

Supplementary Information

Synthesis of S-Aryl Thioesters via Palladium-Catalyzed Thiocarbonylation of Aryl Iodides and Aryl Sulfonyl Hydrazides

Yejin Kim,[†] Kwang Ho Song,^{‡} Sunwoo Lee^{†*}*

[†]Department of Chemistry, Chonnam National University, Gwangju, 61186, Republic of Korea

[‡]Department of Chemical & Biological Engineering, Korea University, Seoul, 02841, Republic of Korea

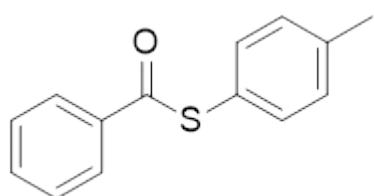
Table of Contents

Experimental Procedure	-S2-
Reference	-S9-
¹H and ¹³C NMR Spectra	-S10-

General Experimental Procedure

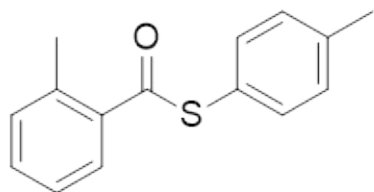
Aryl iodide (1.0 mmol), aryl sulfonyl hydrazide (1.0 mmol), bis(dibenzylideneacetone)dipalladium(0) (29 mg, 0.05 mmol), 1,4-bis(diphenylphosphino)butane (21 mg, 0.05 mmol), 1,4-diazabicyclo[2.2.2]octane (152 mg, 1.0 mmol) and toluene (3 mL) were added to the autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized with 8.0 atm of CO, and then stirred at 80 °C for 12 h. Excess CO was discharged at room temperature. The reaction mixture was quenched with saturated NH₄Cl and diluted with ethyl acetate and washed with saturated NaCl (50 mL × 2). The organic layer was dried over anhydrous Mg₂SO₄, filtered and concentrated under vacuum. Evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography on silica gel (eluent: hexane / ethyl acetate = 40 / 1).

S-p-Tolyl benzothioate (**3aa**)¹



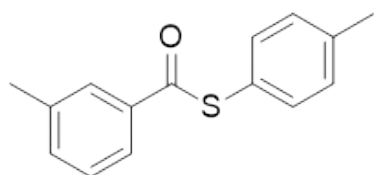
Iodobenzene (204 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3aa** (217 mg, 0.95 mmol, 95%). White solid; Mp. 75 – 76 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.96 - 7.95 (m, 2H), 7.55 – 7.51 (m, 1H), 7.42 – 7.41 (m, 2H), 7.34 – 7.31 (m, 2H), 7.21 – 7.19 (m, 2H), 2.34 (s, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 190.6, 139.8, 136.6, 135.0, 133.6, 130.1, 128.7, 127.4, 123.7, 21.4; MS (EI) m/z = 228 (M⁺).

S-p-Tolyl-2-methylbenzothioate (**3ba**)



2-Iodotoluene (218 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3ba** (179 mg, 0.74 mmol, 74%). White solid; Mp. 78 – 80 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.86 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.36-7.31 (m, 3H), 7.24–7.19 (m, 4H), 2.41 (s, 3H), 2.33 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 192.6, 139.7, 137.4, 136.8, 134.8, 131.9, 131.7, 130.1, 128.6, 125.8, 124.6, 21.4, 20.8; HRMS (FD) m/z cacl. for C₁₅H₁₄OS [M⁺]: 242.0760, found: 242.0760.

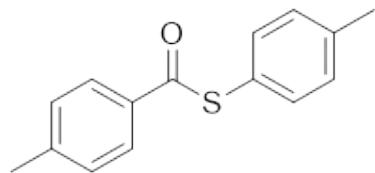
S-p-Tolyl-3-methylbenzothioate (**3ca**)



3-Iodotoluene (218 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3ca** (213 mg, 0.88 mmol, 88%). White solid; Mp. 60 – 61 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, *J* = 6.4 Hz, 2H), 7.35-7.28 (m, 4H), 7.20–7.17 (m, 2H), 2.35 (s, 3H), 2.33 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 190.7, 139.7, 138.6, 136.7, 135.0, 134.3, 130.1, 128.6, 127.3, 124.7, 123.9, 21.4, 21.4; HRMS (FD) m/z cacl. for C₁₅H₁₄OS [M⁺]:

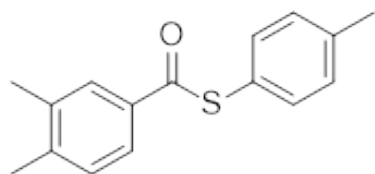
242.0760, found: 242.0758.

S-p-Tolyl-4-methylbenzothioate (3da)²



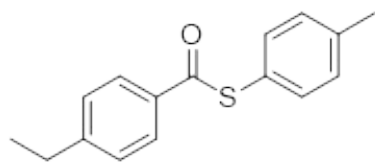
4-Iodotoluene (218 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3da** (143 mg, 0.59 mmol, 59%). Colorless crystals; Mp. 123.8 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.95-7.93 (m, 2H), 7.41-7.40 (m, 2H), 7.30-7.27 (m, 4H), 2.44 (s, 3H), 2.42 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 190.1, 144.5, 139.7, 135.0, 134.2, 130.0, 129.4, 127.5, 123.9, 21.7, 21.4; MS (EI) m/z = 242 (M⁺).

S-p-Tolyl-3,4-dimethylbenzothioate (3ea)



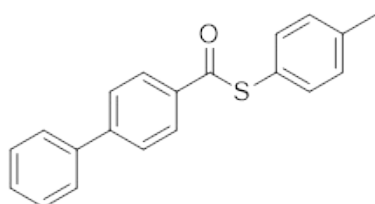
1-Iodo-3,4-dimethylbenzene (232 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3ea** (159 mg, 0.62 mmol, 62%). White solid; Mp. 103 – 105 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.81 – 7.74 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.22 (m, 3H), 2.41 (s, 3H), 2.33 (s, 6H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 190.2, 143.2, 139.6, 137.1, 135.0, 134.5, 130.0, 129.9, 128.5, 125.1, 124.1, 21.4, 20.1, 19.8; HRMS (FD) m/z cacl. for C₁₆H₁₆OS [M⁺]: 256.0916, found: 256.0912.

S-p-Tolyl-4-ethylbenzothioate (3fa)



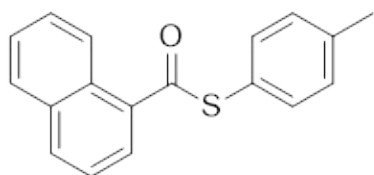
4-Ethyl iodobenzene (232 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3fa** (154 mg, 0.6 mmol, 60%). White solid; Mp. 85 – 87 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.97 – 7.94 (m, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.27 (m, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.28 (t, *J* = 7.6 Hz, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 190.2, 150.6, 139.7, 135.0, 134.3, 130.0, 128.2, 127.6, 123.9, 29.0, 21.4, 15.2; HRMS (FD) m/z cacl. for C₁₆H₁₆OS [M⁺]: 256.0916, found: 256.0920.

S-p-Tolyl-4-phenylbenzothioate (3ga)



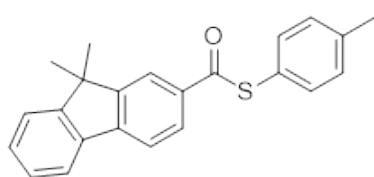
4-Iodobiphenyl (280 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3ga** (256 mg, 0.84 mmol, 84%). White solid; Mp. 134 – 135 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.12 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.68 – 7.63 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 3H), 7.30 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 190.1, 146.3, 139.8, 139.7, 135.4, 135.0, 130.1, 129.0, 128.3, 128.0, 127.4, 127.3, 123.8, 21.4; HRMS (FD) m/z cacl. for C₂₀H₁₆OS [M⁺]: 304.0916, found: 304.0917.

***S-p*-Tolyl naphthothioate (3ha)**



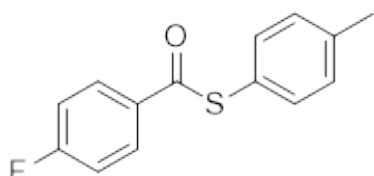
1-Iodonaphthalene (254 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3ha** (214 mg, 0.77 mmol, 77%). White solid; Mp. 79.5 – 80.5 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.51-8.44 (m, 1H), 8.15(dd, *J* = 7.2, 1.1 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.54 – 7.46 (m, 3H), 7.44 – 7.38 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 2.37 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 192.4, 139.6, 134.6, 134.5, 133.5, 132.9, 129.9, 129.1, 128.0, 127.8, 127.7, 126.4, 125.0, 124.5, 124.2, 21.1; HRMS (FD) *m/z* cacl. for C₁₈H₁₄OS [M⁺]: 278.0760, found: 278.0760.

***S-p*-Tolyl-9,9-dimethyl-9H-fluorenothioate (3ia)**



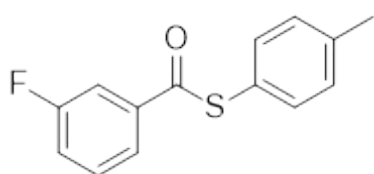
1-Iodo-9,9-dimethyl-9H-fluorene (320 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3ia** (227 mg, 0.66 mmol, 66%). White solid; Mp. 125 – 126 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.08 (dd, *J* = 9.3, 1.1 Hz, 2H), 7.81 (d, *J* = 7.0 Hz, 2H), 7.50 (dd, *J* = 5.6, 2.3 Hz, 1H), 7.46 – 7.40 (m, 4H), 7.30 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H), 1.55 (s, 6H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 190.3, 154.8, 153.9, 144.7, 139.7, 137.8, 135.4, 135.1, 130.1, 128.7, 127.3, 127.2, 124.0, 122.9, 121.7, 121.0, 120.0, 47.1, 26.9, 21.4; HRMS (FD) *m/z* cacl. for C₂₃H₂₀OS [M⁺]: 344.1229, found: 344.1226.

***S-p*-Tolyl-4-fluorobenzothioate (3ja)**



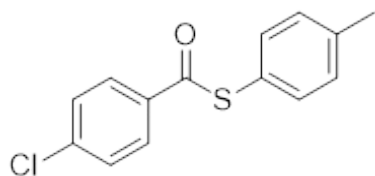
4-Fluoroiodobenzene (222 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3ja** (236 mg, 0.96 mmol, 96%). White solid; Mp. 71 – 72 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.07-8.02 (m, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.18-7.13 (m, 2H), 2.41 (s, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 189.1, 166.0 (d, *J*_{C-F} = 256.7 Hz), 139.9, 134.9, 132.9 (d, *J*_{C-F} = 3.0 Hz), 130.1, 130.0 (d, *J*_{C-F} = 9.1 Hz), 123.4, 115.9 (d, *J*_{C-F} = 21.1 Hz), 21.4; HRMS (FD) *m/z* cacl. for C₁₄H₁₁OFS [M⁺]: 246.0509, found: 246.0507.

***S-p*-Tolyl-3-fluorobenzothioate (3ka)**



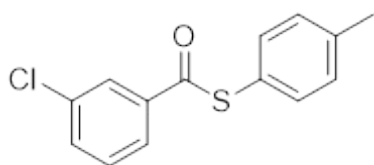
3-Fluoroiodobenzene (222 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3ka** (231 mg, 0.94 mmol, 94%). White solid; Mp. 69.5 – 70.5 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 9.1 Hz, 1H), 7.47 – 7.46 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.26 (m, 3H), 2.41 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 189.5, 162.7 (d, *J*_{C-F} = 249.5 Hz), 140.1, 138.6 (d, *J*_{C-F} = 6.3 Hz), 134.9, 130.3 (d, *J*_{C-F} = 8.8 Hz), 123.2, 120.6, 120.4, 114.3 (d, *J*_{C-F} = 22.7 Hz), 21.4; HRMS (FD) *m/z* cacl. for C₁₄H₁₁OFS [M⁺]: 246.0509, found: 246.0543.

***S-p*-Tolyl-4-chlorobenzothioate (3la)²**



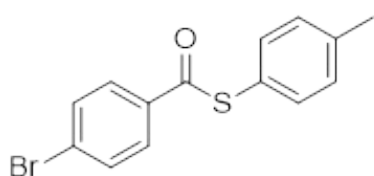
1-Chloro-4-iodobenzene (238 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **31a** (247 mg, 0.94 mmol, 94%). White solid. Mp. 108 – 110 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.91-7.87 (m, 2H), 7.40-7.37 (m, 2H), 7.32-7.29 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 189.5, 140.0, 139.9, 135.1, 135.0, 130.2, 129.0, 128.8, 123.4, 21.4; MS (EI) *m/z* = 262 (M⁺).

***S-p*-Tolyl-3-chlorobenzothioate (3ma)**



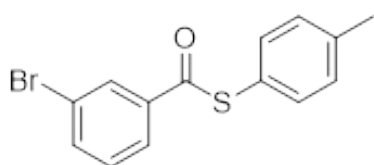
3-Chloroiodobenzene (238 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3ma** (244 mg, 0.93 mmol, 93%). White solid; Mp. 60.5 – 61.5 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.00 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 189.5, 140.1, 138.2, 135.0, 134.9, 133.5, 130.2, 130.0, 127.5, 125.6, 123.2, 21.4; HRMS (FD) *m/z* cacl. for C₁₄H₁₁OSCl [M⁺]: 262.0214, found: 262.0213.

***S-p*-Tolyl-4-bromobenzothioate (3na)**



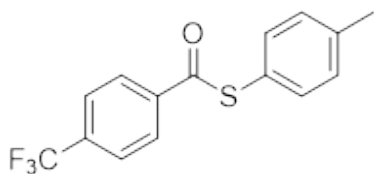
1-Bromo-4-iodobenzene (283 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3na** (295 mg, 0.96 mmol, 96%). White solid; Mp. 123 – 124 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 189.7, 140.0, 135.5, 134.9, 132.0, 130.2, 128.9, 128.6, 123.3, 21.4; HRMS (FD) *m/z* cacl. for C₁₄H₁₁OSBr [M⁺]: 305.9708, found: 305.9706.

***S-p*-Tolyl-3-bromobenzothioate (3oa)**



3-Bromoiodobenzene (283 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3oa** (270 mg, 0.88 mmol, 88%). White solid; Mp. 59.5 – 60.5 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.14 – 8.13 (m, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.38 (t, *J* = 6.8 Hz, 3H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 189.4, 140.1, 138.4, 136.4, 134.9, 130.3, 130.25, 130.20, 125.9, 123.2, 122.9, 21.4; HRMS (FD) *m/z* cacl. for C₁₄H₁₁OSBr [M⁺]: 305.9708, found: 305.9715.

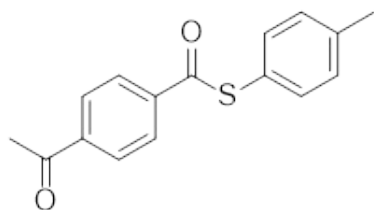
***S-p*-Tolyl-4-trifluoromethylbenzothioate (3pa)**



4-Iodobenzotrifluoride (272 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3pa** (225 mg, 0.76 mmol, 76%). White solid; Mp. 103 – 105 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.9

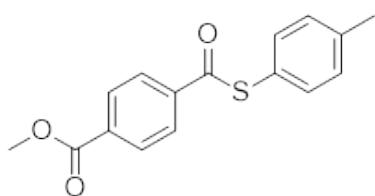
Hz, 2H), 2.43 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 189.8, 140.2, 139.5, 134.8 (q, $J_{\text{C-F}} = 13.9$ Hz), 130.2, 127.8, 125.5 (q, $J_{\text{C-F}} = 3.8$ Hz), 121.3 (q, $J_{\text{C-F}} = 273.4$ Hz), 21.4; HRMS (FD) m/z cacl. for $\text{C}_{15}\text{H}_{11}\text{OF}_3\text{S}$ [M^+]: 296.0477, found: 296.0476.

***S-p*-Tolyl-4-acetylbenzothioate (3qa)**



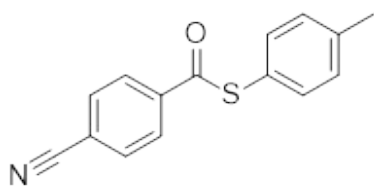
4-Iodoacetophenone (246 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3qa** (230 mg, 0.85 mmol, 85%). White solid; Mp. 103 – 105 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.11 (d, $J = 8.3$ Hz, 2H), 8.05 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 7.9$ Hz, 2H), 2.66 (s, 3H), 2.42 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 197.3, 190.1, 140.6, 140.1, 140.0, 134.9, 130.2, 128.6, 127.7, 123.2, 26.9, 21.4; HRMS (FD) m/z cacl. for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{S}$ [M^+]: 270.0709, found: 270.0704.

***S-p*-Tolyl methylbenzoatethioate (3ra)**



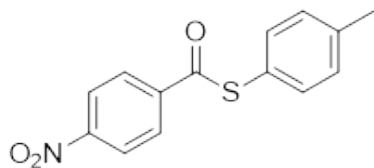
Methyl 4-iodobenzoate (262 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3ra** (189 mg, 0.66 mmol, 66%). White solid; Mp. 108 – 109 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.15 (d, $J = 8.6$ Hz, 2H), 8.08 (d, $J = 8.6$ Hz, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 7.9$ Hz, 2H), 3.97 (s, 3H), 2.42 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 190.1, 166.1, 140.1, 140.0, 134.9, 134.3, 130.2, 129.9, 127.4, 123.2, 52.5, 21.4; HRMS (FD) m/z cacl. for $\text{C}_{16}\text{H}_{14}\text{O}_3\text{S}$ [M^+]: 286.0658, found: 286.0659.

***S-p*-Tolyl-4-cyanobenzothioate (3sa)**



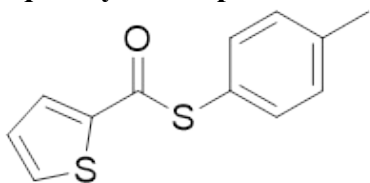
4-Iodobenzonitrile (229 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3sa** (249 mg, 0.87 mmol, 87%). White solid; Mp. 100 – 103 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.11 (d, $J = 8.6$ Hz, 2H), 7.80 (d, $J = 8.6$ Hz, 2H), 7.39 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 2.43 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 189.5, 140.4, 139.9, 134.8, 132.6, 130.3, 127.9, 122.6, 117.8, 116.8, 21.4; HRMS (FD) m/z cacl. for $\text{C}_{15}\text{H}_{11}\text{NOS}$ [M^+]: 253.0556, found: 253.0551.

***S-p*-Tolyl-4-nitrobenzothioate (3ta)^{3,4}**



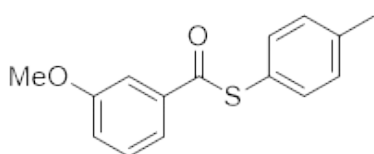
1-Iodo-4-nitrobenzene (249 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3ta** (227 mg, 0.83 mmol, 83%). White solid; Mp. 102 – 104 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.34 (d, $J = 8.9$ Hz, 2H), 8.18 (d, $J = 8.9$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 7.9$ Hz, 2H), 2.43 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 189.3, 150.6, 141.4, 140.5, 134.8, 130.3, 128.5, 123.9, 122.6, 21.4; MS (EI) $m/z = 273$ (M^+).

***S*-*p*-Tolyl-2-thiophenethioate (3ua)**



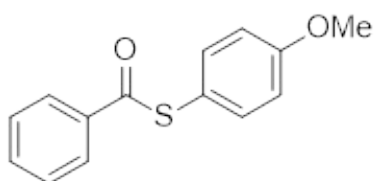
2-Iodothiophenone (210 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3ua** (143 mg, 0.61 mmol, 61%). White solid; Mp. 56 – 59 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.92 – 7.91 (m, 1H), 7.67 – 7.66 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.26 (m, 2H), 7.17 – 7.16 (m, 1H), 2.41 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 182.5, 141.5, 139.9, 134.9, 133.0, 131.5, 130.1, 127.9, 123.3, 21.4; HRMS (FD) *m/z* cacl. for C₁₂H₁₀OS₂ [M⁺]: 234.0168, found: 234.0168.

***S*-*p*-Tolyl-3-methoxybenzothioate (3va)**



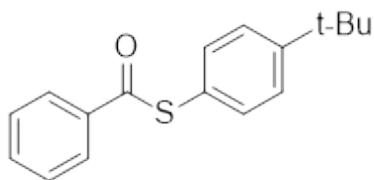
3-Iodoanisole (234 mg, 1.0 mmol) and *p*-tolylsulfonyl hydrazide (186 mg, 1.0 mmol) provided **3va** (163 mg, 0.63 mmol, 63%). Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.51 (m, 1H), 7.41 - 7.40 (m, 1H), 7.39 – 7.38 (m, 2H), 7.29 – 7.26 (m, 2H), 7.15 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.87 (s, 3H), 2.42 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 190.5, 159.8, 139.8, 138.0, 134.9, 130.1, 129.7, 123.8, 120.03, 119.97, 111.7, 55.5, 21.4; HRMS (FD) *m/z* cacl. for C₁₅H₁₄O₂S [M⁺]: 258.0709, found: 258.0709.

