Advanced Synthesis & Catalysis

Supporting Information

Z-Selective Synthesis of α-Sulfanyl Carbonyl Compounds from Internal Alkynes and Thiols via Photoredox Catalysis

Alberto Luridiana, Angelo Frongia, Mariano Andrea Scorciapino, Giuliano Malloci, Barbara Manconi, Simone Serrao, Pier Carlo Ricci, and Francesco Secci*

Z-selective synthesis of α-sulfanyl-carbonyl compounds from internal alkynes and thiols *via* photoredox catalysis

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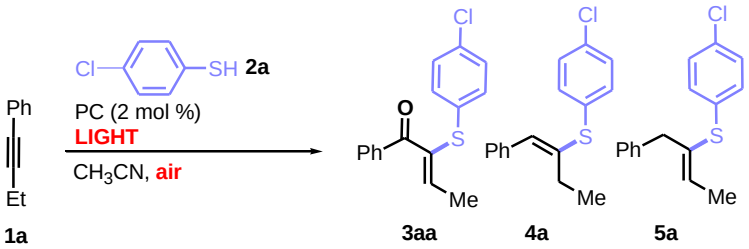
1. Materials and methods

Commercially available reagents were used as received unless otherwise noted. The alkynes **1a**, 1g, **1h**, **1k** and thiols **2a-r** used in this work were purchased from Sigma Aldrich, FluoroChem or TCI and used as received. Alkyne derivatives **1** were prepared following the corresponding literature or by modification of previously published procedures. ^{1}H NMR spectra were recorded on a 500 MHz Varian spectrometers at 25°C using $CDCl_3$ (ref. 7.26 ppm) as a solvent. ^{13}C NMR were recorded at 126 MHz (ref. $CDCl_3$ 77.16 ppm) using $CDCl_3$ as solvent. Chemical shifts (δ) are given in ppm. Coupling constants (*J*) are reported in Hz. Low Mass Spectra Analysis were recorded on an Agilent-HP GC-MS (E.I. 70eV). High Resolution Mass Spectra (HRMS) of compounds **1-13** were obtained using an High Resolution Mass Spectrometer in fast atom bombardment (FAB^+) ionization mode (ESI) acquired using a Bruker micrOTF-Q II or/and Agilent Q-TOF 6520. Melting points were determined with a Büchi M-560 (°C). Analytical thin layer chromatography was performed using 0.25 mm Aldrich silica gel 60-F plates. Flash chromatography was performed using Merck 70-200 mesh silica gel. Yields refer to chromatography and/or spectroscopically pure materials. Acetone, acetonitrile, ethyl acetate were used as received (HPLC grade >99%) or distilled with the appropriate procedure. THF and toluene were distilled from sodium/ benzophenone ketyl. UV-vis analysis were carried out with a Agilent-Cary 5000UV-vis-NIR system. Florescence analysis were carried out with a Varian-Cary Eclipse Fluorescence spectrometer. LED diodes (3W, royal blue (440 nm) or green (530 nm) were purchased from SUIYANR. LEDs were characterized by using a power meter (Newport model 1918-C).

2. Reaction conditions screening

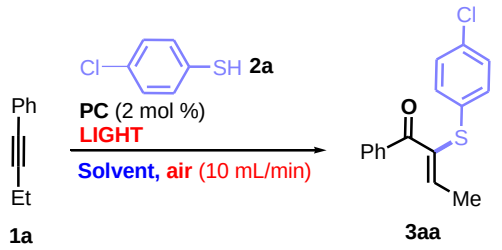
Table S1 Initial reaction conditions screening[a,b,c,d,e]



Entry	Air flow (mL/h)	LED Light source	2a equiv. at starting time (dropwise)	3:4:5 ratio	3aa yield %
1	Open vial	3 Watt (440 nm)	2 (0.0)	12:40:10	-
2	Open vial	3 Watt (440 nm)	1 (1.0)	37:23:10	25
3	Open vial	3 Watt (440 nm)	0 (2.0)	40:17:8	36
4	Open vial	3 Watt (530 nm)	0 (2.0)	50:9:2	45
5	CAP, 0 mL/h	3 Watt (530 nm)	1 (0.0)	2:91:7	-
6	CAP, 0 mL/h	3 Watt (530 nm)	2 (0.0)	3:87:10	-
7	CAP, 2.5 mL/h	3 Watt (530 nm)	0 (2.0)	42:38:17	38
8	CAP, 5 mL/h	3 Watt (530 nm)	0 (2.0)	57:28:12	51
9	CAP, 10 mL/h	3 Watt (530 nm)	0 (2.0)	60:20:8	53
10	CAP, 10 mL/h	3 Watt (530 nm)	0 (1.5)	65:18:9	61
11	CAP, 10 mL/h	3 Watt (530 nm)	0 (1.5)	72:16:7	65
12	CAP, 20 mL/h	3 Watt (530 nm)	0 (1.5)	66:10:2	60
13	CAP, 20 mL/h	3 Watt (530 nm)	0 (2.0)	67:8:3	62
14	CAP, 10 mL/h	3 Watt (440 nm)	0 (1.5)	51:6:2	45
15	CAP, 10 mL/h	3 Watt (white)	0 (1.5)	60:9:3	56

[a] Reactions were performed with (50mg 0.35 mmol) of **1a**, **2a**, Eosin B (2 mol %), solvent (3.0 mL) at room temperature. [b] Thiol **2a** is added one shot or dropwise in acetonitrile (2mL/4 h).[c] Reaction were followed by GC-MS. [d] Isolated yield after flash chromatography. [f] Changing the rate addition of **2a** (2h to 6h) we couldn't see any appreciable the **3** yield improvement. [e] extra EB (2mol%) was added with the thiol.

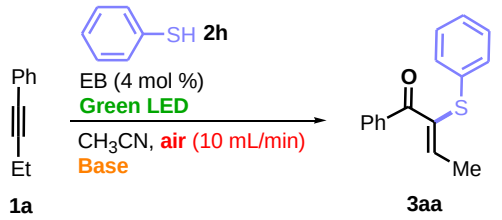
Table S2. Solvent and photocatalyst screening[a,b,c]



Entry	PC	solvent	3aa conversion	3aa Yield%
1	EB	MeCN	65	61
2	EB	AcOEt	60	5
3	EB	THF	64	30
4	EB	Toluene	62	5
5	EB	2-Me-THF	56	50
6	EB	DCE	-	-
7	EB	DMSO	-	-
8	EB	MeCN	64	20
9	EY	MeCN	42	39
10	$[Ru(bpy)_3]Cl_2$	MeCN	52	47
11	DDQ	MeCN	24	21
12	Rhodamine B	MeCN	40	36
13	Fluorescein	MeCN	28	25
14	$(Mes\text{-}Acr)ClO_4$	MeCN	48	43

[a] Reactions were performed with **1a (**50 mg 0.35 mmol), **2a** (82mg 1.5 equiv.), PC (2 mol %), solvent (3.0 mL), rt. Thiol **2a** was added dropwise in acetonitrile (2mL/4 h). [b] Reaction were followed by GC-MS. [c] Isolated yield after flash chromatography.

Table S3. Base additive screening[a,b]



Entry	Base	pKa	Equiv.	Yield %
1	Pyridine	5.2	0.25	37
2	Imidazole	7.0	0.25	25
3	2,4,6-Collidine	7.4	0.25	13
4	Triethyl amine	9.5	0.25	0
5	Diisopropyl amine	10.7	0.25	0
6	pyridine	5.2	0.50	20
7	-	-	-	7

[a] Reactions were performed at room temperature irradiating the reaction suspension with a 5 Watt green LED according with the method B: base (20 mol %), EB (1 mol %), CH_3CN (1.0 mL) **1a** (50 mg 0.35 mmol), were loaded in the reactor vial. A EB (1 mol %) + **2h** (82mg, 1.5 equiv.) suspension in CH_3CN (2 mL) was added dropwise over 4 hours. Reaction is followed by GC-MS. [b] Isolated yield after flash chromatography.

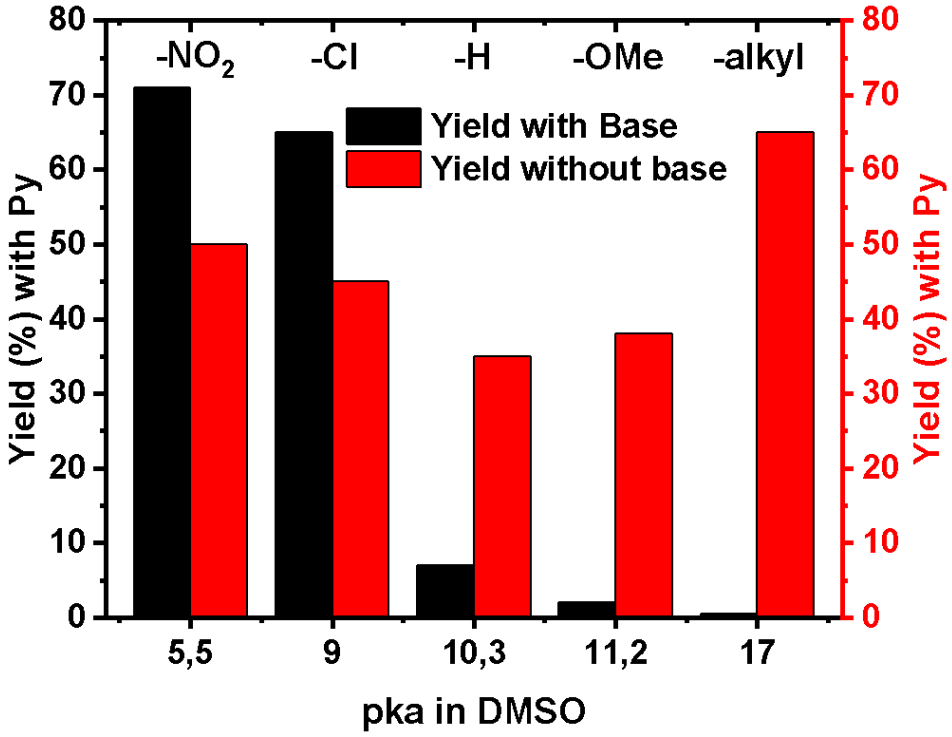


Figure S1. Comparison between method A (black) and method B (red) in the synthesis of selected thiols. pka values were obtained from the literature[1]

3. Emission Quenching Studies

Stern-Volmer experiments were carried out irradiating the samples at 530 nm while the emission was detected at 580 nm. The reported excited-state lifetime for Eosin B in MeCN (280 ps) was used for k_q calculations. [2]

Solutions preparation:

a) Eosin B solution 2,5 $\cdot 10^{-5}$ M: 1.6 mg of EB were added to a 100 mL volumetric flask and filled with ACN.
b) 1-phenylbutine **1** solution 0.065 M: 93 µL of **1** were added to a 10 mL volumetric flask and filled with ACN.
c) 4-chlorobenzenethiol solution 0.066 M: 95 mg of thiol were added to a 10 mL volumetric flask and filled with ACN.

Sample preparation:

1 mL of photocatalyst solution and the amount of quencher (**1a** or **2a)** were loaded in a cuvette and filled with 2 mL CH_3CN. The cuvette was degassed for 5 minutes before starting the measurements.

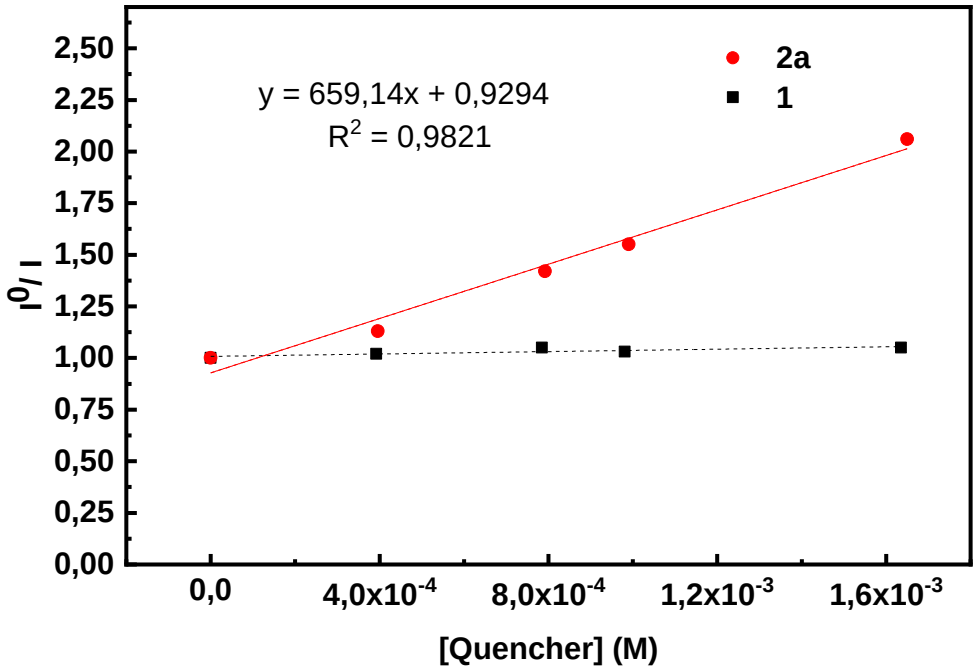


Figure S2. Stern-Volmer quenching experiment of Eosin B with 1-phenyl 1-butine **1a** (black) and **2a (**red).

4. Absorption spectra of compounds 1a, 2a, 3aa and Eosin B

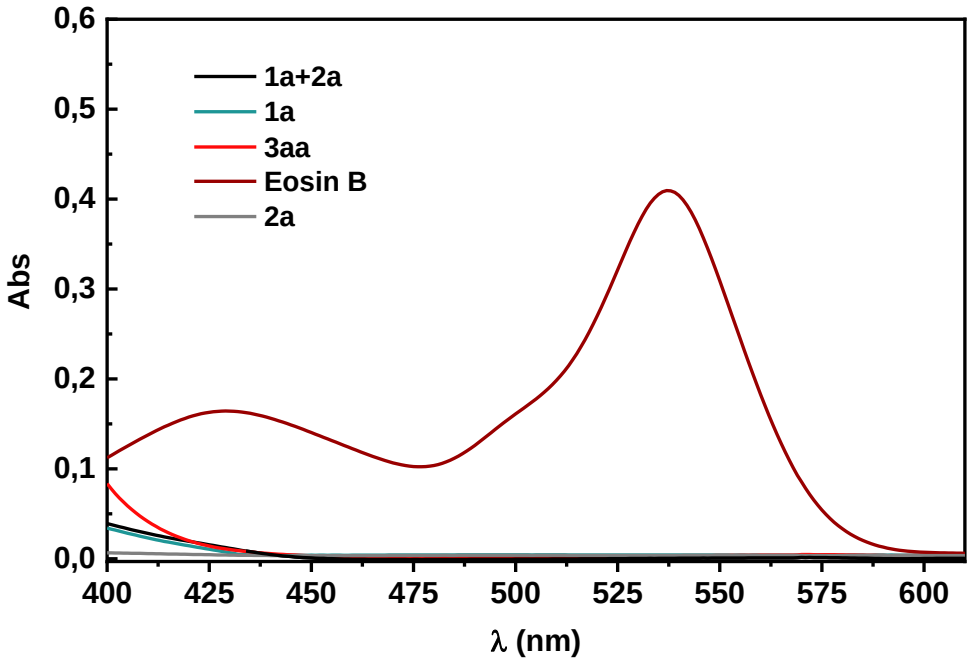


Figure S3. Absorption spectra of compounds **1a** (0.1 mM), **2a** (0.1 mM) and Eosin B ($2.5\ 10^{-5}$ M) 160 μL in 1 mL of CH_3CN.

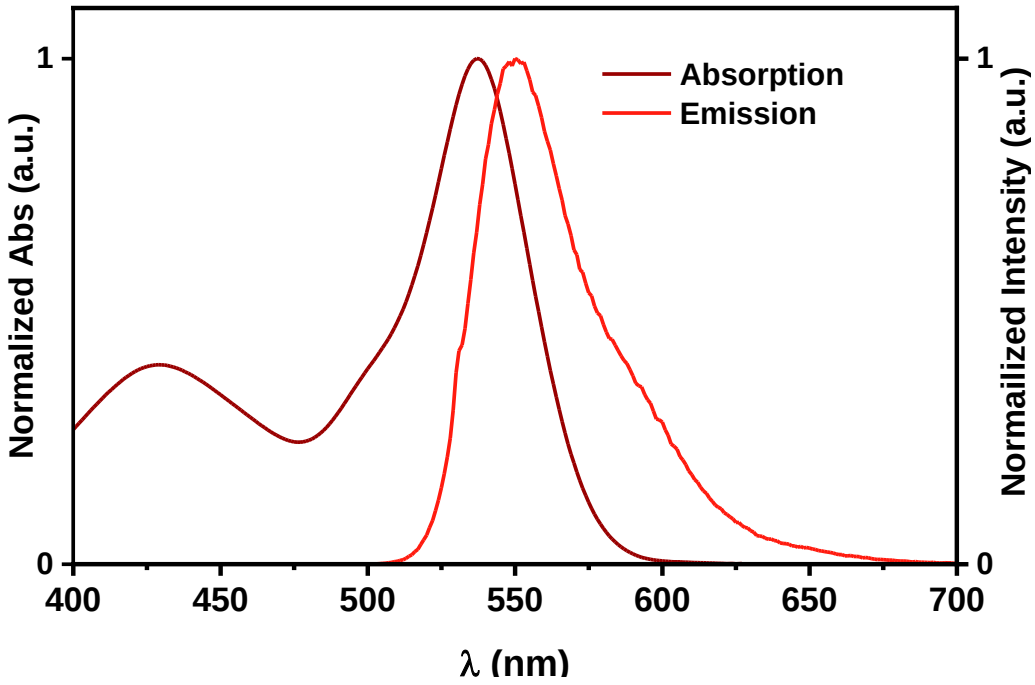


Figure S4. Normalized Absorption and Emission spectra of Eosin B $2.5\ 10^{-6}$ M in CH_3CN.

5. Photocatalyst inactivation studies

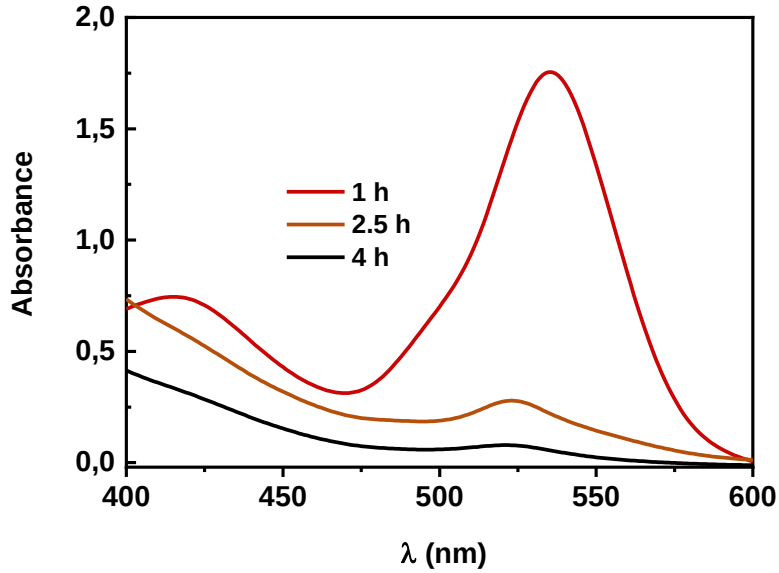


Figure S5. UV Vis monitoring of EB (3 mol %) during the reaction of **1a** with **2a** in CH_3CN at 1hours, 2.5hours and 4 hours. The reaction mixture was submitted to irradiation at 530 nm (5 Watt green LED), air, 34°C (UV-Vis sample dilution 1:100).

6. Photochemical reactor details

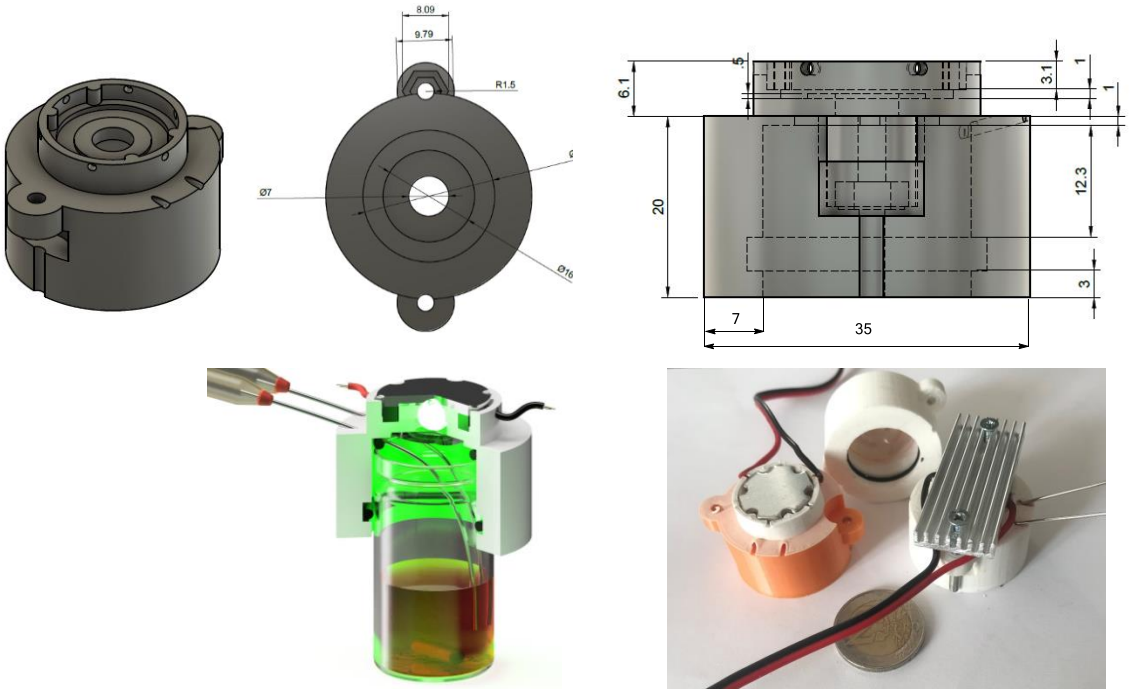


Figure S6. a) Reactor CAP scheme. 3D printed CAP

Inspired by the work of Ananikov and co-workers,[3] we designed a 3D printable CAP able to host a 3 or 5 Watt LED and a glass lens (separated by the led from a PTFE spacer). In this device we realized two inlet (2 mm) for the insertion of syringe needles if necessary. The vial (10 mL glass vials, 14x50 mm). is fixed to the cap with an O-ring. Once the LED is placed on top of the device, it is stuck by an aluminium heat sink. The vials can be covered with aluminium tape to reduce light loss. Alternatively they can be immersed in a cooling solution to lower the reaction temperature.

7. Photon flux characterization of photochemical reactor

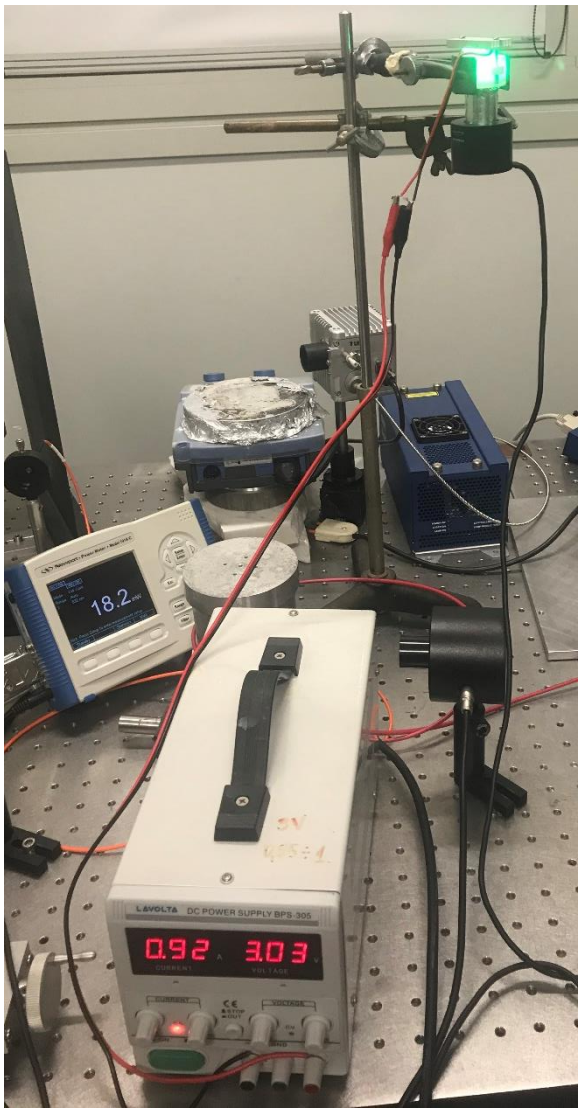


Figure S7. Reactor photophysic characterization

The geometry of the reactor allow to estimate the photons flux going trought the vessel. A photons probe was placed on the bottom of the vial inserted in the reactor (13 mW). Removing the bottom glass a gain of 2mW was registered and covering the vial with aluminum foil the power arise up to (18 mW).

$$E_{530nmphoton} = hv = 6{,}6 \cdot 10^{-34}(J \cdot s) \cdot \frac{3 \cdot 10^{8}(m \cdot s^{-1})}{530 \cdot 10^{-9}(m)}$$

$$= 3{,}74 \cdot 10^{-19}(J)$$

$$Power_{LED\ 530nm} = W\ (J \cdot s^{-1}) = 0{,}2 \cdot 10^{-2}(J \cdot s)$$

$$N.Photons\ per\ second_{LED\ 530nm} = \frac{Power_{LED\ 530nm}}{E_{530nmphoton}}$$

$$= \frac{2 \cdot 10^{-2}(J \cdot s)}{3{,}74 \cdot 10^{-19}(J)} = 5{,}35 \cdot 10^{16}(s^{-1})$$

$$mol\ of\ photons\ per\ second_{LED\ 530nm} = \frac{N.Photons\ per\ second}{N.Avogadro}$$

$$= \frac{5{,}35 \cdot 10^{16} s^{-1}}{6{,}02 \cdot 10^{23}} = 8{,}86 \cdot 10^{-8}(s^{-1})$$

$$mmol\ of\ photons\ per\ hour_{LED\ 530nm}$$

$$= 8{,}86c \cdot 10^{-8}(s^{-1}) \cdot 3600\ (s) \cdot 10^{-3} = 0{,}32$$

8. Quantum Yield measurements

Essentially all incident light (f > 0.999, vide infra) is absorbed by the Eosin B at the reaction conditions used for determining the quantum yield. The setup used for determining the quantum yield is the same used in our reaction and with a photons flux of 18mW no light pass thought the saturated limpid acetonitrile solution of eosin B means that all light is absorbed. Quantum yield experiment: 1-phenil-1-butine (50mg 0.38 mmol), Eosin B saturated solution (10mg in 3mL then filtered), p chlorothiophenol 0.57 mmol in 2 mL dropwised after 2400s yielded 11% of **3a**.

$$\phi = \frac{mol\ product}{flux\ \cdot t \cdot f} = \frac{4{,}18 \cdot 10^{-5} mol}{8{,}86 \cdot 10^{-8} einstein \cdot s^{-1} \cdot 2400s \cdot 1} = 0{,}20$$

Φ (11%) = 0,2

9. NMR studies (determination of (*Z*)-stereochemistry of compounds 3)

Doble Pulsed Field Gradient Spin-Echo was applied in combination with one-dimensional ^{1}H NOESY (DPFGSE-NOESY1d)[4] in order to clarify the E-Z isomerism of the compound **3ac**. Briefly, magnetization of a given group of magnetically equivalent protons is selectively inverted. During the mixing time, magnetization is transferred to close nuclei through cross-relaxation, causing the latter to experience a positive NOE effect. In practice, the selectively inverted intense resonance will be visible in the spectrum together with opposite sign resonances due to those nuclei that have received the magnetization transfer. Transfer takes place through dipolar interaction. Thus, the closer the nuclei (on time average), the larger the NOE effect. The effect decays rapidly with distance (inverse sixth-power), such that, typically, only the nuclei closer than 5 Å to the selectively inverted ones will contribute to the final spectrum. Figure S8 shows the results of two complementary experiments performed on the same **3ac**.

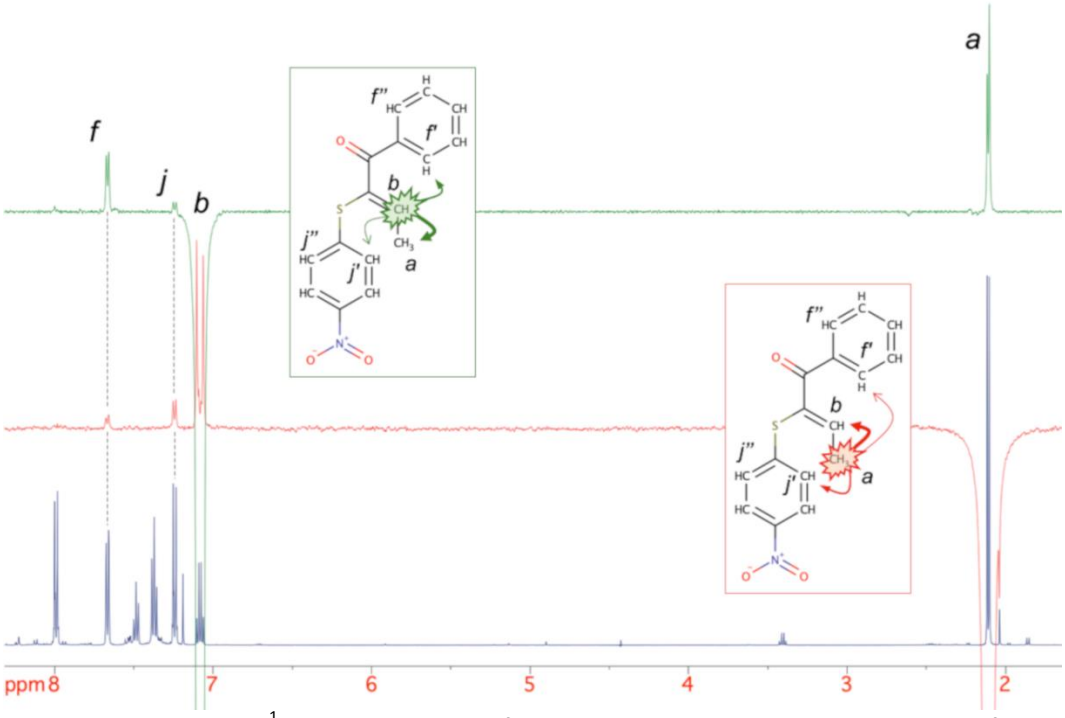


Figure S8. The standard ^{1}H NMR spectrum of compound **3ac** is shown in blue as a reference for resonance frequency. The red spectrum is the results of DPFGSE-NOESY1d acquired with the resonance of the methyl group selectively inverted (resonance a). The green spectrum shows the spectrum resulting from the application of the same pulse-sequence with the olefinic proton selectively inverted (resonance b). In the two insets, arrows width is roughly proportional to the magnitude of the magnetization transfer.

The selective inversion of resonance *a* (methyl group) led to significant NOE enhancement for three resonances. The largest enhancement is observed for the resonance *b* (olefinic proton), which is clearly expected since the time average distance from the methyl group is virtually constant and it is the shortest among all the protons in the molecule. However, when resonance *j* and *f* are compared in the red spectrum in Figure S8, the former shows the largest intensity. This is a clear indication of the shorter distance from the methyl group of the paranitrophenyl moiety than the benzyl group. On

the other hand, the green spectrum in Figure S8 shows the complementary results. In fact, when the resonance *b* was selectively inverted, beside resonance *a* showing the largest NOE enhancement, resonance *f* resulted more intense than the *j* one. This demonstrates that the benzyl group is closer to the olefinic proton than the paranitrophenyl moiety. Thus, we can conclude that compound **3ac** was obtained as the *Z*-**3ac** isomer. The same experiments were carried out for the compound **3aa** leading to the same results.

10. Computational Studies

Radicals were optimized both in vacuum and acetonitrile (polarizable continuum model of solvent)[4] at the DFT level by using the Gaussian09 computer code.[5] We used the hybrid exchange-correlation functional B3LYP[6,7] in combination with the standard Pople-type basis-set 6-31G**. We additionally performed geometry optimizations with the same functional and the larger 6-311++G** basis-set. Subsequent full vibrational analysis calculations confirmed true minima (all eigenvalues of the Hessian matrix were found to be positive). As shown in the following table, adduct **IV** is lower in energy by about 17-18 kcal/mol.

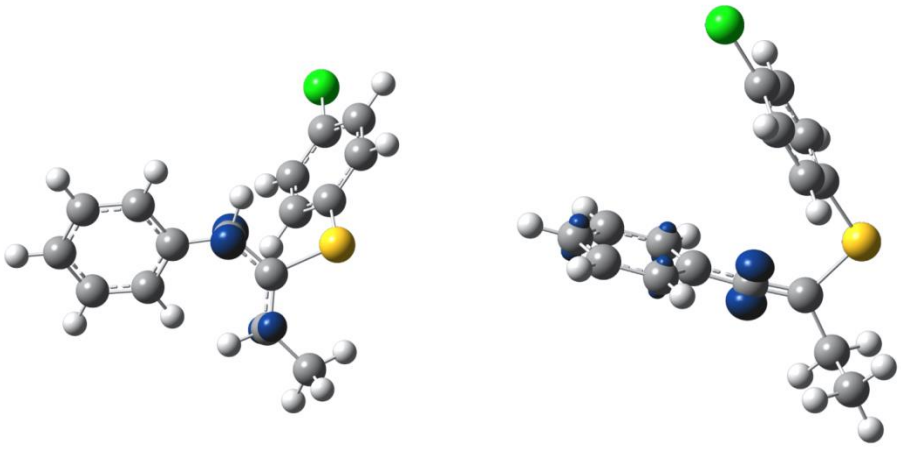
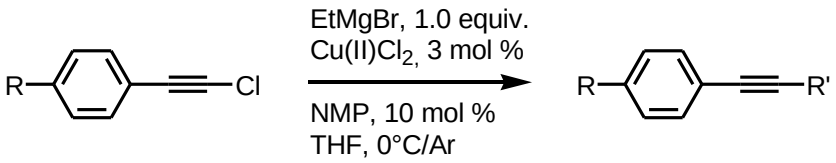


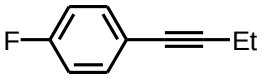
Figure S9. Optimized molecular structure of radical intermediates **III** (right) and **IV** (left). Electron spin density distribution is shown in blue.

