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C-H Functionalization of Terminal Alkynes Towards Stereospecific Synthesis of (*E*) or (*Z*) 2-Methylthio-1,4-ene-diones

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Experimental:

^{1}H spectra were recorded on Brucker-Avance DPX FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$, 7.26ppm). Integration, and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz or 125 MHz.Chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent. Reagents and solvents used were mostly AR grade. Silica gel coated plates were used for TLC.

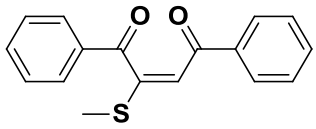
Experimental procedure

General procedure for synthesis of (*E*)-2-methylthio-1,4-ene-dione (Path I);

TMSOTf (222 µl, 1mmol) was added to a solution of terminal alkyne (102 µL, 1mmol) in DMSO (3 ml) followed by the addition of iodine (256 mg, 2mmol).The reaction mixture was heated at 80^{o}C for 18 h and the product formation was monitored by TLC. After completion of reaction, reaction mixture is cooled to room temperature, followed by quenching with 10% $Na_2S_2O_3$ solution, and extraction with ethyl acetate(3 x 50ml). The combined organic layers were washed with brine solution, concentrated under vacuum and purified by column chromatography using ethyl acetate and hexane to afford corresponding products.

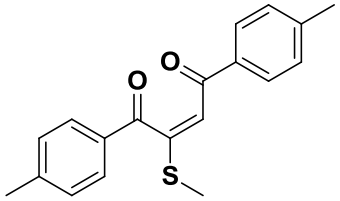
Note: At higher temperatures benzoic acid formation was also observed.

Characterization data:



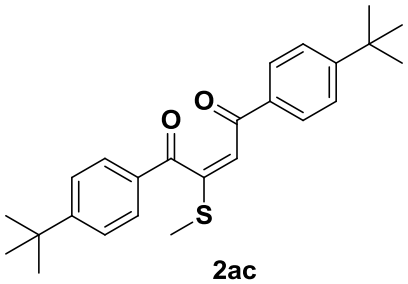
2aa

(*E*)-2-(methylthio)-1,4-diphenylbut-2-ene-1,4-dione (2aa): ^{1}H NMR (400 MHz, CDCl3) δ 8.00 (d, J = 7.6 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H), 7.55 (dd, J = 17.6, 7.4 Hz, 2H), 7.44 (dt, J = 10.8, 7.7 Hz, 4H), 7.03 (s, 2H), 2.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 185.1, 160.8, 137.2, 134.9, 133.6, 132.9, 130.0, 129.1, 128.8, 128.7, 128.6, 128.4, 128.1, 115.9, 14.9.



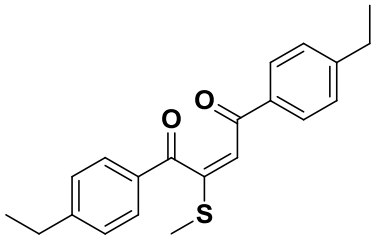
2ab

(*E*)-2-(methylthio)-1,4-di-p-tolylbut-2-ene-1,4-dione (2ab): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.21 (d, *J* = 7.9 Hz, 4H), 7.01 (s, 1H), 2.43 (s, 3H), 2.39 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 184.7, 160.3, 144.6, 143.8, 134.7, 132.4, 130.2, 129.8, 129.5, 129.3, 128.8, 128.6, 128.2, 115.7, 21.8, 21.7, 14.9.



2ac

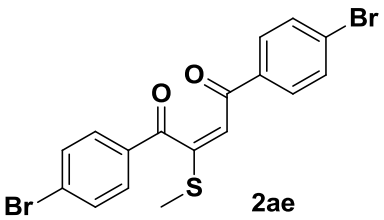
(*E*)-1,4-bis(4-(tert-butyl)phenyl)-2-(methylthio)but-2-ene-1,4-dione(2ac): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.38 (dd, *J* = 8.2, 3.8 Hz, 4H), 6.96 (s, 1H), 2.36 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 184.7, 160.4, 157.2, 156.8, 134.6, 132.2, 128.7, 128.5, 125.8, 125.2, 115.7, 35.2, 35.1, 31.1, 15.0.



2ad

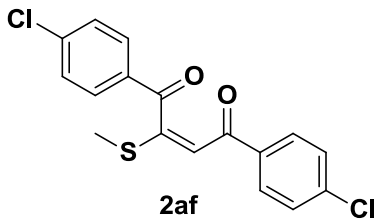
(*E*)-1,4-bis(4-ethylphenyl)-2-(methylthio)but-2-ene-1,4-dione (2ad):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.26 (t, *J* = 8.2 Hz, 4H), 7.02 (s, 1H), 2.69 (q, *J* = 7.6 Hz, 4H), 2.44 (s, 3H), 1.24 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 184.8, 160.4, 150.6, 150.0, 134.9, 132.6, 130.8, 130.3, 128.9, 128.7, 128.4, 128.1, 128.0, 115.8, 29.1, 28.9, 15.2, 15.1, 14.9.



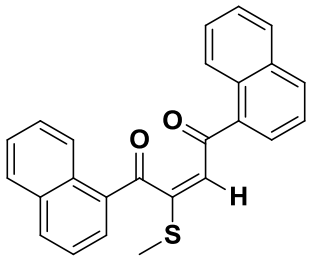
2ae

(*E*)-1,4-bis(4-bromophenyl)-2-(methylthio)but-2-ene-1,4-dione (2ae):^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.59 (t, J = 9.1 Hz, 4H), 6.95 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 184.0, 161.2, 135.8, 133.6, 132.6, 132.2, 132.0, 130.1, 129.9, 128.9, 128.3, 115.4, 15.0.



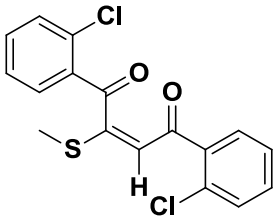
2af

(*E*)-1,4-bis(4-chlorophenyl)-2-(methylthio)but-2-ene-1,4-dione (2af):^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.73 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.53 – 7.45 (m, 4H), 6.87 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 184.1, 161.4, 135.7, 133.5, 132.2, 132.0, 130.1, 130.0, 129.0 128.4, 115.2, 15.1.



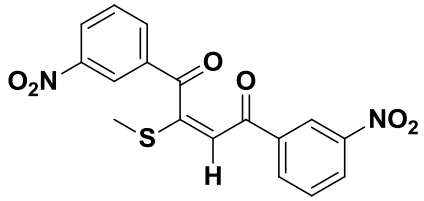
2ag

(*E*)-2-(methylthio)-1,4-di(naphthalen-1-yl)but-2-ene-1,4-dione (2ag): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (d, *J* = 8.7 Hz, 1H), 8.15 – 8.02 (m, 2H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.68 (ddd, *J* = 20.9, 14.9, 7.0 Hz, 3H), 7.51 (dd, *J* = 16.5, 9.4 Hz, 1H), 7.47 – 7.31 (m, 4H), 6.78 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.2, 189.5, 161.6, 136.5, 134.6, 134.0, 133.7, 132.3, 131.8, 131.4, 131.1, 130.1, 128.8, 128.3, 127.6, 127.5, 126.72, 126.69, 126.4, 125.5, 124.4, 124.1, 15.2.



2ah

(*E*)-1,4-bis(2-chlorophenyl)-2-(methylthio)but-2-ene-1,4-dione (2ah): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.50 –7.25 (m, 7H), 6.67 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 187.2, 160.8, 138.6, 134.3, 133.4, 133.3, 132.1, 131.8, 131.4, 130.3, 130.2, 127.1, 126.5, 119.6, 15.2.



2ai

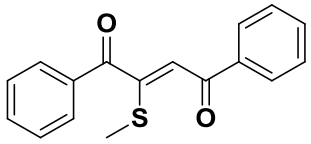
(E)-2-(methylthio)-1,4-bis(3-nitrophenyl)but-2-ene-1,4-dione (2ai): ^{1}H NMR (400 MHz, DMSO) δ 8.67 (s, 1H), 8.58 (s, 1H), 8.46 (dd, *J* = 16.8, 8.4 Hz, 3H), 8.30 (d, *J* = 7.7 Hz, 1H), 7.82 (q, *J* = 7.8 Hz, 2H), 7.32 (s, 1H), 2.74 (s, 3H).^{13}C NMR (100 MHz, DMSO) δ 191.5, 183.1,

161.8, 148.2, 148.0, 137.5, 135.5, 134.7, 134.2, 130.8, 130.5, 127.8, 127.4, 122.9, 122.0, 115.7, 15.1.

General procedure for synthesis of (*Z*)-2-methylthio-1,4-ene-dione (Path II);

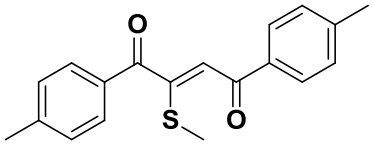
$BF_3.Et_2O$ (122 µl, 1mmol)was added to a solution of terminal alkyne (102 µL, 1mmol) in DMSO (3 ml) followed by the addition of iodine (126 mg, 1mmol).The reaction mixture was heated at 80^oC for 18 h and the product formation was monitored by TLC. After completion of reaction, reaction mixture is cooled to room temperature, followed by quenching with 10% $Na_2S_2O_3$ solution, and extraction with ethyl acetate (3 x 50ml). The combined organic layers were washed with brine solution, concentrated under vacuum and purified by column chromatography using ethyl acetate and hexane to afford corresponding products.

Characterization data:



2ba

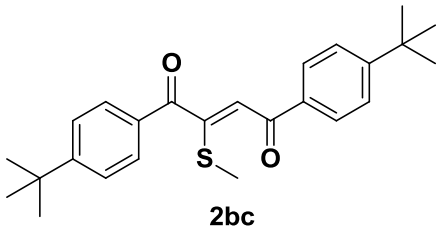
(*Z*)-2-(methylthio)-1,4-diphenylbut-2-ene-1,4-dione (2ba): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.04 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.94 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.70 – 7.65 (m, 1H), 7.53 (t, *J* = 7.9 Hz, 3H), 7.44 (dd, *J* = 10.6, 4.7 Hz, 2H), 7.10 (s, 1H), 2.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.9, 188.2, 160.7, 137.8, 134.89, 132.7, 130.0, 129.2, 128.7, 1281, 116.0, 15.5.



2bb

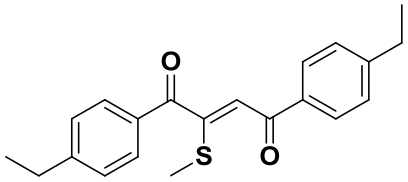
(*Z*)-2-(methylthio)-1,4-dip-tolylbut-2-ene-1,4-dione (2bb): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.06 (s, 1H), 2.45 (s, 3H), 2.39 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 187.9, 160.3, 146.0, 143.5, 135.4, 132.5, 130.2, 129.8, 129.3, 128.2, 116.0, 21.9, 21.6, 15.4.



2bc

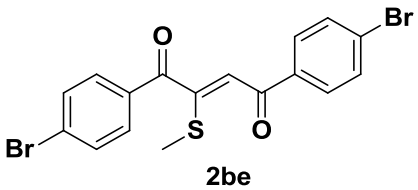
(*Z*)-1,4-bis(4-(tert-butyl)phenyl)-2-(methylthio)but-2-ene-1,4-dione (2bc): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 6.99 (s, 1H), 2.09 (s, 3H), 1.28 (s, 9H), 1.25 (s, 9H);^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 187.9, 160.3, 158.9, 156.4, 135.4, 132.4, 130.0, 128.0, 126.1, 125.6, 116.0, 35.4, 35.1, 31.1, 31.0, 15.4.



2bd

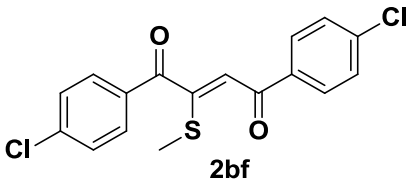
(*Z*)-1,4-bis(4-ethylphenyl)-2-(methylthio)but-2-ene-1,4-dione (2bd):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.07 (s, 1H), 2.72 (dq, *J* = 20.5, 7.6 Hz, 4H), 2.15 (s, 3H), 1.30 – 1.23 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.6, 188.0, 160.4, 152.2, 149.7, 135.6, 132.7, 130.3, 128.7, 128.3, 128.2, 115.9, 29.1, 28.9, 15.4, 15.2, 15.1.



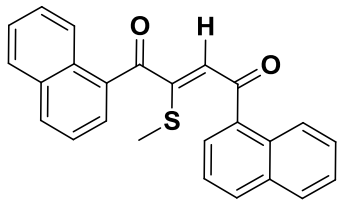
2be

(*Z*)-1,4-bis(4-bromophenyl)-2-(methylthio)but-2-ene-1,4-dione (2be): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 6.94 (s, 1H), 2.08 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 190.8, 187.0, 160.9, 136.4, 133.5, 132.6, 132.0, 131.3, 130.6, 129.6, 128.0, 115.5, 15.5.



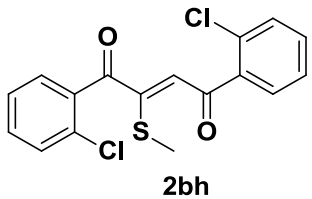
2bf

(*Z*)-1,4-bis(4-chlorophenyl)-2-(methylthio)but-2-ene-1,4-dione (2bf): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 6.8, 1.8 Hz, 2H), 7.73 – 7.68 (m, 2H), 7.60– 7.47 (m, 4H), 6.94 (s, 1H), 2.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.8, 187.0, 160.9, 136.4, 133.5, 132.6, 132.0, 131.3, 130.6, 129.6, 128.0, 115.6, 15.5.



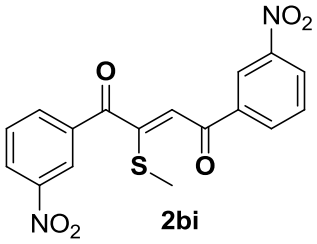
2bg

(Z)-2-(methylthio)-1,4-di(naphthalen-1-yl)but-2-ene-1,4-dione (2bg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 8.6 Hz, 1H), 8.63 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 7.2 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.70 (m, 2H), 7.62 – 7.51 (m, 4H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.03 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 191.9, 161.5, 136.8, 135.7, 134.3, 134.1, 133.9, 132.3, 131.2, 130.9, 130.3, 129.3, 128.9, 128.4, 127.67, 127.64, 127.0, 126.4, 125.8, 124.5, 124.5, 121.1, 15.6.



2bh

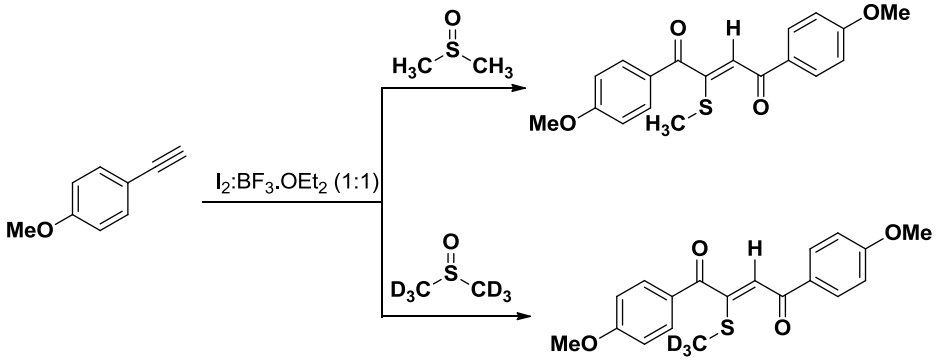
(*Z*)-1,4-bis(2-chlorophenyl)-2-(methylthio)but-2-ene-1,4-dione (2bh): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.51 (m, 3H), 7.41 – 7.32 (m, 4H), 6.82 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 189.8, 159.8, 139.0, 135.5, 133.7, 133.6, 132.0, 132.0, 131.4, 131.2, 130.3, 130.2, 127.1, 127.0, 122.3, 16.0.



2bi

(Z)-2-(methylthio)-1,4-bis(3-nitrophenyl)but-2-ene-1,4-dione (2bi): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.73 (s, 1H), 8.59 – 8.53 (m, 1H), 8.47 – 8.37 (m, 2H), 8.30 (d, *J* = 7.8 Hz, 2H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* = 14.2, 6.1 Hz, 1H), 7.13 (s, 1H), 2.20 (d, *J* = 12.7 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 185.5, 161.6, 148.8, 148.4, 138.8, 136.0, 135.3, 133.7, 130.7, 130.1, 129.1, 127.1, 124.4, 122.8, 115.4, 15.7.

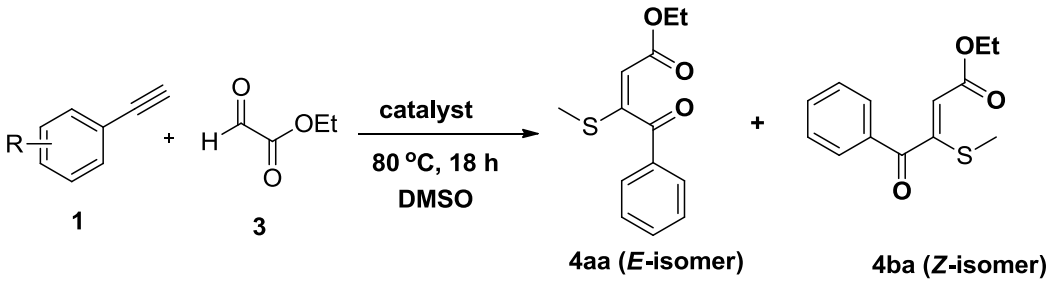
DMSO-d_6 Experiment:



DMSO as a solvent: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.05 (s, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 3.90 (s, 3H), 3.85 (s, 3H), 2.14 (s, 3H).

DMSO-d_6 as a solvent: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.05 (s, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H), 3.86 (s, 3H).

Table S1. Optimization for synthesis of β-methylthio-α,β-unsaturated-γ-ketoesters*

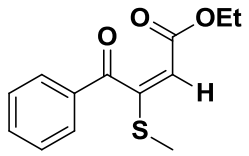


Entry	Iodine	promoter	Equiv.	Yield (%)	*E/Z* [%]
1	I_2	TMSOTf	2:1	72	80:20
2	I_2	TMSOTf	3:1	78	E only
3	I_2	BF_3. Et_2O	1: 1	72	45:55
4	I_2	BF_3. Et_2O	1:2	43**	48:52
5	I_2	BF_3. Et_2O	2:1	51**	49:51
5	I_2	BF_3. Et_2O	3:1	60**	ND

*Reactants: **1** (1 mmol), **3**(1 mmol), DMSO (3 ml), 18 h, 80 ^oC.**In case of BF_3. Et_2O there was also formation of homo coupling products of phenylacetylene (**2aa** and **2ba**), in addition to cross coupling products**4aa** and **4ba**.

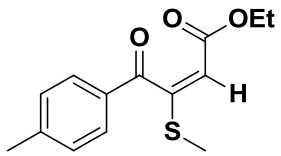
General procedure for synthesis of (*E*)-β-methylthio-α,β-unsaturated-γ-ketoesters(Path I); TMSOTf (222 µl, 1mmol) was added to a solution of terminal alkyne (102 µL, 1mmol) in DMSO (3 ml) followed by the addition of iodine (378mg, 3mmol) and ethyl glyoxylate (102 µL, 1mmol).The reaction mixture was heated at 80^oC for 18 h and the product formation was monitored by TLC. After completion of reaction, reaction mixture is cooled to room temperature, followed by quenching with 10% $Na_2S_2O_3$ solution, and extraction with ethyl acetate(3 x 50ml). The combined organic layers were washed with brine solution, concentrated under vacuum and purified by column chromatography using ethyl acetate and hexane to afford corresponding products.

Characterization data:



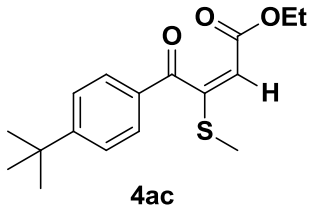
4aa

(*E*)-ethyl 3-(methylthio)-4-oxo-4-phenylbut-2-enoate (4aa): ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.82 (s, 1H), 3.97 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 163.5, 158.2, 134.8, 133.8, 129.0, 128.8, 111.9, 60.6, 14.9, 13.9.



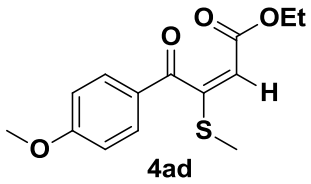
4ab

(*E*)-ethyl 3-(methylthio)-4-oxo-4-(p-tolyl)but-2-enoate (4ab): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.82 (s, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 2.39 (s, 3H), 1.08 (dd, *J* = 8.6, 5.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 163.60, 158.4, 144.9, 132.4, 129.5, 129.2, 111.7, 60.6, 21.8, 14.9, 13.9.



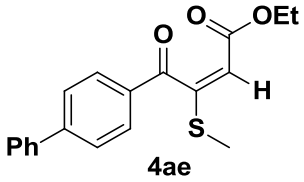
4ac

(*E*)-ethyl 4-(4-(tert-butyl)phenyl)-3-(methylthio)-4-oxobut-2-enoate(4ac): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 5.82 (s, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.33 (s, 9H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 163.6, 158.5, 157.7, 132.2, 129.1, 125.8, 111.7, 60.6, 35.2, 31.1, 14.9, 13.8.



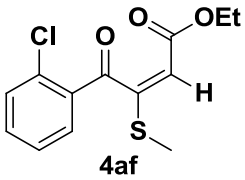
4ad

(*E*)-ethyl 4-(4-methoxyphenyl)-3-(methylthio)-4-oxobut-2-enoate (4ad): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.80 (s, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 2.38 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 131.5, 127.9, 114.1, 111.6, 60.6, 55.6, 14.9, 13.9.



4ae

(*E*)-ethyl 4-([1,1'-biphenyl]-4-yl)-3-(methylthio)-4-oxobut-2-enoate(4ae): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (m, 2H), 7.67 (m, 2H), 7.60 (m, 2H), 7.45 (dd, *J* = 10.2, 4.7 Hz, 2H), 7.38 (m, 1H), 5.83 (s, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 163.7, 158.4, 146.6, 139.8, 133.5, 129.6, 129.0, 128.4, 127.5, 127.3, 111.9, 60.7, 14.9, 13.9.

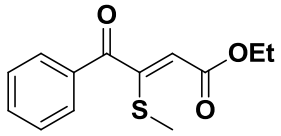


4af

(*E*)-ethyl 4-(2-chlorophenyl)-3-(methylthio)-4-oxobut-2-enoate(4af): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 (m, 2H), 7.36 (m, 1H), 5.76 (s, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.8, 163.7, 158.8, 134.3, 133.6, 133.1, 132.7, 131.9, 126.7, 112.3, 60.8, 15.1, 13.9.

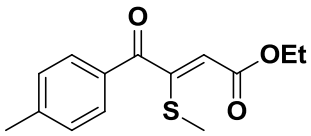
General procedure for synthesis of (*Z*)-β-methylthio-α,β-unsaturated-γ-keto esters(Path II); $BF_3.Et_2O$ (122 µl, 1mmol) was added to a solution of terminal alkyne (102 µL, 1mmol) in DMSO (3 ml) followed by the addition of iodine (126 mg, 1mmol) and ethyl glyoxylate (102 µL, 1mmol).The reaction mixture was heated at 80°C for 18 h and the product formation was monitored by TLC. After completion of reaction, reaction mixture is cooled to room temperature, followed by quenching with 10% $Na_2S_2O_3$ solution, and extraction with ethyl acetate(3 x 50ml). The combined organic layers were washed with brine solution, concentrated under vacuum and purified by column chromatography using ethyl acetate and hexane to afford corresponding products.

Characterization data:



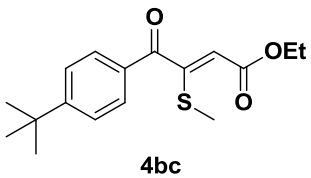
4ba

(*Z*)-ethyl 3-(methylthio)-4-oxo-4-phenylbut-2-enoate (4ba): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 5.82 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.03 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 165.4, 157.9, 134.8, 134.7, 129.9, 129.0, 113.4, 60.5, 14.9, 14.3.



