

A Metal-free Synthesis of Diaryl-1,2-diketones by C–C Triple Bond Cleavage of Alkynones

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 $\text{C}_{16}\text{H}_{14}\text{O}_2^{18}\text{O}_2$.

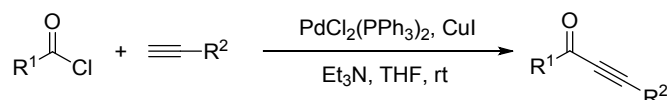
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Experimental Section

All chemicals were obtained from commercial sources and used without further purification. DMSO was dried by CaH_2 . Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. All melting points were determined on a Beijing Science Instrument Dianguang Instrument Factory XT4B melting point apparatus and uncorrected. ^1H and ^{13}C NMR spectra were measured on a 400 MHz Bruker spectrometer (^1H 400 MHz, ^{13}C 100 MHz), using CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. HRMSESI spectra were obtained on Agilent 6450 spectrometer. IR data were recorded on a Nicolet IS10 spectrometer. The products listed below were determined by ^1H , ^{13}C NMR. PE is petroleum ether (60-90 °C).

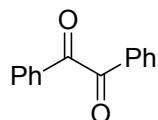
General Procedure for the Preparation of alkynones:



To a solution of the acyl chloride (1.0 mmol) and terminal alkyne (1.1 mmol) in anhydrous THF (5 mL) under N_2 protection, was added $\text{PdCl}_2(\text{PPh}_3)_2$ (14 mg, 2 mol %) and CuI (7.6 mg, 4 mol %). After stirring for 1 min, Et_3N (1.5 mmol) was added and the mixture was stirred for 15 h at r.t. When the reaction was complete (Monitored by TLC), distilled H_2O was added. The mixture was extracted with CH_2Cl_2 . The organic phase was collected, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography [silica gel, PE/EtOAc (50:1)].

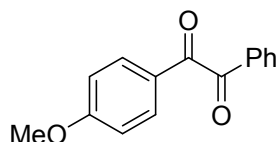
General Procedure for the Synthesis of Diaryl-1,2-diketones 2a-2p:

A mixture of alkynones (0.5 mmol), K_2CO_3 (0.5 mmol) and $\text{H}_2\text{O}/\text{DMSO}$ (40 μl : 2 ml) was stirred at 90 °C for 8h under oxygen atmosphere. After cooling to room temperature, water was added (5 mL). Then the aqueous solution was extracted with ethyl acetate (5ml \times 3). The organic phase was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography [eluent: PE/EtOAc (50:1)] on silica gel to provide the desired product.



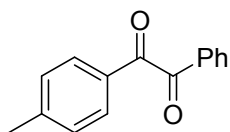
benzil (**2a**)

Yellow solid; ^1H NMR (400 MHz, CDCl_3): δ ppm 8.0 (d, $J = 7.4$ Hz, 4H), 7.66 (t, $J = 7.1$ Hz, 2H), 7.51 (t, $J = 7.2$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ ppm 194.5, 134.9, 133.0, 129.9, 129.0.



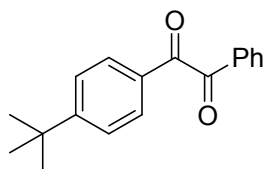
1-(4-methoxyphenyl)-2-phenylethane-1,2-dione(**2b**)

Yellow solid; ^1H NMR (400 MHz, CDCl_3): δ ppm 7.97-7.93 (m, 4H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.8$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ ppm 194.8, 193.1, 165.0, 134.6, 133.1, 132.2, 129.8, 128.9, 126.0, 114.3, 55.6.



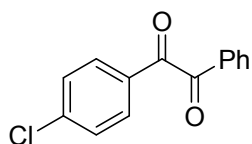
1-phenyl-2-(*p*-tolyl)ethane-1,2-dione(**2c**)

Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ ppm 7.95 (d, $J = 7.1$ Hz, 2H), 7.87 (d, $J = 8.1$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ ppm 194.7, 194.2, 146.1, 134.7, 133.0, 130.5, 129.9, 129.8, 129.7, 128.9, 21.8.



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

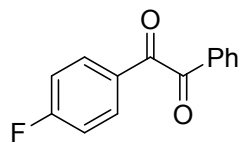
Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ ppm 7.98-7.96 (m, 2H), 7.91 (d, $J = 8.6$ Hz, 2H), 7.66-7.62 (m, 1H), 7.53-7.48 (m, 4H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ ppm 194.7, 194.3, 159.0, 134.7, 133.1, 130.5, 129.9, 128.9, 126.0, 125.4, 35.4, 30.9.



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

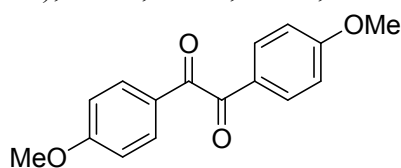
Yellow solid; ^1H NMR (400 MHz, CDCl_3): δ ppm 7.97-7.91 (m, 4H), 7.67 (t, $J = 18.3$ Hz, 1H), 7.54-7.48 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ ppm 193.8, 193.0, 141.6,

135.0, 132.8, 131.4, 131.2, 129.9, 129.4, 129.1.



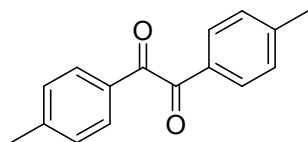
1-(4-fluorophenyl)-2-phenylethane-1,2-dione(**2f**)

Light yellow solid; ^1H NMR (400 MHz, CDCl_3): δ ppm 8.04-7.96 (m, 4H), 7.67 (t, $J = 7.2$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.19 (t, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ ppm 194.0, 192.7, 168.0 ($J_{\text{C,F}} = 256.6$ Hz), 135.0, 132.8, 132.7 ($J_{\text{C,F}} = 9.7$ Hz), 129.9, 129.0, 116.5, 116.3.



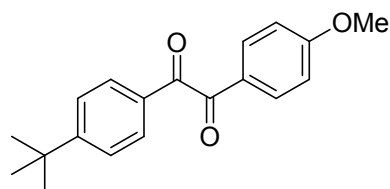
1,2-bis(4-methoxyphenyl)ethane-1,2-dione(**2g**)

Yellow solid; ^1H NMR (400 MHz, CDCl_3): δ ppm 7.94 (d, $J = 9.0$ Hz, 4H), 6.97 (d, $J = 8.9$ Hz, 4H), 3.88 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ ppm 193.5, 164.8, 132.4, 126.3, 114.3, 55.6.



1,2-di-*p*-tolylethane-1,2-dione(**2h**)

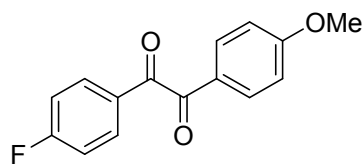
Yellow solid; ^1H NMR (400 MHz, CDCl_3): δ ppm 7.86 (d, $J = 8.2$ Hz, 4H), 7.30 (d, $J = 7.9$ Hz, 4H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ ppm 194.5, 146.0, 130.7, 130.0, 129.7, 21.9.



1-(4-(*tert*-butyl)phenyl)-2-(4-methoxyphenyl)ethane-1,2-dione(**2i**)

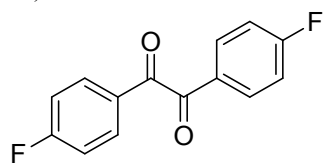
Yellow solid; ^1H NMR (400 MHz, CDCl_3): δ ppm 7.92 (m, 4H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.0 (d, $J = 8.8$ Hz, 2H), 3.87 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ ppm 194.5, 193.4, 164.9, 158.8, 132.3, 130.6, 129.8, 126.2, 125.9, 114.3, 55.6, 35.3,

30.9.



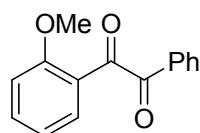
1-(4-fluorophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione(**2j**)

Yellow solid; ^1H NMR(400 MHz, CDCl_3): δ ppm 8.03-8.00 (m, 2H), 7.95 (d, $J = 8.8$ Hz, 2H), 7.18 (t, $J = 8.6$ Hz, 2H), 6.98 (d, $J = 8.8$ Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ ppm 193.0, 192.6, 168.0, 165.2 (d, $J_{\text{C,F}} = 30.7$ Hz), 132.7 (d, $J_{\text{C,F}} = 9.7$ Hz), 132.4, 129.7, 126.0, 116.3 (d, $J_{\text{C,F}} = 22.1$ Hz), 114.4, 55.7.



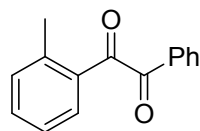
1,2-bis(4-fluorophenyl)ethane-1,2-dione(**2k**)

Yellow solid; ^1H NMR (400 MHz, CDCl_3): δ ppm 8.02 (m, $J = 7.0$ Hz, 4H), 7.20 (m, $J = 8.5$ Hz, 4H) ; ^{13}C NMR (100 MHz, CDCl_3): δ ppm 192.2, 168.1 (d, $J_{\text{C,F}} = 256.9$ Hz), 132.8(d, $J_{\text{C,F}} = 9.8$ Hz), 129.4, 116.5 (d, $J_{\text{C,F}} = 22.1$ Hz).



1-(2-methoxyphenyl)-2-phenylethane-1,2-dione(**2l**)

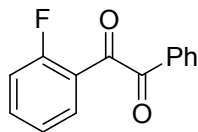
Yellow solid; ^1H NMR(400 MHz, CDCl_3): δ ppm 8.00 (m, 1H), 7.89 (m, 2H), 7.59-7.53 (m, 2H), 7.45 (m, 2H), 7.08 (m, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 3.49 (t, $J = 5.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ ppm 194.5, 193.3, 160.1, 136.4, 133.6, 132.7, 130.1, 129.0, 128.5, 123.5, 121.3, 112.3, 55.4.



1-phenyl-2-(*o*-tolyl)ethane-1,2-dione(**2m**)

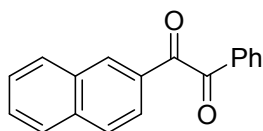
Light yellow solid; ^1H NMR(400 MHz, CDCl_3): δ ppm 7.98 (m, 2H), 7.65 (m, 2H), 7.53-7.46 (m, 3H), 7.35 (d, $J = 7.6$ Hz, 1H), 7.27 (m, 1H), 2.70 (s, 3H); ^{13}C NMR

(100 MHz, CDCl₃): δ ppm 196.8, 194.8, 141.3, 134.7, 133.7, 133.1, 133.0, 132.6, 131.8, 130.0, 129.0, 126.0, 21.9.



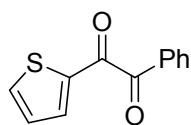
1-(2-fluorophenyl)-2-phenylethane-1,2-dione(**2n**)

Yellow solid; ¹H NMR(400 MHz, CDCl₃): δ ppm 8.07-8.04 (m, 1H), 7.98-7.96 (m, 2H), 7.68-7.61 (m, 2H), 7.54-7.50 (m, 2H), 7.36-7.32 (m, 1H), 7.15-7.10 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ ppm 193.0, 191.9, 164.1(d, $J_{C,F}$ = 256.6 Hz), 136.8 (d, $J_{C,F}$ = 9.1 Hz), 134.7, 132.0, 130.8, 129.8, 129.0, 125.0 (d, $J_{C,F}$ = 3.3 Hz), 122.4 (d, $J_{C,F}$ = 11.1 Hz), 116.6 (d, $J_{C,F}$ = 21.4 Hz).



