Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Porous Organic Polymer as Heterogeneous Ligand for Highly Selective Hydroacylation

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Contents

1. General Methods and Materials

The liquid-state NMR was recorded on a 500 MHz or 400 MHz spectrometer. Chemical shifts were reported in ppm. All ^{13}C NMR spectra were measured with complete proton decoupling. Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. The solid-state ^{13}C CP/MAS NMR was performed on a VARIAN Infinity-plus spectrometer.

Nitrogen sorption isotherms at the temperature of liquid nitrogen were performed on a Quantachrome Autosorb-1 system, and the samples were degassed for 10 h at 393 K before the measurements were obtained. The specific surface areas were calculated from the adsorption data using Brunauer–Emmett–Teller (BET) methods.

Transmission electron microscope (TEM) images were performed using a JEM-2100 with accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy(XPS)was conducted using a Thermo Scientific ESCALAB 250Xi with the Al Kα irradiation at $\theta = 90^{o}$ for X-ray sources, and the spectrometer binding energy was calibrated through the reference C 1s (284.8 eV). The samples were pressed to tablet and were pasted on sample stage using conducting resin and the pressure of vacuum chamber was lower than 10-10mbar when testing while the step size of 0.10 eV was employed.

Scanning electron microscopy (SEM) was performed using a JSM-7800 F. Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (NETZSCH STA 449 F3)，the sample was heated at the rate of $10K•min^{-1}$ from room temperature up to 1073K under a nitrogen atmosphere.

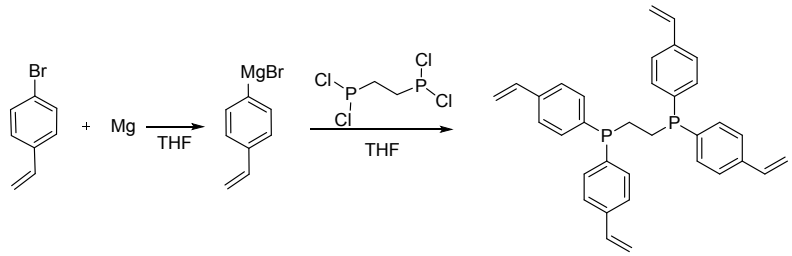
Unless otherwise noted, all reagents were obtained commercially and used without further purification. Solvents were purified according to standard laboratory methods. The β-thio-aldehydes were prepared according to corresponding literature procedures.[1]

Reactions were performed with continuous magnetic stirring, under an atmosphere of nitrogen, unless otherwise stated, using standard Schlenk techniques.

Reference:
[1] M-Y. Lin, A. Das, R-S. Liu, *J. Am. Chem. Soc.*, 2006, **128**, 9340.

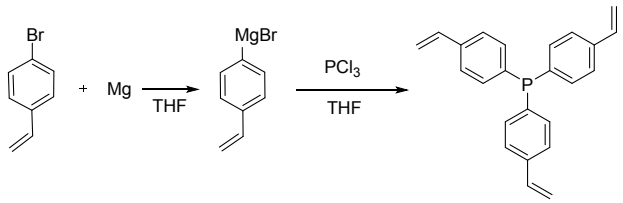
2. Preparation of monomeric ligand

Preparation of vinyl-functionalized dppe ligand monomer (4V-dppe).



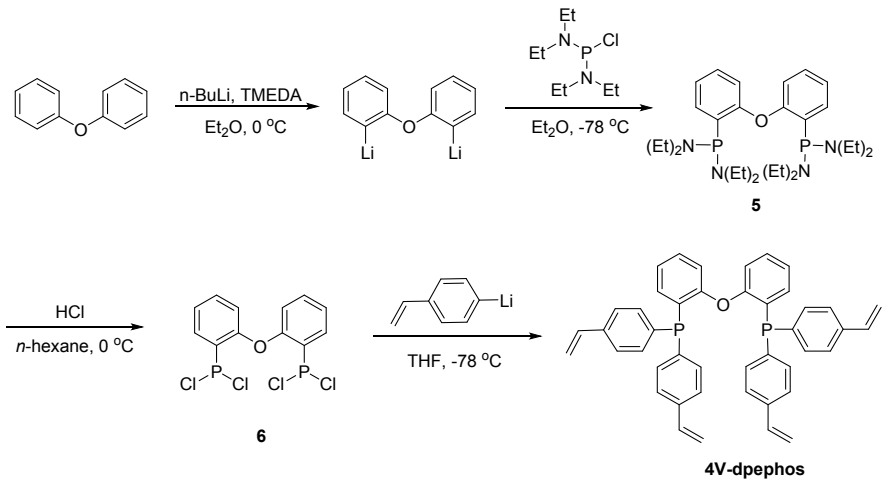
1,2-bis(dichlorophosphino)ethane (10 mmol in 30 mL of THF) was added slowly at 0 °C to the (4-vinylphenyl)magnesium bromide solution, which was synthesized from 4-bromostyrene (60 mmol) and magnesium powder (70 mmol). After stirring at RT for 2 h, 50 mL of saturated NH_4Cl aqueous was added to quench the reaction. The organic phase was separated, and water phase was extracted with an excess of diethyl ether. The combined organic phase was washed with brine, dried over $NaSO_4$, filtered, and concentrated in vacuum. The obtained crude product was purified by silica gel chromatography to afford a white solid.

Preparation of tris(4-vinylphenyl)phosphane



Mg turnings (2.40 g, 100 mmol) was added to a round bottom flask under nitrogen, and were activated by treatment with a grain of I_2 in THF (80 mL). 4-bromostyrene (14.64 g, 80 mmol) was slowly added to the flask, and the mixture was stirred for 1 h at room temperature. Next, PCl_3 (3.43 g, 25 mmol) was slowly added to the solution in the ice water bath over 30 min followed by stirring at room temperature for 4 h. The reaction was quenched with aq.NH_4Cl, and the mixture was extracted with ethyl acetate. The organic layer was washed with H_2O twice, dried over $NaSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford a white solid tris(4-vinylphenyl)phosphane.

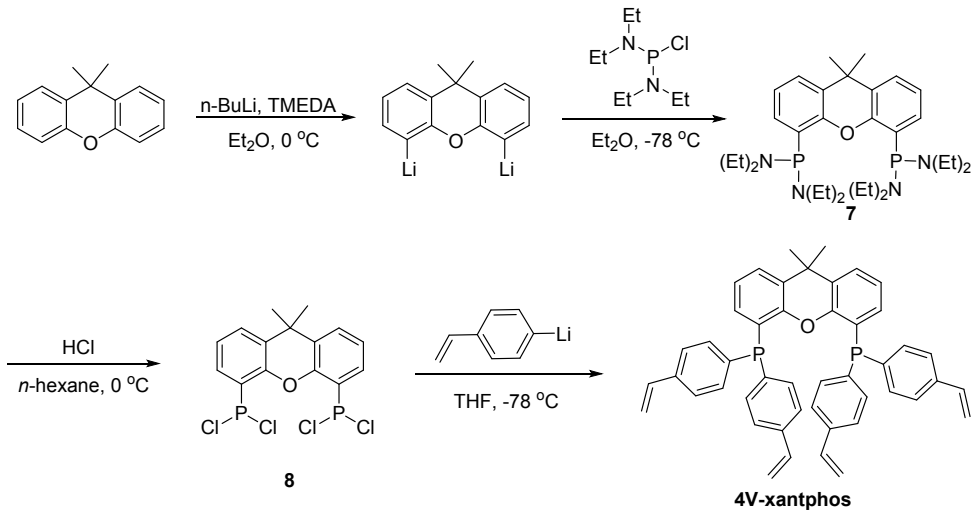
Preparation of vinyl-functionalized dpephos ligand (4V-dpephos)



Diphenyl ether (4.1 g, 24 mmol)，TMEDA (7.0 g, 60 mmol) and anhydrous Et_2O (36 mL) were added to a round bottom flask under nitrogen. To the solution, a 2.5 M solution of n-BuLi (24 mL, 60 mmol) was added slowly at 0 °C, the mixture was stirred at room temperature for 24 h, and cooled to -78 °C, followed by slow addition of $ClP(NEt)_2$ (12.6 g, 60 mmol). the resultant solution was slowly warmed up to room temperature and stirred overnight, and was concentrated to a quarter in vacuo and dry hexane (150 mL) was added to the mixture. After filtration under N_2 atmosphere, dry HCl was passed through the solution at room temperature for 2 h. Prior to filtration under N_2 atmosphere, the solvent was removed in vacuo and the crude product **6** was obtained as a white solid.

A flask was charged with 1-bromo-4-vinylbenzene (4.0 g, 22 mmol) and THF (40 mL). To the solution, n-BuLi (8.8 mL of 2.5 M solution, 22 mmol) was added dropwise at -78 °C and the mixture was stirred at -78 °C for 1 h. To the mixture, a solution of **6** in THF (10 mL) was added dropwise, the resulting solution was slowly warmed up to room temperature and stirred overnight at room temperature. All volatiles were removed in vacuo. Then 40 mL Et_2O and 30 mL saturated salt water were added, and the aqueous layer was extracted twice with 10 mL Et_2O. The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford the fina product **4V-dpephos** (0.9 g, total yield: 6%).

Preparation of vinyl-functionalized dppe ligand monomer (4V-xantphos)

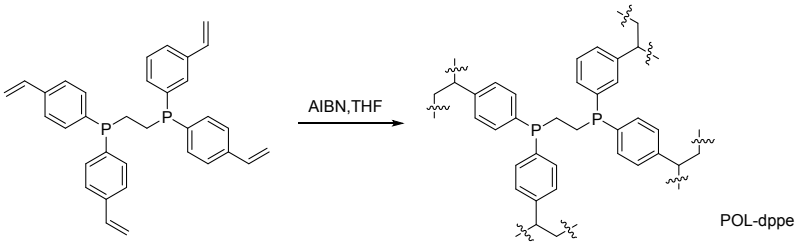


9,9-dimethyl-9H-xanthene (5.0 g, 24 mmol)，TMEDA (7.0 g, 60 mmol) and anhydrous Et_2O (36 mL) were added to a round bottom flask under nitrogen. To the solution, a 2.5 M solution of n-BuLi (24 mL, 60 mmol) was added slowly at 0 °C, the mixture was stirred at room temperature for 24 h, and cooled to -78 °C, followed by slow addition of $ClP(NEt)_2$ (12.6 g, 60 mmol). the resultant solution was slowly warmed up to room temperature and stirred overnight, and was concentrated to a quarter in vacuo and dry hexane (150 mL) was added to the mixture. After filtration under N_2 atmosphere, dry HCl was passed through the solution at room temperature for 2 h. Prior to filtration under N_2 atmosphere, the solvent was removed in vacuo and the crude product **8** was obtained as a white solid.

A flask was charged with 1-bromo-4-vinylbenzene (4.0 g, 22 mmol) and THF (40 mL). To the solution, n-BuLi (8.8 mL of 2.5 M solution, 22 mmol) was added dropwise at -78 °C and the mixture was stirred at -78 °C for 1 h. To the mixture, a solution of **8** in THF (10 mL) was added dropwise, the resulting solution was slowly warmed up to room temperature and stirred overnight at room temperature. All volatiles were removed in vacuo. Then 40 mL Et_2O and 30 mL Saturated salt water were added, and the aqueous layer was extracted twice with 10 mL Et_2O. The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford the fina product **4V-xantphos** (1.3 g, total yield: 8%).

3. Synthesis of polymers

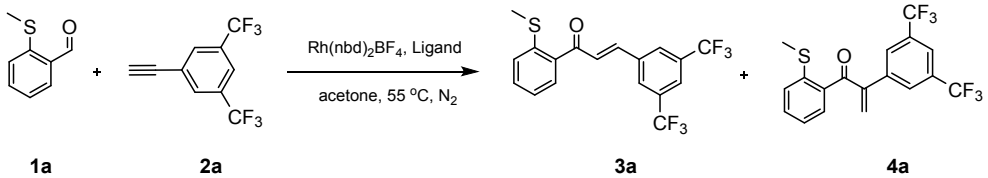
Synthesis of POL-dppe.



1.0 g of vinyl-functionalized dppe monomer was dissolved in 10 mL of THF, followed by addition of 100 mg of azobisisobutyronitrile (AIBN). The mixture was transferred into an autoclave at 100 °C for 24 h. After evaporation of THF under vacuum, a solid product was obtained and denoted as POL-dppe.

4. General Procedure for Rhodium-Catalysed Hydroacylation

General procedure A (Ligand screen, Table 1)

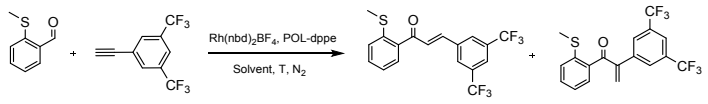


Rh species (0.03 mmol) and the appropriate ligand were dissolved in acetone (2.0 mL) and stirred at RT for 5 min. H_2 (g) was bubbled through the pre-catalyst solution for 2 min, then the solution purged with N_2 (g). 2-methylthiobenzaldehyde (45.7 mg, 0.30 mmol) and 1-ethynyl-3,5-

bis(trifluoromethyl)benzene (107.2 mg, 0.45 mmol) were added and the reaction mixture was stirred at 55 °C for 2-24 h. The reaction mixture was diluted with acetone, 1,3,5-trimethoxybenzene (16.8 mg, 0.10 mmol) was added as an internal standard, filtered through a short plug of celite and the filtrate concentrated in vacuo.

A sample of the crude residue was analysed by ^{1}H NMR in $CDCl_3$, to determine yield and the regioselectivity of the reaction.

Table S1. Impact of different solvents and reaction temperature [a]

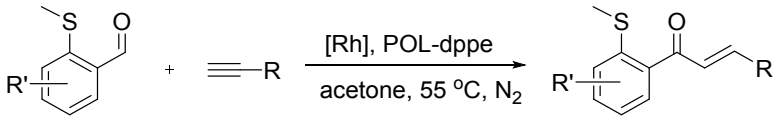


1a 2a 3a 4a

Entry	Solvent	Temperature/°C	yield/%[b]	3a : 4a[c]
1	acetone	55	85	> 20:1
2	acetone	25	50	> 20:1
3	THF	60	36	> 20:1
4	DCE	70	31	10:1
5	Tol	100	< 10	---

[a]Reaction conditions: aldehyde **1a** (0.30 mmol), alkyne **2a** (0.45 mmol), $[Rh(nbd)_2]BF_4$ (10 mol%), POL-dppe (40 mg), 2-24 h. nbd = norbornadiene. [b]Determined by ^{1}H NMR yield, 1,3,5-Trimethoxybenzene as an internal standard, [c]Determined by ^{1}H NMR analysis of crude reaction mixtures.

General procedure B (Reaction scope, Tables 2)



$[Rh(nbd)_2]BF_4$ (11 mg, 0.03 mmol) and POL-dppe (40 mg) were dissolved in acetone (1.0 mL) and stirred at RT for 5 min. H_2 (g) was bubbled through the pre-catalyst solution for 2 min, then the solution purged with N_2 (g). Aldehyde (0.30 mmol) and alkyne (0.45 mmol) were added as a solution in acetone (1.0 mL) and the reaction mixture was stirred at RT for 55 °C for 2-24 h. The reaction mixture was diluted with acetone, filtered through a short plug of celite and the filtrate concentrated in vacuo. The crude residue was purified by flash column chromatography.

A sample of the crude residue was analysed by ^{1}H NMR in $CDCl_3$ to determine the regioselectivity of the reaction.

5. Characterization of polymers and Rh/POL-dppe

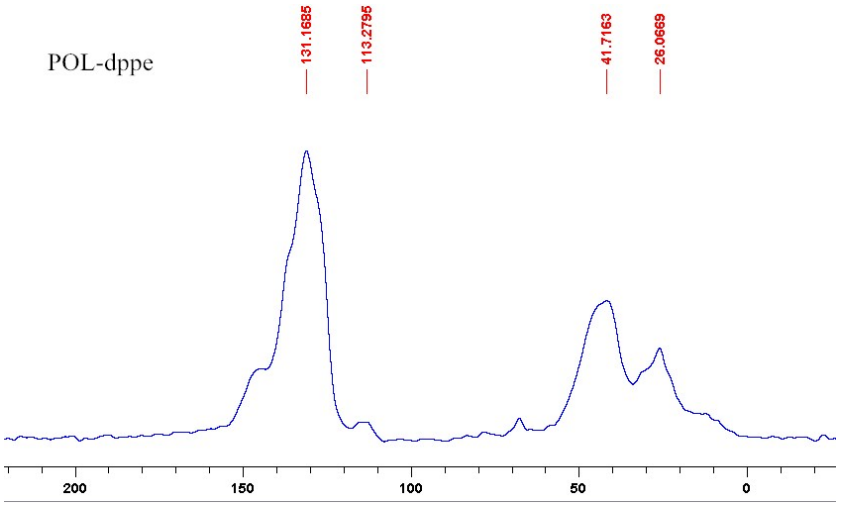


Figure S1. ^{13}C CP/MAS of POL-dppe (100 MHz) δ 26.1, 41.7, 113.3, 131.2.

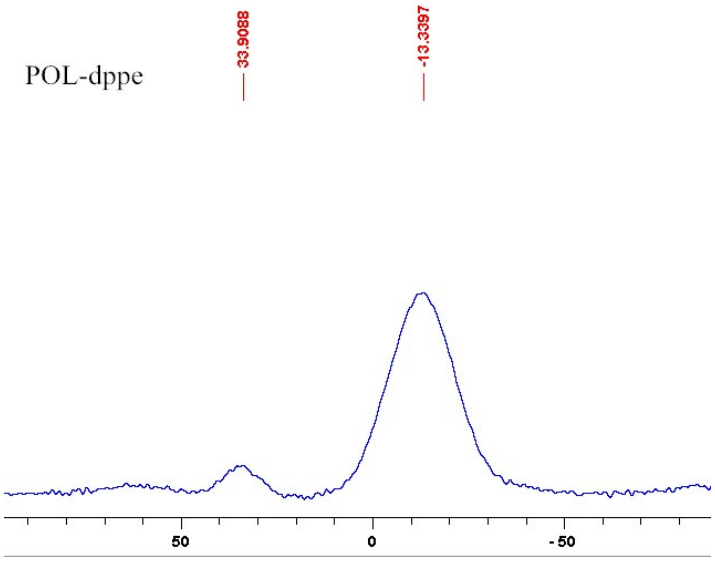


Figure S2. ^{31}P CP/MAS of POL-dppe (162 MHz) δ -13.4.

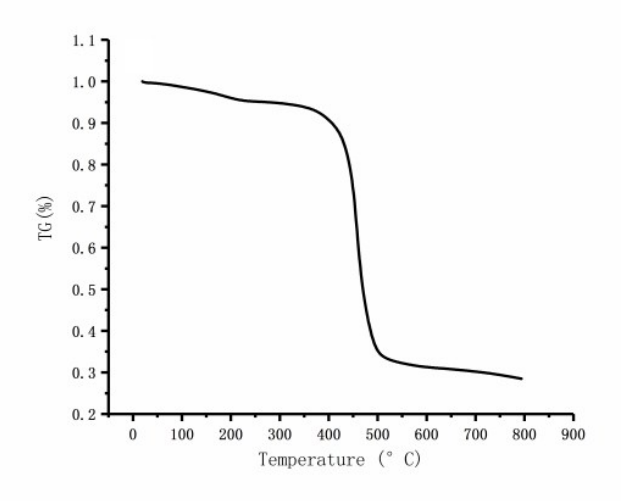


Figure S3. TG curve of POL-dppe

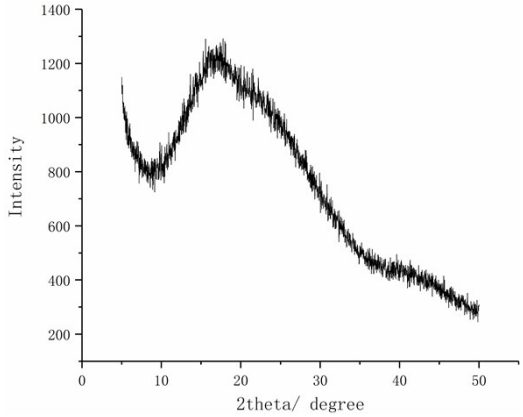


Figure S4. XRD pattern of the POL-dppe polymer. The broad peak ranged from 10 to 45°, indicating the amorphous nature of the sample.

