Supporting Information

Copper (I)-Catalyzed Electrophilic Thiocyanation/Dearomatization/Spirocyclization of Benzofurans to Synthesize Benzannulated Spiroketals

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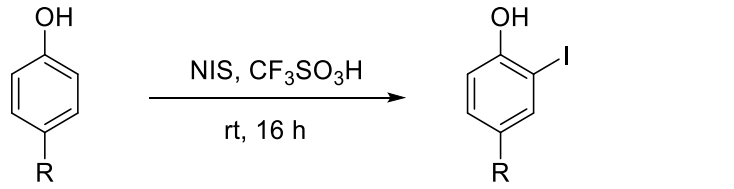
Contents

1. General Experimental Information.

All chemicals were bought from commercial companies and used directly unless noted. Reactions were carried out in a reaction tube with common solvents open to air. ^{1}H NMR spectra were recorded with a Bruker Avance (400 MHz) spectrometer; chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26; DMSO-d_6, δ = 2.50). ^{13}C NMR spectra were recorded with a Bruker Avance (101 or 176 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0; DMSO-d_6, δ = 39.52). ^{19}F NMR spectra were recorded with a Bruker Avance (377 MHz) spectrometer with complete proton decoupling. s = singlet, d = doublet, t = triplet, m = multiplet or unresolved; coupling constants in Hz, integration, assignment. All of the MS of samples were analyzed on an Agilent (Q-TOF6520) unit with an ESI source. All IR spectra were measured on a Shimadzu IR Affinnity-1s spectrometer. Melting points were measured on a digital micro melting point apparatus unless otherwise indicated. Column chromatography was performed using silica gel 60 (particle size 0.06–0.2 mm; 70-230 mesh ASTM). Thin-layer chromatography (TLC) was performed on silica gel F254 TLC glass plates and visualized with UV light.

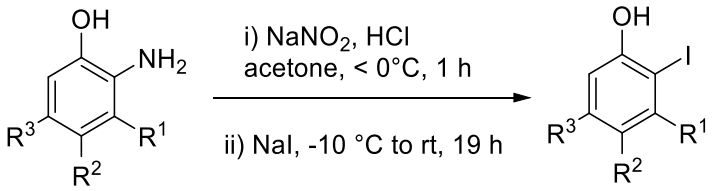
2. Preparation of Substrates

2.1 Iodination of Phenols



R = Me, Et, *t*-Bu, Ph, OPh, CO_2Me, CO_2Et, F, Cl, Br

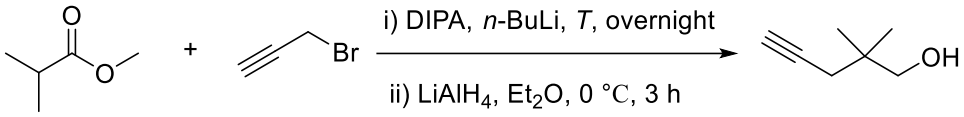
Method A:[1] Phenol (3 mmol) was dissolved in pure TFA (9 mL, 3 M). Then *N*-Iodosuccinimide (NIS) (3.3 mmol, 1.1 equiv.) was added in small portions. The reaction mixture was stirred at ambient temperature for hours until the reaction completed (monitored by TLC). The iodinated products were isolated by pouring the reaction mixture into cold water and then extracting it with DCM (3 × 2.5 mL). The combined organic extracts were washed with 10 % $Na_2S_2O_4$ in water and dried over Na_2SO_4, and the crude product was obtained without purification.



R^1 = H, R^2 = H, R^3 = Me
R^1 = Me, R^2 = H, R^3 = H
R^1 = H, R^2 = CO_2H, R^3 = H

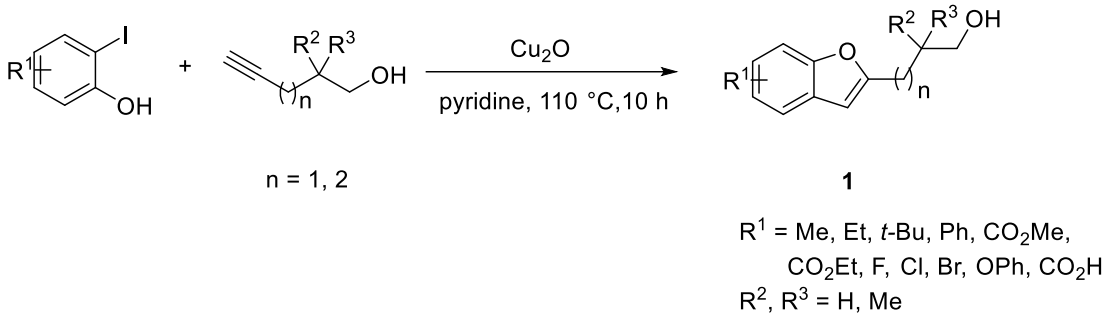
Method B:[2] Phenol (8.1 mmol, 1.0 equiv.) was dissolved in acetone (14 mL) and cooled with an ice / salt mixture. Concentrated HCl (1.7 mL, 20.3 mmol, 2.5 equiv.) was added in that way that the temperature did not rise above 0 °C. Then a solution of $NaNO_2$ (8.1 mmol, 1.0 equiv.) dissolved in 1.7 mL H_2O was added within 15 min below 0 °C. The mixture was further stirred for 1 h at this temperature and then cooled to -10 °C. A solution of NaI (16.2 mmol, 2.0 equiv.) in 2.7 mL H_2O was added within 10 min. Afterwards the temperature was elevated to 0 °C and the mixture was warmed to room temperature. After the addition of H_2O (50 mL) the reaction mixture was extracted four times with ethyl acetate (25 mL) and the organic phase was washed with $Na_2S_2O_3$ solution (50 mL), H_2O (50 mL) and brine (50 mL). The combined aqueous phases were further extracted with ethyl acetate (25 mL). The combined organic phases were dried with Na_2SO_4 and concentrated under reduced pressure without subsequent purification.

2.2 Preparation of 2,2-Dimethyl-4-pentyn-1-ol[3]

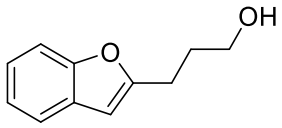


Add 3.1 mL of a 2.5 M *n*-BuLi solution (7.74 mmol, 1.2 equiv.) to a solution of 1.00 mL *N*, *N'*-diisopropylamine (718 mg, 1.1 equiv.) in 11.25 mL of dry THF in a flame-dried round bottomed flask at -78°C. Stir the resulting solution for 10 minutes at -78°C. Add 0.740 mL of methyl isobutyrate (659 mg, 1.0 equiv.) dropwise to the mixture. Warm the solution to 0°C. Recool the mixture to -78°C. Add 0.586 mL (808 mg, 1.05 equiv.) of propargyl bromide dropwise to the mixture. Allow the solution to warm to room temperature overnight. Quench the reaction mixture with saturated NH_4Cl solution (10 mL). Extract the mixture with CH_2Cl_2 (3 × 20 mL). Wash the mixture with brine. Dry the mixture over Na_2SO_4. Remove the solvent in vacuo. Add 15 mL of Et_2O to the crude product. Cool the solution to 0°C. Add 295 mg (7.75 mmol, 1.20 equiv.) of $LiAlH_4$ carefully in portions to the mixture. Continue the mixture to stirring for 15 minutes at 0°C and further 3 hours at room temperature. Terminate the reaction mixture by addition of 0.9 mL of water followed by 0.3 mL of a 4 M NaOH solution at 0°C. After 1 minute, add 0.9 mL of water to the mixture. Warm the suspension to room temperature. Stir the suspension for 15 minutes. Add Na_2SO_4 to the mixture. Filter the suspension. Evaporate solvent under reduced pressure.

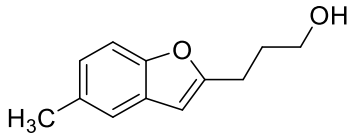
2.3 General Procedure for the Copper-Mediated Heteroannulation[4]



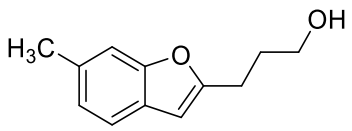
A mixture of 2-iodophenol (5 mol, 1.0 equiv.), alkynol (5.5 mol, 1.1 equiv.) and copper(I) oxide (3.5 mol, 0.7 equiv.) in dry pyridine (5 mL) was stirred at 110 °C for 10 hours. The mixture was allowed to cool to room temperature, diluted with ethyl acetate (10 mL), filtered through a Celite pad (5 cm), and concentrated. The residue was dissolved in ethyl acetate (20 mL), washed with 2 M HCl and brine (20 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to afford the pure desired products **1**.



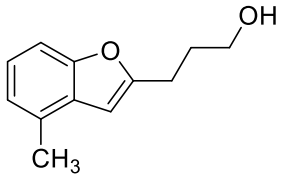
***2-Benzofuranpropanol (1a)*:**[5] eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.2, yellow oil (616 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 6.8 Hz, 1H, Ar-H), 7.41 (d, J = 7.6 Hz, 1H, Ar-H), 7.20 (m, 2H, Ar-H), 6.42 (s, 1H, Het. Ar-H), 3.75 (t, J = 6.2 Hz, 2H, CH_2), 2.89 (t, J = 7.3 Hz, 2H, CH_2), 2.16 (s, 1H, OH), 2.02 (m, 2H, CH_2) ppm.



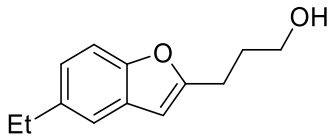
***5-Methyl-2-benzofuranpropanol (1b)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.4, light yellow solid (665 mg, 70% yield), mp: 40-41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.26 (m, 2H, Ar-H), 7.02 (dd, J = 8.3, 1.4 Hz, 1H, Ar-H), 6.34 (s, 1H, Het. Ar-H), 3.73 (t, J = 6.3 Hz, 2H, CH_2), 2.87 (t, J = 7.4 Hz, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.00 (m, 2H, CH_2), 1.64 (s, 0.89H, OH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 153.2, 132.0, 129.1, 124.5, 120.3, 110.4, 102.1, 62.1, 30.8, 24.9, 21.4 ppm. IR (KBr): 3334, 2924, 1475, 1263, 1055, 750 cm^{-1}; HRMS (ESI) m/z $[M - H]^-$ calcd. for $C_{12}H_{13}O_2$ 189.0916 found 189.0912.



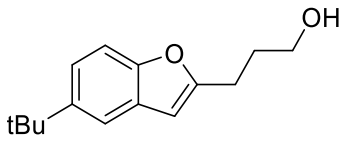
***6-Methyl-2-benzofuranpropanol (1c)*:** eluent petroleum ether/ethyl acetate (3:1, v/v), TLC R_f = 0.4, yellow solid (589 mg, 62% yield), mp: 48-50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.22 (s, 1H, Ar-H), 7.01 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.36 (s, 1H, Het. Ar-H), 3.74 (t, *J* = 6.3 Hz, 2H, CH_2), 2.87 (t, *J* = 7.4 Hz, 2H, CH_2), 2.45 (s, 3H, CH_3), 2.00 (m, 2H, CH_2) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 152.8, 125.9, 124.4, 120.2, 117.9, 112.4, 111.2, 71.0, 55.3, 36.6, 24.6 ppm; IR (KBr): 3332, 2939~2866, 1489, 1055, 815 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd. for $C_{12}H_{15}O_2$ 191.1067 found 191.1076.



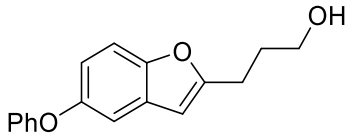
***4-Methyl-2-benzofuranpropanol (1d)*:** eluent petroleum ether/ethyl acetate (3:1, v/v), TLC R_f = 0.4, yellow oil (760 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.0 Hz, 1H, Ar-H), 7.12 (t, *J* = 7.8 Hz, 1H, Ar-H), 6.99 (d, *J* = 7.3 Hz, 1H, Ar-H), 6.44 (s, 1H, Het. Ar-H), 3.75 (t, *J* = 6.3 Hz, 2H, CH_2), 2.90 (t, *J* = 7.4 Hz, 2H, CH_2), 2.48 (s, 3H, CH_3), 2.02 (m, 2H, CH_2), 1.59 (s, 1H, OH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 154.6, 130.3, 128.7, 123.3, 122.93, 108.3, 101.0, 62.1, 30.8, 24.9, 18.7 ppm; IR (KBr): 3342, 2941, 1589, 1423, 1247, 1062, 767 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd. for $C_{12}H_{15}O_2$ 191.1067 found 191.1065.



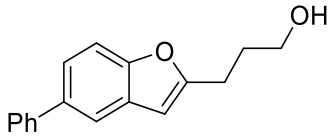
***5-Ethyl-2-benzofuranpropanol (1e)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.5, yellow oil (622 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.29 (m, 2H, Ar-H), 7.05 (dd, *J* = 8.3, 1.7 Hz, 1H, Ar-H), 6.36 (s, 1H, Het. Ar-H), 3.74 (t, *J* = 6.3 Hz, 2H, CH_2), 2.87 (t, *J* = 7.3 Hz, 2H, CH_2), 2.72 (q, *J* = 7.6 Hz, 2H, CH_2), 2.00 (m, 2H, CH_2), 1.50 (s, 1H, OH), 1.27 (t, *J* = 7.6 Hz, 3H, CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 153.4, 138.7, 129.1, 123.5, 119.1, 110.5, 102.2, 62.1, 30.8, 29.0, 25.0, 16.5 ppm; IR (KBr): 3360, 2960~2872, 1714, 1471, 1265, 1056, 750 cm^{-1}; HRMS (ESI) m/z $[M-H]^-$ calcd for $C_{13}H_{15}O_2$ 203.1072 found 203.1072.



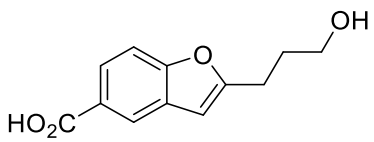
***5-tert-Butyl-2-benzofuranpropanol (1f)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.4, yellow solid (847 mg, 73% yield), mp: 42-43 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 1.7 Hz, 1H, Ar-H), 7.33 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.28 (m, 1H, Ar-H) 6.38 (s, 1H, Het. Ar-H), 3.74 (t, *J* = 6.3 Hz, 2H, CH_2), 2.87 (t, *J* = 7.4 Hz, 2H, CH_2), 2.00 (m, 2H, CH_2), 1.60 (s, 1H, OH), 1.37 (s, 9H, $(CH_3)_3C$) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 153.0, 146.0, 129.0, 121.2, 117.0, 110.1, 102.5, 62.1, 34.8, 32.0, 30.9, 25.0 ppm; IR(KBr): 3329, 2956~2870, 1477, 1271, 1055, 750 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{21}O_2$ 233.1536 found 233.1533.



***5-Phenoxy-2-benzofuranpropanol (1g)*:** eluent petroleum ether/ethyl acetate (3:1, v/v), TLC R_f = 0.4, yellow oil (951 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.22 (m, 3H, Ar-H), 7.16 - 6.80 (m, 5H, Ar-H), 6.42 (s, 1H, Het. Ar-H), 3.76 (m, CH_2), 2.90 (m, 2H, CH_2), 2.02 (m, 2H, CH_2), 1.69 (s, 1H, OH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 158.8, 152.3, 151.4, 129.8, 129.7, 124.5, 122.6, 118.1, 117.9, 116.0, 111.5, 111.0, 102.6, 62.0, 30.7, 25.0 ppm; IR (KBr) 3356, 2939~2877, 1716, 1595, 1219, 752, 692cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{17}O_3$ 269.1168 found 269.1168.

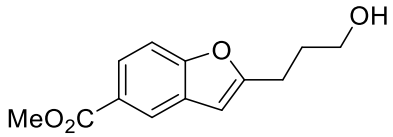


***5-Phenyl-2-benzofuranpropanol (1h)*:** eluent petroleum ether/ethyl acetate (3:1, v/v), TLC R_f = 0.5, yellow solid (857 mg, 68% yield), mp: 87-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H, Ar-H), 7.61 (m, 2H, Ar-H), 7.49 - 7.41 (m, 4H, Ar-H), 7.34 (m, 1H, Ar-H), 6.47 (s, 1H, Het. Ar-H), 3.76 (t, *J* = 6.3 Hz, 2H, CH_2), 2.92 (t, *J* = 7.4 Hz, 2H, CH_2), 2.03 (m, 2H, CH_2), 1.52 (s, 1H, OH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 154.5, 142.0, 136.4, 129.6, 128.8, 127.6, 126.9, 123.1, 119.0, 111.0, 102.6, 62.1, 30.8, 25.0 ppm; IR(KBr): 3282, 2953~2873, 1463, 1265, 1066, 761 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{17}O_2$ 253.1219 found 253.1219.

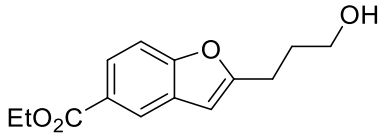


2-(3-Hydroxypropyl)benzofuran-5-carboxylic acid (1i): eluent petroleum ether/ethyl acetate (1:1, v/v), TLC R_f = 0.3, yellow solid (715 mg, 65% yield), mp: 140-143 °C; ^{1}H NMR (400

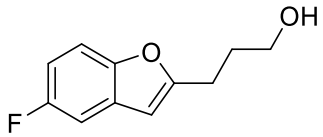
MHz, DMSO-d_6) δ 12.81 (s, 1H, COOH), 8.15 (d, J = 7.7 Hz, 1H, Ar-H), 7.84 (d, J = 8.3 Hz, 1H, Ar-H), 7.57 (d, J = 8.6 Hz, 1H, Ar-H), 6.71 (s, 1H, Het. Ar-H), 4.58 (s, 1H, OH), 3.48 (s, 2H, CH_2), 2.83 (t, J = 7.5 Hz, 2H, CH_2), 1.84 (m, 2H, CH_2) ppm; ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.5, 160.9, 156.5, 128.8, 125.5, 124.9, 122.3, 110.6, 102.5, 59.8, 30.3, 24.4 ppm; IR(KBr): 3333, 2928, 1713, 1267, 750 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{12}H_{13}O_4$ 221.0808 found 221.0804.



Methyl 2-(3-hydroxypropyl)-5-benzofurancarboxylate (1j):[4] eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.4, yellow solid (784 mg, 67% yield), mp: 40-42 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 1.4 Hz, 1H, Ar-H), 7.94 (dd, J = 8.6, 1.7H Hz, 1H, Ar-H), 7.41 (d, J = 8.6 Hz, 1H, Ar-H), 6.47 (s, 1H, Het. Ar-H), 3.92 (s, 3H, CH_3), 3.75 (t, J = 6.3 Hz, 2H, CH_2), 2.90 (t, J = 7.5 Hz, 2H, CH_2), 2.02 (m, 2H, CH_2), 1.63 (s, 1H, OH) ppm.

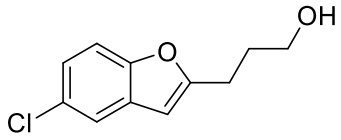


***Ethyl 2-(3-hydroxypropyl)-5-benzofurancarboxylate (1k)*:** eluent petroleum ether/ethyl acetate (3:1, v/v), TLC R_f = 0.5, yellow oil (868 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 1.5 Hz, 1H, Ar-H), 7.95 (dd, J = 8.6, 1.7 Hz, 1H, Ar-H), 7.41 (d, J = 8.6 Hz, 1H, Ar-H), 6.47 (s, 1H, Het. Ar-H), 4.39 (q, J = 7.1 Hz, 2H, CH_2), 3.75 (t, J = 6.3 Hz, 2H, CH_2), 2.91 (t, J = 7.5 Hz, 2H, CH_2), 2.02 (m, 2H, CH_2), 1.56 (s, 1H, OH), 1.41 (t, J = 7.1 Hz, 3H, CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 160.4, 157.4, 129.0, 125.3, 122.8, 110.7, 102.8, 62.0, 61.0, 30.6, 24.9, 14.5 ppm; IR (KBr) 3419, 2953~2852, 1714, 1292, 767cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{17}O_4$ 249.1127 found 249.1128.

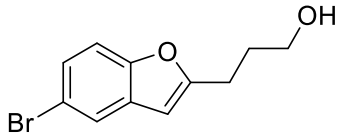


***5-Fluoro-2-benzofuranpropanol (1l)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.2, yellow oil (679 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, J = 8.9, 4.1 Hz, 1H, Ar-H), 7.13 (dd, J = 8.7, 2.6 Hz, 1H, Ar-H), 6.92 (td, J = 9.1, 2.6 Hz, 1H, Ar-H), 6.38 (s, 1H, Het. Ar-H), 3.74 (t, J = 6.3 Hz, 2H, CH_2), 2.87 (t, J = 7.5 Hz, 2H, CH_2), 2.00 (m, 2H, CH_2), 1.62 (s, 1H, OH) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 160.4 (C–F, $^1J_{C-F}$ = 238.2 Hz),

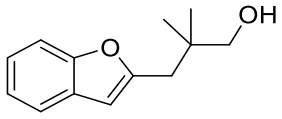
151.0, 129.9 ($^3J_{C-F}$ = 10.8 Hz), 111.4 ($^3J_{C-F}$ = 9.6 Hz), 110.9 ($^2J_{C-F}$ = 26.4 Hz), 106.1 ($^2J_{C-F}$ = 25.1 Hz), 102.7 ($^4J_{C-F}$ = 3.8 Hz), 62.0, 30.6, 25.0 ppm; ^{19}F NMR (377 MHz, $CDCl_3$): δ -121.9 ppm; IR (KBr): 3331, 2941, 1469, 1186, 1055, 750 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd. for $C_{11}H_{12}FO_2$ 195.0816 found 195.0809.



***5-Chloro-2-benzofuranpropanol (1m)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.6, yellow solid (735 mg, 70% yield), mp: 60-61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 2.1 Hz, 1H, Ar-H), 7.31 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.16 (dd, *J* = 8.7, 2.1 Hz, 1H, Ar-H), 6.36 (s, 1H, Het. Ar-H), 3.74 (t, *J* = 6.3 Hz, 2H, CH_2), 2.88 (t, *J* = 7.5 Hz, 2H, CH_2), 2.01 (m, 2H, CH_2), 1.59 (s, 1H, OH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.7, 153.4, 130.6, 128.3, 123.7, 120.2, 112.0, 102.3, 62.2, 30.8, 25.1 ppm; IR (KBr): 3298, 2933, 1452, 1058, 798 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd. for $C_{11}H_{12}FO_2$ 211.0520 found 211.0520.

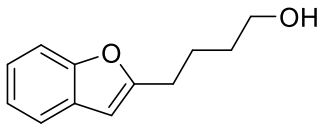


***5-Bromo-2-benzofuranpropanol (1n)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.3, yellow solid (952 mg, 75% yield), mp: 65-66 °C; ^{1}H NMR (400 MHz, DMSO-d6) δ 7.60 (d, *J* = 1.5 Hz, 1H, Ar-H), 7.31 - 7.26 (m, 2H, Ar-H), 6.36 (s, 1H, Het. Ar-H), 3.74 (t, *J* = 6.3 Hz, 2H, CH_2), 2.88 (t, *J* = 7.6 Hz, 2H, CH_2), 2.00 (m, 2H, CH_2), 1.58 (s, 1H, OH) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.4, 153.6, 131.0, 126.2, 123.1, 115.7, 112.3, 102.0, 62.0, 30.6, 24.9 ppm; IR (KBr): 3331, 2926, 1444, 1259, 1049, 796 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd. for $C_{11}H_{12}BrO_2$ 255.0021 found 255.0019.

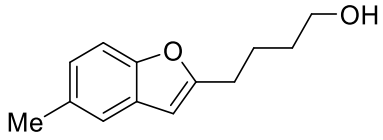


***3-(Benzofuran-2-yl)-2,2-dimethylpropan-1-ol (1o)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.13, yellow oil (607 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 1H, Ar-H), 7.43 (m, 1H, Ar-H), 7.21 (m, 2H, Ar-H), 6.44 (s, 1H, Het. Ar-H), 3.38 (s, 2H, CH_2), 2.75 (s, 2H, CH_2), 1.76 (s, 1H, OH), 1.00 (s, 6H, $(CH_3)_2$) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 154.8, 129.0, 123.4, 122.7, 120.4, 111.0, 104.7, 71.3, 37.4, 36.8, 24.5 ppm; IR(KBr):

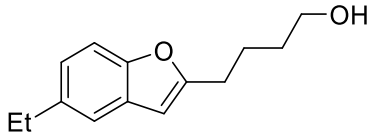
3383, 2957, 1713, 1585, 1454, 1254, 1042, 912, 748 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_{17}O_2$ 205.1223 found 205.1218.



***2-Benzofuranbutanol (1p)*:**[6] eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.3, yellow oil (789 mg, 83% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 - 7.49 (m, 1H, Ar-H), 7.47 - 7.42 (m, 1H, Ar-H), 7.22 (m, 2H, Ar-H), 6.41 (s, 1H, Het. Ar-H), 3.67 (t, J = 6.5 Hz, 2H, CH_2), 2.81 (t, J = 7.5 Hz, 2H, CH_2), 2.42 (s, 1H, OH), 1.87 (m, 2H, CH_2), 1.69 (m, 2H, CH_2) ppm.

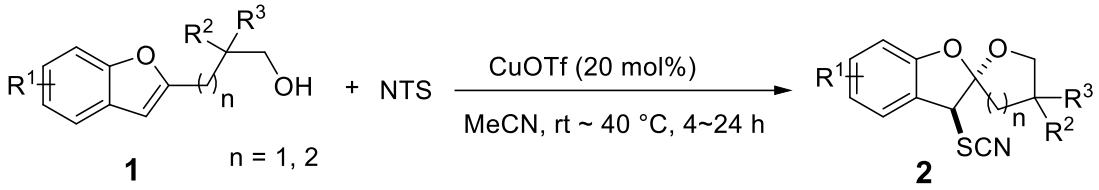


***5-Methyl-2-benzofuranbutanol (1q)*:** eluent petroleum ether/ethyl acetate (3:1, v/v), TLC R_f = 0.4, yellow oil (826 mg, 81% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.23 (m, 2H, Ar-H), 7.01 (d, J = 9.4 Hz, 1H, Ar-H), 6.31 (s, 1H, Het. Ar-H), 3.65 (t, J = 6.5 Hz, 2H, CH_2), 2.77 (t, J = 7.4 Hz, 2H, CH_2), 2.42 (s, 3H, CH_3), 1.97 (s, 1H, OH), 1.81 (m, 2H, CH_2), 1.64 (m, 2H, CH_2) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 153.1, 131.8, 129.1, 124.4, 120.2, 110.3, 101.9, 62.5, 32.2, 28.3, 24.0, 21.4 ppm; IR (KBr) 3041, 2937, 2866, 1598, 1473, 1266, 1058, 798 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_{17}O_2$ 205.1129 found 205.1221.

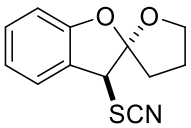


***5-Ethyl-2-benzofuranbutanol (1r)*:** eluent petroleum ether/ethyl acetate (3:1, v/v), TLC R_f = 0.4, yellow oil (992 mg, 91% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.28 (m, 2H, Ar-H), 7.05 (dd, J = 8.3, 1.8 Hz, 1H, Ar-H), 6.34 (s, 1H, Het. Ar-H), 3.69 (t, J = 6.4 Hz, 2H, CH_2), 2.79 (t, J = 7.3 Hz, 2H, CH_2), 2.72 (q, J = 7.6 Hz, 2H, CH_2), 1.83 (m, 2H, CH_2), 1.67 (m, 2H, CH_2), 1.51 (s, 1H, OH), 1.27 (t, J = 7.6 Hz, 3.01H, CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 153.3, 138.6, 129.1, 123.4, 119.1, 110.4, 102.1, 62.7, 32.3, 29.0, 28.3, 24.1, 16.5 ppm; IR (KBr) 3038, 2933, 2868, 1598, 1471, 1265, 1060, 810 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{19}O_2$ 219.1385 found 219.1377.

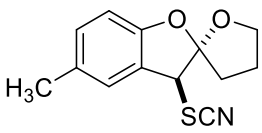
3. Reaction with Substrates and Characterization.



Substrates **1** (1 mmol, 1.0 equiv.) and CuOTf (4.3 mg, 0.2 mmol, 0.2 equiv.) were stirred in CH_3CN (1.0 mL) for 5 min at room temperature under argon atmosphere in dark, the *N*-Thiocyanatosuccinimide (23.3 mg, 1.5 mmol, 1.5 equiv.) was added. After the reaction was completed (monitored by TLC), the reaction mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to afford the pure desired products **2**. *N*-Thiocyanatosuccinimide (31 mg, 2.0 mmol, 2.0 equiv.) was added at 40 ˚C.

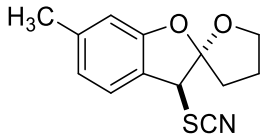


***3-Thiocyanato-4',5'-dihydro-3H,3'H-spirobenzofuran-2,2'-furan (2a)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.5, obtained as a mixture of diastereomers (dr = 1.5:1, determined by ^{1}H NMR), yellow oil (rt, 8 h, 21 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 0.67H), 7.29 (m, 1.67H), 7.00 (t, *J* = 7.5 Hz, 1.67H), 6.87 (d, *J* = 8.1 Hz, 0.67H), 6.82 (d, *J* = 8.1 Hz, 1H), 5.08 (s, 1H), 4.80 (s, 0.67H), 4.26 (m, 1H), 4.19 (m, 0.67H), 4.11 (m, 1.67H), 2.53 (m, 1.67H), 2.47 (m, 0.67H), 2.32 (m, 1H), 2.18 (m, 3.35H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 156.8, 131.6, 131.3, 125.8, 125.1, 124.7, 123.2, 122.2, 122.1, 119.5, 116.7, 112.9 (SCN), 111.1, 110.7 (SCN), 110.6, 71.0, 70.0, 55.4, 55.2, 36.8, 33.4, 24.6, 24.1 ppm; IR (KBr) 2958~2850, 2154 (SCN), 1597, 1475, 876, 752 cm^{-1}; HRMS (ESI) m/z $[M + NH_4]^+$ calcd for $C_{12}H_{15}N_2O_2S$ 251.0849 found 251.0852.

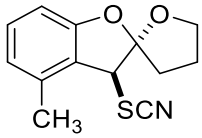


***5-Methyl-3-thiocyanato-4',5'-dihydro-3H,3'H-spirobenzofuran-2,2'-furan (2b)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.8, obtained as a mixture of diastereomers (dr = 1.4:1, determined by ^{1}H NMR), yellow oil (rt, 4 h, 20 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.20 (s, 0.69H), 7.08 (m, 1.69H), 6.75 (d, *J* = 8.2 Hz, 0.69H), 6.70 (d, *J*

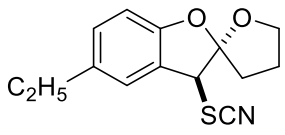
= 8.2 Hz, 1H), 5.04 (s, 1H), 4.75 (s, 0.69H), 4.24 (m, 1H), 4.18 (m, 0.69H), 4.07 (m, 1.69H), 2.52 (m, 1.69H), 2.45 (m, 1H), 2.37 (m, 0.69H), 2.32 (s, 2.99H), 2.31 (s, 2.08H), 2.25 (m, 1..69H), 2.17 (m, 1.69H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 154.7, 132.2, 131.8, 131.7, 131.6, 126.0, 125.4, 124.5, 123.0, 119.6, 116.7, 113.0 (SCN), 110.8 (SCN), 110.6, 110.1, 70.9, 55.7, 36.7, 24.6, 24.1 ppm; IR (KBr) 3283, 2156 (SCN), 1632, 1554, 750 cm^{-1}; HRMS (ESI) m/z [M - H]$^-$ calcd for $C_{13}H_{12}NO_2S$ 246.0589 found 246.0589.



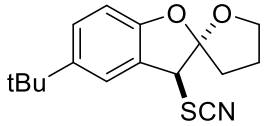
***6-Methyl-3-thiocyanato-4',5'-dihydro-3H,3'H-spirobenzofuran-2,2'-furan (2c)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.6, obtained as a mixture of diastereomers (dr = 1.4:1, determined by ^{1}H NMR), yellow oil (rt, 8 h, 22 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.7 Hz, 1H), 7.27 (d, J = 6.8 Hz, 0.7H), 6.82 (s, 1H), 6.80 (s, 0.7H), 6.68 (s, 0.7H), 6.63 (s, 1H), 5.04 (s, 1H), 4.77 (s, 0.7H), 4.24 (m, 1H), 4.17 (m, 0.7H), 4.09 (m, 1.7H), 2.57 – 2.42 (m, 3.4H), 2.33 (s, 3.0H), 2.31 – 2.21 (m, 3.4H), 2.17 (s, 2.0H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 157.0, 142.3, 142.0, 125.4, 124.7, 123.1, 122.9, 121.6, 120.2, 119.8, 117.0, 113.0 (SCN), 111.6, 111.1, 110.9 (SCN), 70.9, 69.9, 55.5, 55.3, 36.9, 33.4, 31.0, 24.6, 24.1, 21.9, 21.9 ppm; IR (KBr) 2954, 2152 (SCN), 1622, 1494, 1321, 1068, 943, 810 cm^{-1}; HRMS (ESI) m/z [M - H]$^-$ calcd for $C_{13}H_{12}NO_2S$ 246.0589 found 246.0589.



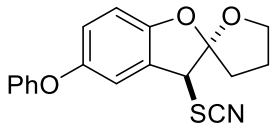
***4-Methyl-3-thiocyanato-4',5'-dihydro-3H,3'H-spirobenzofuran-2,2'-furan (2d)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.6, obtained as a mixture of diastereomers (dr = 2.2:1, determined by ^{1}H NMR), yellow solid (rt, 24 h, 15 mg, 59% yield; 40 ˚C, 8 h, 21 mg, 82% yield;), mp: 88-90 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (m, 1.45H), 6.79 (d, J = 7.6 Hz, 1H), 6.76 (d, J = 7.7 Hz, 0.45H), 6.71 (d, J = 8.1 Hz, 1H), 6.64 (d, J = 8.1 Hz, 0.45H), 4.91 (s, 0.45H), 4.71 (s, 1H), 4.34 (m, 0.29H), 4.18 (m, 0.45H), 4.10 (m, 1.17H), 2.61 (m, 2H), 2.45 (s, 1.35H), 2.41 (s, 3.01H), 2.36 (m, 0.9H), 2.31 (m, 0.9H), 2.23 – 2.12 (m, 2.0H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 157.2, 136.8, 136.4, 131.6, 131.5, 123.5, 123.4, 121.5, 121.0, 119.5, 117.0, 112.4 (SCN), 110.8 (SCN), 108.5, 108.2, 71.1, 70.1, 56.6, 55.0, 38.0, 33.4, 24.9, 24.1, 19.0, 18.6 ppm; IR (KBr) 2956, 2154 (SCN), 1728, 1616, 1489, 1257, 1068, 813, 750 cm^{-1}; HRMS (ESI) m/z [M - H]$^-$ calcd for $C_{13}H_{12}NO_2S$ 246.0589 found 246.0586.



***5-Ethyl-3-thiocyanato-4',5'-dihydro-3H,3'H-spirobenzofuran-2,2'-furan (2e)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.6, obtained as a mixture of diastereomers (dr = 1.5:1, determined by ^{1}H NMR), yellow oil (rt, 8 h, 17 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.22 (d, J = 1.9 Hz, 0.65H), 7.14 – 7.06 (m, 1.65H), 6.78 (d, J = 8.2 Hz, 0.65H), 6.73 (d, J = 8.2 Hz, 1H), 5.06 (s, 1H), 4.77 (s, 0.65H), 4.25 (m, 1H), 4.17 (m, 0.65H), 4.15 – 4.01 (m, 1.65H), 2.67 – 2.57 (m, 3.31H), 2.55 – 2.42 (m, 1.99H), 2.37 – 2.24 (m, 1.32H), 2.22 – 2.10 (m, 3.31H), 1.27 – 1.17 (m, 5H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 154.9, 138.3, 131.1, 130.7, 124.9, 124.5, 124.2, 123.0, 120.0, 113.0 (SCN), 110.8 (SCN), 110.7, 110.2, 70.8, 55.7, 55.4, 36.7, 33.3, 28.5, 28.4, 24.6, 24.1, 16.1, 16.0 ppm; IR (KBr) 2962, 2154 (SCN), 1728, 1618, 1489, 1257, 1070, 823 cm^{-1}; HRMS (ESI) m/z [M - H]$^-$ calcd for $C_{12}H_{12}NO_2S$ 260.0745 found 260.0746.

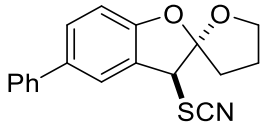


***5-(tert-Butyl)-3-thiocyanato-4',5'-dihydro-3H,3'H-spirobenzofuran-2,2'-furan (2f)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.6, obtained as a mixture of diastereomers (dr = 1.4:1, determined by ^{1}H NMR), yellow oil (rt, 5 h, 24 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.41 (s, 0.7H), 7.34 – 7.28 (m, 1.7H), 6.79 (d, J = 8.5 Hz, 0.7H), 6.74 (d, J = 8.5 Hz, 1H), 5.07 (s, 1H), 4.81 (s, 0.7H), 4.26 (m, 1H), 4.17 (m, 0.7H), 4.13 – 4.03 (m, 1.7H), 2.57 – 2.44 (m, 2.02H), 2.38 – 2.27 (m, 1.4H), 2.25 – 2.13 (m, 3.39H), 1.32 (s, 9.02H), 1.30 (s, 6.27H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 154.6, 145.4, 145.3, 128.7, 128.3, 124.1, 119.7, 116.9, 113.0 (SCN), 111.0 (SCN), 110.3, 109.8, 70.9, 69.9, 55.8, 55.6, 36.8, 34.6, 33.3, 31.7, 24.6, 24.1 ppm; IR (KBr) 2960~2872, 2154 (SCN), 1728, 1490, 833 cm^{-1}; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{16}H_{19}NNaO_2S$ 312.1029 found 312.1028.

