Transition metal-free, photocatalytic arylation and deoxygenation for vicinal diketone synthesis using alkynes and arene diazonium salts

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Content

General ……2

Preparation of Arenediazonium Salts……2

Typical procedure for the products……2

Typical Procedure for products 3a on gram-scale……3

General experimental procedure for the synthesis of desired product via the one-pot, two-step process……3

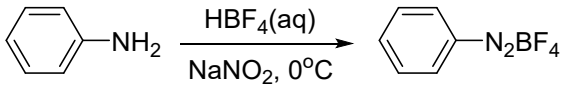
Characterization data of the product……4

References……31

General

Reagents and solvents were used as it is obtained from commercial vendors. Products were purified by column chromatography on silica gel (300–400 mesh). ^{1}H and ^{13}C NMR spectra were obtained on Bruker–400 (500) MHz spectrometers using tetramethylsilane as internal standard in $CDCl_3$. Chemical shifts of ^{1}H NMR and ^{13}C NMR are reported as δ values relative to TMS and $CDCl_3$ respectively. Chemical shifts were reported in parts per million (ppm, δ). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad resonances (br). GC-MS data were collected on Gas Chromatography-mass spectrometer.

Preparation of Arenediazonium Salts



To a suspension of aryl amine (10.0 mmol) in water at room temperature was added HBF_4 (48% in water, 20.0 mmol, 2.0 equiv) and the reaction mixture was stirred for 2 min. The mixture was cooled to 0 °C and a solution of $NaNO_2$ (10.0 mmol, 1.0 equiv) in water (8.3 M) was added drop-wise. After addition the reaction mixture was stirred at 0 °C for 15 min. The solids were filtered, washed with ice-cold water (5 mL) and diethyl ether (10 mL) to give the crude product. This was purified by precipitation with diethyl ether from an acetone solution to obtain arenediazonium salt (**1a**) as

solid.

Typical procedure for the product

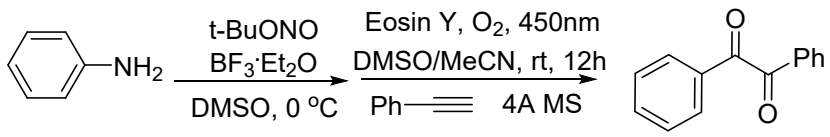
To a 25 mL-schlenk tube charged with a stirring bar, was added arenediazonium tetrafluoroborates (0.5 mmol), aryl acetylenes (0.5 mmol), Eosin Y (2 mol %), 4 Å molecular sieves (40 mg, 2 wt%) and anhydrous MeCN (1.5 mL)/DMSO (0.5 mL) under oxygen (1 atm) with light irradiation using 3 W blue LED for 12 h. The reaction mixture was then diluted with and water, extracted with Et_2O (2 mL×3). The organic layers were dried over Na_2SO_4, then the organic solvent was removed under reduced pressure. The residues were purified by flash column chromatography on silica with an appropriate solvent to afford the pure product.

Typical Procedure for products 3a on gram-scale

To a 100 mL-schlenk tube charged with a stirring bar, was added phenyldiazonium tetrafluoroborates (5 mmol), aryl acetylenes (5 mmol), Eosin Y (2 mol %), 4 Å molecular sieves (400 mg, 2 wt%) and anhydrous MeCN (15 mL)/DMSO (5 mL) under oxygen (1 atm) with light irradiation using 3 W blue LED for 12 h. The reaction mixture was then diluted with and water, extracted with Et_2O (2 mL×3). The organic layers were dried over Na_2SO_4, then the organic solvent was removed under reduced pressure. The residues were purified by flash column chromatography on silica with an appropriate solvent to afford the desired benzil product.

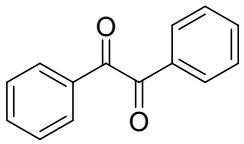
General experimental procedure for the synthesis of desired product via the one-

pot, two-step process

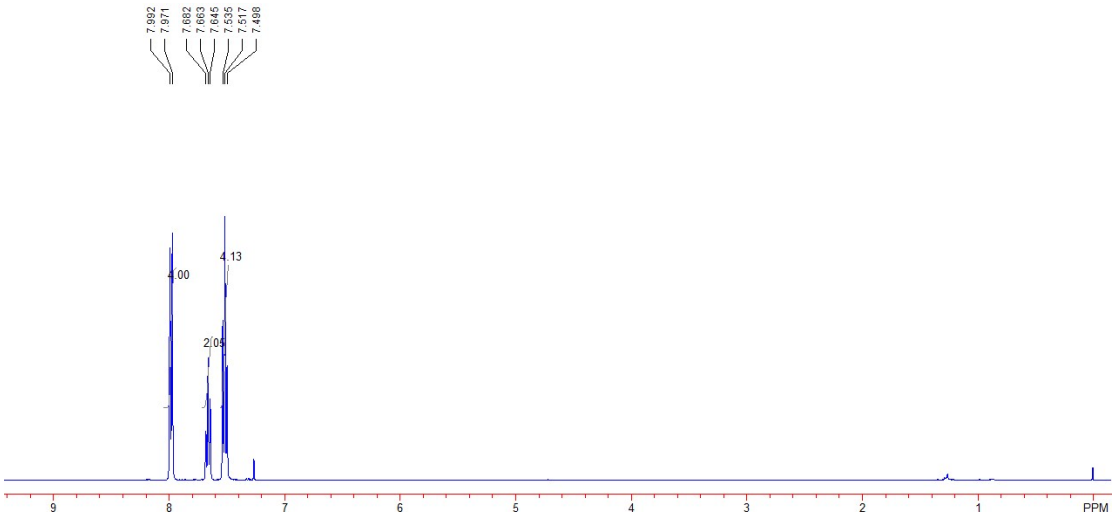


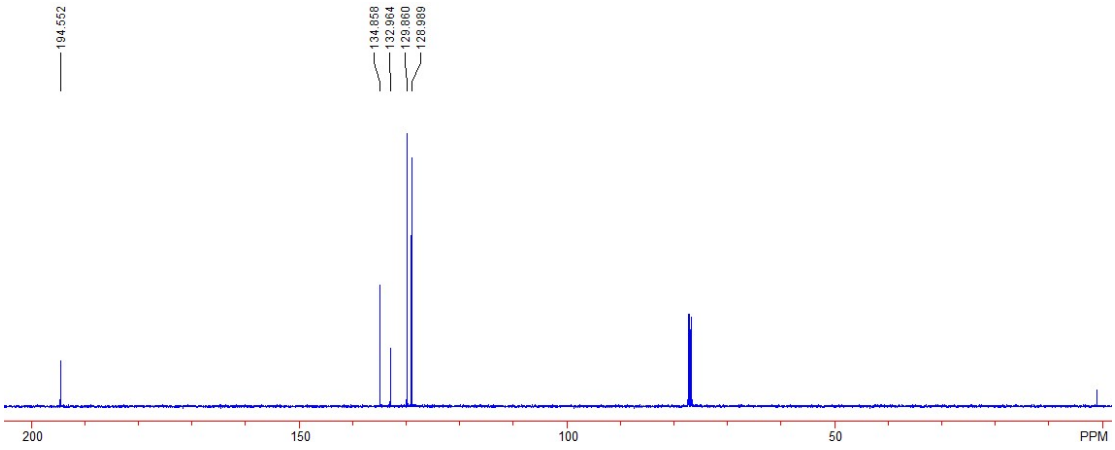
t-BuONO (0.8 mmol) was added dropwisely to a solution of aniline (0.5 mmol) and $BF_3 \cdot Et_2O$ (0.8 mmol) in DMSO (1 mL) under 0 °C. After 10 minutes, the above mixture was added to a solution of phenyl acetylene (0.5 mmol), 4 Å molecular sieves (40 mg, 12 wt %) and eosin Y (0.01 mmol) in MeCN (3 mL) under oxygen protection via a syringe. The reaction was stirred at room temperature under light irradiation using 3 W blue LED for about 12 hours. After completion of reaction as indicated by TLC, the reaction mixture was then diluted with and water, extracted with Et_2O (3 mL×3). The organic layers were dried over Na_2SO_4, then the organic solvent was removed under reduced pressure. The residues were purified by flash column chromatography on silica with an appropriate solvent to to give the desired benzil product.

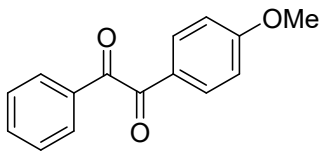
Characterization data of the product



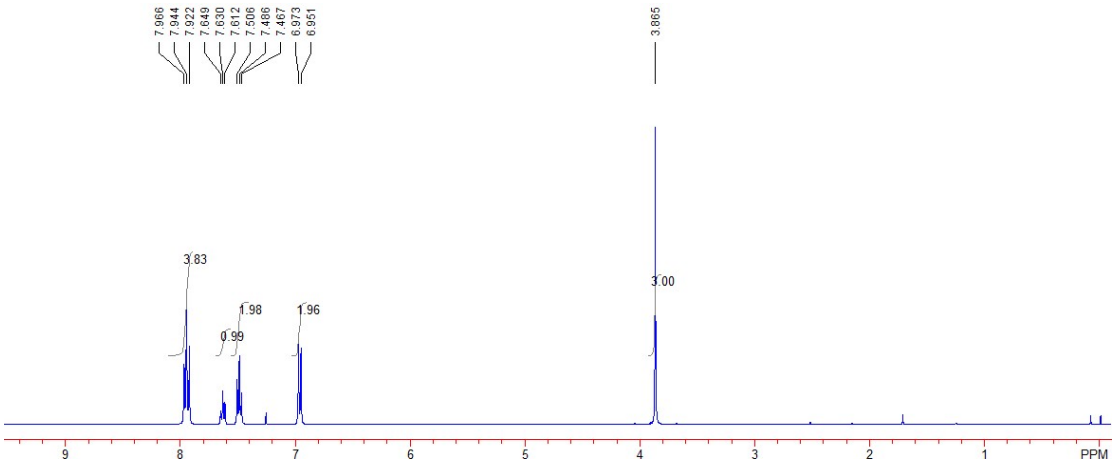
Benzil (3a). 79 mg, 75% yield; white solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 93 – 95 °C (lit.[1] 95 – 97 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.98 (d, J = 8.4 Hz, 4H), 7.67 (t, J = 7.6 Hz, 2H), 7.51 (t, J = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 134.9, 133.0, 129.9, 129.0. GC-MS (EI): m/z=210.09(M^+).

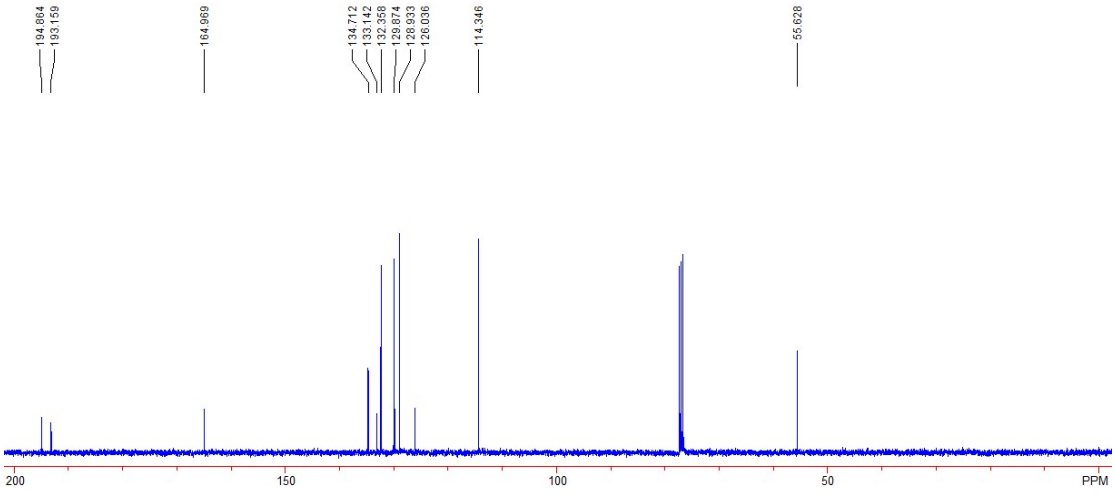


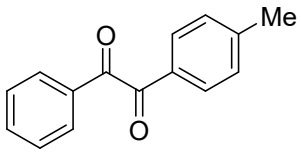




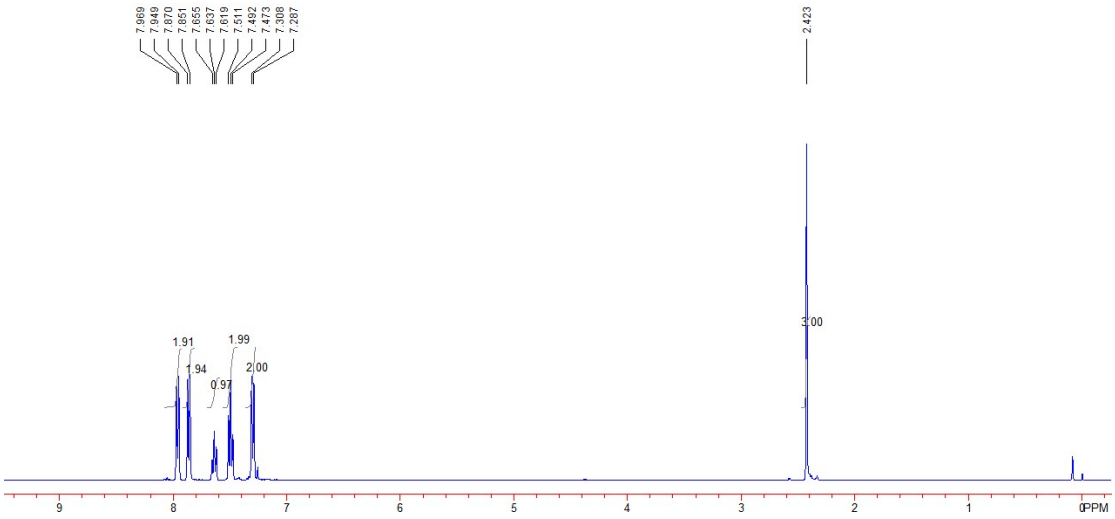
1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (3b). 82 mg, 68% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 62 – 63 °C (lit.[2] 63 – 64 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.94 (t, *J* = 8.8 Hz, 4H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 193.2, 165.0, 134.7, 133.1, 132.4, 129.9, 129.0, 126.0, 114.4, 55.6. GC-MS (EI): m/z=240.09(M^+).

