Electrochemical synthesis of 1,2-diketones from alkynes under transition-metal-catalyst-free conditions

Jie Zhou, Xiang-Zhang Tao, Jian-Jun Dai,* Jun Xu, Hong-Mei Xu, and Hua-Jian Xu*

School of Food and Biological Engineering, Key Laboratory of Metabolism and Regulation for Major Diseases of Anhui Higher Education Institutes, Hefei University of Technology, Hefei 230009, China.

*To whom correspondence should be addressed. E-mail: daijj@hfut.edu.cn; hjxu@hfut.edu.cn

Supporting Information

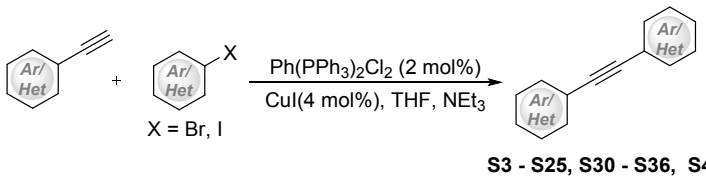
Contents

I. General Information

All reagents were used as received from commercial sources unless specified otherwise or prepared as described in the literature. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on a Bruker Advance 400 or 600 spectrometer at the ambient temperature in $CDCl_3$ unless otherwise noted. Chemical shifts (δ) are reported in parts per million (ppm) using tetramethylsilane (TMS) as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = triplet of doublets, m = multiplet). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration, Chemical shifts were referenced to internal TMS at δ 0.00 ppm or to the signal of residual proton solvent peak: $CDCl_3$ at δ 7.26 ppm. Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm), Chemical shifts were referenced to residual solvent peak: $CDCl_3$ at δ 77.0 ppm. Data for ^{19}F NMR are reported in terms of chemical shift (δ ppm), Chemical shifts were referenced to internal or external $CFCl_3$ at δ 0.00 ppm. GC-MS analyses were performed on Thermo Scientific AS 3000 Series GC-MS System. High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode. Analytical TLC was done on pre-coated silica gel plates. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

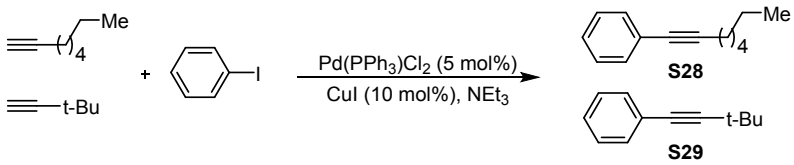
II. Preparation of Substrates

a. Procedure for preparation of substrates S3-S25, S30-S36 and S40[1]



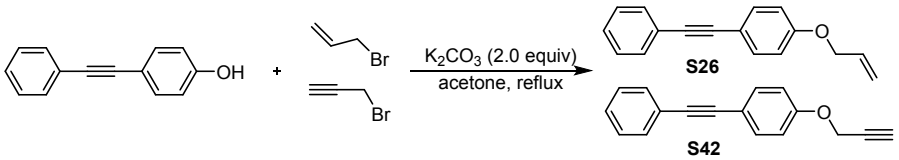
The corresponding iodide or bromo benzene (5 mmol, 1 equiv), $Pd(PPh_3)Cl_2$ (2 mol%, 66.6 mg), CuI (4 mol%, 38 mg) and phenylacetylene (5 mmol, 1 equiv) were added to a 50 mL Schlenk flask with a stir bar under an atmosphere of nitrogen. To this was added tetrahydrofuran (5 mL) and triethylamine (5 mL). The reaction mixture was then stirred at room temperature overnight. Thereafter 25 mL of water were added, and the reaction mixture was extracted with diethyl ether (4 × 25 mL). The combined organic fractions were washed with brine and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The crude product was purified by means of silica gel chromatography using petroleum ether and ethyl acetate as the eluent. The yields were not optimized for the synthesis of alkynes.

b. Procedure for preparation of substrates S28 and S29[2]



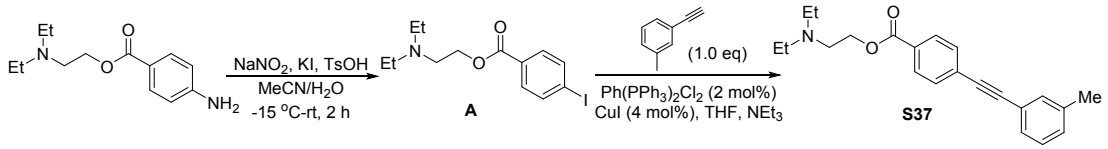
To a mixture of $Pd(PPh_3)_2Cl_2$ (5% mol, 0.25 mmol, 175 mg), CuI (10 mol%,0.5 mmol, 95 mg) and iodobenzene (5 mmol, 1.02 g) was added 10 mL of triethylamine. The solution was stirred for 10 minutes before addition of alkyl acetylene (7.5 mmol). After TLC analysis showed the reaction to be complete, the reaction mixture was filtered through a short plug of silica gel. Filtrate was concentrated and purified by flash column chromatography on silica gel to give the desired product.

c. Procedure for preparation of substrates S26 and S42[2]



To a mixture of 4-(phenylethynyl)phenol (2 mmol, 388 mg) in acetone (25 mL) was added K_2CO_3 (3 mmol, 415 mg) at room temperature. After 15 minutes, propargyl bromide (3 mmol, 357 mg)/allyl bromide (3 mmol, 363 mg) was added slowly and heated to reflux until TLC analysis indicated the disappearance of the starting material. The mixture was cooled to room temperature and filtered. The collected filtrate was concentrated and purified by flash column chromatography on silica gel (hexane) to give the desired product as a white solid.

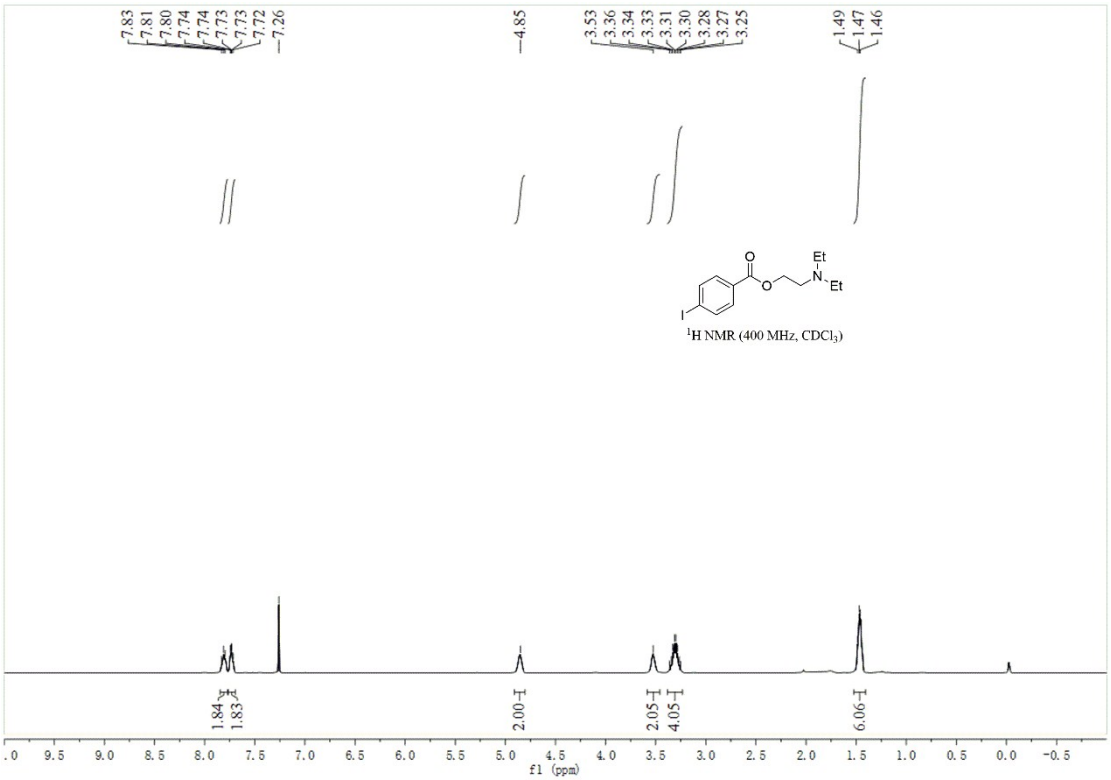
d. Procedure for preparation of substrates S37[3]

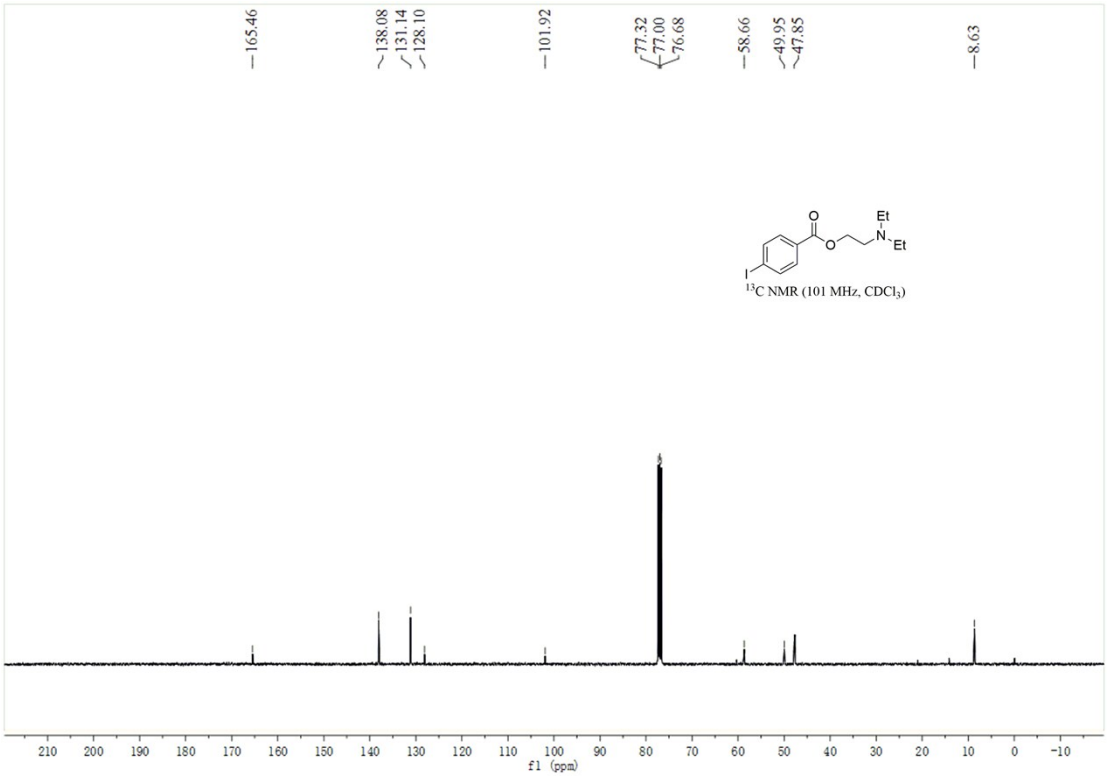


Procain (5 mmol, 1.18 g) and TsOH (15 mmol, 2.58 g) were dissolved in 50 mL of MeCN and cooled to -15 °C. To this mixture was added a solvent of $NaNO_2$ (10 mmol, 690 mg) and KI (12.5 mmol, 2.0 g) in water (15 mL) slowly, and the resulting mixture was then stirred in room temperature for 2 h. After the starting material was totally consumed, water (50 mL) was added, and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic phase was then washed by $NaHCO_3$ (aq.) and NaS_2O_3 (aq.) dried over anhydrous Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography (PE/EA = 10: 1) to give the product 2-(diethylamino)ethyl 4-iodobenzoate as a white solid (1.35 g, 78%).

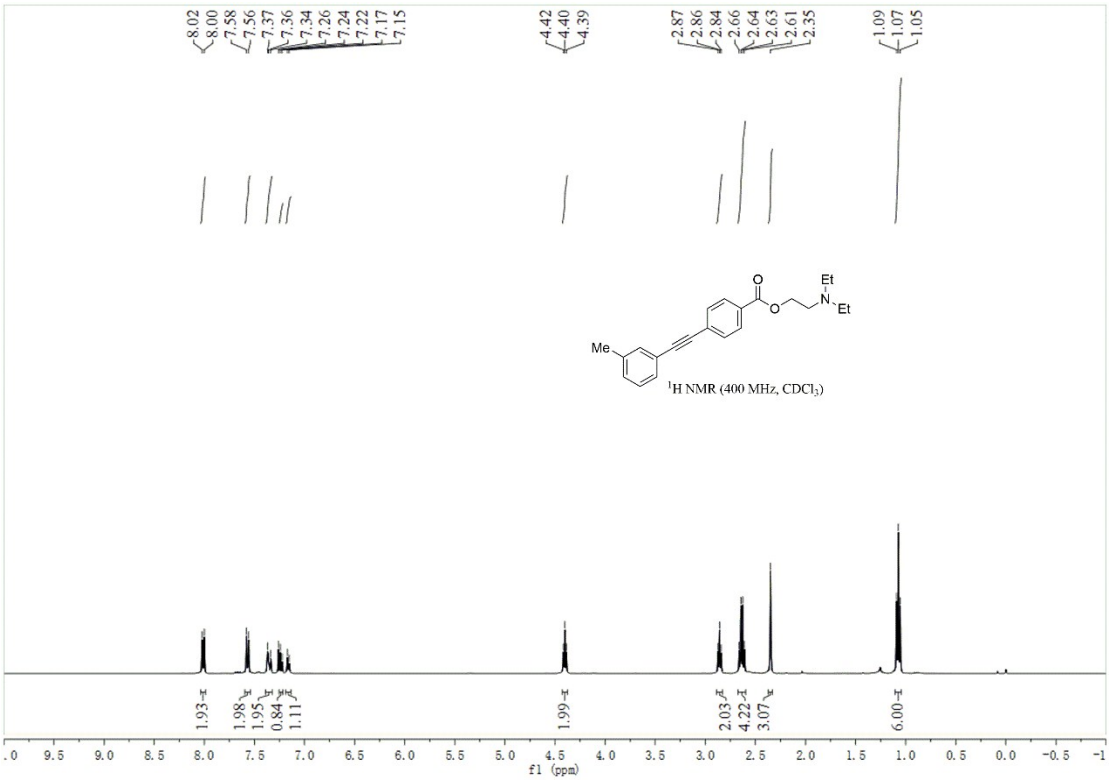
Then, 2-(diethylamino)ethyl 4-iodobenzoate (3.9 mmol, 1.35 g, 1 equiv), $Pd(PPh_3)Cl_2$ (2 mol%, 51.9 mg), CuI (4 mol%, 29.6 mg) and 1-ethynyl-3-methylbenzene (3.9 mmol, 452 mg, 1 equiv) were added to a 50 mL Schlenk flask with a stir bar under an atmosphere of nitrogen. To this was added tetrahydrofuran (5 mL) and triethylamine (5 mL). The reaction mixture was then stirred at room temperature overnight. Thereafter 25 mL of water were added, and the reaction mixture was extracted with diethyl ether (4 × 25 mL). The combined organic fractions were washed with brine and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The crude product was purified by means of silica gel chromatography using petroleum ether and ethyl acetate as the eluent and the desired product 2-(diethylamino)ethyl 4-(m-tolylethynyl)benzoate (**S37**) was obtained as a pale yellow solid (914.6 mg, 70%).

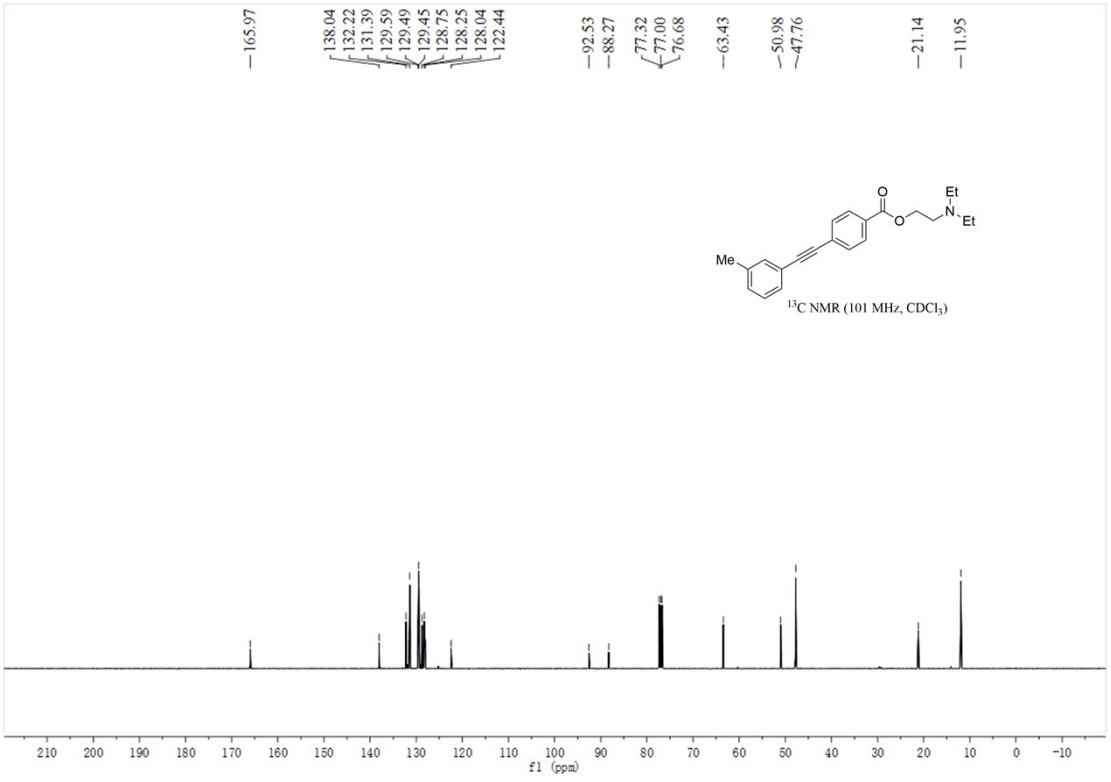
2-(diethylamino)ethyl 4-iodobenzoate (**A**): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 6.6 Hz, 2H), 7.76 – 7.69 (m, 2H), 4.85 (s, 2H), 3.53 (s, 2H), 3.38 – 3.23 (m, 4H), 1.52 – 1.41 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 138.2, 131.1, 128.1, 101.9, 58.7, 50.0, 47.9, 8.6. The spectroscopic characteristics match those reported in the literature.[3]



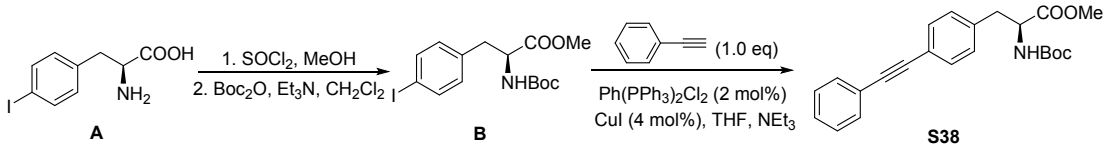


2-(diethylamino)ethyl 4-(m-tolylethynyl)benzoate (**S37**): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 4.40 (t, *J* = 6.2 Hz, 2H), 2.86 (t, *J* = 6.2 Hz, 2H), 2.64 (q, *J* = 7.1 Hz, 4H), 2.35 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.97, 138.04, 132.22, 131.39, 129.59, 129.49, 129.45, 128.75, 128.25, 128.04, 122.44, 92.53, 88.27, 63.43, 50.98, 47.76, 21.14, 11.95. **HRMS** (ESI) Calcd for $C_{22}H_{26}NO_2$ $[M+H]^+$: 336.1958; **Found**: 336.1959.





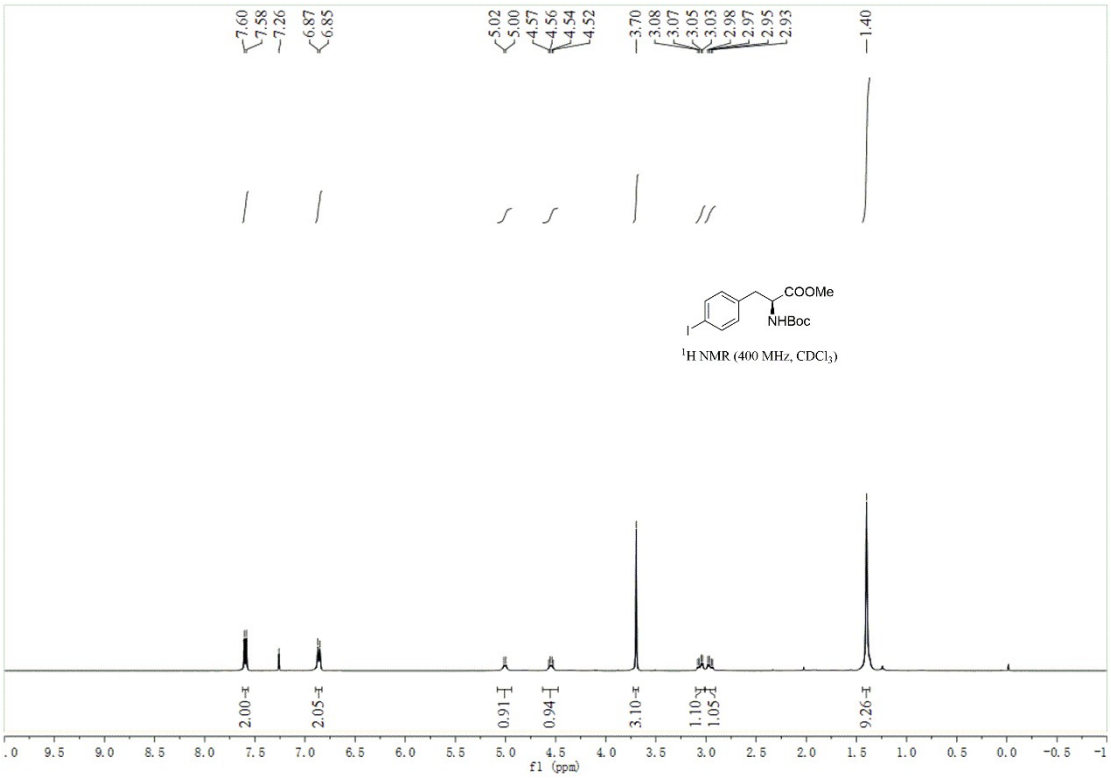
e. Procedure for preparation of substrates S38[4]

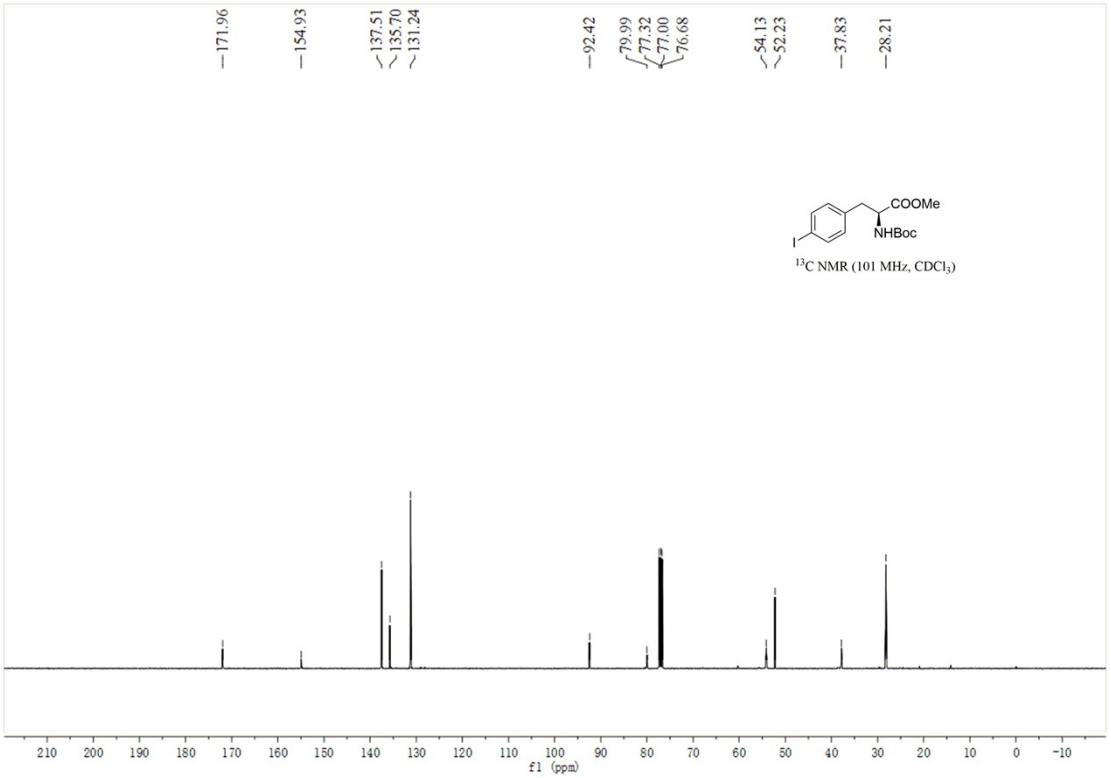


Under a nitrogen atmosphere, to a 100 mL flask, 20 mL of methanol was placed, ice water cooling was carried out, thionyl chloride 2.2 mL (30.3 mmol) was slowly added. After finishing the addition of thionyl chloride, stirred for 10 minutes, **A** (1 g, 6.06 mmol) was added slowly, and stirred. Then returned to room temperature and stirred for 12 hours. The solvent was distilled off, the taken-out crystals were dissolved in a small amount of methanol, recrystallized with diethyl ether. The obtained crystals were added to a 100 mL flask under nitrogen atmosphere, 1,4-dioxane (20 mL) was placed and $(Boc)_2O$ 1.46 g (6.42 mmol) was added. Once the solvent was sufficiently cooled, saturated $NaHCO_3$ (aq.) 20 mL was added slowly and stirred for 2 hours. A small amount of saturated NH_4Cl (aq.) was added, and the mixture was extracted with ethyl acetate. After drying over $MgSO_4$, the solvent was distilled off, the resulting mixture was purified by silica column chromatography (PE/EA = 10: 1 to 3: 1). The methyl (*L*)-2-((tert-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate was obtained as a white solid (1.62 g, 66%).

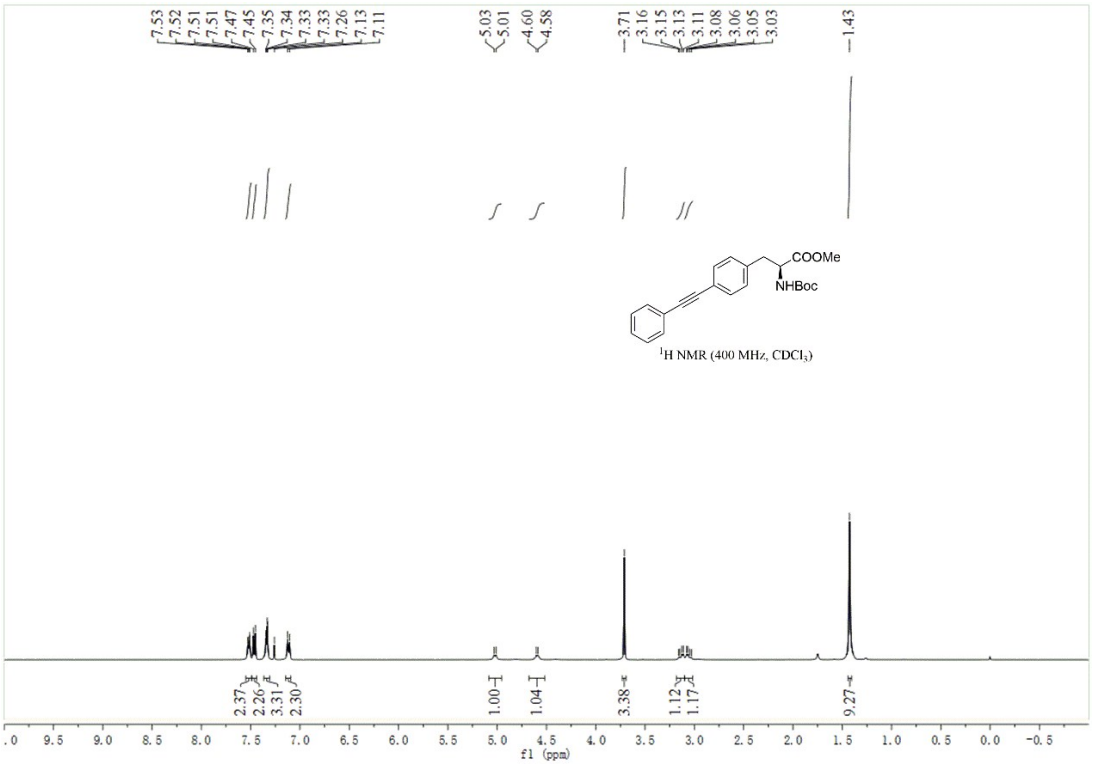
Then, methyl (*L*)-2-((tert-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate (4 mmol, 1.62 g, 1 equiv), $Pd(PPh_3)Cl_2$ (2 mol%, 53.3 mg), CuI (4 mol%, 30.4 mg) and phenylacetylene (4 mmol, 408 mg, 1 equiv) were added to a 50 mL Schlenk flask with a stir bar under an atmosphere of nitrogen. To this was added tetrahydrofuran (1 M) and triethylamine (1 M). The reaction mixture was then stirred at room temperature overnight. Thereafter 25 mL of water were added, and the reaction mixture was extracted with 4 × 25 mL diethyl ether. The combined organic fractions were washed with brine and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The crude product was purified by means of silica gel chromatography using petroleum ether and ethyl acetate as the eluent and methyl (*L*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-(phenylethynyl)phenyl)propanoate (**S38**) was obtained as a pale yellow solid (1.2 g, 79%).

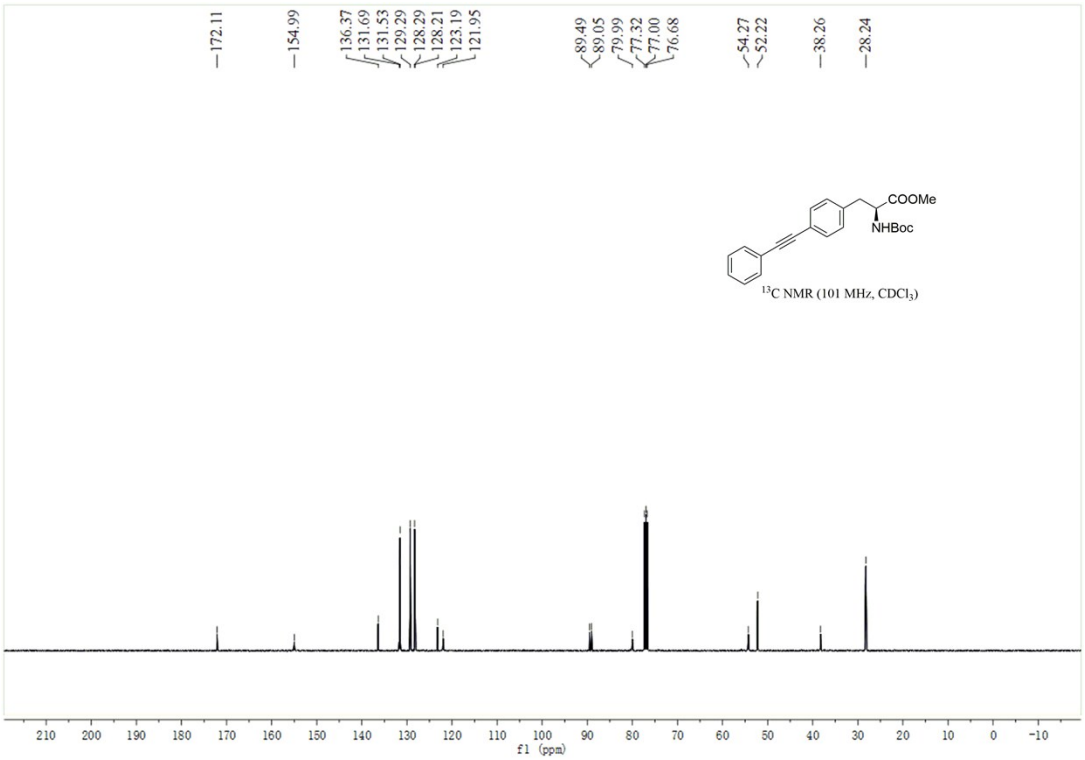
methyl (*L*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate (**B**): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 5.01 (d, *J* = 7.6 Hz, 1H), 4.55 (dd, *J* = 13.1, 6.0 Hz, 1H), 3.70 (s, 3H), 3.06 (dd, *J* = 13.7, 5.6 Hz, 1H), 2.96 (dd, *J* = 13.7, 6.0 Hz, 1H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.96, 154.93, 137.51, 135.70, 131.24, 92.42, 79.99, 54.13, 52.23, 37.83, 28.21. The spectroscopic characteristics match those reported in the literature.[4]





methyl (*L*)-2-((tert-butoxycarbonyl)amino)-3-(4-(phenylethynyl)phenyl)propanoate (S38): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.0, 2.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.34 (dd, *J* = 5.1, 1.8 Hz, 3H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.02 (d, *J* = 7.8 Hz, 1H), 4.59 (d, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 3.14 (dd, *J* = 13.7, 5.7 Hz, 1H), 3.05 (dd, *J* = 13.7, 6.1 Hz, 1H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.11, 154.99, 136.37, 131.69, 131.53, 129.29, 128.29, 128.21, 123.19, 121.95, 89.49, 89.05, 79.99, 54.27, 52.22, 38.26, 28.24. **HRMS** (ESI) Calcd for $C_{23}H_{26}NO_4$ $[M+H]^+$: 380.1856; **Found**: 380.1853.

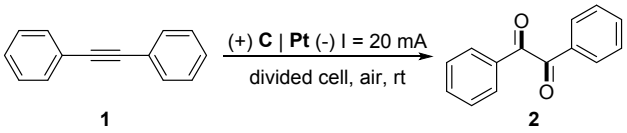




III. General Procedure

a. Optimization of Reaction Conditions

Table S1. Optimization of the reaction conditions.[a]

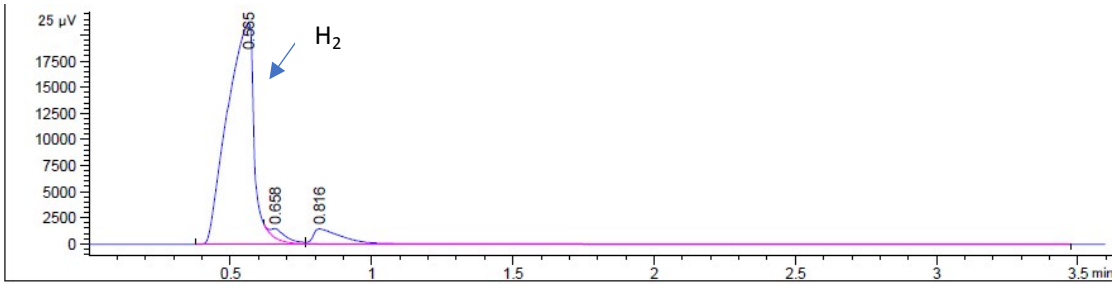


Entry	Variation from the standard conditions	Yield [%][b]
1	**None**	**87**
2	$LiClO_4$ instead of $NaBF_4$	83
3	nBu_4NPF_6 instead of $NaBF_4$	70
4	MeOH instead of DMF	16
5	MeCN instead of DMF	50
6	DMSO instead of DMF	43
7	Without HCO_2H	23
8	TFA instead of HCOOH	62
9	HOAc instead of HCOOH	24
10	O_2 atmosphere	77
11	N_2 atmosphere	Trace
12	10 mA instead of 20 mA, 16 h	61
13	30 mA instead of 20 mA, 5 h	40
14	RVC instead of graphite as anode	60
15	platinum instead of graphite as anode	10
16	graphite instead of platinum as cathode	80
17	No electric current	0

[a]Standard conditions: graphite plate anode (10 mm × 15 mm), **1** (0.3 mmol), $NaBF_4$ (1.0 mmol), DMF (9.0 mL), H_2O (1.0 mL), Platinum plate cathode (10 mm × 10mm), $NaBF_4$ (1.0 mmol), H_2O (9.0 mL), HCO_2H (1.0 mL) in H-type divided cell with an anion exchange membrane, constant current = 20.0 mA (j_{anode} = 13.3 mA/cm^{-2}), 20 F mol^{-1}, r. t., 8 h, [b]Isolated yield.

The cathodic reactions

The cathodic reaction was the formation of H_2 (65 mL, 2.9 mmol) which was identified by GC analysis. Also, the reaction mixture of the cathode was extracted with ether (3 × 10 mL), and 0.71 mL of formic acid was recovered. The consumption of formic acid was 0.29 mL (ca. 7.7 mmol).

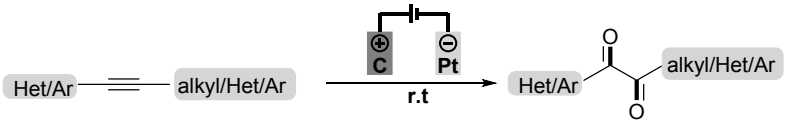


b. Electrolysis Reaction Set-ups

A **B** **C**

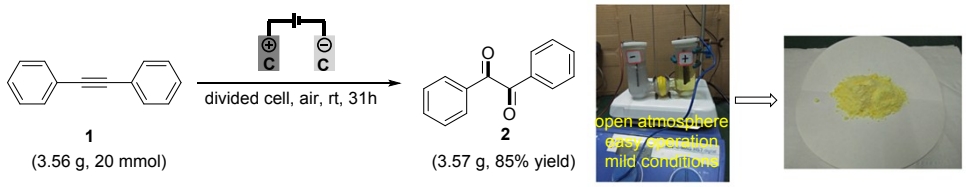
Figure S1. Electrolysis reaction set-ups. **A.** Graphite flat graphite anode and platinum plate cathode; **B.** A device of divided cell; **C.** 0.30 mmol scale reactione.

c. General Procedure for Electrochemical Oxidation of Alkynes



The electrolysis was carried out in an H-type divided cell equipped with stir bars at anode and cathode, respectively. Graphite plate (10 mm × 15 mm) was used as the anode and platinum plate (10 mm × 10 mm) was used as the cathode, which were separated by an anion exchange membrane. The anodic chamber was added with alkyne substrates (0.30 mmol), $NaBF_4$ (108 mg, 1.0 mmol), DMF (9.0 mL) and H_2O (1.0 mL). $NaBF_4$ (108 mg, 1.0 mmol), H_2O (9.0 mL), HCO_2H (1.0 mL) was added to the cathode chamber. Then electrolysis system was stirred at a constant current of 20.0 mA at rt for 8 or 24 h. At the end of the reaction, the reaction mixture of the anodic chamber was washed with water (10.0 mL) and extracted with ethyl acetate (3 × 10.0 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated. The pure product was obtained by flash column chromatography on silica gel (petroleum: ethyl acetate = 40:1).

IV. Larger Scale Reaction



In an 80 mL H-type divided cell equipped with stir bars at anode and cathode, respectively. The anodic chamber was added with substrate **1** (3.6 g, 20 mmol), $NaBF_4$ (6.7 g, 67 mmol), DMF (45 mL) and H_2O (5.0 mL). $NaBF_4$ solution (6.7 g, 67 mmol) H_2O (45 mL) and HCO_2H (5 mL) was added to the cathode chamber. The divided cell was equipped with graphite plate anode (40 mm × 30 mm) and graphite plate cathode (40 mm × 30 mm). Then electrolysis system was stirred at a constant current of 160 mA (j_{anode} = 13.3 mA cm^{-2}) at rt for 31 h. Upon completion (monitored by TLC analysis), the reaction mixture of the anodic chamber was washed with water (50.0 mL) and extracted with ethyl acetate (3 × 50.0 mL). The organic layers were washed with water, $NaHCO_3$ (aq.) and brine, dried over Na_2SO_4 and concentrated. The resulting crude product was then purified on silica gel eluting with ethyl acetate/petroleum ether to furnish the desired product **2**.