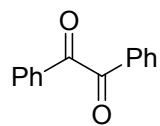
1-(naphthalen-2-yl)-2-phenylethane-1,2-dione(**2o**)

Light yellow solid; ¹H NMR(400 MHz, CDCl₃): δ ppm 8.42 (s, 1H), 8.11-8.09 (m, 1H), 8.03 (m, 2H), 7.97 (d, J = 8.7 Hz, 1H), 7.91 (t, J = 7.2 Hz, 2H), 7.69-7.63(m, 2H), 7.58-7.51 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ ppm 194.6, 136.4, 134.9, 133.5, 133.1, 132.3, 130.3, 130.0, 129.9, 129.5, 129.2, 129.0, 127.9, 127.2, 123.6.

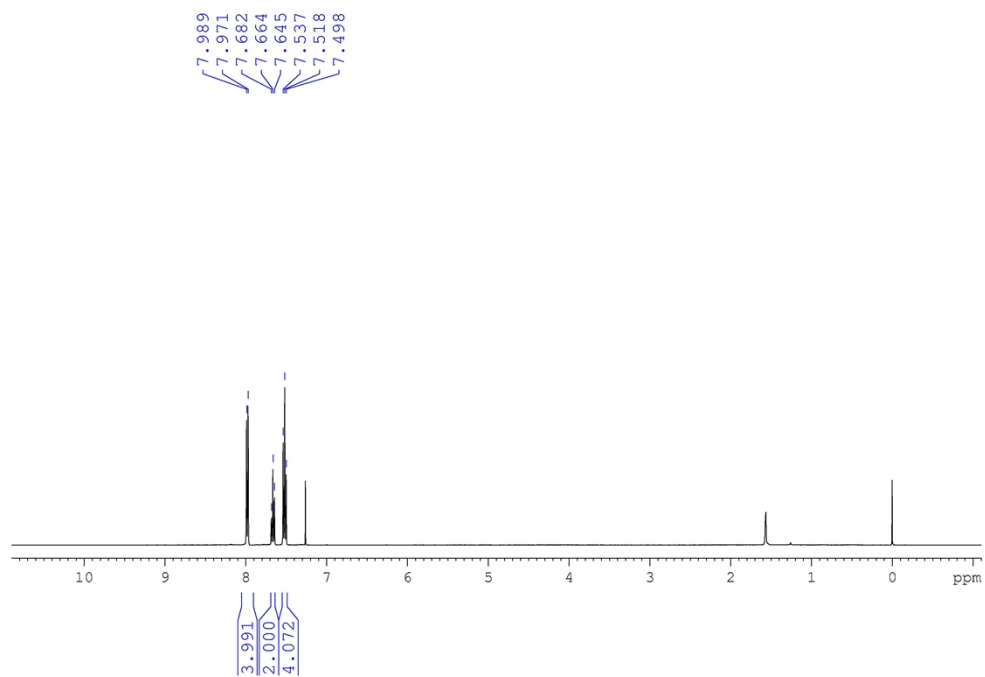


1-phenyl-2-(thiophen-2-yl)ethane-1,2-dione(**2p**)

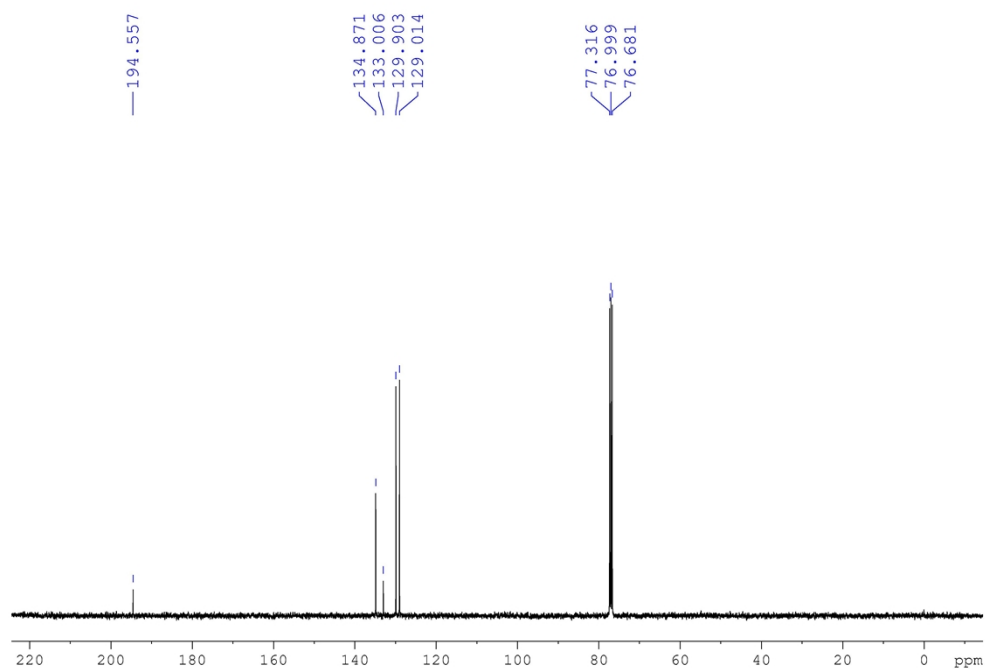
Yellow solid; ¹H NMR(400 MHz, CDCl₃): δ ppm 8.0 (d, J = 7.6 Hz, 2H), 7.85-7.81 (m, 2H), 7.66 (t, J = 7.7 Hz, 1H); 7.52 (m, 2H), 7.19(m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ ppm 192.1, 185.6, 139.9, 136.8, 136.7, 134.8, 132.7, 130.2, 128.9, 128.8.

