

Supporting Information for

Porous Organic Polymer Supported Pd/Cu Bimetallic Catalyst for Heterogeneous Oxidation of Alkynes to 1,2-Diketones

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CONTENES

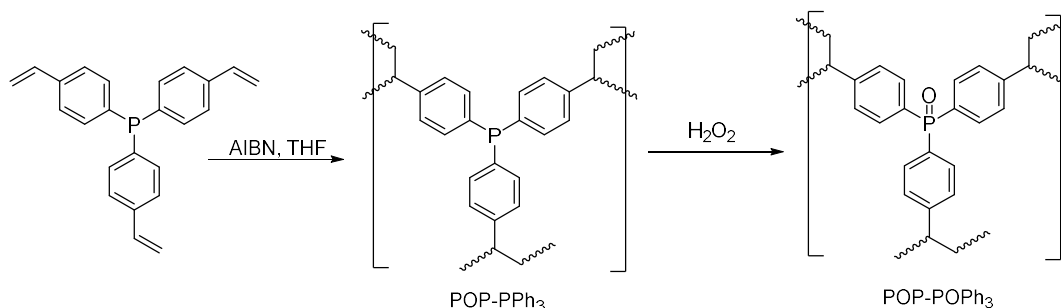
1. General methods	2
2. Synthesis of Pd/Cu@POP-POPh ₃	3
3. FT-IR spectra of POP-POPh ₃ and Pd/Cu@POP-POPh ₃	4
4. XPS spectra of POP-POPh ₃ and Pd/Cu@POP-POPh ₃	5
5. TGA curve of Pd/Cu@POP-POPh ₃	8
6. Characterization data for the oxidation of alkynes products.....	9
7. Recycling tests of the Pd/Cu@POP-POPh ₃ in the oxidation of alkynes.....	13
8. NMR spectra of 1,2-diketones.	14
References:.....	23

1. General methods

Unless otherwise noted, all manipulations involving air- or moisture-sensitive compounds were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. Solvents were dried according to standard procedures. ^1H NMR spectra were recorded on 500 MHz and ^{13}C NMR spectra were recorded on 125 MHz by using a Bruker Avance 500 spectrometer. Chemical shifts (δ values) were reported in ppm with internal TMS (^1H NMR) and CDCl_3 (^{13}C NMR) as the standard, respectively. Solid NMR was recorded on Agilent 600 MHz. HRMS (ESI) were determined on Bruker solanx 70 FT-MS spectrometers. ICP-MS were determined on Thermo iCAP Q. The FT-IR spectra were measured on a Thermo (SCIENTIFIC) NICOLET iS10 spectrometer. KBr pellet was used for FT-IR analysis of solid samples. The SEM and TEM spectra were obtained on a Zeiss sigma 500 and JEOL-2100F spectrometers, respectively. N_2 sorption isotherm was obtained on a Micromeritics ASAP 2460. Thermogravimetric analysis was determined on NETZSCH TG 209 F1. X-ray photoelectron spectroscopy (XPS) was performed on a ThermoScientific ESCALAB 250Xi with the Al $\text{K}\alpha$ radiation as X-ray source ($h\nu=1486.6$ eV). The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

2. Synthesis of Pd/Cu@POP-POPPh₃

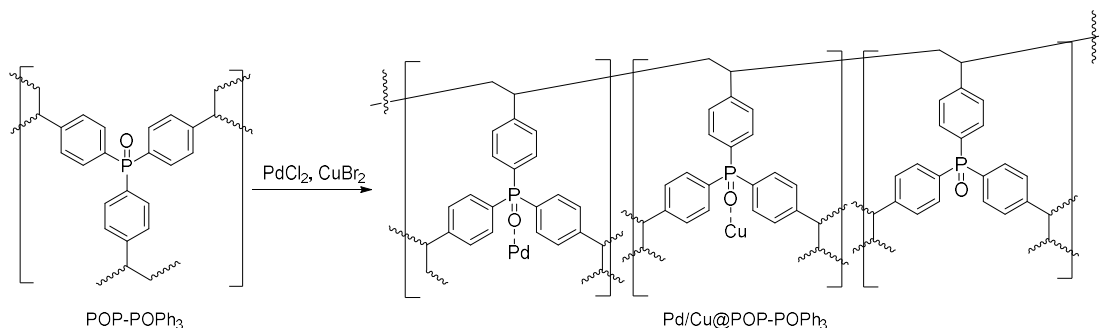
Synthesis of POP-POPPh₃.



Tris(4-vinylphenyl)phosphine (3vPPH₃) was prepared by following the reported literature procedure^[1]. Under nitrogen, the obtained tris(4-vinylphenyl) phosphine (1.0 g, 2.95 mmol), AIBN (24.0 mg, 0.15 mmol) and THF (20 mL) were added into Schlenk flask. After stirring for 30 minutes at room temperature, the mixture was heated to 100 °C for 24 h. The white solid was formed. After evaporation of THF at 40 °C under vacuum, the crude product was washed by THF (3×8 mL) and separated by centrifugation. The white solid POP-PPh₃ (956 mg) was obtained.

A mixture of POP-PPh₃ (200.0 mg) in CH₂Cl₂ (10 mL) was added in 30% H₂O₂ (4 ×2 mL) in Schlenk flask. After stirring for 5 h at room temperature, the resulting product was separated by vacuum filtration. The crude product was washed by H₂O and acetone. The solvent was removed under vacuum, and the white solid POP-POPPh₃ (210 mg) was obtained.

Synthesis of Pd/Cu@POP-POPPh₃



In glove box, POP-POPPh₃ (320 mg), PdCl₂ (13.3 mg), CuBr₂ (35.0 mg) and 1,4-dioxane (10 mL) were added into a Schlenk flask. After stirring for 30 minutes at room temperature, the mixture was heated to 60 °C for 24 h. The resulting product

was separated by centrifugation. The crude product was washed by *n*-hexane (3×8 mL) and dried under vacuum. The dark brown catalyst Pd&Cu/POP-PPh₃ (316 mg) was obtained.

3. FT-IR spectra of POP-POPh₃ and Pd/Cu@POP-POPh₃.

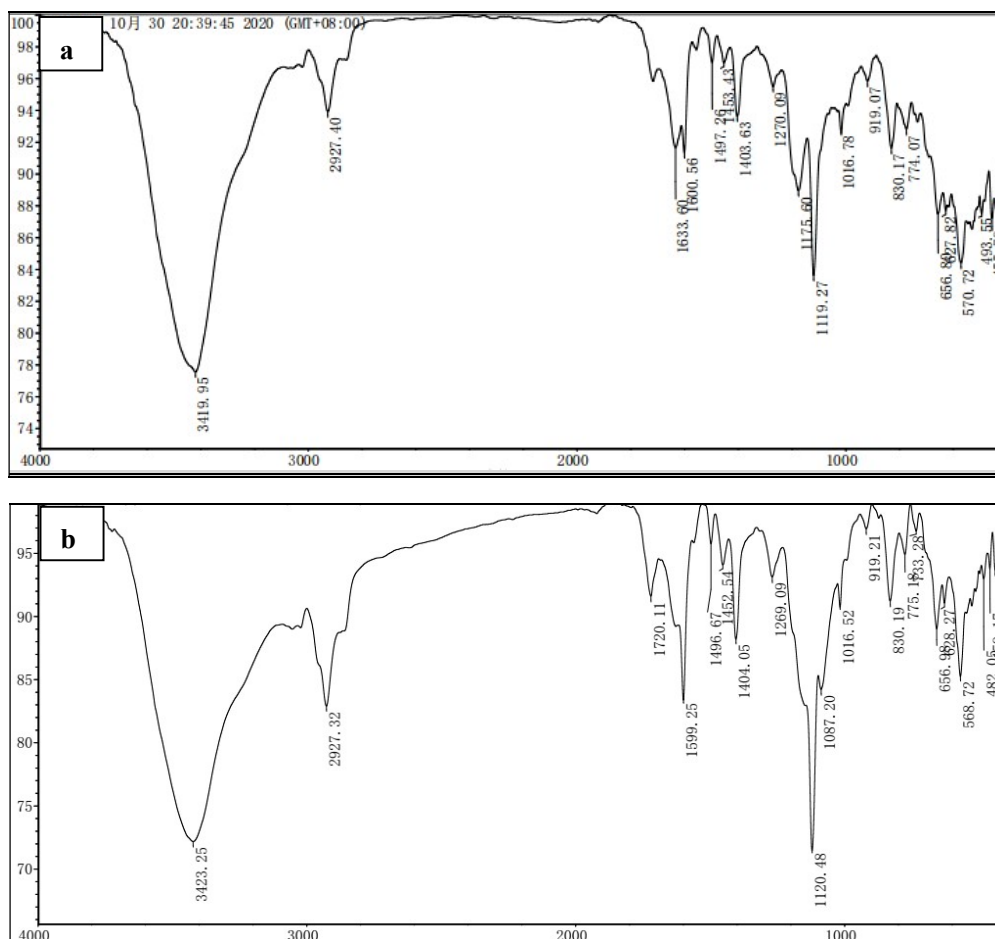


Figure S1. a) FT-IR spectrum of POP-POPh₃, b) FT-IR spectrum of Pd/Cu@POP-POPh₃.