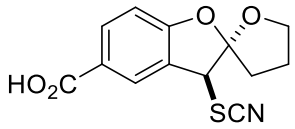


***5-Phenoxy-3-thiocyanato-4',5'-dihydro-3H,3'H-spiro[benzofuran-2,2'-furan] (2g)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.5, obtained as a mixture of diastereomers (dr = 1.4:1, determined by ^{1}H NMR), yellow oil (rt, 24 h, 19 mg, 59% yield; 40 ˚C, 8 h, 27 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (q, J = 8.0 Hz, 3.48H), 7.24 – 7.03 (m, 3.49H), 6.99 – 6.92 (m, 5.22H), 6.85 (d, J = 8.7 Hz, 0.74H), 6.78 (d, J = 8.7 Hz, 1H), 5.04 (s, 1H), 4.72 (s, 0.74H), 4.26 (m, 1H), 4.20 (m, 0.74H), 4.12 (m, 1.74H), 2.57 – 2.48 (m, 2.09H), 2.40 – 2.26 (m, 1.39H), 2.25 – 2.13 (m, 3.50H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 158.1, 154.1, 152.8, 151.5, 151.4, 129.9, 129.8, 129.8, 125.6, 124.1, 123.0, 122.9, 122.9, 122.6, 118.1, 117.9,

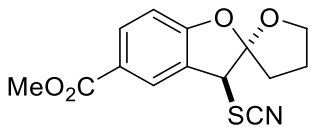
117.7, 117.2, 116.9, 116.7, 112.2 (SCN), 111.7, 111.1, 110.1 (SCN), 70.8, 70.0, 55.4, 55.1, 36.5, 33.4, 24.5, 24.0 ppm; IR (KBr) 3064~2899, 2154 (SCN), 1734, 1475, 1215, 750, 692 cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{15}NNaO_3S$ 348.0665 found 348.0674.



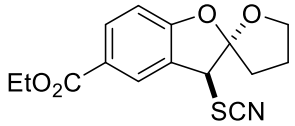
***5-Phenyl-3-thiocyanato-4',5'-dihydro-3H,3'H-spirobenzofuran-2,2'-furan (2h)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.6, obtained as a mixture of diastereomers (dr = 1.5:1, determined by ^1H NMR), yellow oil (rt, 24 h, 14 mg, 45% yield; 40 ˚C, 8 h, 27 mg, 87% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (m, 6.00H), 7.43 (m, 4.01H), 7.33 (m, 1.67H), 6.94 (d, J = 8.4 Hz, 0. 67H), 6.89 (d, J = 8.4 Hz, 1.00H), 5.13 (s, 1.00H), 4.86 (s, 0.67H), 4.32 – 4.25 (m, 1H), 4.26 – 4.17 (m, 0. 67H), 4.19 – 4.08 (m, 1.67H), 2.60 – 2.50 (m, 2.34H), 2.36 – 2.30 (m, 1.H), 2.27 – 2.15 (m, 3.33H). ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 156.3, 140.6, 140.5, 139.7, 138.3, 135.9, 135.8, 130.7, 130.3, 129.1, 129.0, 127.7, 127.2, 127.1, 127.0, 125.3, 124.5, 123.8, 122.9, 120.0, 117.2, 113.7, 112.8 (SCN), 112.3 (SCN), 110.8, 71.0, 70.1, 55.4, 55.2, 36.8, 34.7, 24.6, 24.1 ppm; IR (KBr) 3059~2897, 2152 (SCN), 1730, 1477, 761, 698 cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{18}H_{15}NNaO_2S$ 332.0716 found 332.0724.



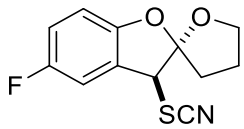
***3-Thiocyanato-4',5'-dihydro-3H,3'H-spiro[benzofuran-2,2'-furan]-5-carboxylic acid (2i)*:** eluent petroleum ether/ethyl acetate (2:1, v/v), TLC R_f = 0.5, obtained as a mixture of diastereomers (dr = 1.5:1, determined by ^1H NMR), yellow oil (40 ˚C, 24 h, 12 mg, 43% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.18 (s, 0.6H), 8.14 – 8.06 (m, 1.6H), 6.93 (d, J = 8.5 Hz, 0.6H), 6.88 (d, J = 8.5 Hz, 1H), 5.07 (s, 1H), 4.80 (s, 0.6H), 4.29 (m, 1H), 4.22 (m, 0.6H), 4.14 (m, 1.6H), 2.64 – 2.50 (m, 2.33H), 2.39 – 2.32 (m, 1.38H), 2.29 – 2.19 (m, 3.20H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 170.8, 162.3, 161.2, 134.7, 134.5, 128.5, 127.8, 125.1, 124.0, 123.5, 123.5, 121.1, 118.2, 112.0, 111.1, 110.6 (SCN), 109.9 (SCN), 71.3, 70.4, 54.3, 54.1, 36.9, 33.7, 24.5, 24.0 ppm; IR (KBr) 2926, 2156 (SCN), 1712, 1688, 1612, 1275, 1242, 914, 750 cm^{-1}; HRMS (ESI) m/z $[M + NH_4]^+$ calcd for $C_{13}H_{11}NNaO_4S$ 300.0301 found 300.0296.



***Methyl-3-thiocyanato-4',5'-dihydro-3H,3'H-spiro[benzofuran-2,2'-furan]-5-carboxylate (2j)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.4, obtained as a mixture of diastereomers (dr = 1.4:1, determined by ^{1}H NMR), yellow oil (rt, 24 h, 14 mg, 48% yield; 40 ˚C, 8 h, 22 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.10 (s, 0.74H), 8.02 (s, 1.74H), 6.89 (d, *J* = 8.5 Hz, 0.74H), 6.84 (d, *J* = 8.5 Hz, 1H), 5.05 (s, 1H), 4.78 (s, 0.74H), 4.26 (m, 1H), 4.19 (m, 0.74H), 4.16 – 4.09 (m, 1.74H), 3.90 (s, 2.98H), 3.89 (s, 2.26H), 2.60 – 2.48 (m, 2.43H), 2.35 (m, 1.06H), 2.30 – 2.15 (m, 3.49H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 166.3, 161.6, 160.5, 134.0, 133.8, 127.8, 126.9, 124.9, 124.5, 124.4, 123.7, 120.9, 112.2 (SCN), 110.9, 110.4, 110.0 (SCN), 77.5, 71.3, 70.3, 54.5, 54.3, 52.3, 52.2, 36.8, 33.7, 24.5 ppm; IR (KBr) 2987~2900, 2156 (SCN), 1714, 1441, 1290, 1087, 974, 918, 771 cm^{-1}; HRMS (ESI) m/z $[M + NH_4]^+$ calcd for $C_{14}H_{17}N_2O_4S$ 309.0904 found 309.0912.

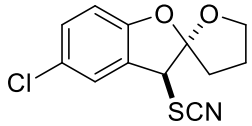


Ethyl-3-thiocyanato-4',5'-dihydro-3H,3'H-spiro[benzofuran-2,2'-furan]-5-carboxylate (2k): eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.4, obtained as a mixture of diastereomers (dr = 1.6:1, determined by ^{1}H NMR), yellow oil (rt, 8 h, 25 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.10 (s, 0.63H), 8.07 – 7.99 (m, 1.63H), 6.89 (d, *J* = 8.5 Hz, 0.63H), 6.84 (d, *J* = 8.5 Hz, 1H), 5.05 (s, 1H), 4.78 (s, 0.63H), 4.40 – 4.32 (m, 3.26H), 4.29 – 4.17 (m, 1.27H), 4.16 – 4.10 (m, 1.99H), 2.63 – 2.45 (m, 1.99H), 2.39 – 2.29 (m, 1.26H), 2.28 – 2.16 (m, 3.26H), 1.38 (t, *J* = 7.1 Hz, 4.89H), 1.25 (t, *J* = 7.1 Hz, 1.99H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 165.8, 161.6, 160.4, 133.9, 133.8, 127.7, 126.9, 124.8, 124.7, 123.7, 120.9, 118.0, 112.1 (SCN), 110.8, 110.4, 110.1 (SCN), 71.3, 70. 3, 61.2, 61.1, 54.5, 54.3, 36.9, 33.7, 24.5, 24.0, 14.5 ppm; IR (KBr) 2981~2902, 2156 (SCN), 1712, 1277, 750 cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{15}NNaO_4S$ 328.0619 found 328.0619.

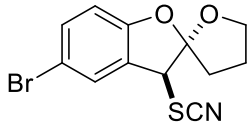


***5-Fluoro-3-thiocyanato-4',5'-dihydro-3H,3'H-spirobenzofuran-2,2'-furan (2l)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.6, obtained as a mixture of diastereomers (dr = 1.4:1, determined by ^{1}H NMR), yellow oil (rt, 24 h, 16 mg, 64% yield; 40 ˚C, 8 h, 18 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 1H), 7.11 (dd, *J* = 7.5, 2.6 Hz, 0.71H), 7.00 (dd, *J* = 8.7, 2.7 Hz, 0.71H), 6.96 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.80 (dd, *J* = 8.8, 4.0 Hz, 0.71H), 6.74 (dd, *J* = 8.8, 4.0 Hz, 1H), 5.05 (s, 1H), 4.71 (s, 0.71H), 4.23 (m, 1H), 4.17 (m, 0.71H),

4.16 – 4.04 (m, 1.71H), 2.57 – 2.44 (m, 2.19H), 2.36 – 2.26 (m, 1.23H), 2.25 – 2.11 (m, 3.42H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 158.9 (C−F, $^1J_{C-F}$ = 241.1 Hz), 153.8 (C−F, $^1J_{C-F}$ = 129.2 Hz), 125.6 ($^3J_{C-F}$ = 9.0 Hz), 124.0 ($^3J_{C-F}$ = 9.0 Hz), 119.8, 118.1 ($^2J_{C-F}$ = 24.4 Hz), 117.6 ($^2J_{C-F}$ = 24.4 Hz), 117.0, 112.3 ($^2J_{C-F}$ = 22.2 Hz), 111.9 ($^2J_{C-F}$ = 25.8 Hz), 111.4 ($^3J_{C-F}$ = 8.5 Hz), 110.8 ($^3J_{C-F}$ = 8.2 Hz), 109.7 (SCN), 77.2, 70.7, 69.8, 55.0 ($^4J_{C-F}$ = 1.9 Hz), 54.7 ($^4J_{C-F}$ = 2.0 Hz), 36.2, 33.2, 24.2, 23.7 ppm; ^{19}F NMR (377 MHz, $CDCl_3$): δ -121.2, -121.3 ppm; IR (KBr) 2960~2872, 2154 (SCN), 1728, 1490, 833 cm^{-1}; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{12}H_{10}FNNaO_2S$ 274.0308 found 273.0316.

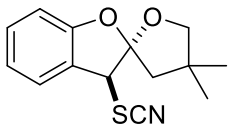


***5-Chloro-3-thiocyanato-4',5'-dihydro-3H,3'H-spirobenzofuran-2,2'-furan (2m)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.5, obtained as a mixture of diastereomers (dr = 1.4:1, determined by ^{1}H NMR), yellow oil (rt, 24 h, 16 mg, 60% yield; 40 ˚C, 8 h, 22 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, J = 1.4 Hz, 1H), 7.37 (d, J = 2.2 Hz, 0.7H), 7.26 – 7.24 (m, 1H), 7.23 – 7.21 (m, 0.7H), 6.80 (d, J = 8.6 Hz, 0.7H), 6.74 (d, J = 8.6 Hz, 1H), 5.03 (s, 1H), 4.71 (s, 0.7H), 4.28 – 4.21 (m, 1H), 4.20 – 4.15 (m, 0.7H), 4.13 – 4.04 (m, 1.7H), 2.62 – 2.45 (m, 2.0H), 2.37 – 2.27 (m, 1.4H), 2.26 – 2.10 (m, 3.39H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 155.4, 131.6, 131.2, 126.9, 126.5, 125.7, 125.1, 125.0, 124.4, 120.2, 117.3, 114.8, 112.2 (SCN), 111.6, 110.0 (SCN), 71.1, 70.2, 54.9, 54.6, 36.6, 33.5, 24.5, 24.0 ppm; IR (KBr) 2953~2899, 2154 (SCN), 1734, 1469, 815 cm^{-1}; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{12}H_{10}ClNNaO_2S$ 290.0013 found 290.0021.

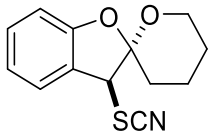


***5-Bromo-3-thiocyanato-4',5'-dihydro-3H,3'H-spirobenzofuran-2,2'-furan (2n)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.5, obtained as a mixture of diastereomers (dr = 1.4:1, determined by ^{1}H NMR), yellow oil (rt, 24 h, 15 mg, 48% yield; 40 ˚C, 8 h, 29 mg, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 2.7 Hz, 1H), 7.51 (d, J = 1.9 Hz, 0.69H), 7.40 – 7.35 (m, 1.69H), 6.76 (d, J = 8.6 Hz, 0.69H), 6.70 (d, J = 8.6 Hz, 1H), 5.04 (s, 1H), 4.71 (s, 0.69H), 4.24 (m, 1H), 4.17 (m, 0.69H), 4.14 – 4.03 (m, 1.69H), 2.56 – 2.46 (m, 2H), 2.35 – 2.26 (m, 1.39H), 2.25 – 2.15 (m, 3.39H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 155.9, 134.4, 134.1, 128.6, 127.9, 127.0, 125.5, 120.2, 117.3, 115.2, 113.8, 112.7, 112.3 (SCN), 112.2, 110.0 (SCN), 71.1, 70.2, 54.8, 54.5, 36.6, 33.5, 24.5, 24.0 ppm; IR (KBr) 3064~2897, 2154

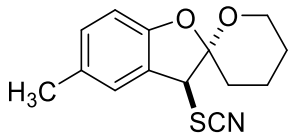
(SCN), 1732, 1465, 813 cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{12}H_{10}BrNNaO_2S$ 333.9508 found 333.9516.



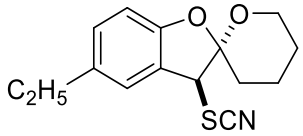
***4',4'-Dimethyl-3-thiocyanato-4',5'-dihydro-3H,3'H-spirobenzofuran-2,2'-furan (2o)*:** eluent petroleum ether/ethyl acetate (6:1, v/v), TLC R_f = 0.5, obtained as a mixture of diastereomers (dr = 1.2:1, determined by ^1H NMR), yellow oil (rt, 15 h, 21 mg, 81% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (m, 0.85H), 7.54 (d, J = 7.5 Hz, 1H), 7.41 (d, J = 7.6 Hz, 0.85H), 7.29 (m, 1H), 7.00 (m, 1.85H), 6.89 (d, J = 8.1 Hz, 0.85H), 6.83 (d, J = 8.1 Hz, 1H), 5.03 (s, 1H), 4.72 (s, 0.85H), 3.93 – 3.88 (m, 1.84H), 3.77 (m, 1.84H), 2.43 – 2.35 (m, 1.84H), 2.26 – 2.15 (m, 1.84H), 1.34 (s, 2.53H), 1.32 (s, 2.99H), 1.24 (s, 2.53H), 1.23 (s, 2.99H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 157.0, 131.5, 131.2, 125.9, 125.1, 124.6, 123.4, 122.2, 122.1, 120.2, 117.6, 113.4, 112.9, 111.2 (SCN), 110.5 (SCN), 82.7, 81.9, 57.0, 56.3, 51.2, 47.4, 39.5, 39.2, 28.0, 27.3, 26.4, 26.3 ppm; IR (KBr) 2960, 2872, 2154 (SCN), 1730, 1612, 1465, 1034, 912, 748 cm^{-1}; HRMS (ESI) m/z $[M + NH_4]^+$ calcd for $C_{14}H_{15}NNaO_2S$ 284.0716 found 284.0706.



***3-Thiocyanato-3',4',5',6'-tetrahydro-3H-spiro[benzofuran-2,2'-pyran] (2p)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.5, obtained as a mixture of diastereomers (dr = 1.3:1, determined by ^1H NMR), yellow oil (rt, 24 h, 13 mg, 51% yield; 40 ˚C, 8 h, 19 mg, 77% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 1H), 7.41 (d, J = 7.4 Hz, 0.75H), 7.34 – 7.26 (m, 1.75H), 7.00 (t, J = 7.7 Hz, 1.75H), 6.91 (d, J = 8.1 Hz, 0.75H), 6.86 (d, J = 8.1 Hz, 1H), 4.82 (s, 1H), 4.62 (s, 0.75H), 4.11 – 3.97 (m, 1.74H), 3.86 (dd, J = 11.3, 4.7 Hz, 1H), 3.74 (dd, J = 11.3, 4.8 Hz, 0.75H), 2.13 – 1.97 (m, 3.5H), 1.98 – 1.88 (m, 2.0H), 1.89 – 1.77 (m, 1.5H), 1.77 – 1.62 (m, 3.5H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 157.1, 131.4, 131.1, 126.2, 125.4, 125.3, 123.6, 122.2, 122.1, 113.4, 111.3, 110.8, 110.2 (SCN), 108.3 (SCN), 64.3, 63.9, 58.1, 57.7, 32.8, 30.6, 24.5, 24.3, 19.6, 19.2 ppm; IR (KBr) 3051~2851, 2152 (SCN), 1576, 1463, 1242, 1045, 877, 750 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_{14}NO_2S$ 248.0740 found 248.0734.

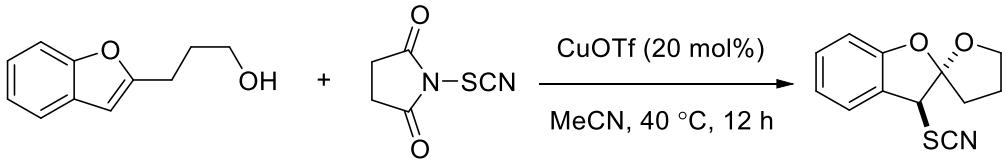


***5-Methyl-3-thiocyanato-3',4',5',6'-tetrahydro-3H-spiro[benzofuran-2,2'-pyran] (2q)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.8, obtained as a mixture of diastereomers (dr = 1.2:1, determined by ^{1}H NMR), yellow oil (rt, 24 h, 11 mg, 42% yield; 40 ˚C, 8 h, 19 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.21 (s, 0.82H), 7.08 (t, J = 7.1 Hz, 1.82H), 6.80 (d, J = 8.2 Hz, 0.82H), 6.74 (d, J = 8.2 Hz, 1H), 4.78 (s, 1H), 4.57 (s, 0.82H), 4.03 (m, 1.82H), 3.84 (dd, J = 11.3, 4.7 Hz, 1H), 3.72 (dd, J = 11.3, 4.7 Hz, 0.82H), 2.32 (s, 3H), 2.31 (s, 2.46H), 2.08 – 1.97 (m, 3.65H), 1.95 – 1.81 (m, 3.67H), 1.77 – 1.61 (m, 3.66H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 155.0, 132.0, 131.8, 131.7, 131.6, 126.5, 125.6, 125.2, 123.5, 113.6, 111.0, 110.9, 110.4, 110.2 (SCN), 108.3 (SCN), 64.2, 63.8, 58.4, 57.8, 32.7, 30. 6, 24. 6, 24.3, 21.0, 20.9, 19.6, 19.2 ppm; IR (KBr) 2947, 2154 (SCN), 1489, 1230, 1045, 912, 744 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{16}NO_2S$ 262.0896 found 262.0897.



***5-Ethyl-3-thiocyanato-3',4',5',6'-tetrahydro-3H-spiro[benzofuran-2,2'-pyran] (2r)*:** eluent petroleum ether/ethyl acetate (5:1, v/v), TLC R_f = 0.8, obtained as a mixture of diastereomers (dr = 1.3:1, determined by ^{1}H NMR), yellow oil (rt, 24 h, 18 mg, 67% yield; 40 ˚C, 8 h, 22 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.23 (s, 0.8H), 7.14 – 7.07 (m, 1.8H), 6.82 (d, J = 8.3 Hz, 0.8H), 6.77 (d, J = 8.2 Hz, 1H), 4.80 (s, 1H), 4.60 (s, 0.8H), 4.10 – 3.98 (m, 1.8H), 3.84 (dd, J = 11.3, 4.7 Hz, 1H), 3.73 (dd, J = 11.3, 4.7 Hz, 0.8H), 2.67 – 2.56 (m, 3.61H), 2.10 – 1.98 (m, 3.61H), 1.96 – 1.83 (m, 3.60H), 1.77 – 1.60 (m, 3.60H), 1.25 – 1.22 (m, 3.03H), 1.22 – 1.19 (m, 2.37H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 155.2, 138.4, 138. 3, 131.0, 130.5, 125.4, 125.2, 124.5, 123.5, 113.6, 111.0, 110. 9, 110.5, 110.2 (SCN), 108.4 (SCN), 64.2, 63.8, 58.4, 57.9, 32.7, 30.6, 28.5, 28. 4, 24. 6, 24.3, 19.6, 19.2, 16.2, 16.0 ppm; IR (KBr) 2960~2872, 2154 (SCN), 1489, 1228, 1045, 912, 742 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{18}NO_2S$ 276.1053 found 276.1053.

4. Gram-scale reaction of 2a



1a (6 mmol, 1.06 g) **(2.0 equiv.)** **2a (1.20 g, 86% yield, dr = 1.5:1)**

1a (6 mmol, 1.0 equiv.) and CuOTf (25.8 mg, 1.2 mmol, 0.2 equiv.) were stirred in CH_3CN (6.0 mL) for 5 min at room temperature under argon atmosphere in dark, after the *N*-Thiocyanatosuccinimide (186 mg, 12 mmol, 2.0 equiv.) was added, heating the reaction to 40 °C for 12 hours until the reaction completed (monitored by TLC). The reaction mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5/1, v/v) to afford the pure desired products **2a** with good 86% yield.

5. Single Crystal X-Ray data for compound 2d（CCDC 2248480）

The single crystal was cultivated in the solution of **2d** (50 mg) in EtOAc (1.0 mL) and PE (3.0 mL) evaporated at room temperature.

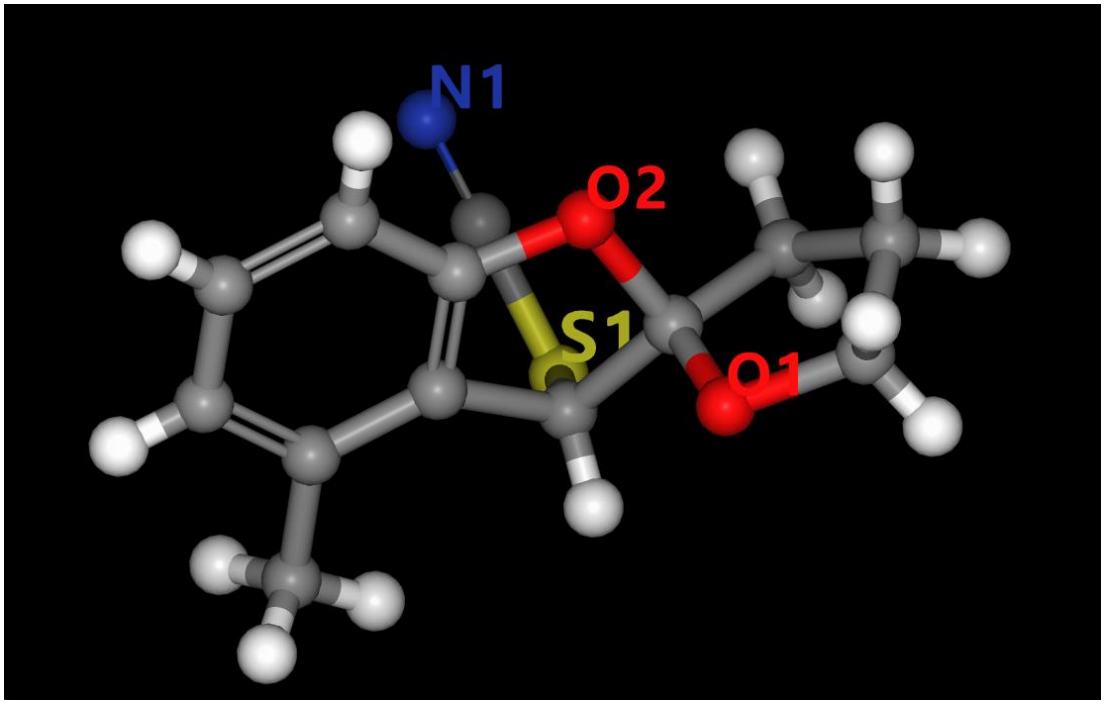


Table S1. **Crystal data and structure refinement for 2d**.

Identification code	CCDC 2248480	
Empirical formula	C13 H13 N O2 S	
Formula weight	247.30	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 16.128(6) Å	a= 90°.
	b = 5.8764(19) Å	b= 90°.

	c = 26.359(9) Å g = 90°.
Volume	2498.3(15) $Å^3$
Z	8
Density (calculated)	1.315 Mg/m^3
Absorption coefficient	0.248 mm^{-1}
F(000)	1040
Crystal size	0.200 x 0.200 x 0.200 mm^3
Theta range for data collection	2.526 to 24.992°.
Index ranges	-16<=h<=19, -6<=k<=6, -30<=l<=31
Reflections collected	29056
Independent reflections	4260 [R(int) = 0.1676]
Completeness to theta = 24.992°	99.3 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4260 / 229 / 283
Goodness-of-fit on F^2	0.996
Final R indices [I>2sigma(I)]	R1 = 0.1322, wR2 = 0.2315
R indices (all data)	R1 = 0.2397, wR2 = 0.2698
Absolute structure parameter	0.48(8)
Extinction coefficient	n/a
Largest diff. peak and hole	0.541 and -0.404 $e.Å^{-3}$

6. References

[1] Bergström M, Suresh G, Naidu V R, *Eur. J. Org. Chem.*, 2017, **2017**, 3234.
[2] Marsch N, Kock M, Lindel T. *Beilstein J. Org. Chem.*, 2016, **12**, 334.
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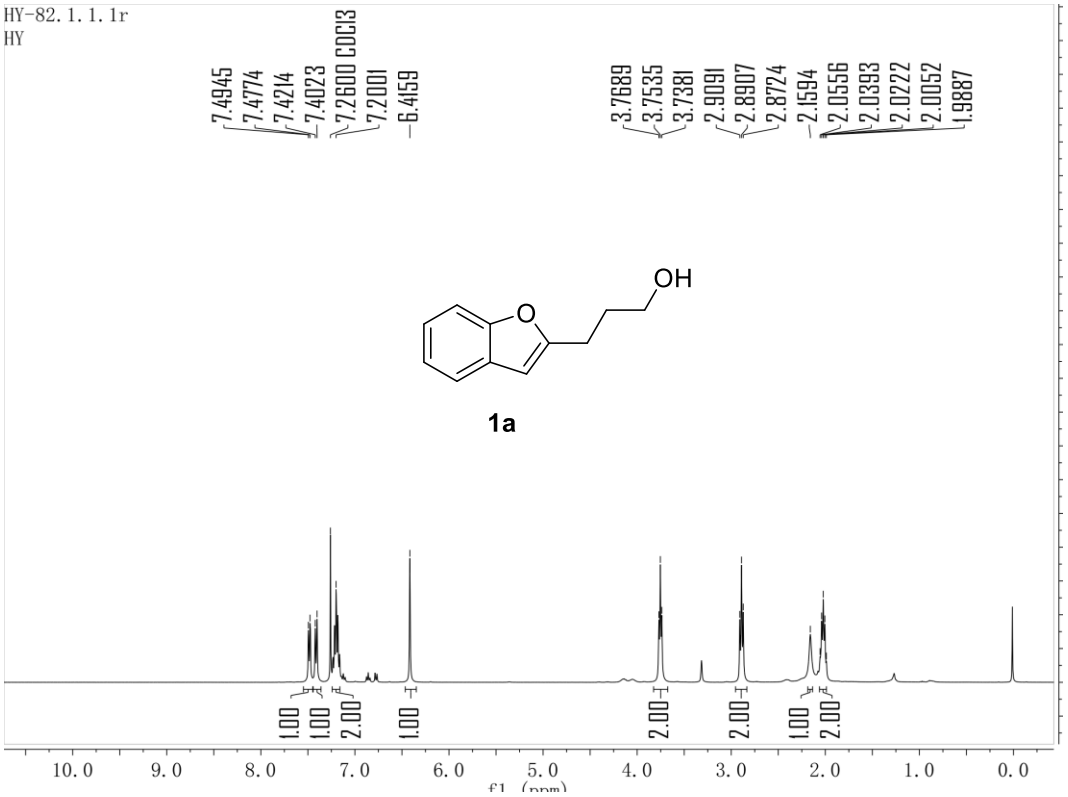
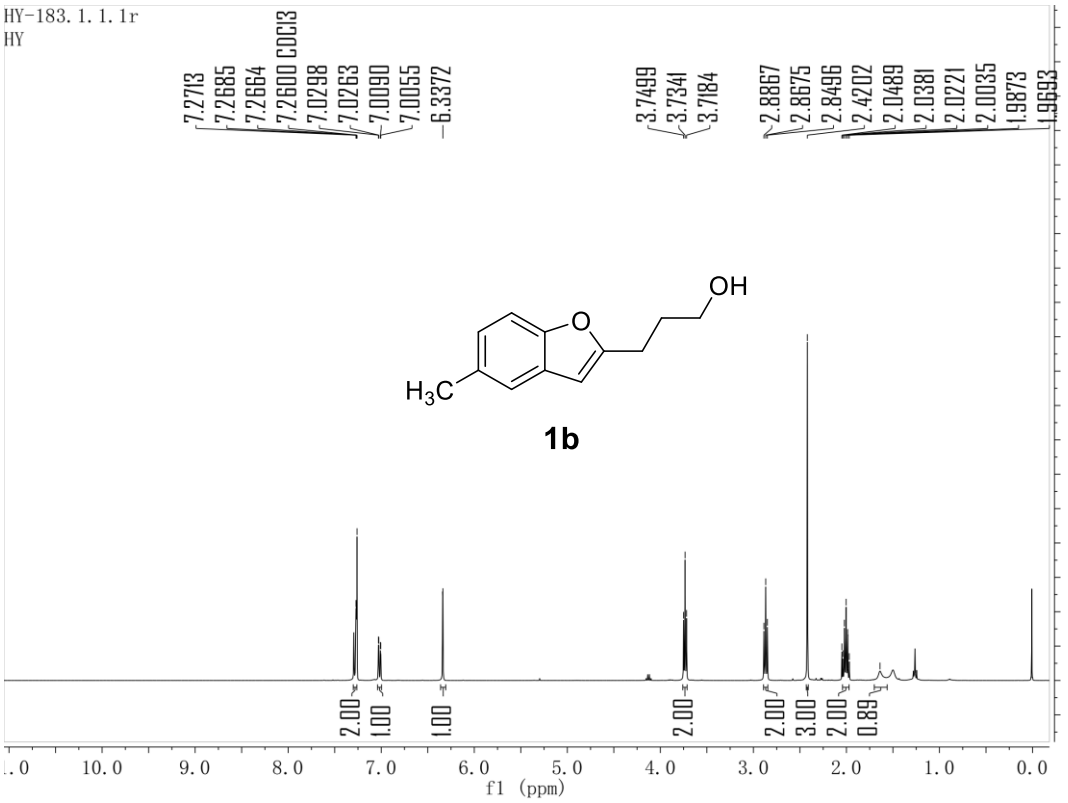
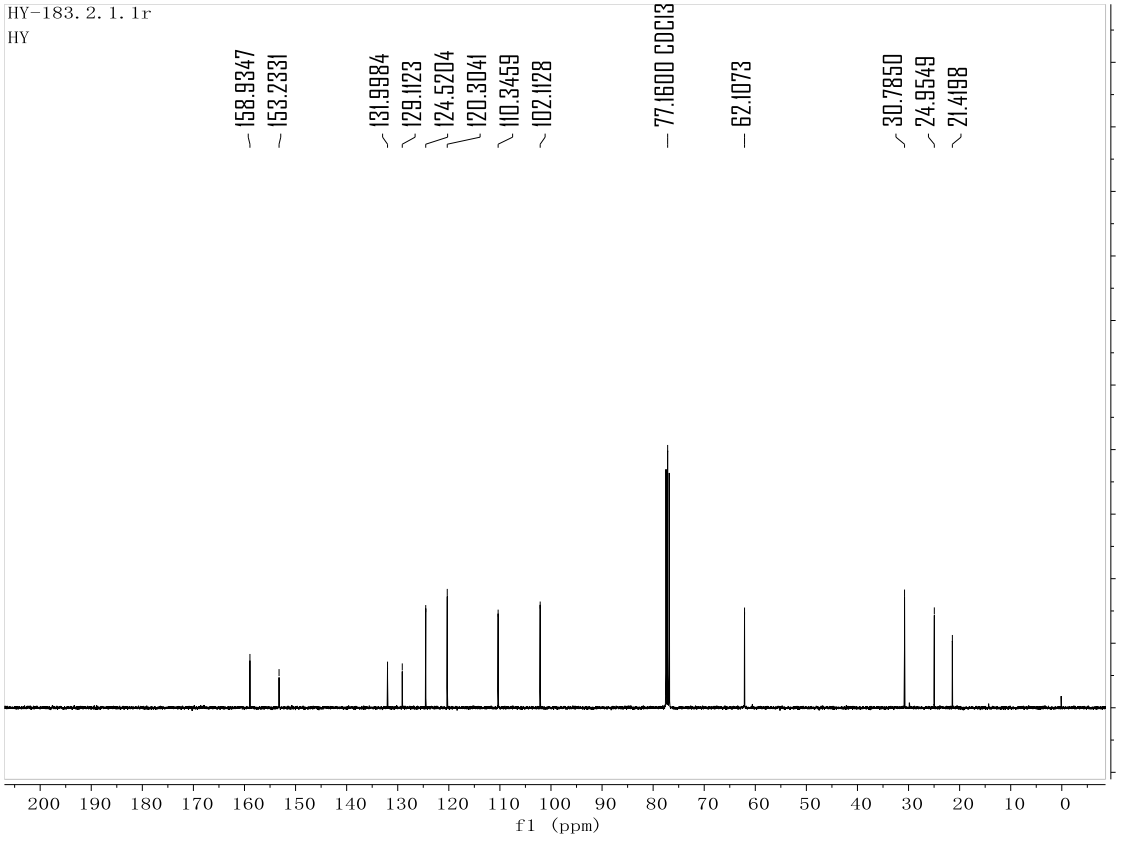
[4] Bakunova S M, Bakunov S A, Wenzler T, *J. Med. Chem.*, 2007, **50**, 5807.
[5] Zhou L, Shi Y, Xiao Q, *Org. Lett.*, 2011, **13**, 968.
[6] Xiang K, Tong P, Yan B, *Org. Lett.*, 2018, **21**, 412.

7. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra



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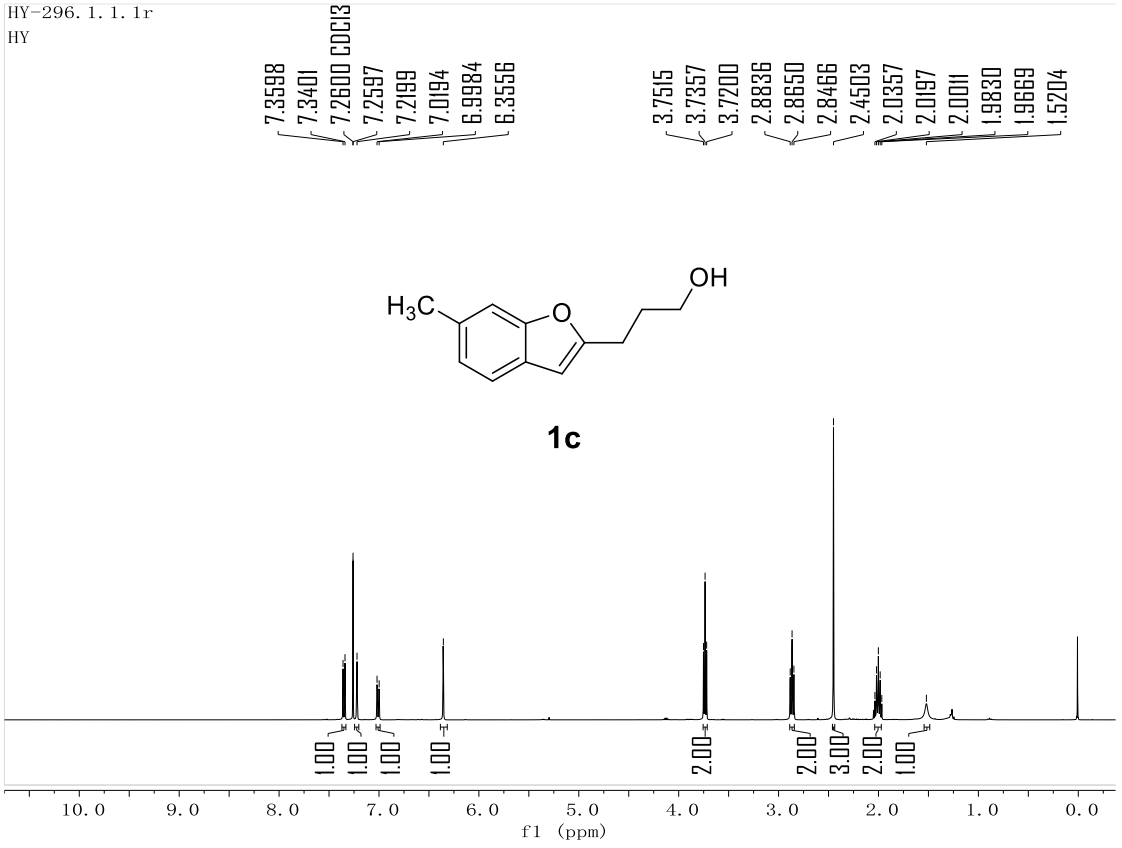
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1.00
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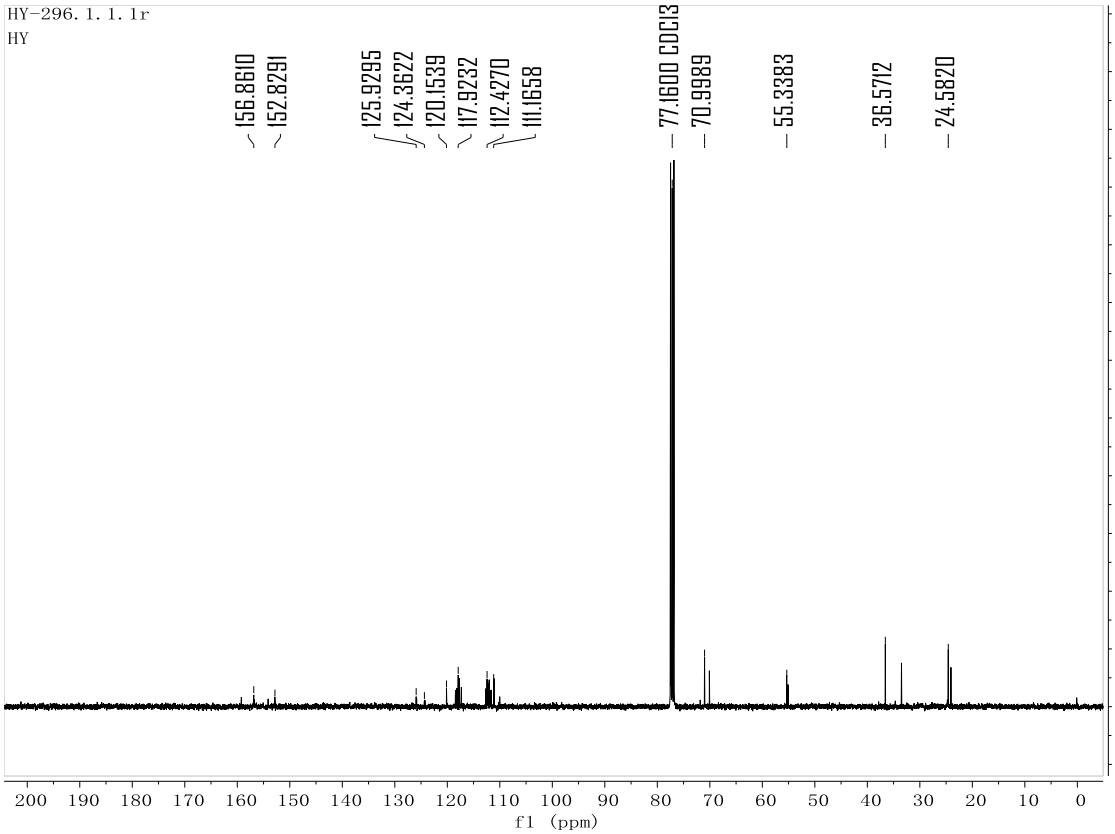
f1 (ppm)

H3C
O
OH

1c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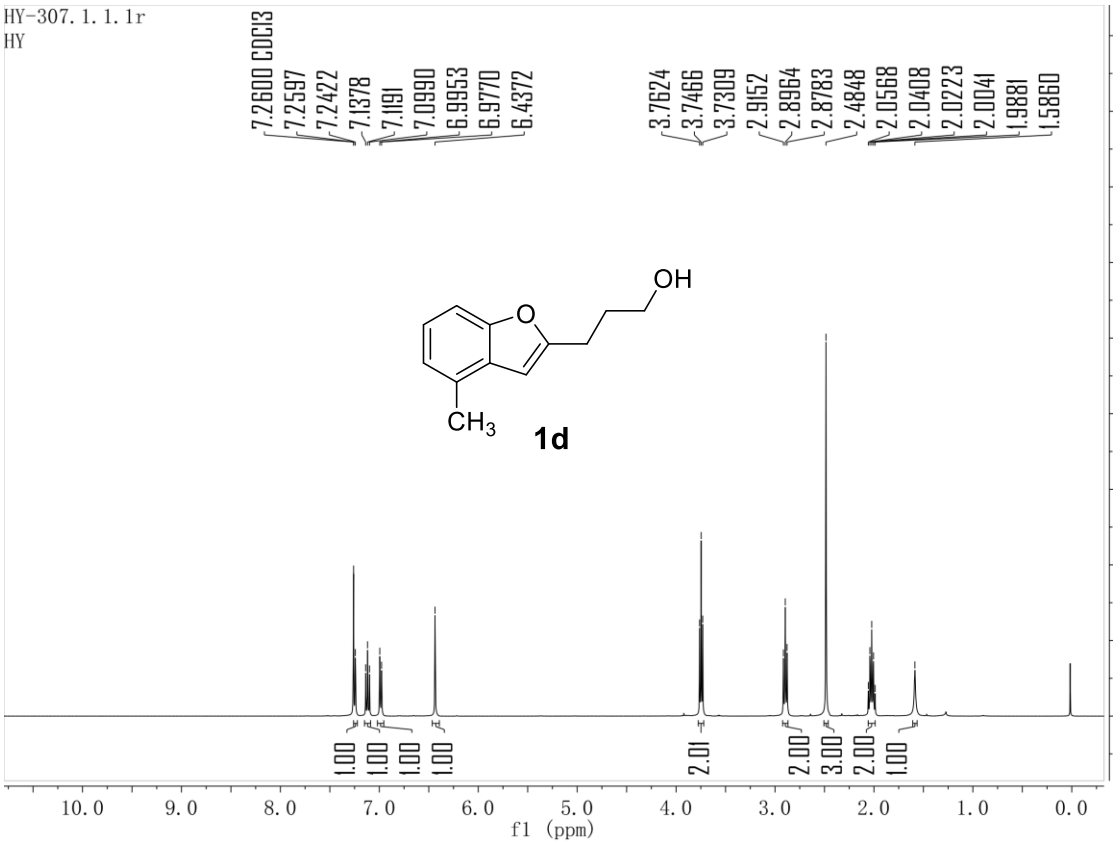
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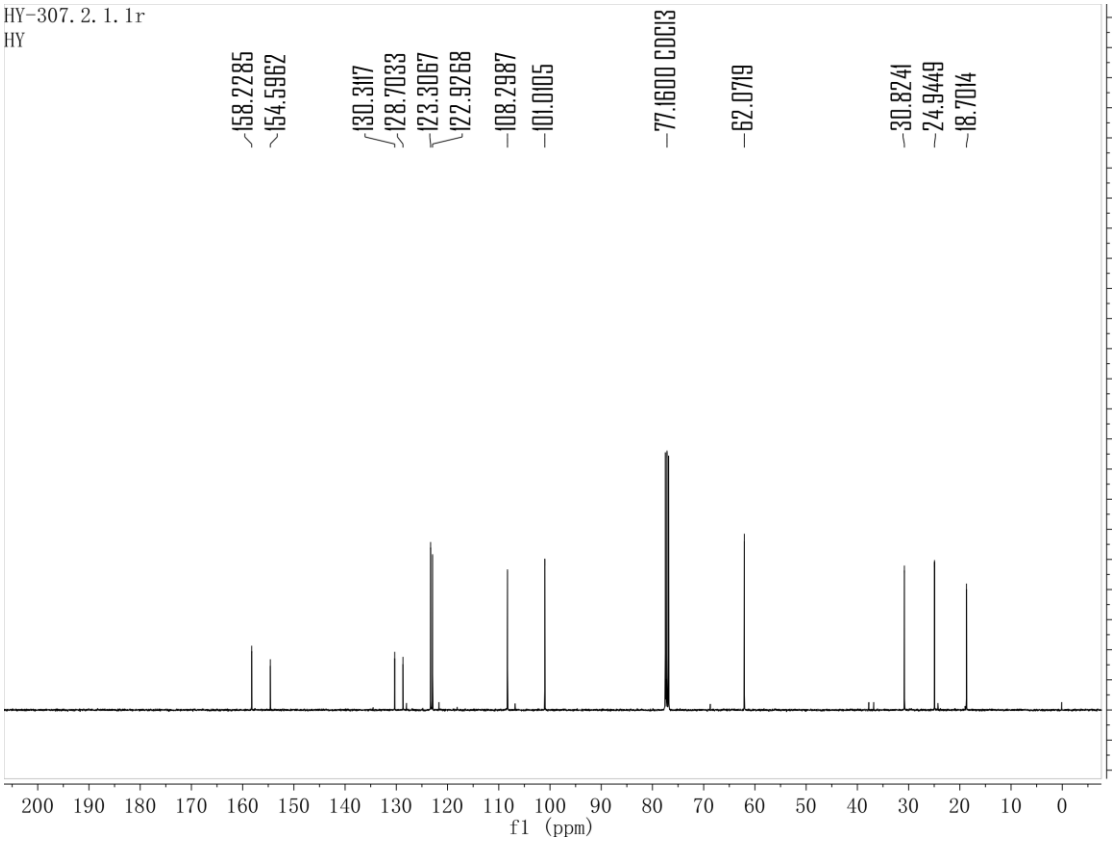
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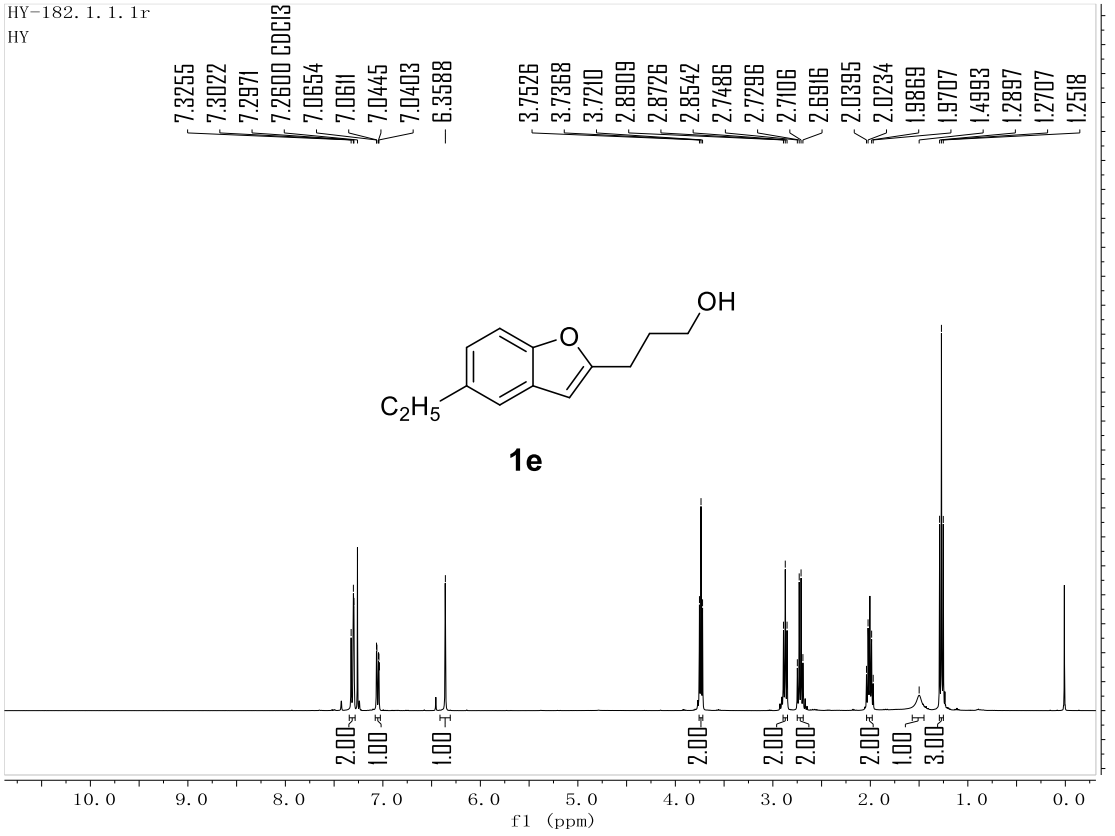
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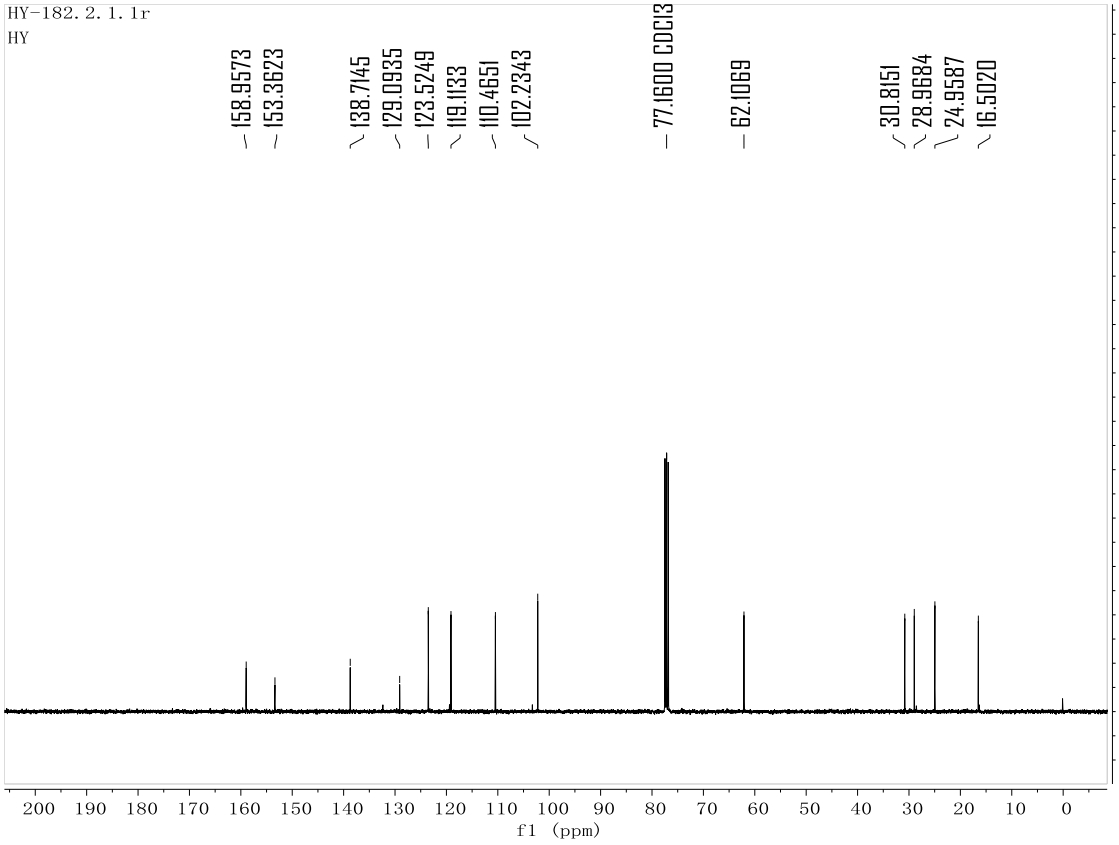
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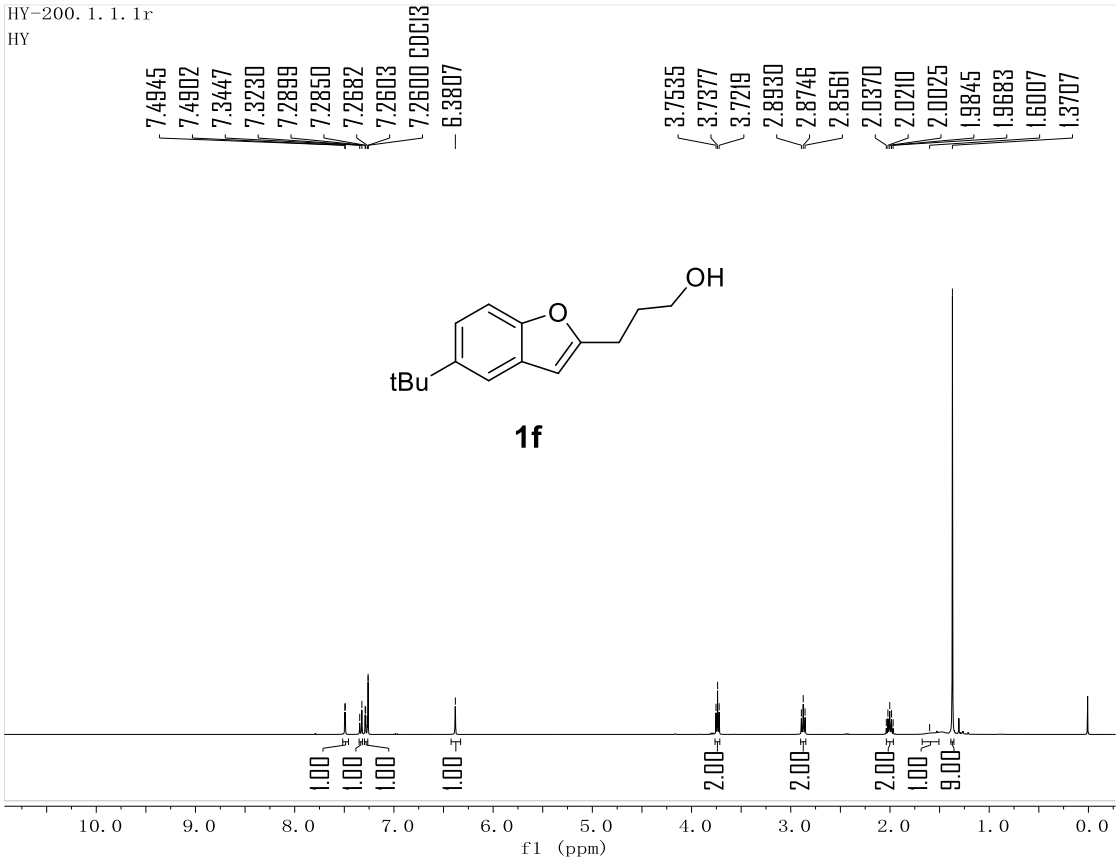
f1 (ppm)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O
tBu
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1.00
1.00
1.00
2.00
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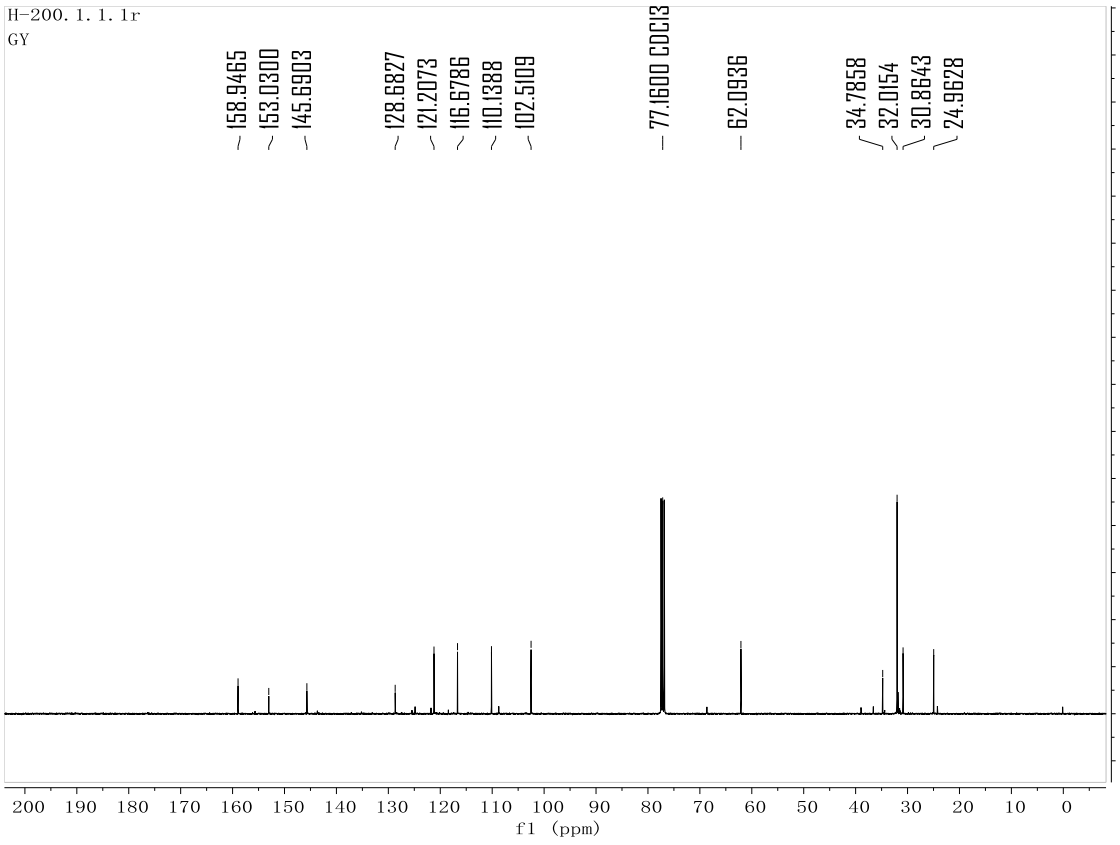
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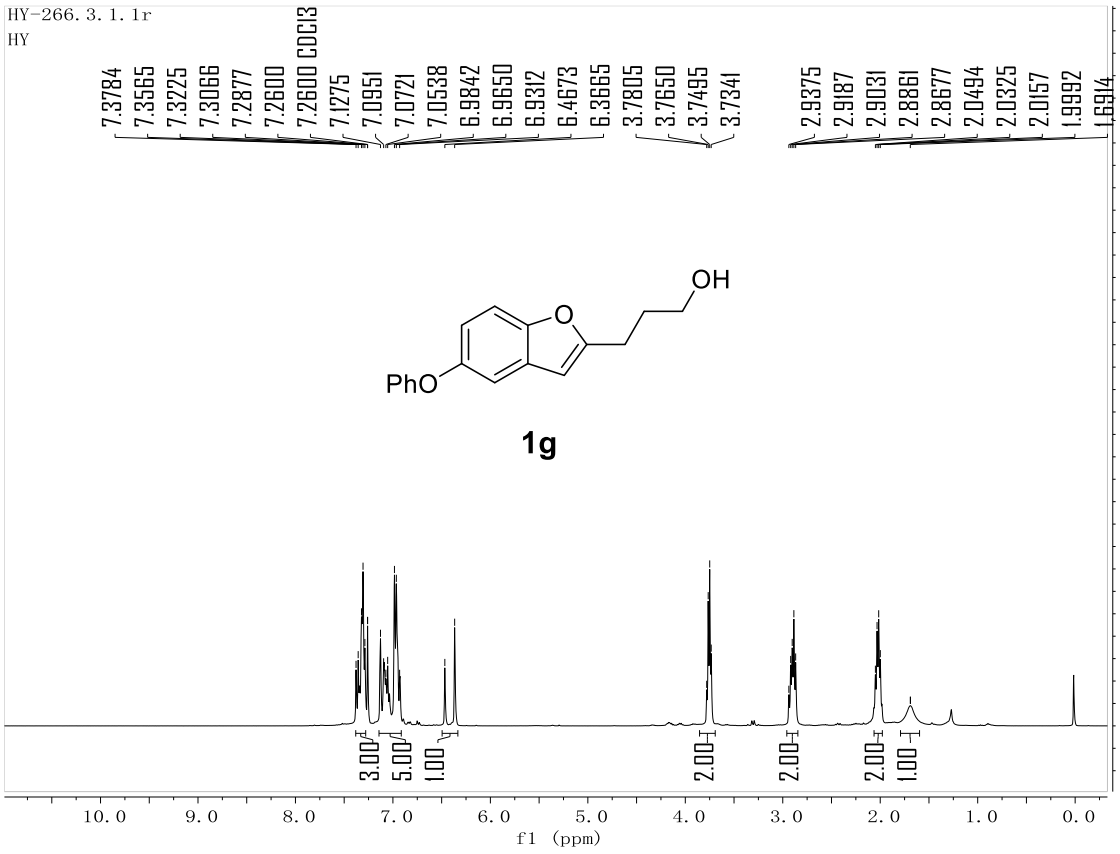
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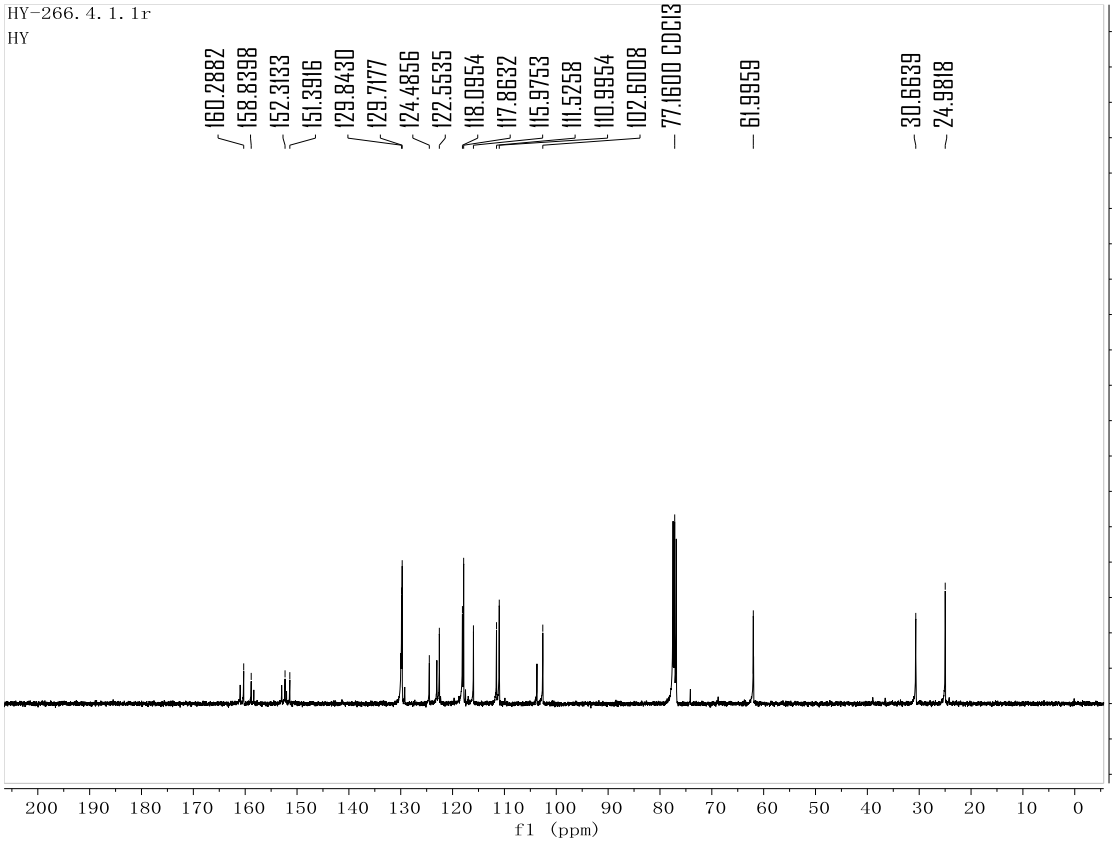
PhO

1g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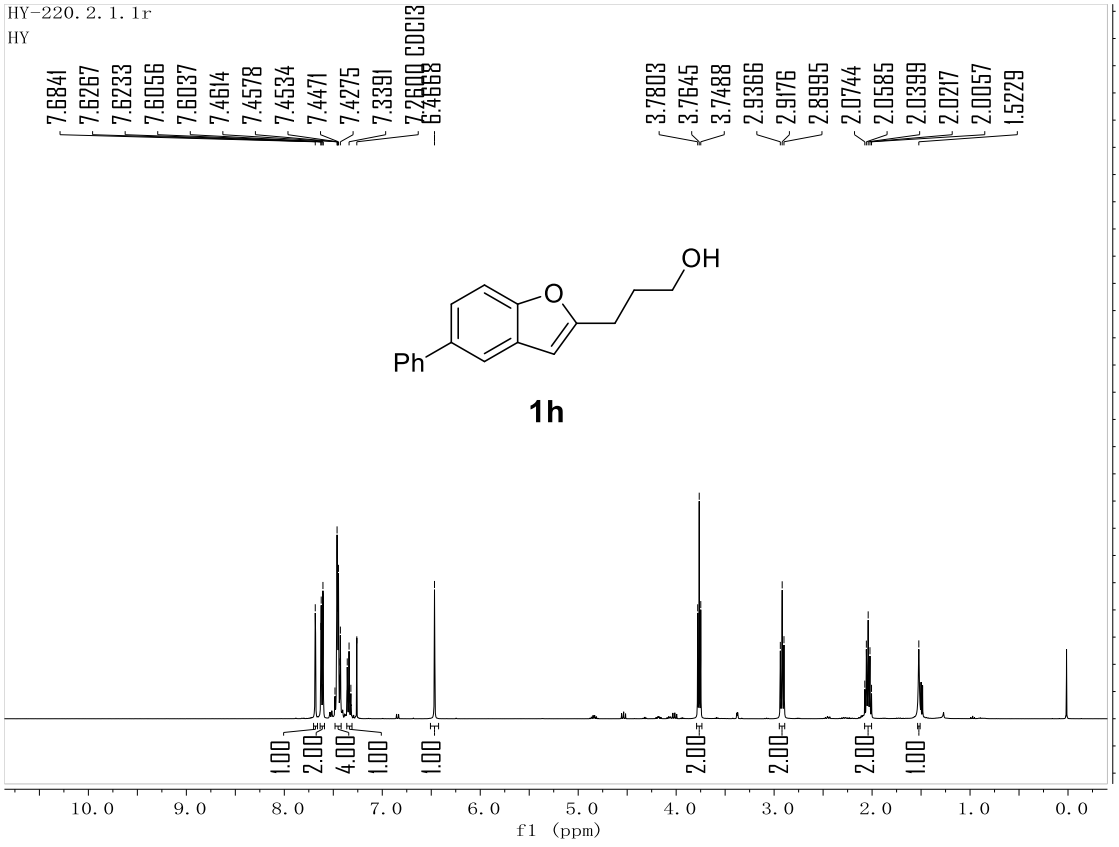
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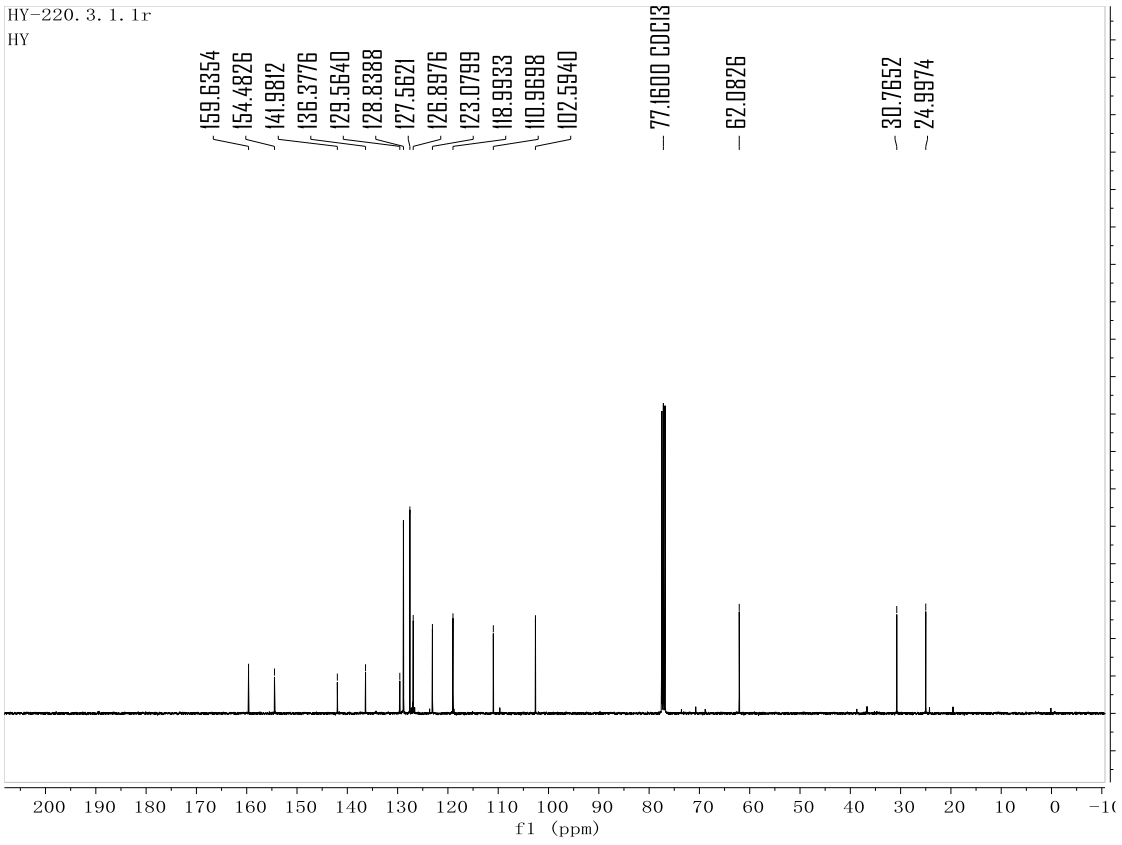
O
Ph

1h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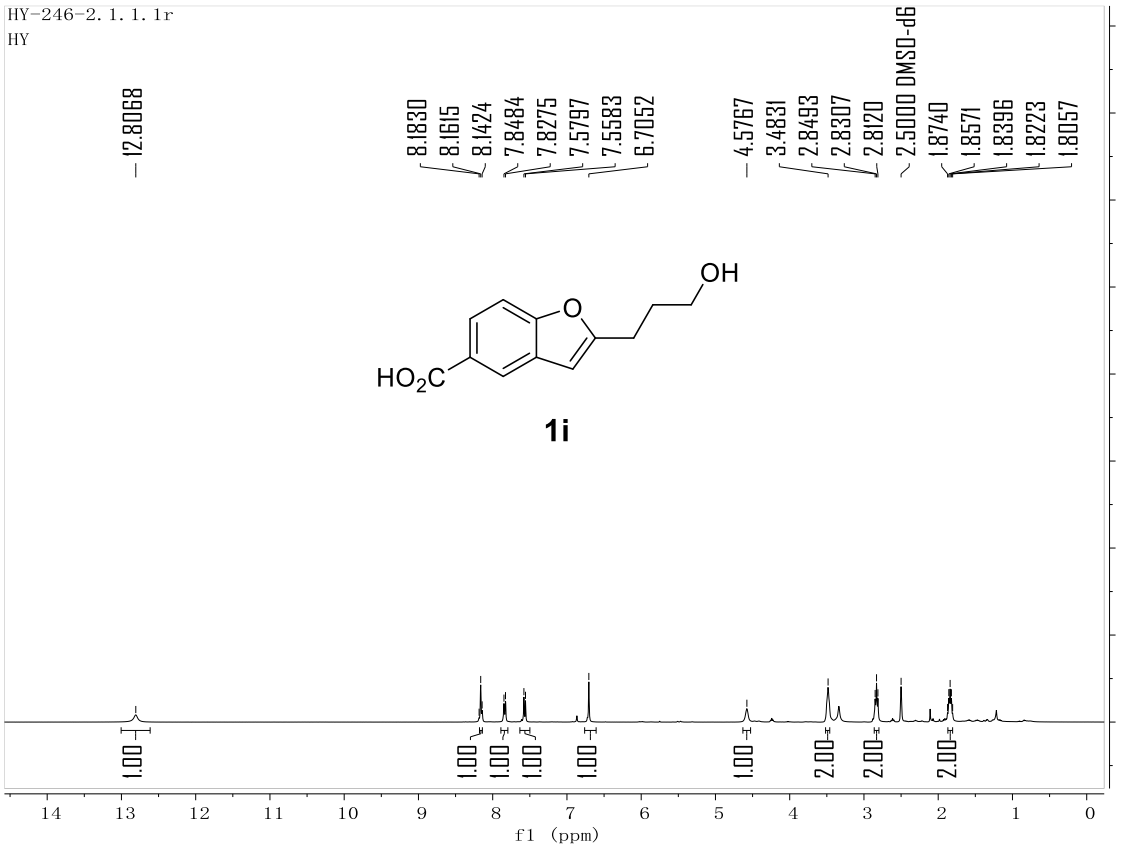
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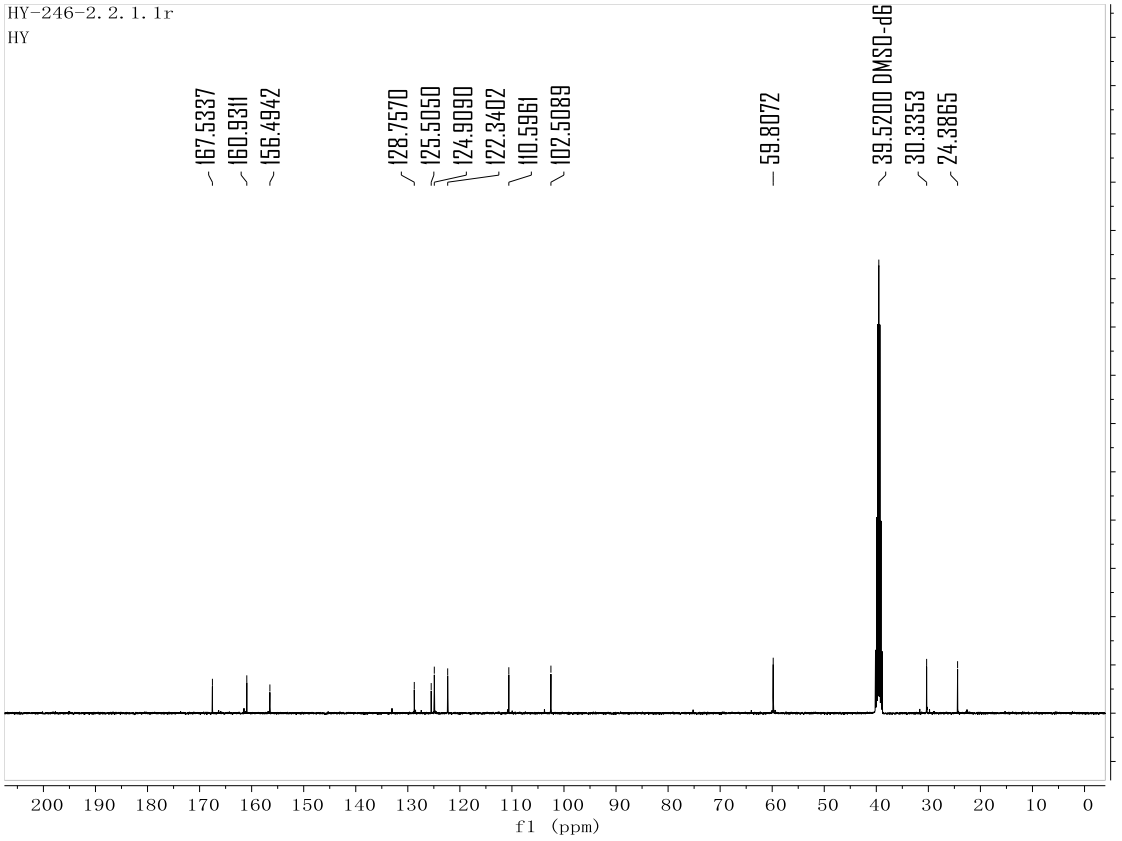
f1 (ppm)