	B3LYP/6-31G** (vacuum)	B3LYP/6-31G** (acetonitrile)	B3LYP/6-311++G** (acetonitrile)
IV	-1476.5	-1476.5	-1476.7
III	-1476.5	-1476.5	-1476.7
Δ (kcal/mol)	17.9	17.8	17.0

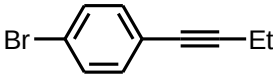
11.General procedure for the synthesis of alkynes 1



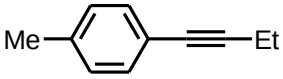
Chloroethynyl-benzene and the corresponding aryl-alkyl alkynes were following the procedure developed by Cahiez and co-workers.[8]
Chloroethynyl-benzene (800 mg, 5.88 mmol) was reacted with a 2.0 M ethylmagnesium bromide solution (8.82 mmol, 4.41 mL), in the presence of NMP (57 mg, 0.58 mmol) and $CuCl_2$ (24 mg, 0.011 mmol) in dry THF (6 mL) at 0°C. After one hour, the reaction mixture was quenched with HCl 1.0 M solution (5 mL) and extracted with Et_2O (2x10 mL). the organic phase was dried on Na_2SO_4 and concentrated under reduced pressure. Flash chromatography (hexanes/Et_2O 95:5) afforded the compound I as a colorless oil in 86% yield (657 mg).



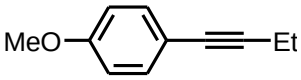
1-But-1-ynyl-4-fluoro-benzene 1b. 1-Chloroethynyl-4-fluoro-benzene (905 mg, 5.88 mmol) ethylmagnesium bromide 3.0 M solution in Et_2O (8.82 mmol, 2.9 mL), NMP (57 mg, 0.58 mmol), $CuCl_2$ (24 mg, 0.011 mmol), dry THF (6 mL) at 0°C. Spectroscopic data in accordance with the literature.[9]



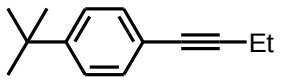
1-bromo-4-(but-1-yn-1-yl)benzene 1c. Chloroethynyl-benzene (1.25 g, 5.88 mmol) ethylmagnesium bromide 3.0 M solution in Et_2O (8.82 mmol, 2.9 mL), NMP (57 mg, 0.58 mmol), $CuCl_2$ (24 mg, 0.011 mmol), dry THF (6 mL) at 0°C. Spectroscopic data in accordance with the literature.[10]



1-(but-1-yn-1-yl)-4-methylbenzene 1d. 1-Chloroethynyl-4-methyl-benzene (882 mg, 5.88 mmol) ethylmagnesium bromide 3.0 M solution in Et_2O (8.82 mmol, 2.9 mL), NMP (57 mg, 0.58 mmol), $CuCl_2$ (24 mg, 0.011 mmol), dry THF (6 mL) at 0°C. Spectroscopic data in accordance with the literature.[9]

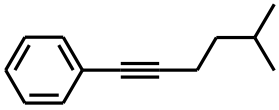


1-But-1-ynyl-4-methoxy-benzene 1e. 1-Chloroethynyl-4-methoxy-benzene (963 mg, 5.88 mmol) ethylmagnesium bromide 3.0 M solution in Et_2O (8.82 mmol, 2.9 mL), NMP (57 mg, 0.58 mmol), $CuCl_2$ (24 mg, 0.011 mmol), dry THF (6 mL) at 0°C. Spectroscopic data in accordance with the literature.[9]

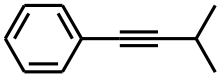


1-(but-1-yn-1-yl)-4-(tert-butyl)benzene 1f. Chloroethynyl-benzene (1.13 g, 5.88 mmol) ethylmagnesium bromide 3.0 M solution in Et_2O (8.82 mmol, 2.9 mL), NMP (57 mg, 0.58 mmol), $CuCl_2$ (24 mg, 0.011 mmol), dry THF (6 mL) at 0°C. ^1H NMR (500 MHz,

$CDCl_3$) δ: 7.36-7.29 (m, 4H), 2.45-2.38 (m, 2H), 1.31 (d, *J* = 1.1 Hz, 9H), 1.24 (td, *J* = 7.5, 1.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 130.10, 127.63, 125.49, 125.08, 123.08, 91.26, 77.06, 75.05, 14.01, 13.20); HRMS (ESI), calcd. for $C_{14}H_{18}$ [M-H^+]: 186,1409, found: 186,1415.

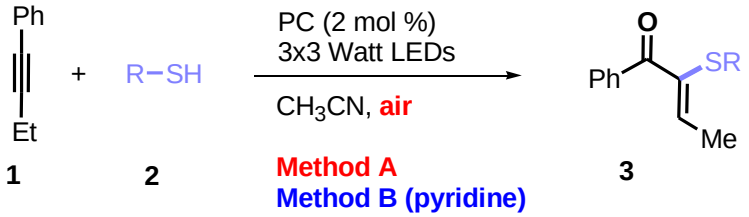


(5-Methyl-hex-1-ynyl)-benzene 1i. Chloroethynyl-benzene (800 mg, 5.88 mmol) 2-Methyl-propylmagnesium bromide 1.2 M solution in Et_2O (8.82 mmol, 7.4 mL), NMP (57 mg, 0.58 mmol), CuCl2 (24 mg, 0.011 mmol), dry THF (6 mL) at 0°C. Spectroscopic data in accordance with the literature.[11]



(3-methylbut-1-yn-1-yl)benzene 1j. Chloroethynyl-benzene (800 mg, 5.88 mmol) isopropenylmagnesium bromide 2.0 M solution in THF (8.82 mmol, 4.41 mL), NMP (57 mg, 0.58 mmol), CuCl2 (24 mg, 0.011 mmol), dry THF (6 mL) at 0°C. Spectroscopic data in accordance with the literature.[12]

12. General Procedure for the Synthesis of enones 3



Method A

In a 10 mL vial (A) equipped with a stirring bar, EB (2% mol) is suspended in CH_3CN (1mL) and stirred at room temperature. In a second vial (B), EB (2 mol %) and 4-chloro benzene thiol **2a** (0.57 mmol, 1.5 equiv) are dissolved in 2mL of CH_3CN. This solution is then drawn into a syringe and placed on a syringe pump. In the meantime, 1-phenil-1-butine **1a** (50 mg 0.38 mmol) is added to the vial A. The vial A is then closed with the 3D printed cap. The needle of the syringe containing the EB+thiol **2a**/CH_3CN solution was inserted into one of the inlets of the cap. With a second needle, the reactor was connected with an air line. Finally, the LED light was switched and both reagents and air were added to the solution contained in the vial A. The reaction was followed by GC-MS. After 4-8 hours, CH_3CN was evaporated under reduced pressure, and the crude product was loaded on a silica gel column to be purified by flash chromatography (eluents hexanes-Et_2O 7:1).

Method B

In a 10 mL vial (A) equipped with a stirring bar, EB (2% mol) is suspended in CH_3CN (1mL) and stirred at room temperature. In a second vial (B), EB (2 mol %) and 4-chloro benzene thiol **2a** (0.57 mmol, 1.5 equiv) are dissolved in 2mL of CH_3CN. This solution is then drawn into a syringe and placed on a syringe pump. Then, 1-phenil-1-butine **1a** (50 mg 0.38 mmol) and pyridine (25 mol %) were added to the vial A. The vial A is closed with the 3D printed cap. The needle of the syringe containing the EB+thiol **2a**/CH_3CN solution was inserted into one of the inlets of the cap. With a second needle, the reactor was connected with an air line. Finally, the LED light was switched and both reagents and air were added to the solution contained in the vial A. The reaction was followed by GC-MS. After 4-8 hours, CH_3CN was evaporated under reduced pressure, and the crude product was loaded on a silica gel column to be purified by flash chromatography (eluents hexanes-Et_2O 7:1).

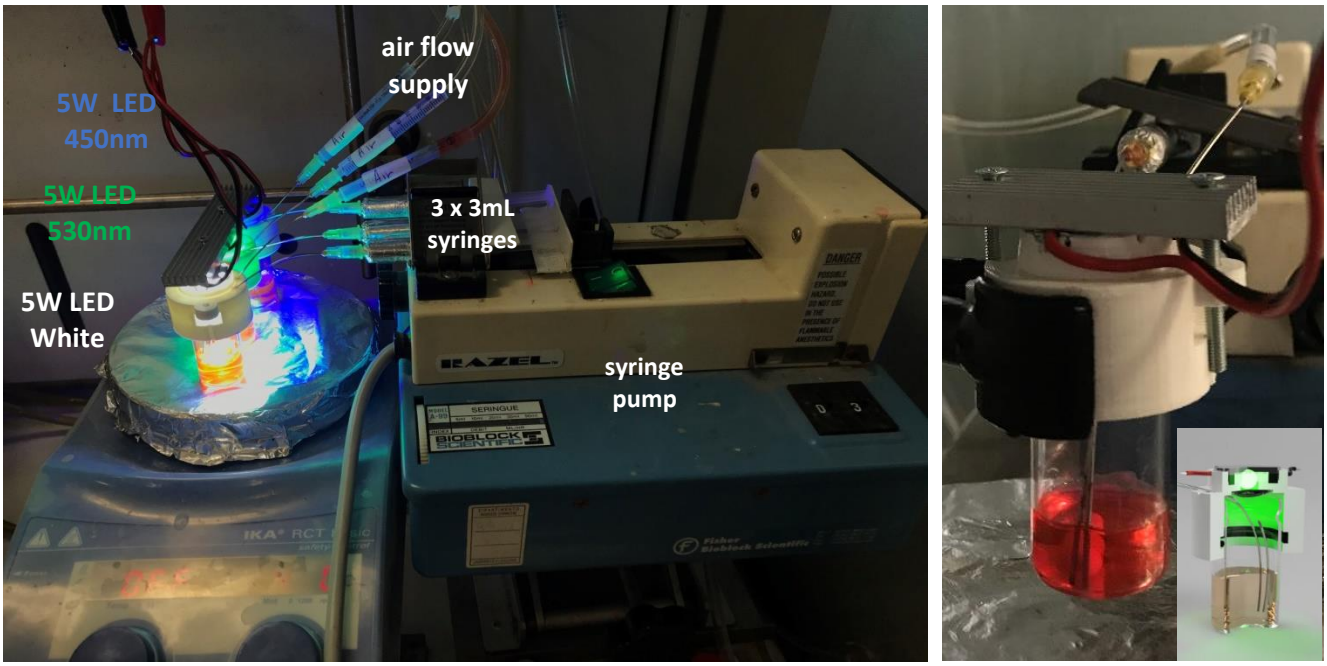
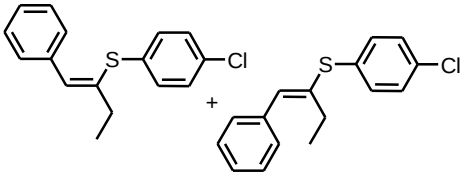


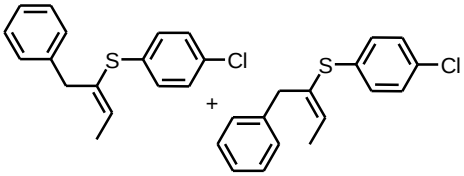
Figure S10. Photochemical reactor. a) in image (a), three reactions irradiated at different wavelengths are conducted in parallel, using three 10 mL reactors. b) Single reaction. details of the reactor used for the preparation of the compounds 3

12.1. Identification of secondary products 4a, 5a, 6a, 7a

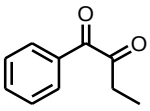


(*E/Z*)-1-(1-Benzyl-propenylsulfanyl)-4-chloro-benzene 4a. ^1H and ^{13}C NMR were extracted from a *E/Z* mixture of isomers **4**. Major (*E*): ^1H NMR (600 MHz, $CDCl_3$) δ: 7.47-7.43 (m, 2H), 7.38-7.08 (m, 7H), 6.75 (s, 1H), 2.23 (qd, *J* = 7.4, 1.2 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 137.03, 136.69, 133.21, 133.14, 132.81, 132.11, 129.32, 129.18, 128.17, 127.47, 31.69, 13.97; Minor (*Z*): ^1H NMR (600

MHz, $CDCl_3$), δ: 7.38-7.08 (m, 9H) 6.66 (s, 1H), 2.42 (q, *J* = 7.4 Hz, 2H), 1.18 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 140.49, 136.96, 133.45, 133.14, 133.09, 131.98, 129.41, 128.55, 128.50, 127.19, 24.96, 13.70; FTIR (film) cm^{-1} ν: 2974, 2930, 1595, 1449, 1471, 1442,1384, 1092, 1012, 818; HRMS (ESI), calcd. for $C_{16}H_{16}ClS$ [M-H^+]: 275.0661, found: 275.0670.

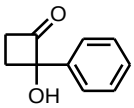


(***E/Z*)-(4-chlorophenyl)(1-phenylbut-2-en-2-yl)sulfane 5a.** ^1H and ^{13}C NMR were extracted from a *E/Z* mixture of isomers **5**. ^1H NMR (600 MHz, $CDCl_3$) Major (*Z*) δ : 7.42-7.04 (m, 9H), 5.97 (q, *J* = 6.7 Hz, 1H), 3.44 (s, 2H), 2.02-1.73 (m, 3H); ^1H NMR (600 MHz, $CDCl_3$) Minor (*E*) δ: 7.42-7.04 (m, 9H), 6.06 (q, *J* = 7.0 Hz, 1H), 3.52 (s, 2H), 2.02-1.73 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) (*E/Z* mixture) δ: 138.94, 138.76, 136.67, 134.01, 133.92, 133.51, 133.08, 133.04, 132.72, 132.42, 130.97, 129.50, 129.10, 128.67, 128.41, 126.53, 126.44, 44.03, 36.57, 15.87, 15.32. HRMS (ESI), calcd. for $C_{16}H_{16}ClOS$: 275.0661 [M-H^+], found: 275.1039.



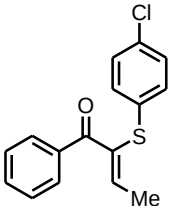
1-Phenyl-butane-1,2-dione 6a

^1H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 2.90 (q, *J* = 7.3 Hz, 2H), 1.18 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 203.8, 192.4, 132.0, 130.0, 128.7, 32.0, 6.8. Yellow oil. Spectral data are in agreement with the literature.[13]

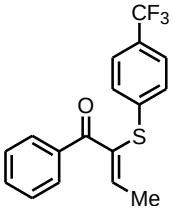


2-Hydroxy-2-phenyl-cyclobutanone 7a. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.65-7.22 (m, 5H), 3.66 (s, 1H), 3.02-2.91 (m, 2H), 2.74-2.63 (m, 1H), 2.36 (dd, *J* = 22.1, 10.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 209.2, 138.8, 129.0, 128.8, 126.1, 92.6, 41.0, 28.0. Spectral data are in agreement with the literature.[13]

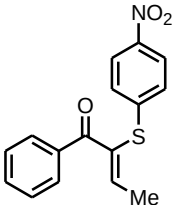
13.Synthesis and characterization of enones 3.



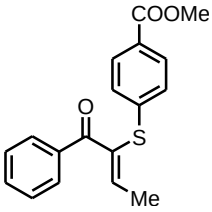
(*Z*)-2-((4-chlorophenyl)thio)-1-phenylbut-2-en-1-one 3aa. 1-phenyl-butine (50 mg, 0.38 mmol), *p*-chlorothiophenol (99 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3 mL). Flash chromatography *Rf* = 0.3 (petroleum ether/EtOAc 7:1), yield 72% (79 mg**),** yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.69 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.18-7.14 (m, 3H), 6.84 (q, *J* = 6.9 Hz, 1H), 2.14 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.8, 145.1, 137.3, 136.6, 132.9, 132.8, 132.5, 131.2, 129.4, 129.1, 128.3, 77.1, 16.5; FTIR (film) cm^{-1} ν: 2969, 2906, 2872, 1705, 1660, 1477, 1260, 1090, 1010, 815, 698; HRMS (ESI): calcd. for $C_{16}H_{14}ClOS$ [M-H^+]: 289.0448, found: 289.0448.



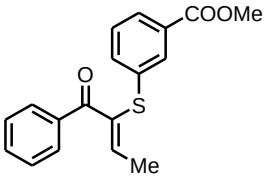
(*Z*)-1-phenyl-2-((4-(trifluoromethyl)phenyl)thio)but-2-en-1-one 3ab. 1-phenyl-butine (50 mg, 0.38 mmol) 4-(trifluoromethyl)benzenethiol (137.19 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3mL). Flash chromatography, *Rf* = 0.5 (petroleum ether/Et_2O 5:1), yield 51% (63 mg), colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.72 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H) (m, 1H), 7.45-7.40 (m, 4H), 7.34-7.28 (m, 2H), 7.03 (q, *J* = 6.9 Hz, 1H), 2.17 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.6, 148.0, 141.2-139.2 (m), 137.2, 135.2, 132.7, 130.0, 129.5, 128.4, 128.4, 125.9 (q, *J* = 3.8 Hz), 16.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ: - 62.59; FTIR (film), cm^{-1} ν: 3260, 2967, 1657, 1606, 1599, 1438, 1406, 1336, 1249, 1125, 1066, 829; HRMS (ESI): calcd. for $C_{17}H_{14}F_3OS$ [M-H$^+$]: 323.0712, found: 323.0709.



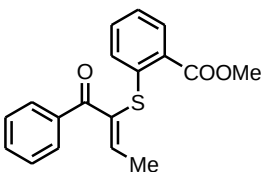
(*Z*)-2-((4-nitrophenyl)thio)-1-phenylbut-2-en-1-one 3ac. 1-phenyl-butine (50 mg, 0.38 mmol), *p*-nitrothiophenol (120 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3 mL). Flash chromatography *Rf* = 0.3 (petroleum ether/EtOAc 7:1), yield 71% (82 mg), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.12-8.00 (m, 2H), 7.78-7.70 (m, 2H), 7.56 (ddt, *J* = 7.9, 7.0, 1.3 Hz, 1H), 7.48-7.41 (m, 2H), 7.36-7.26 (m, 2H), 7.16 (q, *J* = 6.9 Hz, 1H), 2.18 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.28, 150.12, 145.87, 145.12, 136.93, 134.18, 132.93, 129.55, 128.59, 127.59, 124.21, 17.08; FTIR (film), cm^{-1} ν: 1660 1579 1511 1335 1260 1084 852 745 716; HRMS (ESI): calcd. for $C_{16}H_{14}NO_3S$ [M-H$^+$]: 300.0689, found: 300.0685.



(*Z*)-methyl-4-((1-oxo-1-phenylbut-2-en-2-yl)thio)benzoate 3ad. 1-phenyl-butine (50 mg, 0.38 mmol) methyl-4-mercaptobenzoato (129.5 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3mL). Flash chromatography, *Rf* = 0.3 (petroleum ether/Et_2O 5:1), yield 55 % (66 mg) colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.89-7.82 (m, 2H), 7.75-7.69 (m, 2H), 7.56-7.49 (m, 1H), 7.44-7.39 (m, 2H), 7.25 (m, 2H), 7.03 (q, *J* = 6.9 Hz, 1H), 3.87 (s, 3H), 2.15 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): 193.8, 166.4, 146.4, 137.5, 136.4, 135.5, 133.8, 132.5, 131.0, 130.4, 129.5, 129.1, 128.3, 127.8, 52.3, 16.7; FTIR (film), cm^{-1} ν: 3062, 2953, 1718, 1662, 1541, 1462, 1440, 1310, 1241, 1118, 1068, 962, 756, 712; HRMS (ESI): calcd. for $C_{18}H_{17}O_3S$ [M-H+]: 313.0893, found: 313.0891.

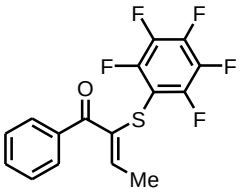


(*Z*)-methyl-3-((1-oxo-1-phenylbut-2-en-2-yl)thio)benzoate 3ae. 1-phenyl-butine (50 mg, 0.38 mmol) methyl-3-mercaptobenzoato (129.5 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3mL). Flash chromatography, *Rf* = 0.3 (petroleum ether/Et_2O 5:1), yield 53% (64 mg), colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (t, *J* = 1.8 Hz, 1H), 7.79 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.74-7.68 (m, 2H), 7.54-7.47 (m, 1H), 7.45 (ddd, *J* = 7.9, 2.1, 1.1 Hz, 1H), 7.43-7.36 (m, 2H), 7.31-7.26 (m, 1H), 6.92 (q, *J* = 6.9 Hz, 1H), 3.87 (s, 3H), 2.16 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.8, 166.4, 146.4, 137.5, 136.4, 135.5, 133.8, 132.5, 131.0, 130.4, 129.5, 129.1, 128.3, 127.8, 52.3, 16.7; FTIR (film), cm^{-1} ν: 3062, 2969, 2871, 1665, 1603, 1526, 1456, 1419, 1308, 1232, 1126, 1074, 992, 945 758 721; HRMS (ESI): calcd. for $C_{18}H_{17}O_3S$ [M-H$^+$]: 313.0898, found: 313.0890.

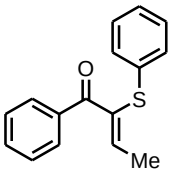


(*Z*)-methyl-2-((1-oxo-1-phenylbut-2-en-2-yl)thio)benzoate 3af. 1-phenyl-butine (50 mg, 0.38 mmol) 2-methyl thiosalicylate (129.5 mg, 0.77 mmol), eosin B (9.6

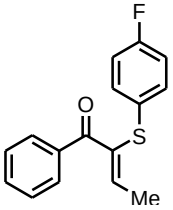
mg, 4% mol), acetonitrile (3mL). Flash chromatography, *Rf* = 0.3 (petroleum ether/Et_2O 5:1), yield 66% (62.3 mg), colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.88 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.53-7.46 (m, 1H), 7.42-7.34 (m, 2H), 7.32 (td, *J* = 7.6, 7.2, 1.5 Hz, 1H), 7.27-7.21 (m, 1H), 7.16-7.05 (m, 2H), 3.90 (s, 3H), 2.16 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.50, 166.76, 148.90, 139.61, 137.23, 135.93, 132.46, 131.37, 129.51, 128.27, 128.02, 127.79, 125.45, 124.94, 52.25, 16.70; FTIR (film), cm^{-1} ν: 3061, 2949, 1712, 1658, 1539, 1463, 1433, 1247, 1108, 1053, 959, 741, 701, 659; HRMS (ESI): calcd. for $C_{18}H_{17}O_3S$ [M-H$^+$]: 313.0898, found: 313.0891.



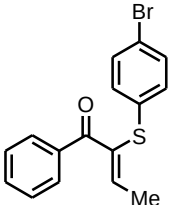
(*Z*)-1-phenyl-2-((4-(trifluoromethyl)phenyl)thio)but-2-en-1-one 3ag. 1-phenyl-butine (50 mg, 0.38 mmol) 2,3,4,5,6-Pentafluorothiophenol (154.1 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3mL). Flash chromatography, *Rf* = 0.5 (petroleum ether/Et_2O 5:1), yield 49% (mg 60), colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75-7.69 (m, 2H), 7.55-7.52 (m, 1H), 7.45-7.40 (m, 4H), 7.34-7.28 (m, 2H), 7.03 (q, *J* = 6.9 Hz, 1H), 2.17 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.3, 148.0, 139.2, 136.7, 134.7, 134.6, 132.3, 131.5, 131.4, 131.0, 130.5, 18.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -132.11 – -135.02 (m), -152.52 – -152.89 (m), -160.97 – -161.21 (m); FTIR (film), cm^{-1} ν: 3435, 2361, 2339, 1655, 1637, 1514, 1489, 1261, 1088, 979, 856, 805; HRMS (ESI): calcd. for $C_{16}H_{10}F_5OS$ [M-H$^+$]: 345.0372, found: 345.0528.



(*Z*)-1-phenyl-2-(phenylthio)but-2-en-1-one 3ah. 1-phenyl-butine (50 mg, 0.38 mmol) thiophenol (99mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3mL). Flash chromatography, *Rf* = 0.3 (petroleum ether/Et_2O 10:1), yield 37% (35 mg), colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.73-7.65 (m, 2H), 7.51-7.47 (m, 1H), 7.41-7.35 (m, 2H), 7.25-7.21 (m, 2H), 7.21-7.14 (m, 2H), 7.14-7.10 (m, 1H), 6.84 (q, *J* = 6.9 Hz, 1H), 2.14 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.1, 144.5, 137.5, 137.0, 134.4, 132.4, 129.9, 129.4, 129.0, 128.2, 126.7, 16.5; FTIR (film), cm^{-1} ν: 3058, 1718, 1662, 1597, 1477, 1437, 1260, 742; HRMS (ESI): calcd. for $C_{16}H_{15}OS$ [M-H$^+$]: 255.0838, found: 255.0835.

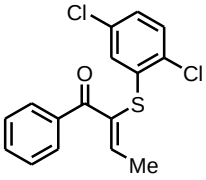


(Z)-2-((4-fluorophenyl)thio)-1-phenylbut-2-en-1-one 3ai. 1-phenyl-butine (50 mg, 0.38 mmol) *p*-fluorotiophenol (99mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3mL). Flash chromatography, *Rf* = 0.7 (petroleum ether/Et_2O 10:1), yield 40% (42 mg) colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.72-7.66 (m, 2H), 7.55-7.48 (m, 1H), 7.41-7.37 (m, 2H), 7.34-7.27 (m, 2H), 7.15-7.05 (m, 2H), 6.86 (q, *J* = 6.9 Hz, 1H), 2.14 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.0, 162.1 (d, *J* = 247.2 Hz), 143.2, 137.5, 137.4, 132.9 (d, *J* = 8.1 Hz), 132.5, 129.4, 128.6, 128.3, 116.2 (d, *J* = 22.1 Hz), 16.42; FTIR (film), cm^{-1} ν: 1660, 1597, 1477, 1437, 1260, 742, 713, 695; HRMS (ESI): calcd. for $C_{16}H_{14}FOS$ [M-H$^+$]: 273.0744 found: 273.0738.

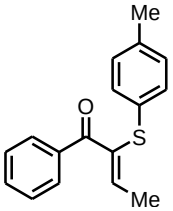


(*Z*)-2-((4-bromophenyl)thio)-1-phenylbut-2-en-1-one 3aj. 1-phenyl-butine (50 mg, 0.38 mmol) (50 mg, 0.38 mmol), *p*-bromothiophenol (144mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3mL). Flash chromatography, *Rf* = 0.3 (petroleum ether/Et_2O

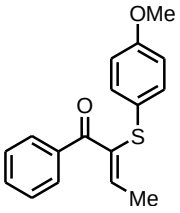
10:1), yield 58% (74 mg), colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 8.0, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.86 (q, *J* = 6.9 Hz, 1H), 2.14 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.8, 145.4,137.3, 136.5, 132.6, 132.1, 131.4, 129.4, 128.3, 16.6; FTIR (film), cm^{-1} ν: 1660, 1600, 1471, 1257, 1087, 1066, 1009, 810, 695, 475; HRMS (ESI): calcd for $C_{16}H_{14}BrOS$ [M-H$^+$]: 332.9943, found: 332,9915.



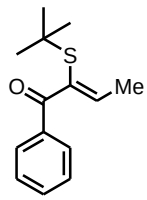
(*Z*)-2-((2,5-dichlorophenyl)thio)-1-phenylbut-2-en-1-one 3ak. 1-phenyl-butine (50 mg, 0.38 mmol) 2,5-dichlorobenzenethiol (137 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3mL). Flash chromatography, *Rf* = 0.4 (petroleum ether/Et_2O 10:1), yield 59% (73 mg)**,** colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.72 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.47-7.39 (m, 2H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.07 (q, *J* = 6.9 1H), 7.04 (dd, *J* = 8.5, 2.5 Hz, 1H), 2.17 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.3, 149.1, 137.2, 135.9, 134.8, 133.0, 132.6, 131.9, 130.7, 129.5, 129.5, 128.4, 127.5, 16.9; FTIR (film), cm^{-1} ν: 3062, 2952, 2919, 1665, 1603, 1570, 1449, 1256, 1095, 1030, 800; HRMS (ESI): calcd. for $C_{16}H_{13}Cl_2OS$ [M-H$^+$]: 323.0059, found: 323.0056.



(*Z*)-1-phenyl-2-(p-tolylthio)but-2-en-1-one 3al. 1-phenyl-butine (50 mg, 0.38 mmol) p-methyl thiophenol (99mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), pyridine (25%mmol, 7.6mg 0.09625 mmol,) acetonitrile (3mL). Flash chromatography, *Rf* = 0.3 (petroleum ether/Et_2O 10:1), yield 45% (46 mg), colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.77-7.66 (m, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.74 (q, *J* = 6.9 Hz, 1H), 2.25 (s, 3H), 2.13 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.2, 143.2, 137.6, 137.6, 136.9, 132.4, 130.6, 130.5, 129.8, 129.5, 128.2, 21.1, 16.4; FTIR (film), cm^{-1} ν: 3100, 3030, 2920, 2836, 2601, 2449, 1654, 1602, 1580, 1508, 1336, 1260, 1179, 1084, 851, 737, 679; HRMS (ESI): calcd. for $C_{17}H_{17}OS$ [M-H$^+$]: 269.0995, found: 269.0993.

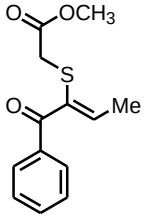


(*Z*)-2-((4-methoxyphenyl)thio)-1-phenylbut-2-en-1-one 3am. 1-phenyl-butine (50 mg, 0.38 mmol) p-methoxy thiophenol (99mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), pyridine (25%mmol, 7.6mg 0.09625 mmol,) acetonitrile (3mL). Flash chromatography, *Rf* = 0.4 (petroleum ether/Et_2O 5:1), 38% (42 mg), colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.71 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.50 (td, *J* = 7.2, 1.4 Hz, 1H), 7.41-7.33 (m, 2H), 7.09 (t, *J* = 8.0 Hz, 1H) 6.85 (q, *J* = 6.9 Hz, 1H), 6.78 – 6.74 (m, 1H), 6.71-6.61 (m, 2H), 3.70 (s, 3H), 2.14 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.1, 159.9, 144.9, 133.3, 132.4, 129.5, 128.7, 128.2, 121.9, 114.8, 112.8, 55.4, 16.60; FTIR (film), cm^{-1} ν: 3062, 3002, 2937, 2835, 1663, 1589, 1575, 1478, 1425, 1283, 1247, 1040, 860, 776, 688; HRMS (ESI): calcd. for $C_{17}H_{18}OS$ [M-H$^+$]: 285.0949, found: 285.0935.

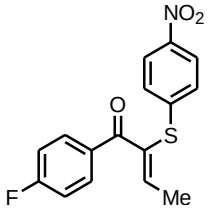


(*Z*)-2-(tert-butylthio)-1-phenylbut-2-en-1-one 3an. 1-phenyl-butine (50 mg, 0.38 mmol) *tert*-butylthiol (68.5 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3mL). Flash chromatography, *Rf* = 0.3 (petroleum ether/Et_2O 95:1), 65% (59 mg), colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83-7.77 (m, 2H), 7.57-7.49 (m, 1H), 7.46-7.42 (m, 2H), 6.96 (q, *J* = 6.8 Hz, 2H), 2.15 (d, *J* = 6.8 Hz, 3H), 1.29 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 197.0,

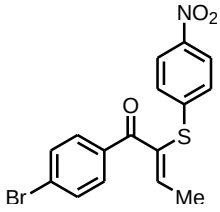
149.2, 137.4, 136.1, 132.4, 130.0, 128.3, 48.3, 31.5, 17.0; FTIR (film), cm^{-1} ν: 3064, 2965, 2927, 2860, 1727, 1662, 1603, 1598, 1455, 1365, 1252, 1165, 1023, 871, 800, 716, 710; HRMS (ESI): calcd. for $C_{14}H_{19}OS$ [M-H^+]: 235.1156, found: 235.1147.



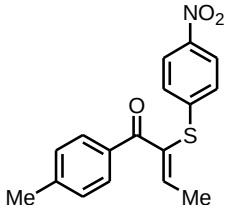
(*Z*)-methyl-2-((1-oxo-1-phenylbut-2-en-2-yl)thio)benzoate 3ao. 1-phenyl-butine (50 mg, 0.38 mmol) methylthyoglicolate (80.66 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3mL). Flash chromatography, *Rf* = 0.3 (petroleum ether/Et_2O 5:1), yield 58% (56 mg), colourless oil. ^{1}H NMR (500 MHz , $CDCl_3$) δ: 7.75 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 6.64 (q, *J* = 6.9 Hz, 1H), 3.65 (s, 3H), 3.51 (s, 2H), 2.08 (d, J = 6.9 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.6, 170.3, 145.5, 137.9, 136.4, 132.4, 129.9, 128.3, 52.4, 33.2, 16.4; FTIR (film), cm^{-1} ν: 3060, 2952, 2848, 1736, 1656, 1597, 1578, 1447, 1436, 1374, 1265, 1128, 1009, 818, 713, 665. HRMS (ESI): calcd. for $C_{13}H_{15}O_3S$ [M-H^+]: 251.0741, found: 251.0733.



(*Z*)-1-(4-fluorophenyl)-2-((4-nitrophenyl)thio)but-2-en-1-one 3bc. 1-(but-1-yn-1-yl)-4-fluorobenzene (56 mg, 0.38 mmol), *p*-nitrothiophenol (120 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3 mL). Flash chromatography *Rf* = 0.4 (petroleum ether/Et_2O 1:1), yield 48% (58 mg), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): 8.09-8.03 (m, 2H), 7.78 (ddd, *J* = 10.0, 5. 3, 2.5 Hz, 2H), 7.32-7.28 (m, 2H), 7.14-7.09 (m, 3H), 2.18 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.3, 168.1 (d, *J* = 255.0 Hz), 151.7, 147.2, 136.3, 135.4 (d, *J* = 3.1 Hz), 134.7 (d, *J* = 9.2 Hz), 130.2, 129.0, 127.0, 126.7, 118.2 (d, *J* = 22.0 Hz), 19.4; FTIR (film), cm^{-1} ν: 3100, 3295, 2849, 1715, 1662, 1597, 1579, 1505, 1335, 1249, 1158, 1084, 847, 742; HRMS (ESI): calcd. for $C_{16}H_{13}FNO_3S$ [M-H^+]: 318.0595, found: 318.0591.