4. XPS spectra of POP-POPh₃ and Pd/Cu@POP-POPh₃.

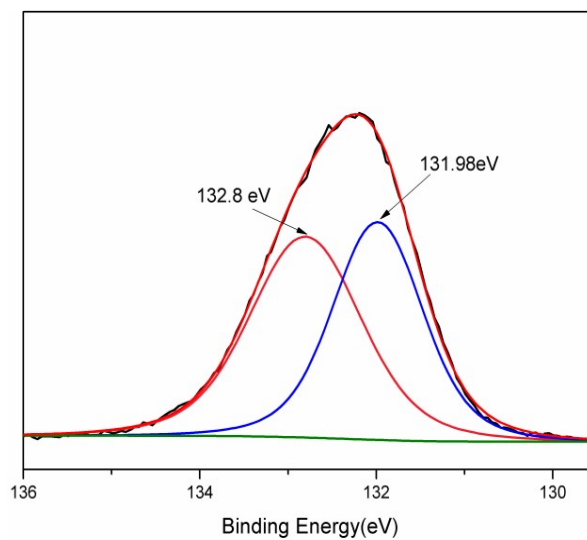


Figure S2. P 2p XPS spectra of POP-POPh₃

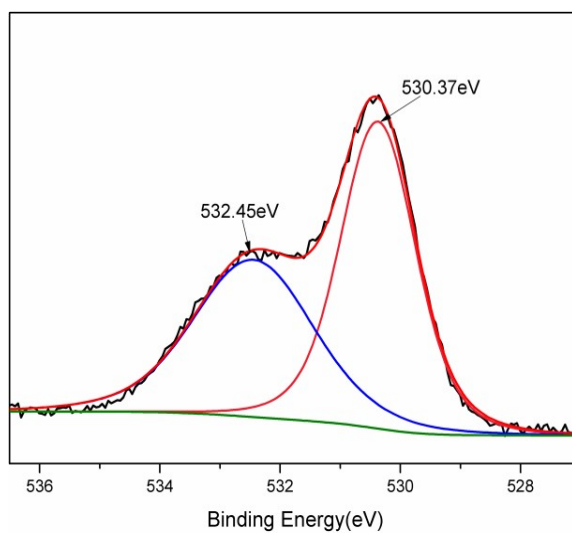


Figure S3. O 1s XPS spectra of POP-POPh₃

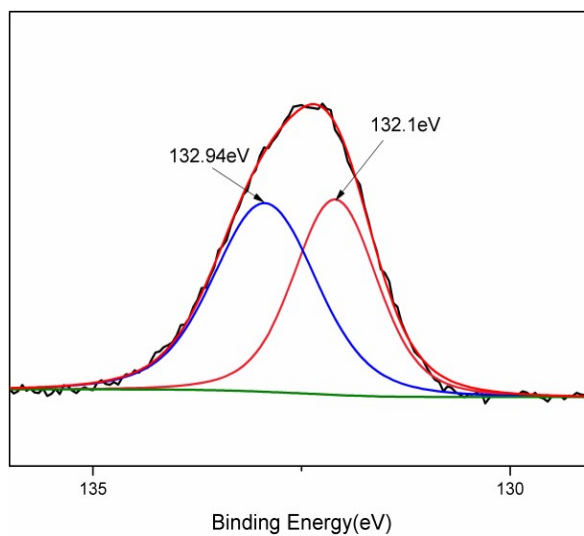


Figure S4. P 2p XPS spectra of Pd/Cu@POP-POPh₃

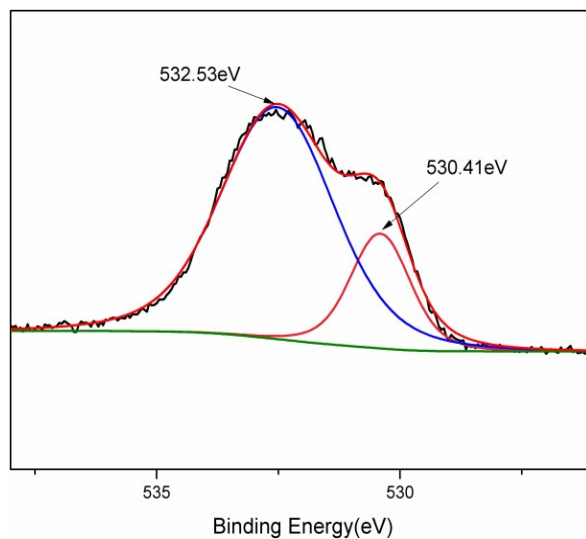


Figure S5. O 1s XPS spectra of Pd/Cu@POP-POPh₃

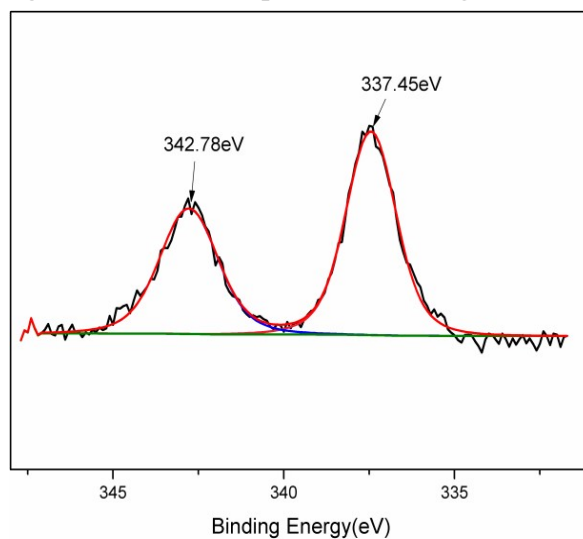


Figure S6. Pd 3d XPS spectra of Pd/Cu@POP-POPh₃

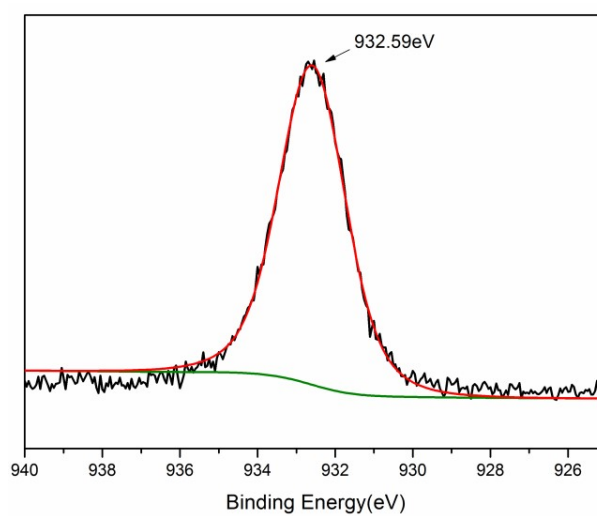


Figure S7. Cu 2p XPS spectra of Pd/Cu@POP-POPh₃

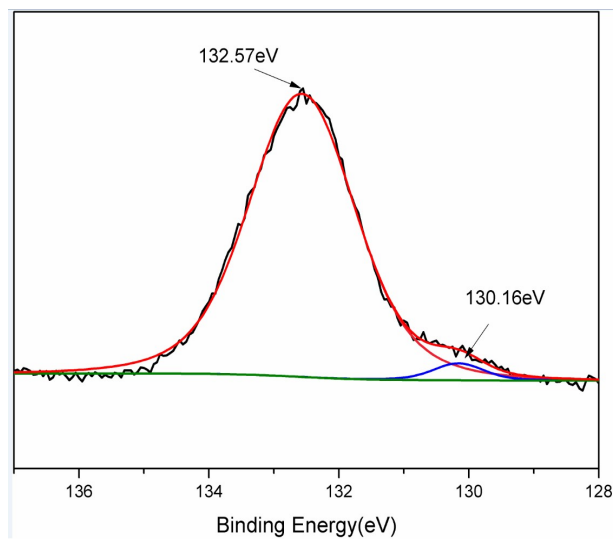


Figure S8. P 2p XPS spectra of recovered Pd/Cu@POP-POPh₃

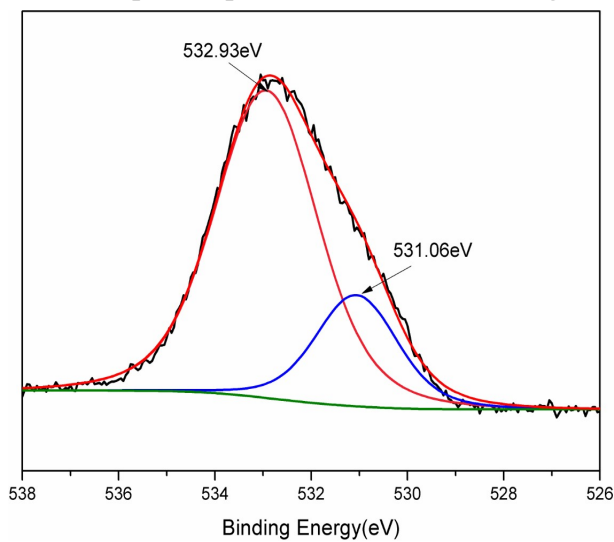


Figure S9. O 1s XPS spectra of recovered Pd/Cu@POP-POPh₃

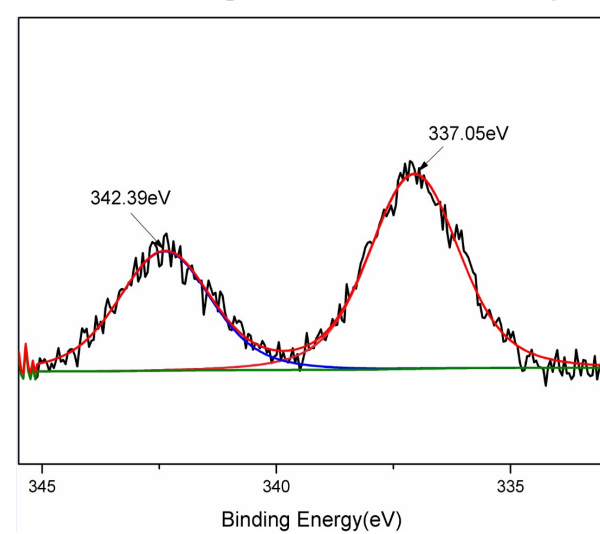


Figure S10. Pd 3d XPS spectra of recovered Pd/Cu@POP-POPh₃

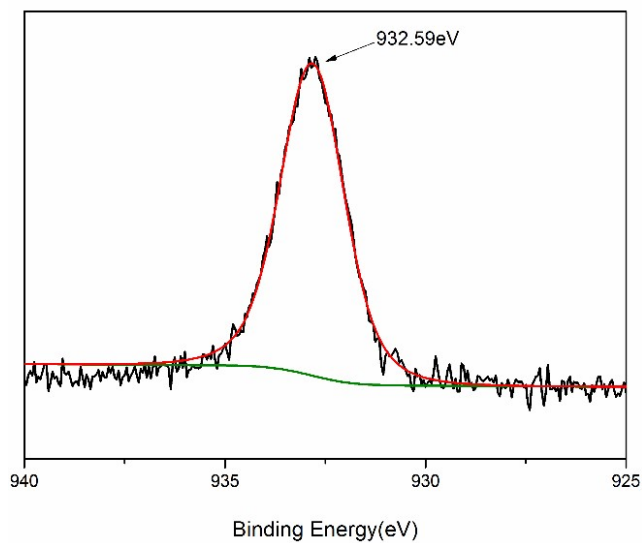


Figure S11. Cu 2p XPS spectra of recovered Pd/Cu@POP-POPh₃

5. TGA curve of Pd/Cu@POP-POPh₃.

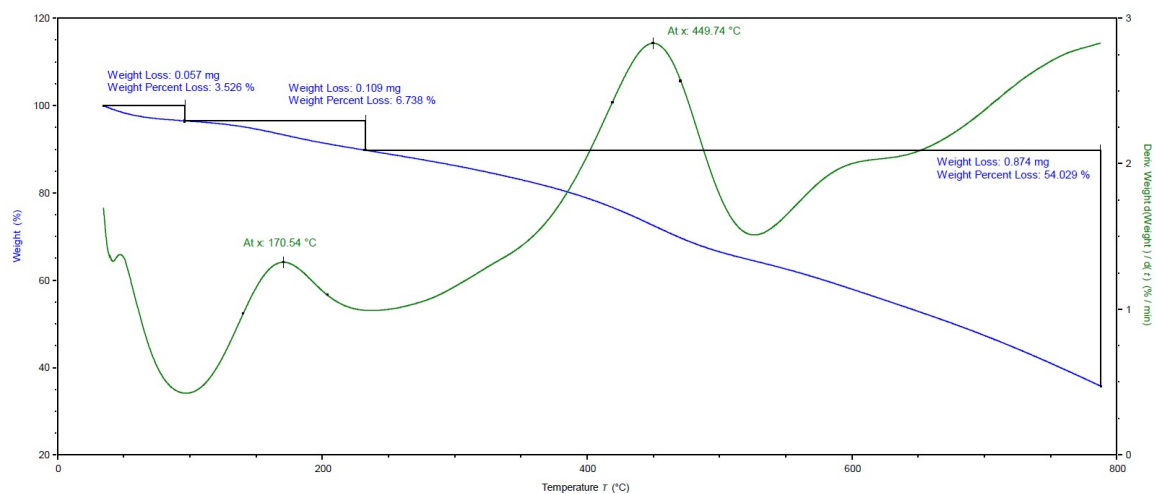
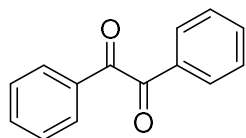
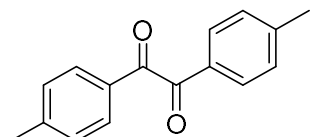


Figure S12. TGA curve of Pd/Cu@POP-POPh₃

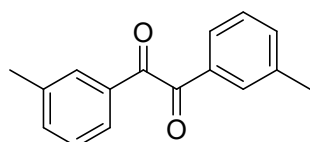
6. Characterization data for the oxidation of alkynes products.



