

Supporting Information

A Cascade Synthesis of *S*-allyl Benzoylcarbamothioates *via* Mumm-type Rearrangement

Anjali Dahiya, Wajid Ali, Tipu Alam and Bhisma K. Patel*

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati-781039, India

Fax: (+91)361-26909762.

E-mail: patel@iitg.ernet.in

List of contents

General information: All the compounds were commercial grade and used without further purification. Organic extracts were dried over anhydrous sodium sulfate. Solvents were removed in a rotary evaporator under reduce pressure. Silica gel (60–120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25 mm).

NMR spectra were recorded in DMSO with tetramethylsilane as internal standard for proton NMR (400, 600 MHz) DMSO and $CDCl_3$ solvent as internal standard for ^{13}C NMR (100 and 150 MHz). HRMS spectra were recorded using ESI mode (Q-TOF MS Analyzer). IR spectra were recorded in KBr or neat.

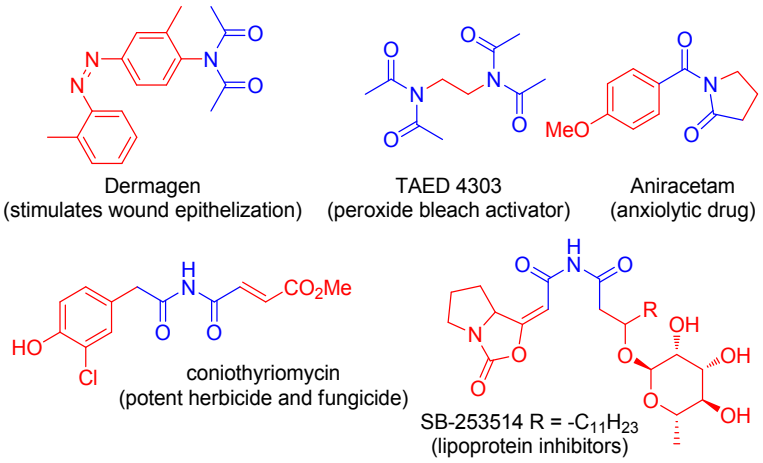
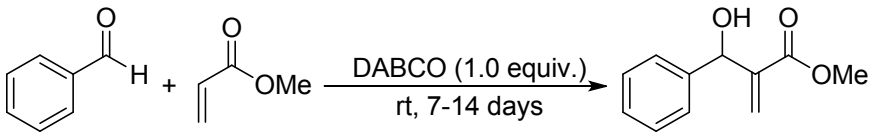


Figure S1 Examples of Biologically Active Imides

Experimental procedure:

***General Procedure for the Synthesis of methyl 2-(hydroxy(phenyl)methyl)acrylate (1-18)*:**



The synthesis of all the MBH alcohols (**1-18**, **15**,[1] **16**[2]) was according to the following reported procedure. Benzaldehyde (5 mmol), methyl acrylate (2.5 equiv.) and DABCO (1.0 equiv.) were taken in a 25 mL oven dried round bottom flask and sealed with a rubber septum. The resultant reaction mixture was stirred at room temperature under solvent free condition for 7-14 days. The progress of the reaction was monitored by TLC. After completion was admixed with ethyl acetate (30 mL) and washed successively with saturated solution of sodium bicarbonate (2 x 5

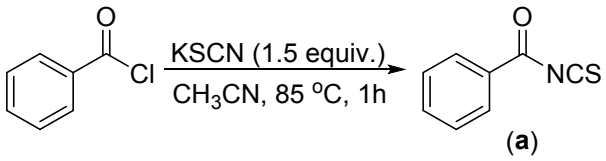
mL) and brine solution (2 x 5 mL). The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated in vacuum. The crude product thus obtained was purified using column chromatography with hexane and EtOAc as eluent to afford the desired MBH alcohols in quantitative yield.

References:

1) S. Chandrasekhar, Ch. Narsihmulu, B. Saritha and S. S. Sultana, *Tetrahedron Letters,* 2004, **45**, 5865.

2) V. K. Aggarwal and A. Mereu, *Chem. Commun.,* 1999, 2311.

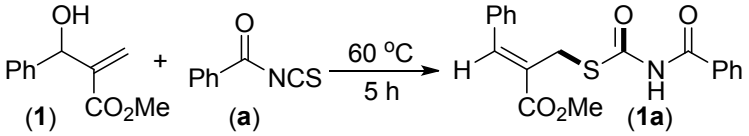
***General Procedure for the Synthesis of Aroyl Isothiocyanate (a-k)*:**



(**a**)

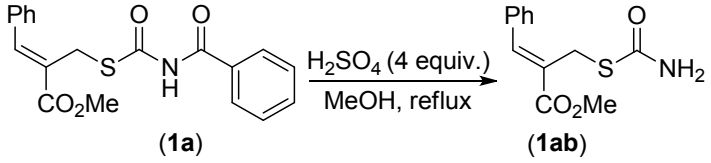
The synthesis of all the aroyl isothiocyanates (**a-k**) were according to the following procedure Benzoyl chloride (5 mmol), KSCN (1.5 equiv.) and CH_3CN (15 ml) were taken in a 25 mL oven dried round bottom flask. Then it was fitted with a condenser and the resultant reaction mixture was stirred in a pre-heated oil bath maintained at 85 ^oC. The progress of the reaction was monitored by TLC. After completion (color changes from white to yellow) the reaction mixture was cooled to room temperature. The reaction mixture was evaporated under reduced pressure to remove CH_3CN. Then it was admixed with ethyl acetate (30 mL) and washed successively with saturated solution of sodium bicarbonate (2 x 5 mL) and brine solution (2 x 5 mL). The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated in vacuum. The crude product thus obtained was purified using column chromatography with hexane as eluent to afford the desired benzoyl isothiocyanate in quantitative yield.

***General Procedure for the Synthesis of (Z)-methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (1a)*:**



Methyl 2-(hydroxy(phenyl)methyl)acrylate (**1**) (0.50 mmol, 87.5 mg) and benzoyl isothiocyanate (**a**) (0.50 mmol, 81.5 mg) were combined in an 5 mL oven-dried round bottom flask equipped with a magnetic needle. The reaction mixture was then stirred at 60 ^{o}C for 6 h. The progress of the reaction was monitored by TLC. After completion of the reaction, (indicated by formation of white solid) the crude product so obtained was then purified by silica gel column chromatography using EtOAc and hexane (20:80) as eluent to remove all the side product and the final product (**1a)** was obtained using 100% DCM as eluent (170 mg, 96%). The identity and purity of the product was confirmed by spectroscopic analysis.

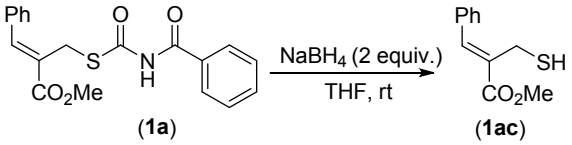
General Procedure for Synthesis of Methyl 2-((carbamoylthio)methyl)-3-phenylacrylate (1ab):



Z-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (**1**) (0.14 mmol, 49.7 mg), MeOH (1 mL) and conc. H_2SO_4 (0.56 mmol, 54.92 mg) were combined in an 5 mL oven-dried round bottom flask equipped with a magnetic needle. The reaction mixture was then refluxed for overnight. The progress of the reaction was monitored by TLC. After completion of the reaction, mixture was diluted with EtOAc (10 mL), washed with saturated $NaHCO_3$ solution (1×10 mL) and finally washed with saturated NaCl solution (1×10 mL), dried over anhydrous sodium

sulphate (Na_2SO_4), and evaporated under reduced pressure., the crude product thus obtained was then purified by silica gel column chromatography using EtOAc and hexane (19:81) as eluent. The identity and purity of the product **1ab** (25.30 mg, 72%) was confirmed by spectroscopic analysis and was consistent with the reported product.

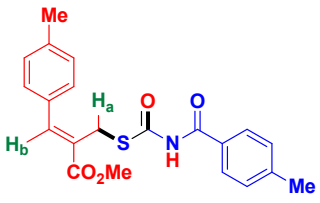
General Procedure for Synthesis of Methyl 2-(mercaptomethyl)-3-phenylacrylate (1ac):

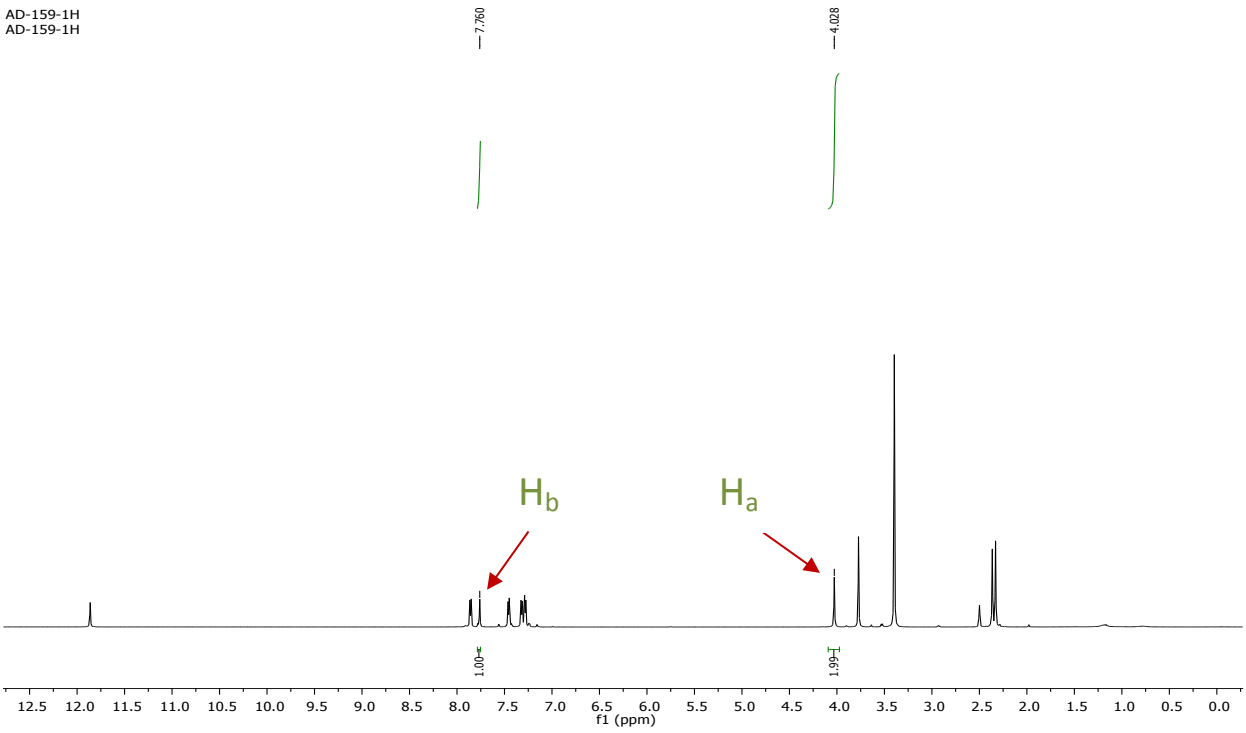


(**1a**) (**1ac**)

Z-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (**1**) (0.14 mmol, 49.7 mg), MeOH (1 mL) and sodium borohydride (0.28 mmol, 10.59 mg) and THF (1 mL) were combined in an 5 mL oven-dried round bottom flask equipped with a magnetic needle. The reaction mixture was then stirred overnight. After completion of the reaction, mixture was diluted with EtOAc (10 mL), washed with saturated $NaHCO_3$ solution (1×10 mL) and finally washed with saturated NaCl solution (1×10 mL), dried over anhydrous sodium sulfate (Na_2SO_4), and evaporated under reduced pressure., the crude product thus obtained was then purified by silica gel column chromatography using EtOAc and hexane (10:90) as eluent. The identity and purity of the product **1ac** (23 mg, 79%) was confirmed by spectroscopic analysis.

NOE Experiment:

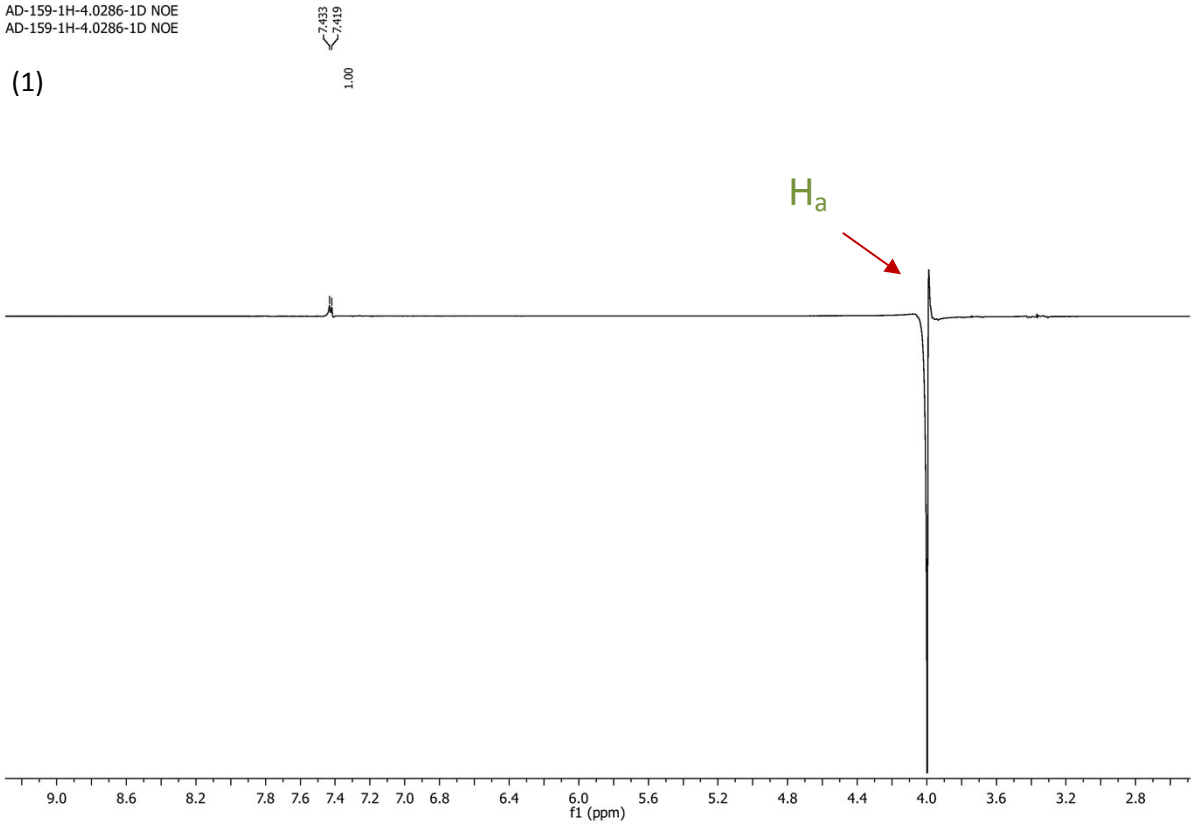




The relative stereochemistry in the product (**1a**–**13b**) was determined by the 1D NOE experiment of (**2b**) as the representative example. When proton H_a was irradiated in the compound (**2b**), no peak enhancement for H_a along with very weak peak enhancement of the proton of phenyl ring of MBH alcohol was observed. On the other hand, when proton H_b was irradiated, no peak enhancement for the proton H_b was observed as expected. All these NOE observations ultimately suggests that the relative stereochemistry of the product (**2b**) as ***Z*-Methyl 2-((((4-methylbenzoyl)carbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate**. The spatial interactions of the protons are shown in the figures given below.

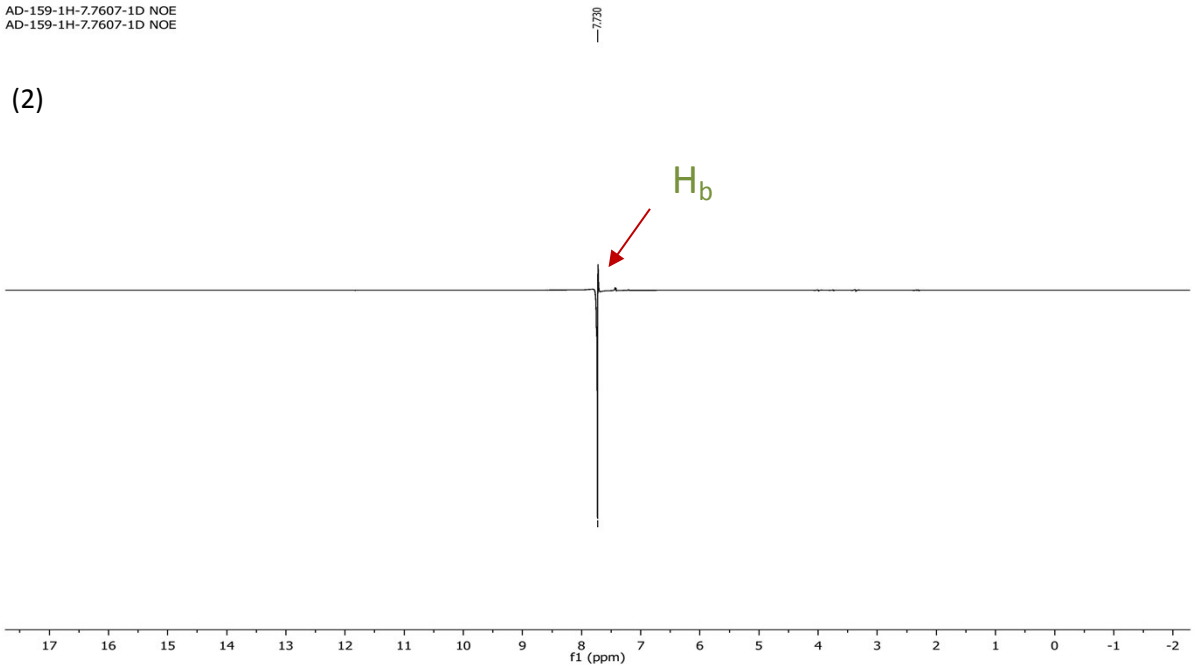
AD-159-1H-4.0286-1D NOE
AD-159-1H-4.0286-1D NOE

(1)



AD-159-1H-7.7607-1D NOE
AD-159-1H-7.7607-1D NOE

(2)



Mechanistic Investigation:

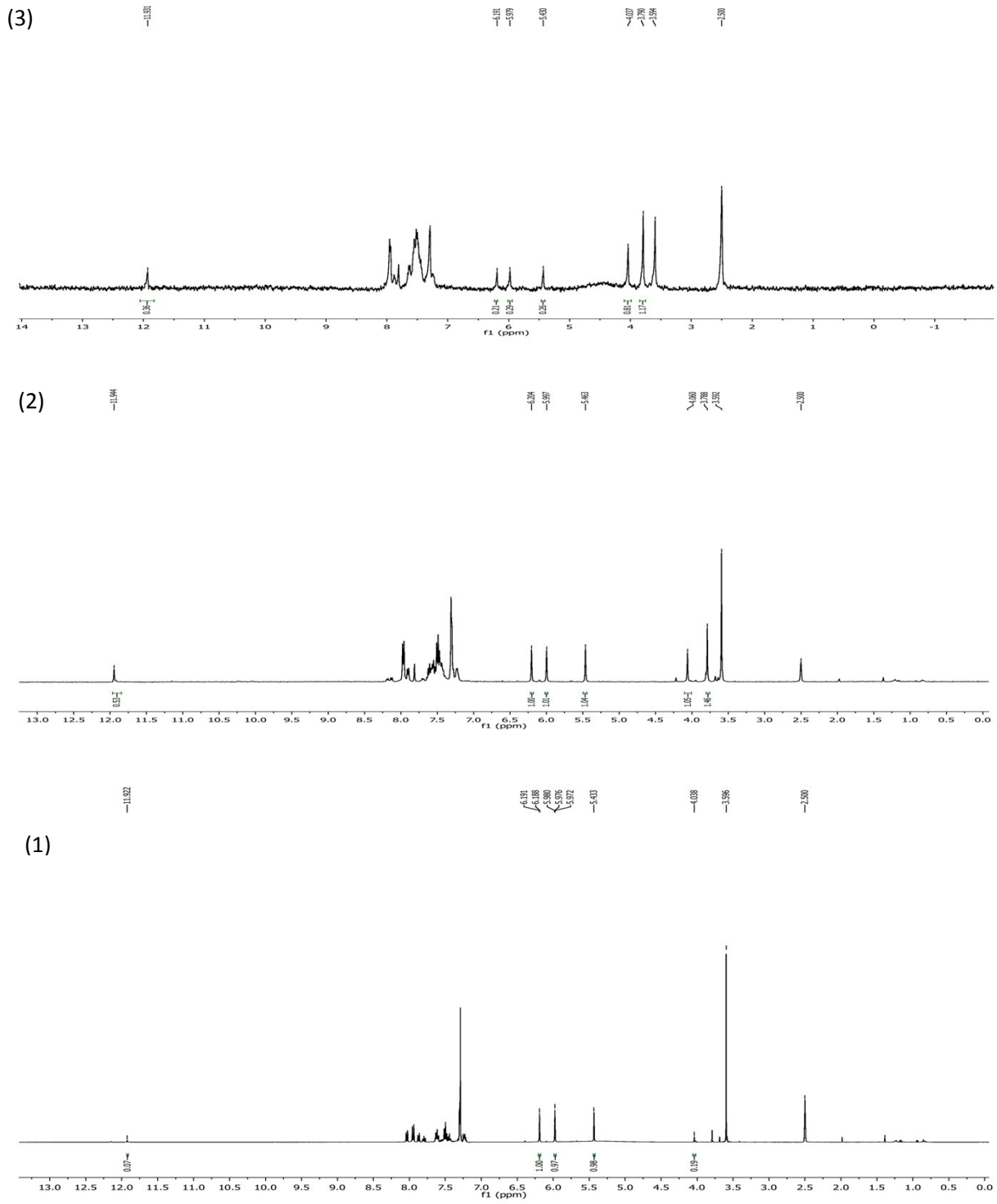
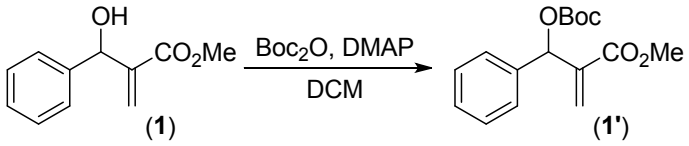


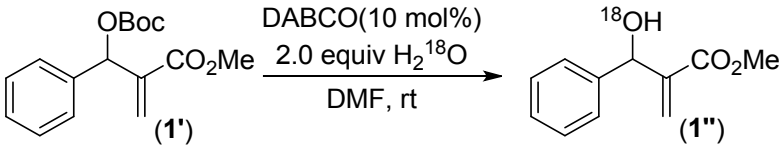
Figure S2 [1]HNMR analysis of reaction mixture at (1) 10 min (2) 30 min (3) 1 h.

***^{1}H NMR study for the detection of reaction intermediates*:** In order to detect the intermediate species in the reaction mixture for this transformation ^{1}H NMR spectroscopy was performed. In this study (**1a**) was taken as representative example. A 5 mL oven-dried flask was charged with methyl 2-(hydroxy(phenyl)methyl)acrylate (**1**) (0.50 mmol, 87.5 mg) and benzoyl isothiocyanate (**a**) (0.50 mmol, 81.5 mg). Then the reaction mixture was stirred in a pre-heated oil bath at 60 ^{o}C. After 5 min of reaction, small aliquot was withdrawn from the reaction mixture. The crude product so obtained was used for ^{1}H NMR study in DMSO-d_6 with tetramethylsilane as the internal standard for ^{1}H NMR (400 MHz). In the ^{1}H NMR spectra, both starting material and product were observed. There was no indication for the formation of cyclic intermediate 1,3-oxathiane. This suggests that the reaction is going through concerted path.

Experimental Procedure for the Formation of labeled MBH alcohol (1″):



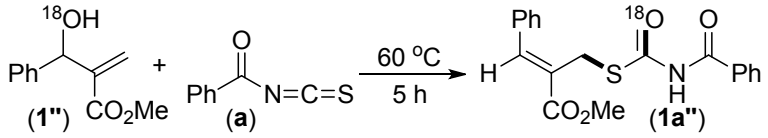
To a MBH alcohol (2.5 mmol) in DCM (4 mL) was added Boc_2O (2.55 mmol) in DCM (4 mL) dropwise in an ice bath. The mixture was stirred for 30 min, and DMAP (0.25 mmol) was added in a portion. The reaction was monitored with TLC. Then the mixture was diluted with DCM (20 mL), washed with 4 N HCl (1×10 mL) and saturated $NaHCO_3$ aqueous (1×10 mL) and finally washed with saturated NaCl aqueous (1×10 mL), dried over anhydrous sodium sulphate (Na_2SO_4), and evaporated under reduced pressure. The crude product so obtained was then purified by silica gel column chromatography using EtOAc and hexane (10:90) as eluent.



To MBH carbonate (**1'**) (58.4 mg, 0.2 mmol, 1.0 equiv), $H_2{}^{18}O$ (8.0 μL, 0.4 mmol, 2.0 equiv), were dissolved in DMF (700 μL) and stirred at rt for 10.0 min, and stirred at room temperature for 2.0 min, followed by DABCO (2.24 mg, 0.02 mmol, 0.1 equiv). The reaction mixture was stirred at room temperature and monitored by TLC. After four hour and complete consumption of 1′, the reaction mixture was directly loaded onto a short silica gel column, followed by gradient elution with EtOAc and hexane (15:85). Removal of the solvent in *vacuo* affords product 1″ (18.1 mg) as pale yellow oil in 88% yield.

^{18}O Labeling Experiment:

***Typical Experimental Procedure for the Formation of labeled S-allyl benzoylcarbamothioate (1a")*:**



Labeled methyl 2-(hydroxy(phenyl)methyl)acrylate (**1''**) (0.10 mmol, 19.4 mg) and benzoyl isothiocyanate (**a**) (0.10 mmol, 16.3 mg) were combined in an 5 mL oven-dried round bottom flask equipped with a magnetic needle. The reaction mixture was then stirred at 60^{o} C for 6h. The crude mixture thus obtained was used for ^{13}CNMR study in DMSO-d_6 with tetramethylsilane as the internal standard for ^{13}CNMR (150 MHz). Formation of labeled *S*-allyl benzoylcarbamothioate (1a) was confirmed by spectroscopic and HRMS analysis.

HRMS Spectra of *Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (1a) from $H_2{}^{18}O$ labelling experiment:

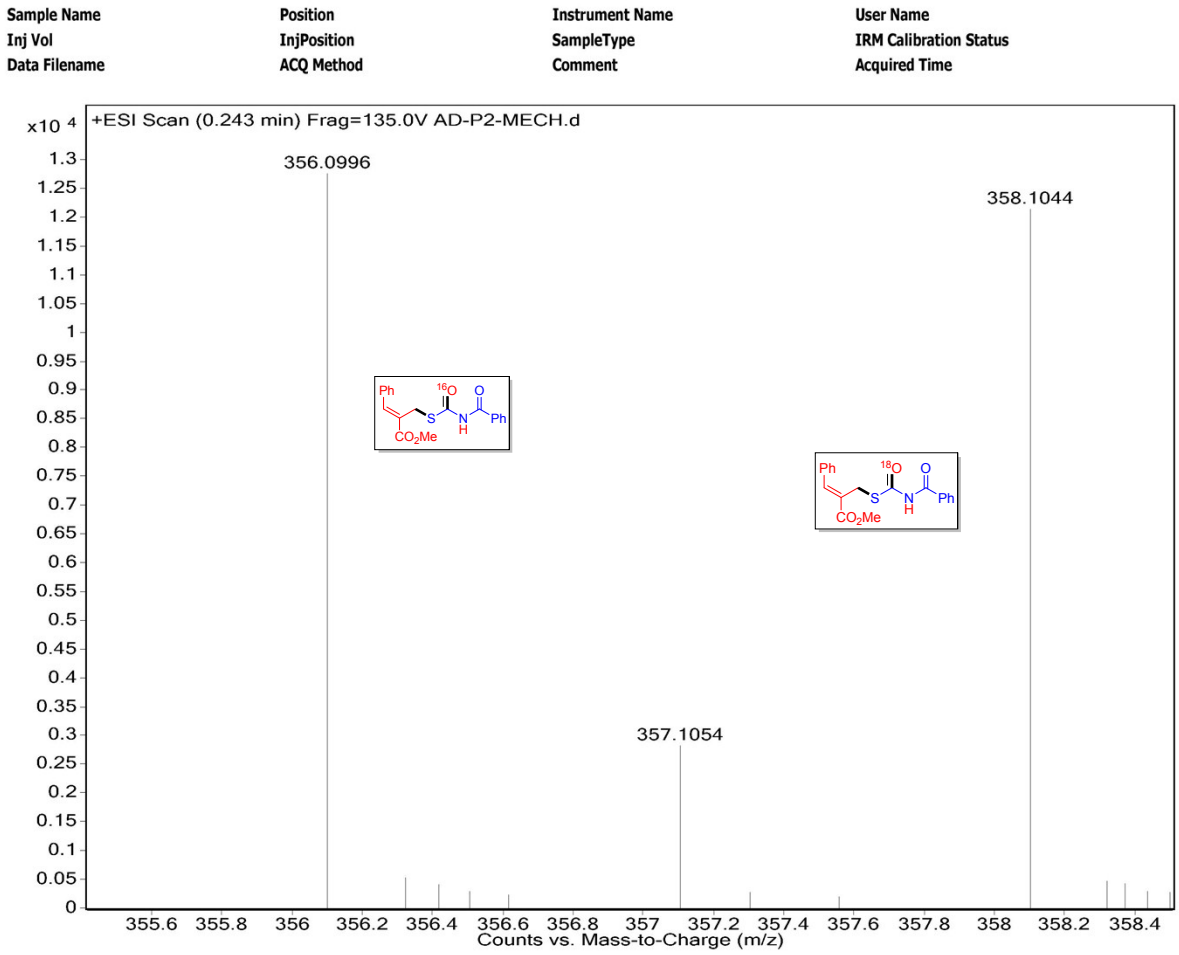


Figure S3 HRMS spectrum of ^{18}O labeled (**1a"**).

Labeled *E*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (1a): ^{13}CNMR (DMSO-d$_6$, 150 MHz):

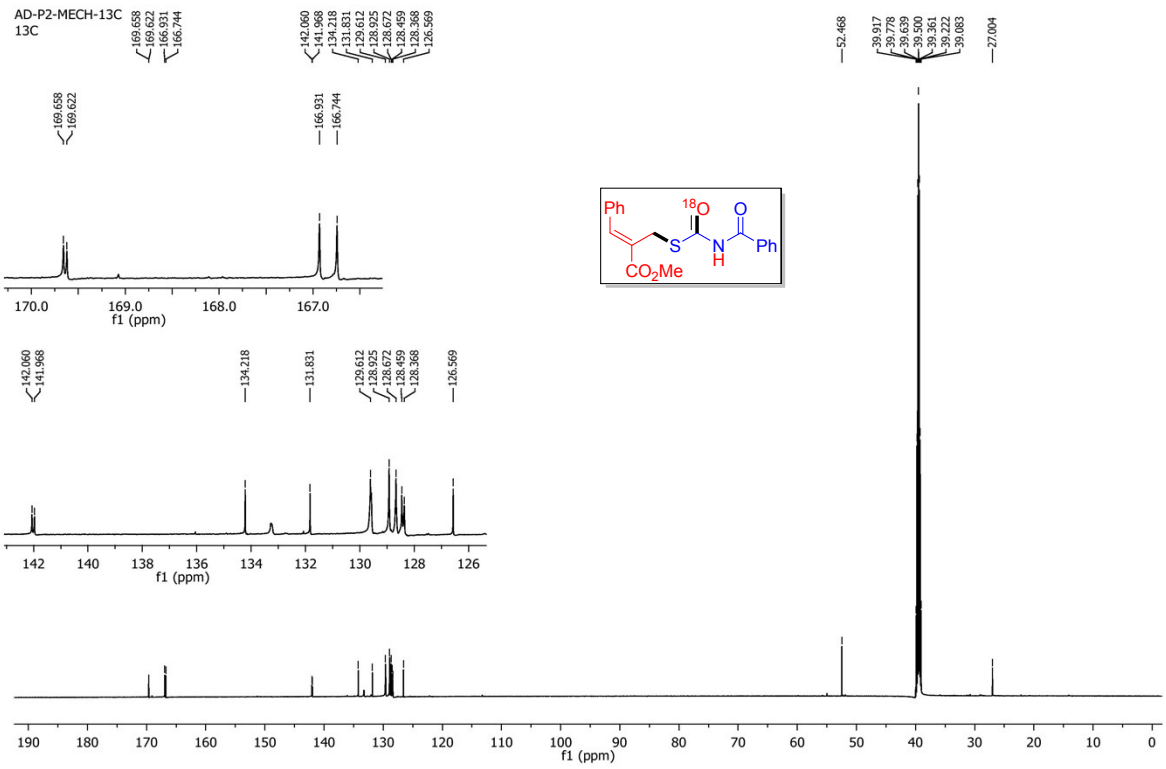


Figure S4 ^{13}CNMR spectrum of ^{18}O labeled (**1a"**).

(8) Crystallographic Description:

Crystal data were collected with Bruker Smart Apex-II CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073Å) at 298 K. Cell parameters were retrieved using SMART [a] software and refined with SAINT[a] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS[b]. The structure was solved by direct methods implemented in SHELX-2014[c] program and refined by full-matrix least-squares

methods on F2. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. Yellow crystals were isolated in block shape from methanol at room temperature.

a. SMART V 4.043 Software for the CCD Detector System; Siemens Analytical Instruments Division: Madison, WI, 2008.

b. SAINT Plus (v 6.14) Bruker AXS Inc., Madison, WI, 2008.

c. Sheldrick, G. M. SHELXL-2014, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen (Germany), 1997.

Crystallographic description of *Z*-Methyl-2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (1a): $C_{21}H_{21}NO_4S$, crystal dimensions 0.35 x 0.32 x 0.29mm, M_r = 383.45, triclinic, space group P -1 -1 -1,a = 5.2634(5), b = 12.909(2),c = 14.964(2)Å, α = 73.896(14)°, β = 89.385(10)°, γ = 80.113(11)°, V = 961.6(2)Å^3, Z = 2, ρ_{calcd} = 1.324g/cm^3, μ = 0.195mm^{-1}, F(000)= 404.0, reflection collected / unique = 3376 / 2129, refinement method = full-matrix least-squares on F^2, final R indices [I > 2\s(I)]: R_1 = 0.1253, wR_2 = 0.1960, R indices (all data): R_1 = 0.0786, wR_2 = 0.1430, goodness of fit = 1.134. CCDC-1844331 for ***Z*-Methyl-2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (1a)** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

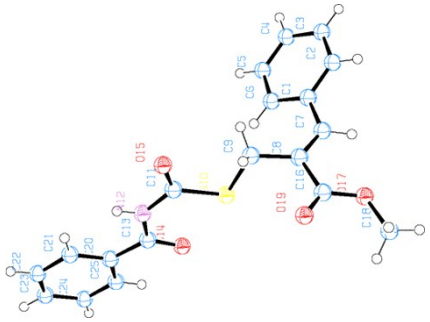
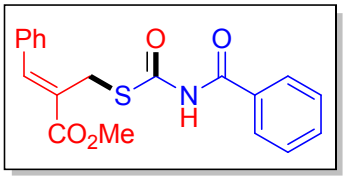


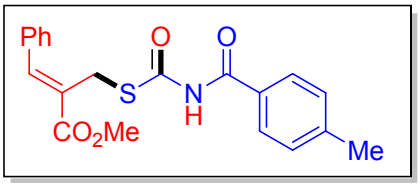
Figure S5. ORTEP view of (**1a)** with 50% thermal ellipsoid probability.

Spectral data of product



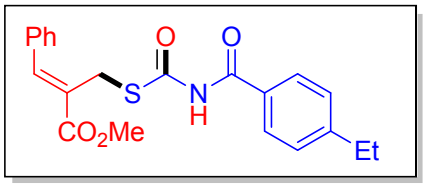
***Z*-Methyl-2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (1a):**

White solid (96%, 170.4 mg); m.p. 173–175 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.79 (s, 3H), 4.05 (s, 2H), 7.48 (m, 7H), 7.63 (t, 1H, *J* = 7.6 Hz), 7.80 (s, 1H), 7.95 (d, 2H, *J* = 7.6 Hz), 11.92 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 27.0, 52.4, 126.6, 128.4, 128.6, 128.9, 129.5, 129.6, 131.8, 133.2, 134.2, 142.0, 166.7, 166.9, 169.6; IR (KBr): 3443, 2953, 2923, 2853, 1714, 1696, 1633, 1434, 1261, 1217 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{18}NO_4S^+$ [M + H$^+$] 356.0951; found 356.0954.



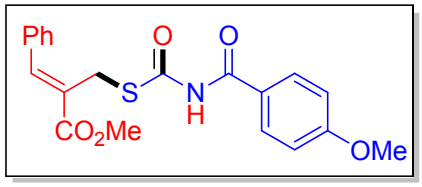
***Z*-Methyl 2-((((4-methylbenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1b):**

White solid (92%, 169.7 mg); m.p. 199–201 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 2.36 (s, 3H), 3.79 (s, 3H), 4.03 (s, 2H), 7.32 (d, 2H, *J* = 8.0 Hz), 7.42 (t, 1H, *J* = 6.8 Hz), 7.48 (t, 2H, *J* = 7.6 Hz), 7.56 (d, 2H, *J* = 7.2 Hz), 7.80 (s, 1H), 7.86 (d, 2H, *J* = 8.0 Hz), 11.84 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 21.1, 26.9, 52.4, 126.6, 128.4, 128.8, 128.9, 129.1, 129.46, 129.54, 134.2, 141.9, 143.6, 166.4, 166.9, 169.6; IR (KBr): 3459, 2957, 2856, 1711, 1694, 1615, 1436, 1381 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{20}NO_4S^+$ [M + H$^+$] 370.1108; found 370.1114.



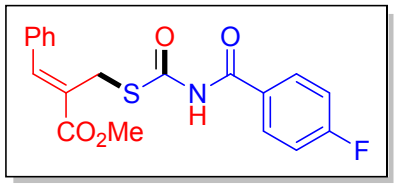
***Z*-Methyl 2-((((4-ethylbenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1c):**

White solid (90%, 172.3 mg); m.p. 170–172 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 1.18 (t, 3H, *J* = 7.6 Hz), 2.66 (q, 2H, *J* = 7.6 Hz), 3.79 (s, 3H), 4.03 (s, 2H), 7.35 (d, 2H, *J* = 8.0 Hz), 7.42 (m, 1H), 7.48 (t, 2H, *J* = 7.6 Hz), 7.55 (d, 2H, *J* = 7.6 Hz), 7.80 (s, 1H), 7.88 (d, 2H, *J* = 8.4 Hz), 11.84 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 15.2, 27.0, 28.2, 52.4, 126.6, 128.0, 128.6, 128.9, 129.2, 129.5, 129.6, 134.2, 141.9, 149.0, 166.5, 166.9, 169.6; IR (KBr): 3448, 2967, 2923, 2853, 1715, 1636, 1578, 1384, 1262 cm^{-1}; HRMS (ESI): calcd. for $C_{21}H_{22}NO_4S^+$ [M + H$^+$] 384.1264; found 384.1267.



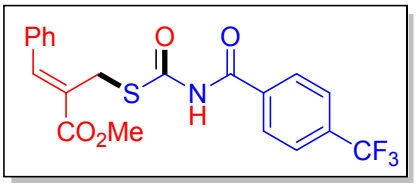
***Z*-Methyl 2-((((4-methoxybenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1d):**

White solid (81%, 155.9 mg); m.p. 181–183 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.79 (s, 3H), 3.83 (s, 3H), 4.02 (s, 2H), 7.05 (d, 2H, *J* = 8.8 Hz), 7.43 (m, 1H), 7.48 (t, 2H, *J* = 7.6 Hz), 7.56 (d, 2H, *J* = 7.6 Hz), 7.80 (s, 1H), 7.96 (d, 2H, *J* = 8.8 Hz), 11.77 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 26.9, 52.4, 55.6, 113.9, 123.7, 126.7, 128.8, 129.47, 129.54, 130.6, 134.2, 141.8, 163.2, 165.8, 166.9, 169.7; IR (KBr): 3449, 3004, 2924, 2849, 1690, 1630, 1607, 1469, 1249 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{20}NO_5S^+$ [M + H$^+$] 386.1057; found 386.1067.



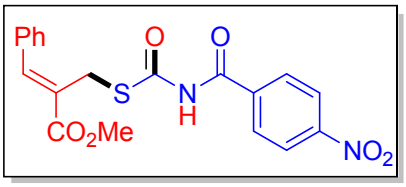
***Z*-Methyl 2-((((4-fluorobenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1e):**

White solid (95%, 177.1 mg); m.p. 190–192 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.79 (s, 3H), 4.03 (s, 2H), 7.35 (t, 2H, *J* = 8.8 Hz), 7.46 (m, 3H), 7.55 (d, 2H, *J* = 7.2 Hz), 7.80 (s, 1H), 8.02 (t, 2H, *J* = 7.6 Hz), 11.94 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 27.0, 52.4, 115.7 (d, *J* = 21.9 Hz), 126.6, 128.4 (d, *J* = 2.7 Hz), 128.9, 129.6, 131.4 (d, *J* = 9.5 Hz), 134.2, 142.0, 163.8, 165.6, 166.3, 166.9, 169.6; ^{19}F NMR (DMSO-d_6 +Hexafluorobenzene): δ (ppm) -108.34 (s); IR (KBr): 3438, 3277, 2950, 2855, 1710, 1693, 1639, 1511, 1260 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{17}FNO_4S^+$ [M + H$^+$] 374.0857; found 374.0864.



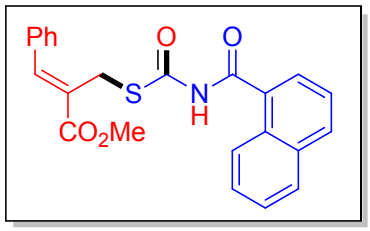
***Z*-Methyl 3-phenyl-2-((((4-(trifluoromethyl)benzoyl)carbamoyl)thio)methyl)acrylate (1f):**

White solid (98%, 207.2 mg); m.p. 195–197 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.79 (s, 3H), 4.05 (s, 2H), 7.47 (m, 3H), 7.56 (d, 2H, *J* = 7.2 Hz), 7.81 (s, 1H), 7.90 (d, 2H, *J* = 8.0 Hz), 8.12 (d, 2H, *J* = 8.0 Hz), 12.13 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 27.0, 52.4, 122.4, 125.5 (q, *J* = 3.6 Hz), 126.5, 128.4, 128.9, 129.3, 129.5, 129.6, 134.2, 135.8, 142.1, 165.8, 166.9, 169.5; ^{19}F NMR (DMSO-d_6 + Hexafluorobenzene): δ (ppm) -64.35 (s); IR (KBr): 3432, 2957, 2853, 1720, 1627, 1523, 1444, 1326 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{17}F_3NO_4S^+$ [M + H$^+$] 424.0825; found 424.0827.



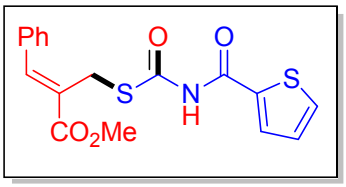
***Z*-Methyl 2-((((4-nitrobenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1g):**

Pale Yellow solid (91%, 182.1 mg); m.p. 144–146 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.68 (s, 3H), 6.06 (s, 1H), 6.41 (s, 1H), 6.59 (s,1H), 7.38 (m, 5H), 8.08 (d, 2H, *J* = 6.0 Hz), 8.31 (d, 2H, *J* = 6.0 Hz), 11.48 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 52.1, 73.9, 123.4, 126.6, 127.5, 128.6, 128.6, 129.8, 137.1, 138.8, 138.9, 149.6, 150.2, 164.79, 164.83; IR (KBr): 3448, 2957, 2924, 2854, 1759, 1713, 1635, 1526, 1349, 1263, 1196 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{17}N_2O_6S^+$ [M + H$^+$] 401.0802; found 401.0806.



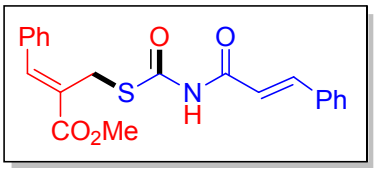
***Z*-Methyl 2-((((1-naphthoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1h):**

White solid (93%, 188.3 mg); m.p. 124–126 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.82 (s, 3H), 4.14 (s, 2H), 7.48 (m, 3H), 7.62 (m, 5H), 7.82 (d, 1H, *J* = 7.2 Hz), 7.86 (s, 1H), 8.01 (d, 1H, *J* = 7.6 Hz), 8.11 (d, 1H, *J* = 8.4 Hz), 8.21 (d, 1H, *J* = 8.8 Hz), 12.15 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 27.0, 52.4, 124.7, 124.8, 126.6, 127.1, 127.6, 128.6, 128.9, 129.5, 129.6, 131.0, 131.8, 133.2, 134.2, 142.1, 166.9, 168.4, 169.1; IR (KBr): 3438, 2951, 2930, 2853, 1715, 1694, 1634, 1469, 1250, 1188, 1075 cm^{-1}; HRMS (ESI): calcd. for $C_{23}H_{20}NO_4S^+$ [M + H$^+$] 406.1108; found 406.1118.



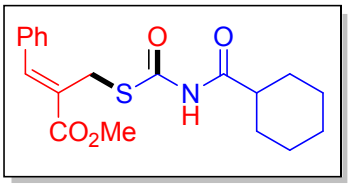
***Z*-Methyl 3-phenyl-2-((((thiophene-2-carbonyl)carbamoyl)thio)methyl)acrylate (1i):**

Brown solid (78%, 141.2 mg); m.p. 179–181 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.78 (s, 3H), 4.03 (s, 2H), 7.22 (t, 1H, *J* = 8.0 Hz), 7.45 (m, 3H), 7.54 (d, 2H, *J* = 7.2 Hz), 7.79 (s, 1H), 8.00 (d, 1H, *J* = 4.8 Hz), 8.16 (d, 1H, *J* = 3.6 Hz), 11.99 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 27.0, 52.4, 126.6, 128.7, 128.9, 129.5, 129.6, 132.1, 134.2, 135.1, 136.8, 142.0, 160.8, 166.9, 169.3; IR (KBr): 3441, 3227, 2922, 1709, 1682, 1633, 1470, 1268 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{16}NO_4S_2^+$ [M + H$^+$] 362.0515; found 362.0521.



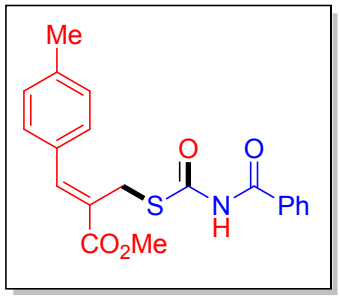
***Z*-Methyl 2-(((cinnamoylcarbamoyl)thio)methyl)-3-phenylacrylate (1j):**

White solid (74%, 140.9 mg); m.p. 194–196 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.79 (s, 3H), 4.02 (s, 2H), 6.81 (d, 1H, *J* = 16.0 Hz), 7.46 (m, 6H), 7.54 (d, 2H, *J* = 7.2 Hz), 7.62 (d, 2H, *J* = 3.6 Hz), 7.70 (d, 1H, *J* = 16.0 Hz), 7.80 (s, 1H), 11.65 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 26.8, 52.4, 119.5, 126.5, 128.2, 128.8, 129.1, 129.49, 129.52, 130.7, 134.0, 134.1, 142.0, 144.0, 164.5, 166.8, 168.9; IR (KBr): 3438, 2921, 2851, 1704, 1693, 1634, 1507, 1438, 1195, 1153, 1021 cm^{-1}; HRMS (ESI): calcd. for $C_{21}H_{20}NO_4S^+$ [M + H$^+$] 382.1108; found 382.1109.



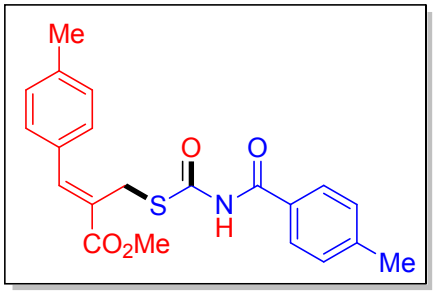
***Z*-Methyl 2-((((cyclohexanecarbonyl)carbamoyl)thio)methyl)-3-phenylacrylate (1k):**

Pale yellow gummy (89%, 160.7 mg); **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 1.24 (m, 4H), 1.44 (m, 2H), 1.76 (m, 2H) 1.88 (d, 2H, J = 13.2 Hz), 2.36 (m, 1H) 3.83 (s, 3H), 4.11 (s, 2H), 7.40 (m, 5H), 7.88 (s, 1H), 9.50 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 25.4, 25.6, 27.7, 28.9, 45.3, 52.5, 126.2, 128.8, 129.4, 129.6, 134.6, 143.6, 167.4, 171.2, 175.8; IR (KBr): 3450, 3063, 2922, 2855, 1715, 1663, 1642, 1448, 1268, 1081 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{24}NO_4S^+$ [M + H^+] 362.1421; found 362.1428.



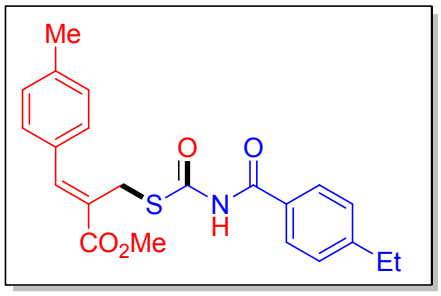
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2a):**

White solid (84%, 154.9 mg); m.p. 193–195 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 2.34 (s, 3H), 3.83 (s, 3H), 4.19 (s, 2H), 7.20 (d, 2H, J = 8.0 Hz), 7.41 (dd, 4H, J_1 = 8.4 Hz, J_2 = 7.6 Hz), 7.55 (t, 1H, J = 7.2 Hz), 7.89 (s, 1H), 7.95 (d, 2H, J = 7.6 Hz), 9.92 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 20.9, 27.1, 52.3, 125.5, 128.4, 128.6, 129.5, 129.7, 131.3, 131.8, 133.1, 139.4, 142.0, 166.6, 167.0, 169.7 ; IR (KBr): 3420, 2920, 2853, 1710, 1687, 1638, 1512, 1433, 1258, 1183, 1150 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{20}NO_4S^+$ [M + H^+] 370.1108; found 370.1116.



***Z*-Methyl 2-((((4-methylbenzoyl)carbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2b):**

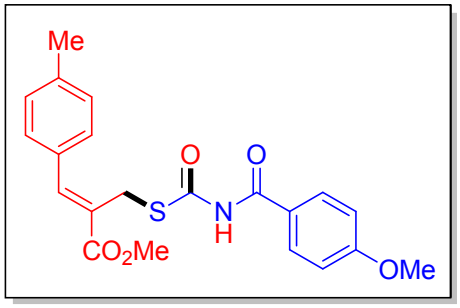
White solid (79%, 151.2 mg); m.p. 208–210 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 2.33 (s, 3H), 2.36 (s, 3H), 3.78 (s, 3H), 4.04 (s, 2H), 7.29 (dd, 4H, J_1 = 8.0 Hz, , J_2 = 8.4 Hz), 7.45 (d, 2H, J = 8.0 Hz), 7.76 (s, 1H), 7.87 (d, 2H, J = 8.4 Hz), 11.84 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 20.9, 21.1, 27.0, 52.3, 125.5, 128.4, 128.9, 129.1, 129.5, 129.7, 131.3, 139.5, 142.0, 143.6, 166.4, 167.0, 169.7 ; IR (KBr): 3447, 2961, 2923, 2855, 1715, 1687, 1639, 1384, 1263 cm^{-1}; HRMS (ESI): calcd. for $C_{21}H_{22}NO_4S^+$ [M + H^+] 384.1264; found 384.1269.



