Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Triphenylphosphine mediated photo-rearrangement and methanol addition of aryl chalcones to 1-propanones

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1) General procedure for preparation of α , β -unsaturated ketones 1a-1h and 1j-1n.

To a stirred solution of acetophenone (10 mmol) in methanol (5 mL) was added dropwise a solution of sodium hydroxide (13 mmol) in methanol (10 mL). Fifteen minutes later, the resulting mixture was further treated with substituted benzaldehydes (10 mmol) and stirred at room temperature. When the reaction was complete (disappearance of acetophenone, monitored by TLC), 40 mL of water was added. The solid products were filtered off, washed with water (3 × 25 mL), cold methanol (3 × 25 mL) and dried to give the corresponding α,β-unsaturated ketones.[1]

(E)-3-Phenyl-1-(thiophen-2-yl)prop-2-en-1-one (1a). Pale yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.81 (m, 2H), 7.69 (dd, *J* = 4.9, 0.9 Hz, 1H), 7.67 -7.67 (m, 2H), 7.47 – 7.39 (m, 4H), 7.20 (dd, *J* = 4.9, 3.9 Hz, 1H). The spectroscopic data are in accordance with literature.[2]

(E)-3-(4-Fluorophenyl)-1-(thiophen-2-yl)prop-2-en-1-one (1b). Pale yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.77 (m, 2H), 7.70 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.35 (d, *J* = 15.6 Hz, 1H), 7.23 – 7.16 (m, 1H), 7.16 – 7.07 (m, 2H). The spectroscopic data are in accordance with literature.[3]

(E)-3-(4-Bromophenyl)-1-(thiophen-2-yl)prop-2-en-1-one (1c). Pale yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.78 (d, *J* = 15.6 Hz, 1H), 7.70 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.59 – 7.48 (m, 4H), 7.45 – 7.35 (m, 1H), 7.20 (dd, *J* = 4.9, 3.9 Hz, 1H). The spectroscopic data are in accordance with literature.[4]

(E)-3-(4-Chlorophenyl)-1-(thiophen-2-yl)prop-2-en-1-one (1d). White powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 3.8, 0.9 Hz, 1H), 7.80 (d, *J* = 15.6 Hz, 1H), 7.70 (dt, *J* = 9.3, 4.7 Hz, 1H), 7.59 (dd, *J* = 8.8, 2.2 Hz, 2H), 7.44 – 7.34 (m, 3H), 7.20 (dd, *J* = 4.9, 3.9 Hz, 1H). The spectroscopic data are in accordance with literature.[5]

(E)-3-(3-Bromophenyl)-1-(thiophen-2-yl)prop-2-en-1-one (1e). White powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.78 (dd, *J* = 11.1, 8.9 Hz, 2H), 7.71 (dd, *J* = 4.9,

1.0 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.41 (d, *J* = 15.5 Hz, 1H), 7.29 (dd, *J* = 13.2, 5.3 Hz, 1H), 7.21 (dd, *J* = 4.9, 3.9 Hz, 1H). The spectroscopic data are in accordance with literature.[3]

(E)-1-(Thiophen-2-yl)-3-(p-tolyl)prop-2-en-1-one (1f). White powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 2H), 7.68 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.34 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.19 (dd, *J* = 4.9, 3.8 Hz, 1H), 2.40 (s, 3H). The spectroscopic data are in accordance with literature.[3]

(E)-3-(4-Methoxyphenyl)-1-(thiophen-2-yl)prop-2-en-1-one (1g). White powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.75 (m, 2H), 7.67 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.37 – 7.28 (m, 1H), 7.18 (dd, *J* = 4.9, 3.8 Hz, 1H), 6.99 – 6.90 (m, 2H). The spectroscopic data are in accordance with literature.[3]

(E)-4-(3-Oxo-3-(thiophen-2-yl)prop-1-en-1-yl)benzonitrile (1h). White powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.82 (d, *J* = 15.6 Hz, 1H), 7.76 – 7.69 (m, 5H), 7.48 (d, *J* = 15.6 Hz, 1H), 7.22 (dd, *J* = 4.9, 3.9 Hz, 1H). The spectroscopic data are in accordance with literature.[6]

(E)-1-Phenyl-3-(p-tolyl)prop-2-en-1-one (1j). White powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.80 (d, *J* = 15.7 Hz, 1H), 7.62 – 7.45 (m, 6H), 7.23 (d, *J* = 8.0 Hz, 2H). The spectroscopic data are in accordance with literature.[7]

(E)-3-(4-Bromophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (1k). White powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 – 7.95 (m, 2H), 7.73 (d, *J* = 15.7 Hz, 1H), 7.59 – 7.45 (m, 5H), 7.04 – 6.93 (m, 2H), 3.90 (s, 3H). The spectroscopic data are in accordance with literature.[8]

(E)-1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-one (1l). White powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 – 8.00 (m, 2H), 7.87 – 7.74 (m, 1H), 7.70 – 7.61 (m, 2H), 7.60 – 7.50 (m, 1H), 7.43-7.41 (m, 3H), 7.04 – 6.94 (m, 2H), 3.89 (s, 3H). The spectroscopic data are in accordance with literature.[9]

(E)-1-(2-Nitrophenyl)-3-phenylprop-2-en-1-one (1m). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21–8.18 (dd, *J* = 0.1, 8.2 Hz,1H), 7.81–7.75 (m, 1H), 7.70–7.64 (m, 1H), 7.54–7.50 (m, 3H), 7.41–7.36 (m, 3H), 7.26 (d, *J* = 16.3 Hz, 1H), 7.02 (d, *J* = 16.3 Hz, 1H). The spectroscopic data are in accordance with literature.[10]

(E)-1-(Naphthalen-2-yl)-3-phenylprop-2-en-1-one (1n). White powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.11 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.04 – 7.98 (m, 1H), 7.98 – 7.85 (m, 3H), 7.75 – 7.67 (m, 3H), 7.60 (pd, *J* = 6.9, 1.5 Hz, 2H), 7.48 – 7.42 (m, 3H). The spectroscopic data are in accordance with literature.[11]

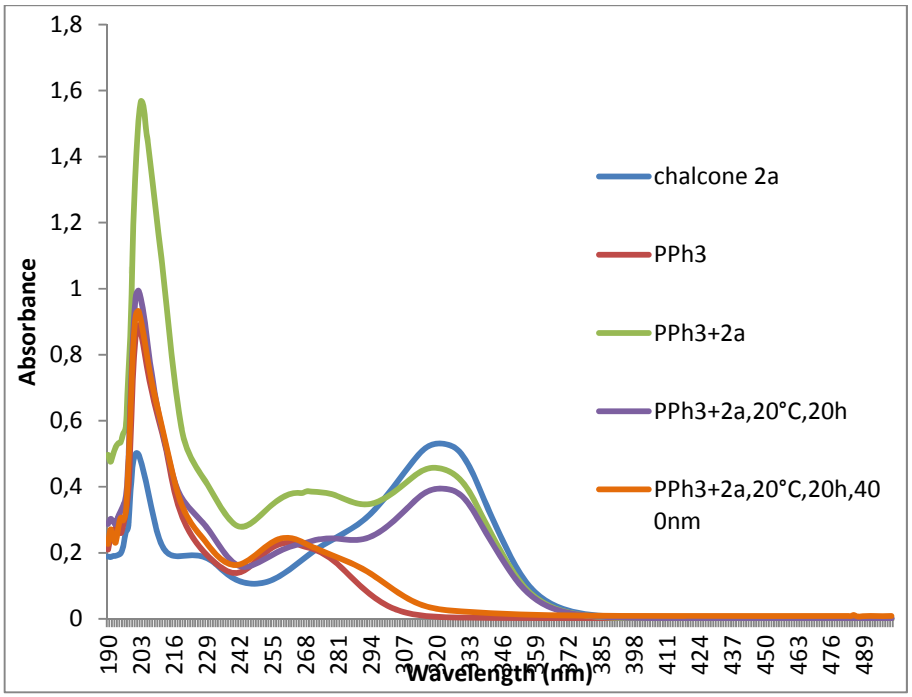
2) ^{1}H NMR data for [2 + 2] cycloaddition products

