Supporting Information

An Efficient and Straightforward Approach for Accessing Thionoester via Palladium-Catalyzed C-N Cleavage of Thioamides

Yinbo Liu,[a] Xiaofeng Mo,[a] Majeed Irfan,[a] Mei Zhang,[a] Hui Wang,[a] Zhuo Zeng[ab,*]

[a] School of Chemistry, South China Normal University, Guangzhou 510006, People's Republic of China

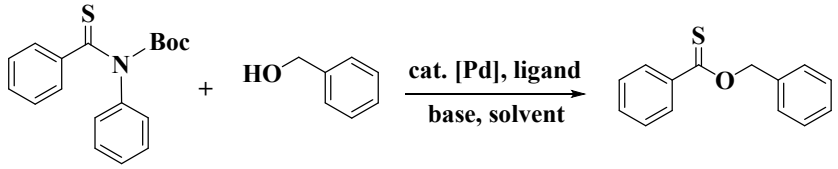
Fax:(+86)-20-3931-0187 E-mail: zhuoz@scun.edu.cn;

[b] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 345 Lingling Road, Shanghai 200032, China

List of Contents

Table S1 Referred to from the Main Manuscript

Table S1 Summary of key optimization studies in the esterification of thioamides[a]



1a **2a** **3a**

Entry	Catalyst	Ligand[c]	Base	Solvent	Yield[b]
1	$Pd(PPh_3)_2Cl_2$	none	K_2CO_3	toluene	24
2	$Pd(OAc)_2$	PPh_3	K_2CO_3	toluene	52
3	$Pd_2(dba)_3$	none	K_2CO_3	toluene	＜5
4	$PdCl_2$	PCy_3	K_2CO_3	toluene	＜5
5	$PdCl_2$	dppp	K_2CO_3	toluene	＜5
6	$PdCl_2$	dppf	K_2CO_3	toluene	trace
7	$PdCl_2$	Xantphos	K_2CO_3	toluene	trace
8	$Pd(OAc)_2$	PPh_3	K_3PO_4	toluene	73
9	$Pd(OAc)_2$	PCy_3	K_3PO_4	toluene	50
10	$Pd(OAc)_2$	$P(C_6F_5)_3$	K_3PO_4	toluene	81
11	$Pd(OAc)_2$	$(4\text{-}MeOPh)_3P$	K_3PO_4	toluene	28
12	$Pd(OAc)_2$	Rac-Binap	K_3PO_4	toluene	55
13	$Pd(OAc)_2$	dppp	K_3PO_4	toluene	25
14	$Pd(OAc)_2$	dppf	K_3PO_4	toluene	＜5
15	$Pd(OAc)_2$	$P(C_6F_5)_3$	K_3PO_4	DMSO	trace
16	$Pd(OAc)_2$	$P(C_6F_5)_3$	K_3PO_4	DMF	trace
17	$Pd(OAc)_2$	$P(C_6F_5)_3$	K_3PO_4	CH_3CN	＜5
18[d]	$Pd(OAc)_2$	$P(C_6F_5)_3$	K_3PO_4	toluene	56
19[e]	$Pd(OAc)_2$	$P(C_6F_5)_3$	K_3PO_4	toluene	62
20[f]	$Pd(OAc)_2$	$P(C_6F_5)_3$	K_3PO_4	toluene	43

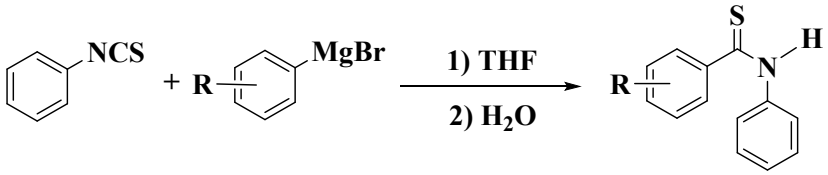
[a] Reaction condition: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), catalyst (5 mol%), ligand (20 mol%), base (3.0 equiv), solvent (2.0 ml), 110 ° C, 12h. [b] Isolated yield. [c] Full name of all ligands: PPh_3(Triphenylphosphine), PCy_3(Tricyclohexyl phosphine), dppp (1,3-Bis(diphenylphosphino)propane), dppf (1,1'-Bis(diphenylphosphino)ferrocene), Xantphos(9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene), $P(C_6F_5)_3$ (Tris(pentafluorophenyl)phosphine), $(4\text{-}MeOPh)_3P$(Tris(p-methoxyphenyl)phosphine), Rac-Binap(1.1'-Binaphthyl-2.2'-diphemyl phosphine). [d] $Pd(OAc)_2$ (3 mol%). [e] $P(C_6F_5)_3$ (10 mol%). [f] At 90 ° C.

List of Known Compounds

The reactions were conducted in sealed tube under nitrogen atmosphere. All reactants reported in the manuscript are commercially available and have been prepared by the method reported previously. All solvents were purchased at the China suppliers and used without any purification. Flash chromatography was performed using 200-300 mesh silica gel. ^{1}H and ^{13}C and ^{19}F NMR data were recorded with AVANCE NEO Bruker (600 MHz) and Varian AS (400 MHz) spectrometers in $CDCl_3$ or $(CD_3)_2SO_2$ with tetramethylsiliane as an internal standard. ^{1}H NMR data are given for all compounds in the Supporting Experimental. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS data are reported for all new compounds.

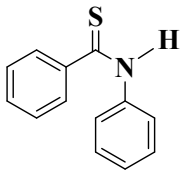
Experimental Procedures and Characterization Data

Experimental procedures for the synthesis of *N*-phenylbenzothioamides.

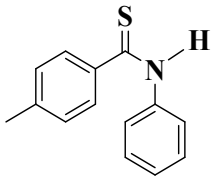


1-3

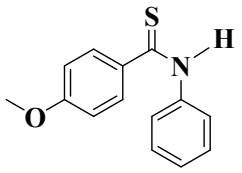
To a solution of phenylisothiocyanate (10.0 mmol, 1.0 equiv) in dry THF (5 mL) was added dropwise a dry THF solution of Grignard reagent (10.0 mmol, 1.0 equiv) at 0 ºC. The reaction mixture was left to warm up to room temperature, and stirred for another 2 h. The reaction was quenched with water (10 mL), extracted with dichloromethane (3 x 20 mL). The combined organic solution was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to give the desired compound.



***N*-phenylbenzothioamide (1).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (petroleum ether/ethyl acetate =10/1) yielded the target compound **1** in 74% (1.58 g) as a yellow solid; R_f = 0.52 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.75 (s, 1H), 7.83 (d, J = 7.8 Hz, 4H), 7.53 (t, J = 7.3 Hz, 1H), 7.49 – 7.42 (m,4H), 7.28 (t, J = 7.4 Hz, 1H). These data are corresponding to the literature.[1]



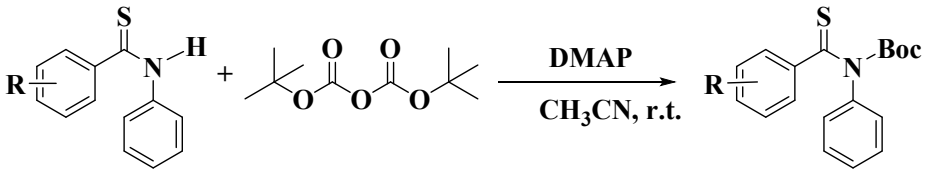
4-methyl-*N*-phenylbenzothioamide (2). The representative general procedure mentioned above was followed. Purification by flash column chromatography (petroleum ether/ethyl acetate =10/1) yielded the target compound **2** in 76% (1.72 g) as a yellow solid; R_f = 0.61 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.63 (s, 1H), 7.78 (dd, J = 14.0 Hz, J = 7.9 Hz, 4H), 7.43 (t, J = 7.9 Hz, 2H), 7.27 (t, J = 7.7 Hz, 3H), 2.37 (s, 3H). These data are corresponding to the literature.[2]



4-methoxy-*N*-phenylbenzothioamide (3). The representative general procedure mentioned above was followed. Purification by flash column chromatography (petroleum ether/ethyl acetate =10/1) yielded the target compound **3** in 81% (1.97 g) as a yellow solid; R_f = 0.35 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.54 (s, 1H), 7.90 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 7.8 Hz, 2H), 7.43 (t,

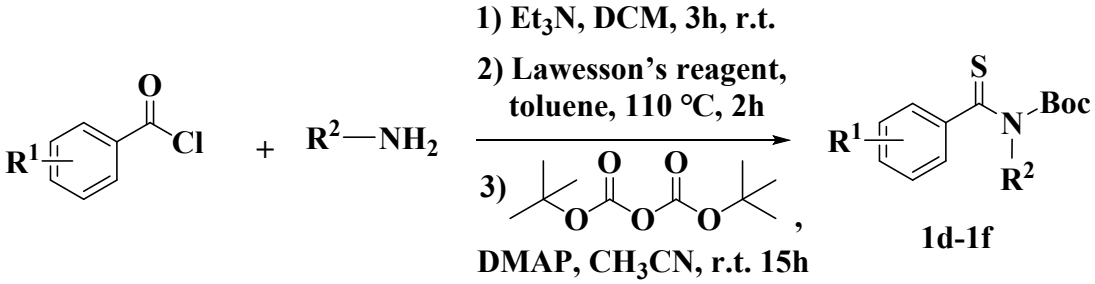
J = 7.7 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H). These data are corresponding to the literature.[3]

Experimental procedures for the synthesis of tert-butyl phenyl(phenylcarbonothioyl)carbamates.



1a-1c

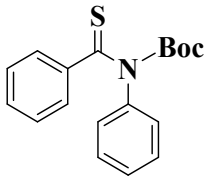
An oven-dried round-bottomed flask equipped with a stir bar was charged with a *N-phenylbenzothioamides* substrate (5.0 mmol, 1.0 equiv), 4-(dimethylamino)pyridine (1.0 mmol, 0.2 equiv), di-tert-butyl dicarbonate (15.0 mmol, 3.0 equiv) and acetonitrile (10.0 mL). The mixture was allowed to stir at room temperature for 15 h. After the indicated time, the reaction was quenched with aqueous HCl (1.0 M, 25 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. Purification by flash column chromatography (petroleum ether/ethyl acetate) afforded pure products.



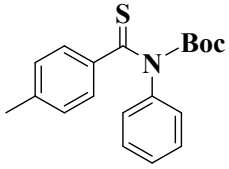
1d-1f

To a mixture of the aniline (5 mmol), Et_3N (6.5 mmol) and CH_2Cl_2 (10 mL) was added benzoyl chloride (5.5 mmol) slowly at room temperature for 3 h. Then, the reaction mixture was washed with water and extracted with CH_2Cl_2 (20 mL × 2). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure to obtain pure benzamide. The solution of the benzamide (2.5mmol) and Lawesson's reagent (1.5 mmol) in dry toluene (40 mL) was heated at reflux under an atmosphere of nitrogen for 2 h, after which it was concentrated, recrystallized from hexane/ethyl acetate.

An oven-dried round-bottomed flask equipped with a stir bar was charged with a N-phenylbenzothioamides substrate (5.0 mmol, 1.0 equiv), 4-(dimethylamino)pyridine (1.0 mmol, 0.2 equiv), di-tert-butyl dicarbonate (15.0 mmol, 3.0 equiv) and acetonitrile (10.0 mL). The mixture was allowed to stir at room temperature for 15 h. After the indicated time, the reaction was quenched with aqueous HCl (1.0 M, 25 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. Purification by flash column chromatography (petroleum ether/ethyl acetate) afforded pure products.

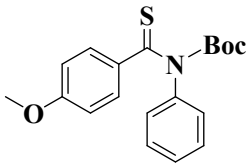


tert-butyl phenyl(phenylcarbonothioyl)carbamate (1a). The representative general procedure mentioned above was followed. Purification by flash column chromatography (petroleum ether/ethyl acetate =20/1) yielded the target compound **1a** in 60% (0.94 g) as an orange-yellow solid; R_f=0.68 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 3H), 7.37 (t, *J* = 7.8 Hz, 3H), 7.30 (d, *J* = 7.4 Hz, 2H), 1.19 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.11, 152.69, 146.50, 144.05, 130.91, 129.62, 128.30, 128.22, 128.02, 127.05, 84.59, 27.40. HRMS (ESI-MS) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}O_2NNaS$ 336.1034; Found 336.1029 for the compounds: **1a**.

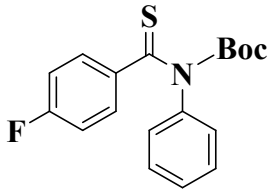


tert-butyl (4-methylphenylcarbonothioyl)(phenyl)carbamate (1b). The representative general procedure mentioned above was followed. Purification by flash column chromatography (petroleum ether/ethyl acetate =20/1) yielded the target compound **1b** in 65% (1.06 g) as an orange-red solid; R_f =0.72 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.25 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.86

(s, 3H), 1.25 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 210.24, 162.49, 152.88, 144.23, 139.28, 129.49, 129.36, 127.84, 127.79, 113.43, 83.99, 55.58, 27.45. HRMS (ESI-MS) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}O_2NNaS$ 350.1191; Found 350.1372 for the compounds: **1b**.

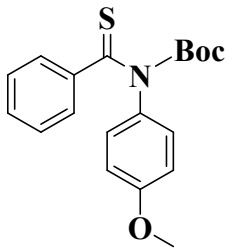


tert-butyl (4-methoxyphenylcarbonothioyl)(phenyl)carbamate (1c). The representative general procedure mentioned above was followed. Purification by flash column chromatography (petroleum ether/ethyl acetate =10/1) yielded the target compound **1c** in 58% (0.99 g) as an orange-yellow solid; R_f =0.43 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.8 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.24 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 210.24, 162.26, 152.88, 144.29, 139.28, 129.50, 129.36, 127.85, 127.79, 113.44, 83.99, 55.59, 27.46. HRMS (ESI-MS) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}O_3NNaS$ 336.1140; Found 336.1146 for the compounds: **1c**.

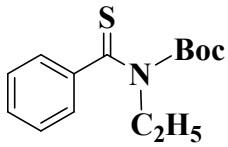


tert-butyl (4-fluorophenylcarbonothioyl)(phenyl)carbamate (1d). The representative general procedure mentioned above was followed. Purification by flash column chromatography (petroleum ether/ethyl acetate =30/1) yielded the target compound **1d** in 70% (1.16 g) as an orange-yellow solid; R_f=0.73 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 2H), 1.29 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 209.25, 164.40 (d, *J* = 252.7 Hz), 152.54, 143.90, 142.55 (d, *J* = 3.1 Hz), 129.53, 129.26 (d, *J* = 8.6 Hz), 128.15, 127.86, 115.24 (d, *J* = 21.9 Hz), 84.57, 27.42. ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.65. HRMS

(ESI-MS) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}O_2NFS$ 332.1121; Found 332.1125 for the compounds: **1d**.

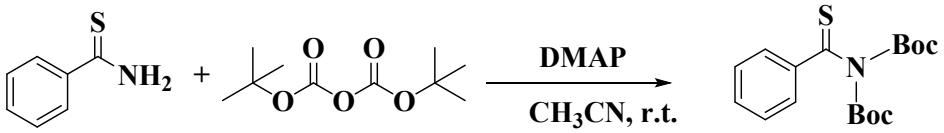


tert-butyl (4-methoxyphenyl)(phenylcarbonothioyl)carbamate (1e). The representative general procedure mentioned above was followed. Purification by flash column chromatography (petroleum ether/ethyl acetate =10/1) yielded the target compound **1e** in 86% (1.47 g) as an orange-red solid; R_f =0.45 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 5.2 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 6.7 Hz, 2H), 3.83 (s, 3H), 1.18 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.03, 159.10, 152.76, 146.41, 136.74, 130.68, 128.92, 128.16, 126.88, 114.72, 84.41, 55.45, 27.29. HRMS (ESI-MS) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}O_3NS$ 344.1320; Found 344.1323 for the compounds: **1e**.



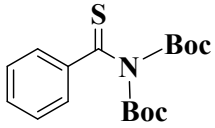
tert-butyl ethyl(phenylcarbonothioyl)carbamate (1f). The representative general procedure mentioned above was followed. Purification by flash column chromatography (petroleum ether/ethyl acetate =30/1) yielded the target compound **1f** in 88% (1.16g) as an orange-yellow solid; R_f =0.76 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 2H), 4.33 (q, *J* = 7.0 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.10 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 209.05, 152.34, 147.21, 129.86, 127.87, 126.37, 83.76, 47.79, 27.15, 12.73. HRMS (ESI-MS) m/z: $[M+H]^+$ Calcd for $C_{14}H_{20}O_2NS$ 266.1215; Found 266.1219 for the compounds: **1f**.

Experimental procedures for the synthesis of tert-butyl (tert-butoxycarbonyl)(phenylcarbonothioyl)carbamate.



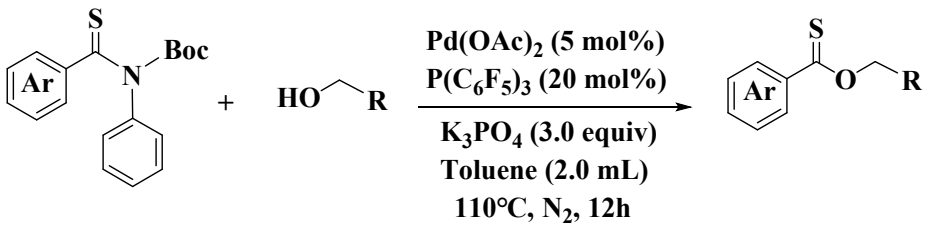
4a

An oven-dried round-bottomed flask equipped with a stir bar was charged with a benzothioamide substrate (5.0 mmol, 1.0 equiv), 4-(dimethylamino)pyridine (1.0 mmol, 0.2 equiv), di-tert-butyl dicarbonate (15.0 mmol, 3.0 equiv) and acetonitrile (10.0 mL). The mixture was allowed to stir at room temperature for 15 h. After the indicated time, the reaction was quenched with aqueous HCl (1.0 M, 25 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. Purification by flash column chromatography (petroleum ether/ethyl acetate) afforded pure product.

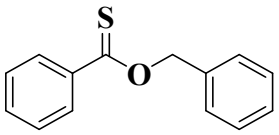


tert-butyl (tert-butoxycarbonyl)(phenylcarbonothioyl)carbamate (4a). The representative general procedure mentioned above was followed. Purification by flash column chromatography (petroleum ether/ethyl acetate =20/1) yielded the target compound **4a** in 68% (1.14 g) as a yellow solid; R_f =0.62 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.8 Hz, 2H), 1.49 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 203.82, 149.30, 142.37, 131.67, 128.22, 127.22, 83.61, 27.96.

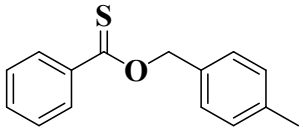
Experimental procedures for the synthesis of thionoester via tert-butyl phenyl(phenylcarbonothioyl)carbamates.



A sealed tube equipped with a stir bar was charged with tert-butyl phenyl(phenylcarbonothioyl)carbamates (0.2 mmol, 1.0 equiv), alcohols (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (5 mol%), $P(C_6F_5)_3$ (20 mol%), K_3PO_4 (3.0 equiv) and toluene (2.0 ml) under a N_2 atmosphere. The reaction mixture was placed in an oil bath and stirred for 12 h at 110 °C. Then the mixture was cooled to room temperature, washed with H_2O (20 mL), saturated NaCl (20 mL) and extracted with CH_2Cl_2 (20 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuo. The desired product was isolated by flash column chromatography using 100% petroleum ether as eluent to afford thionoester and calculate the yields. [$P(C_6F_5)_3$ = Tris(pentafluorophenyl)phosphine]

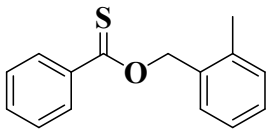


***O*-benzyl benzothioate (3aa).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (100% petroleum ether) yielded the target compound **3aa** in 81% (36.40 mg) as a yellow liqiud; R_f=0.80 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.3 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 7.1 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 3H), 5.71 (s, 2H). These data are corresponding to the literature.[4]

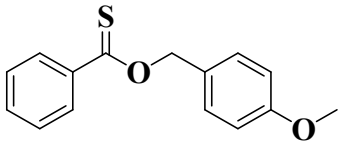


***O*-(4-methylbenzyl) benzothioate (3ab).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (100% petroleum ether) yielded the target compound **3ab** in 74% (35.86 mg) as a yellow liqiud; R_f =0.86 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* =

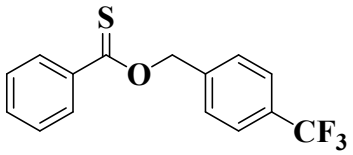
7.3 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 6.8 Hz, 4H), 7.23 (d, *J* = 7.8 Hz, 2H), 5.66 (s, 2H), 2.39 (s, 3H). These data are corresponding to the literature.[5]



***O*-(2-methylbenzyl) benzothioate (3ac).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (100% petroleum ether) yielded the target compound **3ac** in 71% (35.86 mg) as a yellow liqiud; R_f=0.85 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.5 Hz, *J* = 1.2 Hz, 2H), 7.56 (t, *J* = 6.8 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.25 (m, 2H), 5.73 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.06, 138.21, 137.45, 133.40, 132.83, 130.52, 129.75, 128.91, 128.87, 128.13, 126.10, 72.91, 19.08. HRMS (EI-MS) m/z: [M] Calcd for $C_{15}H_{14}OS$ 242.0765; Found 242.0763 for the compounds: **3ac**.

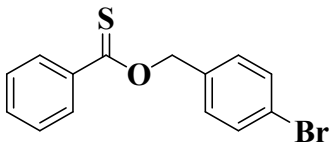


***O*-(4-methoxybenzyl) benzothioate (3ad).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1) yielded the target compound **3ad** in 36% (18.60 mg) as a yellow liqiud; R_f=0.53 (petroleum ether/ethyl acetate = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 5.64 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.18, 159.88, 138.34, 132.77, 130.29, 128.89, 128.08, 127.37, 114.06, 74.14, 55.33. HRMS (EI-MS) m/z: [M] Calcd for $C_{15}H_{14}O_2S$ 258.0715; Found 258.0705 for the compounds: **3ad**.

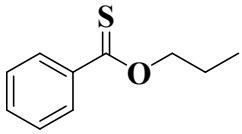


***O*-(4-(trifluoromethyl)benzyl) benzothioate (3ae).** The representative general procedure mentioned above was followed. Purification by flash column

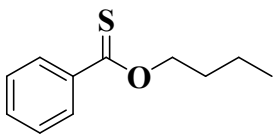
chromatography (100% petroleum ether) yielded the target compound **3ae** in 68% (40.29 mg) as a yellow liqiud; R_f=0.65 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.5 Hz, *J* = 1.2, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.56 (m, 3H), 7.44 – 7.42 (m, 2H), 5.71 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 210.72, 139.35, 138.01, 133.10, 130.63 (q, *J* = 32.6 Hz), 128.92, 128.31, 128.24, 125.68 (q, *J* = 3.8 Hz), 124.00 (q, *J* = 272.0 Hz), 72.79 (s). ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.64. HRMS (EI-MS) m/z: [M] Calcd for $C_{15}H_{11}OF_3S$ 296.0483; Found 296.0483 for the compounds: **3ae**.



