Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

A Convenient Base-mediated Synthesis of 3-Aryol-4-methyl (or benzyl)-2-(methylthio) Furans from α-Oxo Ketene Dithioacetals and Propargyl Alcohols via the Domino Coupling/annulations

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Experimental

General

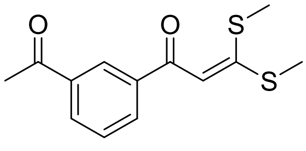
All the reagents and solvents were obtained from commercial suppliers. The solvents for reaction were distilled to remove water over Na, CaH_2, P_2O_5 or K_2CO_3. All reactions were monitored by TLC (Merck silica gel 60 F_{254}) and analysed under UV (254 nm). For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. Melting points were measured on a RY–I apparatus and uncorrected. ^1H, ^{19}F and ^{13}C NMR spectra were recorded at 400 MHz, 376 MHz and 100 MHz with a Bruker AV 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. HRMS were recorded on an IonSpec FT-ICR mass spectrometer with Electron Spray Ionization (ESI) resource.

1. Synthesis of starting materials

1.1. General procedure for the synthesis of 3,3-bis(methylthio)-1-aryl/hetaroary-2-propen-1-ones (1a-1y)

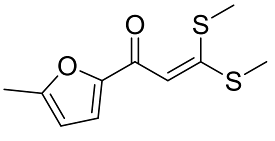
t-BuOK (2.0 equiv) in dry THF was stirred at 0 ˚C under N_2 for 10 min. The appropriate ketone (1.0 equiv) was added and the mixture was stirred for 15 min. Subsequently, carbon disulfide (1.0 equiv) was added and the solution was stirred at 0 ˚C for 4 h. Then, dimethylsulfate (2.0 equiv) was added at 0 ˚C and the reaction mixture was stirred at room temperature for 4 h. Water was added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate, washed with brine, and the combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was recrystallized from ethyl acetate and petroleum ether. The synthesis of **1a-n**, **1p-r**, **1t-v** and **1x, y** has been previously reported[1-6].

1.1.1. 3,3-Bis(methylthio)-1-(3-acetylphenyl)-2-propen-1-one (**1o**)



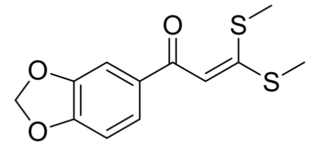
Starting with 1,3-diacetylbenzene (1.622 g, 10.0 mmol), potassium tert-butanolate (2.245 g, 20.0 mmol), carbon disulfide (0.61 mL, 10.0 mmol) and dimethylsulfate (1.89 mL, 20.0 mmol) in THF (80 mL), **1o** was obtained as a yellow solid (1.065 g, 38%). mp: 105-106 ˚C; ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.49 (t, $^4J_{H\text{-}H}$ = 1.6 Hz, 1H, ArH), 8.15-8.06 (m, 2H, ArH), 7.55 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 1H, ArH), 6.79 (s, 1H, 2-H), 2.66 (s, 3H, $COCH_3$), 2.60 (s, 3H, SCH_3), 2.56 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 197.69, 184.51, 168.35, 139.71, 137.26, 132.08, 131.19, 128.88, 127.57, 108.78, 26.80, 17.48, 15.17; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{13}H_{15}O_2S_2$: 267.0513, found: 267.0507.

1.1.2. 3,3-Bis(methylthio)-1-(5-methylfuran-2-yl)-2-propen-1-one (**1s**)



Starting with 5-methyl-2-acetylfuran (1.241 g, 10.0 mmol), potassium tert-butanolate (2.245 g, 20.0 mmol), carbon disulfide (0.61 mL, 10.0 mmol) and dimethylsulfate (1.89 mL, 20.0 mmol) in THF (80 mL), **1s** was obtained as a pale brown powder (1.369 g, 60%). mp: 115-116 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.05 (d, $^{3}J_{\text{H-H}}$ = 3.4 Hz, 1H, ArH), 6.64 (s, 1H, 2-H), 6.13 (d, $^{3}J_{\text{H-H}}$ = 3.4 Hz, 1H, ArH), 2.55 (s, 3H, SCH$_3$), 2.51 (s, 3H, SCH$_3$), 2.38 (s, 3H, ArCH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 174.38, 164.98, 156.02, 152.75, 116.77, 108.99, 108.91, 17.29, 15.09, 14.13; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{10}H_{13}O_2S_2$: 229.0357, found: 229.0353.

1.1.3. 3, 3-Bis(methylthio)-1-[3,4-(methylenedioxy)phenyl]-2-propen-1-one (**1w**)

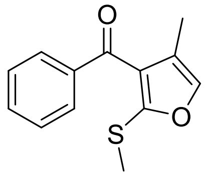


Using 3,4-(methylenedioxy)acetophenone (1.642 g, 10.0 mmol), potassium tert-butanolate (2.245 g, 20.0 mmol), carbon disulfide (0.61 mL, 10.0 mmol) and dimethylsulfate (1.89 mL, 20.0 mmol) in dry THF (80 mL), **1w** was obtained as a pale brown powder (1.798 g, 67%). mp: 127-128 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.50 (dd, $^{3}J_{\text{H-H}}$ = 8.1 Hz, $^{4}J_{\text{H-H}}$ = 1.7 Hz, 1H, ArH), 7.43 (d, $^{4}J_{\text{H-H}}$ = 1.6 Hz, 1H, ArH), 6.84 (d, $^{3}J_{\text{H-H}}$ = 8.1 Hz, 1H, ArH), 6.69 (s, 1H, 2-H), 6.03 (s, 2H, OCH$_2$O), 2.55 (s, 3H, SCH$_3$), 2.52 (s, 3H, SCH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 183.98, 165.56, 150.68, 148.01, 133.93, 123.21, 109.17, 107.96, 107.79, 101.71, 17.36, 15.07; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{12}H_{13}O_3S_2$: 269.0306, found: 269.0305.

2. Cyclization reactions

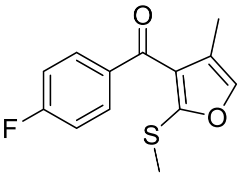
2.1. General procedure for the synthesis of 3-aryol-4-methyl-2-methylthio-furans (2a-x)

t-BuOK (123 mg, 1.1 mmol) and propargyl alcohol **b** (62 mg, 1.1 mmol) in dry THF (10 mL) were stirred at room temperature under N$_2$ for 15 min. Subsequently, α-oxoketene dithioacetal **1a-x** (0.5 mmol) was added and the reaction mixture was stirred at room temperature for the stipulated period of time. After completion of the reaction (monitored by TLC), Water (10 mL) was added and the whole mixture was extracted with ethyl acetate (3×15 mL), and the combined organic extract was washed with brine (2×15 mL), dried over MgSO$_4$. The solvent was evaporated under vacuum and the residue was purified by column chromatography over silica gel using ethyl acetate/petroleum ether (1:100, v/v) as eluent to give the desired product in excellent purity. The physical and spectral data of the synthesized compounds are listed as follows.

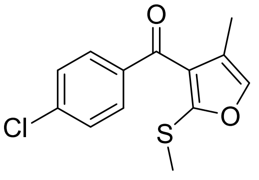


2.1.1. 3-Benzoyl-4-methyl-2-methylthio-furan (**2a**). Yield 75 mg (65%), colourless viscous liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.75 (dd, $^{3}J_{\text{H-H}}$ =8.4 Hz, $^{4}J_{\text{H-H}}$ = 1.4 Hz, 2H, ArH), 7.57 (tt, $^{3}J_{\text{H-H}}$ = 8.4 Hz, $^{4}J_{\text{H-H}}$ = 1.3 Hz, 1H, ArH), 7.47(td, $^{3}J_{\text{H-H}}$ = 8.4 Hz, $^{4}J_{\text{H-H}}$ =

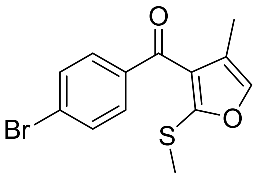
1.4 Hz, 2H, ArH), 7.30 (q, ${}^4J_{H\text{-}H}$ = 1.2 Hz, 1H, 5-H), 2.42 (s, 3H, SCH$_3$), 1.98 (d, ${}^4J_{H\text{-}H}$ = 1.2 Hz, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 191.86, 153.60, 141.24, 139.14, 132.58, 129.13, 128.39, 125.08, 122.04, 15.88, 9.63; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{13}H_{13}O_2S$: 233.0636, found: 233.0638.



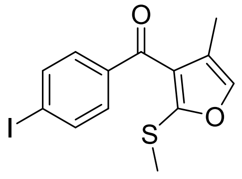
2.1.2. 3-(4-Flourbenzoyl)-4-methyl-2-methylthio-furan (**2b**). Yield 56 mg (45%), colourless viscous liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.80-7.75 (m, 2H, ArH), 7.30 (q, ${}^4J_{H\text{-}H}$ = 1.2 Hz, 1H, 5-H), 7.16-7.11 (m, 2H, ArH), 2.42 (s, 3H, SCH$_3$), 1.98 (d, ${}^4J_{H\text{-}H}$ = 1.2 Hz, 3H, CH$_3$); ^{19}F NMR (CDCl$_3$, 376 MHz): δ = −105.84; ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 190.22, 165.51 (d, ${}^1J_{C\text{-}F}$ = 254.9 Hz), 153.25, 141.35, 135.32 (d, ${}^4J_{C\text{-}F}$ = 3.0 Hz), 131.76 (d, ${}^3J_{C\text{-}F}$ = 9.1 Hz), 124.96, 121.99, 115.52 (d, ${}^2J_{C\text{-}F}$ = 21.8 Hz), 15.90, 9.51; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{13}H_{12}FO_2S$: 251.0542, found: 251.0531.



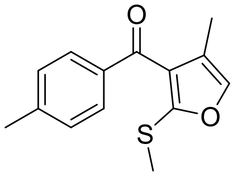
2.1.3. 3-(4-Chlorobenzoyl)-4-methyl-2-methylthio-furan (**2c**). Yield 76 mg (57%), pale yellow solid. mp: 65-66 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.69 (d, ${}^3J_{H\text{-}H}$ =7.5 Hz, 2H, ArH), 7.44 (d, ${}^3J_{H\text{-}H}$ = 7.5 Hz, 2H, ArH), 7.30 (s, 1H, 5-H), 2.42 (s, 3H, SCH$_3$), 1.98 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 190.45, 153.90, 141.36, 138.90, 137.41, 130.55, 128.70, 124.59, 121.97, 15.78, 9.63; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{13}H_{12}ClO_2S$: 267.0247, found: 267.0245.



2.1.4. 3-(4-Bromobenzoyl)-4-methyl-2-methylthio-furan (**2d**). Yield 96 mg (62%), pale yellow viscous liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.60 (s, 4H, ArH), 7.29 (q, ${}^4J_{H\text{-}H}$ = 1.2 Hz, 1H, 5-H), 2.43 (s, 3H, SCH$_3$), 1.98 (d, ${}^4J_{H\text{-}H}$ = 1.2 Hz, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 190.64, 154.01, 141.36, 137.87, 131.70, 130.67, 127.58, 124.55, 121.99, 15.78, 9.65; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{13}H_{12}BrO_2S$: 310.9741 and 312.9721, found: 310.9740 and 312.9721.

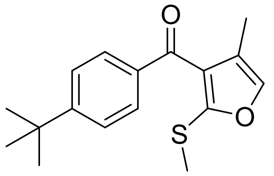


2.1.5. 3-(4-Iodobenzoyl)-4-methyl-2-methylthio-furan (**2e**). Yield 113 mg (63%), pale yellow viscous liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.82 (d, ${}^3J_{H\text{-}H}$ = 8.4 Hz, 2H, ArH), 7.45 (d, ${}^3J_{H\text{-}H}$ = 8.4 Hz, 2H, ArH), 7.29 (q, ${}^4J_{H\text{-}H}$ = 1.1 Hz, 1H, 5-H), 2.43(s, 3H, SCH$_3$), 1.98 (d, ${}^3J_{H\text{-}H}$ = 1.1 Hz, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 190.81, 154.12, 141.35, 138.38, 137.65, 130.57, 124.38, 121.94, 100.31, 15.77, 9.74; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{13}H_{12}IO_2S$: 358.9603, found: 358.9595.

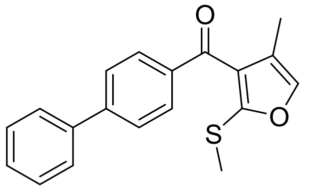


2.1.6. 4-Methyl-3-(4-methylbenzoyl)-2-methylthio-furan (**2f**). Yield 69 mg (56%), colourless viscous liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.67 (d, ${}^3J_{H\text{-}H}$ = 7.4 Hz, 2H, ArH), 7.29 (s, 1H, 5-

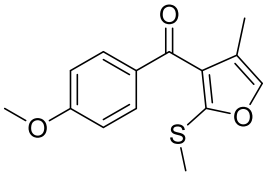
H), 7.26 (d, $^{3}J_{\text{H-H}}$ = 7.4 Hz, 2H, ArH), 2.43 (s, 3H, SCH_3), 2.42 (s, 3H, $ArCH_3$), 1.98 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.43, 152.55, 143.49, 141.24, 136.34, 129.41, 129.09, 125.56, 122.00, 21.71, 16.08, 9.53; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{14}H_{15}O_2S$: 247.0793, found: 247.0791.



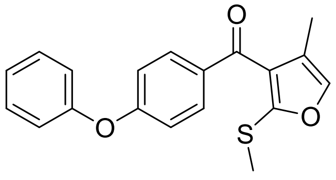
2.1.7. 3-(4-*tert*-Butylbenzoyl)-4-methyl--2-methylthio-furan (**2g**). Yield 72 mg (50%), colourless viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.71 (d, $^{3}J_{\text{H-H}}$ = 8.5 Hz, 2H, ArH), 7.47 (d, $^{3}J_{\text{H-H}}$ = 8.5 Hz, 2H, ArH), 7.29 (q, $^{4}J_{\text{H-H}}$ = 1.2 Hz, 1H, 5-H), 2.41 (s, 3H, SCH_3), 1.97 (d, $^{4}J_{\text{H-H}}$ =1.2 Hz, 3H, CH_3), 1.35 (s, 9H, *t*-Bu); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.47, 156.51, 152.42, 141.20, 136.15, 129.29, 125.71, 125.35, 122.00, 35.14, 31.17, 16.20, 9.58; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{17}H_{21}O_2S$: 289.1262, found: 289.1262.



2.1.8. 3-(Biphenyl-4-carbonyl)-4-methyl-2-methylthio-furan (**2h**). Yield 91 mg (59%), pale yellow powder. mp: 104-105 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (d, $^{3}J_{\text{H-H}}$ = 8.3 Hz, 2H, ArH), 7.70 (d, $^{3}J_{\text{H-H}}$ = 8.3 Hz, 2H, ArH), 7.66 (d, $^{3}J_{\text{H-H}}$ = 7.2 Hz, 2H, ArH), 7.48 (t, $^{3}J_{\text{H-H}}$ = 7.2 Hz, 2H, ArH), 7.40 (t, $^{3}J_{\text{H-H}}$ = 7.2 Hz, 1H, ArH), 7.32 (q, $^{4}J_{\text{H-H}}$ = 1.1 Hz, 1H, 5-H), 2.44(s, 3H, SCH_3), 2.02 (d, $^{4}J_{\text{H-H}}$ = 1.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.16, 152.07, 144.17, 140.21, 138.76, 136.57, 128.75, 127.84, 127.07, 126.15, 125.89, 124.18, 120.91, 14.87, 8.55; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{19}H_{17}O_2S$: 309.0949, found: 309.0948.

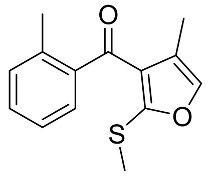


2.1.9. 4-Methyl-3-(4-methoxybenzoyl)-2-methylthio-furan (**2i**). Yield 68 mg (52%), colourless viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78 (d, $^{3}J_{\text{H-H}}$ = 8.8 Hz, 2H, ArH), 7.30 (d, $^{4}J_{\text{H-H}}$ = 1.1 Hz, 1H, 5-H), 6.95 (d, $^{3}J_{\text{H-H}}$ = 8.8 Hz, 2H, ArH), 3.88 (s, 3H, OCH_3), 2.40 (s, 3H, SCH_3), 1.99 (d, $^{4}J_{\text{H-H}}$ = 1.1 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 189.40, 162.47, 150.30, 140.24, 130.73, 130.51, 125.10, 120.99, 112.59, 54.43, 15.44, 8.36; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{14}H_{15}O_3S$: 236.0742, found: 236.0740.

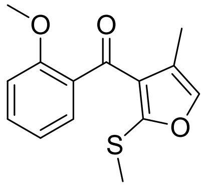


2.1.10. 4-Methyl-3-(4-phenoxybenzoyl)-2-methylthio-furan (**2j**). Yield 91 mg (56%), pale yellow viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.76, (d, $^{3}J_{\text{H-H}}$ = 8.7 Hz, 2H, ArH), 7.40 (t, $^{3}J_{\text{H-H}}$ = 7.7 Hz, 2H, ArH), 7.30 (q, $^{4}J_{\text{H-H}}$ = 1.1 Hz, 1H, 5-H), 7.20 (t, $^{3}J_{\text{H-H}}$ = 7.4 Hz, 1H, ArH), 7.09 (d, $^{3}J_{\text{H-H}}$ = 7.7 Hz, 2H, ArH), 7.01 (d, $^{3}J_{\text{H-H}}$ = 8.7 Hz, 2H, ArH), 2.42 (s, 3H, SCH_3), 2.00 (d, $^{4}J_{\text{H-H}}$ = 1.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.41, 161.84, 155.51, 141.34, 133.35, 131.69, 130.08, 125.67, 124.60, 122.01, 120.19, 117.22, 16.28, 9.54; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{19}H_{17}O_3S$: 325.0898, found: 325.0897.

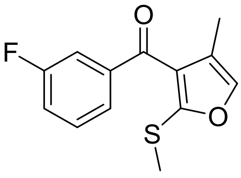
2.1.11. 4-Methyl-3-(2-methylbenzoyl)-2-methylthio-furan (**2k**). Yield 52 mg (42%), colourless viscous liquid. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 7.65 (q, $^4J_{\text{H-H}}$ = 1.2 Hz, 1H, 5-H), 7.40 (td, $^3J_{\text{H-H}}$ = 7.4 Hz, $^4J_{\text{H-H}}$ = 1.3 Hz, 1H, ArH), 7.31-7.26 (m, 2H, ArH), 7.22 (dd, $^3J_{\text{H-H}}$ = 7.2 Hz, $^4J_{\text{H-H}}$ = 0.8 Hz, 1H, ArH), 2.44 (s, 3H, SCH_3), 2.22 (s, 3H, $ArCH_3$), 1.73 (d, $^4J_{\text{H-H}}$ =1.1 Hz, 3H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 193.30, 157.89, 140.76, 140.61, 135.51, 130.83, 130.09, 127.44, 125.72, 123.24, 122.00, 19.45, 14.12, 9.69; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{14}H_{15}O_2S$: 247.0793, found: 247.0682.



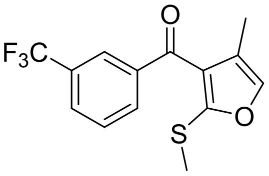
2.1.12. 4-Methyl-3-(2-methoxylbenzoyl)-2-methylthio-furan (**2l**). Yield 52 mg (40%), colourless viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.42 (t, $^3J_{\text{H-H}}$ = 7.7 Hz, 1H, ArH), 7.28 (s, 1H, 5-H), 7.19 (s, 1H, ArH), 7.01 (t, $^3J_{\text{H-H}}$ = 7.1 Hz, 1H, ArH), 6.94 (d, $^3J_{\text{H-H}}$ = 8.0 Hz, 1H, ArH), 3.78 (s, 3H, OCH_3), 2.45 (s, 3H, SCH_3), 1.87 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 189.61, 156.67, 155.76, 139.40, 130.59, 129.80, 127.59, 125.49, 122.53, 121.05, 119.65, 110.22, 54.66, 13.10, 8.53; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{14}H_{15}O_3S$: 236.0742, found: 236.0739.



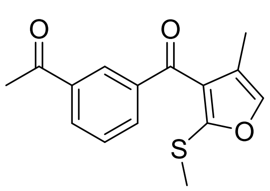
2.1.13. 3-(3-Flourbenzoyl)-4-methyl-2-methylthio-furan (**2m**). Yield 56 mg (45%), pale yellow viscous liquid. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 7.72 (s, 1H, 5-H), 7.60-7.55 (m, 1H, ArH), 7.51-7.43 (m, 3H, ArH), 2.43 (s, 3H, SCH_3), 1.88 (s, 3H, CH_3); ^{19}F NMR ($CDCl_3$, 376 MHz): δ = −112.24; ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 189.92 (d, $^4J_{\text{C-F}}$ = 1.8 Hz), 162.47 (d, $^1J_{\text{C-F}}$ = 246.4 Hz), 154.52, 142.75, 141.44 (d, $^3J_{\text{C-F}}$ = 6.2 Hz), 131.27 (d, $^3J_{\text{C-F}}$ = 8.1 Hz), 125.31 (d, $^4J_{\text{C-F}}$ = 2.4 Hz), 124.15, 121.61, 119.88 (d, $^2J_{\text{C-F}}$ = 20.9 Hz), 115.34 (d, $^2J_{\text{C-F}}$ = 22.4 Hz), 15.44, 9.76; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{13}H_{12}FO_2S$: 251.0542, found: 251.0540.



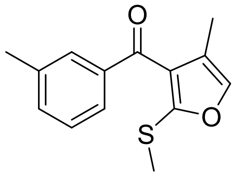
2.1.14. 3-(3-Trifluoromethylbenzoyl)-4-methyl-2-methylthio-furan (**2n**). Yield 65 mg (43%), pale yellow viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.97 (s, 1H, ArH), 7.92 (d, $^3J_{\text{H-H}}$ = 7.8 Hz, 1H, ArH), 7.81 (d, $^3J_{\text{H-H}}$ = 7.7 Hz, 1H, ArH), 7.61 (t, $^3J_{\text{H-H}}$ = 7.7 Hz, 1H, ArH), 7.32 (q, $^4J_{\text{H-H}}$ =1.0 Hz, 1H, 5-H), 2.44 (s, 3H, SCH_3), 1.98 (d, $^4J_{\text{H-H}}$ = 0.9 Hz, 3H, CH_3); ^{19}F NMR ($CDCl_3$, 376 MHz): δ= − 62.73; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.16, 155.03, 141.52, 139.71, 132.14, 130.82 (q, $^2J_{\text{C-F}}$ = 32.6 Hz), 129.08, 128.78 (q, $^3J_{\text{C-F}}$ = 3.5 Hz), 126.05 (d, $^3J_{\text{C-F}}$ = 3.7 Hz), 123.99, 123.77 (d, $^1J_{\text{C-F}}$ = 270.9 Hz), 121.96, 15.46, 9.66; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{14}H_{12}F_3O_2S$: 301.0510, found: 301.0501.



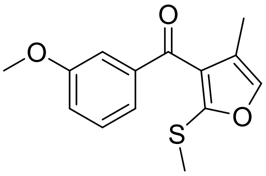
2.1.15. 3-(3-Acetylbenzoyl)-4-methyl-2-methylthio-furan (**2o**). Yield 56 mg (41%), colourless viscous liquid. ^{1}H NMR



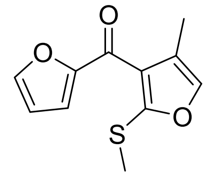
(CDCl$_3$, 400 MHz): δ = 8.29 (t, $^{4}J_{\text{H-H}}$ = 1.5 Hz, 1H, ArH), 8.16 (td, $^{3}J_{\text{H-H}}$ = 7.8 Hz, $^{4}J_{\text{H-H}}$ = 1.5 Hz, 1H, ArH), 7.94 (td, $^{3}J_{\text{H-H}}$ = 7.8 Hz, $^{4}J_{\text{H-H}}$ = 1.4 Hz, 1H, ArH), 7.58 (t, $^{3}J_{\text{H-H}}$ = 7.7 Hz, 1H, ArH), 7.32 (d, $^{4}J_{\text{H-H}}$ = 1.2 Hz, 1H, 5-H), 2.65 (s, 3H, COCH$_3$), 2.43 (s, 3H, SCH$_3$), 1.99 (d, $^{4}J_{\text{H-H}}$ = 1.1 Hz, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 197.34, 190.77, 154.63, 141.44, 139.47, 137.04, 133.34, 131.89, 129.06, 128.88, 124.17, 122.03, 26.79, 15.57, 9.71; HRMS *m/z* [M + H]$^+$ calculated for $C_{15}H_{15}O_3S$: 275.0742. Found: 275.0742.



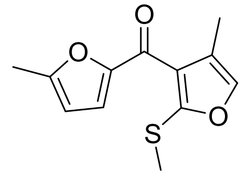
2.1.16. 4-Methyl-3-(3-methylbenzoyl)-2-methylthio-furan (**2p**). Yield 63 mg (51%), colourless viscous liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.57 (s, 1H, ArH), 7.53 (d, $^{3}J_{\text{H-H}}$ = 7.2 Hz, 1H, ArH), 7.38 (d, $^{3}J_{\text{H-H}}$ = 7.5 Hz, 1H, ArH), 7.34 (t, $^{3}J_{\text{H-H}}$ = 7.5 Hz, 1H, ArH), 7.29 (s, 1H, 5-H), 2.41 (s, 6H, ArCH$_3$ and SCH$_3$), 1.98 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 191.95, 153.29, 141.20, 139.10, 138.18, 133.38, 129.60, 128.25, 126.45, 125.27, 122.07, 21.33, 15.91, 9.59; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{14}H_{15}O_2S$: 247.0793, found: 247.0793.



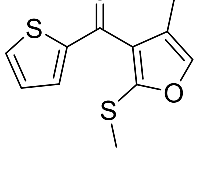
2.1.17. 3-(3-Methoxylbenzoyl)-4-methyl-2-methylthio-furan (**2q**). Yield 83 mg (63%), colourless viscous liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.36 (t, $^{3}J_{\text{H-H}}$ = 7.8 Hz, 1H, ArH), 7.31 (s, 1H, 5-H), 7.30-7.27 (m, 2H, ArH), 7.11 (dd, $^{3}J_{\text{H-H}}$ = 7.2 Hz, $^{4}J_{\text{H-H}}$ = 1.5 Hz, 1H, ArH), 3.86 (s, 3H, OCH$_3$), 2.42 (s, 3H, SCH$_3$), 1.99 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 191.50, 159.63, 153.61, 141.21, 140.40, 129.40, 125.00, 122.03, 121.90, 119.04, 113.19, 55.41, 15.84, 9.60; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{14}H_{15}O_3S$: 263.0742, found: 263.0736.



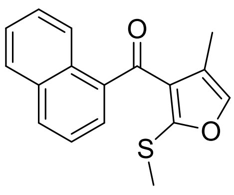
2.1.18. 3-(Furan-2-carbonyl)-4-methyl-2-methylthio-furan (**2r**). Yield 52 mg (47%), colourless viscous liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.64 (s, 1H, ArH), 7.29 (q, $^{4}J_{\text{H-H}}$ = 0.6 Hz, 1H, 5-H), 7.18 (d, $^{3}J_{\text{H-H}}$ = 3.5 Hz, 1H, ArH), 6.58 (dd, $^{3}J_{\text{H-H}}$ = 3.4 Hz, $^{4}J_{\text{H-H}}$ = 1.5 Hz, 1H, ArH), 2.44 (s, 3H, SCH$_3$), 2.07 (d, $^{4}J_{\text{H-H}}$ = 0.6 Hz, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 178.03, 152.82, 152.26, 146.74, 141.36, 125.33, 121.72, 119.44, 112.43, 16.33, 9.21; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{11}H_{11}O_3S$: 233.0429, found: 233.0429.



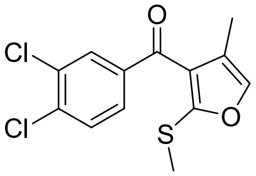
2.1.19. 4-Methyl-3-(5-methylfuran-2-carbonyl)-2-methylthio-furan (**2s**). Yield 59 mg (50%), pale yellow viscous liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.28 (q, $^{4}J_{\text{H-H}}$ = 1.1 Hz, 1H, 5-H), 7.06 (d, $^{3}J_{\text{H-H}}$ = 3.4 Hz, 1H, ArH), 6.20 (d, $^{3}J_{\text{H-H}}$ = 3.3 Hz, 1H, ArH), 2.42 (s, 6H, ArCH$_3$ and SCH$_3$), 2.06 (d, $^{4}J_{\text{H-H}}$ = 1.0 Hz, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 177.43, 158.51, 151.63, 150.88, 141.34, 125.89, 122.02, 121.80, 109.24, 16.74, 14.09, 9.12; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{12}H_{13}O_3S$: 237.0585, found: 237.0583.



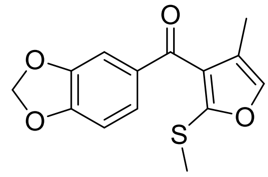
2.1.20. 4-Methyl-2-methylthio-3-(thien-2-carbonyl)-furan (**2t**). Yield 64 mg (54%), pale yellow viscous liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.71 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 1H, ArH), 7.59 (d, $^3J_{H\text{-}H}$ = 3.6 Hz, 1H, ArH), 7.30 (s, 1H, 5-H), 7.13 (d, $^3J_{H\text{-}H}$ = 4.1 Hz, 1H, ArH), 2.44 (s, 3H, SCH$_3$), 2.05 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 183.31, 150.64, 144.67, 141.51, 134.55, 134.47, 127.96, 126.63, 121.74, 16.90, 9.17; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{11}H_{11}O_2S_2$: 239.0200, found: 239.0200.



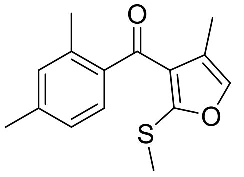
2.1.21. 4-Methyl-2-methylthio-3-(1-naphthoyl)-furan (**2u**). Yield 72 mg (51%), colourless viscous liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 8.10-8.08 (m, 1H, ArH), 7.97 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 1H, ArH), 7.91-7.88 (m, 1H, ArH), 7.56-7.48 (m, 4H, ArH), 7.24 (q, $^4J_{H\text{-}H}$ = 1.2 Hz, 1H, 5-H), 2.41 (s, 3H, SCH$_3$), 1.78 (d, $^4J_{H\text{-}H}$ = 1.2 Hz, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 192.52, 158.20, 140.87, 138.26, 133.69, 130.96, 130.17, 128.37, 127.21, 126.52, 126.41, 125.22, 124.88, 124.01, 122.12, 14.28, 9.81; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{17}H_{15}O_2S$: 283.0793, found: 283.0791.



2.1.22. 3-(3,4-Dichlorobenzoyl)-4-methyl-2-methylthio-furan (**2v**). Yield 60 mg (40%), brown solid. mp: 59-60 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.81 (d, $^4J_{H\text{-}H}$ = 1.6 Hz, 1H, ArH), 7.57 (dd, $^3J_{H\text{-}H}$ = 8.3 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz, 1H, ArH), 7.54 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H, ArH), 7.30 (q, $^4J_{H\text{-}H}$ = 1.2 Hz, 1H, 5-H), 2.45 (s, 3H, SCH$_3$), 2.00 (d, $^4J_{H\text{-}H}$ = 1.2 Hz, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 189.12, 154.71, 141.51, 138.69, 136.89, 132.89, 131.06, 130.57, 128.14, 123.96, 121.96, 15.62, 9.68; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{13}H_{11}Cl_2O_2S$: 300.9857, found: 300.9845.

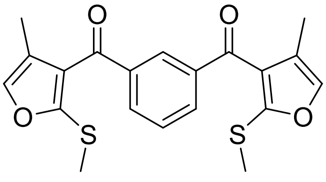


2.1.23. 4-Methyl-3-(3,4-methylenedioxybenzoyl)-2-methylthio-furan (**2w**). Yield 72 mg (52%), pale yellow viscous liquid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.34 (dd, $^3J_{H\text{-}H}$ = 8.1 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz, 1H, ArH), 7.31 (d, $^4J_{H\text{-}H}$ = 1.6 Hz, 1H, ArH), 7.29 (q, $^4J_{H\text{-}H}$ = 1.2 Hz, 1H, 5-H), 6.84 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 1H, ArH), 6.06 (s, 2H, OCH$_2$O), 2.40 (s, 3H, SCH$_3$), 1.99 (d, $^4J_{H\text{-}H}$ = 1.2 Hz, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 189.98, 151.79, 151.52, 148.10, 141.30, 133.35, 126.23, 126.00, 122.00, 108.83, 107.78, 101.90, 16.44, 9.37; HRMS (ESI) *m/z* [M + H]$^+$ calculated for $C_{14}H_{13}O_4S$: 277.0535, found: 277.0528.



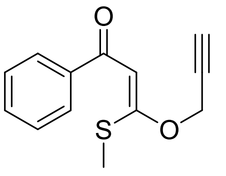
2.1.24. 4-Methyl-3-(2,4-dimethylbenzoyl)-2-methylthio-furan (**2x**). Yield 77 mg (59%), pale yellow solid. mp: 61-62 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.22 (d, $^4J_{H\text{-}H}$ = 1.2 Hz, 1H, 5-H), 7.19 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 1H, ArH), 7.06 (s, 1H, ArH), 7.03 (d, $^3J_{H\text{-}H}$ = 7.9 Hz, 1H, ArH), 2.44 (s, 3H, SCH$_3$), 2.36 (s, 3H, ArCH$_3$), 2.34 (s, 3H, ArCH$_3$), 1.87 (d, $^4J_{H\text{-}H}$ = 1.2 Hz, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 193.29, 156.92, 140.74, 140.50, 137.58, 136.02, 131.76, 128.24, 126.30, 123.88, 122.04, 21.45, 19.61, 14.35, 9.72; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{15}H_{17}O_2S$: 261.0949, found: 261.0945.

2.2. General procedure for the synthesis of 1,3-bis[(4-methyl-2-methylthio) furan-3-carbonyl]benzene (2y)



t-BuOK (246 mg, 2.2 mmol) and propargyl alcohol **b** (123 mg, 2.2 mmol) in dry THF (20 mL) were stirred at room temperature under N_2 for 15 min. Then, **1y** (185 mg, 0.5 mmol) was added and the reaction mixture was stirred at room temperature for 4 h. Water (15 mL) was added and the whole mixture was extracted with ethyl acetate (3×15 mL), and the combined organic extract was washed with brine (2×15 mL), dried over $MgSO_4$. The solvent was evaporated under vacuum and the residue was purified by column chromatography over silica gel using ethyl acetate/petroleum ether (1:80, v/v) to generate 1,3-bis[(4-methyl-2-methylthio)furan-3-carbonyl]benzene (**2y**) as pale yellow viscous liquid (68 mg, 35%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 8.06 (s, 1H, ArH), 7.91 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 2H, ArH), 7.56 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 1H, ArH), 7.29 (s, 2H, 5-H), 2.43(s, 6H, SCH$_3$), 1.98 (s, 6H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 190.94, 154.68, 141.39, 139.35, 132.61, 129.70, 128.50, 124.41, 121.94, 15.62, 9.77; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{20}H_{19}O_4S_2$: 387.0725, found: 387.0724.