V. Mechanism Studies

a. Cyclic Voltammetry Experiments

Cyclic voltammograms were recorded with a CHI600D potentiostat at room temperature in MeCN. $LiClO_4$ (0.1 M) was used as the supporting electrolyte, and following analysis was performed with Origin 8.0 software. A glassy-carbon electrode (3.0 mm-diameter, disc-electrode) was used as the working electrode, a Pt wire as auxiliary electrode and a SCE electrode was used as the reference. The measurements were carried out at a scan rate of 100 mV s^{-1}.

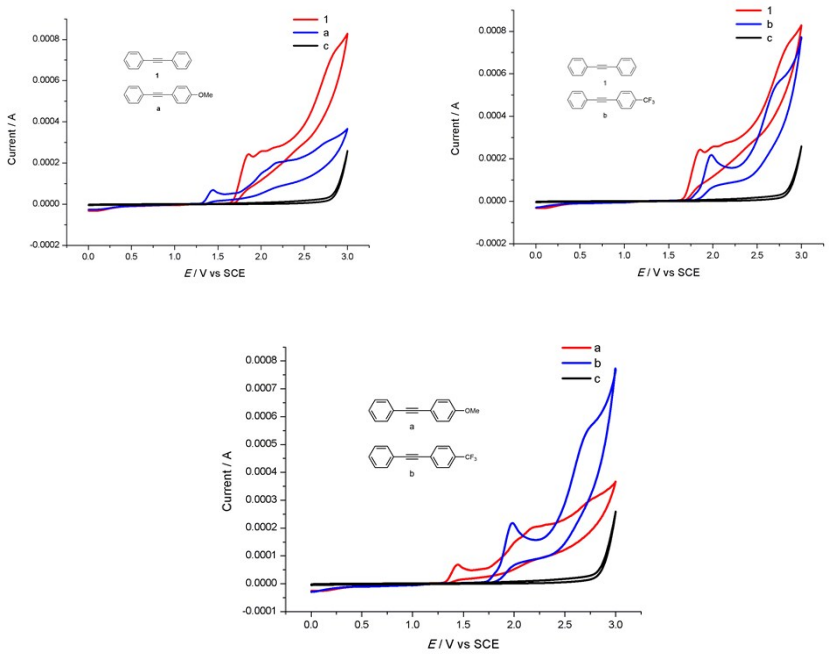
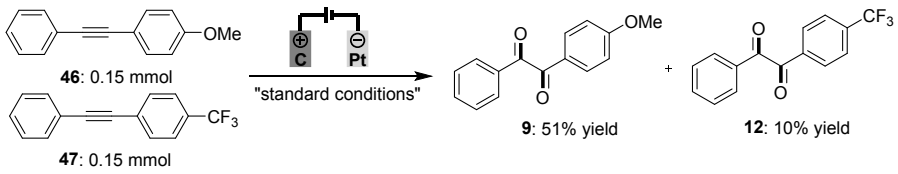
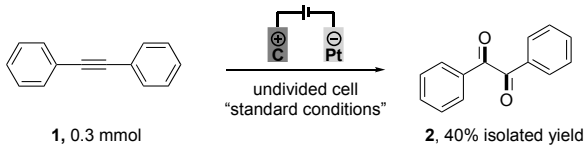


Figure S2. Cyclic voltammetry of **1** (0.3 mmol/L), **a** (0.3 mmol/L), and **b** (0.3 mmol/L) in CH_3CN with $LiClO_4$ (0.1 M) using a platinum-disk electrode working electrode, platinum wire and SCE as counter and reference electrodes at a scan rate of 100 mV s^{-1}.

b. Competitive Experiments

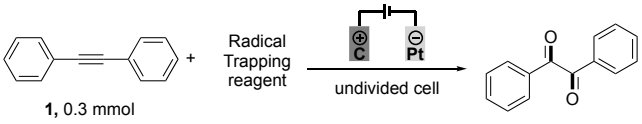


c. Radical Trapping Experiments



1, 0.3 mmol

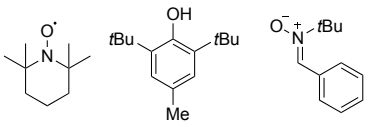
2, 40% isolated yield



1, 0.3 mmol

2

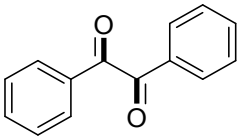
Entry	Radical Trapping reagent	GC yield of **2**
1	**TEMPO** (2. 0 or 3.0 equiv))	0%
2	**BHT** (2.0 equiv)	10%
3	**PBN**, 2.0 equiv	< 5%



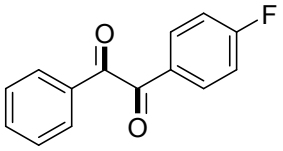
TEMPO **BHT** **PBN**

To a 25 mL undivided cell were sequentially added the substrate **1** (0.3 mmol), $NaBF_4$ (1.0 mmol), radical-trapping reagent (TEMPO, BHT or PBN) (0.3 mmol, 2 equiv), DMF (9.0 mL) and H_2O (1.0 mL). The cell was equipped with a graphite plate anode: (10 mm × 15 mm) and a platinum plate cathode: (10 mm × 10 mm). The electrolysis was carried out at rt using a constant current of 20 mA after 8 hours. It was found that the addition of the radical-trapping reagent inhibited the reaction. These results indicated that the reaction probably proceeded via a free radical process.

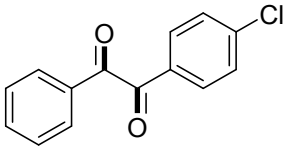
VI. Spectroscopic Data of Products



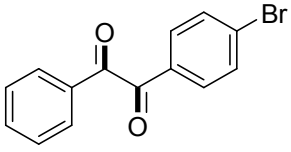
Benzil (2): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (54.8 mg, 87% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.67 – 7.63 (m, 1H), 7.50 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 194.52, 134.84, 132.88, 129.81, 128.96. The spectroscopic characteristics match those reported in the literature.[5]



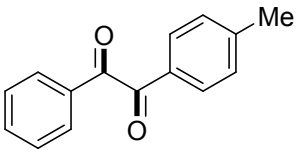
1-(4-fluorophenyl)-2-phenylethane-1,2-dione (3): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (69.1 mg, 80% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.04 – 7.99 (m, 2H), 7.97 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 8.6 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 194.05, 192.71, 167.60, 165.89, 135.00, 132.74 (t, *J* = 8.0 Hz), 129.91, 129.44 (d, *J* = 2.8 Hz), 129.03, 116.38 (d, *J* = 22.2 Hz). **^{19}F NMR** (564 MHz, $CDCl_3$): δ -101.21 (s, 1F). The spectroscopic characteristics match those reported in the literature.[5]



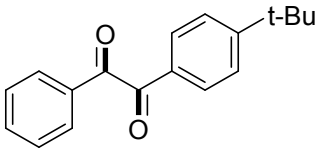
1-(4-chlorophenyl)-2-phenylethane-1,2-dione (4): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (46.1 mg, 63% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 193.83, 193.01, 141.54, 135.03, 132.69, 131.26, 131.17, 129.89, 129.39, 129.03. The spectroscopic characteristics match those reported in the literature.[5]



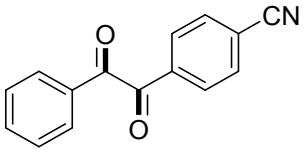
1-(4-bromophenyl)-2-phenylethane-1,2-dione (5): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (53.8 mg, 62% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.85 – 7.82 (m, 2H), 7.68 – 7.64 (m, 3H), 7.51 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 193.77, 193.20, 135.02, 132.69, 132.37, 131.66, 131.18, 130.44, 129.88, 129.02. The spectroscopic characteristics match those reported in the literature.[5]



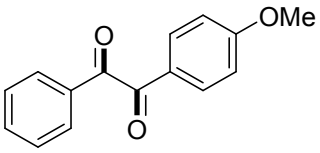
1-phenyl-2-(p-tolyl)ethane-1,2-dione (6): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (47.0 mg, 70% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.65 (td, *J* = 7.5, 0.9 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 194.73, 194.26, 146.19, 134.75, 133.02, 130.51, 129.97, 129.83, 129.70, 128.93, 21.89. The spectroscopic characteristics match those reported in the literature.[5]



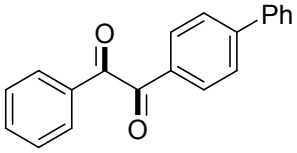
1-(4-(*tert*-butyl)phenyl)-2-phenylethane-1,2-dione (7): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (68.6 mg, 86% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.00 – 7.96 (m, 2H), 7.94 – 7.90 (m, 2H), 7.67 – 7.62 (m, 1H), 7.55 – 7.48 (m, 4H), 1.35 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 194.71, 194.23, 158.97, 134.70, 133.07, 133.07, 130.43, 129.84, 128.91, 125.99, 35.34, 30.92. The spectroscopic characteristics match those reported in the literature.[6]



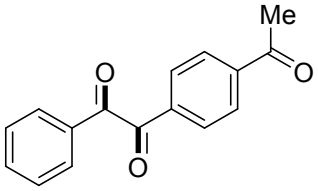
4-(2-oxo-2-phenylacetyl) benzonitrile (8): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (35.3 mg, 50% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 7.3 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 192.96, 192.36, 135.80, 135.37, 132.71, 132.36, 130.16, 129.98, 129.16, 117.83, 117.54. The spectroscopic characteristics match those reported in the literature.[5]



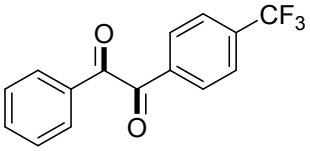
1-(4-methoxyphenyl)-2-phenylethane-1,2-dione (9): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (48.2 mg, 67% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 14.0, 8.3 Hz, 4H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 194.83, 193.14, 164.96, 134.70, 133.13, 132.36, 129.87, 128.92, 126.03, 114.33, 55.63. The spectroscopic characteristics match those reported in the literature.[5]



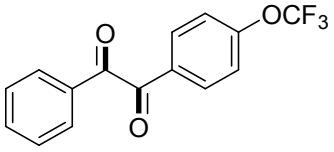
1-([1,1'-biphenyl]-4-yl)-2-phenylethane-1,2-dione (10): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (62.6 mg, 73% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.4 Hz, 2H), 8.02 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.49 (dd, *J* = 10.3, 4.7 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H).**^{13}C NMR** (151 MHz, $CDCl_3$): δ 194.49, 194.08, 147.52, 139.37, 134.84, 132.94, 131.59, 130.43, 129.88, 128.98, 128.97, 128.59, 127.58, 127.28. The spectroscopic characteristics match those reported in the literature.[2]



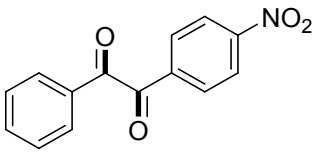
1-(4-acetylphenyl)-2-phenylethane-1,2-dione (11): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (53.7 mg, 71% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 0.5 Hz, 4H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.70 – 7.65 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 2.64 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 197.20, 193.70, 193.54, 141.22, 135.89, 135.13, 132.59, 130.04, 129.90, 129.07, 128.65, 26.92. The spectroscopic characteristics match those reported in the literature.[6]



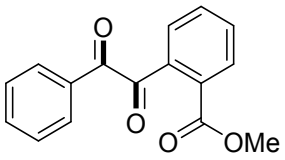
1-phenyl-2-(4-(trifluoromethyl) phenyl) ethane-1,2-dione (12): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (63.4 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 2H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 193.44, 193.00, 135.83 (q, *J* = 32.8 Hz), 135.61, 135.21, 132.60, 130.20, 129.96, 129.13, 126.02 (q, *J* = 3.6 Hz), 123.32 (q, *J* = 273.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.37 (s, 3F). The spectroscopic characteristics match those reported in the literature.[5]



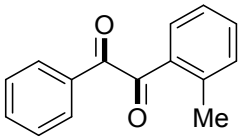
1-phenyl-2-(4-(trifluoromethoxy)phenyl)ethane-1,2-dione (13): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (62.6 mg, 71% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.06 – 8.03 (m, 2H), 7.99 – 7.96 (m, 2H), 7.67 (t, *J* = 6.4 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 193.75, 192.59, 153.80 (q, *J* = 1.7 Hz), 135.09, 132.68, 132.01,131.07, 129.92, 129.07, 120.60, 120.18 (q, *J* = 259.6 Hz). **^{19}F NMR** (564 MHz, $CDCl_3$): δ -57.60 (s, 3F). The spectroscopic characteristics match those reported in the literature.[7]



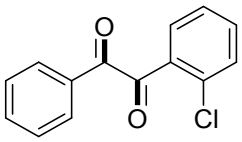
1-(4-nitrophenyl)-2-phenylethane-1,2-dione (14): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (39.0 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.39 – 8.32 (m, 2H), 8.21 – 8.14 (m, 2H), 8.03 – 7.95 (m, 2H), 7.71 (t, *J* = 6.2 Hz, 1H), 7.58 – 7.52 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 192.84, 192.06, 151.12, 137.25, 135.47, 132.32, 130.95, 130.04, 129.22, 124.11. The spectroscopic characteristics match those reported in the literature.[5]



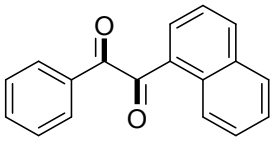
methyl 2-(2-oxo-2-phenylacetyl)benzoate (15): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (61.1 mg, 76% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.20 (d, *J* = 7.3 Hz, 2H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 5.2 Hz, 2H), 7.67 – 7.62 (m, 2H), 7.54 (t, *J* = 7.7 Hz, 2H), 3.66 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 193.54, 188.96, 166.81, 138.71, 133.80, 133.08, 132.92, 131.51, 130.73, 130.02, 129.63, 129.61, 128.38, 52.58. The spectroscopic characteristics match those reported in the literature.[8]



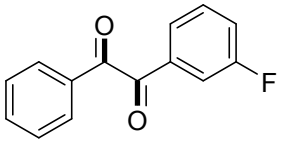
1-phenyl-2-(o-tolyl) ethane-1,2-dione (16): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (47.7 mg, 71% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.99 – 7.96 (m, 2H), 7.65 (t, *J* = 7.2 Hz, 2H), 7.50 (dt, *J* = 15.4, 7.6 Hz, 3H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.24 (m, 1H), 2.71 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 196.73, 194.78, 141.30, 134.65, 133.74, 133.06, 132.99, 132.51, 131.71, 129.86, 128.96, 125.97, 21.86. The spectroscopic characteristics match those reported in the literature.[5]



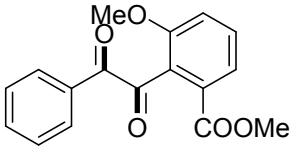
1-(2-chlorophenyl)-2-phenylethane-1,2-dione (17): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (52.7 mg, 72% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.53 (dd, *J* = 10.8, 4.4 Hz, 3H), 7.43 (t, *J* = 7.8 Hz, 2H).**^{13}C NMR** (151 MHz, $CDCl_3$): δ 193.61, 192.00, 134.53, 134.47, 133.93, 133.79, 132.38, 132.05, 130.46, 130.15, 128.84, 127.31. The spectroscopic characteristics match those reported in the literature.[6]



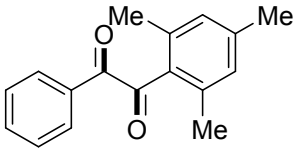
1-(naphthalen-1-yl)-2-phenylethane-1,2-dione (18): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (28.1 mg, 36% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 9.31 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 7.3 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.68 – 7.62 (m, 2H), 7.51 (dt, *J* = 17.6, 7.8 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 197.13, 194.56, 135.96, 135.09, 134.73, 134.05, 133.32, 130.91, 130.01, 129.45, 129.02, 128.77, 128.57, 127.11, 125.93, 124.41. The spectroscopic characteristics match those reported in the literature.[12]



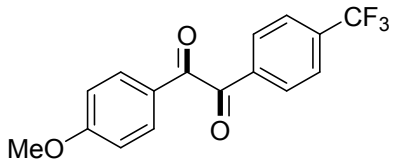
1-(3-fluorophenyl)-2-phenylethane-1,2-dione (19): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (47.9 mg, 70% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.75 – 7.64 (m, 3H), 7.50 (m, *J* = 13.3, 11.8, 6.6 Hz, 3H), 7.36 (td, *J* = 8.2, 1.8 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 193.66, 193.01, 163.61, 161.96, 135.08, 132.62, 130.77 (d, *J* = 7.6 Hz), 129.89, 129.05, 125.95 (d, *J* = 3.1 Hz), 121.97 (d, *J* = 21.5 Hz), 116.03 (d, *J* = 22.6 Hz). **^{19}F NMR** (564 MHz, $CDCl_3$): δ -110.57 (s, 1F). The spectroscopic characteristics match those reported in the literature.[5]



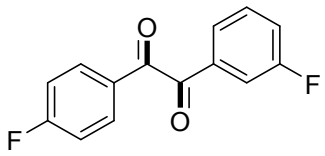
methyl 3-methoxy-2-(2-oxo-2-phenylacetyl)benzoate (20): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (61.7 mg, 69% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 2.3 Hz, 1H), 7.15 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.91 (s, 3H), 3.60 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 192.58, 189.93, 166.93, 162.58, 133.87, 133.14, 132.71, 130.54, 129.14, 128.45, 117.79, 114.91, 55.78, 52.61. **HRMS** (APCI) Calcd for $C_{17}H_{15}O_5$ $[M+H]^+$: 299.0914; found: 299.0913.



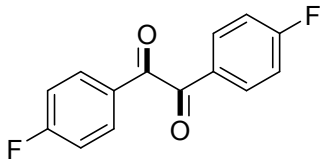
1-mesityl-2-phenylethane-1,2-dione (21): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (48.4 mg, 64% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.17 – 8.11 (m, 2H), 7.67 (dd, *J* = 11.7, 4.2 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 6.90 (s, 2H), 2.32 (s, 3H), 2.29 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 197.78, 191.60, 141.57, 137.38, 134.38, 133.05, 132.05, 130.40, 129.45, 128.87, 21.28, 20.82. The spectroscopic characteristics match those reported in the literature.[10]



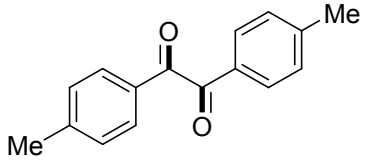
1-(4-methoxyphenyl)-2-(4-(trifluoromethyl) phenyl) ethane-1,2-dione (22): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (75.7 mg, 82% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.97 – 7.92 (m, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 193.25, 191.94, 165.24, 135.77, 135.60 (q, *J* = 32.8 Hz), 132.46, 130.17, 125.99 – 125.84 (m), 125.57, 123.31 (q, *J* = 272.9 Hz), 114.46, 55.65. **^{19}F NMR** (564 MHz, $CDCl_3$): δ -63.32 (s, 3F). The spectroscopic characteristics match those reported in the literature.[11]



1-(3-fluorophenyl)-2-(4-fluorophenyl)ethane-1,2-dione (23)： Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (53.8 mg, 73% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.01 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.49 (td, *J* = 7.9, 5.5 Hz, 1H), 7.36 (td, *J* = 8.2, 2.5 Hz, 1H), 7.19 (t, *J* = 8.5 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 192.49, 191.80, 166.86 (d, *J* = 258.6 Hz), 162.80 (d, *J* = 249.7 Hz), 134.74 (d, *J* = 6.4 Hz), 132.78 (d, *J* = 9.9 Hz), 130.81 (d, *J* = 7.6 Hz), 129.15 (d, *J* = 2.8 Hz), 125.98 (d, *J* = 3.0 Hz), 122.09 (d, *J* = 21.5 Hz), 116.45 (d, *J* = 22.3 Hz), 116.11 (d, *J* = 22.6 Hz). **^{19}F NMR** (564 MHz, $CDCl_3$): δ -100.75 (s, 1F), -110.49 (s, 1F). **HRMS** (APCI) Calcd for $C_{14}H_9F_2O_2$ $[M+H]^+$: 247.0565; found: 247.0564.

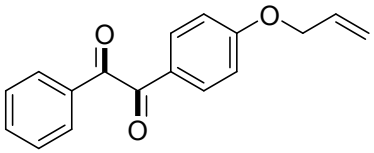


1,2-bis(4-fluorophenyl)ethane-1,2-dione (24): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (65.7 mg, 89% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.07 – 7.95 (m, 4H), 7.18 (t, *J* = 8.6 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 192.13, 166.84 (d, *J* = 258.4 Hz), 132.75 (d, *J* = 9.8 Hz), 129.43 (d, *J* = 2.9 Hz), 116.39 (d, *J* = 22.2 Hz). **^{19}F NMR** (564 MHz, $CDCl_3$): δ -101.08 (s, 2F). The spectroscopic characteristics match those reported in the literature.[5]

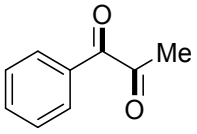


1,2-di-p-tolylethane-1,2-dione (25): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (44.9 mg, 63% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.2 Hz, 4H), 7.29 (d, *J* = 8.0 Hz, 4H), 2.42

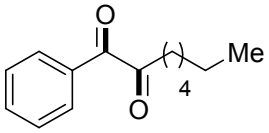
(s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 194.46, 146.04, 130.6, 129.94, 129.64, 21.87. The spectroscopic characteristics match those reported in the literature.[5]



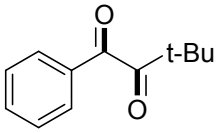
1-(4-(allyloxy)phenyl)-2-phenylethane-1,2-dione (26): Following the general procedure (*I* = 10.0 mA, the reaction time was 5 h), the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (38.3 mg, 48% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.99 – 7.95 (m, 2H), 7.95 – 7.92 (m, 2H), 7.65 (t, *J* = 6.9 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.03 (m, *J* = 10.6, 7.0, 5.3 Hz, 1H), 5.42 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.33 (dd, *J* = 10.5, 1.2 Hz, 1H), 4.62 (d, *J* = 5.3 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 194.84, 193.12, 163.91, 134.74, 133.03, 132.34, 132.00, 129.87, 128.92, 126.01, 118.49, 114.97, 69.00. The spectroscopic characteristics match those reported in the literature.[2]



1-phenylpropane-1,2-dione (27)： Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired product as a yellow oil (18.5 mg, 42% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.63 (dd, *J* = 10.9, 3.9 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 2.52 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 200.50, 191.34, 134.54, 131.71, 130.27, 128.80, 26.34. The spectroscopic characteristics match those reported in the literature.[12]

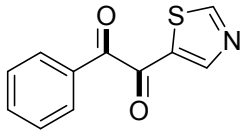


1-phenylpentane-1,2-dione (28)： Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired product as a yellow oil (26.3 mg, 50% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.96 (t, *J* = 8.7 Hz, 2H), 7.63 (dd, *J* = 11.1, 3.8 Hz, 1H), 7.49 (dd, *J* = 14.4, 6.7 Hz, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 1.72 – 1.66 (m, 2H), 1.37 (dd, *J* = 14.7, 7.1 Hz, 2H), 1.33 – 1.28 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 203.51, 192.56, 134.52, 131.97, 130.11, 128.81, 38.77, 31.47, 28.80, 22.80, 22.42, 13.98. The spectroscopic characteristics match those reported in the literature.[13]

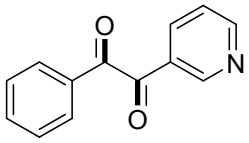


3,3-dimethyl-1-phenylbutane-1,2-dione (29)： Following the general procedure (*I* = 30.0 mA, the reaction time was 10 h), the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to

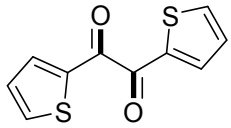
give the desired product as a yellow oil (31.8 mg,56% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 1.30 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 210.80, 195.39, 134.49, 132.84, 129.44, 128.89, 42.62, 26.23. The spectroscopic characteristics match those reported in the literature.[14]



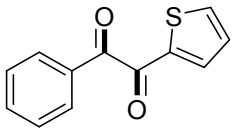
1-phenyl-2-(thiazol-5-yl) ethane-1,2-dione (30): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 10:1) to give the desired product as a yellow solid (29.8 mg, 46% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.61 (s, 1H), 8.08 (d, *J* = 7.3 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 190.43, 184.42, 161.10, 151.53, 135.18, 132.08, 130.44, 129.00. **HRMS** (ESI) Calcd for $C_{11}H_8NO_2S$ $[M+H]^+$: 218.0270; found: 218.0272.



1-phenyl-2-(pyridin-3-yl) ethane-1,2-dione (31): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 10:1) to give the desired product as a yellow solid (25.3 mg, 40% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 9.16 (s, 1H), 8.86 (d, *J* = 3.4 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.72 – 7.65 (m, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.48 (dd, *J* = 7.8, 4.8 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 192.86, 192.70, 154.79, 151.30, 136.85, 135.25, 132.41, 130.02, 129.11, 128.65, 123.86. The spectroscopic characteristics match those reported in the literature.[15]

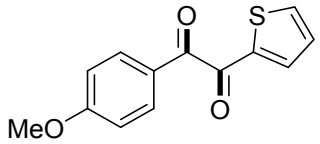


1,2-di(thiophen-2-yl)ethane-1,2-dione (32): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (35.3 mg, 53% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 3.8 Hz, 2H), 7.84 (d, *J* = 4.9 Hz, 2H), 7.20 (t, *J* = 4.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 182.37, 138.57, 137.45, 137.22, 128.63. The spectroscopic characteristics match those reported in the literature.[17]

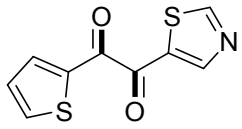


1-phenyl-2-(thiophen-2-yl)ethane-1,2-dione (33): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired product as a yellow solid (32.4 mg, 50% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.85 (dd, *J* = 4.8, 1.0 Hz, 1H), 7.80 (dd, *J* = 3.8, 0.9 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.19 (dd,

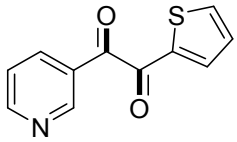
J = 4.8, 4.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 192.05, 185.58, 139.80, 136.90, 136.76, 134.87, 132.51, 130.19, 128.90, 128.80. The spectroscopic characteristics match those reported in the literature.[12]



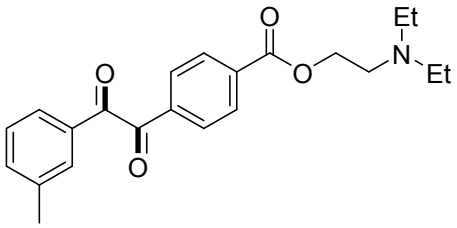
1-(4-methoxyphenyl)-2-(thiophen-2-yl) ethane-1,2-dione (34): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (37.5 mg, 51% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 4.8 Hz, 1H), 7.80 (d, *J* = 3.8 Hz, 1H), 7.17 (t, *J* = 4.4 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 1H), 3.88 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 190.62, 185.98, 164.98, 140.07, 136.56, 136.55, 132.72, 128.69, 125.59, 114.26, 55.62. The spectroscopic characteristics match those reported in the literature.[16]



1-(thiazol-5-yl)-2-(thiophen-2-yl)ethane-1,2-dione (35): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 5:1) to give the desired product as a yellow solid (30.0 mg, 45% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 9.13 (s, 1H), 8.86 (s, 1H), 8.18 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.89 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.23 (t, *J* = 4.4 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 181.73, 180.43, 161.69, 152.20, 138.38, 137.82, 137.53, 128.81. **HRMS** (ESI) Calcd for $C_9H_6NO_2S_2$ $[M+H]^+$: 223.9835; found: 223.9828.

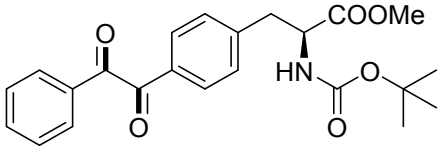


1-(pyridin-3-yl)-2-(thiophen-2-yl)ethane-1,2-dione (36): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 10:1) to give the desired product as a yellow solid (24.6 mg, 38% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 9.27 (s, 1H), 8.86 (d, *J* = 2.6 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 3.8 Hz, 1H), 7.88 (d, *J* = 4.9 Hz, 1H), 7.48 (dd, *J* = 7.8, 4.9 Hz, 1H), 7.22 (t, *J* = 4.4 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 190.15, 183.41, 154.60, 151.56, 139.05, 137.67, 137.42, 137.19, 128.94, 123.74. **HRMS** (ESI) Calcd for $C_{11}H_8NO_2S$ $[M+H]^+$: 218.0270; found: 218.0271.

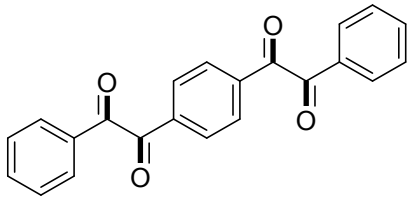


2-(diethylamino)ethyl 4-(2-oxo-2-(m-tolyl)acetyl)benzoate (37): Following the general procedure (*I* = 10.0 mA, CH_3CN instead of DMF, $LiClO_4$ instead of $NaBF_4$, the reaction time was 4 h), the resulting mixture was purified by flash chromatography (PE: EA:CH_2Cl_2 = 5:1:1) to give the desired

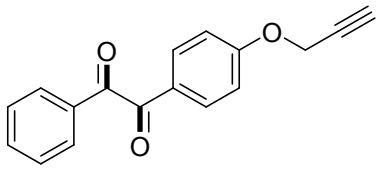
product as a yellow solid (0.2 mmol, 31.4 mg ,43% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.19 – 8.12 (m, 2H), 8.05 – 7.99 (m, 2H), 7.76 (d, *J* = 13.6 Hz, 2H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.41 (td, *J* = 7.6, 2.1 Hz, 1H), 4.48 – 4.42 (m, 2H), 2.91 – 2.87 (m, 2H), 2.69 – 2.63 (m, 4H), 2.41 (s, 3H), 1.08 (td, *J* = 7.1, 2.3 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 194.07, 193.80, 165.35, 139.10, 136.03, 136.00, 135.35, 132.64, 130.23, 130.07, 129.74, 128.98, 127.26, 63.75, 50.80, 47.68, 21.26, 11.77. **HRMS** (ESI) Calcd for $C_{22}H_{26}NO_4$ $[M+H]^+$: 368.1856; found: 368.1852.



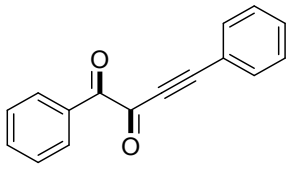
methyl2-((*tert*-butoxycarbonyl)amino)-3-(4-(2-oxo-2-phenylacetyl)phenyl)propanoate (38): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 5:1) to give the desired product as a yellow solid (93.6 mg, 76% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.98 – 7.90 (m, 2H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.60 (m, 1H), 7.50 – 7.45 (m, 2H), 7.29 – 7.25 (m, 2H), 5.09 (d, *J* = 6.8 Hz, 1H), 4.60 (d, *J* = 5.8 Hz, 1H), 3.69 (s, 3H), 3.21 (dd, *J* = 13.4, 4.9 Hz, 1H), 3.08 (dd, *J* = 13.1, 5.9 Hz, 1H), 1.37 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 194.35, 193.95, 171.68, 154.86, 144.01, 134.80, 132.82, 131.66, 129.97, 129.79, 128.91, 80.04, 54.01, 52.32, 38.41, 28.14. **HRMS** (ESI) Calcd for $C_{23}H_{25}NO_6Na$ $[M+Na]^+$: 434.1574; found: 434.1570.



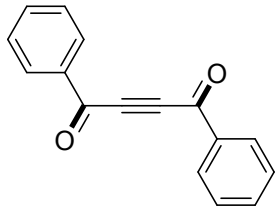
2,2'-(1,4-phenylene)bis(1-phenylethane-1,2-dione) (40): Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 30:1) to give the desired product as a yellow solid (69.8 mg, 68% yield).**^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.11 (s, 4H), 7.97 (d, *J* = 7.3 Hz, 4H), 7.69 (t, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 193.42, 193.26, 137.12, 135.26, 132.56, 130.25, 129.98, 129.15. The spectroscopic characteristics match those reported in the literature.[9]



1-phenyl-2-(4-(prop-2-yn-1-yloxy)phenyl)ethane-1,2-dione (42): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (52% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.99 – 7.94 (m, 4H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 4.77 (d, *J* = 2.4 Hz, 2H), 2.56 (t, *J* = 2.4 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 194.64, 193.04, 162.68, 134.72, 133.08, 132.24, 129.85, 128.92, 126.74, 115.17, 77.35, 76.46, 55.94. The spectroscopic characteristics match those reported in the literature.[2]



1,4-diphenylbut-3-yne-1,2-dione (44): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (11.0 mg, 15% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.11 – 8.07 (m, 2H), 7.70 – 7.63 (m, 3H), 7.57 – 7.48 (m, 3H), 7.41 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 188.42, 178.52, 134.87, 133.64, 131.66, 131.61, 130.50, 128.91, 128.73, 119.20, 99.14, 87.04. The spectroscopic characteristics match those reported in the literature.[6]



1,4-diphenylbut-2-yne-1,4-dione (45): Following the general procedure, the resulting mixture was purified by flash chromatography (PE: EA = 40:1) to give the desired product as a yellow solid (49.7 mg, 71% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.24 – 8.10 (m, 4H), 7.68 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 176.52, 135.80, 135.13, 129.78, 128.95, 85.84. The spectroscopic characteristics match those reported in the literature.[18]

VII. Reference

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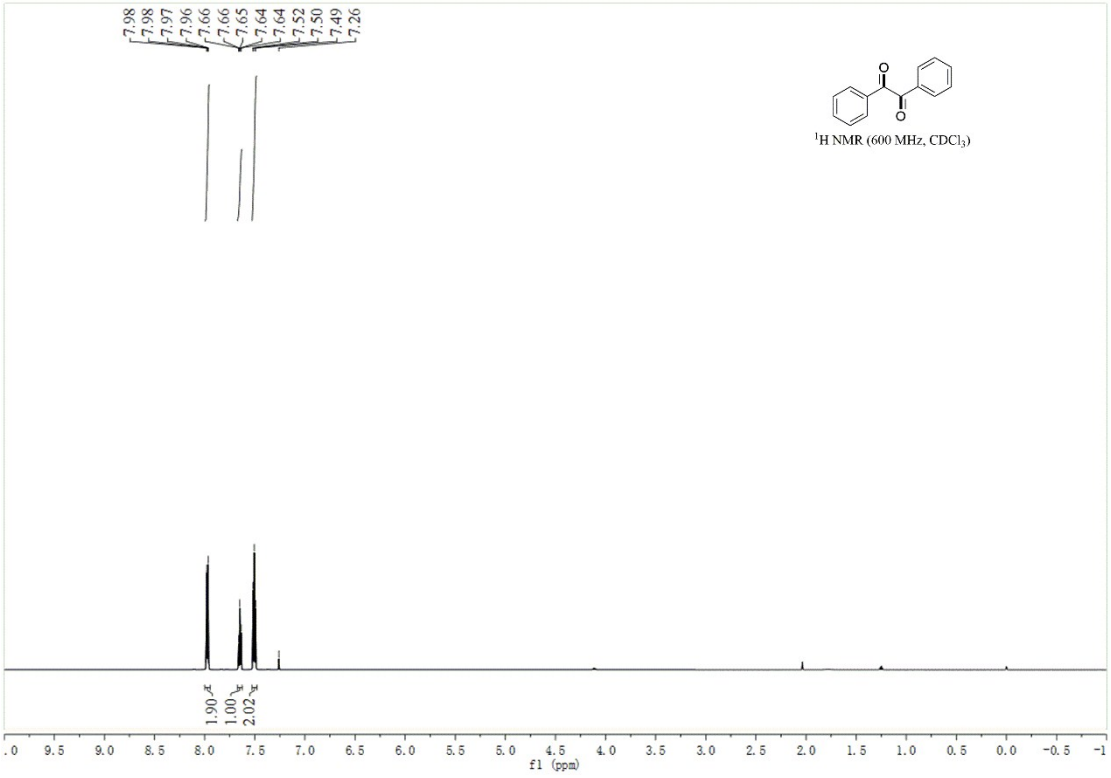
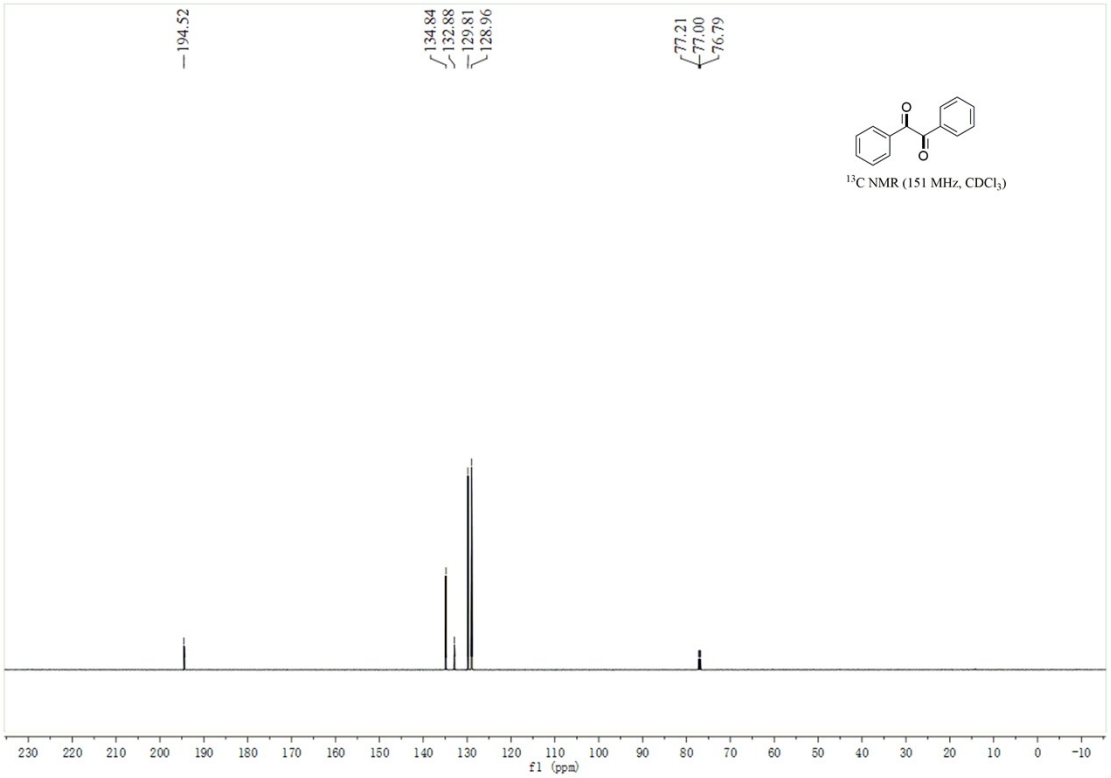
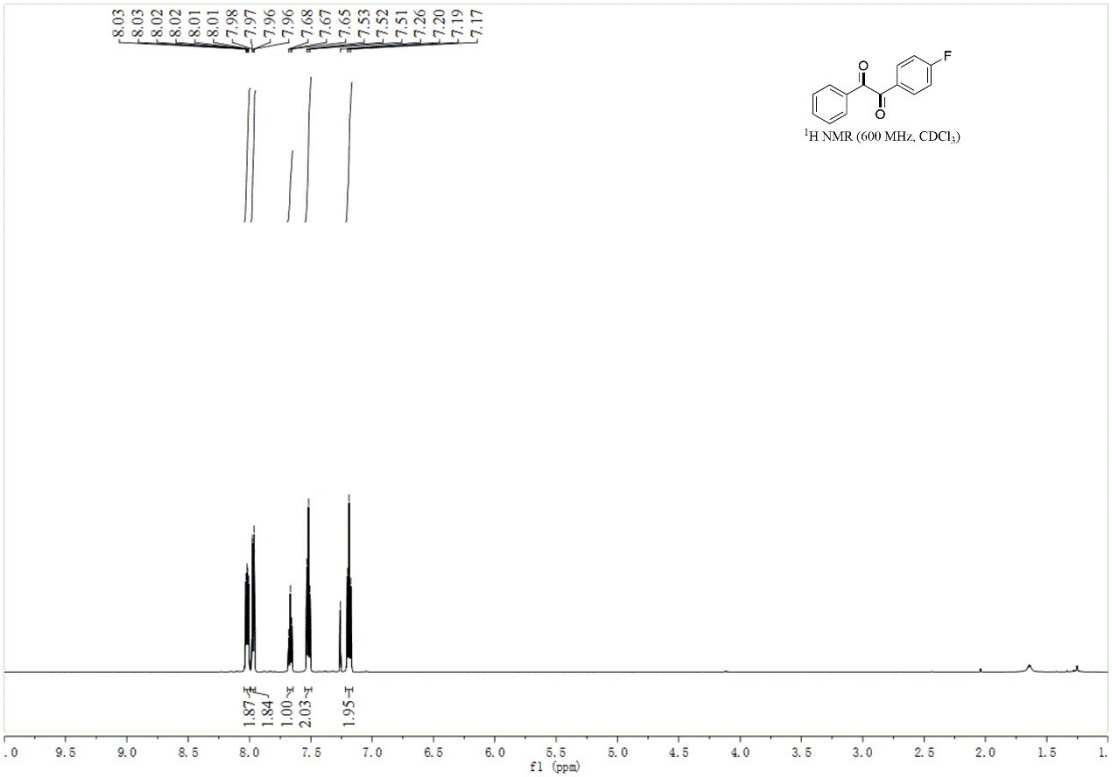
VIII. Copies of NMR Spectra