***S*-(4-Methoxyphenyl) benzothioate (3ab)¹**



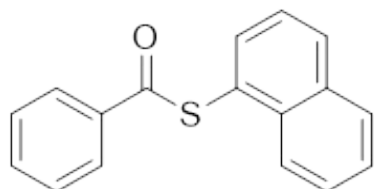
Iodobenzene (204 mg, 1.0 mmol) and 4-methoxyphenylsulfonyl hydrazide (202 mg, 1.0 mmol) provided **3ab** (222 mg, 0.91 mmol, 91%). White solid; Mp. 90 – 91 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.05 – 7.99 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 191.0, 160.8, 136.65, 136.62, 133.5, 128.7, 127.4, 117.9, 114.9, 55.4; MS (EI) *m/z* = 244 (M⁺).

***S*-(4-*tert*-Butylphenyl) benzothioate (3ac)**



Iodobenzene (204 mg, 1.0 mmol) and 4-*tert*-butylphenylsulfonyl hydrazide (228 mg, 1.0 mmol) provided **3ac** (243 mg, 0.90 mmol, 90%). White solid; Mp. 79 – 81 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.43 (m, 6H), 1.37 (s, 9H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 190.6, 152.8, 136.7, 134.7, 133.6, 128.7, 127.5, 126.4, 123.8, 34.8, 31.2; HRMS (FD) *m/z* cacl. for C₁₇H₁₈OS [M⁺]: 270.1073, found: 270.1074.

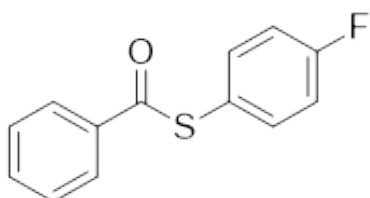
***S*-(1-Naphthalenyl) benzothioate (3ad)**



Iodobenzene (204 mg, 1.0 mmol) and 1-naphthalenylsulfonyl hydrazide (222 mg, 1.0 mmol) provided **3ad** (233 mg, 0.88

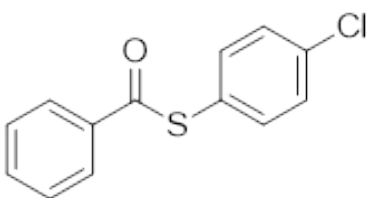
mmol, 88%). White solid; Mp. 133 – 135 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.25 (d, *J* = 7.1 Hz, 1H), 8.13 (d, *J* = 7.3 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.94 – 7.90 (m, 1H), 7.81 (d, *J* = 7.1 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.51 (m, 5H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 189.7, 136.7, 135.5, 134.6, 134.2, 133.7, 131.0, 128.8, 128.7, 127.7, 127.2, 126.4, 125.6, 125.4, 124.8; HRMS (FD) *m/z* cacl. for C₁₇H₁₂OS [M⁺]: 264.0603, found: 264.0603.

S-(4-Fluorophenyl) benzothioate (3ae)¹



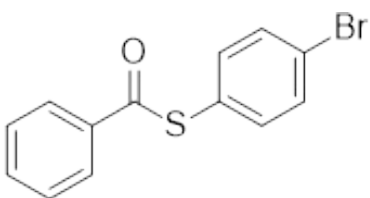
Iodobenzene (204 mg, 1.0 mmol) and 4-fluorophenylsulfonyl hydrazide (190 mg, 1.0 mmol) provided **3ae** (188 mg, 0.81 mmol, 81%). White solid; Mp. 47 – 49 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.07 – 8.01 (m, 2H), 7.67 – 7.60 (m, 1H), 7.53 – 7.47 (m, 4H), 7.17 (t, *J* = 8.7 Hz, 2H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 190.1, 163.6 (d, *J*_{C-F} = 250.7 Hz), 137.1 (d, *J*_{C-F} = 8.8 Hz), 136.4, 133.8, 129.3, 128.8, 127.5, 122.6 (d, *J*_{C-F} = 3.8 Hz), 116.5 (d, *J*_{C-F} = 21.4 Hz); MS (EI) *m/z* = 232 (M⁺).

S-(4-Chlorophenyl) benzothioate (3af)¹



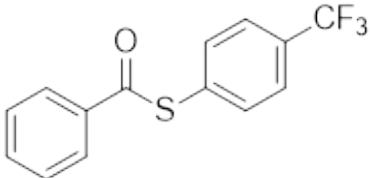
Iodobenzene (204 mg, 1.0 mmol) and 4-chlorophenylsulfonyl hydrazide (207 mg, 1.0 mmol) provided **3af** (211 mg, 0.85 mmol, 85%). White solid; Mp. 72 – 74 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.04 – 8.01 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.47 – 7.43 (m, 4H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 189.6, 136.4, 136.3, 136.0, 133.8, 129.5, 128.8, 127.5, 125.8; MS (EI) *m/z* = 248 (M⁺).

S-(4-Bromophenyl) benzothioate (3ag)¹



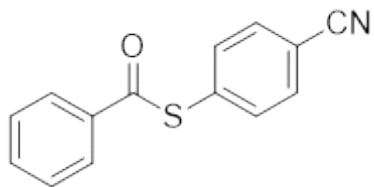
Iodobenzene (204 mg, 1.0 mmol) and 4-bromophenylsulfonyl hydrazide (251 mg, 1.0 mmol) provided **3ag** (254 mg, 0.87 mmol, 87%). White solid; Mp. 82 – 84 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.04 – 8.00 (m, 2H), 7.61 (dd, *J* = 12.8, 8.0 Hz, 3H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 189.5, 136.5, 136.3, 133.9, 132.4, 128.8, 127.5, 126.5, 124.2; MS (EI) *m/z* = 292 (M⁺).

S-(4-Trifluoromethylphenyl) benzothioate (3ah)



Iodobenzene (204 mg, 1.0 mmol) and 4-trifluoromethylphenylsulfonyl hydrazide (240 mg, 1.0 mmol) provided **3ah** (223 mg, 0.79 mmol, 79%). White solid; Mp. 100 – 103 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.74 – 7.71 (m, 2H), 7.68 – 7.64 (m, 3H), 7.52 (t, *J* = 7.8 Hz, 2H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 188.9, 136.7, 136.2, 135.2, 134.1, 132.1, 131.6, 131.3, 128.9, 127.9, 127.6, 126.5, 126.3, 126.0 (q, *J*_{C-F} = 3.8 Hz), 123.8 (q, *J*_{C-F} = 273.4 Hz); HRMS (FD) *m/z* cacl. for C₁₄H₉OF₃S [M⁺]: 282.0321, found: 282.0317.

S-(4-Cyanophenyl) benzothioate (3ai)



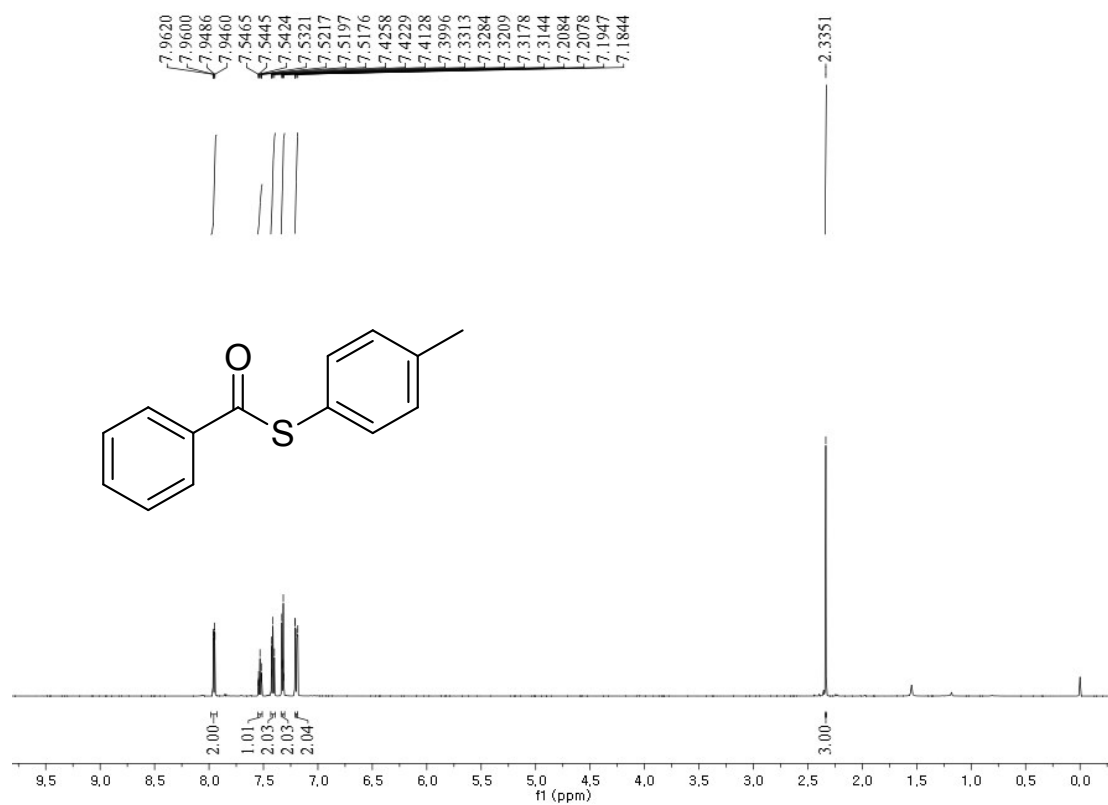
Iodobenzene (204 mg, 1.0 mmol) and 4-cyanophenylsulfonyl hydrazide (197 mg, 1.0 mmol) provided **3ai** (156 mg, 0.65 mmol, 65%). White solid; Mp. 97 – 99 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.04 – 8.00 (m, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.66 (dd, *J* = 8.3, 2.0 Hz, 3H), 7.53 (t, *J* = 7.8 Hz, 2H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 188.3, 135.9, 135.3, 134.2, 133.9, 132.5, 128.9, 127.6, 118.3, 113.1; HRMS (FD) *m/z* calcd. for C₁₄H₉NOS [M⁺]: 239.0399, found: 239.0399.

Reference

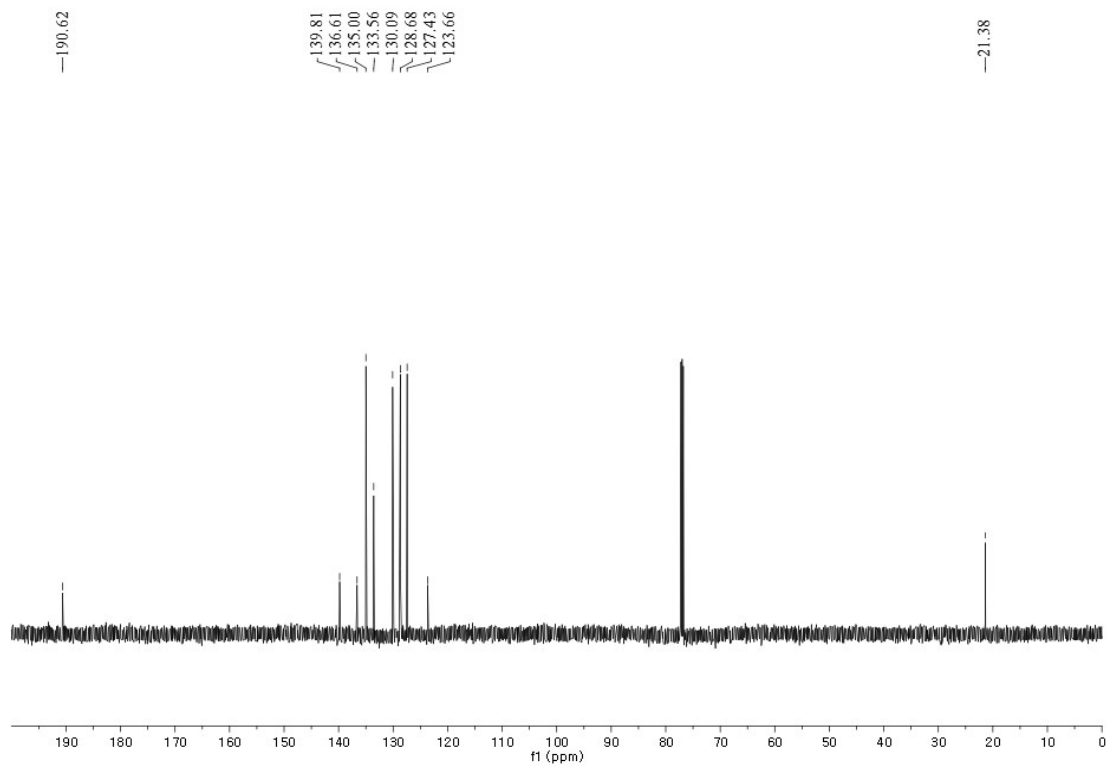
1. H. Cao, L. McNamee and H. Alper, *J. Org. Chem.* 2008, **73**, 3530-3534.
2. M. Arisawa, T. Yamada and M. Yamaguchi, *Tetrahedron Lett.* 2010, **51**, 6090-6092.
3. M. J. Strauss and Z. Rappoport, *J. Org. Chem.* 1982, **47**, 4809-4812.
4. C. A. Kingsbury and G. Ebert, *G. PHOSPHORUS SULFUR* 1981, **9**, 315-321.

S-p-Tolyl benzothioate (3a)