***Z*-Methyl 2-((((4-ethylbenzoyl)carbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2c):**

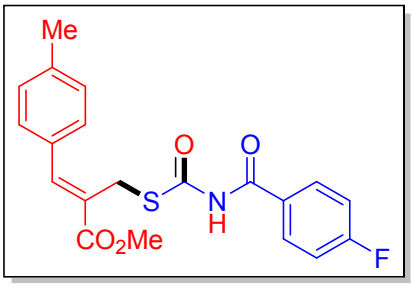
White solid (80%, 158.8 mg); m.p. 171–173 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 1.18 (t, 3H, J = 7.6 Hz) 2.32(s, 3H), 2.63 (q, 2H, J = 7.6 Hz), 3.83 (s, 3H), 4.20 (s, 2H), 7.19 (d, 4H, J = 7.2 Hz), 7.40 (d, 2H, J = 8.0 Hz), 7.91 (d, 3H, J = 8.0 Hz), 10.20 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 15.2, 21.0, 27.0, 28.2, 52.3, 125.6, 128.0, 128.6, 129.2, 129.5, 129.7, 131.4, 139.5, 142.0, 149.7, 166.5, 167.0, 169.7 ; IR (KBr): 3442, 2957, 2923, 2853, 1710, 1638, 1576,

1380, 1262, 1020 cm^{-1}; HRMS (ESI): calcd. for $C_{22}H_{24}NO_4S^+$ [M + H^+] 398.1421; found 398.1430.



***Z*-Methyl 2-((((4-methoxybenzoyl)carbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2d):**

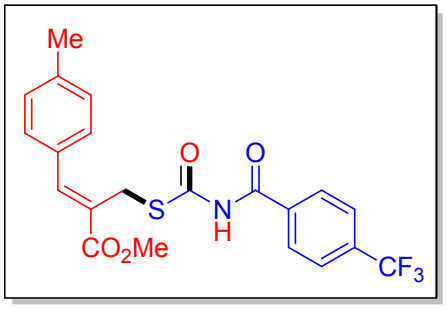
White solid (71%, 141.6 mg); m.p. 195–197 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 2.33 (s, 3H), 3.77 (s, 3H), 3.83 (s, 3H), 4.02(s, 2H), 7.04 (d, 2H, *J* = 9.2 Hz), 7.28 (d, 2H, *J* = 8.0 Hz), 7.45 (d, 2H, *J* = 8.0 Hz), 7.75 (s, 1H), 7.96 (d, 2H, *J* = 8.8Hz), 11.76 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 21.0, 27.0, 52.3, 55.6, 113.9, 123.7, 125.6, 129.5, 129.7, 130.6, 131.4, 139.5, 142.0, 163.2, 165.8, 167.0 , 169.8; IR (KBr): 3438, 2954, 2924, 2853, 1719, 1635, 1461, 1384, 1262, 1180, 1020 cm^{-1}; HRMS (ESI): calcd. for $C_{21}H_{22}NO_5S^+$ [M + H^+] 400.1213; found 400.1217.



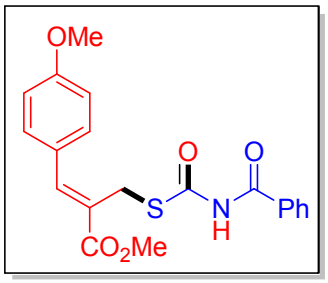
***Z*-Methyl 2-((((4-fluorobenzoyl)carbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2e):**

White solid (91%, 176.1 mg); m.p. 180–182 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 2.33 (s, 3H), 3.78 (s, 3H), 4.04(s, 2H), 7.29 (d, 2H, *J* = 7.6 Hz), 7.36 (t, 2H, *J* = 8.4 Hz), 7.46 (d, 2H, *J*

= 7.6 Hz), 7.77 (s, 1H), 8.03 (m, 2H), 11.97 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 20.9, 27.0, 52.3, 115.6 (d, *J* = 22.0 Hz), 125.5, 126.9, 128.34, 128.37, 129.6 (d, *J* = 21.7 Hz), 131.4 (d, *J* = 9.2 Hz), 139.5, 142.0, 163.7, 165.5, 166.2, 167.0, 169.7; ^{19}F NMR (DMSO-d_6 + Hexafluorobenzene): δ (ppm) -110.98 (s); IR (KBr): 3442, 2959, 2924, 2853, 1707, 1634, 1462, 1383, 1259, 1182, 1022 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{19}FNO_4S^+$ [M + H$^+$] 388.1013; found 388.1019.

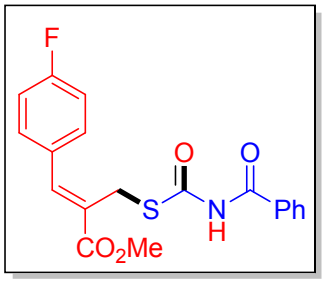


***Z*-Methyl 3-(p-tolyl)-2-((((4-(trifluoromethyl)benzoyl)carbamoyl)thio)methyl)acrylate (2f):** Pale Yellow solid (90%, 196.6 mg); m.p. 172–174 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 2.34 (s, 3H), 3.78 (s, 3H), 4.06 (s, 2H), 7.29 (d, 2H, *J* = 8.0 Hz), 7.46 (d, 2H, *J* = 8.0 Hz), 7.77(s, 1H), 7.90 (d, 2H, *J* = 8.4 Hz), 8.12 (d, 2H, *J* = 8.0 Hz), 12.12 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 20.9, 27.0, 52.3, 125.1, 125.5 (q, *J* = 7.0 Hz), 129.3, 129.5, 129.7, 131.3, 132.3, 132.7, 135.8, 139.5, 142.1, 165.7, 166.9, 169.5; ^{19}F NMR (DMSO-d_6 + Hexafluorobenzene): δ (ppm) -63.95; IR (KBr): 3441, 2955, 2925, 2854, 1715, 1696, 1633, 1331, 1260, 1129, 1067 cm^{-1}; HRMS (ESI): calcd. for $C_{21}H_{19}F_3NO_4S^+$ [M + H$^+$] 438.0981; found 438.0990.



***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-methoxyphenyl)acrylate (3a):**

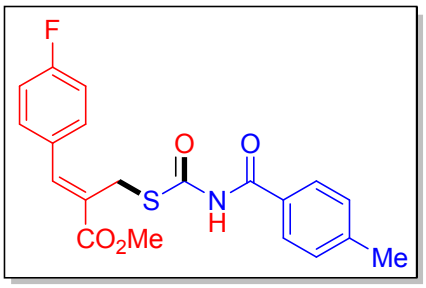
White solid (77%, 148.2 mg); m.p. 148–150 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.77 (s, 3H), 3.80 (s, 3H), 4.06 (s, 2H), 7.04 (d, 2H, *J* = 8.8 Hz), 7.54 (m, 4H), 7.64(t, 1H, *J* = 7.2 Hz), 7.76 (s, 1H), 7.95 (t, 2H, *J* = 8.8 Hz), 11.93 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 27.2, 52.2, 55.3, 114.4, 123.5, 126.5, 128.4, 128.6, 131.77, 131.84, 133.1, 141.9, 160.4, 166.7, 167.1, 169.8; IR (KBr): 3453, 3003, 2952, 2838, 1719, 1698, 1665, 1511, 1439, 1176, 1031 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{20}F_3NO_5S^+$ [M + H^+] 386.1057; found 386.1058.



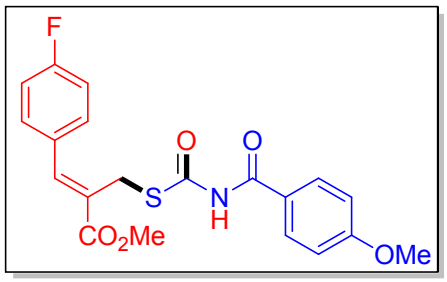
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-fluorophenyl)acrylate (4a):**

White solid (95%, 177.1 mg); m.p. 164–166 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.78 (s, 3H), 4.03 (s, 2H), 7.31 (t, 2H, *J* = 8.8 Hz), 7.51 (t, 2H, *J* = 7.6 Hz), 7.62 (dd, 3H, J_1= 5.2 Hz, J_2= 2.8 Hz), 7.78 (s, 1H), 7.95 (d, 2H, *J* = 7.6 Hz), 11.92 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 26.8, 52.4, 115.9 (d, *J* = 21.5 Hz), 126.5, 128.5 (d, *J* = 23.9 Hz), 130.8 (d, *J* = 3.1 Hz), 131.8, 132.0 (d, *J* = 8.5 Hz), 133.2, 140.8, 161.3, 163.8, 166.7, 166.9, 169.6 ; ^{19}F NMR (DMSO-d_6 + Hexafluorobenzene): δ (ppm) –113.27 (s); IR (KBr): 3438, 2921, 2851, 1634,

1507, 1438, 1255, 1195, 1153, 1021 cm $^{-1}$; HRMS (ESI): calcd. for $C_{19}H_{17}FNO_4S^+$ [M + H^+] 374.0857; found 374.0863.

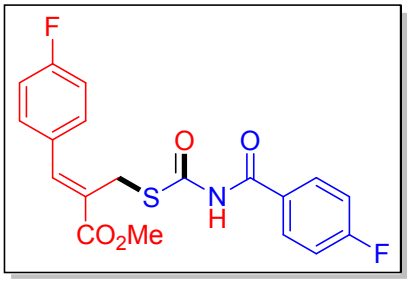


***Z*-Methyl 3-(4-fluorophenyl)-2-((((4-methylbenzoyl)carbamoyl)thio)methyl)acrylate (4b):** White solid (93%, 179.9 mg); m.p. 193–195 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 2.37 (s, 3H), 3.78 (s, 3H), 4.01 (s, 2H), 7.33 (m, 4H), 7.62 (m, 2H), 7.78 (s, 1H), 7.86 (d, 2H, *J* = 8.0 Hz), 11.84 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 21.1, 26.8, 52.4, 115.9 (d, *J* = 21.6 Hz), 126.51, 126.53, 128.4, 128.9, 129.2, 130.7 (d, *J* = 3.2 Hz), 132.0 (d, *J* = 8.6 Hz), 140.7, 143.6, 163.7, 166.4, 166.8, 169.6; ^{19}F NMR (DMSO-d_6 + Hexafluorobenzene): δ (ppm) -113.33; IR (KBr): 3452, 2922, 2855, 1639, 1508, 1435, 1384, 1262, 1161 cm $^{-1}$; HRMS (ESI): calcd. for $C_{20}H_{19}FNO_4S^+$ [M + H^+] 388.1013; found 388.1020.



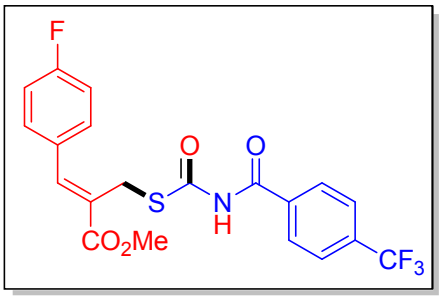
***Z*-Methyl 3-(4-fluorophenyl)-2-((((4-methoxybenzoyl)carbamoyl)thio)methyl)acrylate (4d):** White solid (86%, 173.3 mg); m.p. 188–190 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.79 (s, 3H), 3.84 (s, 3H), 4.00 (s, 2H), 7.05 (d, 2H, *J* = 8.8 Hz), 7.33 (t, 2H, *J* = 8.4 Hz), 7.63 (dd, 2H, J_1 = 5.6 Hz, J_2 = 2.8 Hz), 7.78 (s, 1H), 7.96 (d, 2H, *J* = 8.8 Hz), 11.77 (s, 1H); **^{13}C NMR**

(100 MHz, DMSO-d_6): δ (ppm) 26.8, 52.4, 55.6, 113.9, 115.9 (d, J = 21.5 Hz), 123.6, 126.5, 130.6, 130.8(d, J = 3.1 Hz), 132.0 (d, J = 8.6 Hz), 140.6, 163.2, 165.8, 166.8, 169.6 ; ^{19}F NMR (DMSO-d_6 + Hexafluorobenzene): δ (ppm) -113.36; IR (KBr): 3435, 2955, 2924, 2854, 1719, 1688, 1636, 1607, 1507, 1469, 1255, 1195 cm $^{-1}$; HRMS (ESI): calcd. for $C_{20}H_{19}FNO_5S^+$ [M + H^+] 404.0962; found 404.0963.

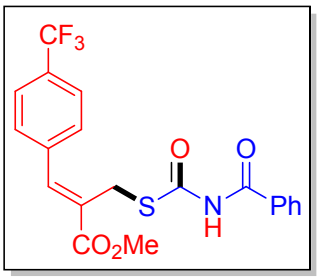


***Z*-Methyl 2-((((4-fluorobenzoyl)carbamoyl)thio)methyl)-3-(4-fluorophenyl)acrylate (4e):**

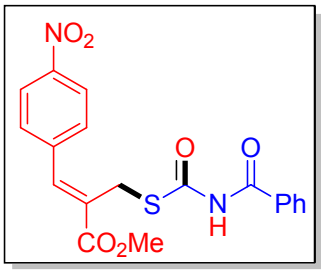
White solid (97%, 208.2 mg); m.p. 189–191 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.79 (s, 3H), 4.02 (s, 2H), 7.34 (m, 4H), 7.63 (dd, 2H, J_1 = 5.6 Hz, J_2 = 2.8 Hz), 7.78 (s, 1H), 8.03 (dd, 2H, J_1 = 5.2 Hz, J_2 = 3.2 Hz), 11.94 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 26.8, 52.4, 115.7 (d, J = 20.8 Hz), 115.9 (d, J = 20.3 Hz), 126.5, 128.3 (d, J = 2.7 Hz), 130.7 (d, J = 3.2 Hz), 131.4 (d, J = 9.5 Hz), 132.0 (d, J = 8.5 Hz), 140.7, 161.3, 163.7, 165.5, 166.8, 169.6; ^{19}F NMR (DMSO-d_6 + Hexafluorobenzene): δ (ppm) -111.02, -107.93; (s); IR (KBr): 3440, 2924, 2849, 1713, 1634, 1601, 1508, 1437, 1257, 1195, 1159, 1071 cm $^{-1}$; HRMS (ESI): calcd. for $C_{19}H_{16}F_2NO_4S^+$ [M + H^+] 392.0763; found 392.0772.



***Z*-Methyl 3-(4-fluorophenyl)-2-((((4-(trifluoromethyl)benzoyl)carbamoyl)thio)methyl)acrylate (4f):** White solid (96%, 211.6 mg); m.p. 192–194 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.79 (s, 3H), 4.04 (s, 2H), 7.32 (t, 2H, J = 8.8 Hz), 7.62 (dd, 2H, J_1 = 8.4 Hz, J_2 = 8.4 Hz), 7.79 (s, 1H), 7.89 (d, 2H, J = 8.4 Hz), 8.11 (d. 2H, J = 8.4 Hz), 12.13 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 26.8, 52.4, 115.9 (d, J = 21.6 Hz), 125.5 (q, J = 3.6 Hz), 126.4 (d, J = 1.2 Hz), 129.3, 130.8 (d, J = 3.2 Hz), 132.0 (d, J = 8.5 Hz), 135.8, 140.8, 161.3, 163.8, 165.8, 166.8, 169.5; ^{19}F NMR (DMSO-d_6 +Hexafluorobenzene): δ (ppm) -113.36, -64.00; IR (KBr): 3438, 2955, 2922, 2853, 2727, 2632, 2598, 2505, 1441, 1327, 1259, 1184, 1155, 1067 cm $^{-1}$; HRMS (ESI): calcd. for $C_{20}H_{16}F_4NO_4S^+$ [M + H^+] 442.0731; found 442.0741.

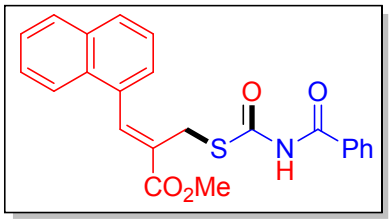


***Z*-methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-(trifluoromethyl)phenyl)acrylate (5a):** White solid (93%, 196.7 mg); m.p. 172–174 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.80 (s, 3H), 4.02 (s, 2H), 7.50 (t, 2H, J = 8.0 Hz), 7.62 (t, 1H, J = 7.2 Hz), 7.73 (d, 2H, J = 8.0 Hz), 7.81 (d, 3H, J = 9.6 Hz), 7.95 (d, 2H, J = 7.6 Hz), 11.91 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 26.6, 52.4, 125.5 (q, J = 3.6 Hz), 128.3, 128.6, 129.0, 129.3, 129.4, 130.0, 131.8, 133.1, 138.5, 139.9, 166.57, 166.62, 169.5; ^{19}F NMR (DMSO-d_6 + Hexafluorobenzene): δ (ppm) -63.68; IR (KBr): 3438, 2956, 2921, 2851, 1722, 1695, 1636, 1471, 1326, 1250, 1107, 1015 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{17}F_3NO_4S^+$ [M + H^+] 424.0825; found 424.0829.



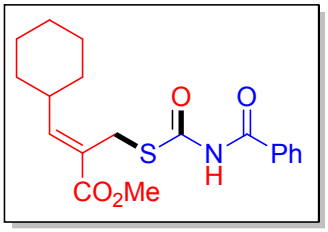
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-nitrophenyl)acrylate (6a):**

Yellow solid (88%, 176.2 mg); m.p. 183–185 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.81 (s, 3H), 4.01 (s, 2H), 7.51 (t, 2H, *J* = 7.6 Hz), 7.61 (m, 1H), 7.79 (d, 2H, *J* = 8.8 Hz), 7.84 (s, 1H), 7.93 (t, 2H, *J* = 8.4 Hz), 8.30 (d, 2H, *J* = 8.8 Hz), 11.90 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 26.5, 52.5, 123.7, 128.3, 128.6, 130.5, 130.6, 131.7, 133.2, 139.1, 141.1, 147.2, 166.4, 166.6, 169.4; IR (KBr): 3434, 2952, 2923, 2851, 1719, 1638, 1541, 1515, 1471, 1344, 1278, 1068 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{17}N_2O_6S^+$ [M + H$^+$] 401.0802; found 401.0809.



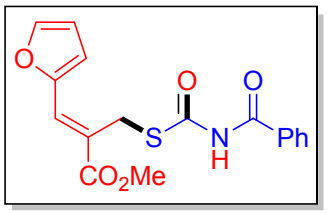
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(naphthalen-1-yl)acrylate (7a):**

White solid (95%, 192.3 mg); m.p. 161–163 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.81 (s, 3H), 4.17 (s, 2H), 7.51 (t, 2H, *J* = 7.2 Hz), 7.56 (m, 2H), 7.64 (m, 2H), 7.94 (t, 6H, *J* = 10.0 Hz), 8.09 (s, 1H), 11.93 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 26.9, 52.4, 126.5, 126.8, 127.1, 127.4, 127.5, 127.6, 128.3, 128.4, 128.5, 128.6, 129.8, 131.9, 132.7, 133.0, 133.2, 141.8, 166.7, 167.0, 169.7; IR (KBr): 3439, 2950, 2920, 2853, 1704, 1694, 1638, 1510, 1432, 1259, 1064 cm^{-1}; HRMS (ESI): calcd. for $C_{23}H_{20}NO_4S^+$ [M + H$^+$] 406.1108; found 406.1118.



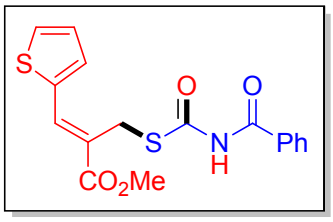
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-cyclohexylacrylate (8a):**

Pale yellow gummy (73%, 131.7 mg); **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 1.24 (m, 4H), 1.47 (m, 2H), 1.77 (t, 2H, J = 9.2 Hz) 1.89 (d, 2H, J = 13.2 Hz), 2.37 (m, 1H) 3.83 (s, 3H), 4.11 (s, 2H), 7.41 (m, 5H), 7.88 (s, 1H), 9.50 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 25.4, 25.6, 27.7, 28.9, 45.3, 52.5, 126.2, 128.8, 129.4, 129.6, 134.6, 143.6, 167.4, 171.2, 175.8; IR (KBr): 3453, 2955, 2922, 2838, 1729, 1663, 1605, 1435, 1257, 1031cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{24}NO_4S^+$ [M + H^+] 362.1421; found 362.1427.



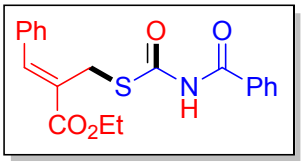
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(furan-2-yl)acrylate (9a):**

Yellow solid (81%, 139.7 mg); m.p. 142–144 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 3.83 (s, 3H), 4.36 (s, 2H), 7.11 (dd, 1H, J_1 = 4.8 Hz, J_2 = 5.2 Hz), 7.38 (d, 1H, , J = 3.6 Hz), 7.48 (t, 2H, , J = 7.6 Hz), 7.53 (d, 1H, J = 4.8 Hz), 7.59 (t, 1H, , J = 14.4 Hz), 7.94 (d, 2H, J = 7.6 Hz), 8.01 (s, 1H), 9.72 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 28.3, 52.7, 122.0, 127.9, 128.0, 129.2, 130.3, 131.2, 131.8, 133.6, 135.8, 137.5, 165.8, 167.6, 172.2; IR (KBr): 3434, 2952, 2925, 2853, 1699, 1662, 1636, 1468, 1436, 1257, 1207, 1072 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{16}NO_5S^+$ [M + H^+] 346.0744; found 346.0745.



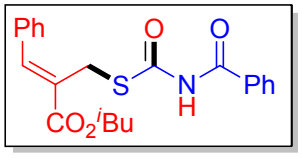
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(thiophen-2-yl)acrylate (10a):**

Brown solid (83%, 150.2 mg); m.p. 164–166 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 3.71 (s, 3H), 4.35 (s, 2H), 6.40 (dd, 1H, J_1 = 3.6 Hz, J_2 = 3.6 Hz), 6.65 (d, 1H, , J = 3.2 Hz), 7.39 (t, 2H, , J = 7.6 Hz), 7.48 (m, 3H), 7.84 (d, 2H, J = 7.6 Hz), 9.59 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 28.3, 52.7, 122.0, 127.9, 128.0, 128.1, 129.2, 131.2, 131.8, 133.6, 135.8, 137.5, 165.8, 167.6, 172.2; IR (KBr): 3439, 2952, 2924, 2853, 1700, 1661, 1633, 1506, 1472, 1259, 1191,1020 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{16}NO_4S_2^+$ [M + H^+] 362.0515; found 363.0520.



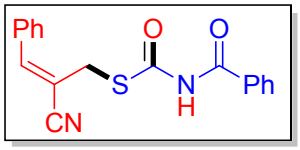
***Z*-Ethyl 2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (11a):**

White solid (94%, 173.4 mg); m.p. 149–151 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 1.28 (t, 3H, J = 7.2 Hz), 4.05 (s, 2H), 4.24 (q, 2H, J = 7.2 Hz), 7.48 (m, 7H), 7.63 (t, 1H, J = 7.2 Hz), 7.79 (s, 1H), 7.94 (d, 2H, J = 7.2 Hz), 11.91 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 14.1, 26.9, 61.1, 127.0, 128.4, 128.6, 128.9, 129.4, 129.5, 131.8, 133.2, 134.3, 141.7, 166.4, 166.7, 169.6; IR (KBr): 3437, 2955, 2921, 2851, 1708, 1696, 1632, 1462, 1260, 1199, 1074 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{20}NO_4S^+$ [M + H^+] 370.1108; found 370.1116.



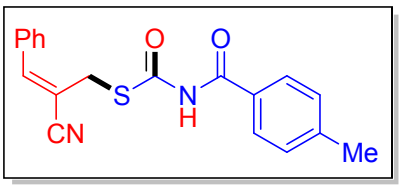
***Z*-Isobutyl 2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (12a):**

White solid (89%, 165.9 mg); m.p. 168–170 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 0.94 (s, 3H), 0.96 (s, 3H), 1.98 (m, 1H), 3.99 (d, 2H, *J* = 6.4 Hz) 4.06 (s, 2H), 7.49 (m, 7H), 7.64 (t, 1H, *J* = 7.2 Hz), 7.81 (s, 1H), 7.95 (t, 2H, *J* = 7.2 Hz), 11.92 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 18.9. 26.9, 27.4, 70.8, 126.9, 128.4, 128.6, 128.8, 129.4, 129.5, 131.8, 133.2, 134.2, 141.8, 166.3, 166.6, 169.6; IR (KBr): 3436, 2962, 2921, 2851, 1711, 1694, 1636, 1511, 1467, 1259, 1193, 1068 cm^{-1}; HRMS (ESI): calcd. for $C_{22}H_{24}NO_4S^+$ [M + H$^+$] 398.1421; found 398.1426.



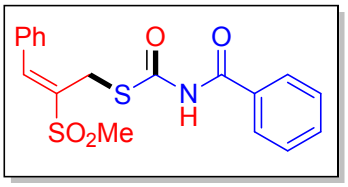
***Z*-S-(2-Cyano-3-phenylallyl) benzoylcarbamothioate (13a):**

White solid (77%, 123.6 mg); m.p. 138–140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 3.84 (s, 2H), 7.11 (s, 1H), 7.30 (s, 3H), 7.42 (m, 2H), 7.52 (m, 1H), 7.60 (d, 2H, *J* = 1.6 Hz), 7.84 (dd, 2H, *J* = 6.8 Hz), 9.65 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 34.7, 106.9, 118.0, 128.1, 129.0, 129.1, 129.2, 130.8, 131.6, 133.1, 133.8, 146.3, 166.0, 170.5; IR (KBr): 3448, 2922, 2851, 2215, 1697, 1661, 1643, 1505, 1470, 1180 cm^{-1}; HRMS (ESI): calcd. for $C_{18}H_{15}N_2O_2S^+$ [M + H$^+$] 323.0849; found 323.0855.



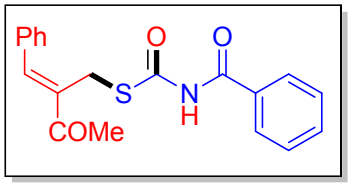
***Z*-S-(2-Cyano-3-phenylallyl) (4-methylbenzoyl)carbamothioate (13b):**

White solid (71%, 119.3 mg); m.p. 173–175 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 2.33 (s, 3H), 3.85 (s, 2H), 7.14 (s, 1H), 7.22 (d, 2H, *J* = 8.0 Hz), 7.32 (d, 4H, *J* = 3.2 Hz), 7.62 (d, 1H, *J* = 3.2 Hz), 7.73 (d, 2H, *J* = 8.0 Hz), 9.44 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 21.9, 34.7, 107.0, 118.1, 128.1, 128.7, 129.0, 129.1, 129.9, 130.8, 133.2, 144.9, 146.3, 165.8, 170.4; IR (KBr): 3437, 2986, 2928, 2853, 2212, 1691, 1638, 1610, 1462, 1263, 1198 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{17}N_2O_2S^+$ [M + H$^+$] 337.1005; found 337.1113.



***E*-S-(2-(Methylsulfonyl)-3-phenylallyl) benzoylcarbamothioate (14a):**

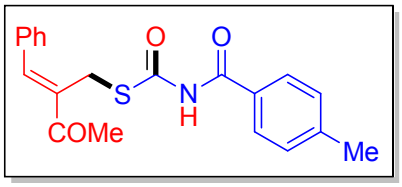
Gummy (69%, 129.4 mg); **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.20 (s, 3H), 4.24 (s, 2H), 7.50-7.55 (m, 5H), 7.63 (dd, 3H, J_1 = 7.6 Hz, J_2 = 7.6 Hz), 7.73 (s, 1H), 7.95 (t, 2H, *J* = 8.4 Hz), 12.04 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 25.8, 41.9, 128.4, 128.6, 129.1, 129.8, 130.3, 131.7, 132.6, 133.3, 136.7, 141.1, 166.8, 169.3; IR (KBr): 3418, 3259, 2955, 2925, 2855, 1693, 1628, 1487, 1302, 1256, 1178, 1120, 1025 cm^{-1}; HRMS (ESI): calcd. for $C_{18}H_{18}NO_4S_2^+$ [M + H$^+$] 376.0672; found 376.0679.



***Z*-S-(2-Benzylidene-3-oxobutyl) benzoylcarbamothioate (15a):**

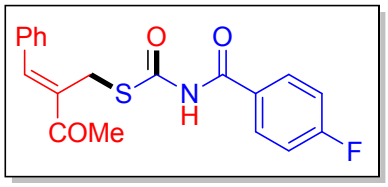
White solid (78%, 132.2 mg); m.p. 172–174 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 2.49 (s, 3H), 4.14 (s, 2H), 7.42 (dd, 5H, J_1 = 14.4 Hz, J_2 = 8.0 Hz), 7.49 (dd, 3H, J_1 = 10.8 Hz, J_2 = 12.4

Hz), 7.72 (s, 1H), 7.92 (t, 2H, J = 8.4 Hz), 9.91 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 26.0, 29.7, 128.0, 128.97, 128.99, 129.7, 130.2, 131.8, 133.5, 134.7, 135.6, 143.8, 165.9, 171.7, 198.4; IR (KBr): 3448, 2983, 2925, 2851, 1664, 1637, 14691381, 1255, 1178, 1024 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{18}NO_3S^+$ [M + H^+] 340.1002; found 340.1113.



***Z*-S-(2-Benzylidene-3-oxobutyl) (4-methylbenzoyl)carbamothioate (15b):**

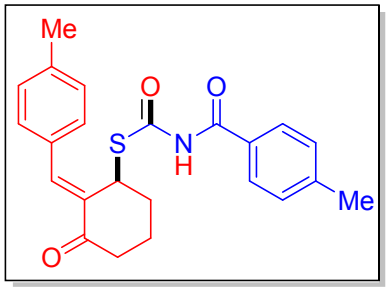
White solid (74%, 130.6 mg); m.p. 158–160 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 2.40 (s, 3H), 2.53 (s, 3H), 4.03 (s, 2H), 7.35 (d, 2H, J = 8.4 Hz), 7.48 (t, 1H, J = 7.2 Hz), 7.54 (dd, 2H, J_1 = 7.6 Hz, J_2 = 7.2 Hz), 7.65 (d, 2H, J = 7.2 Hz), 7.90 (s, 1H), 7.92 (d, 2H, J = 3.2 Hz), 11.82 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) 21.1, 25.5, 25.9, 127.5, 128.4, 128.8, 129.1, 129.4, 129.6, 134.7, 135.2, 143.3, 143.5, 166.4, 169.9, 198.6; IR (KBr): 3436, 2952, 2923, 2852, 1659, 1636, 1485, 1258, 1025 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{20}NO_3S^+$ [M + H^+] 354.1158; found 354.1160.



***Z*-S-(2-Benzylidene-3-oxobutyl) (4-fluorobenzoyl)carbamothioate (15e):**

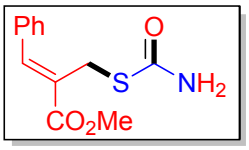
White solid (81%, 144.6 mg); m.p. 138–140 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 3.01 (s, 3H), 4.51 (s, 2H), 7.86 (t, 2H, J = 8.8 Hz), 7.96 (d, 1H, J = 7.2 Hz), 8.01 (t, 2H, J = 7.6 Hz), 8.12 (d, 2H, J = 7.2 Hz), 8.41 (s, 1H), 8.54-8.58 (m, 2H), 12.40 (s, 1H); **^{13}C NMR** (100 MHz,

DMSO-d_6): δ (ppm) 25.5, 25.8, 115.5, 115.7, 128.8, 129.5, 129.6, 131.3, 131.4, 134.7, 135.1, 143.3, 165.5, 169.9, 198.6; ^{19}F NMR (DMSO-d_6 +Hexafluorobenzene): δ (ppm) -108.49 (s); IR (KBr): 3432, 2975, 2922, 2851, 1668, 1630, 1453, 1256, 1025 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{17}FNO_3S^+$ [M + H$^+$] 358.0986; found 358.0989.



***Z*-S-(2-(4-Methylbenzylidene)-3-oxocyclohexyl) (4-methylbenzoyl)carbamothioate (16b):**

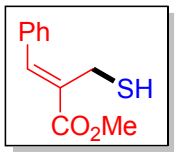
Gummy (55%, 108.1 mg); **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 0.83-0.90 (m, 3H), 1.91-1.97 (m, 1H), 2.03-2.11 (m, 1H), 2.32 (s, 3H), 2.40 (s, 3H), 2.73 (d, 1H, *J* = 13.6 Hz), 5.34 (s, 1H), 7.18 (d, 2H, *J* = 8.0 Hz), 7.24 (d, 1H, *J* = 7.6 Hz), 7.41 (d, 2H, *J* = 8.0 Hz), 7.56 (s, 1H), 7.80 (d, 2H, *J* = 8.0 Hz), 9.37 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 19.6, 21.6, 21.8, 29.9, 39.9, 44.3, 128.0, 129.0, 129.7, 129.9, 131.0, 131.9, 133.8, 139.6, 140.1, 144.7, 165.5, 170.5, 200.0; IR (KBr): 3439, 3125, 2956, 2922, 2857, 1668, 1635, 1566, 1453, 1256, 1025 cm^{-1}; HRMS (ESI): calcd. for $C_{23}H_{24}NO_3S^+$ [M + H$^+$] 394.1471; found 394.1479.



Methyl 2-((carbamoylthio)methyl)-3-phenylacrylate (1ab):

Pale Yellow solid (72%, 25.3 mg); m.p. 99–101 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 3.84 (s, 3H), 4.10 (s, 2H), 5.66 (s, 2H), 7.37 (m, 1H), 7.41 (m, 2H), 7.45 (d, 2H, *J* = 7.2 Hz), 7.81 (s, 1H) ; **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 28.0, 52.6, 127.2, 128.9, 129.5, 129.8, 134.6, 142.8,

167.8, 168.7 ; IR (KBr): 3459, 3327, 2950, 2924, 2854, 1702, 1662, 1629, 1384, 1268 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_{14}NO_3S^+$ [M + H^+] 252.0689; found 252.0692.

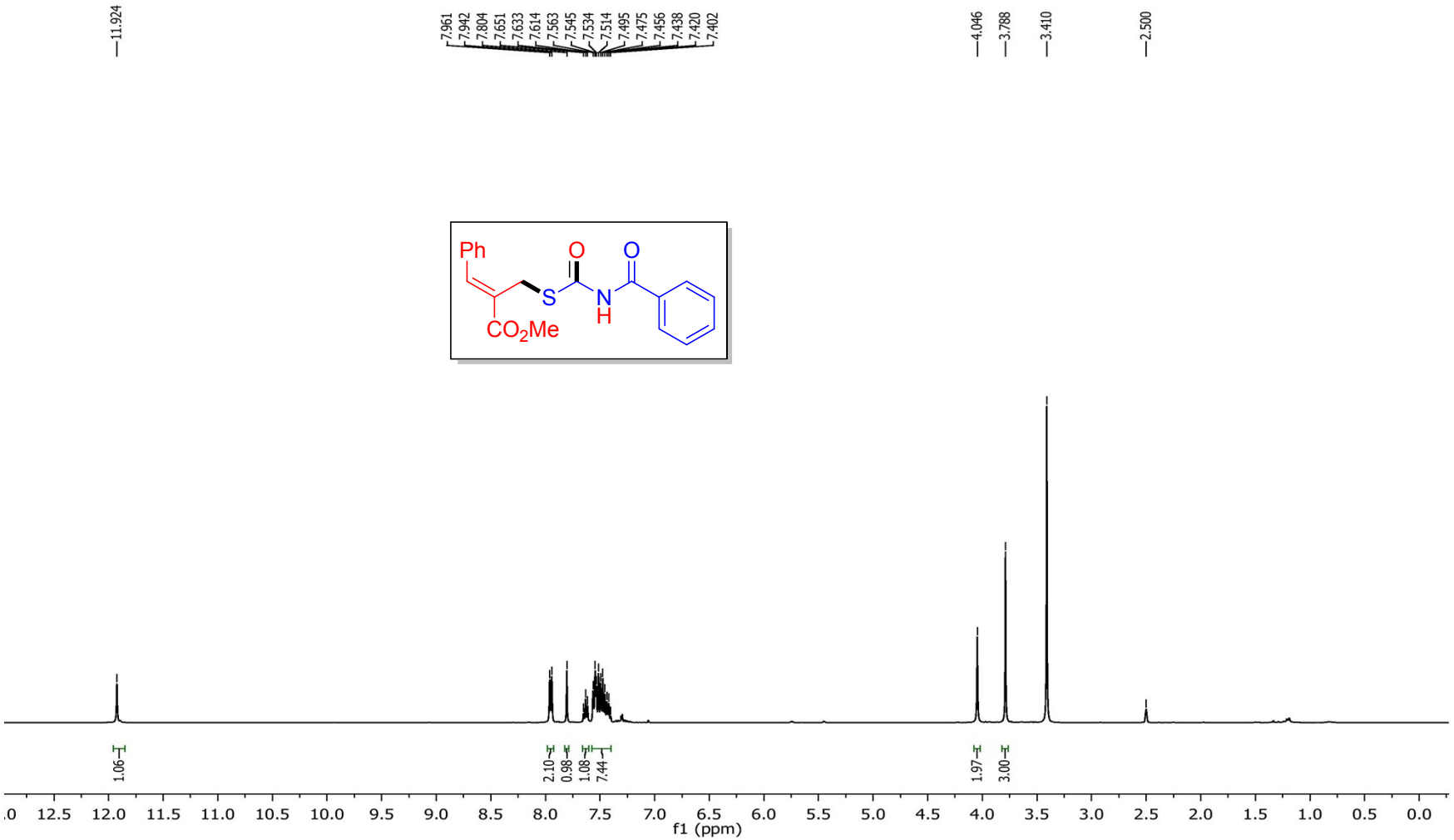


Methyl 2-(mercaptomethyl)-3-phenylacrylate (1ac):

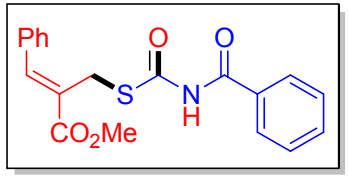
Gummy white solid (79%, 23.1 mg); **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 1.65 (s, 1H), 3.74 (s, 2H), 3.84 (s, 3H), 7.36 (d, 1H, *J* = 7.8 Hz), 7.40 (t, 2H, *J* = 7.8 Hz), 7.50 (d, 2H, *J* = 7.2 Hz), 7.76 (s, 1H) ; **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 30.3, 52.5, 128.8, 128.9, 129.2, 129.9, 135.0, 141.4, 168.0 ; IR (KBr): 3051, 2950, 2851, 2929, 1712, 1632, 1434, 1265,, 1080 cm^{-1}; HRMS (ESI): calcd. for $C_{11}H_{13}O_2S^+$ [M + H^+] 209.0631; found 209.0638.

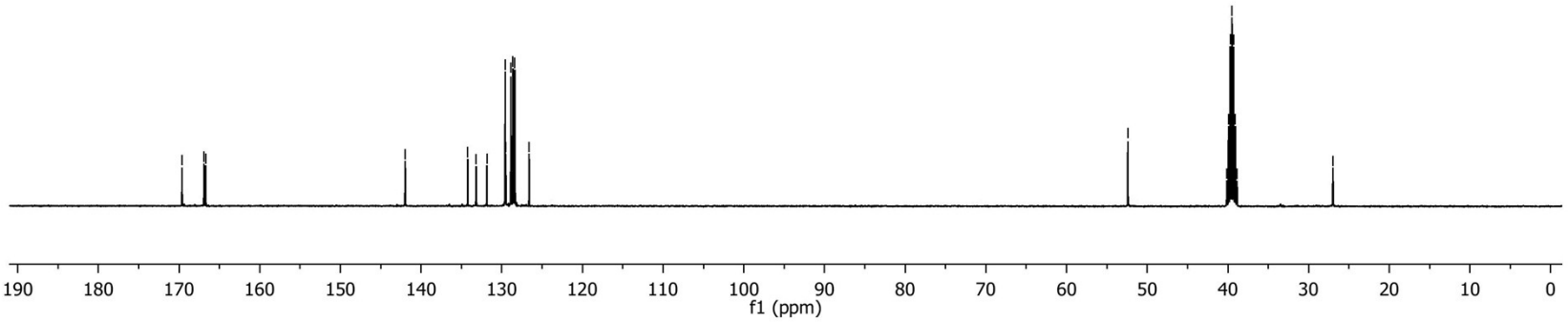
Spectra of products

***Z*-Methyl-2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (1a): ^{1}HNMR (400 MHz, DMSO-d_6)**

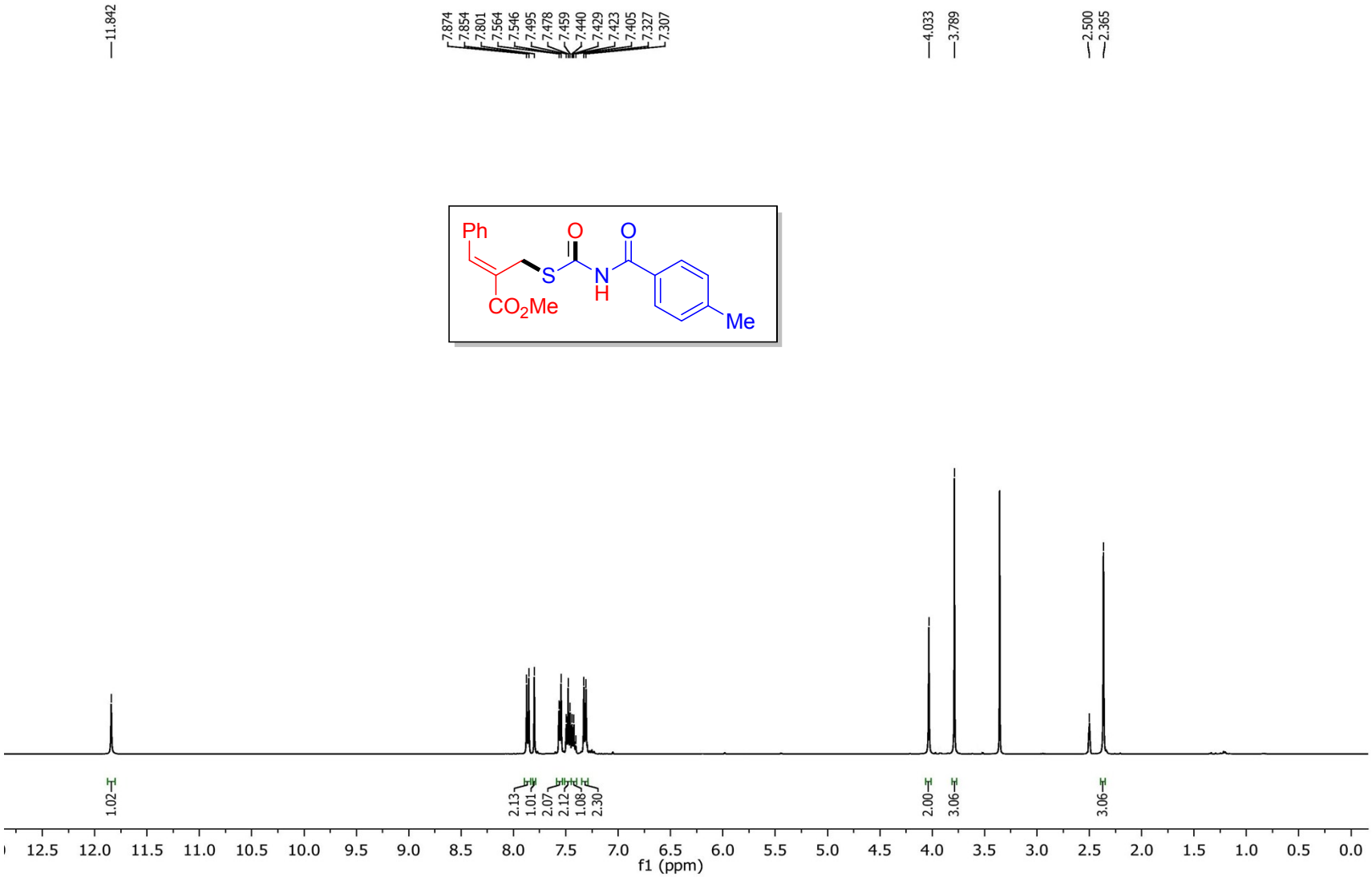


_Z_-Methyl-2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (1a): ^{13}CNMR (100 MHz, DMSO-d_6)

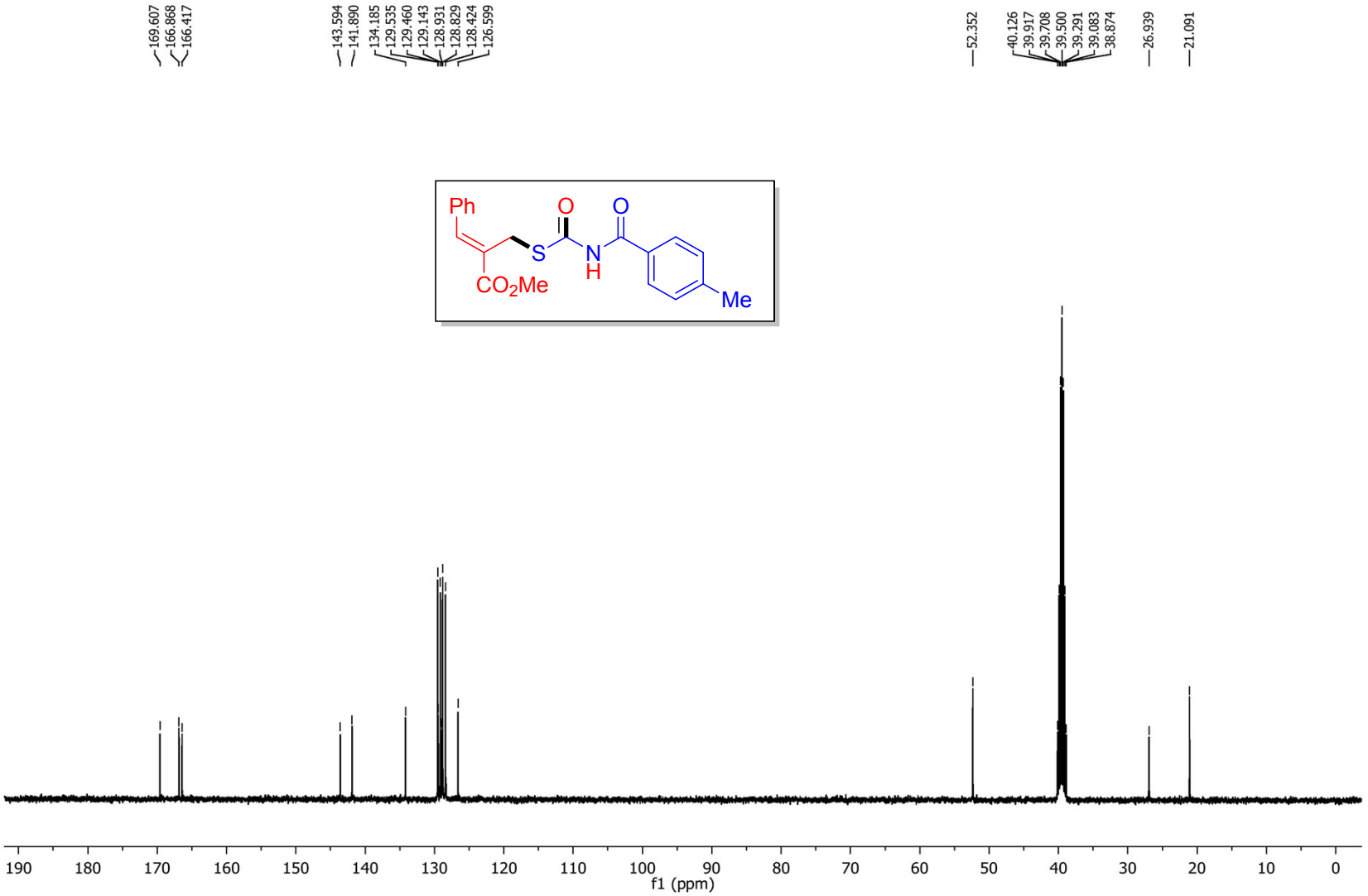




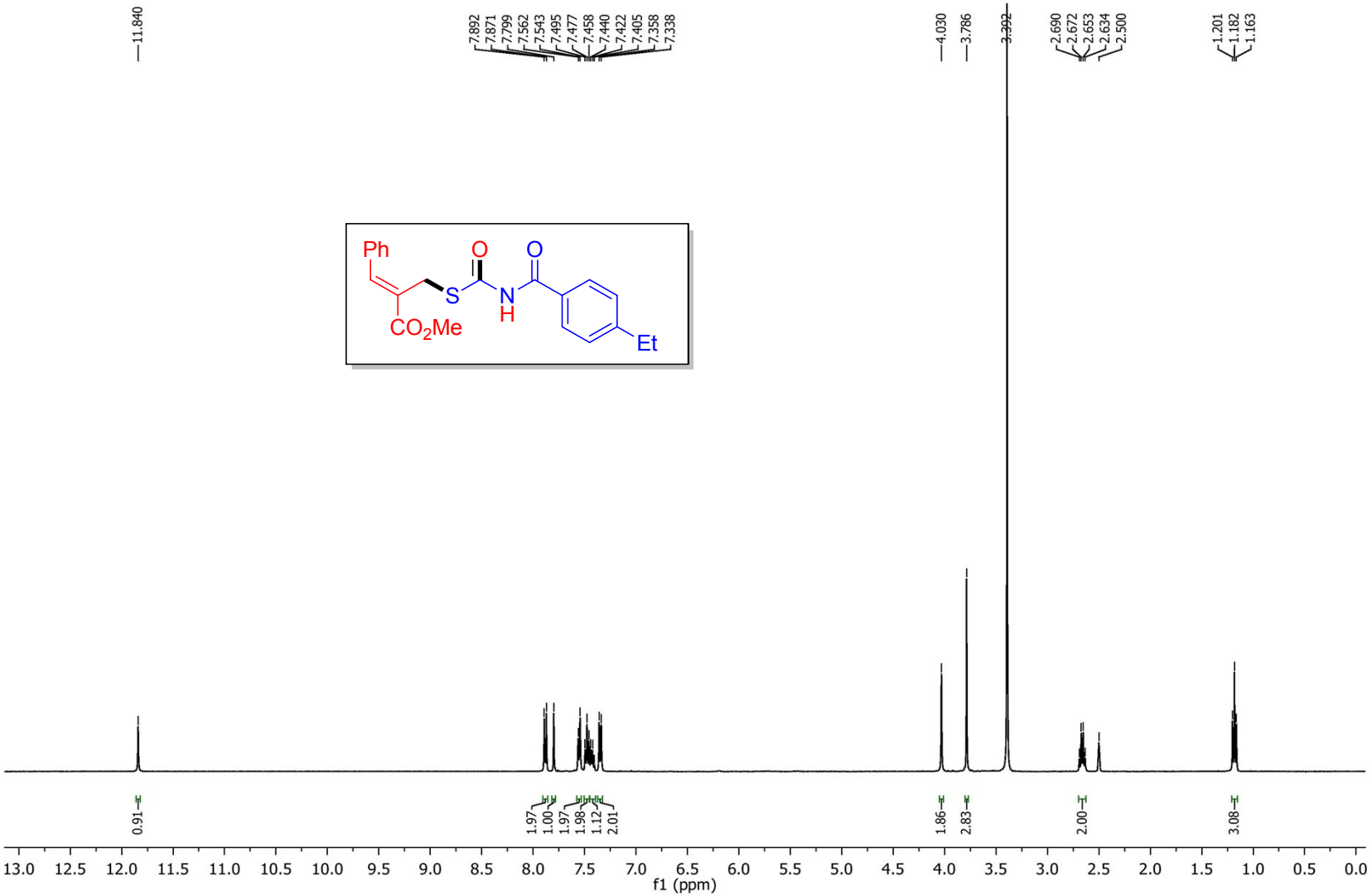
_Z_-Methyl 2-((((4-methylbenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1b): ^{1}HNMR (400 MHz, DMSO-d_6)



