Supporting Information

Chemoselective Transition-Metal-Free Acylation of Thioamides by N–C(S) Bond Cleavage using Acyclic Twisted Thioamides

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1.General Information

Commercially available chemicals were purchased from commercial suppliers and used as received without further purification. All reactions were performed in oven-dried or flame-dried glassware. TLC analysis was carried out on glass plates coated with silica gel 60 F254. The plates were visualized using a 254 nm ultraviolet lamp. Purification was performed by chromatography using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Ascend spectrometers at 400 or 600 MHz (^{1}H NMR), 100 MHz or 150 MHz (^{13}C NMR) and 376 MHz (^{19}F NMR). For ^{1}H NMR, tetramethylsilane (TMS) (δ = 0) in $CDCl_3$ was used as an internal standard. For ^{13}C NMR, $CDCl_3$ (δ = 77.0) was used as an internal standard. The following abbreviations were used: s = singlet, d=doublet, t = triplet, m = multiplet, and br = broad. All coupling constants (*J*) are reported in hertz (Hz). Single crystal diffraction data were recorded on a Bruker APEX-II CCD diffractometer with Mo *K*a radiation. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Information for characterization purposes.

2. Experimental Procedures

All starting materials reported in the manuscript have been previously described in literature and prepared by the method reported previously unless indicated otherwise. Thioamides were prepared by amides and P_2S_5 that have been previously described in literature.[1]

General procedure for the synthesis N-mono-Boc thioamides

An oven-dried flask equipped with a stir bar was charged with *N*-Phenylbenzothioamide (10.0 mmol, 1.0 equiv), dimethylaminopyridine (0.5 mmol, 5 mol%) and THF (1.0 M). Di-*tert*-butyl dicarbonate (1.5 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 ℃, and the reaction mixture was stirred for 15 h at 25 °C. After the indicated time, the reaction mixture was diluted with ethyl acetate (50.0 mL), the organic layer was washed with water (1 × 30 mL), brine (1 × 30 mL), dried over Na_2SO_4, and concentrated. The crude reaction mixture was purified by chromatography on aluminium oxide (PE/EA = 40:1) to afford pure product.

General procedure for the coupling of N-Ph-Boc thioamides with ketones

An oven-dried vial equipped with a stir bar was charged with thioamide substrate **1** (0.2 mmol, 1.0 equiv), acetophenone **2** (typically, 0.3 mmol, 1.5 equiv) THF (typically, 1.0 M) and KHMDS (1.0 M in THF, typically, 0.5 mL, 2.5 equiv) were sequentially added with vigorous stirring at 25 ℃, and the reaction mixture was stirred at 25 ℃ for 15 h. After the indicated time, the reaction mixture was quenched with NH_4Cl (aq., 1.0 M, 1 mL). The solution was diluted with EtOAc (10 mL), and the organic layer was washed with water (1 × 10 mL), HCl (1.0 M, 1 × 10 mL), dried and concentrated. The products were purified by chromatography on silica gel (EtOAc/hexane) and afforded the products

3. Selectivity in Acylation of Thioamides

A: Effect of amide distortion on acylation of thioamides by chemoselective N–C(S) cleavage.

An oven-dried vial equipped with a stir bar was charged with **1** (1.0 equiv), acetophenone (2.0 equiv), THF (1.0 M) and KHMDS (2.5 equiv) were sequentially added with vigorous stirring at 25 °C, and the reaction mixture was stirred at 25 °C for an indicated time. After the indicated time, the reaction mixture was quenched with NH_4Cl (aq., 1.0 M, 15 mL) and filtered with Celite then dried and concentrated. A sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

B: Competition studies between electron-deficient and electron-rich thioamide

An oven-dried vial equipped with a stir bar was charged with tert-butyl(4-methoxyphenylcarbonothioyl)(phenyl)carbamate (2.0 equiv), tert-butyl(4-chlorophenylcarbonothioyl)(phenyl)carbamate (2.0 equiv), acetophenone

(1.0 equiv), THF (1.0 M) and KHMDS (2.5 equiv) were sequentially added with vigorous stirring at 25 °C, and the reaction mixture was stirred at 25 °C for an indicated time. After the indicated time, the reaction mixture was quenched with NH_4Cl (aq., 1.0 M, 15 mL) and filtered with Celite then dried and concentrated. A sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

C: Competition studies between electron-deficient and electron-rich acetophenone

An oven-dried vial equipped with a stir bar was charged with tert-butyl phenyl(phenylcarbonothioyl)carbamate (1.0 equiv), 4-Methylacetophenone (2.0 equiv), 4-Fluoroacetophenone (2.0 equiv) THF (1.0 M) and KHMDS (2.5 equiv) were sequentially added with vigorous stirring at 25 °C, and the reaction mixture was stirred at 25 °C for an indicated time. After the indicated time, the reaction mixture was quenched with NH_4Cl (aq., 1.0 M, 15 mL) and filtered with Celite then dried and concentrated. A sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples.

4. Characterization Data of Products

(*Z*)-3-Hydroxy-1,3-diphenylprop-2-ene-1-thione (3a). According to the general procedure, the reaction of tert-butyl phenyl(phenylcarbonothioyl)carbamate (0.20 mmol, 1.0 equiv), acetophenone (1.5 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 70 % yield (33.6 mg). Yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.27 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 6.9 Hz, 1H), 7.48 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 203.3, 179.9, 145.5, 135.8, 132.6, 131.1, 128.9, 128.5, 127.3, 126.8, 110.7. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}OS^+$: 241.0682; Found: 241.0678.

(*Z*)-3-hydroxy-1-phenyl-3-(*p*-tolyl)prop-2-ene-1-thione (3b). According to the general procedure, the reaction of tert-butyl phenyl(phenylcarbonothioyl)carbamate (0.20 mmol, 1.0 equiv), 1-(p-tolyl)ethan-1-one (2.0 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 74 % yield (37.6 mg). Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 15.34 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.37 (s, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 203.4, 179.8, 145.7, 143.7, 132.8, 131.0, 129.7, 128.5, 127.3, 126.8, 110.4, 21.8. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}OS^+$: 255.0838; Found: 255.0835.

(*Z*)-3-hydroxy-1-phenyl-3-(*m*-tolyl)prop-2-ene-1-thione (3c). According to the general procedure, the reaction of tert-butyl phenyl(phenylcarbonothioyl)carbamate (0.20 mmol, 1.0 equiv), 1-(m-tolyl)ethan-1-one (2.0 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 50 % yield (25.4 mg). Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 15.34 (s, 1H), 7.80 (t, *J* = 7.0 Hz, 4H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.45 – 7.41 (m, 3H), 7.37 (d, *J* = 4.9 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 203.8, 180.0, 145.6, 138.7, 135.7, 133.5, 131.1, 128.8, 128.5, 127.8, 126.9, 124.5, 110.7, 21.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}OS^+$: 255.0838; Found: 255.0842.

(*Z*)-3-hydroxy-3-(3-methoxyphenyl)-1-phenylprop-2-ene-1-thione (3d). According to the general procedure, the reaction of tert-butyl phenyl(phenylcarbonothioyl)carbamate (0.20 mmol, 1.0 equiv), 1-(3-methoxyphenyl)ethan-1-one (2.0 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 61 % yield (33.0 mg). Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 14.94 (s, 1H), 7.72 (d, *J* = 7.2, 1.9 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.45 (s, 1H), 7.40 (t, *J* = 6.9 Hz, 1H), 7.34 (m, 3H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 202.3, 179.9, 160.0, 145.4, 137.3, 131.1, 129.9, 128.6, 126.7, 119.6, 118.7, 112.3, 110.9, 55.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}O_2S^+$: 271.0787; Found: 271.0783.

(*Z*)-3-hydroxy-1-phenyl-3-(*o*-tolyl)prop-2-ene-1-thione (3e). According to the general procedure, the reaction of tert-butyl phenyl(phenylcarbonothioyl)carbamate (0.20 mmol, 1.0 equiv), 1-(o-tolyl)ethan-1-one (2.0 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 55 % yield (28.0 mg). Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 14.65 (s, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 6.4 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.03 (s, 1H), 2.48 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 199.8, 184.8, 144.8, 137.2, 137.1, 131.6, 131.2, 130.9, 128.6, 128.3, 126.9, 126.0, 114.8, 20.8. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}OS^+$: 255.0838; Found: 255.0835.

(*Z*)-3-hydroxy-3-mesityl-1-phenylprop-2-ene-1-thione (3f). According to the general procedure, the reaction of tert-butyl phenyl(phenylcarbonothioyl)carbamate (0.20 mmol, 1.0 equiv), 1-mesitylethan-1-one (2.0 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 50 % yield (28.2 mg). Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 14.85 (s, 1H), 7.70 (d, *J* = 9.3 Hz, 2H), 7.39 (t, *J* = 6.8 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 6.84 (s, 2H), 6.81 (s, 1H), 2.24 (s, 6H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 201.4, 185.76, 144.40, 139.28, 135.10, 131.34, 128.59, 128.52, 126.92, 19.74. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for

$C_{18}H_{19}OS^+$: 283.1151; Found: 283.1149.