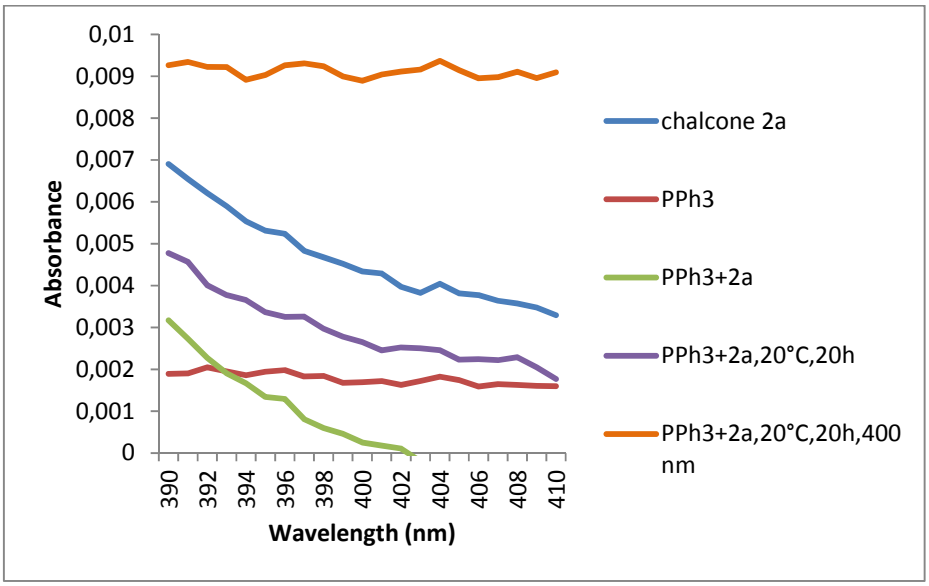
(3,4-Diphenylcyclobutane-1, 2-diyl)bis (thiophen-2-yl methanone). Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 4.9, 1.0 Hz, 2H), 7.43 (dd, *J* = 3.8, 1.0 Hz, 2H), 7.32 (d, *J* = 4.4 Hz, 4H), 6.96 (dd, *J* = 4.9, 3.9 Hz, 1H), 4.49 – 4.37 (m, 2H), 4.05 – 3.92 (m,2). The spectroscopic data are in accordance with literature.[12]

(3,4-Diphenylcyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone). White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 4H), 7.31 – 7.29 (m, 8H), 7.25 – 7.21 (m, 2H), 6.82 – 6.74 (m, 4H), 4.59 – 4.49 (m, 2H), 4.02 – 3.93 (m, 2H), 3.79 (s, 6H). The spectroscopic data are in accordance with literature.[13]

3) UV spectra of chalcone 2a and PPh_3 before and after irradiation

UV–visible spectra of the compounds were determined in MeOH solution (conc. 2×10^{-5}M).





The absorbance in the range of 390-410 nm is very weak. Molar absorptivity at 390 nm was in the range of 100-500 cm^{-1}. After 20h of irradiation, the reaction mixture turns to light yellow color and showed stronger absorption at 390 nm. The peak of chalcone **2a** at 324 nm dramatically decreases demonstrating the consumption of chalcone **2a**.

4) References

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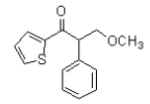
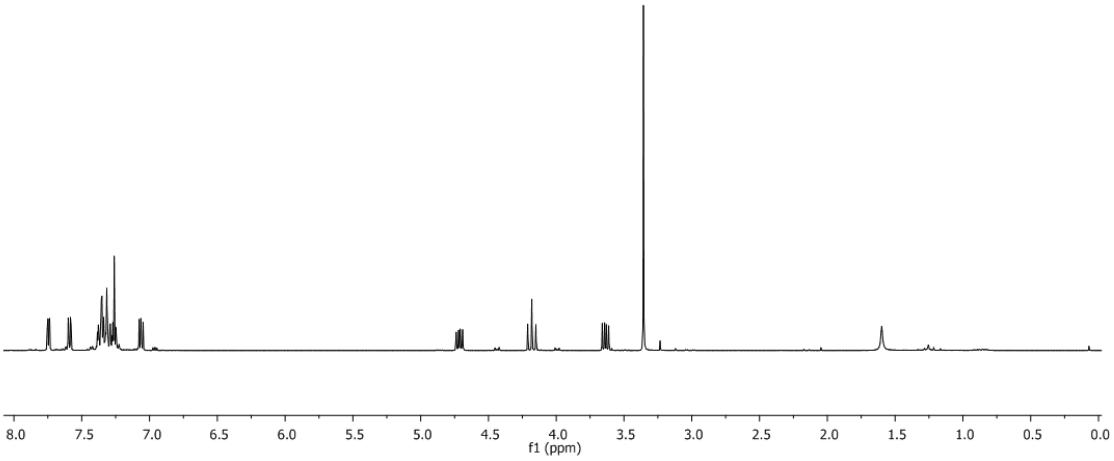
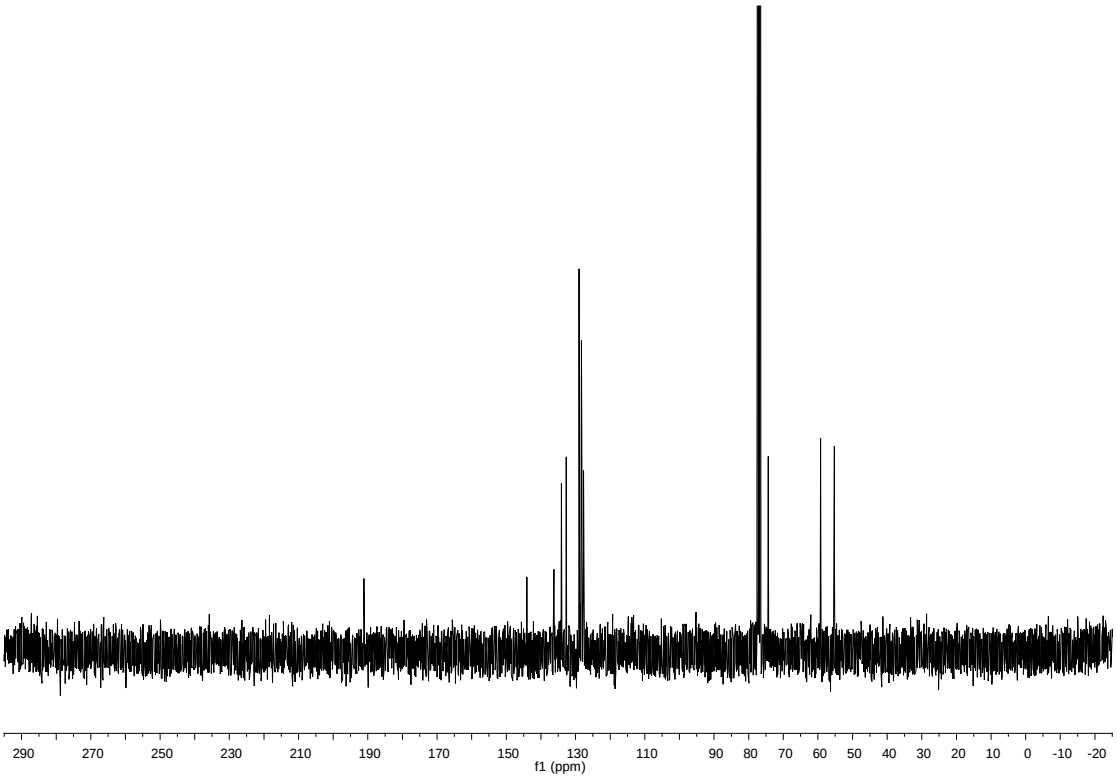
5) ^{1}H and ^{13}C NMR spectra of prepared compounds