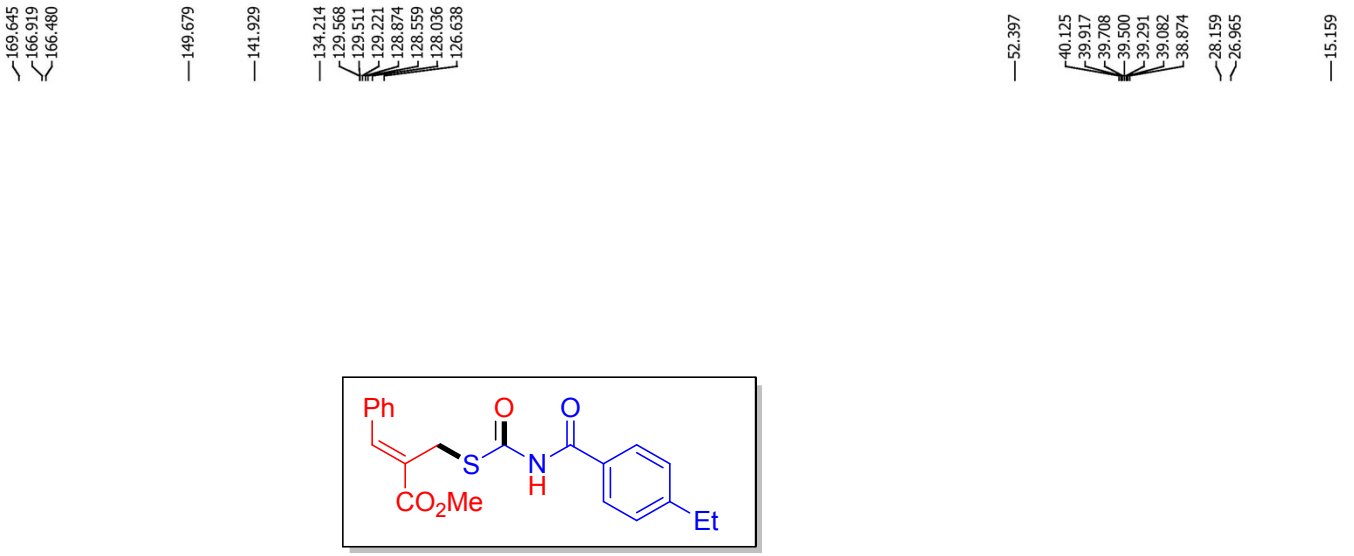
_Z_-Methyl 2-((((4-methylbenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1b): ^{13}CNMR (100 MHz, DMSO-d_6)



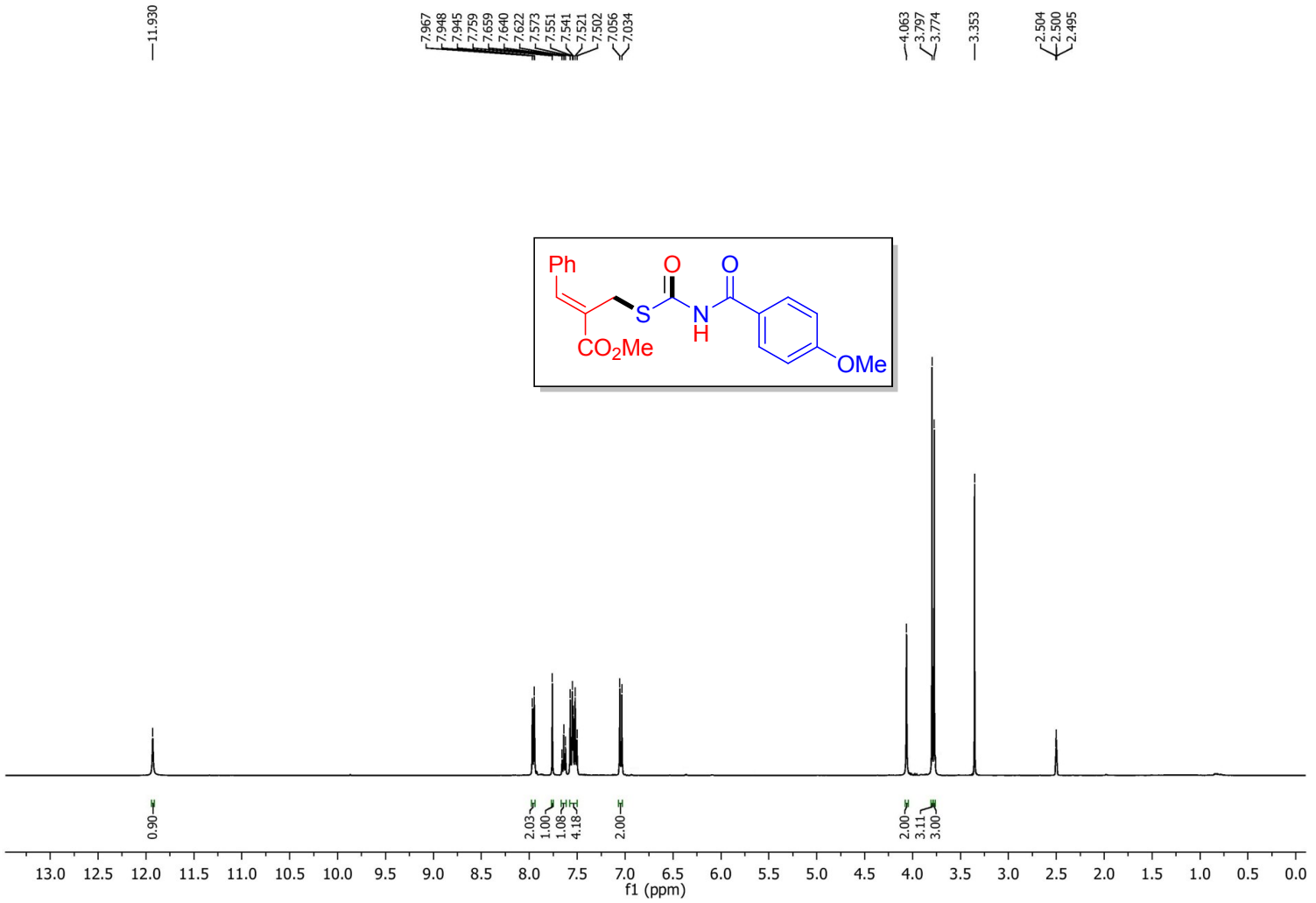
_Z_-Methyl 2-((((4-ethylbenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1c): ^{1}HNMR (400 MHz, DMSO-d_6)



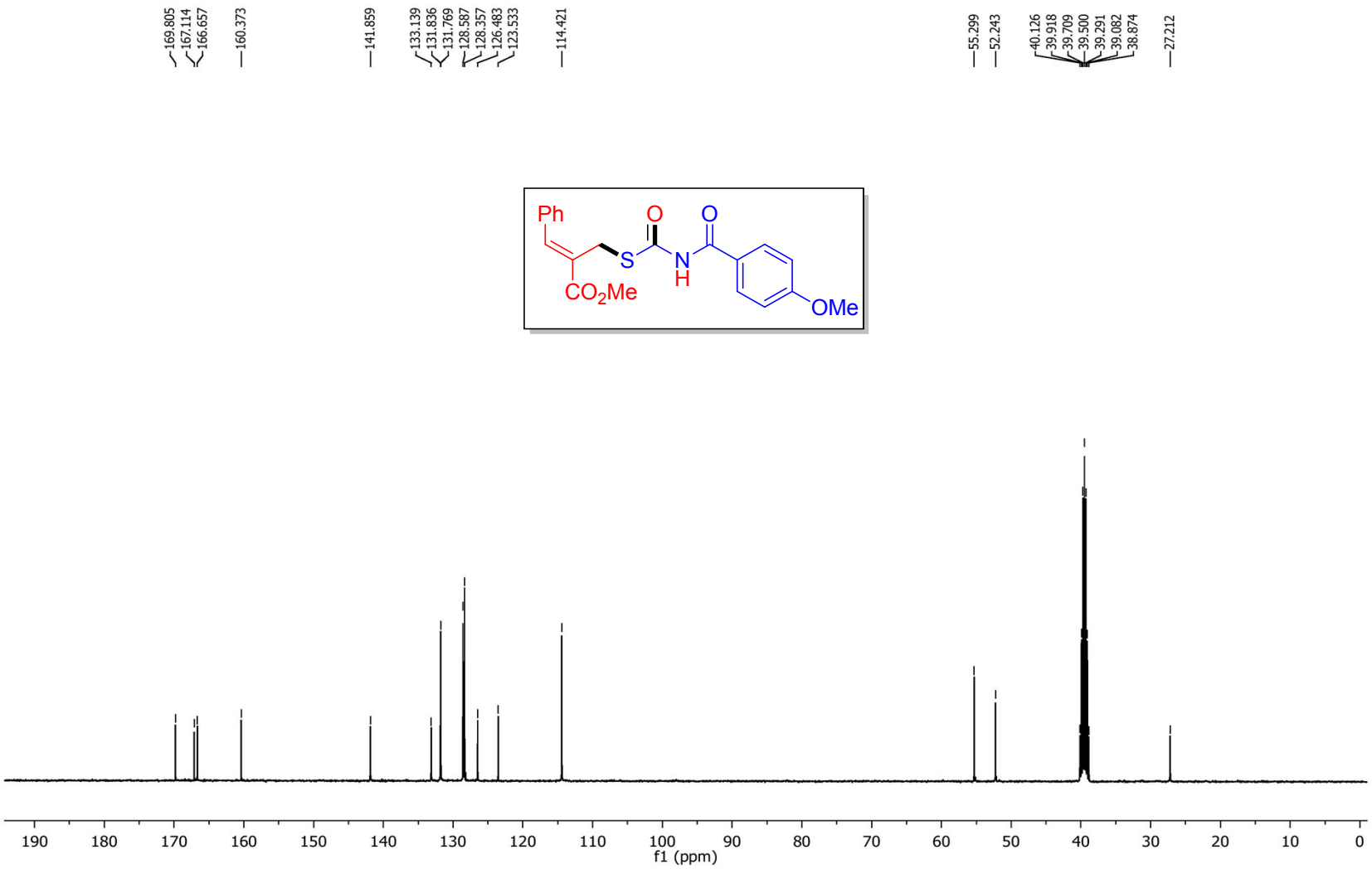
_Z_-Methyl 2-((((4-ethylbenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1c): ^{13}CNMR (100 MHz, DMSO-d_6)



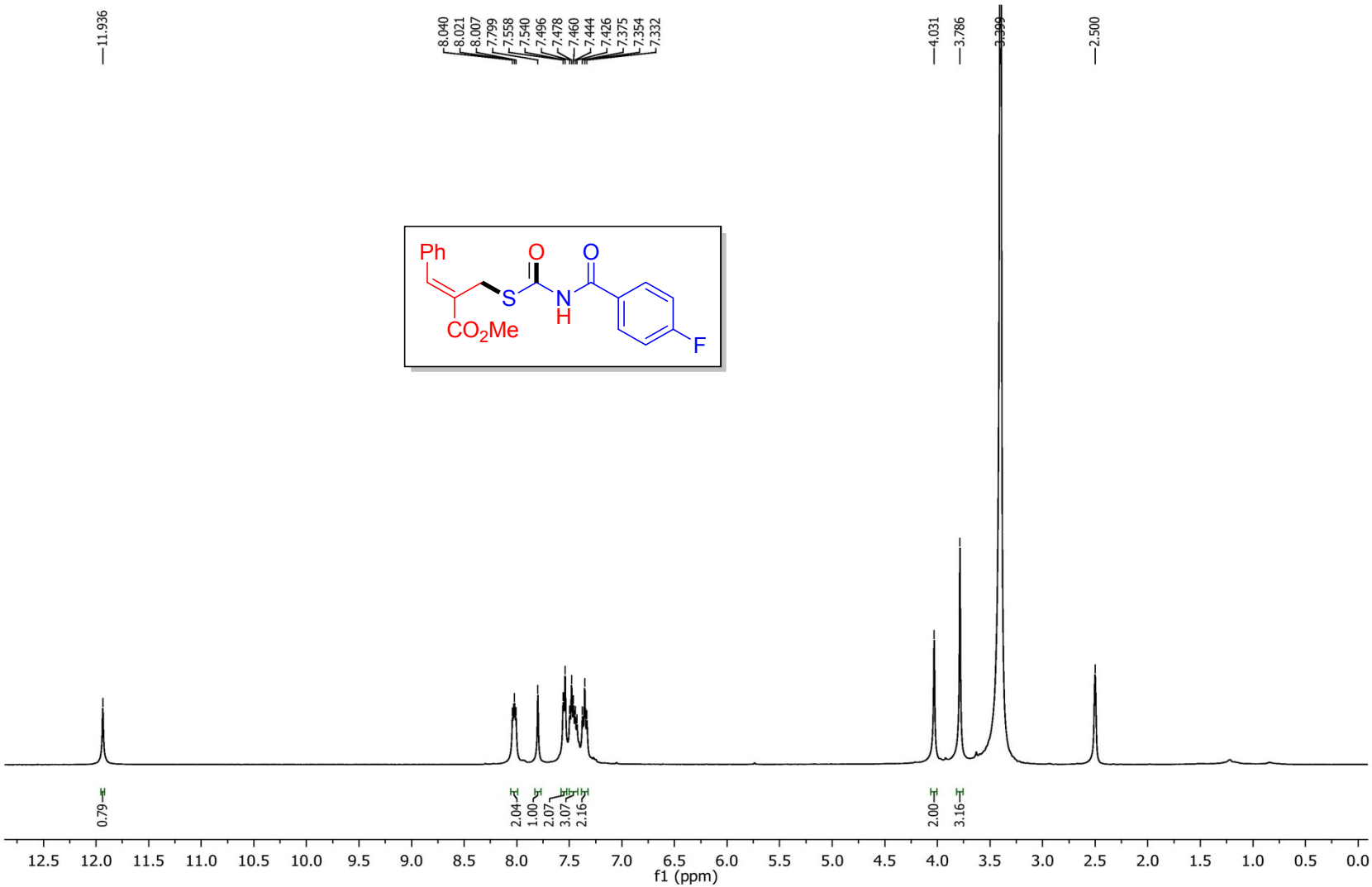
_Z_-Methyl 2-((((4-methoxybenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1d): ^{1}HNMR (400 MHz, DMSO-d_6)



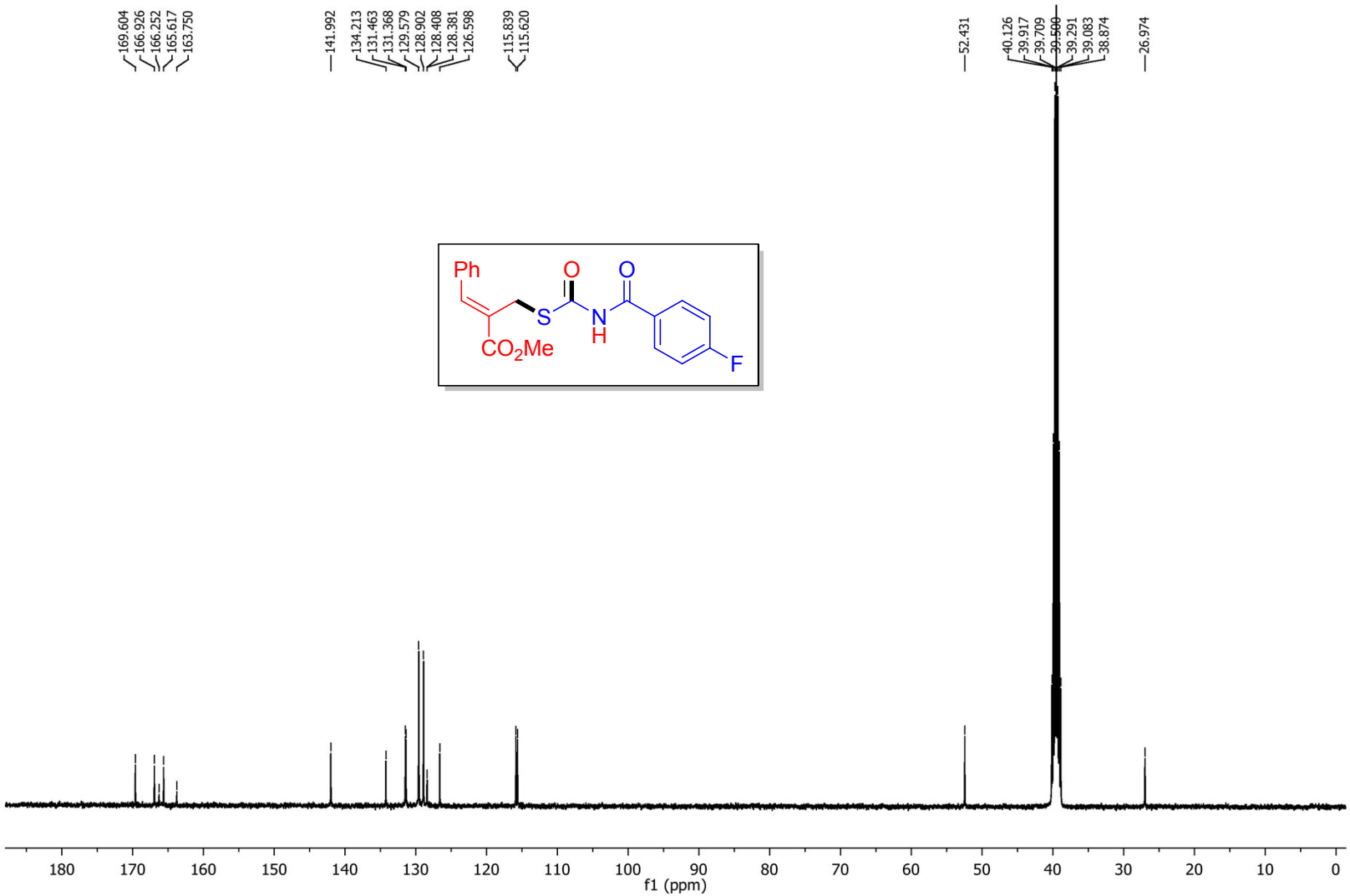
_Z_-Methyl 2-((((4-methoxybenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1d): ^{13}CNMR (100 MHz, DMSO-d_6)



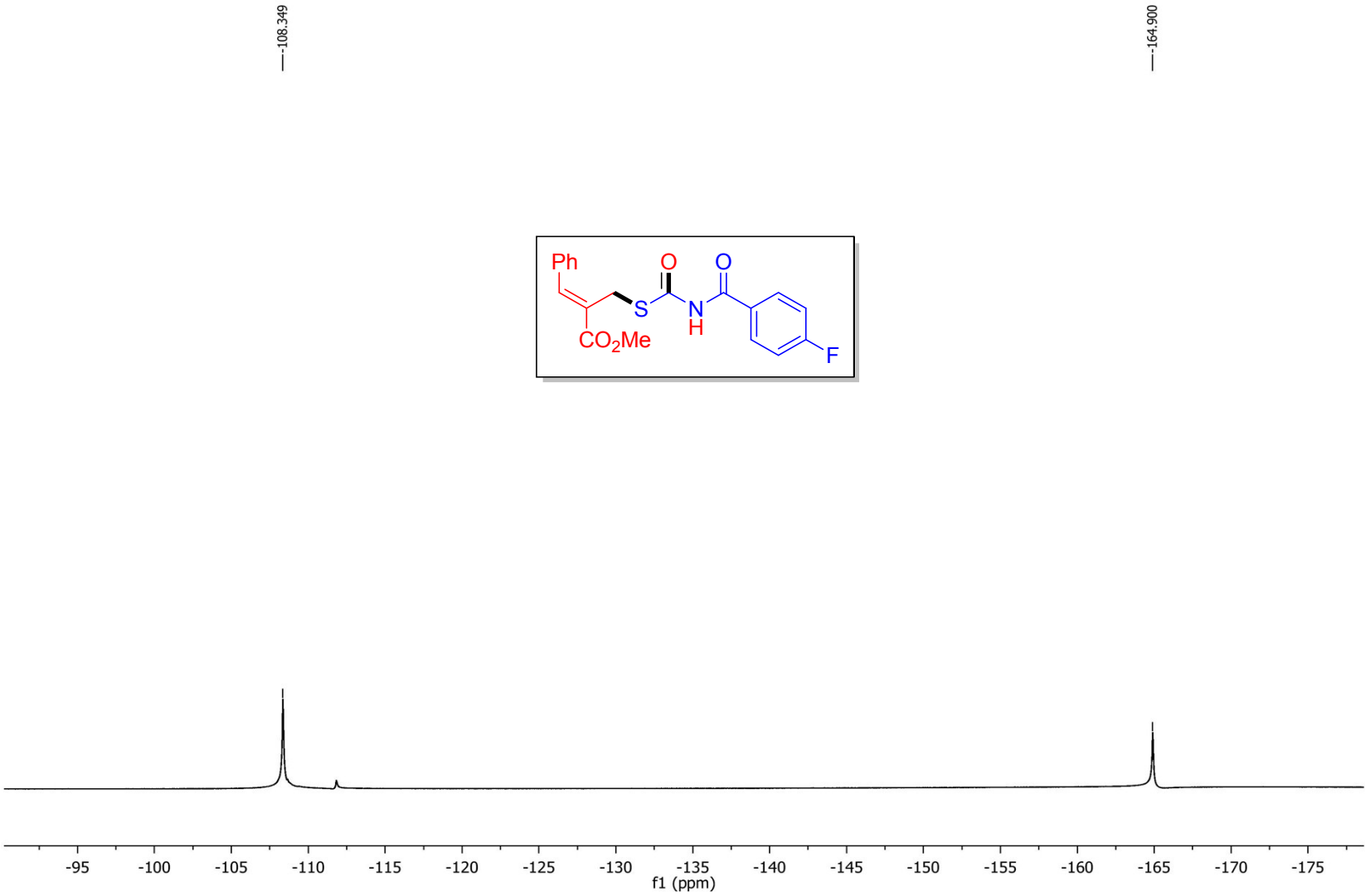
***Z*-Methyl 2-((((4-fluorobenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1e): ^{1}HNMR (400 MHz, DMSO-d_6)**



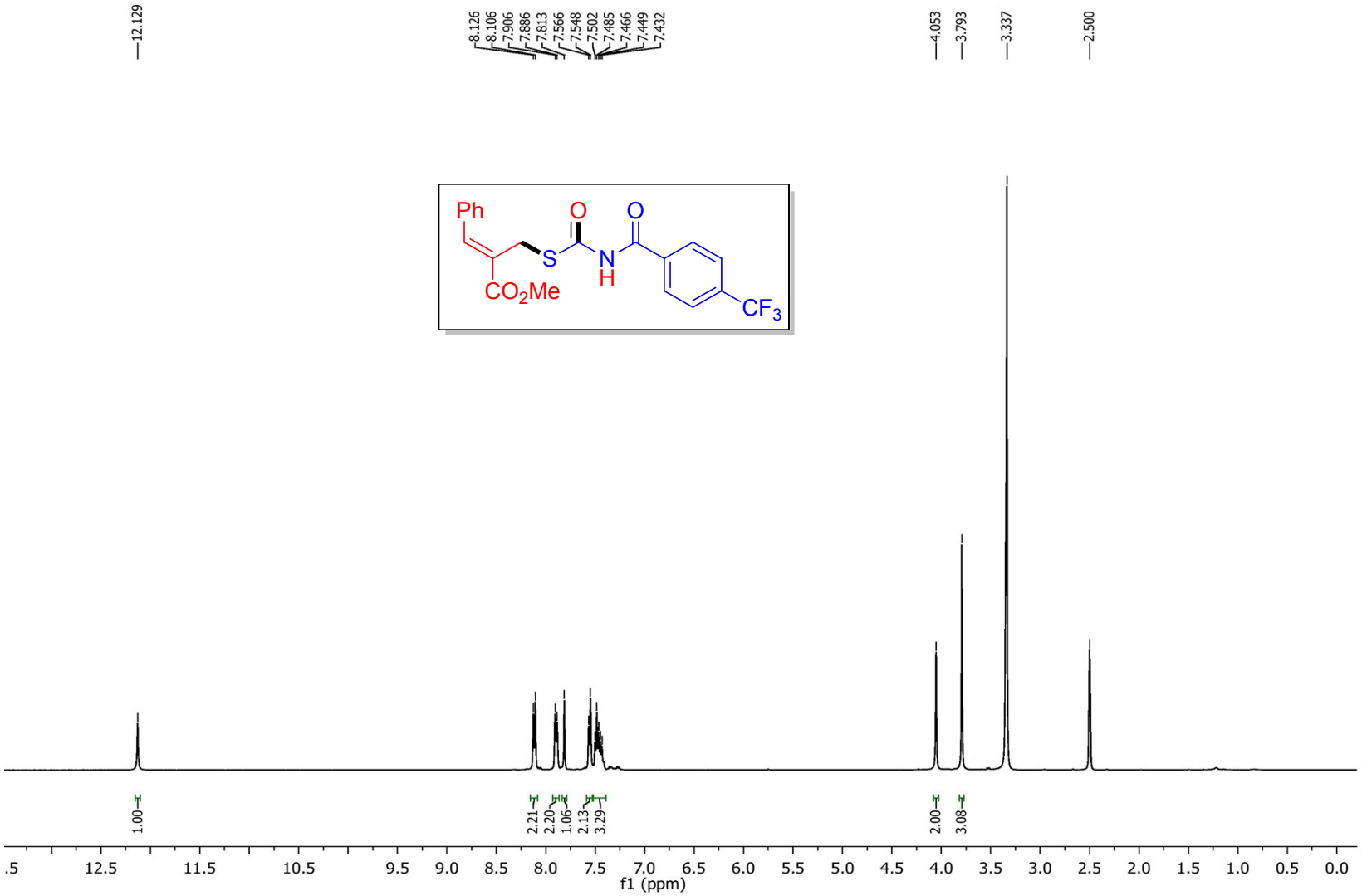
_Z_-Methyl 2-((((4-fluorobenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1e): ^{13}CNMR (100 MHz, DMSO-d$_6$)



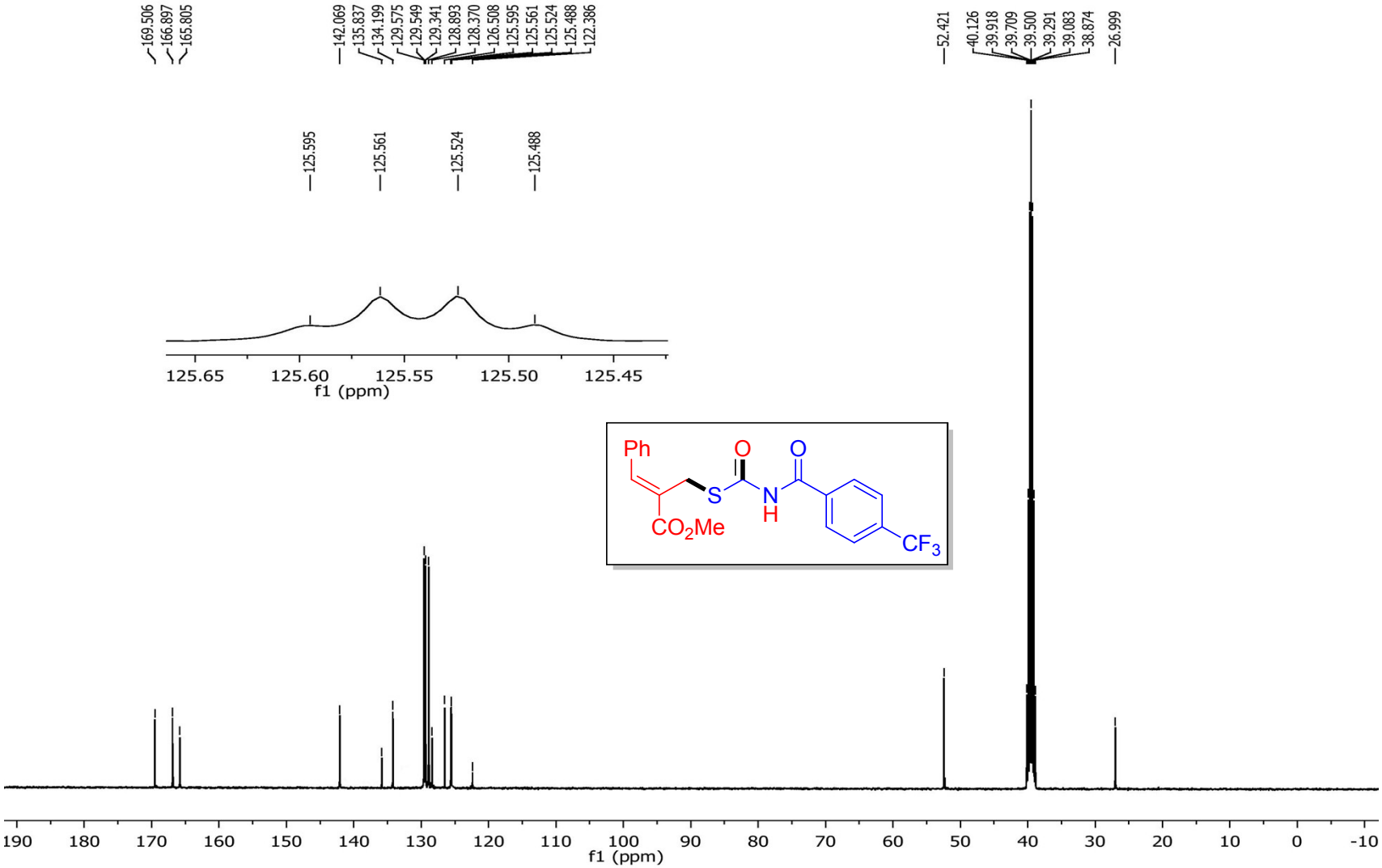
_Z_-Methyl 2-((((4-fluorobenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1e): ^{19}FNMR (DMSO-d_6 + C_6F_6)



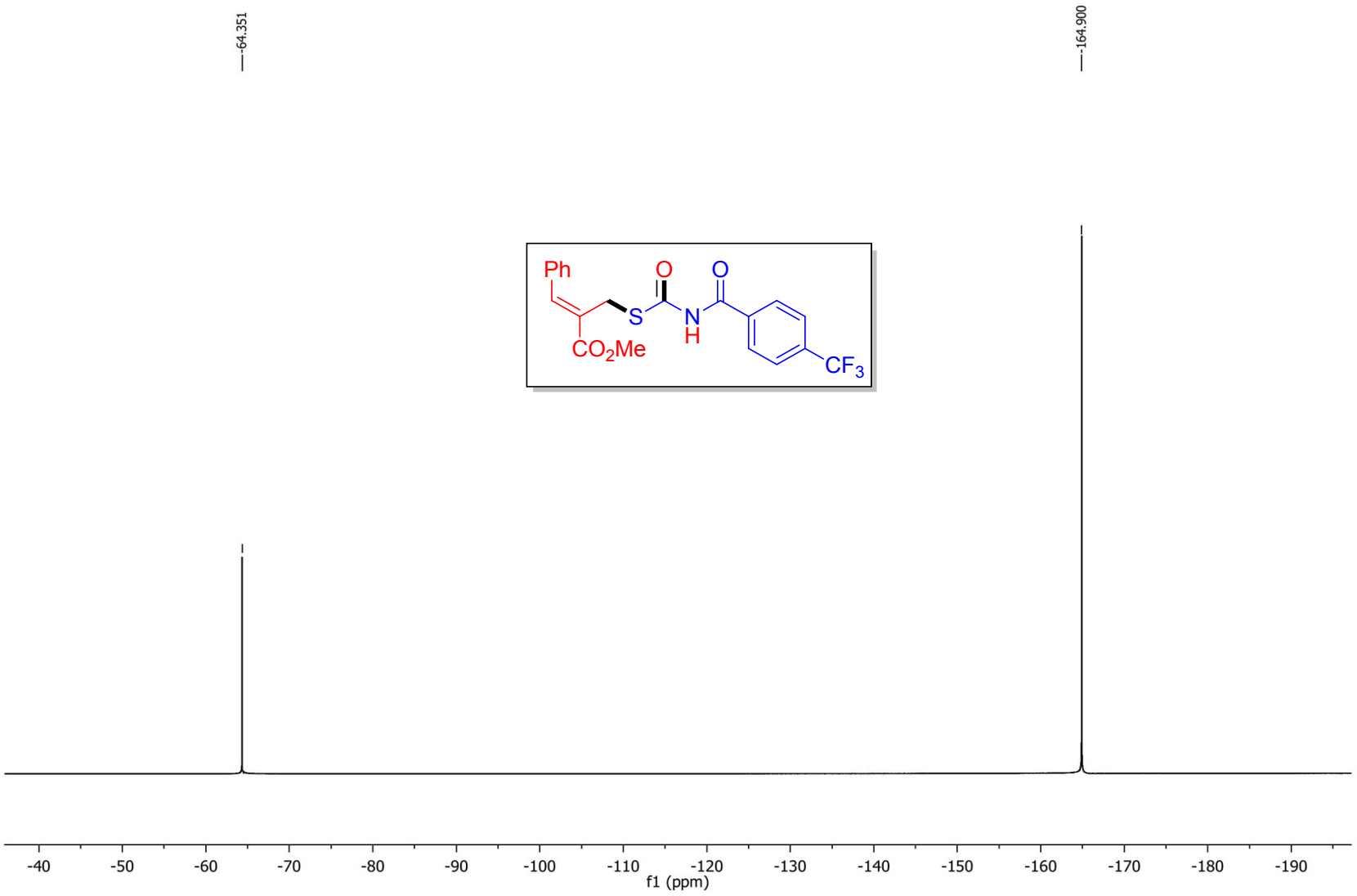
_Z_-Methyl 3-phenyl-2-((((4-(trifluoromethyl)benzoyl)carbamoyl)thio)methyl)acrylate (1f): ^{1}HNMR (400 MHz, DMSO-d_6)



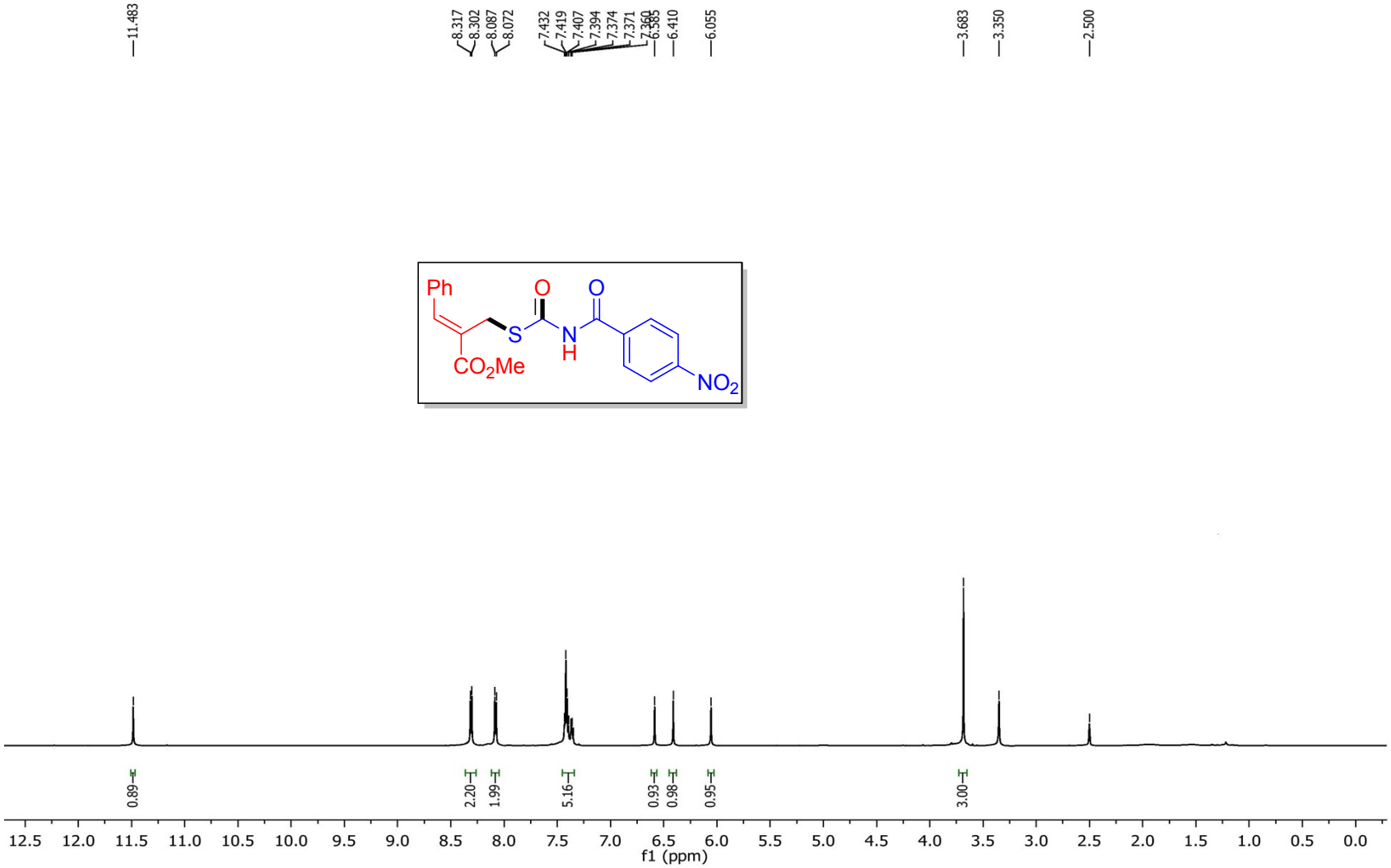
***Z*-Methyl 3-phenyl-2-((((4-(trifluoromethyl)benzoyl)carbamoyl)thio)methyl)acrylate (1f): ^{13}CNMR (100 MHz, DMSO-d_6)**



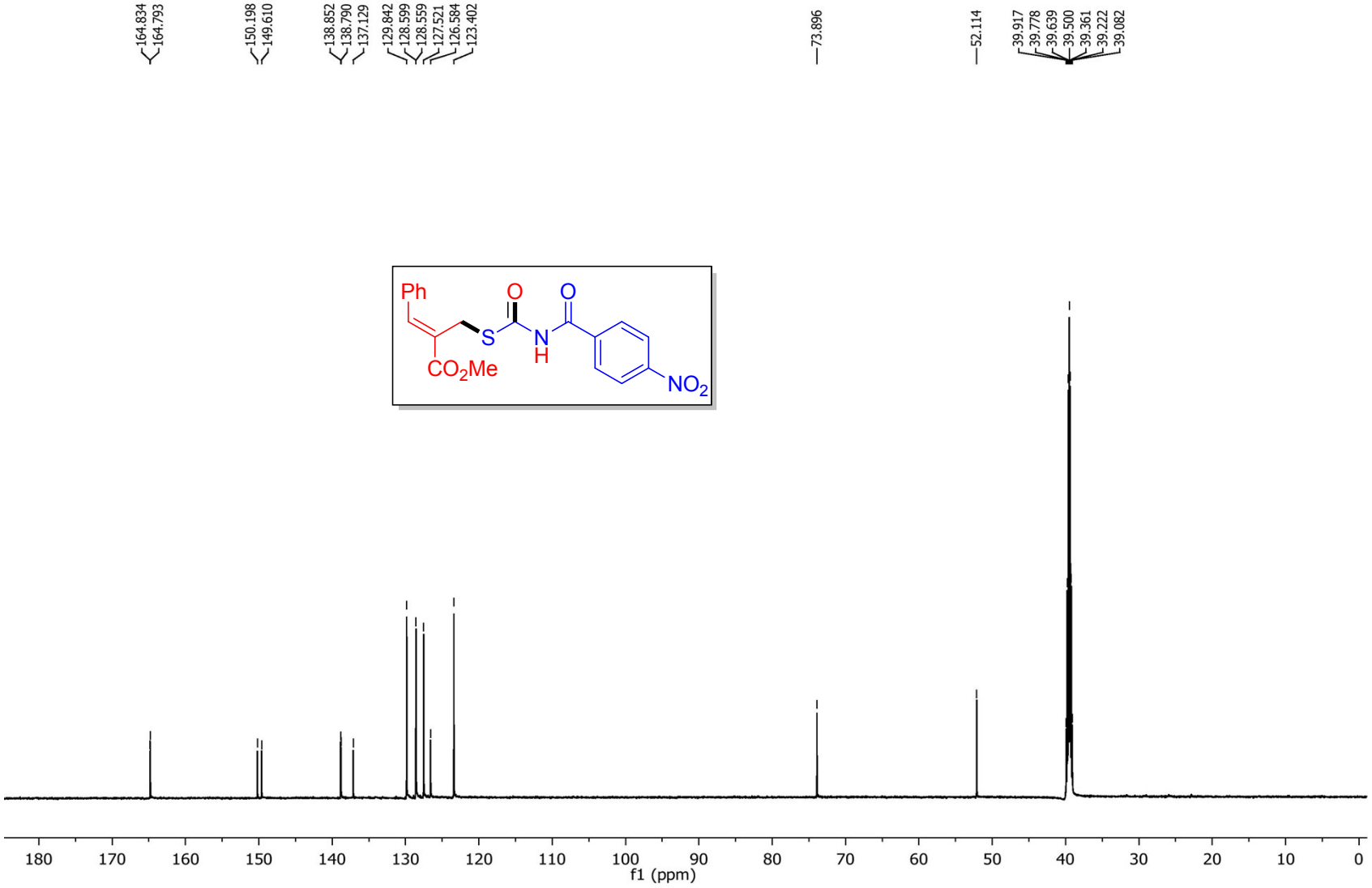
_Z_-Methyl 3-phenyl-2-((((4-(trifluoromethyl)benzoyl)carbamoyl)thio)methyl)acrylate (1f): ^{19}FNMR (DMSO-d_6 + C_6F_6)



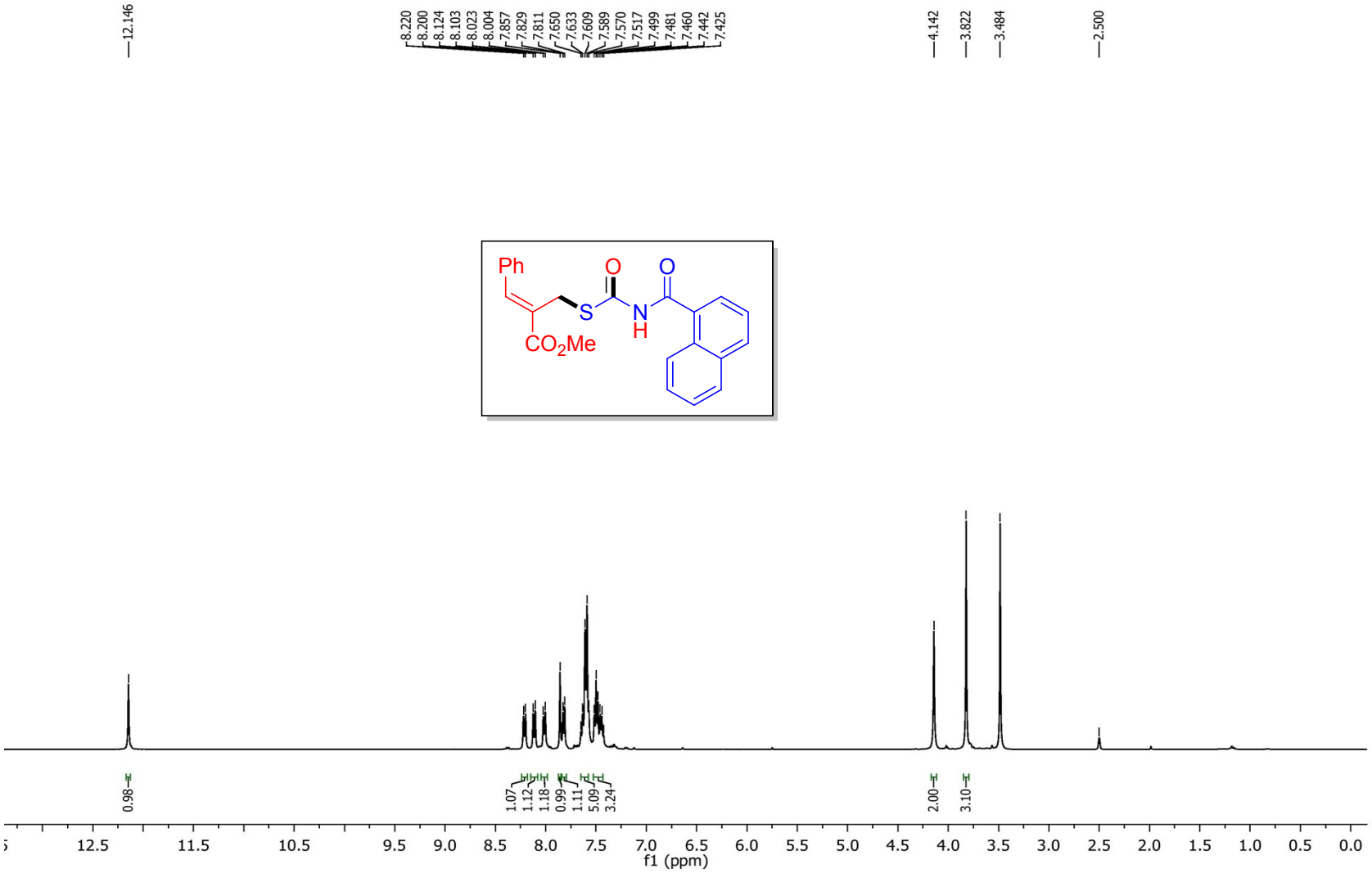
_Z_-Methyl 2-((((4-nitrobenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1g): ^{1}HNMR (400 MHz, DMSO-d_6)



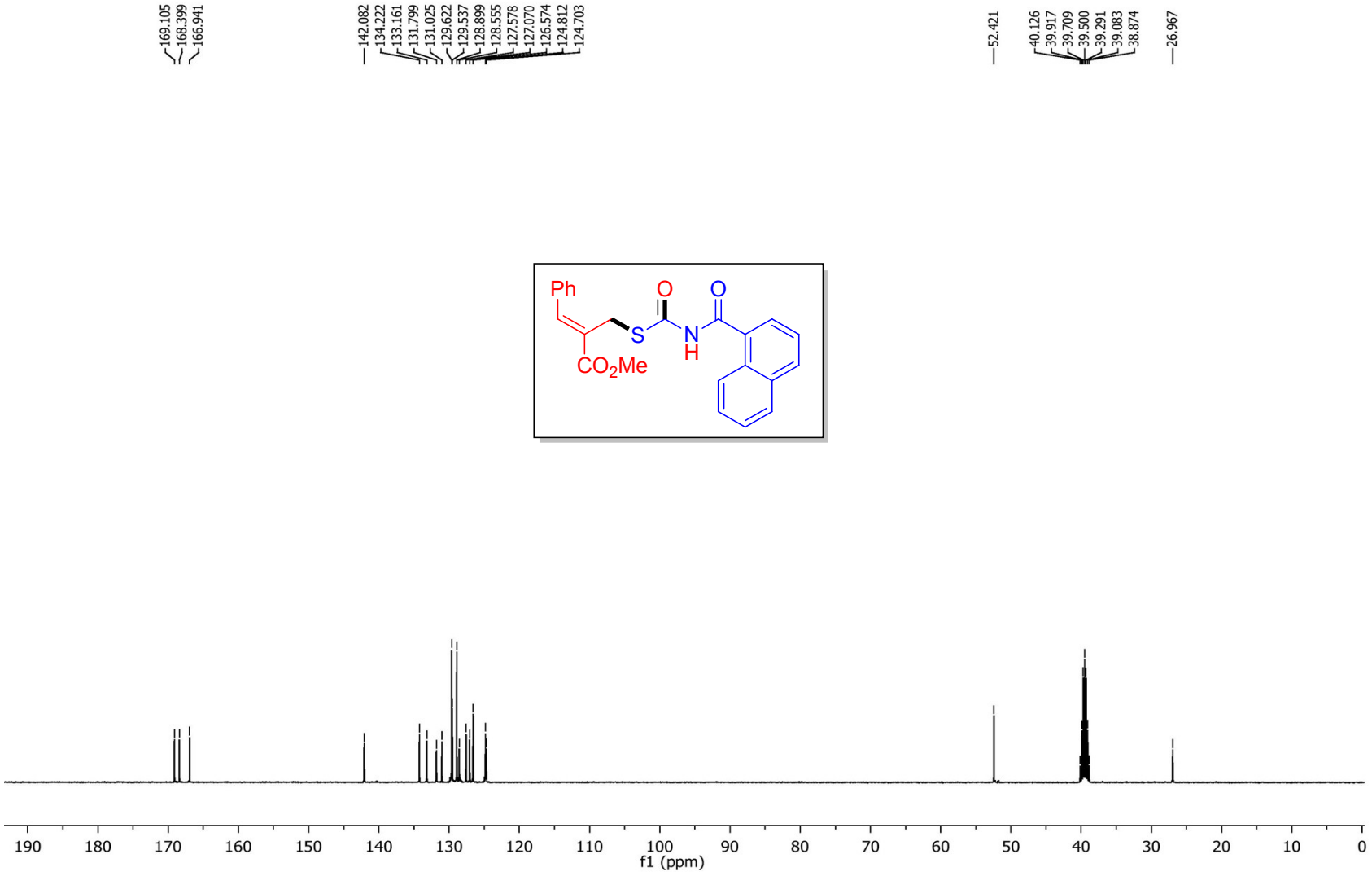
_Z_-Methyl 2-((((4-nitrobenzoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1g): ^{13}CNMR (100 MHz, DMSO-d$_6$)



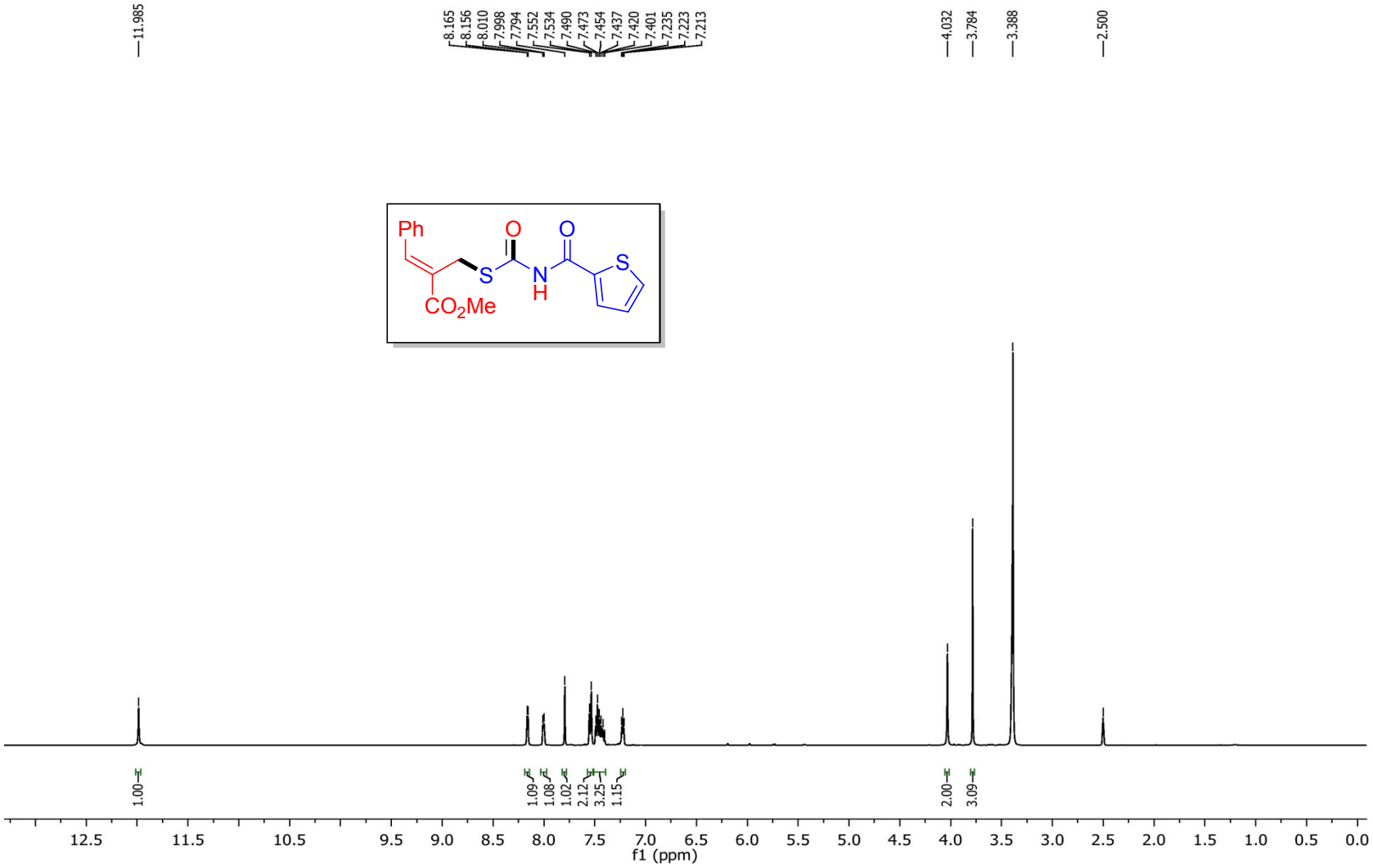
_Z_-Methyl 2-((((1-naphthoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1h): ^{1}HNMR (400 MHz, DMSO-d_6)



