Supporting Information

Blue Light-Mediated Carbene Transfer Reaction of Thioesters with Diazoesters: Efficient Synthesis of Tetrasubstituted *Z*-Enol Esters

Shuncheng Wang, Hua Zhang, Jin Yang, Dongfang Zhang and Xin-Ping Hui*

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China

Corresponding author: Prof. Xin-Ping Hui

E-mail: huixp@lzu.edu.cn

Contents

1. General information

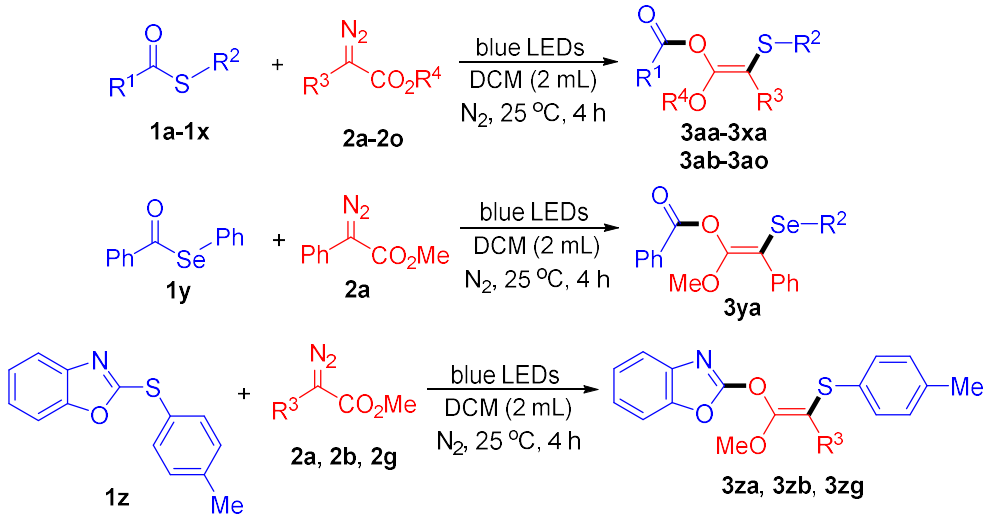
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer using tetramethylsilane (TMS) as an internal reference, and chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The HRMS analysis was obtained on a Thermo Scientific mass spectrometer (ESI) with an Orbitrap analyzer. The X-ray data were detected by Agilent SuperNOVA X-ray single crystal diffractometer. Melting points were taken on an X–4 melting point apparatus and were uncorrected. Toluene was freshly distilled from a deep-blue solution of sodium-benzophenone under nitrogen. DCE and MeCN were freshly distilled from phosphorous pentoxide and freshly distilled under nitrogen atmosphere. DCM, $CHCl_3$ and CCl_4 were dried by calcium hydride and freshly distilled under nitrogen atmosphere. EtOAc (GR) was purchased from commercial supplier and used directly. Methanol, 1,4-dioxane and other chemicals (AR) were purchased from commercial suppliers and used directly. All syntheses and manipulations were carried out under dry nitrogen atmosphere. Flash column chromatography was carried out utilizing 200–300 mesh silica gel.

S-Substituted thioesters **1a**–**1x**[1], *Se*-phenyl benzoselenoate (**1y**)[2], 2-(4-tolylthio)benzo[*d*]oxazole (**1z**)[3], aryldiazo esters **2a**–**2o**[4] and alkyl diazoester **2p**[5] were synthesized according to the literature methods, respectively.

The blue LEDs (model: ouying 5313, wavelength: 400 – 500 nm, wavelength of peak intensity: 452 nm, light intensity: 44.0 mw/cm^2) was used as light source. The Schlenk tube was placed in the 25 °C and the distance from the center of light source to the Schlenk tube was 2 centimeter.

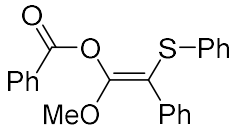
Figure S1. The setup of the photo reaction

2. General procedure for visible-light induced carbene transfer reaction of thioesters with aryl diazoesters



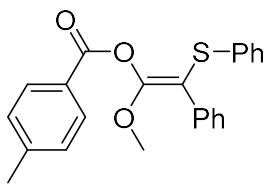
To an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added **1** (0.6 mmol, 6.0 equiv.), **2** (0.1 mmol). The tube was evacuated, backfilled with nitrogen for 3 times and DCM (2.0 mL) was added under nitrogen atmosphere. The solution was stirred from Blue LEDs at room temperature for 4 h. After the reaction was completed, the reaction was quenched with saturated brine solution (2 mL), extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography with petroleum ether/EtOAc as eluent on silica gel to afford products **3**.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl benzoate (3aa)



29 mg, 80% yield, white solid, mp 94.8 – 95.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.27 – 7.19 (m, 4H), 7.16 – 7.09 (m, 3H), 7.00 (t, J = 7.2 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.91, 154.35, 136.11, 135.64, 134.12, 130.49, 129.37, 128.65, 128.56, 127.96, 127.83, 127.76, 126.95, 125.44, 101.02, 57.18. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{19}O_3S$ $(M+H)^+$: 363.1049, Found: 363.1054.

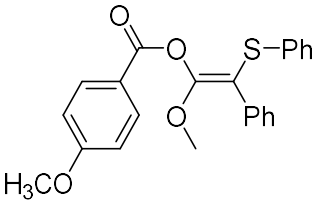
(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl 4-methylbenzoate (3ba)



31.6 mg, 84% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 6.8 Hz, 2H), 7.68 (d, J = 6.8

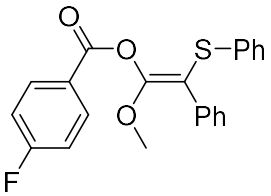
Hz, 2H), 7.26 – 7.21 (m, 6H), 7.17 – 7.10 (m, 3H), 7.04 – 7.00 (m, 1H), 3.72 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.90, 154.49, 145.10, 136.29, 135.82, 135.82, 130.54, 129.37, 128.53, 127.80, 126.87, 125.40, 125.25, 100.87, 57.05, 21.75. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{21}O_3S$ $(M+H)^+$: 377.1206, Found: 377.1218.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl 4-methoxybenzoate (3ca)



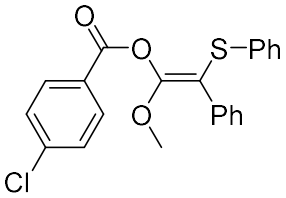
31.8 mg, 81% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 7.6 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.15 – 7.09 (m, 3H), 7.01 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.31, 163.49, 154.56, 136.36, 135.86, 132.65, 129.33, 128.51, 127.77, 127.70, 126.81, 125.34, 120.16, 113.94, 100.59, 56.94, 55.45. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{21}O_4S$ $(M+H)^+$: 393.1155, Found: 393.1166.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl 4-fluorobenzoate (3da)



28.9 mg, 76% yield, white solid, mp 77.9 – 79.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 7.6, 5.6 Hz, 2H), 7.67 (d, J = 7.6 Hz, 2H), 7.28 – 7.20 (m, 4H), 7.17 – 7.10 (m, 5H), 7.03 (t, J = 7.2 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.71, 165.16, 162.96, 154.28, 136.03, 135.58, 133.20, 133.11, 129.37, 128.60, 127.86, 127.82, 127.03, 125.54, 124.33, 124.30, 116.04, 115.81, 101.40, 57.31. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{18}FO_3S$ $(M+H)^+$: 381.0955, Found: 381.0966.

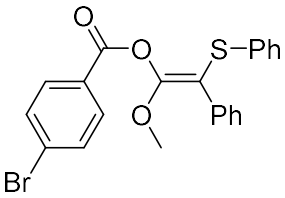
(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl 4-chlorobenzoate (3ea)



21 mg, 54% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 7.2 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.28 – 7.11 (m, 7H), 7.03 (t, J = 7.2 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.13, 154.21, 140.72, 135.94, 135.48, 131.80, 129.35, 129.04, 128.60, 127.86, 127.77, 127.05, 126.47, 125.54, 101.43, 57.35. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{18}ClO_3S$ $(M+H)^+$: 397.0660, Found:

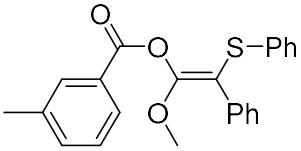
397.0660.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl 4-bromobenzoate (3fa)



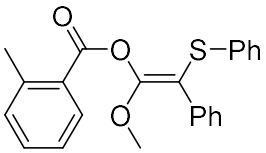
18 mg, 41% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 7.17 – 7.11 (m, 2H), 7.04 (t, J = 7.2 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.33, 154.23, 135.97, 135.53, 132.07, 131.91, 129.50, 129.39, 128.63, 127.89, 127.84, 127.09, 127.00, 125.59, 101.56, 57.42. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{17}BrO_3SNa$ $(M+Na)^+$: 462.9974, Found: 462.9983.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl 3-methylbenzoate (3ga)



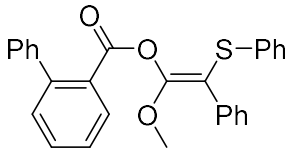
27.4 mg, 73% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 10.0 Hz, 2H), 7.68 (d, J = 7.2 Hz, 2H), 7.43 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.28 (s, 1H), 7.24 – 7.21 (m, 3H), 7.17 – 7.11 (m, 3H), 7.03 (t, J = 7.2 Hz, 1H), 3.73 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.06, 154.43, 138.53, 136.30, 135.78, 134.90, 130.98, 129.39, 128.56, 127.95, 127.83, 127.79, 127.66, 126.92, 125.42, 100.96, 57.12, 21.21. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{21}O_3S$ $(M+H)^+$: 377.1206, Found: 377.1216.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl 2-methylbenzoate (3ha)



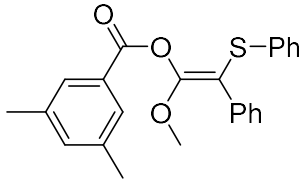
26.7 mg, 71% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 7.2 Hz, 2H), 7.48 – 7.44 (m, 1H), 7.29 – 7.22 (m, 6H), 7.17 – 7.11 (m, 3H), 7.02 (t, J = 7.6 Hz, 1H), 3.74 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.32, 154.55, 141.91, 136.27, 135.83, 133.22, 131.91, 131.52, 129.40, 128.57, 127.83, 127.75, 127.04, 126.90, 125.97, 125.42, 100.84, 57.10, 21.77. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{21}O_3S$ $(M+H)^+$: 377.1206, Found: 377.1213.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl [1,1'-biphenyl]-2-carboxylate (3ia)



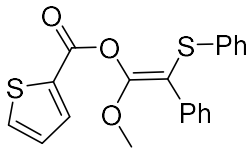
24.5 mg, 56% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 1H), 7.59 – 7.56 (m, 3H), 7.43 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.33 – 7.31 (m, 2H), 7.29 – 7.26 (m, 2H), 7.24 – 7.18 (m, 5H), 7.13 – 7.10 (m, 3H), 7.03 (t, J = 7.2 Hz, 1H), 3.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.67, 154.19, 144.09, 140.65, 135.97, 135.57, 132.37, 131.32, 130.78, 129.35, 128.66, 128.58, 128.11, 128.02, 127.93, 127.75, 127.41, 127.32, 126.88, 125.44, 101.22, 57.09. HRMS (ESI): Exact Mass Calcd for $C_{28}H_{23}O_3S$ $(M+H)^+$: 439.1362, Found: 439.1373.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl 3,5-dimethylbenzoate (3ja)



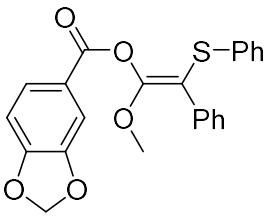
25.6 mg, 66% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.68 (m, 4H), 7.28 – 7.24 (m, 4H), 7.22 (s, 1H), 7.14 (q, J = 7.2 Hz, 3H), 7.03 (t, J = 7.2 Hz, 1H), 3.73 (s, 3H), 2.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.20, 154.47, 138.38, 136.43, 135.83, 129.37, 128.55, 128.19, 127.83, 127.71, 126.89, 125.37, 100.74, 57.03, 21.10. HRMS (ESI): Exact Mass Calcd for $C_{24}H_{23}O_3S$ $(M+H)^+$: 391.1362, Found: 391.1373.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl thiophene-2-carboxylate (3ka)



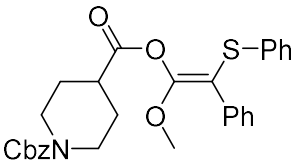
22.5 mg, 61% yield, white solid, mp 113.7 – 115.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 3.6, 1.2 Hz, 1H), 7.66 – 7.64 (m, 3H), 7.27 – 7.22 (m, 4H), 7.17 – 7.11 (m, 4H), 7.03 (t, J = 7.6 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.10, 153.81, 135.91, 135.59, 134.43, 131.04, 129.38, 128.55, 128.18, 128.06, 127.83, 127.00, 125.56, 101.76, 57.29. HRMS (ESI): Exact Mass Calcd for $C_{20}H_{17}O_3S_2$ $(M+H)^+$: 369.0614, Found: 369.0623.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl benzo[*d*][1,3]dioxole-5-carboxylate (3la)



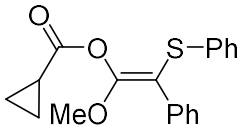
33.7 mg, 83% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.4, 1.6 Hz, 1H), 7.66 (d, J = 7.6 Hz, 2H), 7.49 (d, J = 1.6 Hz, 1H), 7.27 – 7.20 (m, 4H), 7.17 – 7.11 (m, 3H), 7.02 (t, J = 7.2 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.03 (s, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.19, 154.42, 152.68, 147.94, 136.22, 135.76, 129.36, 128.55, 127.81, 127.79, 126.89, 126.81, 125.44, 121.77, 110.10, 108.25, 102.02, 100.93, 57.09. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{19}O_5S$ $(M+H)^+$: 407.0948, Found: 407.0960.

(*Z*)-1-benzyl 4-(1-methoxy-2-phenyl-2-(phenylthio)vinyl) piperidine-1,4-dicarboxylate (3ma)



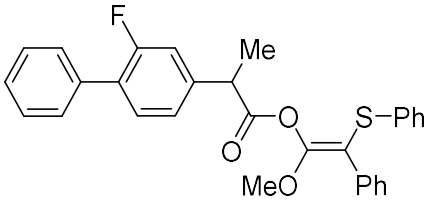
29.7 mg, 59% yield, white solid, mp 83.3 – 86.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.6 Hz, 2H), 7.35 – 7.31 (m, 5H), 7.25 – 7.18 (m, 4H), 7.13 (t, J = 7.6 Hz, 3H), 7.03 (t, J = 7.2 Hz, 1H), 5.12 (s, 2H), 4.08 (br s, 2H), 3.64 (s, 3H), 3.00 – 2.95 (m, 2H), 2.75 – 2.68 (m, 1H), 1.98 (br s, 2H), 1.78 – 1.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.51, 155.03, 154.07, 136.58, 135.69, 135.36, 129.25, 128.62, 128.44, 127.98, 127.86, 127.79, 127.54, 126.98, 125.52, 100.92, 67.12, 57.10, 42.92, 40.50, 27.53. HRMS (ESI): Exact Mass Calcd for $C_{29}H_{30}NO_5S$ $(M+H)^+$: 504.1839, Found: 504.1851.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl cyclopropanecarboxylate (3na)



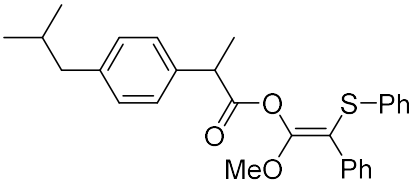
26.3 mg, 81% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.6 Hz, 2H), 7.24 – 7.21 (m, 4H), 7.15 – 7.11 (m, 3H), 7.03 (t, J = 7.2 Hz, 1H), 3.67 (s, 3H), 1.80 – 1.74 (m, 1H), 1.19 – 1.15 (m, 2H), 1.03 – 0.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.90, 154.16, 136.18, 135.75, 129.31, 128.56, 127.76, 127.72, 126.83, 125.42, 100.59, 56.90, 12.63, 9.48. HRMS (ESI): Exact Mass Calcd for $C_{19}H_{19}O_3S$ $(M+H)^+$: 327.1049, Found: 327.1057.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (3oa)



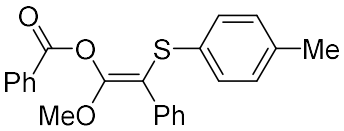
27.6 mg, 57% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.2 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.24 – 7.18 (m, 3H), 7.16 – 7.10 (m, 6H), 7.05 – 7.01 (m, 1H), 3.95 (q, J = 7.2 Hz, 1H), 3.51 (s, 3H), 1.62 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.05, 160.87, 158.40, 154.27, 140.27, 140.20, 135.97, 135.59, 135.30, 130.83, 130.79, 129.28, 128.93, 128.90, 128.59, 128.43, 128.23, 128.10, 127.82, 127.73, 127.48, 126.98, 125.45, 123.84, 123.81, 115.67, 115.44, 100.97, 57.07, 44.75, 17.96. HRMS (ESI): Exact Mass Calcd for $C_{30}H_{26}FO_3S$ $(M+H)^+$: 485.1581, Found: 485.1582.

(*Z*)-1-methoxy-2-phenyl-2-(phenylthio)vinyl 2-(4-isobutylphenyl)propanoate (3pa)



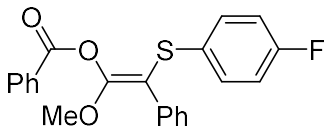
27.2 mg, 61% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.25 – 7.21 (m, 4H), 7.19 – 7.18 (m, 1H), 7.16 – 7.14 (m, 2H), 7.13 – 7.08 (m, 2H), 7.06 – 7.01 (m, 3H), 3.89 (q, J = 7.2 Hz, 1H), 3.37 (s, 3H), 2.44 (d, J = 7.2 Hz, 2H), 1.87 – 1.77 (m, 1H), 1.57 (d, J = 6.8 Hz, 3H), 0.88 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.65, 154.20, 141.02, 136.30, 136.24, 135.78, 129.40, 129.28, 128.54, 127.75, 127.64, 127.46, 126.82, 125.37, 100.51, 56.60, 44.99, 44.90, 30.16, 22.31, 22.29, 17.84. HRMS (ESI): Exact Mass Calcd for $C_{28}H_{31}O_3S$ $(M+H)^+$: 447.1988, Found: 447.2000.

(*Z*)-1-methoxy-2-phenyl-2-(p-tolylthio)vinyl benzoate (3qa)



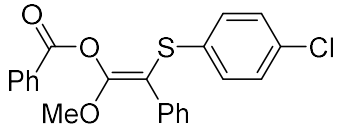
23.6 mg, 63% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.6 Hz, 2H), 7.67 – 7.60 (m, 3H), 7.47 (t, J = 7.6 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.17 – 7.11 (m, 3H), 6.93 (d, J = 8.0 Hz, 2H), 3.72 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.98, 154.03, 135.80, 135.43, 134.05, 132.29, 130.50, 129.46, 129.37, 128.64, 128.35, 128.16, 127.81, 126.91, 101.96, 57.25, 20.90. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{21}O_3S$ $(M+H)^+$: 377.1206, Found: 377.1215.

(*Z*)-2-((4-fluorophenyl)thio)-1-methoxy-2-phenylvinyl benzoate (3ra)



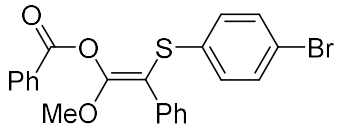
25.9 mg, 68% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 2H), 7.66 – 7.61 (m, 3H), 7.49 (t, J = 7.6 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 6.83 – 6.79 (m, 2H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.96, 162.61, 160.17, 153.80, 135.39, 134.18, 130.71, 130.68, 130.57, 130.47, 129.45, 128.72, 128.04, 127.88, 127.05, 115.75, 115.53, 102.13, 57.22. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{18}FO_3S$ $(M+H)^+$: 381.0955, Found: 381.0970.

(*Z*)-2-((4-chlorophenyl)thio)-1-methoxy-2-phenylvinyl benzoate (3sa)



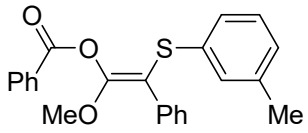
27.6 mg, 69% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.2 Hz, 2H), 7.66 – 7.62 (m, 3H), 7.49 (t, J = 7.6 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.19 – 7.13 (m, 3H), 7.09 (d, J = 8.4 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.88, 154.47, 135.33, 134.68, 134.23, 131.38, 130.48, 129.35, 129.16, 128.73, 128.70, 127.94, 127.11, 100.75, 57.17. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{17}ClO_3SNa$ $(M+Na)^+$: 419.0479, Found: 419.0488.

(*Z*)-2-((4-bromophenyl)thio)-1-methoxy-2-phenylvinyl benzoate (3ta)



30.8 mg, 70% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.2 Hz, 2H), 7.66 – 7.62 (m, 3H), 7.48 (t, J = 7.6 Hz, 2H), 7.29 – 7.22 (m, 4H), 7.18 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 8.4 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.86, 154.60, 135.46, 135.32, 134.23, 131.60, 130.48, 129.34, 129.33, 127.95, 127.91, 127.13, 119.23, 100.50, 57.16. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{18}BrO_3S$ $(M+H)^+$: 441.0155, Found: 441.0171.

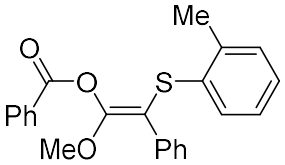
(*Z*)-1-methoxy-2-phenyl-2-(m-tolylthio)vinyl benzoate (3ua)



24.9 mg, 66% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.02

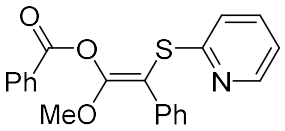
(d, J = 5.2 Hz, 3H), 6.84 (d, J = 3.6 Hz, 1H), 3.73 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.89, 154.38, 138.23, 135.92, 135.85, 134.06, 130.50, 129.41, 128.63, 128.44, 128.43, 128.09, 127.83, 126.93, 126.36, 124.85, 101.25, 57.22, 21.26. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{21}O_3S$ $(M+H)^+$: 377.1206, Found: 377.1208.

(*Z*)-1-methoxy-2-phenyl-2-(*o*-tolylthio)vinyl benzoate (3va)



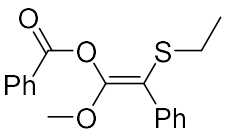
20.7 mg, 55% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.29 – 7.24 (m, 3H), 7.16 (t, J = 7.2 Hz, 1H), 7.03 – 6.93 (m, 3H), 3.74 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.90, 154.41, 136.00, 135.81, 135.28, 134.06, 130.46, 129.76, 129.32, 128.61, 128.08, 127.83, 127.62, 126.95, 126.20, 125.30, 100.76, 57.28, 19.95. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{21}O_3S$ $(M+H)^+$: 377.1206, Found: 377.1214.

(*Z*)-1-methoxy-2-phenyl-2-(pyridin-2-ylthio)vinyl benzoate (3wa)



19.5 mg, 54% yield, white solid, mp 101.6 – 102.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 4.0 Hz, 1H), 8.07 (d, J = 7.2 Hz, 2H), 7.79 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.48 – 7.39 (m, 3H), 7.30 (t, J = 7.6 Hz, 2H), 7.22 – 7.18 (m, 2H), 6.89 (dd, J = 6.4, 4.2 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.69, 160.21, 155.24, 149.11, 136.38, 135.51, 134.16, 130.41, 129.19, 128.61, 127.88, 127.68, 126.98, 120.79, 119.47, 98.53, 56.95. HRMS (ESI): Exact Mass Calcd for $C_{21}H_{18}NO_3S$ $(M+H)^+$: 364.1002, Found: 364.1011.

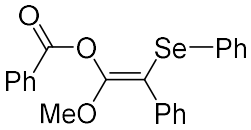
(*Z*)-2-(ethylthio)-1-methoxy-2-phenylvinyl benzoate (3xa)



15.2 mg, 48% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.19 (m, 2H), 7.69 – 7.63 (m, 3H), 7.55 – 7.52 (m, 2H), , 7.39 – 7.35 (m, 2H), 7.28 – 7.24 (m, 1H), 3.63 (s, 3H), 2.30 (q, J = 7.2 Hz, 2H), 1.07 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.87, 151.88, 135.41, 133.91, 130.38, 129.66, 128.65, 128.42, 127.99, 127.01, 103.57, 57.38, 26.34, 14.76. HRMS (ESI): Exact Mass Calcd for $C_{18}H_{18}O_3SNa$

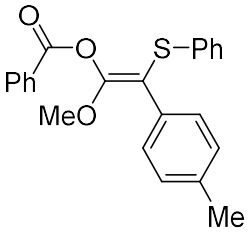
$(M+Na)^+$: 337.0869, Found: 337.0866.

(*Z*)-1-methoxy-2-phenyl-2-(phenylselanyl)vinyl benzoate (3ya)



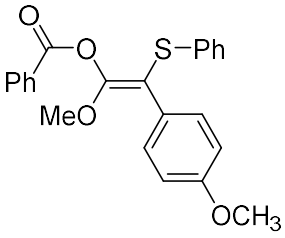
12.3 mg, 30% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.35 – 7.33 (m, 2H), 7.26 – 7.22 (m, 2H), 7.16 – 7.11 (m, 4H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.03, 153.14, 136.86, 134.04, 131.20, 130.93, 130.45, 129.88, 128.81, 128.65, 128.24, 127.81, 126.90, 126.37, 99.07, 57.58. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{18}O_3SeK$ $(M+K)^+$: 449.0053, Found: 449.0057.

(*Z*)-1-methoxy-2-(phenylthio)-2-(*p*-tolyl)vinyl benzoate (3ab)



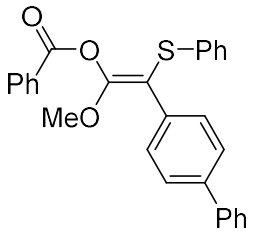
26.3 mg, 70% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.24 – 7.21 (m, 2H), 7.13 (t, J = 7.6 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 7.02 (t, J = 7.2 Hz, 1H), 3.73 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.98, 154.14, 136.71, 136.29, 134.05, 132.69, 130.48, 129.25, 128.63, 128.61, 128.55, 128.12, 127.78, 125.38, 101.21, 57.22, 21.15. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{21}O_3S$ $(M+H)^+$: 377.1206, Found: 377.1214.

(*Z*)-1-methoxy-2-(4-methoxyphenyl)-2-(phenylthio)vinyl benzoate (3ac)



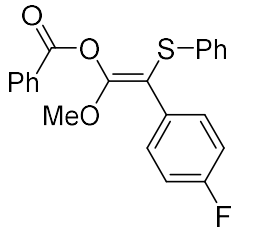
12.1 mg, 31% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 2H), 7.63 – 7.59 (m, 3H), 7.46 (t, J = 8.0 Hz, 2H), 7.24 – 7.21 (m, 2H), 7.15 – 7.11 (m, 2H), 7.04 – 7.01 (m, 1H), 6.82 – 6.79 (m, 2H), 3.75 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.01, 158.38, 153.67, 136.16, 134.04, 130.55, 130.44, 128.61, 128.54, 128.06, 127.80, 125.38, 113.25, 101.03, 57.21, 55.10. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{21}O_4S$ $(M+H)^+$: 393.1155, Found: 393.1167.

(*Z*)-2-([1,1'-biphenyl]-4-yl)-1-methoxy-2-(phenylthio)vinyl benzoate (3ad)



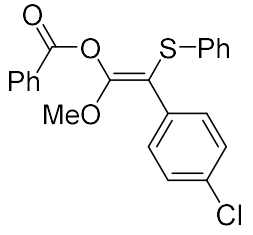
27.1 mg, 62% yield, white solid, mp 112.2 – 113.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.6 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.56 (d, J = 7.2 Hz, 2H), 7.52 – 7.45 (m, 4H), 7.40 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 7.6 Hz, 1H), 7.24 (s, 2H), 7.15 (t, J = 7.6 Hz, 2H), 7.04 (t, J = 7.6 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.91, 154.61, 140.69, 139.52, 136.29, 134.79, 134.13, 130.51, 129.71, 128.67, 128.64, 128.01, 127.68, 127.16, 126.92, 126.53, 125.46, 100.59, 57.16. HRMS (ESI): Exact Mass Calcd for $C_{28}H_{23}O_3S$ $(M+H)^+$: 439.1362, Found: 439.1371.

(*Z*)-2-(4-fluorophenyl)-1-methoxy-2-(phenylthio)vinyl benzoate (3ae)



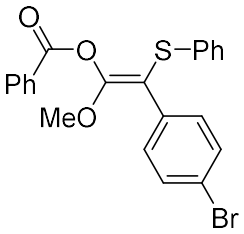
26.2 mg, 69% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.2 Hz, 2H), 7.67 – 7.60 (m, 3H), 7.47 (t, J = 7.6 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 7.6 Hz, 2H), 7.04 (t, J = 7.2 Hz, 1H), 6.94 (t, J = 8.8 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.89, 162.77, 160.32, 154.12, 135.75, 134.17, 131.58, 131.55, 131.10, 131.03, 130.49, 128.68, 128.63, 128.02, 127.93, 125.67, 114.86, 114.64, 100.33, 57.07. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{18}FO_3S$ $(M+H)^+$: 381.0955, Found: 381.0961.

(*Z*)-2-(4-chlorophenyl)-1-methoxy-2-(phenylthio)vinyl benzoate (3af)



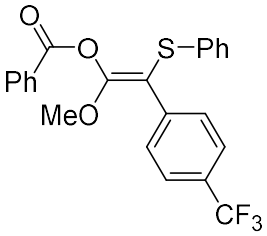
26.5 mg, 67% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.6 Hz, 2H), 7.64 – 7.60 (m, 3H), 7.47 (t, J = 7.6 Hz, 2H), 7.24 – 7.19 (m, 4H), 7.13 (t, J = 7.6 Hz, 2H), 7.04 (t, J = 7.2 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.81, 154.47, 135.71, 134.23, 134.22, 132.47, 130.67, 130.50, 128.70, 128.67, 128.02, 127.91, 127.86, 125.70, 100.05, 57.03. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{17}ClO_3SNa$ $(M+Na)^+$: 419.0479, Found: 419.0486.

(*Z*)-2-(4-bromophenyl)-1-methoxy-2-(phenylthio)vinyl benzoate (3ag)



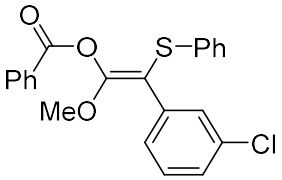
34.8 mg, 79% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.21 – 7.18 (m, 2H), 7.13 (t, J = 7.6 Hz, 2H), 7.04 (t, J = 7.2 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.77, 154.49, 135.70, 134.75, 134.22, 130.99, 130.96, 130.50, 128.69, 128.68, 127.88, 127.84, 125.70, 120.68, 100.04, 57.02. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{18}BrO_3S$ $(M+H)^+$: 441.0155, Found: 441.0161.

(*Z*)-1-methoxy-2-(phenylthio)-2-(4-(trifluoromethyl)phenyl)vinyl benzoate (3ah)



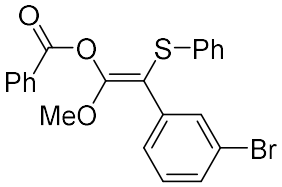
24.1 mg, 56% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.6 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.52 – 7.47 (m, 4H), 7.20 (d, J = 7.6 Hz, 2H), 7.15 (t, J = 7.2 Hz, 2H), 7.05 (t, J = 7.2 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.71, 155.34, 139.70, 135.67, 134.34, 130.56, 129.53, 128.75, 127.75, 127.72, 125.78, 124.80, 124.76, 99.47, 56.96. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{18}F_3O_3S$ $(M+H)^+$: 431.0923, Found: 431.0929.

(*Z*)-2-(3-chlorophenyl)-1-methoxy-2-(phenylthio)vinyl benzoate (3ai)



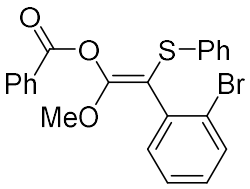
28.5 mg, 72% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.6 Hz, 2H), 7.71 (s, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.21 – 7.12 (m, 6H), 7.05 (t, J = 7.2 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.74, 154.91, 137.73, 135.75, 134.25, 133.69, 130.53, 129.32, 129.01, 128.71, 127.84, 127.81, 127.55, 126.96, 125.71, 99.63, 57.03. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{18}ClO_3SNa$ $(M+Na)^+$: 419.0479, Found: 419.0485.

(*Z*)-2-(3-bromophenyl)-1-methoxy-2-(phenylthio)vinyl benzoate (3aj)



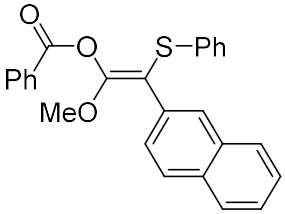
29.5 mg, 67% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.2 Hz, 2H), 7.86 (s, 1H), 7.65 – 7.61 (m, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.21 – 7.10 (m, 5H), 7.05 (t, J = 7.2 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.72, 154.92, 138.00, 135.71, 134.25, 132.17, 130.52, 129.85, 129.29, 128.70, 127.99, 127.84, 127.78, 125.72, 121.91, 99.49, 57.03. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{17}BrO_3SNa$ $(M+Na)^+$: 462.9974, Found: 462.9986.

(*Z*)-2-(2-bromophenyl)-1-methoxy-2-(phenylthio)vinyl benzoate (3ak)



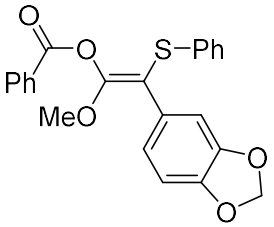
28.6 mg, 65% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.36 – 7.31 (m, 3H), 7.18 – 7.09 (m, 4H), 7.07 – 7.02 (m, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.73, 154.15, 137.06, 134.57, 134.16, 132.83, 132.09, 130.53, 130.41, 128.77, 128.70, 128.53, 128.00, 126.91, 126.52, 124.74, 100.36, 56.93. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{18}BrO_3S$ $(M+H)^+$: 441.0155, Found: 441.0163.

(*Z*)-1-methoxy-2-(naphthalen-2-yl)-2-(phenylthio)vinyl benzoate (3al)



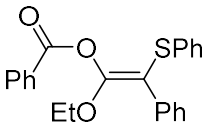
14.0 mg, 34% yield, light yellow solid, mp 88.7 – 90.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.11 (m, 3H), 7.84 – 7.72 (m, 4H), 7.63 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.27 – 7.24 (m, 2H), 7.12 – 7.08 (m, 2H), 6.99 (t, J = 7.6 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.98, 154.69, 136.01, 134.15, 133.17, 133.08, 132.40, 130.52, 128.68, 128.60, 128.10, 127.99, 127.85, 127.42, 127.39, 127.28, 125.83, 125.52 101.29, 57.33. HRMS (ESI): Exact Mass Calcd for $C_{26}H_{21}O_3S$ $(M+H)^+$: 413.1206, Found: 413.1209.

(*Z*)-2-(benzo[*d*][1,3]dioxol-5-yl)-1-methoxy-2-(phenylthio)vinyl benzoate (3am)



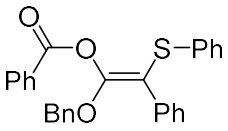
17.9 mg, 44% yield, Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.24 – 7.13 (m, 6H), 7.04 (t, J = 7.6 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 5.90 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.95, 153.84, 147.13, 146.41, 135.98, 134.09, 130.46, 129.38, 128.64, 128.59, 127.98, 127.87, 125.50, 123.30, 109.85, 107.73, 101.02, 100.93, 57.17. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{18}O_5SNa$ $(M+Na)^+$: 429.0767, Found: 429.0779.

(*Z*)-1-ethoxy-2-phenyl-2-(phenylthio)vinyl benzoate (3an)



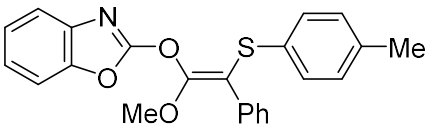
31.2 mg, 83% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.17 – 7.10 (m, 3H), 7.02 (t, J = 7.2 Hz, 1H), 4.04 (q, J = 7.2 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.85, 153.87, 136.26, 135.85, 134.00, 130.44, 129.42, 128.62, 128.55, 128.24, 127.83, 127.75, 126.83, 125.42, 101.89, 66.62, 14.87. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{21}O_3S$ $(M+H)^+$: 377.1206, Found: 377.1210.