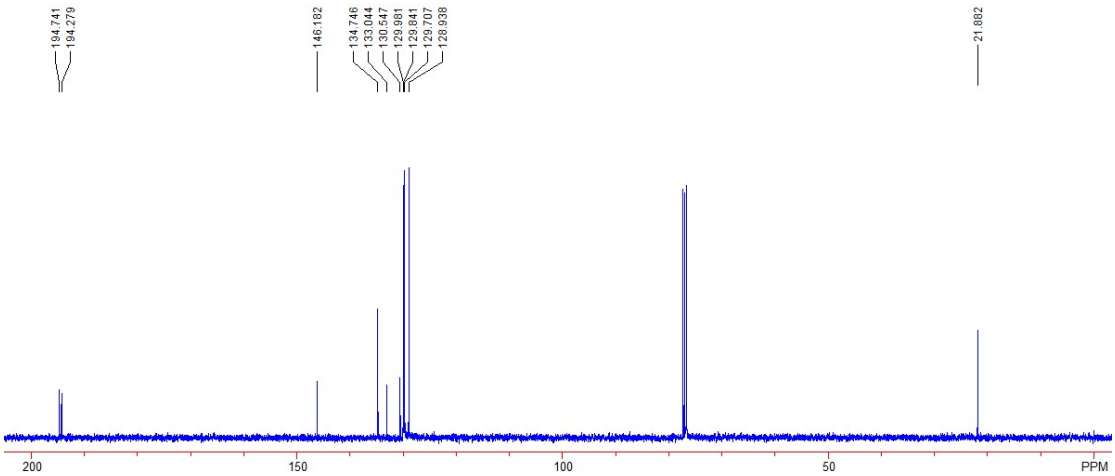


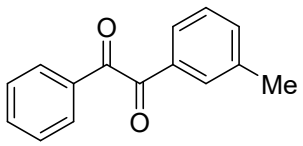




1-Phenyl-2-p-tolylethane-1,2-dione (3c). 82 mg, 73% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 32 – 33 °C (lit.[1] 30 – 31 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 194.3, 146.2, 134.8, 133.0, 130.6, 130.0, 129.8, 129.7, 128.9, 21.9; GC-MS (EI): m/z=224.07(M^+).

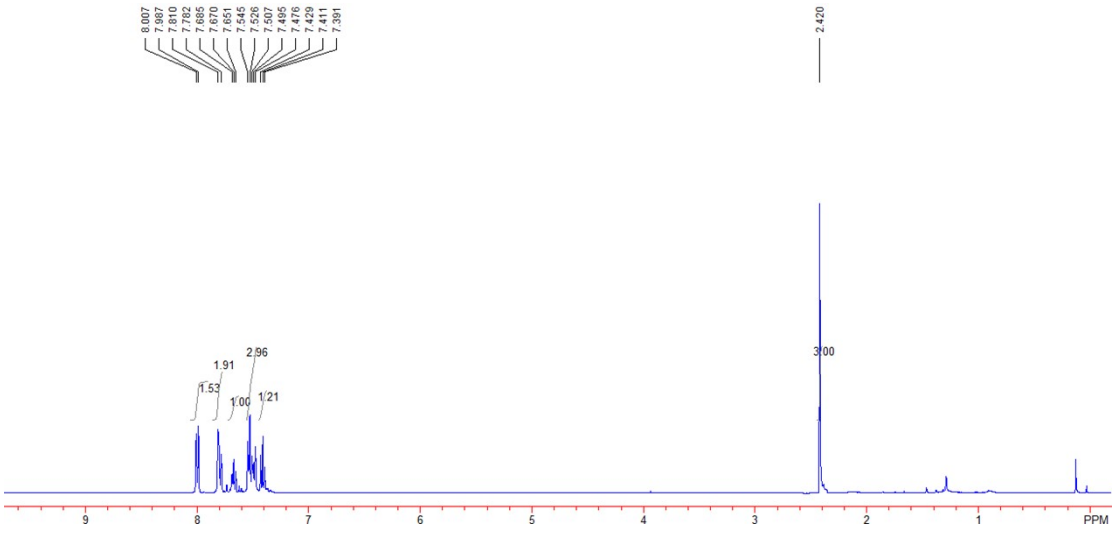


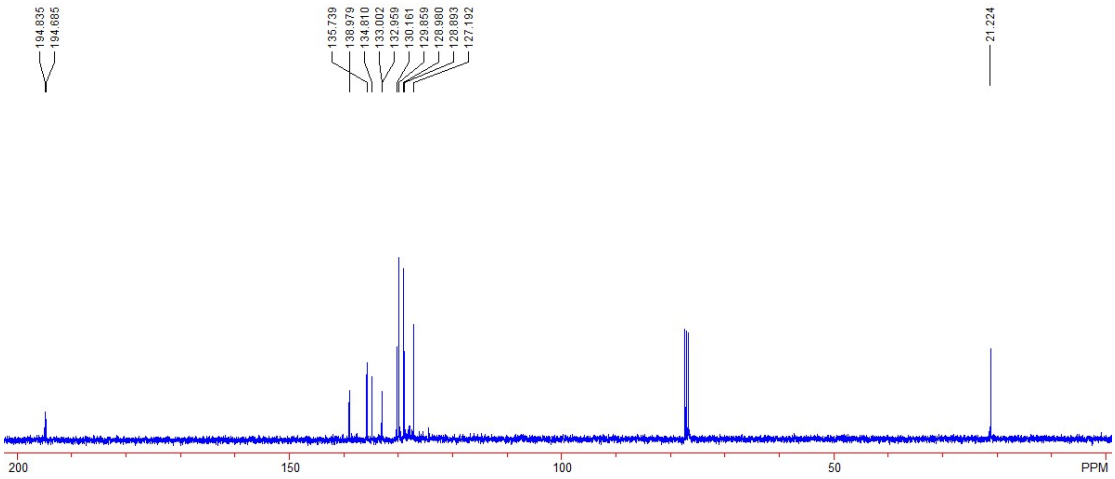




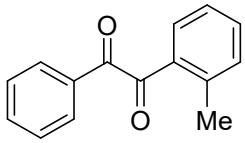
1-Phenyl-2-m-tolylethane-1,2-dione (3d). 77 mg, 69% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 57 – 59 °C (lit.[3] 56 – 57 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 11.2 Hz, 2H), 7.67 (t, *J* = 6.8 Hz, 1H), 7.47 – 7.55 (m, 3 H), 7.41 (t, *J* = 7.6 Hz, 1H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 194.7, 139.0, 135.7, 134.8, 133.0, 133.0, 130.2, 129.9, 129.0, 128.9,

127.2, 21.2; GC-MS (EI): m/z=224.08(M^+).

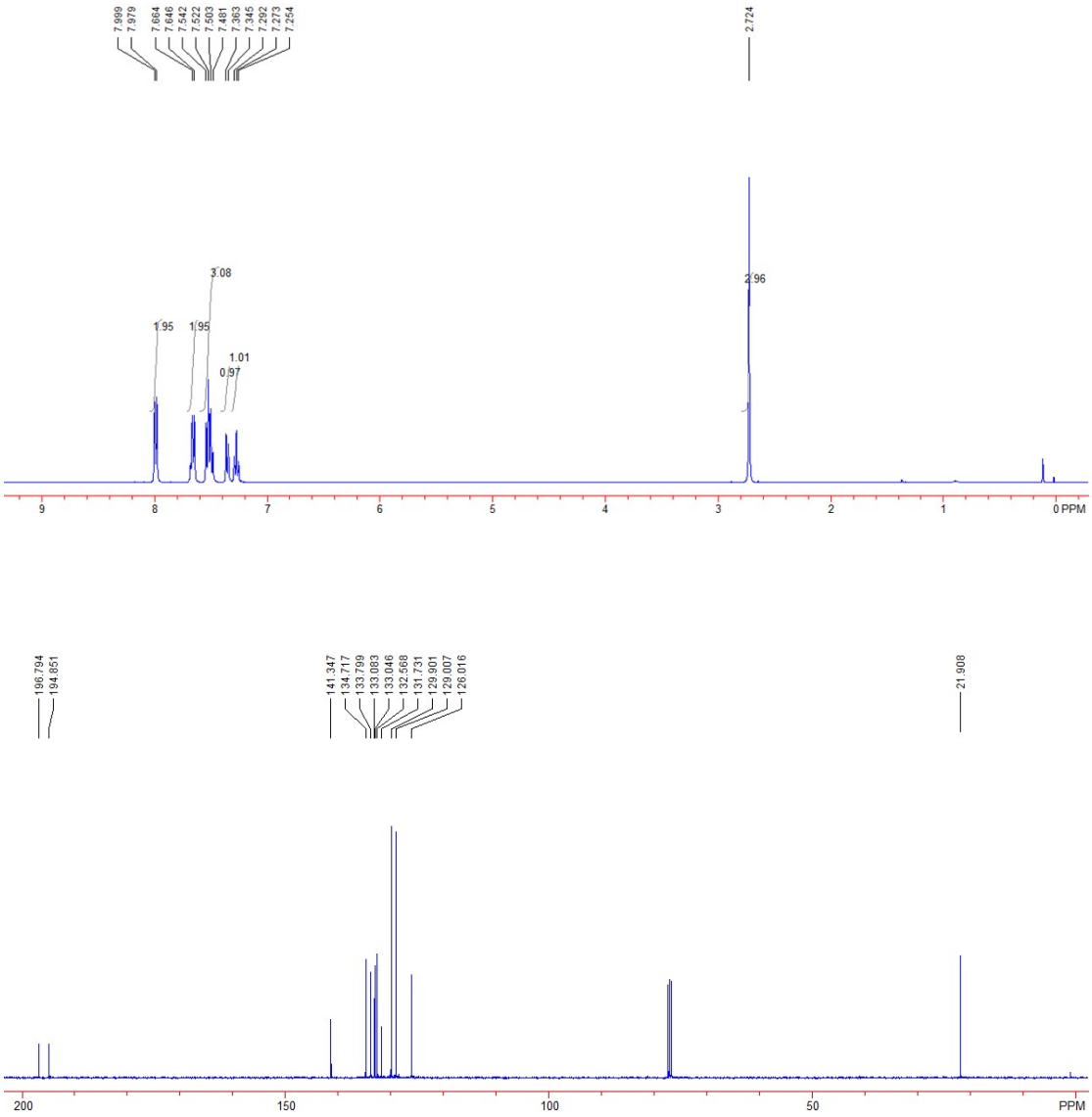


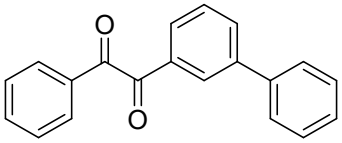


(4) 1-Phenyl-2-o-tolylethane-1,2-dione (2e)

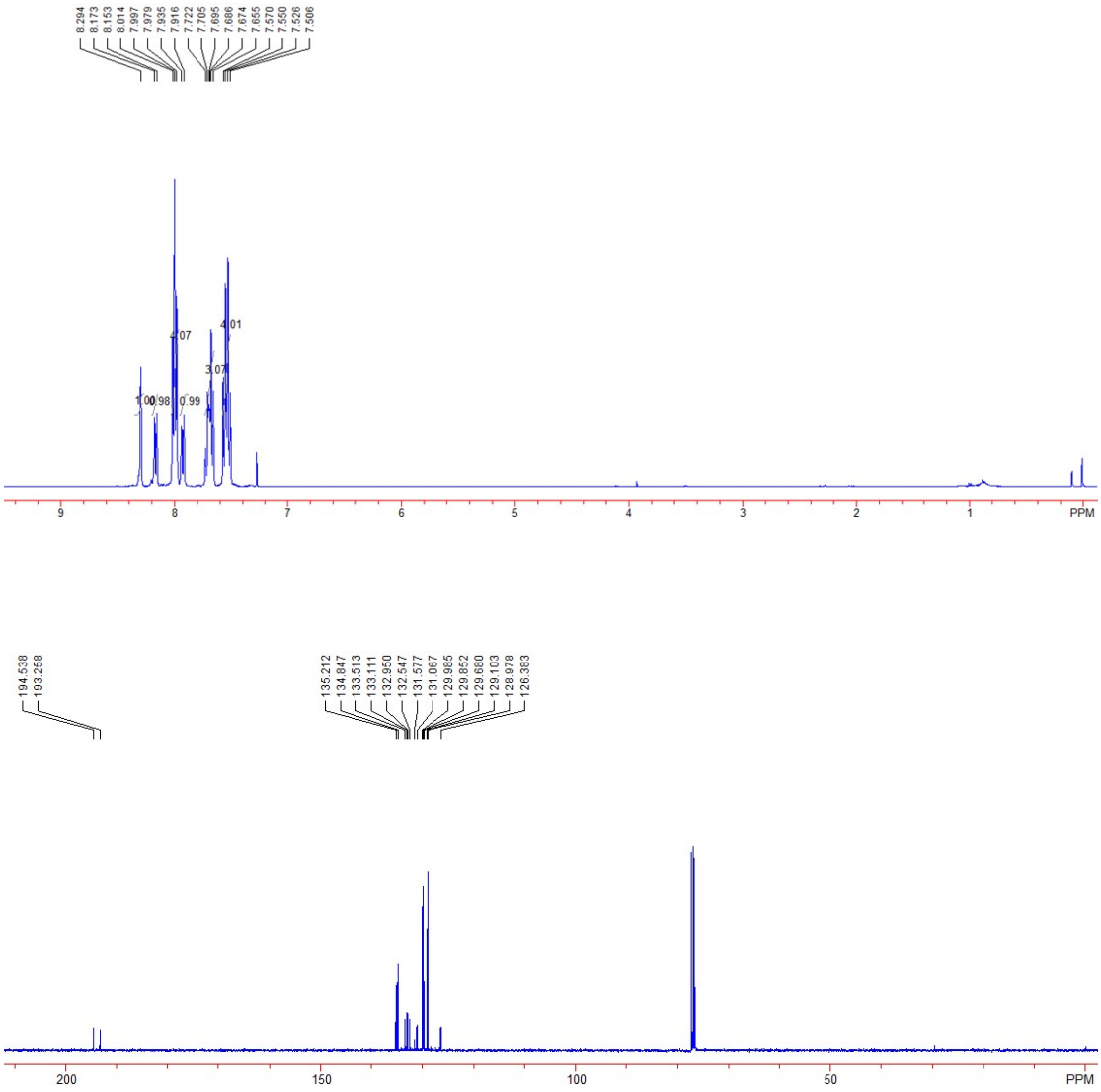


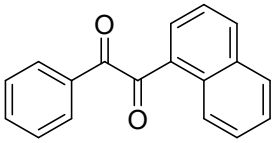
1-Phenyl-2-o-tolylethane-1,2-dione (3d). 62 mg, 55% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:10, v/v); mp 55 – 56 °C (lit.[3] 56 – 57 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.55 (m, 3H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 194.9, 141.4, 134.7, 133.8, 133.1, 133.1, 132.6, 131.7, 129.9, 129.0, 126.0, 21.9; GC-MS (EI): m/z=224.09(M^+).