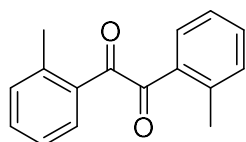
Benzil (2a)^[2]: yellow solid, 104 mg, 99% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.98 (dd, *J* = 8.0, 1.5 Hz, 4H), 7.68-7.65 (m, 2H), 7.54-7.50 (m, 4H) ppm.



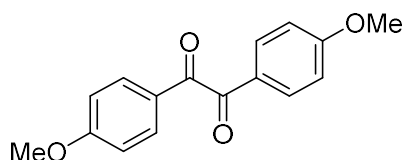
1,2-Di(p-tolyl)ethane-1,2-dione (2b)^[3]: yellow solid, 116 mg, 98% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.86 (d, *J* = 7.5 Hz, 4H), 7.30 (d, *J* = 7.5 Hz, 4H), 2.42 (s, 6H) ppm.



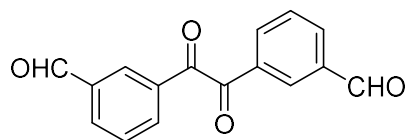
1,2-Di-m-tolyethane-1,2-dione (2c)^[4]: yellow solid, 112 mg, 94% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.78-7.76 (m, 4H), 7.48-7.46 (m, 2H), 7.41-7.38 (m, 2H), 2.41 (s, 6H) ppm.



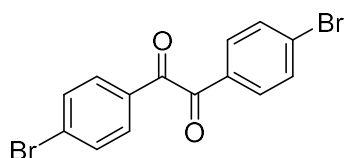
1,2-Bis(2-methylphenyl)ethane-1,2-dione (2d)^[4]: yellow solid, 113 mg, 95% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.67 (d, *J* = 7.5 Hz, 2H), 7.51-7.48 (m, 2H), 7.35 (d, 2H, *J*=7.5), 7.29-7.26 (m, 2H), 2.71 (s, 6H) ppm.



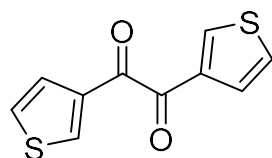
1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (2e)^[4]: yellow solid, 127 mg, 95% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.93 (d, *J* = 8.5 Hz, 4H), 6.95 (d, *J* = 8.5 Hz, 4H), 3.86 (s, 6H) ppm.



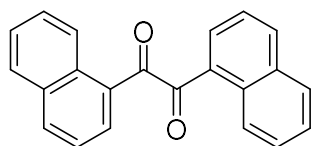
3,3'-(1,2-Dioxo-1,2-ethanediyl)bis-benzaldehyde (2f): yellow solid, melting point 142 °C, 124 mg, 93% yield. ^1H NMR (500 MHz, CDCl_3): δ 10.02 (s, 2H), 8.39 (s, 2H), 8.22 (d, $J = 8.0$ Hz, 2H), 8.14 (d, $J = 7.5$ Hz, 2H), 7.67 (t, $J = 7.5$ Hz, 2H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ 190.7, 136.9, 135.1, 135.0, 133.4, 131.4, 130.1 ppm. IR (KBr): 3076, 2921, 2849, 2744, 1704, 1669, 1598, 1433, 1386, 1320, 1293, 1247, 1189, 1150, 920, 839, 803, 746, 711, 694, 670 cm^{-1} . HRMS (ESI) m/z : Calcd. For $\text{C}_{16}\text{H}_{10}\text{NaO}_4^+$: 289.0470 $[\text{M}+\text{Na}^+]$, found: 289.0470.



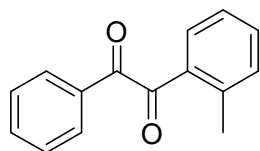
1,2-Bis(4-bromophenyl)ethane-1,2-dione (2g)^[4]: yellow solid, 182 mg, 99% yield. ^1H NMR (500 MHz, CDCl_3): δ 7.84 (d, $J = 8.0$ Hz, 4H), 7.68 (d, $J = 8.0$ Hz, 4H) ppm.



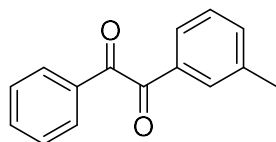
1,2-Di(thiophen-3-yl)ethane-1,2-dione (2h)^[5]: brown solid, 84.4 mg, 76% yield. ^1H NMR (500 MHz, CDCl_3): δ 8.28 (s, 2H), 7.62 (d, $J = 5.5$ Hz, 2H), 7.32-7.30 (m, 2H), ppm.



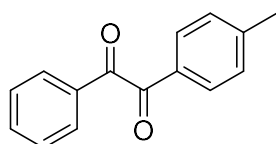
1,2-Di(naphthalen-1-yl)ethane-1,2-dione (2i)^[4]: brown liquid, 147.2 mg, 95% yield. ^1H NMR (500 MHz, CDCl_3): δ 9.39 (d, $J = 8.5$ Hz, 2H), 8.13 (d, $J = 8.0$ Hz, 2H), 8.04 (d, $J = 7.5$ Hz, 2H), 7.96 (d, $J = 8.5$ Hz, 2H), 7.70 (t, $J = 7.5$ Hz, 2H), 7.65 (t, $J = 7.5$ Hz, 2H), 7.49 (t, $J = 7.5$ Hz, 2H) ppm.



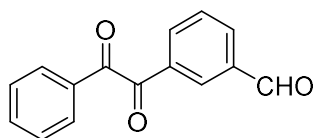
1-Phenyl-2-(o-tolyl)ethane-1,2-dione (2j)^[2]: yellow solid, 98.6 mg, 88% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.58-7.55 (m, 2H), 7.44-7.39 (m, 3H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 2H), 2.62 (s, 3H) ppm.



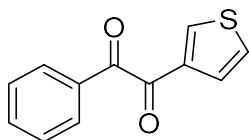
1-Phenyl-2-m-tolylolethane-1,2-dione (2k)^[6]: yellow solid, 105.4 mg, 94% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.97 (d, *J* = 7.5 Hz, 2H), 7.78-7.76 (m, 2H), 7.66 (t, *J* = 7.0 Hz, 2H), 7.53-7.46 (m, 3H), 7.40 (t, *J* = 7.5 Hz, 2H), 2.41 (s, 3H) ppm.



1-Phenyl-2-(p-tolyl)ethane-1,2-dione (2l)^[7]: yellow solid, 100.8 mg, 90% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.57-7.54 (m, 1H), 7.43-7.40 (m, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 2.35 (s, 3H) ppm.

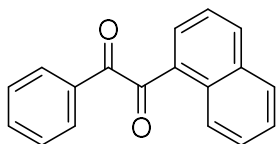


3-(2-Oxo-2-phenylacetyl)benzaldehyde (2m): yellow liquid, 118 mg, 99% yield. ¹H NMR (500 MHz, CDCl₃): δ 9.99 (s, 1H), 8.37 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 6.5 Hz, 2H), 7.65-7.59 (m, 2H), 7.47-7.44 (m, 2H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ 193.5, 192.9, 190.9, 136.9, 135.2, 135.1, 134.7, 133.8, 132.6, 131.4, 130.1, 129.9, 129.1 ppm. IR (neat): 3062, 2923, 2852, 2733, 1703, 1674, 1597, 1449, 1381, 1320, 1294, 1228, 1151, 1077, 1025, 1001, 910, 844, 794, 747, 716, 695 cm⁻¹. HRMS (ESI) *m/z*: Calcd. For C₁₅H₁₀NaO₃⁺: 261.0522 [M+Na⁺], found: 261.0514.



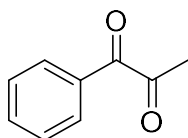
1-Phenyl-2-(thiophen-3-yl)ethane-1,2-dione (2n)^[8]: brown solid, 92 mg, 85% yield.

¹H NMR (500 MHz, CDCl₃): δ 8.23 (d, *J* = 2.0 Hz, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.68-7.65 (m, 2H), 7.54-7.51 (m, 2H), 7.42-7.41 (m, 1H) ppm.

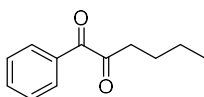


1-(1-Naphthyl)-2-phenylethane-1,2-dione (2o)^[9]: yellow solid, 125 mg, 96% yield.

¹H NMR (500 MHz, CDCl₃): δ 9.32 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 2H), 7.95-7.91 (m, 2H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.68-7.62 (m, 2H), 7.54-7.47 (m, 3H) ppm.



1-Phenylpropane-1,2-dione (2p)^[10]: brown liquid, 71.2 mg, 96% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 2.53 (s, 3H) ppm.