¹H NMR

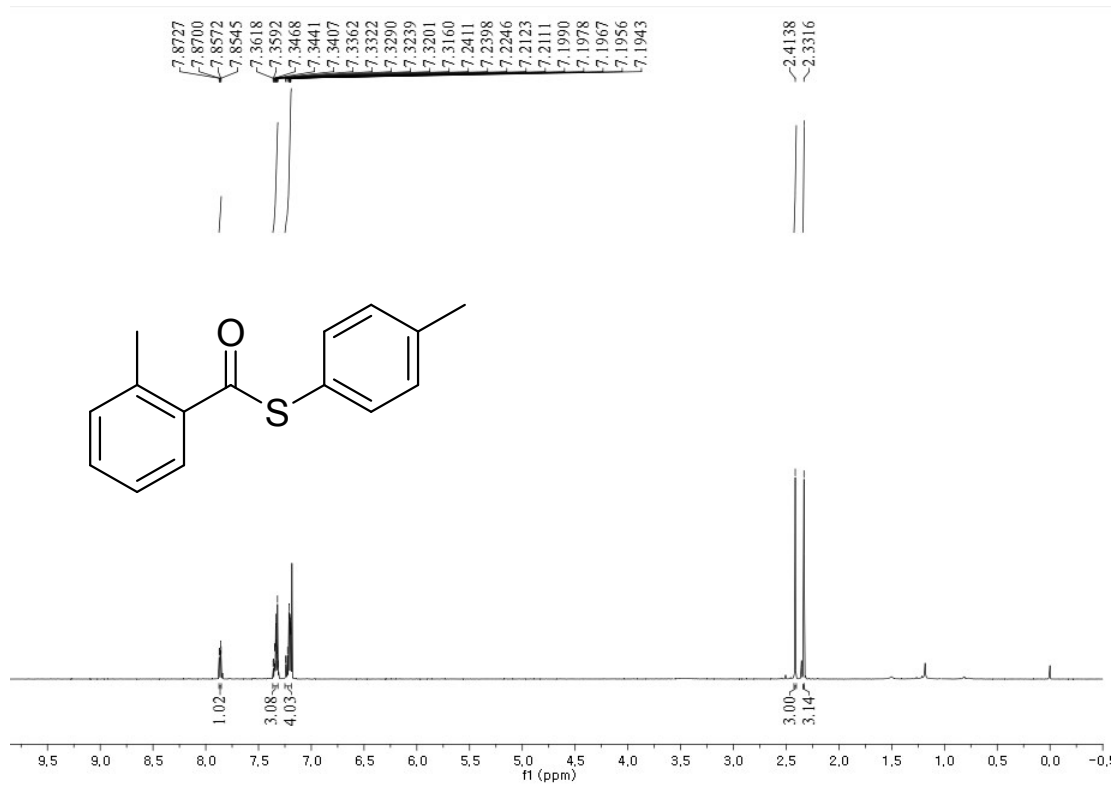


¹³C NMR

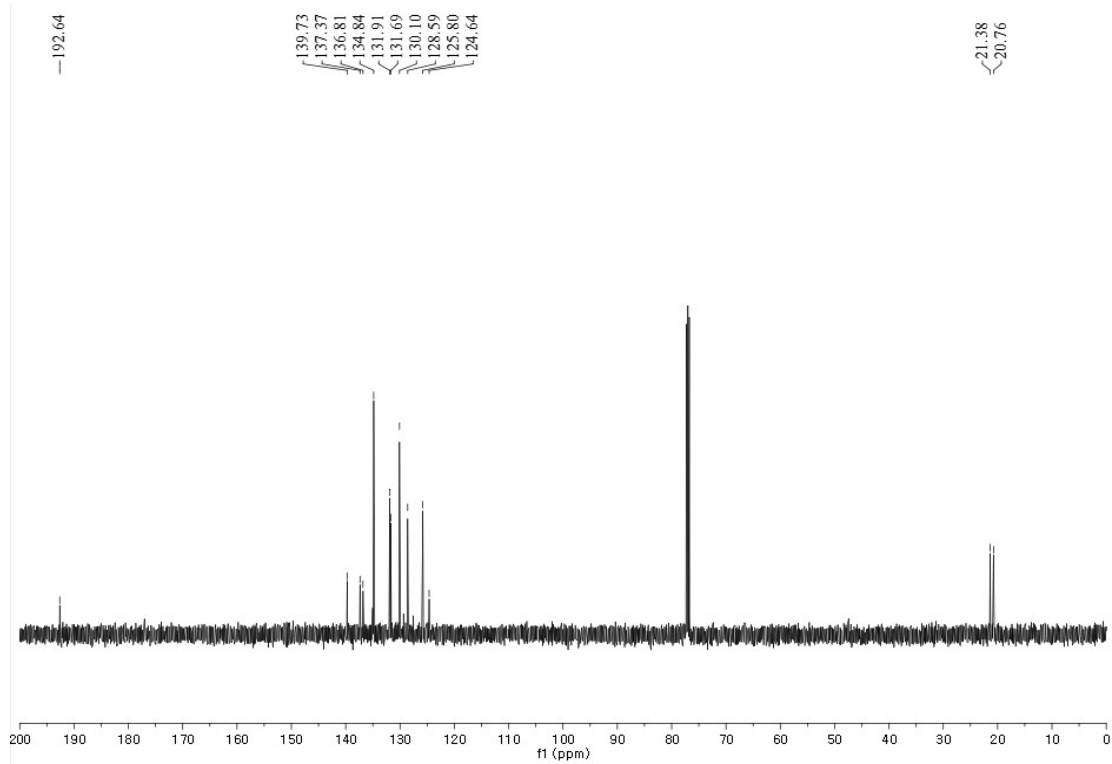


***S-p*-Tolyl-2-methylbenzothioate (3ba)**

¹H NMR

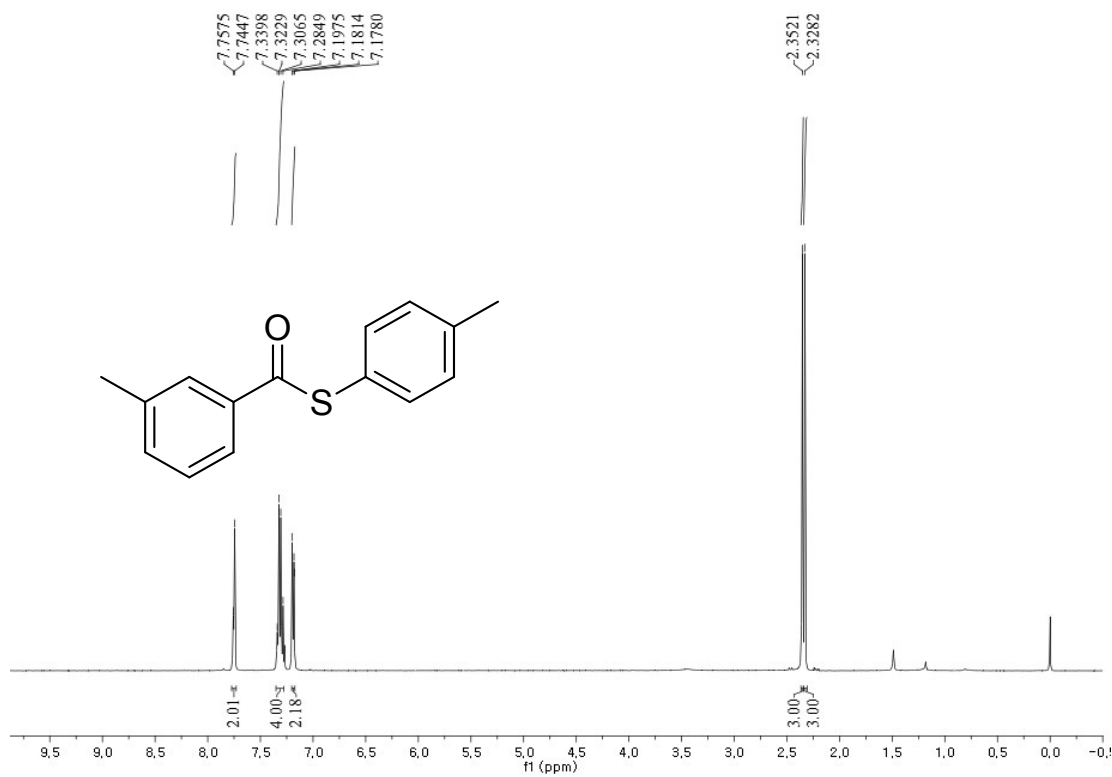


¹³C NMR

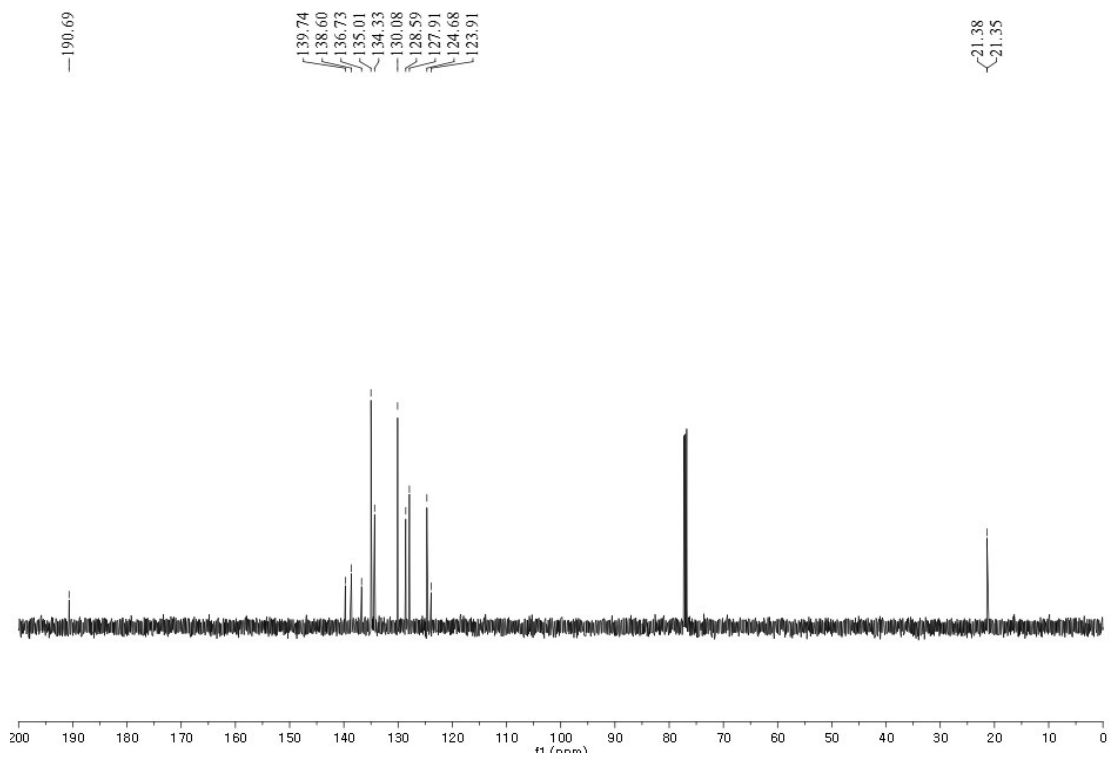


***S-p*-Tolyl-3-methylbenzothioate (3ca)**

¹H NMR

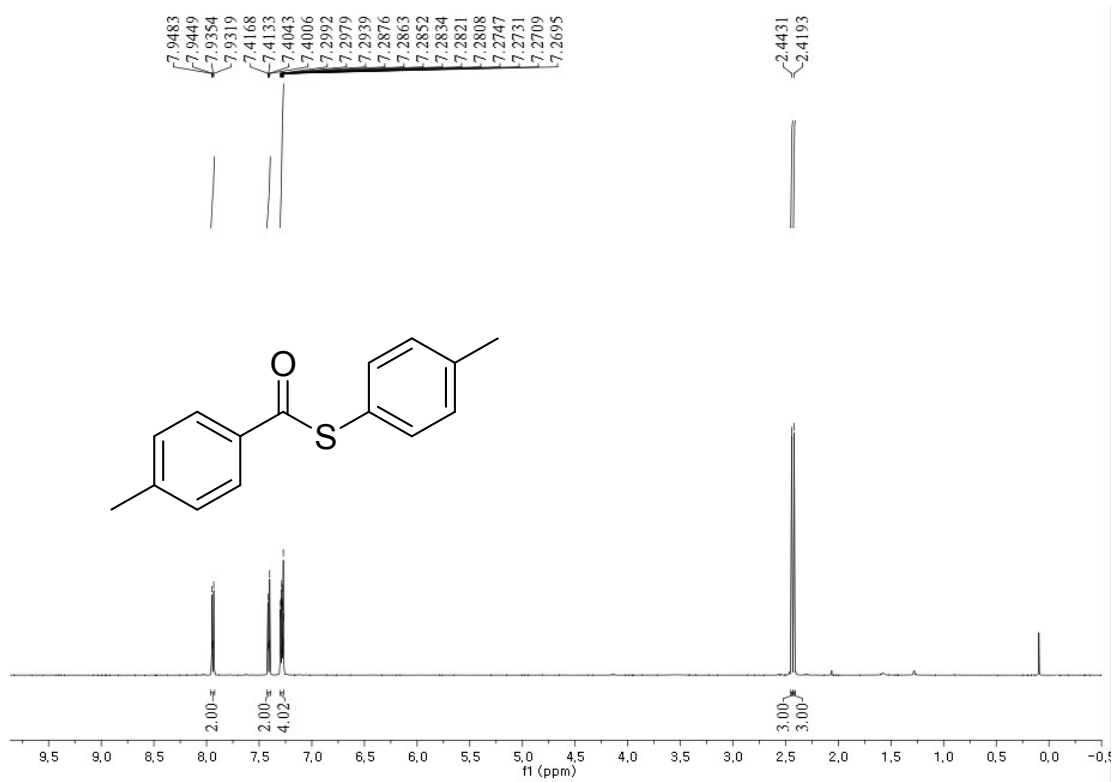


¹³C NMR

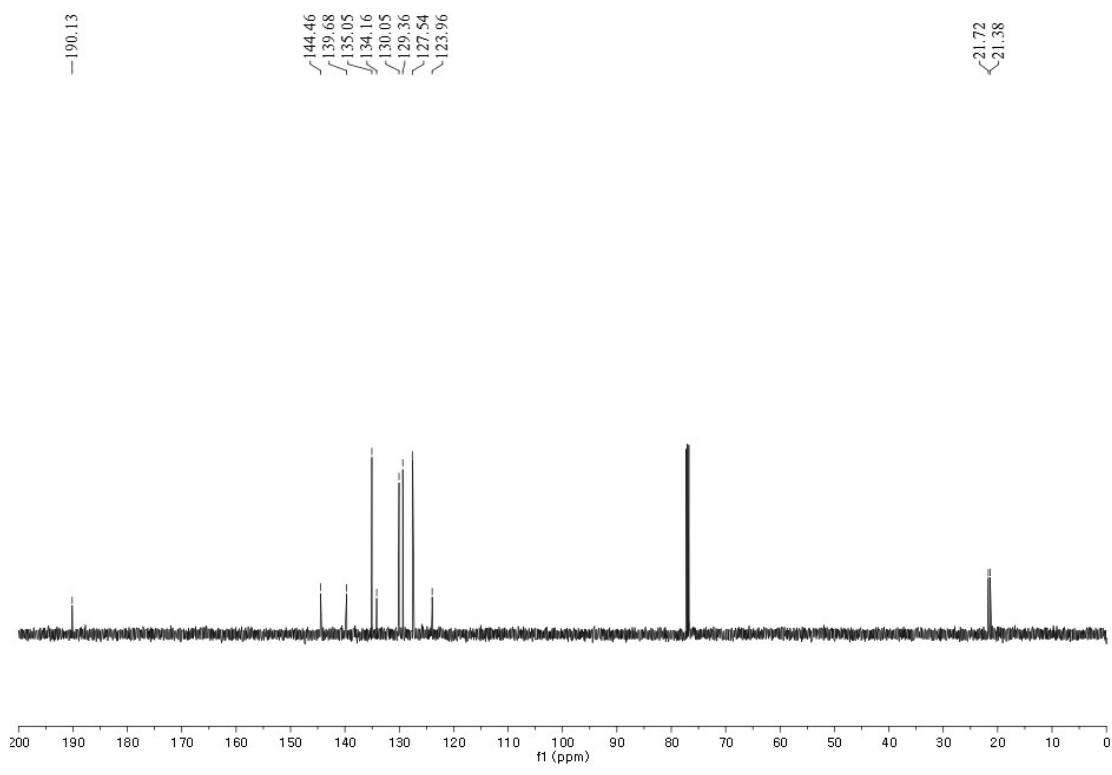


***S-p*-Tolyl-4-methylbenzothioate (3da)**

¹H NMR

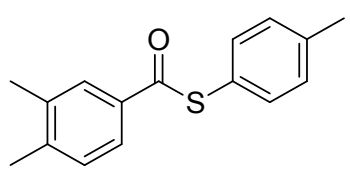
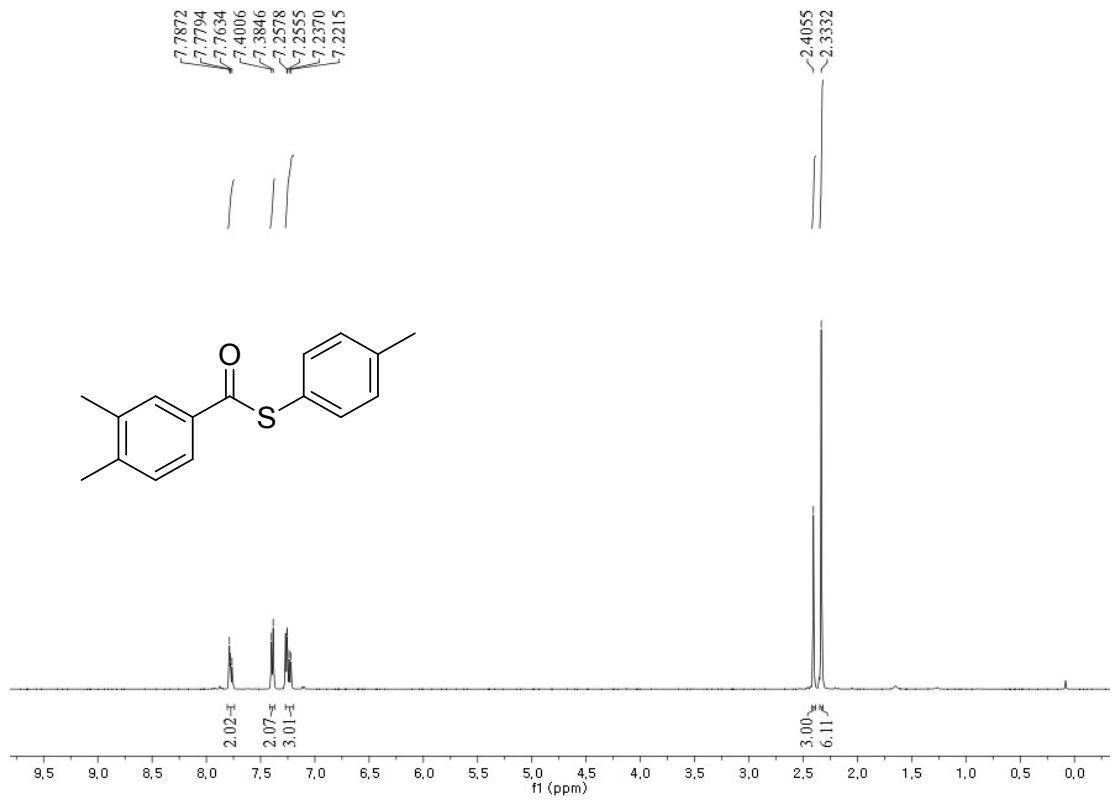