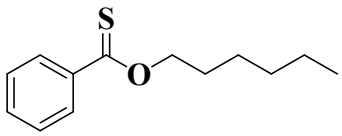
***O*-(4-bromobenzyl) benzothioate (3af).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (100% petroleum ether) yielded the target compound **3af** in 62% (38.09 mg) as a yellow liqiud; R_f=0.71 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.5 Hz, *J* = 1.2 Hz, 2H), 7.54 (t, *J* = 6.6 Hz, 3H), 7.41 – 7.33 (m, 4H), 5.66 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 210.85, 138.10, 134.34, 132.99, 131.87, 130.04, 128.90, 128.19, 122.57, 73.14. HRMS (EI-MS) m/z: [M] Calcd for $C_{14}H_{11}OBrS$ 305.9714; Found 305.9715 for the compounds: **3af**.



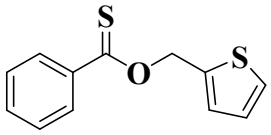
***O*-propyl benzothioate (3ag).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (100% petroleum ether) yielded the target compound **3ag** in 67% (24.15 mg) as a yellow liqiud; R_f=0.78 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.5, *J* = 1.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 – 7.36 (m, 2H), 4.63 (t, *J* = 6.6 Hz, 2H), 1.99 – 1.91 (m, 2H), 1.10 (t, *J* = 7.4 Hz, 3H). These data are corresponding to the literature.[6]



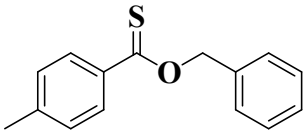
***O*-butyl benzothioate (3ah).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (100% petroleum ether) yielded the target compound **3ah** in 70% (27.28 mg) as a yellow liqiud; R_f=0.76 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.5, *J* = 1.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 – 7.37 (m, 2H), 4.68 (t, *J* = 6.5 Hz, 2H), 1.94 – 1.87 (m, 2H), 1.55 (h, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).These data are corresponding to the literature.[7]



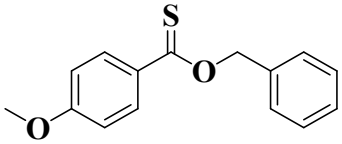
***O*-hexyl benzothioate (3ai).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (100% petroleum ether) yielded the target compound **3ai** in 72% (32.02 mg) as a yellow liqiud; R_f=0.74 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 4.66 (t, *J* = 6.6 Hz, 2H), 1.94 – 1.88 (m, 2H), 1.53 – 1.46 (m, 2H), 1.36 (tt, *J* = 13.0, *J* = 6.4 Hz, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). These data are corresponding to the literature.[5]



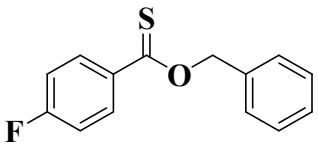
***O*-(thiophen-2-ylmethyl) benzothioate (3aj).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (100% petroleum ether) yielded the target compound **3aj** in 58% (27.18 mg) as a yellow liqiud; R_f=0.63 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.5, *J* = 1.2 Hz, 2H), 7.53 (t, *J* = 6.8 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 3H), 7.22 (d, *J* = 3.4 Hz, 1H), 7.06 – 7.03 (m, 1H), 5.88 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 210.63, 138.09, 137.09, 132.94, 128.98, 128.63, 128.13, 127.17, 126.88, 68.31. HRMS (EI-MS) m/z: [M] Calcd for $C_{12}H_{10}OS_2$ 234.0173; Found 234.0169 for the compounds: **3aj**.



***O*-benzyl 4-methylbenzothioate (3ba).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (100% petroleum ether) yielded the target compound **3ba** in 76% (36.83 mg) as a yellow liqiud; R_f =0.68 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 5.69 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.01, 143.82, 135.90, 135.51, 129.05, 128.87, 128.68, 128.46, 128.36, 73.93, 21.65. HRMS (EI-MS) m/z: [M] Calcd for $C_{15}H_{14}OS$ 242.0765; Found 242.0761 for the compounds: **3ba**.



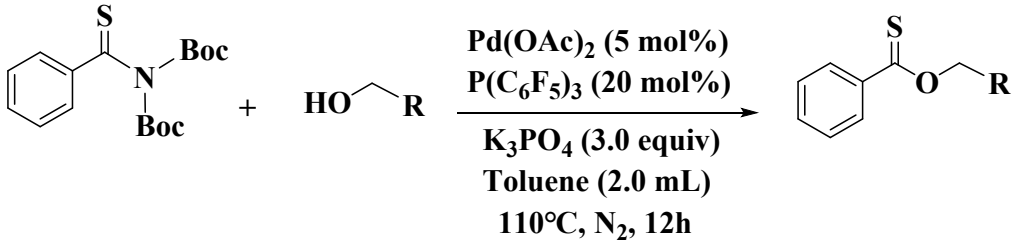
***O*-benzyl 4-methoxybenzothioate (3ca).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1) yielded the target compound **3ca** in 69% (35.65 mg) as a yellow liqiud; R_f =0.52 (petroleum ether/ethyl acetate = 50/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.1 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.40 (m, 3H), 6.86 (d, *J* = 9.1 Hz, 2H), 5.69 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 210.11, 163.74, 135.65, 131.21, 128.71, 128.65, 128.40, 128.32, 113.31, 73.74, 55.51. HRMS (EI-MS) m/z: [M] Calcd for $C_{15}H_{14}O_2S$ 258.0715; Found 258.0716 for the compounds: **3ca.**



***O*-benzyl 4-fluorobenzothioate (3da).** The representative general procedure mentioned above was followed. Purification by flash column chromatography (100% petroleum ether) yielded the target compound **3da** in 87% (42.81 mg) as a yellow liqiud; Rf =0.74 (100% petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (dd, *J* =

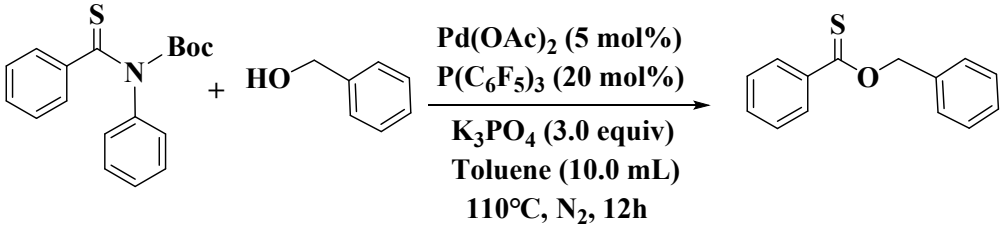
8.9, *J* = 5.5 Hz, 2H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.07 – 7.01 (m, 2H), 5.68 (s, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -106.05.

Experimental procedures for the synthesis of thionoester via tert-butyl (tert-butoxycarbonyl)(phenylcarbonothioyl)carbamate.



A sealed tube equipped with a stir bar was charged with tert-butyl (tert-butoxycarbonyl)(phenylcarbonothioyl)carbamate (0.2 mmol, 1.0 equiv), alcohols (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (5 mol%), $P(C_6F_5)_3$ (20 mol%), K_3PO_4 (3.0 equiv) and toluene (2.0 ml) under a N_2 atmosphere. The reaction mixture was placed in an oil bath and stirred for 12 h at 110 °C. Then the mixture was cooled to room temperature, washed with H_2O (20 mL), saturated NaCl (20 mL) and extracted with CH_2Cl_2 (20 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuo. The desired product was isolated by flash column chromatography using petroleum ether as eluent to afford thionoester and calculate the yields. [$P(C_6F_5)_3$ = Tris(pentafluorophenyl)phosphine]

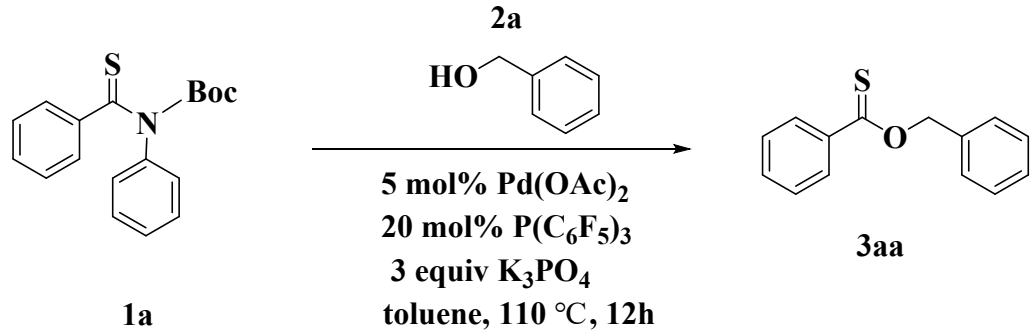
Experimental procedures for the for scale-up of the reaction.

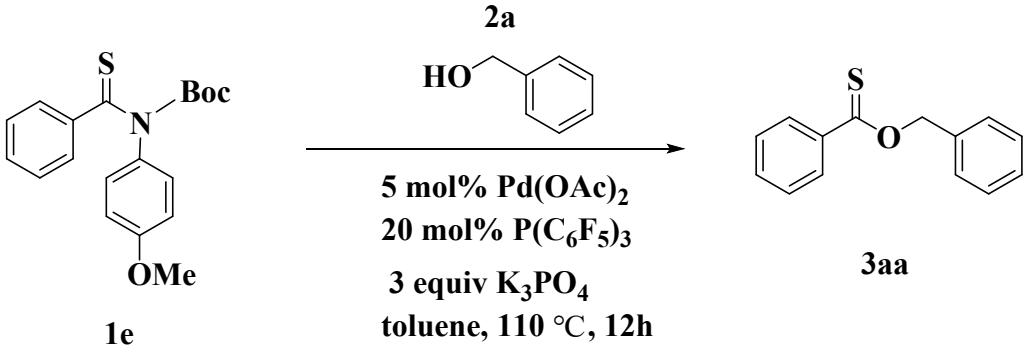


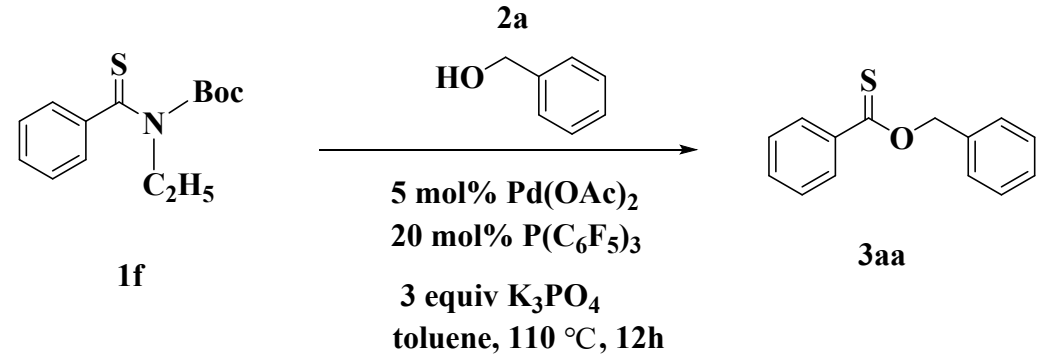
A sealed tube equipped with a stir bar was charged with tert-butyl phenyl(phenylcarbonothioyl)carbamate (5 mmol, 1.0 equiv, 1.57 g), phenylmethanol

(10 mmol, 2.0 equiv, 1.08 g), $Pd(OAc)_2$ (5 mol%, 56 mg), $P(C_6F_5)_3$ (20 mol%, 0.53 g), K_3PO_4 (3.0 equiv, 3.18 g) and toluene (10.0 ml) under a N_2 atmosphere. The reaction mixture was placed in an oil bath and stirred for 12 h at 110 °C. Then the mixture was cooled to room temperature, washed with H_2O (20 mL), saturated NaCl (20 mL) and extracted with CH_2Cl_2 (20 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuo. The desired product was isolated by flash column chromatography using petroleum ether as eluent to afford *O*-benzyl benzothioate (yellow liquid) and the yields is 75% (85.6 mg). [$P(C_6F_5)_3$ = Tris(pentafluorophenyl)phosphine]

Experimental procedures for control reaction.







A sealed tube equipped with a stir bar was charged with thioamides (5 mmol, 1.0 equiv, 1.57 g), phenylmethanol (10 mmol, 2.0 equiv, 1.08 g), $Pd(OAc)_2$ (5 mol%, 56 mg), $P(C_6F_5)_3$ (20 mol%, 0.53 g), K_3PO_4 (3.0 equiv, 3.18 g) and toluene (10.0 ml) under a N_2 atmosphere. The reaction mixture was placed in an oil bath and stirred for 12 h at 110 °C. Then the mixture was cooled to room temperature, washed with H_2O (20 mL), saturated NaCl (20 mL) and extracted with CH_2Cl_2 (20 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuo. The desired product was isolated by flash column

chromatography using petroleum ether as eluent to afford *O*-benzyl benzothioate (yellow liquid) and the yields were calculated. [$P(C_6F_5)_3$ = Tris(pentafluorophenyl)phosphine]

References

[1] H. Jin, X. Chen, C. Qian, X. Ge, S. Zhou, *Eur. J. Org. Chem.* **2021**, *2021*, 3403-3406.

[2] N. T. Do, K. M. Tran, H. T. Phan, T. A. To, T. T. Nguyen, N. T. Phan, *Org. Biomol. Chem.* **2019**, *17*, 8987-8991.

[3] A. A. Folgueiras-Amador, X.-Y. Qian, H. Xu, T. Wirth, *Chem. Eur. J.* **2018**, *24*, 487-491.

[4] M. A. Shalaby, H. Rapoport, *J. Org. Chem.* **1999**, *64*, 1065-1070.

[5] J. J. Newton, R. Britton, C. M. Friesen, *J. Org. Chem.* **2018**, *83*, 12784-12792.

[6] S.-K. Yeo, B.-G. Choi, J.-D. Kim, J.-H. Lee, *Bull. Korean Chem. Soc.* **2002**, *23*, 1029-1030.

[7] J. Newton, D. Driedger, M. B. Nodwell, P. Schaffer, R. E. Martin, R. Britton, C. M. Friesen, *Chem. Eur. J.* **2019**, *25*, 15993-15997.

Copies of ^{1}H, ^{13}C, ^{19}F, NMR, Mass Spectra and HRMS

Figure S1. *N*-phenylbenzothioamide (1)

^{1}H NMR (600 MHz, DMSO-d_6)

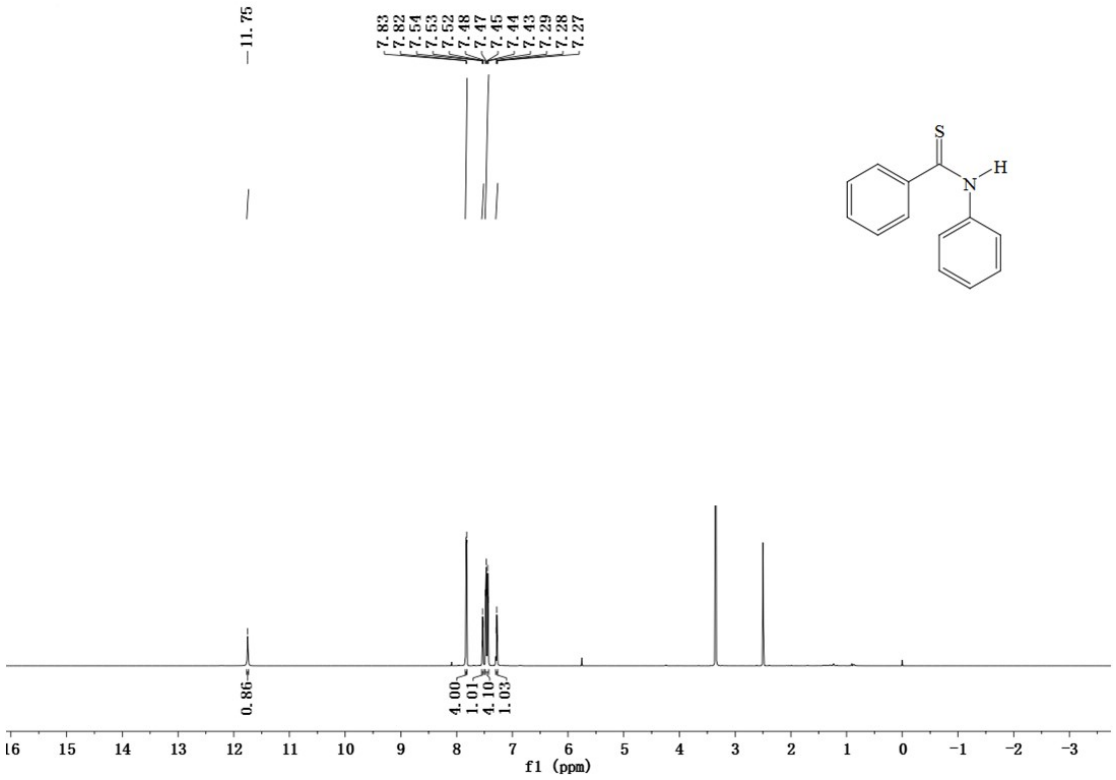


Figure S2. 4-methyl-*N*-phenylbenzothioamide (2)
^{1}H NMR (600 MHz, DMSO-d_6)

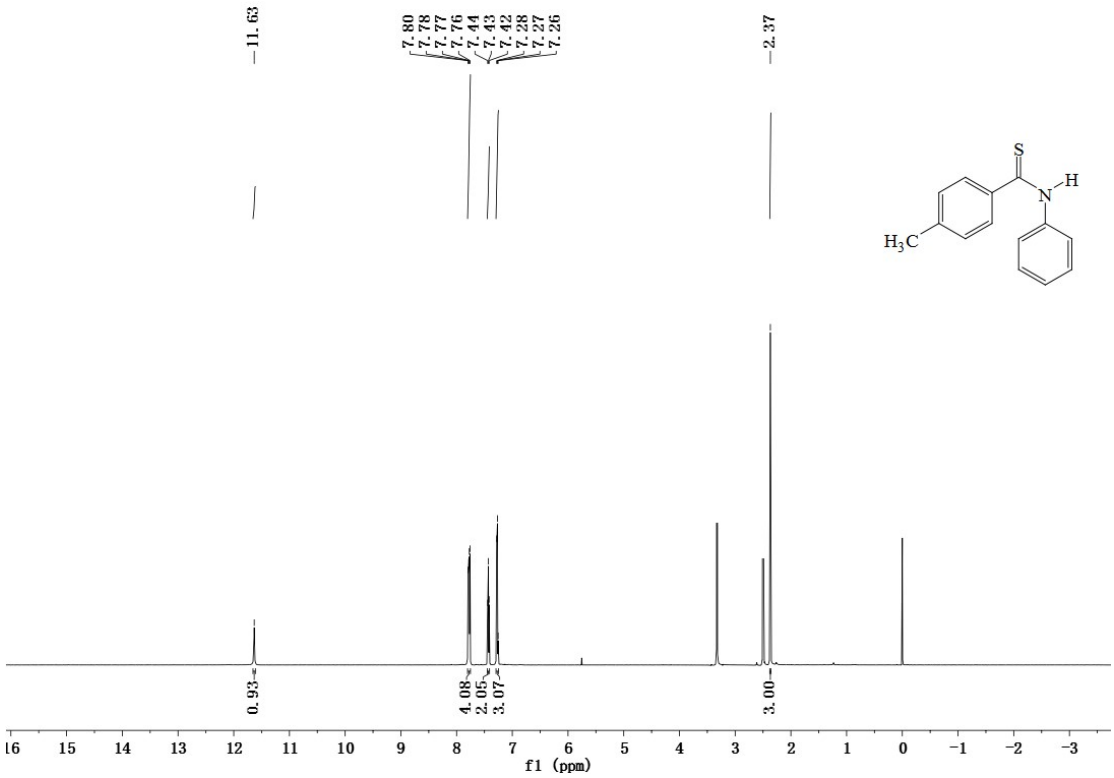


Figure S3. 4-methoxy-*N*-phenylbenzothioamide (3)
^{1}H NMR (600 MHz, DMSO-d_6)

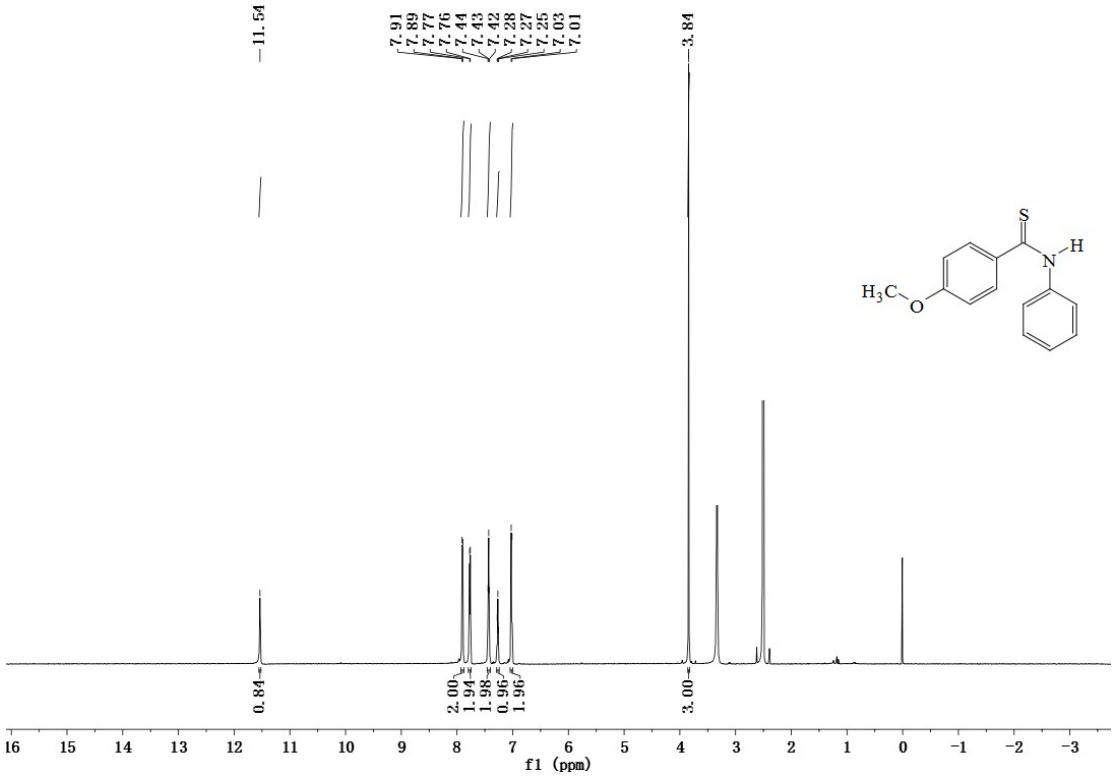


Figure S4. tert-butyl phenyl(phenylcarbonothioyl)carbamate (1a)
^{1}H NMR (600 MHz, $CDCl_3$)