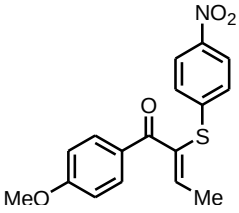


(*Z*)-1-(4-bromophenyl)-2-((4-nitrophenyl)thio)but-2-en-1-one 3cc. 1-(but-1-yn-1-yl)-4-bromobenzene (79 mg, 0.38 mmol), *p*-nitrothiophenol (120 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3 mL). Flash chromatography *Rf* = 0.5 (petroleum ether/Et_2O 1:1), yield 56% (81 mg), yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.08-8.05 (m, 2H), 7.62-7.57 (m, 4H), 7.30-7.27 (m, 2H), 7.13 (q, *J* = 6.9 Hz, 1H), 2.18 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.7, 166.7, 148.0, 141.6, 137.2, 135.3, 132.6, 130.2, 130.2, 129.5, 128.4, 127.8, 52.2, 16.9; FTIR (film), cm^{-1} ν: 3433, 3080, 2450, 2238, 1656, 1575, 1583, 1510, 1334, 1257, 1066, 1008, 848, 744, 664; HRMS (ESI): calcd. for $C_{16}H_{13}BrNO_3S$ [M-H^+]: 377,9799, found: 377.9803.

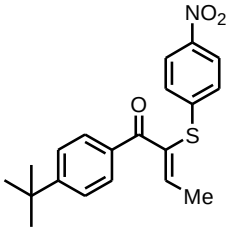


(*Z*)-2-((4-nitrophenyl)thio)-1-(p-tolyl)but-2-en-1-one 3dc. 1-(but-1-yn-1-yl)-4-methylbenzene (55 mg, 0.38 mmol), *p*-chlorothiophenol (120 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3 mL). Flash chromatography *Rf* = 0.5 (petroleum ether/Et_2O 5:1), 55% (56 mg) yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.06 (dq, *J* = 9.6, 2.6, 2.1 Hz, 2H), 7.70-7.64 (m, 2H), 7.32 (dq, *J* = 9.6, 2.6, 2.1 Hz, 2H), 7.29-7.21 (m, 2H), 7.10 (q, *J* = 6.9 Hz, 1H), 2.41 (s, 3H), 2.16 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 192.9, 149.1, 145.8, 145.2, 143.9, 134.1, 134.0, 129.8, 129.3, 129.2, 127.5, 124.1, 21.8,

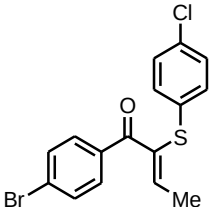
16.9; FTIR (film), cm^{-1} n: 3100, 3030, 2836, 2601, 2447, 1654, 1602, 1579, 1508, 1334, 1260, 1179, 1084, 852, 737. HRMS (ESI): calcd for $C_{17}H_{16}NO_3S^+$: 314.0843 (M+-H+), found: 314.0845.



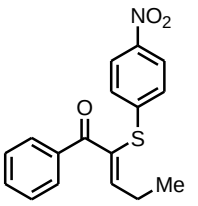
(*Z*)-1-(4-methoxyphenyl)-2-((4-nitrophenyl)thio)but-2-en-1-one 3ec. 1-(but-1-yn-1-yl)-4-methoxybenzene (60.9 mg, 0.38 mmol), *p*-nitrothiophenol (120 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3 mL). Flash chromatography *Rf* = 0.4 (petroleum ether/Et_2O 1:1), 74% (93 mg)**,** yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ: 8.05 (d, *J* = 8.9 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 9.1 Hz, 2H), 7.05 (q, *J* = 6.9 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H), 2.16 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 192.0, 163.7, 147.7, 145.8, 145.2, 133.8, 132.1, 132.0, 129.2, 127.6, 124.1, 113.9, 77.1, 55.6, 16.8; FTIR (film), cm^{-1} ν: 3100, 2972, 2841, 1649, 1597, 1576, 1511, 1335, 1254, 1171, 1087, 1027, 844, 745. HRMS (ESI): calcd. for $C_{17}H_{16}NO_4S$ [M-H^+]: 330,0795, found: 330.0791.



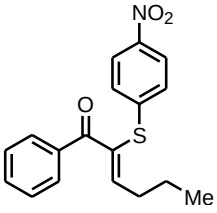
(*Z*)-1-(4-tert-butylphenyl)-2-((4-nitrophenyl)thio)but-2-en-1-one 3fc. 1-(but-1-yn-1-yl)-4-(tert-butyl)benzene (71 mg, 0.38 mmol), *p*-nitrothiophenol (120 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3 mL). Flash chromatography Rf = 0.4 (petroleum ether/Et2O 1:1), yield 50% (58 mg), yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.50-7.44 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.13 (q, *J* = 6.9 Hz, 1H), 2.17 (d, *J* = 6.9 Hz, 3H), 1.34 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 192.9, 178.7, 149.5, 134.1, 129.6, 127.5, 126.5, 125.6, 124.6, 124.2, 35.3, 31.2, 17.0; FTIR (film), cm^{-1} ν: HRMS (ESI): calcd. for $C_{20}H_{22}NO_3S$ [M-H^+]: 356.1320 found: 356.1329.



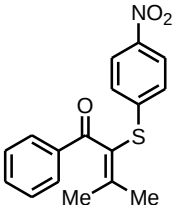
(*Z*)-1-(4-Bromo-phenyl)-2-(4-chloro-phenylsulfanyl)-but-2-en-1-one 3ca. 1-bromo-4-(but-1-yn-1-yl)benzene (71 mg, 0.38 mmol), *p*-chorothiophenol (110 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3 mL). Flash chromatography *Rf* = 0.4 (petroleum ether/Et_2O 1:1), yield 56% (79 mg), yellow oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.57-7.51 (m, 4H), 7.17-7.12 (m, 4H), 6.82 (d, *J* = 6.9 Hz, 1H), 2.14 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 192.8, 144.8, 136.3, 136.0, 133.1, 132.6, 131.6, 131.4, 130.9, 129.3, 127.7, 16.5; FTIR (film), cm^{-1} ν: 2969, 2904, 2871, 1706, 1662, 1479, 1262, 1092, 1011, 812, 696. HRMS (ESI): calcd. for $C_{16}H_{13}BrClNaOS$ [M-Na-H^+]: 389.94567, found: 389.9424.



(*Z*)-2-((4-nitrophenyl)thio)-1-phenylpent-2-en-1-one 3gc. pent-1-yn-1-ylbenzene (55 mg, 0.38 mmol), *p*-nitrothiophenol (120 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3 mL). Flash chromatography *Rf* = 0.4 (petroleum ether/Et_2O 1:1), yield 40% (48 mg), yellow oil. ^1H NMR (600 MHz $CDCl_3$) δ: 8.01-7.88 (m, 2H), 7.71-7.57 (m, 2H), 7.45 (td, *J* = 7.3, 1.4 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 2.50 (p, *J* = 7.5 Hz, 2H), 1.04 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 193.2, 156.4, 145.7, 145.3, 136.8, 132.8, 132.1, 129.4, 128.4, 127.4, 124.0, 24.5, 12.9; FTIR (film), cm^{-1} ν: 2973, 2874, 1660, 1591, 1580, 1518, 1342, 1269, 1242, 1168, 1112,1081, 1008, 909, 844, 729; HRMS (ESI): calcd. for $C_{18}H_{18}NO_3S$ [M-H^+]: 314,0845, found: 314.0841.

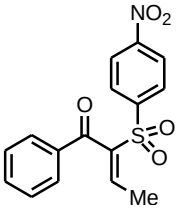


(*Z*)-2-((4-nitrophenyl)thio)-1-phenylhex-2-en-1-one 3hc. Hex-1-yn-1-ylbenzene (60 mg, 0.38 mmol), *p*-nitrothiophenol (120 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3 mL). Flash chromatography *Rf* = 0.4 (petroleum ether/Et_2O 1:1), yield 58% (72 mg), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 8.9 Hz, 2H), 7.79 – 7.69 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 2.58 (q, *J* = 7.3 Hz, 2H), 1.58 (q, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.2, 154.7, 145.2, 136.9, 133.1, 132.9, 129.5, 128.5, 127.7, 126.5, 124.6, 124.1, 33.1, 21.9, 14.1; FTIR (film), cm^{-1} ν: 3100, 2962, 2930, 2873, 1660, 1600, 1579, 1513, 1477, 1333, 1247, 1087, 854, 742 713; HRMS (ESI): calcd. for $C_{18}H_{18}NO_3S$ [M-H$^+$]: 328.1002, found: 328.0998.

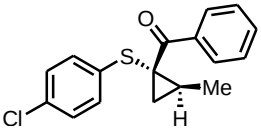


3-methyl-2-((4-nitrophenyl)thio)-1-phenylbut-2-en-1-one 3jc. (3-methylbut-1-yn-1-yl)benzene (55 mg, 0.38 mmol), *p*-nitrothiophenol (120 mg, 0.77 mmol), eosin B (9.6 mg, 4% mol), acetonitrile (3 mL). Flash chromatography *Rf* = 0.4 (petroleum ether/Et_2O 1:1), yield 45% (54 mg), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.12-8.03 (m, 2H), 7.87-7.78 (m, 2H), 7.58-7.55 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.40-7.34 (m, 2H), 2.20 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.0, 152.7, 145.6, 135.7, 133.7, 129.6, 128.8, 127.0, 126.5, 124.6, 124.1, 23.1, 22.5; FTIR (film), cm^{-1} ν: 3098, 3065, 2962, 2918, 2851, 1659, 1595, 1578, 1512, 1336, 1259, 1177, 1109, 1086, 1023, 852, 840, 742, 682; HRMS (ESI): calcd. for: $C_{17}H_{16}NO_3S$ [M-H$^+$]: 314.0845, found: 314.0841.

14.Synthesis and characterization of compounds 9-13.

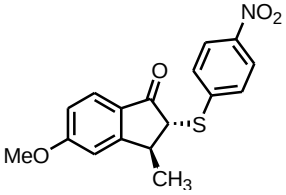


(*Z*)-2-((4-nitrophenyl)sulfonyl)-1-phenylbut-2-en-1-one 9. To an ice-cooled solution of **3ac** (150 mg, 0.5 mmol) in CH_2Cl_2 (30 mL), MCPBA (172 mg, 1 mmol) was added in small portions. The solution was stirred at room temperature for 12 h and then it was diluted with CH_2Cl_2 and washed with a saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the residue was chromatographed on silica gel. Flash chromatography *Rf* = 0.4 (AcOEt/Et_2O 1:1), gave the adduct **9** in 88 % yield (145 mg) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.26-8.16 (m, 2H), 7.77-7.71 (m, 2H), 7.62-7.56 (m, 3H), 7.39 (dd, *J* = 8.3, 7.4 Hz, 2H), 6.98 (q, *J* = 7.4 Hz, 1H), 1.81 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 192.2, 150.1, 149.6, 144.8, 137.2, 136.9, 134.5, 129.2, 129.1, 125.9, 124.3, 16.5; FTIR (film), cm^{-1} ν: 3061, 2245, 1665, 1549, 1583, 1514, 1449, 1341, 1048, 849, 740, 686; HRMS (ESI): calcd for $C_{16}H_{14}NO_5S$ [M-Na-H$^+$]: 355.0490 found: 355.0699.

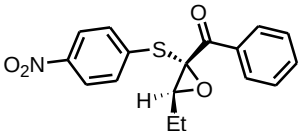


(1-((4-chlorophenyl)thio)-2-methylcyclopropyl)(phenyl)methanone 10. Trimethylsulfoxonium iodide (950 mg, 0.44 mmol 1.1 eq) was rapidly added to a stirred suspension of pentane-washed NaH (10.6 mg, 0.44 mmol, 60 % in mineral oil) in DMSO (0.5 mL) under an argon atmosphere. After keeping the reaction mixture at room temperature for 2 h, **3aa** (127 mg, 0.4 mmol) was added in 1 mL of DMSO and the reaction mixture was heated at 50 °C for 1 h. The mixture was diluted with diethyl ether, washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced

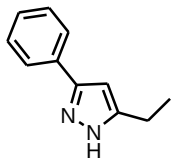
pressure and the crude product was purified by flash chromatography on silica gel. Rf = 0.4 (petroleum ether/Et_2O 10:1), yielding the adduct **10** in 65 % (79 mg) as colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.95-7.87 (m, 2H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.22-7.16 (m, 4H), 2.04 (dd, *J* = 9.1, 4.9 Hz, 1H), 1.93 (ddt, *J* = 13.4, 9.1, 6.2 Hz, 1H), 1.50 (d, *J* = 6.2 Hz, 3H), 1.03-0.99 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 198.3, 135.6, 134.9, 132.7, 131.8, 129.3, 129.1, 128.8, 128.3, 37.5, 23.1, 22.8, 14.2; HRMS (ESI): calcd. for $C_{17}H_{16}ClOS$ [M-H$^+$]: 303.0605, found : 303.0603.



(*trans*)-5-methoxy-3-methyl-2-((4-nitrophenyl)thio)-2,3-dihydro-1H-inden-1-one 11. $SnCl_2{\cdot}2H_2O$ (104mg, 0.46 mmol) was added to a solution of **3ec** (184mg, 0.55 mmol) in ethanol (5 mL). The resulting heterogeneous solution was refluxed and stirred for 4 h then the solvent was removed under reduced pressure. The residue was washed with $NaHCO_3$ aqueous solution (100 mL) and extracted with ethyl acetate. The organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (hexanes/EtOAc 2:1) Rf = 0.8, afforded the compound **11** in 91% (165 mg) as a white solid. Mp = 110-115 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.14-8.08 (m, 1H), 7.74 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.59-7.53 (m, 1H), 6.97 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.90-6.87 (m, 1H), 3.91 (s, 3H), 3.72 (dd, *J* = 4.7, 1.0 Hz, 1H), 3.32-3.25 (m, 1H), 1.56 (dd, *J* = 7.1, 1.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 199.0, 166.4, 159.2, 146.2, 145.3, 129.1, 127.6, 126.5, 124.0, 116.1, 108.5, 57.9, 55.9, 40.9, 19.7; FTIR (film), cm^{-1} ν: 3106, 3066, 2976, 2878, 2361, 1684, 1598, 1576, 1514, 1478, 1449, 1344, 1232, 1183, 1106, 1084, 1008, 1001, 936, 874, 845, 816, 780, 737, 679, 682, 675., 623; HRMS (ESI): calcd. for $C_{17}H_{16}NO_4S$ [M-H$^+$]: 330.0800, found: 330.0793.



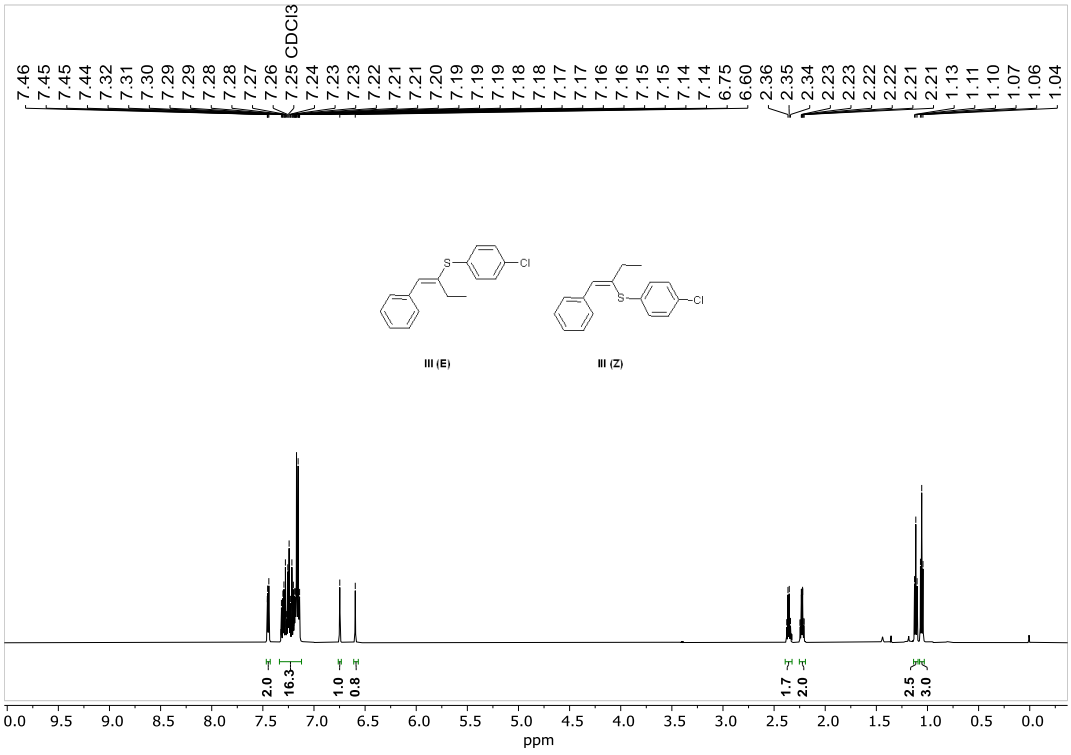
(3-ethyl-2-((4-nitrophenyl)thio)oxiran-2-yl)(phenyl)methanone 12. Hydrogen peroxide (0.8 mL, 30%, 7.5 equiv) was added in one portion to a stirred ethanol solution (3 mL) of enone **3fc** (323 mg 1.03 mmol). Then NaOH (10%, 1 mL) was added dropwise. After completion (1 h), addition of water caused the precipitation of a white solid which was purified by a flash chromatography (petroleum ether/AcOEt 5:1), *Rf* = 0,4 affording the oxirane **12** in 90% yield (305 mg) as a white solid. Mp = 120-122 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.02-7.95 (m, 2H), 7.86-7.73 (m, 2H), 7.52-7.45 (m, 3H), 7.38-7.31 (m, 2H), 3.32 (t, *J* = 6.2 Hz, 1H), 2.05-1.95 (m, 2H), 1.21-1.12 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 190.6, 146.9, 140.3, 134.0, 133.5, 130.9, 129.3, 128.6, 124.0, 71.6, 63.7, 22.4, 10.3; FTIR (film), cm^{-1} ν: 3106, 3066, 2976, 2878, 2361, 1684, 1598, 1576, 1514, 1478, 1449, 1344, 1232, 1183, 1106, 1084, 1008, 1001, 936, 874, 845, 816, 780, 737, 679, 682, 675, 623.

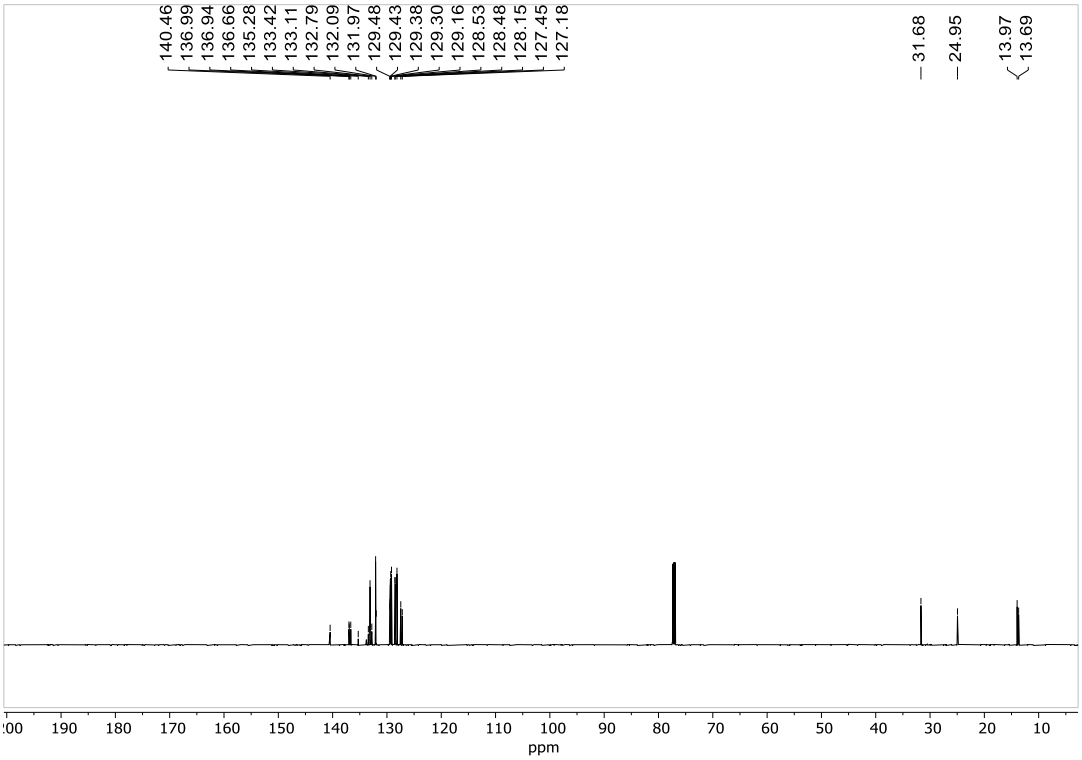


5-ethyl-3-phenyl-1H-pyrazole 13. (*Z*)-2-((4-nitrophenyl)thio)-1-phenylpent-2-en-1-one **3fc** (50 mg, 0.16 mmol) and hydrazine hydrate (0.32 mmol 2eq) were refluxed in EtOH (5mL) overnight. Extraction with EtOAc yielded the compound 13 in 78% (22 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.80 (s, 2H), 7.75-7.63 (m, 2H), 7.36-7.30 (m, 2H), 7.28-7.24 (m, 1H), 6.34 (s, 1H), 2.61 (qd, *J* = 7.6, 0.7 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 149.8, 149.5, 132.6, 128.7, 127.8, 125.8, 100.6, 19.8, 13.5. Spectroscopic data are in accordance with the literature[7].

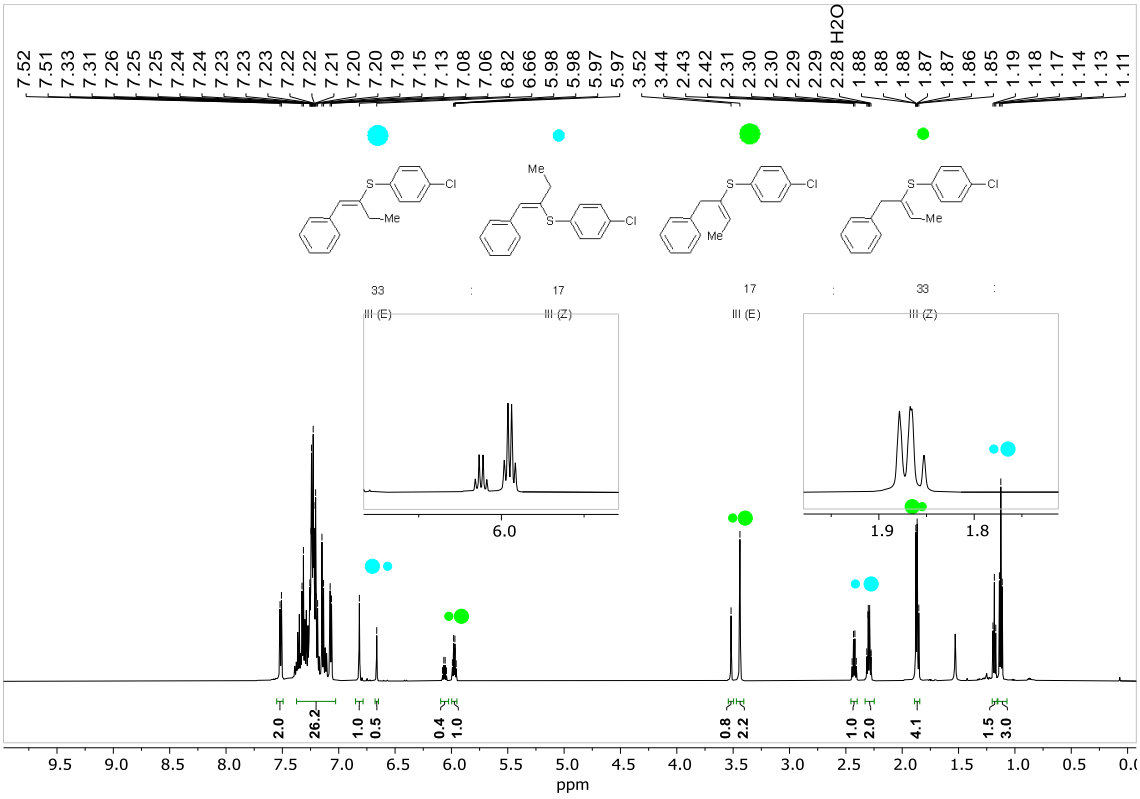
15. ^{1}H and ^{13}C NMR spectra of compounds 4a and 5a (mixtures of isomers)

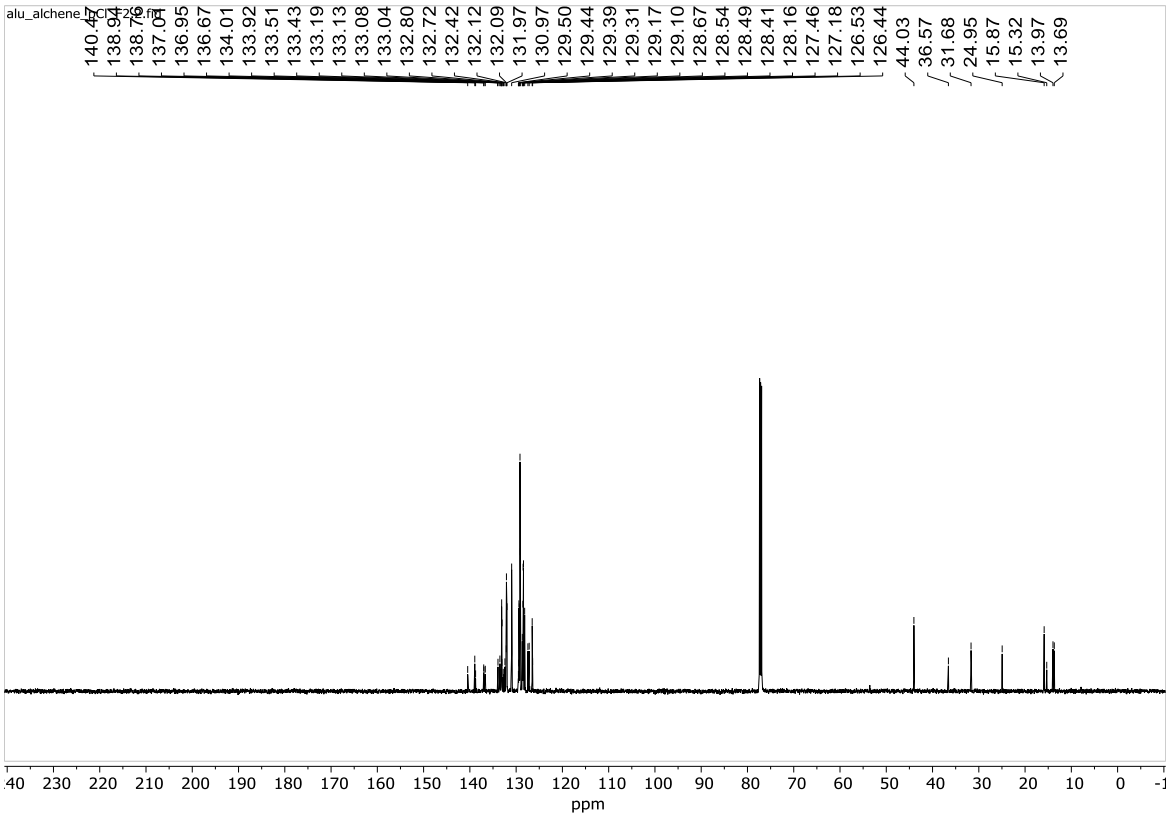
(4-chlorophenyl)(1-phenylbut-2-en-2-yl)sulfane (Isolated E : Z ratio = 54 : 46)





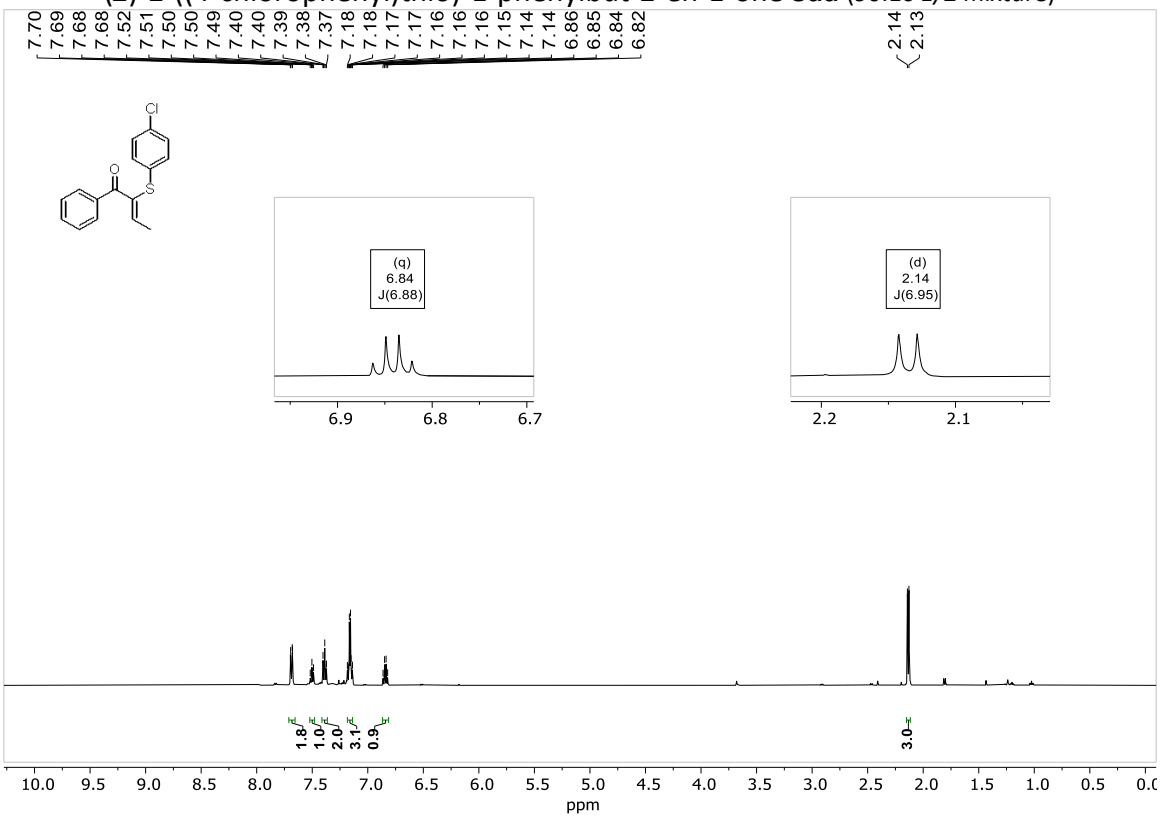
(4-chlorophenyl)(1-phenylbut-2-en-2-yl)sulfane (Isolated E : Z ratio = 33 : 17 : 17 : 33)

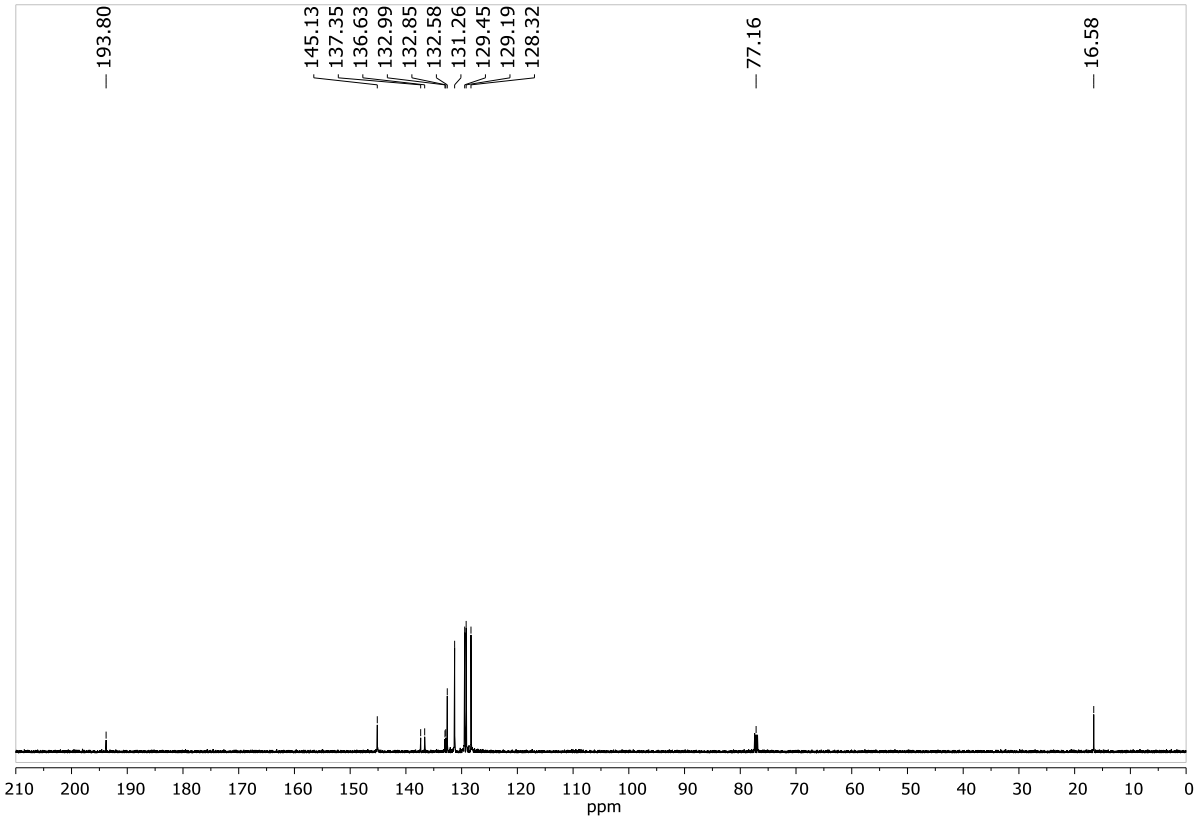




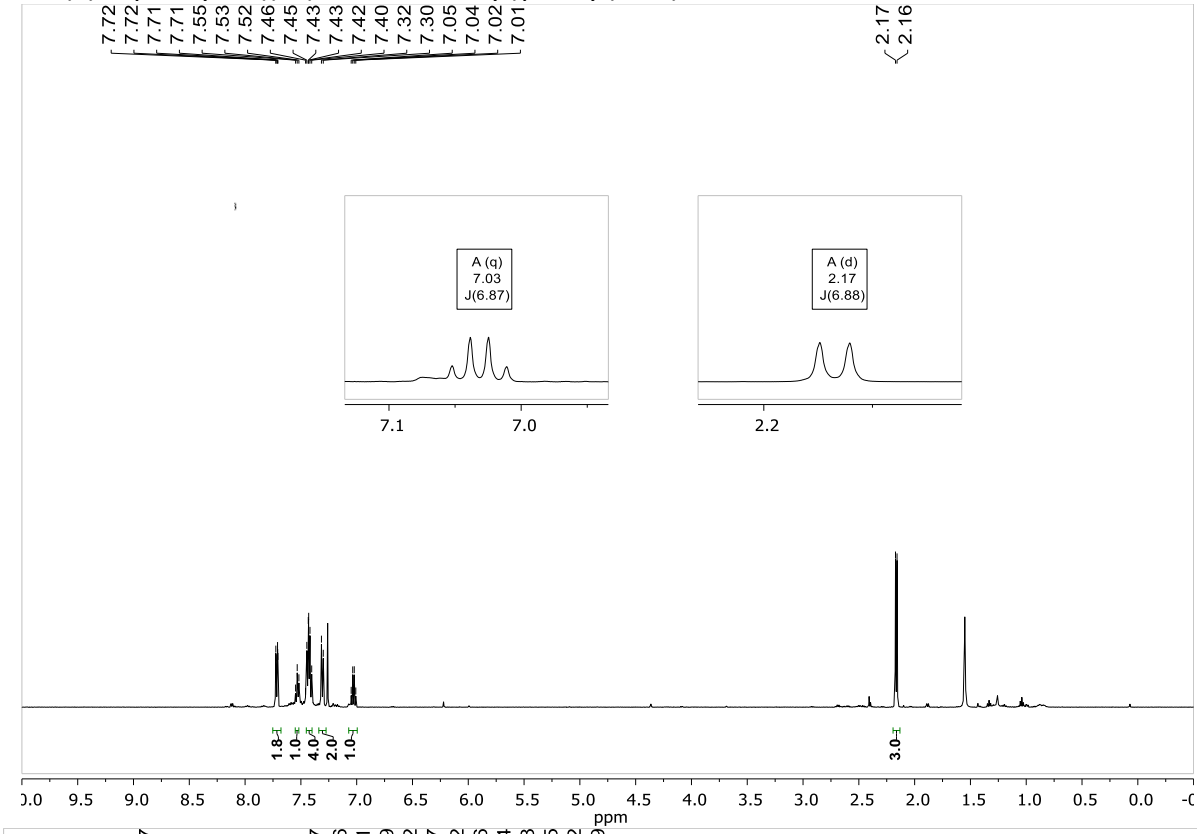
16. ^{1}H and ^{13}C NMR spectra of enones 3