¹³C NMR

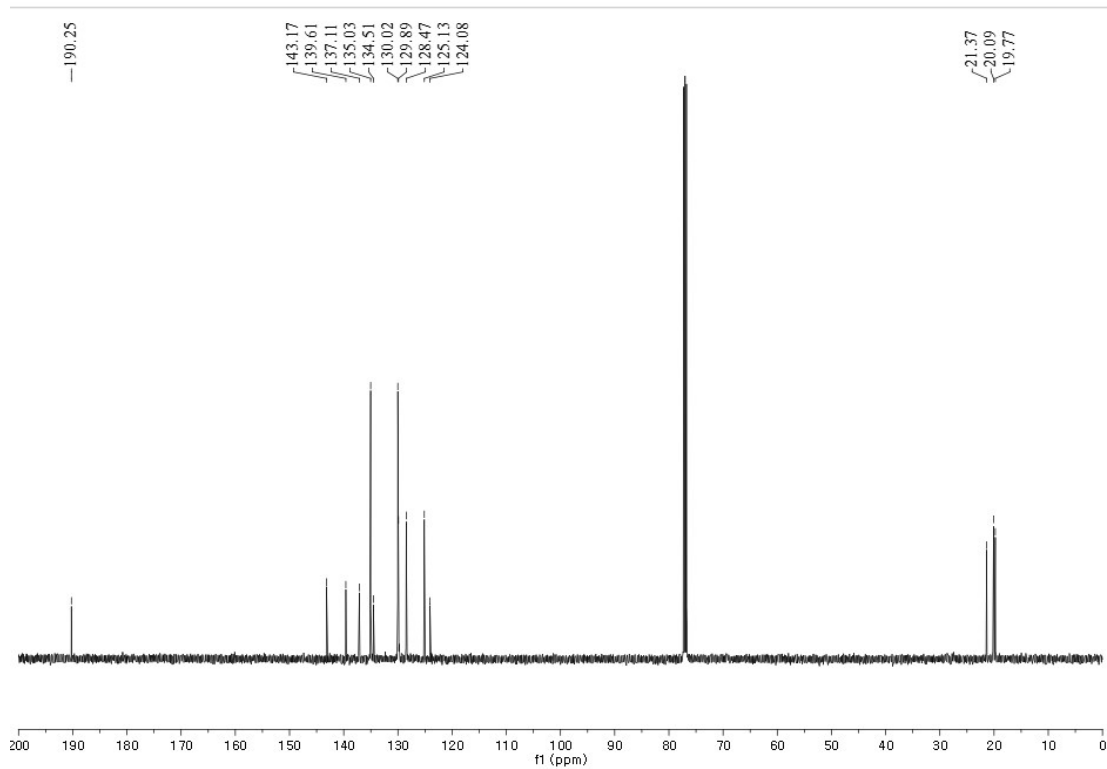


***S-p*-Tolyl-3,4-dimethylbenzothioate (3ea)**

¹H NMR

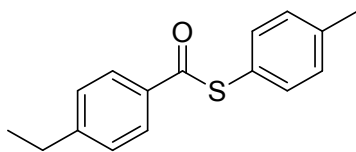


¹³C NMR

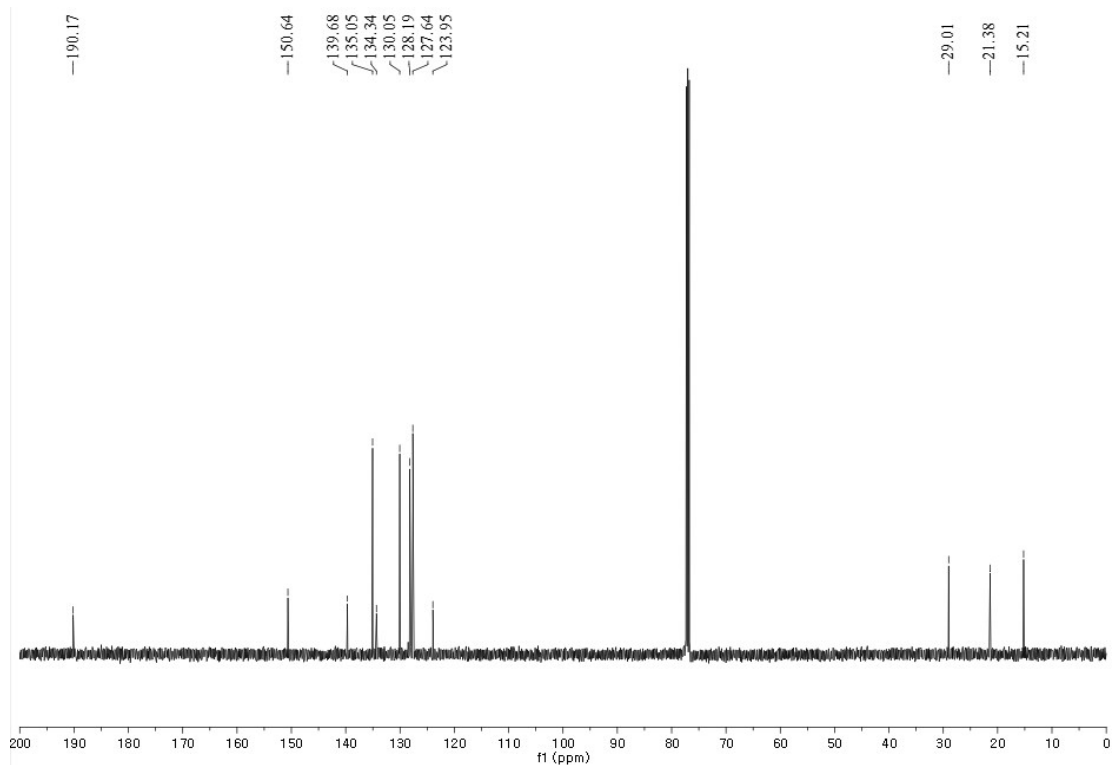


***S-p*-Tolyl-4-ethylbenzothioate (3fa)**

¹H NMR

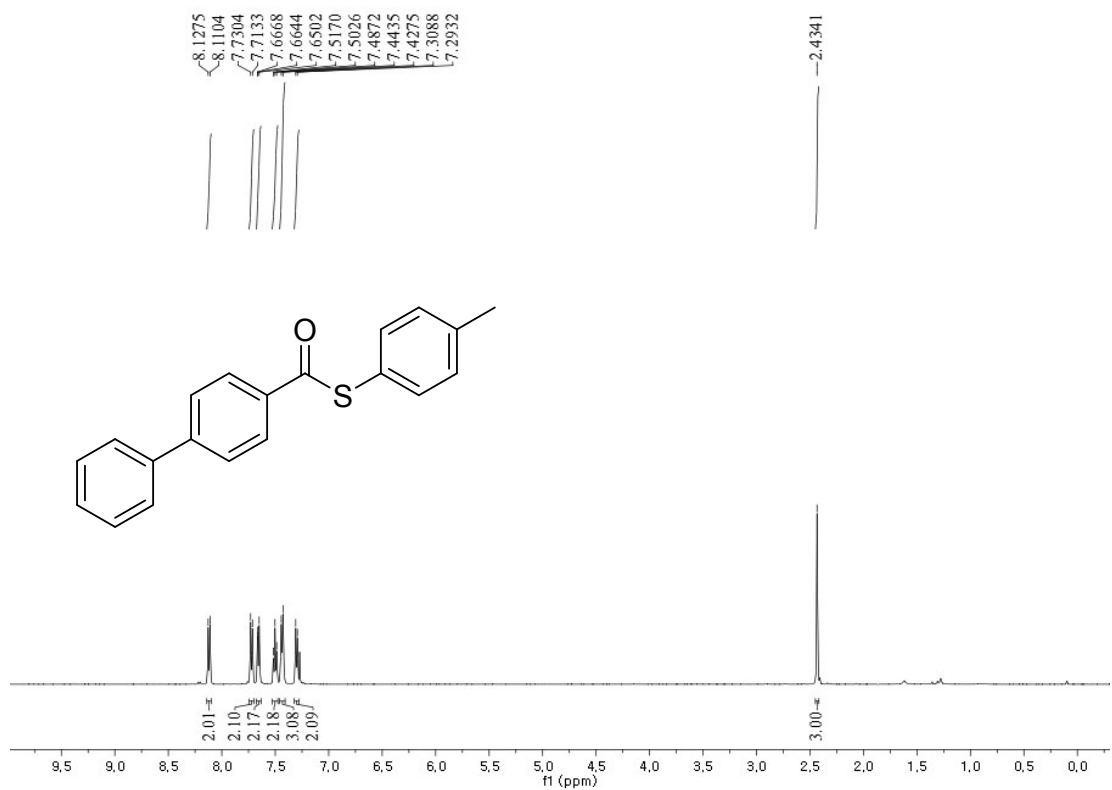


¹³C NMR

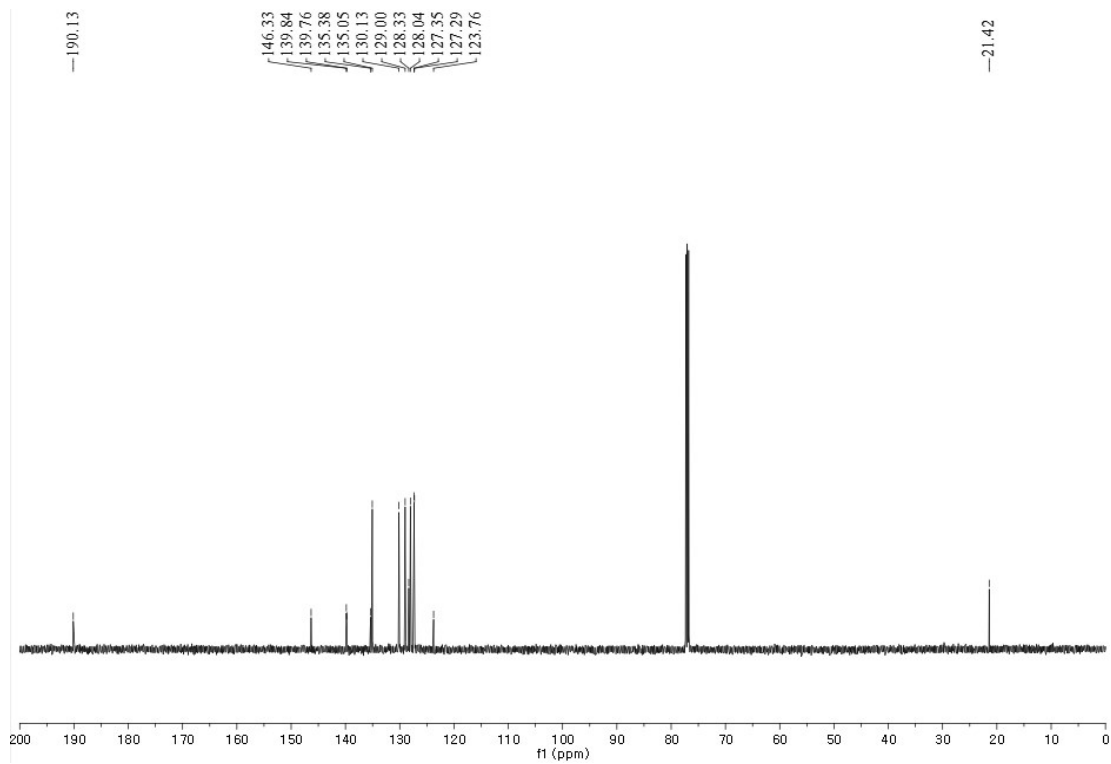


***S-p*-Tolyl-4-phenylbenzothioate (3ga)**

¹H NMR

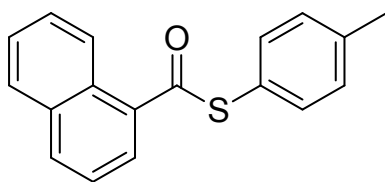
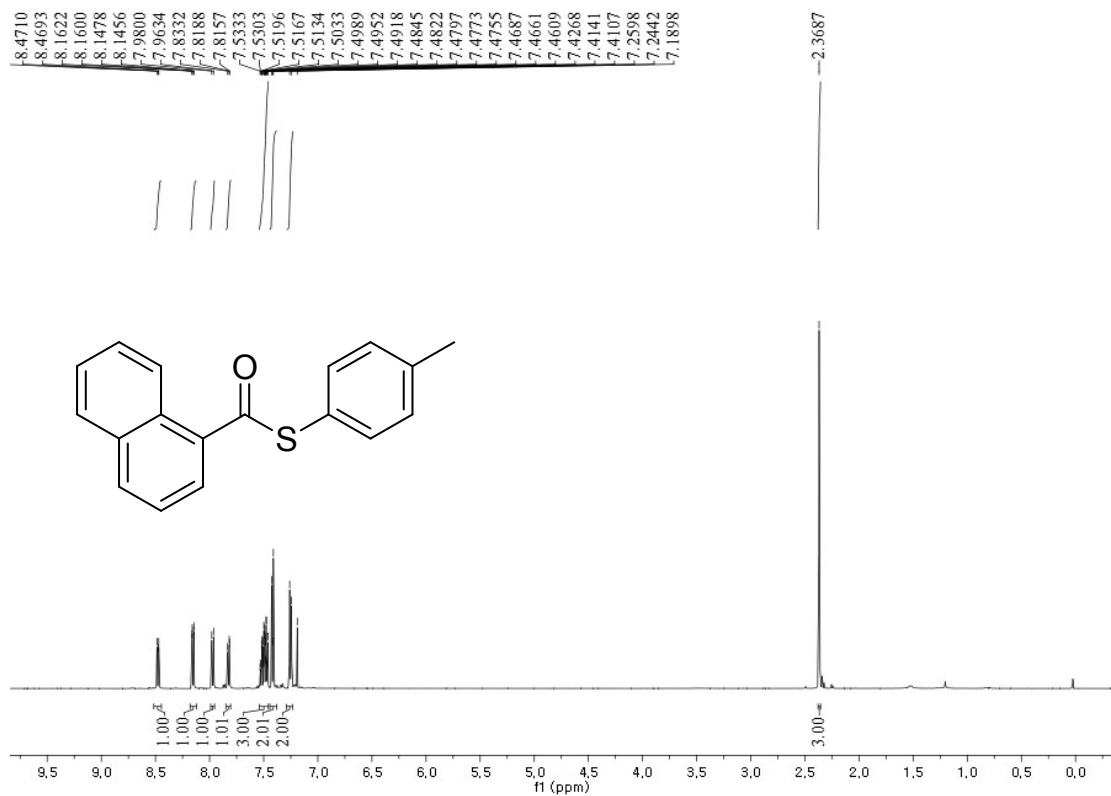


¹³C NMR

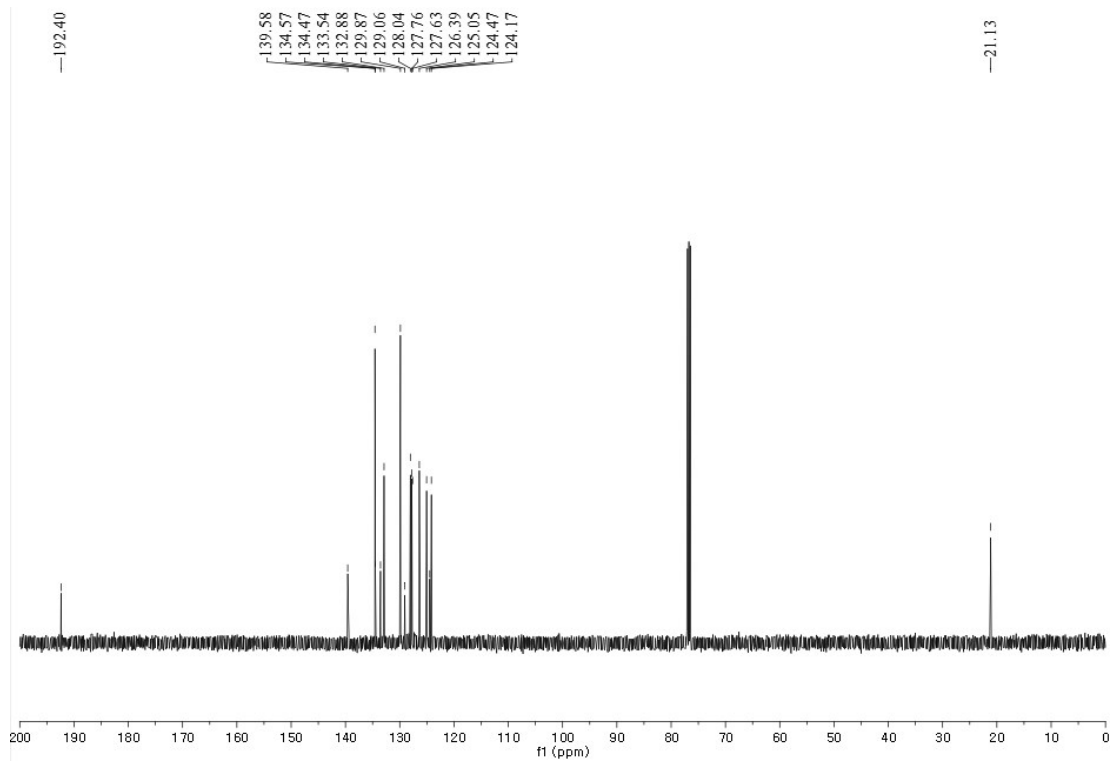


S-p-Tolyl naphthothioate (3ha)

¹H NMR



¹³C NMR

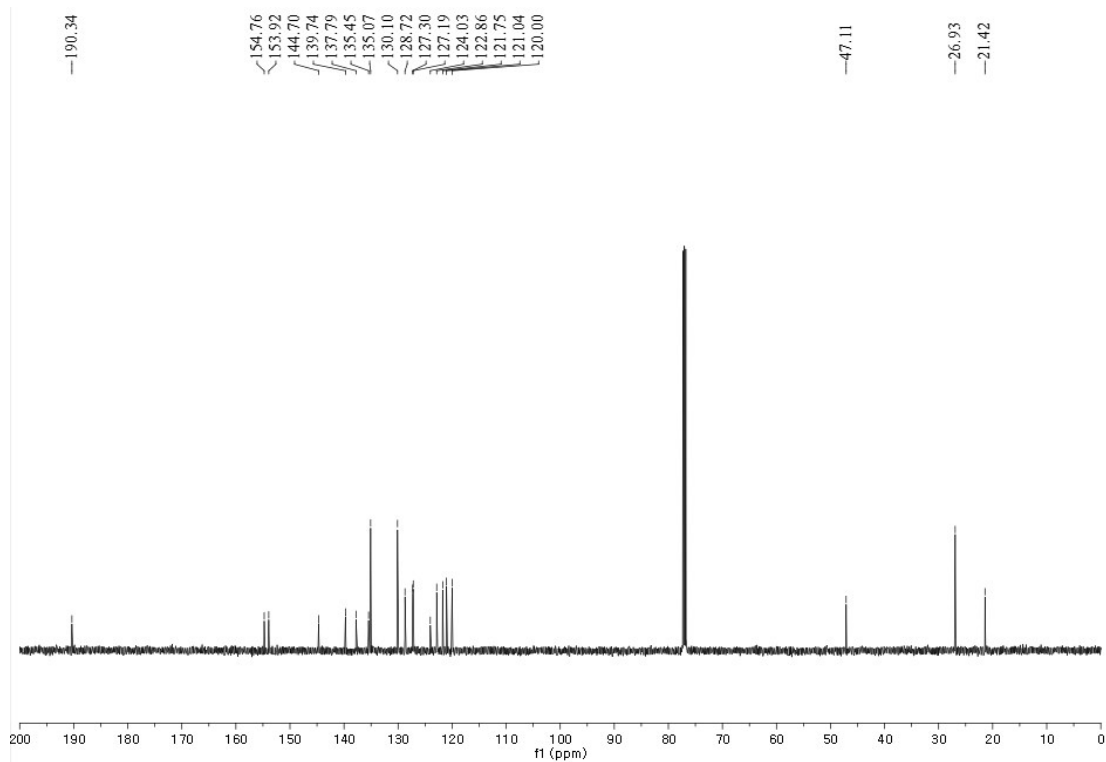


S-p-Tolyl-9,9-dimethyl-9H-fluorenothioate (3ia)

¹H NMR

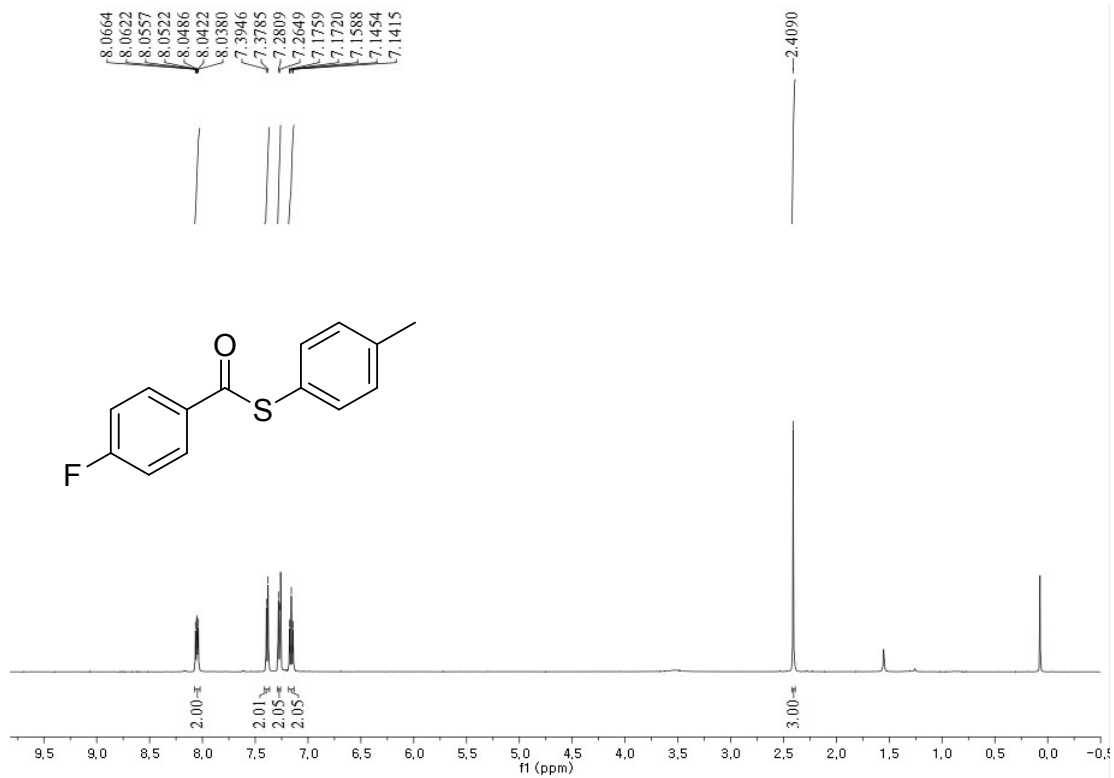


¹³C NMR

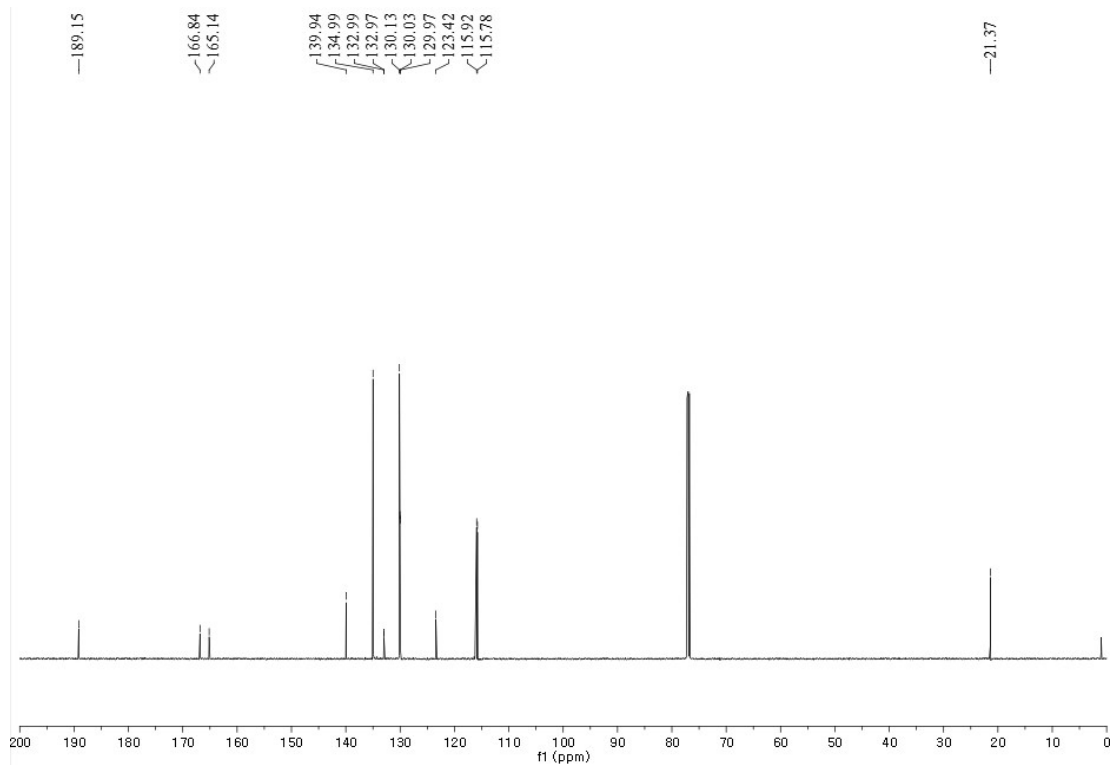


S-p-Tolyl-4-fluorobenzothioate (3ja)

¹H NMR

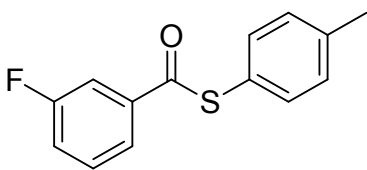
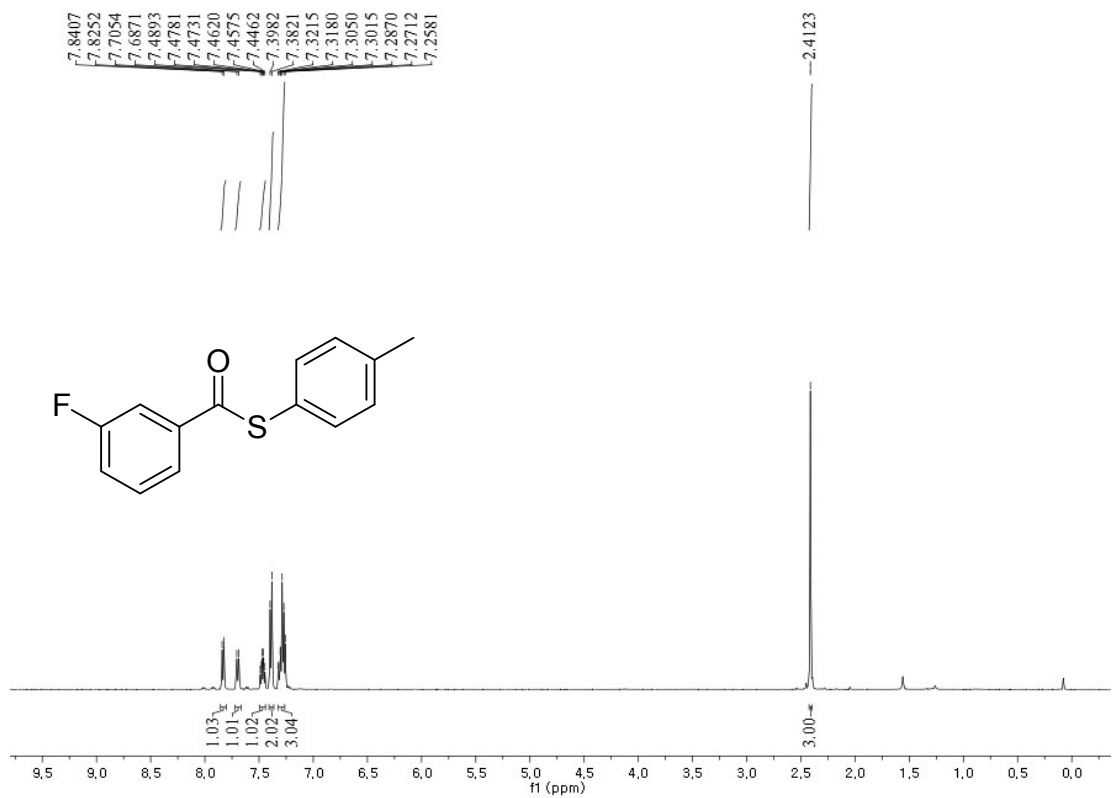