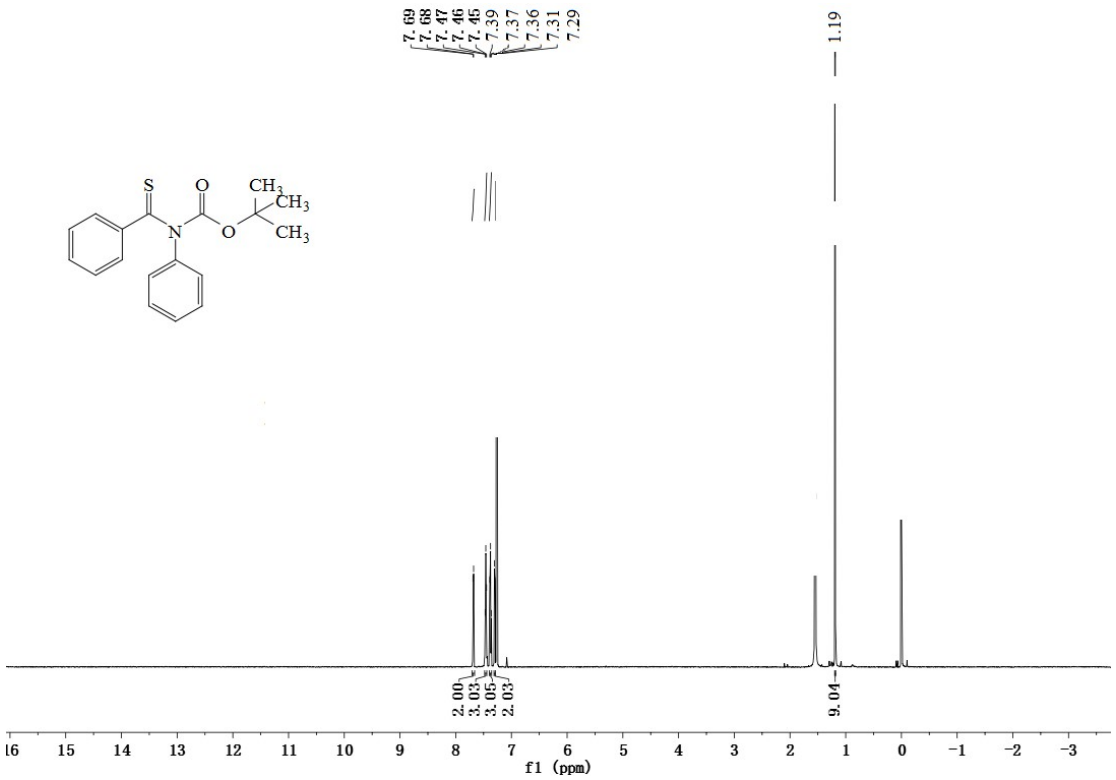


Figure S5. tert-butyl phenyl(phenylcarbonothioyl)carbamate (1a)

^{13}C NMR (150 MHz, $CDCl_3$)

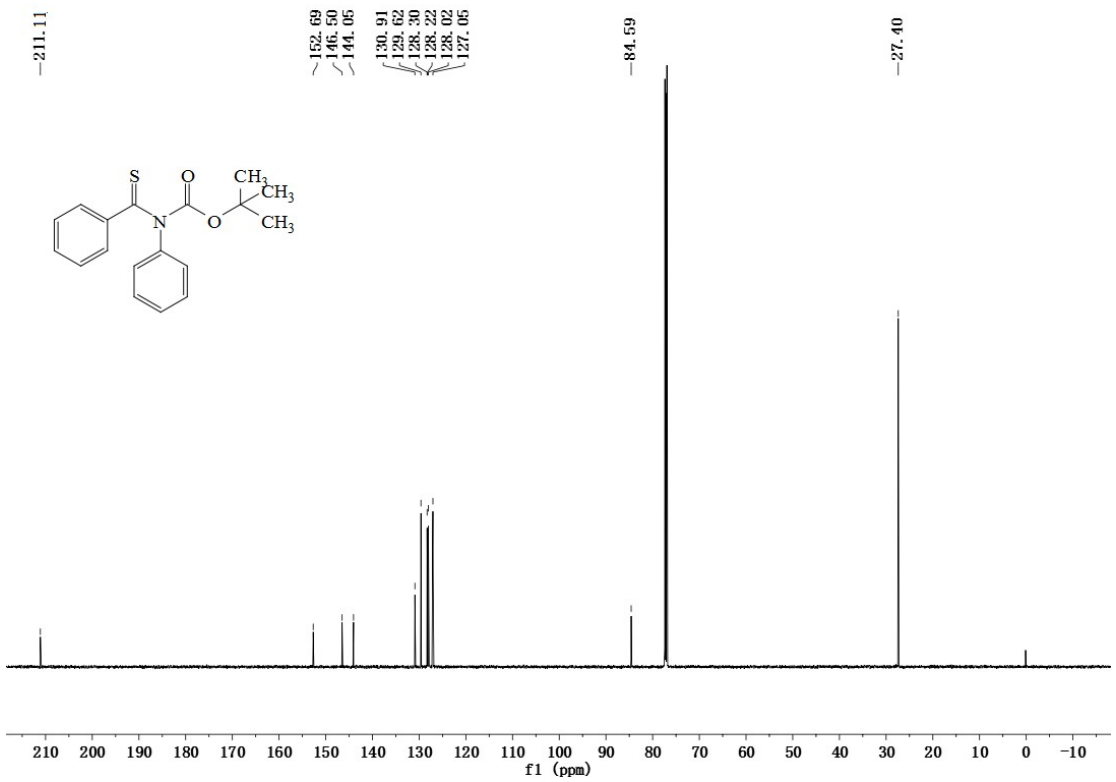


Figure S6. tert-butyl phenyl(phenylcarbonothioyl)carbamate (1a)

Mass spectrum

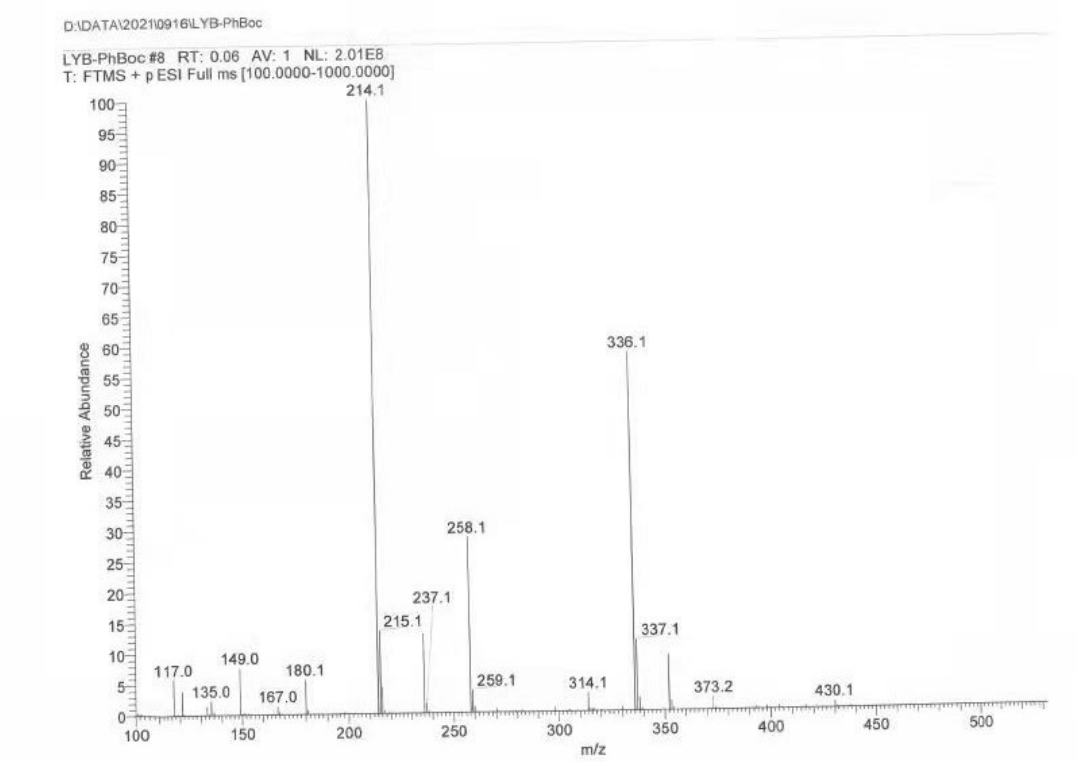


Figure S7. tert-butyl phenyl(phenylcarbonothioyl)carbamate (1a) HRMS

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution ESI-MS REPORT

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: E212376

Sample Serial Number: LYB-PhBoc

Operator: Songw Date: 2021/09/16

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 336.1029

m/z= 331.1029-341.1029

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
336.1029	336.1029	0.21	9.5	$C_{18}H_{19}O_2NNaS$

Figure S8. tert-butyl (4-methylphenylcarbonothioyl)(phenyl)carbamate (1b)

^{1}H NMR (600 MHz, $CDCl_3$)

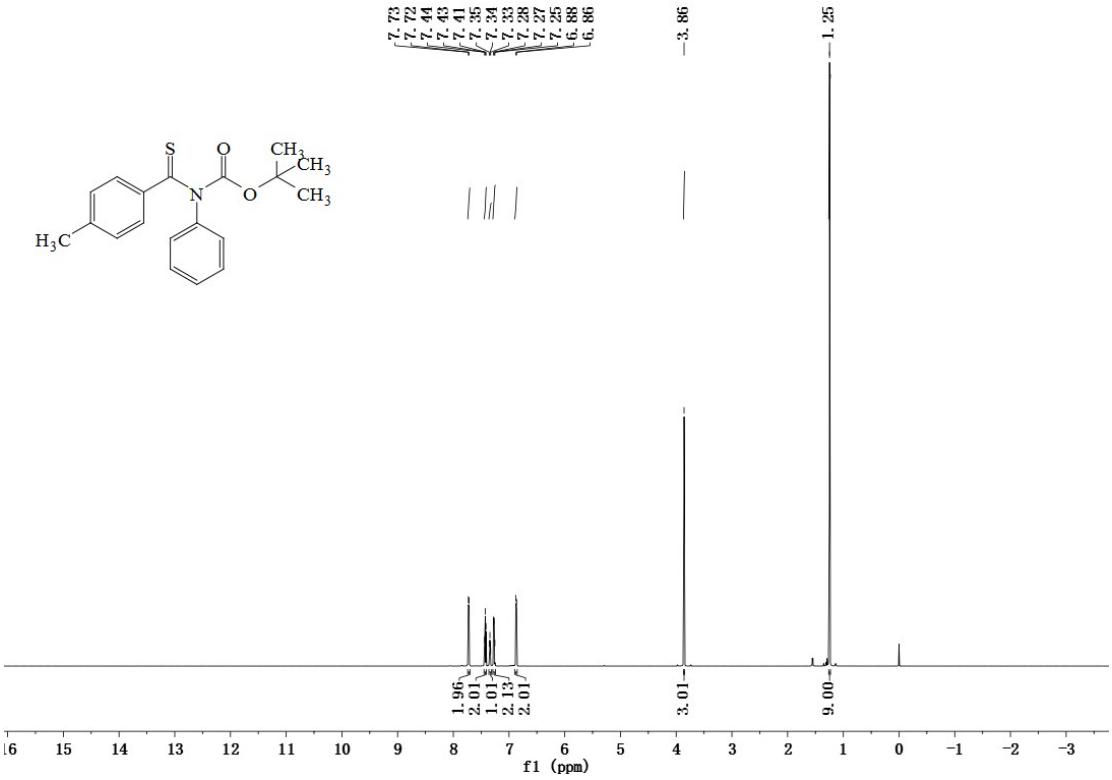


Figure S9. tert-butyl (4-methylphenylcarbonothioyl)(phenyl)carbamate (1b)

^{13}C NMR (150 MHz, $CDCl_3$)

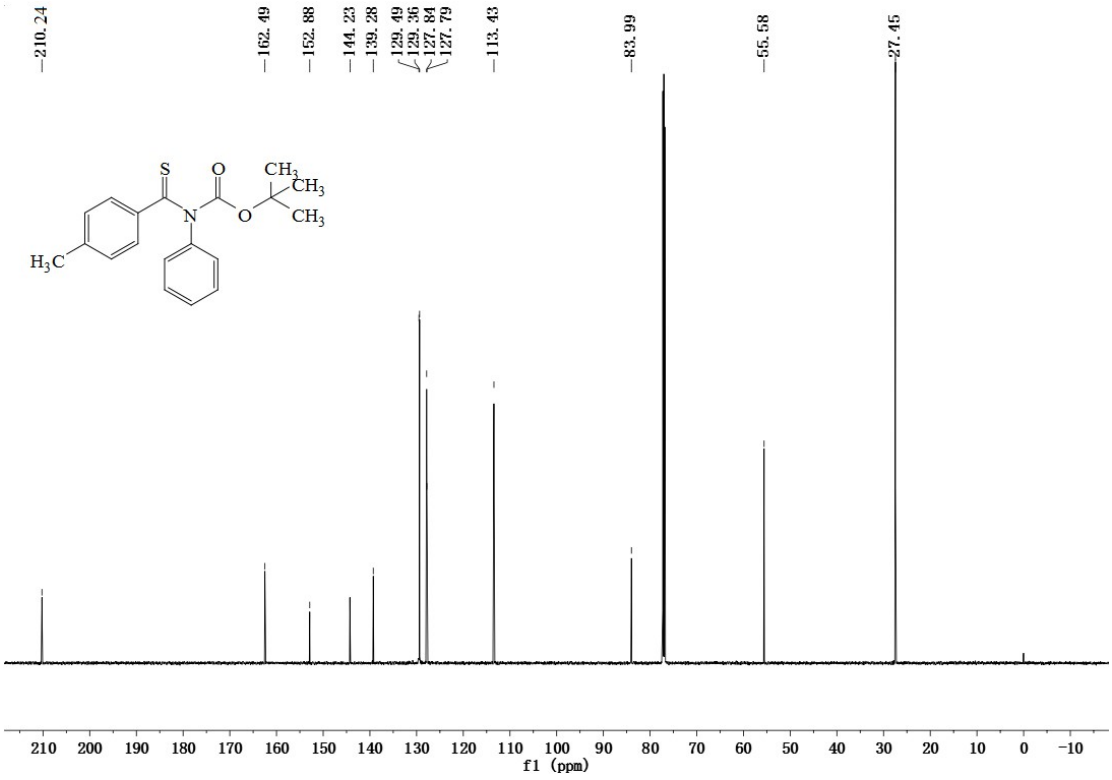


Figure S10. tert-butyl (4-methylphenylcarbonothioyl)(phenyl)carbamate (1b) Mass spectrum

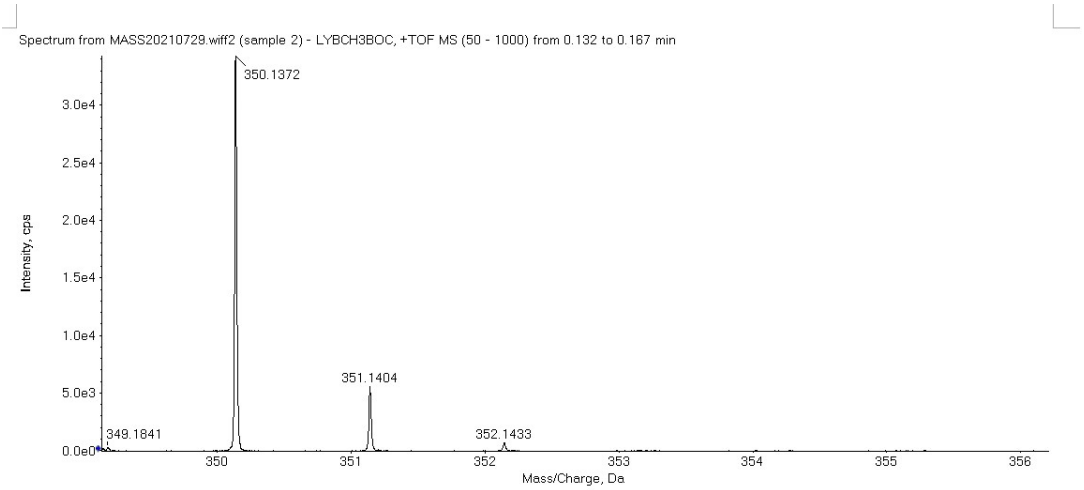


Figure S11. tert-butyl (4-methoxyphenylcarbonothioyl)(phenyl)carbamate (1c)

^{1}H NMR (600 MHz, $CDCl_3$)

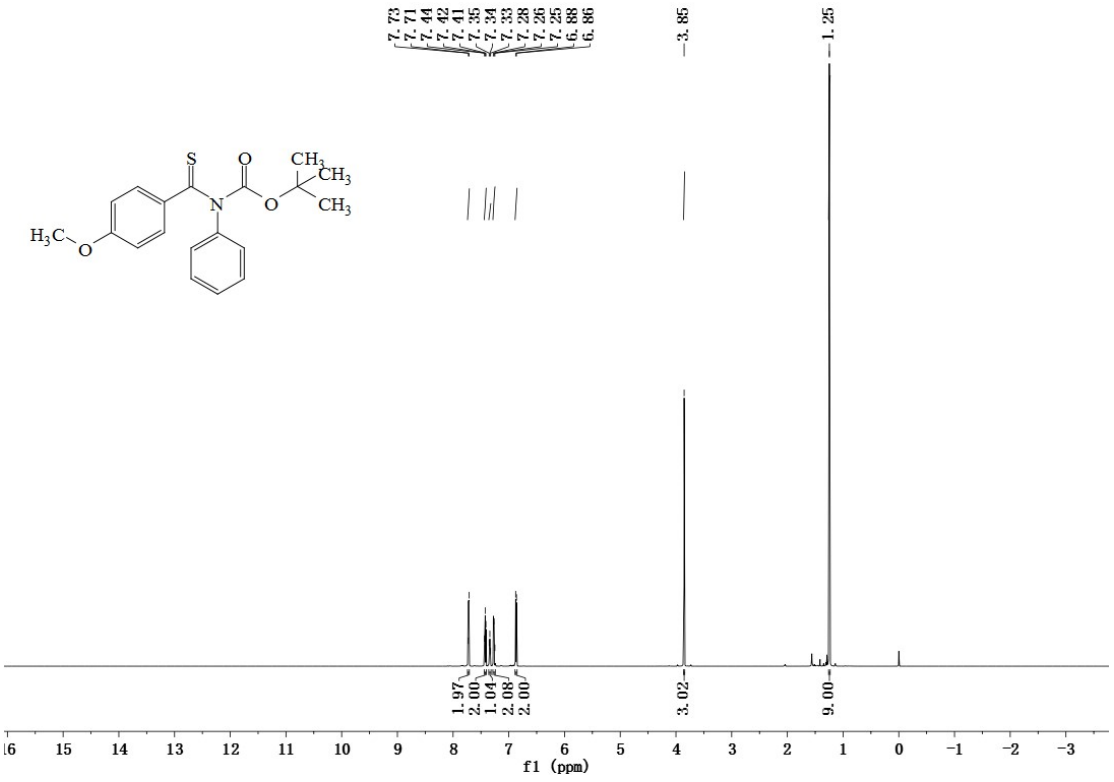


Figure S12. tert-butyl (4-methoxyphenylcarbonothioyl)(phenyl)carbamate (1c)

^{13}C NMR (150 MHz, $CDCl_3$)

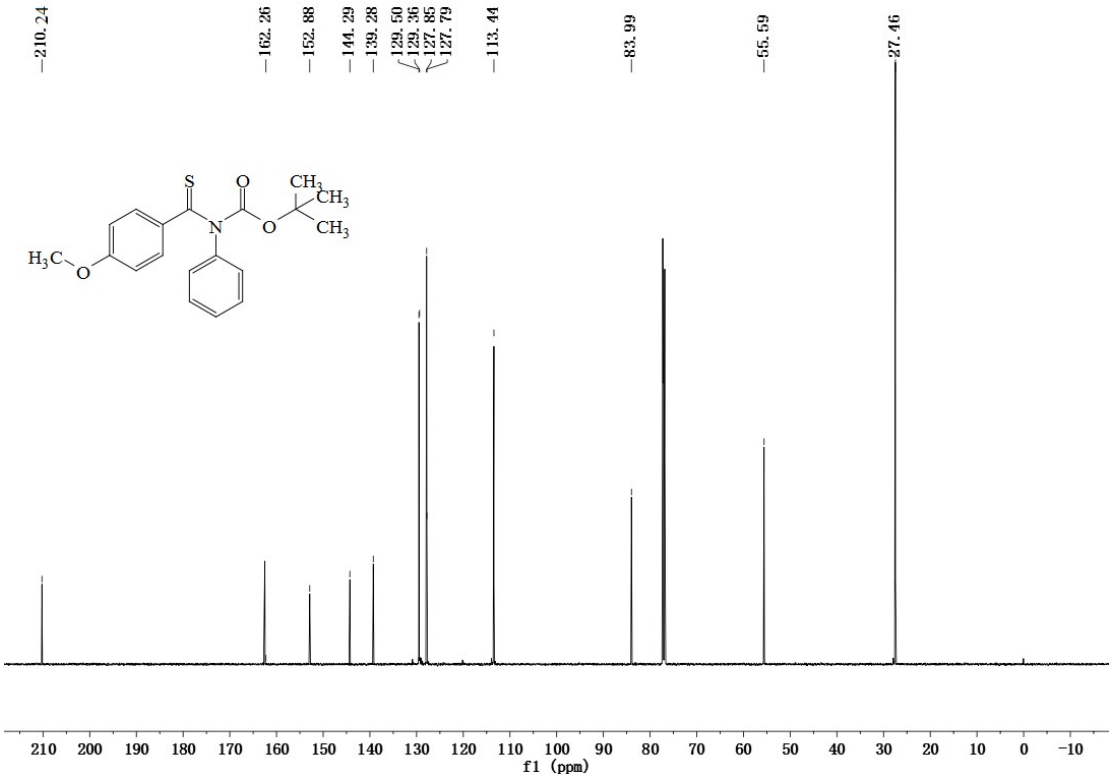
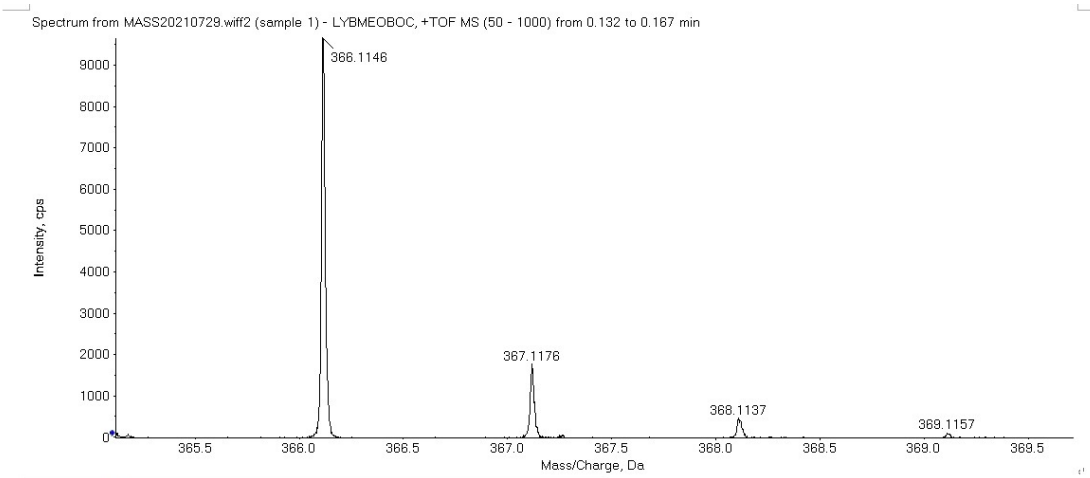


