Supporting Information

Carboxylation of α, β-Unsaturated Ketones by CO_2 Fixation through Photoelectro-chemistry

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1. Materials and equipments

Acetonitrile (99.9%, super dry with molecular sieve, Meryer), chalcone (>98.0%, Energy Chemical), tetrabutylammonium bromide (99%, J&K), HF solution (48 wt.% in H_2O, Sigma-Aldrich) and $AgNO_3$ (>98%, Sigma-Aldrich) are used without further purification. P-Si (100) wafers (10^{15} cm^{-3} B doped; ρ:10~20 Ω•cm; Wafernet, CA, USA) and Al foil (99.9995%, Alfa Aesar) are polished before use. CO_2 (99.9%) is purchased from Airgas, while Ag epoxy (MG Chemicals 8331) from SPI supplies and non-conductive hysol epoxy (EA615) from Loctite. All other reagents and materials, unless otherwise noted, are purchased from commercial vendors and used without further purification.

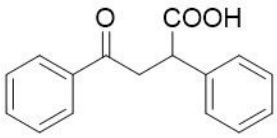
Xenon lamp (300W, Newport, model 71228, CA, USA) is used as light source by AM 1.5G filter to simulate sunlight and the light intensity is about 100 mW/cm^2. The sputtering of Al on Si plate is operated on radio frequency magnetron sputtering instrument (AJA International). All reactions are monitored by thin-layer chromatography (TLC) performed on pre-coated TLC plates (silica gel, 0.2 mm, HSGF254). Visualization is accomplished with UV light (254 nm) and phosphomolybdic acid in ethanol by heating. Flash column chromatography is performed on silica gel (200-300 mesh, Huanghai Ltd.). ^{1}H NMR and ^{13}C NMR spectra are recorded on a JEOL or Broker 400 MHz spectrometer at ambient temperature. High resolution mass spectra (HRMS) are obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QTof) using electrospray ionization (ESI) in positive or negative mode. Electrochemical data are recorded on AutoLab XM (Ameteck, PSTAT) ECS or CHI Electrochemical Test System.

2. General procedure and experimental results

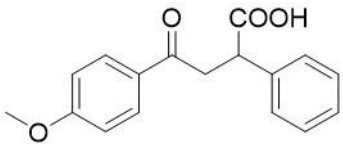
Synthesis of SiNWs electrode. The synthesis method of SiNWs was reported before.[1] A p-Si (100) was cleaned sequentially in acetone, methanol, and isopropanol and then oxidized in H_2O_2/H_2SO_4 (1:3) at 90˚C for 15 min to remove heavy metals and organic species. After rinsing with deionized (DI) water, the substrate was cut into approximately 1.0 cm×5.0 cm pieces and then immersed into an HF/$AgNO_3$ aqueous solution (containing 4.6 M HF and 0.02 M $AgNO_3$) for 30 min at 50˚C for a varying duration of time to produce SiNWs of varying lengths. A film of Al (300 nm) is then sputtered onto the backside of the SiNWs substrate by radio frequency magnetron sputtering. The resulted samples are then annealed in Ar (flow rate: 5000 standard cubic centimeter per minute, SCCM) at 450 ℃ for 5 min. Afterward, tinned Cu wires were fixed to the Al film by Ag epoxy. Lastly, non-conductive hysol epoxy was used to seal the entire substrates except the regions where SiNWs resided. Before use, SiNWs electrode was immersed in HF (aqueous, 5%) for 5 min and then dried in a stream of N_2.

General photoelectro-catalysis procedure. In an oven-dried three-neck round-bottom flask equipped with a magnetic stir bar, tetrabutylammonium bromide (0.644 g, 2.00 mmol), α, β-unsaturated ketone (0.4mmol), and acetonitrile (20mL) were added under Ar. Then the flask is set up in photoelectro-catalysis system with Ag/AgBr as the reference electrode, Al foil as the counter electrode and SiNWs as the working electrode. CO_2 is bubbled into the vessel continuously at controlled flow rate for several minutes to saturate the solution, then a suitable

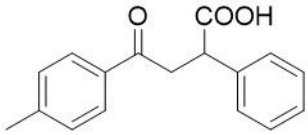
potential was applied to the reaction mixture with light irradiation and vigorously stirring. After reaction, the crude mixture is concentrated in vacuo and quenched with 1 N HCl (2 mL), followed by extraction with ethyl acetate (3 x 20 mL). The combined organic layers are dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to afford the crude product. After purification on column chromatography (Hexane/Ethyl acetate), pure compound is isolated.



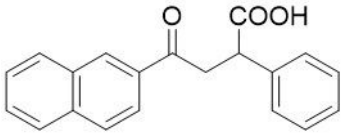
^{1}H NMR (d^6-DMSO, 400 MHz) δ 12.40 (s, 1H), δ 8.04 – 8.02 (d, *J*=8 Hz, 2H), δ 7.06-7.58 (d, *J*=8 Hz, 2H), δ 7.40-7.33 (m, 5H), δ 7.29-7.26 (m, 1H), δ 4.12-4.08 (dd, *J*=4, 4 Hz, 1H), δ 3.92-3.85 (dd, *J*=12, 8 Hz, 1H), δ 3.32-3.26 (dd, *J*=4, 4 Hz, 1H); **^{13}C NMR** (d^6-DMSO, 101 MHz) δ 197.96, 174.26, 139.04, 136.30, 133.36, 128.76, 128.63, 128.01, 127.97, 127.16, 46.17, 42.03; **Exact mass calcd** for [MNa^+] requires *m/z* 277.0841 Found 277.0820 (ES+).



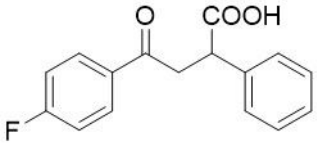
^{1}H NMR (d^6-DMSO, 400 MHz) δ 12.38 (s, 1H), δ 8.00 – 7.98 (d, *J*=8 Hz, 2H),δ 7.40-7.25 (m, 5H), δ 7.04-7.02 (d, *J*=8 Hz, 2H), δ 4.13-4.09 (dd, *J*=4, 4 Hz, 1H), δ 3.87-3.80 (m, 4H), δ 3.25-3.20 (dd, *J*=4, 4 Hz, 1H); **^{13}C NMR** (d^6-DMSO, 101 MHz) δ 196.21, 174.28, 163.22, 139.14, 130.30, 129.30, 128.58, 127.94, 127.08, 113.87, 55.53, 46.21, 41.66; **Exact mass calcd** for [MNa^+] requires m/z 307.0946 Found 307.0923 (ES+).



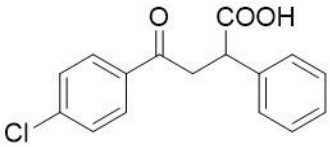
^{1}H NMR (d^6-DMSO, 400 MHz) δ 12.37 (s, 1H), δ 7.92 – 7.90 (d, *J*=8 Hz, 2H), δ 7.40-7.25 (m, 7H), δ 4.12-4.09 (dd, *J*=4, 4 Hz,1H), δ 3.89-3.82 (dd, *J*=8, 8 Hz, 1H), δ 3.28-3.22 (dd, *J*=4, 4 Hz, 1H), δ 2.37 (s, 3H); **^{13}C NMR** (d^6-DMSO, 101 MHz) δ 197.40, 174.24, 143.69, 139.07, 133.84, 129.26, 128.58, 128.10, 127.93, 127.10, 49.13, 41.88, 21.16; **Exact mass calcd** for [MNa^+] requires *m/z* 291.0997 Found 291.0988 (ES+).



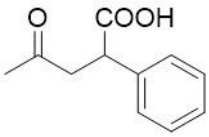
^{1}H NMR (d^6-DMSO, 400 MHz) δ 12.46 (s, 1H), δ 8.80 (s, 1H), δ 8.15-8.13 (d, *J*=8 Hz, 1H), δ 8.01-7.98 (m, 3H), δ 7.69-7.60 (m, 2H), δ 7.45-7.43 (d, *J*=8 Hz, 2H), δ 7.40-7.36 (t, 2H), δ 7.32-7.28 (m, 1H), δ 4.20-4.17 (dd, *J*=4, 4 Hz, 1H), δ 34.09-4.01 (dd, *J*=12, 12 Hz, 1H), δ 3.47-3.41 (dd, *J*=4, 4 Hz, 1H); **^{13}C NMR** (d^6-DMSO, 101 MHz) δ 197.88, 174.34, 139.12, 135.14, 133.53, 132.28, 130.24, 129.68, 128.73, 128.67, 128.31, 128.01, 127.70, 127.19, 126.97, 124.43, 46.24, 42.15; **Exact mass calcd** for [MNa^+] requires *m/z* 327.0997 Found 327.1021 (ES+).



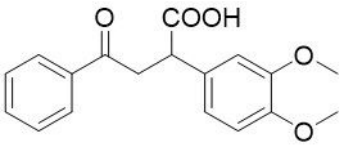
^{1}H NMR (d^{6}-DMSO, 400 MHz) δ 12.42 (s, 1H), δ 8.12 – 8.09 (m, 2H), δ 7.40-7.28 (m, 7H), δ 4.13-4.09 (dd, *J*=4, 4 Hz, 1H), δ 3.92-3.85 (dd, *J*=12, 8 Hz, 1H), δ 3.31-3.26 (dd, *J*=4 Hz, 1H); **^{13}C NMR** (d^{6}-DMSO, 101 MHz) δ 196.60, 174.20, 166.37, 163.87, 138.95, 133.05, 133.03, 131.08, 130.99, 128.59, 127.95, 115.83, 115.61, 46.13, 41.92; **Exact mass calcd** for [MNa^{+}] requires *m/z* 295.0746 Found 295.0750 (ES+).



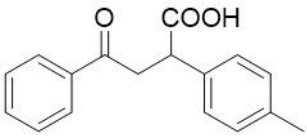
^{1}H NMR (d^{6}-DMSO, 400 MHz) δ 12.44 (s, 1H), δ 7.34-7.23 (m, 5H),δ 3.91-3.88 (dd, *J*=4, 4 Hz, 1H), δ 3.28-3.21 (dd, *J*=8, 12 Hz, 1H), δ 2.78-2.72 (dd, *J*=8, 4 Hz, 1H), **^{13}C NMR** (d^{6}-DMSO, 101 MHz) δ 197.02, 174.13, 138.89, 138.26, 134.94, 129.94, 128.83, 128.59, 127.93, 127.14, 46.10, 41.96; **Exact mass calcd** for [MNa^{+}] requires *m/z* 311.0451 Found 311.0481 (ES+).



^{1}H NMR (d^{6}-DMSO, 400 MHz) δ 12.38 (s, 1H), δ 8.04 – 8.02 (d, *J*=8 Hz, 2H), δ 7.60-7.57 (d, *J*=12 Hz, 2H), δ 7.40-7.33 (m, 4H), δ 7.29-7.26 (m, 1H), δ 4.12-4.09 (dd, *J*=4, 4 Hz, 1H), δ 3.92-3.84 (dd, *J*=12, 12 Hz, 1H), δ 3.32-3.26 (dd, *J*=4, 4 Hz, 1H); **^{13}C NMR** (d^{6}-DMSO, 101 MHz) δ 206.43, 174.16, 138.99, 128.61, 127.75, 127.09, 46.31, 45.89, 29.68; **Exact mass calcd** for [MNa^{+}] requires *m/z* 215.0684 Found 215.0658 (ES+).

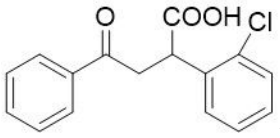


^{1}H NMR (d^{6}-DMSO, 400 MHz) δ 12.31 (s, 1H), δ 8.01 – 8.00 (m, 2H), δ 7.66-7.62 (m, 1H), δ 7.54-7.51 (m, 2H), δ 6.98 (d, 1H), δ 6.93-6.87 (m, 2H), δ 4.07-4.03 (dd, *J*=4, 4 Hz, 1H), δ 3.92-3.85 (dd, *J*=12, 8 Hz, 1H), δ 3.76-3.73 (d, *J*=12 Hz, 6H), δ 3.28-3.22 (dd, *J*=4, 4 Hz, 1H); **^{13}C NMR** (d^{6}-DMSO, 101 MHz) δ 198.09, 174.41, 148.72, 147.97, 136.33, 133.29, 131.37, 128.70, 127.97, 119.83, 111.96, 111.84, 55.57, 55.53, 45.67, 42.18; **Exact mass calcd** for [MNa^{+}] requires *m/z* 337.1052 Found 337.1027 (ES+).