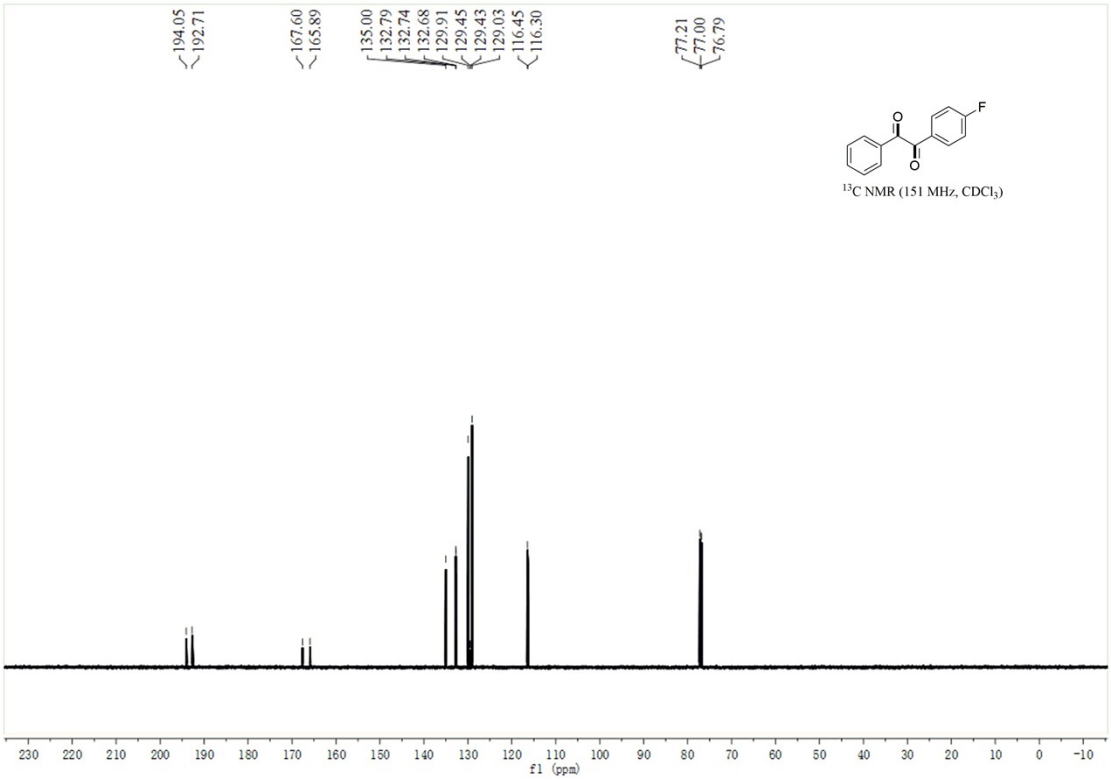
Benzil (2)

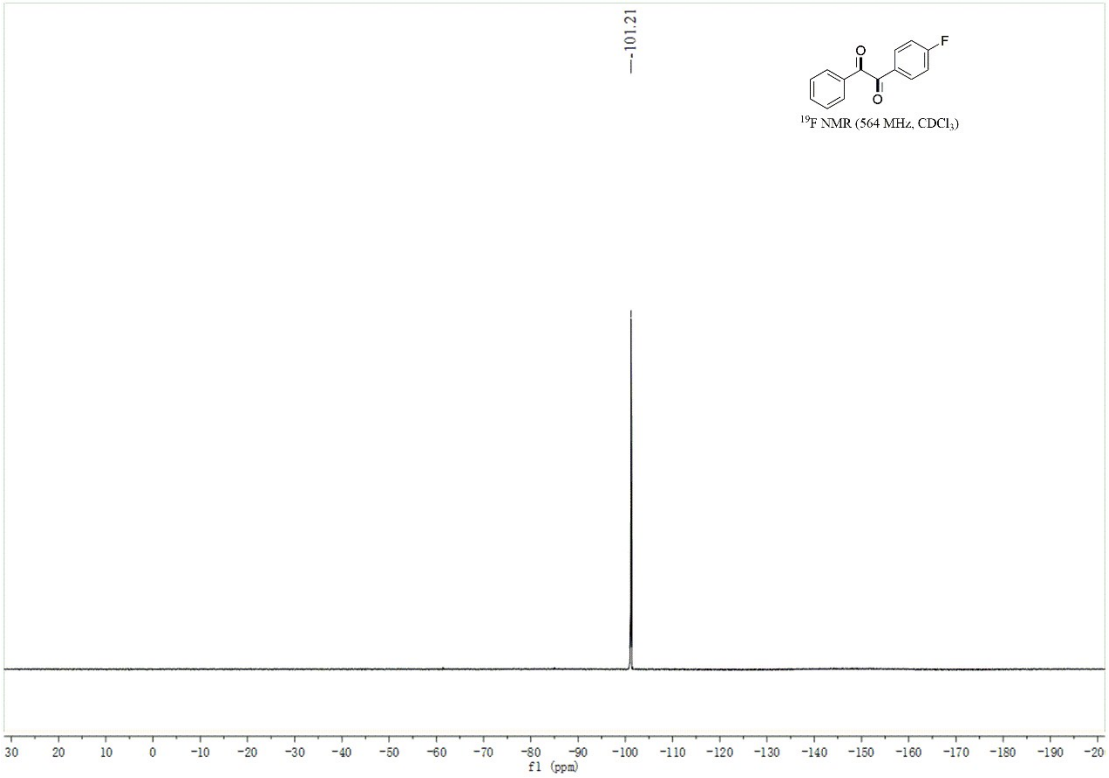




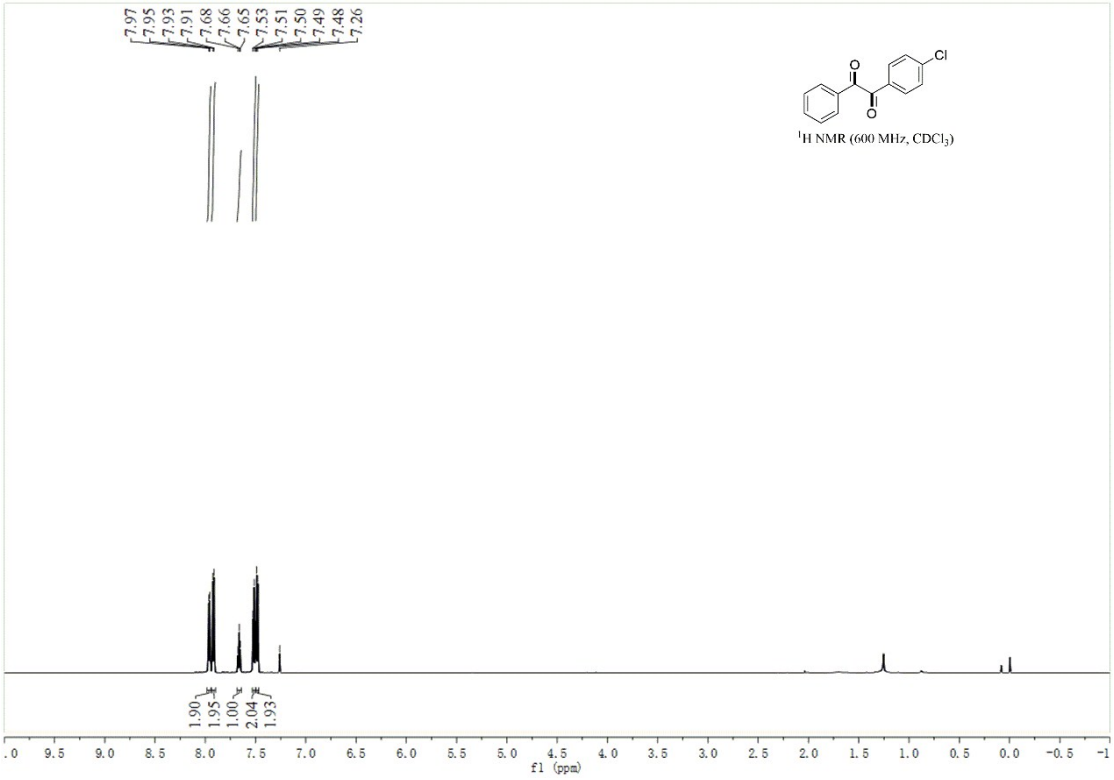
1-(4-fluorophenyl)-2-phenylethane-1,2-dione (3)

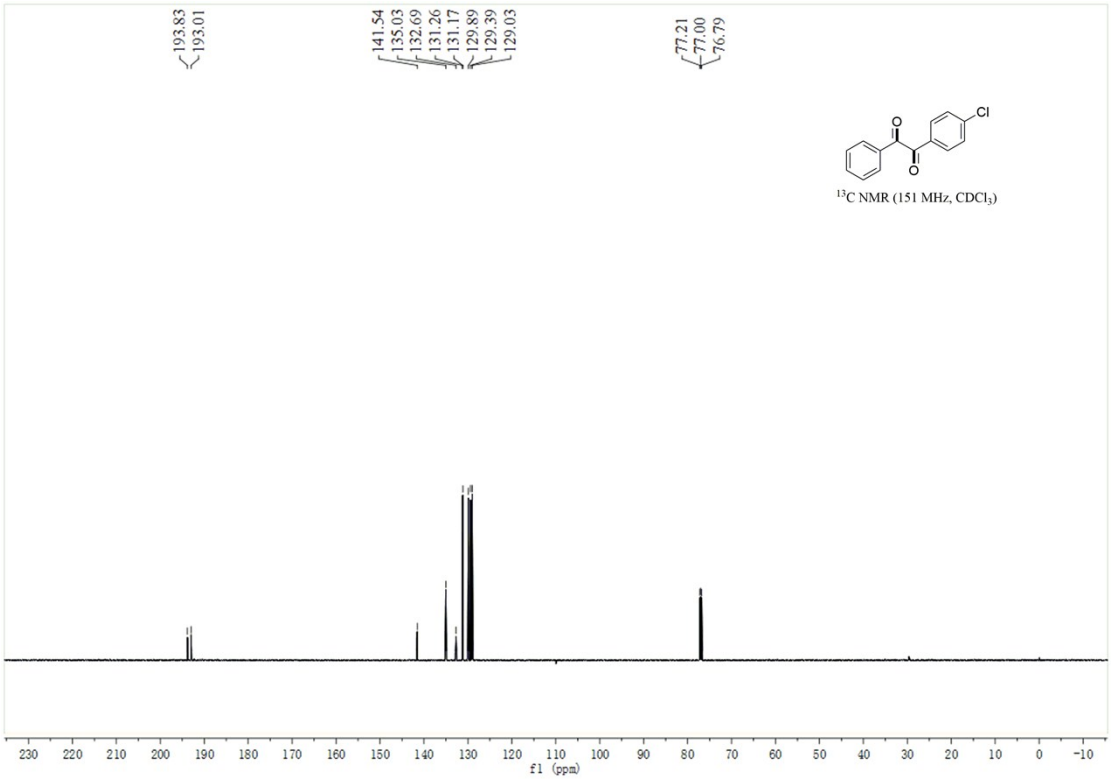




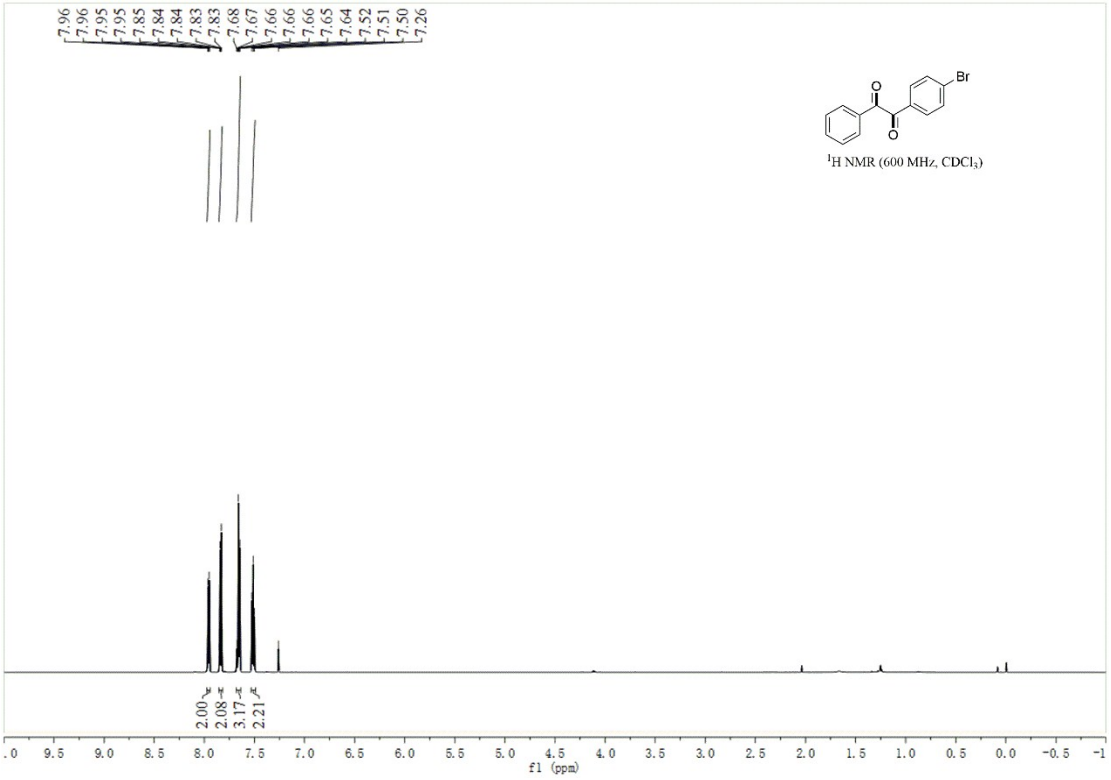

-101.21
F
O
O
^{19}F NMR (564 MHz, $CDCl_3$)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

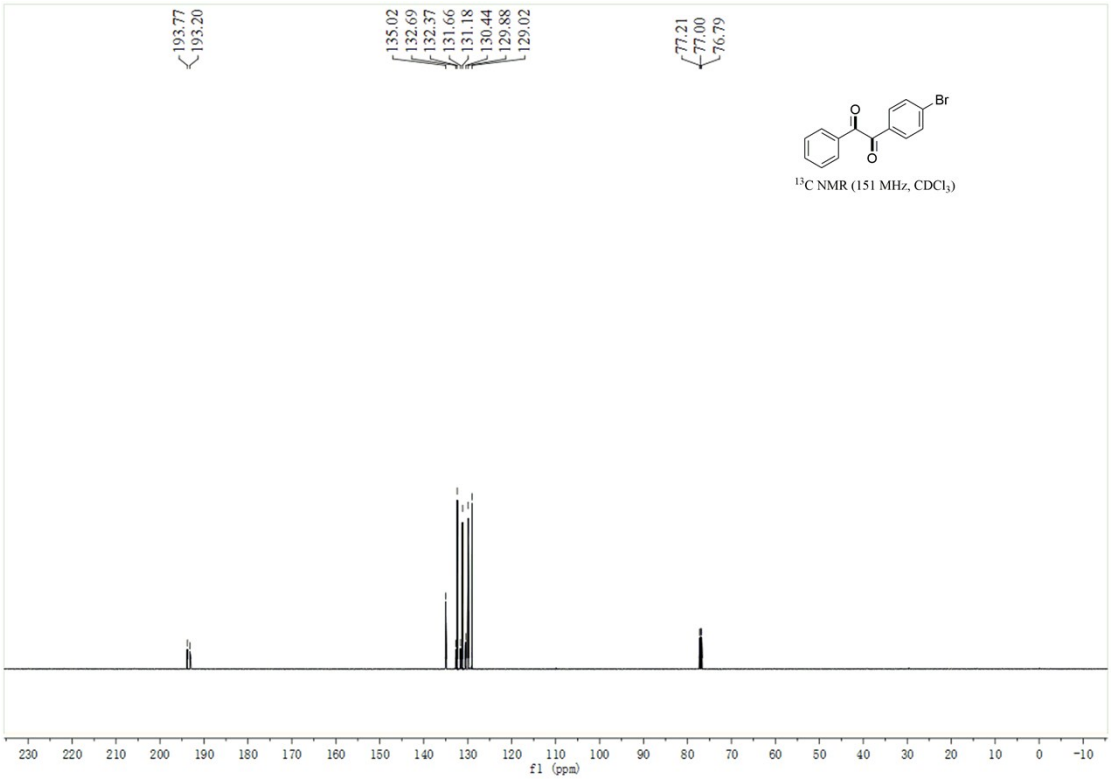
1-(4-chlorophenyl)-2-phenylethane-1,2-dione (4)



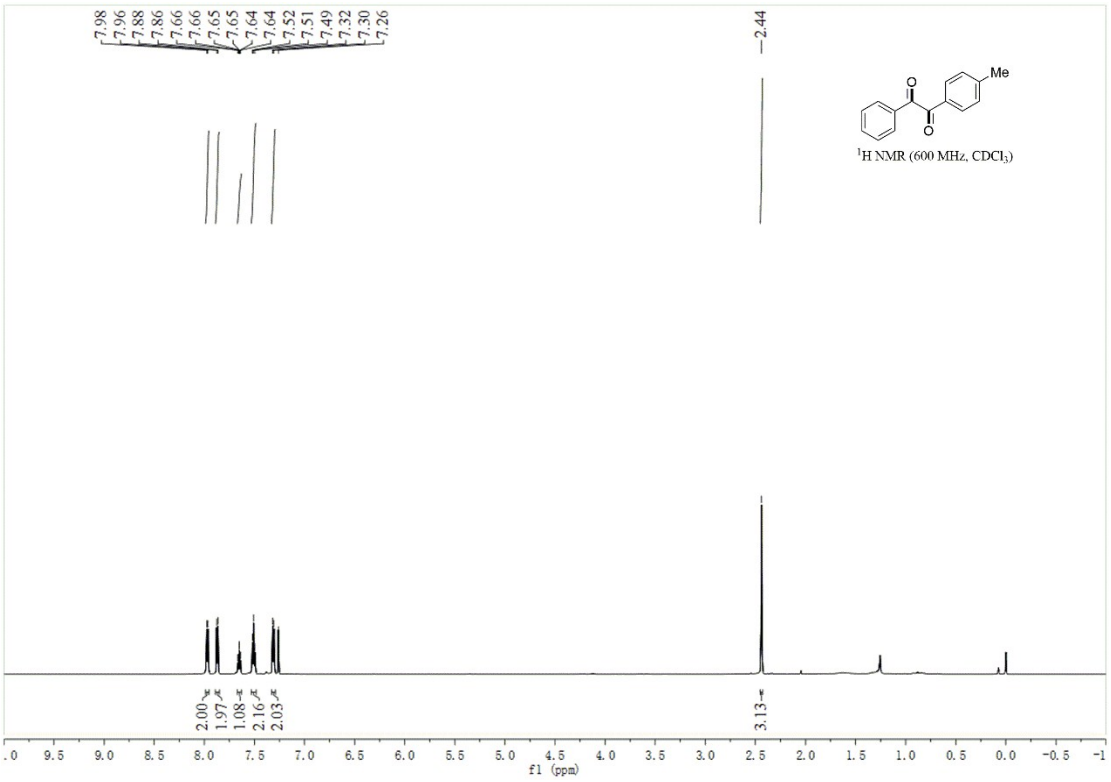


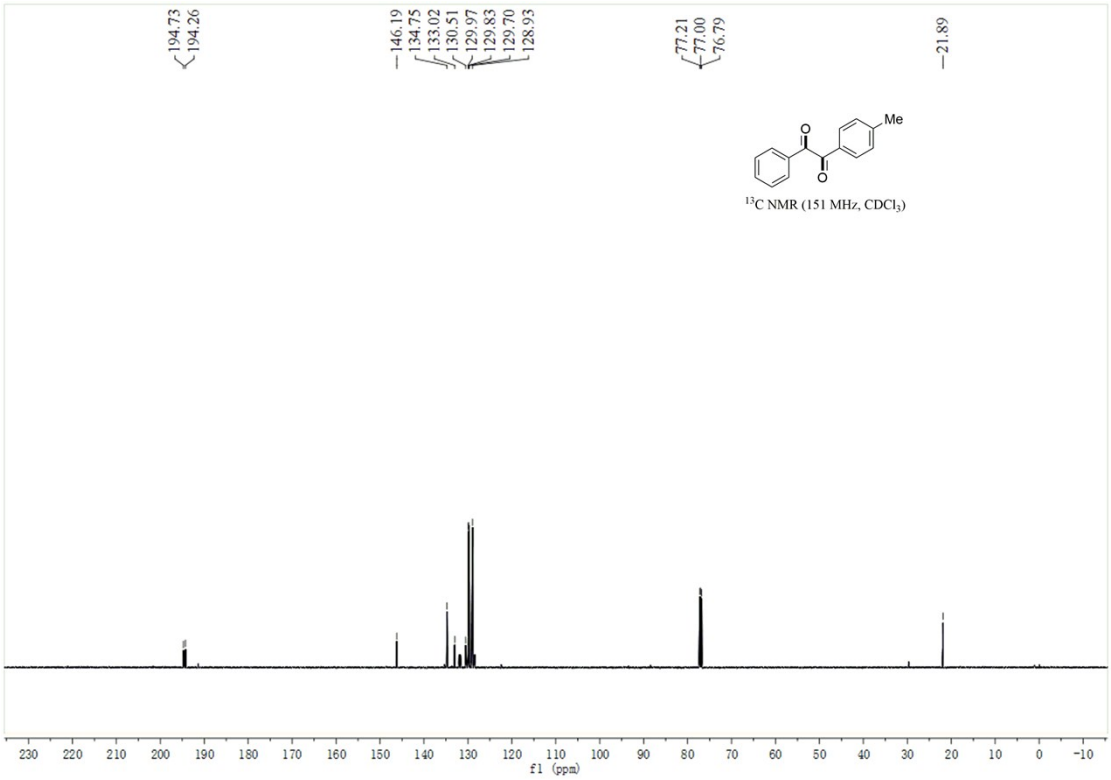
1-(4-bromophenyl)-2-phenylethane-1,2-dione (5)



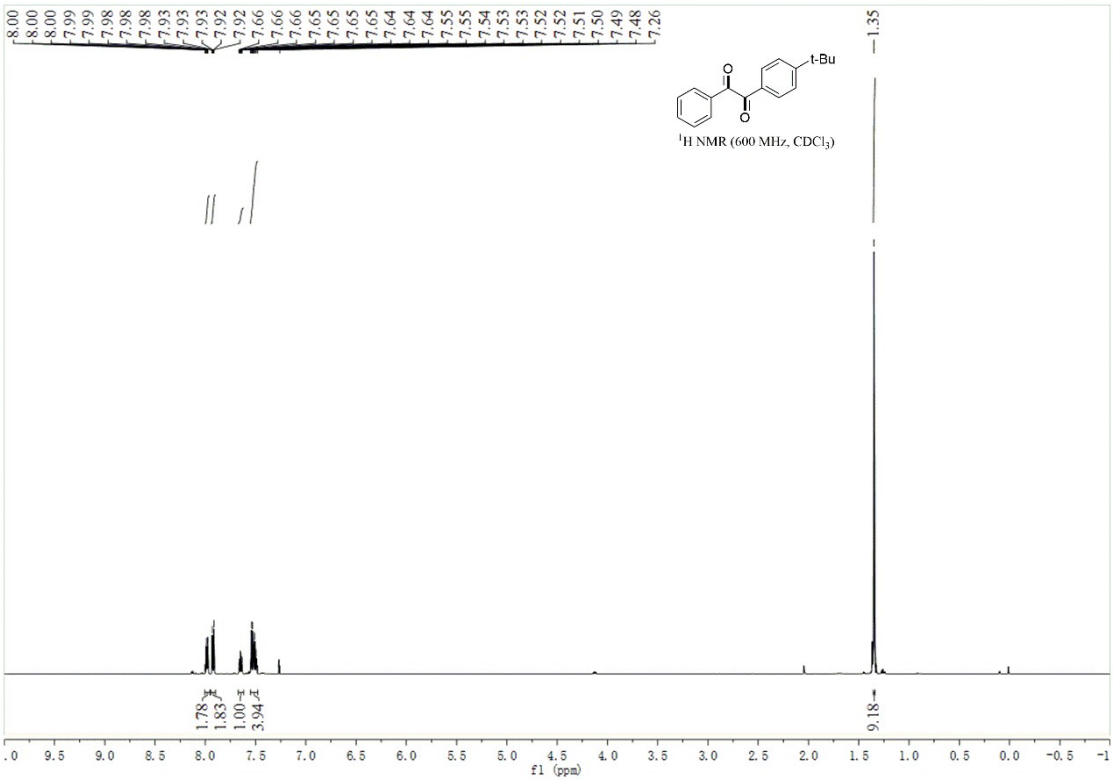


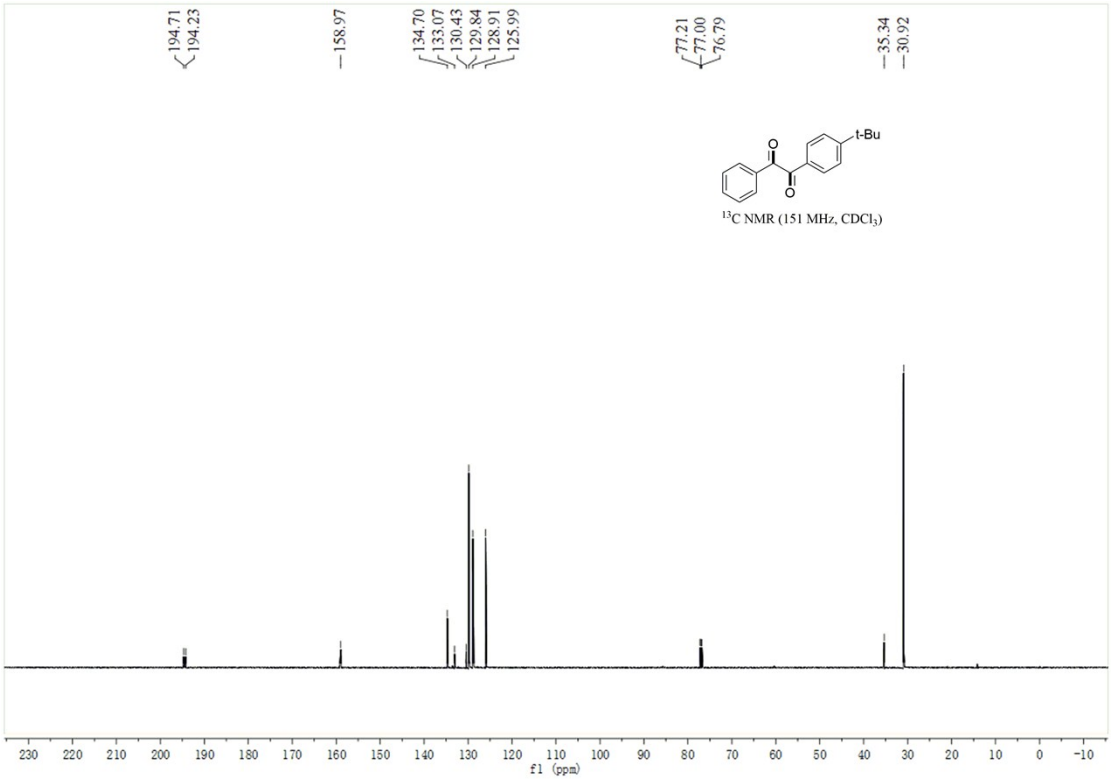
1-phenyl-2-(p-tolyl)ethane-1,2-dione (6)



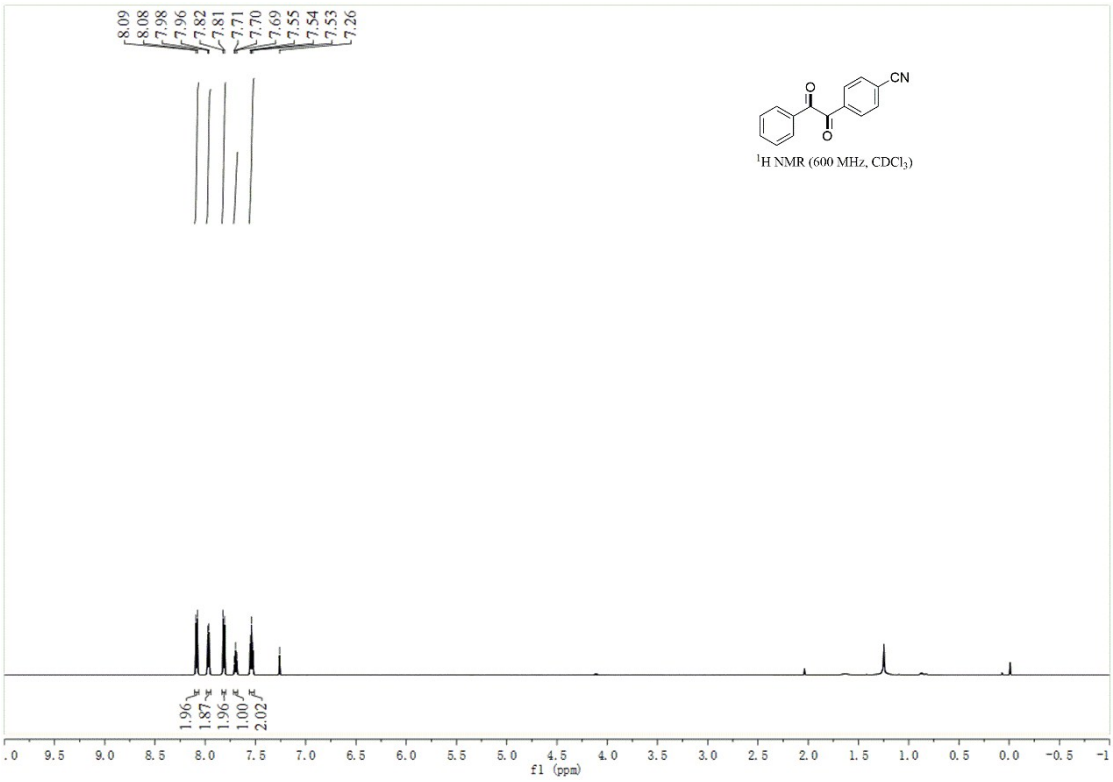


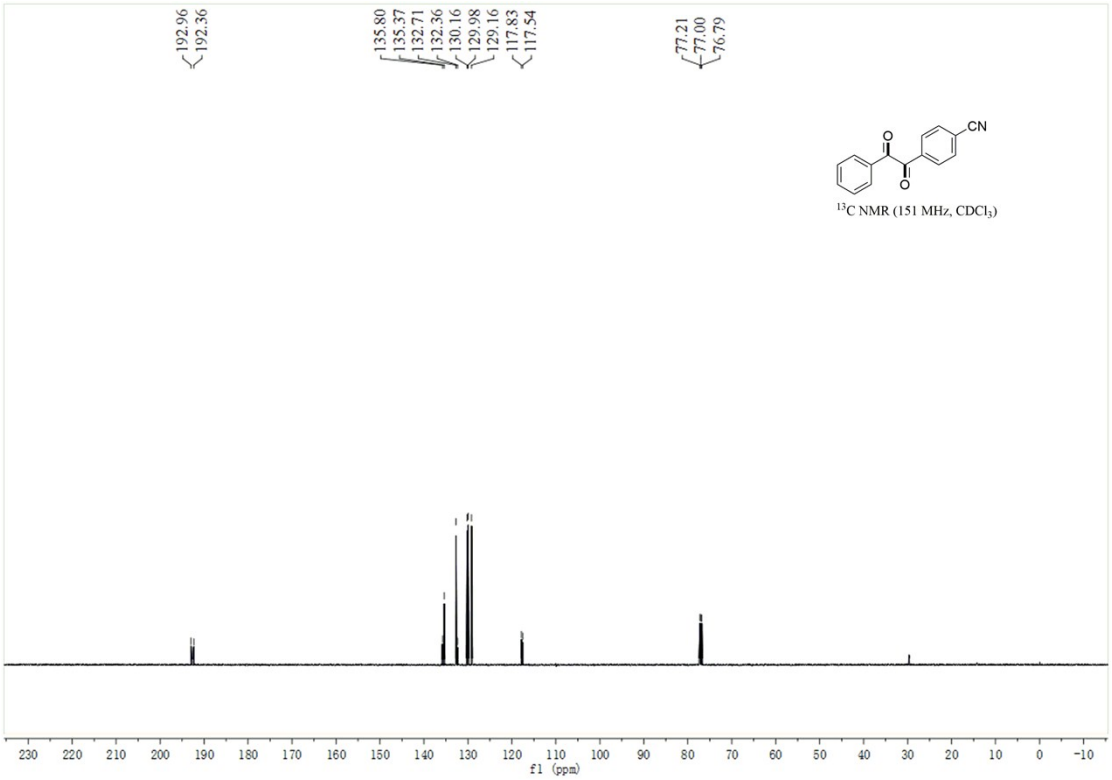
1-(4-(tert-butyl)phenyl)-2-phenylethane-1,2-dione (7)



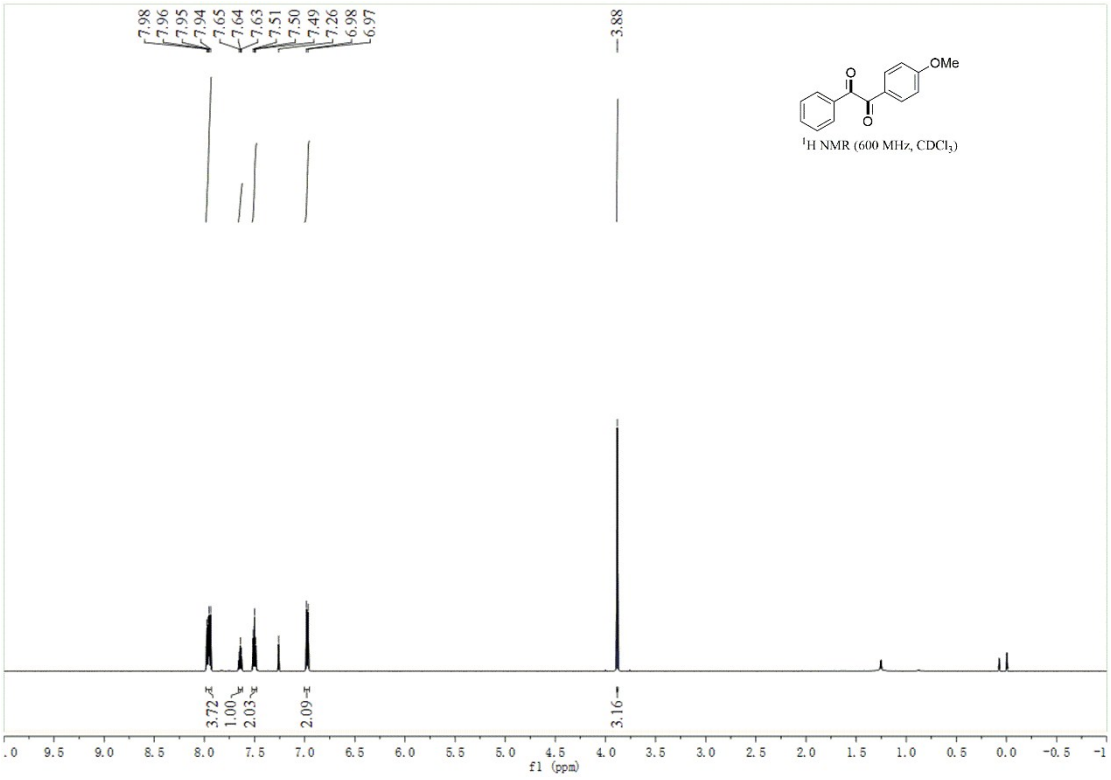


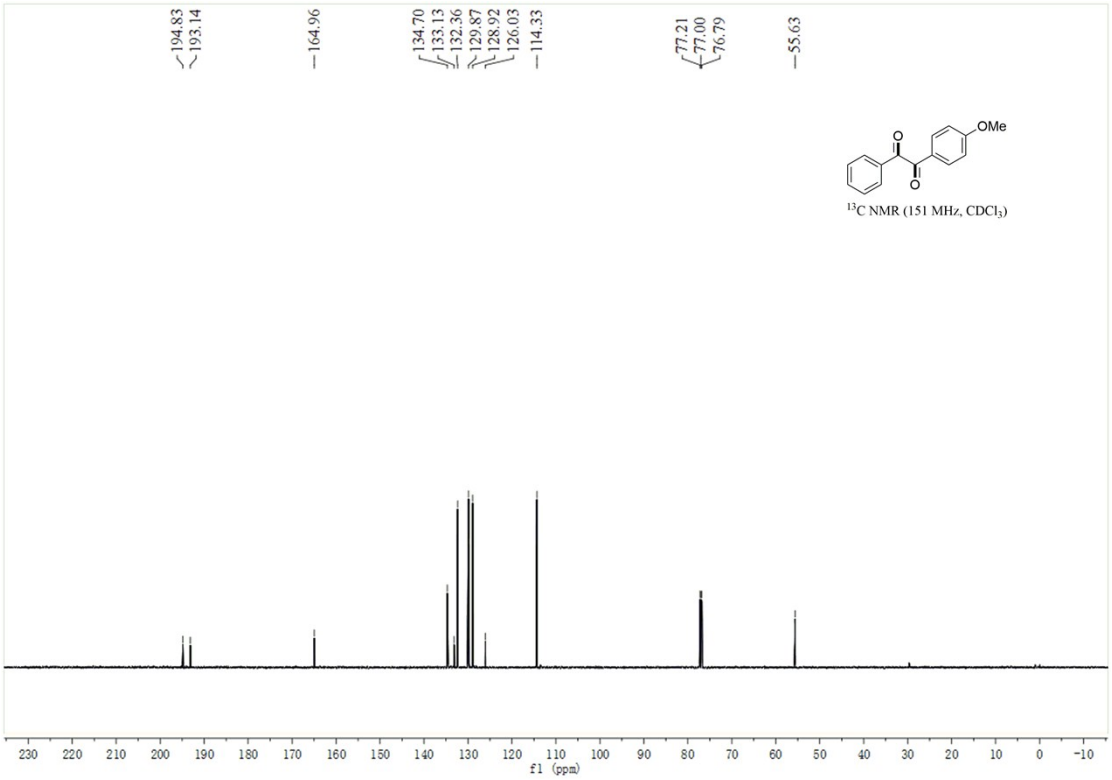
4-(2-oxo-2-phenylacetyl) benzonitrile (8)