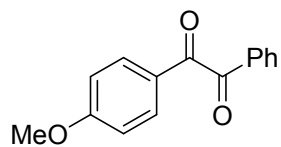


^1H NMR spectrum of **2a**

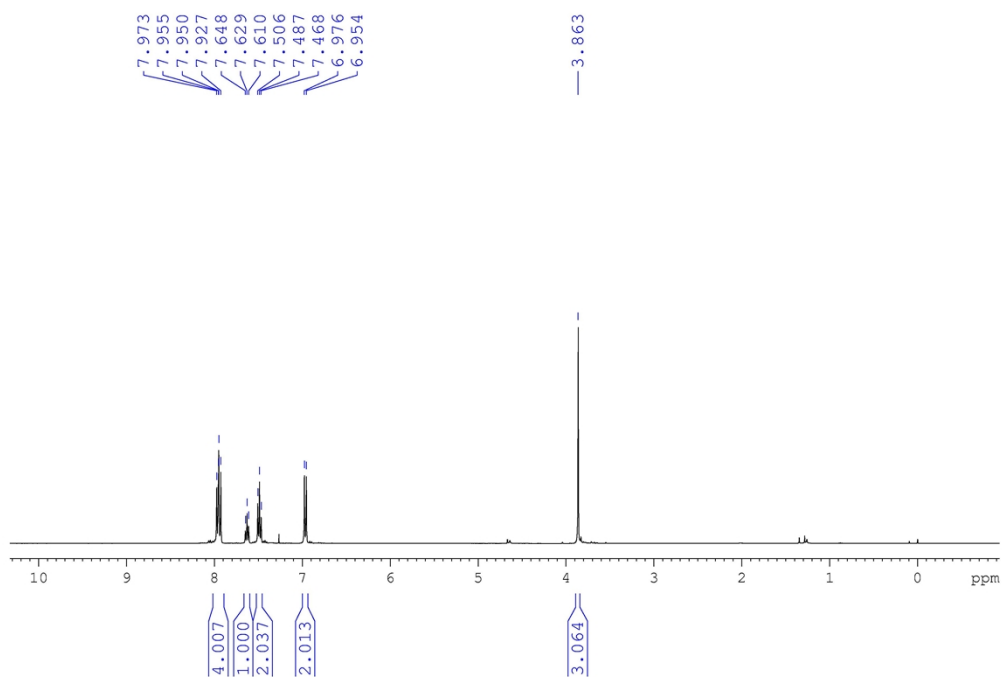


^{13}C NMR spectrum of **2a**

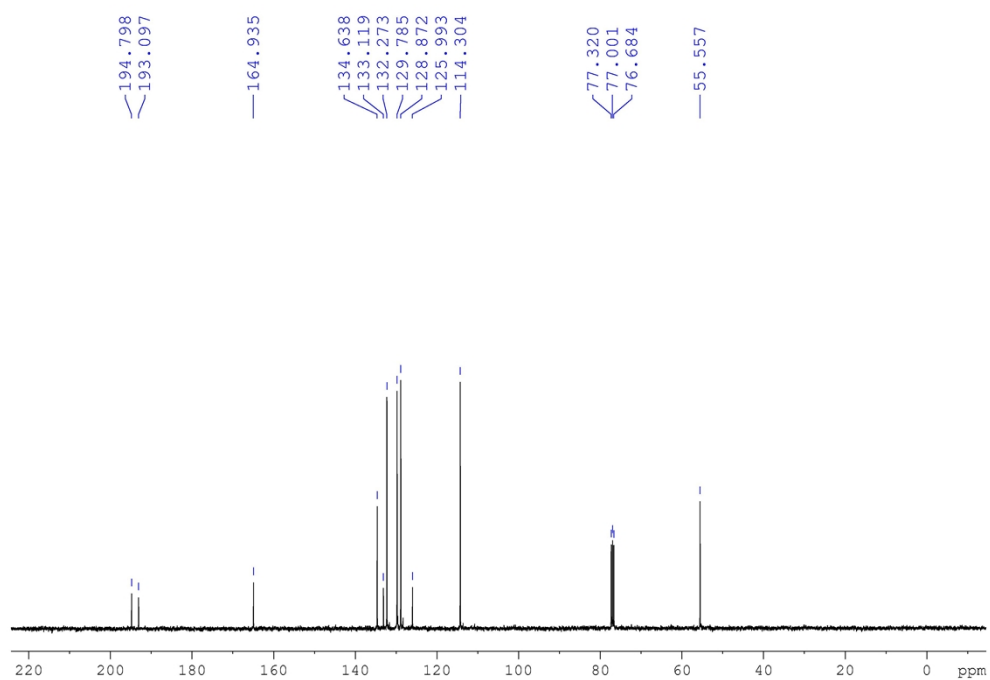


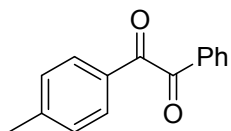


^1H NMR spectrum of **2b**

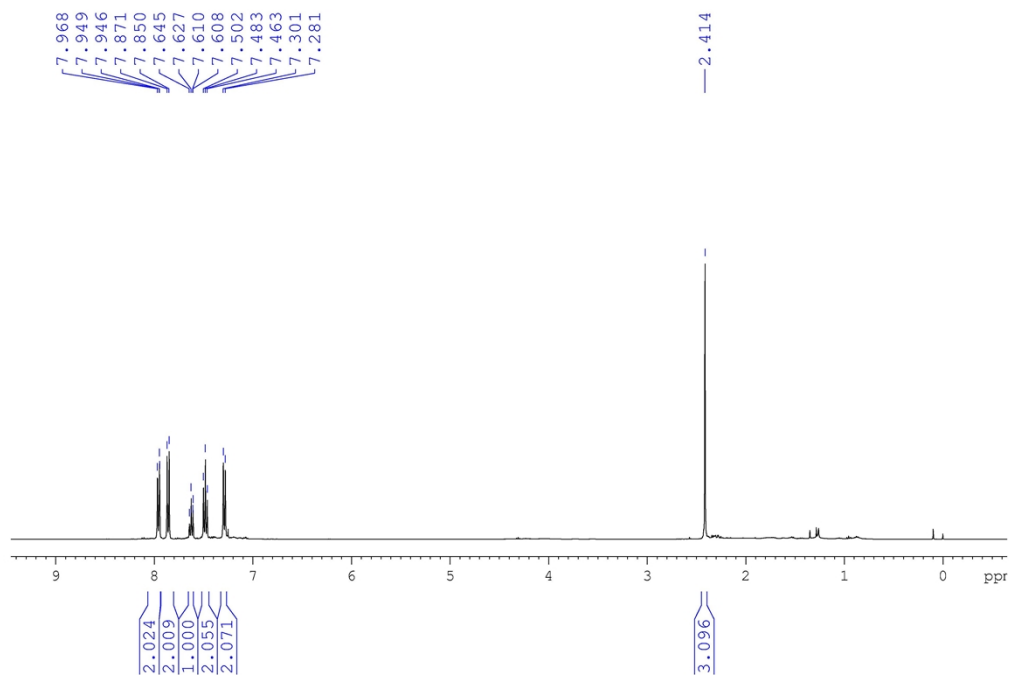


^{13}C NMR spectrum of **2b**

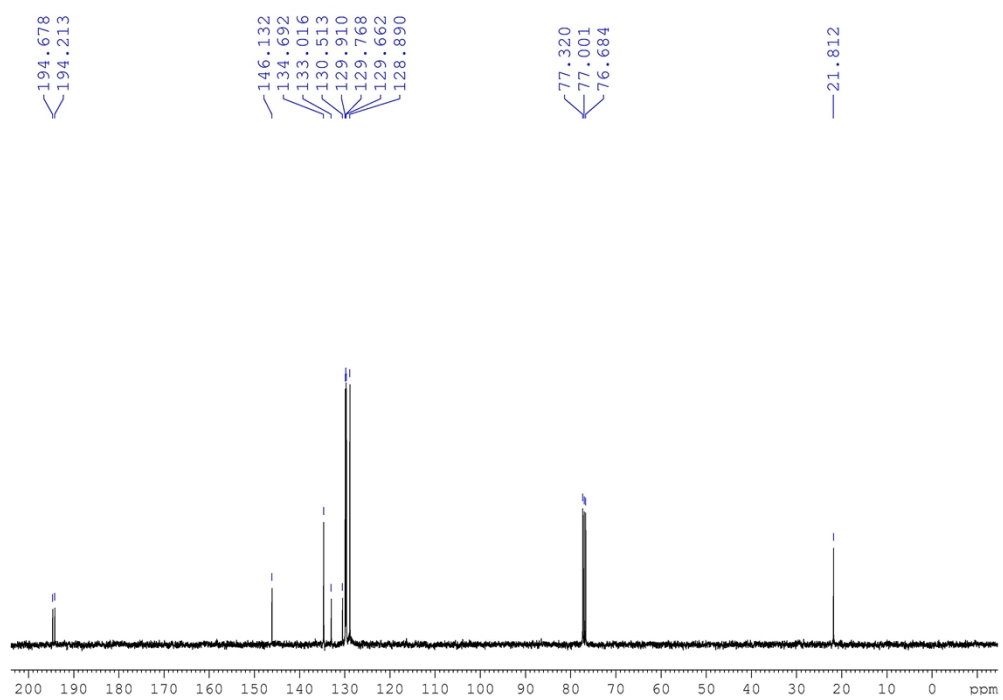


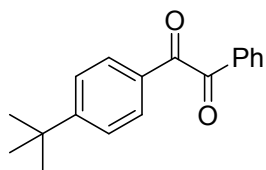


^1H NMR spectrum of **2c**

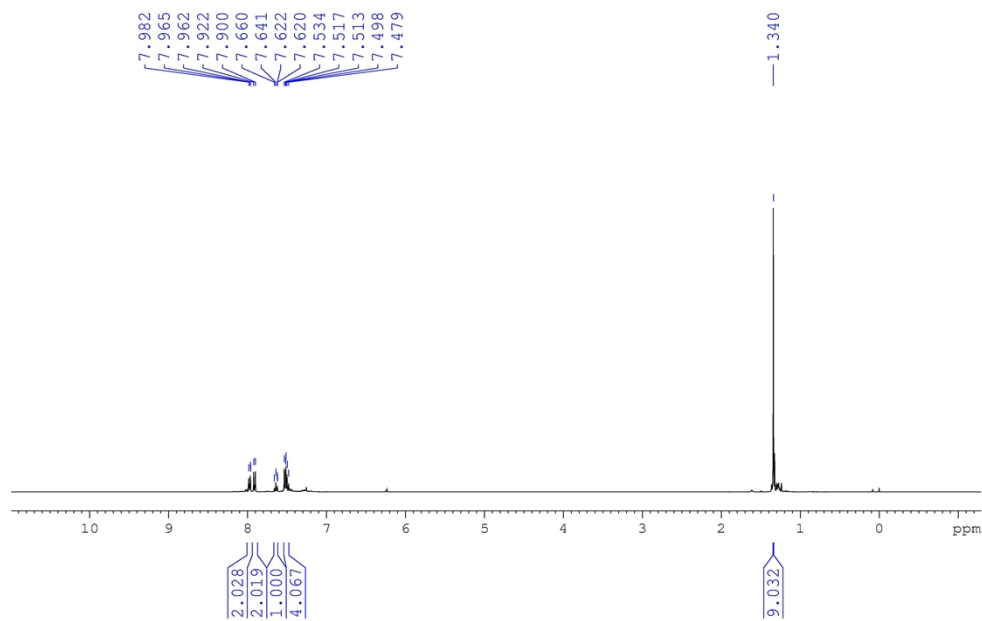


^{13}C NMR spectrum of **2c**

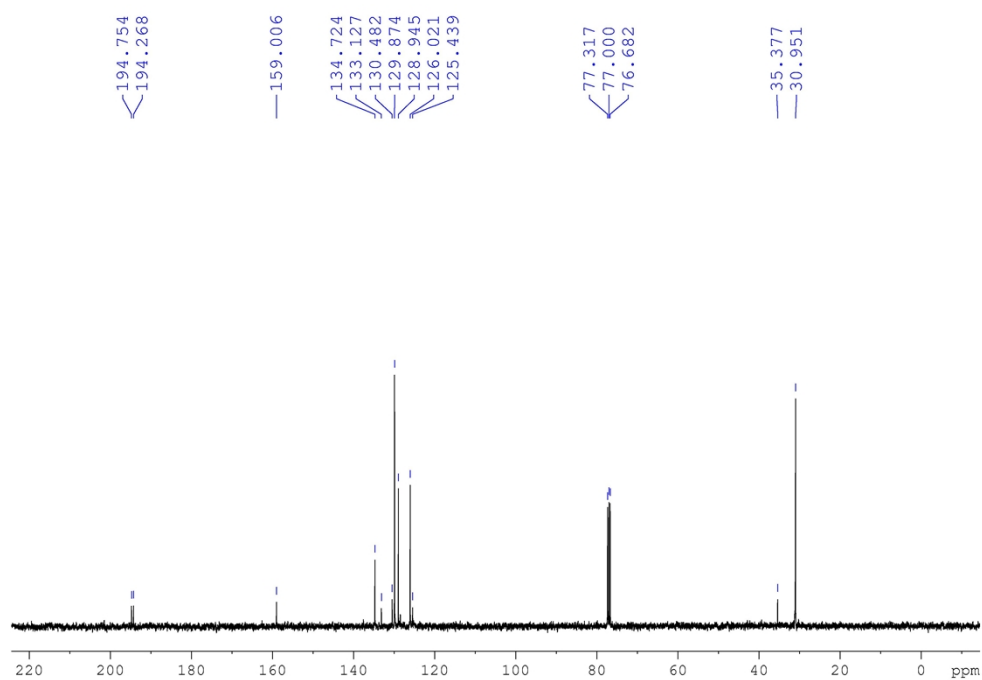


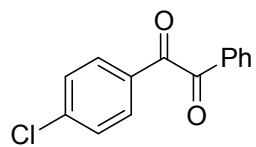


^1H NMR spectrum of **2d**

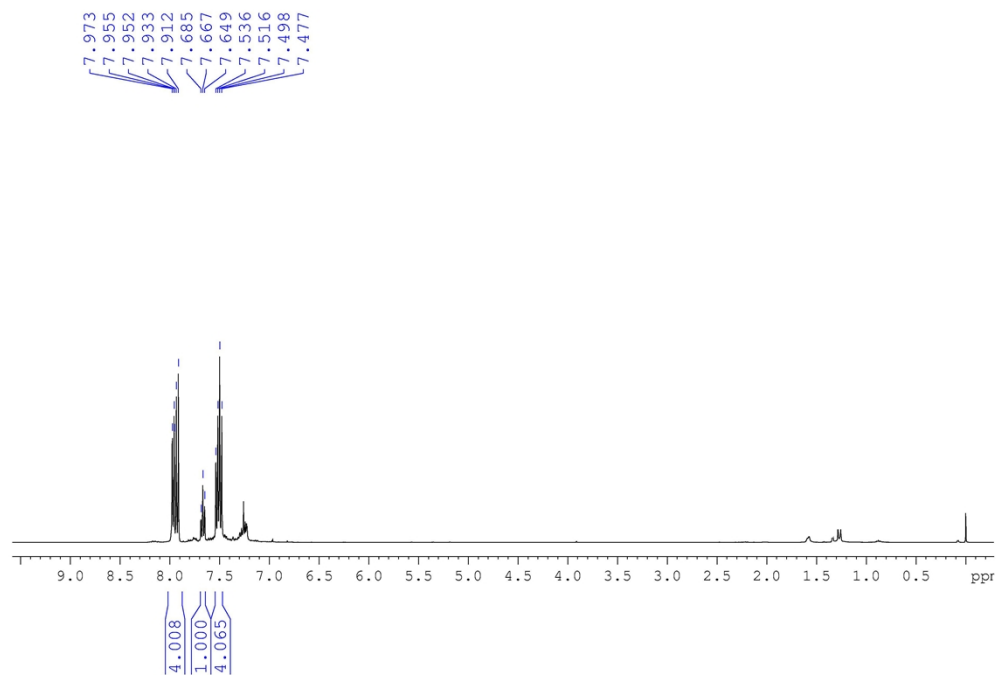


^{13}C NMR spectrum of **2d**