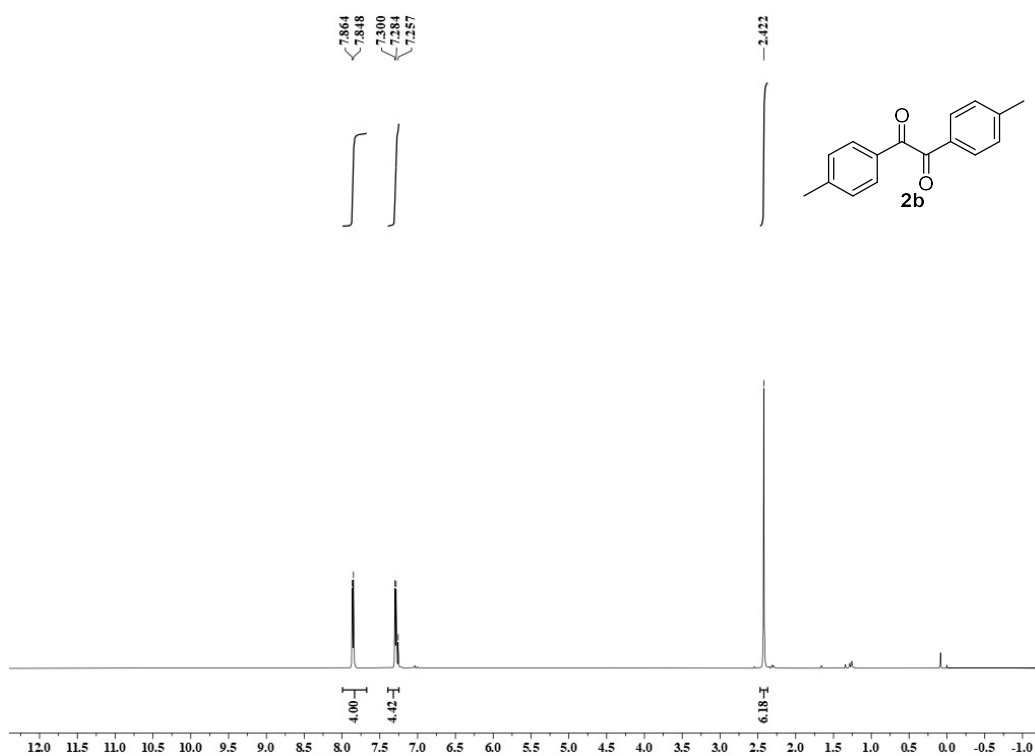
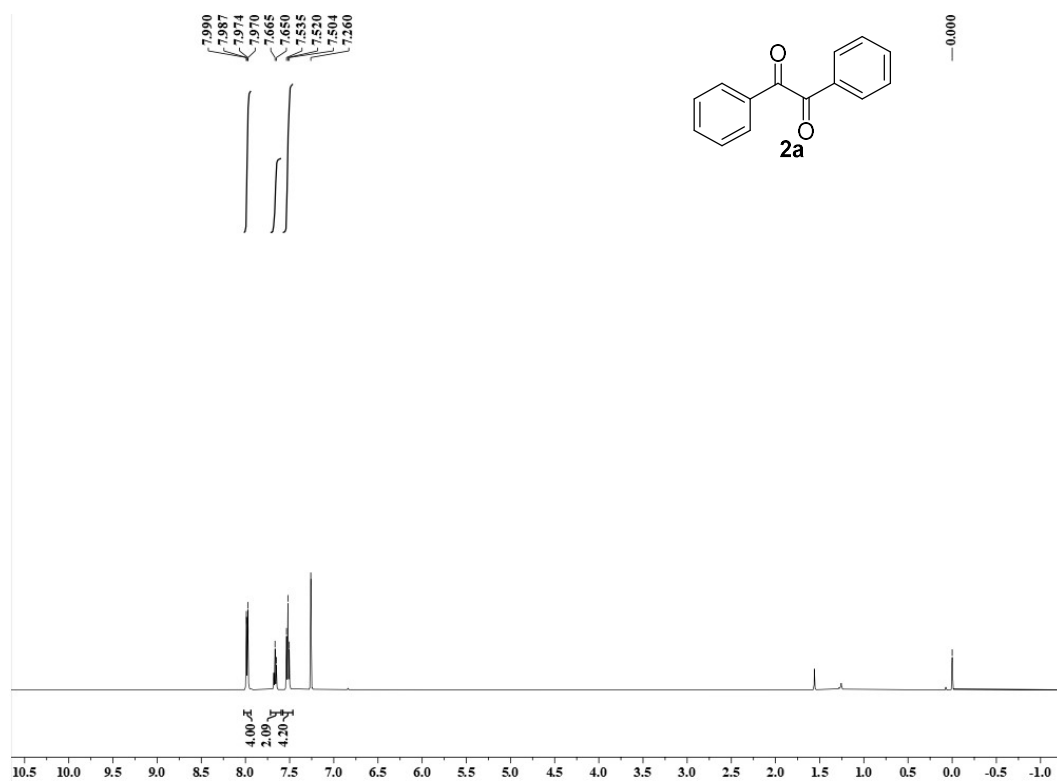


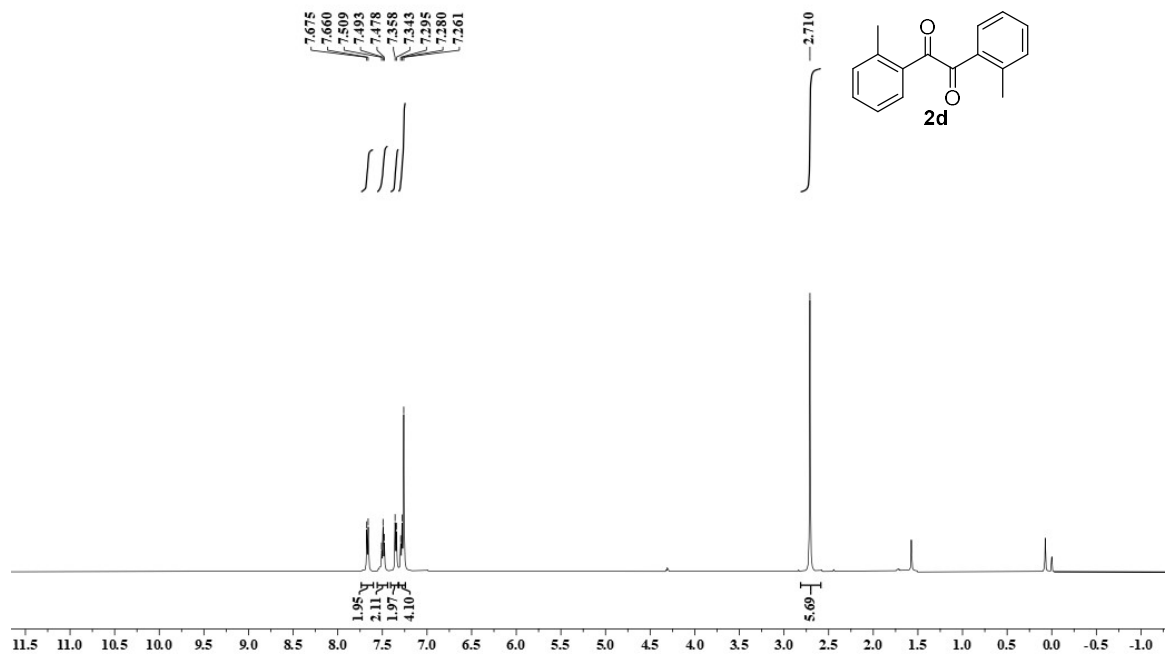
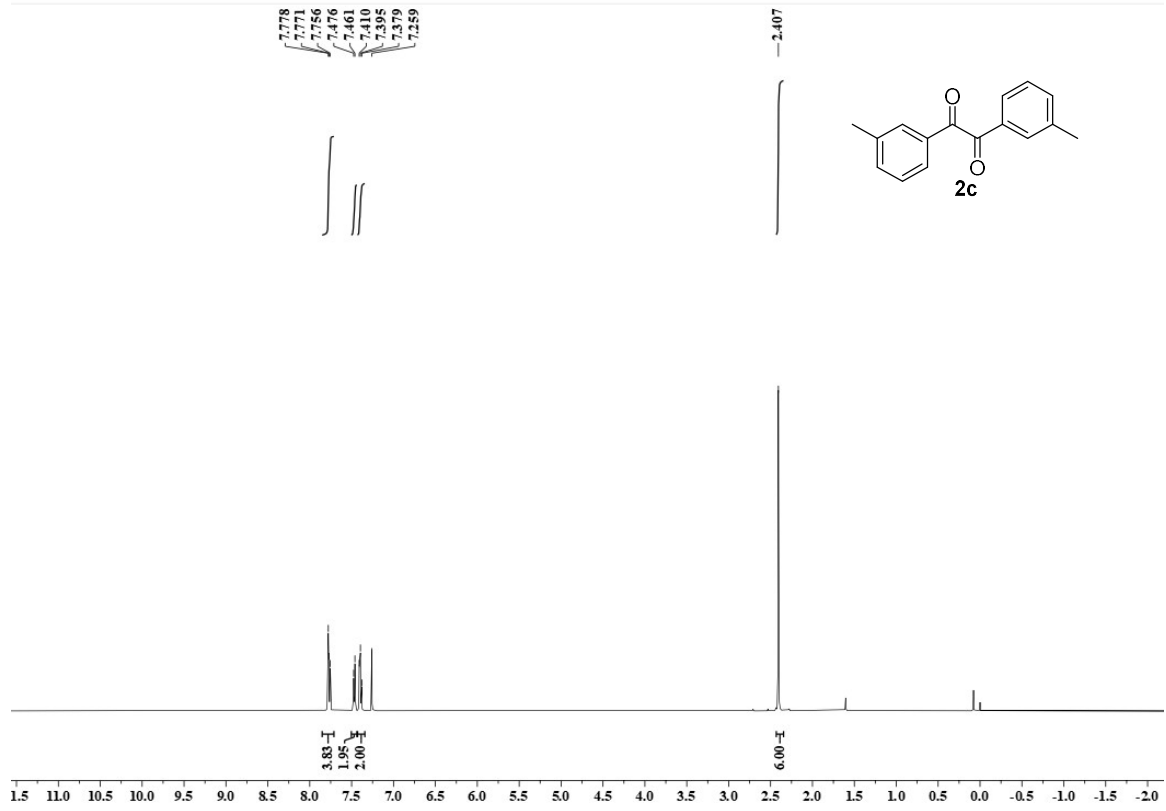
1-Phenylhexane-1,2-dione (2q)^[7]: yellow liquid, 85.6 mg, 90% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.98 (d, *J* = 7.0 Hz, 1H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 2.88 (t, *J* = 7.5 Hz, 2H), 1.71-1.65 (m, 2H), 1.43-1.39 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H) ppm.

