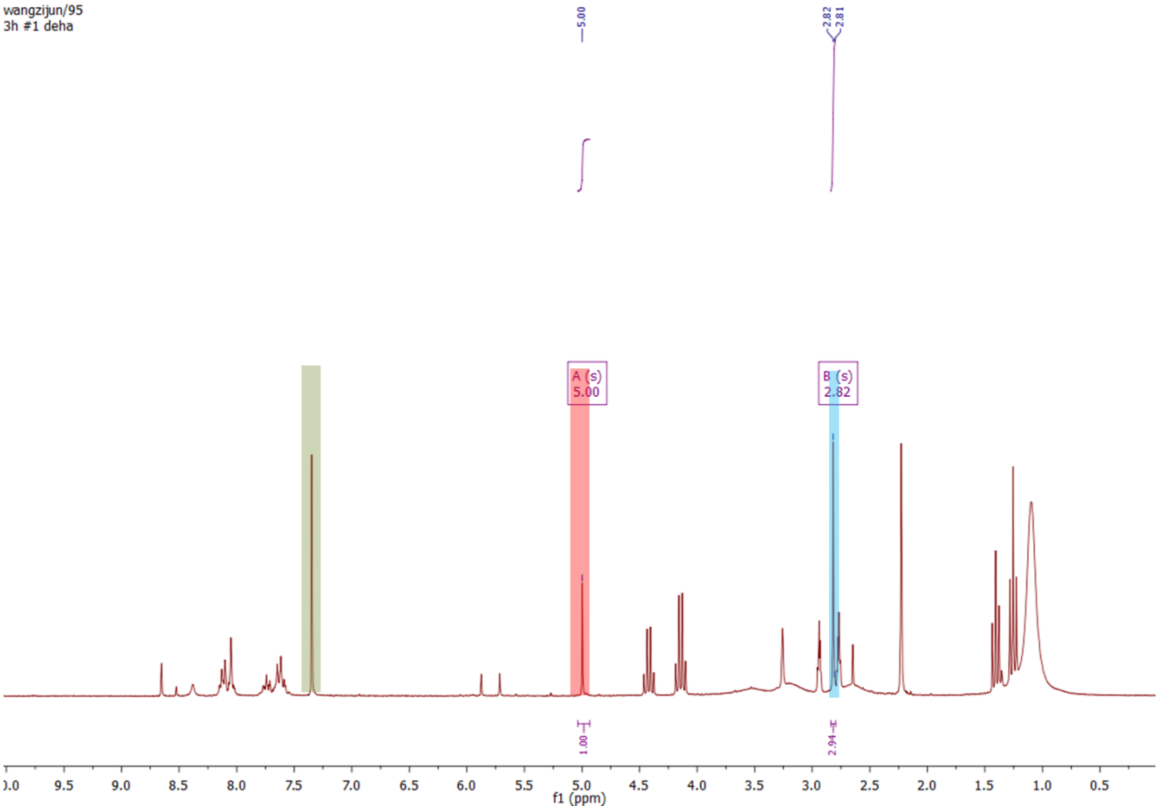


Fig S10. ^{1}H-NMR spectrum for estimation of the apparent quantum yield (AQY) of B$_2$-FL$_2$-BBT after a reaction time of 3 h. $\delta = 7.35$ ppm (s, 1H, trichloroethylene), 4.98 ppm (s, 2H, C(O)-C**H**$_2$-Br, starting material), 2.80 ppm (s, 3H, C(O)-C**H**$_3$, product).

1. Maschmeyer, T.; Che, M., *Angew. Chem. Int. Ed.* **2010,** 49, (9), 1536-1539.

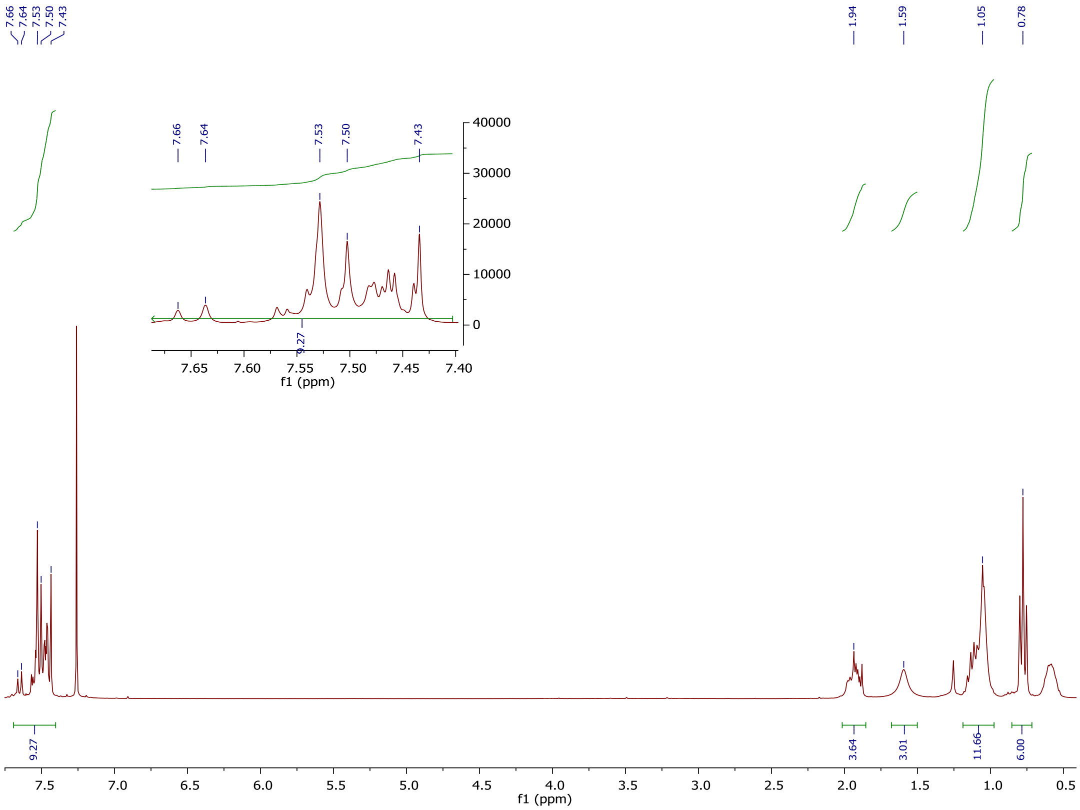


Fig S11: ^{1}H NMR spectrum of the linear polymer B_2-FL_2-BBT-L.