Figure S13. tert-butyl (4-methoxyphenylcarbonothioyl)(phenyl)carbamate (1c) Mass spectrum



Hit	Formula	m/z	RDB	ppm	MS Rank	MSMS ppm	MSMS Rank	Found
1	C19H21NO3S	366.1134	10.0	3.2	1			NA/NA

Figure S14. tert-butyl (4-fluorophenylcarbonothioyl)(phenyl)carbamate (1d) ^{1}H NMR (600 MHz, $CDCl_3$)

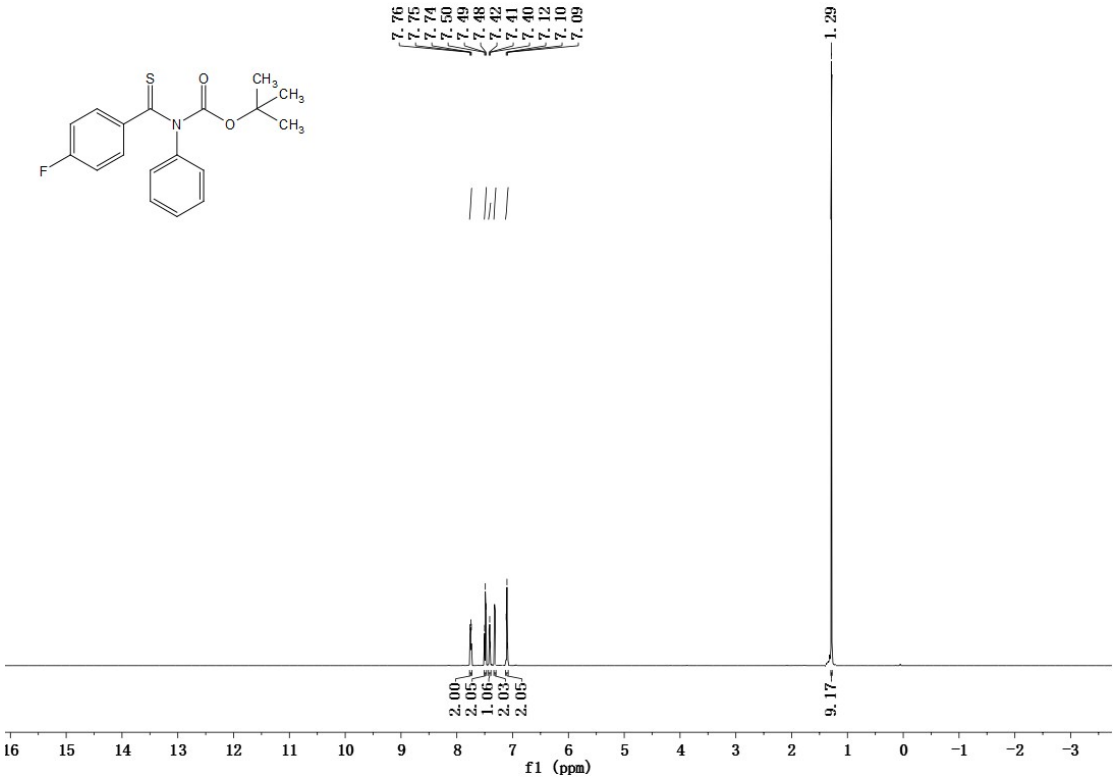


Figure S15. tert-butyl (4-fluorophenylcarbonothioyl)(phenyl)carbamate (1d) ^{13}C NMR (150 MHz, $CDCl_3$)

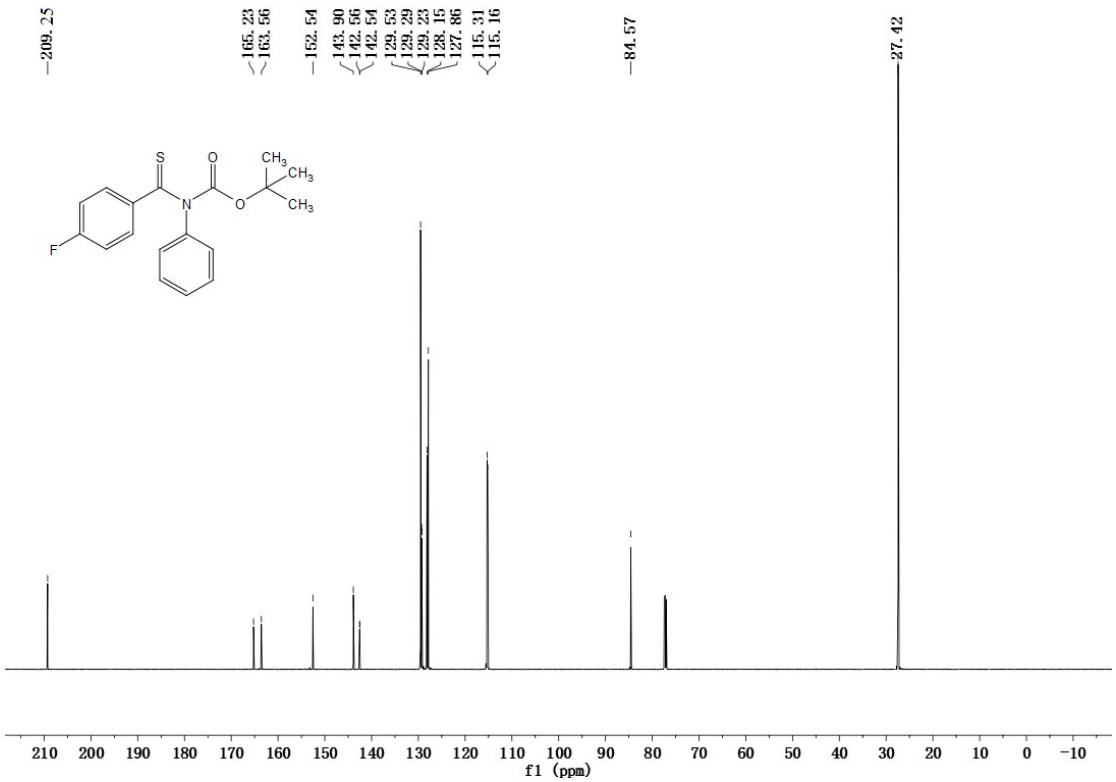


Figure S16. tert-butyl (4-fluorophenylcarbonothioyl)(phenyl)carbamate (1d) ^{19}F NMR (565 MHz, $CDCl_3$)

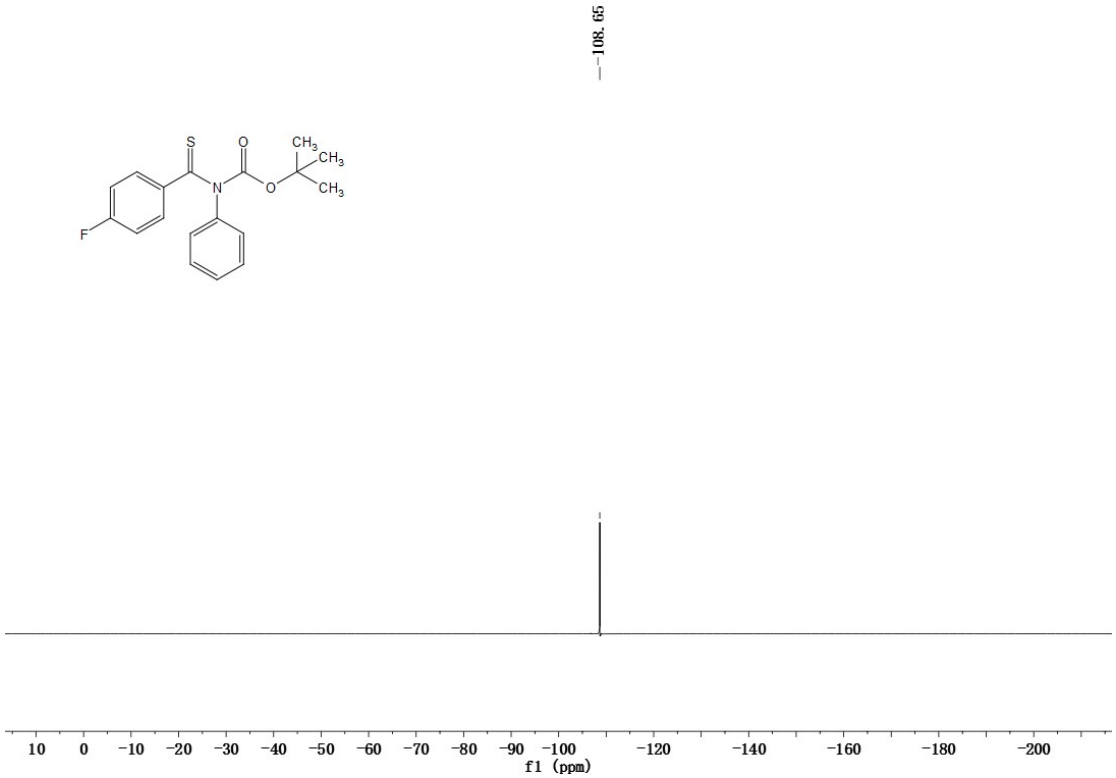


Figure S17. tert-butyl (4-fluorophenylcarbonothioyl)(phenyl)carbamate (1d)

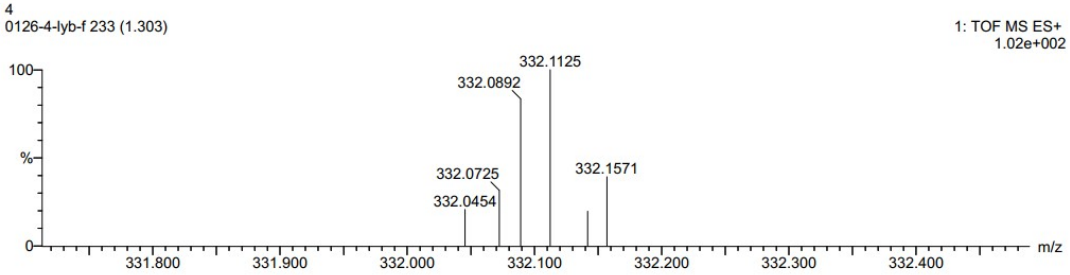
HRMS

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
550 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 18-18 H: 5-45 N: 1-2 O: 1-9 S: 1-3 I: 0-3 F: 1-12

4
0126-4-lyb-f 233 (1.303)



Minimum:				-1.5				
Maximum:		5.0	30.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
332.1125	332.1121	0.4	1.2	9.5	31.0	n/a	n/a	C18 H19 N O2 S F

Figure S18. tert-butyl (4-methoxyphenyl)(phenylcarbonothioyl)carbamate (1e)

^{1}H NMR (600 MHz, $CDCl_3$)

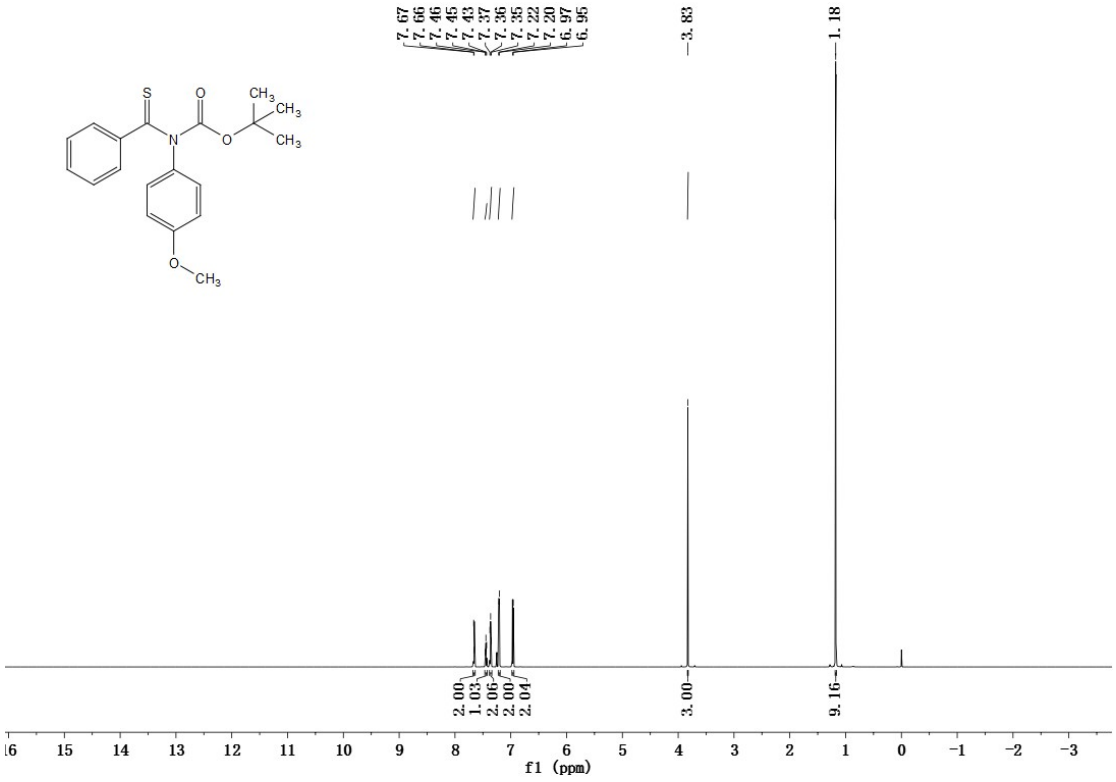


Figure S19. tert-butyl (4-methoxyphenyl)(phenylcarbonothioyl)carbamate (1e)

^{13}C NMR (150 MHz, $CDCl_3$)

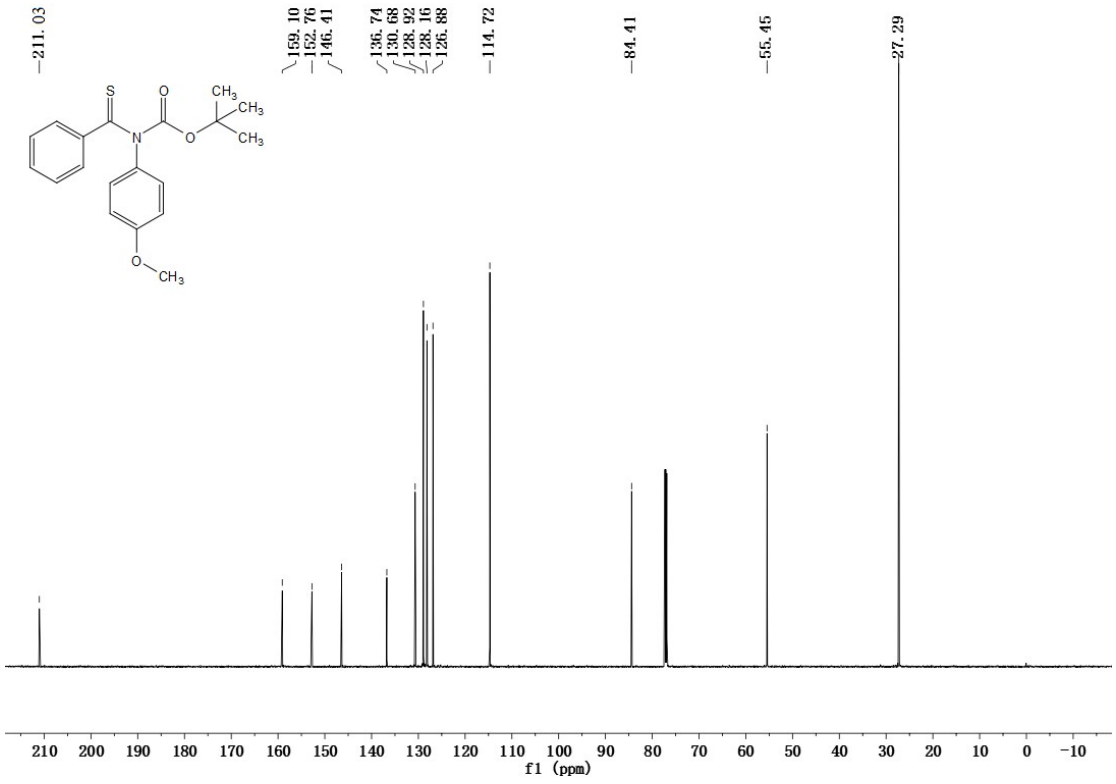


Figure S20. tert-butyl (4-methoxyphenyl)(phenylcarbonothioyl)carbamate (1e)

HRMS

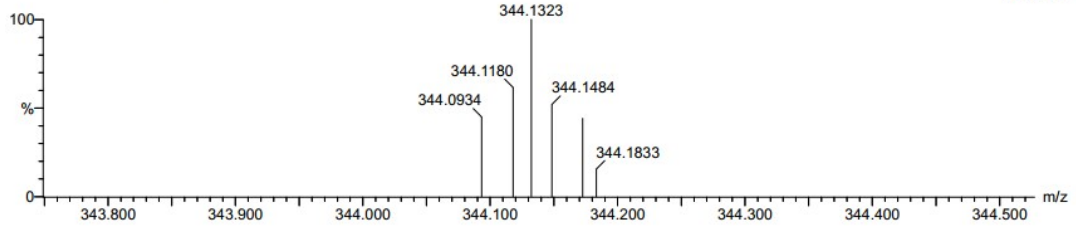
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
101 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 19-19 H: 5-45 N: 1-2 O: 1-9 S: 1-3 I: 0-3

4
0126-4-lyb-phboc 164 (0.925)

1: TOF MS ES+
1.01e+003



Minimum:			-1.5		
Maximum:		5.0	30.0	50.0	

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
344.1323	344.1320	0.3	0.9	9.5	58.5	n/a	n/a	C19 H22 N O3 S

Figure S21. tert-butyl ethyl(phenylcarbonothioyl)carbamate (1f)

^{1}H NMR (600 MHz, $CDCl_3$)

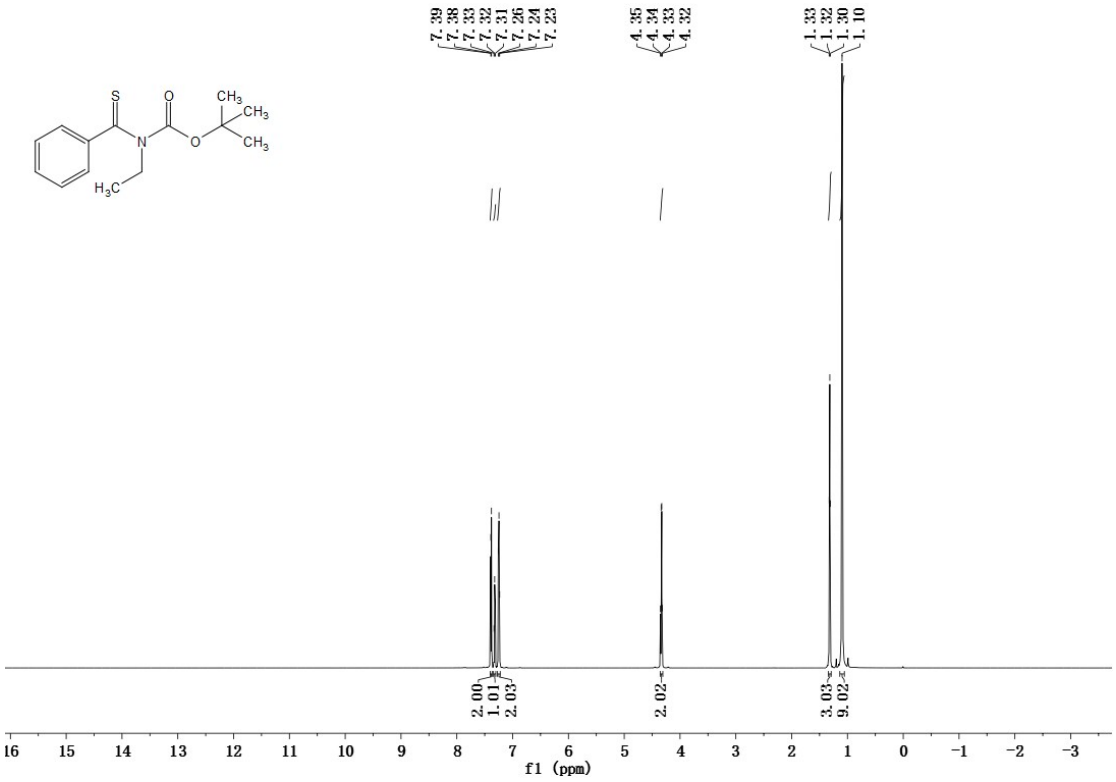


Figure S22. tert-butyl ethyl(phenylcarbonothioyl)carbamate (1f)

^{13}C NMR (150 MHz, $CDCl_3$)

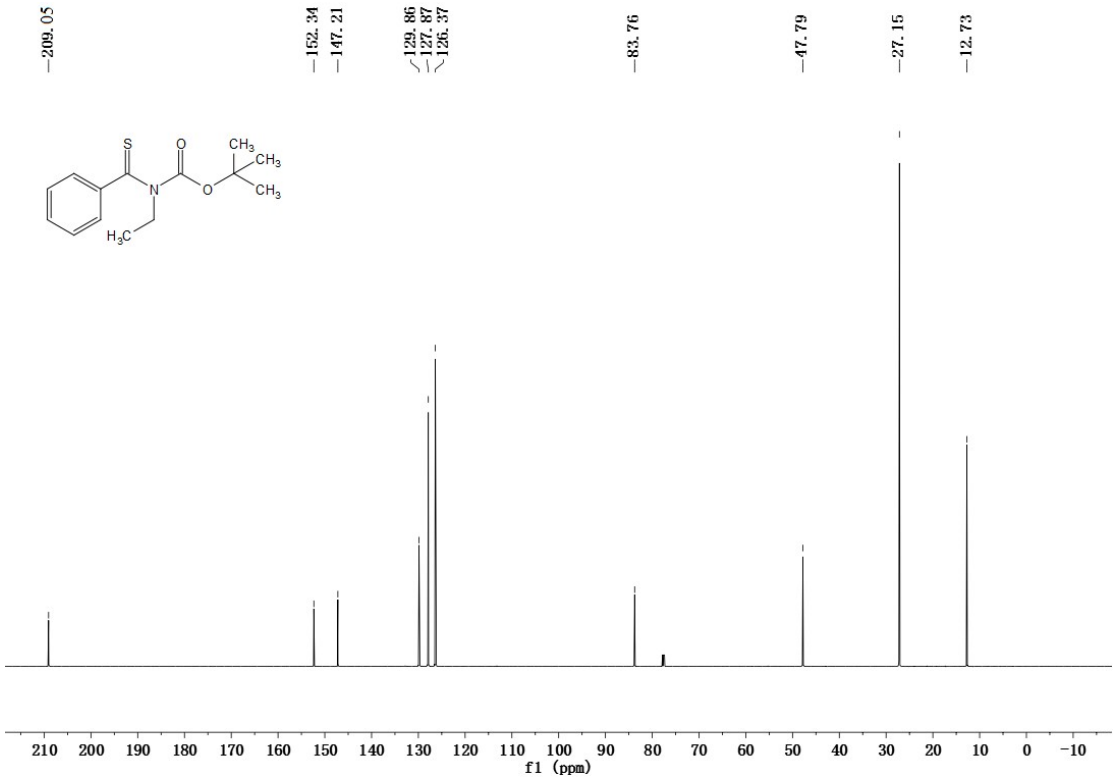


Figure S23. tert-butyl ethyl(phenylcarbonothioyl)carbamate (1f)