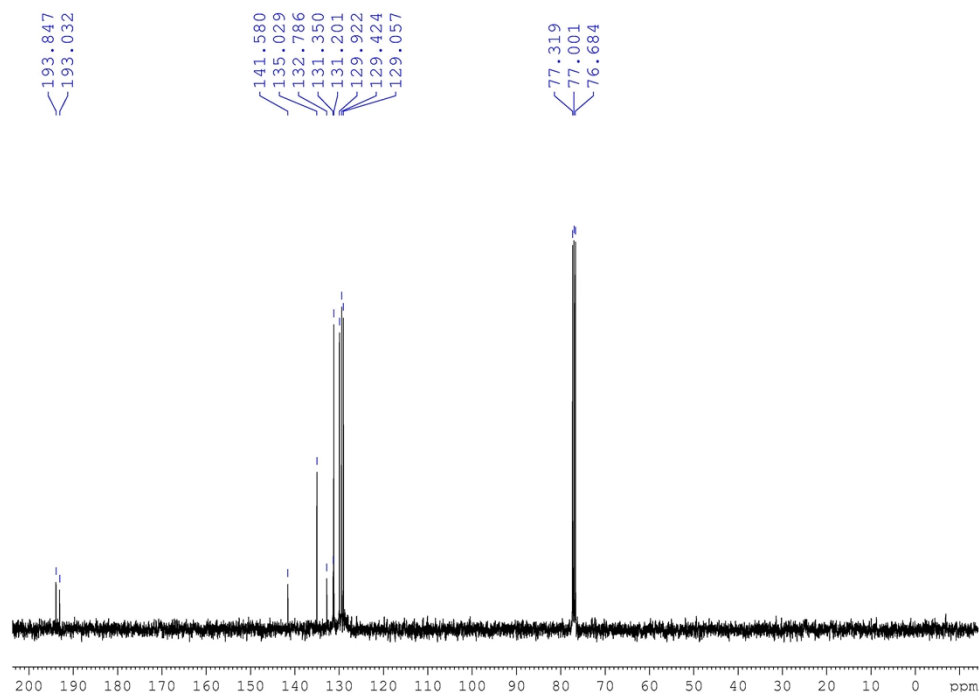


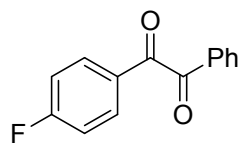


^1H NMR spectrum of **2e**

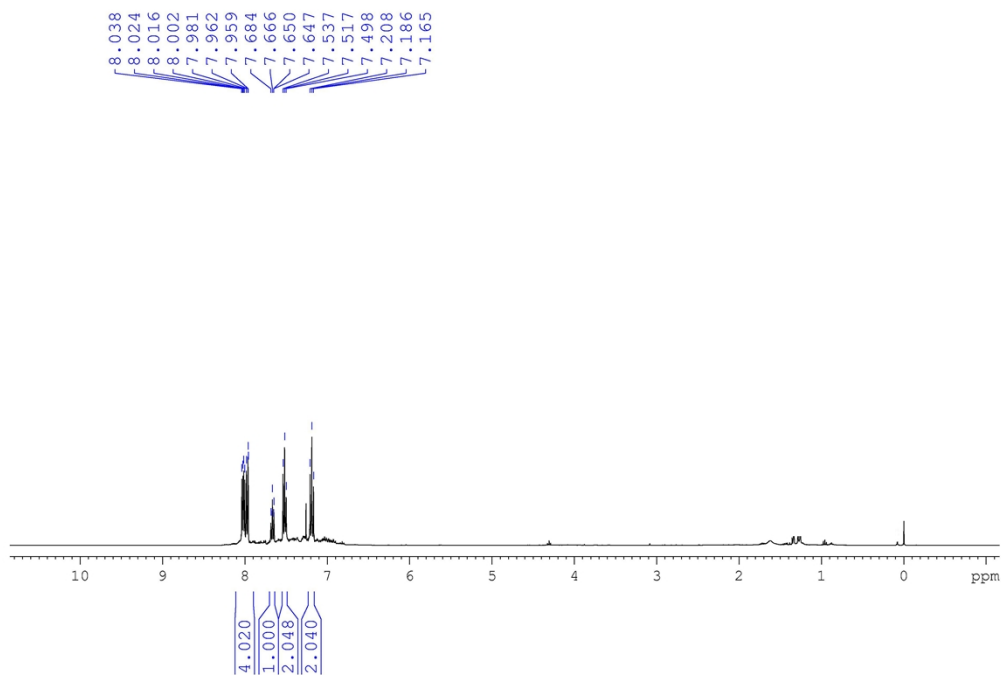


^{13}C NMR spectrum of **2e**

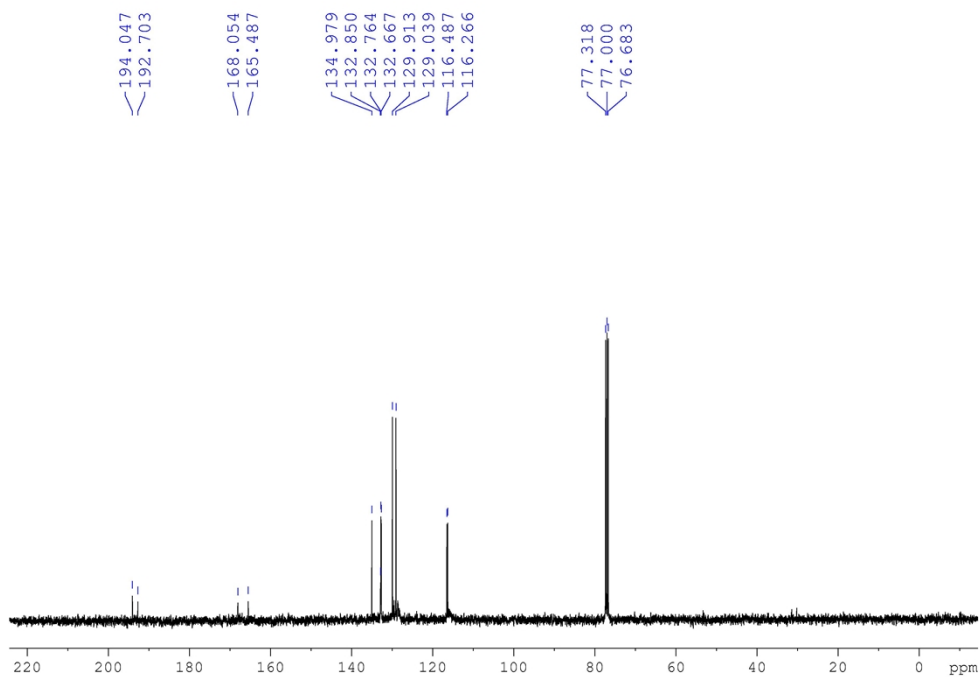


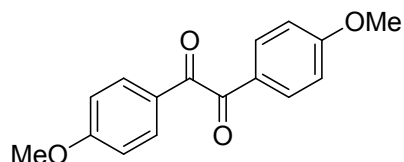


^1H NMR spectrum of **2f**

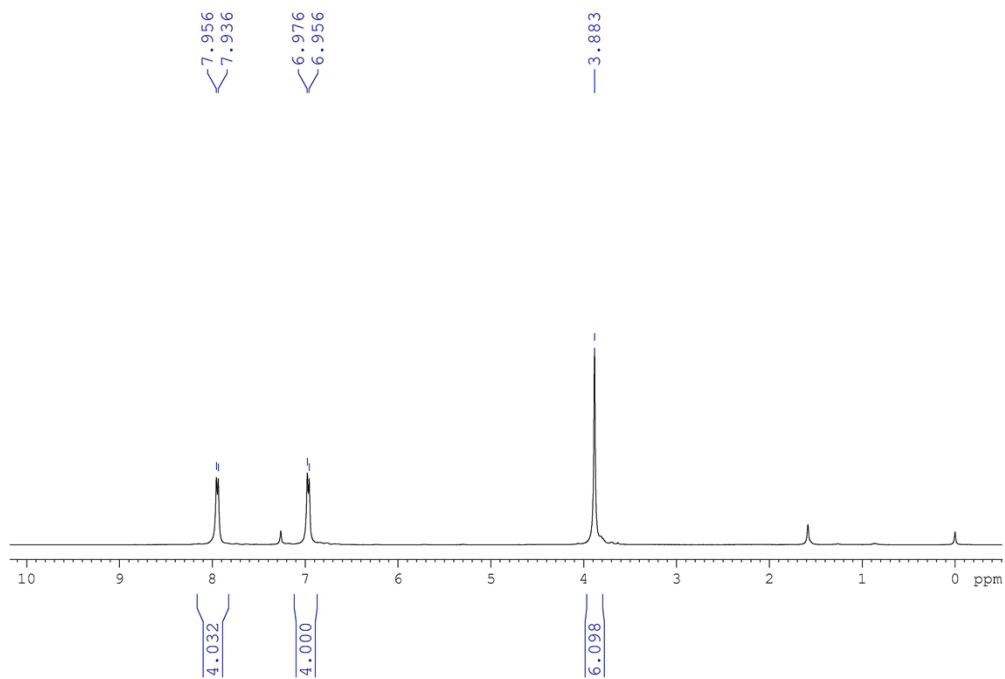


^{13}C NMR spectrum of **2f**

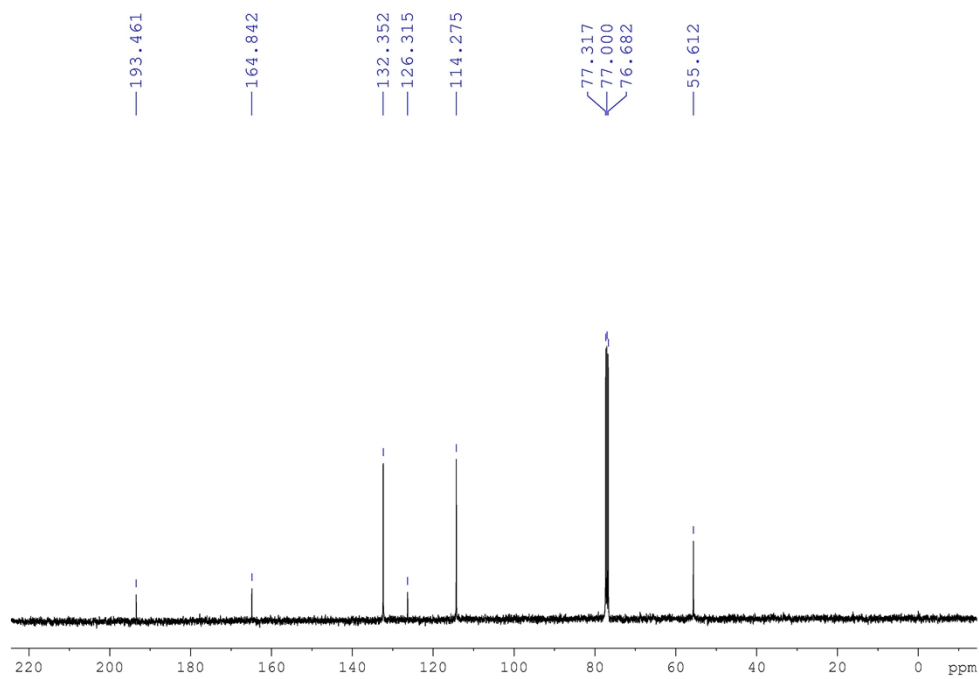


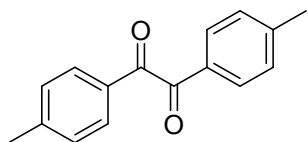


^1H NMR spectrum of **2g**

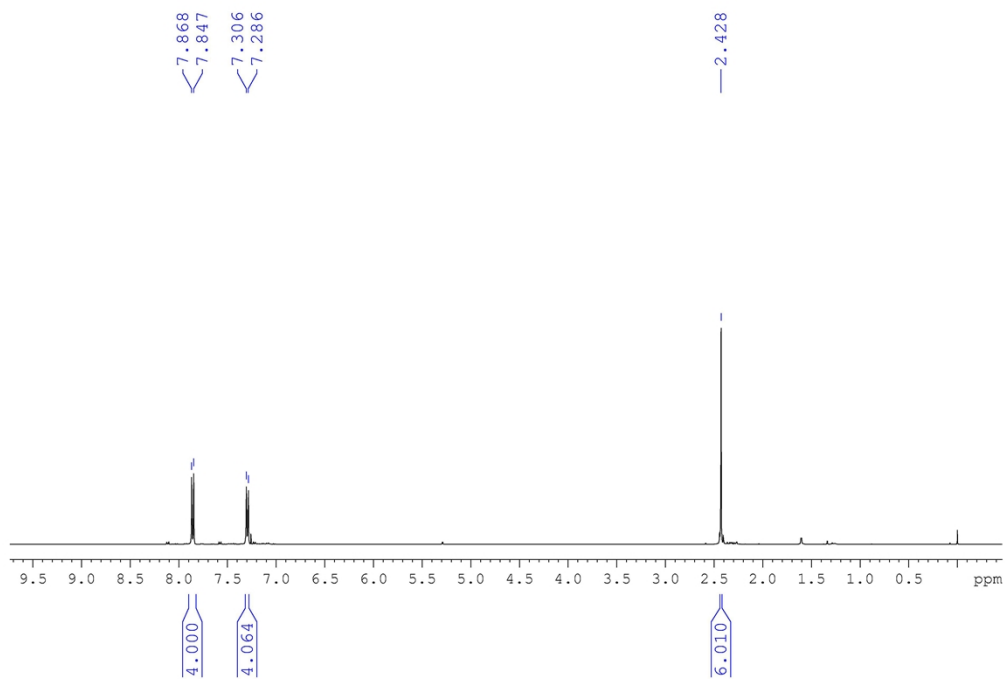


^{13}C NMR spectrum of **2g**

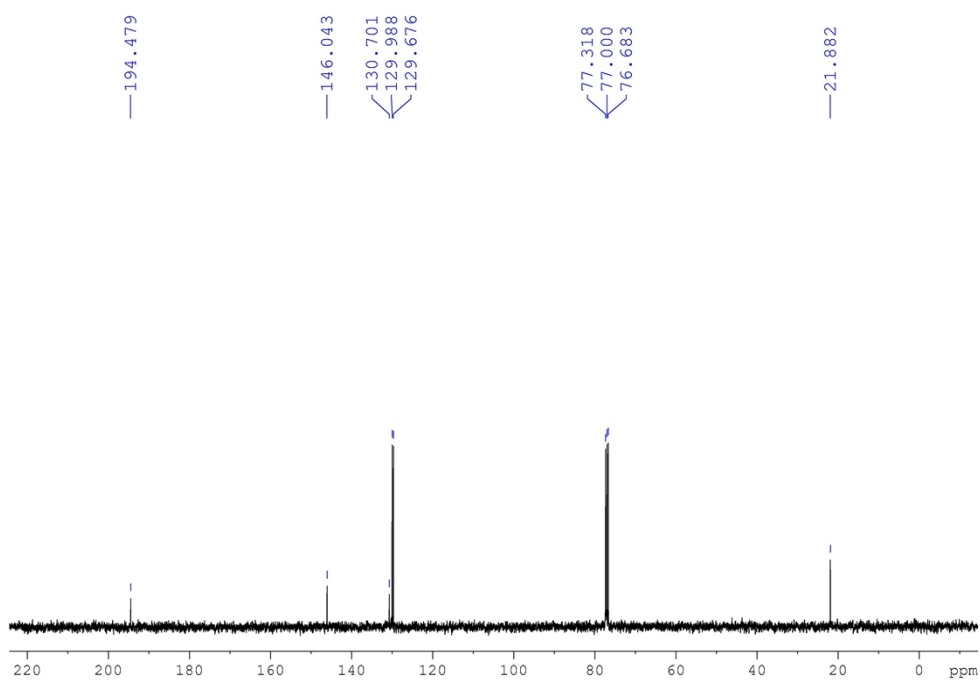


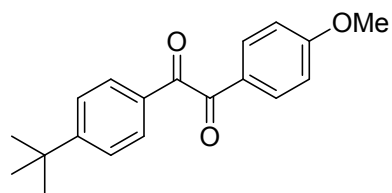


^1H NMR spectrum of **2h**