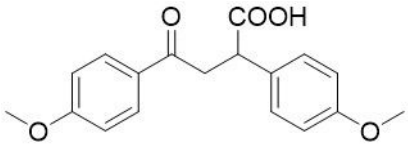


^{1}H NMR (d^{6}-DMSO, 400 MHz) δ 12.34 (s, 1H), δ 8.02 – 8.00 (d, *J*=8 Hz, 2H), δ 7.66-7.62 (t, 1H), δ 7.54-7.50 (t, 2H), δ 7.28-7.26 (d, *J*=8 Hz, 2H), δ 7.16-7.14 (d, *J*=8 Hz, 2H), δ 4.09-4.06 (dd, *J*=4, 4 Hz, 1H), δ 3.90-3.83 (dd, *J*=12, 8 Hz, 1H), δ 3.28-3.23 (dd,

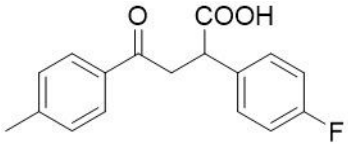
J=4, 4 Hz, 1H), δ 2.28(s, 3H); **^{13}C NMR** (d^6-DMSO, 101 MHz) δ 197.98, 174.36, 136.30, 136.25, 135.98, 133.32, 129.13, 128.73, 127.97, 127.79, 45.70, 42.00, 20.64; **Exact mass calcd** for [MNa$^+$] requires *m/z* 291.0997 Found 291.0993 (ES+).



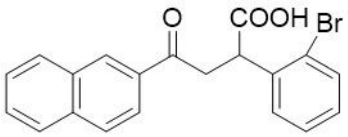
^{1}H NMR (d^6-DMSO, 400 MHz) δ 12.67 (s, 1H), δ 8.02 – 8.01 (d, *J*=4 Hz, 2H), δ 7.66-7.62 (t, 1H), δ 7.54-7.48 (m, 3H), δ 45-7.43 (dd, 1H), δ 7.37-7.29 (m, 2H), δ 4.66-4.63 (dd, *J*=4, 4 Hz, 1H), δ 3.93-3.85 (dd, *J*=12, 12 Hz, 1H), δ 3.30-3.24 (dd, *J*=4, 4 Hz, 1H); **^{13}C NMR** (d^6-DMSO, 101 MHz) δ 197.60, 173.52, 136.82, 136.16, 133.48, 133.07, 129.69, 129.11, 128.92, 128.79, 128.09, 127.67, 42.85, 40.81; **Exact mass calcd** for [MNa$^+$] requires *m/z* 311.0451 Found 311.0446 (ES+).



^{1}H NMR (d^6-DMSO, 400 MHz) δ 12.29 (s, 1H), δ 7.99 – 7.97 (d, *J*=12 Hz, 2H), δ 7.31-7.29 (d, *J*=8 Hz, 2H), δ 7.03-7.01 (d, *J*=8 Hz, 2H), δ 6.91-6.89 (d, *J*=8 Hz, 2H), δ 4.06-4.02 (dd, *J*=4, 4 Hz, 1H), δ 3.83-3.73 (m, 7H), δ 3.21-3.15 (dd, *J*=4, 4 Hz, 1H); **^{13}C NMR** (d^6-DMSO, 101 MHz) δ 196.32, 174.56, 163.20, 158.37, 131.03, 130.28, 129.34, 128.95, 113.96, 113.87, 55.52, 55.08, 45.31, 41.73; **Exact mass calcd** for [MNa$^+$] requires *m/z* 337.1052 Found 337.1031 (ES+).

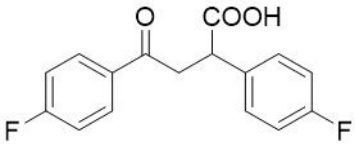


^{1}H NMR (d^6-DMSO, 400 MHz) δ 12.40 (s, 1H), δ 7.92-7.90 (d, *J*=8 Hz, 2H), δ 7.45-7.41 (dd, *J*=4, 8 Hz, 2H), δ 7.33-7.31 (d, *J*=8 Hz, 2H), δ 7.19-7.15 (t, , *J*=8 Hz, 2H), δ 4.15-4.11 (dd, *J*=4, 4 Hz, 1H), δ 3.88-3.81 (dd, *J*=8, 12 Hz, 1H), δ 3.29-3.23 (dd, *J*=4, 4 Hz, 1H), δ 2.37 (s, 3H); **^{13}C NMR** (d^6-DMSO, 101 MHz) δ 197.29, 174.16, 143.70, 133.81, 129.91, 129.83, 129.24, 128.10, 115.38, 115.17, 45.32, 41.82, 21.14; **Exact mass calcd** for [MNa$^+$] requires *m/z* 309.0884 Found 309.0903 (ES+).

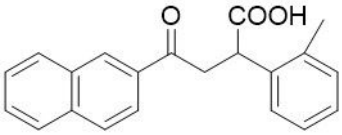


^{1}H NMR (d^6-DMSO, 400 MHz) δ 12.68 (s, 1H), δ 8.80(s, 1H), δ 8.14 – 8.12 (d, *J*=8 Hz, 1H), δ 8.01-7.99 (d, *J*=8 Hz, 3H), δ 7.70-7.60 (m, 3H), δ 7.48-7.40 (m, 2H), δ 7.27-7.23 (m, 1H), δ 4.70-4.66 (dd, *J*=4, 4 Hz, 1H), δ 4.05-3.98 (m, 1H), δ 3.42-3.36 (dd, *J*=4, 4 Hz, 1H); **^{13}C NMR** (d^6-DMSO, 101 MHz) δ 197.46, 173.59, 138.60, 135.18, 133.36, 133.00, 132.26, 130.36, 129.68, 129.20, 128.93, 128.78, 128.34, 128.27, 127.70, 126.99, 124.16,

123.42, 45.57, 41.16; **Exact mass calcd** for [MNa$^+$] requires *m/z* 405.0102 Found 405.0202 (ES+).



^{1}H NMR (d^6-DMSO, 400 MHz) δ 12.48 (s, 1H), δ 8.13-8.09 (dd, *J*=8, 4 Hz, 2H), δ 7.46-7.42 (dd, *J*=4, 8 Hz, 2H), δ 7.36-7.32 (t, 2H), δ 7.20-7.15 (t, *J*=8, 12 Hz, 2H), δ 4.15-4.11 (dd, *J*=4, 4 Hz, 1H), δ 3.93-3.86 (dd, *J*=12, 8 Hz, 1H), δ 3.32-3.26 (dd, *J*=4, 4 Hz, 1H); **^{13}C NMR** (d^6-DMSO, 101 MHz) δ 196.56, 174.23, 166.44, 163.94, 162.61, 160.20, 135.18, 135.15, 133.04, 133.01, 131.15, 131.05, 129.99, 129.91, 115.88, 115.66, 115.46, 115.25, 45.37, 41.91; **Exact mass calcd** for [MNa$^+$] requires *m/z* 313.0652 Found 313.0628 (ES+).



^{1}H NMR (d^6-DMSO, 400 MHz) δ 12.39 (s, 1H), δ 8.78 (s, 1H), δ 8.15-8.13 (d, *J*=8 Hz, 1H), δ 8.01-7.98 (d, *J*=12 Hz, 3H), δ 7.69-7.60 (m, 2H), δ 7.35-7.33 (d, *J*=8 Hz, 1H), δ 7.24-7.17 (m, 3H), δ 4.44-4.41 (dd, *J*=4, 4 Hz, 1H), δ 4.04-3.96 (dd, *J*=12, 12 Hz, 1H), δ 3.42-3.37 (m, 1H), δ 2.43 (s, 3H); **^{13}C NMR** (d^6-DMSO, 101 MHz) δ 197.97, 174.53, 137.65, 135.97, 135.10, 133.56, 132.25, 130.49, 129.64, 128.67, 128.25, 127.65, 126.94, 126.73, 126.28, 123.42, 41.95, 41.44, 19.39; **Exact mass calcd** for [MNa$^+$] requires *m/z* 341.1154 Found 341.1174 (ES+).

3. Supplementary Figures

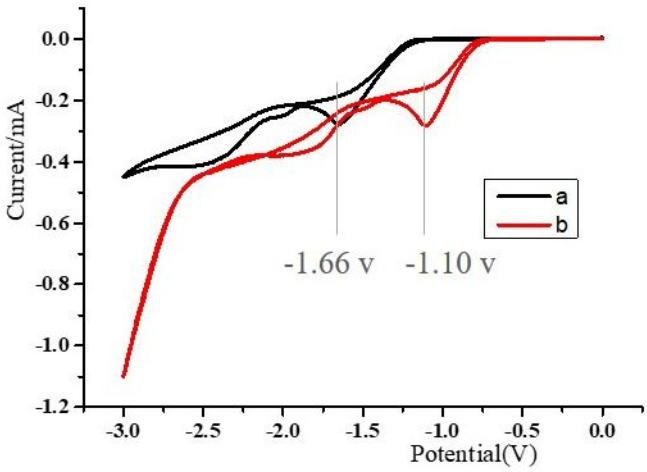


Figure S1. Cyclic voltammograms on the glassy carbon electrode of chalcone (0.4 mmol) in the electrolyte (0.1 M of Bu_4NBr in 20 mL of CH_3CN) with CO_2 bubbling using (a) Ag/AgCl or (b) Ag/AgBr as the reference electrode.

It is observed that the onset potential with the Ag/AgBr reference electrode is *ca.* 0.5 V

more positively than the Ag/AgCl electrode. Also, the current density detected when using Ag/AgBr electrode is much higher than the Ag/AgCl electrode. Obviously, the Ag/AgBr reference electrode is more favorable in our experimental system.

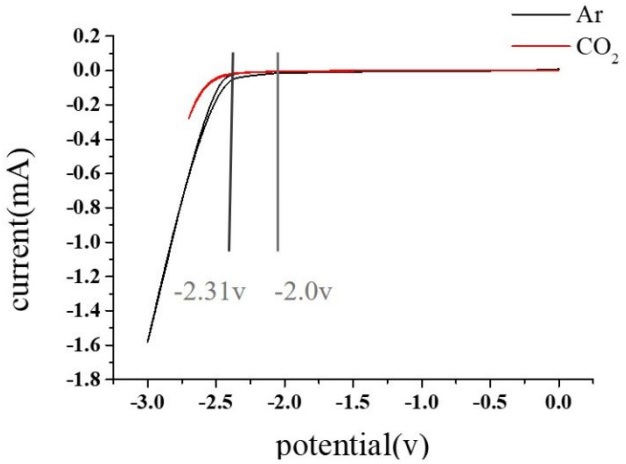


Figure S2. Cyclic voltammograms (E *vs.* Ag/AgBr) on the glassy carbon electrode of the electrolyte (0.1 M of Bu_4NBr in 20 mL of acetonitrile) with (red trace) and without CO_2 bubbling (black trace).

It is observed that when applied potential is more positive than -2.0 V, the interference on the reaction from the decomposition of electrolyte and CO_2 is negligible.