(*Z*)-1-(benzyloxy)-2-phenyl-2-(phenylthio)vinyl benzoate (3ao)



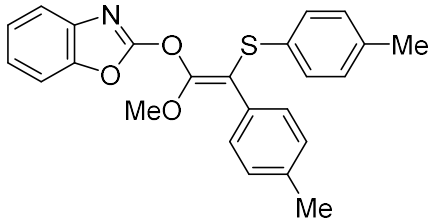
31.1 mg, 71% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 2H), 7.64 – 7.58 (m, 3H), 7.46 – 7.42 (m, 2H), 7.29 – 7.20 (m, 7H), 7.17 – 7.13 (m, 3H), 7.11 – 7.07 (m, 2H), 7.03 – 6.99 (m, 1H), 4.98 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.72, 153.30, 135.95, 135.63, 135.38, 134.02, 130.42, 129.55, 128.60, 128.54, 128.39, 128.34, 128.11, 127.82, 127.73, 127.02, 125.43, 103.61, 72.39. HRMS (ESI): Exact Mass Calcd for $C_{28}H_{23}O_3S$ $(M+H)^+$: 439.1362, Found: 439.1374.

(*Z*)-2-((1-methoxy-2-phenyl-2-(*p*-tolylthio)vinyl)oxy)benzo[*d*]oxazole (3za)



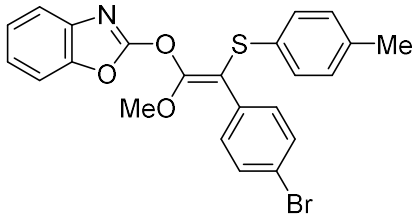
24.5 mg, 63% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.29 – 7.16 (m, 5H), 7.12 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 3.80 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.56, 154.64, 148.85, 140.70, 135.94, 135.01, 131.17, 129.49, 129.35, 129.14, 127.89, 127.34, 124.57, 123.57, 118.93, 110.08, 103.38, 58.82, 20.88. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{20}NO_3S$ $(M+H)^+$: 390.1158, Found: 390.1157.

(*Z*)-2-((1-methoxy-2-(*p*-tolyl)-2-(*p*-tolylthio)vinyl)oxy)benzo[*d*]oxazole (3zb)



27.0 mg, 67% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.4 Hz, 3H), 7.39 (d, J = 8.4 Hz, 1H), 7.29 – 7.20 (m, 2H), 7.12 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 3.79 (s, 3H), 2.28 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.62, 154.47, 148.82, 140.71, 137.13, 135.79, 131.96, 131.34, 129.33, 128.97, 128.65, 124.53, 123.52, 118.90, 110.05, 103.34, 58.81, 21.17, 20.87. HRMS (ESI): Exact Mass Calcd for $C_{24}H_{22}NO_3S$ $(M+H)^+$: 404.1315, Found: 404.1316.

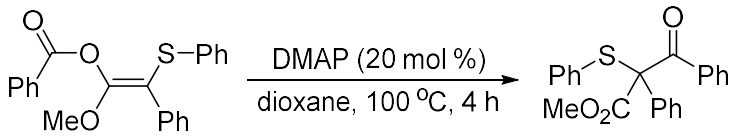
(*Z*)-2-((2-(4-bromophenyl)-1-methoxy-2-(*p*-tolylthio)vinyl)oxy)benzo[*d*]oxazole (3zg)



21.5 mg, 46% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 3H), 7.42 – 7.37 (m, 3H), 7.30 – 7.22 (m, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 3.82 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.43, 154.65, 148.86, 140.58, 136.23, 134.03, 131.11, 131.05, 130.72, 129.48, 129.18, 124.66, 123.69, 121.21, 118.95, 110.13, 102.37, 58.63, 20.90. HRMS (ESI): Exact Mass Calcd for $C_{23}H_{19}BrNO_3S$ $(M+H)^+$: 468.0264, Found: 428.0263.

3. Synthetic applications of compound 3aa

3.1 Synthesis of compound 4

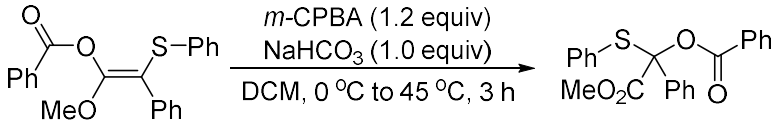


3aa **4,** 81%

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added **3aa** (72.4 mg, 0.2 mmol), DMAP (4.9 mg, 0.04 mmol, 0.2 equiv.) and dioxane (2 mL). The mixture was refluxed at 100 °C for 4 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (20:1) as eluent.

methyl 3-oxo-2,3-diphenyl-2-(phenylthio)propanoate (4). 58.6 mg, 81% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2H), 7.60 – 7.57 (m, 2H), 7.40 (t, J = 7.6 Hz, 1H), 7.29 – 7.25 (m, 3H), 7.22 – 7.20 (m, 3H), 7.17 – 7.11 (m, 4H), 3.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.91, 168.48, 137.12, 135.81, 134.82, 132.71, 130.15, 129.57, 128.60, 128.28, 128.24, 127.94, 72.13, 52.67. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{19}O_3S$ $(M+H)^+$: 363.1049, Found: 363.1057.

3.2 Synthesis of compound 5

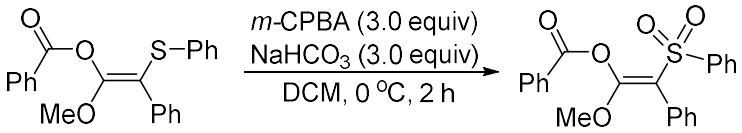


3aa **5,** 81%

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added **3aa** (36.2 mg, 0.1 mmol), $NaHCO_3$ (8.4 mg, 0.1 mmol, 1.0 equiv.) and DCM (1 mL). A solution of *m*-CPBA (24.3 mg, 0.12 mmol, 1.2 equiv., 85%) in DCM (1 mL) was added dropwise at 0 °C. The reaction was stirred at 0 °C for 2 h and then warmed up to 45 °C and stirred for 1 h. The mixture was cooled to room temperature and saturated brine solution (5 mL) was added. The mixture was extracted with DCM (10 mL×3) and the combined organic layer was washed with saturated $NaHCO_3$ solution (10 mL×2), dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (20:1) as eluent.

methyl 2-methoxy-2-oxo-1-phenyl-1-(phenylthio)ethyl benzoate (5). 30.6 mg, 81% yield, white solid, mp 110.7 – 112.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.8 Hz, 2H), 7.67 – 7.63 (m, 1H), 7.53 – 7.49 (m, 4H), 7.31 – 7.19 (m, 4H), 7.04 (d, J = 4.0 Hz, 4H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.45, 163.94, 136.90, 136.84, 133.75, 129.89, 129.38, 129.29, 129.24, 128.62, 128.47, 128.25, 128.13, 125.71, 91.22, 53.48. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{18}O_4SNa$ $(M+Na)^+$: 401.0818, Found: 401.0825.

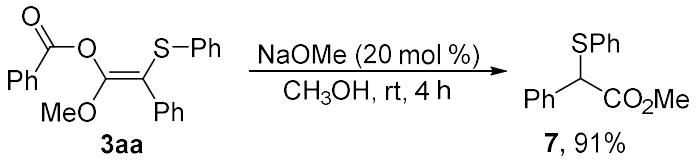
3.3 synthesis of compound 6



To a 10 mL Schlenk tube equipped with a magnetic stir bar was added **3aa** (36.2 mg, 0.1 mmol), $NaHCO_3$ (25.2 mg, 0.3 mmol, 3.0 equiv.) and DCM (1 mL). A solution of *m*-CPBA (60.7 mg, 0.3 mmol, 3.0 equiv., 85%) in DCM (1 mL) was added dropwise at 0 °C. The reaction was stirred at 0 °C for 2 h. After the reaction was completed, saturated brine solution (5 mL) was added. The mixture was extracted with DCM (10 mL×3) and the combined organic layer was washed with saturated $NaHCO_3$ solution (10 mL×2), dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (10:1) as eluent.

(*Z*)-1-methoxy-2-phenyl-2-(phenylsulfonyl)vinyl benzoate (6). 27.6 mg, 70% yield, white solid, mp 147.6 – 148.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.4 Hz, 2H), 7.72 – 7.68 (m, 1H), 7.60 – 7.55 (m, 4H), 7.50 – 7.46 (m, 1H), 7.36 – 7.24 (m, 7H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.22, 156.22, 141.19, 134.57, 132.69, 131.95, 130.84, 129.77, 128.57, 128.42, 128.15, 127.81, 127.45, 109.97, 56.08. HRMS (ESI): Exact Mass Calcd for $C_{22}H_{19}O_5S$ $(M+H)^+$: 395.0948, Found: 395.0961.

3.4 Synthesis of compound 7



To a 10 mL Schlenk tube equipped with a magnetic stir bar was added **3aa** (72.4 mg, 0.2 mmol), NaOMe (2.2 mg, 0.04 mmol, 0.2 equiv.) and MeOH (4 mL). The mixture was stirred at 25 °C for 4 h and flushed through a short column of silica gel with EtOAc. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (30:1) as eluent.

methyl 2-phenyl-2-(phenylthio)acetate (7). 47.0 mg, 91% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.0, 1.2 Hz, 2H), 7.38 – 7.24 (m, 8H), 4.91 (s, 1H), 3.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.84, 135.57, 133.66, 132.62, 128.93, 128.64, 128.46, 128.28, 127.97, 56.30, 52.66. HRMS (ESI): Exact Mass Calcd for $C_{15}H_{15}O_2S$ $(M+H)^+$: 259.0787, Found: 259.0791.

4. References

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[4] (a) Bess, E. N.; Guptill, D. M.; Davies, H. M. L.; Sigman, M. S. Using IR vibrations to quantitatively describe and predict site-selectivity in multivariate Rh-catalyzed C–H functionalization. *Chem. Sci.* **2015**, *6*, 3057−3062. (b) Song, Z.; Wu, Y.; Xin, T.; Jin, C.; Wen, X.; Sun, H.; Xu, Q.-L. The Rh(II)-catalyzed formal N–S bond insertion reaction of aryldiazoacetates into *N*-phenyl-sulfenyl phthalimide. *Chem. Commun.* **2016**, *52*, 6079−6082.

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5. X-Ray crystal structure of compounds 3wa and 5

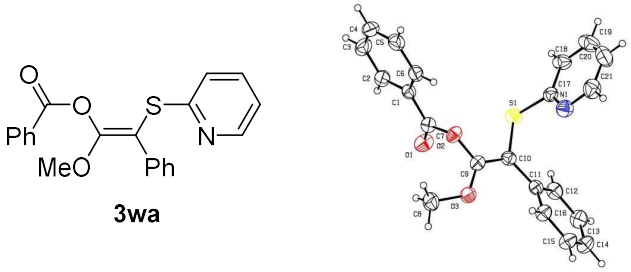


Figure 1. X-ray crystallography of compound **3wa**

(Displacement ellipsoids are drawn at 30% probability level)

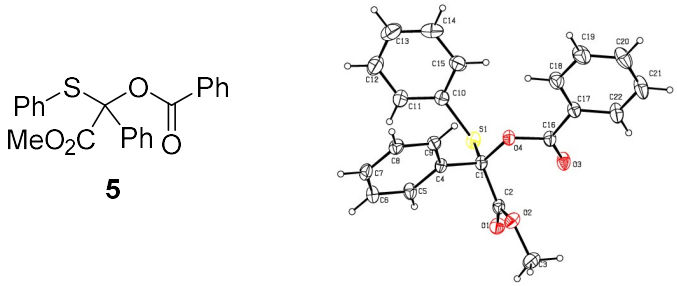


Figure 2. X-ray crystallography of compound **5**

(Displacement ellipsoids are drawn at 30% probability level)

Table 1. Crystallographic data and refinement details for compound **3wa**

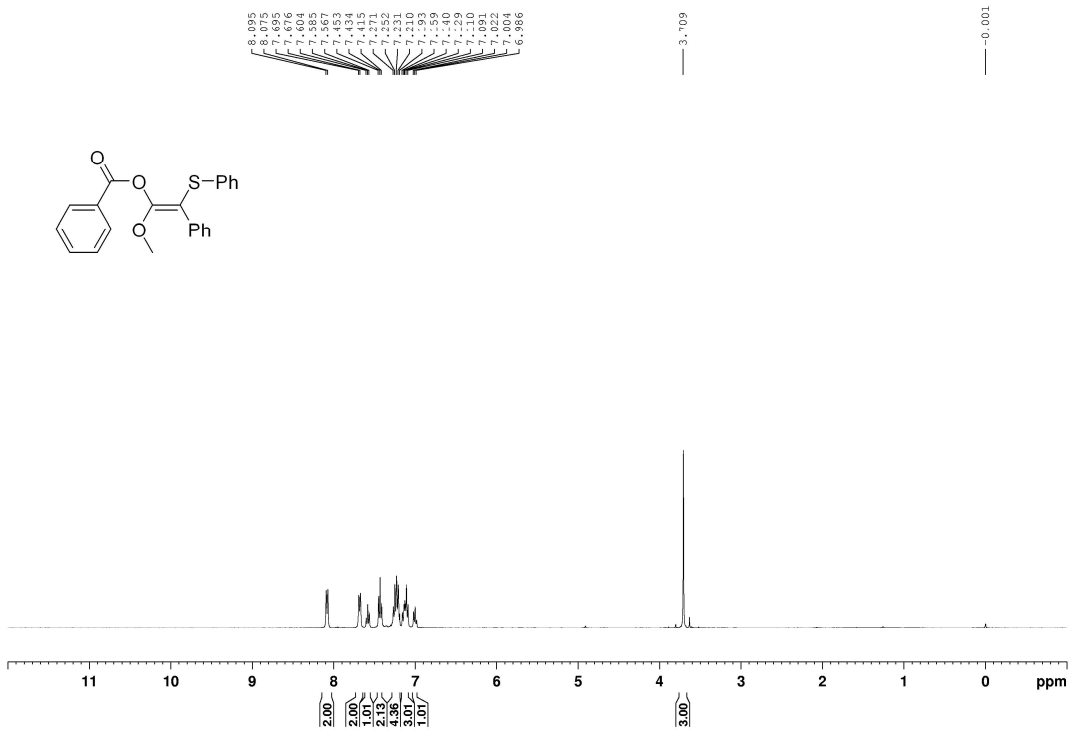
Identification code	wangshch_0103
Empirical formula	$C_{21}H_{17}NO_3S$
Formula weight	363.42
Temperature/K	293.63(10)
Crystal system	orthorhombic
Space group	Pnna
a/Å	12.2870(4)
b/Å	34.0526(14)
c/Å	8.7274(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3651.6(2)
Z	8
ρ_{calc} g/cm^3	1.322
μ/mm^{-1}	1.743
F(000)	1520.0
Crystal size/mm^3	0.19 × 0.16 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/	10.392 to 133.196
Index ranges	$-7 \le h \le 14$, $-40 \le k \le 31$, $-10 \le l \le 10$
Reflections collected	7945
Independent reflections	3226 [R_{int} = 0.0193, R_{sigma} = 0.0238]
Data/restraints/parameters	3226/0/236
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.1071
Final R indexes [all data]	R_1 = 0.0528, wR_2 = 0.1159
Largest diff. peak/hole / e Å^{-3}	0.23/-0.23

Table 2. Crystallographic data and refinement details for compound **5**

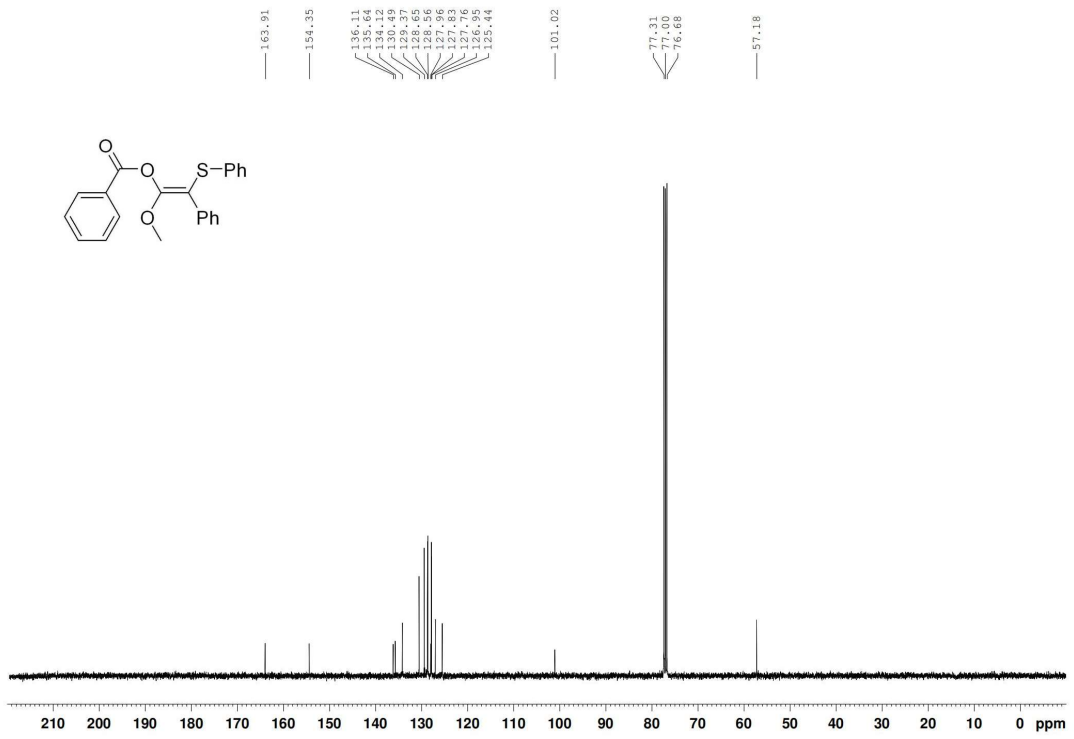
Identification code	wangshunch_0222-2_auto
Empirical formula	$C_{22}H_{18}O_4S$
Formula weight	380.42
Temperature/K	295.83(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.4800(3)
b/Å	10.7260(5)
c/Å	11.5506(5)
α/°	94.424(4)
β/°	109.645(4)
γ/°	96.794(3)
Volume/Å^3	974.79(8)
Z	2
ρ_{calc} g/cm^3	1.296
μ/mm^{-1}	1.694
F(000)	398.0
Crystal size/mm^3	0.18 × 0.13 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/	8.192 to 154.918
Index ranges	$-10 \le h \le 10$, $-13 \le k \le 13$, $-12 \le l \le 14$
Reflections collected	11134
Independent reflections	3899 [R_{int} = 0.0269, R_{sigma} = 0.0258]
Data/restraints/parameters	3899/0/246
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.1156
Final R indexes [all data]	R_1 = 0.0429, wR_2 = 0.1176
Largest diff. peak/hole / e Å^{-3}	0.23/-0.29

6. NMR spectra of compounds 3aa–3ya, 3ab–3ao, 3za, 3zb, 3zg and 4–7

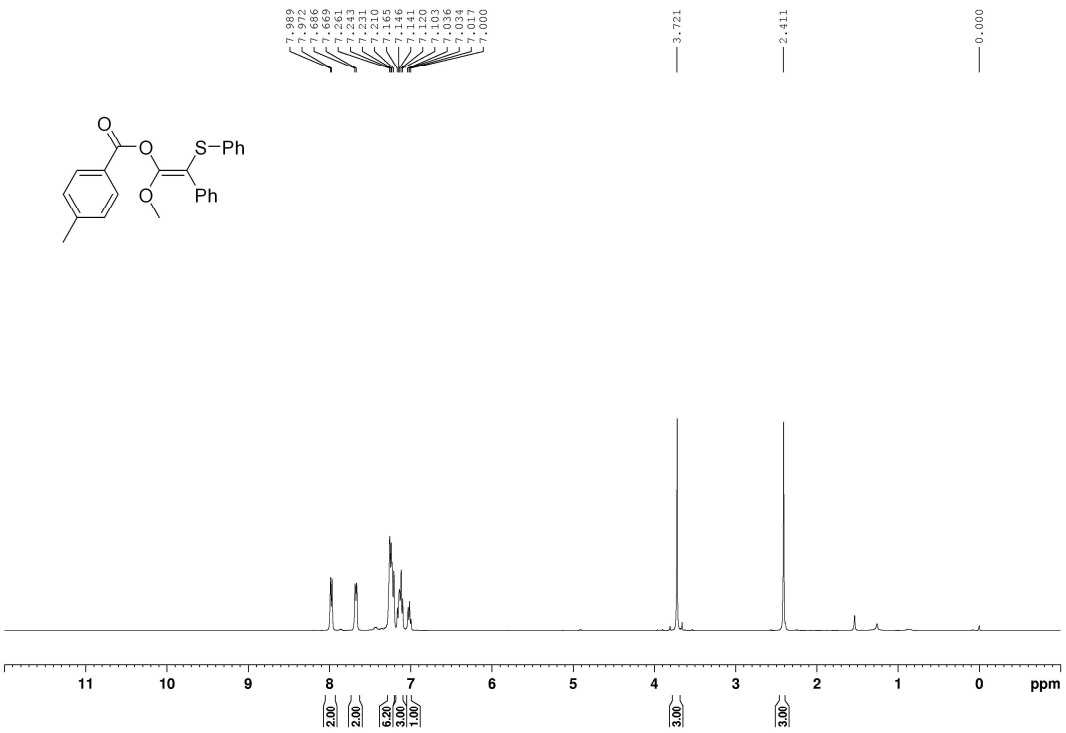
^{1}H NMR spectrum of compound **3aa** ($CDCl_3$, 400 MHz)



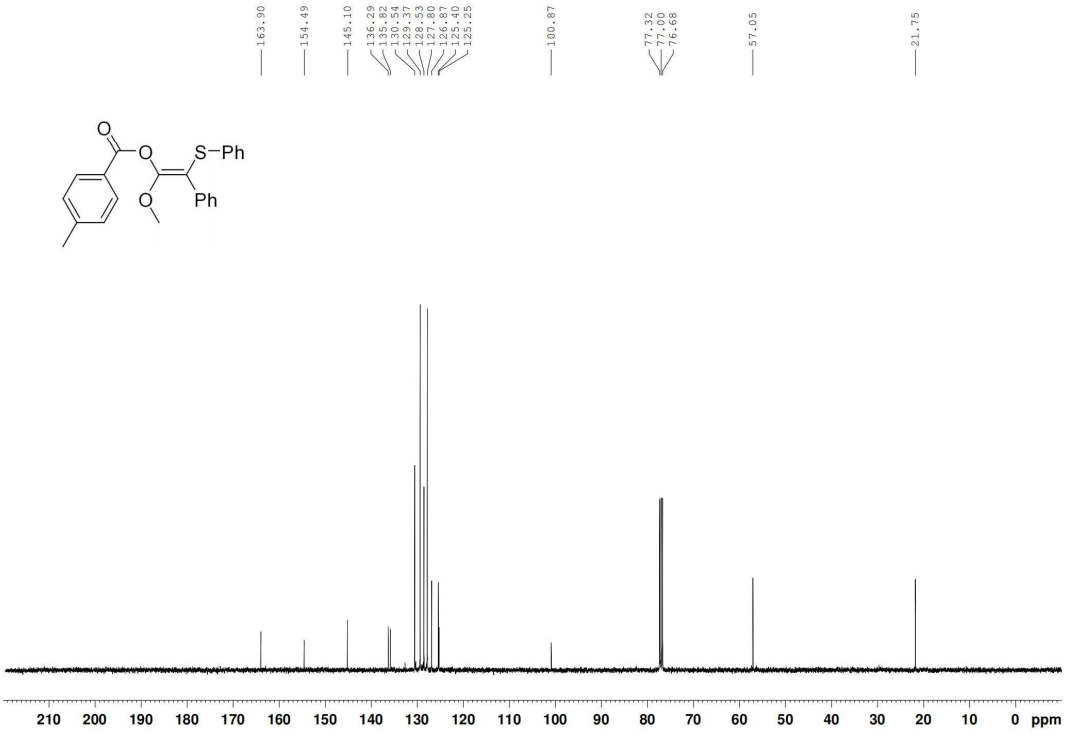
^{13}C NMR spectrum of compound **3aa** ($CDCl_3$, 100 MHz)



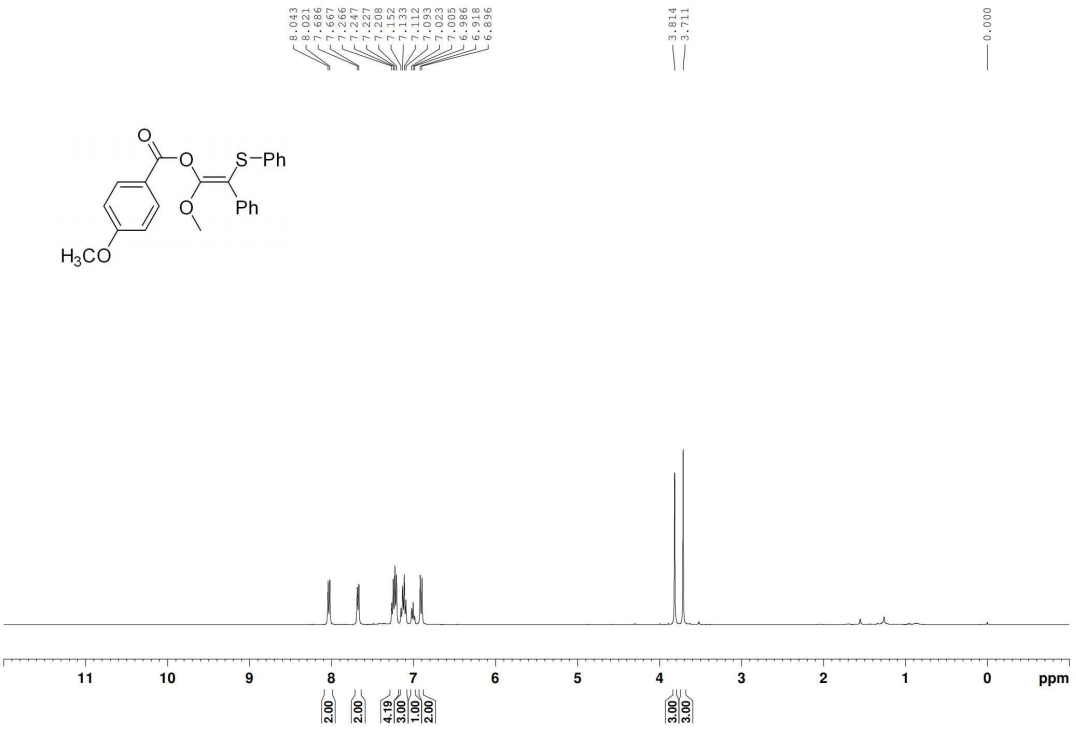
^{1}H NMR spectrum of compound **3ba** ($CDCl_3$, 400 MHz)



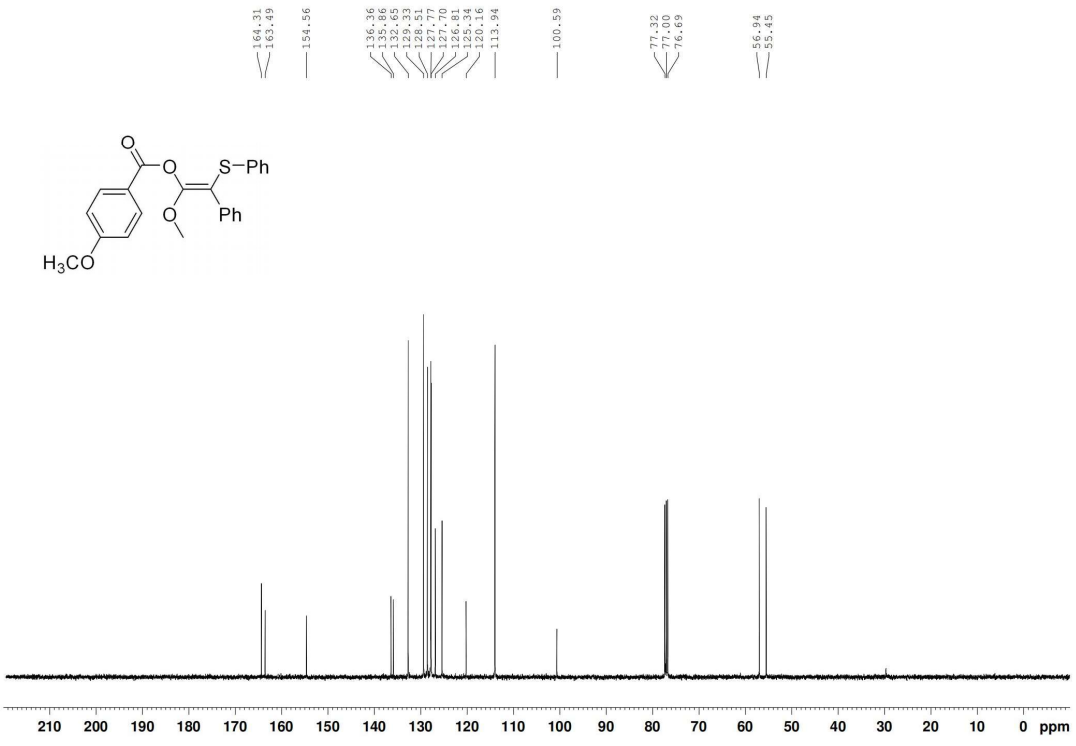
^{13}C NMR spectrum of compound **3ba** ($CDCl_3$, 100 MHz)



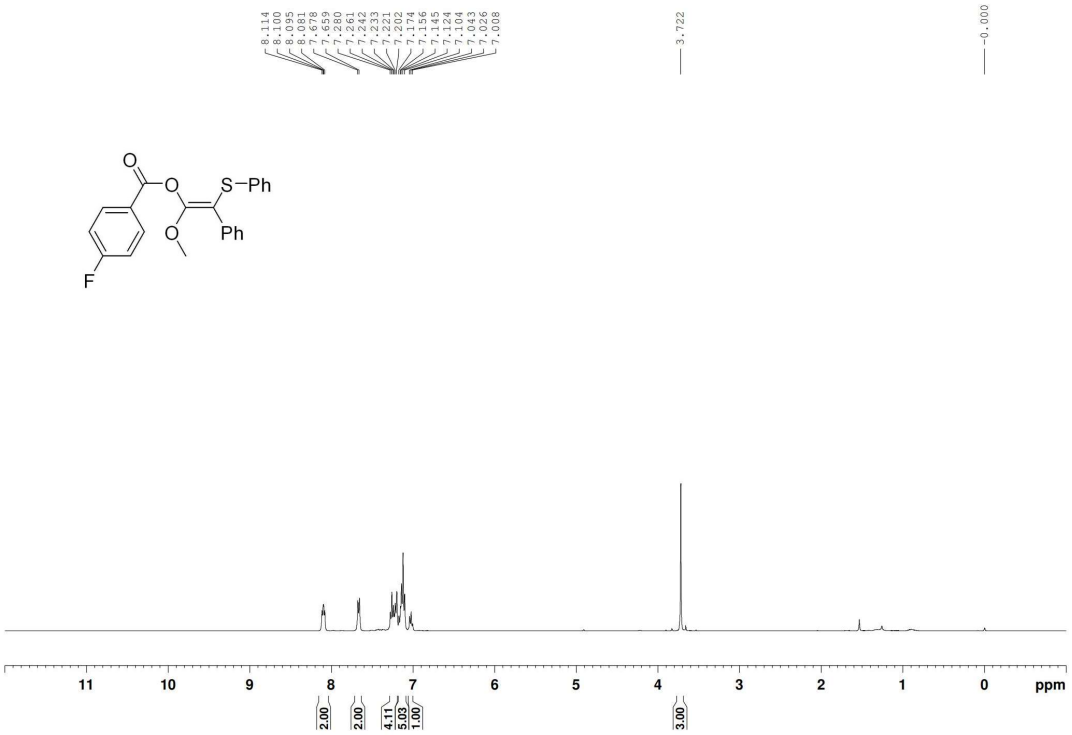
^{1}H NMR spectrum of compound **3ca** ($CDCl_3$, 400 MHz)



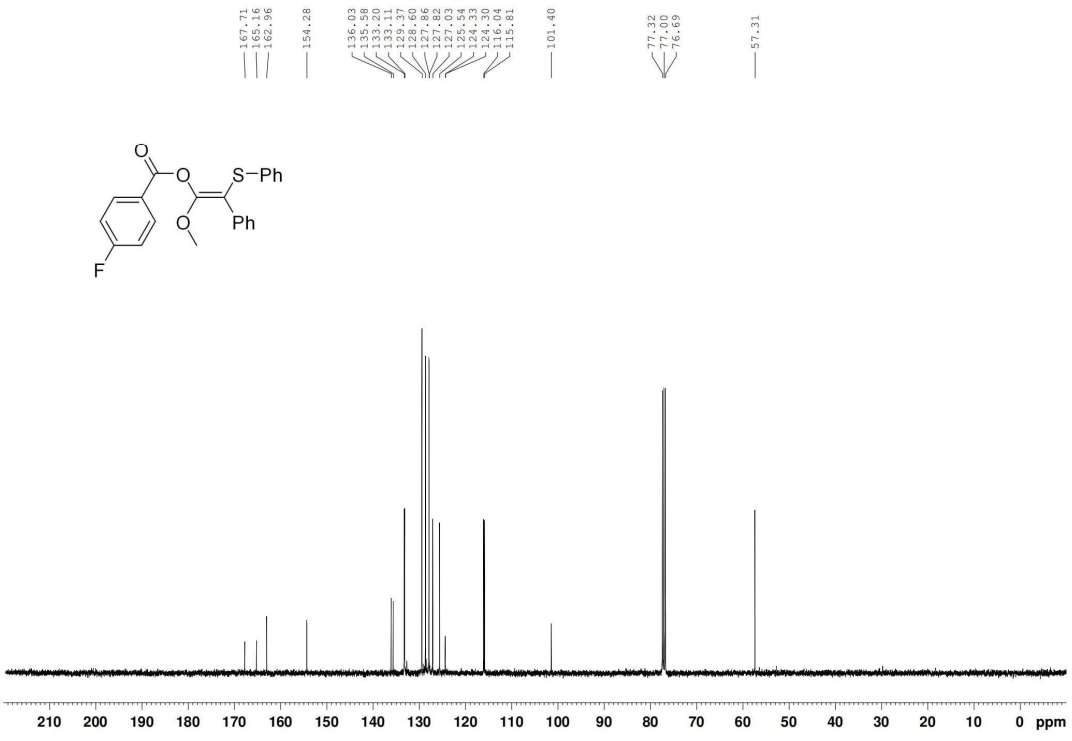
^{13}C NMR spectrum of compound **3ca** ($CDCl_3$, 100 MHz)



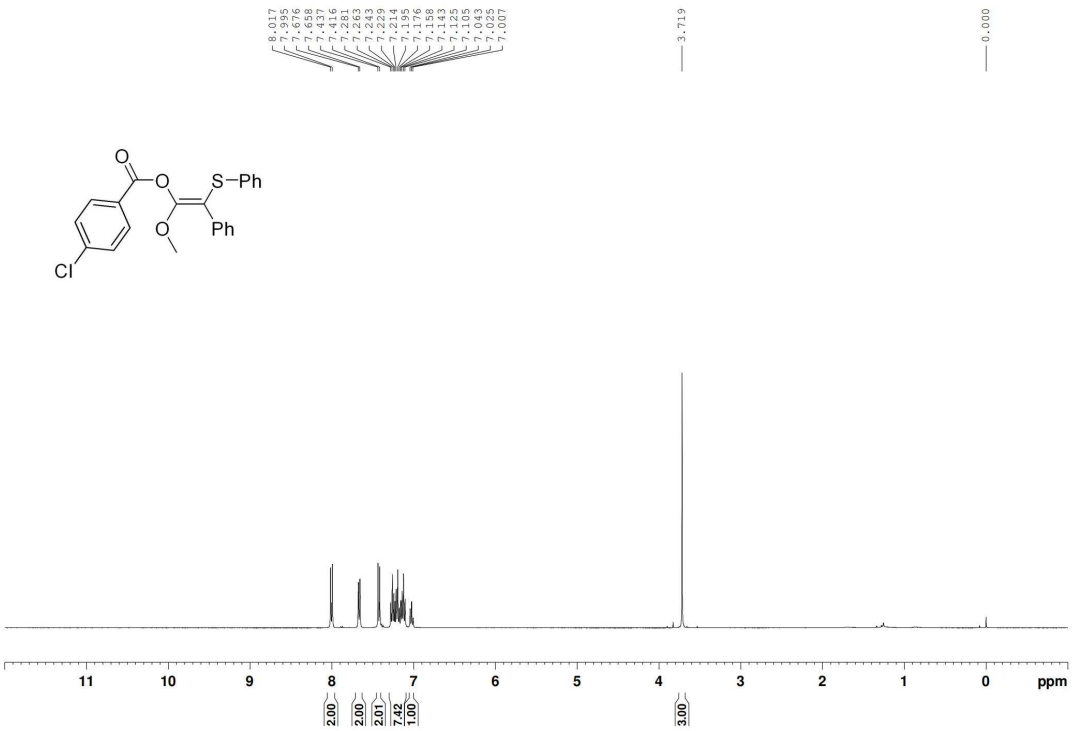
^{1}H NMR spectrum of compound **3da** ($CDCl_3$, 400 MHz)