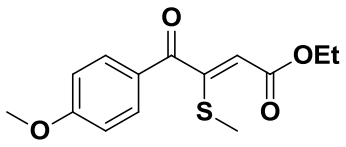
4bb

(*Z*)-ethyl 3-(methylthio)-4-oxo-4-(p-tolyl)but-2-enoate (4bb): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 5.89 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.42 (d, *J* = 17.2 Hz, 3H), 2.11 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 165.6, 158.2, 145.9, 132.4, 130.1, 129.7, 113.2, 60.5, 21.8, 14.9, 14.3.



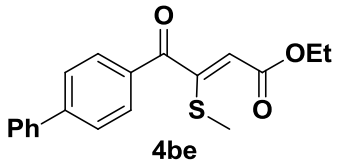
4bc

(*Z*)-ethyl 4-(4-(tert-butyl)phenyl)-3-(methylthio)-4-oxobut-2-enoate (4bc): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (t, *J* = 7.9 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 5.89 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.13 (s, 3H), 1.35 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.2, 165.6, 158.8, 158.3, 132.2, 130.0, 126.0, 113.1, 60.5, 35.4, 31.0, 14.9, 14.3.



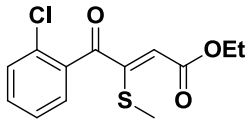
4bd

(*Z*)-ethyl 4-(4-methoxyphenyl)-3-(methylthio)-4-oxobut-2-enoate (4bd): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99(d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 5.89 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 2.12 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 165.7, 164.8, 158.4, 132.5, 127.8, 114.3, 112.9, 60.5, 55.7, 14.9, 14.3.



4be

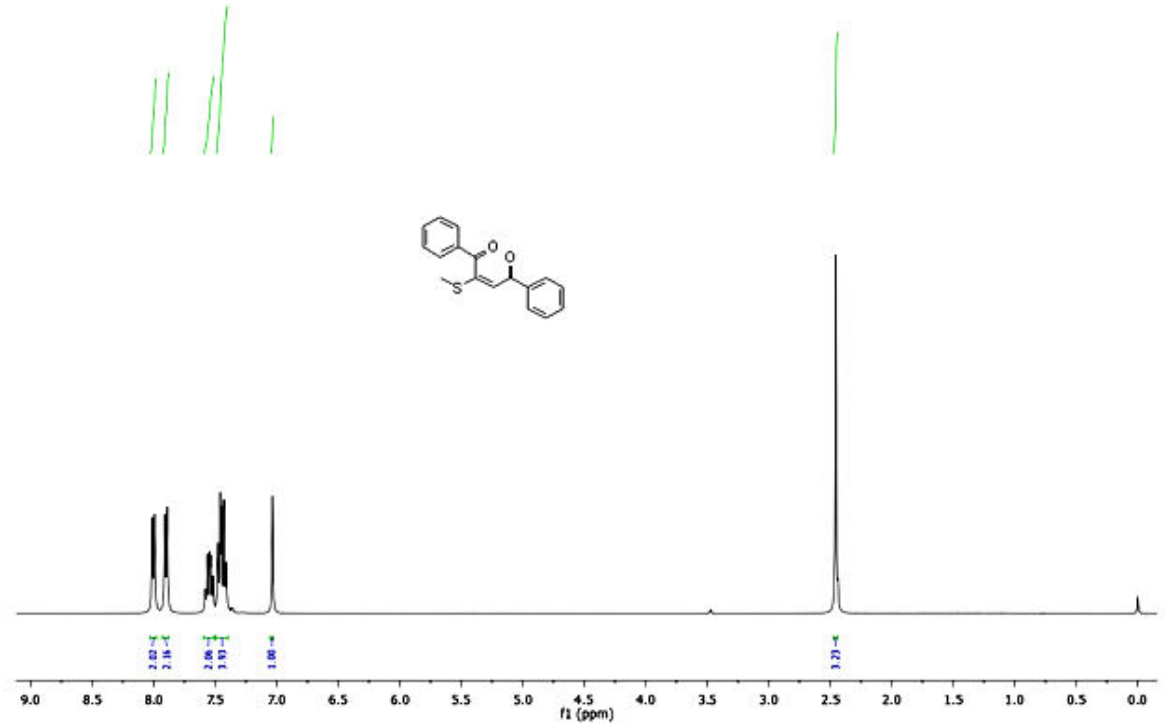
(*Z*)-ethyl 4-([1,1'-biphenyl]-4-yl)-3-(methylthio)-4-oxobut-2-enoate (4be): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (m, 2H), 7.77 (m, 2H), 7.65 (m, 2H), 7.50 (dd, *J* = 10.2, 4.7 Hz, 2H), 7.44 (m, 1H), 5.95 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.16 (s, 3H), 1.33 (m, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 191.2, 165.7, 158.2, 147.2, 139.4, 133.5, 130.6, 129.1, 128.7, 127.7, 127.3, 113.4, 60.6, 15.0, 14.3.

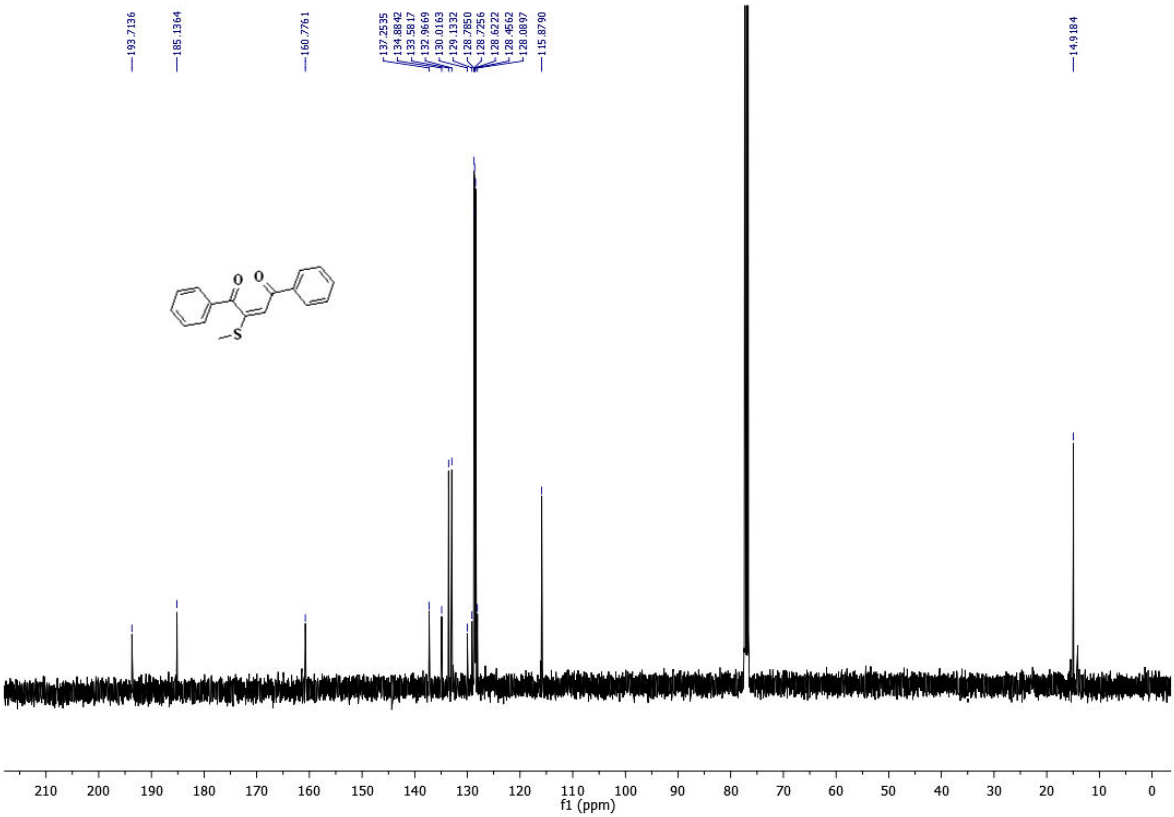


4bf

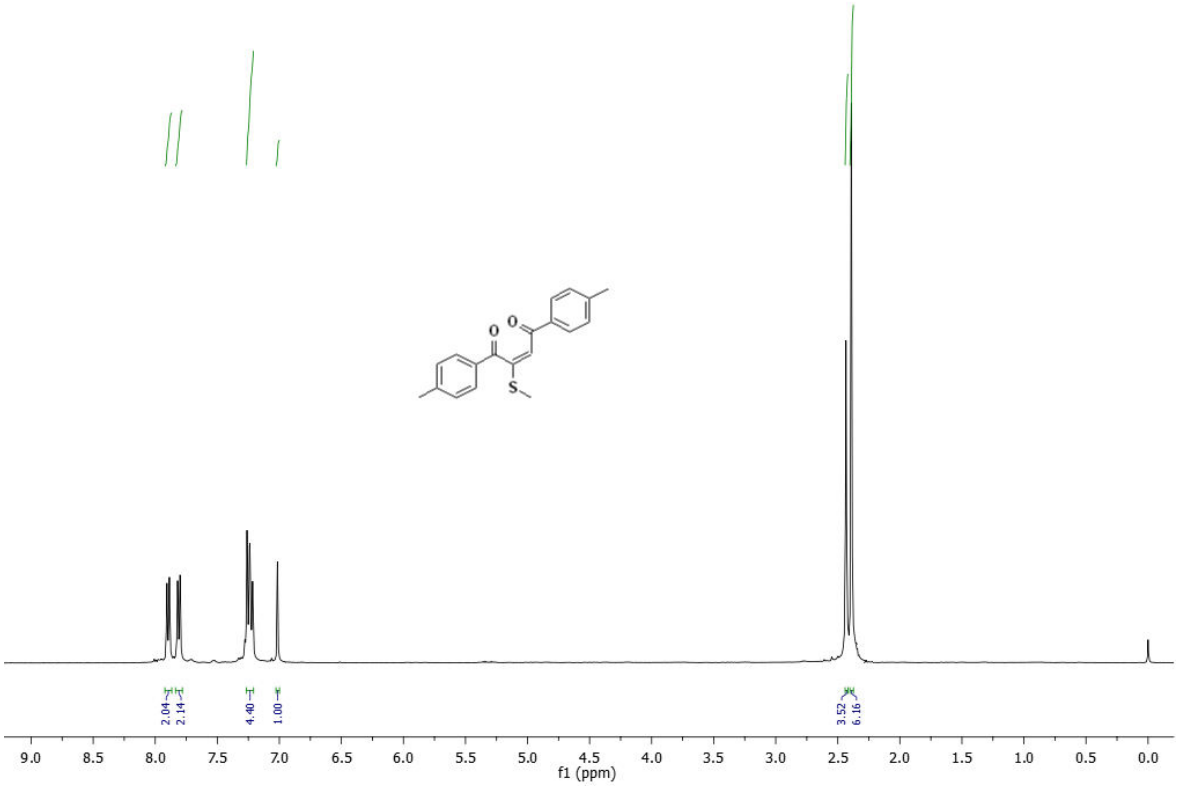
(*Z*)-ethyl 4-(2-chlorophenyl)-3-(methylthio)-4-oxobut-2-enoate (4bf): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.7 Hz, 1H), 7.49 (q, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.1 Hz, 1H), 5.95 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.28 (t,*J* = 7.1 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 165.3, 158.2, 135.7, 133.5, 133.3, 131.8, 131.2, 127.0, 117.1, 60.7, 15.5, 14.2.

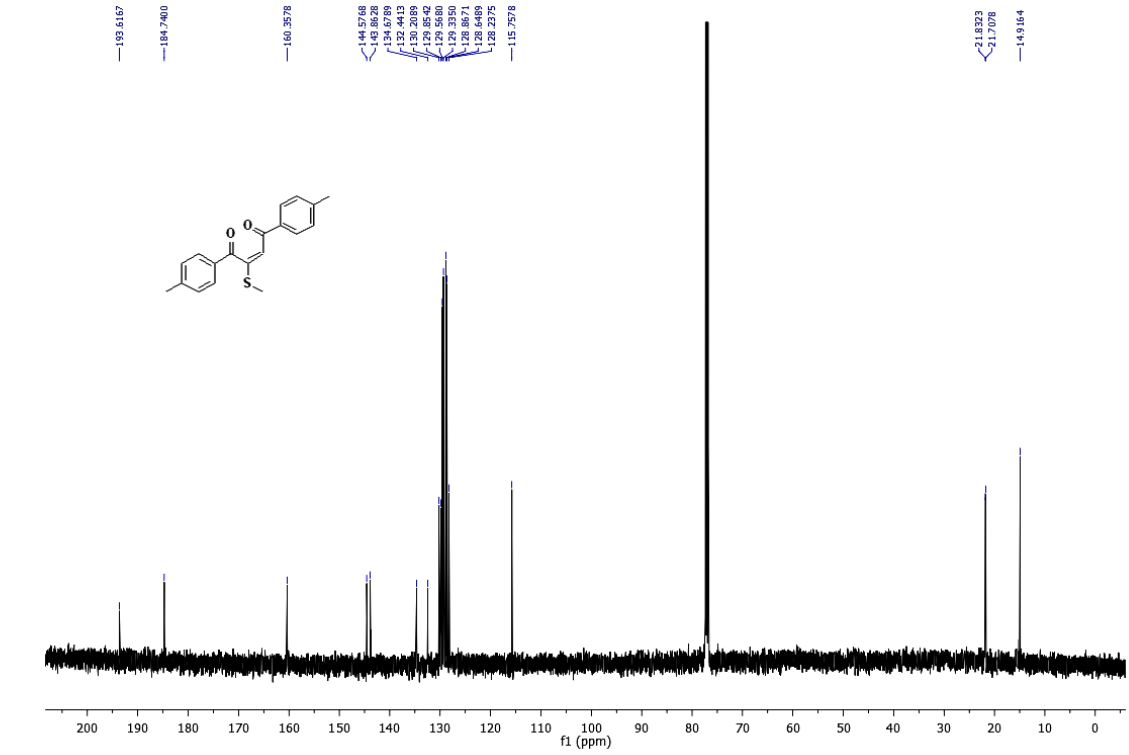
^{1}H NMR ^{13}C-NMR of 2aa:



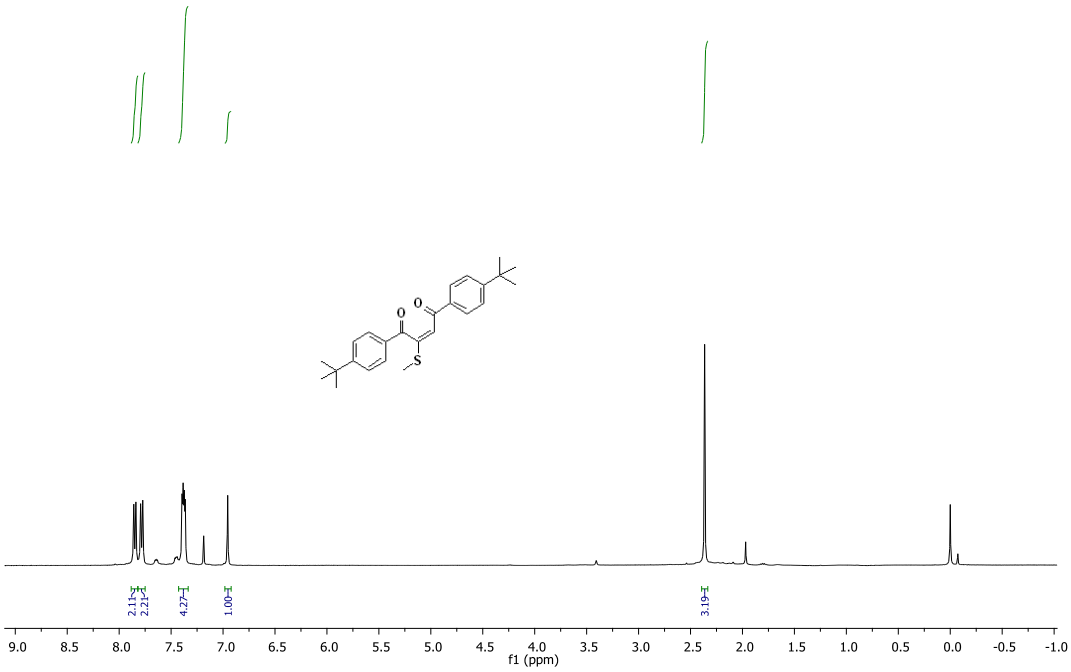


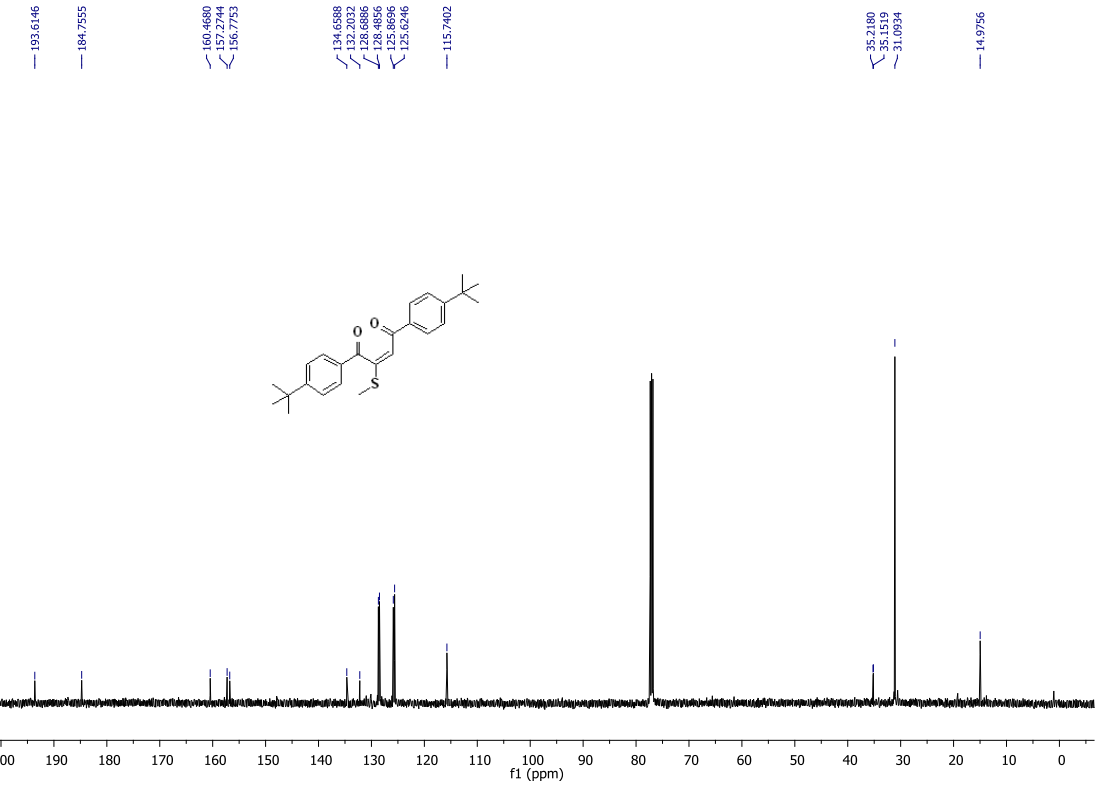
^{1}H and ^{13}C-NMR of 2ab:



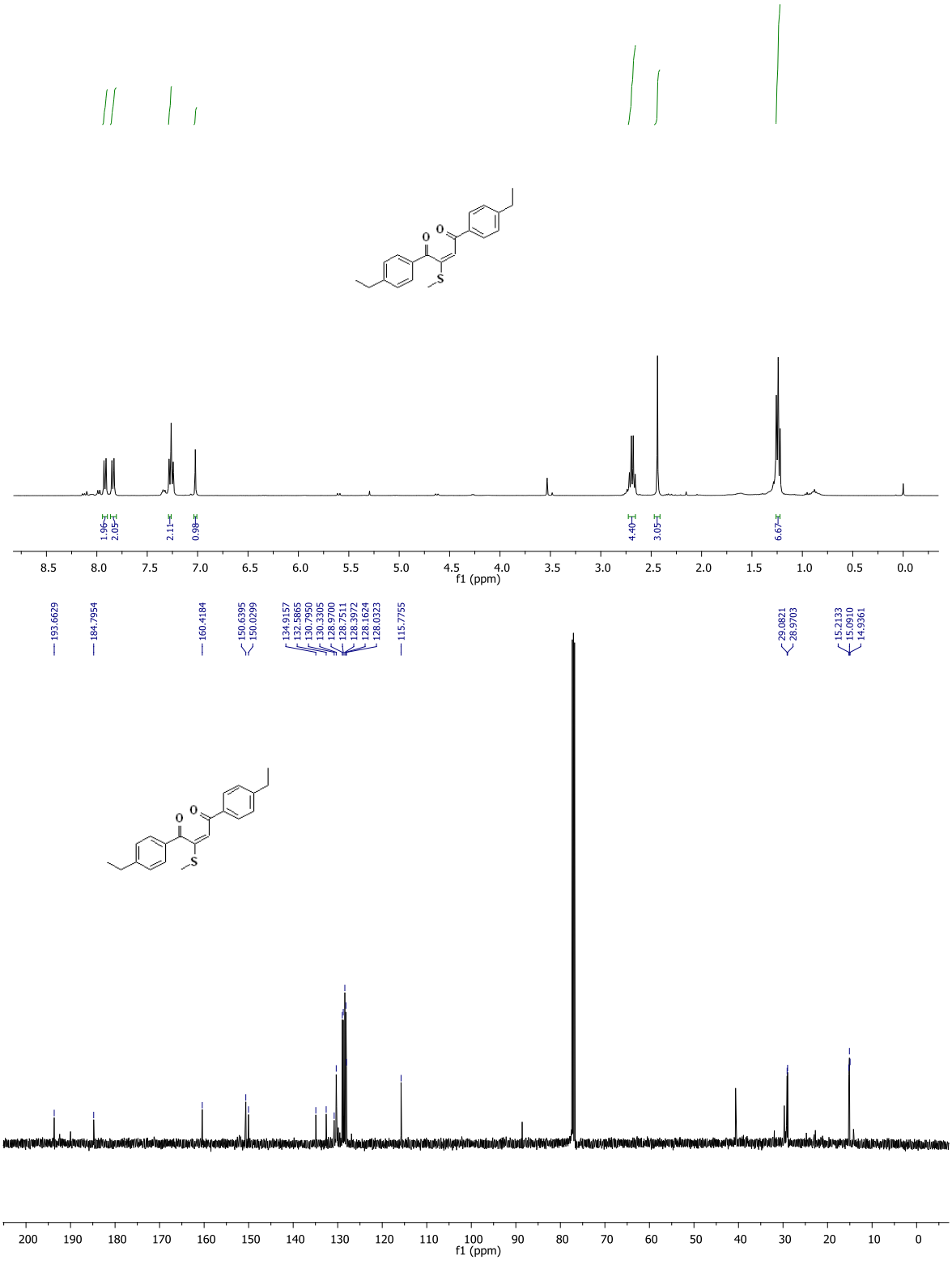


^{1}H and^{13}C-NMR of 2ac:

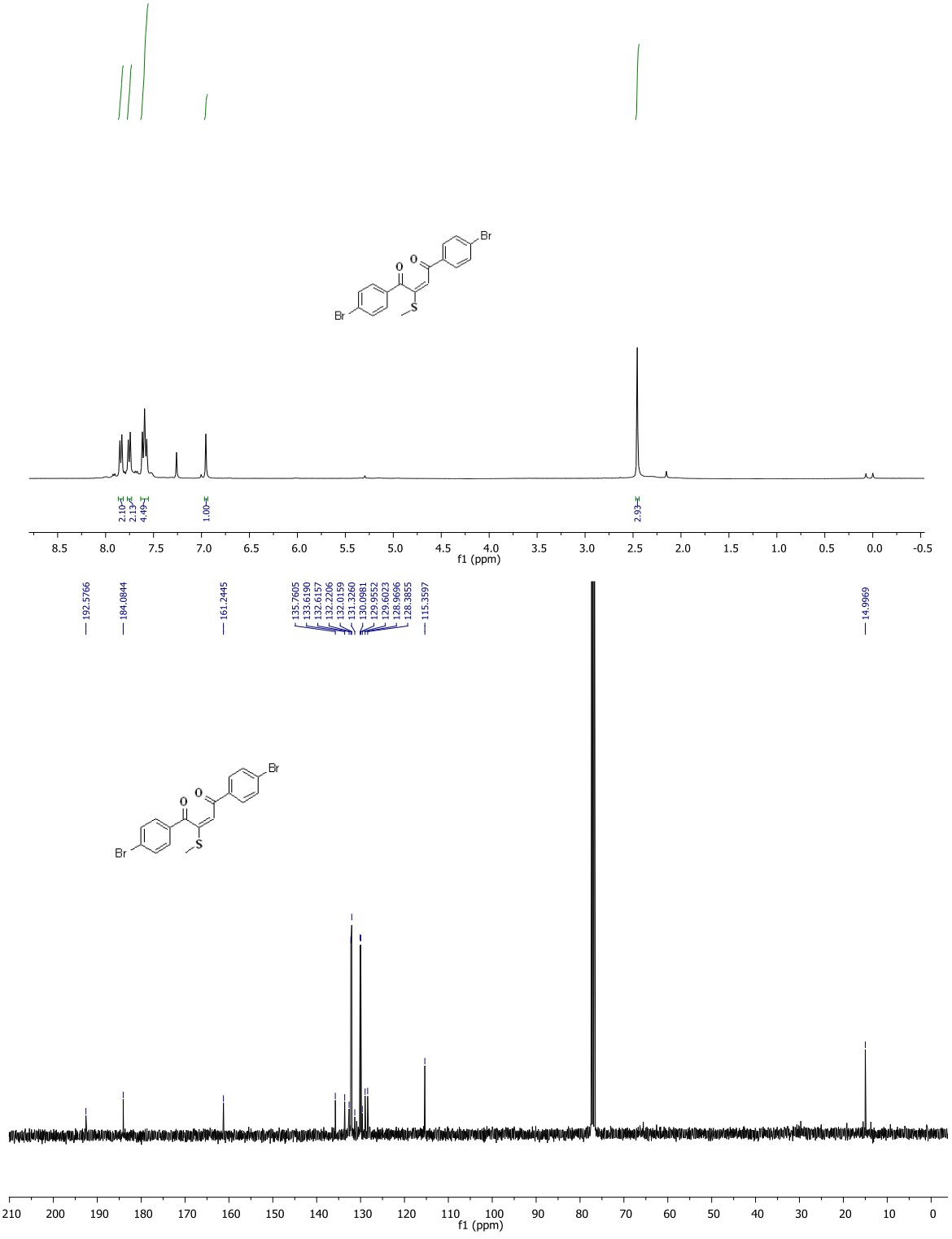




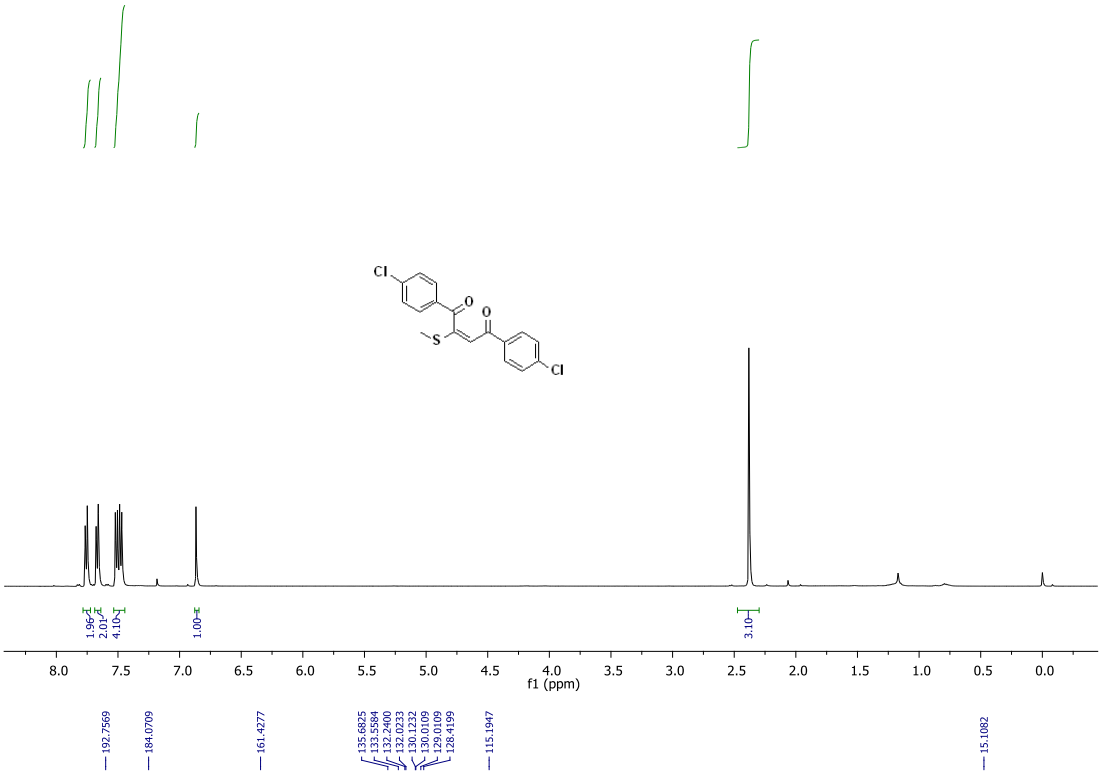
^{1}H and^{13}C-NMR of 2ad:

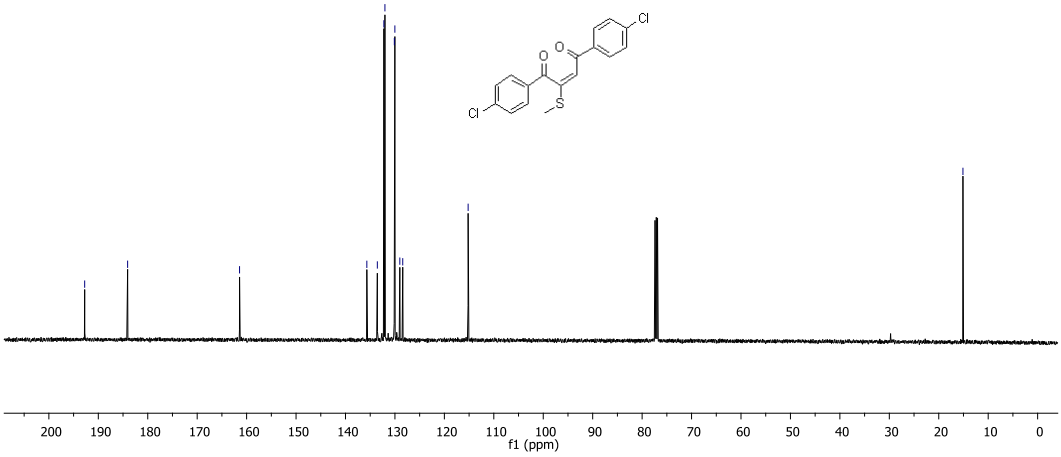


^{1}H and ^{13}C-NMR of 2ae:

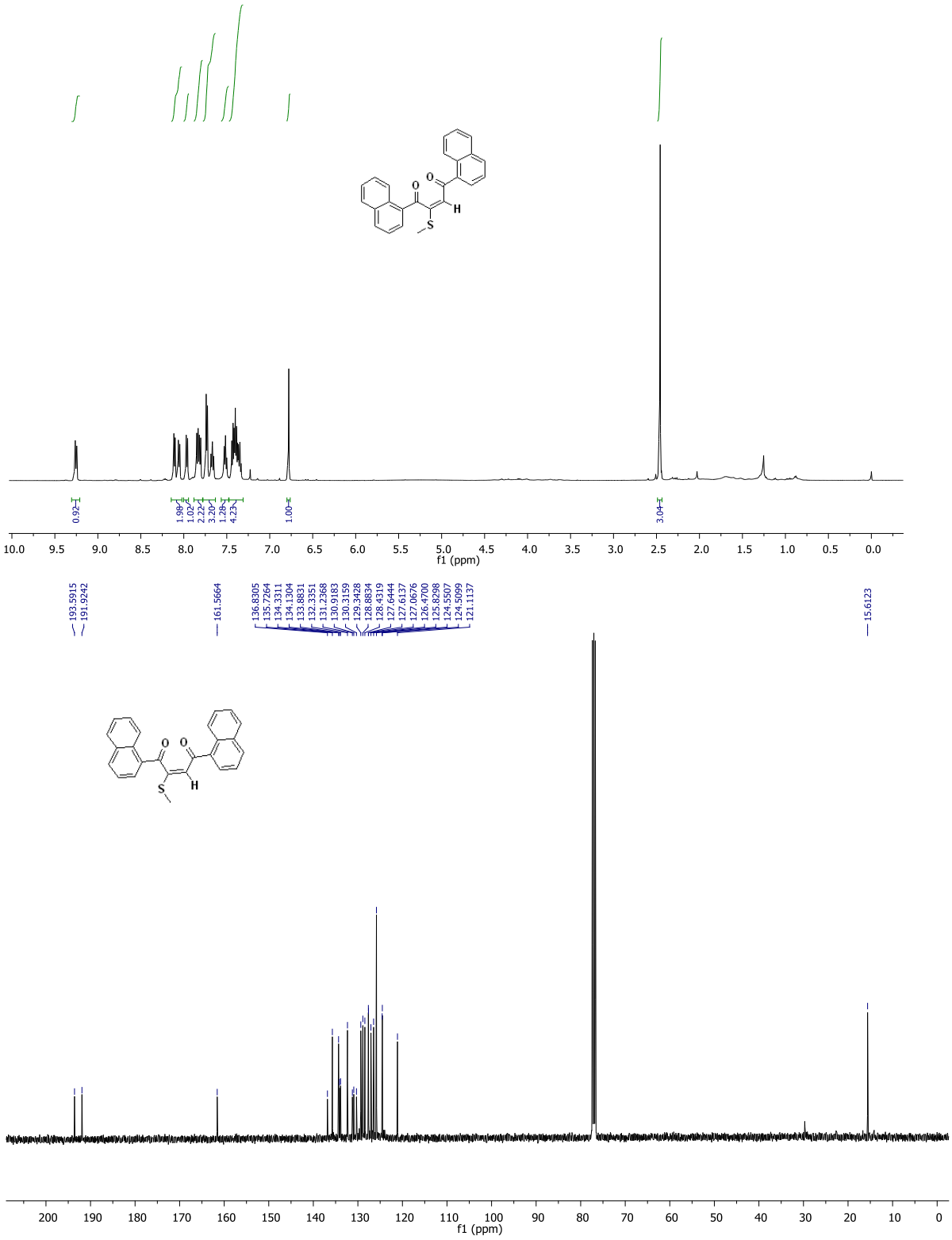


^{1}H and^{13}C-NMR of 2af:

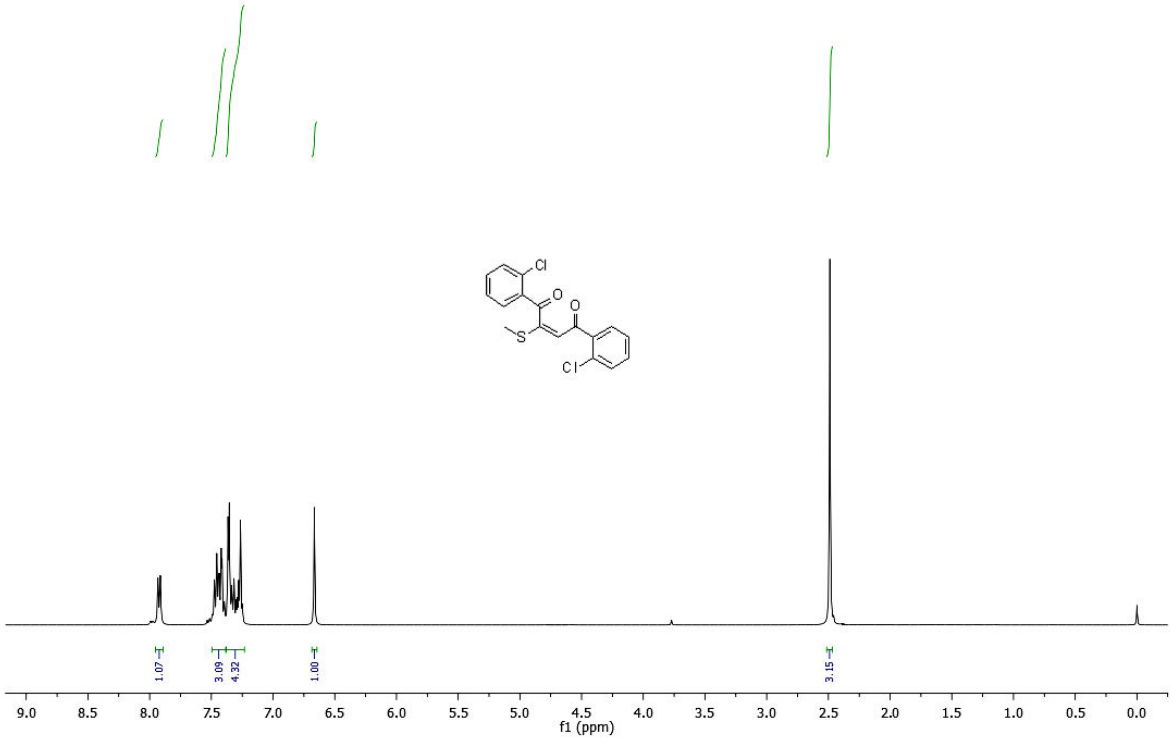


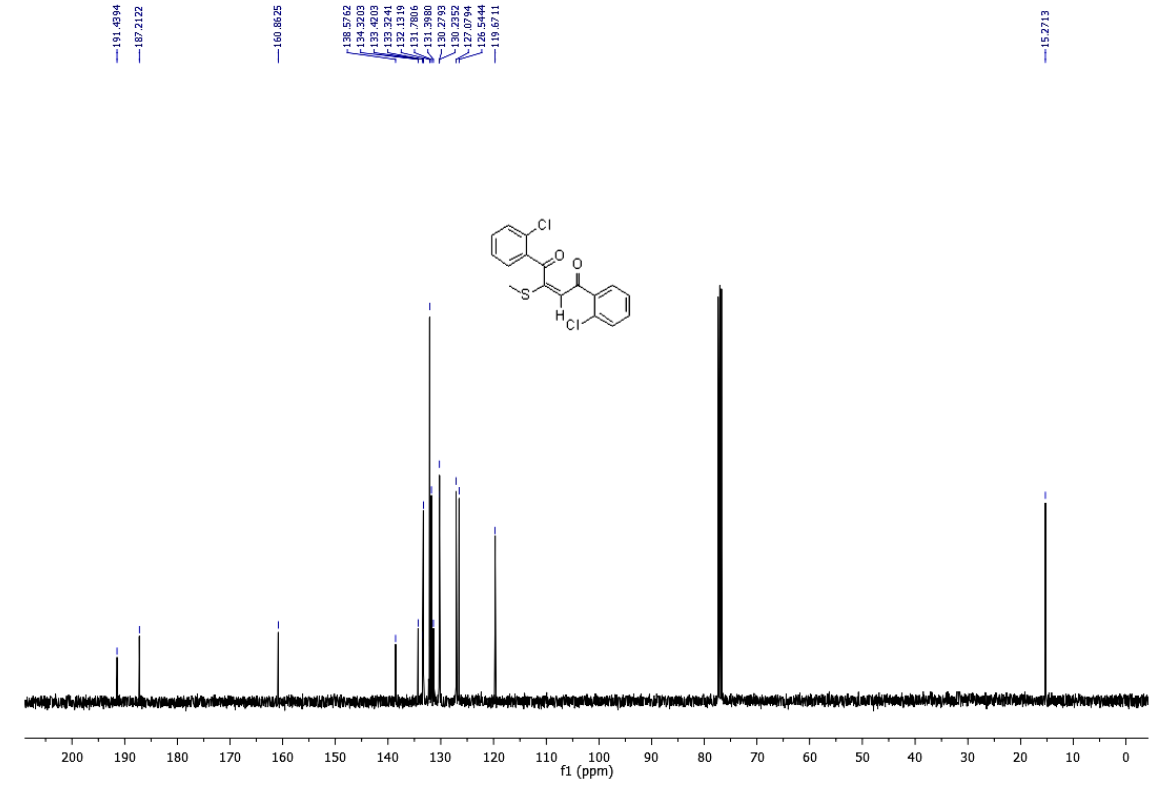


^{1}H and^{13}C-NMR of 2ag:

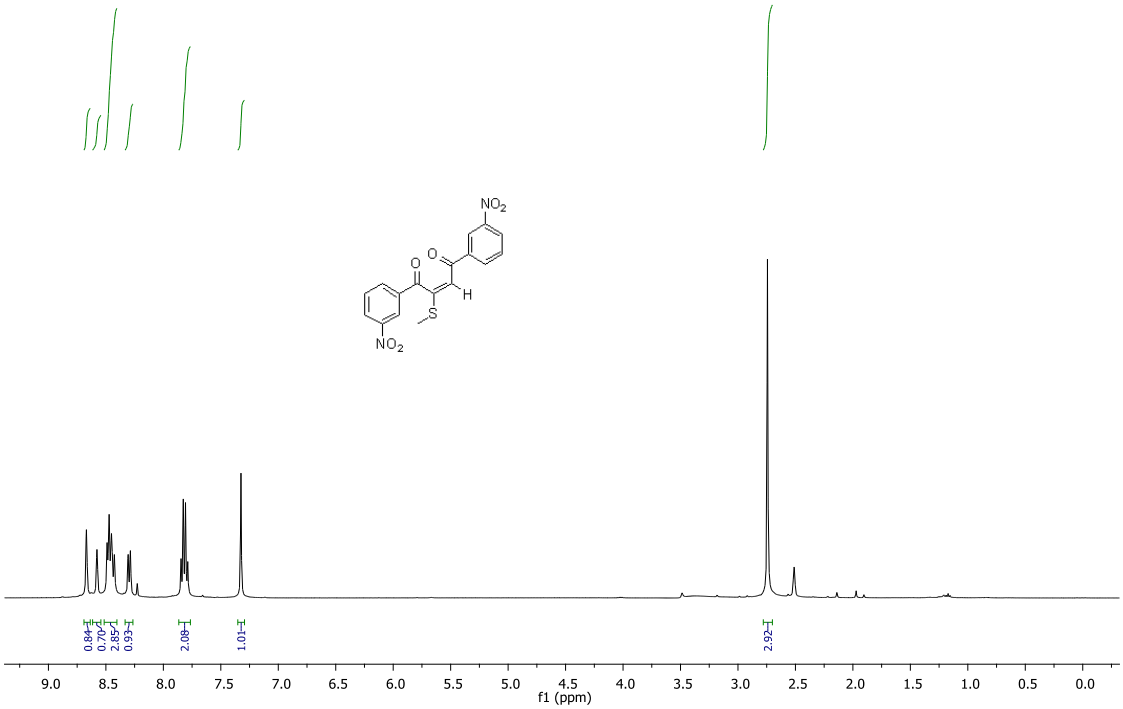


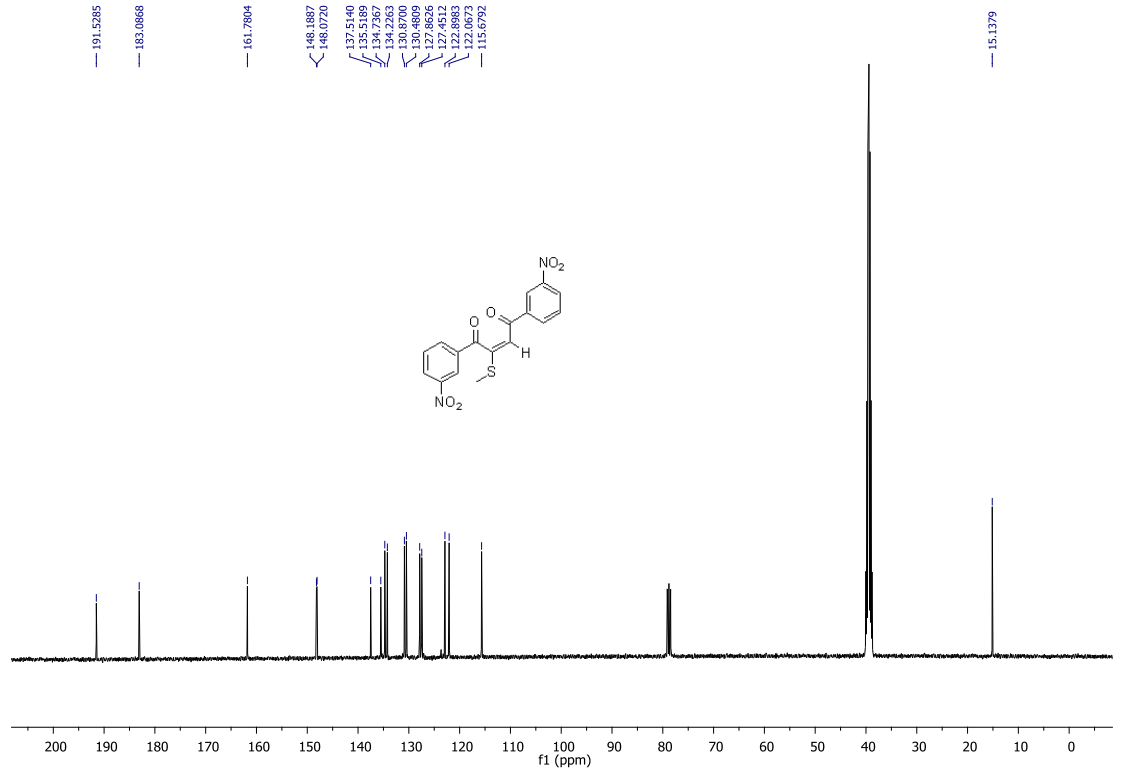
^{1}H and ^{13}C-NMR of 2ah



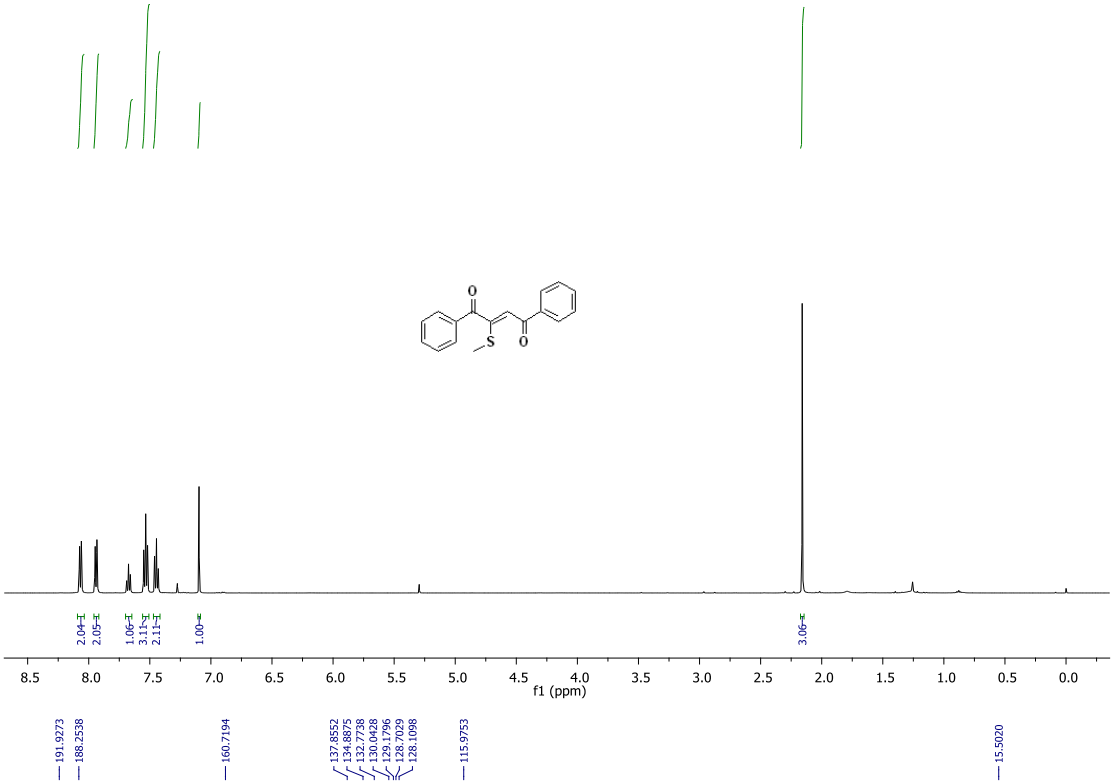


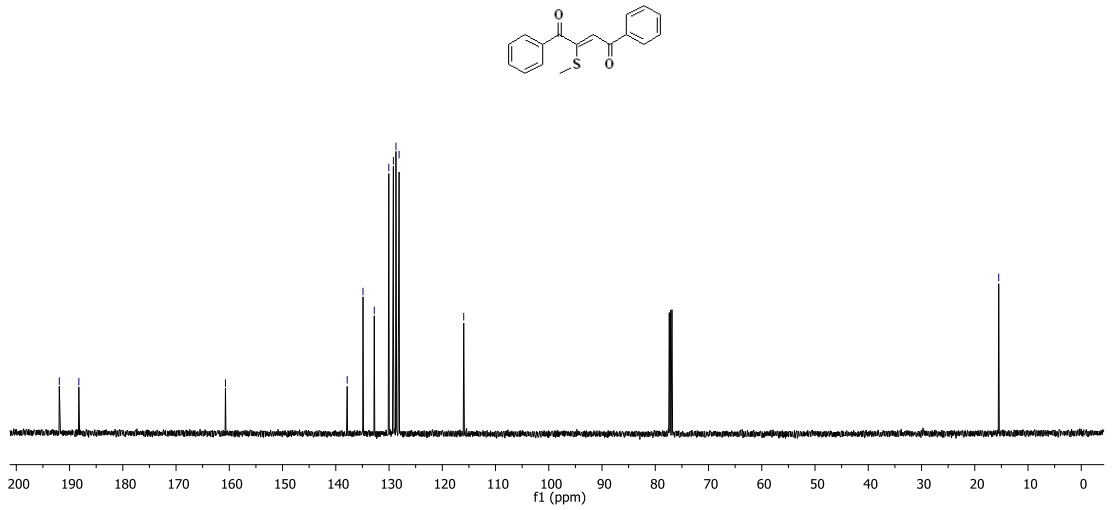
^{1}H and ^{13}C-NMR of 2ai



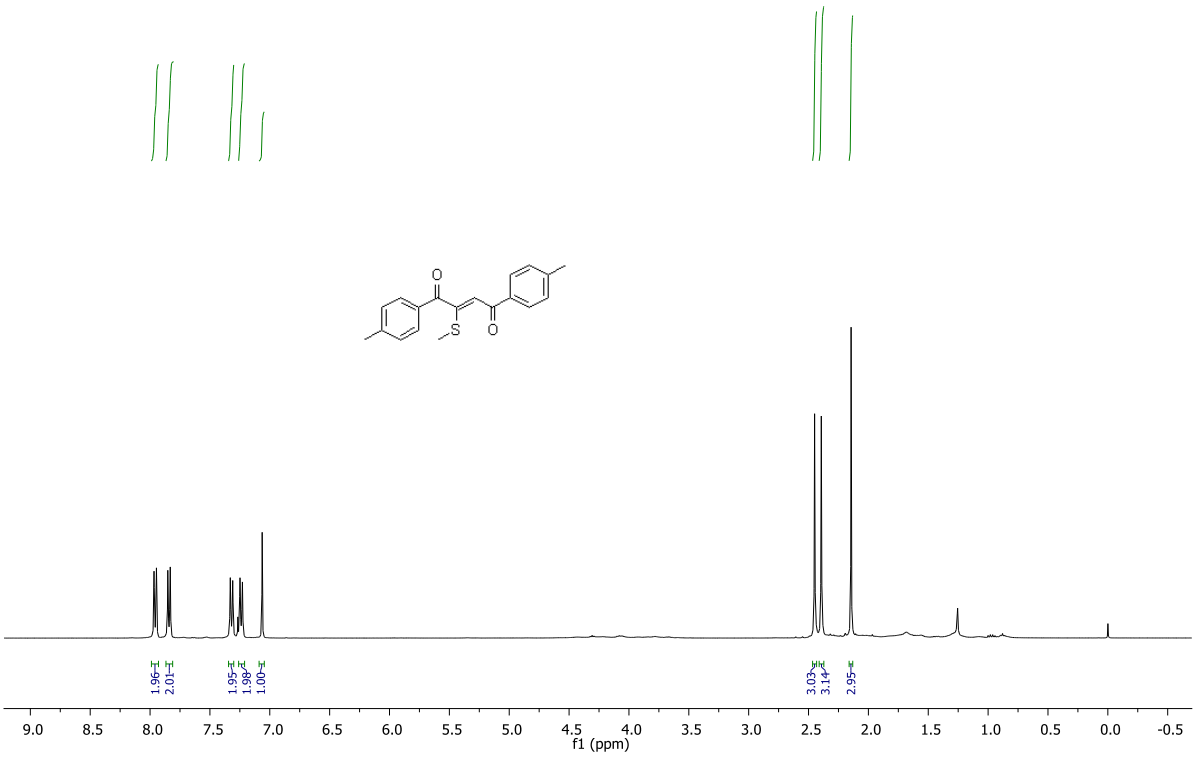


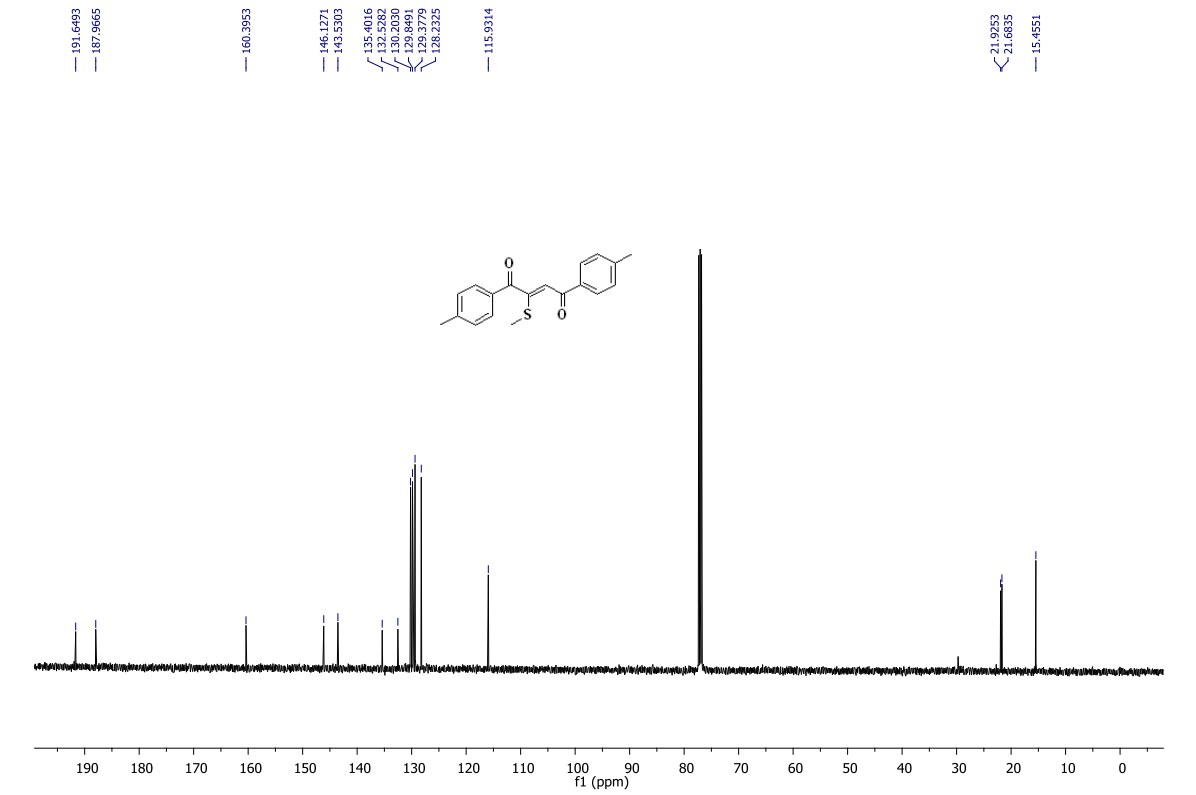
^{1}H and ^{13}C-NMR of 2ba:



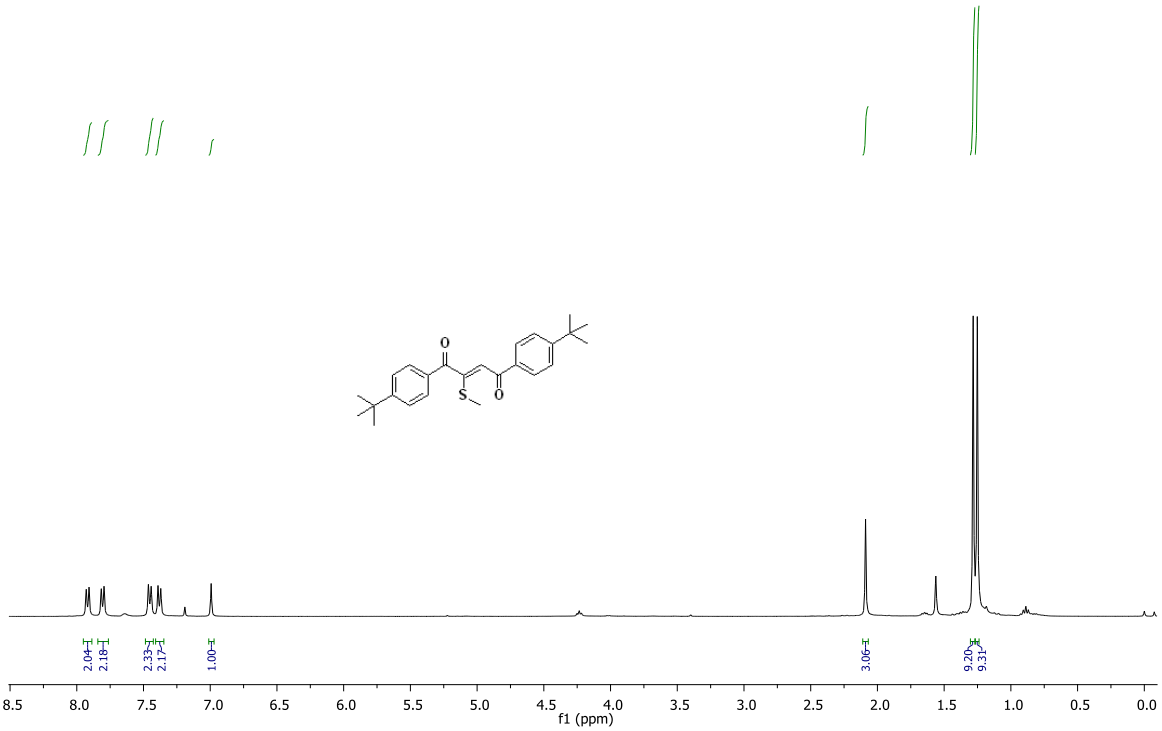


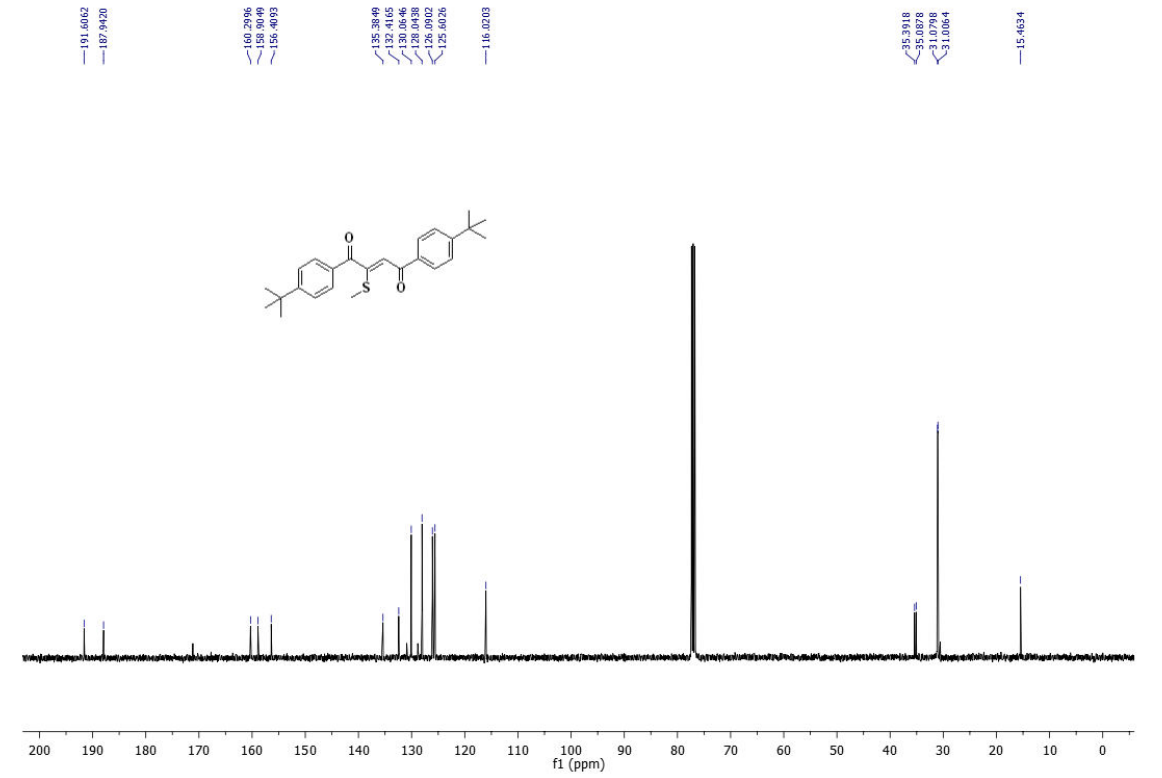
^{1}H and ^{13}C-NMR of 2bb:



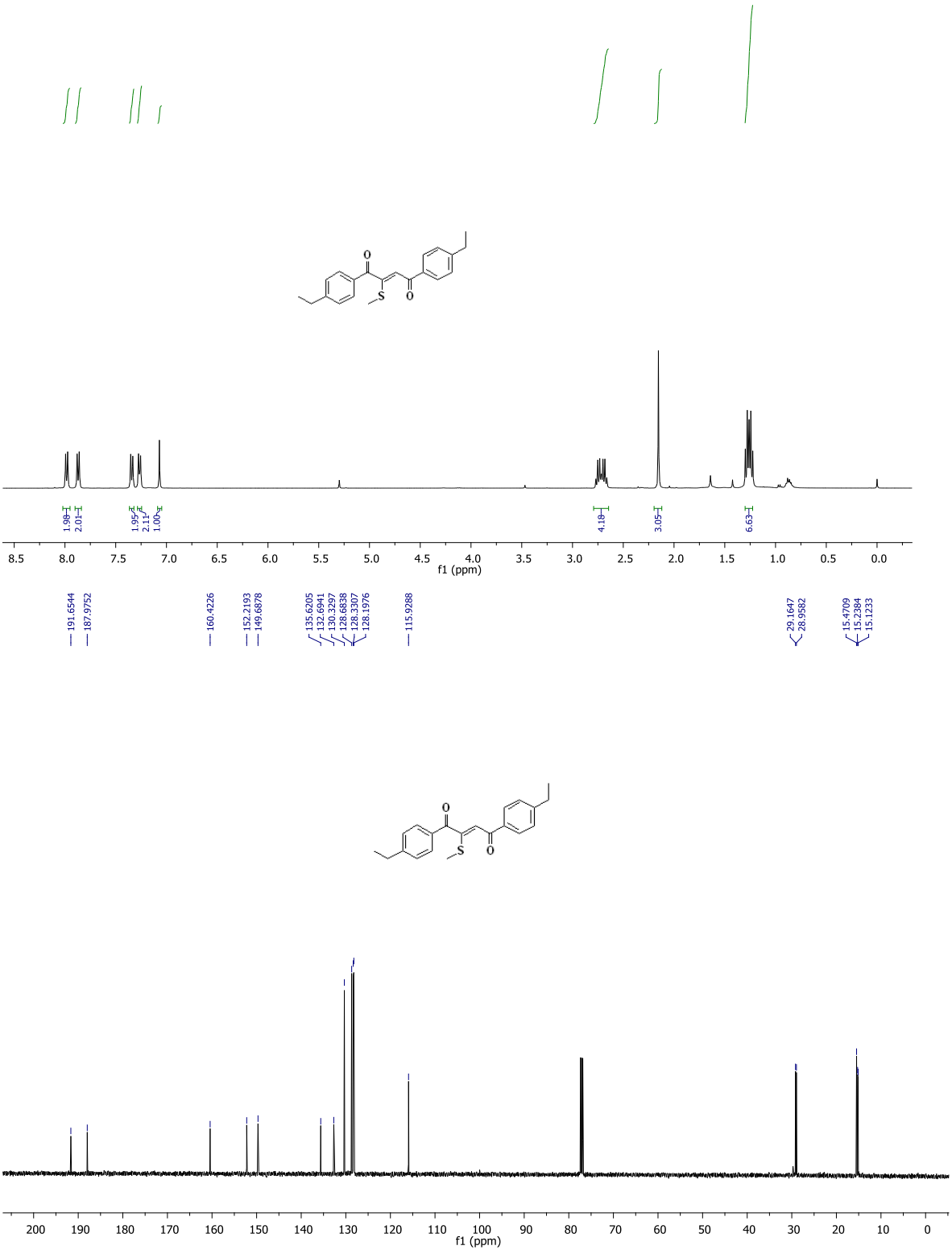


^{1}H and ^{13}C-NMR of 2bc:

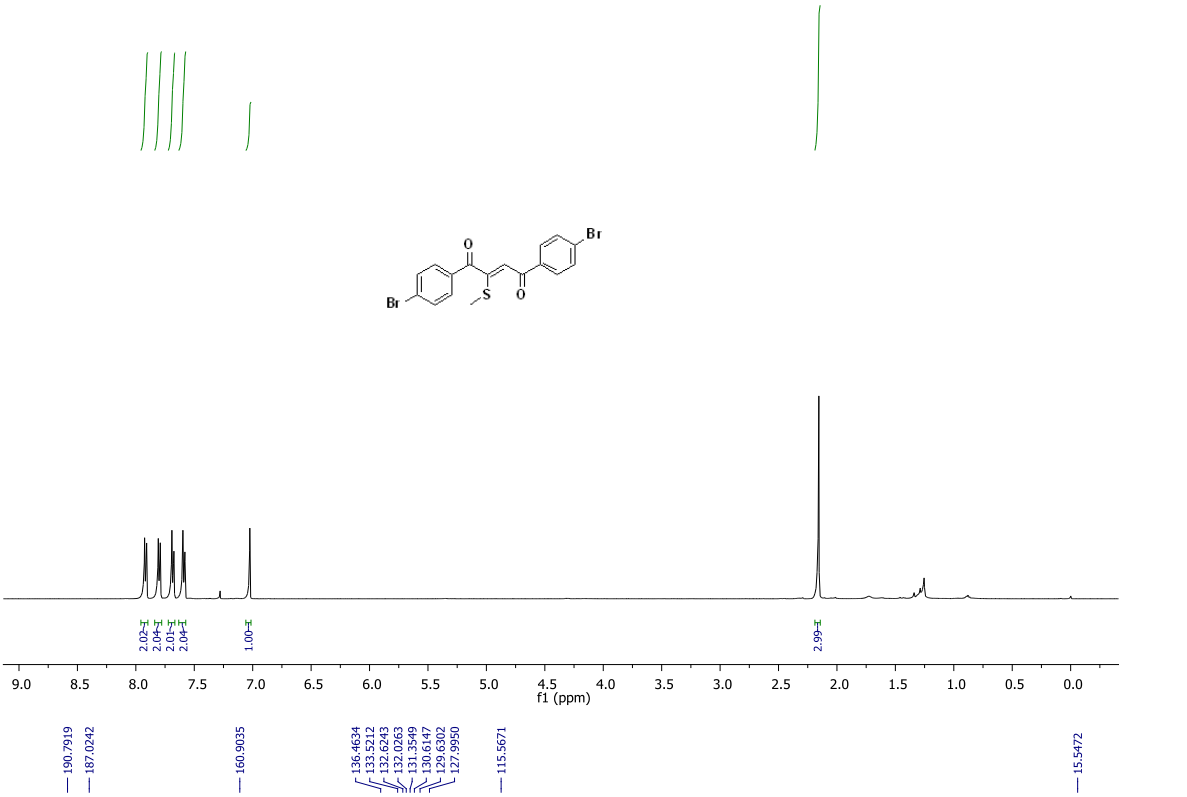


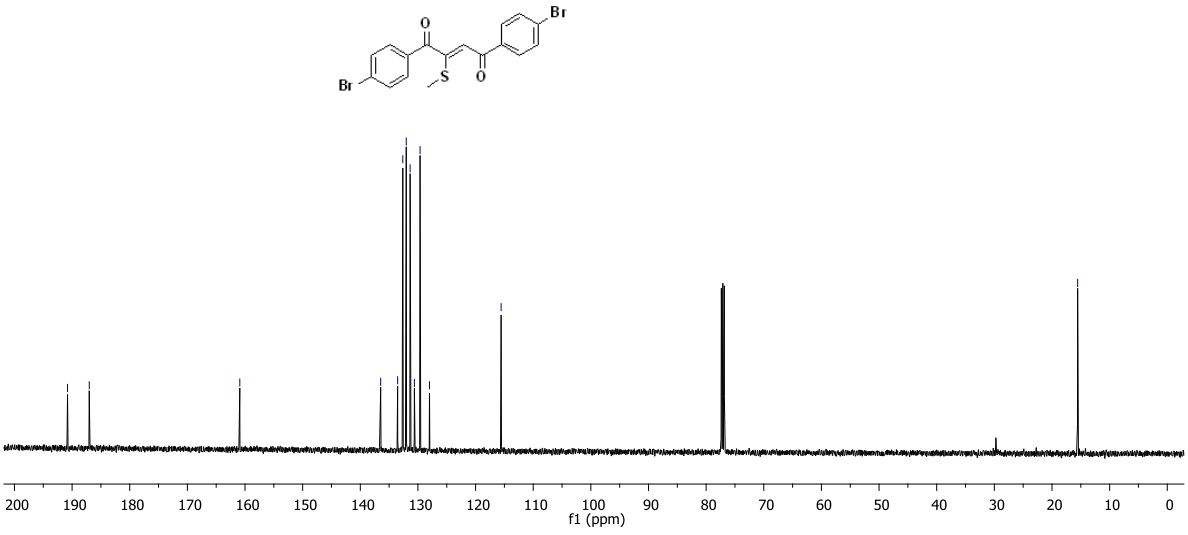


^{1}H and ^{13}C-NMR of 2bd:

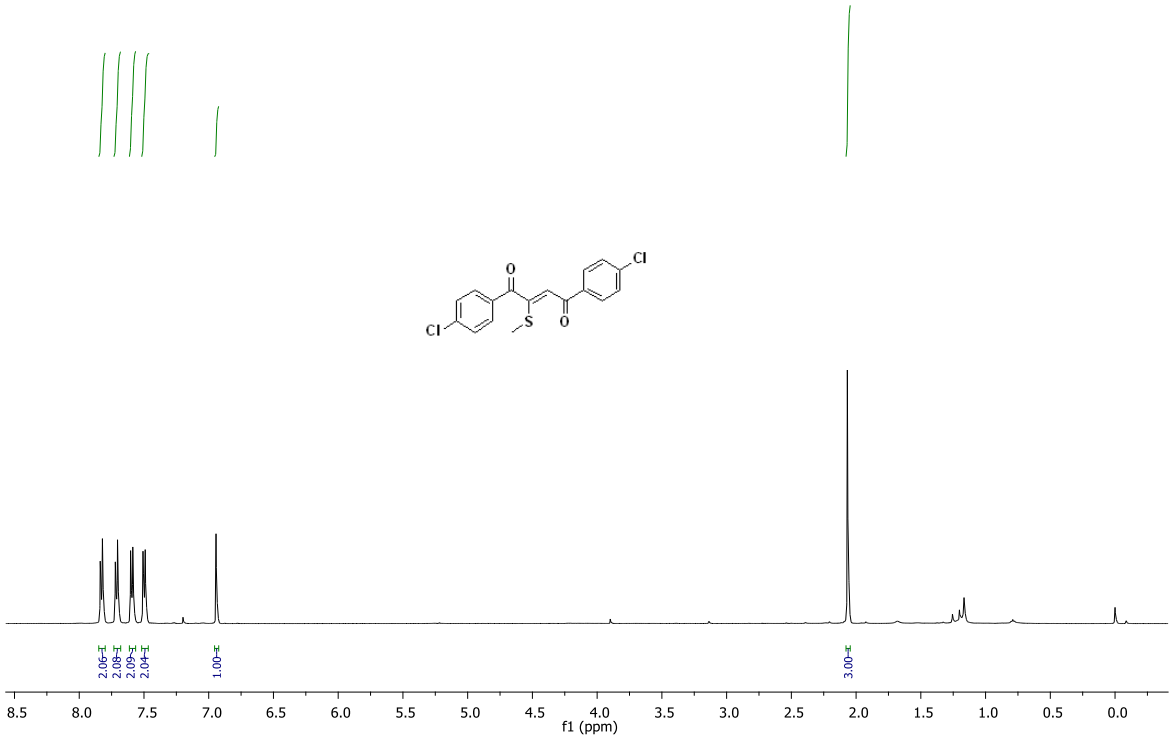


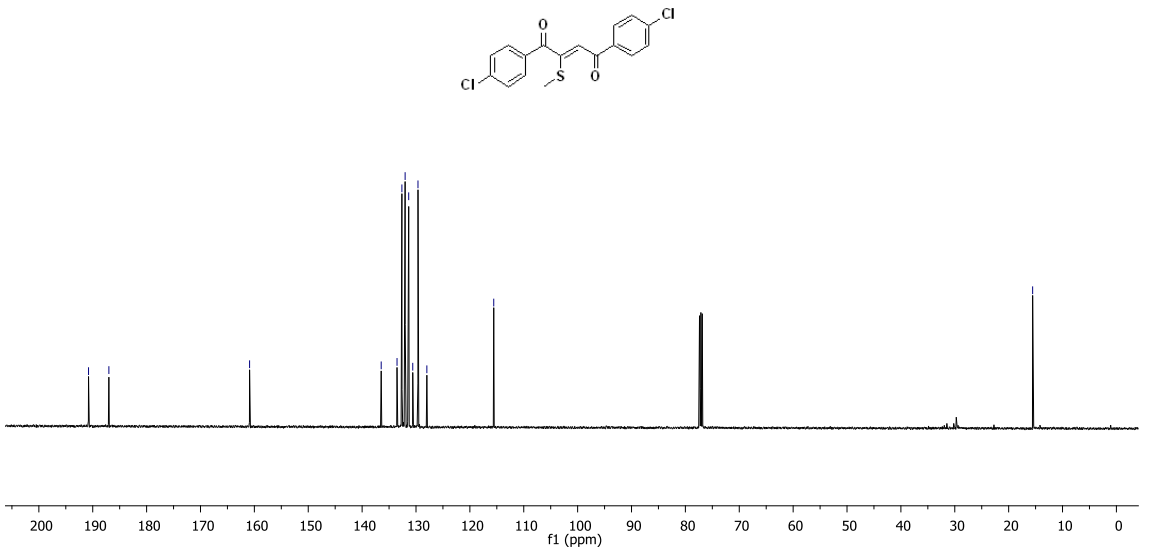
^{1}H and ^{13}C-NMR of 2be:



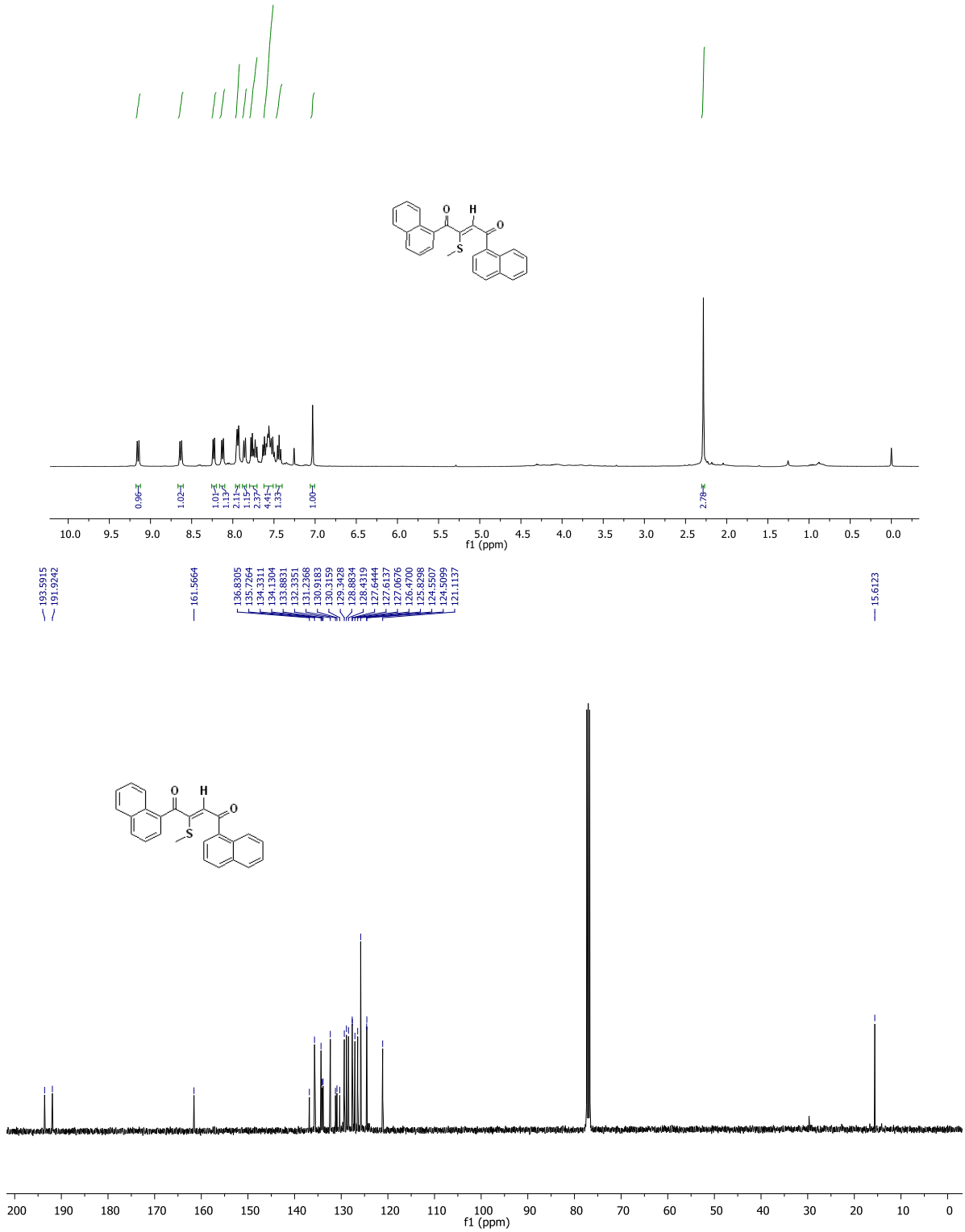


^{1}H and ^{13}C-NMR of 2bf:

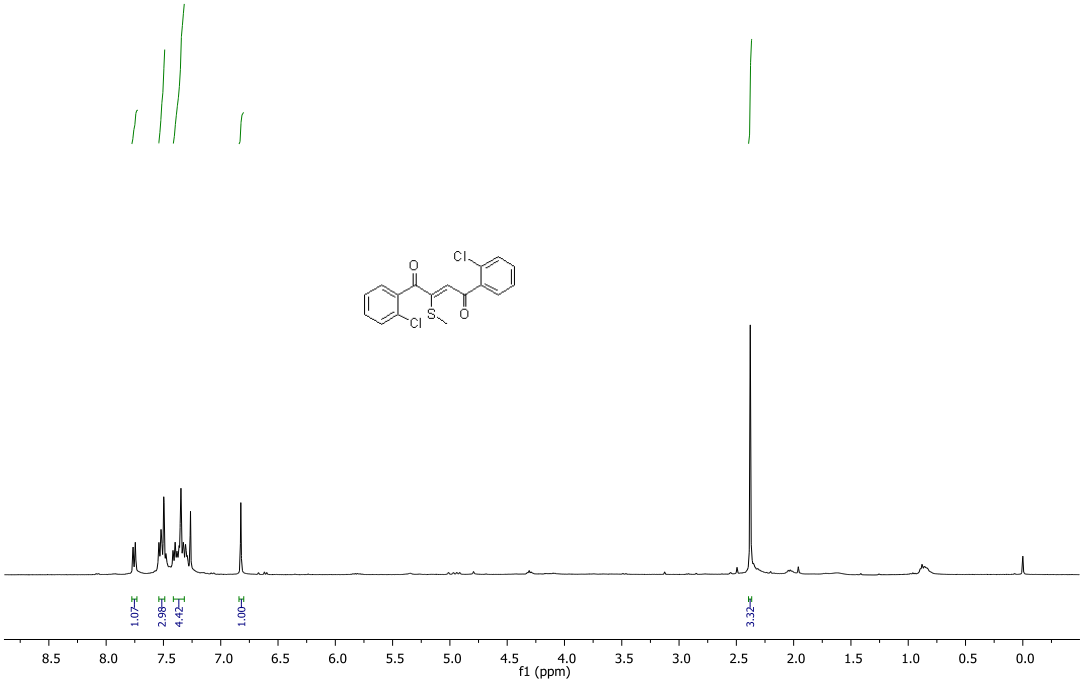


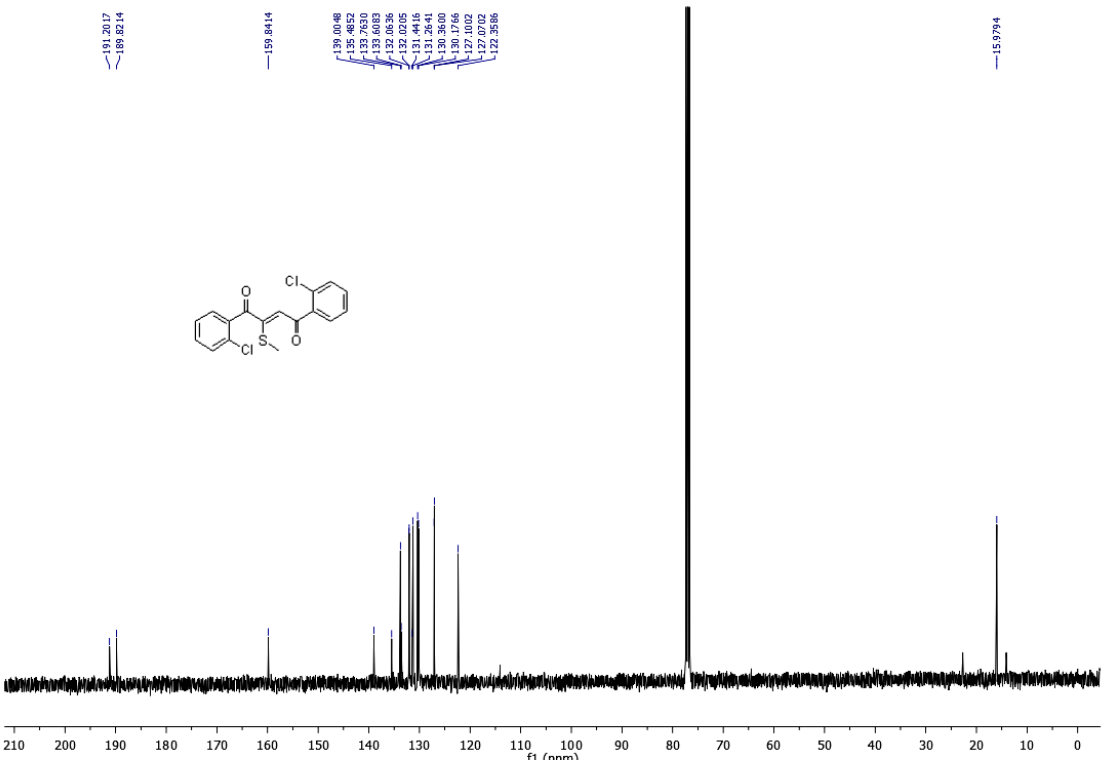


^{1}H and ^{13}C-NMR of 2bg:

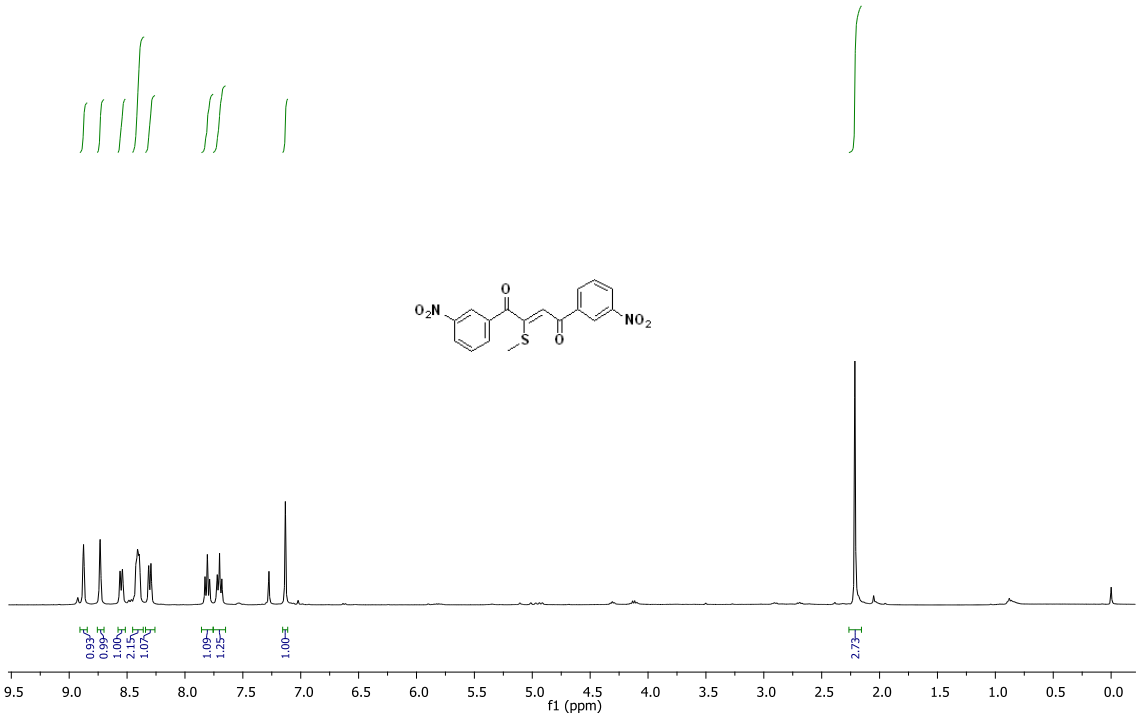


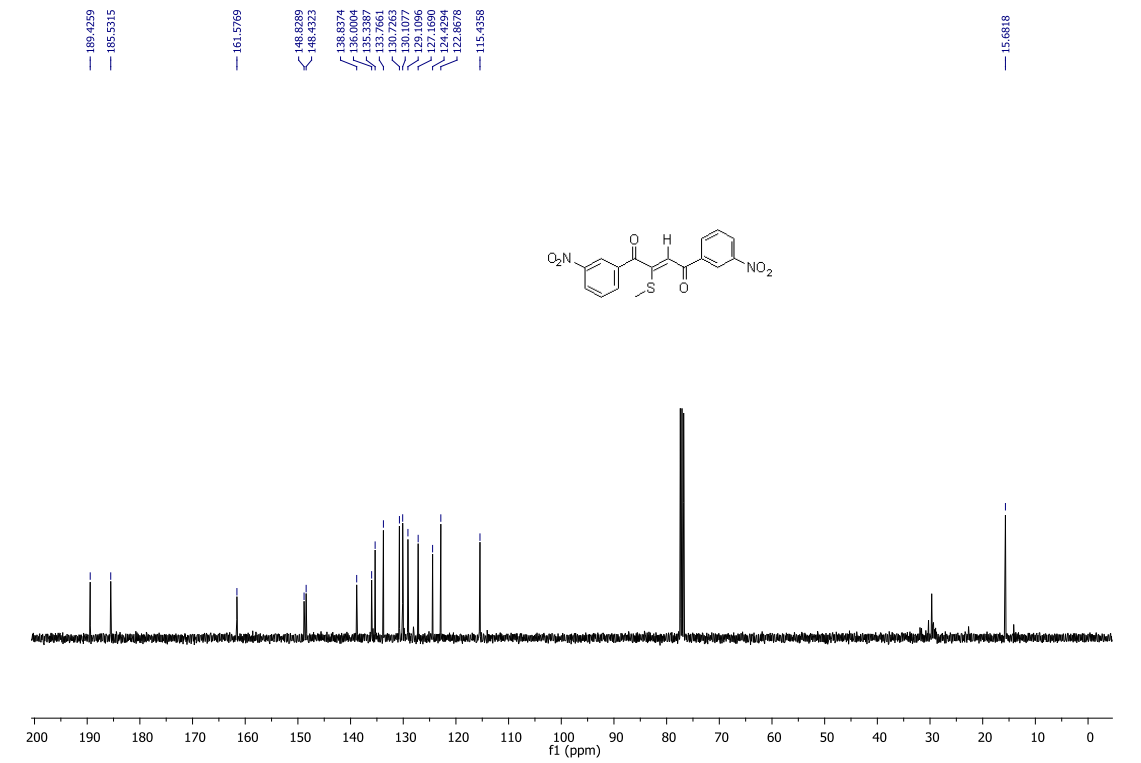
^{1}H and ^{13}C-NMR of 2bh



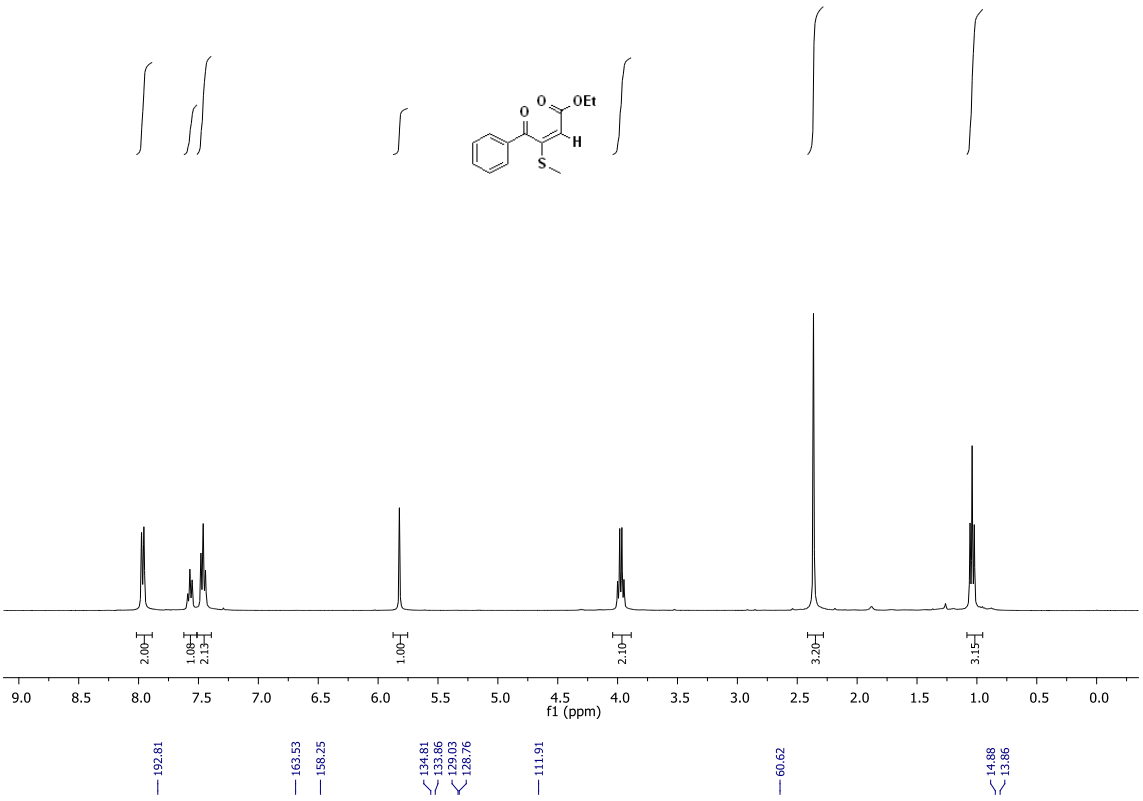


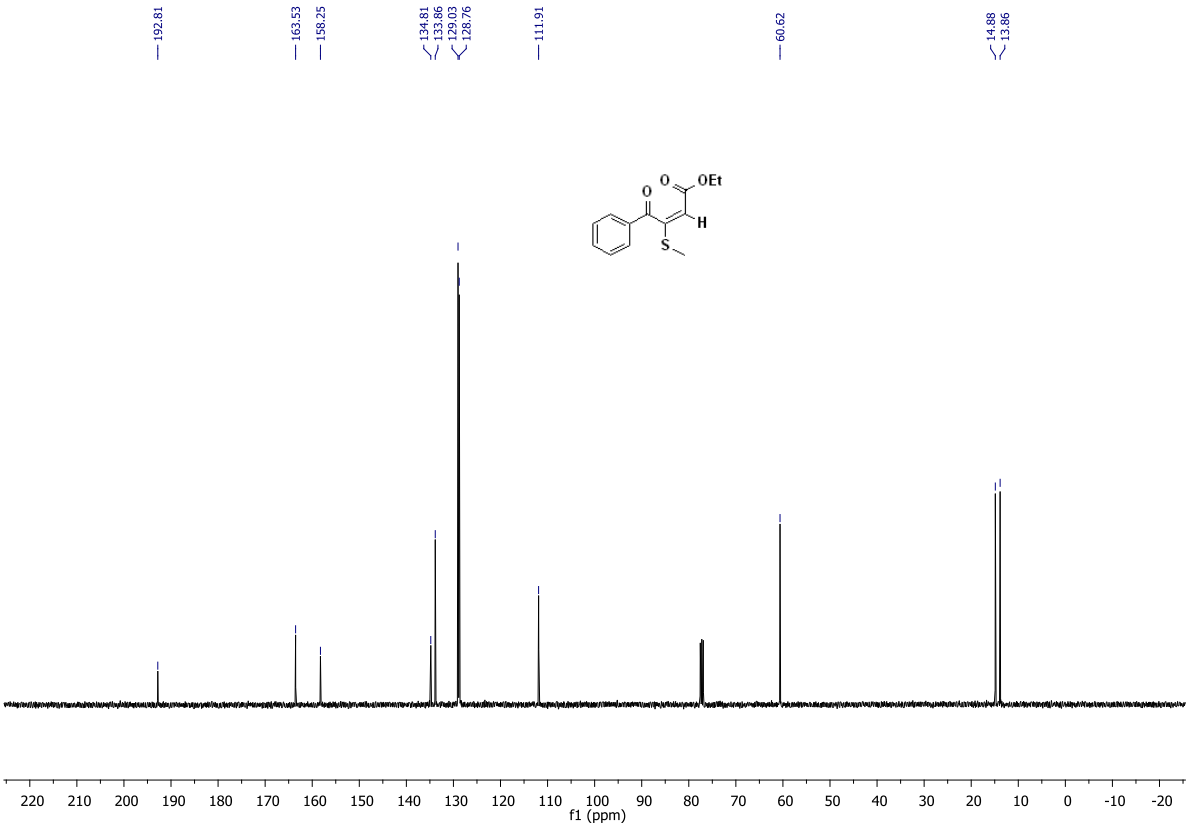
^{1}H and ^{13}C-NMR of 2bi



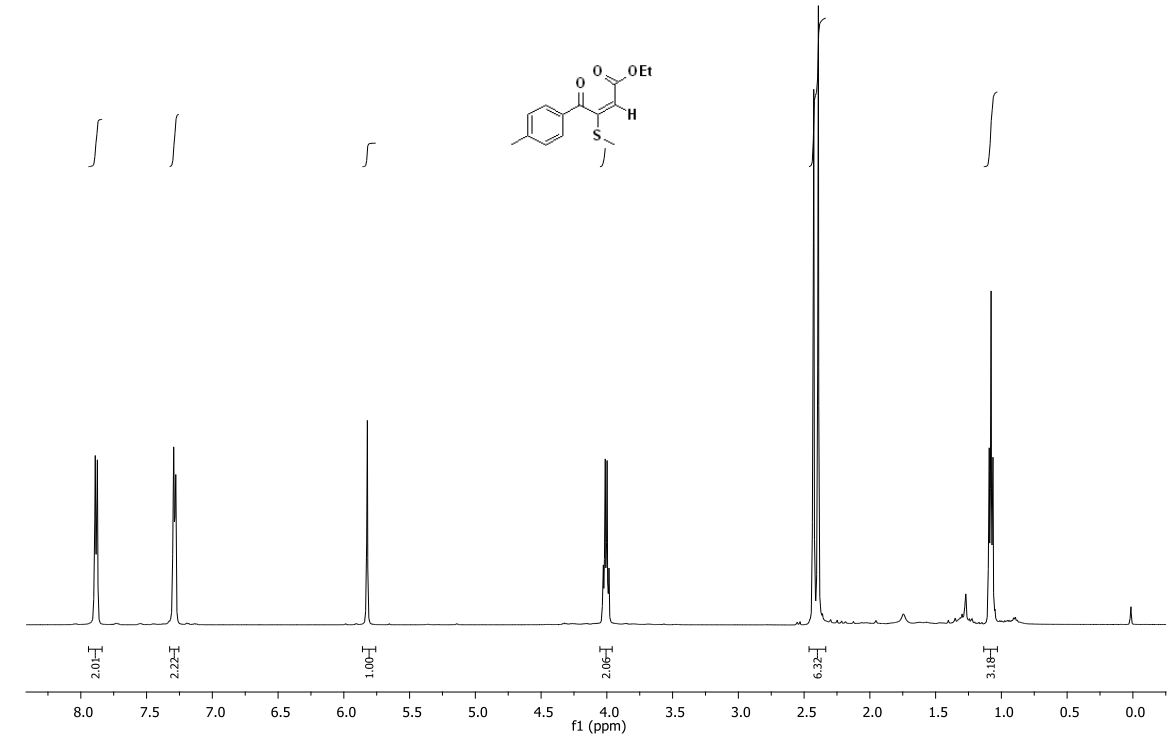


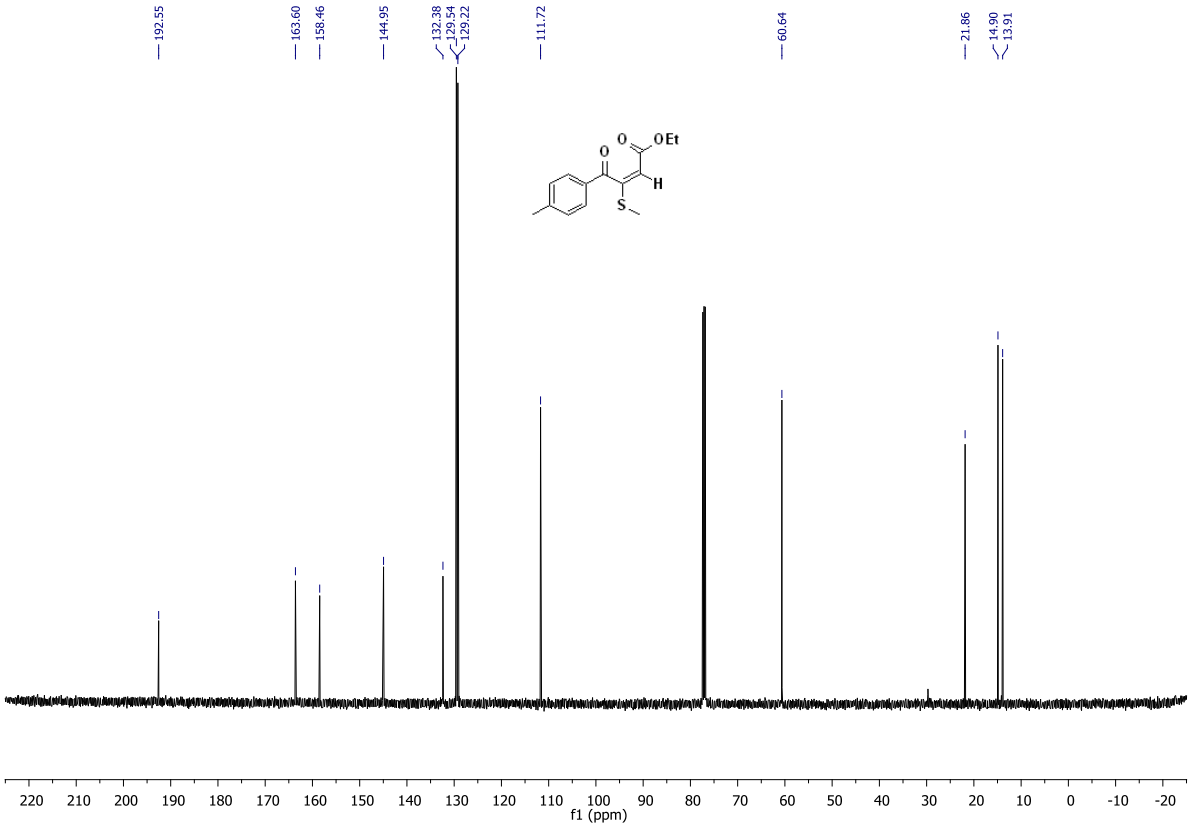
^{1}H and ^{13}C-NMR spectra of 4aa:



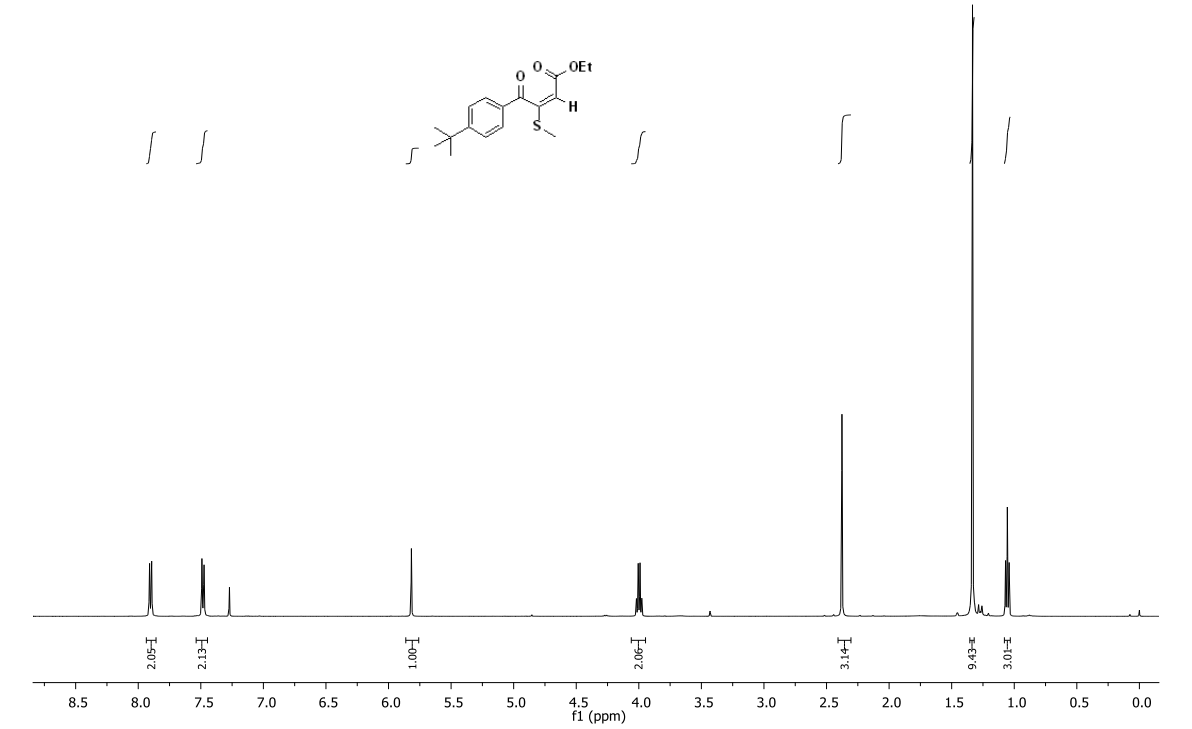


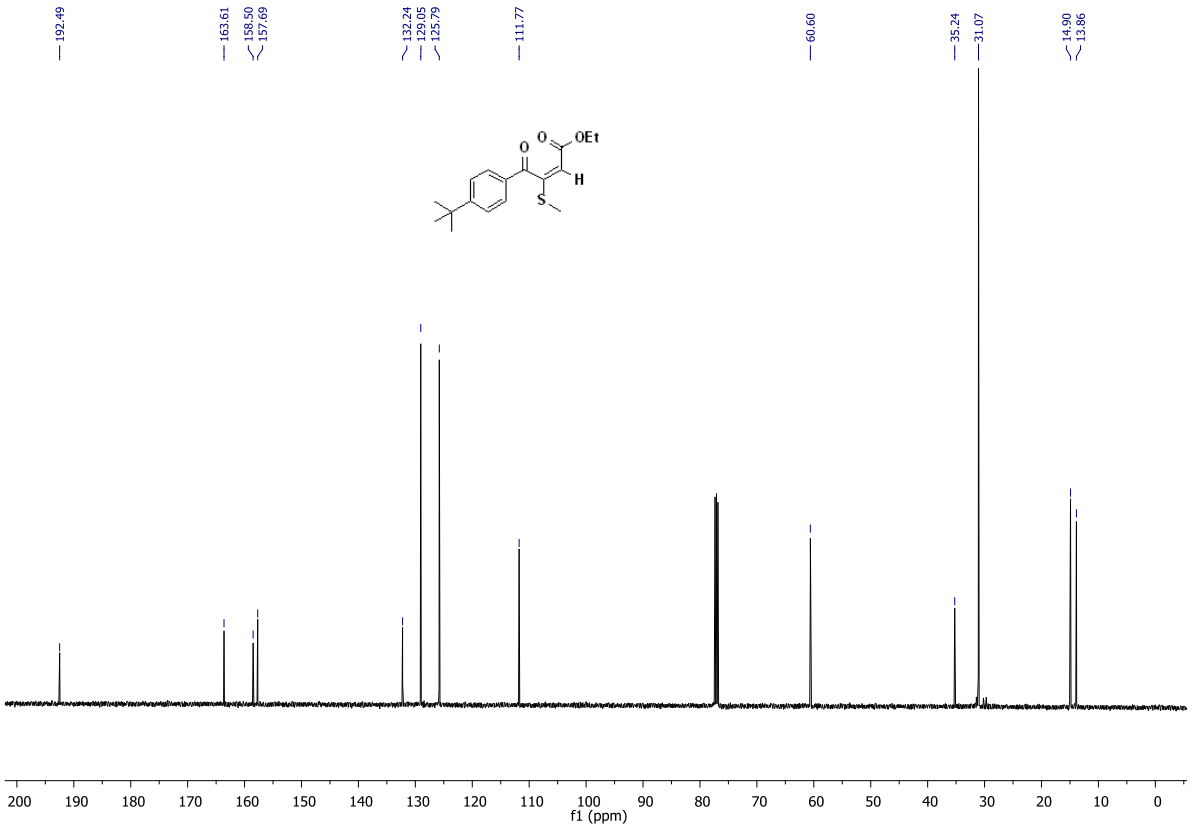
^{1}H and ^{13}C-NMR spectra of 4ab:



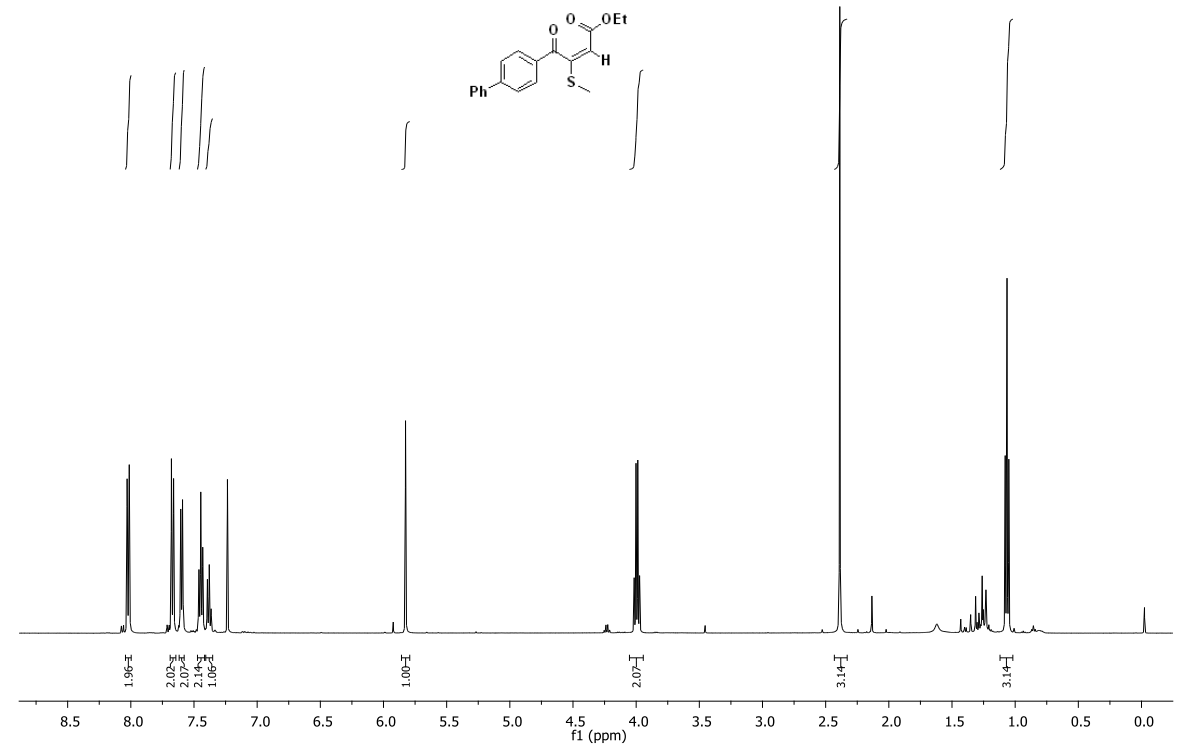


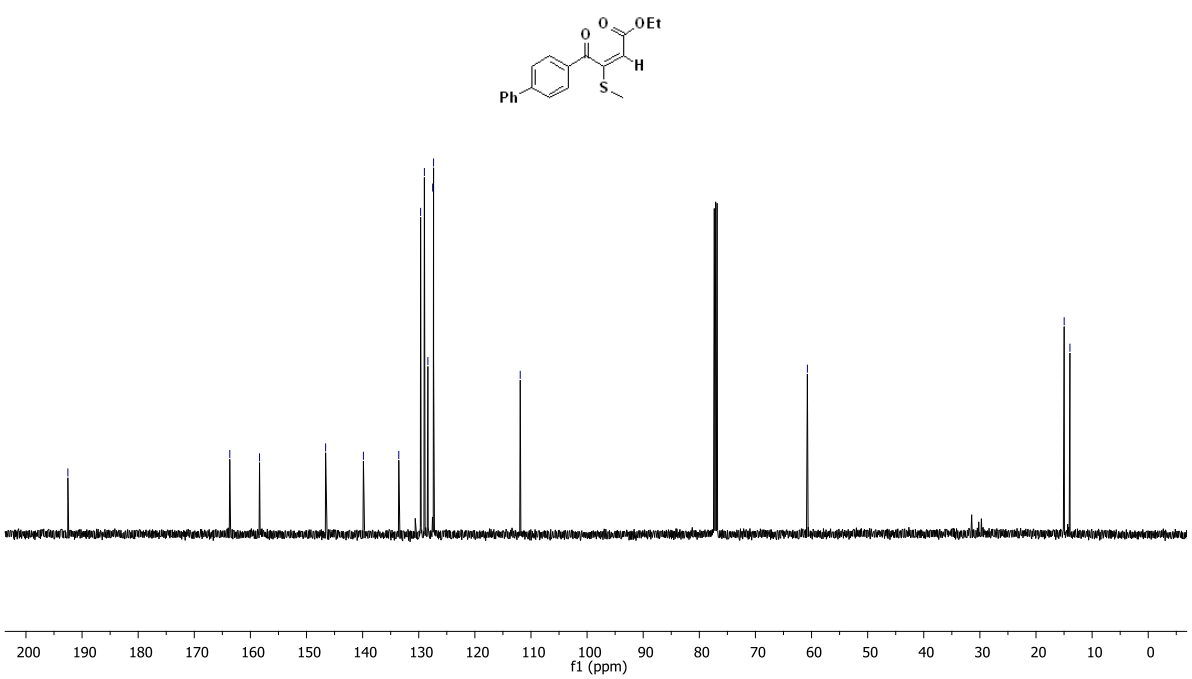
^{1}H and ^{13}C-NMR spectra of 4ac:



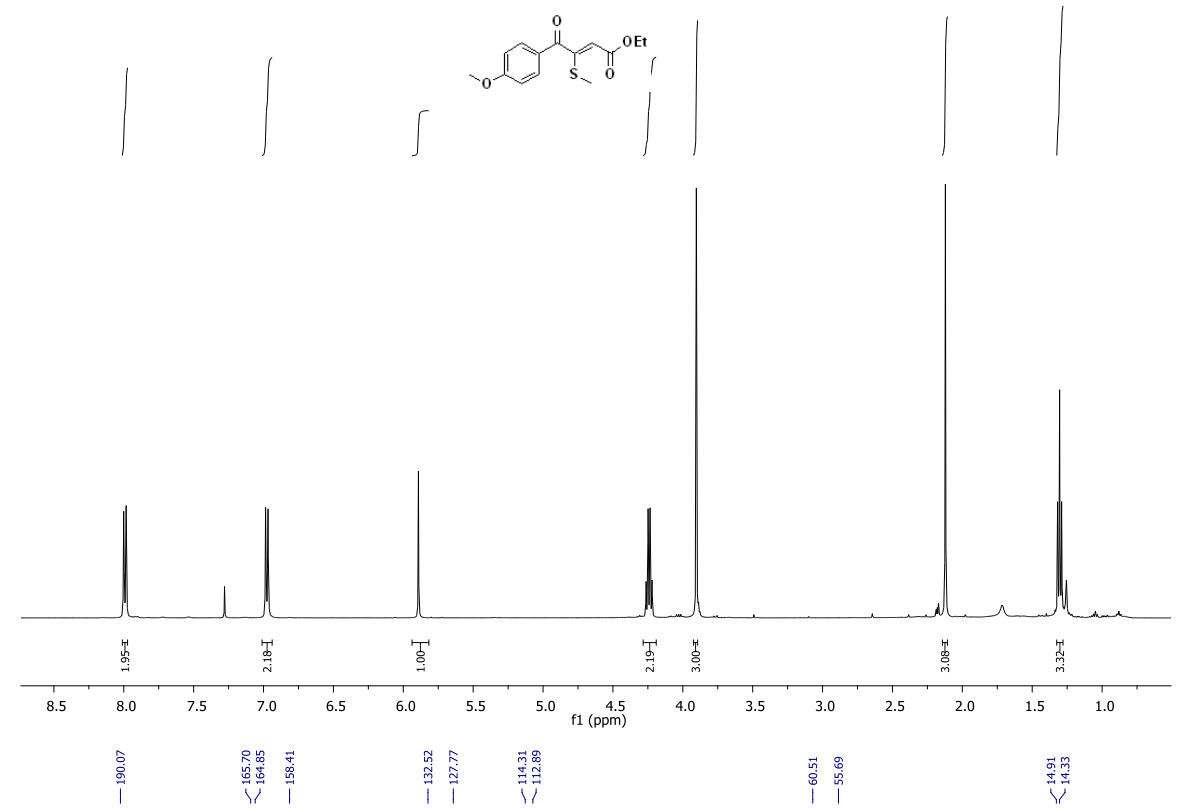


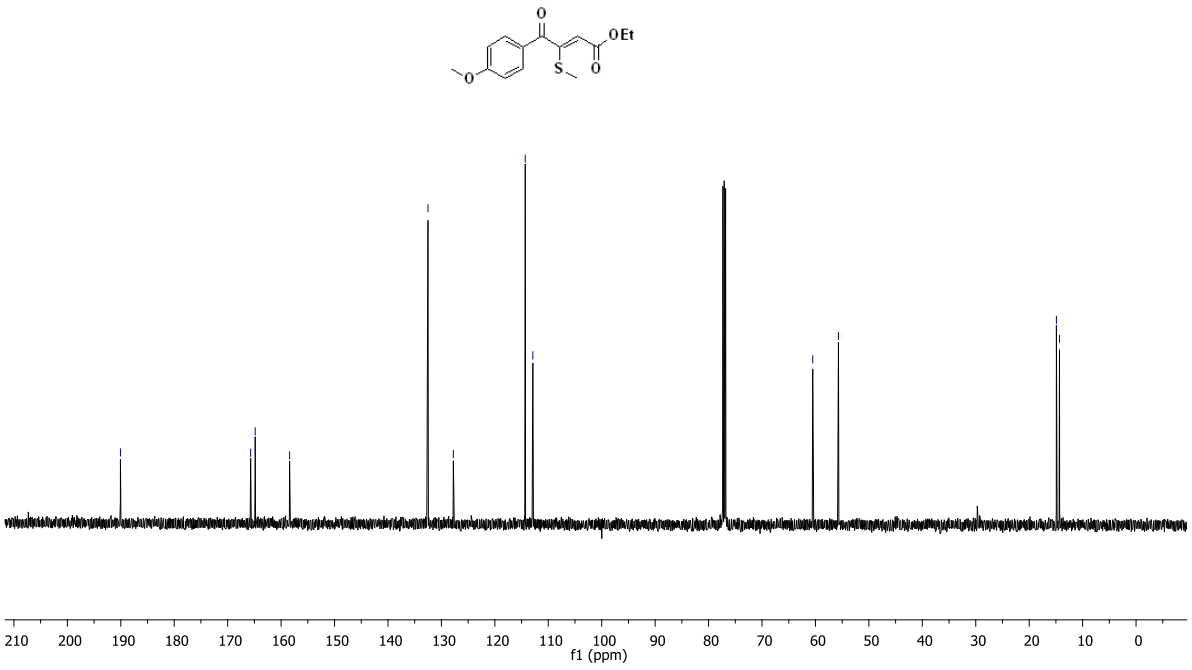
^{1}H and ^{13}C-NMR spectra of 4ad:



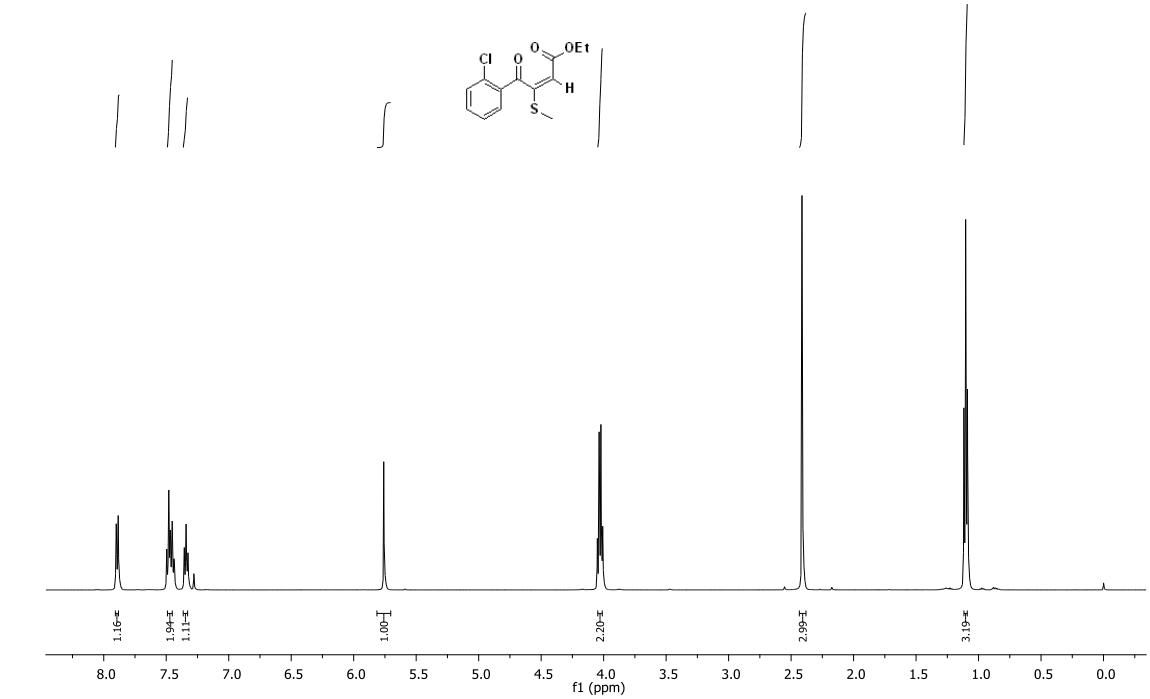


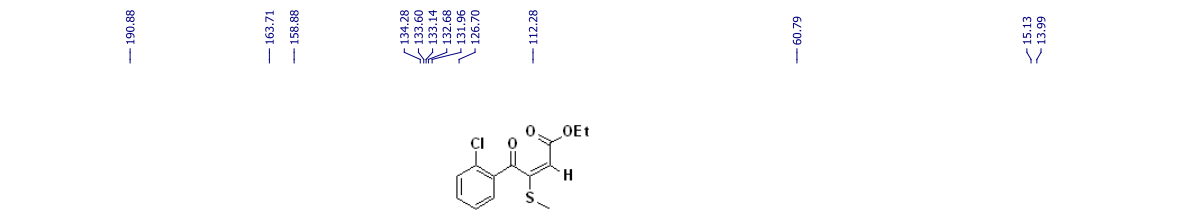
^{1}H and ^{13}C-NMR spectra of 4ae:

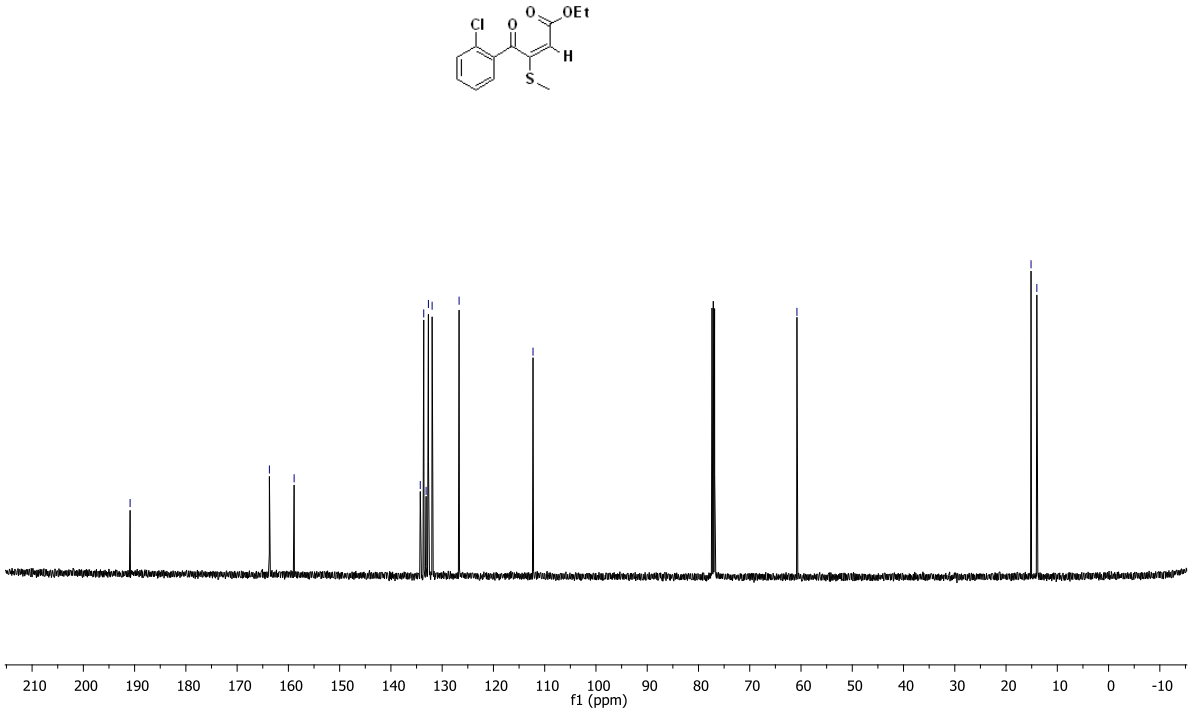




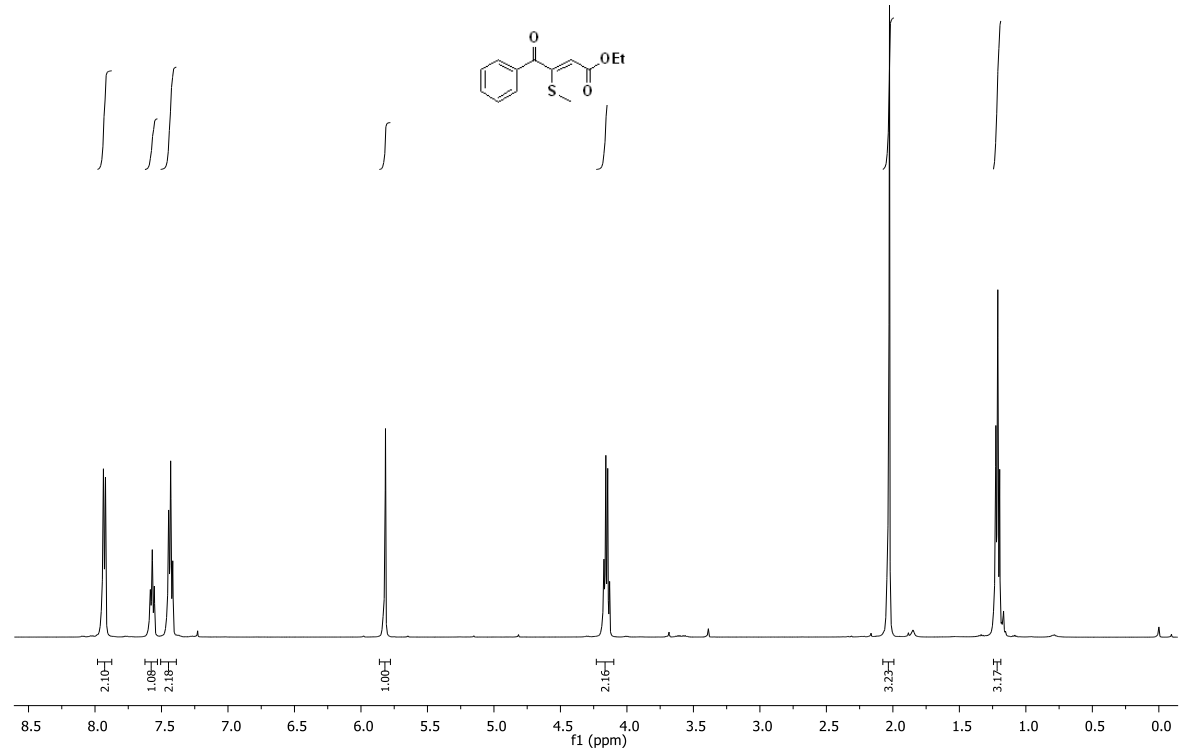
^{1}H and ^{13}C-NMR spectra of 4af:

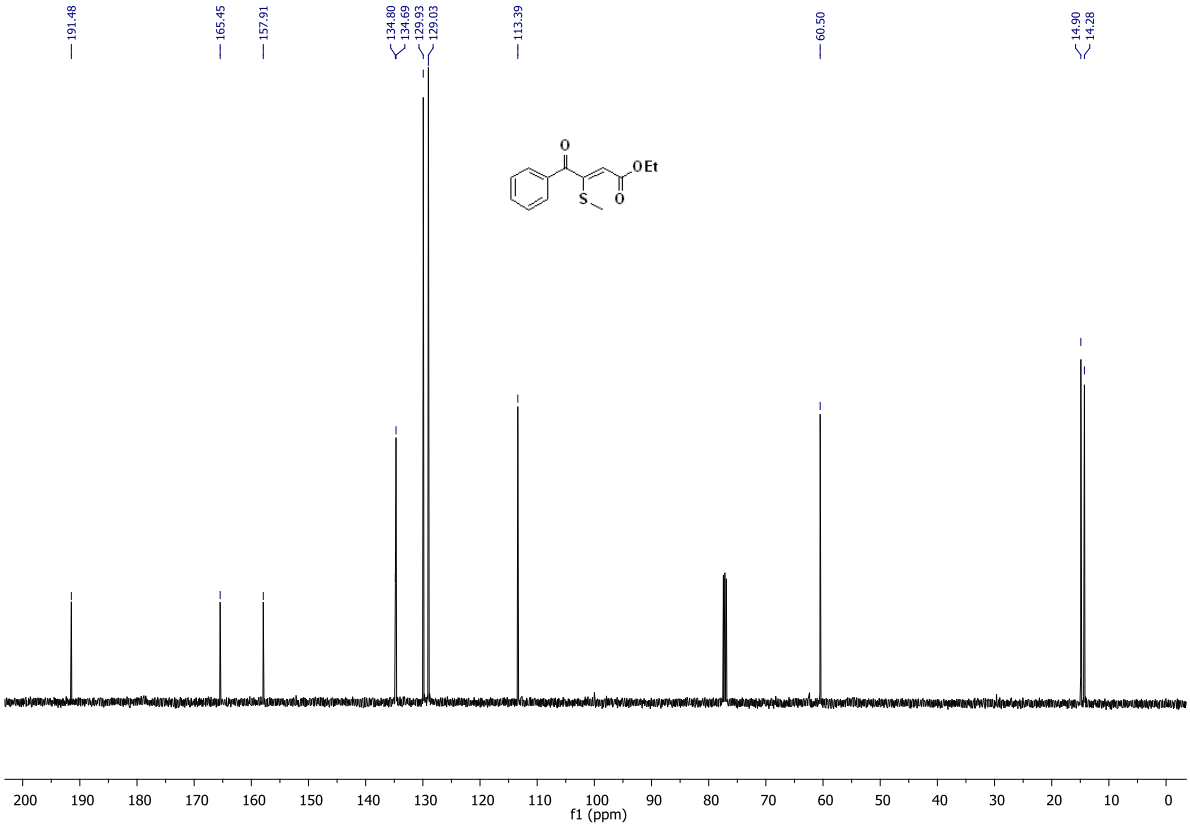




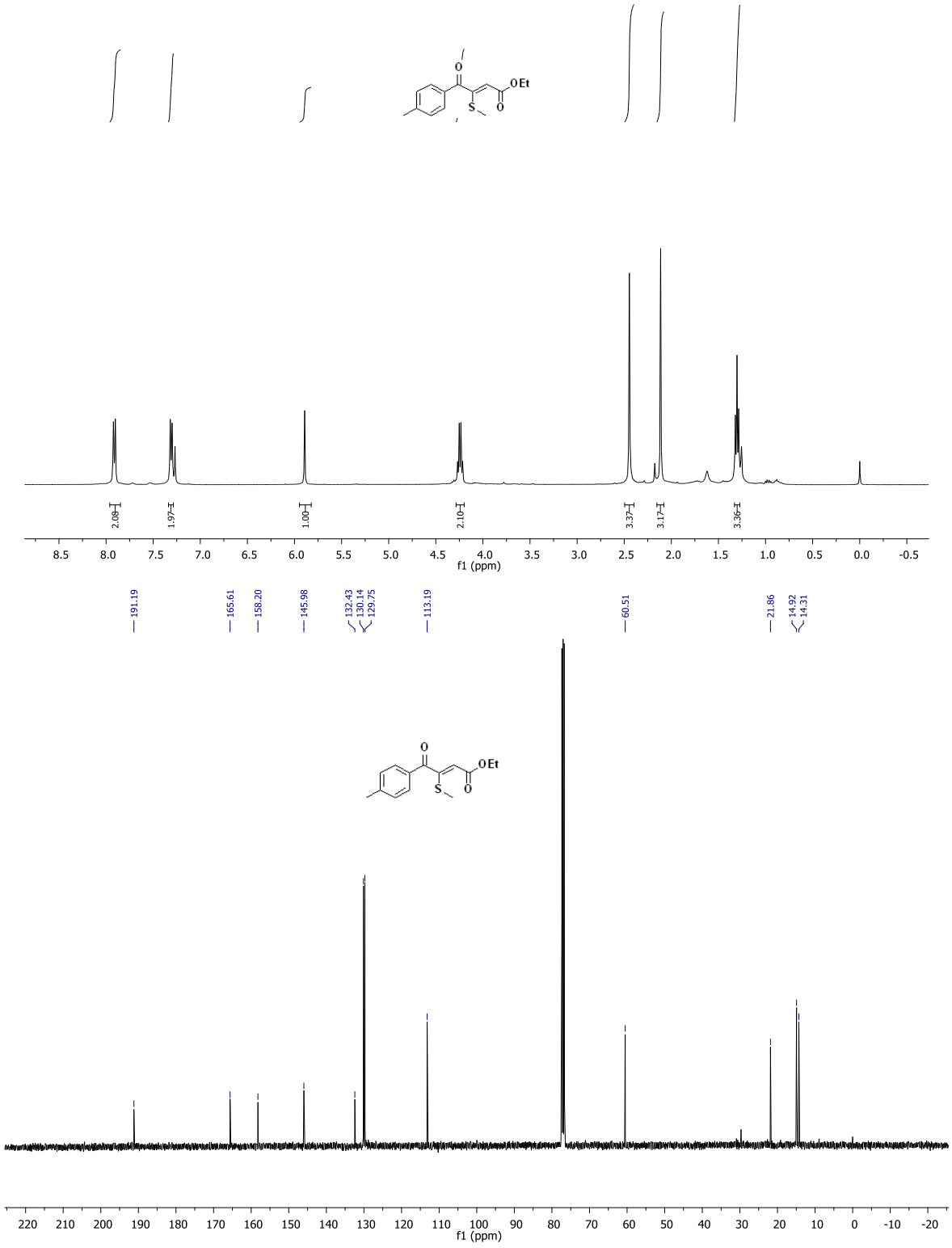


^{1}H and ^{13}C-NMR spectra of 4ba:

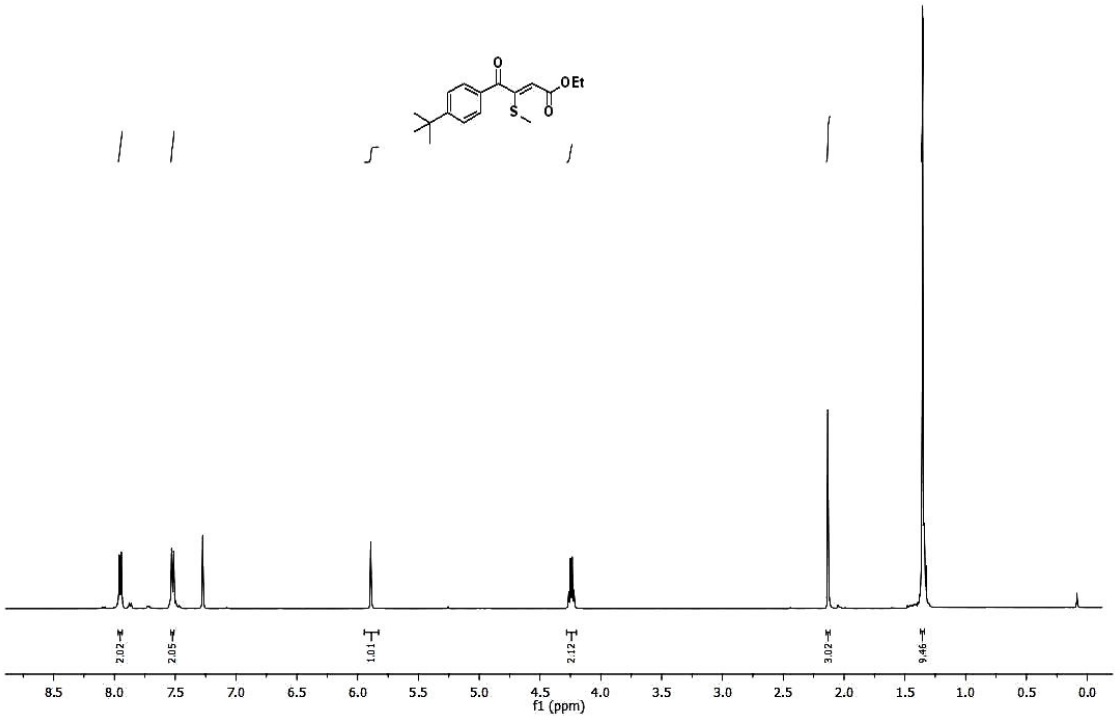


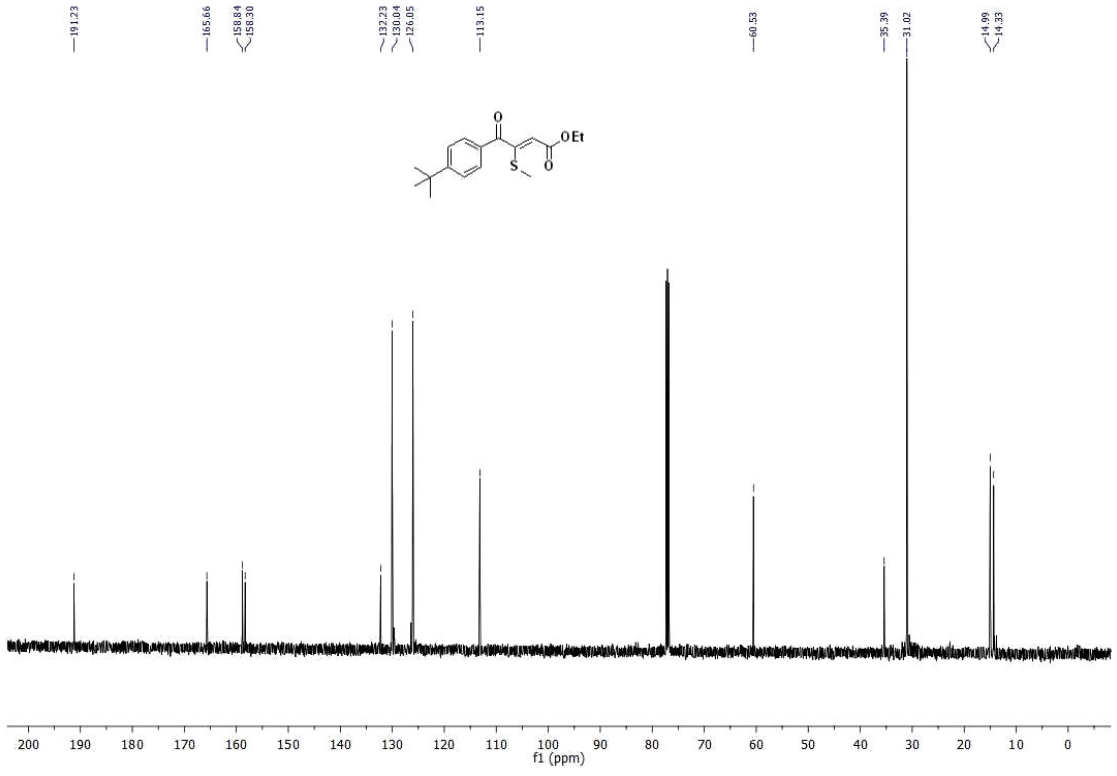


^{1}H and ^{13}C-NMR spectra of 4bb:

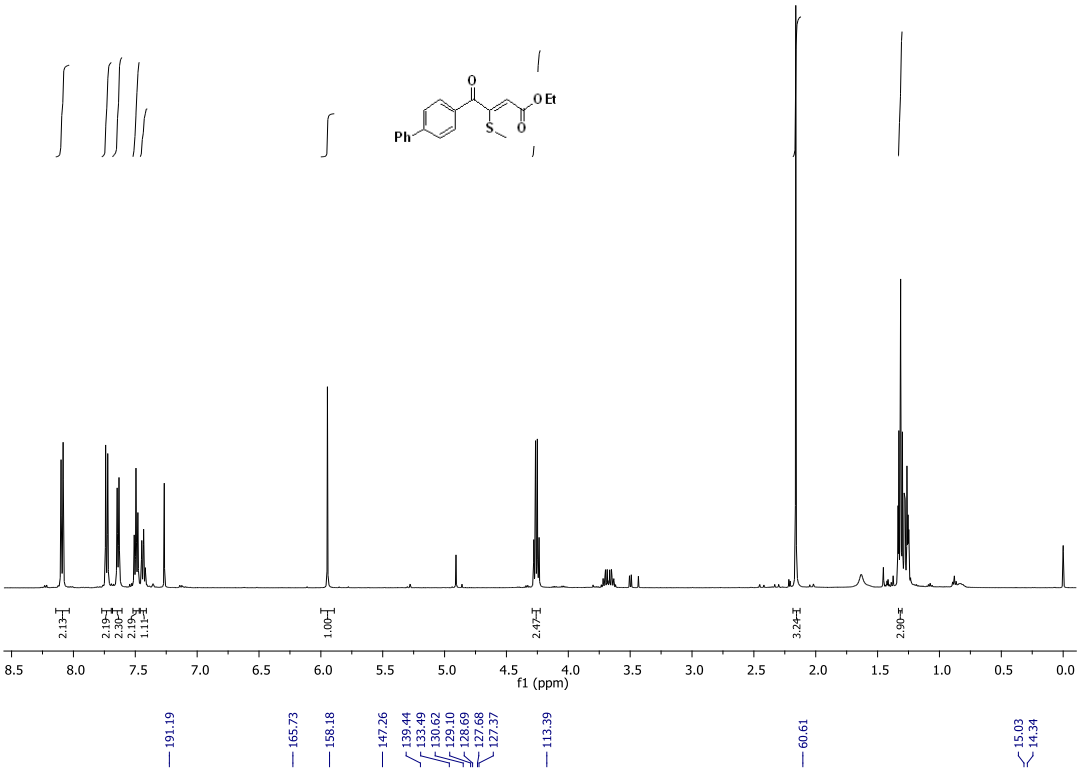


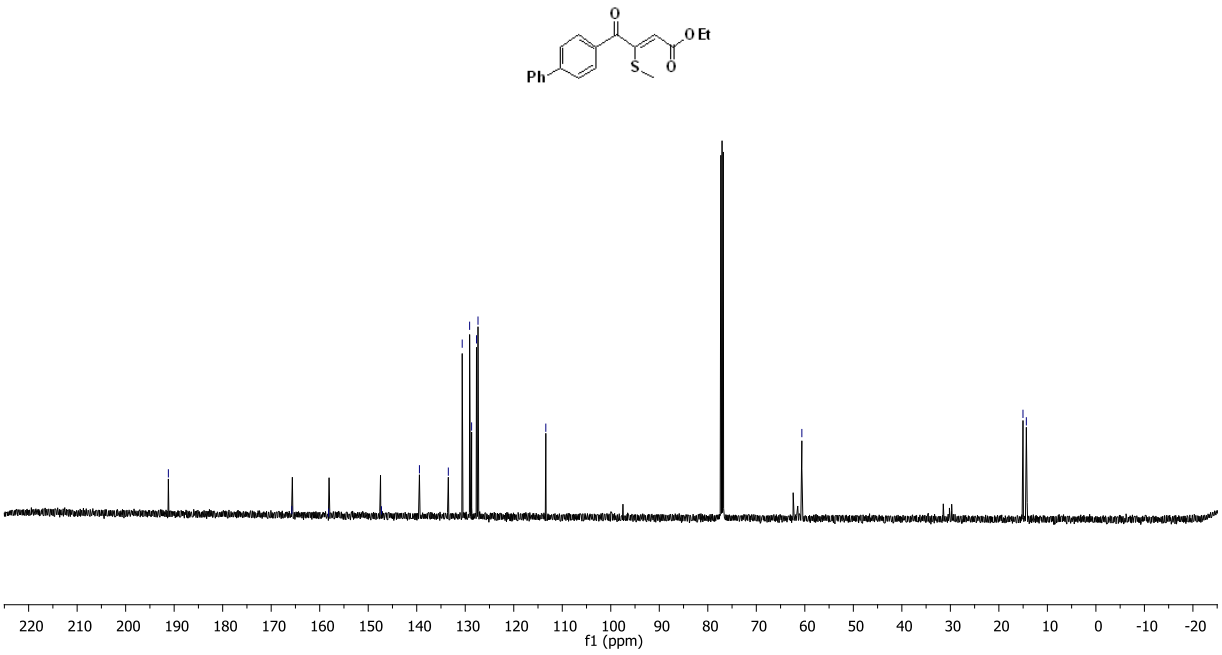
^{1}H and ^{13}C-NMR spectra of 4bc:



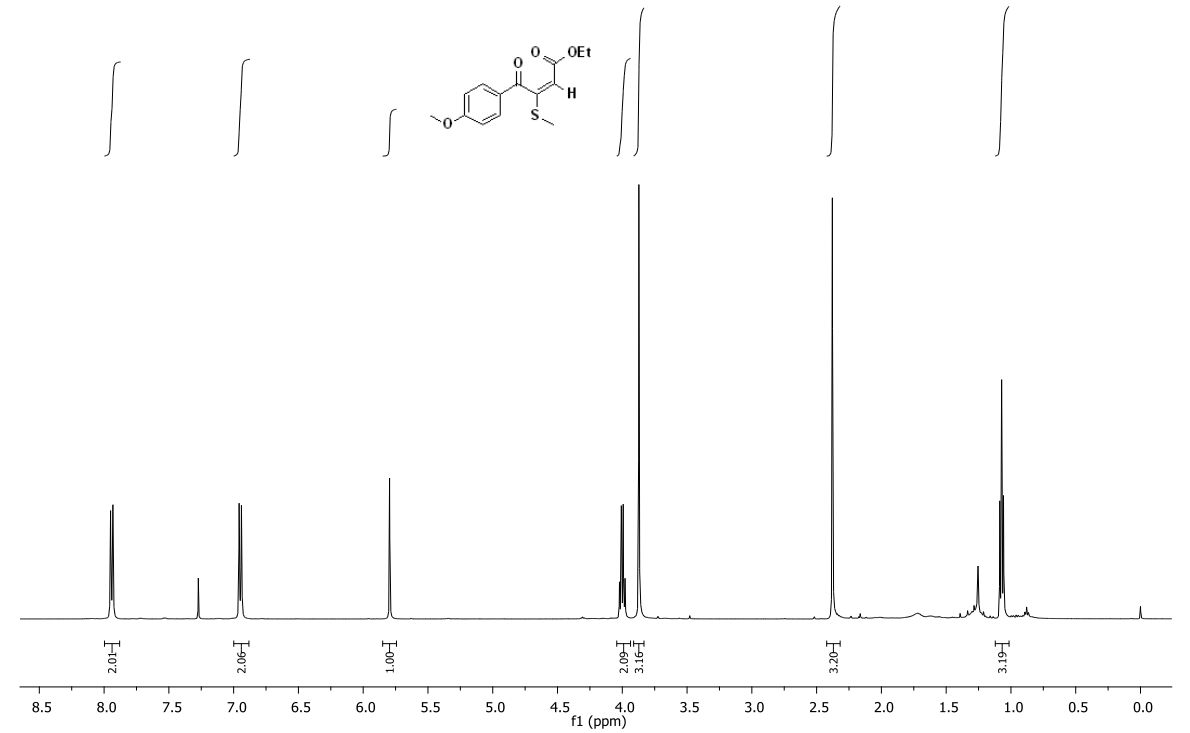


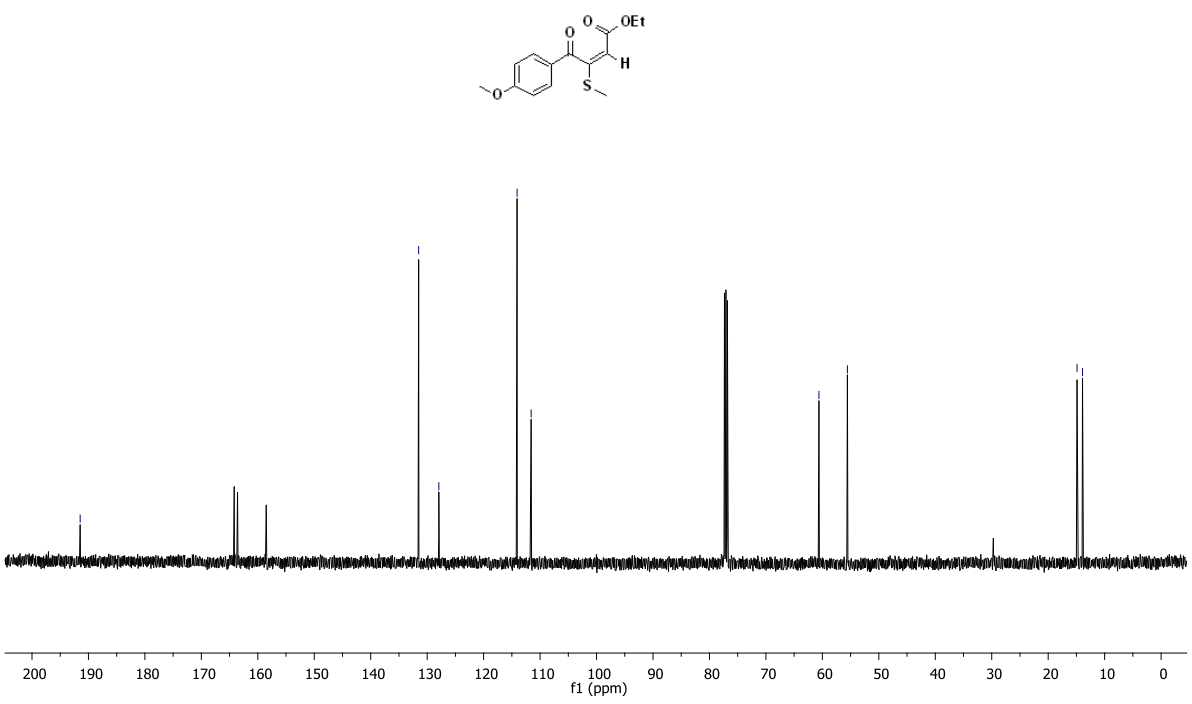
^{1}H and ^{13}C-NMR spectra of 4bd:



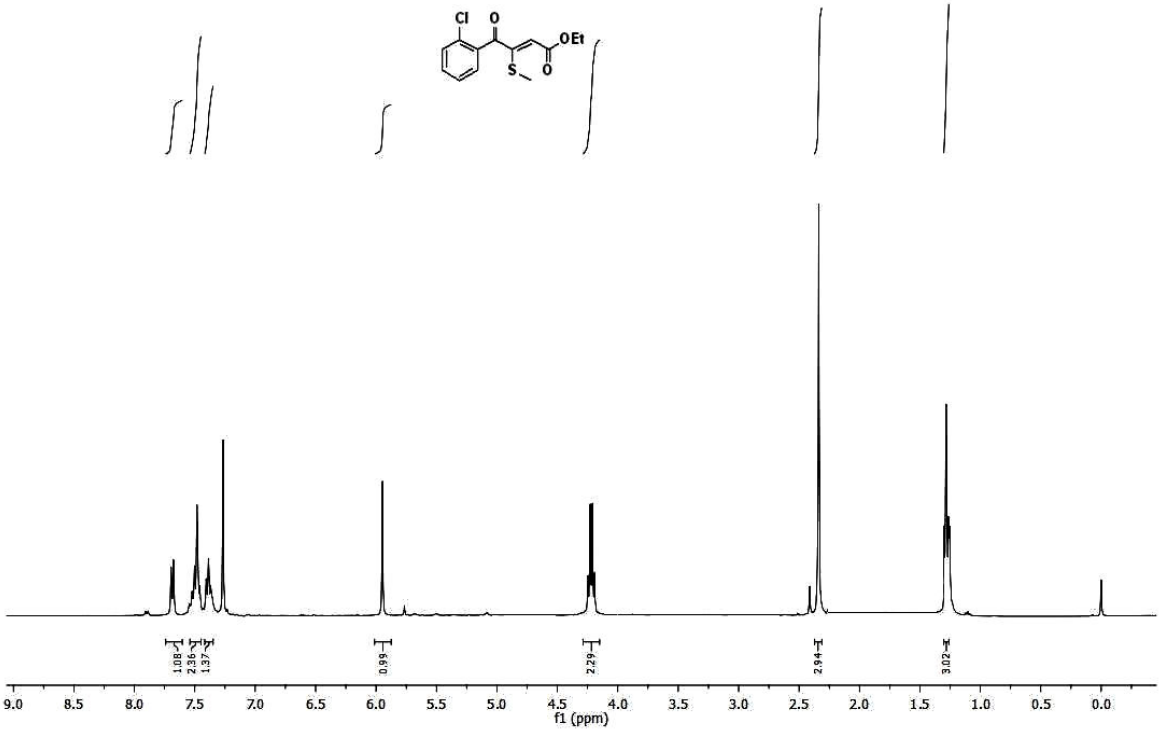


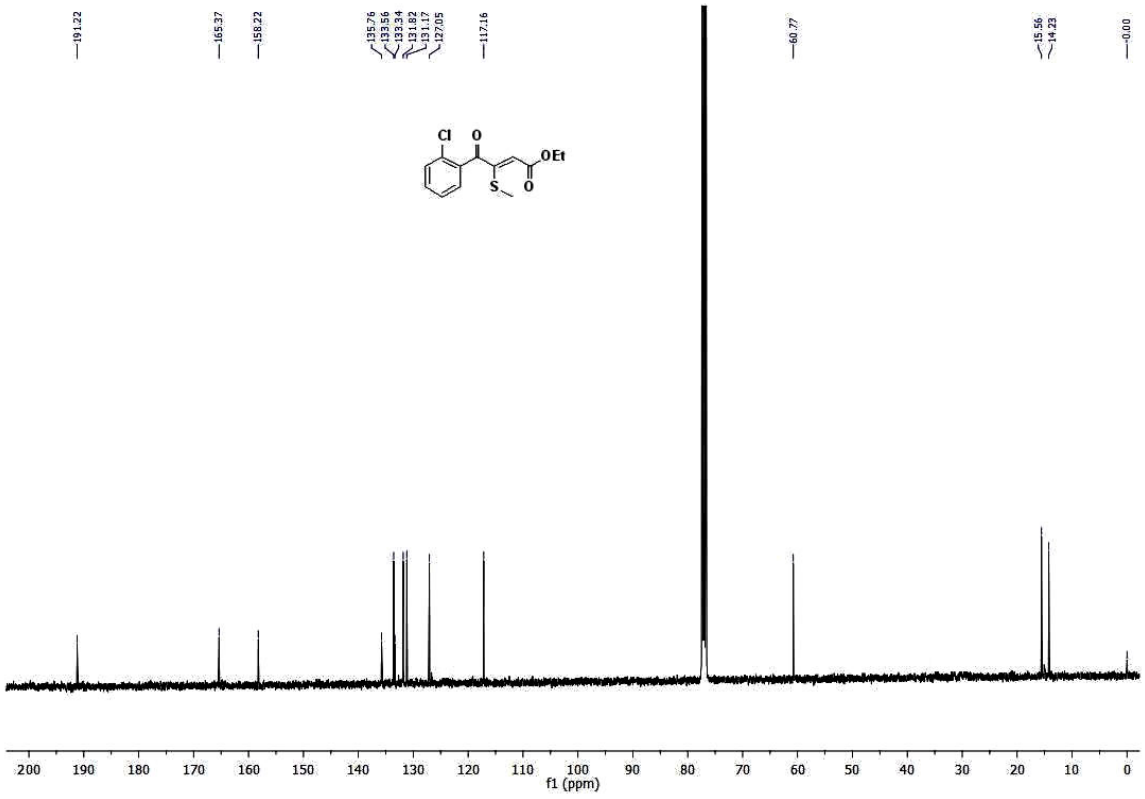
^{1}H and ^{13}C-NMR spectra of 4be:



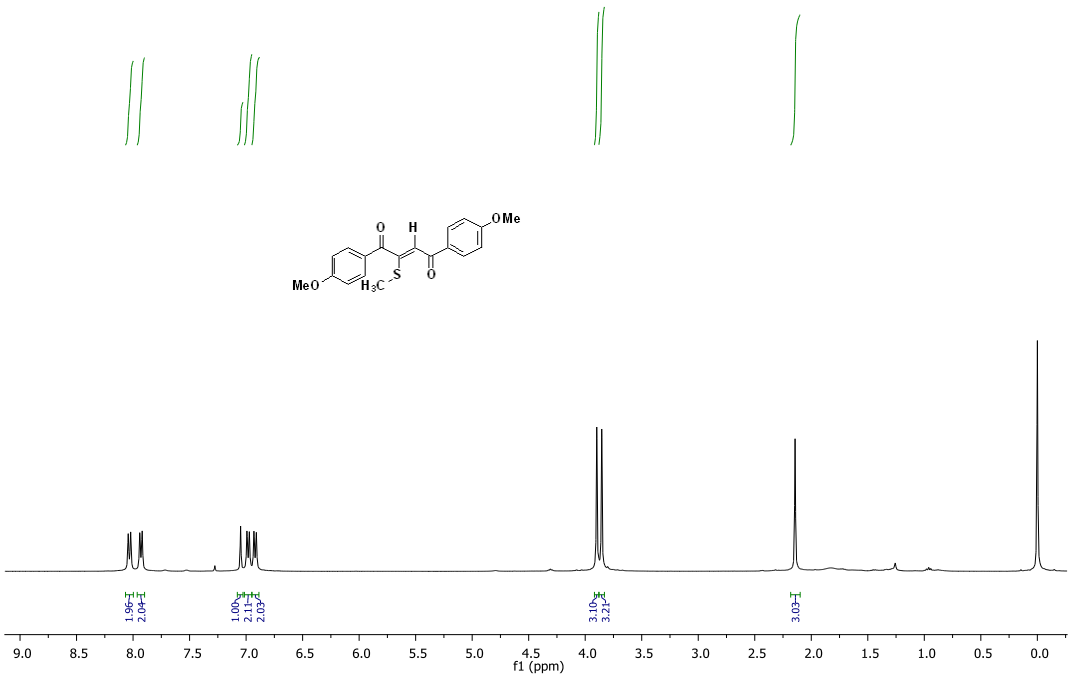


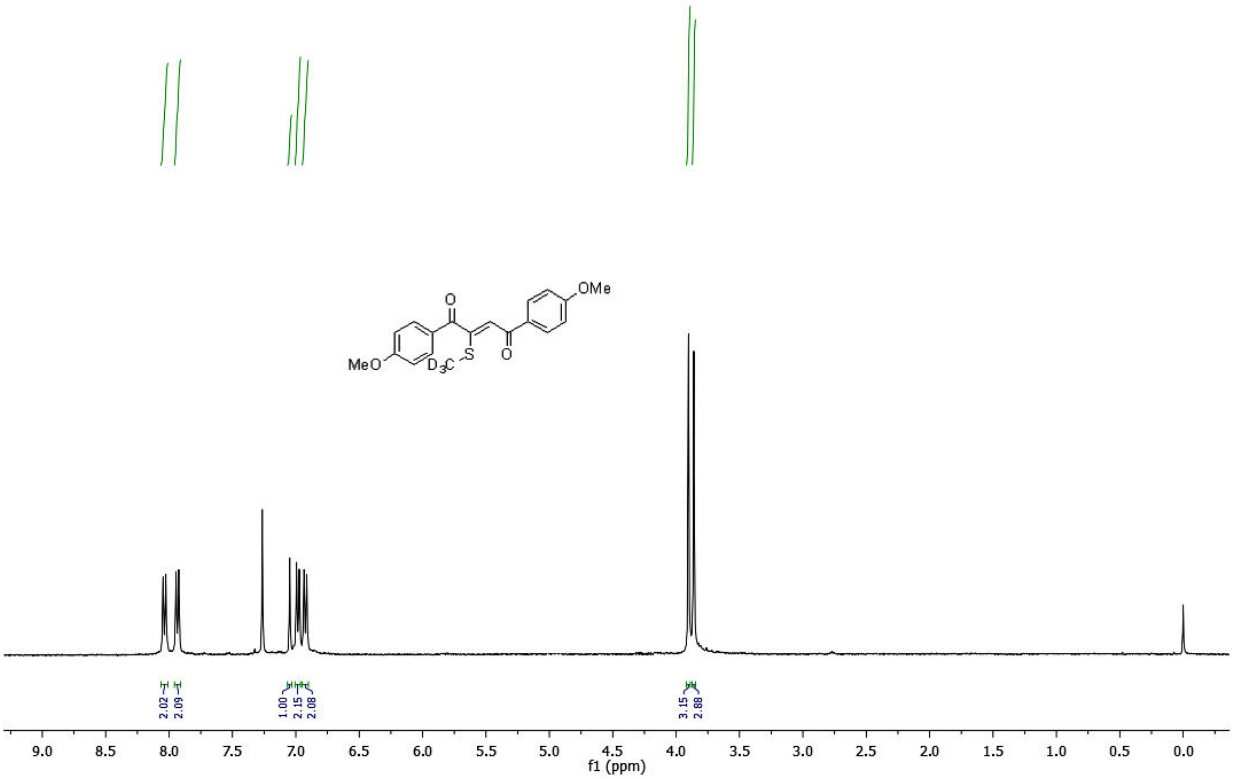
^{1}H and ^{13}C-NMR spectra of 4bf:





DMSO-d_6Experiment





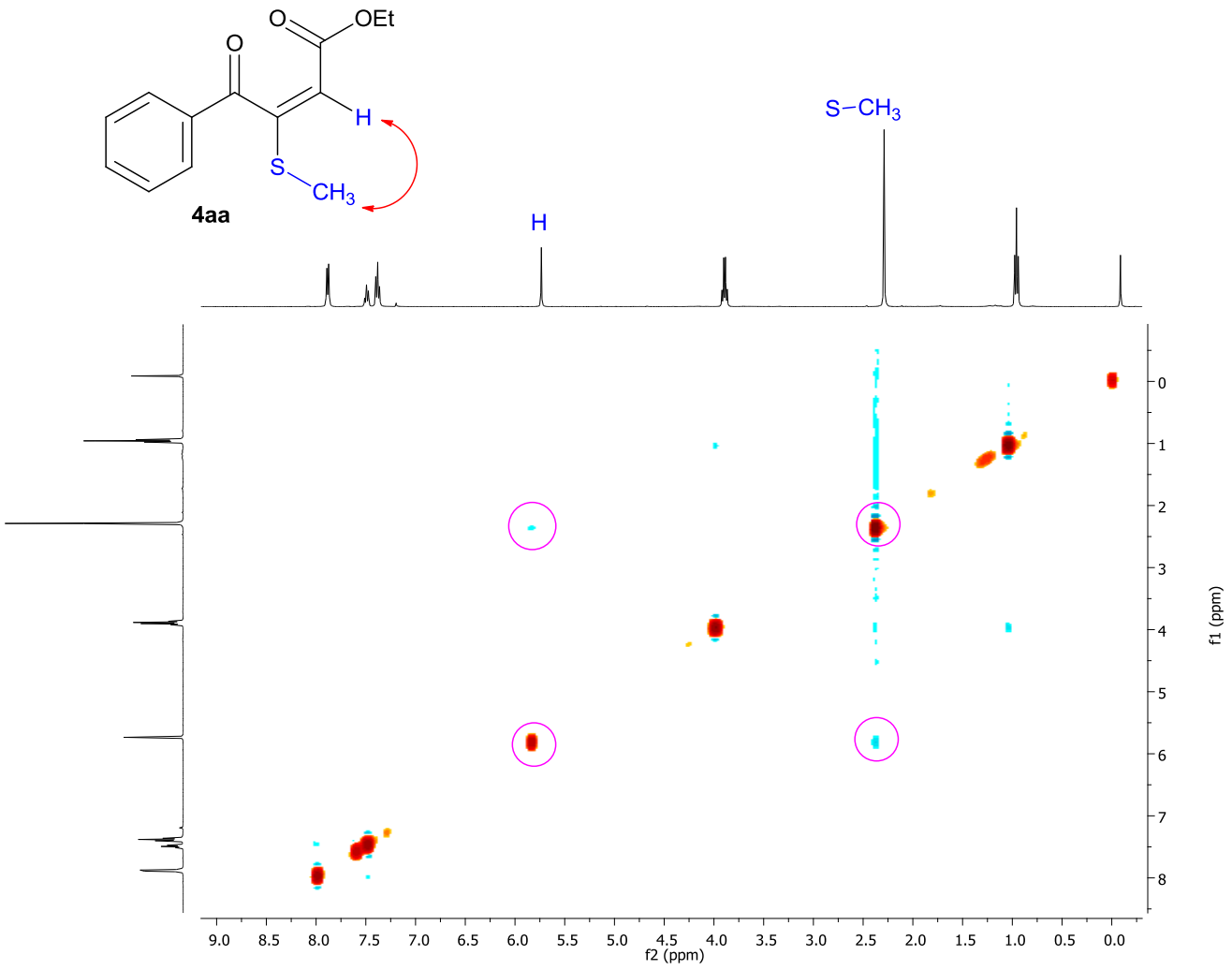


Figure: 1NOESY spectrum of compound **4aa**. ($CDCl_3$, 400 MHz)

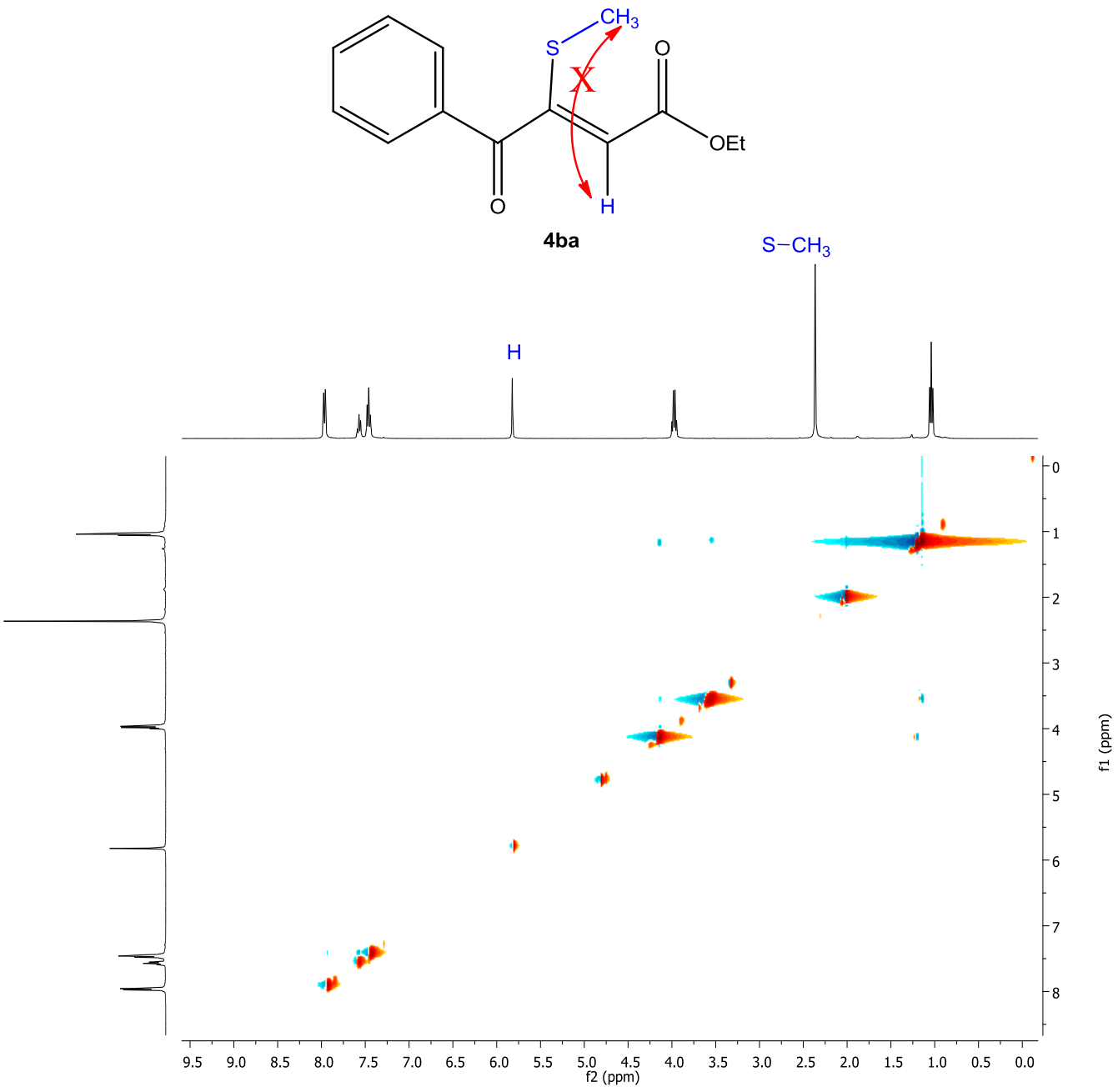


Figure: 2NOESY spectrum of compound **4ba**. ($CDCl_3$, 400 MHz)