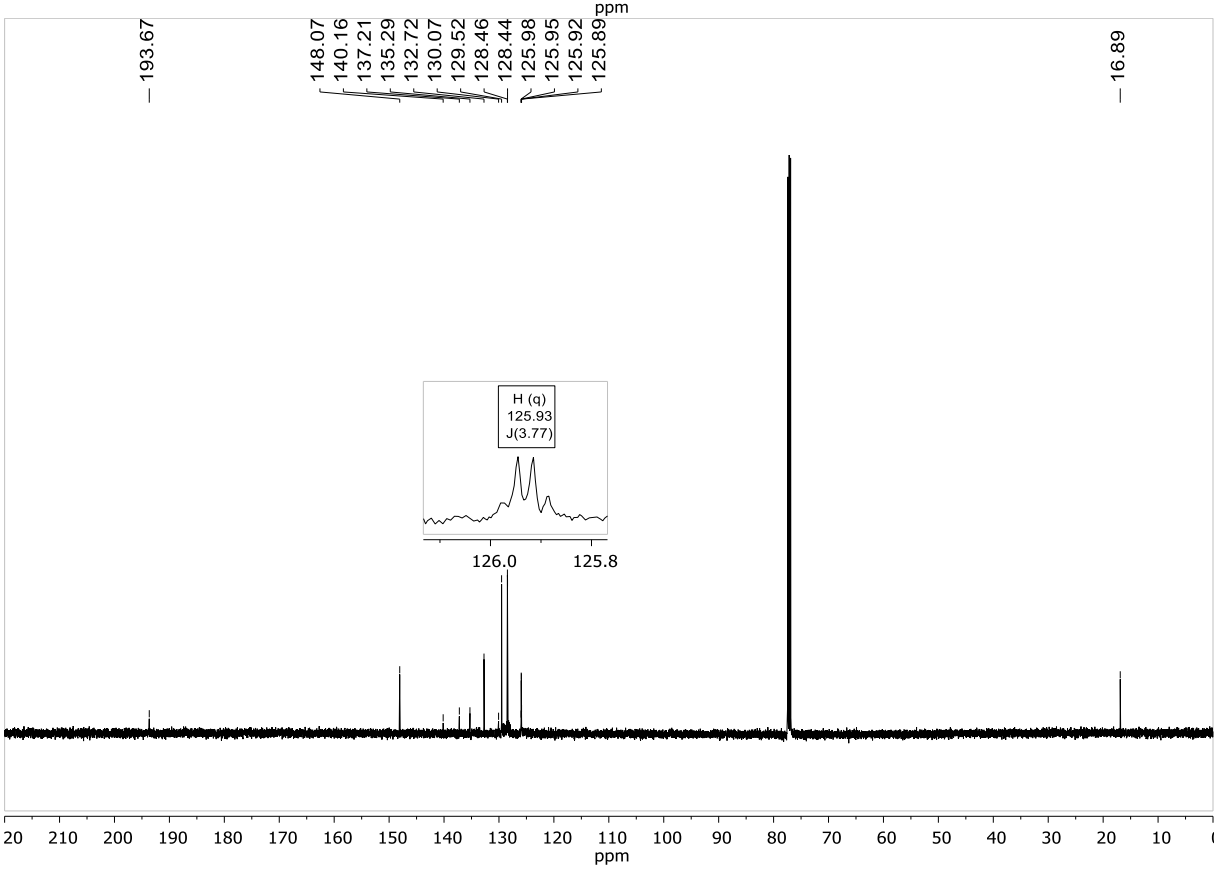
(*Z*)-2-((4-chlorophenyl)thio)-1-phenylbut-2-en-1-one **3aa** (90:10 *E/Z* mixture)



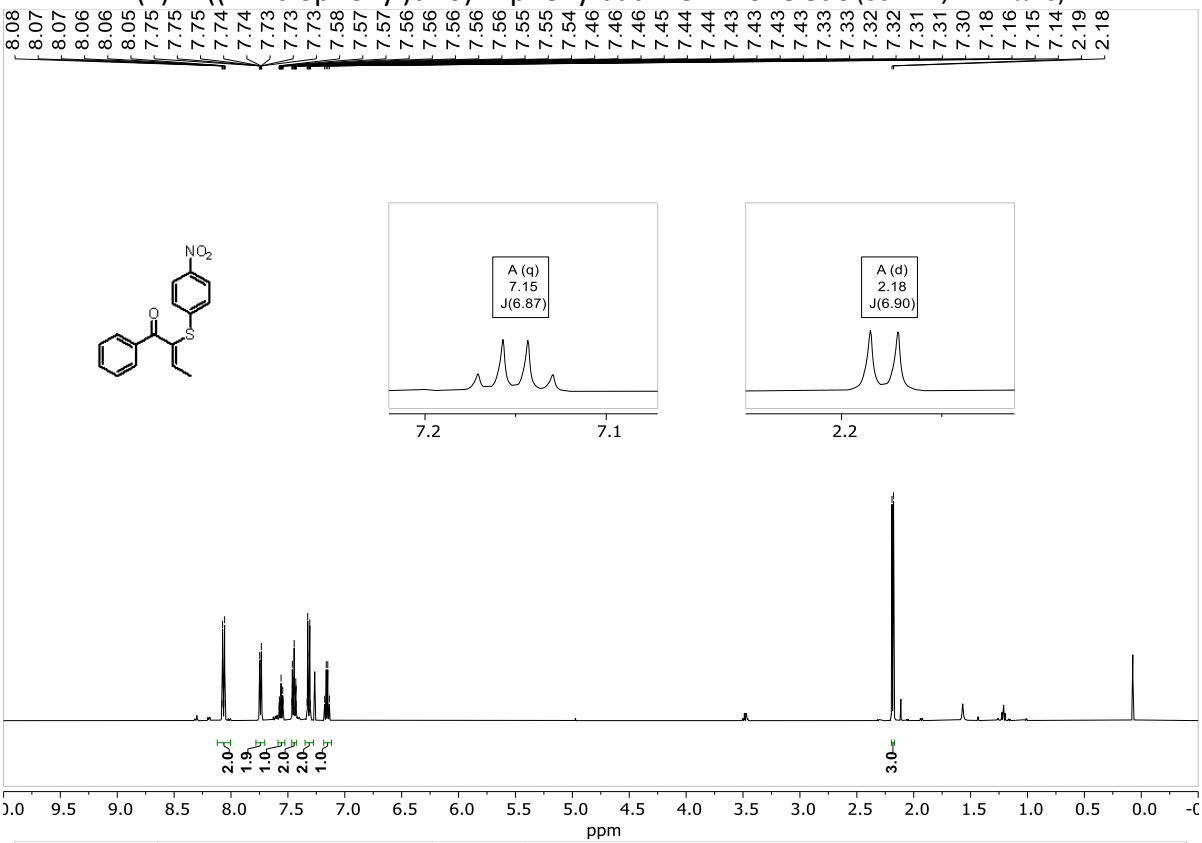


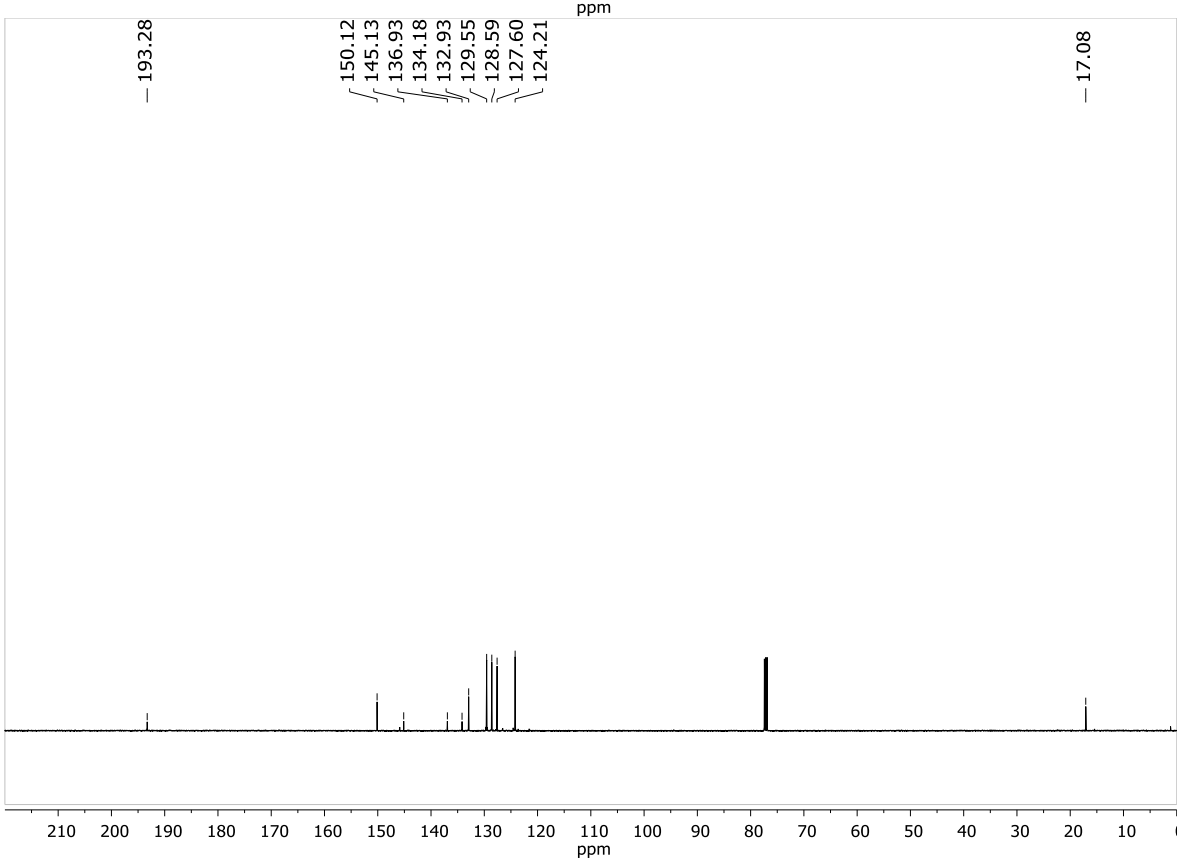
(*Z*)-1-phenyl-2-((4-(trifluoromethyl)phenyl)thio)but-2-en-1-one **3ab** (89:11 *E/Z* mixture)



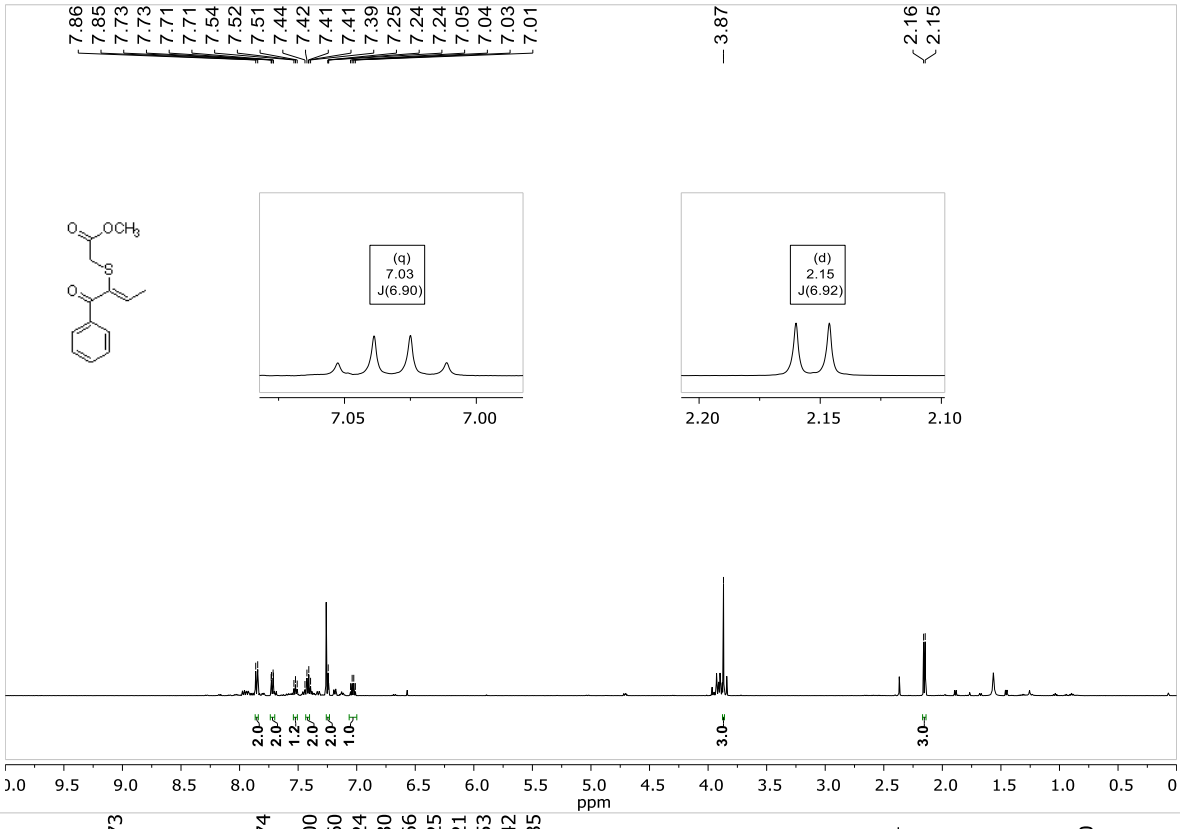


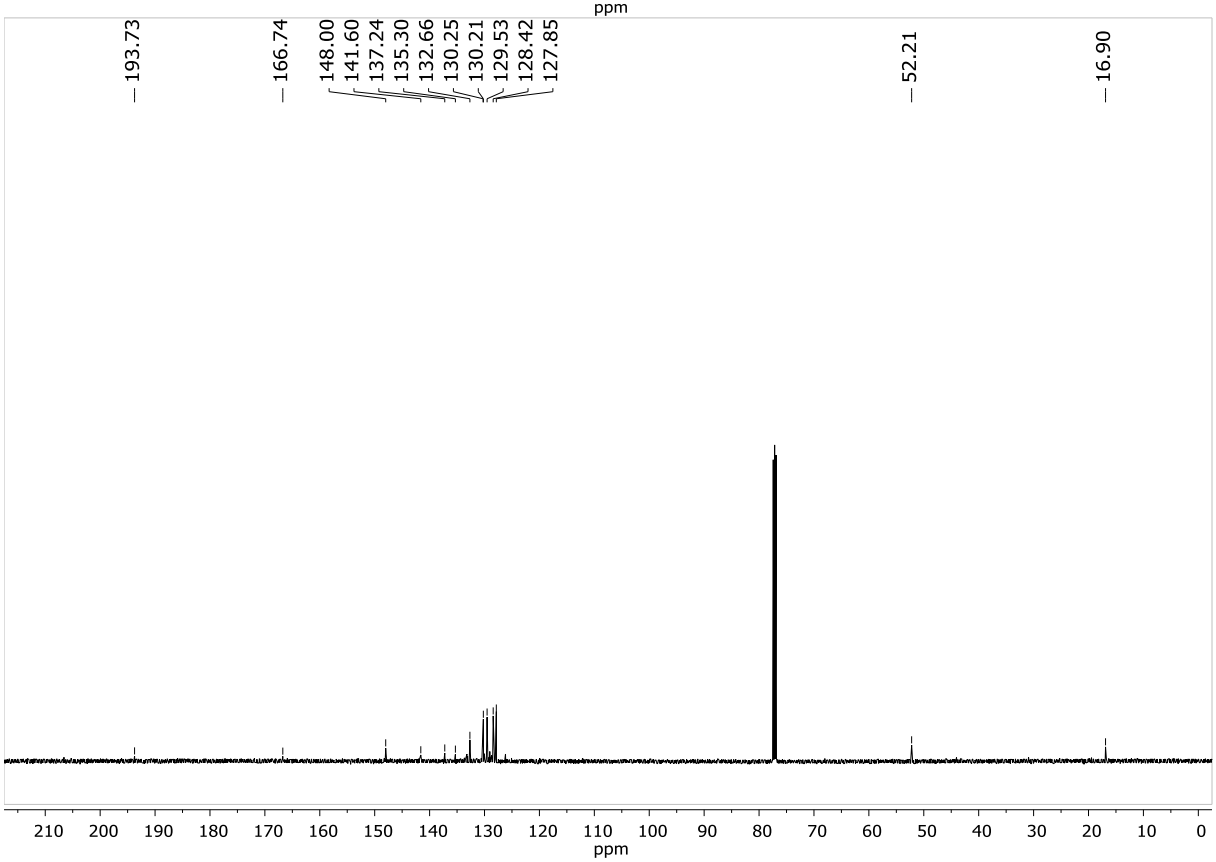
(*Z*)-2-((4-nitrophenyl)thio)-1-phenylbut-2-en-1-one **3ac** (88:12 *E/Z* mixture)



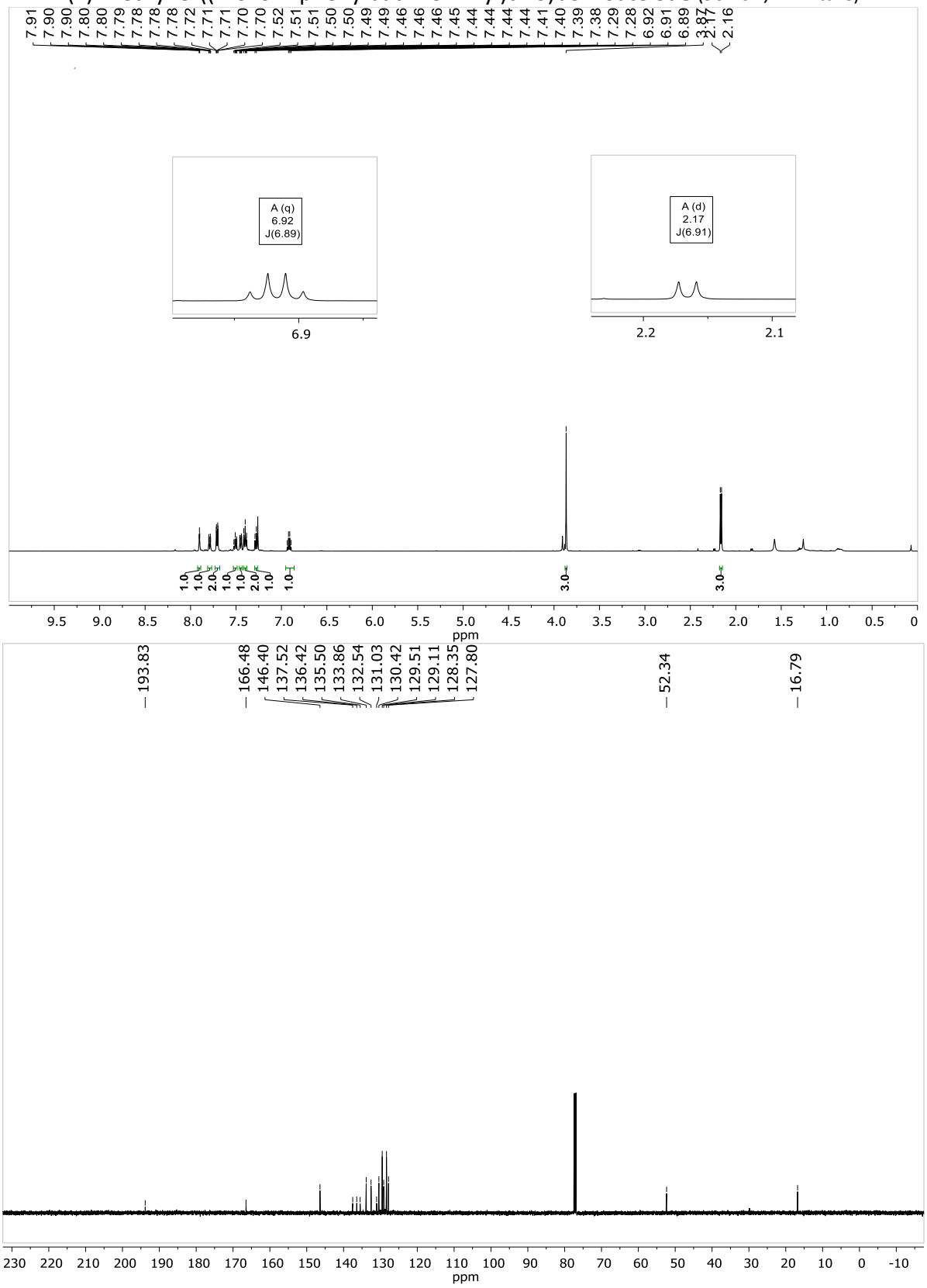


(*Z*)- 4-(1-Benzoyl-propenylsulfanyl)-benzoic acid methyl ester **3ad** (90:10 *E/Z* mixture)

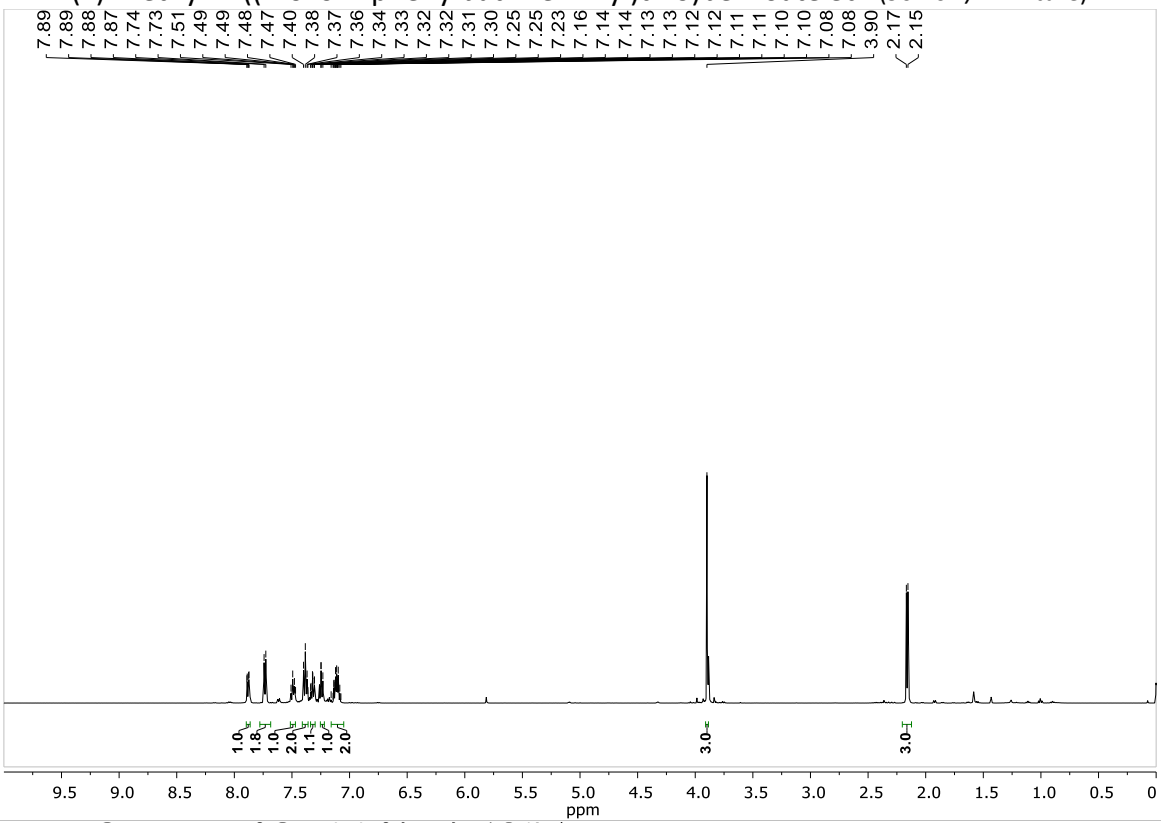


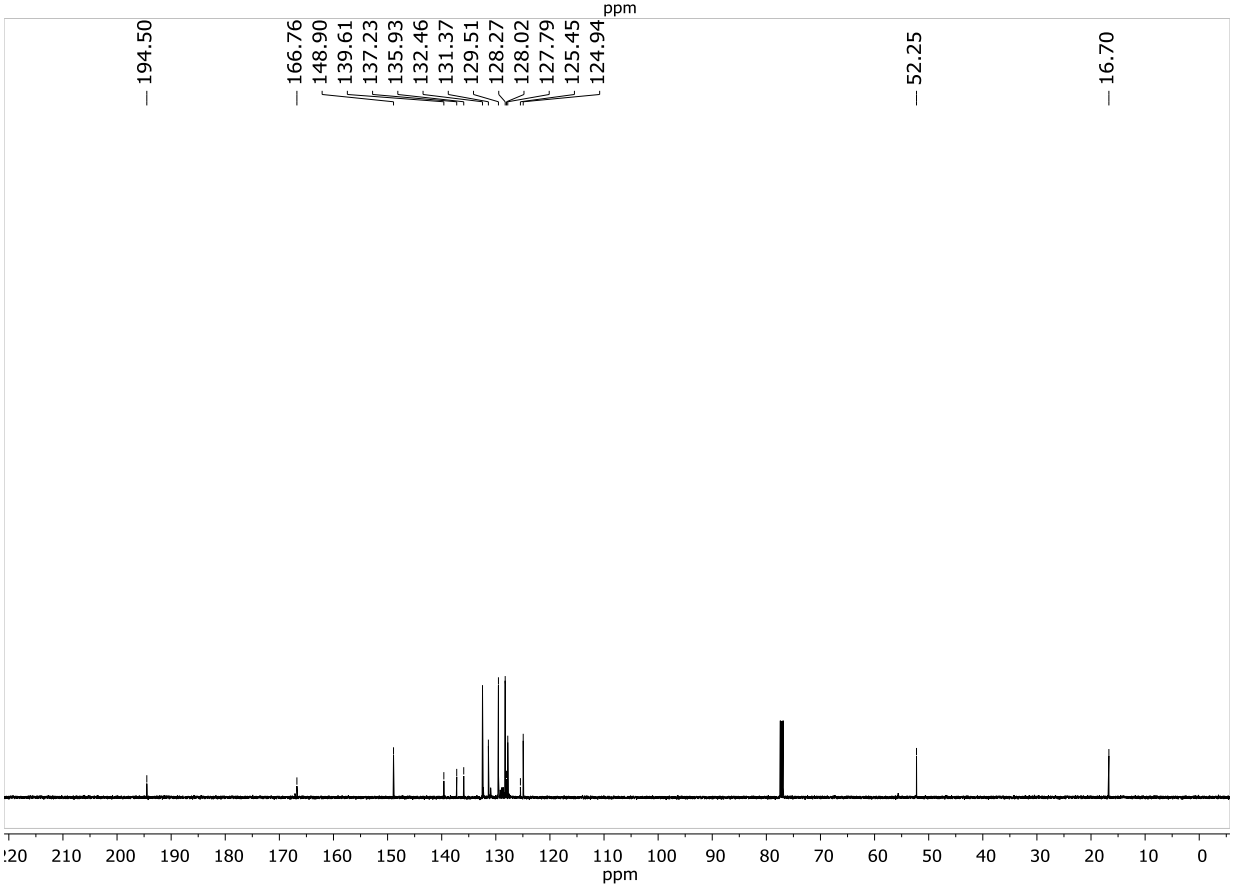


(*Z*)-methyl-3-((1-oxo-1-phenylbut-2-en-2-yl)thio)benzoate **3ae** (90:10 *E/Z* mixture)

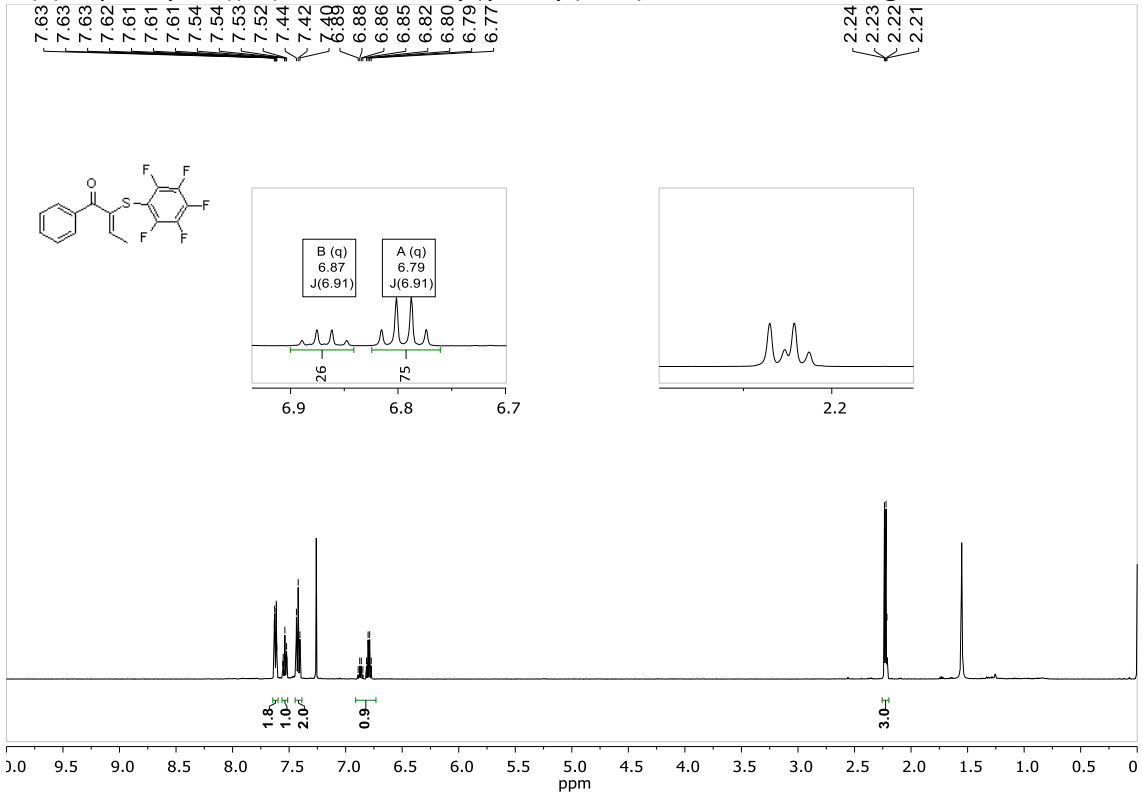


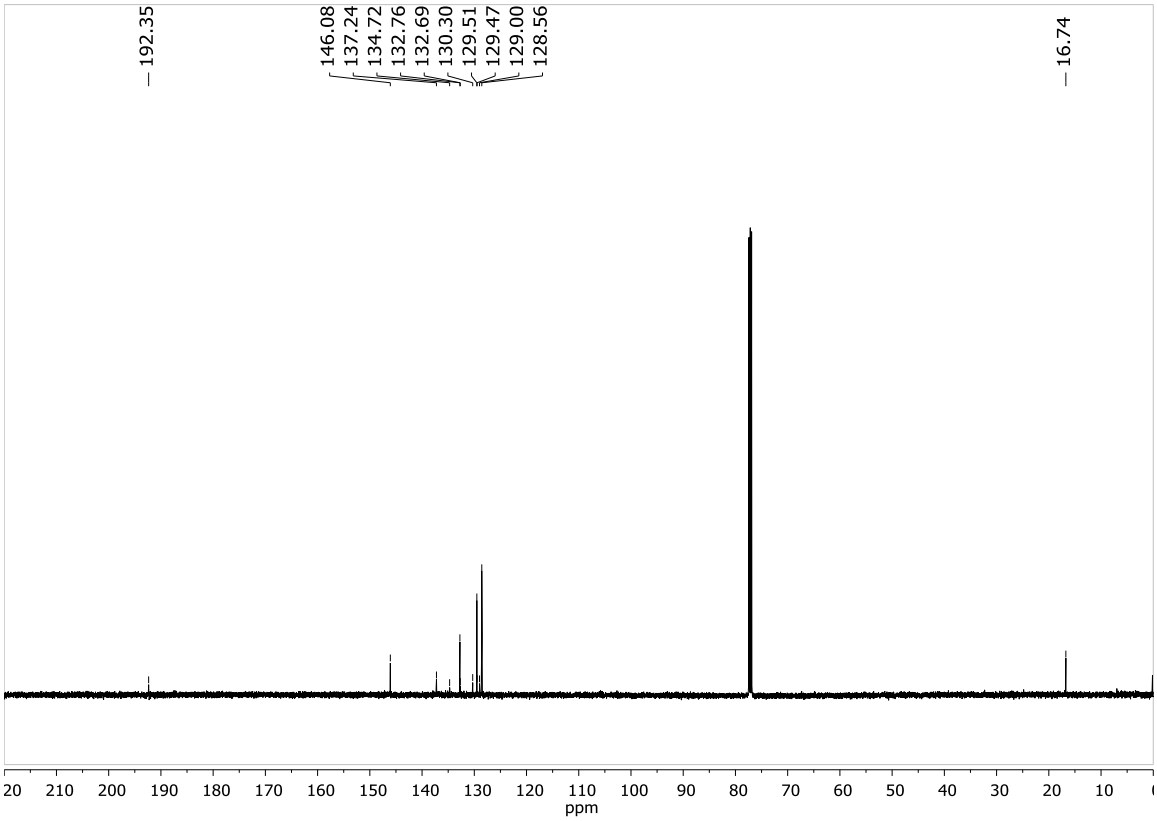
(*Z*)-methyl-2-((1-oxo-1-phenylbut-2-en-2-yl)thio)benzoate **3af** (90:10 *E/Z* mixture)