2.3. Synthesis of 3-benzoyl-4-methyl-2-methylthio-furan 2a from 3



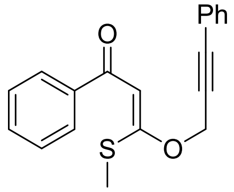
3-methylthio-1-phenyl-3-(prop-2-ynyloxy)prop-2-en-1-one (3). A similar procedures as reported references[7-9], **1a** (2.243 g, 10 mmol) and dimethylsulfate (2.523 g, 30 mmol) were stirred at 80 °C for 3h. The reaction was cooled to room temperature, diluted with dry diethyl ether (20 mL). 70% perchloric acid (1.435 g, 10 mmol) was added and the mixture was stirred for 10 min to form solid. The yellow dimethylsulfonium perchlorate salt was collected by filtration, washed using diethyl ether (3.286 g, 97%). A stirred suspension of prop-2-ynyl alcohol (0.841 g, 15 mmol) and anhydrous K_2CO_3 (6.219 g, 45 mmol) in anhydrous ethyl methyl ketone (40 mL) was refluxed for 3 h. The resulting mixture was cooled to 0-5°C and dimethylsulfonium perchlorate salt (1.694 g, 5 mmol) was added in small portions with stirring. The mixture was further stirred at the same temperature for 2 h and then for a further 10 h at room temperature, filtered, washed with ethyl methyl ketone, and the filtrate concentrated under reduced pressure. The residue was added water (30 mL) and extracted with ethyl acetate (2×30 mL**)**. The combined extracts were washed with brine (2×40 mL), dried over Na_2SO_4. The solvent was evaporated under vacuum and the residue was purified by column chromatography silica gel eluting with EtOAc/ petroleum (1/70, v/v) to give **3** (0.48 g, 50%). Pale yellow solid; ^{1}H NMR (CDCl$_3$, 400 MHz) δ = 7.90 (dd, $^3J_{H\text{-}H}$ = 7.0 Hz, $^4J_{H\text{-}H}$ = 1.5 Hz, 2H, ArH), 7.50 (td, $^3J_{H\text{-}H}$ = 7.3

Hz, ${}^4J_{\text{H-H}}$ = 1.5 Hz, 1H, ArH), 7.44 (t, ${}^3J_{\text{H-H}}$ = 7.6 Hz, 2H, ArH), 6.55 (s, 1H, 2-H), 4.83 (d, ${}^4J_{\text{H-H}}$ = 2.4 Hz, 2H, CH_2), 2.70 (t, ${}^4J_{\text{H-H}}$ = 2.4 Hz, ≡CH), 2.36 (s, 3H, SCH_3).

3-benzoyl-4-methyl-2-methylthio-furan 2a. *t*-BuOK (62 mg, 0.55 mmol) in 10 mL of dry THF was stirred at room temperature under N_2 for 15 min. Then, **3** (116 mg, 0.5 mmol) was added and the mixture was stirred at room temperature for 1.5 h. Water (10 mL) was added and the whole mixture was extracted with ethyl acetate (3×15 mL), and the combined organic extract was washed with brine (2×15 mL), dried over $MgSO_4$. The solvent was evaporated under vacuum and the residue was purified by column chromatography over silica gel using ethyl acetate/petroleum ether (1:100, v/v) to give 4-Methyl-3-benzoyl-2-methylthiofuran **2a** (73 mg, 63%).

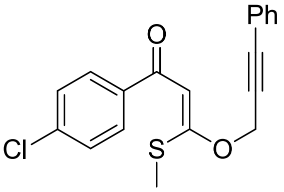
2.4. General procedure for the synthesis of 1-aryol-3-methylthio-3-(3-phenylprop-2-ynyloxy)prop-2-en-1-one (4a-e)

2.4.1. 3-methylthio-1-phenyl-3-(3-phenylprop-2-ynyloxy)prop-2-en-1-one (**4a**)



Intermediate **4a** was synthesized following the general procedure of **3.** Using 3-phenylpropargyl alcohol **c** (0.793 g, 6 mmol), K_2CO_3 (2.488 g, 18 mmol), (3-(phenyl)-1-(methylthio)-3-oxo-prop-1-en-1-yl)dimethylsulfonium perchlorate salt (0.678 g, 2 mmol) in anhydrous ethyl methyl ketone (20 mL), **4a** was obtained as yellow solid (0.247 g, 40%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.93 (d, ${}^3J_{\text{H-H}}$ = 7.2 Hz, 2H, ArH), 7.49-7.46 (m, 3H, ArH), 7.43 (t, ${}^3J_{\text{H-H}}$ = 7.3 Hz, 2H, ArH), 7.37-7.31 (m, 3H, ArH), 6.68 (s, 1H, C=CH), 5.06 (s, 2H, CH_2), 2.38 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 188.11, 174.68, 139.48, 131.91, 131.71, 129.23, 128.49, 128.43, 127.51, 121.60, 95.85, 89.22, 81.45, 59.82, 12.66; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{19}H_{17}O_2S$: 309.0949, found: 309.0946.

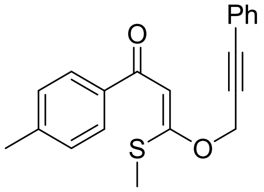
2.4.2. 1-(4-chlorophenyl)-3-methylthio-3-(3-phenylprop-2-ynyloxy)prop-2-en-1-one (**4b**)



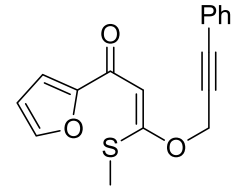
Intermediate **4b** was synthesized following the general procedure of **3.** Using 3-phenylpropargyl alcohol **c** (0.793 g, 6 mmol), K_2CO_3 (2.488 g, 18 mmol), (3-(4-chlorophen- yl)-1-(methylthio)-3-oxoprop-1-en-1-yl)dimethylsulfonium perchlorate salt (0.747 g, 2 mmol) in anhydrous ethyl methyl ketone (20 mL), **4b** was obtained as yellow solid (0.425 g, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.86 (d, ${}^3J_{\text{H-H}}$ = 8.5 Hz, 2H, ArH), 7.45 (d, ${}^3J_{\text{H-H}}$ = 7.9 Hz, 2H, ArH), 7.40-7.31 (m, 5H, ArH), 6.62 (s, 1H, C=CH), 5.06 (s, 2H, CH_2), 2.38 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 186.66, 175.35, 137.89, 137.82, 131.87, 129.29, 128.92, 128.67, 128.52, 121.53, 95.47, 89.37, 81.35, 59.93, 12.66; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{19}H_{16}ClO_2S$: 343.0560, found: 343.0555.

2.4.3. 1-(4-methylphenyl)-3-methylthio-3-(3-phenylprop-2-ynyloxy)prop-2-en-1-one

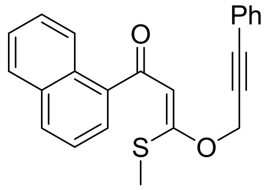
(**4c**) Intermediate **4c** was synthesized following the general procedure of **3.** Using 3-phenylpropargyl alcohol **c** (0.793 g, 6 mmol), K_2CO_3 (2.488 g, 18 mmol), (3-(4-methylphenyl)-1-(methylthio)-3-oxoprop-1-en-1-yl)dimethylsulfonium perchlo- rate salt (0.706 g, 2 mmol) in anhydrous ethyl methyl ketone (20 mL), **4c** was obtained as yellow solid (0.316 g, 49%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.84 (d, $^{3}J_{\text{H-H}}$ = 8.2 Hz, 2H, ArH), 7.46 (dd, $^{3}J_{\text{H-H}}$ = 8.0 Hz, $^{4}J_{\text{H-H}}$ = 1.9 Hz, 2H, ArH), 7.37-7.31 (m, 3H, ArH), 7.23 (d, $^{3}J_{\text{H-H}}$ = 8.2 Hz, 2H, ArH), 6.66 (s, 1H, C=CH), 5.05 (s, 2H, CH_2), 2.39 (s, 3H, $ArCH_3$) 2.38 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 187.83, 174.21, 142.26, 136.85, 131.91, 129.19, 129.12, 128.48, 127.60, 121.64, 95.80, 89.14, 81.53, 59.76, 21.57, 12.66; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{20}H_{19}O_2S$: 323.1106, found: 323.1103.



2.4.4. 1-(furan-2-yl)-3-methylthio-3-(3-phenylprop-2-ynyloxy)prop-2-en-1-one (**4d**) Intermediate **4d** was synthesized following the general procedure of **3.** Using 3-phenylpropargyl alcohol **c** (0.793 g, 6 mmol), K_2CO_3 (2.488 g, 18 mmol), (3-(furan-2-yl)-1-(methylthio)-3-oxo-prop-1-en-1-yl)dimethylsulfonium perchlorate salt (0.658 g, 2 mmol) in anhydrous ethyl methyl ketone (20 mL), **4d** was obtained as yellow solid (0.269 g, 45%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.51 (s, 1H, ArH), 7.46 (dd, $^{3}J_{\text{H-H}}$ = 8.4 Hz, $^{4}J_{\text{H-H}}$ = 1.6 Hz, 2H, ArH), 7.37-7.30 (m, 3H, ArH), 7.14 (d, $^{3}J_{\text{H-H}}$ = 3.4 Hz, 1H, ArH), 6.58 (s, 1H, C=CH), 6.50 (dd, $^{3}J_{\text{H-H}}$ = 3.5 Hz, $^{3}J_{\text{H-H}}$ = 3.5 Hz, 1H, ArH), 5.04 (s, 2H, CH_2), 2.37 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 177.11, 174.50, 154.24, 144.61, 131.93, 129.17, 128.43, 121.69, 114.44, 112.31, 95.16, 89.09, 81.37, 59.92, 12.63; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{17}H_{15}O_3S$: 299.0742, found: 299.0732.



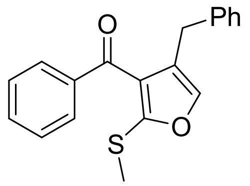
2.4.4. 1-(naphthalen-1-yl)-3-methylthio-3-(3-phenylprop-2-ynyloxy)prop-2-en-1-one (**4e**) Intermediate **4e** was synthesized following the general procedure of **3.** Using 3-phenylpropargyl alcohol **c** (0.793 g, 6 mmol), K_2CO_3 (2.488 g, 18 mmol), (3-(naphthalen-1-yl)-1-(methylthio)-3-oxoprop-1-en-1-yl)dimethylsulfonium perchlorate salt (0.778 g, 2 mmol) in anhydrous ethyl methyl ketone (20 mL), **4e** was obtained as yellow solid (0.373 g, 52%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.46 (d, $^{3}J_{\text{H-H}}$ = 8.5 Hz, 1H, ArH), 7.91 (d, $^{3}J_{\text{H-H}}$ = 8.2 Hz, 1H, ArH), 7.86 (d, $^{3}J_{\text{H-H}}$ = 8.0 Hz, 1H, ArH), 7.72 (d, $^{3}J_{\text{H-H}}$ = 7.0 Hz, 1H, ArH), 7.49-7.41 (m, 5H, ArH), 7.39-7.31 (m, 3H, ArH), 6.46 (s, 1H, C=CH), 4.99 (s, 2H, CH_2), 2.43 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.92, 174.10, 139.47, 133.80, 131.91, 130.81, 130.13, 129.22, 128.47, 128.26, 126.96, 126.16, 126.00, 125.97, 124.70, 121.63, 100.35, 89.17, 81.49, 59.82, 12.61; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{23}H_{19}O_2S$: 359.1106, found: 359.1098.



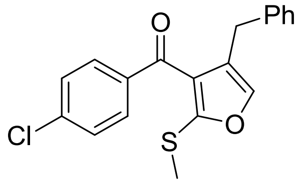
2.5. General procedure for the synthesis of 3-aryol-4-benzyl-2-methylthio-furan (5a-e)

t-BuOK (62 mg, 0.55 mmol) in 10 mL of dry THF was stirred at room temperature under N_2 for 15 min. Then, **4a-e** (0.5 mmol) was added and the mixture was stirred at room temperature for 2-3 hours. Water (10 mL) was added and the whole mixture was extracted with ethyl acetate (3×15 mL), and the combined organic extract was washed with brine (2×15 mL), dried over $MgSO_4$. The solvent was evaporated under vacuum and the residue was purified by column chromatography over silica gel using ethyl acetate/petroleum ether (1:100, v/v)) as eluent to give the desired product **5a-e** in excellent purity. The physical and spectral data of the synthesized compounds are listed as follows.

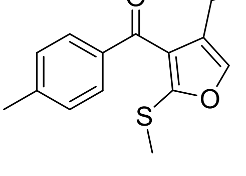
2.5.1 3-benzoyl-4-benzyl-2-methylthio-furan (**5a**). Yield 85 mg (55%), yellow viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.67 (dd, $^3J_{H\text{-}H}$ = 7.0 Hz, $^4J_{H\text{-}H}$ = 1.4 Hz, 2H, ArH), 7.55 (tt, $^3J_{H\text{-}H}$ = 7.4 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz, 1H, ArH), 7.43 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, ArH), 7.21 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H, ArH), 7.16-7.13 (m, 2H, ArH, 5-H), 7.08 (d, $^3J_{H\text{-}H}$ = 7.0 Hz, 2H, ArH), 3.78 (s, 2H, CH_2), 2.40 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.86, 153.76, 141.98, 139.17, 139.12, 132.64, 129.09, 128.75, 128.40, 126.97, 126.31, 124.43, 30.68, 15.98; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{19}H_{17}O_2S$: 309.0949, found: 309.0948.



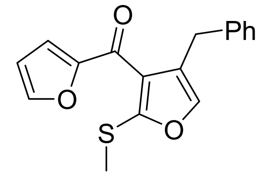
2.5.2 4-benzyl-3-(4-chlorobenzoyl)-2-methylthio-furan (**5b**). Yield 115 mg (67%), yellow viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.60 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H, ArH), 7.39 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H, ArH), 7.21 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 2H, ArH), 7.16-7.13 (m, 2H, 5-H, ArH), 7.07 (d, $^3J_{H\text{-}H}$ = 7.0 Hz, 2H, ArH), 3.78 (s, 2H, CH_2), 2.41 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 190.53, 153.81, 142.08, 139.02, 138.97, 137.35, 130.46, 128.69, 128.41, 126.89, 126.34, 124.09, 30.59, 15.94; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{19}H_{16}ClO_2S$: 343.0560, found: 343.0558.



2.5.3 4-benzyl-3-(4-methylbenzoyl)-2-methylthio-furan (**5c**). Yield 97 mg (60%), yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.61 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 2H, ArH), 7.24-7.19 (m, 4H, 5-H, ArH), 7.15 (tt, $^3J_{H\text{-}H}$ = 7.2 Hz, $^4J_{H\text{-}H}$ = 2.3 Hz, 1H, ArH), 7.12-7.09 (m, 3H, ArH), 3.78 (s, 2H, CH_2), 2.42 (s, 3H, $ArCH_3$), 2.39 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.56, 152.66, 143.60, 141.95, 139.24, 136.38, 129.42, 129.12, 128.78, 128.40, 127.07, 126.29, 124.99, 30.62, 21.79, 16.26; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{20}H_{19}O_2S$: 323.1106, found: 323.1103.

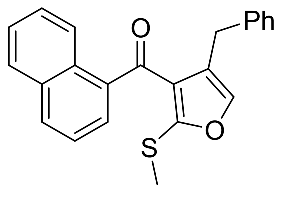


2.5.4 4-benzyl-3-(furan-2-carbonyl)-2-methylthio-furan (**5d**). Yield 60 mg (40%), yellow viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.62 (s, 1H, ArH), 7.23 (t, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, ArH), 7.16 (t, $^3J_{H\text{-}H}$ = 7.1



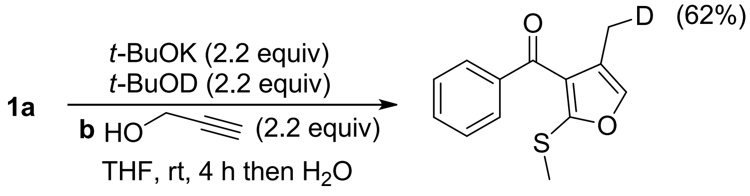
Hz, 3H, ArH), 7.12-7.11 (m, 2H, 5-H, ArH), 6.54 (dd, $^3J_{H\text{-}H}$ = 3.5 Hz, $^3J_{H\text{-}H}$ = 3.5 Hz, 1H, ArH), 3.85 (s, 2H, CH_2), 2.43 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.07, 152.86, 152.32, 146.73, 142.06, 139.13, 128.74, 128.40, 126.75, 126.32, 124.79, 119.45, 112.48, 30.42, 16.50; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{17}H_{15}O_3S$: 299.0742, found: 299.0741.

2.5.5 4-benzyl-2-methylthio-3-(1-naphthoyl)-furan (**5e**). Yield 113 mg (63%), yellow viscous liquid. ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.96 (t, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, ArH), 7.87 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 1H, ArH), 7.52-7.43 (m, 4H, ArH), 7.17-7.10 (m, 3H, ArH), 7.08 (s, 1H, 5-H), 7.99 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, ArH), 3.67 (s, 2H, CH_2), 2.36 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 192.43, 158.26, 141.80, 139.16, 138.02, 133.74, 131.26, 130.27, 128.71, 128.32, 127.26, 126.93, 126.90, 126.41, 126.29, 125.24, 124.83, 123.61, 30.89, 14.52; HRMS (ESI) *m/z* $[M + H]^+$ calculated for $C_{23}H_{19}O_2S$: 359.1106, found: 359.1107.



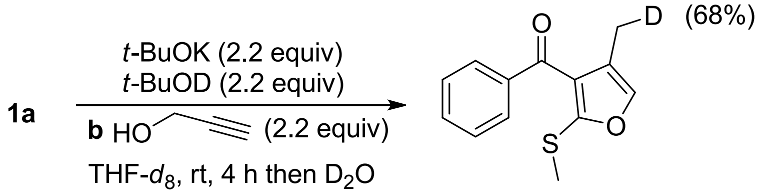
3. Mechanistic investigation.

*Cyclization of **1a** with added t-BuOD*: *t*-BuOK (123 mg, 1.1 mmol), propargyl alcohol **b** (62 mg, 1.1 mmol) and *t*-BuOD (83 mg, 1.1 mmol) in dry THF (10 mL) were stirred at room temperature under N_2 for 15 min. Then, **1a** (112 mg, 0.5 mmol) was added and the reaction mixture was stirred for 4 h at room temperature. Water (10 mL) was added and the whole mixture was extracted with ethyl acetate (3×15 mL), and the combined organic extract was washed with brine (2×15 mL), dried over $MgSO_4$. The solvent was evaporated under vacuum and the residue was purified by column chromatography over silica gel using ethyl acetate/petroleum ether (1:100, v/v) to give **2aa-*d*** (47 mg, 62% atom D, yield 40%). ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.73 (dd, $^3J_{H\text{-}H}$ = 7.1 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz, 2H, ArH), 7.56 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 1H, ArH), 7.46 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 2H, ArH), 7.29 (s, 1H, 5-H), 2.42 (s, 3H, SCH_3), 1.97-1.96 (m, 2.38H, CH_3).



2aa-*d*

*Cyclization of **1a** using deuterated reagents*: *t*-BuOK (123 mg, 1.1 mmol), propargyl alcohol **b** (62 mg, 1.1 mmol) and *t*-BuOD (83 mg, 1.1 mmol) in dry THF-d_8 (10 mL) were stirred at room temperature under N_2 for 15 min. Then, **1a** (112 mg, 0.5 mmol) was added and the reaction mixture was stirred for 4 h at room temperature. D_2O (10 mL) was added and the whole mixture was extracted with ethyl acetate (3×15 mL), and the combined organic extract was washed with brine (2×15 mL), dried over $MgSO_4$. The solvent was evaporated under vacuum and the residue was purified by column chromatography over silica gel using ethyl acetate/petroleum ether (1:100, v/v) to give **2ab-*d*** (42 mg, 68% atom D, yield 36%) ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.74 (dd, $^3J_{H-H}$ = 7.0 Hz, $^4J_{H-H}$ = 1.4 Hz, 2H, ArH), 7.57 (tt, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-H}$ = 1.3 Hz, 1H, ArH), 7.46 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, ArH), 7.29 (s, 1H, 5-H), 2.42 (s, 3H, SCH_3), 1.97-1.95 (m, 2.32H, CH_3).



2ab-*d*

3. ^{1}H, ^{19}F and ^{13}C NMR Spectra

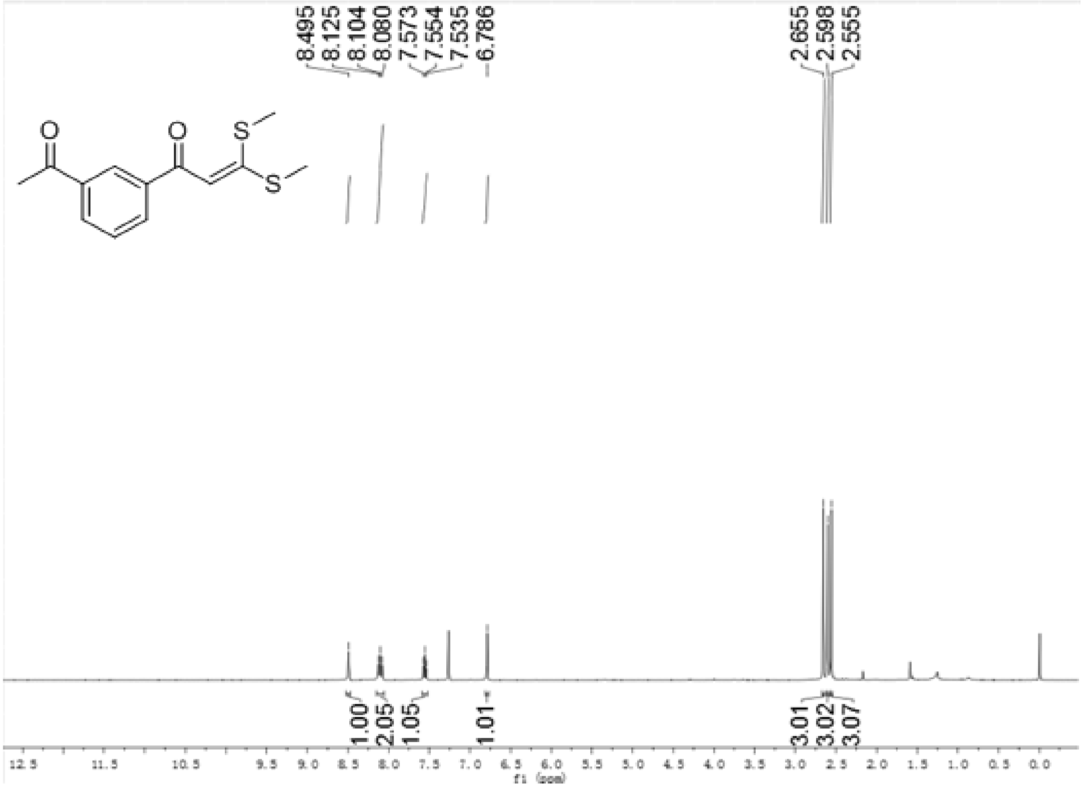


Figure S1. ^{1}H NMR spectra of 1-(3-acetylphenyl)-3,3-bis(methylthio)-2-propen-1-one (**1o**) in $CDCl_3$.

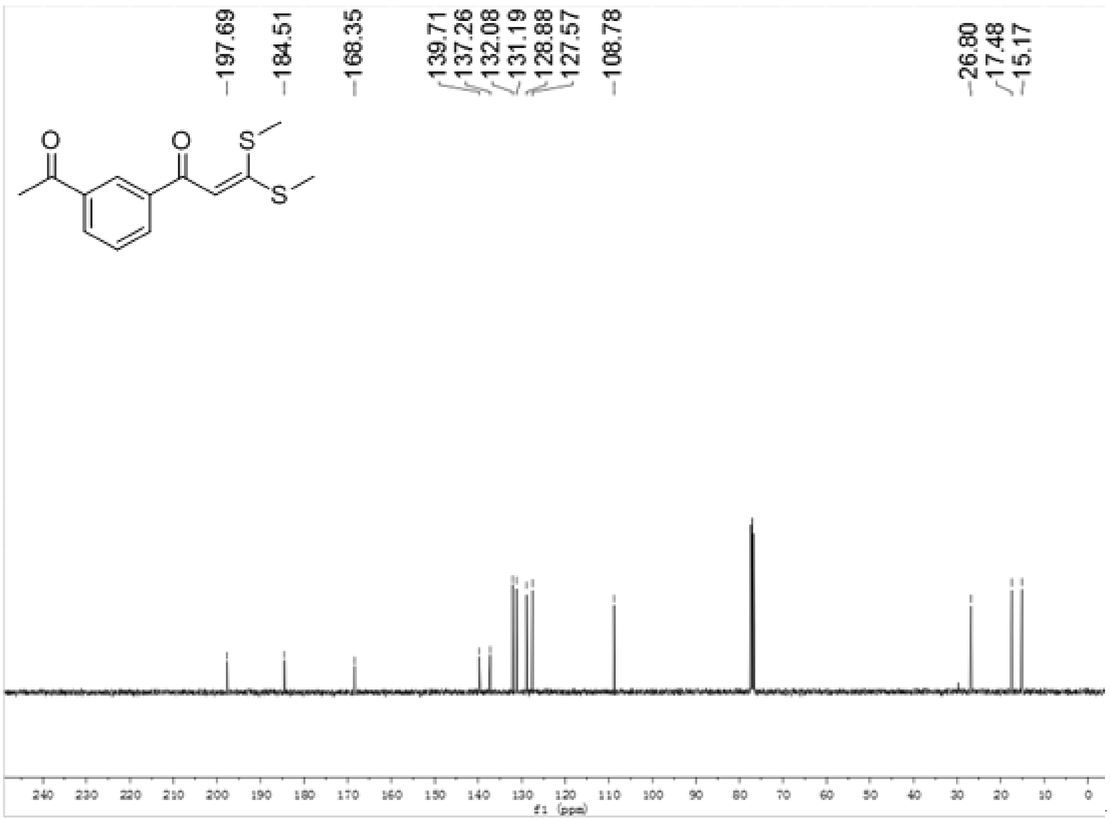


Figure S2. ^{13}C NMR spectra of 1-(3-acetylphenyl)-3,3-bis(methylthio)-2-propen-1-one (**1o**) in $CDCl_3$.

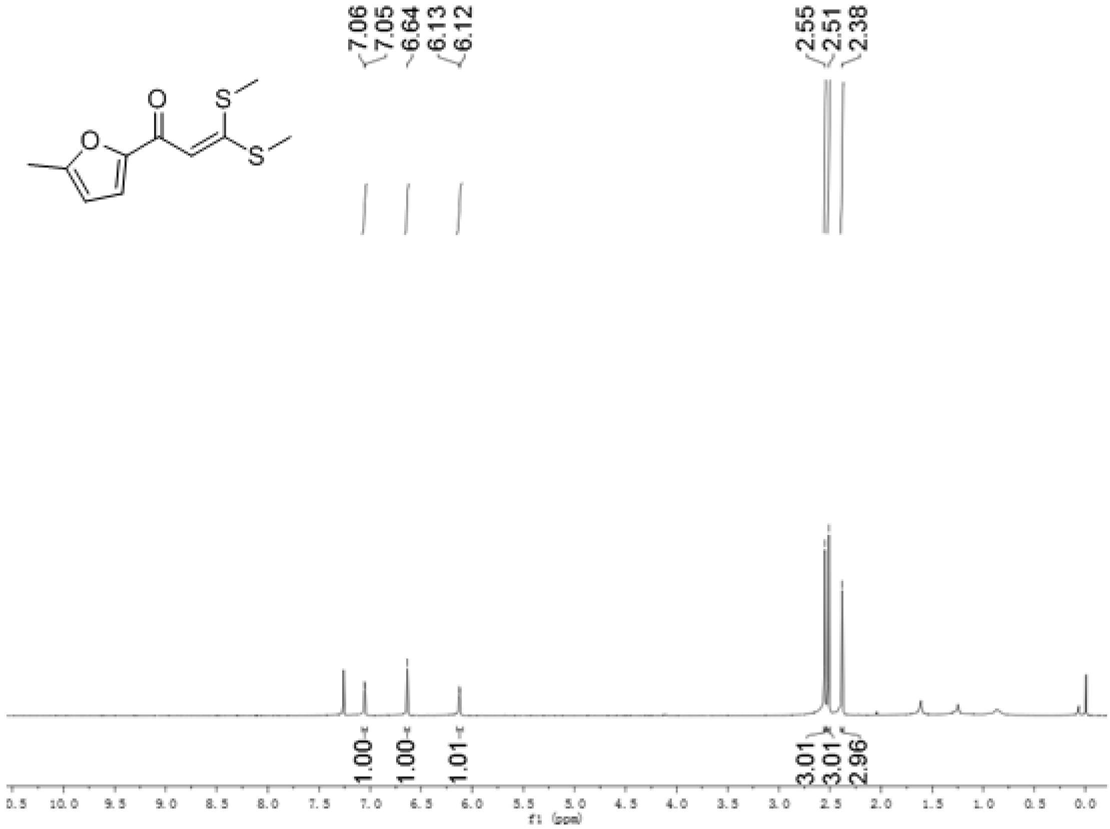


Figure S3. ^{1}H NMR spectra of 1-(5-methylfuran-2-yl)-3,3-bis(methylthio)-2-propen-1-one (**1s**) in $CDCl_3$.

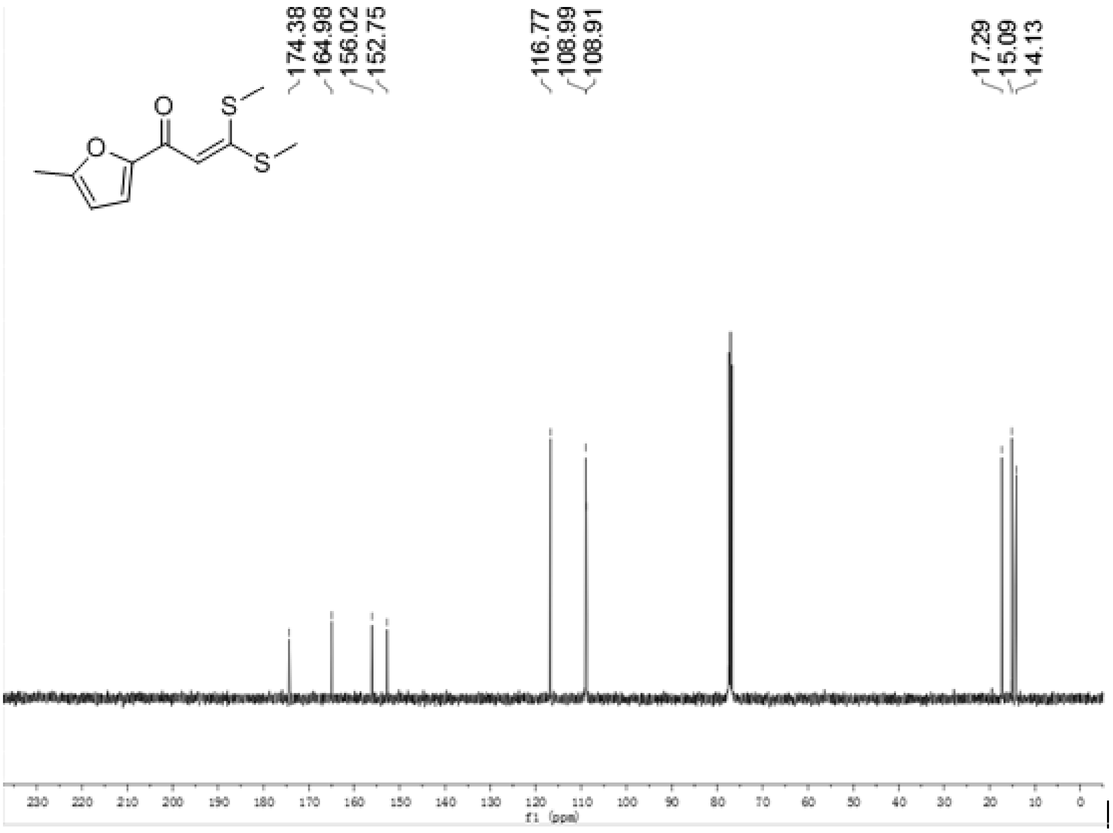


Figure S4. ^{13}C NMR spectra of 1-(5-methylfuran-2-yl)-3,3-bis(methylthio)-2-propen-1-one (**1s**) in $CDCl_3$.

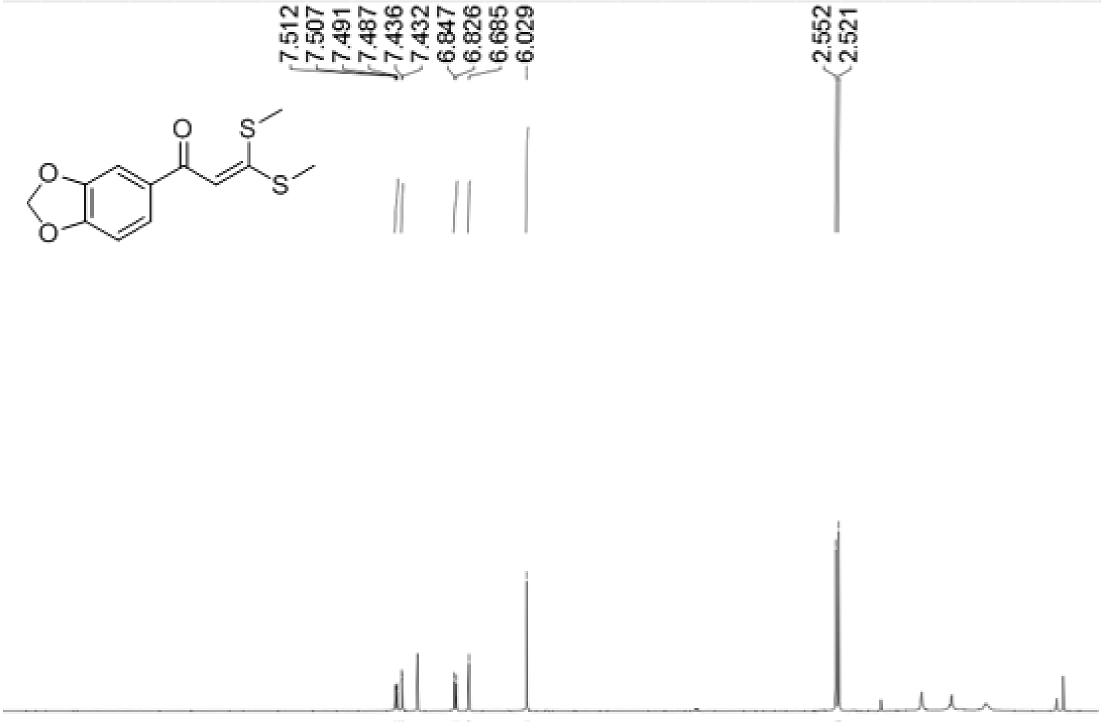


Figure S5. ^{1}H NMR spectra of 3,3-bis(methylthio)-1-[3,4-(methylenedioxy)phenyl]-2-propen-1-one (**1w**) in $CDCl_3$.

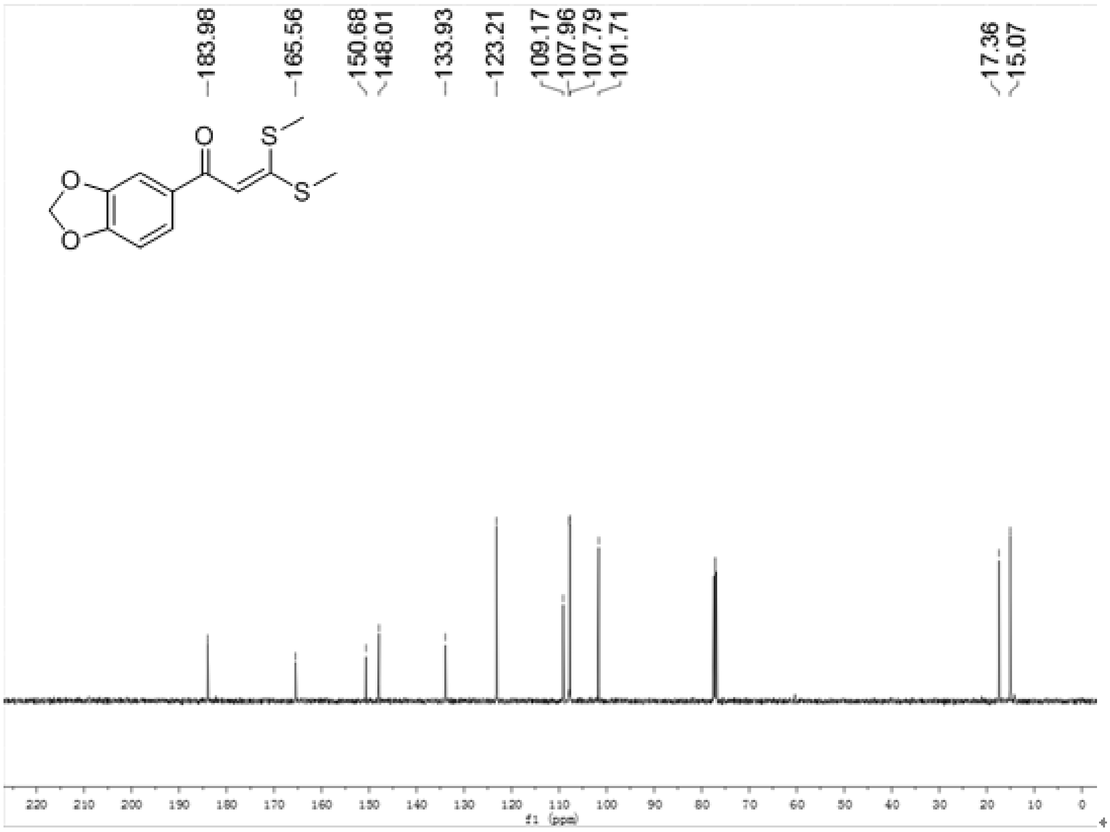


Figure S6. ^{13}C NMR spectra of 3,3-bis(methylthio)-1-[3,4-(methylenedioxy)phenyl]-2-propen-1-one (**1w**) in $CDCl_3$.