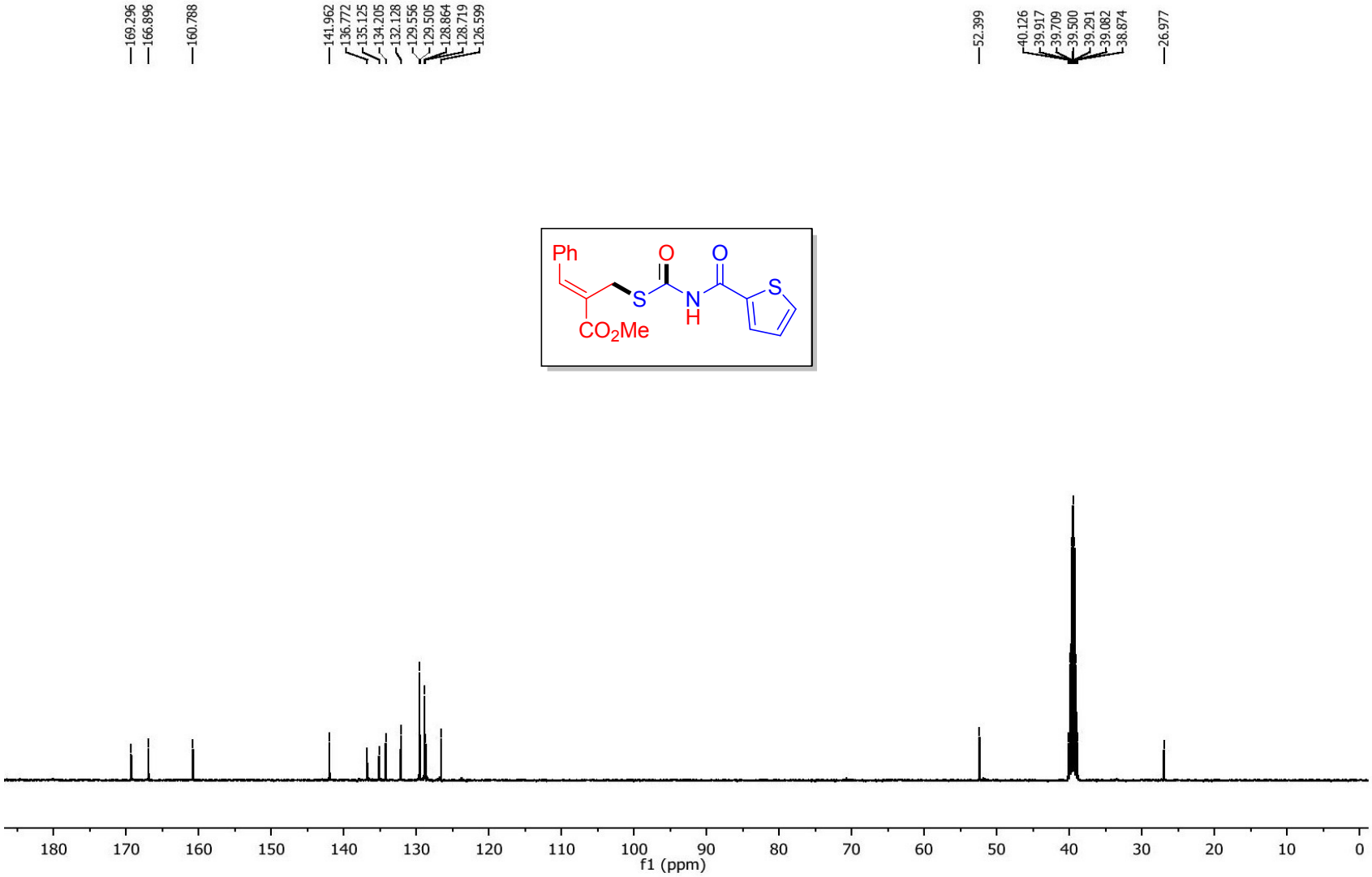
_Z_-Methyl 2-((((1-naphthoyl)carbamoyl)thio)methyl)-3-phenylacrylate (1h): ^{13}CNMR (100 MHz, DMSO-d_6)



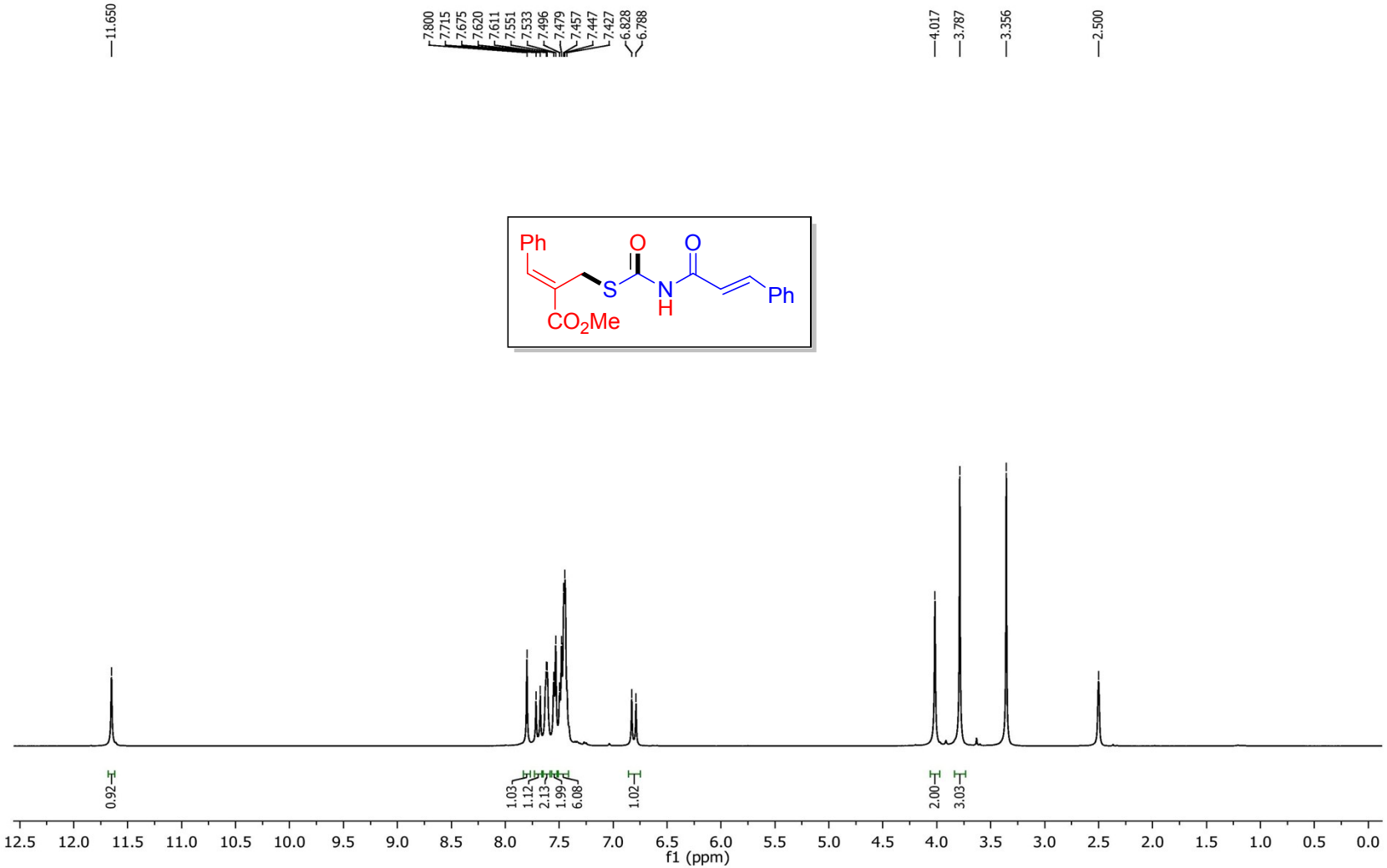
_Z_-Methyl 3-phenyl-2-((((thiophene-2-carbonyl)carbamoyl)thio)methyl)acrylate (1i): ^{1}HNMR (400 MHz, DMSO-d$_6$)



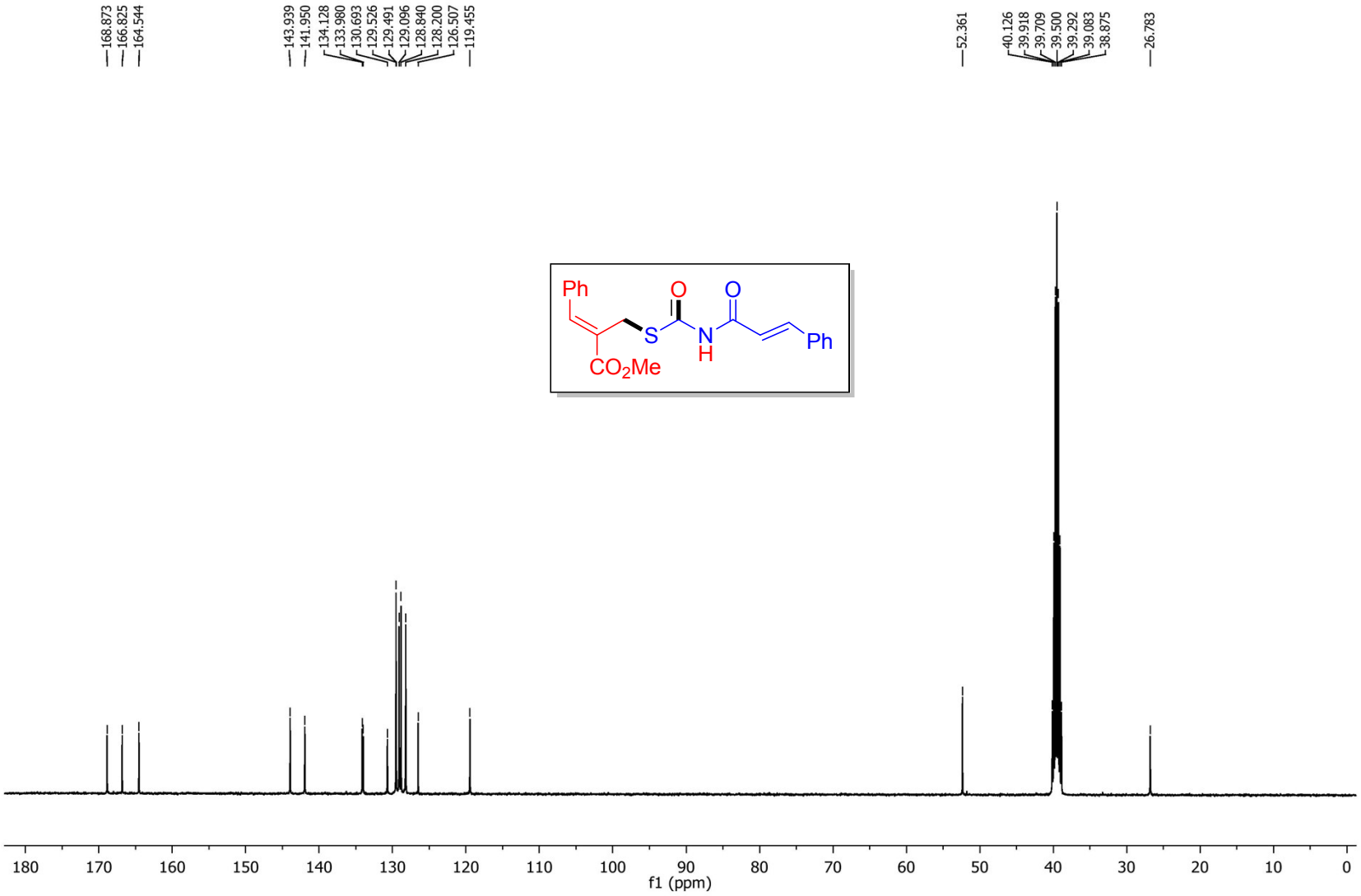
_Z_-Methyl 3-phenyl-2-((((thiophene-2-carbonyl)carbamoyl)thio)methyl)acrylate (1i): ^{13}CNMR (100 MHz, DMSO-d_6)



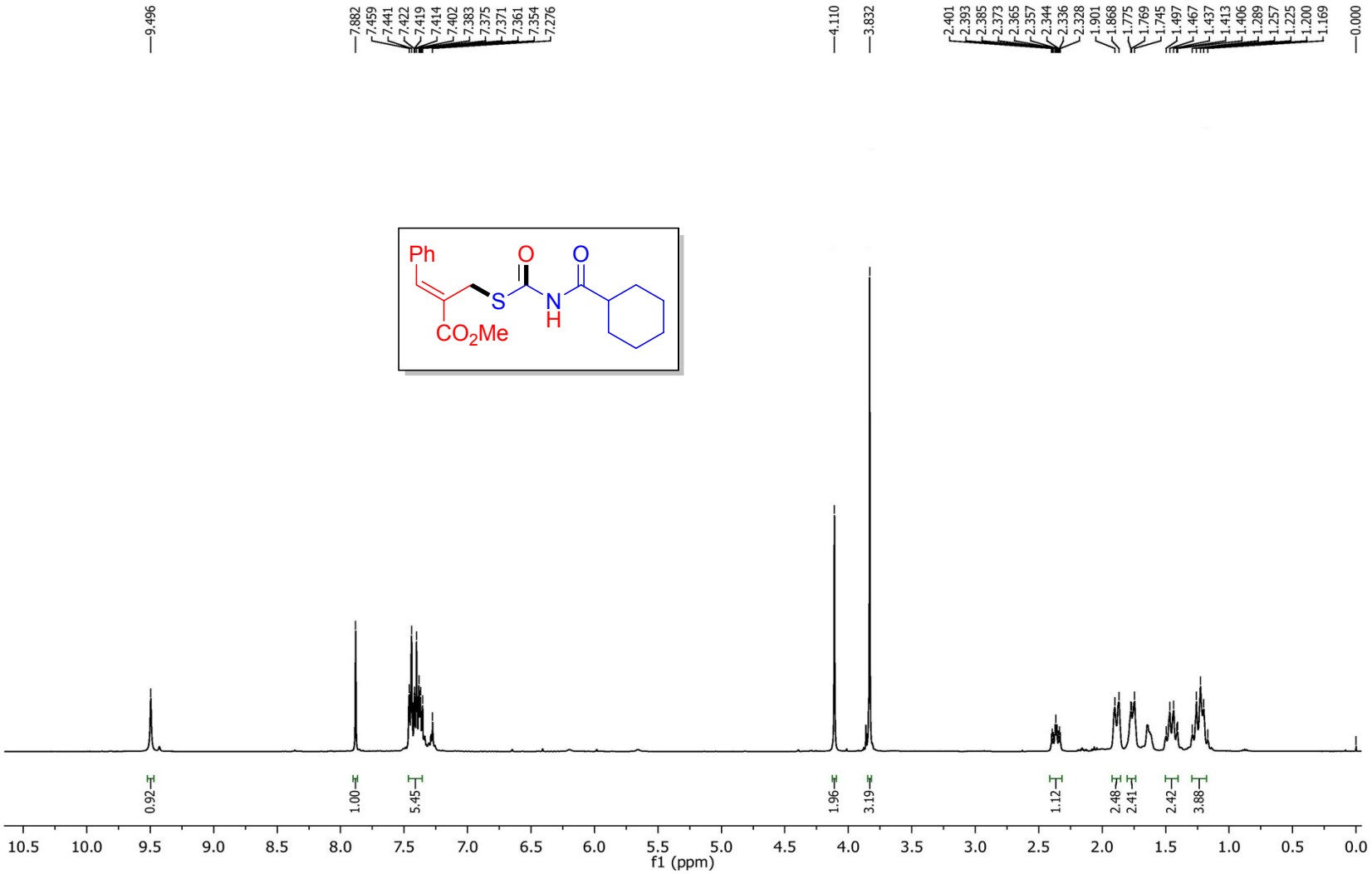
_Z_-Methyl 2-(((cinnamoylcarbamoyl)thio)methyl)-3-phenylacrylate (1j): ^{1}HNMR (400 MHz, DMSO-d_6)



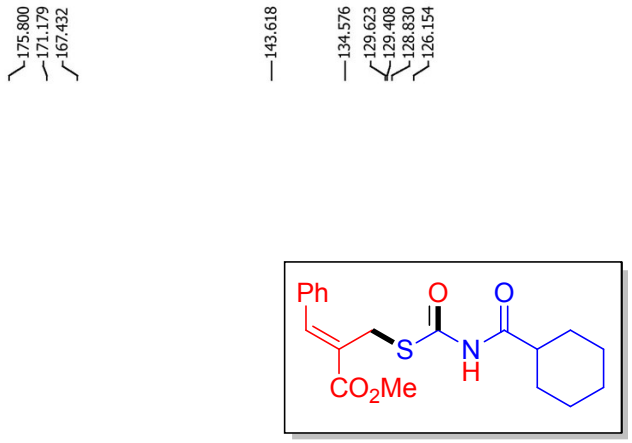
_Z_-Methyl 2-(((cinnamoylcarbamoyl)thio)methyl)-3-phenylacrylate (1j): ^{13}CNMR (100 MHz, DMSO-d_6)

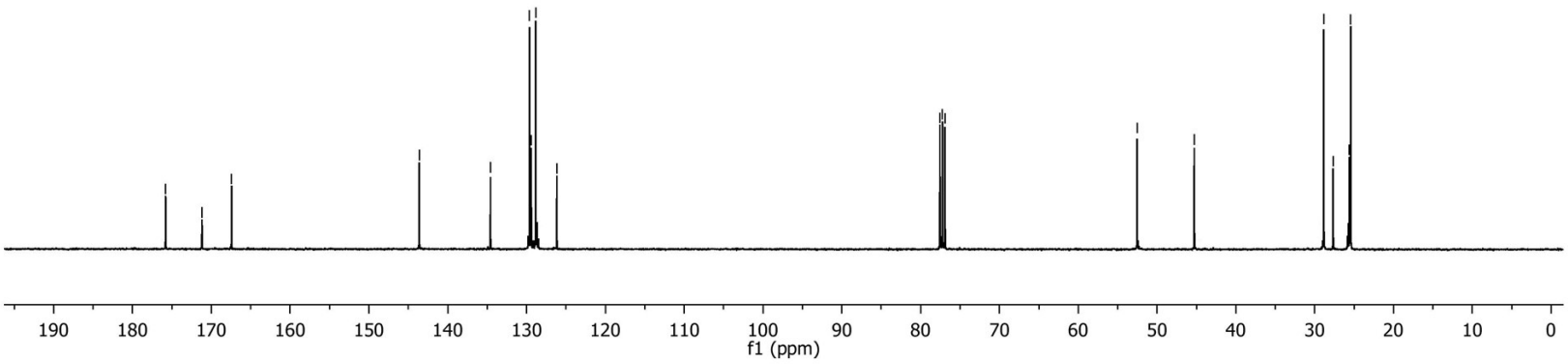


_Z_-Methyl 2-((((cyclohexanecarbonyl)carbamoyl)thio)methyl)-3-phenylacrylate (1k): ^{1}HNMR (400 MHz, $CDCl_3$)

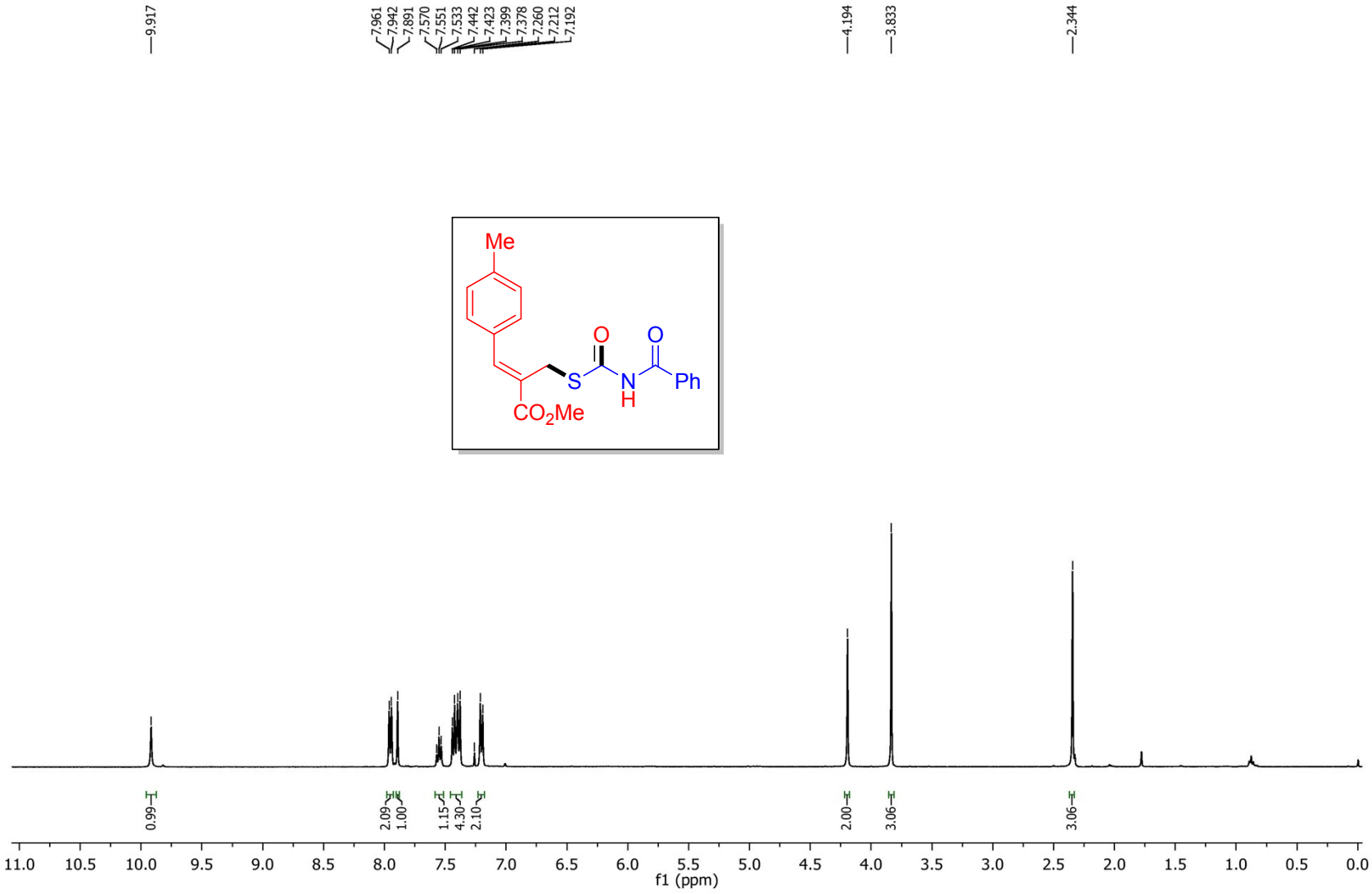


_Z_-Methyl 2-((((cyclohexanecarbonyl)carbamoyl)thio)methyl)-3-phenylacrylate (1k): ^{13}CNMR (100 MHz, $CDCl_3$)

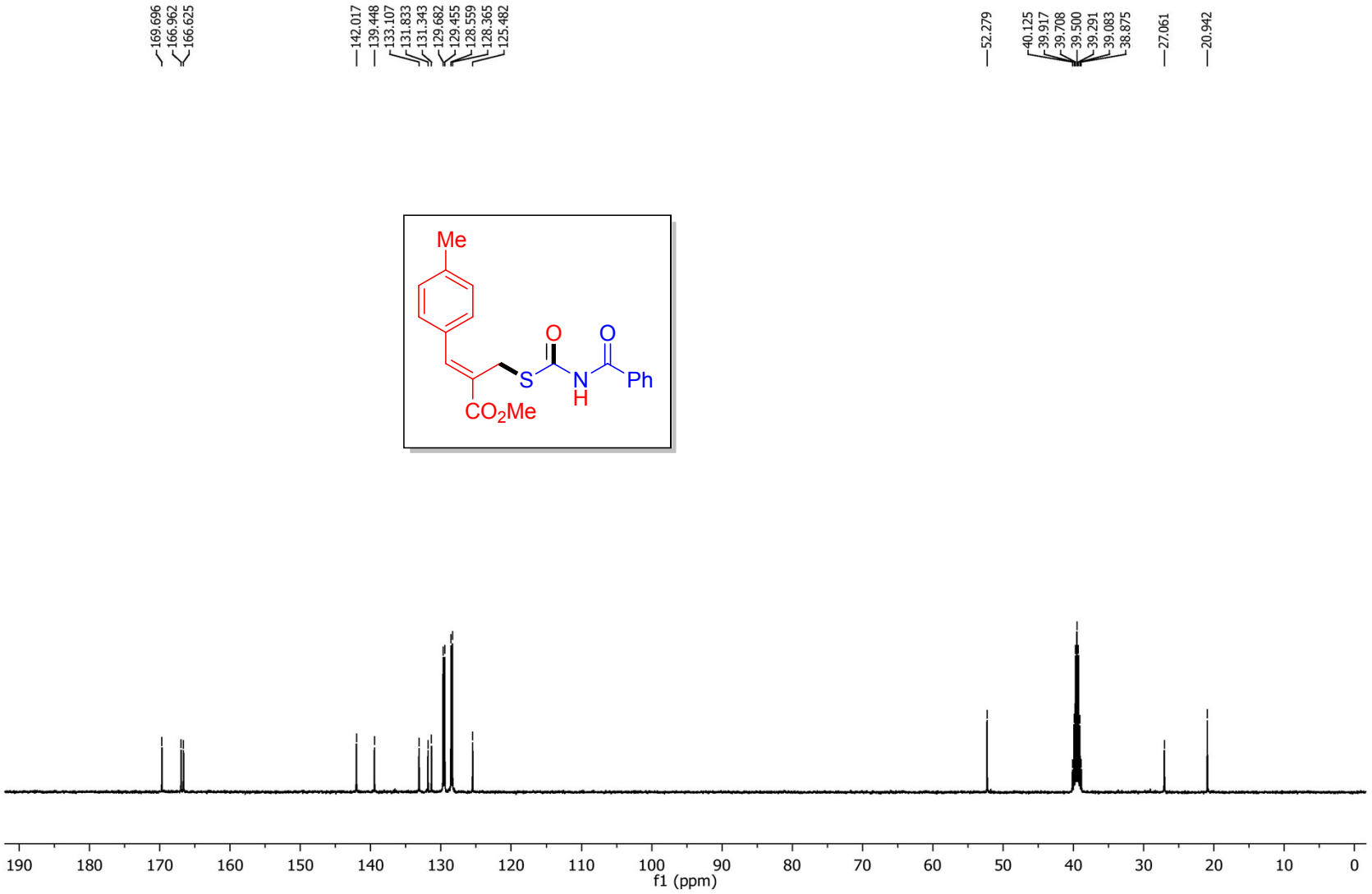




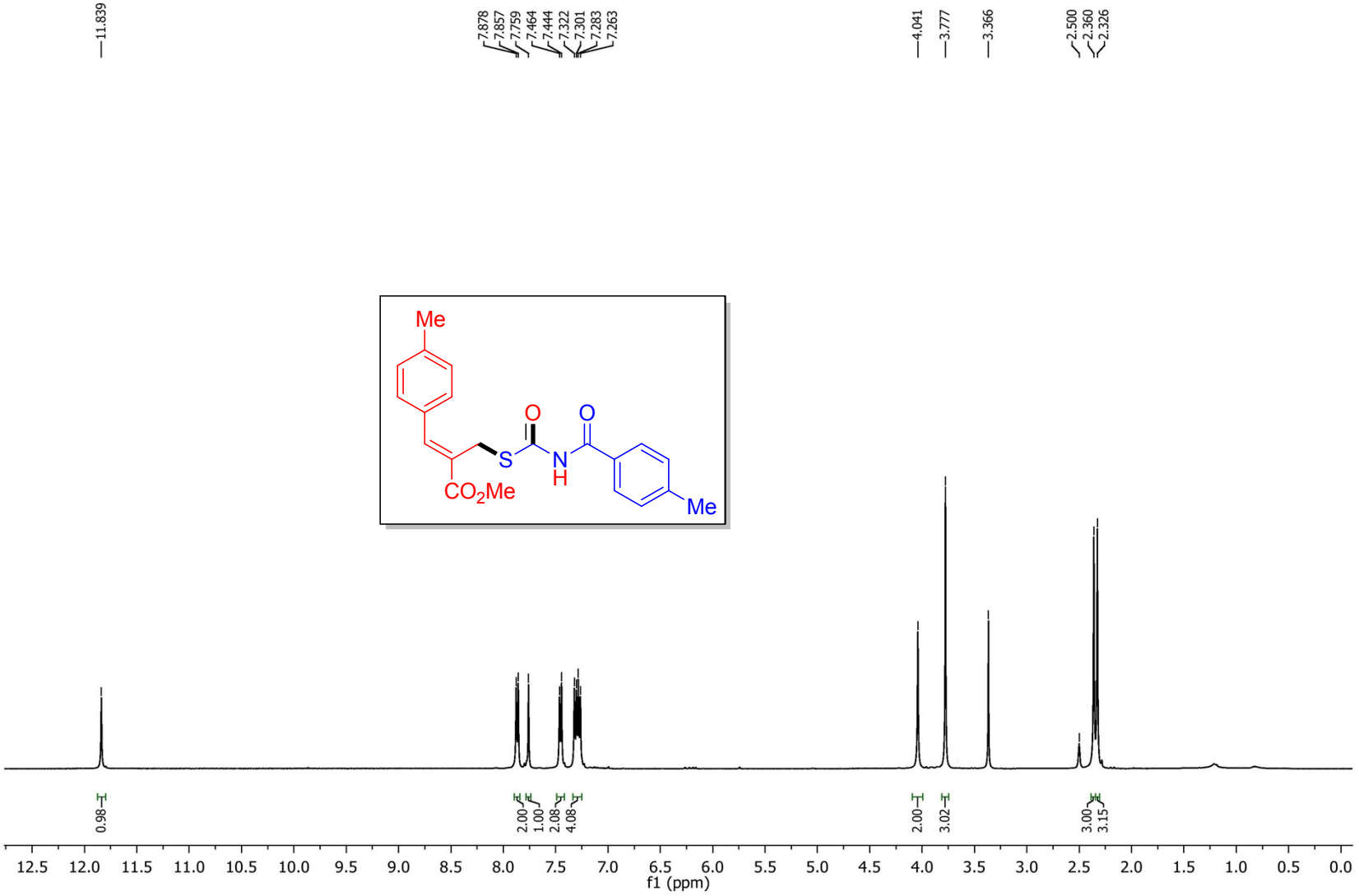
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2a): ^{1}HNMR (400 MHz, $CDCl_3$)**



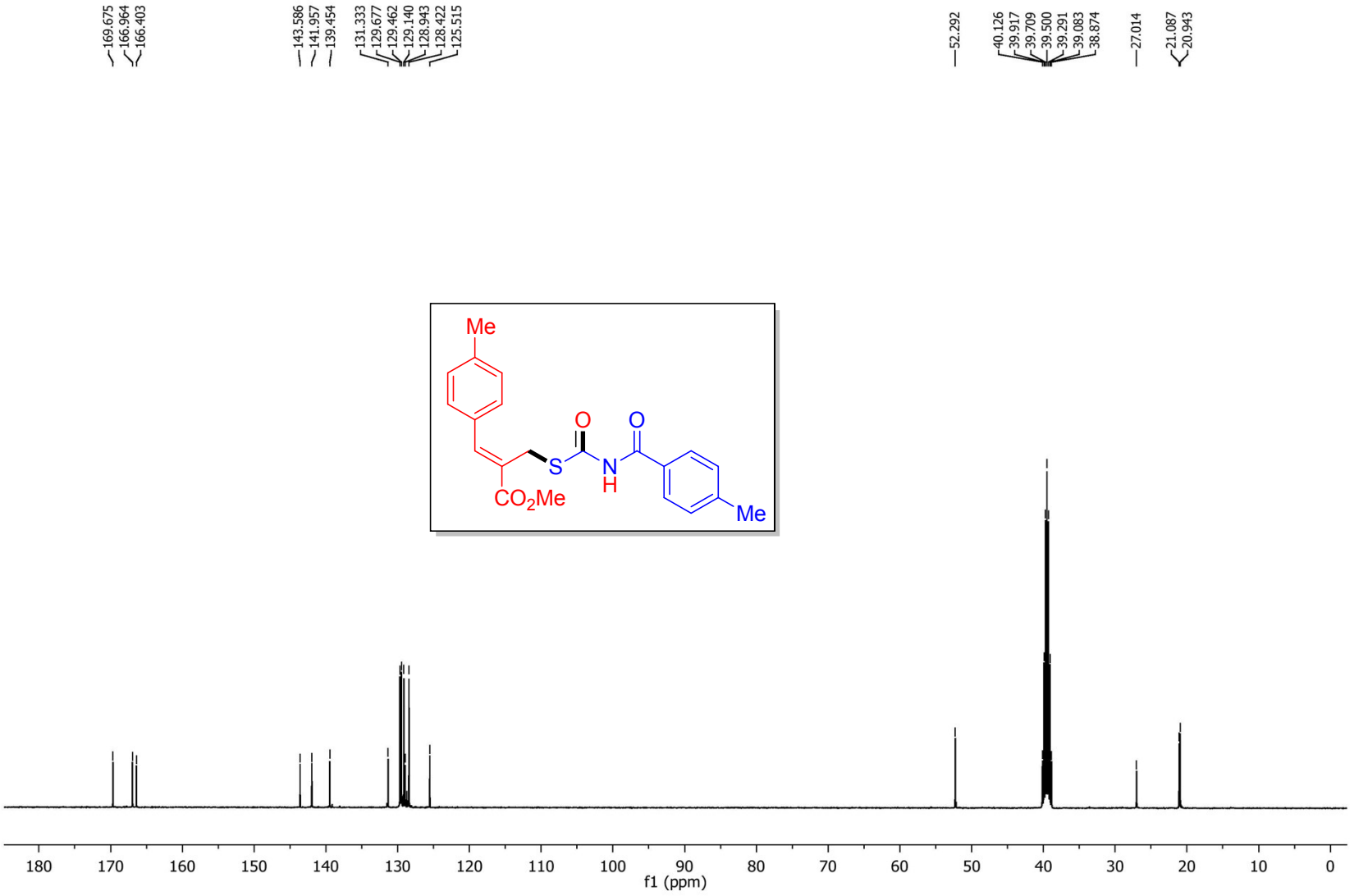
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2a): ^{13}CNMR (100 MHz, DMSO-d_6)**



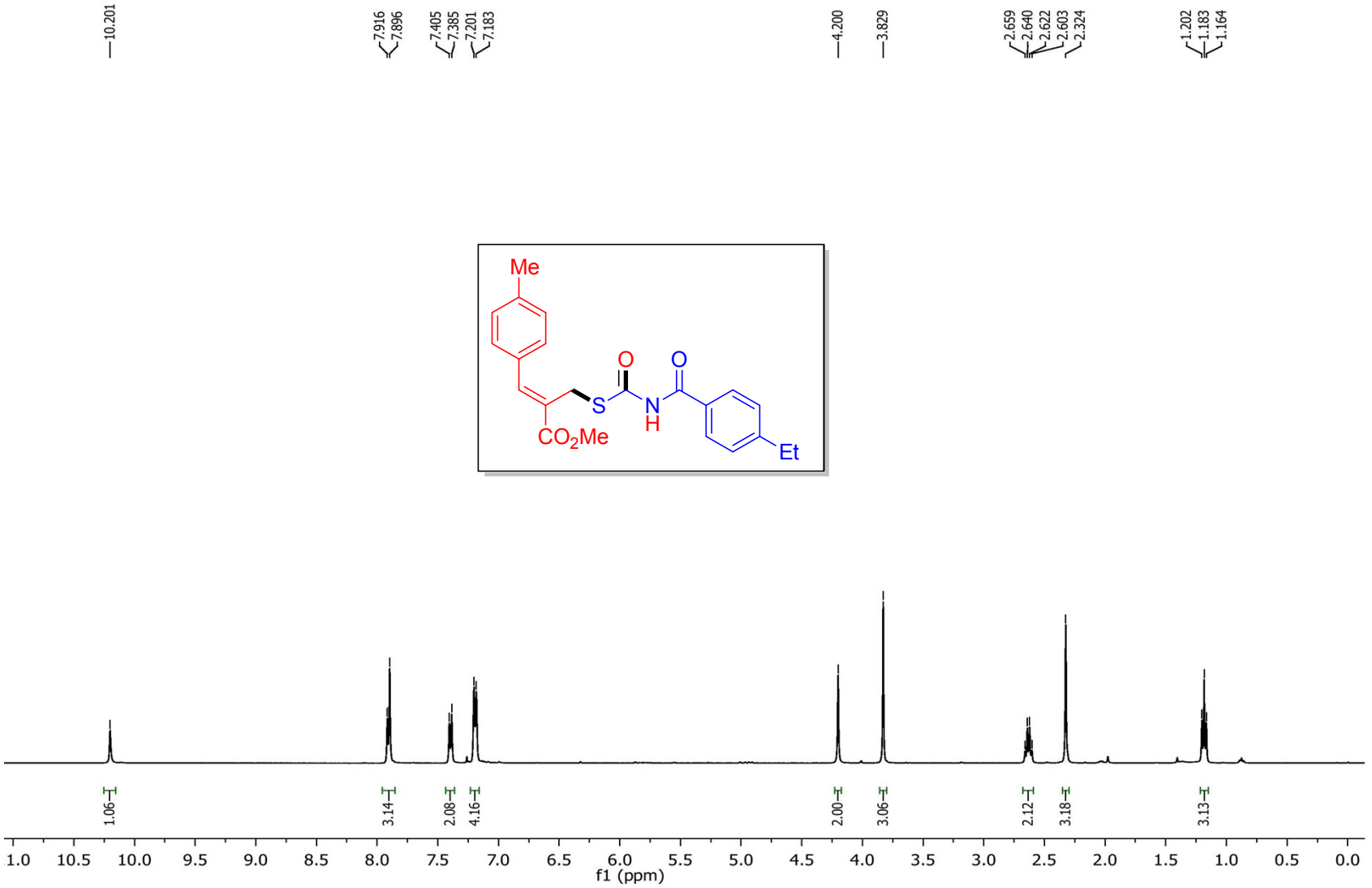
_Z_-Methyl 2-((((4-methylbenzoyl)carbamoyl)thio)methyl)-3-(_p_-tolyl)acrylate (2b): ^{1}HNMR (400 MHz, DMSO-d$_6$)



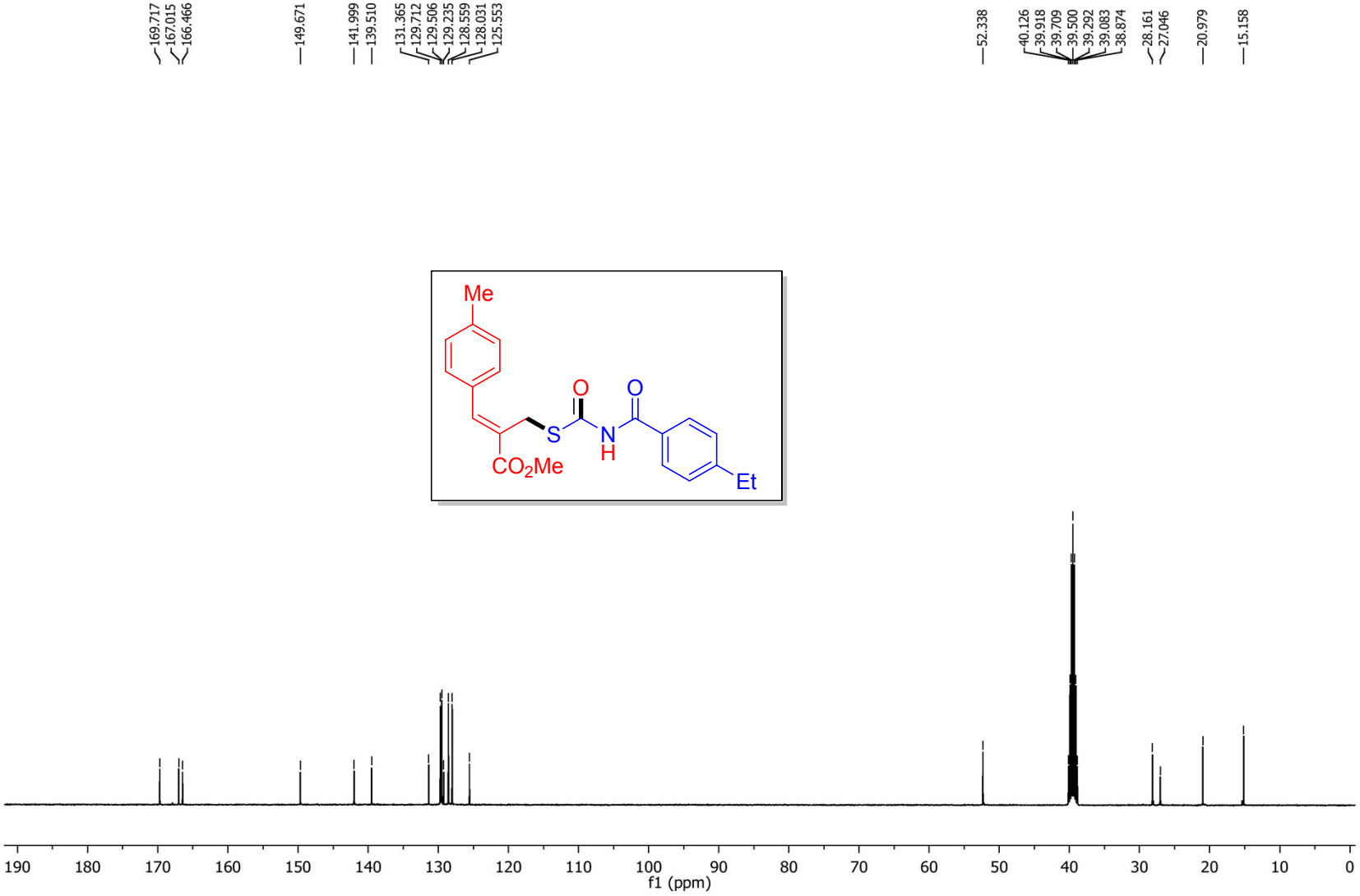
***Z*-Methyl 2-((((4-methylbenzoyl)carbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2b): ^{13}CNMR (100 MHz, DMSO-d_6)**



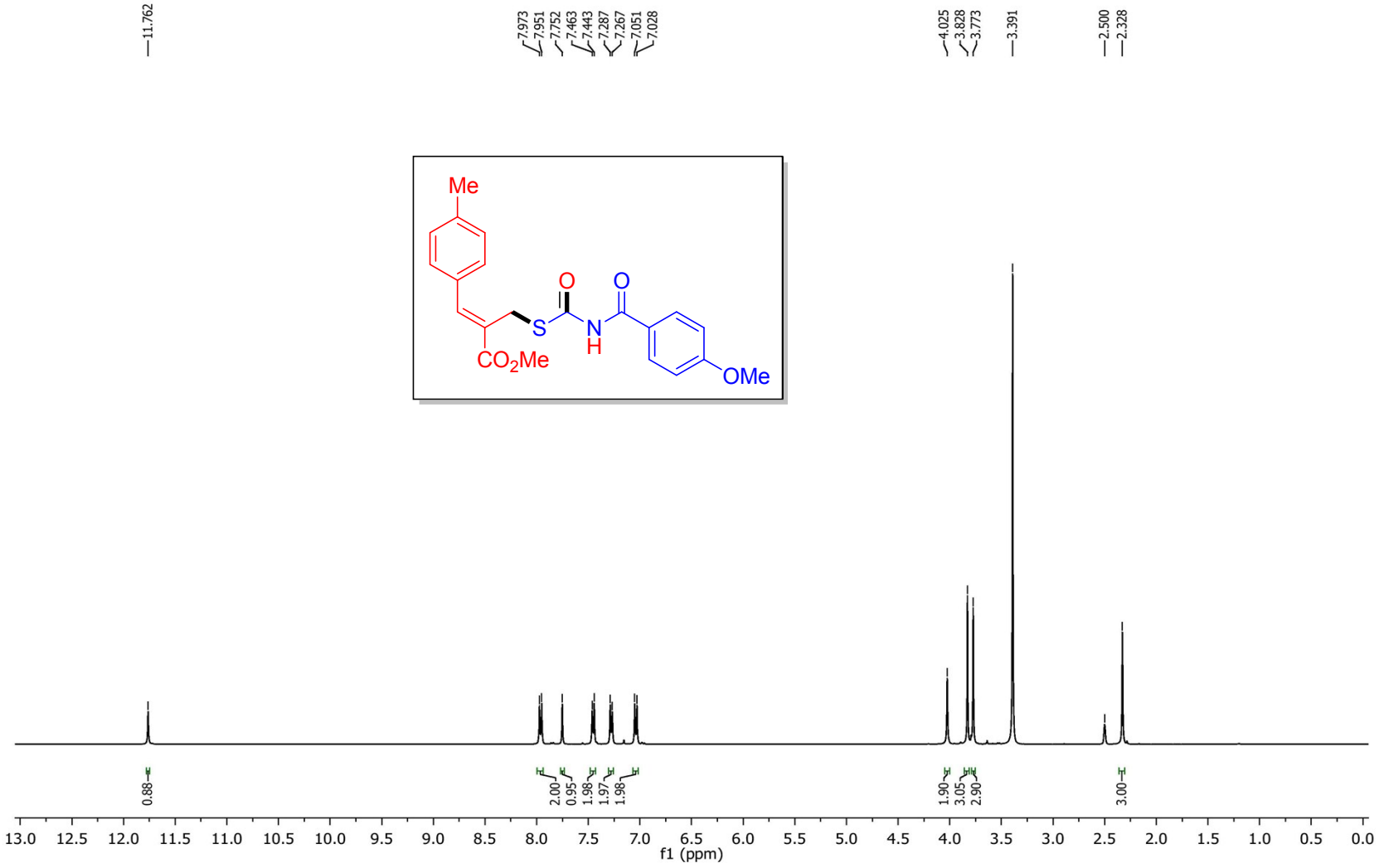
_Z_-Methyl 2-((((4-ethylbenzoyl)carbamoyl)thio)methyl)-3-(_p_-tolyl)acrylate (2c): ^{1}HNMR (400 MHz, $CDCl_3$)



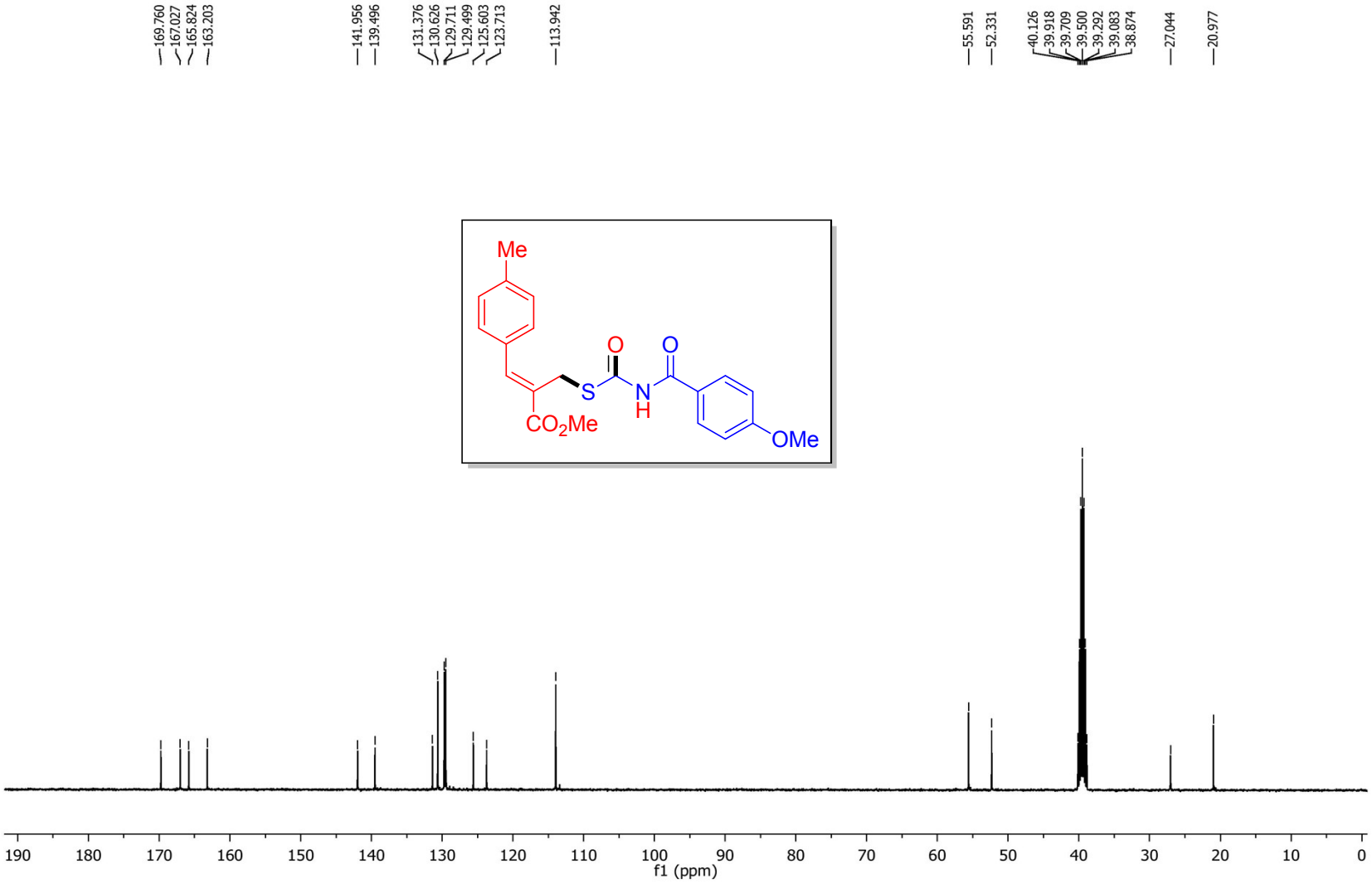
***Z*-Methyl 2-((((4-ethylbenzoyl)carbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2c): ^{13}CNMR (100 MHz, DMSO-d_6)**



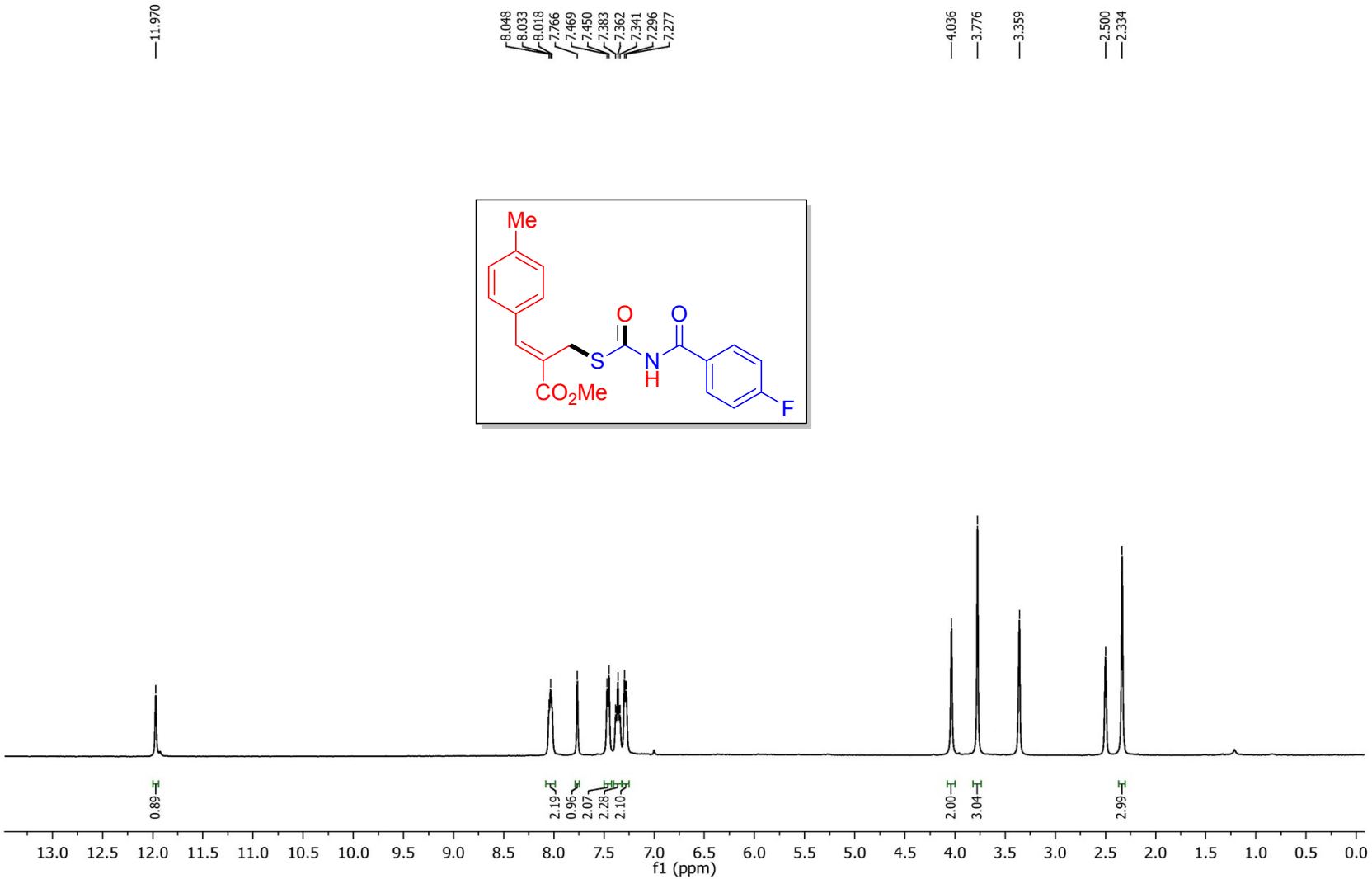
***Z*-Methyl 2-((((4-methoxybenzoyl)carbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2d): ^{1}HNMR (400 MHz, DMSO-d_6)**