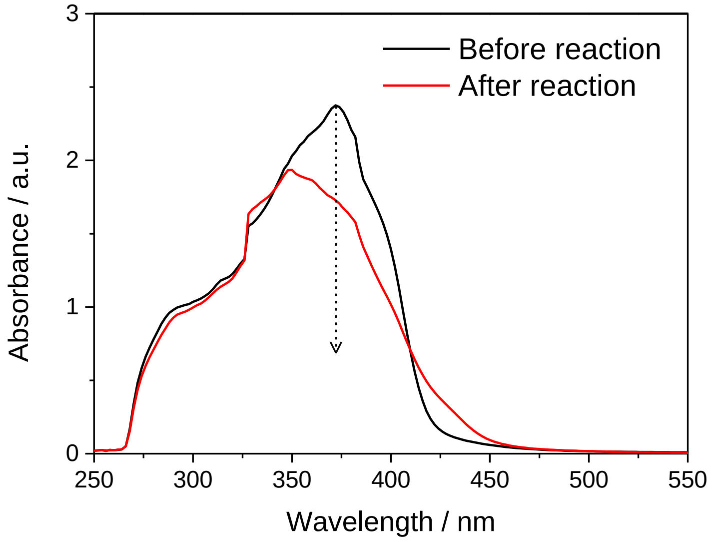


Fig S12: UV/vis spectra of the linear polymer before and after the photo dehaloganation reaction.

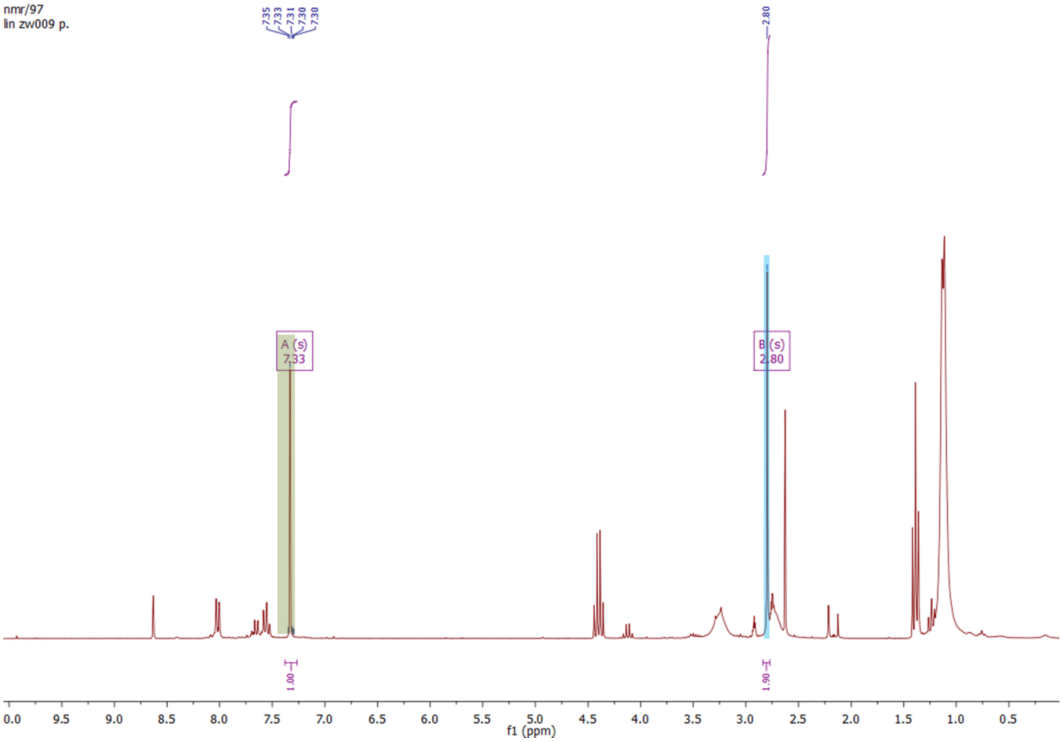


Fig S13: ^{1}H NMR spectrum of the reaction mixture using linear polymer after light irradiation. $\delta = 7.35$ ppm (s, 1H, trichloroethylene), 2.80 ppm (s, 3H, $C(O)\text{-}C\mathbf{H}_3$, product).

5. Repeating experiments of dehalogenation of 2-bromoacetophenone

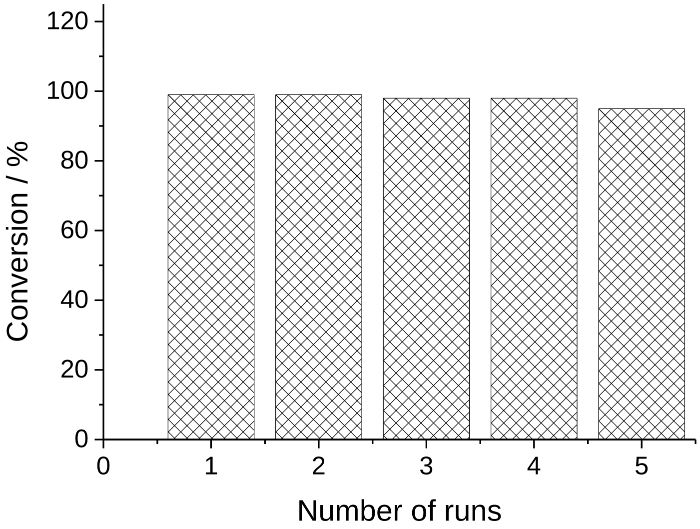
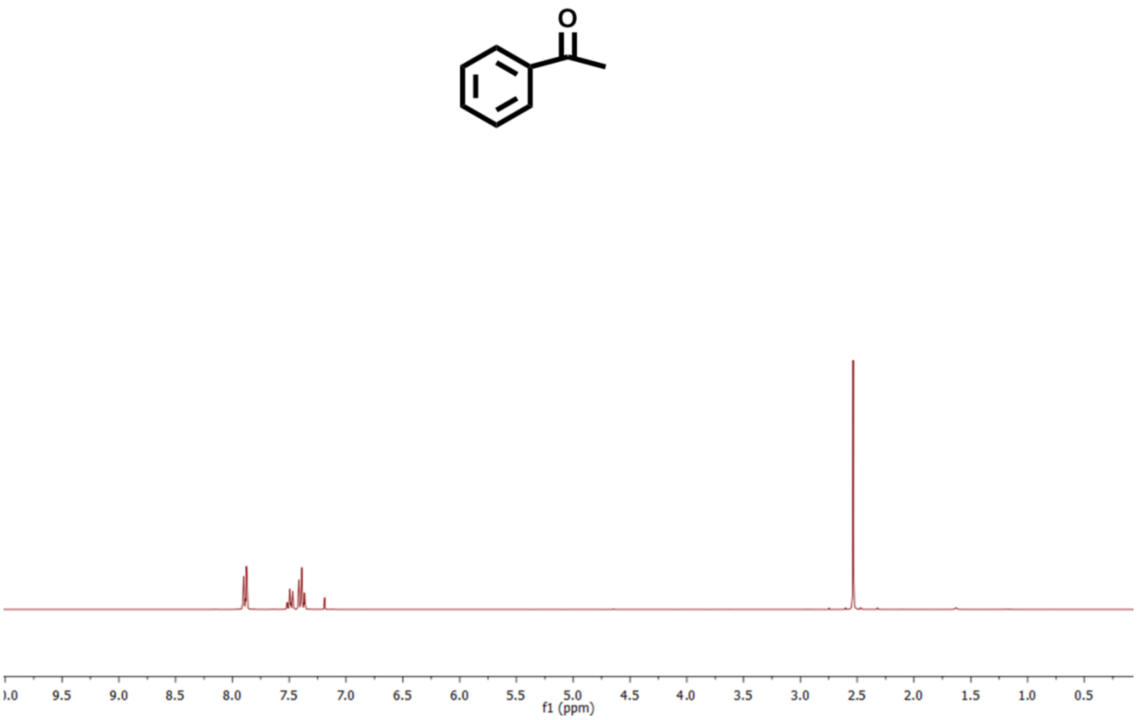


Fig S14: Reapeating experiment of the dehalogenation of 2-bromoacetophenone using B_2-FL_2-BBT as photocatalyst.