¹³C NMR

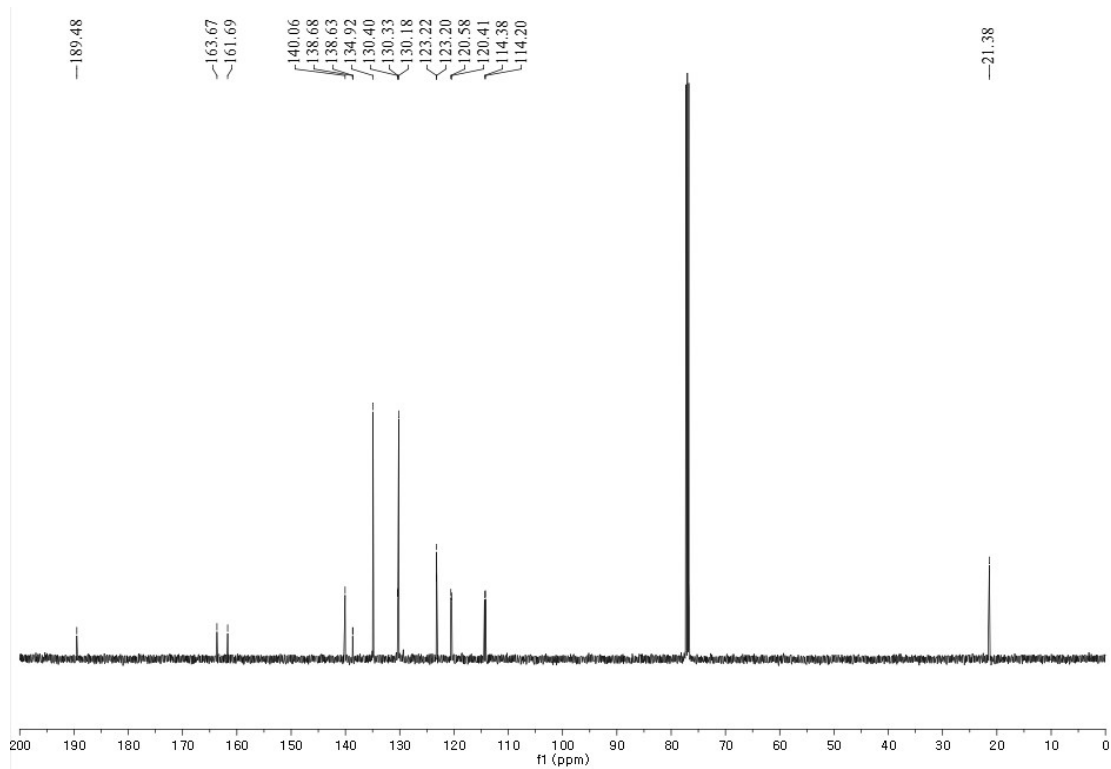


S-p-Tolyl-3-fluorobenzothioate (3ka)

¹H NMR



¹³C NMR

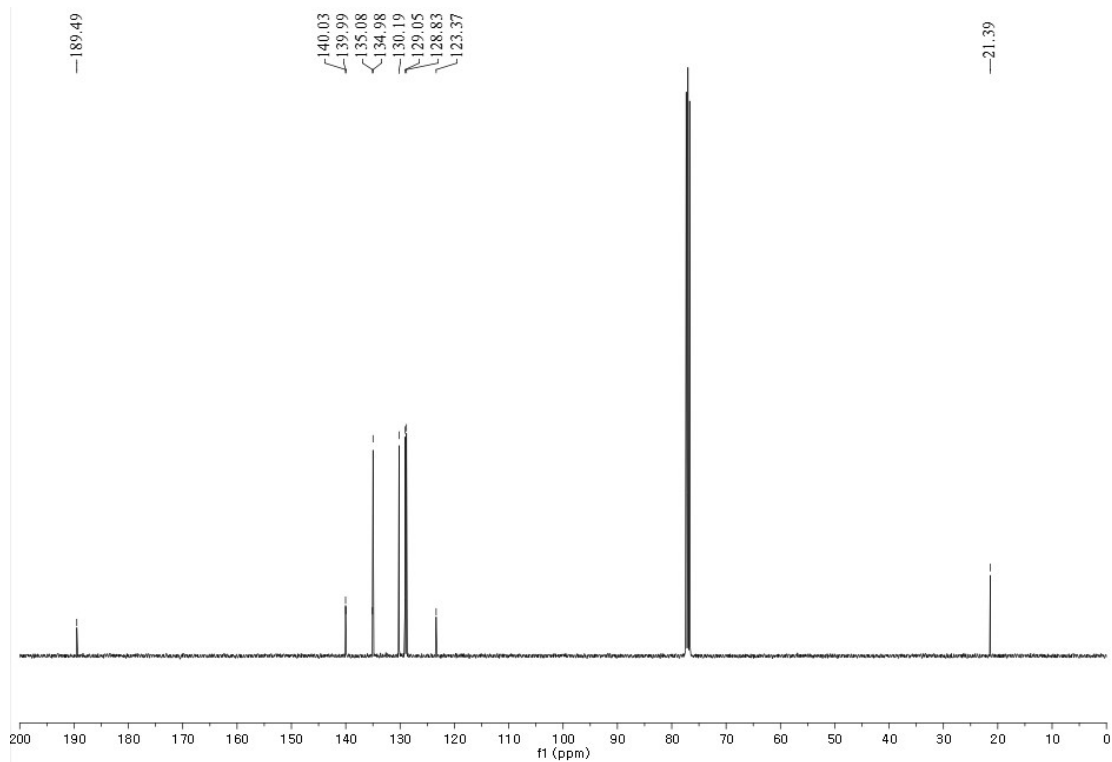


S-p-Tolyl-4-chlorobenzothioate (3la)

¹H NMR

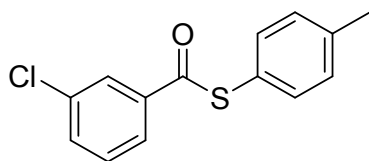


¹³C NMR

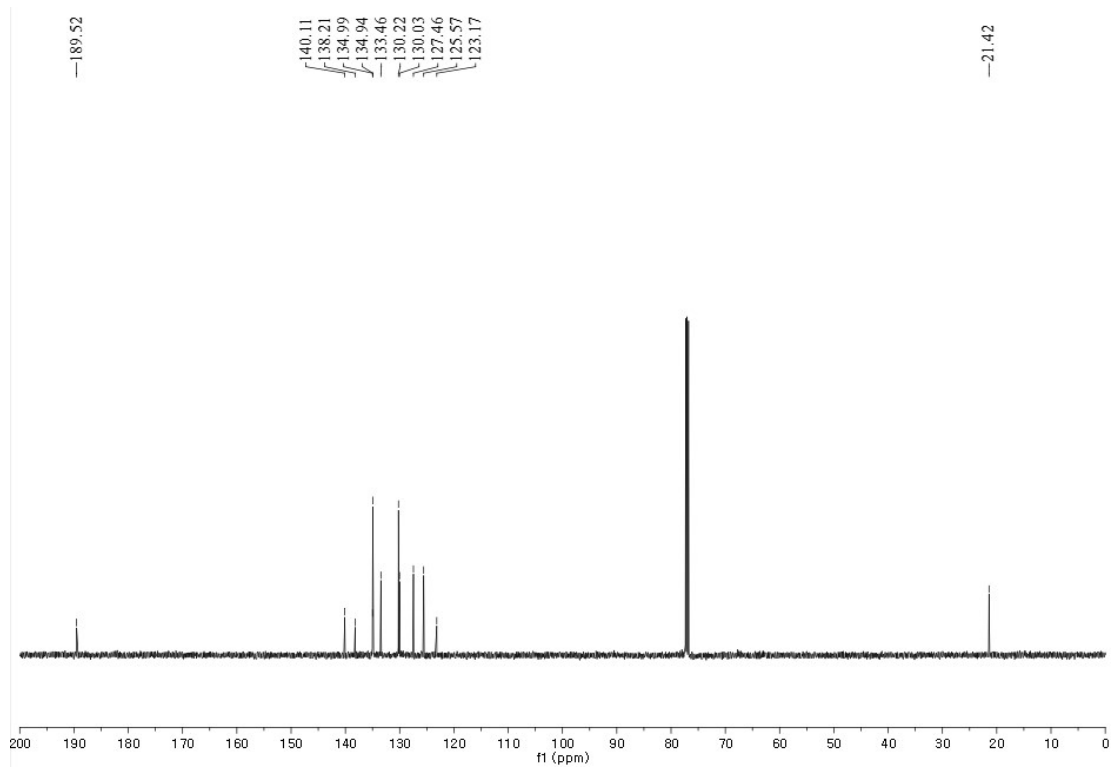


***S-p*-Tolyl-3-chlorobenzothioate (3ma)**

¹H NMR

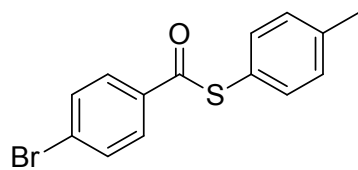
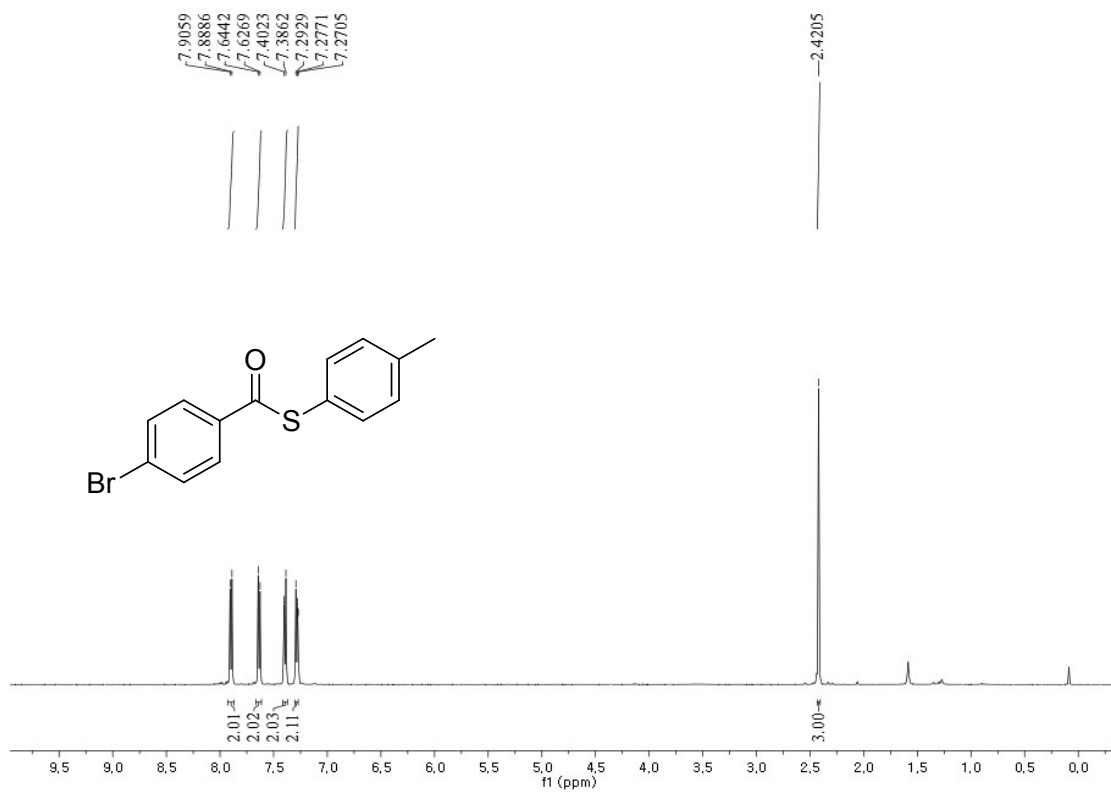


¹³C NMR

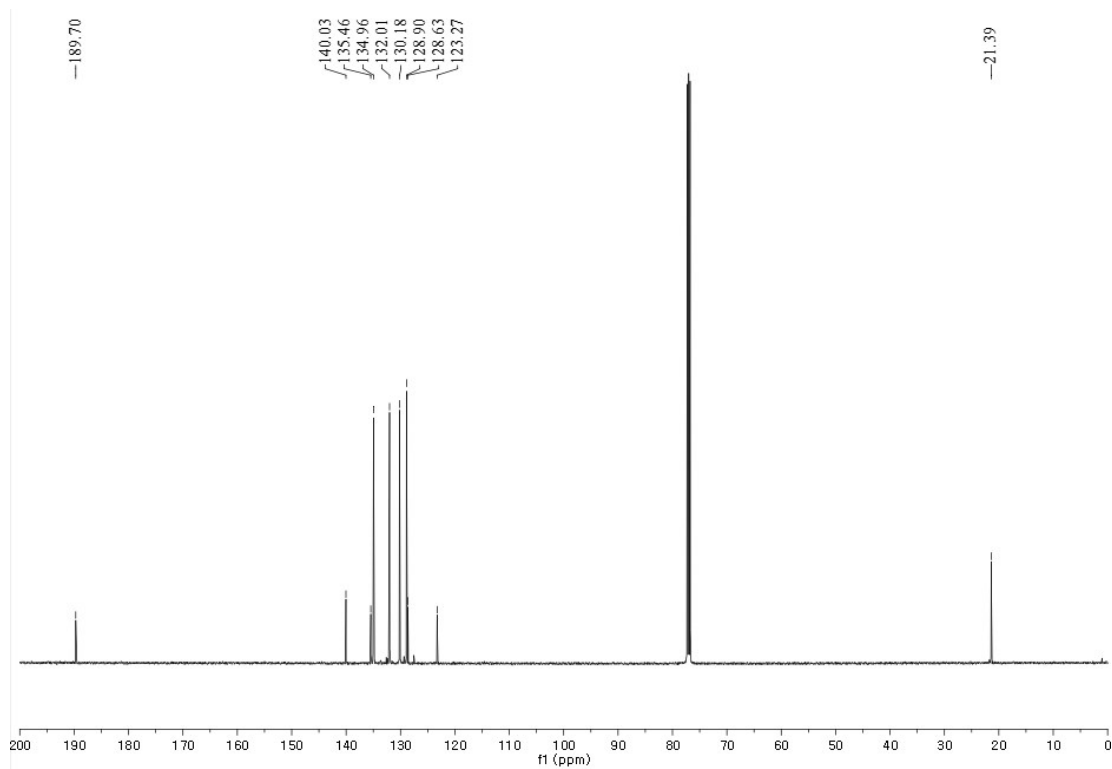


***S-p*-Tolyl-4-bromobenzothioate (3na)**

¹H NMR

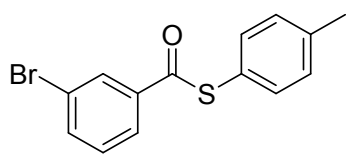


¹³C NMR

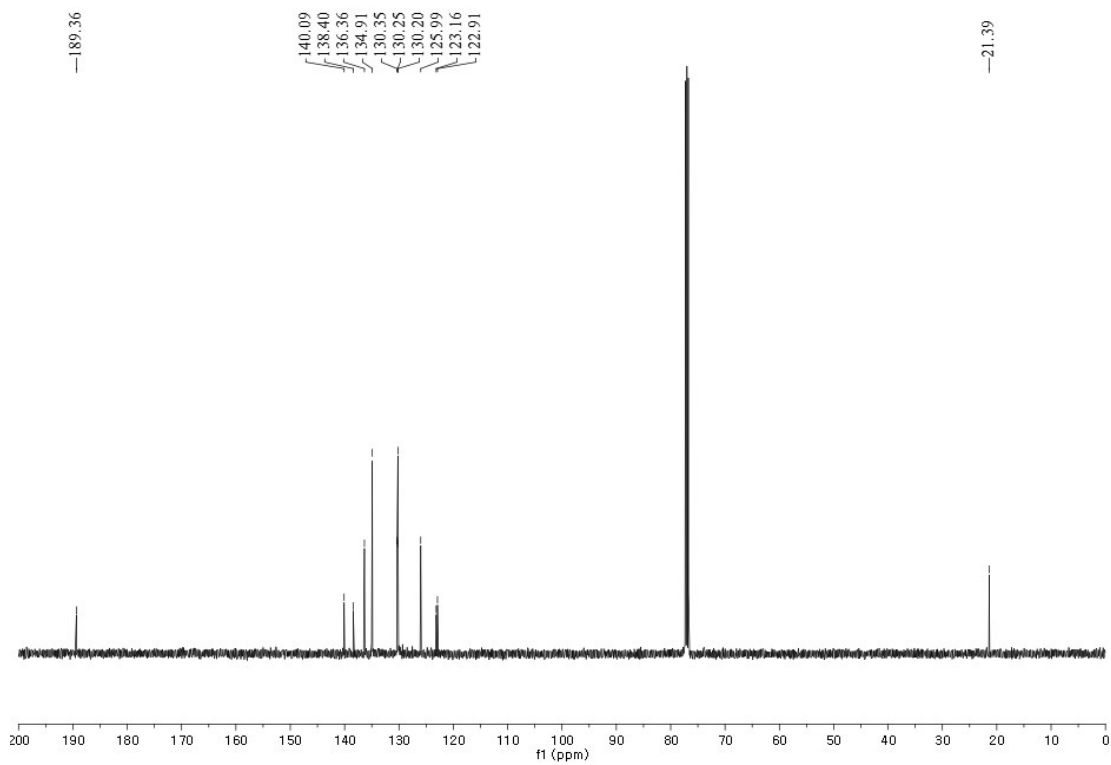


S-p-Tolyl-3-bromobenzothioate (30a)

¹H NMR

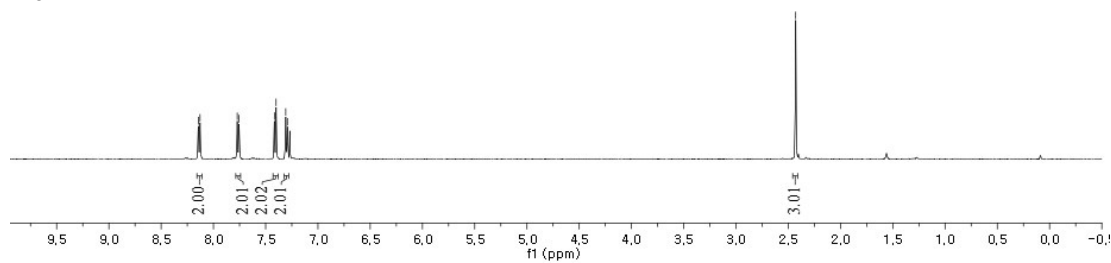
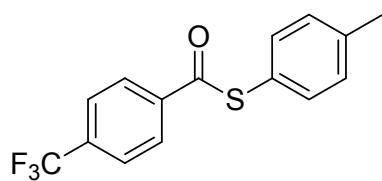