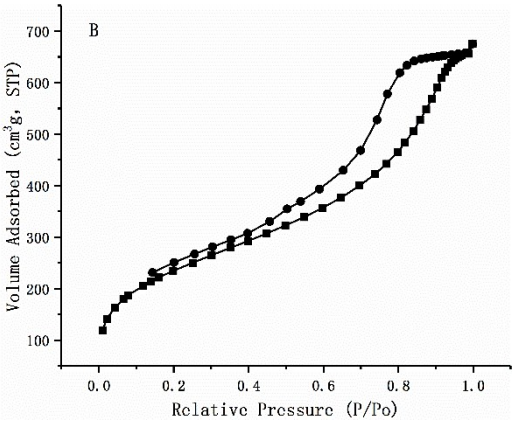


Figure S5. N_2 sorption isotherms of POL-dppe.

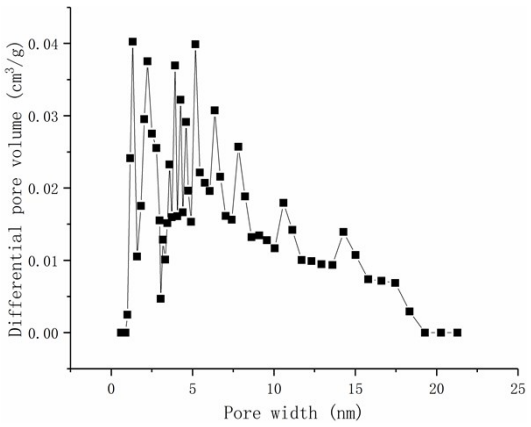


Figure S6. Pore size distribution of the POL-dppe polymer calculated from non-local density functional theory (NLDFT). This result indicates that the presence of hierarchical porosity in the sample.

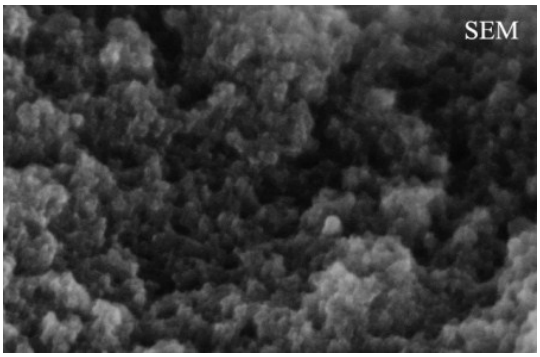


Figure S7. Scanning electron microscopy (SEM) of POL-dppe.

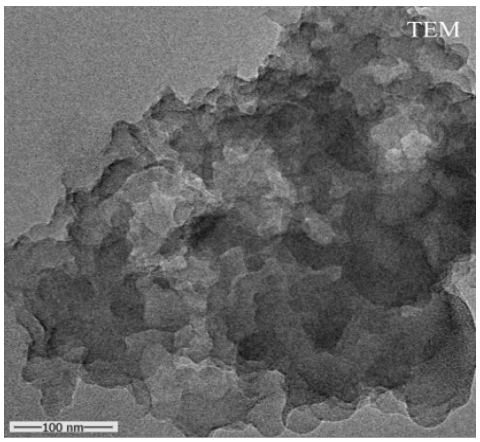


Figure S8. Transmission electron microscopy (TEM) of POL-dppe

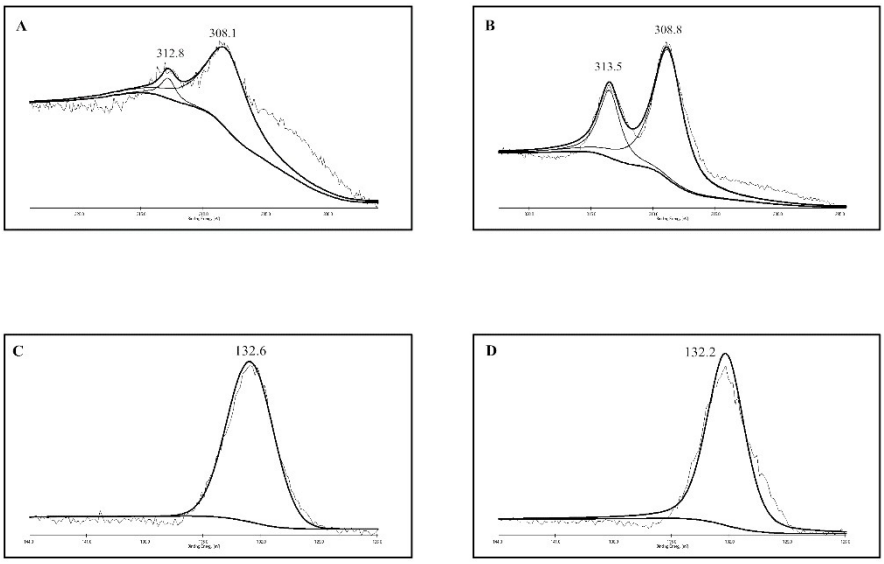


Figure S9. Rh3d XPS spectra of (A) Rh/POL-dppe and (B) $[Rh(nbd)_2]BF_4$
P2p XPS spectra of (C) Rh/POL-dppe and (D) POL-dppe samples
X-ray photoelectron spectroscopy (XPS) spectra of the Rh/POL-dppe catalyst demonstrate the values of Rh 3d5/2 and Rh 3d3/2 about 308.1 and 312.8 eV, which are lower than the values 308.8 and 313.5 eV of $[Rh(nbd)_2]BF_4$. Simultaneously, the P2d binding energy of the Rh/POL-dppe catalyst exhibits a higher value (132.6 eV) than that (132.2 eV) of the POL-dppe polymer.

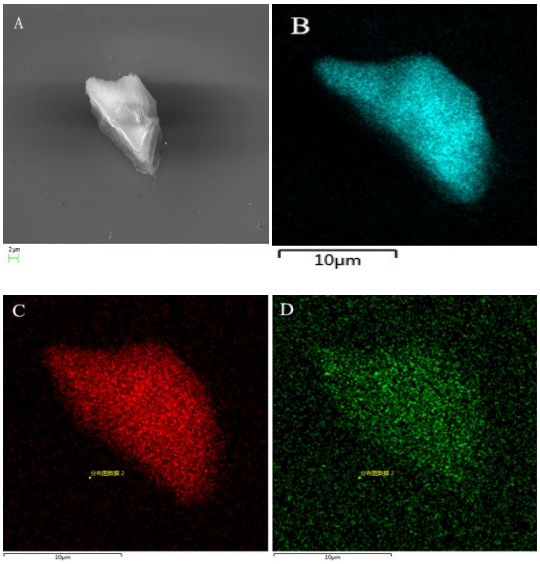
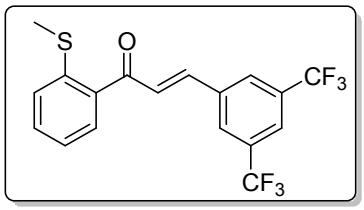


Figure S10. Elemental distribution in $[Rh(nbd)_2]BF_4$/POL-dppe determined by SEM-EDS mapping, (A) SEM images, (B) Carbon, (C) Phosphorus and (D) Rhodium.

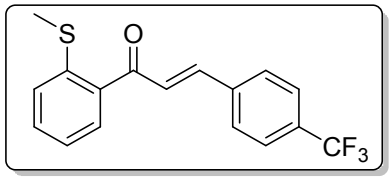
6. Analytical data for compounds

3a. (E)-3-(3,5-bis(Trifluoromethyl)phenyl)-1-(2-(methylthio)phenyl)prop-2-en-1-one



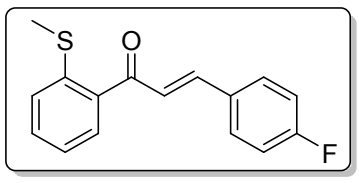
Prepared according to General Procedure B using 2-(methylthio)benzaldehyde (46 mg, 0.30 mmol) and 1-ethynyl-3,5-bis(trifluoromethyl)benzene (107 mg, 0.45 mmol), $[Rh(nbd)_2]BF_4$ (11 mg, 0.03 mmol), POL-dppe (40 mg) in acetone (2.0 mL) at 55 ^oC for 24 h. Purification by flash chromatography afforded the title compound 3a as a bright yellow solid (90 mg, 77%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (2H, s), 7.89 (1H, s), 7.75 (1H, apparent d, *J*= 7.7 Hz), 7.67 (1H, d, *J*= 15.9 Hz), 7.51 (1H, apparent t, *J*= 7.7 Hz), 7.45 (1H, d, *J*= 15.9 Hz), 7.41(1H, apparent d, *J*= 8.0 Hz), 7.30-7.25 (1H, m), 2.48 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.5, 141.3, 140.8, 137.0, 136.3, 132.5 (q, *J*= 33.5 Hz), 132.1, 129.8, 127.9, 127.8, 126.3, 124.3, 123.5-123.3 (m), 123.0 (q, *J*= 273.0 Hz), 16.4.

3b. (*E*)-1-(2-(Methylthio)phenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one



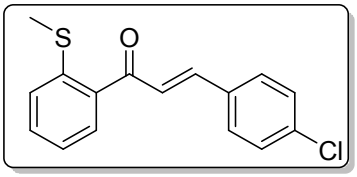
yellow solid (63 mg, 65%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75-7.62 (6H, m), 7.53-7.47 (1H, apparent t, *J*= 7.6 Hz), 7.43-7.36 (1H d, *J*= 15.6 Hz overlapping 1H, m), 7.27-7.22 (1H, m), 2.47 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.2, 142.9, 141.0, 138.3, 136.7, 131.9, 131.9 (q, *J*= 33.0 Hz), 129.6, 128.5, 126.8, 126.3 , 125.9 (q, *J*= 3.8 Hz), 124.2, 123.8 (q, *J*= 273.0 Hz), 16.5.

3c. (*E*)-3-(4-Fluorophenyl)-1-(2-(methylthio)phenyl)prop-2-en-1-one



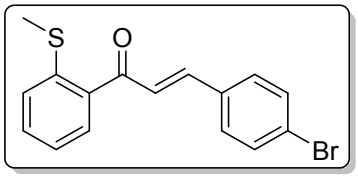
yellow solid (62 mg, 76%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (1H, apparent d, *J*= 7.7 Hz), 7.6-7.55 (3H, m), 7.51-7.44 (1H, m), 7.38 (1H, apparent d, *J*= 8.0 Hz), 7.28-7.20 (2H, m), 7.09 (2H, apparent t, *J*= 8.5 Hz), 2.46 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.7, 164.0 (d, *J*= 252.2 Hz), 143.9, 140.5, 137.3, 131.6, 131.1 (d, *J*= 3.5 Hz), 130.4 (d, *J*= 8.8 Hz), 129.4, 126.3, 124.6, 124.5, 116.1 (d, *J*= 21.9 Hz), 16.5.

3d. (*E*)-3-(4-Chlorophenyl)-1-(2-(methylthio)phenyl)prop-2-en-1-one



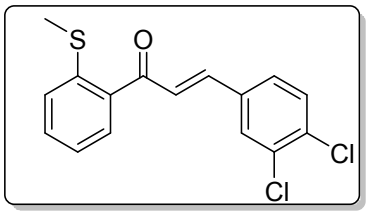
yellow solid (62 mg, 71%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (1H, apparent d, *J*= 7.6 Hz), 7.57 (1H, d, *J*= 15.9 Hz), 7.51 (2H, d, *J*= 8.0 Hz), 7.47 (1H, apparent t, *J*= 7.6 Hz), 7.4-7.34 (3H, m), 7.28 (1H, d, *J*= 15.8 Hz), 7.23 (1H, apparent t, *J*= 7.5 Hz), 2.45 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.5, 143.6, 140.7, 137.1, 136.4, 133.3, 131.7, 129.6, 129.5, 129.2, 126.3, 125.2, 124.2, 16.5.

3e. (*E*)-3-(4-Bromophenyl)-1-(2-(methylthio)phenyl)prop-2-en-1-one



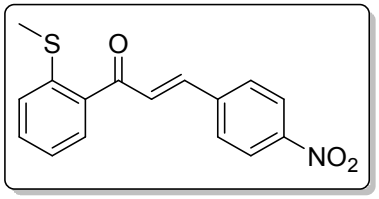
yellow solid (87 mg, 87%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (1H, dd, J_1= 7.7 Hz, J_2= 1.3 Hz), 7.60-7.41 (6H, m), 7.37 (1H, apparent d, *J*= 7.9 Hz), 7.30 (1H, d, *J*= 15.9 Hz), 7.25-7.20 (1H, m), 2.45 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.5, 143.6, 140.7, 137.1, 133.8, 132.2, 131.7, 129.8, 129.5, 126.3, 125.3, 124.8, 124.2, 16.5.

3f. (*E*)-3-(3,4-Dichlorophenyl)-1-(2-(methylthio)phenyl)prop-2-en-1-one



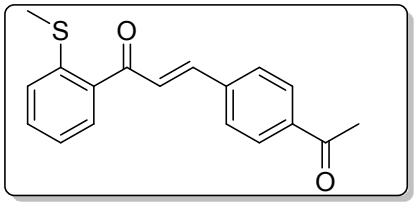
yellow solid (72.8 mg, 75%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (1H, apparent d, *J*= 7.6 Hz), 7.66 (1H, s), 7.56-7.44 (2H, m), 7.44-7.35 (2H, m), 7.30 (1H, d, *J*= 15.9 Hz), 7.27-7.21 (1H, m), 2.46 (1H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.0, 142.0, 140.9, 136.7, 134.9, 134.4, 133.3, 131.9, 130.9, 129.8, 129.6, 127.4, 126.3, 126.1, 124.2, 16.5.

3g. (*E*)-1-(2-(Methylthio)phenyl)-3-(4-nitrophenyl)prop-2-en-1-one



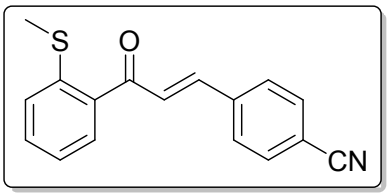
yellow solid (43.2 mg, 48%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (2H, apparent d, *J*= 8.8 Hz), 7.78-7.72 (3H, m), 7.68 (1H, d, *J*= 16 Hz), 7.55-7.48 (1H, m), 7.46 (1H, d, *J*= 15.9 Hz), 7.40 (1H, apparent d, *J*= 7.9 Hz), 7.30-7.23 (1H, m), 2.48 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.7, 148.6, 141.5, 141.3, 141.1, 136.4, 132.1, 129.8, 128.9, 128.2, 126.3, 124.3, 124.2, 16.5.

3h. (*E*)-3-(4-acetylphenyl)-1-(2-(Methylthio)phenyl)prop-2-en-1-one



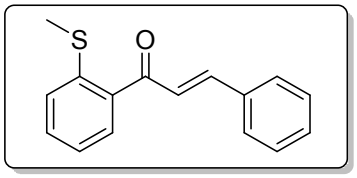
yellow solid (72 mg, 81%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (2H, apparent d, *J*= 8.1 Hz), 7.72 (1H, apparent d, *J*= 7.7 Hz), 7.69-7.61 (3H, m), 7.52-7.46 (1H, m), 7.44-7.36 (2H, m), 7.29-7.22 (1H, m), 2.62 (3H, s), 2.47 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.3, 192.2, 143.2, 140.9, 139.2, 138.1, 136.8, 131.8, 129.6, 128.9, 128.5, 126.8, 126.3, 124.2, 26.7, 16.5.

3i. (*E*)-3-(4-cyanophenyl)-1-(2-(Methylthio)phenyl)prop-2-en-1-one



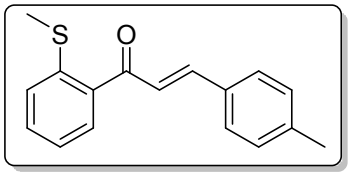
yellow solid (62.8 mg, 75%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (1H, apparent d, *J*= 7.7 Hz), 7.70-7.67 (4H, s), 7.62 (1H, d, *J*= 15.9 Hz), 7.50 (1H, apparent t, *J*= 7.7 Hz), 7.44-7.38 (2H, m), 7.25 (1H, apparent t, *J*= 7.5 Hz), 2.47 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.8, 142.1, 141.2, 139.2, 136.5, 132.7, 132.1, 129.7, 128.7, 127.6, 126.3, 124.2, 118.4, 113.4, 16.5.

3j. (*E*)-1-(2-(Methylthio)phenyl)-3-(phenyl)prop-2-en-1-one



yellow oil (63.3 mg, 83%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (1H, apparent d, *J*= 7.7 Hz), 7.62 (1H, d, *J*= 15.9 Hz), 7.6-7.56 (2H, m), 7.48-7.43 (1H, m), 7.41-7.35 (4H, m), 7.30 (1H, apparent d, *J*= 15.9 Hz), 7.25-7.20 (1H, m), 2.45 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.0, 145.3, 140.5, 137.3, 134.8, 131.5, 130.6, 129.4, 129.0, 128.5, 126.3, 124.8, 124.2, 16.5.

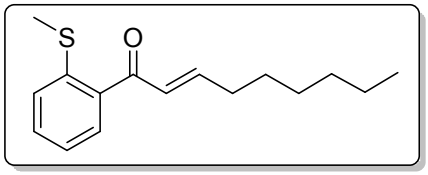
3k. (*E*)-1-(2-(Methylthio)phenyl)-3-(4-methylphenyl)prop-2-en-1-one



yellow solid (57.9 mg, 72%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (1H, apparent d, *J*= 7.7 Hz), 7.59 (1H, d, *J*= 15.9 Hz), 7.50-7.42 (3H, m), 7.37 (1H, apparent d, *J*= 8.0 Hz), 7.28-7.17 (4H, m), 2.45 (3H, s), 2.37 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.2, 145.5, 141.1, 140.3, 137.5, 132.1,

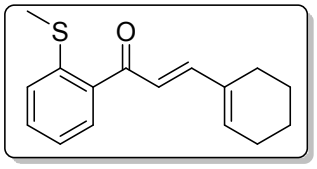
131.4, 129.7, 129.3, 128.5, 126.3, 124.2, 123.9, 21.5, 16.5.