(*Z*)-3-(4-fluorophenyl)-3-hydroxy-1-phenylprop-2-ene-1-thione (3g). According to the general procedure, the reaction of tert-butyl phenyl(phenylcarbonothioyl)carbamate (0.20 mmol, 1.0 equiv), 1-(4-fluorophenyl)ethan-1-one (2.0 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 57 % yield (29.4 mg). Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 14.72 (s, 1H), 7.97 – 7.93 (m, 2H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.32 (s, 1H), 7.10 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 200.9, 179.1, 165.5 (d, *J*=300.2 Hz), 145.2, 132.1(d, *J*=3.0 Hz), 131.2, 129.7 (d, *J*=9.2 Hz), 128.6, 126.8, 116.1 (d, *J*=22.0 Hz), 110.5. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -105.59 (s, 1F). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}FOS^+$: 259.0587; Found: 259.0583.

(*Z*)-3-(4-chlorophenyl)-3-hydroxy-1-phenylprop-2-ene-1-thione (3g). According to the general procedure, the reaction of tert-butyl phenyl(phenylcarbonothioyl)carbamate (0.20 mmol, 1.0 equiv), 1-(4-chlorophenyl)ethan-1-one (2.0 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 71 % yield (39.0 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 14.70 (s, 1H), 7.93 (d, *J* = 7.1 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.46 (m, 5H), 7.39 (s, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 202.5, 178.6, 145.3, 138.9, 134.3, 131.3, 129.2, 128.6, 128.6, 126.8, 110.4. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}ClOS^+$: 275.0292; Found: 275.0288.

(*Z*)-3-(4-bromophenyl)-3-hydroxy-1-phenylprop-2-ene-1-thione (3h). According to the general procedure, the reaction of tert-butyl phenyl(phenylcarbonothioyl)carbamate (0.20 mmol, 1.0 equiv), 1-(4-bromophenyl)ethan-1-one (2.0 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 85 % yield (54.3 mg).^{1}H NMR (600 MHz, Chloroform-*d*) δ 14.82 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.32 (s, 1H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 202.6, 178.7, 145.3, 134.7, 132.2, 131.3, 128.7,

128.6, 127.5, 126.8, 110.4. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}BrOS^+$: 318.9787; Found: 318.9783.

(*Z*)-3-(3-bromophenyl)-3-hydroxy-1-phenylprop-2-ene-1-thione (3j).According to the general procedure, the reaction of tert-butyl phenyl(phenylcarbonothioyl)carbamate (0.20 mmol, 1.0 equiv), 1-(3-bromophenyl)ethan-1-one (2.0 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 54 % yield (34.5 mg).^{1}H NMR (600 MHz, Chloroform-*d*) δ 14.61 (s, 1H), 8.02 (s, 1H), 7.82 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.25 (m, 2H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 202.1, 178.4, 145.1, 138.0, 135.3, 131.3, 130.4, 130.2, 128.6, 126.9, 125.7, 123.1, 110.6. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}BrOS^+$: 318.9787; Found: 318.9783.

(*Z*)-3-hydroxy-1-phenyl-3-(pyridin-3-yl)prop-2-ene-1-thione (3k).According to the general procedure, the reaction of tert-butyl phenyl(phenylcarbonothioyl)carbonate (0.20 mmol, 1.0 equiv), 1-(pyridin-3-yl)ethan-1-one (2.0 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 30 % yield (14.5 mg).^{1}H NMR (600 MHz, Chloroform-*d*) δ 14.54 (s, 1H), 9.21 (d, *J* = 2.2 Hz, 1H), 8.77 (d, *J* = 3.2 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.1 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.43 (m, 3H), 7.42 (s, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 201.8, 177.9, 152.8, 148.4, 144.9, 134.6, 131.9, 131.5, 128.7, 126.8, 123.7, 110.6. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}NOS^+$: 242.0635; Found: 242.0629.

(*Z*)-3-hydroxy-1-phenyl-3-(thiophen-3-yl)prop-2-ene-1-thione (3l). According to the general procedure, the reaction of tert-butyl phenyl(phenylcarbonothioyl)carbamate (0.20 mmol, 1.0 equiv), 1-(thiophen-3-yl)ethan-1-one (2.0 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 20 % yield (9.9 mg).^{1}H NMR (600 MHz, Chloroform-*d*) δ 13.17 (s, 1H), 7.78 (d, *J* = 3.3 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.59 (d, *J* = 4.6 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.22 (s, 1H), 7.11 – 7.08 (m, 1H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 189.1, 176.6, 144.0, 142.6,

132.9, 130.9, 130.6, 128.6, 128.6, 126.8, 111.4. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}OS_2^+$: 247.0246; Found: 247.0241.

(*Z*)-3-hydroxy-1-(4-methoxyphenyl)-3-phenylprop-2-ene-1-thione (3m). According to the general procedure, the reaction of tert-butyl (4-methoxyphenylcarbonothioyl)(phenyl)carbamate (0.20 mmol, 1.0 equiv), acetophenone (1.5 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 72 % yield (38.9 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 16.00 (s, 1H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.9 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.45 (s, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 206.4, 178.0, 162.7, 138.4, 135.7, 132.4, 128.9, 128.9, 127.1, 113.8, 108.7, 55.5. Spectroscopic properties matched those described previously.[2]

(*Z*)-3-hydroxy-3-phenyl-1-(*p*-tolyl)prop-2-ene-1-thione (3n). According to the general procedure, the reaction of tert-butyl (4-methylphenylcarbonothioyl)(phenyl)carbamate (0.20 mmol, 1.0 equiv), acetophenone (1.5 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 50 % yield (25.4 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 15.48 (s, 1H), 7.99 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 6.7 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.45 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 204.8, 179.1, 142.9, 142.0, 135.7, 132.5, 129.2, 128.9, 127.2, 126.9, 109.9, 21.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}OS^+$: 255.0838; Found: 255.0841.

(*Z*)-1-(4-(tert-butyl)phenyl)-3-hydroxy-3-phenylprop-2-ene-1-thione (3o). According to the general procedure, the reaction of tert-butyl (4-(tert-butyl)phenylcarbonothioyl)(phenyl)carbamate (0.20 mmol, 1.0 equiv), acetophenone (1.5 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 70 % yield (41.5 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.46 (s, 1H), 8.00 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.53 – 7.41 (m, 5H), 1.35 (s, 9H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 204.7, 179.2, 155.0, 142.9, 135.8, 132.6, 128.9, 127.2, 126.8, 125.6, 110.1, 35.0, 31.2.HRMS

(ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}OS^+$: 297.1308; Found: 297.1300.

(*Z*)-1-(4-chlorophenyl)-3-hydroxy-3-phenylprop-2-ene-1-thione (3p). According to the general procedure, the reaction of tert-butyl (4-chlorophenylcarbonothioyl)(phenyl)carbamate (0.20 mmol, 1.0 equiv), acetophenone (1.5 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 61 % yield (33.5 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 15.59 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.43 – 7.37 (m, 3H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 203.7, 179.6, 143.8, 137.5, 135.3, 132.8, 129.0, 128.7, 128.2, 127.3, 110.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}ClOS^+$: 275.0292; Found: 275.0285.

(*Z*)-1-(3-chlorophenyl)-3-hydroxy-3-phenylprop-2-ene-1-thione (3q). According to the general procedure, the reaction of tert-butyl (3-chlorophenylcarbonothioyl)(phenyl)carbamate (0.20 mmol, 1.0 equiv), acetophenone (1.5 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 51 % yield (28.0 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 15.37 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.77 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 1H), 7.42 (s, 1H), 7.36 (t, *J* = 7.9 Hz, 1H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 202.4, 180.0, 147.0, 135.3, 134.6, 132.9, 130.8, 129.8, 129.0, 127.3, 126.9, 125.0, 110.7. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}ClOS^+$: 275.0292; Found: 275.0296.

(***Z***)**-1-(4-bromophenyl)-3-hydroxy-3-phenylprop-2-ene-1-thione (3r).** According to the general procedure, the reaction of tert-butyl (4-bromophenylcarbonothioyl)(phenyl)carbamate (0.20 mmol, 1.0 equiv), acetophenone (1.5 equiv) and KHMDS (2.5 equiv) in THF (1.0 M) at 25 °C for 15 h, afforded after the standard work-up as described above and chromatography the title compound in 61 % yield (38.9 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 15.48 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 3H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.35 (s, 1H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 203.5, 179.7, 144.3, 135.4, 132.8, 131.7, 129.0, 128.3, 127.3, 126.0, 110.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}BrOS^+$: 318.9787; Found: 318.9779.

5. Crystallographic Studies

Single crystal suitable for X-ray study was grown from Petroleum ether/ether (20:1, V/V) solvent by slow evaporation in 2 days.

X-ray crystallographic data were collected using a Bruker APEX-II CCD diffractometer, equipped with a sealed tube Mo-Kα radiation (λ = 0.71076 Å) at low temperature or at ambient temperature under liquid N_2 flow. The crystal structure was solved with the Superflip, structure solution program using Charge Flipping and refined by direct methods using SHELXL-2018/3 and with full-matrix least squares on F^2 using SHELXL-2018/3. All the non−hydrogen atoms were refined anisotropically.

Crystal structure of **3a**.

Scheme S1. Crystal structure of **3a** (*50% ellipsoids*). (Crystallographic data has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2346234.)

Table S1. Crystal Data and Structure Refinement Summary for 3a.