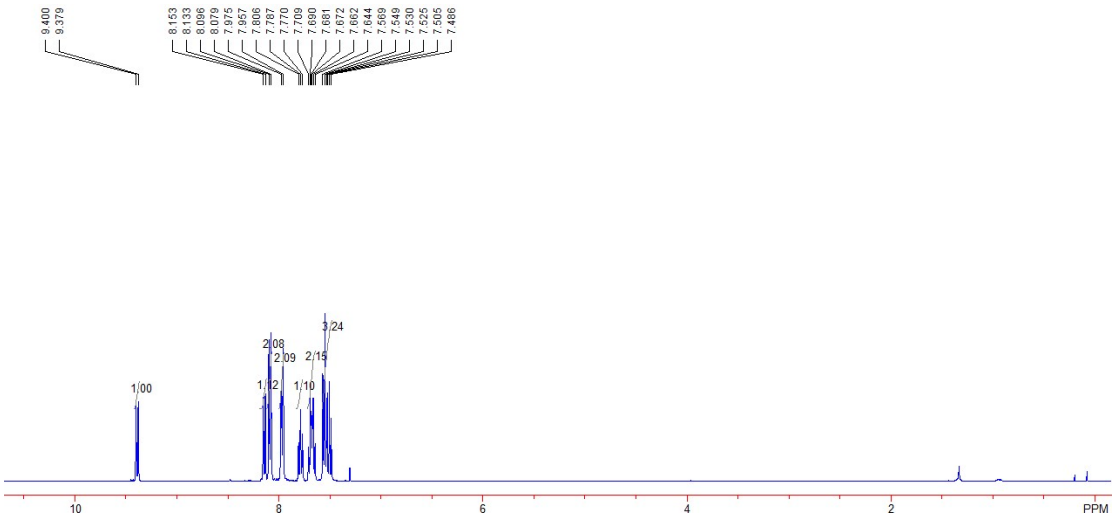


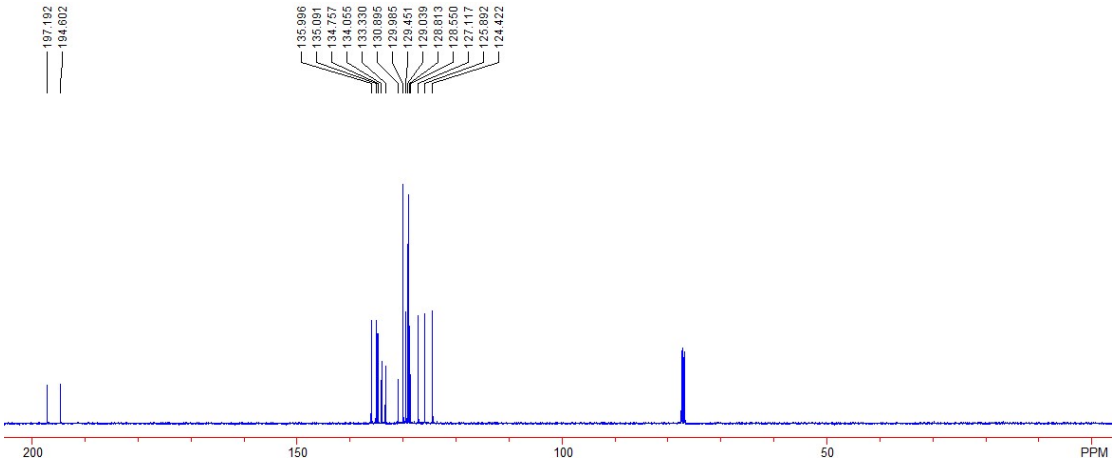
1-Phenyl-2-m-phenylethane-1,2-dione (3f). 99 mg, 69% yield; white solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:20, v/v); mp 89 – 91 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.29 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.00 (t, *J* = 7.2 Hz, 4H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.73 (m, 3H), 7.50 – 7.57 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 193.3, 135.2, 134.9, 133.5, 133.1, 133.0, 132.6, 131.6, 131.1, 130.0, 129.9, 129.7, 129.1, 129.0, 126.4; GC-MS (EI): m/z=286.11(M^+).

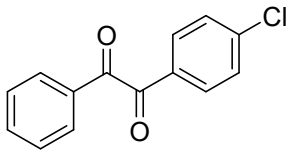




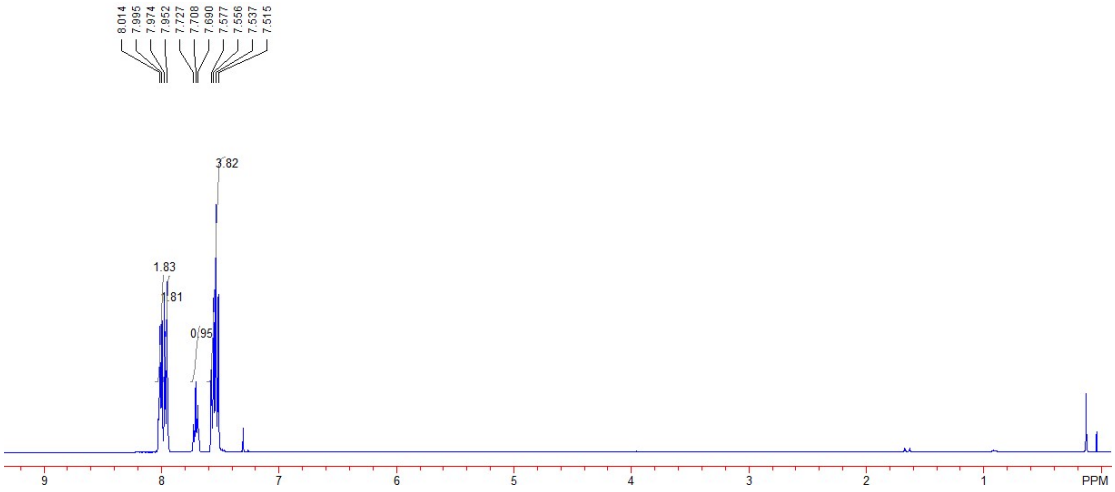
1-(Naphthalen-1-yl)-2-phenylethane-1,2-dione (3g). 68 mg, 52% yield; white solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:20, v/v); mp 99 – 101 °C (lit.[4] 98 – 99 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.39 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 6.8 Hz, 2H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.78 (t, *J* = 7.2 Hz, 1H), 7.64 – 7.71 (m, 2H), 7.48 – 7.57 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 194.6, 136.0, 135.1, 134.8, 134.1, 133.3, 130.9, 130.0, 129.4, 129.0, 128.8, 128.5, 127.1, 125.9, 124.4; GC-MS (EI): m/z=260.07(M^+).

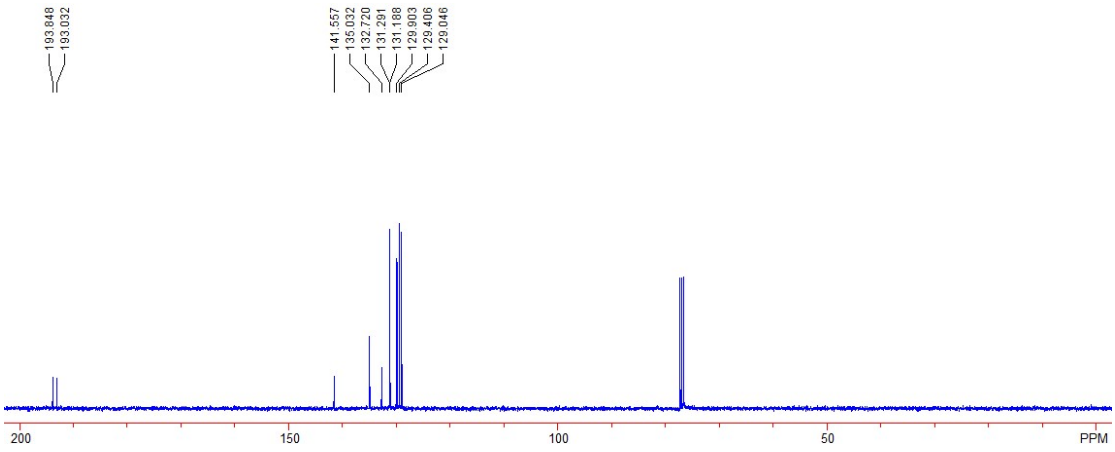


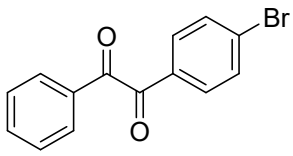




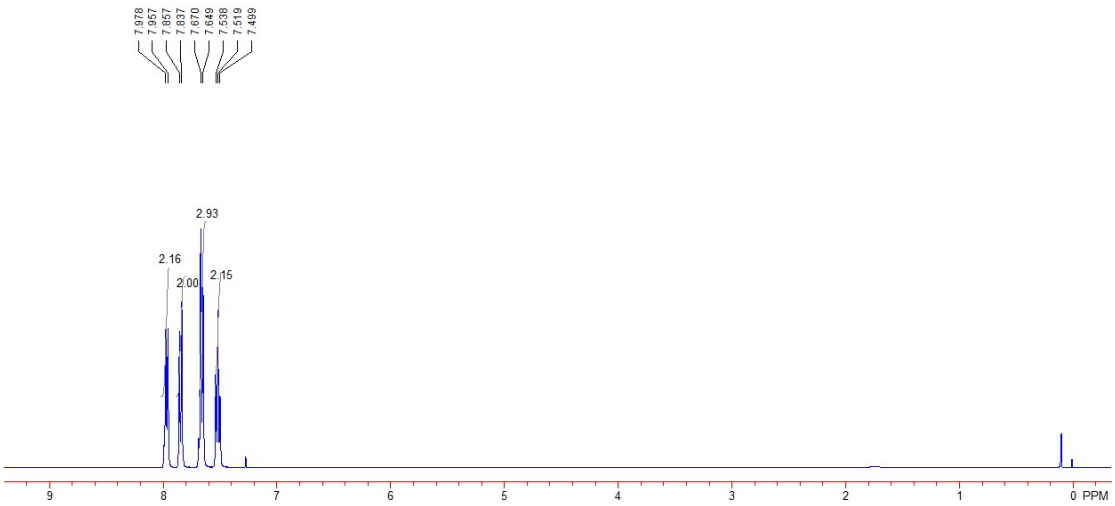
1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (3h). 76 mg, 62% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 71 – 73 °C (lit.[1] 73 – 74 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.71 (t, *J* = 7.2 Hz, 1H), 7.51 – 7.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 193.0, 141.6, 135.0, 132.7, 131.3, 131.2, 129.9, 129.4, 129.0; GC-MS (EI): m/z=244.02(M^+).

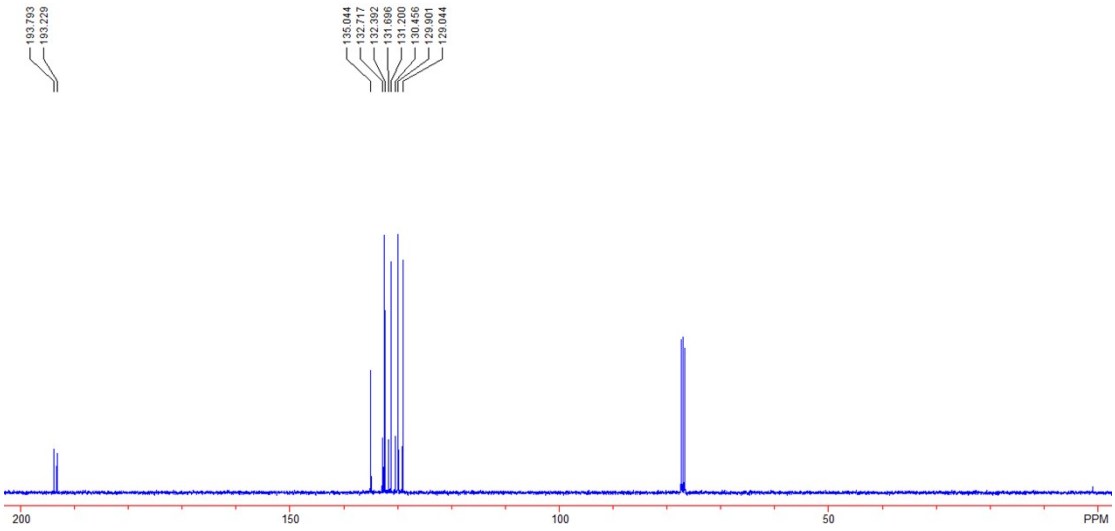


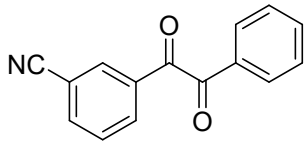




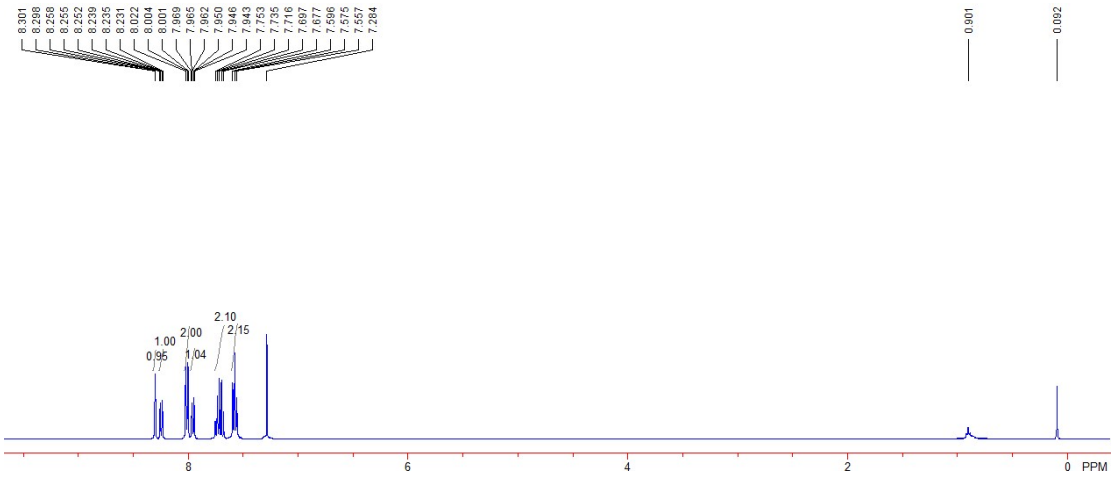
1-(4-Bromophenyl)-2-phenylethane-1,2-dione (3i). 94 mg, 65% yield; yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 88 – 90 °C (lit.[3] 86 – 87 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 3H), 7.52 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 193.2, 135.0, 132.7, 132.4, 131.7, 131.2, 130.5, 129.9, 129.0; GC-MS (EI): m/z=288.00(M^+).

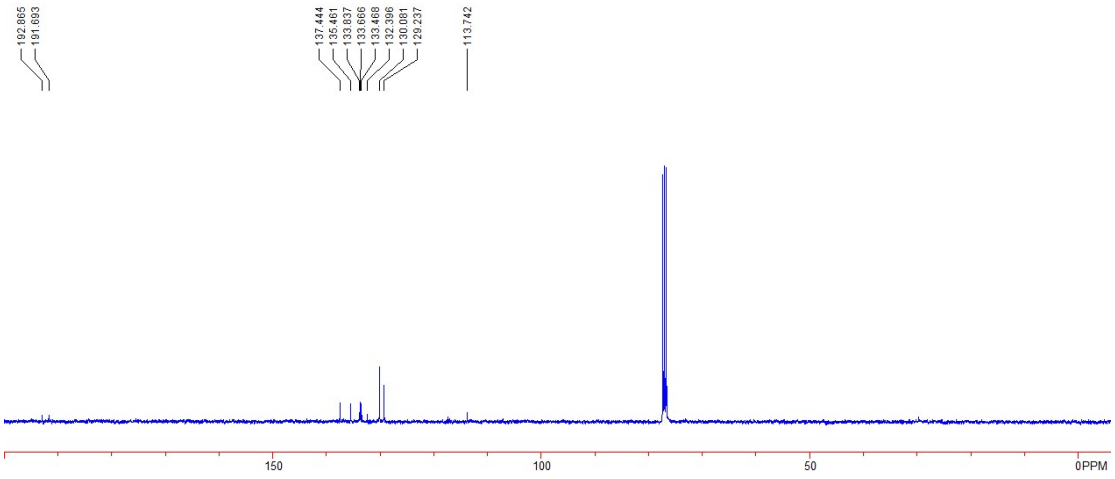


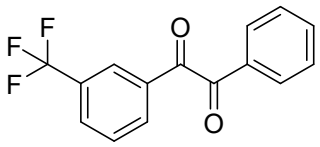




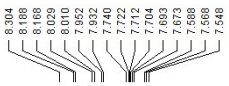
3-(2-Oxo-2-phenylacetyl)benzonitrile (3j). 68 mg, 58% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:20, v/v); mp 95 – 97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.2 Hz, 1H), 8.26-8.23 (m, 1H), 8.02-8.00 (m, 2H), 7.97-7.94 (m, 1H), 7.75 – 7.68 (m, 2H), 7.58 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 191.7, 137.4, 135.5, 133.8, 133.7, 133.5, 132.4, 130.1, 129.2, 113.7; GC-MS (EI): m/z=235.05(M^+).