1i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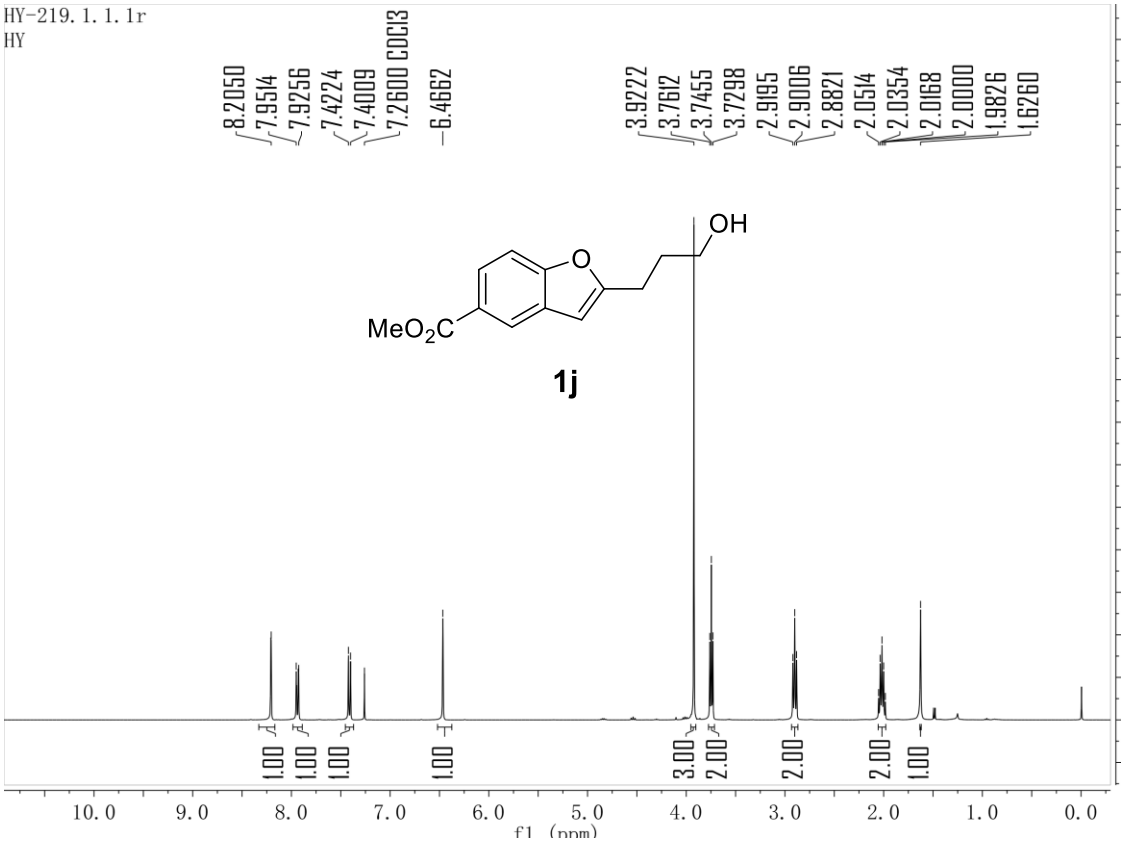
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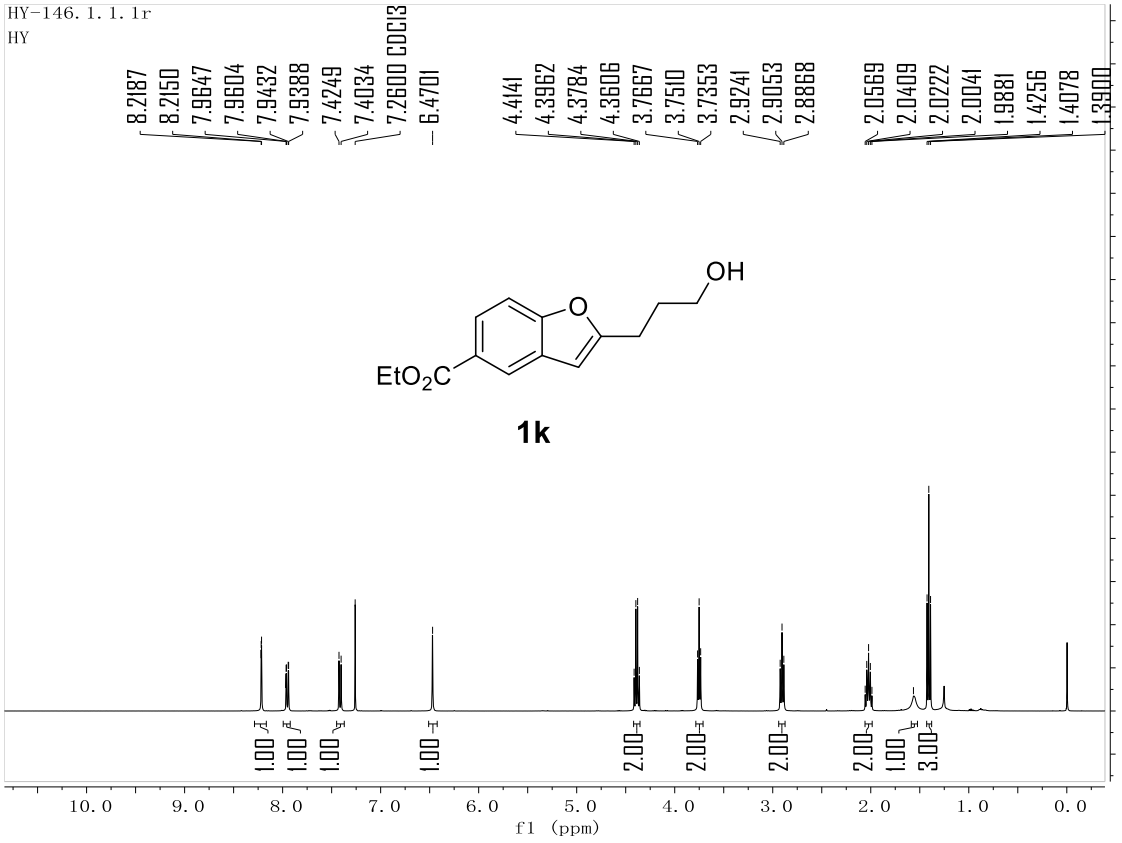
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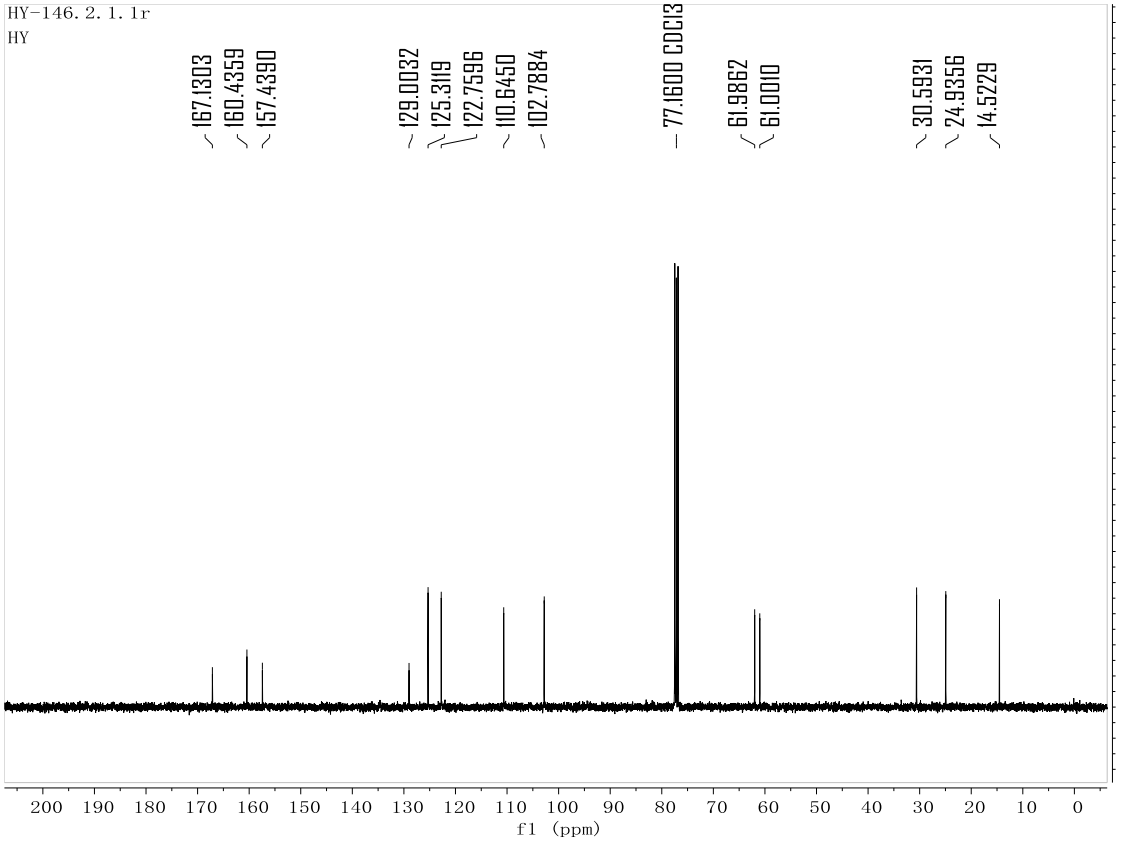
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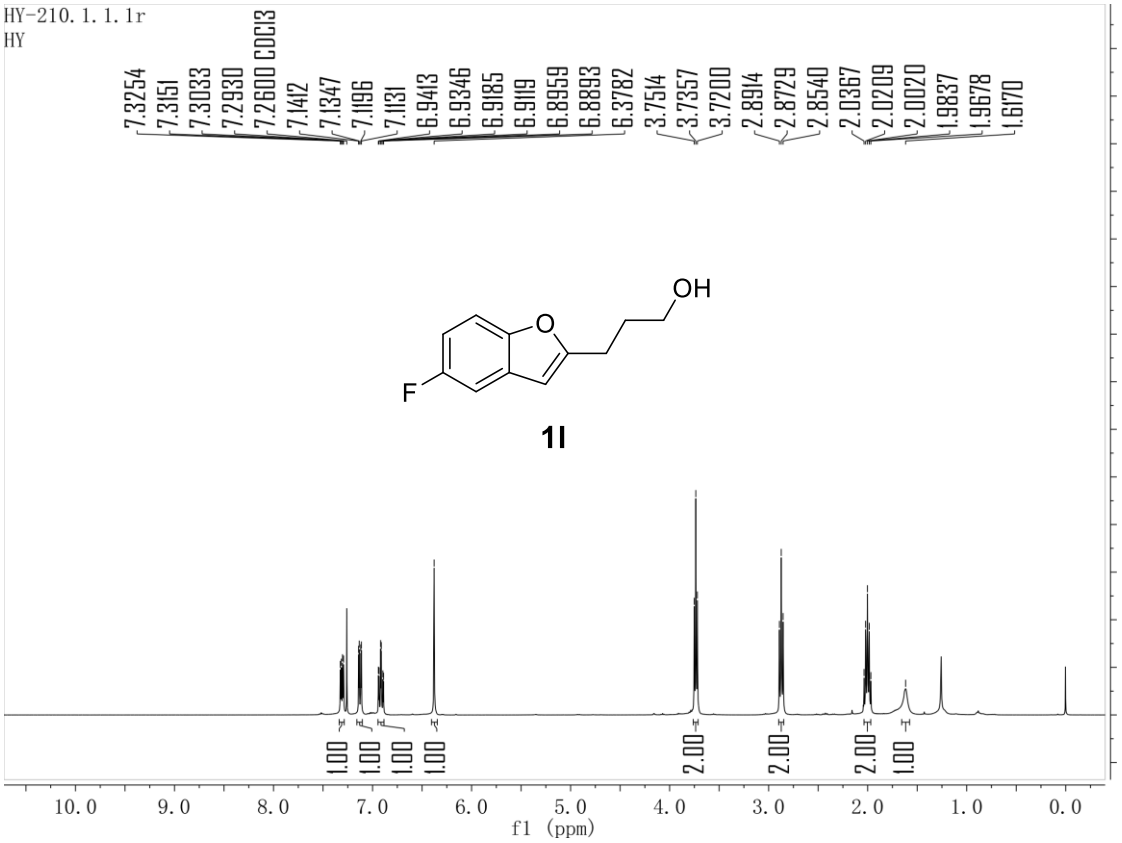
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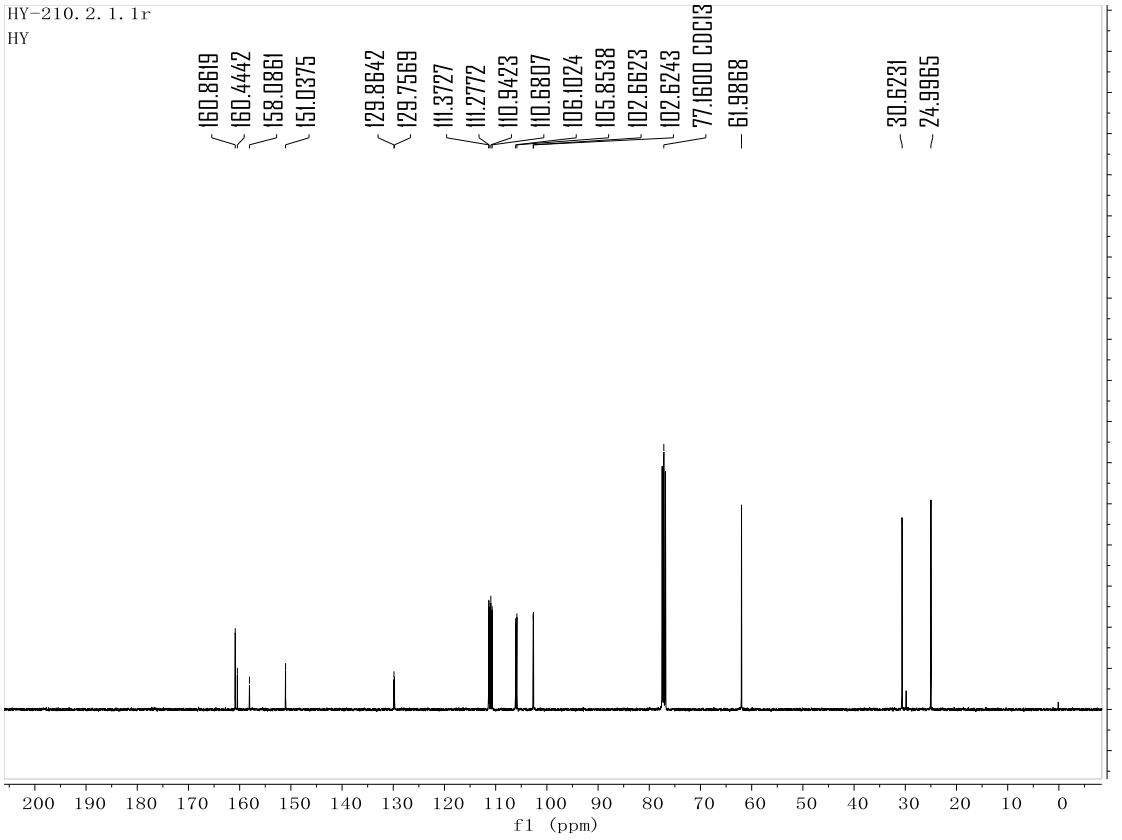
1l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190
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50
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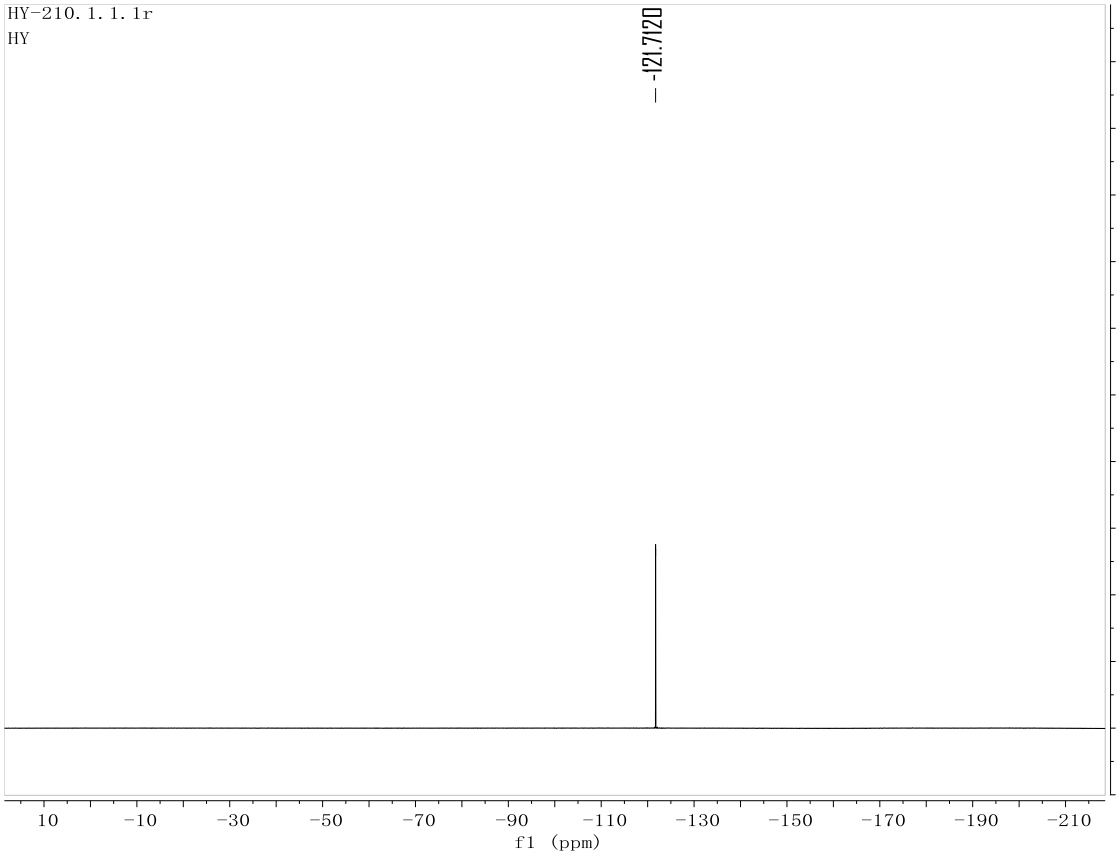
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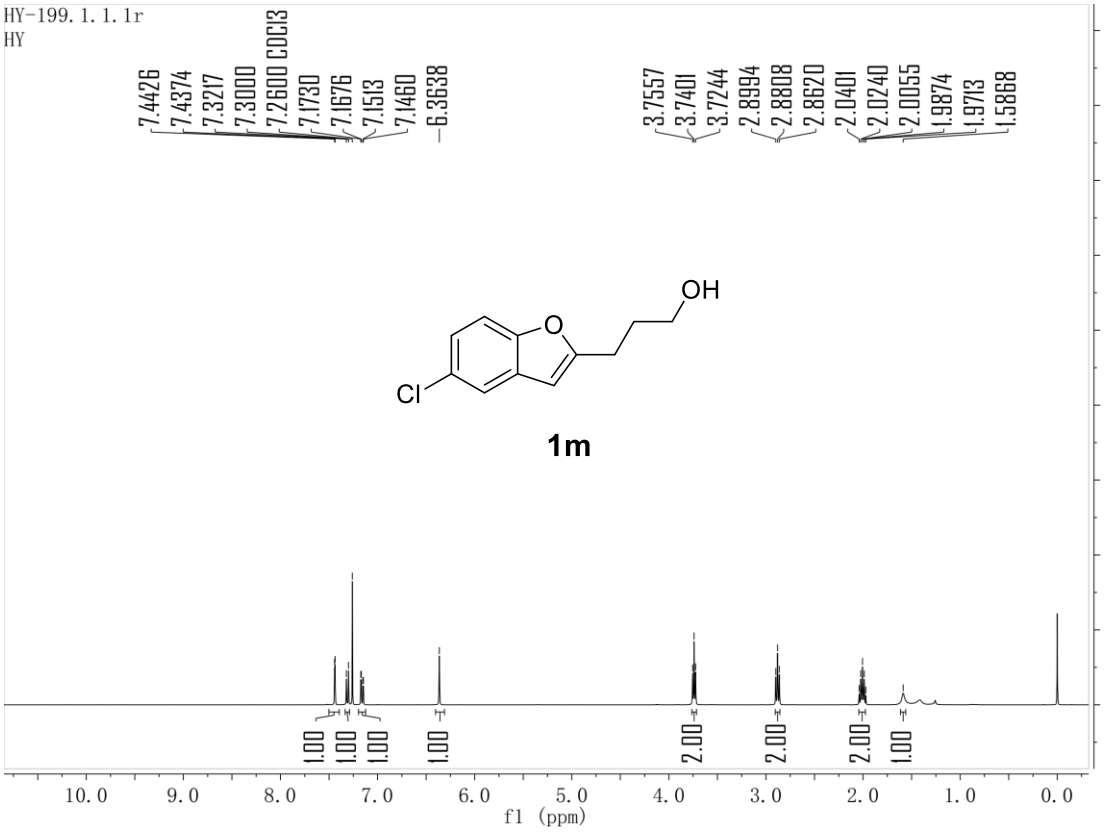
f1 (ppm)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7.4426
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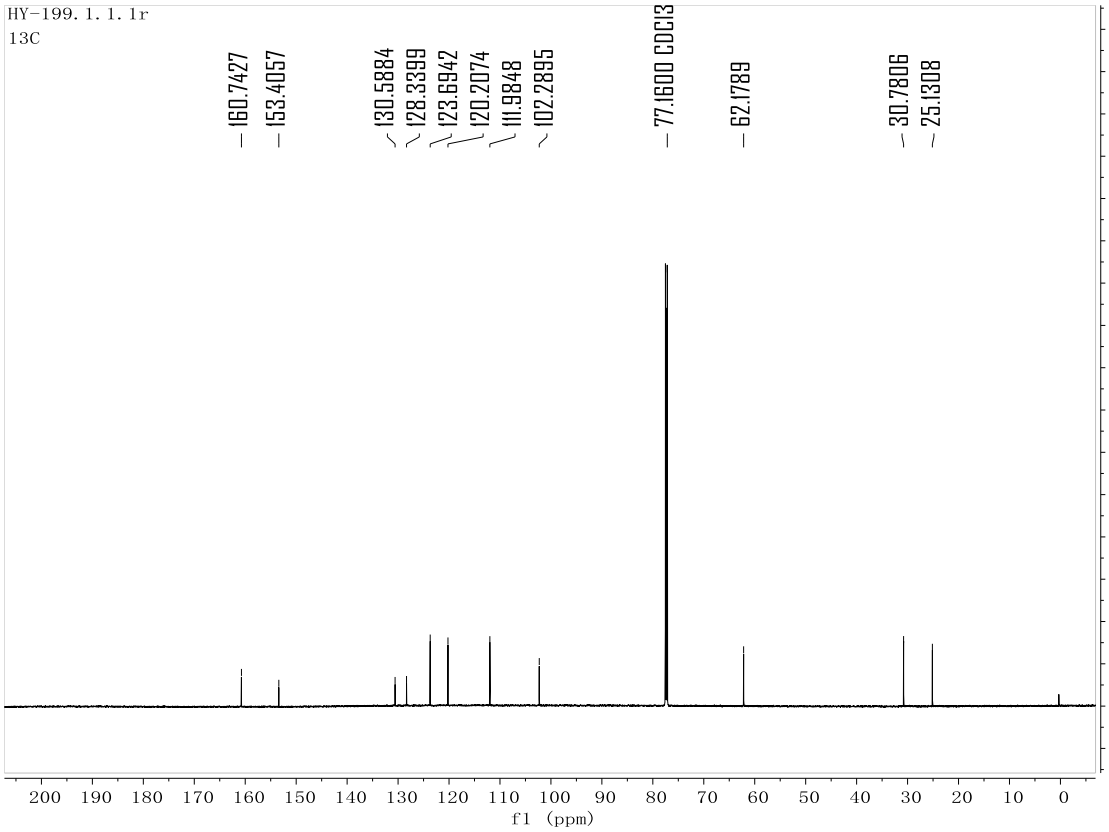
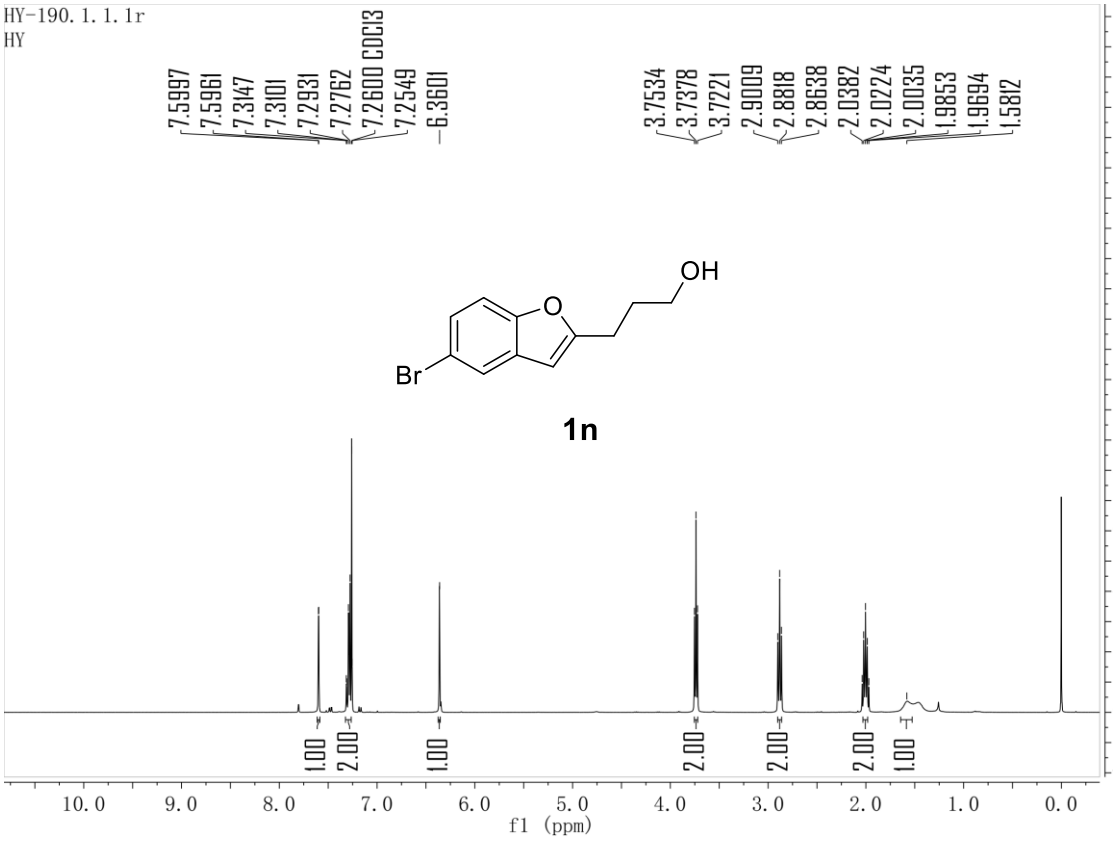
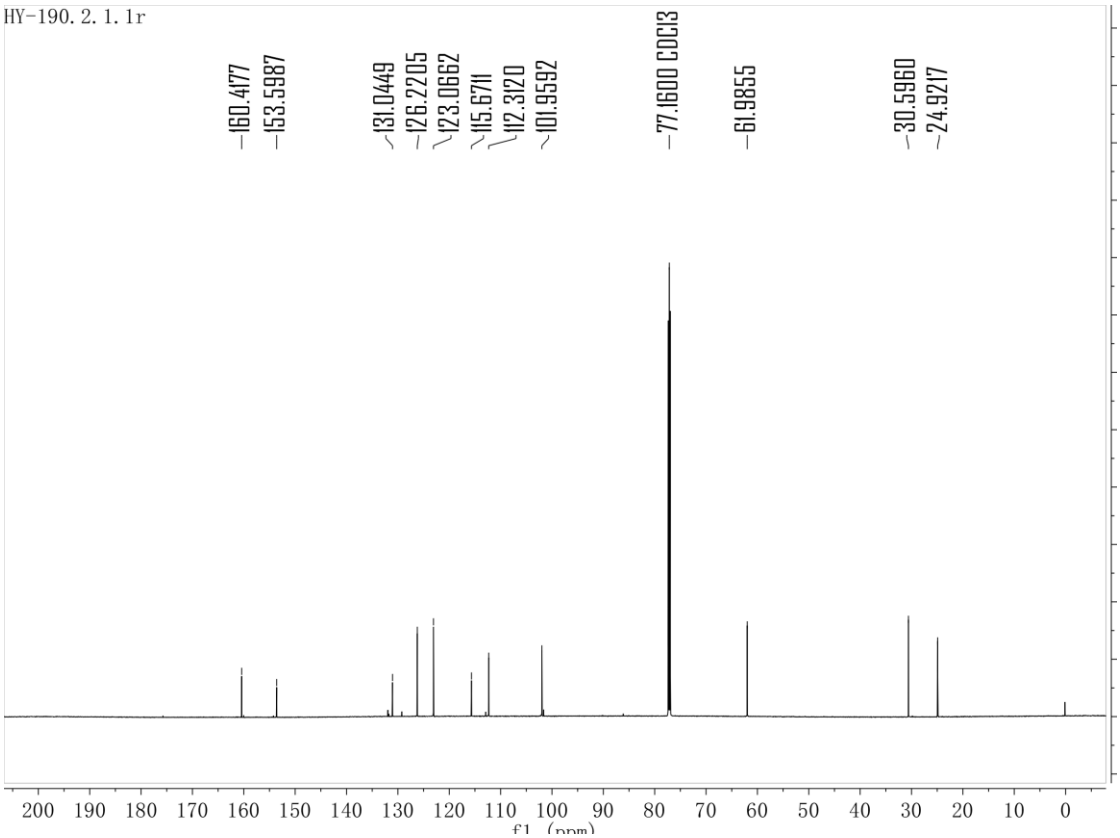
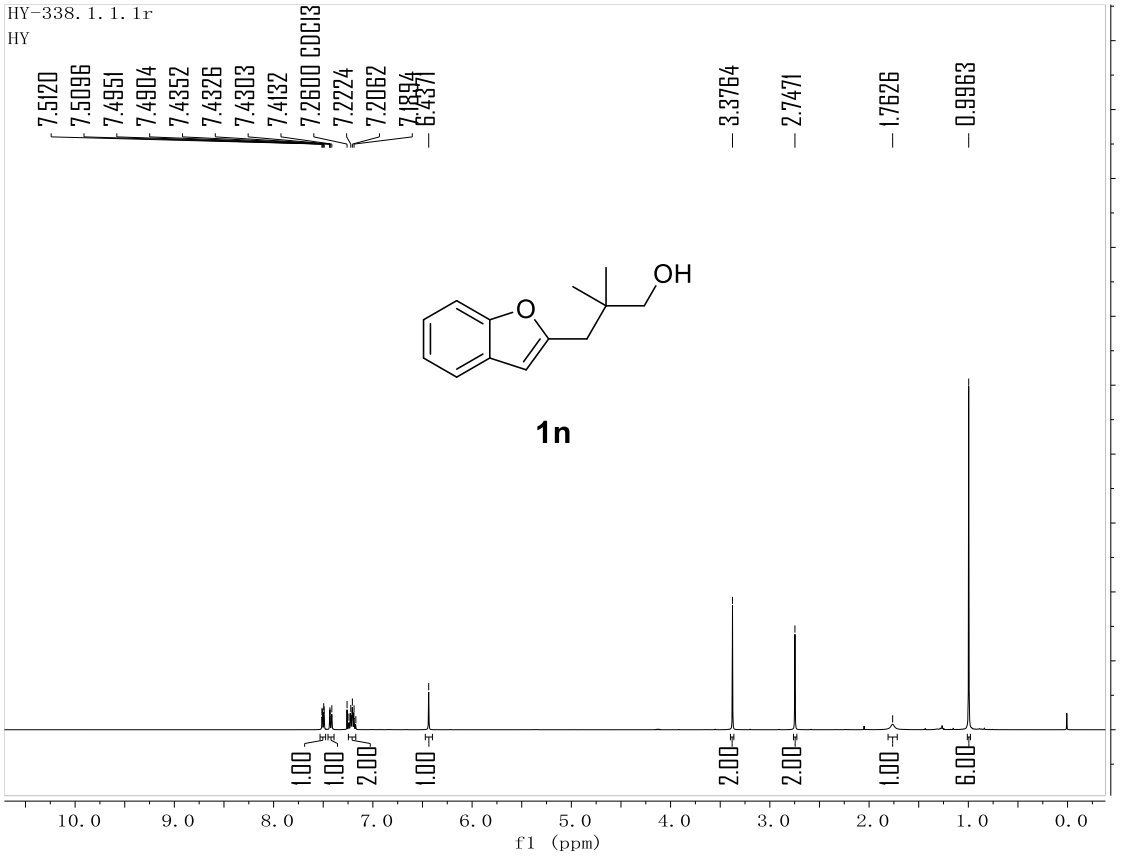
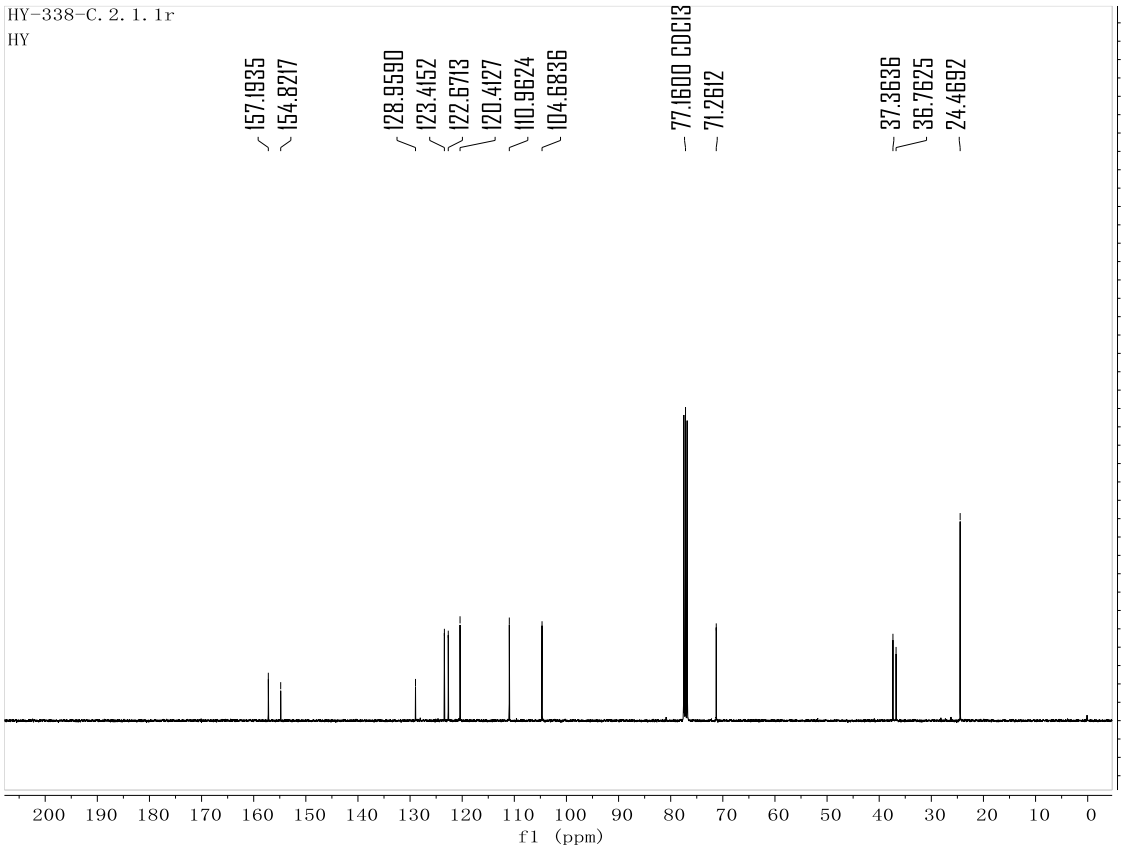
7.3217
7.3000
7.2600 CDCl3
7.1730
7.1676
7.1513
7.1460
6.3638
3.7557
3.7401
3.7244
2.8994
2.8808
2.8620
2.0401
2.0240
2.0055
1.9874
1.9713
1.5868
OH
O
Cl
1m
1.00
1.00
1.00
1.00
2.00
2.00
2.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