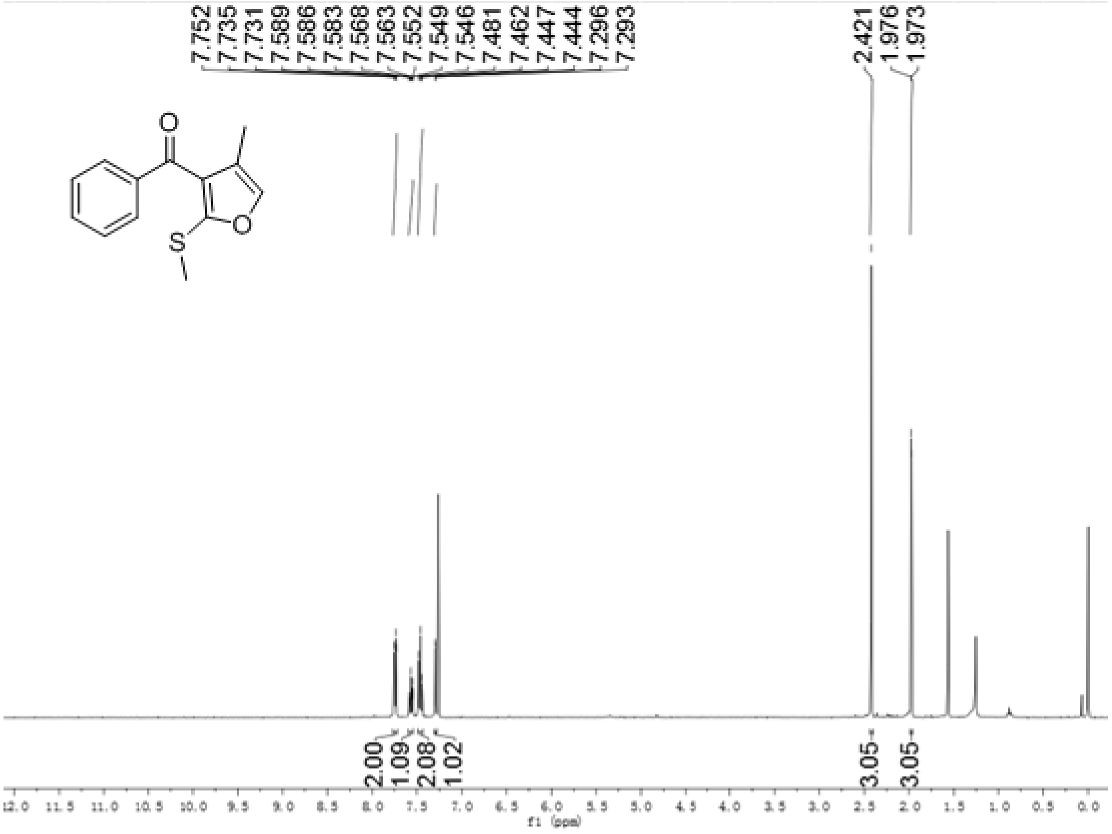


Figure S7. ^{1}H NMR spectra of 3-benzoyl-4-methyl-2-methylthio-furan (**2a**) in $CDCl_3$.

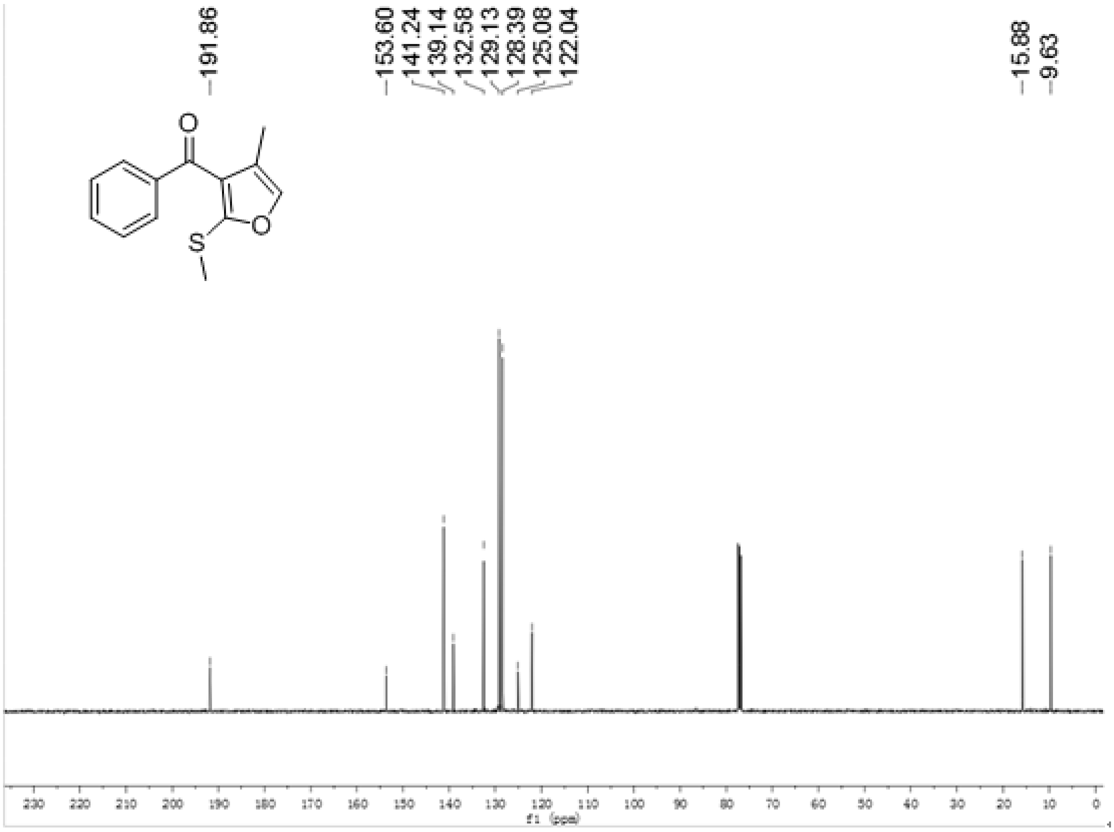


Figure S8. ^{13}C NMR spectra of 3-benzoyl-4-methyl-2-methylthio-furan (**2a**) in CDCl$_3$.

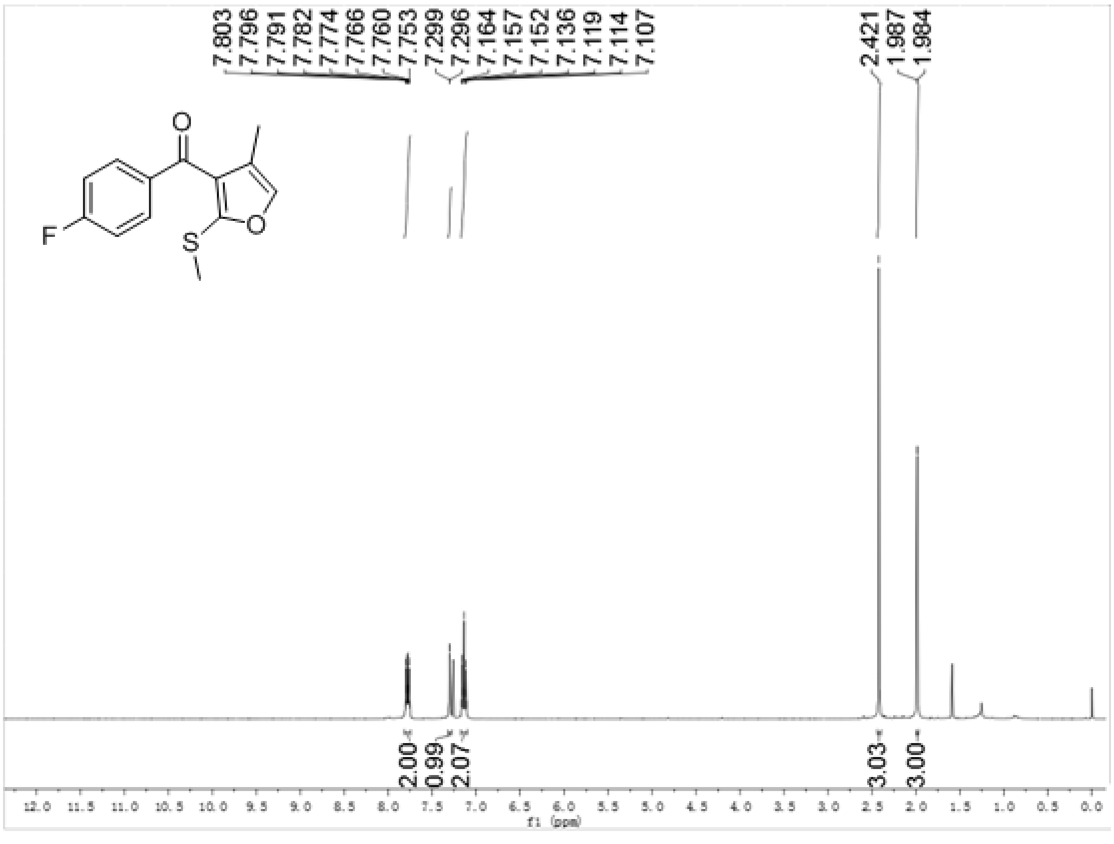


Figure S9. ^{1}H NMR spectra of 3-(4-flourbenzoyl)-4-methyl-2-methylthio-furan (**2b**) in CDCl$_3$.

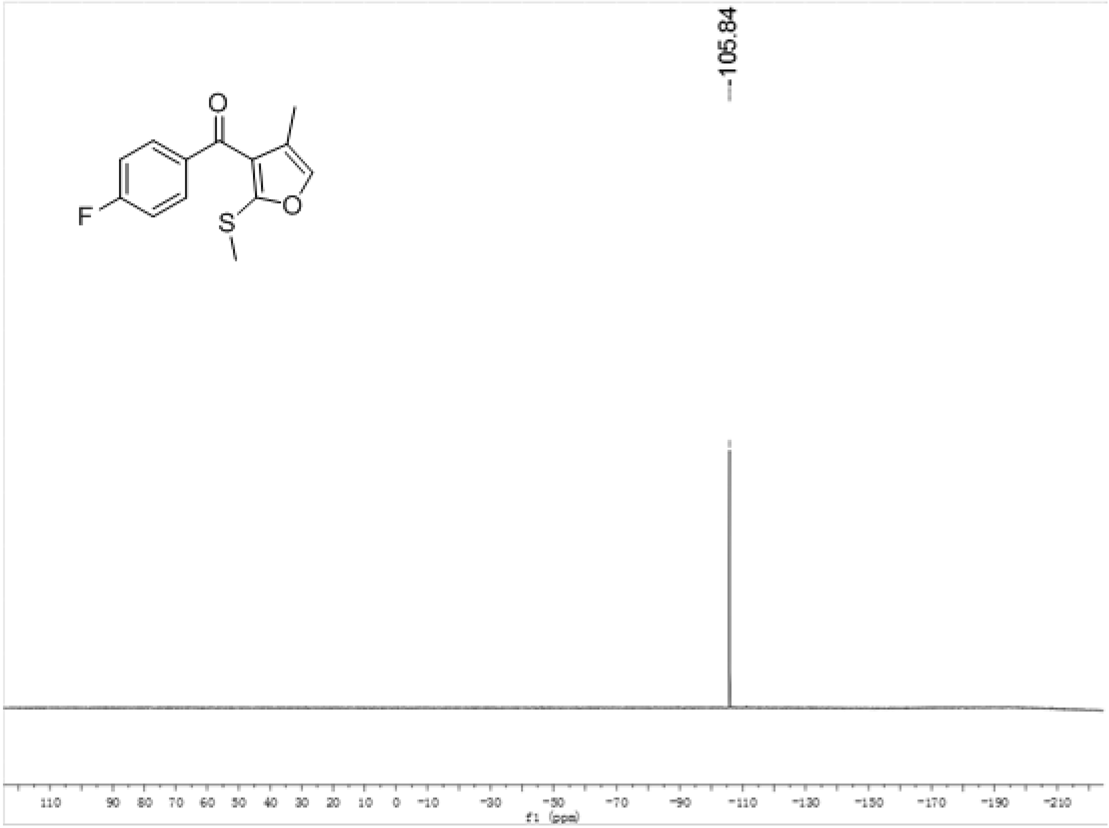


Figure S10. ^{19}F NMR spectra of 3-(4-flourbenzoyl)-4-methyl-2-methylthio-furan (**2b**) in $CDCl_3$.

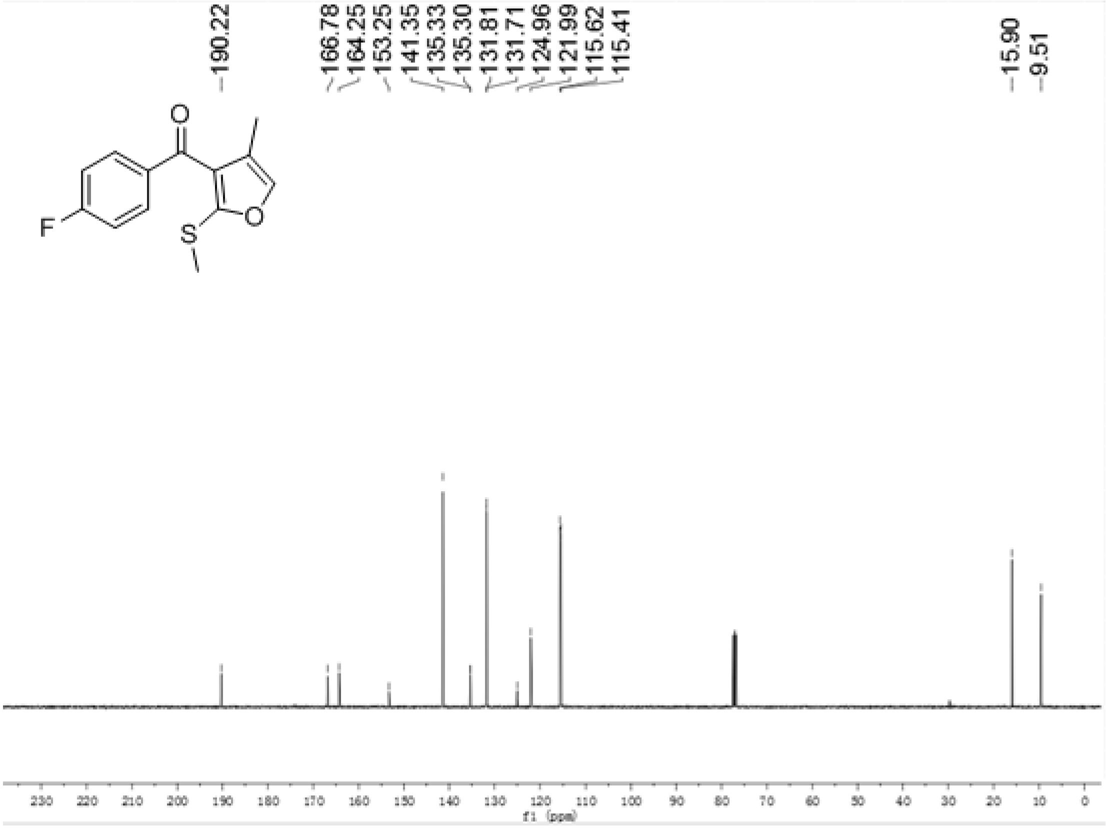


Figure S11. ^{13}C NMR spectra of 3-(4-flourbenzoyl)-4-methyl-2-methylthio-furan (**2b**) in $CDCl_3$.

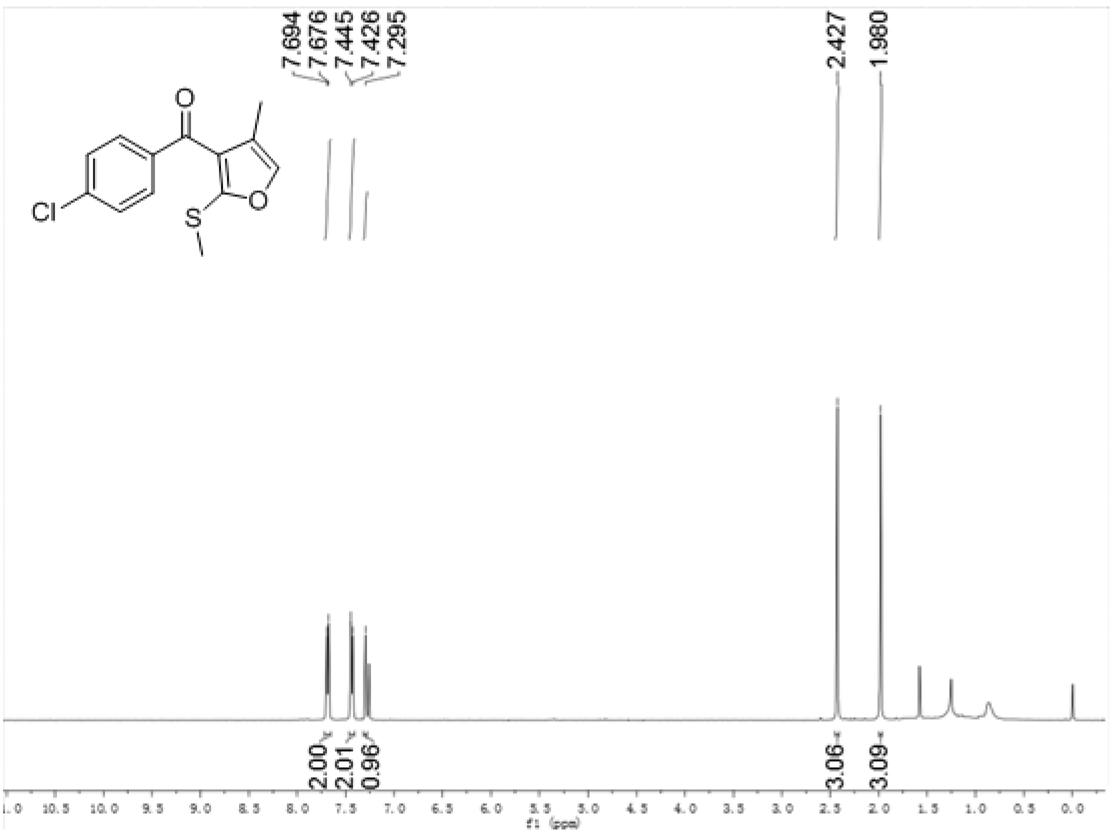


Figure S12. ^{1}H NMR spectra of 3-(4-chlorobenzoyl)-4-methyl-2-methylthio-furan (**2c**) in $CDCl_3$.

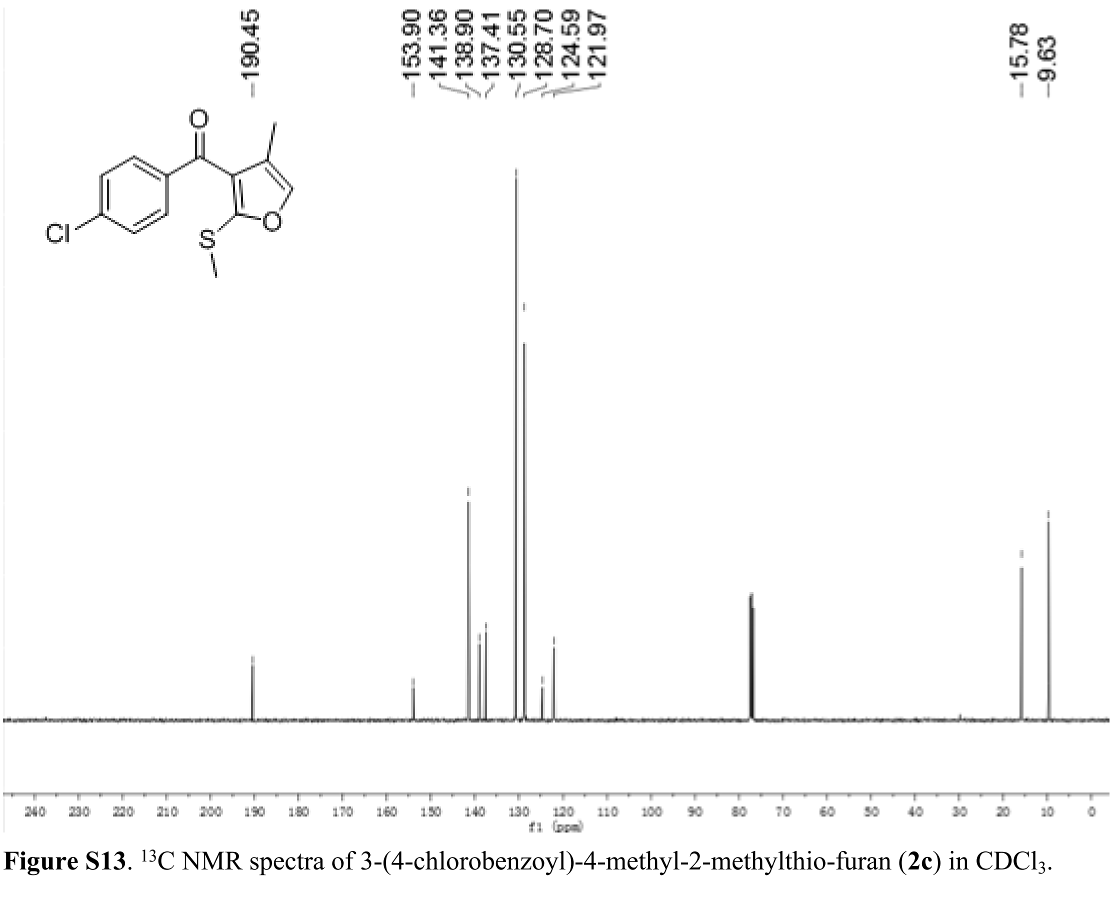


Figure S13. ^{13}C NMR spectra of 3-(4-chlorobenzoyl)-4-methyl-2-methylthio-furan (**2c**) in $CDCl_3$.

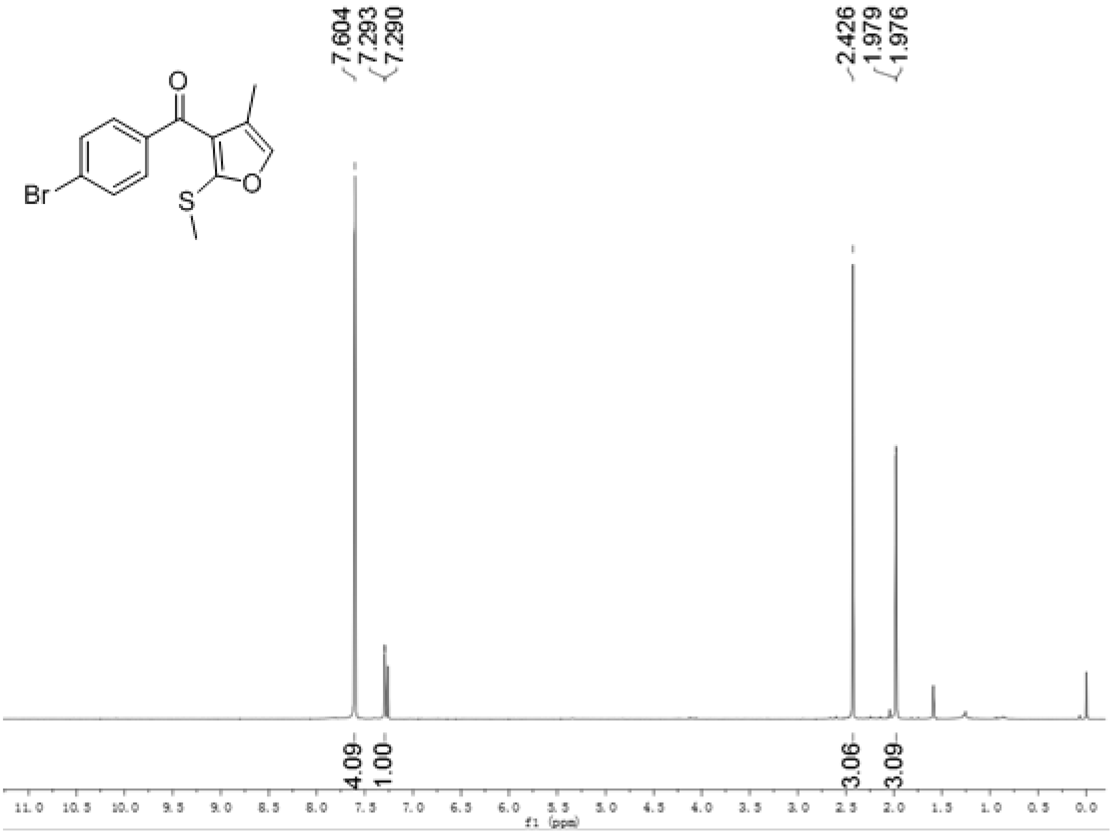


Figure S14. ^{1}H NMR spectra of 3-(4-bromobenzoyl)-4-methyl-2-methylthio-furan (**2d**) in CDCl$_3$.

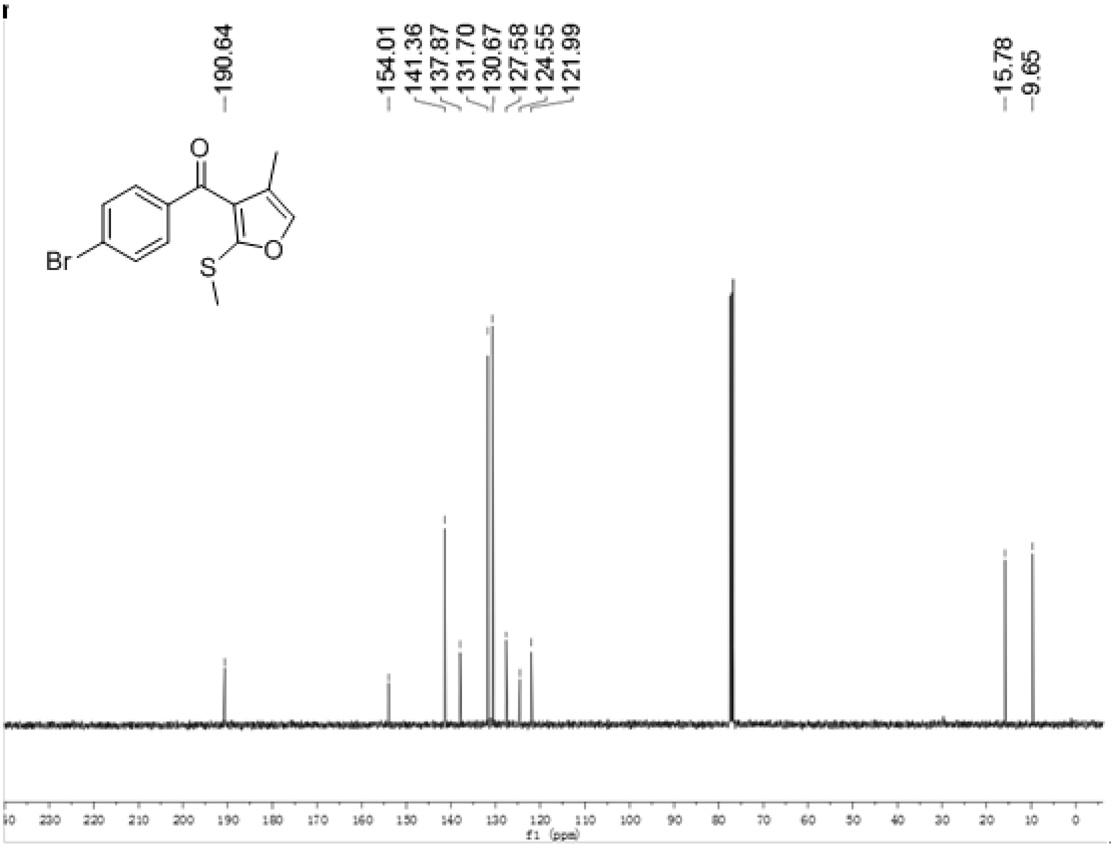


Figure S15. ^{13}C NMR spectra of 3-(4-bromobenzoyl)-4-methyl-2-methylthio-furan (**2d**) in CDCl$_3$.

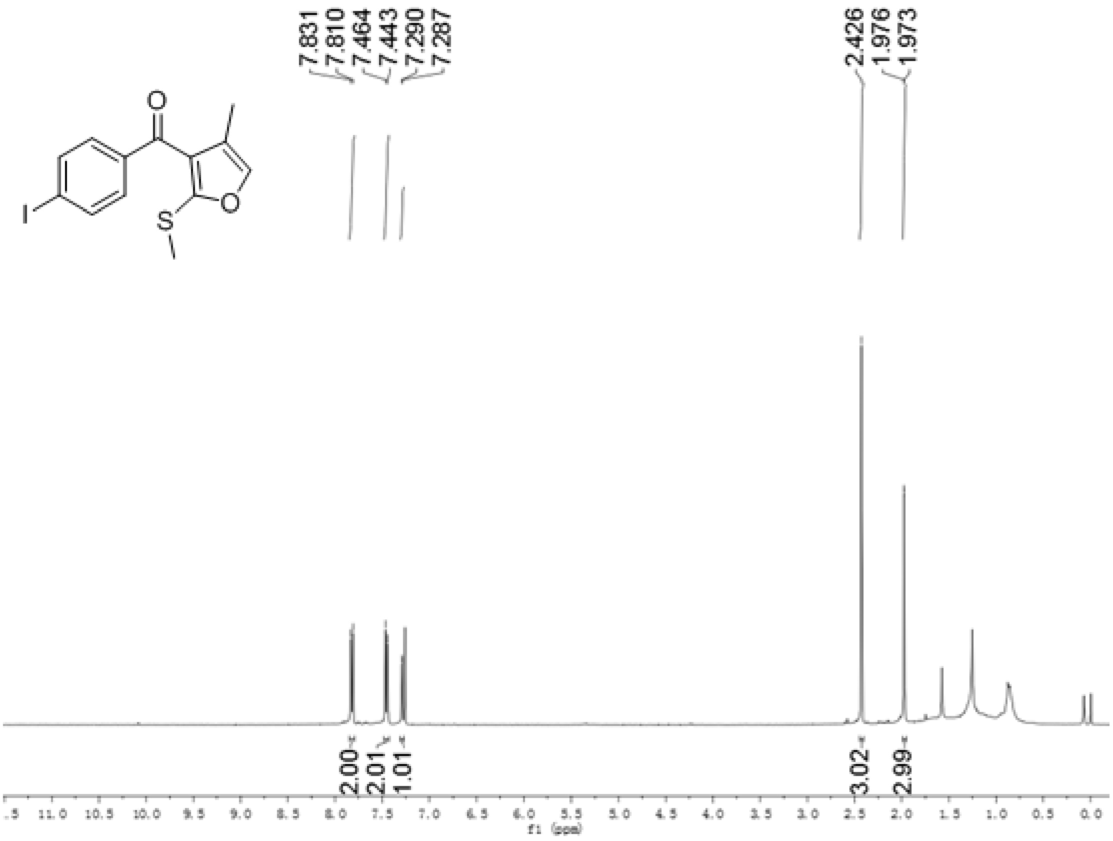


Figure S16. ^{1}H NMR spectra of 3-(4-iodobenzoyl)-4-methyl-2-methylthio-furan (**2e**) in CDCl$_3$.

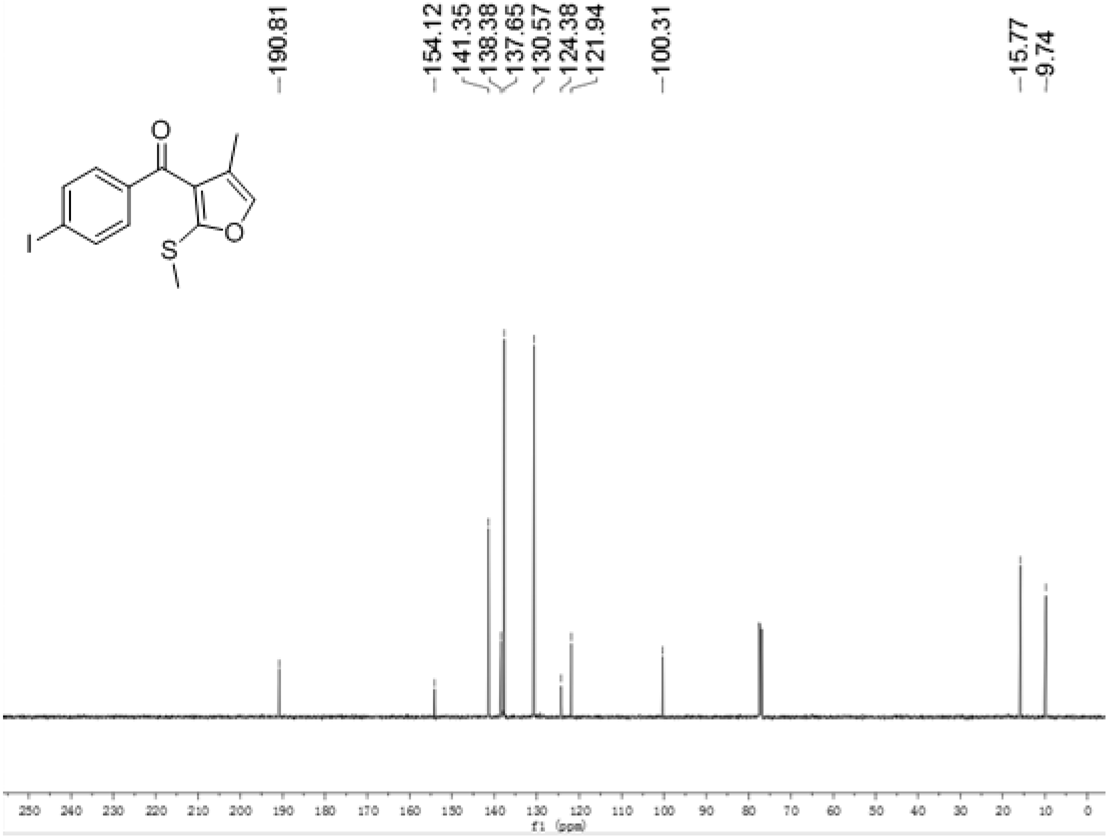


Figure S17. ^{13}C NMR spectra of 3-(4-iodobenzoyl)-4-methyl-2-methylthio-furan (**2e**) in CDCl$_3$.