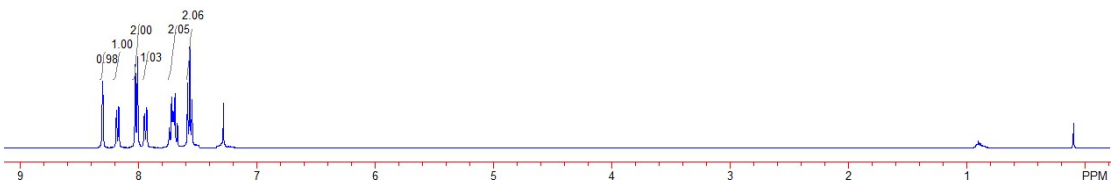


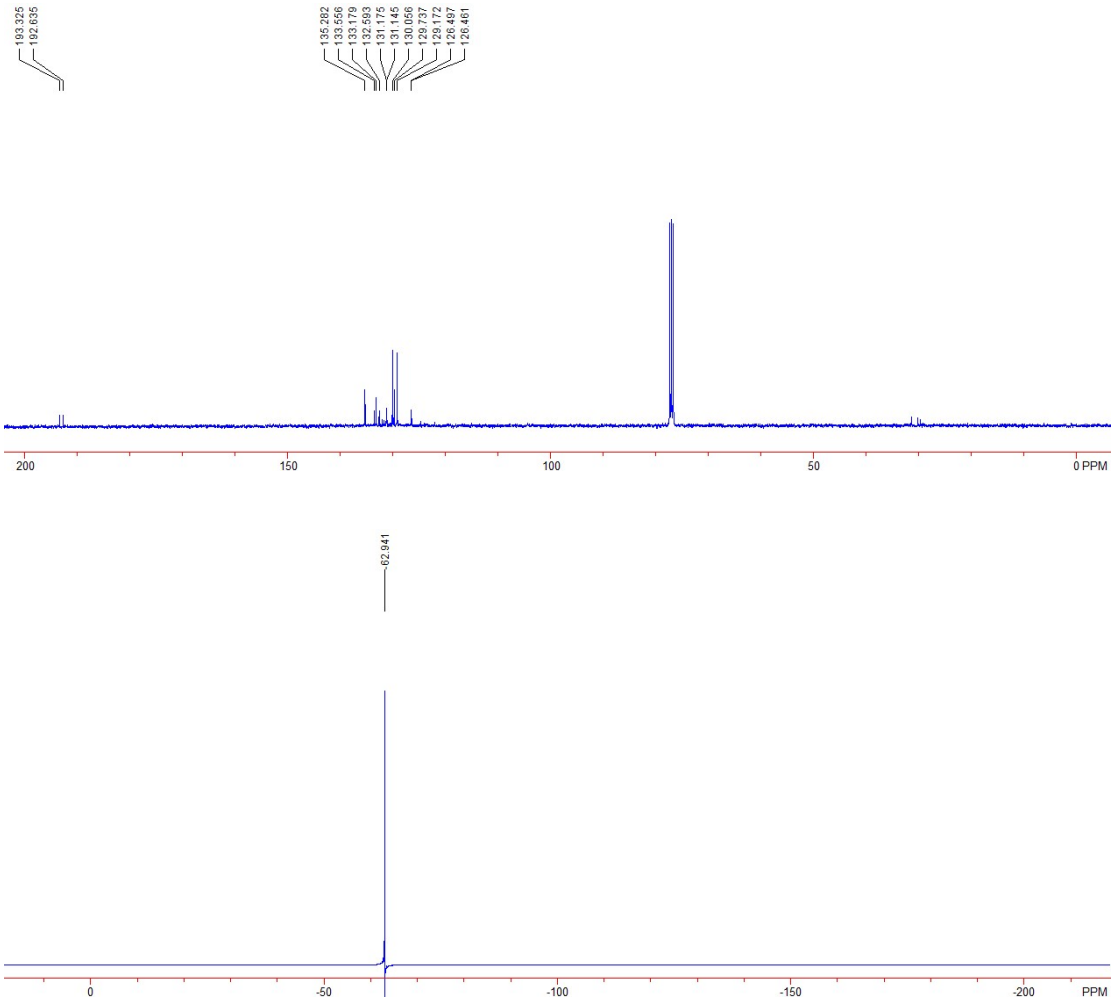


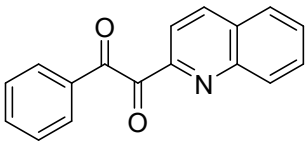


1-Phenyl-2-(3-(trifluoromethyl)phenyl)ethane-1,2-dione (3k). 85 mg, 61% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 68–70 °C (lit.[3] 69–70 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.18 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 7.9 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.57 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 192.6, 135.3, 133.6, 133.2, 132.6, 132.2 (J = 124.8 Hz), 131.1 (J = 10.0 Hz), 130.0, 129.7, 129.1, 126.4 (J = 12.4 Hz). ^{19}F NMR (250 MHz, $CDCl_3$) δ −62.94; GC-MS (EI): m/z=278.07(M^+).

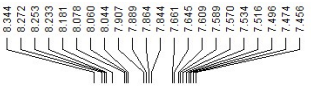


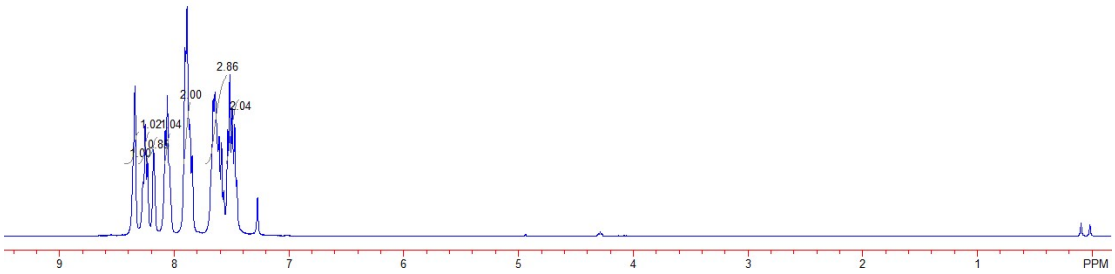


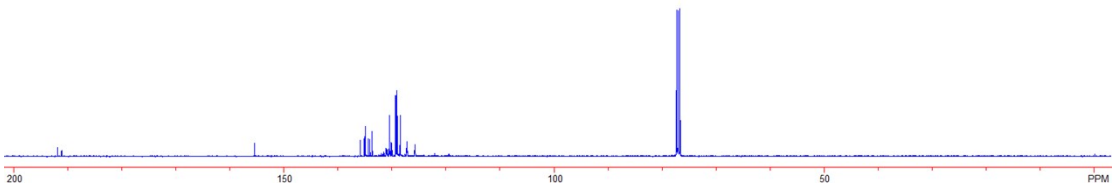


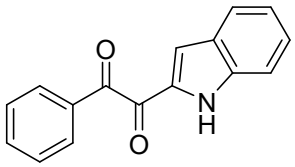


1-Phenyl-2-(quinolin-2-yl)ethane-1,2-dione (3l). 56 mg, 43% yield; brown solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:10, v/v); mp 137 – 140 °C (lit.[5] 140 – 143 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.34 (s, 1H), 8.25 (t, J = 7.6 Hz, 1H), 8.18 (s, 1H), 8.06 (t, J = 6.8 Hz, 4 H), 7.84 – 7.91 (m, 2H), 7.57 – 7.66 (m, 3H), 7.45 – 7.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 191.1, 155.4, 135.1, 134.95, 134.4, 134.1, 133.6, 130.5, 131.1, 129.8, 129.7, 129.3, 129.0, 128.5, 127.2, 125.7; GC-MS (EI): m/z=261.09(M^+).

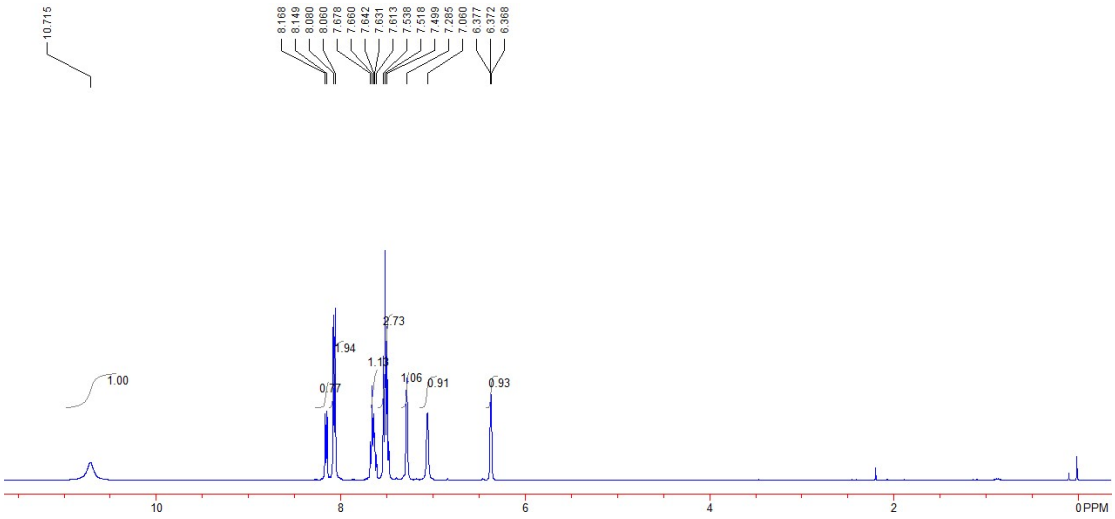


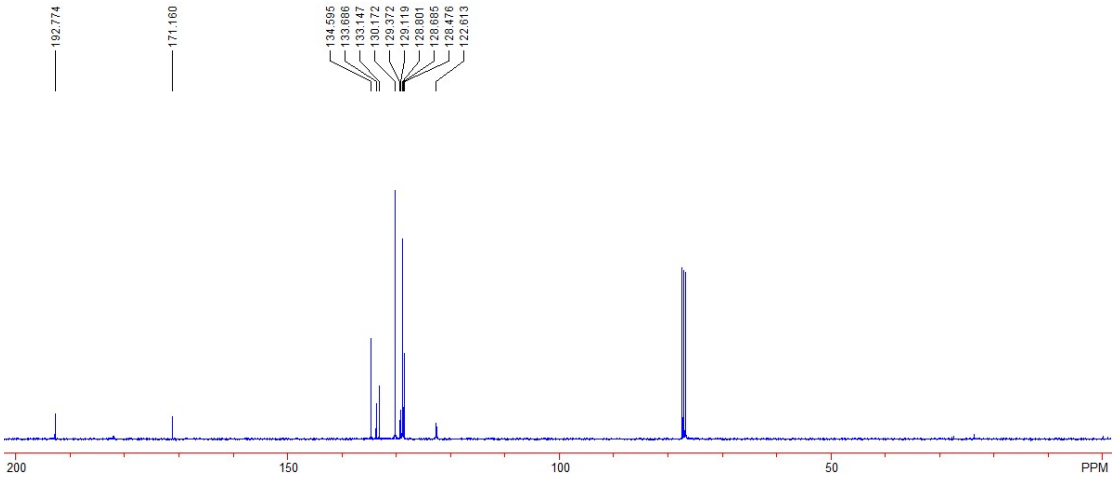


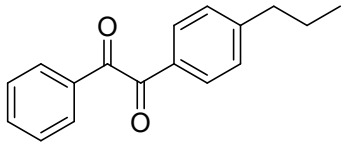




1-(1H-indol-2-yl)-2-phenylethane-1,2-dione (3m). 63 mg, 51% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:20, v/v); mp 112 – 115 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.71 (s, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.68 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 3H), 7.28 (s, 1H), 7.06 (s, 1H), 6.37 (t, *J* = 2.0 Hz, 1H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 192.8, 171.2, 134.6, 133.7, 133.2, 130.2, 129.4, 129.1, 128.8, 128.7, 128.5, 122.6; GC-MS (EI): m/z=249.07(M^+).