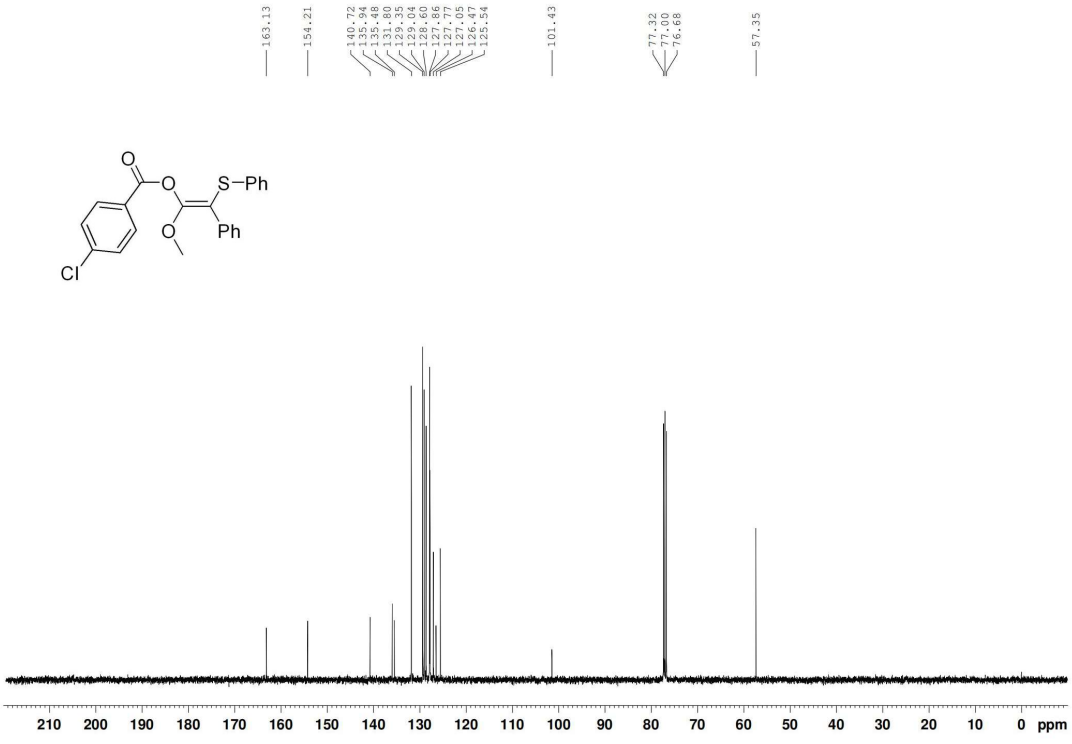
^{13}C NMR spectrum of compound **3da** ($CDCl_3$, 100 MHz)



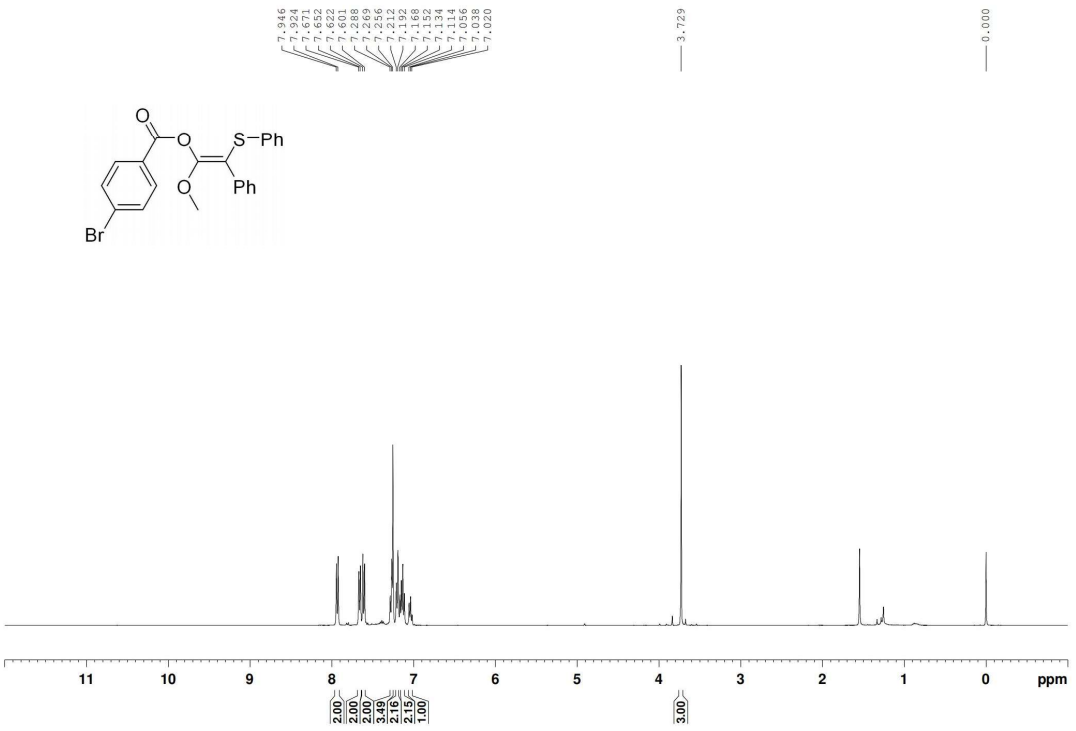
^{1}H NMR spectrum of compound **3ea** ($CDCl_3$, 400 MHz)



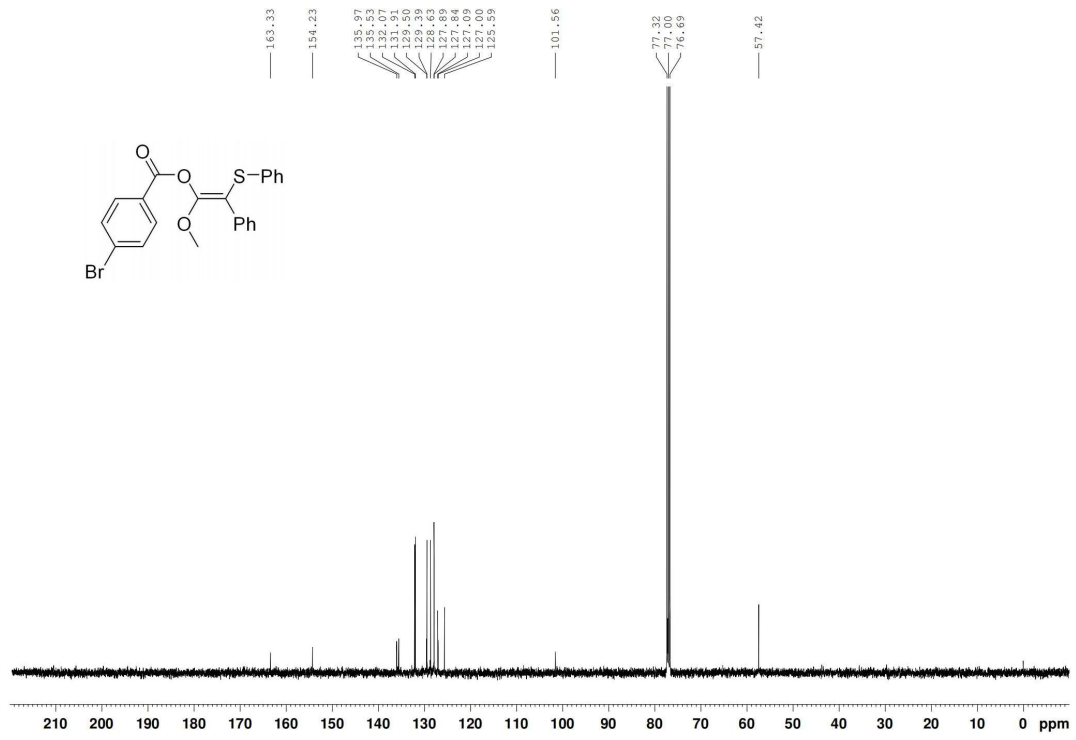
^{13}C NMR spectrum of compound **3ea** ($CDCl_3$, 100 MHz)



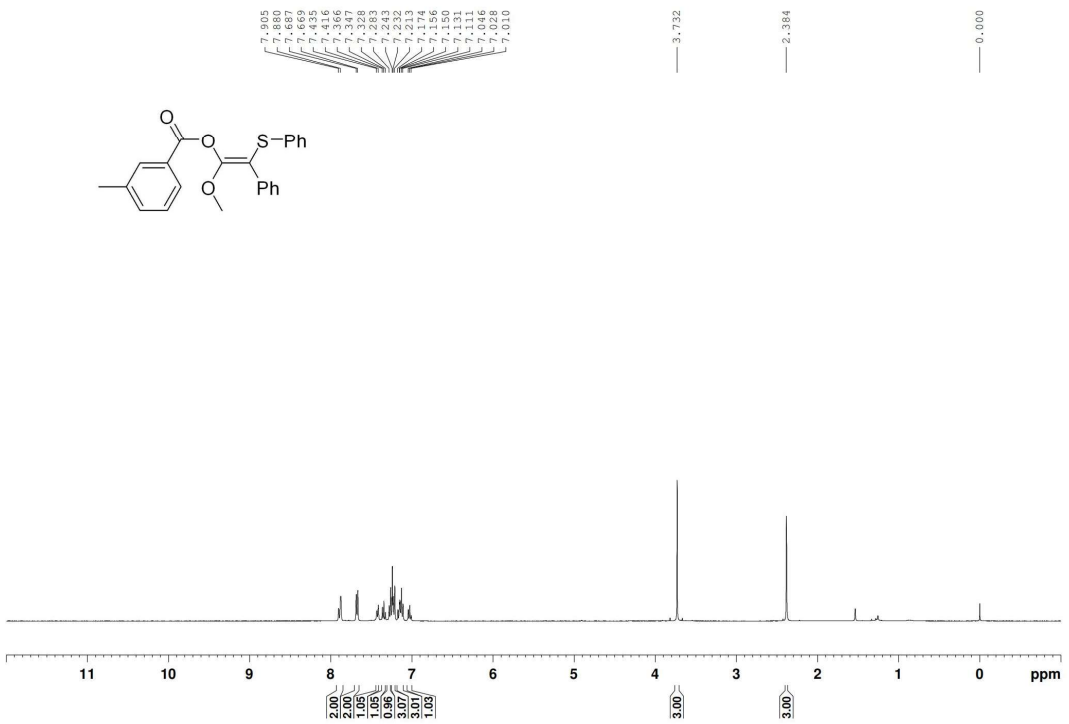
^{1}H NMR spectrum of compound **3fa** ($CDCl_3$, 400 MHz)



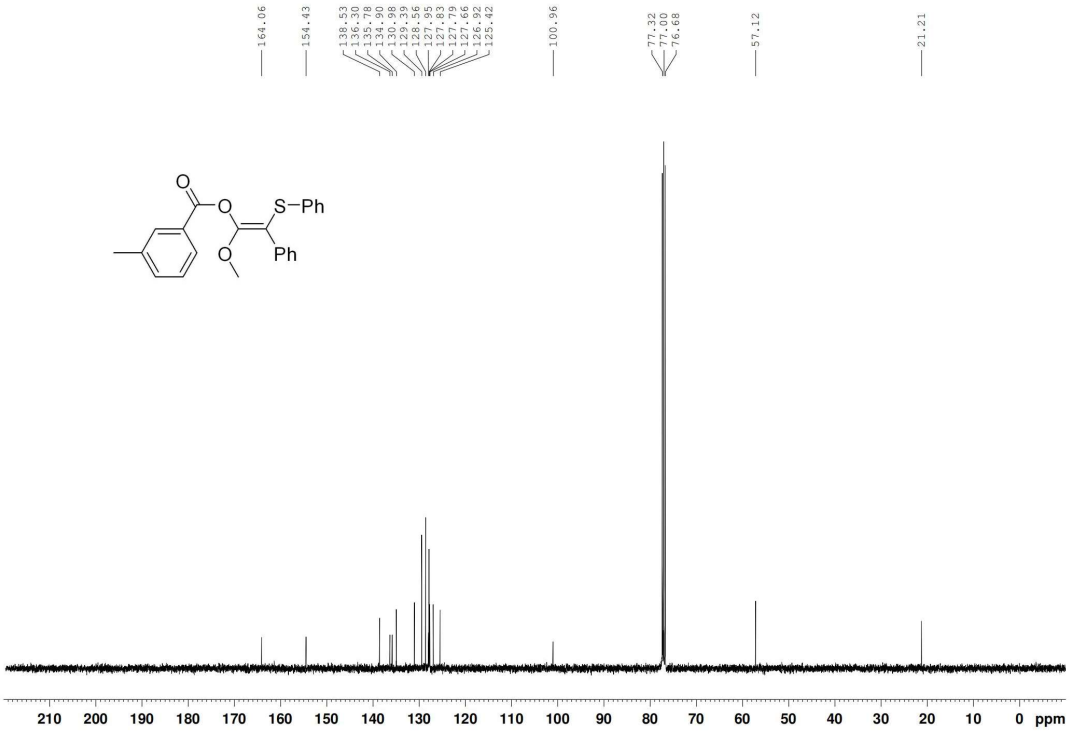
^{13}C NMR spectrum of compound **3fa** ($CDCl_3$, 100 MHz)



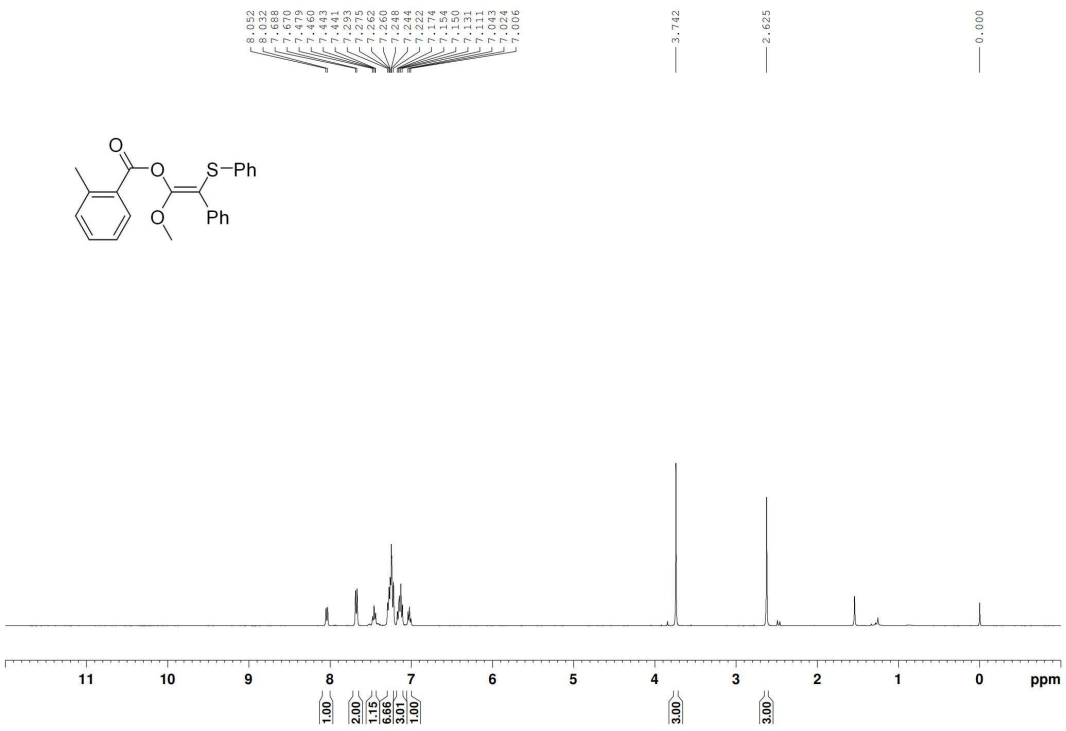
^{1}H NMR spectrum of compound **3ga** ($CDCl_3$, 400 MHz)



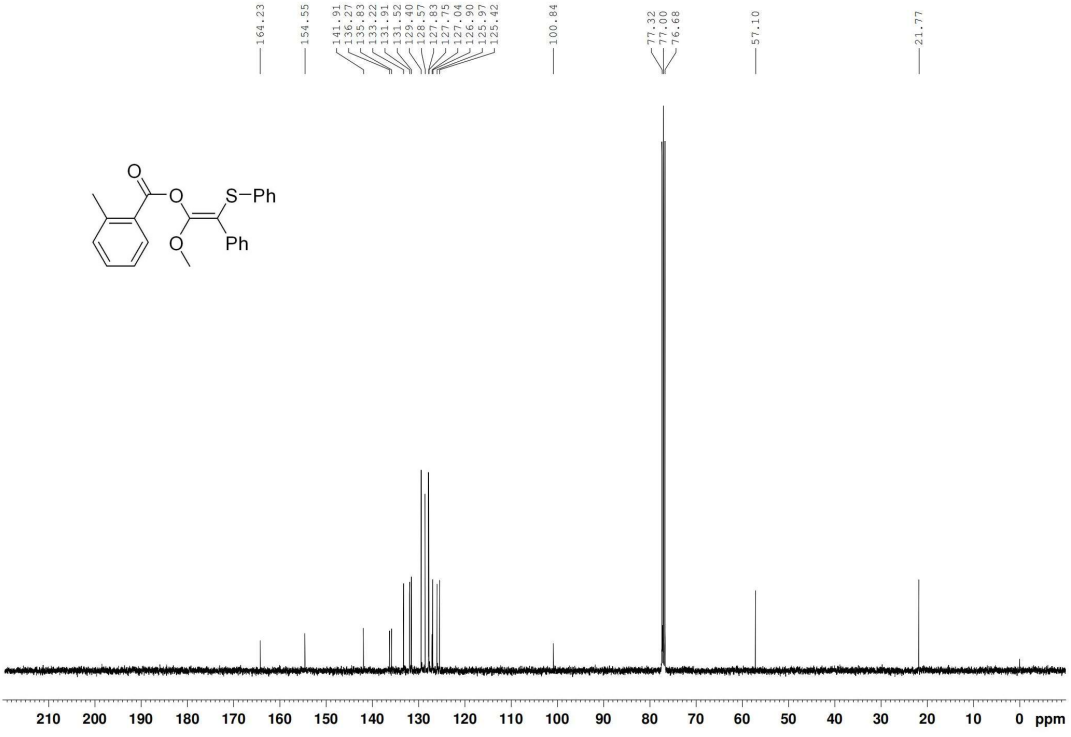
^{13}C NMR spectrum of compound **3ga** ($CDCl_3$, 100 MHz)



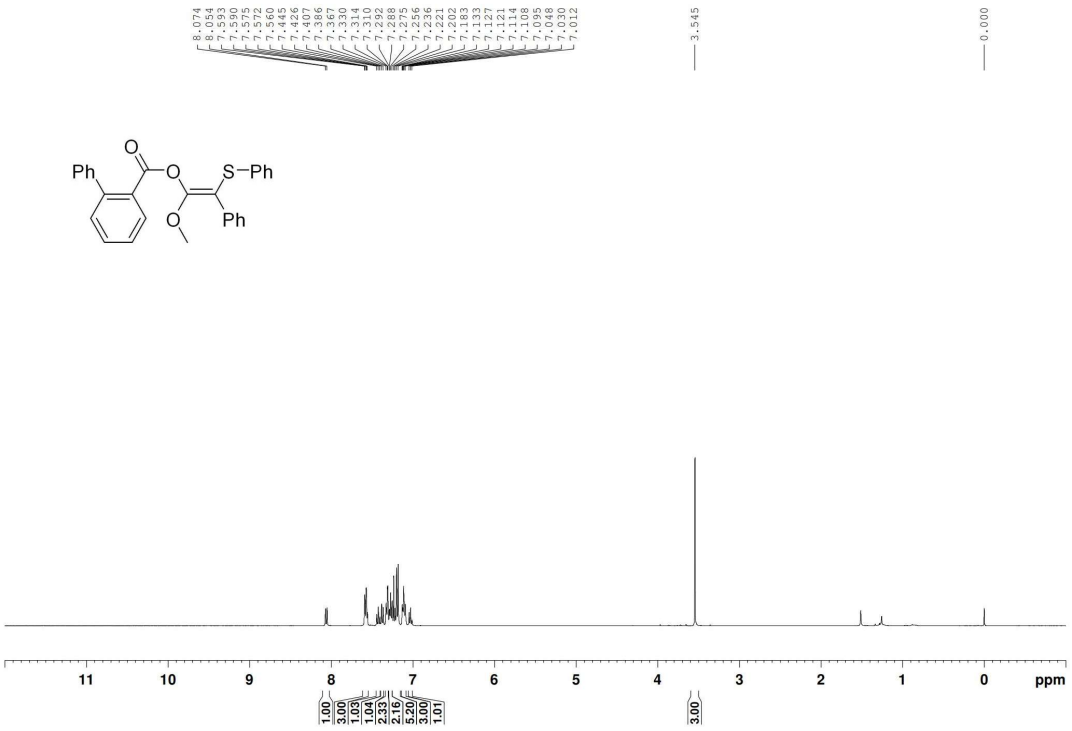
^{1}H NMR spectrum of compound **3ha** ($CDCl_3$, 400 MHz)



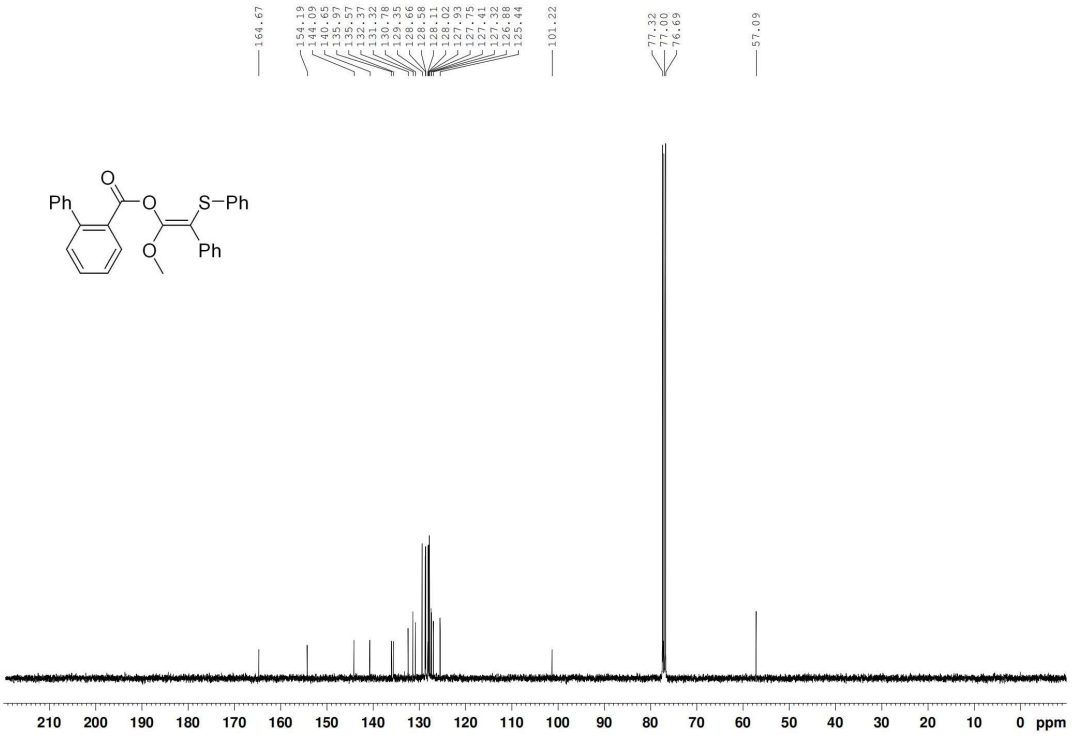
^{13}C NMR spectrum of compound **3ha** ($CDCl_3$, 100 MHz)



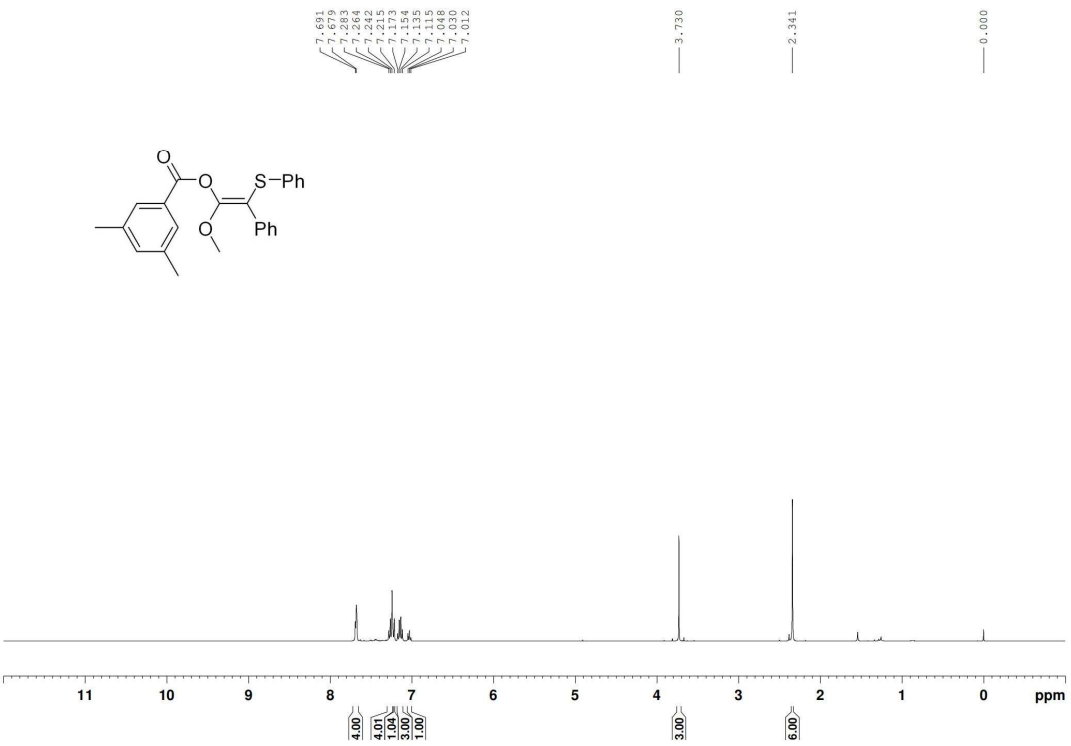
^{1}H NMR spectrum of compound **3ia** ($CDCl_3$, 400 MHz)



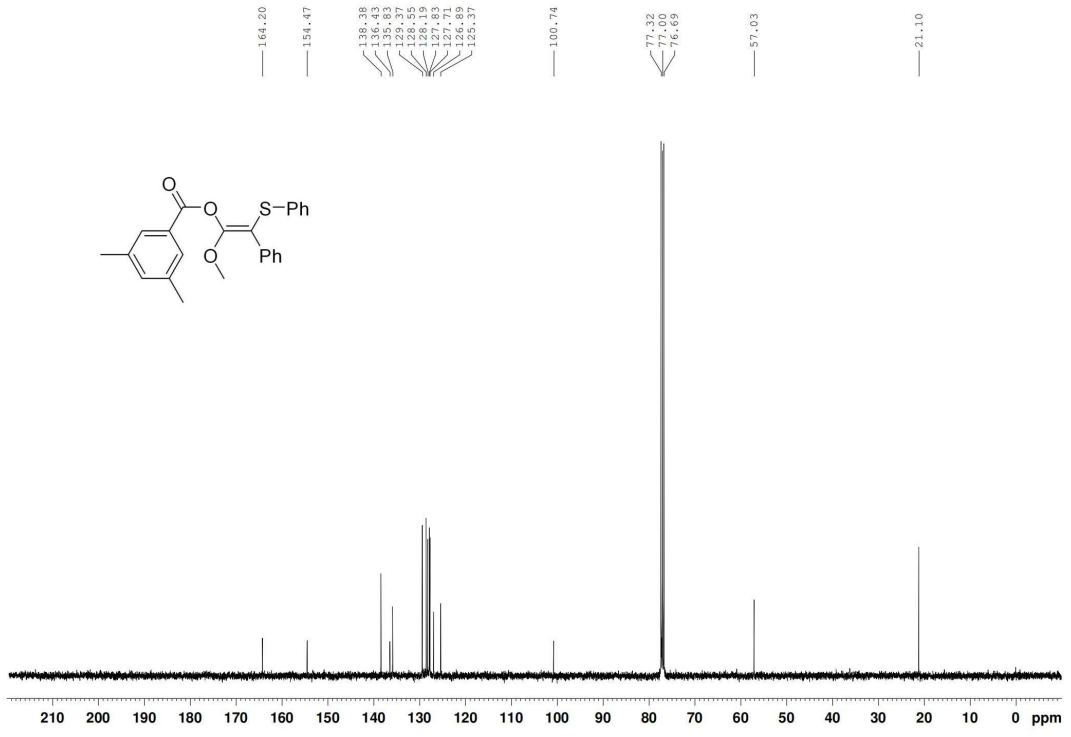
^{13}C NMR spectrum of compound **3ia** ($CDCl_3$, 100 MHz)



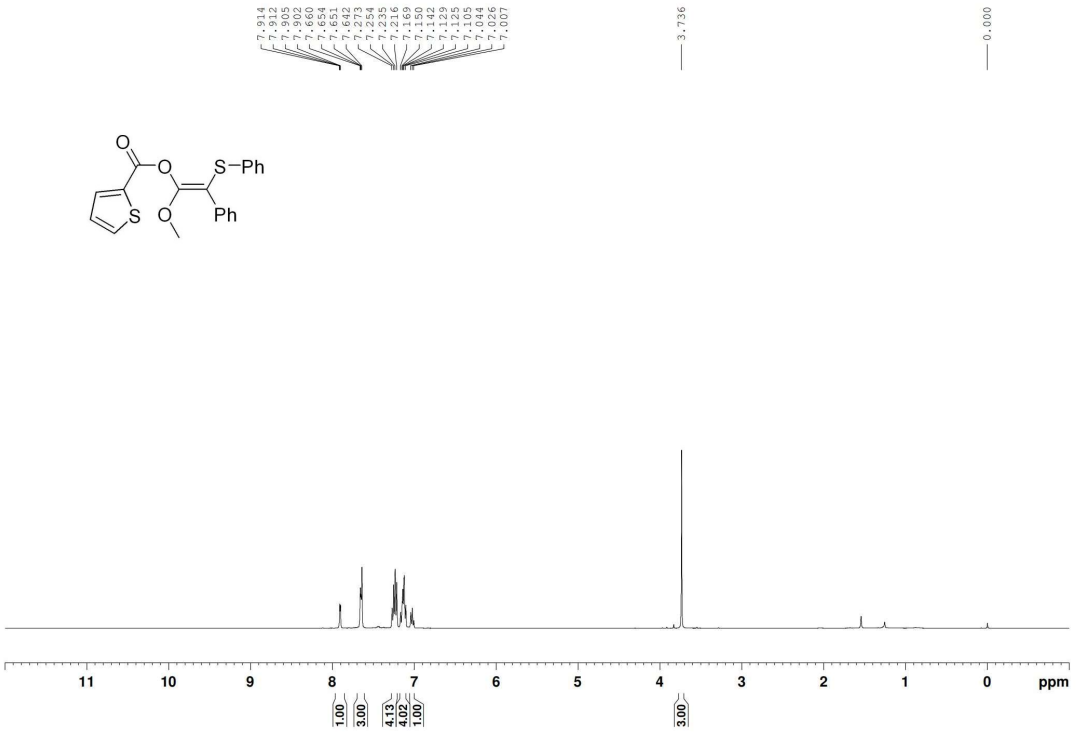
^{1}H NMR spectrum of compound **3ja** ($CDCl_3$, 400 MHz)



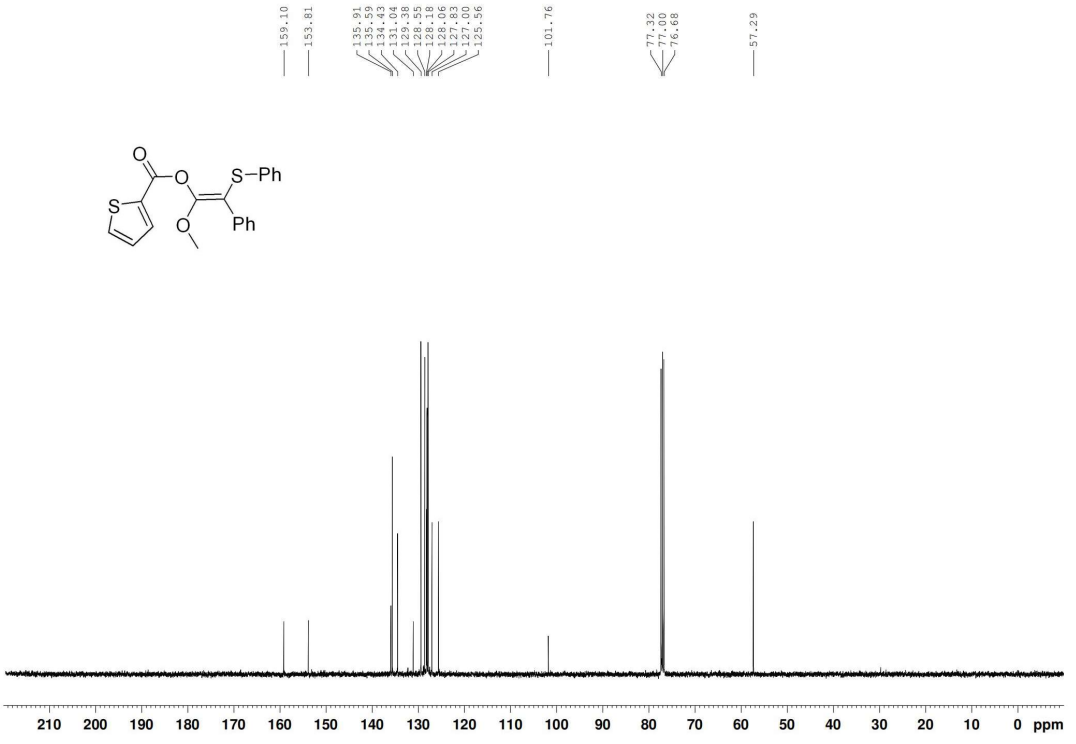
^{13}C NMR spectrum of compound **3ja** ($CDCl_3$, 100 MHz)