HRMS

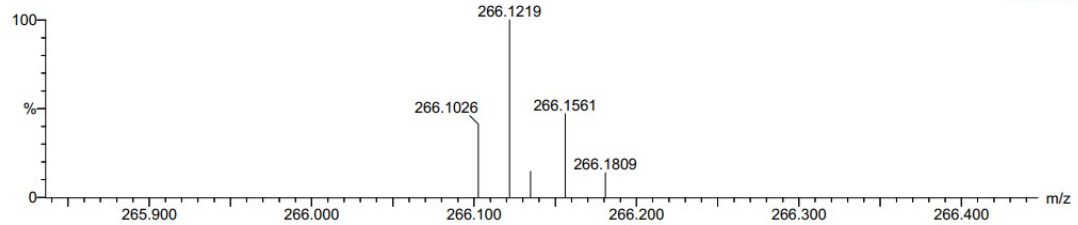
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
66 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 14-14 H: 5-45 N: 1-2 O: 1-9 S: 1-3 I: 0-3

4
0126-lyb-ya 121 (0.692)

1: TOF MS ES+
1.44e+002



Minimum:				-1.5				
Maximum:		5.0	30.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
266.1219	266.1215	0.4	1.5	5.5	38.6	n/a	n/a	C14 H20 N O2 S

Figure S24. tert-butyl (tert-butoxycarbonyl)(phenylcarbonothioyl)carbamate (4a)

^{1}H NMR (600 MHz, $CDCl_3$)

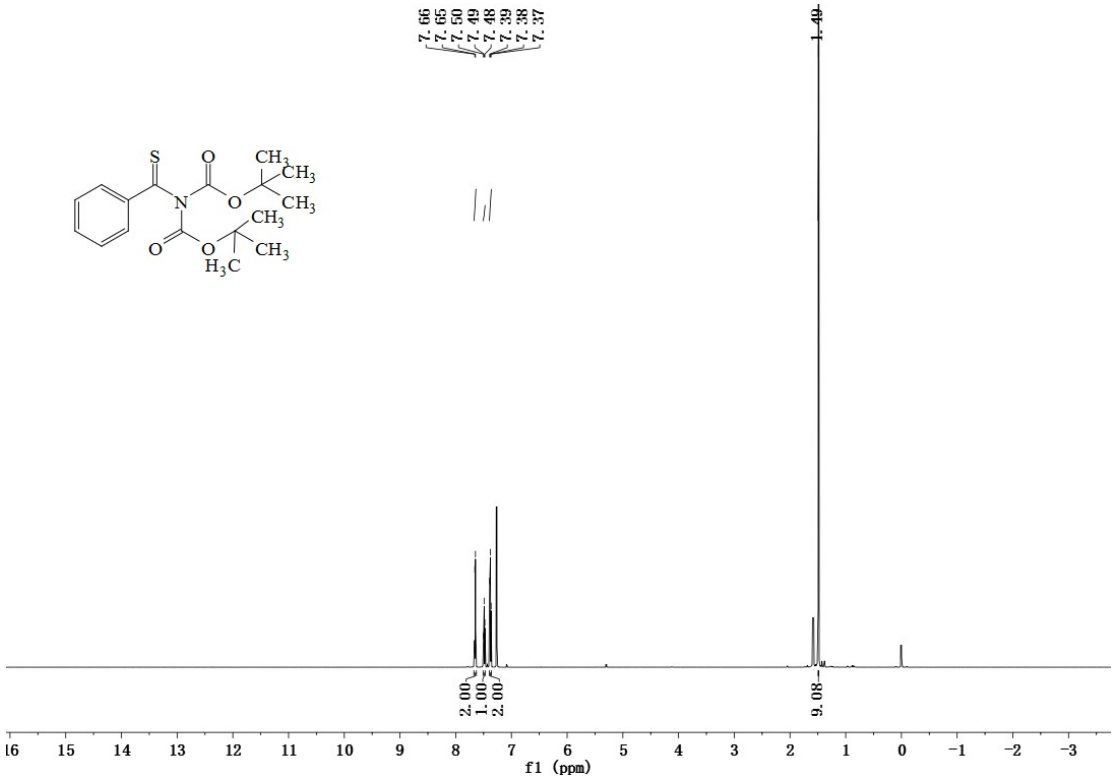


Figure S25. tert-butyl (tert-butoxycarbonyl)(phenylcarbonothioyl)carbamate (4a)
^{13}C NMR (101 MHz, $CDCl_3$)

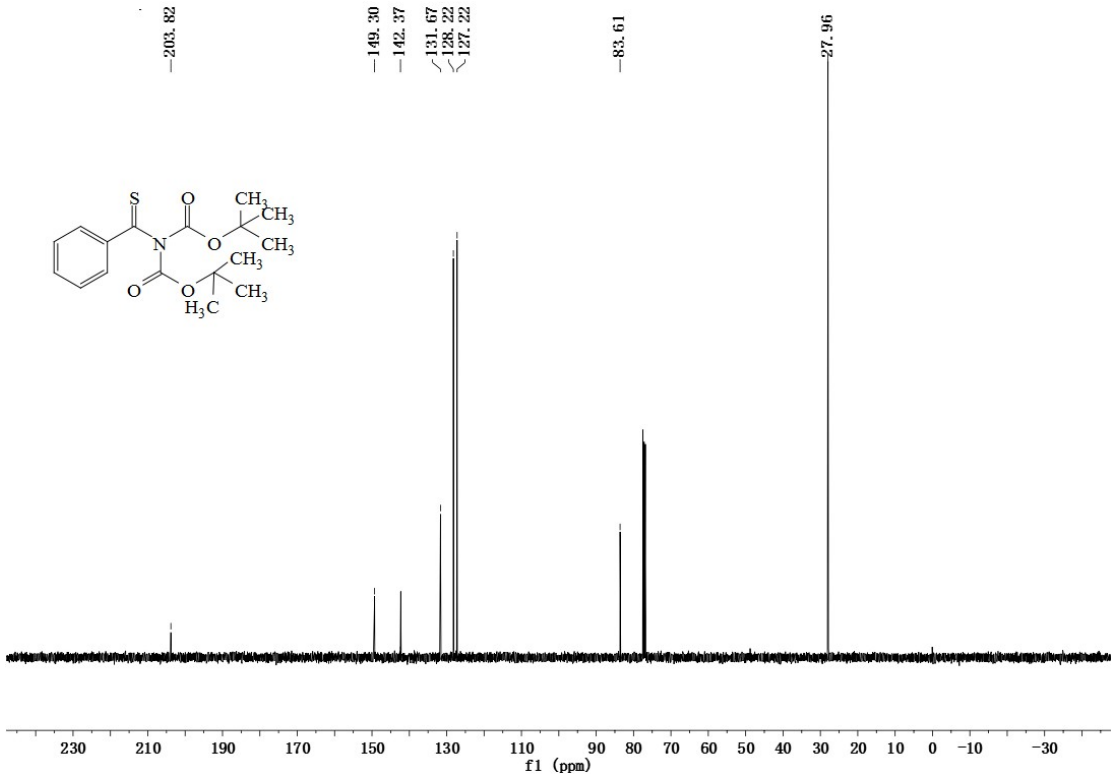


Figure S26. *O*-benzyl benzothioate (3aa)
^{1}H NMR (600 MHz, $CDCl_3$)

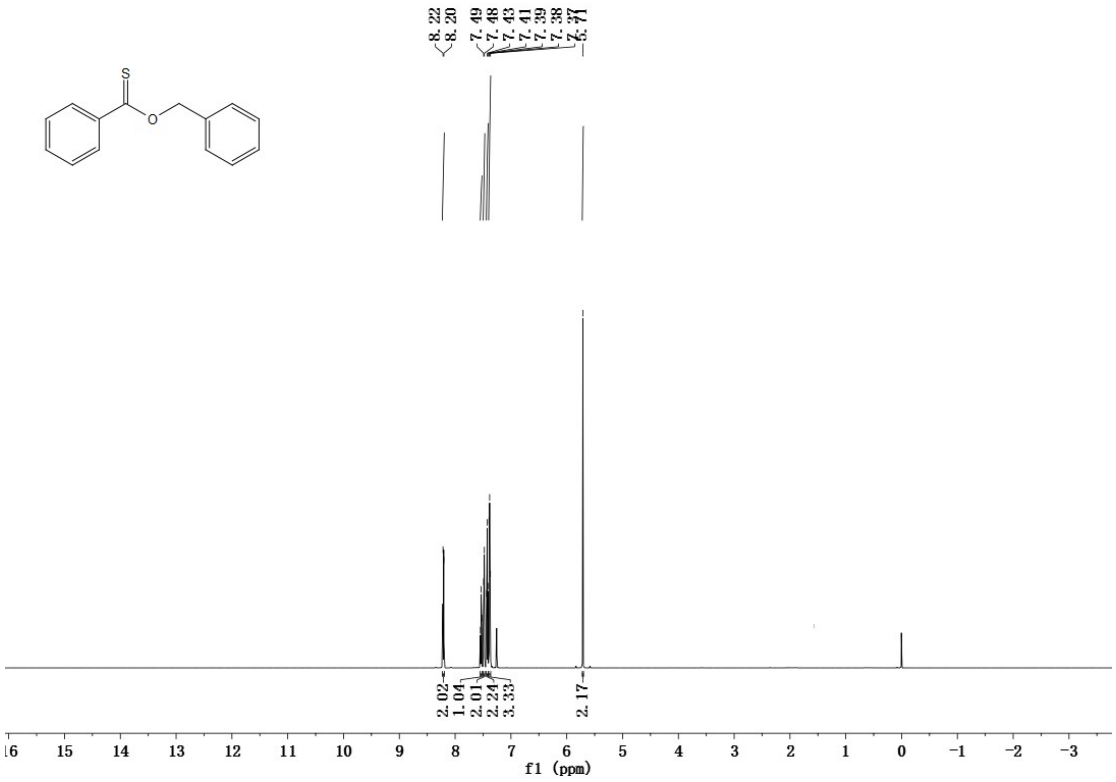


Figure S27. *O*-(4-methylbenzyl) benzothioate (3ab)
^{1}H NMR (600 MHz, $CDCl_3$)

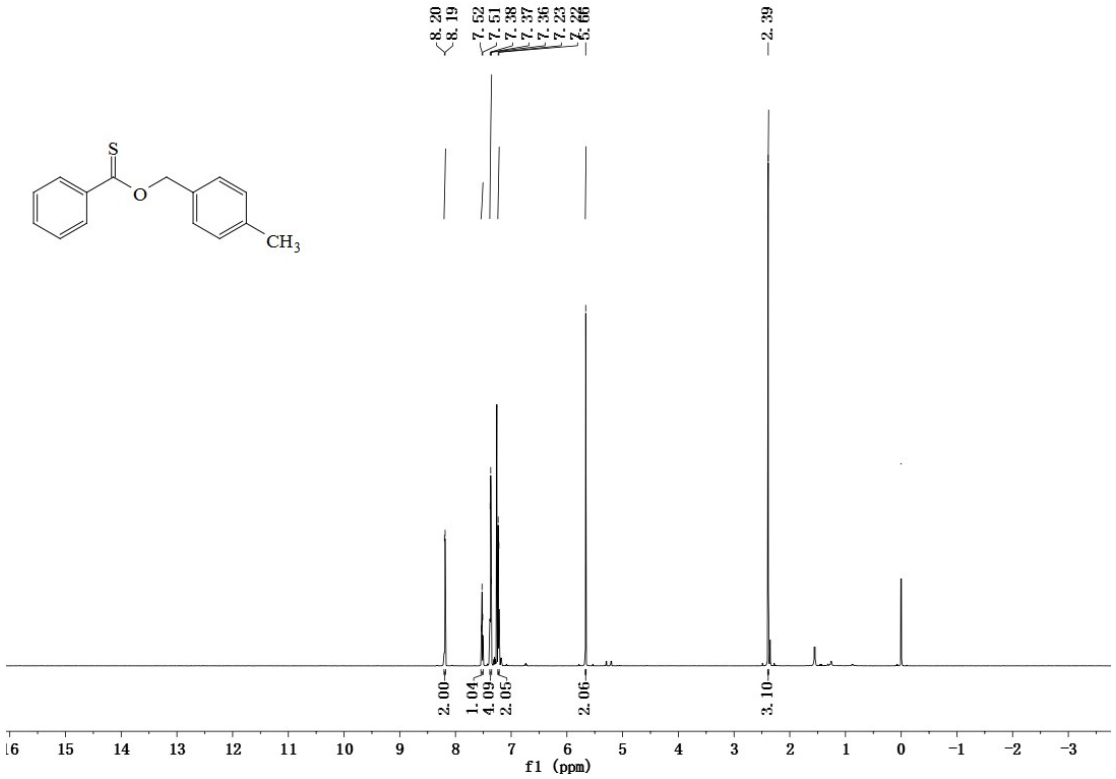


Figure S28. *O*-(2-methylbenzyl) benzothioate (3ac)
^{1}H NMR (600 MHz, $CDCl_3$)

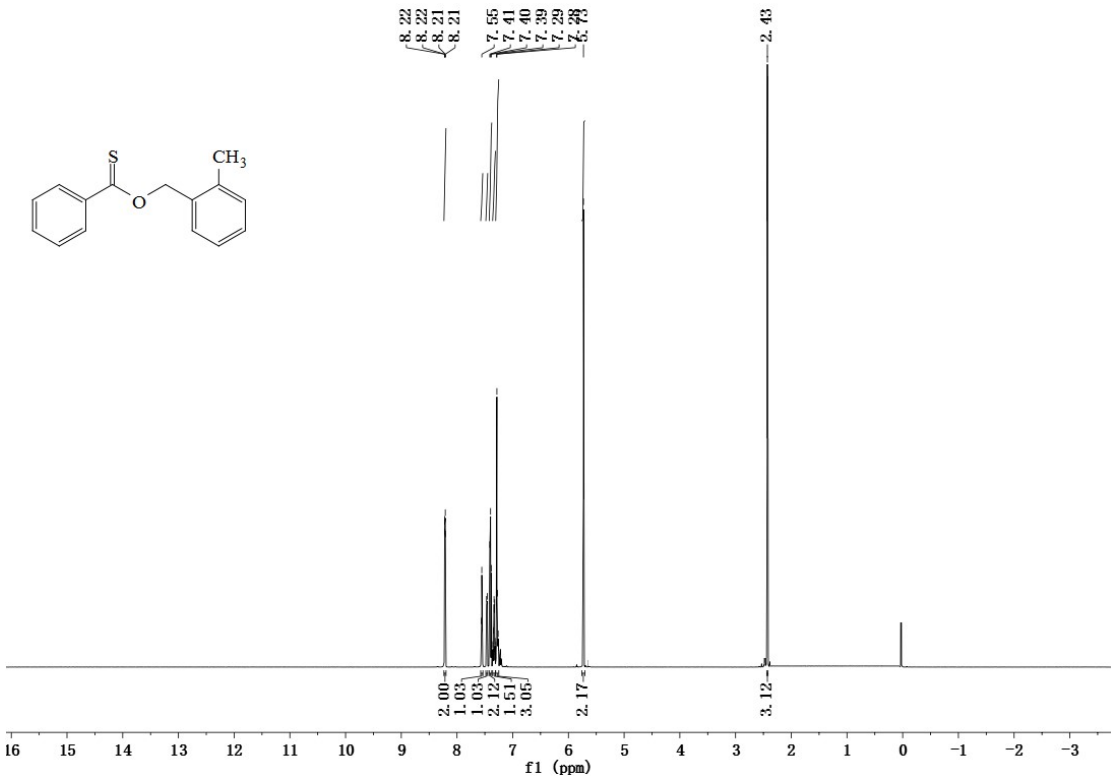


Figure S29. *O*-(2-methylbenzyl) benzothioate (3ac)

^{13}C NMR (150 MHz, $CDCl_3$)

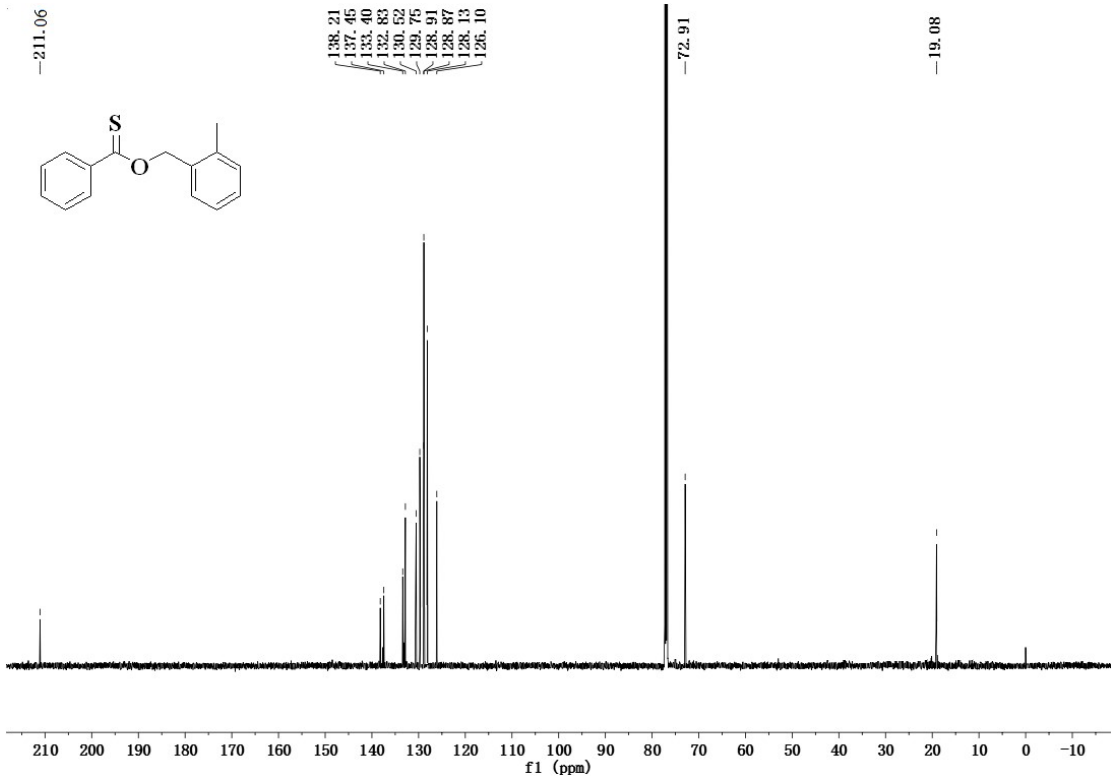


Figure S30. *O*-(2-methylbenzyl) benzothioate (3ac)

Mass spectrum

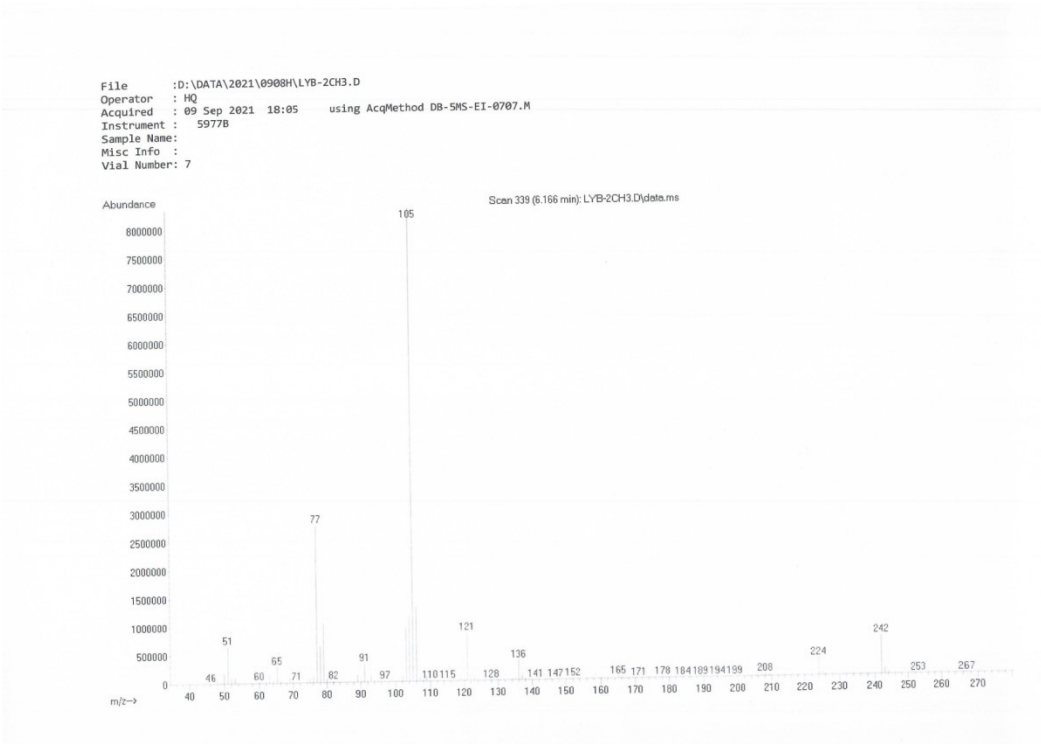


Figure S31. *O*-(2-methylbenzyl) benzothioate (3ac)
HRMS

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution EI-MS Report
Low Resolution EI-MS Report

Instrument: Waters Premier GC-TOF MS

Operation Mode: **EI** Positive Ion Mode (Electron Energy: 70eV)

Card Serial Number: GCT-P-EI-T21-2408

Sample Serial Number: 2019551-LYB-2CH3

Operator: Li Date: 2021/09/14

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
242.0763	242.0762	0.57	-5.5	$C_5H_{22}O_3NBrF$
	242.0760	1.05	2.0	$C_9H_{13}O_4F_3$
	242.0760	1.29	9.0	$C_{15}H_{14}OS$
	242.0759	1.47	-9.5	$C_3H_{24}NBrF_3S$
	242.0771	-3.25	-13.5	$H_{25}ONBrF_4S$

Figure S32. *O*-(4-methoxybenzyl) benzothioate (3ad)
^{1}H NMR (600 MHz, $CDCl_3$)