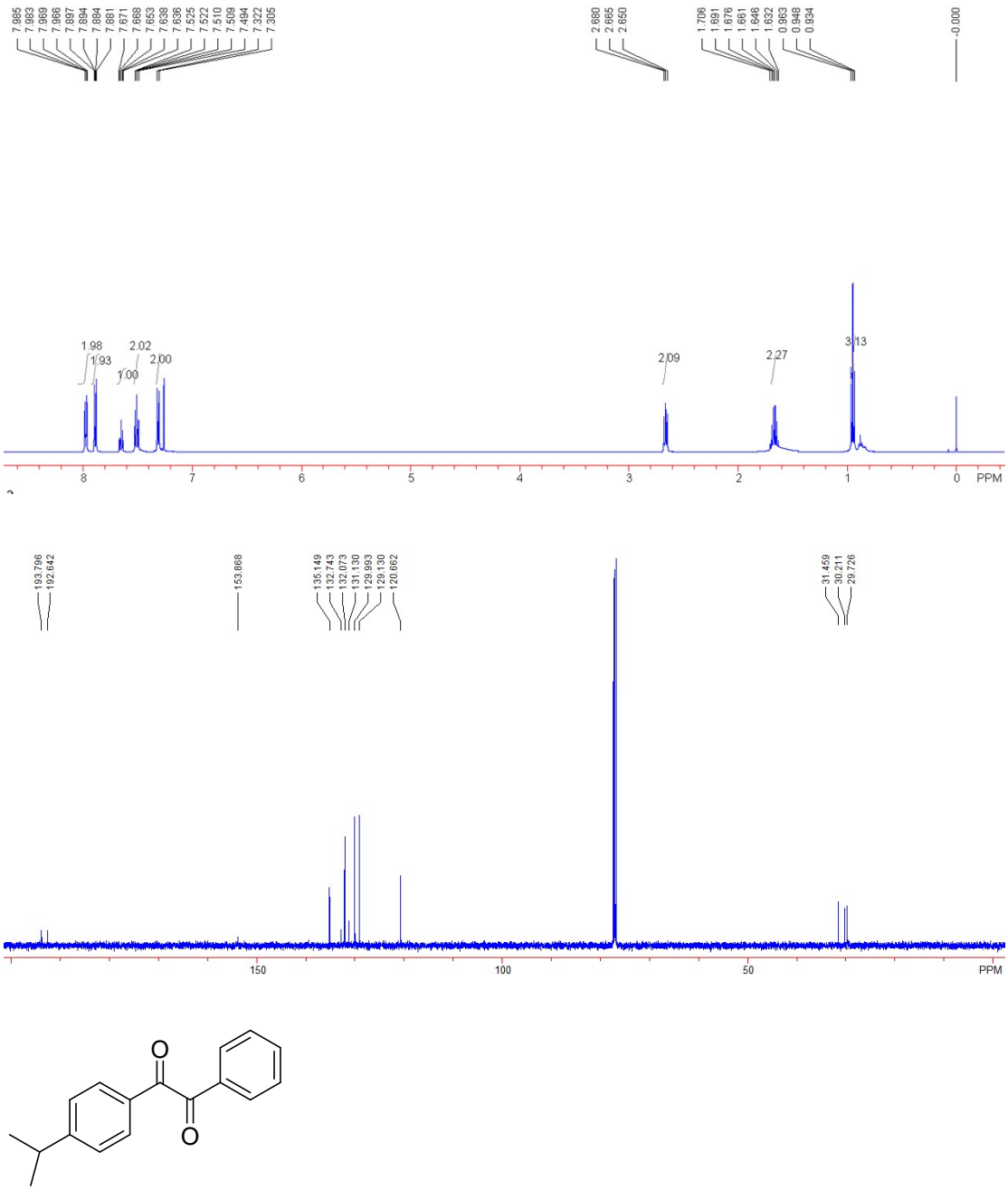






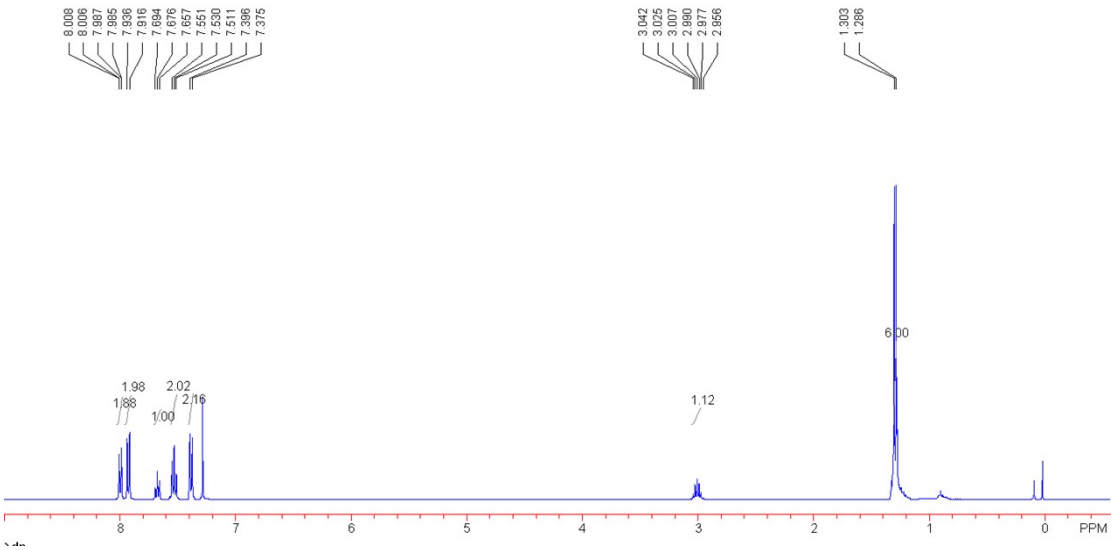
1-phenyl-2-(4-propylphenyl)ethane-1,2-dione (3n). 86 mg, 68% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 45 – 46 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.90 – 7.88 (m, 2H), 7.67 – 7.64 (m, 1H), 7.53 – 7.49 (m, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 2.67 (d, *J* = 7.5 Hz, 2H), 1.71 – 1.63 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 192.6, 135.2, 132.7, 132.1, 131.1,

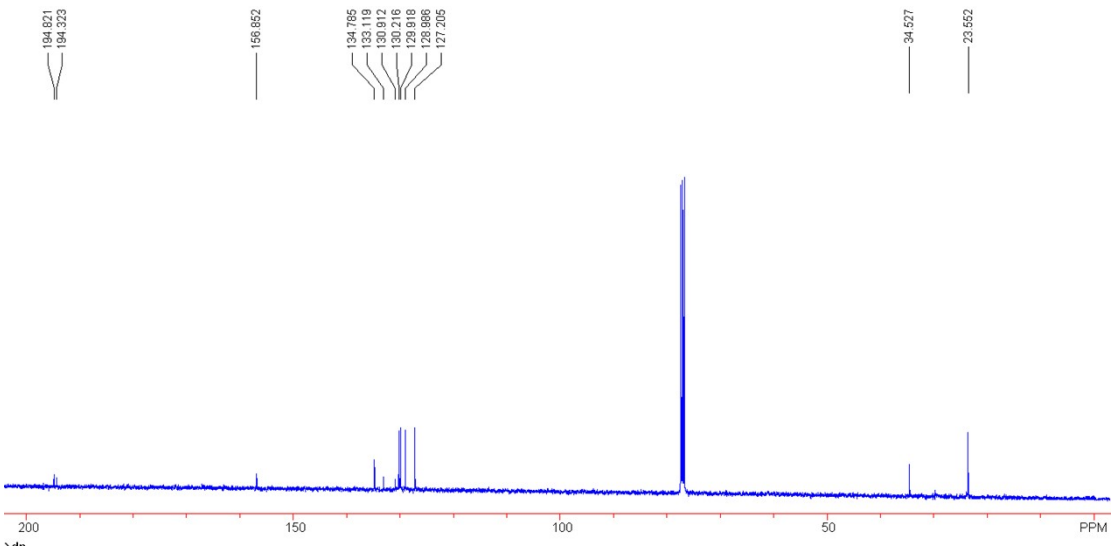
130.0, 129.1, 120.7, 31.5, 30.2, 29.7; GC-MS (EI): m/z=252.13(M^+).

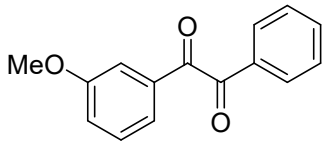


1-(4-isopropylphenyl)-2-phenylethane-1,2-dione (3o). 88 mg, 70% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 41 – 42 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 8.4, 0.8 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.68 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 8.4 Hz, 2H), 7.39 (t, J = 8.4 Hz, 2H), 3.04 – 2.96 (m, 1H), 1.29 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 194.3, 156.9, 141.6, 134.8, 133.1 , 130.9,

130.2, 129.9, 129.0, 127.2, 34.5, 23.6; GC-MS (EI): m/z=252.10(M^+).

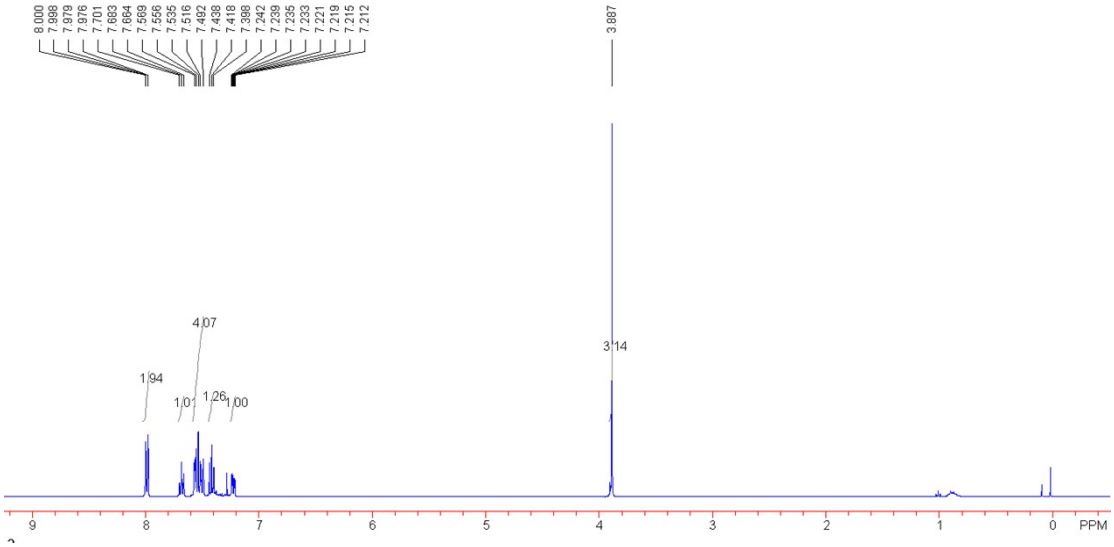


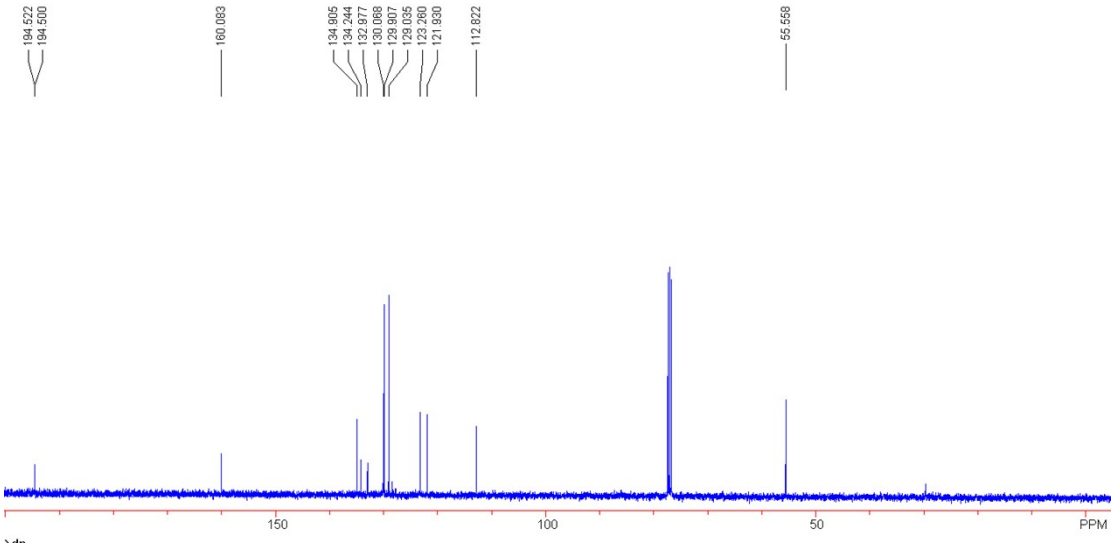


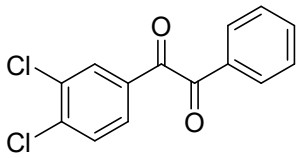


1-(3-methoxyphenyl)-2-phenylethane-1,2-dione (3p). 88 mg, 73% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 93 – 94 °C (lit.[6] 91 – 93 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.4, 0.8 Hz, 2H), 7.68 (t, J = 7.2 Hz, 1H), 7.57 – 7.49 (m, 4H), 7.42 (t, J = 8.0 Hz, 1H), 7.24 – 7.21 (m, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.52, δ 194.50, 160.1, 134.9, 134.2, 133.0, 130.1, 129.9, 129.0, 123.3,

121.9, 112.8, 55.6; GC-MS (EI): m/z=240.07(M^+).

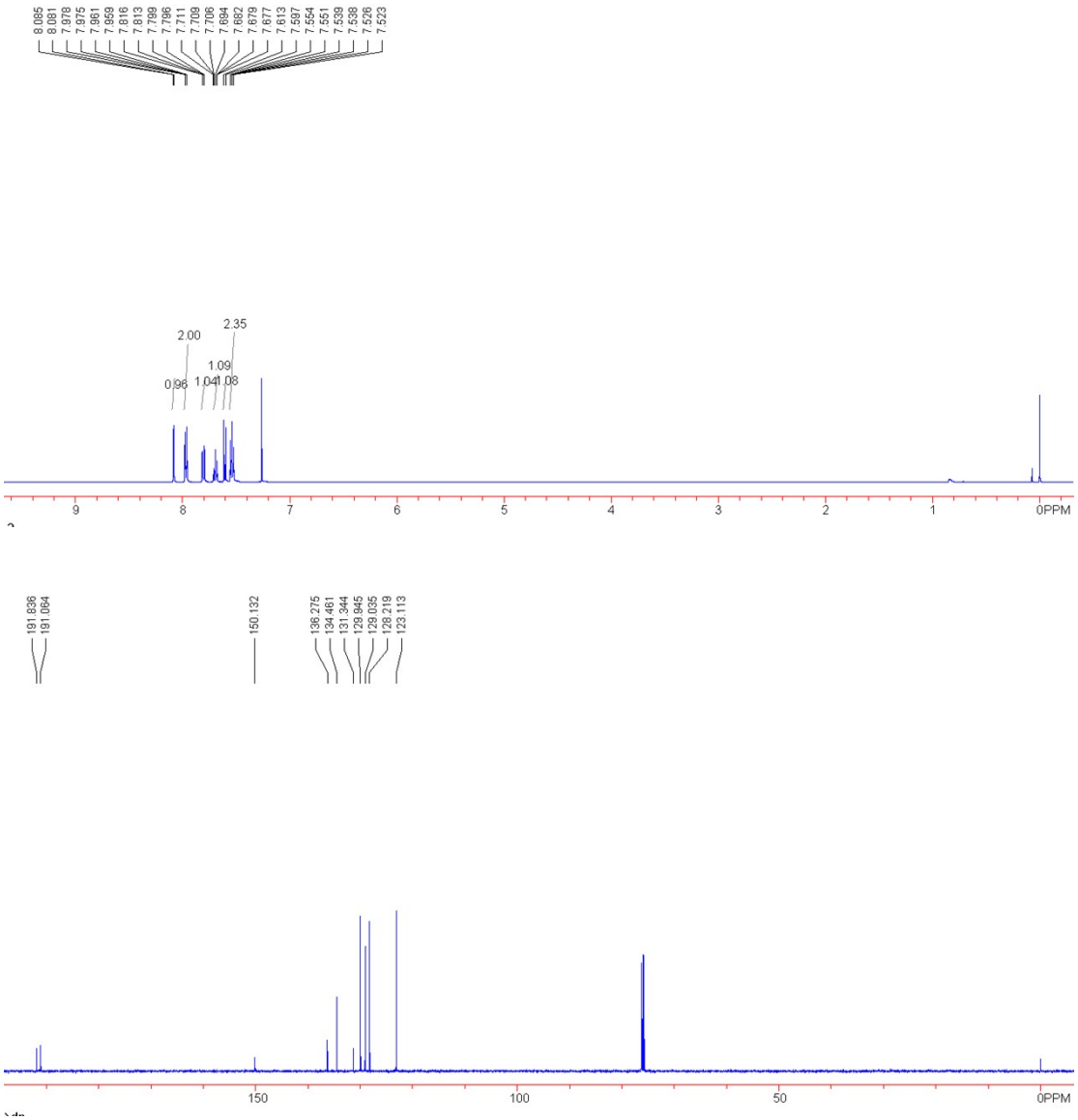


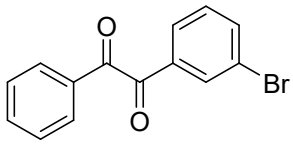




1-(3,4-dichlorophenyl)-2-phenylethane-1,2-dione (3q). 81 mg, 58% yield; yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:20, v/v); mp 61 – 62 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2 Hz, 1H), 7.80 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.81