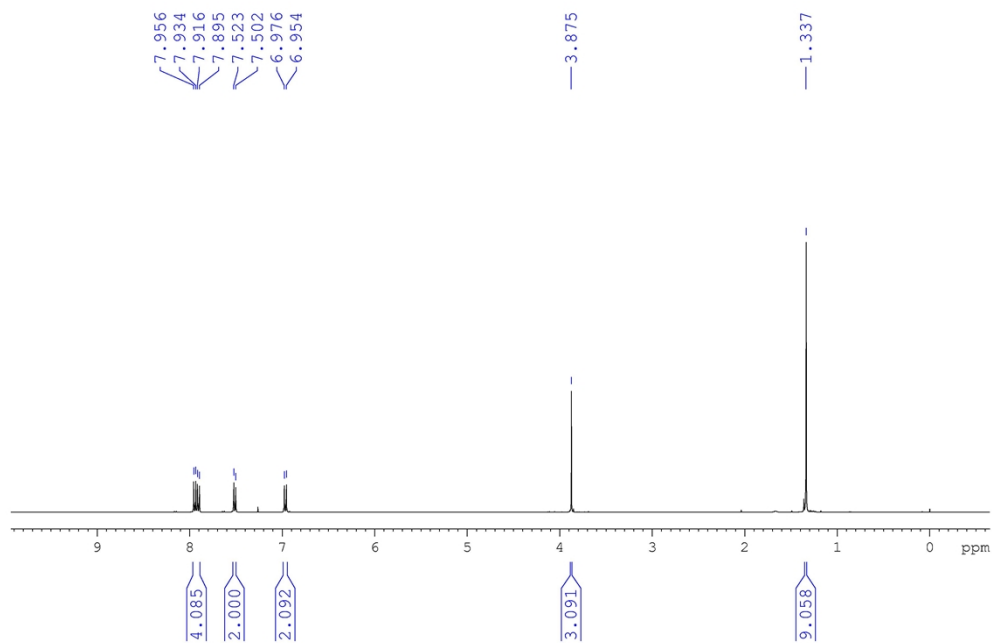


^{13}C NMR spectrum of **2h**

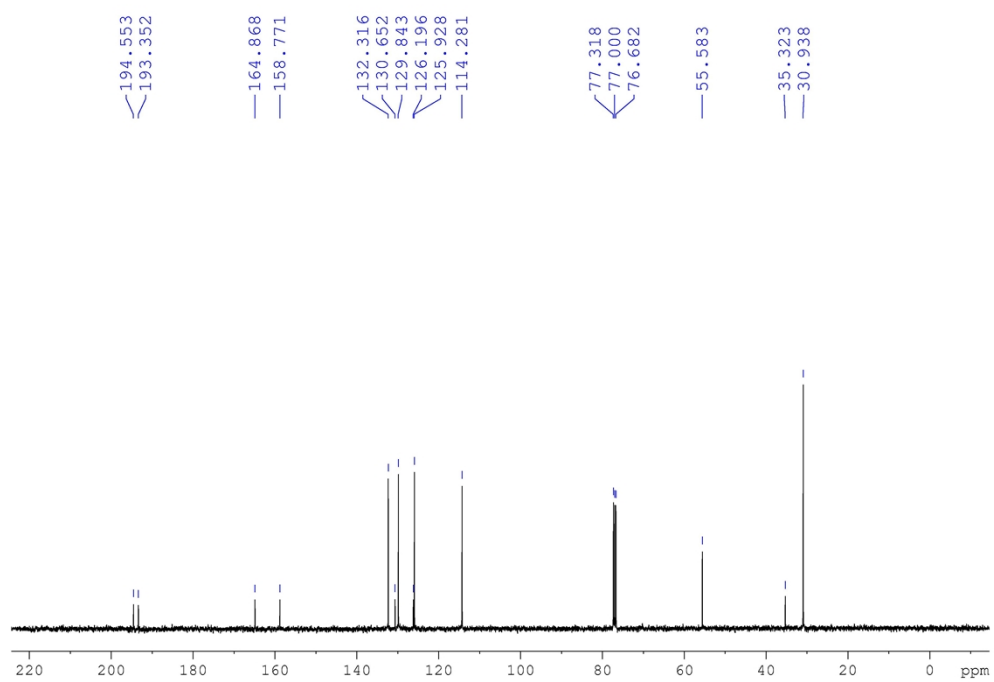


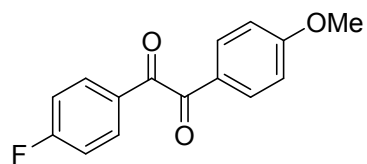


^1H NMR spectrum of **2i**

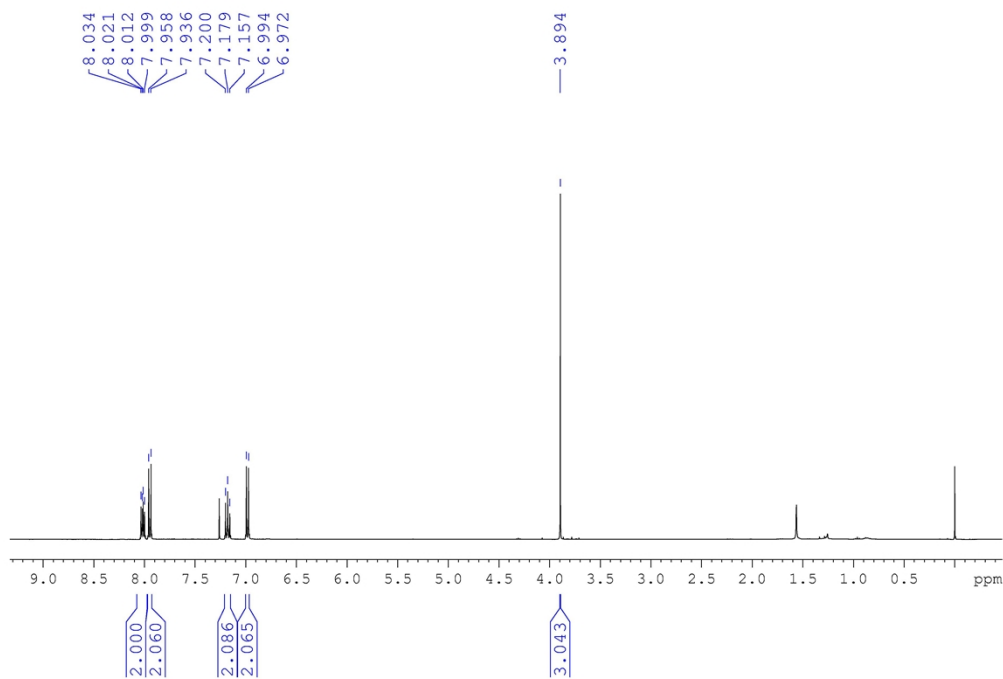


^{13}C NMR spectrum of **2i**

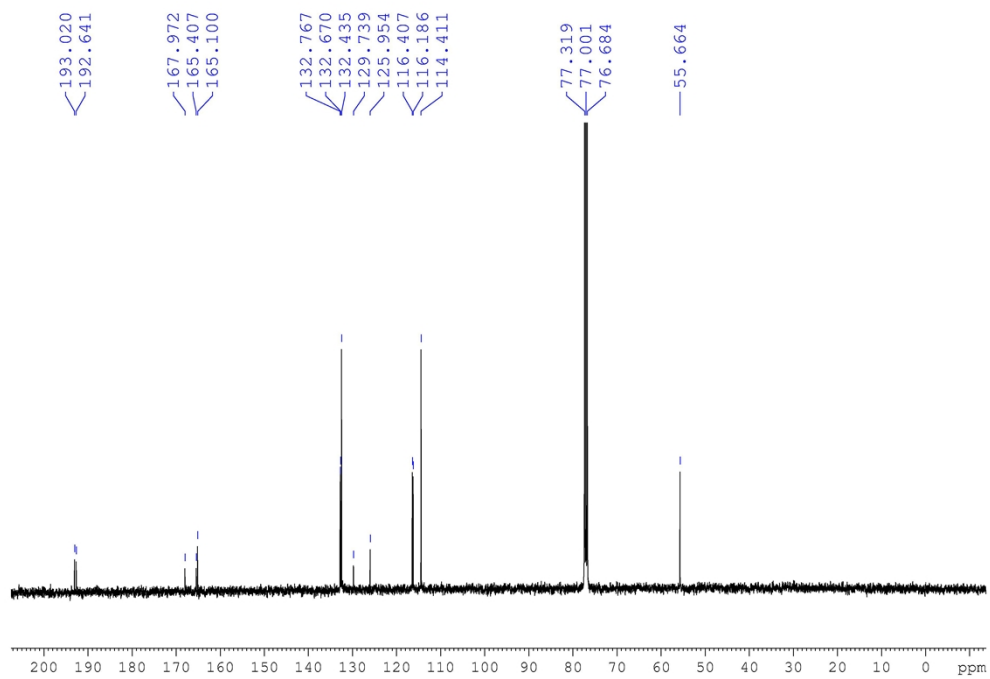


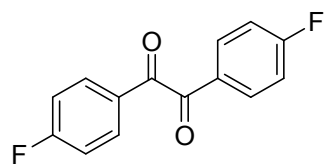


^1H NMR spectrum of **2j**

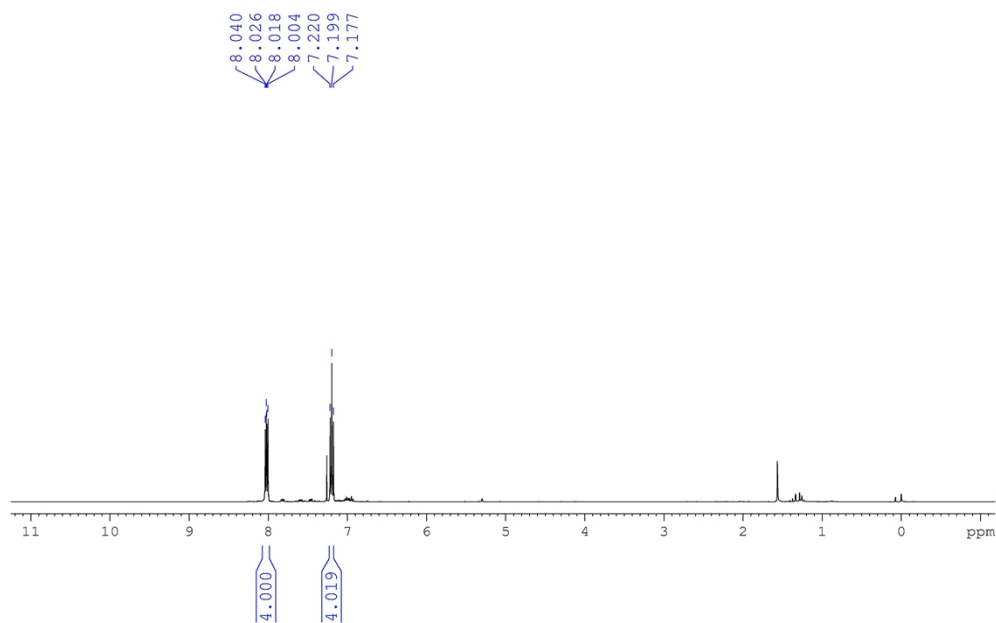


^{13}C NMR spectrum of **2j**

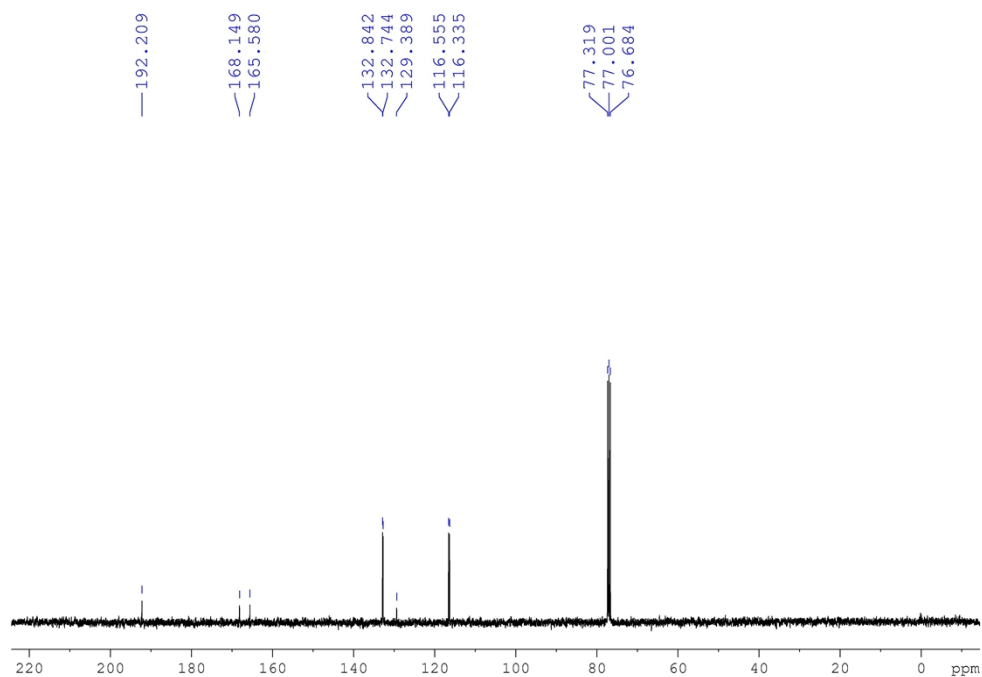


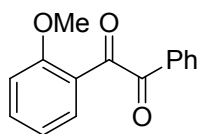


^1H NMR spectrum of **2k**

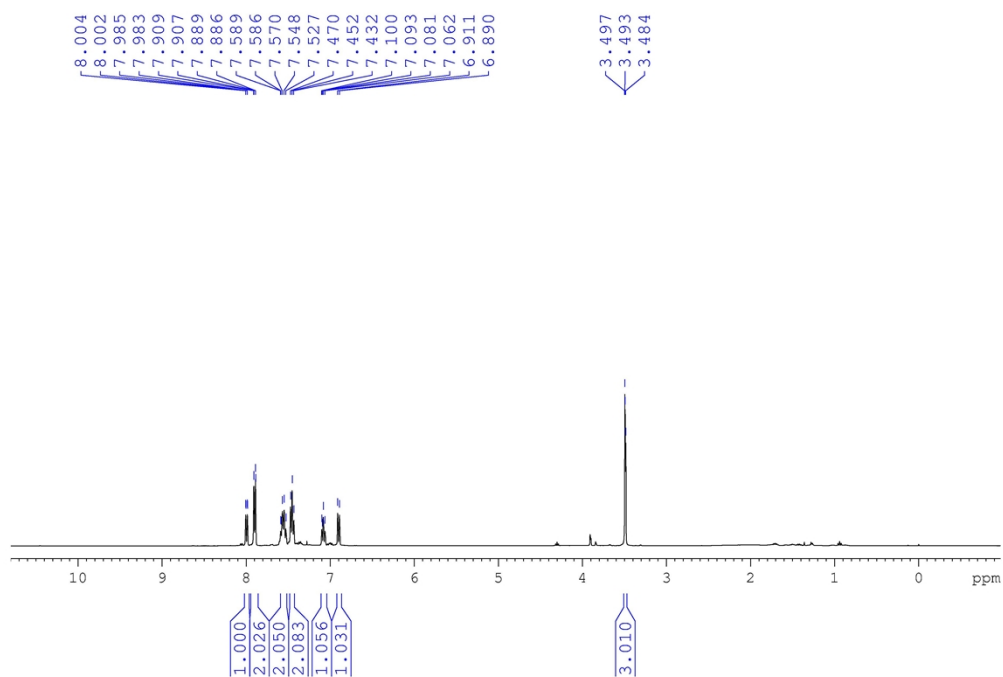


^{13}C NMR spectrum of **2k**

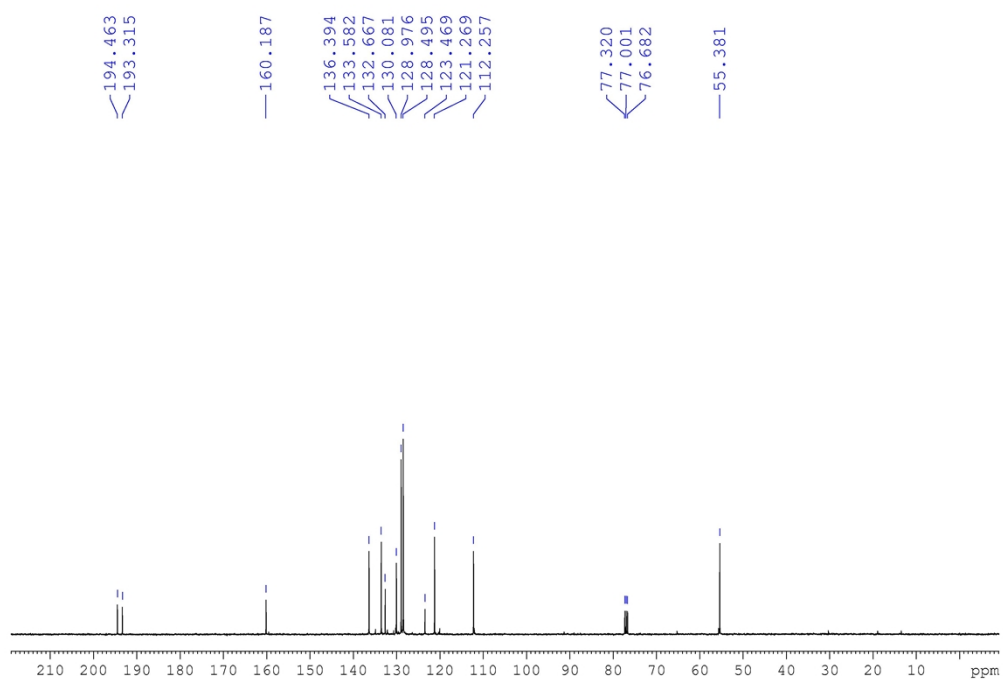


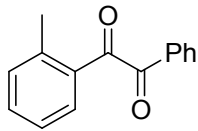