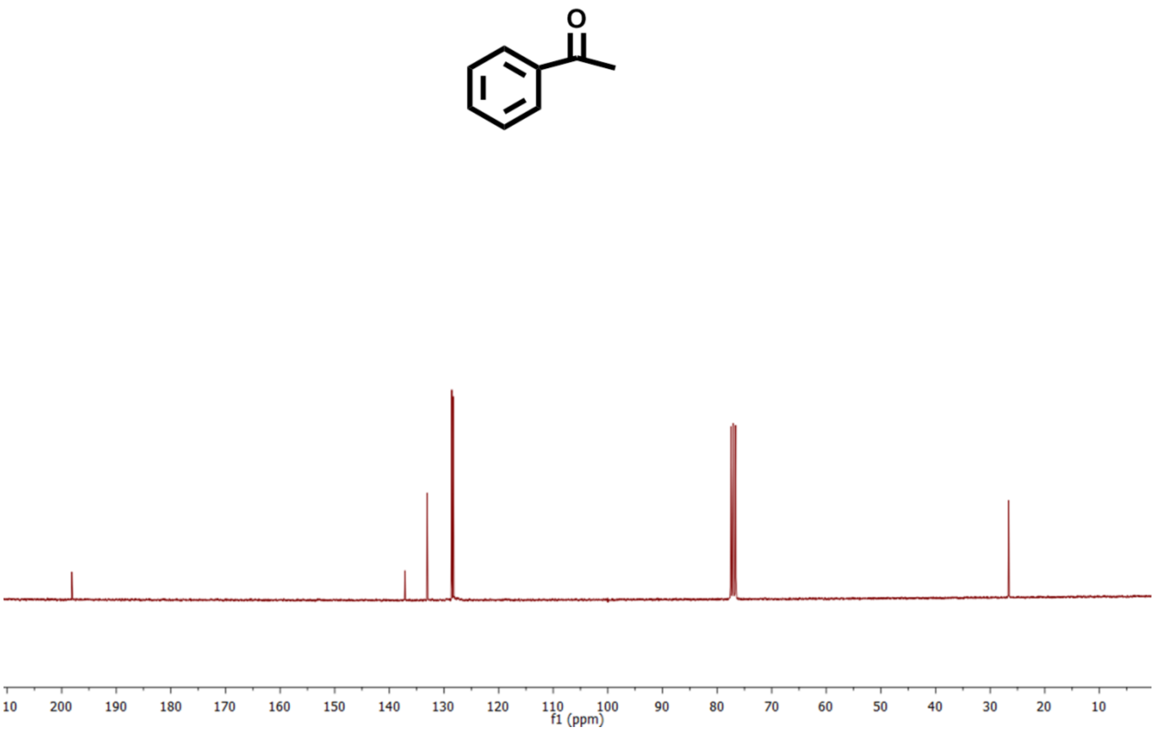
Fig S15: Simple set-up of the dehalogenation of haloketones a 23 W household energy saving light bulb.

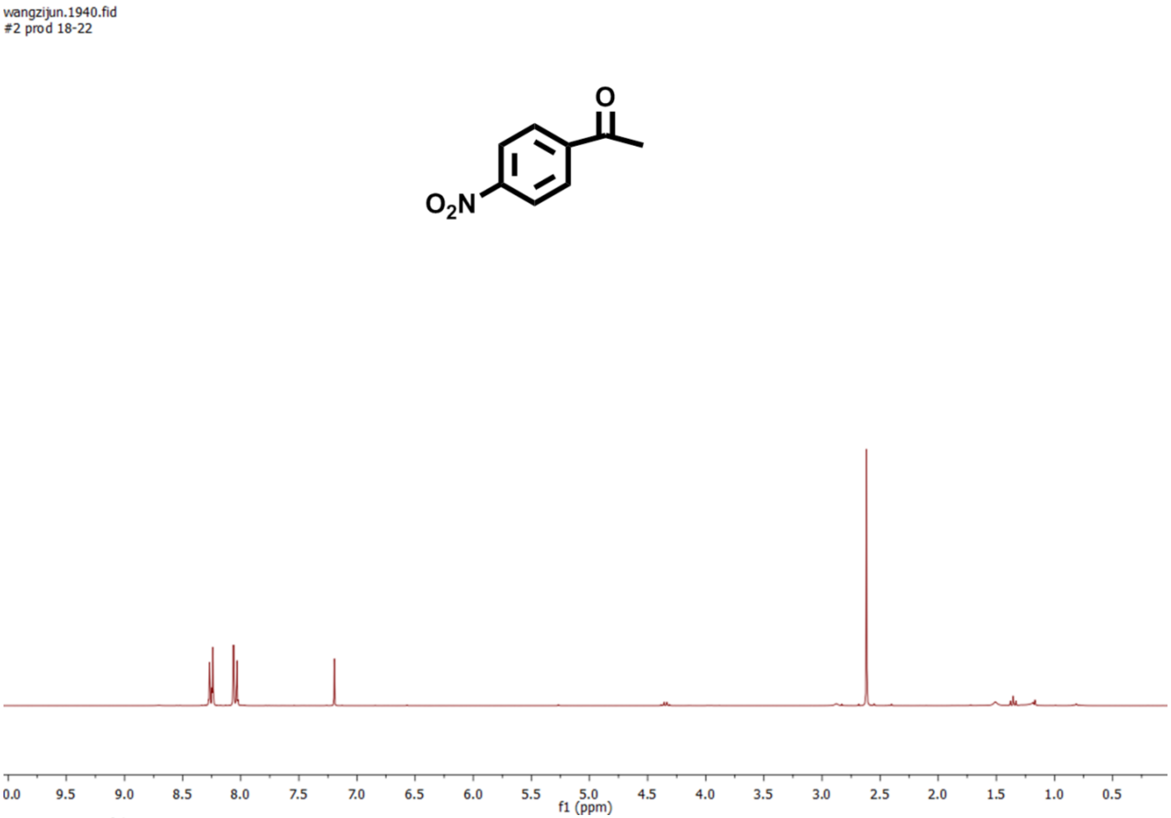
6. ^{1}H NMR, ^{13}C NMR Spectra of Dehalogenated Products