Crystal data

$C_{15}H_{12}OS$	$F(000)$ = 504
M_r = 240.31	D_x = 1.310 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo *K*a radiation, l = 0.71076 Å
a = 12.5206 (13) Å	Cell parameters from 7019 reflections
b = 7.4108 (8) Å	q = 3.2-24.9°
c = 13.2690 (14) Å	m = 0.24 mm^{-1}
b = 98.254 (3)°	*T* = 100 K
V = 1218.4 (2) Å^3	Block, colourless
Z = 4	
Bruker diffractometer	R_{int} = 0.032
Absorption correction: multi-scan SADABS-2016/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.0521 before and 0.0442 after correction. The Ratio of	q_{max} = 25.1°, q_{min} = 3.2°

minimum to maximum transmission is 0.8914. The l/2 correction factor is Not present.	
T_{min} = 0.664, T_{max} = 0.745	h = -14→14
14813 measured reflections	k = -7→8
2126 independent reflections	l = -15→13
1725 reflections with $I > 2s(I)$	
Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2s(F^2)]$ = 0.036	H-atom parameters constrained
$wR(F^2)$ = 0.086	$w = 1/[s^2(F_o^2) + (0.0288P)^2 + 0.4633P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.07	$(D/s)_{max}$ = 0.001
2126 reflections	$D\rho_{max}$ = 0.19 e Å^{-3}
155 parameters	$D\rho_{min}$ = -0.20 e Å^{-3}
0 restraints	

6. NMR Spectra

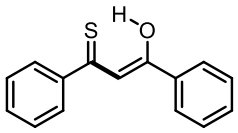

Figure S1 ^{1}H NMR Spectrum of compound **3a** (400 MHz, Chloroform-*d*).

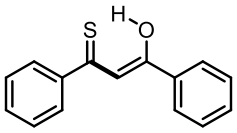

Figure S2 ^{13}C NMR Spectrum of compound **3a** (101 MHz, Chloroform-*d*).

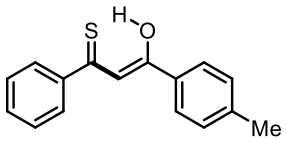

Figure S3 ^{1}H NMR Spectrum of compound **3b** (600 MHz, Chloroform-*d*).

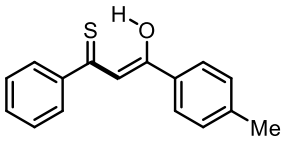

Figure S4 ^{13}C NMR Spectrum of compound **3b** (151 MHz, Chloroform-*d*).

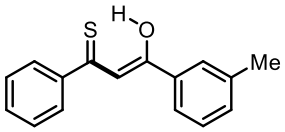

Figure S5 ^{1}H NMR Spectrum of compound **3c** (600 MHz, Chloroform-*d*).

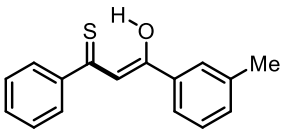

Figure S6 ^{13}C NMR Spectrum of compound **3c** (151 MHz, Chloroform-*d*).

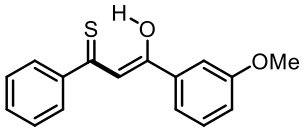

Figure S7 ^{1}H NMR Spectrum of compound **3d** (600 MHz, Chloroform-*d*).

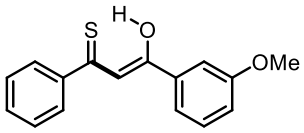

Figure S8 ^{13}C NMR Spectrum of compound **3d** (151 MHz, Chloroform-*d*).

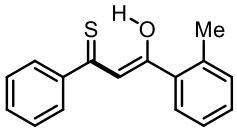

Figure S9 ^{1}H NMR Spectrum of compound **3e** (600 MHz, Chloroform-*d*).

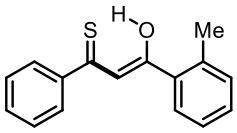

Figure S10 ^{13}C NMR Spectrum of compound **3e** (151 MHz, Chloroform-*d*).

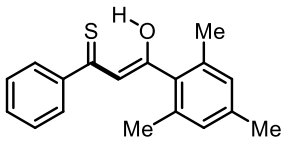

Figure S11 ^{1}H NMR Spectrum of compound **3f** (600 MHz, Chloroform-*d*).

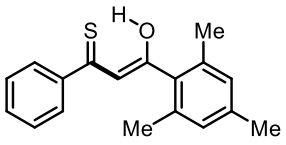

Figure S12 ^{13}C NMR Spectrum of compound **3f** (151 MHz, Chloroform-*d*).

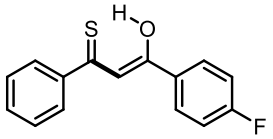

Figure S13 ^{1}H NMR Spectrum of compound **3g** (600 MHz , Chloroform-*d*).

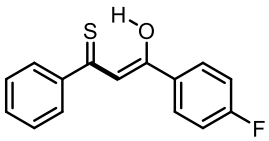

Figure S14 ^{13}C NMR Spectrum of compound **3g** (151 MHz, Chloroform-*d*).

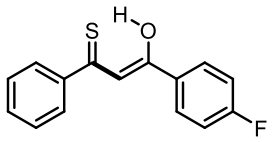

Figure S15 ^{19}F NMR Spectrum of compound **3g** (565 MHz MHz, Chloroform-*d*)..

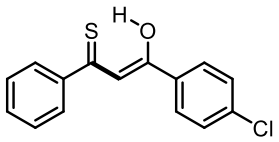

Figure S16 ^{1}H NMR Spectrum of compound **3h** (400 MHz, Chloroform-*d*).

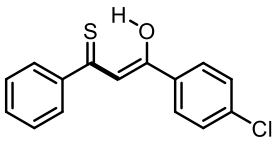

Figure S17 ^{13}C NMR Spectrum of compound **3h** (101 MHz, Chloroform-*d*).

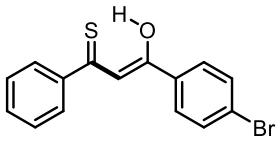

Figure S18 ^{1}H NMR Spectrum of compound **3i** (600 MHz, Chloroform-*d*).

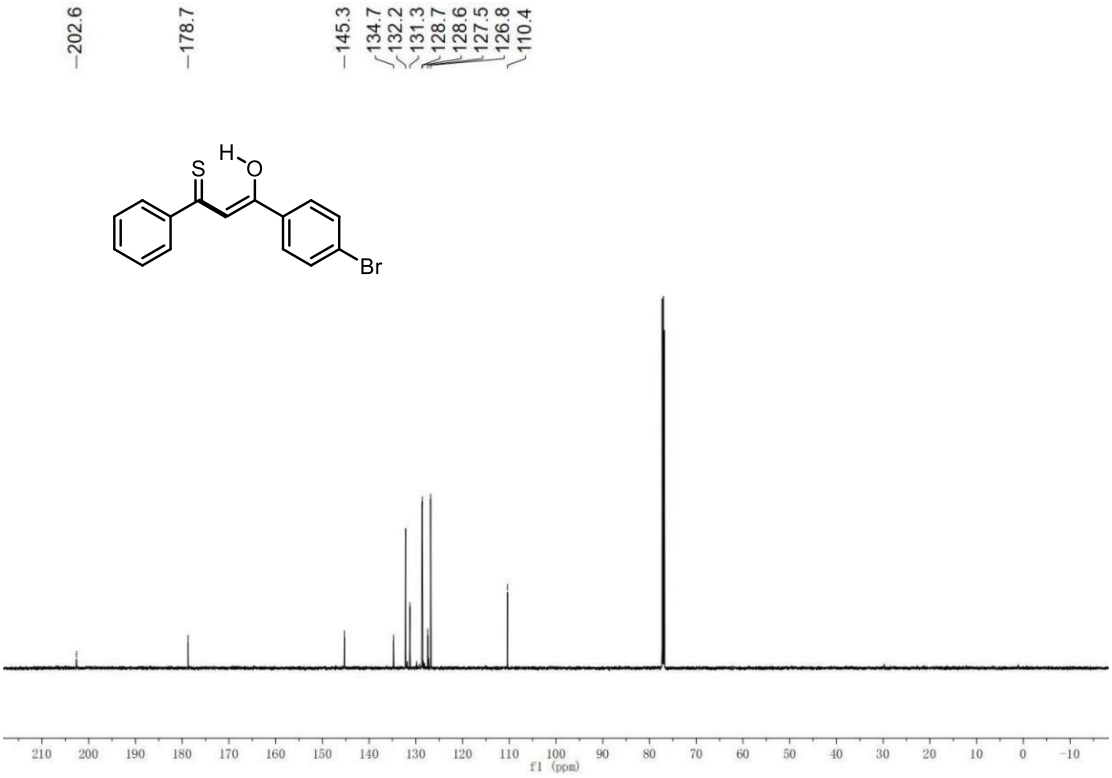

Figure S19 ^{13}C NMR Spectrum of compound **3i** (151 MHz, Chloroform-*d*).