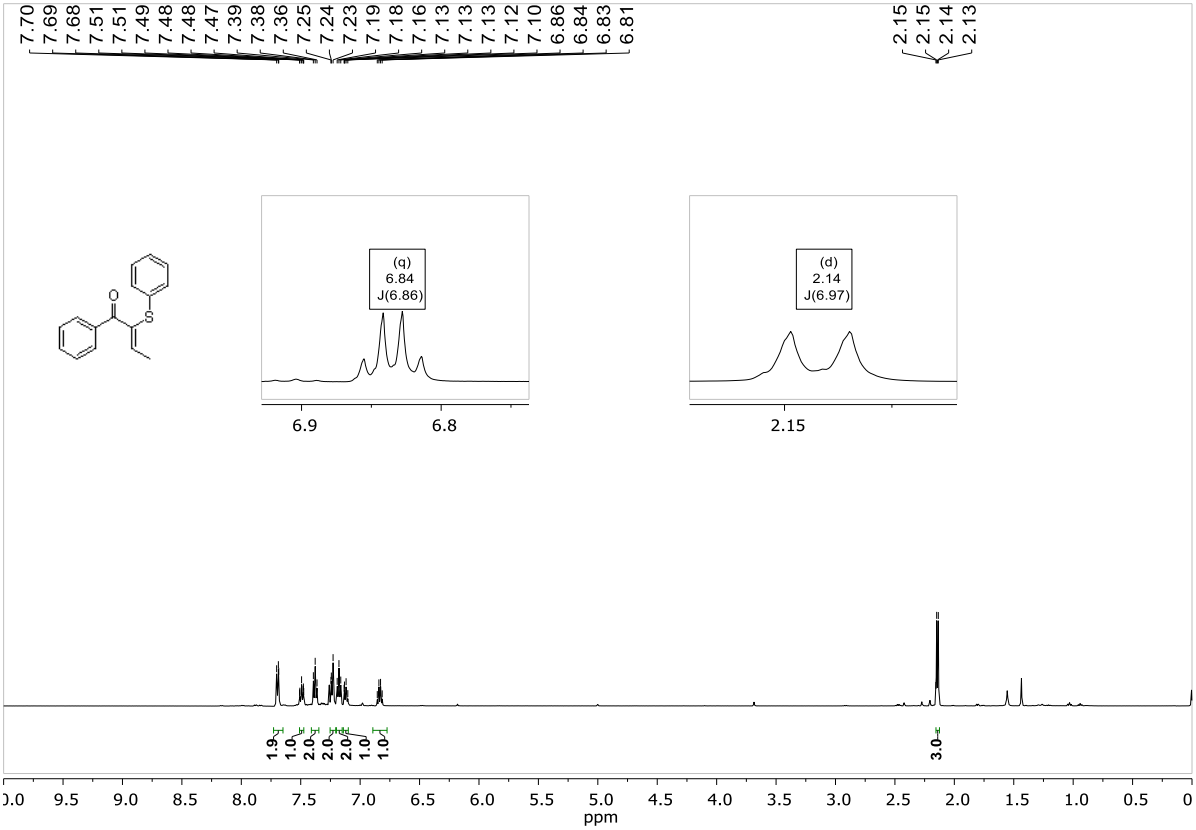


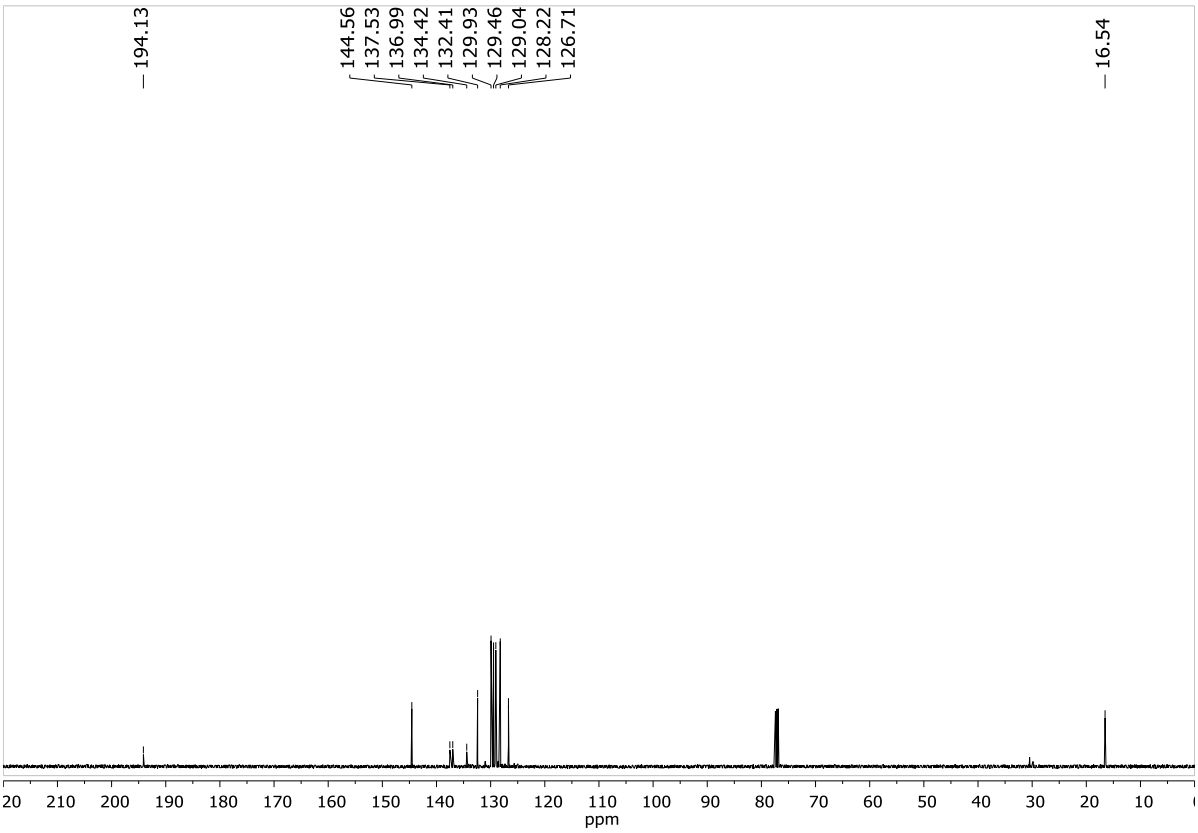
(*Z*)-1-phenyl-2-((4-(trifluoromethyl)phenyl)thio)but-2-en-1-one **3ag** (90:10 *E/Z* mixture)



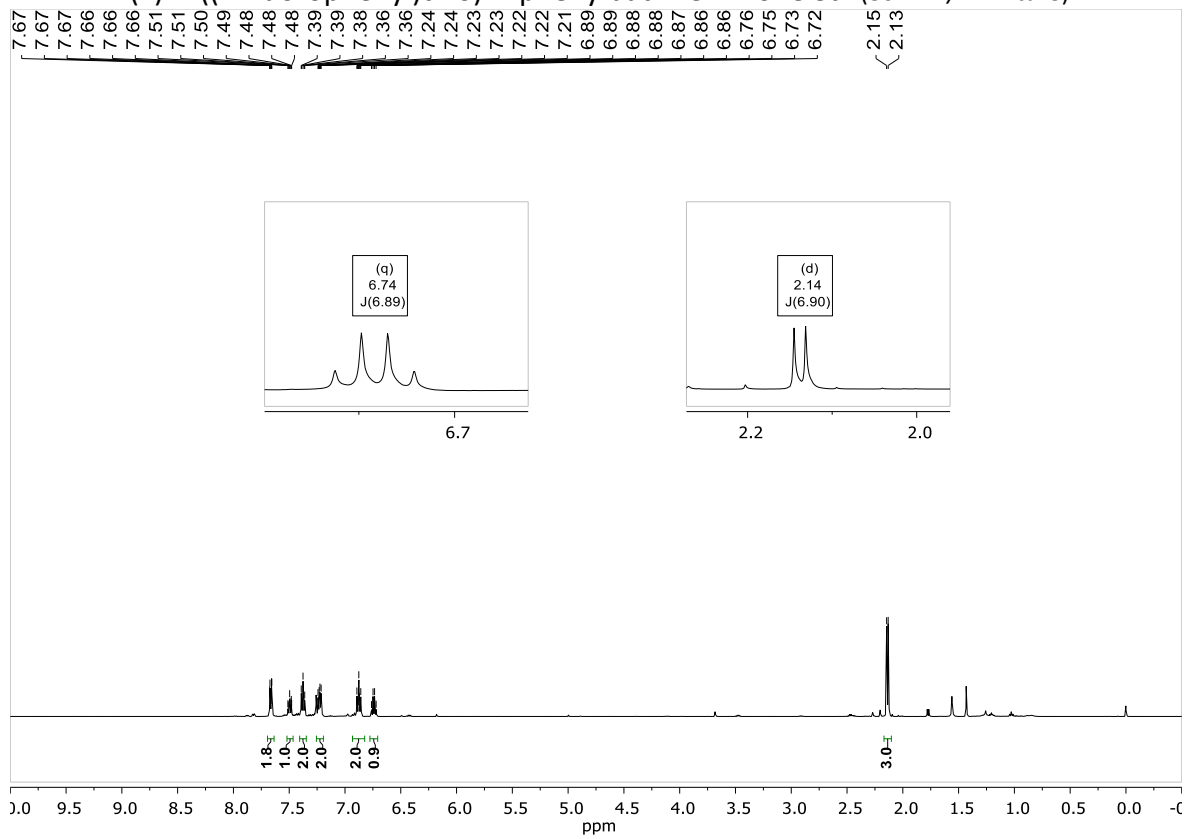


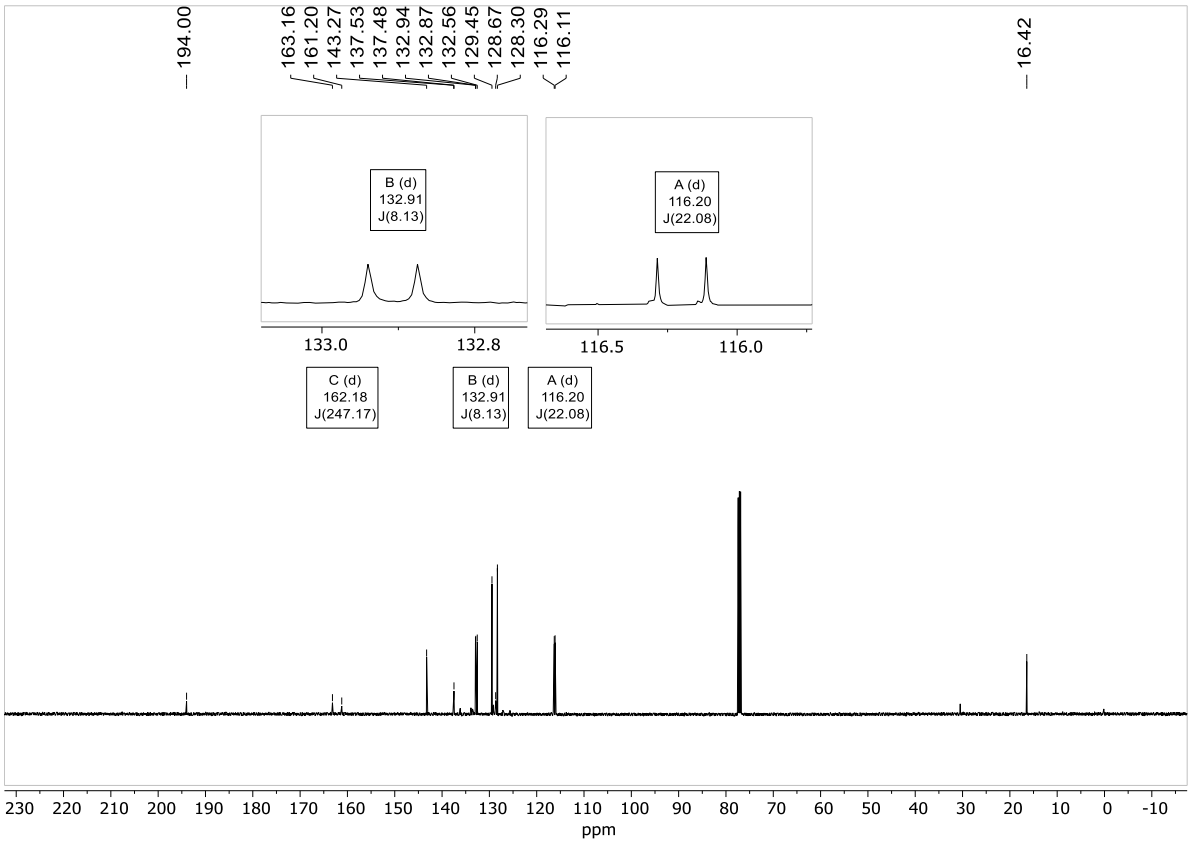
(*Z*)-1-phenyl-2-(phenylthio)but-2-en-1-one **3ah** (85:15 *E/Z* mixture)



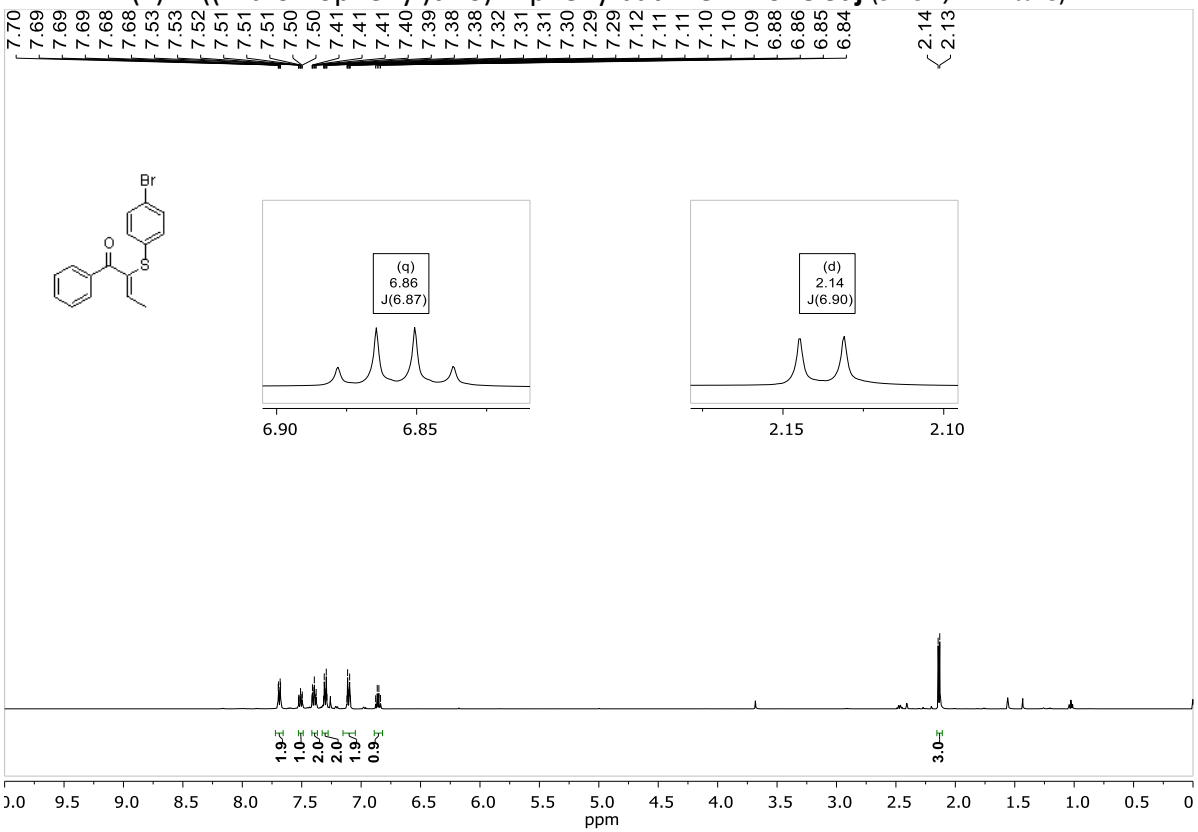


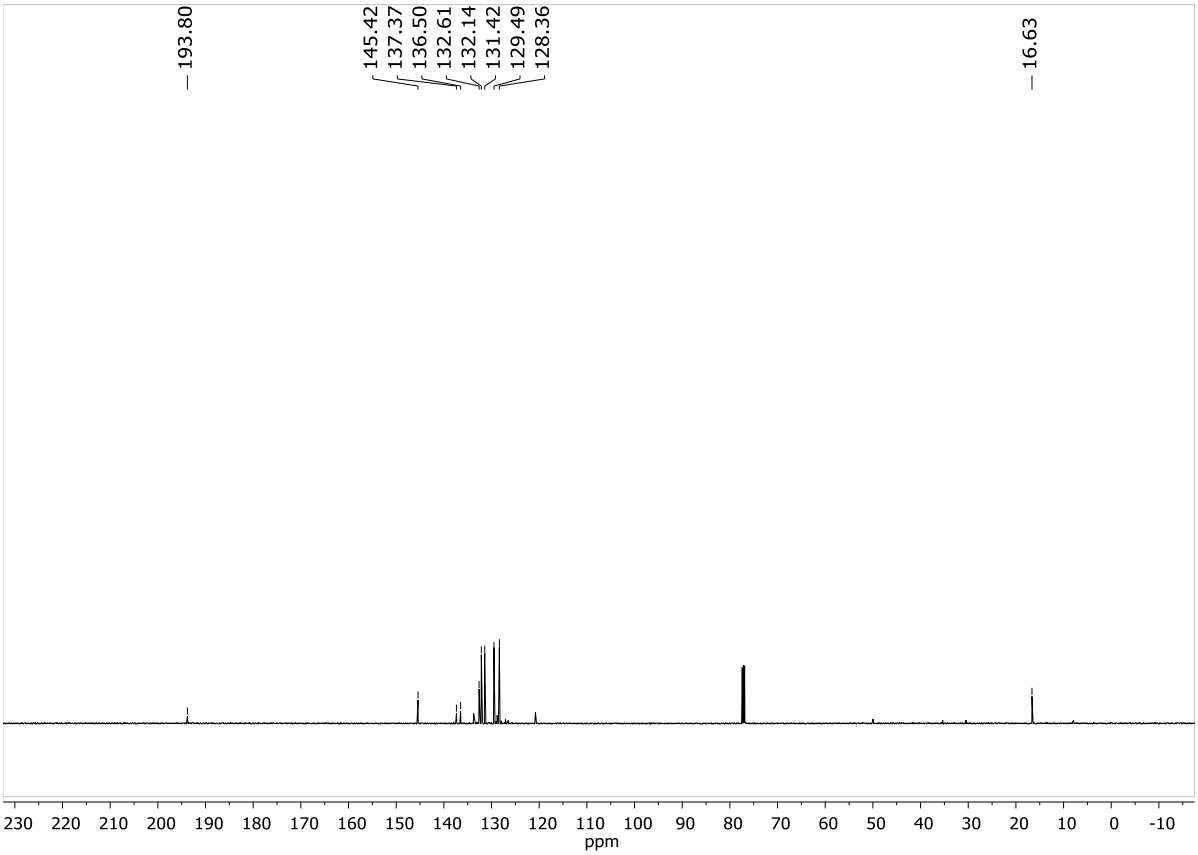
(*Z*)-2-((4-fluorophenyl)thio)-1-phenylbut-2-en-1-one **3ai** (86:14 *E/Z* mixture)



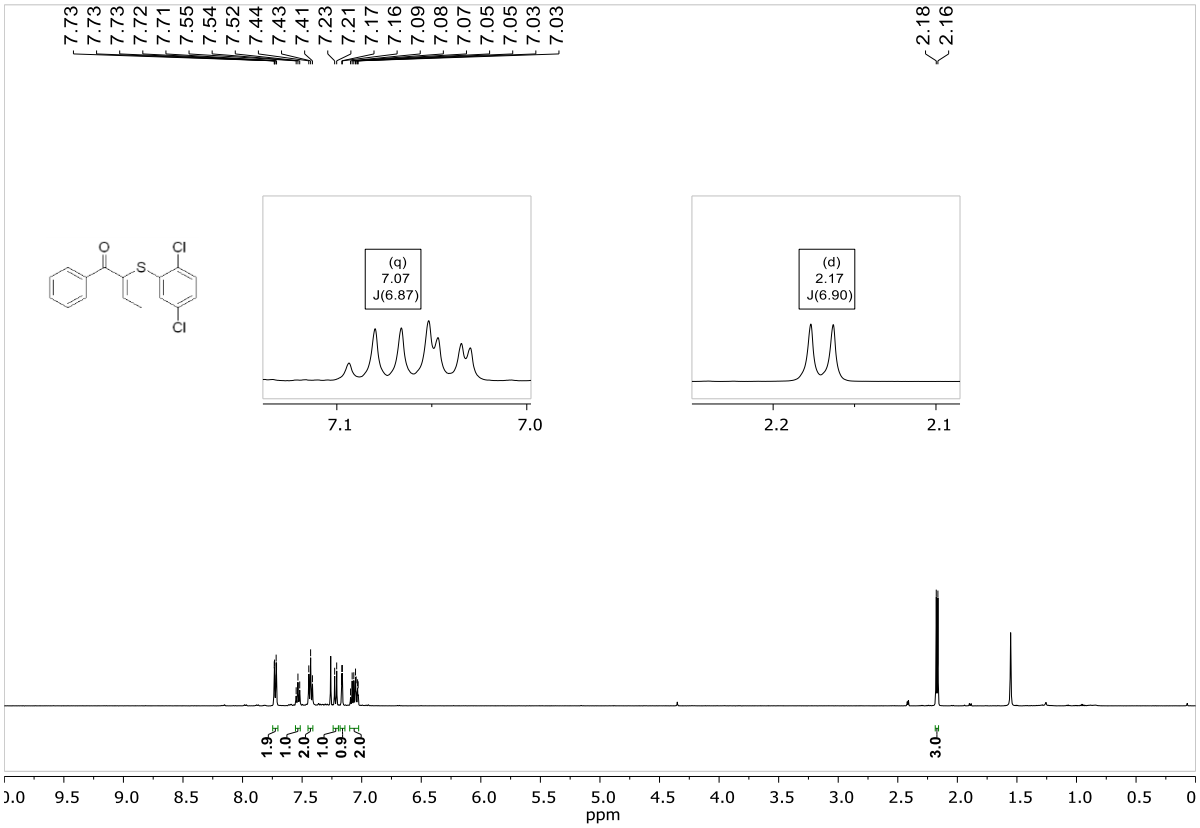


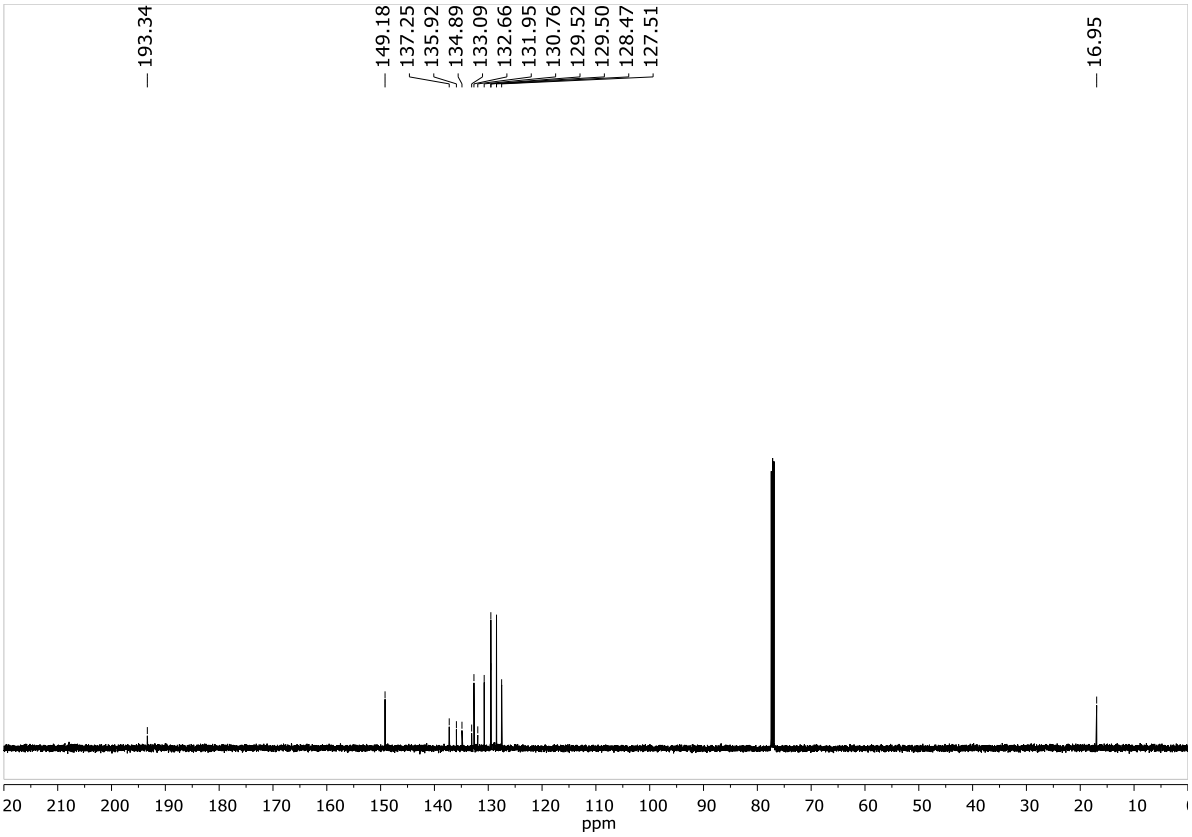
(*Z*)-2-((4-bromophenyl)thio)-1-phenylbut-2-en-1-one **3aj** (91:9 *E/Z* mixture)



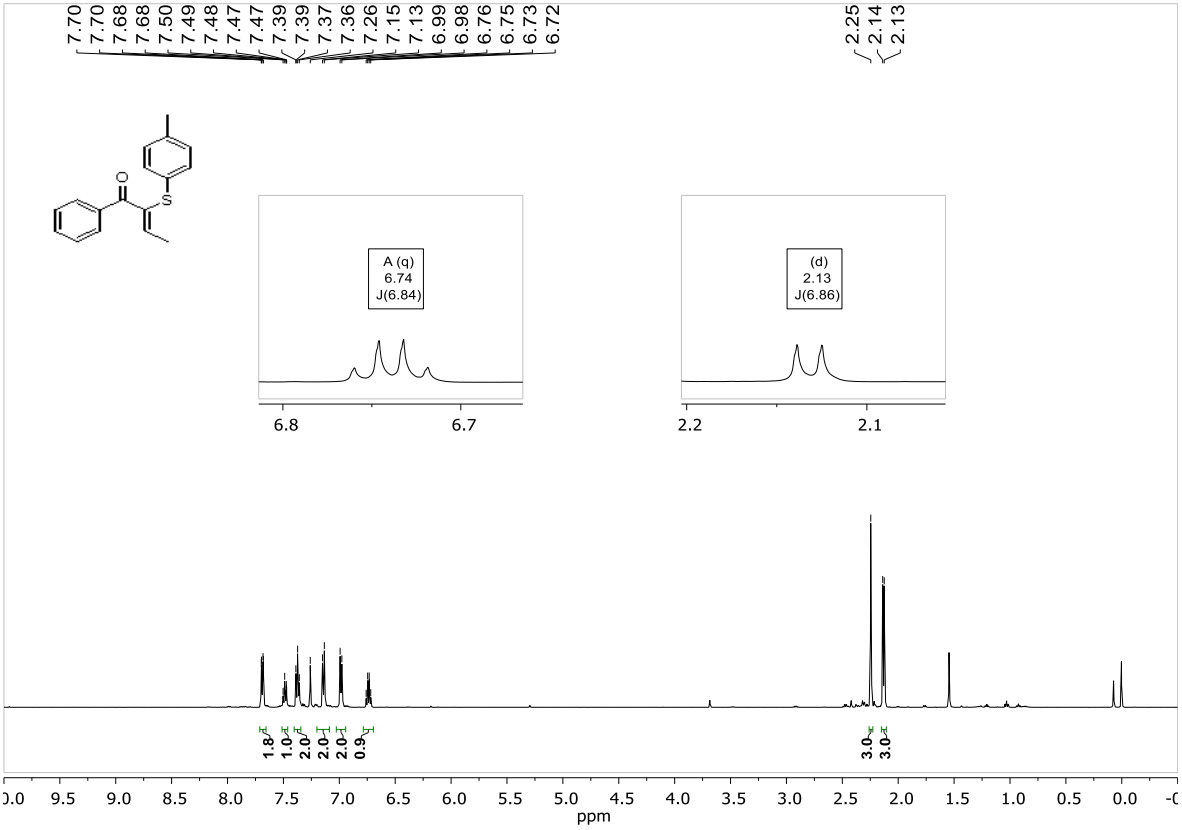


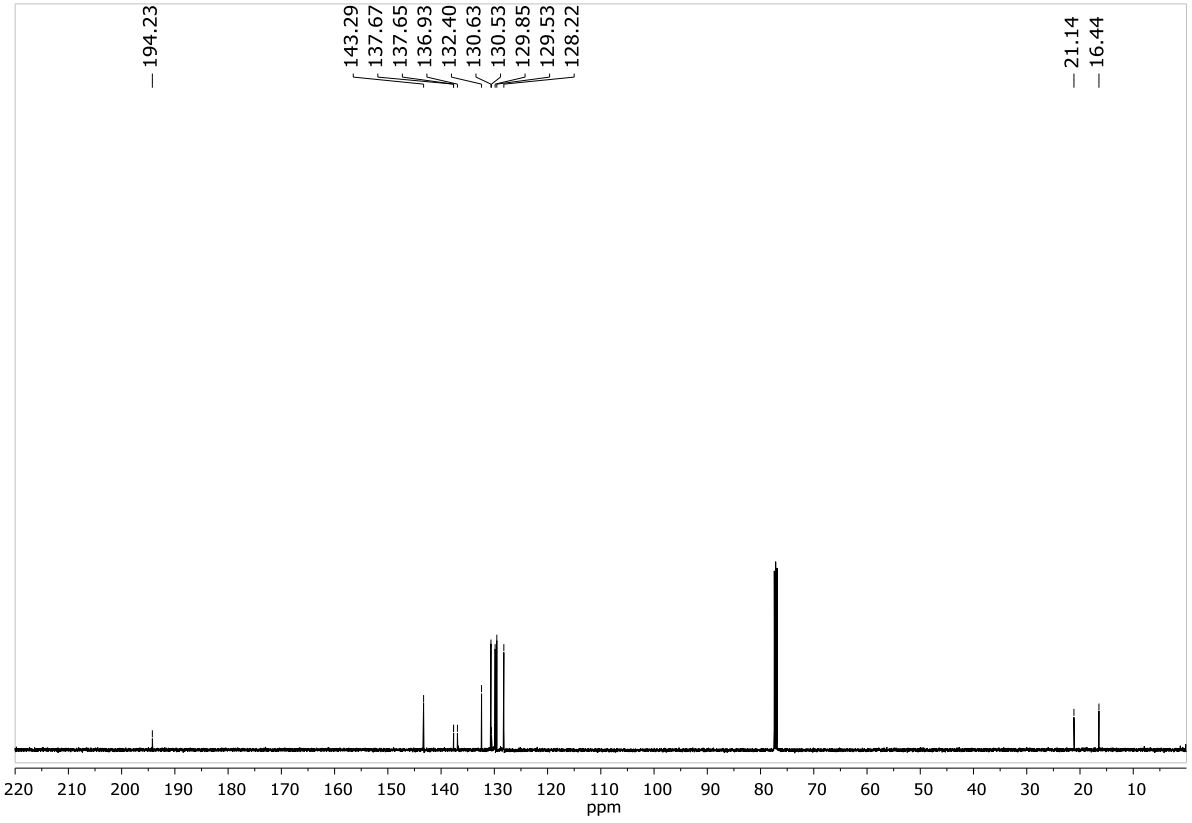
(*Z*)-2-((2,5-dichlorophenyl)thio)-1-phenylbut-2-en-1-one **3ak** (89:11 *E/Z* mixture)