¹³C NMR

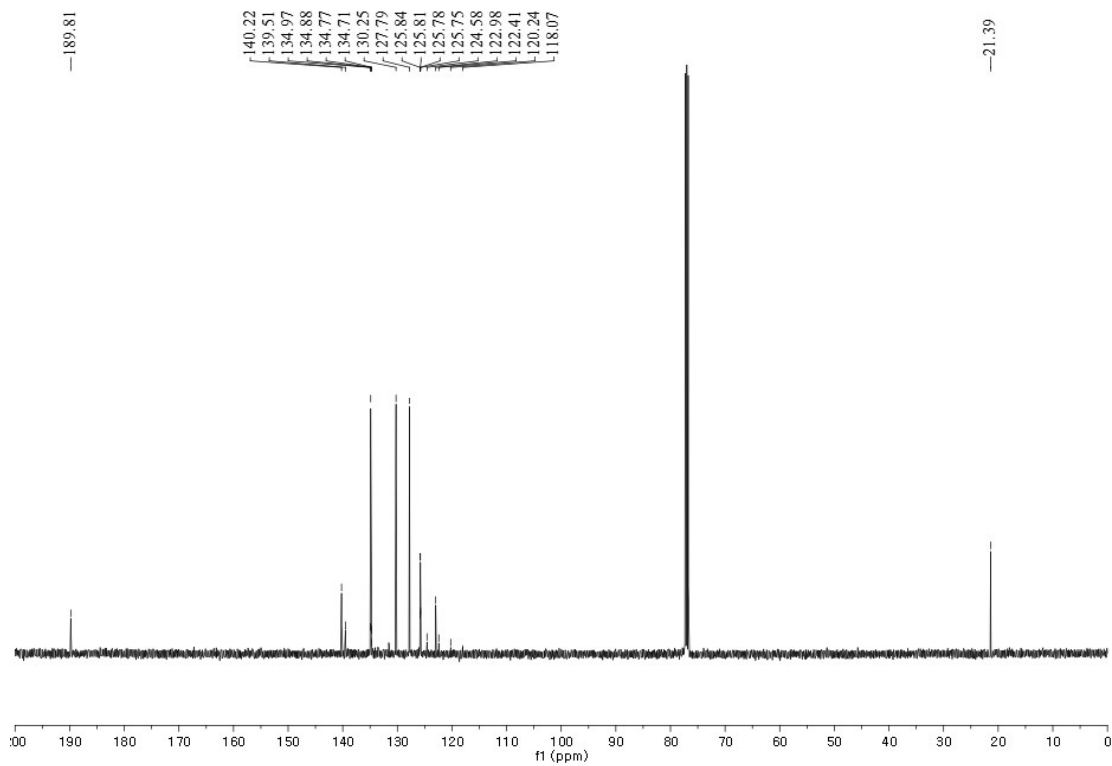


***S-p*-Tolyl-4-trifluoromethylbenzothioate (3pa)**

¹H NMR

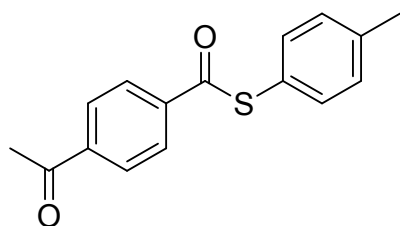
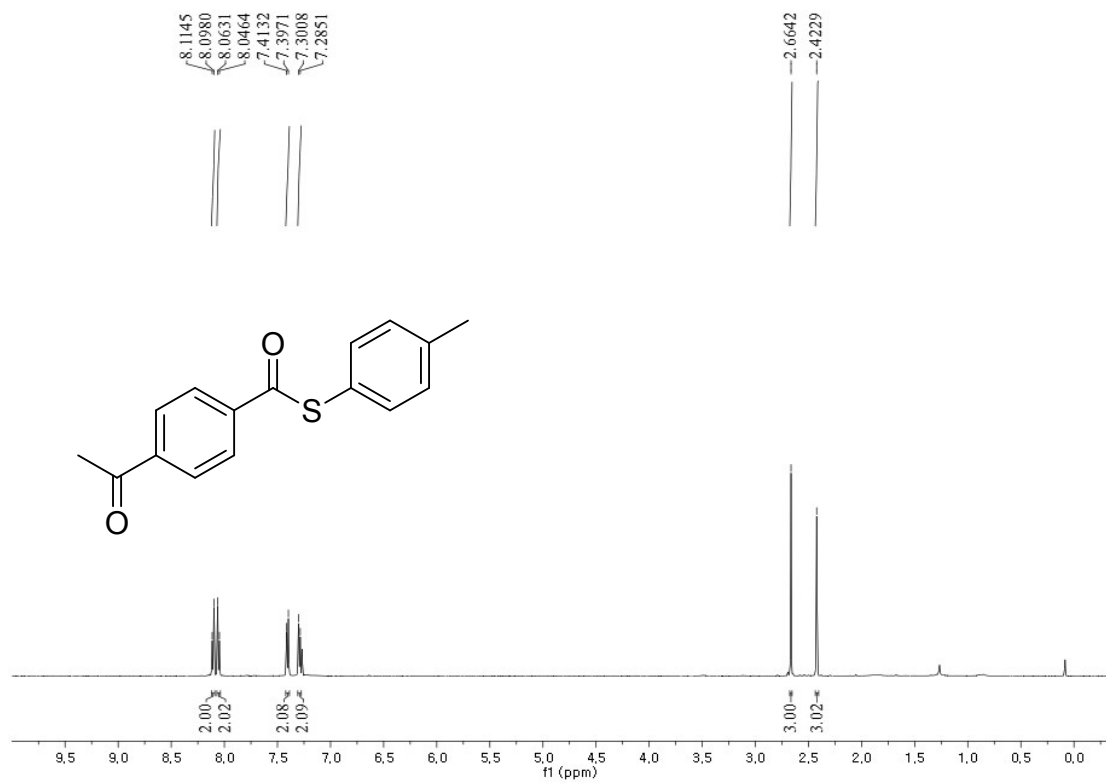


¹³C NMR

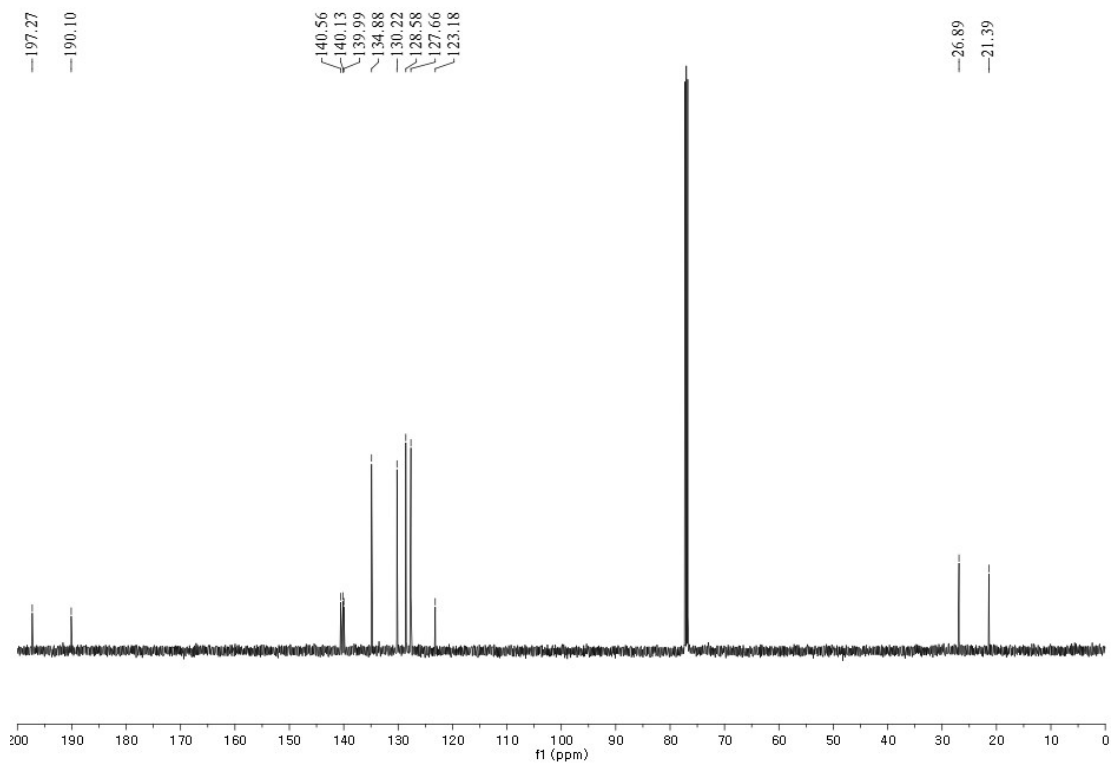


S-p-Tolyl-4-acetylbenzothioate (3qa)

¹H NMR



¹³C NMR

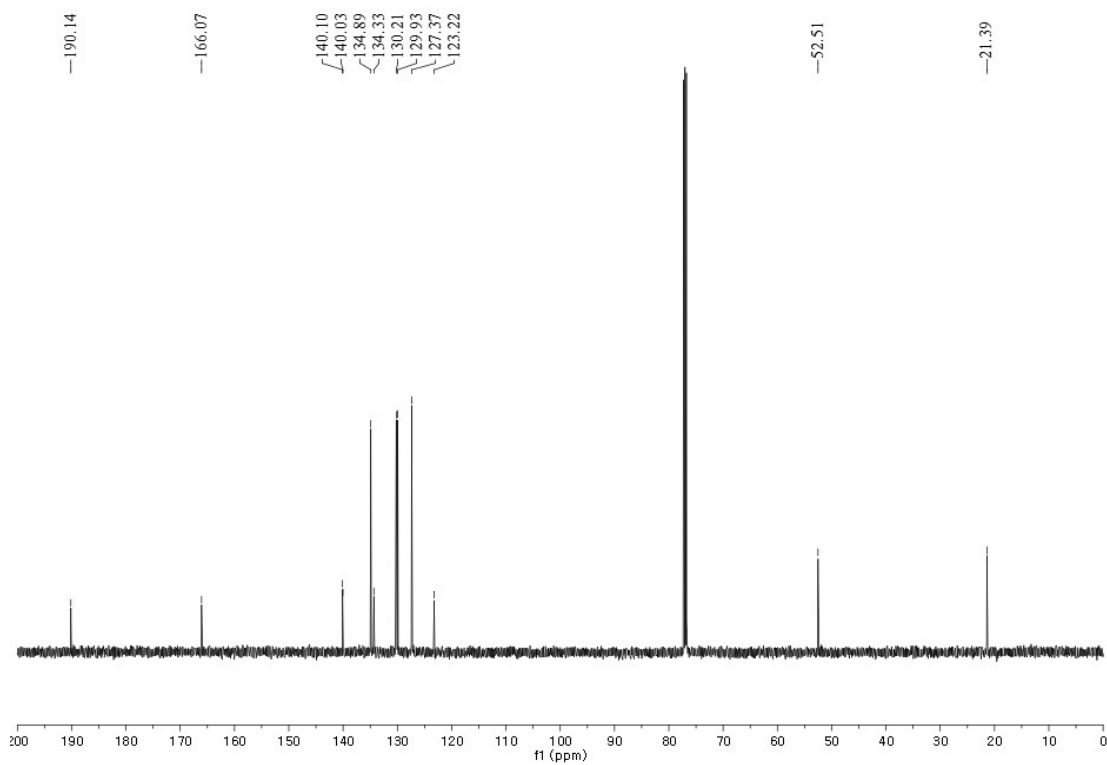


***S-p*-Tolyl methylbenzoatethioate (3ra)**

¹H NMR

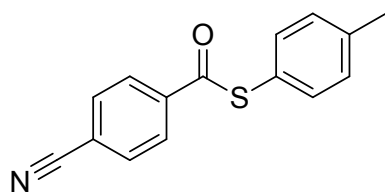
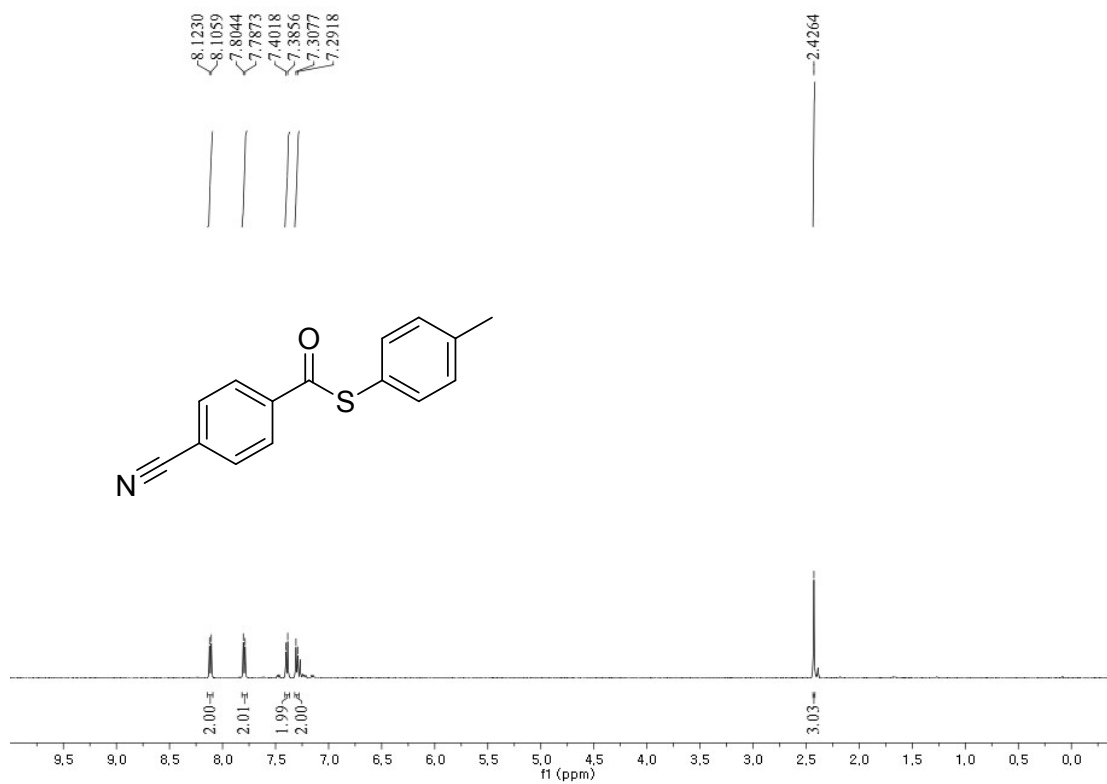


