Supplementary Information

Rh(I)-catalyzed site-selective hydroacylation of alkenyl-bearing allylic alcohols with non-chelating aldehydes controlled by in situ generated carbonyl group

Fu-Gang Wang,‡[a] Fei-Yuan Gong,‡[a] Juan Cao,[a] Ji-Cong Wang,[b] Kai-Qiang Tian,[a] Jinbo Zhao*[a] and Hong-Shuang Li*[a]

[a] School of Pharmaceutical Sciences, Shandong First Medical University & Shandong Academy of Medical Sciences, 619 Changcheng Road, Taian 271016, P. R. China
E-mail: jinbozhao1982@hotmail.com; hsli@sdfmu.edu.cn

[b] People's Hospital of Juxian, 151 Shennong Road, Rizhao 276599, P. R. China

‡ F.G.W. and F.Y.G. contributed equally.

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1. General Experiment Information

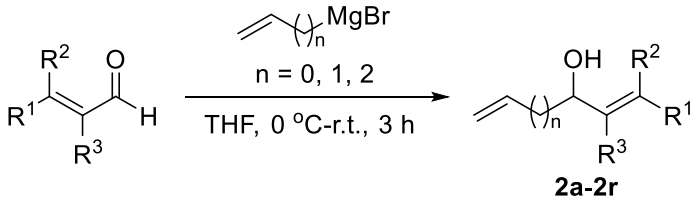
Unless specified otherwise, all the rhodium(I)-catalyzed reactions were carried out in the glove box (filled with N_2). All chemicals of commercial grade were directly used without further purification. Aldehydes and Grignard reagents were commercially available. Toluene was dried by silica gel column chromatography prior to use (200−300 mesh).

$CDCl_3$ was purchased from Innochem Reagents (Beijing). ^1H NMR spectra were recorded on the Bruker Ascend^{TM} 400 with 400 MHz frequencies, and ^{13}C NMR spectra were recorded on the Bruker Ascend^{TM} 400 with 100 MHz frequencies. Chemical shifts are given in ppm and coupling constants in Hertz (Hz), respectively. ^1H spectra were calibrated in relation to the reference measurement of TMS (δ_H = 0.000 ppm) or the residual solvent signal of $CDCl_3$ (δ_H = 7.260 ppm). ^{13}C spectra were calibrated in relation to $CDCl_3$ (δ_C = 77.10 ppm). The following abbreviations were used for ^1H NMR and ^{13}C NMR spectra to indicate the signal multiplicities: bs (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplets), together with combinations of them.

Organic solvents were concentrated under reduced pressure on a EYELA rotary evaporator (Japan). Analytical thin-layer chromatography (TLC) was performed on 0.25 mm commercial silica gel plates (purchased from Qingdao Haiyang Chemical, China, silica gel GF254), and the compounds were visualized with the UV light at 254 nm and 365 nm, respectively. Column chromatography was performed on silica gel 200−300 mesh (purchased from Qingdao Haiyang Chemical, China). High-resolution mass spectra (HRMS) were performed on an Agilent 6546 LC/Q-TOF.

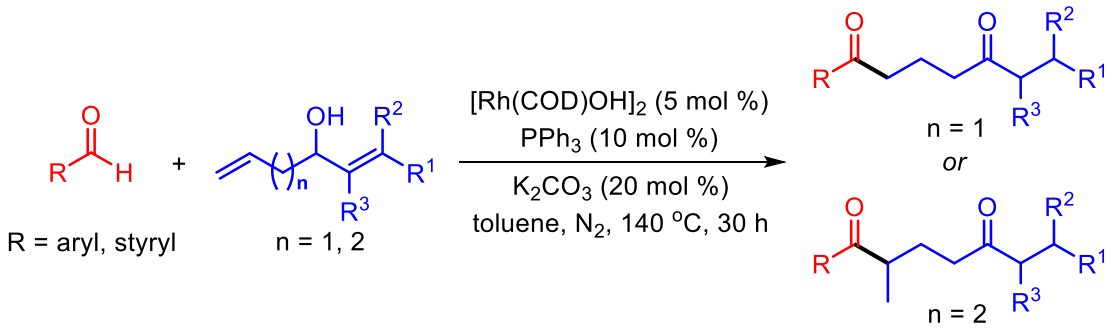
2. General Procedures

(1) General Procedure for the Preparation of Alkenyl-Substituted Allylic Alcohols (2a–2r)



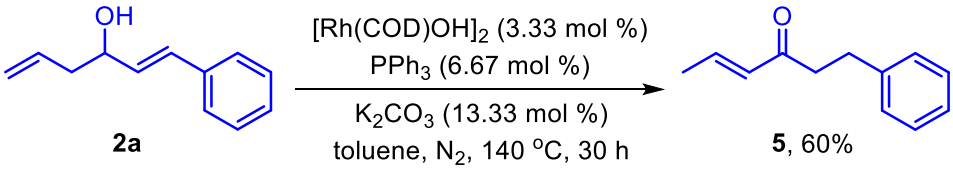
Alkenyl-substituted allylic alcohols (**2a**–**2r**) were prepared through the Grignard reaction according to the literature procedure.[1]

(2) General Procedure for the Synthesis of 1,5-Diketones 3



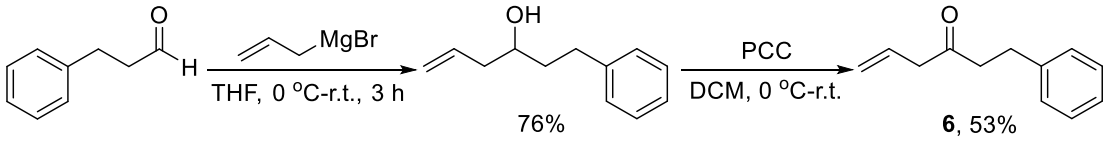
To an oven-dried sealed tube (10 mL) equipped with a stirrer bar in the glove box (filled with N_2) was added $[Rh(COD)OH]_2$ (4.6 mg, 0.01 mmol, 5 mol %), PPh_3 (5.2 mg, 0.02 mmol, 10 mol %), K_2CO_3 (5.5 mg, 0.04 mmol, 20 mol %), aldehyde **1** (0.2 mmol, 1.0 equiv), and alkenyl-substituted allylic alcohol **2** (0.3 mmol, 1.5 equiv). Then anhydrous toluene (1.0 mL, 0.2 M) was added. The tube was sealed and removed from the glove box. The mixture was stirred at room temperature for 15 min, and then heated at 140 °C for 30 h using a Heidolph MR Hei-Tec heating magnetic stirrer (Heidolph Instruments, Germany). Upon completion, the reaction mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc) to afford the desired 1,5-dikeone **3**.

(3) Synthesis of (*E*)-1-phenylhex-4-en-3-one 5



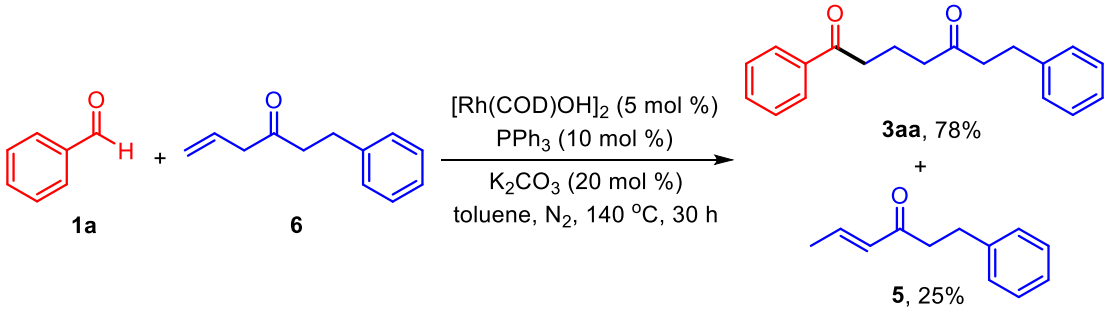
To an oven-dried sealed tube (10 mL) equipped with a stirrer bar in the glove box (filled with N_2) was added $[Rh(COD)OH]_2$ (6.1 mg, 0.0133 mmol, 3.33 mol %), PPh_3 (7.0 mg, 0.0267 mmol, 6.67 mol %), K_2CO_3 (7.4 mg, 0.0533 mmol, 13.33 mol %), and (*E*)-1-phenylhexa-1,5-dien-3-ol **2a** (69.7 mg, 0.4 mmol, 1 equiv). Then anhydrous toluene (1.0 mL) was added. The tube was sealed and removed from the glove box. The mixture was stirred at room temperature for 15 min, and then heated at 140 °C for 30 h using a Heidolph MR Hei-Tec heating magnetic stirrer (Heidolph Instruments, Germany). Upon completion, the reaction mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc = 300:1) to afford **5** as a light-yellow oil, 41.8 mg (60%).

(4) Preparation of 1-Phenylhex-5-en-3-one 6



1-Phenylhex-5-en-3-one **6** was prepared through the Grignard reaction[1] and PCC oxidation[2] according to the literature procedure.

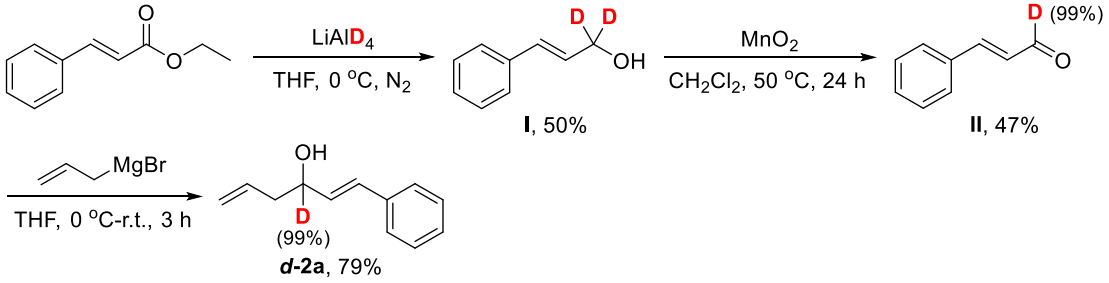
(5) Synthesis of 3aa from 1-Phenylhex-5-en-3-one 6



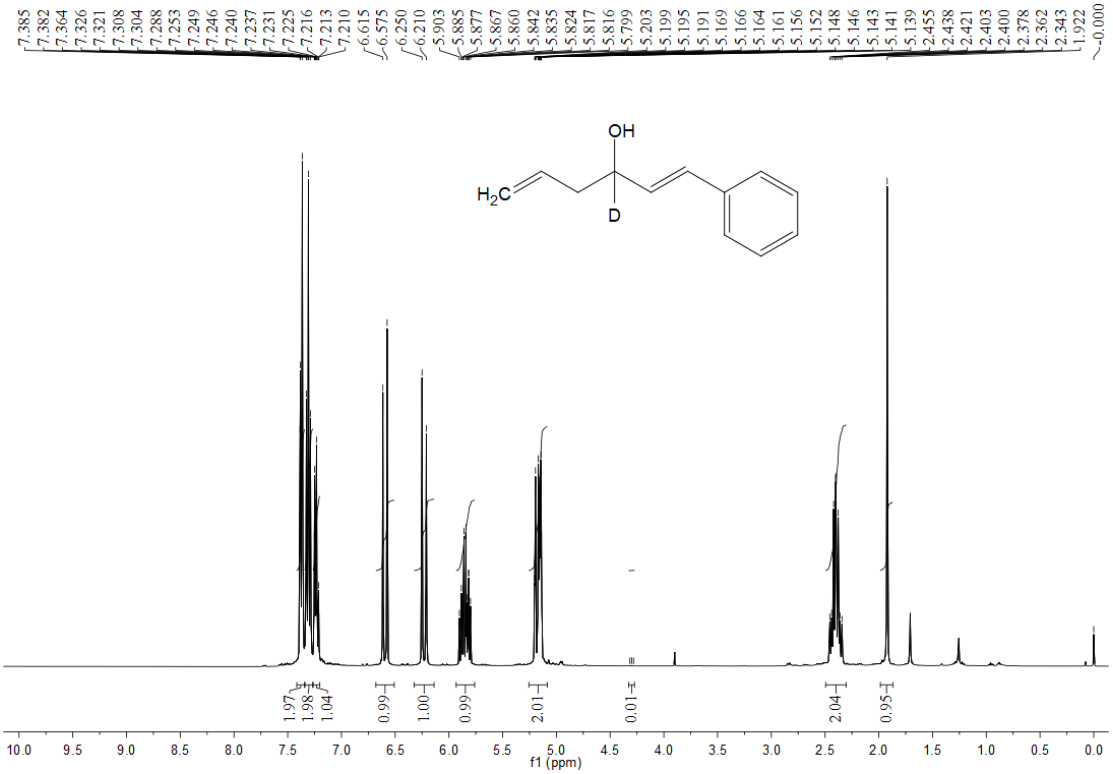
To an oven-dried sealed tube (10 mL) equipped with a stirrer bar in the glove box (filled with N_2) was added $[Rh(COD)OH]_2$ (4.6 mg, 0.01 mmol, 5 mol %), PPh_3 (5.2 mg, 0.02 mmol, 10 mol %), K_2CO_3 (5.5 mg, 0.04 mmol, 20 mol %), benzaldehyde **1a**

(21.2 mg, 0.2 mmol, 1.0 equiv), and 1-phenylhex-5-en-3-one **6** (52.3 mg, 0.3 mmol, 1.5 equiv). Then anhydrous toluene (1.0 mL, 0.2 M) was added. The tube was sealed and removed from the glove box. The mixture was stirred at room temperature for 15 min, and then heated at 140 ℃ for 30 h using a Heidolph MR Hei-Tec heating magnetic stirrer (Heidolph Instruments, Germany). Upon completion, the reaction mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc = 200:1) to afford the desired 1,5-dikeone **3aa** (a light-yellow oil, 43.7 mg, 78%) and (*E*)-1-phenylhex-4-en-3-one **5** (a light-yellow oil, 13.0 mg, 25%).

(6) Preparation of (*E*)-1-Phenylhexa-1,5-dien-3-*d*-3-ol (*d*-2a)

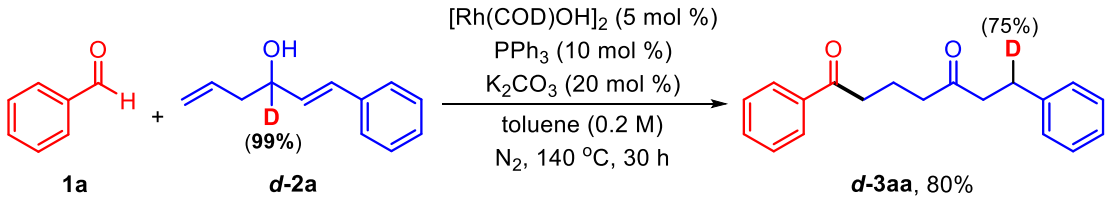


(*E*)-1-Phenylhexa-1,5-dien-3-*d*-3-ol (***d*-2a**, 99% D-incorporation) was prepared from ethyl cinnamate through reduction with $LiAlD_4$,[3] oxidation with MnO_2,[4] and the Grignard reaction[1] according to the literature procedure.



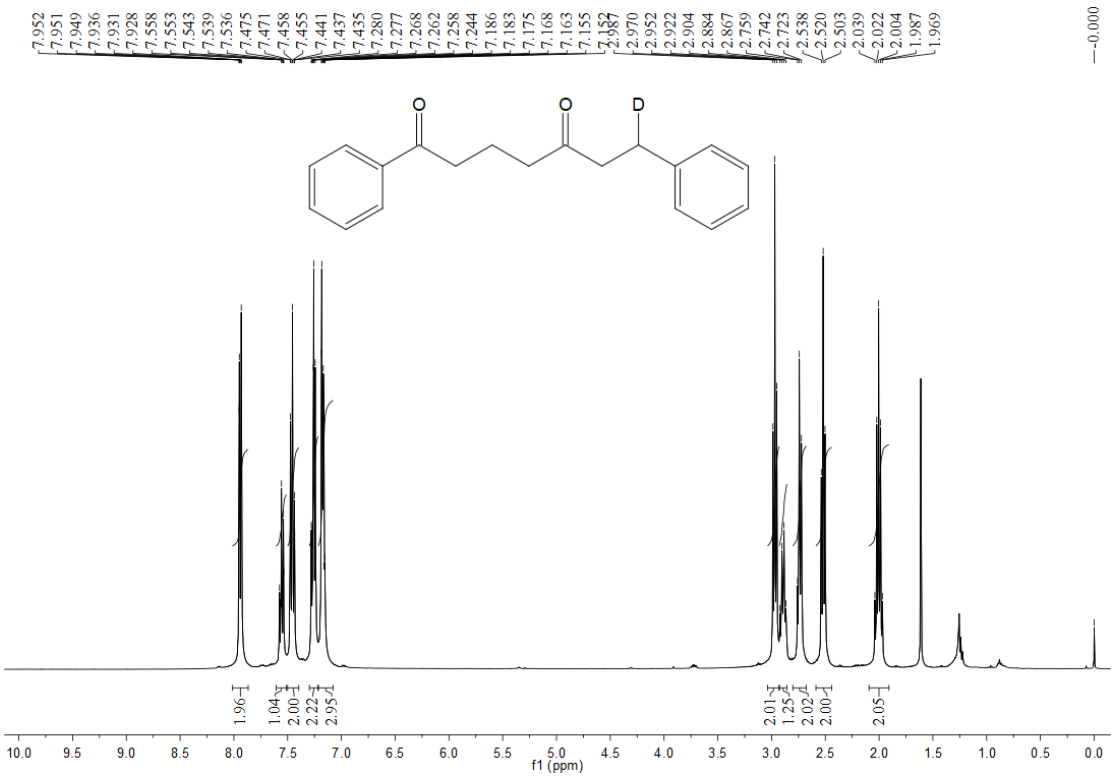
^{1}H NMR (400 MHz, $CDCl_3$) of ***d*-2a**

(7) Isotopic Labelling Experiment: Synthesis of *d*-3aa



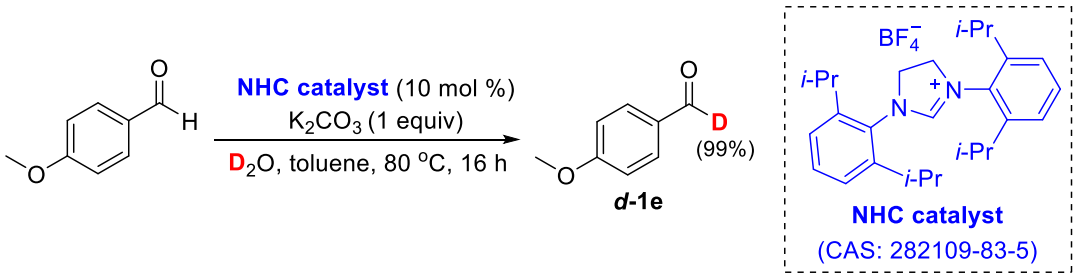
To an oven-dried sealed tube (10 mL) equipped with a stirrer bar in the glove box (filled with N_2) was added $[Rh(COD)OH]_2$ (4.6 mg, 0.01 mmol, 5 mol %), PPh_3 (5.2 mg, 0.02 mmol, 10 mol %), K_2CO_3 (5.5 mg, 0.04 mmol, 20 mol %), benzaldehyde **1a** (21.2 mg, 0.2 mmol, 1.0 equiv), and (*E*)-1-Phenylhexa-1,5-dien-3-*d*-3-ol ***d*-2a** (52.6 mg, 0.3 mmol, 1.5 equiv). Then anhydrous toluene (1.0 mL, 0.2 M) was added. The tube was sealed and removed from the glove box. The mixture was stirred at room temperature for 15 min, and then heated at 140 ℃ for 30 h using a Heidolph MR Hei-Tec heating magnetic stirrer (Heidolph Instruments, Germany). Upon completion, the reaction mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc = 200:1) to

afford ***d*-3aa** as a colorless oil, 45.0 mg (80%), approximately 75% D-incorporation.



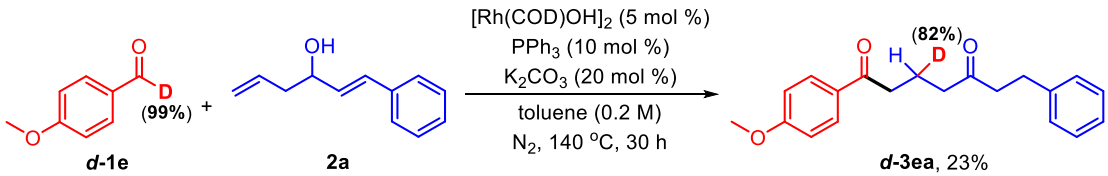
^{1}H NMR (400 MHz, $CDCl_3$) of ***d*-3aa**

(8) Preparation of 4-Methoxybenzaldehyde-*α*-d_1 (*d*-1e)



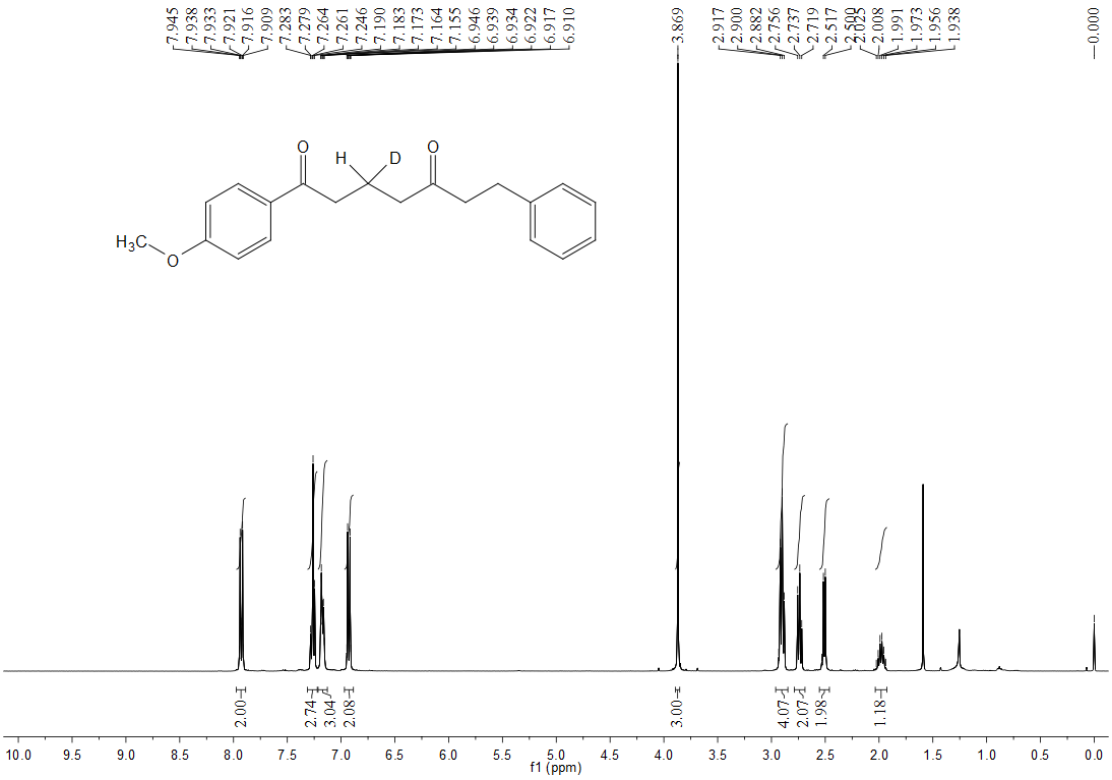
4-Methoxybenzaldehyde-*α*-d_1 (***d*-1e**) was prepared according to the literature procedure with 99% D-incorporation.[5]

(9) Isotopic Labelling Experiment: Synthesis of *d*-3ea



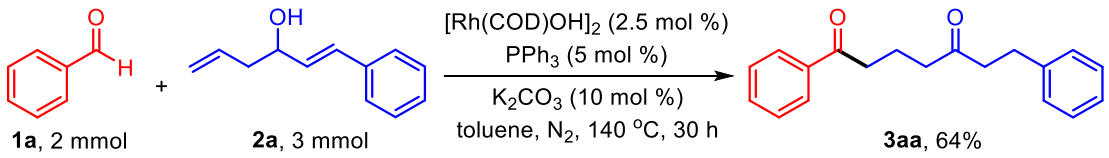
To an oven-dried sealed tube (10 mL) equipped with a stirrer bar in the glove box (filled with N_2) was added $[Rh(COD)OH]_2$ (4.6 mg, 0.01 mmol, 5 mol %), PPh_3 (5.2

mg, 0.02 mmol, 10 mol %), K_2CO_3 (5.5 mg, 0.04 mmol, 20 mol %), 4-methoxybenzaldehyde-α-d_1 (***d*-1e**, 0.2 mmol, 27.4 mg, 1.0 equiv), and (*E*)-1-phenylhexa-1,5-dien-3-ol (**2a**, 0.3 mmol, 52.3 mg, 1.5 equiv). Then anhydrous toluene (1.0 mL, 0.2 M) was added. The tube was sealed and removed from the glove box. The mixture was stirred at room temperature for 15 min, and heated at 140 ℃ for 30 h. Upon completion, the reaction mixture was cooled to room temperature and concentrated. The residue was purified by silica gel chromatography (*n*-hexane/EtOAc = 150:1) to afford the desired product ***d*-3ea** as a light-yellow oil, 14.3 mg (23%), approximately 82% D-incorporation.



^{1}H NMR (400 MHz, $CDCl_3$) of ***d*-3ea**

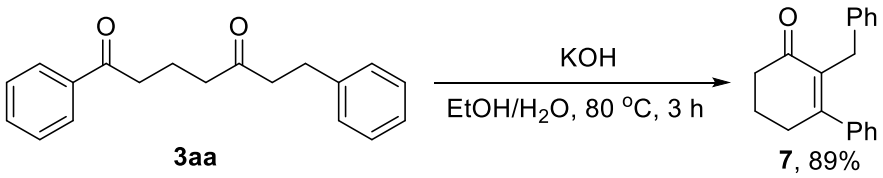
(10) Scale-Up Synthesis of 3aa



To an oven-dried sealed tube (30 mL) equipped with a stirrer bar in the glove box (filled with N_2) was added $[Rh(COD)OH]_2$ (22.8 mg, 0.05 mmol, 2.5 mol %), PPh_3

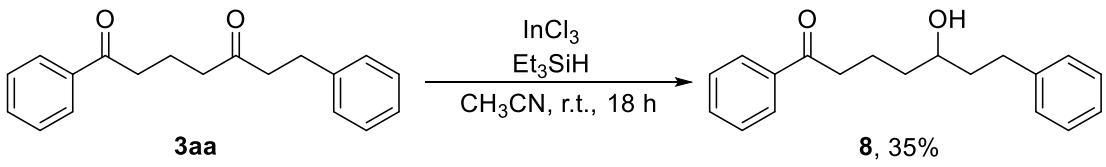
(26.2 mg, 0.1 mmol, 5 mol %), K_2CO_3 (27.6 mg, 0.2 mmol, 10 mol %), benzaldehyde **1a** (212.2 mg, 2 mmol, 1.0 equiv), and (*E*)-1-phenylhexa-1,5-dien-3-ol **2a** (522.7 mg, 3 mmol, 1.5 equiv). Then anhydrous toluene (10 mL, 0.2 M) was added. The tube was sealed and removed from the glove box. The mixture was stirred at room temperature for 15 min, and then heated at 140 ℃ for 30 h using a Heidolph MR Hei-Tec heating magnetic stirrer (Heidolph Instruments, Germany). Upon completion, the reaction mixture was cooled to room temperature and concentrated. The residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc = 200:1) to afford **3aa** as a light-yellow oil (358.9 mg, 64%).

(11) Synthesis of 2-Benzyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (7)



2-Benzyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (**7**) was prepared according to the literature procedure.[6] To a solution of 1,7-diphenylheptane-1,5-dione (**3aa**, 56 mg, 0.2 mmol) in EtOH (0.5 mL) and H_2O (0.5 mL) was added KOH (22 mg, 0.4 mmol). The mixture was stirred at 80 ℃ for 3 h and then extracted three times with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel flash chromatography (*n*-hexane/EtOAc = 10:1) to give the target product **7** (46.7 mg, 89% yield) as colorless oil.

(12) Synthesis of 5-Hydroxy-1,7-diphenylheptan-1-one (8)

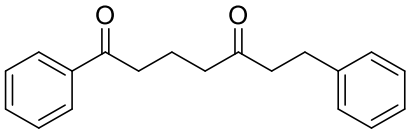


To a stirred solution of **3aa** (112.2 mg, 0.4 mmol, 1 equiv) and $InCl_3$ (44.2 mg, 0.2 mmol, 0.5 equiv) in dry acetonitrile (2 mL) was added Et_3SiH (186.0 mg, 1.6 mmol, 4 equiv). The reaction mixture was stirred at room temperature for 18 h. After completion of the reaction, water was added to the reaction mixture, which was

extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated in vacuo, and purified by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1) to afford the target product **8** (39.5 mg, 35% yield) as a colorless oil.

3. Characterization of Materials

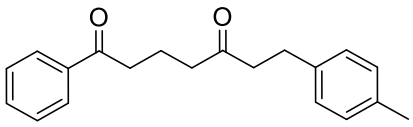
1,7-diphenylheptane-1,5-dione (3aa)



3aa

According to the General Procedure, the product **3aa** (a known compound[6]) was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 200:1), 42.1 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.95 (m, 2H), 7.54-7.58 (m, 1H), 7.44-7.48 (m, 2H), 7.25-7.28 (m, 2H), 7.15-7.18 (m, 3H), 2.97 (t, J = 7.2 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H), 2.74 (t, J = 7.6 Hz, 2H), 2.52 (t, J = 7.2 Hz, 2H), 1.97-2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 199.8, 141.0, 136.8, 133.2, 128.7, 128.5, 128.4, 128.1, 126.2, 44.3, 41.9, 37.4, 29.8, 18.2.

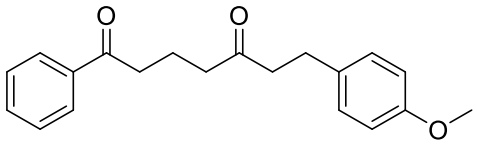
1-phenyl-7-(*p*-tolyl)heptane-1,5-dione (3ab)



3ab

According to the General Procedure, the product **3ab** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 40.6 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.95 (m, 2H), 7.54-7.58 (m, 1H), 7.44-7.48 (m, 2H), 7.02-7.09 (m, 4H), 2.96 (t, J = 6.8 Hz, 2H), 2.86 (t, J = 7.6 Hz, 2H), 2.72 (t, J = 7.6 Hz, 2H), 2.52 (t, J = 6.8 Hz, 2H), 2.29 (s, 3H), 1.96-2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 199.8, 137.9, 136.8, 135.7, 133.1, 129.2, 128.7, 128.2, 128.1, 44.4, 41.9, 37.5, 29.5, 21.0, 18.2; HRMS (ESI-TOF) calcd for $C_{20}H_{23}O_2$ $[M+H]^+$ (295.1698), found 295.1697.

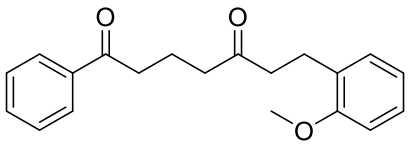
7-(4-methoxyphenyl)-1-phenylheptane-1,5-dione (3ac)



3ac

According to the General Procedure, the product **3ac** was obtained as a yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 45.9 mg (74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.95 (m, 2H), 7.53-7.57 (m, 1H), 7.43-7.47 (m, 2H), 7.08-7.11 (m, 2H), 6.78-6.82 (m, 2H), 3.75 (s, 3H), 2.96 (t, *J* = 6.8 Hz, 2H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.51 (t, *J* = 6.8 Hz, 2H), 1.96-2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 199.8, 158.0, 136.8, 133.1, 133.0, 129.3, 128.6, 128.1, 113.9, 55.3, 44.5, 41.9, 37.4, 29.0, 18.2; HRMS (ESI-TOF) calcd for $C_{20}H_{23}O_3$ $[M+H]^+$ (311.1647), found 311.1644.

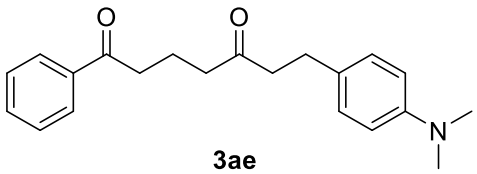
7-(2-methoxyphenyl)-1-phenylheptane-1,5-dione (3ad)



3ad

According to the General Procedure, the product **3ad** was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 80:1), 18.6 mg (30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.55-7.58 (m, 1H), 7.45-7.48 (m, 2H), 7.16-7.19 (m, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.82-6.88 (m, 2H), 3.81 (s, 3H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 1.97-2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 199.9, 157.5, 136.8, 133.2, 130.1, 129.3, 128.7, 128.1, 127.5, 120.5, 110.2, 55.2, 42.7, 41.8, 37.6, 25.2, 18.3; HRMS (ESI-TOF) calcd for $C_{20}H_{23}O_3$ $[M+H]^+$ (311.1647), found 311.1646.

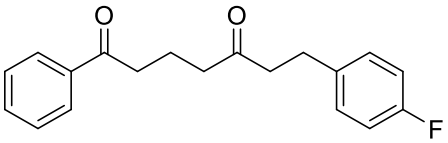
7-(4-(dimethylamino)phenyl)-1-phenylheptane-1,5-dione (3ae)



3ae

According to the General Procedure, the product **3ae** was obtained as a yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 100:1), 40.8 mg (63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.96 (m, 2H), 7.54-7.58 (m, 1H), 7.44-7.48 (m, 2H), 7.05 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 8.8 Hz, 2H)), 2.97 (t, J = 7.2 Hz, 2H), 2.89 (s, 6H), 2.81 (t, J = 7.6 Hz, 2H), 2.69 (t, J = 7.6 Hz, 2H), 2.52 (t, J = 7.2 Hz, 2H), 1.96-2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.4, 199.9, 149.3, 136.9, 133.1, 129.0, 128.7, 128.1, 113.1, 44.8, 42.0, 40.9, 37.5, 29.0, 18.2; HRMS (ESI-TOF) calcd for $C_{21}H_{26}NO_2$ $[M+H]^+$ (324.1964), found 324.1968.

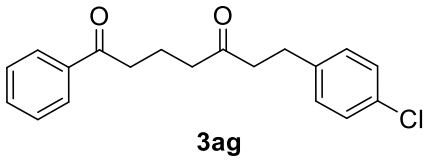
7-(4-fluorophenyl)-1-phenylheptane-1,5-dione (3af)



3af

According to the General Procedure, the product **3af** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 40.6 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.95 (m, 2H), 7.54-7.59 (m, 1H), 7.44-7.48 (m, 2H), 7.11-7.15 (m, 2H), 6.91-6.97 (m, 2H), 2.98 (t, J = 7.2 Hz, 2H), 2.87 (t, J = 7.6 Hz, 2H), 2.72 (t, J = 7.6 Hz, 2H), 2.52 (t, J = 7.2 Hz, 2H), 1.97-2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 199.8, 161.4 (d, J = 242.4 Hz), 136.8, 136.7 (d, J = 3.4 Hz), 133.2, 129.8 (d, J =7.8 Hz), 128.7, 128.1, 115.3 (d, J = 21.0 Hz), 44.3, 42.0, 37.4, 29.0, 18.2; HRMS (ESI-TOF) calcd for $C_{19}H_{20}FO_2$ $[M+H]^+$ (299.1447), found 299.1441.