3l. (*E*)-1-(2-(Methylthio)phenyl)- non-2-en-1-one



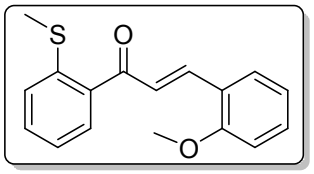
yellow oil (47.3 mg, 60%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (1H, apparent d, *J*= 7.7 Hz), 7.42 (1H, apparent t, *J*= 7.7 Hz), 7.34 (1H, apparent d, *J*= 8.0 Hz), 7.18 (1H, apparent t, *J*= 7.5 Hz), 6.87 (1H, dt, J_1= 15.5 Hz, J_2= 7.5 Hz), 6.63 (1H, apparent d, *J*= 15.5 Hz), 2.43 (3H, s), 2.32-2.25 (2H, m), 1.54-1.44 (2H, m), 1.37-1.25 (6H, m), 0.92-0.85 (3H, m); **^{13}C NMR** (125 MHz, CDCl3) δ 193.5, 151.2, 140.1, 137.2, 131.2, 129.3, 128.7, 126.3, 124.0, 32.8, 31.6, 28.9, 28.0, 22.5, 16.5, 14.0.

3m. (*E*)-3-(1-cyclohexenyl)-1-(2-(Methylthio)phenyl)prop-2-en-1-one



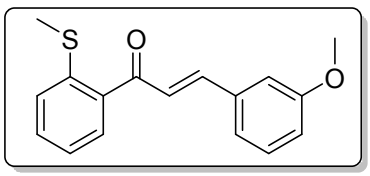
yellow solid (52.7 mg, 68%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (1H, apparent d, *J*= 7.7 Hz), 7.42 (1H, apparent t, *J*= 7.7 Hz), 7.34 (1H, apparent d, *J*= 8.0 Hz), 7.23-7.16 (2H, m), 6.60 (1H, d, *J*= 15.7 Hz), 6.26-6.19 (1H, m), 2.44 (3H, s), 2.26-2.19 (4H, m), 1.78-1.67 (2H, m), 167-1.58 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.1, 149.3, 140.8, 139.7, 138.0, 135.6, 131.0, 129.1, 126.3, 124.1, 121.9, 26.7, 24.3, 22.1, 22.0, 16.5.

3n. (*E*)-3-(2-methoxyphenyl)-1-(2-(Methylthio)phenyl)prop-2-en-1-one



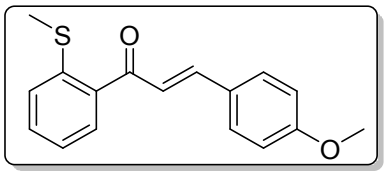
yellow solid (53 mg, 62%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (1H, d, *J*= 16.0 Hz), 7.68 (1H, apparent d, *J*= 7.7 Hz), 7.58 (1H, apparent d, *J*= 7.7 Hz), 7.48-7.33 (4H, m), 7.25-7.20 (1H, m), 6.97 (1H, apparent t, *J*= 7.5 Hz), 6.91 (1H, apparent d, *J*= 8.3 Hz), 3.87 (3H, s), 2.45 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.6, 158.8, 140.9, 140.3, 137.8, 131.8, 131.3, 129.4, 129.2, 126.4, 125.5, 124.2, 123.9, 120.8, 111.3, 55.5, 16.6.

3o. (*E*)-3-(3-methoxyphenyl)-1-(2-(Methylthio)phenyl)prop-2-en-1-one



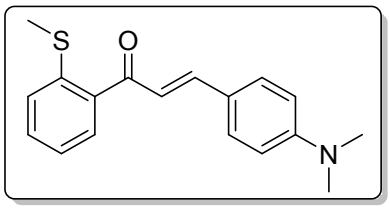
yellow solid (63.2 mg, 74%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (1H, apparent d, *J*= 7.7 Hz), 7.58 (1H, d, *J*= 15.8 Hz), 7.50-7.44 (1H, m), 7.38 (1H, apparent d, *J*= 8.0 Hz), 7.34-7.20 (3H, m), 7.18 (1H, apparent d, *J*= 7.6 Hz), 7.10 (1H, s), 6.95 (1H, dd, J_1= 8.3 Hz, J_2= 2.1 Hz), 3.84 (3H, s), 2.46 (3H, s);**^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.0, 160.0, 145.2, 140.4, 137.3, 136.2, 131.5, 129.9, 129.4, 126.4, 125.2, 124.2, 121.2, 116.4, 113.3, 55.4, 16.5.

3p. (*E*)-3-(4-methoxyphenyl)-1-(2-(Methylthio)phenyl)prop-2-en-1-one



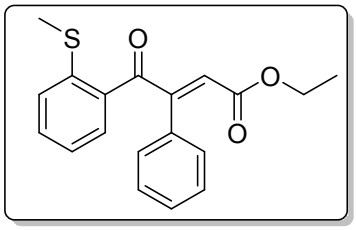
yellow solid (65.7 mg, 77%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (1H, dd, J_1= 7.7 Hz, J_2= 1.4 Hz), 7.60-7.50 (3H, m), 7.48-7.41 (1H, m), 7.47-7.42 (1H, m), 7.37 (1H, apparent d, *J*= 7.6 Hz), 7.22 (1H, td, J_1= 7.5 Hz, J_2= 1.1 Hz), 6.96-6.86 (2H, m), 3.83 (3H, s), 2.45 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.2, 161.7, 145.3, 140.1, 137.8, 131.3, 130.3, 129.2, 127.5, 126.3, 124.2, 122.7, 114.3, 55.4, 16.5.

3q. (*E*)-3-(4-dimethylamino)-1-(2-(Methylthio)phenyl)prop-2-en-1-one



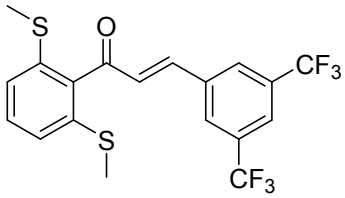
yellow solid (60.6 mg, 68%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (1H, apparent d, *J*= 7.6 Hz), 7.54 (1H, d, *J*= 15.8 Hz), 7.47 (2H, apparent d, *J*= 8.8 Hz), 7.44-7.39 (1H, m), 7.35 (1H, apparent d, *J*= 7.9 Hz), 7.21 (1H, apparent t, *J*= 7.5 Hz), 7.06 (1H, d, *J*= 15.7 Hz), 6.66 (2H, d, *J*= 8.9 Hz), 3.02 (3H, s), 2.44 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.7, 152.1, 146.8, 139.4, 138.6, 130.8, 130.5, 128.9, 126.4, 124.2, 122.5, 120.1, 111.8, 40.1, 16.6.

3r. ethyl (E)-4-(2-(methylthio)phenyl)-4-oxo-3-phenylbut-2-enoate



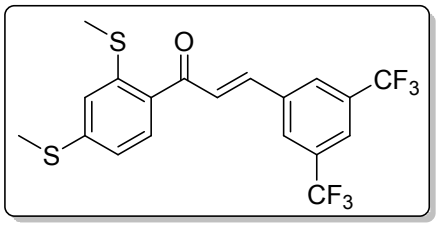
yellow solid (63.6 mg, 65%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.9 (1H, s), 7.74 (1H, apparent d, *J*= 7.8 Hz), 7.47-7.41 (1H, m), 7.36-7.30 (3H, m), 7.28-7.20 (3H, m), 7.0 (1H, apparent t, *J*= 7.5 Hz), 4.23 (2H, q, *J*= 7.1 Hz), 2.49 (3H, s), 1.18 (3H, t, *J*= 7.1 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.1, 165.2, 144.5, 142.3, 133.1, 133.0, 132.8, 132.7, 131.8, 130.3, 130.2, 128.7, 124.5, 123.3, 61.5, 15.6, 14.1.

3s. (*E*)-1-(2,6-bis(Methylthio)phenyl)-3-(3,5-bis(trifluoromethyl)phenyl)prop-2-en-1-one



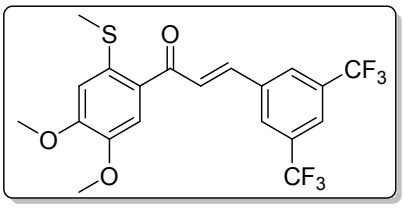
yellow solid (91.6 mg, 70%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (2H, s), 8.04 (1H, s), 7.59-7.54 (1H, m), 7.51 (1H, d, *J*= 16.1 Hz), 7.44 (2H, apparent d, *J*= 7.9 Hz), 7.26 (1H, d, *J*= 16.2 Hz), 2.61 (6H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.1, 141.2, 140.4, 136.8, 136.0, 132.5 (q, *J*= 33.5 Hz), 130.5, 130.2, 128.0 (q, *J*= 3.5 Hz), 126.2, 123.5 (q, *J*= 3.8 Hz), 123.0 (q, *J*= 273.0 Hz), 17.8.

3t. (*E*)-1-(2,4-bis(Methylthio)phenyl)-3-(3,5-bis(trifluoromethyl)phenyl)prop-2-en-1-one



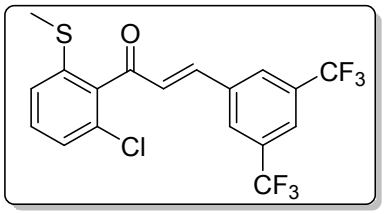
yellow solid (106 mg, 81%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.0 (2H, s), 7.88 (1H, s), 7.76 (1H, apparent d, *J*= 8.2 Hz), 7.70 (1H, d, *J*= 15.8 Hz), 7.50 (1H, d, *J*= 15.8 Hz), 7.17 (1H, s), 7.06 (1H, apparent d, *J*= 8.2 Hz), 2.56 (3H, s), 2.47 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 189.5, 145.5, 143.4, 140.4, 137.2, 132.5 (q, *J*= 33.5 Hz), 131.7, 130.6, 127.9 (q, *J*= 3.4 Hz), 127.2, 123.3 (q, *J*= 3.8 Hz) , 123.0 (q, *J*= 270.4 Hz), 122.0, 120.3, 16.2, 14.9.

3u. (*E*)-3-(3,5-bis(Trifluoromethyl)phenyl)-1-(4,5-dimethoxy-2-(methylthio)phenyl)prop-2-en-1-one



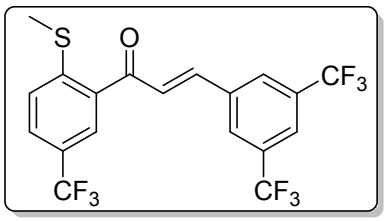
yellow solid (74.6 mg, 65%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (2H, s), 7.88 (1H, s), 7.67 (1H, d, *J*= 15.8 Hz), 7.50 (1H, d, *J*= 15.8 Hz), 7.25 (1H, s), 6.93 (1H, s), 3.98 (3H, s), 3.94 (3H, s), 3.47 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.4, 152.4, 146.8, 139.5, 137.3, 133.7, 132.4 (q, *J*= 33.8 Hz), 130.5, 128.4, 127.8 (q, *J*= 3.5 Hz), 123.2 (q, *J*= 3.8 Hz), 123.0 (q, *J*= 273 Hz), 113.0, 111.1, 56.4, 56.1, 18.0.

3v. (*E*)-3-(3,5-bis(Trifluoromethyl)phenyl)-1-(2-chloro-6-(methylthio)phenyl)prop-2-en-1-one



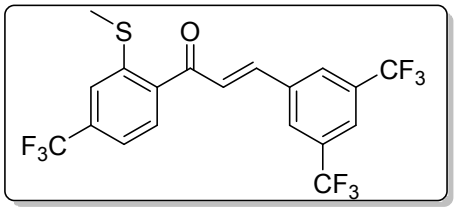
yellow solid (91.8 mg, 72%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (2H, s), 7.89 (1H, s), 7.40-7.26 (4H, m), 7.07 (1H, d, *J*= 16.2 Hz), 2.46 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.5, 142.2, 138.4, 137.8, 136.5, 132.5 (q, *J*= 33.5 Hz), 130.9, 130.7, 130.0, 128.1 (q, *J*= 3.6 Hz), 127.1, 126.6, 123.9-123.7 (m), 122.9 (q, *J*= 271.2 Hz), 17.6.

3w. (*E*)-3-(3,5-bis(Trifluoromethyl)phenyl)-1-(2-(methylthio)-5-(trifluoromethyl)phenyl)prop -2-en-1-one



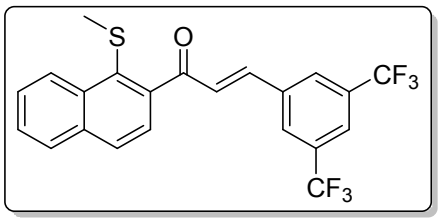
yellow solid (103.1 mg, 75%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (2H, s), 7.92 (2H, apparent d, *J*= 11 Hz), 7.76-7.68 (2H, m), 7.48 (1H, apparent d, *J*= 8.5 Hz), 7.43 (1H, d, *J*= 15.9 Hz), 2.52 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.3, 146.4, 141.9, 136.7, 136.0, 132.6 (q, *J*= 33.7 Hz), 128.3 (q, *J*= 3.3 Hz), 128.1 (q, *J*= 3.0 Hz), 127.0, 126.5, 126.3 (q, *J*= 3.2 Hz), 125.9, 123.8 (q, *J*= 3.5 Hz), 123.8 (q, *J*= 273.0 Hz), 123.0 (q, *J*= 273.0 Hz), 16.1.

3x. (*E*)-3-(3,5-bis(Trifluoromethyl)phenyl)-1-(2-(methylthio)-4-(trifluoromethyl)phenyl) prop -2-en-1-one



yellow solid (90.7 mg, 66%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (2H, s), 7.91 (1H, s), 7.77 (1H, apparent d, *J*= 7.9 Hz), 7.64 (1H, d, *J*= 16.0 Hz), 7.60 (1H, s), 7.50 (1H, apparent d, *J*= 8.0 Hz), 7.39 (1H, d, *J*= 15.9 Hz), 2.53(3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.3, 142.0, 141.9, 139.3, 136.6, 133.6 (q, *J*= 32.3 Hz), 132.6 (q, *J*= 33.5 Hz), 129.7, 128.0 (q, *J*= 3.5 Hz), 127.6, 123.9-123.7 (m), 123.4 (q, *J*= 273.2 Hz), 123.0 (q, *J*= 273.0 Hz), 122.9 (q, *J*= 4.0 Hz), 121.1 (q, *J*= 3.6 Hz), 16.3.

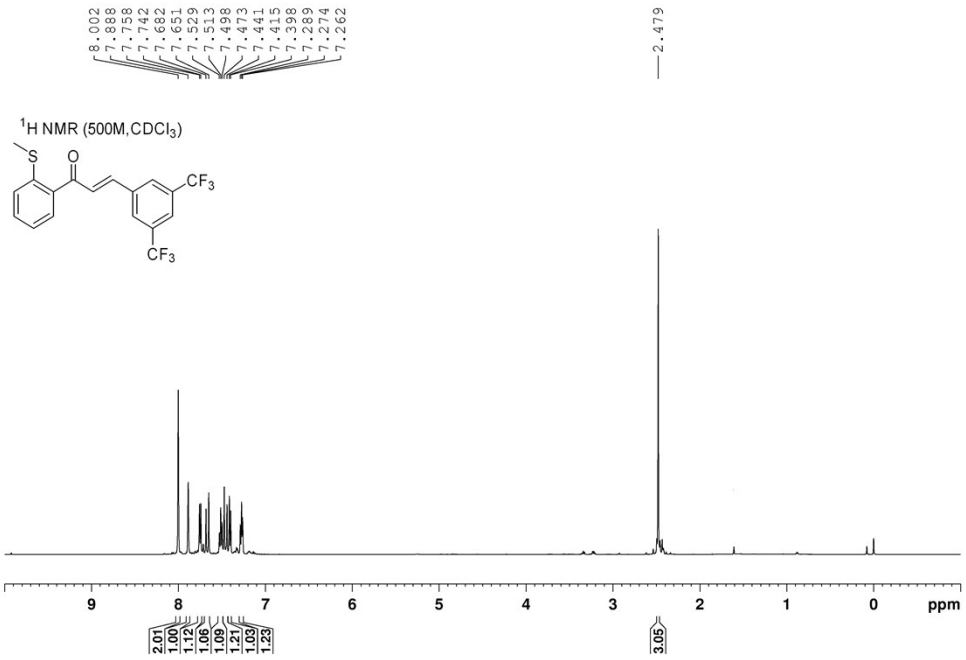
3y. (E)-3-(3,5-bis(Trifluoromethyl)phenyl)-1-(2-(methylthio)naphthyl)prop-2-en-1-one

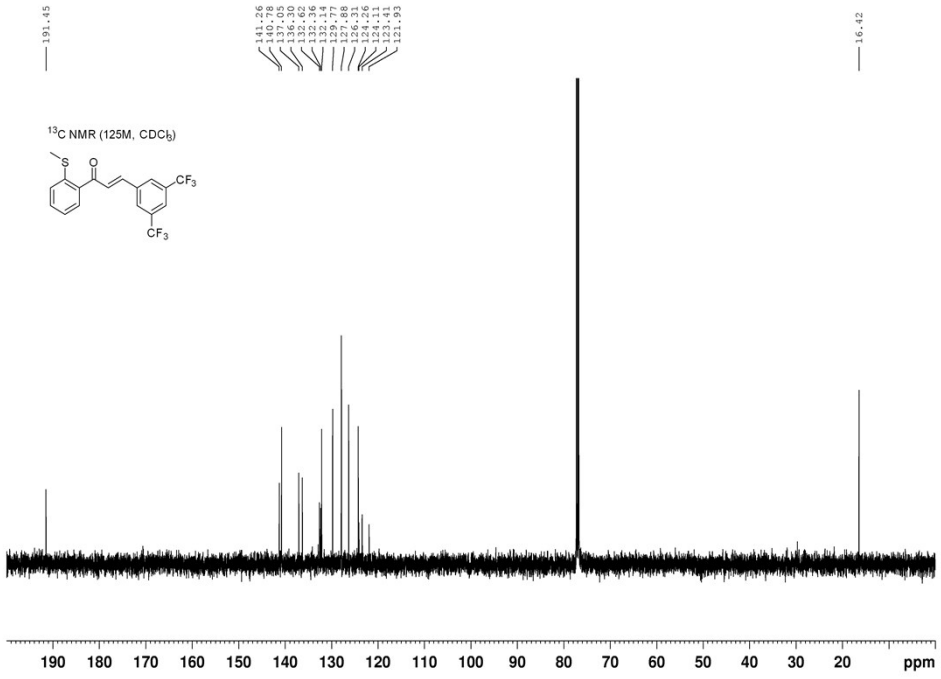


yellow solid (103.1 mg, 78%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.69 (1H, d, *J*= 8.4 Hz), 7.96-7.91 (4H, m), 7.87 (1H, s), 7.72-7.68 (1H, m), 7.65-7.1 (1H, m), 7.44 (1H, d, *J*= 8.4 Hz), 7.40-7.29 (2H, m), 2.37 (3H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.9, 142.5, 139.3, 135.9, 133.6, 133.2, 131.5 (q, *J*= 33.5 Hz), 130.2, 130.1, 129.0, 127.8, 127.0, 126.9-126.8 (m), 126.5, 125.0, 123.0, 122.0 (q, *J*= 270.1 Hz), 122.5-122.4 (m), 19.9.