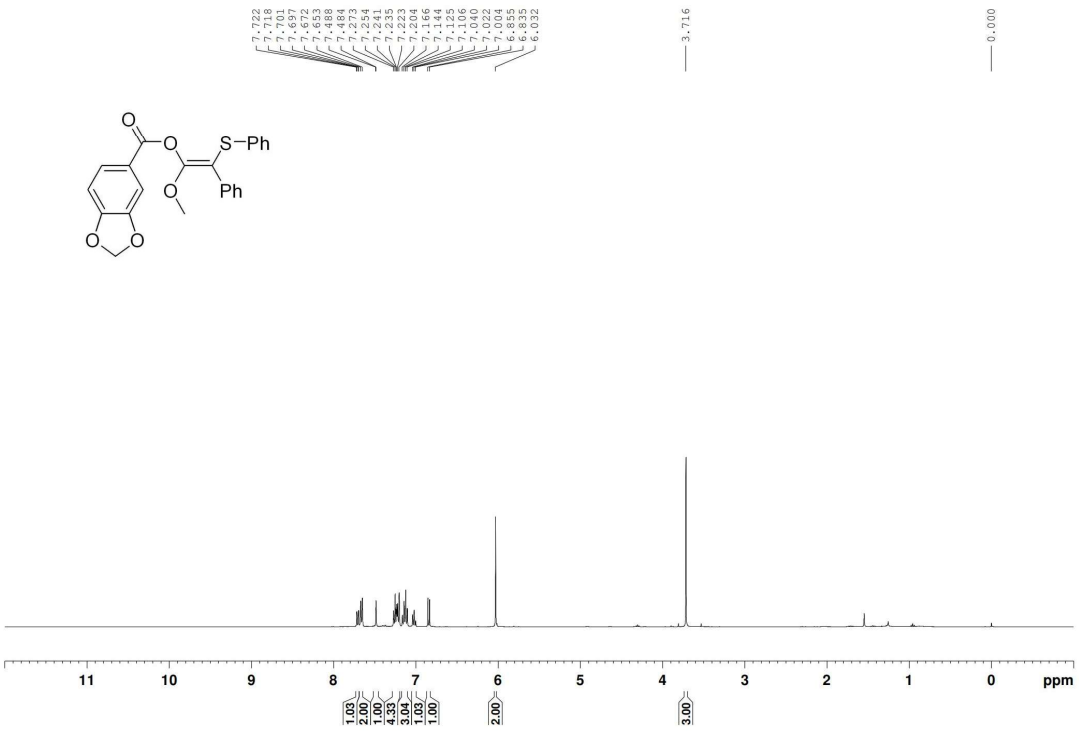
^{1}H NMR spectrum of compound **3ka** ($CDCl_3$, 400 MHz)



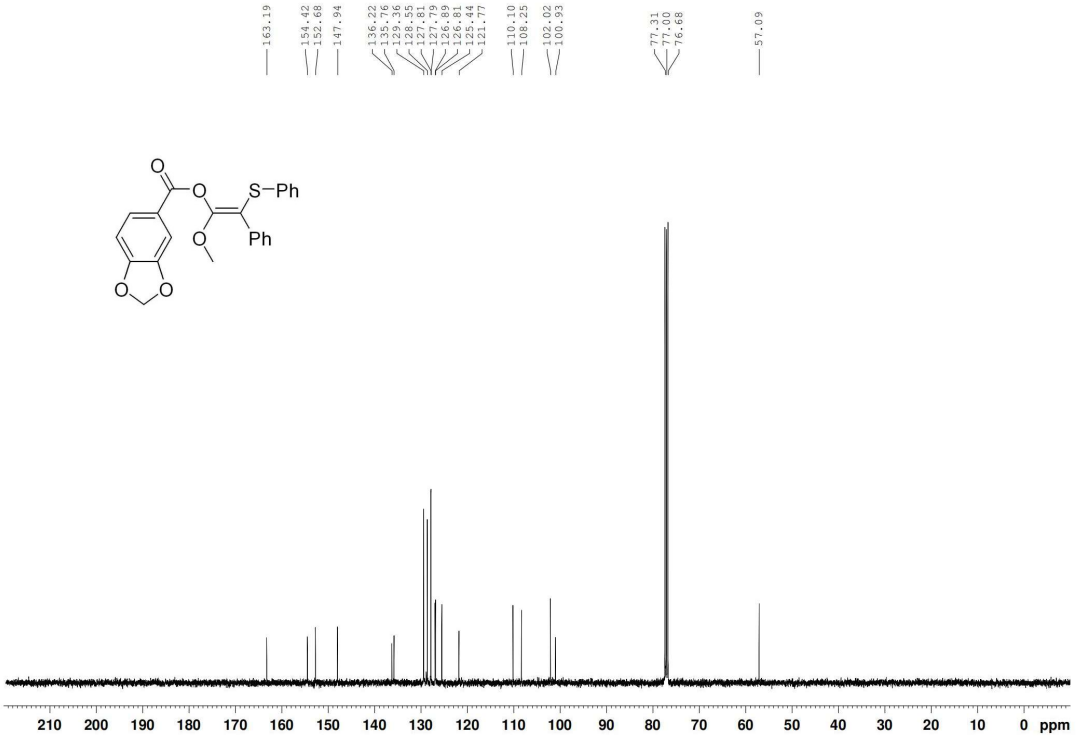
^{13}C NMR spectrum of compound **3ka** ($CDCl_3$, 100 MHz)



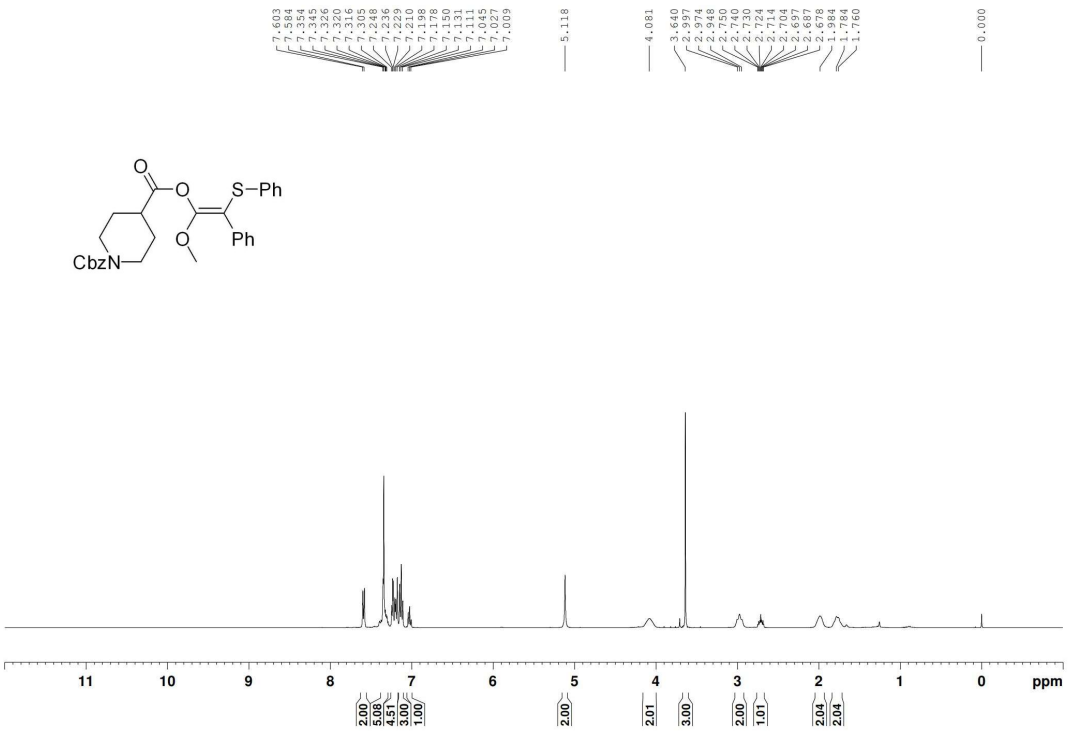
^{1}H NMR spectrum of compound **3la** ($CDCl_3$, 400 MHz)



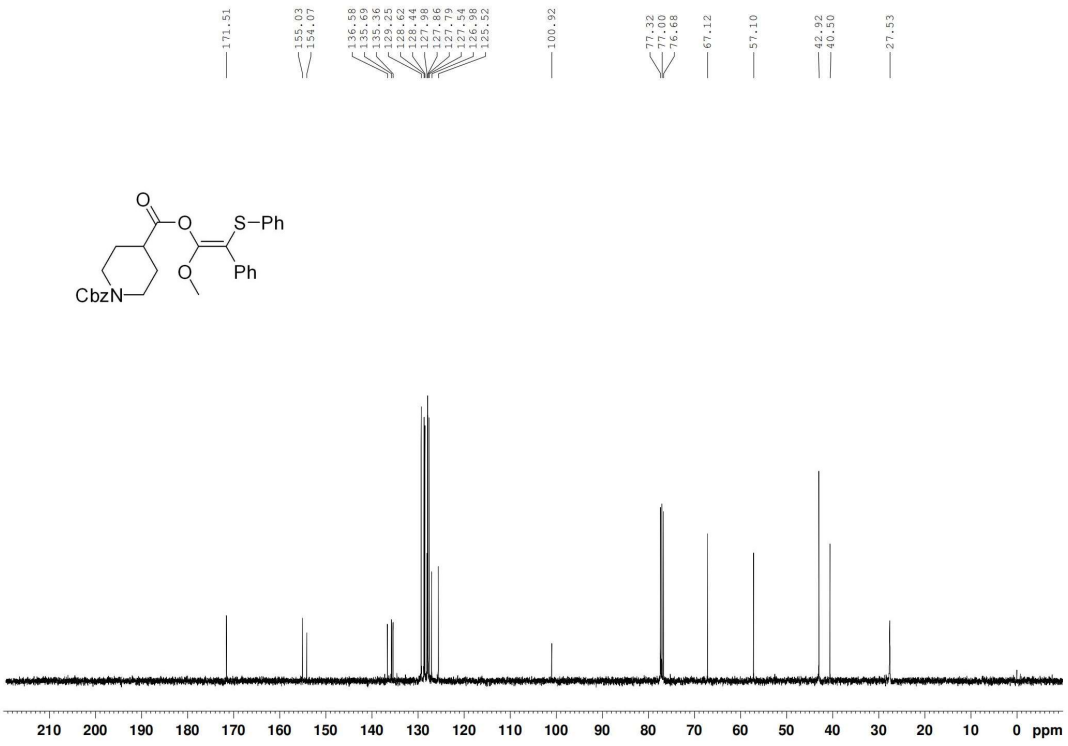
^{13}C NMR spectrum of compound **3la** ($CDCl_3$, 100 MHz)



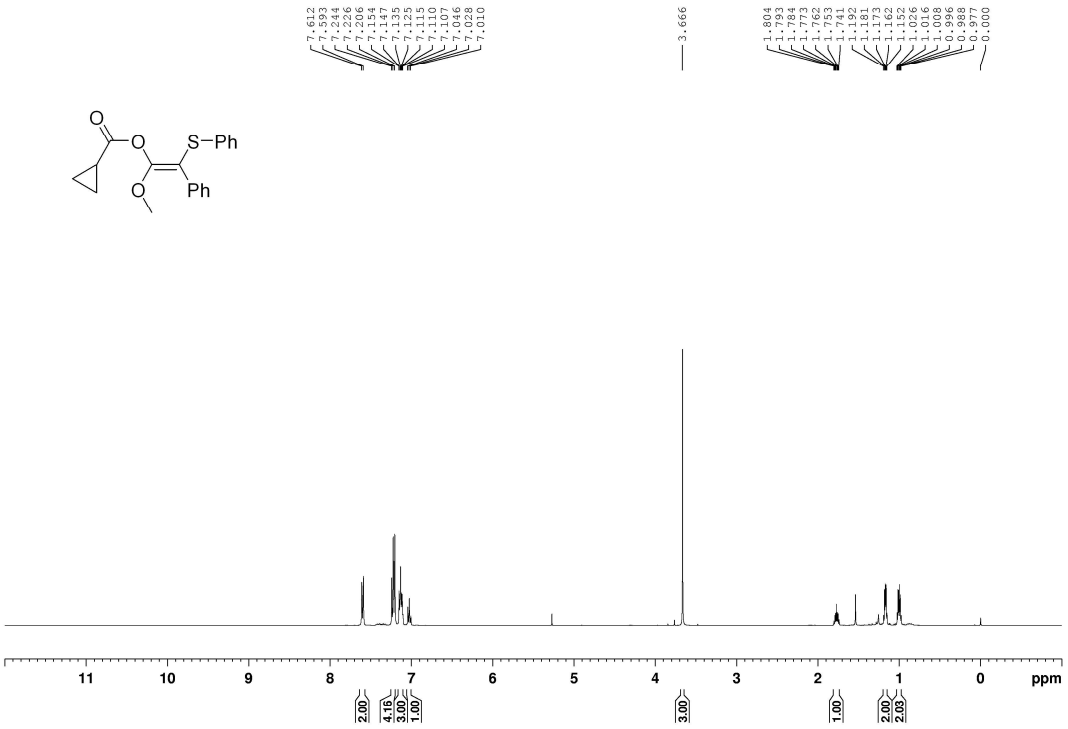
^{1}H NMR spectrum of compound **3ma** ($CDCl_3$, 400 MHz)



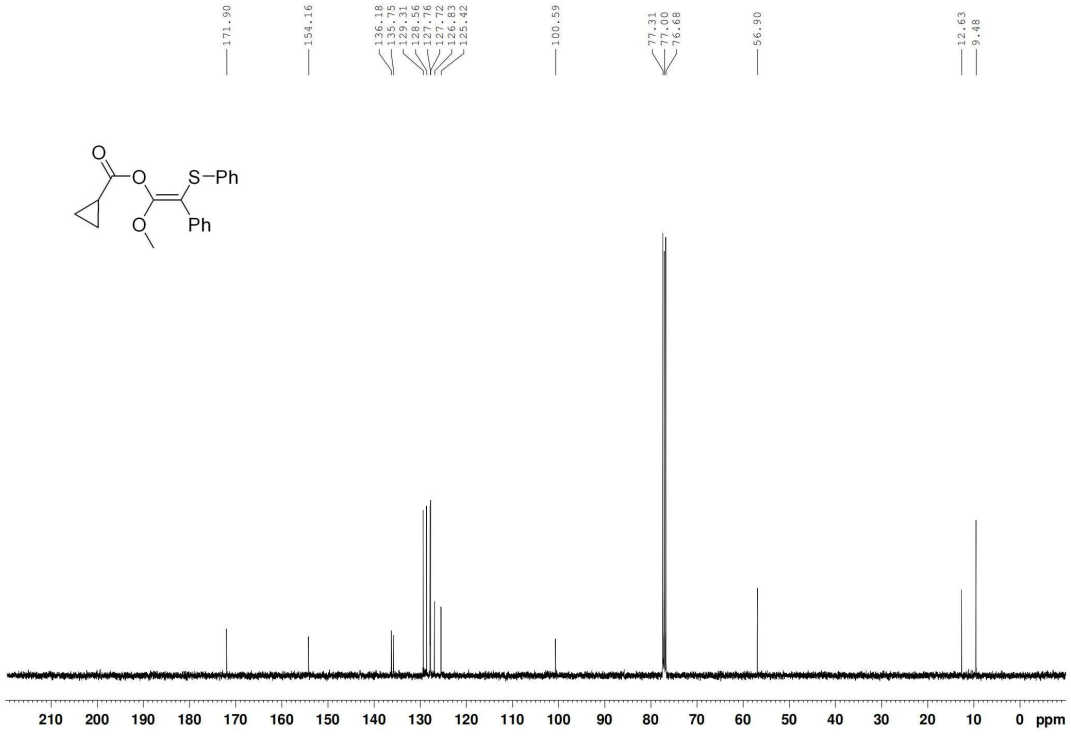
^{13}C NMR spectrum of compound **3ma** ($CDCl_3$, 100 MHz)



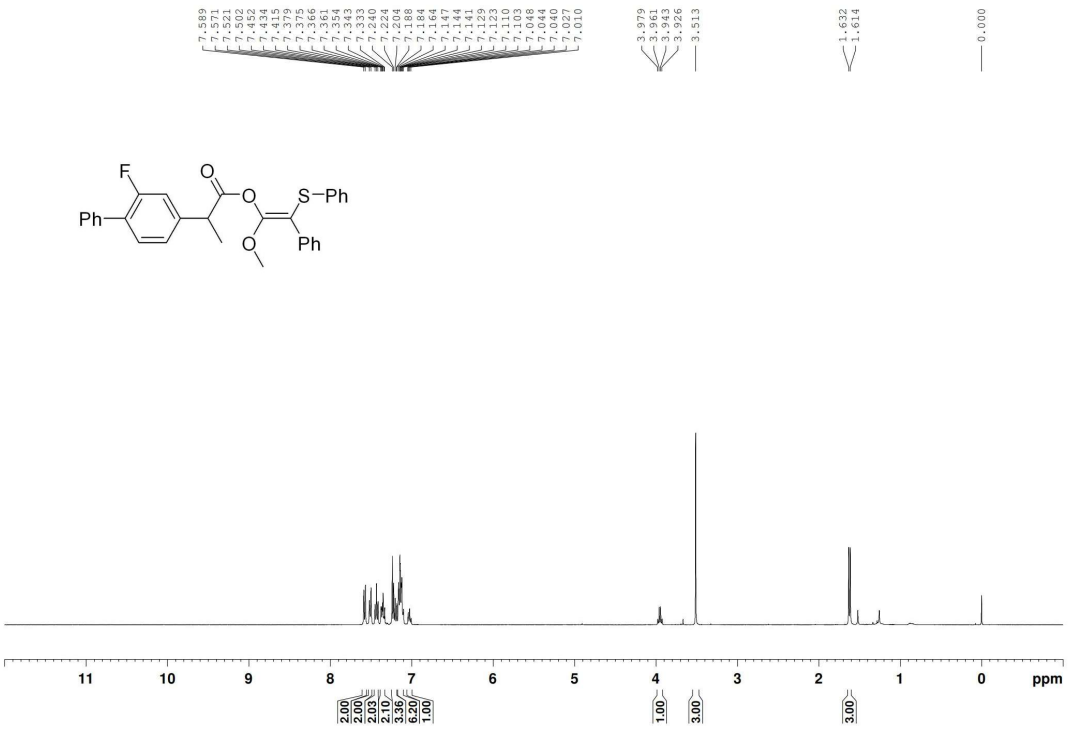
^{1}H NMR spectrum of compound **3na** ($CDCl_3$, 400 MHz)



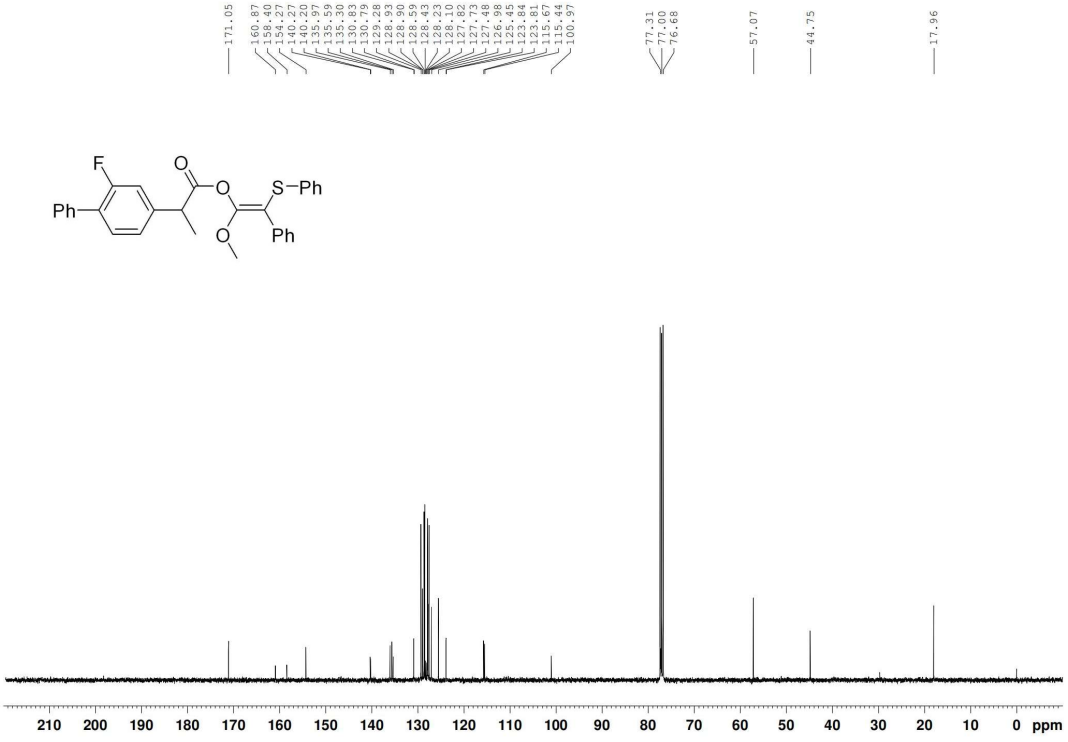
^{13}C NMR spectrum of compound **3na** ($CDCl_3$, 100 MHz)



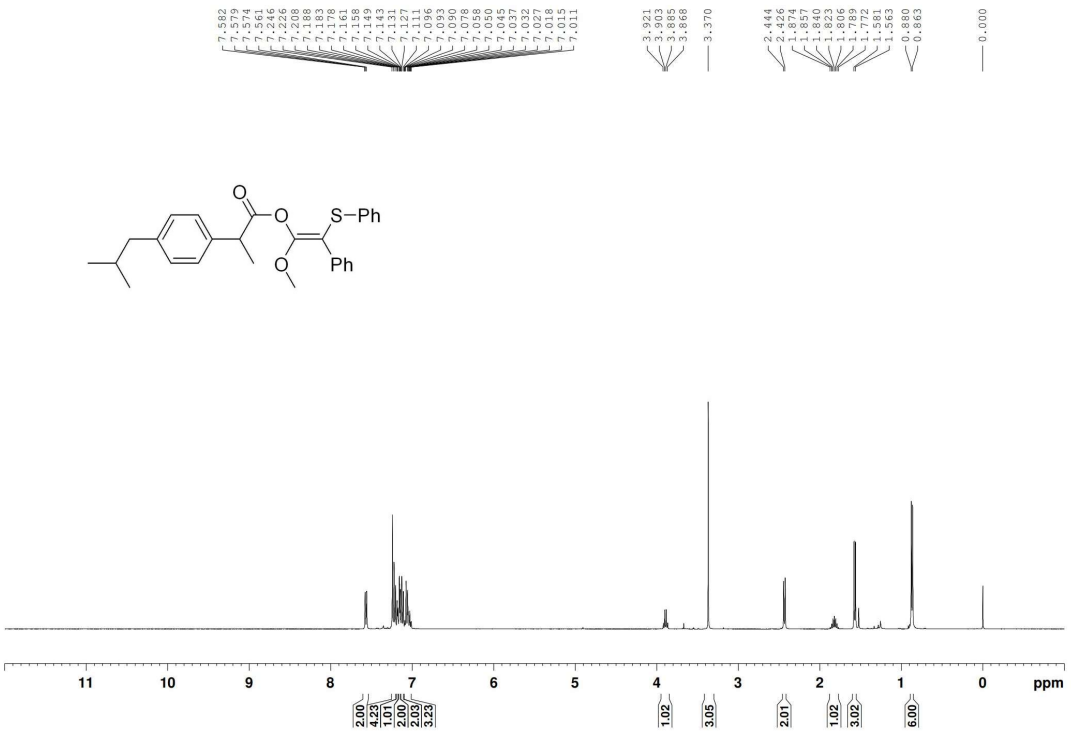
^{1}H NMR spectrum of compound **3oa** ($CDCl_3$, 400 MHz)



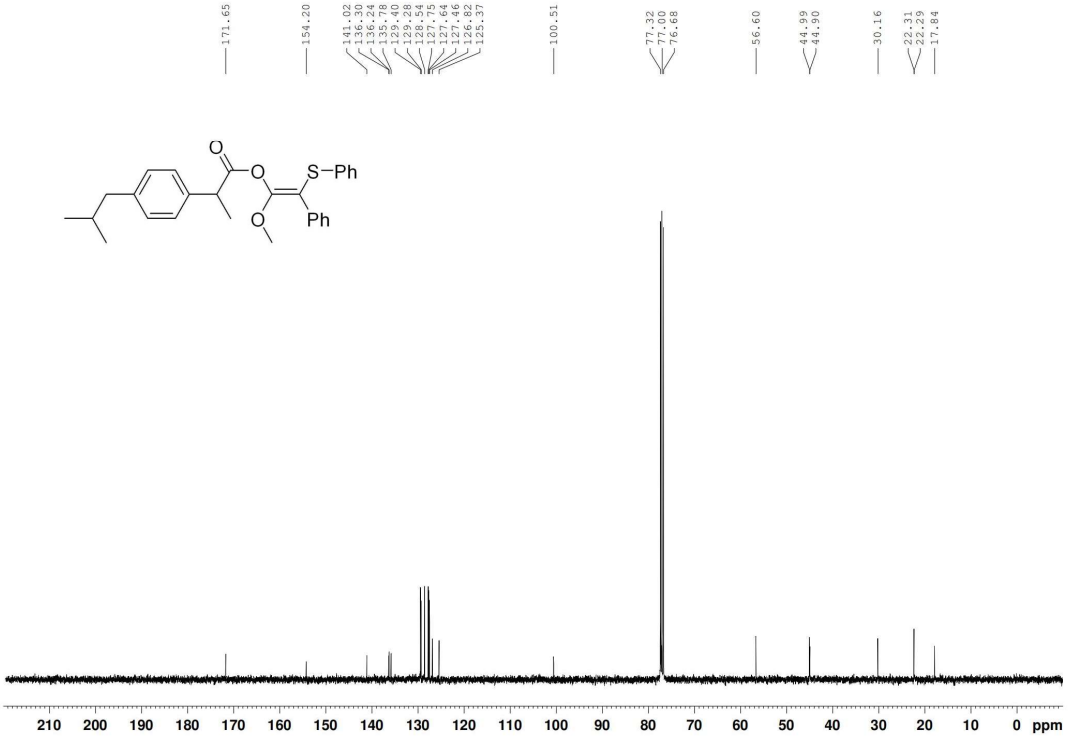
^{13}C NMR spectrum of compound **3oa** ($CDCl_3$, 100 MHz)



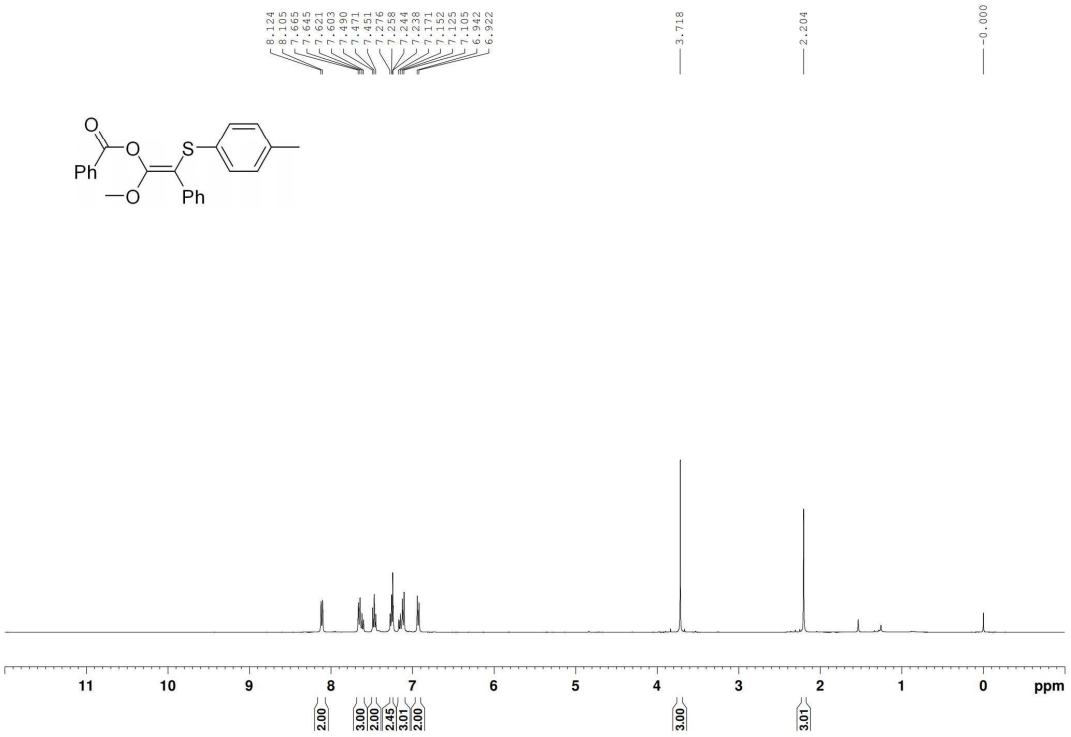
^{1}H NMR spectrum of compound **3pa** ($CDCl_3$, 400 MHz)



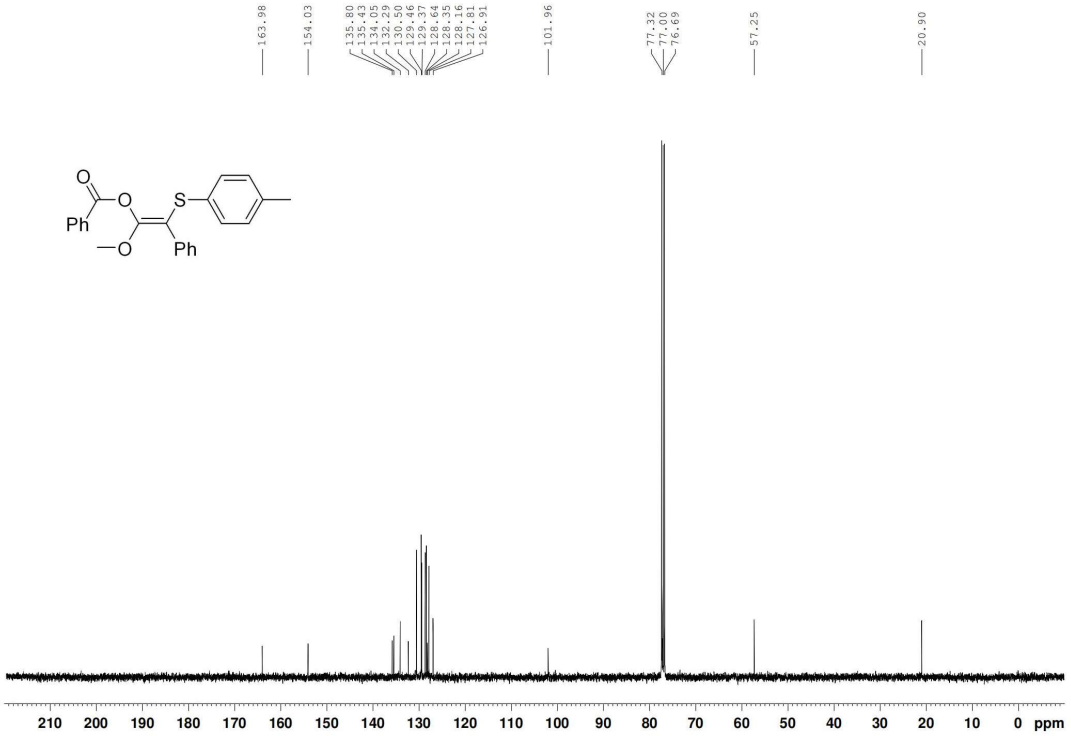
^{13}C NMR spectrum of compound **3pa** ($CDCl_3$, 100 MHz)



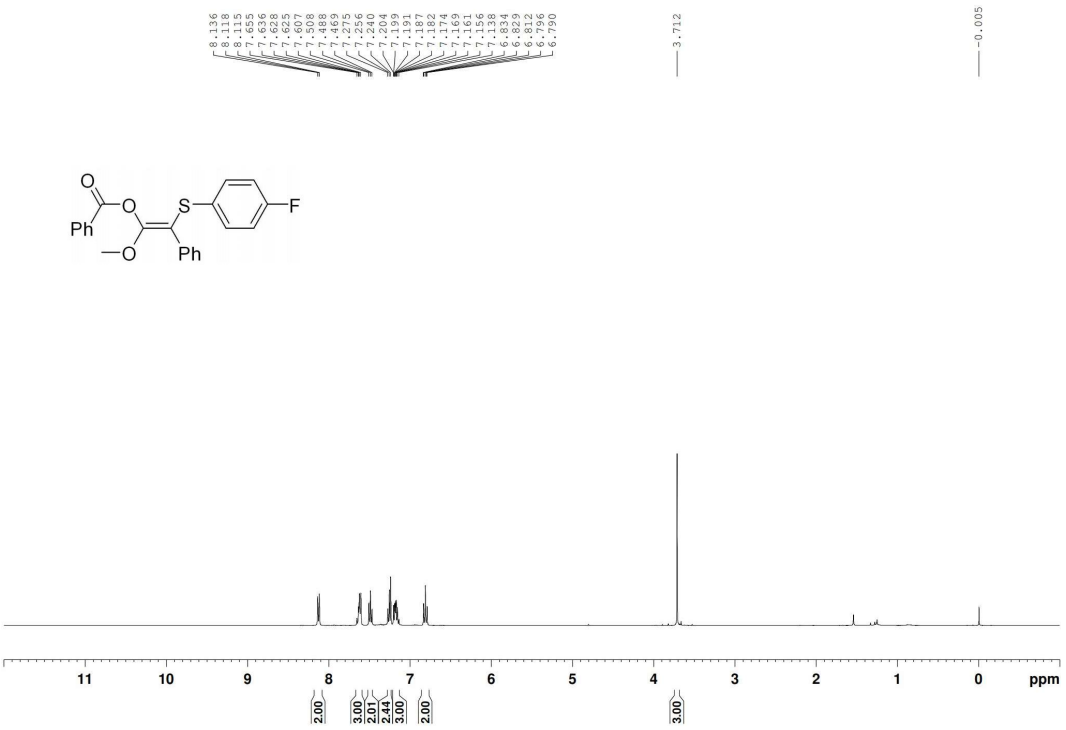
^{1}H NMR spectrum of compound **3qa** ($CDCl_3$, 400 MHz)



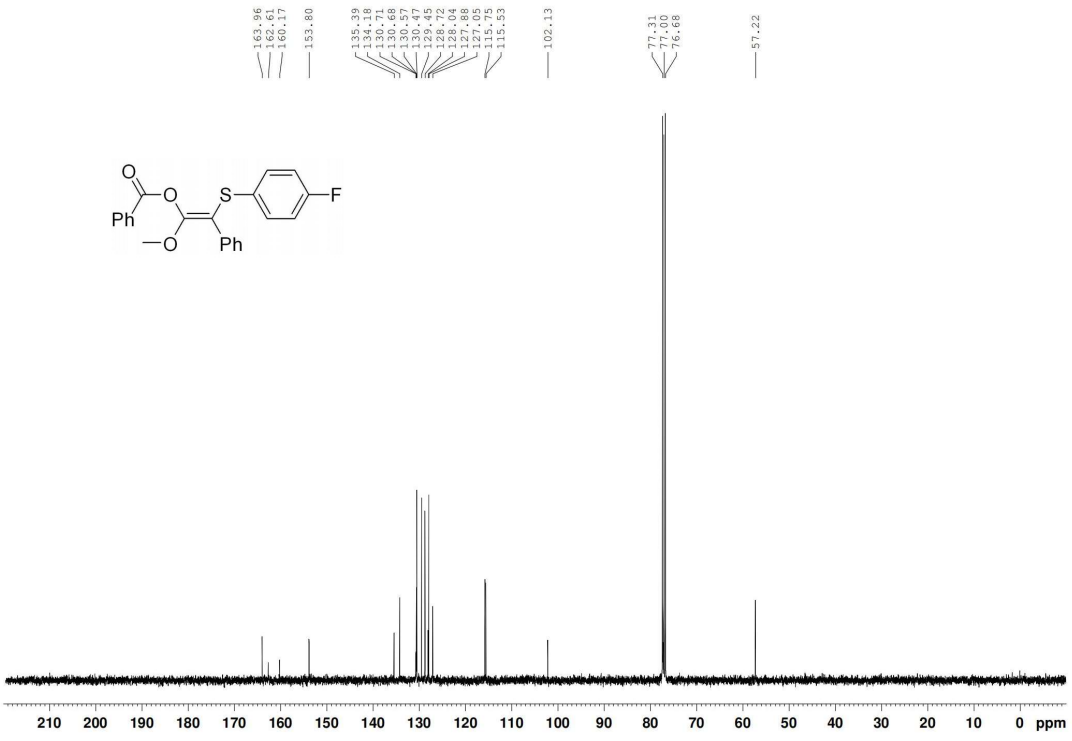
^{13}C NMR spectrum of compound **3qa** ($CDCl_3$, 100 MHz)