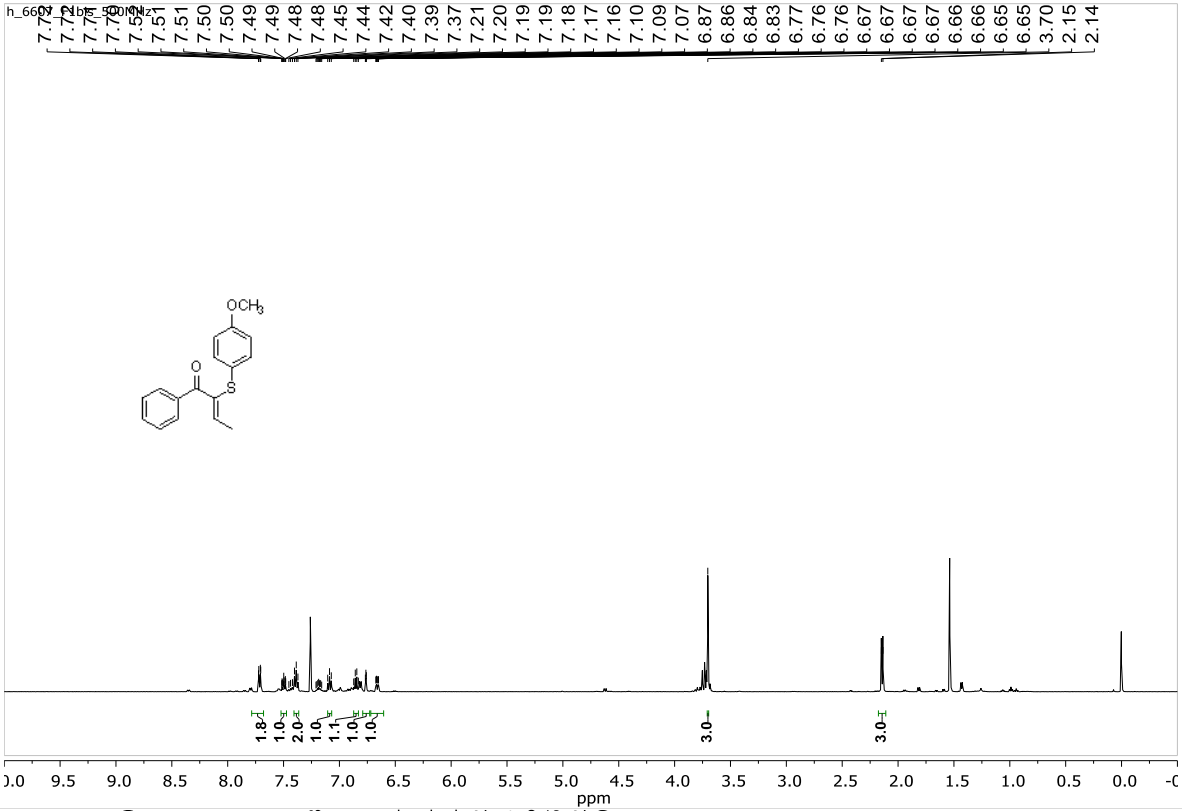


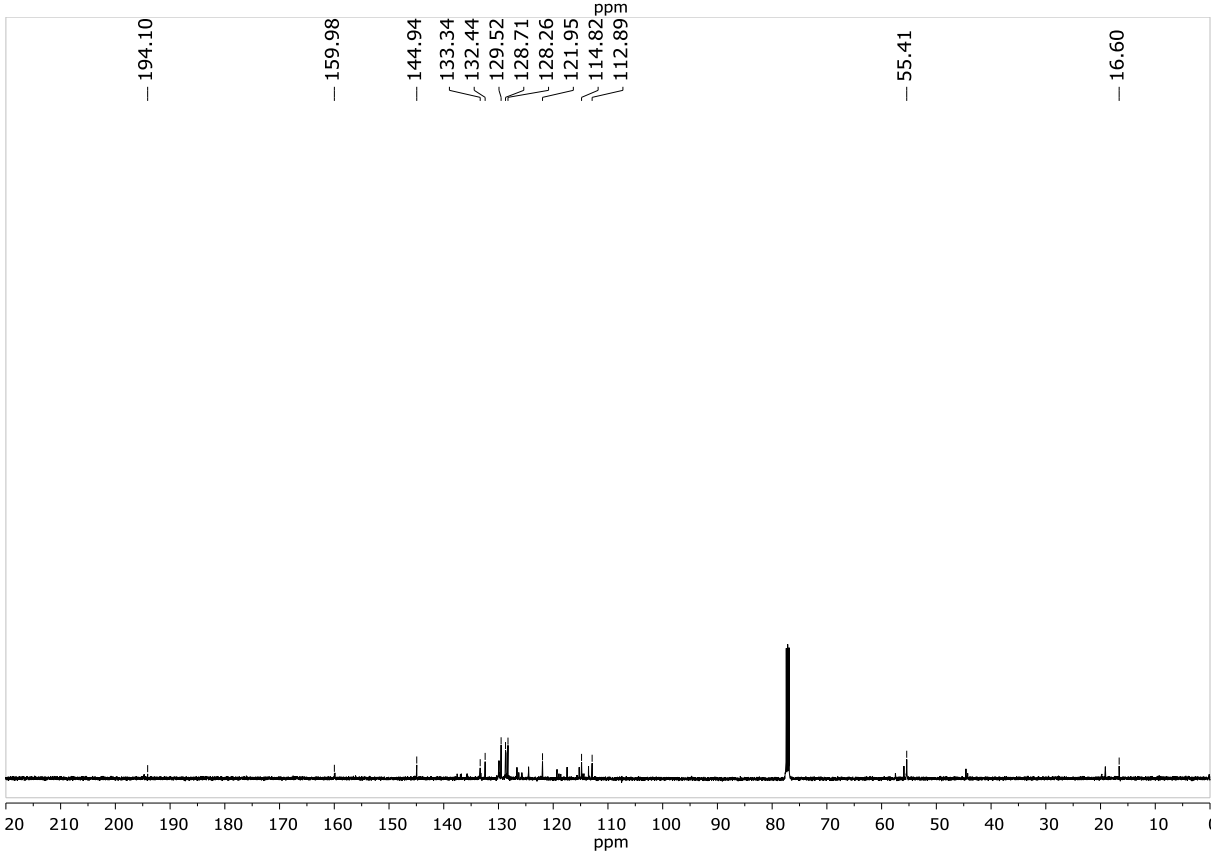
(*Z*)-1-phenyl-2-(p-tolylthio)but-2-en-1-one **3al** (83:17 *E/Z* mixture)



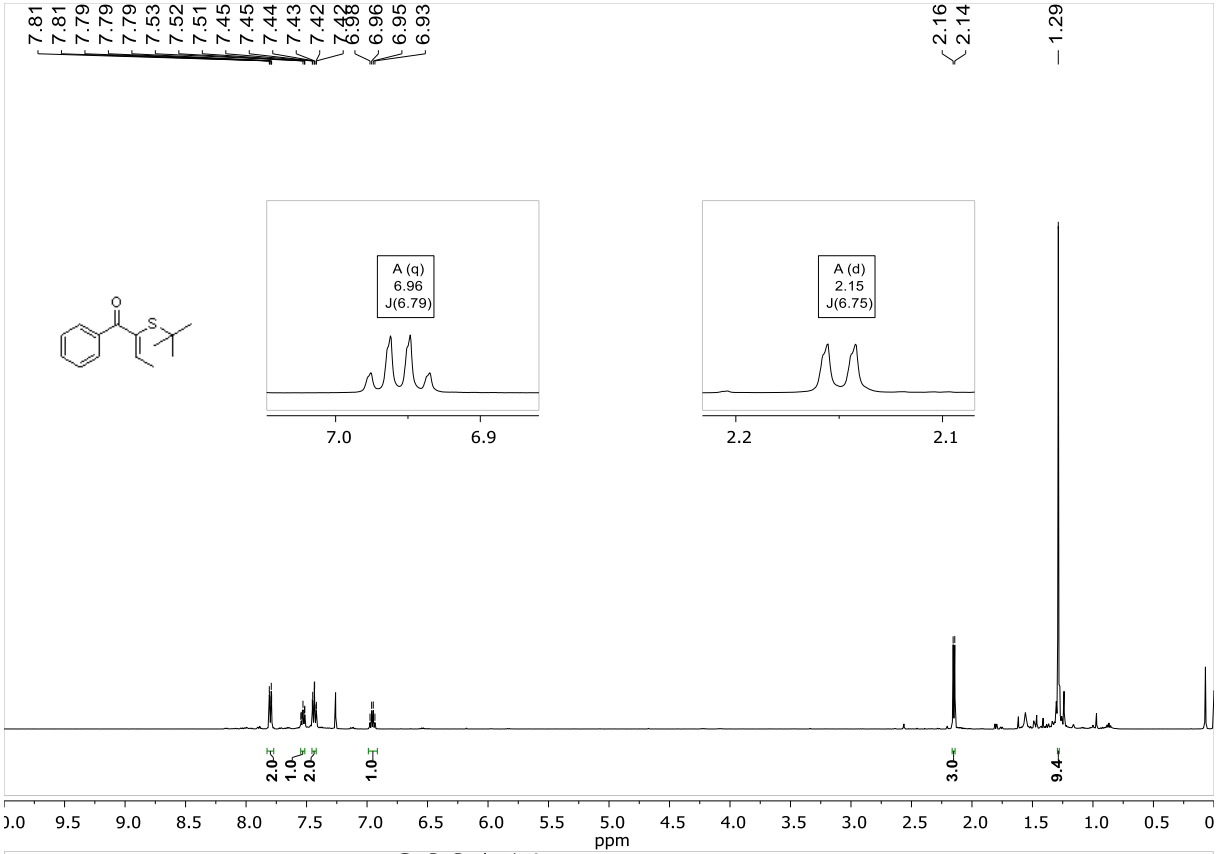


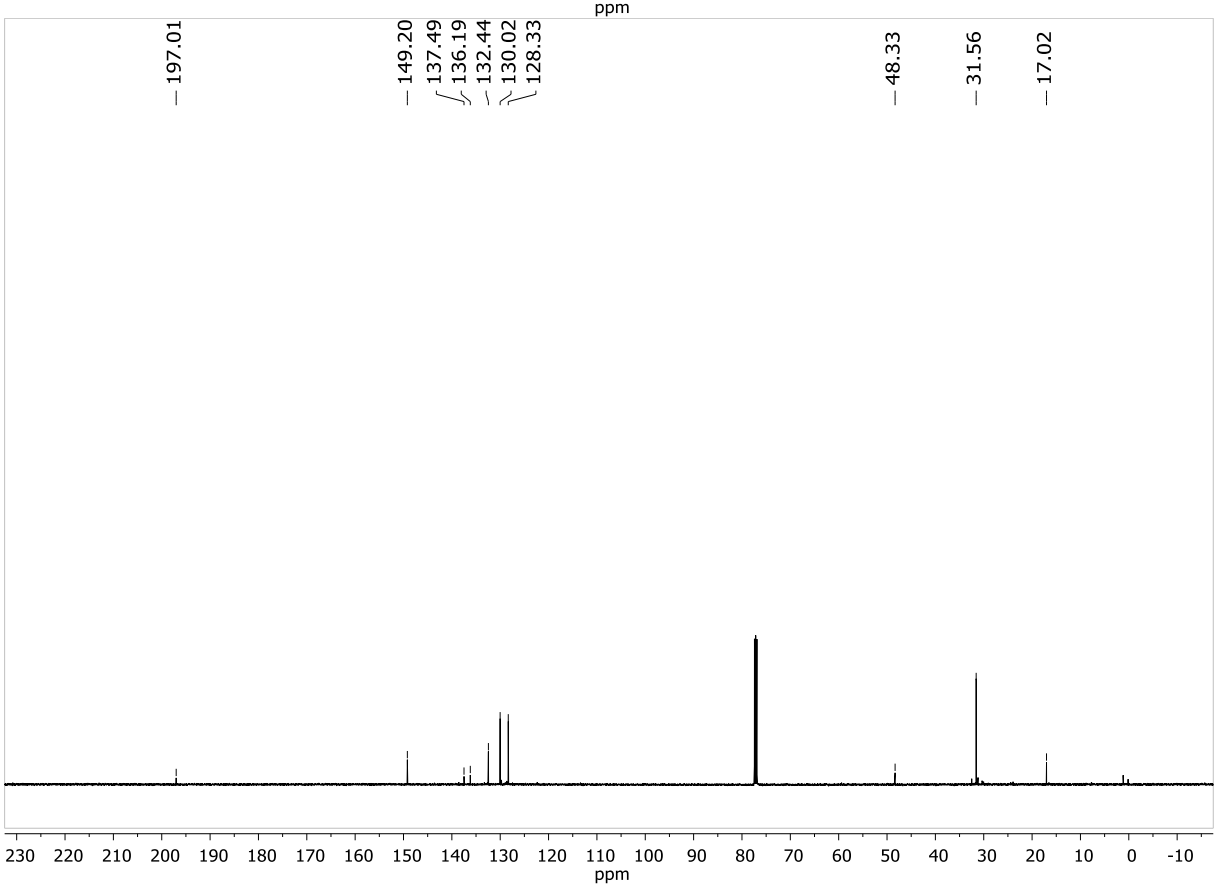
(*Z*)-2-((4-methoxyphenyl)thio)-1-phenylbut-2-en-1-one **3am** (85:15 *E/Z* mixture)



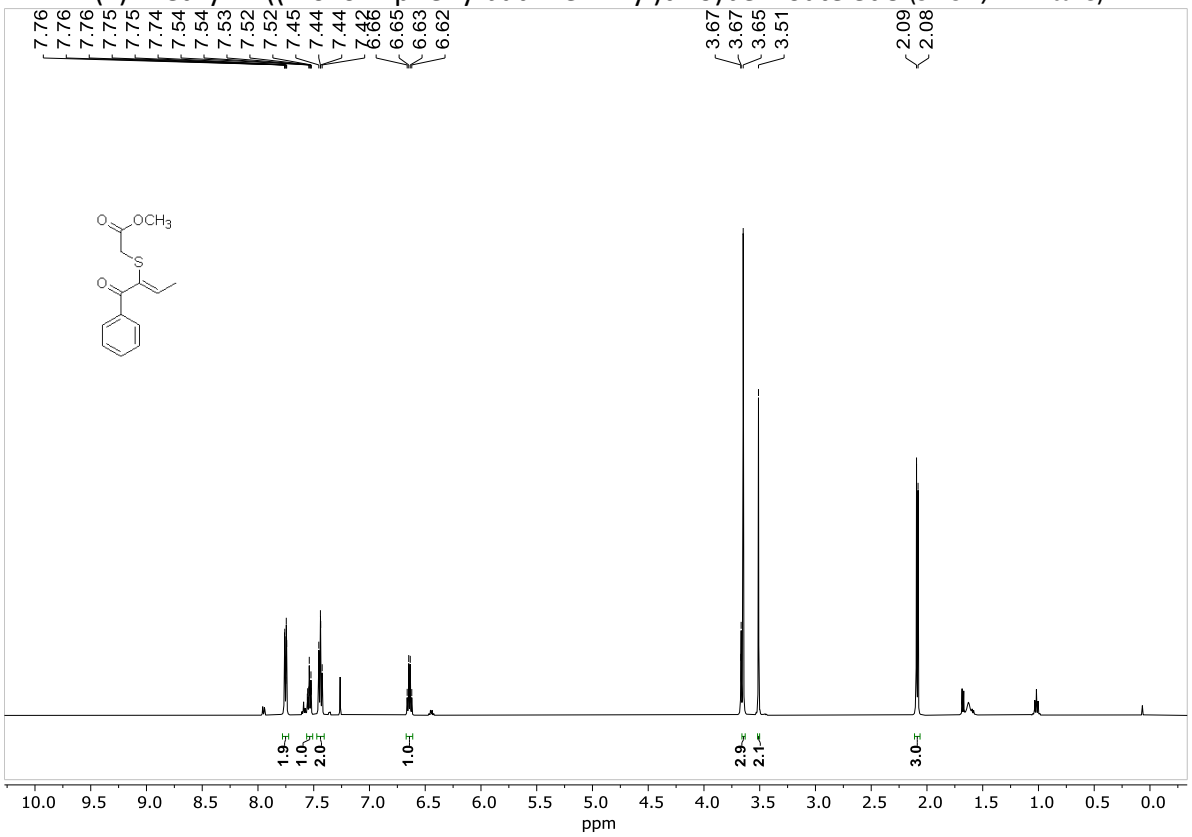


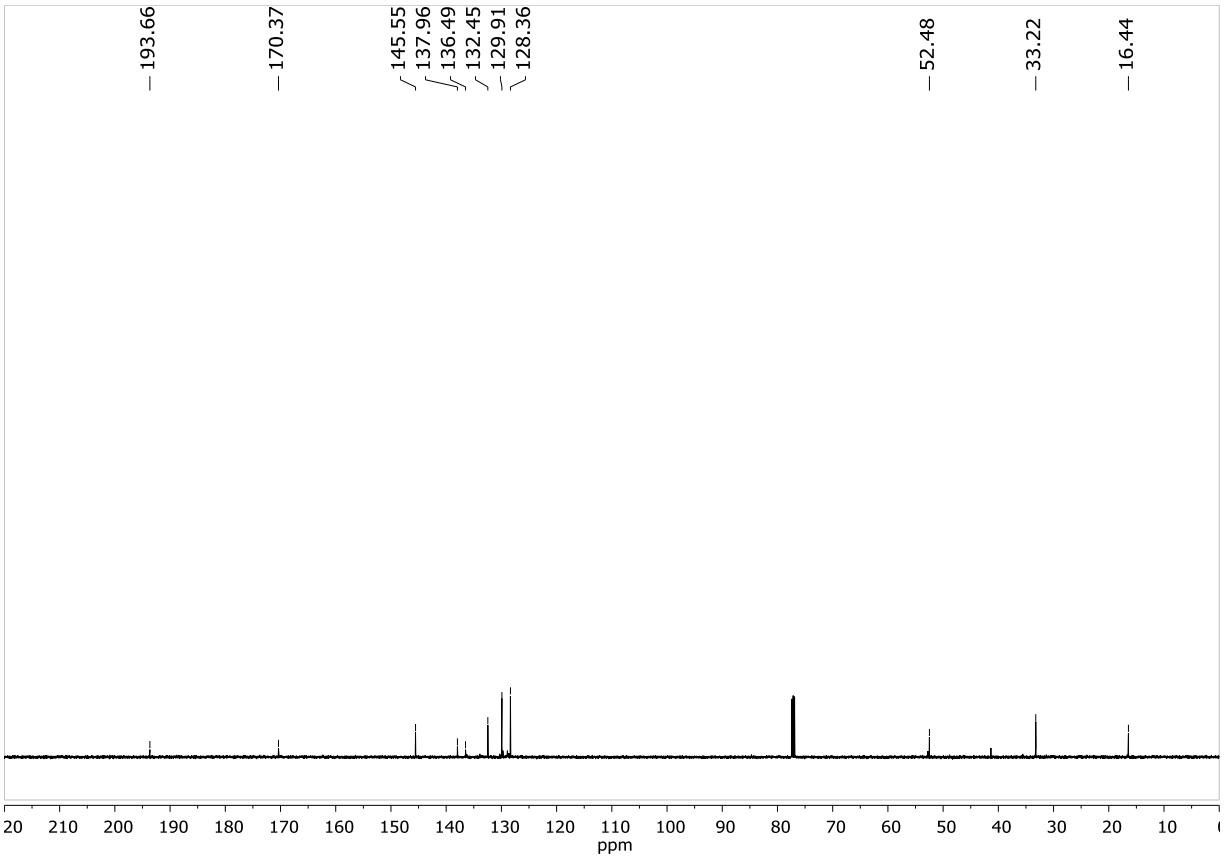
(*Z*)-2-(tert-butylthio)-1-phenylbut-2-en-1-one **3an** (92:8 *E/Z* mixture)



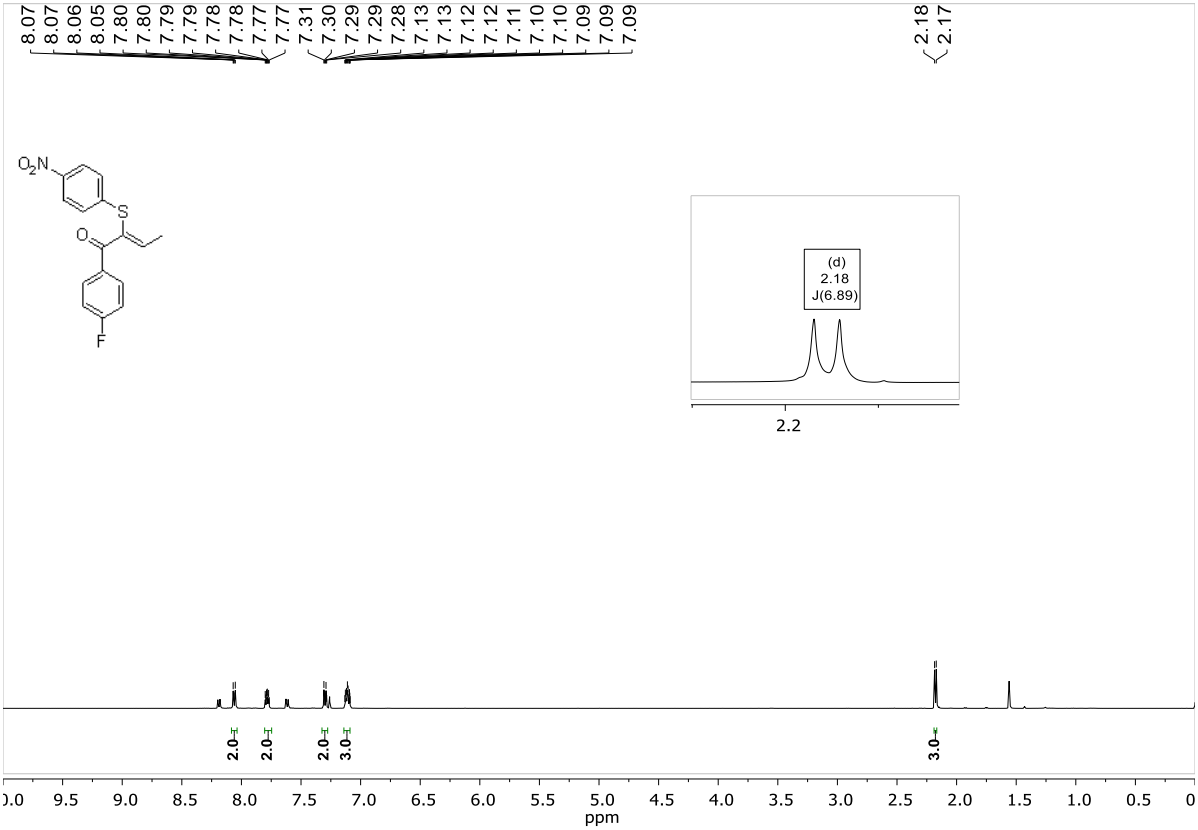


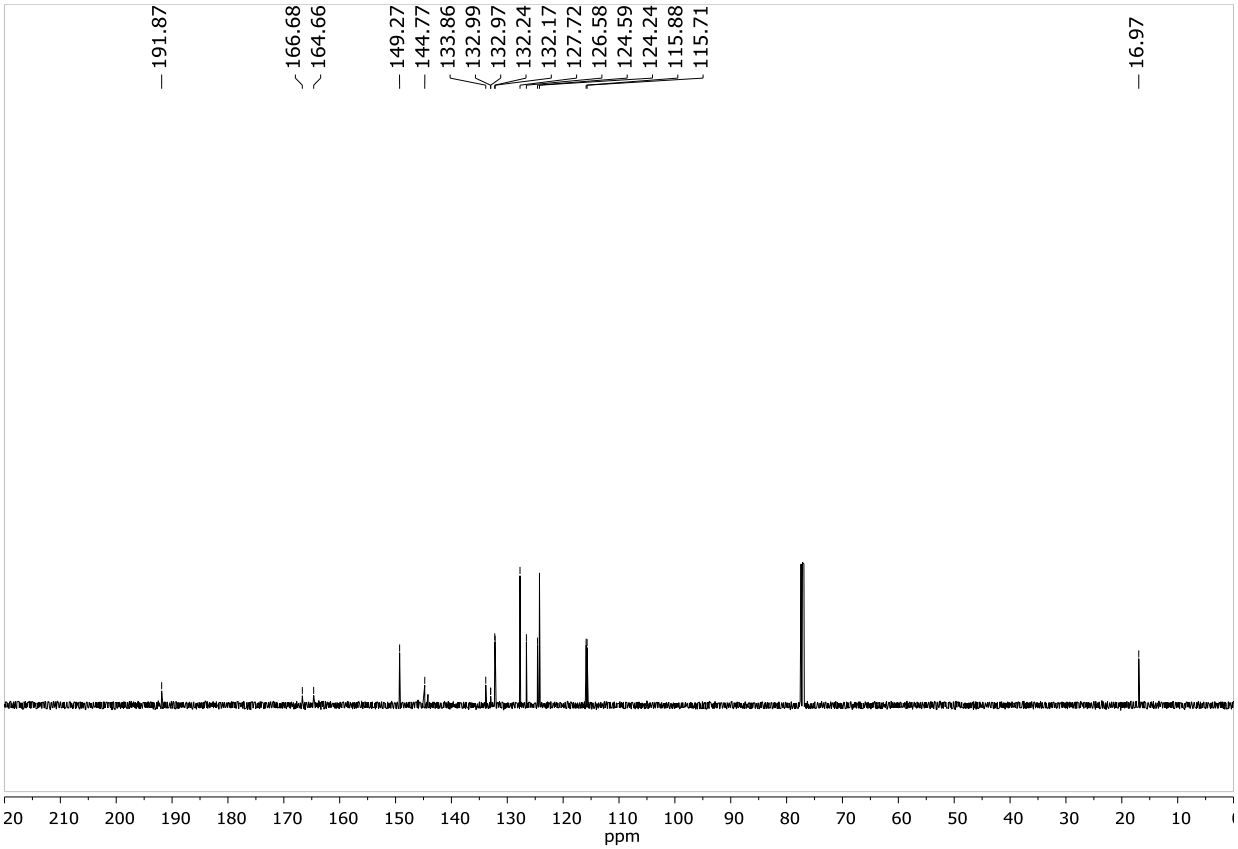
(*Z*)-methyl-2-((1-oxo-1-phenylbut-2-en-2-yl)thio)benzoate **3ao** (91:9 *E/Z* mixture)



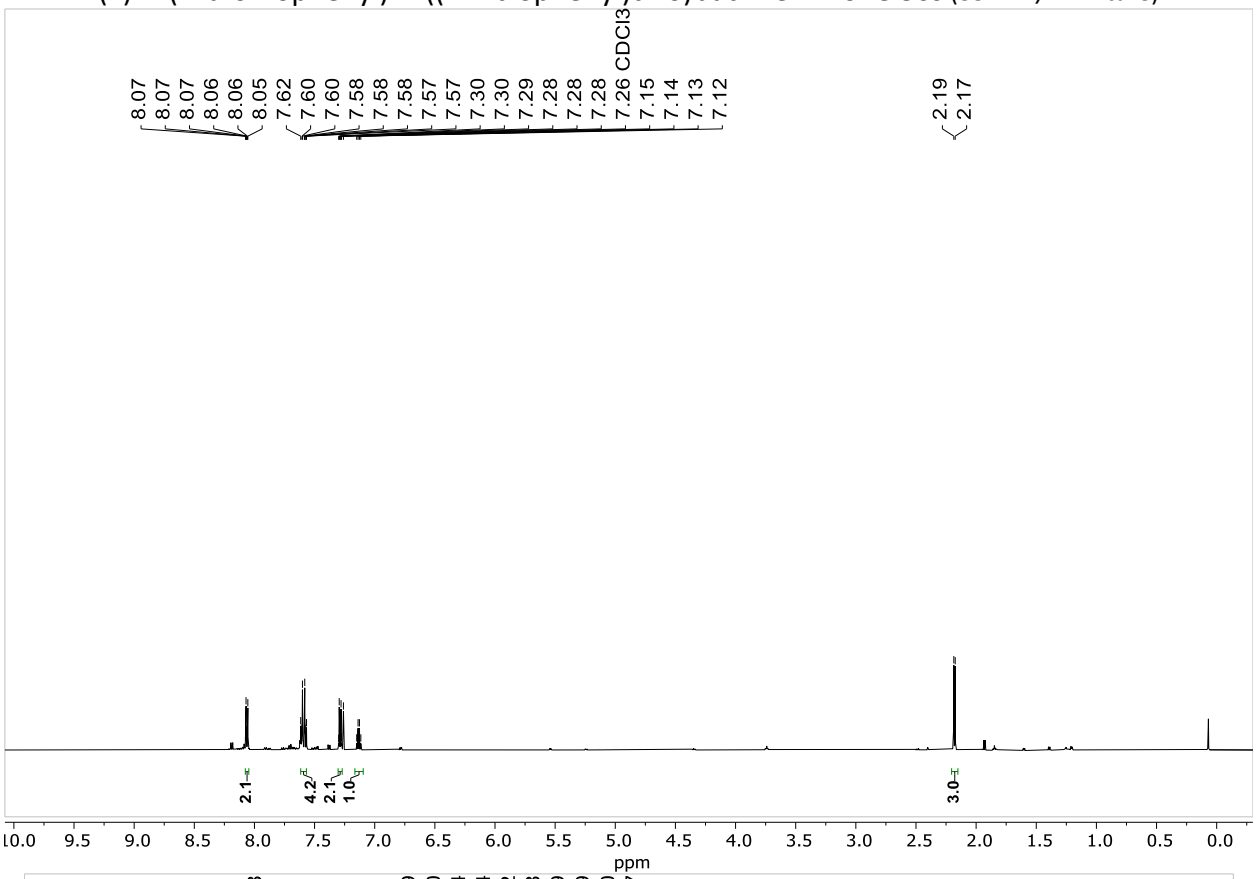


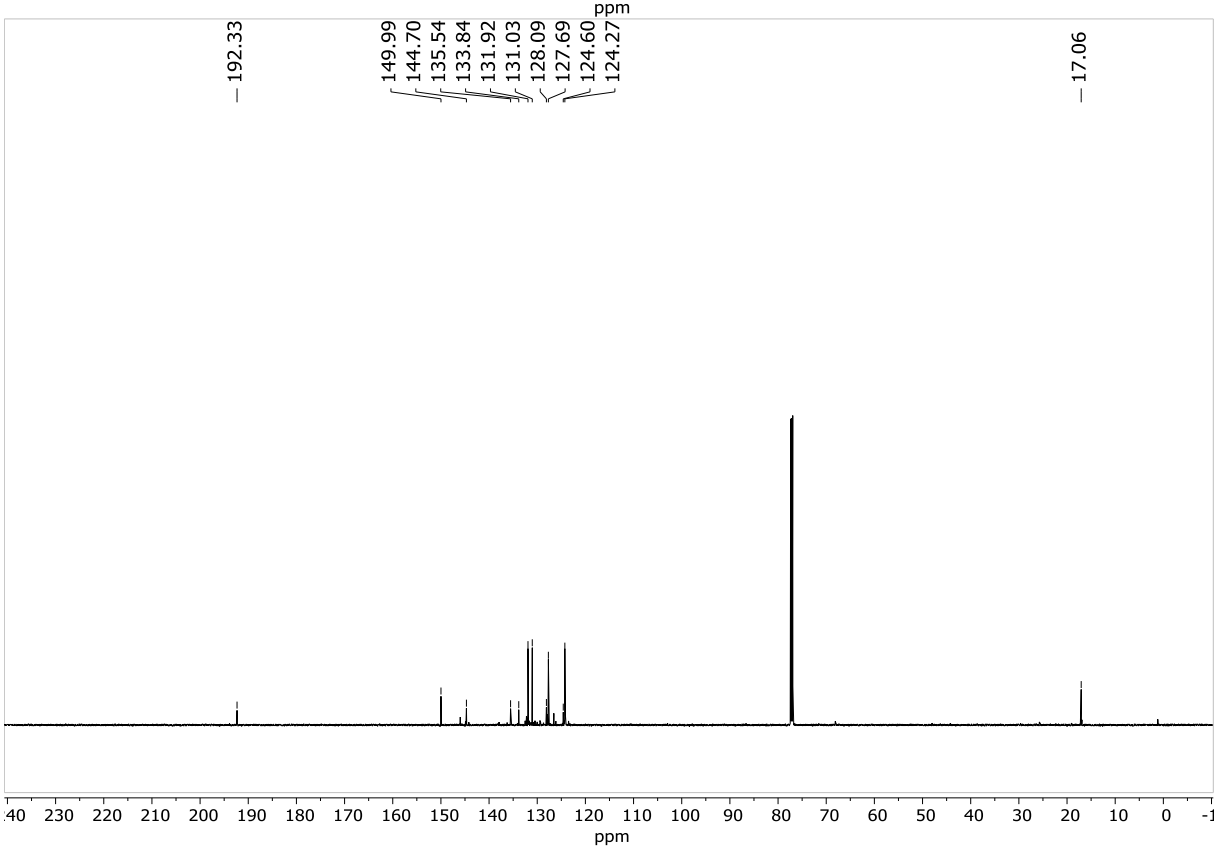
(*Z*)-1-(4-fluorophenyl)-2-((4-nitrophenyl)thio)but-2-en-1-one **3bc** (85:15 *Z/E* mixture)



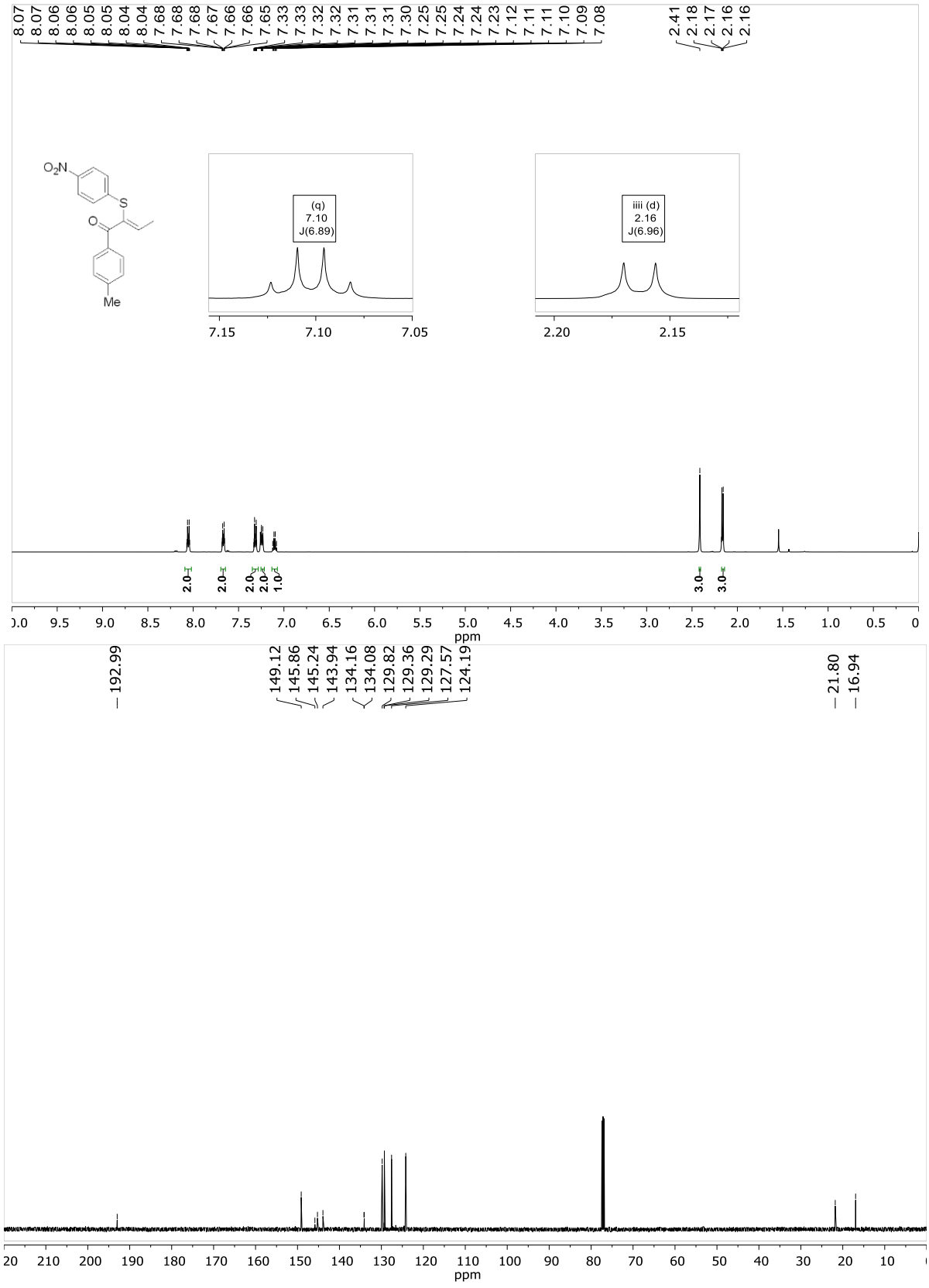


(*Z*)-1-(4-bromophenyl)-2-((4-nitrophenyl)thio)but-2-en-1-one **3cc** (88:12 *Z/E* mixture)