^1H NMR spectrum of **21**

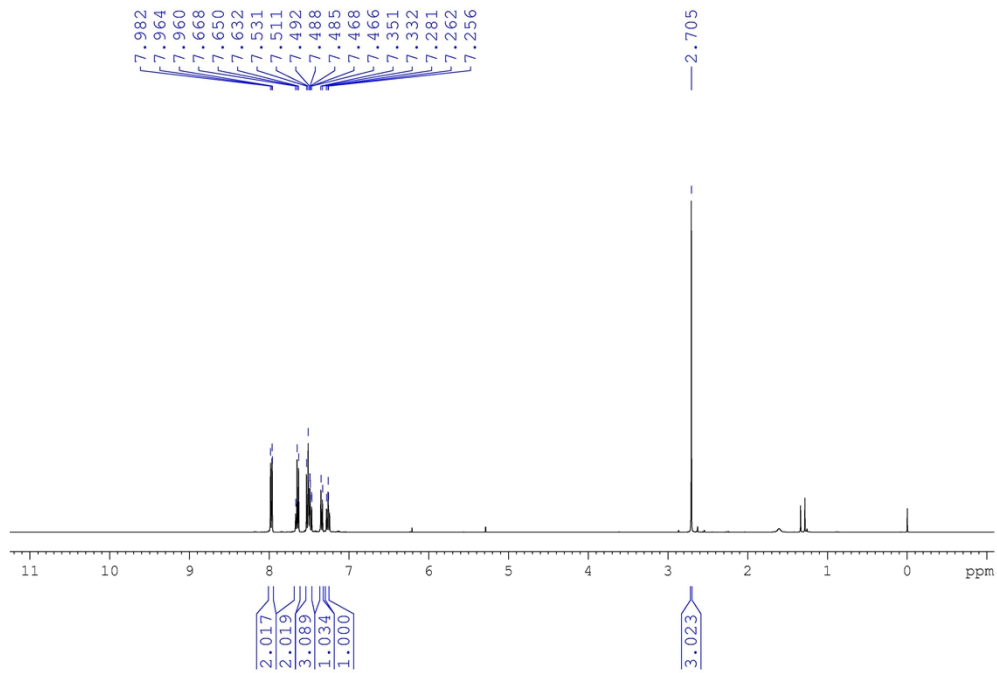


^{13}C NMR spectrum of **21**

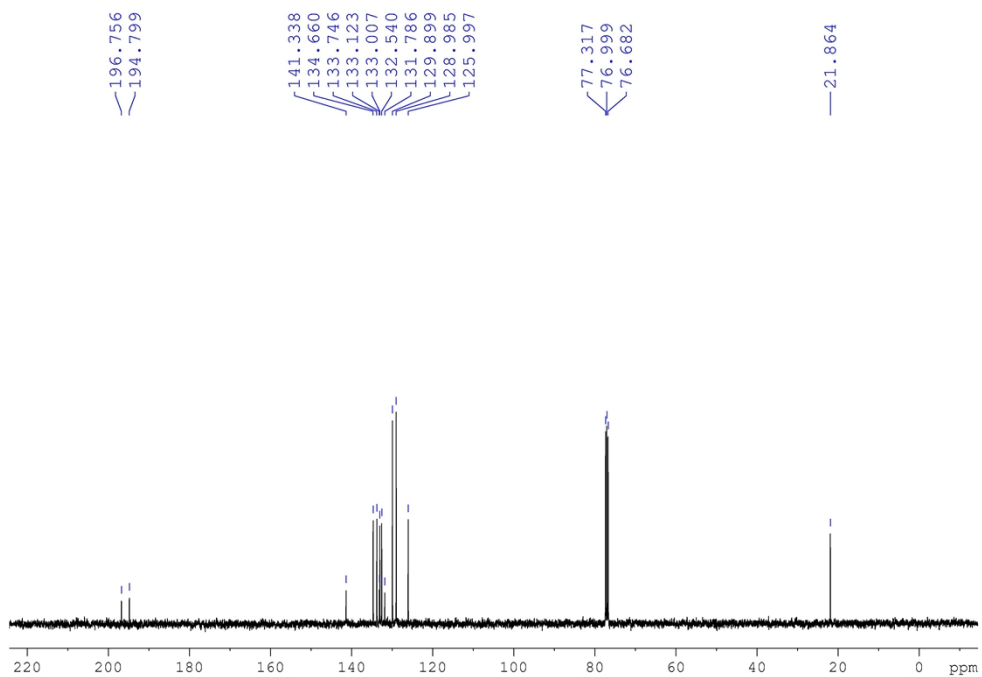


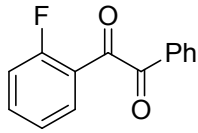


^1H NMR spectrum of **2m**

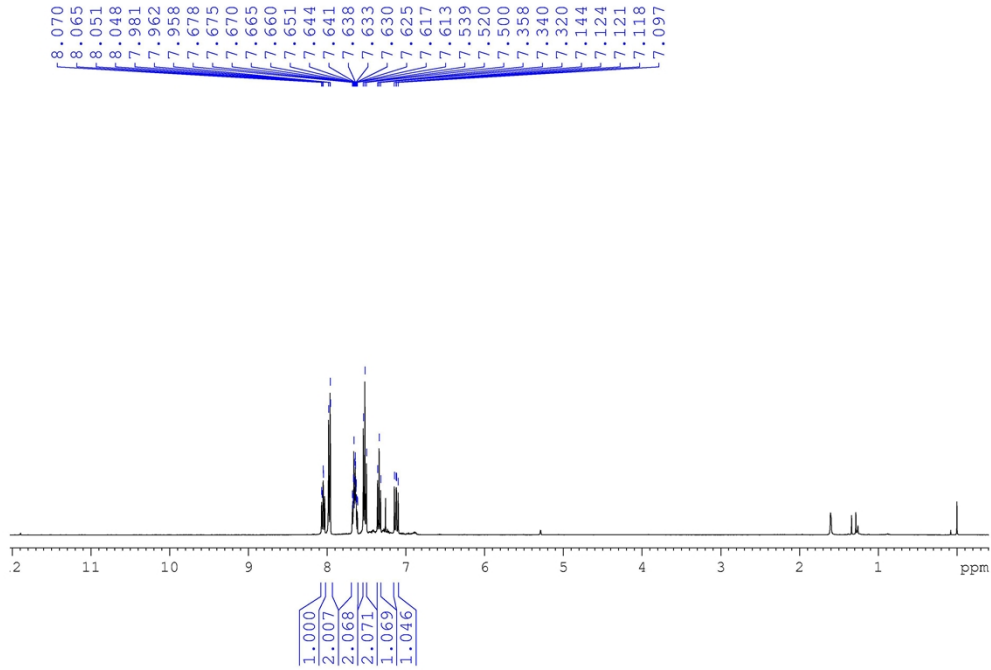


^{13}C NMR spectrum of **2m**

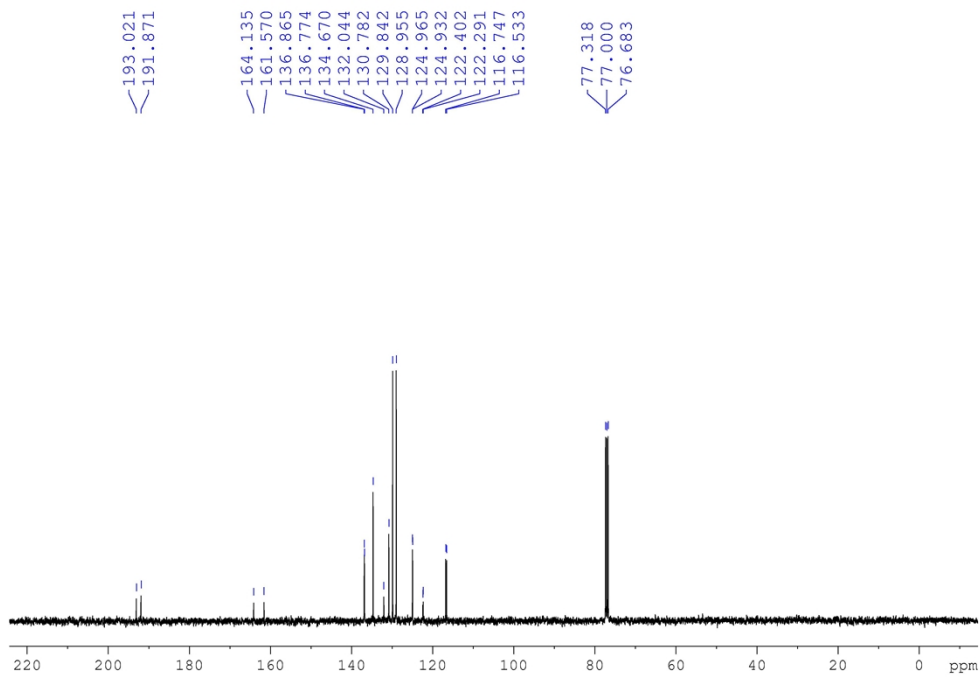


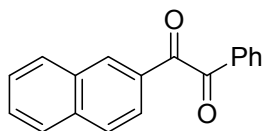


^1H NMR spectrum of **2n**

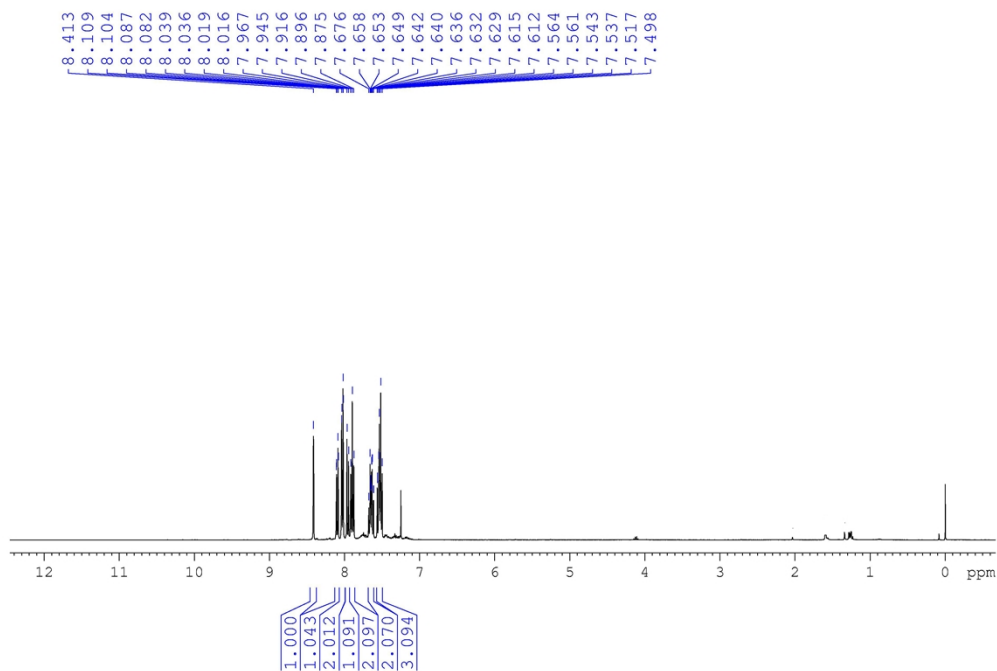


^{13}C NMR spectrum of **2n**

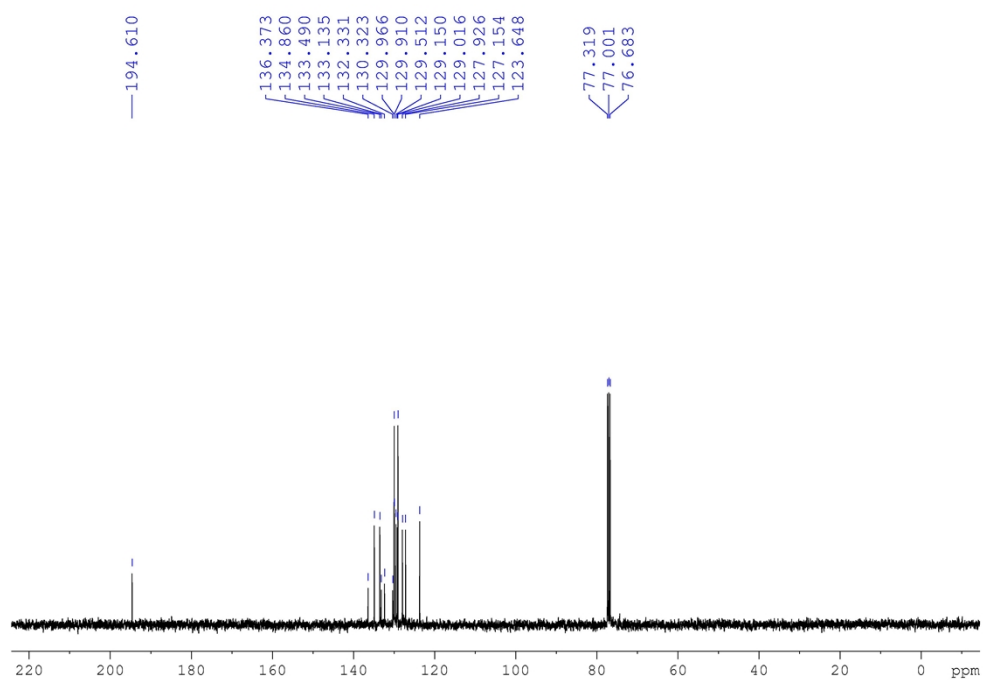


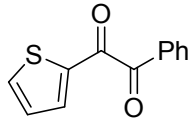


^1H NMR spectrum of **2o**

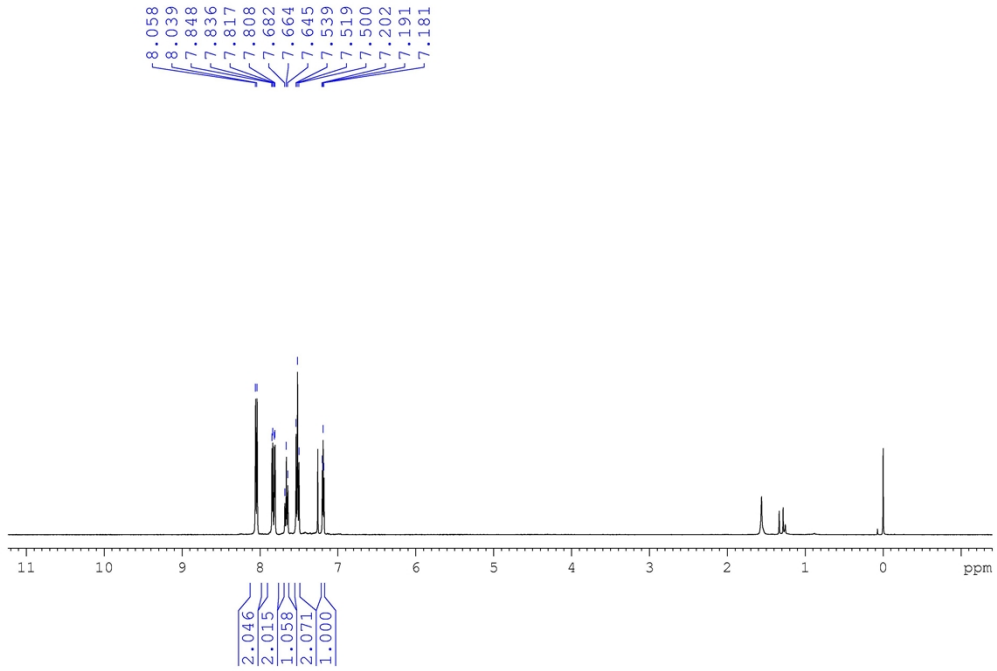


^{13}C NMR spectrum of **2o**

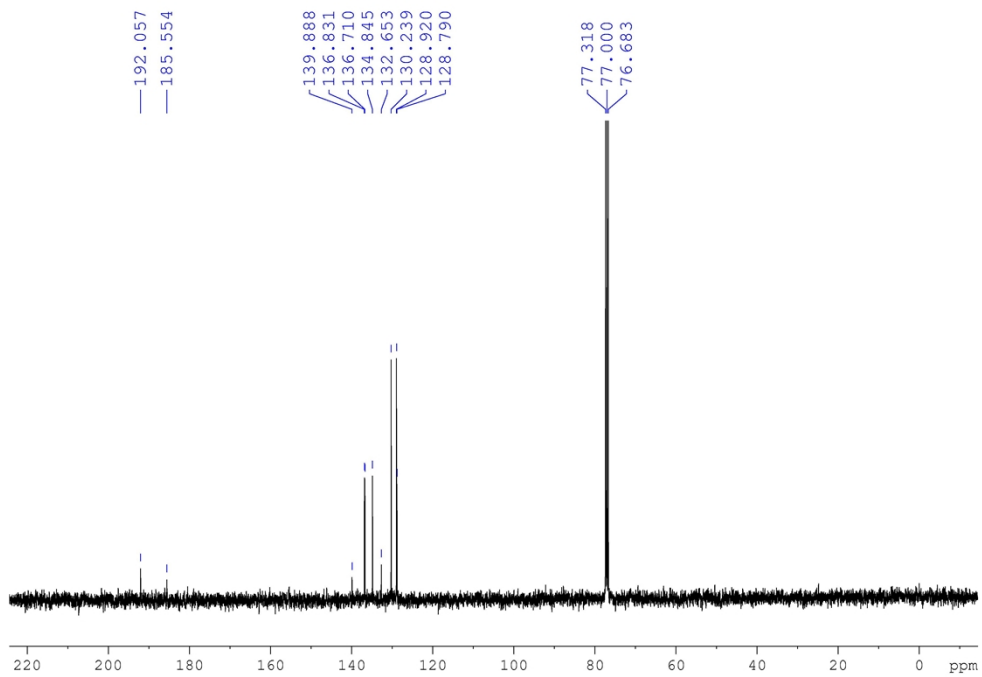