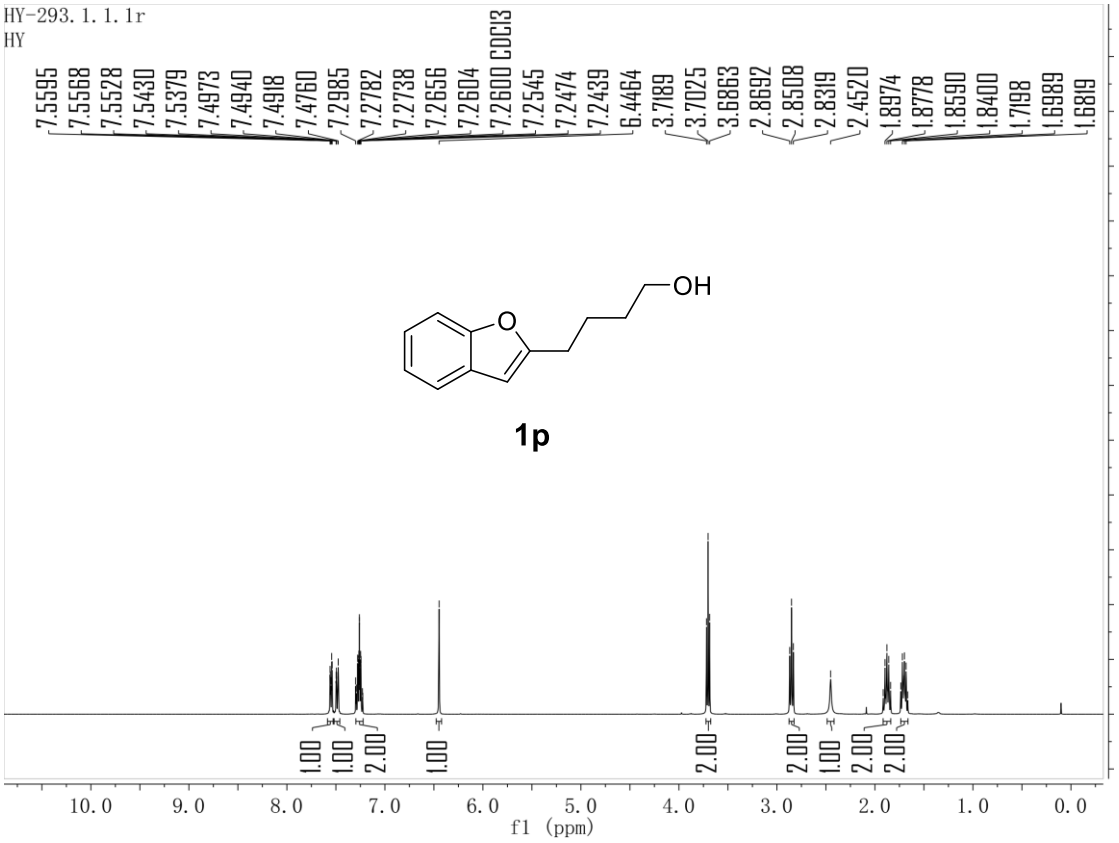

HY-199.1.1.1r
13C
160.7427
153.4057
130.5884
128.3399
123.6942
120.2074
111.9848
102.2895
77.1600 CDCl3
62.1789
30.7806
25.1308
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HY-190.1.1.1r
HY
7.5997
7.5961
7.3147
7.3101
7.2931
7.2762
7.2600 CDCl3
7.2549
6.3601
3.7534
3.7378
3.7221
2.9009
2.8818
2.8638
2.0382
2.0224
2.0035
1.9853
1.9694
1.5812
OH
O
Br
1n
1.00
2.00
1.00
2.00
2.00
2.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

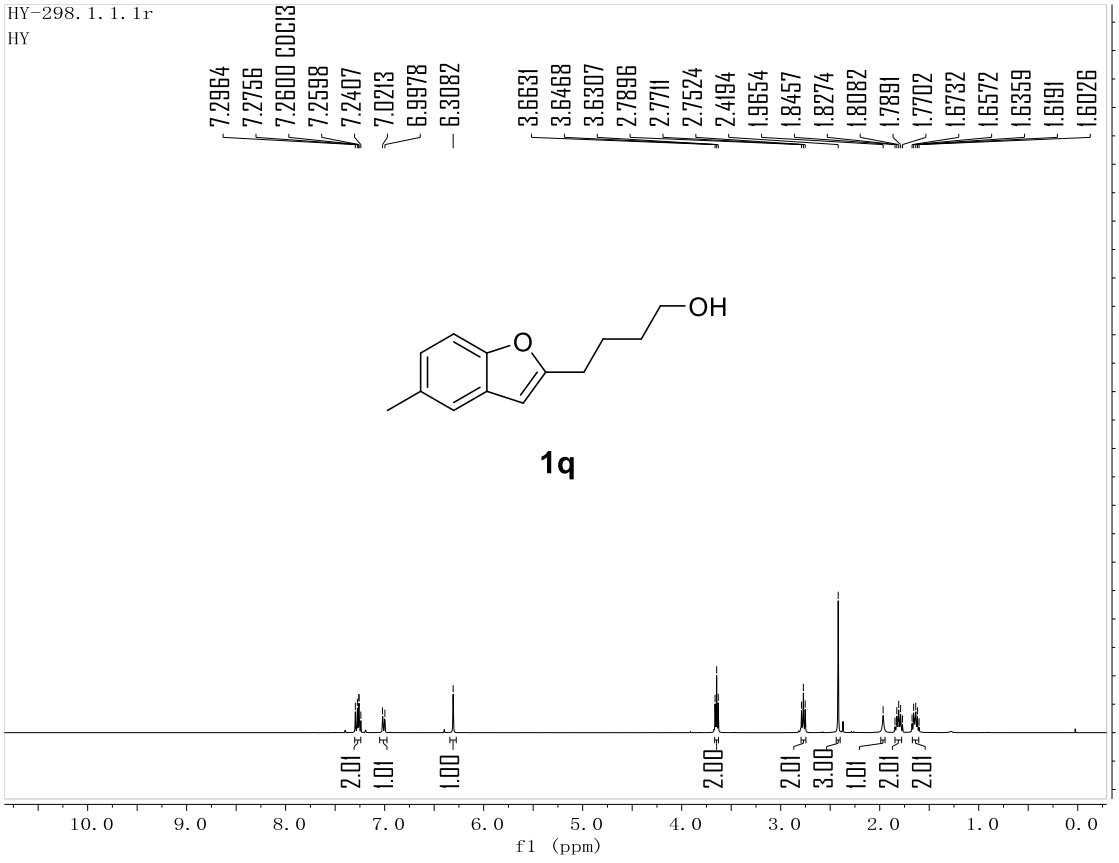

HY-190.2.1.1r
160.4177
153.5987
131.0449
126.2205
123.0662
115.6711
112.3120
101.9592
77.1600 CDCl3
61.9855
30.5960
24.9217
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HY-338.1.1.1r
HY
7.5120
7.5096
7.4951
7.4904
7.4352
7.4326
7.4303
7.4132
7.2600 CDCl3
7.2224
7.2062
6.4371
3.3764
2.7471
1.7626
0.9963
OH
O
1n
1.00
1.00
2.00
1.00
2.00
2.00
1.00
6.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

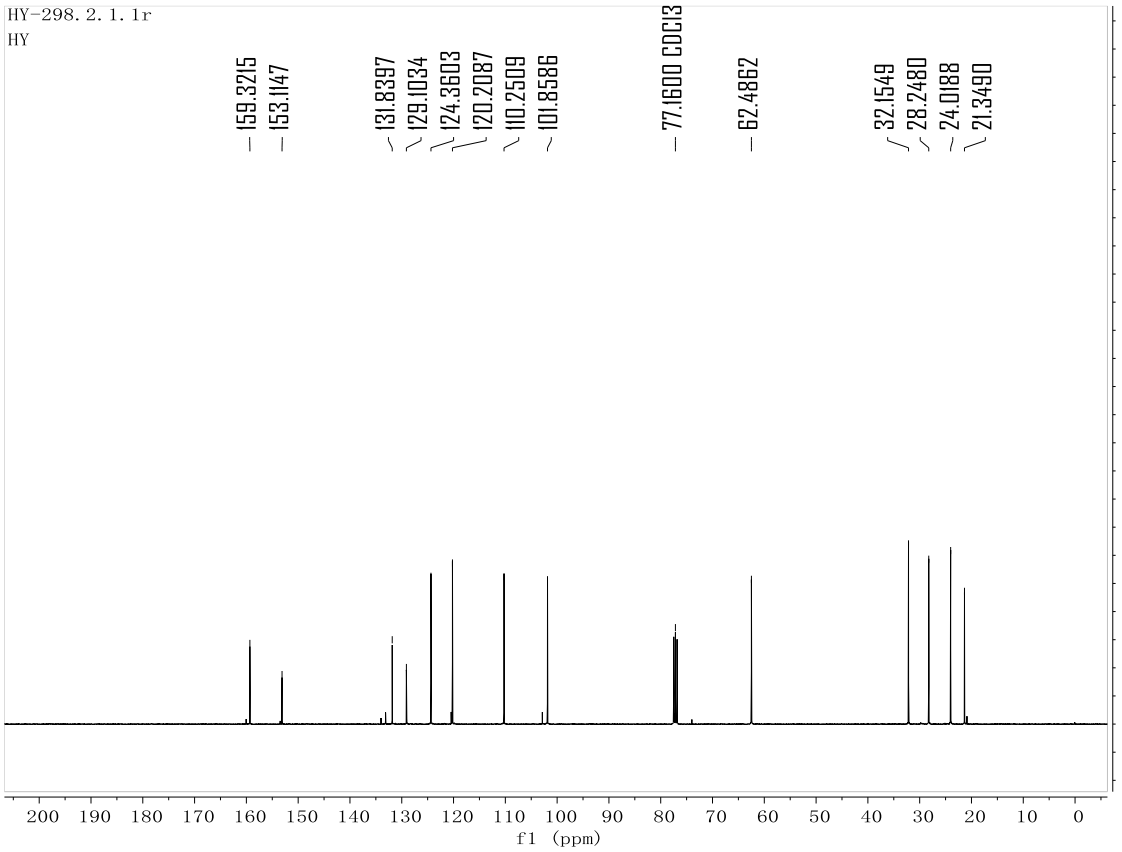

HY-338-C.2.1.1r
HY
157.1935
154.8217
128.9590
123.4152
122.6713
120.4127
110.9624
104.6836
77.1600 CDCl3
71.2612
37.3636
36.7625
24.4692
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

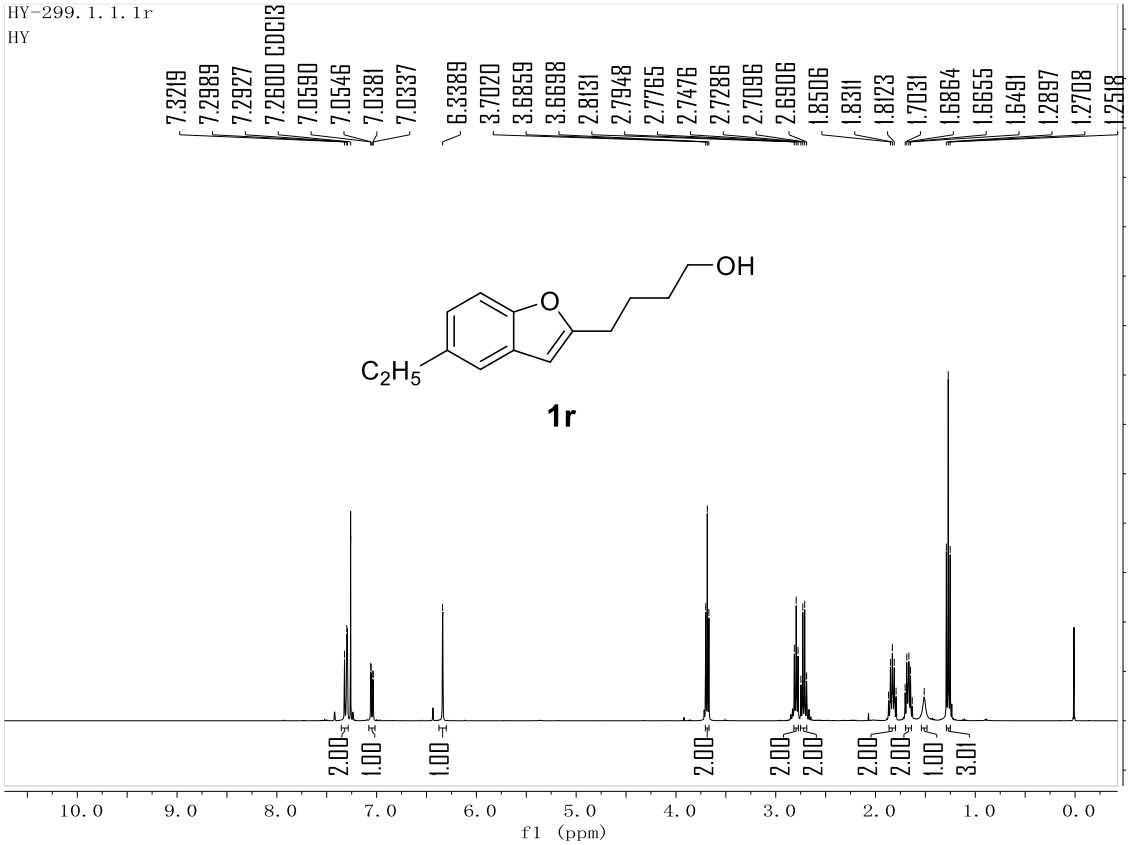

HY-293.1.1.1r
HY
7.5595
7.5568
7.5528
7.5430
7.5379
7.4973
7.4940
7.4918
7.4760
7.2985
7.2782
7.2738
7.2656
7.2604
7.2600 CDCl3
7.2545
7.2474
7.2439
6.4464
3.7189
3.7025
3.6863
2.8692
2.8508
2.8319
2.4520
1.8974
1.8778
1.8590
1.8400
1.7198
1.6989
1.6819
OH
O
1.00
1.00
2.00
1.00
2.00
2.00
1.00
2.00
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

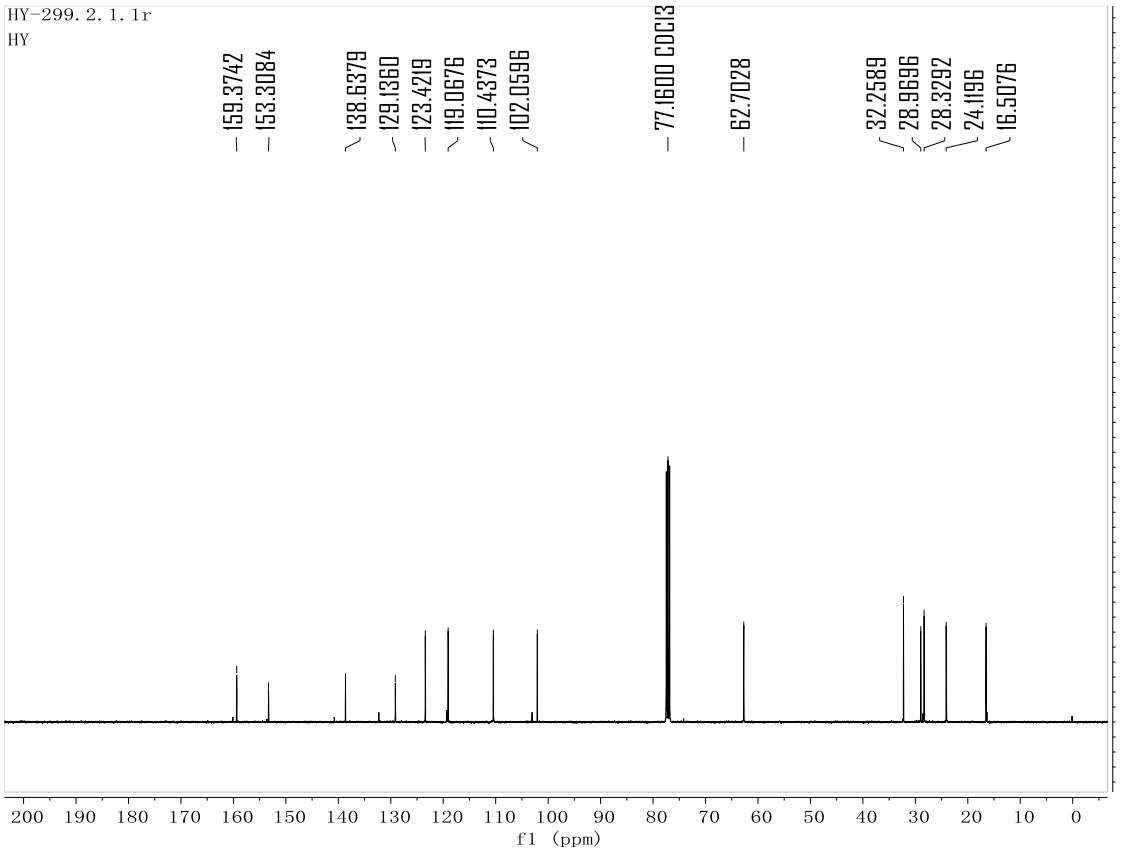
1p

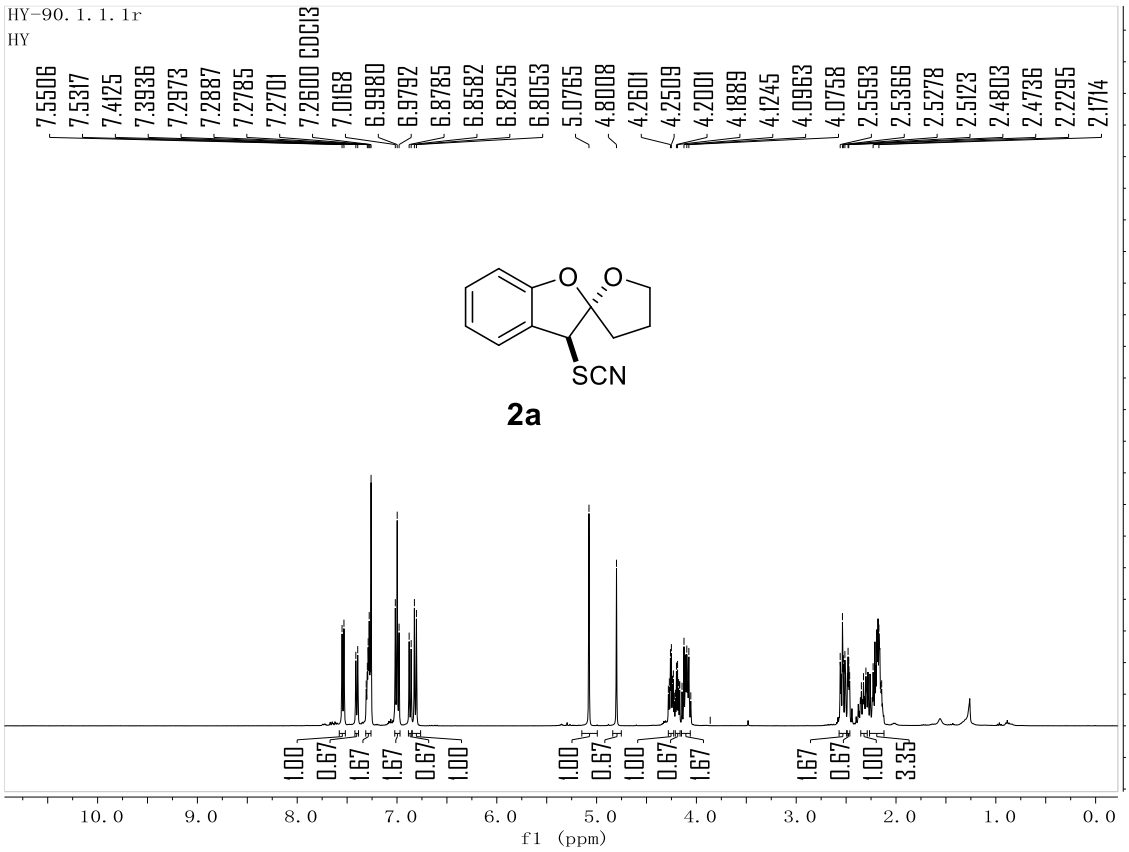

HY-298.1.1.1r
HY
7.2964
7.2756
7.2600 CDCl3
7.2598
7.2407
7.0213
6.9978
6.3082
3.6631
3.6468
3.6307
2.7896
2.7711
2.7524
2.4194
1.9654
1.8457
1.8274
1.8082
1.7891
1.7702
1.6732
1.6572
1.6359
1.6191
1.6026
OH
O
2.01
1.01
1.00
2.00
2.01
3.00
1.01
2.01
2.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

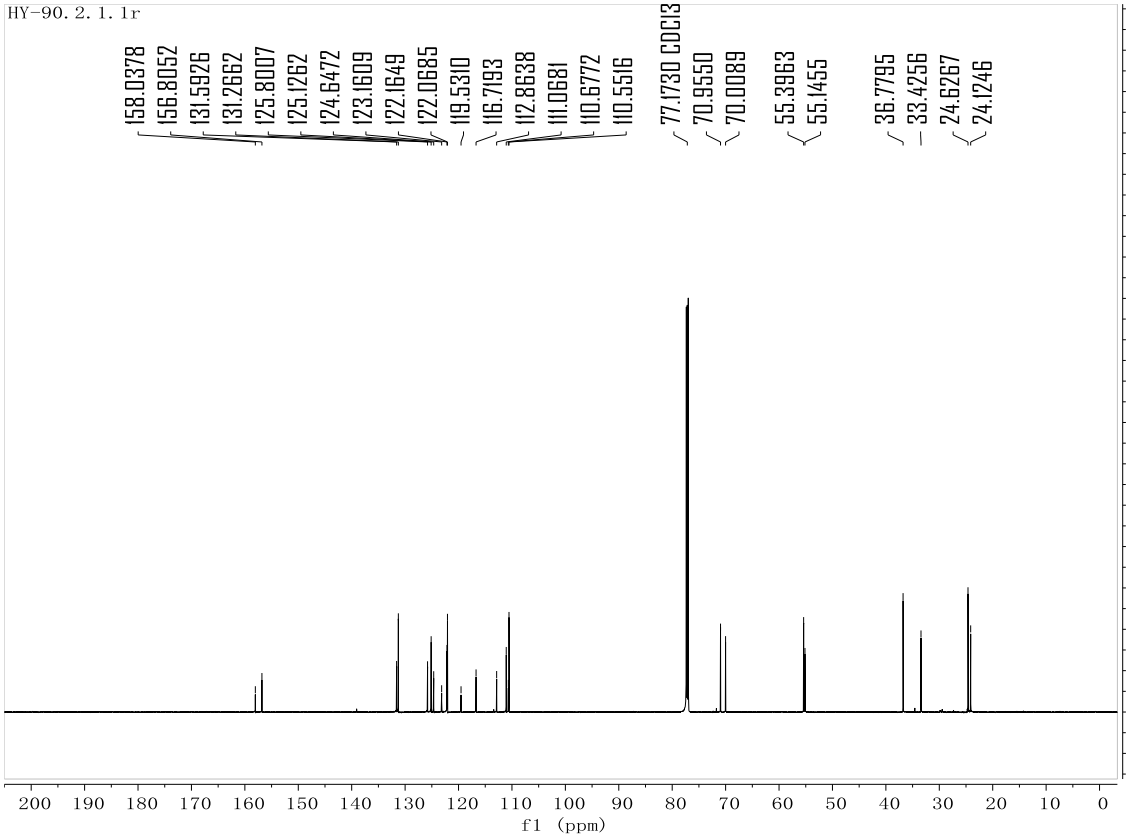
1q

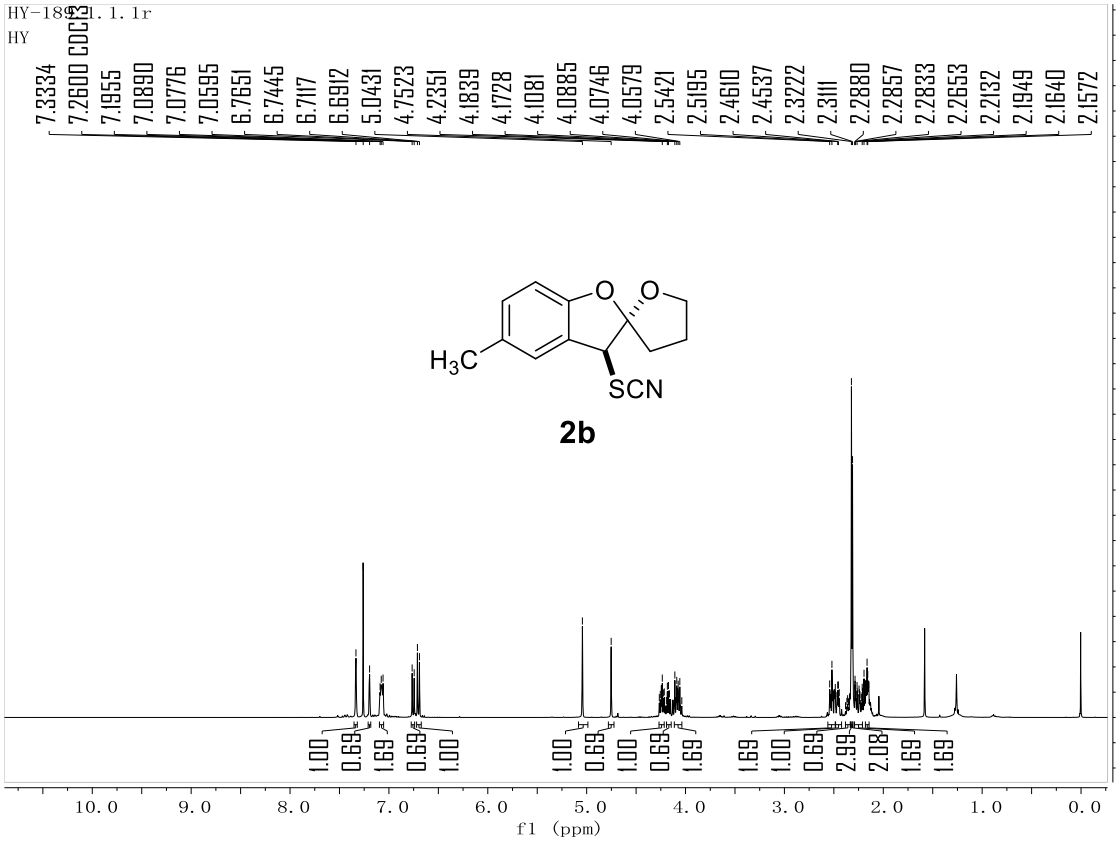

HY-298.2.1.1r
HY
159.3215
153.1147
131.8397
129.1034
124.3603
120.2087
110.2509
101.8586
77.1600 CDCl3
62.4862
32.1549
28.2480
24.0188
21.3490
f1 (ppm)


HY-299.1.1.1r
HY
7.3219
7.2989
7.2927
7.2600 CDCl3
7.0590
7.0546
7.0381
7.0337
6.3389
3.7020
3.6859
3.6698
2.8131
2.7948
2.7765
2.7476
2.7286
2.7096
2.6906
1.8506
1.8311
1.8123
1.7031
1.6864
1.6655
1.6491
1.2897
1.2708
1.2518
OH
O
C2H5
1r
2.00
1.00
1.00
2.00
2.00
2.00
2.00
2.00
1.00
3.01
f1 (ppm)

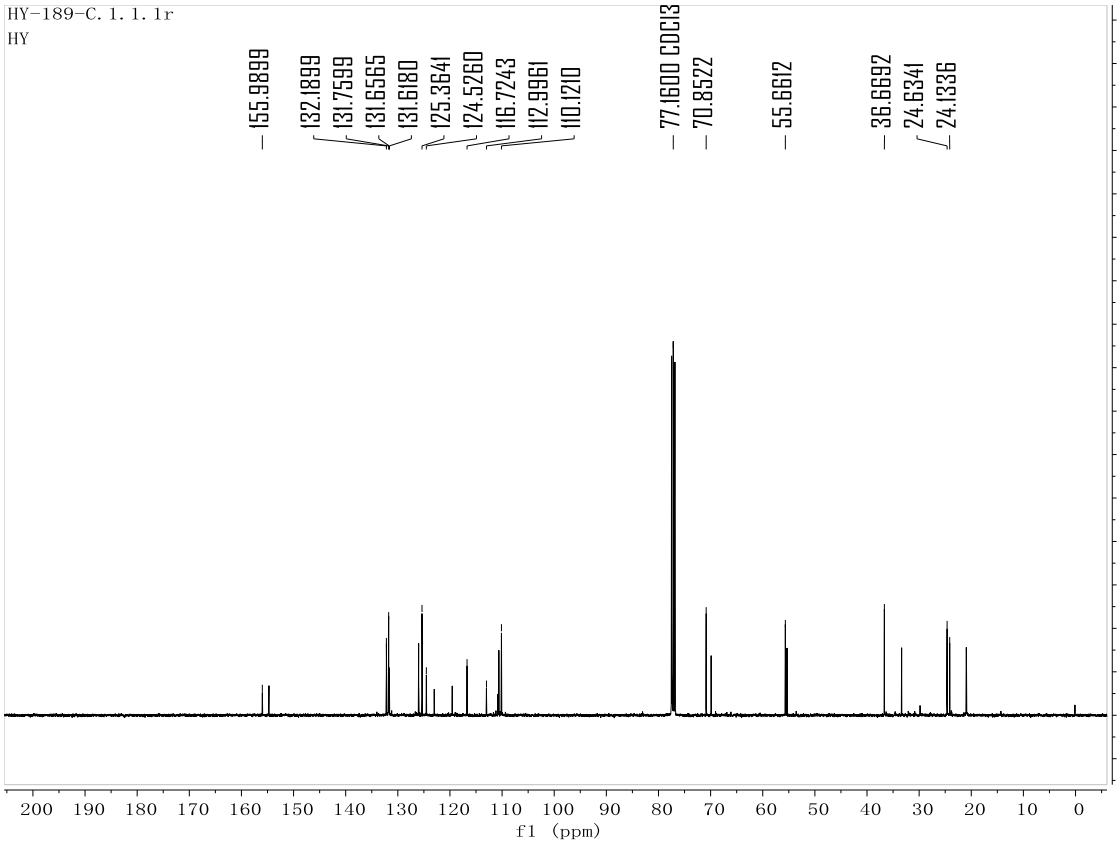

HY-299.2.1.1r
HY
159.3742
153.3084
138.6379
129.1360
123.4219
119.0676
110.4373
102.0596
77.1600 CDCl3
62.7028
32.2589
28.9696
28.3292
24.1196
16.5076
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

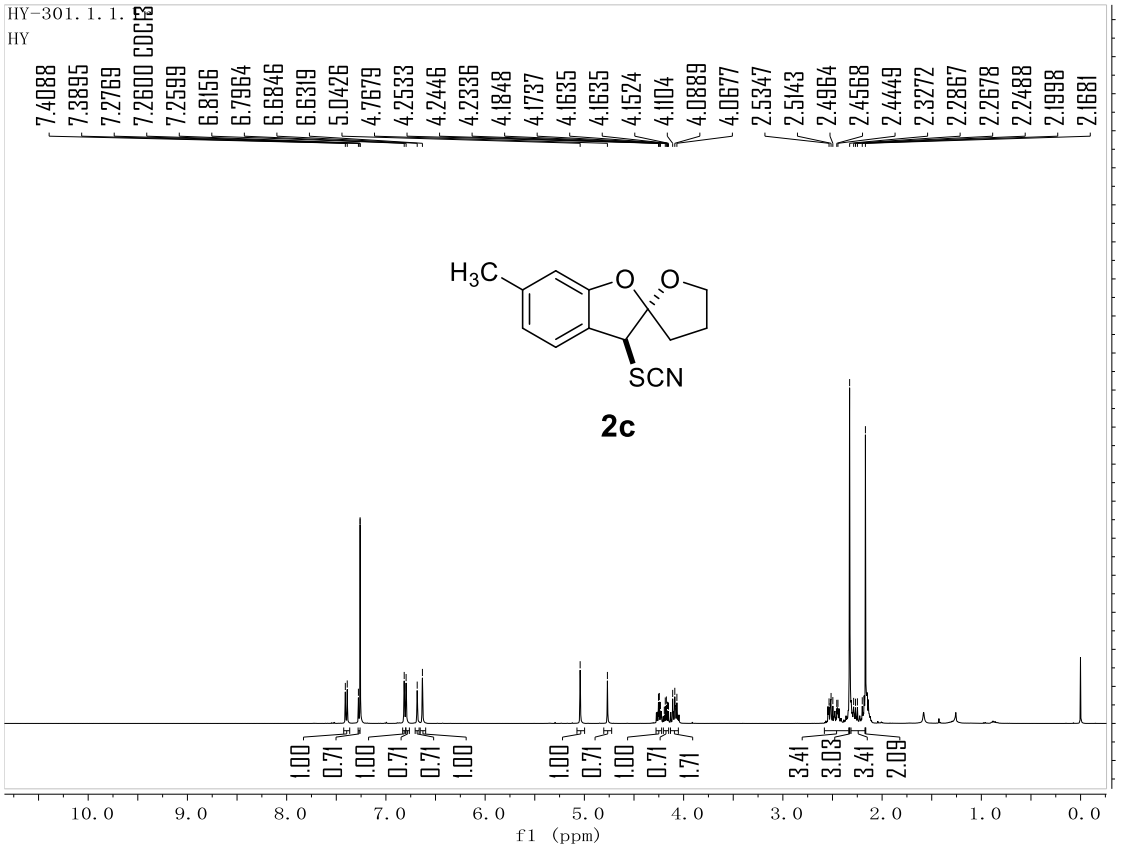

HY-90.1.1.1r
HY
7.5506
7.5317
7.4125
7.3936
7.2973
7.2887
7.2785
7.2701
7.2600 CDCl3
7.0168
6.9980
6.9792
6.8785
6.8582
6.8256
6.8053
5.0765
4.8008
4.2601
4.2509
4.2001
4.1889
4.1245
4.0963
4.0758
2.5593
2.5386
2.5278
2.5123
2.4803
2.4736
2.2295
2.1714
O
O
SCN
2a
1.00
0.67
1.67
1.67
0.67
1.00
1.00
0.67
1.00
0.67
1.67
1.67
0.67
1.00
3.35
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


HY-90.2.1.1r
158.0378
156.8052
131.5926
131.2662
125.8007
125.1262
124.6472
123.1609
122.1649
122.0685
119.5310
116.7193
112.8638
111.0681
110.6772
110.5516
77.1730 CDCl3
70.9550
70.0089
55.3963
55.1455
36.7795
33.4256
24.6267
24.1246
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HY-189-H.1.1.1r
HY
7.3334
7.2600 CDCl3
7.1955
7.0890
7.0776
7.0595
6.7651
6.7445
6.7117
6.6912
5.0431
4.7523
4.2351
4.1839
4.1728
4.1081
4.0885
4.0746
4.0579
2.5421
2.5195
2.4610
2.4537
2.3222
2.3111
2.2880
2.2857
2.2833
2.2653
2.2132
2.1949
2.1640
2.1572
O
O
H3C
SCN
1.00
0.69
1.69
0.69
1.00
1.00
0.69
1.00
0.69
1.69
1.69
1.00
0.69
2.99
2.08
1.69
1.69
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