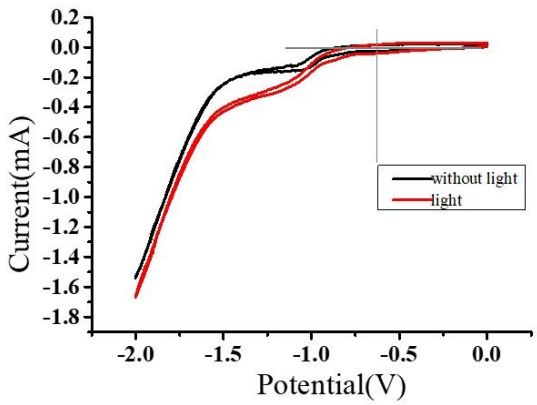
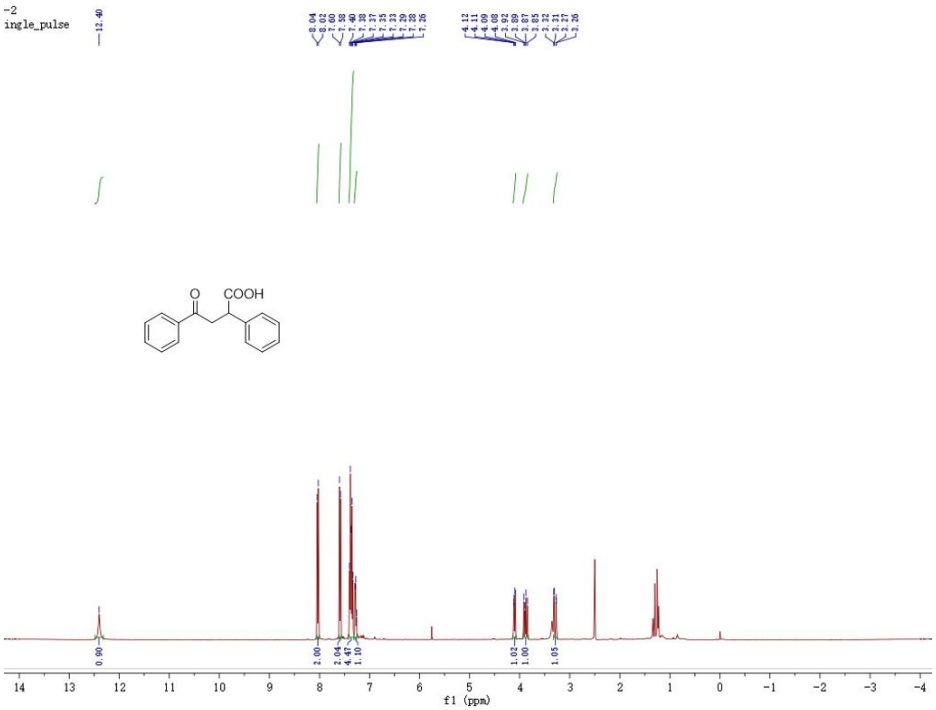


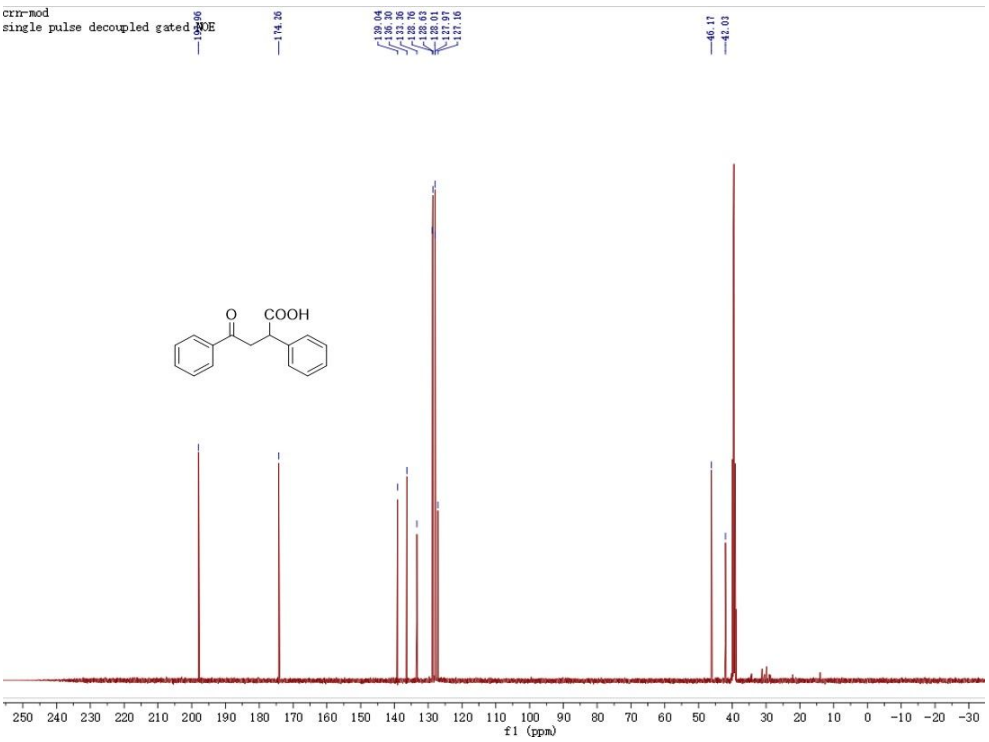
Figure S3. Cyclic voltammograms of chalcone on SiNWs electrode with CO_2 bubbling in dark (black trace) and in light (red trace). The solution consists of supporting electrolyte (0.1 M of Bu_4NBr) and chalcone (20 mM) in 20 mL of acetonitrile.

It is observed that the onset potentials on two curves are similar, but the current density is enhanced with light irradiation.

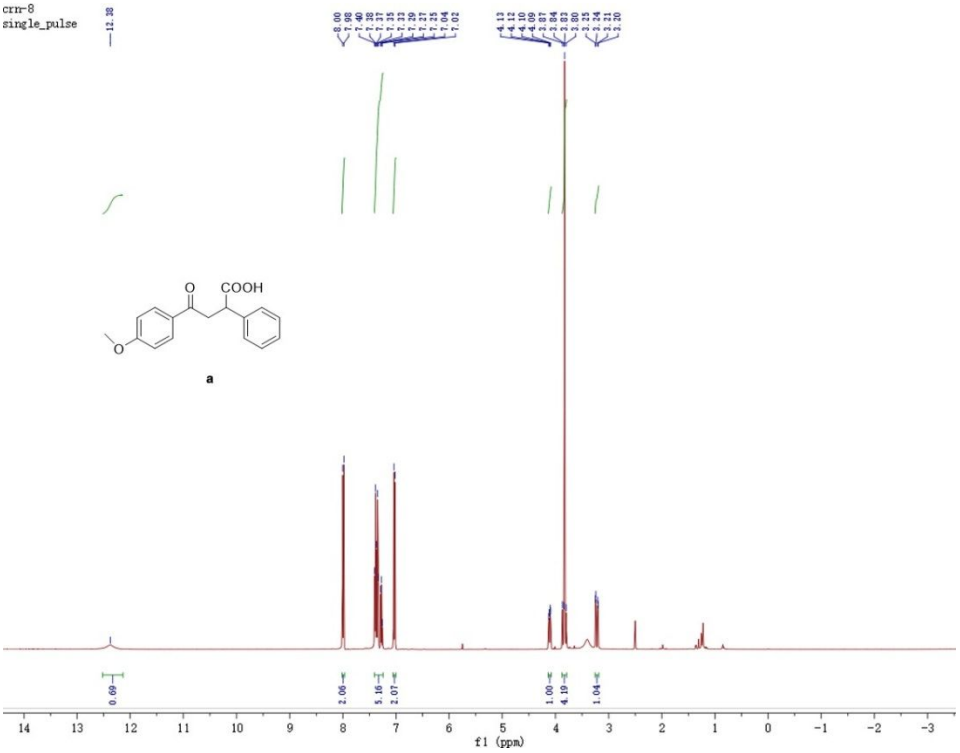
NMR Spectra of Compounds



^{1}H NMR (d^6-DMSO, 400 MHz)



^{13}C NMR (d^6-DMSO, 101 MHz)



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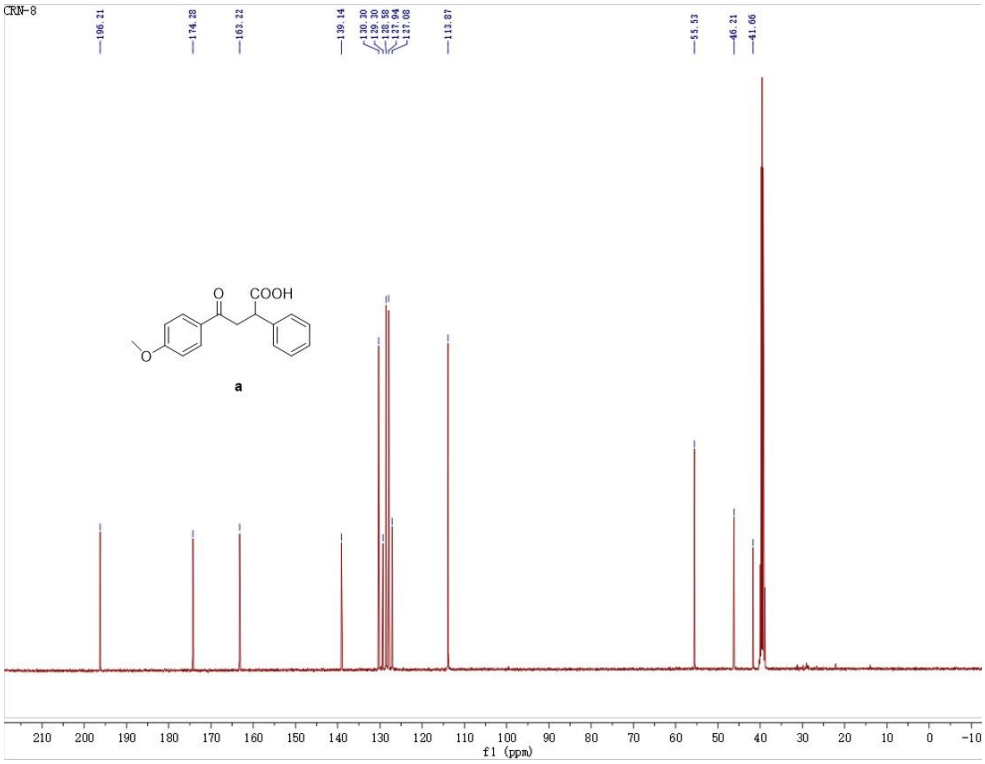

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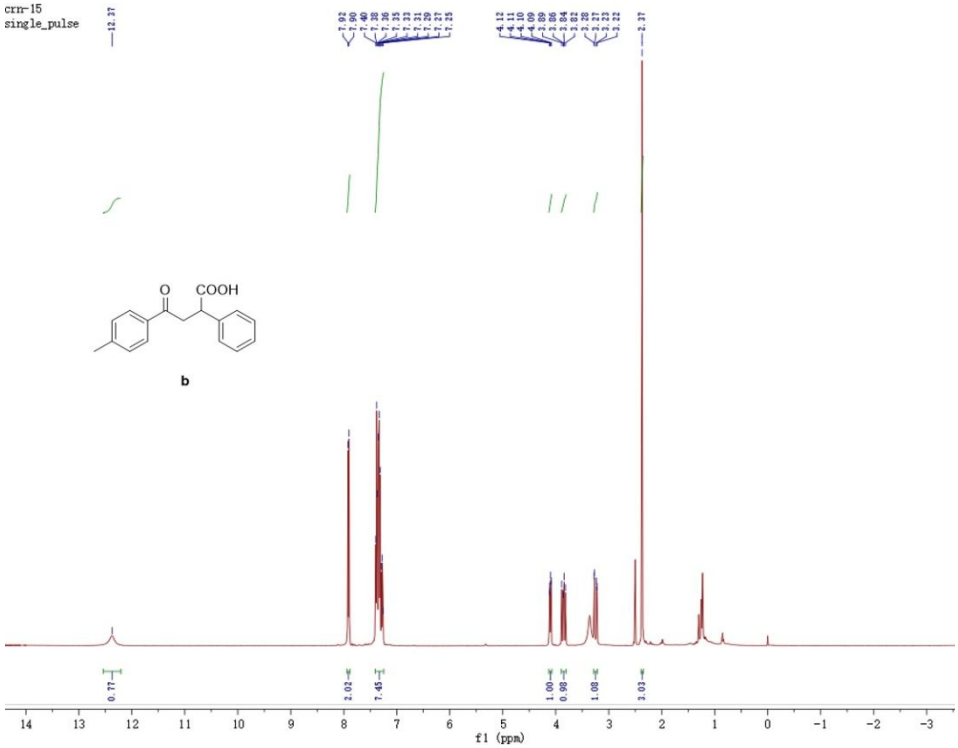

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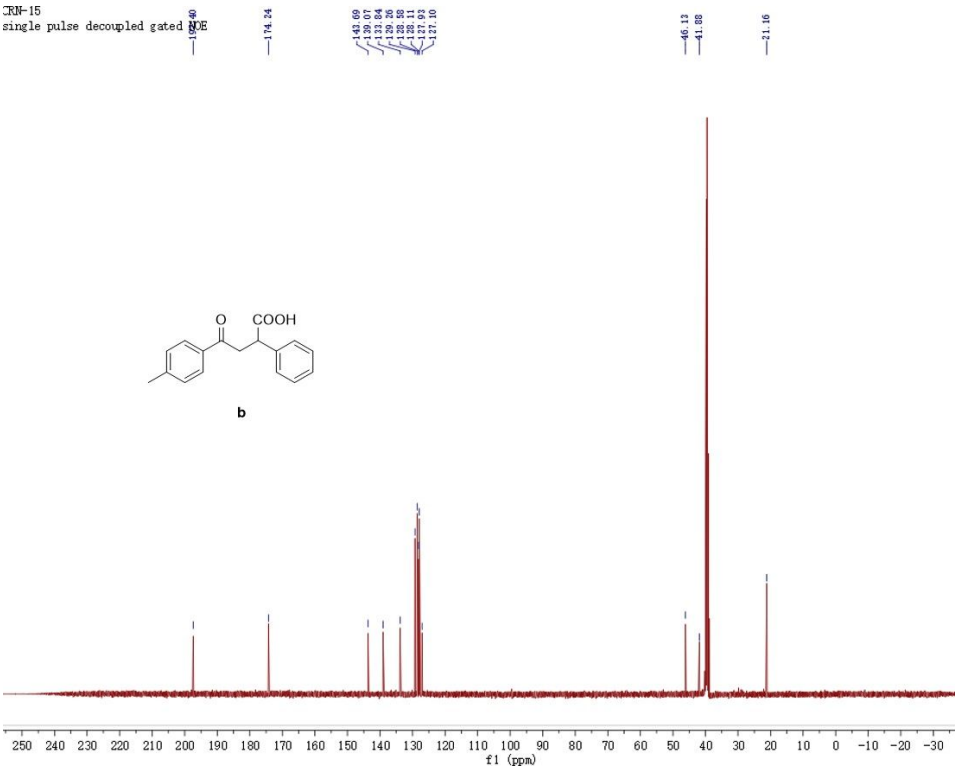