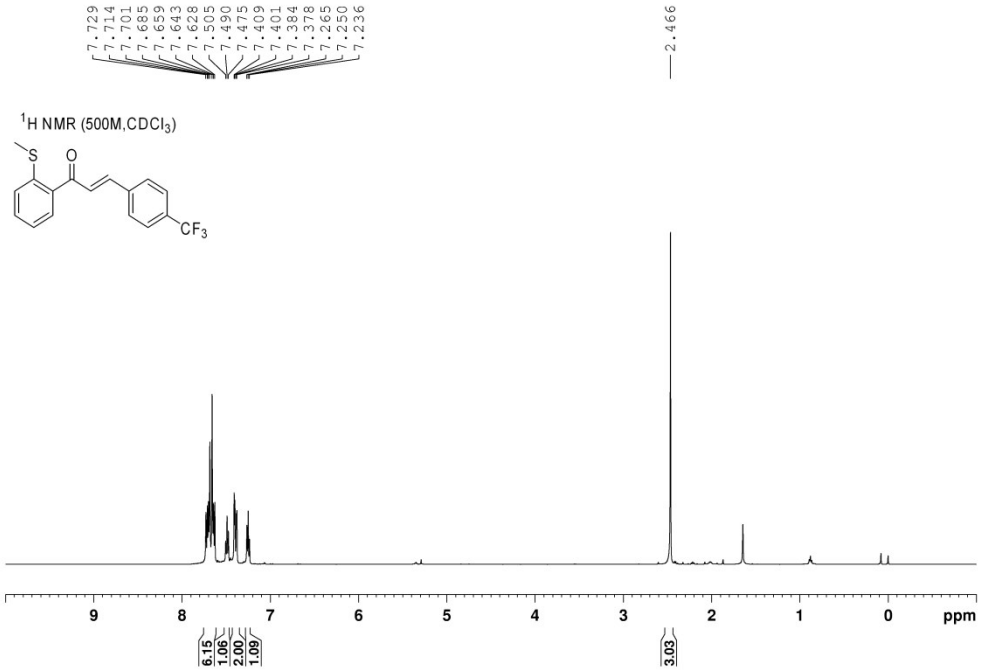
7. NMR spectra

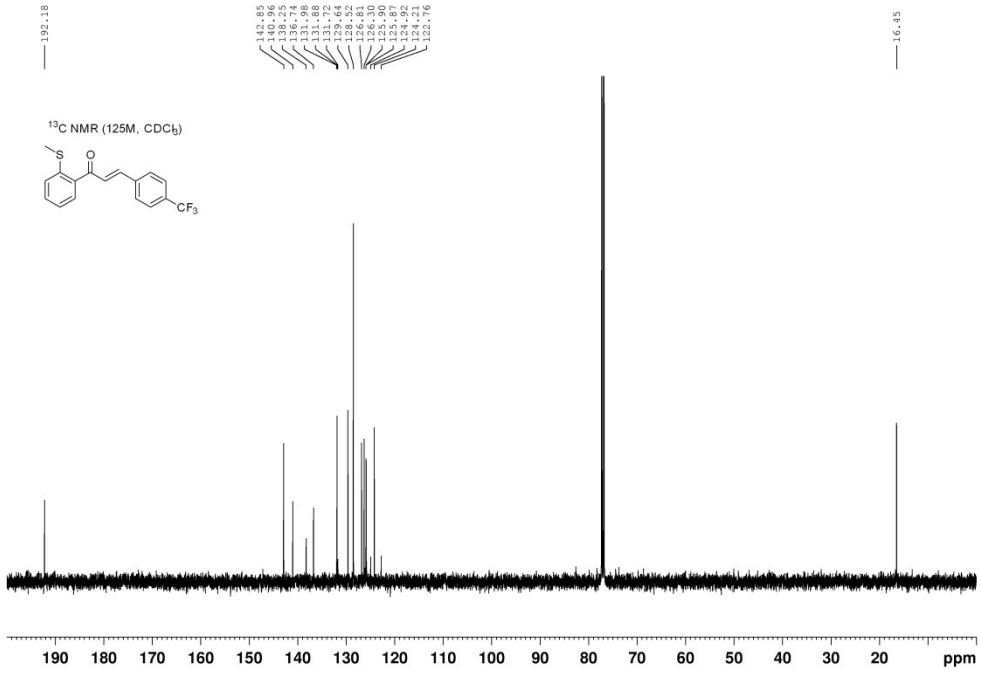
3a. (E)-3-(3,5-bis(Trifluoromethyl)phenyl)-1-(2-(methylthio)phenyl)prop-2-en-1-one



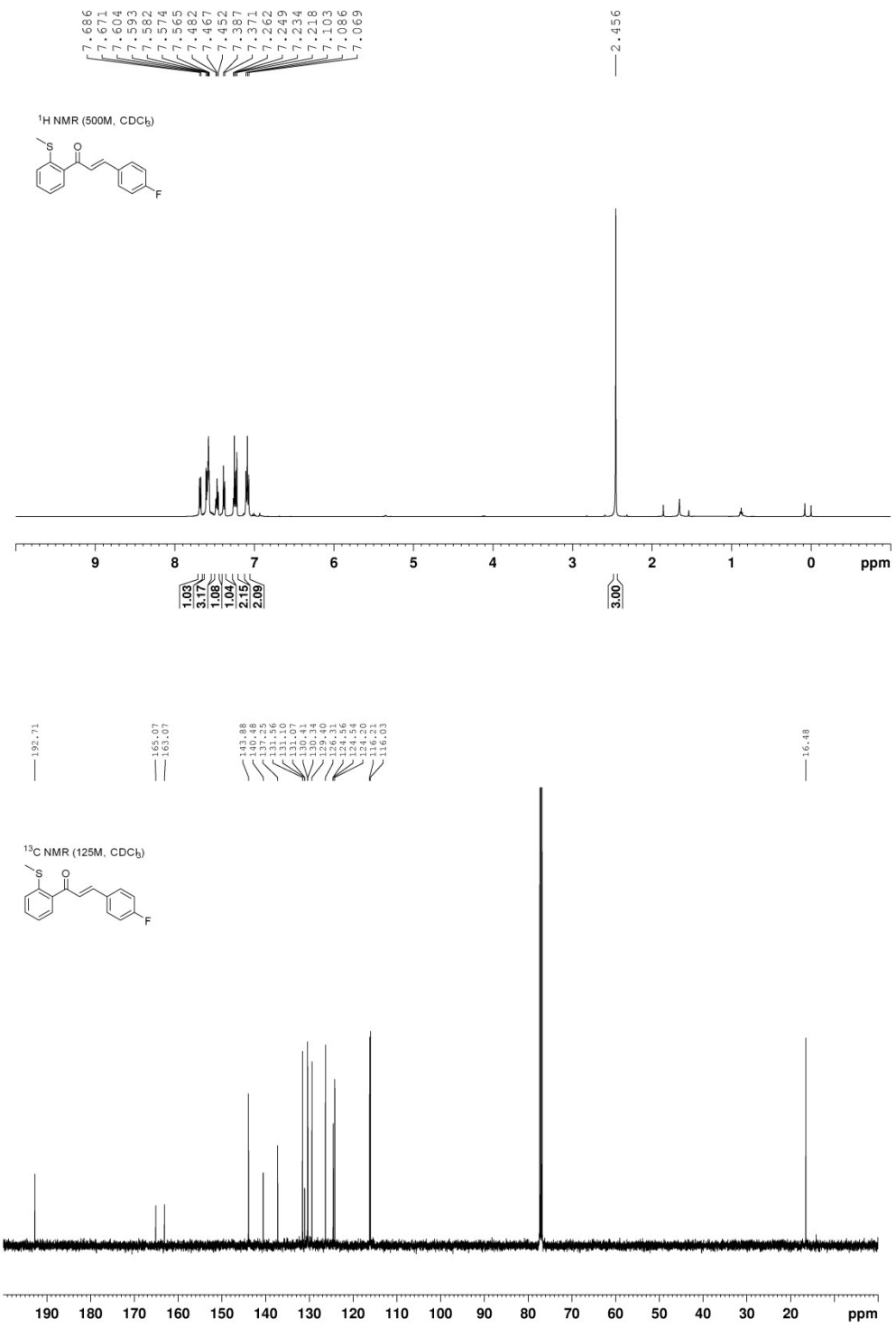


3b. (*E*)-1-(2-(Methylthio)phenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one

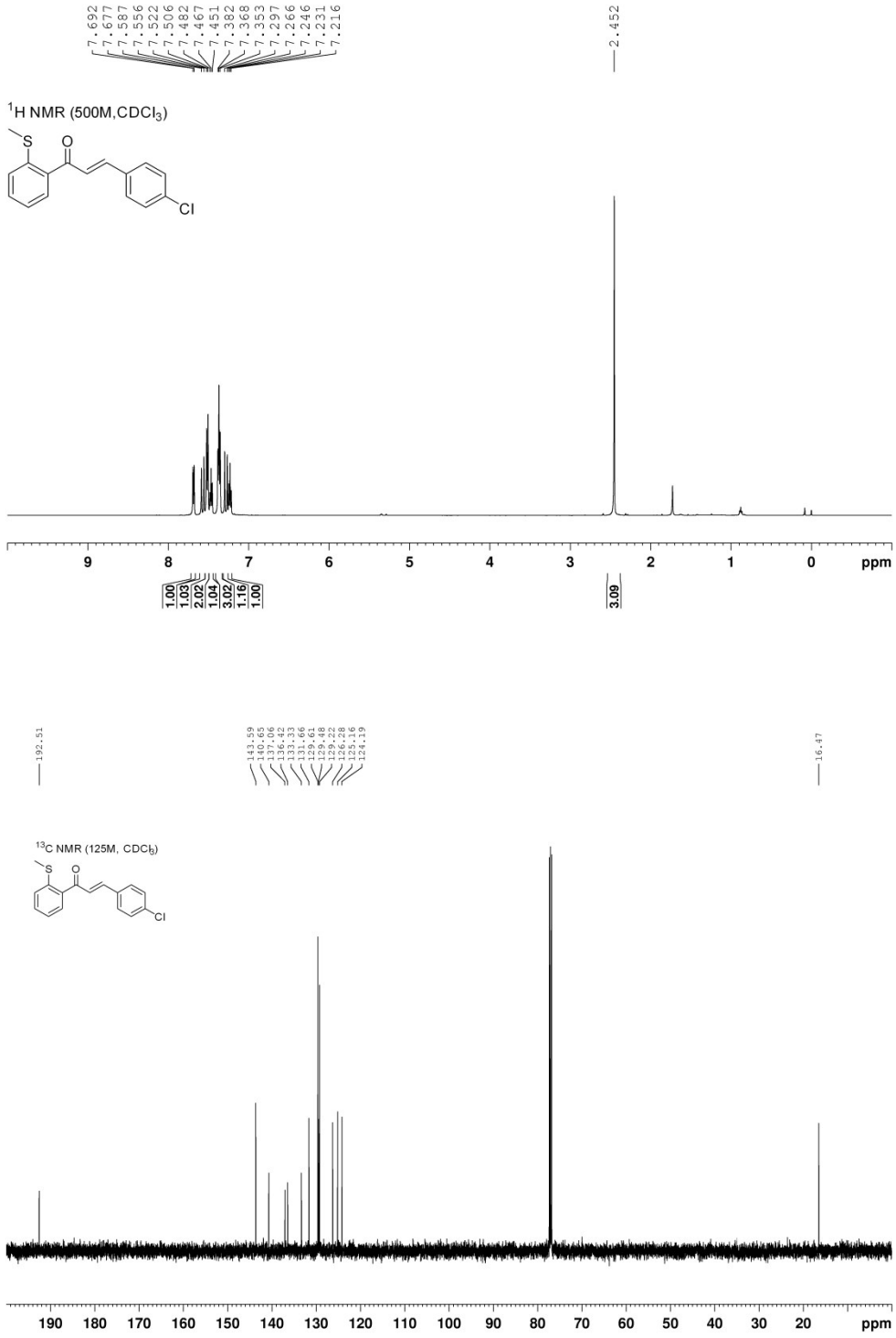




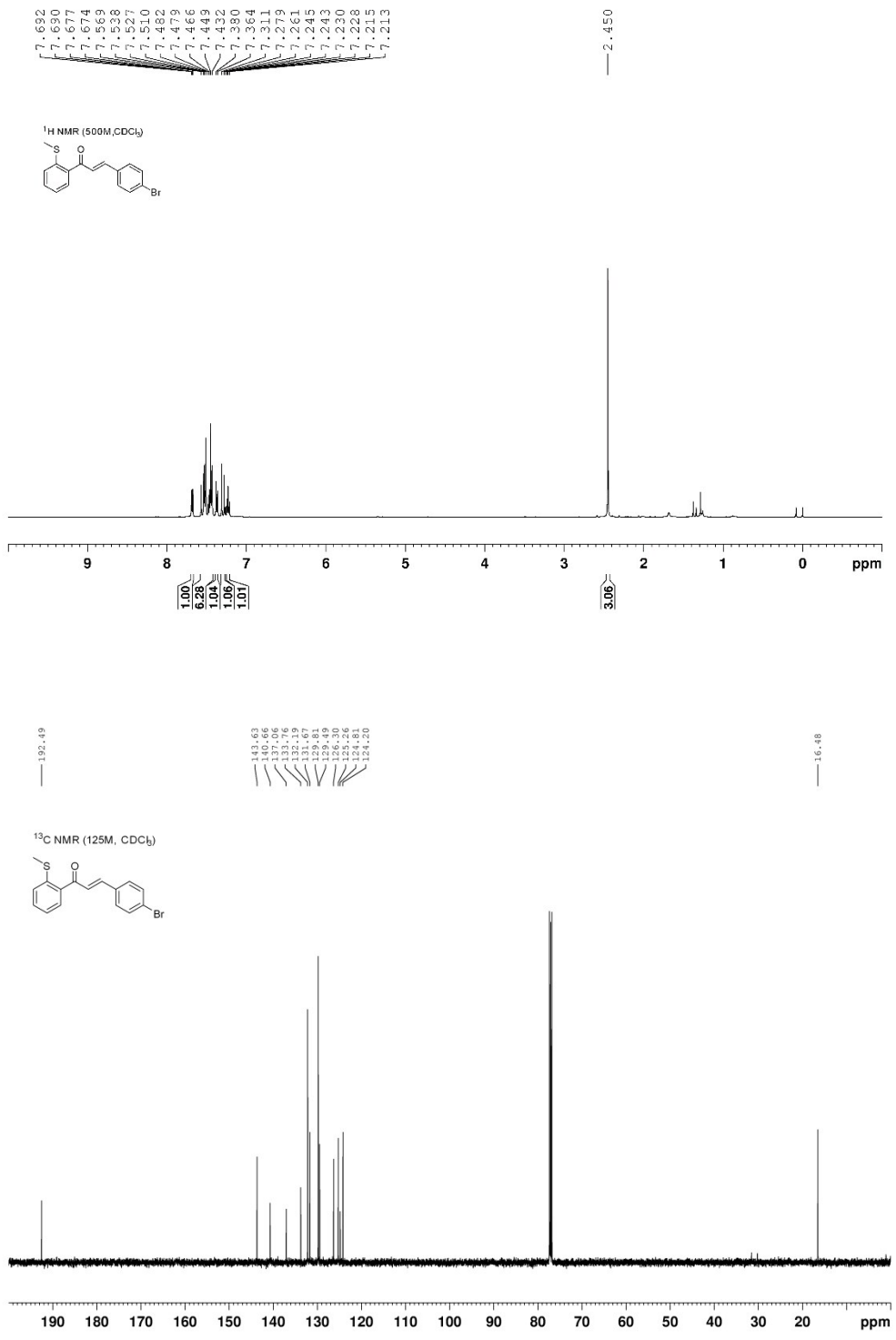
3c. (*E*)-3-(4-Fluorophenyl)-1-(2-(methylthio)phenyl)prop-2-en-1-one



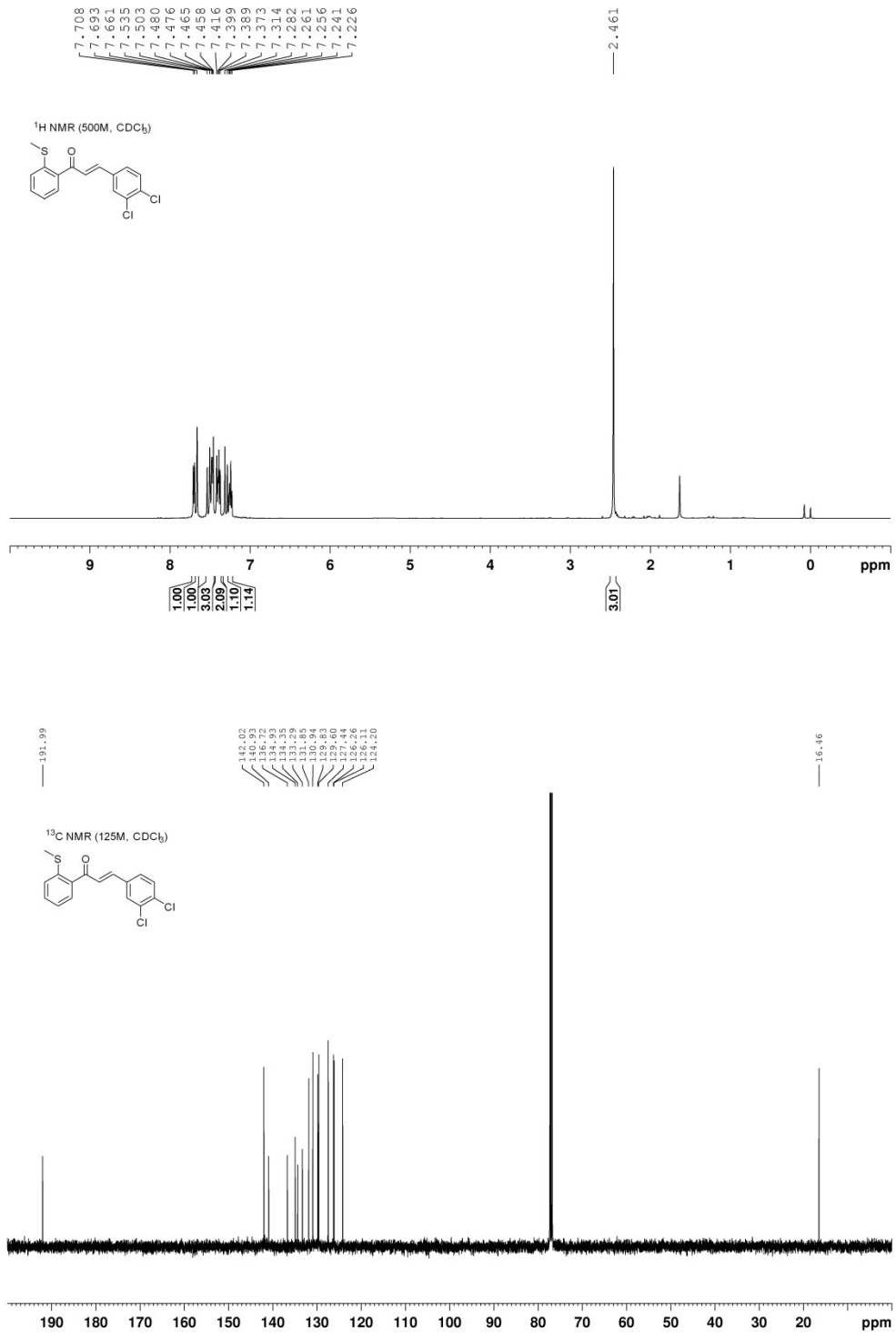
3d. (*E*)-3-(4-Chlorophenyl)-1-(2-(methylthio)phenyl)prop-2-en-1-one