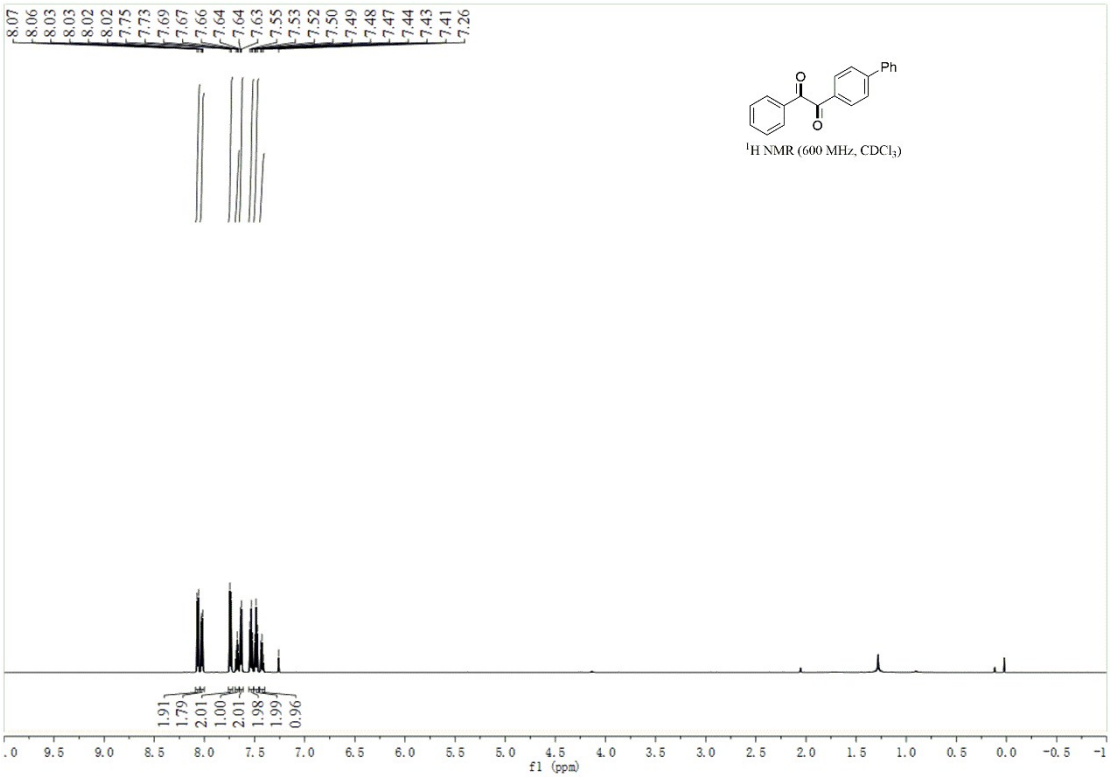


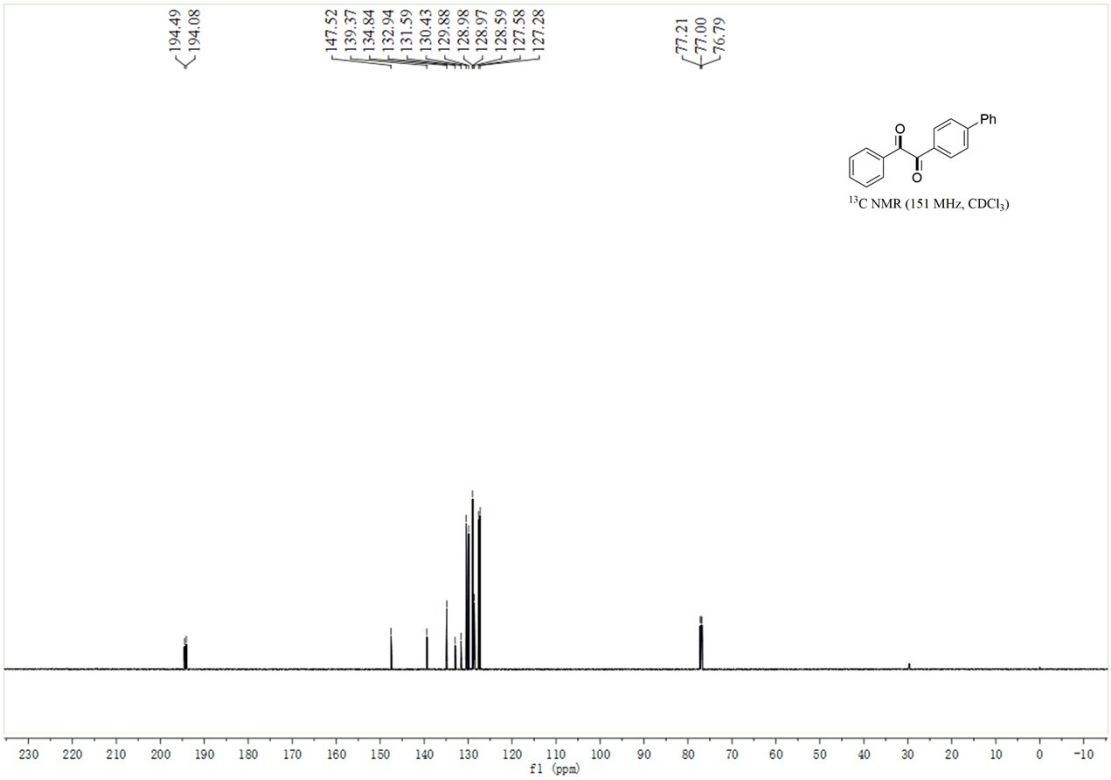
1-(4-methoxyphenyl)-2-phenylethane-1,2-dione (9)



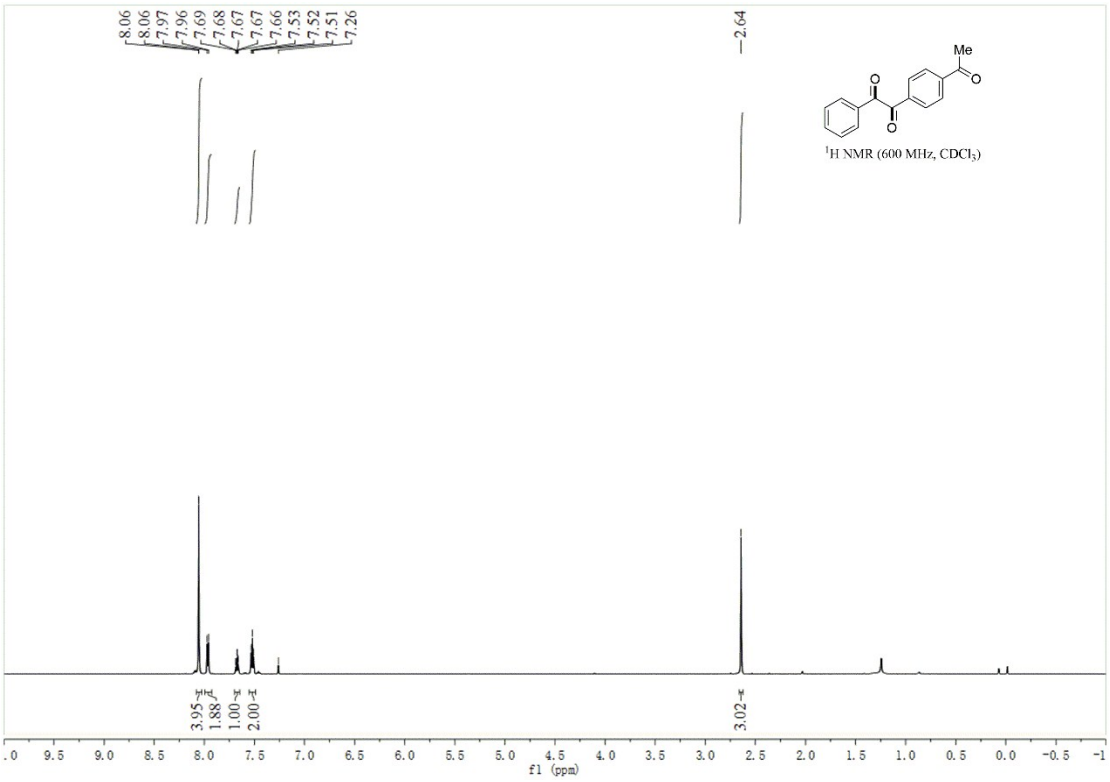


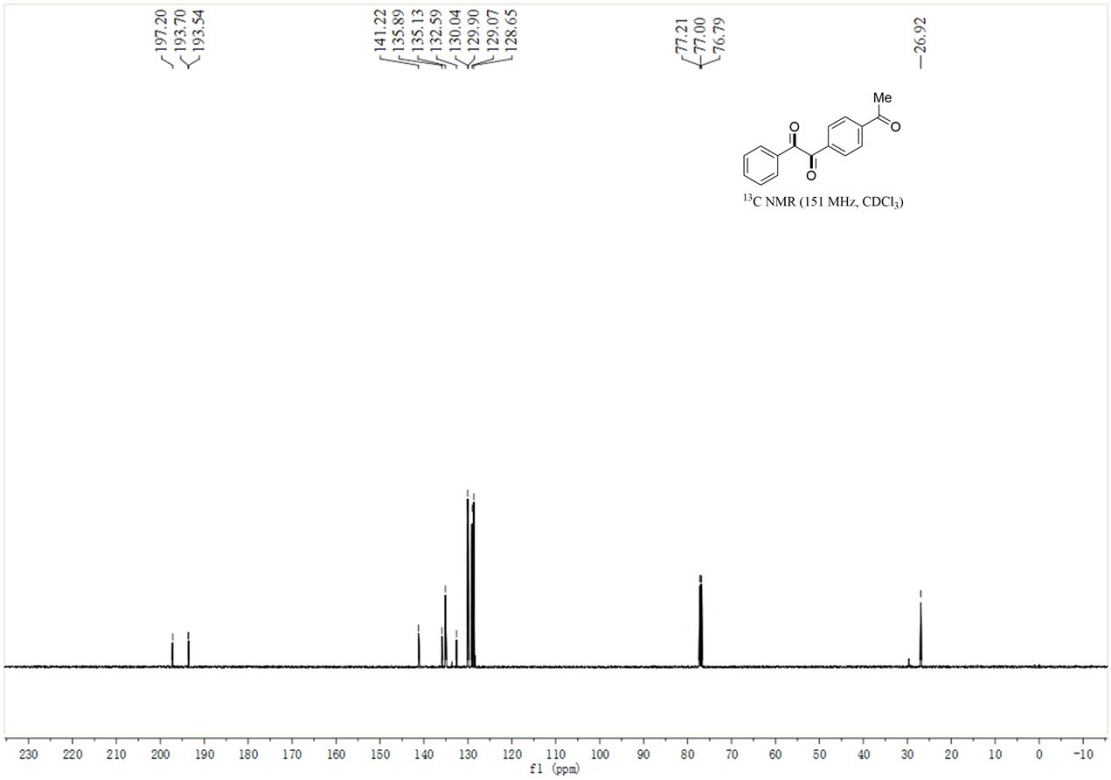
1-([1,1'-biphenyl]-4-yl)-2-phenylethane-1,2-dione (10)



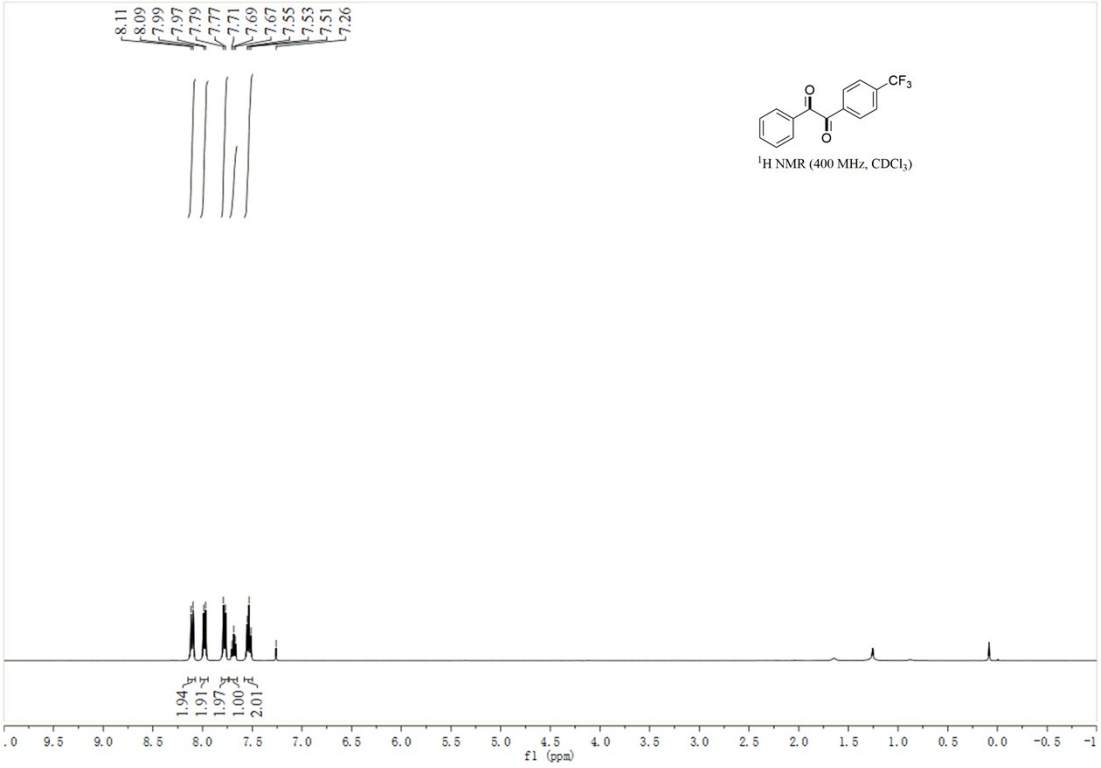


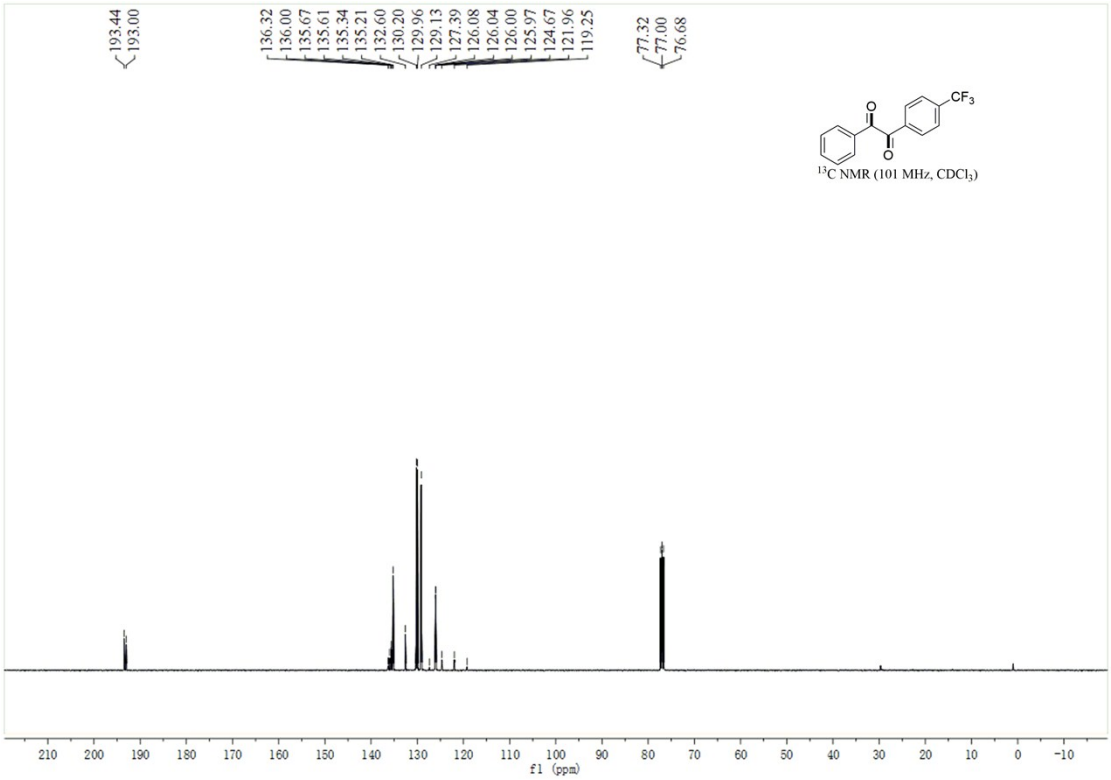
1-(4-acetylphenyl)-2-phenylethane-1,2-dione (11)

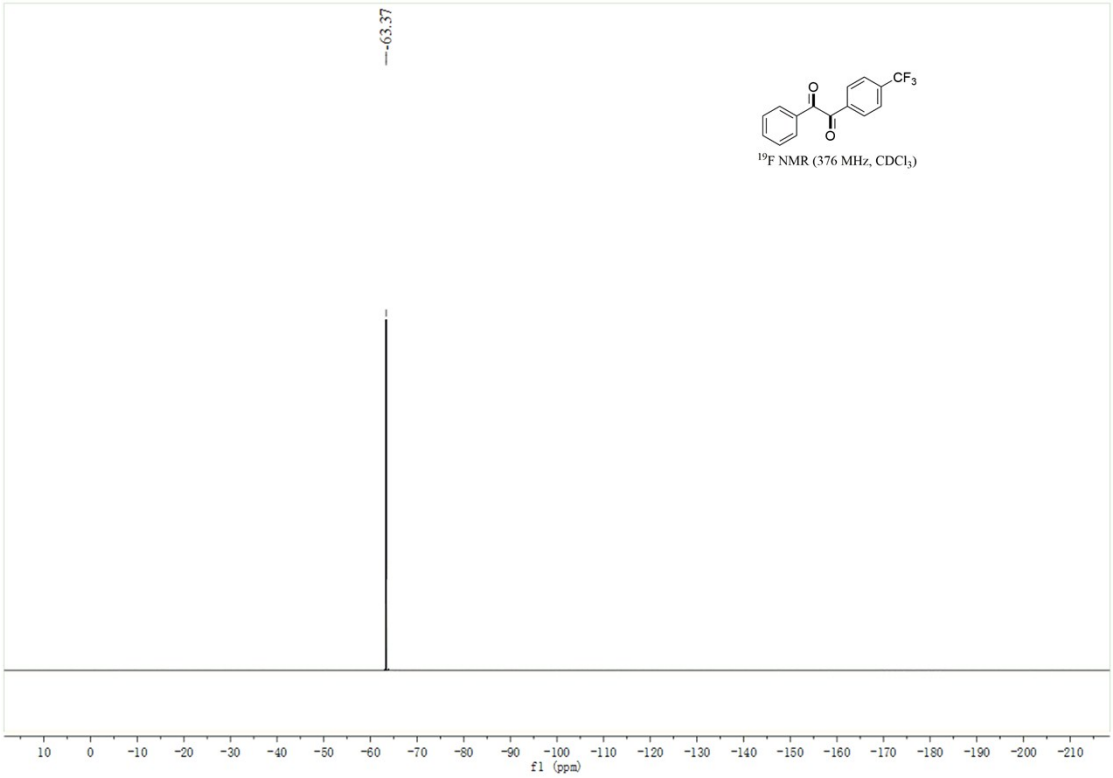




1-phenyl-2-(4-(trifluoromethyl) phenyl) ethane-1,2-dione (12)

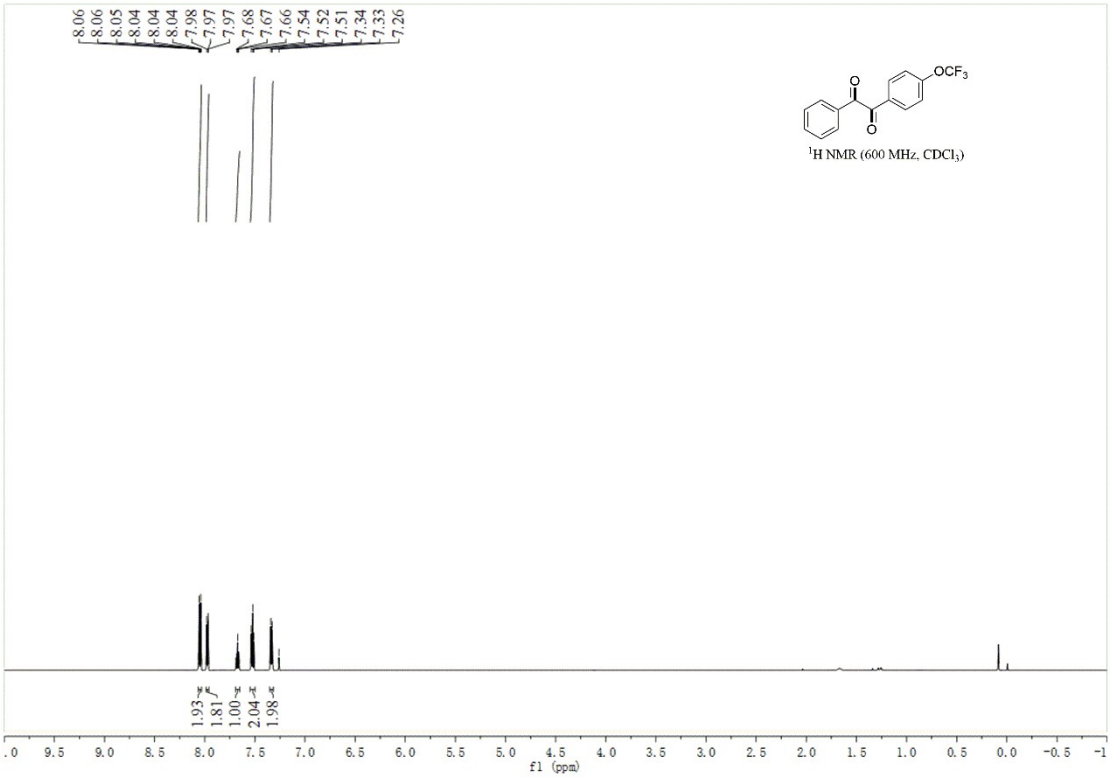


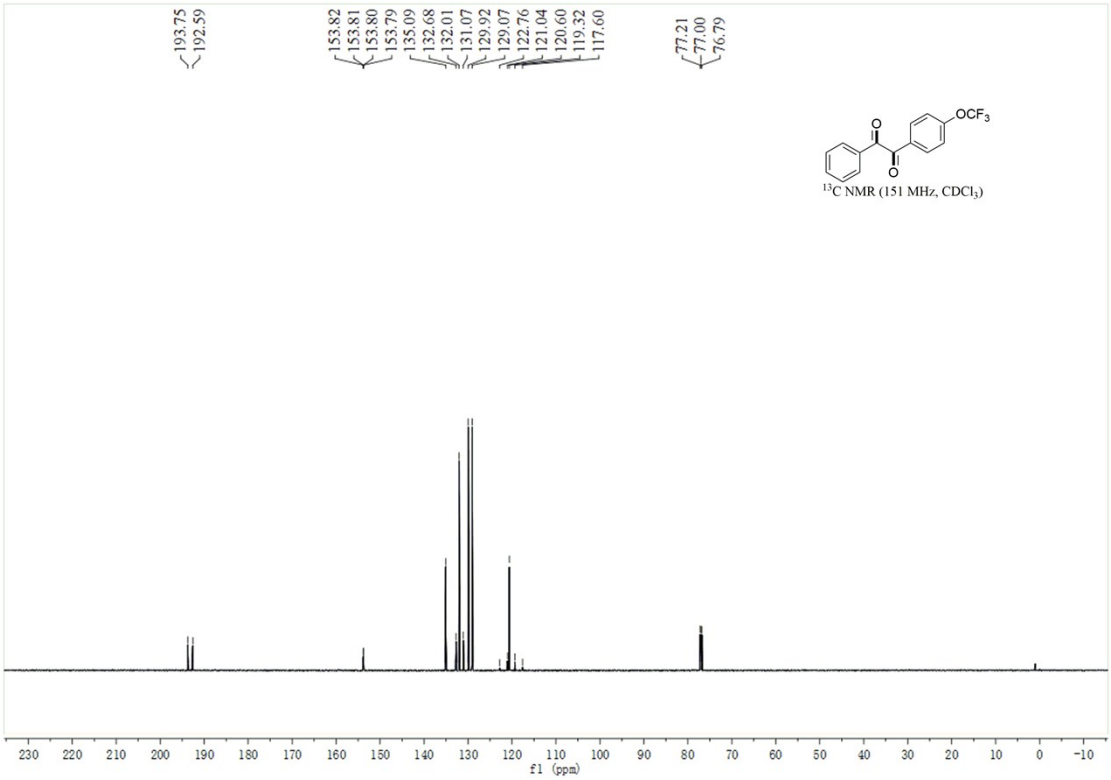


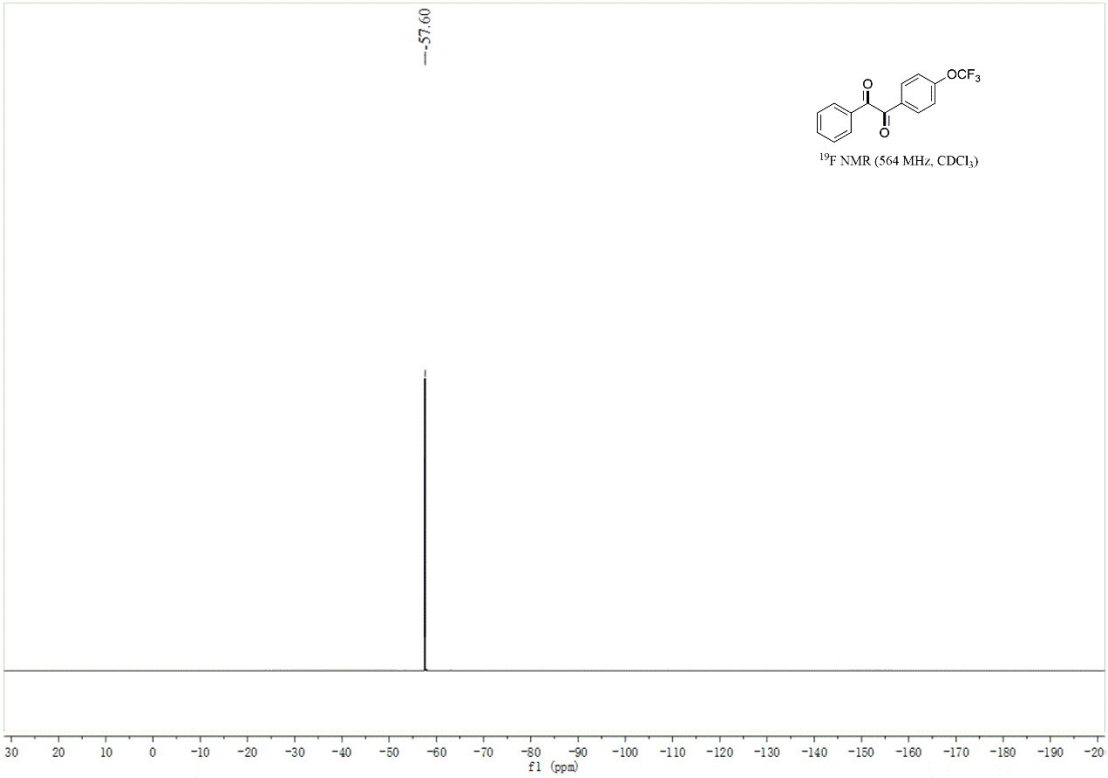


^{19}F NMR (376 MHz, $CDCl_3$)

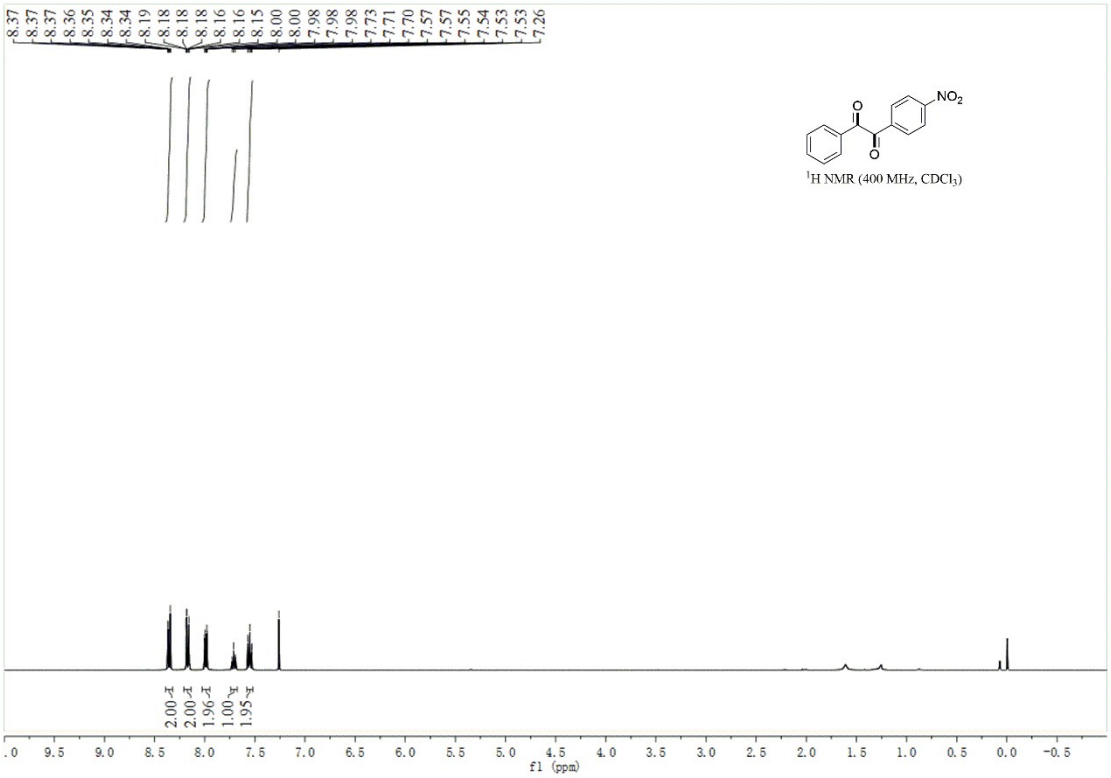
1-phenyl-2-(4-(trifluoromethoxy)phenyl)ethane-1,2-dione (13)

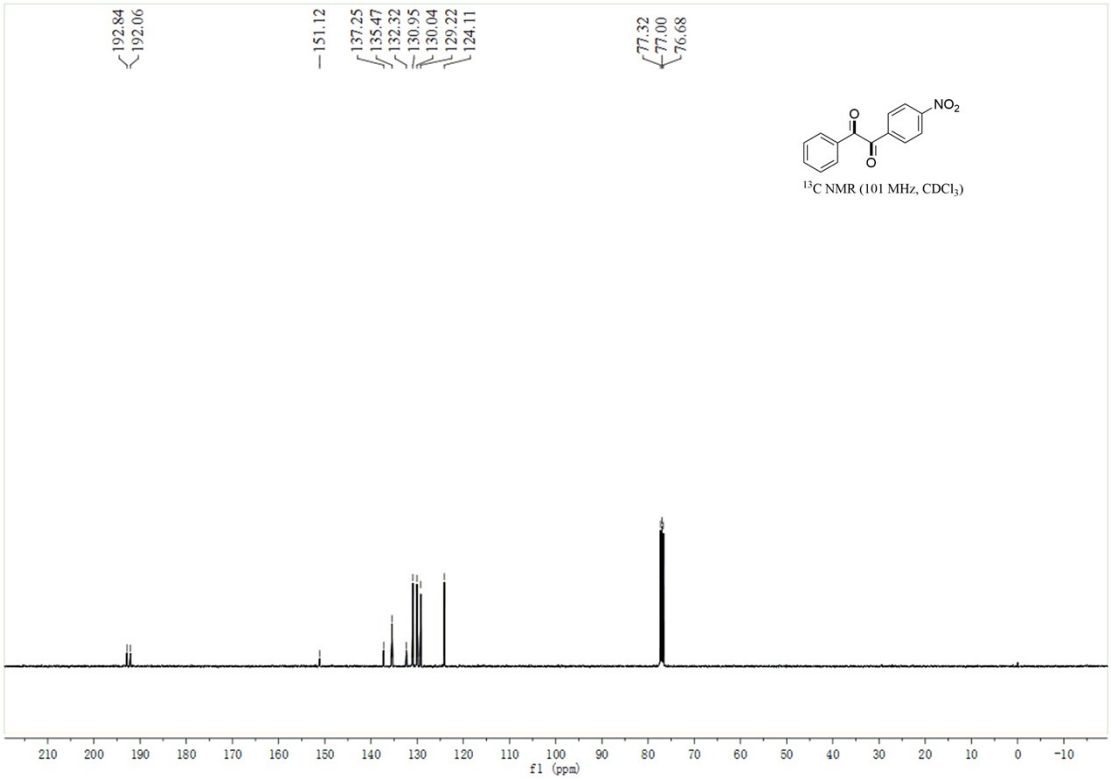




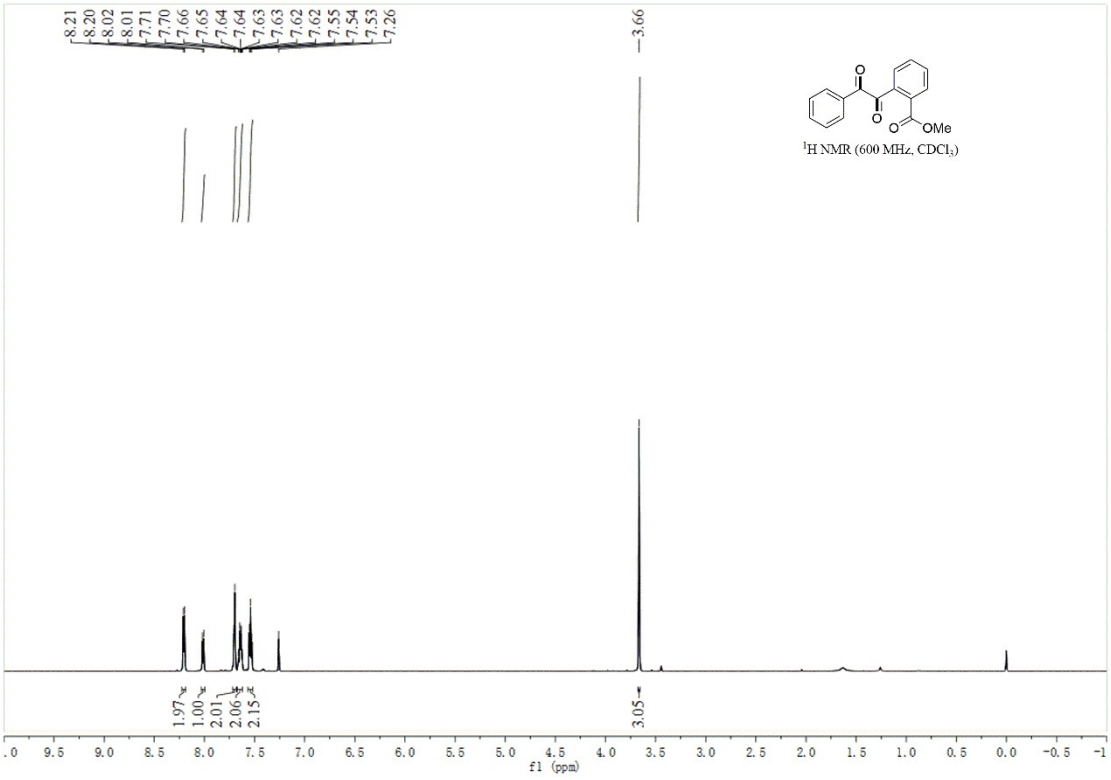

-57.60
OCF3
O
O
19F NMR (564 MHz, CDCl3)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

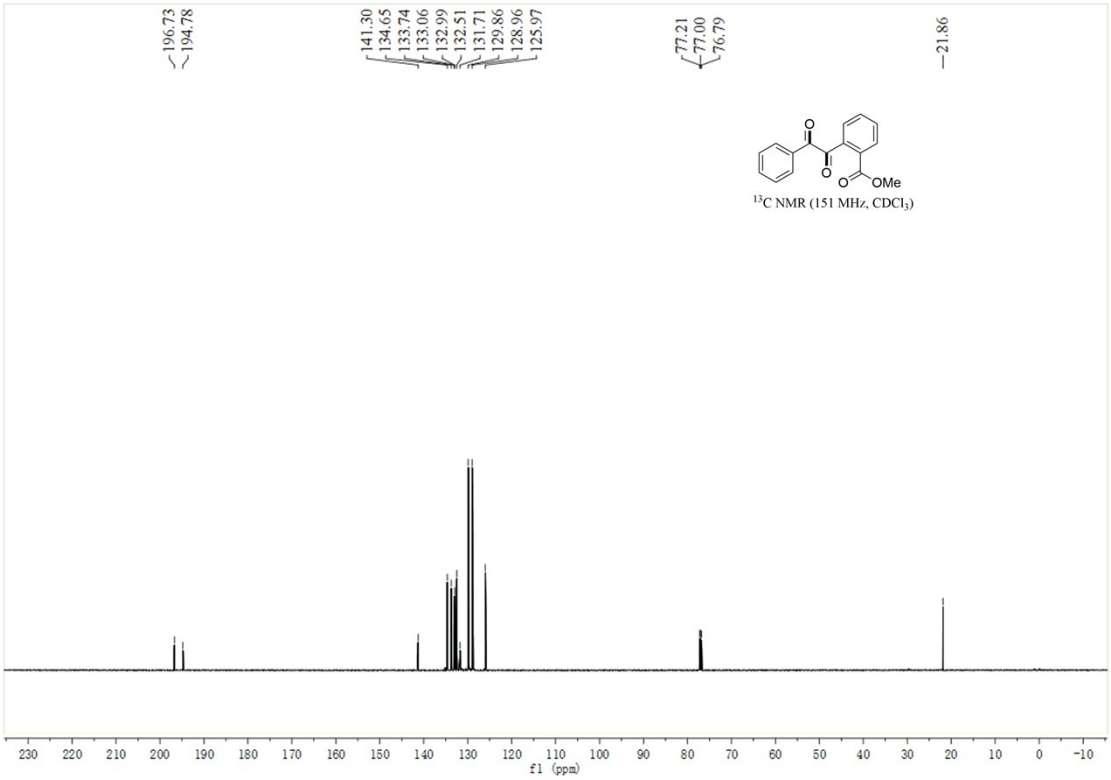
1-(4-nitrophenyl)-2-phenylethane-1,2-dione (14)