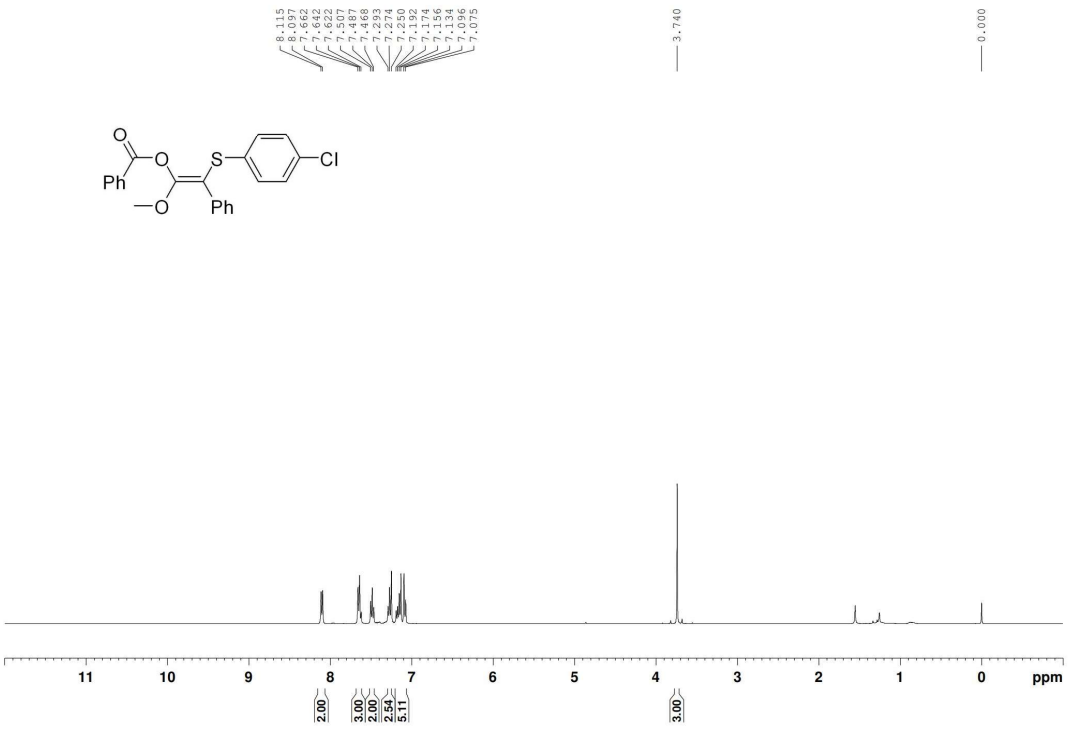
^{1}H NMR spectrum of compound **3ra** ($CDCl_3$, 400 MHz)



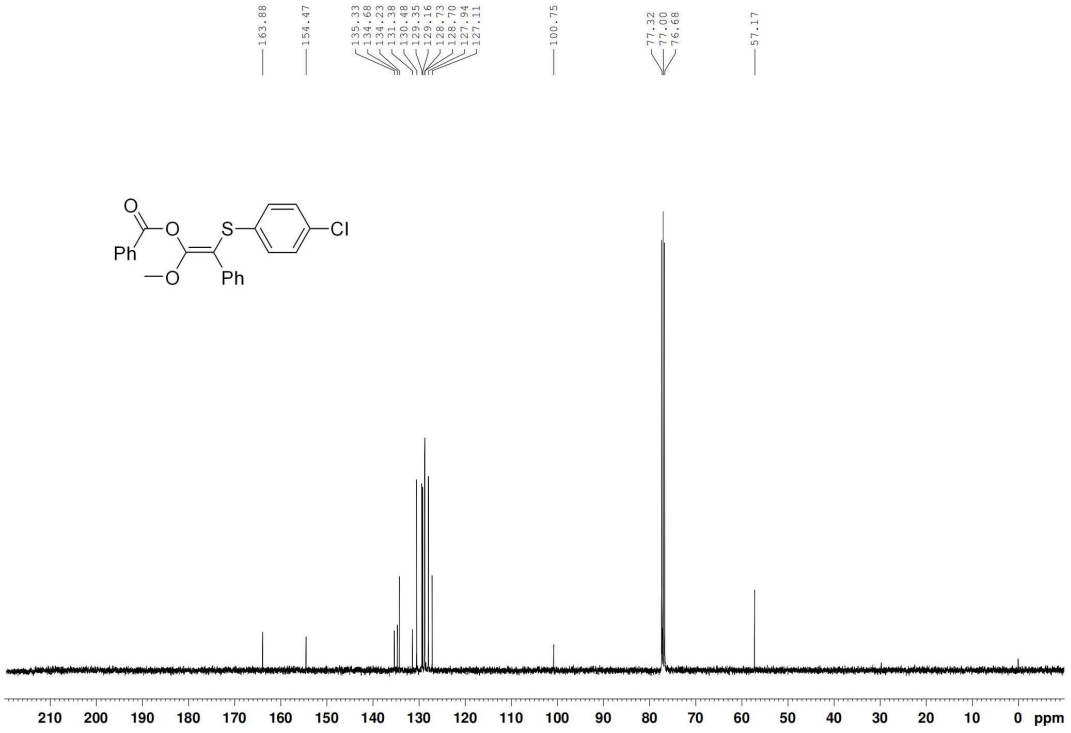
^{13}C NMR spectrum of compound **3ra** ($CDCl_3$, 100 MHz)



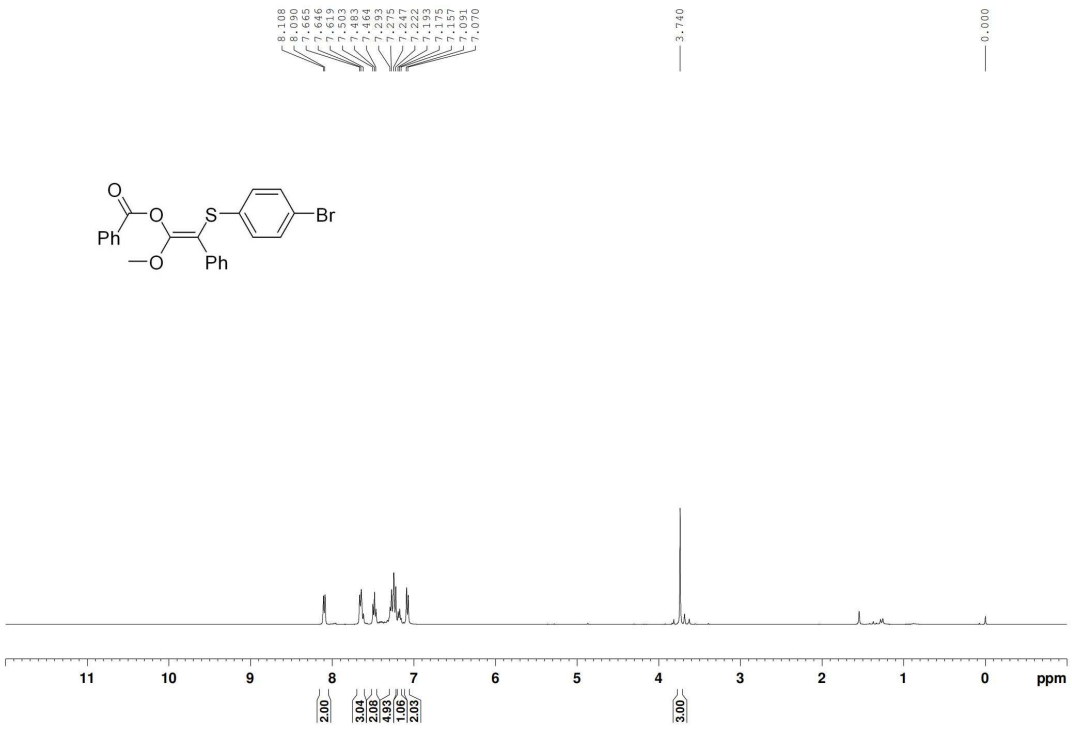
^{1}H NMR spectrum of compound **3sa** ($CDCl_3$, 400 MHz)



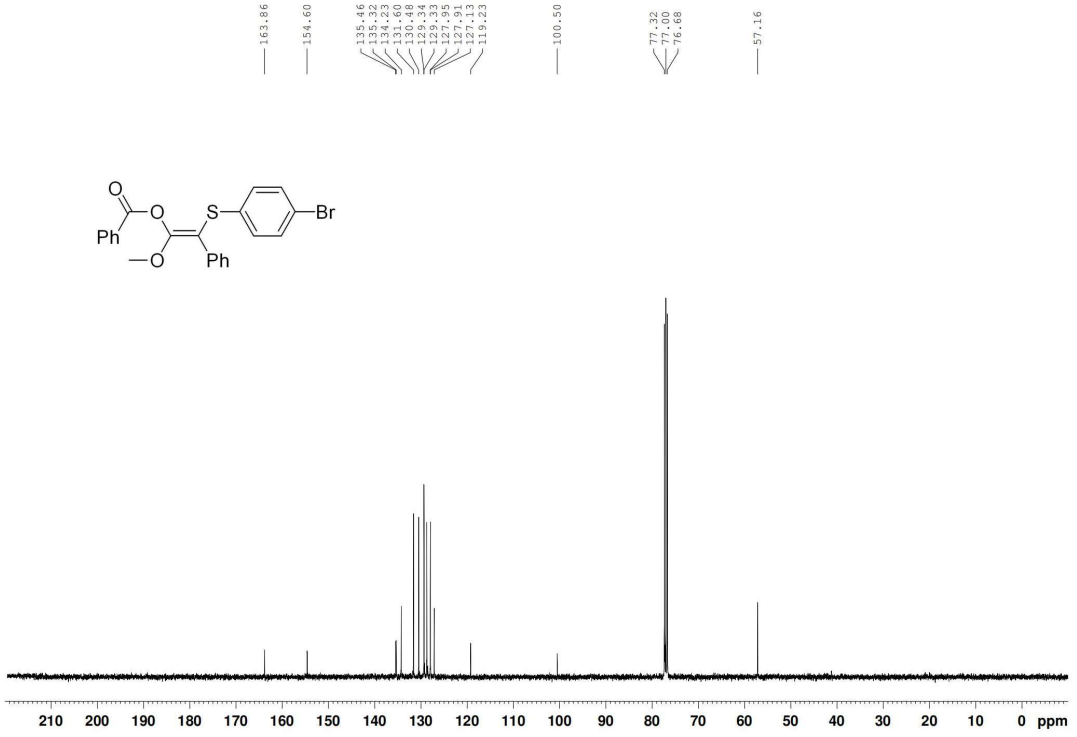
^{13}C NMR spectrum of compound **3sa** ($CDCl_3$, 100 MHz)



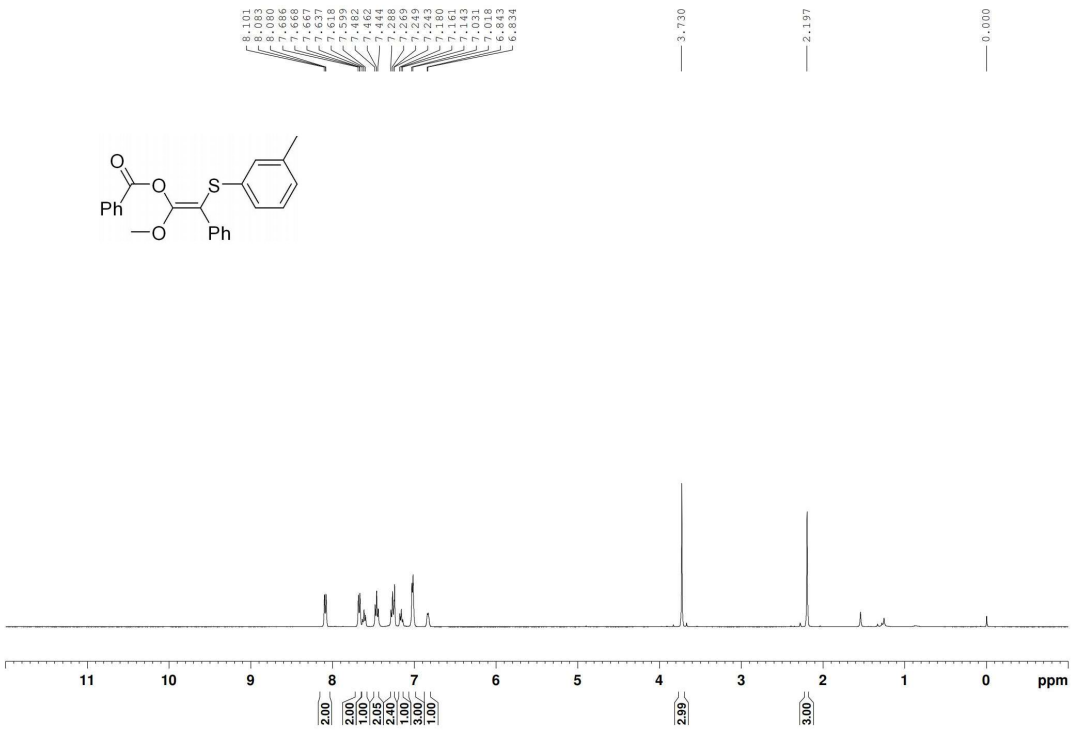
^{1}H NMR spectrum of compound **3ta** ($CDCl_3$, 400 MHz)



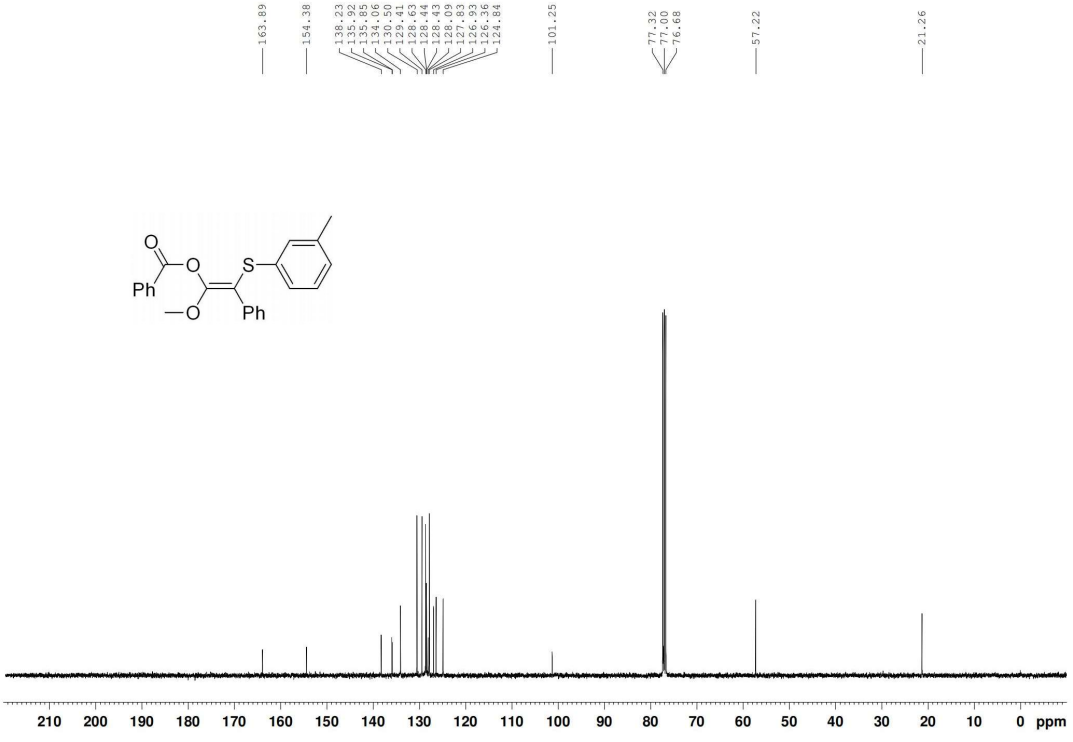
^{13}C NMR spectrum of compound **3ta** ($CDCl_3$, 100 MHz)



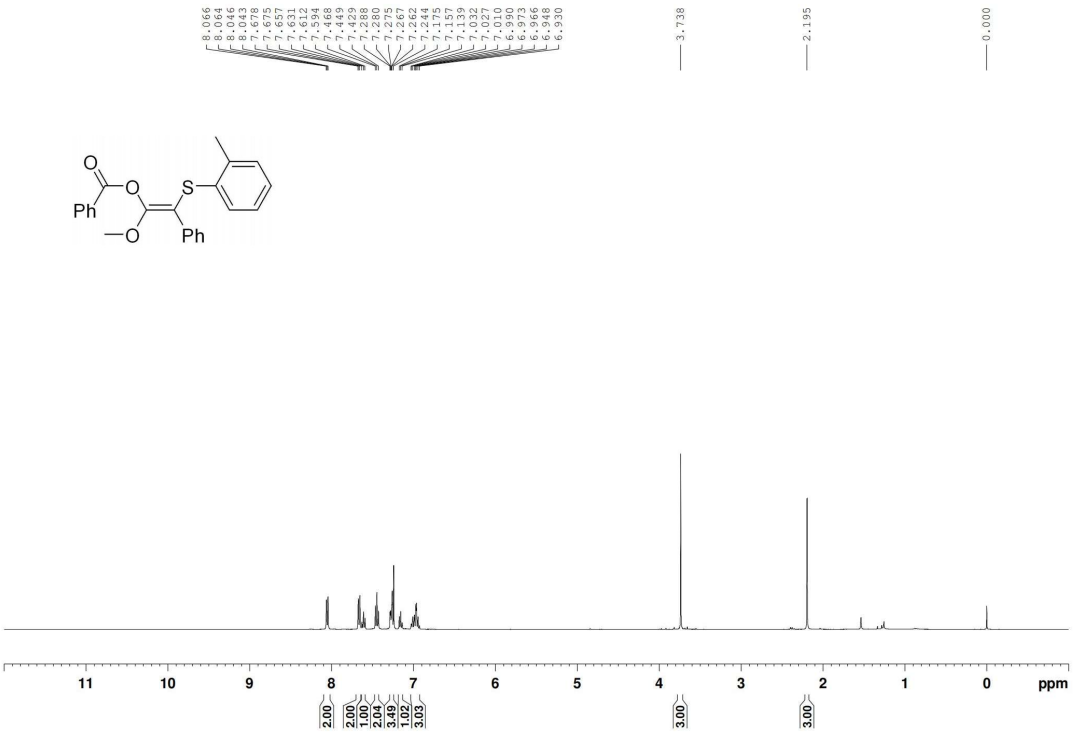
^{1}H NMR spectrum of compound **3ua** ($CDCl_3$, 400 MHz)



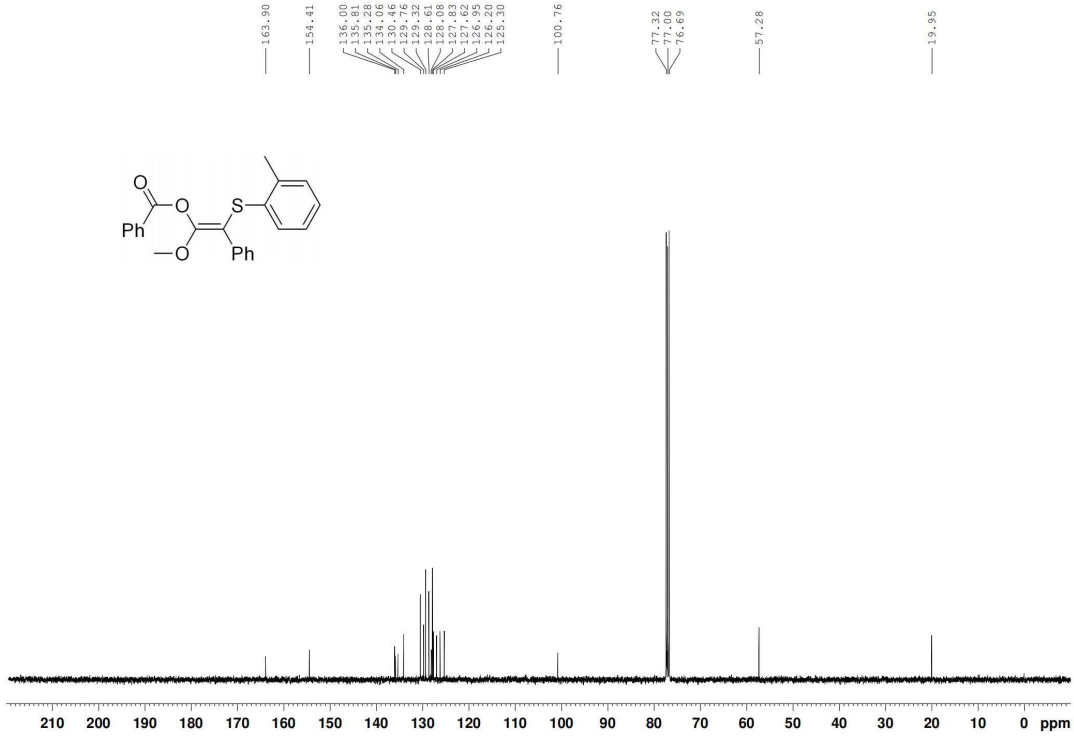
^{13}C NMR spectrum of compound **3ua** ($CDCl_3$, 100 MHz)



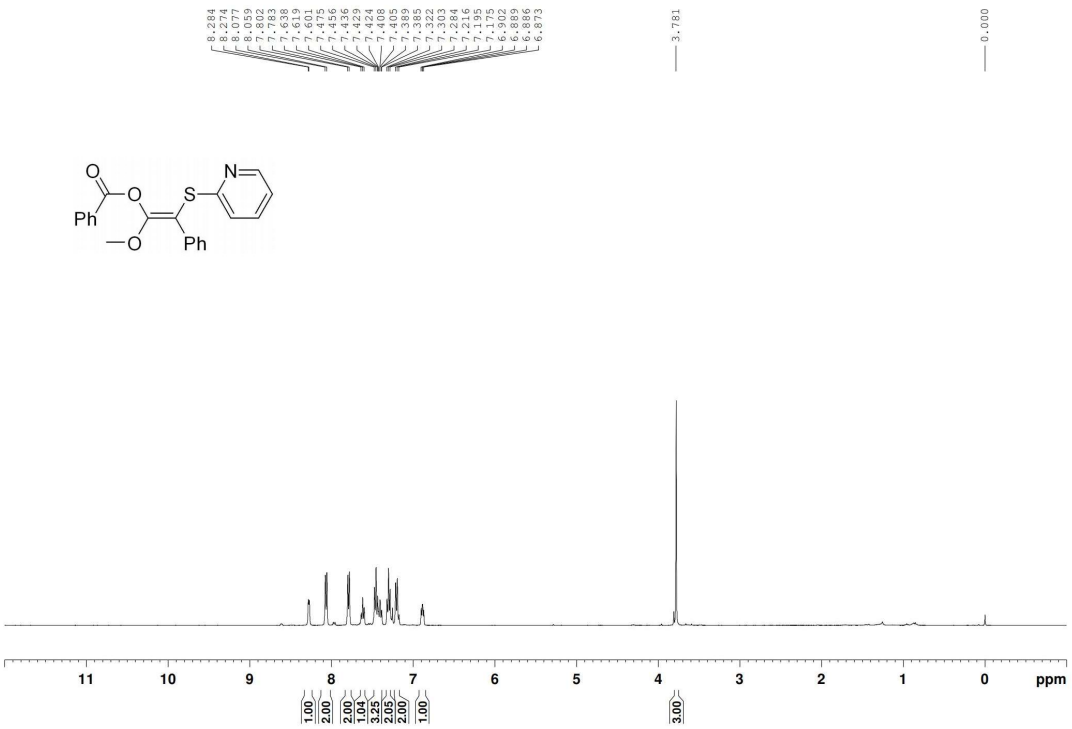
^{1}H NMR spectrum of compound **3va** ($CDCl_3$, 400 MHz)



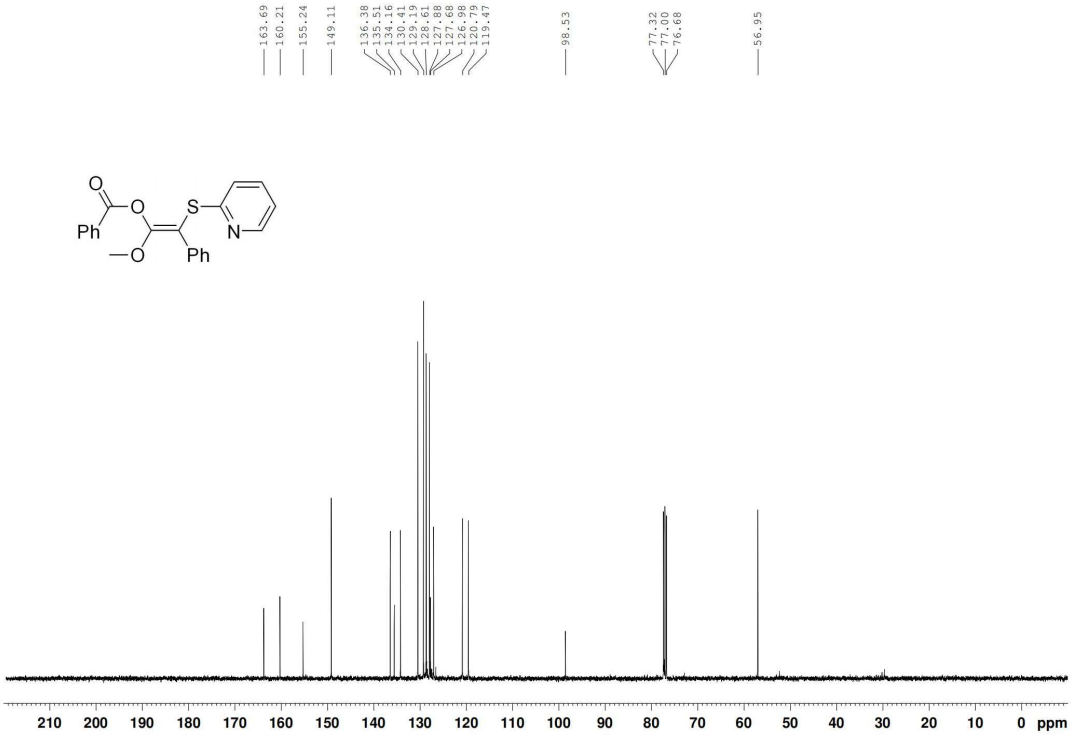
^{13}C NMR spectrum of compound **3va** ($CDCl_3$, 100 MHz)



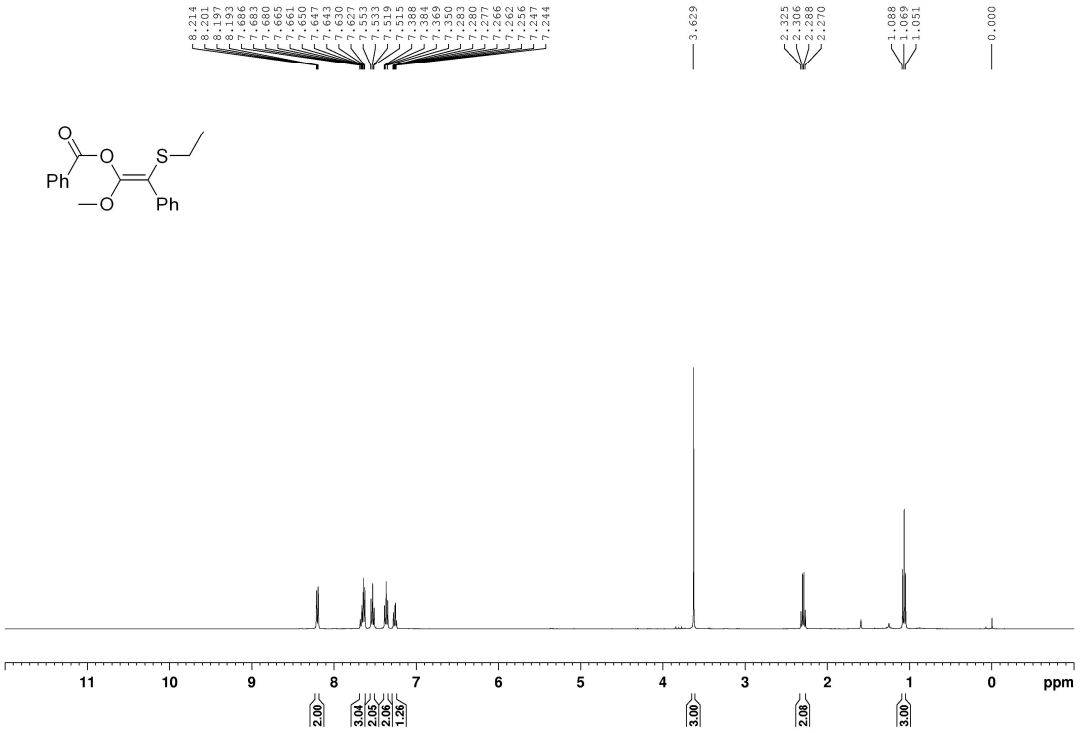
^{1}H NMR spectrum of compound **3wa** ($CDCl_3$, 400 MHz)



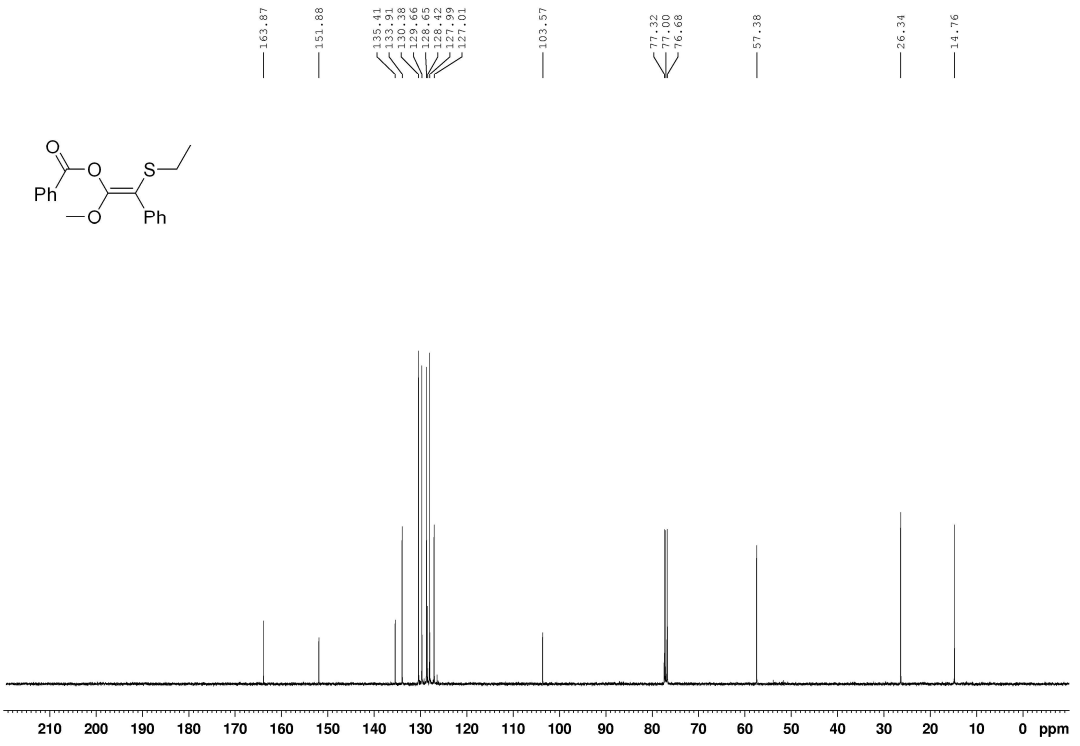
^{13}C NMR spectrum of compound **3wa** ($CDCl_3$, 100 MHz)



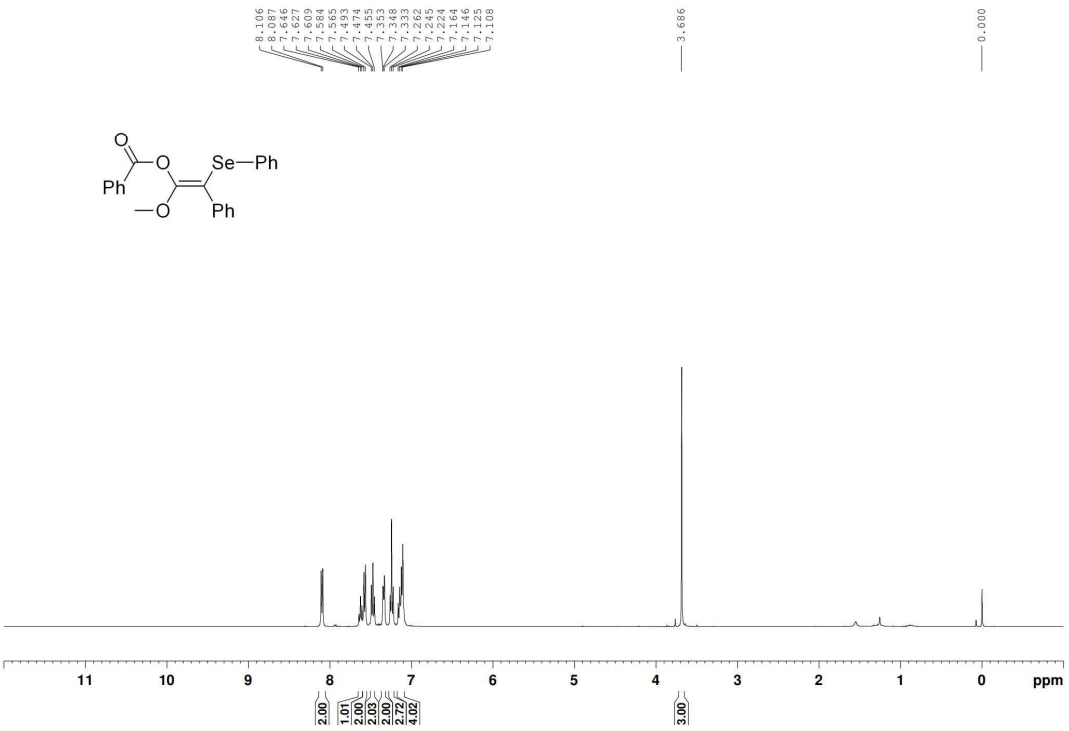
^{1}H NMR spectrum of compound **3xa** $CDCl_3$, 400 MHz)



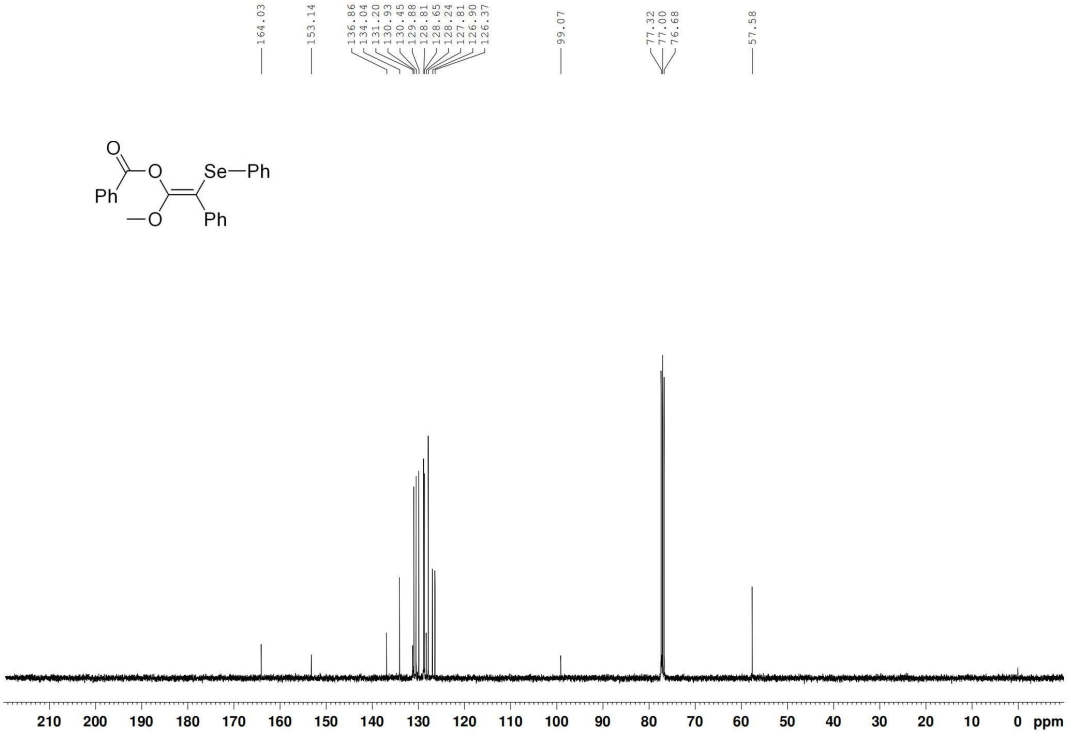
^{13}C NMR spectrum of compound **3xa** ($CDCl_3$, 100 MHz)