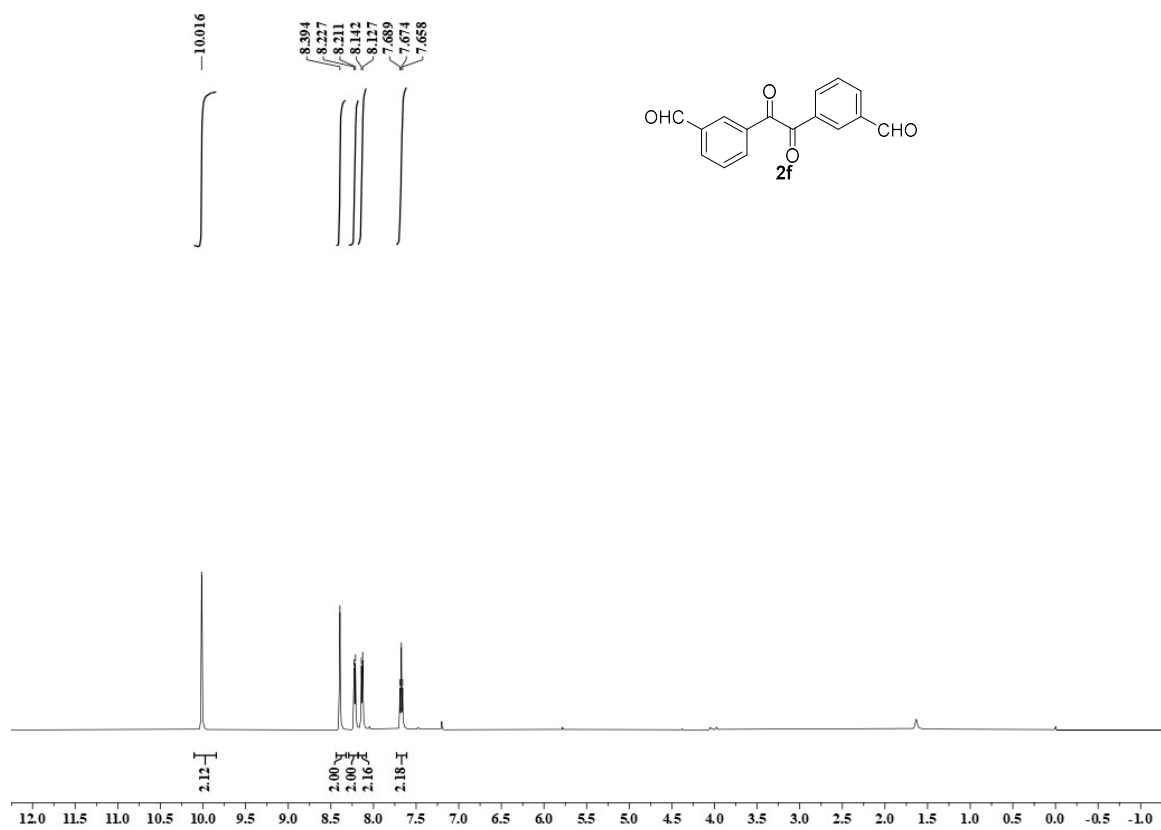
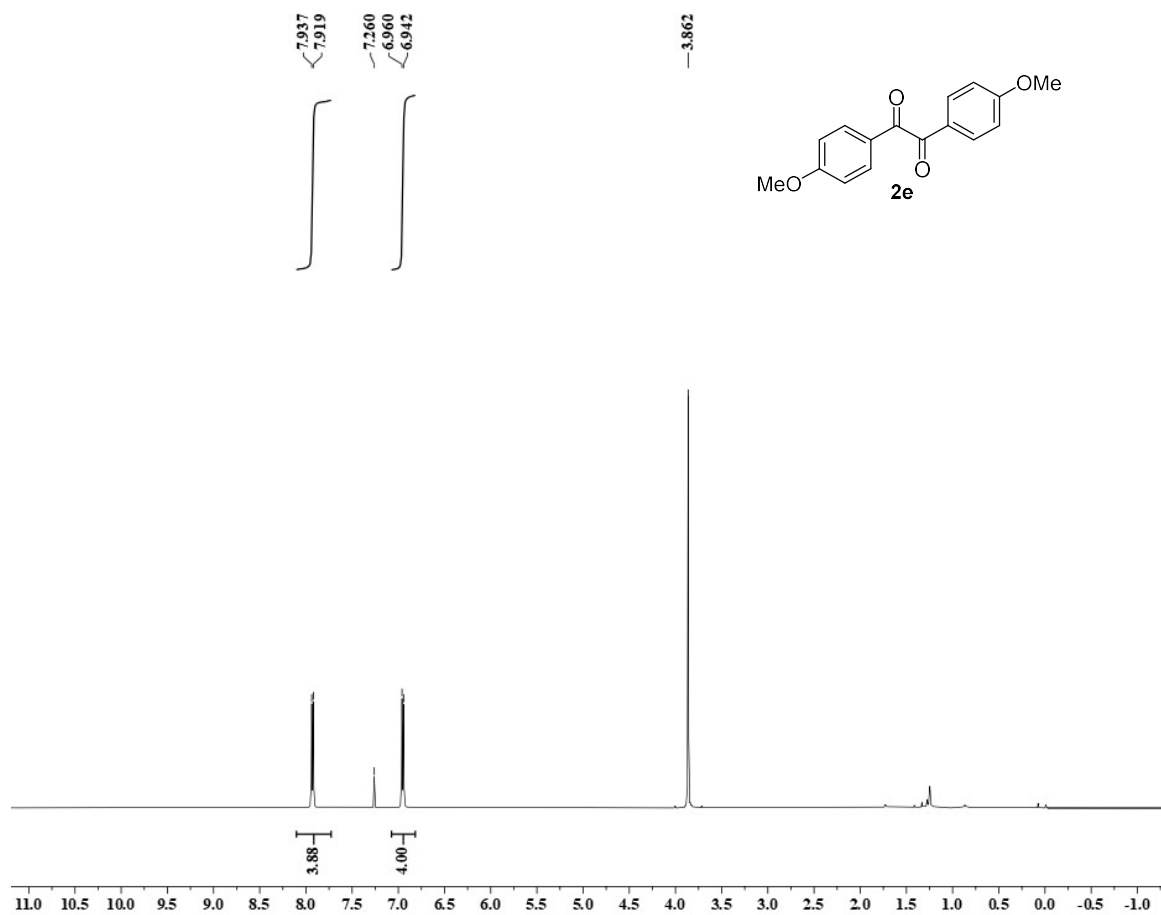
7. Recycling tests of the Pd/Cu@POP-POPh₃ in the oxidation of alkynes.

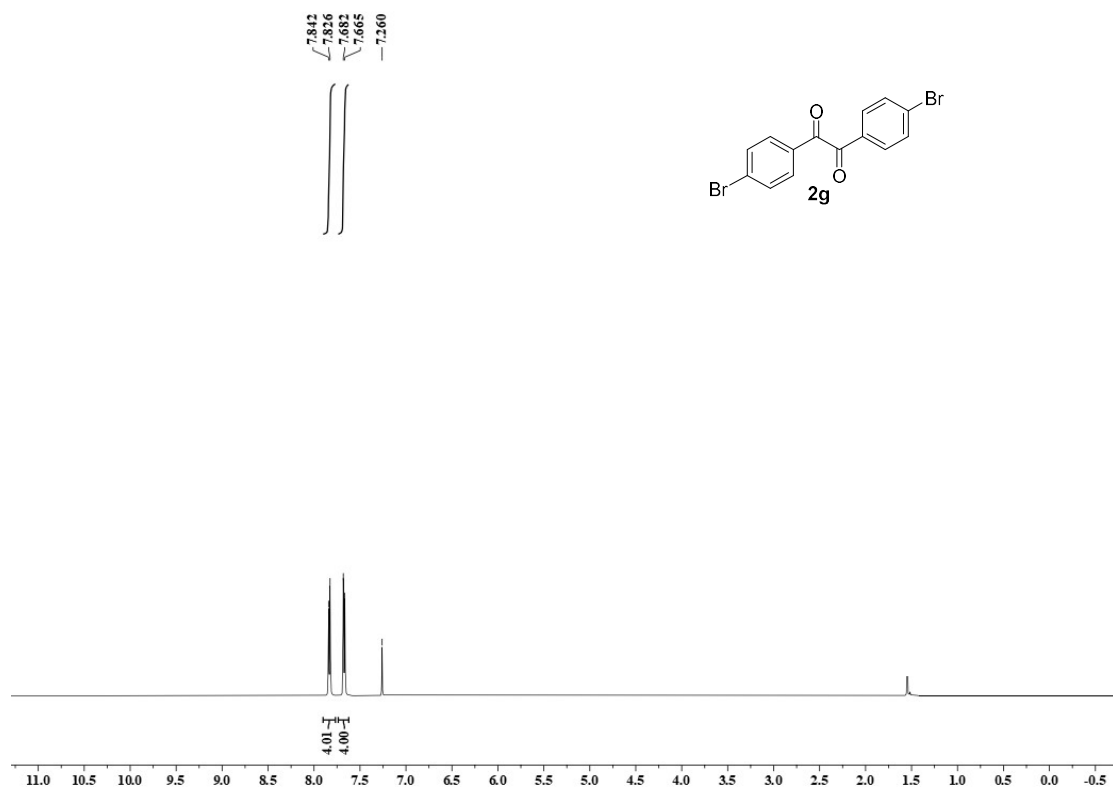
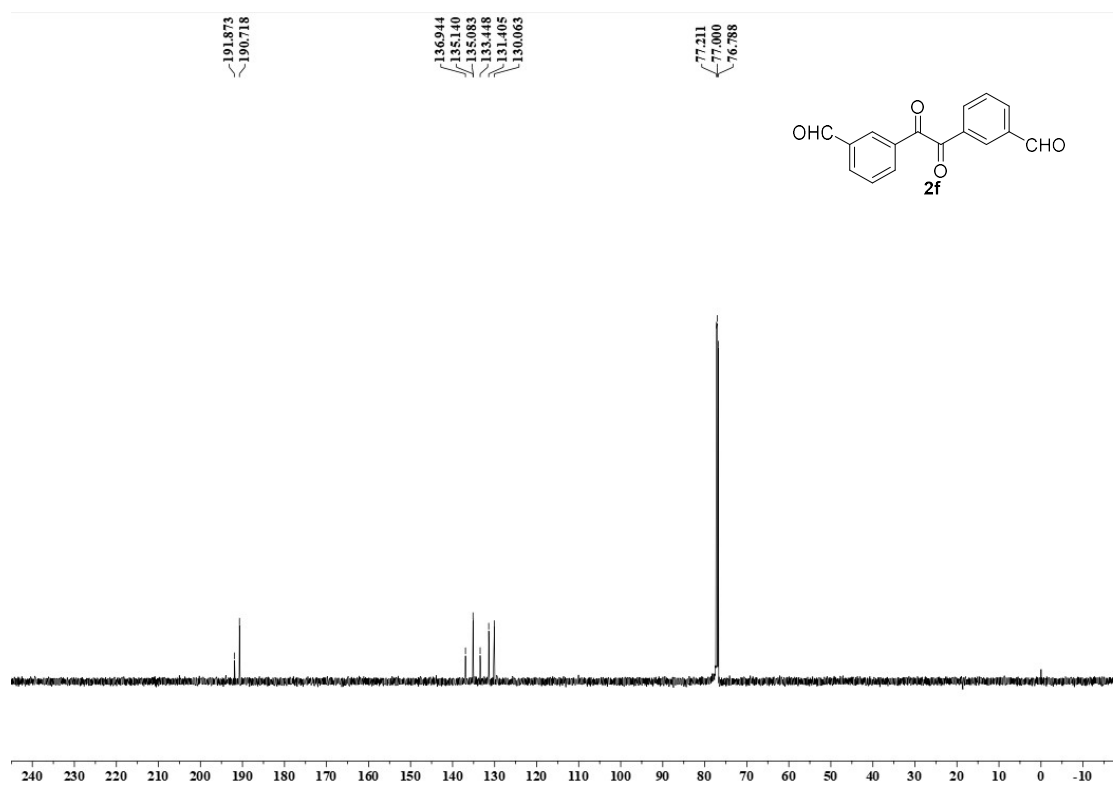
A Schlenk flask with a magnetic stirring bar was successively charged with alkynes (0.5 mol), Pd/Cu@POP-POPh₃ (61 mg), dioxane (2 mL) and H₂O (0.3 mL). The Schlenk flask was purged with O₂ for three times. The mixture was stirred under an oxygen (balloon) atmosphere at 60 °C for 15 h. After the reaction, the mixture was diluted with *n*-hexane (3×2 mL). The catalyst of Pd&Cu/POP-POPh₃ was recovered by centrifugation. Then the recovered catalyst used to test next recycling reaction with the same condition and procedure. Yields of **2a** were determined on the basis of GC analysis. GC analysis condition: SE-54, 30 m×0.32 mm×0.33 mm, flow rate 2.0 mL min⁻¹, method: 50 °C was maintained for 5 min, and then ramped from 50 °C to 250 °C at a rate of 20 °C min⁻¹, 250 °C was maintained for 10 min.