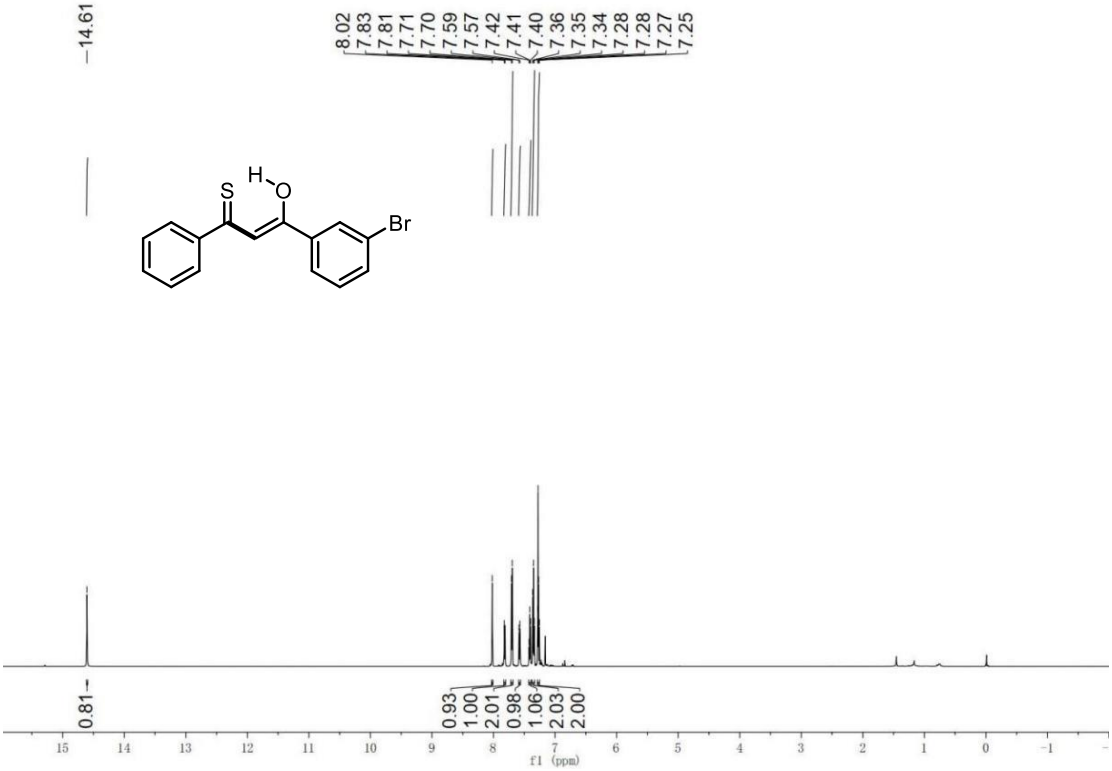

Figure S20 ^{1}H NMR Spectrum of compound **3j** (600 MHz, Chloroform-*d*).

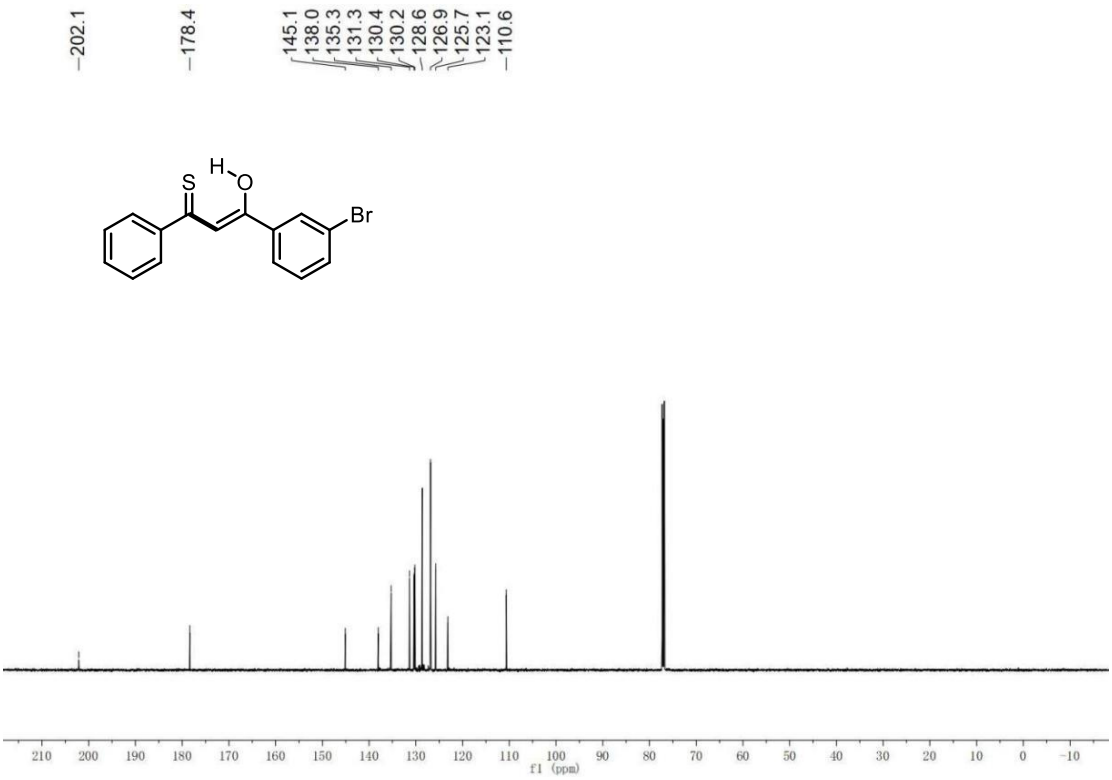

Figure S21 ^{13}C NMR Spectrum of compound **3j** (151 MHz, Chloroform-*d*).

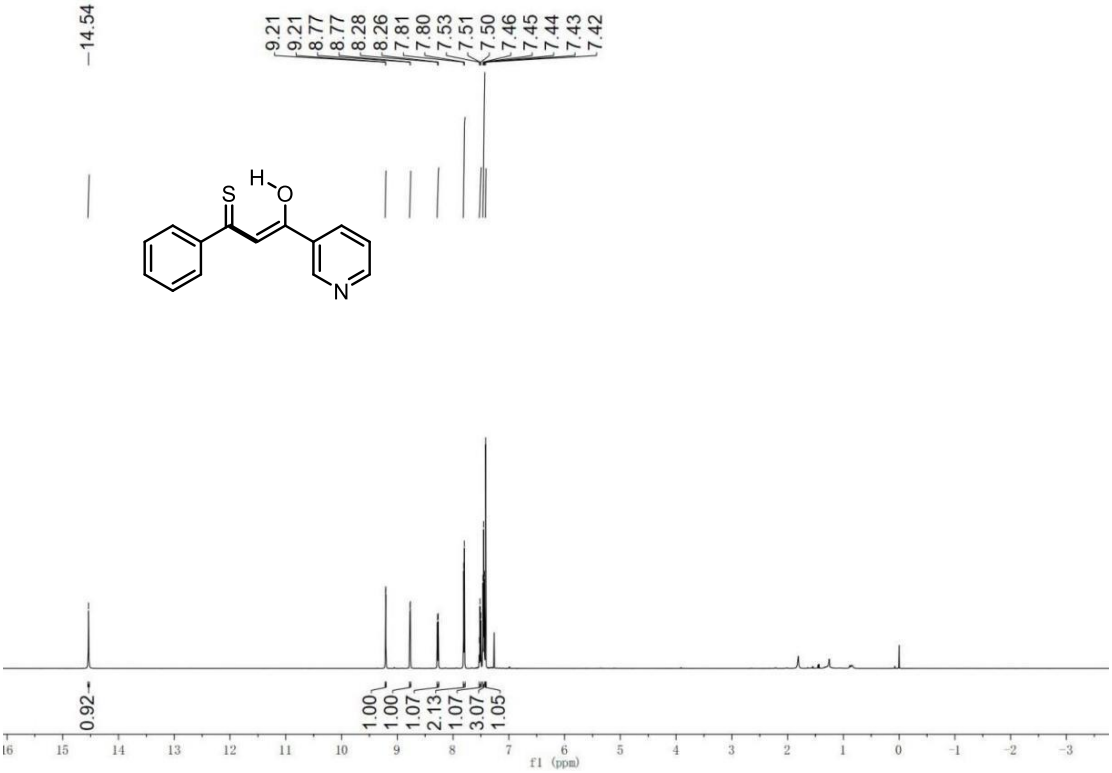

Figure S22 ^{1}H NMR Spectrum of compound **3k** (600 MHz, Chloroform-*d*).