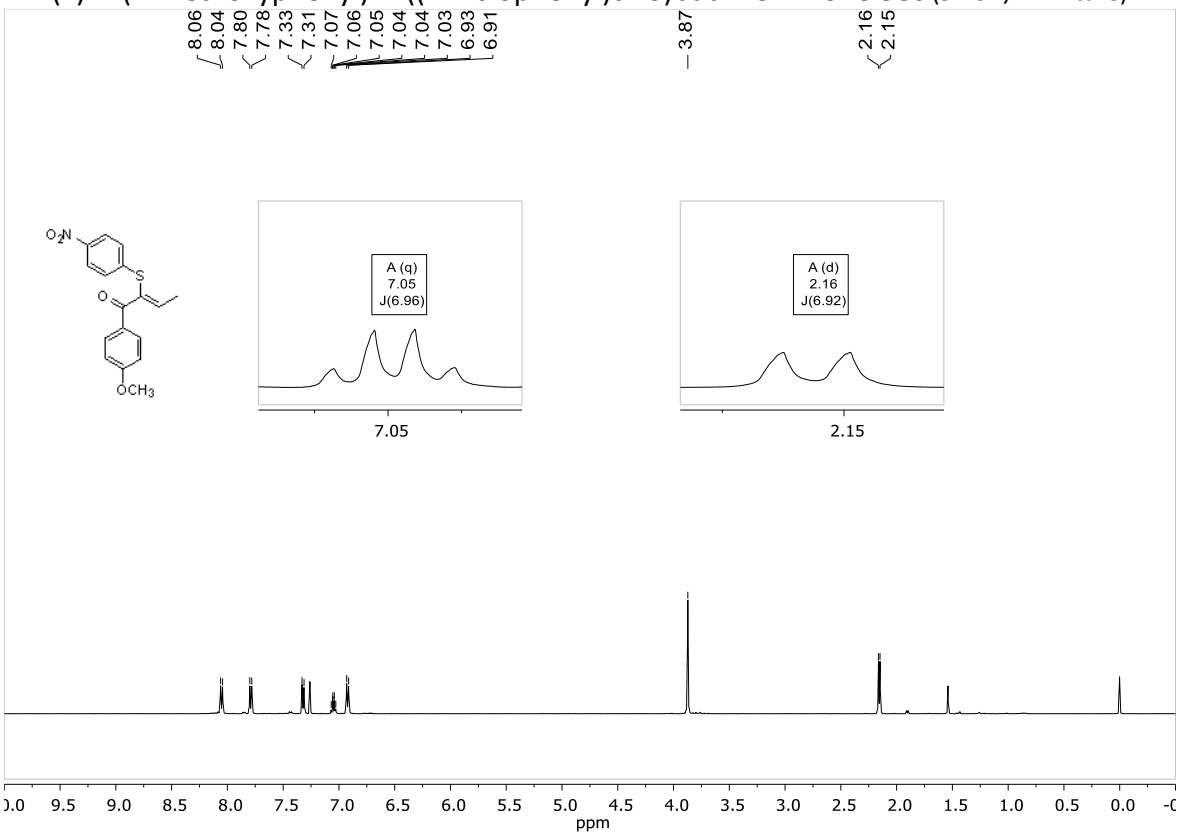


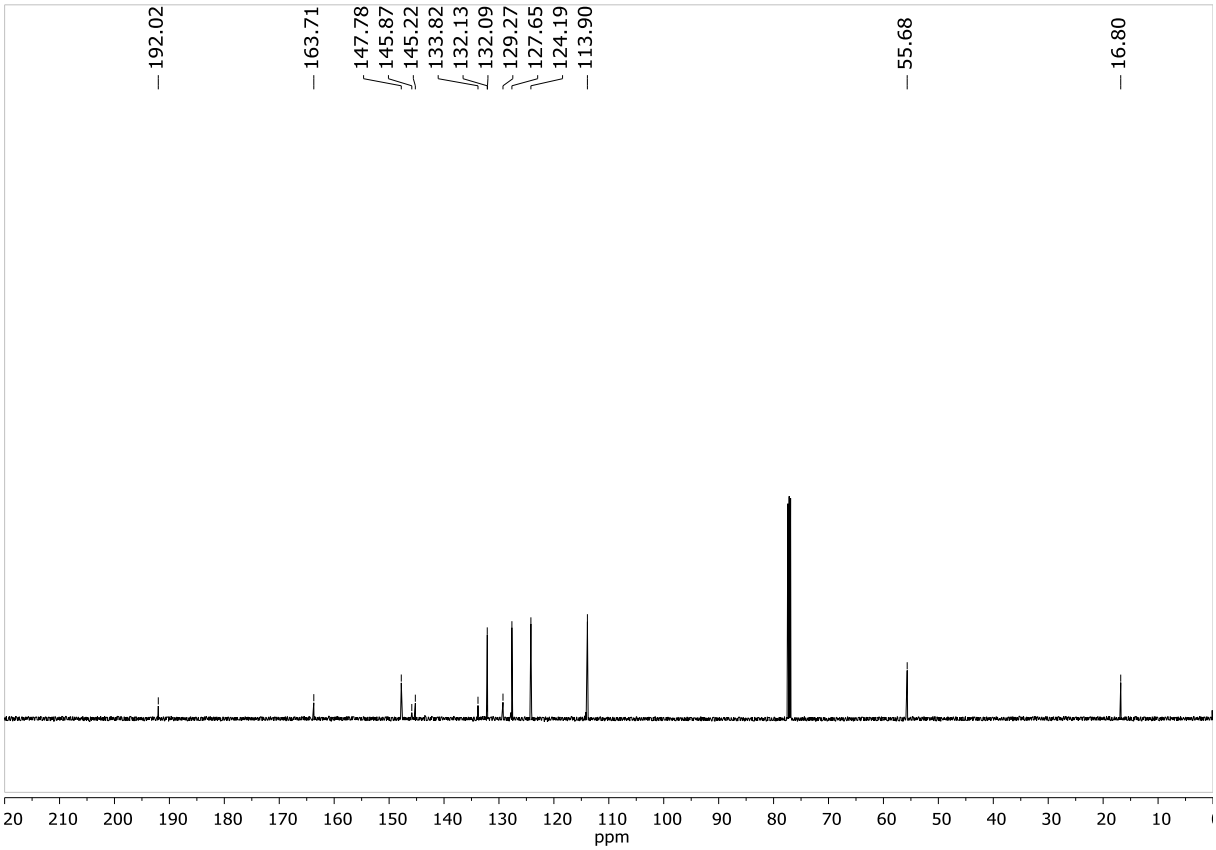


(*Z*)-2-((4-nitrophenyl)thio)-1-(p-tolyl)but-2-en-1-one **3dc** (88:12 *Z/E* mixture)

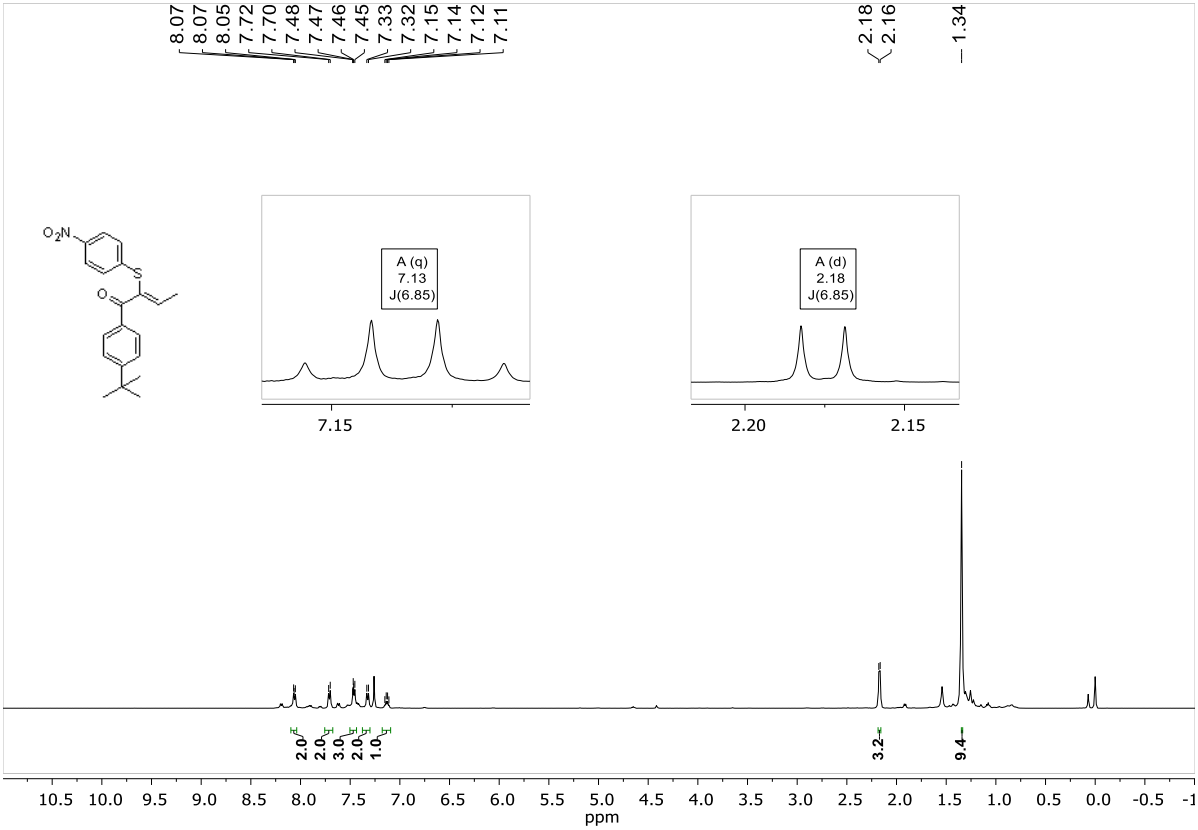


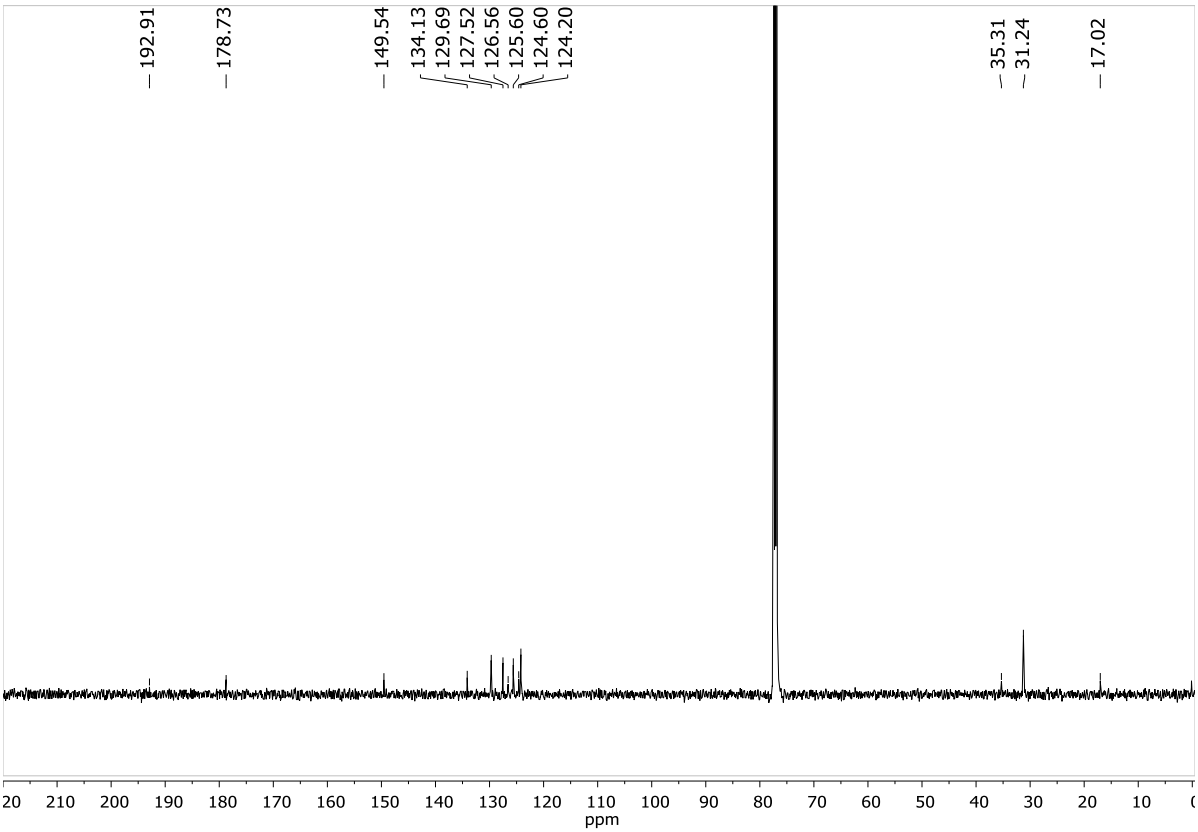
(*Z*)-1-(4-methoxyphenyl)-2-((4-nitrophenyl)thio)but-2-en-1-one **3ec** (92:8 *Z/E* mixture)



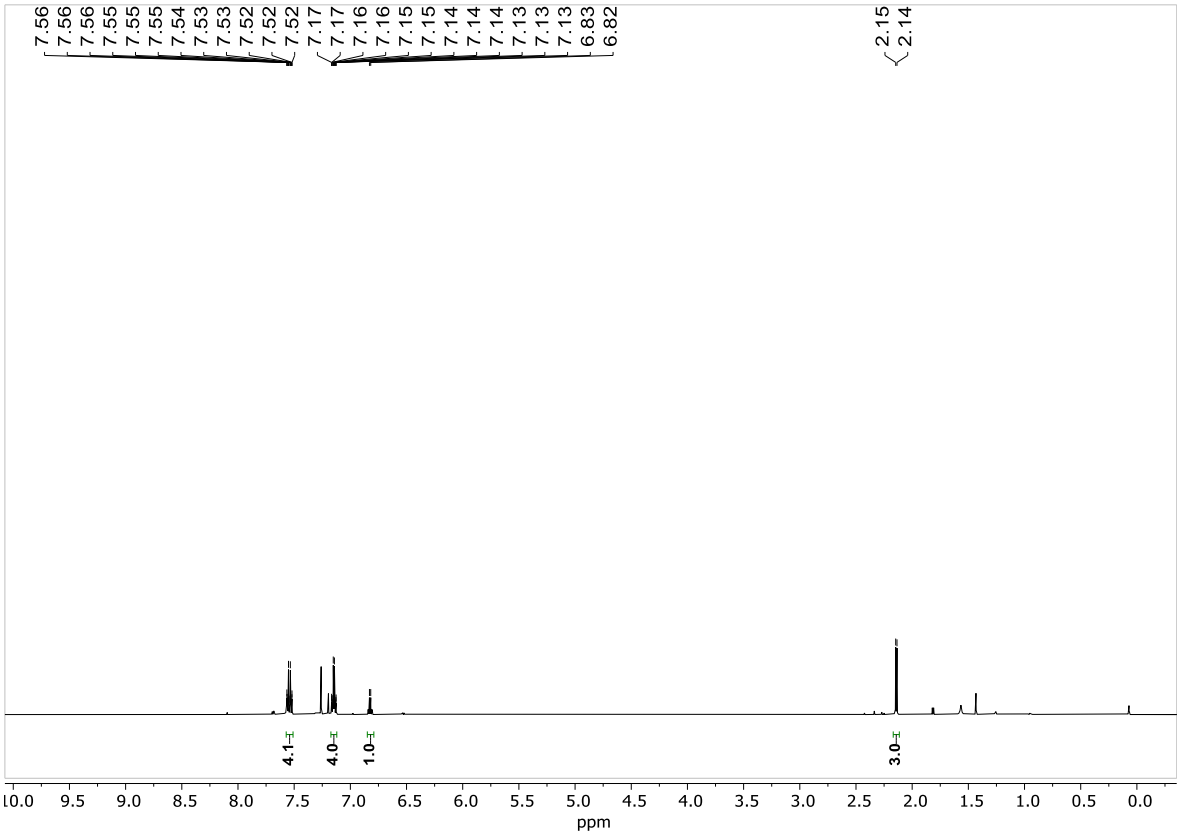


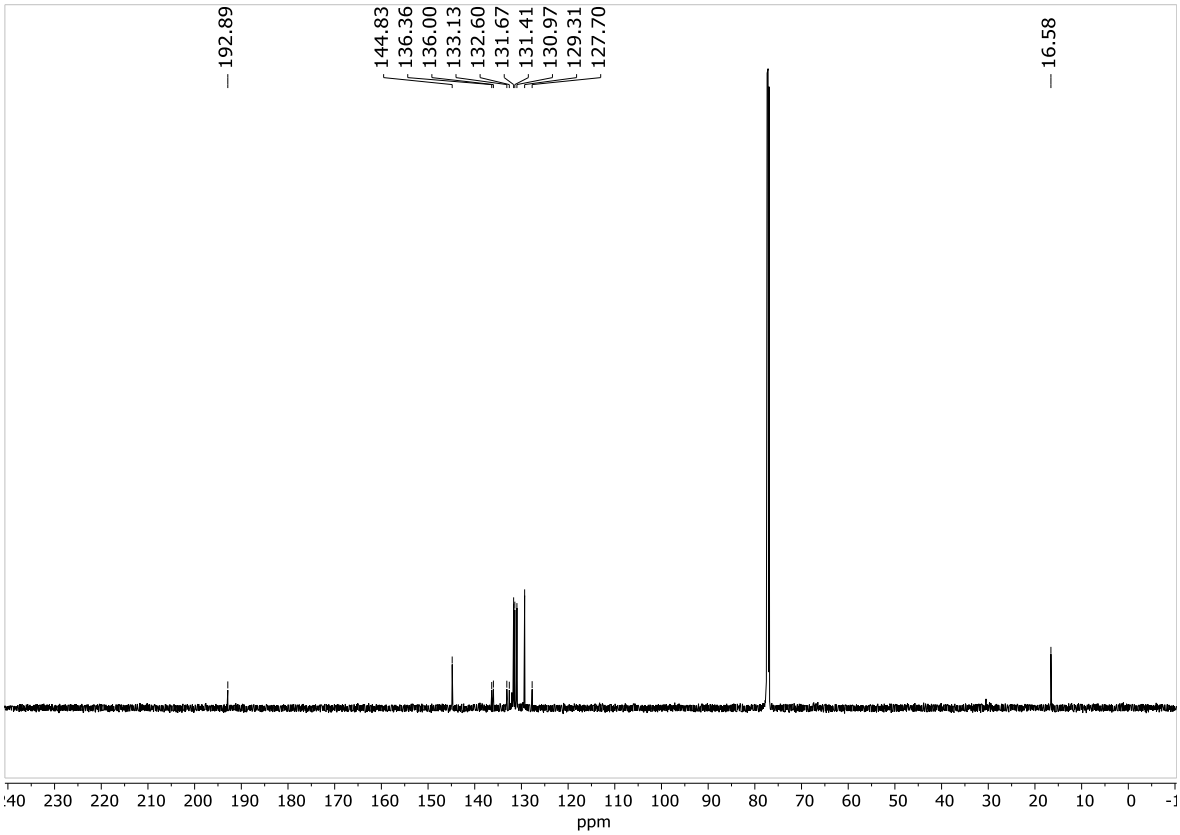
(*Z*)-1-(4-(tert-butyl)phenyl)-2-((4-nitrophenyl)thio)but-2-en-1-one **3fa** (89:11 *Z/E* mixture)



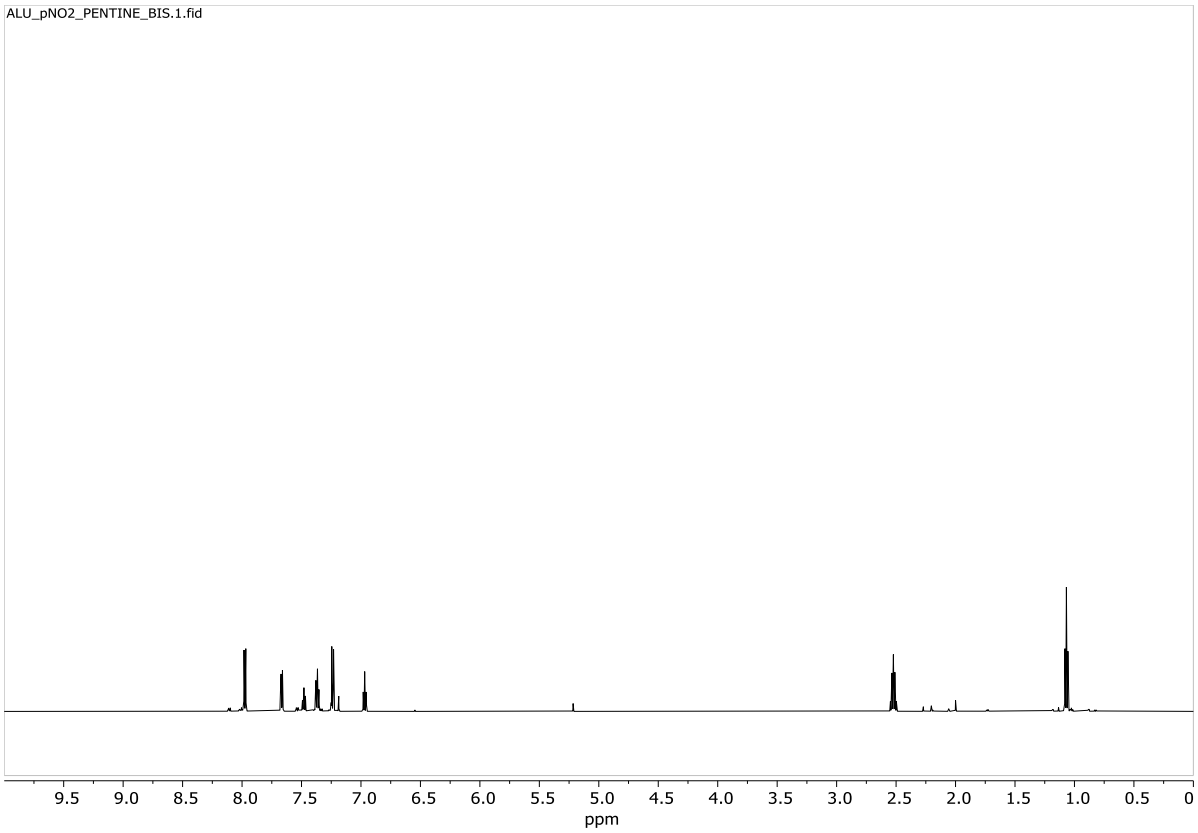


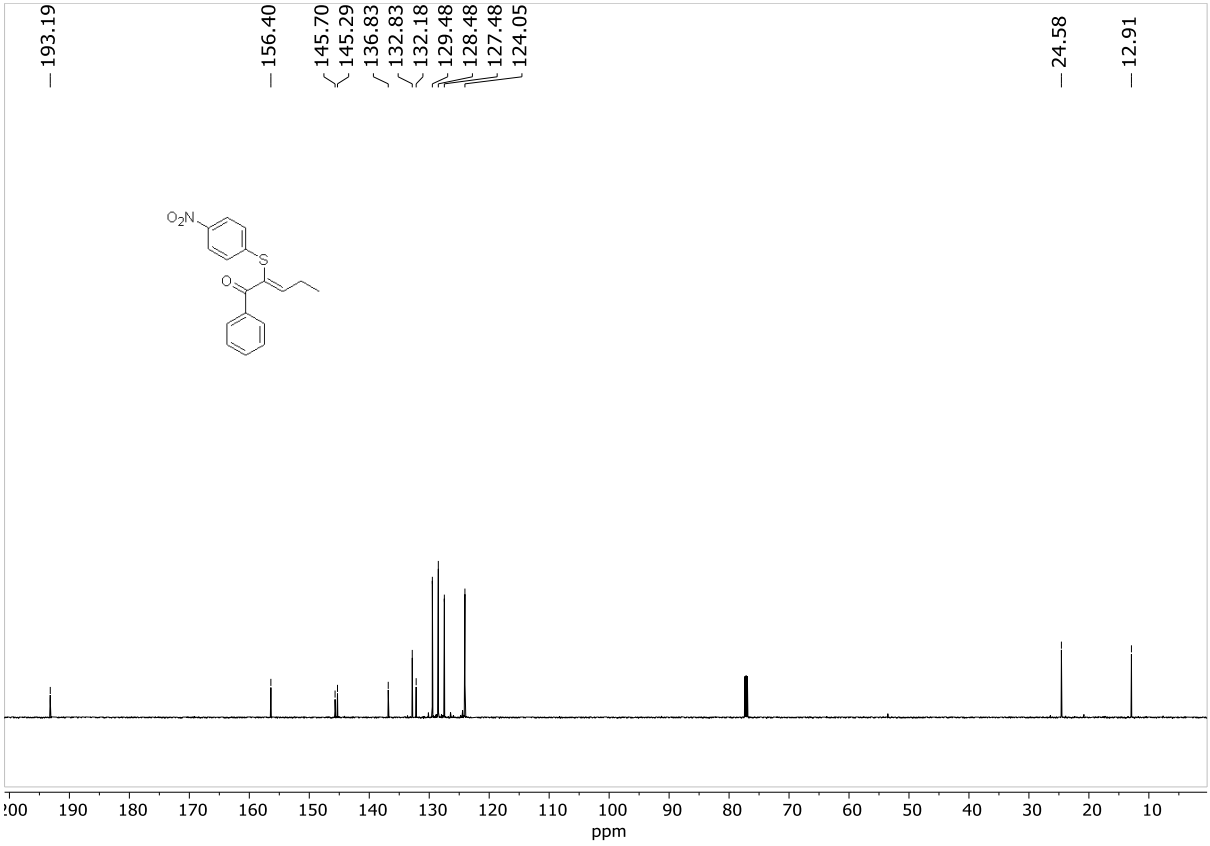
(*Z*)-1-(4-bromophenyl)-2-((4-chlorophenyl)thio)but-2-en-1-one **3ca** (88:12 *Z/E* mixture)



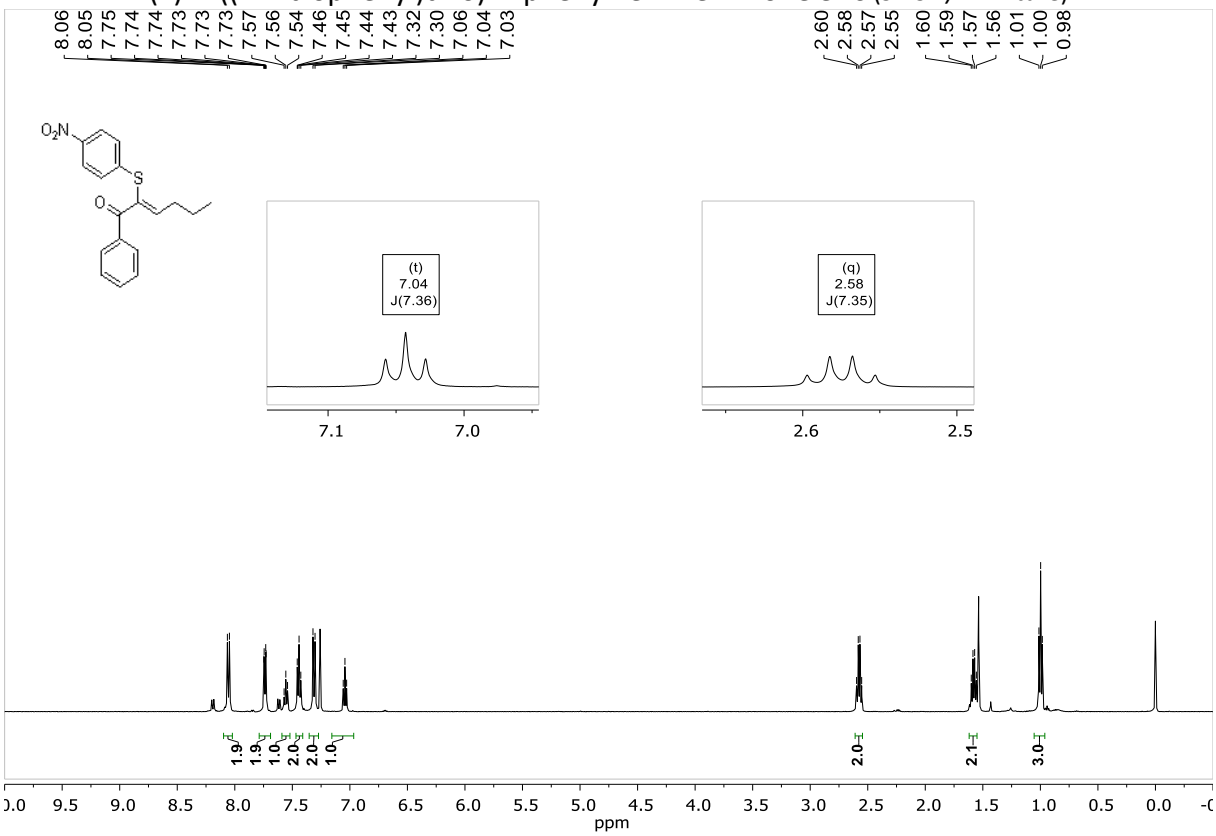


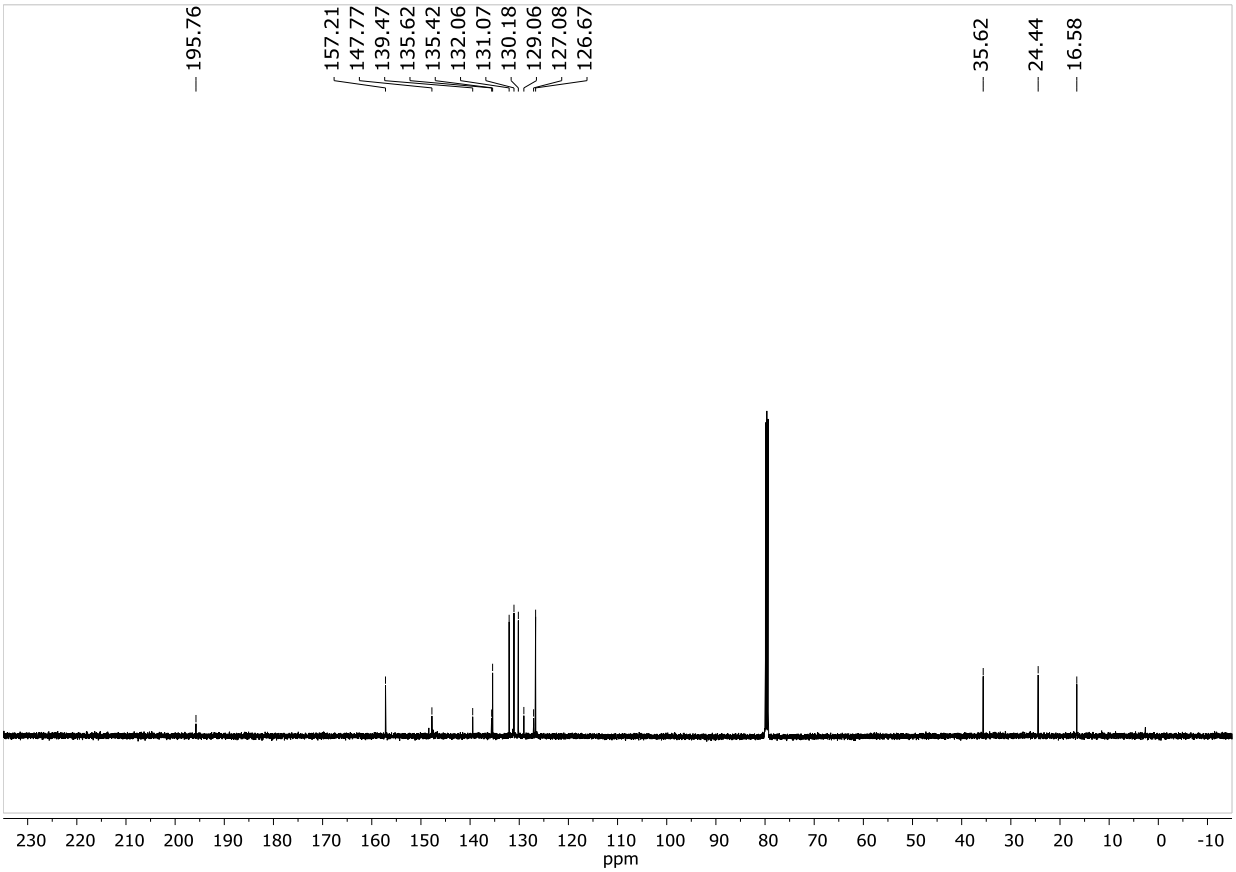
(*Z*)-2-((4-nitrophenyl)thio)-1-phenylpent-2-en-1-one **3gc** (86:14 *Z/E* mixture)