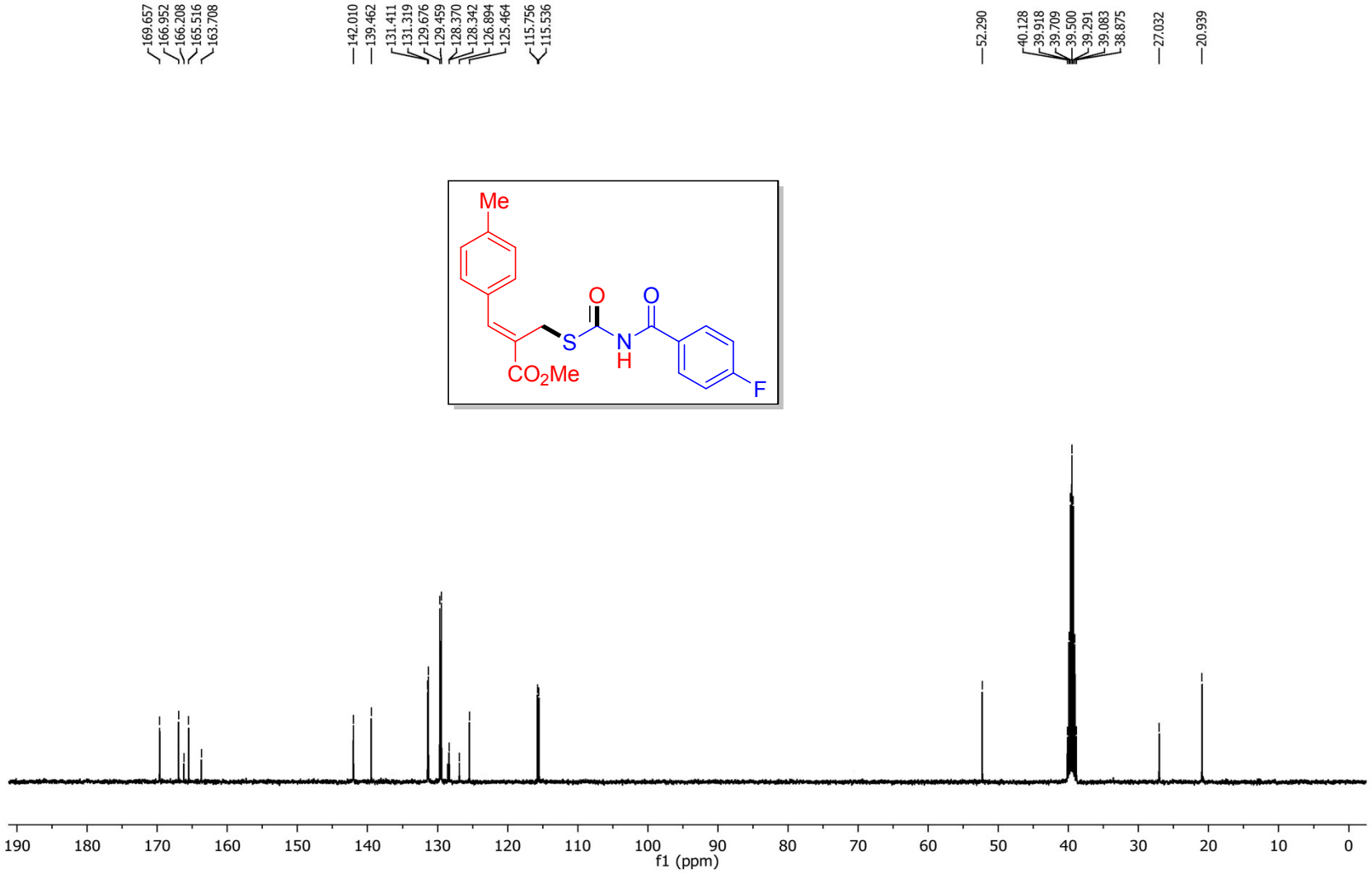
***Z*-Methyl 2-((((4-methoxybenzoyl)carbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2d): ^{13}CNMR (100 MHz, DMSO-d_6)**



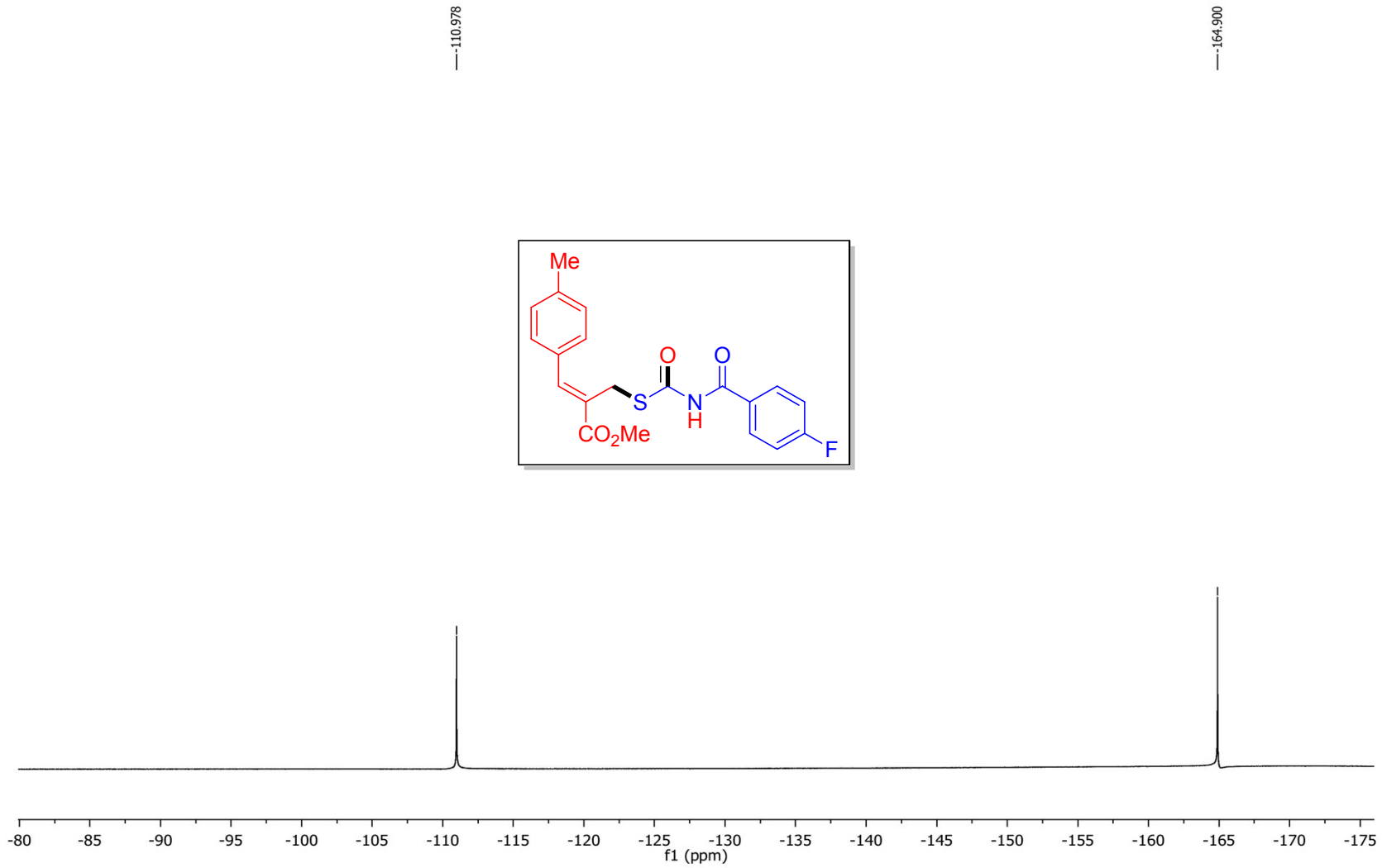
***Z*-Methyl 2-((((4-fluorobenzoyl)carbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2e): ^{1}HNMR (400 MHz, DMSO-d_6)**



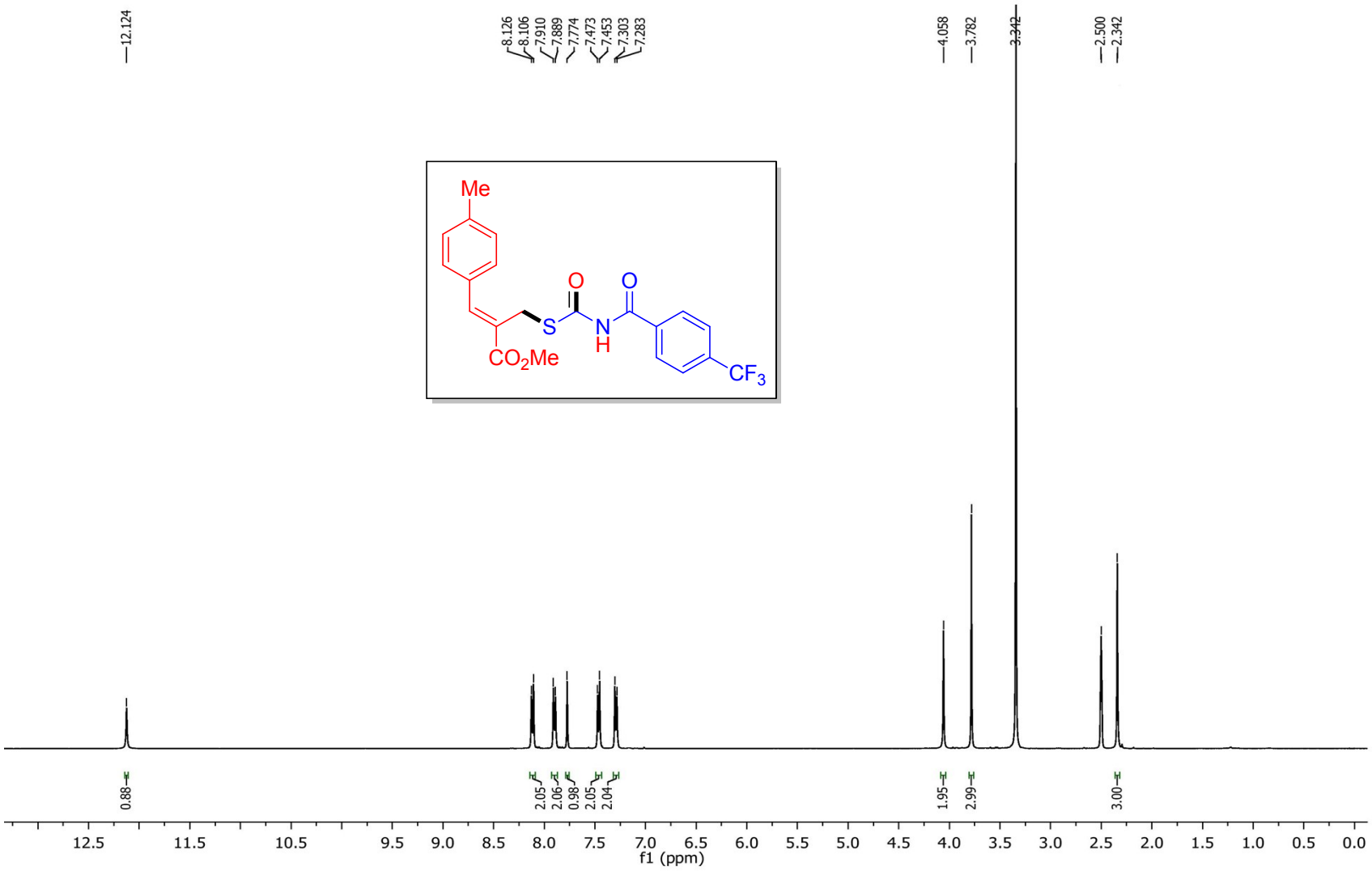
***Z*-Methyl 2-((((4-fluorobenzoyl)carbamoyl)thio)methyl)-3-(*p*-tolyl)acrylate (2e): ^{13}CNMR (100 MHz, DMSO-d_6)**



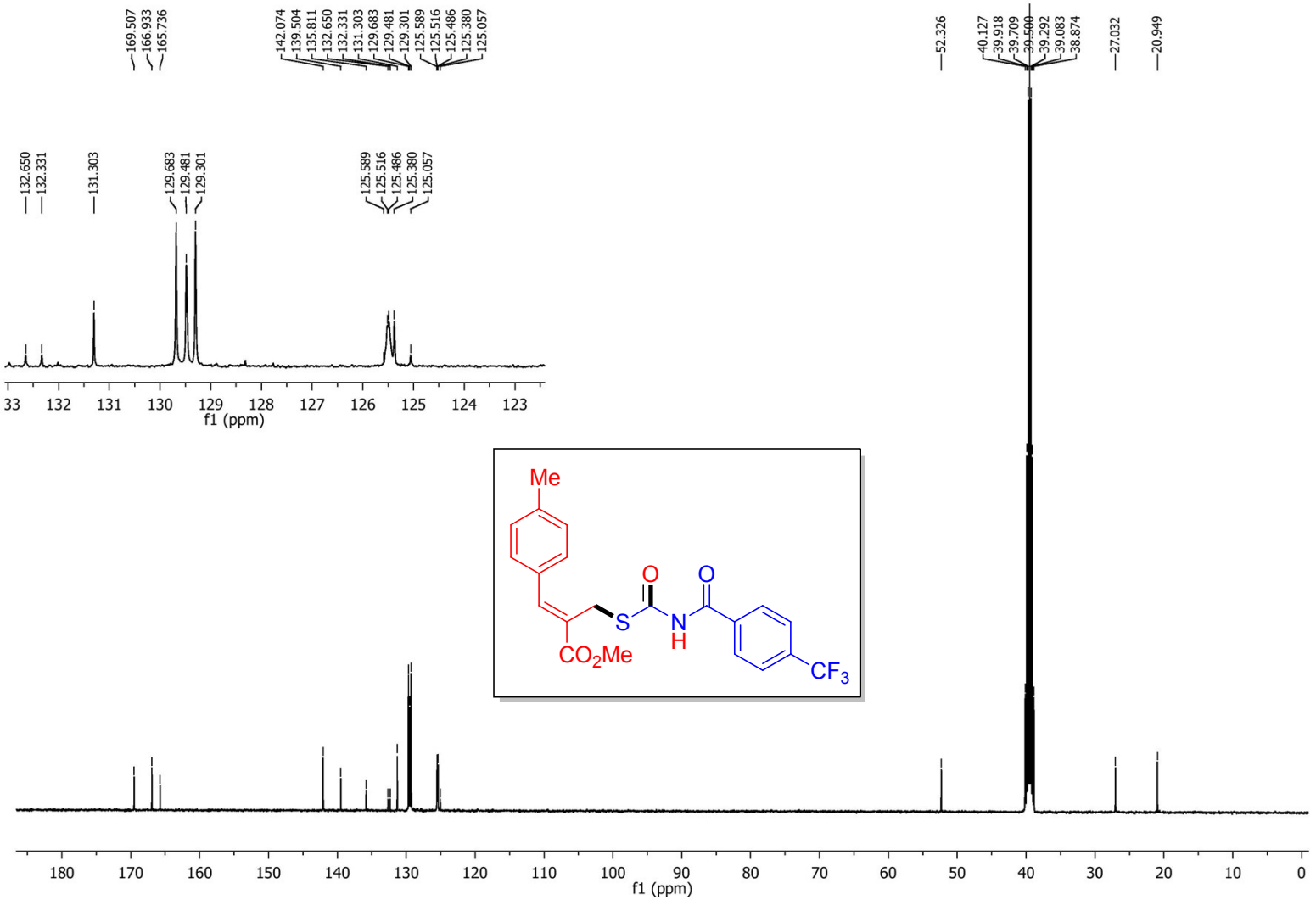
_Z_-Methyl 2-((((4-fluorobenzoyl)carbamoyl)thio)methyl)-3-(_p_-tolyl)acrylate (2e): ^{19}FNMR (DMSO-d_6 + Hexafluorobenzene)



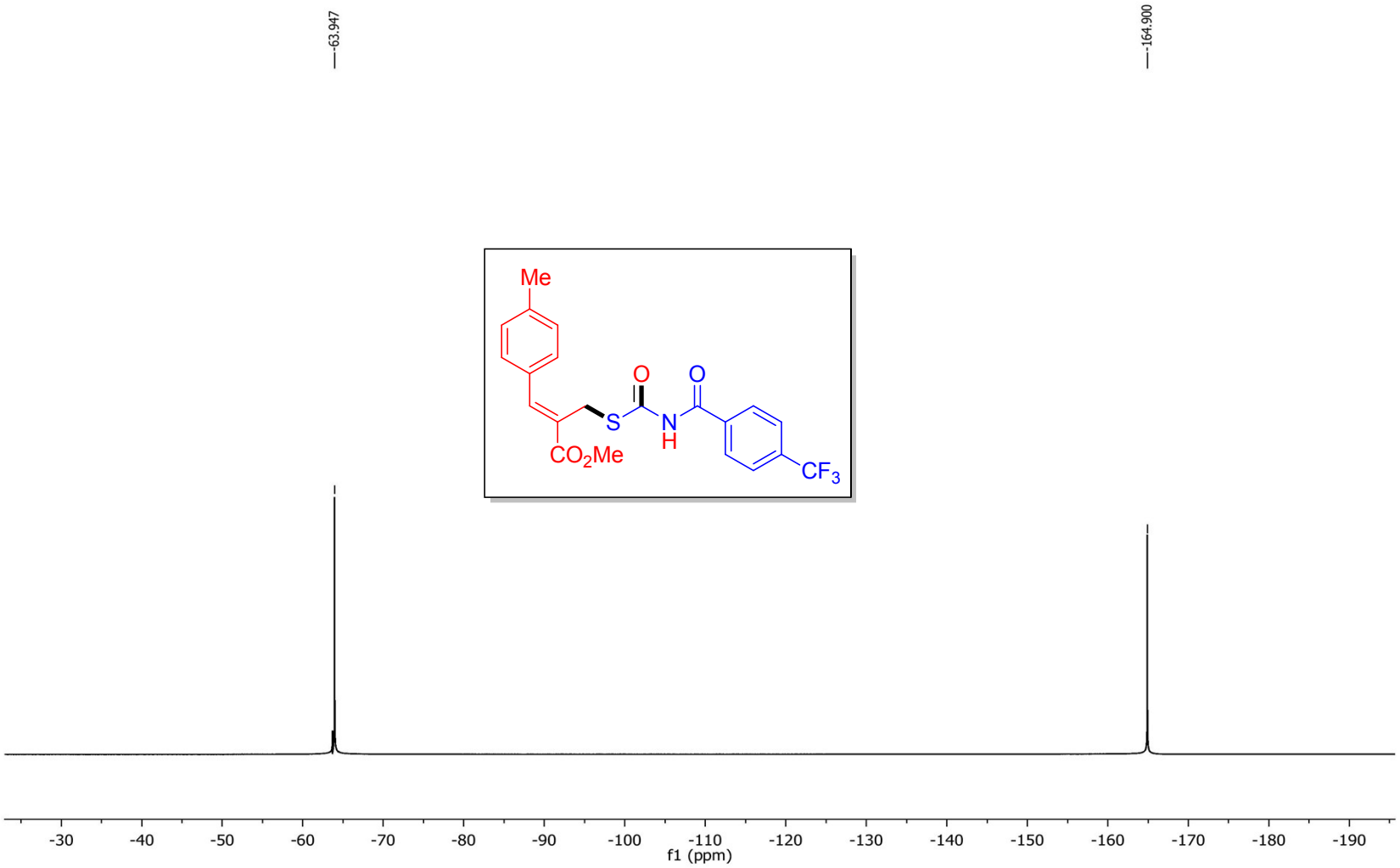
_Z_-Methyl 3-(p-tolyl)-2-((((4-(trifluoromethyl)benzoyl)carbamoyl)thio)methyl)acrylate (2f): ^{1}HNMR (400 MHz, DMSO-d_6)



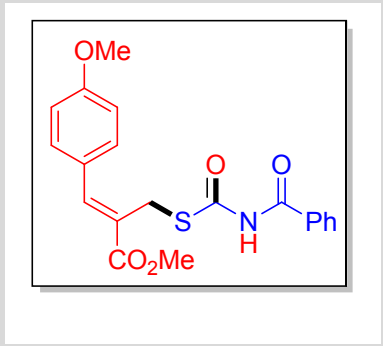
_Z_-Methyl 3-(p-tolyl)-2-((((4-(trifluoromethyl)benzoyl)carbamoyl)thio)methyl)acrylate (2f): ^{13}CNMR (100 MHz, DMSO-d_6)



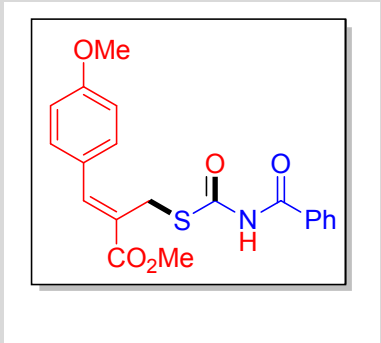
_Z_-Methyl 3-(p-tolyl)-2-((((4-(trifluoromethyl)benzoyl)carbamoyl)thio)methyl)acrylate (2f): ^{19}FNMR (DMSO-d_6 + C_6F_6)



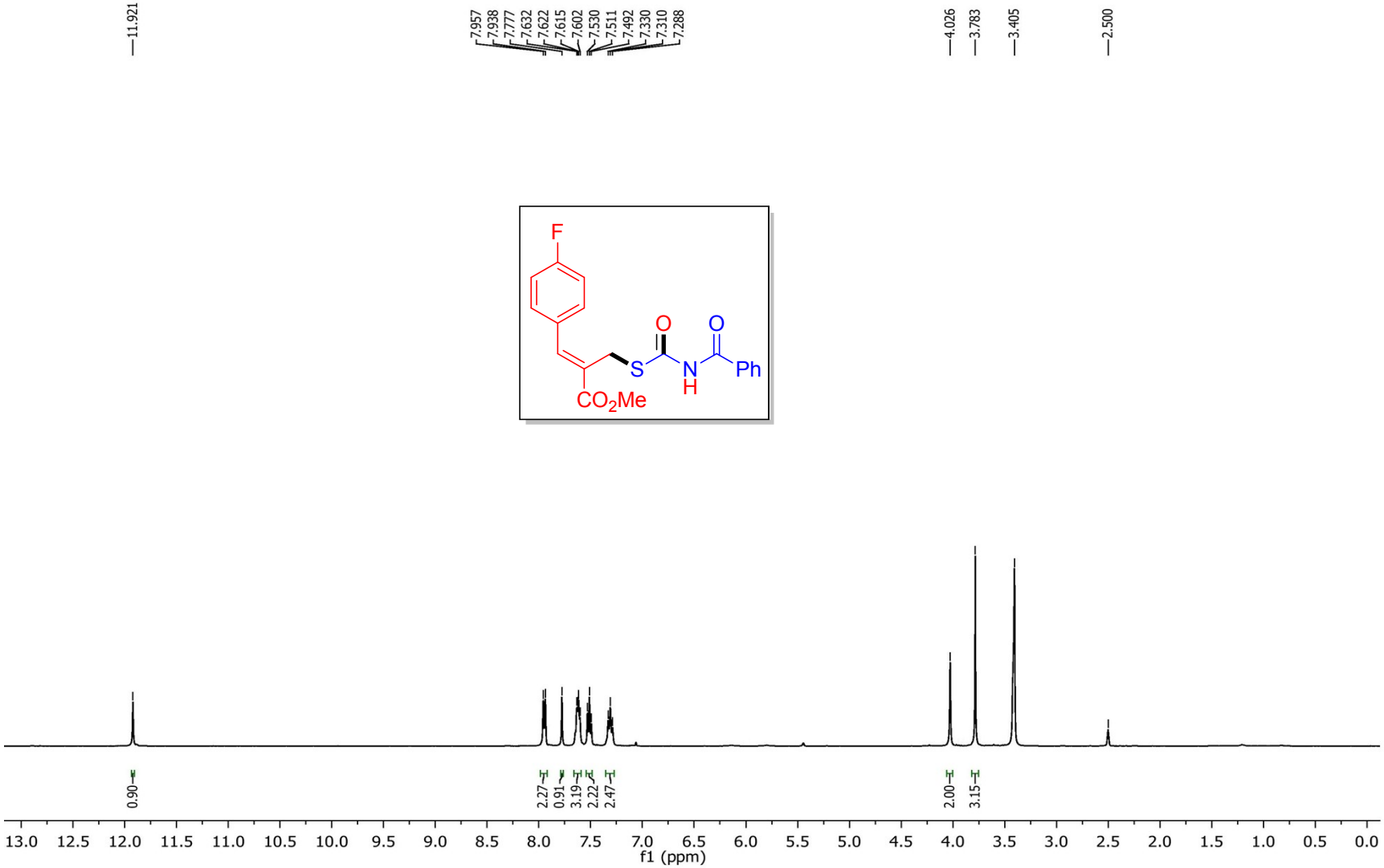
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-methoxyphenyl)acrylate (3a): ^{1}HNMR (400 MHz, DMSO-d_6)**



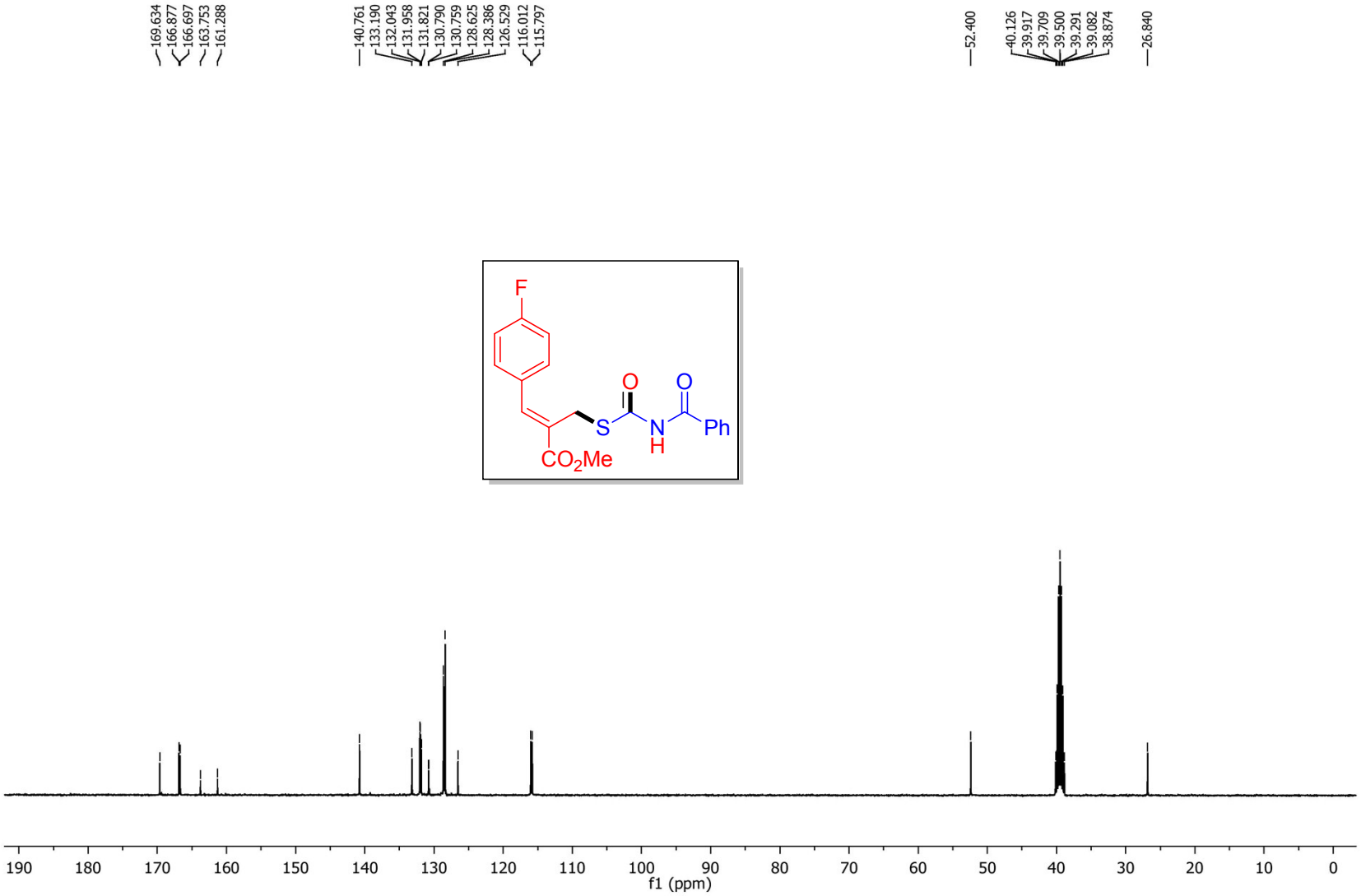
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-methoxyphenyl)acrylate (3a): ^{13}CNMR (100 MHz, DMSO-d_6)**



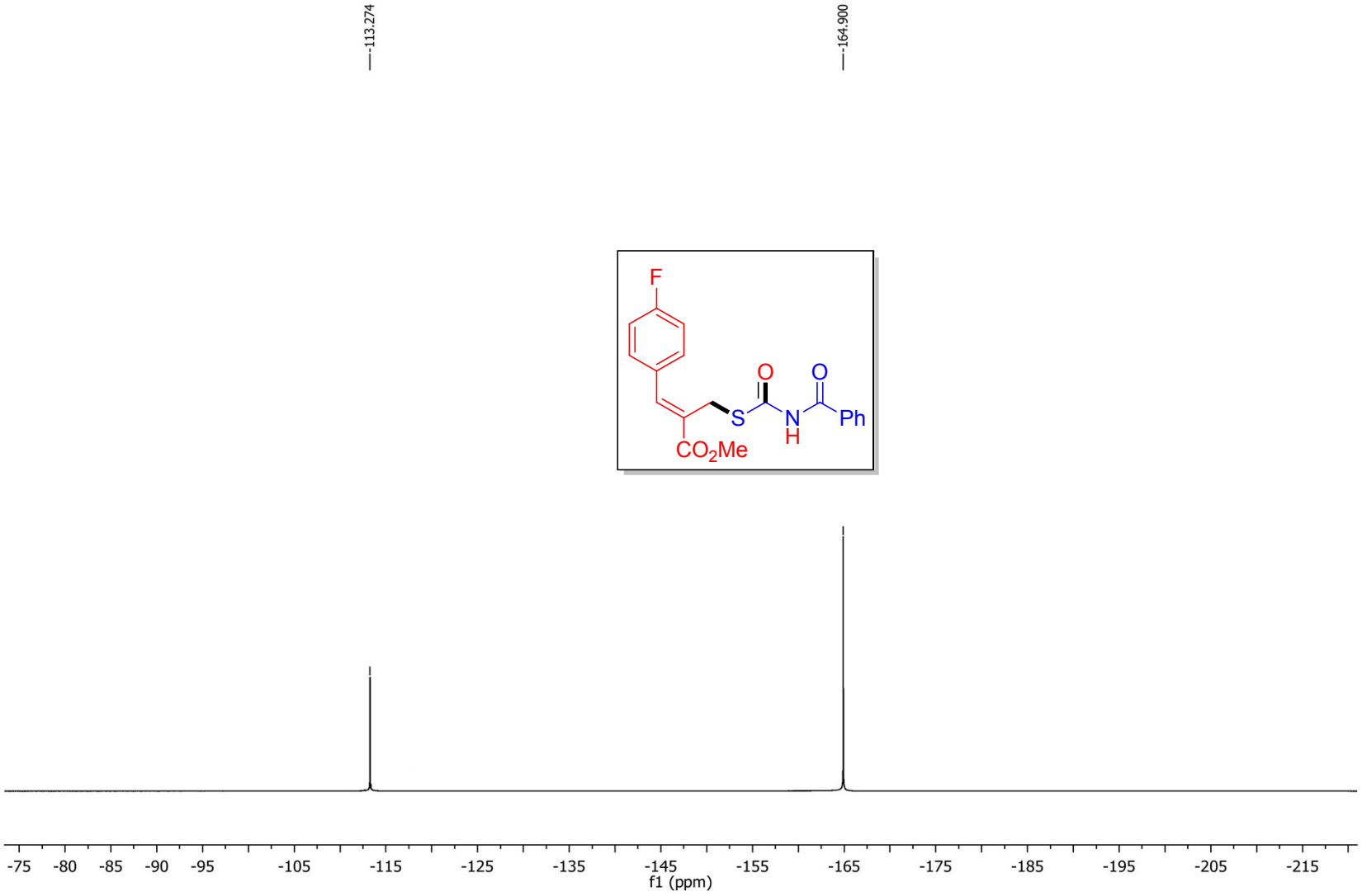
_Z_-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-fluorophenyl)acrylate (4a): ^{1}HNMR (400 MHz, DMSO-d_6)



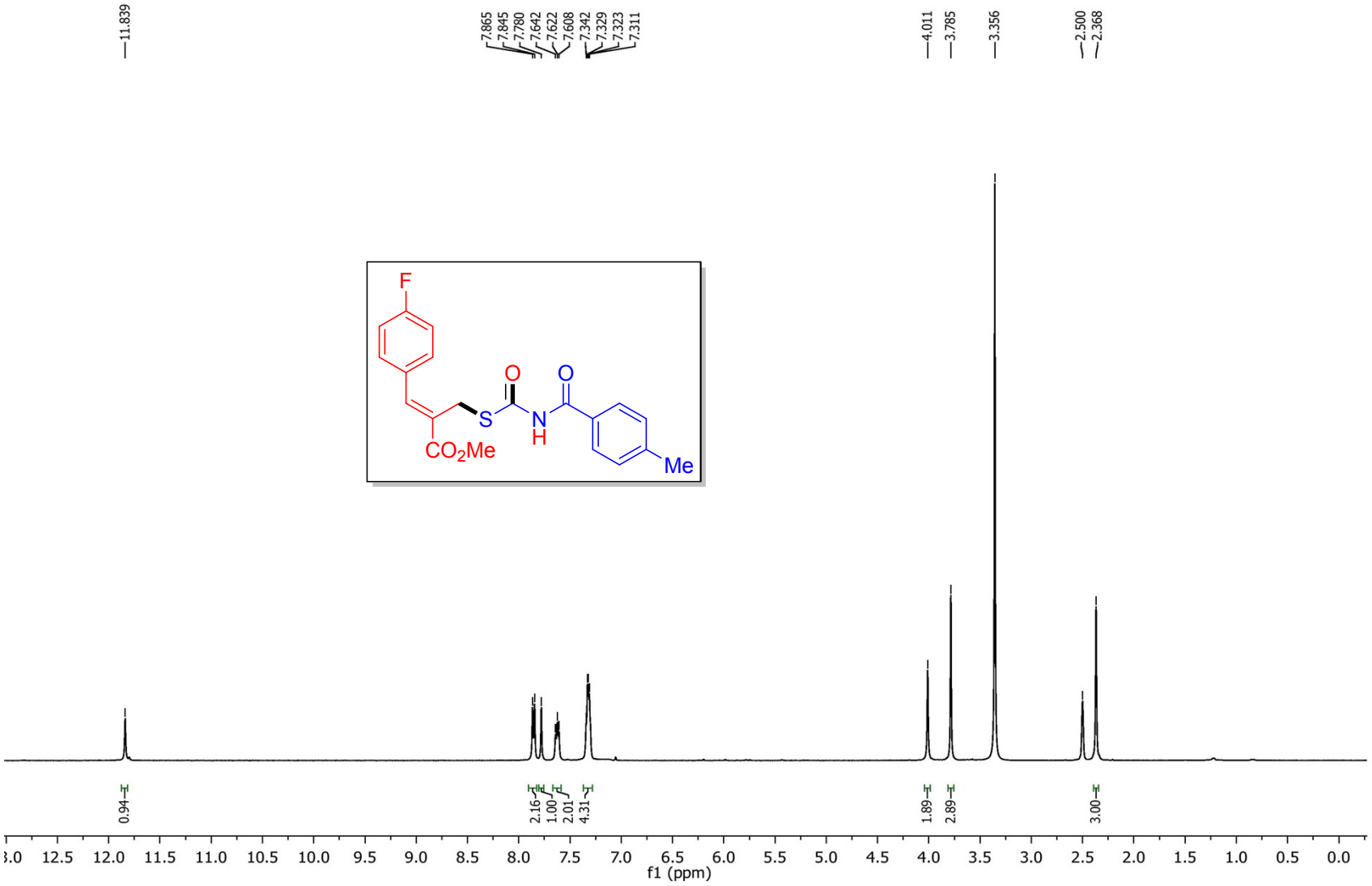
_Z_-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-fluorophenyl)acrylate (4a): ^{13}CNMR (100 MHz, DMSO-d$_6$)



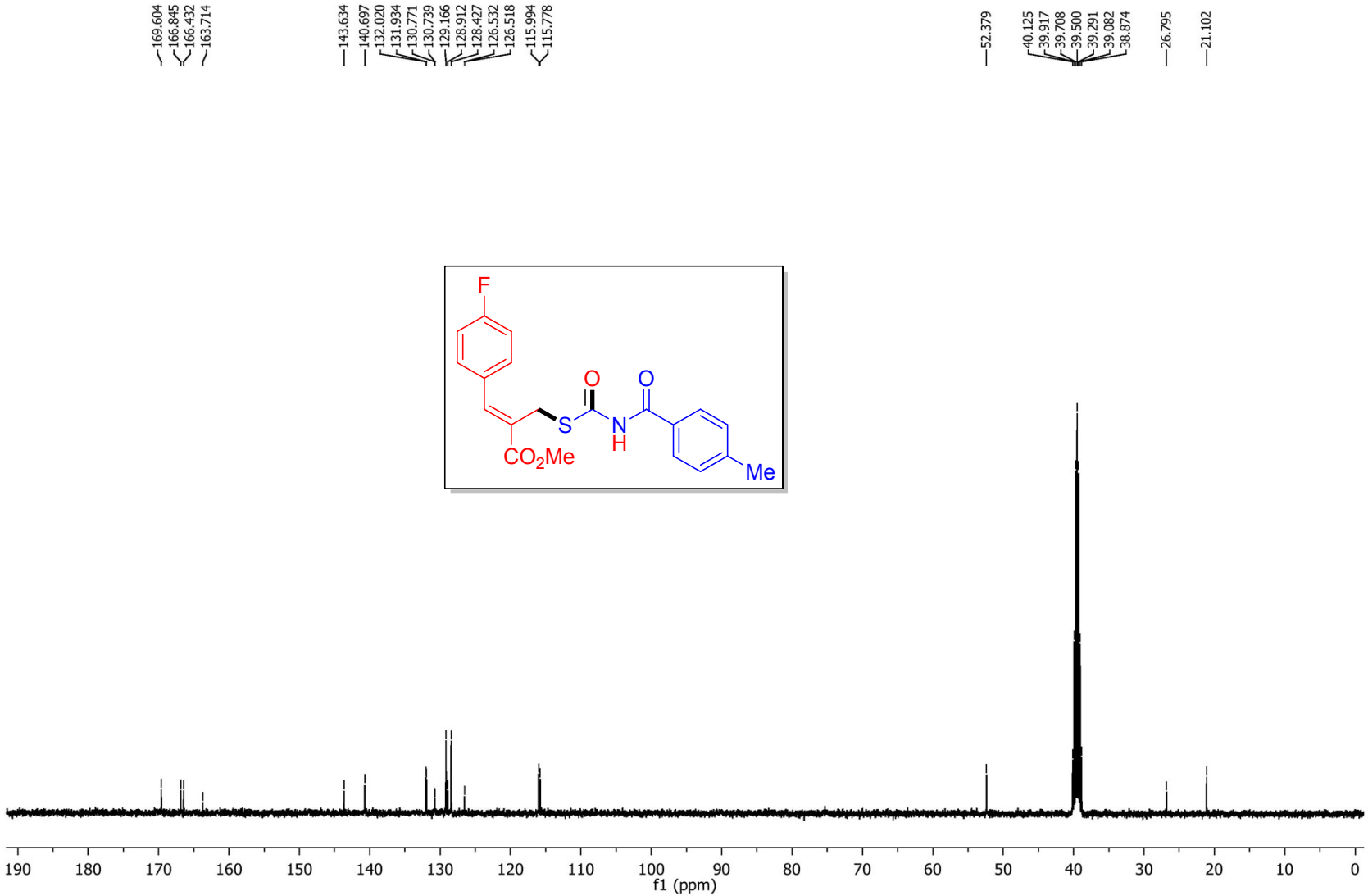
_Z_-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-fluorophenyl)acrylate (4a): ^{13}CNMR (100 MHz, DMSO-d_6)



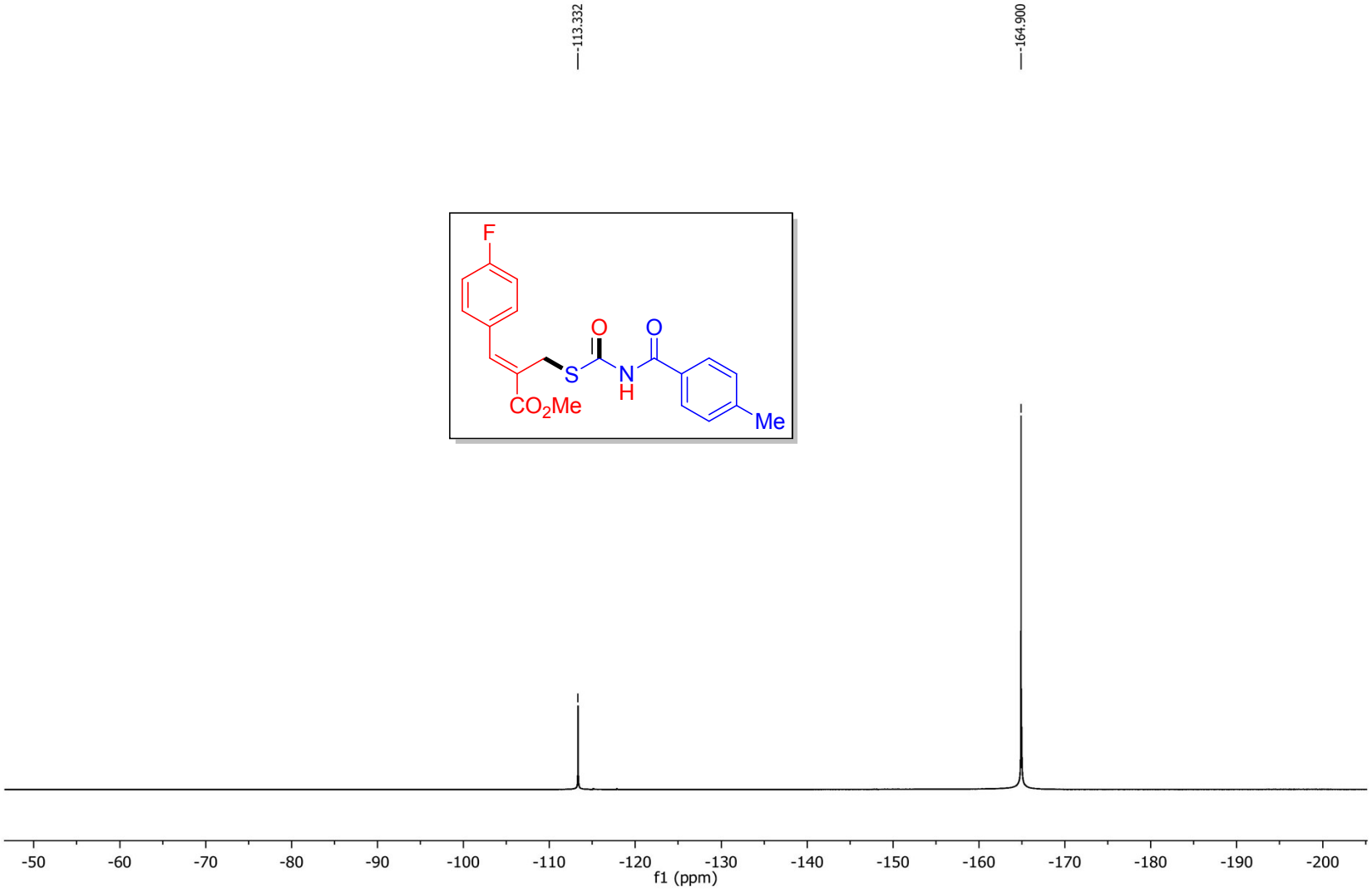
_Z_-Methyl 3-(4-fluorophenyl)-2-((((4-methylbenzoyl)carbamoyl)thio)methyl)acrylate (4b): ^{1}HNMR (400 MHz, DMSO-d_6)



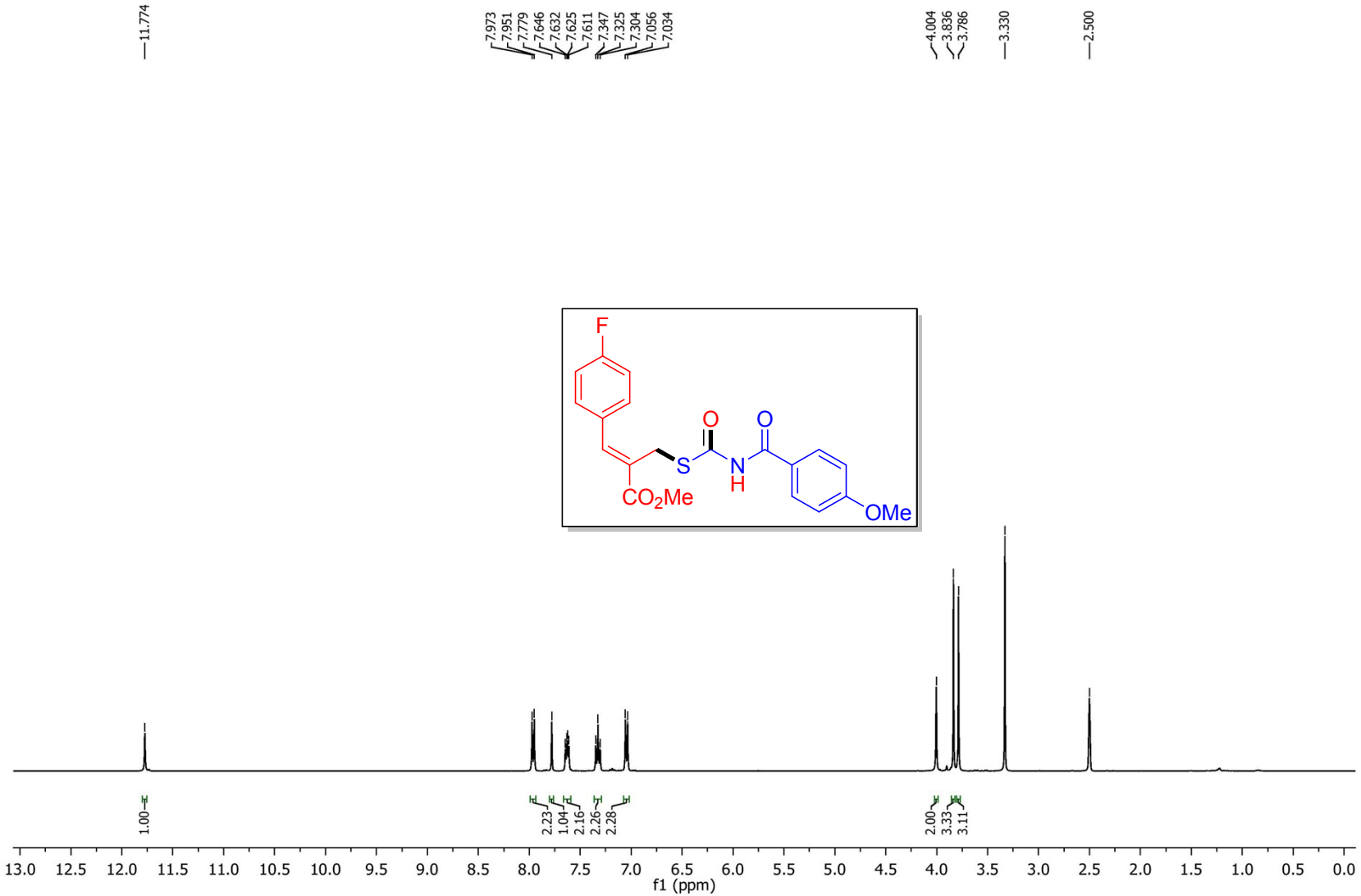
_Z_-Methyl 3-(4-fluorophenyl)-2-((((4-methylbenzoyl)carbamoyl)thio)methyl)acrylate (4b): ^{13}CNMR (100 MHz, DMSO-d_6)



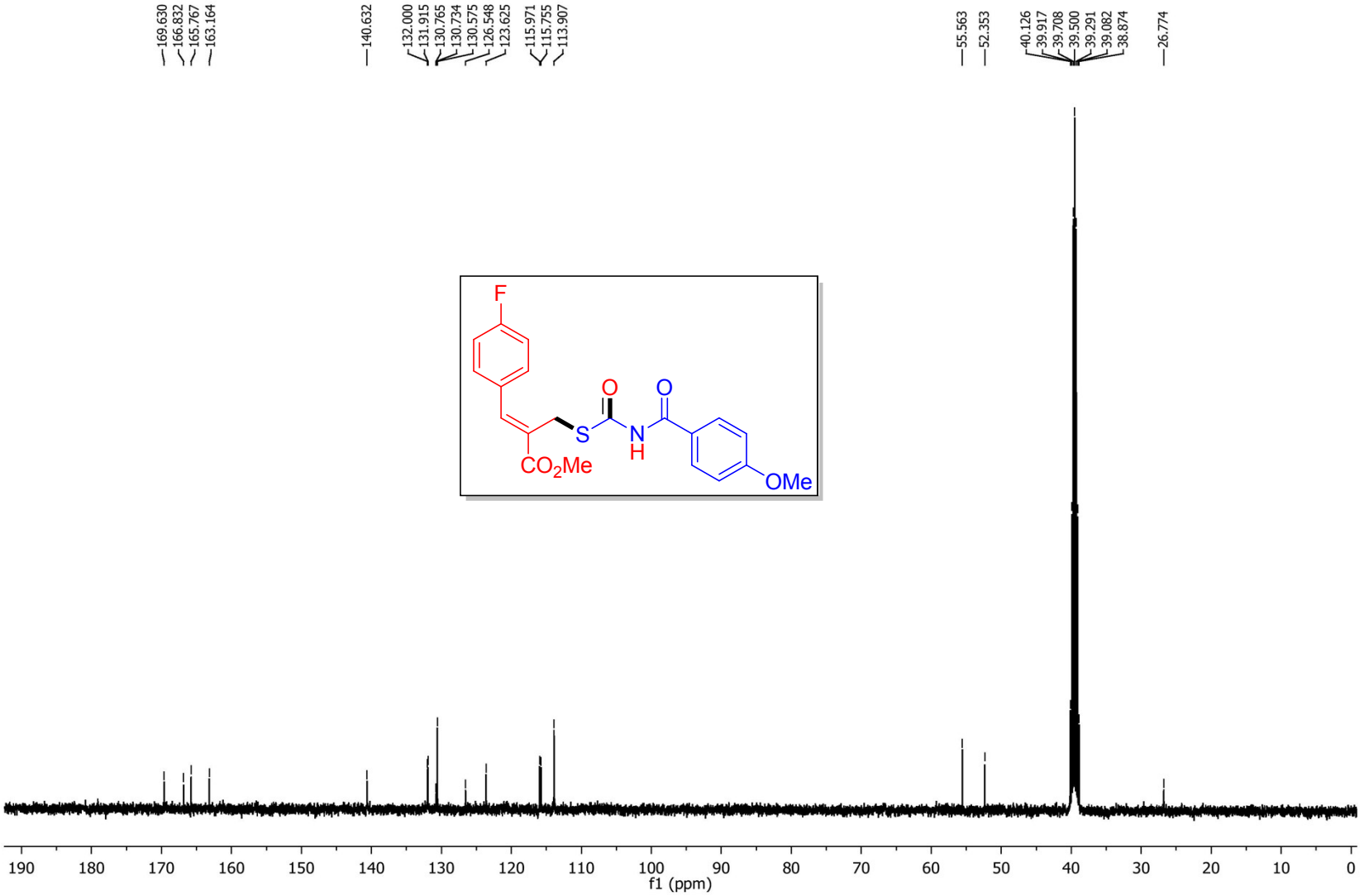
_Z_-Methyl 3-(4-fluorophenyl)-2-((((4-methylbenzoyl)carbamoyl)thio)methyl)acrylate (4b): ^{19}FNMR (DMSO-d_6 + C_6F_6)