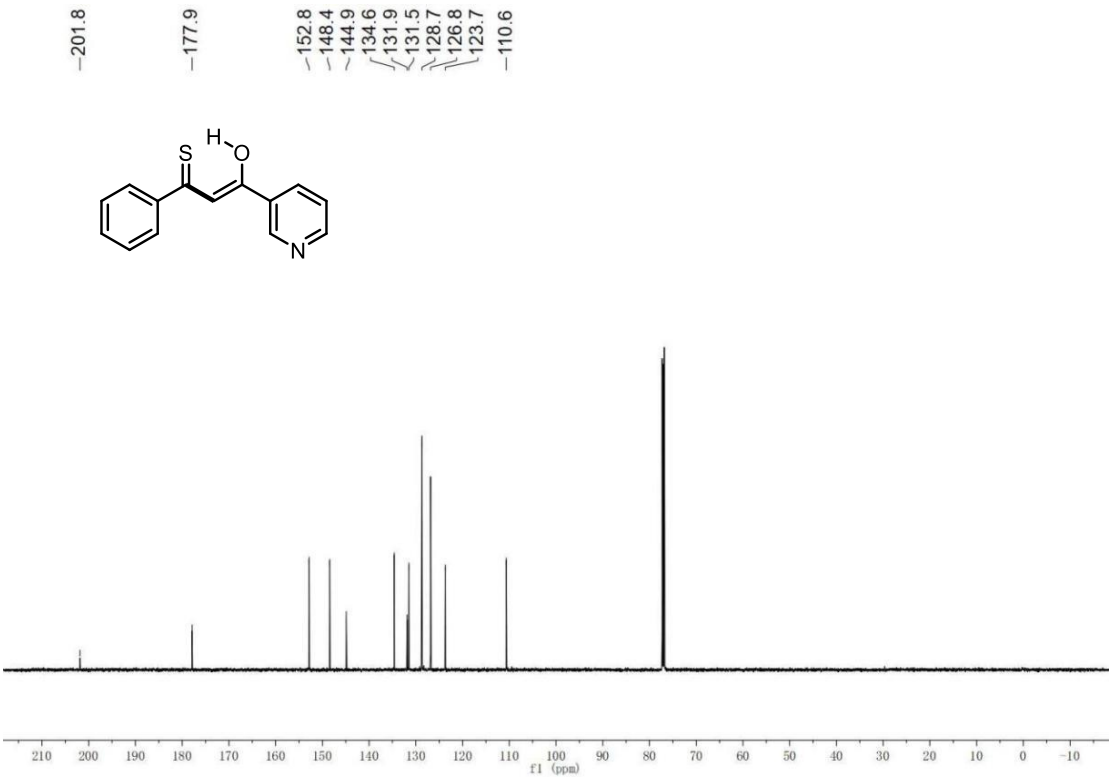

Figure S23 ^{13}C NMR Spectrum of compound **3k** (151 MHz, Chloroform-*d*).

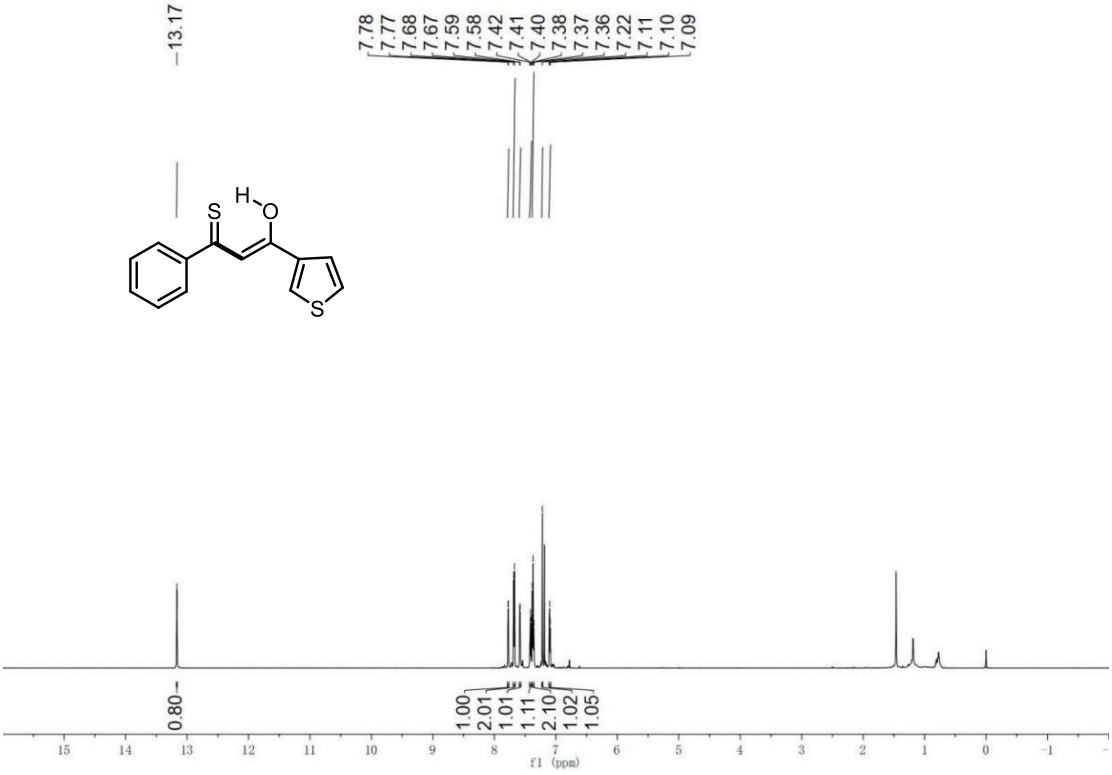

Figure S24 ^{1}H NMR Spectrum of compound **3l** (600 MHz, Chloroform-*d*).

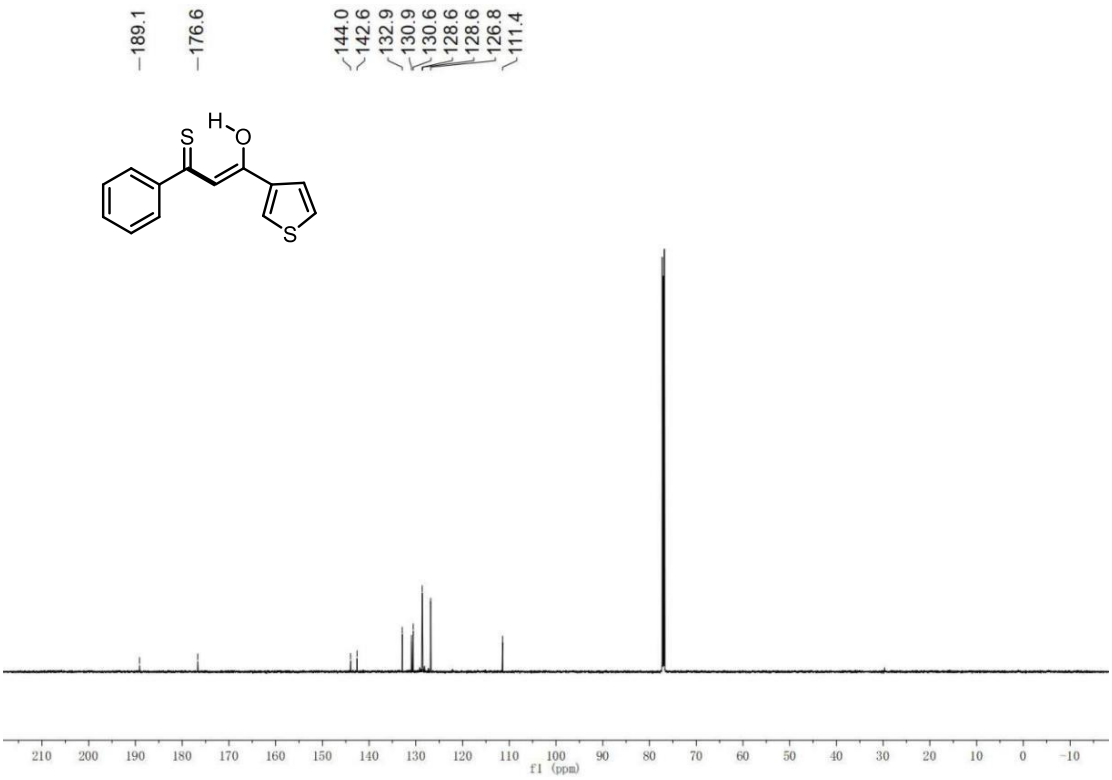

Figure S25 ^{13}C NMR Spectrum of compound **3l** (151 MHz, Chloroform-*d*).

Figure S26 ^{1}H NMR Spectrum of compound **3m** (600 MHz, Chloroform-*d*).

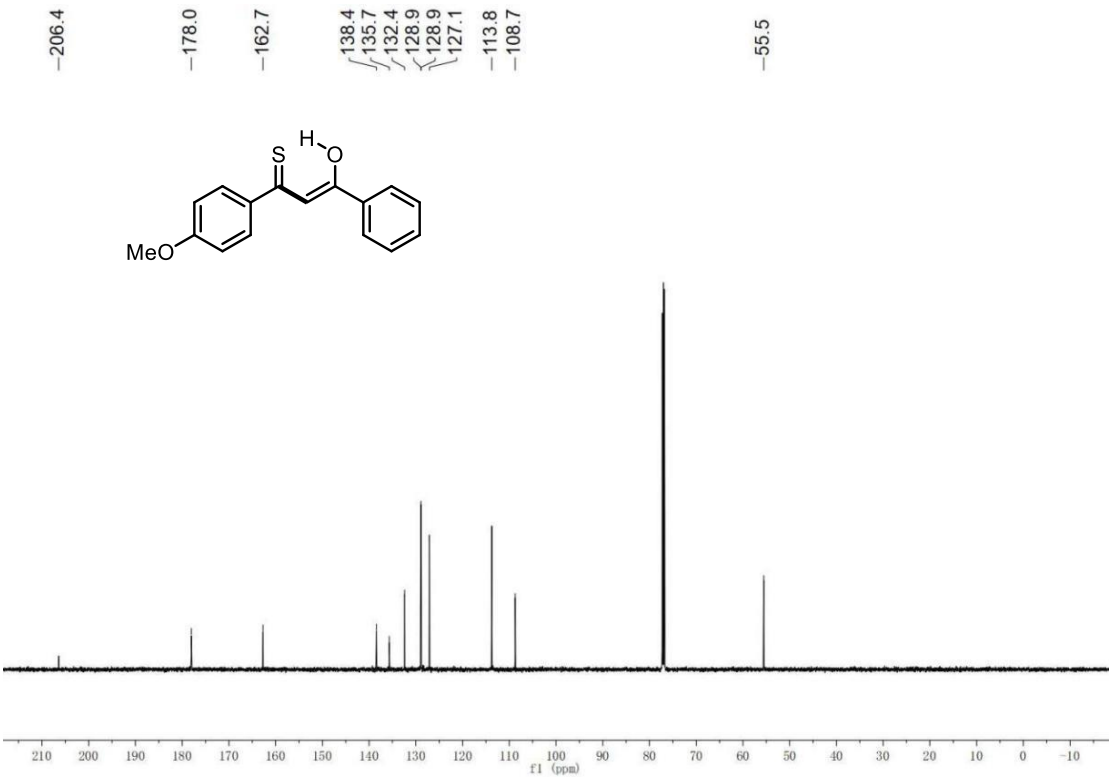

Figure S27 ^{13}C NMR Spectrum of compound **3m** (151 MHz, Chloroform-*d*).