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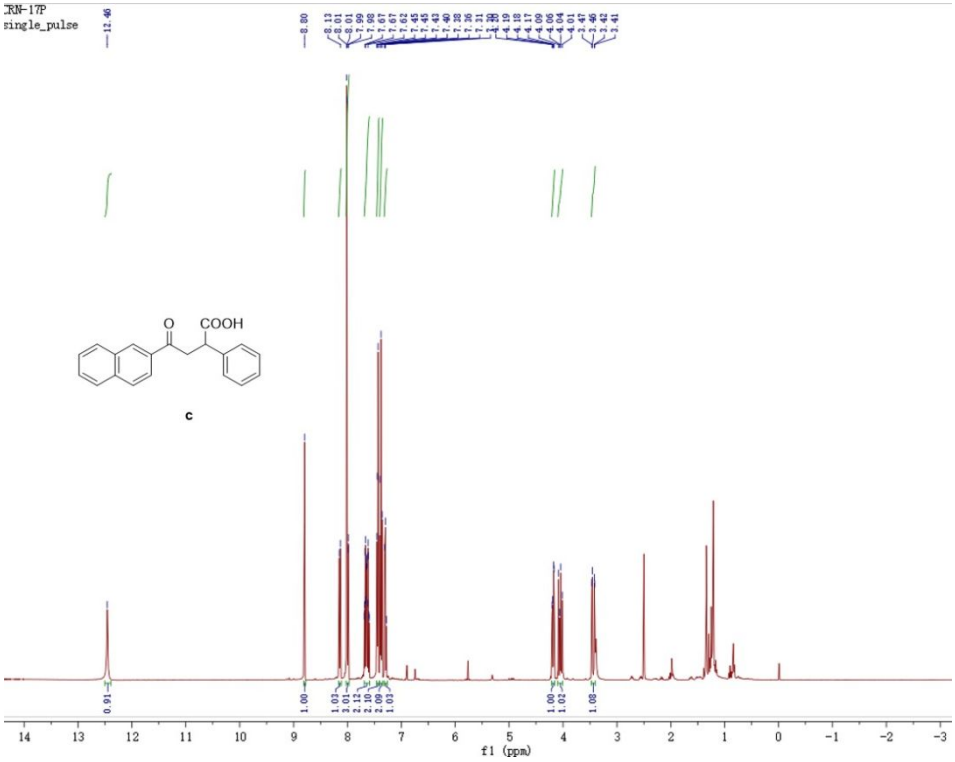

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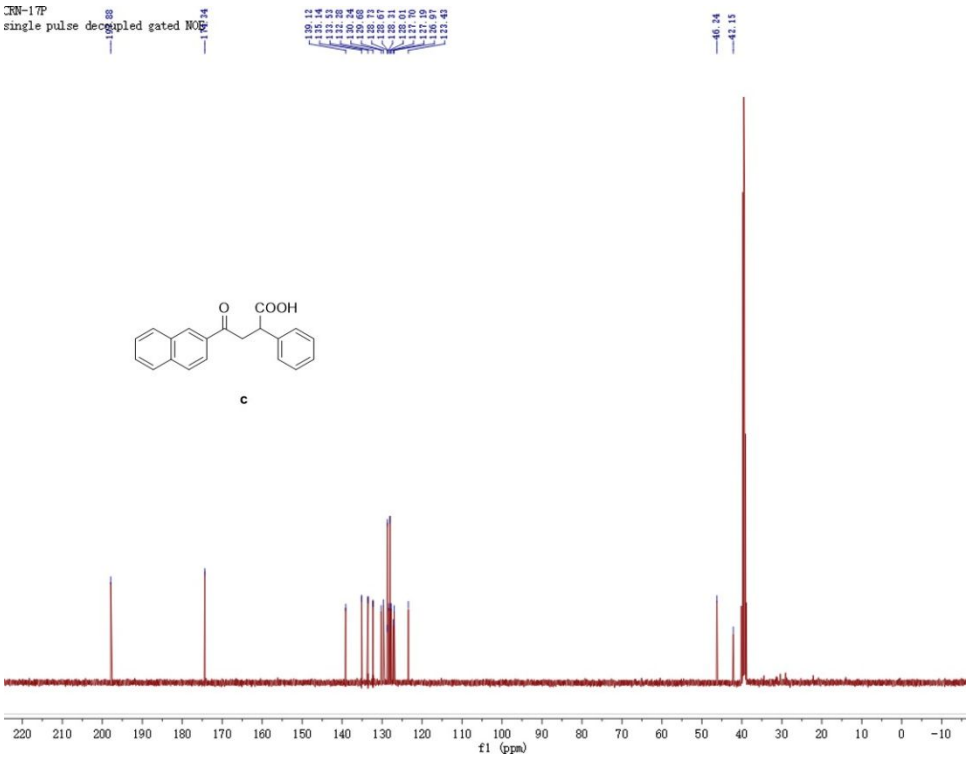

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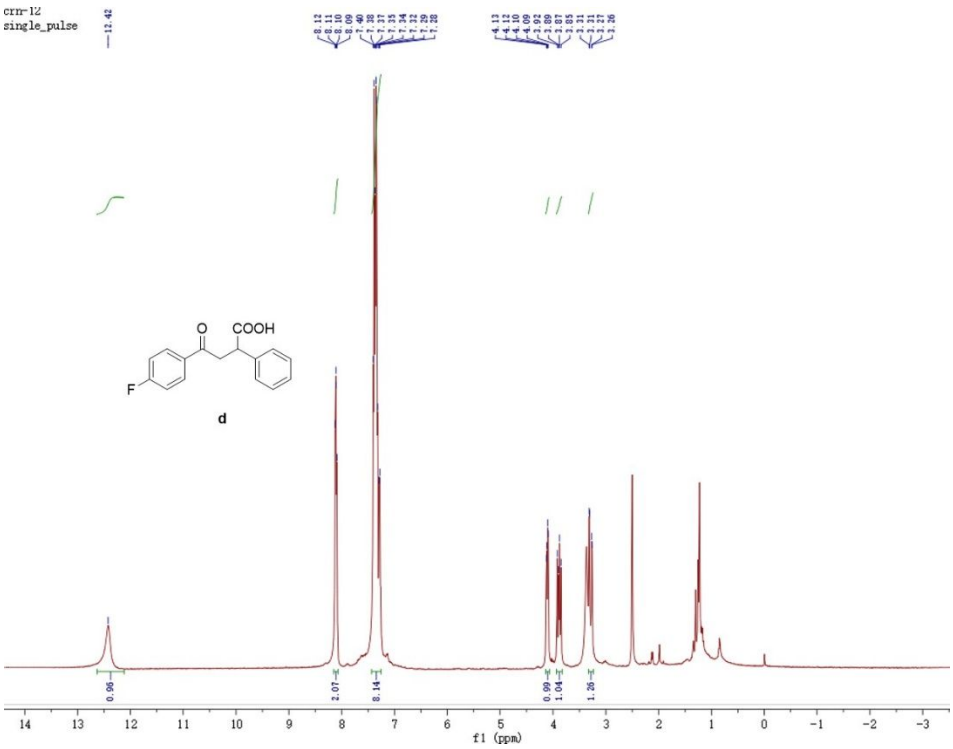

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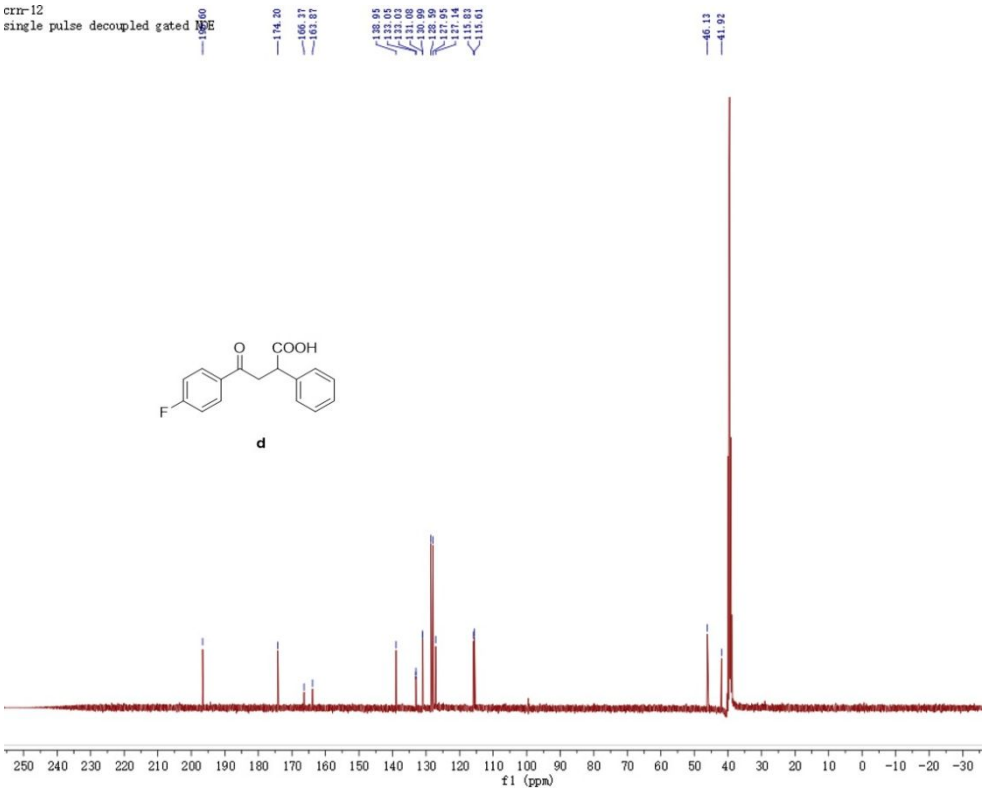

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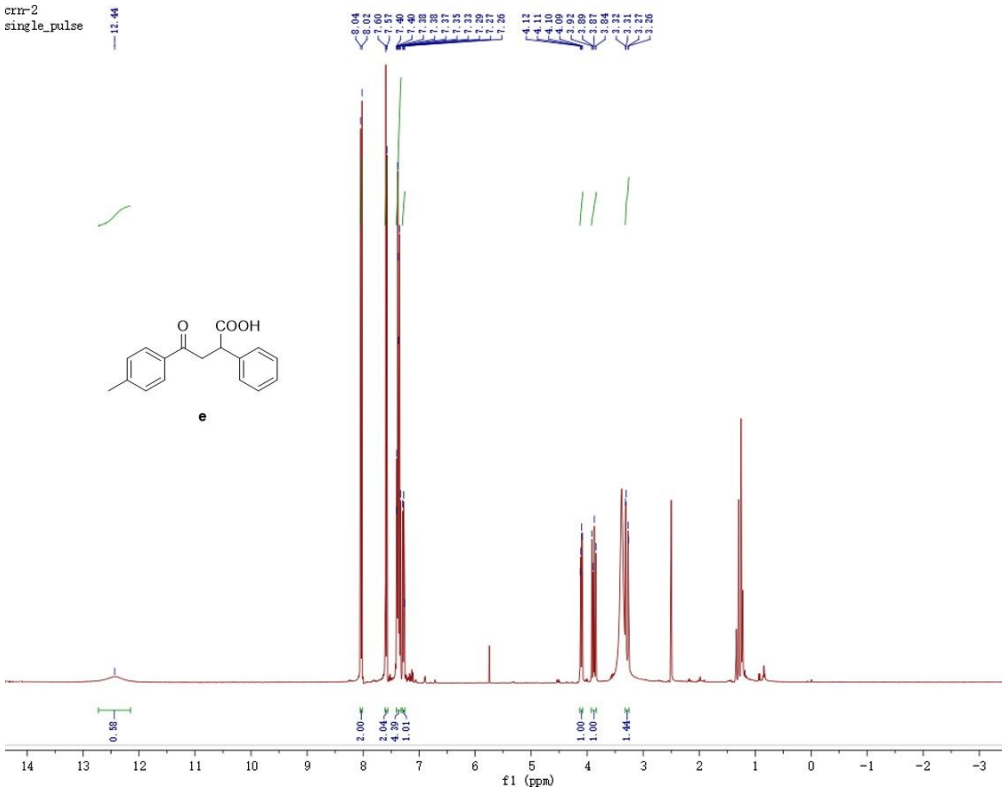