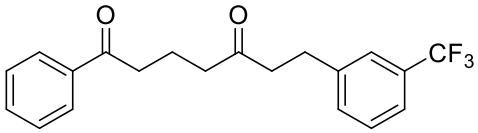
7-(4-chlorophenyl)-1-phenylheptane-1,5-dione (3ag)



3ag

According to the General Procedure, the product **3ag** was obtained as a yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 47.2 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.95 (m, 2H), 7.54-7.59 (m, 1H), 7.44-7.48 (m, 2H), 7.21-7.24 (m, 2H), 7.10-7.12 (m, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 1.97-2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4, 199.7, 139.5, 136.8, 133.2, 131.9, 129.8, 128.7, 128.6, 128.1, 44.0, 41.9, 37.4, 29.1, 18.2; HRMS (ESI-TOF) calcd for $C_{19}H_{20}ClO_2$ $[M+H]^+$ (315.1152), found 315.1152.

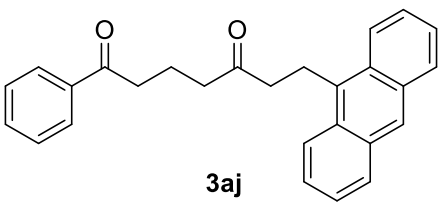
1-phenyl-7-(3-(trifluoromethyl)phenyl)heptane-1,5-dione (3ai)



3ai

According to the General Procedure, the product **3ai** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 52.5 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.95 (m, 2H), 7.54-7.58 (m, 1H), 7.44-7.48 (m, 4H), 7.36-7.38 (m, 2H), 2.94-3.00 (m, 4H), 2.77 (t, *J* = 7.2 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.98-2.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 199.7, 142.0, 136.8, 133.2, 131.9, 130.8 (q, *J* = 31.8 Hz), 129.0, 128.7, 128.1, 125.1 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 270.5 Hz), 123.1 (q, *J* = 3.7 Hz), 43.8, 41.9, 37.4, 29.4, 18.2; HRMS (ESI-TOF) calcd for $C_{20}H_{20}F_3O_2$ $[M+H]^+$ (349.1415), found 349.1418.

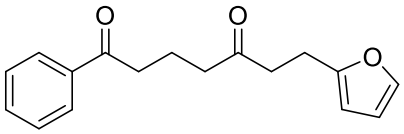
7-(anthracen-9-yl)-1-phenylheptane-1,5-dione (3aj)



3aj

According to the General Procedure, the product **3aj** was obtained as a yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 100:1), 60.9 mg (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.19-8.22 (m, 2H), 7.97-8.00 (m, 2H), 7.92-7.95 (m, 2H), 7.43-7.57 (m, 7H), 3.88-3.92 (m, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.86-2.90 (m, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.00-2.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 199.7, 136.8, 133.1, 131.6, 129.5, 129.4, 128.7, 128.1, 126.2, 125.9, 125.0, 124.0, 43.6, 42.0, 37.5, 21.8, 18.3; HRMS (ESI-TOF) calcd for $C_{27}H_{25}O_2$ $[M+H]^+$ (381.1855), found 381.1850.

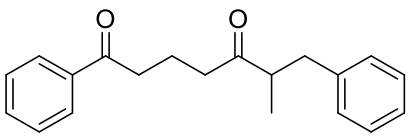
7-(furan-2-yl)-1-phenylheptane-1,5-dione (3ak)



3ak

According to the General Procedure, the product **3ak** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 40.0 mg (74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.96 (m, 2H), 7.55-7.58 (m, 1H), 7.44-7.48 (m, 2H), 7.27 (d, *J* = 2.0 Hz, 1H), 6.25 (dd, *J* = 2.8 Hz, 2.0 Hz, 1H), 5.98 (d, *J* = 2.8 Hz, 1H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.77 (t, *J* = 7.2 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 1.99-2.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 199.8, 154.6, 141.2, 136.8, 133.2, 128.7, 128.1, 110.3, 105.3, 41.8, 40.8, 37.5, 22.3, 18.2; HRMS (ESI-TOF) calcd for $C_{17}H_{19}O_3$ $[M+H]^+$ (271.1334), found 271.1329.

6-methyl-1,7-diphenylheptane-1,5-dione (3al)

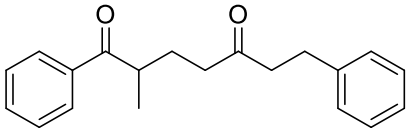


3al

According to the General Procedure, the product **3al** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 28.8 mg (49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.93 (m, 2H), 7.54-7.58 (m, 1H), 7.44-7.47 (m, 2H),

7.22-7.26 (m, 2H), 7.12-7.17 (m, 3H), 2.80-2.99 (m, 4H), 2.51-2.61 (m, 2H), 2.37 (dt, *J* = 17.6 Hz, 6.8 Hz, 1H), 1.90-1.97 (m, 2H), 1.09 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.0, 199.9, 139.7, 136.8, 133.1, 129.0, 128.6, 128.5, 128.1, 126.3, 48.1, 41.0, 39.3, 37.4, 18.0, 16.7; HRMS (ESI-TOF) calcd for $C_{20}H_{23}O_2$ $[M+H]^+$ (295.1698), found 295.1697.

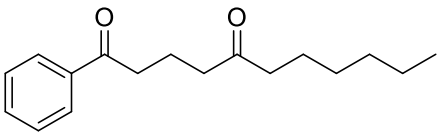
2-methyl-1,7-diphenylheptane-1,5-dione (3am)



3am

According to the General Procedure, the product **3am** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 30.0 mg (51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.97 (m, 2H), 7.55-7.79 (m, 1H), 7.45-7.49 (m, 2H), 7.24-7.27 (m, 2H), 7.14-7.19 (m, 3H), 3.48-3.57 (m, 1H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.62-2.75 (m, 2H), 2.44-2.52 (m, 1H), 2.31-2.39 (m, 1H), 2.03-2.12 (m, 1H), 1.70-1.78 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 203.9, 141.0, 136.4, 133.2, 128.8, 128.6, 128.41, 128.35, 126.2, 44.3, 40.2, 39.5, 29.8, 27.1, 17.6; HRMS (ESI-TOF) calcd for $C_{20}H_{23}O_2$ $[M+H]^+$ (295.1698), found 295.1699.

1-phenylundecane-1,5-dione (3an)

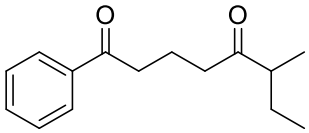


3an

According to the General Procedure, the product **3an** (a known compound[7]) was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 200:1), 34.9 mg (67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.98 (m, 2H), 7.54-7.58 (m, 1H), 7.44-7.48 (m, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 1.98-2.05 (m, 2H), 1.53-1.60 (m, 2H), 1.24-1.32 (m, 6H), 0.87 (t, *J* =

7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 199.9, 136.9, 133.1, 128.7, 128.1, 43.0, 41.6, 37.6, 31.7, 29.0, 23.9, 22.5, 18.3, 14.1.

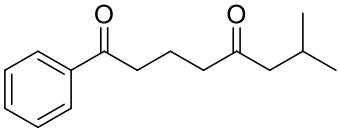
6-methyl-1-phenyloctane-1,5-dione (3ao)



3ao

According to the General Procedure, the product **3ao** (a known compound[6]) was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 16.7 mg (36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.98 (m, 2H), 7.54-7.58 (m, 1H), 7.44-7.48 (m, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.56-2.60 (m, 2H), 2.41-2.50 (m, 1H), 1.98-2.05 (m, 2H), 1.63-1.73 (m, 1H), 1.33-1.44 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.6, 200.0, 136.9, 133.1, 128.7, 128.1, 48.0, 40.1, 37.6, 26.0, 18.3, 16.0, 11.8.

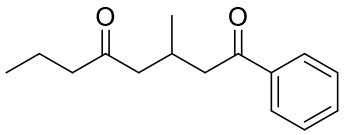
7-methyl-1-phenyloctane-1,5-dione (3ap)



3ap

According to the General Procedure, the product **3ap** was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 19.5 mg (42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.99 (m, 2H), 7.52-7.58 (m, 1H), 7.44-7.48 (m, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.29 (d, *J* = 6.8 Hz, 2H), 2.09-2.19 (m, 1H), 1.98-2.05 (m, 2H), 0.91 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 199.9, 136.9, 133.2, 128.7, 128.1, 52.0, 42.3, 37.6, 24.7, 22.7, 18.3; HRMS (ESI-TOF) calcd for $C_{15}H_{21}O_2$ $[M+H]^+$ (233.1542), found 233.1531.

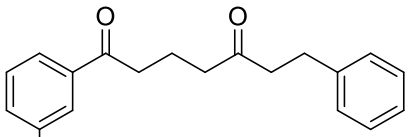
3-methyl-1-phenyloctane-1,5-dione (3ap')



3ap'

According to the General Procedure, the product **3ap'** (a known compound[6]) was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 9.8 mg (21%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-8.00 (m, 2H), 7.54-7.58 (m, 1H), 7.45-7.49 (m, 2H), 3.06 (dd, *J* = 15.6 Hz, 6.0 Hz, 1H), 2.79 (dd, *J* = 15.6 Hz, 7.2 Hz, 1H), 2.64-2.73 (m, 1H), 2.54 (dd, *J* = 16.0 Hz, 6.0 Hz, 1H), 2.35-2.41 (m, 3H), 1.56-1.65 (m, 2H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 199.8, 137.1, 133.1, 128.7, 128.3, 49.5, 45.23, 45.18, 26.2, 20.3, 17.3, 13.8.

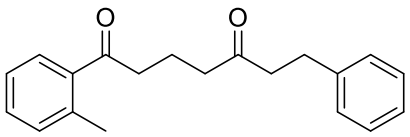
7-phenyl-1-(*m*-tolyl)heptane-1,5-dione (3ba)



3ba

According to the General Procedure, the product **3ba** was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 40.0 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.75 (m, 2H), 7.32-7.38 (m, 2H), 7.25-7.28 (m, 2H), 7.15-7.18 (m, 3H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.96-2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 200.0, 141.1, 138.4, 136.9, 133.9, 128.62, 128.55, 128.4, 126.2, 125.3, 44.3, 42.0, 37.5, 29.9, 21.4, 18.2; HRMS (ESI-TOF) calcd for $C_{20}H_{23}O_2$ $[M+H]^+$ (295.1698), found 295.1702.

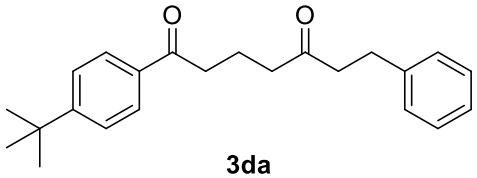
7-phenyl-1-(*o*-tolyl)heptane-1,5-dione (3ca)



3ca

According to the General Procedure, the product **3ca** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 31.8 mg (54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 1H), 7.34-7.38 (m, 1H), 7.23-7.28 (m, 4H), 7.16-7.19 (m, 3H), 2.87-2.92 (m, 4H), 2.74 (t, J = 7.2 Hz, 2H), 2.50 (t, J = 7.2 Hz, 2H), 2.48 (s, 3H), 1.94-2.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 203.8, 141.1, 138.1, 137.8, 132.0, 131.4, 128.57, 128.55, 128.4, 126.2, 125.8, 44.3, 42.0, 40.3, 29.8, 21.4, 18.4; HRMS (ESI-TOF) calcd for $C_{20}H_{23}O_2$ $[M+H]^+$ (295.1698), found 295.1701.

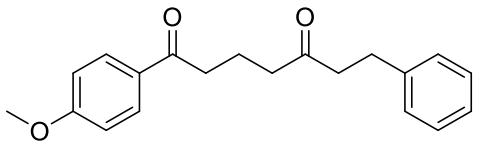
1-(4-(*tert*-butyl)phenyl)-7-phenylheptane-1,5-dione (3da)



3da

According to the General Procedure, the product **3da** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 34.3 mg (51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.90 (m, 2H), 7.45-7.49 (m, 2H), 7.25-7.28 (m, 2H), 7.15-7.19 (m, 3H), 2.95 (t, J = 7.2 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H), 2.74 (t, J = 7.6 Hz, 2H), 2.52 (t, J = 7.2 Hz, 2H), 1.96-2.03 (m, 2H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 199.5, 156.9, 141.1, 134.3, 128.6, 128.4, 128.1, 126.2, 125.6, 44.3, 42.0, 37.4, 35.2, 31.2, 29.9, 18.3; HRMS (ESI-TOF) calcd for $C_{23}H_{29}O_2$ $[M+H]^+$ (337.2168), found 337.2154.

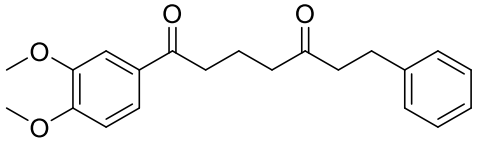
1-(4-methoxyphenyl)-7-phenylheptane-1,5-dione (3ea)



3ea

According to the General Procedure, the product **3ea** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 43.4 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.95 (m, 2H), 7.25-7.28 (m, 2H), 7.16-7.19 (m, 3H), 6.91-6.95 (m, 2H), 3.87 (s, 3H), 2.88-2.93 (m, 4H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 1.96-2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 198.4, 163.5, 141.1, 130.4, 130.0, 128.6, 128.4, 126.2, 113.8, 55.5, 44.3, 42.0, 37.1, 29.9, 18.4; HRMS (ESI-TOF) calcd for $C_{20}H_{23}O_3$ $[M+H]^+$ (311.1647), found 311.1646.

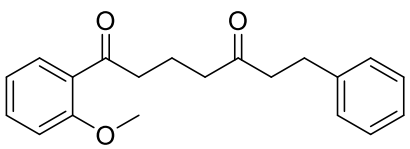
1-(3,4-dimethoxyphenyl)-7-phenylheptane-1,5-dione (3fa)



3fa

According to the General Procedure, the product **3fa** was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 100:1), 50.4 mg (74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.25-7.29 (m, 2H), 7.17-7.19 (m, 3H), 6.88 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 2.89-2.95 (m, 4H), 2.74 (d, *J* = 7.2 Hz, 2H), 2.52 (d, *J* = 7.2 Hz, 2H), 1.96-2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 199.5, 154.3, 150.1, 142.1, 131.1, 129.6, 129.4, 127.2, 123.9, 111.2, 111.1, 57.2, 57.1, 45.3, 43.0, 38.1, 30.9, 19.6; HRMS (ESI-TOF) calcd for $C_{21}H_{25}O_4$ $[M+H]^+$ (341.1753), found 341.1757.

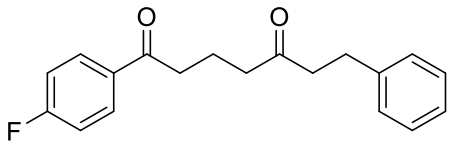
1-(2-methoxyphenyl)-7-phenylheptane-1,5-dione (3ga)



3ga

According to the General Procedure, the product **3ga** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 46.5 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.43-7.47 (m, 1H), 7.24-7.28 (m, 2H), 7.16-7.19 (m, 3H), 6.94-7.01 (m, 2H), 3.88 (s, 3H), 2.98 (t, J = 7.2 Hz, 2H), 2.89 (t, J = 7.2 Hz, 2H), 2.73 (t, J = 7.2 Hz, 2H), 2.48 (t, J = 7.2 Hz, 2H), 1.92-1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 202.1, 158.6, 141.1, 133.5, 130.3, 128.5, 128.4, 128.3, 126.1, 120.7, 111.6, 55.5, 44.3, 42.7, 42.2, 29.8, 18.4; HRMS (ESI-TOF) calcd for $C_{20}H_{23}O_3$ $[M+H]^+$ (311.1647), found 311.1644.

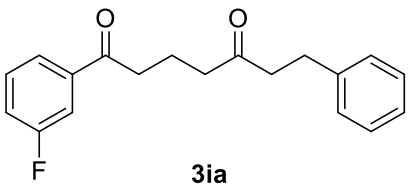
1-(4-fluorophenyl)-7-phenylheptane-1,5-dione (3ha)



3ha

According to the General Procedure, the product **3ha** was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 44.8 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.99 (m, 2H), 7.25-7.28 (m, 2H), 7.09-7.18 (m, 5H), 2.89-2.95 (m, 4H), 2.74 (t, J = 7.2 Hz, 2H), 2.52 (t, J = 6.8 Hz, 2H), 1.96-2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 198.2, 165.8 (d, J = 253.2 Hz), 141.0, 133.3 (d, J = 3.0 Hz), 130.8 (d, J = 9.3 Hz), 128.6, 128.4, 126.2, 115.7 (d, J = 21.6 Hz), 44.3, 41.9, 37.4, 29.9, 18.2; HRMS (ESI-TOF) calcd for $C_{19}H_{20}FO_2$ $[M+H]^+$ (299.1447), found 299.1450.

1-(3-fluorophenyl)-7-phenylheptane-1,5-dione (3ia)

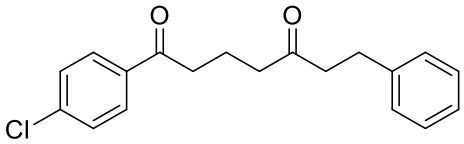


3ia

According to the General Procedure, the product **3ia** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 24.4 mg (41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 9.2 Hz, 1H),

7.41-7.47 (m, 1H), 7.25-7.29 (m, 3H), 7.17-7.19 (m, 3H), 2.89-2.96 (m, 4H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 1.96-2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 198.5 (d, *J* = 2.1 Hz), 162.9 (d, *J* = 246.4 Hz), 141.0, 138.9 (d, *J* = 6.0 Hz), 130.3 (d, *J* = 7.4 Hz), 128.5 (d, *J* = 18.1 Hz), 126.2, 123.9 (d, *J* = 3.1 Hz), 120.2 (d, *J* = 21.2 Hz), 114.9 (d, *J* = 21.9 Hz), 44.3, 41.8, 37.6, 29.9, 18.1; HRMS (ESI-TOF) calcd for $C_{19}H_{20}FO_2$ $[M+H]^+$ (299.1447), found 299.1449.

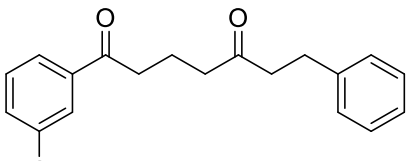
1-(4-chlorophenyl)-7-phenylheptane-1,5-dione (3ja)



3ja

According to the General Procedure, the product **3ja** was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 37.8 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.90 (m, 2H), 7.41-7.45 (m, 2H), 7.25-7.28 (m, 2H), 7.16-7.19 (m, 3H), 2.89-2.95 (m, 4H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 1.95-2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 198.6, 141.0, 139.6, 135.1, 129.6, 129.0, 128.6, 128.4, 126.2, 44.3, 41.8, 37.5, 29.9, 18.1; HRMS (ESI-TOF) calcd for $C_{19}H_{20}ClO_2$ $[M+H]^+$ (315.1152), found 315.1152.

1-(3-chlorophenyl)-7-phenylheptane-1,5-dione (3ka)

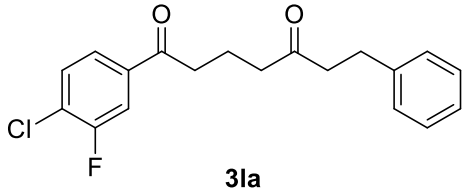


3ka

According to the General Procedure, the product **3ka** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 42.8 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.91 (m, 1H), 7.80-7.83 (m, 1H), 7.53 (ddd, *J* = 8.0 Hz, 2.4 Hz, 1.2 Hz, 1H), 7.38-7.42 (m, 1H), 7.25-7.29 (m, 2H), 7.16-7.19 (m, 3H), 2.89-2.95 (m, 4H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 6.8 Hz, 2H), 1.96-2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 198.5, 141.0, 138.3, 135.0, 133.1, 130.0,

128.6, 128.4, 128.2, 126.2, 44.3, 41.8, 37.6, 29.9, 18.0; HRMS (ESI-TOF) calcd for $C_{19}H_{20}ClO_2$ $[M+H]^+$ (315.1152), found 315.1150.

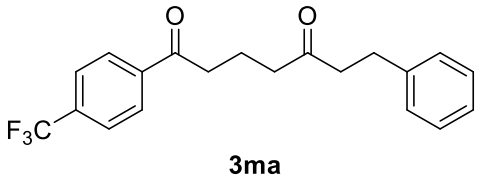
1-(4-chloro-3-fluorophenyl)-7-phenylheptane-1,5-dione (3la)



3la

According to the General Procedure, the product **3la** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 46.6 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.72 (m, 2H), 7.48-7.52 (m, 1H), 7.25-7.29 (m, 2H), 7.16-7.19 (m, 3H), 2.89-2.93 (m, 4H), 2.75 (t, J = 7.6 Hz, 2H), 2.52 (t, J = 7.2 Hz, 2H), 1.95-2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 197.5 (d, J = 1.5 Hz), 158.3 (d, J = 249.4 Hz), 141.0, 137.0 (d, J = 5.4 Hz), 131.0, 128.6, 128.4, 126.5 (d, J = 17.9 Hz), 126.2, 124.5 (d, J = 3.6 Hz), 116.0 (d, J = 21.7 Hz), 44.3, 41.7, 37.5, 29.9, 18.0; HRMS (ESI-TOF) calcd for $C_{19}H_{19}ClFO_2$ $[M+H]^+$ (333.1058), found 333.1055.

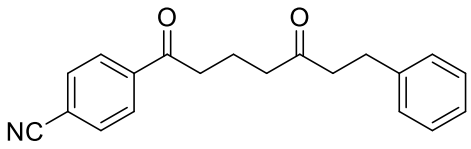
7-phenyl-1-(4-(trifluoromethyl)phenyl)heptane-1,5-dione (3ma)



3ma

According to the General Procedure, the product **3ma** was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 45.3 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.18-7.21 (m, 2H), 7.08-7.12 (m, 3H), 2.91 (t, J = 6.8 Hz, 2H), 2.84 (t, J = 7.2 Hz, 2H), 2.68 (t, J = 7.2 Hz, 2H), 2.46 (t, J = 6.8 Hz, 2H), 1.90-1.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 198.8, 141.0, 139.4, 134.5 (q, J = 32.6 Hz), 128.6, 128.5, 128.4, 126.2, 125.8 (q, J = 3.7 Hz), 123.7 (q, J = 270.8 Hz), 44.3, 41.7, 37.8, 29.9, 18.0; HRMS (ESI-TOF) calcd for $C_{20}H_{20}F_3O_2$ $[M+H]^+$ (349.1415), found 349.1415.

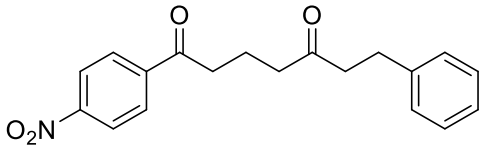
4-(5-oxo-7-phenylheptanoyl)benzonitrile (3na)



3na

According to the General Procedure, the product **3na** was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 100:1), 38.5 mg (63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-8.04 (m, 2H), 7.76-7.78 (m, 2H), 7.25-7.29 (m, 2H), 7.17-7.19 (m, 3H), 2.97 (t, J = 6.8 Hz, 2H), 2.91 (t, J = 7.6 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 2.53 (t, J = 6.8 Hz, 2H), 1.96-2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 198.4, 140.9, 139.7, 132.6, 128.59, 128.56, 128.4, 126.3, 118.0, 116.4, 44.3, 41.7, 37.8, 29.9, 17.9; HRMS (ESI-TOF) calcd for $C_{20}H_{20}NO_2$ $[M+H]^+$ (306.1494), found 306.1489.

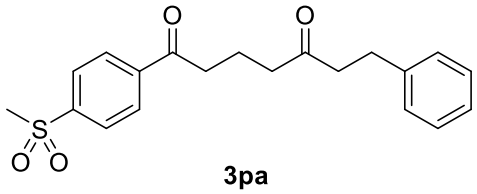
1-(4-nitrophenyl)-7-phenylheptane-1,5-dione (3oa)



3oa

According to the General Procedure, the product **3oa** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 100:1), 35.1 mg (54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29-8.32 (m, 2H), 8.08-8.11 (m, 2H), 7.25-7.29 (m, 2H), 7.17-7.19 (m, 3H), 3.00 (t, J = 7.2 Hz, 2H), 2.91 (t, J = 7.2 Hz, 2H), 2.76 (t, J = 7.2 Hz, 2H), 2.54 (t, J = 6.8 Hz, 2H), 1.98-2.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 198.2, 150.4, 141.2, 140.9, 129.2, 128.6, 128.4, 126.2, 123.9, 44.3, 41.6, 38.1, 29.9, 17.9; HRMS (ESI-TOF) calcd for $C_{19}H_{20}NO_4$ $[M+H]^+$ (326.1392), found 326.1388.

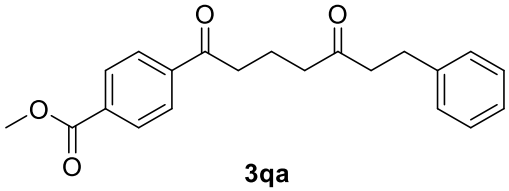
1-(4-(methylsulfonyl)phenyl)-7-phenylheptane-1,5-dione (3pa)



3pa

According to the General Procedure, the product **3pa** was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 30:1), 45.9 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.12 (m, 2H), 8.04-8.06 (m, 2H), 7.25-7.29 (m, 2H), 7.17-7.20 (m, 3H), 3.09 (s, 3H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.54 (t, *J* = 6.8 Hz, 2H), 1.98-2.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 198.5, 144.2, 141.0, 140.8, 129.0, 128.6, 128.4, 127.9, 126.3, 44.4, 44.3, 41.7, 38.0, 29.9, 18.0; HRMS (ESI-TOF) calcd for $C_{20}H_{23}O_4S$ $[M+H]^+$ (359.1317), found 359.1317.

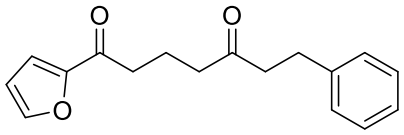
methyl 4-(5-oxo-7-phenylheptanoyl)benzoate (3qa)



3qa

According to the General Procedure, the product **3qa** was obtained as a yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 100:1), 38.6 mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.25-7.28 (m, 2H), 7.15-7.19 (m, 3H), 3.95 (s, 3H), 2.99 (t, *J* = 6.8 Hz, 2H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 6.8 Hz, 2H), 1.97-2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 199.3, 166.3, 141.0, 140.0, 133.9, 129.9, 128.6, 128.4, 128.0, 126.2, 52.6, 44.3, 41.8, 37.8, 29.9, 18.0; HRMS (ESI-TOF) calcd for $C_{21}H_{23}O_4$ $[M+H]^+$ (339.1596), found 339.1600.

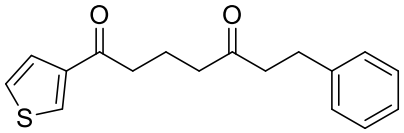
1-(furan-2-yl)-7-phenylheptane-1,5-dione (3ra)



3ra

According to the General Procedure, the product **3ra** was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 100:1), 25.4 mg (47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, J = 0.8 Hz, 1H), 7.25-7.29 (m, 2H), 7.16-7.20 (m, 4H), 6.53 (dd, J = 3.2 Hz, 1.6 Hz, 1H), 2.90 (t, J = 7.2 Hz, 2H), 2.83 (t, J = 7.2 Hz, 2H), 2.73 (t, J = 7.2 Hz, 2H), 2.50 (t, J = 7.2 Hz, 2H), 1.95-2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 189.0, 152.6, 146.4, 141.0, 128.6, 128.4, 126.2, 117.2, 112.3, 44.3, 41.8, 37.3, 29.8, 18.1; HRMS (ESI-TOF) calcd for $C_{17}H_{19}O_3$ $[M+H]^+$ (271.1334), found 271.1337.

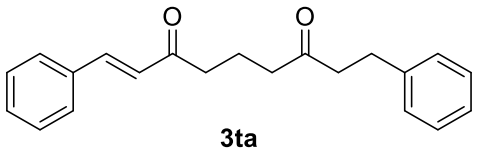
7-phenyl-1-(thiophen-3-yl)heptane-1,5-dione (3sa)



3sa

According to the General Procedure, the product **3sa** was obtained as a yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 100:1), 32.1 mg (56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 2.8 Hz, 1.2 Hz, 1H), 7.53 (dd, J = 5.2 Hz, 1.2 Hz, 1H), 7.31 (dd, J = 5.2 Hz, 2.8 Hz, 1H), 7.25-7.29 (m, 2H), 7.16-7.19 (m, 3H), 2.85-2.92 (m, 4H), 2.74 (t, J = 7.2 Hz, 2H), 2.52 (t, J = 6.8 Hz, 2H), 1.95-2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 194.3, 142.2, 141.0, 132.1, 128.6, 128.4, 127.0, 126.4, 126.2, 44.3, 41.9, 38.7, 29.9, 18.3; HRMS (ESI-TOF) calcd for $C_{17}H_{19}O_2S$ $[M+H]^+$ (287.1106), found 287.1108.

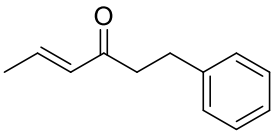
(*E*)-1,9-diphenylnon-1-ene-3,7-dione (3ta)



3ta

According to the General Procedure, the product **3ta** was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 150:1), 16.5 mg (27%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.57 (m, 3H), 7.38-7.41 (m, 3H), 7.25-7.29 (m, 2H), 7.17-7.20 (m, 3H), 6.70 (d, J = 16.4 Hz, 1H), 2.91 (t, J = 7.6 Hz, 2H), 2.74 (t, J = 7.6 Hz, 2H), 2.68 (t, J = 7.2 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H), 1.91-1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 199.9, 142.8, 141.1, 134.6, 130.6, 129.1, 128.6, 128.41, 128.37, 126.20, 126.17, 44.3, 41.9, 39.6, 29.9, 18.2; HRMS (ESI-TOF) calcd for $C_{21}H_{23}O_2$ $[M+H]^+$ (307.1698), found 307.1699.

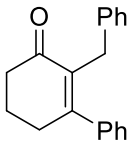
(*E*)-1-phenylhex-4-en-3-one (5)



5

The product **5** (a known compound[8]) was obtained as a light-yellow oil after silica gel chromatography (*n*-hexane/EtOAc = 300:1), 41.8 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.31 (m, 2H), 7.17-7.21 (m, 3H), 6.85 (dq, J = 16.0 Hz, 6.8 Hz, 1H), 6.13 (dq, J = 16.0 Hz, 1.6 Hz, 1H), 2.92-2.96 (m, 2H), 2.83-2.88 (m, 2H), 1.89 (dd, J = 6.8 Hz, 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 142.9, 141.4, 132.0, 128.5, 128.4, 126.1, 41.7, 30.1, 18.4.

2-benzyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (7)

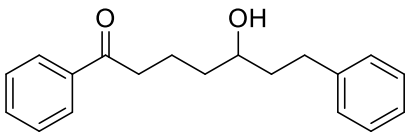


7

The product **7** (a known compound[9]) was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 10:1), 46.7 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.38 (m, 3H), 7.08-7.19 (m, 5H), 6.95-6.97 (m, 2H), 3.57 (s, 2H), 2.68 (t, J = 6.0 Hz, 2H), 2.53-2.56 (m, 2H), 2.09-2.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 158.6, 141.2, 141.0, 135.1, 128.5, 128.3, 128.2, 128.0, 126.8, 125.6,

38.1, 33.6, 32.0, 22.8.

5-hydroxy-1,7-diphenylheptan-1-one (8)



8

The product **8** was obtained as a colorless oil after silica gel chromatography (*n*-hexane/EtOAc = 100:1), 39.5 mg (35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.96 (m, 2H), 7.54-7.57 (m, 1H), 7.44-7.47 (m, 2H), 7.25-7.29 (m, 2H), 7.15-7.20 (m, 3H), 3.59-3.70 (m, 1H), 3.01 (t, J = 7.2 Hz, 2H), 2.76-2.83 (m, 1H), 2.64-2.71 (m, 1H), 1.73-1.93 (m, 5H), 1.49-1.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 142.2, 137.1, 133.1, 128.7, 128.50, 128.48, 128.1, 125.9, 70.9, 39.2, 38.4, 37.1, 32.2, 20.1; HRMS (ESI-TOF) calcd for $C_{19}H_{21}O$ $[M+H-H_2O]^+$ (265.1592), found 265.1588.