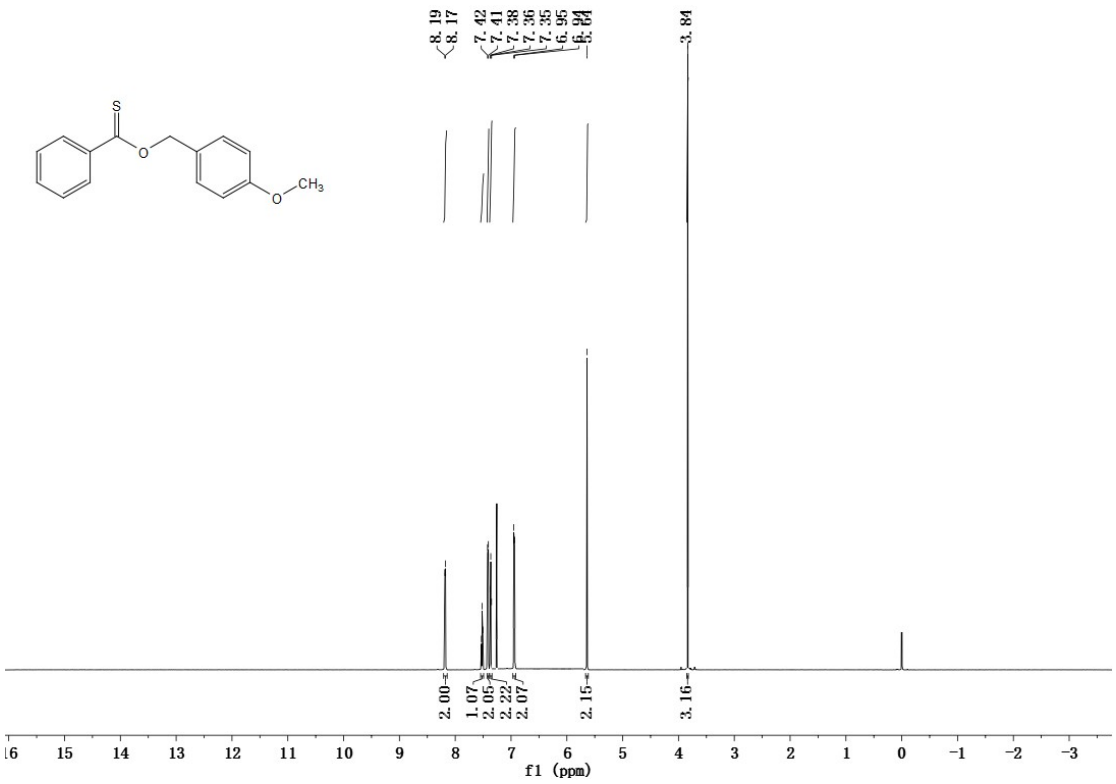


Figure S33. *O*-(4-methoxybenzyl) benzothioate (3ad)

^{13}C NMR (150 MHz, $CDCl_3$)

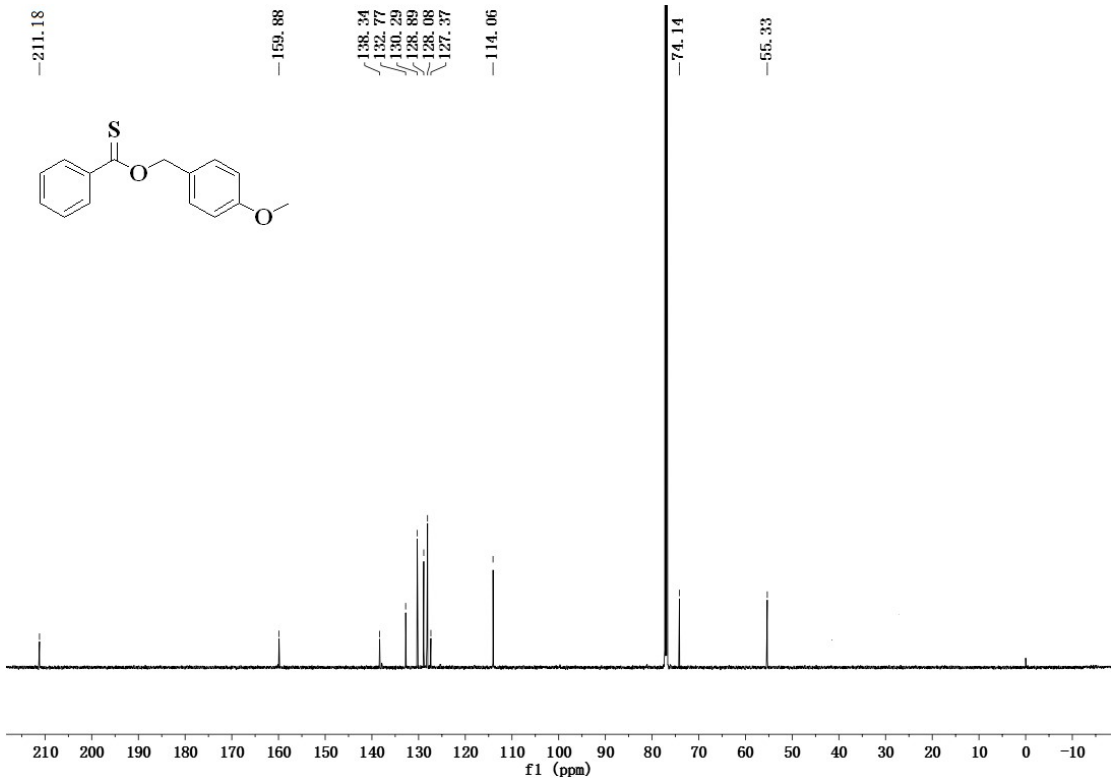


Figure S34. *O*-(4-methoxybenzyl) benzothioate (3ad)

Mass spectrum

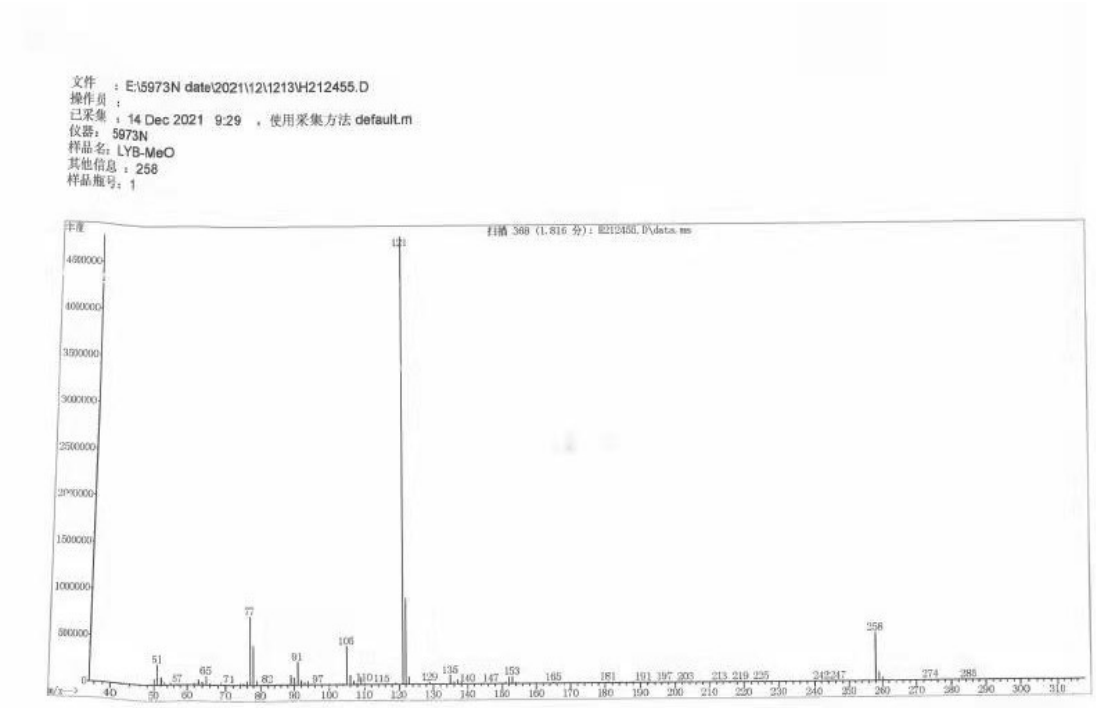
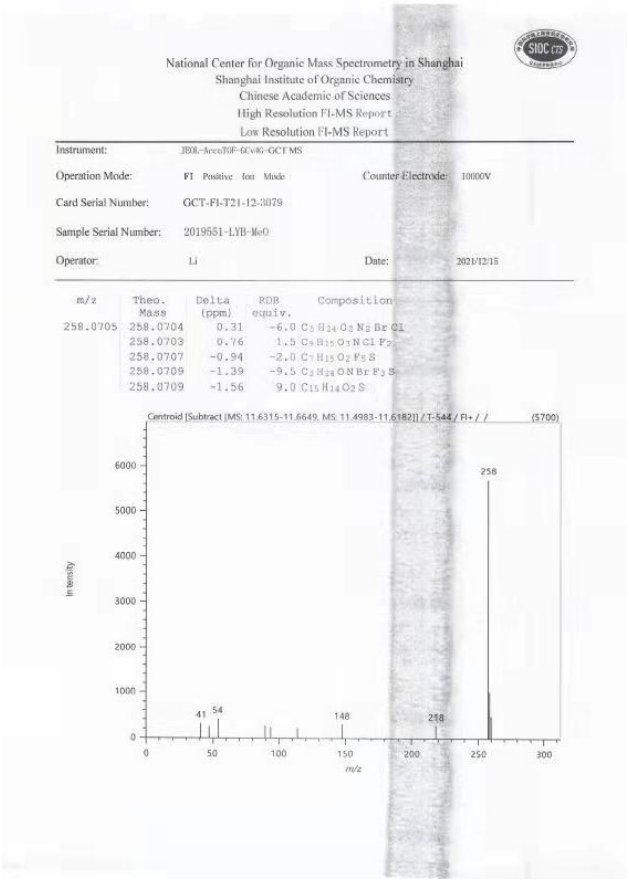


Figure S35. *O*-(4-methoxybenzyl) benzothioate (3ad)

HRMS



National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution FI-MS Report
Low Resolution FI-MS Report

Instrument: JEOL-AccuTOF-GCv4G-GCT MS
Operation Mode: FI Positive Ion Mode — Counter Electrode: 10000V
Card Serial Number: GCT-FI-T21-12-3079
Sample Serial Number: 2019551-LYB-MeO
Operator: Li — Date: 2021/12/15

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
258.0705	258.0704	0.31	-6.0	$C_5H_{24}O_2N_2BrCl$
	258.0703	0.76	1.5	$C_9H_{15}O_7NClF_2$
	258.0707	-0.94	-2.0	$C_7H_{15}O_2F_5S$
	258.0709	-1.39	-9.5	$C_3H_{24}ONBrF_3S$
	258.0709	-1.56	9.0	$C_{15}H_{14}O_2S$

Figure S36. *O*-(4-(trifluoromethyl)benzyl) benzothioate (3ae)
^{1}H NMR (600 MHz, $CDCl_3$)

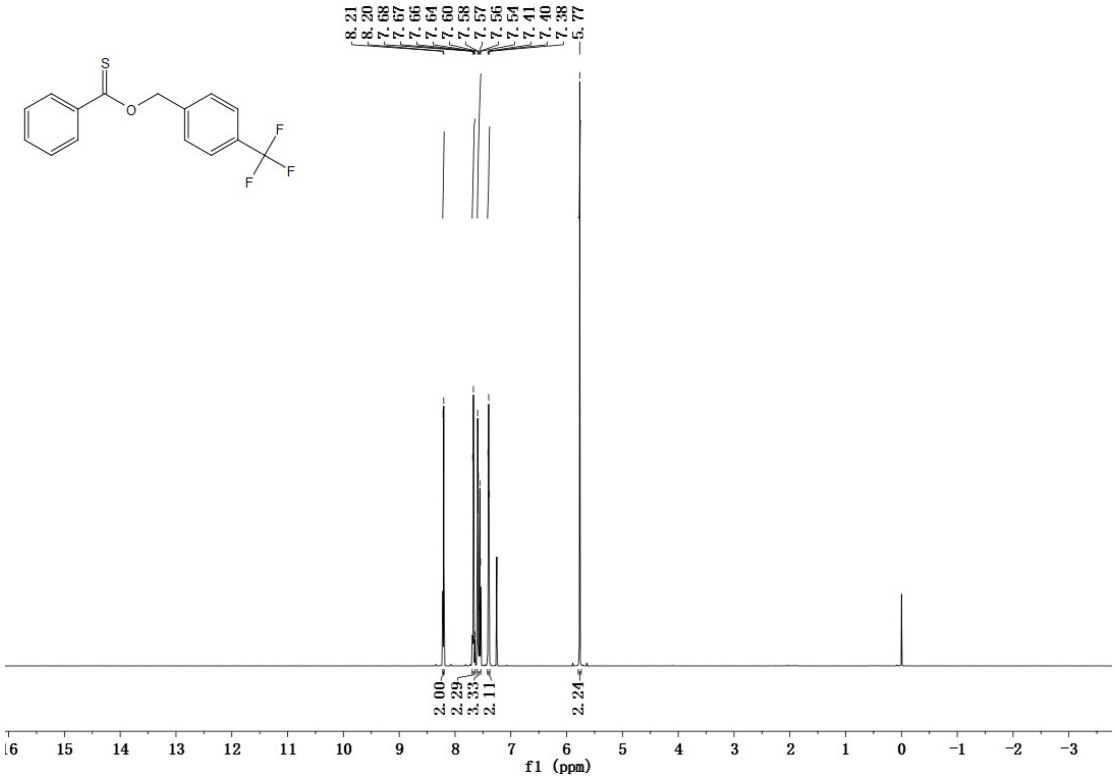


Figure S37. *O*-(4-(trifluoromethyl)benzyl) benzothioate (3ae)
^{13}C NMR (150 MHz, $CDCl_3$)

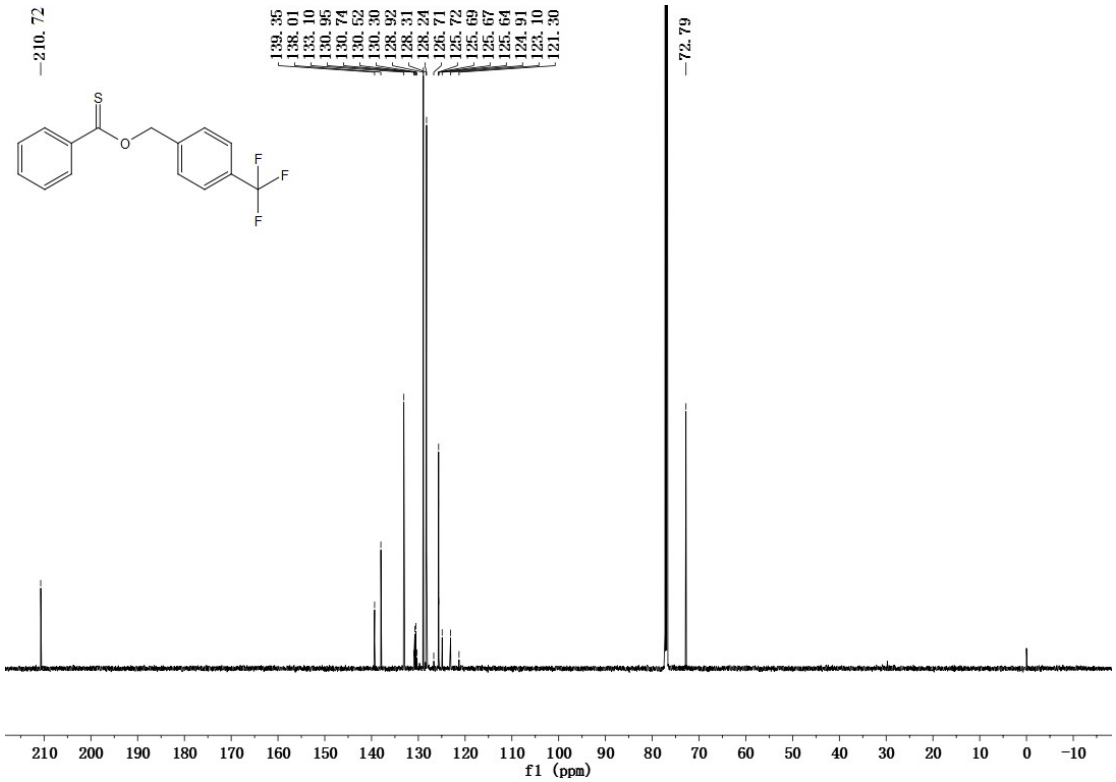


Figure S38. *O*-(4-(trifluoromethyl)benzyl) benzothioate (3ae) Mass spectrum

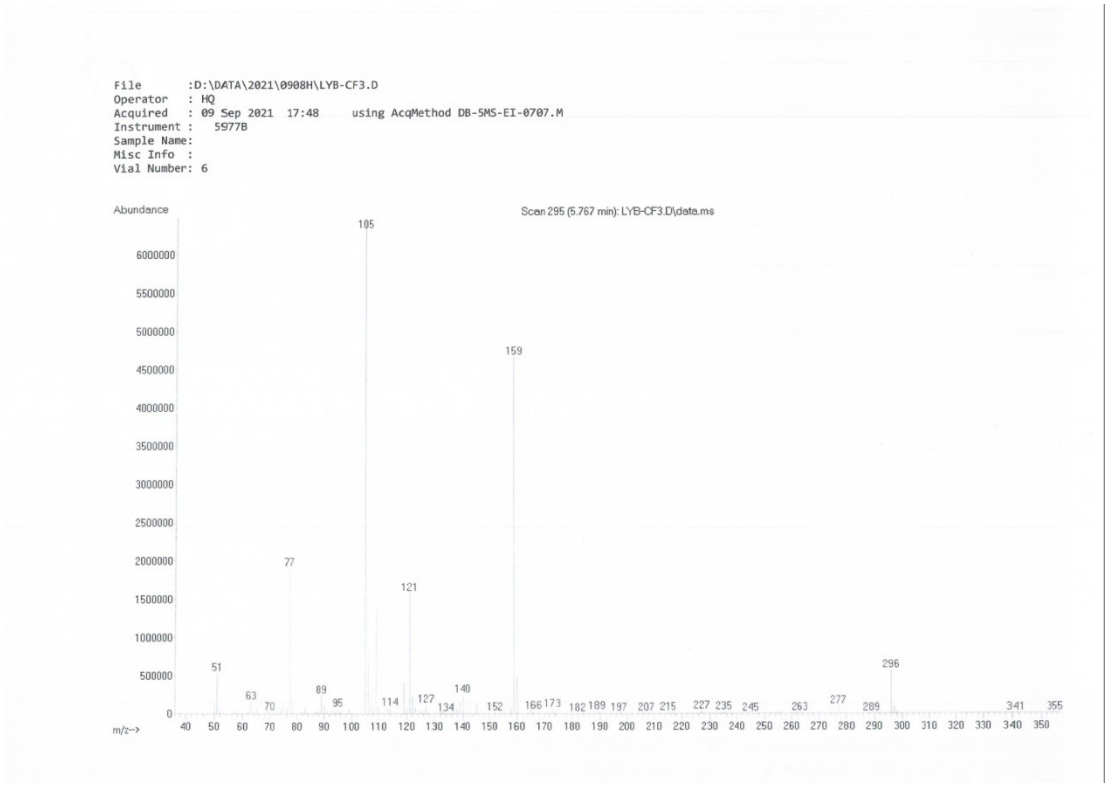


Figure S39. *O*-(4-(trifluoromethyl)benzyl) benzothioate (3ae) HRMS

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution FI-MS Report
Low Resolution FI-MS Report

Instrument: JEOL-AccuTOF-GCv4G-GCT MS

Operation Mode: FI Positive Ion Mode (Counter Electrode: 10000V)

Card Serial Number: GCT-FI-T21-09-2410

Sample Serial Number: 2019551-LYB-CF3

Operator: Li Date: 2021/09/14

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
296.0483	296.0479	1.22	13.0	$C_{17}H_9O_4F$
	296.0478	1.76	2.0	$C_9H_{10}O_4F_6$
	296.0489	-1.91	5.0	$C_{12}H_{12}O_2F_4S$
	296.0477	1.95	9.0	$C_{15}H_{11}OF_3S$
	296.0493	-3.43	10.5	$C_{15}H_7NF_5$

Figure S40. *O*-(4-bromobenzyl) benzothioate (3af)
^{1}H NMR (600 MHz, $CDCl_3$)

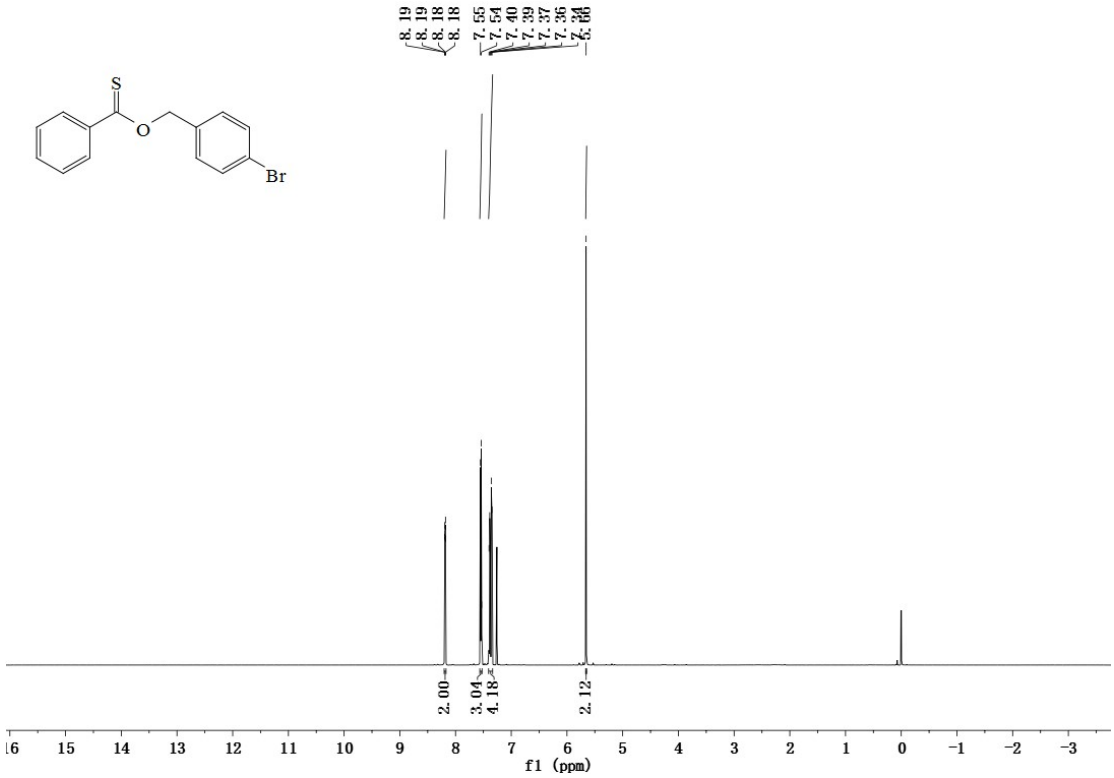


Figure S41. *O*-(4-bromobenzyl) benzothioate (3af)
^{13}C NMR (150 MHz, $CDCl_3$)