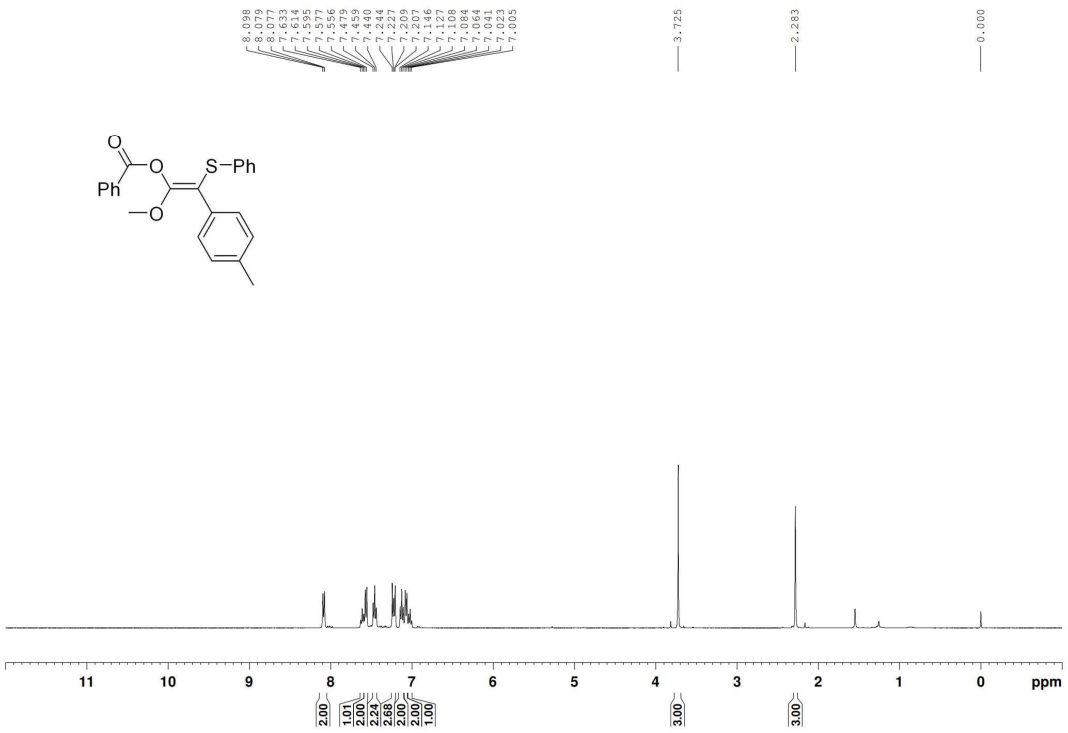
^{1}H NMR spectrum of compound **3ya** ($CDCl_3$, 400 MHz)



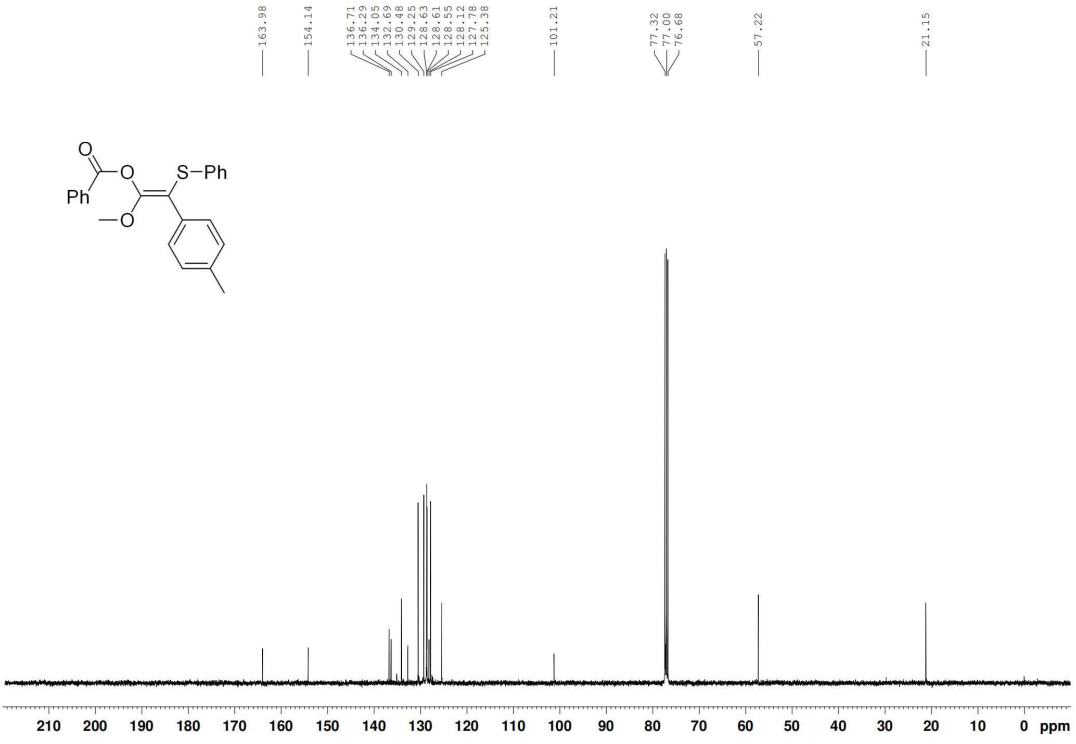
^{13}C NMR spectrum of compound **3ya** ($CDCl_3$, 100 MHz)



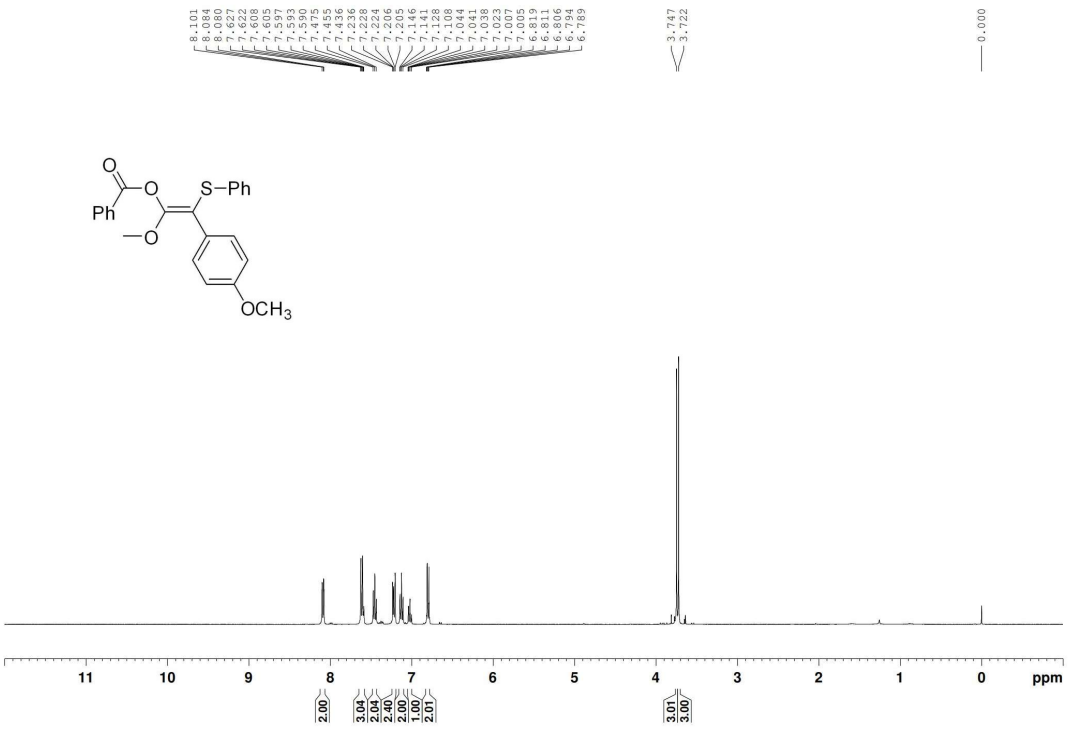
^{1}H NMR spectrum of compound **3ab** ($CDCl_3$, 400 MHz)



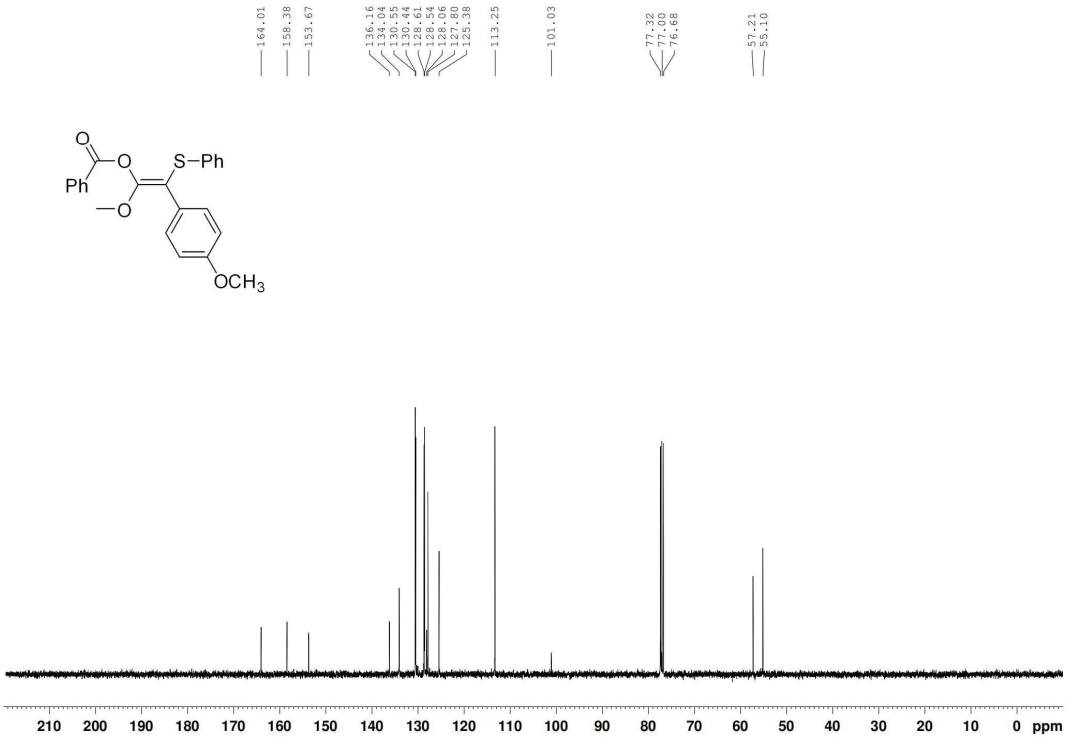
^{13}C NMR spectrum of compound **3ab** ($CDCl_3$, 100 MHz)



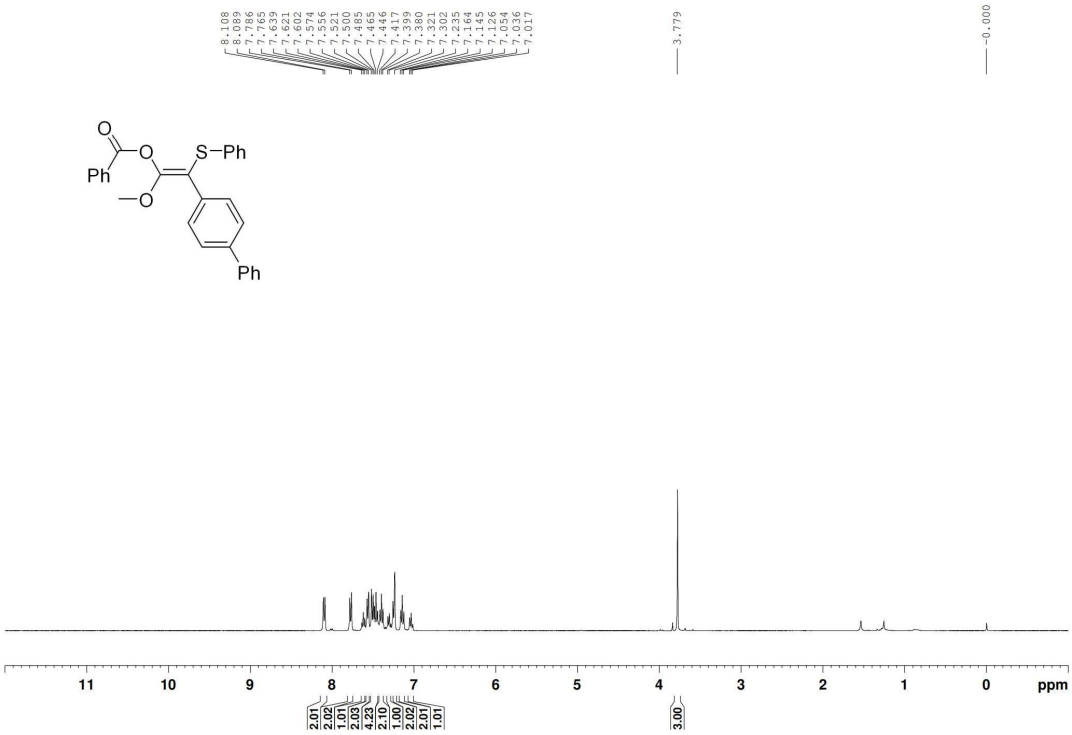
^{1}H NMR spectrum of compound **3ac** ($CDCl_3$, 400 MHz)



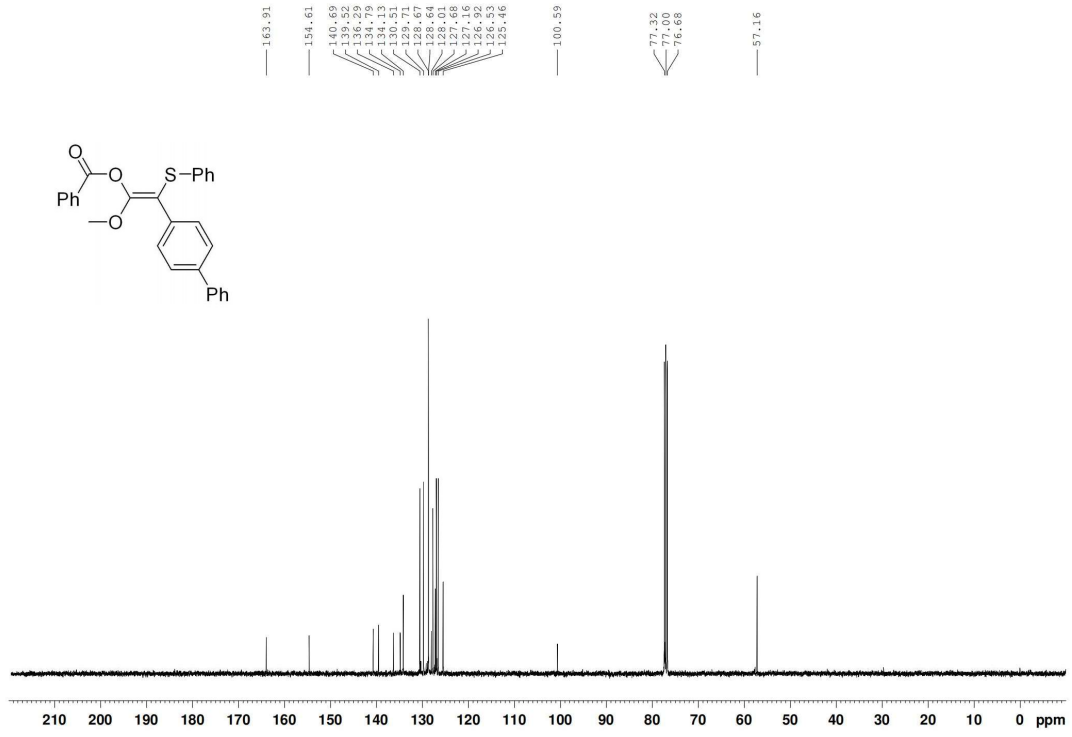
^{13}C NMR spectrum of compound **3ac** ($CDCl_3$, 100 MHz)



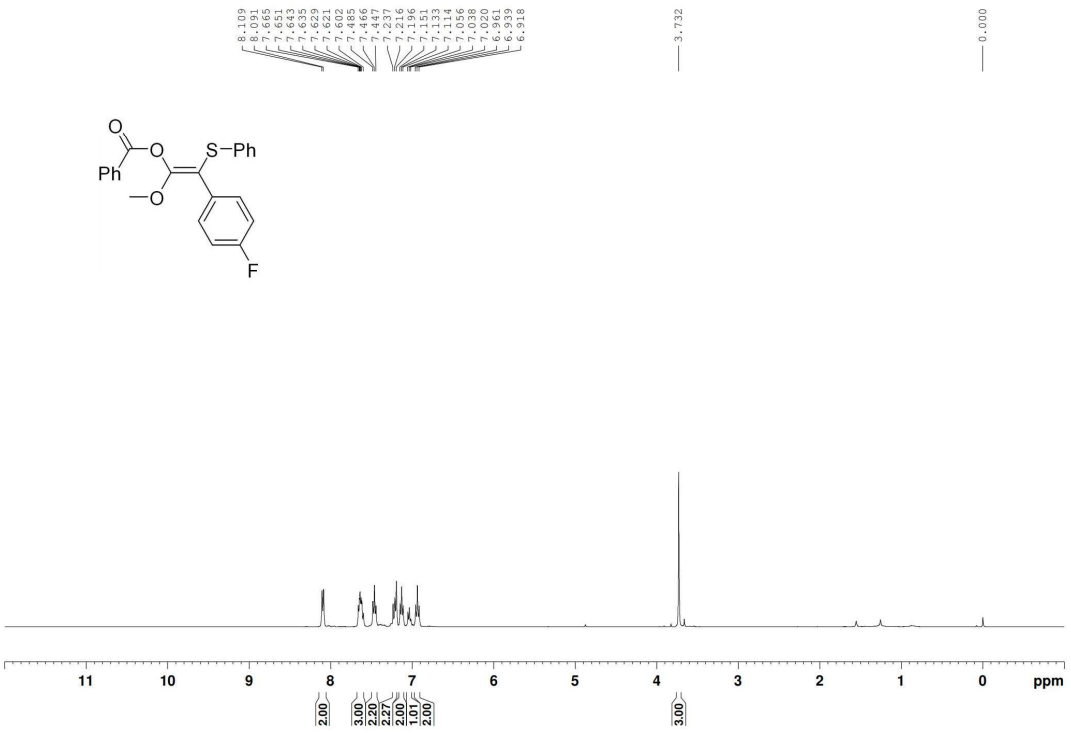
^{1}H NMR spectrum of compound **3ad** ($CDCl_3$, 400 MHz)



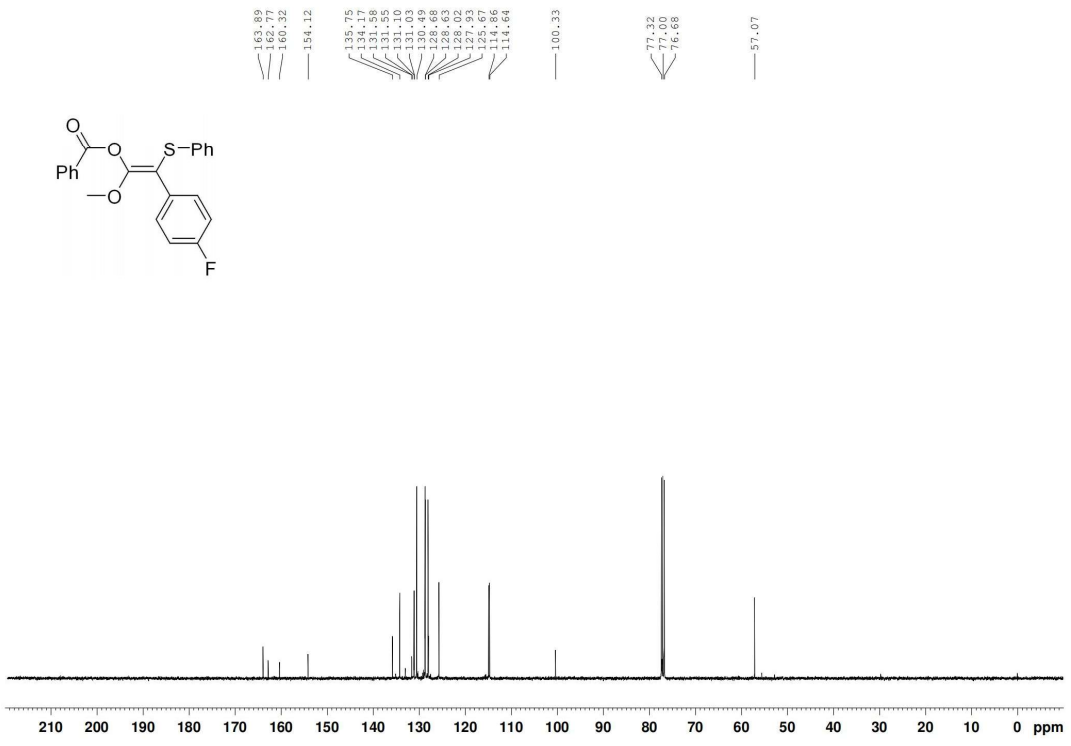
^{13}C NMR spectrum of compound **3ad** ($CDCl_3$, 100 MHz)



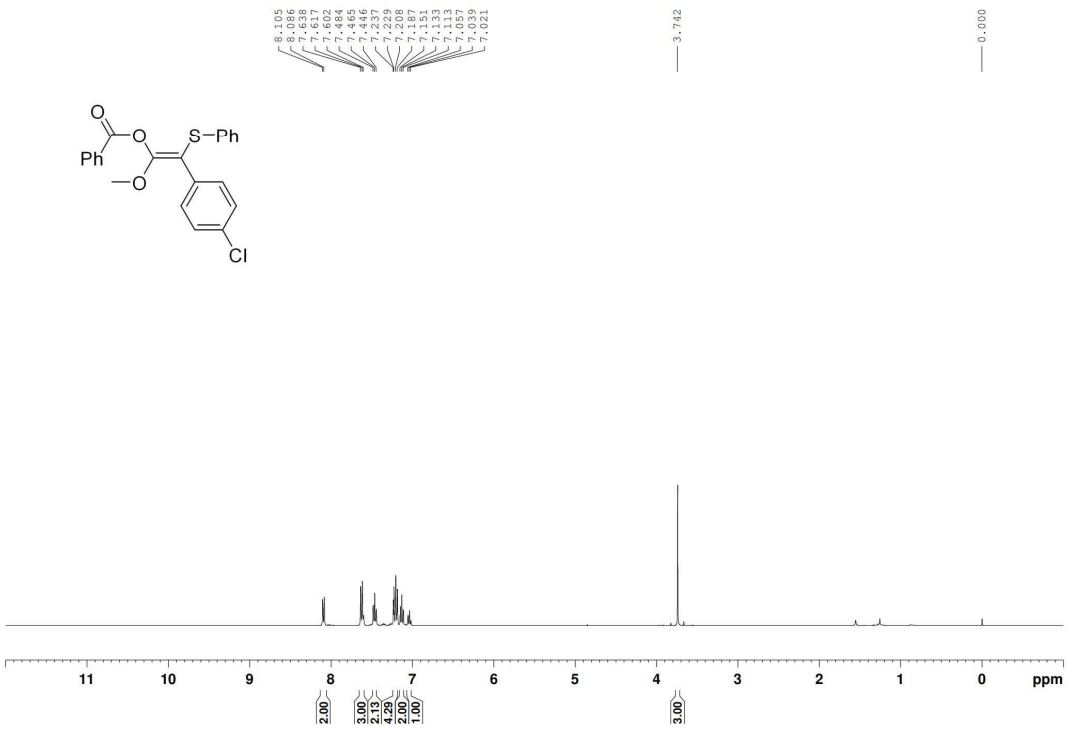
^{1}H NMR spectrum of compound **3ae** ($CDCl_3$, 400 MHz)



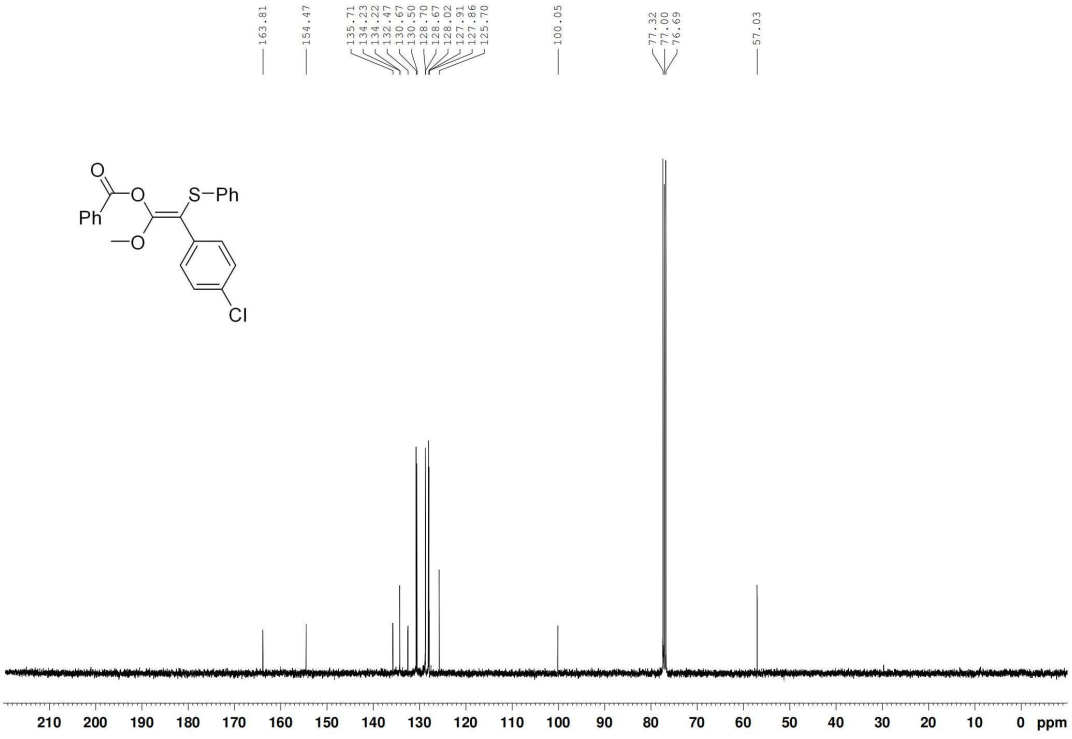
^{13}C NMR spectrum of compound **3ae** ($CDCl_3$, 100 MHz)



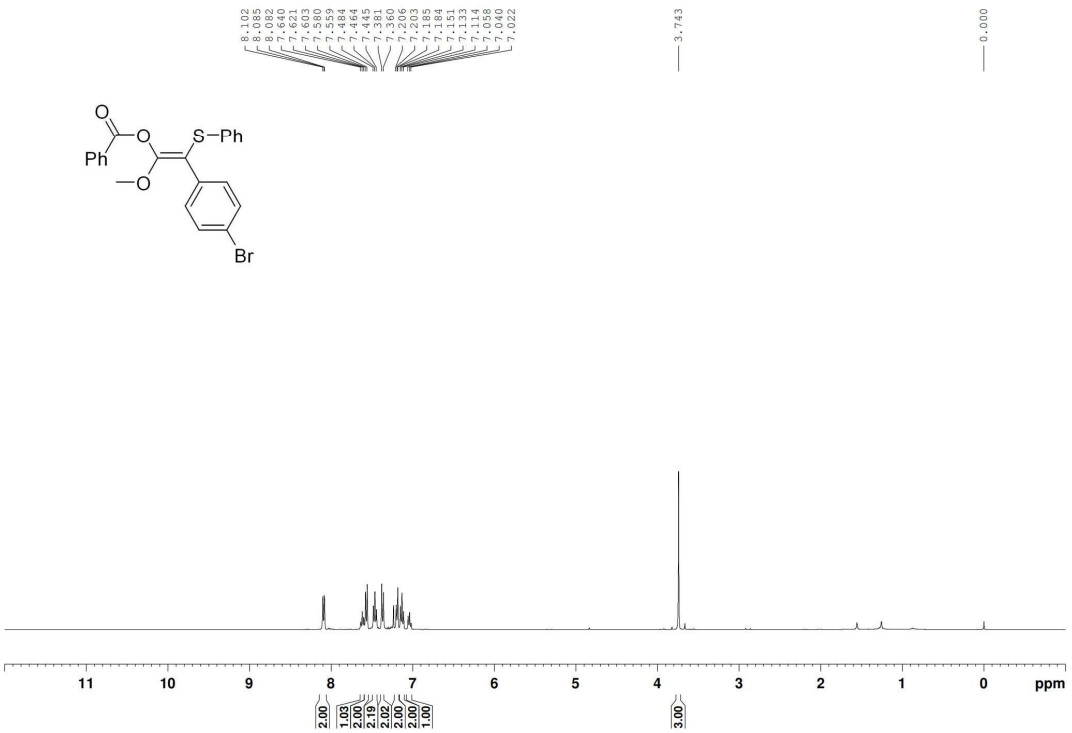
^{1}H NMR spectrum of compound **3af** ($CDCl_3$, 400 MHz)



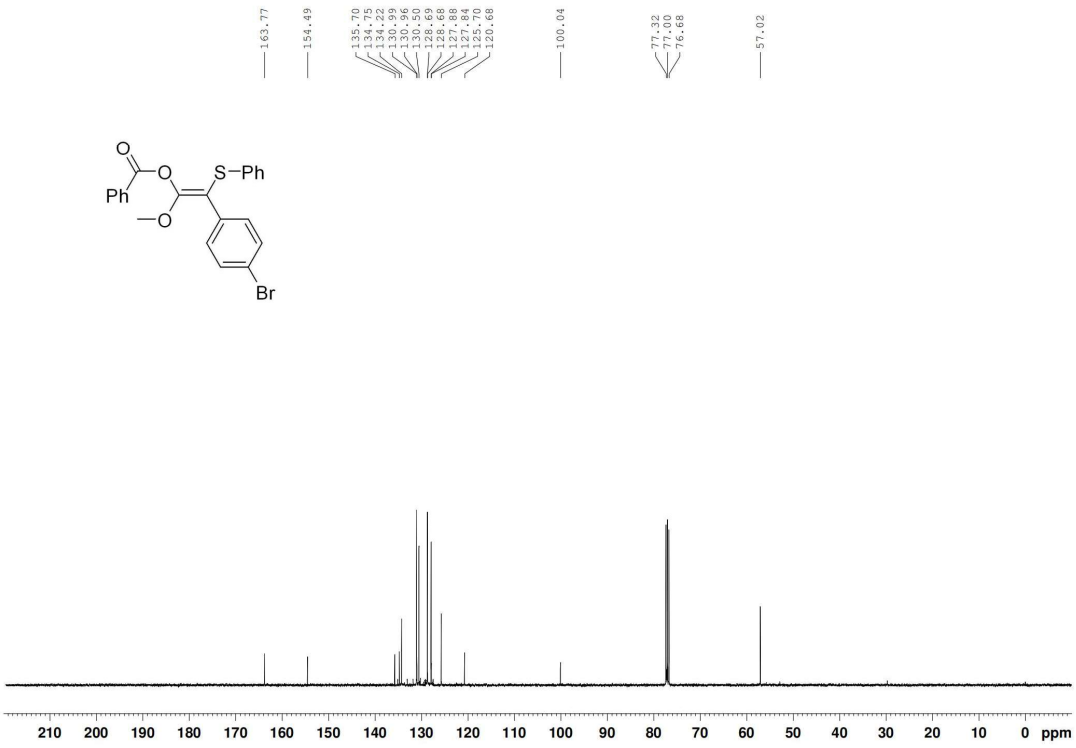
^{13}C NMR spectrum of compound **3af** ($CDCl_3$, 100 MHz)



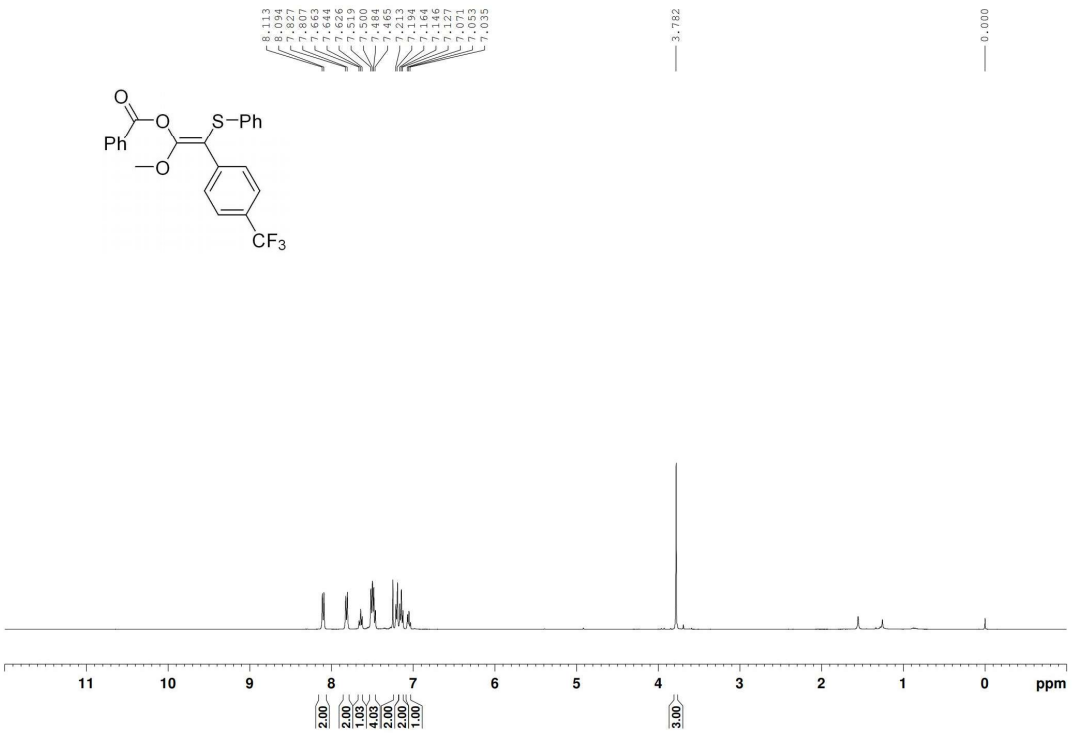
^{1}H NMR spectrum of compound **3ag** ($CDCl_3$, 400 MHz)



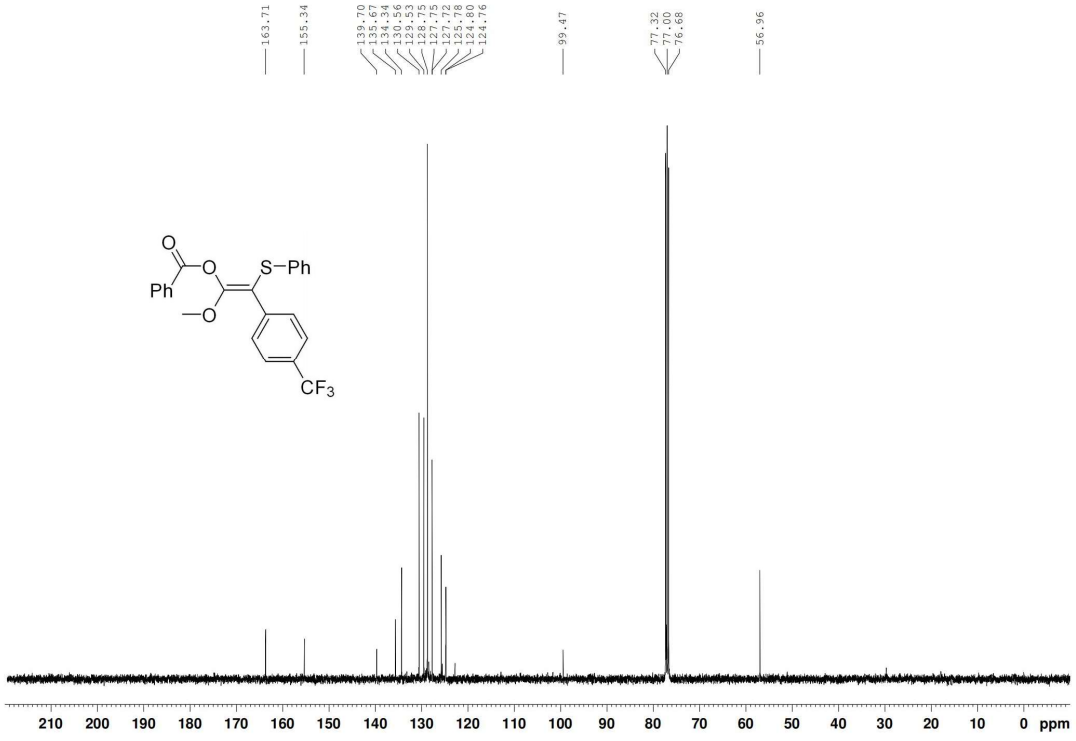
^{13}C NMR spectrum of compound **3ag** ($CDCl_3$, 100 MHz)