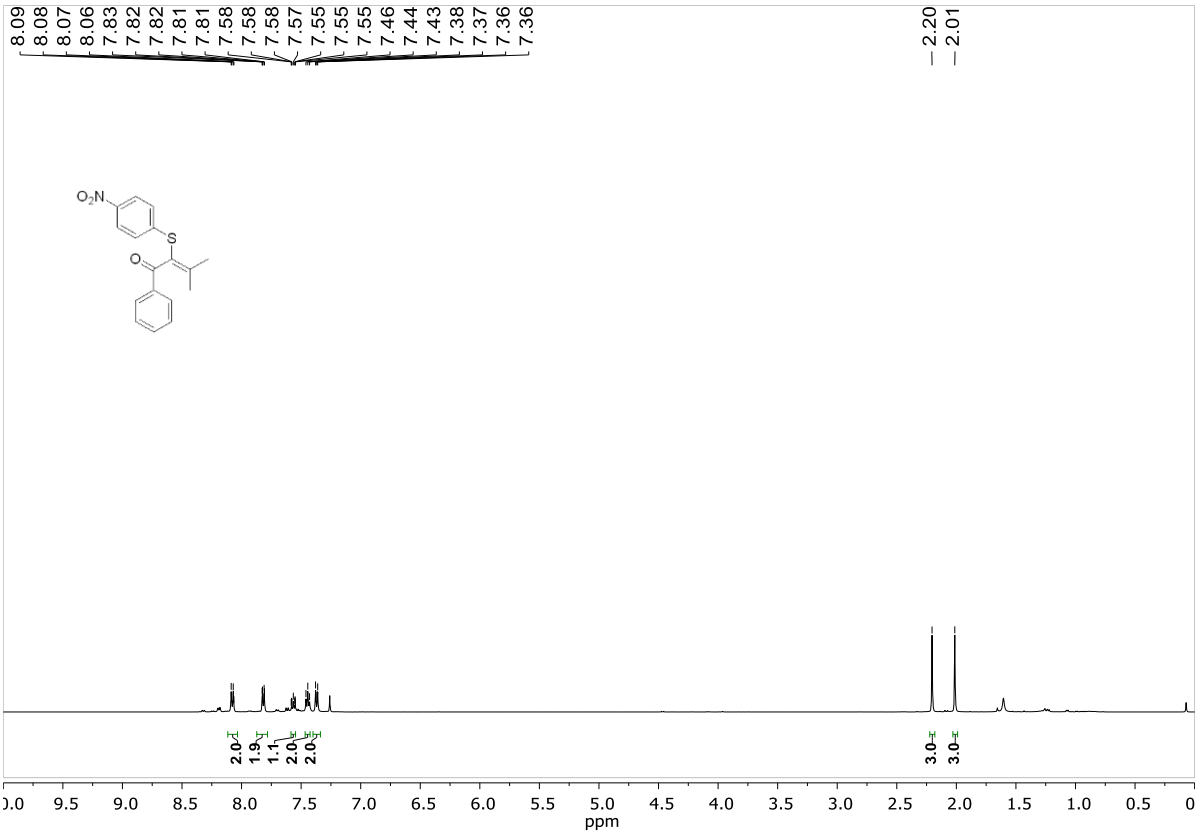


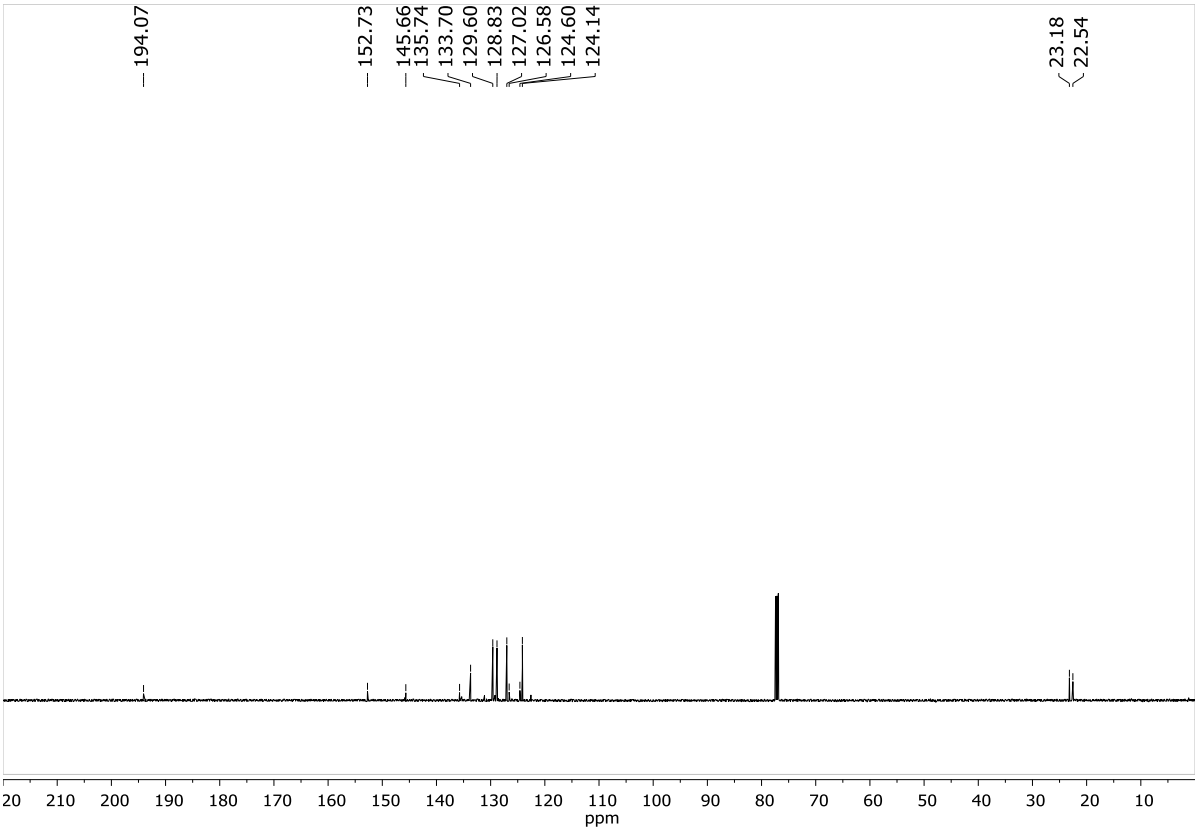
(*Z*)-2-((4-nitrophenyl)thio)-1-phenylhex-2-en-1-one **3hc** (91:9 *Z/E* mixture)





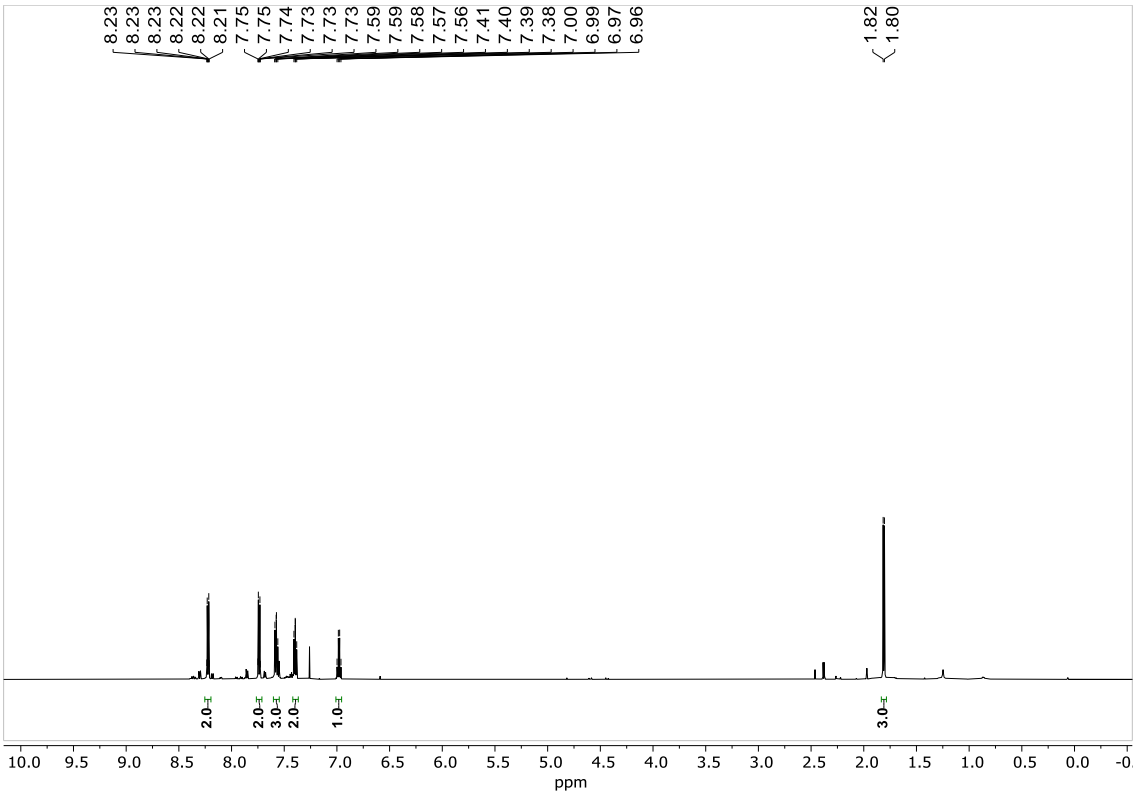
3-methyl-2-((4-nitrophenyl)thio)-1-phenylbut-2-en-1-one **3jc**

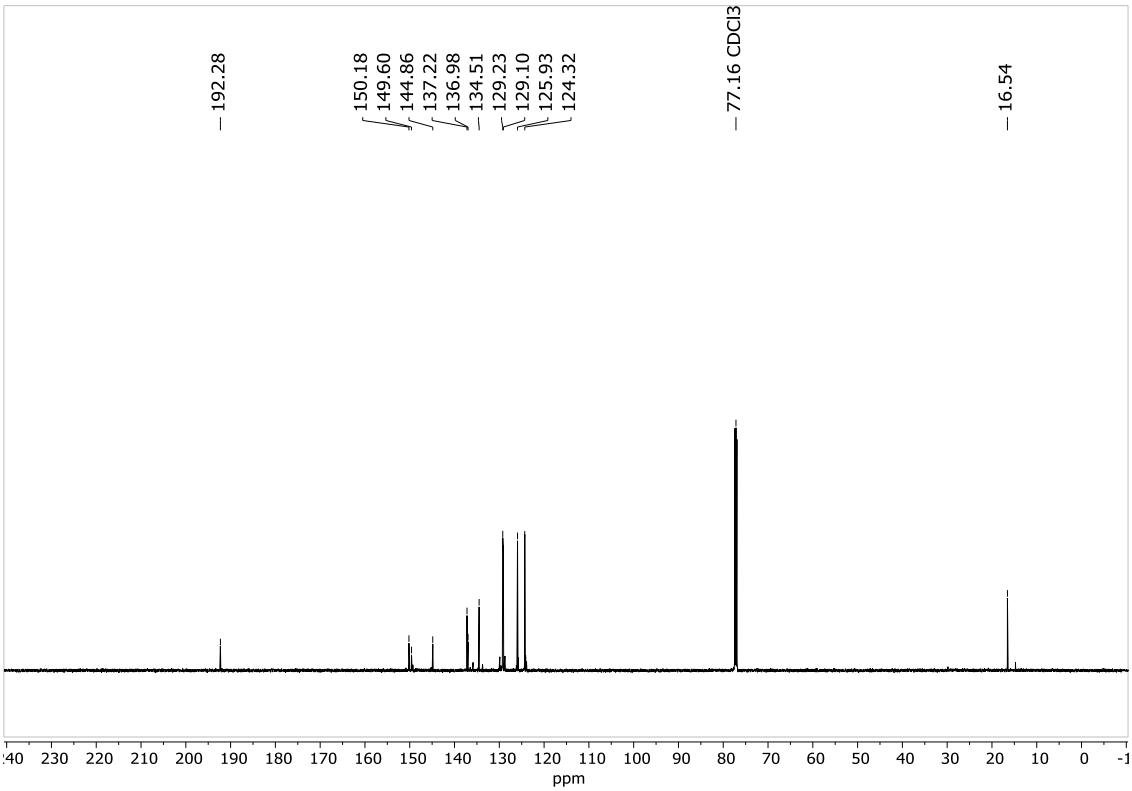




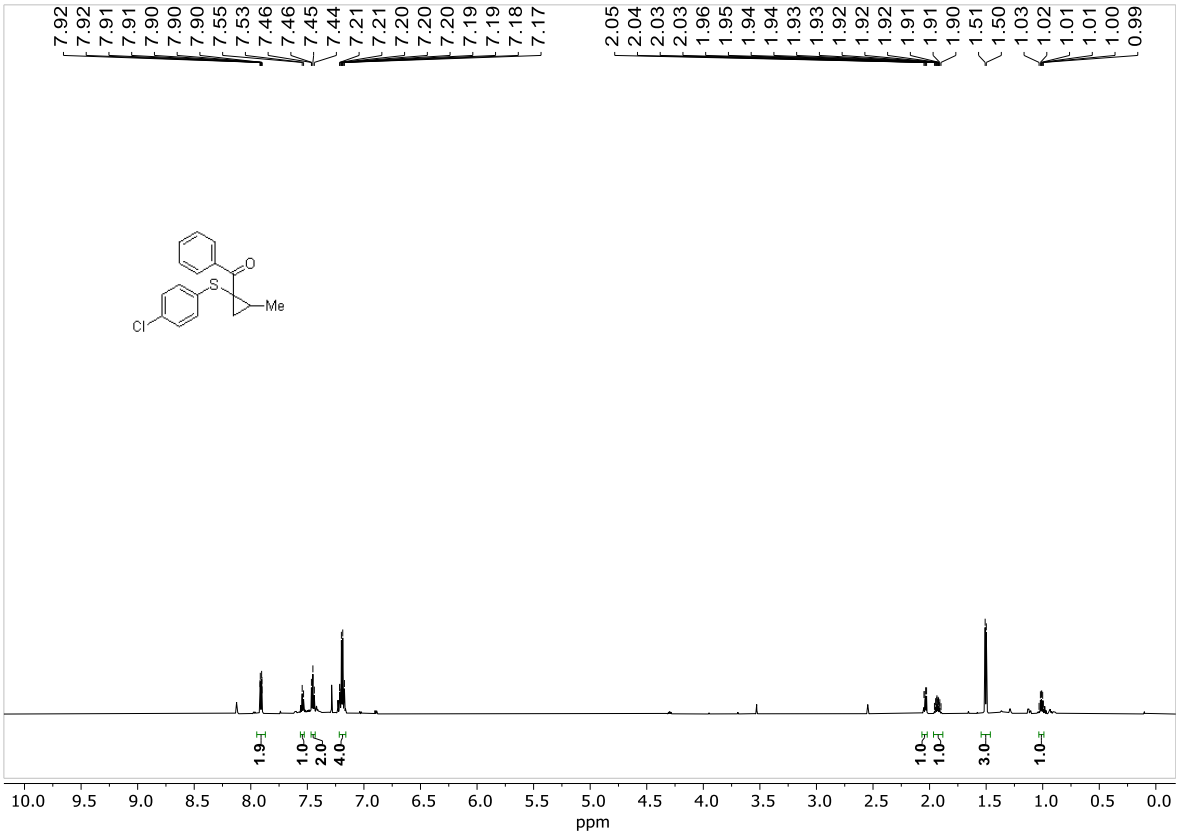
17. ^{1}H and ^{13}C NMR spectra of compounds 9-13

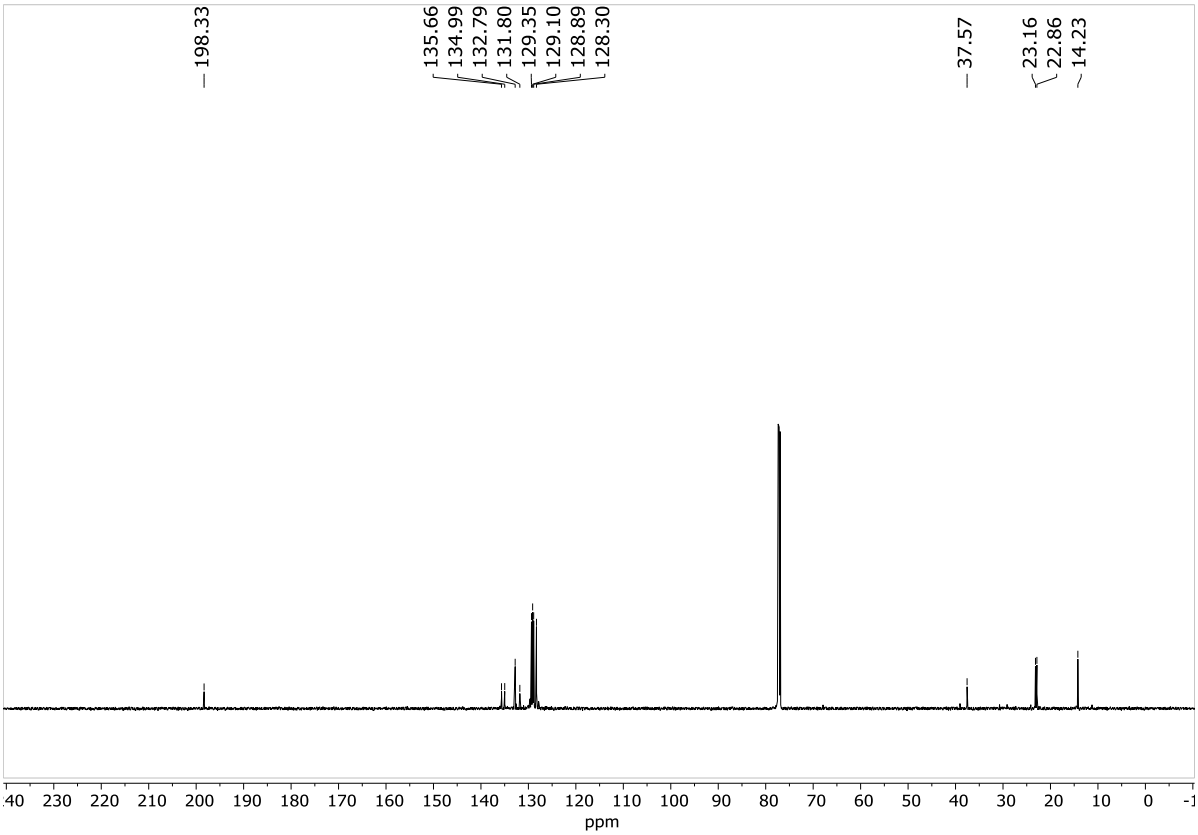
(*Z*)-2-((4-nitrophenyl)sulfonyl)-1-phenylbut-2-en-1-one **9**



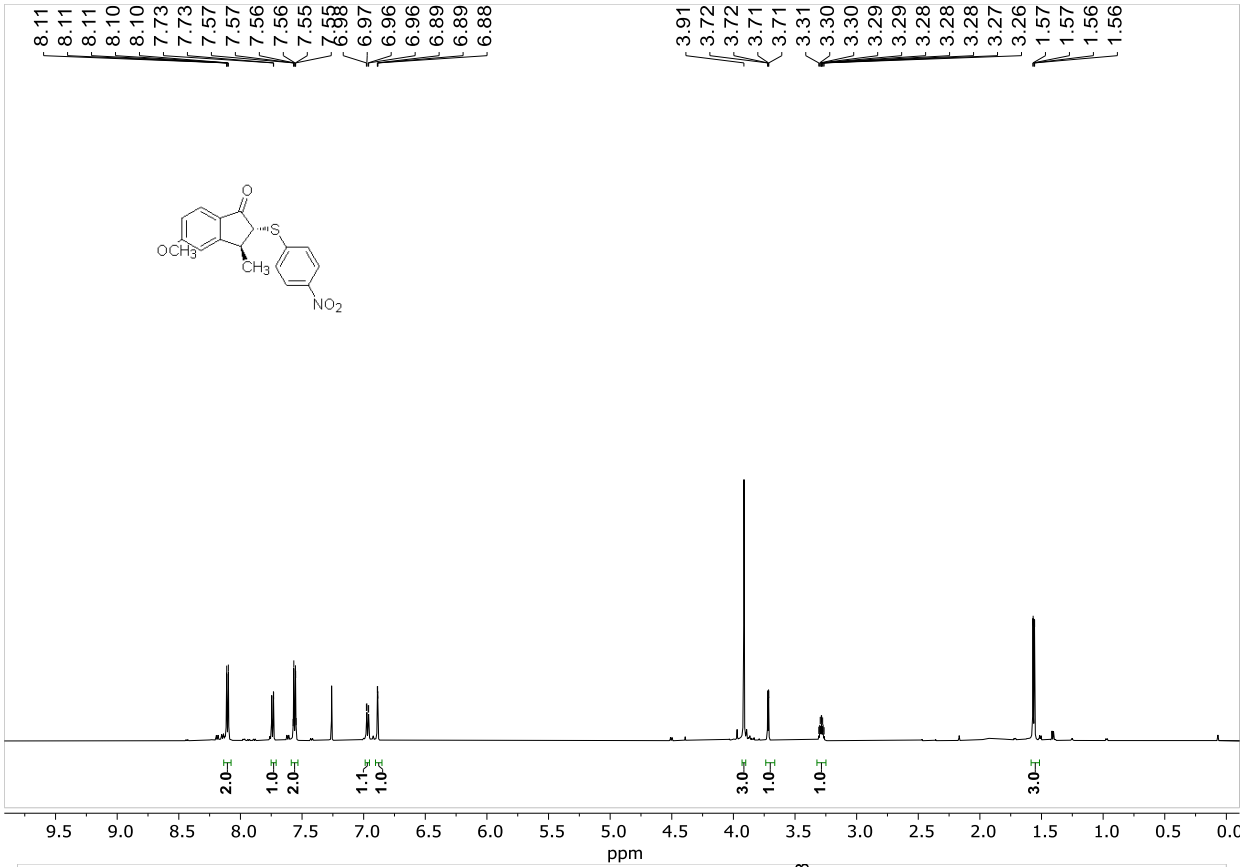


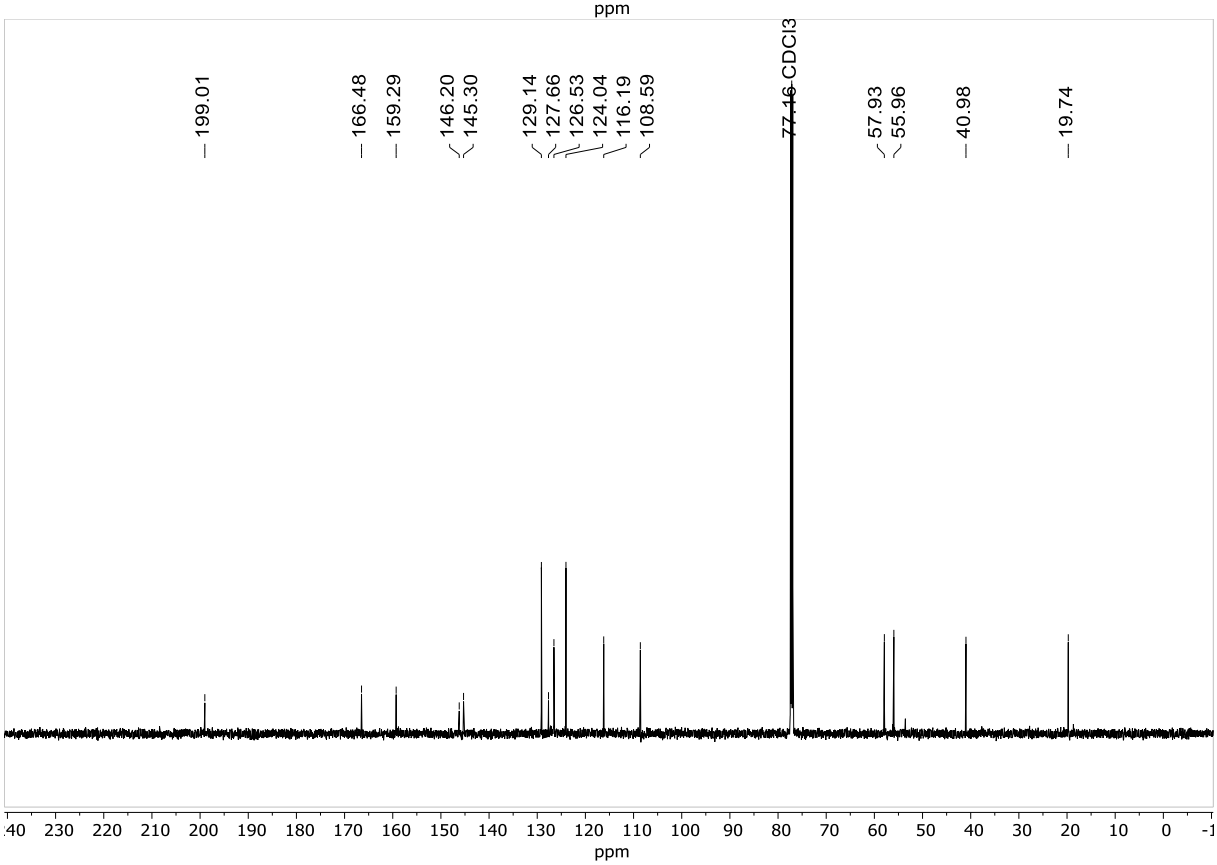
(1-((4-chlorophenyl)thio)-2-methylcyclopropyl)(phenyl)methanone **10**



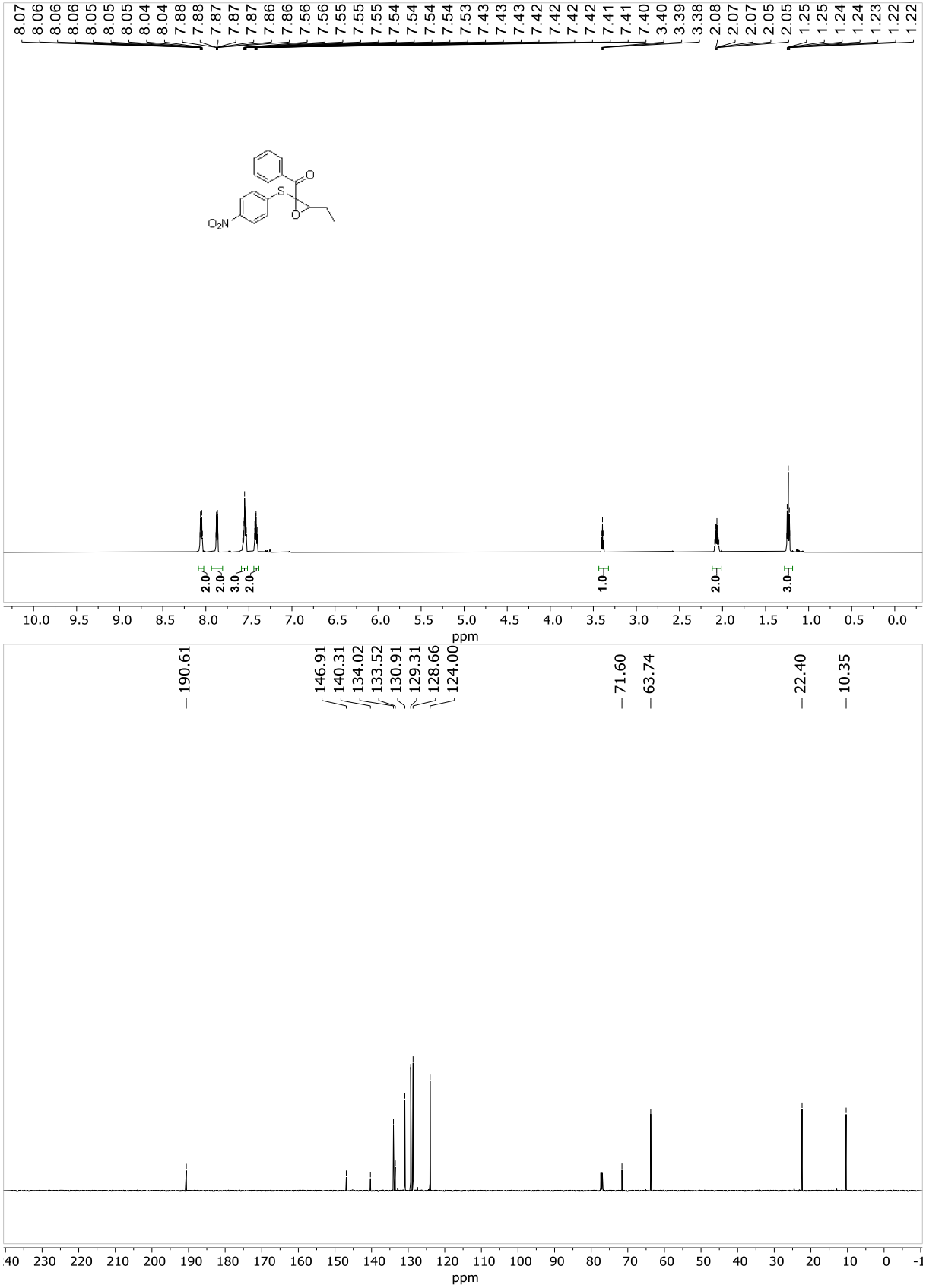


(*trans*)-5-methoxy-3-methyl-2-((4-nitrophenyl)thio)-2,3-dihydro-1H-inden-1-one **11**

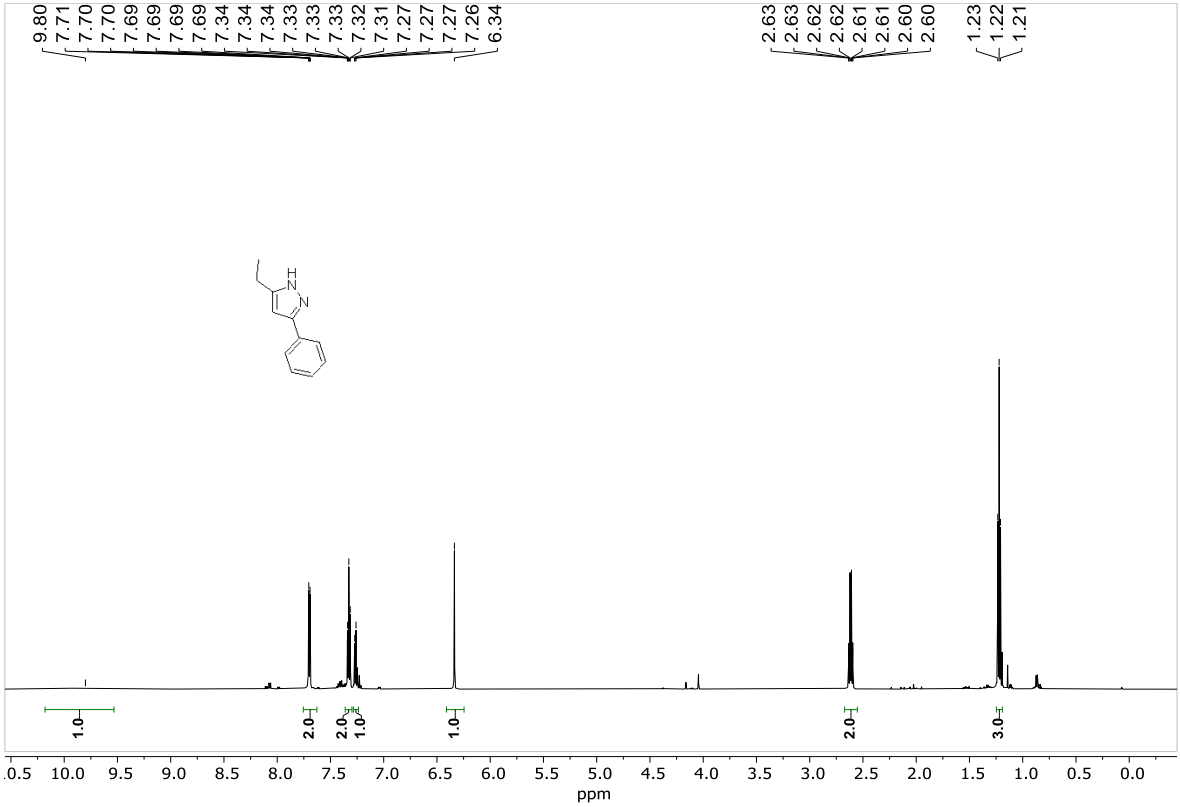


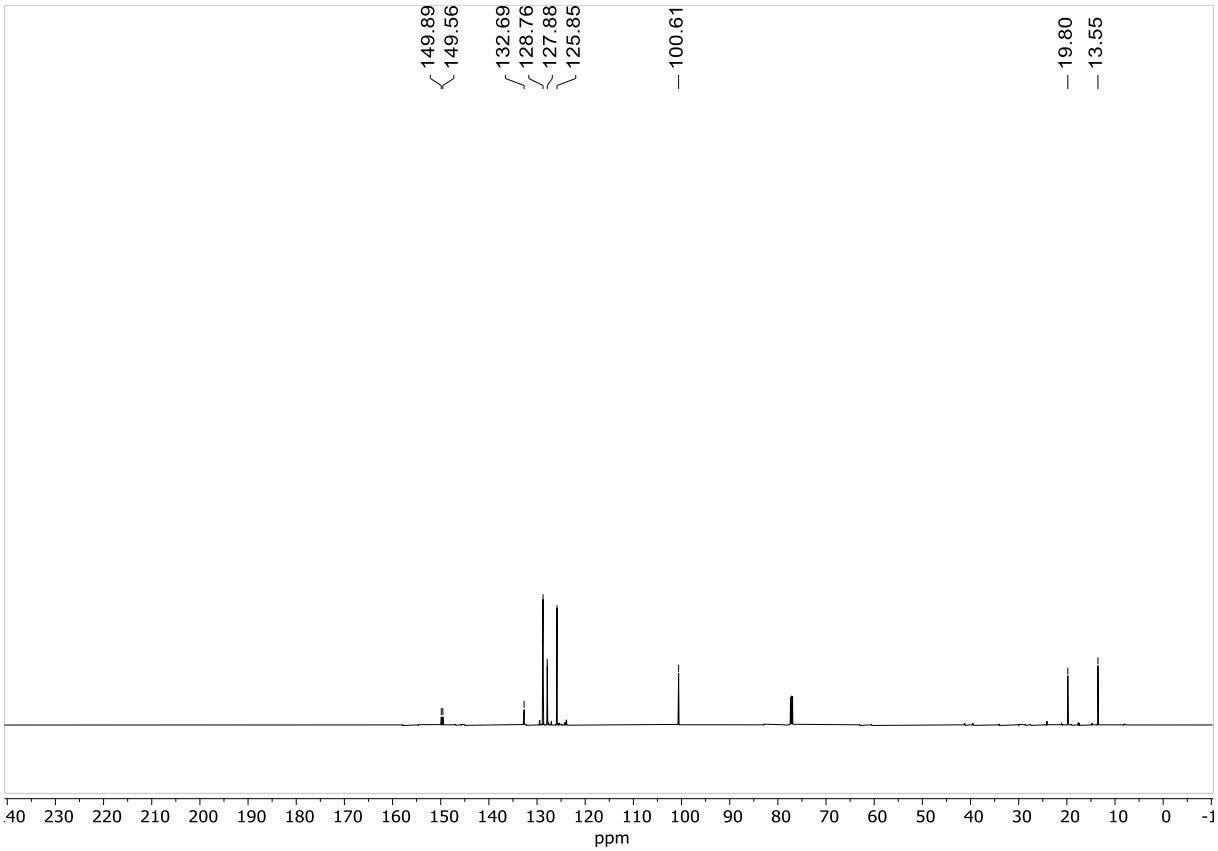


(3-ethyl-2-((4-nitrophenyl)thio)oxiran-2-yl)(phenyl)methanone **12**



5-ethyl-3-phenyl-1H-pyrazole **13**





18. References and notes

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