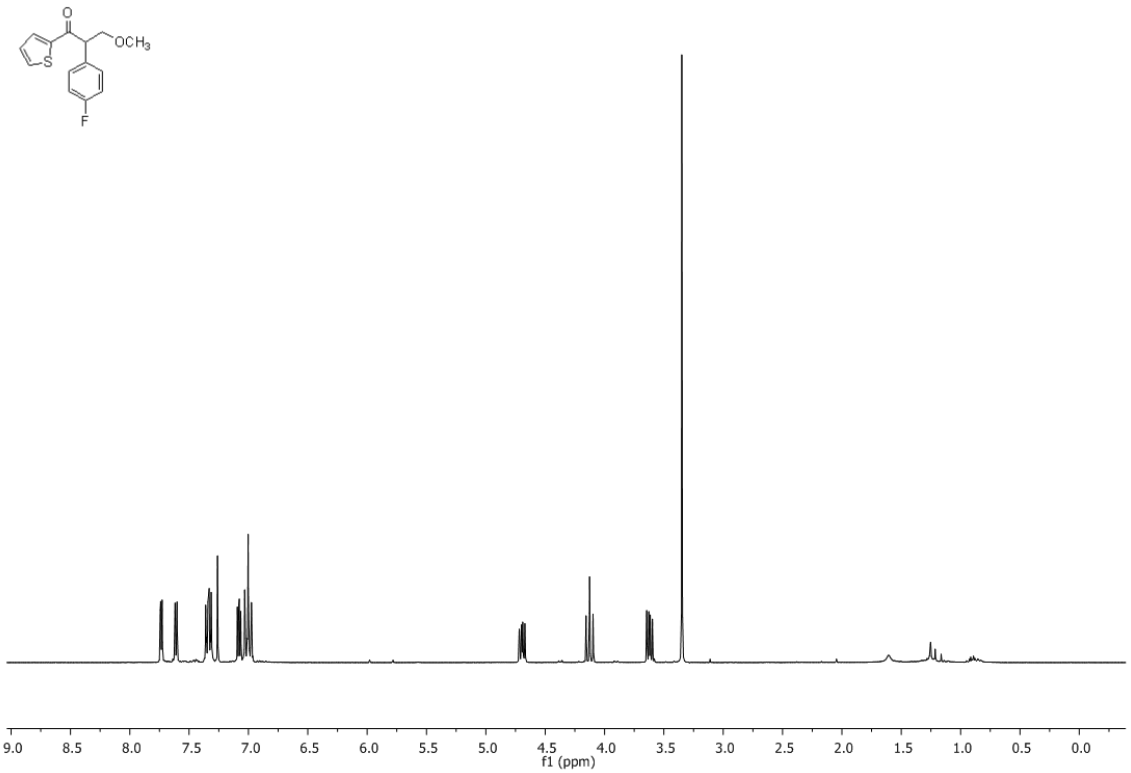
^{1}H and ^{13}C NMR spectra for 3-methoxy-2-phenyl-1-(thiophen-2-yl)propan-1-one (2a)