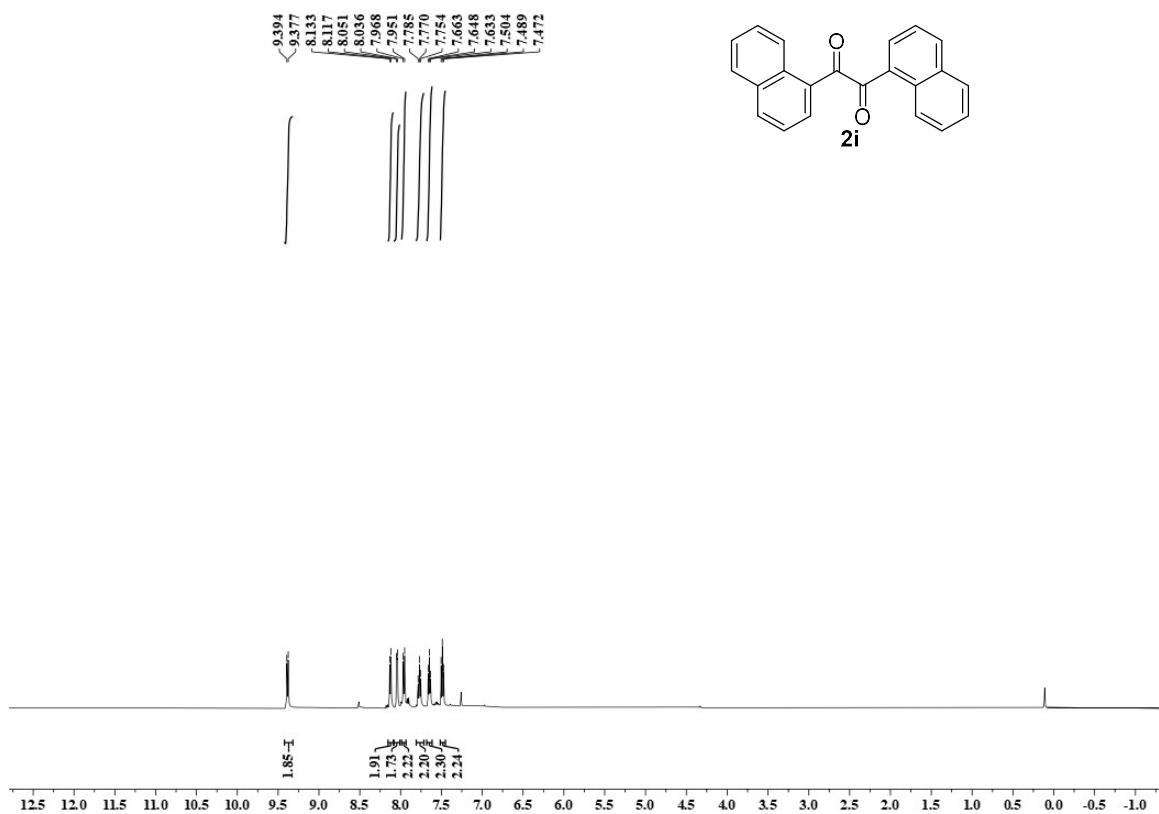
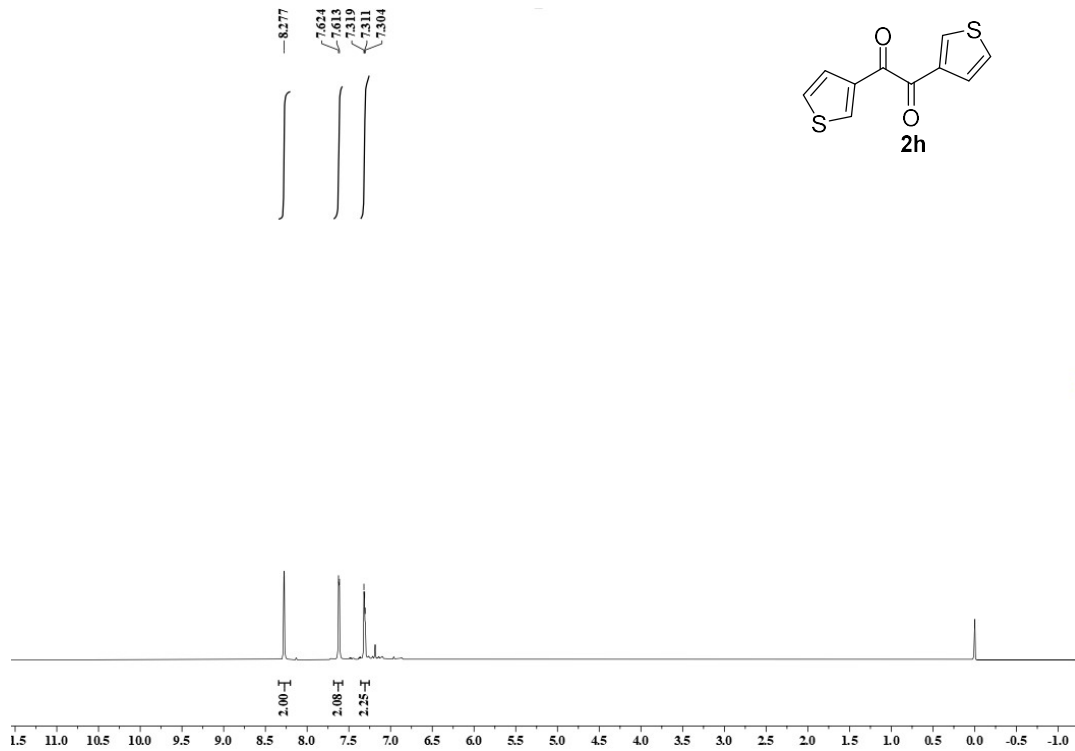
8. NMR spectra of 1,2-diketones.

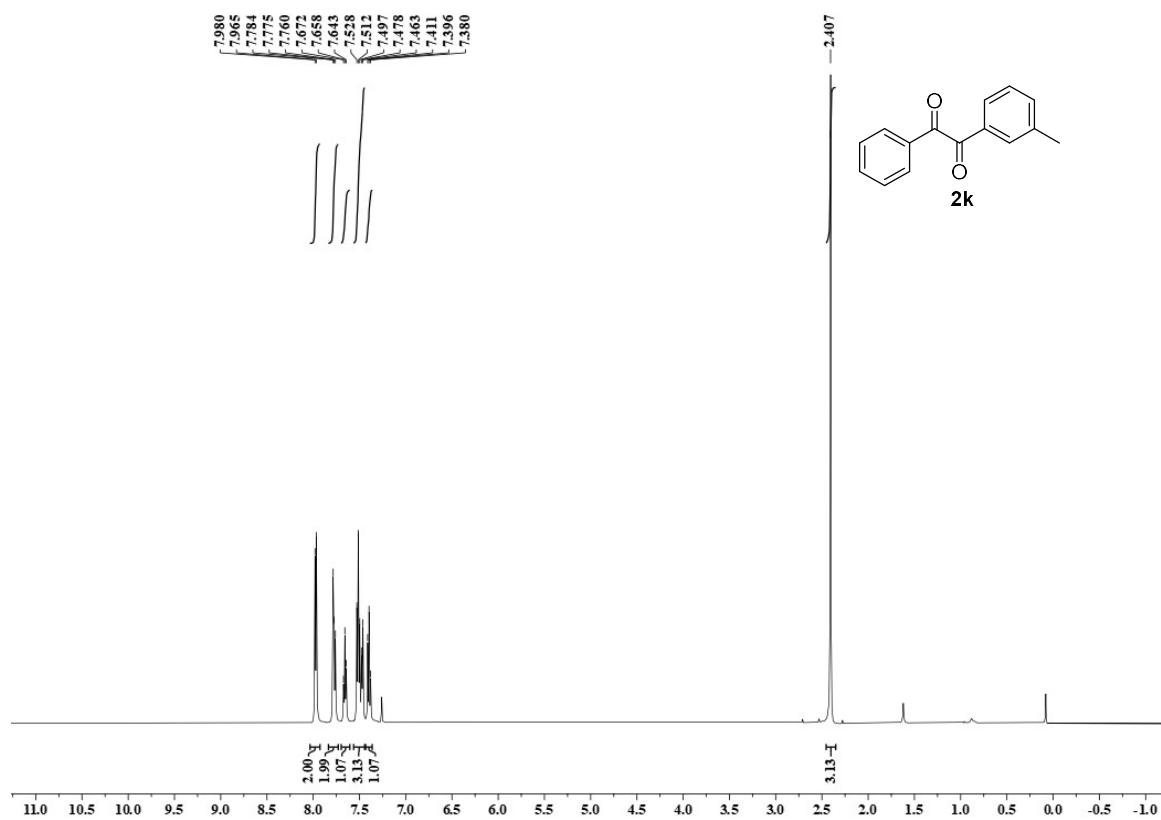
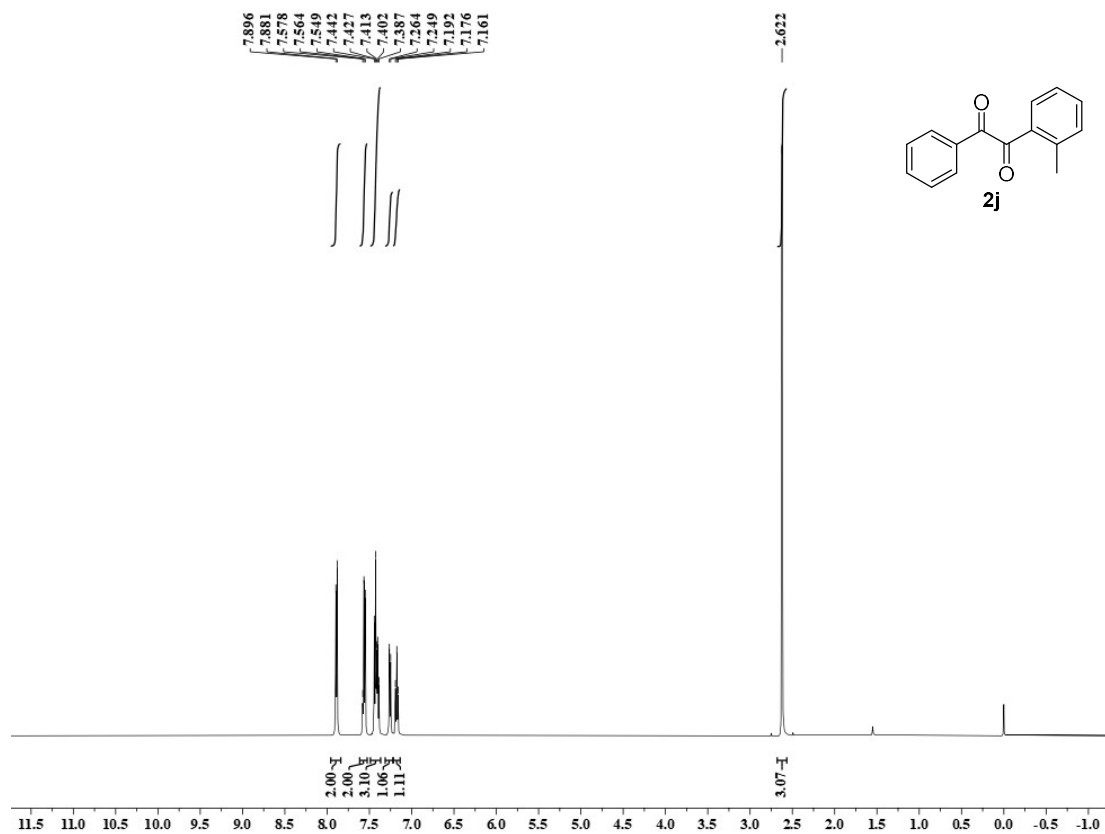