4. References

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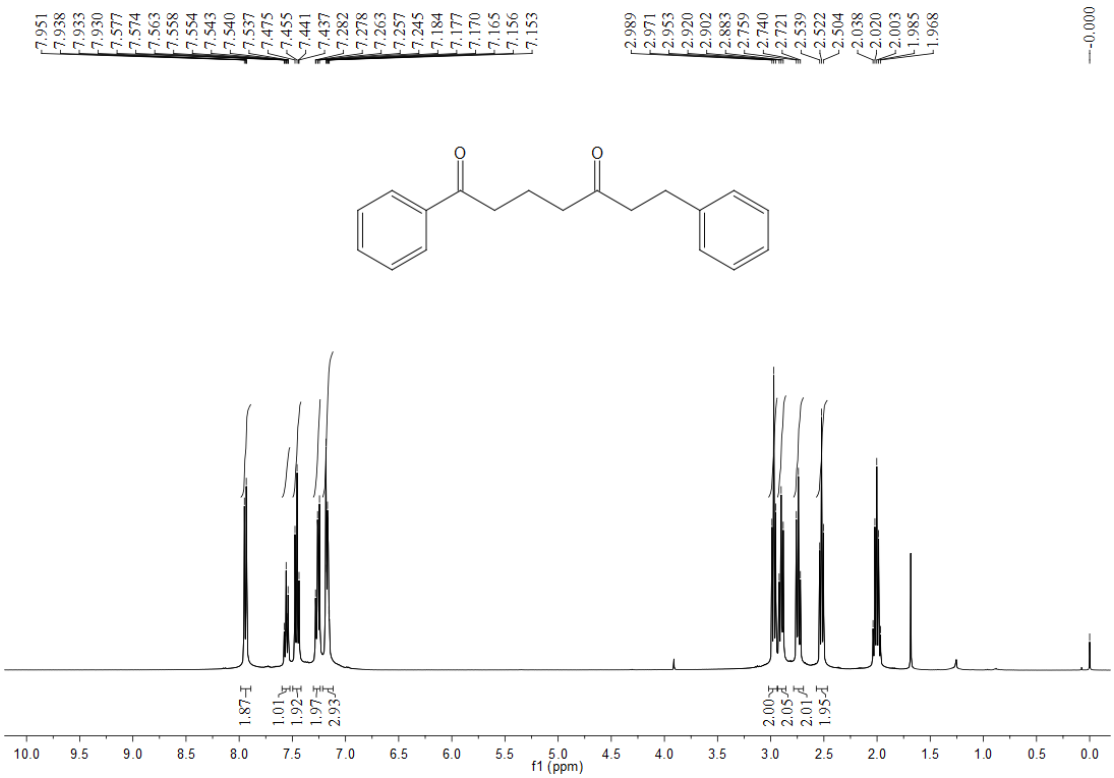
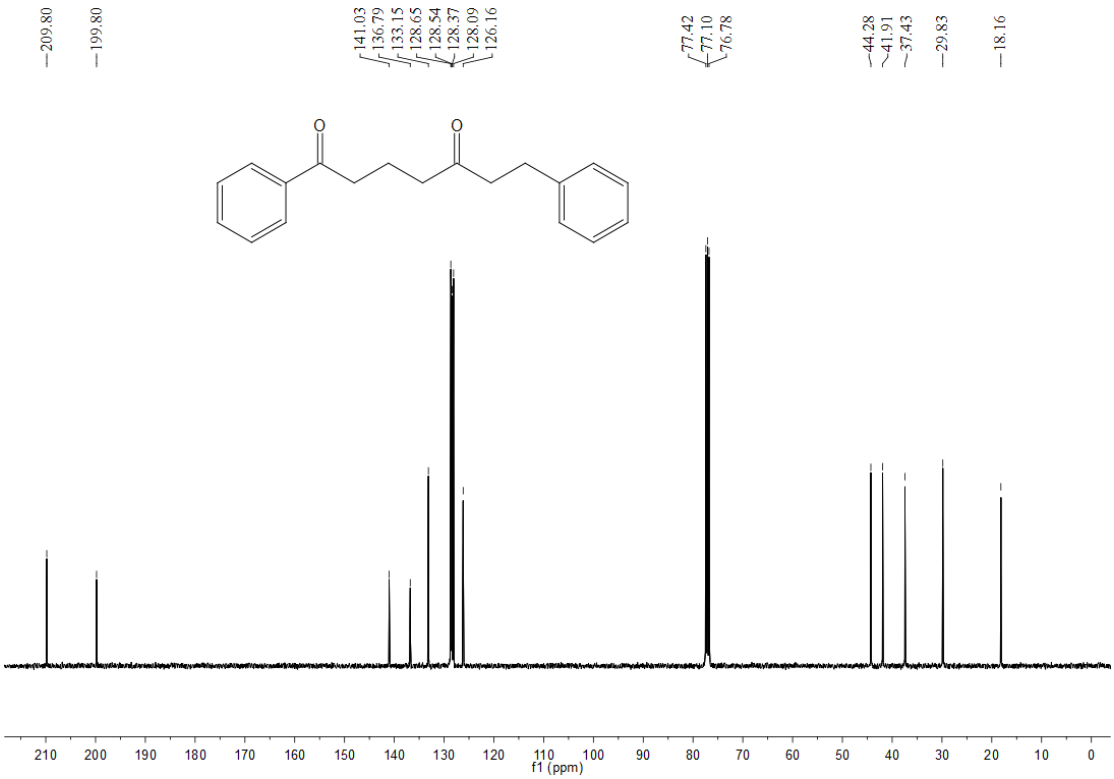
5. Copies of NMR Spectra

1,7-diphenylheptane-1,5-dione (3aa)

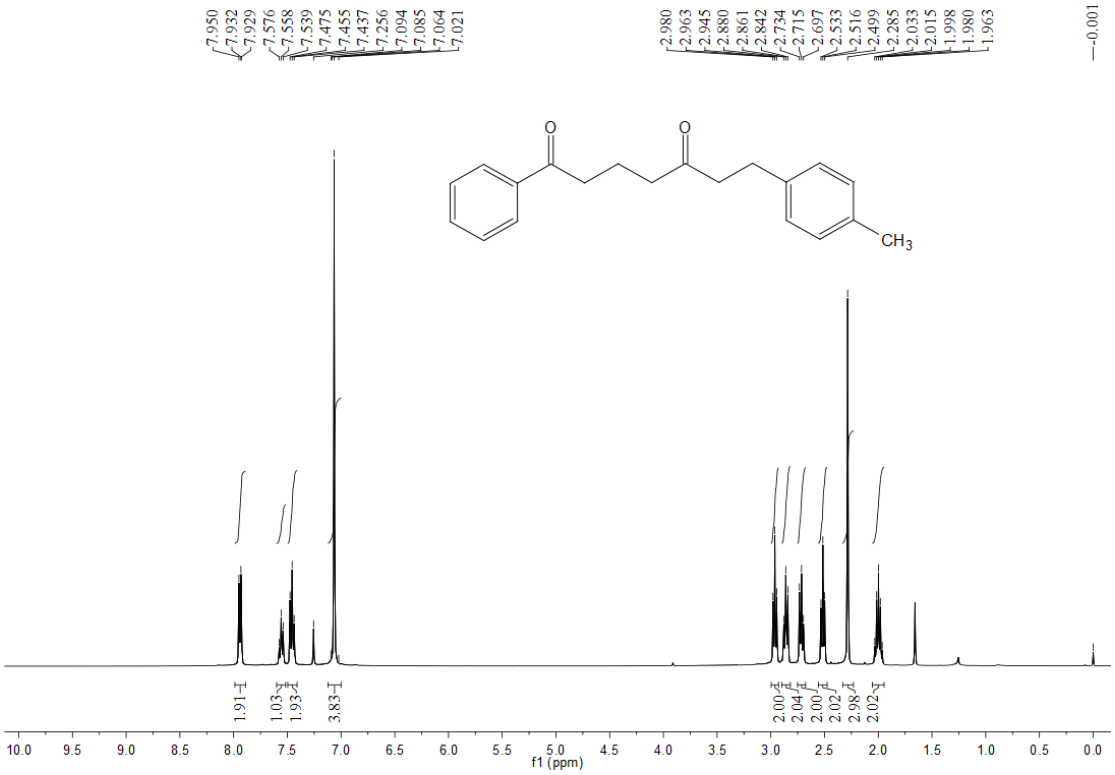


^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**

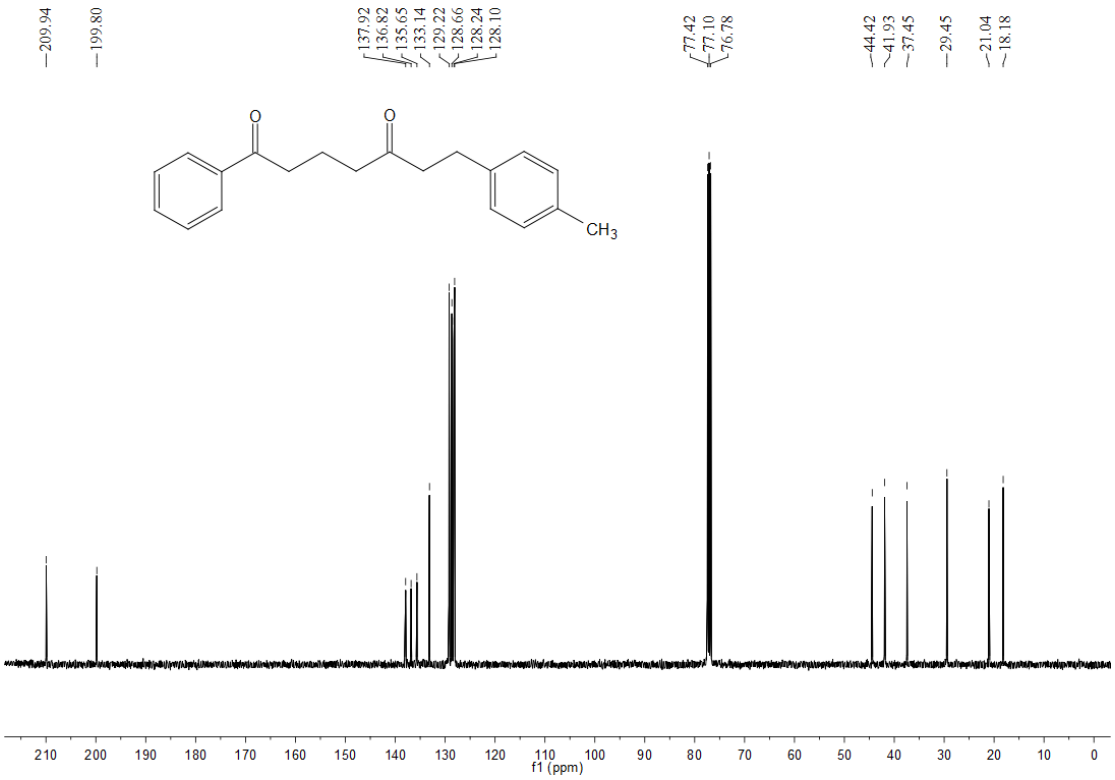


^{13}C NMR (100 MHz, $CDCl_3$) of **3aa**

1-phenyl-7-(*p*-tolyl)heptane-1,5-dione (3ab)

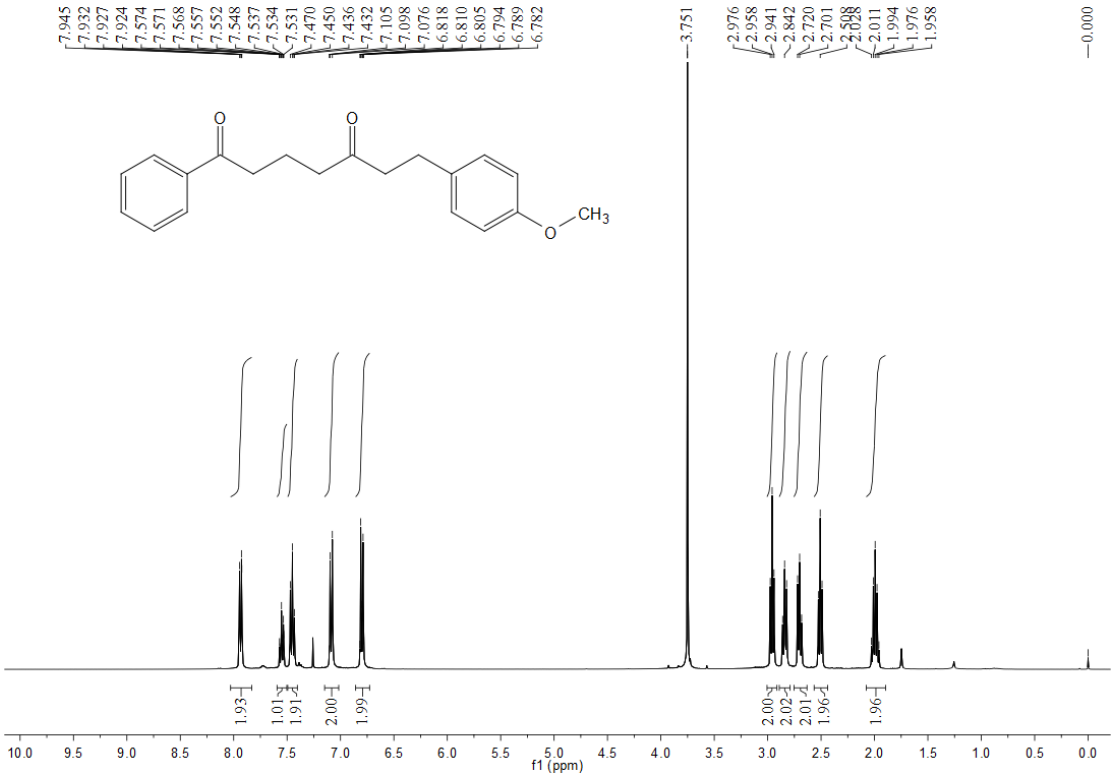


^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**

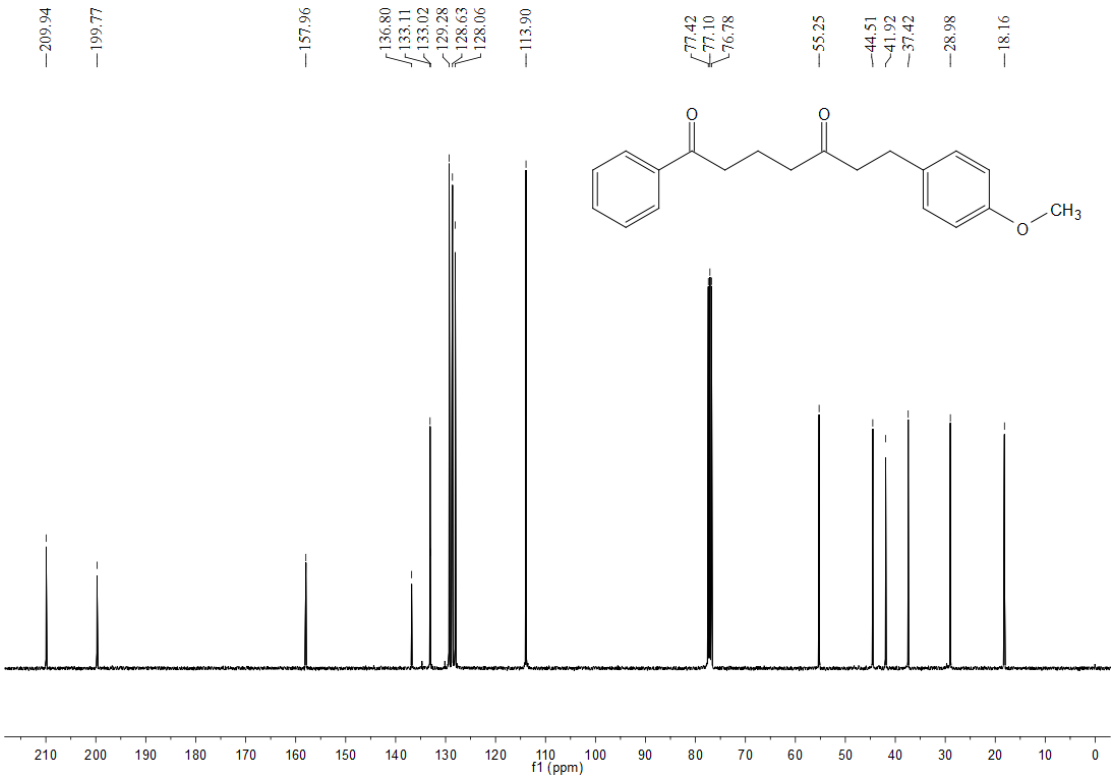


^{13}C NMR (100 MHz, $CDCl_3$) of **3ab**

7-(4-methoxyphenyl)-1-phenylheptane-1,5-dione (3ac)

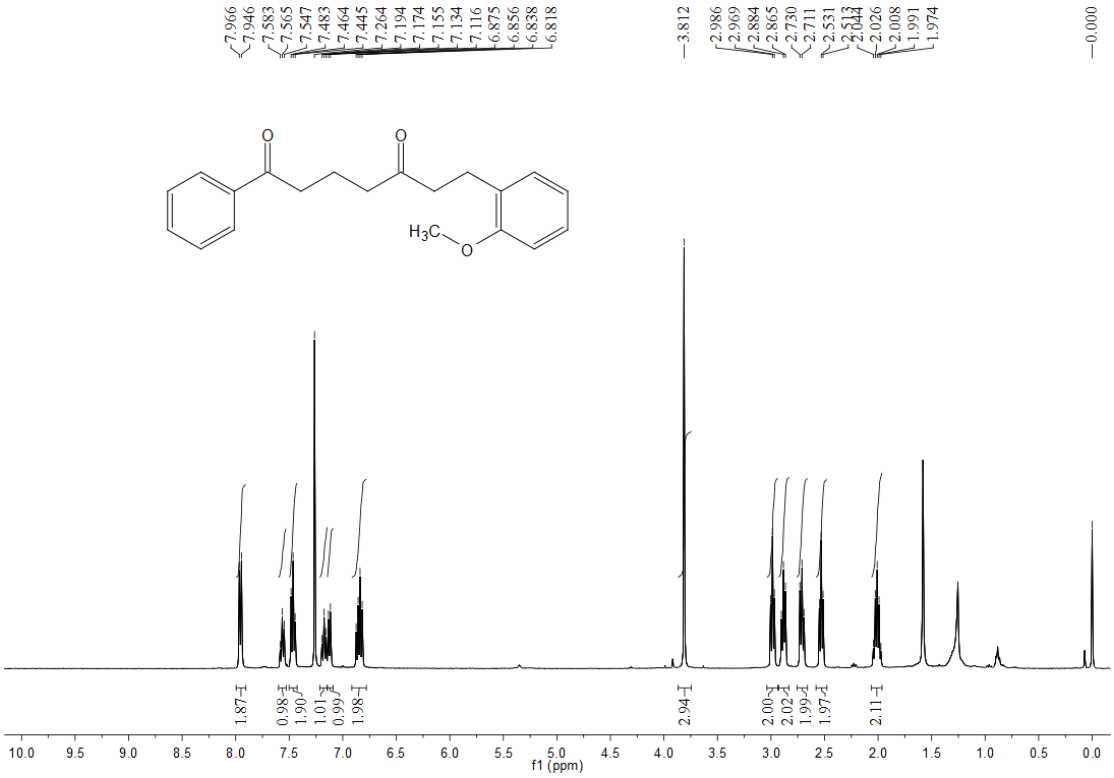


^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**

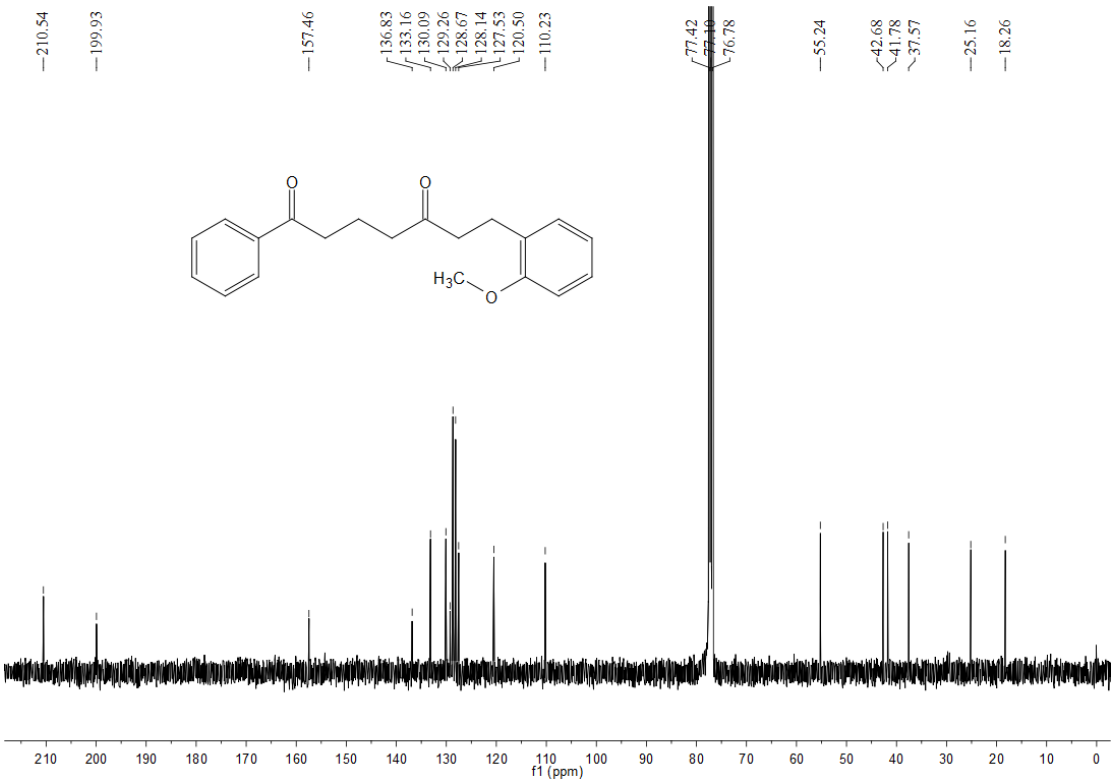


^{13}C NMR (100 MHz, $CDCl_3$) of **3ac**

7-(2-methoxyphenyl)-1-phenylheptane-1,5-dione (3ad)

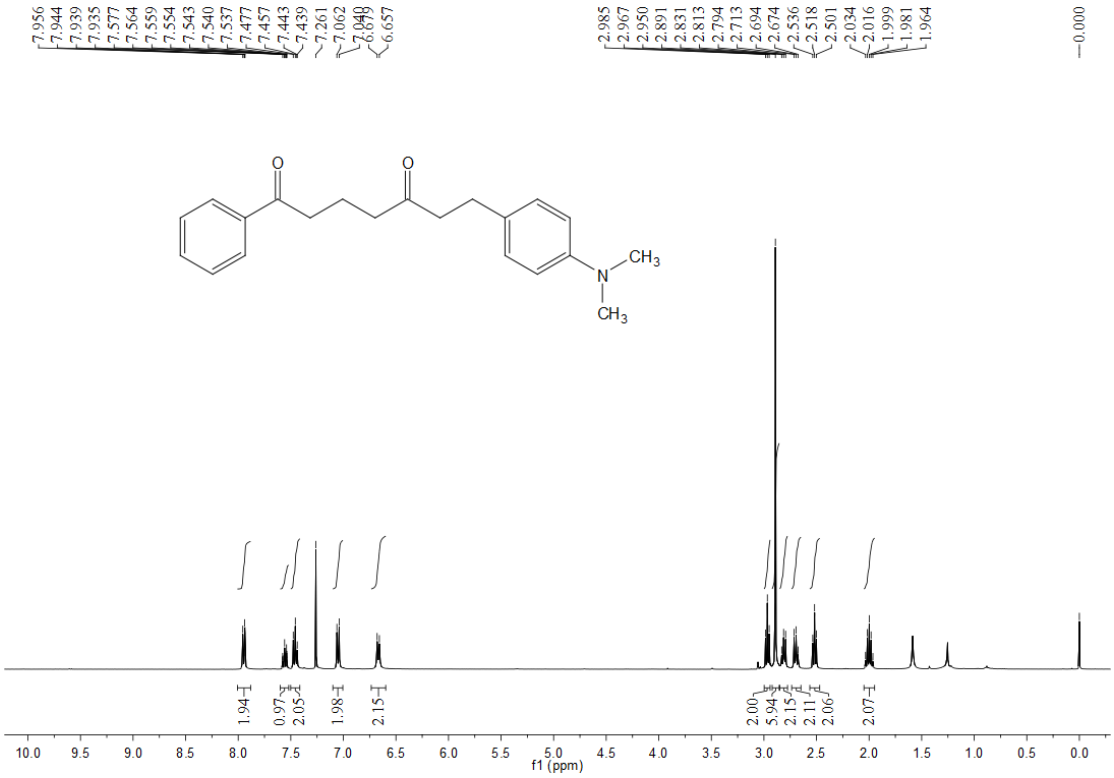


^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**

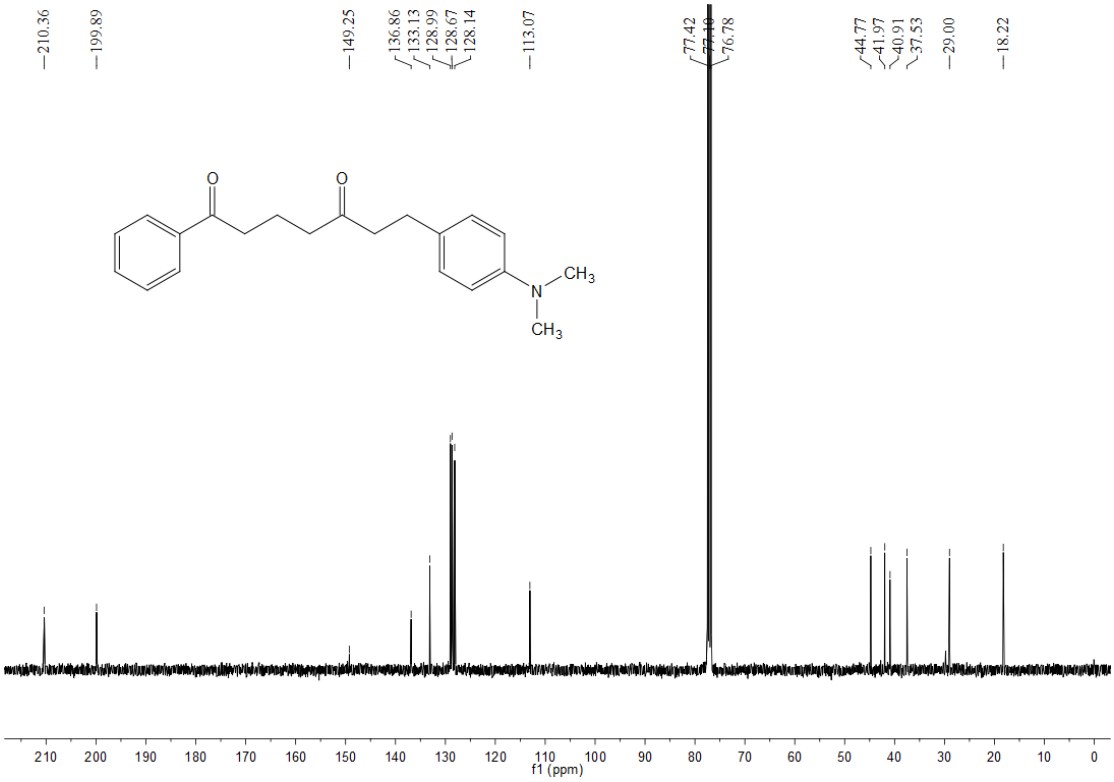


^{13}C NMR (100 MHz, $CDCl_3$) of **3ad**

7-(4-(dimethylamino)phenyl)-1-phenylheptane-1,5-dione (3ae)

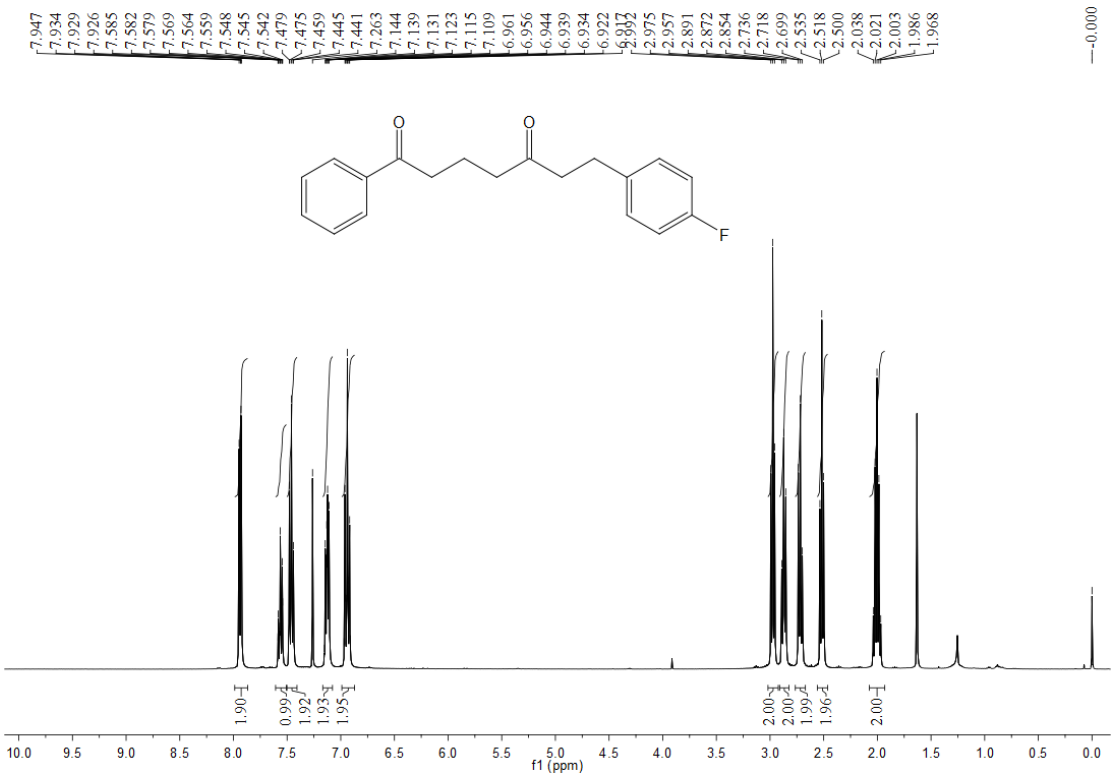


^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**

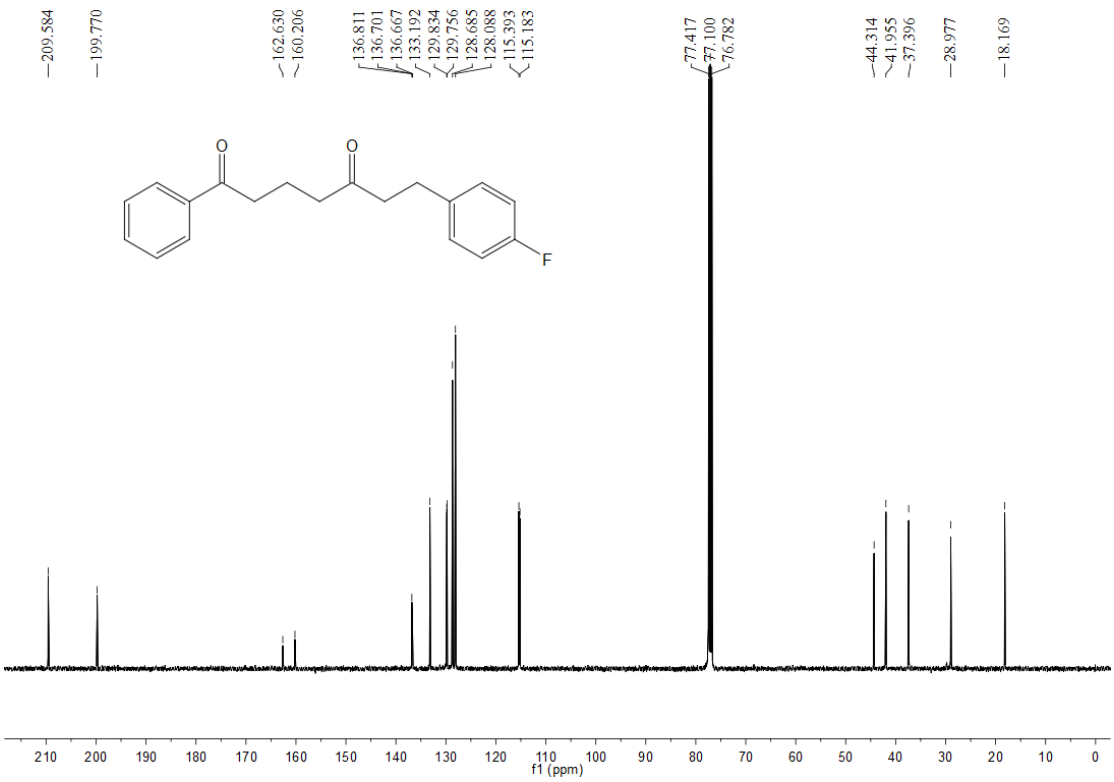


^{13}C NMR (100 MHz, $CDCl_3$) of **3ae**

7-(4-fluorophenyl)-1-phenylheptane-1,5-dione (3af)

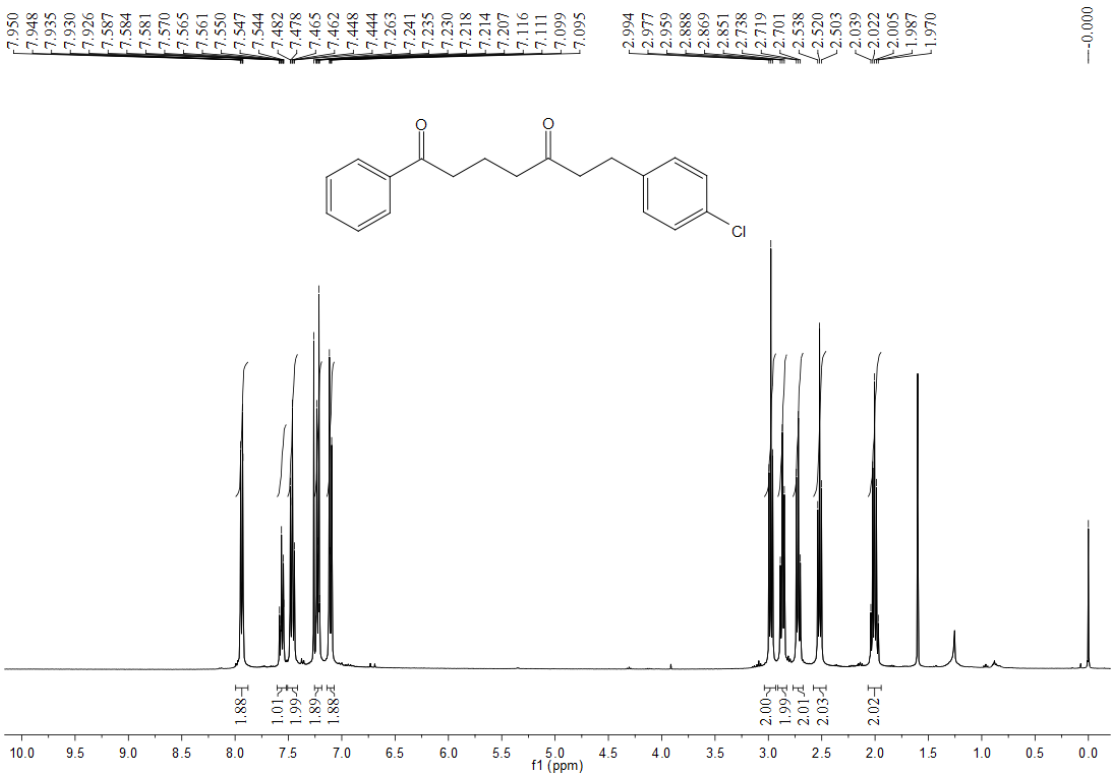


^{1}H NMR (400 MHz, $CDCl_3$) of **3af**

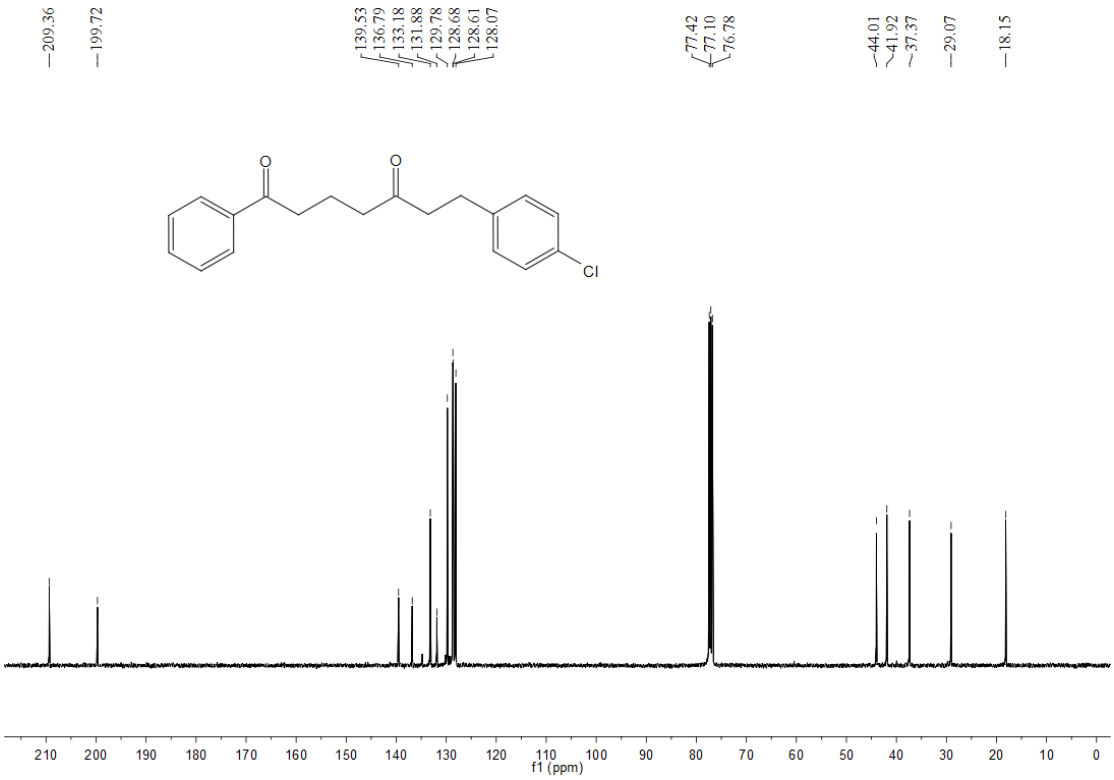


^{13}C NMR (100 MHz, $CDCl_3$) of **3af**

7-(4-chlorophenyl)-1-phenylheptane-1,5-dione (3ag)