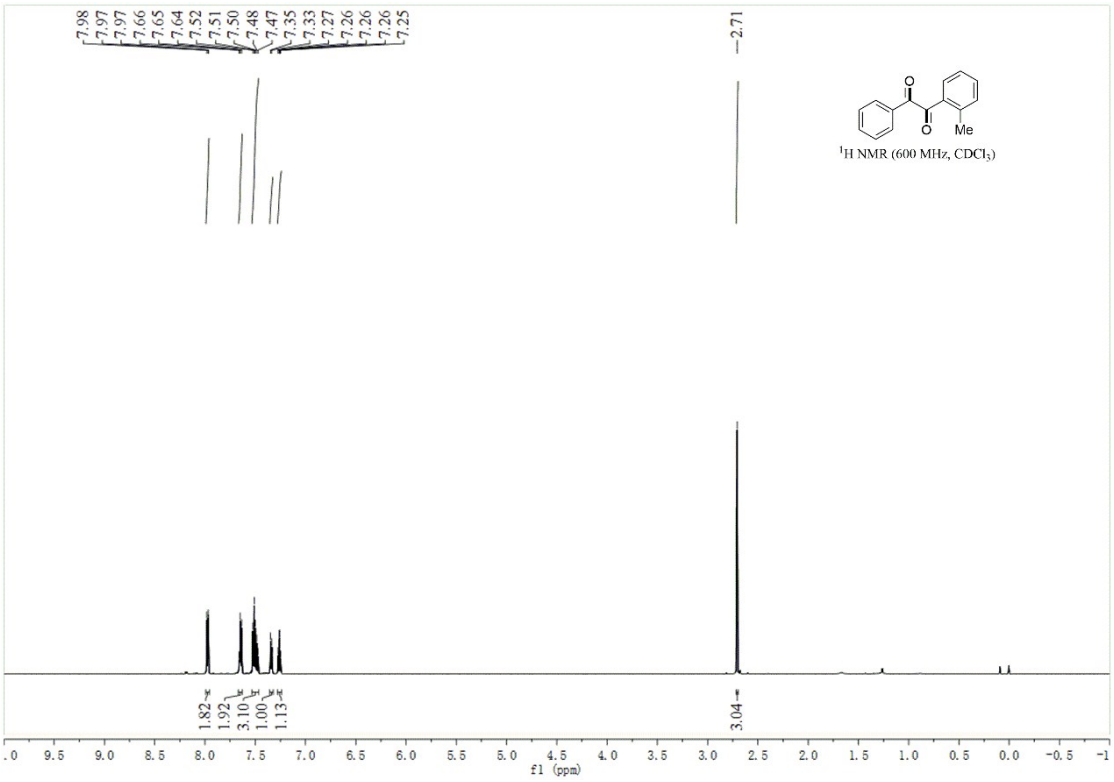


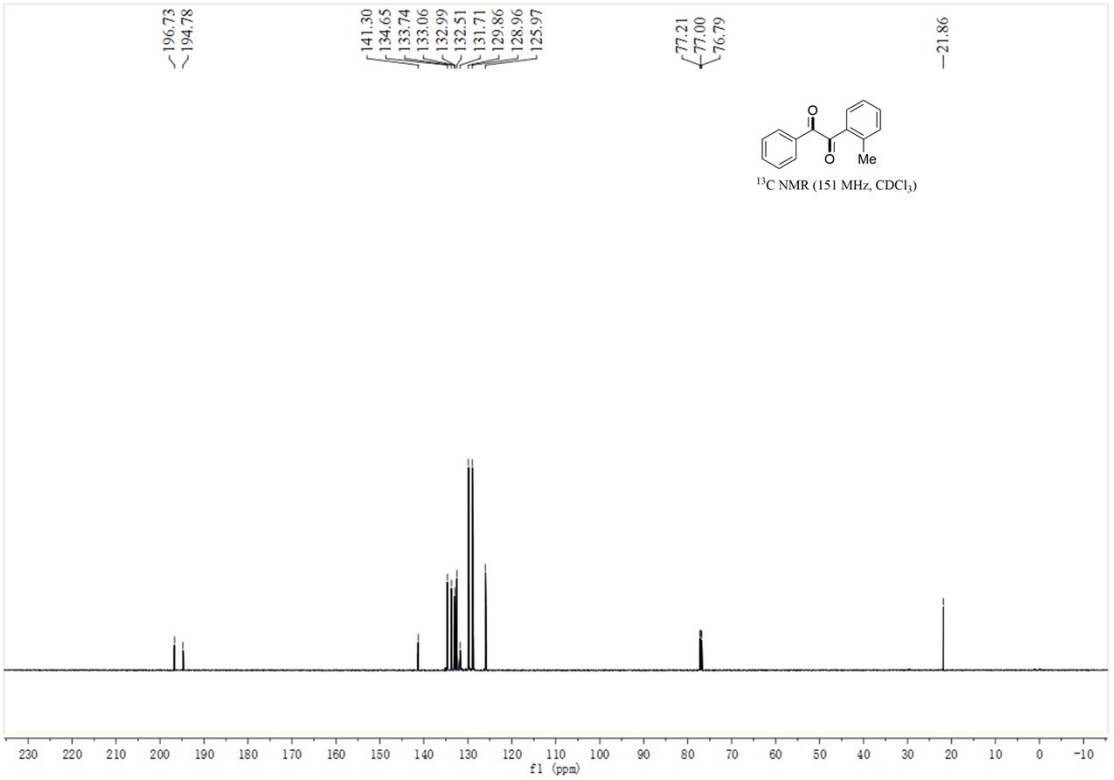
methyl 2-(2-oxo-2-phenylacetyl)benzoate (15)



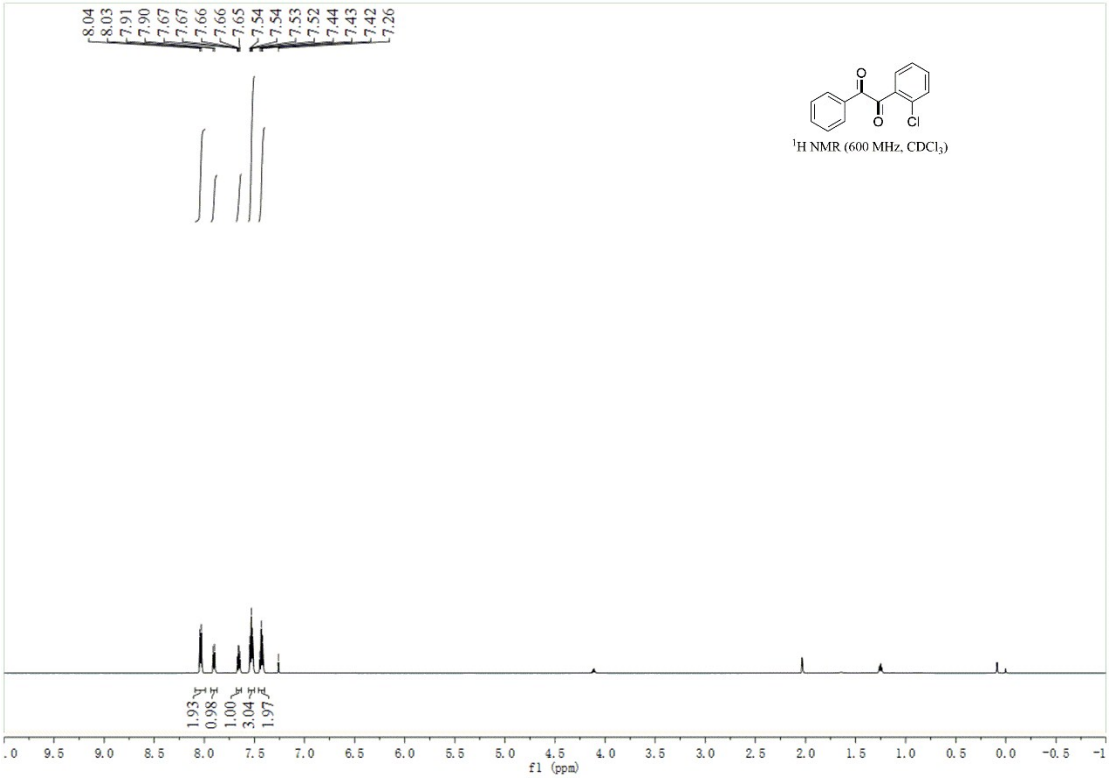


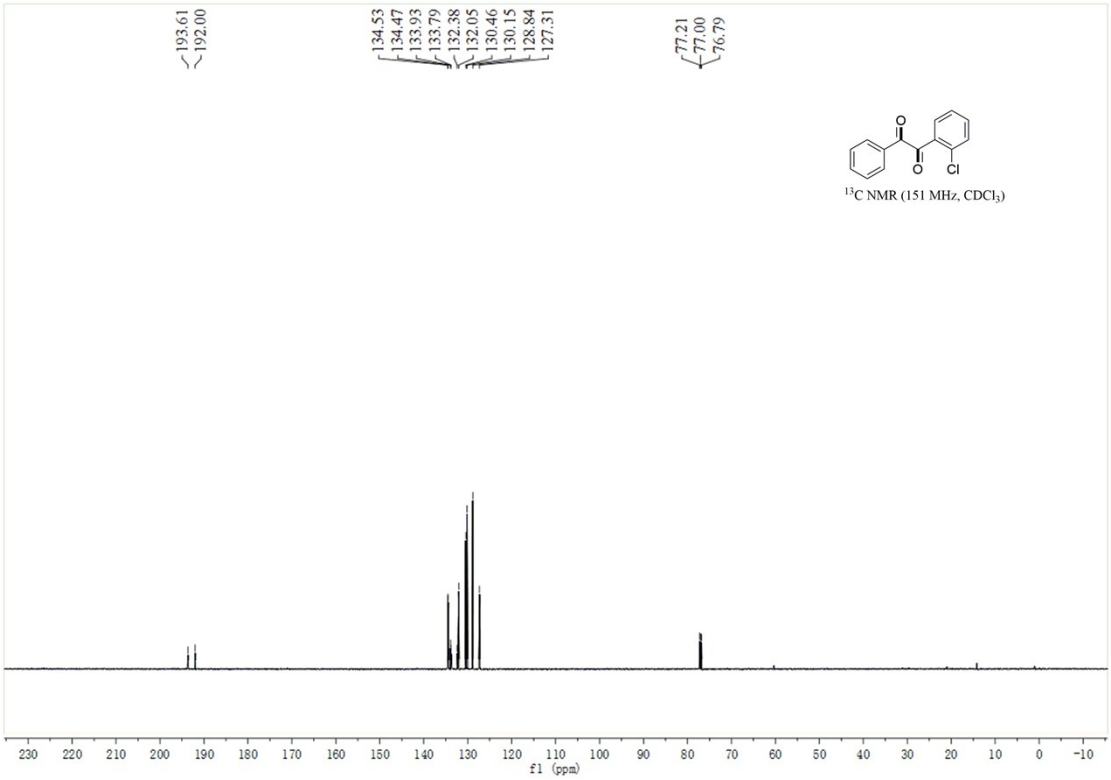
1-phenyl-2-(o-tolyl) ethane-1,2-dione (16)



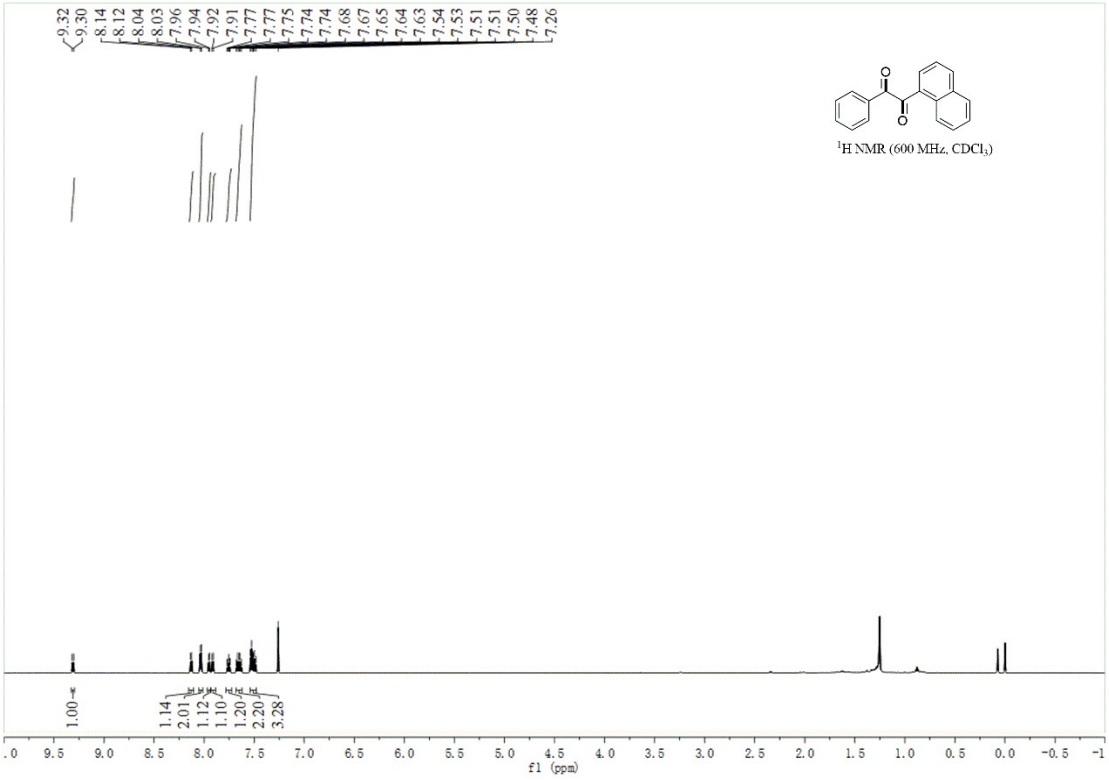


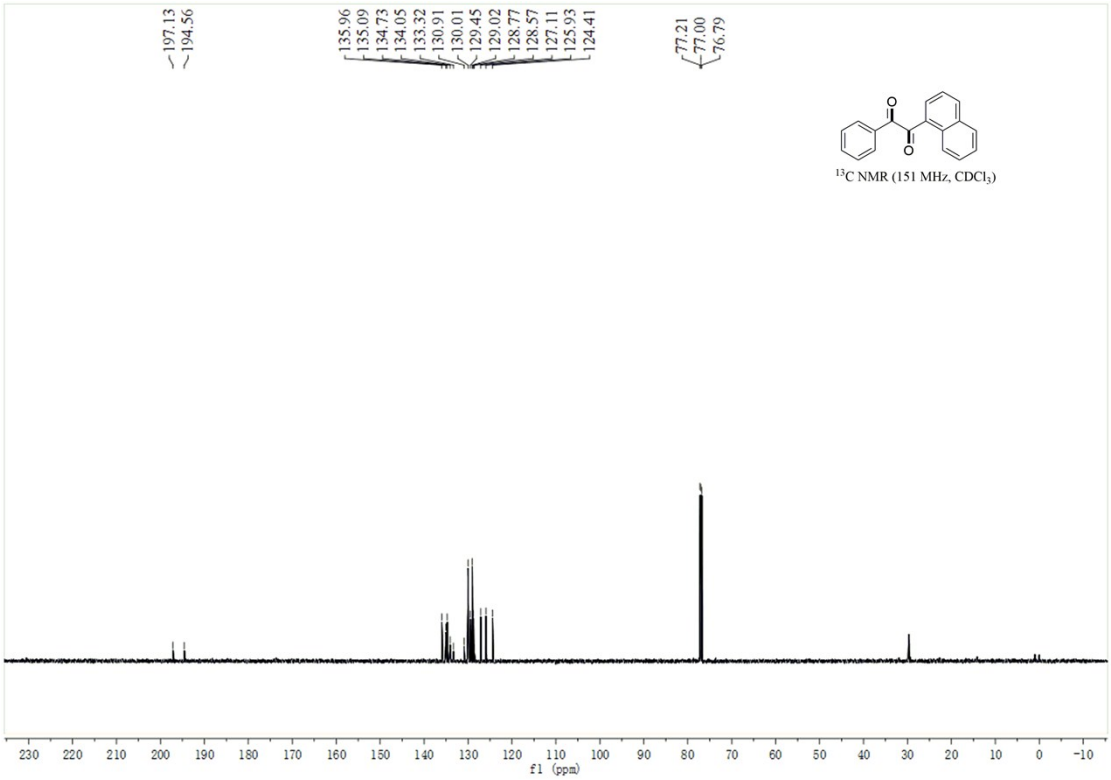
1-(2-chlorophenyl)-2-phenylethane-1,2-dione (17)



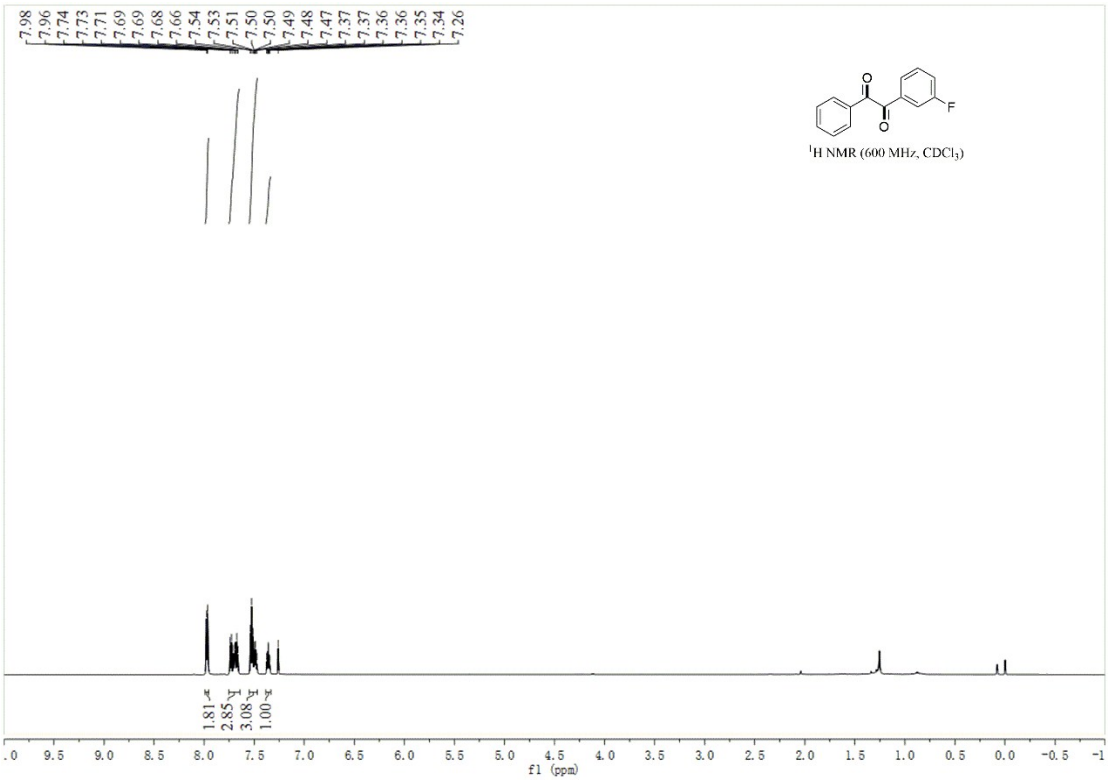


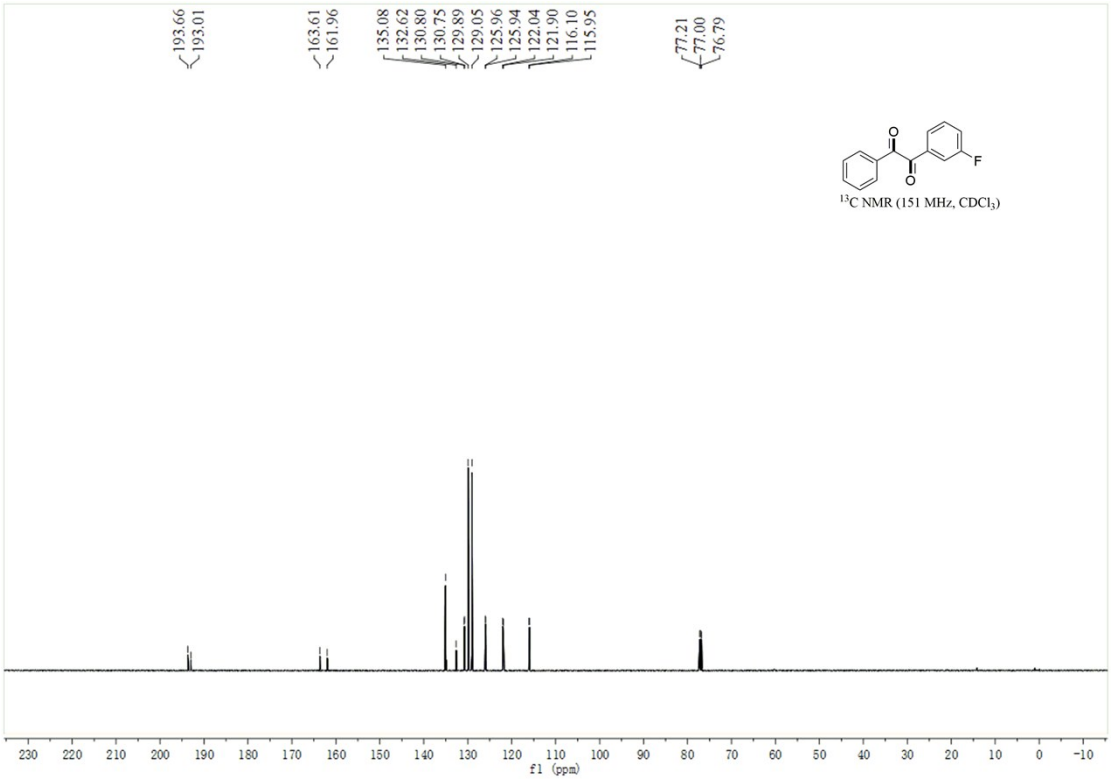
1-(naphthalen-1-yl)-2-phenylethane-1,2-dione (18)

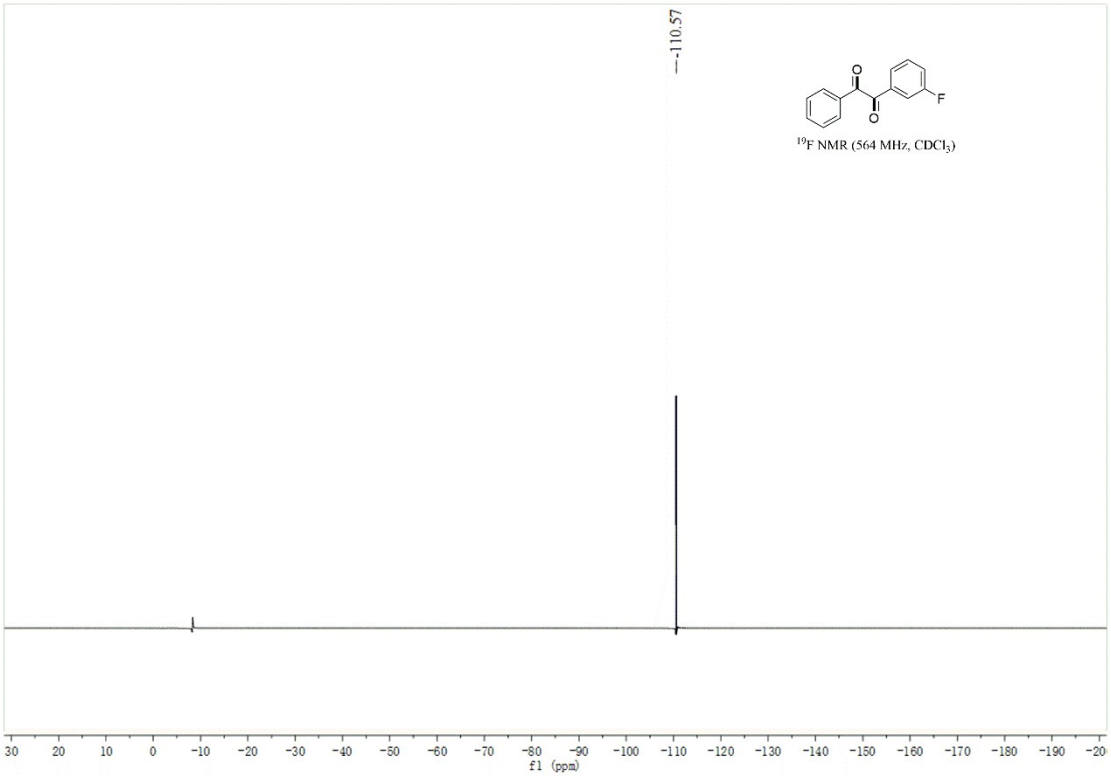




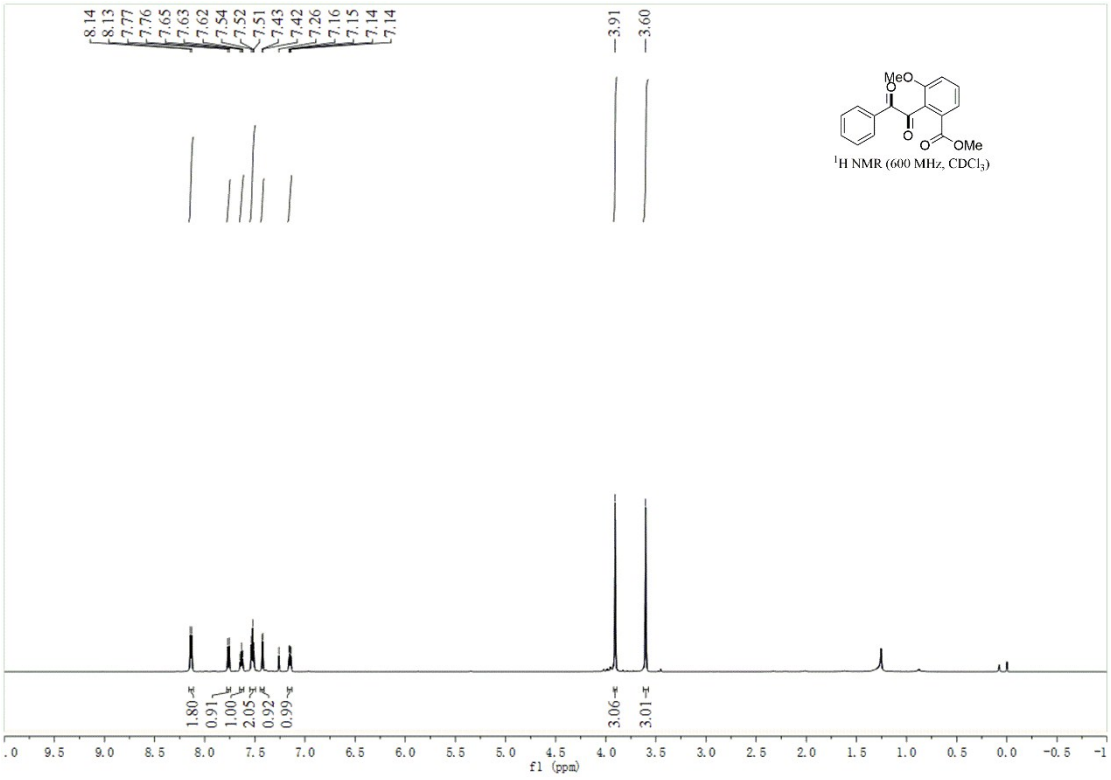
1-(3-fluorophenyl)-2-phenylethane-1,2-dione (19)

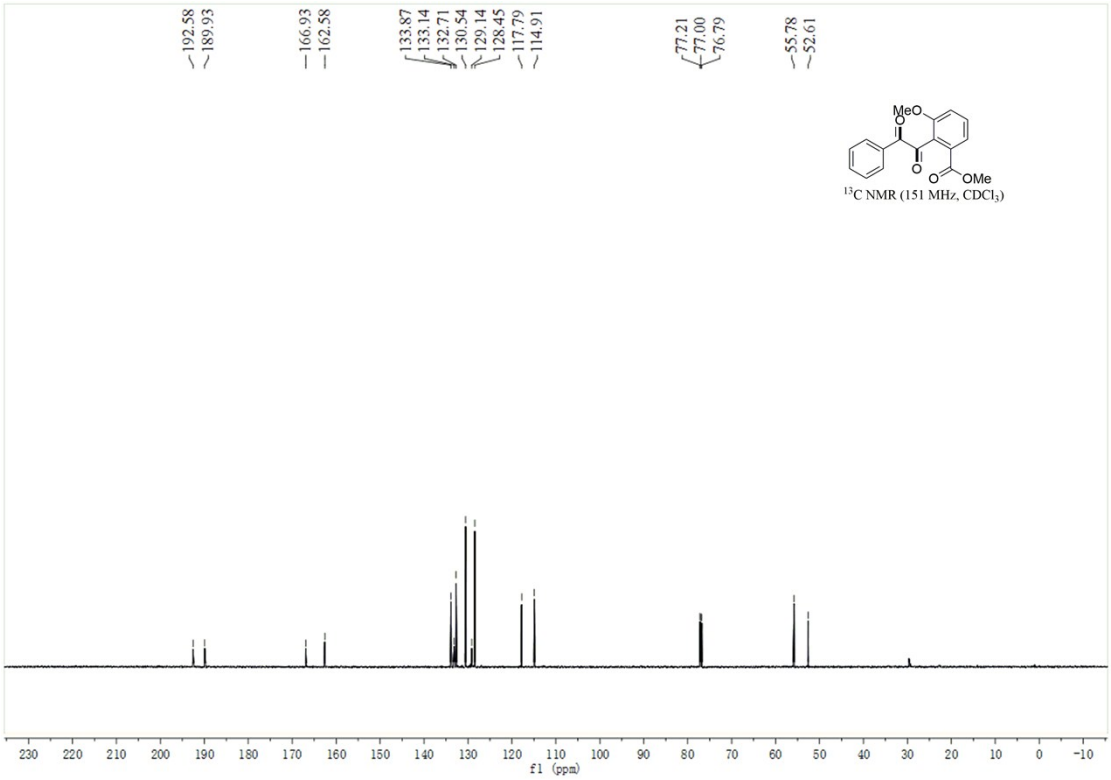




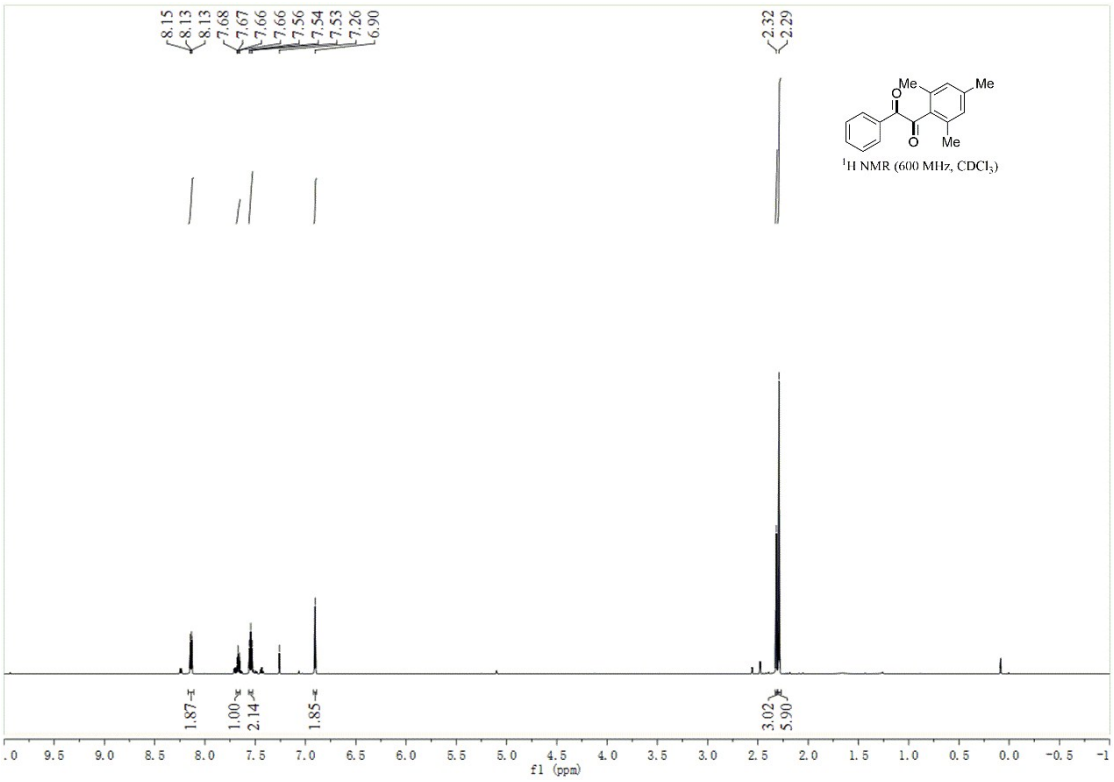

-110.57
O
O
F
^{19}F NMR (564 MHz, $CDCl_3$)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

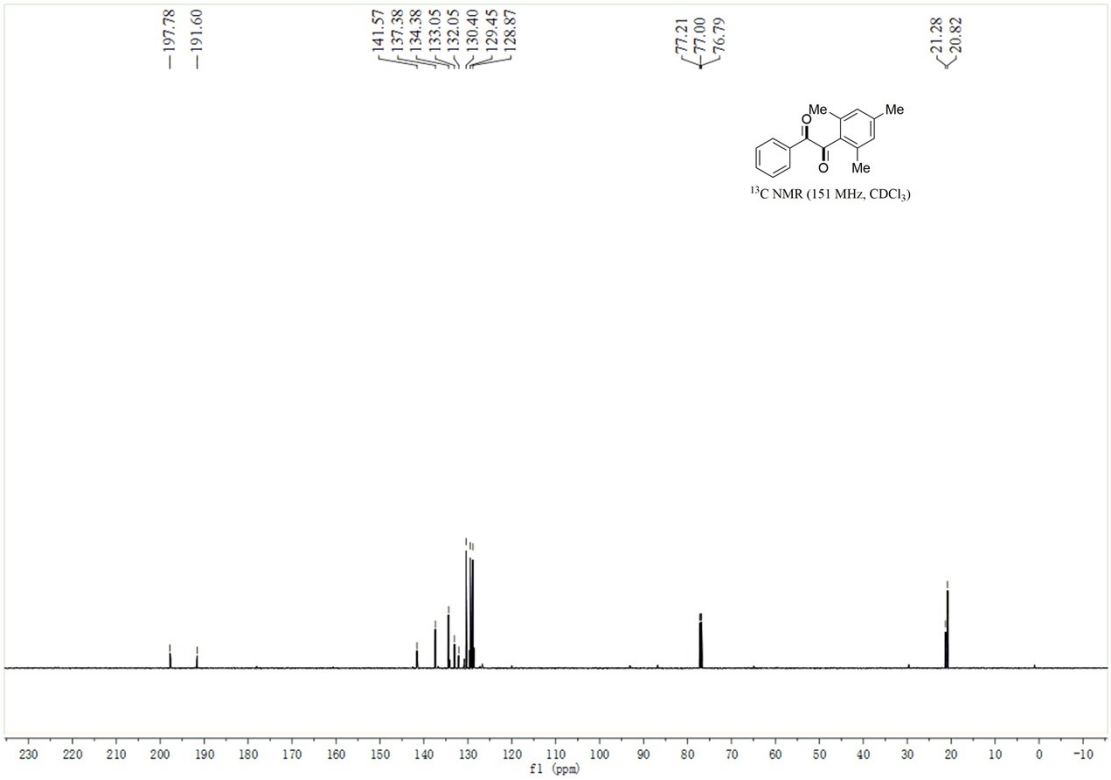
methyl 3-methoxy-2-(2-oxo-2-phenylacetyl)benzoate (20)



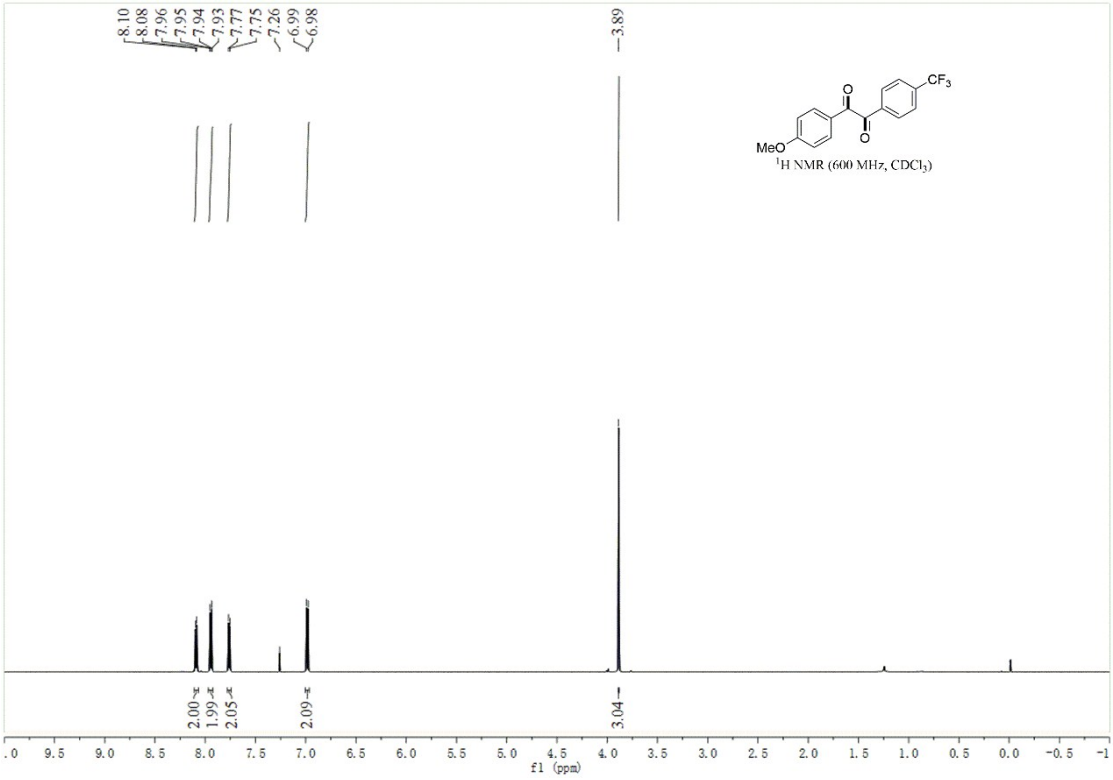


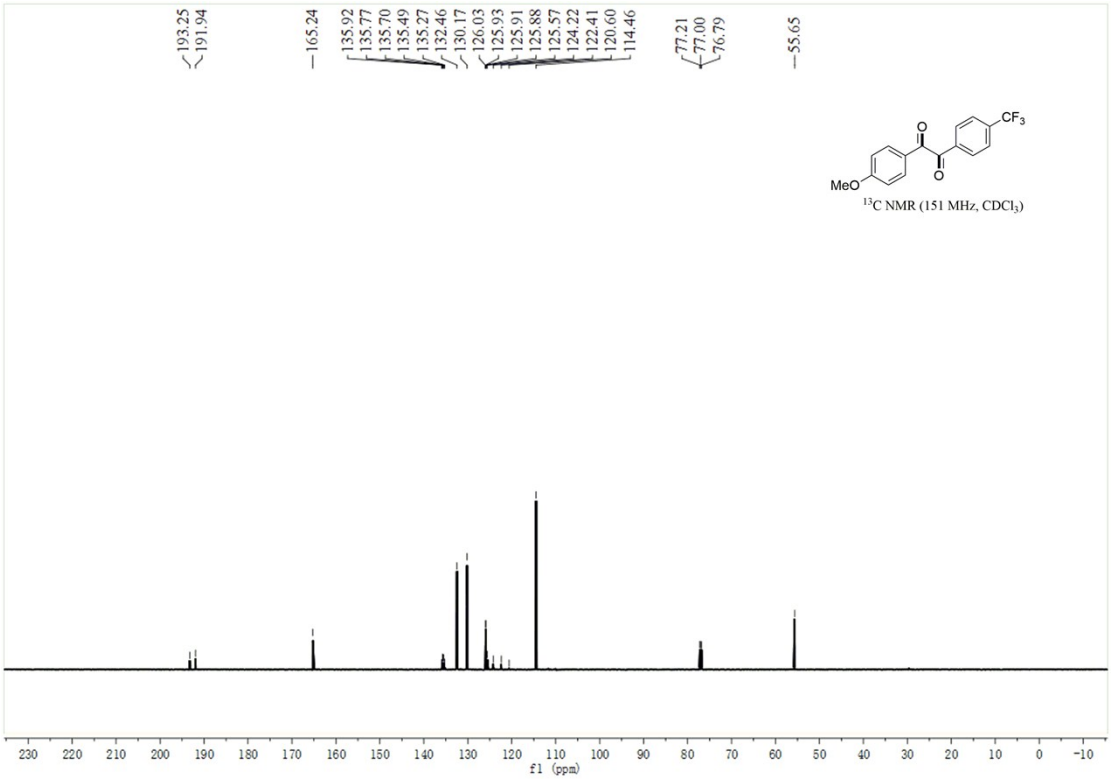
mesityl-2-phenylethane-1,2-dione (21)