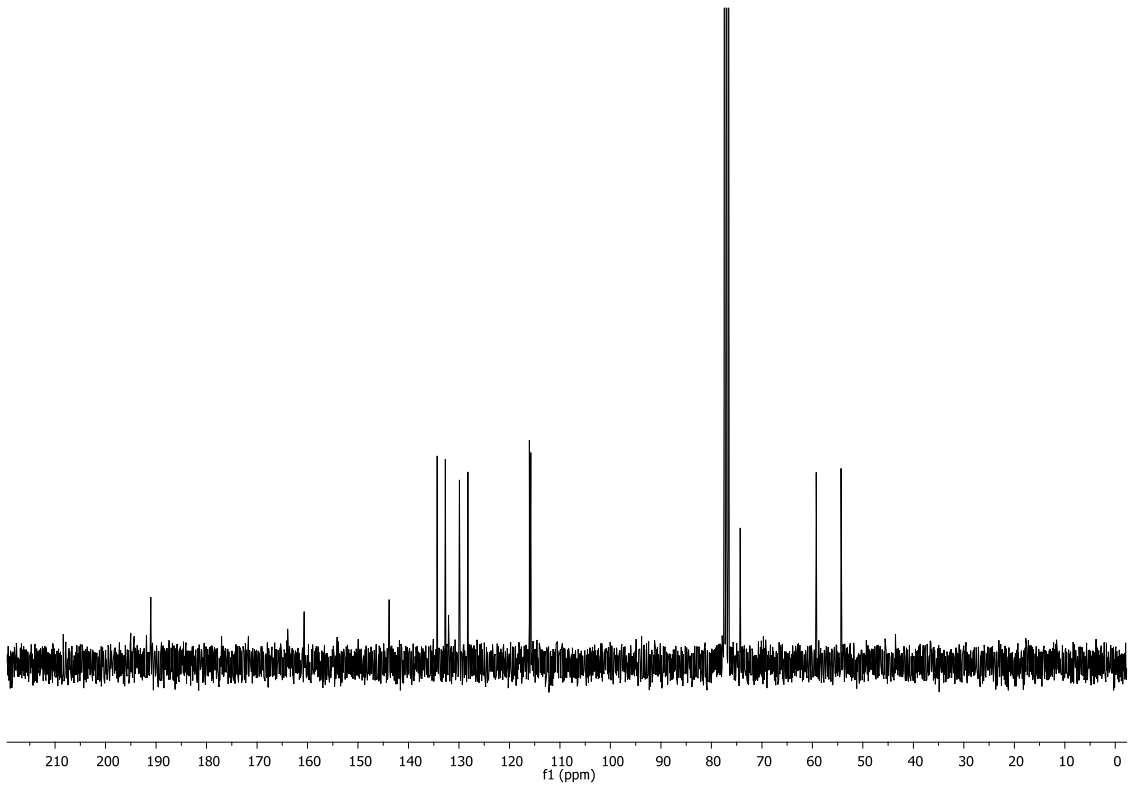




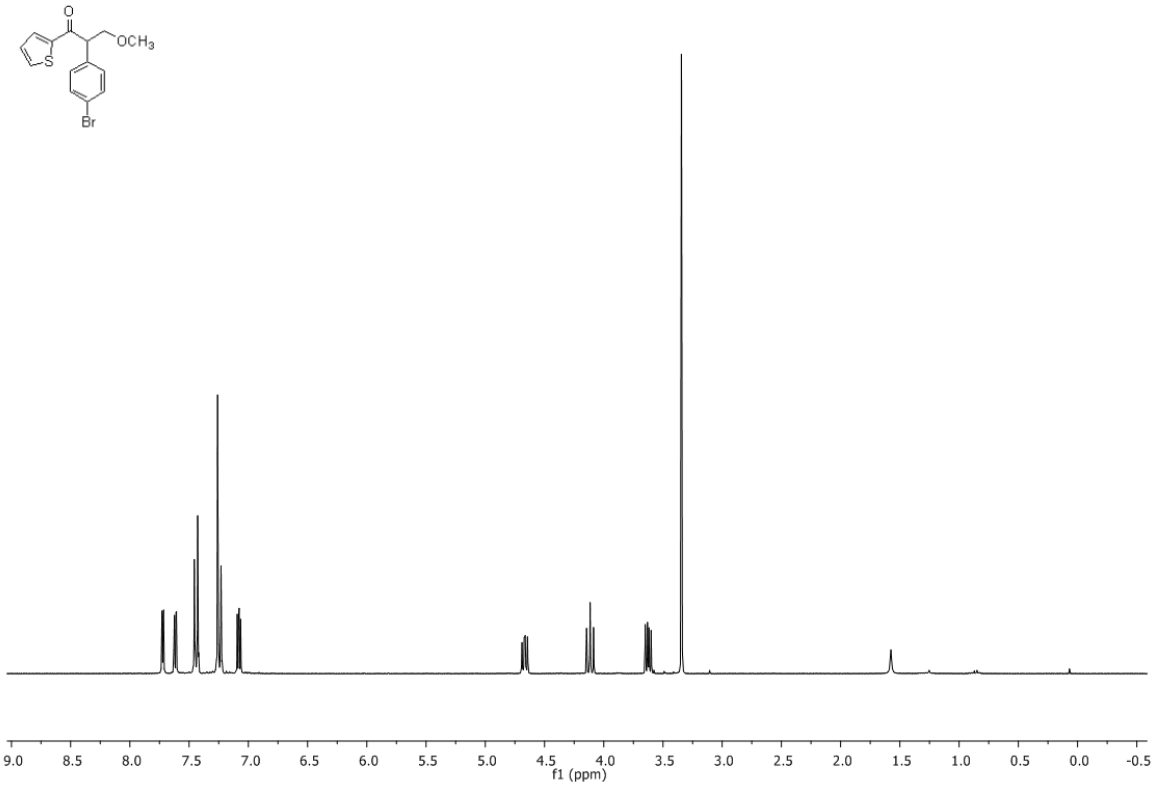


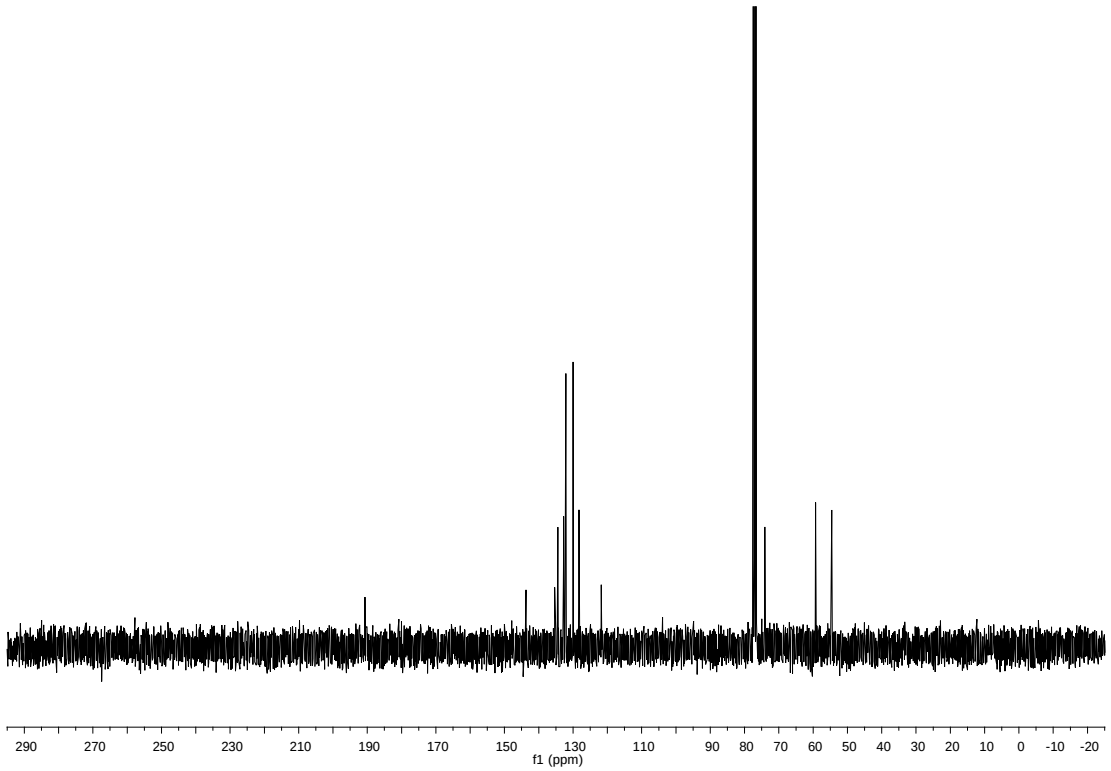
^{1}H and ^{13}C NMR spectra for 2-(4-fluorophenyl)-3-methoxy-1-(thiophen-2-yl)propan-1-one (2b)



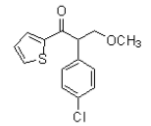


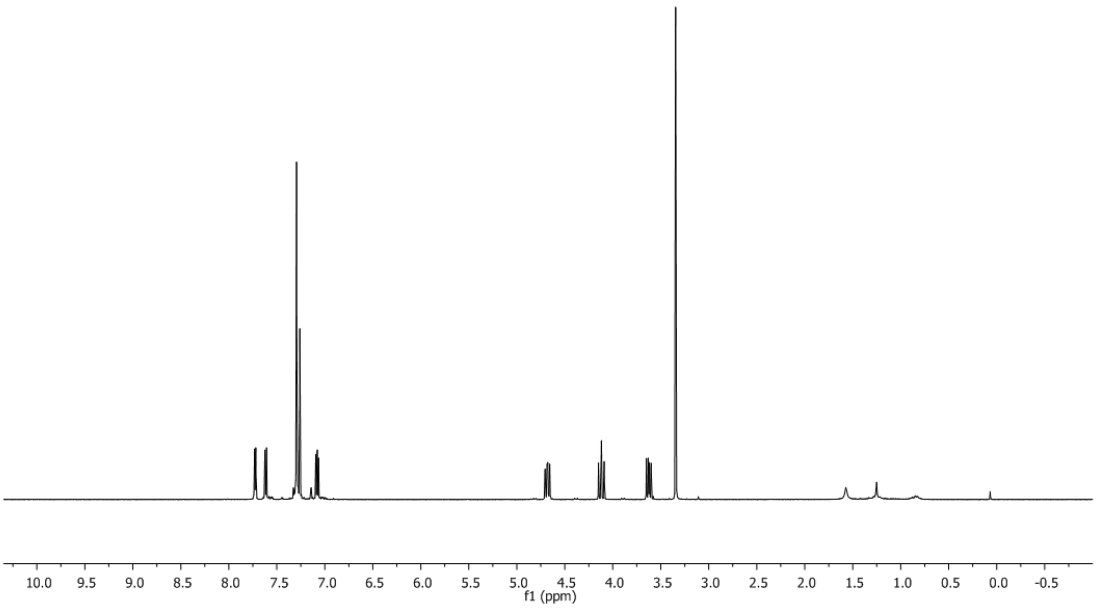
^{1}H and ^{13}C NMR spectra for 2-(4-bromophenyl)-3-methoxy-1-(thiophen-2-yl)propan-1-one (2c)