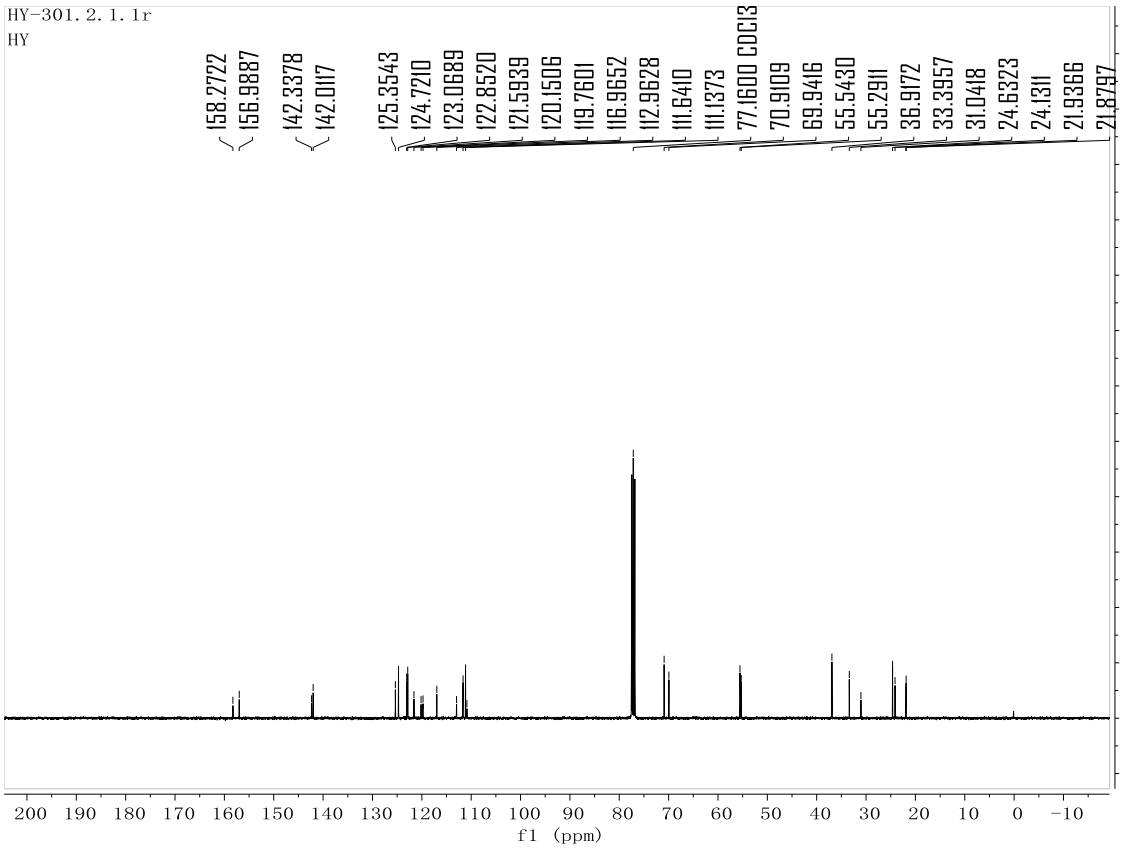
2b

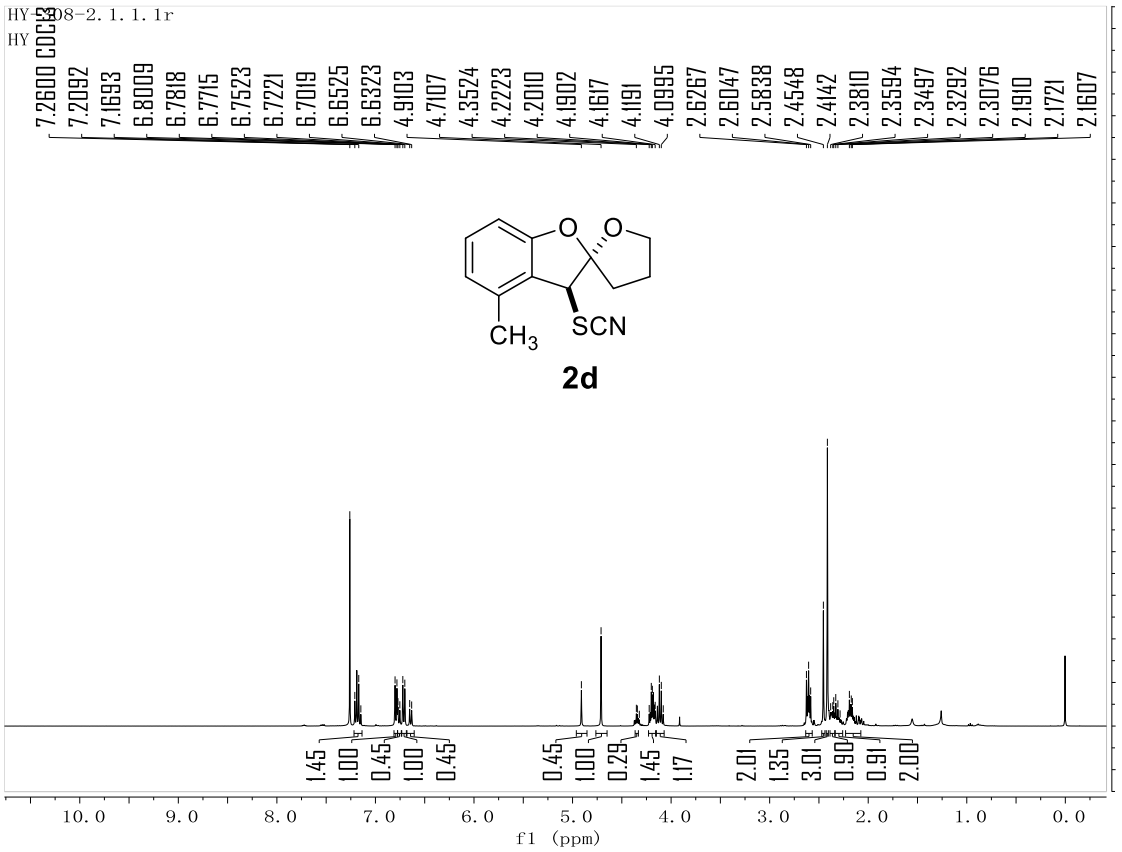

HY-189-C.1.1.1r
HY
155.9899
132.1899
131.7589
131.6565
131.6180
125.3641
124.5260
116.7243
112.9961
110.1210
77.1600 CDCl3
70.8522
55.6612
36.6692
24.6341
24.1336
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

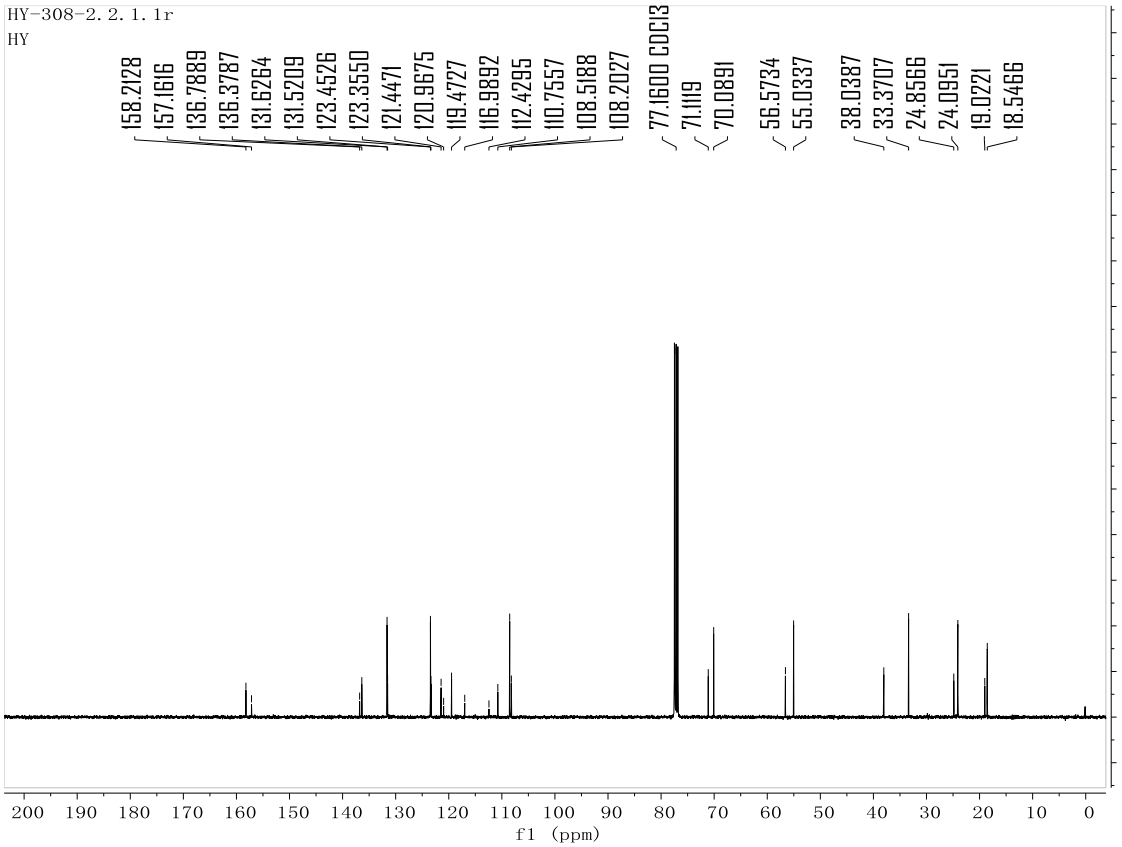

HY-301.1.1.
HY
7.4088
7.3895
7.2769
7.2600 CDCl3
7.2599
6.8156
6.7964
6.6846
6.6319
5.0426
4.7679
4.2533
4.2446
4.2336
4.1848
4.1737
4.1635
4.1635
4.1524
4.1104
4.0889
4.0677
2.5347
2.5143
2.4964
2.4568
2.4449
2.3272
2.2867
2.2678
2.2488
2.1998
2.1681
1.00
0.71
1.00
0.71
0.71
1.00
1.00
0.71
1.00
0.71
1.71
3.41
3.03
3.41
2.09
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

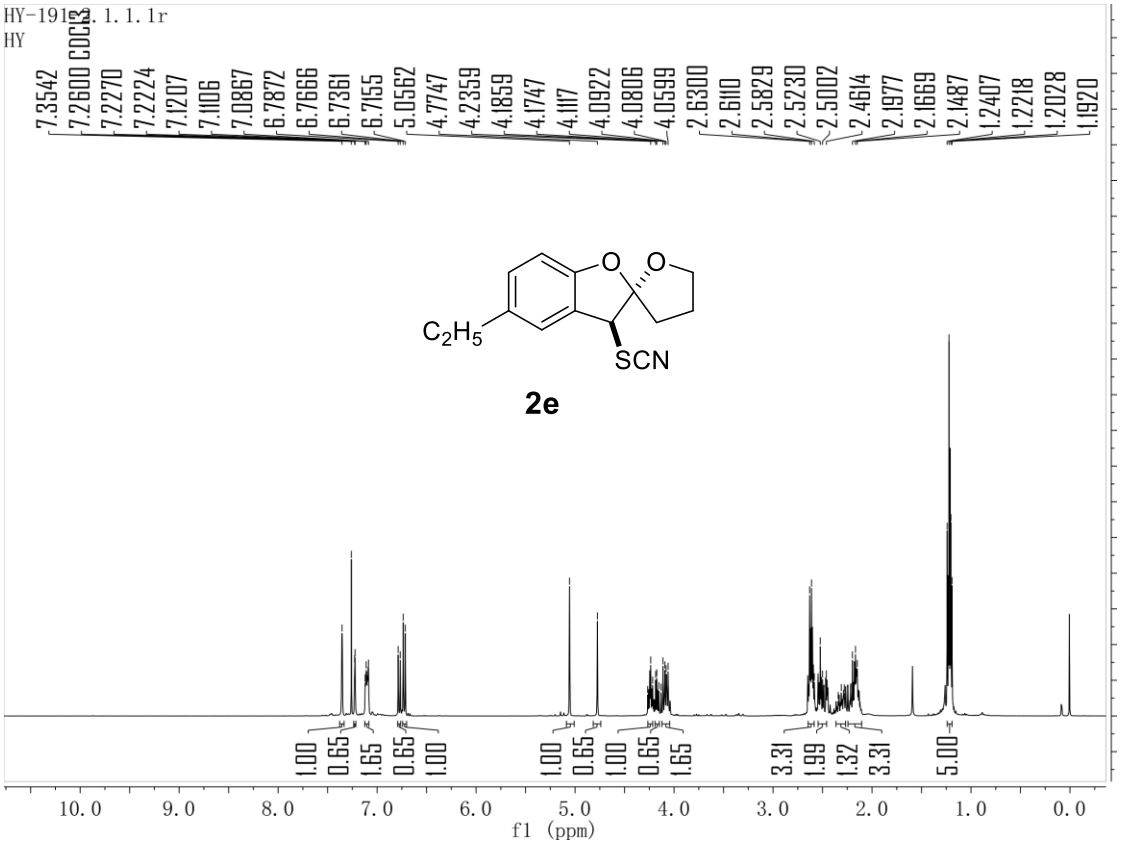
H3C
O
O
SCN

2c

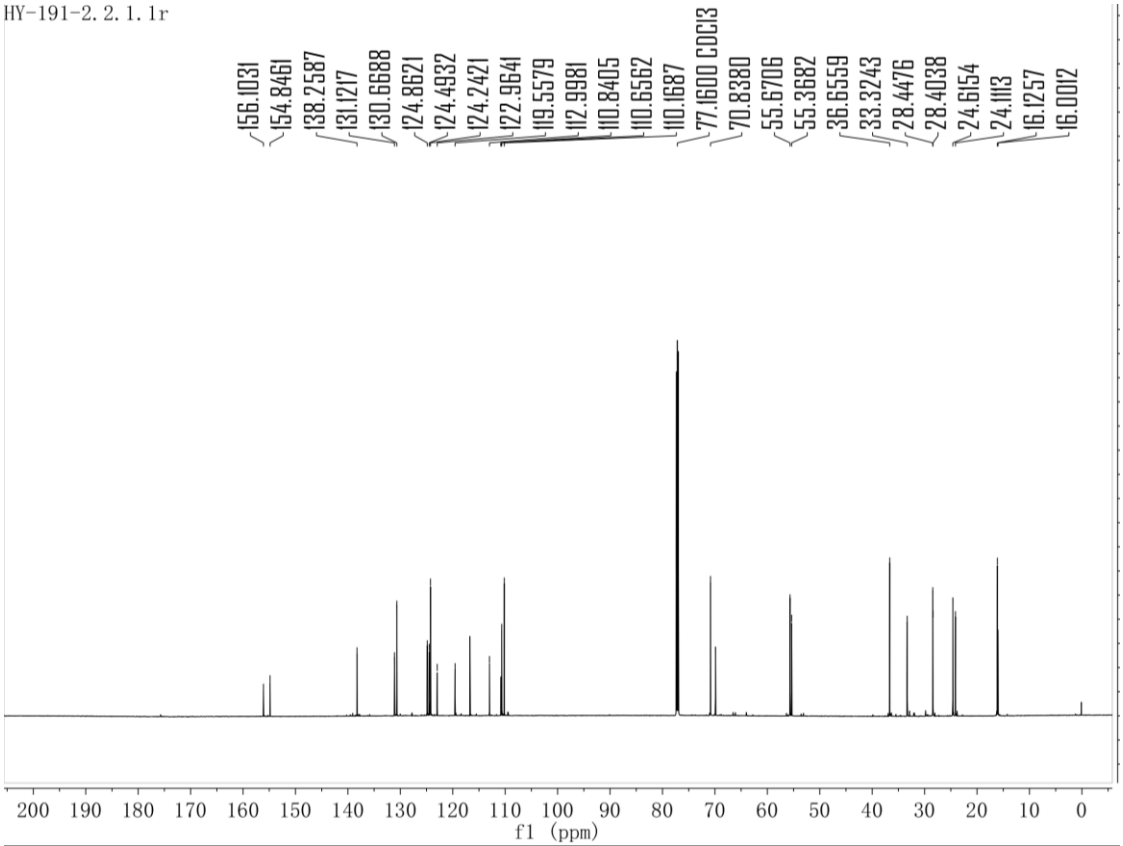

HY-301.2.1.1r
HY
158.2722
156.9887
142.3378
142.0117
125.3543
124.7210
123.0689
122.8520
121.5939
120.1506
119.7601
116.9652
112.9628
111.6410
111.1373
77.1600 CDCl3
70.9109
69.9416
55.5430
55.2911
36.9172
33.3957
31.0418
24.6323
24.1311
21.9366
21.8797
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

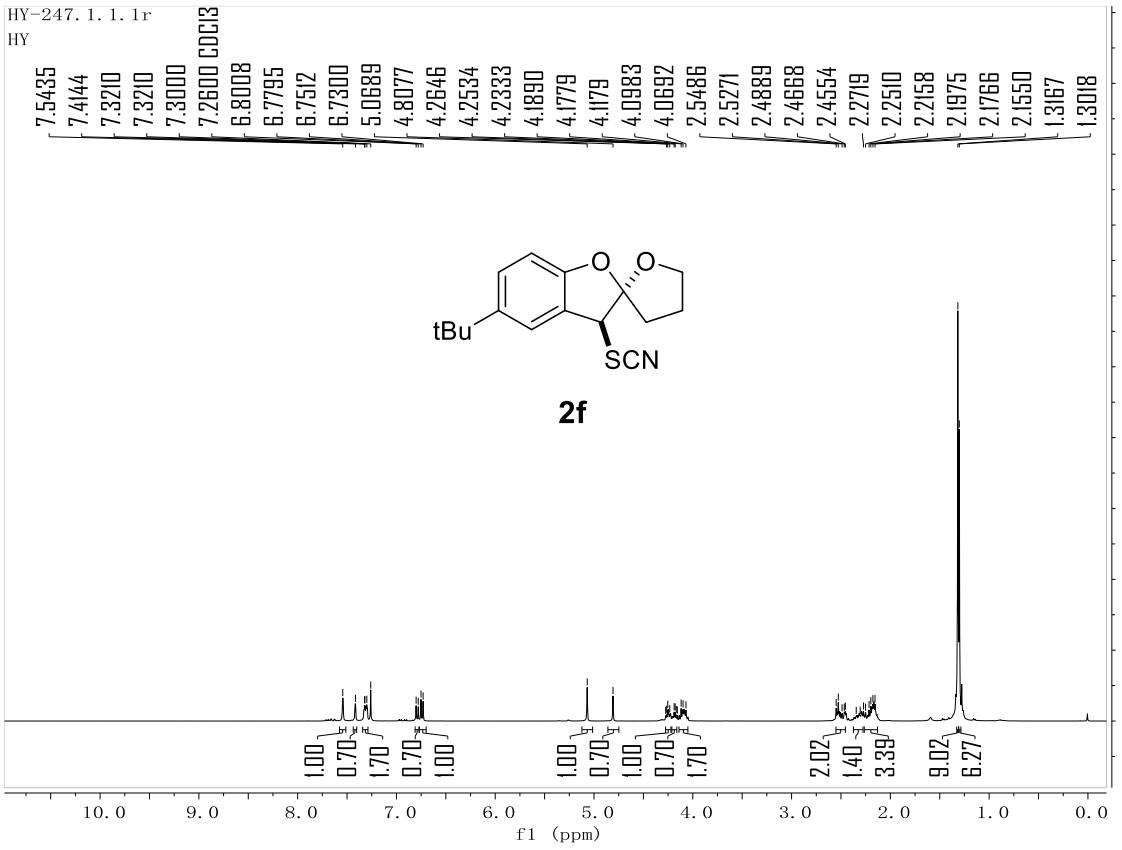

HY-308-2.1.1.1r
HY
7.2600 CDCl3
7.2092
7.1693
6.8009
6.7818
6.7715
6.7523
6.7221
6.7019
6.6525
6.6323
4.9103
4.7107
4.3524
4.2223
4.2010
4.1902
4.1617
4.1191
4.0995
2.6267
2.6047
2.5838
2.4548
2.4442
2.3810
2.3594
2.3497
2.3292
2.3076
2.1910
2.1721
2.1607
O
O
SCN
CH3
2d
1.45
1.00
0.45
1.00
0.45
0.45
1.00
0.29
1.45
1.17
2.01
1.35
3.01
0.90
0.91
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


HY-308-2.2.1.1r
HY
158.2128
157.1616
136.7889
136.3787
131.6264
131.5209
123.4526
123.3550
121.4471
120.9675
119.4727
116.9892
112.4295
110.7557
108.5188
108.2027
77.1600 CDCl3
71.1119
70.0891
56.5734
55.0337
38.0387
33.3707
24.8566
24.0951
19.0221
18.5466
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

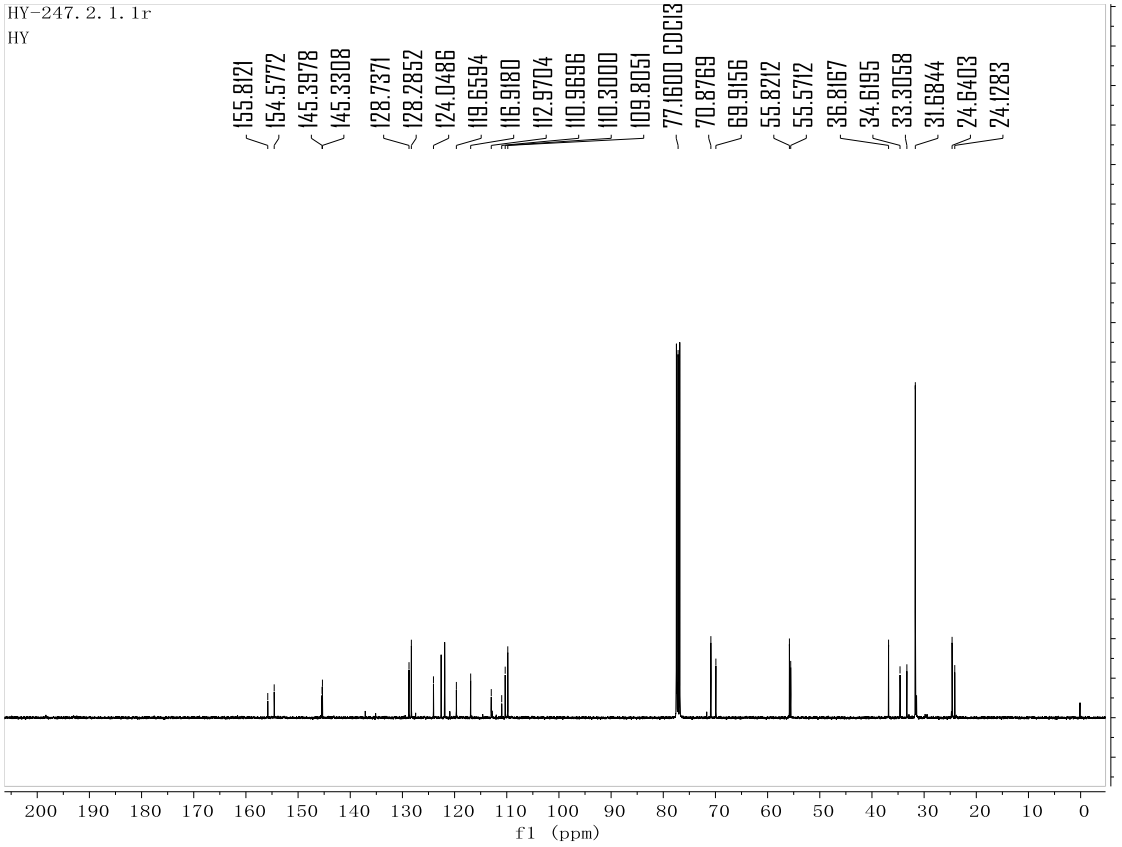

HY-191-2.1.1.1r
HY
7.3542
7.2600 CDCl3
7.2270
7.2224
7.1207
7.1106
7.0867
6.7872
6.7666
6.7361
6.7155
5.0562
4.7747
4.2359
4.1859
4.1747
4.1117
4.0922
4.0806
4.0599
2.6300
2.6110
2.5829
2.5230
2.5002
2.4614
2.1977
2.1669
2.1487
1.2407
1.2218
1.2028
1.1920
O
O
C2H5
SCN
1.00
0.65
1.65
0.65
1.00
1.00
0.65
1.00
0.65
1.65
3.31
1.99
1.32
3.31
5.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

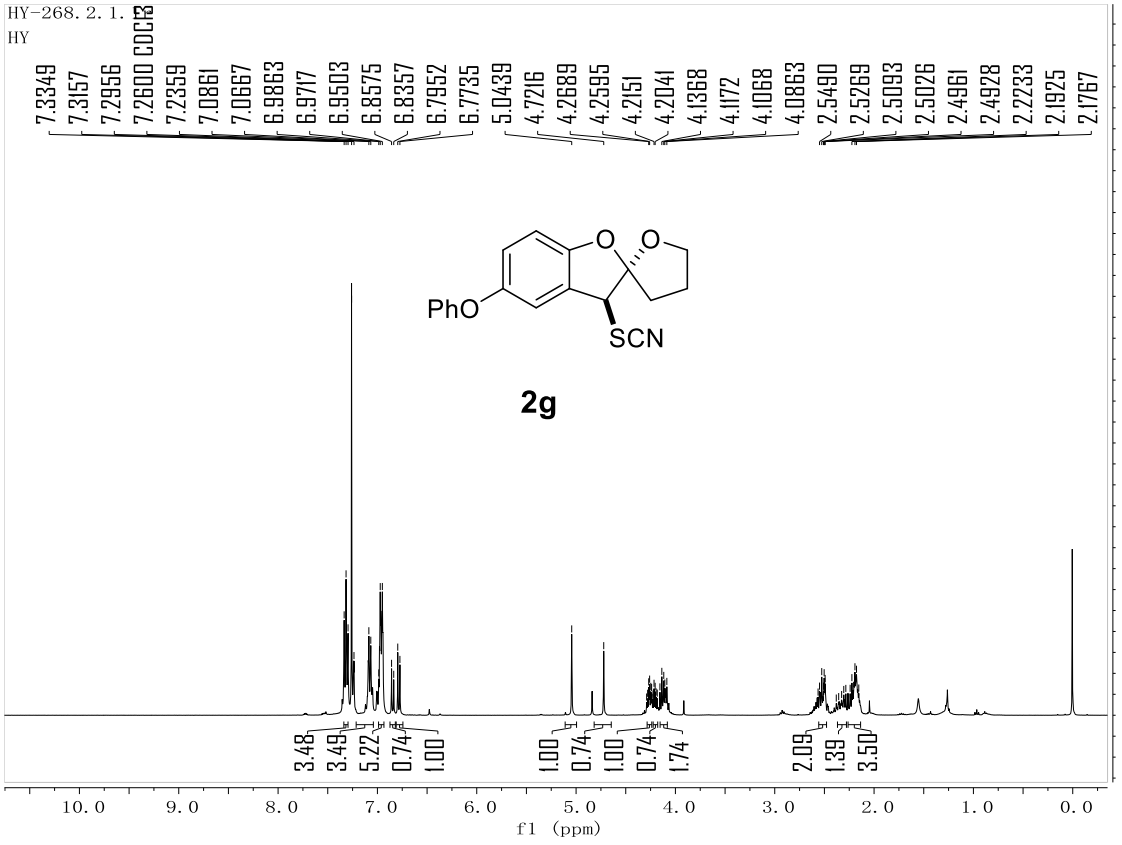
2e


HY-191-2.2.1.1r
156.1031
154.8461
138.2587
131.1217
130.6688
124.8621
124.4932
124.2421
122.9641
119.5579
112.9981
110.8405
110.6562
110.1687
77.1600 CDCl3
70.8380
55.6706
55.3682
36.6559
33.3243
28.4476
28.4038
24.6154
24.1113
16.1257
16.0012
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HY-247.1.1.1r
HY
7.5435
7.4144
7.3210
7.3210
7.3000
7.2600 CDCl3
6.8008
6.7795
6.7512
6.7300
5.0689
4.8077
4.2646
4.2534
4.2333
4.1890
4.1779
4.1179
4.0983
4.0692
2.5486
2.5271
2.4889
2.4668
2.4554
2.2719
2.2510
2.2158
2.1975
2.1766
2.1550
1.3167
1.3018
O
O
tBu
SCN
1.00
0.70
1.70
0.70
1.00
1.00
0.70
1.00
0.70
1.70
2.02
1.40
3.39
9.02
6.27
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

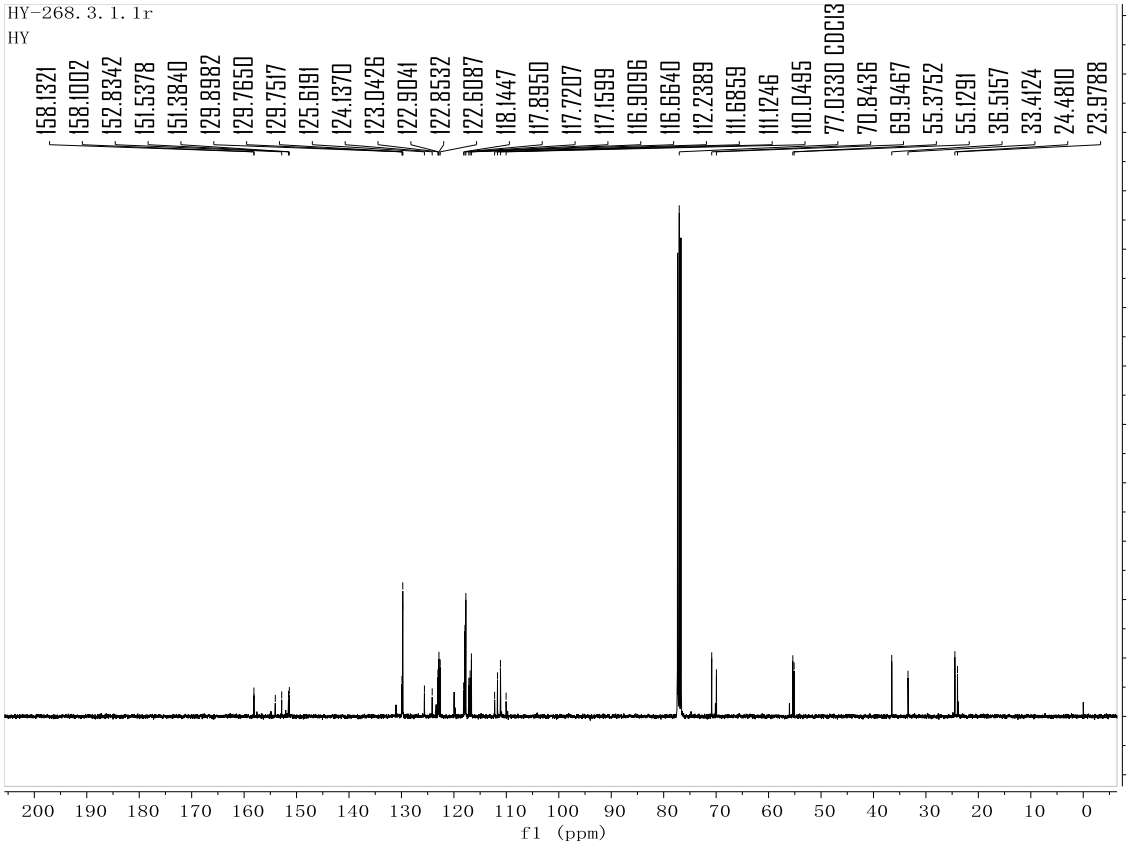
2f

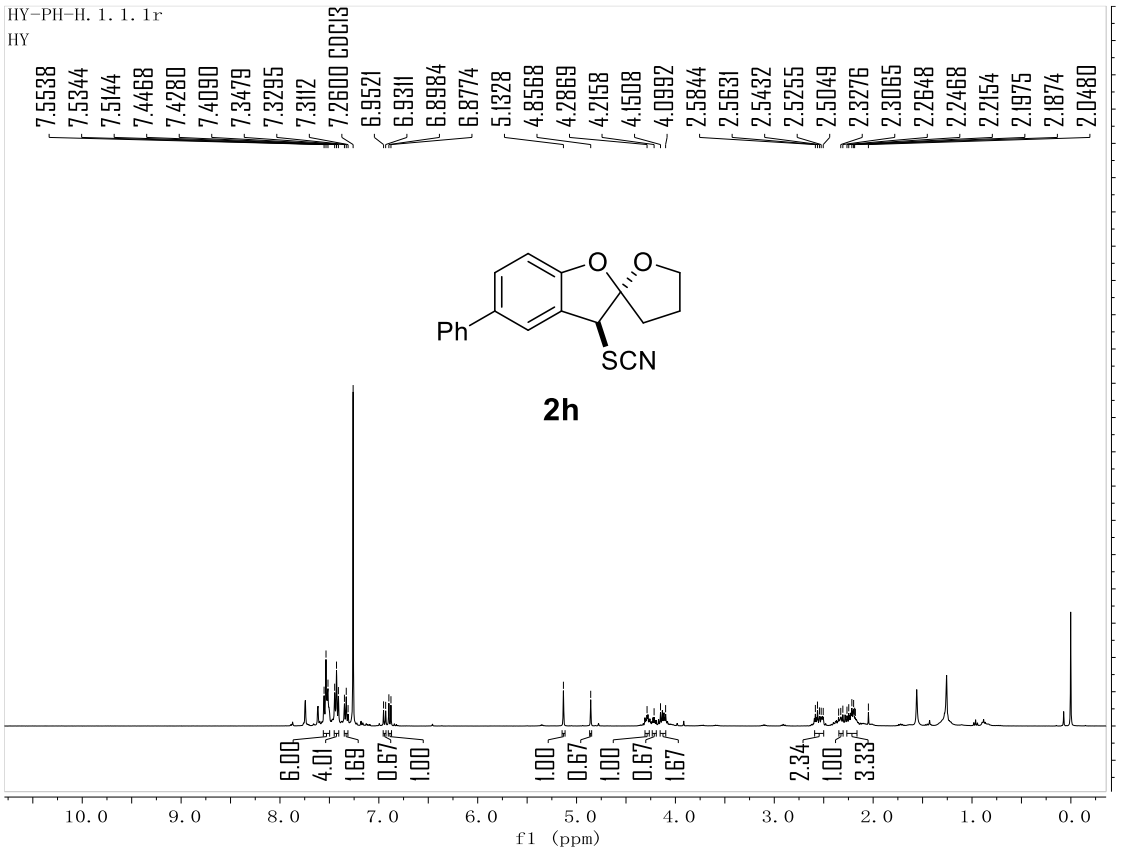

HY-247.2.1.1r
HY
155.8121
154.5772
145.3978
145.3308
128.7371
128.2852
124.0486
119.6594
116.9180
112.9704
110.9696
110.8000
109.8051
77.1600 CDCl3
70.8769
69.9156
55.8212
55.5712
36.8167
34.6195
33.8058
31.6844
24.6403
24.1283
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HY-268.2.1.
HY
7.3349
7.3157
7.2956
7.2600 CDCl3
7.2359
7.0861
7.0667
6.9863
6.9717
6.9503
6.8575
6.8357
6.7952
6.7735
5.0439
4.7216
4.2689
4.2595
4.2151
4.2041
4.1368
4.1172
4.1068
4.0863
2.5490
2.5269
2.5093
2.5026
2.4961
2.4928
2.2233
2.1925
2.1767
3.48
3.49
5.22
0.74
1.00
1.00
0.74
1.00
0.74
1.74
2.09
1.39
3.50
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

O
O
PhO
SCN

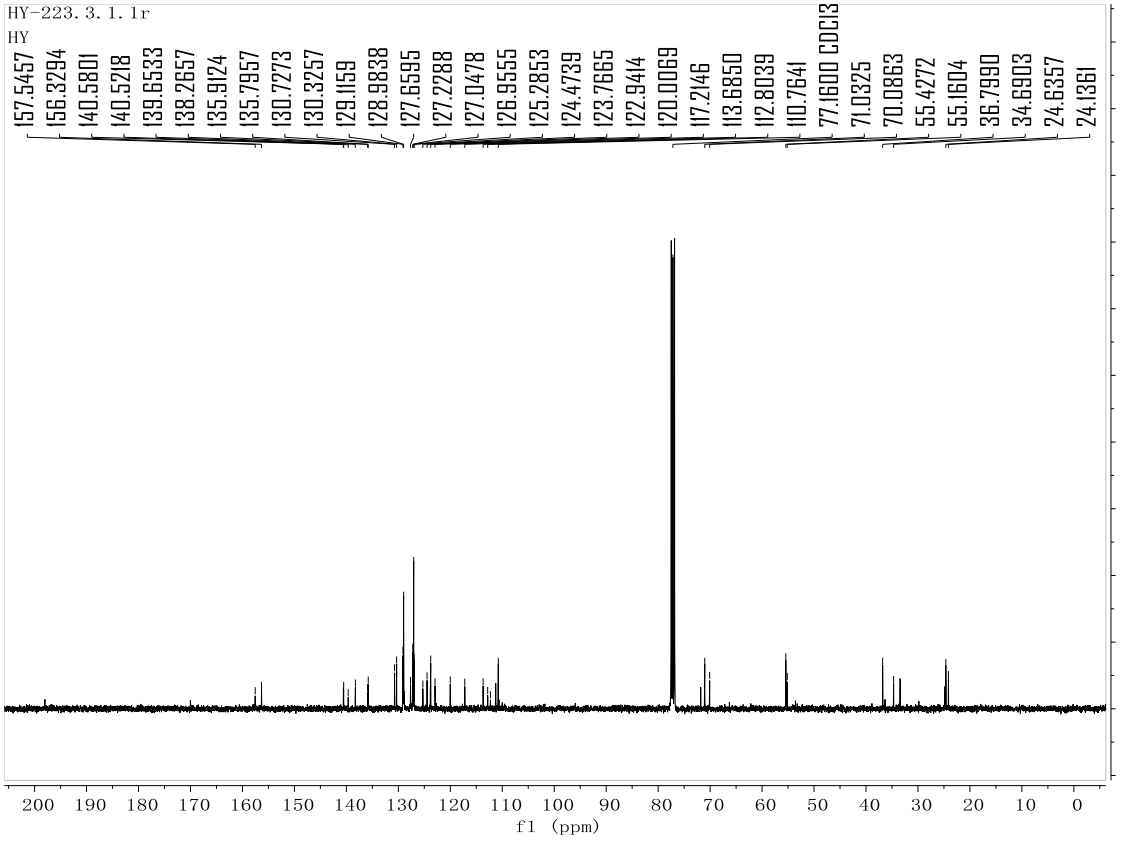
2g

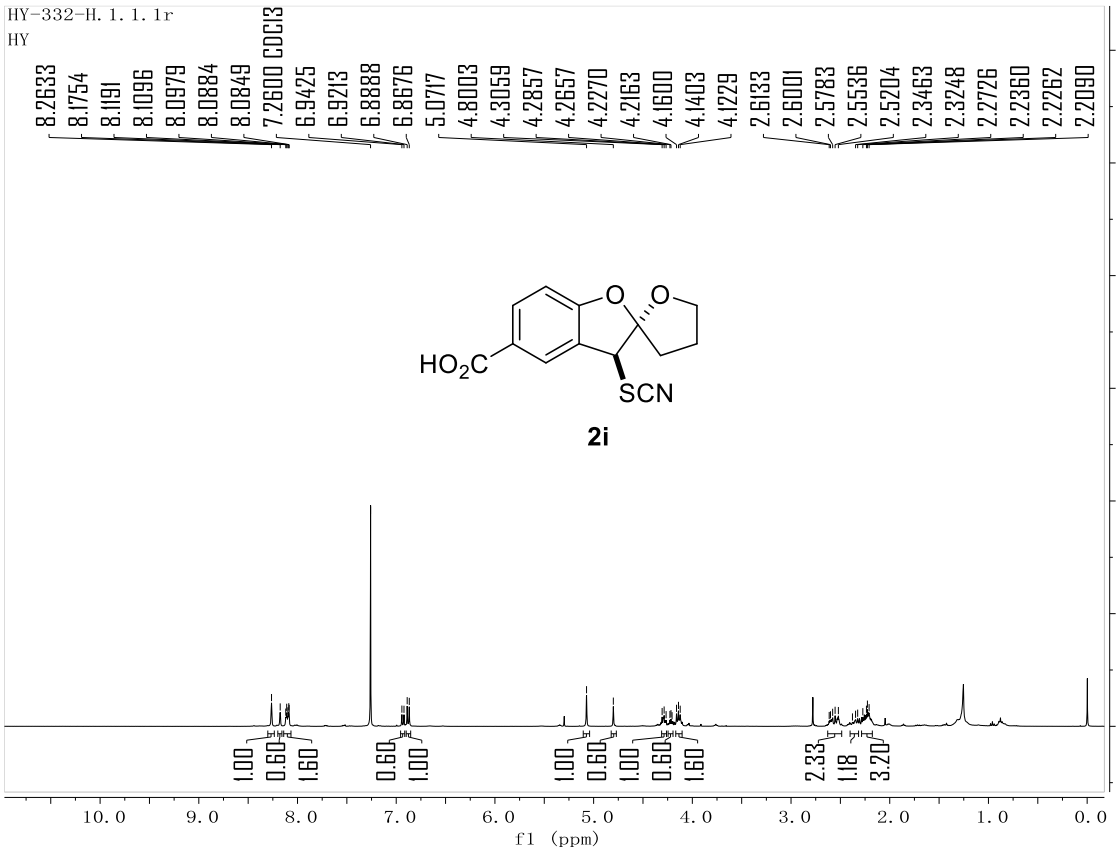

HY-268.3.1.1r
HY
158.1321
158.1002
152.8342
151.5378
151.3840
129.8982
129.7650
129.7517
125.6191
124.1370
123.0426
122.9041
122.8532
122.6087
118.1447
117.8950
117.7207
117.1599
116.9096
116.6640
112.2389
111.6859
111.1246
110.0495
77.0330 CDCl3
70.8436
69.9467
55.3752
55.1291
36.5157
33.4124
24.4810
23.9788
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