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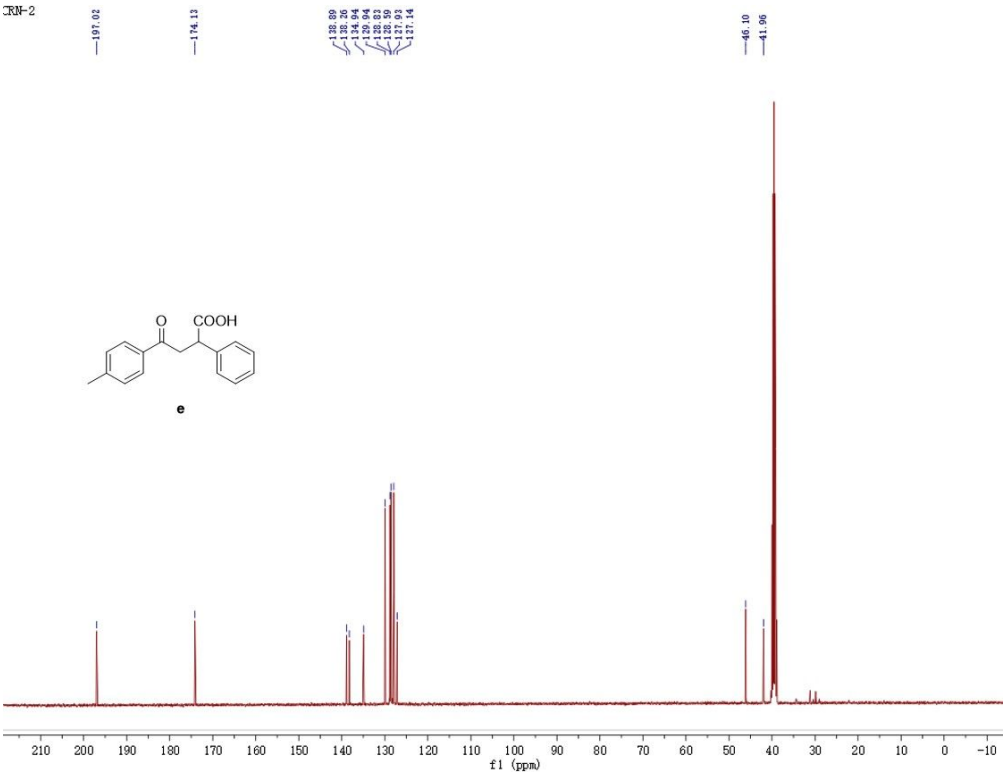

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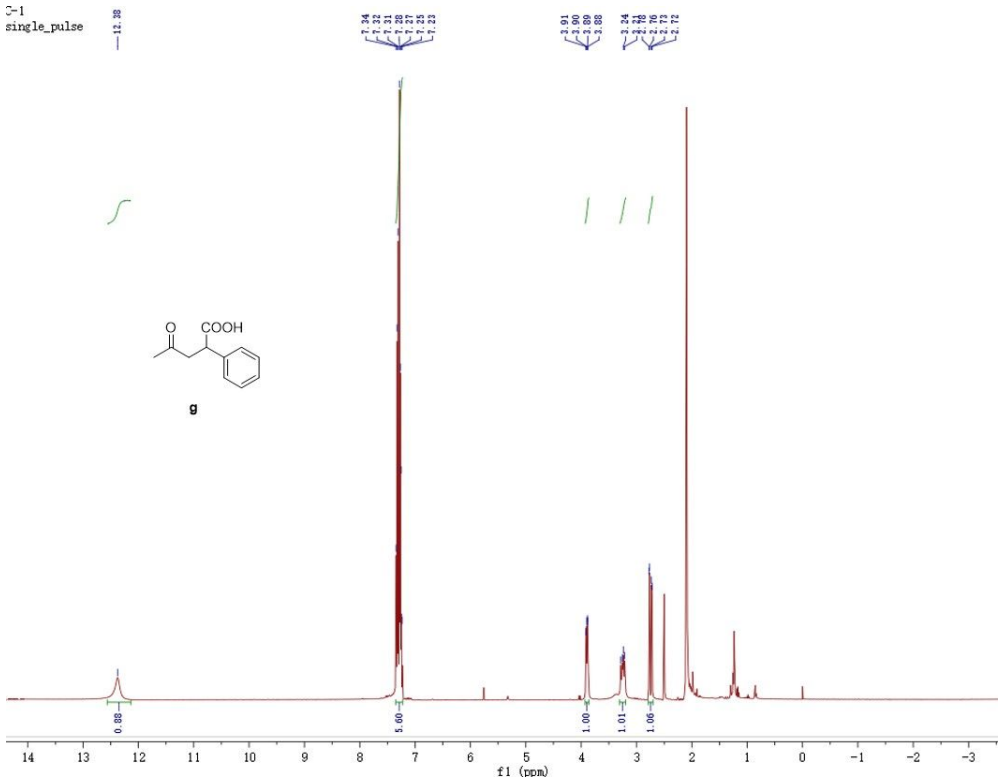

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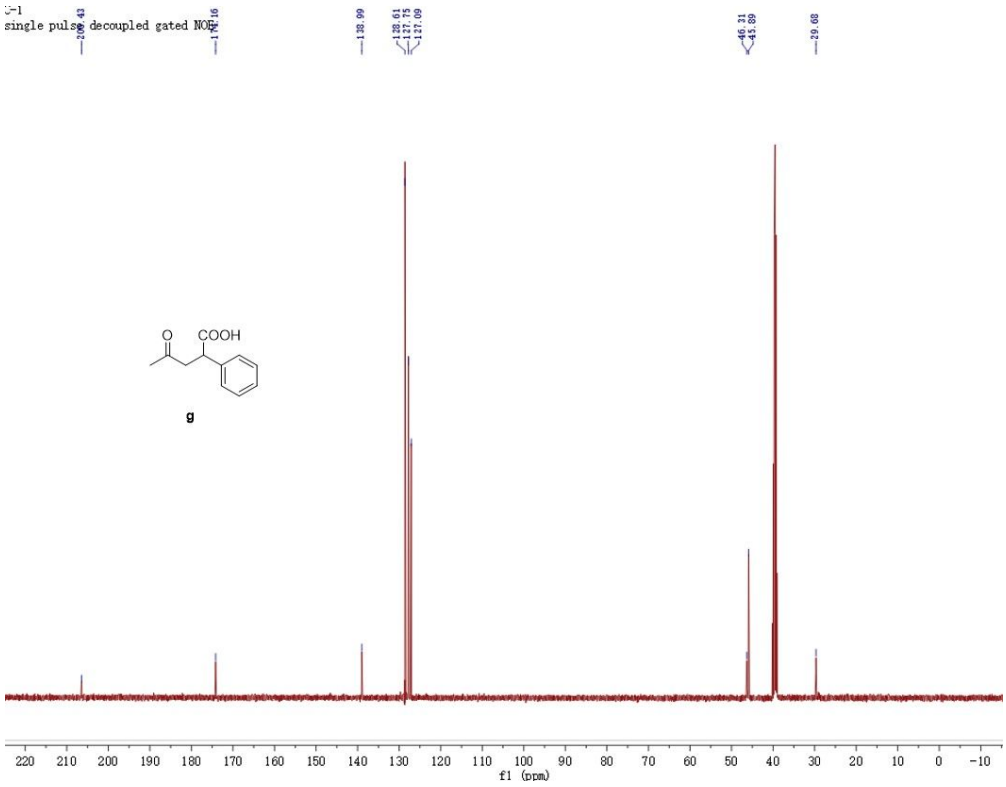

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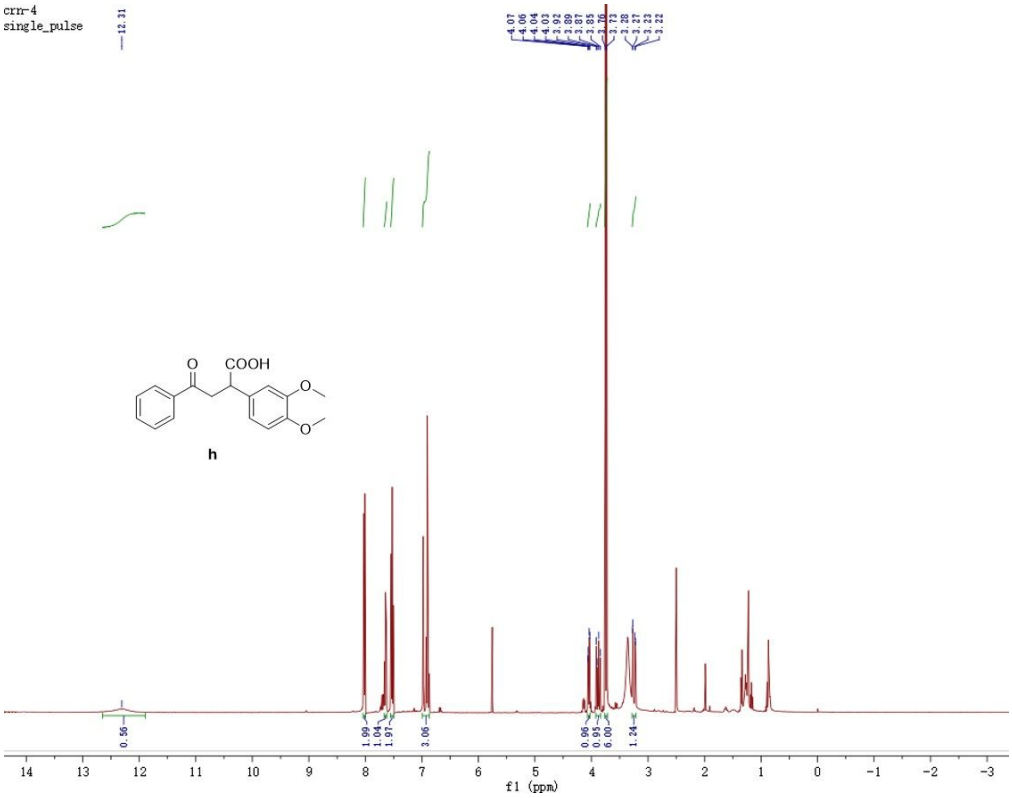

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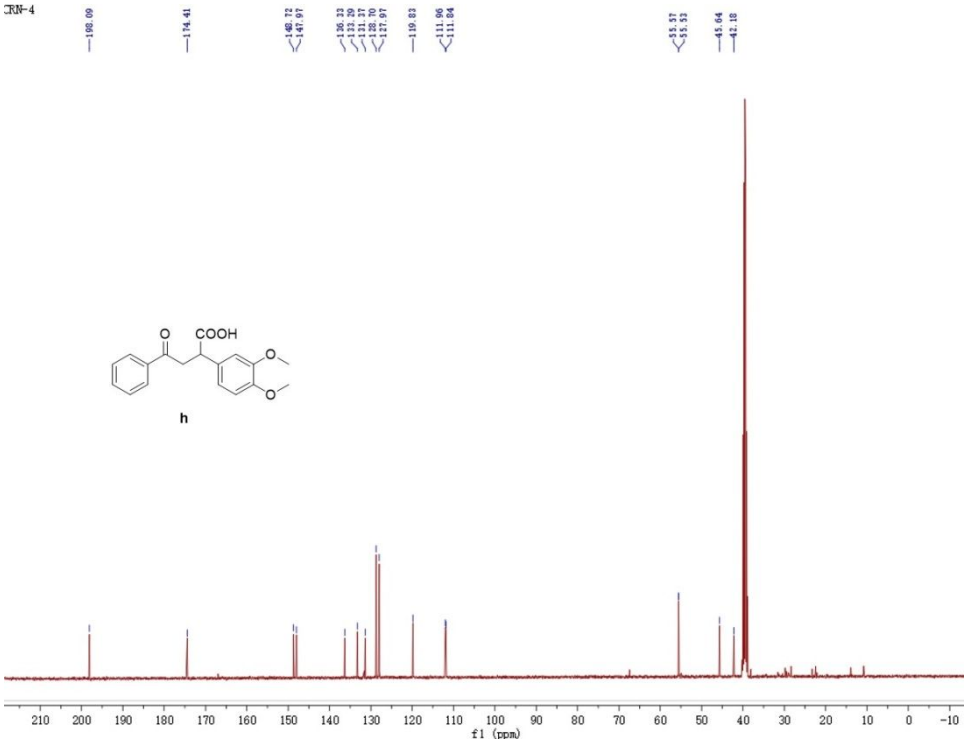