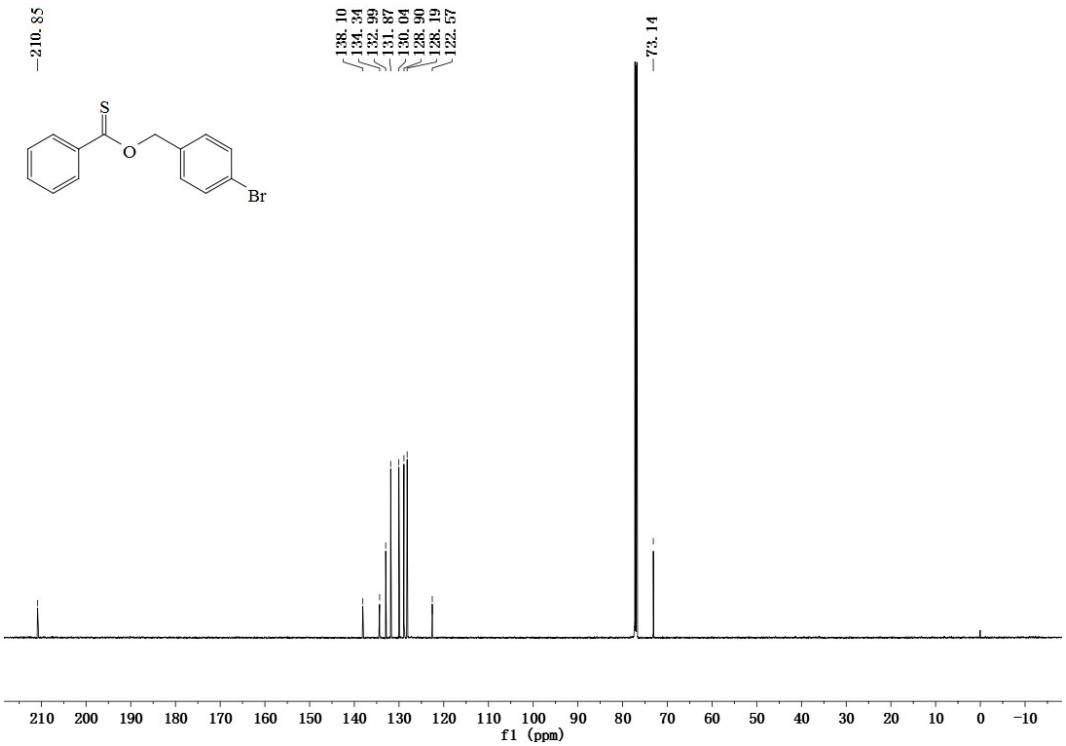


Figure S42. *O*-(4-bromobenzyl) benzothioate (3af)

Mass spectrum

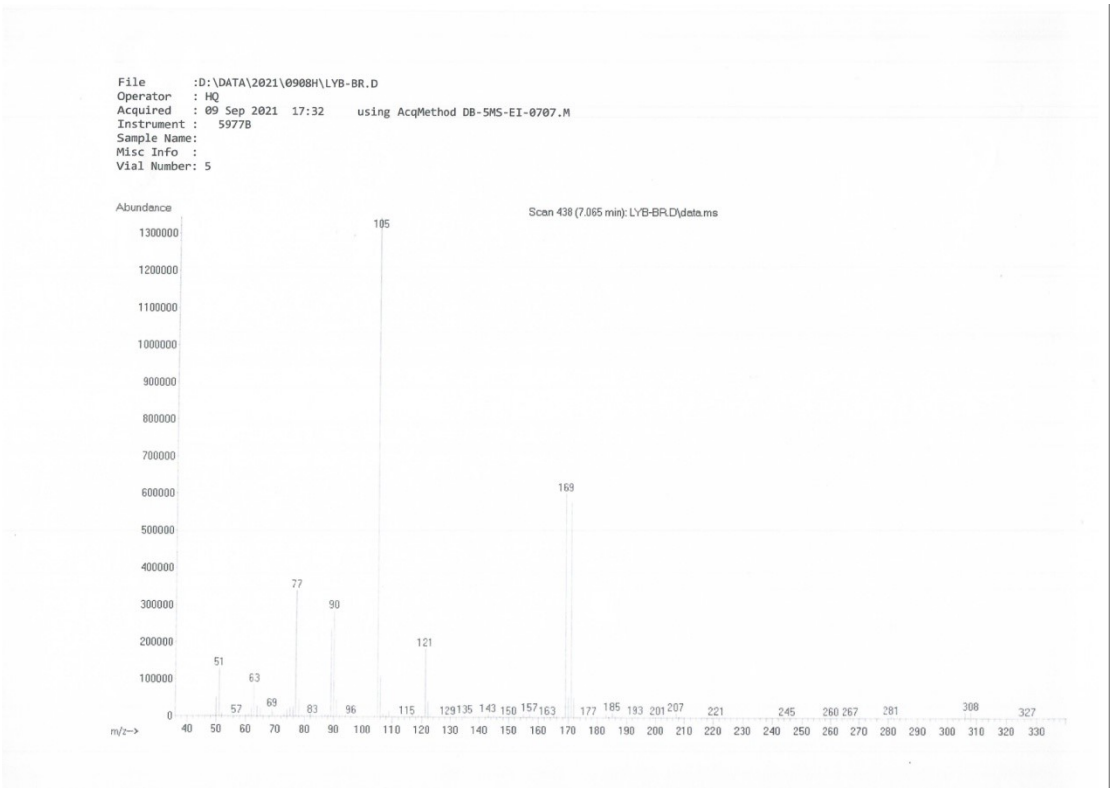


Figure S43. *O*-(4-bromobenzyl) benzothioate (3af)

HRMS

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution FI-MS Report
Low Resolution FI-MS Report

Instrument: JEOL-AccuTOF-GCv4G-GCT MS

Operation Mode: FI Positive Ion Mode (Counter Electrode: 10000V)

Card Serial Number: GCT-FI-T21-09-2411

Sample Serial Number: 2019551-LYB-Br

Operator: Li Date: 2021/09/14

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
305.9715	305.9717	-0.58	9.0	$C_{10}H_2O_3N_2F_4S$
	305.9718	-1.09	-6.0	$C_3H_{13}O_2BrF_6S$
	305.9720	-1.61	5.0	$C_{11}H_{12}O_2BrFS$
	305.9709	1.94	2.0	$C_8H_{10}O_4BrF_3$
	305.9708	2.12	9.0	$C_{14}H_{11}OBrS$

Figure S44. *O*-propyl benzothioate (3ag)
^{1}H NMR (600 MHz, $CDCl_3$)

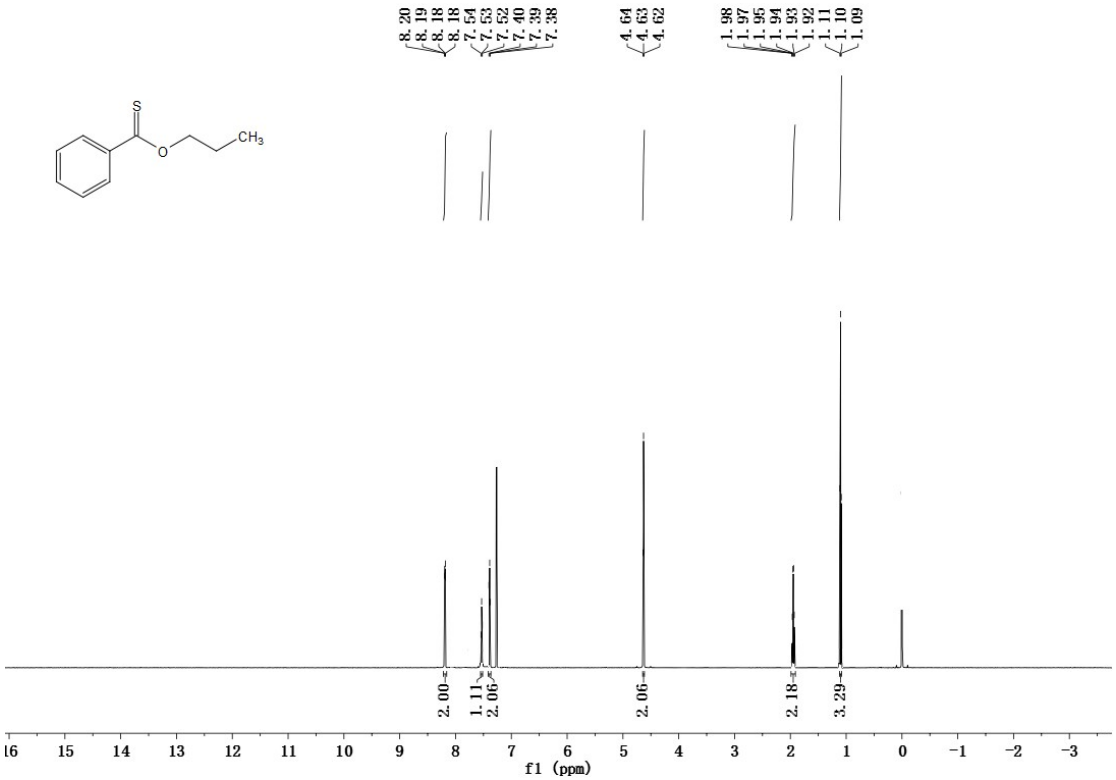


Figure S45. *O*-butyl benzothioate (3ah)
^{1}H NMR (600 MHz, $CDCl_3$)

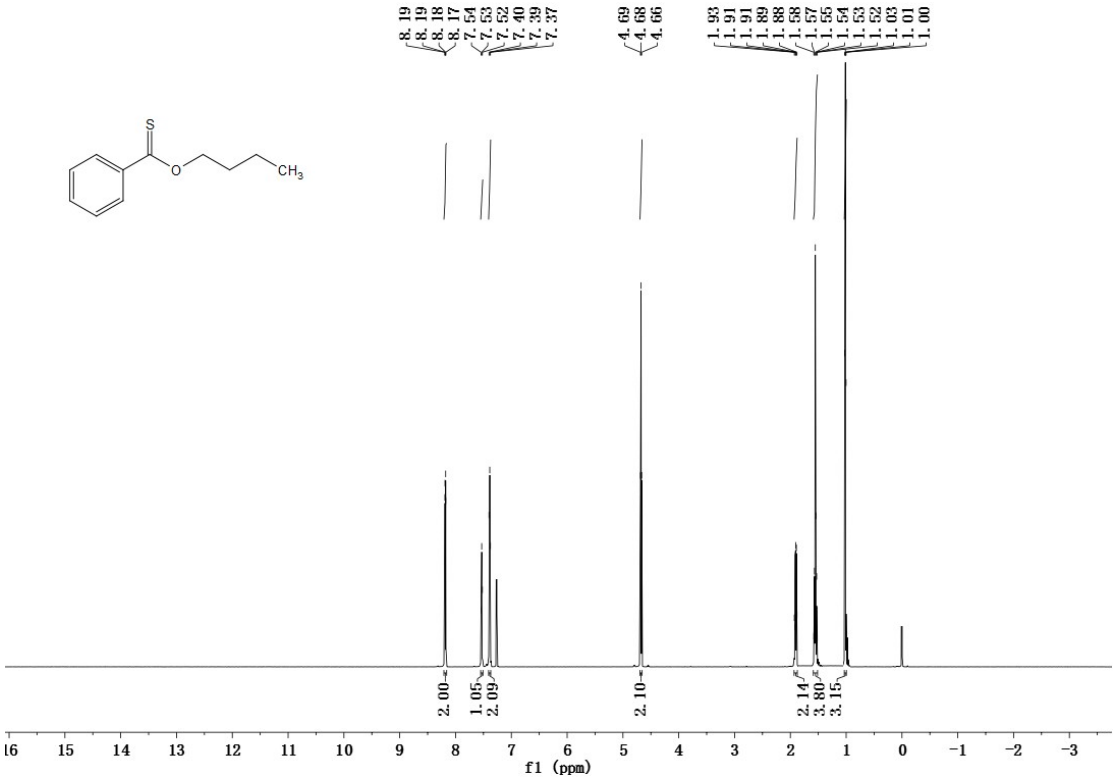


Figure S46. *O*-hexyl benzothioate (3ai)

^{1}H NMR (600 MHz, $CDCl_3$)

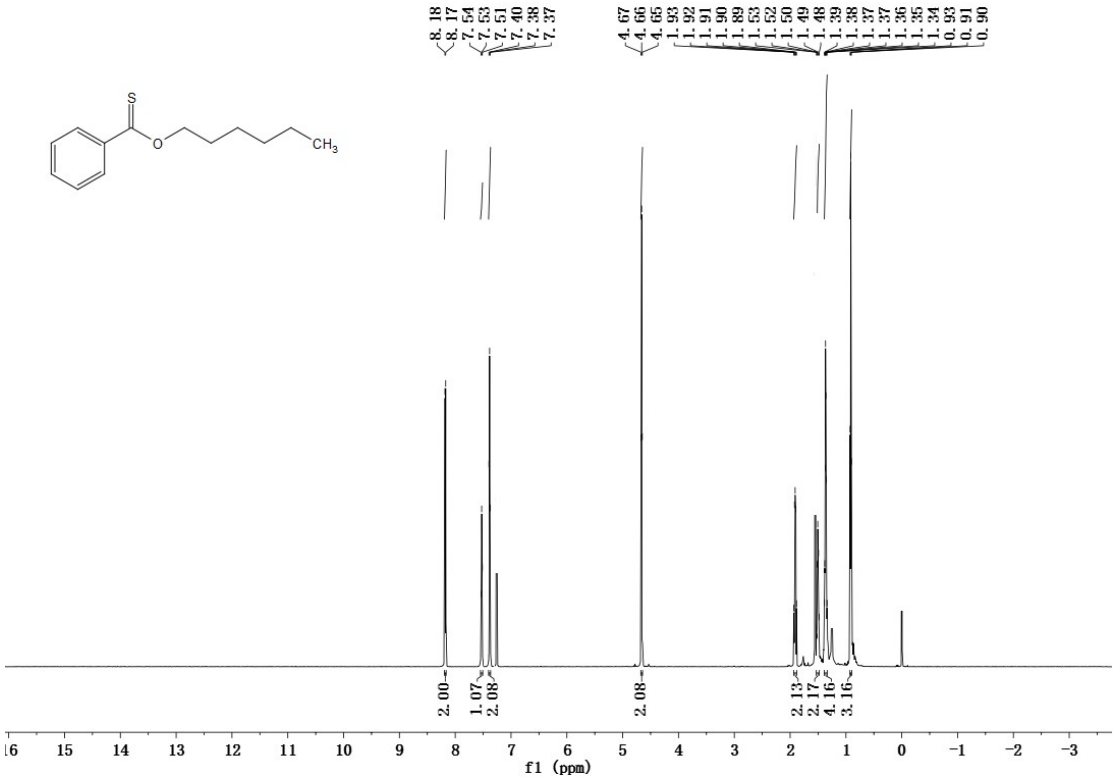


Figure S47. *O*-(thiophen-2-ylmethyl) benzothioate (3aj)

^{1}H NMR (600 MHz, $CDCl_3$)

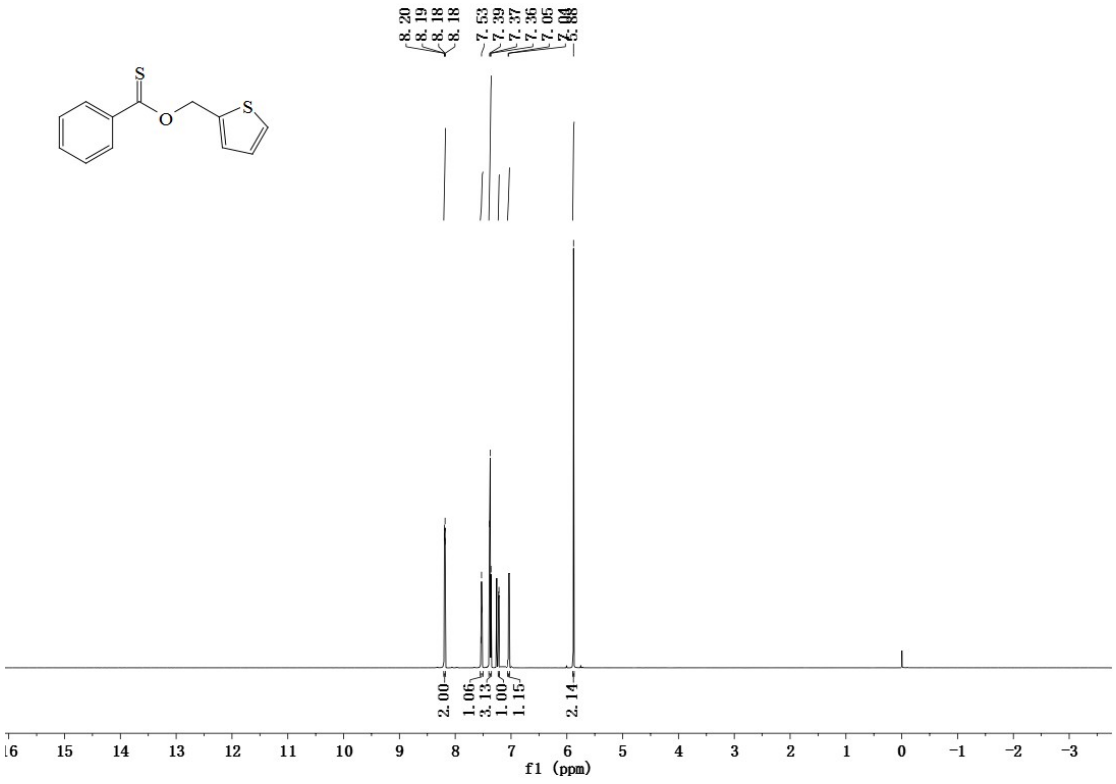


Figure S48. *O*-(thiophen-2-ylmethyl) benzothioate (3aj)
^{13}C NMR (150 MHz, $CDCl_3$)

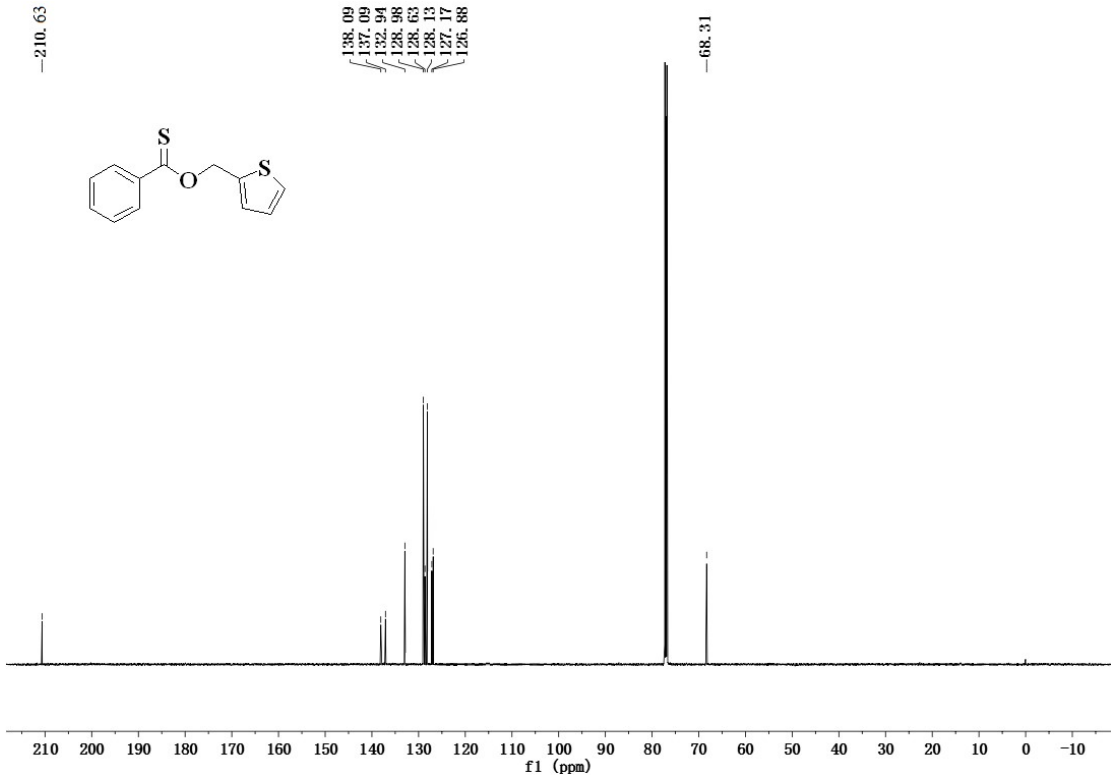


Figure S49. *O*-(thiophen-2-ylmethyl) benzothioate (3aj)
Mass spectrum

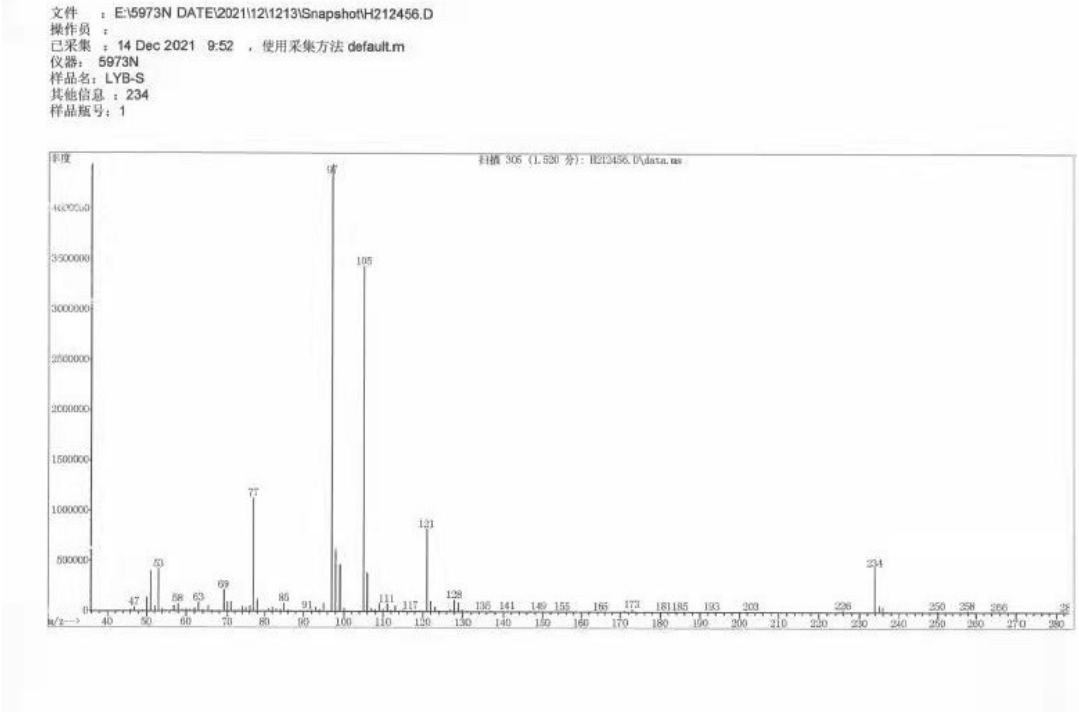


Figure S50. *O*-(thiophen-2-ylmethyl) benzothioate (3aj)

HRMS

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution FI-MS Report
Low Resolution FI-MS Report

Instrument:	JEOL-AccuTOF-GCv4G-GCT MS		
Operation Mode:	FI Positive Ion Mode	Counter Electrode:	10000V
Card Serial Number:	GCT-FI-T21-12-3080		
Sample Serial Number:	2019551-LYB-S		
Operator:	Li	Date:	2021/12/16

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
234.0169	234.0168	0.36	1.0	$C_6H_9O_4F_3S$
	234.0168	0.61	8.0	$C_{12}H_{10}OS_2$
	234.0166	1.29	-3.0	$C_4H_{11}OF_5S_2$
	234.0173	-1.57	6.5	$C_9H_4O_2NF_4$
	234.0161	3.31	10.5	$C_{12}H_3ONF_3$