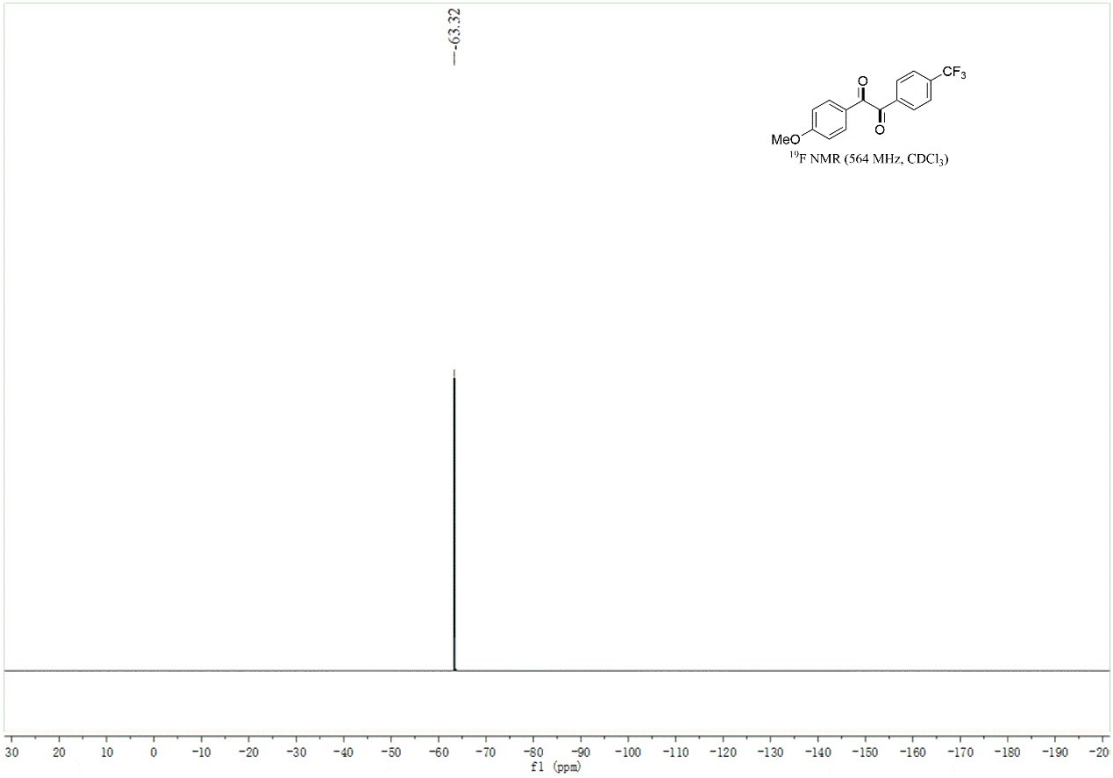




1-(4-methoxyphenyl)-2-(4-(trifluoromethyl) phenyl) ethane-1,2-dione (22)

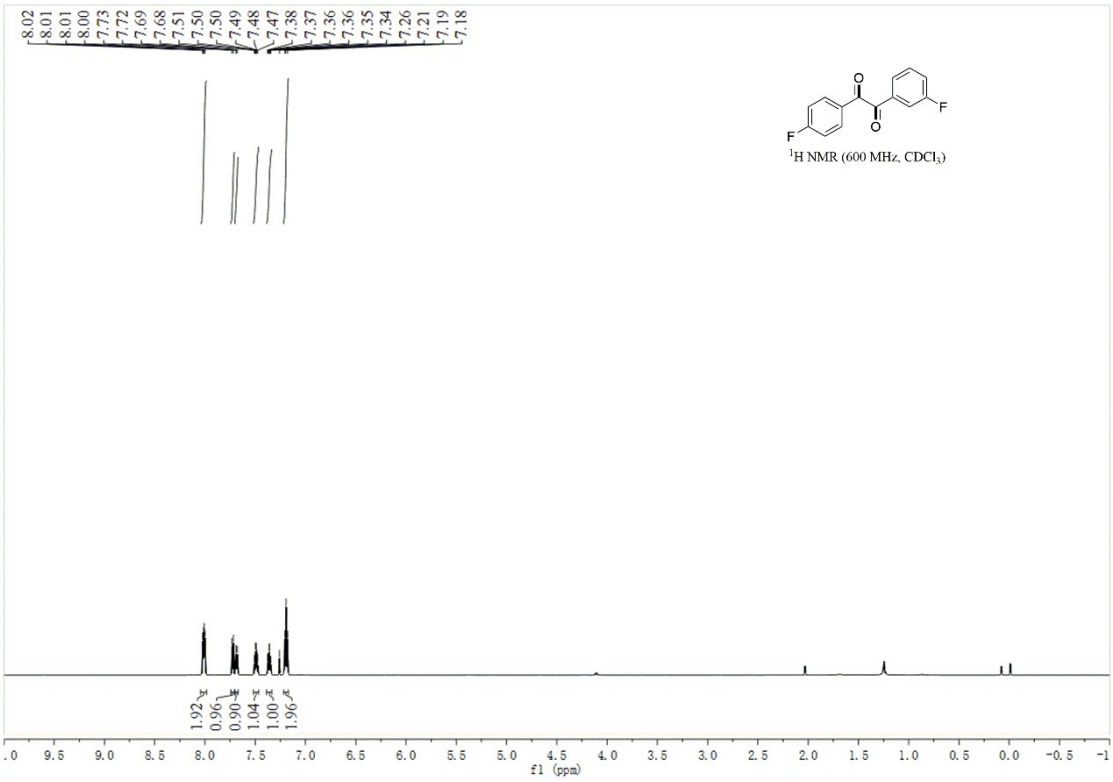


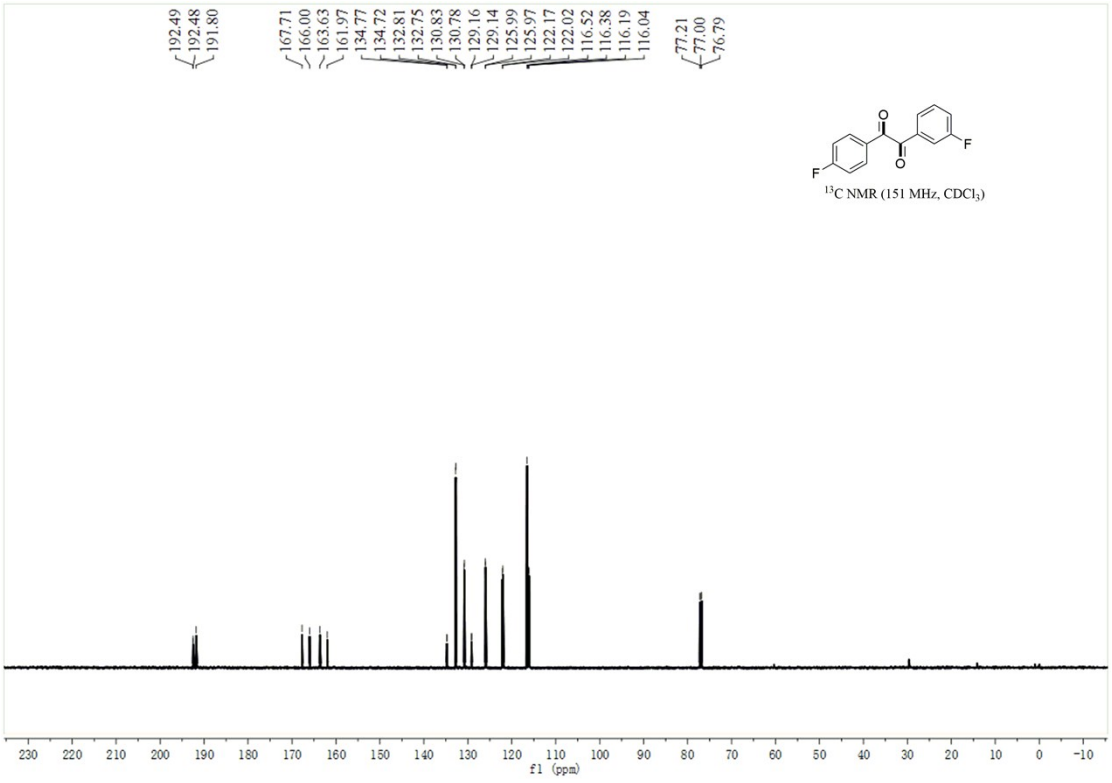


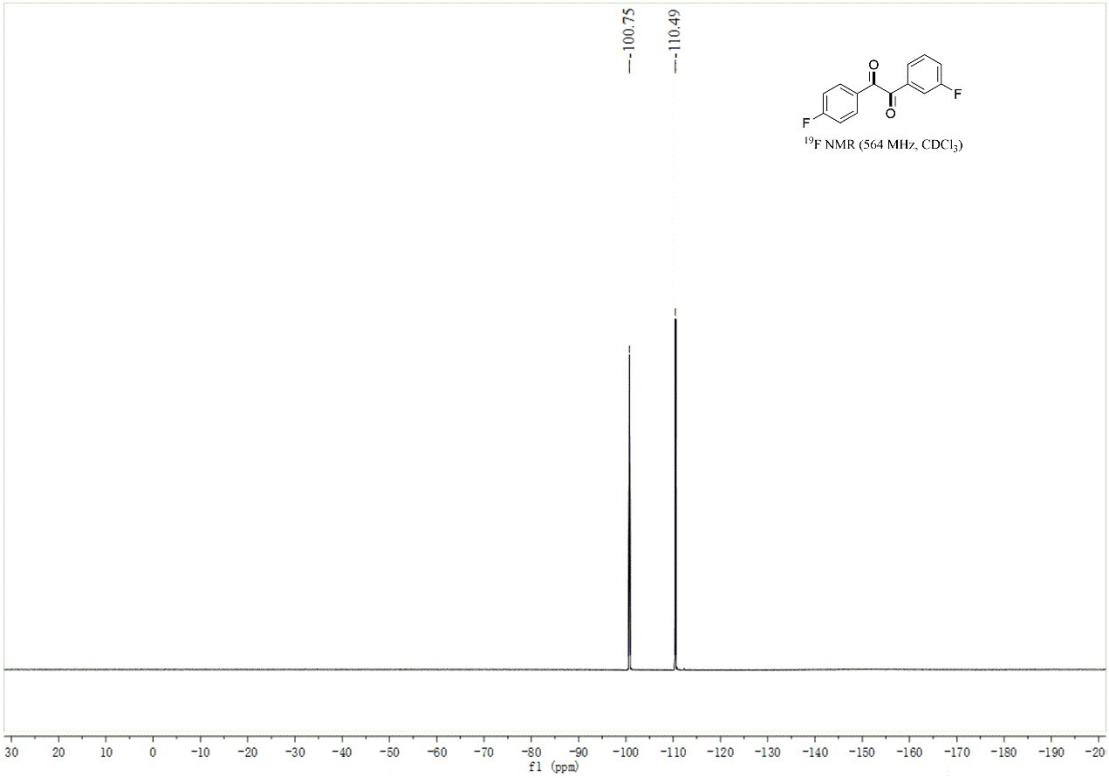


^{19}F NMR (564 MHz, $CDCl_3$)

1-(3-fluorophenyl)-2-(4-fluorophenyl)ethane-1,2-dione (23)

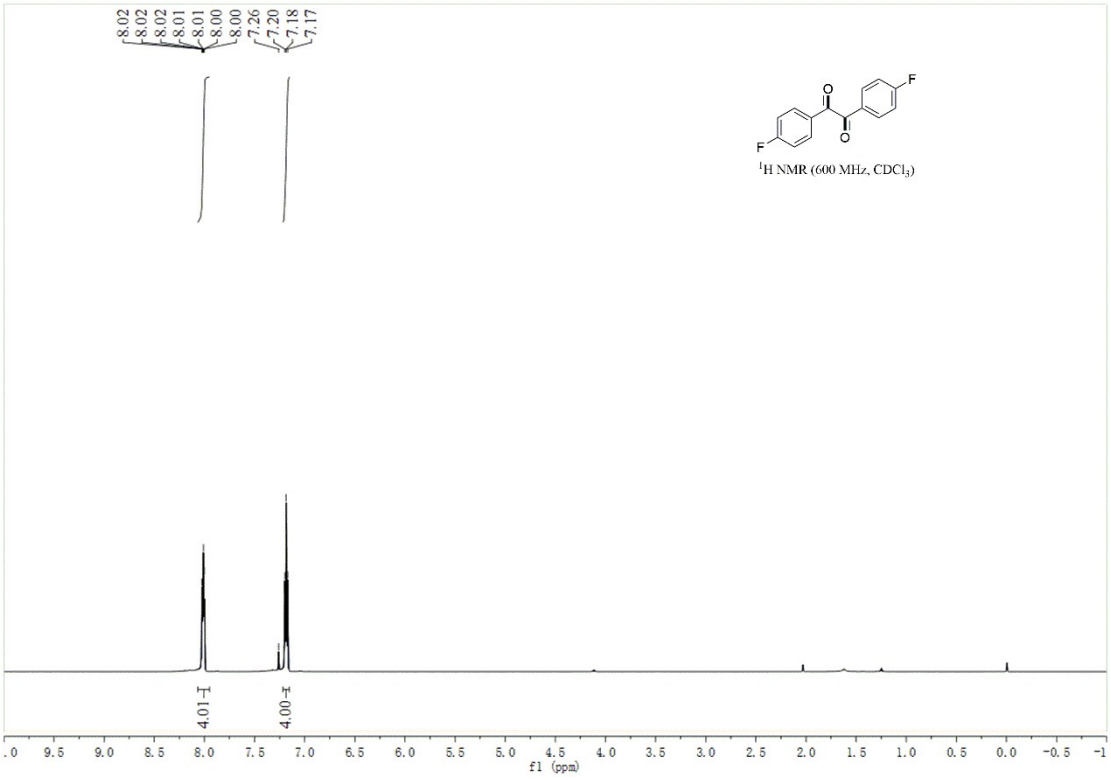


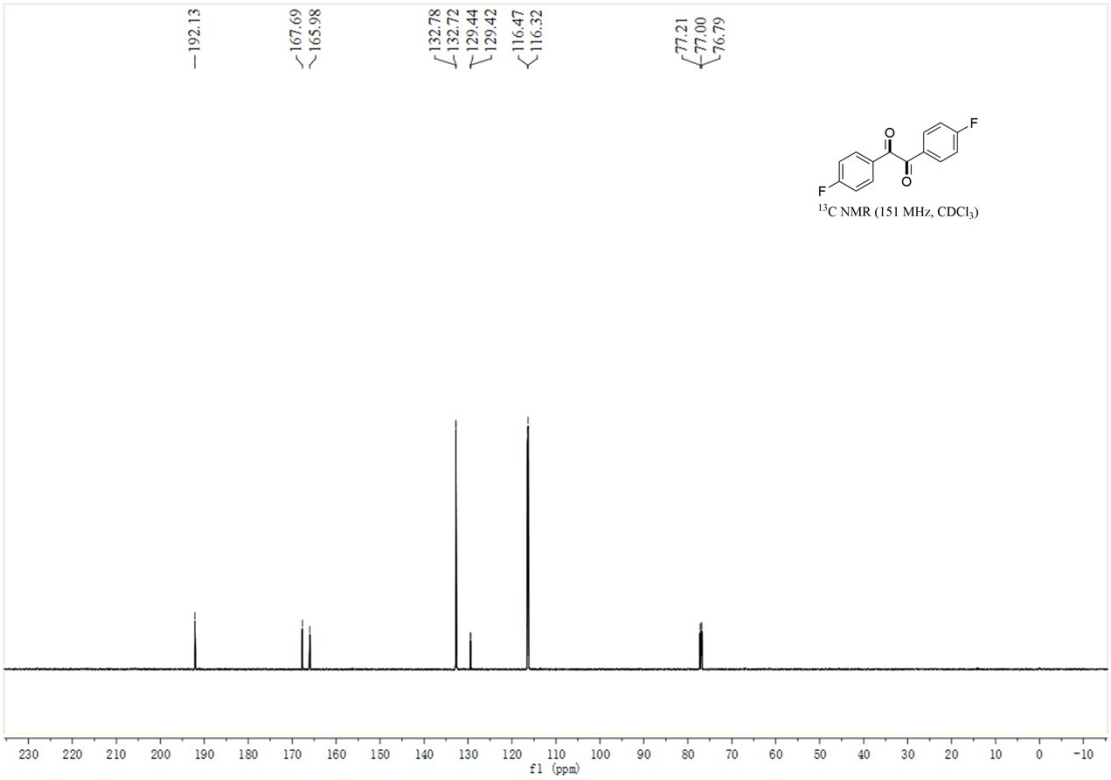


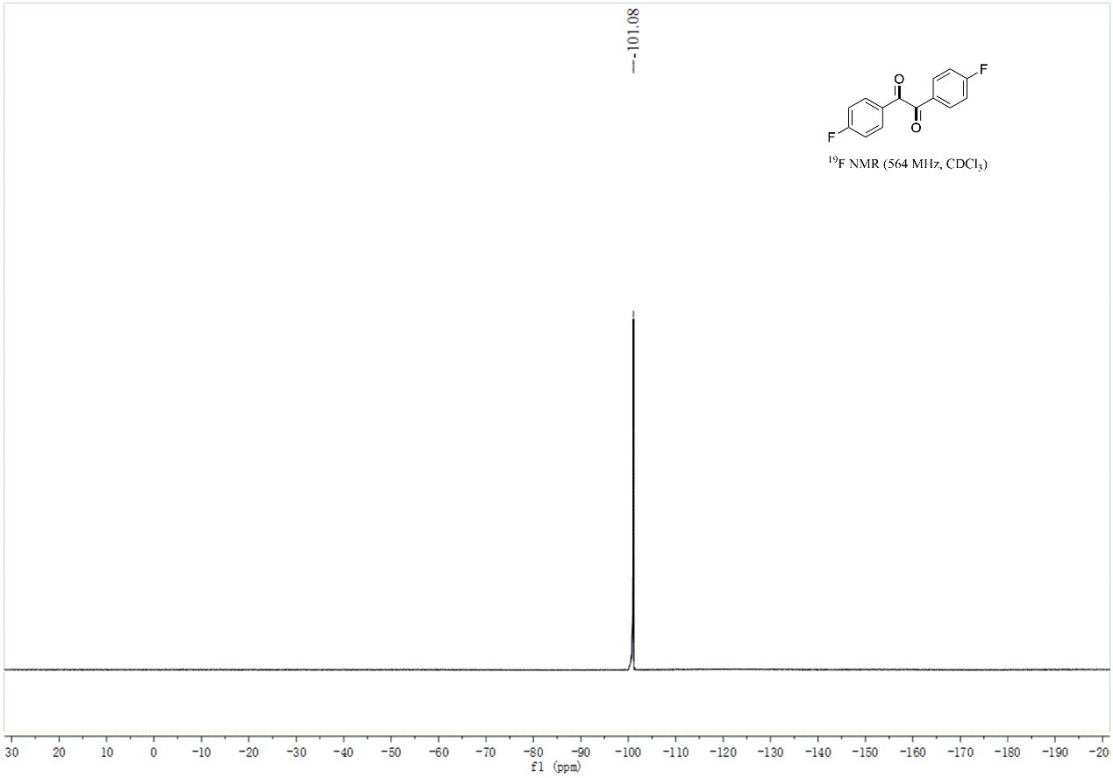


^{19}F NMR (564 MHz, $CDCl_3$)

1,2-bis(4-fluorophenyl)ethane-1,2-dione (24)

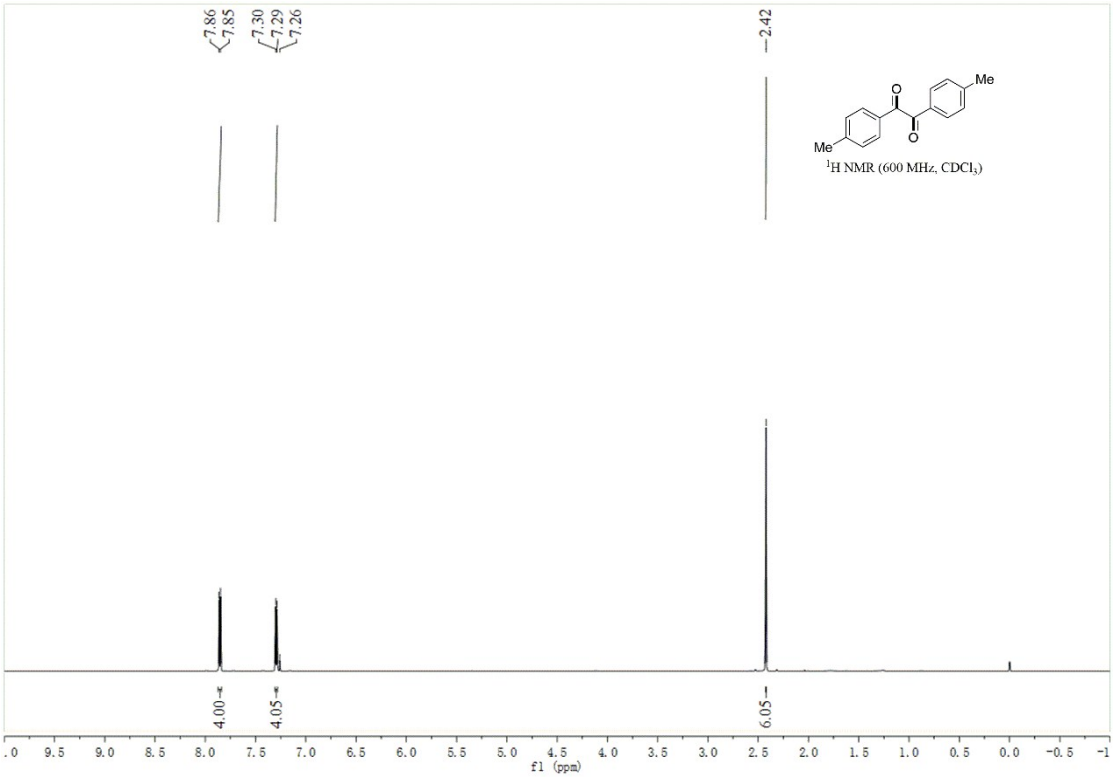




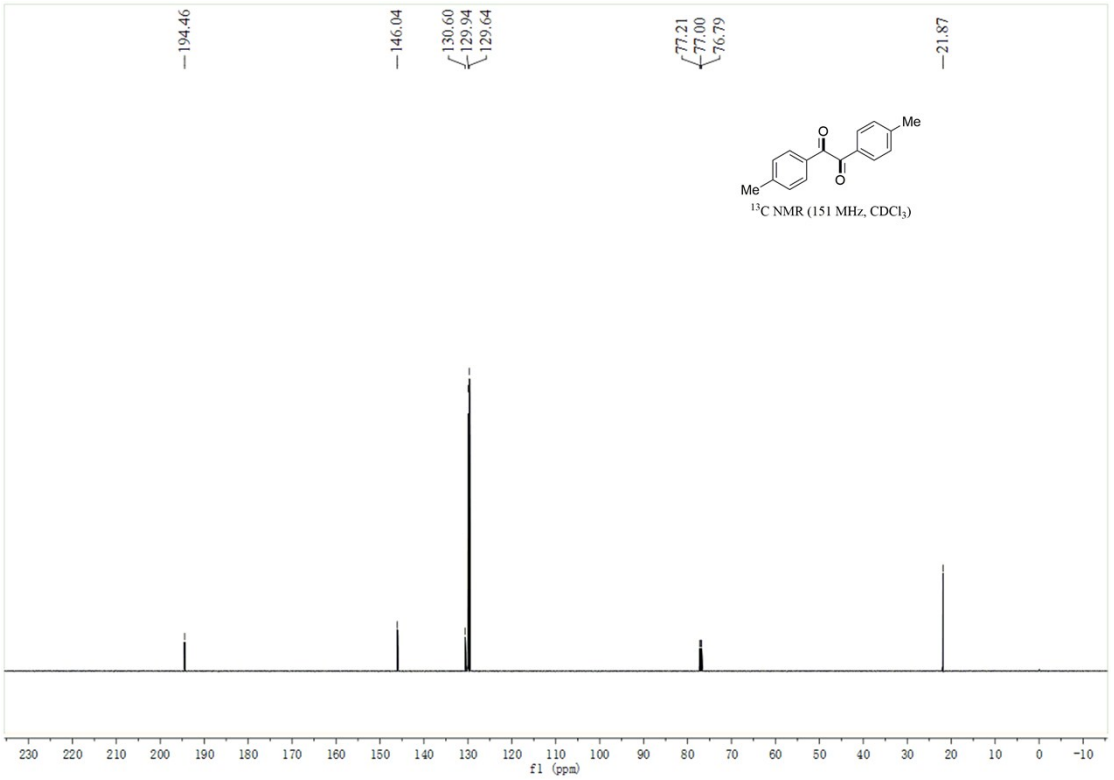


^{19}F NMR (564 MHz, $CDCl_3$)

1,2-di-p-tolylethane-1,2-dione (25)

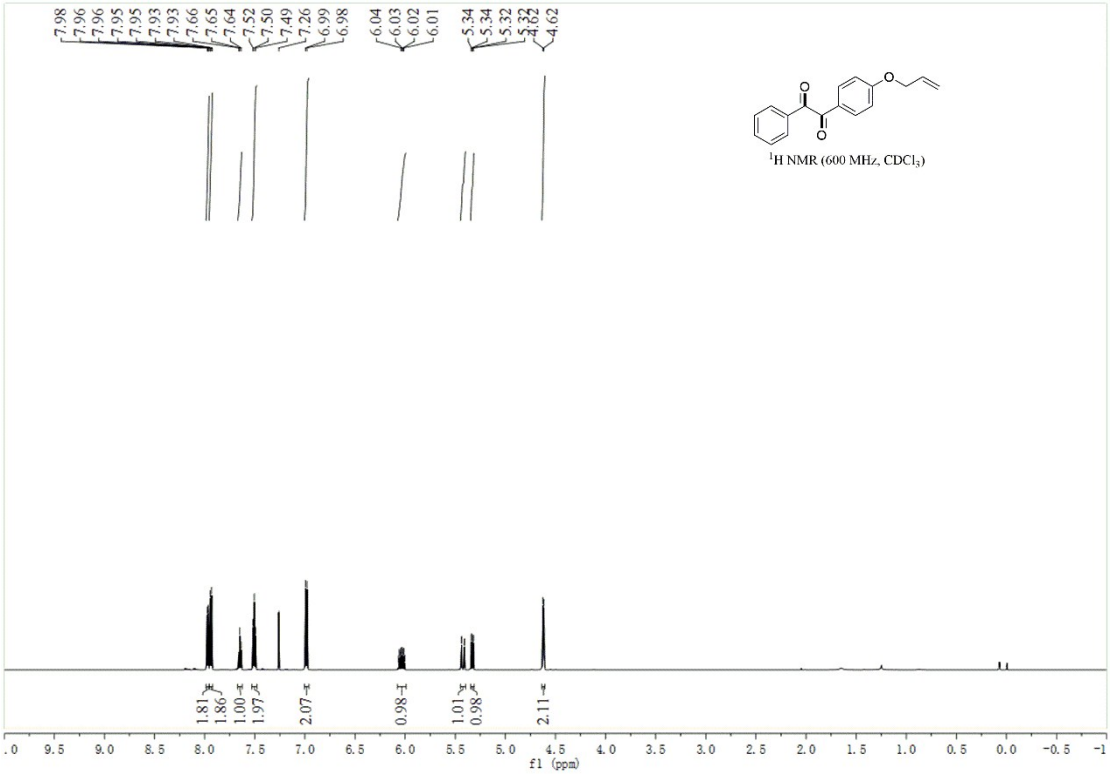


^{1}H NMR (600 MHz, $CDCl_3$)

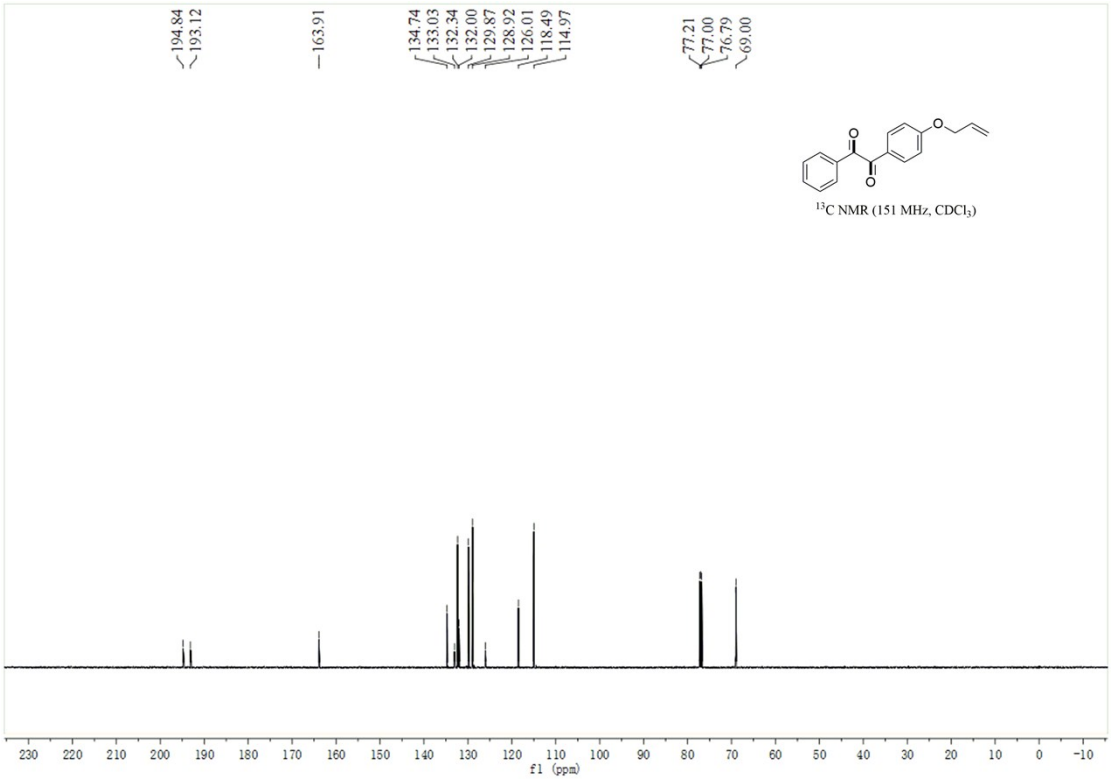


^{13}C NMR (151 MHz, $CDCl_3$)

1-(4-(allyloxy)phenyl)-2-phenylethane-1,2-dione (26)

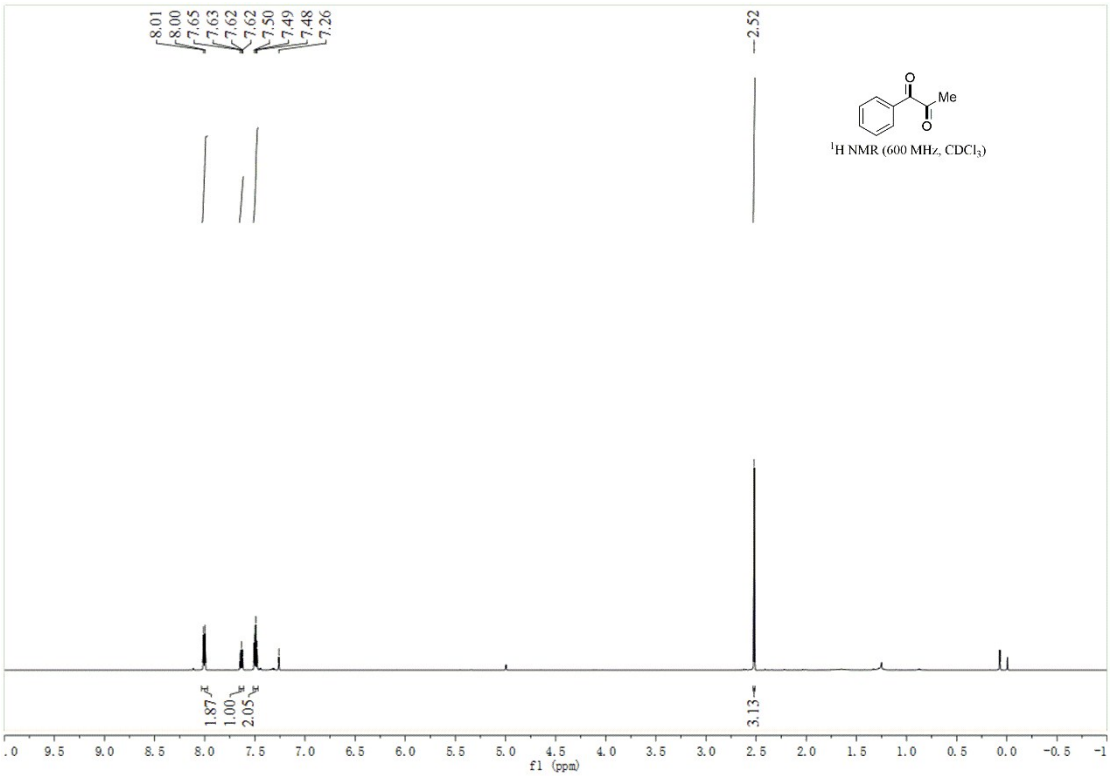


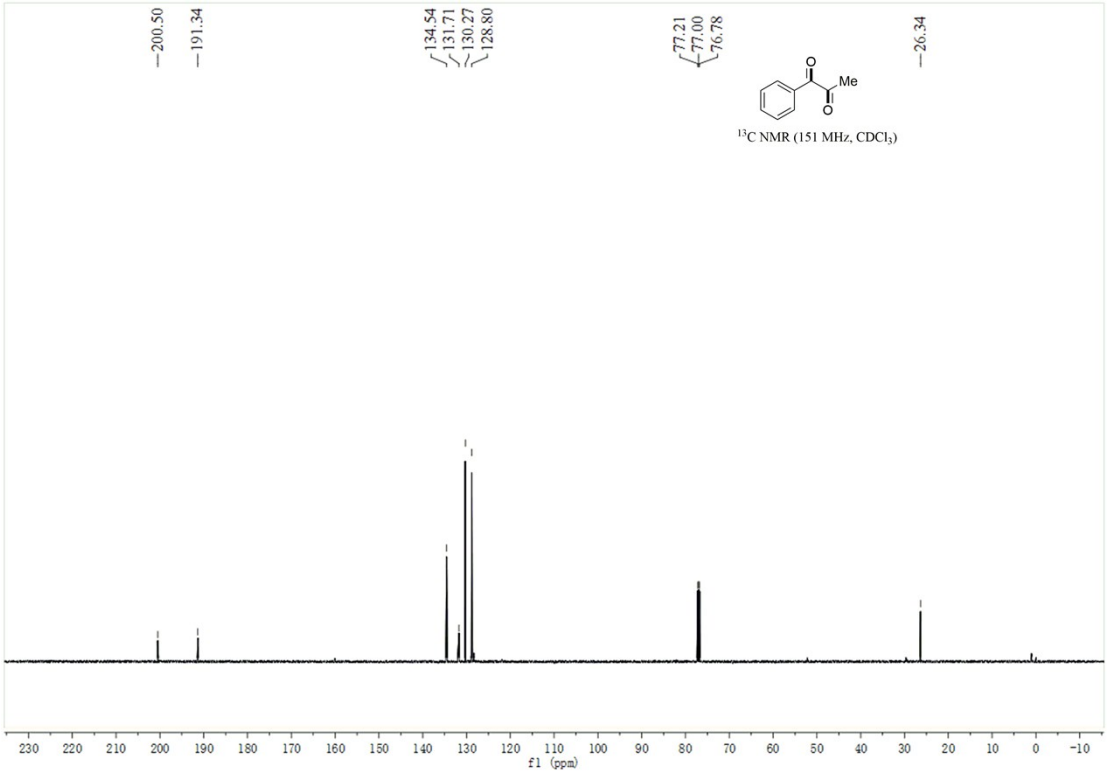
^{1}H NMR (600 MHz, $CDCl_3$)



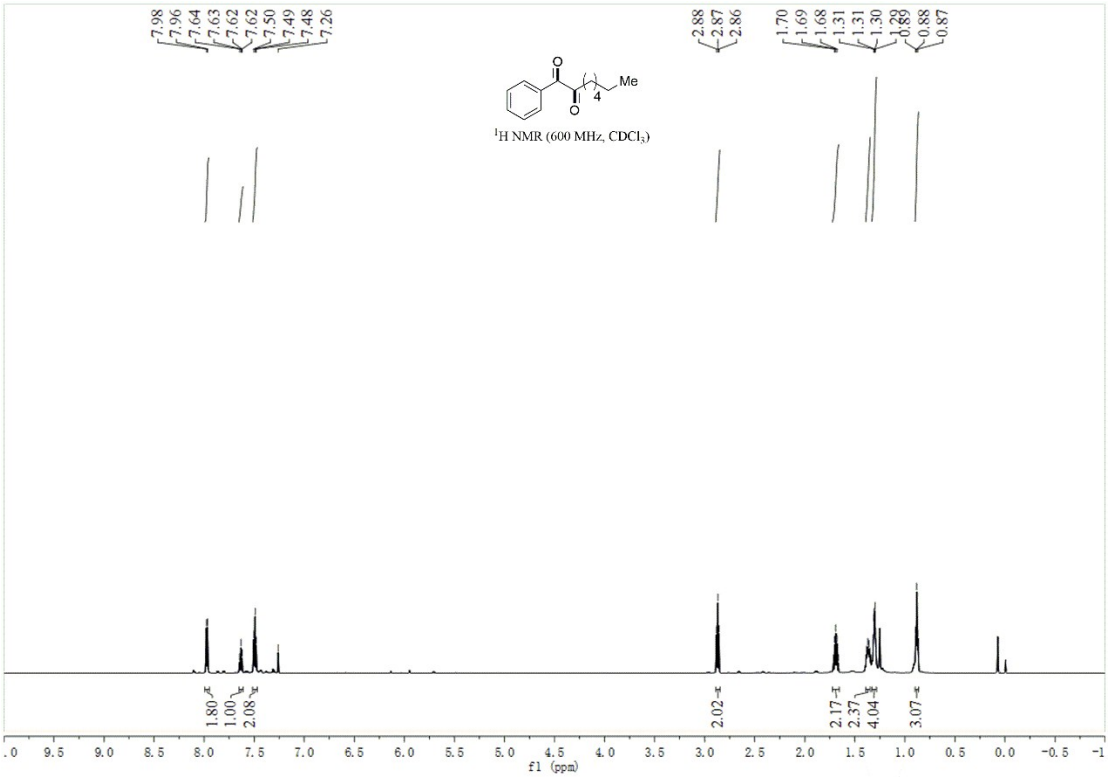
^{13}C NMR (151 MHz, $CDCl_3$)