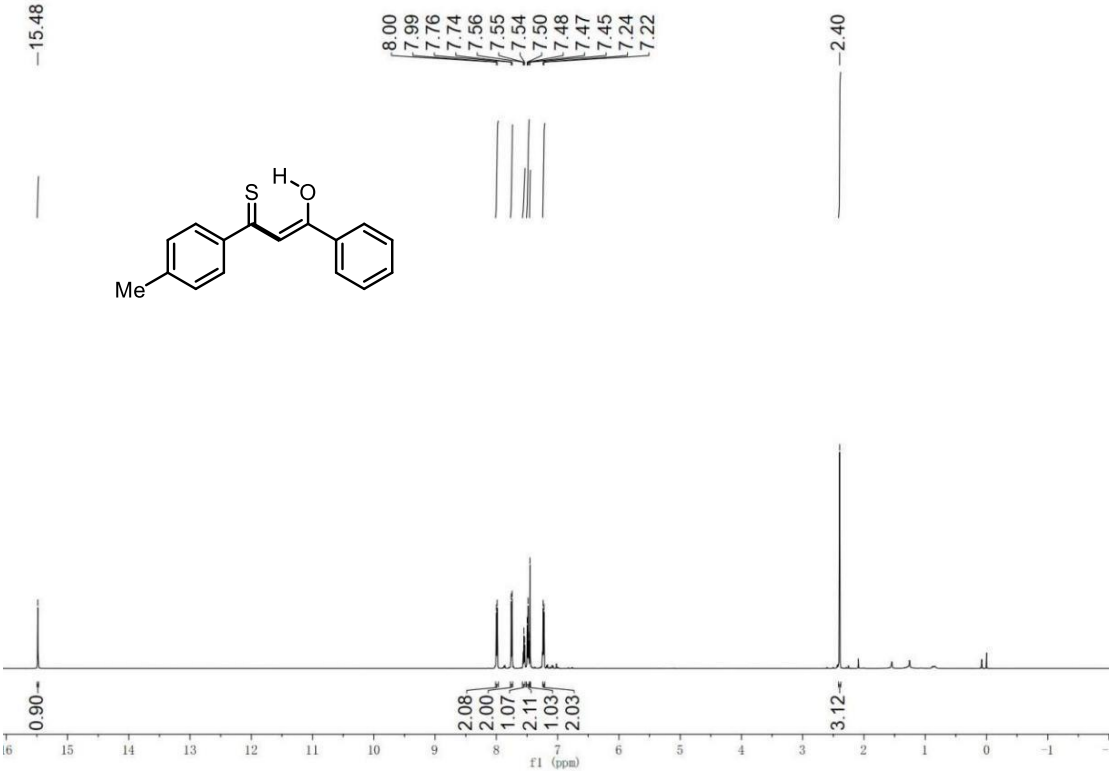

Figure S28 ^{1}H NMR Spectrum of compound **3n** (600 MHz, Chloroform-*d*).

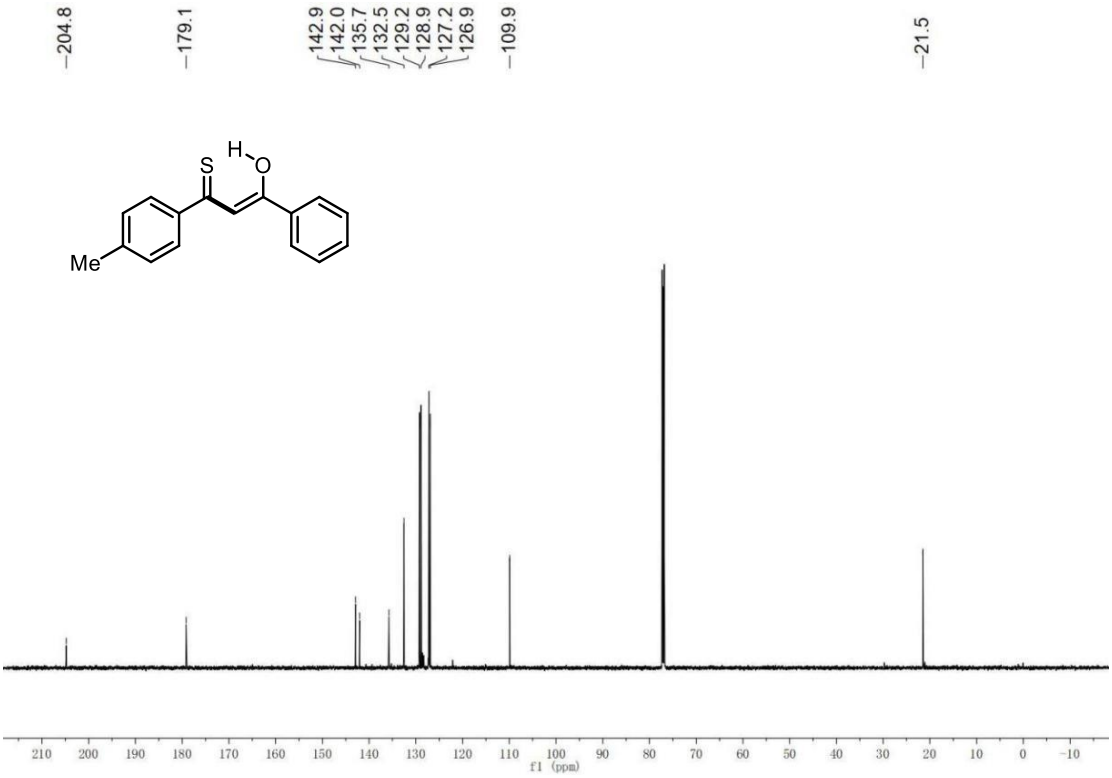

Figure S29 ^{13}C NMR Spectrum of compound **3n** (151 MHz, Chloroform-*d*).

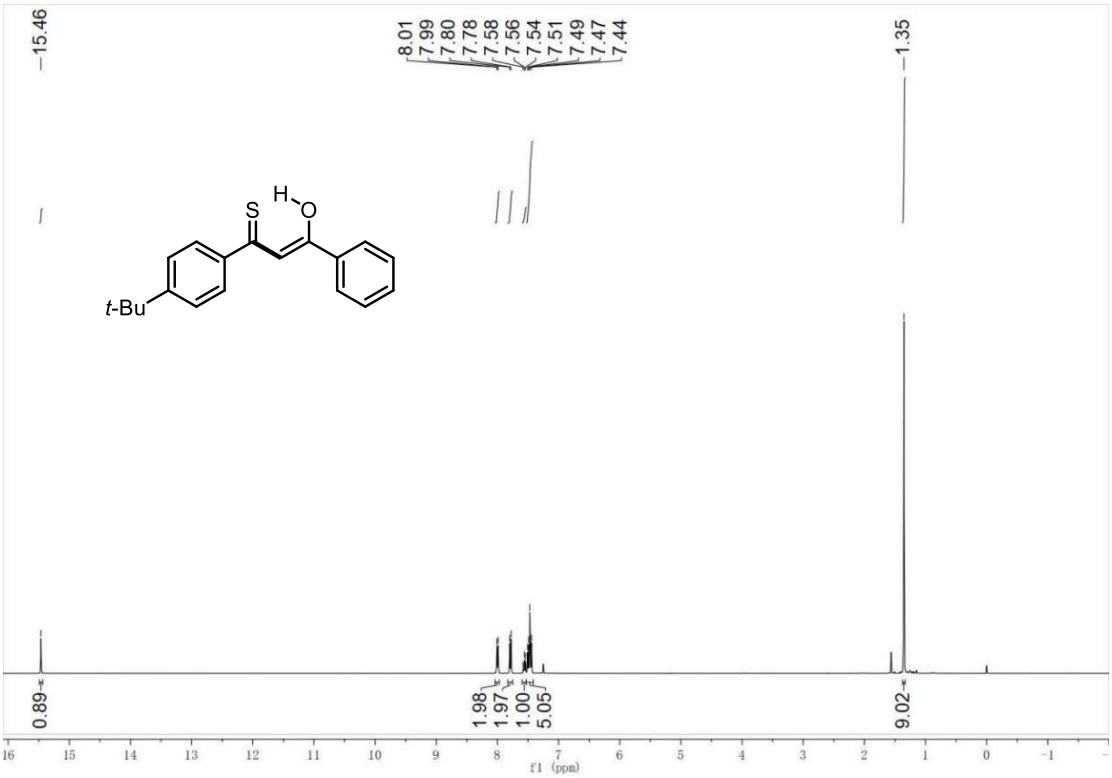

Figure S30 ^{1}H NMR Spectrum of compound **3o** (400 MHz, Chloroform-*d*).