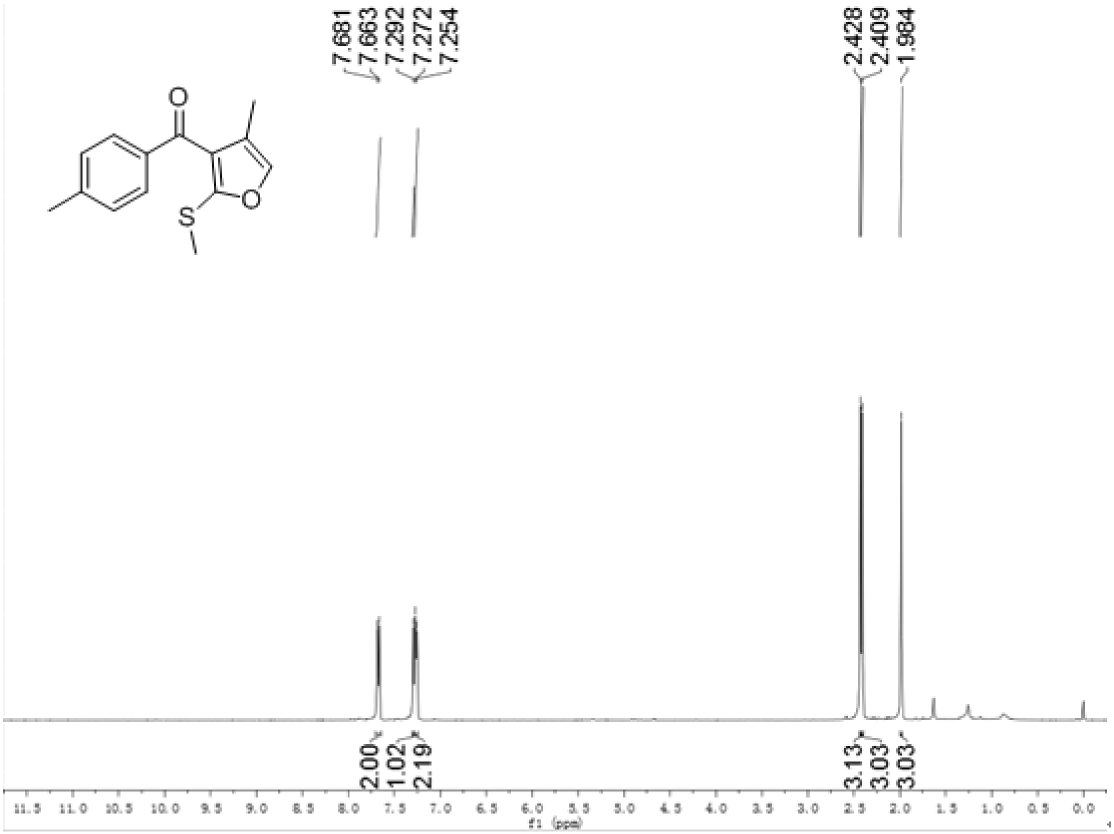


Figure S18. ^{1}H NMR spectra of 4-methyl-3-(4-methylbenzoyl)-2-methylthio-furan (**2f**) in $CDCl_3$.

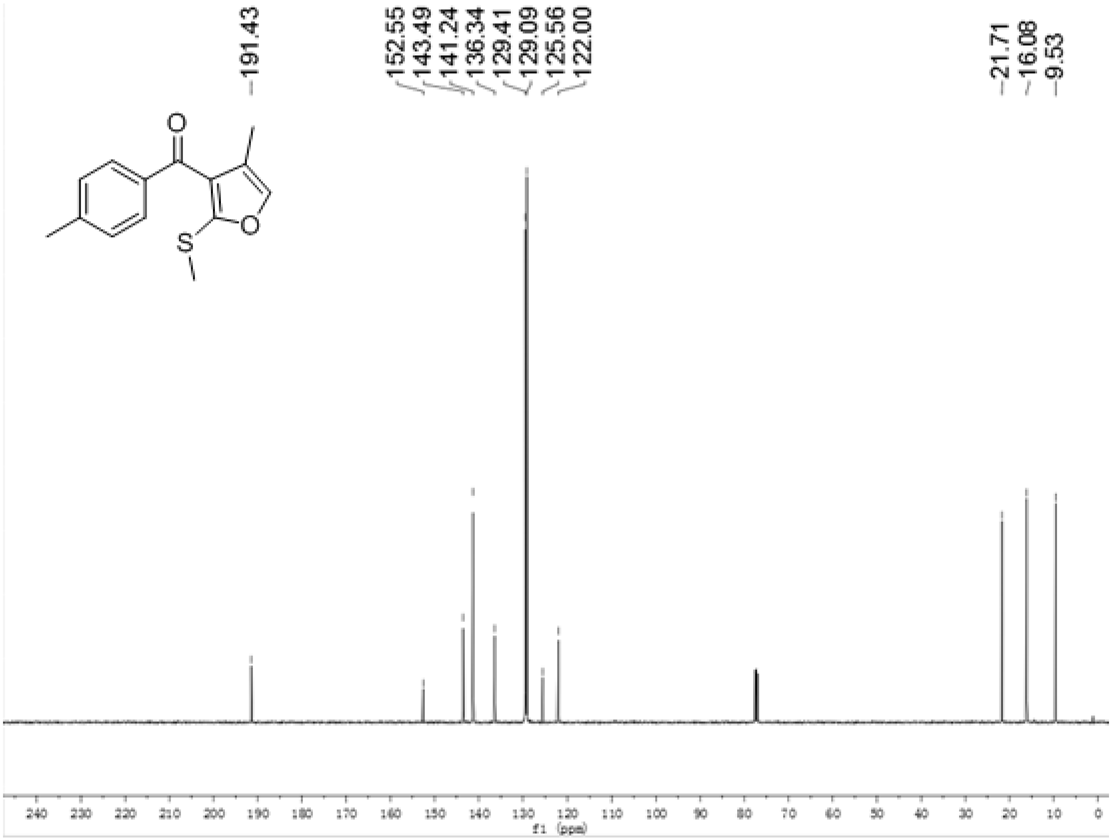


Figure S19. ^{13}C NMR spectra of 4-methyl-3-(4-methylbenzoyl)-2-methylthio-furan (**2f**) in $CDCl_3$.

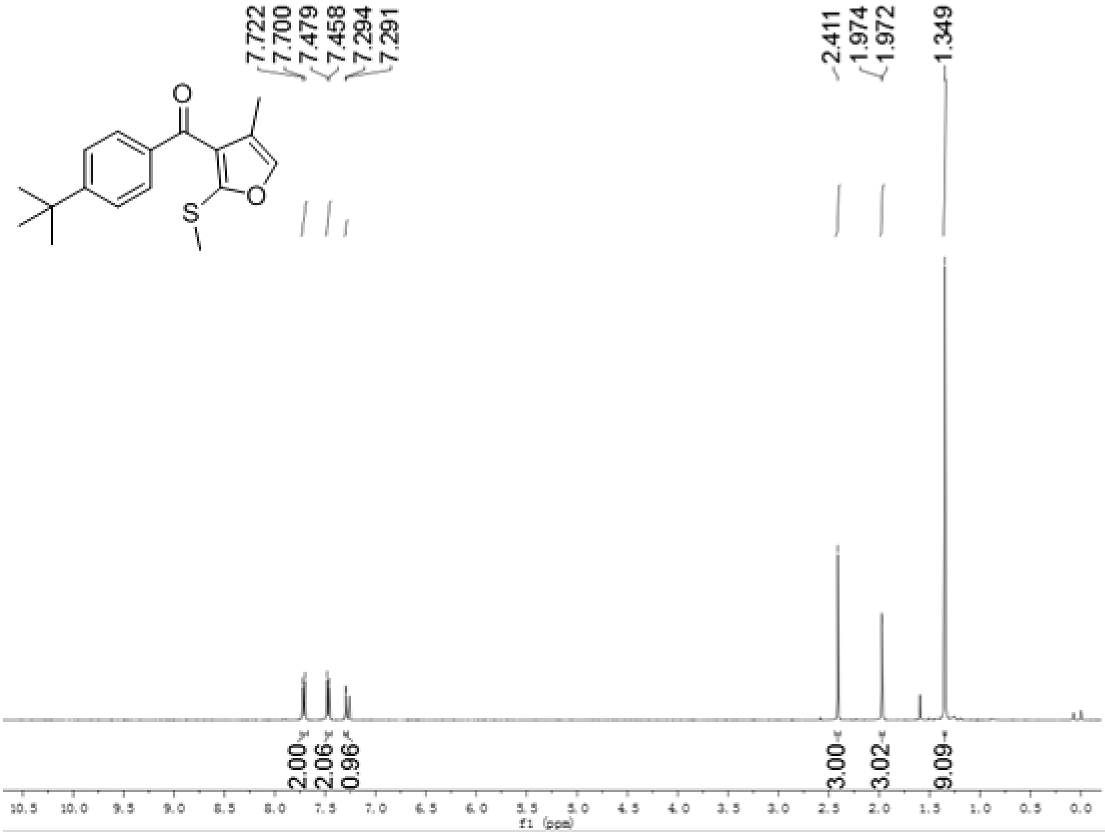


Figure S20. ^{1}H NMR spectra of 3-(4-*tert*-butylbenzoyl)-4-methyl--2-methylthio-furan (**2g**) in CDCl$_3$.

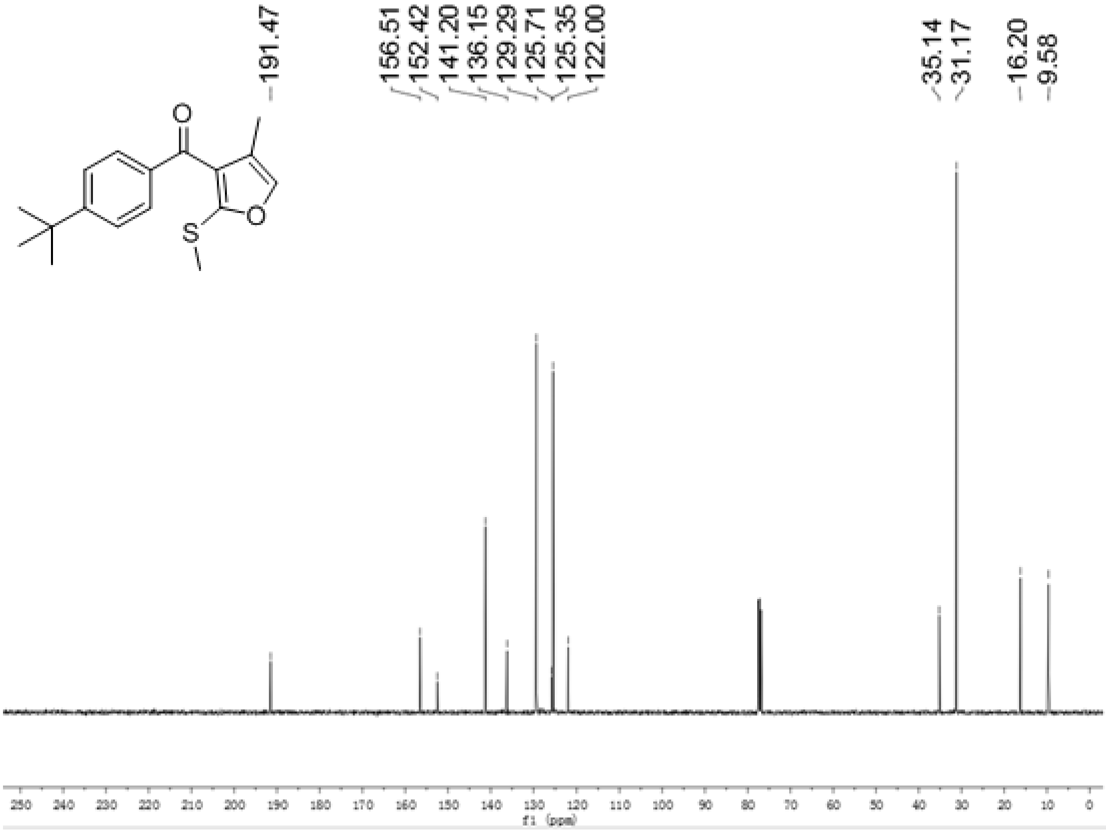


Figure S21. ^{13}C NMR spectra of 3-(4-*tert*-butylbenzoyl)-4-methyl--2-methylthio-furan (**2g**) in CDCl$_3$.

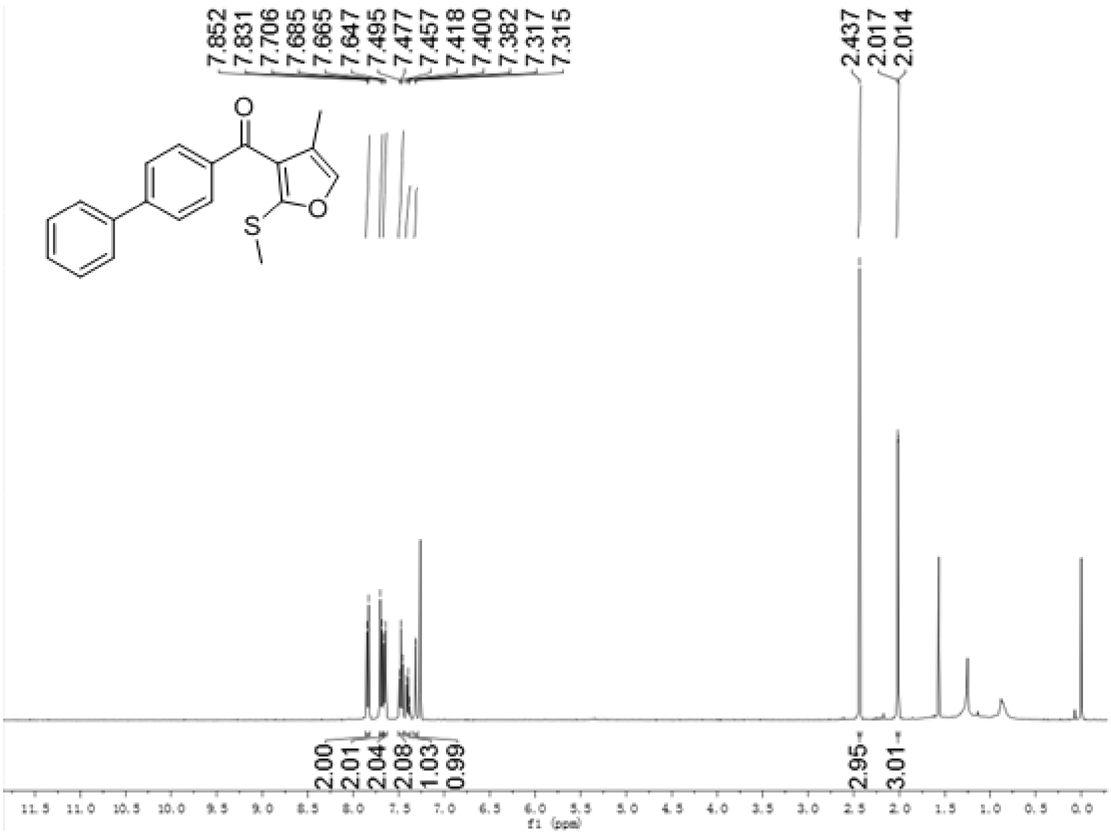


Figure S22. ^{1}H NMR spectra of 3-(biphenyl-4-carbonyl)-4-methyl-2-methylthio-furan (**2h**) in CDCl$_3$.

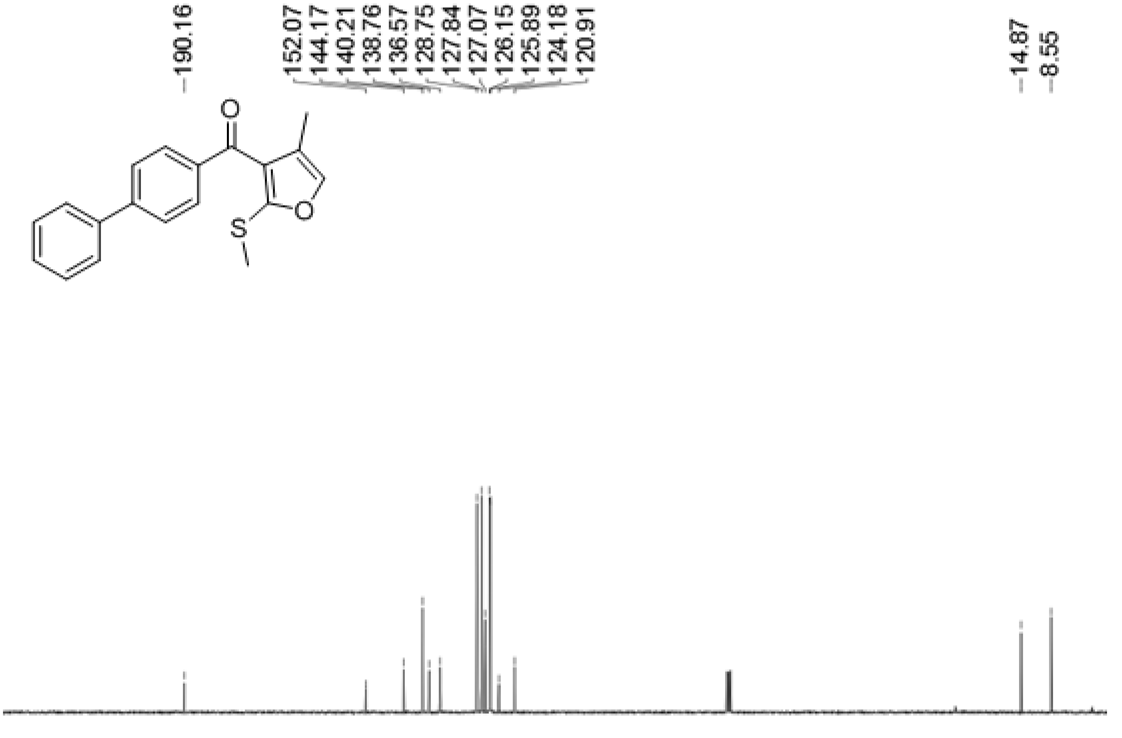


Figure S23. ^{13}C NMR spectra of 3-(biphenyl-4-carbonyl)-4-methyl-2-methylthio-furan (**2h**) in CDCl$_3$.

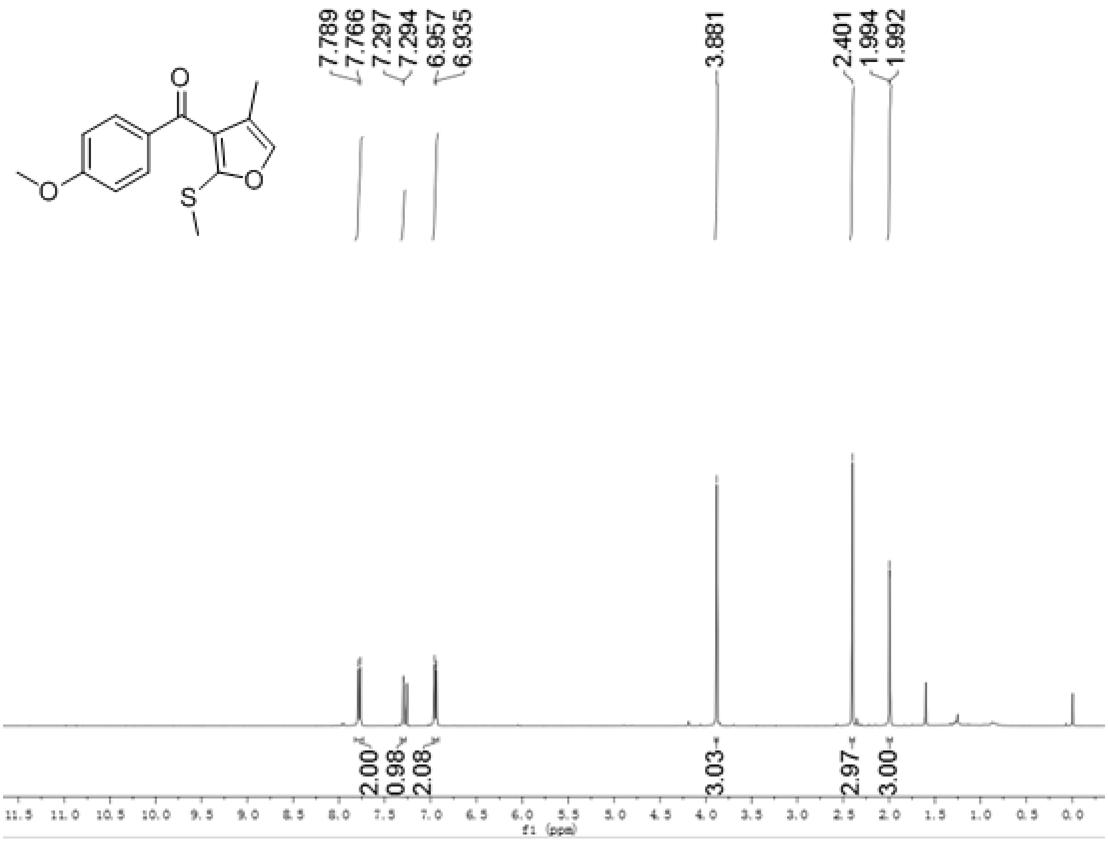


Figure S24. ^{1}H NMR spectra of 4-methyl-3-(4-methoxybenzoyl)-2-methylthio-furan (**2i**) in $CDCl_3$.

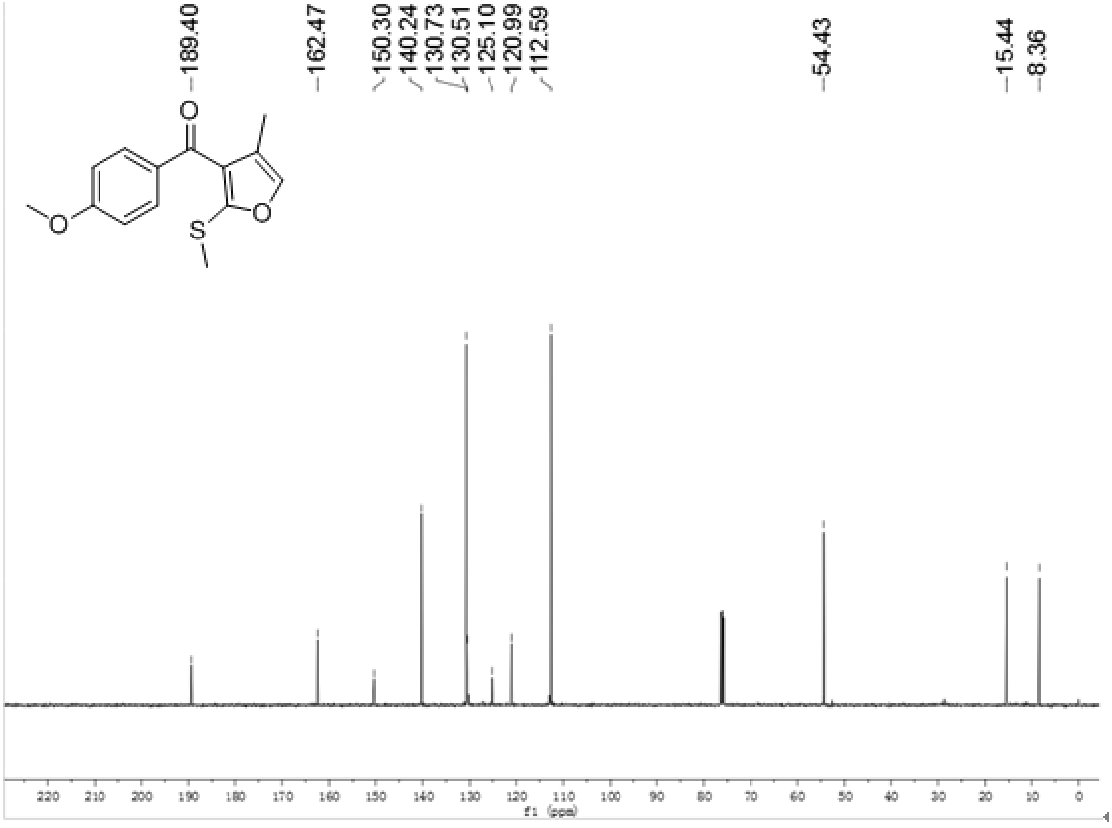


Figure S25. ^{13}C NMR spectra of 4-methyl-3-(4-methoxybenzoyl)-2-methylthio-furan (**2i**) in $CDCl_3$.

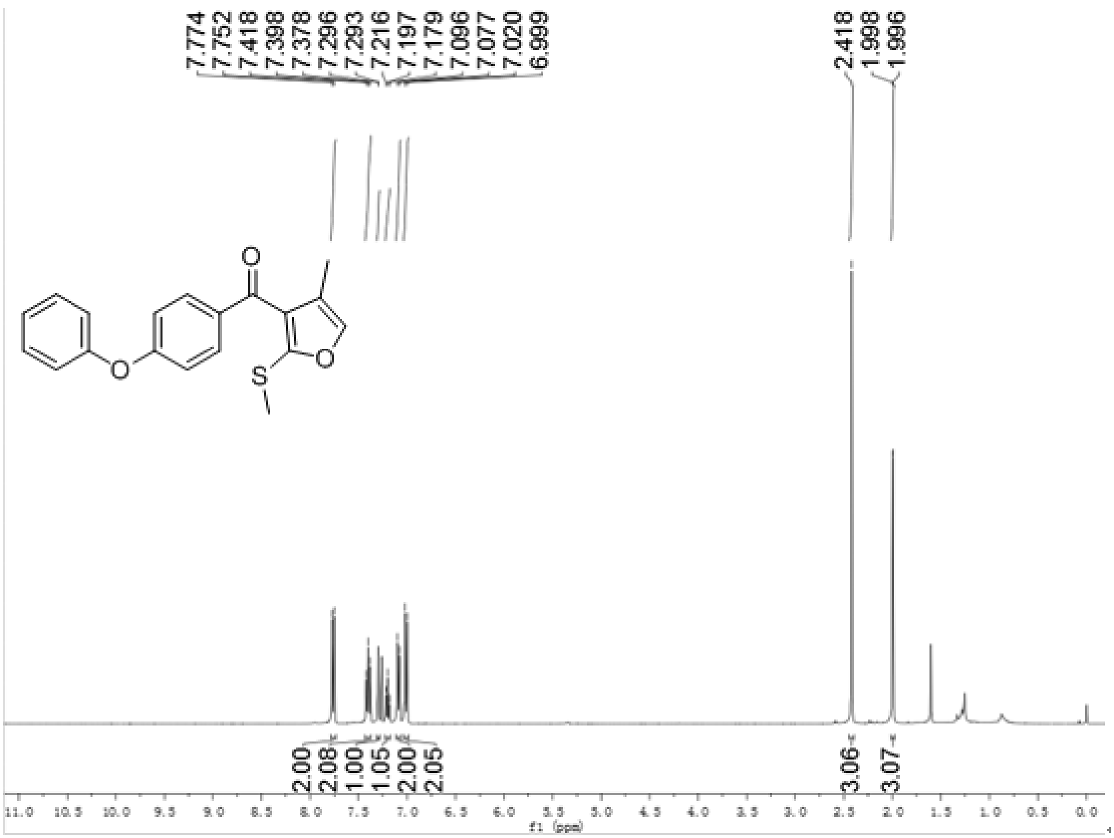


Figure S26. ^{1}H NMR spectra of 4-methyl-3-(4-phenoxybenzoyl)-2-methylthio-furan (**2j**) in $CDCl_3$.

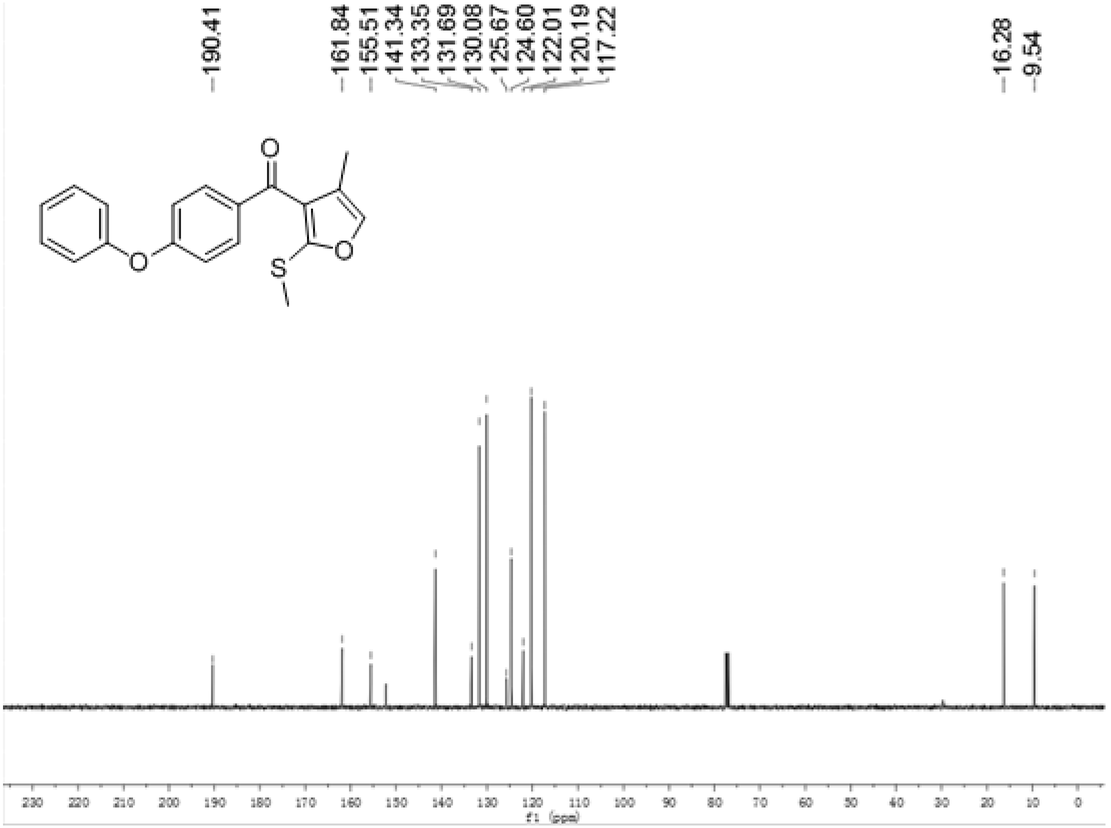


Figure S27. ^{13}C NMR spectra of 4-methyl-3-(4-phenoxybenzoyl)-2-methylthio-furan (**2j**) in $CDCl_3$.

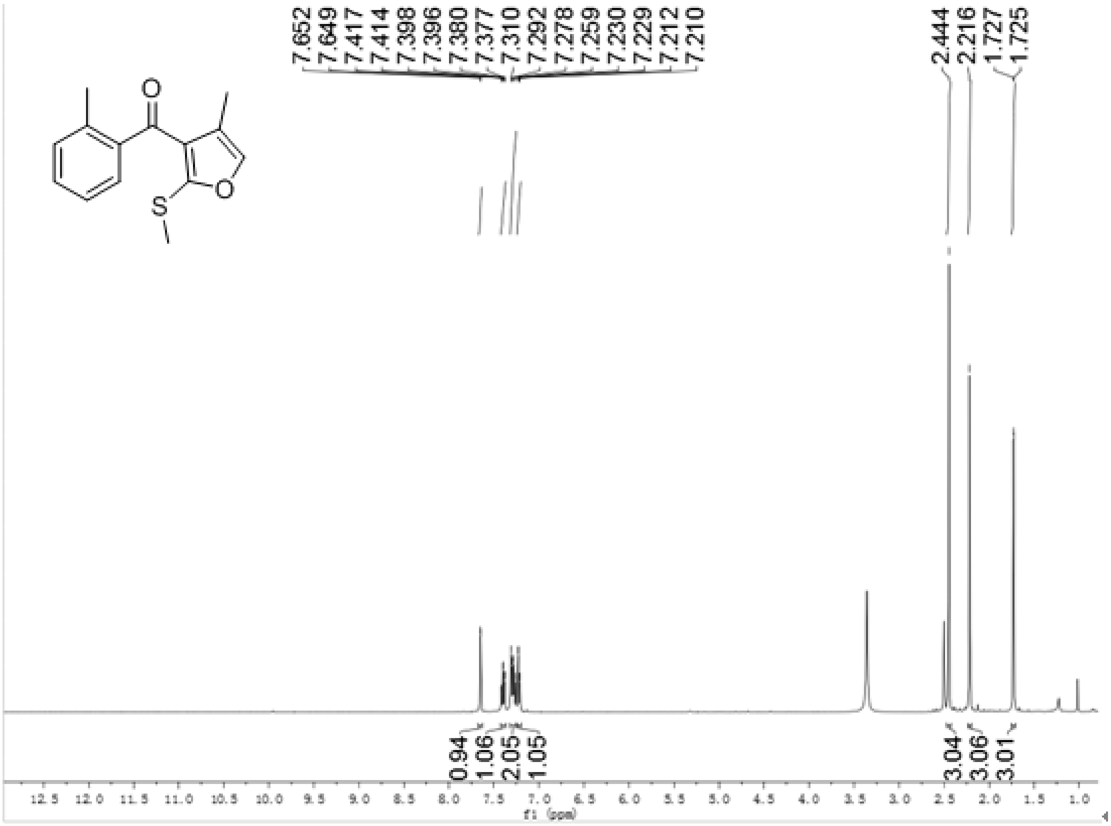


Figure S28. ^{1}H NMR spectra of 4-methyl-3-(2-methylbenzoyl)-2-methylthio-furan (**2k**) in DMSO-d_6.

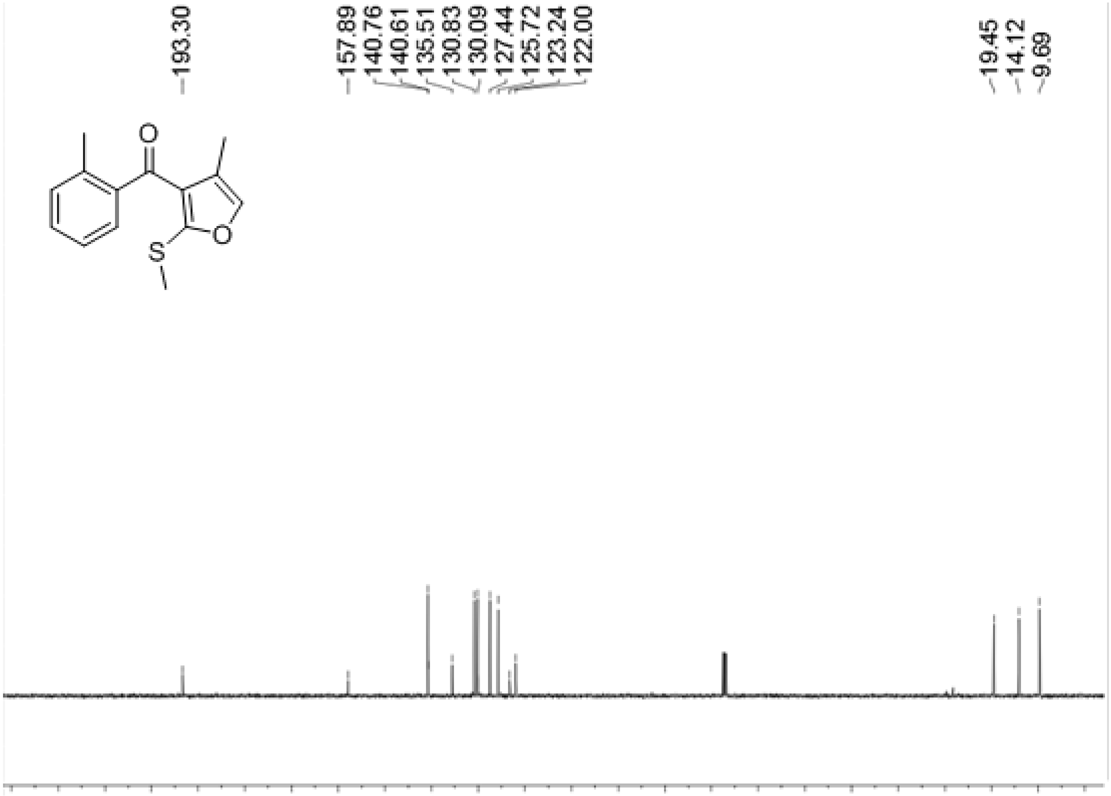


Figure S29. ^{13}C NMR spectra of 4-methyl-3-(2-methylbenzoyl)-2-methylthio-furan (**2k**) in CDCl$_3$.