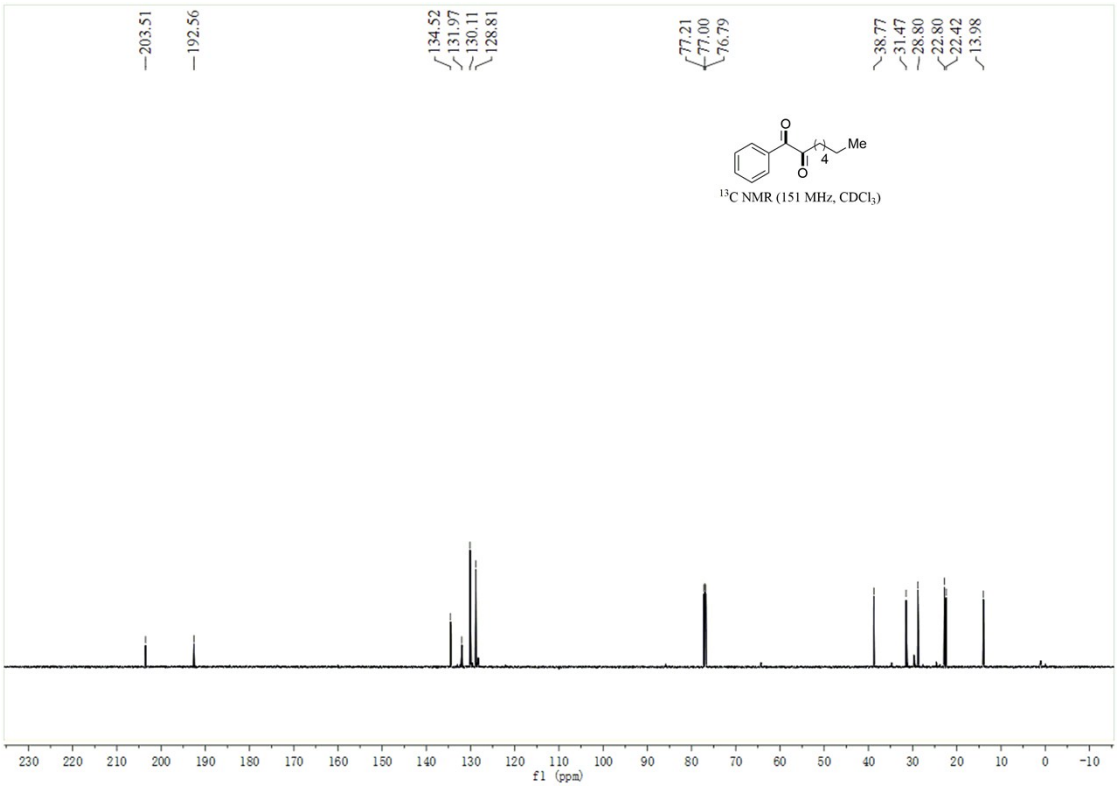
1-phenylpropane-1,2-dione (27)



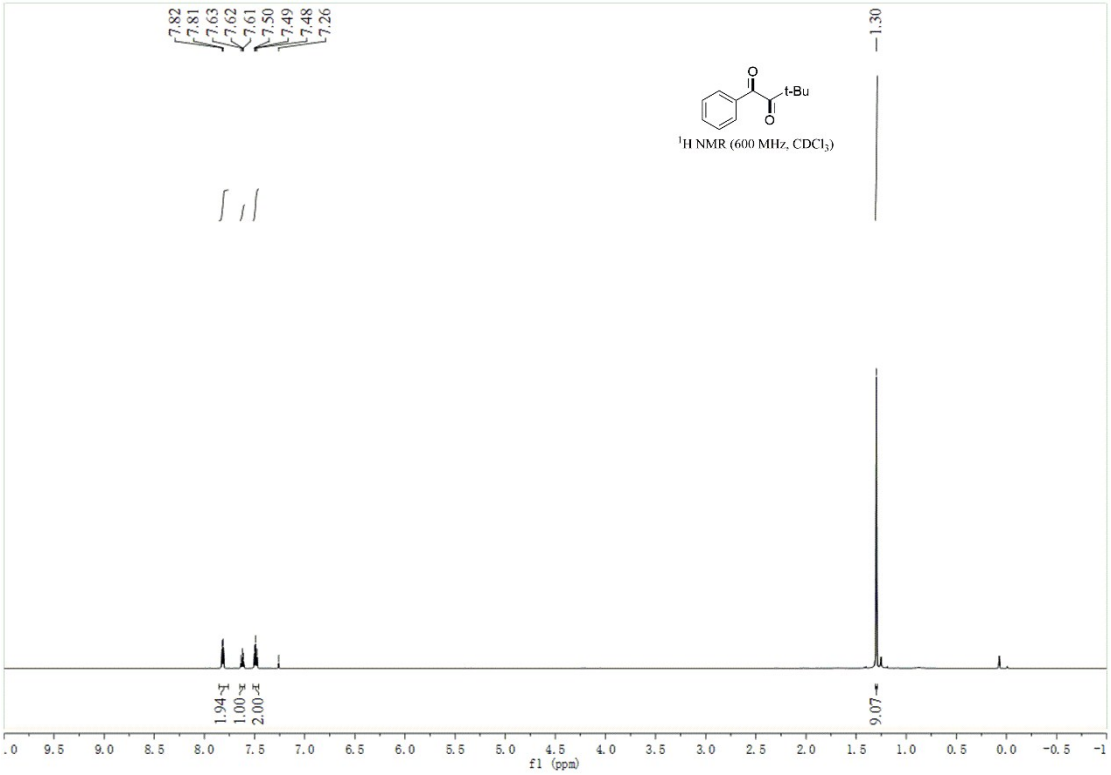


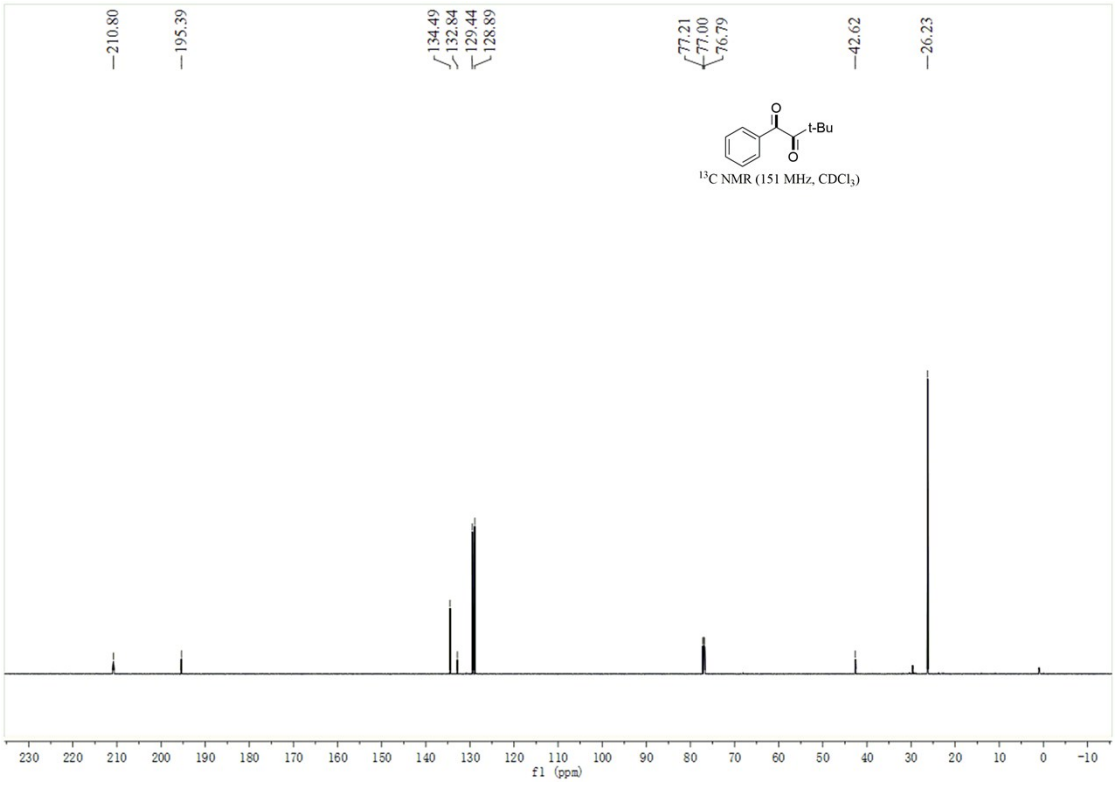
1-phenylpentane-1,2-dione (28)



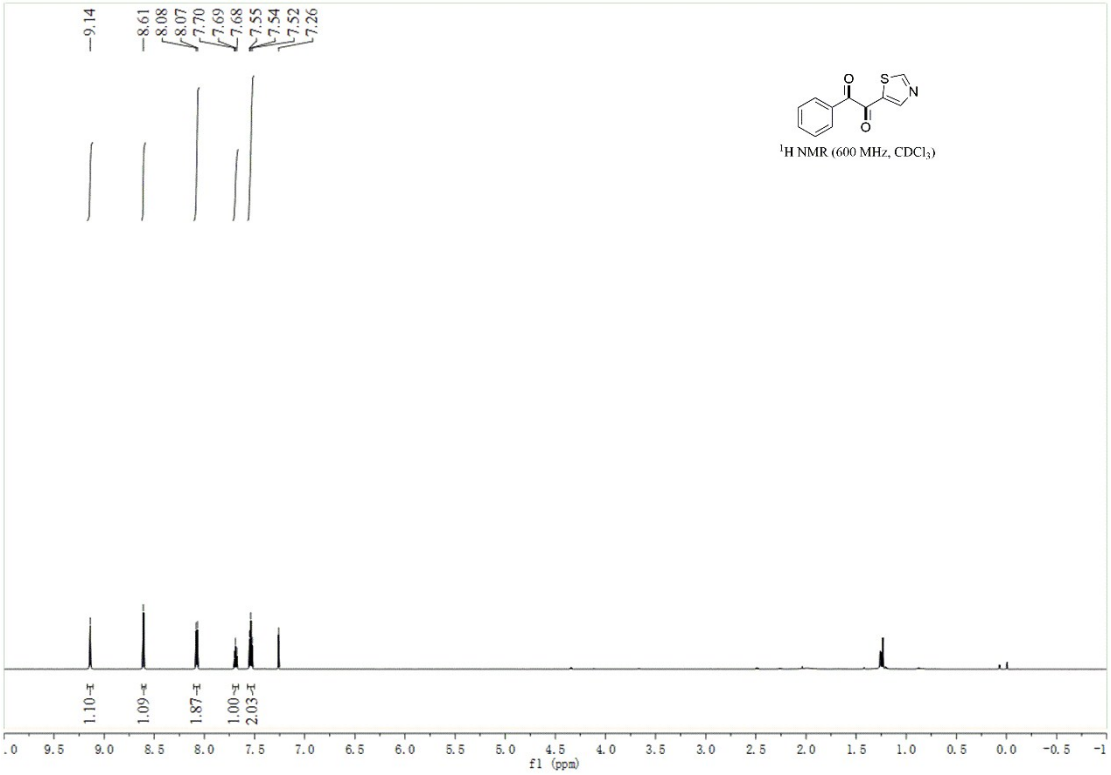


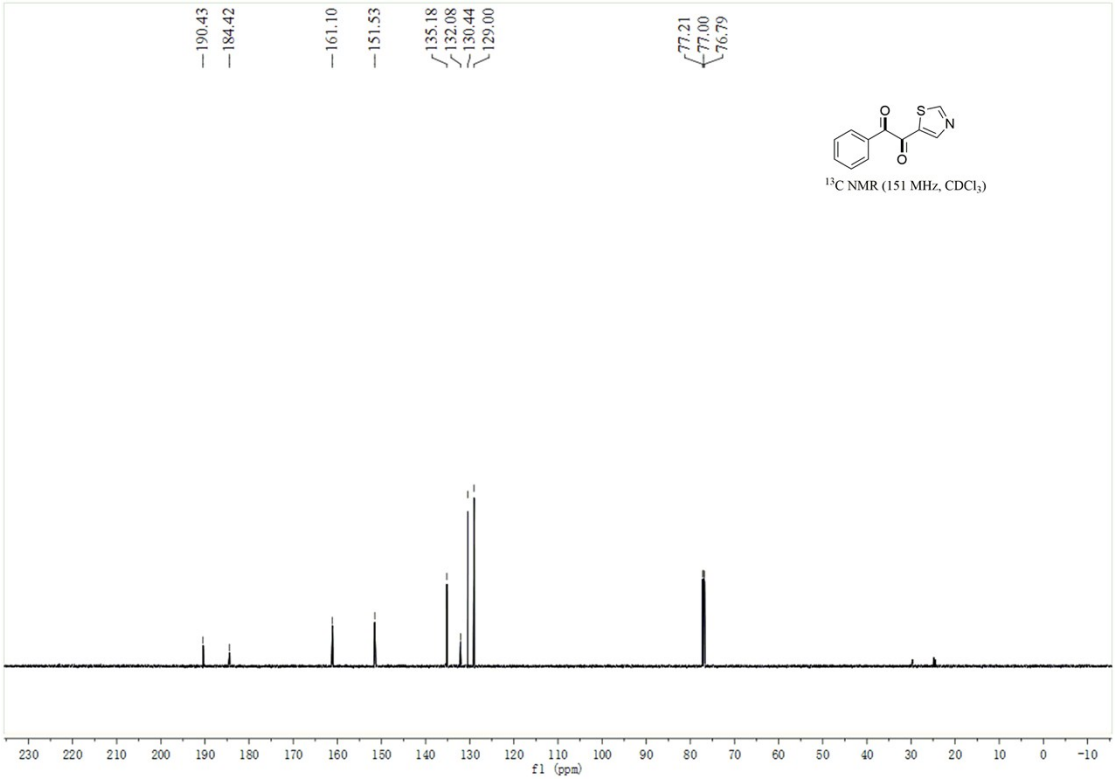
3,3-dimethyl-1-phenylbutane-1,2-dione (29)



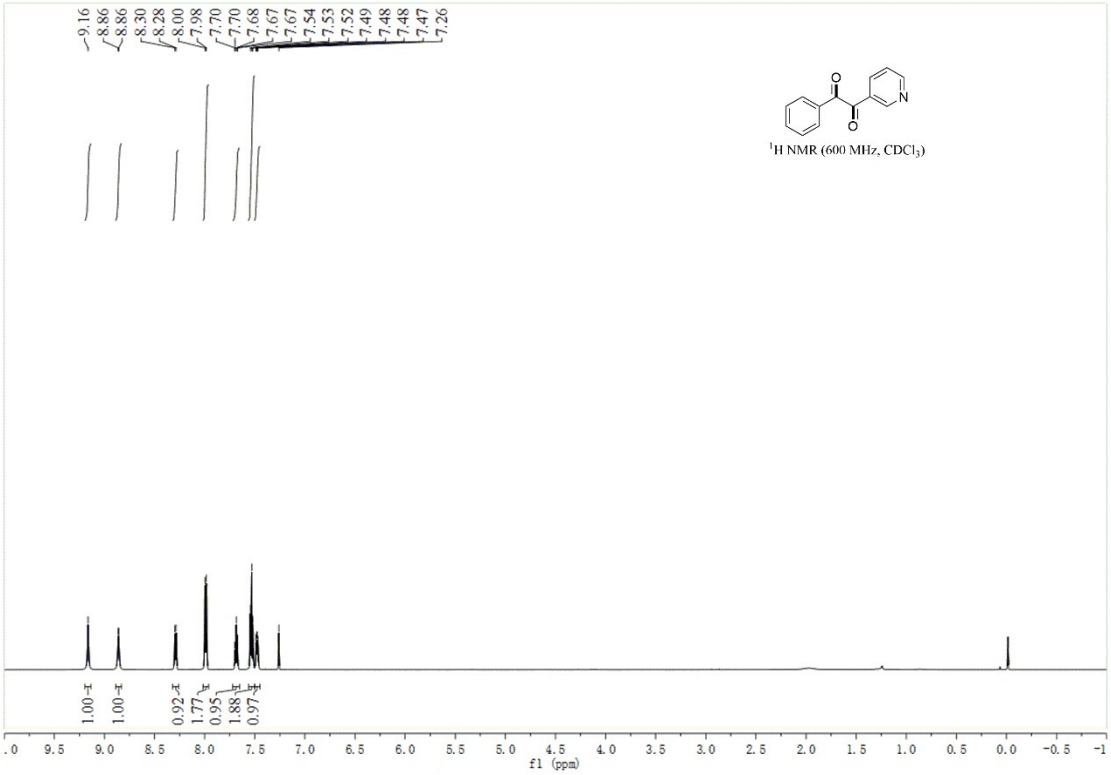


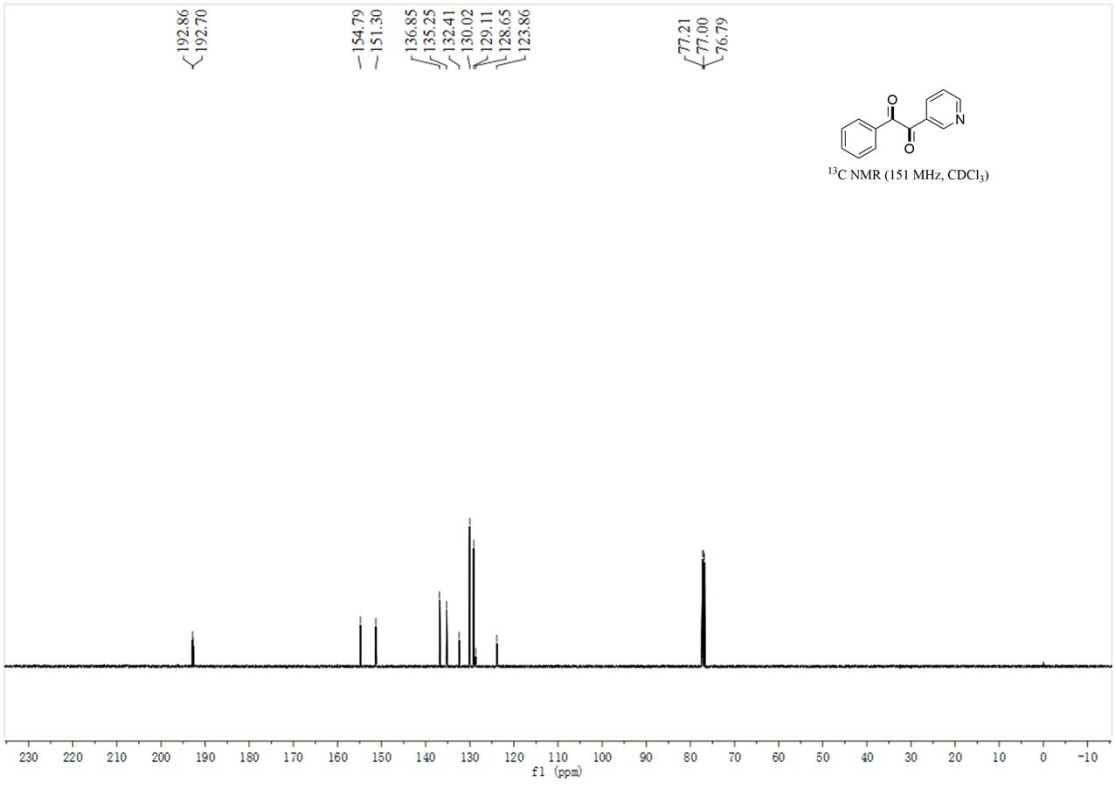
1-phenyl-2-(thiazol-5-yl) ethane-1,2-dione (30)



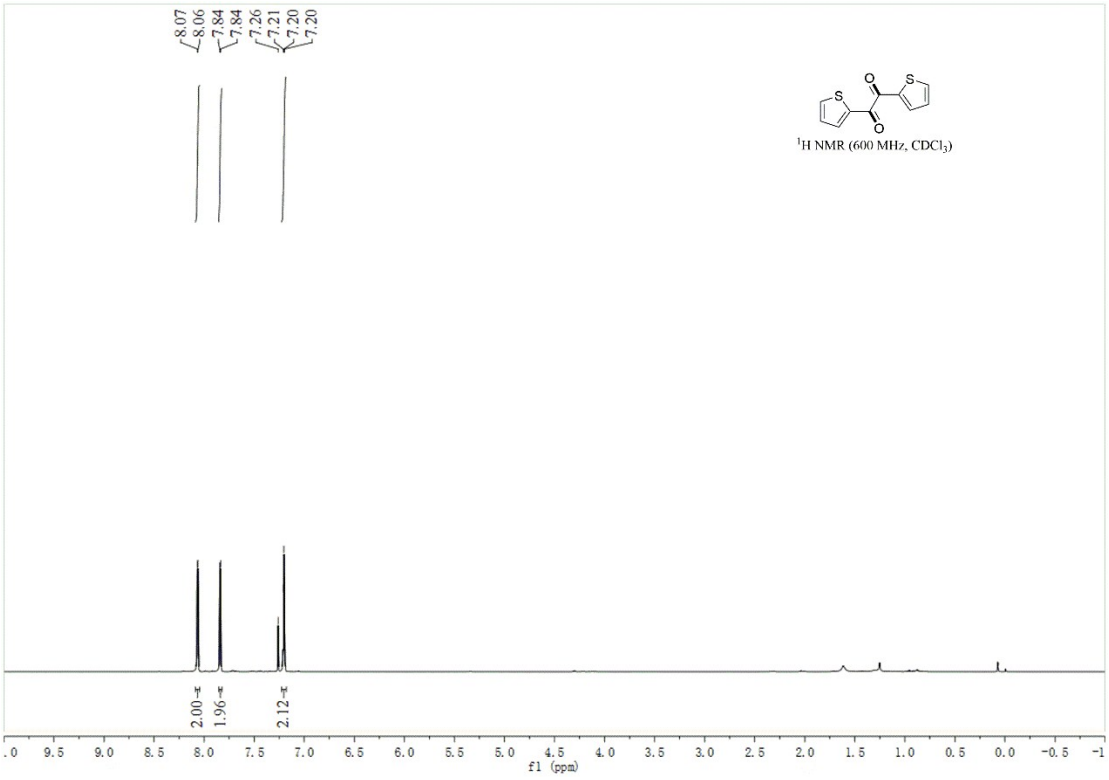


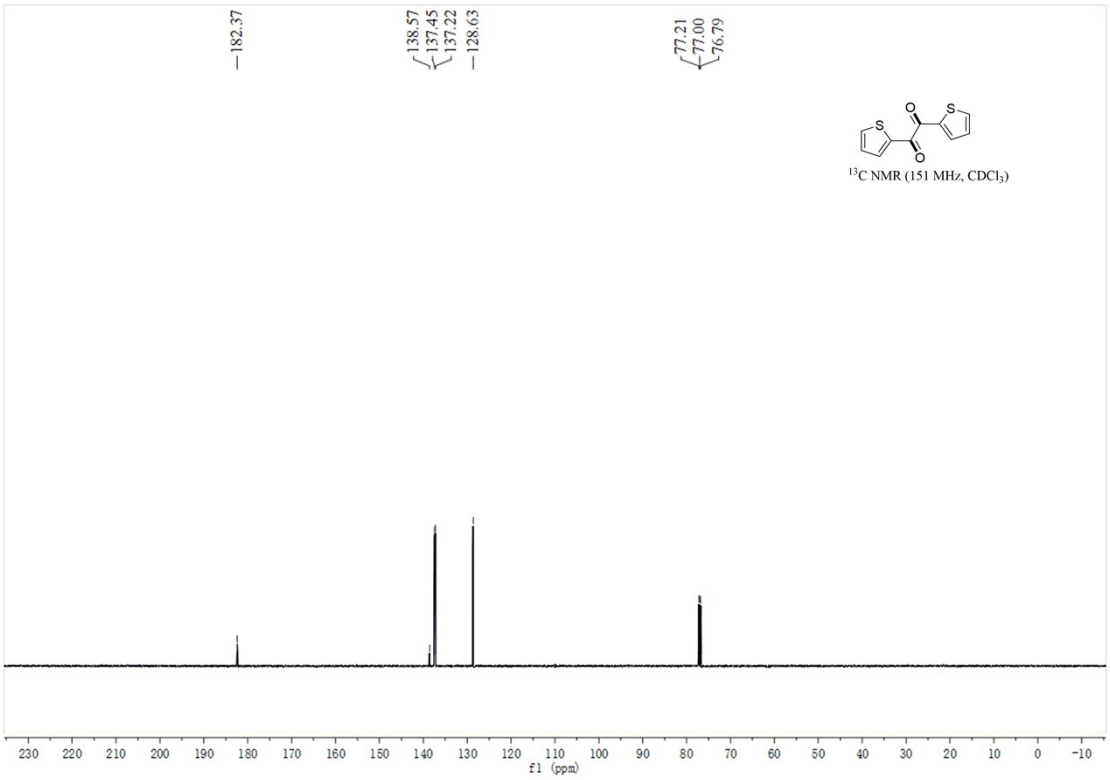
1-phenyl-2-(pyridin-3-yl) ethane-1,2-dione (31)



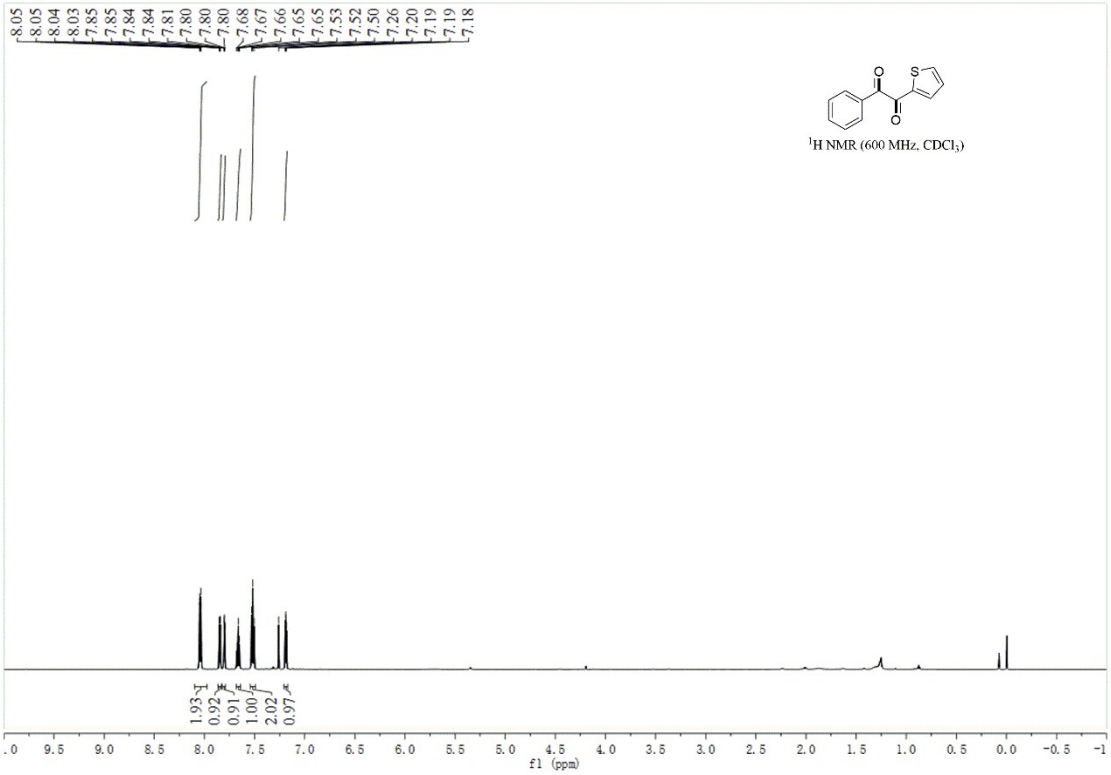


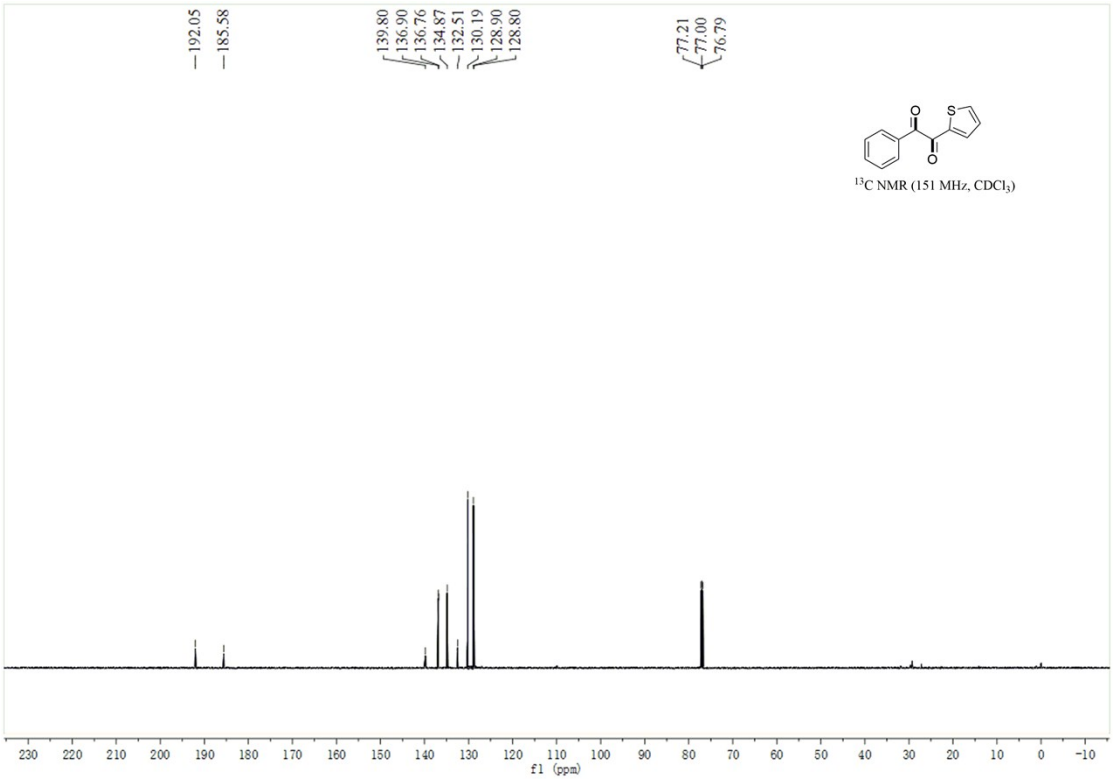
1,2-di(thiophen-2-yl)ethane-1,2-dione (32)



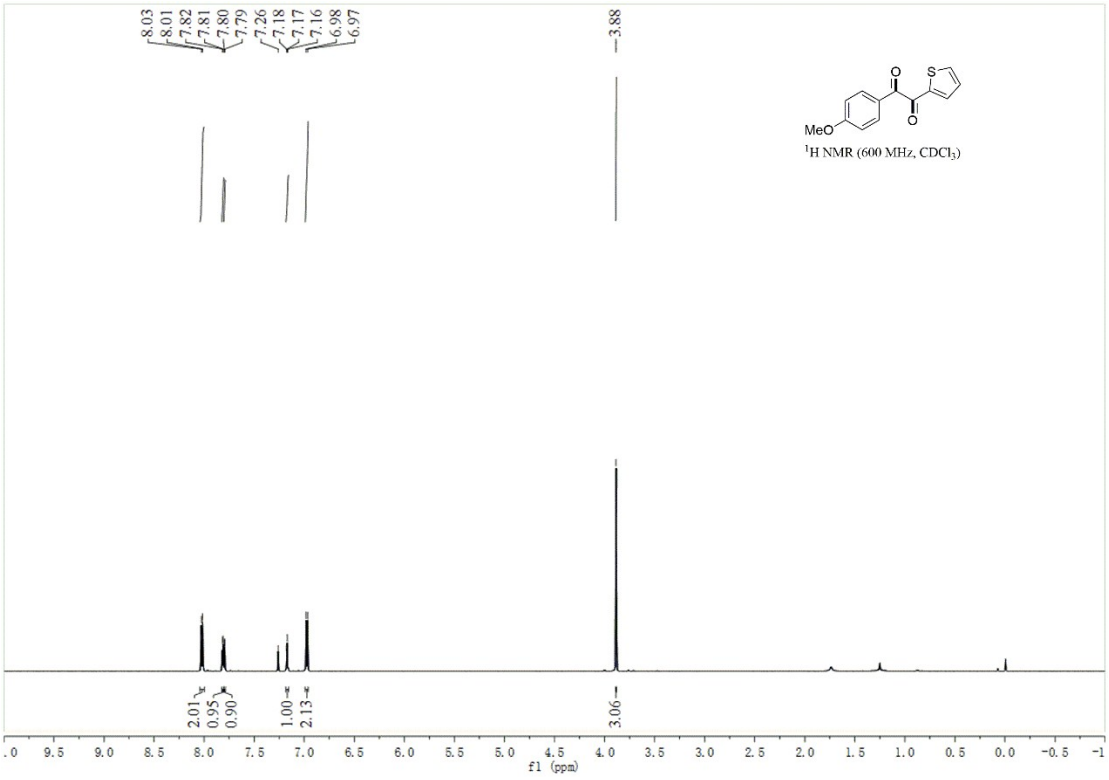


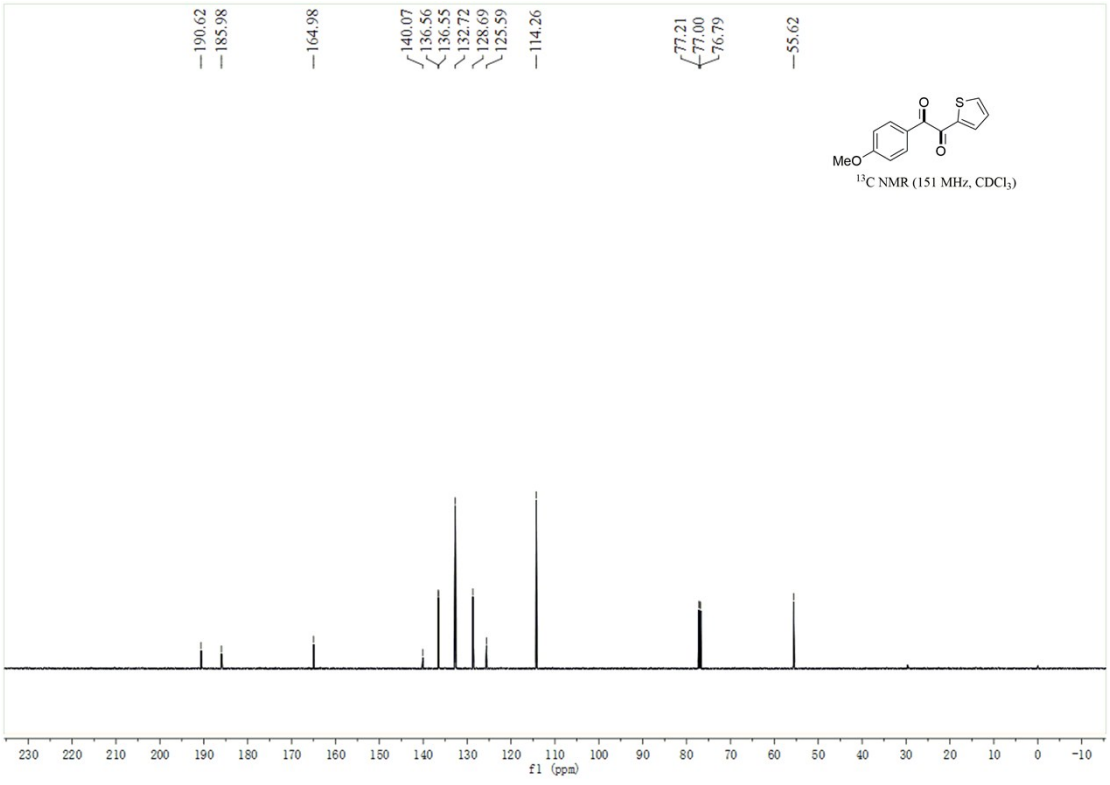
1-phenyl-2-(thiophen-2-yl)ethane-1,2-dione (33)



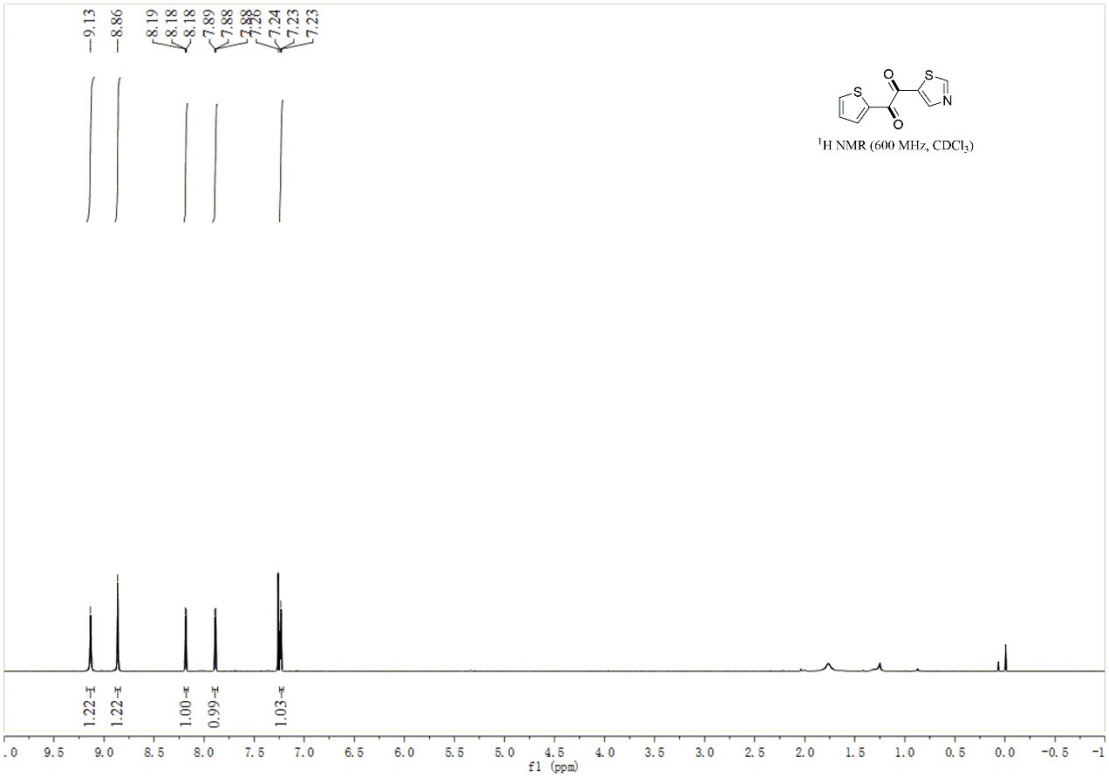


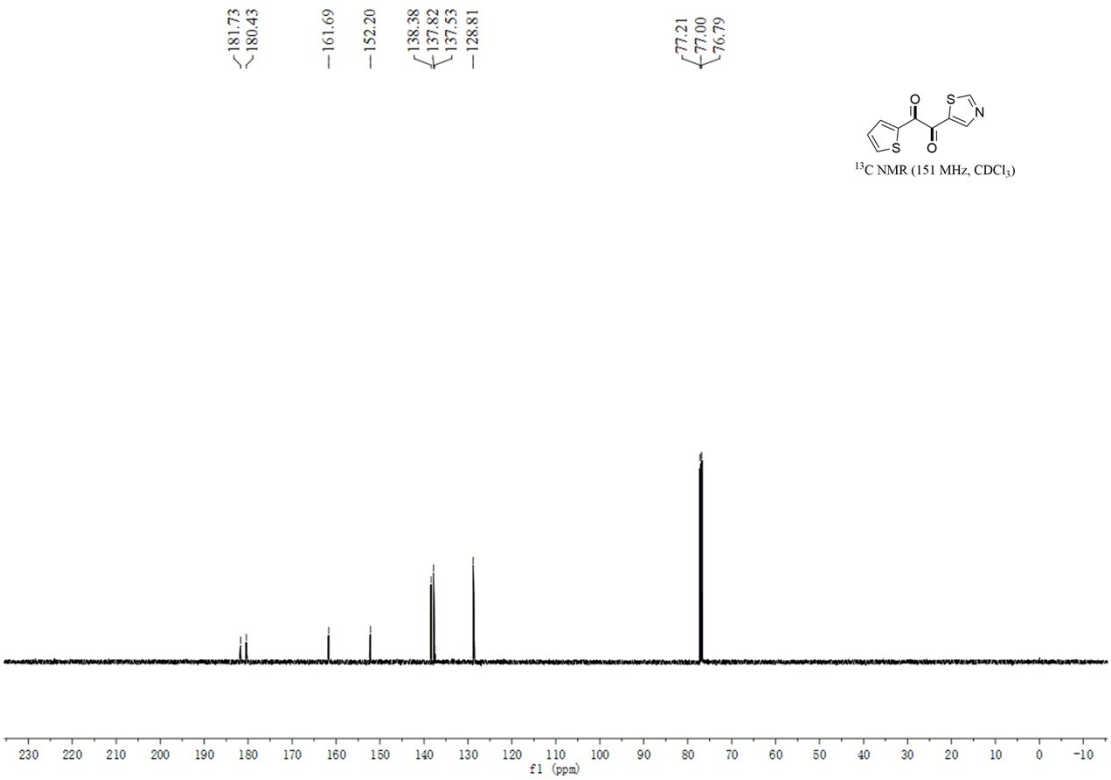
1-(4-methoxyphenyl)-2-(thiophen-2-yl) ethane-1,2-dione (34)