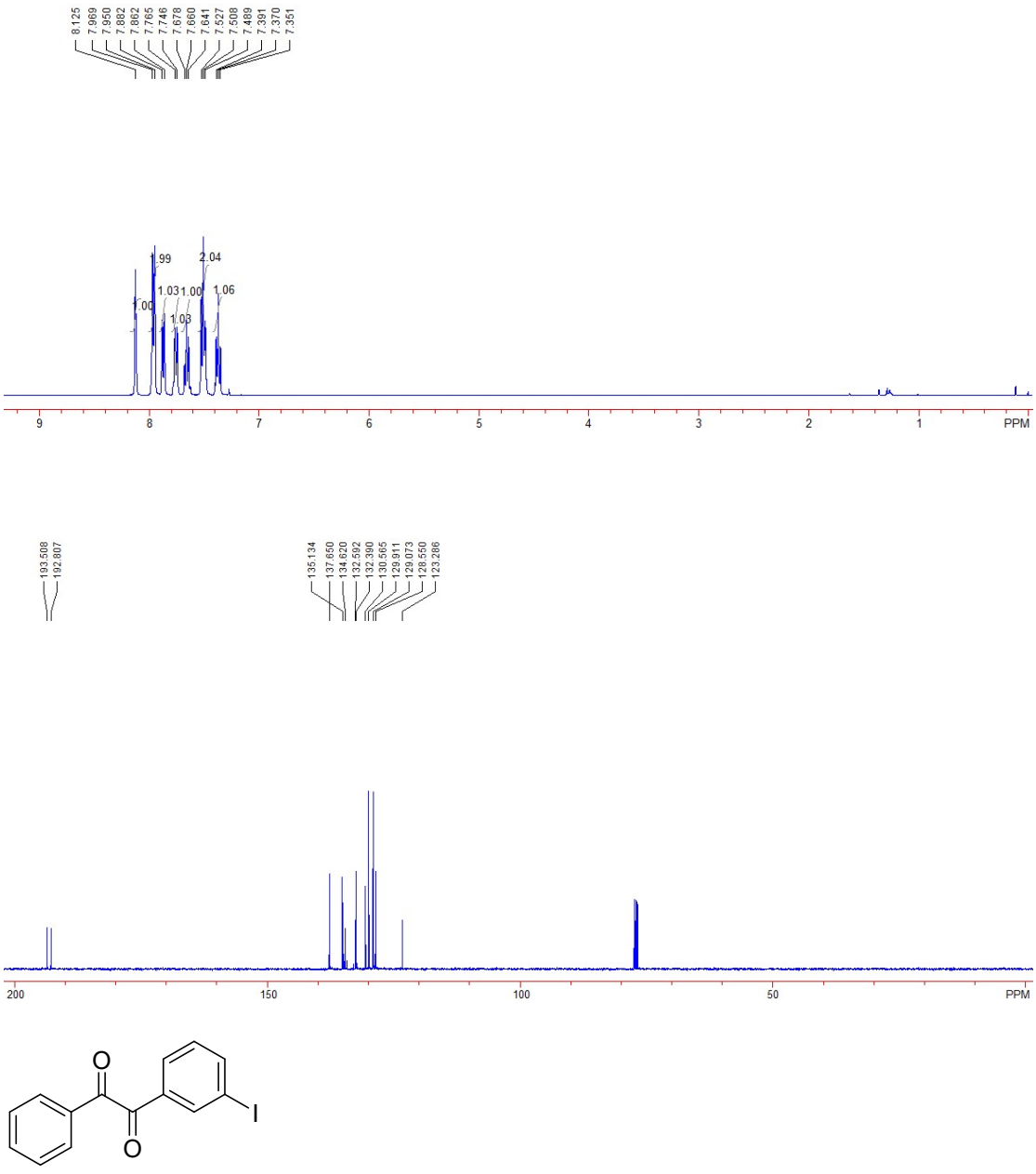
(dd, J = 8.5, 1.5 Hz, 1H), 7.71-7.68 (m, 1H), 7.61 (d, J = 8 Hz, 1H), 7.55 – 7.52 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.8, 191.1, 150.1, 136.3, 134.5, 131.3, 129.9, 129.0, 128.2, 123.1; GC-MS (EI): m/z=278.00(M^+).





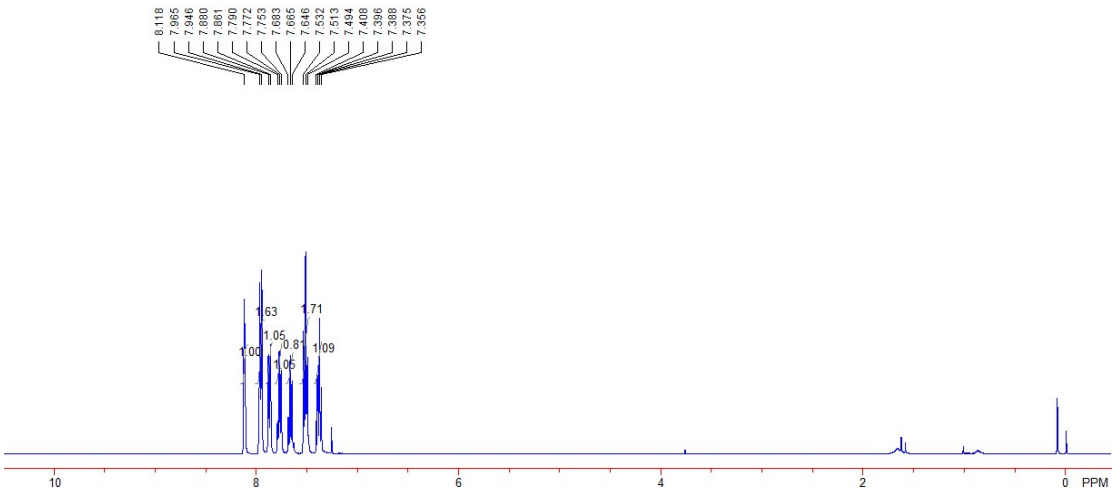
1-(3-Bromophenyl)-2-phenylethane-1,2-dione (3r). 101 mg, 70% yield; yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:20, v/v); mp 82 – 83 °C (lit.[7] 80 – 81 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.12 (s, 1H), 7.96 (d, J = 7.6 Hz,

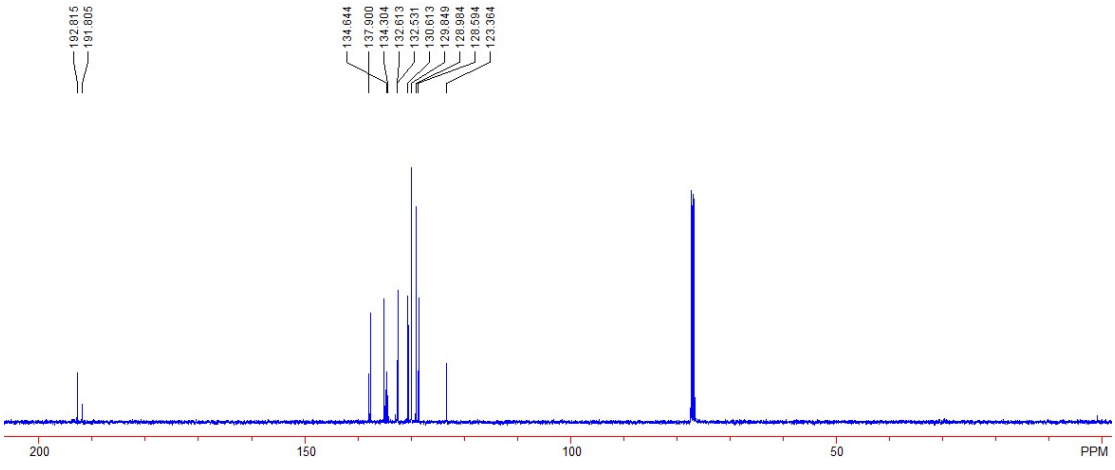
2H), 7.87 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 192.8, 137.7, 135.1, 134.6, 132.6, 132.4, 130.6, 129.9, 129.1, 128.6, 123.3; GC-MS (EI): m/z=287.99(M^+).

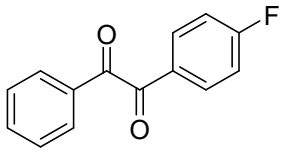


1-(3-iodophenyl)-2-phenylethane-1,2-dione (3s). 128 mg, 76% yield; light brown solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 117 – 119 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.11 (s, 1 H), 7.95 (d, J = 7.6 Hz, 2 H), 7.86 (d, J =

7.6 Hz, 1 H), 7.77 (t, *J* = 7.2 Hz, 1 H), 7.67 (t, *J* = 7.6 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 2 H), 7.35- – 7.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 191.8, 137.9, 134.6, 134.3, 132.6, 132.4, 130.6, 129.8, 129.0, 128.6, 123.4; GC-MS (EI): m/z=335.94(M^+).

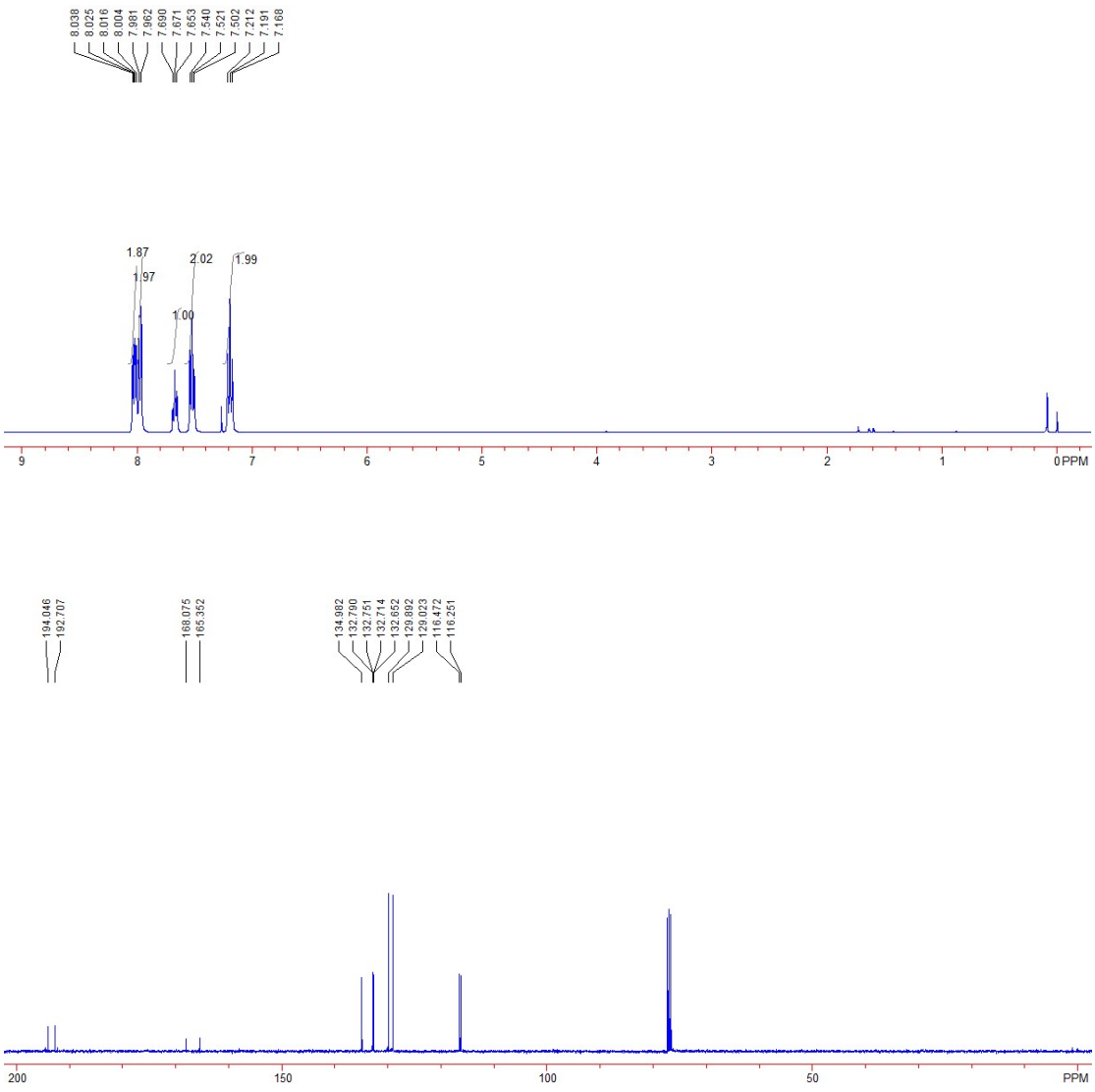


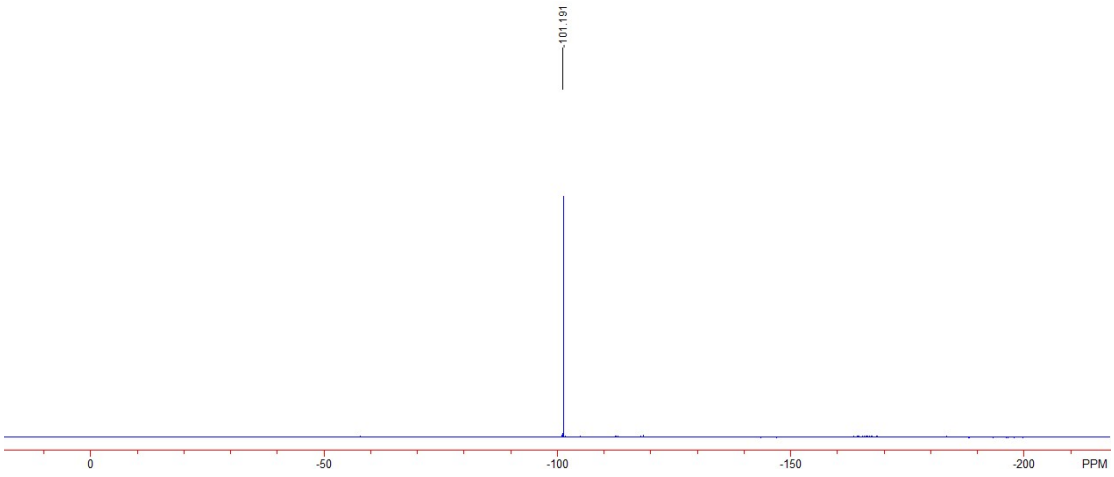


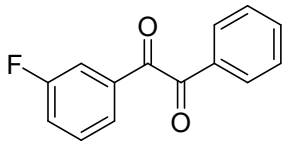


1-(4-Fluorophenyl)-2-phenylethane-1,2-dione (3t). 74 mg, 65% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:20, v/v); mp 63 – 65 °C (lit.[8] 62 – 63.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.00 – 8.04 (m, 2 H), 7.97 (d, *J* =

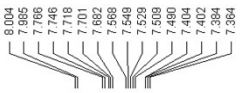
7.6 Hz, 2 H), 7.67 (t, J = 7.6 Hz, 1 H), 7.52 (t, J = 7.6 Hz, 2 H), 7.19 (t, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 192.7, 166.7 (J = 272.3 Hz), 135.0, 132.8 (t, J = 3.8 Hz), 132.7, 129.9, 129.0, 116.5, 116.3. ^{19}F NMR (250 MHz, $CDCl_3$) δ −101.19; GC-MS (EI): m/z=228.05(M^+).