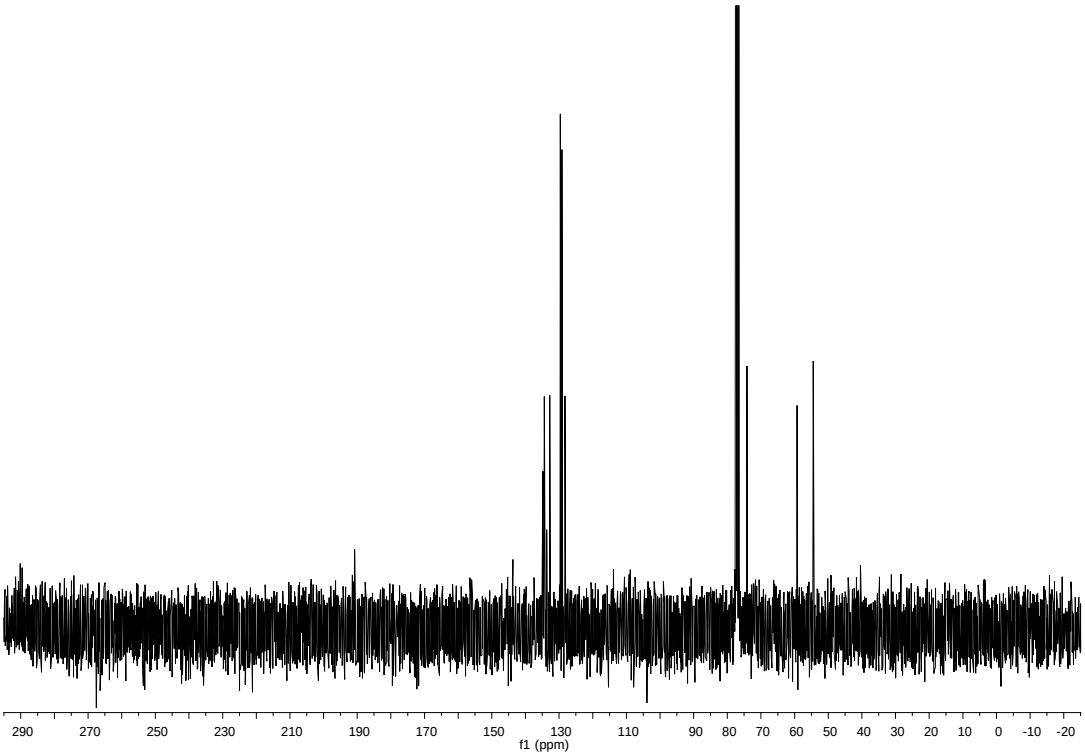




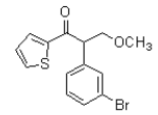
^{1}H and ^{13}C NMR spectra for 2-(4-chlorophenyl)-3-methoxy-1-(thiophen-2-yl)propan-1-one (2d)

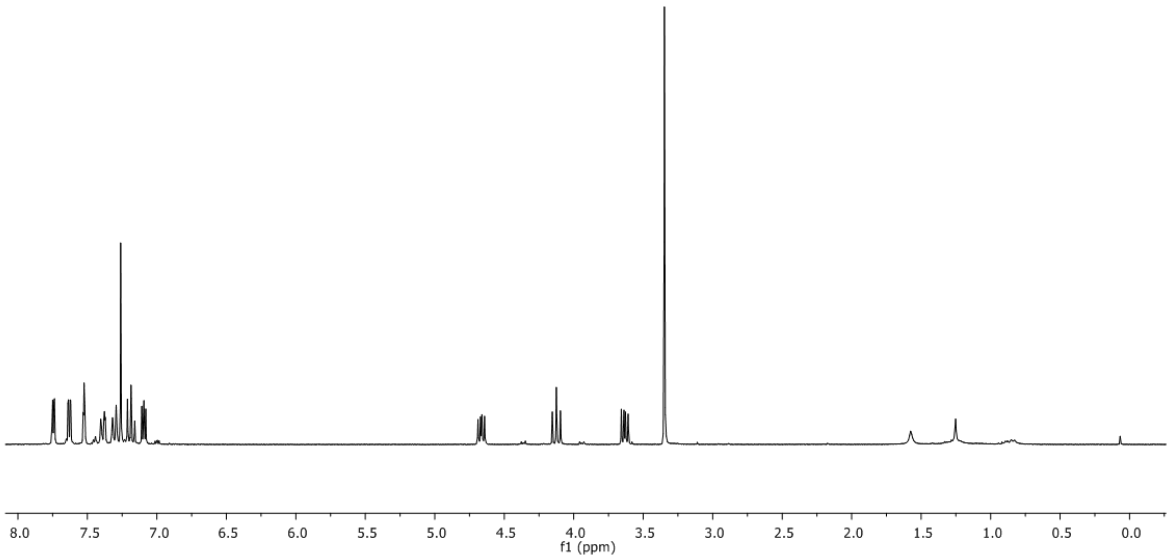


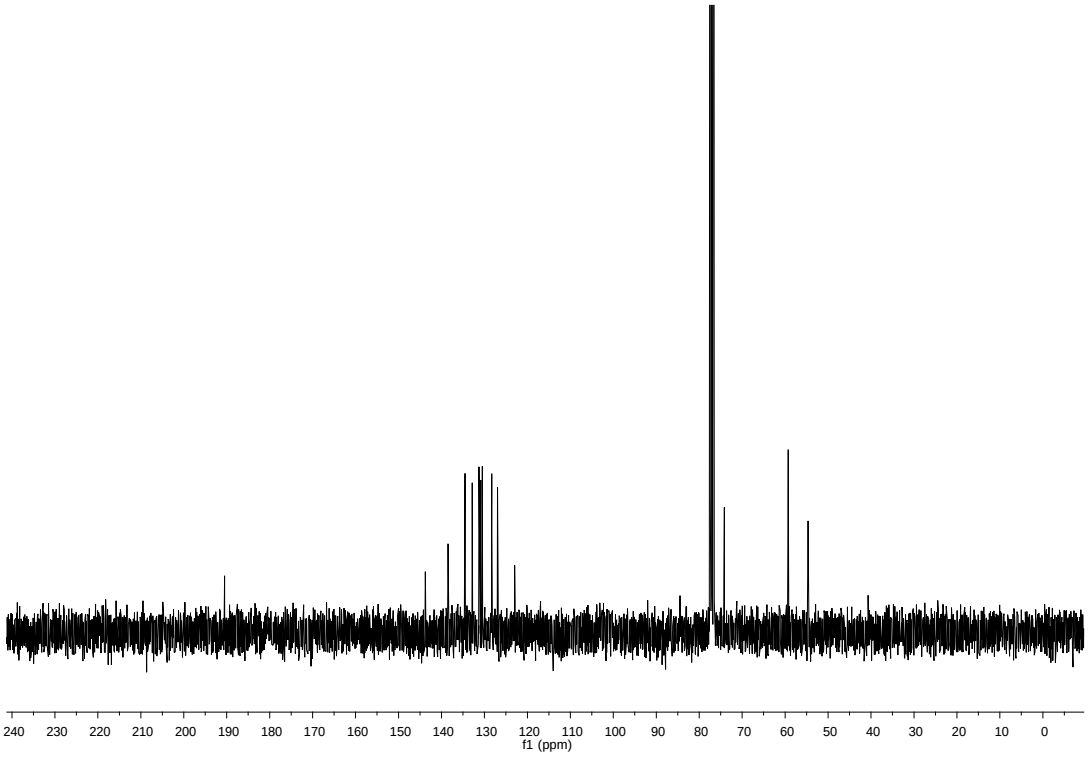




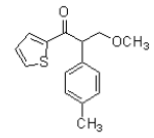
^{1}H and ^{13}C NMR spectra for 2-(3-bromophenyl)-3-methoxy-1-(thiophen-2-yl)propan-1-one (2e)