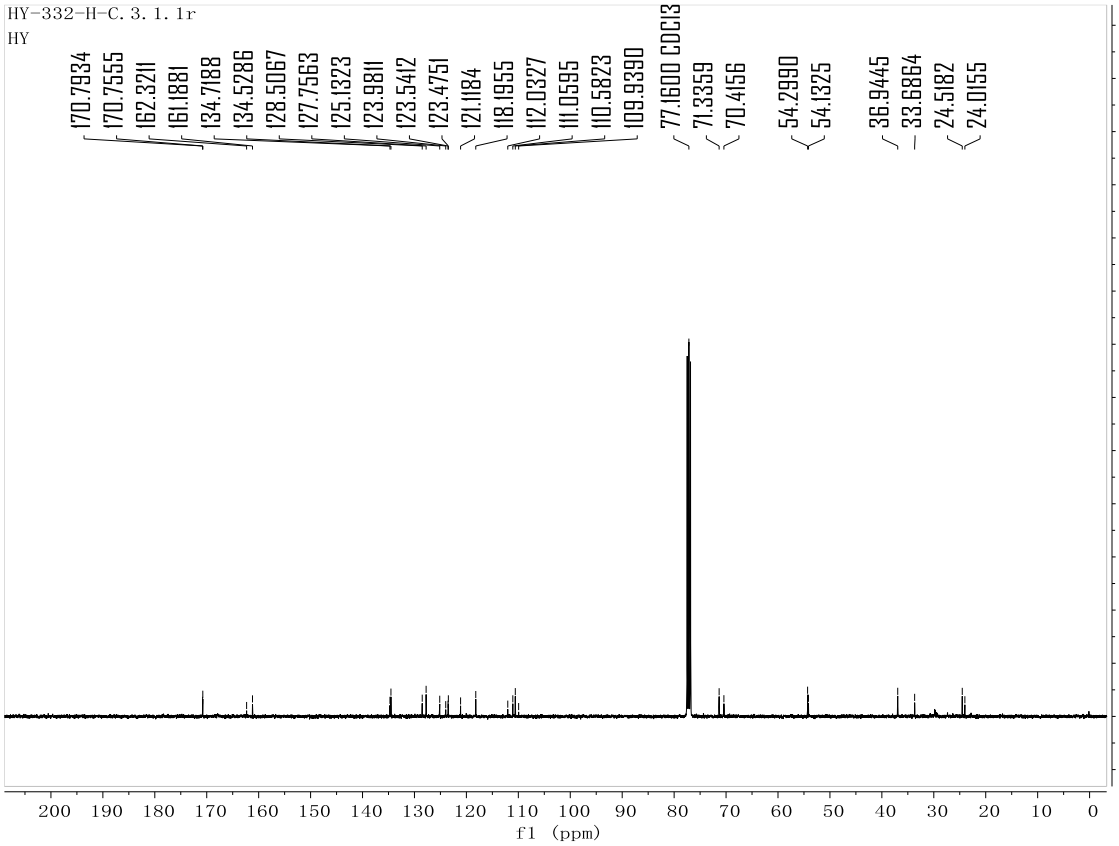

HY-PH-H.1.1.1r
HY
7.5538
7.5344
7.5144
7.4468
7.4280
7.4090
7.3479
7.3295
7.3112
7.2600 CDCl3
6.9521
6.9311
6.8984
6.8774
5.1328
4.8568
4.2869
4.2158
4.1508
4.0992
2.5844
2.5631
2.5432
2.5255
2.5049
2.3276
2.3065
2.2648
2.2468
2.2154
2.1975
2.1874
2.0480
6.00
4.01
1.69
0.67
1.00
1.00
0.67
1.00
0.67
1.67
2.34
1.00
3.33
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

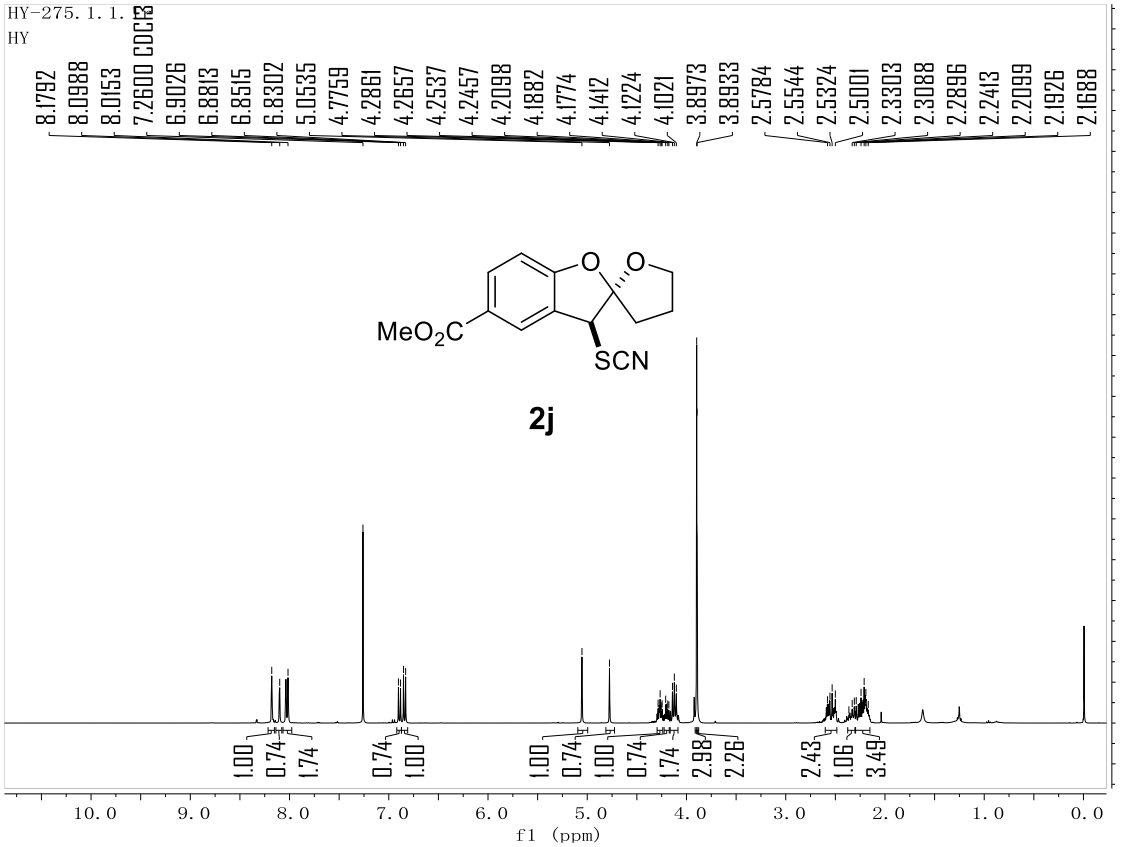
O
O
Ph
SCN

2h

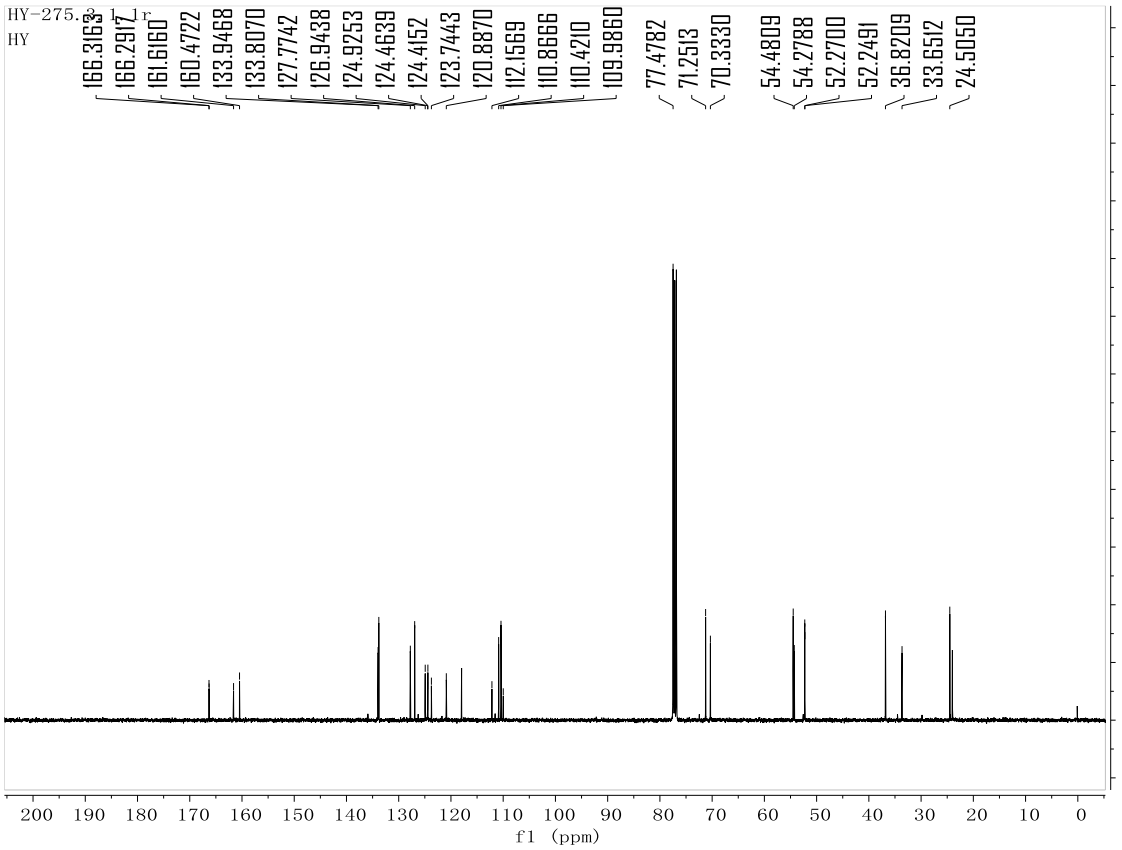

HY-223.3.1.1r
HY
157.5457
156.3294
140.5801
140.5218
139.6533
138.2657
135.9124
135.7957
130.7273
130.3257
129.1159
128.9838
127.6595
127.2288
127.0478
126.9555
125.2853
124.4739
123.7665
122.9414
120.0069
117.2146
113.6850
112.8039
110.7841
77.1600 CDCl3
71.0325
70.0863
55.4272
55.1604
36.7990
34.6803
24.6357
24.1361
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

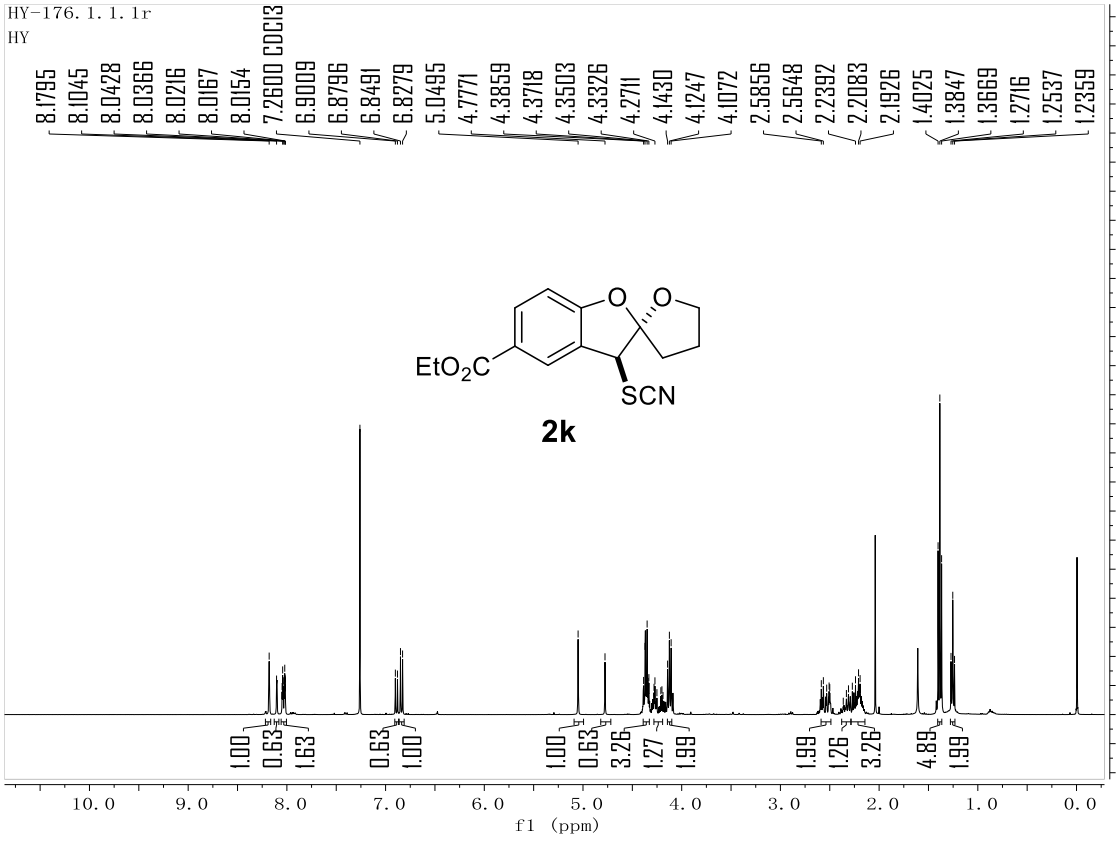

HY-332-H. 1. 1. 1r
HY
8.2633
8.1754
8.1191
8.1096
8.0979
8.0884
8.0849
7.2600 CDCl3
6.9425
6.9213
6.8888
6.8676
5.0717
4.8003
4.3059
4.2857
4.2657
4.2270
4.2163
4.1600
4.1403
4.1229
2.6133
2.6001
2.5783
2.5536
2.5204
2.3463
2.3248
2.2726
2.2360
2.2262
2.2090
1.00
0.60
1.60
0.60
1.00
1.00
0.60
1.00
0.60
1.60
2.33
1.18
3.20
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


HY-332-H-C. 3. 1. 1r
HY
170.7934
170.7555
162.3211
161.1881
134.7188
134.5286
128.5067
127.7563
125.1323
123.9811
123.5412
123.4751
121.1184
118.1955
112.0327
111.0595
110.5823
109.9390
77.1600 CDCl3
71.3359
70.4156
54.2990
54.1325
36.9445
33.6864
24.5182
24.0155
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HY-275.1.1.
HY
8.1792
8.0988
8.0153
7.2600 CDCl3
6.9026
6.8813
6.8515
6.8302
5.0535
4.7759
4.2861
4.2657
4.2537
4.2457
4.2098
4.1882
4.1774
4.1412
4.1224
4.1021
3.8973
3.8933
2.5784
2.5544
2.5324
2.5001
2.3303
2.3088
2.2896
2.2413
2.2099
2.1926
2.1688
MeO2C
O
O
SCN
1.00
0.74
1.74
0.74
1.00
1.00
0.74
1.00
0.74
1.74
2.98
2.26
2.43
1.06
3.49
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

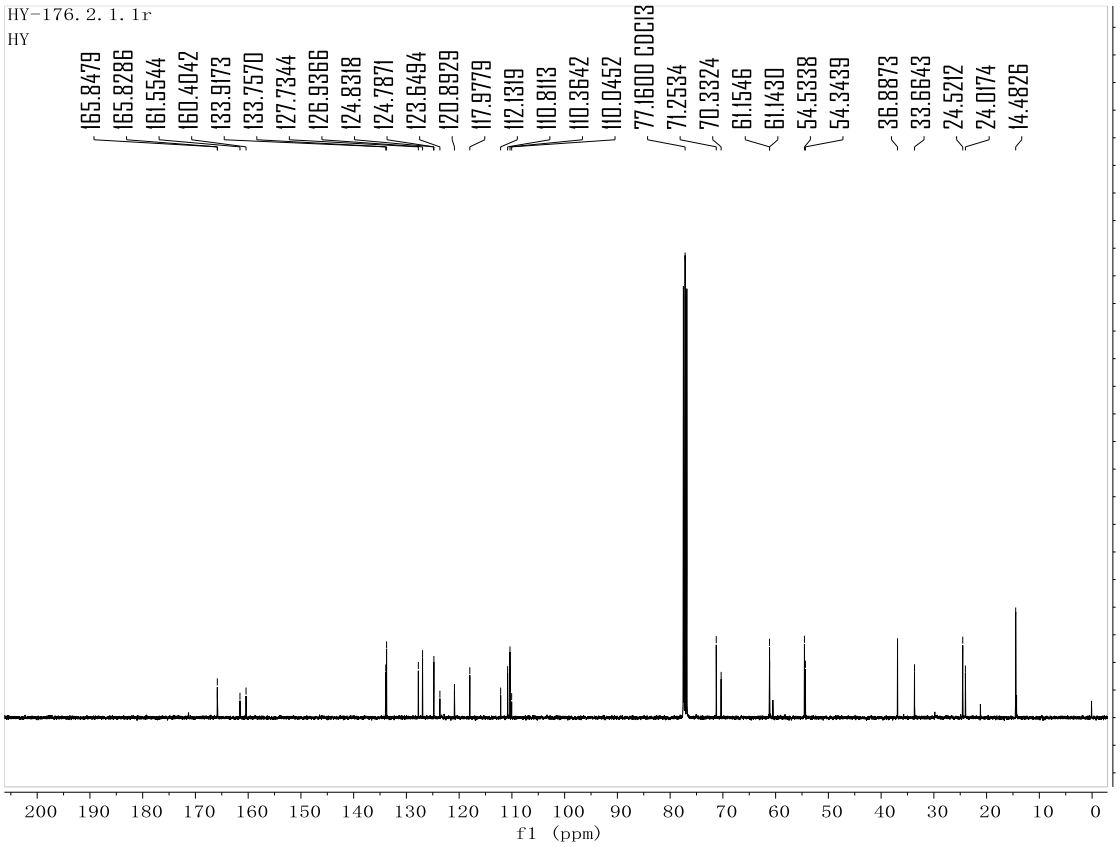
2j

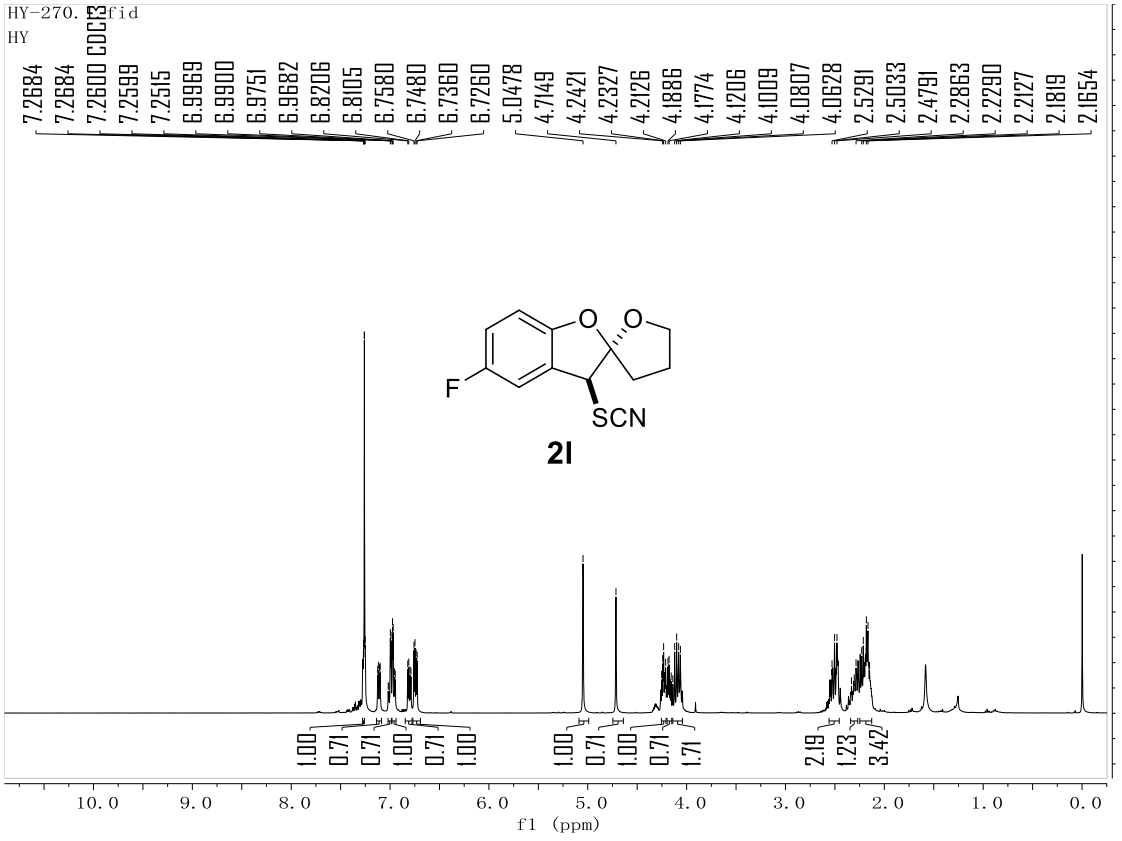

HY-275.3.1.r
HY
166.3163
166.2917
161.6160
160.4722
133.9468
133.8070
127.7742
126.9438
124.9253
124.4639
124.4152
123.7443
120.8870
112.1569
110.8666
110.4210
109.9860
77.4782
71.2513
70.3330
54.4809
54.2788
52.2700
52.2491
36.8209
33.6512
24.5050
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

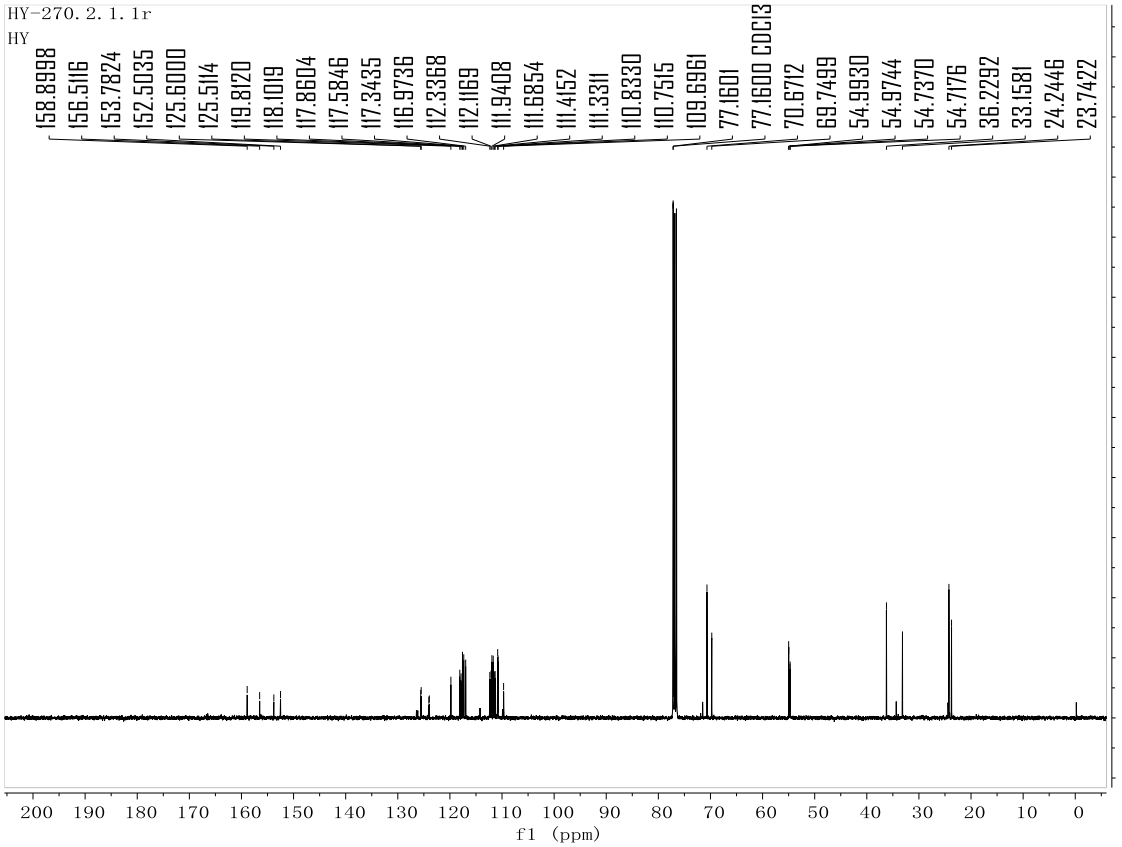

HY-176.1.1.1r
HY
8.1795
8.1045
8.0428
8.0366
8.0216
8.0167
8.0154
7.2600 CDCl3
6.9009
6.8796
6.8491
6.8279
5.0495
4.7771
4.3859
4.3718
4.3503
4.3326
4.2711
4.1430
4.1247
4.1072
2.5856
2.5648
2.2392
2.2083
2.1926
1.4025
1.3847
1.3669
1.2716
1.2537
1.2359
1.00
0.63
1.63
0.63
1.00
1.00
0.63
3.26
1.27
1.99
1.99
1.26
3.26
4.89
1.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

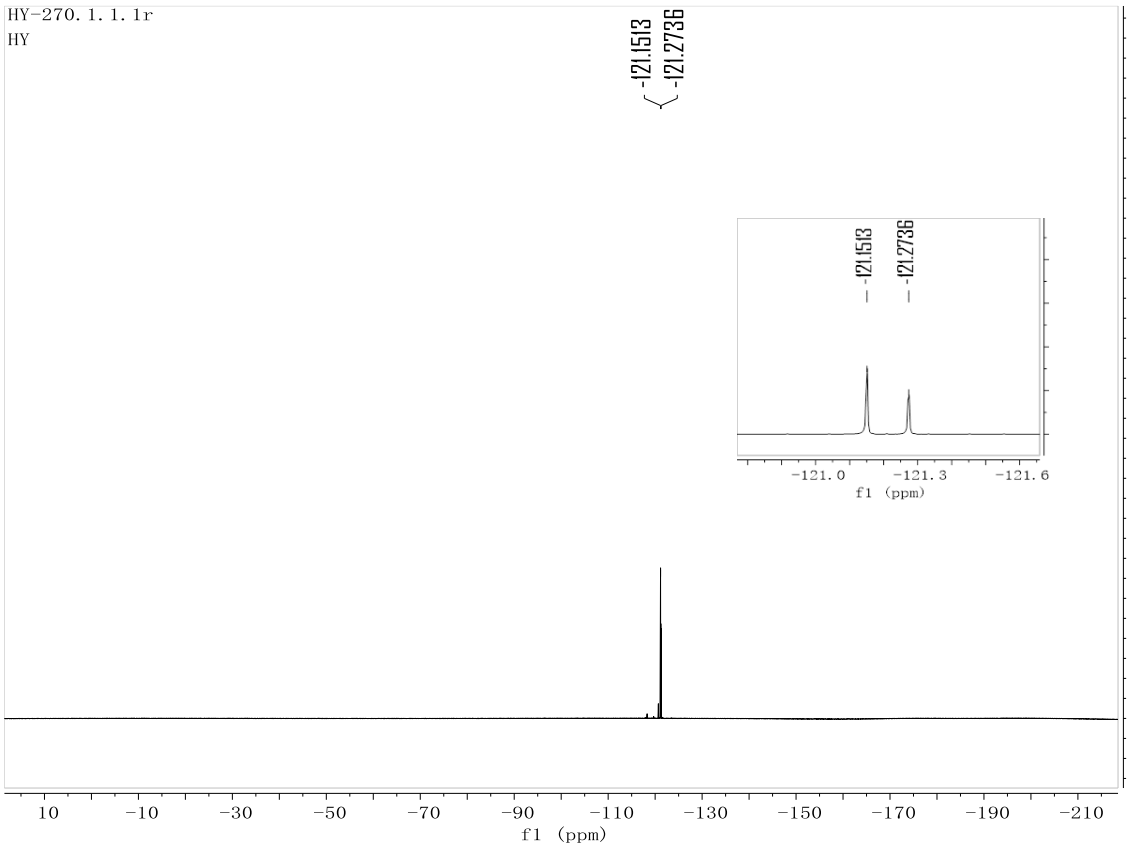
EtO2C
O
O
SCN

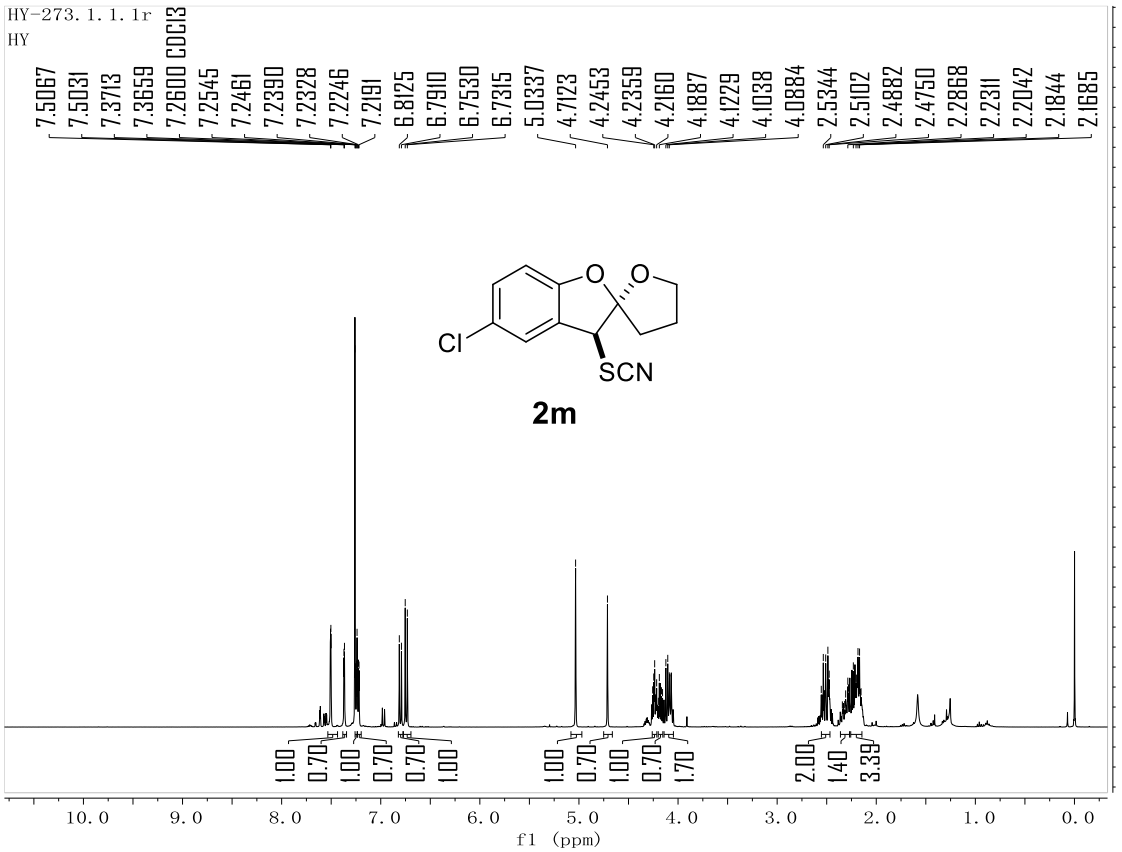
2k

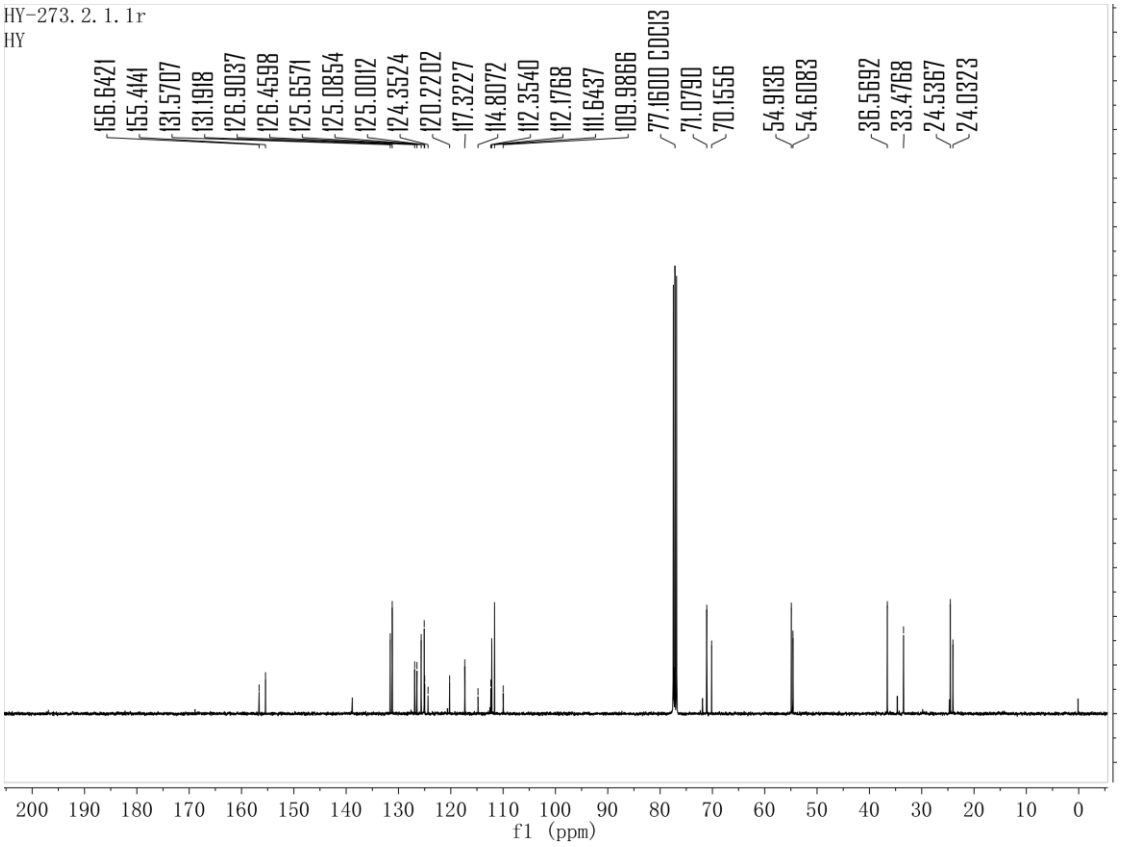

HY-176.2.1.1r
HY
165.8479
165.8286
161.5544
160.4042
133.9173
133.7570
127.7344
126.9366
124.8318
124.7871
123.6494
120.8929
117.9779
112.1319
110.8113
110.3642
110.0452
77.1600 CDCl3
71.2534
70.3324
61.1546
61.1430
54.5338
54.3439
36.8873
33.6643
24.5212
24.0174
14.4826
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