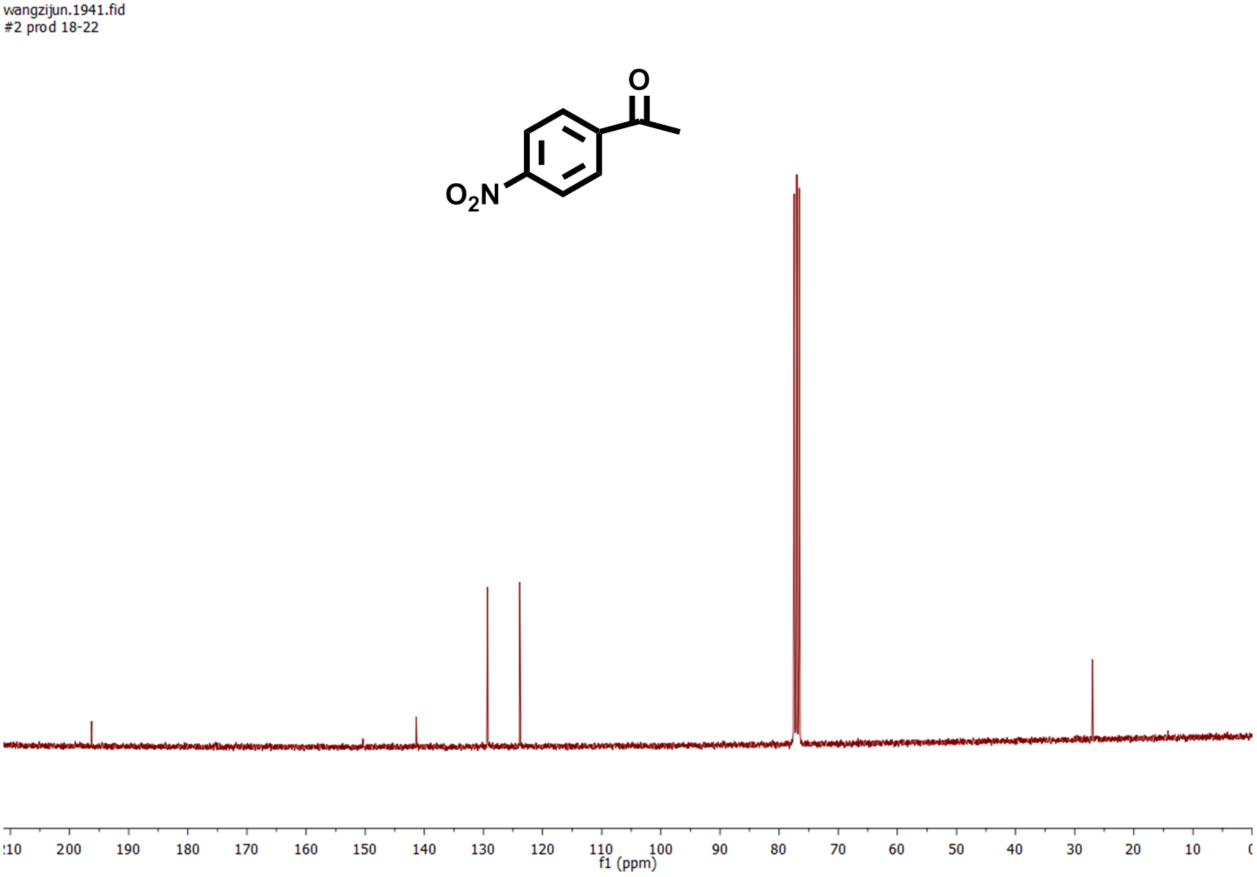
wangzijun.1960.fid
#1 prod



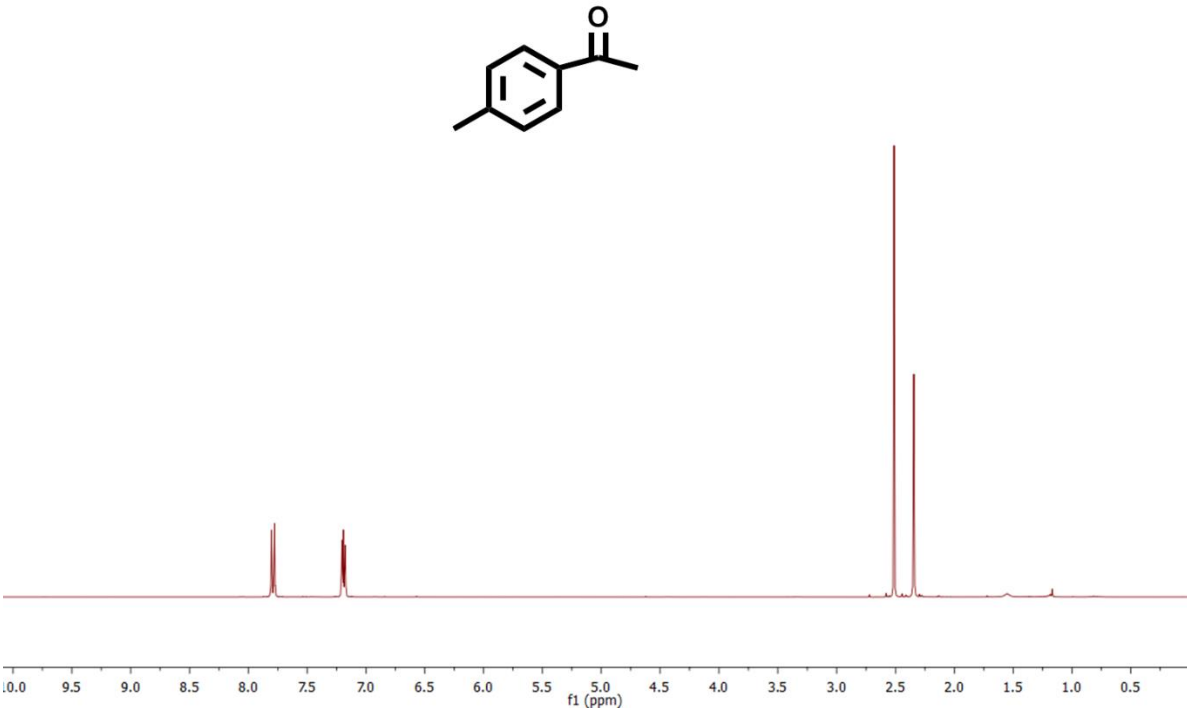
wangzijun.1961.fid
#1 prod



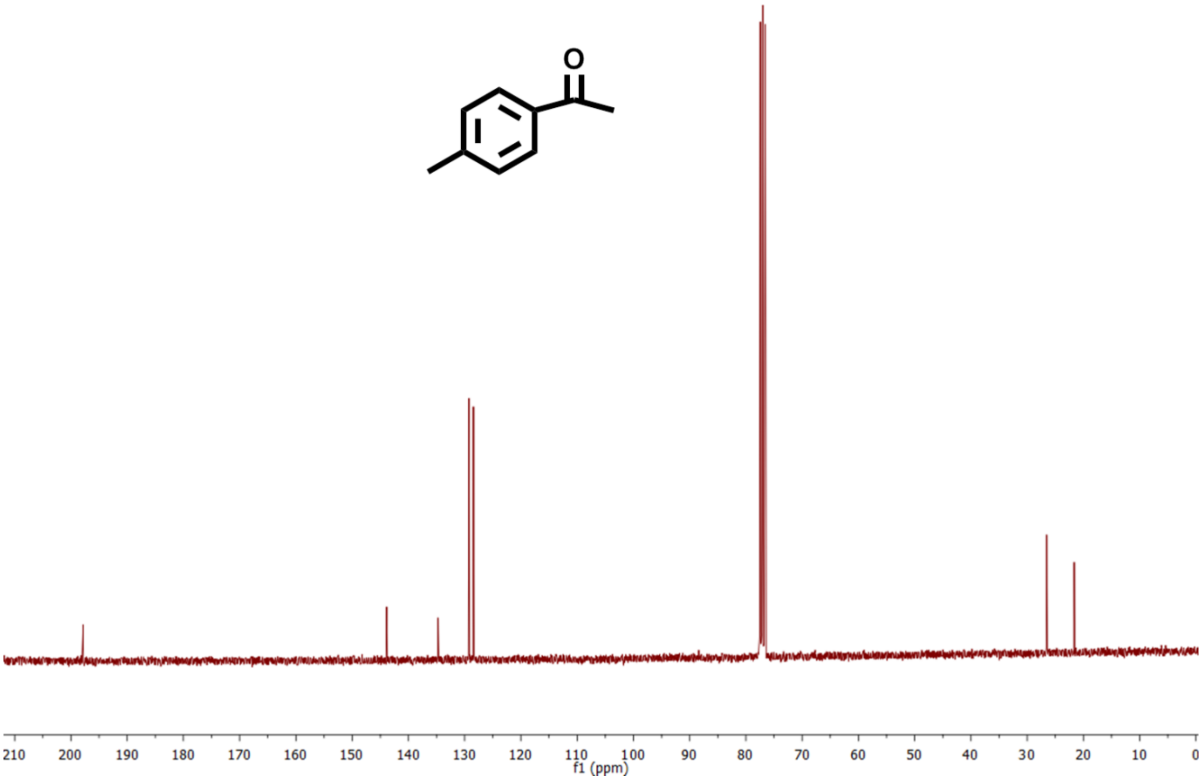

wangzijun.1940.fid
#2 prod 18-22
O
O2N
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


wangzijun.1941.fid
#2 prod 18-22
O
O2N
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