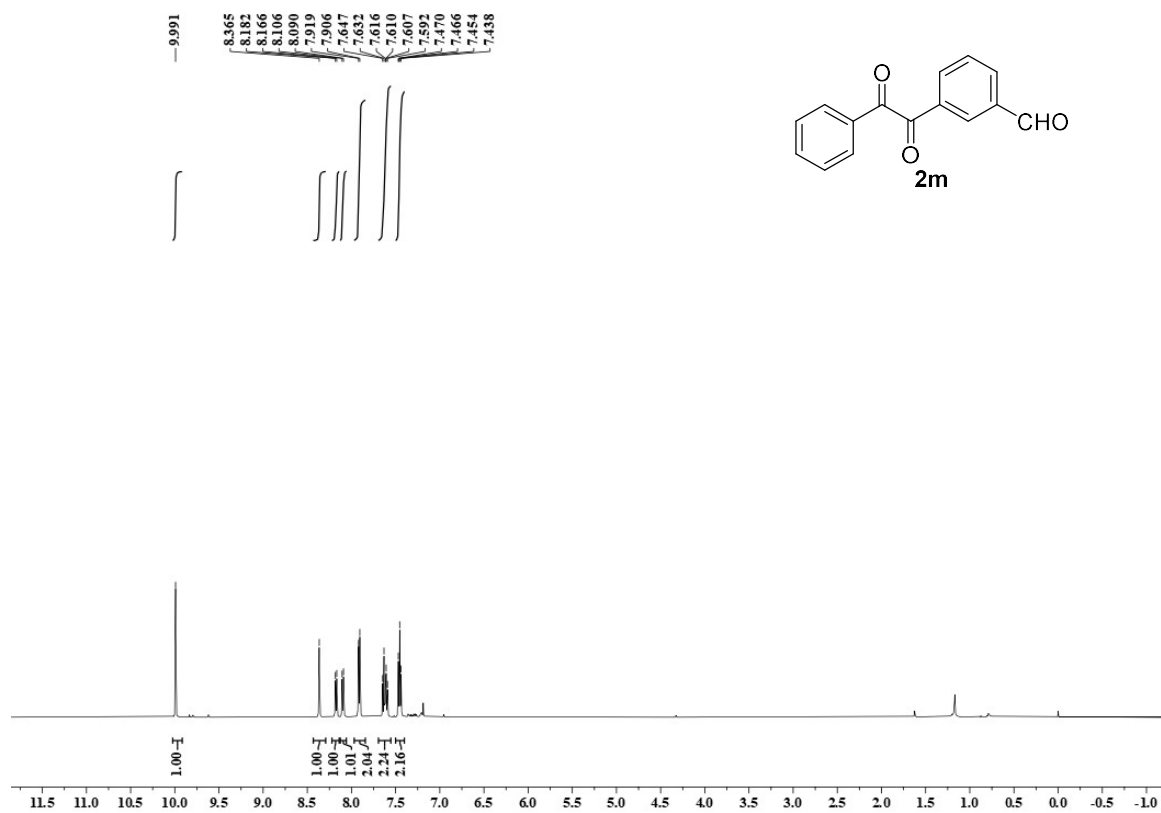
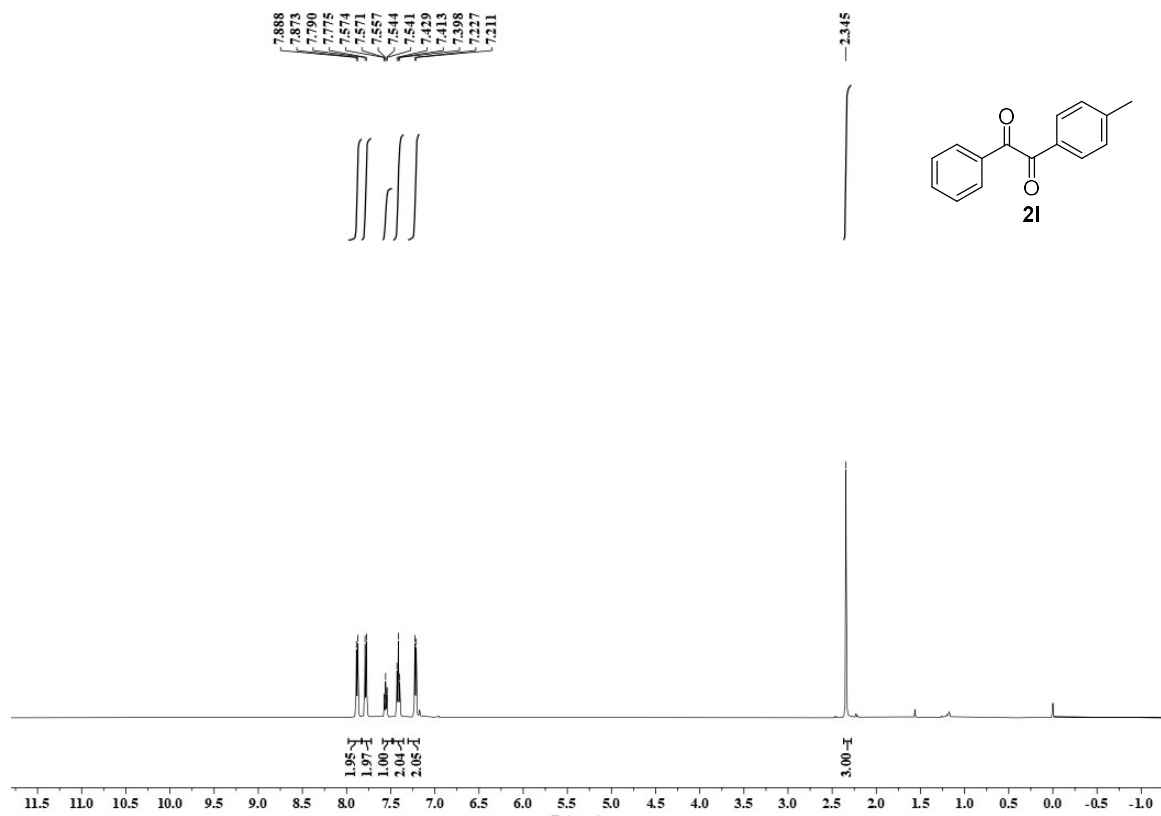


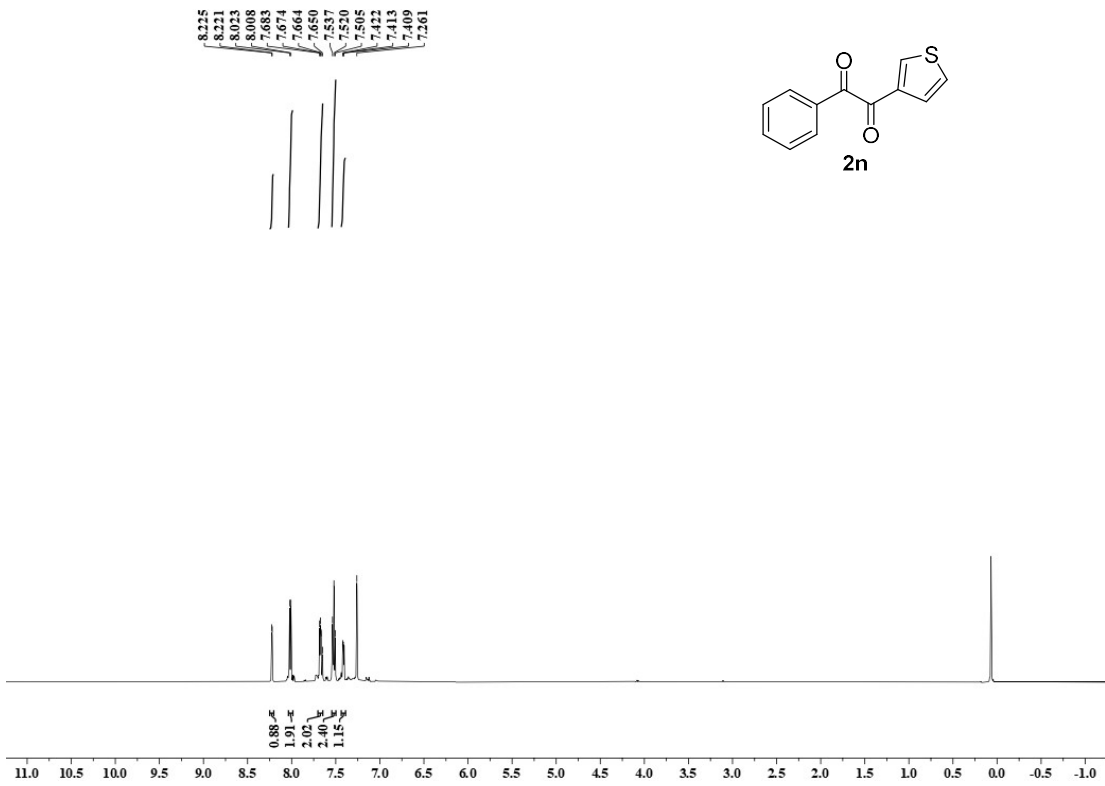
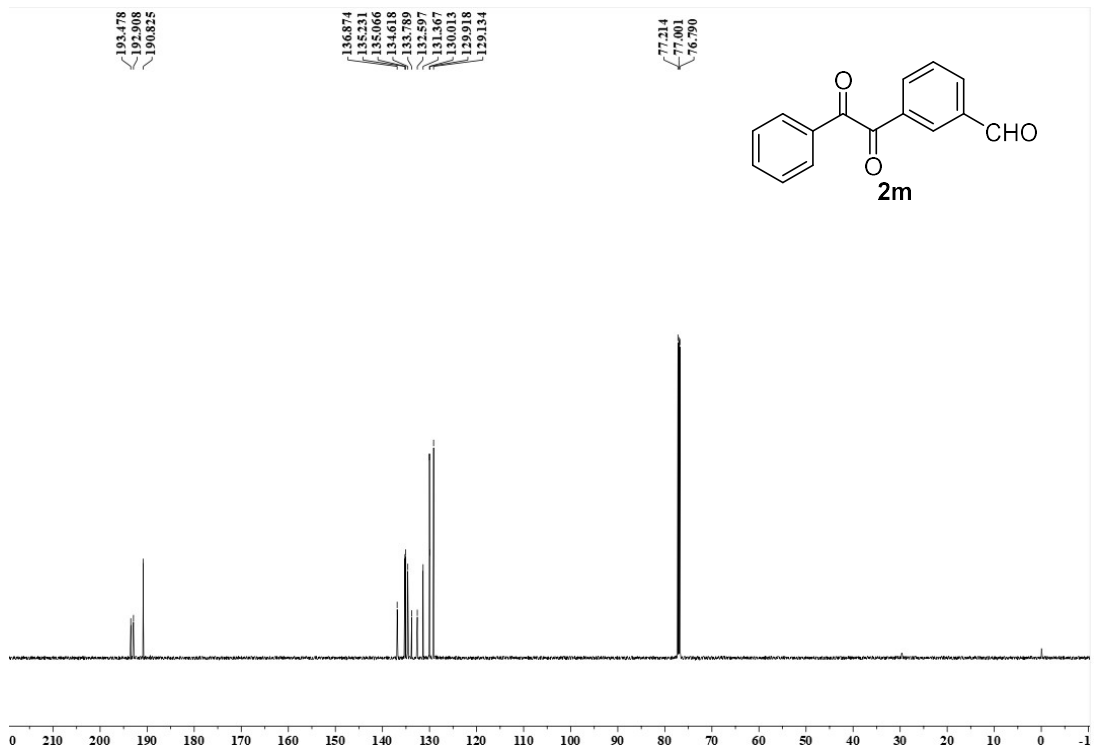