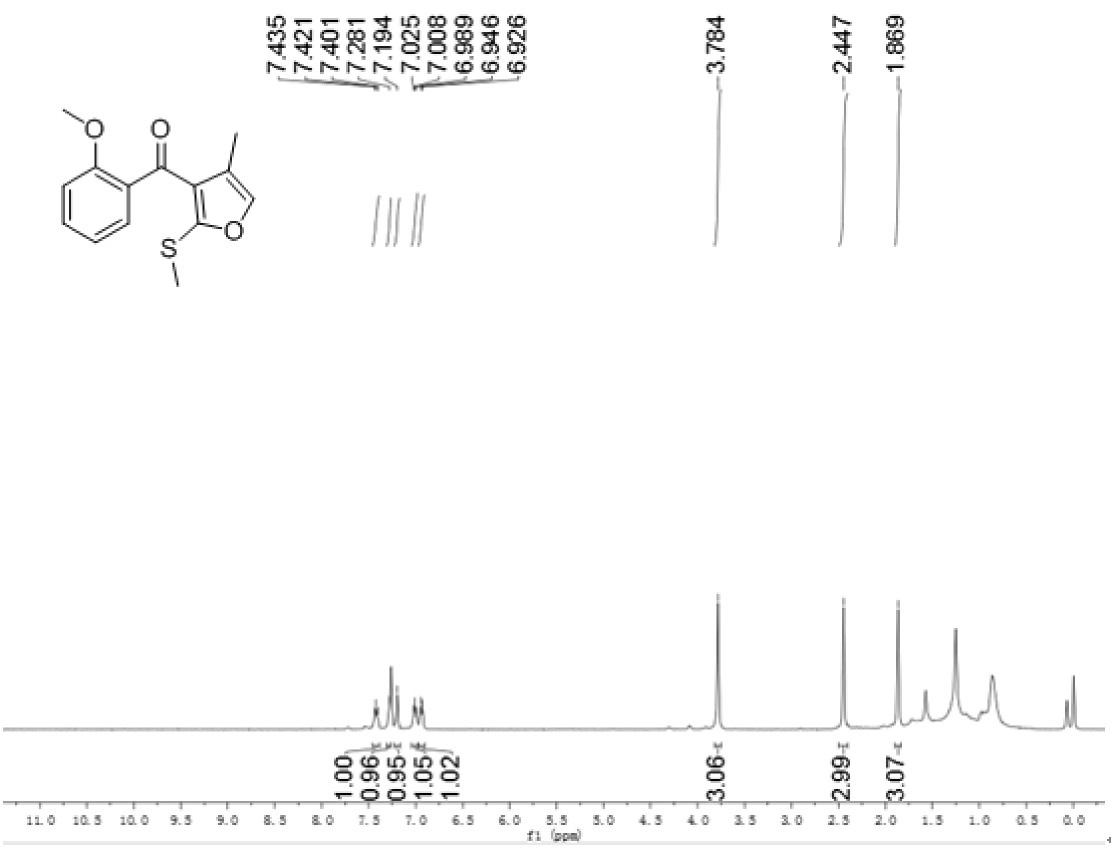


Figure S30. ^{1}H NMR spectra of 4-methyl-3-(2-methoxylbenzoyl)-2-methylthio-furan (**2l**) in $CDCl_3$.

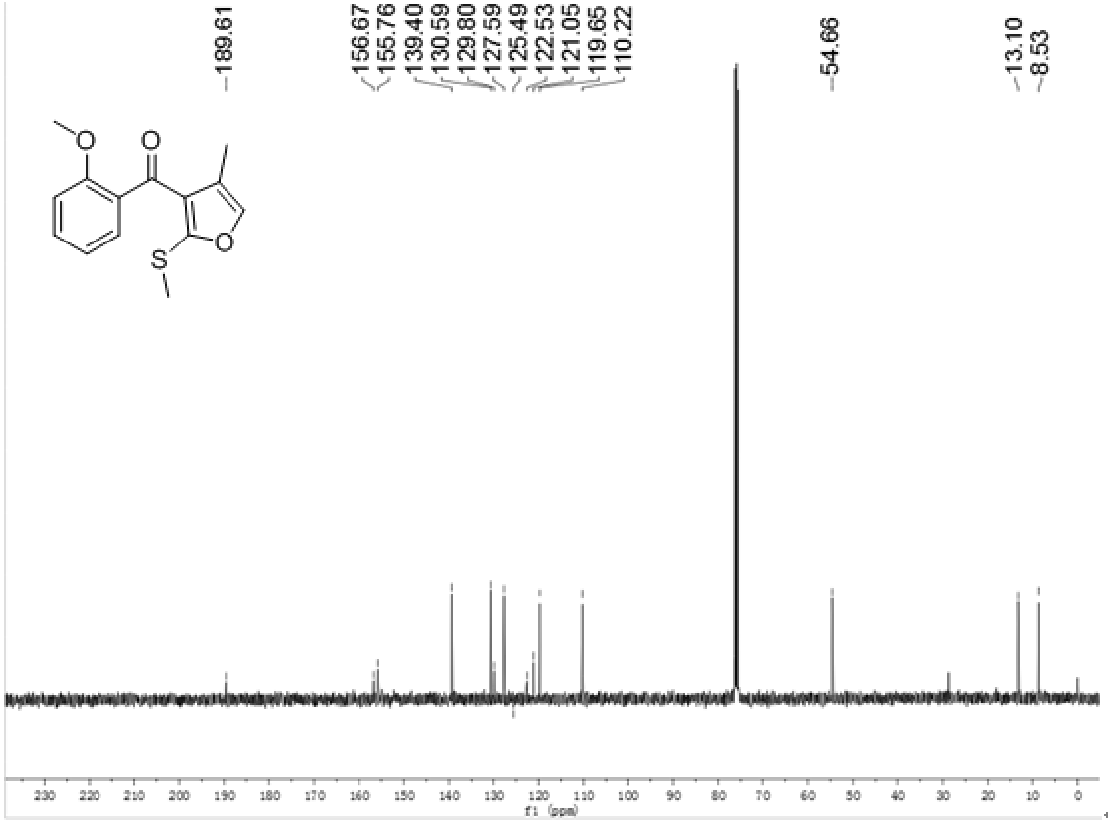


Figure S31. ^{13}C NMR spectra of 4-methyl-3-(2-methoxylbenzoyl)-2-methylthio-furan (**2l**) in $CDCl_3$.

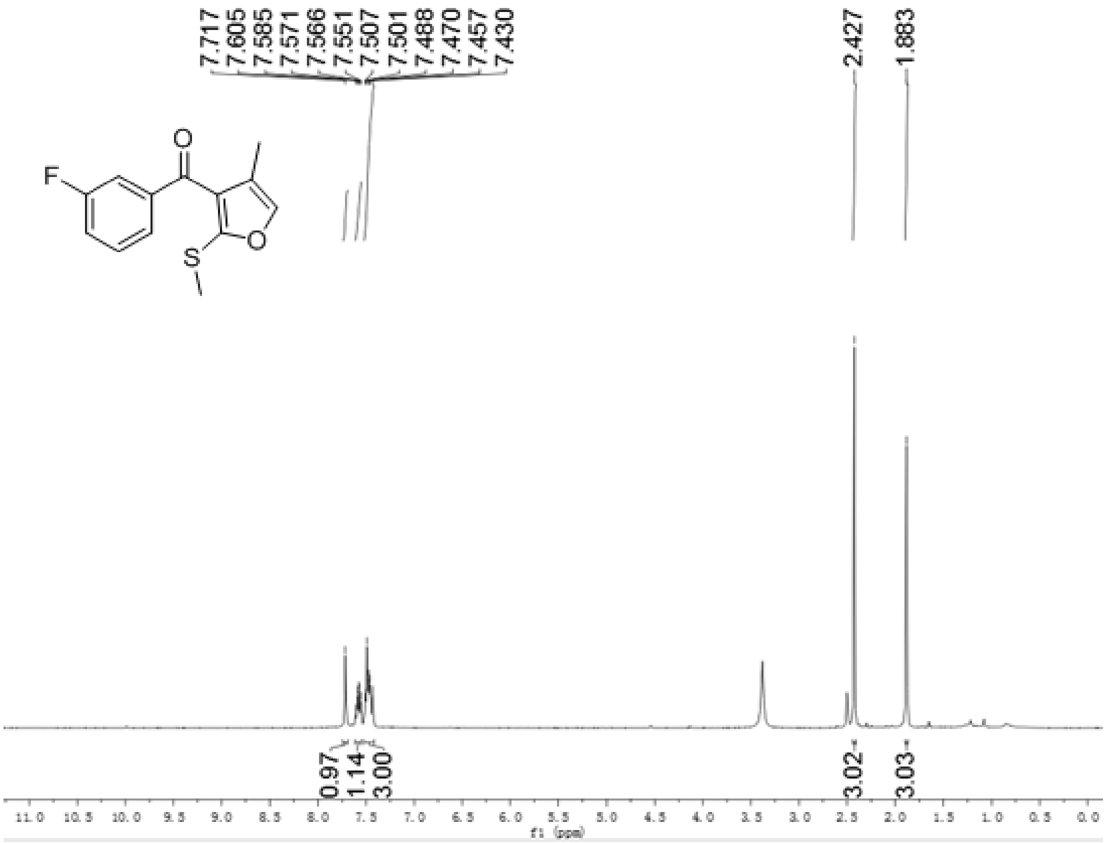


Figure S32. ^{1}H NMR spectra of 3-(3-flourbenzoyl)-4-methyl-2-methylthio-furan (**2m**) in DMSO-d_6.

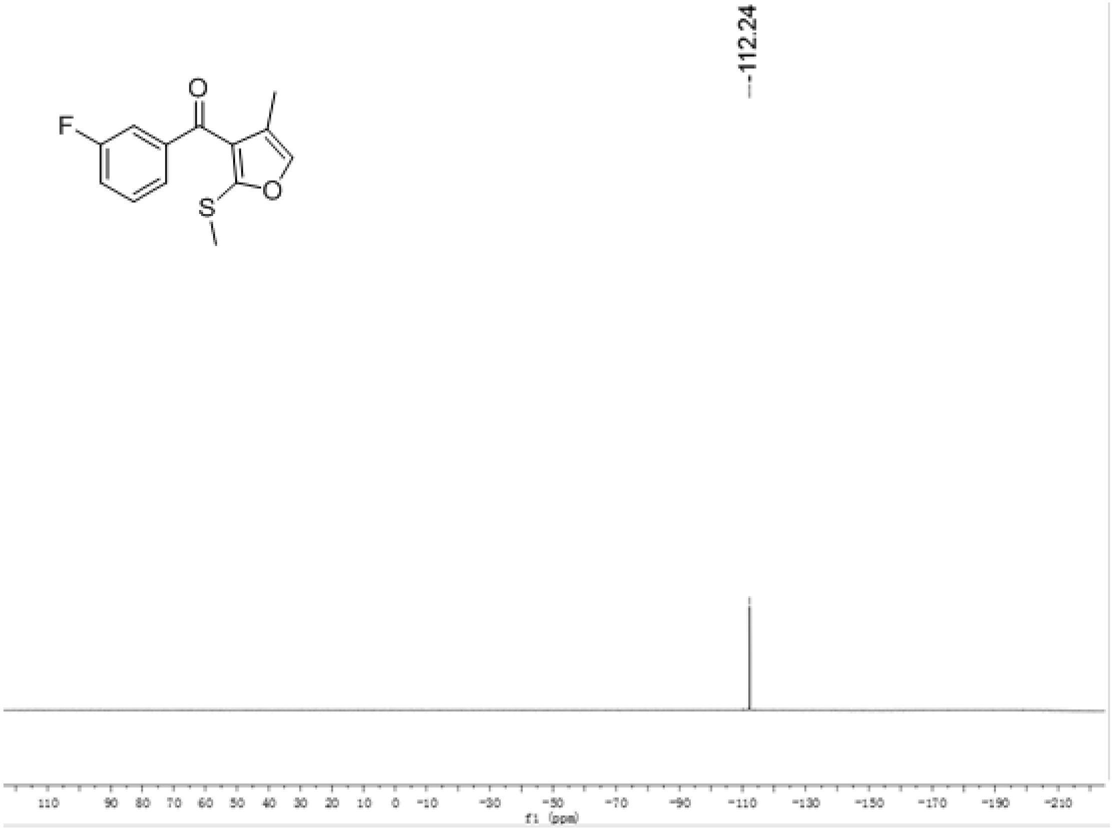


Figure S33. ^{19}F NMR spectra of 3-(3-flourbenzoyl)-4-methyl-2-methylthio-furan (**2m**) in CDCl$_3$.

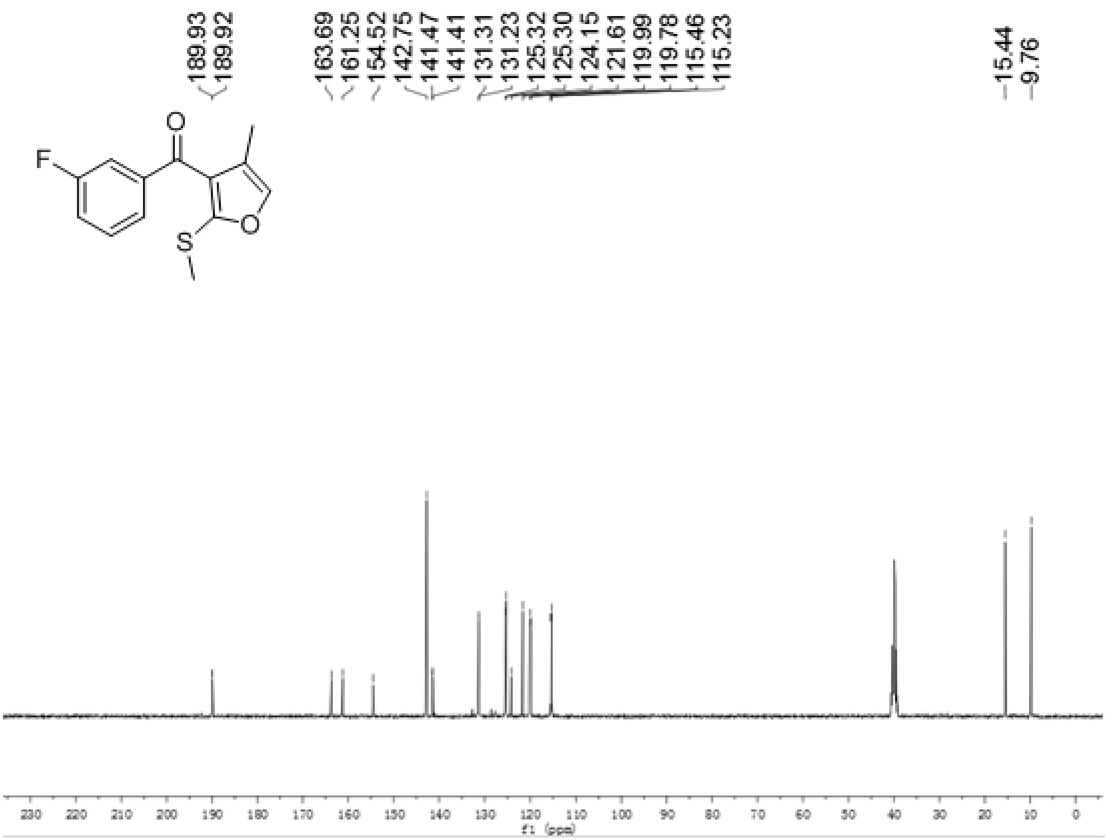


Figure S34. ^{13}C NMR spectra of 3-(3-flourbenzoyl)-4-methyl-2-methylthio-furan (**2m**) in DMSO-d_6.

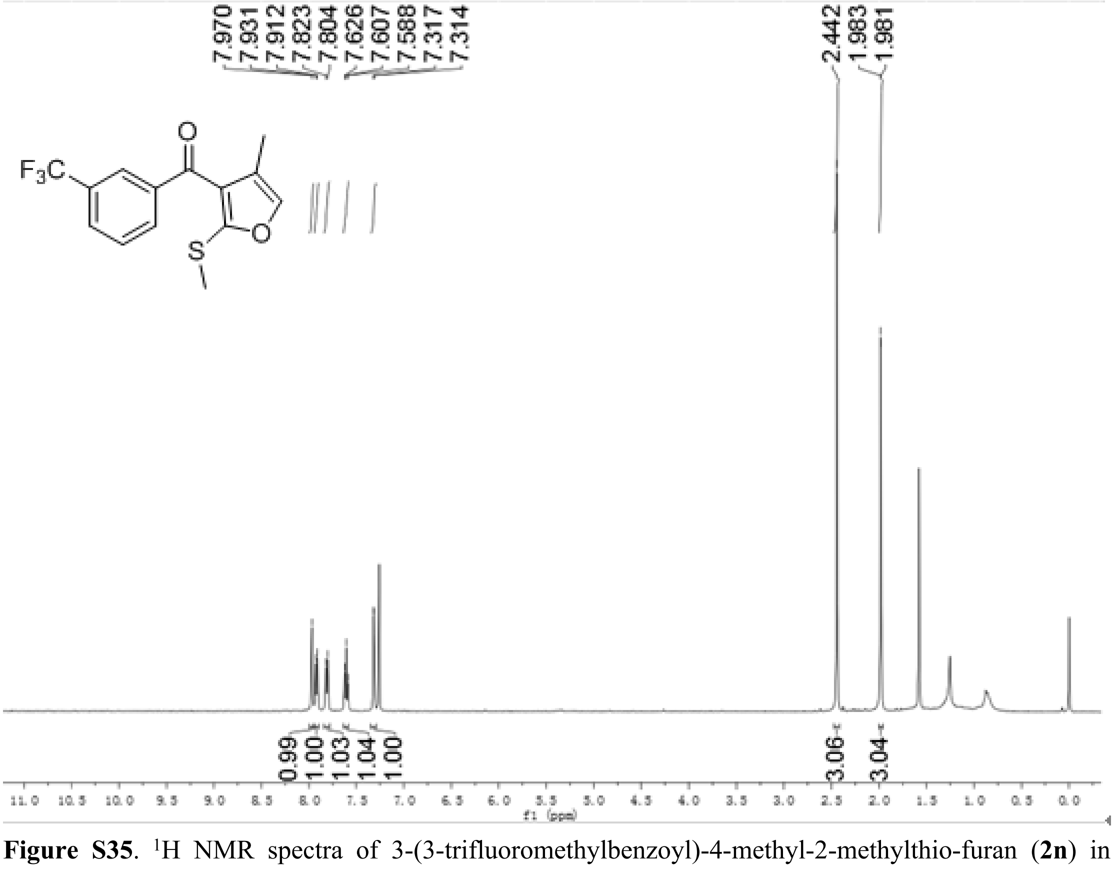


Figure S35. ^{1}H NMR spectra of 3-(3-trifluoromethylbenzoyl)-4-methyl-2-methylthio-furan (**2n**) in CDCl$_3$.

Figure S36. ^{19}F NMR spectra of 3-(3-trifluoromethylbenzoyl)-4-methyl-2-methylthio-furan (**2n**) in CDCl$_3$.

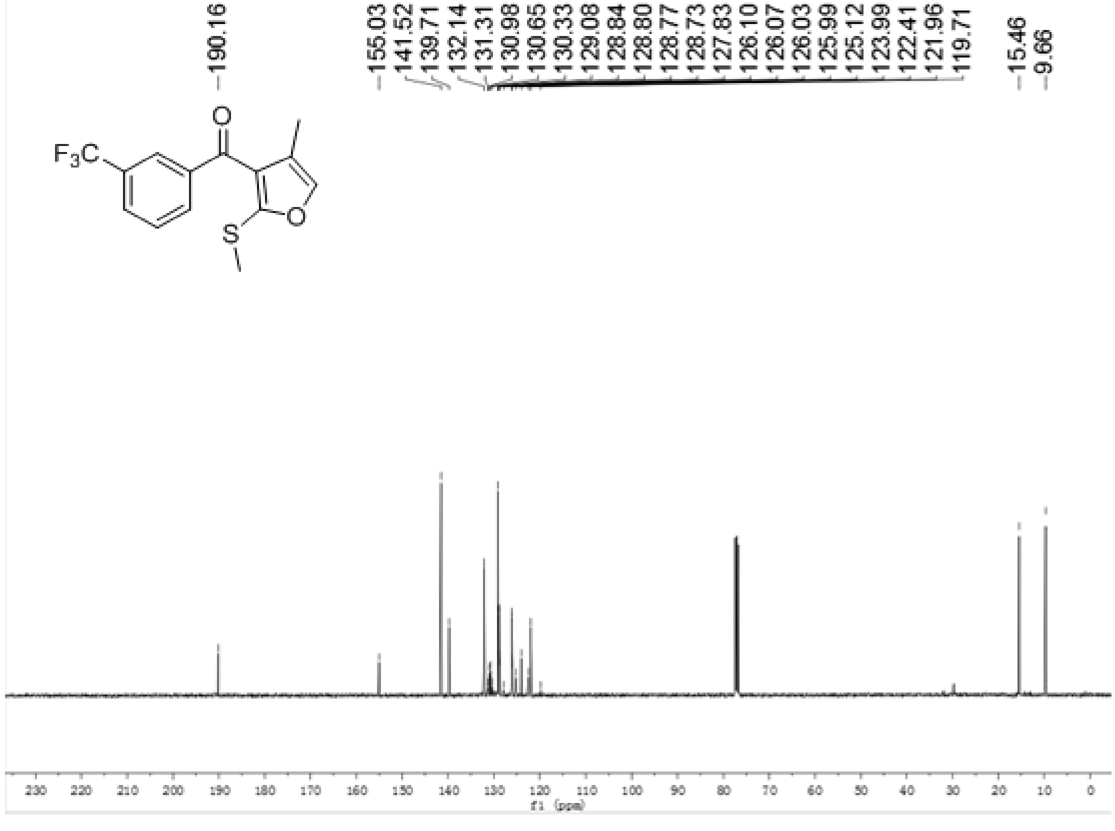


Figure S37. ^{13}C NMR spectra of 3-(3-trifluoromethylbenzoyl)-4-methyl-2-methylthio-furan (**2n**) in CDCl$_3$.

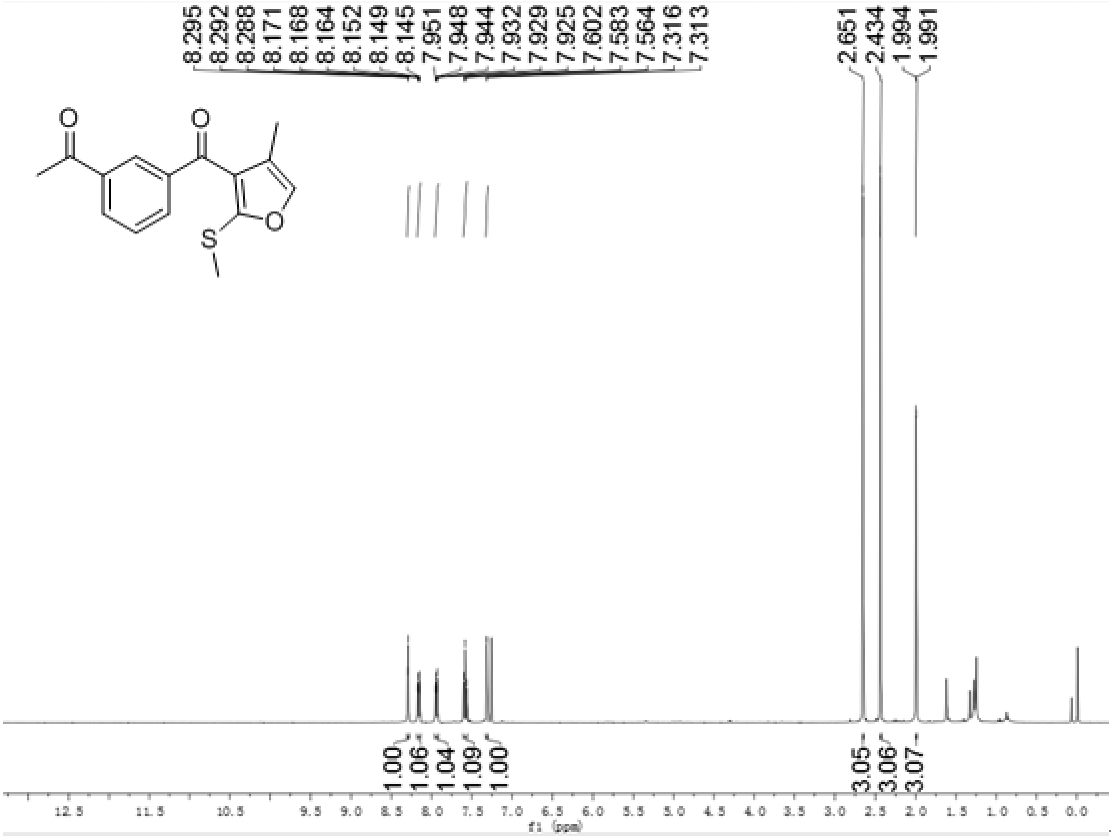


Figure S38. ^{1}H NMR spectra of 3-(3-acetylbenzoyl)-4-methyl-2-methylthio-furan (**2o**) in CDCl$_3$.

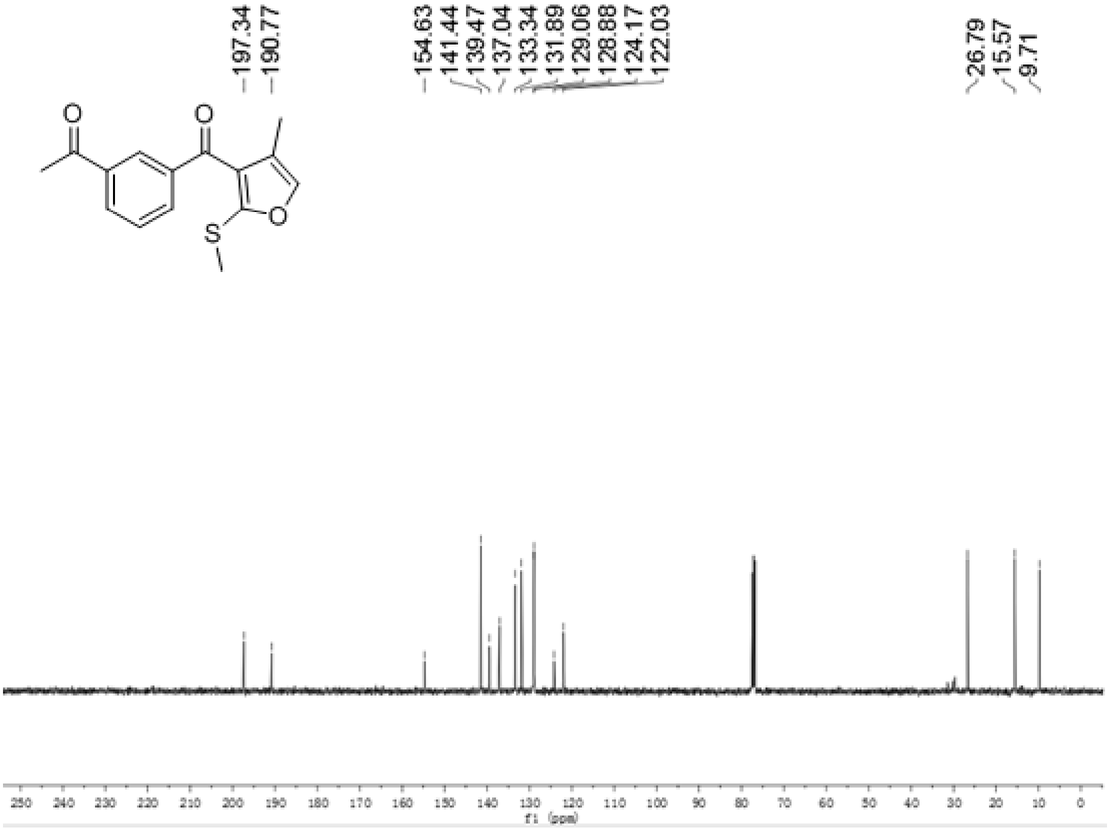


Figure S39. ^{13}C NMR spectra of 3-(3-acetylbenzoyl)-4-methyl-2-methylthio-furan (**2o**) in CDCl$_3$.

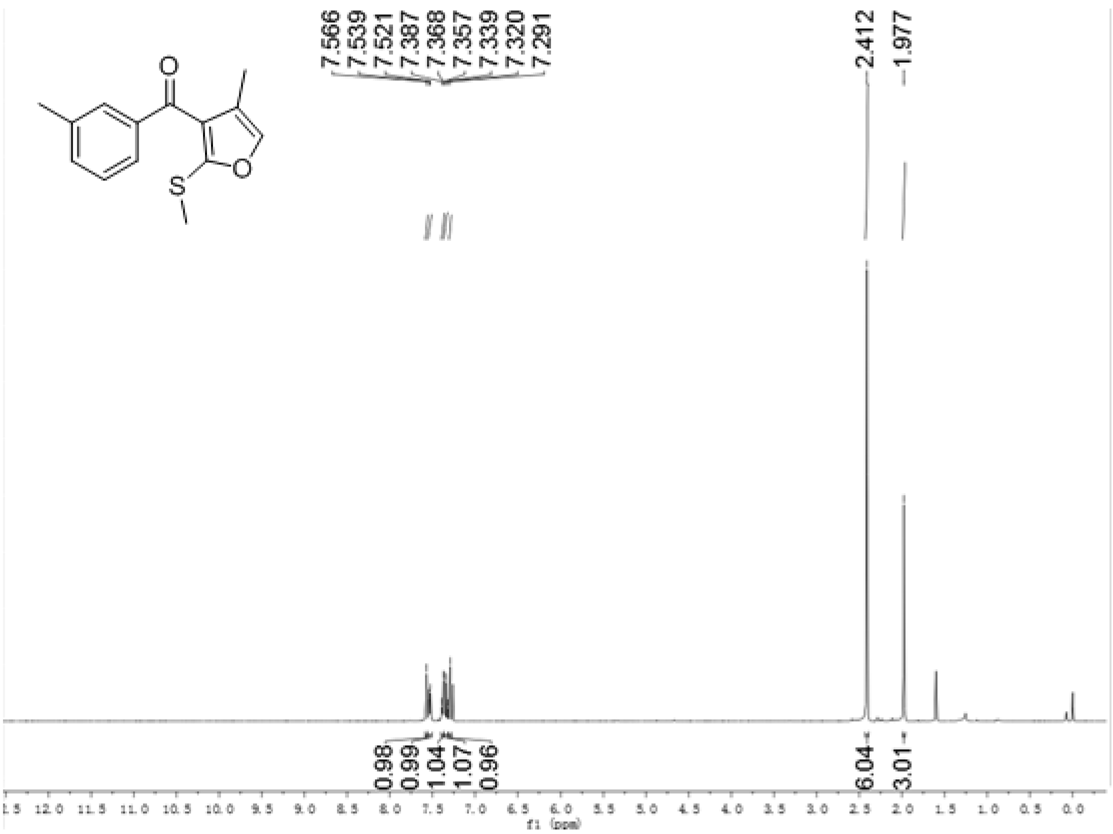


Figure S40. ^{1}H NMR spectra of 4-methyl-3-(3-methylbenzoyl)-2-methylthio-furan (**2p**) in $CDCl_3$.

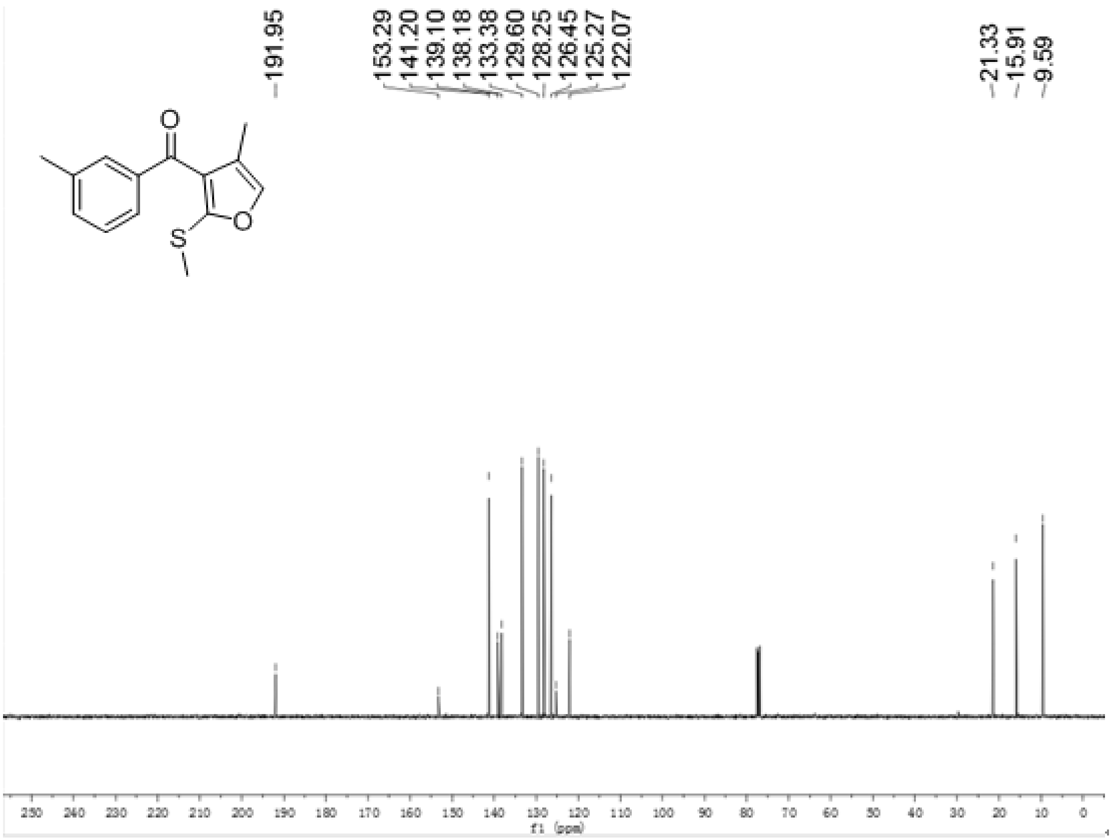


Figure S41. ^{13}C NMR spectra of 4-methyl-3-(3-methylbenzoyl)-2-methylthio-furan (**2p**) in CDCl$_3$.