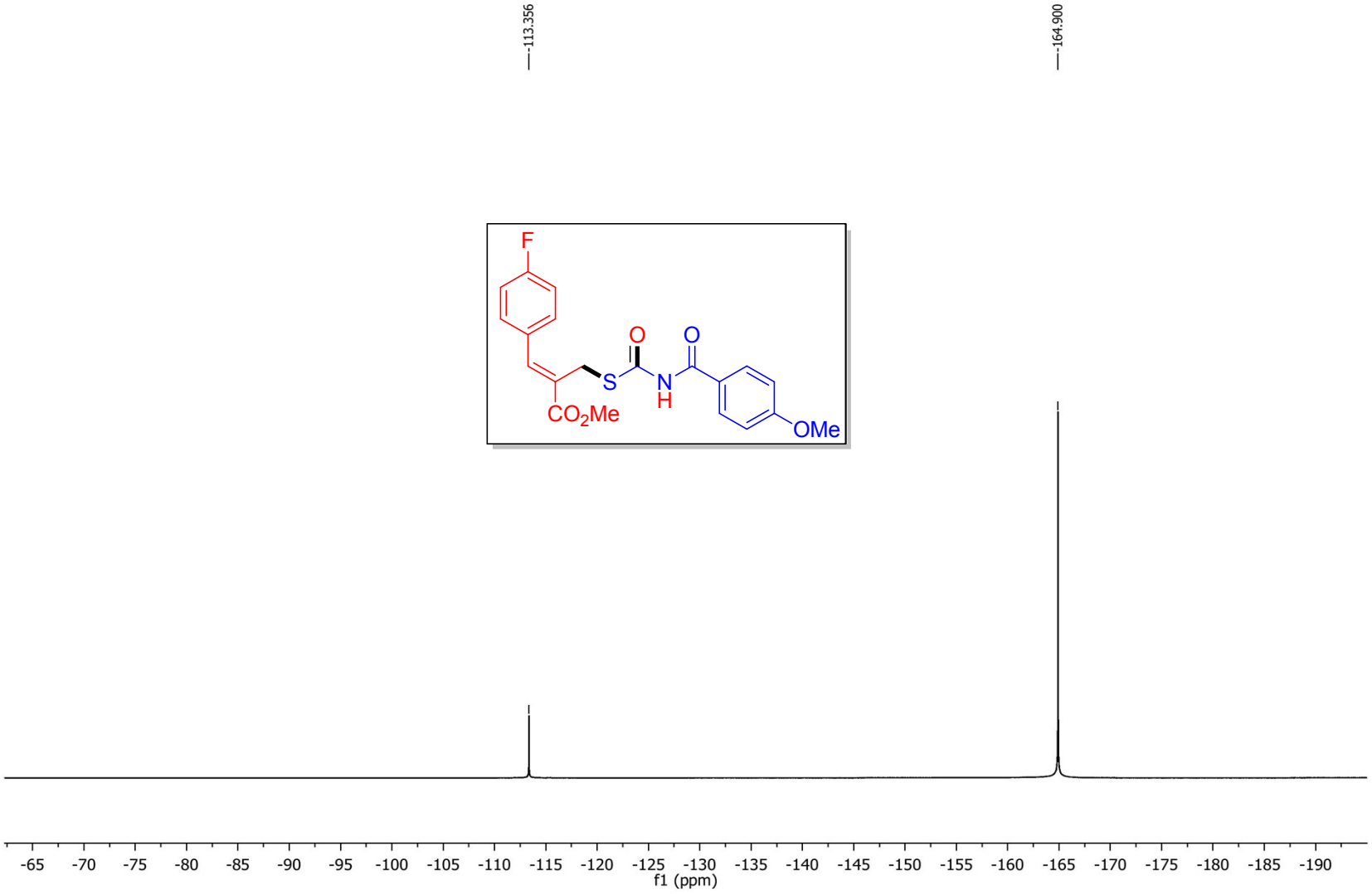
_Z_-Methyl 3-(4-fluorophenyl)-2-((((4-methoxybenzoyl)carbamoyl)thio)methyl)acrylate (4d): ^{1}HNMR (400 MHz, DMSO-d_6)



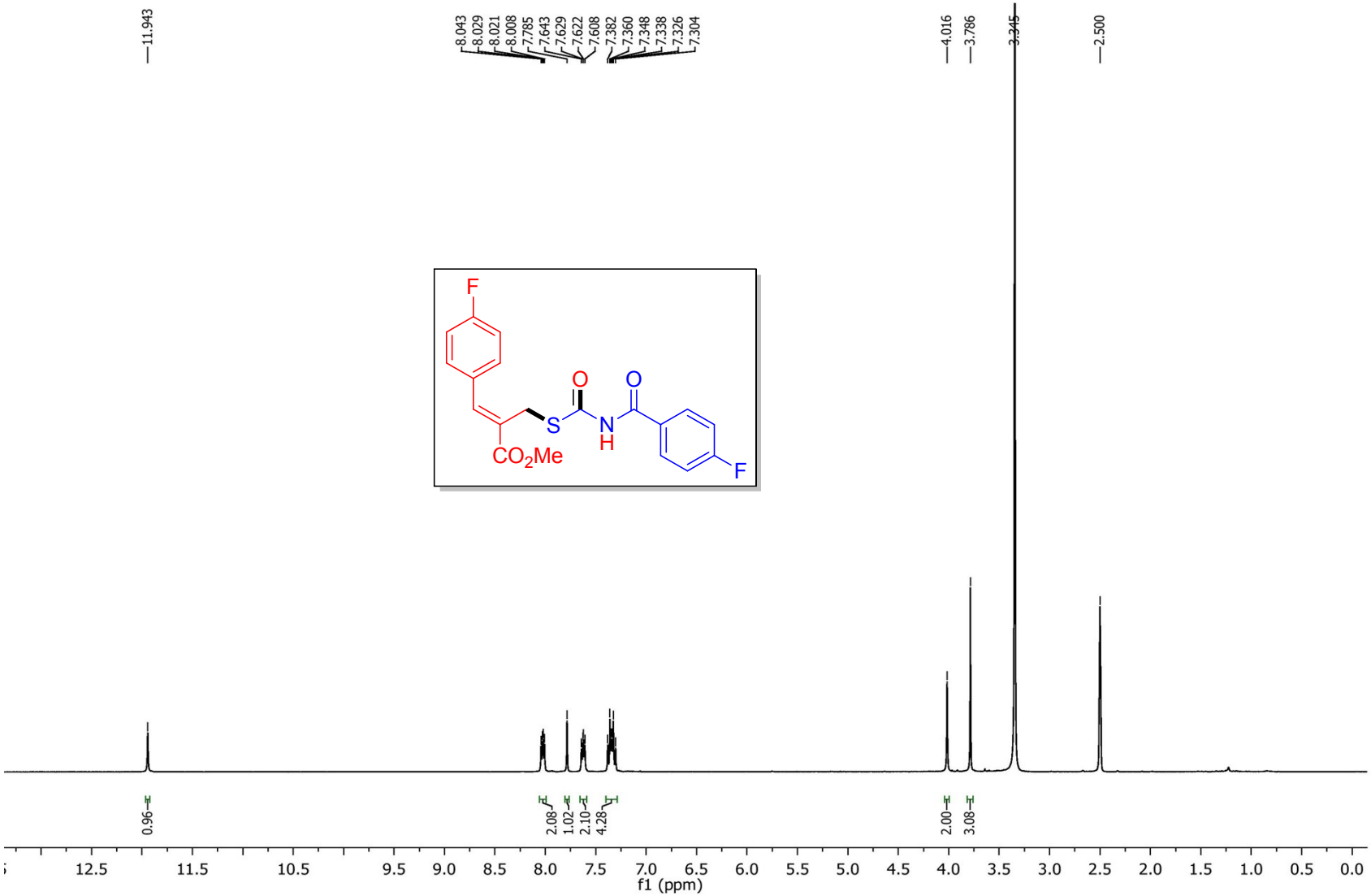
_Z_-Methyl 3-(4-fluorophenyl)-2-((((4-methoxybenzoyl)carbamoyl)thio)methyl)acrylate (4d): ^{13}CNMR (100 MHz, DMSO-d_6)



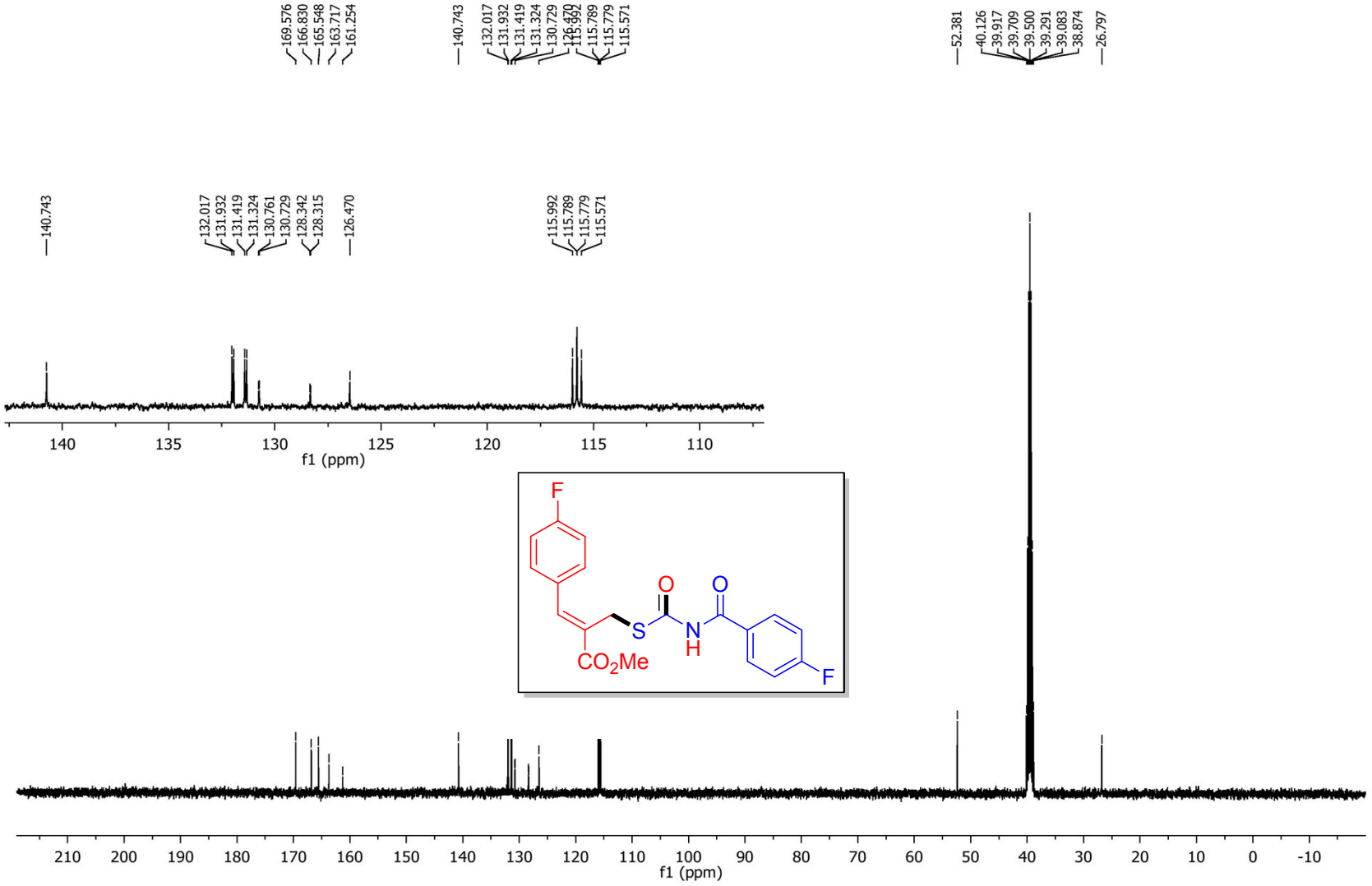
***Z*-Methyl 3-(4-fluorophenyl)-2-((((4-methoxybenzoyl)carbamoyl)thio)methyl)acrylate (4d): ^{19}FNMR (DMSO-d_6 + C_6F_6)**



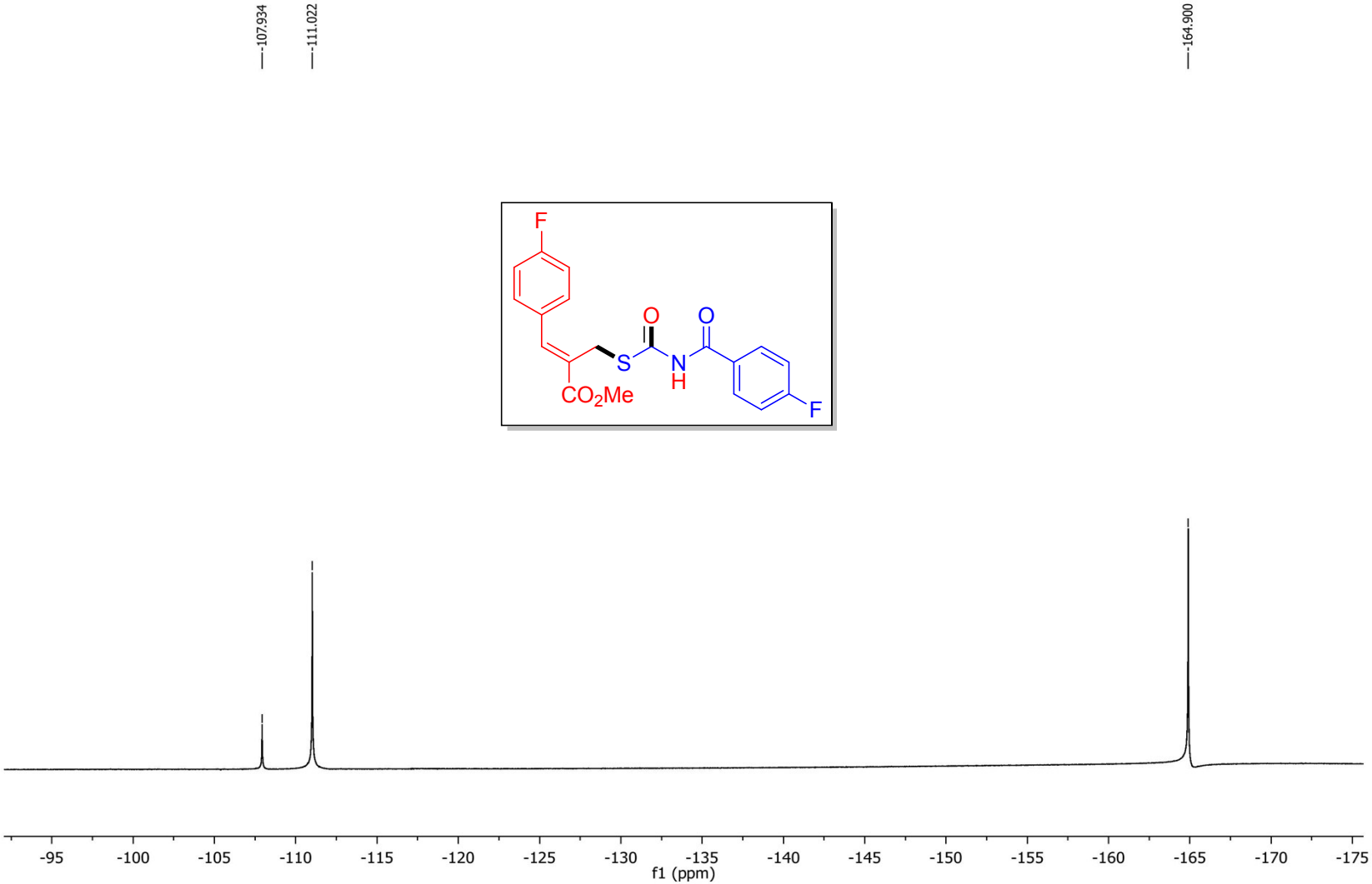
***Z*-Methyl 2-((((4-fluorobenzoyl)carbamoyl)thio)methyl)-3-(4-fluorophenyl)acrylate (4e): ^{1}HNMR (400 MHz, DMSO-d_6)**



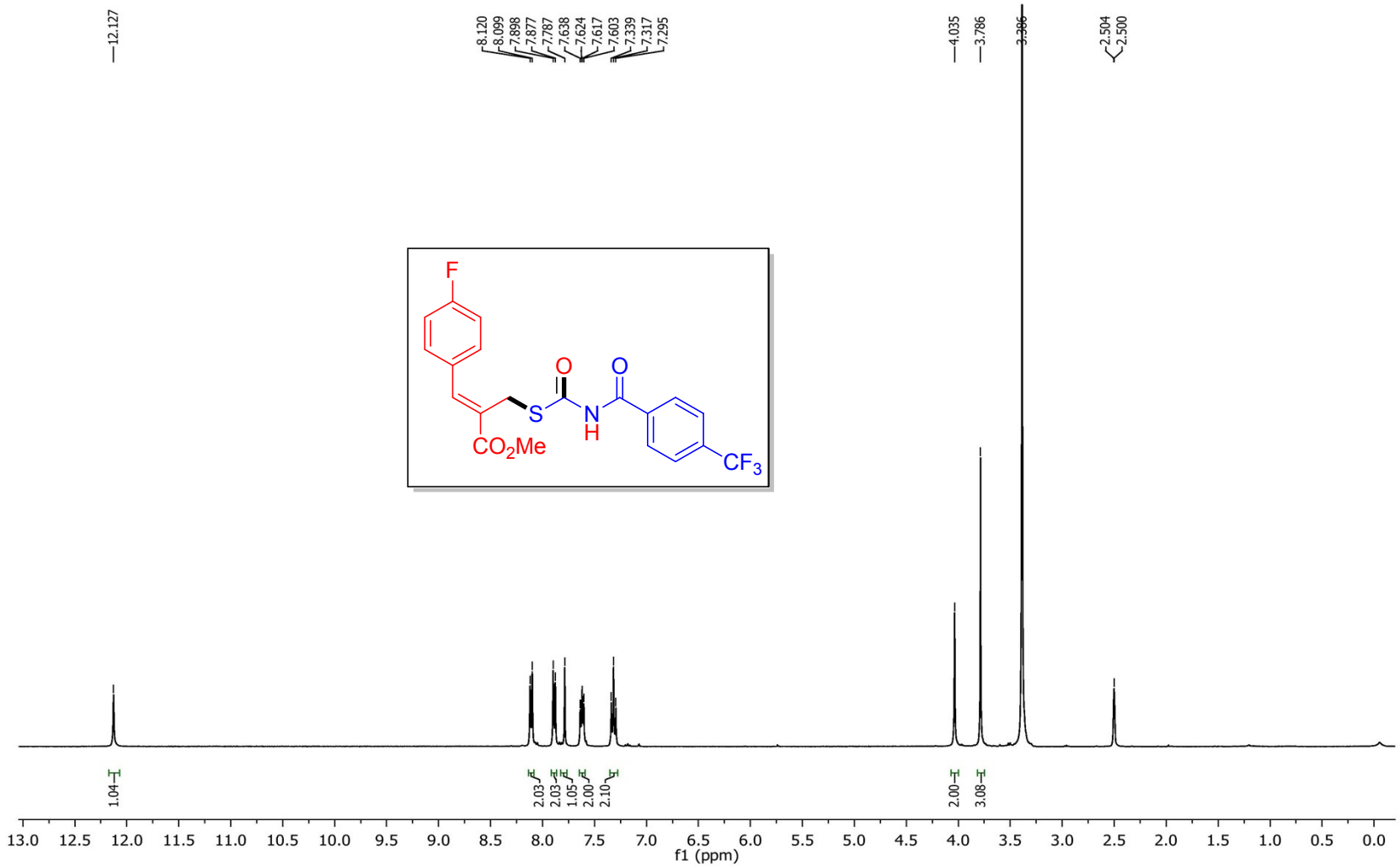
_Z_-Methyl 2-((((4-fluorobenzoyl)carbamoyl)thio)methyl)-3-(4-fluorophenyl)acrylate (4e): ^{13}CNMR (100 MHz, DMSO-d_6)



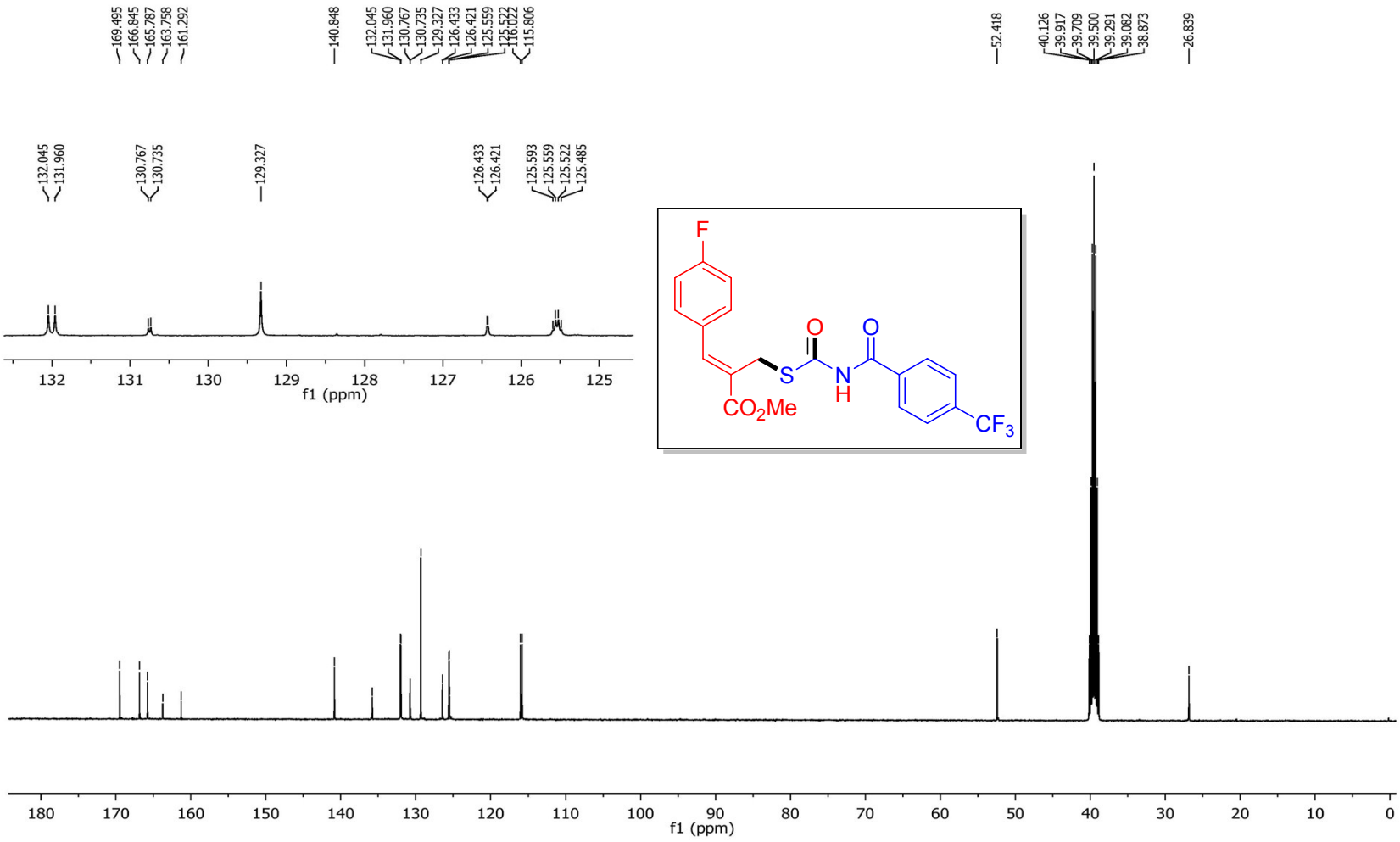
_Z_-Methyl 2-((((4-fluorobenzoyl)carbamoyl)thio)methyl)-3-(4-fluorophenyl)acrylate (4e): ^{13}CNMR (100 MHz, DMSO-d_6)



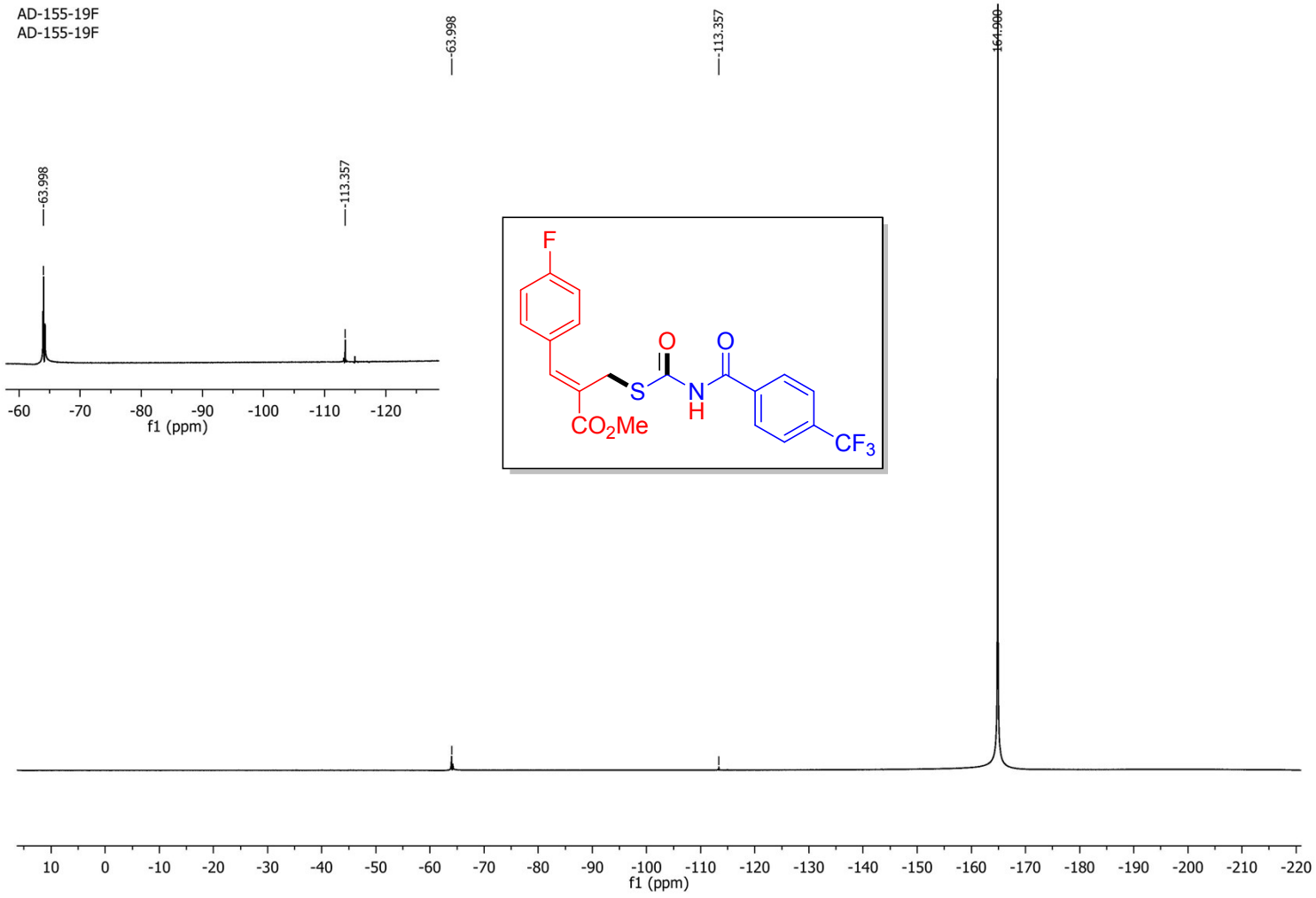
_Z_-Methyl 3-(4-fluorophenyl)-2-((((4-(trifluoromethyl)benzoyl)carbamoyl)thio)methyl)acrylate (4f): ^{1}HNMR (400 MHz, DMSO-d_6)



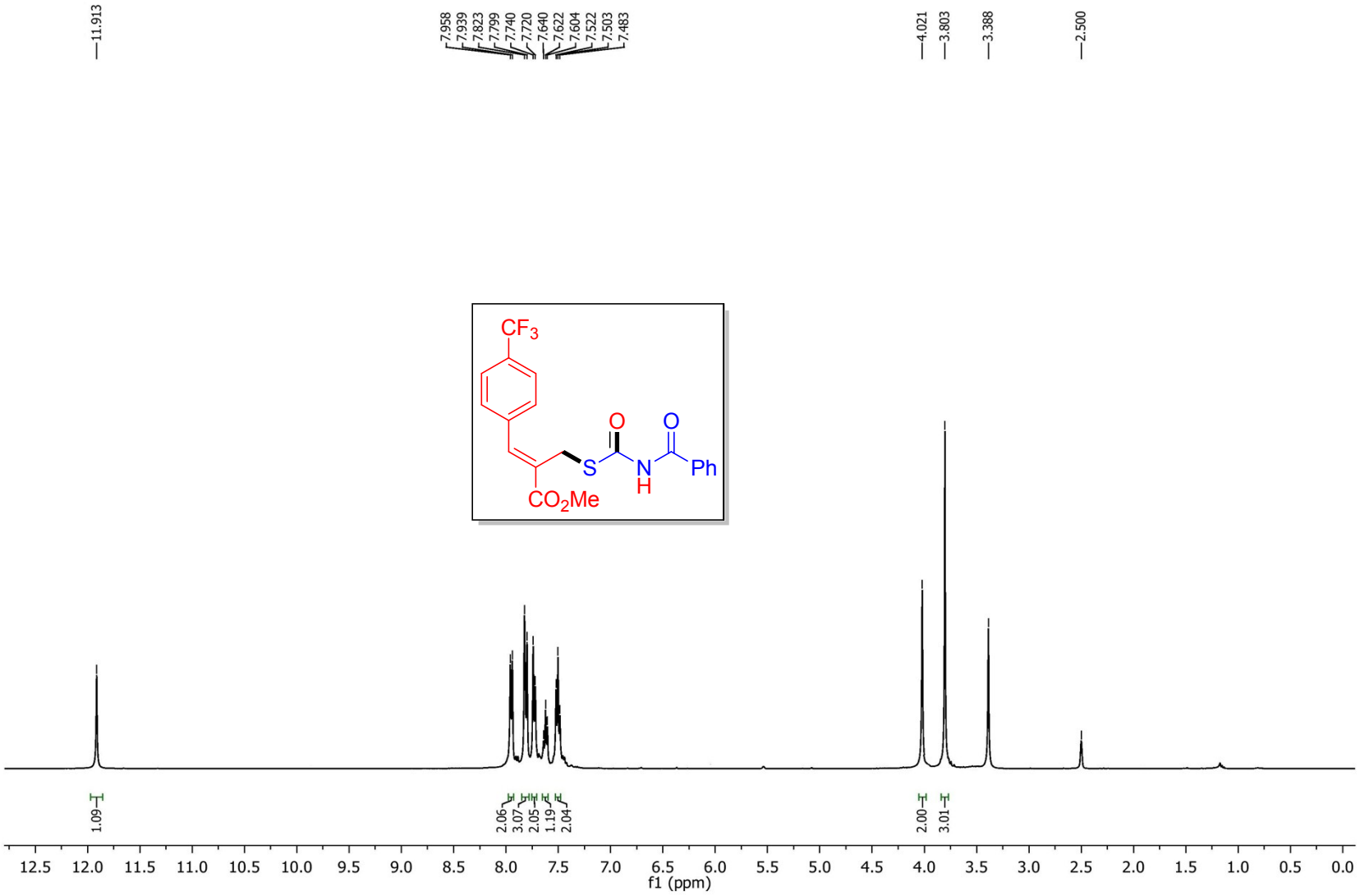
***Z*-Methyl 3-(4-fluorophenyl)-2-((((4-(trifluoromethyl)benzoyl)carbamoyl)thio)methyl)acrylate (4f): ^{13}CNMR (100 MHz, DMSO-d_6)**



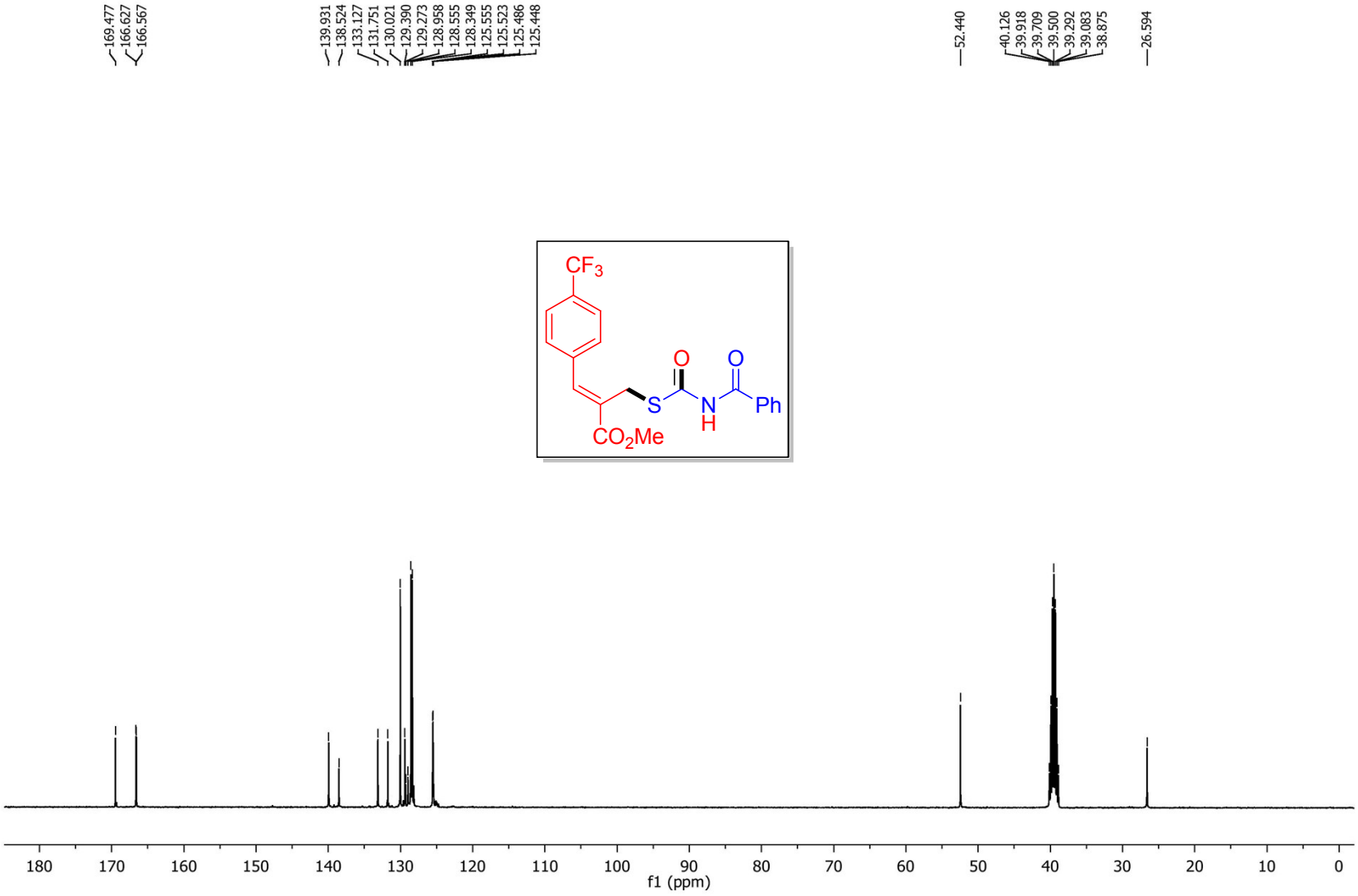
_Z_-Methyl 3-(4-fluorophenyl)-2-((((4-(trifluoromethyl)benzoyl)carbamoyl)thio)methyl)acrylate (4f): ^{19}FNMR (DMSO-d_6 + C_6F_6)



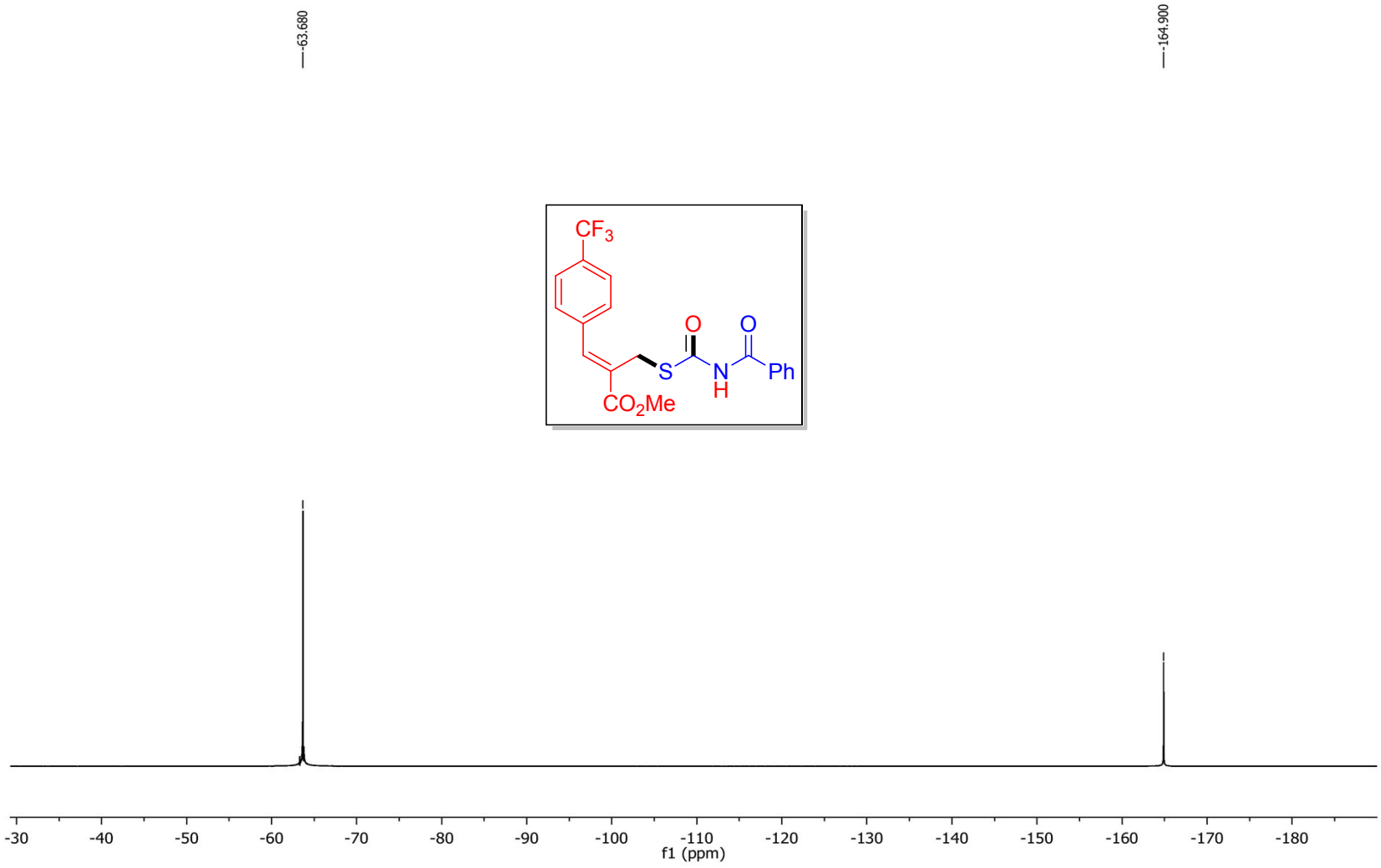
_Z_-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-(trifluoromethyl)phenyl)acrylate (5a): ^{1}HNMR (400 MHz, DMSO-d_6)



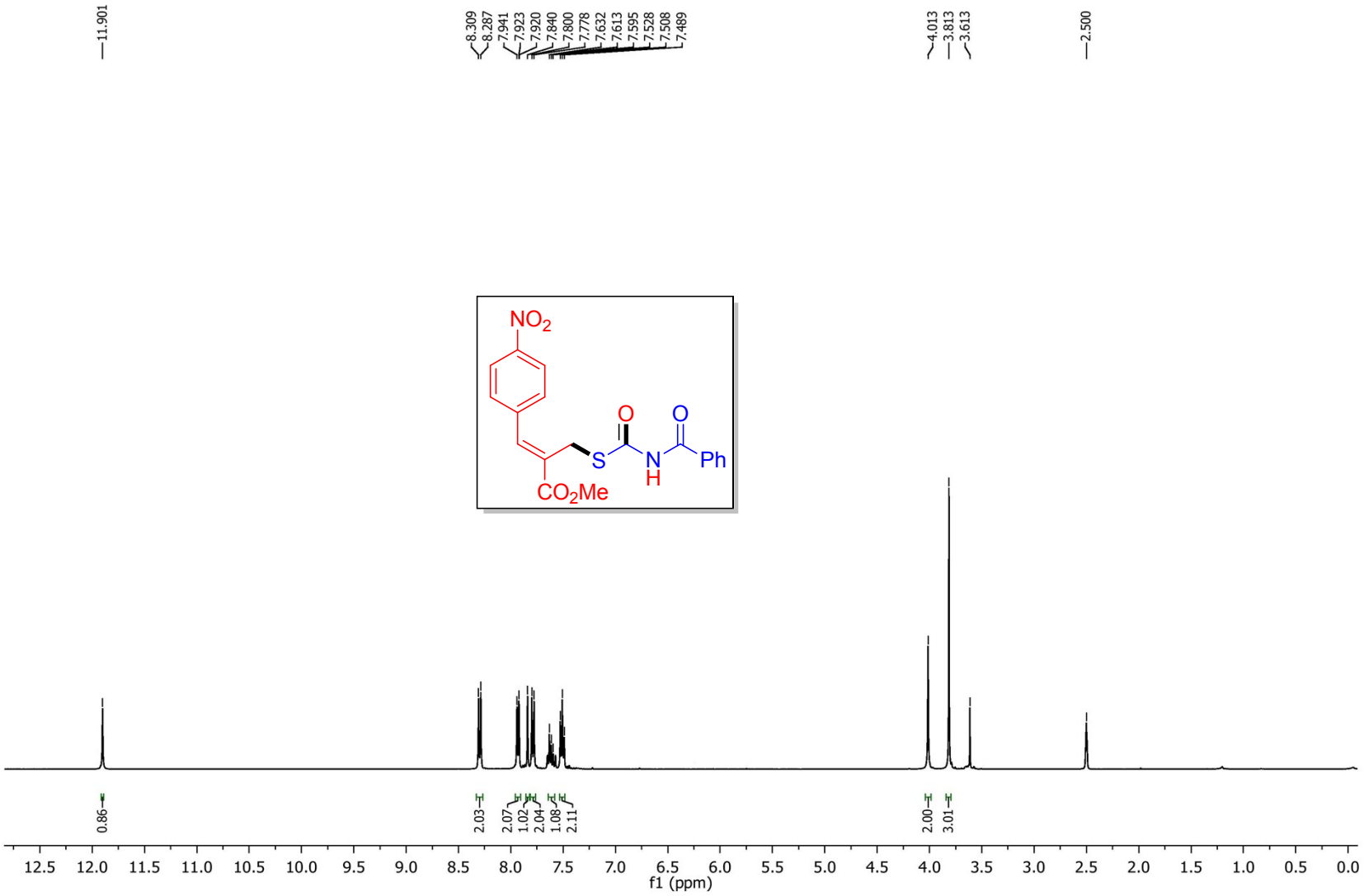
_Z_-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-(trifluoromethyl)phenyl)acrylate (5a): ^{13}CNMR (100 MHz, DMSO)



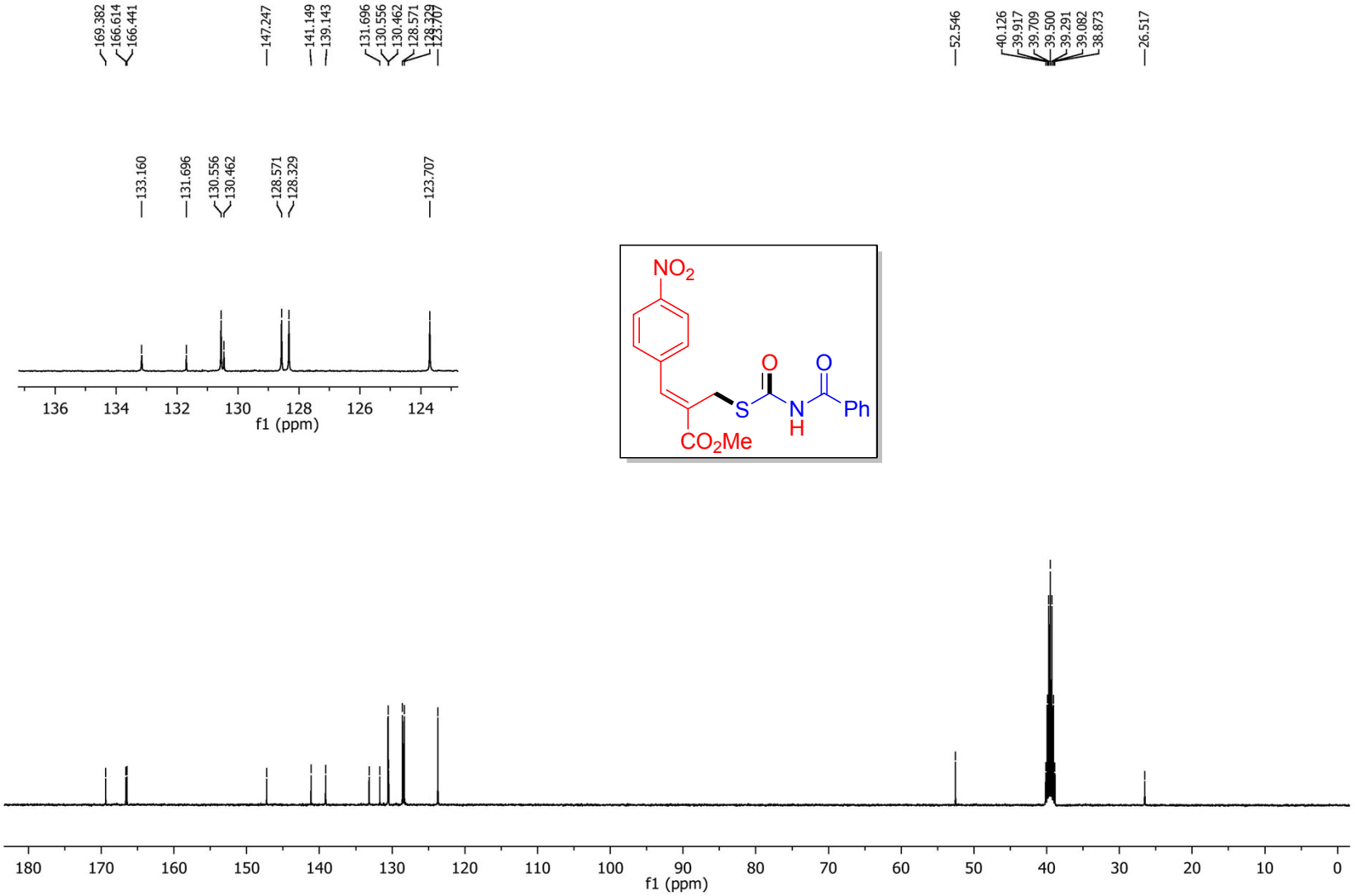
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-(trifluoromethyl)phenyl)acrylate (5a): ^{19}FNMR (DMSO-d_6 + C_6F_6)**



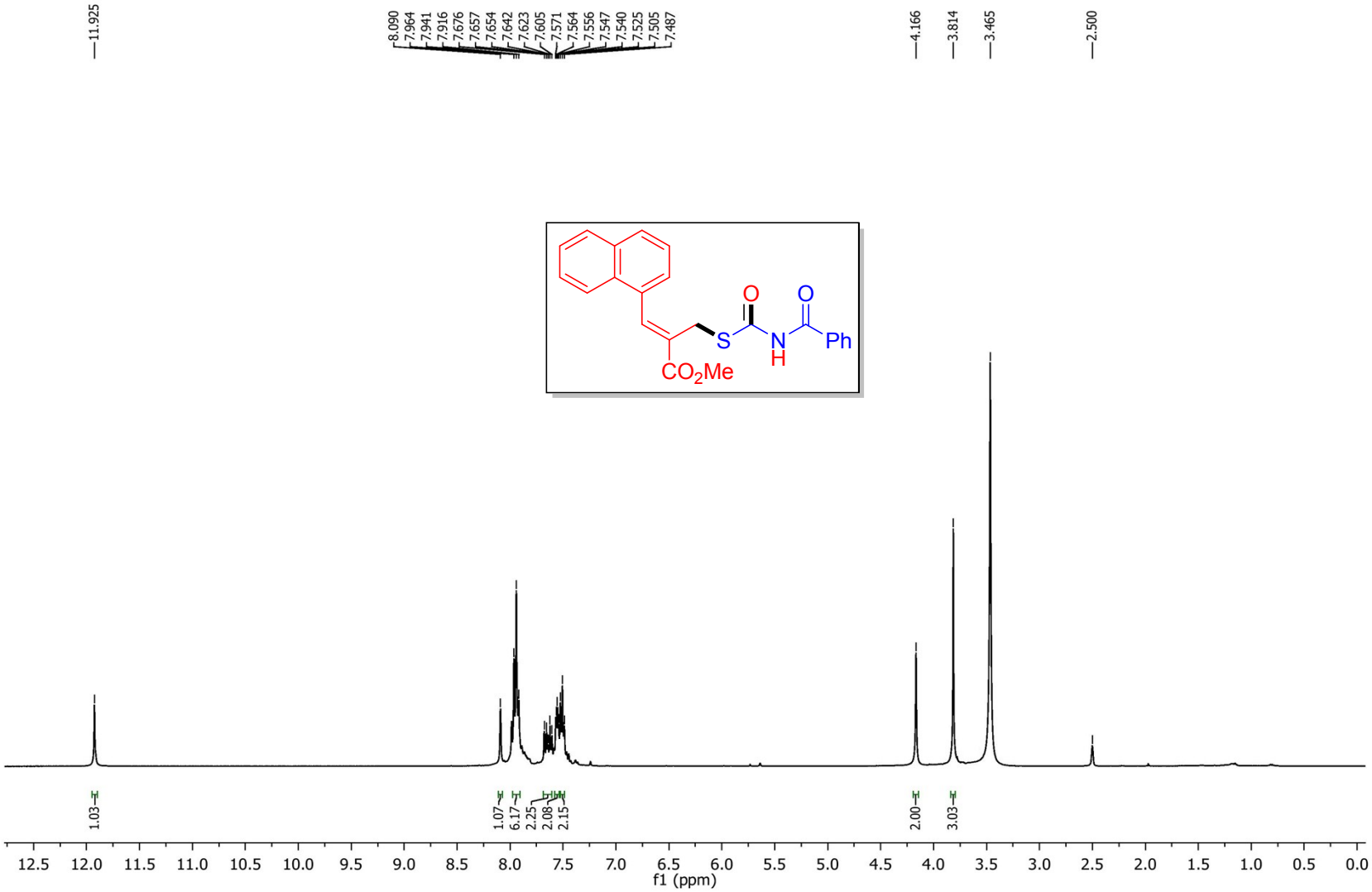
_Z_-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-nitrophenyl)acrylate (6a): ^{1}HNMR (400 MHz, DMSO-d_6)