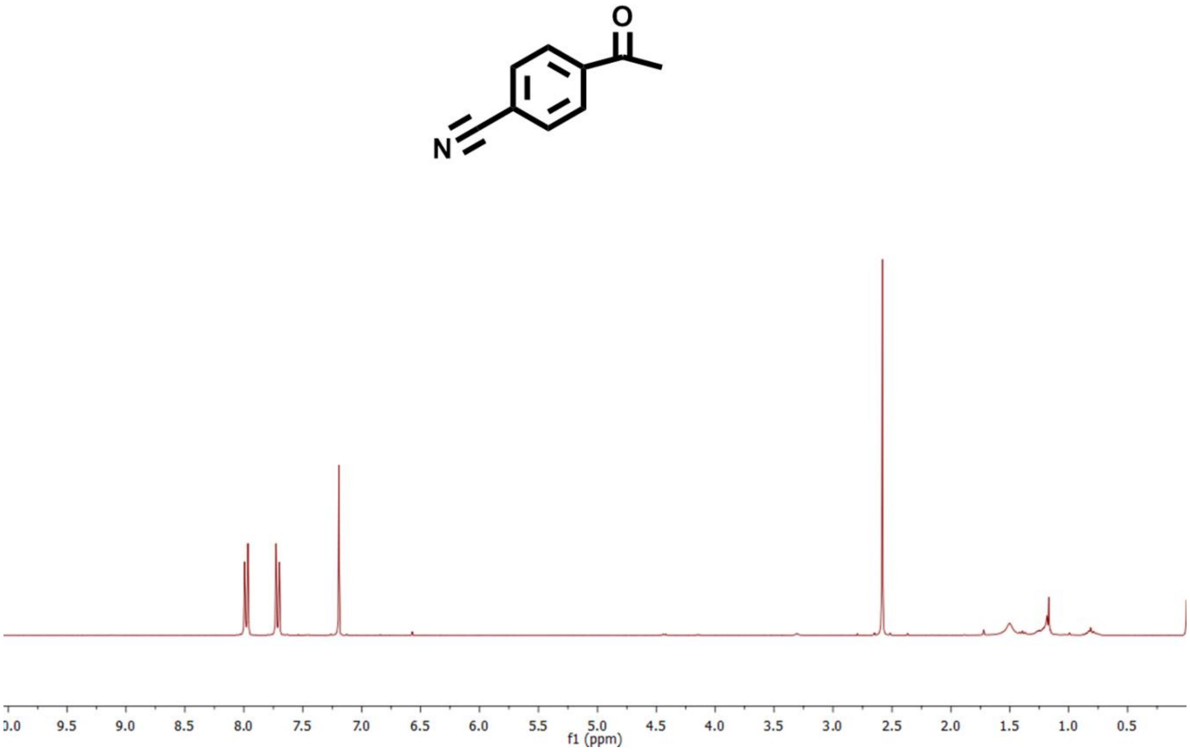
wangzijun.1920.fid
#3 prod methyl 7-9



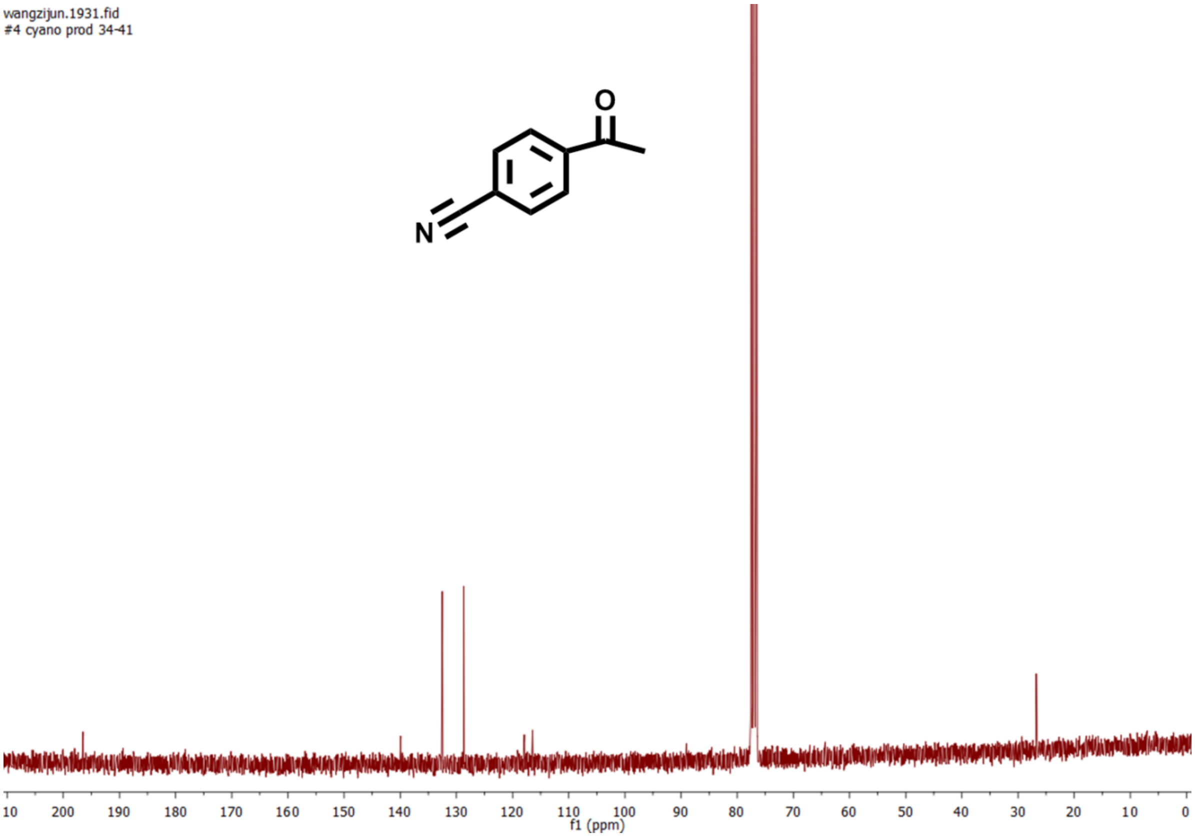
wangzijun.1921.fid
#3 prod methyl 7-9

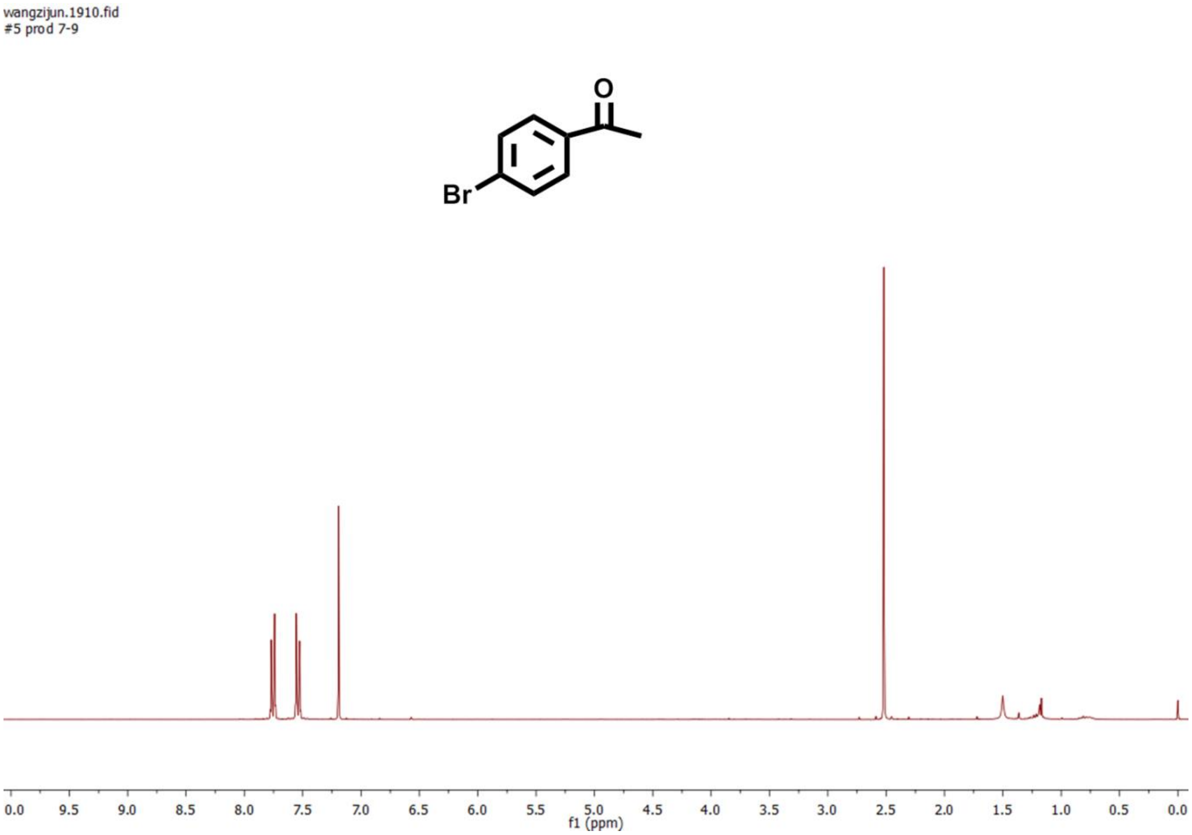


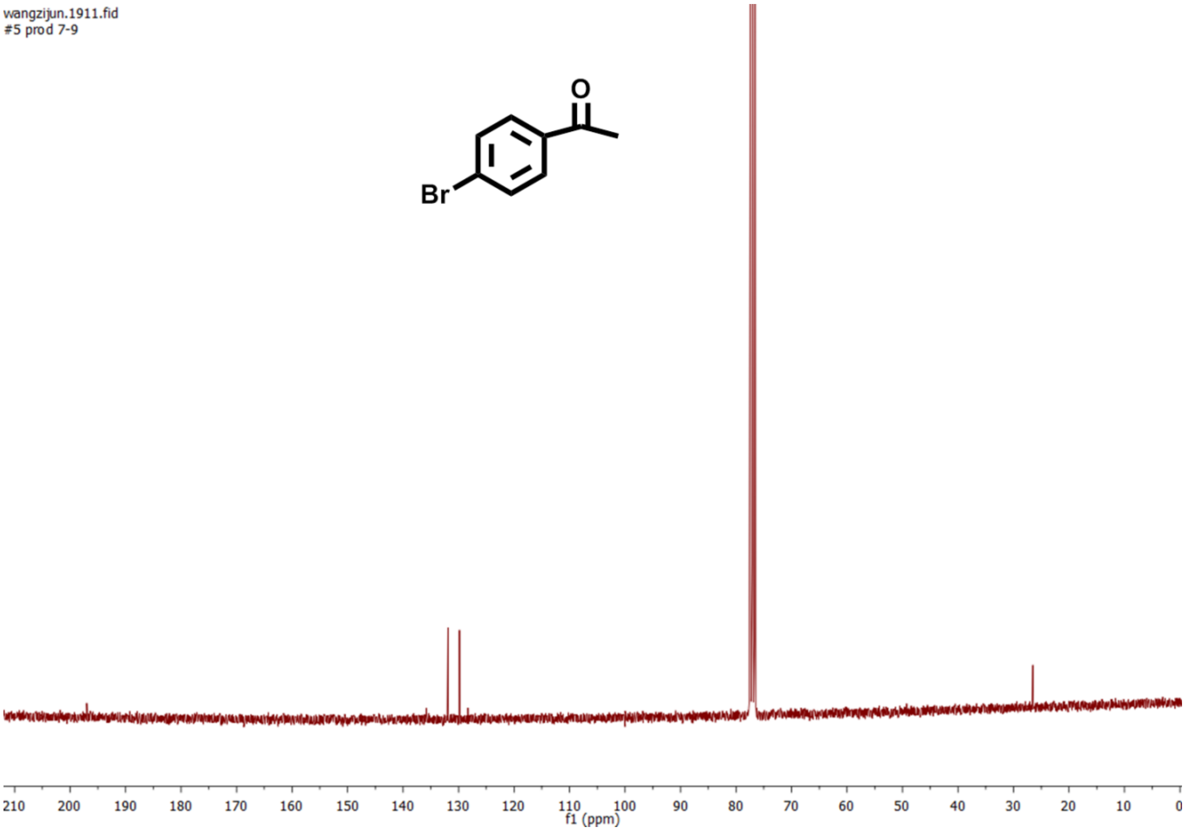
wangzijun.1930.fid