¹³C NMR

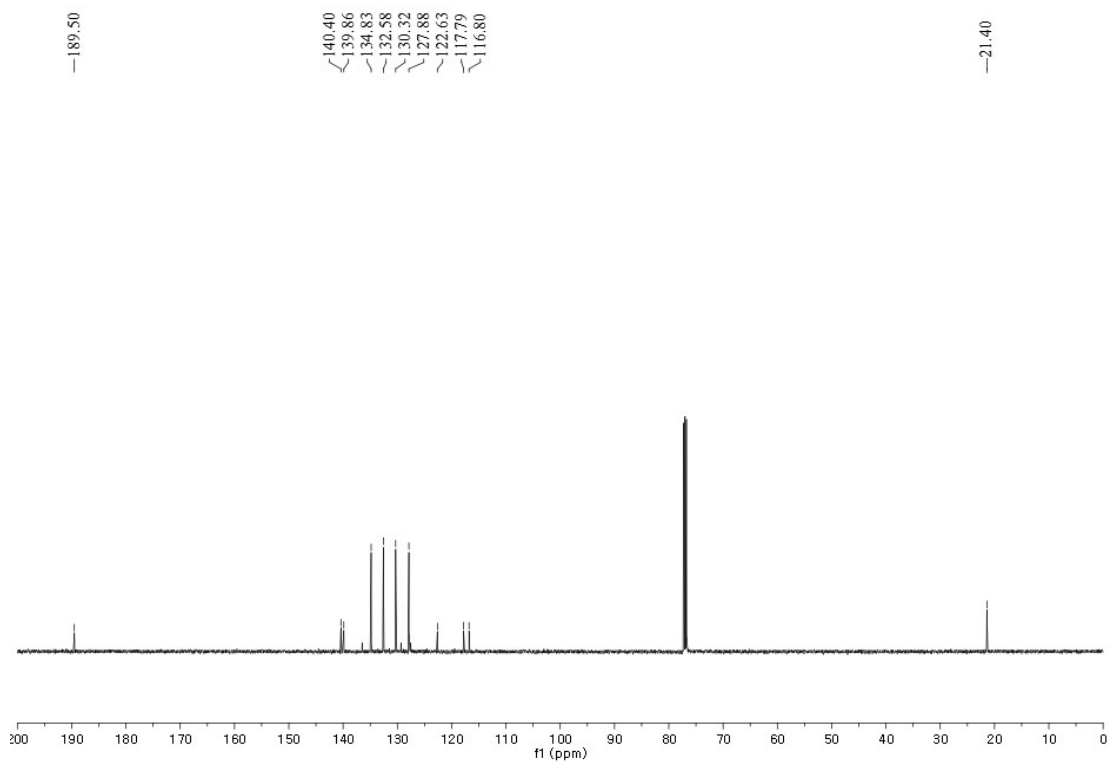


***S-p*-Tolyl-4-cyanobenzothioate (3sa)**

¹H NMR



¹³C NMR

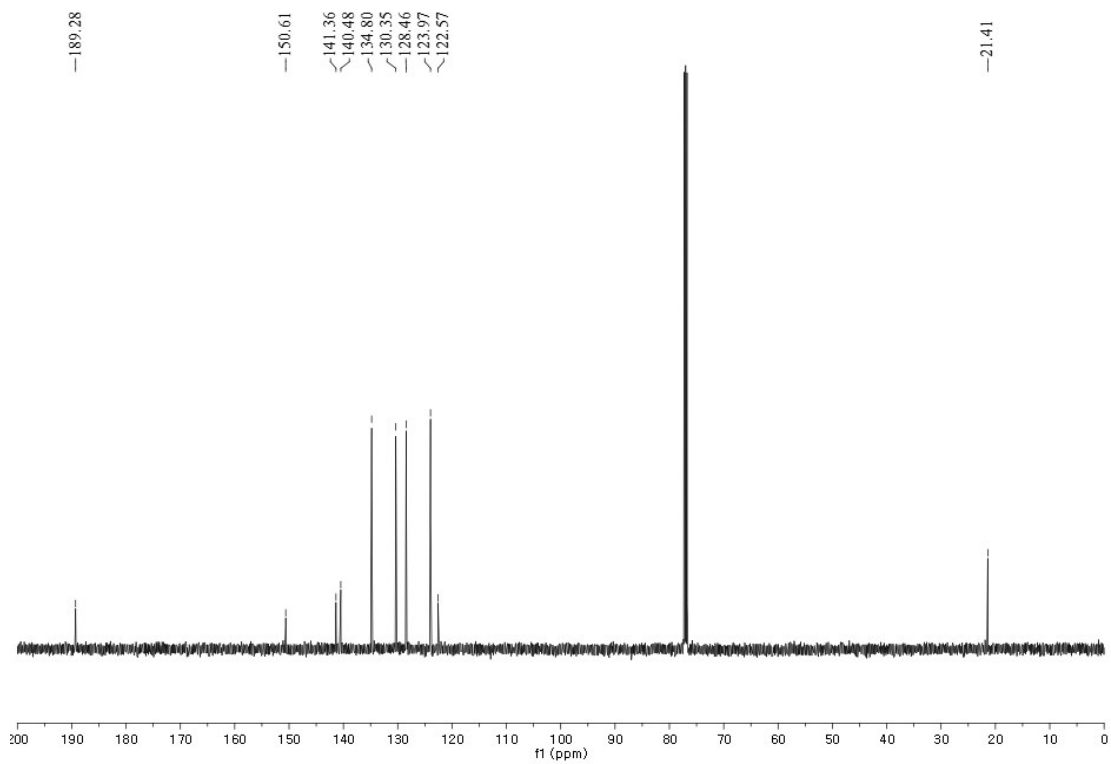


***S-p*-Tolyl-4-nitrobenzothioate (3ta)**

¹H NMR

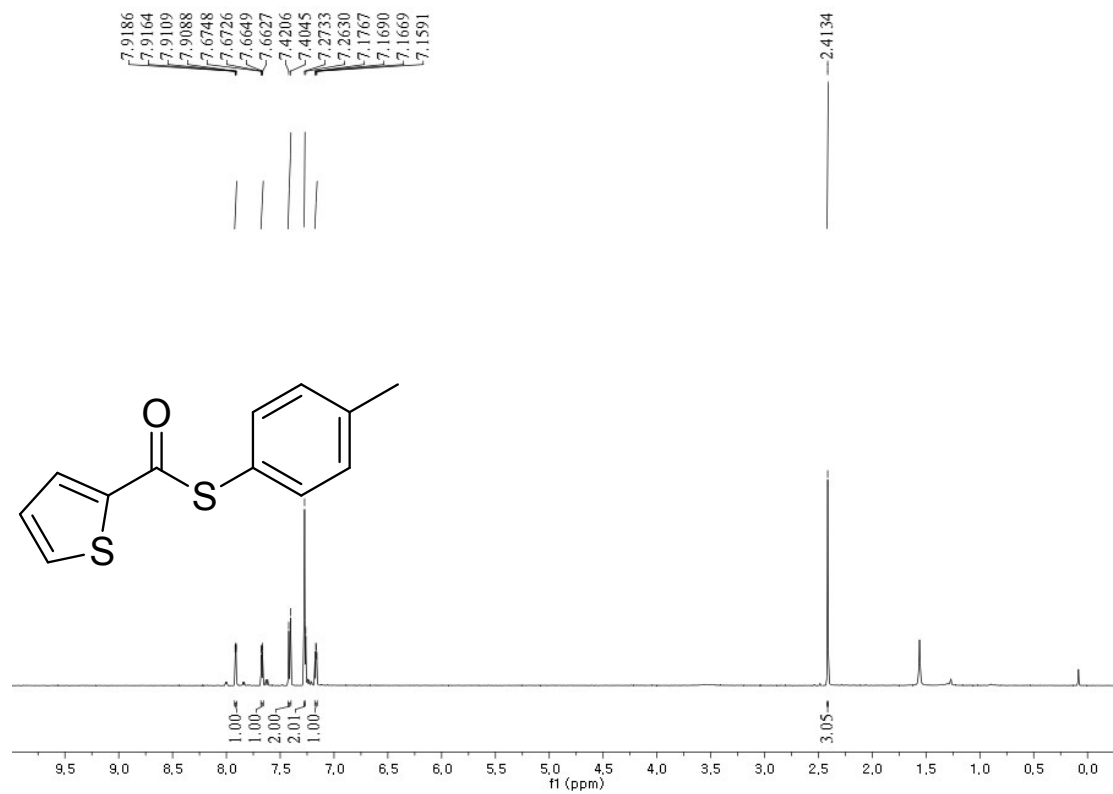


¹³C NMR

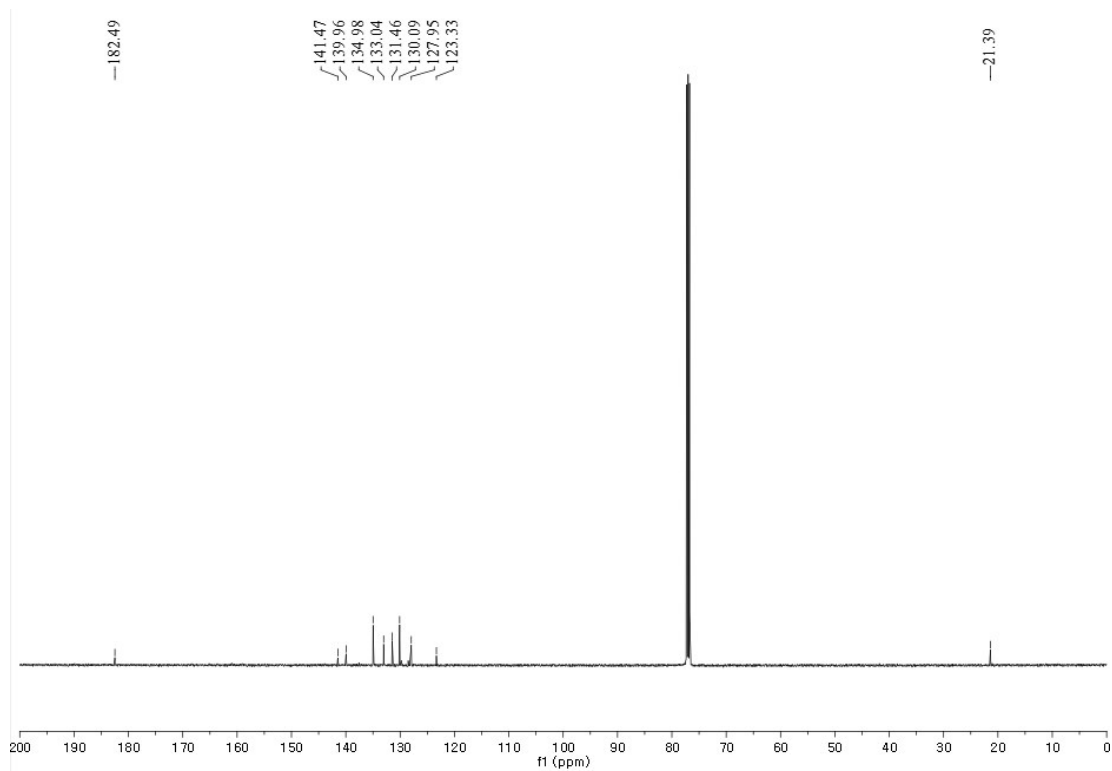


***S-p*-Tolyl-2-thiophenethioate (3ua)**

^1H NMR

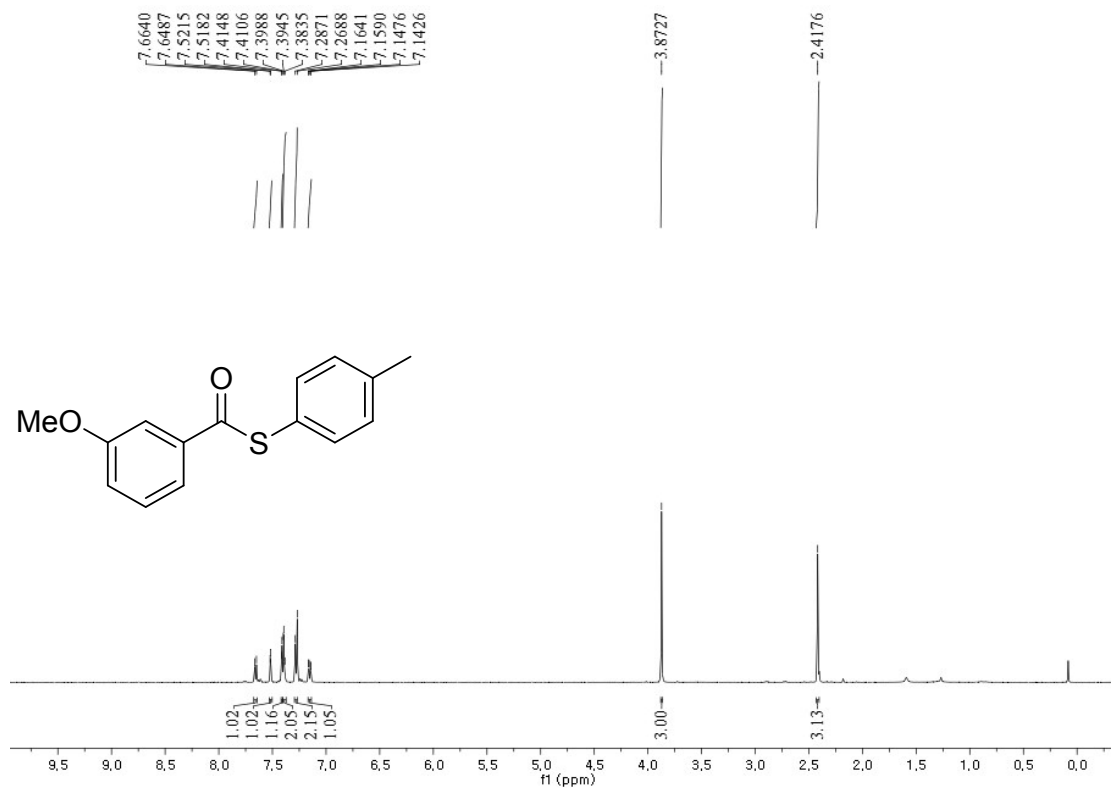


^{13}C NMR

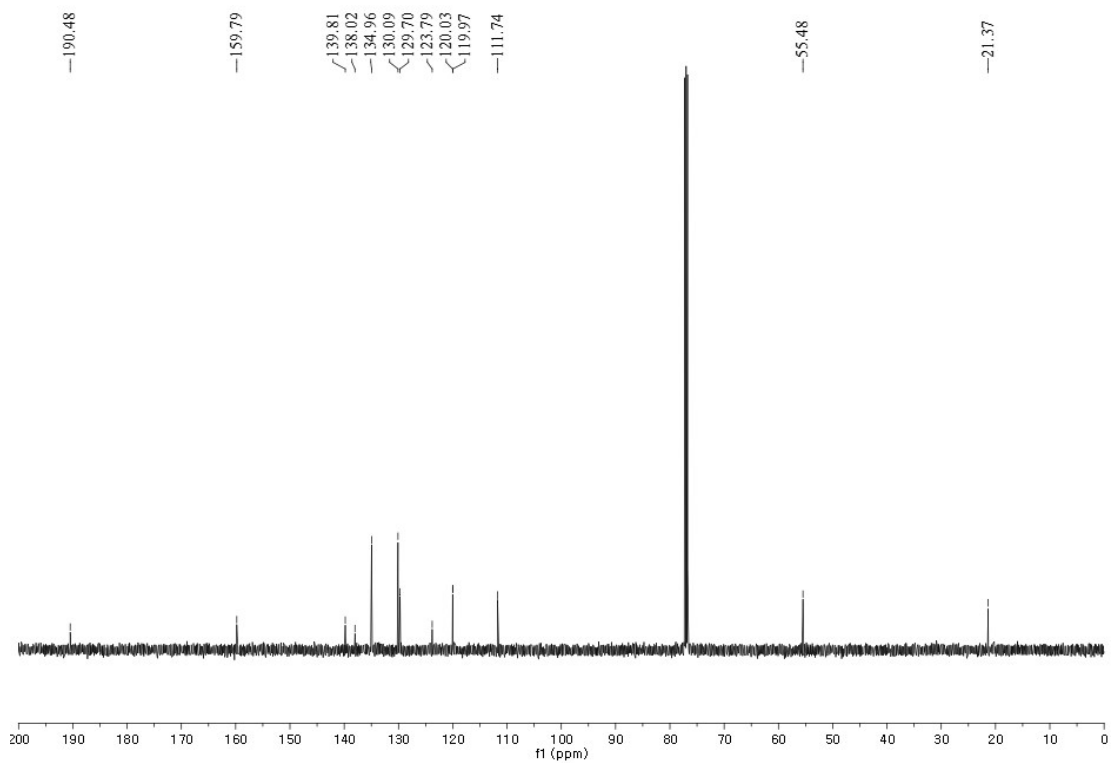


S-p-Tolyl-3-methoxybenzothioate (3va)

¹H NMR

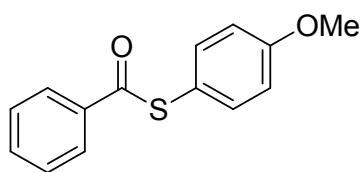
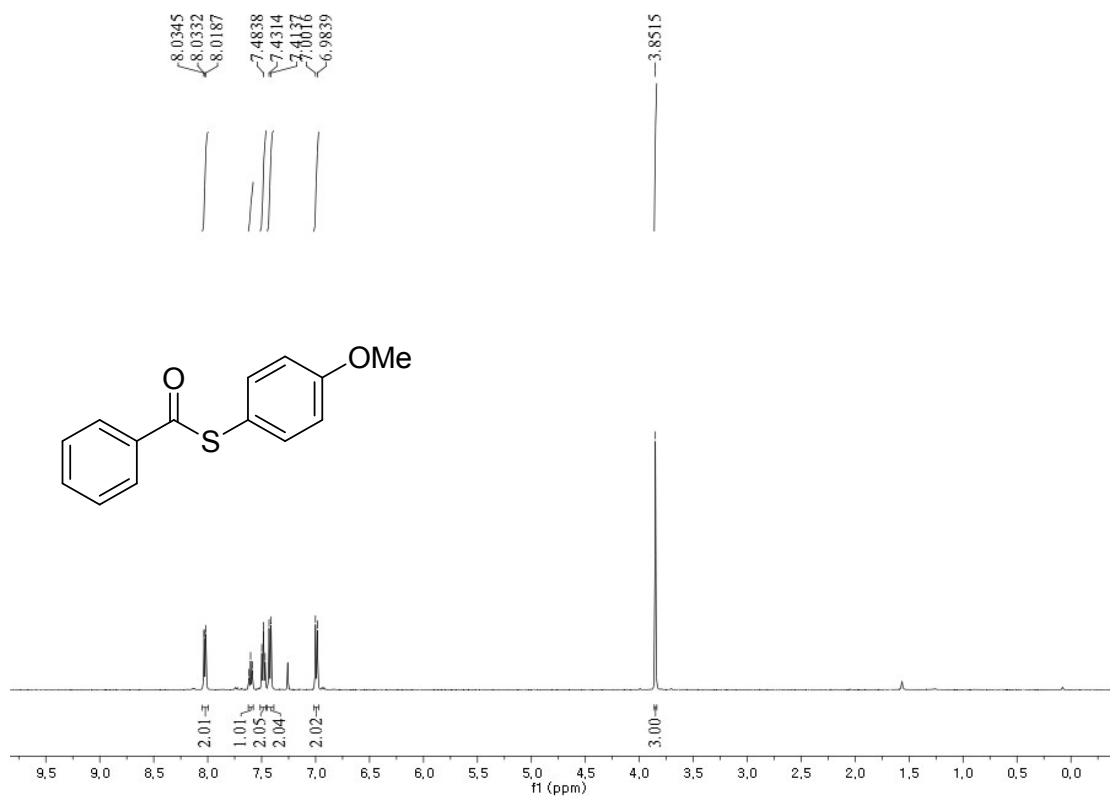


¹³C NMR

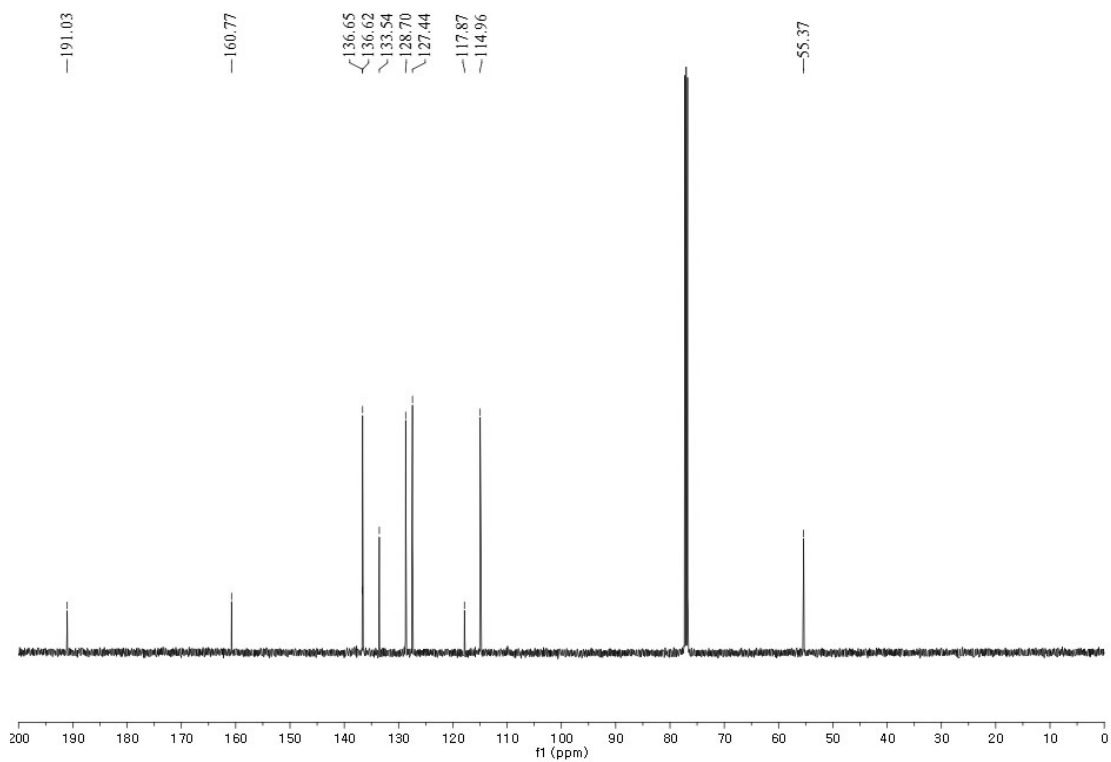


S-(4-Methoxyphenyl)-3-methylbenzothioate (3ab)

¹H NMR

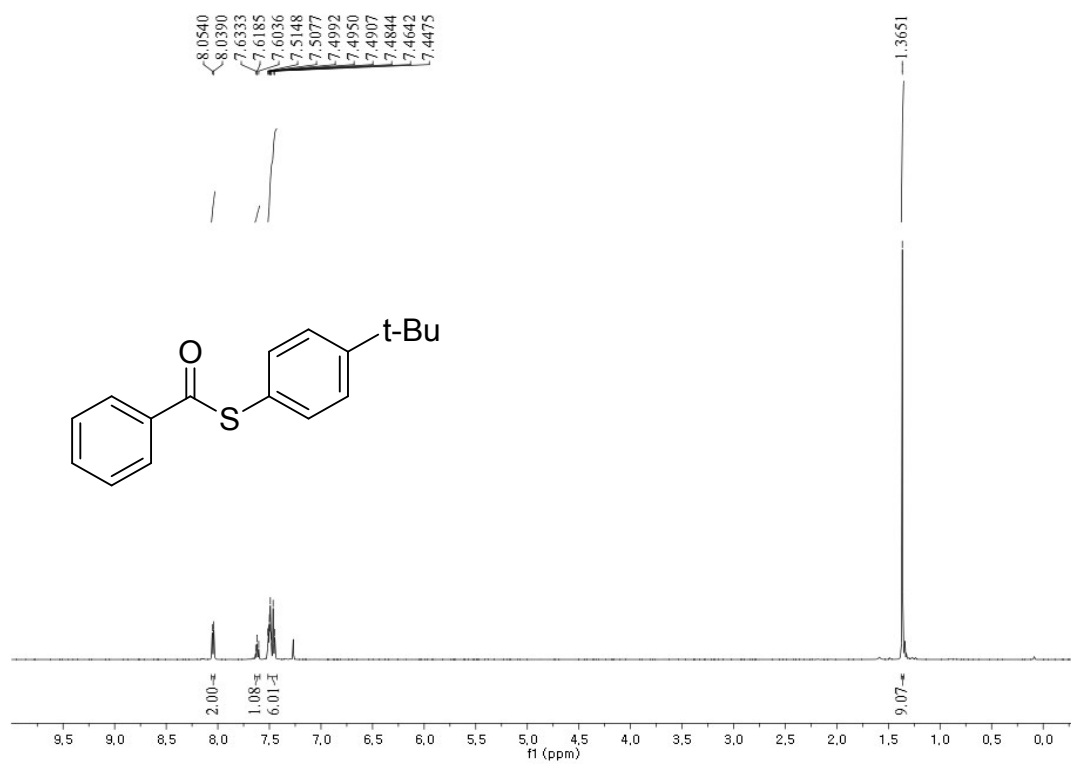


¹³C NMR

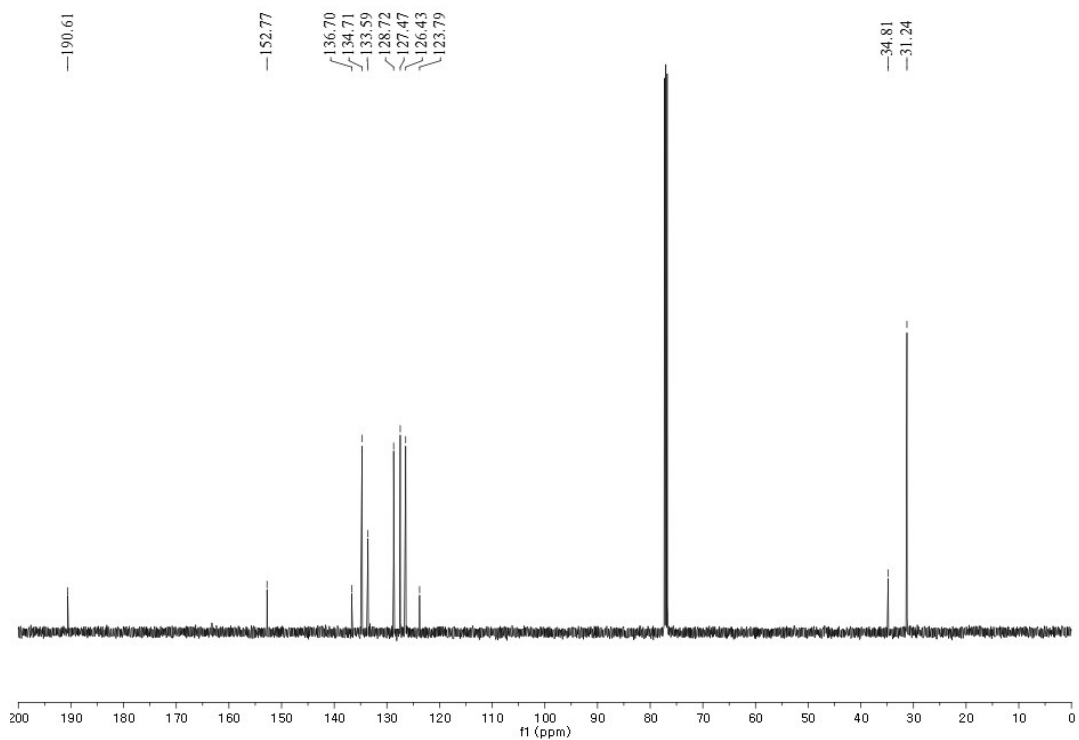


***S*-(4-*tert*-Butylphenyl)-3-methylbenzothioate(3ac)**

¹H NMR

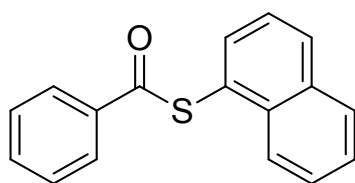


¹³C NMR

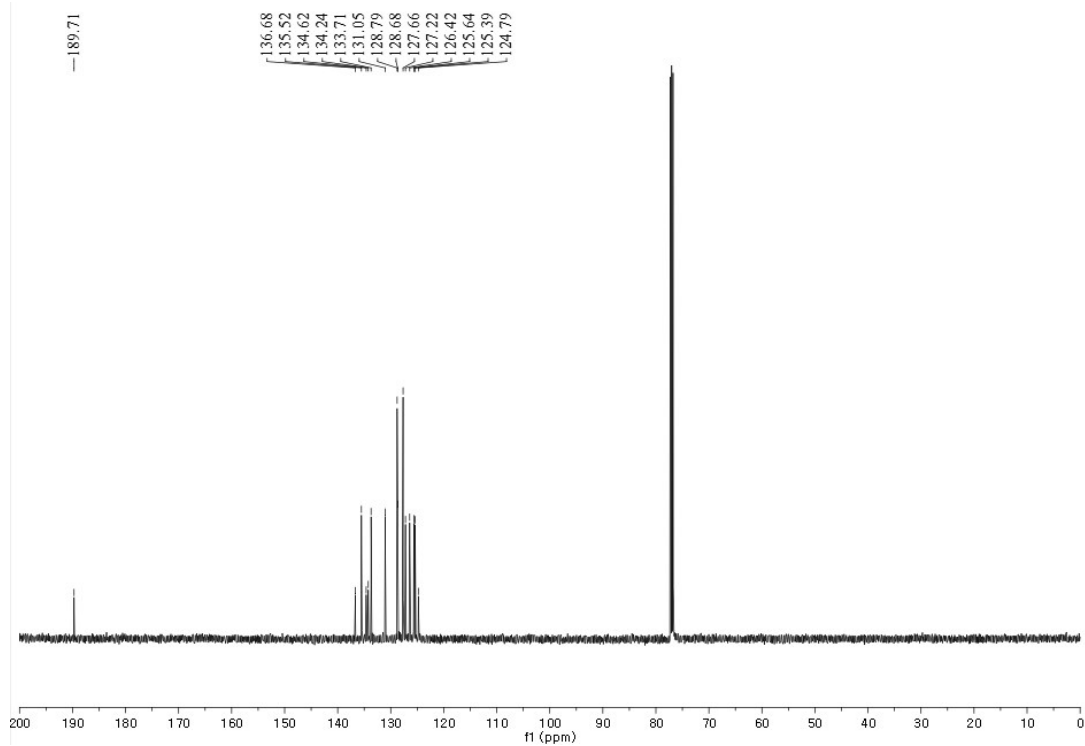


S-(1-Naphthalenyl)-3-methylbenzothioate (3ad)