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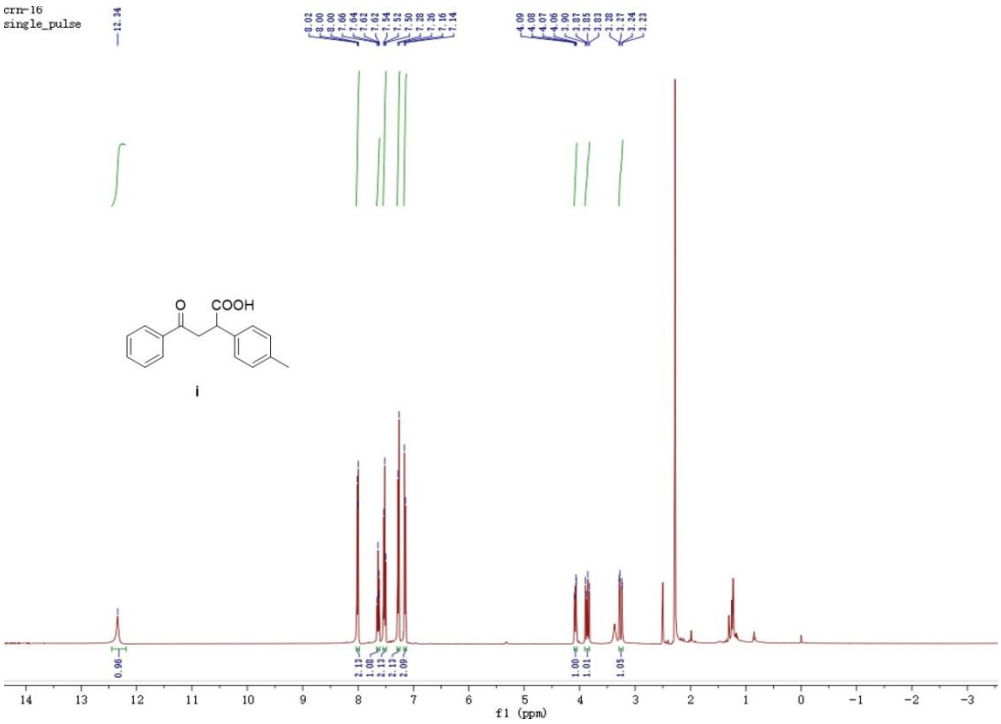

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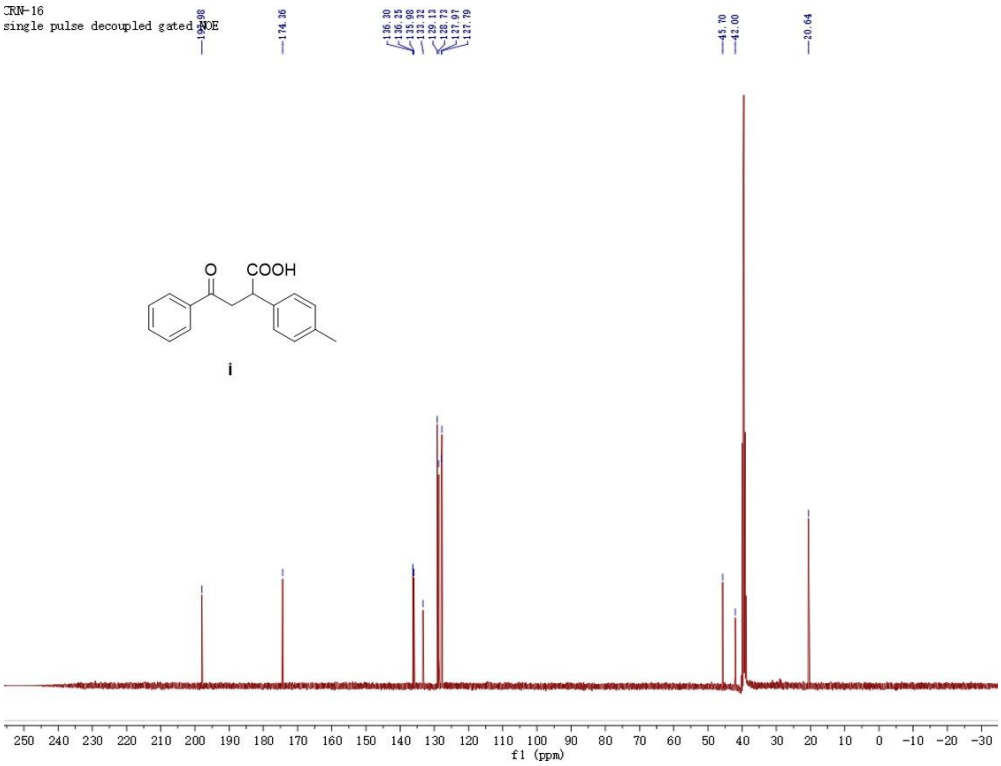

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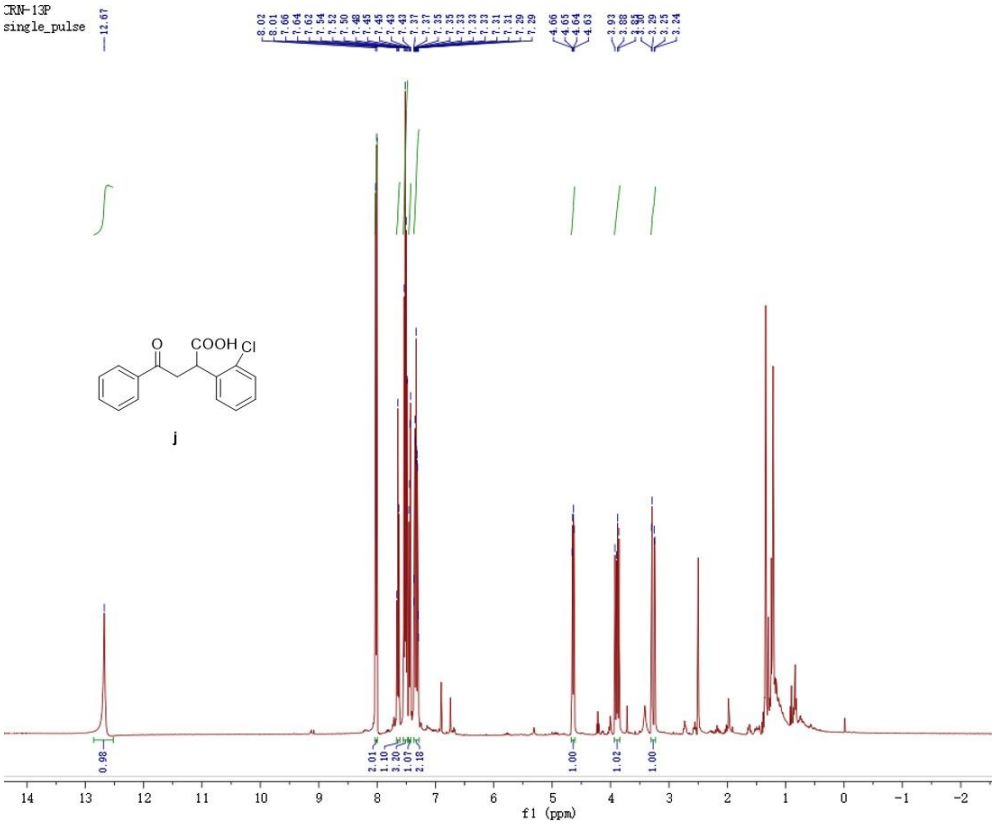

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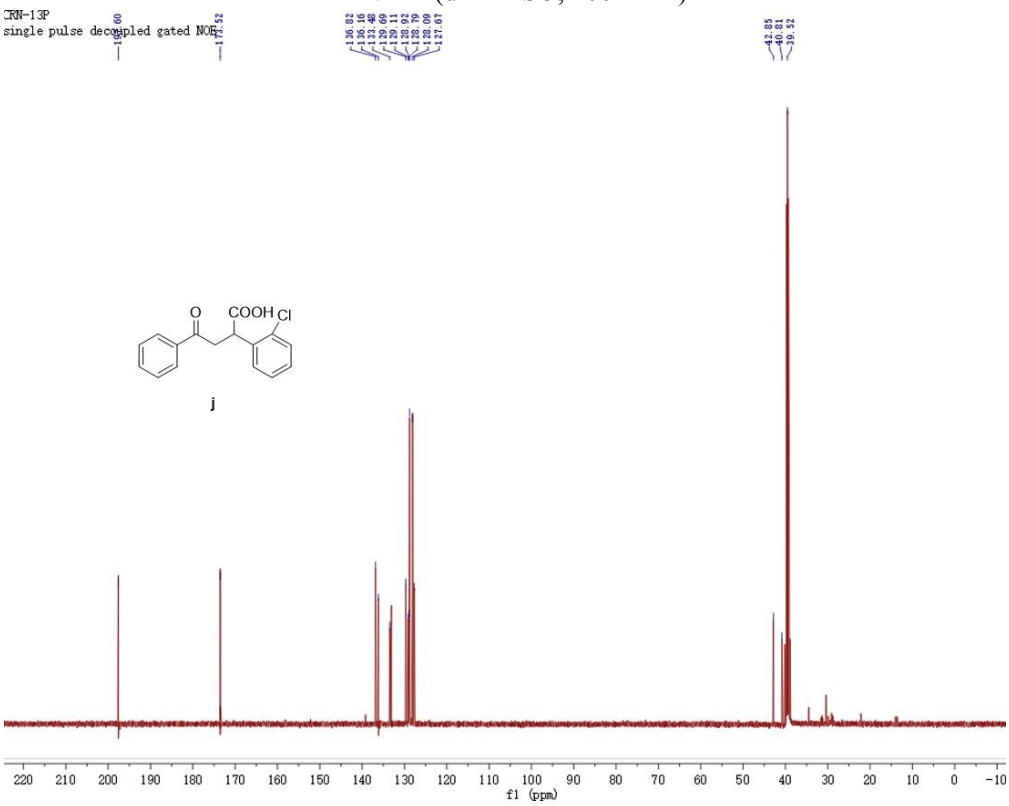

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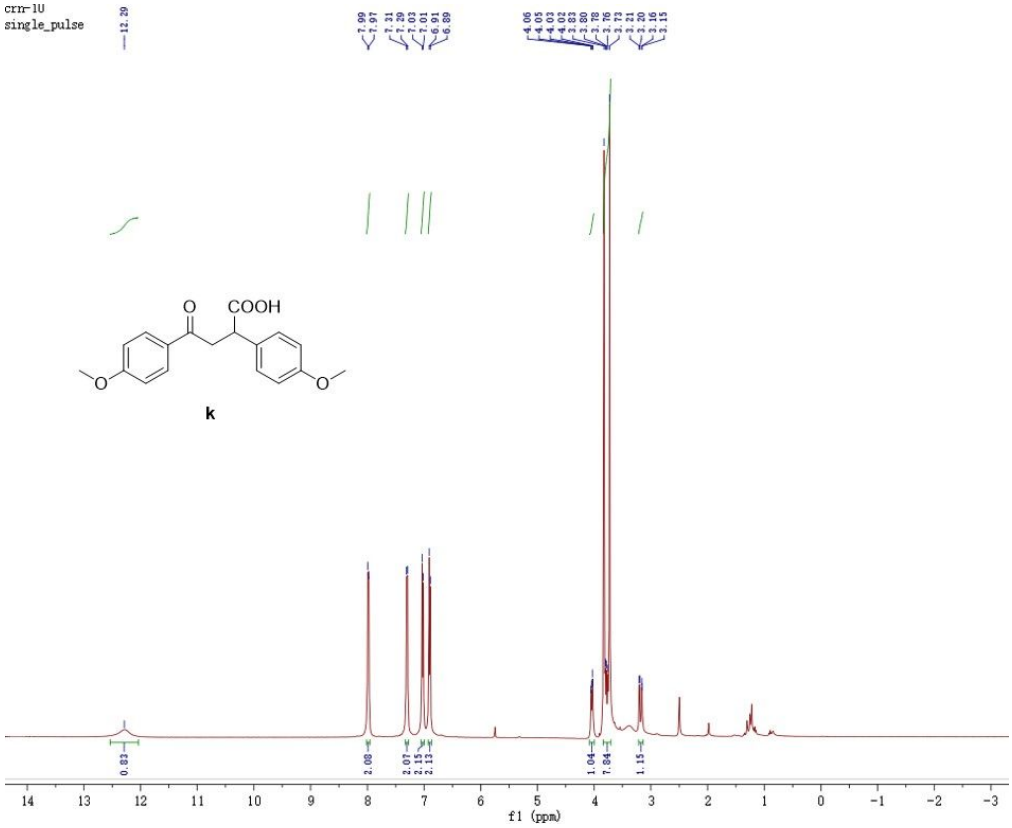