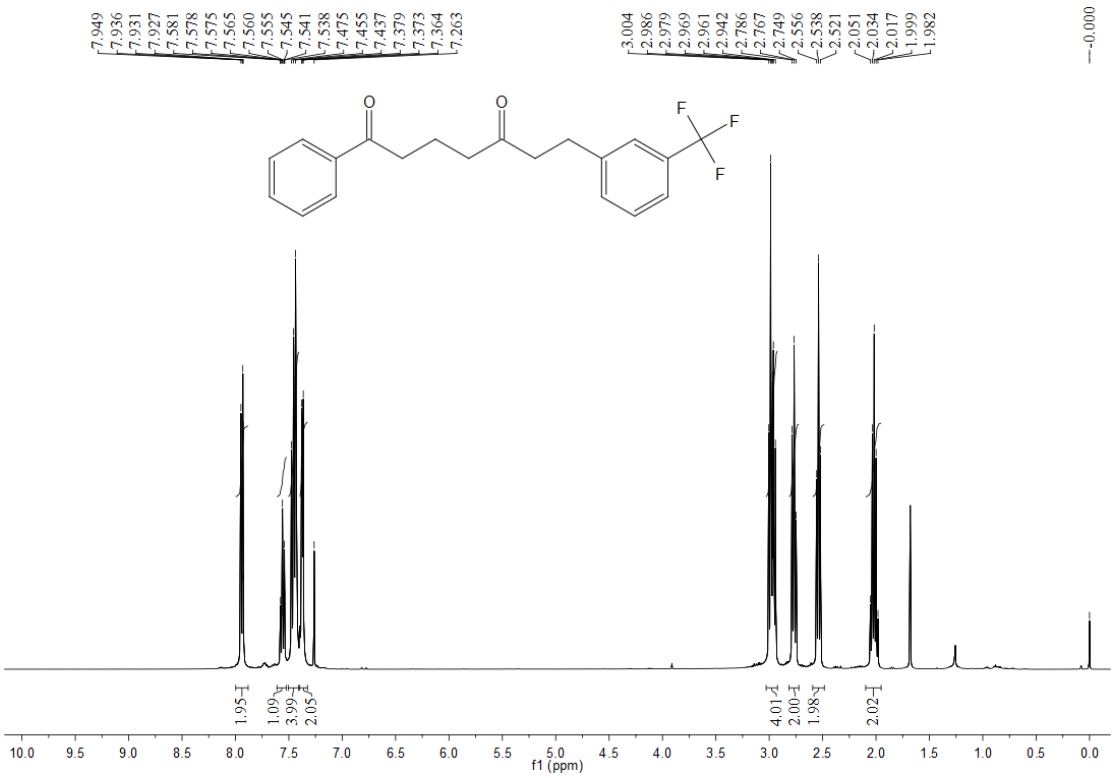


^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**

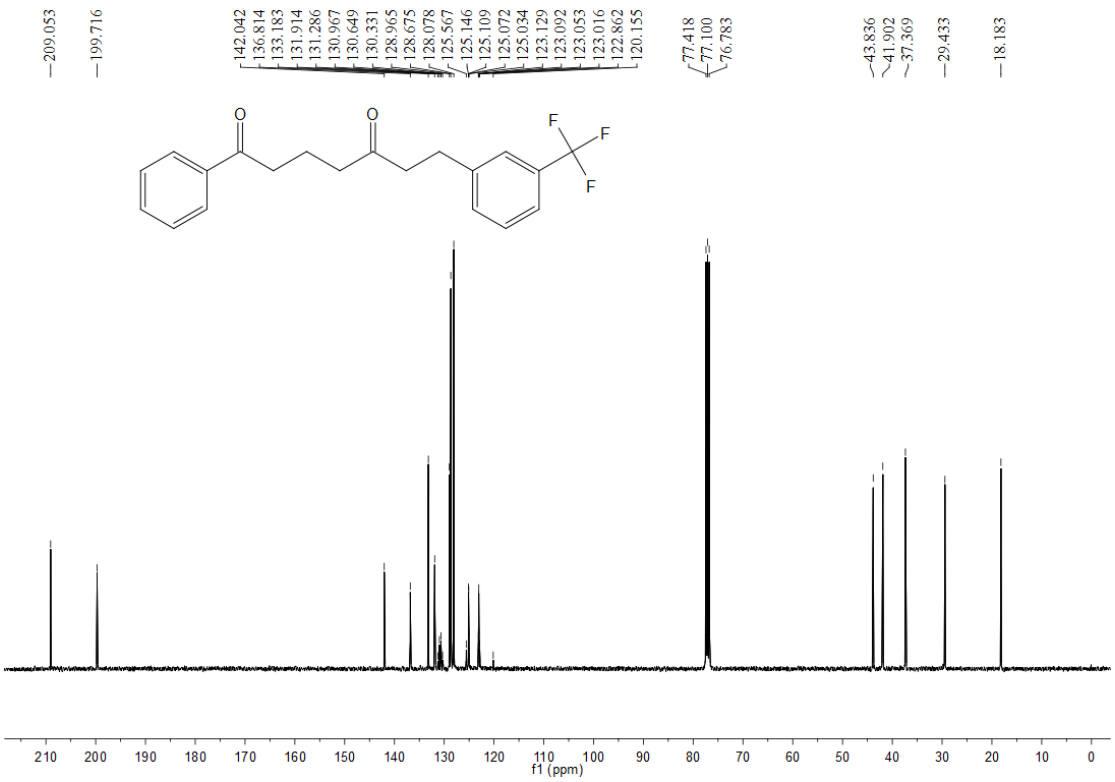


^{13}C NMR (100 MHz, $CDCl_3$) of **3ag**

1-phenyl-7-(3-(trifluoromethyl)phenyl)heptane-1,5-dione (3ai)

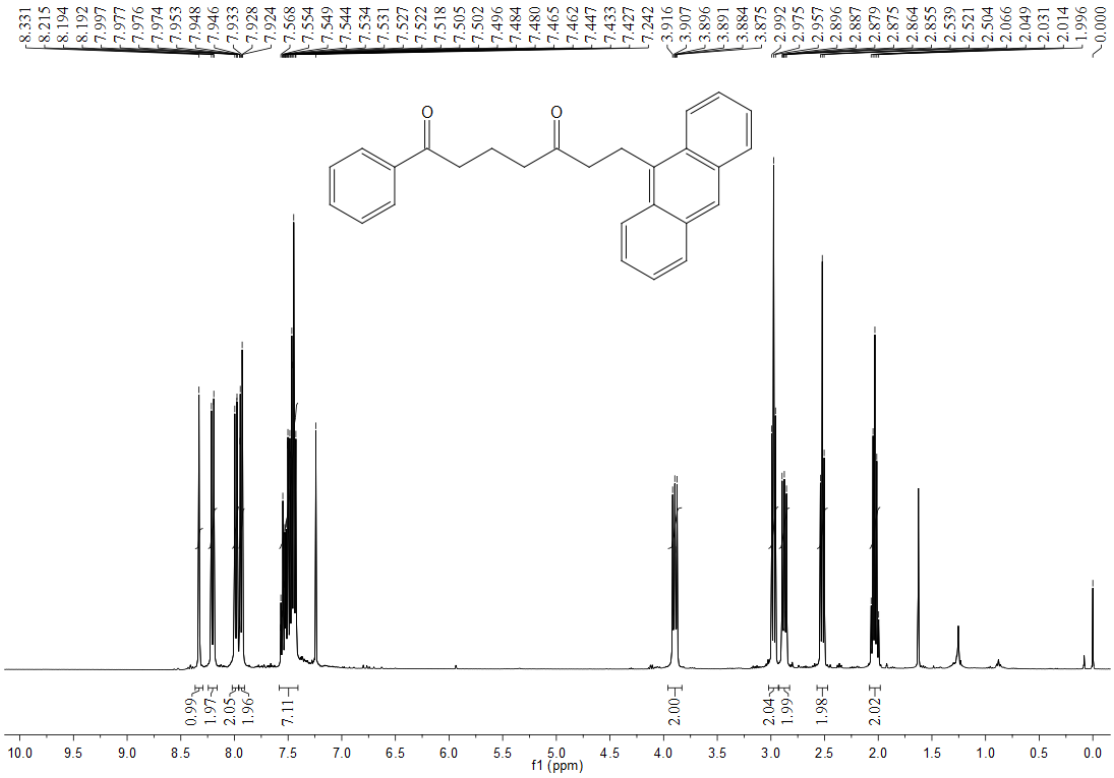


^{1}H NMR (400 MHz, $CDCl_3$) of **3ai**

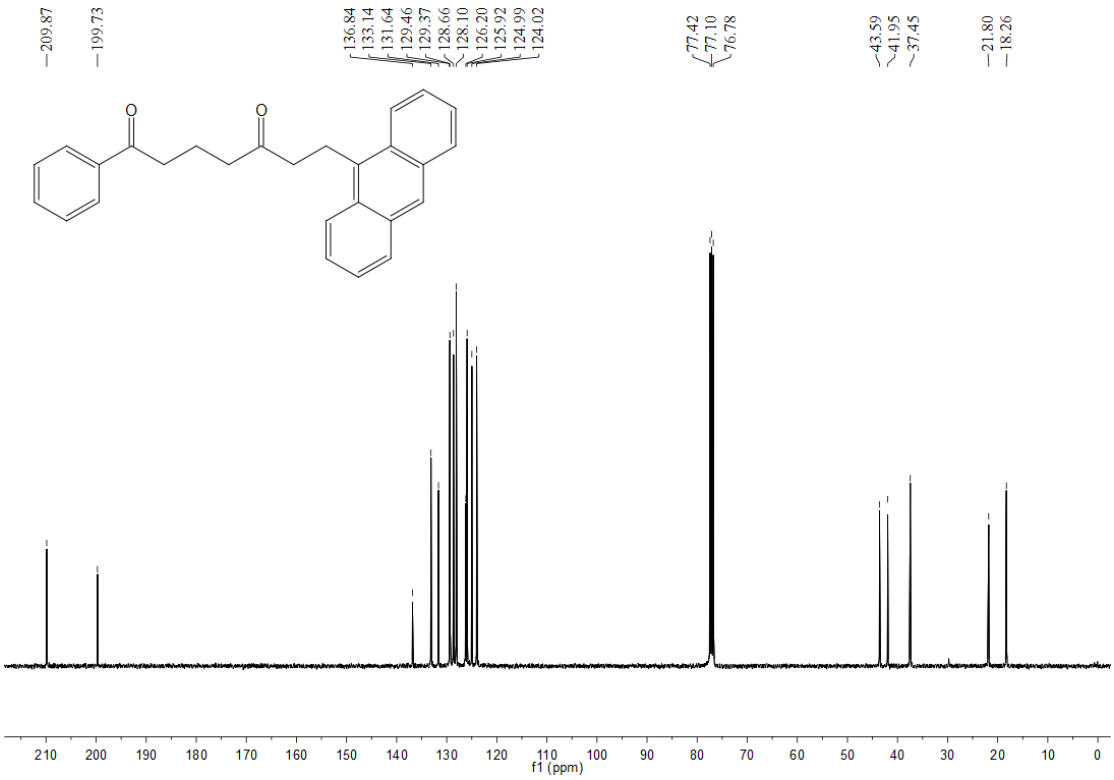


^{13}C NMR (100 MHz, $CDCl_3$) of **3ai**

7-(anthracen-9-yl)-1-phenylheptane-1,5-dione (3aj)

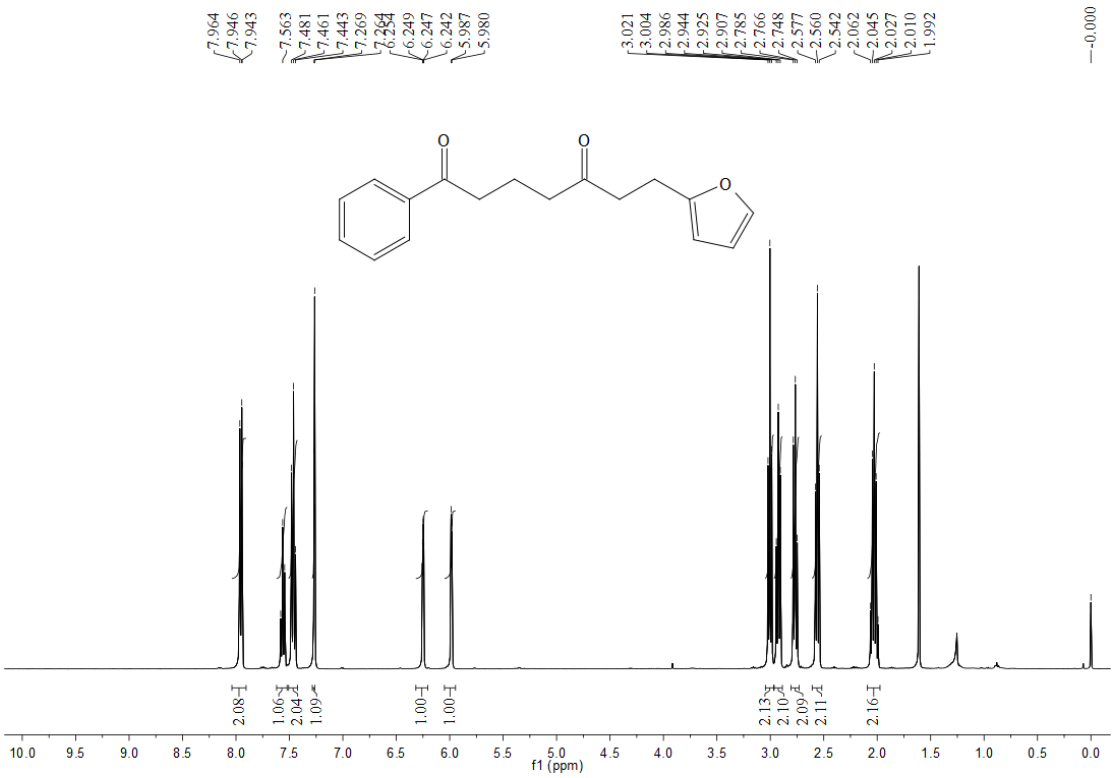


^{1}H NMR (400 MHz, $CDCl_3$) of **3aj**

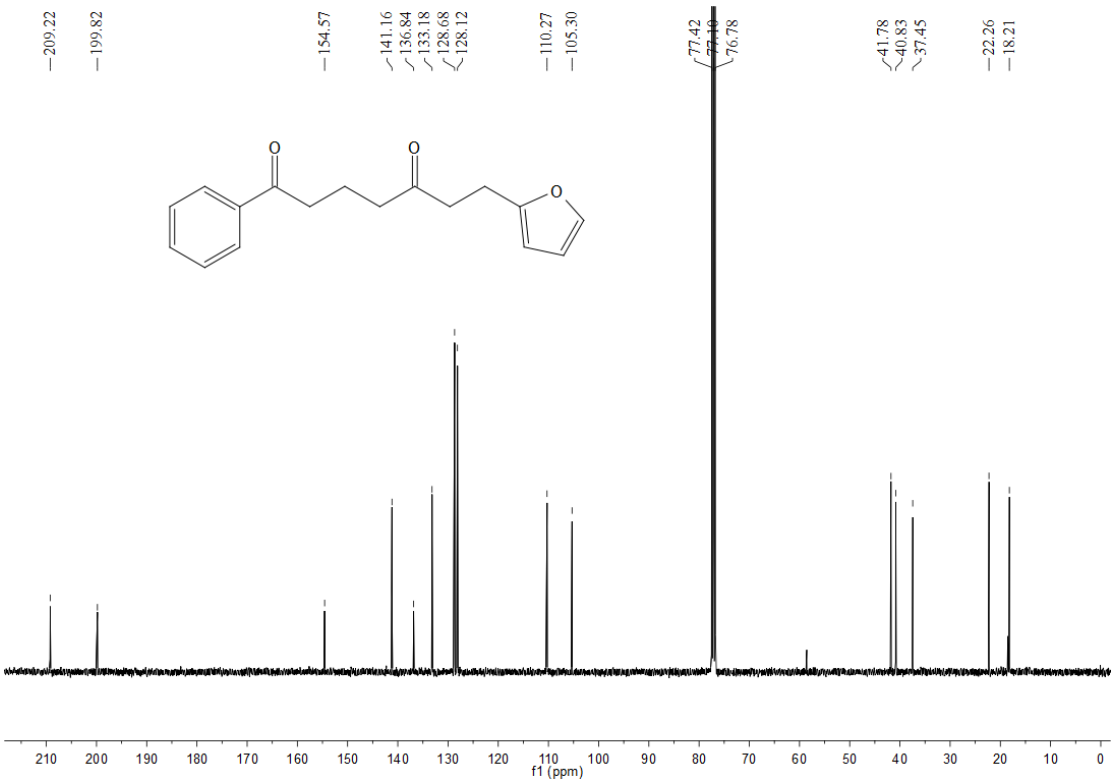


^{13}C NMR (100 MHz, $CDCl_3$) of **3aj**

7-(furan-2-yl)-1-phenylheptane-1,5-dione (3ak)

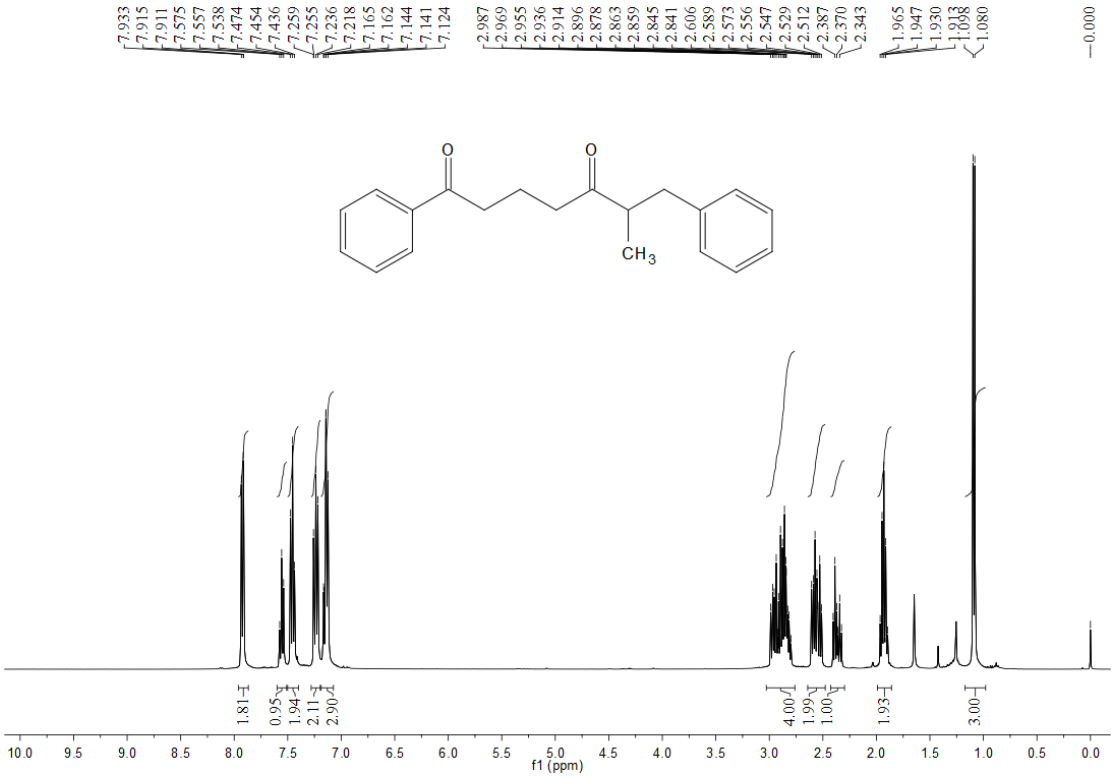


^{1}H NMR (400 MHz, $CDCl_3$) of **3ak**

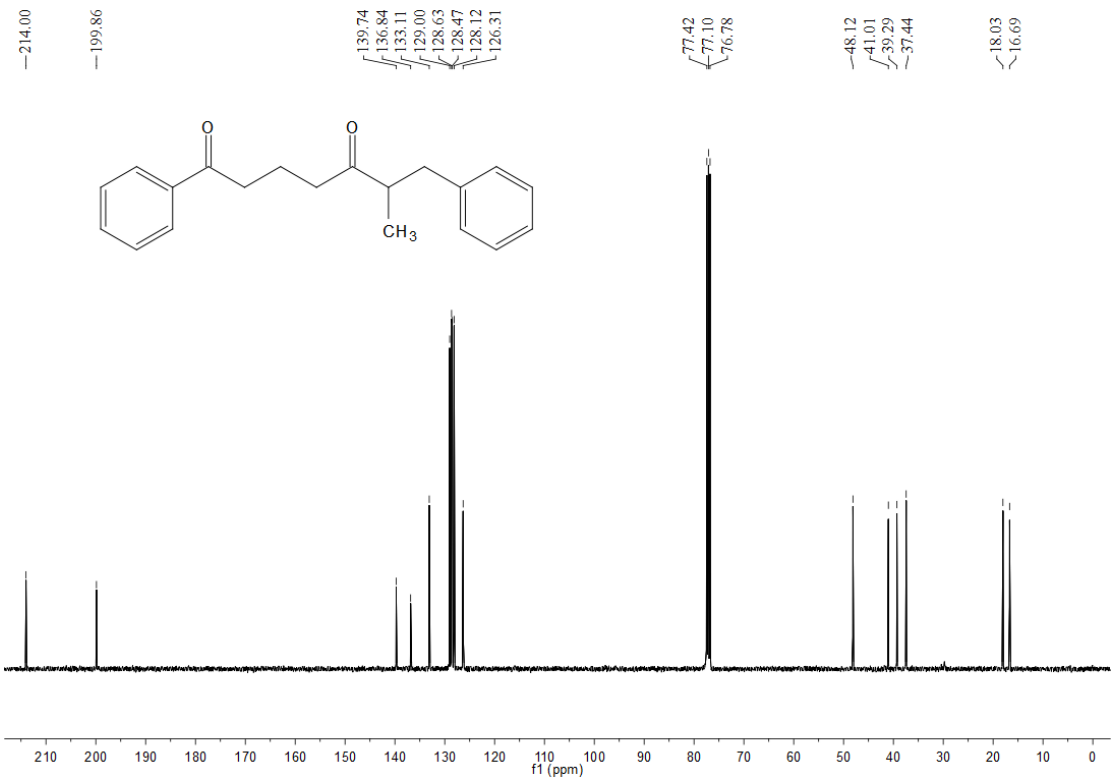


^{13}C NMR (100 MHz, $CDCl_3$) of **3ak**

6-methyl-1,7-diphenylheptane-1,5-dione (3al)

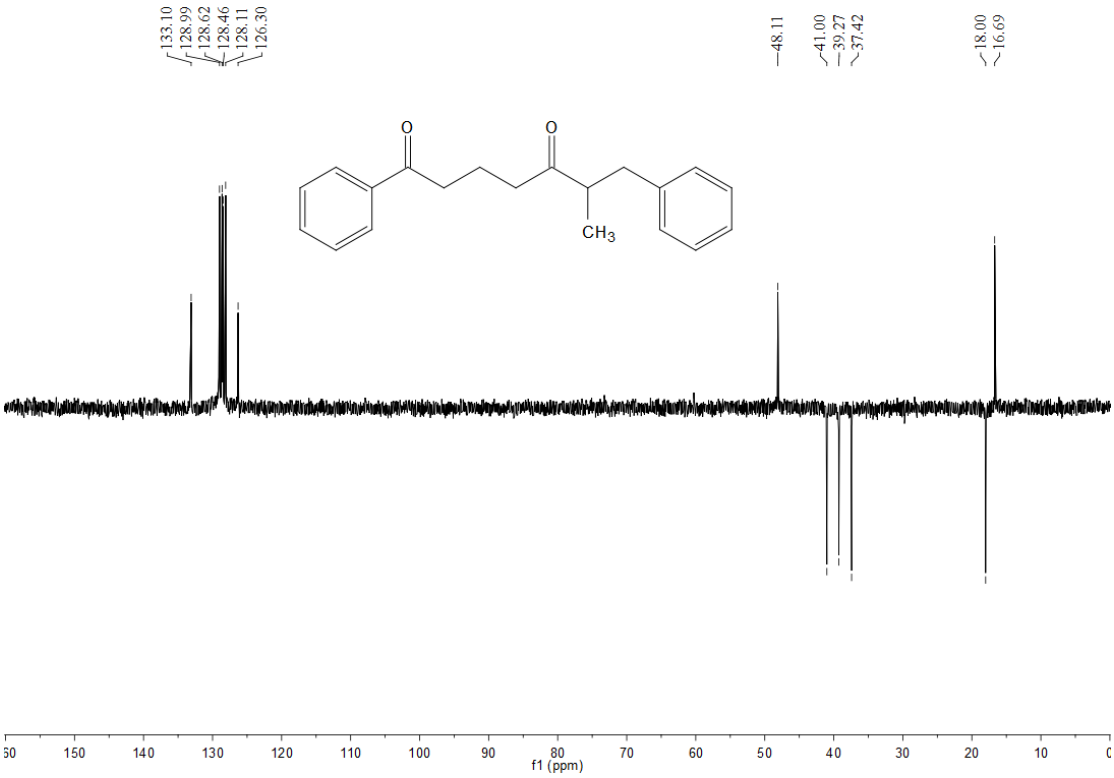


^{1}H NMR (400 MHz, $CDCl_3$) of **3al**



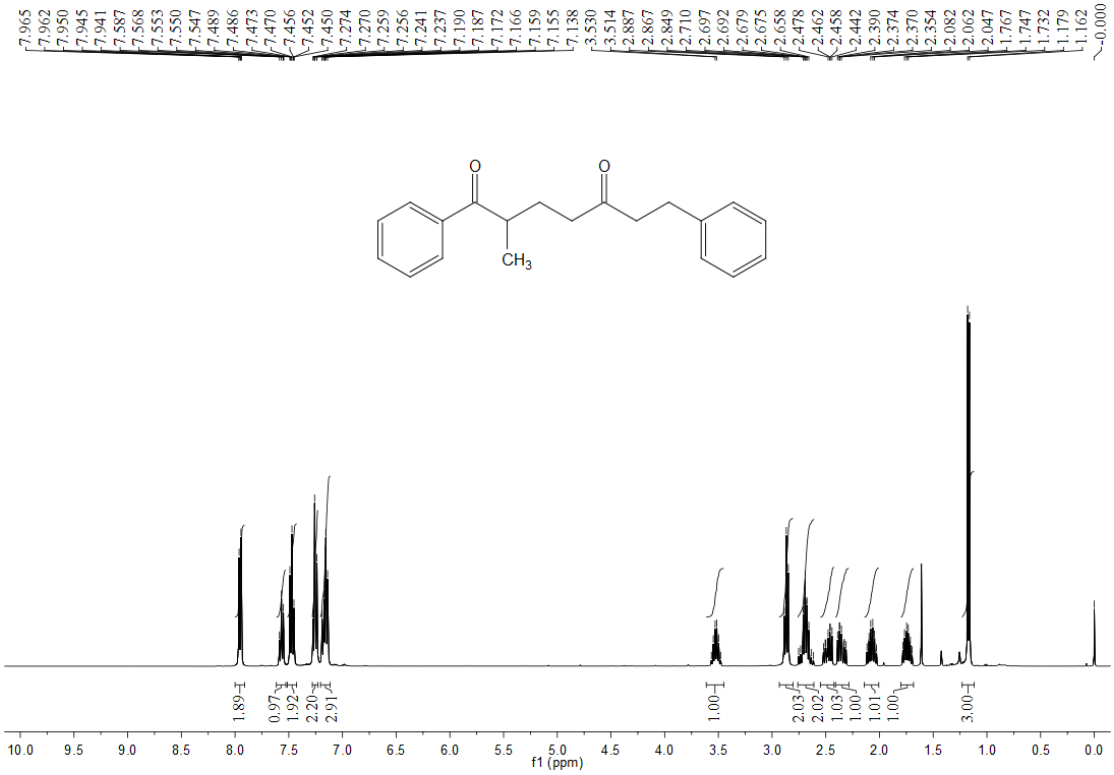
^{13}C NMR (100 MHz, $CDCl_3$) of **3al**

6-methyl-1,7-diphenylheptane-1,5-dione (3al)



DEPT135 (100 MHz, $CDCl_3$) of **3al**

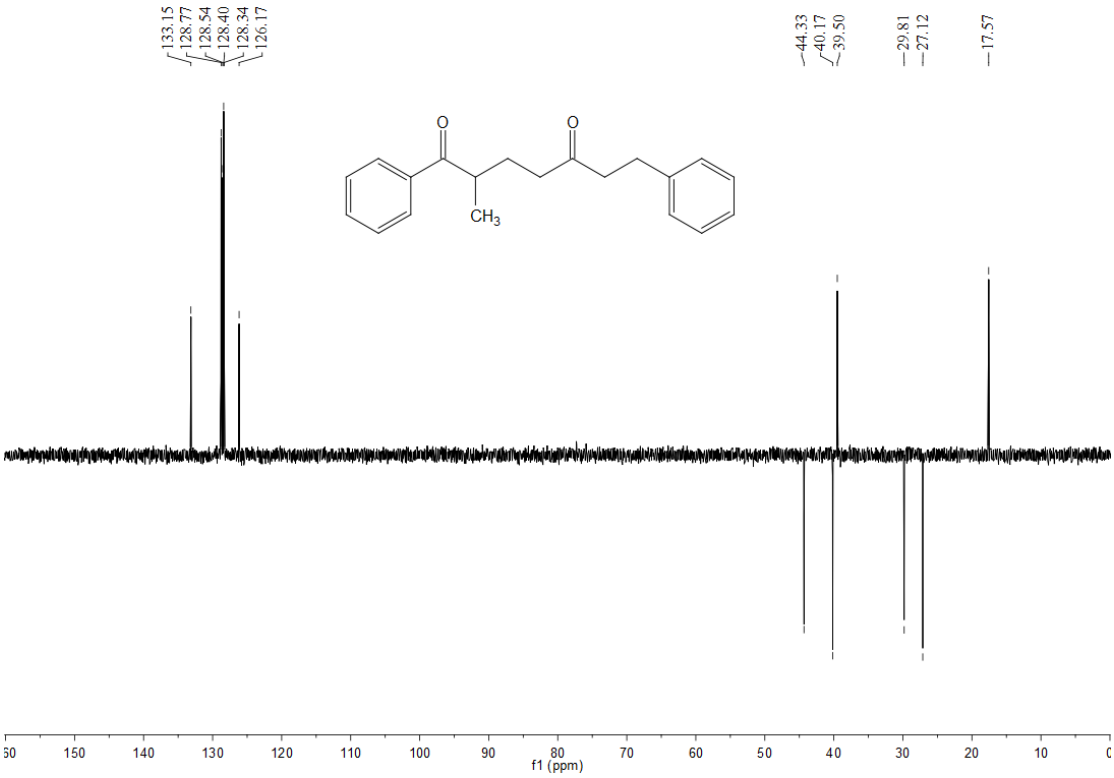
2-methyl-1,7-diphenylheptane-1,5-dione (3am)



^{1}H NMR (400 MHz, $CDCl_3$) of **3am**

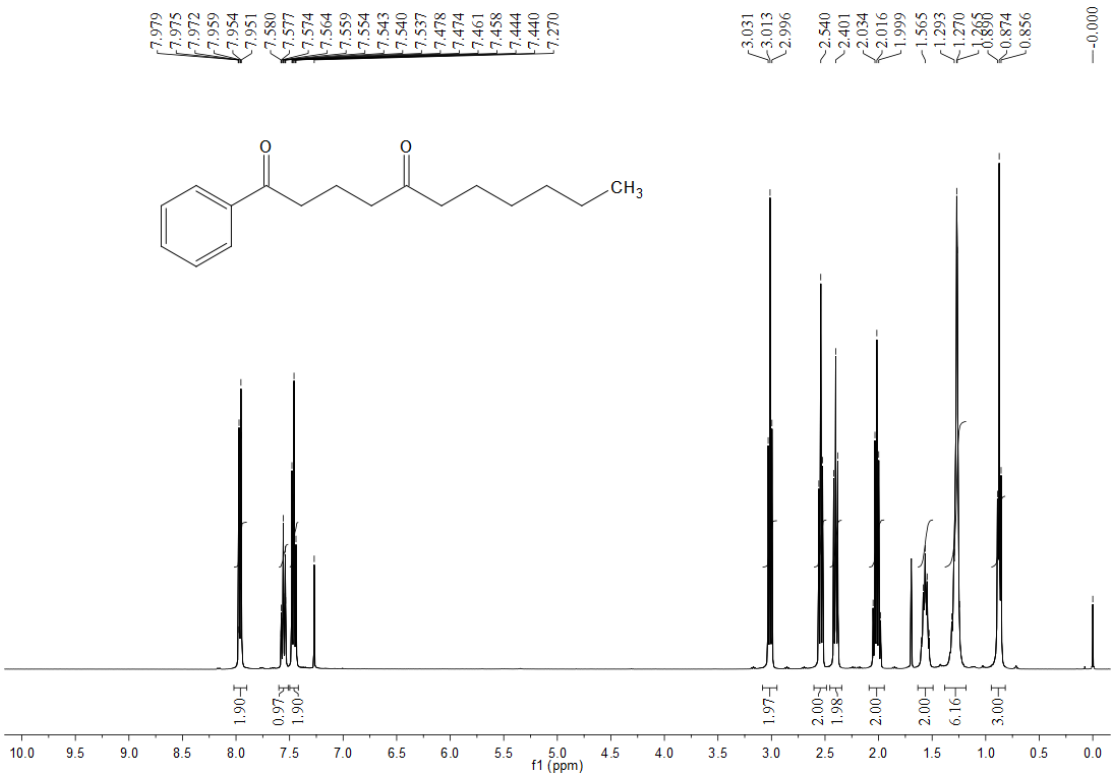
^{13}C NMR (100 MHz, $CDCl_3$) of **3am**

2-methyl-1,7-diphenylheptane-1,5-dione (3am)

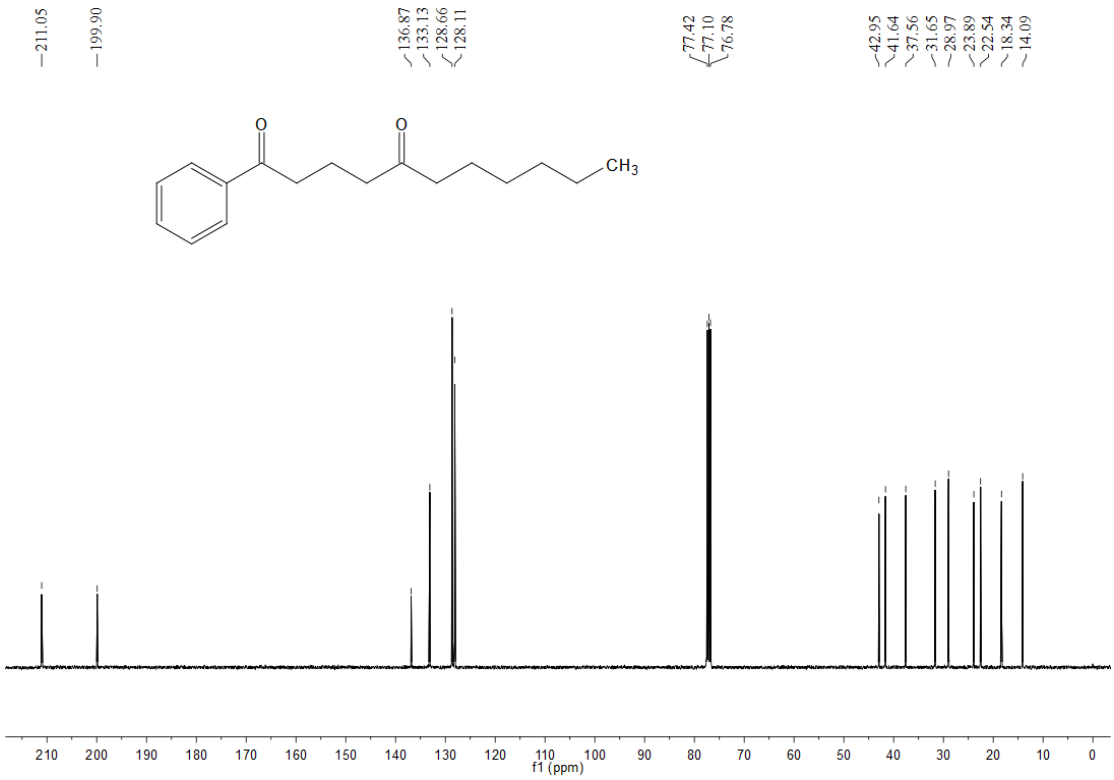


DEPT135 (100 MHz, $CDCl_3$) of **3am**

1-phenylundecane-1,5-dione (3an)