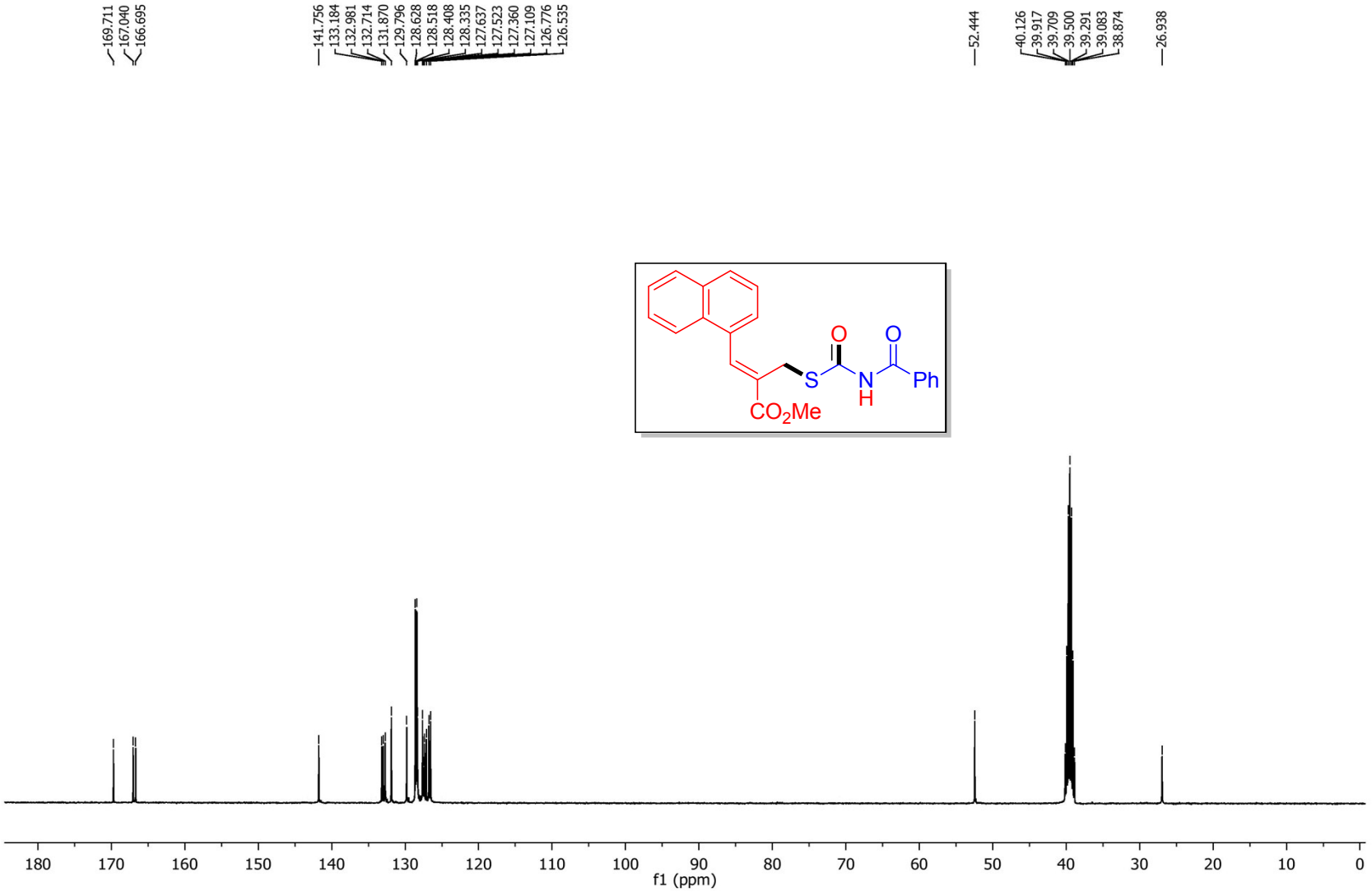
_Z_-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(4-nitrophenyl)acrylate (6a): ^{13}CNMR (100 MHz, DMSO)



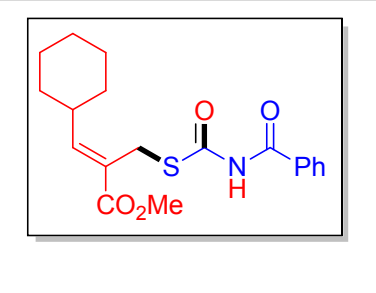
_Z_-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(naphthalen-1-yl)acrylate (7a): ^{1}HNMR (400 MHz, DMSO-d_6)



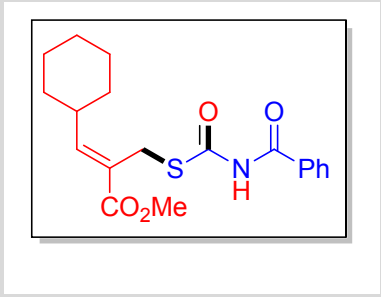
_Z_-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(naphthalen-1-yl)acrylate (7a): ^{13}CNMR (100 MHz, DMSO)



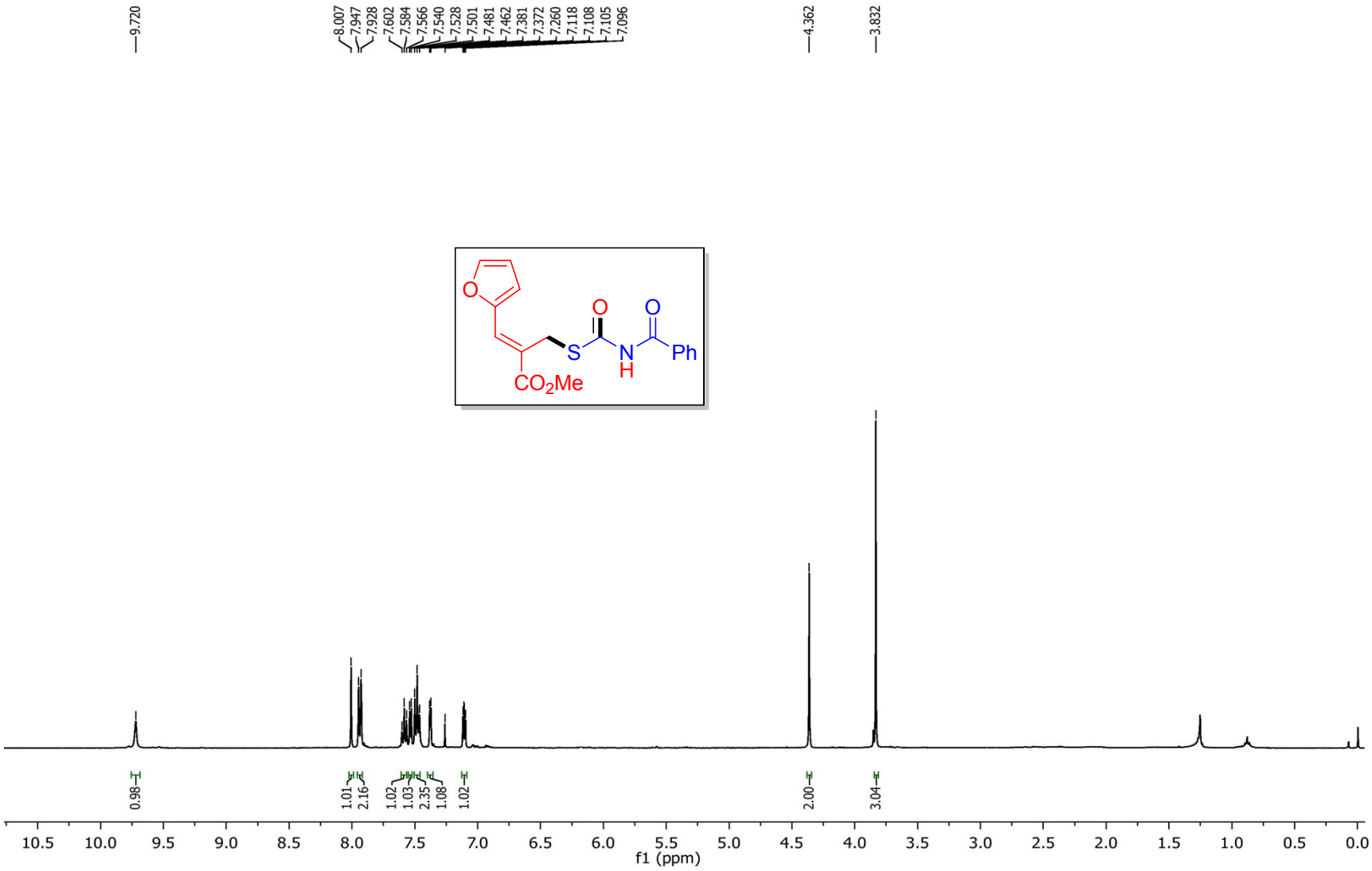
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-cyclohexylacrylate (8a): ^{1}HNMR (400 MHz, $CDCl_3$)**



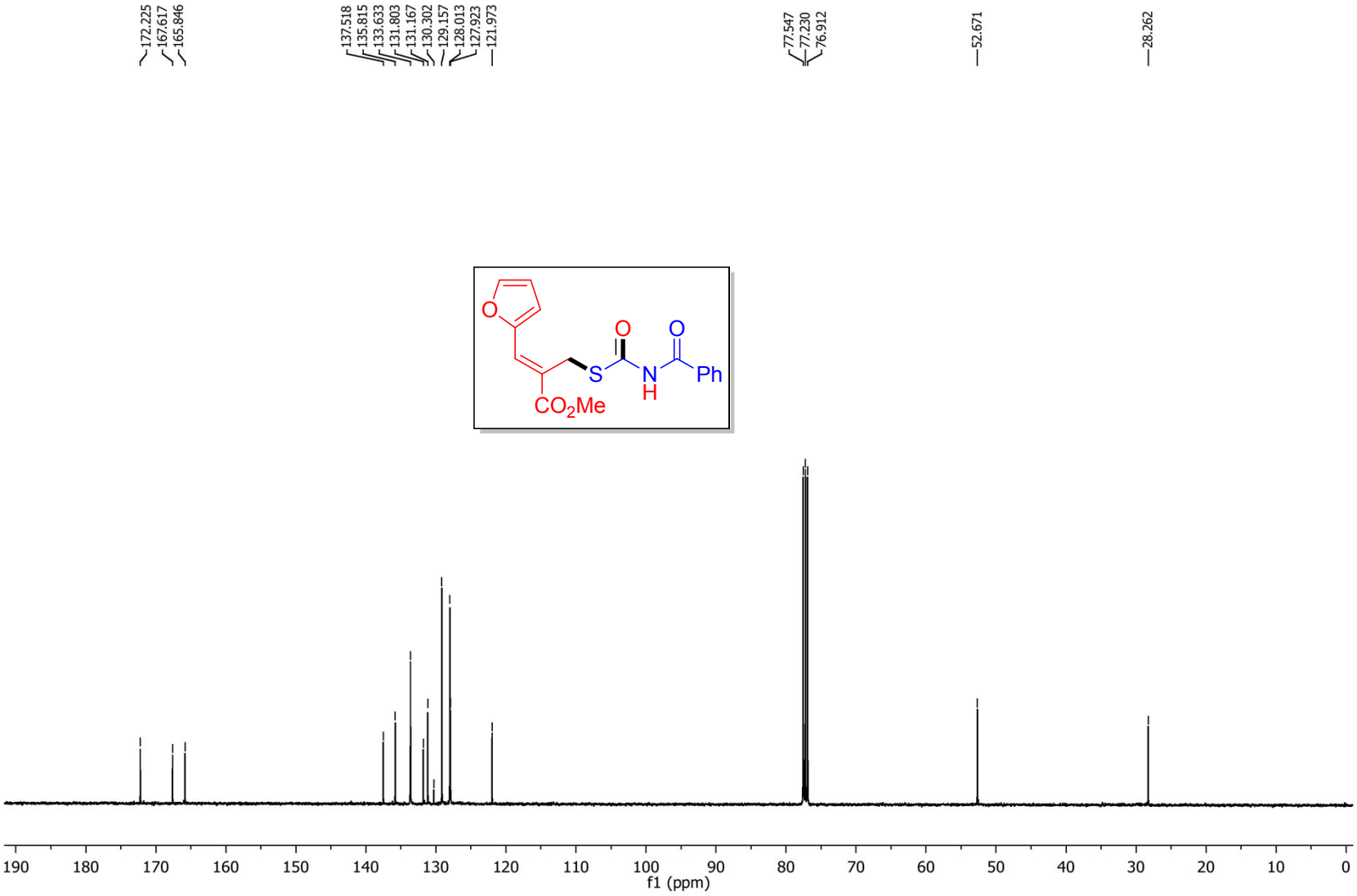
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-cyclohexylacrylate (8a): ^{13}CNMR (100 MHz, $CDCl_3$)**



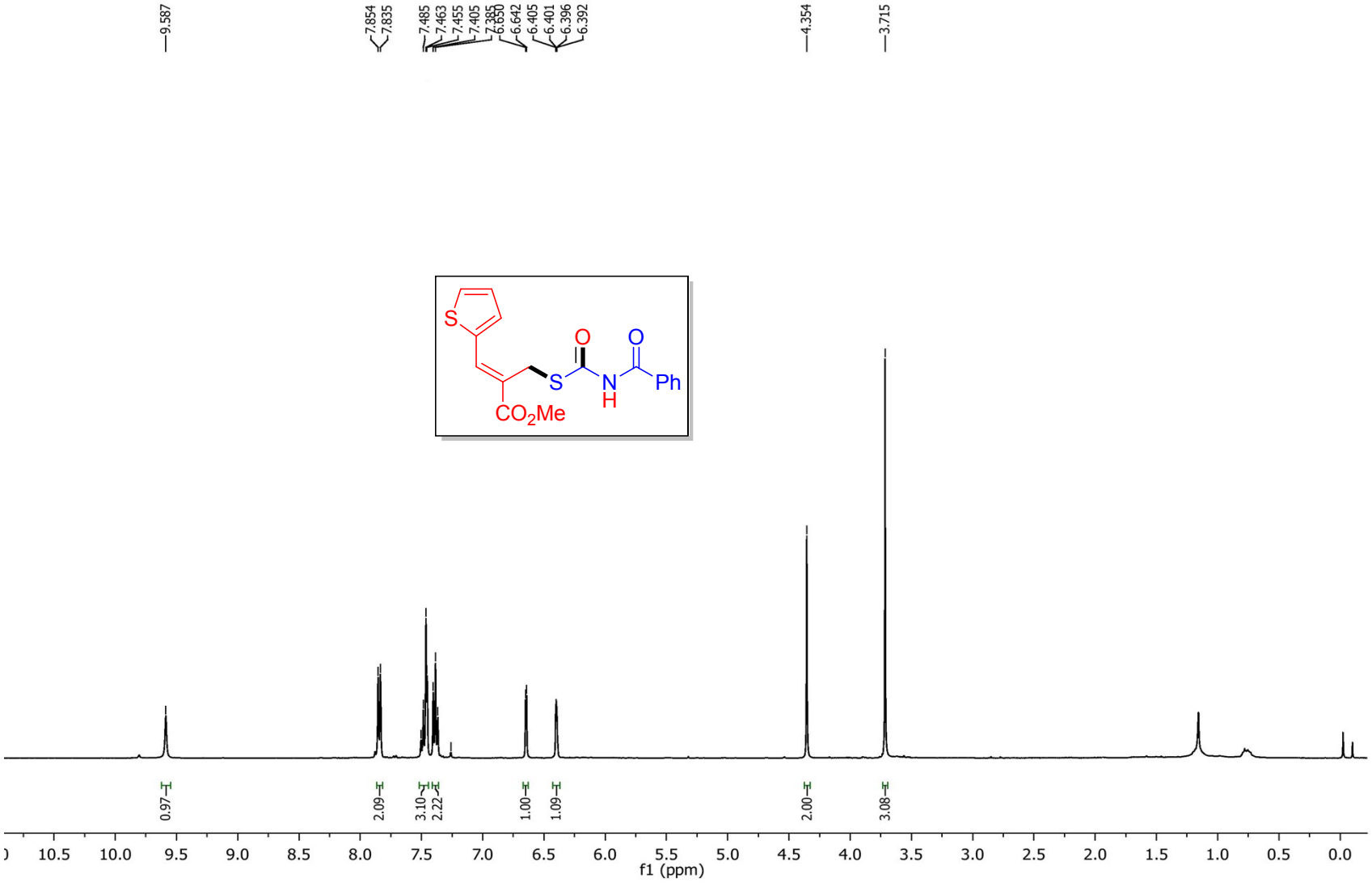
***Z*-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(furan-2-yl)acrylate (9a): ^{1}HNMR (400 MHz, $CDCl_3$)**



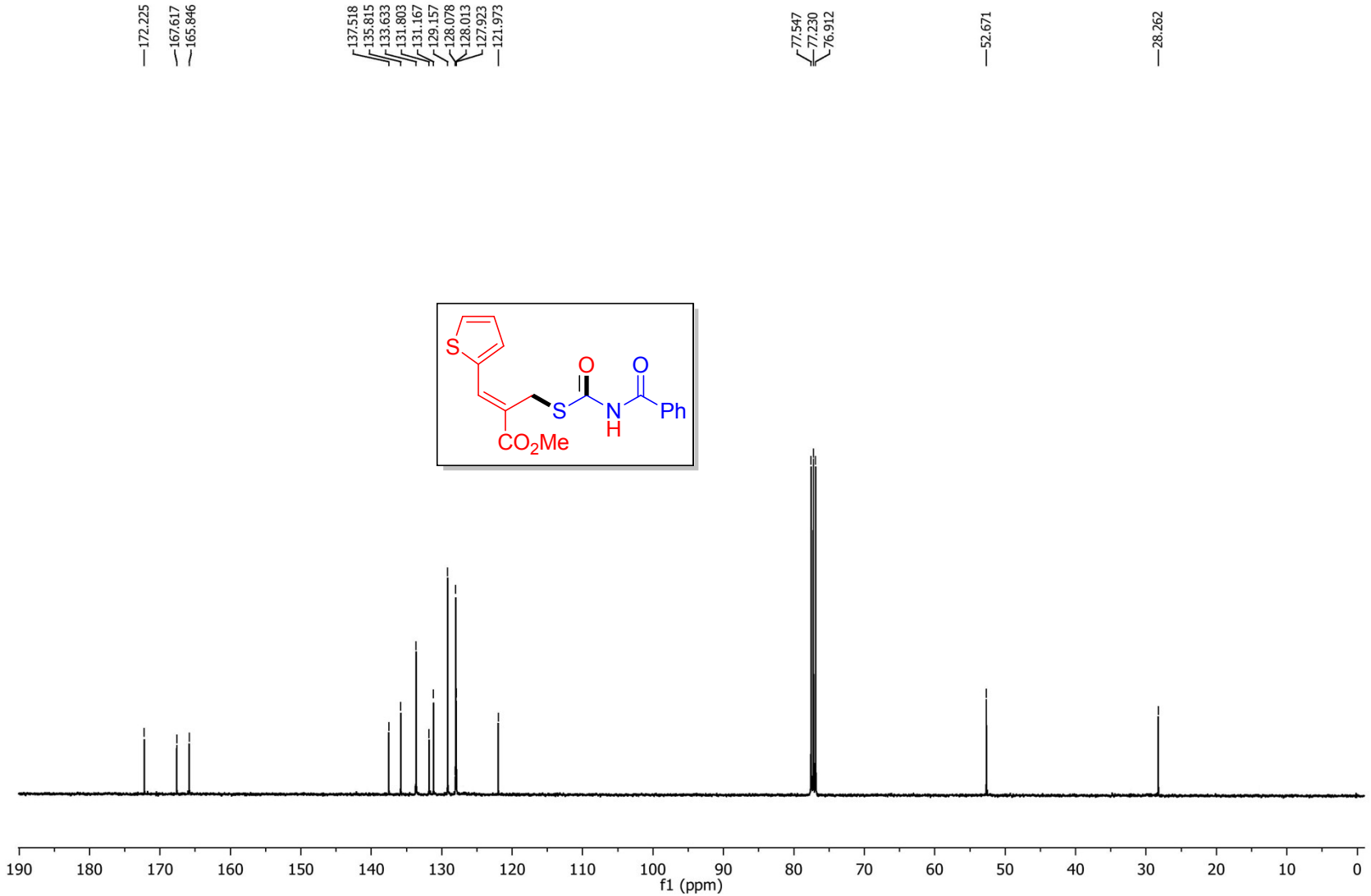
_Z_-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(furan-2-yl)acrylate (9a): ^{13}CNMR (100 MHz, $CDCl_3$)



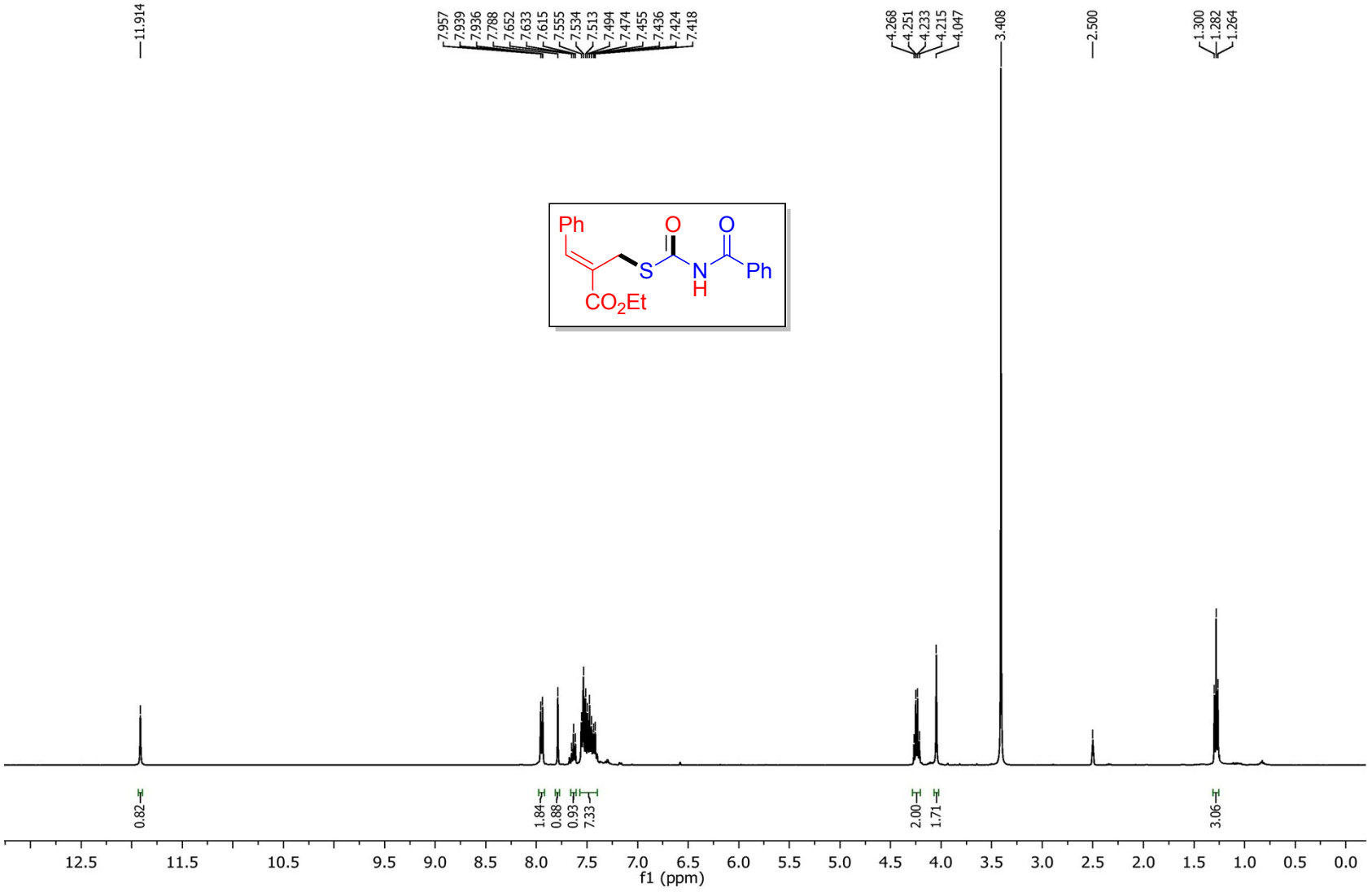
_Z_-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(thiophen-2-yl)acrylate (10a): ^{1}HNMR (400 MHz, $CDCl_3$)



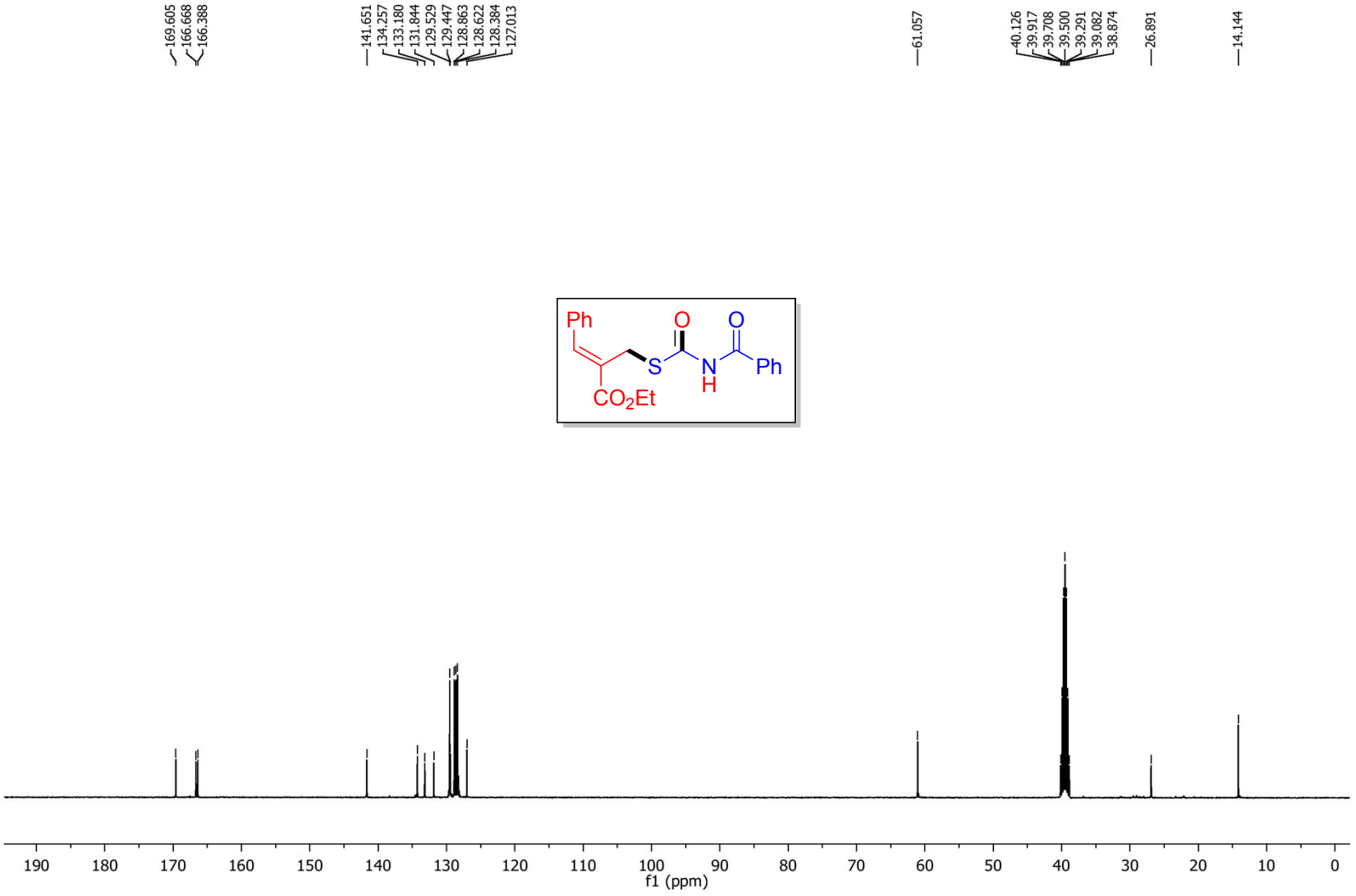
_Z_-Methyl 2-(((benzoylcarbamoyl)thio)methyl)-3-(thiophen-2-yl)acrylate (10a): ^{13}CNMR (100 MHz, $CDCl_3$)



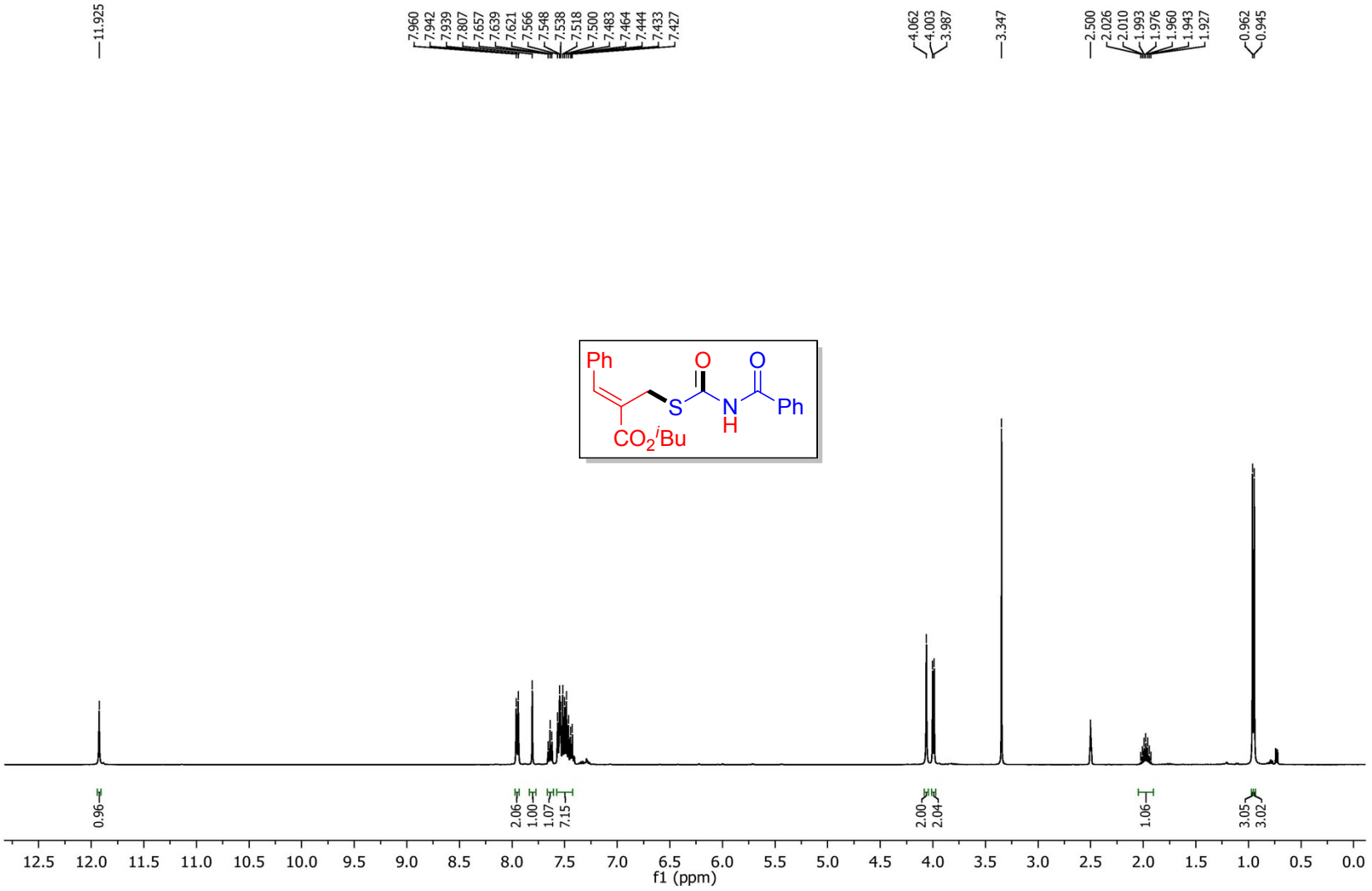
_Z_-Ethyl 2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (11a): ^{1}HNMR (400 MHz, DMSO-d_6)



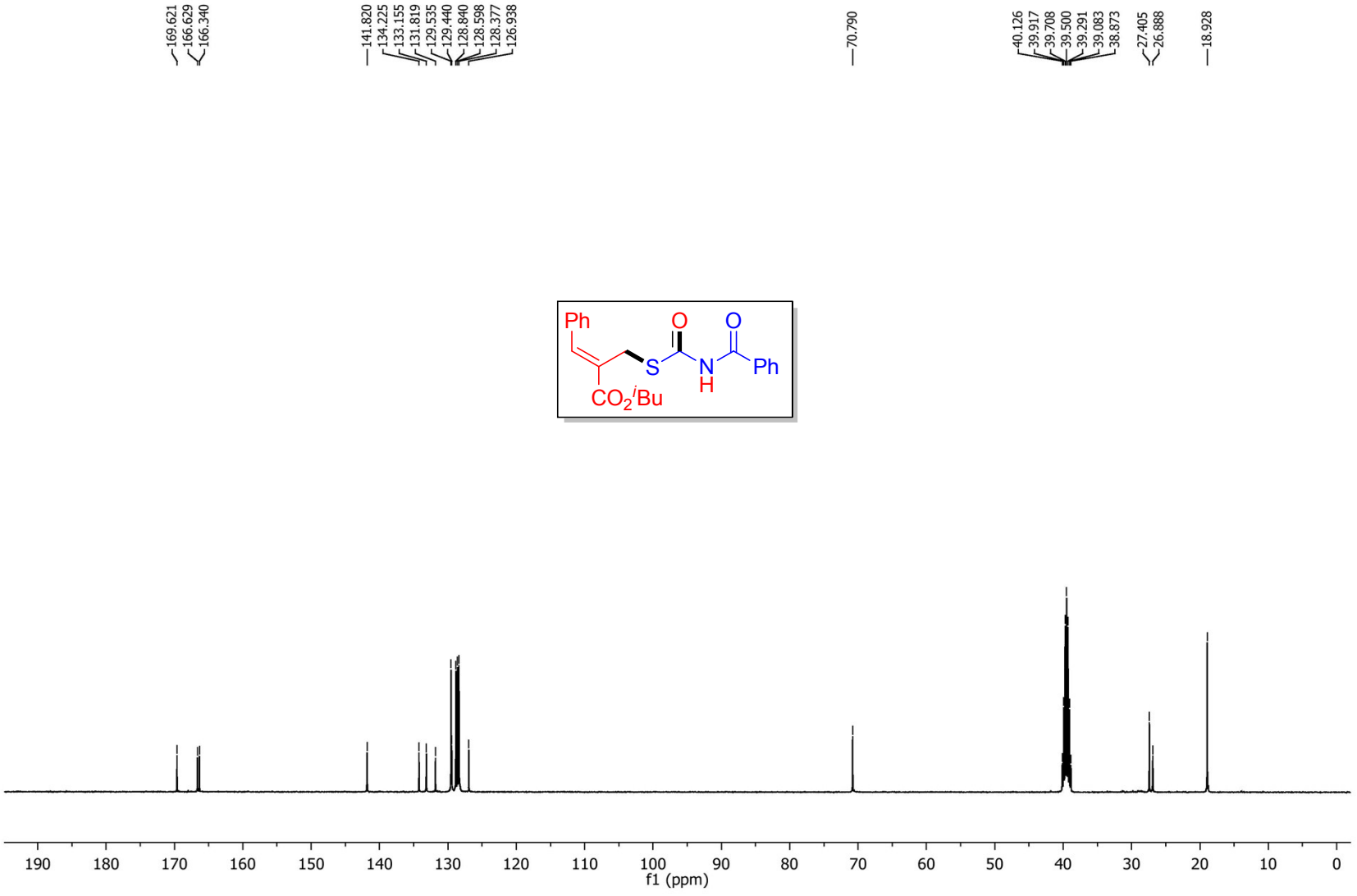
_Z_-Ethyl 2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (11a): ^{13}CNMR (100 MHz, DMSO-d_6)



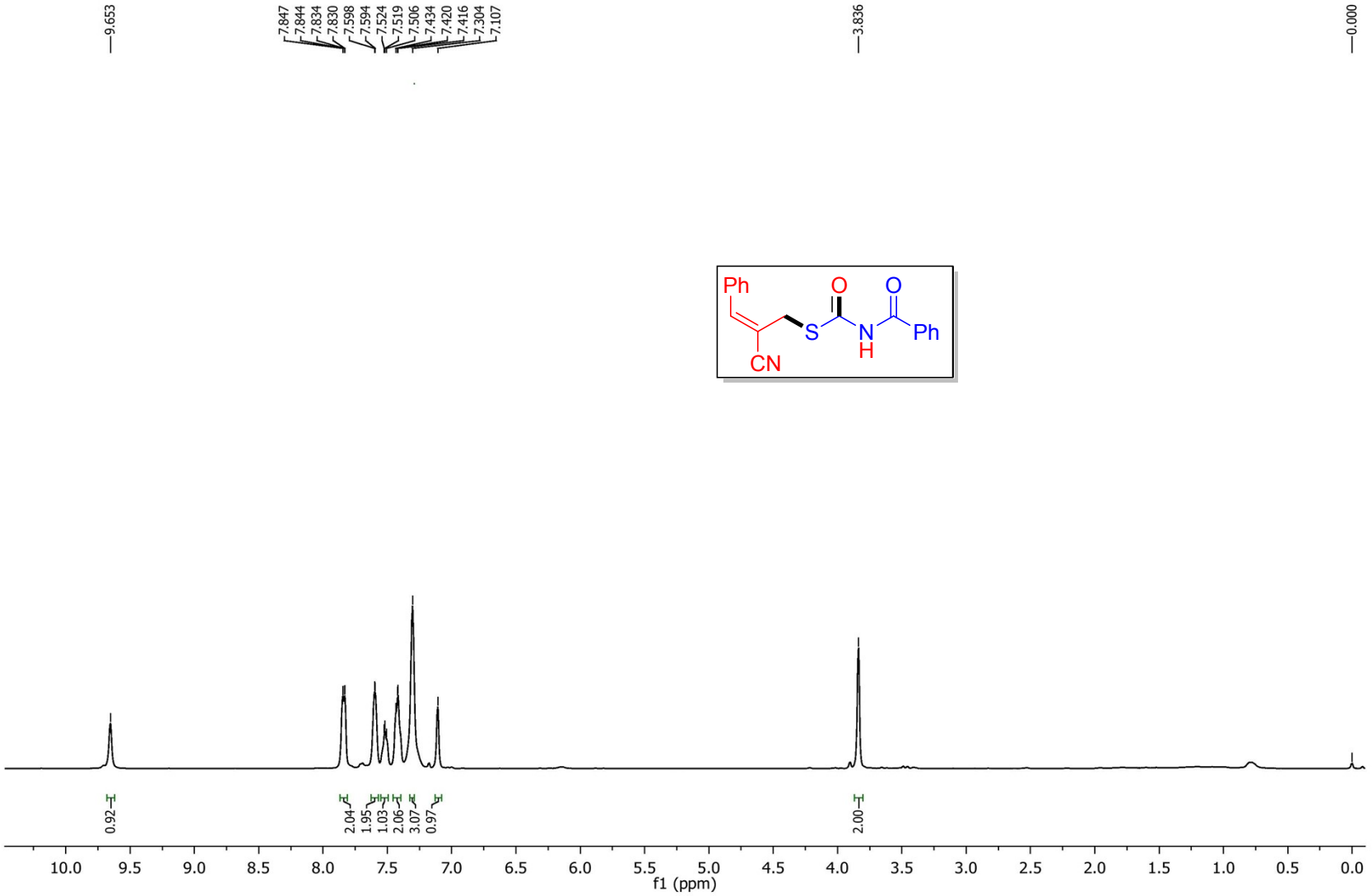
_Z_-Isobutyl 2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (12a): ^{1}HNMR (400 MHz, DMSO-d_6)



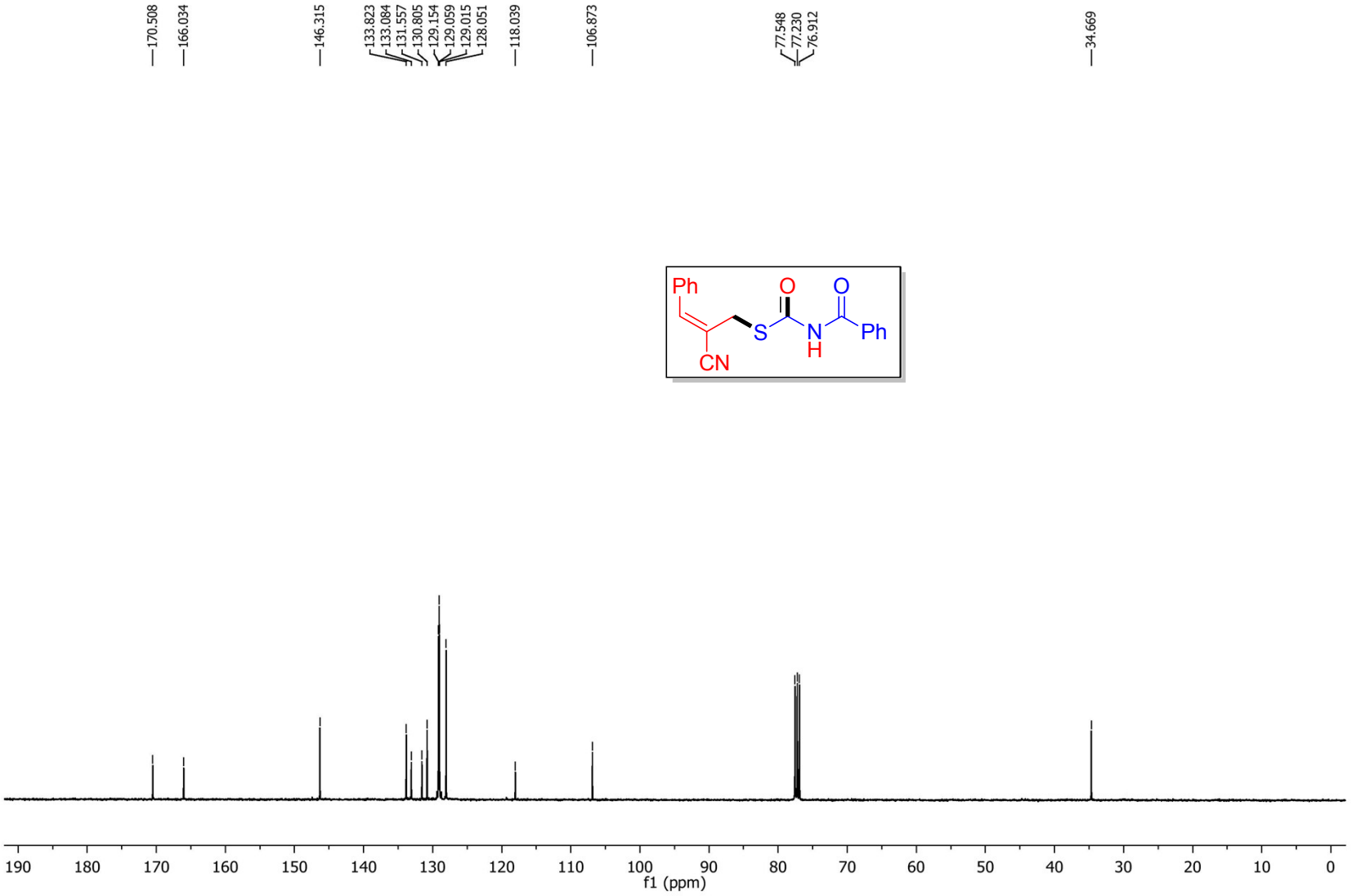
_Z_-Isobutyl 2-(((benzoylcarbamoyl)thio)methyl)-3-phenylacrylate (12a): ^{13}CNMR (100 MHz, DMSO-d$_6$)



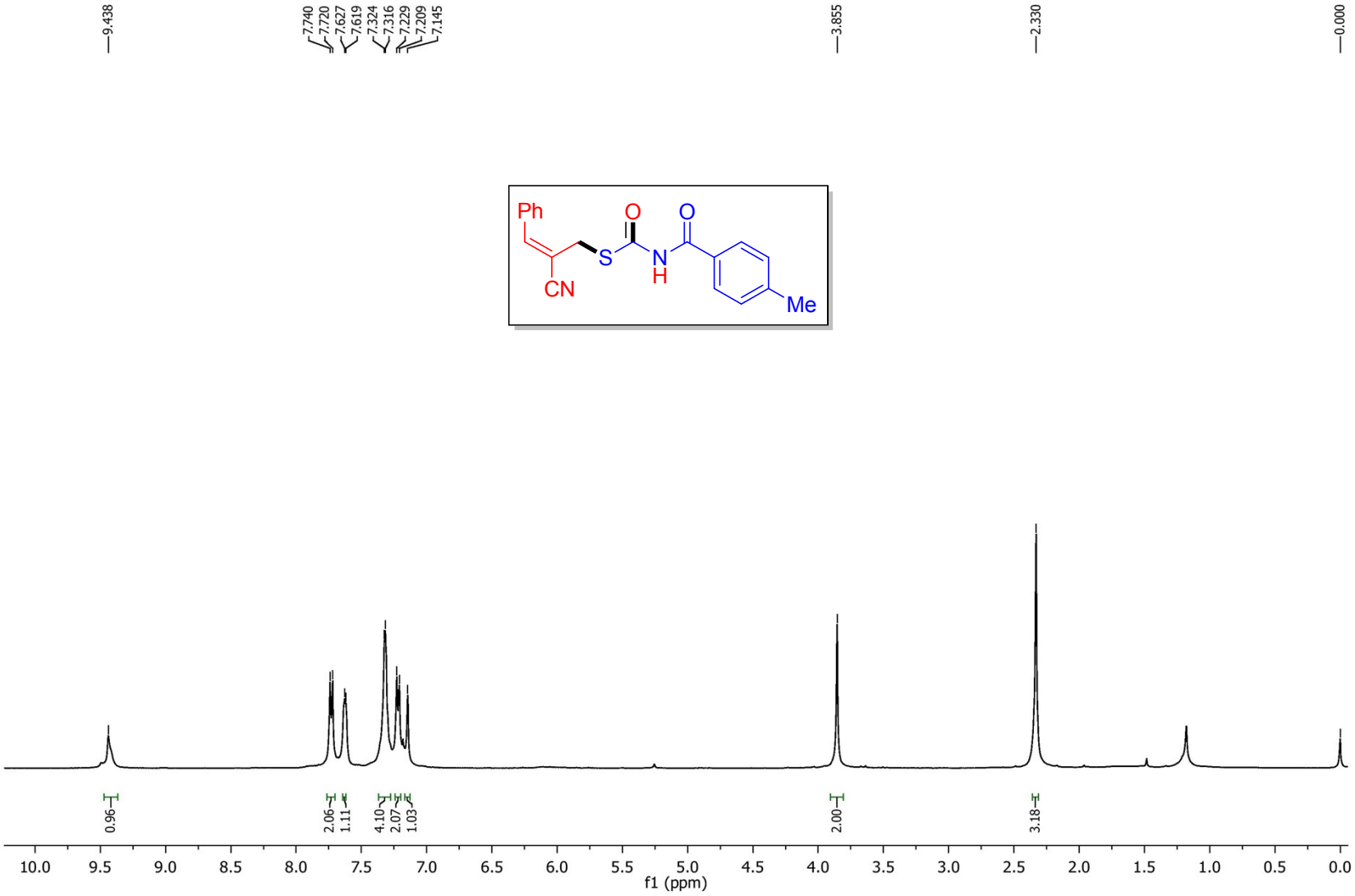
_Z_-S-(2-Cyano-3-phenylallyl) benzoylcarbamothioate (13a): ^{1}HNMR (400 MHz, $CDCl_3$)



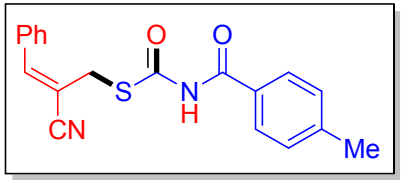
_Z_-S-(2-Cyano-3-phenylallyl) benzoylcarbamothioate (13a): ^{13}CNMR (100 MHz, $CDCl_3$)

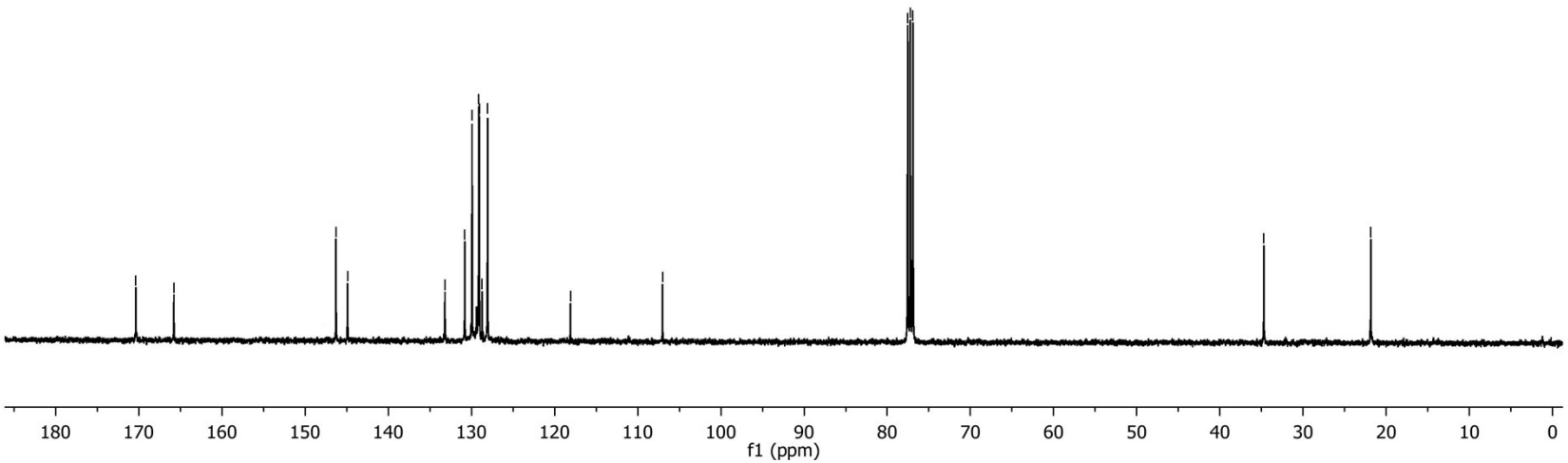


_Z_-S-(2-Cyano-3-phenylallyl) (4-methylbenzoyl)carbamothioate (13b): ^{1}HNMR (400 MHz, $CDCl_3$):