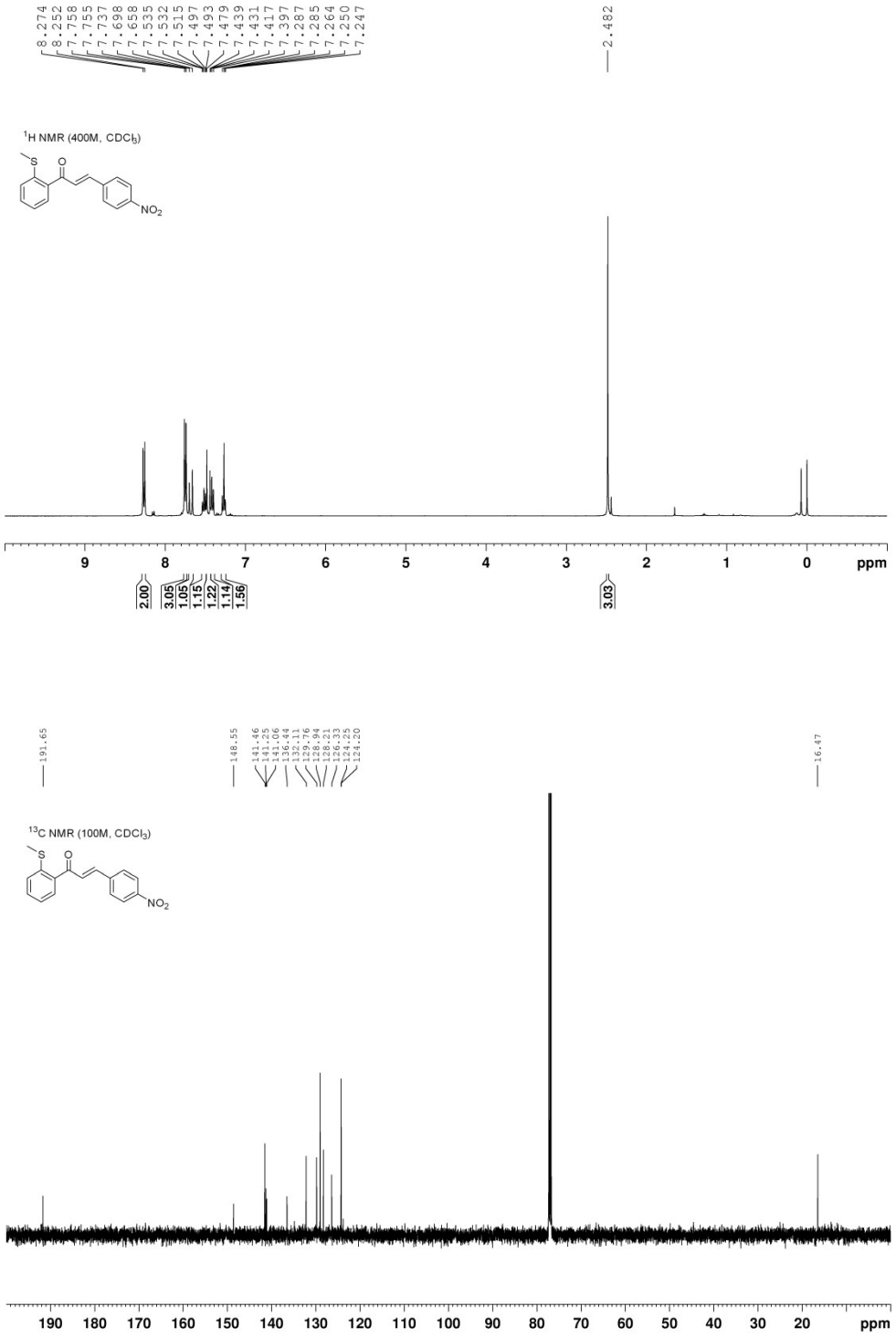
3e. (*E*)-3-(4-Bromophenyl)-1-(2-(methylthio)phenyl)prop-2-en-1-one



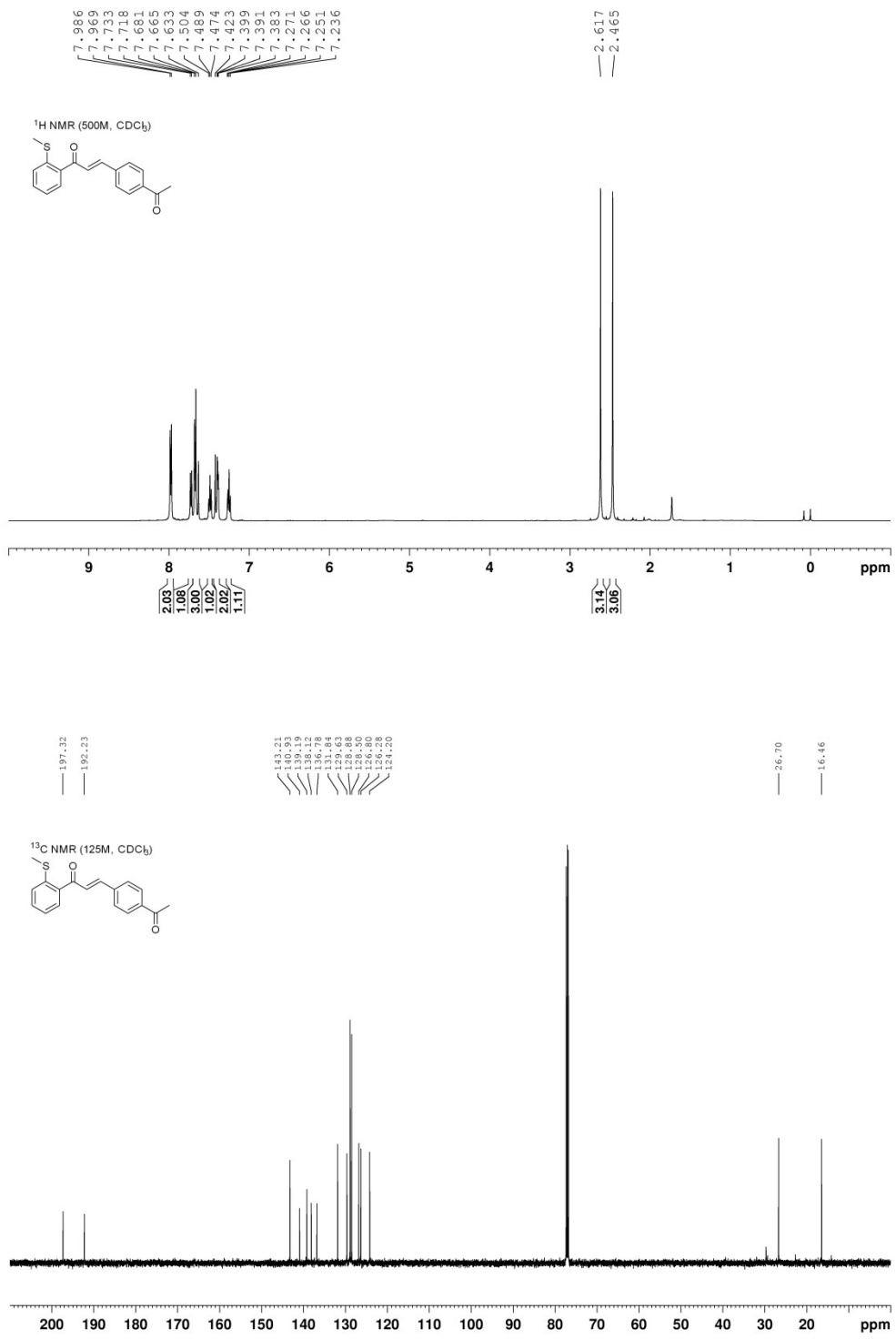
3f. (*E*)-3-(3,4-Dichlorophenyl)-1-(2-(methylthio)phenyl)prop-2-en-1-one



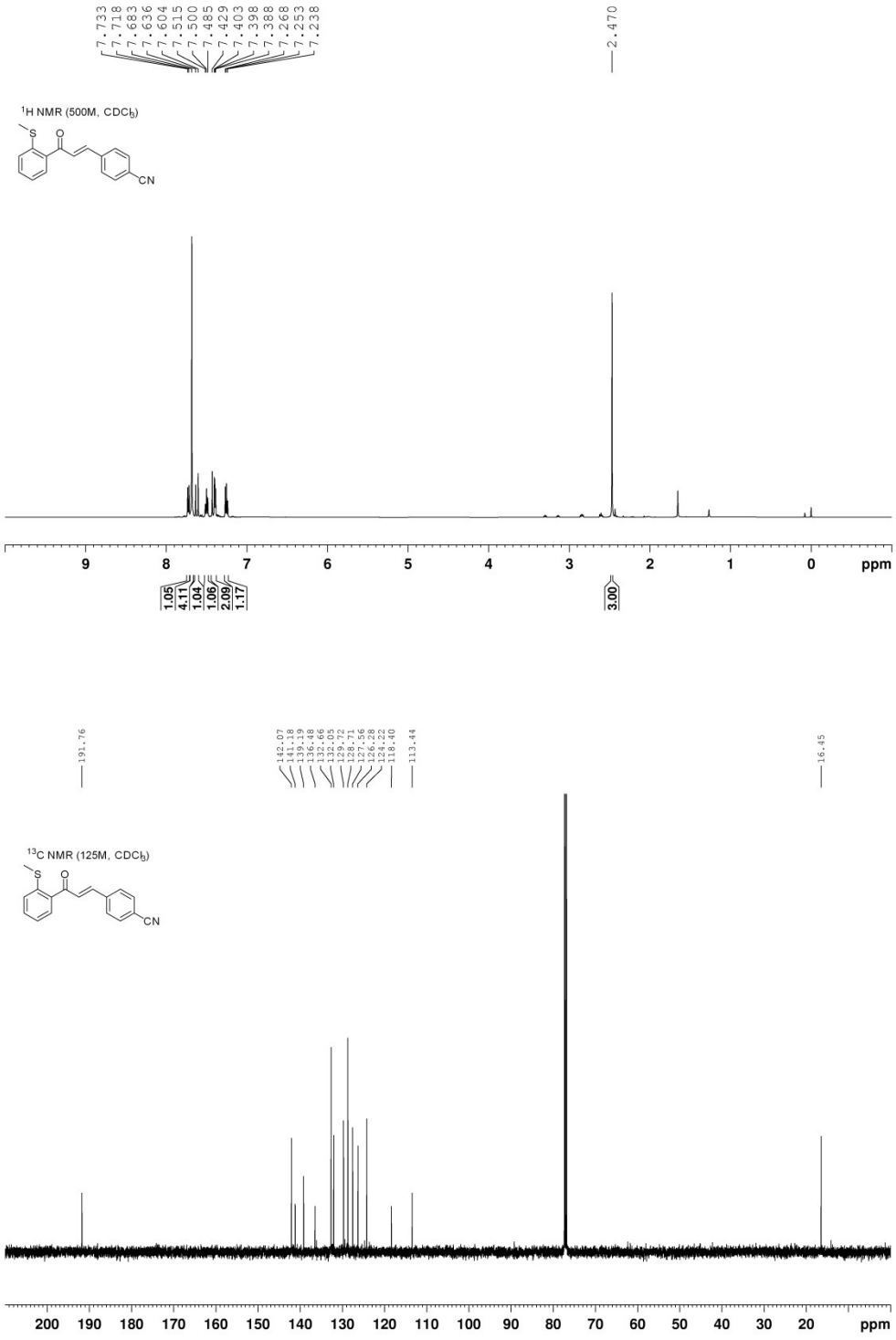
3g. (*E*)-1-(2-(Methylthio)phenyl)-3-(4-nitrophenyl)prop-2-en-1-one



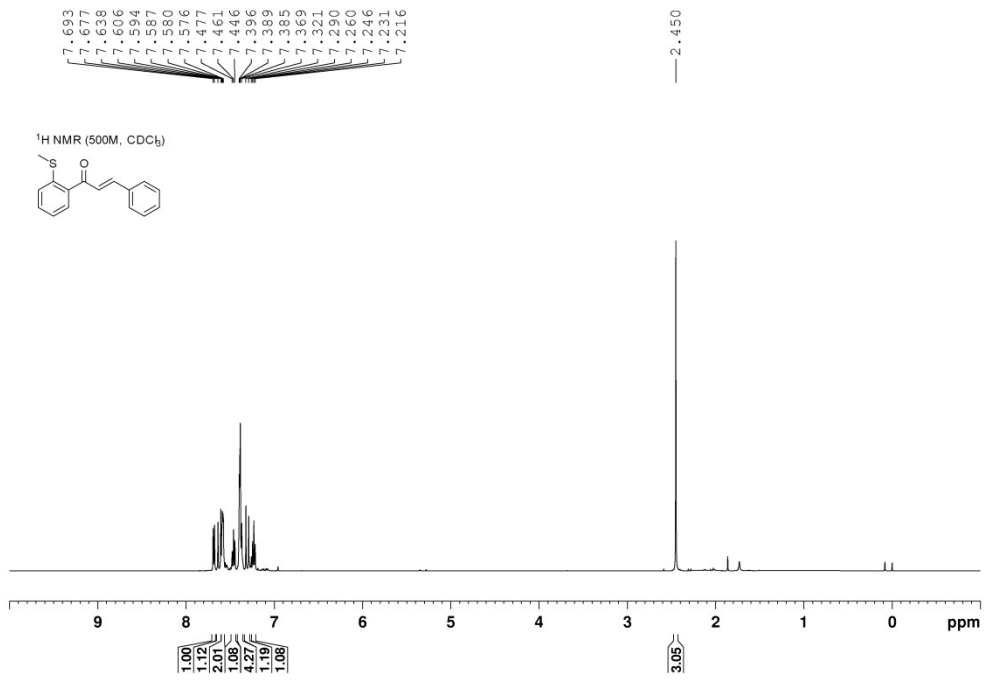
3h. (*E*)-3-(4-acetylphenyl)-1-(2-(Methylthio)phenyl)prop-2-en-1-one