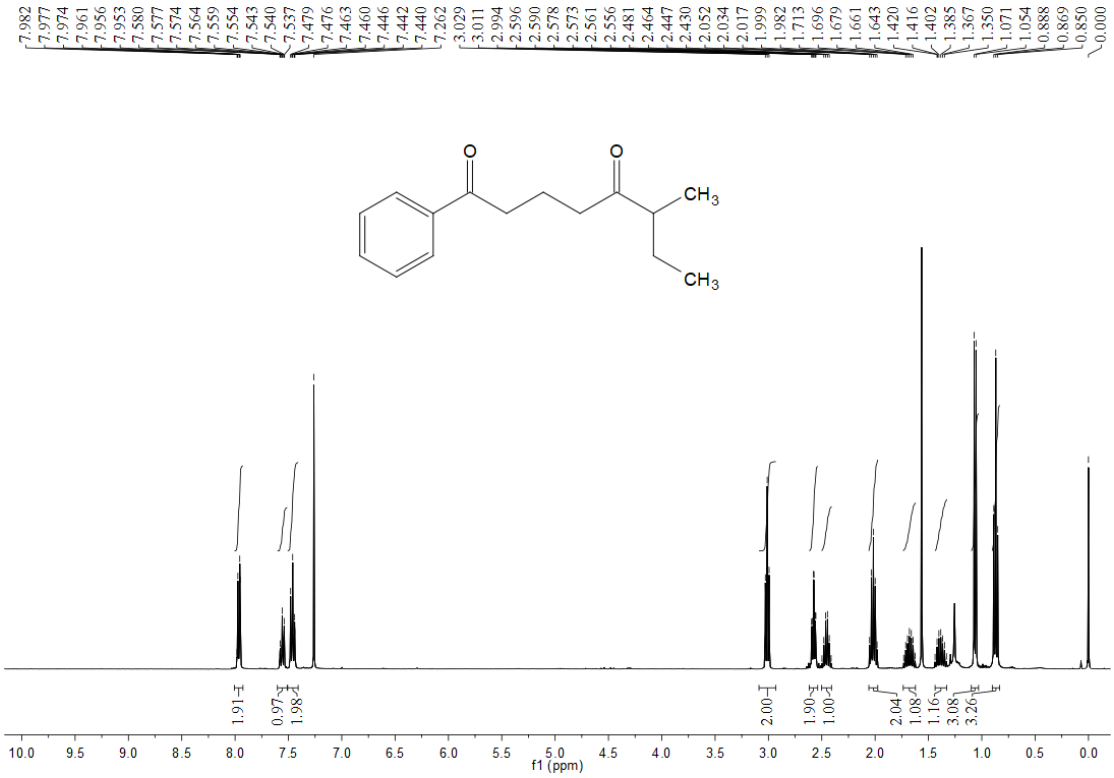


^{1}H NMR (400 MHz, $CDCl_3$) of **3an**

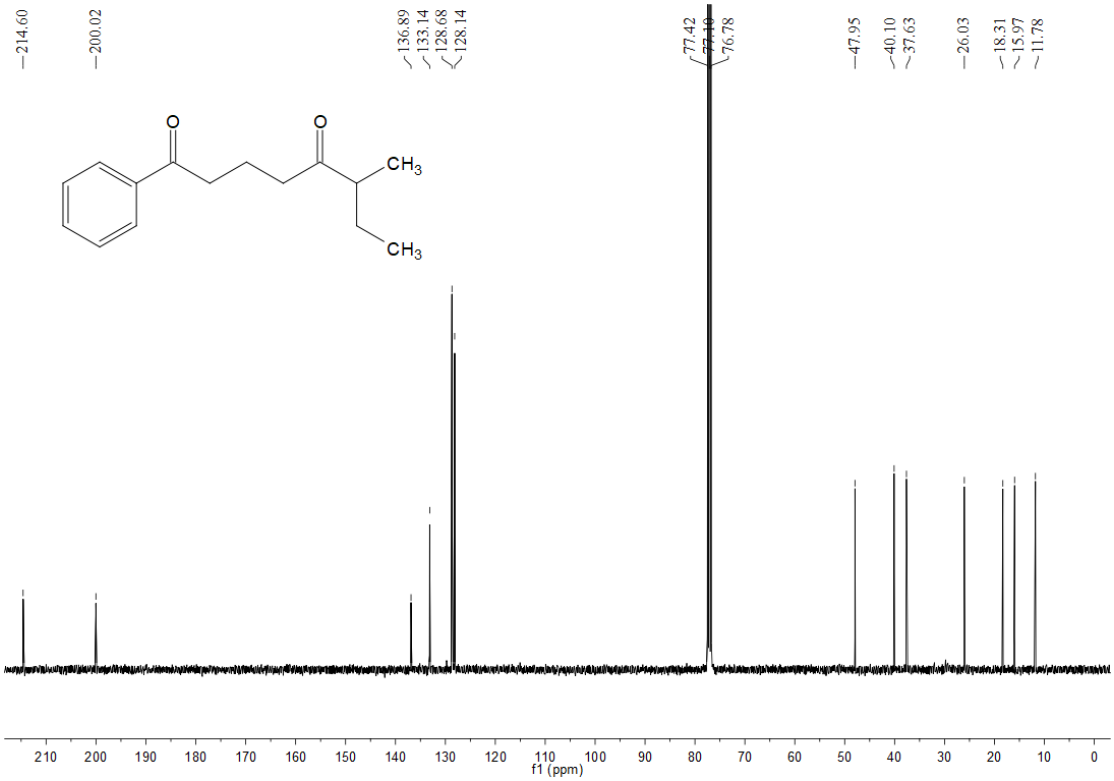


^{13}C NMR (100 MHz, $CDCl_3$) of **3an**

6-methyl-1-phenyloctane-1,5-dione (3ao)

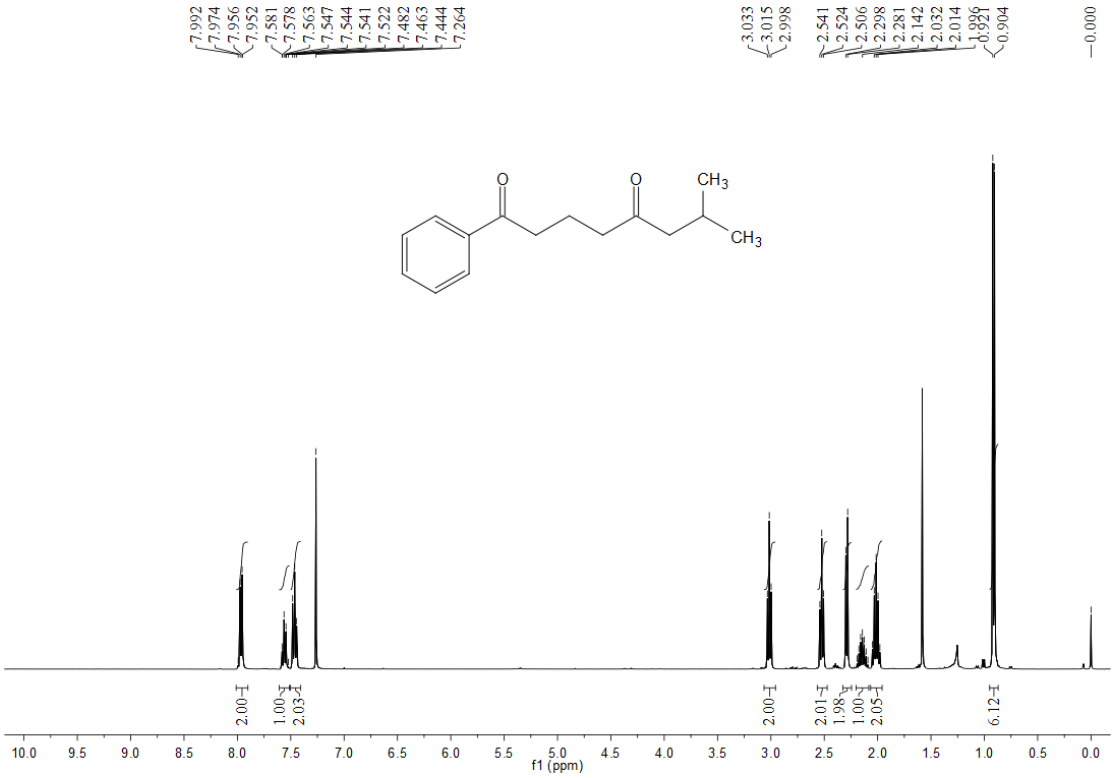


^{1}H NMR (400 MHz, $CDCl_3$) of **3ao**

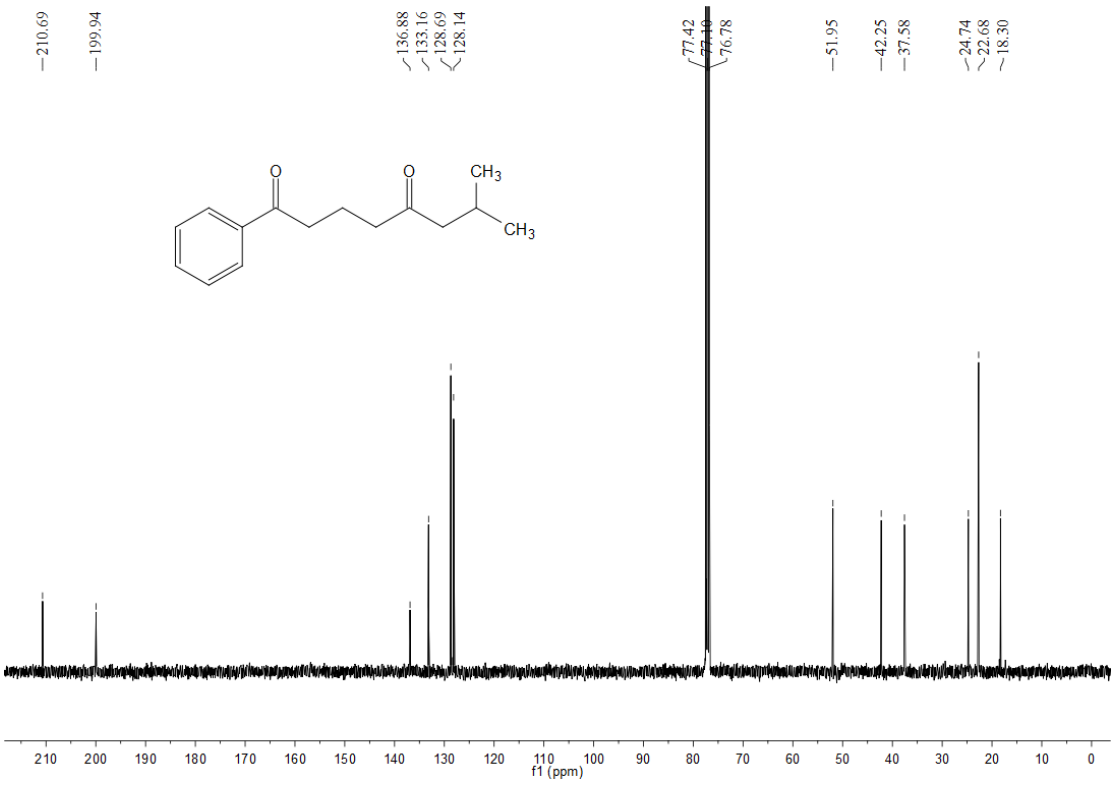


^{13}C NMR (100 MHz, $CDCl_3$) of **3ao**

7-methyl-1-phenyloctane-1,5-dione (3ap)

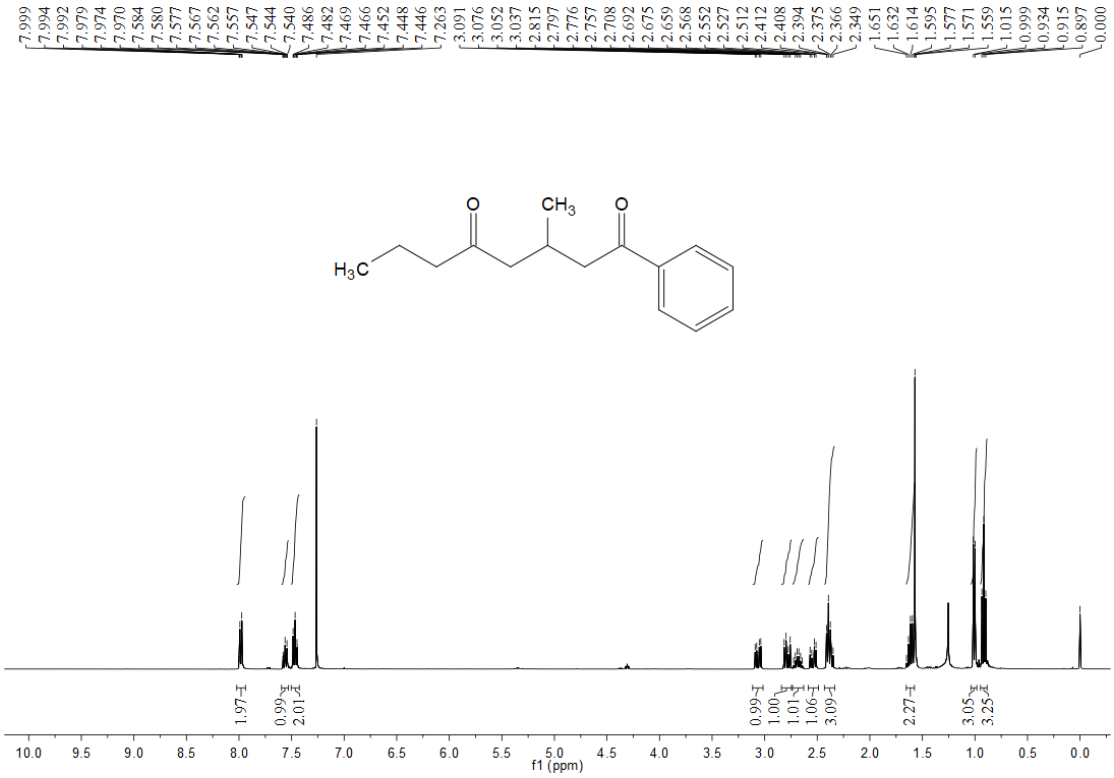


^{1}H NMR (400 MHz, $CDCl_3$) of **3ap**



^{13}C NMR (100 MHz, $CDCl_3$) of **3ap**

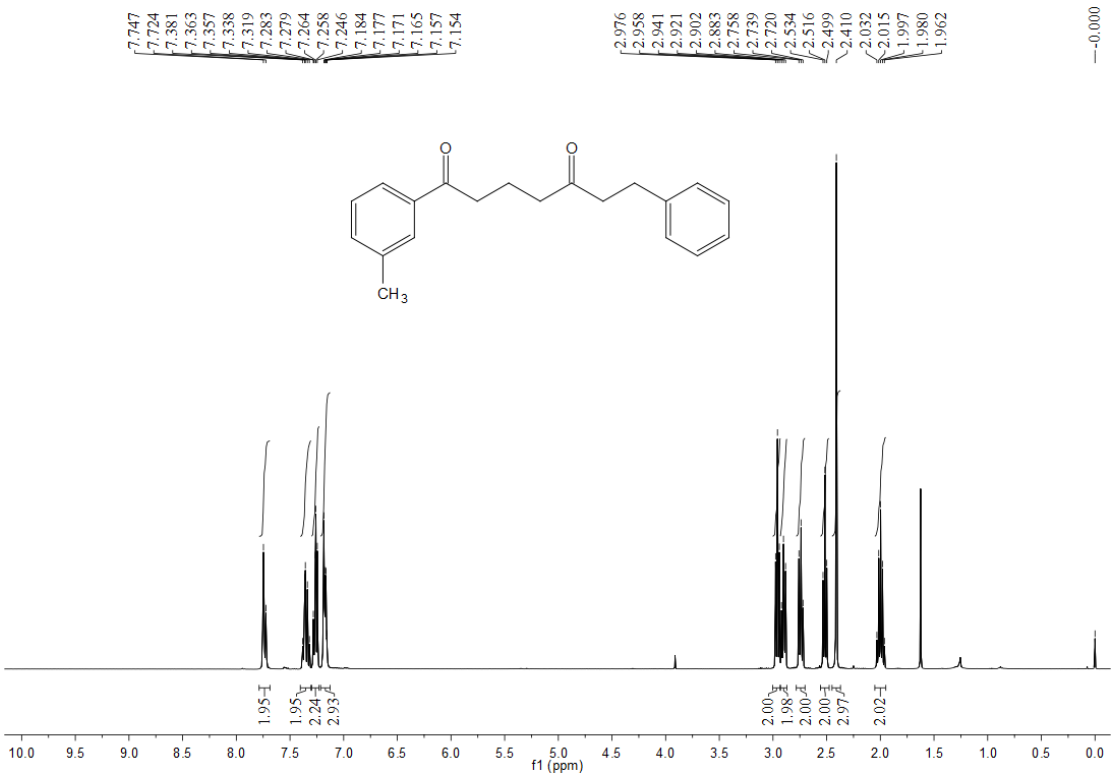
3-methyl-1-phenyloctane-1,5-dione (3ap')



^{1}H NMR (400 MHz, $CDCl_3$) of **3ap'**

^{13}C NMR (100 MHz, $CDCl_3$) of **3ap'**

7-phenyl-1-(*m*-tolyl)heptane-1,5-dione (3ba)



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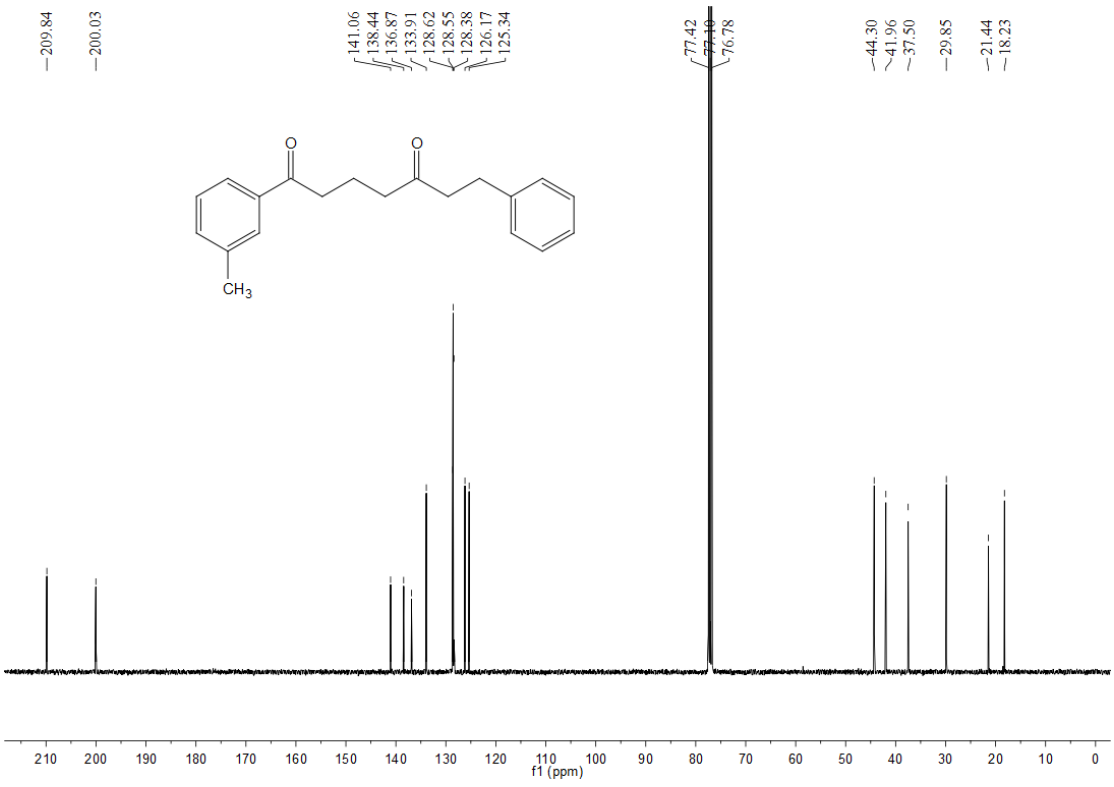

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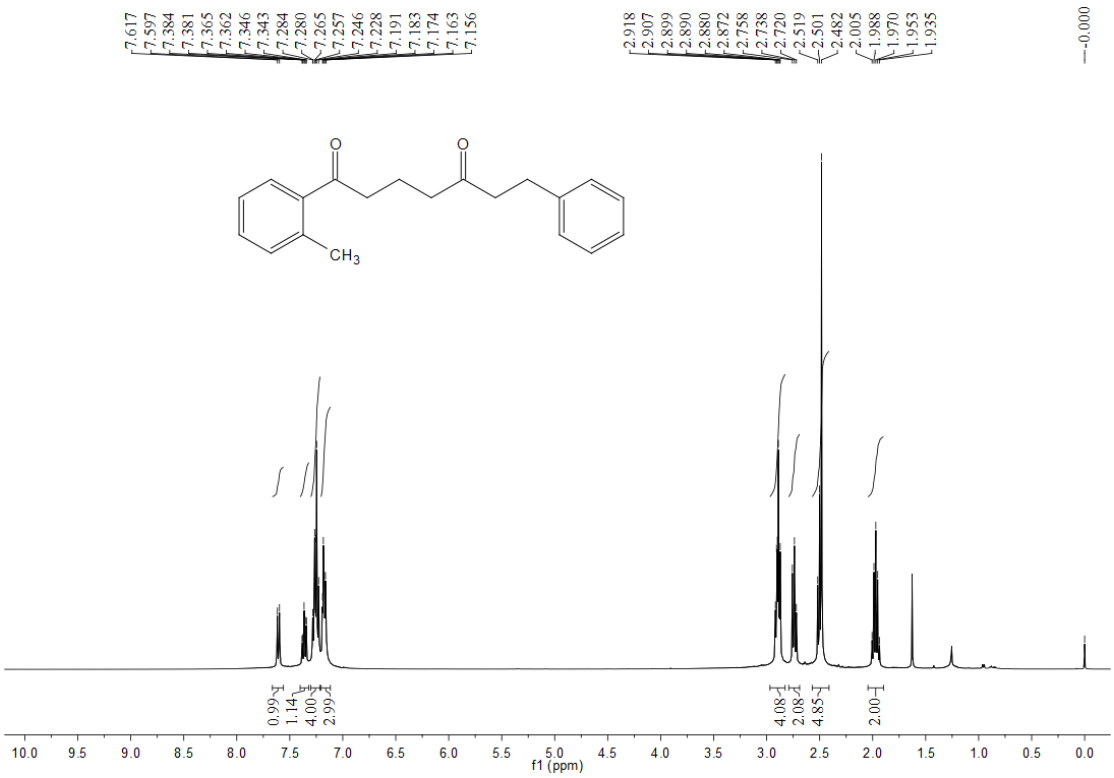
7-phenyl-1-(*o*-tolyl)heptane-1,5-dione (3ca)



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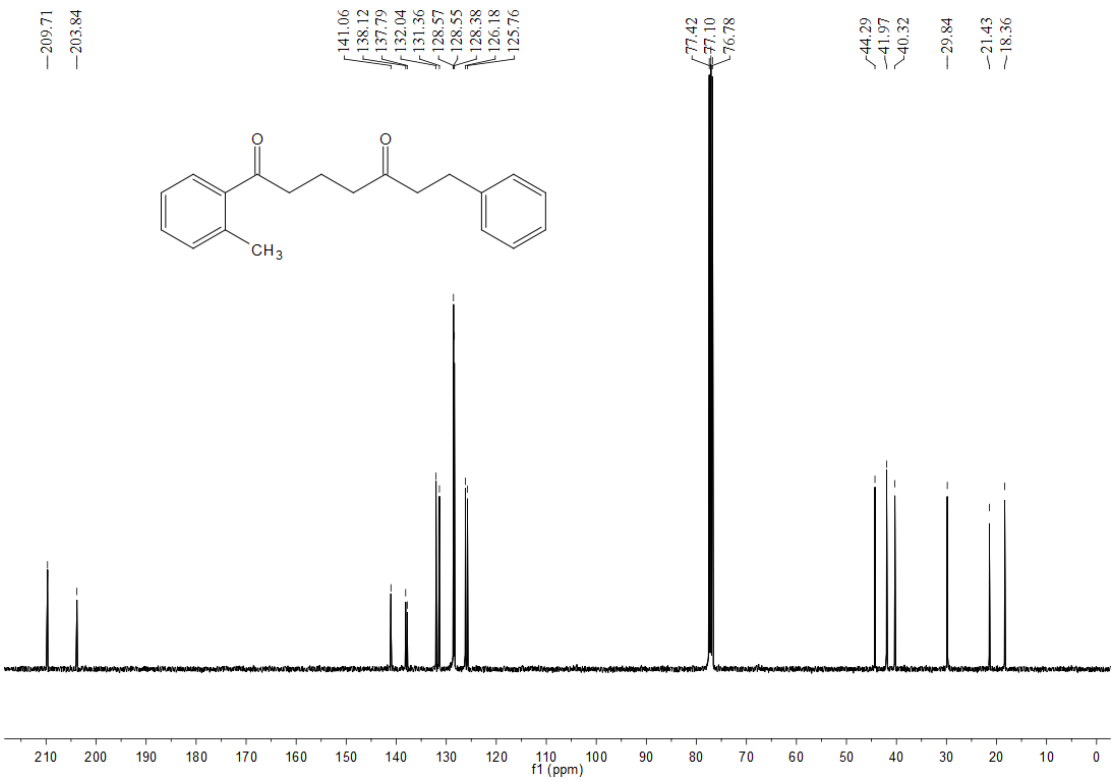
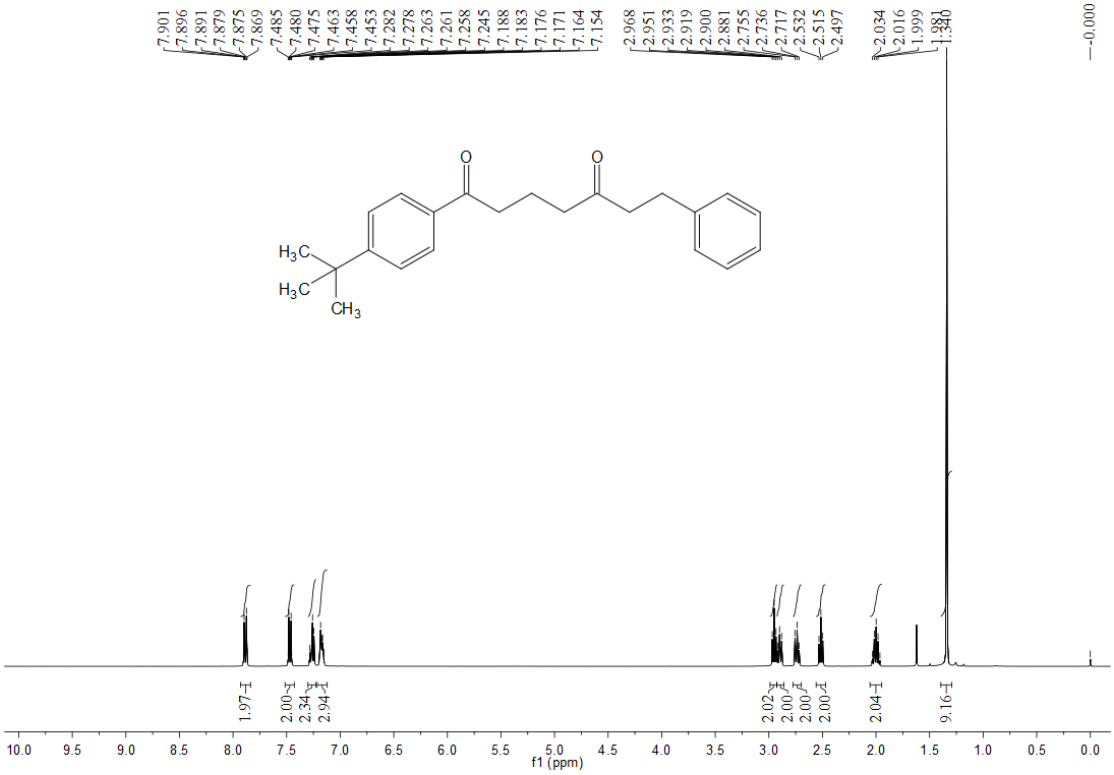
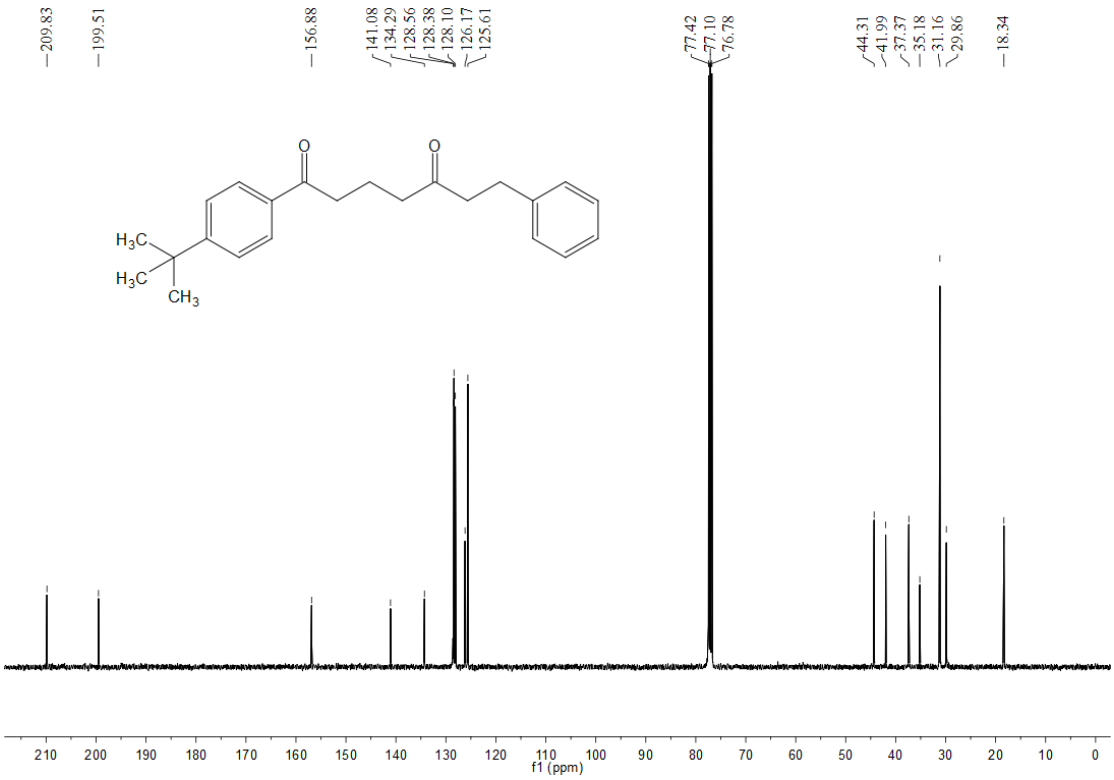


^{13}C NMR (100 MHz, $CDCl_3$) of **3ca**

1-(4-(*tert*-butyl)phenyl)-7-phenylheptane-1,5-dione (3da)

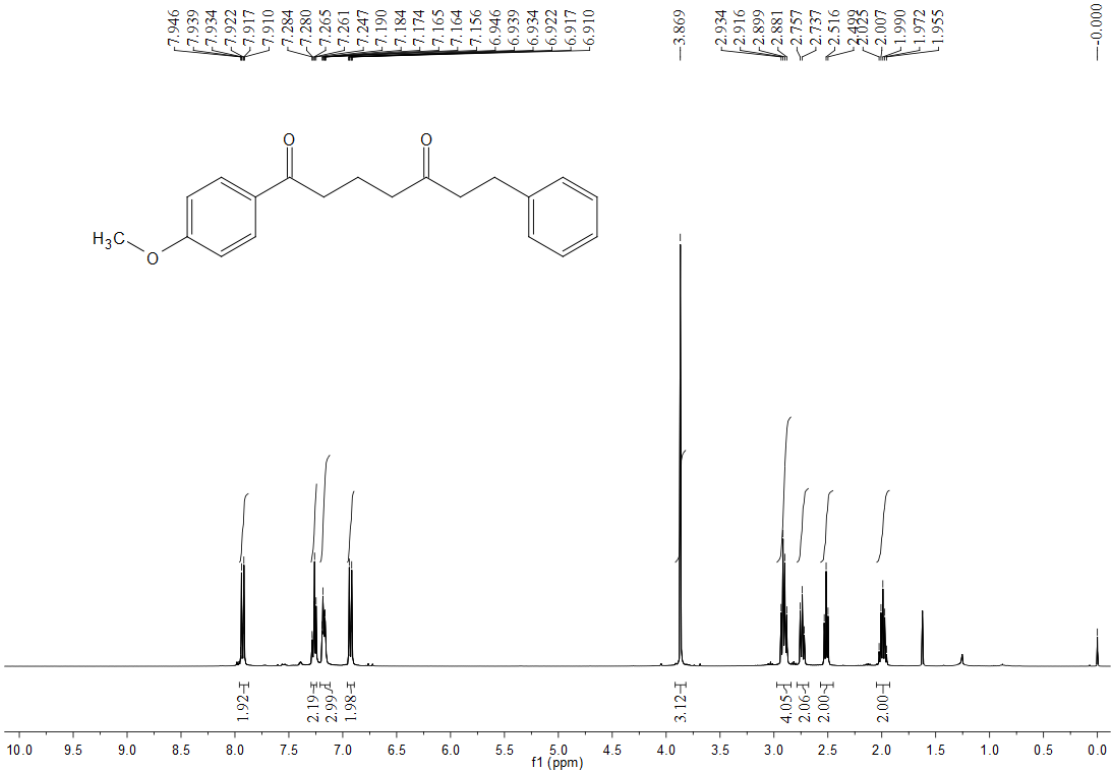


^{1}H NMR (400 MHz, $CDCl_3$) of **3da**

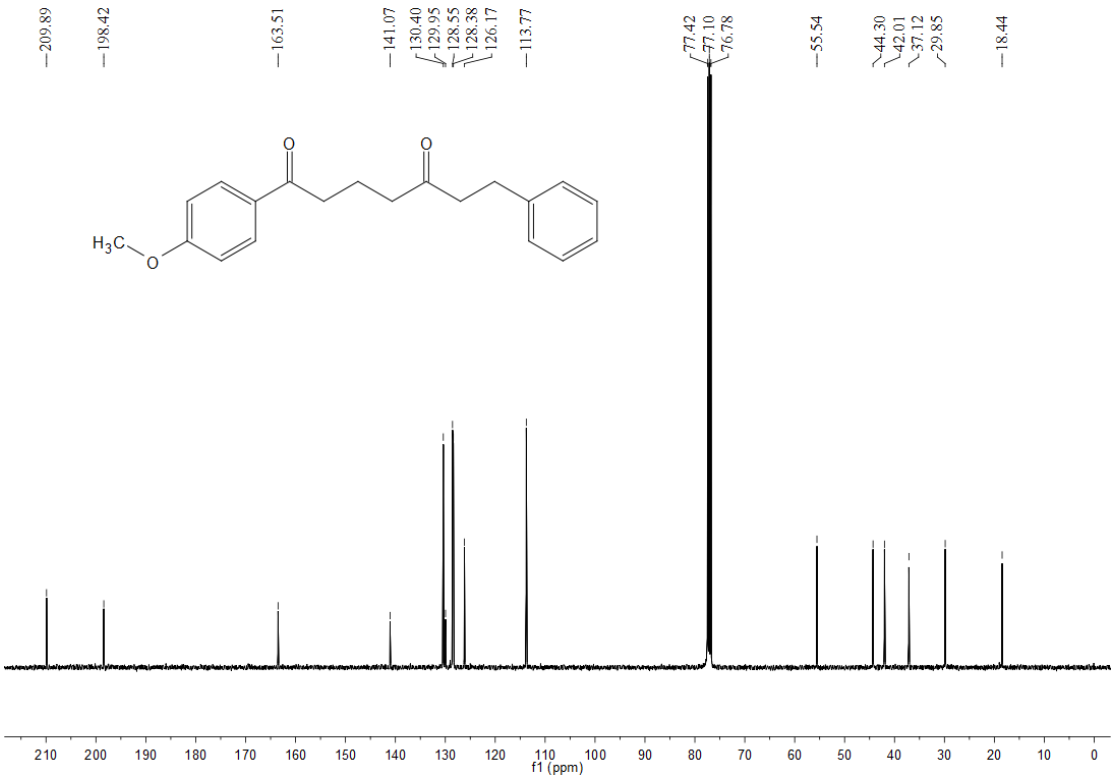


^{13}C NMR (100 MHz, $CDCl_3$) of **3da**

1-(4-methoxyphenyl)-7-phenylheptane-1,5-dione (3ea)