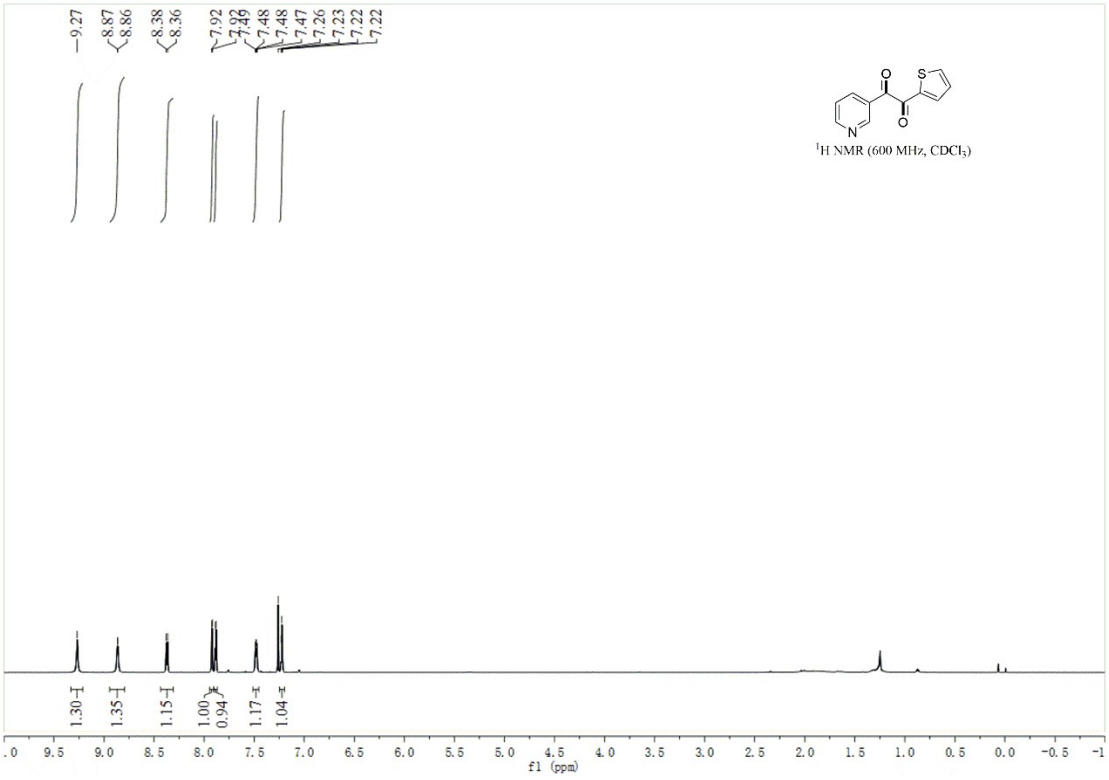


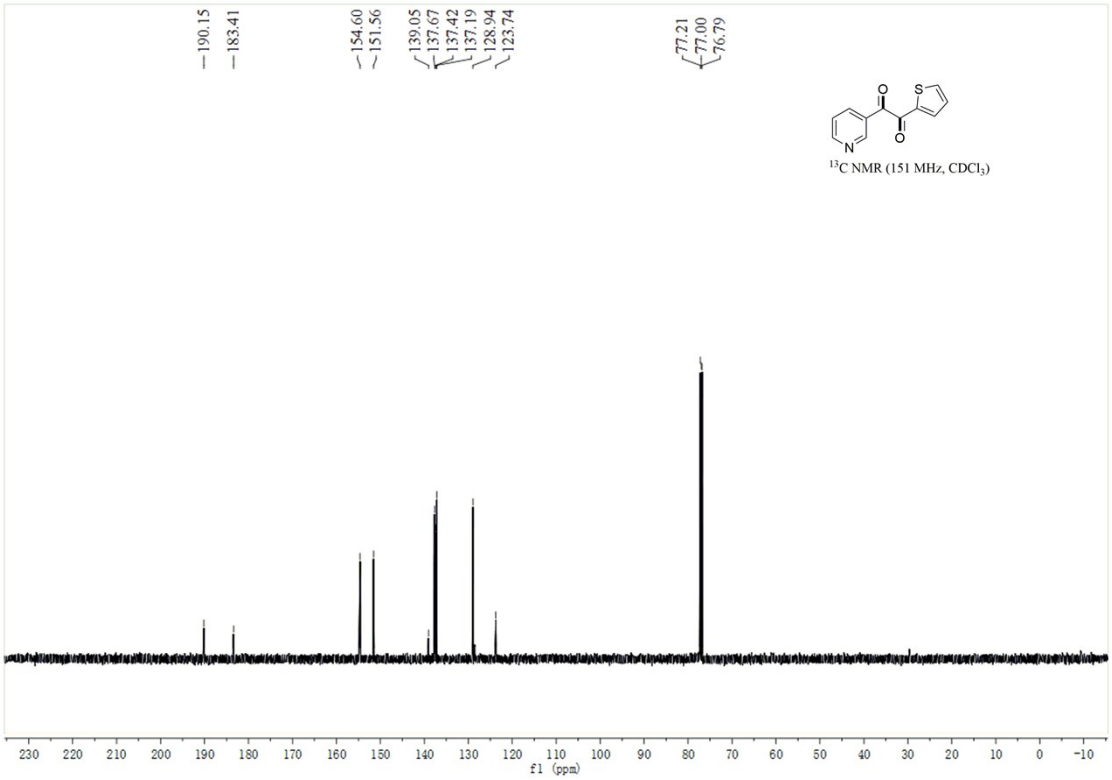
1-(thiazol-5-yl)-2-(thiophen-2-yl)ethane-1,2-dione (35)



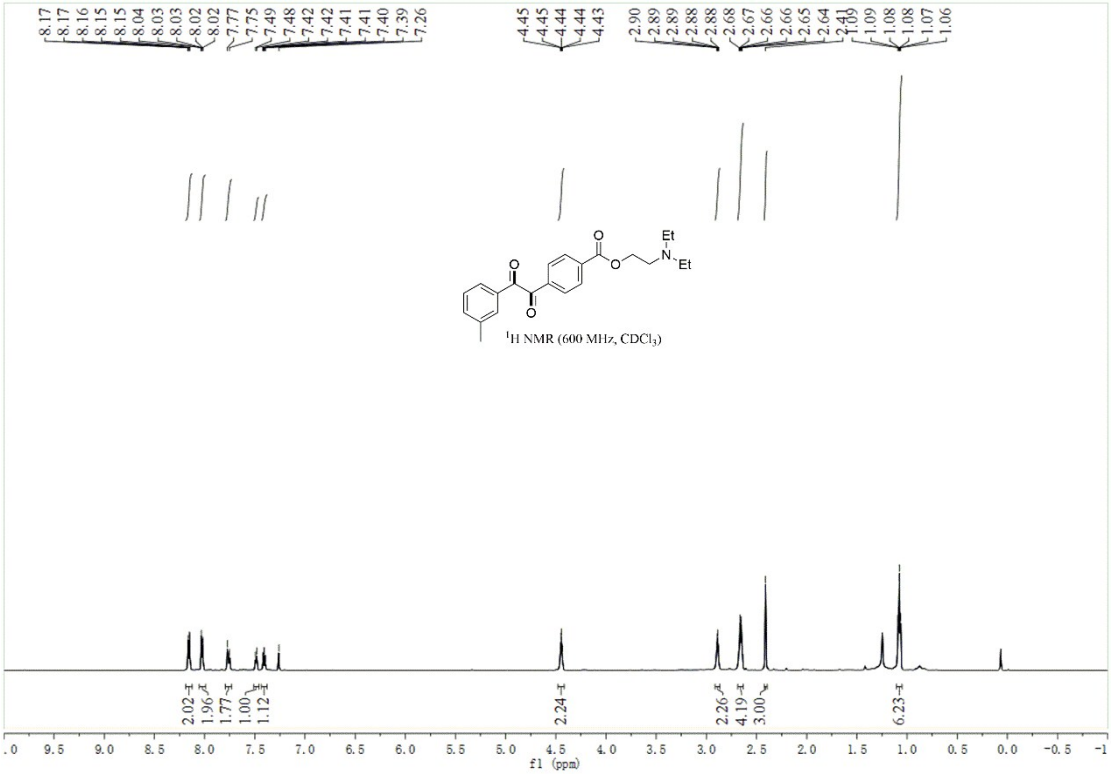


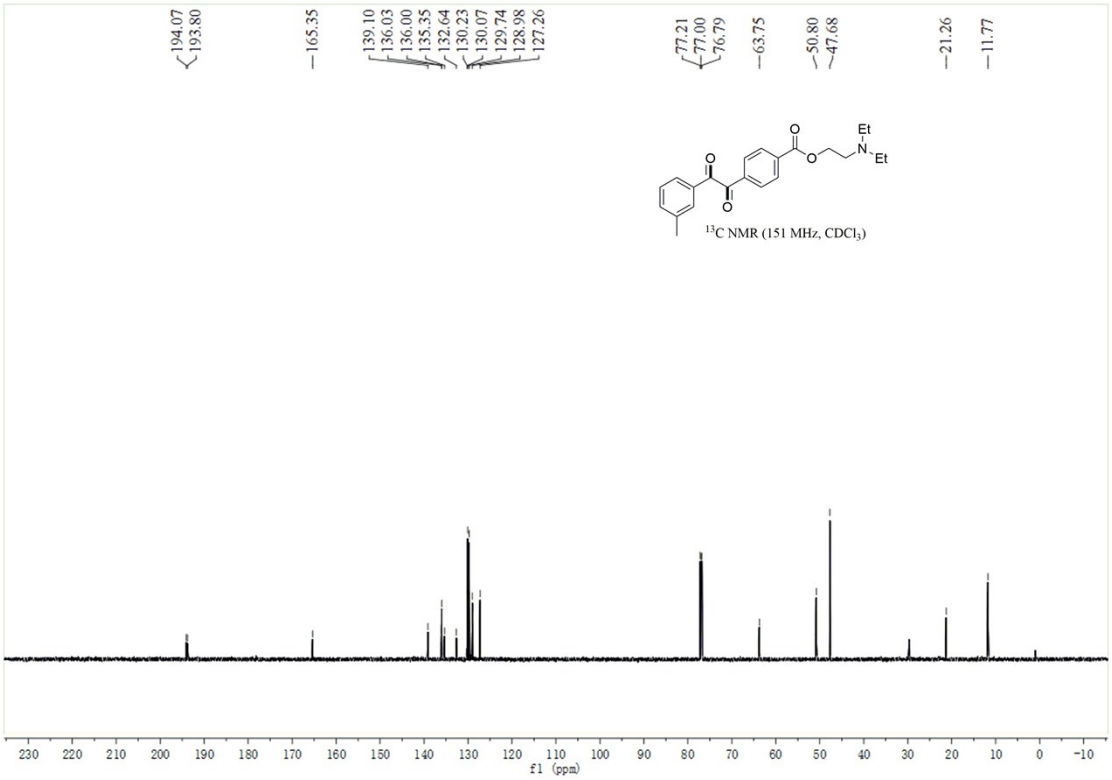
1-(pyridin-3-yl)-2-(thiophen-2-yl)ethane-1,2-dione (36)



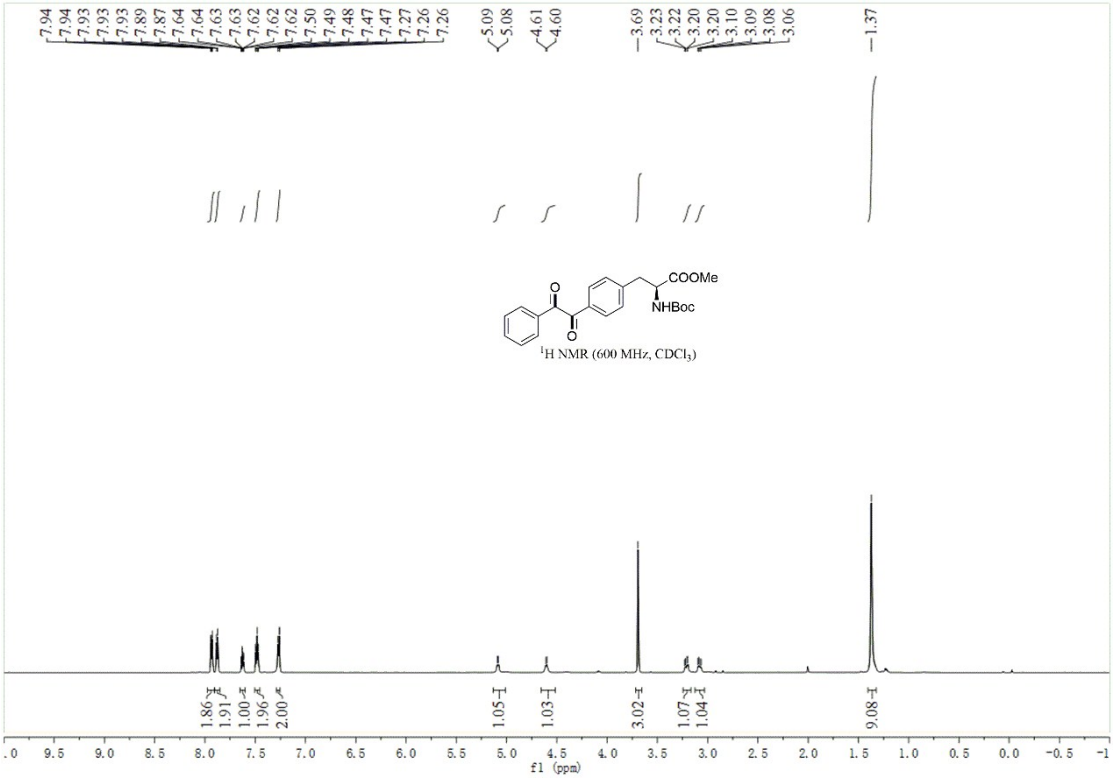


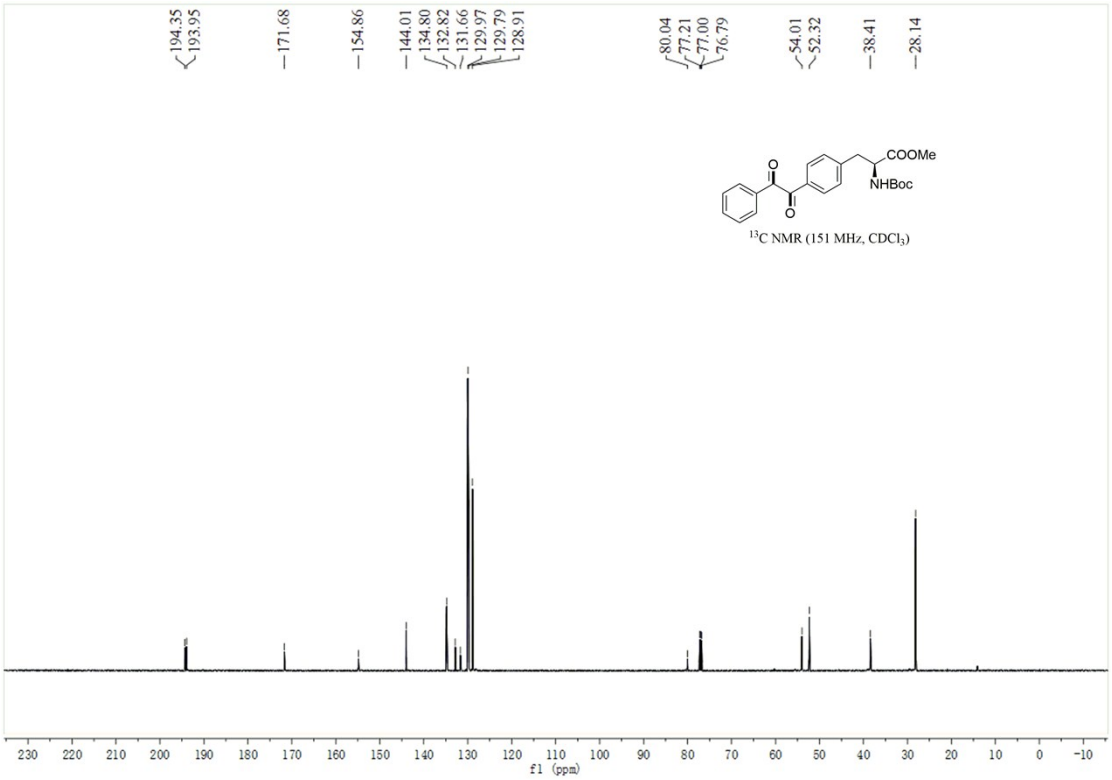
2-(diethylamino)ethyl 4-(2-oxo-2-(m-tolyl)acetyl)benzoate (37)



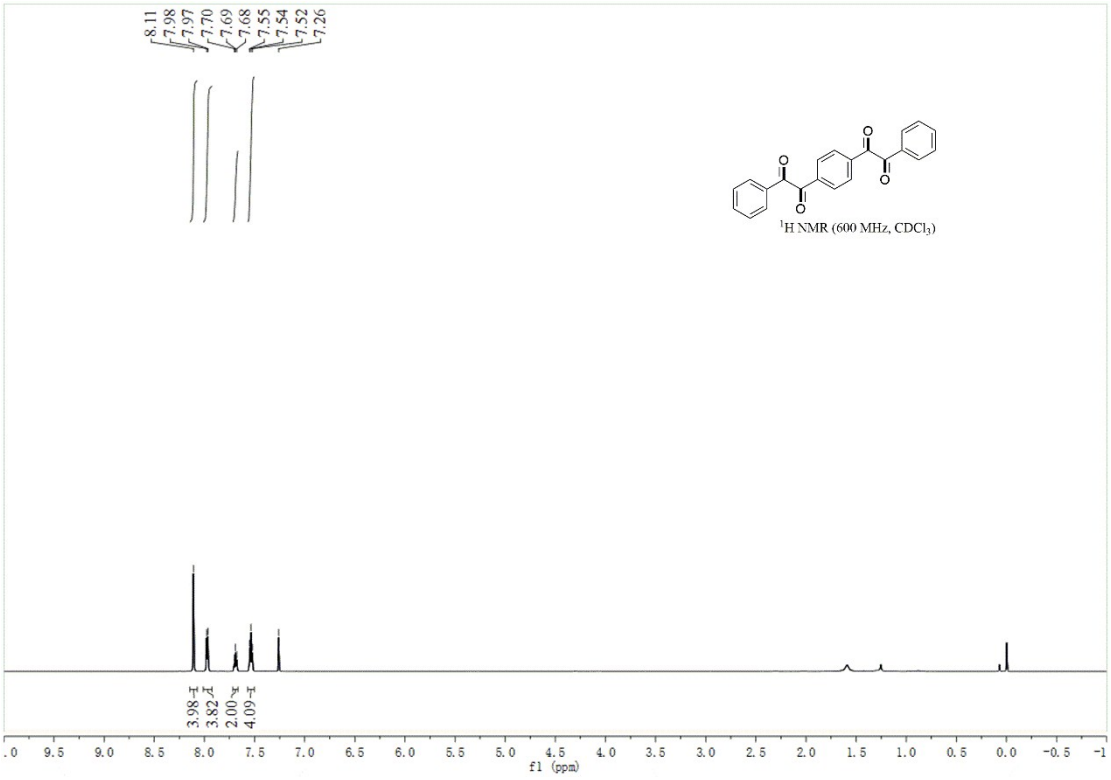


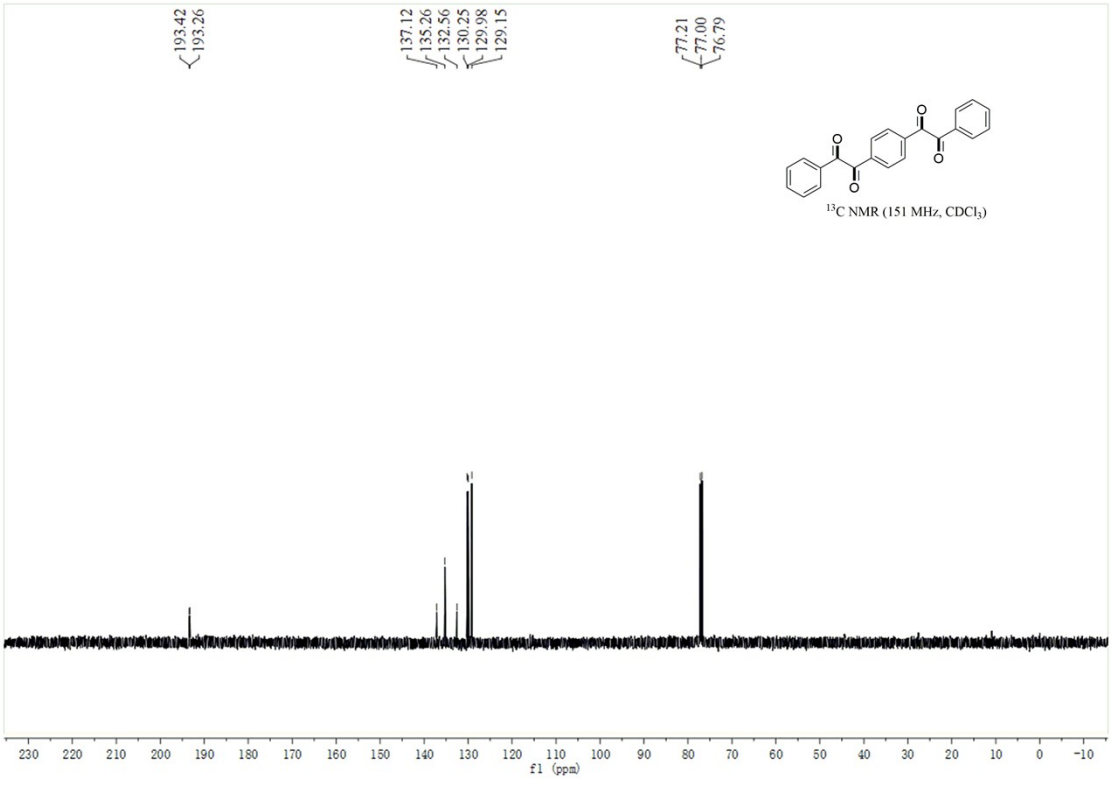
methyl2-((tert-butoxycarbonyl)amino)-3-(4-(2-oxo-2-phenylacetyl)phenyl)propanoate (38)



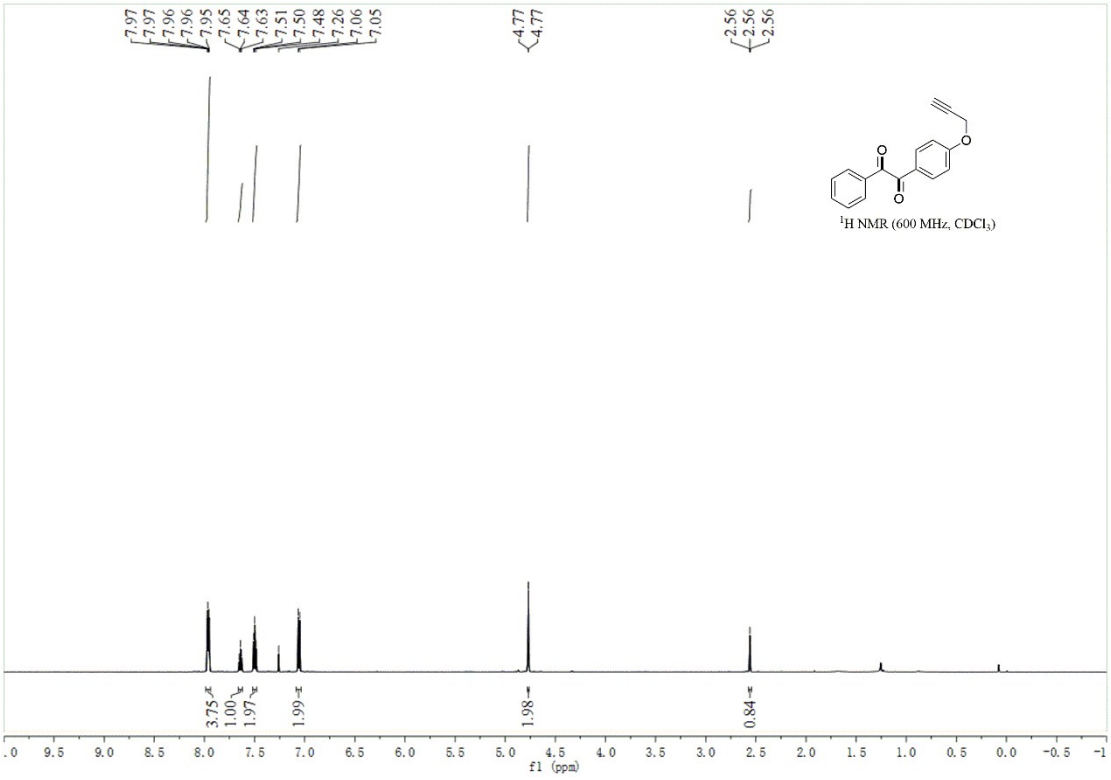


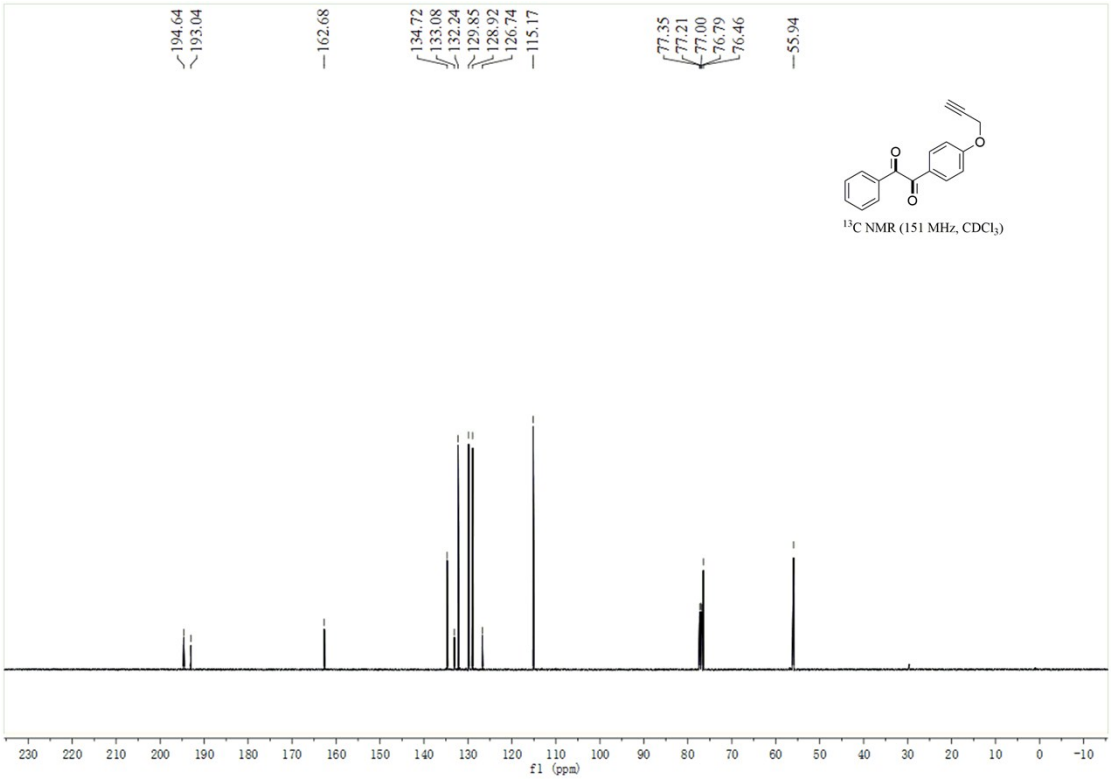
2,2'-(1,4-phenylene)bis(1-phenylethane-1,2-dione) (40)



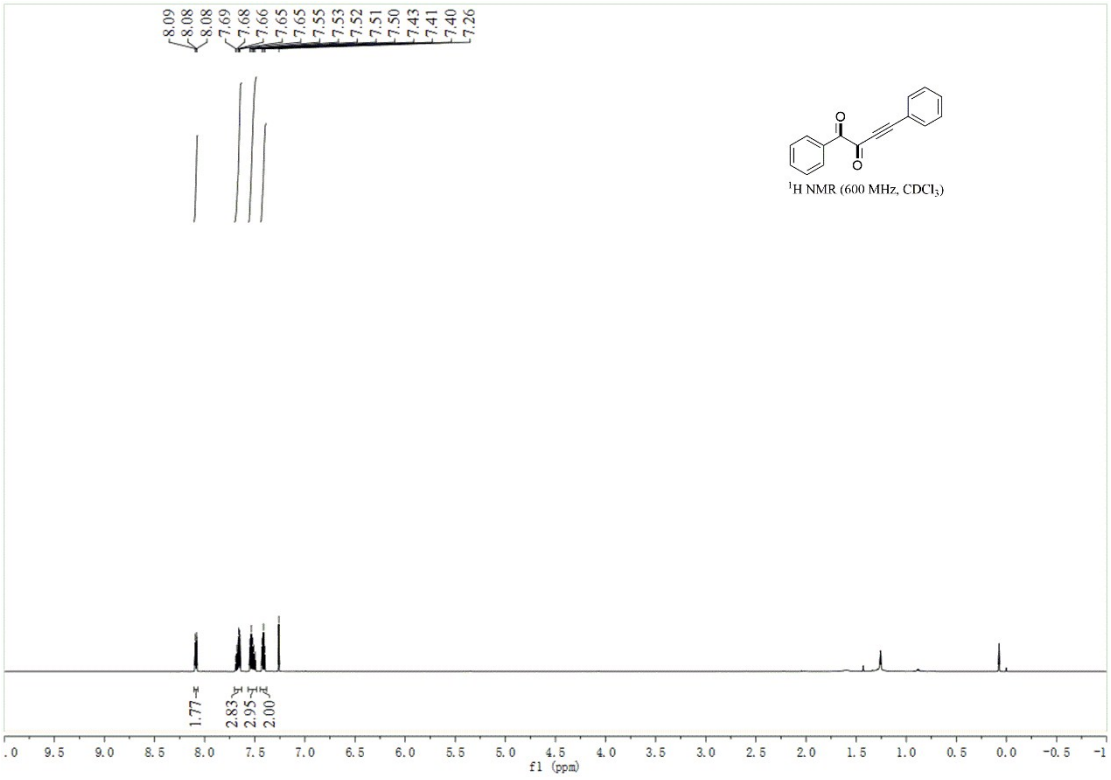


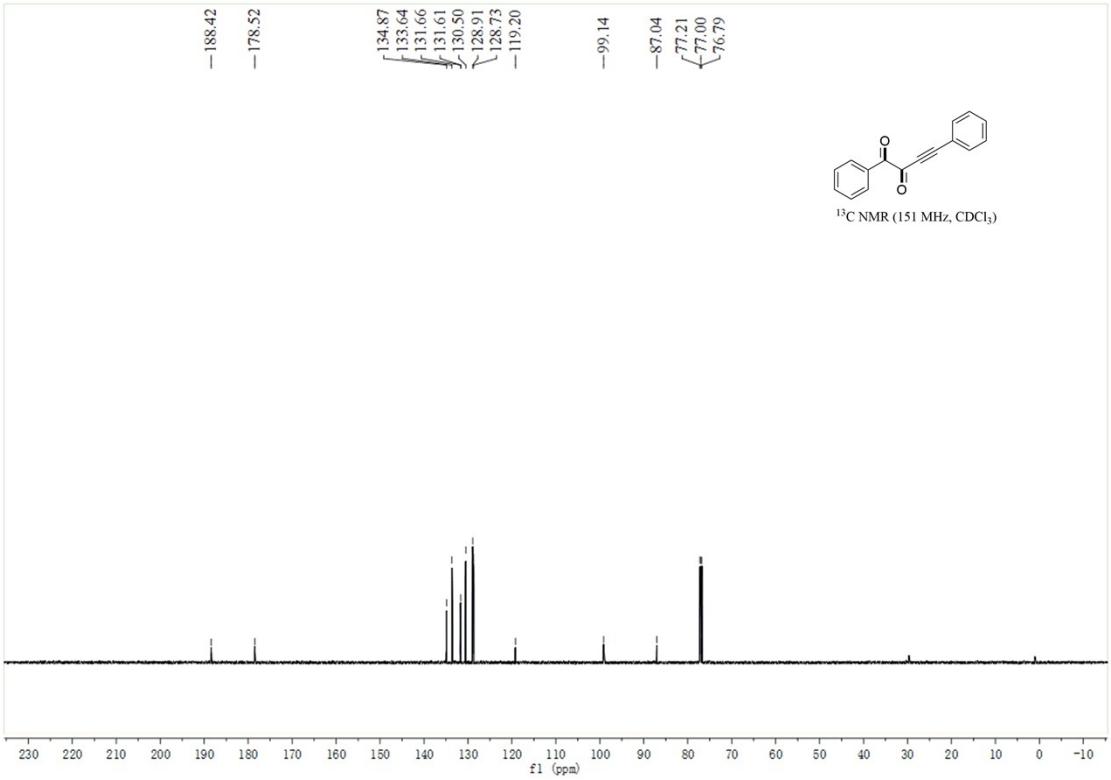
1-(4-(allyloxy)phenyl)-2-phenylethane-1,2-dione (42)



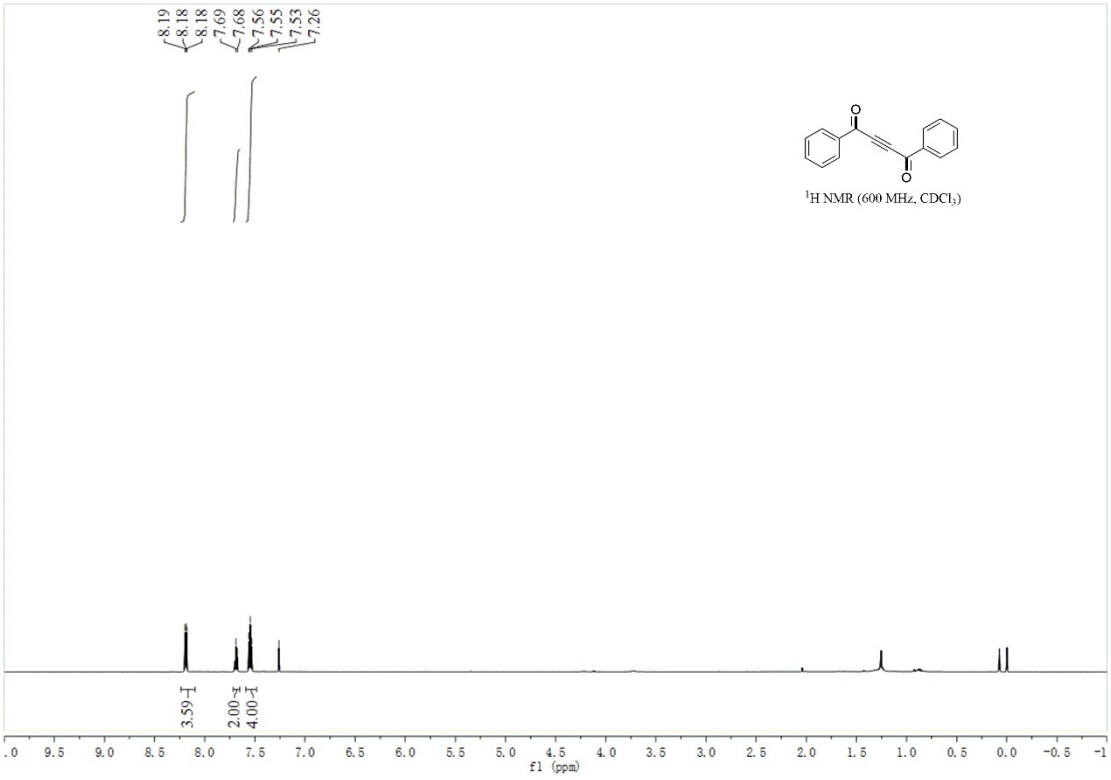


1,4-diphenylbut-3-yne-1,2-dione (44)

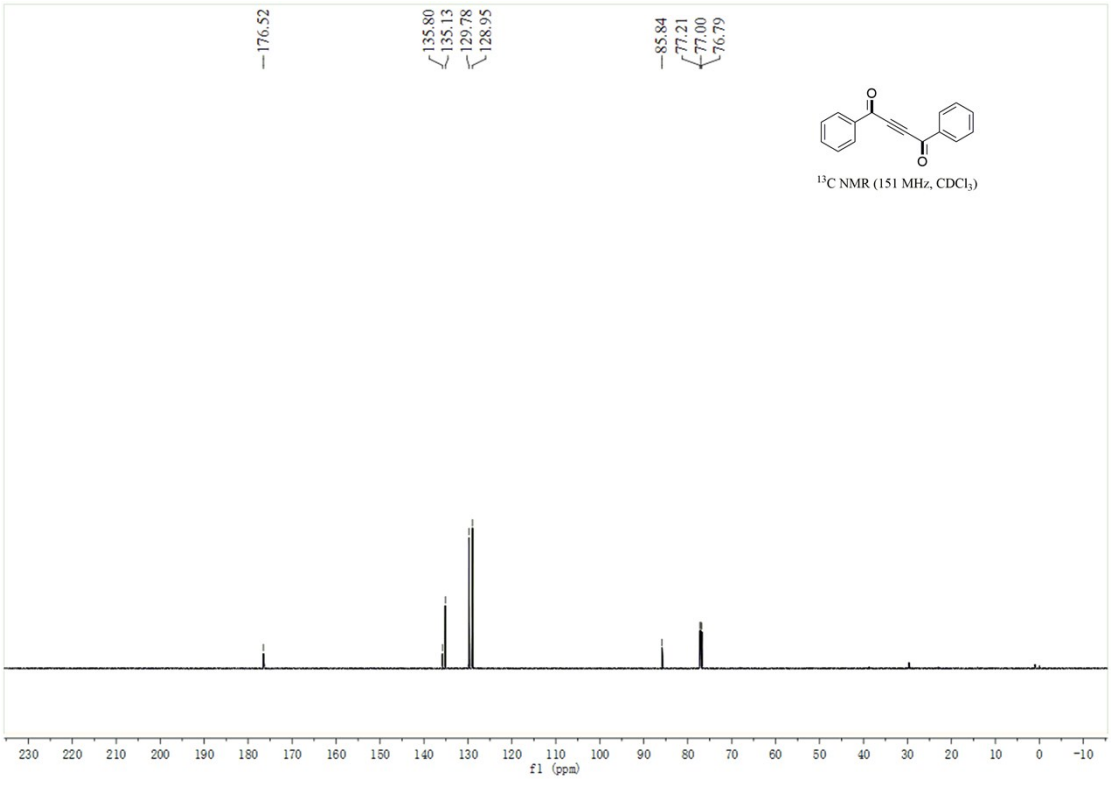




1,4-diphenylbut-2-yne-1,4-dione (45):



^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)