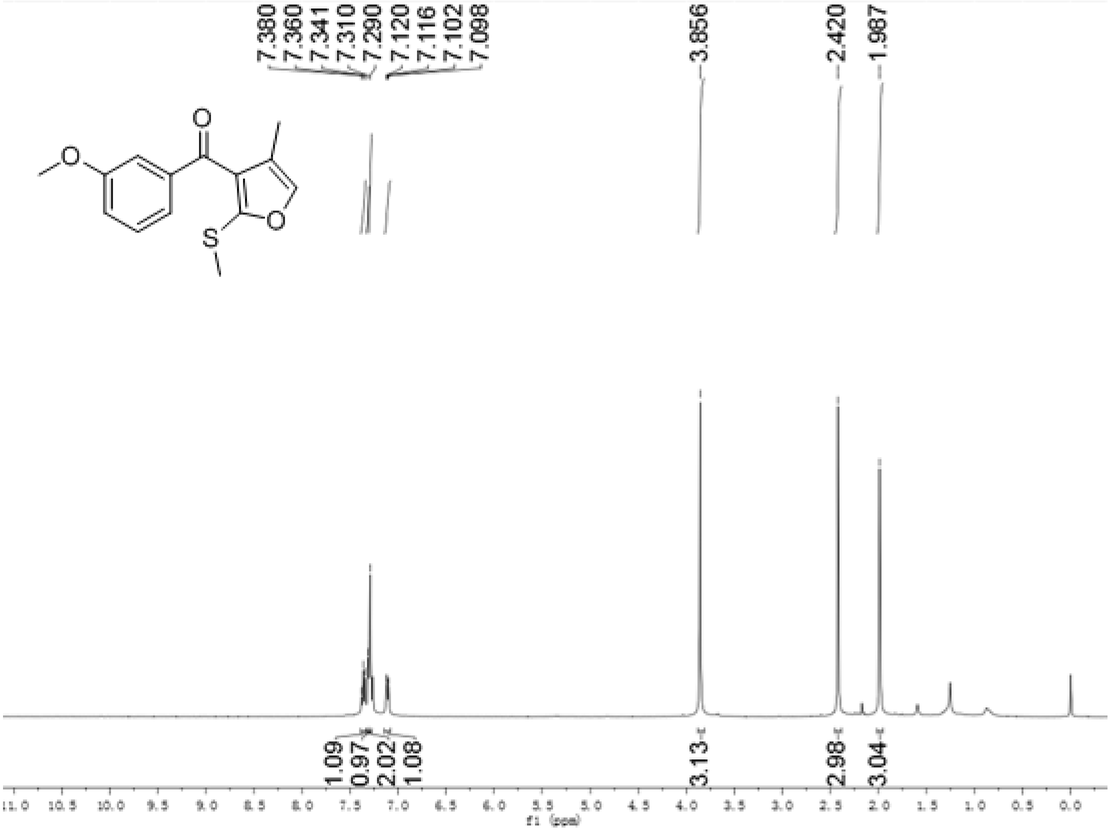


Figure S42. ^{1}H NMR spectra of 3-(3-methoxylbenzoyl)-4-methyl-2-methylthio-furan (**2q**) in CDCl$_3$.

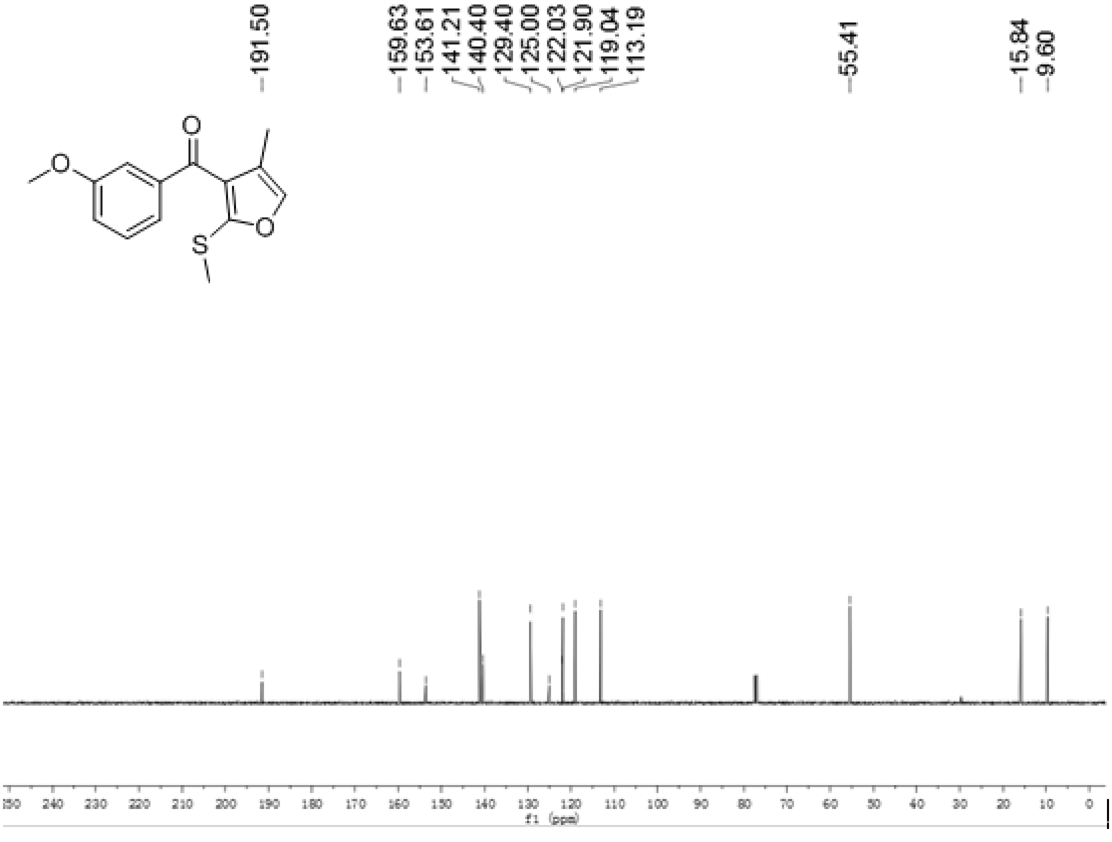


Figure S43. ^{13}C NMR spectra of 3-(3-methoxylbenzoyl)-4-methyl-2-methylthio-furan (**2q**) in CDCl$_3$.

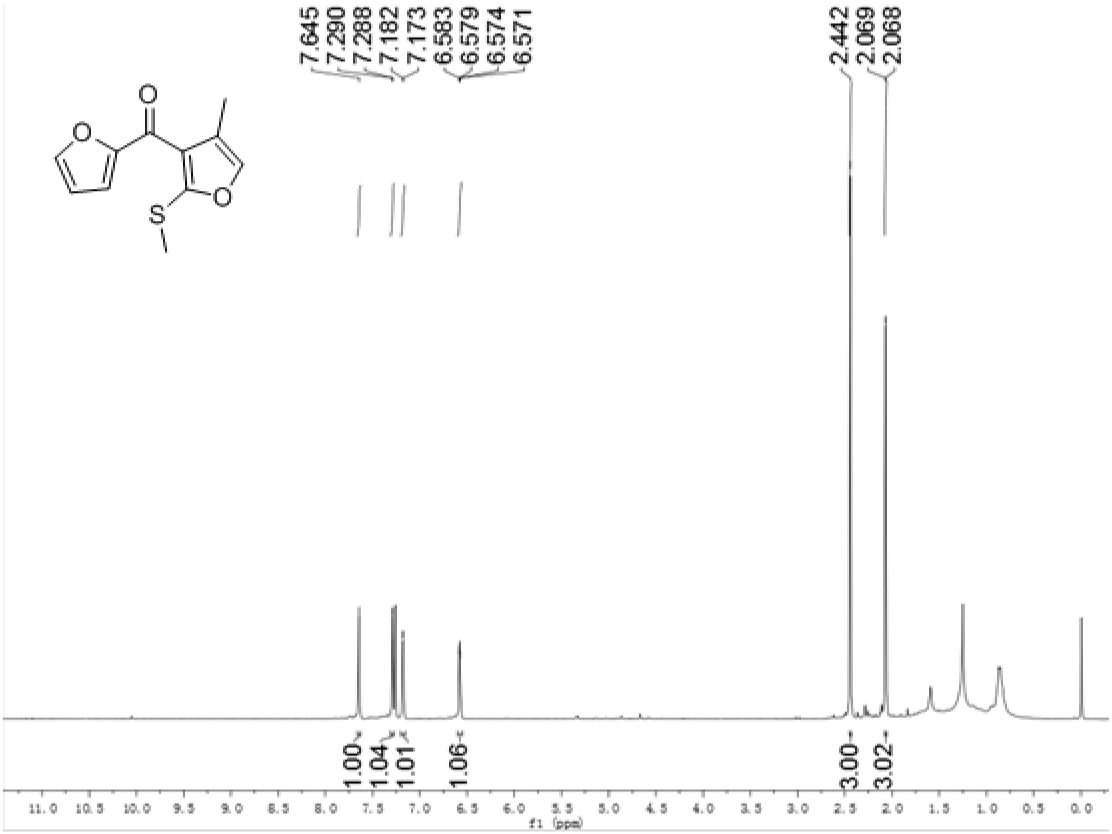


Figure S44. ^{1}H NMR spectra of 3-(furan-2-carbonyl)-4-methyl-2-methylthio-furan (**2r**) in CDCl$_3$.

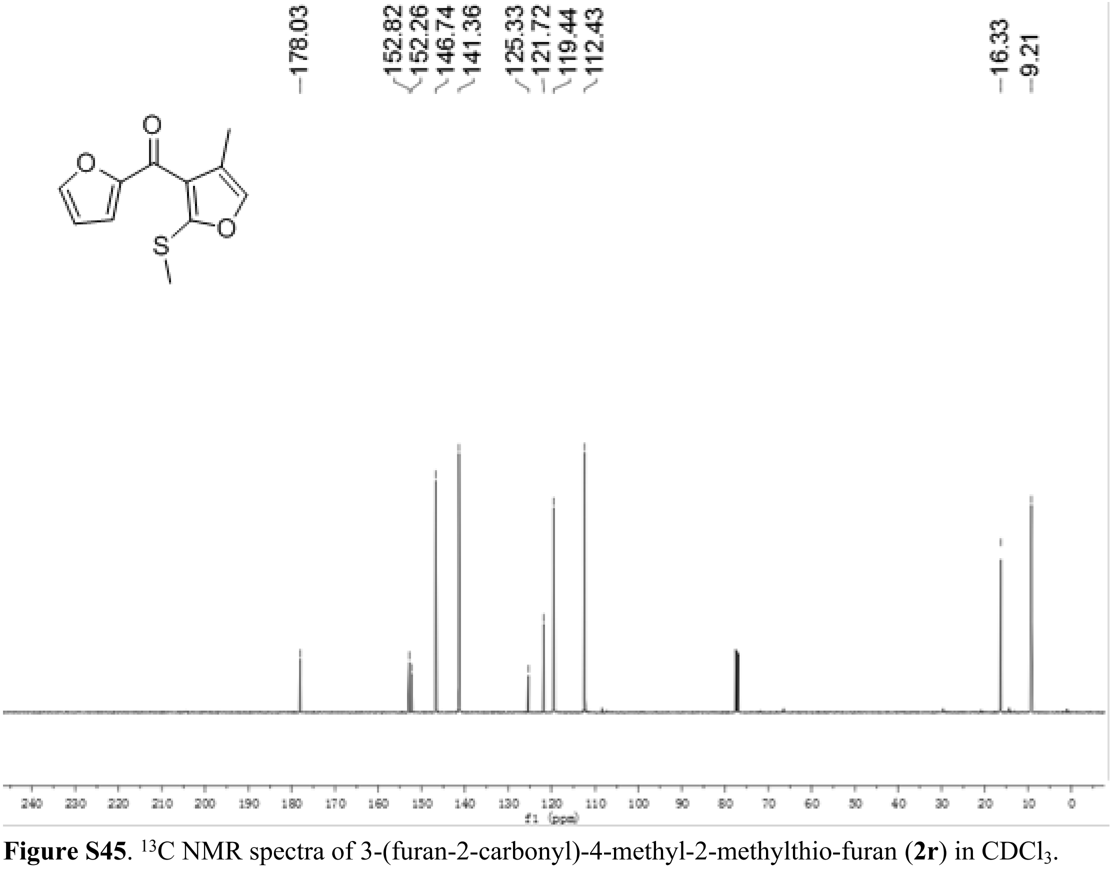


Figure S45. ^{13}C NMR spectra of 3-(furan-2-carbonyl)-4-methyl-2-methylthio-furan (**2r**) in CDCl$_3$.

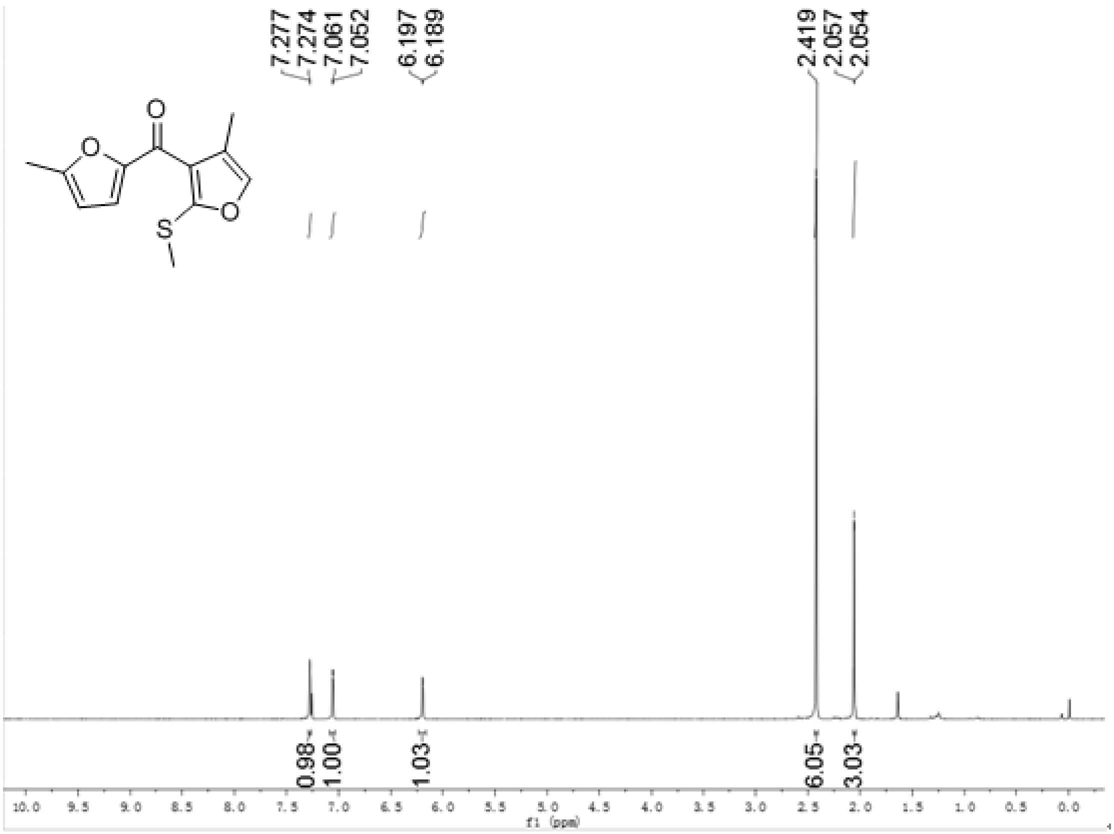


Figure S46. ^{1}H NMR spectra of 4-methyl-3-(5-methylfuran-2-carbonyl)-2-methylthio-furan (**2s**) in $CDCl_3$.

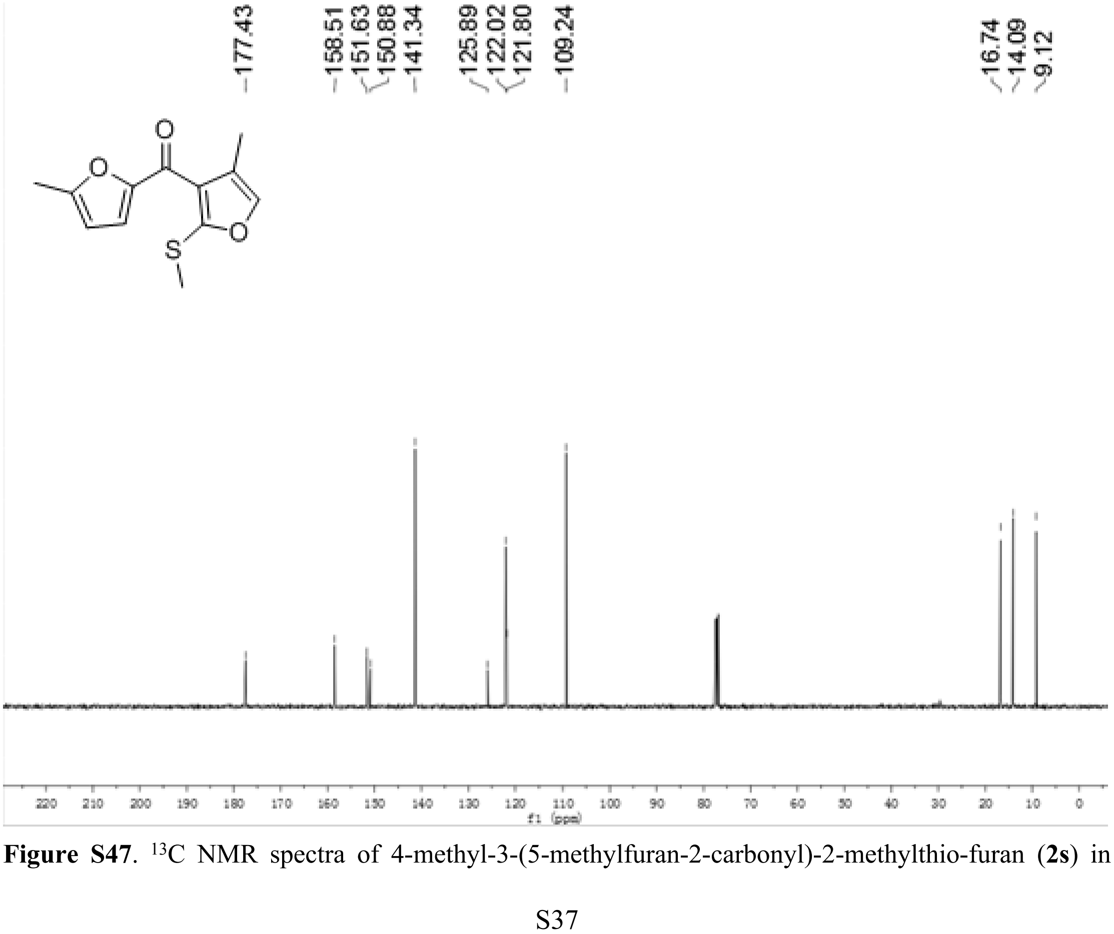


Figure S47. ^{13}C NMR spectra of 4-methyl-3-(5-methylfuran-2-carbonyl)-2-methylthio-furan (**2s**) in

CDCl$_3$.

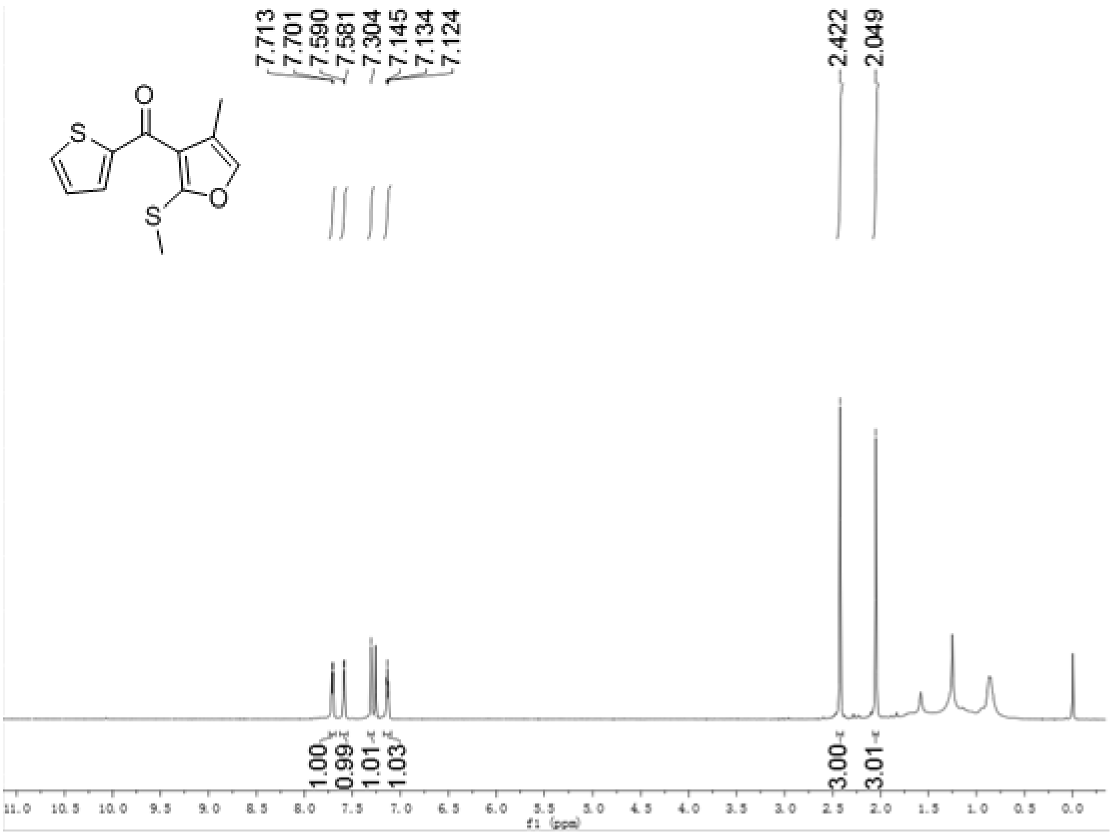


Figure S48. ^{1}H NMR spectra of 4-methyl-2-methylthio-3-(thien-2-carbonyl)-furan (**2t**) in CDCl$_3$.

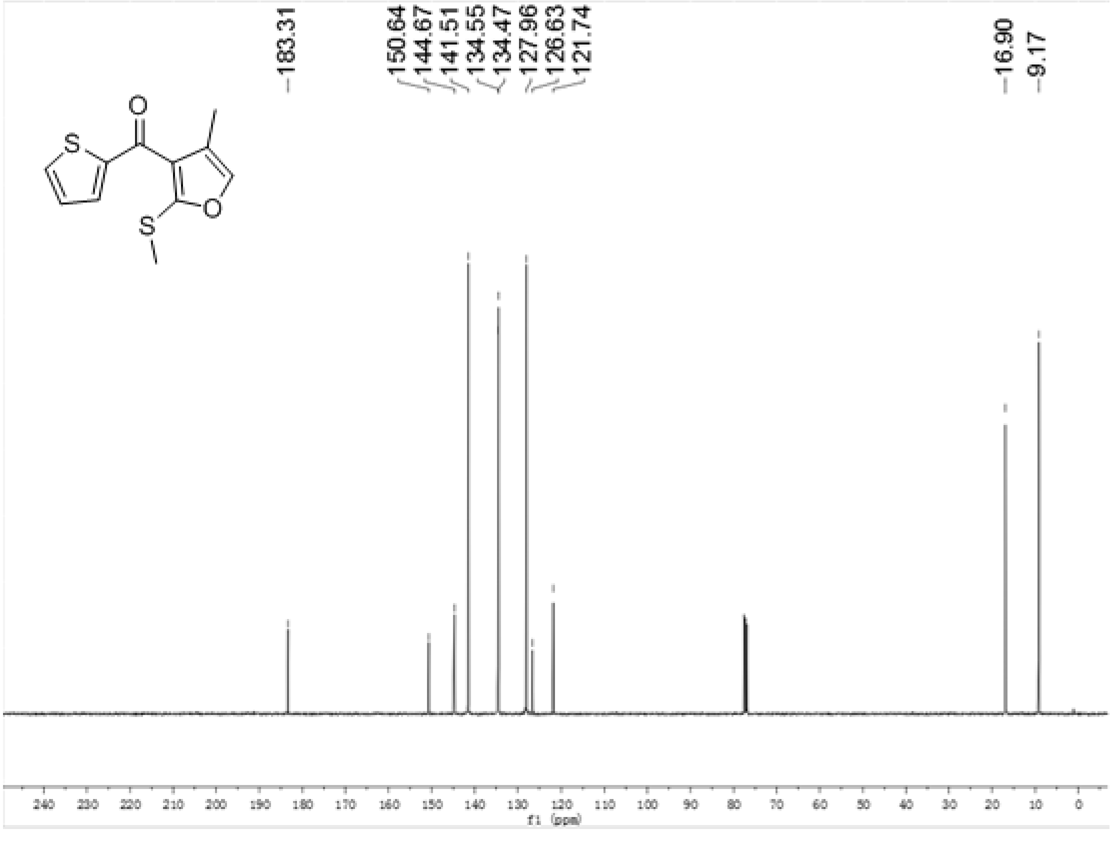


Figure S49. ^{13}C NMR spectra of 4-methyl-2-methylthio-3-(thien-2-carbonyl)-furan (**2t**) in CDCl$_3$.

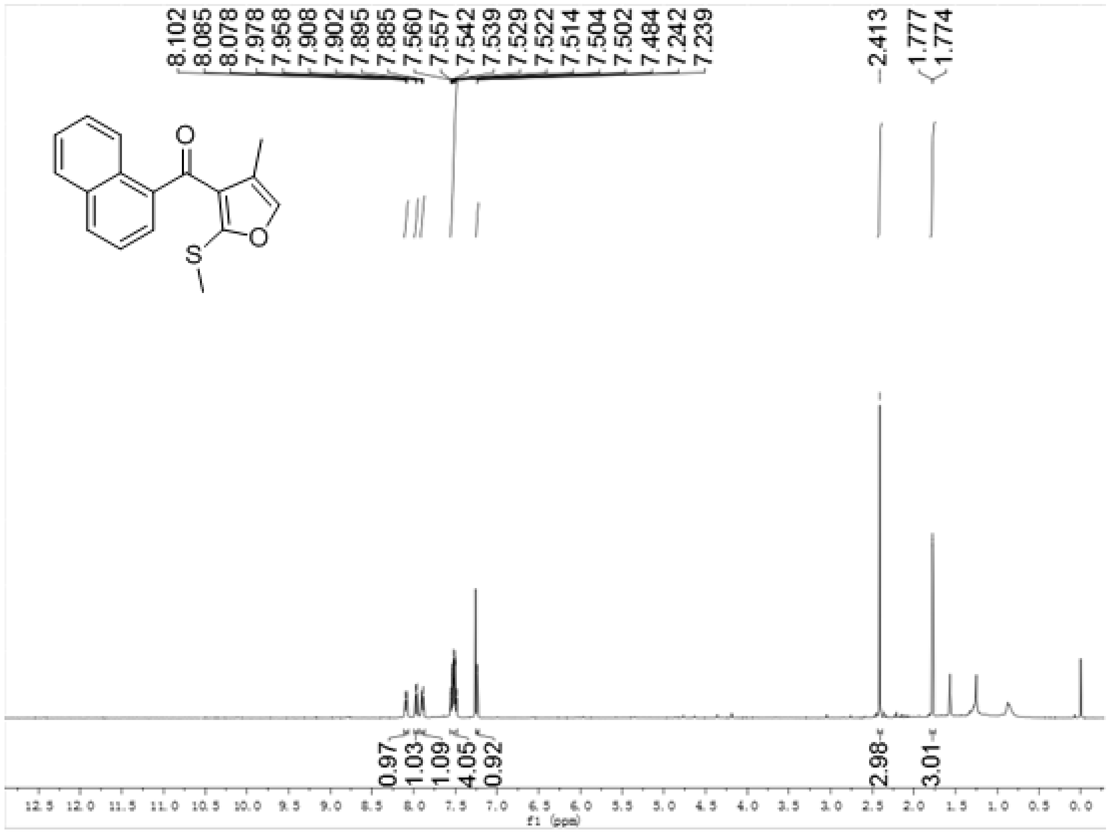


Figure S50. ^{1}H NMR spectra of 4-methyl-2-methylthio-3-(1-naphthoyl)-furan (**2u**) in $CDCl_3$.

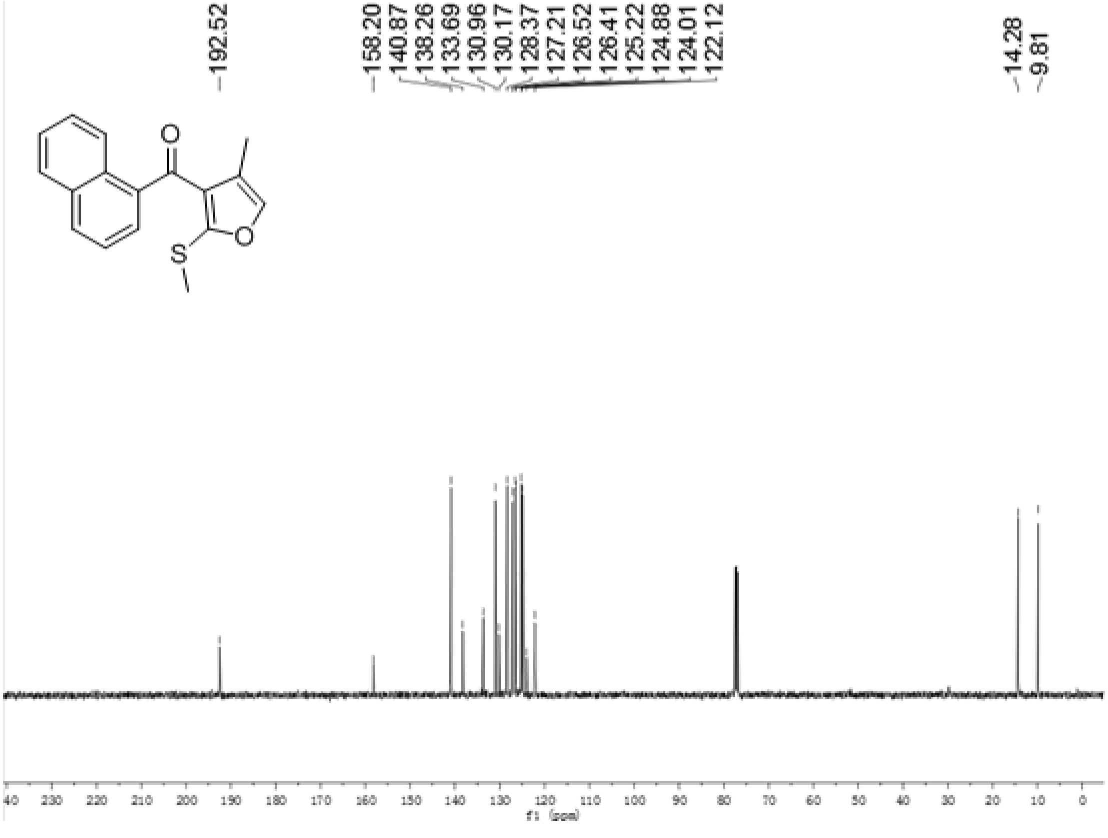


Figure S51. ^{13}C NMR spectra of 4-methyl-2-methylthio-3-(1-naphthoyl)-furan (**2u**) in $CDCl_3$.

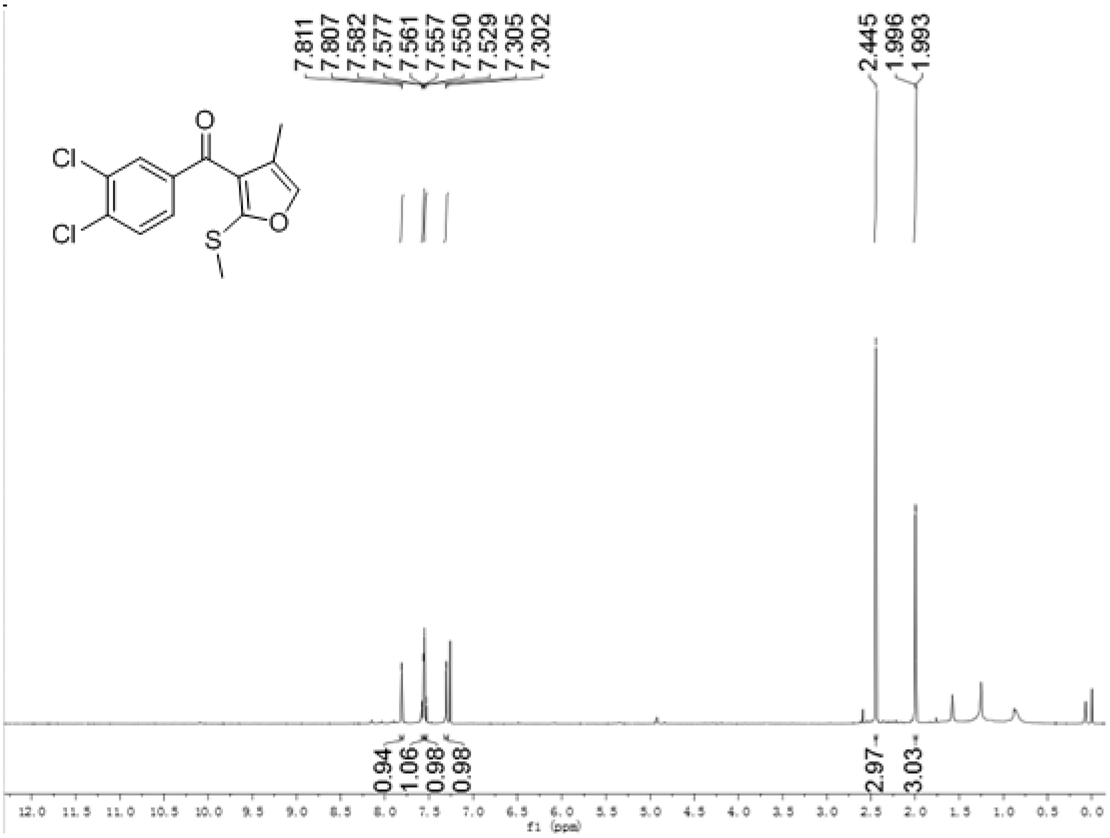


Figure S52. ^{1}H NMR spectra of 3-(3,4-dichlorobenzoyl)-4-methyl-2-methylthio-furan (**2v**) in CDCl$_3$.

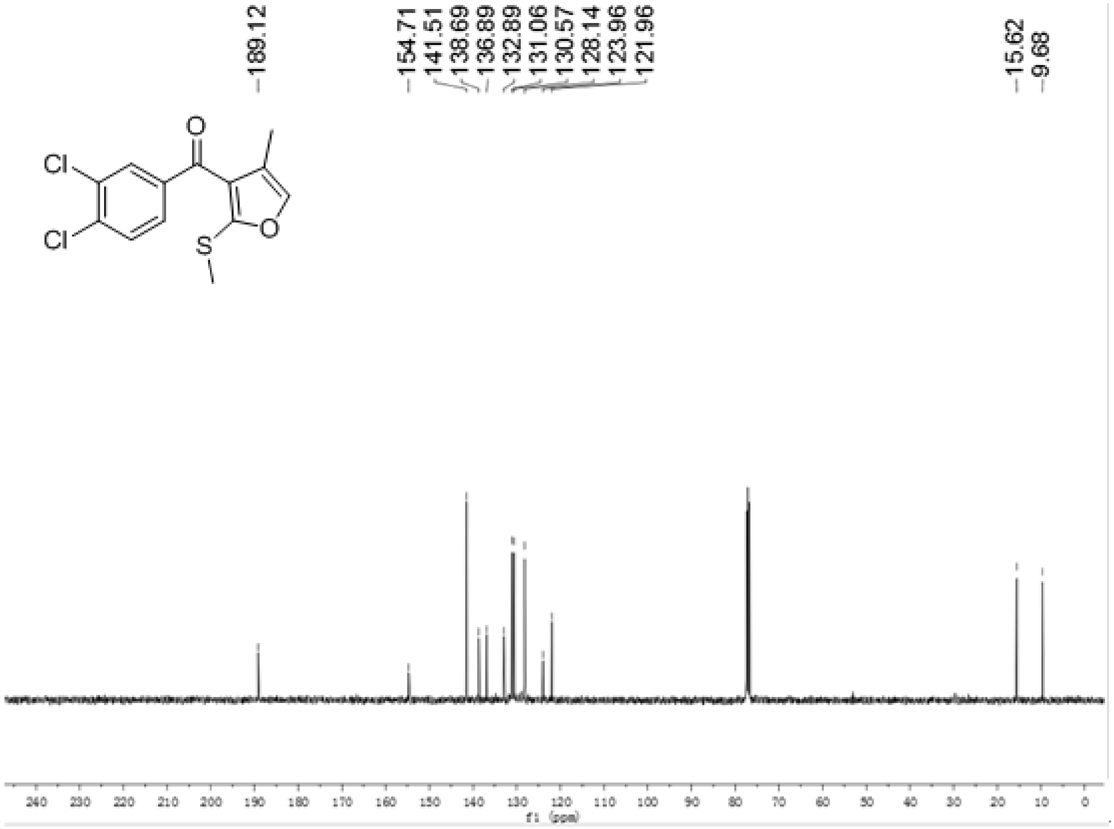


Figure S53. ^{13}C NMR spectra of 3-(3,4-dichlorobenzoyl)-4-methyl-2-methylthio-furan (**2v**) in CDCl$_3$.