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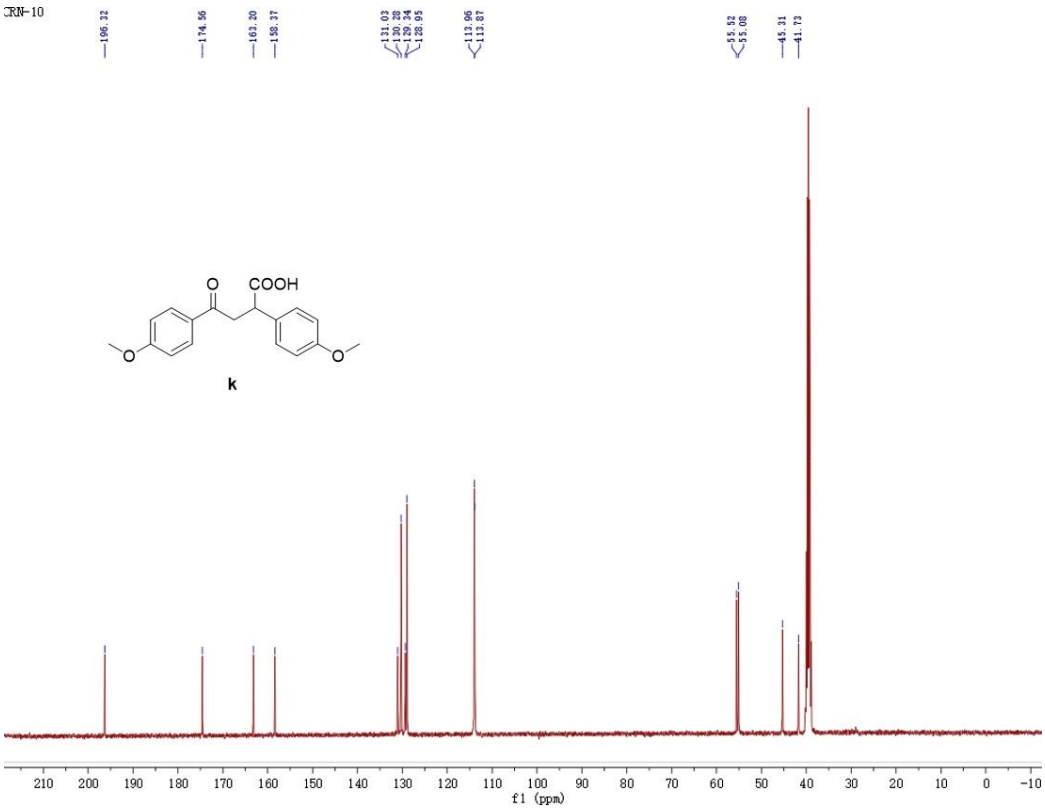

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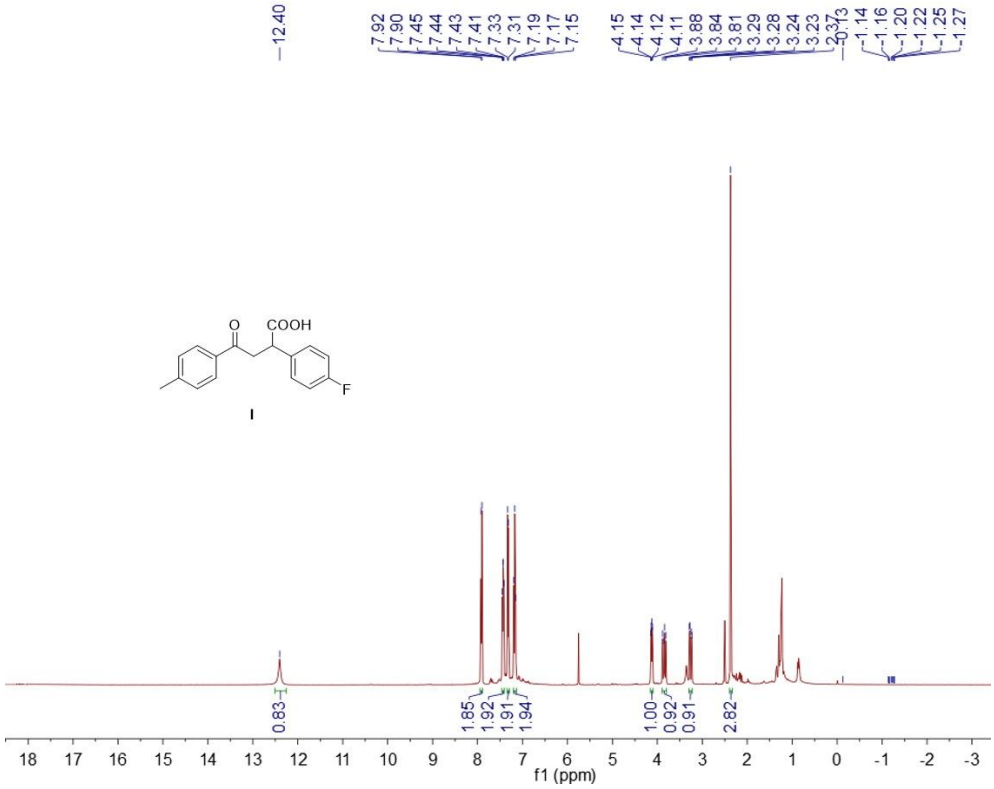

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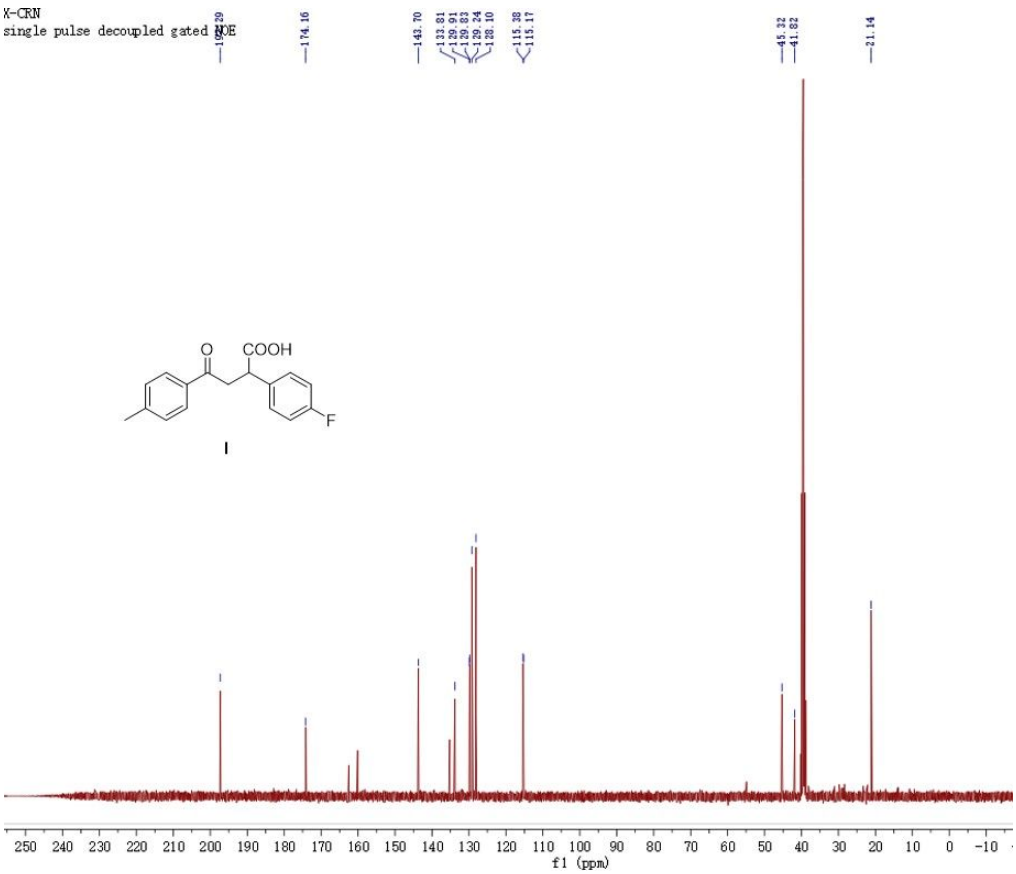

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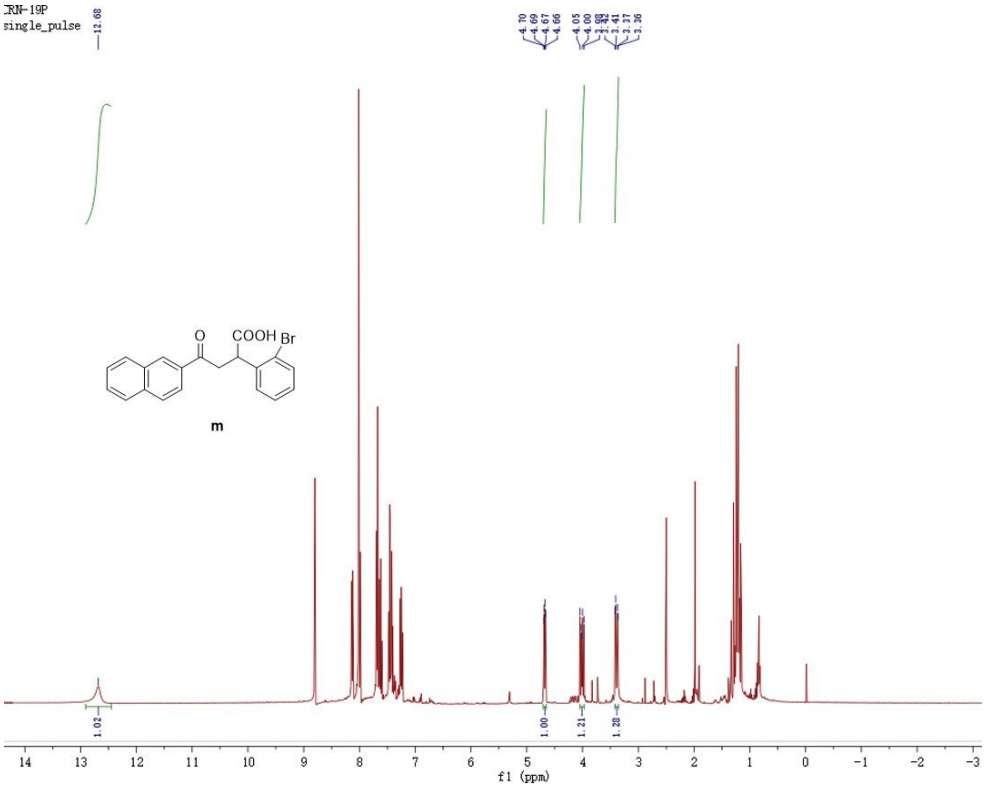