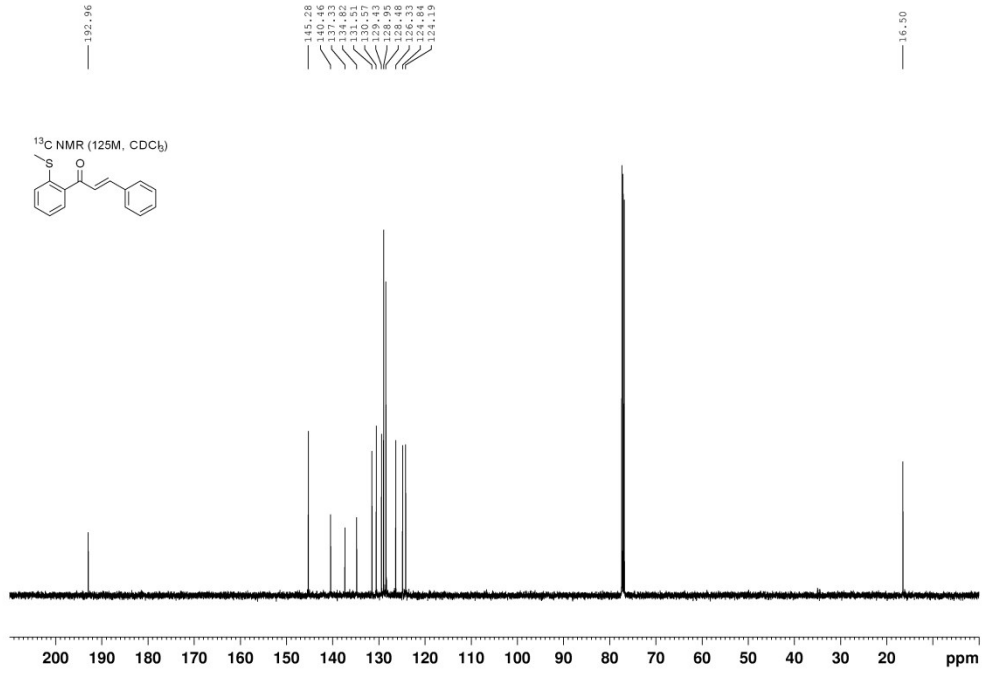


3i. (*E*)-3-(4-cyanophenyl)-1-(2-(Methylthio)phenyl)prop-2-en-1-one

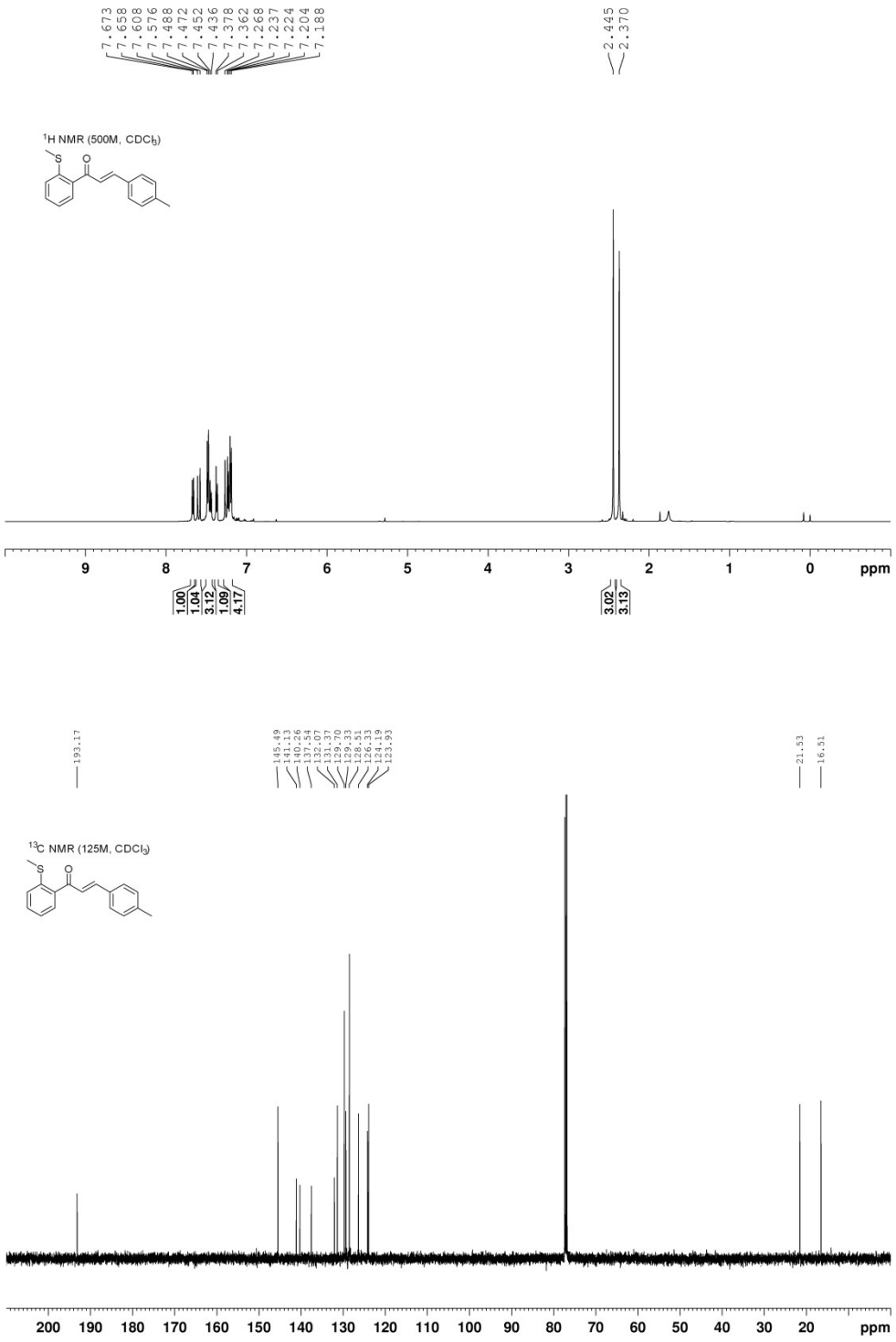


3j. (*E*)-1-(2-(Methylthio)phenyl)-3-(phenyl)prop-2-en-1-one

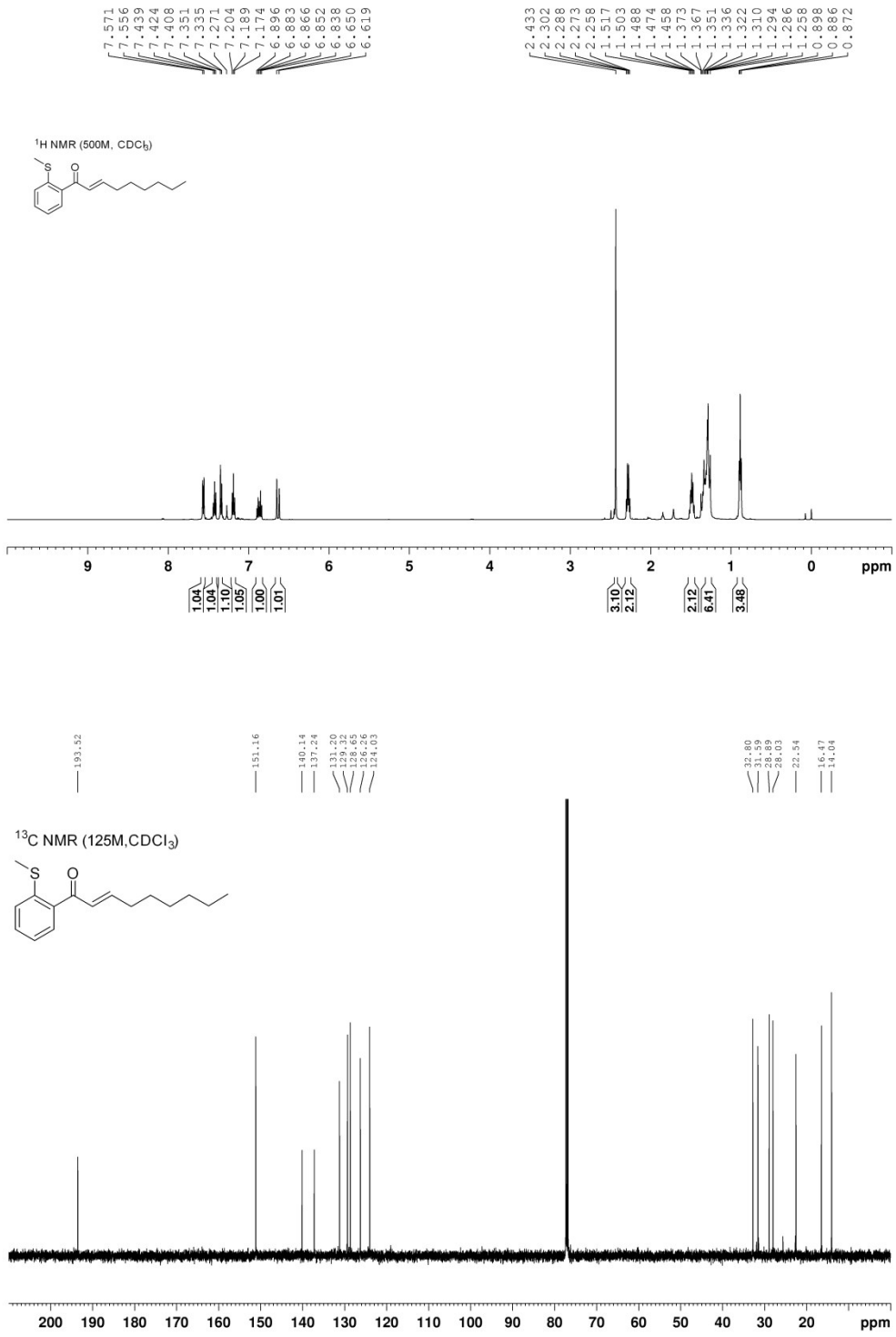




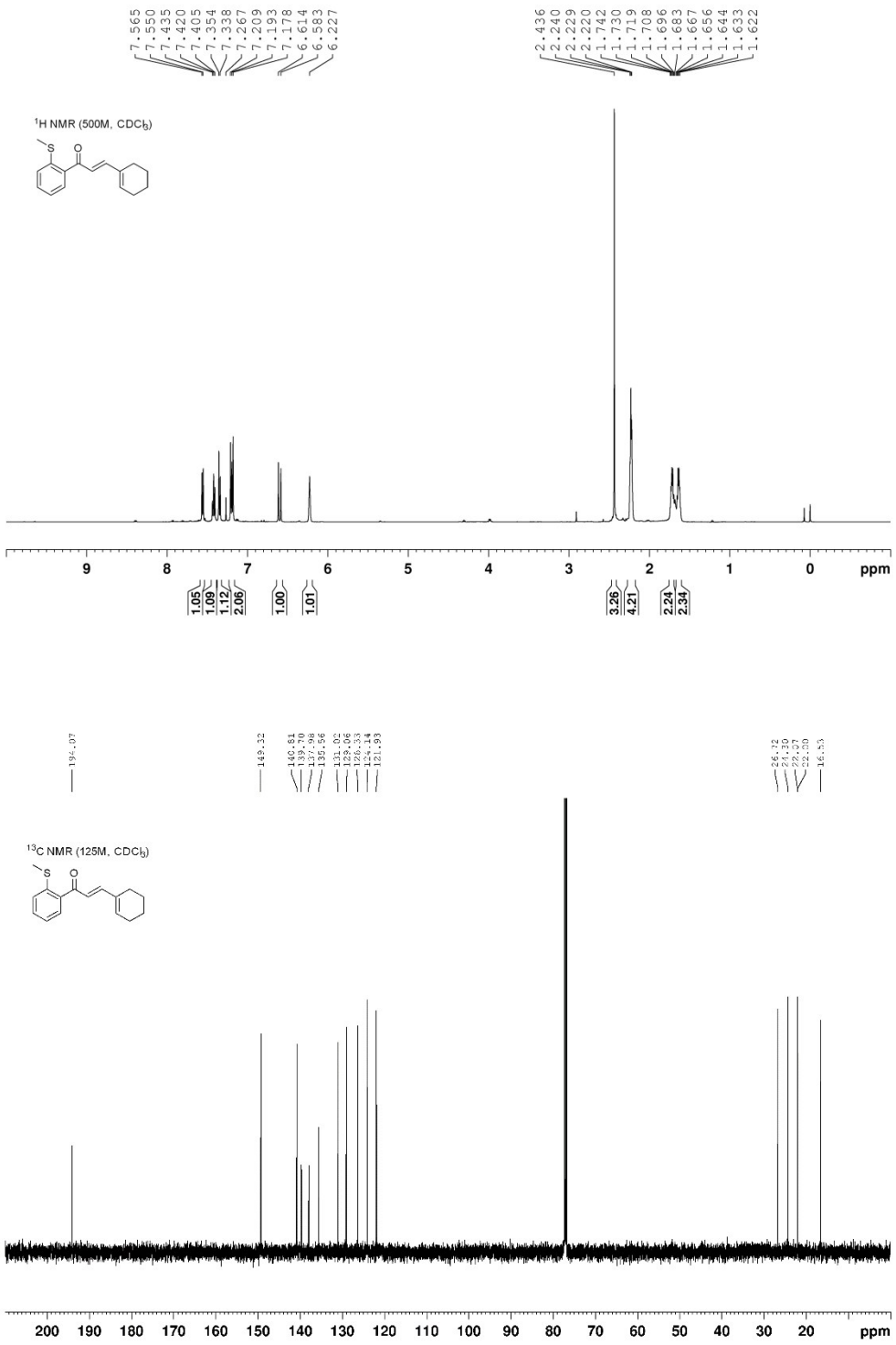
3k. (*E*)-1-(2-(Methylthio)phenyl)-3-(4-methylphenyl)prop-2-en-1-one



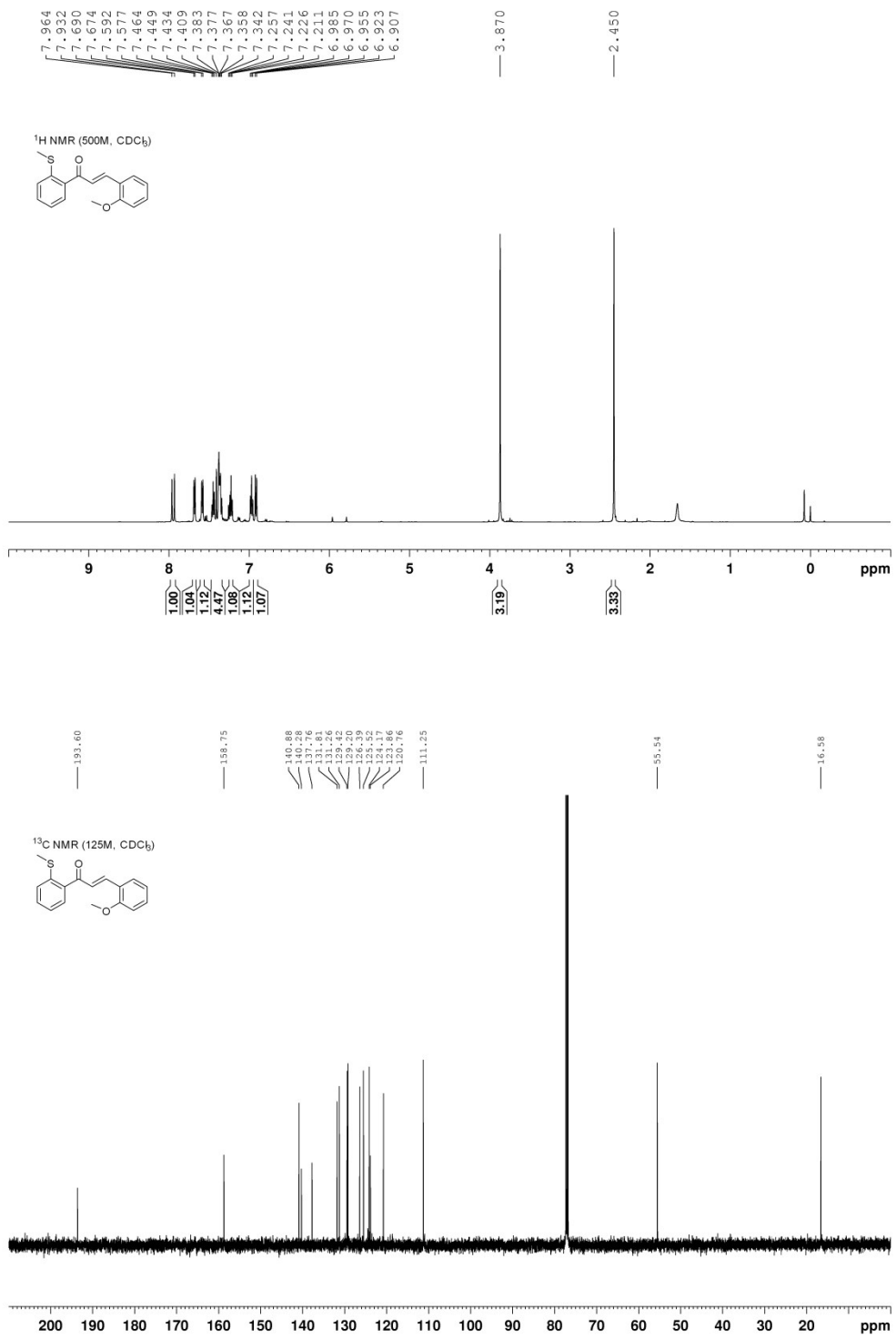
3l. (*E*)-1-(2-(Methylthio)phenyl)- non-2-en-1-one



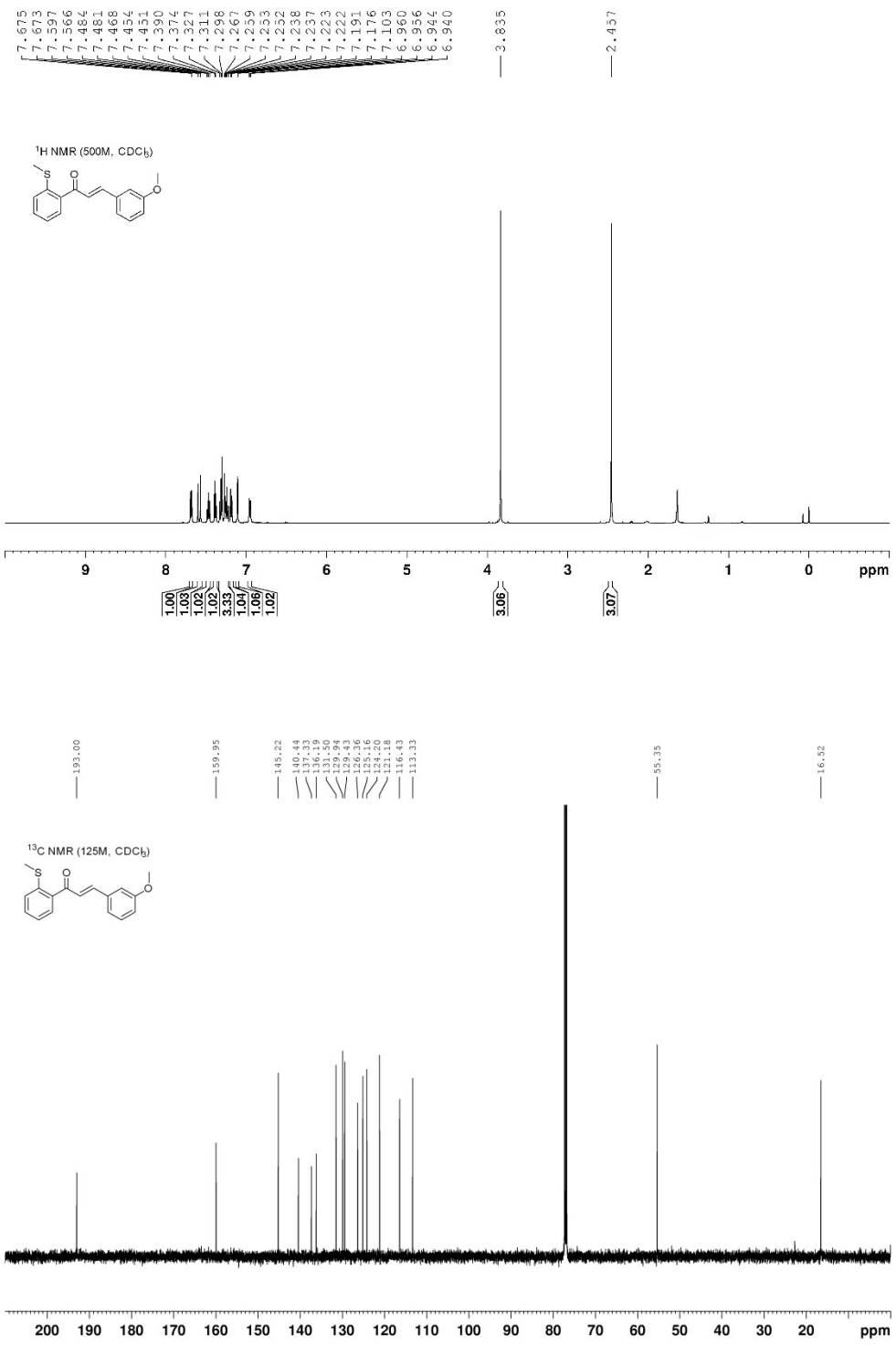
3m. (*E*)-3-(1-cyclohexenyl)-1-(2-(Methylthio)phenyl)prop-2-en-1-one



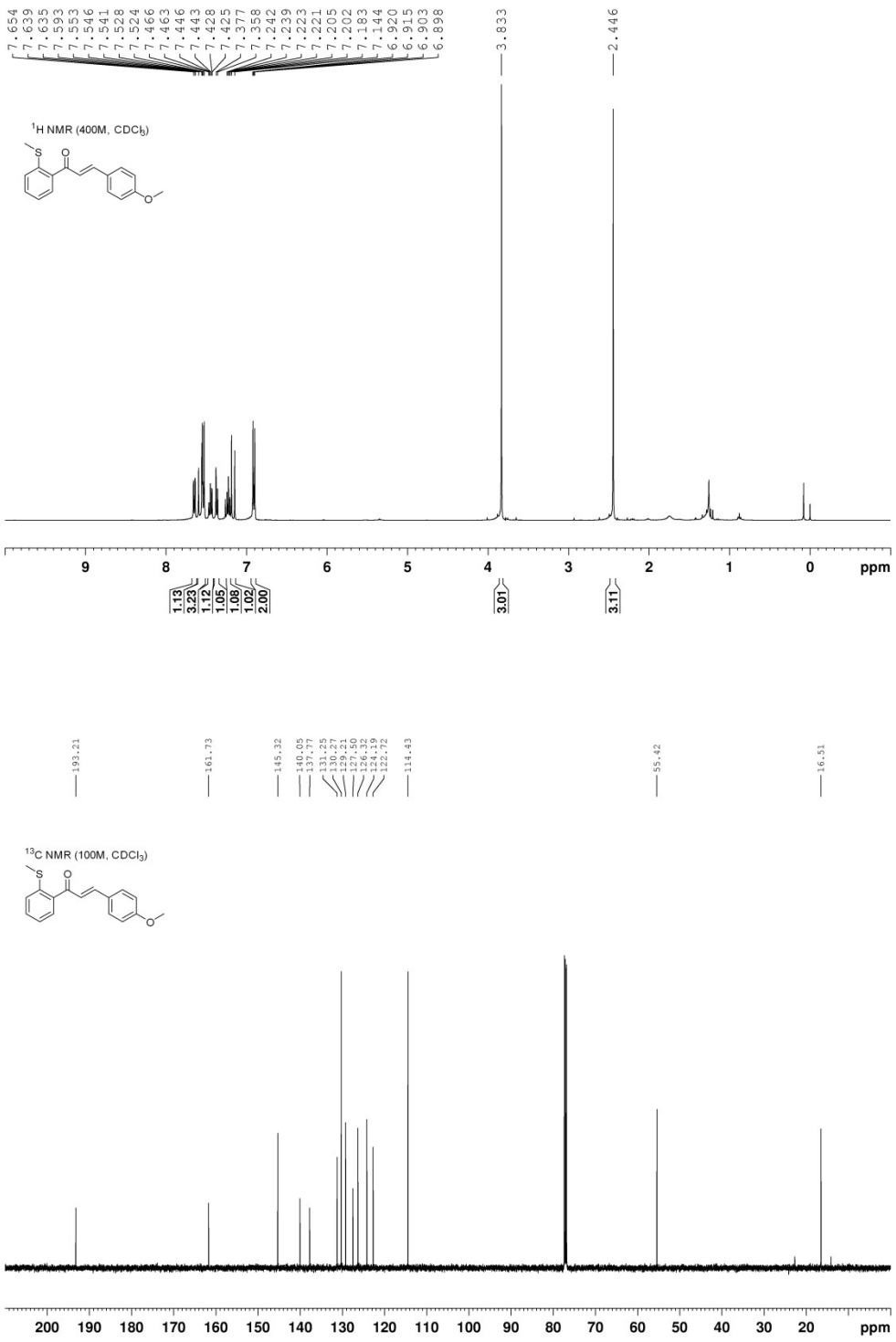
3n. (*E*)-3-(2-methoxyphenyl)-1-(2-(Methylthio)phenyl)prop-2-en-1-one