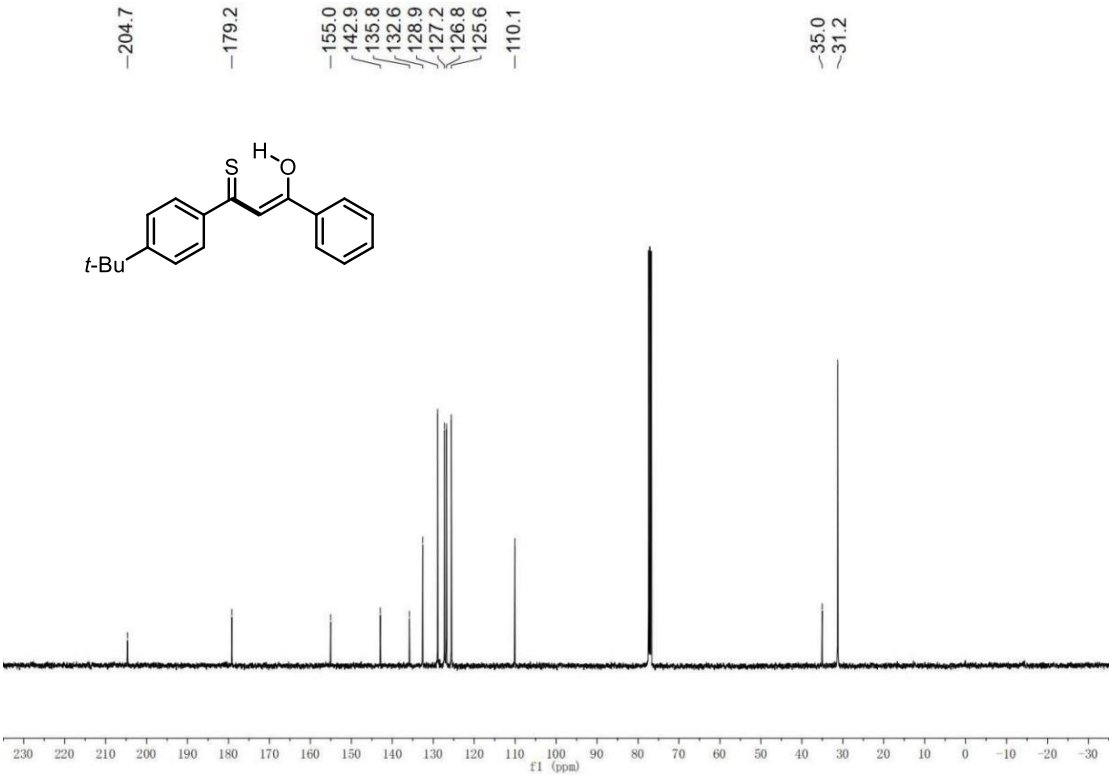

Figure S31 ^{13}C NMR Spectrum of compound **3o** (151 MHz, Chloroform-*d*).

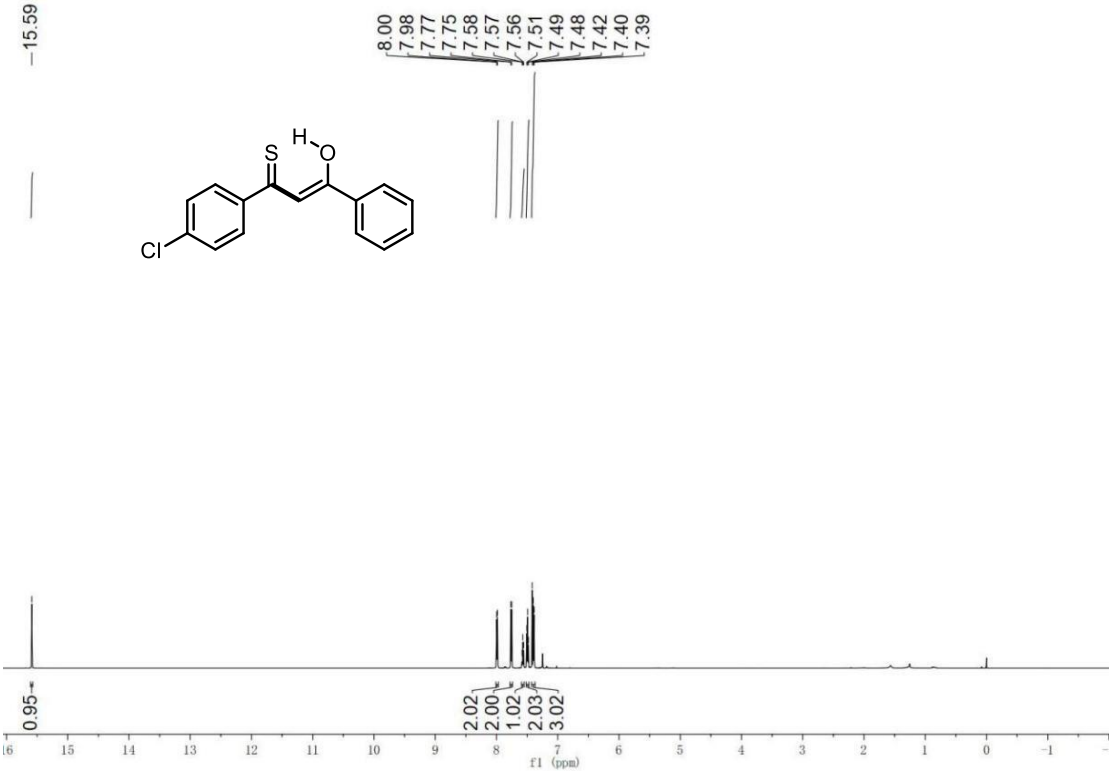

Figure S32 ^{1}H NMR Spectrum of compound **3p** (600 MHz, Chloroform-*d*).

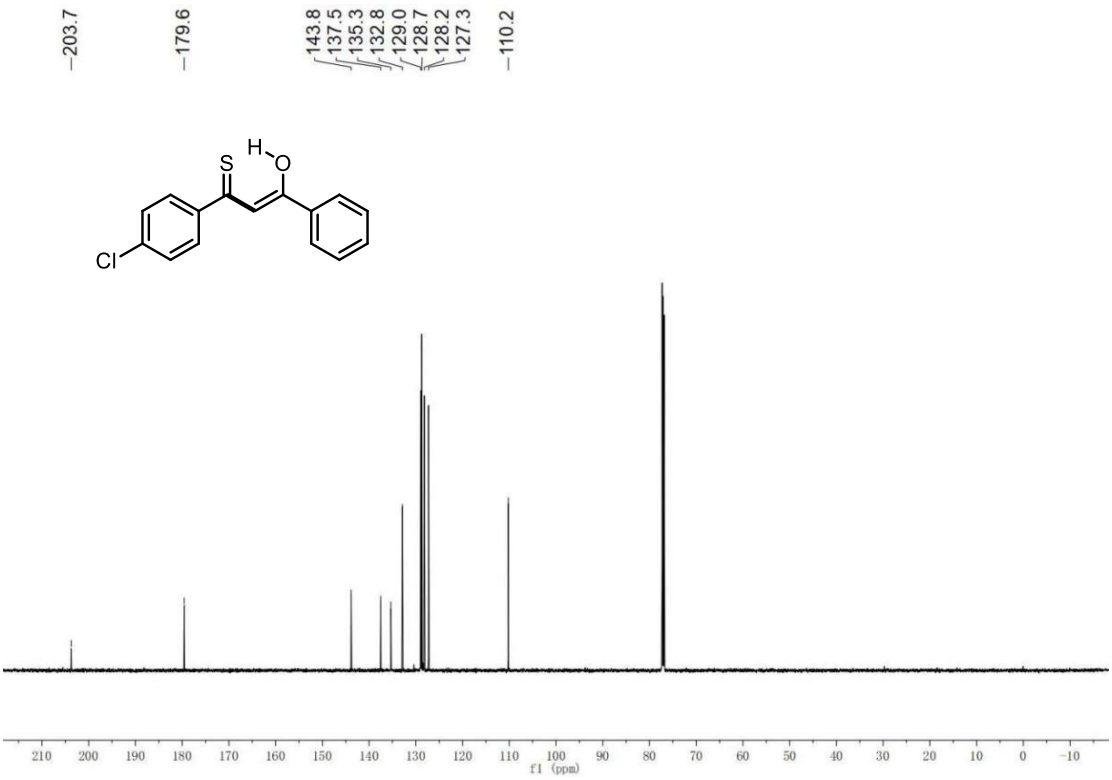

Figure S33 ^{13}C NMR Spectrum of compound **3p** (151 MHz, Chloroform-*d*).