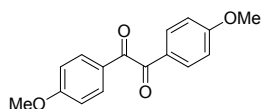


^1H NMR spectrum of **2p**



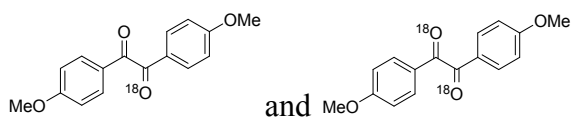
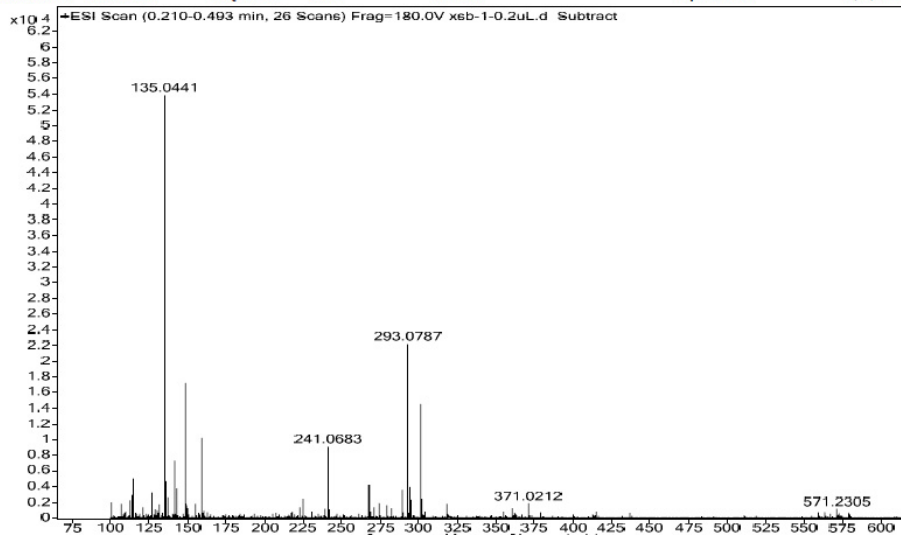
^{13}C NMR spectrum of **2p**





The controlled experiment was conducted involving H_2O^{18} , and $\text{C}_{16}\text{H}_{14}\text{O}_3^{18}\text{O}$ was not observed. HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{14}\text{O}_4$ ($\text{M} + \text{Na}$) $^+$ 293.0790, found 293.0787.

Sample Name	Position	Instrument Name	Instrument 1	User Name	Agilent FSE
xs5-1	P1-D4	Instrument 1	Sample	IRM Calibration Status	Success
Inj Vol	InjPosition	SampleType	Sample	IRM Calibration Status	Success
1				Acquired Time	12/24/13 Tue 11:50:25
Data Filename	ACQ Method	Comment			
xs5-1-0.2uL.d	test.m				



The controlled experiment was conducted involving O_2^{18} , and HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{14}\text{O}_3^{18}\text{O}$ ($\text{M} + \text{Na}$) $^+$ 295.0832, found 295.0830; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2^{18}\text{O}_2$ ($\text{M} + \text{Na}$) $^+$ 297.0875, found 297.0872.

Sample Name	Position	Instrument Name	Instrument 1	User Name	Agilent FSE
xs5-2	P1-D5	Instrument 1	Sample	IRM Calibration Status	Success
Inj Vol	InjPosition	SampleType	Sample	IRM Calibration Status	Success
1				Acquired Time	12/24/13 Tue 11:51:36
Data Filename	ACQ Method	Comment			
xs5-2-0.2uL.d	test.m				