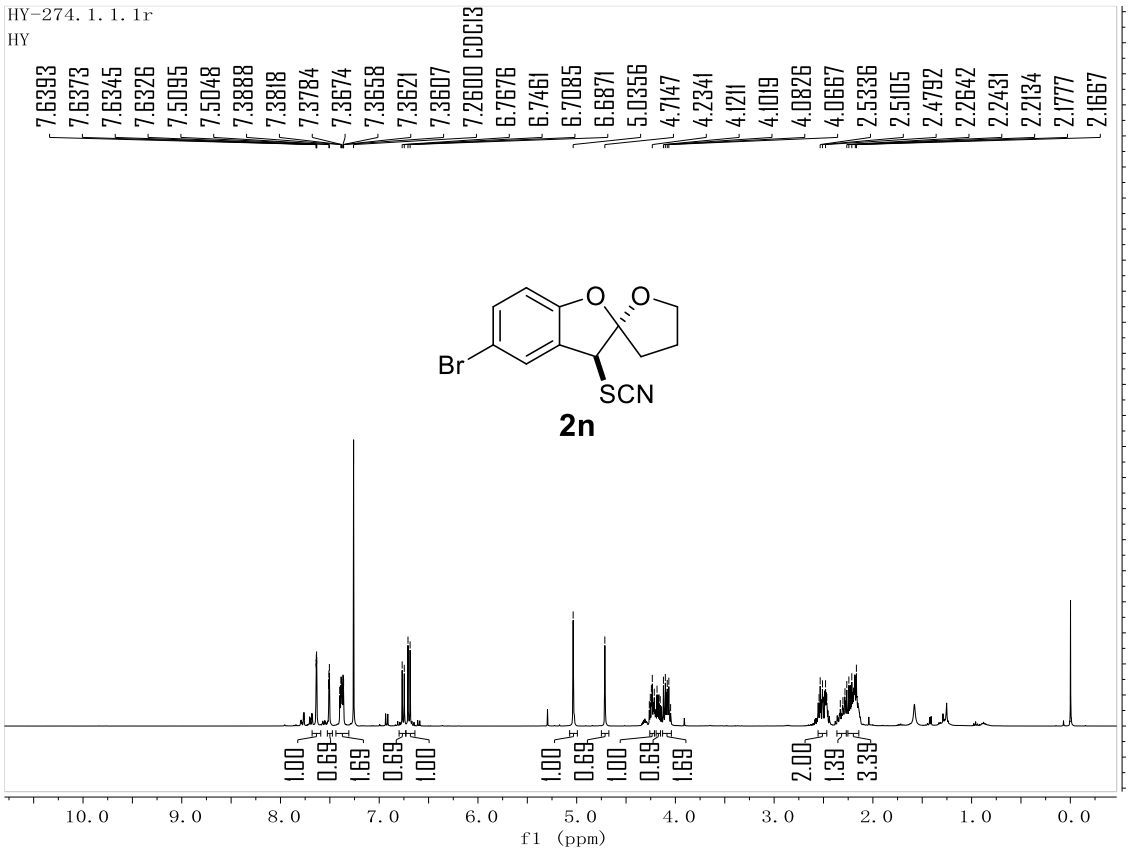

HY-270.fid
HY
7.2684
7.2684
7.2600 CDCl3
7.2599
7.2515
6.9969
6.9900
6.9751
6.9682
6.8206
6.8105
6.7580
6.7480
6.7360
6.7260
5.0478
4.7149
4.2421
4.2327
4.2126
4.1886
4.1774
4.1206
4.1009
4.0807
4.0628
2.5291
2.5033
2.4791
2.2863
2.2290
2.2127
2.1819
2.1654
1.00
0.71
0.71
1.00
0.71
1.00
1.00
0.71
1.00
0.71
1.71
2.19
1.23
3.42
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

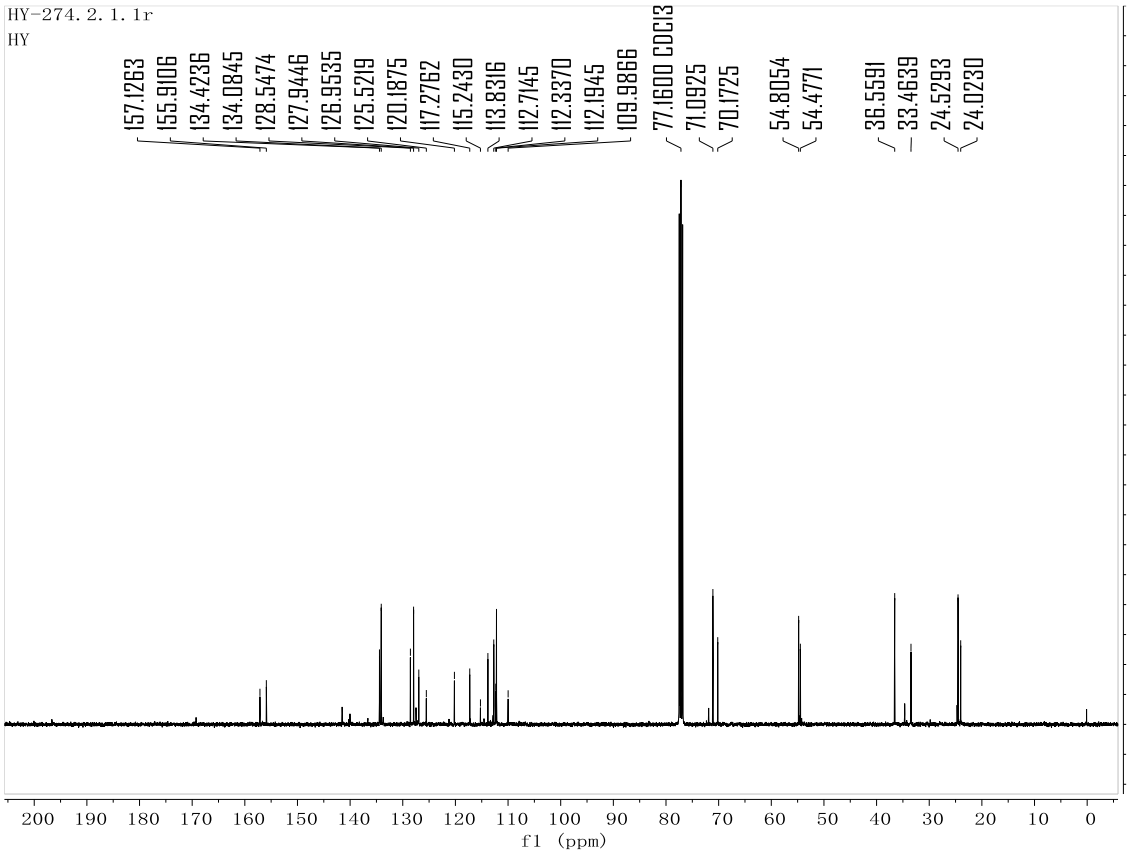

HY-270.2.1.1r
HY
158.8998
156.5116
153.7824
152.5035
125.6000
125.5114
119.8120
118.1019
117.8604
117.5846
117.3435
116.9736
112.3368
112.1169
111.9408
111.6854
111.4152
111.3311
110.8330
110.7515
109.6961
77.1601
77.1600 CDCl3
70.6712
69.7499
54.9930
54.9744
54.7370
54.7176
36.2292
33.1581
24.2446
23.7422
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

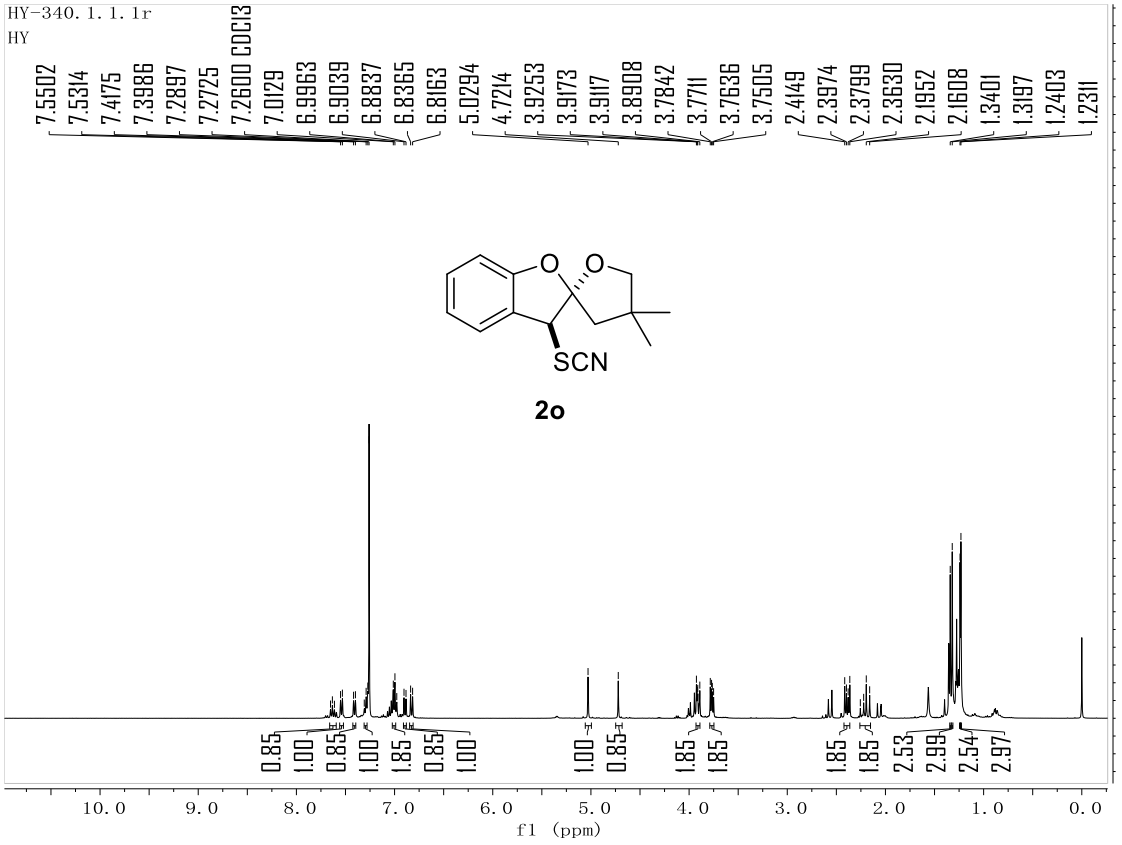

HY-270.1.1.1r
HY
-121.1513
-121.2736
-121.1513
-121.2736
-121.0
-121.3
-121.6
f1 (ppm)
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


HY-273.1.1.1r
HY
7.5067
7.5031
7.3713
7.3659
7.2600 CDCl3
7.2545
7.2461
7.2390
7.2328
7.2246
7.2191
6.8125
6.7910
6.7530
6.7315
5.0337
4.7123
4.2453
4.2359
4.2160
4.1887
4.1229
4.1038
4.0884
2.5344
2.5102
2.4882
2.4750
2.2868
2.2311
2.2042
2.1844
2.1685
Cl
O
O
SCN
2m
1.00
0.70
1.00
0.70
0.70
1.00
1.00
0.70
1.00
0.70
1.70
2.00
1.40
3.39
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


HY-273.2.1.1r
HY
156.6421
155.4141
131.5707
131.1918
126.9037
126.4598
125.6571
125.0854
125.0012
124.3524
120.2202
117.3227
114.8072
112.3540
112.1768
111.6437
109.9866
77.1600 CDCl3
71.0790
70.1556
54.9136
54.6083
36.5692
33.4768
24.5367
24.0323
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HY-274.1.1.1r
HY
7.6393
7.6373
7.6345
7.6326
7.5095
7.5048
7.3888
7.3818
7.3784
7.3674
7.3658
7.3621
7.3607
7.2600 CDCl3
6.7676
6.7461
6.7085
6.6871
5.0356
4.7147
4.2341
4.1211
4.1019
4.0826
4.0667
2.5336
2.5105
2.4792
2.2642
2.2431
2.2134
2.1777
2.1667
Br
O
O
SCN
2n
1.00
0.69
1.69
0.69
1.00
1.00
0.69
1.00
0.69
1.69
2.00
1.39
3.39
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


HY-274.2.1.1r
HY
157.1263
155.9106
134.4236
134.0845
128.5474
127.9446
126.9535
125.5219
120.1875
117.2762
115.2430
113.8316
112.7145
112.3370
112.1945
109.9866
77.1600 CDCl3
71.0925
70.1725
54.8054
54.4771
36.5591
33.4639
24.5293
24.0230
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HY-340.1.1.1r
HY
7.5502
7.5314
7.4175
7.3986
7.2897
7.2725
7.2600 CDCl3
7.0129
6.9963
6.9039
6.8837
6.8365
6.8163
5.0294
4.7214
3.9253
3.9173
3.9117
3.8908
3.7842
3.7711
3.7636
3.7505
2.4149
2.3974
2.3799
2.3630
2.1952
2.1608
1.3401
1.3197
1.2403
1.2311
0.85
1.00
0.85
1.00
1.85
0.85
1.00
1.00
0.85
1.85
1.85
1.85
1.85
2.53
2.99
2.54
2.97
10.0
9.0
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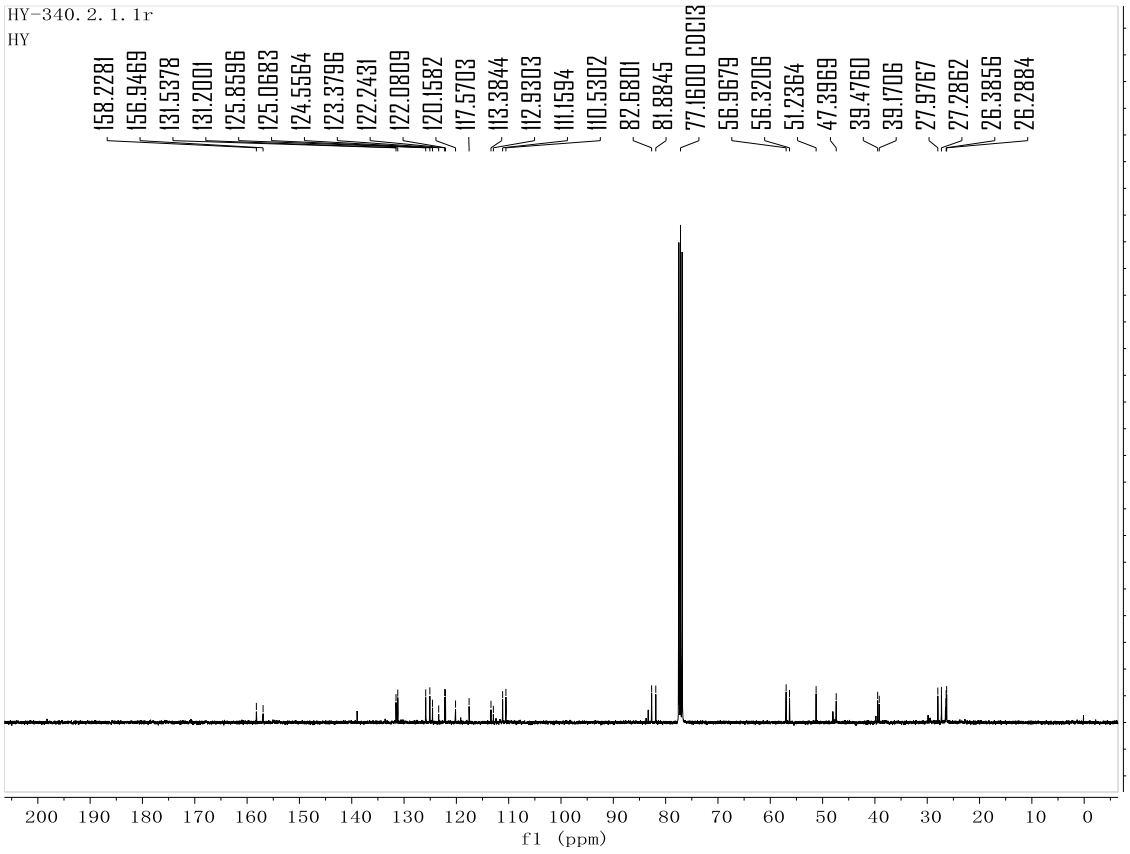
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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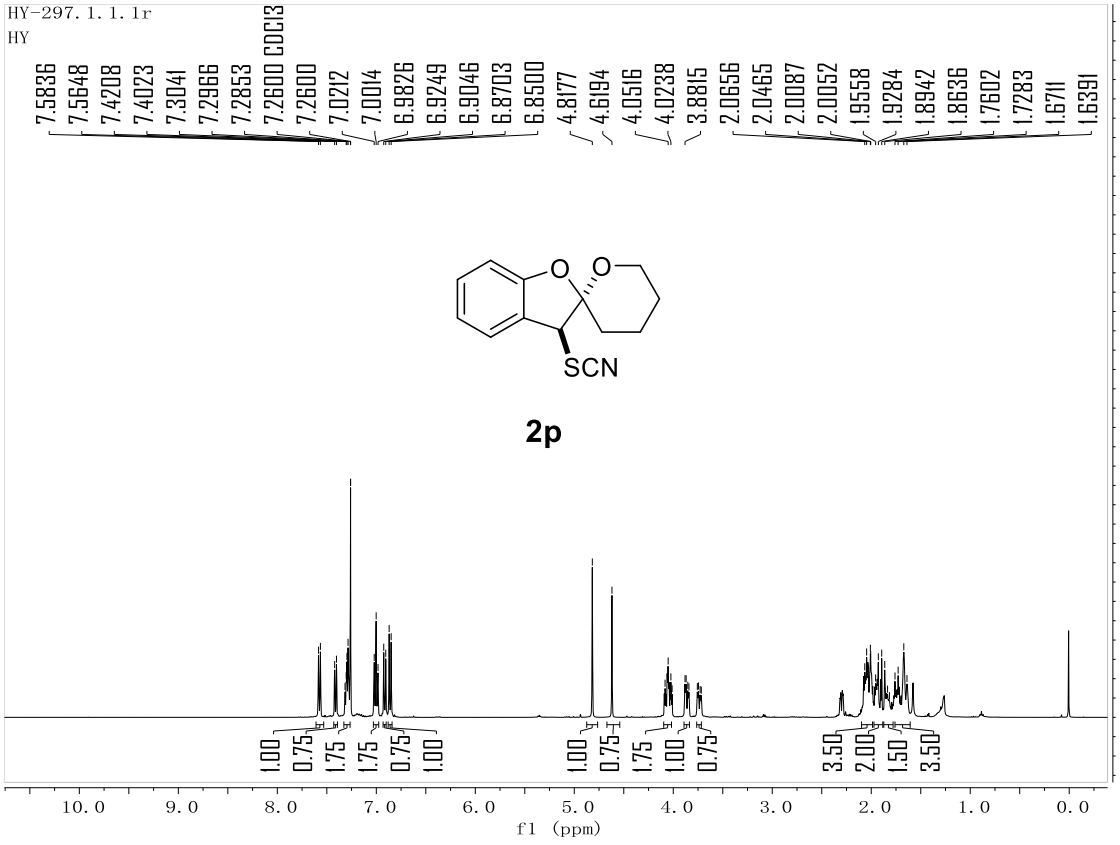
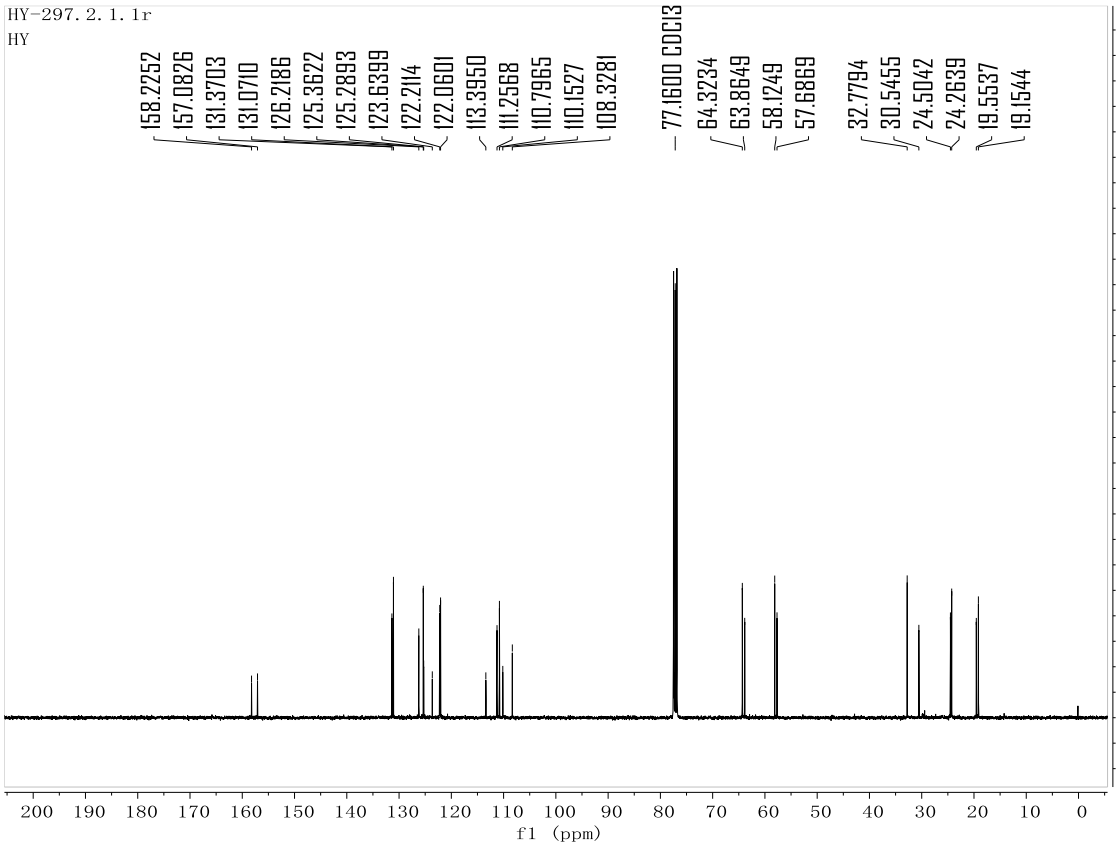
131.5378
131.2001
125.8596
125.0683
124.5564
123.3796
122.2431
122.0809
120.1582
117.5703
113.3844
112.9303
111.1594
110.5302
82.6801
81.8845
77.1600 CDCl3
56.9679
56.3206
51.2364
47.3969
39.4760
39.1706
27.9767
27.2862
26.3856
26.2884
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HY-297.1.1.1r
HY
7.5836
7.5648
7.4208
7.4023
7.3041
7.2966
7.2853
7.2600 CDCl3
7.2600
7.0212
7.0014
6.9826
6.9249
6.9046
6.8703
6.8500
4.8177
4.6194
4.0516
4.0238
3.8815
2.0656
2.0465
2.0087
2.0052
1.9558
1.9284
1.8942
1.8636
1.7602
1.7283
1.6711
1.6391
O
O
SCN
1.00
0.75
1.75
1.75
0.75
1.00
1.00
0.75
1.75
1.00
0.75
3.50
2.00
1.50
3.50
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

2p


HY-297.2.1.1r
HY
158.2252
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131.3703
131.0710
126.2186
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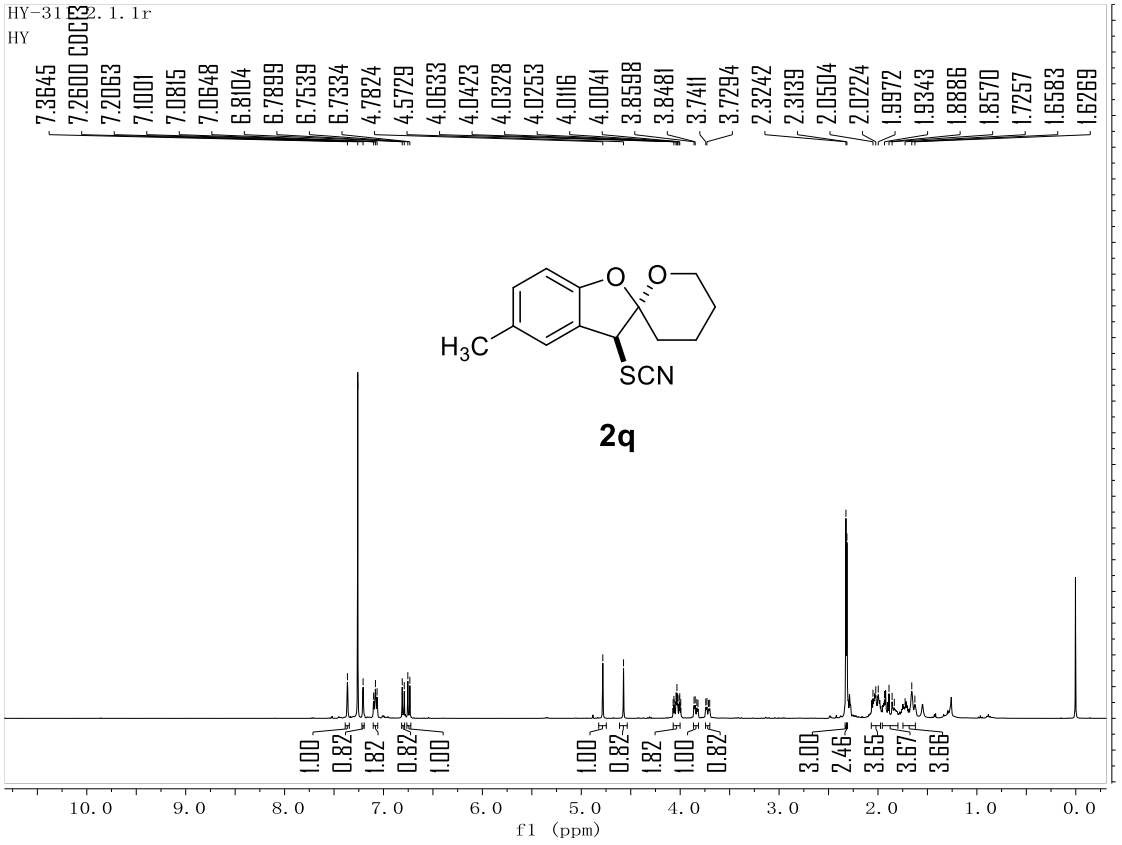
125.2893
123.6399
122.2114
122.0601
113.3950
111.2568
110.7965
110.1527
108.3281
77.1600 CDCl3
64.3234
63.8649
58.1249
57.6869
32.7794
30.5455
24.5042
24.2639
19.5537
19.1544
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.2600 CDCl3
7.2063
7.1001
7.0815
7.0648
6.8104
6.7899
6.7539
6.7334
4.7824
4.5729
4.0633
4.0423
4.0328
4.0253
4.0116
4.0041
3.8598
3.8481
3.7411
3.7294
2.3242
2.3139
2.0504
2.0224
1.9972
1.9343
1.8886
1.8570
1.7257
1.6583
1.6269
1.00
0.82
1.82
0.82
1.00
1.00
0.82
1.82
1.00
0.82
3.00
2.46
3.65
3.67
3.66
10.0
9.0
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7.0
6.0
5.0
4.0
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2.0
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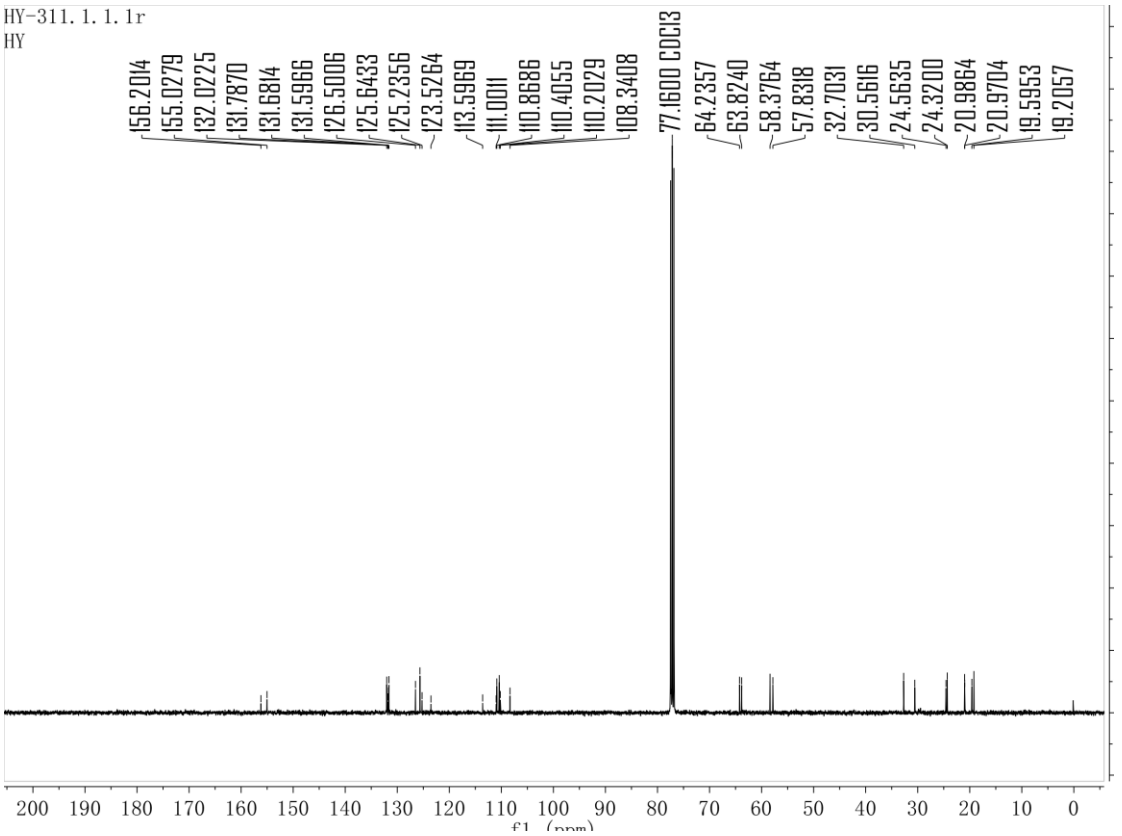
0.0
f1 (ppm)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131.6814
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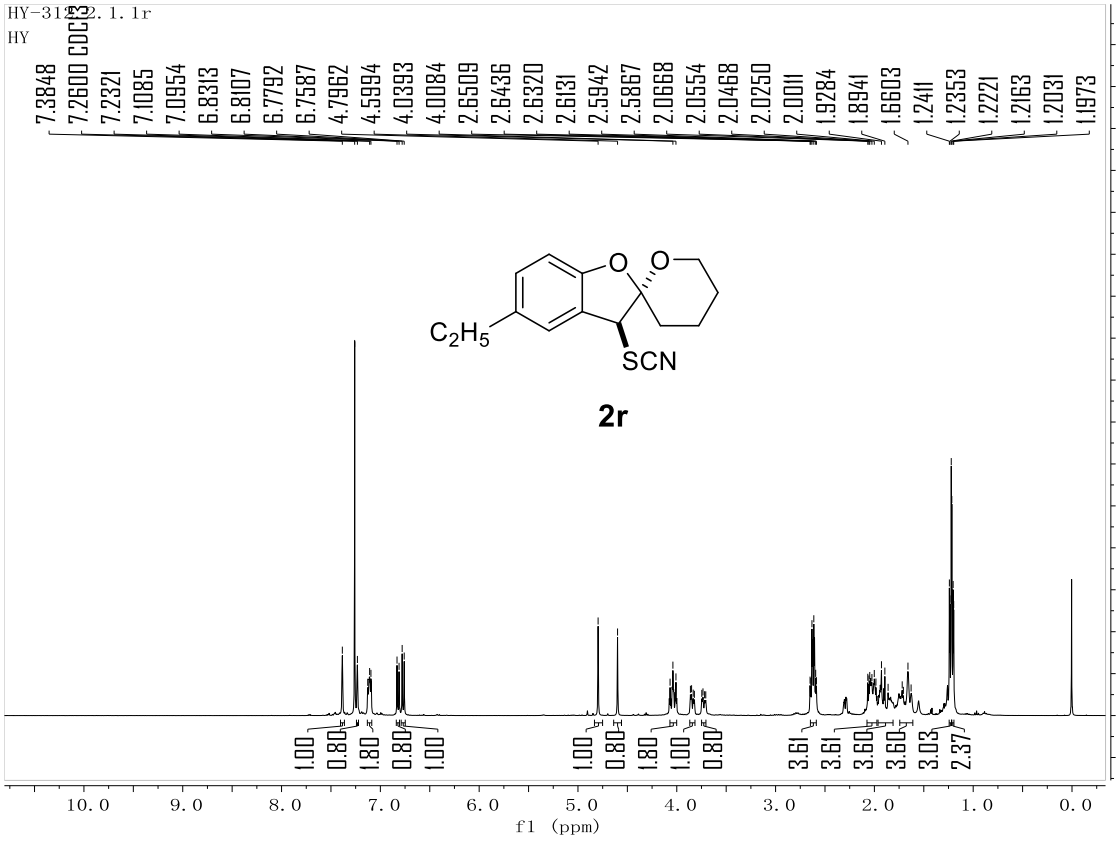
125.2356
123.5264
113.5969
111.0011
110.8686
110.4055
110.2029
108.3408
77.1600 CDCl3
64.2357
63.8240
58.3764
57.8318
32.7031
30.5616
24.5635
24.3200
20.9864
20.9704
19.5953
19.2057
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

H_3C

SCN

2q


HY-312.1.1.1r
HY
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7.2600 CDCl3
7.2321
7.1085
7.0954
6.8313
6.8107
6.7792
6.7587
4.7962
4.5994
4.0393
4.0084
2.6509
2.6436
2.6320
2.6131
2.5942
2.5867
2.0668
2.0554
2.0468
2.0250
2.0011
1.9284
1.8941
1.6603
1.2411
1.2353
1.2221
1.2163
1.2031
1.1973
1.00
0.80
1.80
0.80
1.00
1.00
0.80
1.80
1.00
0.80
3.61
3.61
3.60
3.60
3.03
2.37
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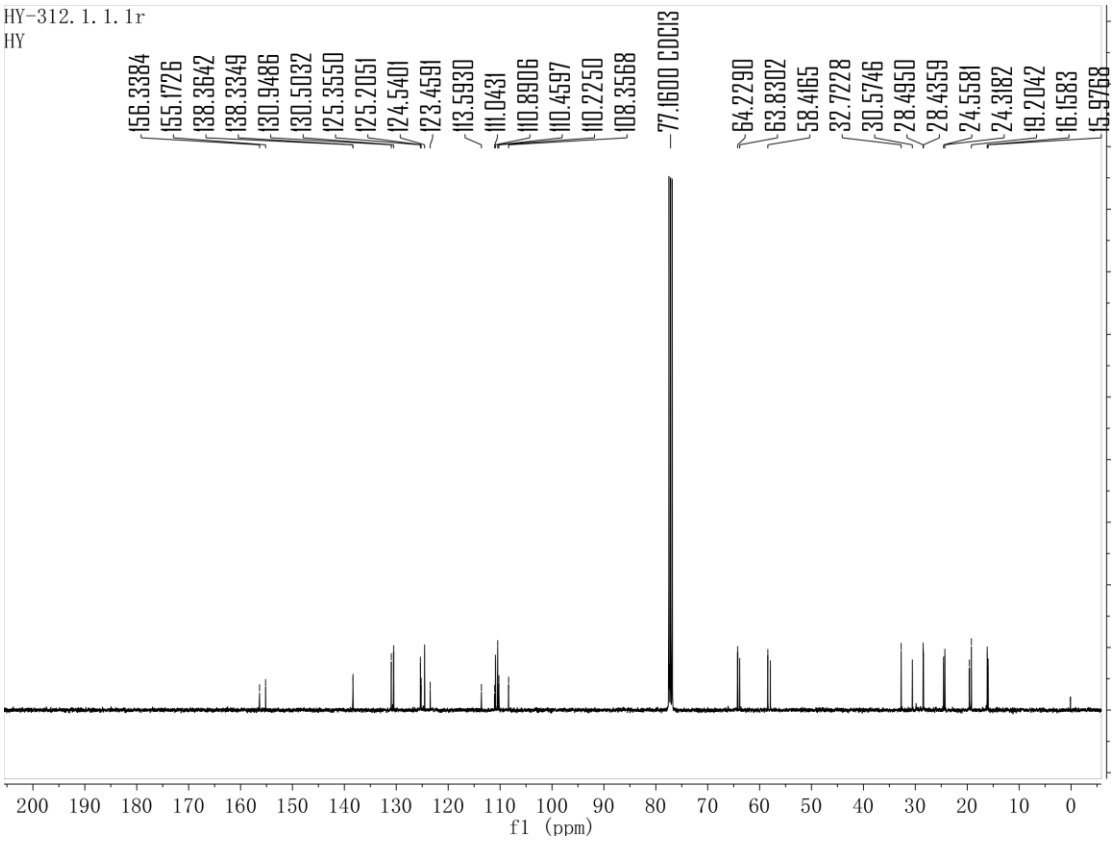
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


HY-312.1.1.1r
HY
156.3384
155.1726
138.3642
138.3349
130.9486
130.5032
125.3550
125.2051
124.5401
123.4591
113.5930
111.0431
110.8906
110.4597
110.2250
108.3568
77.1600 CDCl3
64.2290
63.8302
58.4165
32.7228
30.5746
28.4950
28.4359
24.5581
24.3182
19.2042
16.1583
15.9768
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)