1-(3-fluorophenyl)-2-phenylethane-1,2-dione (3u). 79 mg, 69% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 52 – 54 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.77 – 7.68 (m, 3H), 7.57 – 7.49 (m, 3H), 7.40 – 7.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 193.0, 162.9 (d, J = 248 Hz), 135.0 (t, *J* = 6.6 Hz), 132.7 (d, *J* = 6.7 Hz), 132.7, 130.8 (d, *J* = 6.8 Hz), 130.0, 129.1 , 126.0 (d, *J* = 1.9 Hz), 122.0 (d, *J* = 21.3 Hz), 116.1 (d, *J* = 22.7 Hz); ^{19}F NMR (250 MHz, $CDCl_3$) δ −110.56; GC-MS (EI): m/z=228.07(M^+).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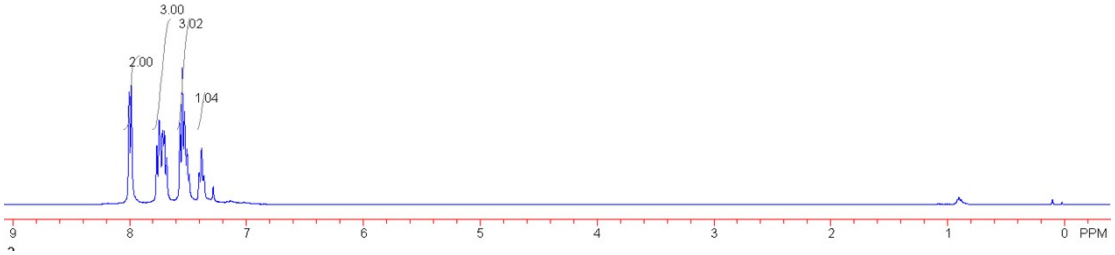
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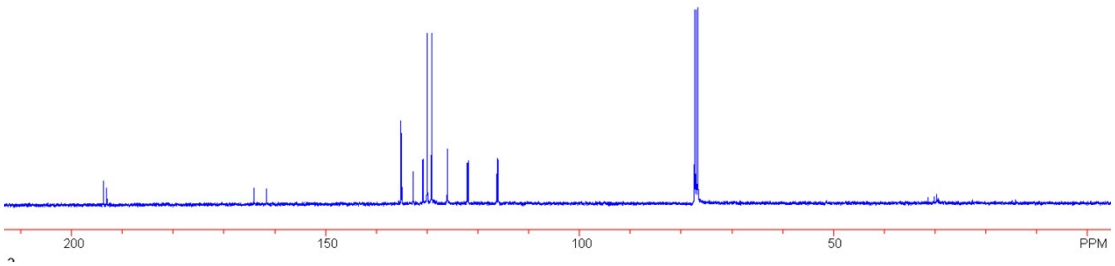
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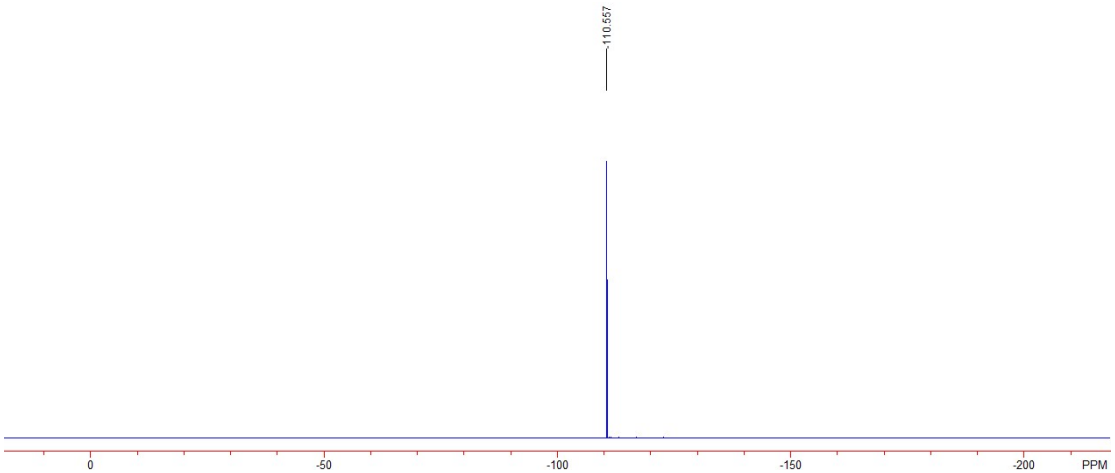
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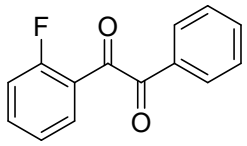
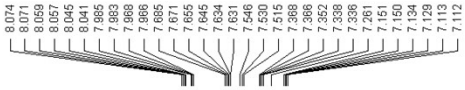
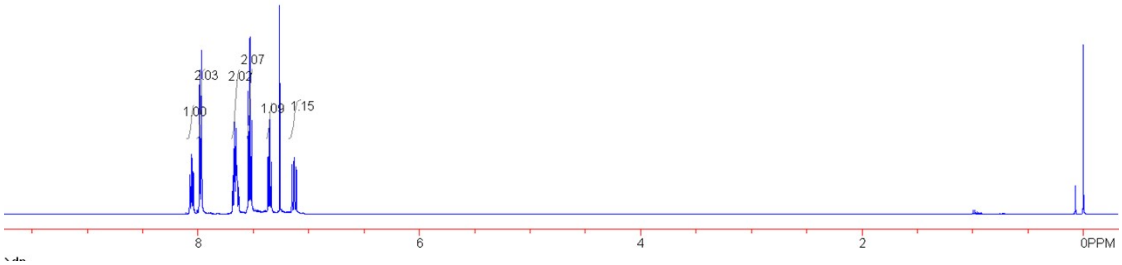
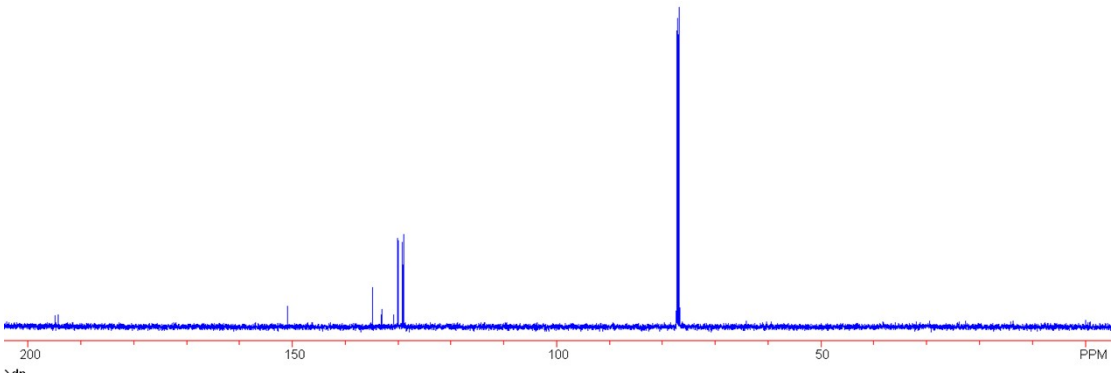
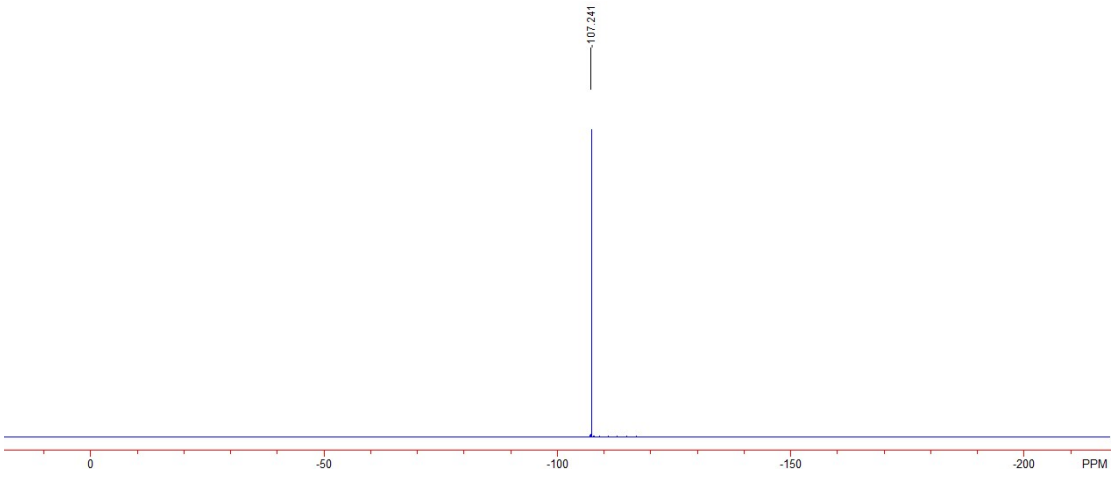


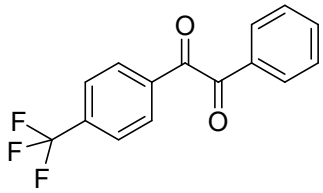
1-(2-fluorophenyl)-2-phenylethane-1,2-dione (3v). 68 mg, 60% yield; white solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 55 – 57 °C (lit.[9] 58 – 60 °C); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.06 (td, *J* = 7.5, 1.5 Hz, 1H), 7.99 – 7.97 (m, 2H), 7.69 – 7.63 (m, 2H), 7.55 – 7.52 (m, 2H), 7.3 – 7.34 (m, 1H), 7.15 – 7.11 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.8, 194.4, 150.9, 134.8, 133.1, 130.8, 130.1, 129.9, 129.2, 129.0; ^{19}F NMR (250 MHz, $CDCl_3$) δ −107.24; GC-MS (EI): m/z=228.04(M^+).



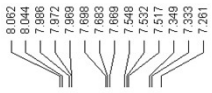


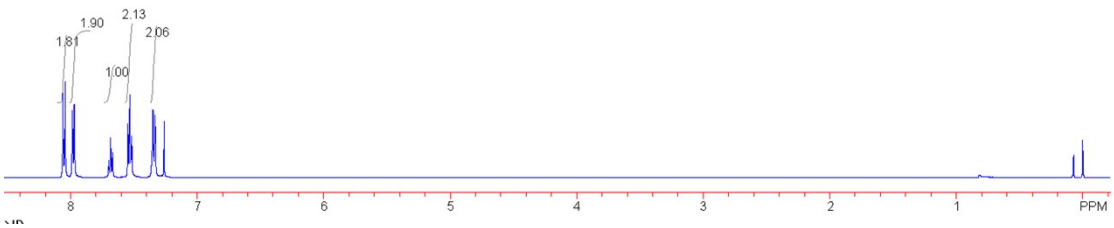


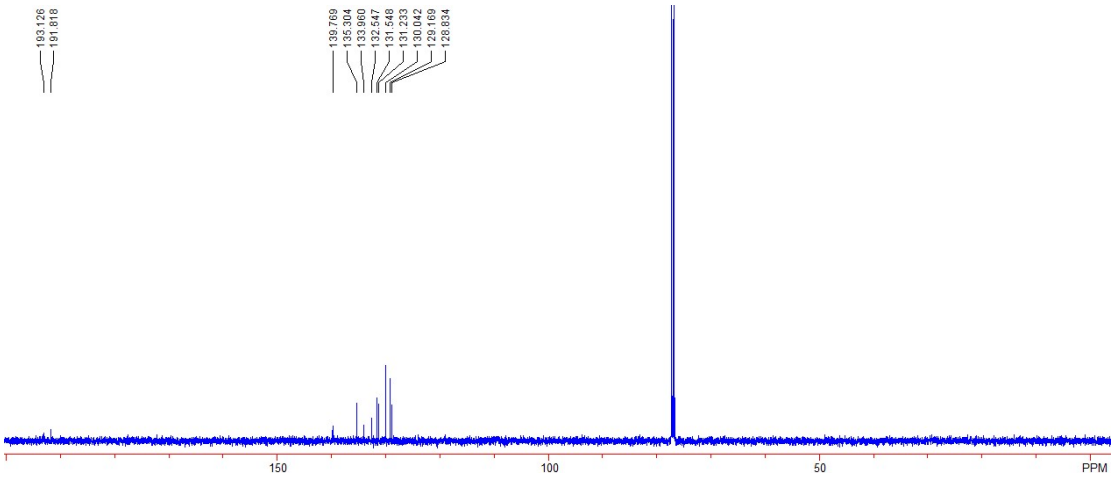


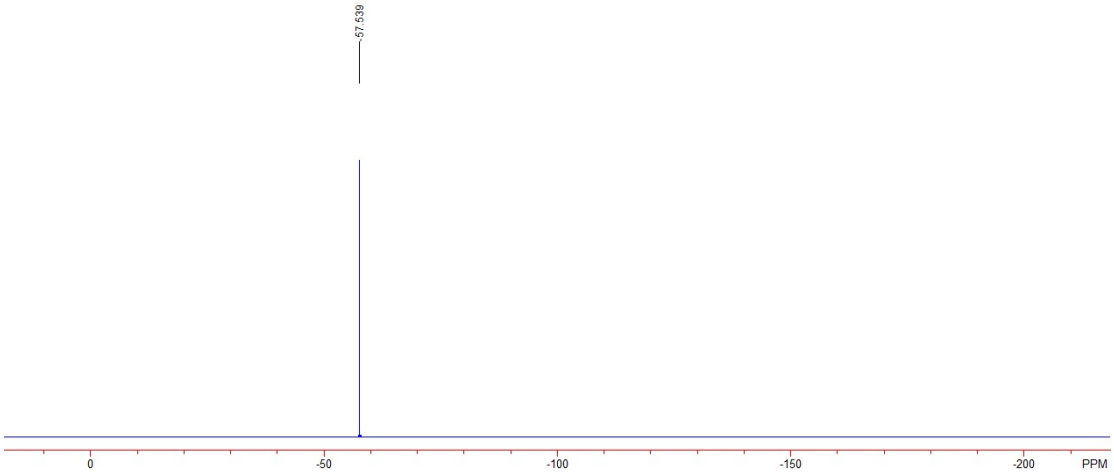


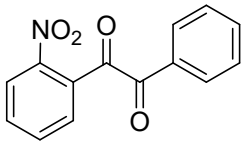
1-phenyl-2-(4-(trifluoromethyl)phenyl)ethane-1,2-dione (3w). 72 mg, 52% yield; yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 84 – 86 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 9.0 Hz, 2H), 7.98 (m, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1 , 191.8, 135.6 (*J* = 32.8 Hz), 135.3, 134.0, 132.5, 131.5, 131.2, 130.0, 125.8 (*J* = 3.6 Hz), 122.9 (*J* = 272.8 Hz); ^{19}F NMR (250 MHz, $CDCl_3$) δ −57.54; GC-MS (EI): m/z=278.05(M^+).