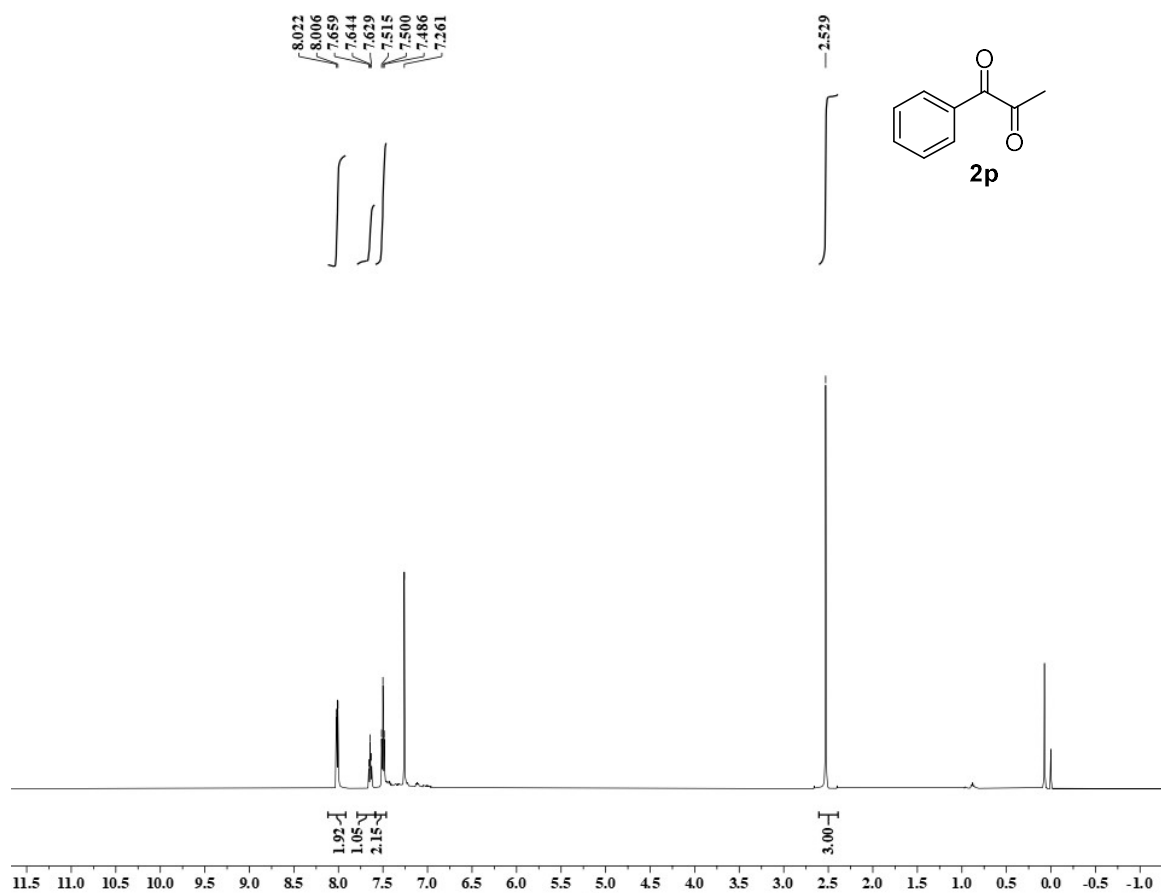
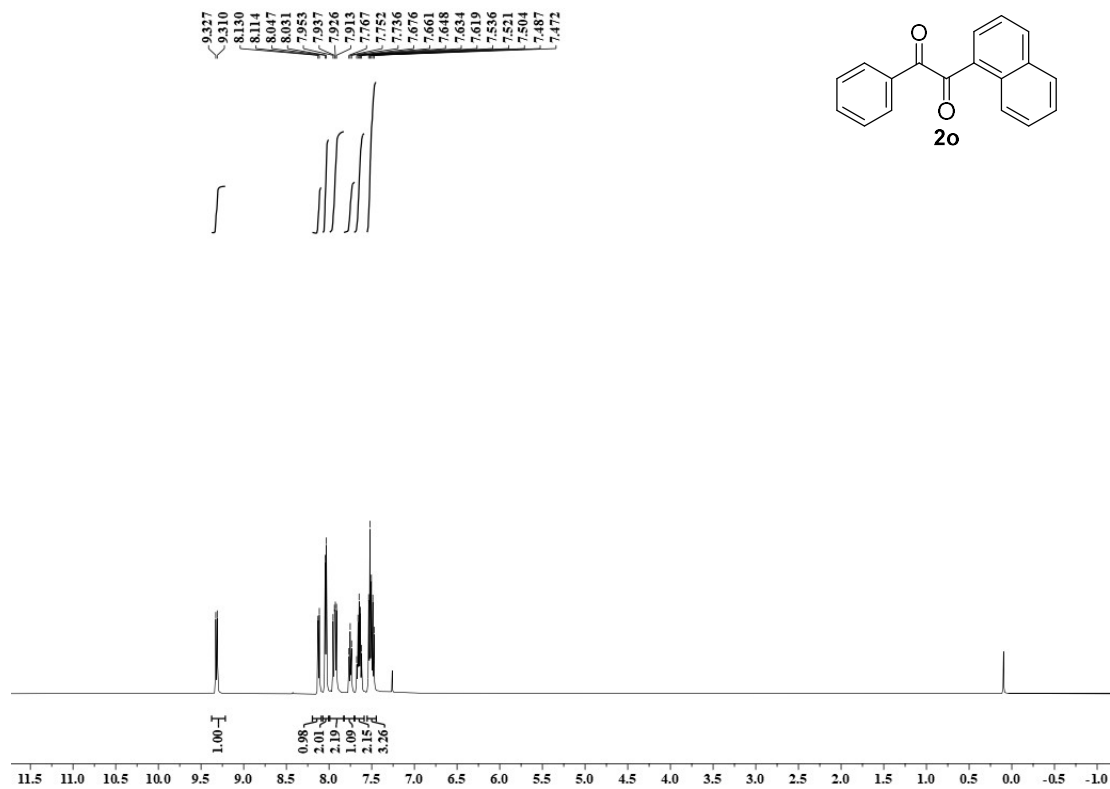


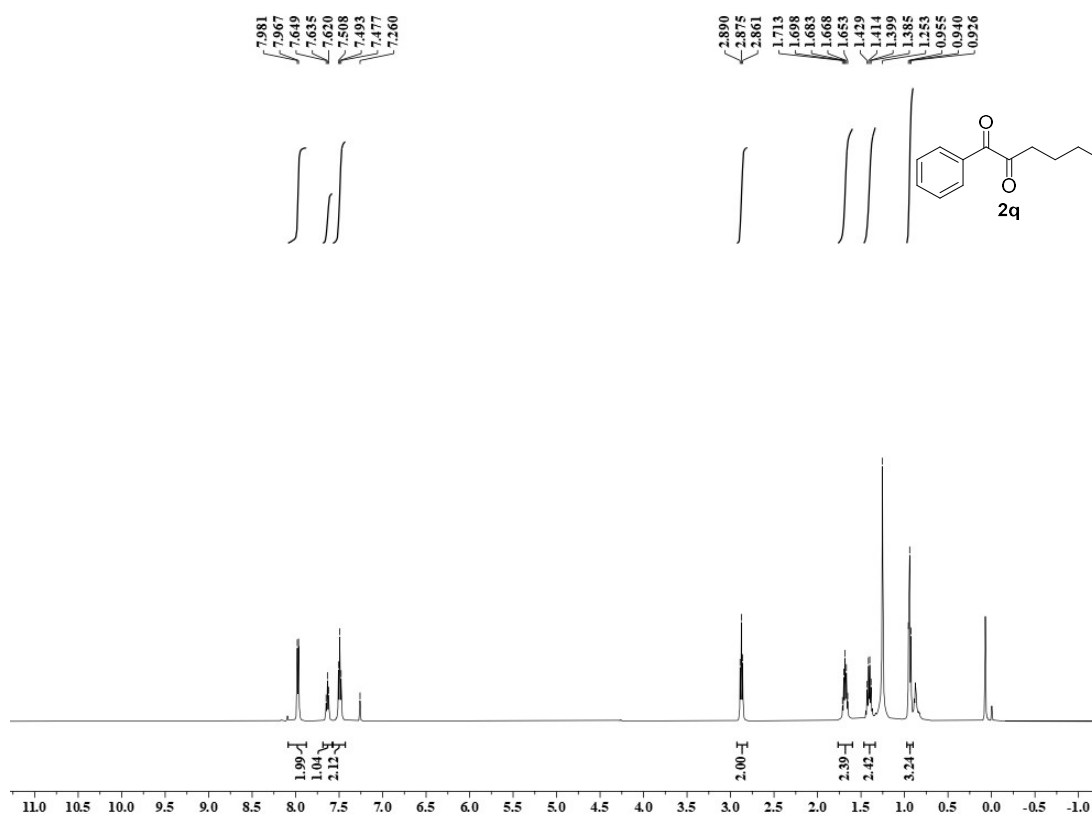












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