¹H NMR

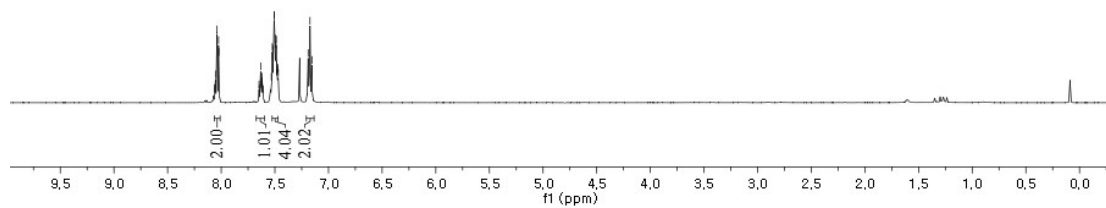
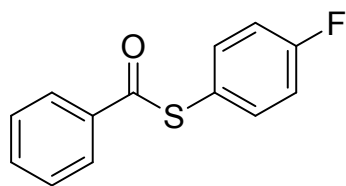
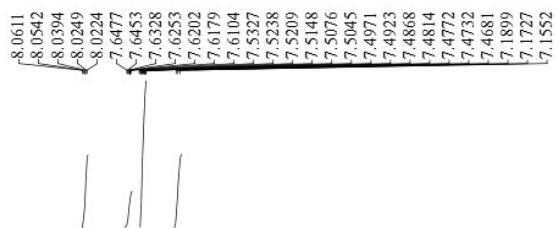


¹³C NMR

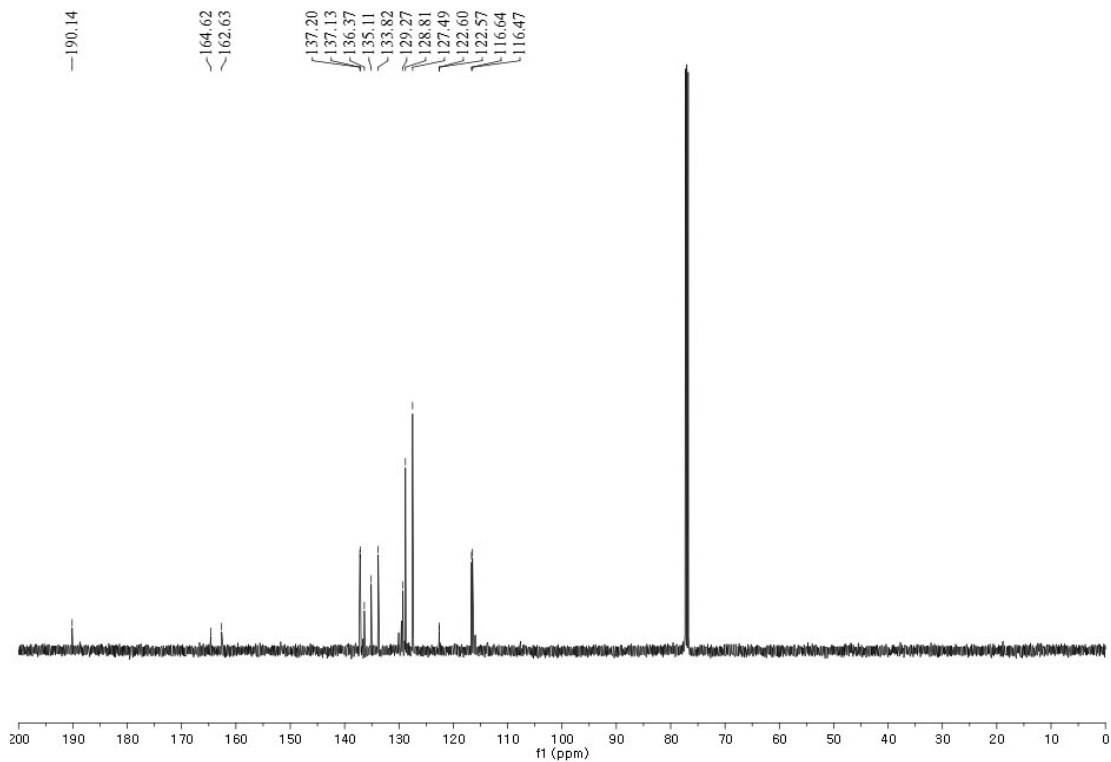


***S*-(4-Fluorophenyl)-3-methylbenzothioate (3ae)**

¹H NMR

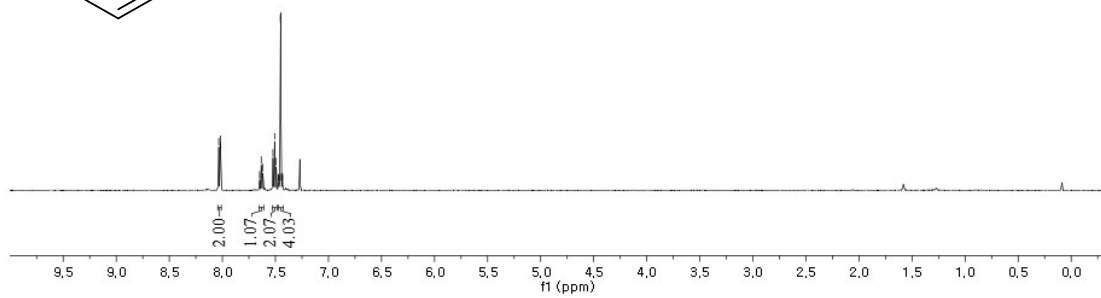
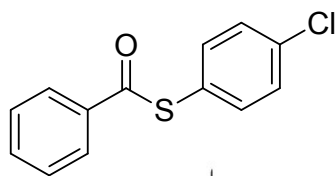
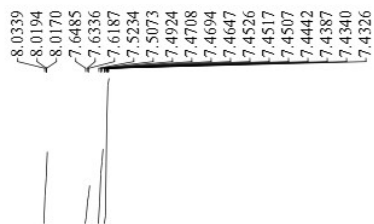


¹³C NMR

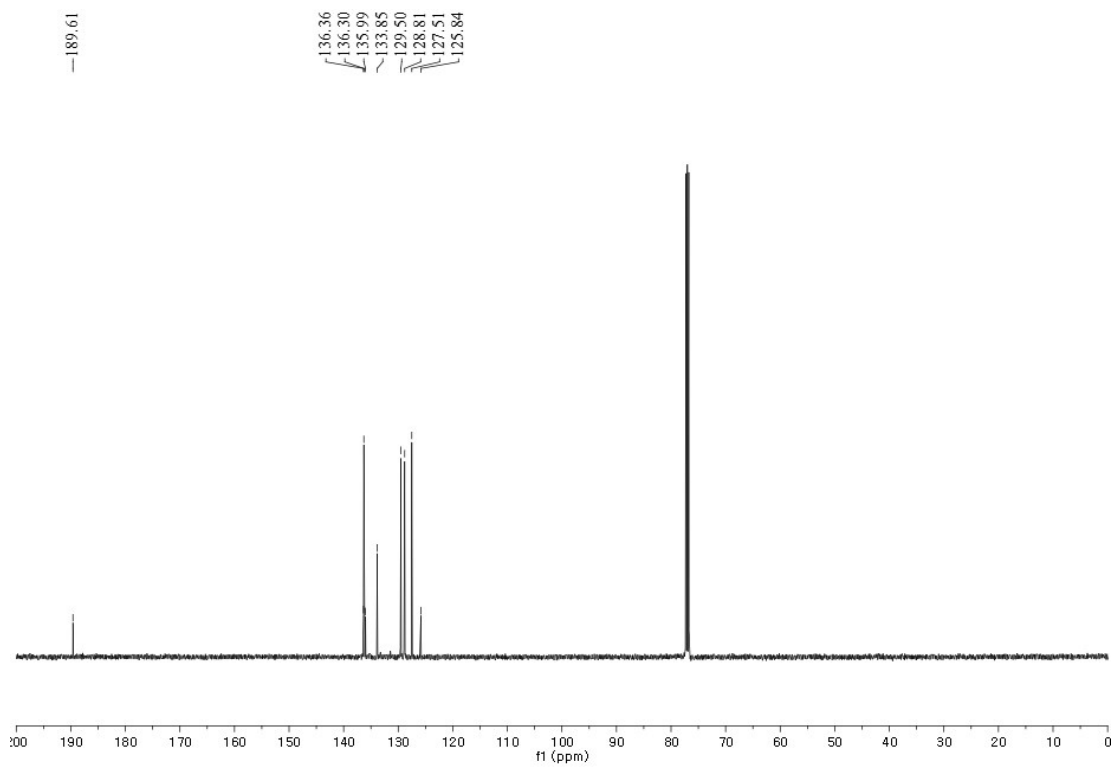


S-(4-Chlorophenyl)-3-methylbenzothioate (3af)

¹H NMR

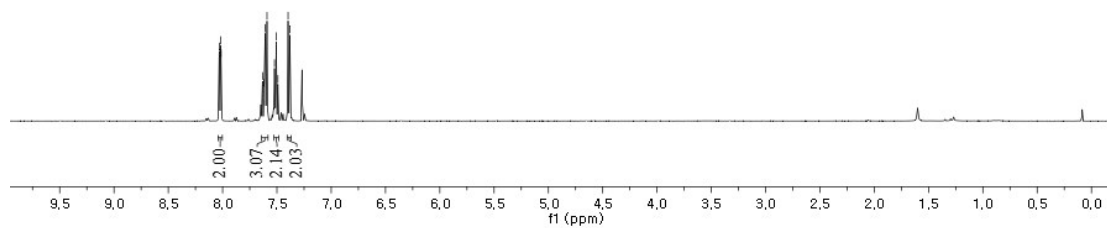
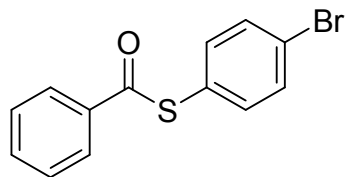
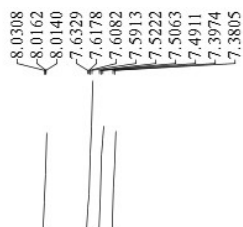


¹³C NMR

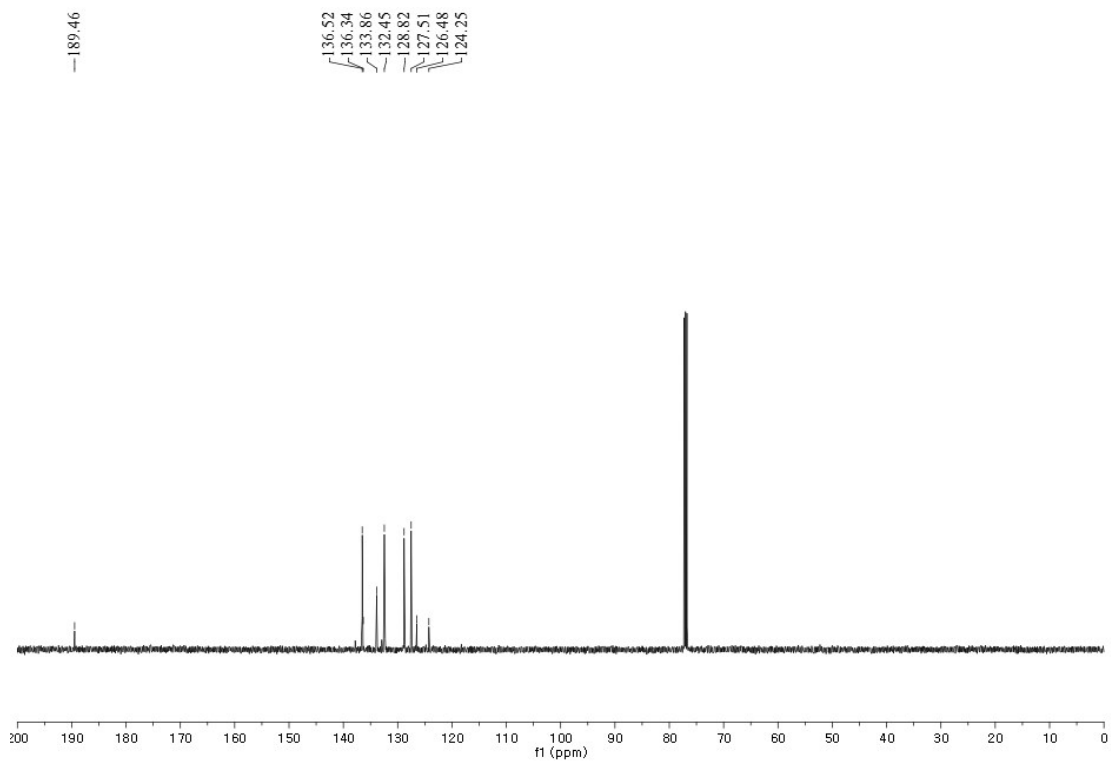


S-(4-Bromophenyl)-3-methylbenzothioate (3ag)

¹H NMR



¹³C NMR

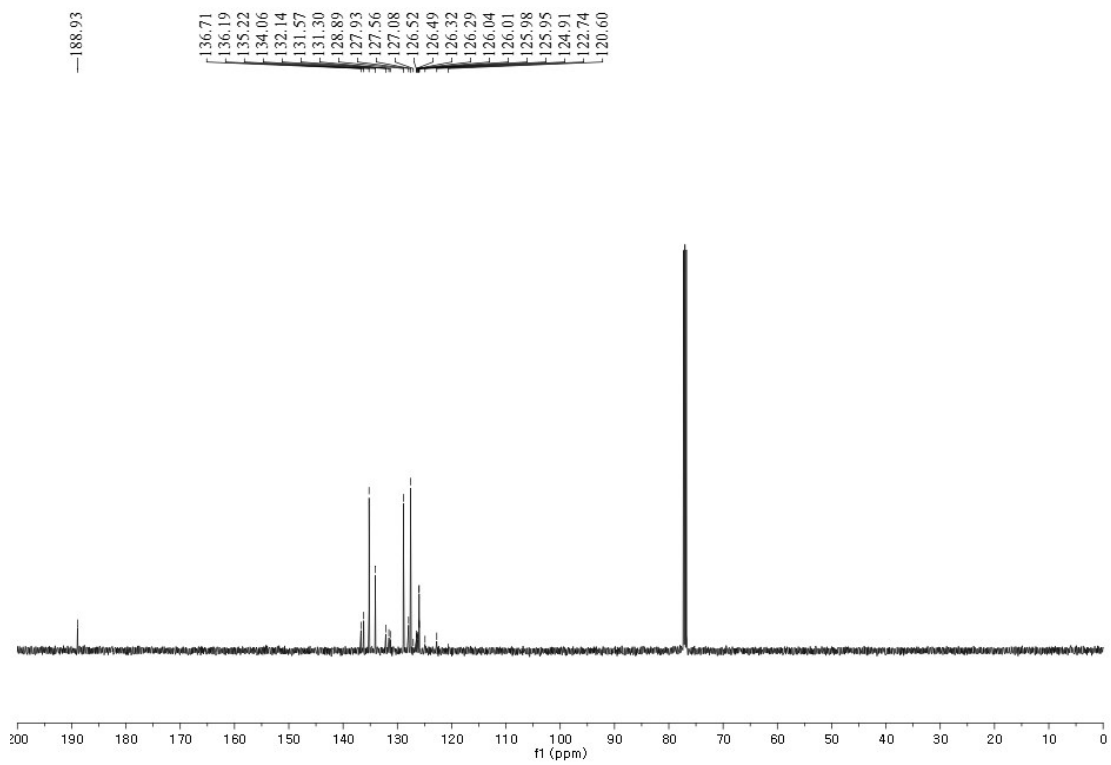


S-(4-Trifluoromethylphenyl)-3-methylbenzothioate (3ah)

¹H NMR

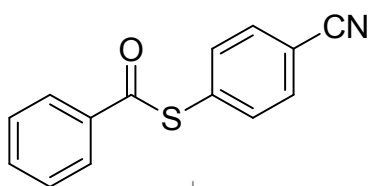
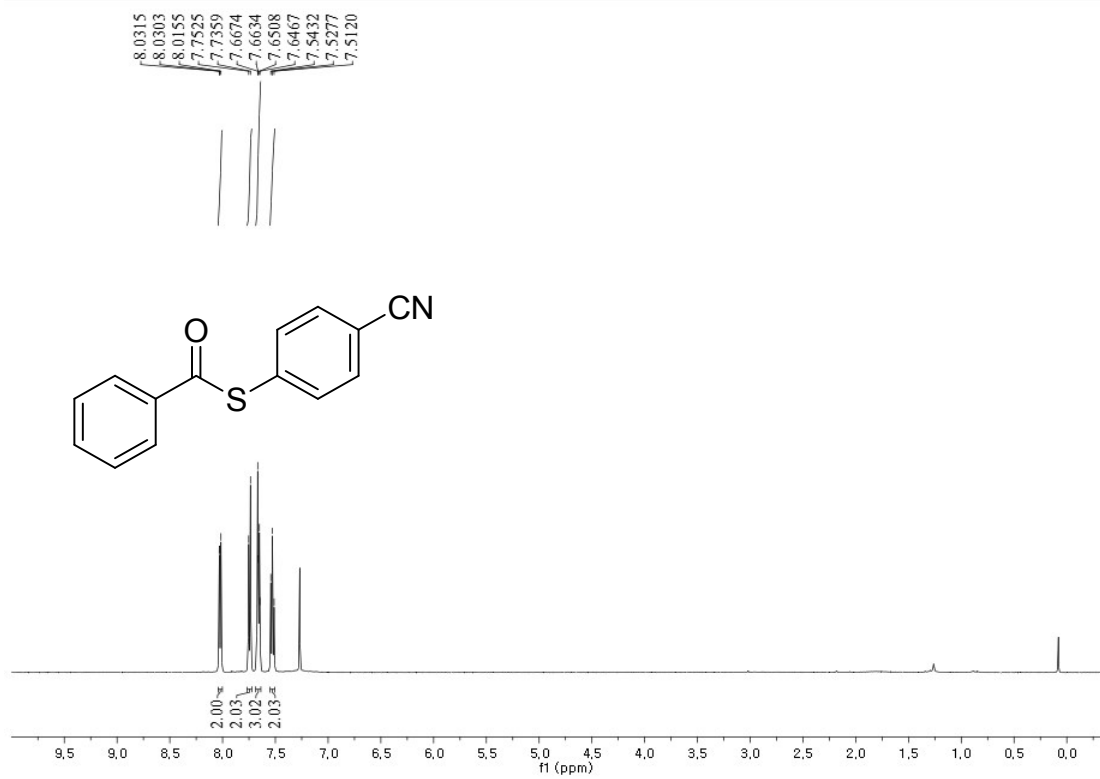


¹³C NMR



S-(4-Cyanophenyl)-3-methylbenzothioate (3ai)

¹H NMR



¹³C NMR