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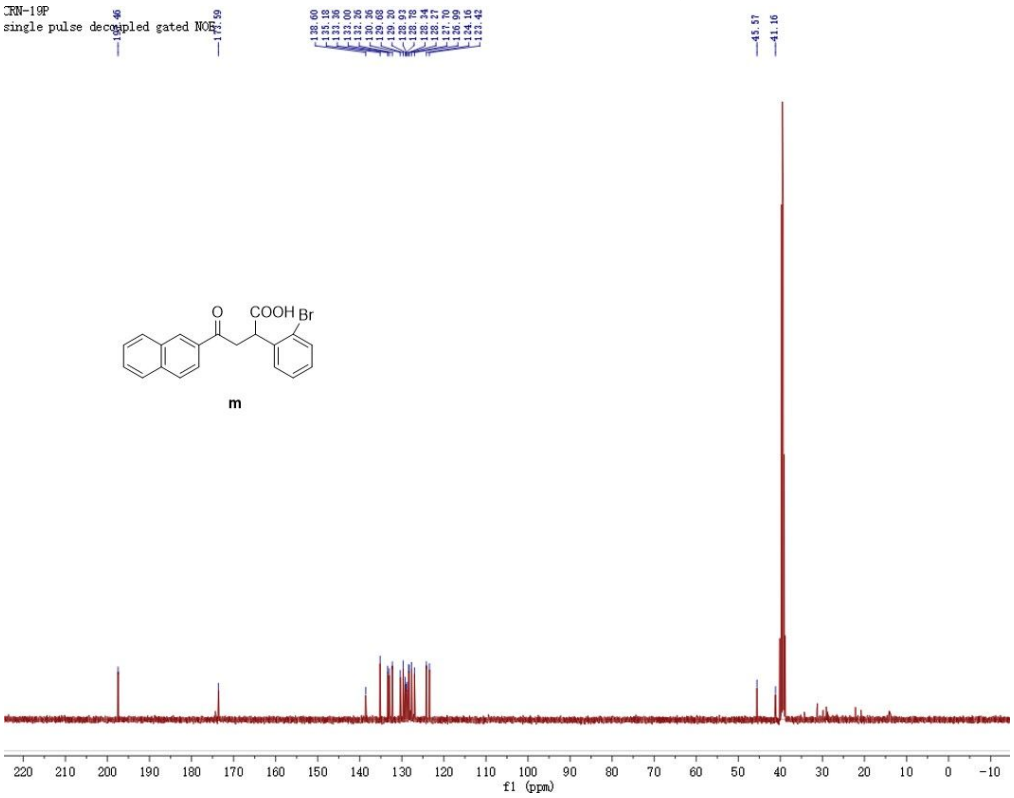

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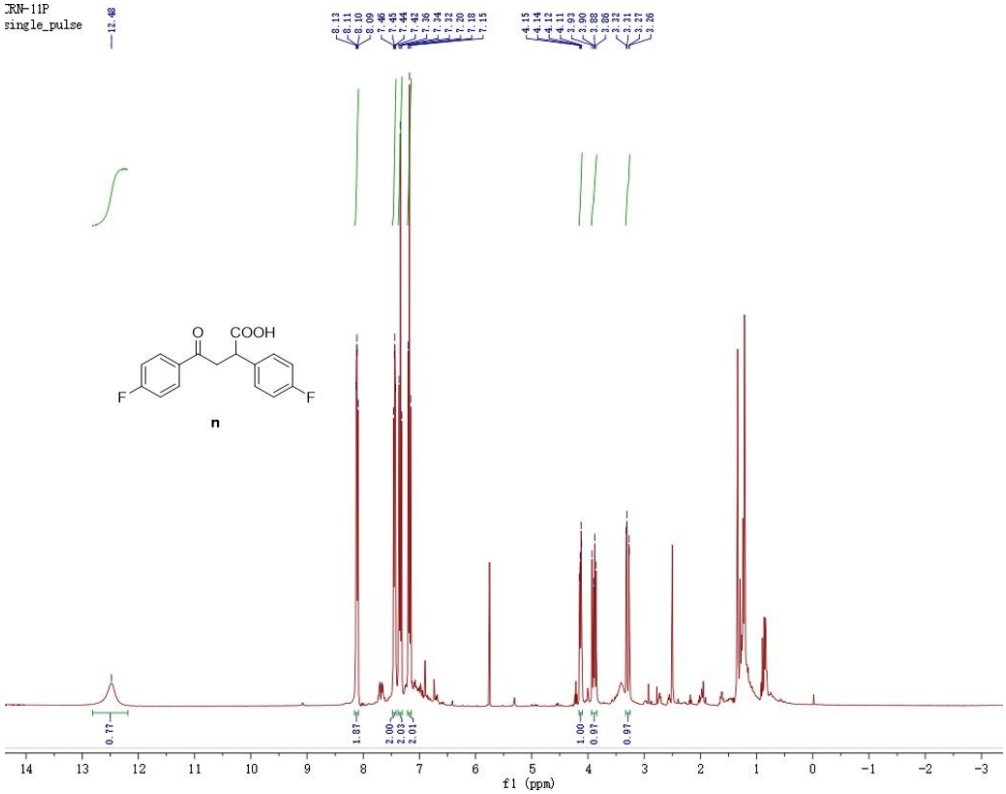

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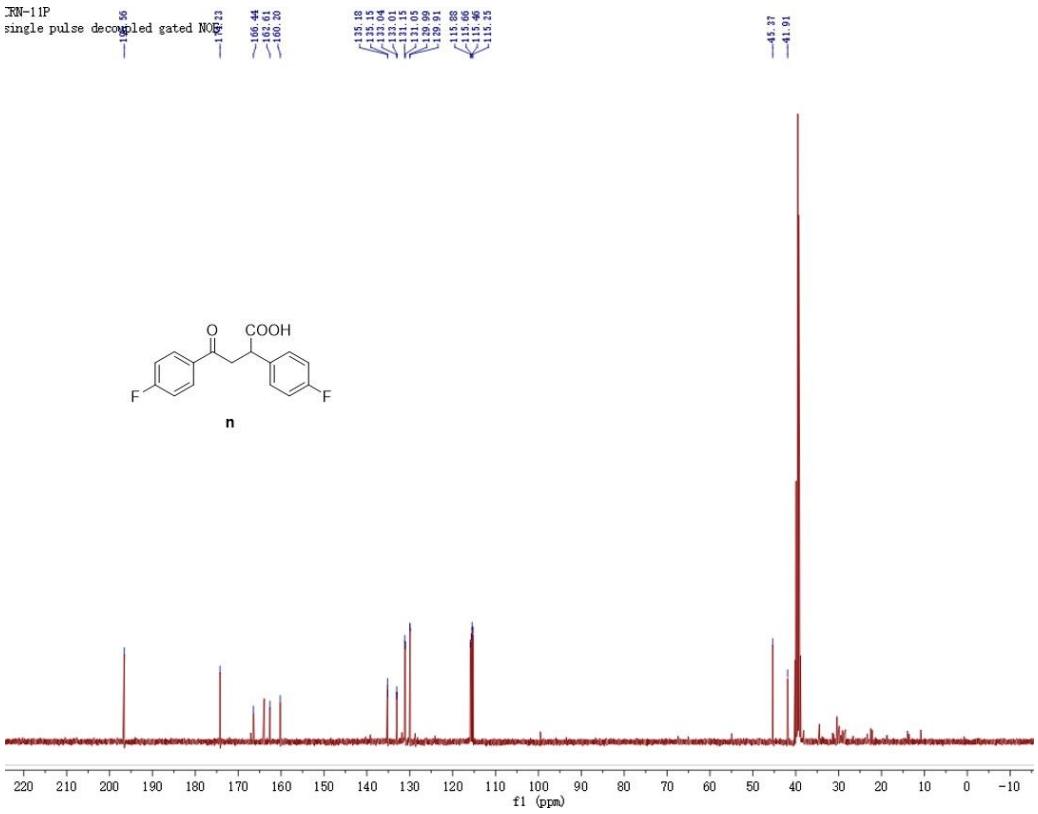

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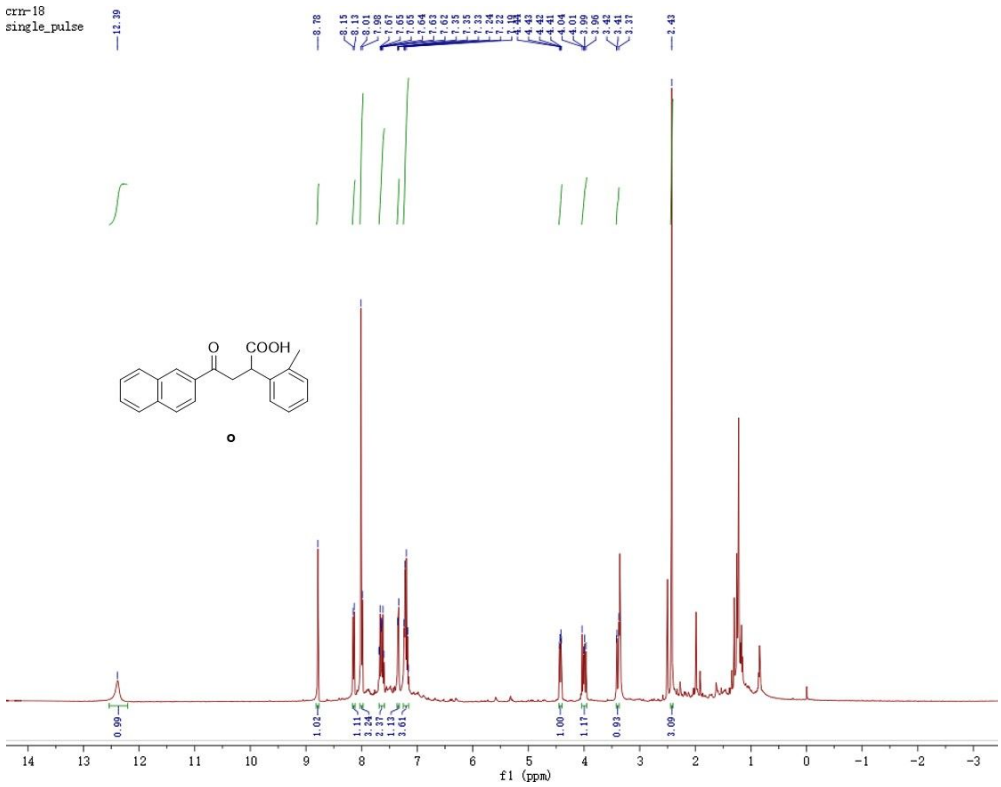

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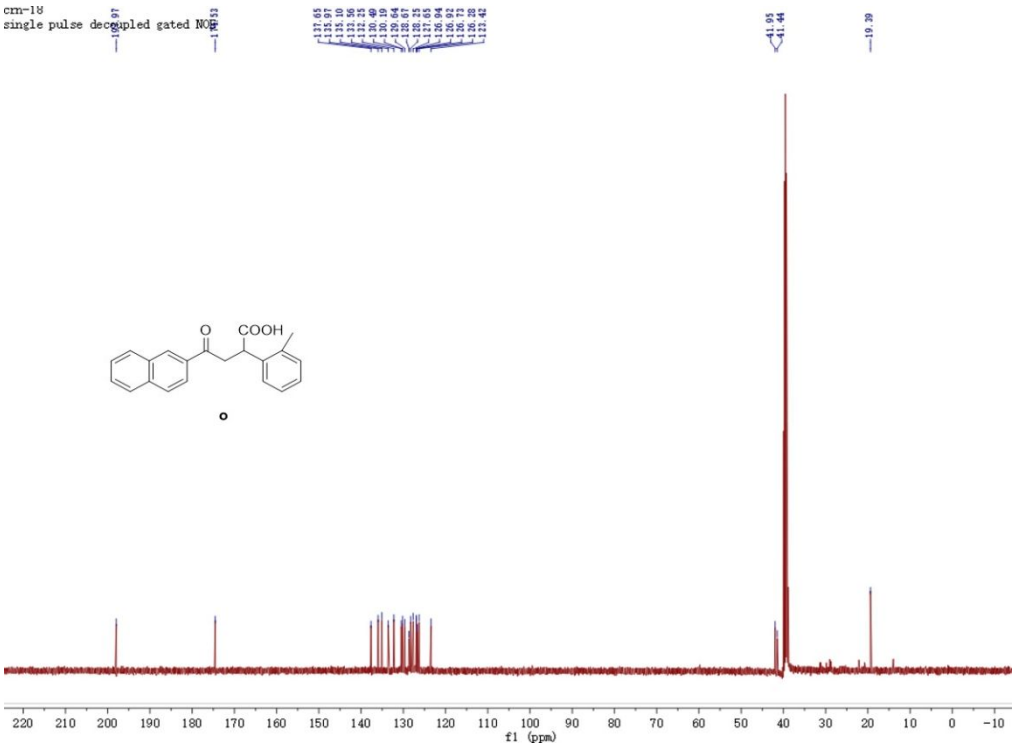

^{13}C NMR (d^{6}-DMSO, 101 MHz)

References

1.Yuan, G.; Aruda, K.; Zhou, S.; Levine, A.; Xie, J.; Wang, D., Understanding the Origin of the Low Performance of Chemically Grown Silicon Nanowires for Solar Energy Conversion. *Angew. Chem. Int. Ed.* **2011**, 50 (10), 2334-2338.