Figure S34 ^{1}H NMR Spectrum of compound **3q** (600 MHz, Chloroform-*d*).

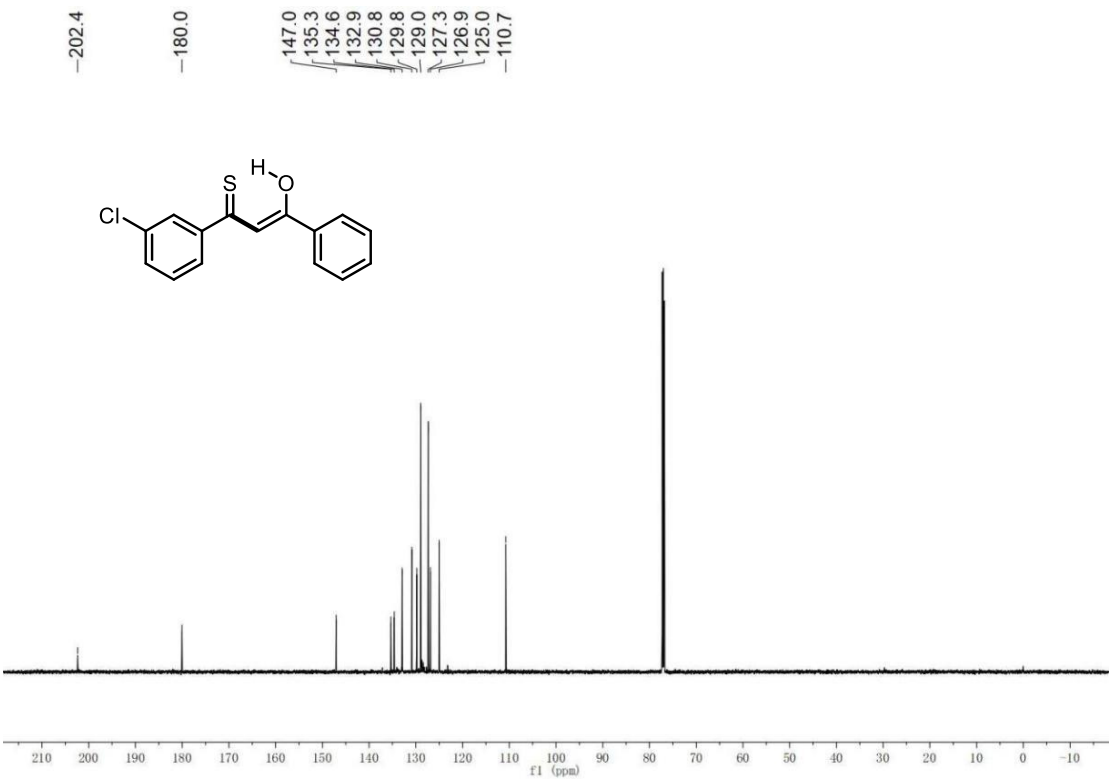

Figure S35 ^{13}C NMR Spectrum of compound **3q** (151 MHz, Chloroform-*d*).

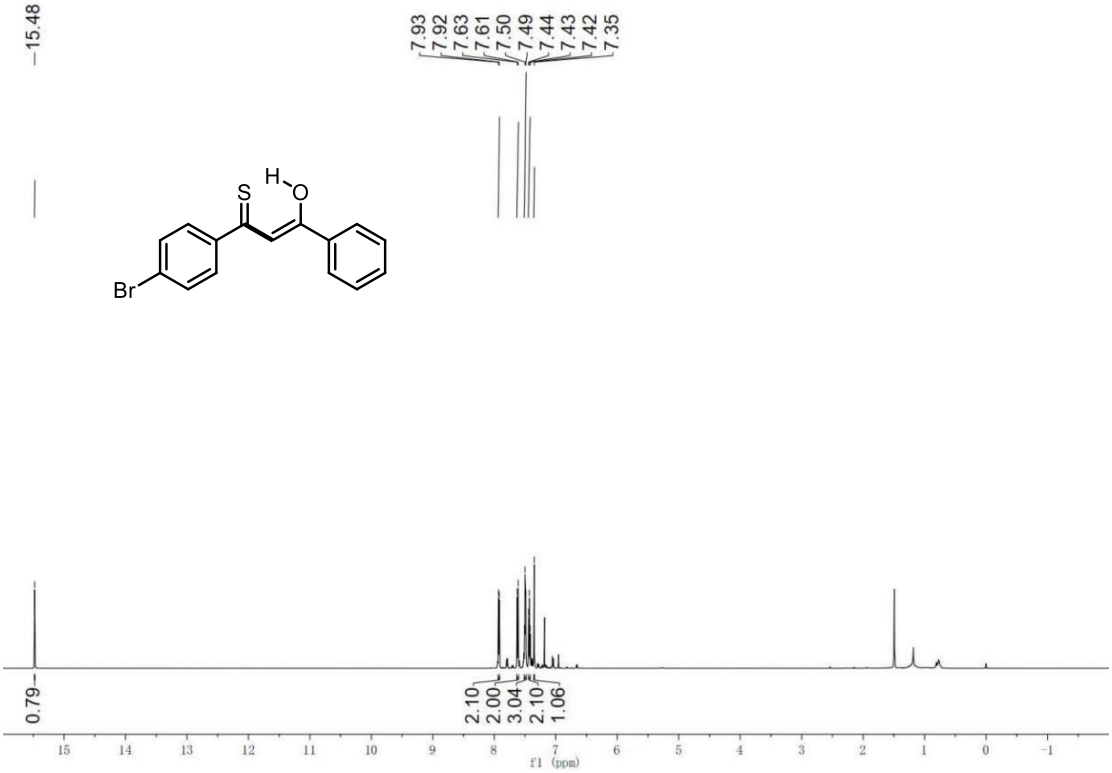

Figure S36 ^{1}H NMR Spectrum of compound **3r** (600 MHz, Chloroform-*d*).

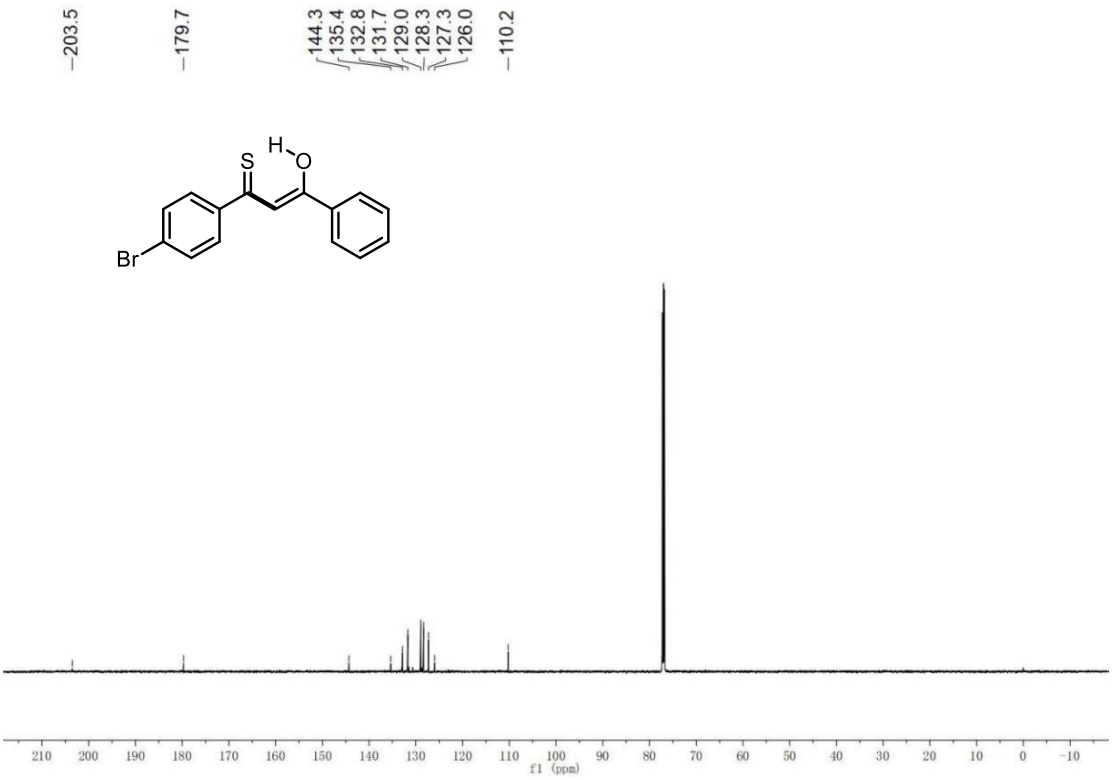

Figure S37 ^{13}C NMR Spectrum of compound **3r** (151 MHz, Chloroform-*d*).

7. References

1. Zhang, J.; Liu, Z.; Yin, Z.; Yang, X.; Ma, Y.; Szostak, R.; Szostak, M., Preference of cis-Thioamide Structure in N-Thioacyl-N-methylanilines. *Organic Letters*, **2020**, 22(24), 9500-9505.

2. Hansen, P.; Duus, F, Schmitt, P. Deuterium Isotope Effects on ^{13}C Nuclear Shielding as a Measure of Tautomeric Equilibria. *Organic Magnetic Resonance*, **1982,** 18(1), 58-61.