Figure S54. ^{1}H NMR spectra of 4-methyl-3-(3,4-methylenedioxybenzoyl)-2-methylthio-furan (**2w**) in $CDCl_3$.

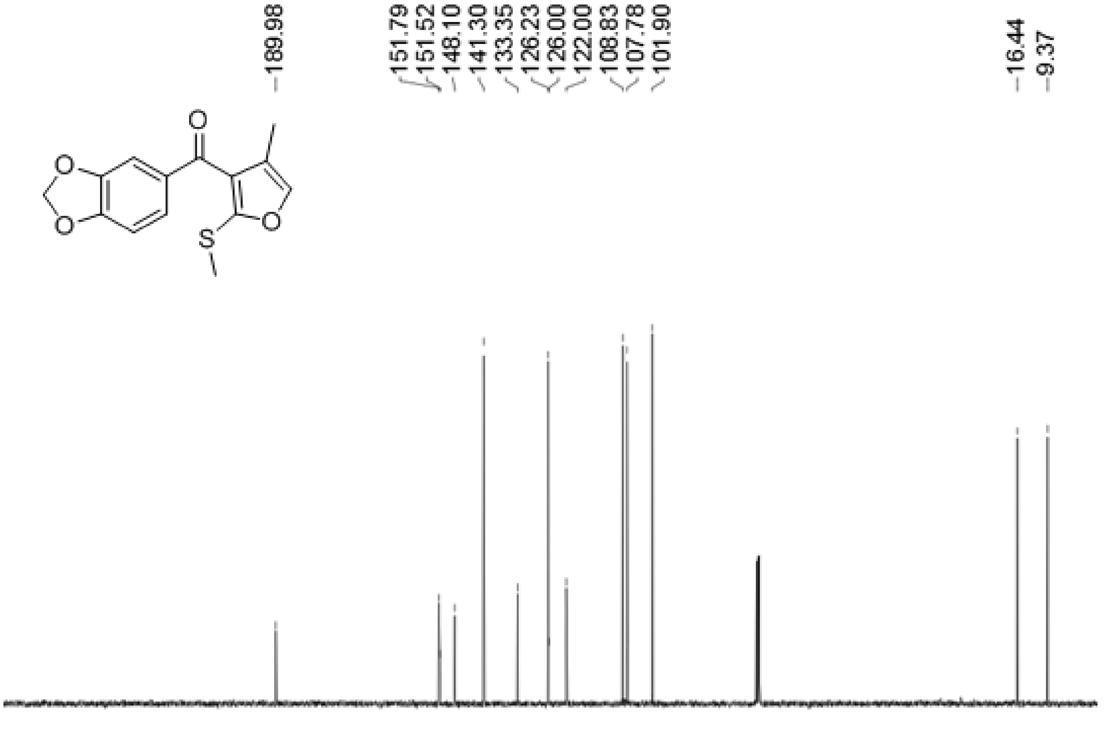


Figure S55. ^{13}C NMR spectra of 4-methyl-3-(3,4-methylenedioxybenzoyl)-2-methylthio-furan (**2w**) in

$CDCl_3$.

Figure S56. ^{1}H NMR spectra of 4-methyl-3-(2,4-dimethylbenzoyl)-2-methylthio-furan (**2x**) in $CDCl_3$.

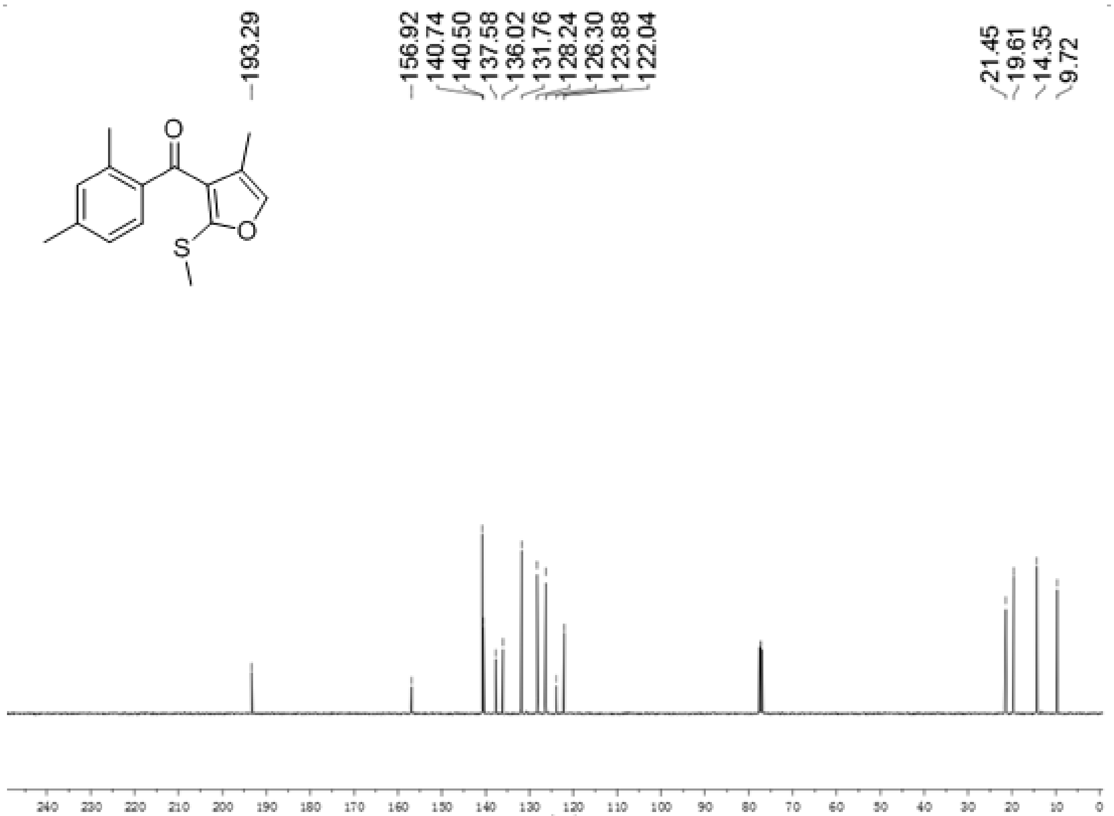


Figure S57. ^{13}C NMR spectra of 4-methyl-3-(2,4-dimethylbenzoyl)-2-methylthio-furan (**2x**) in $CDCl_3$.

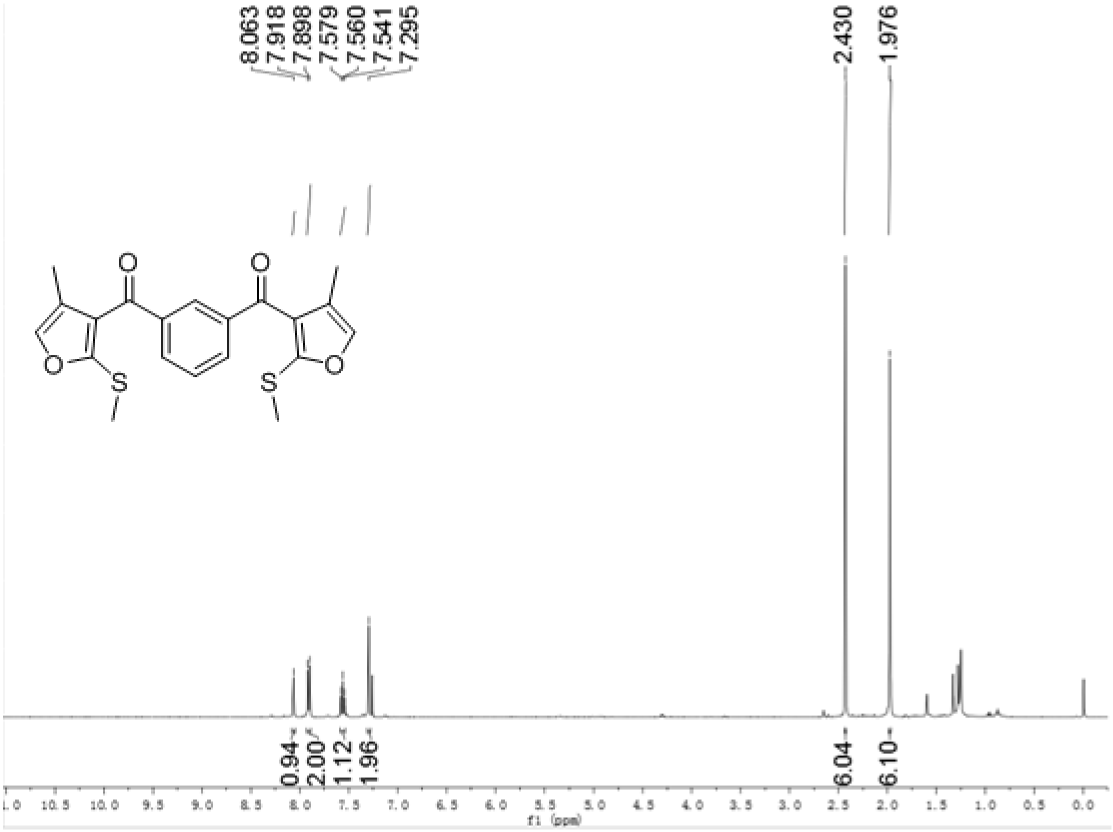


Figure S58. ^{1}H NMR spectra of 1,3-bis[(4-methyl-2-methylthio)furan-3-carbonyl]benzene (**2y**) in $CDCl_3$.

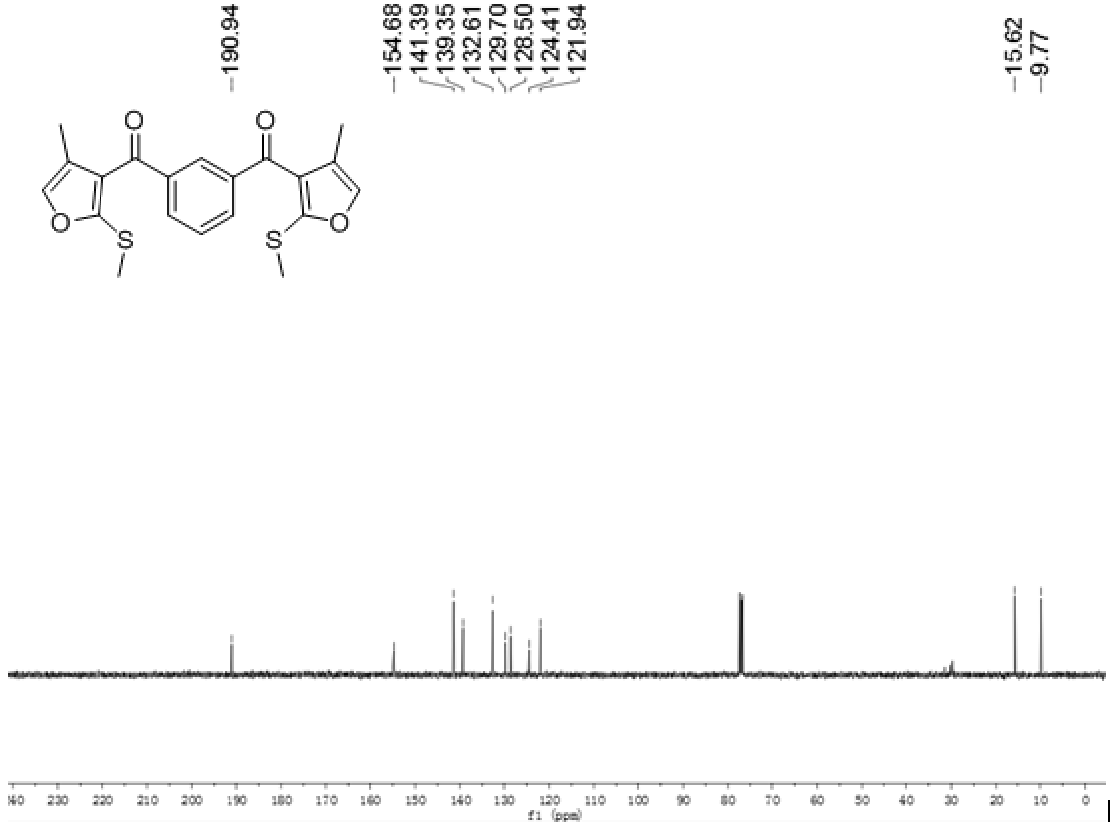


Figure S59. ^{13}C NMR spectra of 1,3-bis[(4-methyl-2-methylthio)furan-3-carbonyl]benzene (**2y**) in $CDCl_3$.

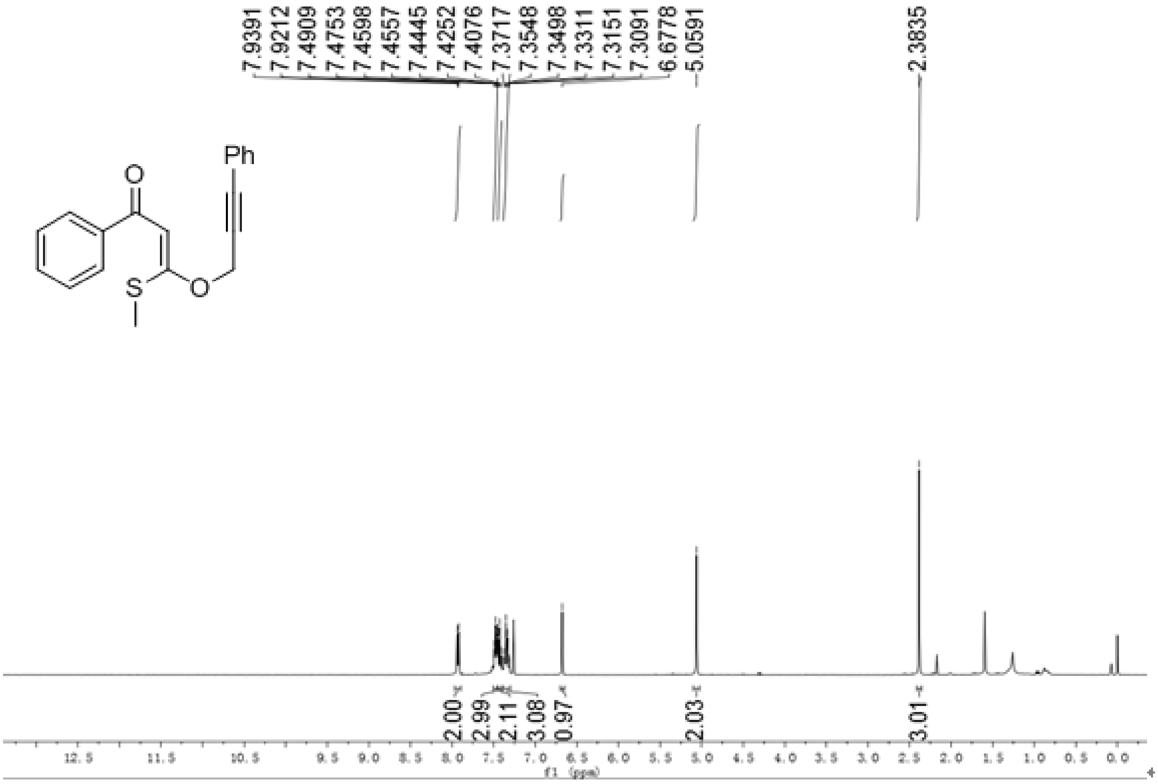


Figure S60. ^{1}H NMR spectra of 3-methylthio-1-phenyl-3-(3-phenylprop-2-ynyloxy)prop-2-en-1-one (**4a**) in $CDCl_3$.

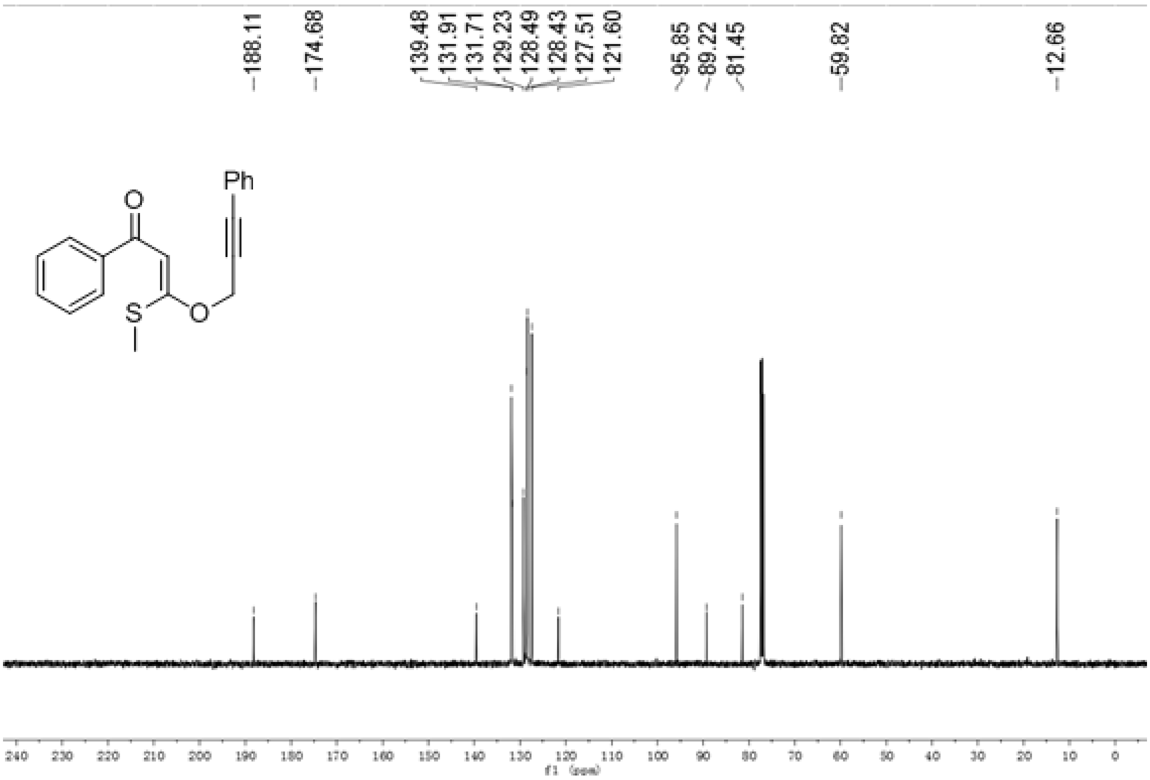


Figure S61. ^{13}C NMR spectra of 3-methylthio-1-phenyl-3-(3-phenylprop-2-ynyloxy)prop-2-en-1-one (**4a**) in $CDCl_3$.

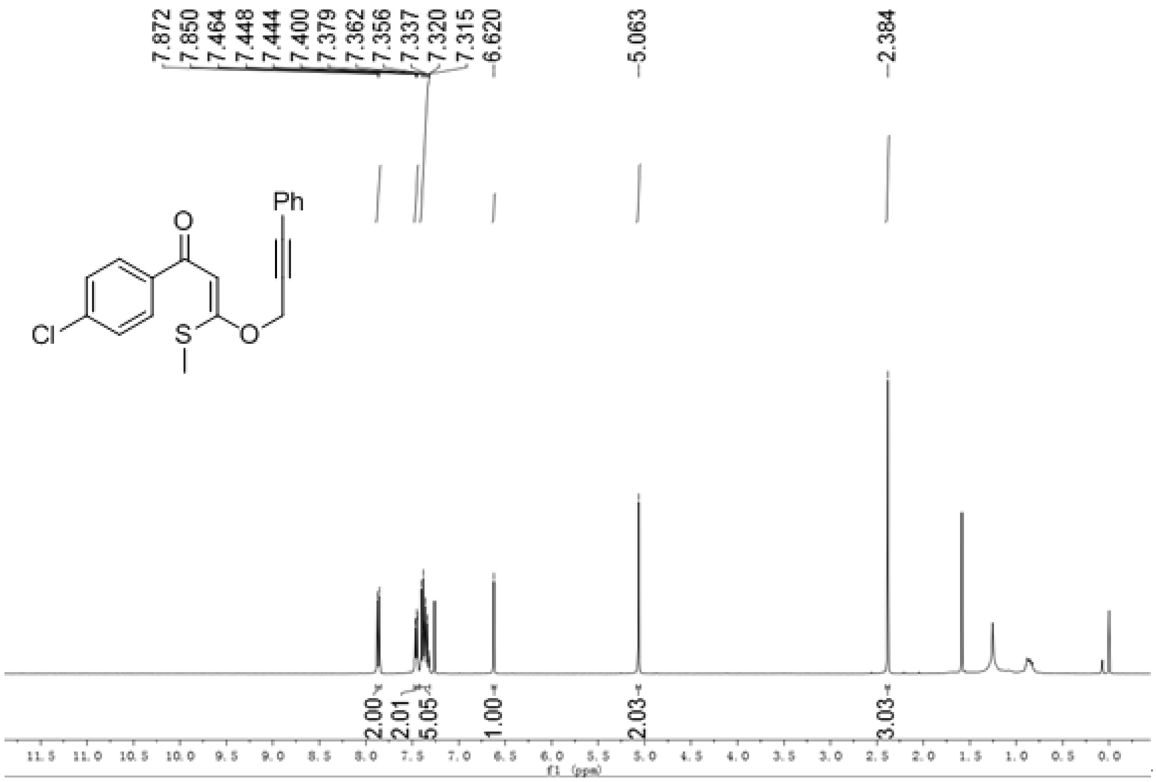


Figure S62. ^{1}H NMR spectra of 1-(4-chlorophenyl)-3-methylthio-3-(3-phenylprop-2-ynyloxy)pro- p-2-en-1-one (**4b**) in $CDCl_3$.

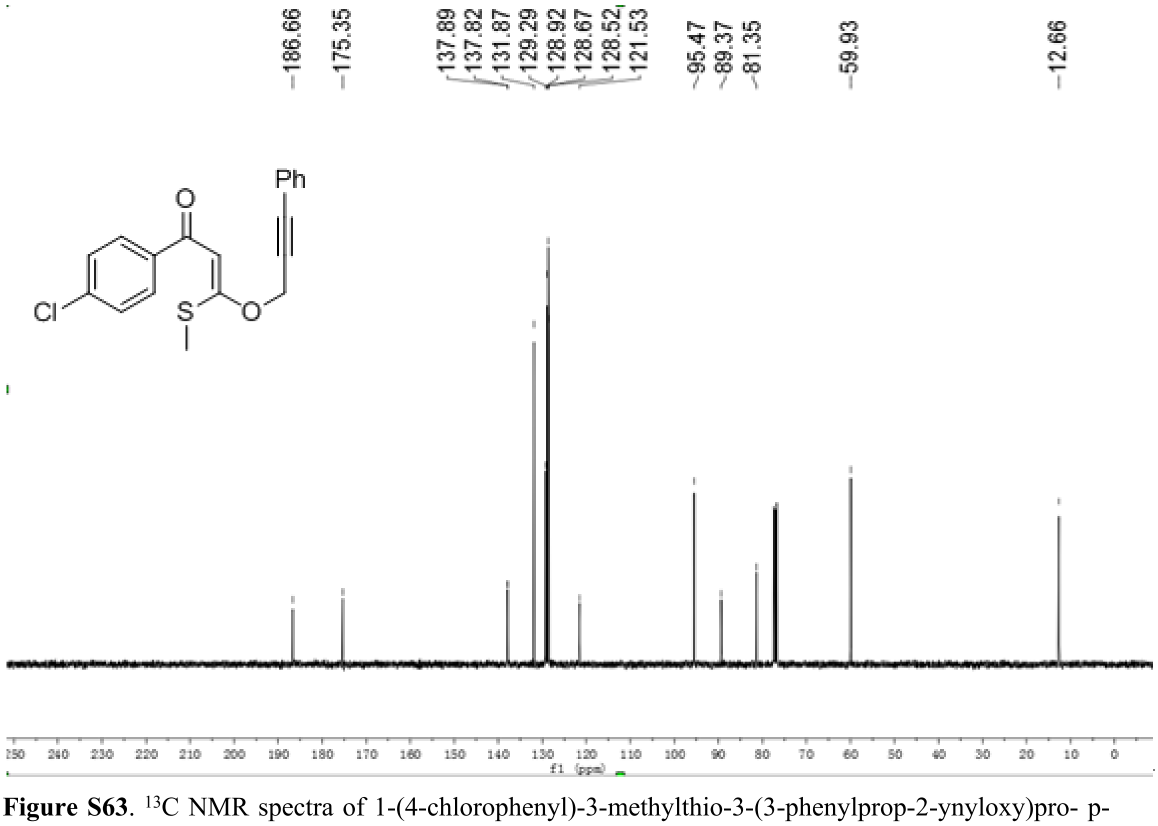


Figure S63. ^{13}C NMR spectra of 1-(4-chlorophenyl)-3-methylthio-3-(3-phenylprop-2-ynyloxy)pro- p-2-en-1-one (**4b**) in $CDCl_3$.

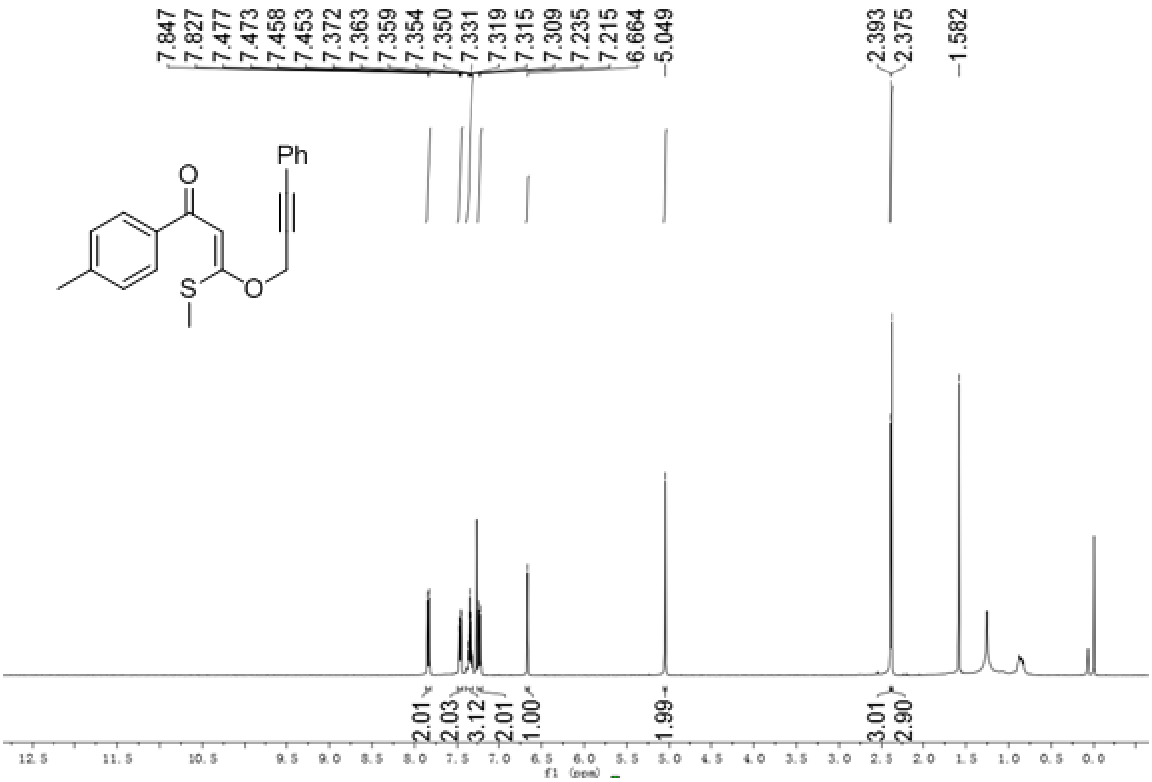


Figure S64. ^{1}H NMR spectra of 1-(4-methylphenyl)-3-methylthio-3-(3-phenylprop-2-ynyloxy)pro- p-2-en-1-one (**4c**) in $CDCl_3$.

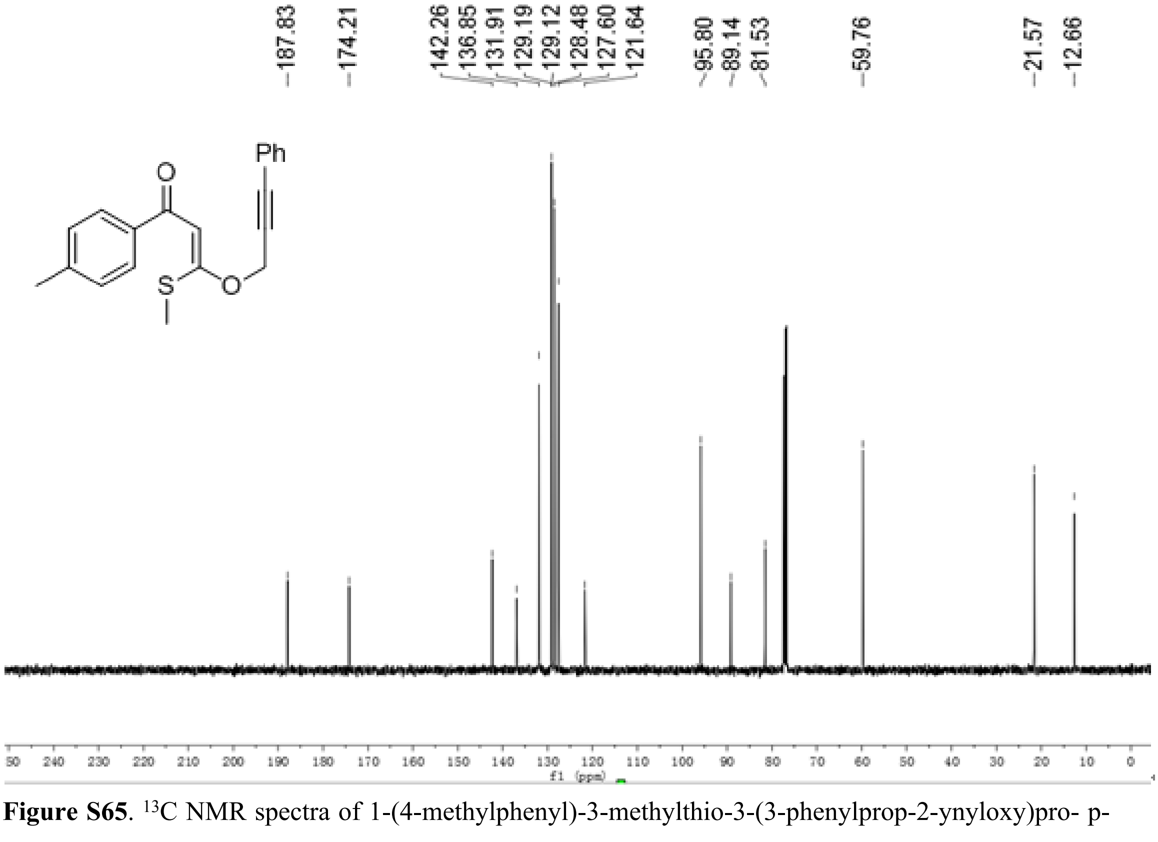


Figure S65. ^{13}C NMR spectra of 1-(4-methylphenyl)-3-methylthio-3-(3-phenylprop-2-ynyloxy)pro- p-2-en-1-one (**4c**) in $CDCl_3$.

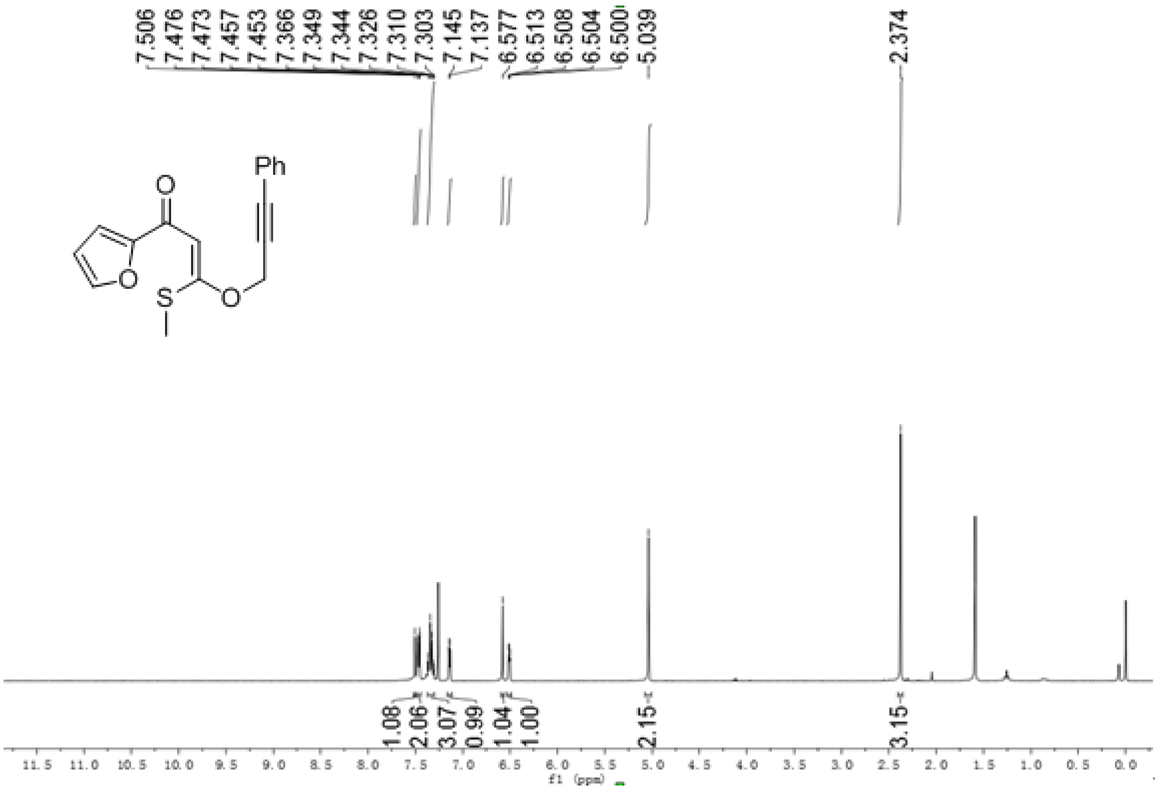


Figure S66. ^{1}H NMR spectra of 1-(furan-2-yl)-3-methylthio-3-(3-phenylprop-2-ynyloxy)pro- p-2-en-1-one (**4d**) in $CDCl_3$.