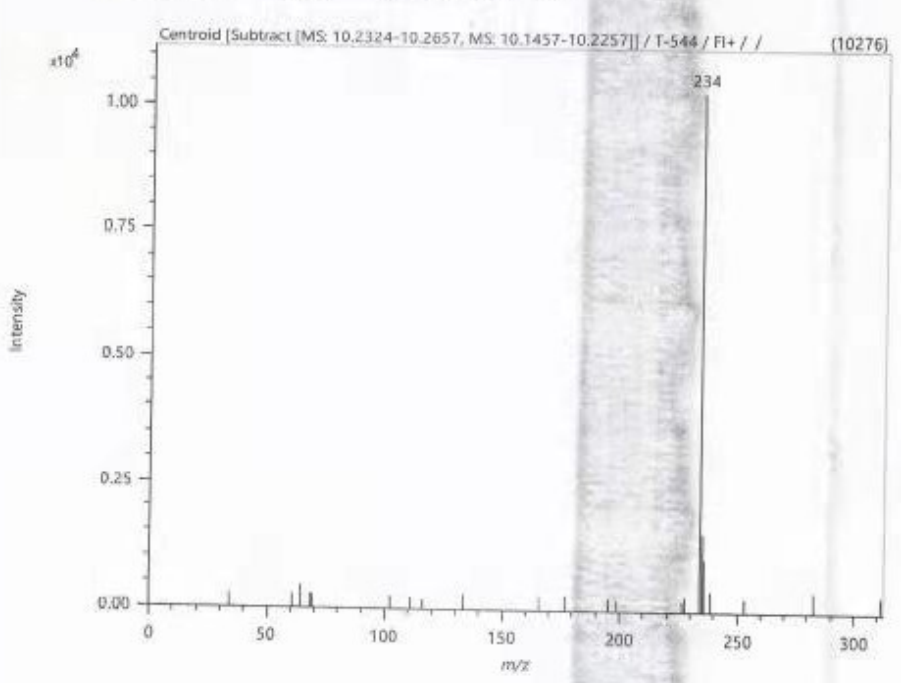


Figure S51. *O*-benzyl 4-methylbenzothioate (3ba)
^{1}H NMR (600 MHz, $CDCl_3$)

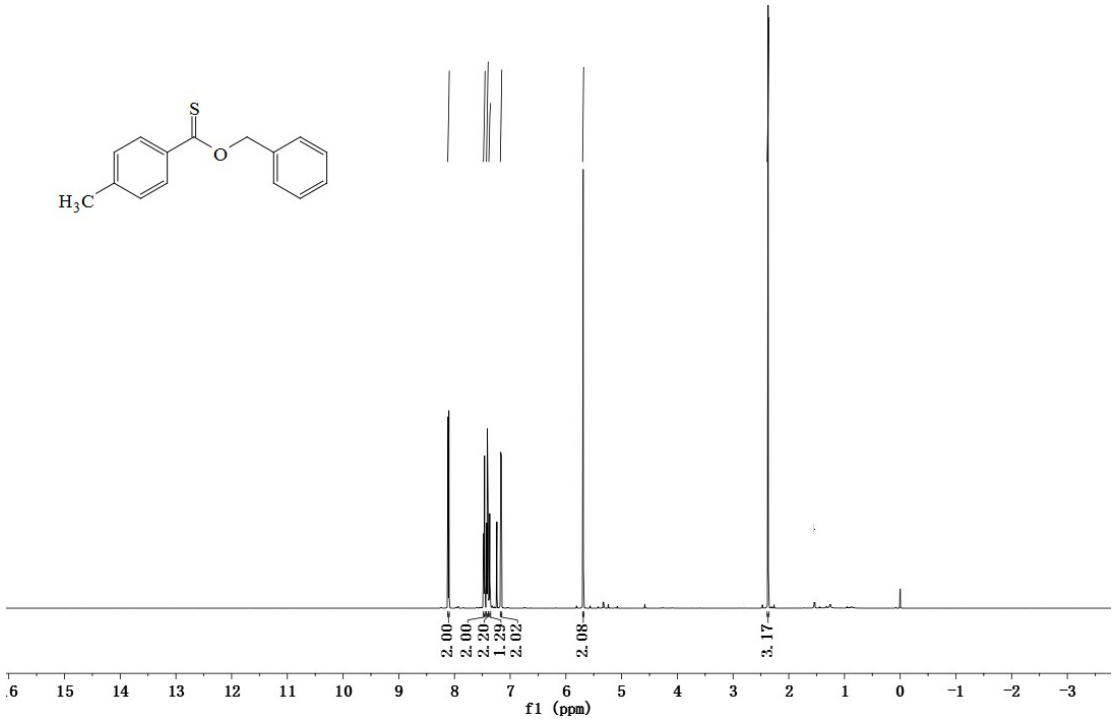


Figure S52. *O*-benzyl 4-methylbenzothioate (3ba)
^{13}C NMR (150 MHz, $CDCl_3$)

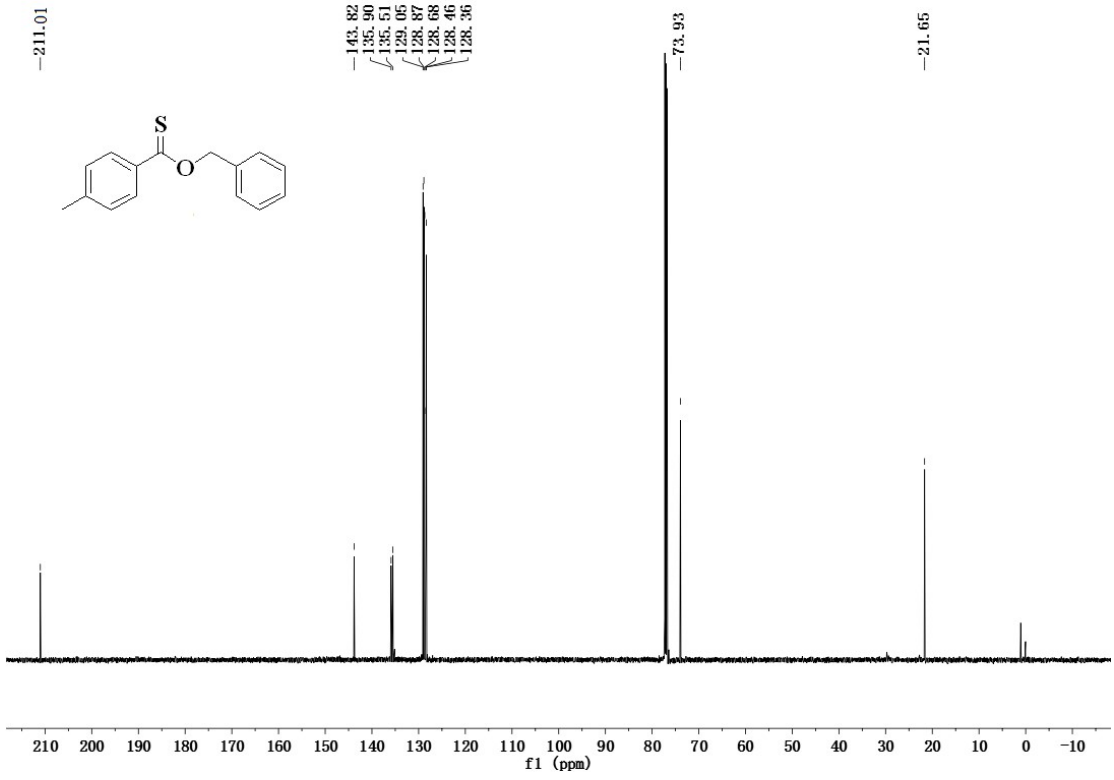


Figure S53. *O*-benzyl 4-methylbenzothioate (3ba)

Mass spectrum

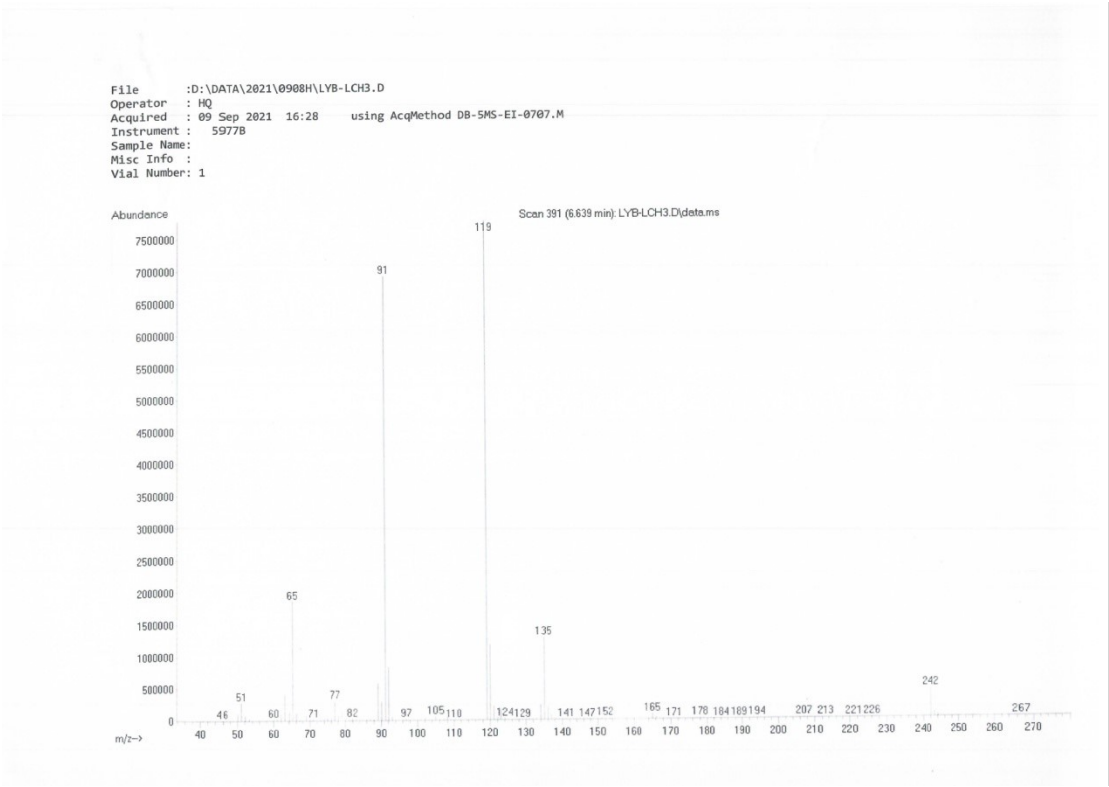


Figure S54. *O*-benzyl 4-methylbenzothioate (3ba)

HRMS

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution FI-MS Report
Low Resolution FI-MS Report

Instrument: JEOL-AccuTOF-GCv4G-GCT MS

Operation Mode: FI Positive Ion Mode (Counter Electrode: 10000V)

Card Serial Number: GCT-FI-T21-09-2409

Sample Serial Number: 2019551-LYB-LCH3

Operator: Li Date: 2021/09/14

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
242.0761	242.0760	0.23	2.0	$C_9H_{13}O_4F_3$
	242.0760	0.47	9.0	$C_{15}H_{14}OS$
	242.0758	1.12	-2.0	$C_7H_{15}OF_5S$
	242.0770	-3.60	-6.0	$C_4H_{16}O_2F_6S$
	242.0771	-4.26	5.0	$C_{12}H_{15}O_2FS$

Figure S55. *O*-benzyl 4-methoxybenzothioate (3ca)

^{1}H NMR (600 MHz, $CDCl_3$)

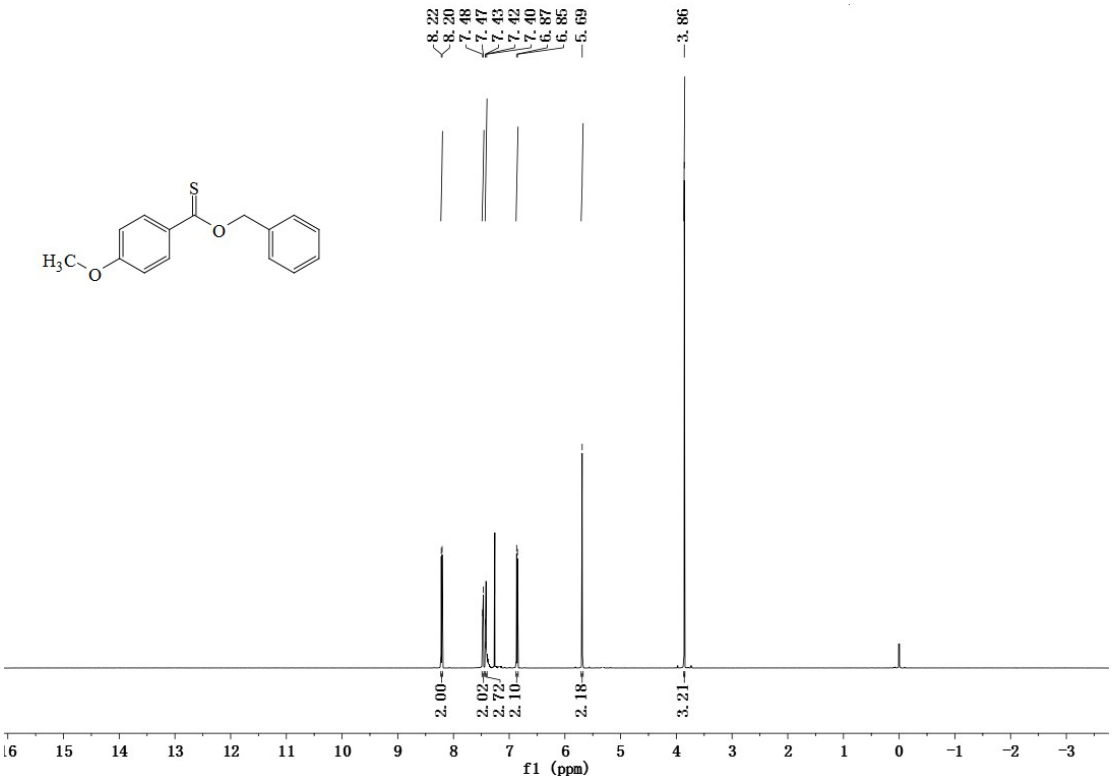


Figure S56. *O*-benzyl 4-methoxybenzothioate (3ca)

^{13}C NMR (150 MHz, $CDCl_3$)

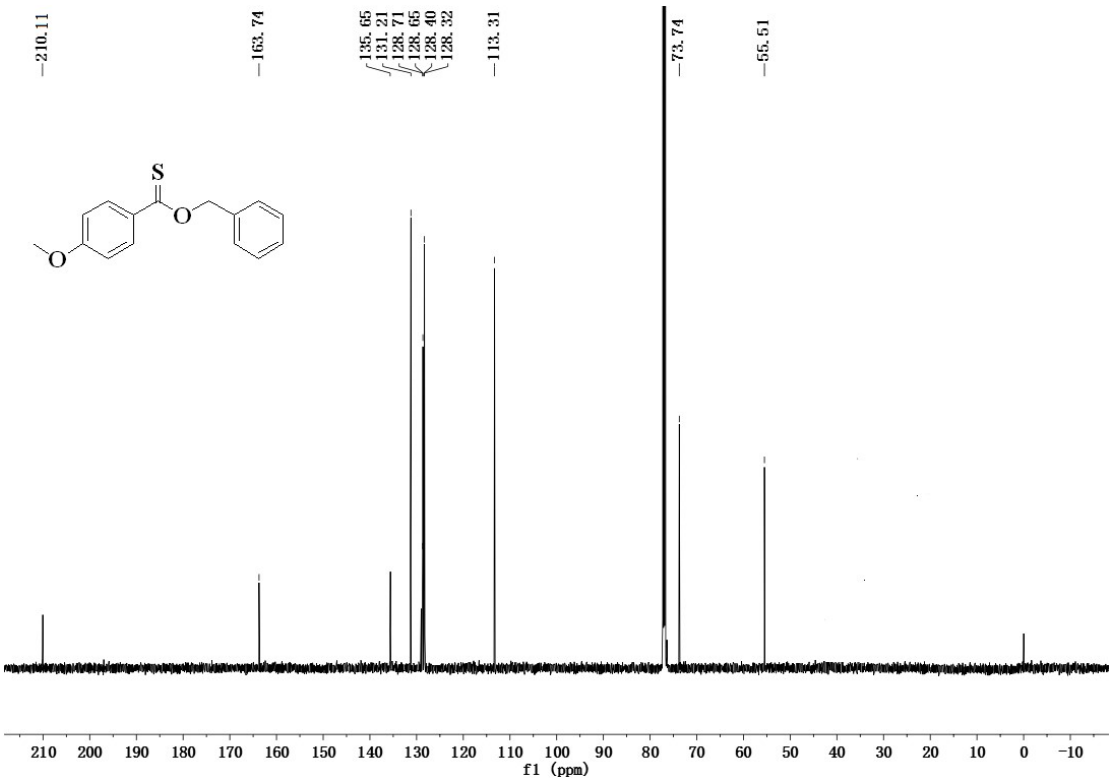


Figure S57. *O*-benzyl 4-methoxybenzothioate (3ca)

Mass spectrum

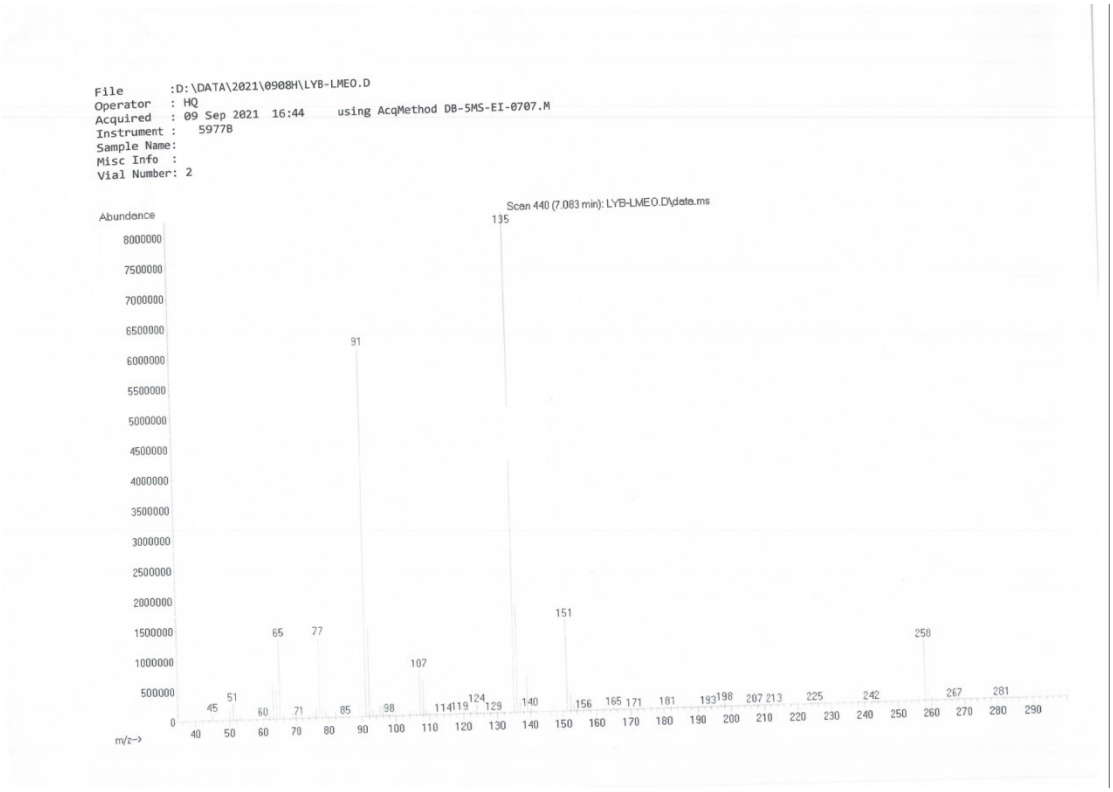


Figure S58. *O*-benzyl 4-methoxybenzothioate (3ca)

HRMS

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution EI-MS Report
Low Resolution EI-MS Report

Instrument: Waters Premier GC-TOF MS
Operation Mode: EI Positive Ion Mode (Electron Energy: 70eV)
Card Serial Number: GCT-P-EI-T21-2407
Sample Serial Number: 2019551-LYB-LMeO
Operator: Li Date: 2021/09/14

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
258.0716	258.0714	0.95	14.5	$C_{18}H_9NF$
	258.0720	-1.56	-13.5	$H_{25}O_2NBrF_4S$
	258.0720	-1.72	5.0	$C_{12}H_{15}O_3FS$
	258.0711	2.03	-5.5	$C_5H_{22}O_4NBrF$
	258.0709	2.70	9.0	$C_{15}H_{14}O_2S$

Figure S59. *O*-benzyl 4-fluorobenzothioate (3da)
^{1}H NMR (600 MHz, $CDCl_3$)

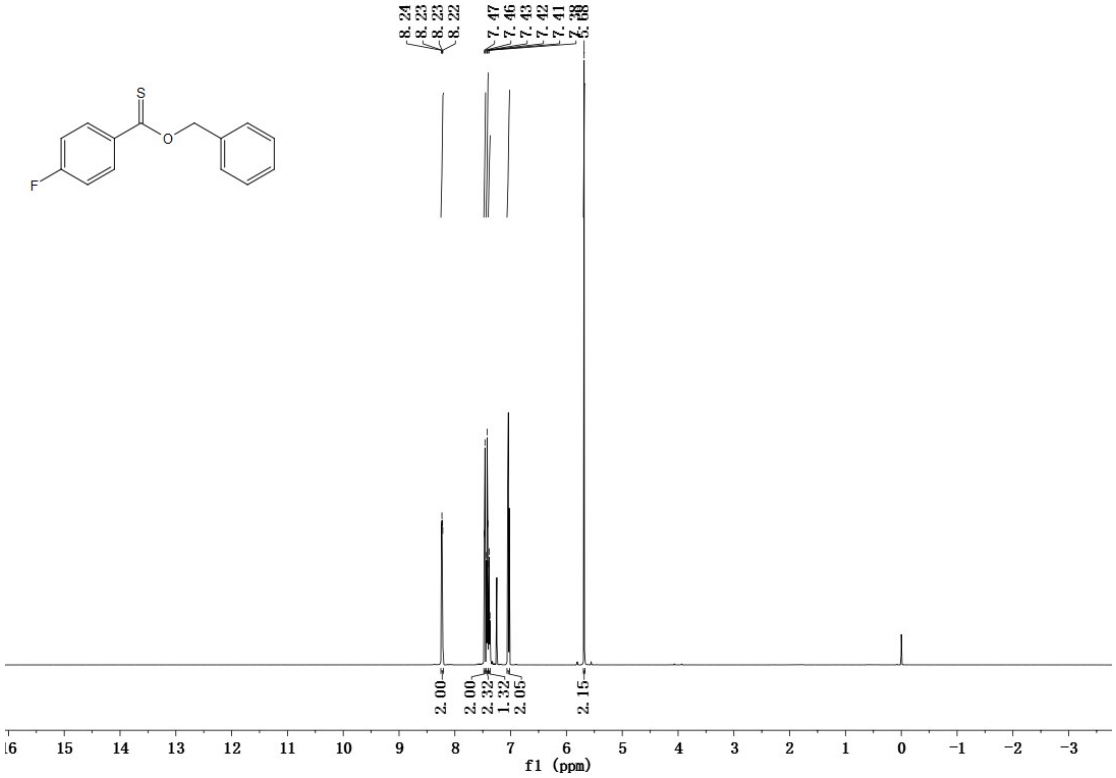


Figure S60. *O*-benzyl 4-fluorobenzothioate (3da)
^{19}F NMR (565 MHz, $CDCl_3$)