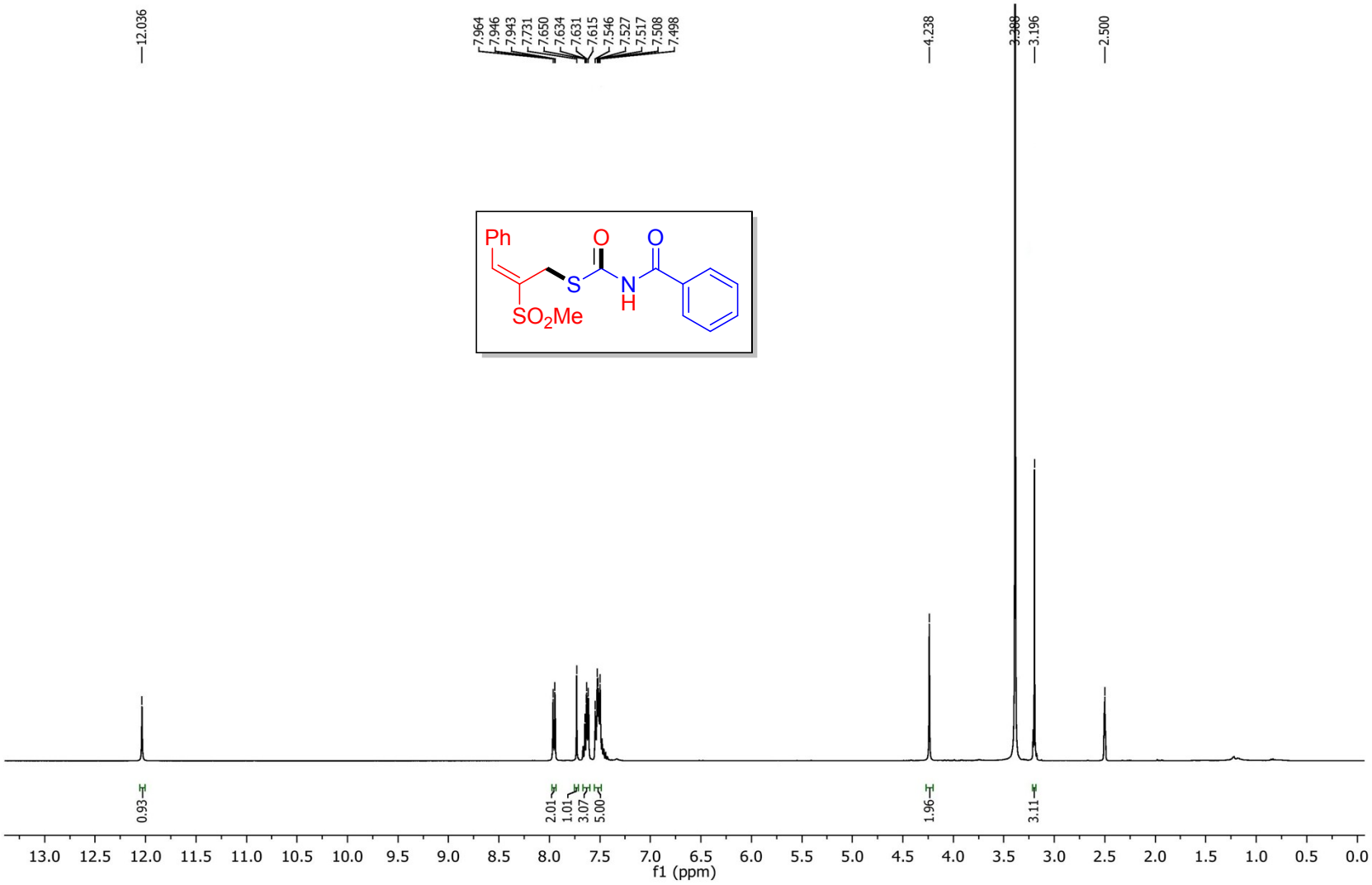


_Z_-S-(2-Cyano-3-phenylallyl) (4-methylbenzoyl)carbamothioate (13b): ^{13}CNMR (100 MHz, $CDCl_3$):

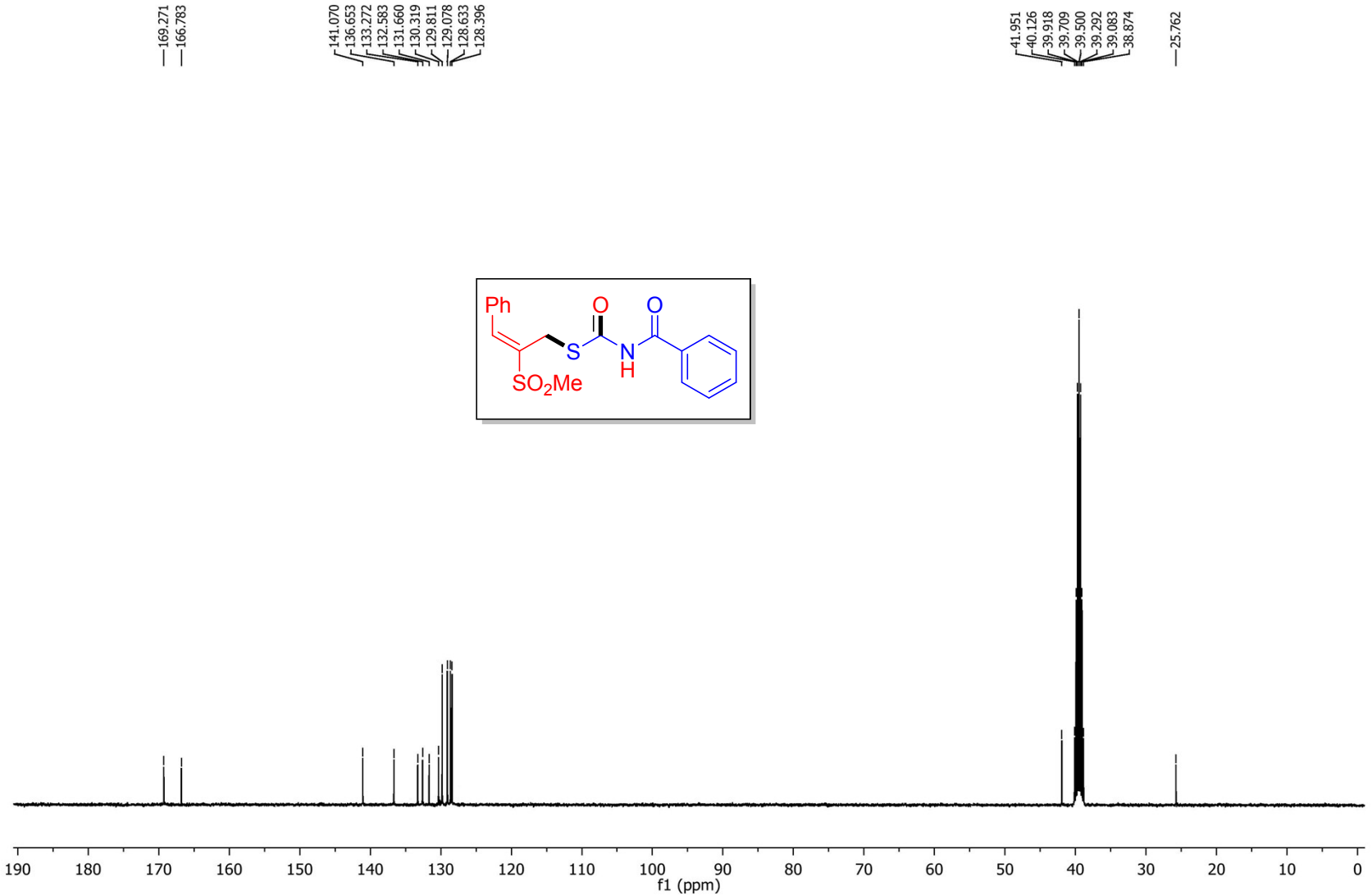




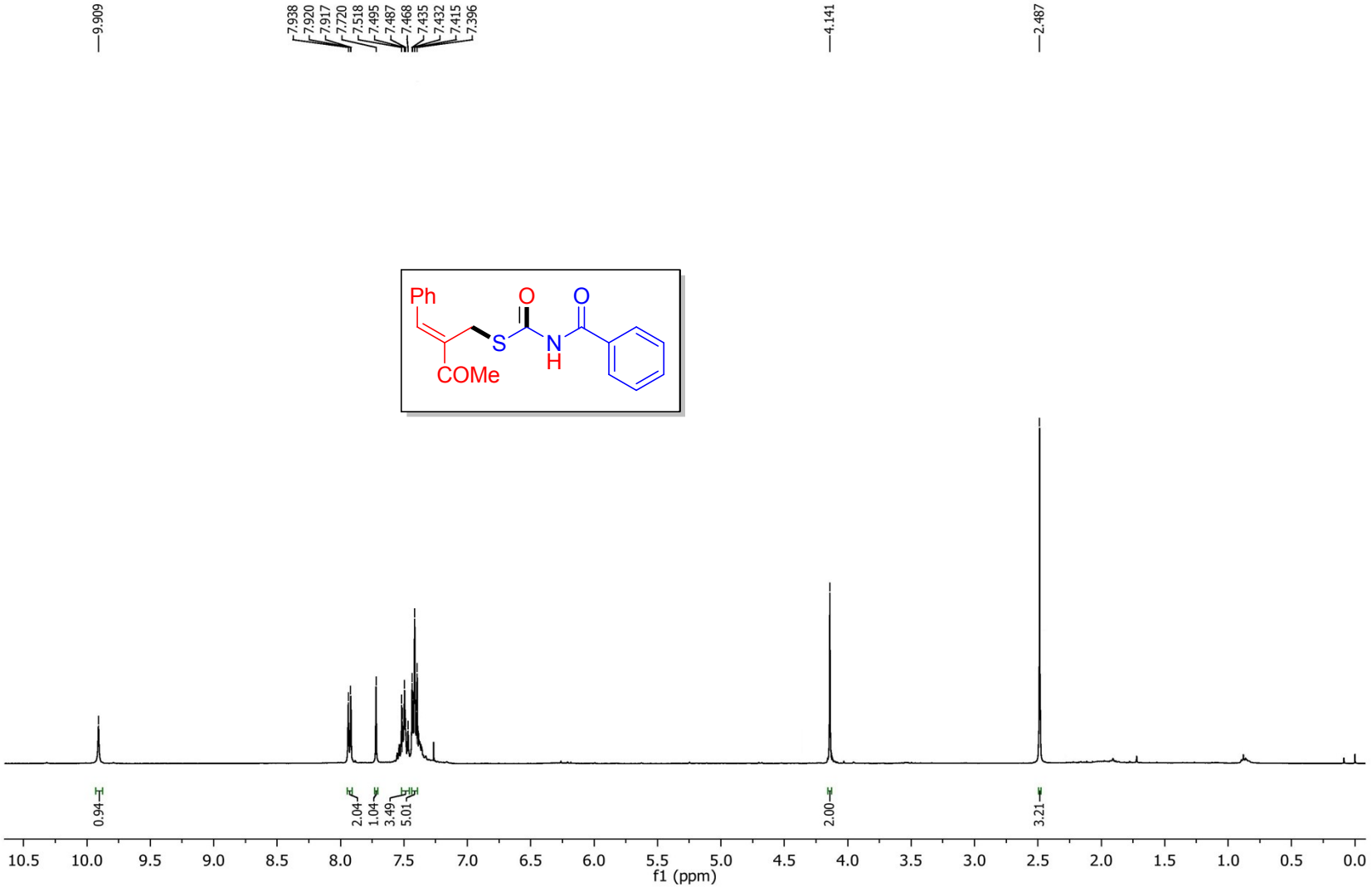
_E_-S-(2-(Methylsulfonyl)-3-phenylallyl) benzoylcarbamothioate (14a): ^{1}HNMR (400 MHz, DMSO-d_6)



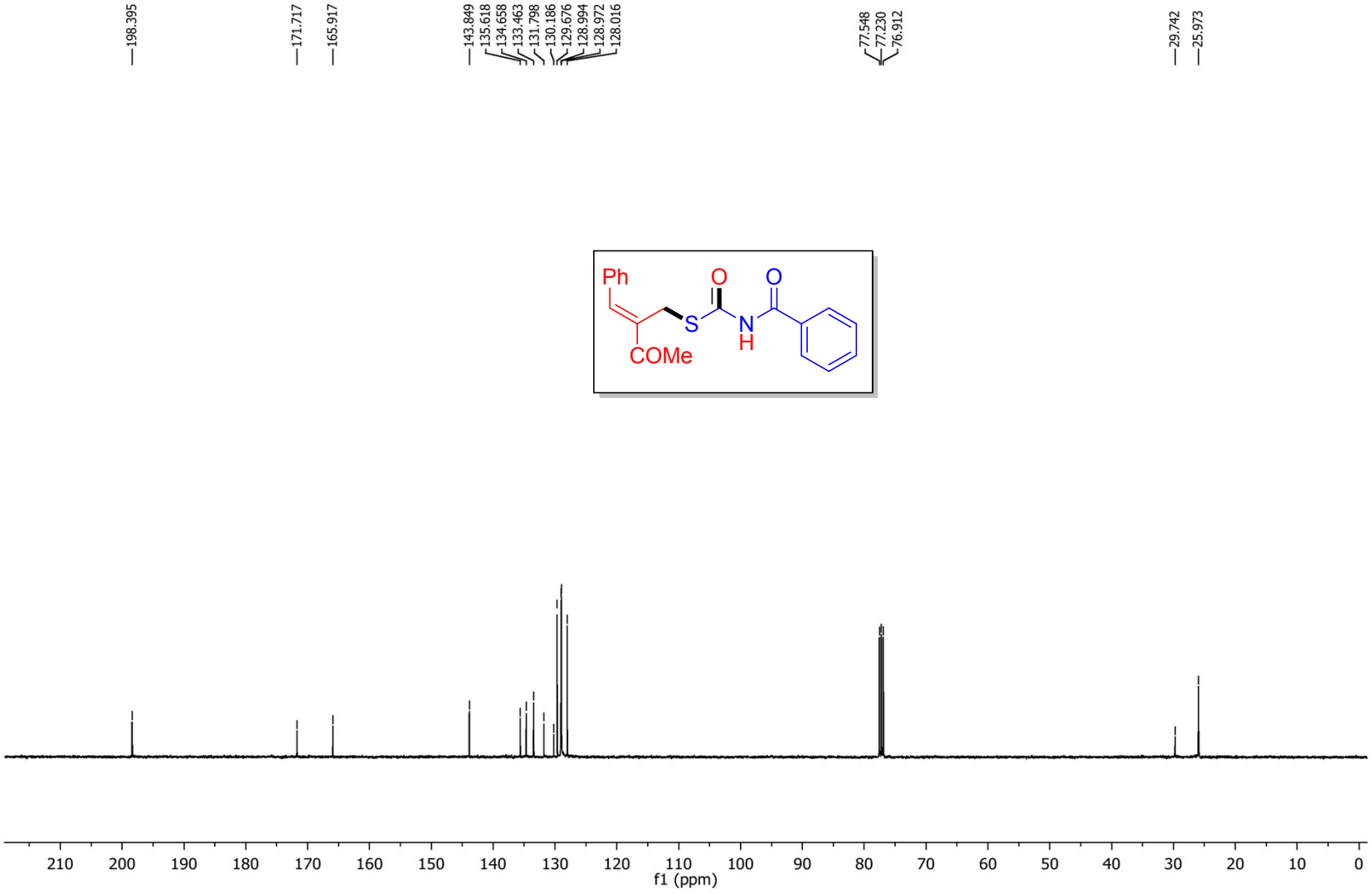
_E_-S-(2-(Methylsulfonyl)-3-phenylallyl) benzoylcarbamothioate (14a): ^{13}CNMR (100 MHz, DMSO-d$_6$)



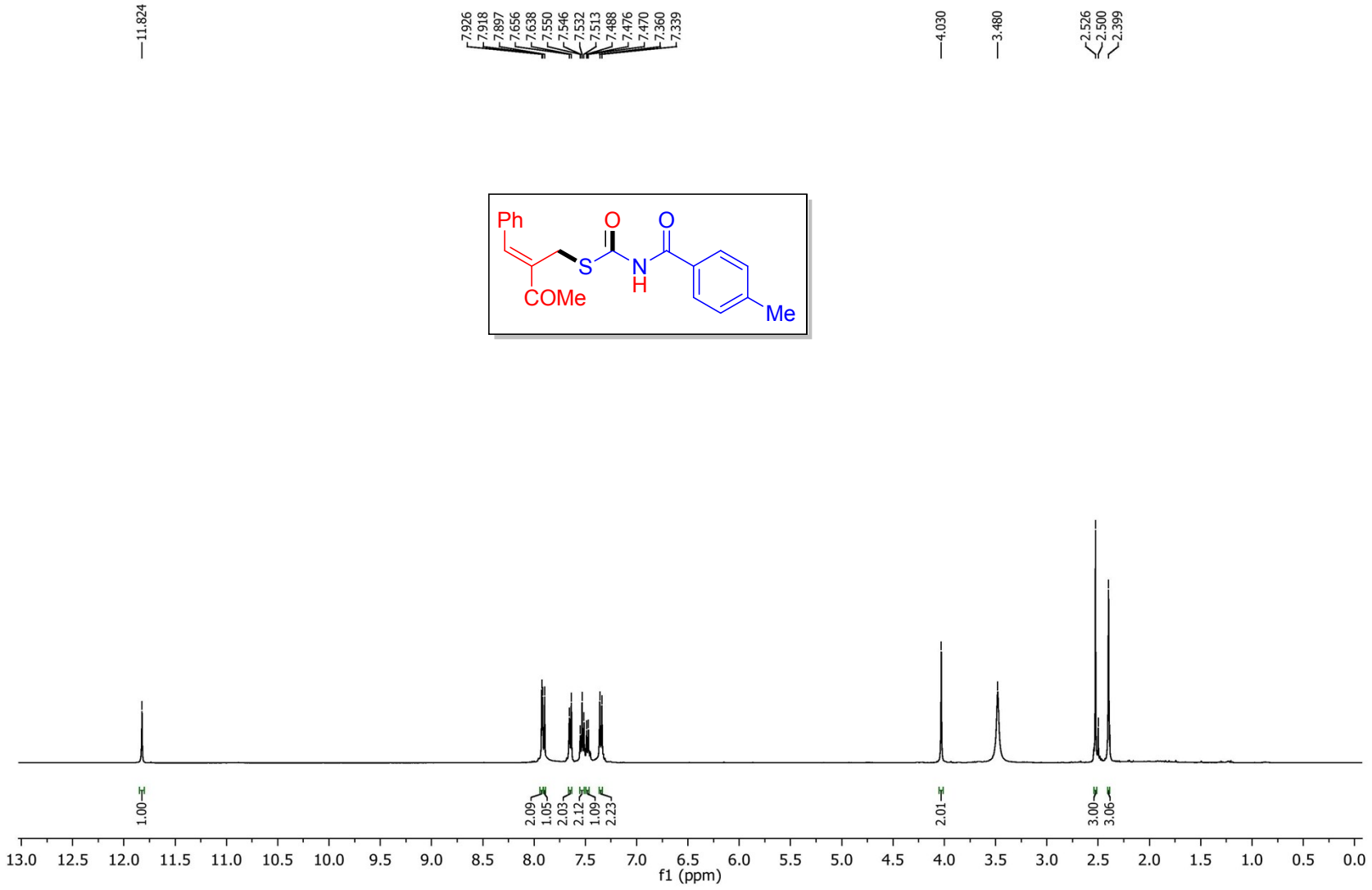
_Z_-S-(2-Benzylidene-3-oxobutyl) benzoylcarbamothioate (15a): ^{1}HNMR (400 MHz, $CDCl_3$)



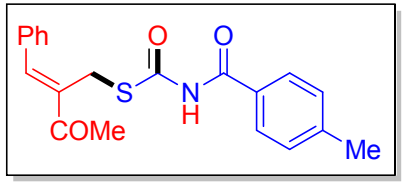
_Z_-S-(2-Benzylidene-3-oxobutyl) benzoylcarbamothioate (15a): ^{13}CNMR (100 MHz, $CDCl_3$)

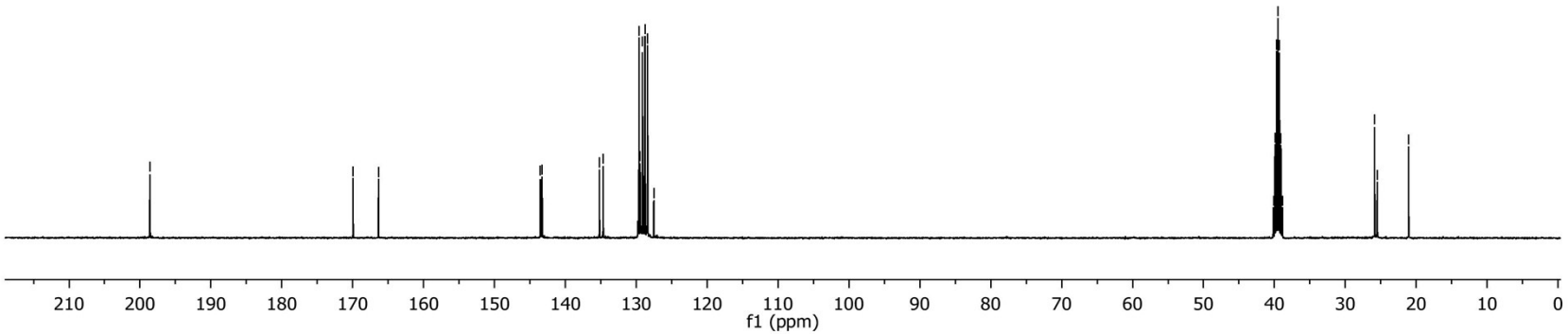


_Z_-S-(2-Benzylidene-3-oxobutyl) (4-methylbenzoyl)carbamothioate (15b): ^{1}HNMR (400 MHz, DMSO-d_6)

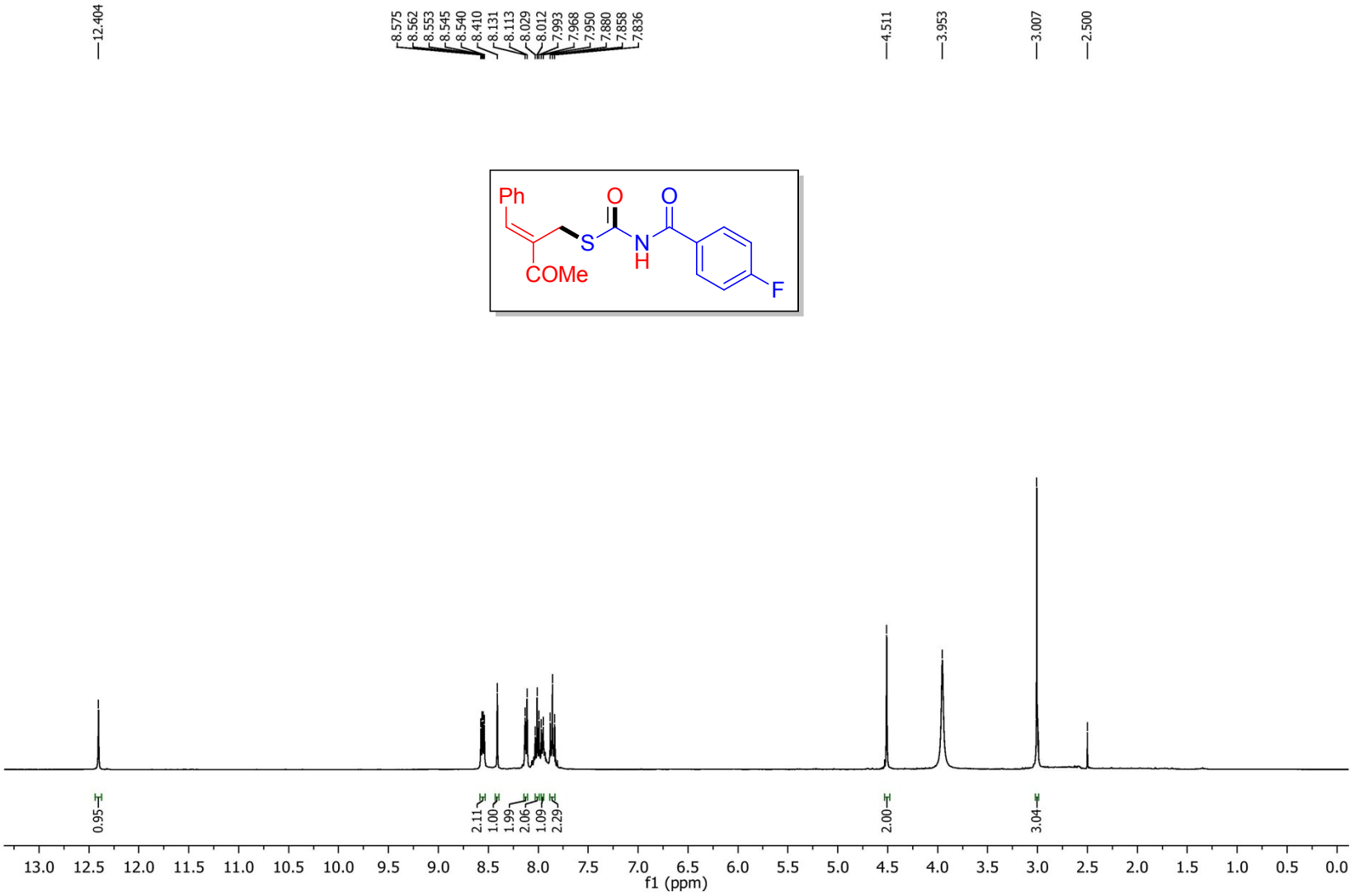


_Z_-S-(2-Benzylidene-3-oxobutyl) (4-methylbenzoyl)carbamothioate (15b): ^{13}CNMR (100 MHz, DMSO-d_6)

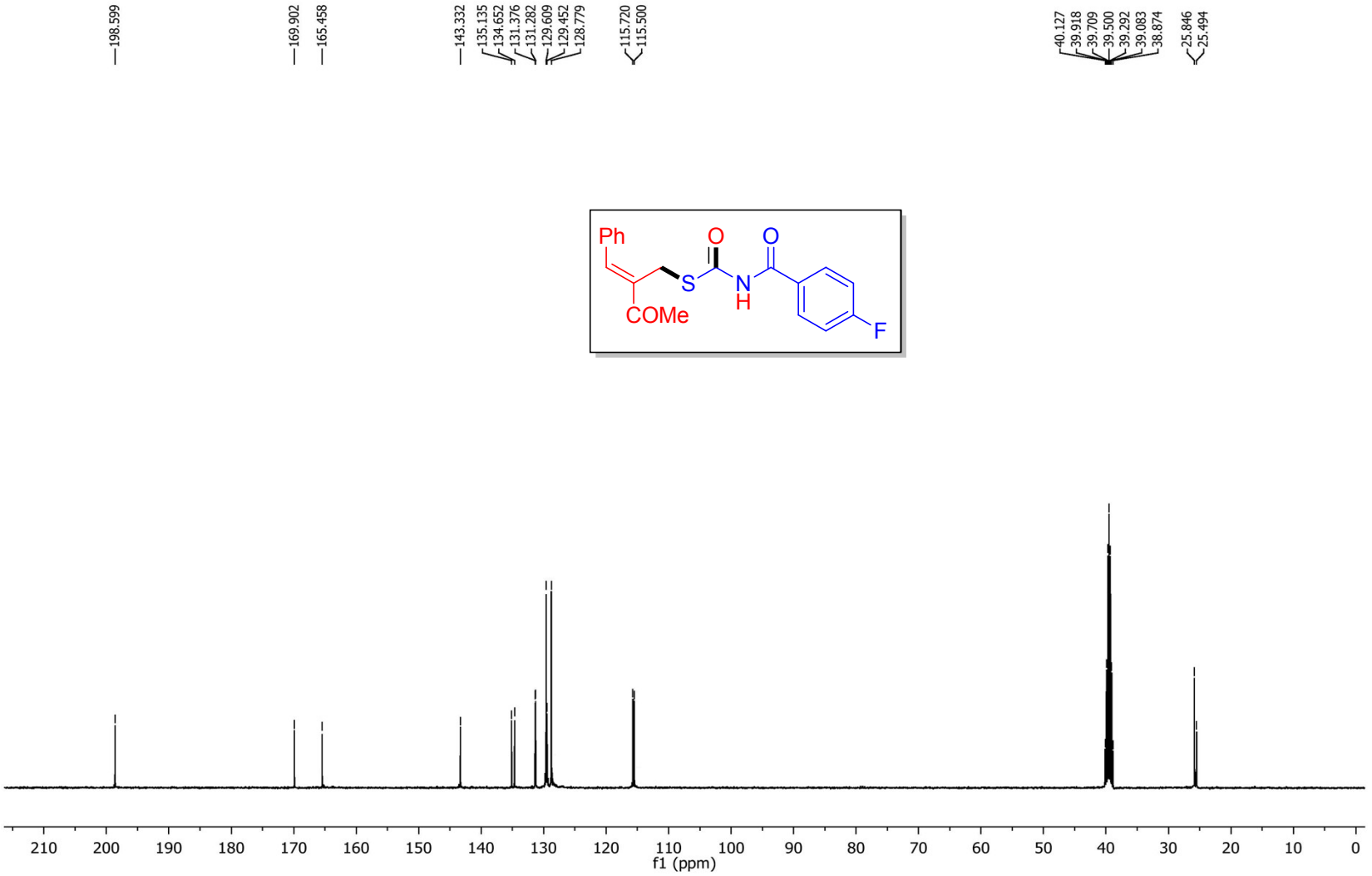




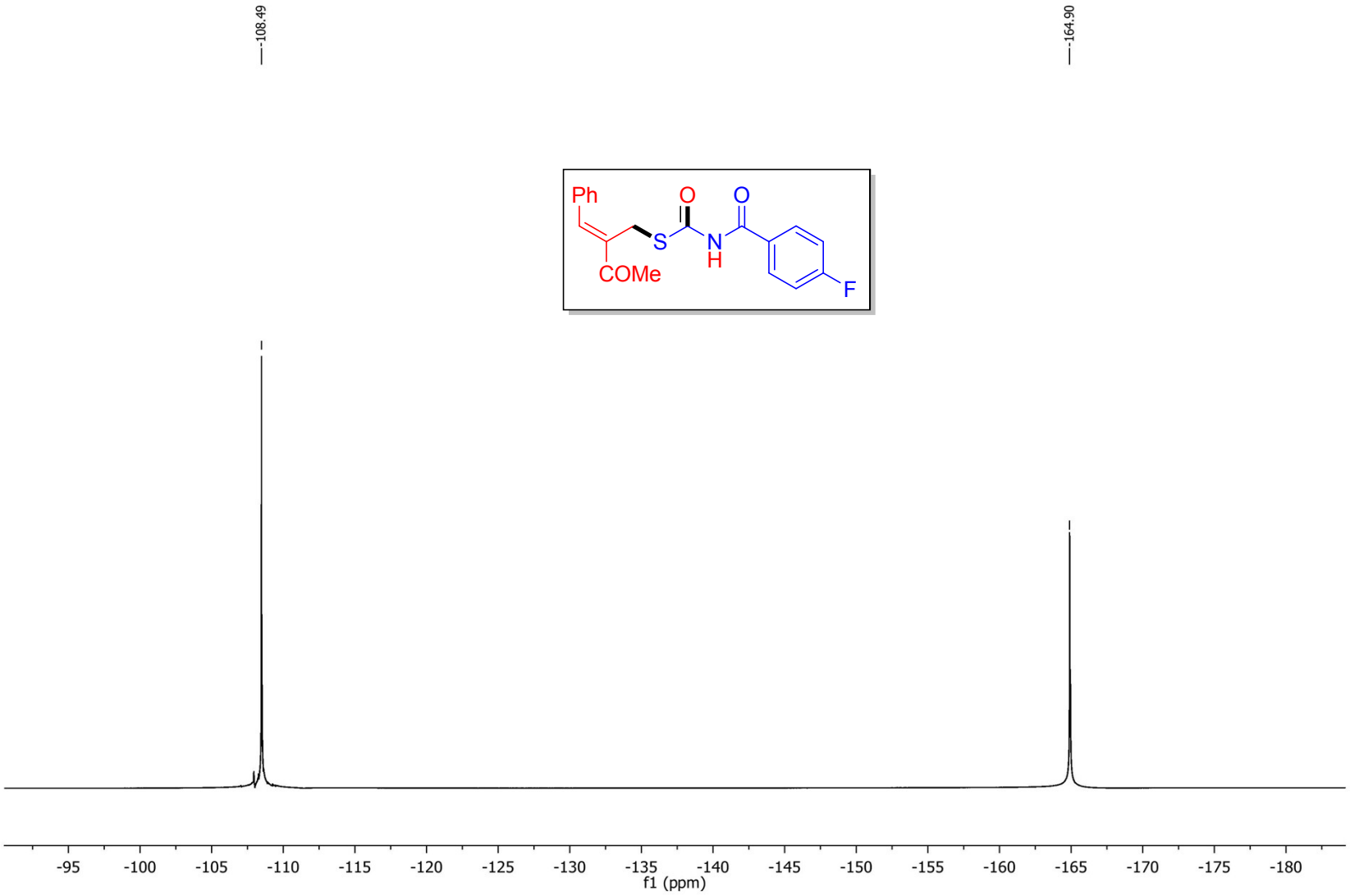
_Z_-S-(2-Benzylidene-3-oxobutyl) (4-fluorobenzoyl)carbamothioate (15e): ^{1}HNMR (400 MHz, DMSO-d_6)



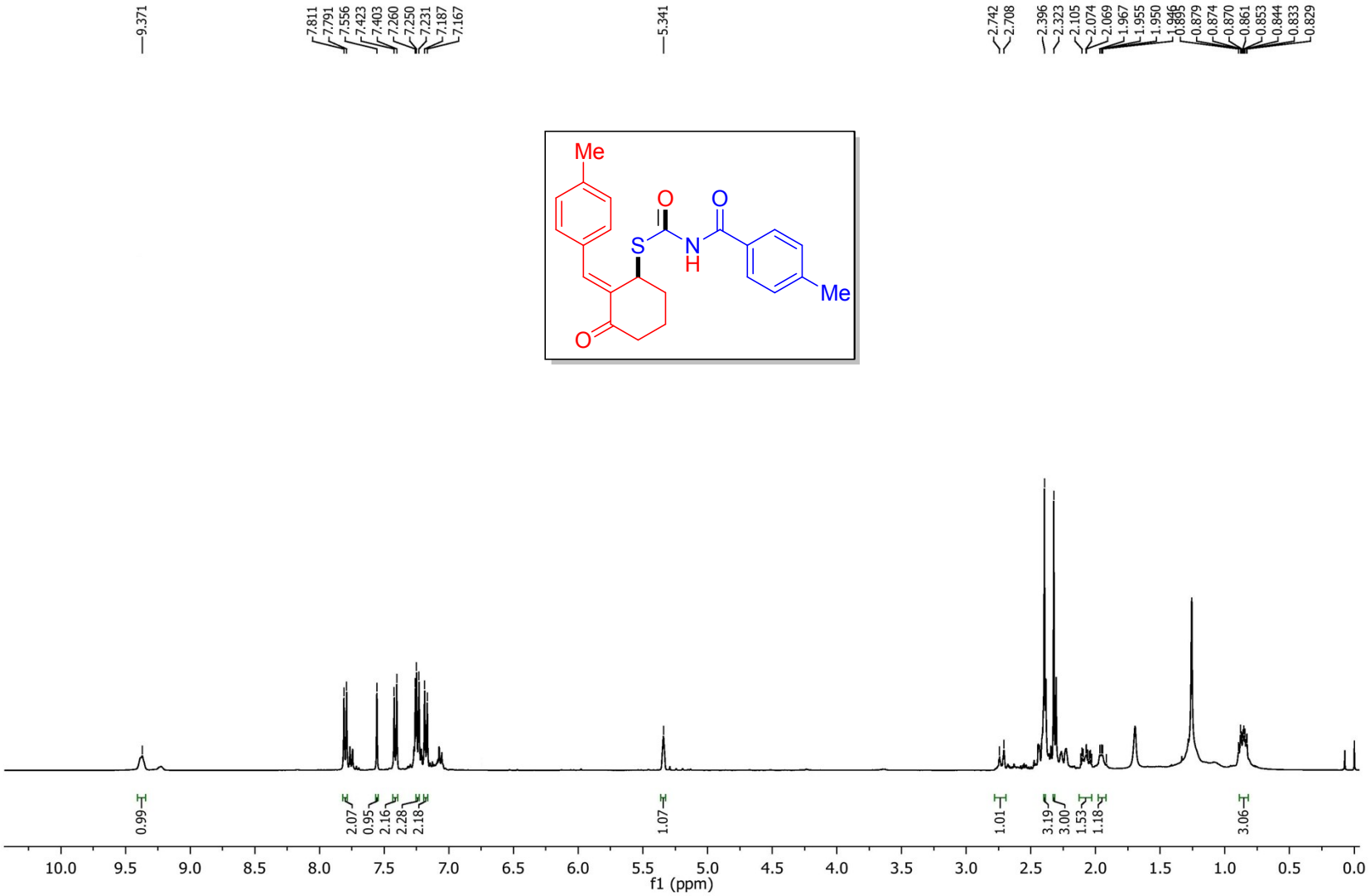
_Z_-S-(2-Benzylidene-3-oxobutyl) (4-fluorobenzoyl)carbamothioate (15e): ^{13}CNMR (100 MHz, DMSO-d$_6$)



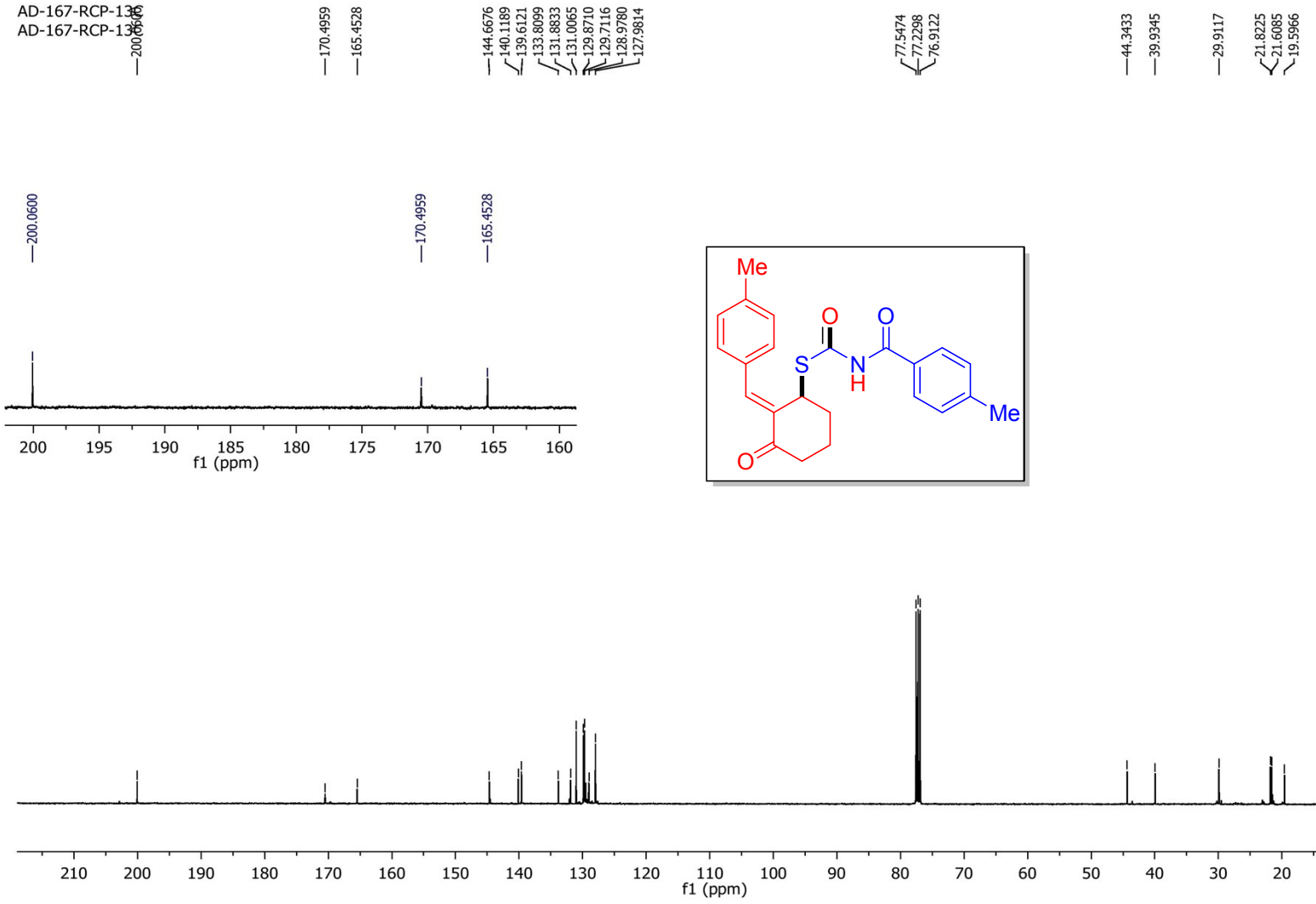
_Z_-S-(2-Benzylidene-3-oxobutyl) (4-fluorobenzoyl)carbamothioate (15e): ^{19}FNMR (DMSO-d_6 + C_6F_6)



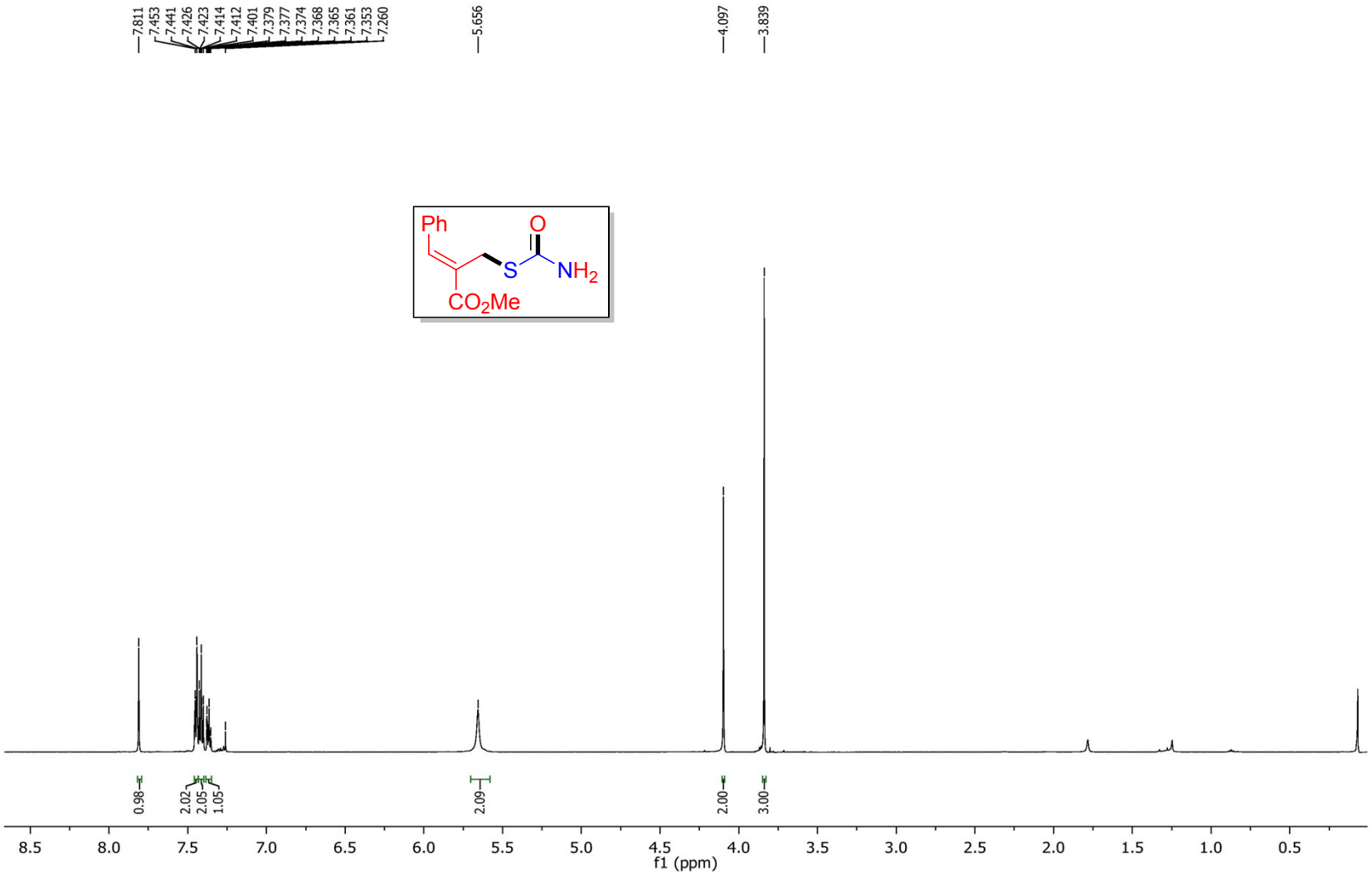
_Z_-S-(2-(4-Methylbenzylidene)-3-oxocyclohexyl) (4-methylbenzoyl)carbamothioate (16b): ^{1}HNMR (400 MHz, DMSO-d$_6$)



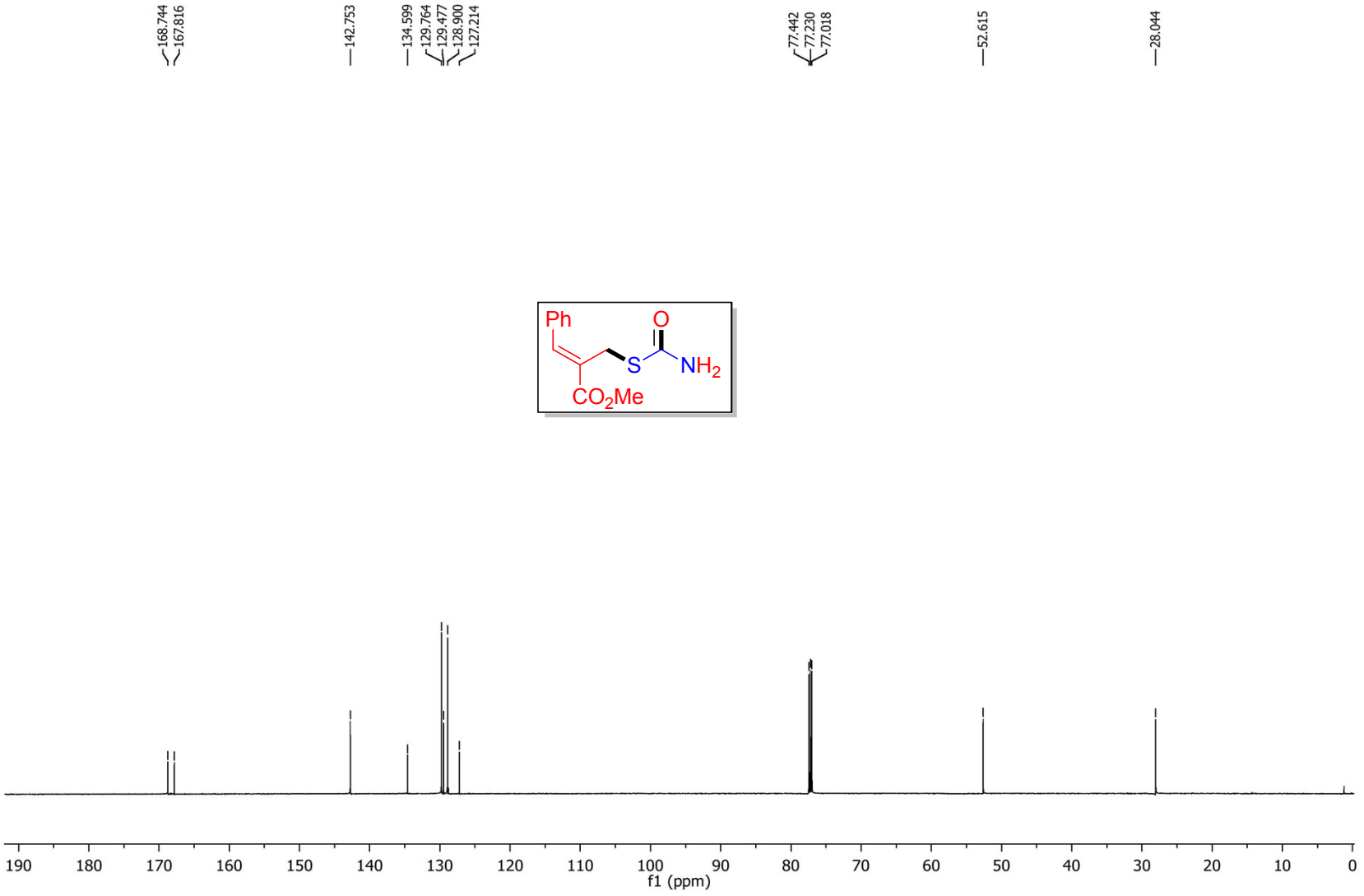
_Z_-S-(2-(4-Methylbenzylidene)-3-oxocyclohexyl) (4-methylbenzoyl)carbamothioate: ^{13}CNMR (100 MHz, DMSO-d_6)



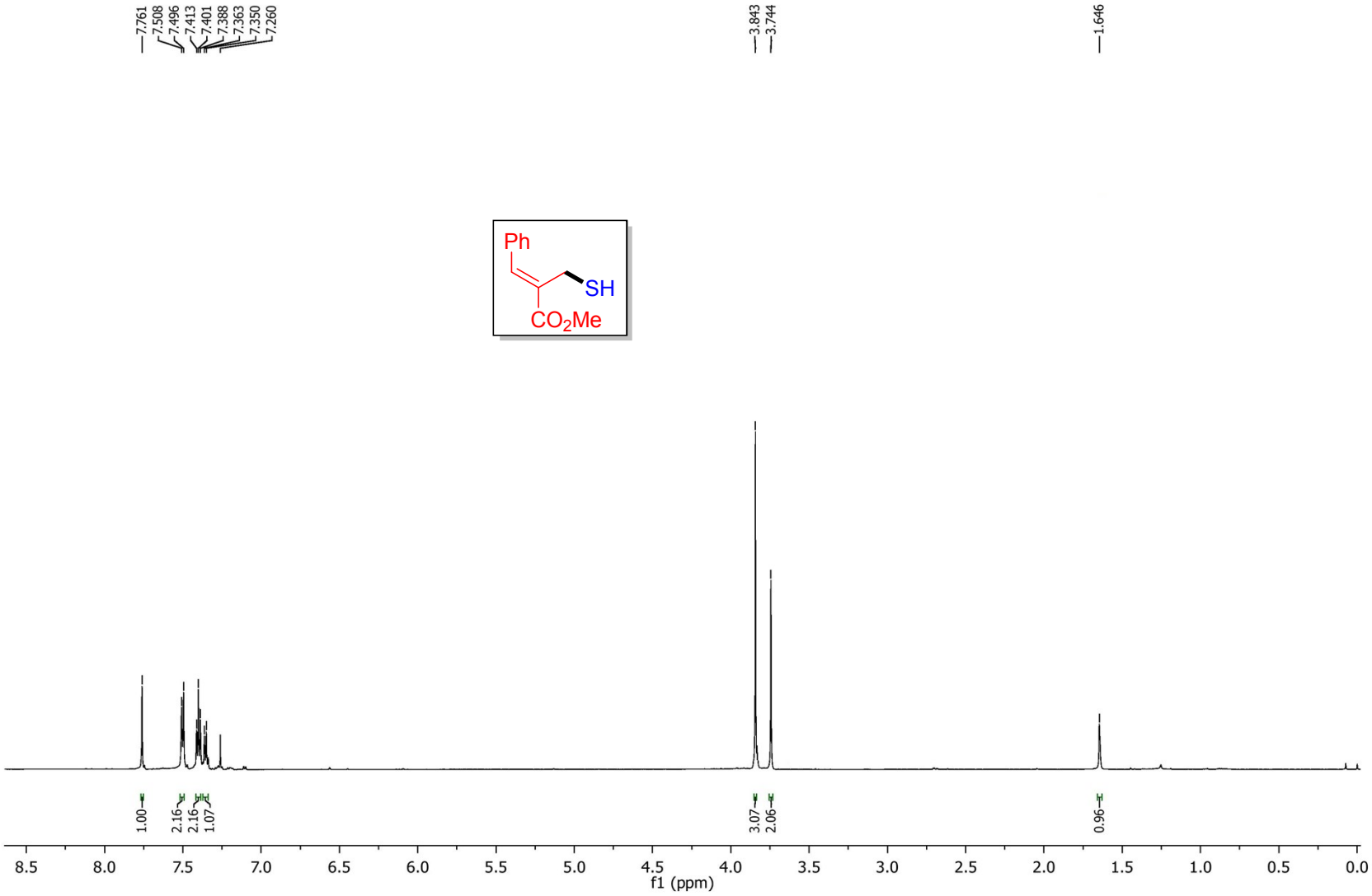
Methyl 2-((carbamoylthio)methyl)-3-phenylacrylate (1ab): ^{1}HNMR (600 MHz, $CDCl_3$):



Methyl 2-((carbamoylthio)methyl)-3-phenylacrylate (1ab): ^{13}CNMR (150 MHz, $CDCl_3$):



Methyl 2-(mercaptomethyl)-3-phenylacrylate (1ac) ^{1}HNMR (600 MHz, $CDCl_3$):



Methyl 2-(mercaptomethyl)-3-phenylacrylate (1ac) ^{13}CNMR (150 MHz, $CDCl_3$):