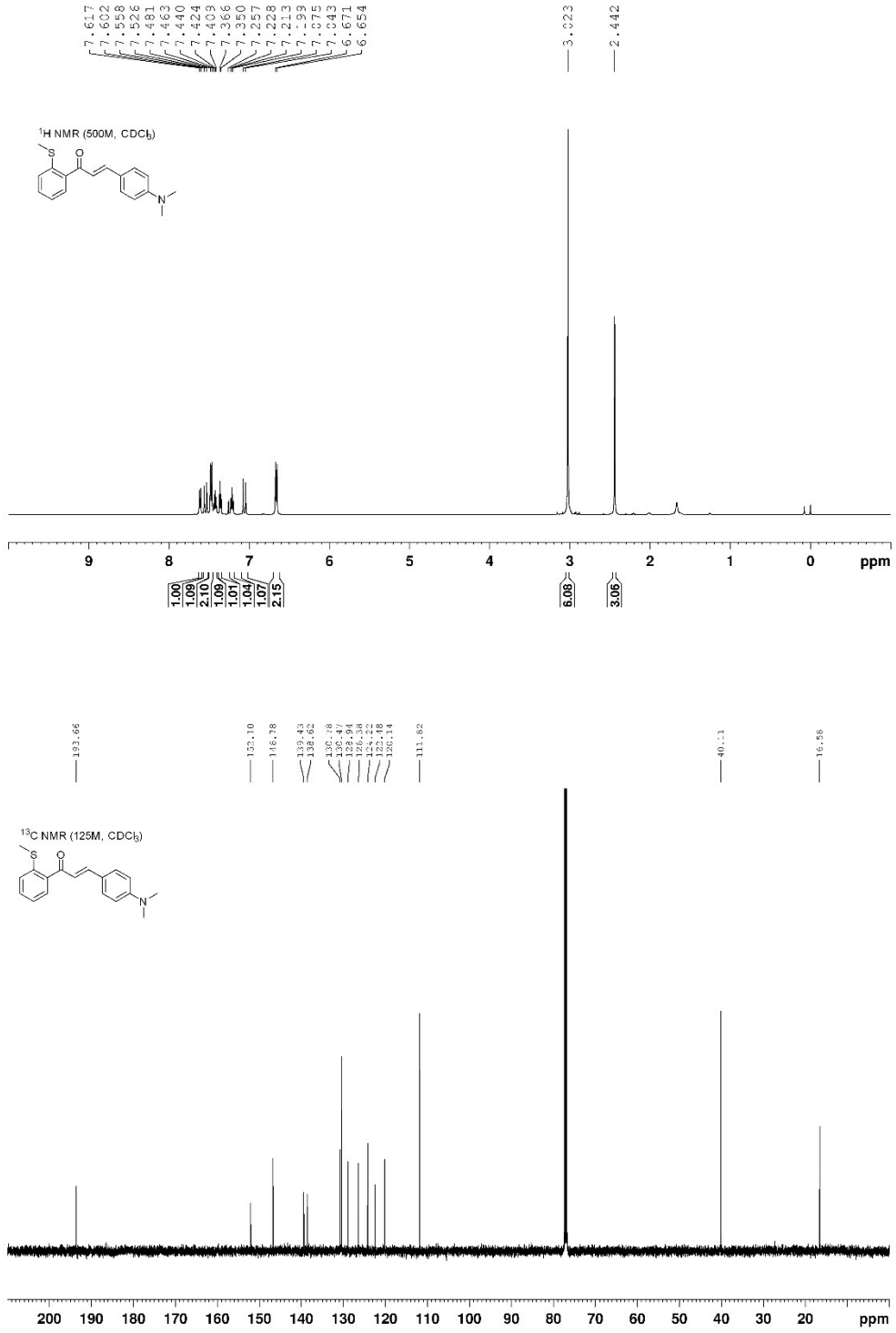
3o. (*E*)-3-(3-methoxyphenyl)-1-(2-(Methylthio)phenyl)prop-2-en-1-one



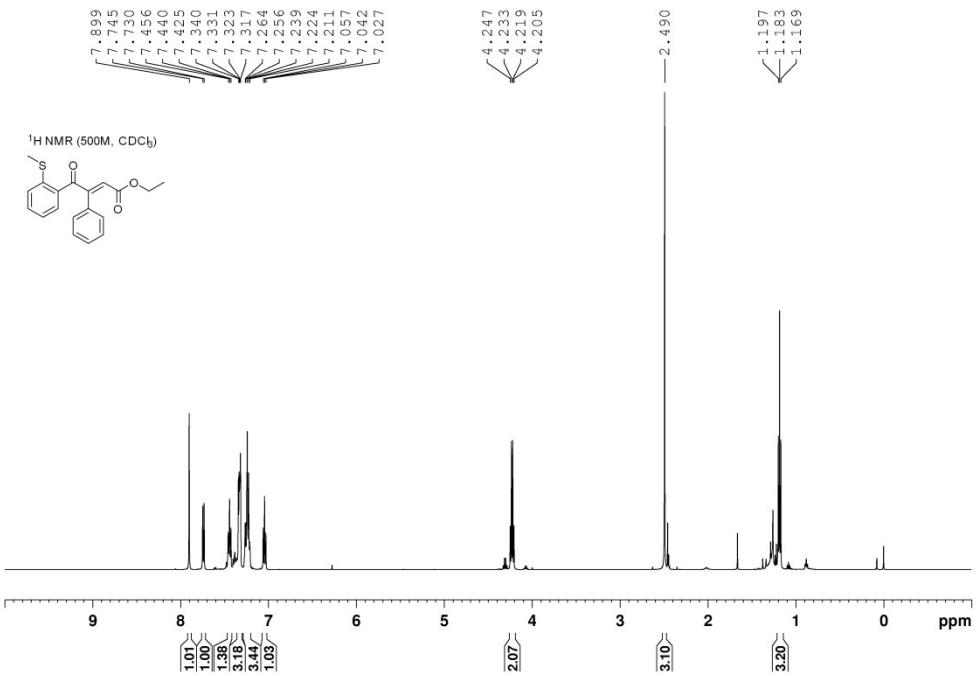
3p. (*E*)-3-(4-methoxyphenyl)-1-(2-(Methylthio)phenyl)prop-2-en-1-one

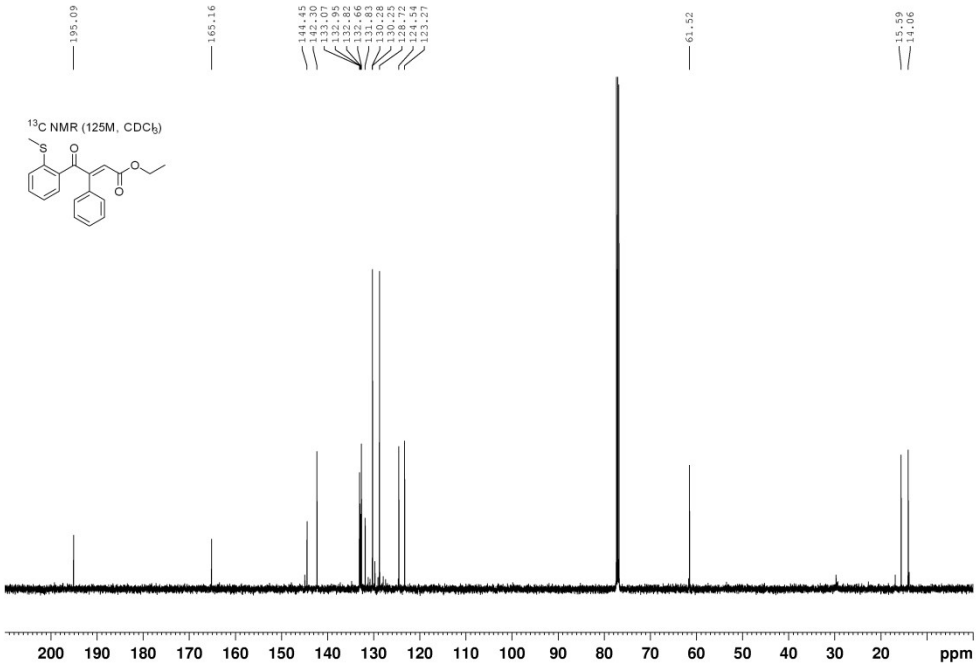


3q. (*E*)-3-(4-dimethylamino)-1-(2-(Methylthio)phenyl)prop-2-en-1-one

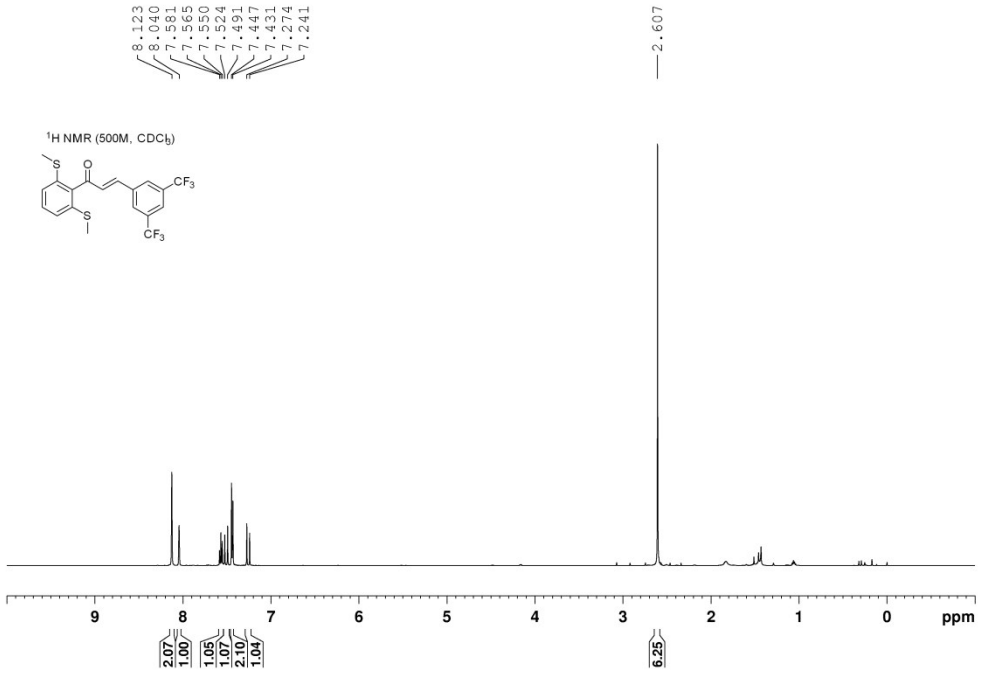


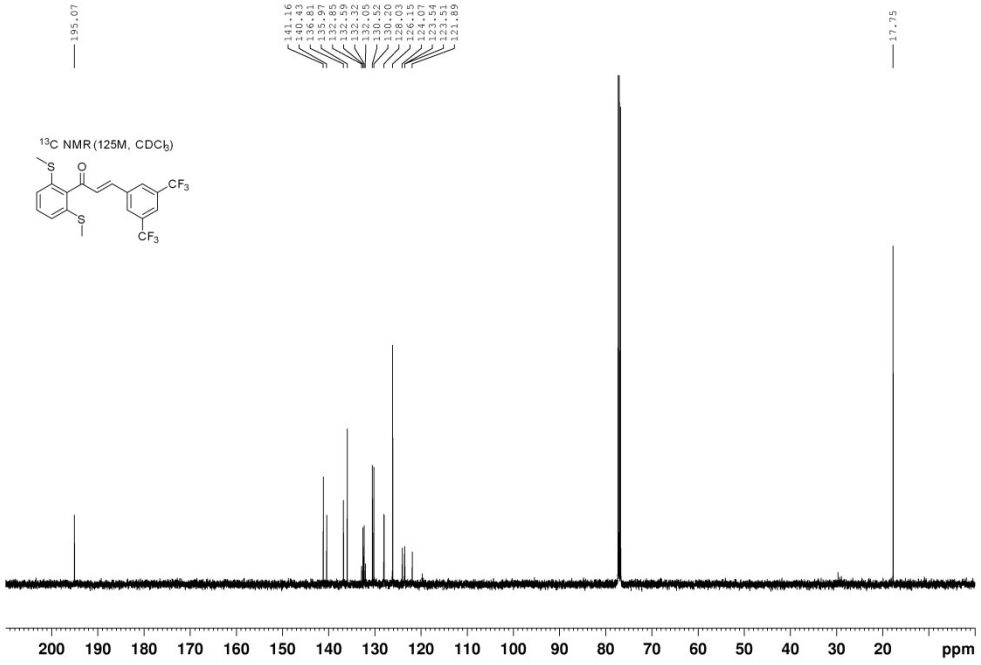
3r. ethyl (E)-4-(2-(methylthio)phenyl)-4-oxo-3-phenylbut-2-enoate



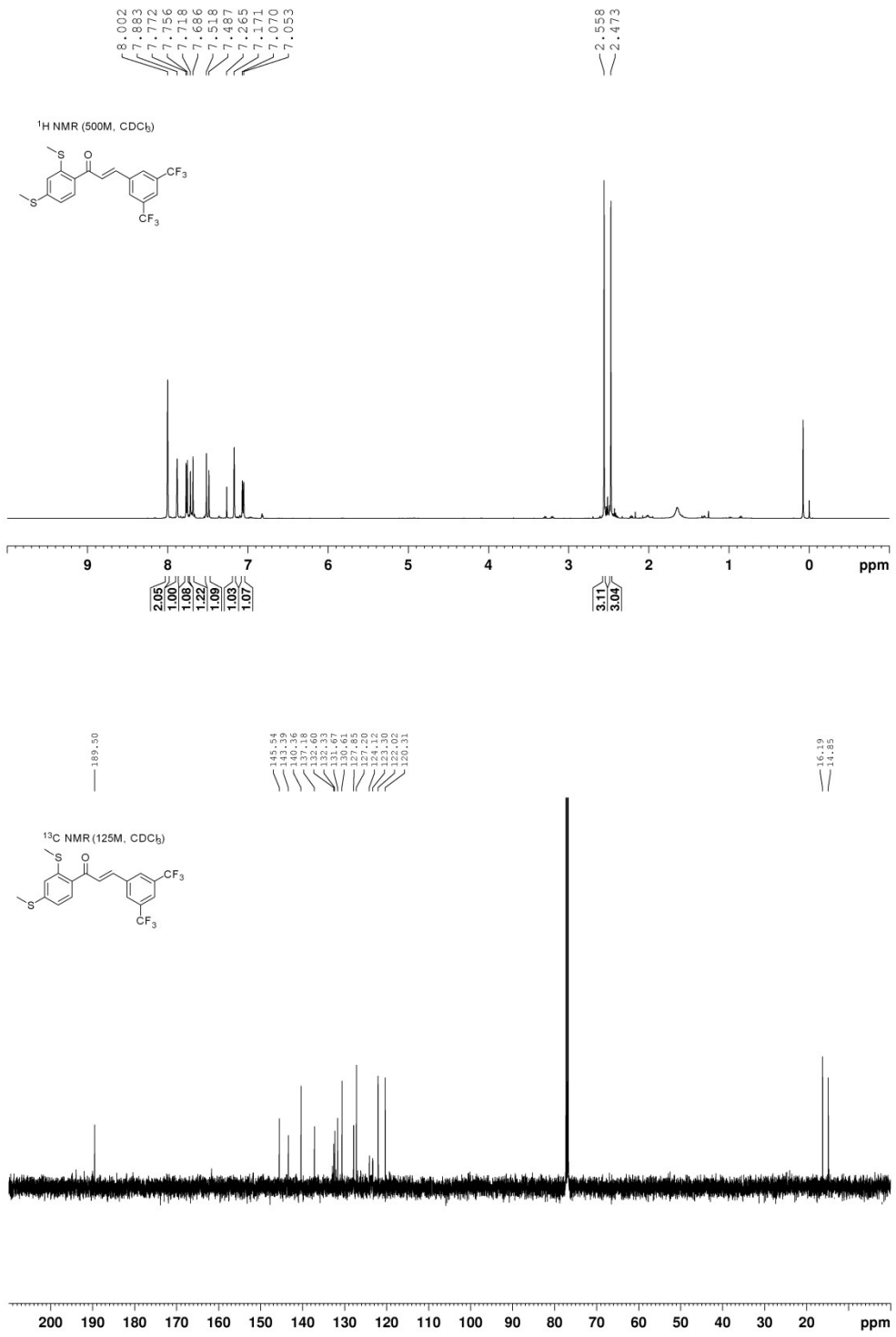


3s. (*E*)-1-(2,6-bis(Methylthio)phenyl)-3-(3,5-bis(trifluoromethyl)phenyl)prop-2-en-1-one

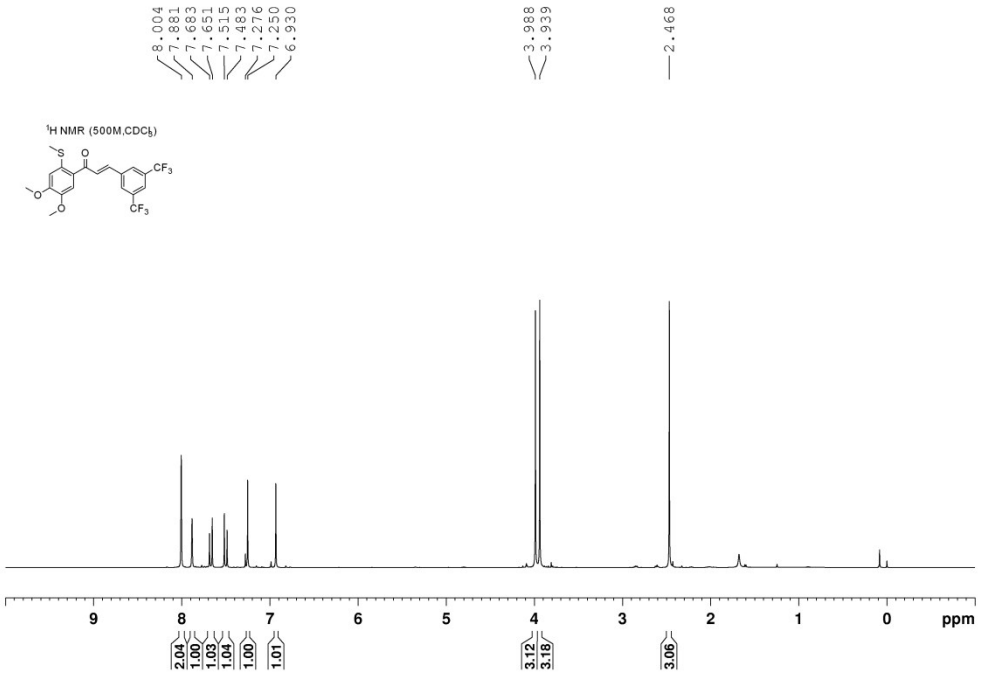


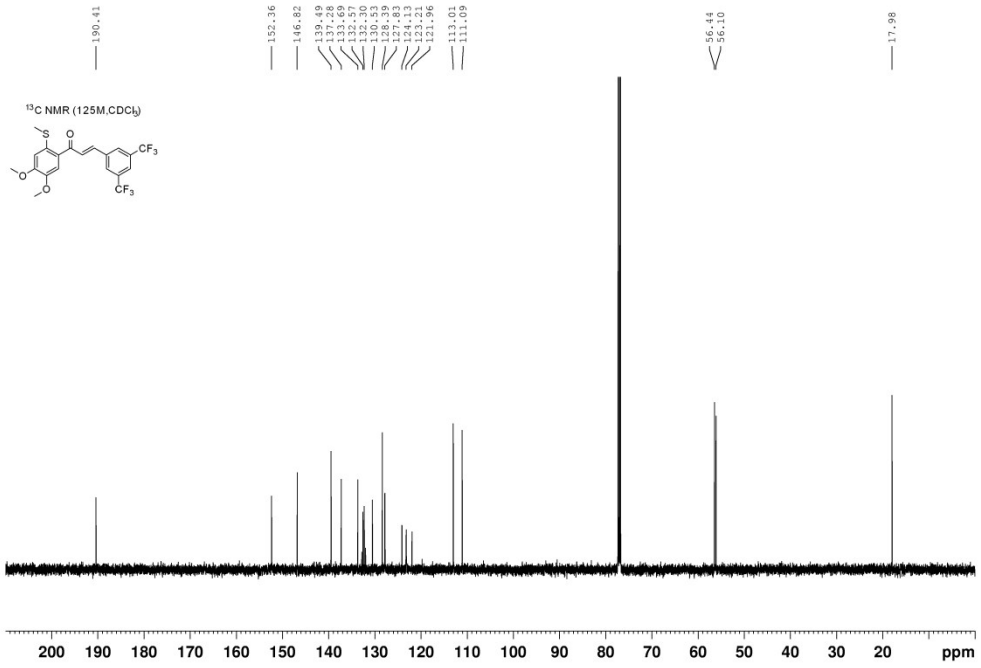


3t. (*E*)-1-(2,4-bis(Methylthio)phenyl)-3-(3,5-bis(trifluoromethyl)phenyl)prop-2-en-1-one