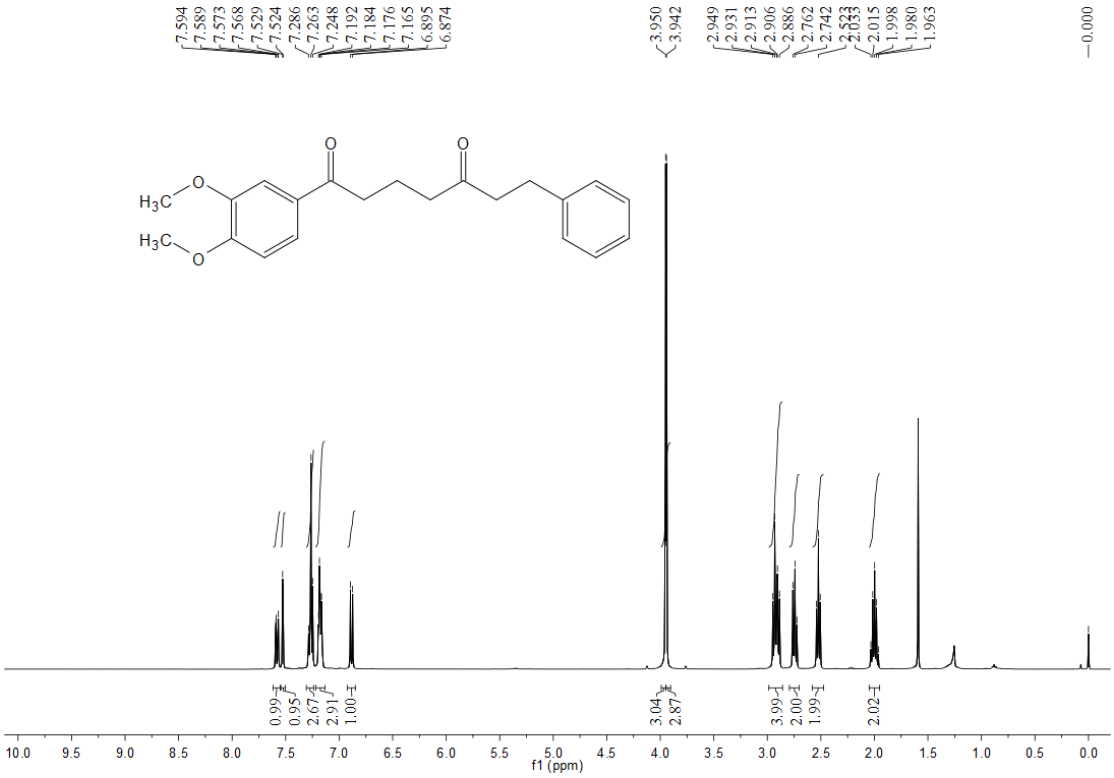


^{1}H NMR (400 MHz, $CDCl_3$) of **3ea**

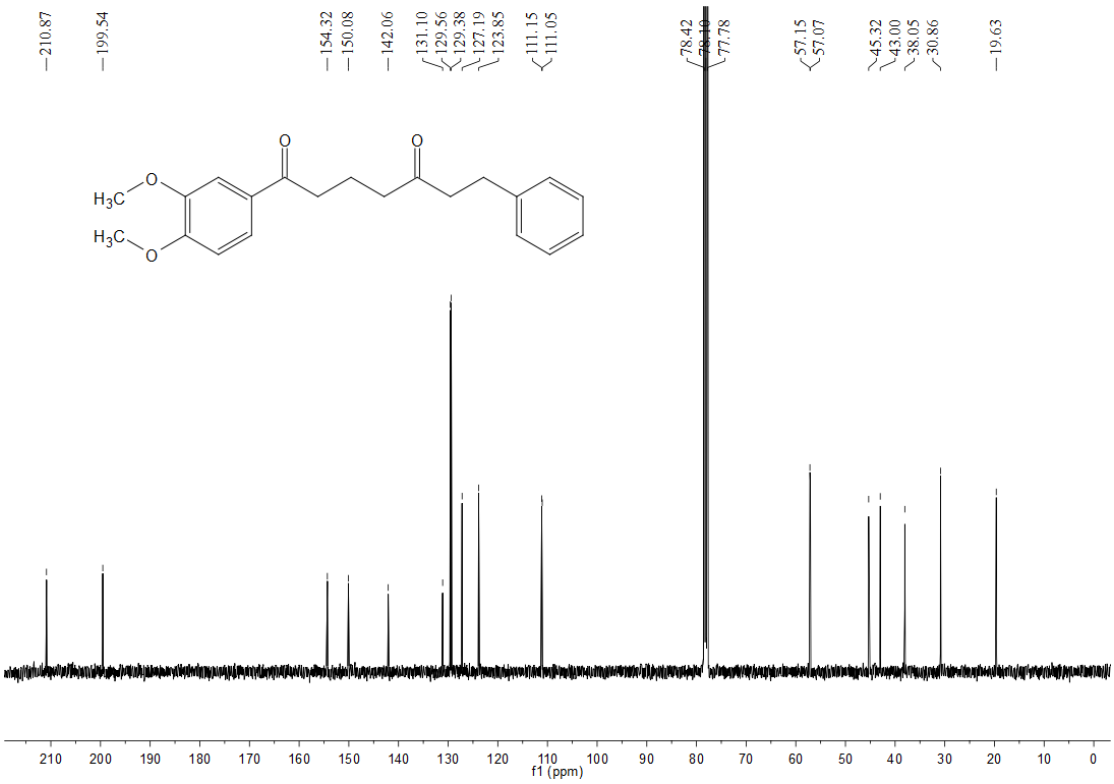


^{13}C NMR (100 MHz, $CDCl_3$) of **3ea**

1-(3,4-dimethoxyphenyl)-7-phenylheptane-1,5-dione (3fa)

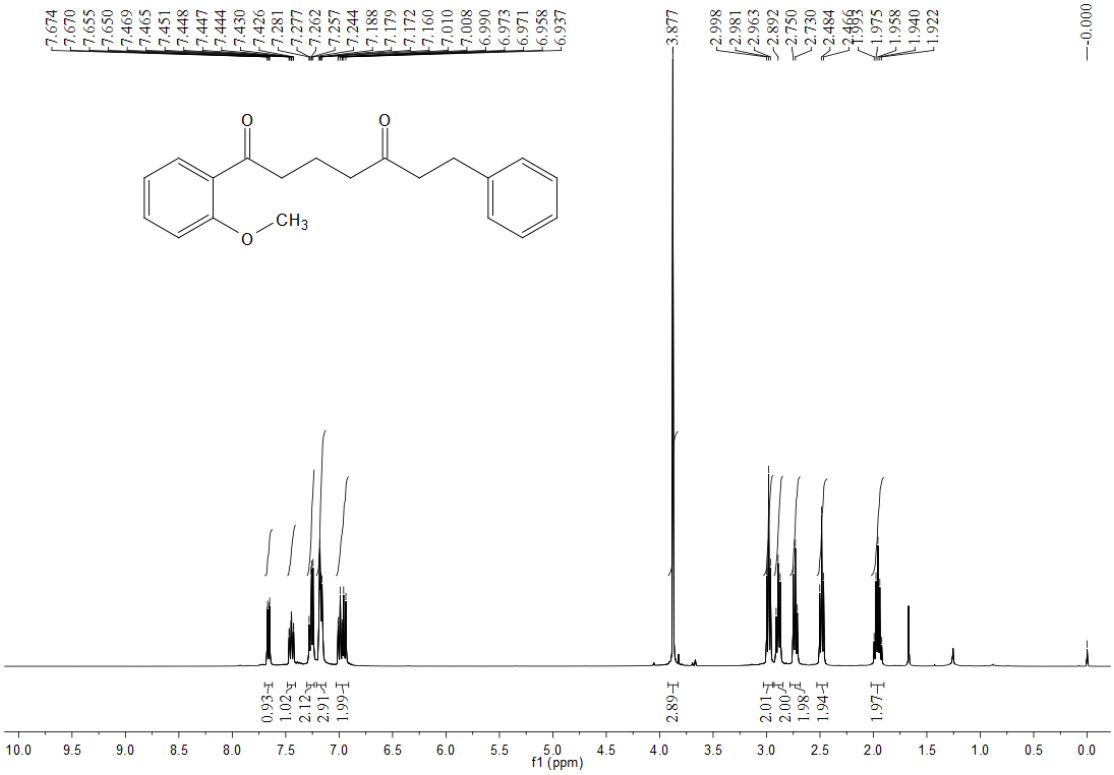


^{1}H NMR (400 MHz, $CDCl_3$) of **3fa**

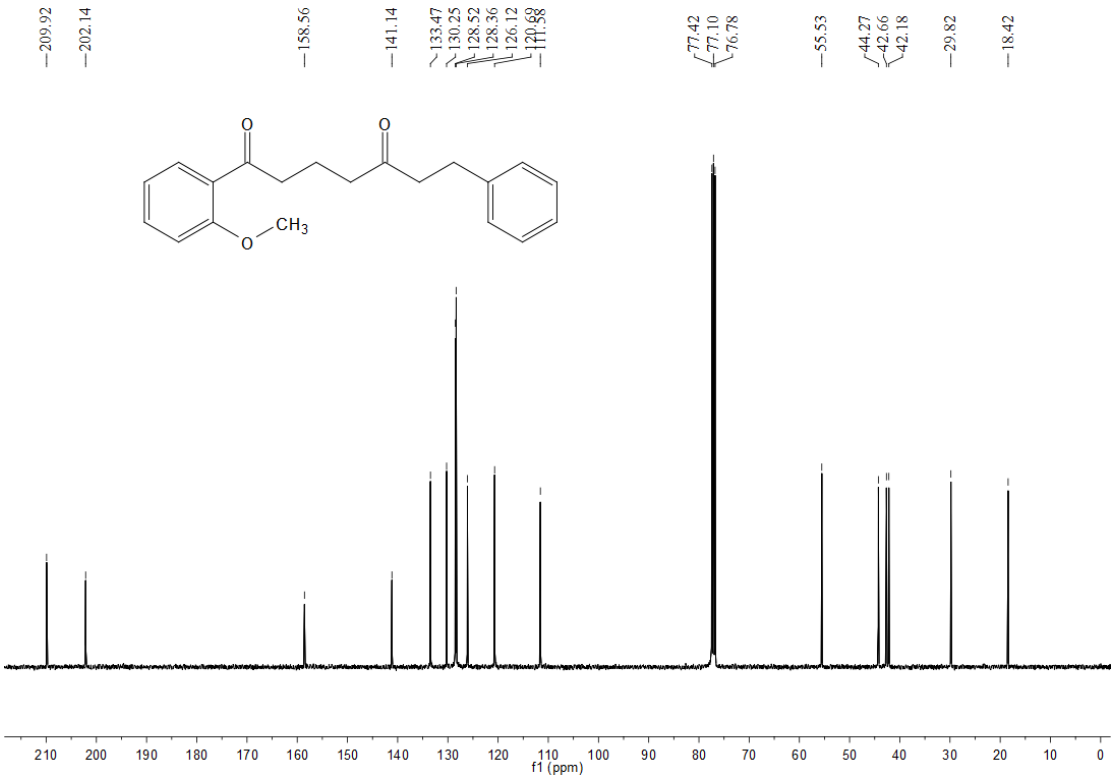


^{13}C NMR (100 MHz, $CDCl_3$) of **3fa**

1-(2-methoxyphenyl)-7-phenylheptane-1,5-dione (3ga)

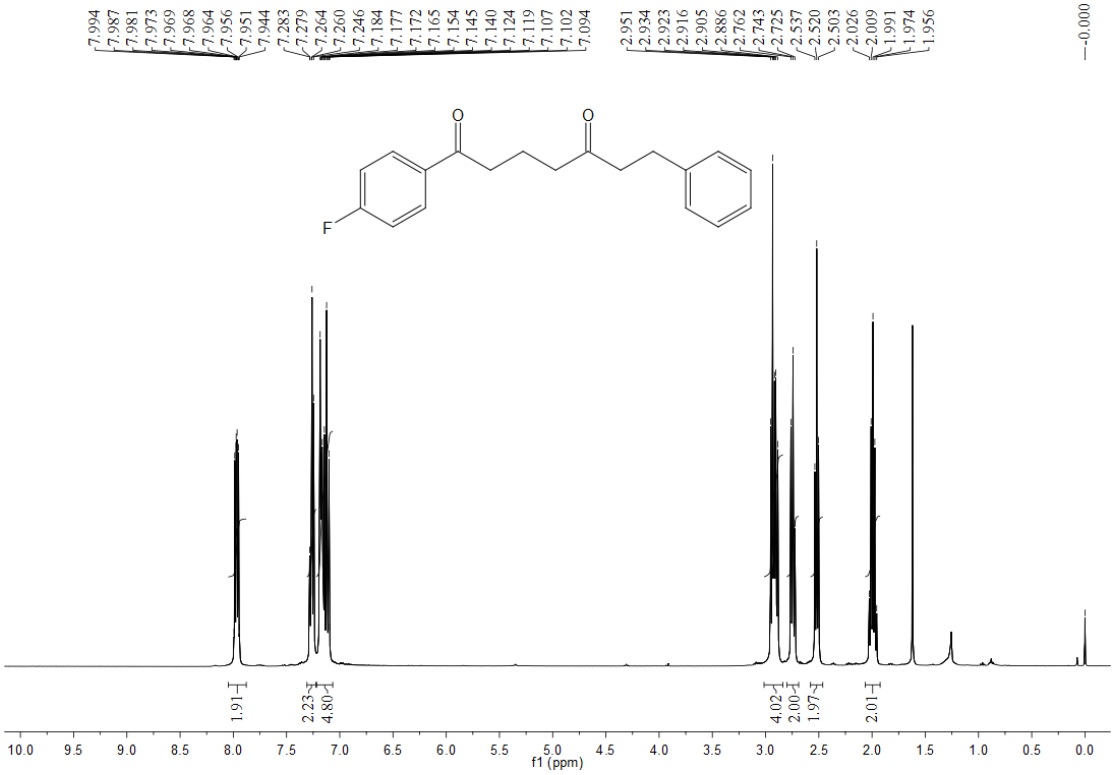


^{1}H NMR (400 MHz, $CDCl_3$) of **3ga**

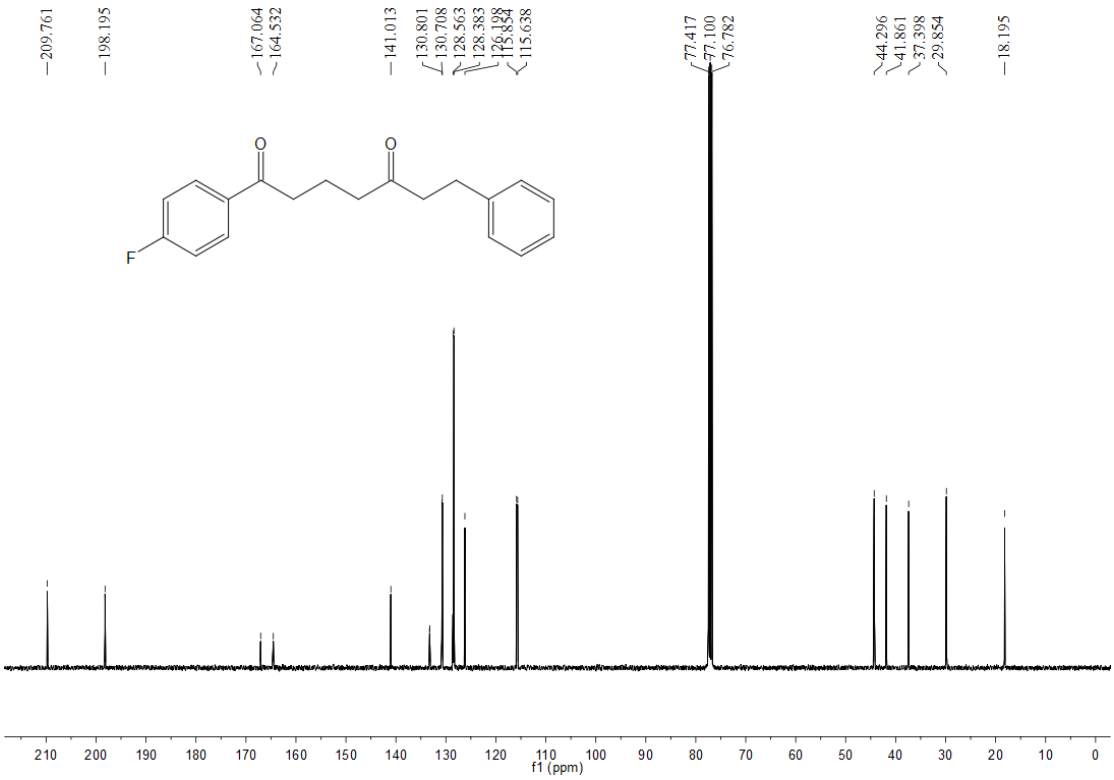


^{13}C NMR (100 MHz, $CDCl_3$) of **3ga**

1-(4-fluorophenyl)-7-phenylheptane-1,5-dione (3ha)

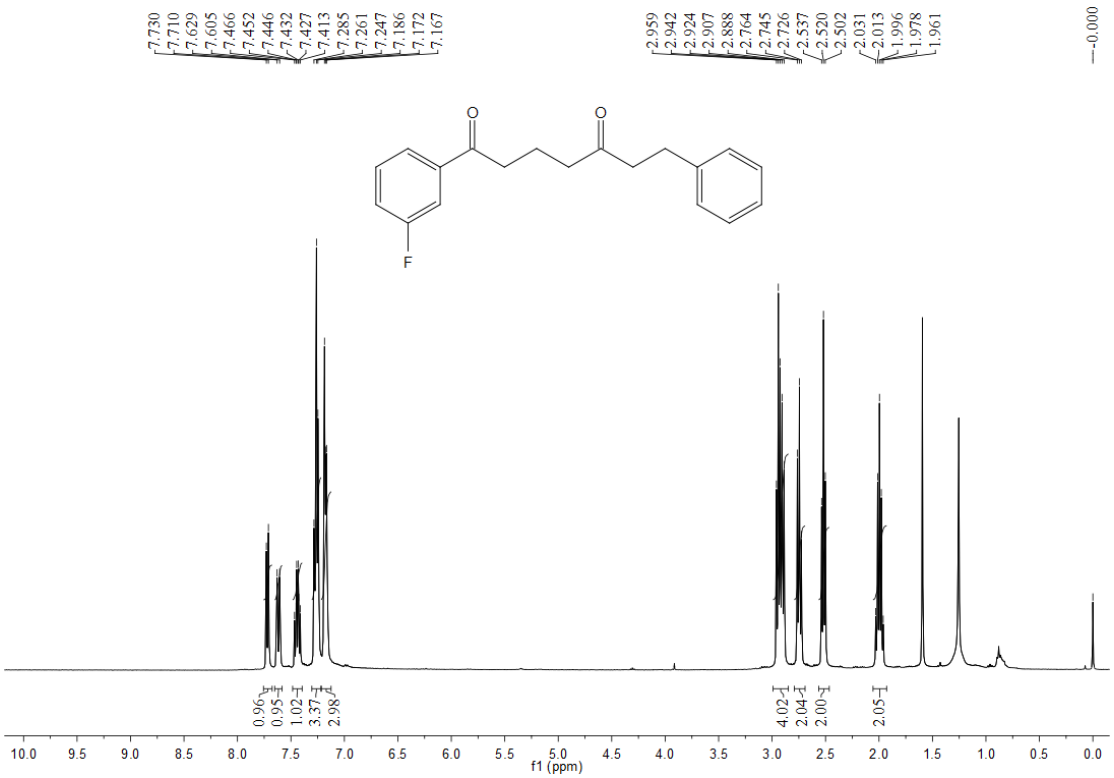


^{1}H NMR (400 MHz, $CDCl_3$) of **3ha**

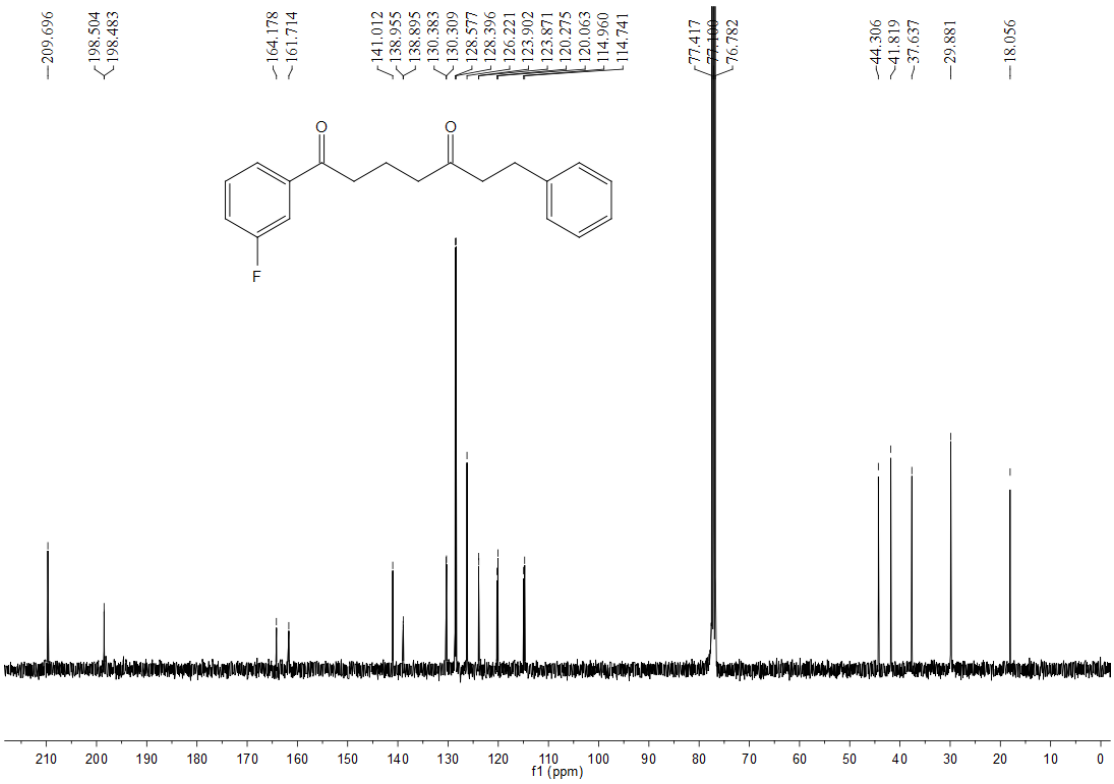


^{13}C NMR (100 MHz, $CDCl_3$) of **3ha**

1-(3-fluorophenyl)-7-phenylheptane-1,5-dione (3ia)

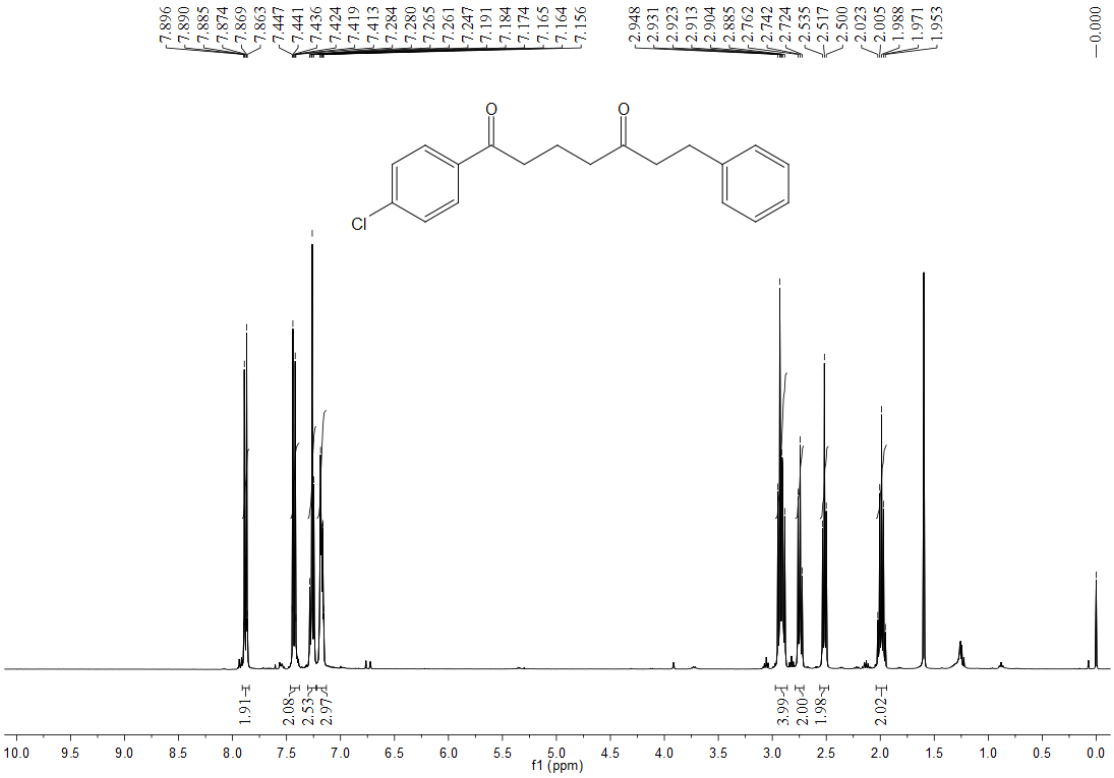


^{1}H NMR (400 MHz, $CDCl_3$) of **3ia**

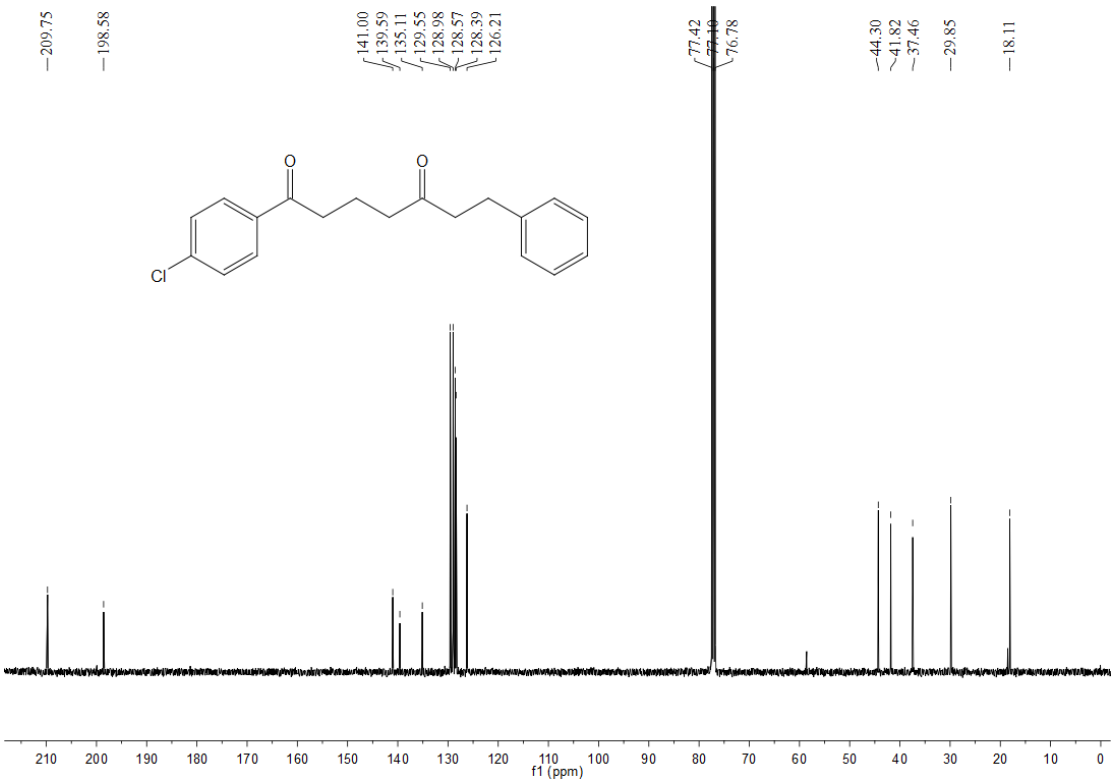


^{13}C NMR (100 MHz, $CDCl_3$) of **3ia**

1-(4-chlorophenyl)-7-phenylheptane-1,5-dione (3ja)

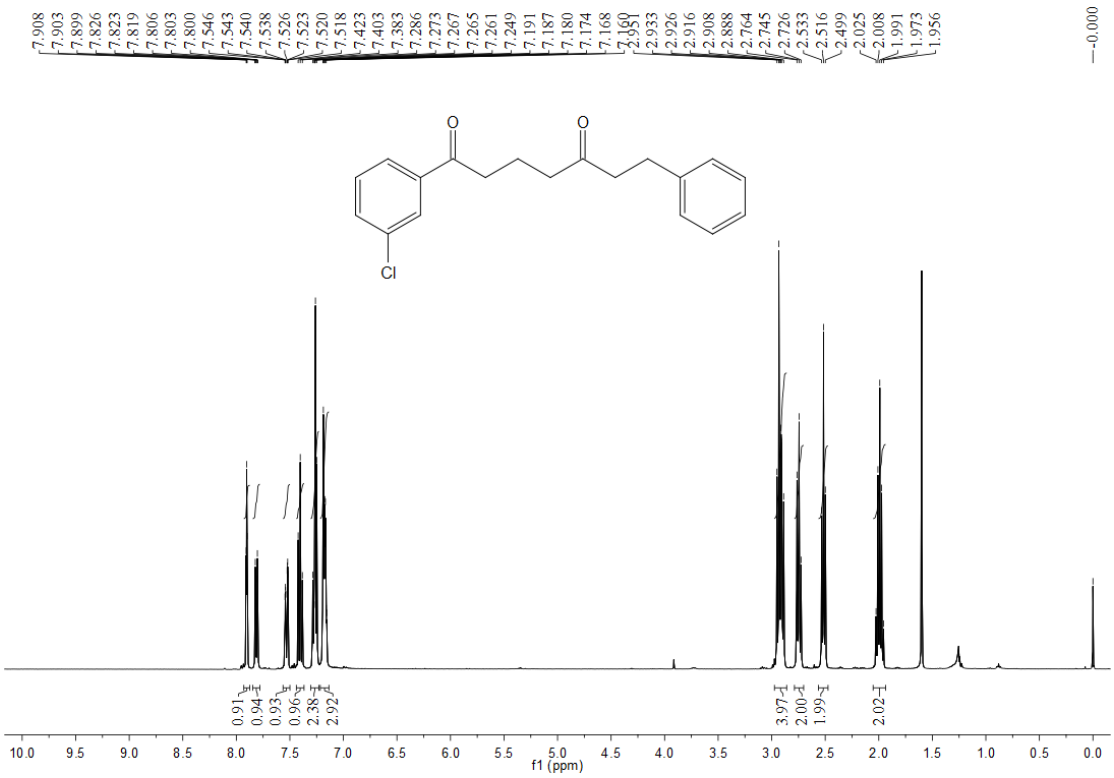


^{1}H NMR (400 MHz, $CDCl_3$) of **3ja**

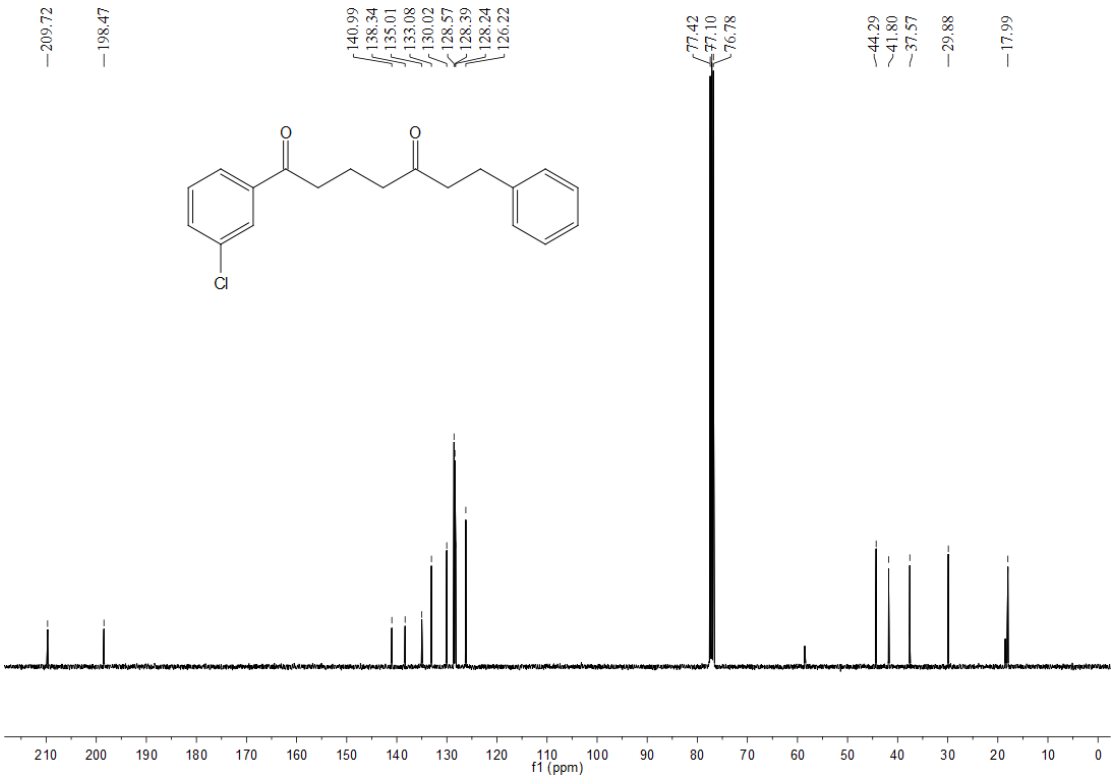


^{13}C NMR (100 MHz, $CDCl_3$) of **3ja**

1-(3-chlorophenyl)-7-phenylheptane-1,5-dione (3ka)