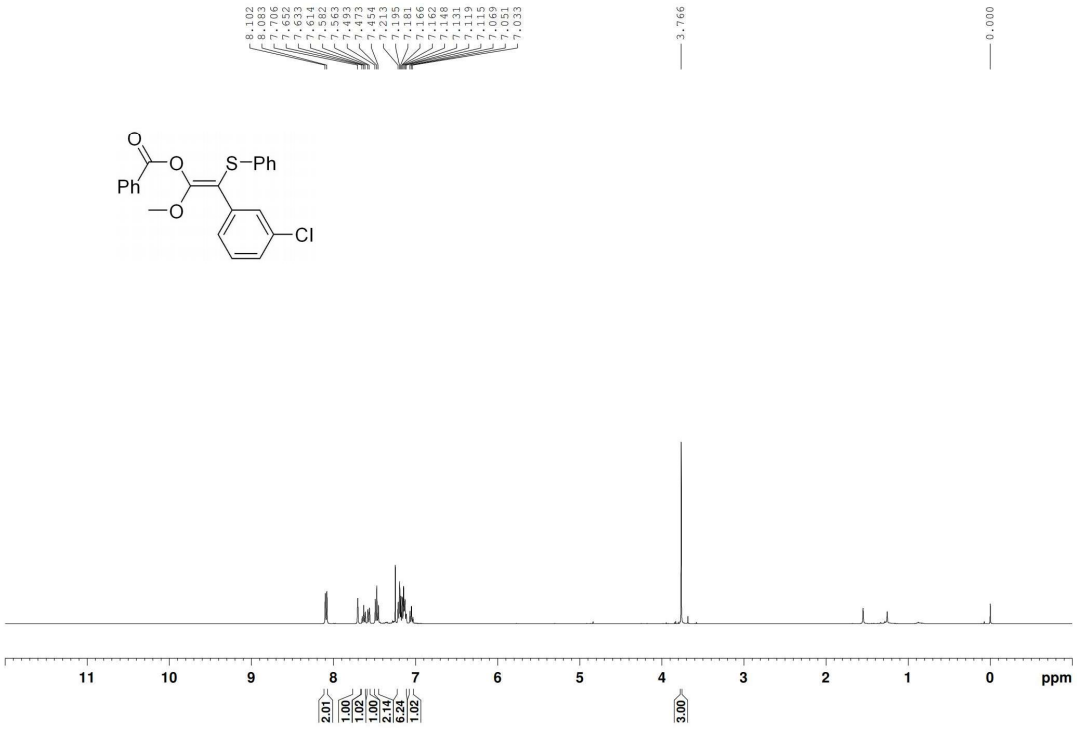
^{1}H NMR spectrum of compound **3ah** ($CDCl_3$, 400 MHz)



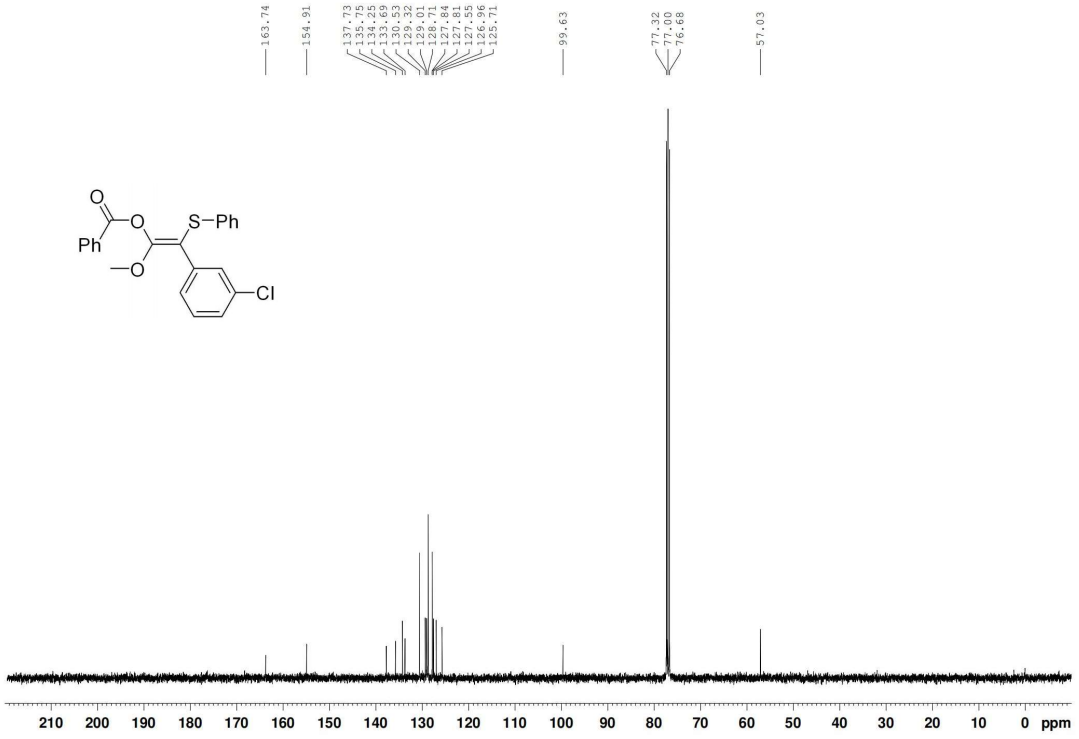
^{13}C NMR spectrum of compound **3ah** ($CDCl_3$, 100 MHz)



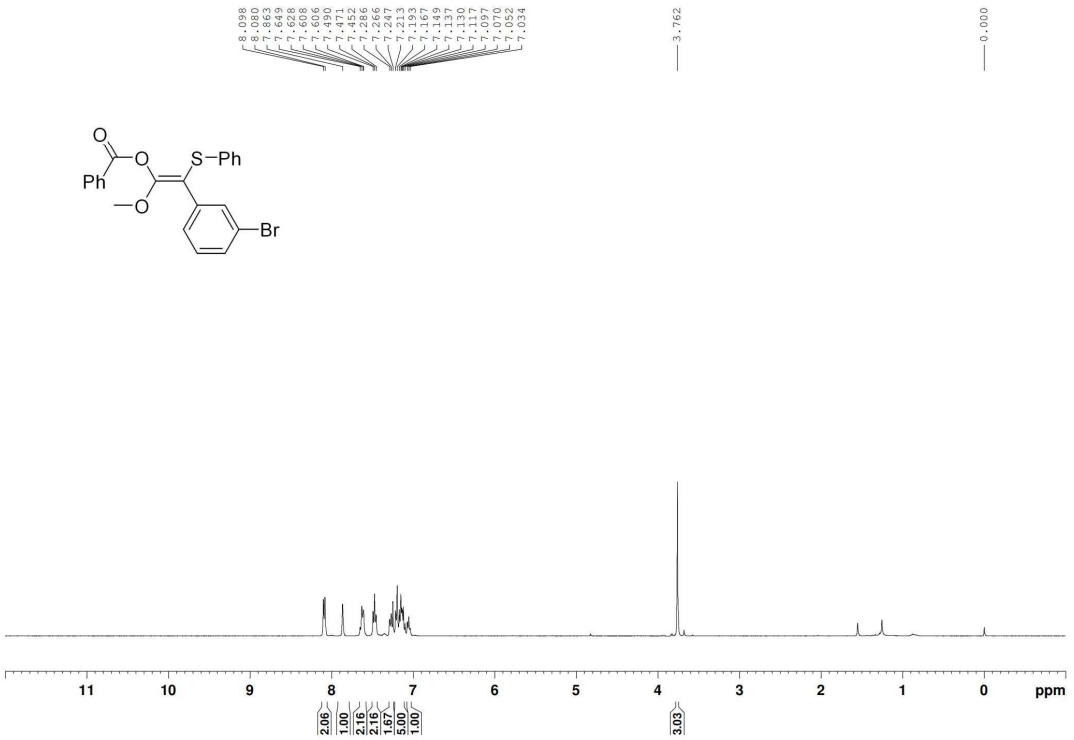
^{1}H NMR spectrum of compound **3ai** ($CDCl_3$, 400 MHz)



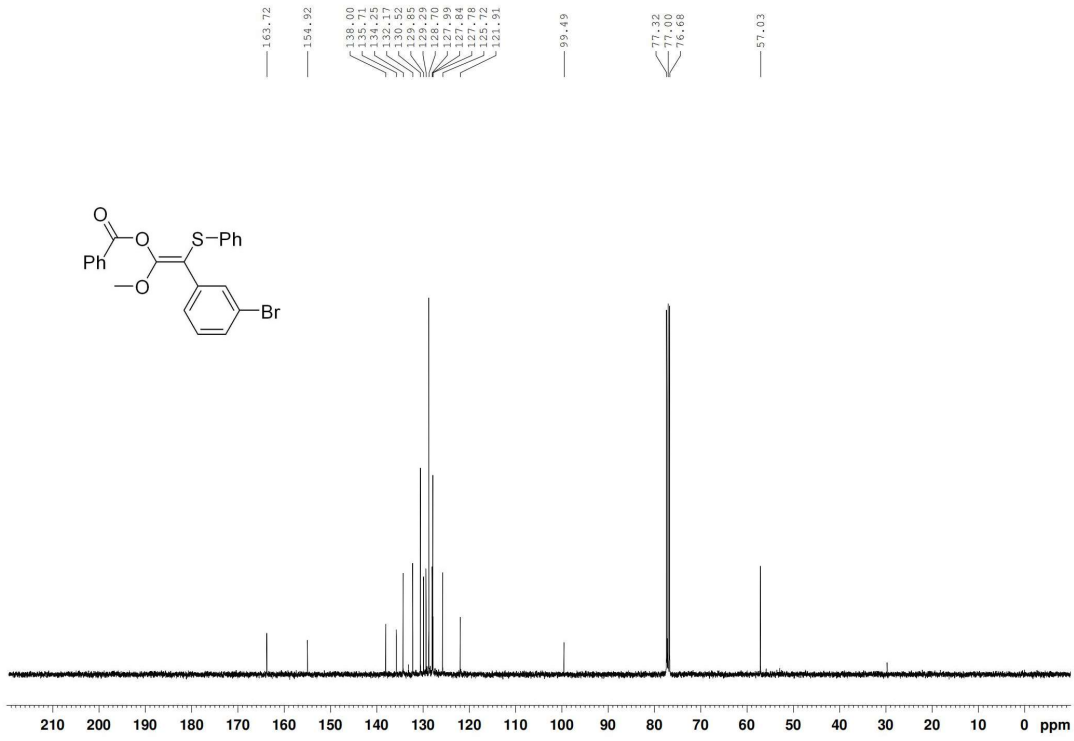
^{13}C NMR spectrum of compound **3ai** ($CDCl_3$, 100 MHz)



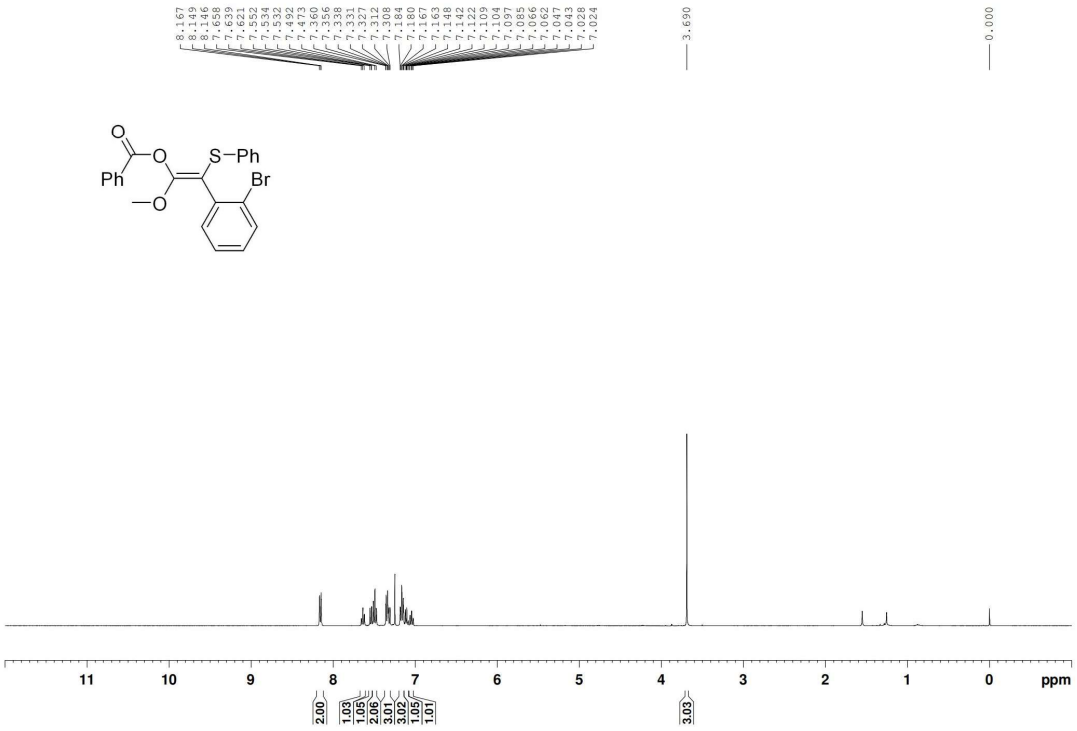
^{1}H NMR spectrum of compound **3aj** ($CDCl_3$, 400 MHz)



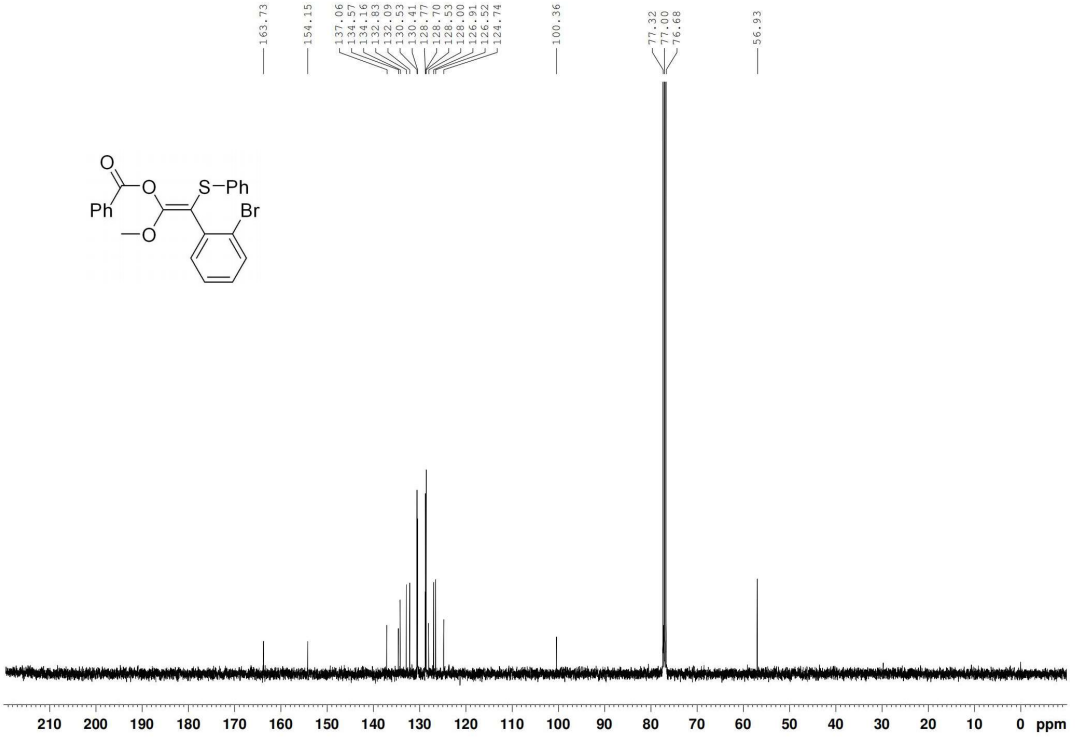
^{13}C NMR spectrum of compound **3aj** ($CDCl_3$, 100 MHz)



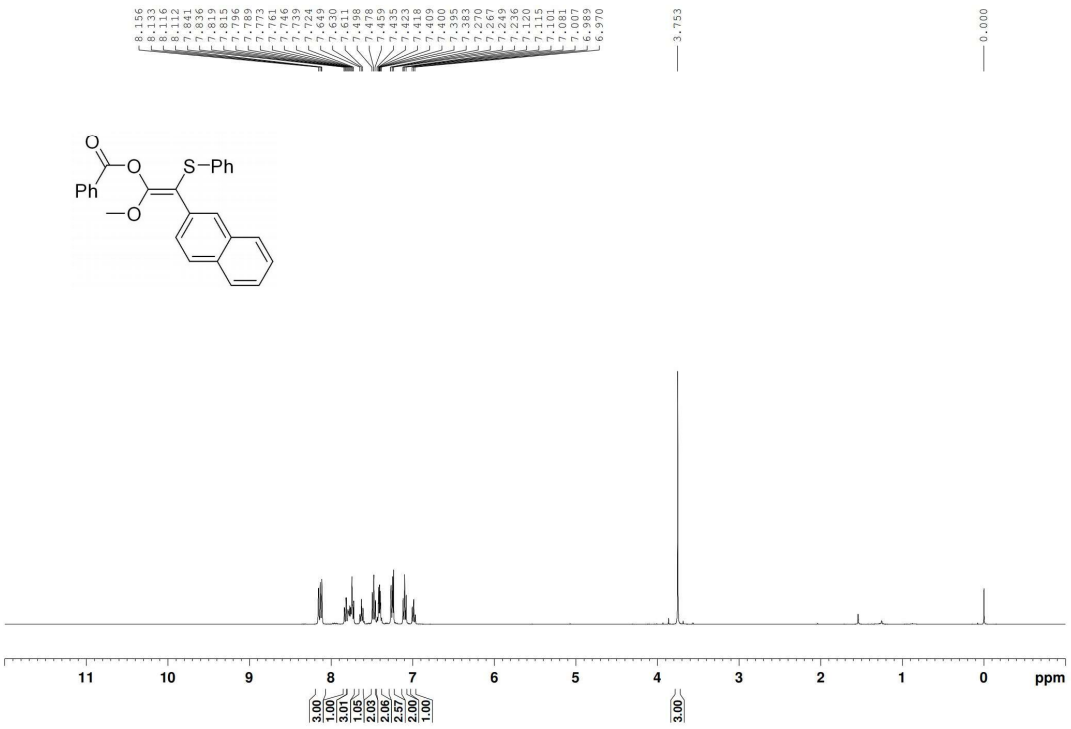
^{1}H NMR spectrum of compound **3ak** ($CDCl_3$, 400 MHz)



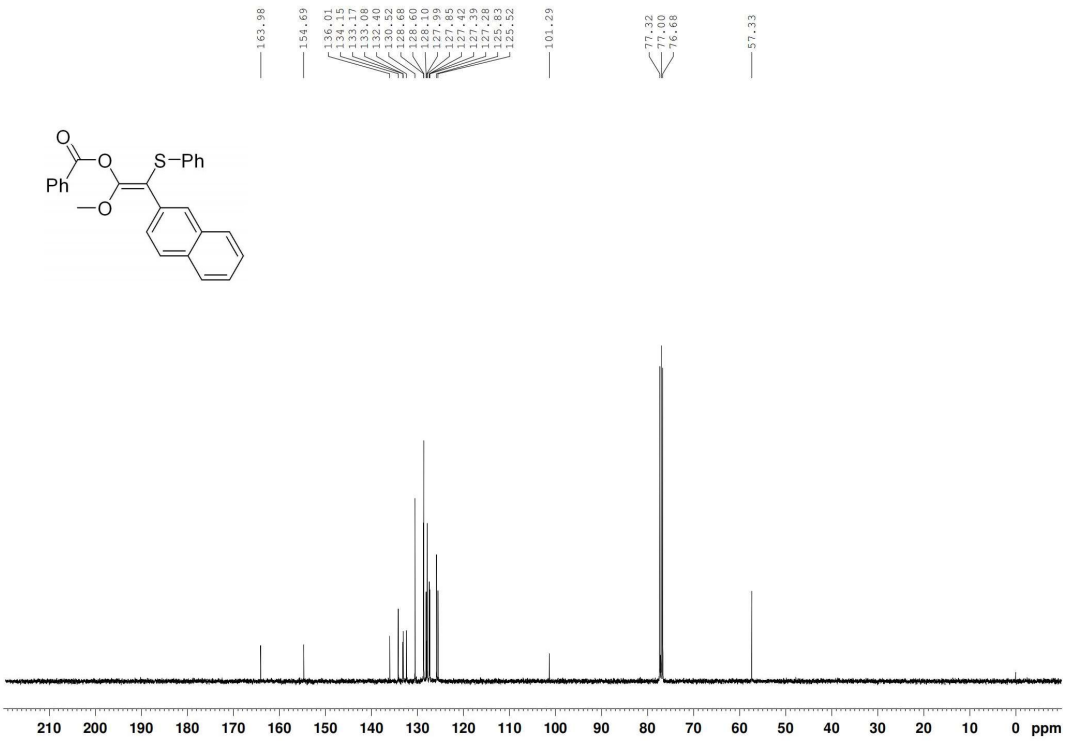
^{13}C NMR spectrum of compound **3ak** ($CDCl_3$, 100 MHz)



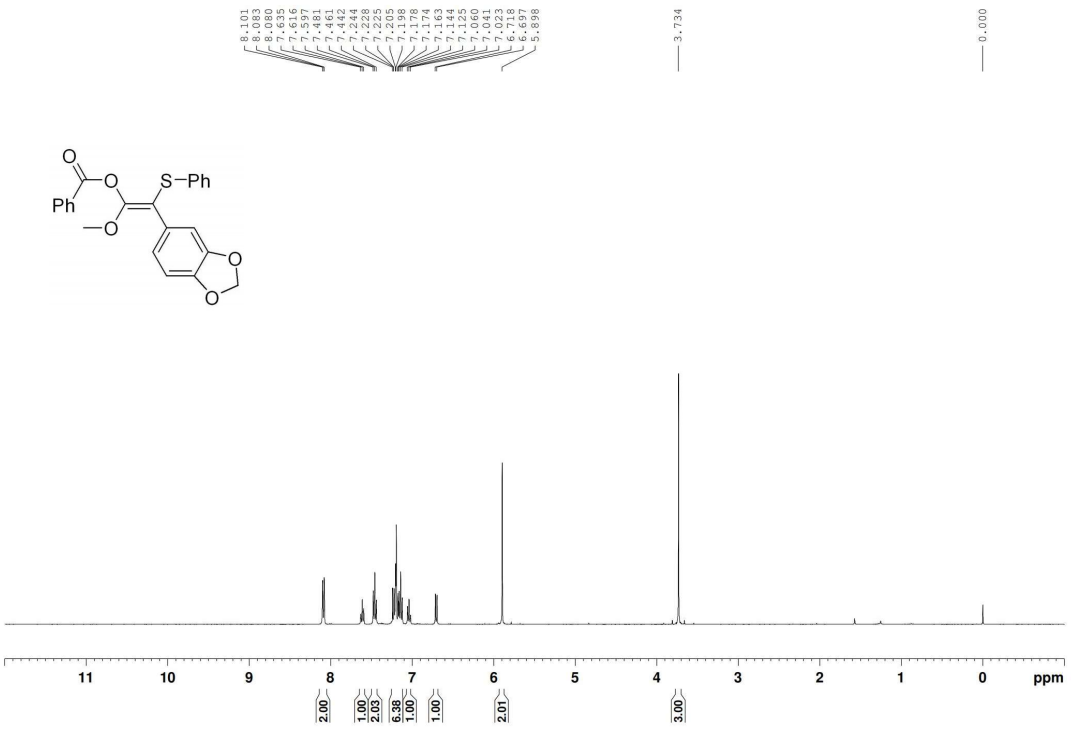
^{1}H NMR spectrum of compound **3al** ($CDCl_3$, 400 MHz)



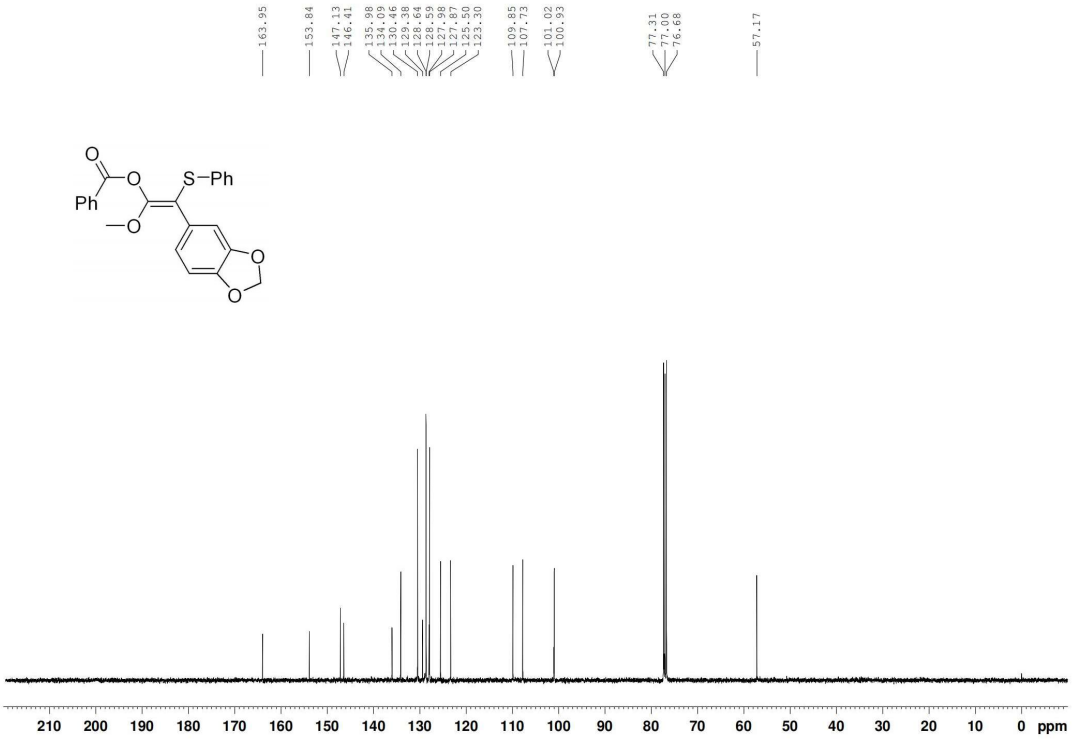
^{13}C NMR spectrum of compound **3al** ($CDCl_3$, 100 MHz)



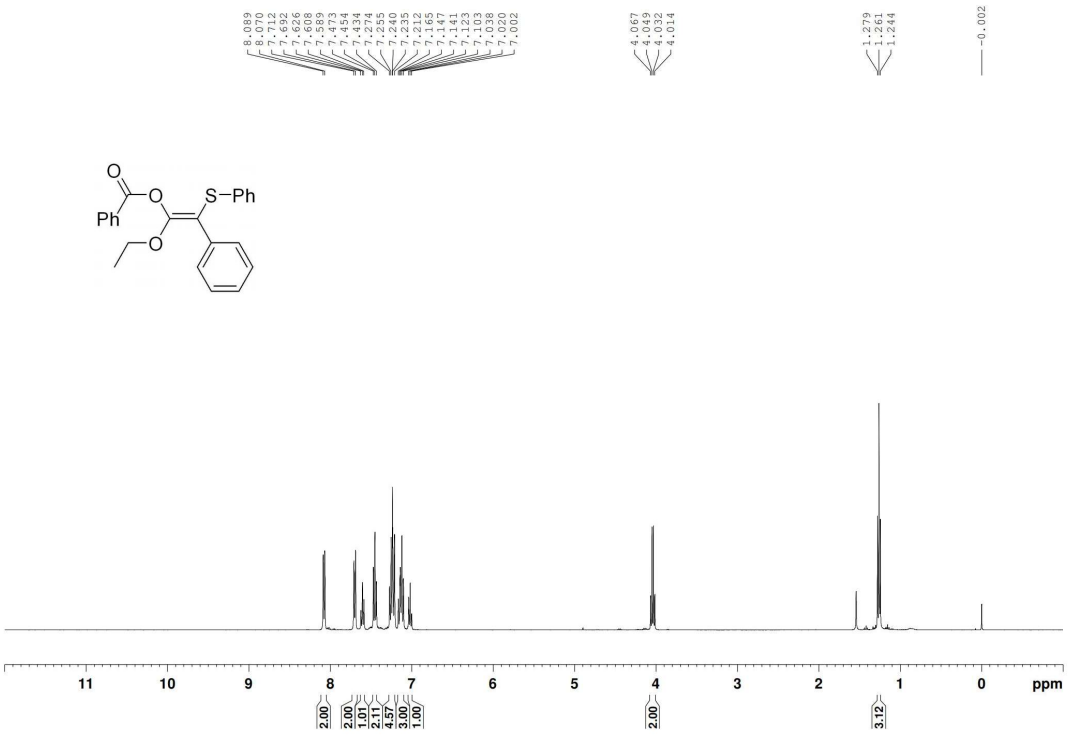
^{1}H NMR spectrum of compound **3am** ($CDCl_3$, 400 MHz)



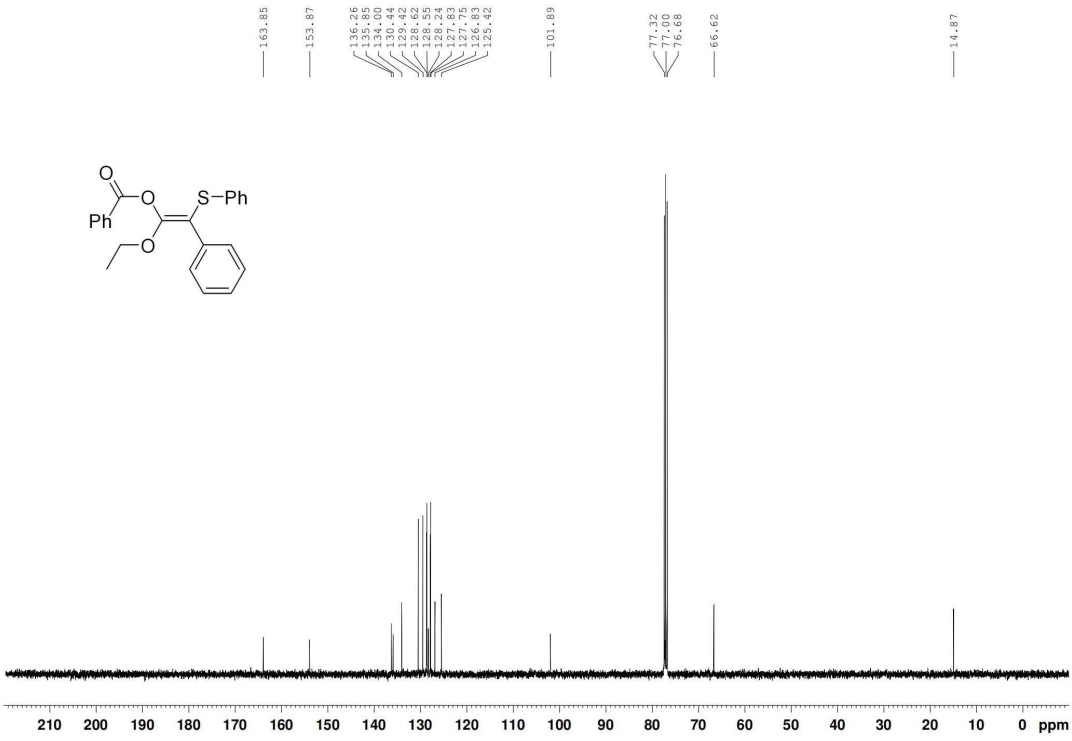
^{13}C NMR spectrum of compound **3am** ($CDCl_3$, 100 MHz)



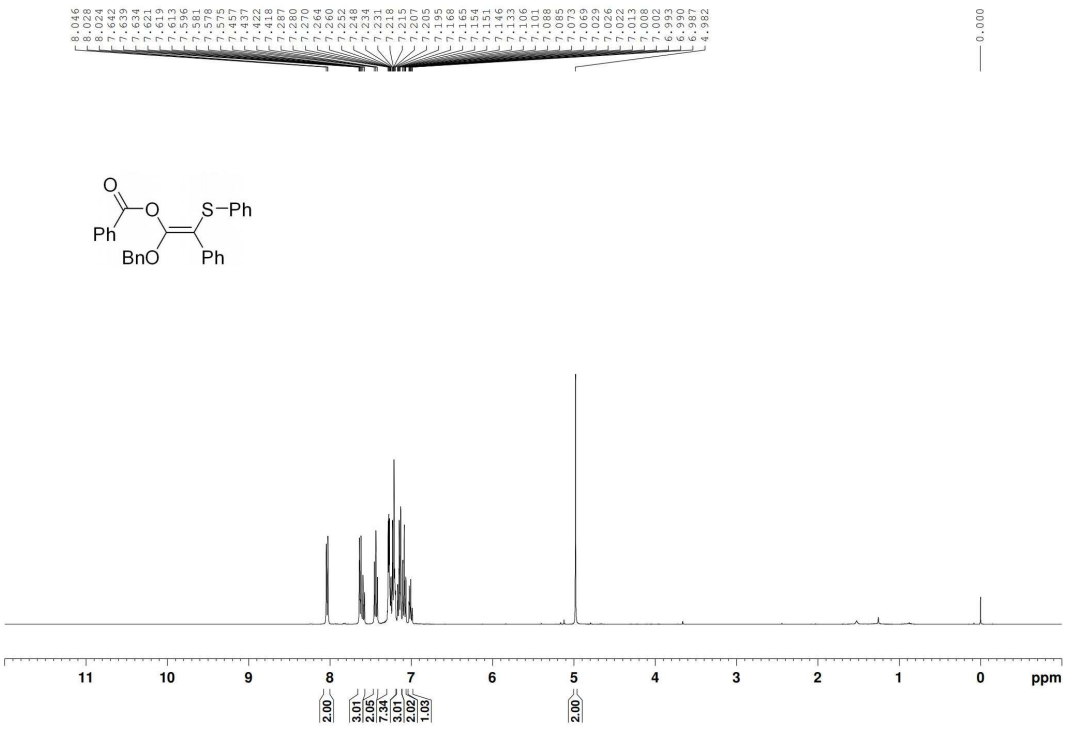
^{1}H NMR spectrum of compound **3an** ($CDCl_3$, 400 MHz)