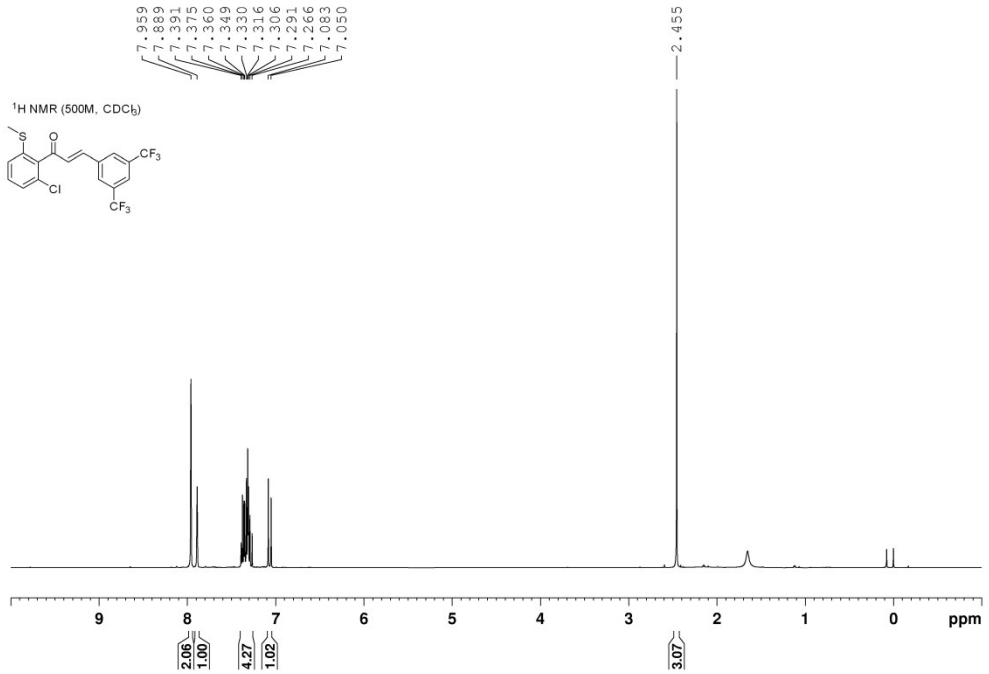


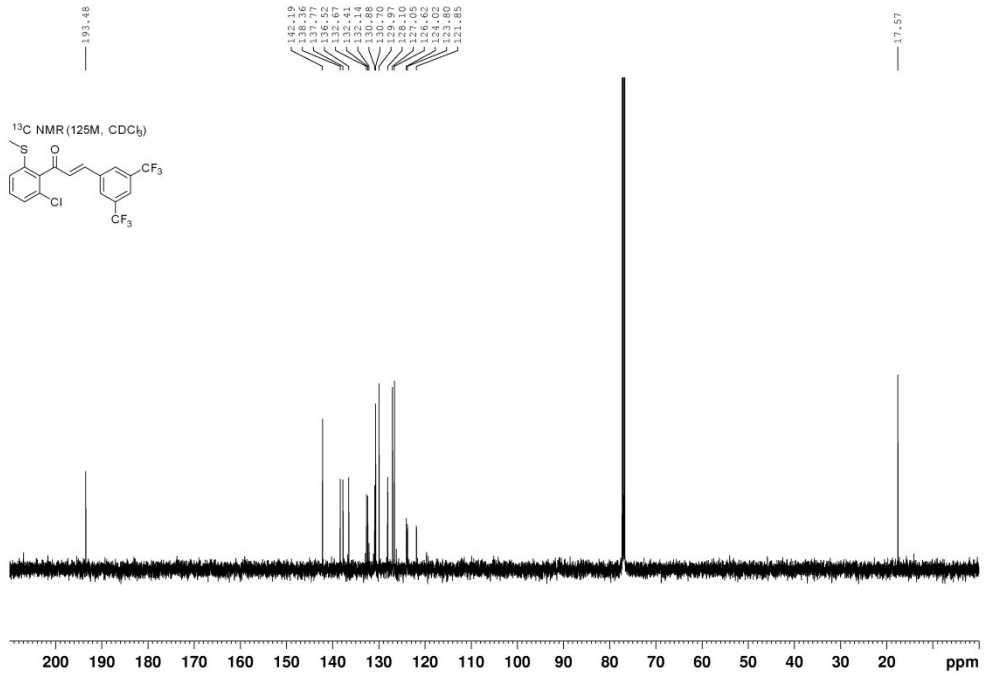
3u. (*E*)-3-(3,5-bis(Trifluoromethyl)phenyl)-1-(4,5-dimethoxy-2-(methylthio)phenyl)prop-2-en-1-one



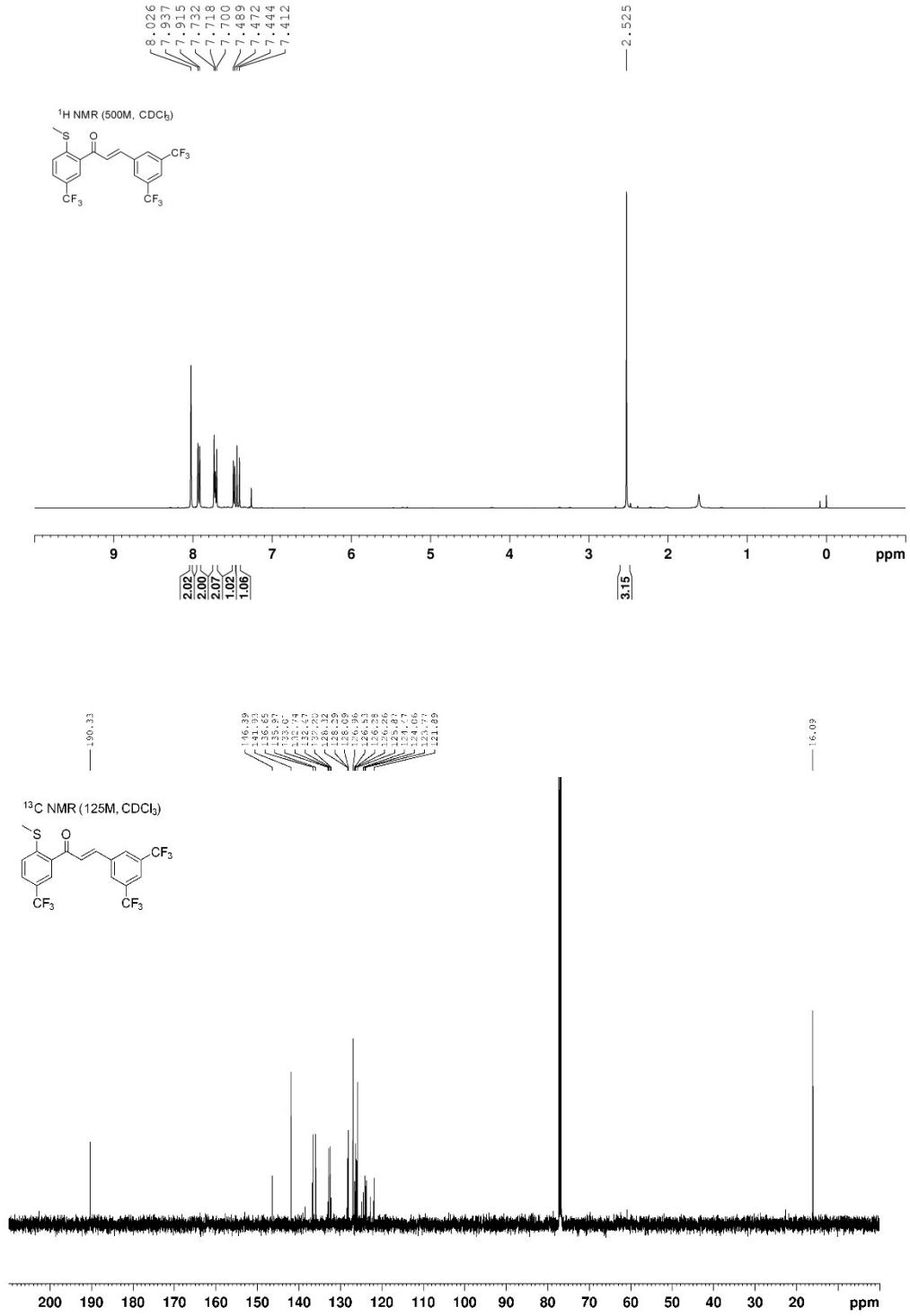


3v. (*E*)-3-(3,5-bis(Trifluoromethyl)phenyl)-1-(2-chloro-6-(methylthio)phenyl)prop-2-en-1-one

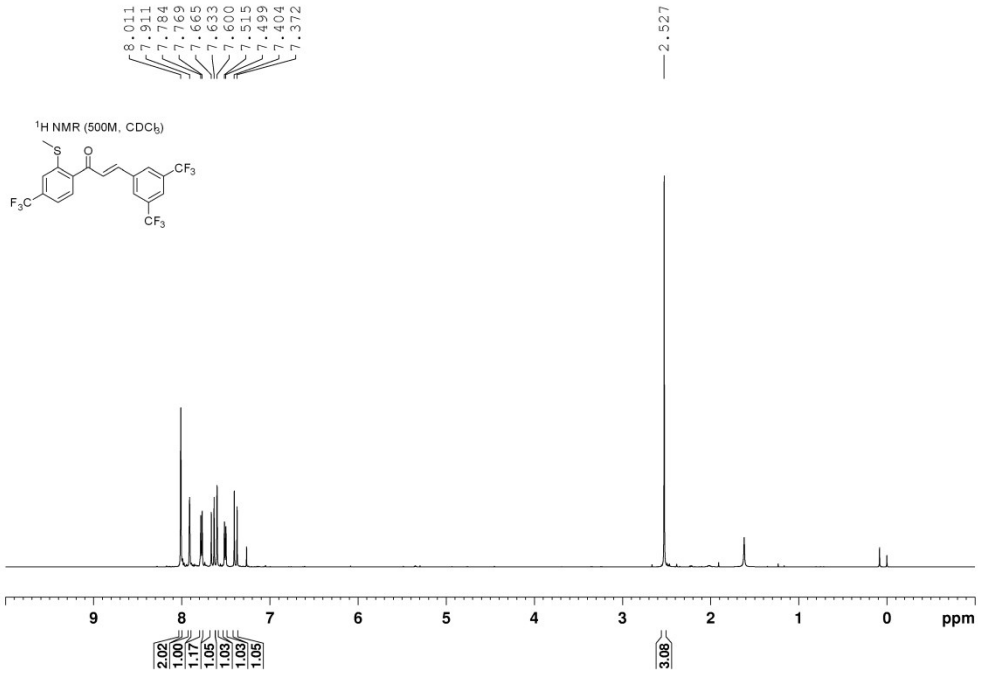


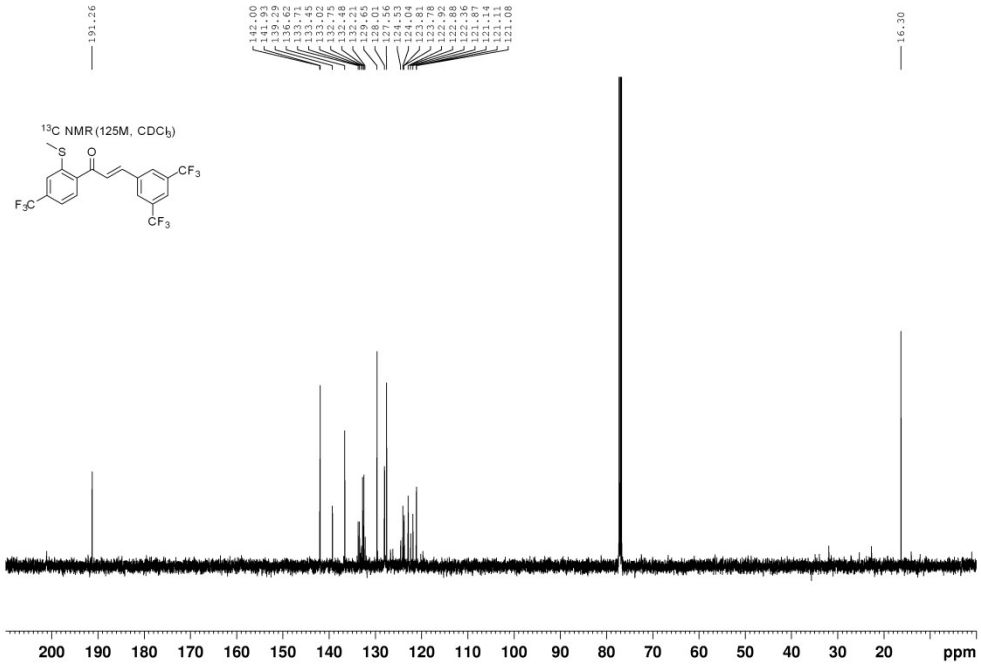


3w. (*E*)-3-(3,5-bis(Trifluoromethyl)phenyl)-1-(2-(methylthio)-5-(trifluoromethyl)phenyl)prop-2-en-1-one

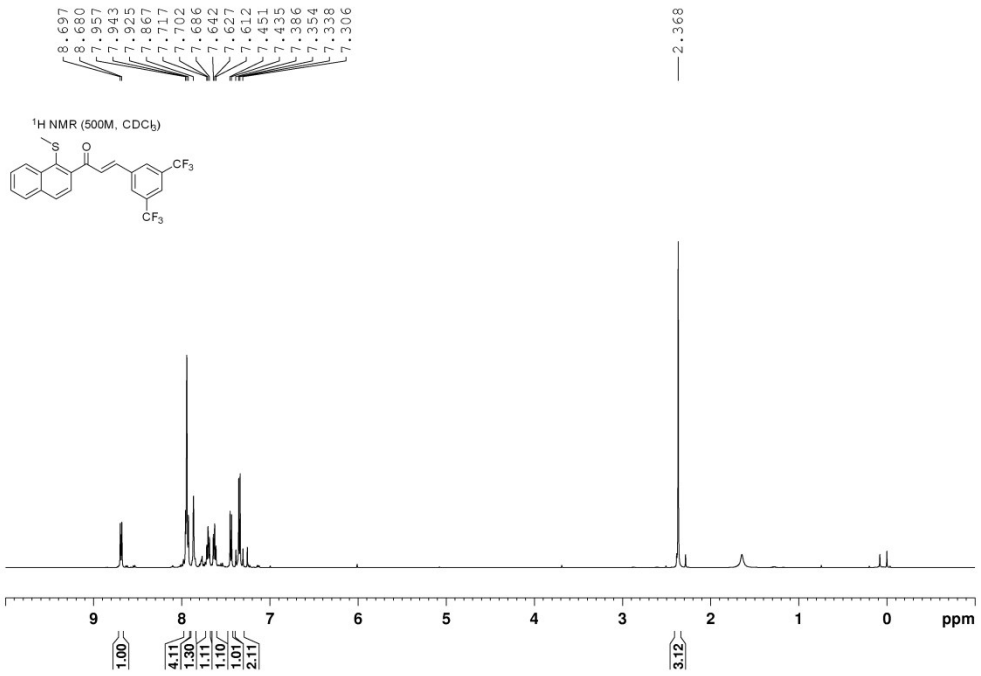


3x. (*E*)-3-(3,5-bis(Trifluoromethyl)phenyl)-1-(2-(methylthio)-4-(trifluoromethyl)phenyl) prop -2-en-1-one





3y. (E)-3-(3,5-bis(Trifluoromethyl)phenyl)-1-(2-(methylthio)naphthyl)prop-2-en-1-one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7.642
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7.451
7.435
7.386
7.354
7.338
7.306
2.368
1H NMR (500M, CDCl3)
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O
CF3
CF3
9
8
7
6
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4
3
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1
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1.11
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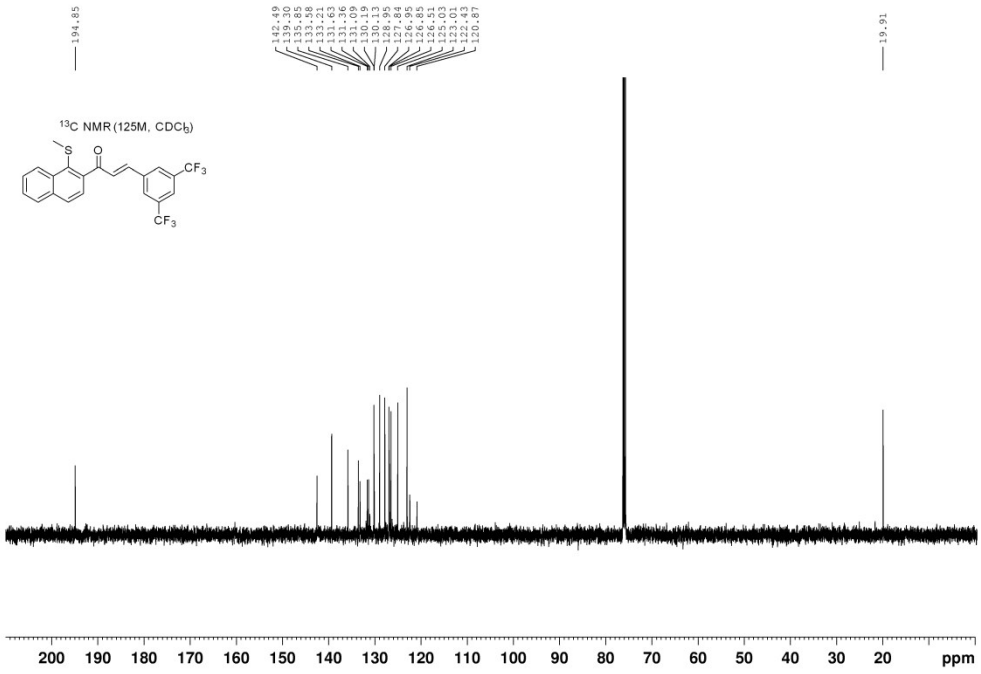
2.11
3.12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122.43
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19.91
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CF3
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20
ppm