#4 cyano prod 34-41

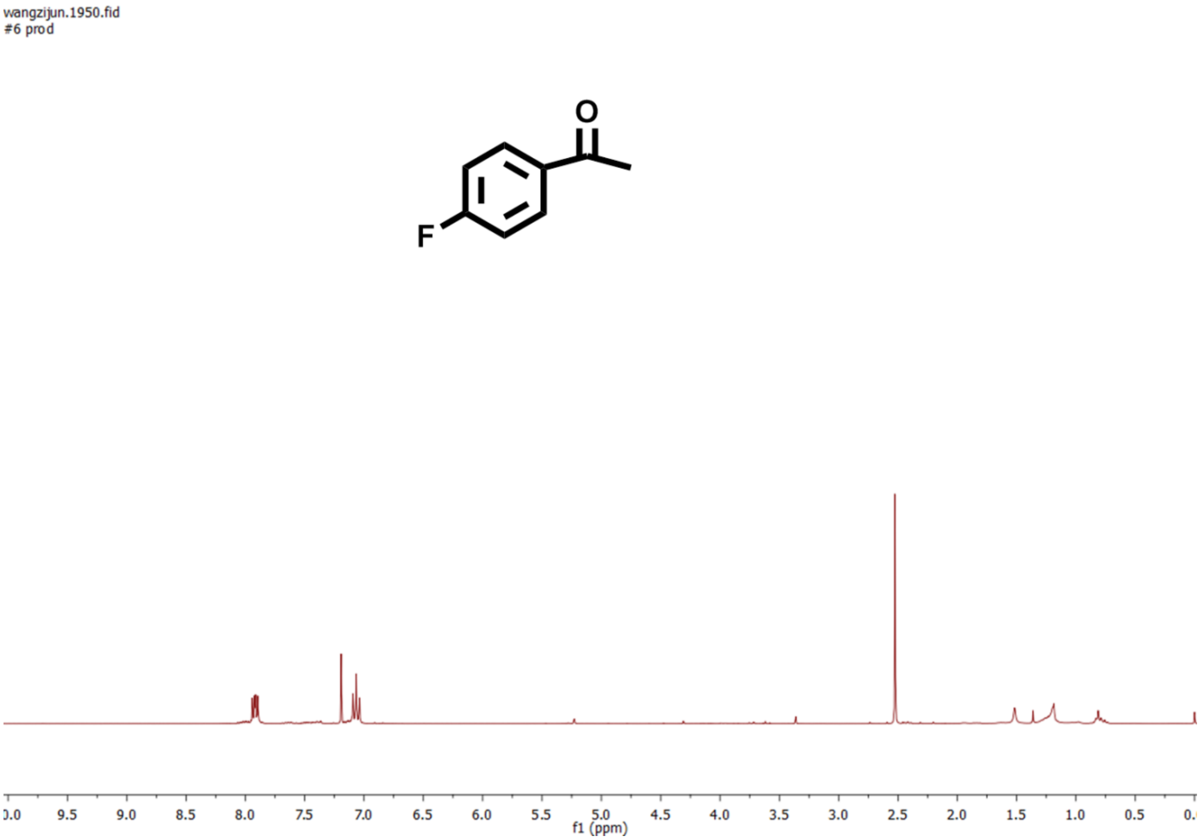


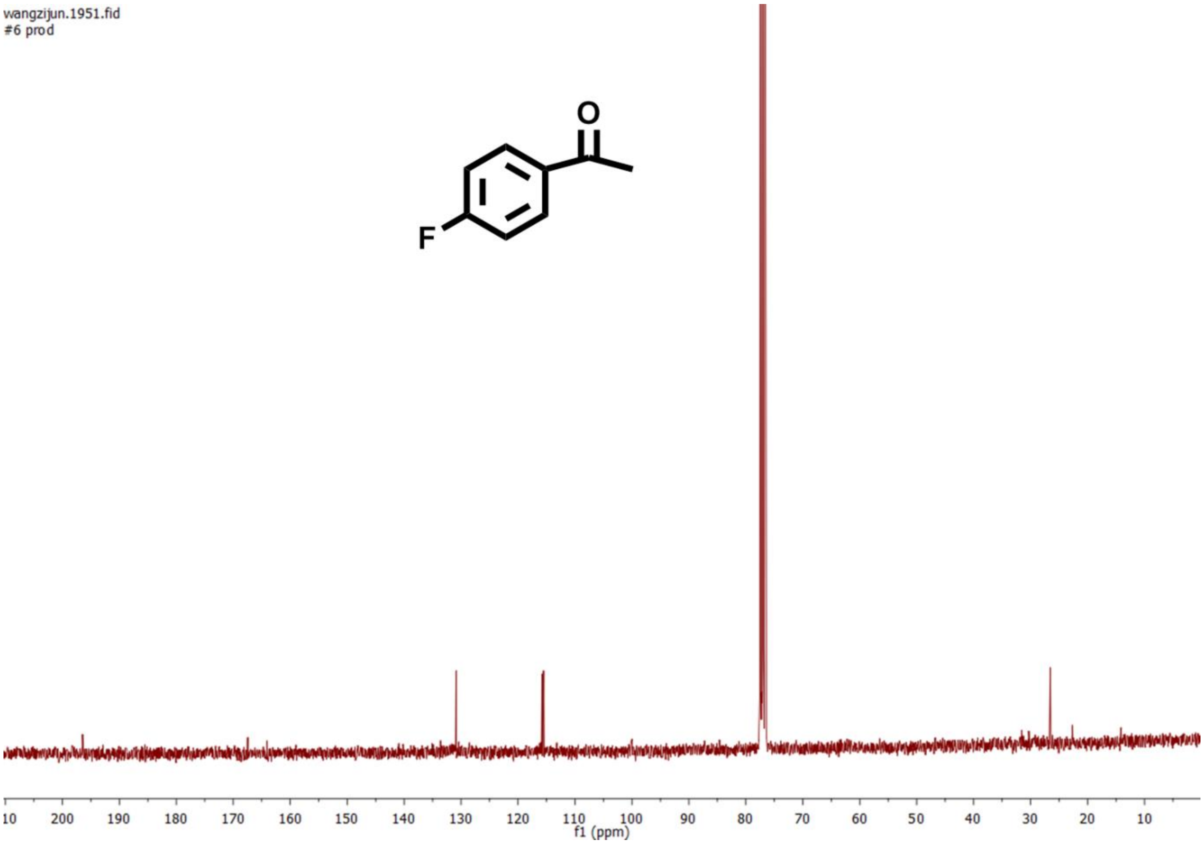
wangzijun.1931.fid
#4 cyano prod 34-41

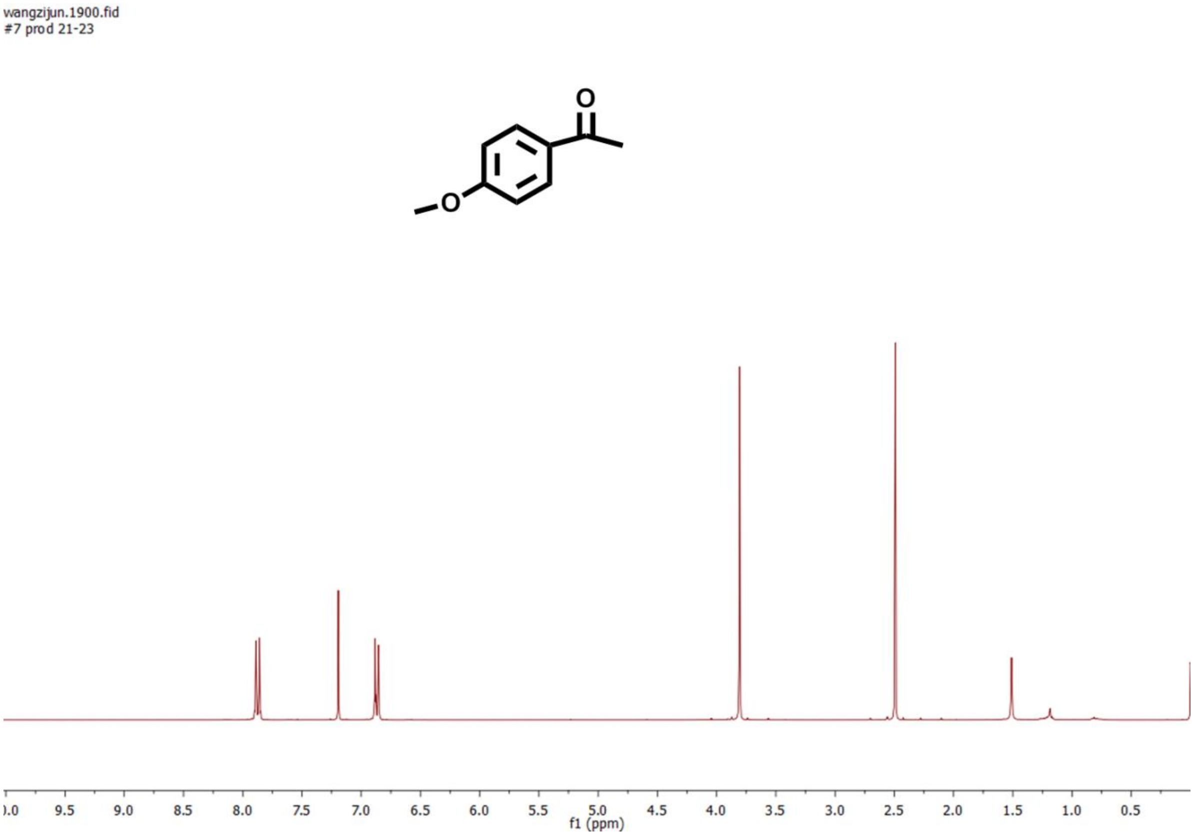


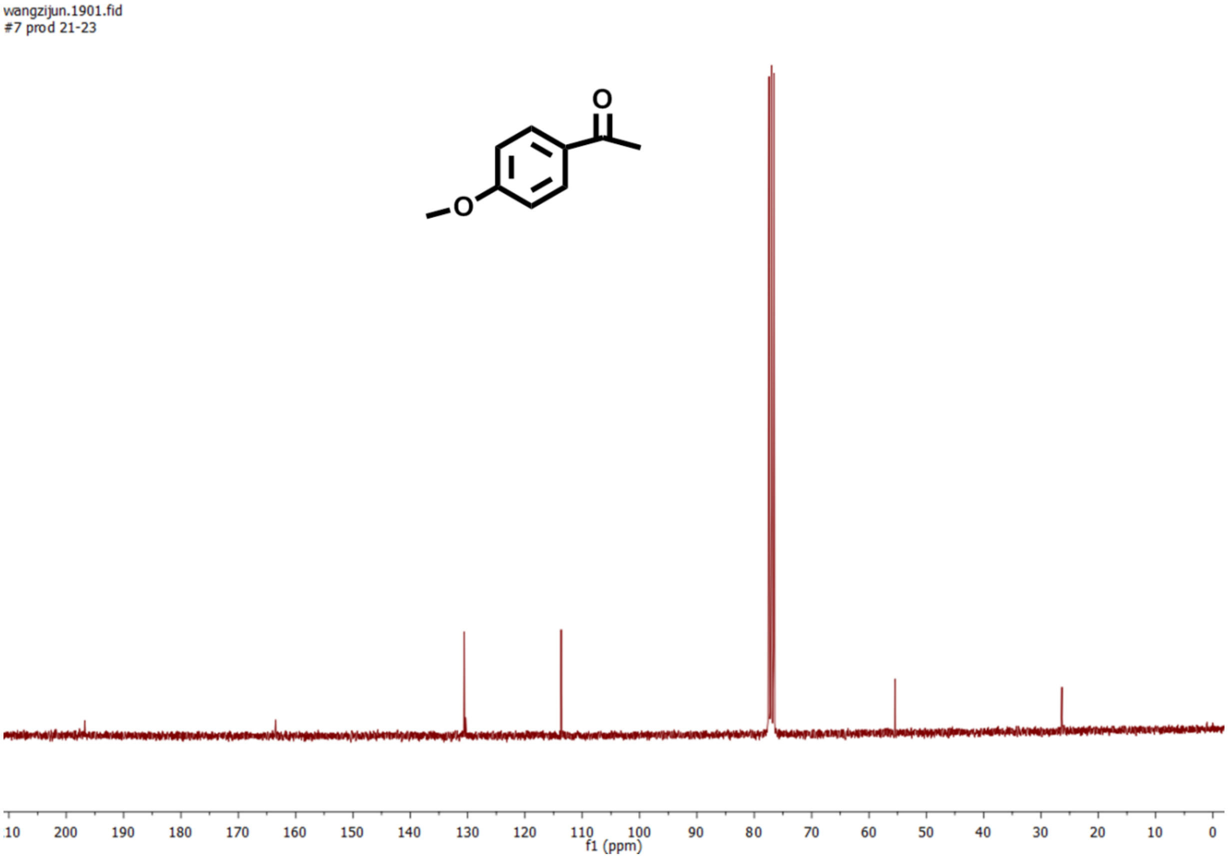

wangzijun.1910.fid
#5 prod 7-9
Br
O
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


wangzijun.1911.fid
#5 prod 7-9
Br
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


wangzijun.1950.fid
#6 prod
O
F
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


wangzijun.1951.fid
#6 prod
O
F
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


wangzijun.1900.fid
#7 prod 21-23
O
O
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


wangzijun.1901.fid
#7 prod 21-23
O
O
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)