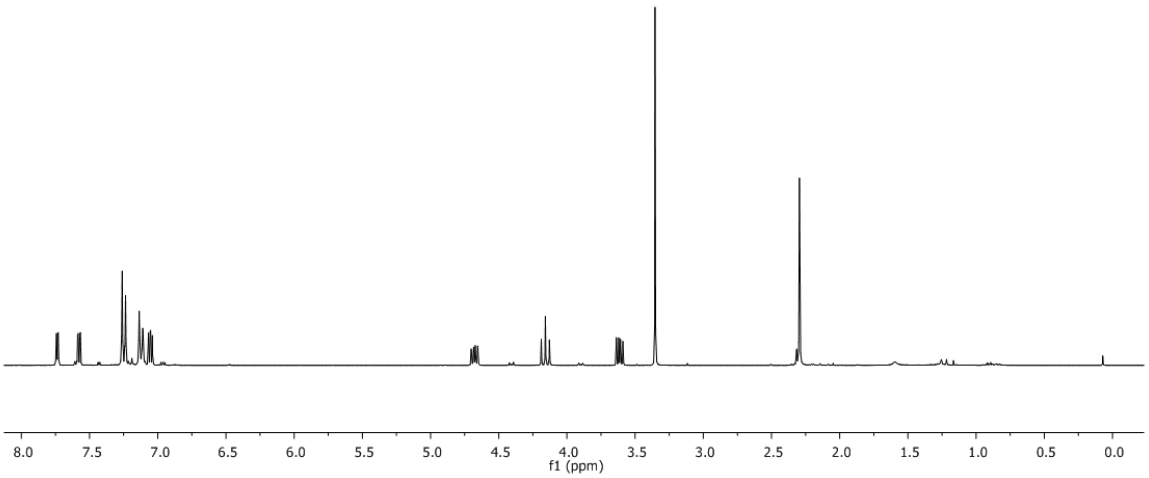


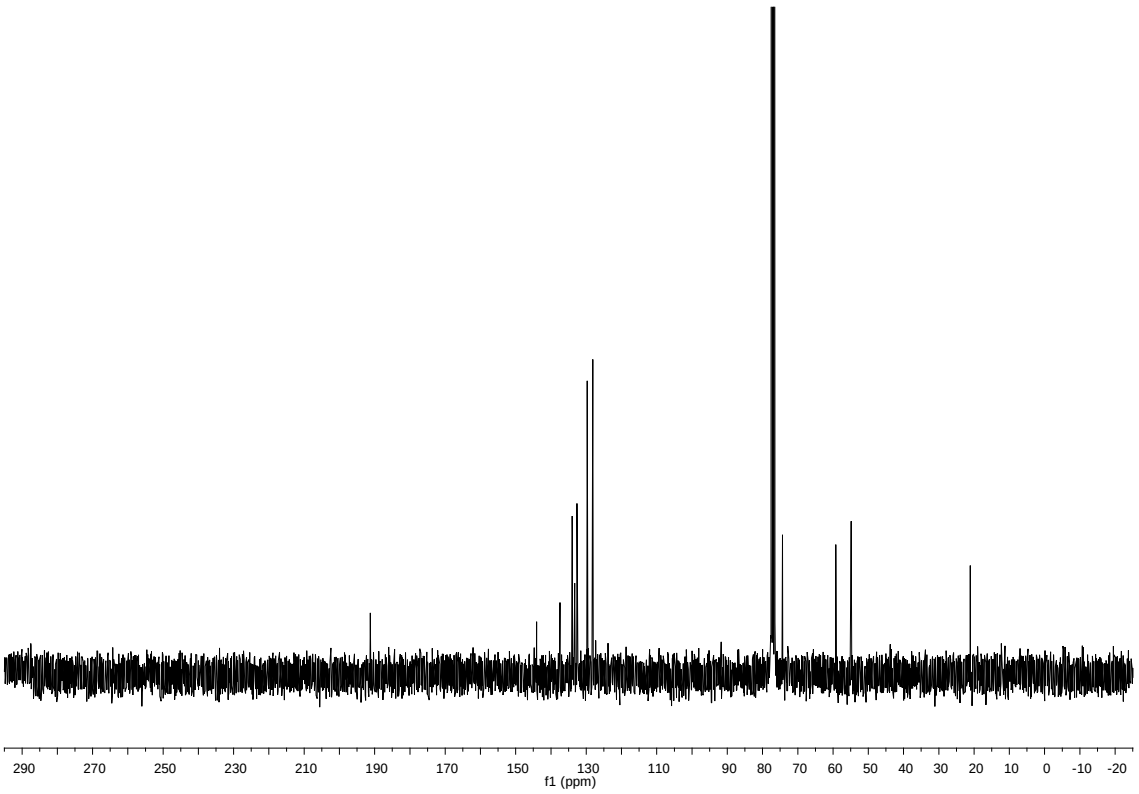




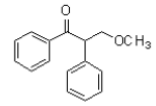
^{1}H and ^{13}C NMR spectra for 3-methoxy-1-(thiophen-2-yl)-2-(p-tolyl)propan-1-one (2f)