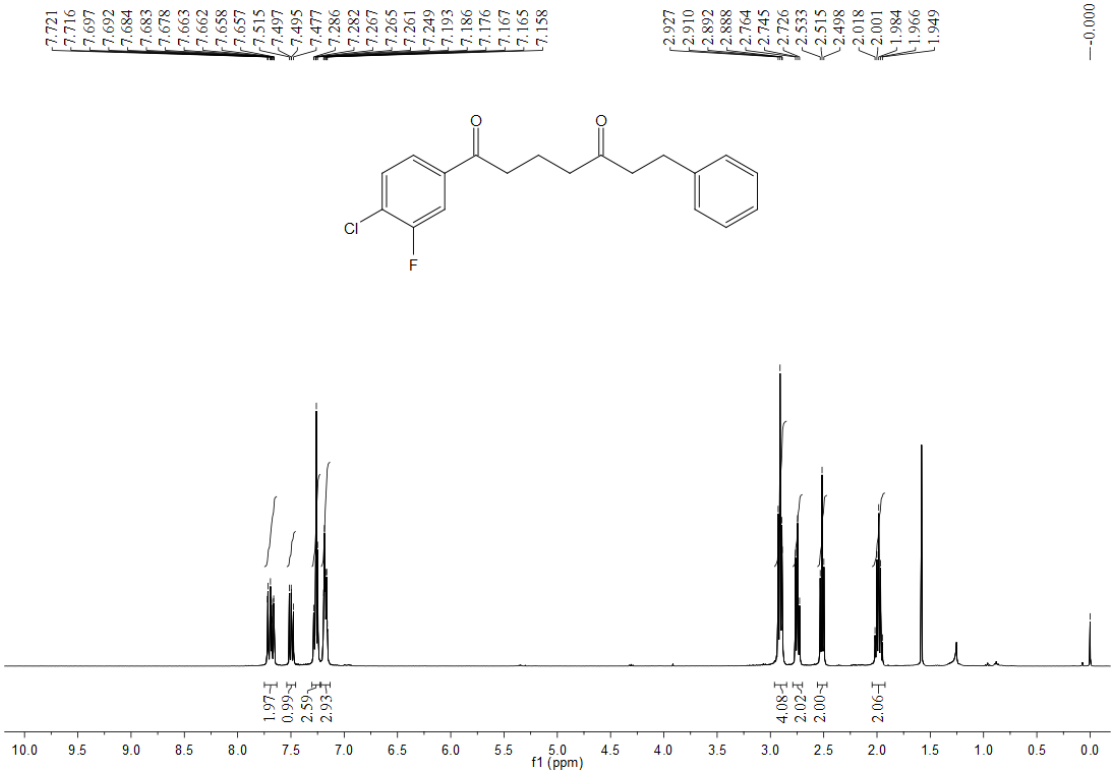


^{1}H NMR (400 MHz, $CDCl_3$) of **3ka**

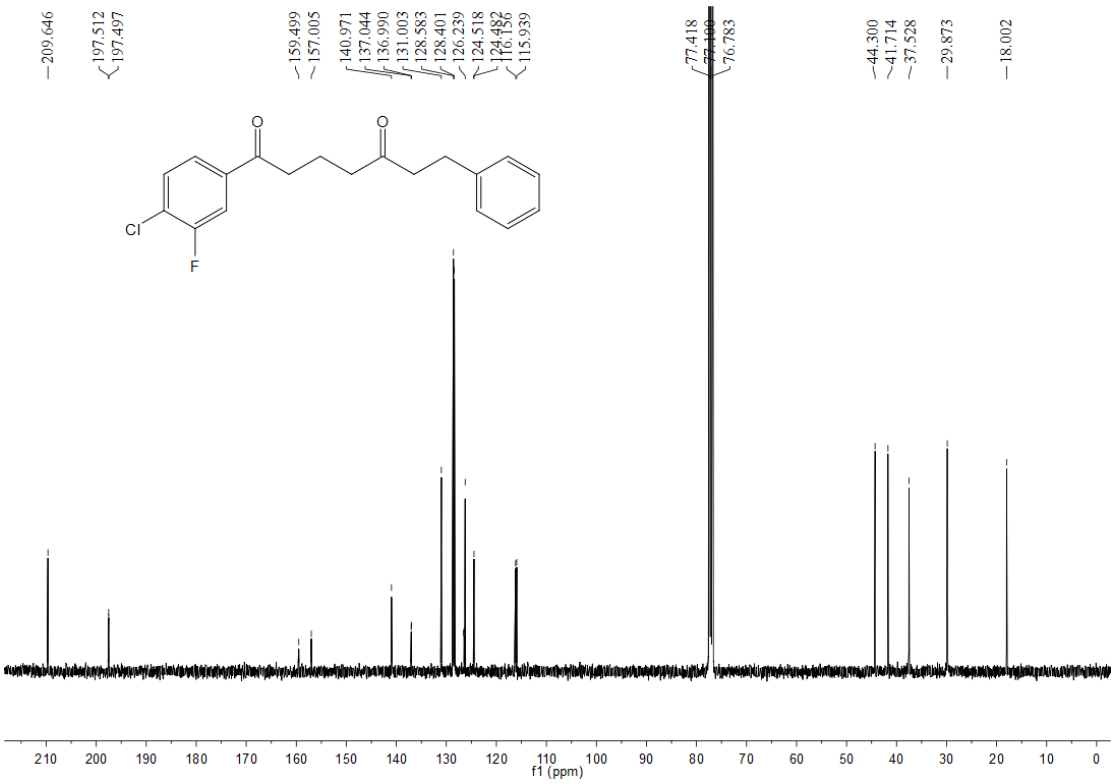


^{13}C NMR (100 MHz, $CDCl_3$) of **3ka**

1-(4-chloro-3-fluorophenyl)-7-phenylheptane-1,5-dione (3la)

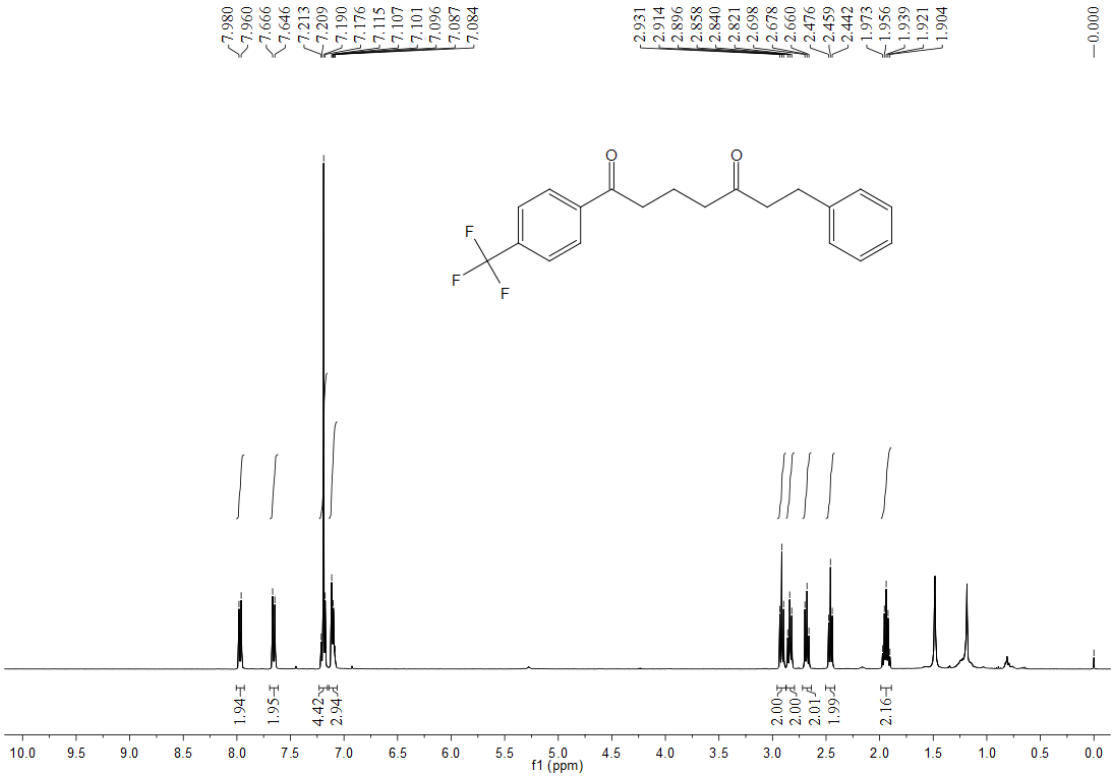


^{1}H NMR (400 MHz, $CDCl_3$) of **3la**

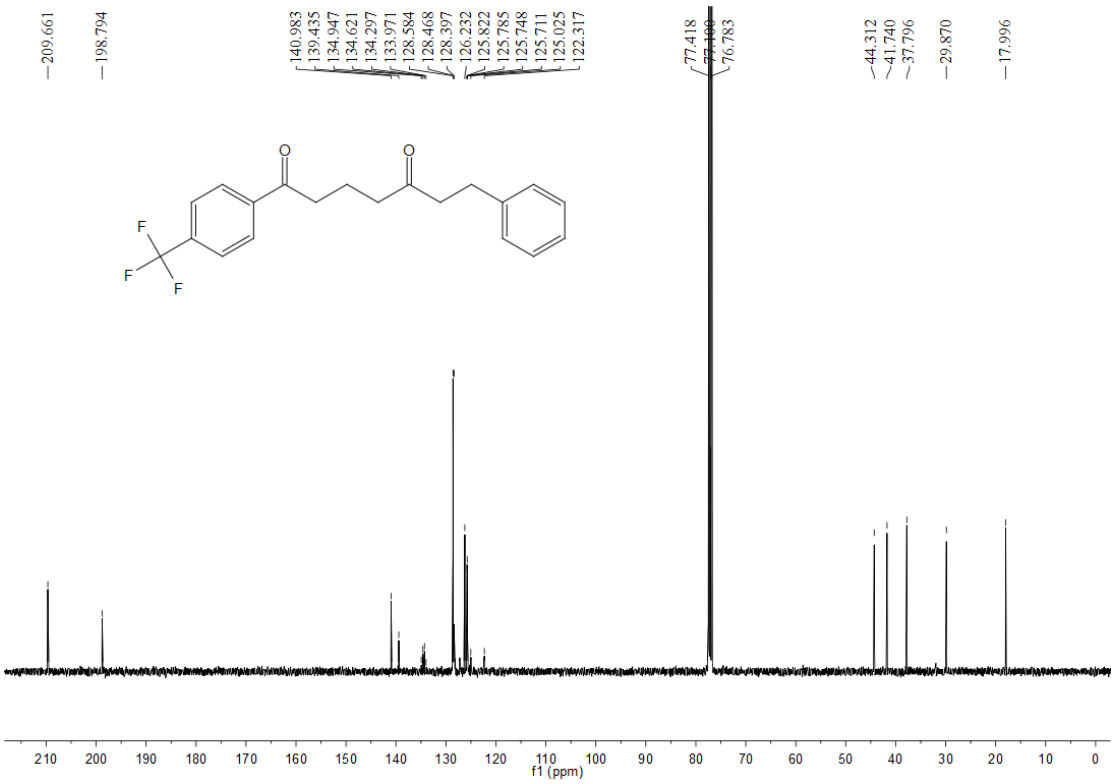


^{13}C NMR (100 MHz, $CDCl_3$) of **3la**

7-phenyl-1-(4-(trifluoromethyl)phenyl)heptane-1,5-dione (3ma)

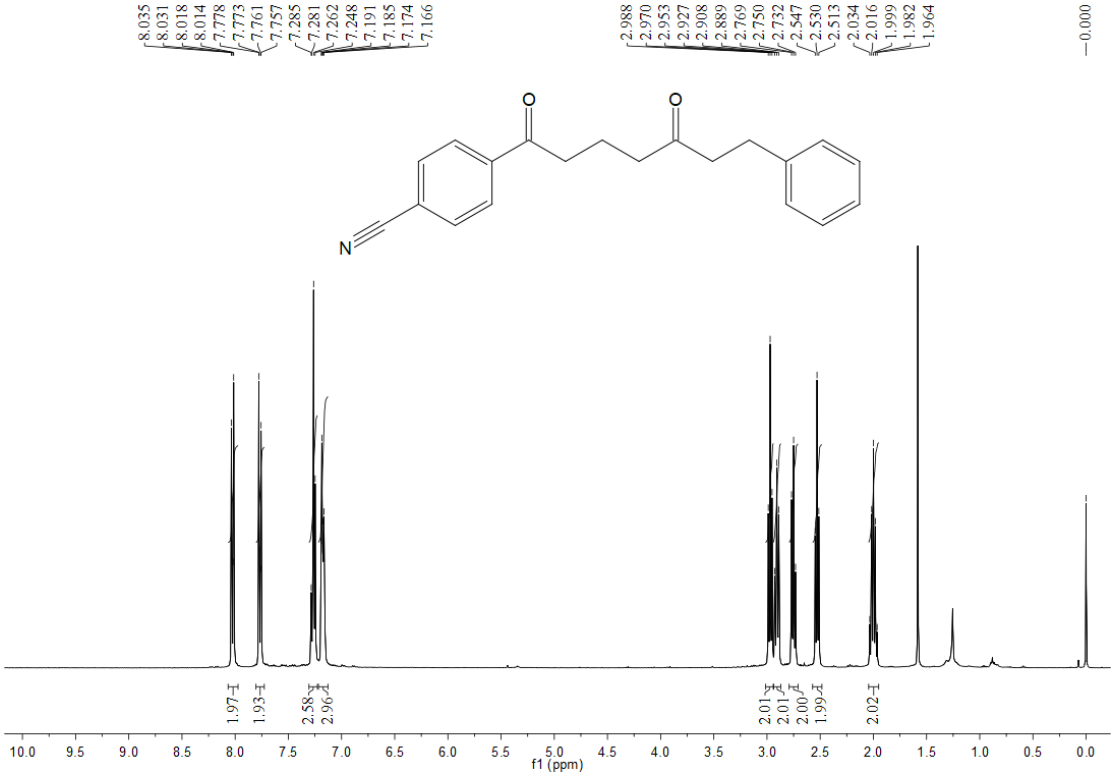


^{1}H NMR (400 MHz, $CDCl_3$) of **3ma**

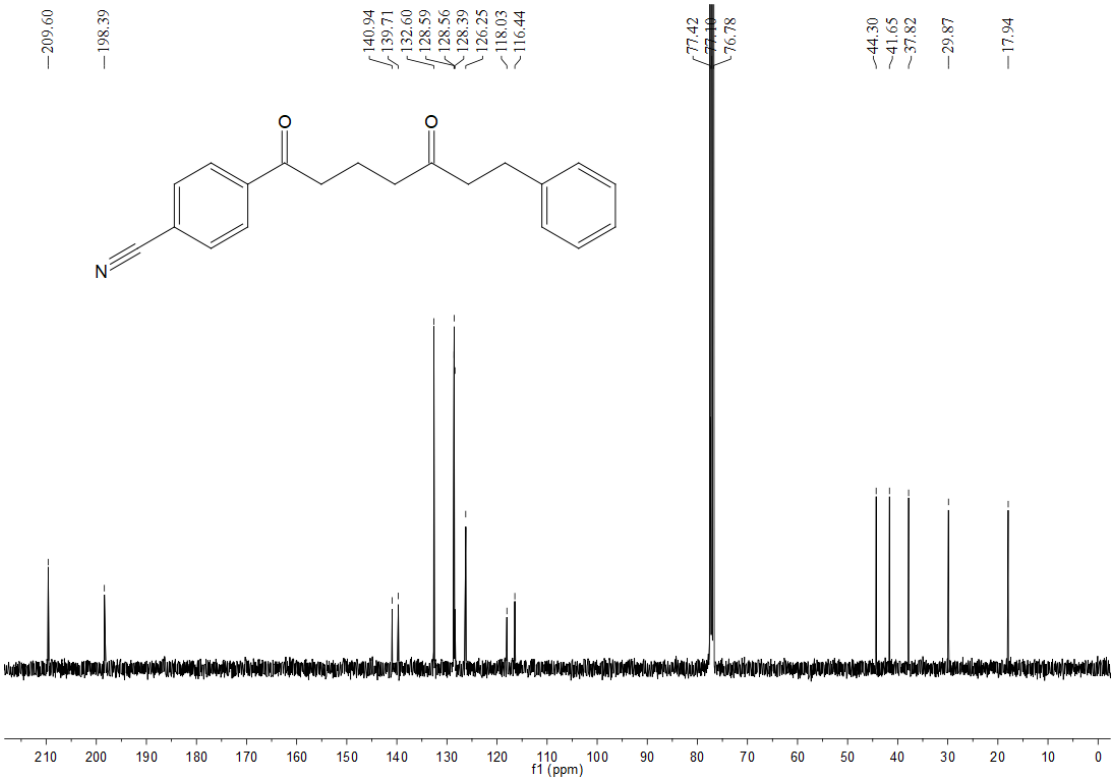


^{13}C NMR (100 MHz, $CDCl_3$) of **3ma**

4-(5-oxo-7-phenylheptanoyl)benzonitrile (3na)

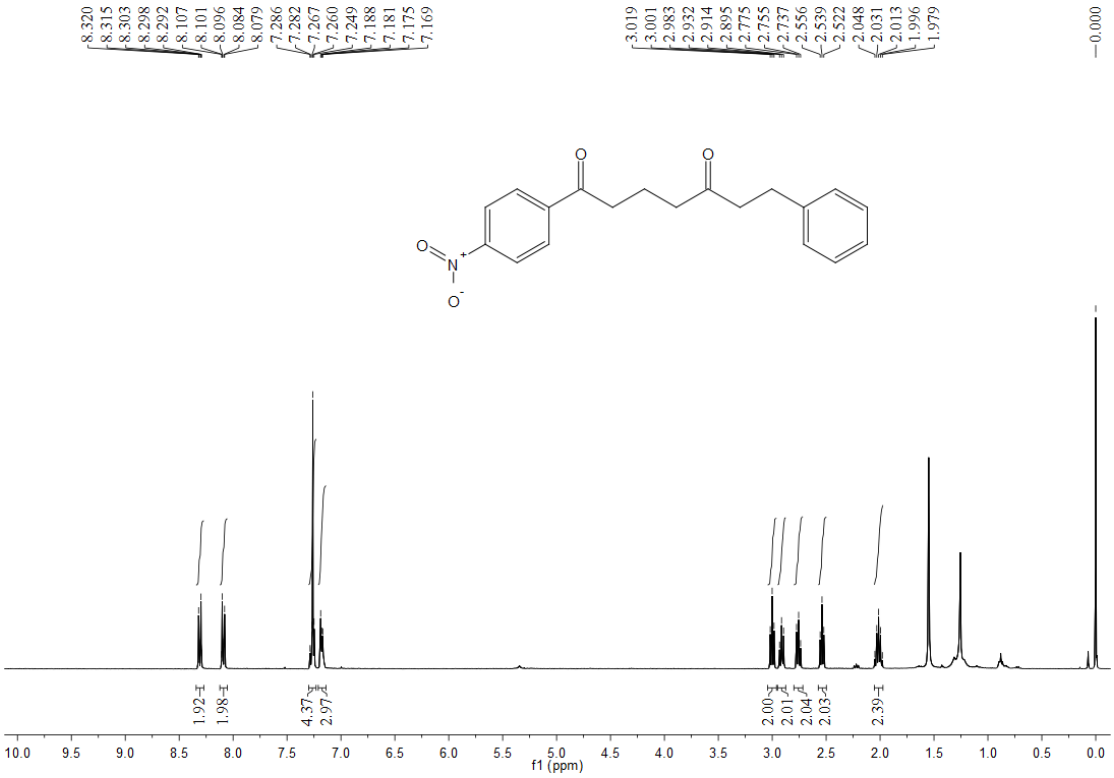


^{1}H NMR (400 MHz, $CDCl_3$) of **3na**

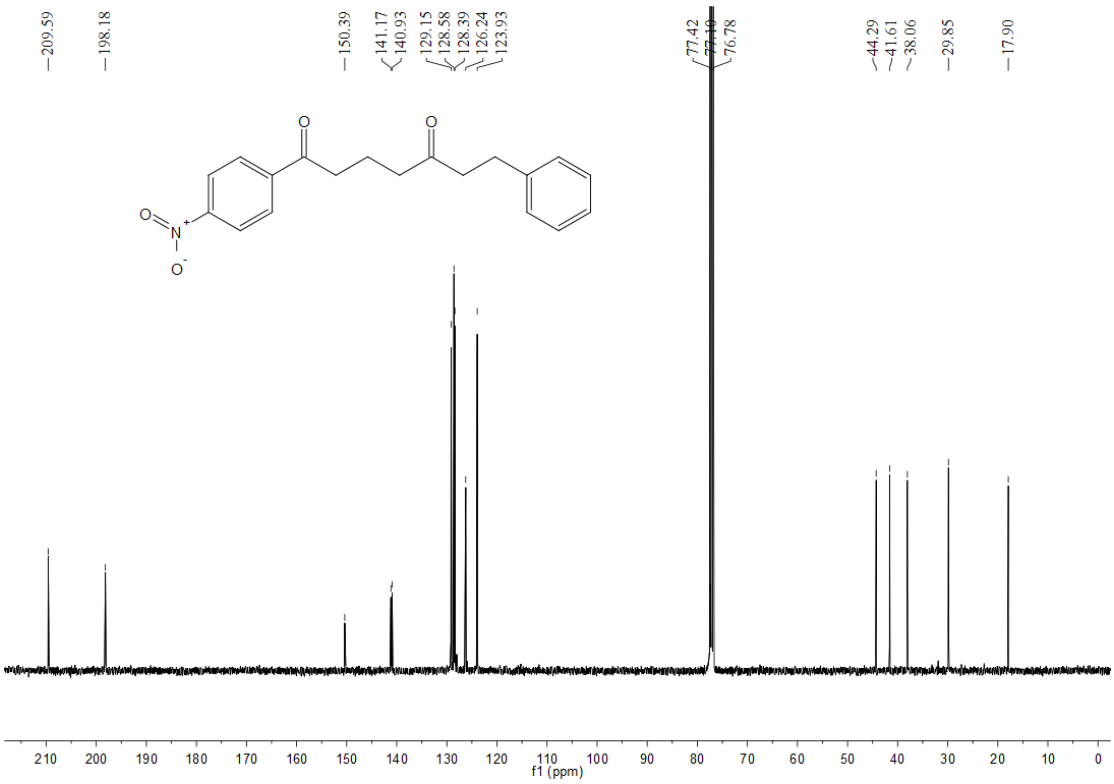


^{13}C NMR (100 MHz, $CDCl_3$) of **3na**

1-(4-nitrophenyl)-7-phenylheptane-1,5-dione (3oa)

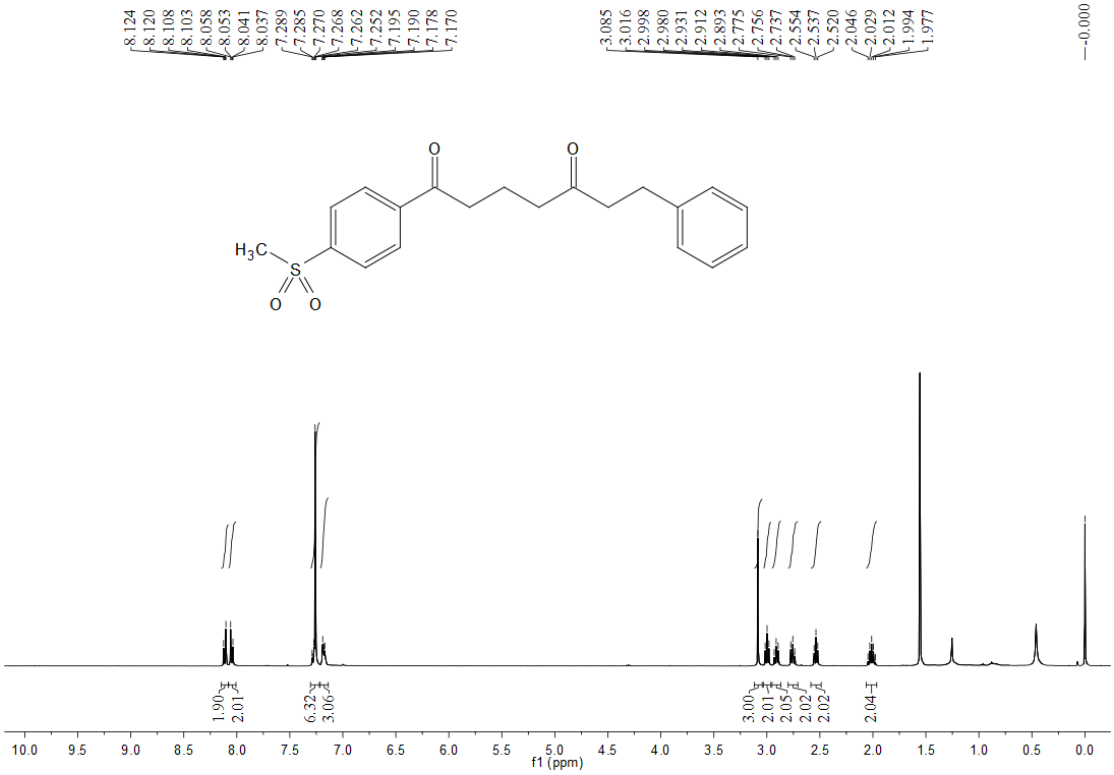


^{1}H NMR (400 MHz, $CDCl_3$) of **3oa**

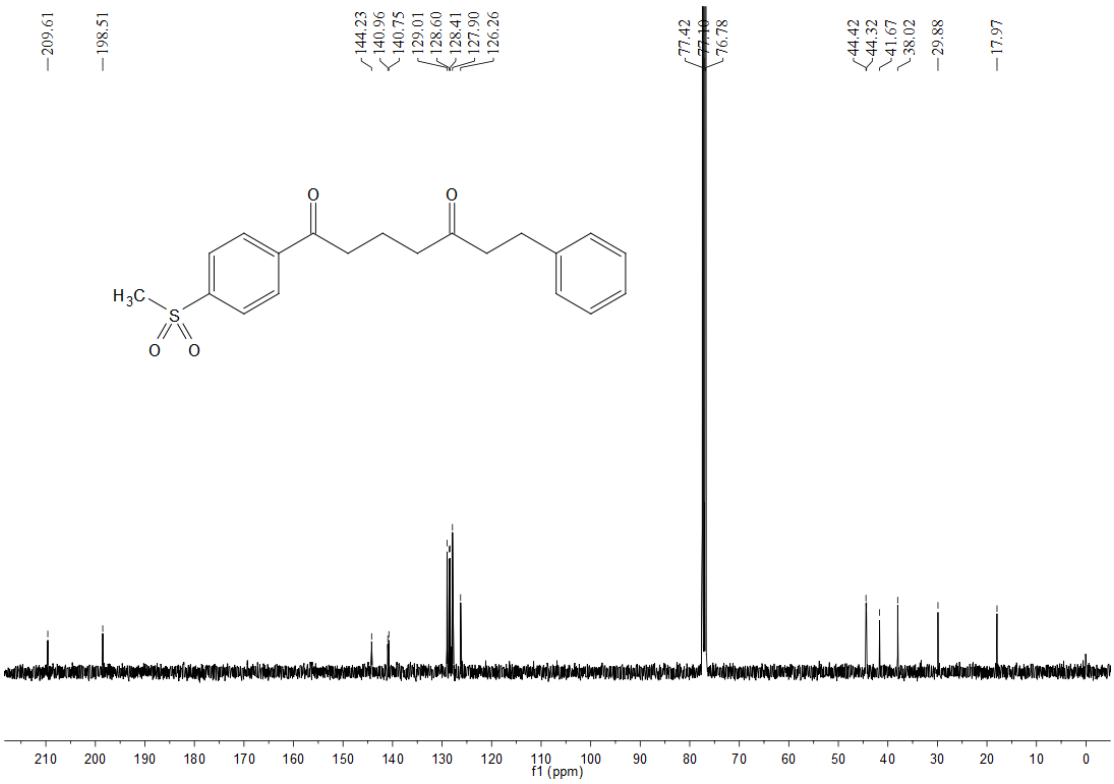


^{13}C NMR (100 MHz, $CDCl_3$) of **3oa**

1-(4-(methylsulfonyl)phenyl)-7-phenylheptane-1,5-dione (3pa)

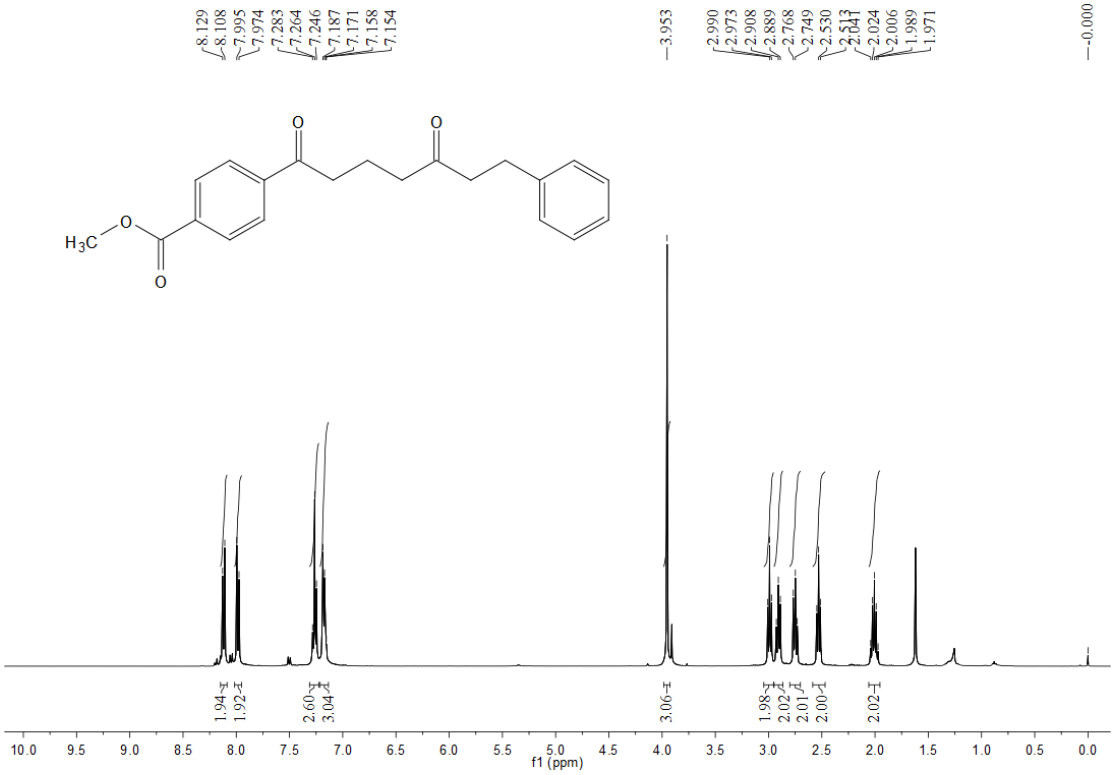


^{1}H NMR (400 MHz, $CDCl_3$) of **3pa**

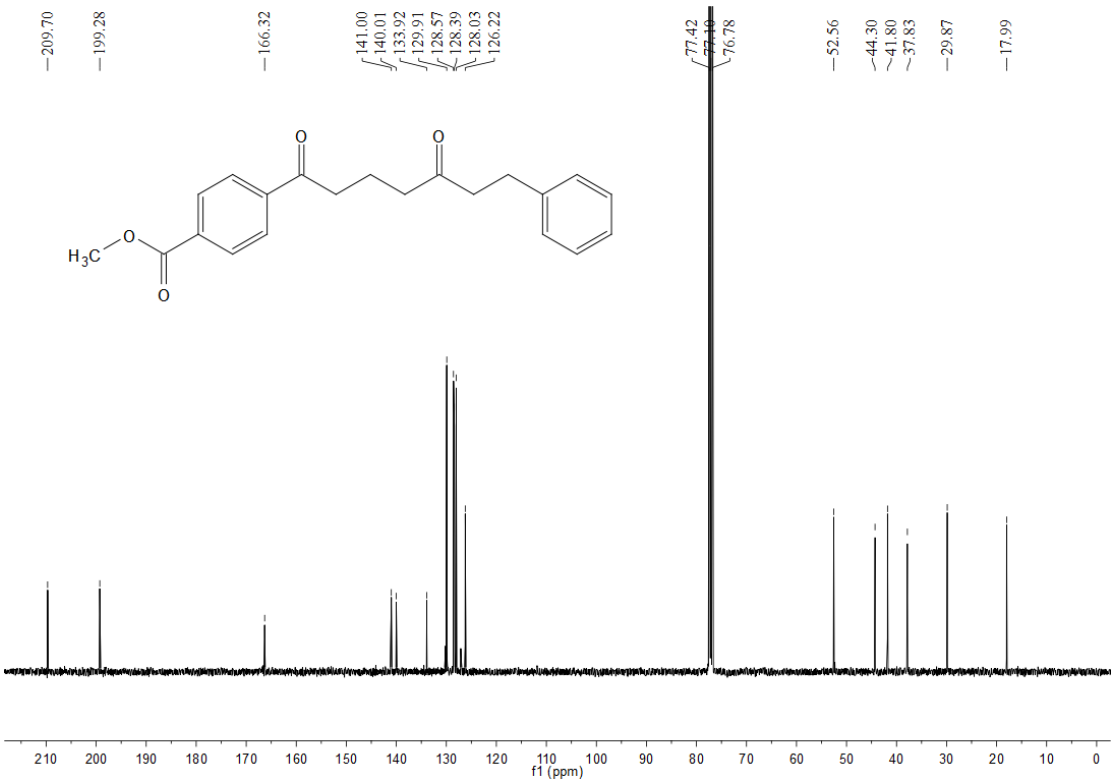


^{13}C NMR (100 MHz, $CDCl_3$) of **3pa**

methyl 4-(5-oxo-7-phenylheptanoyl)benzoate (3qa)