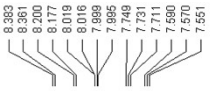


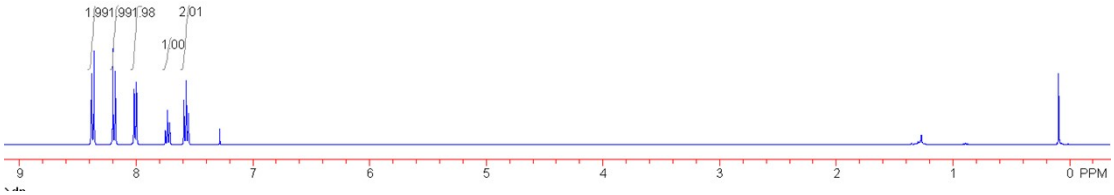


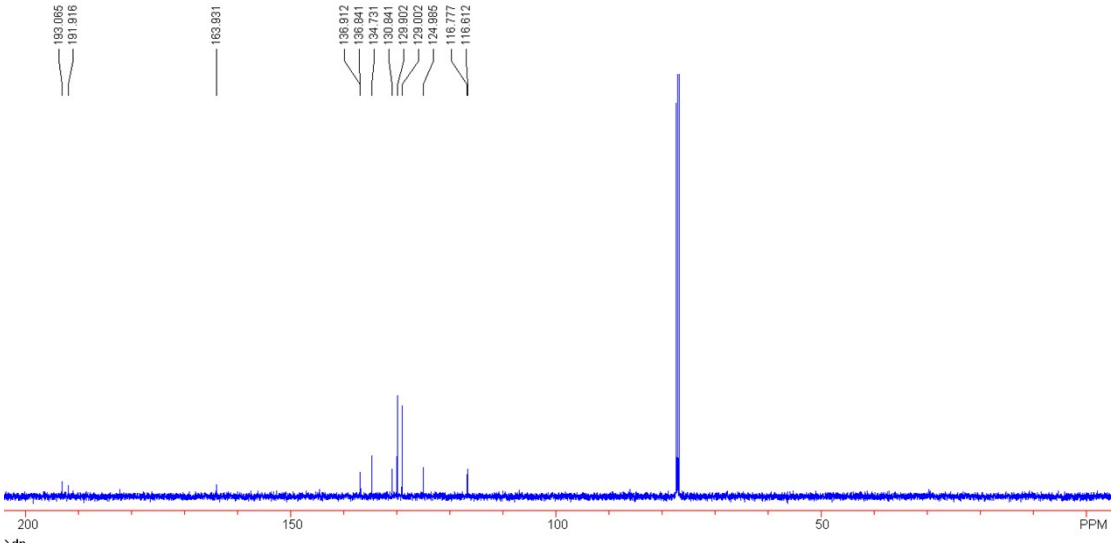


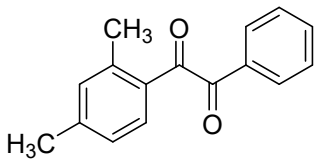


1-(2-nitrophenyl)-2-phenylethane-1,2-dione (3x). 64 mg, 50% yield; yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 125 – 126 °C (lit.[9] 124 – 126 °C); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.37 (d, *J* = 1.0 Hz, 2H),8.19 (d, *J* = 11.5 Hz, 2H), 8.4 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 2H), 7.75-7.71 (m, 1H), 7.57 (t, *J* = 10.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1, 191.9, 163.9, 136.9, 136.8, 134.7, 130.8, 129.9, 129.0, 125.0 (s), 116.8, 116.6; GC-MS (EI): m/z=255.06(M^+).



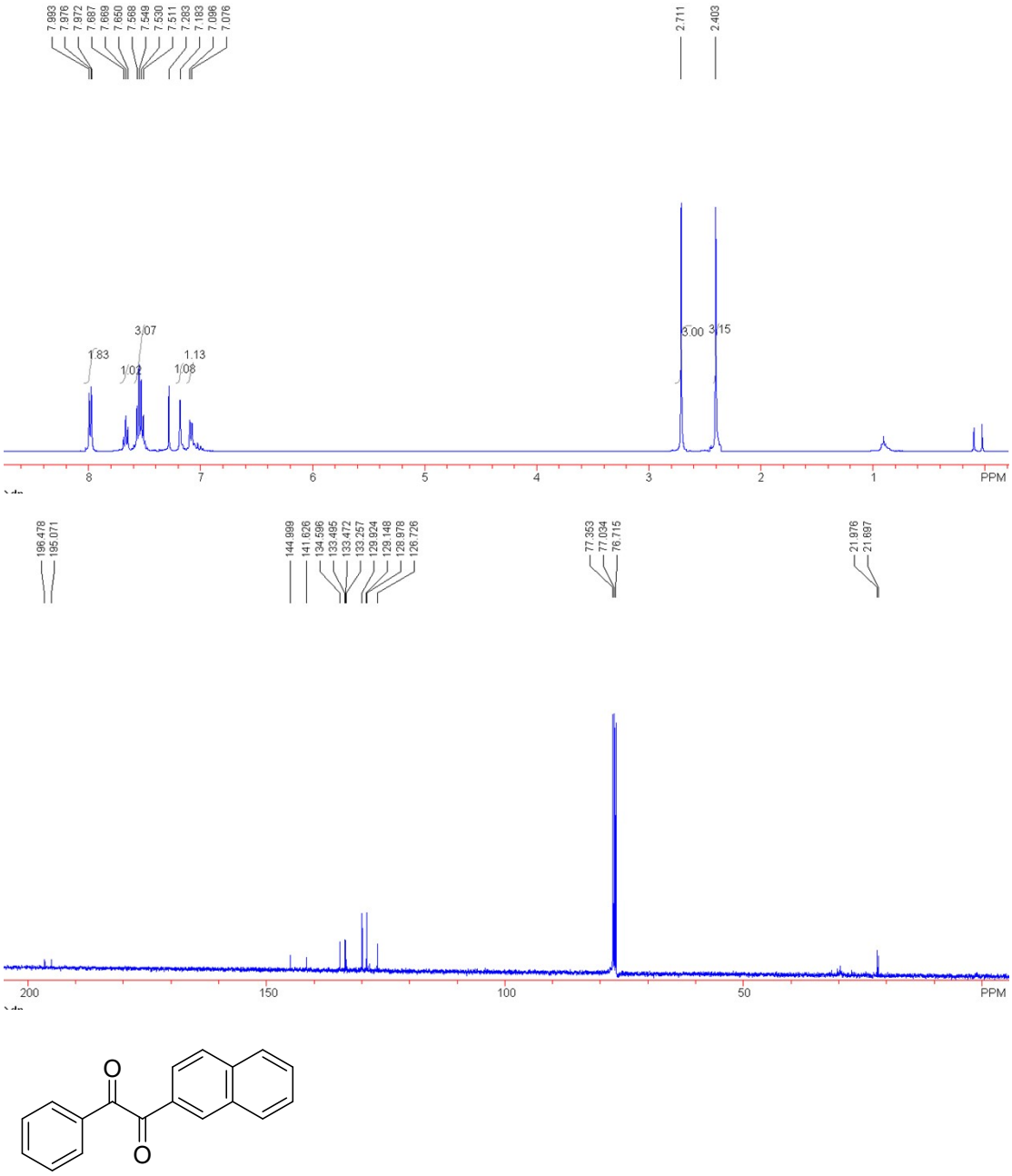




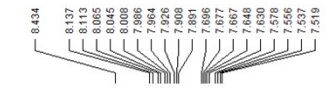


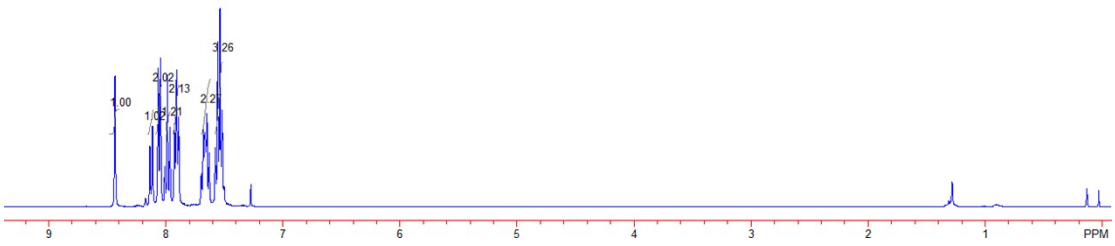
1-(2,4-dimethylphenyl)-2-phenylethane-1,2-dione (3y). 64 mg, 54% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:30, v/v); mp 34 – 36 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.97 (m, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.18 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 2.71 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 195.1, 145.0, 141.6, 134.6, 133.5, 133.5, 133.3, 129.9, 129.2, 129.0, 126.7, 22.0,

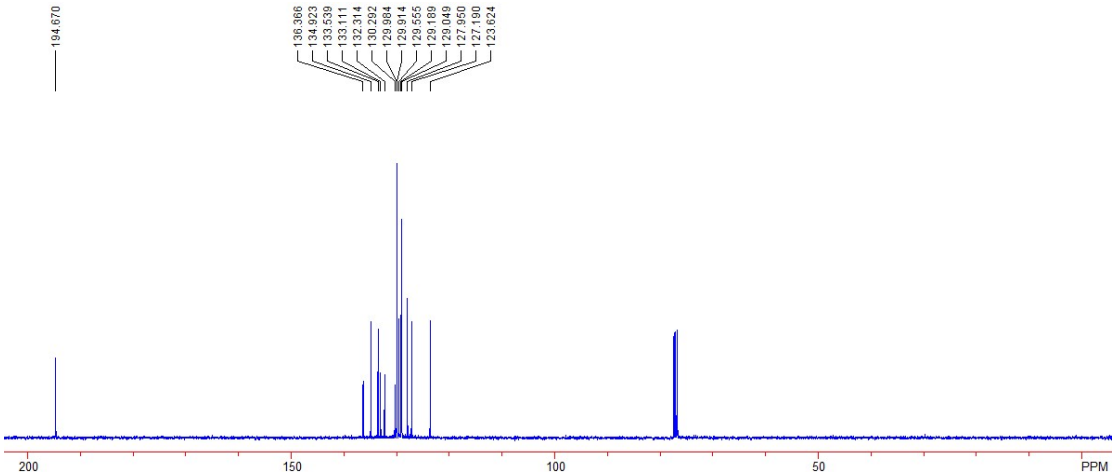
21.7; GC-MS (EI): m/z=238.11(M^+).

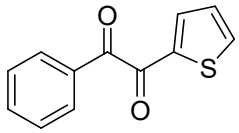


1-(Naphthalen-2-yl)-2-phenylethane-1,2-dione (3z). 87 mg, 67% yield; white solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:10, v/v); mp 85 – 97 °C (lit.[2] 85 – 86 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.44 (s, 1H), 8.12 (d, *J* = 9.6 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.98 (t, *J* = 8.8 Hz, 1H), 7.90 (t, *J* = 6.8 Hz, 2H), 7.63 – 7.69 (m, 2H), 7.51 – 7.58 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 136.4, 134.9, 133.5, 133.1, 132.3, 130.3, 130.0, 129.9, 129.6, 129.2, 129.0, 128.0, 127.2, 123.6; GC-MS (EI): m/z=260.10(M^+).



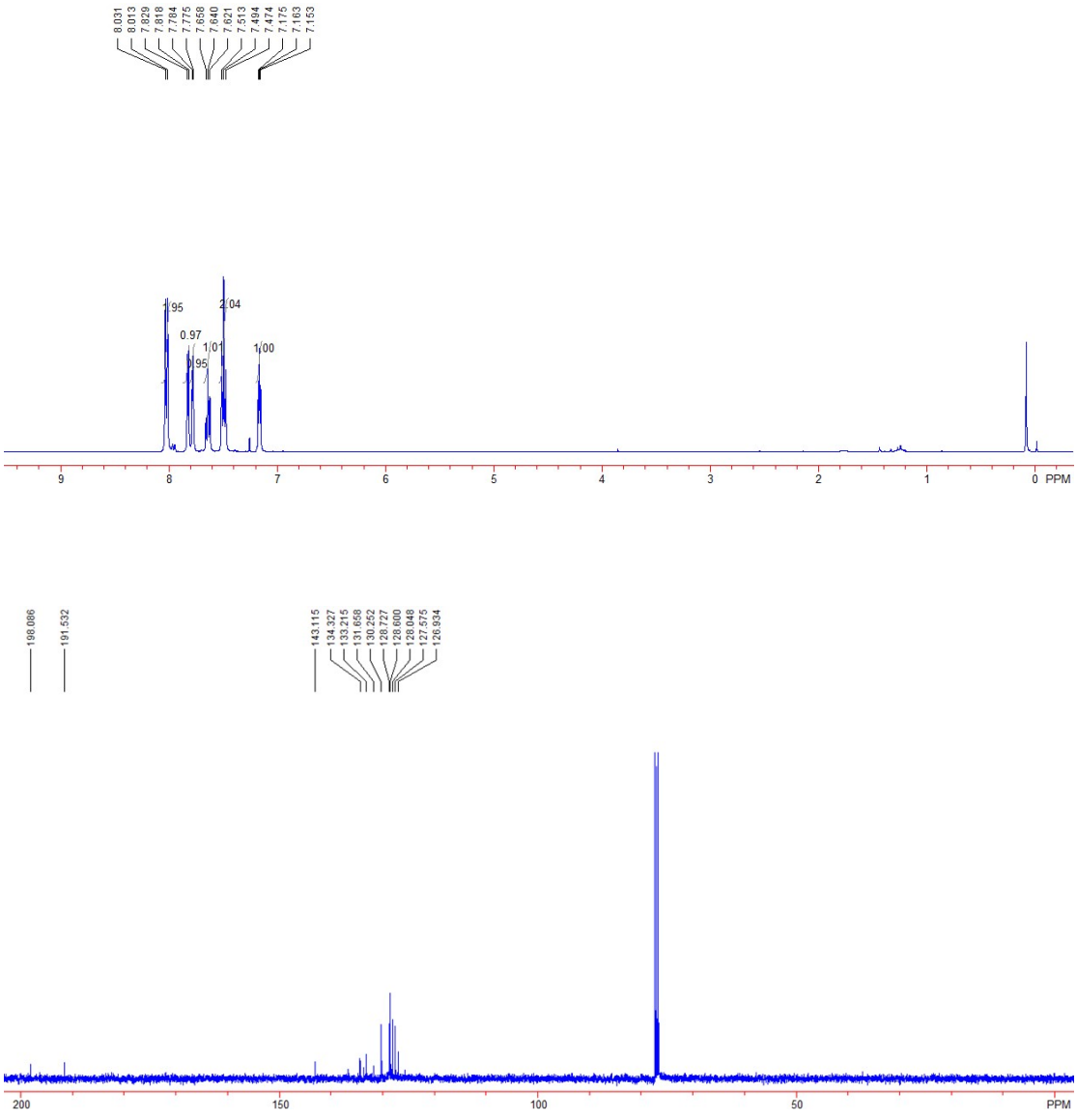






1-Phenyl-2-(thiophen-2-yl)ethane-1,2-dione (3aa). 47 mg, 44% yield; light yellow solid after purification by column chromatography (eluent, ethyl acetate/petroleum ether = 1:10, v/v); mp 65 – 66 °C (lit.[10] 63 – 65 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.82 (d, *J* = 4.4 Hz, 1H), 7.78 (d, *J* = 3.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 4.4 Hz, 1H); ^{13}CNMR(100 MHz, $CDCl_3$) δ 198.1, 191.5, 143.1, 134.3, 133.2, 131.7, 130.3, 128.7,

128.6, 128.0, 127.6, 126.9; GC-MS (EI): m/z=216.01(M^+).



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