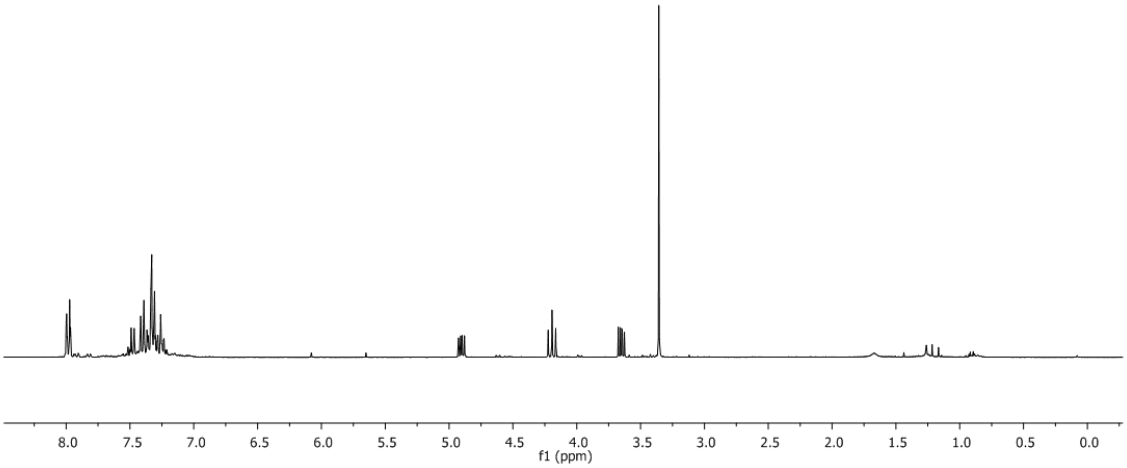


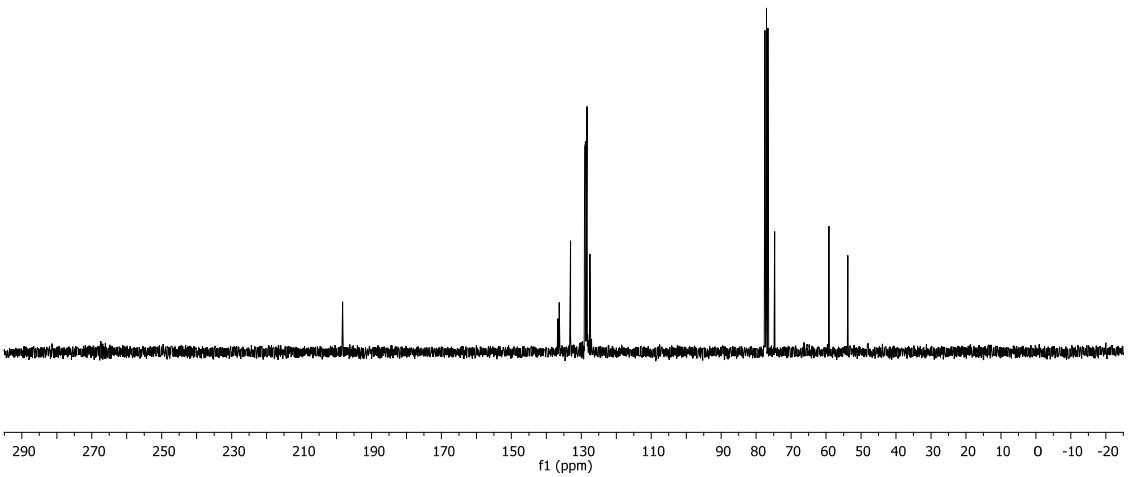




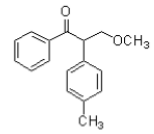
^{1}H and ^{13}C NMR spectra for 3-methoxy-1,2-diphenylpropan-1-one (2i)

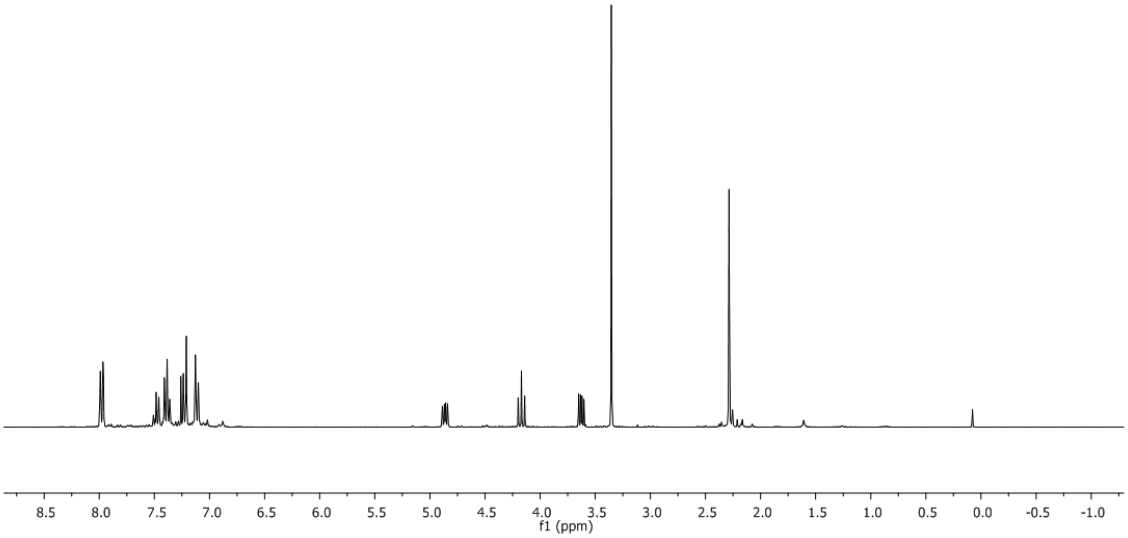


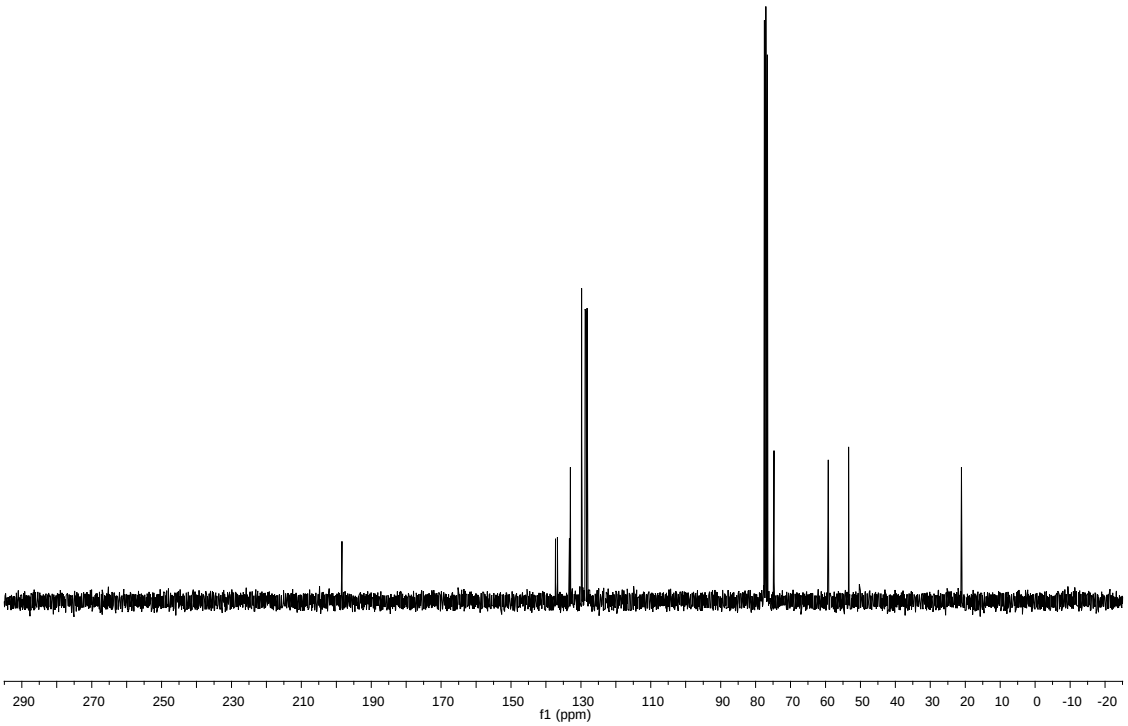




^{1}H and ^{13}C NMR spectra for 3-methoxy-1-phenyl-2-(p-tolyl)propan-1-one (2j)