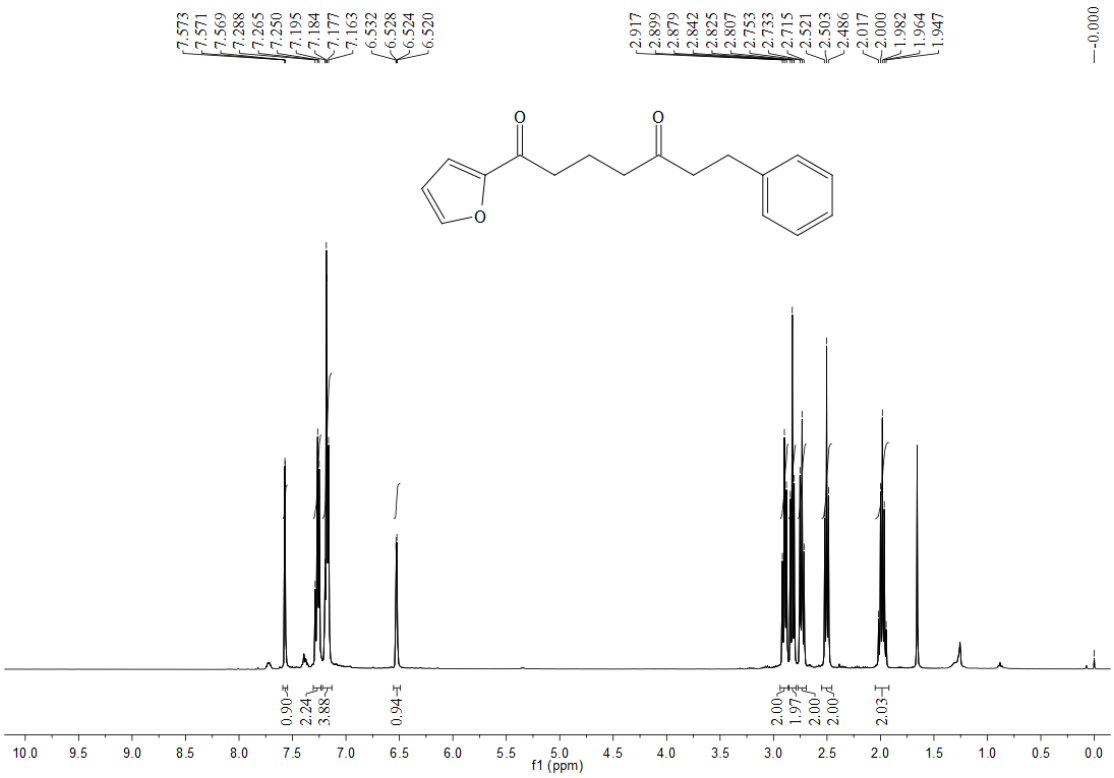


^{1}H NMR (400 MHz, $CDCl_3$) of **3qa**

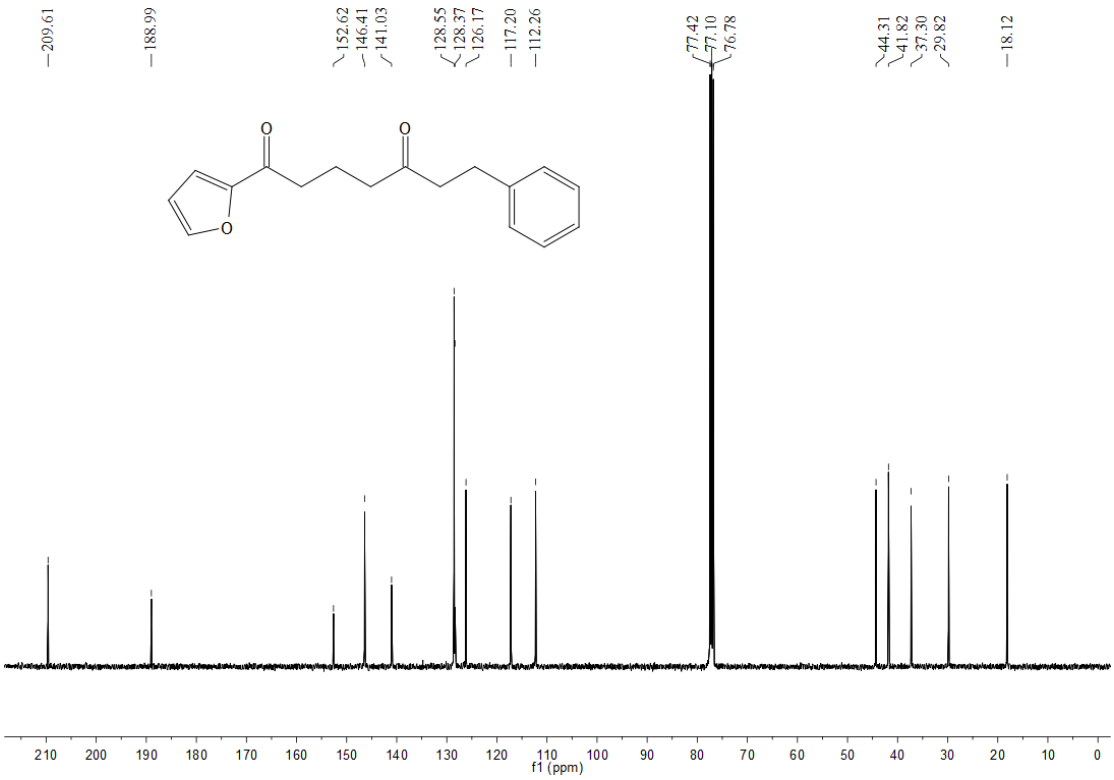


^{13}C NMR (100 MHz, $CDCl_3$) of **3qa**

1-(furan-2-yl)-7-phenylheptane-1,5-dione (3ra)

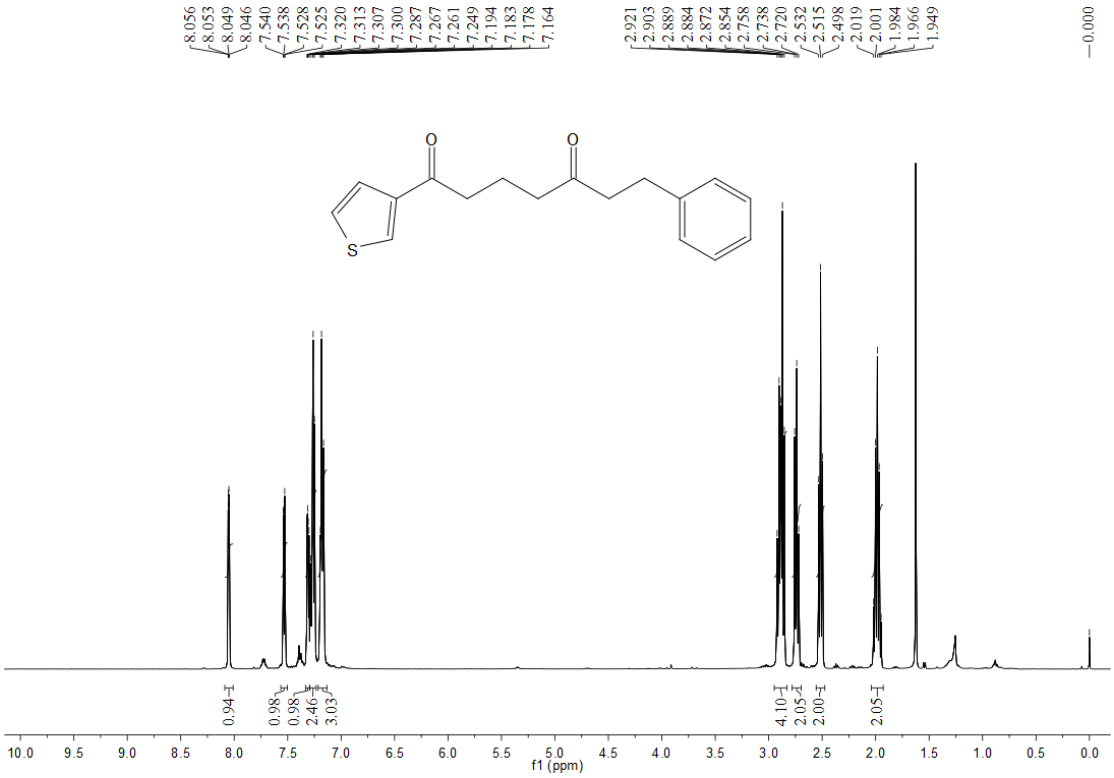


^{1}H NMR (400 MHz, $CDCl_3$) of **3ra**

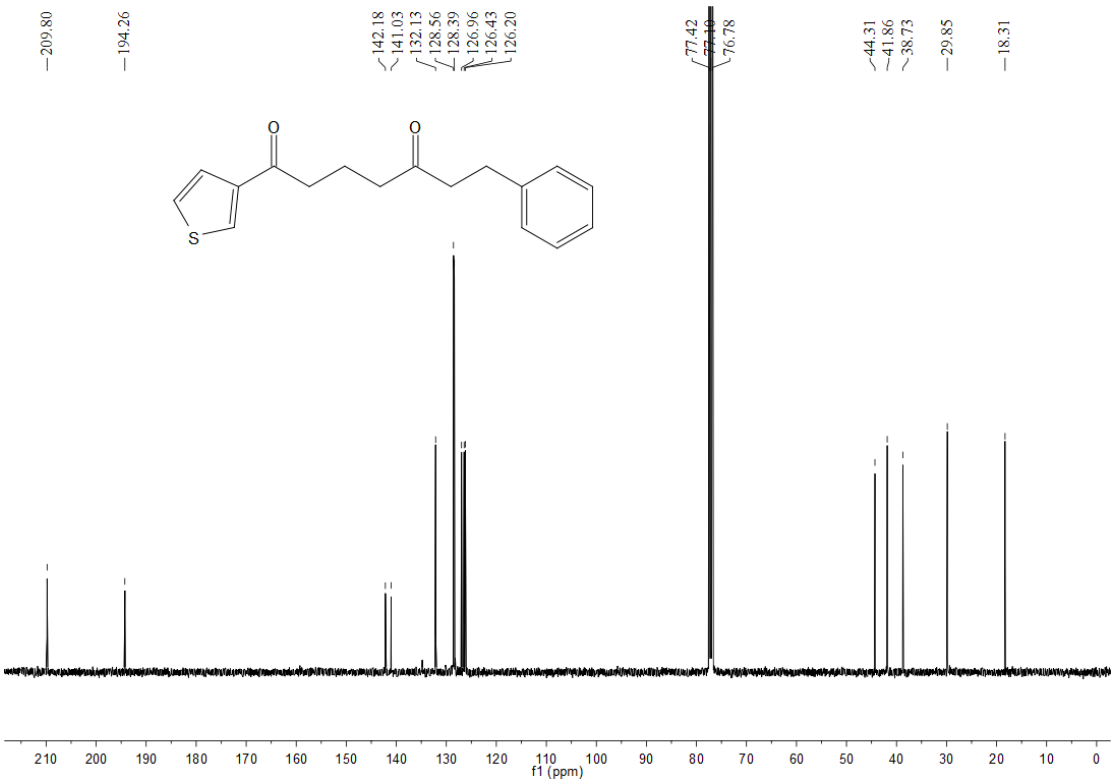


^{13}C NMR (100 MHz, $CDCl_3$) of **3ra**

7-phenyl-1-(thiophen-3-yl)heptane-1,5-dione (3sa)

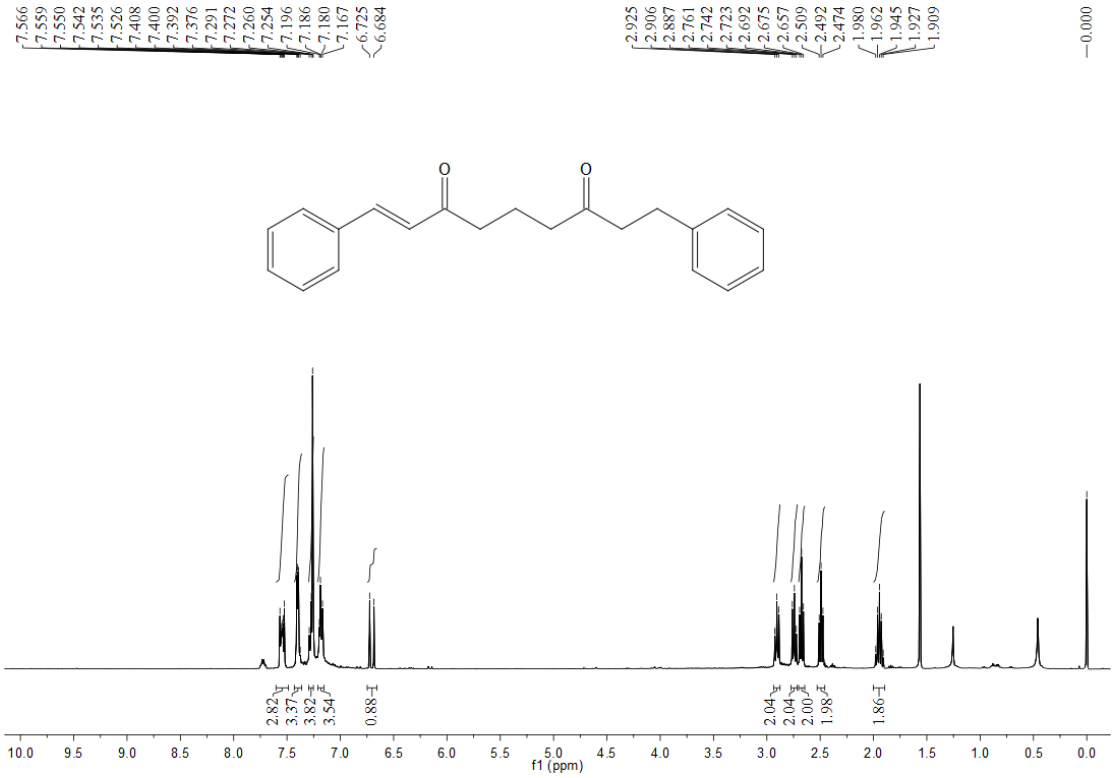


^{1}H NMR (400 MHz, $CDCl_3$) of **3sa**

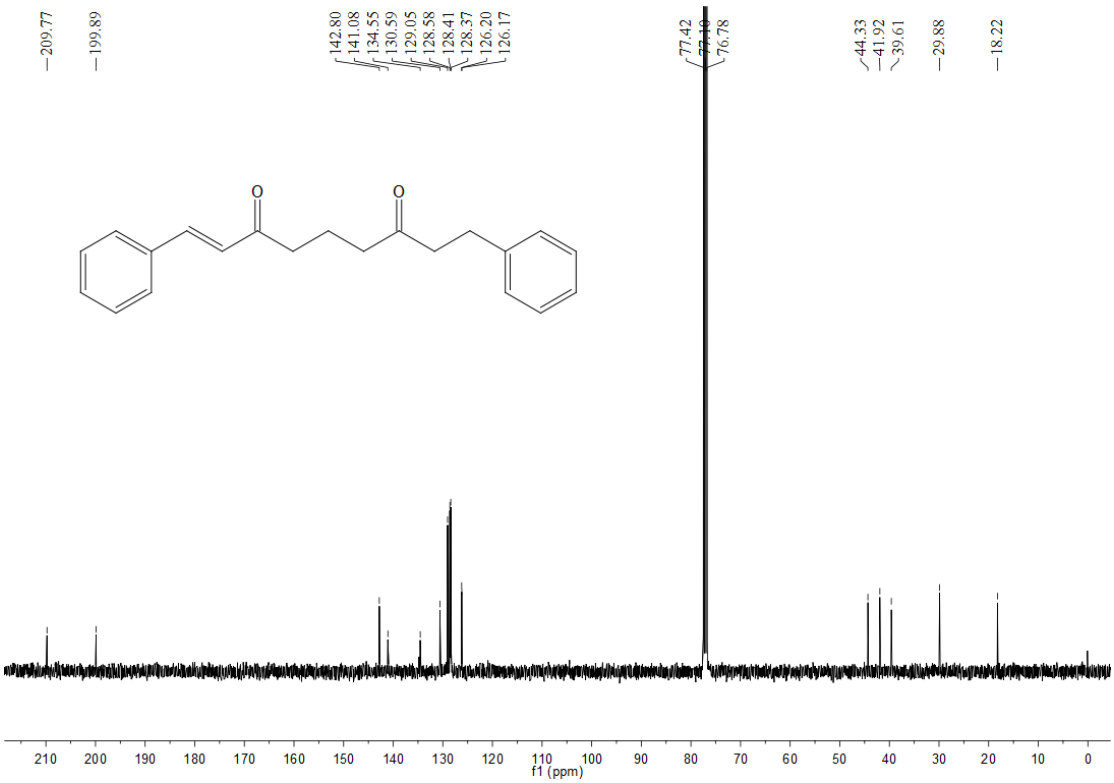


^{13}C NMR (100 MHz, $CDCl_3$) of **3sa**

(*E*)-1,9-diphenylnon-1-ene-3,7-dione (3ta)

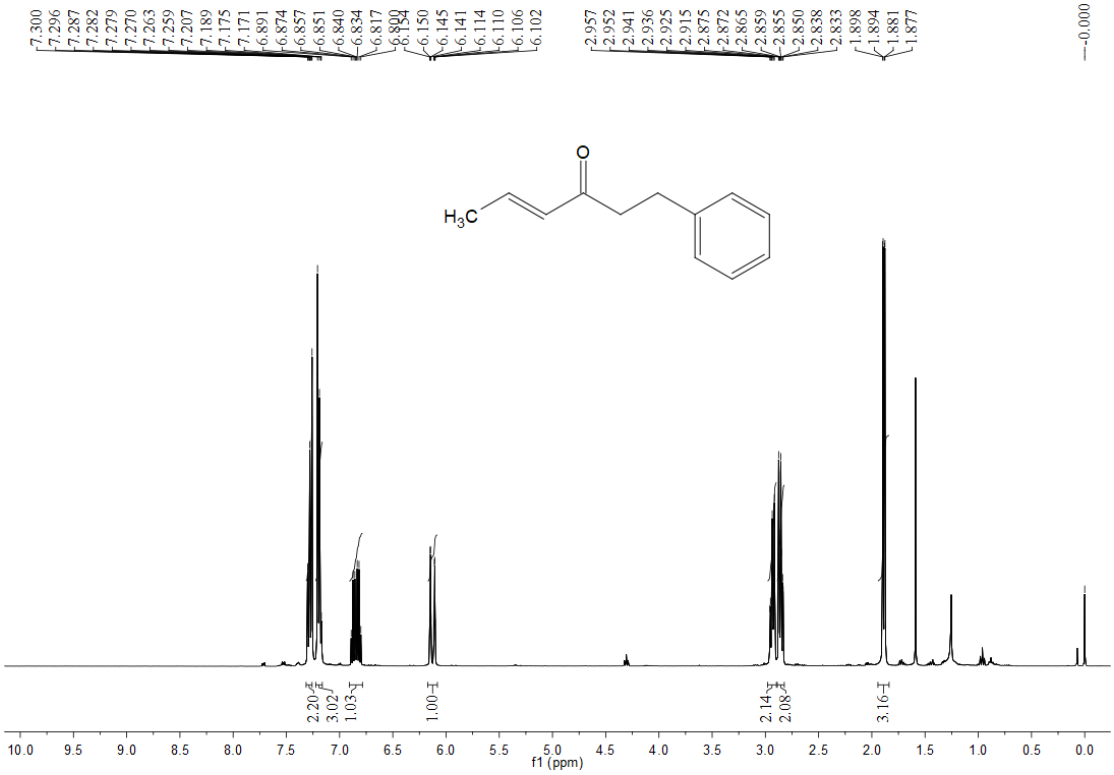


^{1}H NMR (400 MHz, $CDCl_3$) of **3ta**

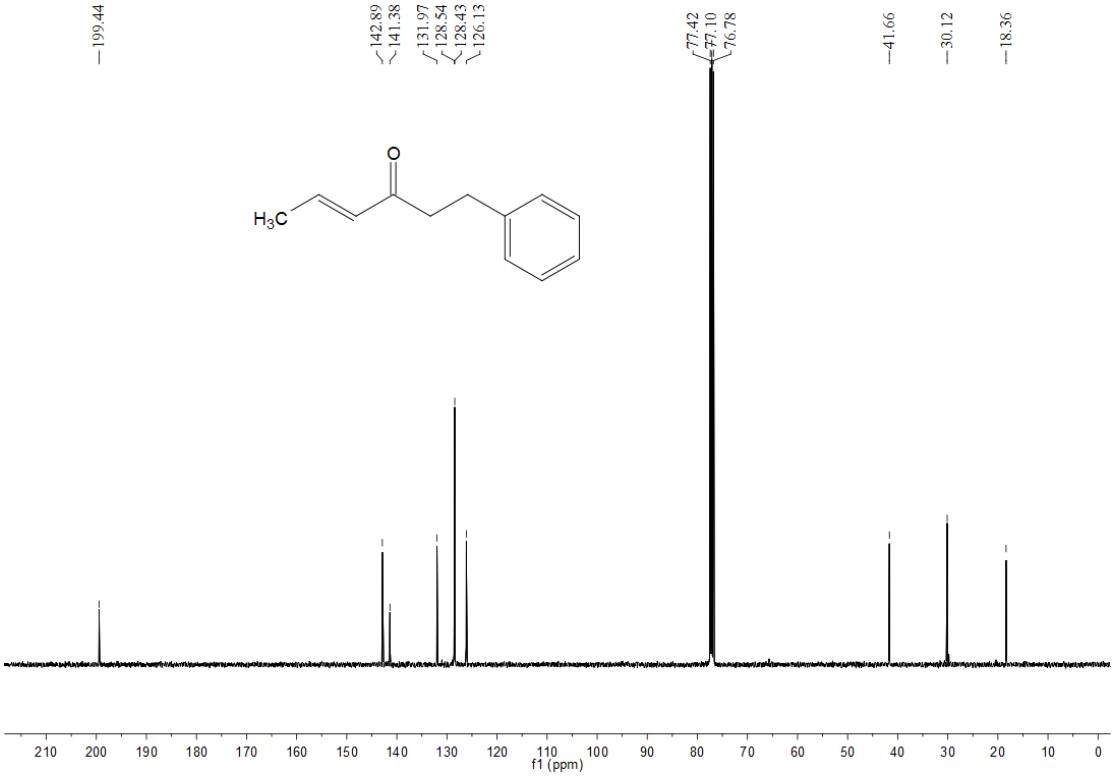


^{13}C NMR (100 MHz, $CDCl_3$) of **3ta**

(*E*)-1-phenylhex-4-en-3-one (5)

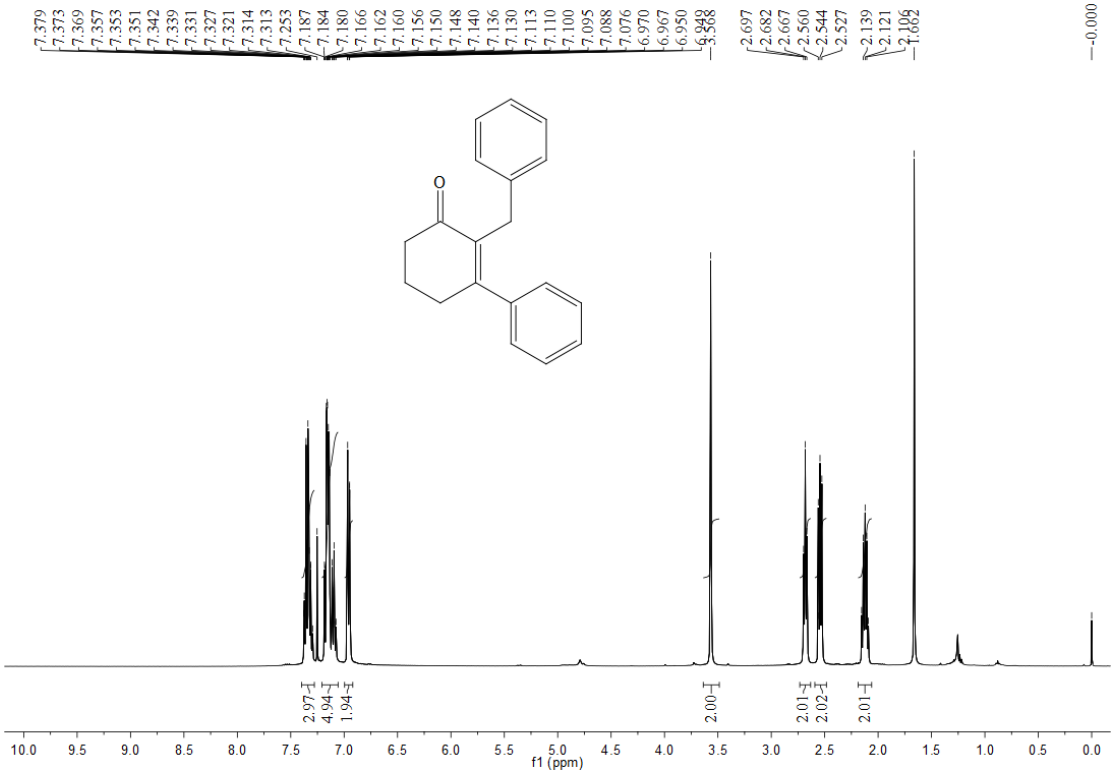


^{1}H NMR (400 MHz, $CDCl_3$) of **5**

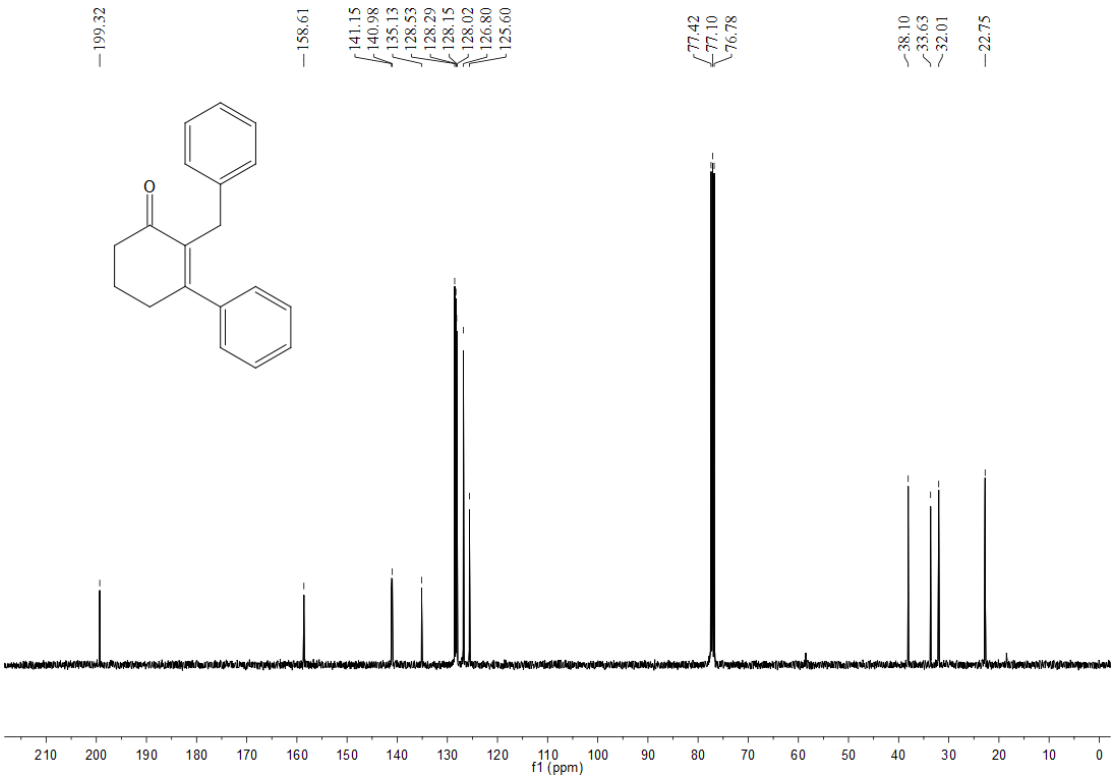


^{13}C NMR (100 MHz, $CDCl_3$) of **5**

2-benzyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (7)

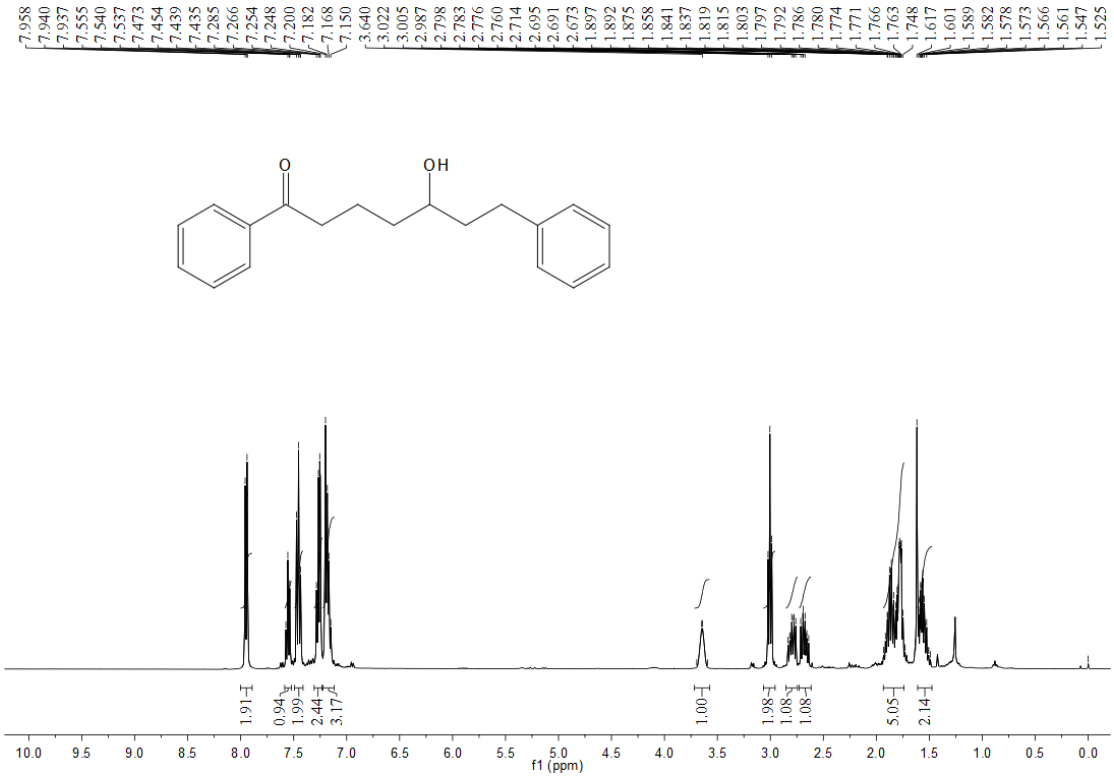


^{1}H NMR (400 MHz, $CDCl_3$) of **7**

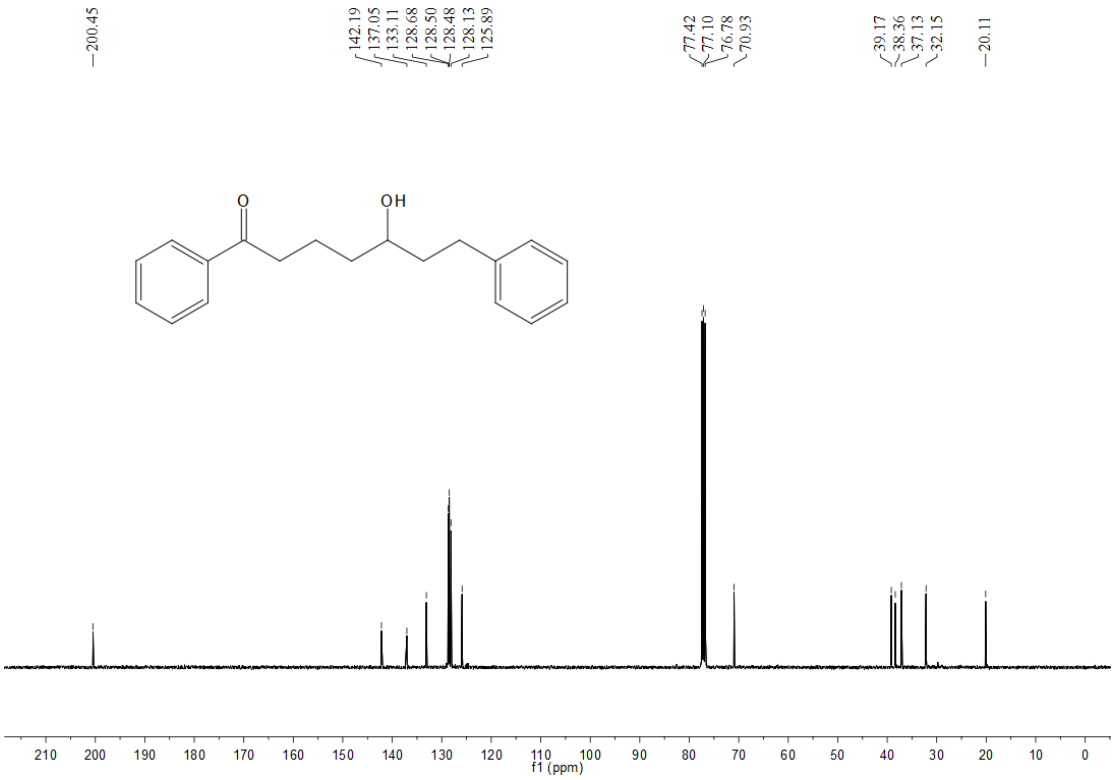


^{13}C NMR (100 MHz, $CDCl_3$) of **7**

5-hydroxy-1,7-diphenylheptan-1-one (8)

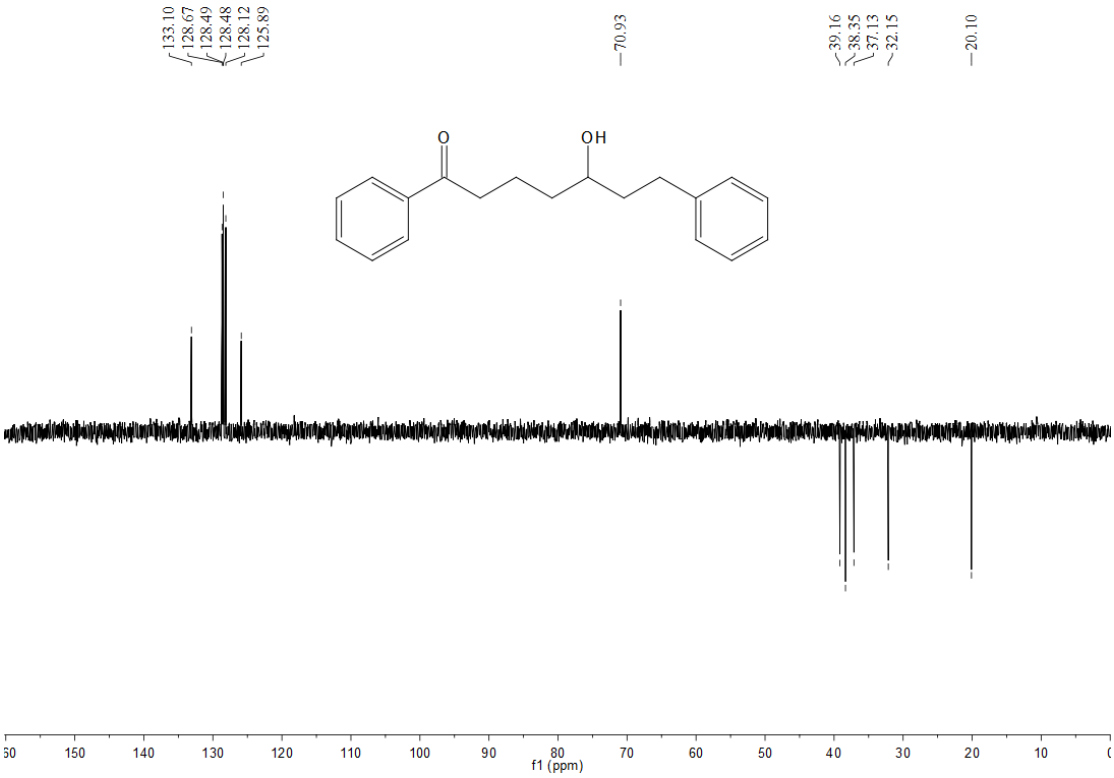


^{1}H NMR (400 MHz, $CDCl_3$) of **8**



^{13}C NMR (100 MHz, $CDCl_3$) of **8**

5-hydroxy-1,7-diphenylheptan-1-one (8)



DEPT135 (100 MHz, $CDCl_3$) of **8**