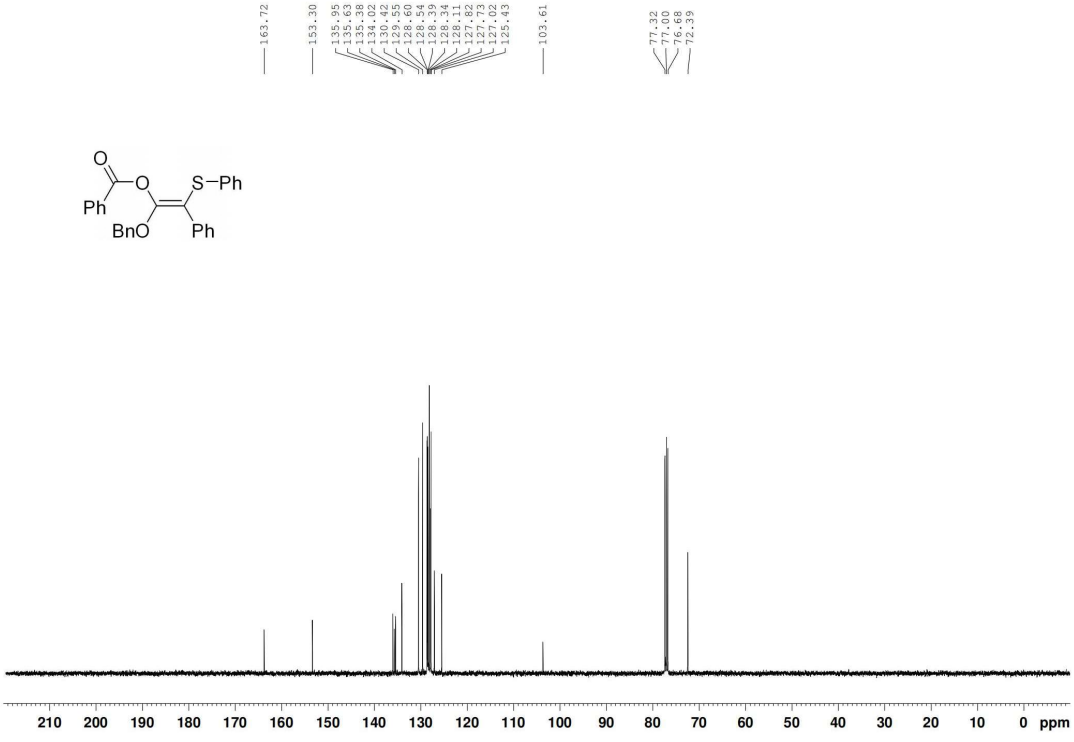
^{13}C NMR spectrum of compound **3an** ($CDCl_3$, 100 MHz)



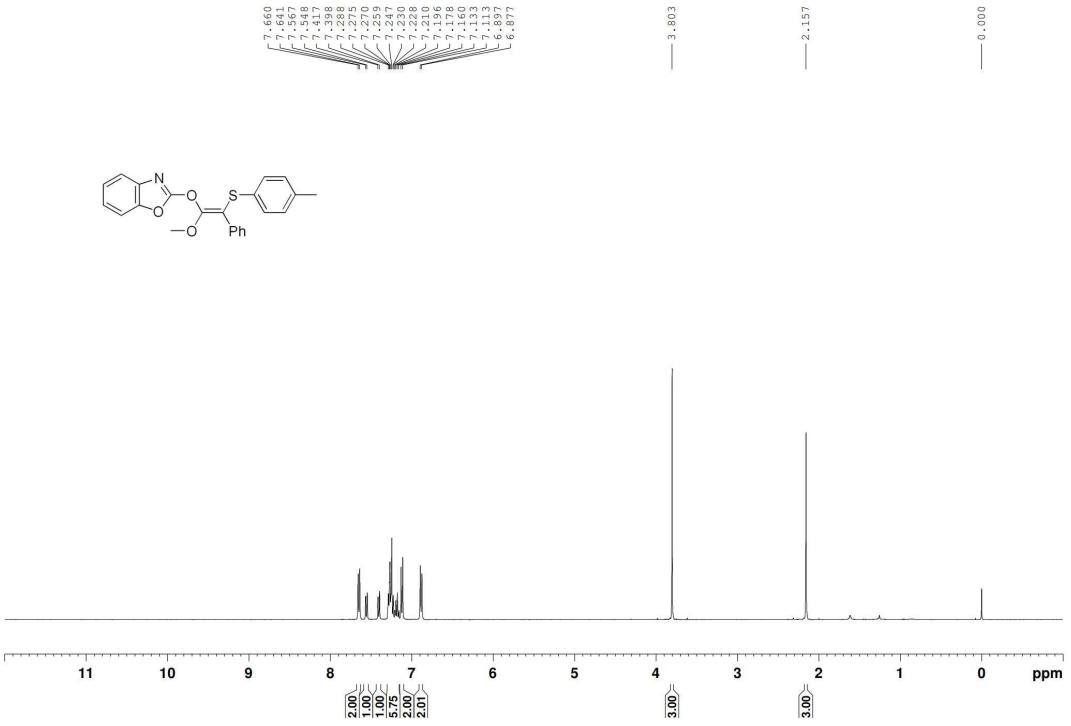
^{1}H NMR spectrum of compound **3ao** ($CDCl_3$, 400 MHz)



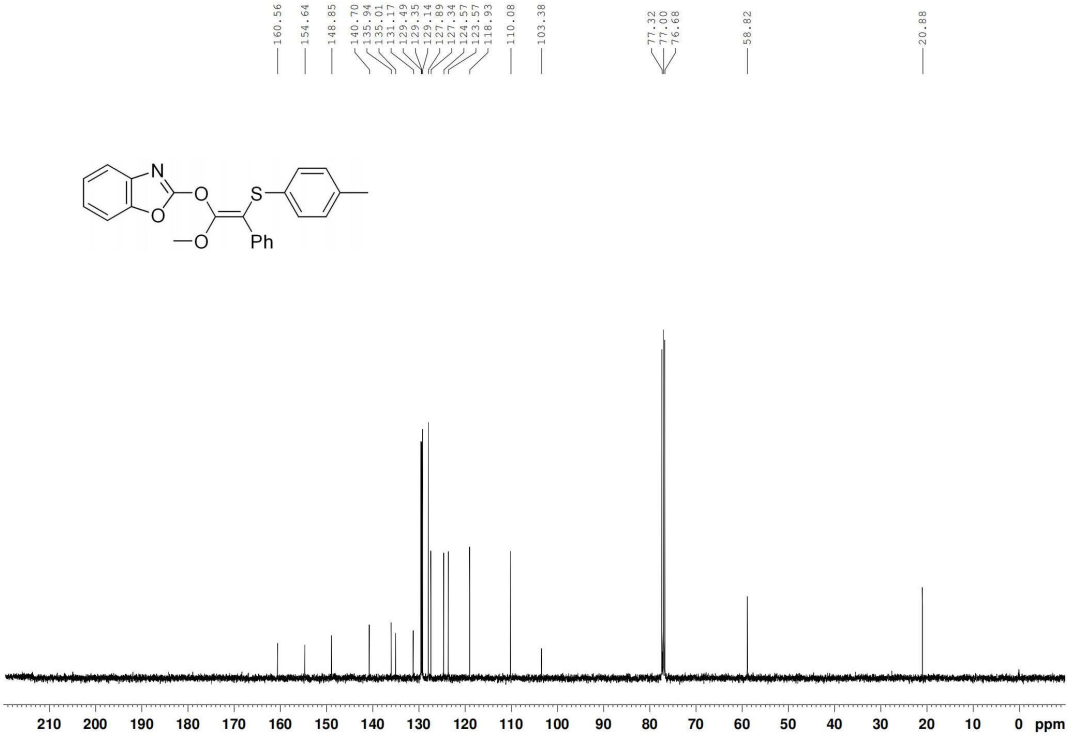
^{13}C NMR spectrum of compound **3ao** ($CDCl_3$, 100 MHz)



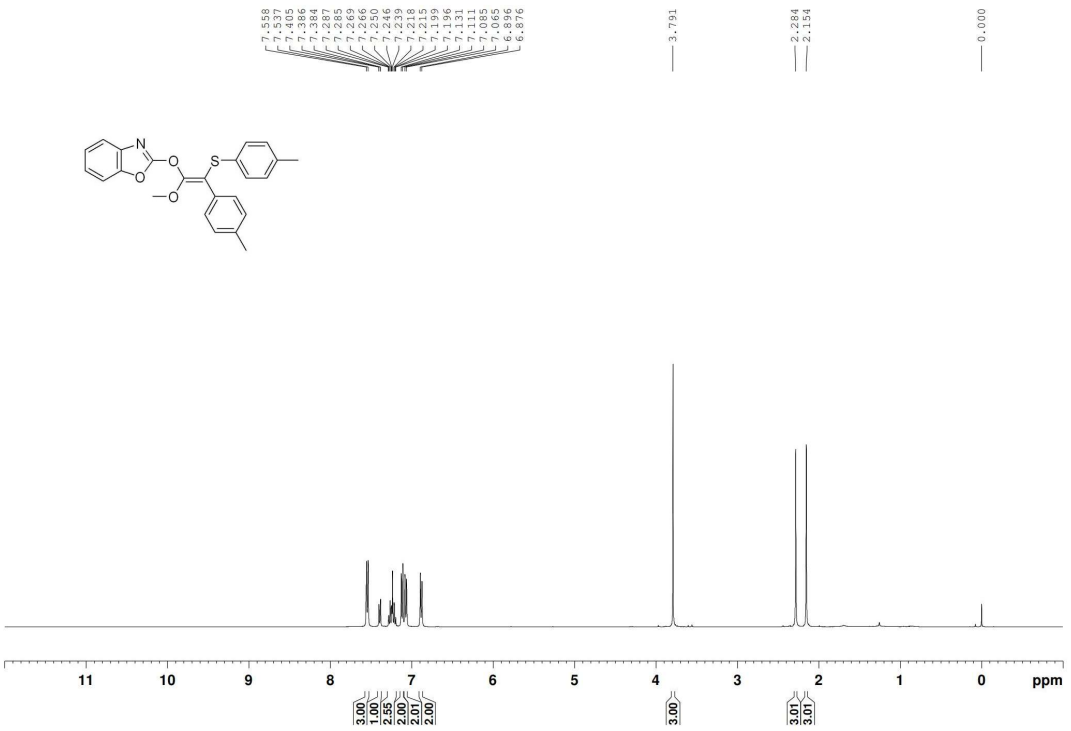
^{1}H NMR spectrum of compound **3za** ($CDCl_3$, 400 MHz)



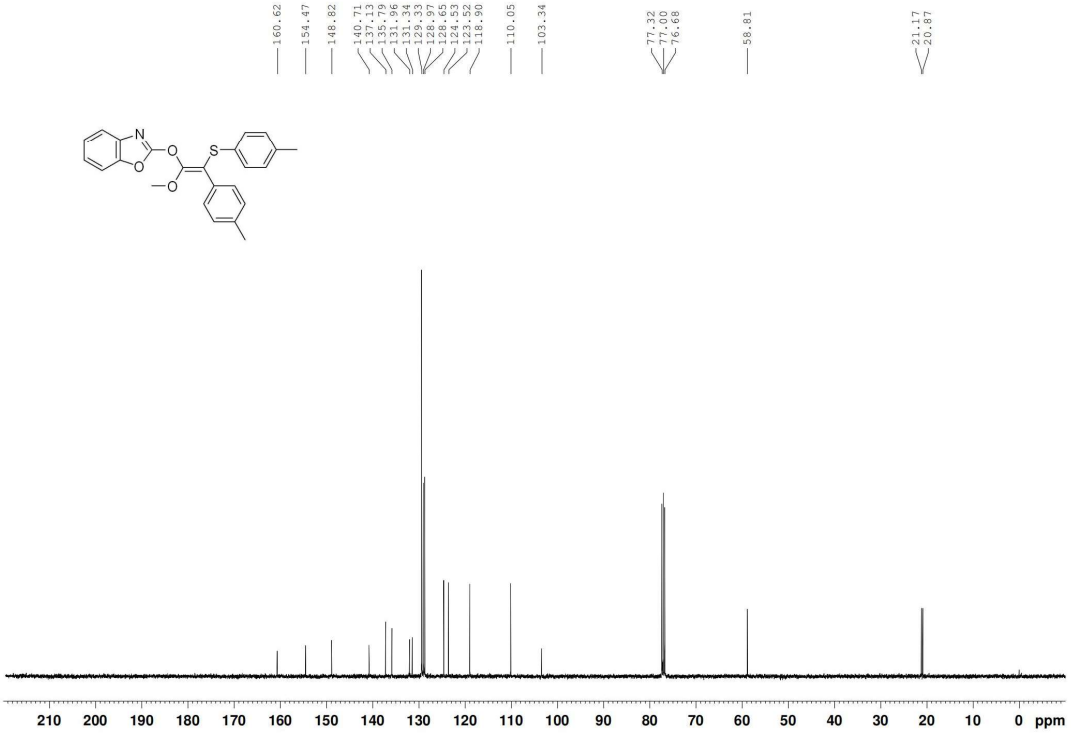
^{13}C NMR spectrum of compound **3za** ($CDCl_3$, 100 MHz)



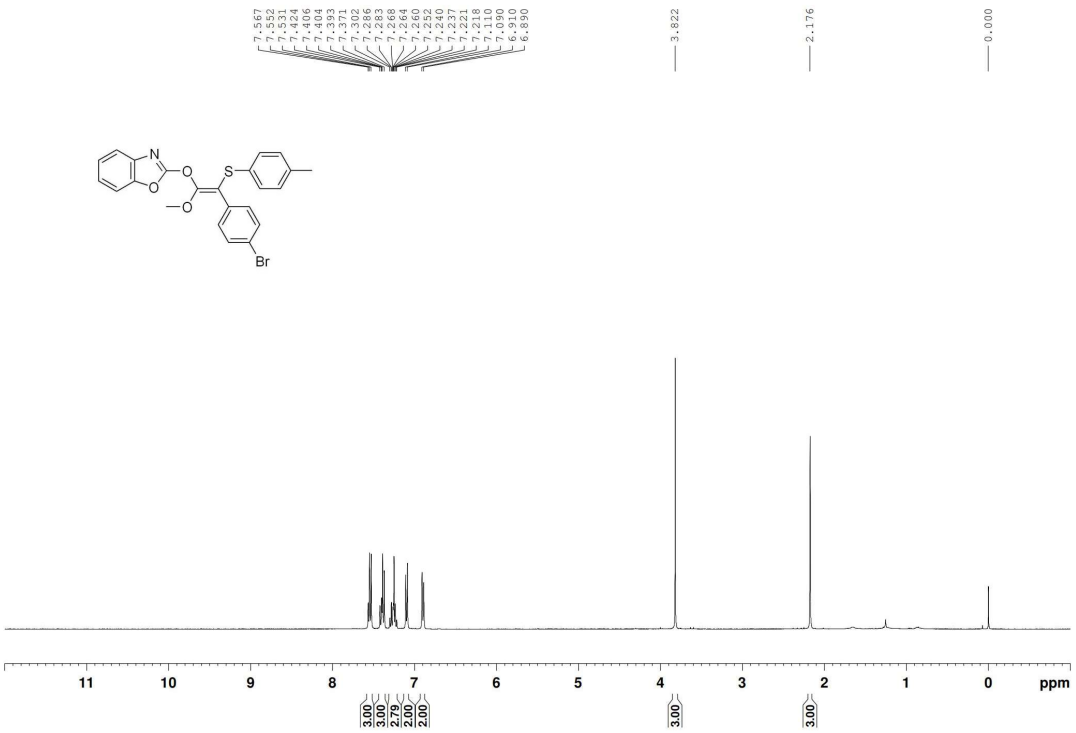
^{1}H NMR spectrum of compound **3zb** ($CDCl_3$, 400 MHz)



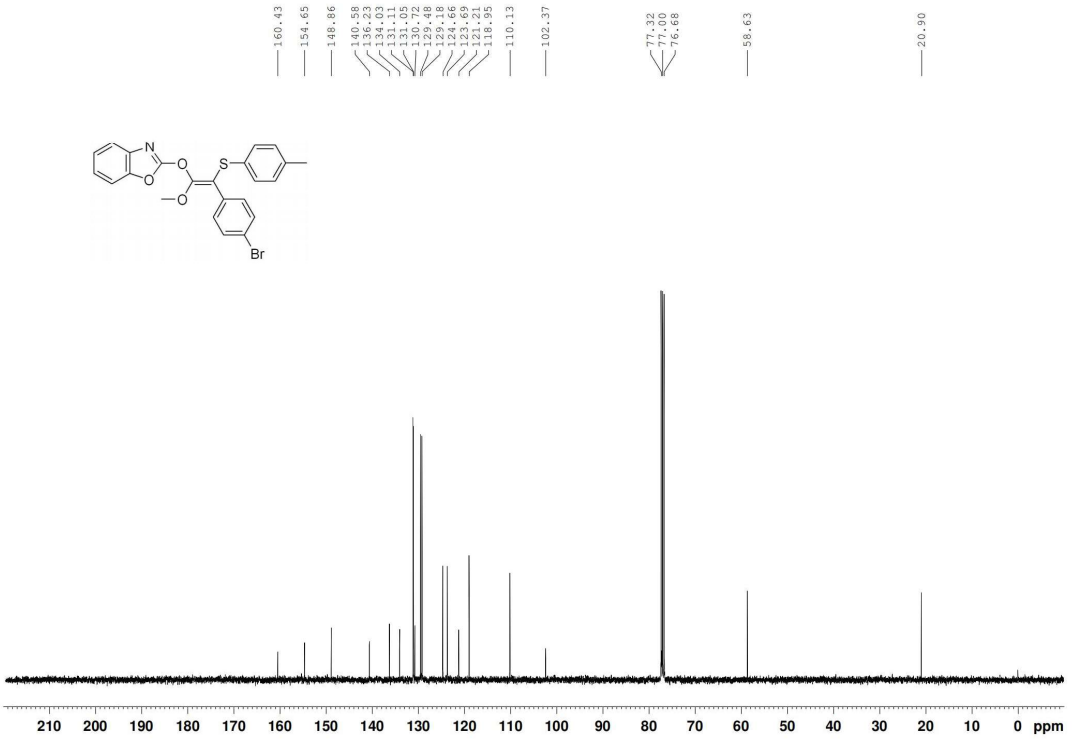
^{13}C NMR spectrum of compound **3zb** ($CDCl_3$, 100 MHz)



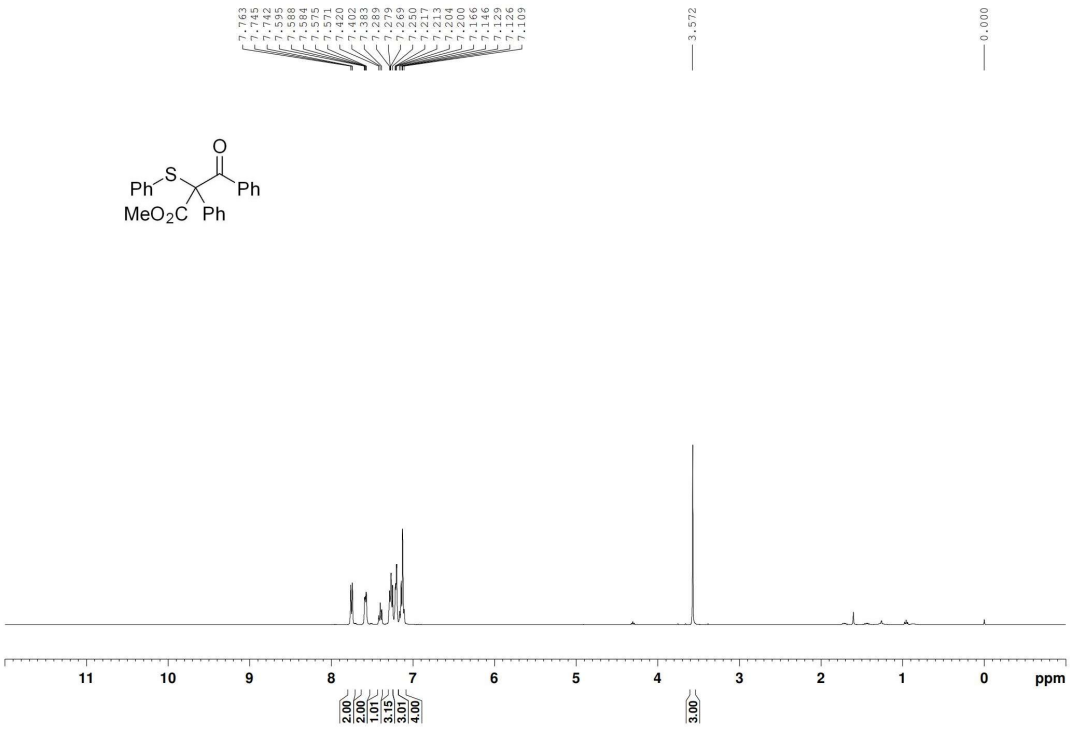
^{1}H NMR spectrum of compound **3zg** ($CDCl_3$, 400 MHz)



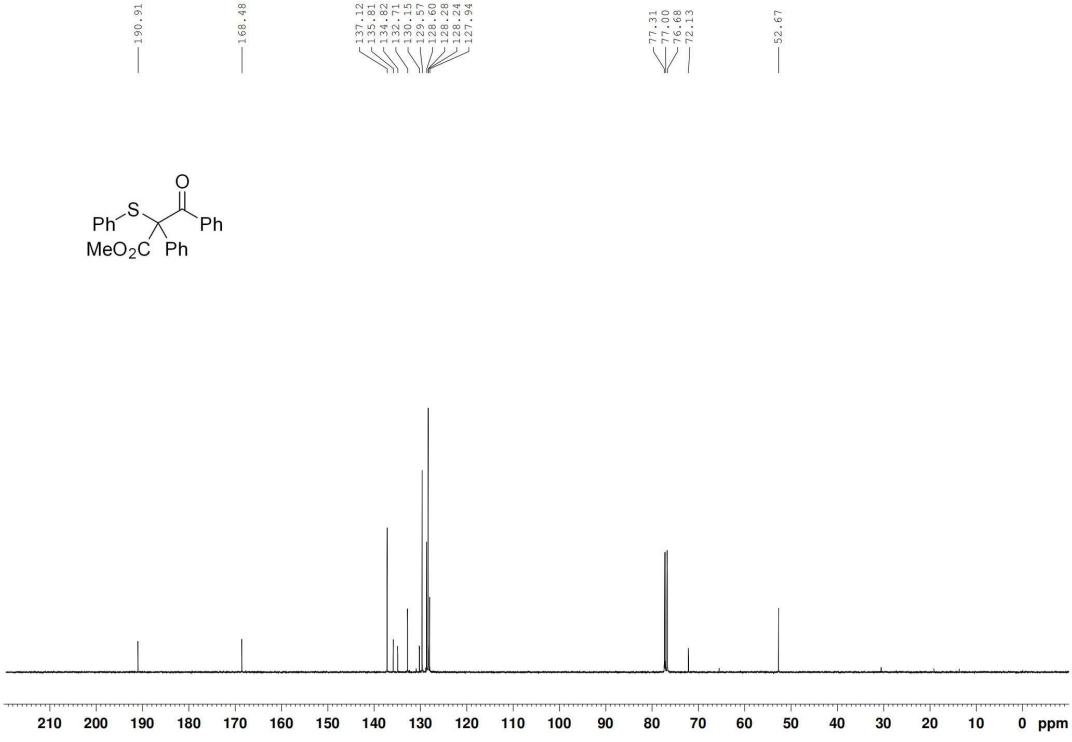
^{13}C NMR spectrum of compound **3zg** ($CDCl_3$, 100 MHz)



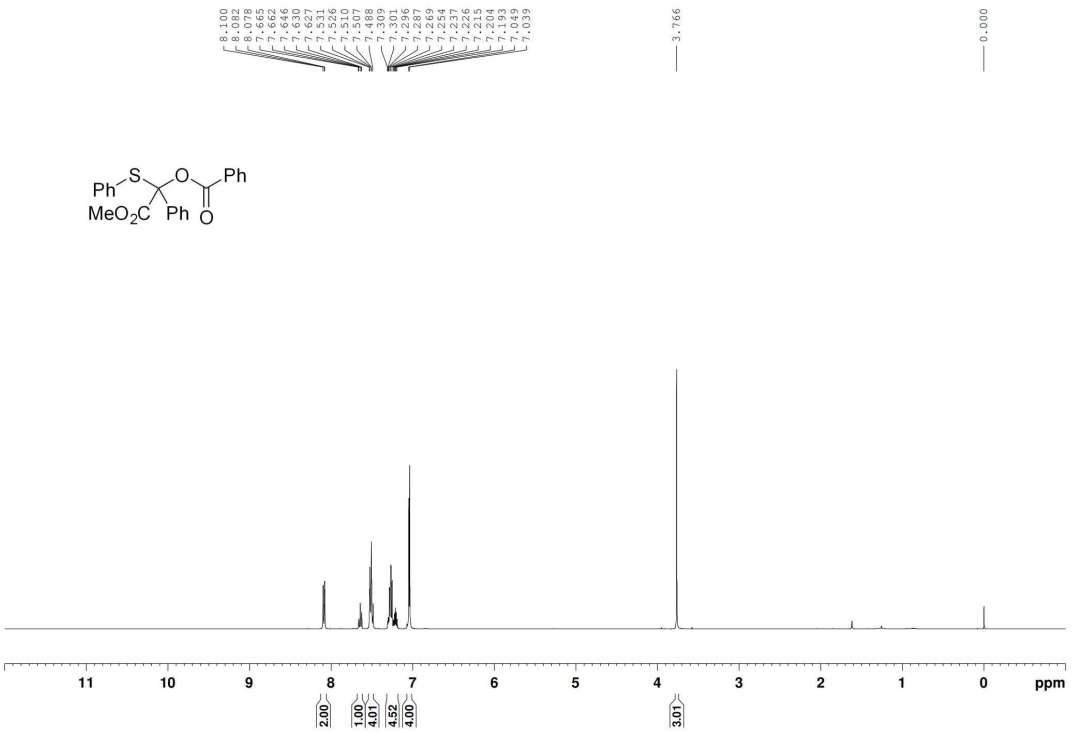
^{1}H NMR spectrum of compound **4** ($CDCl_3$, 400 MHz)



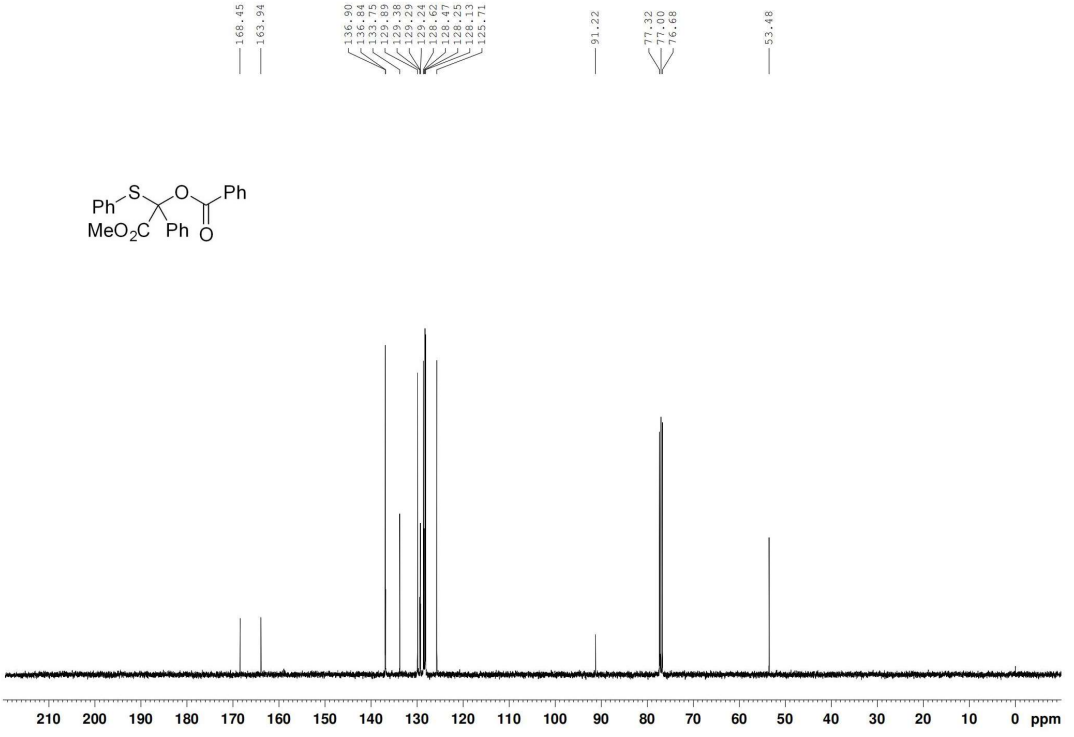
^{13}C NMR spectrum of compound **4** ($CDCl_3$, 100 MHz)



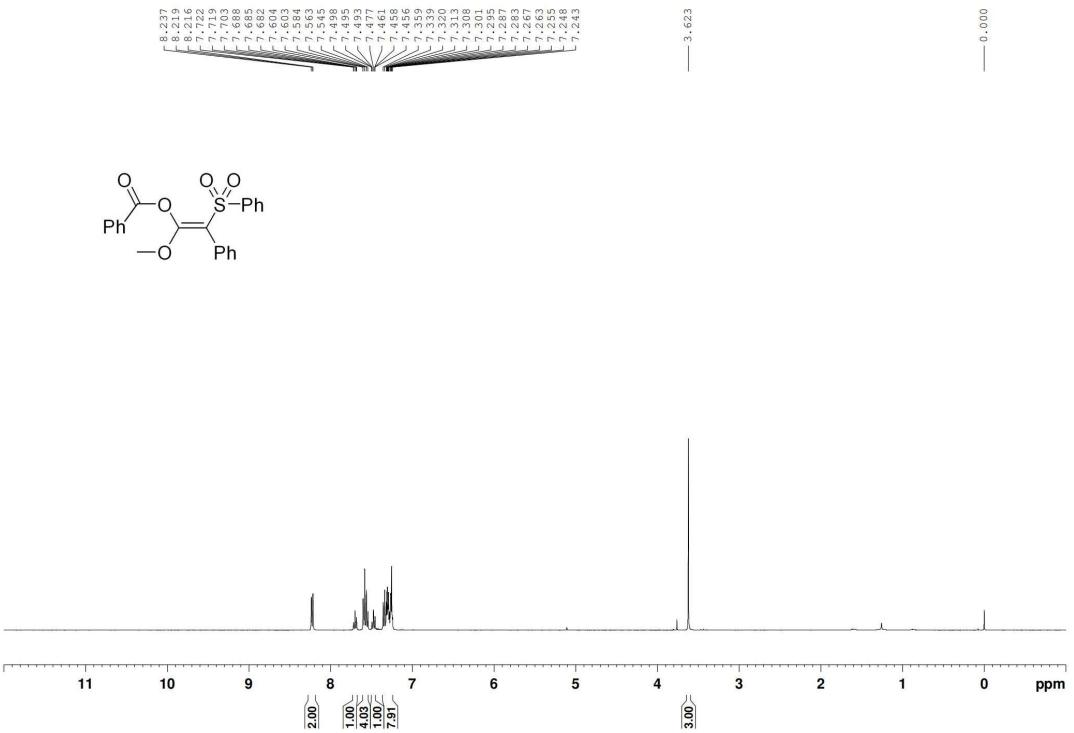
^{1}H NMR spectrum of compound **5** ($CDCl_3$, 400 MHz)



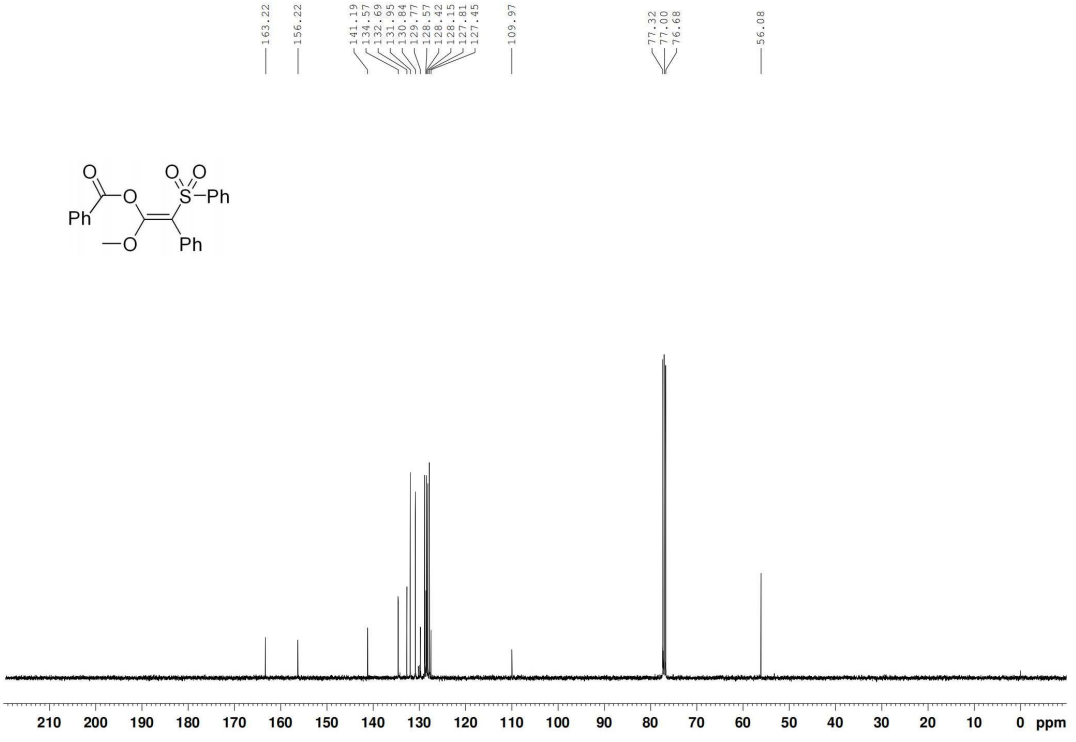
^{13}C NMR spectrum of compound **5** ($CDCl_3$, 100 MHz)



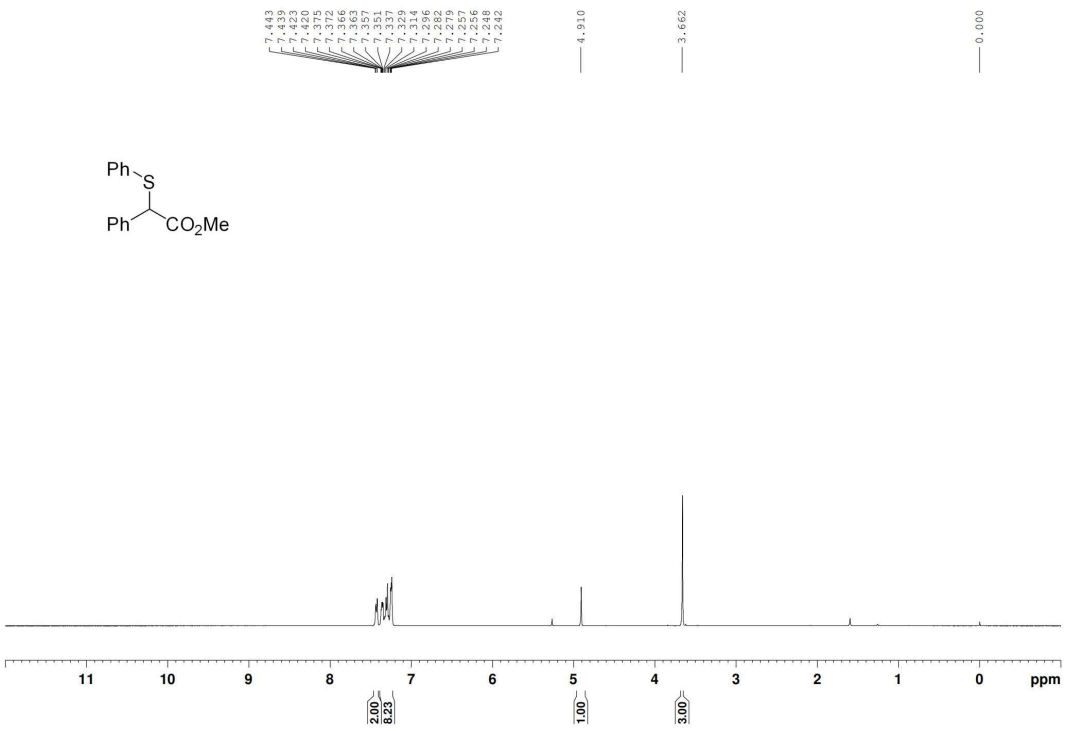
^{1}H NMR spectrum of compound **6** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of compound **6** ($CDCl_3$, 100 MHz)



^{1}H NMR spectrum of compound **7** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of compound **7** ($CDCl_3$, 100 MHz)