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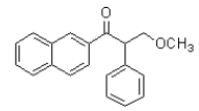
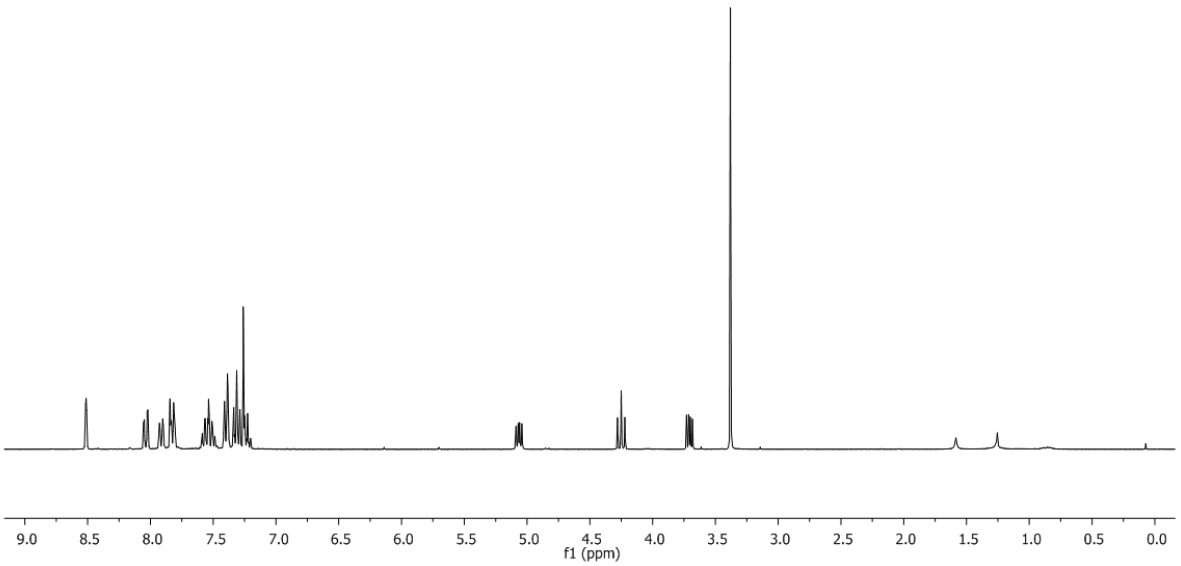
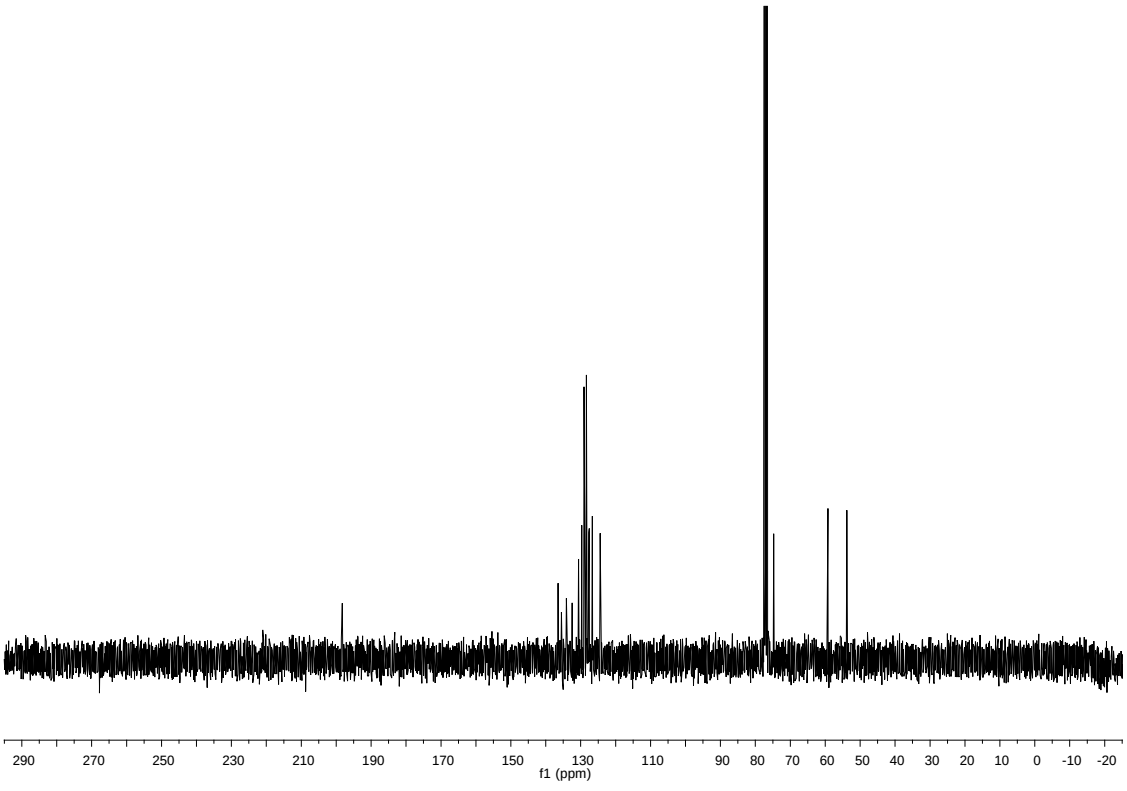
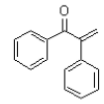


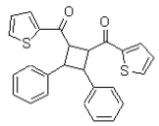


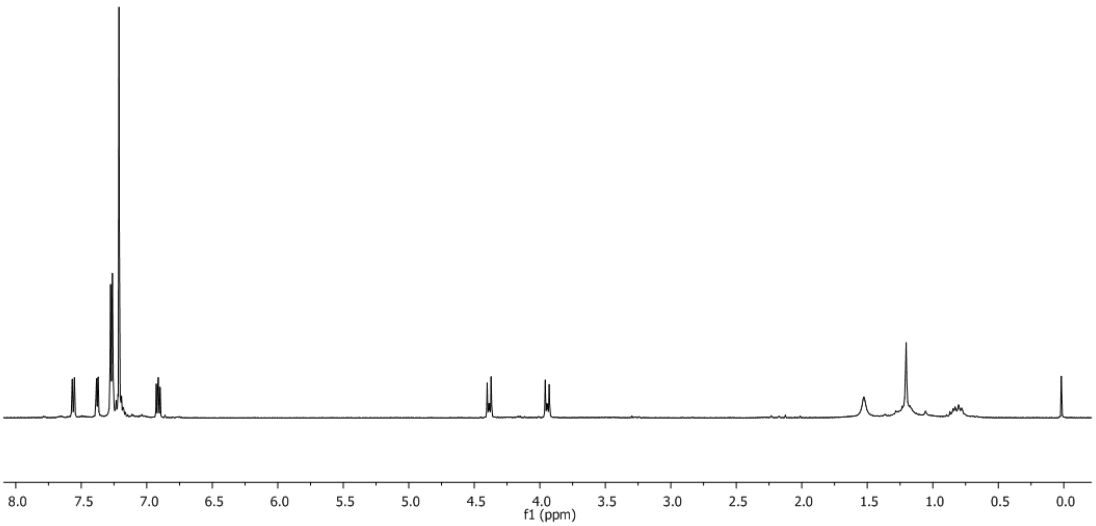


^{1}H spectra for 1,2-Diphenylprop-2-en-1-one (8)



^{1}H spectra for (3,4-diphenylcyclobutane-1, 2-diyl)bis (thiophen-2-yl methanone)





^{1}H spectra for (3,4-diphenylcyclobutane-1,2-diyl)bis((4-methoxyphenyl)methanone).