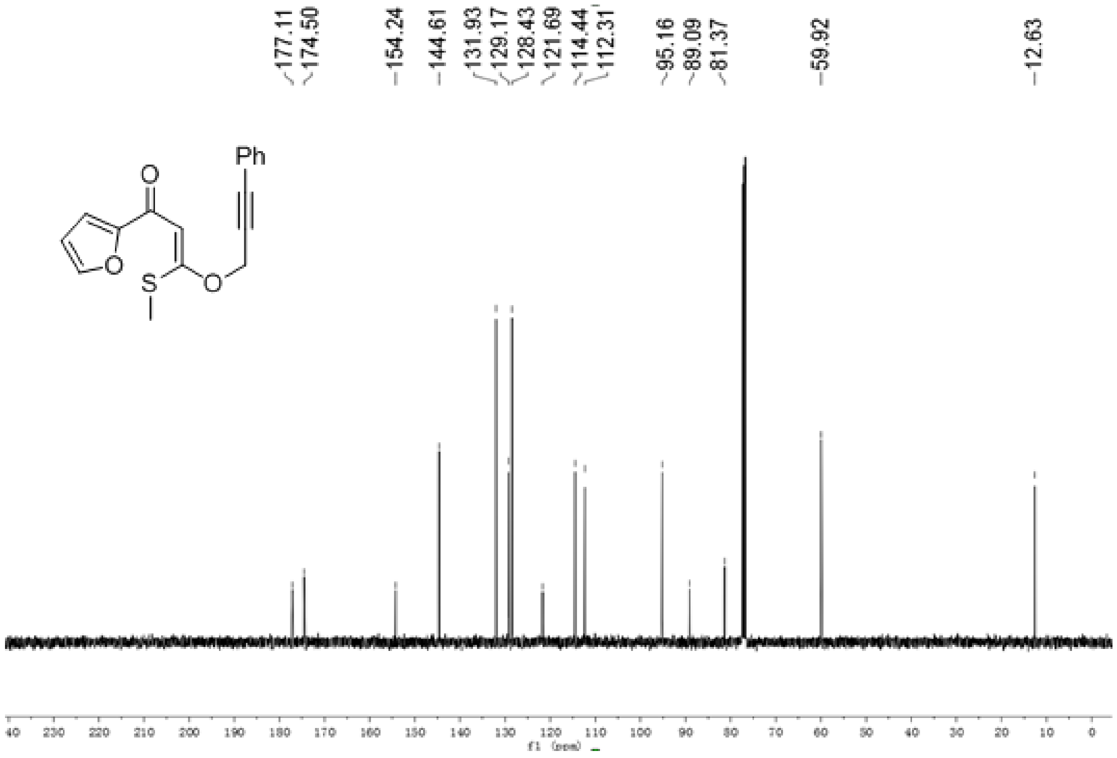


Figure S67. ^{13}C NMR spectra of 1-(furan-2-yl)-3-methylthio-3-(3-phenylprop-2-ynyloxy)pro- p-2-en-1-one (**4d**) in $CDCl_3$.

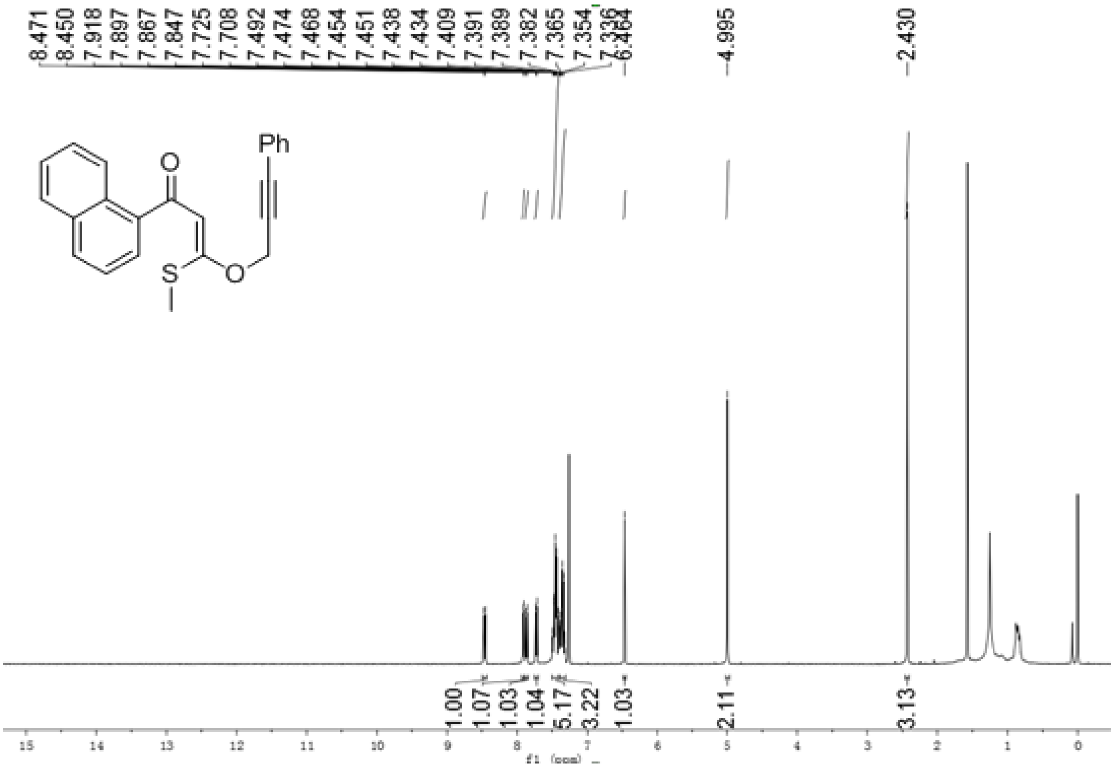


Figure S68. ^{1}H NMR spectra of 1-(naphthalen-1-yl)-3-methylthio-3-(3-phenylprop-2-ynyloxy)pro- p-2-en-1-one (**4e**) in $CDCl_3$.

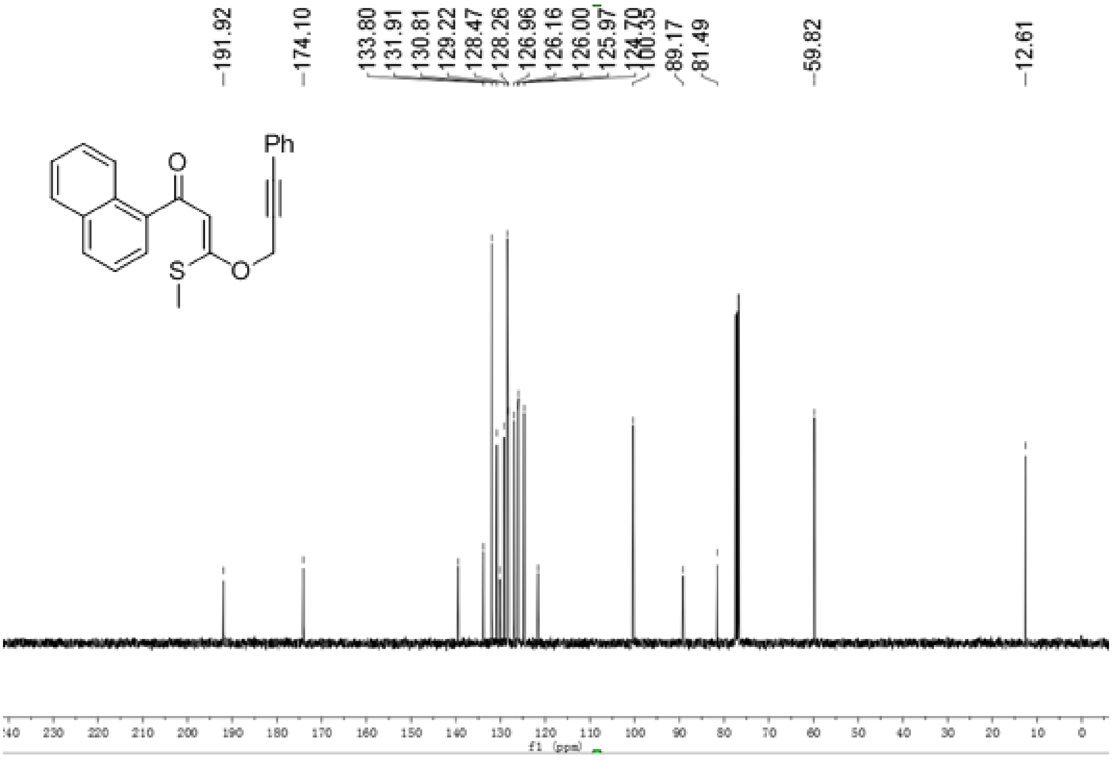


Figure S69. ^{13}C NMR spectra of 1-(naphthalen-1-yl)-3-methylthio-3-(3-phenylprop-2-ynyloxy)pro- p-2-en-1-one (**4e**) in $CDCl_3$.

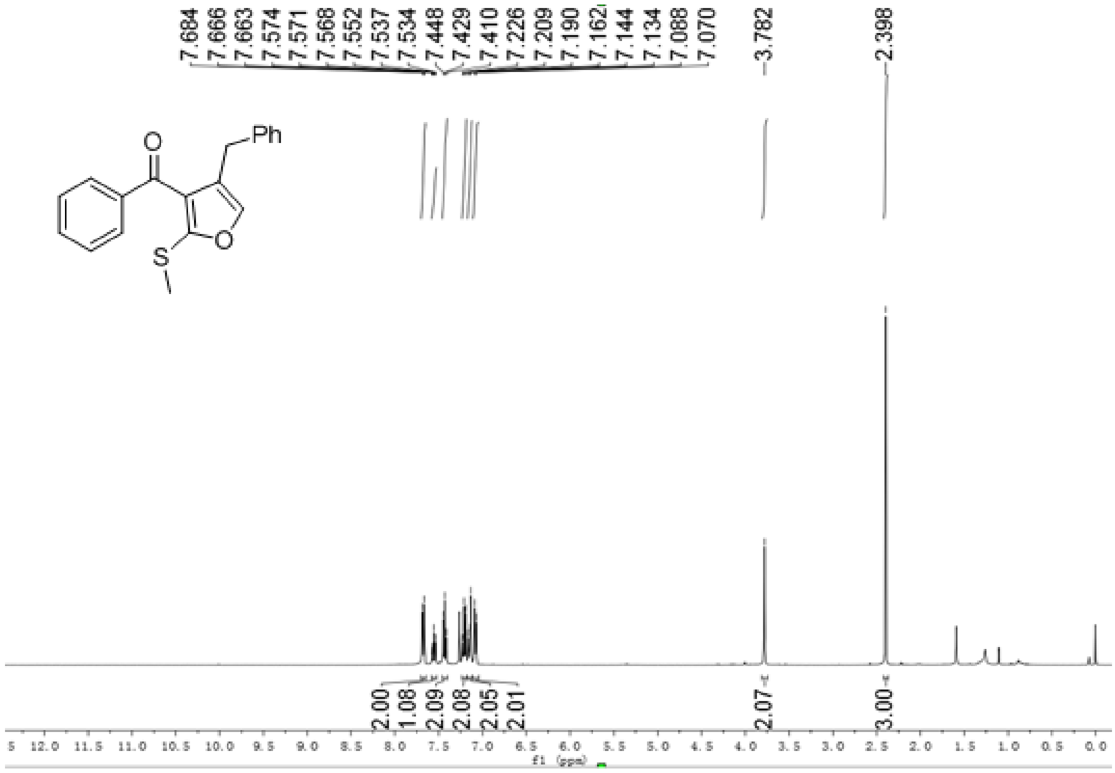


Figure S70. ^{1}H NMR spectra of 3-benzoyl-4-benzyl-2-methylthio-furan (**5a**) in $CDCl_3$.

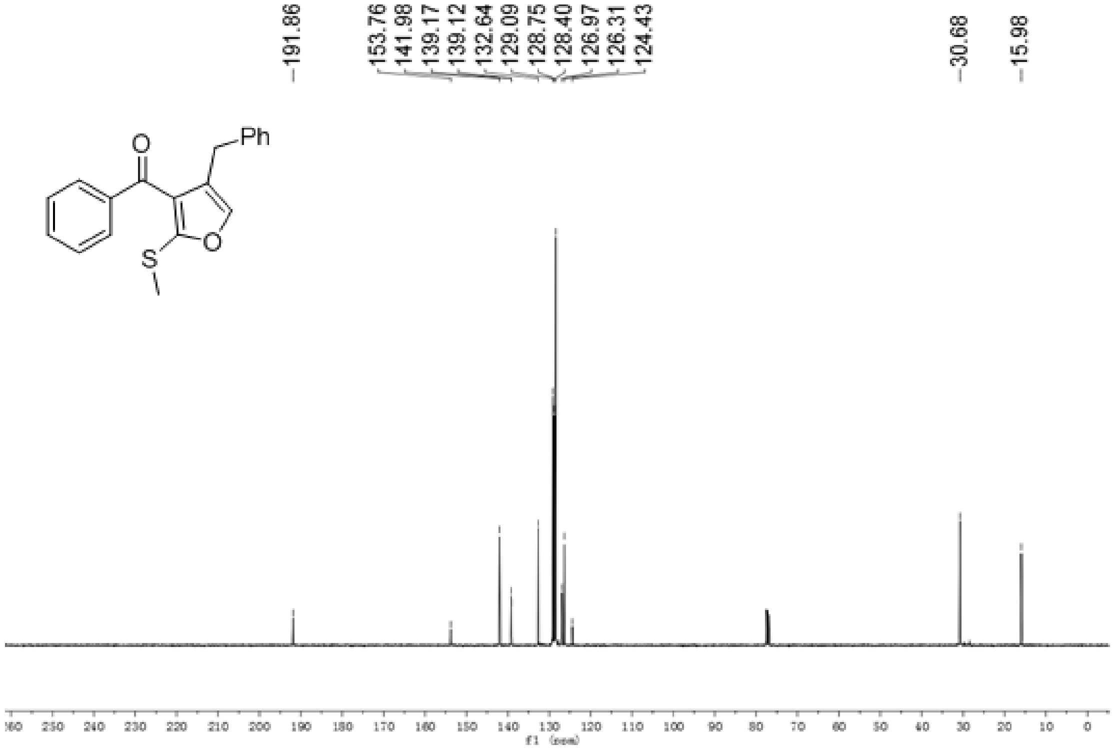


Figure S71. ^{13}C NMR spectra of 3-benzoyl-4-benzyl-2-methylthio-furan (**5a**) in $CDCl_3$.

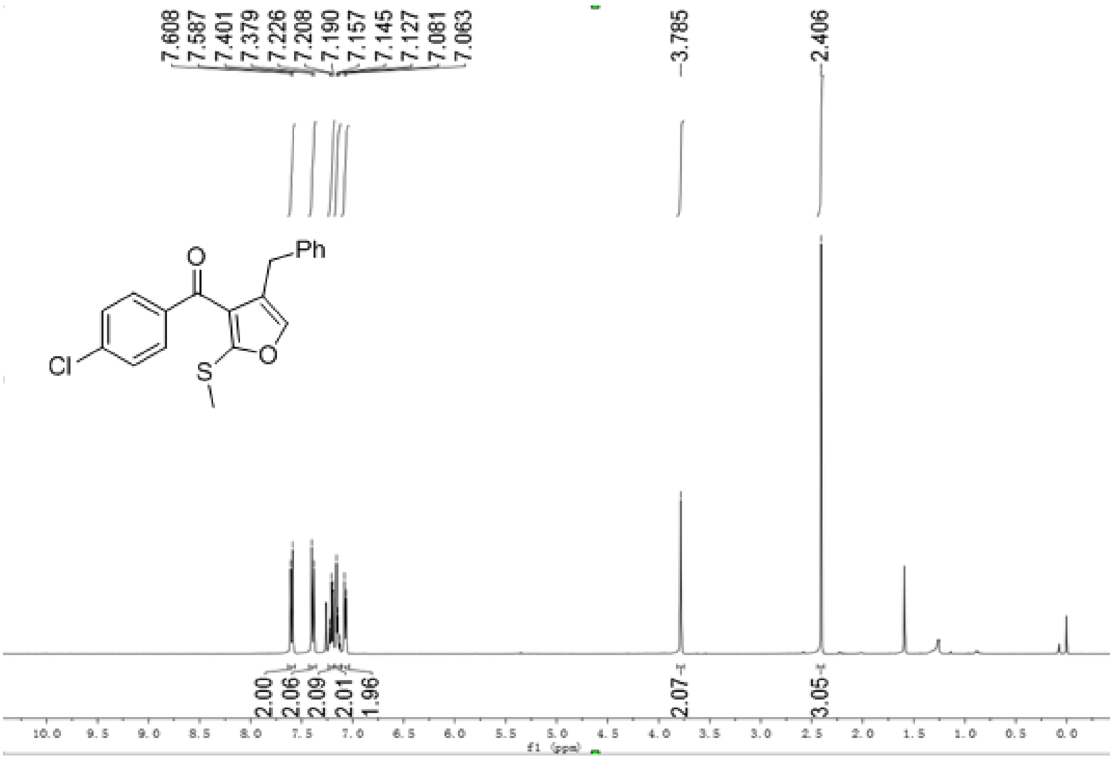


Figure S72. ^{1}H NMR spectra of 4-benzyl-3-(4-chlorobenzoyl)-2-methylthio-furan (**5b**) in $CDCl_3$.

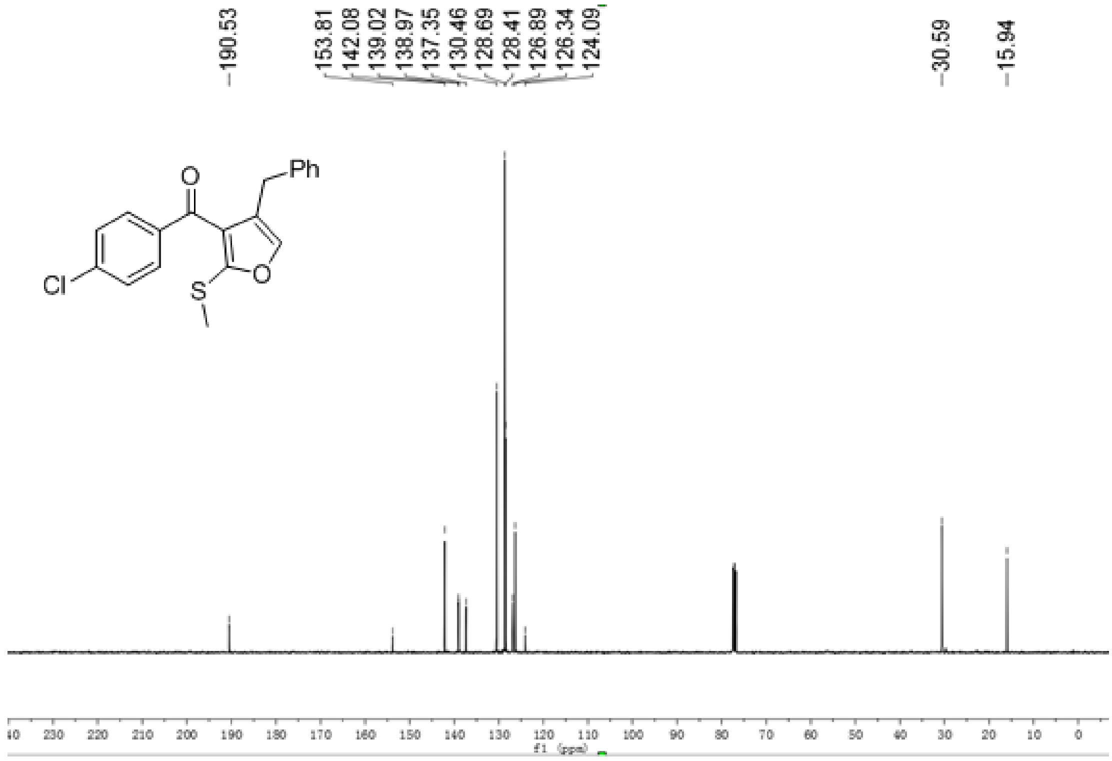


Figure S73. ^{1}H NMR spectra of 4-benzyl-3-(4-chlorobenzoyl)-2-methylthio-furan (**5b**) in $CDCl_3$.

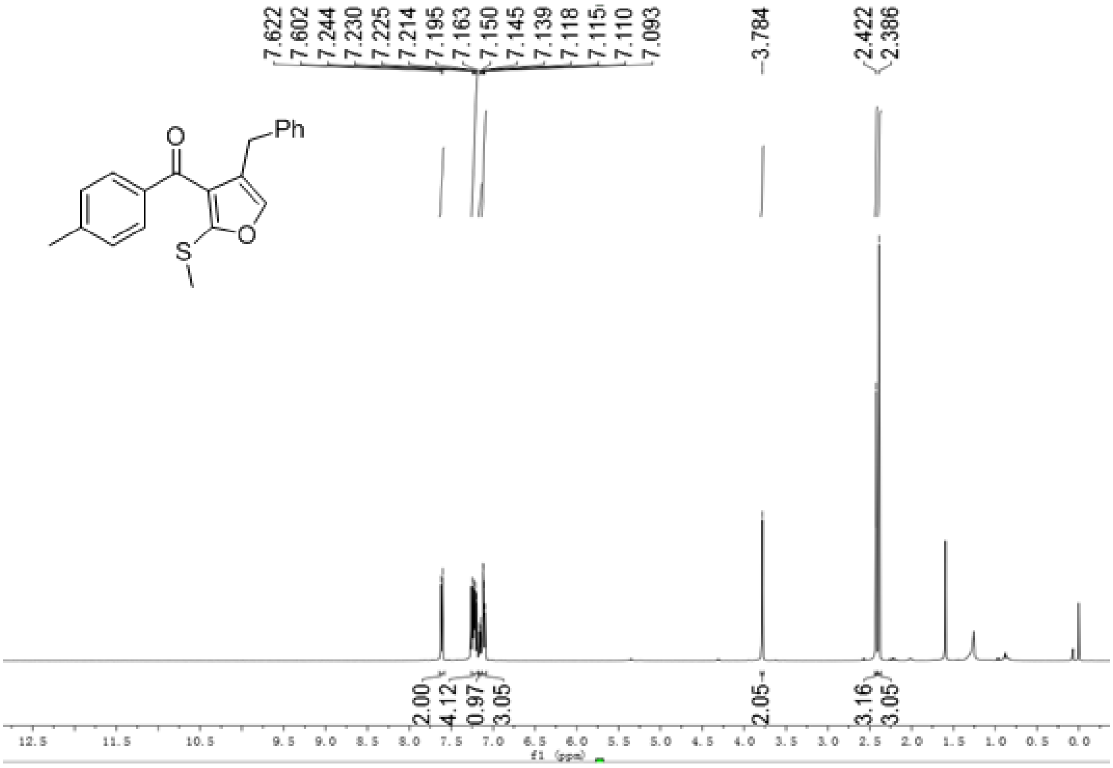


Figure S74. ^{1}H NMR spectra of 4-benzyl-3-(4-methylbenzoyl)-2-methylthio-furan (**5c**) in CDCl$_3$.

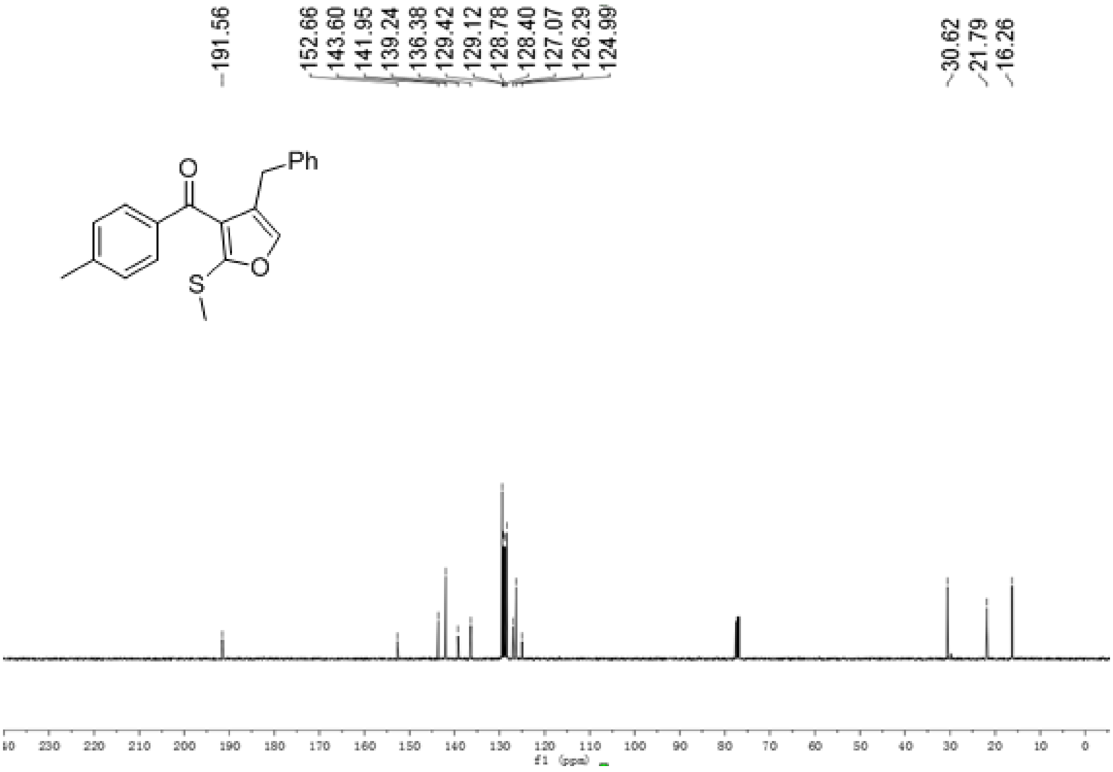


Figure S75. ^{1}H NMR spectra of 4-benzyl-3-(4-methylbenzoyl)-2-methylthio-furan (**5c**) in CDCl$_3$.

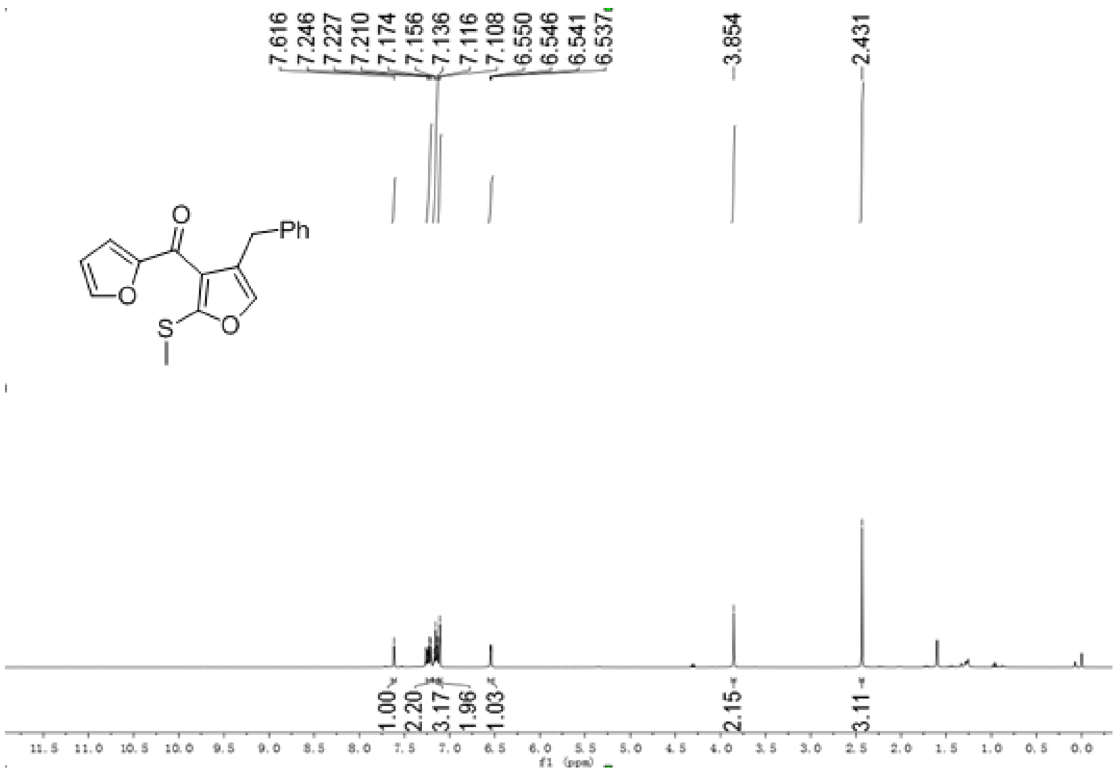


Figure S76. ^{1}H NMR spectra of 4-benzyl-3-(furan-2-carbonyl)-2-methylthio-furan (**5d**) in CDCl$_3$.

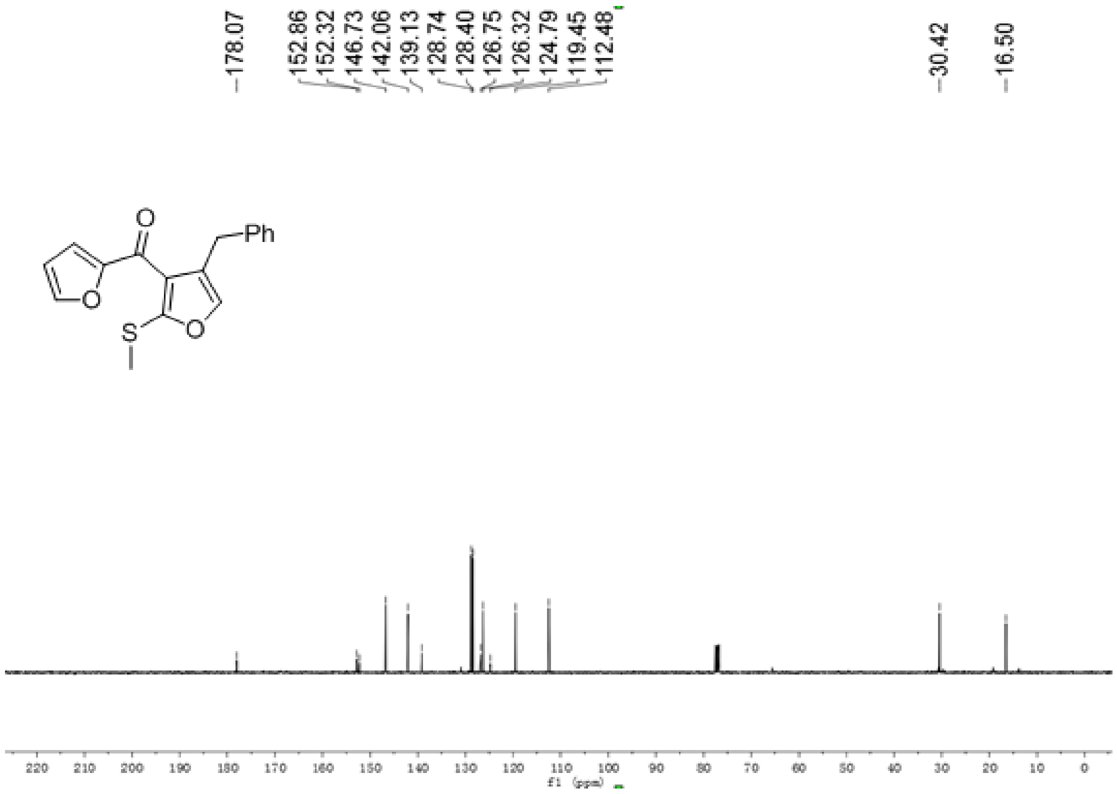


Figure S77. ^{1}H NMR spectra of 4-benzyl-3-(furan-2-carbonyl)-2-methylthio-furan (**5d**) in CDCl$_3$.

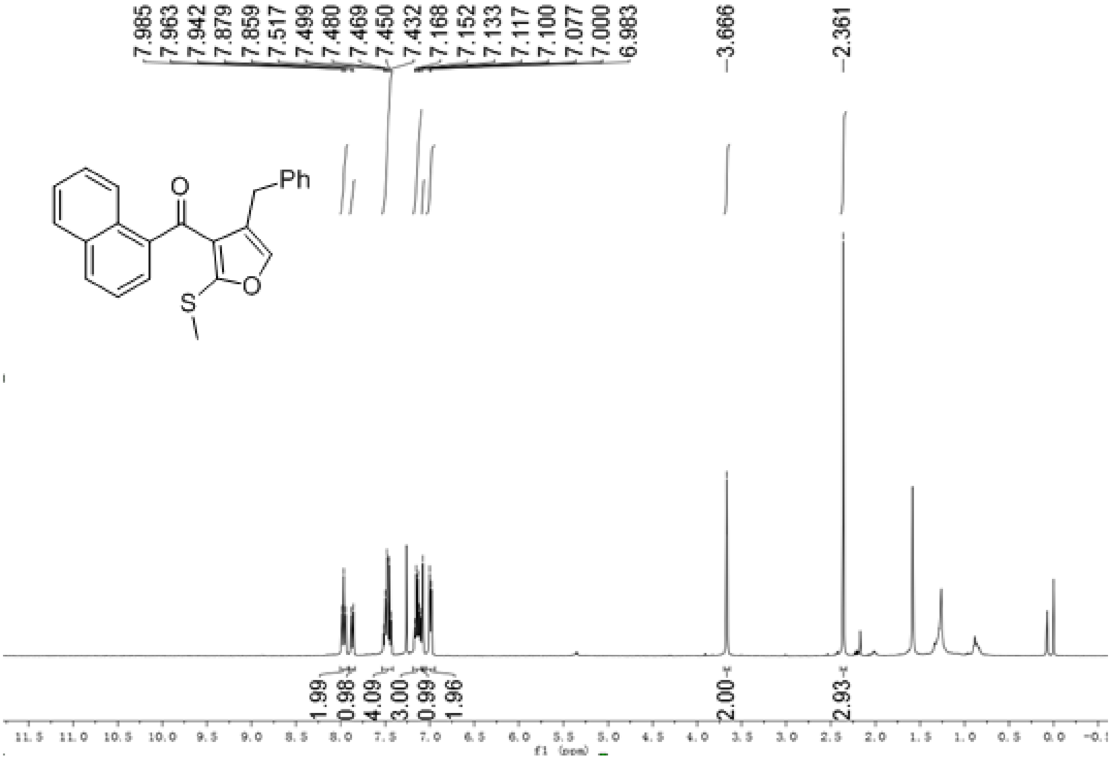


Figure S78. ^{1}H NMR spectra of 4-benzyl-2-methylthio-3-(1-naphthoyl)-furan (**5e**) in $CDCl_3$.

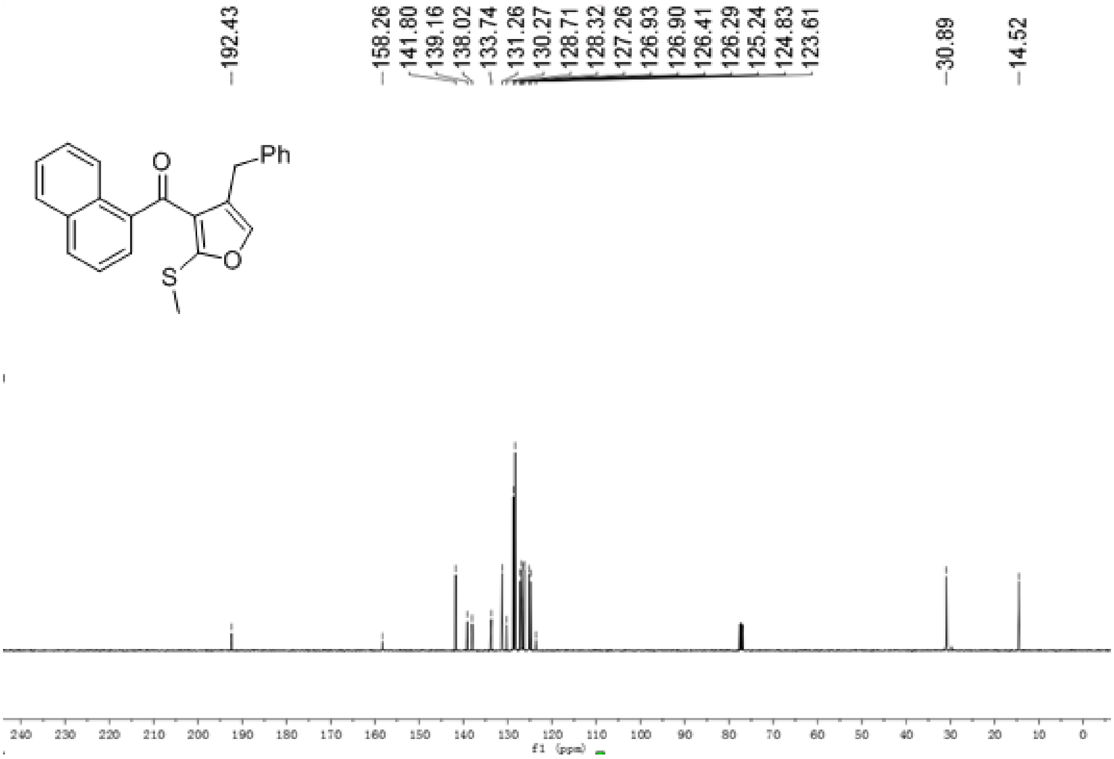


Figure S79. ^{1}H NMR spectra of 4-benzyl-2-methylthio-3-(1-naphthoyl)-furan (**5e**) in $CDCl_3$.

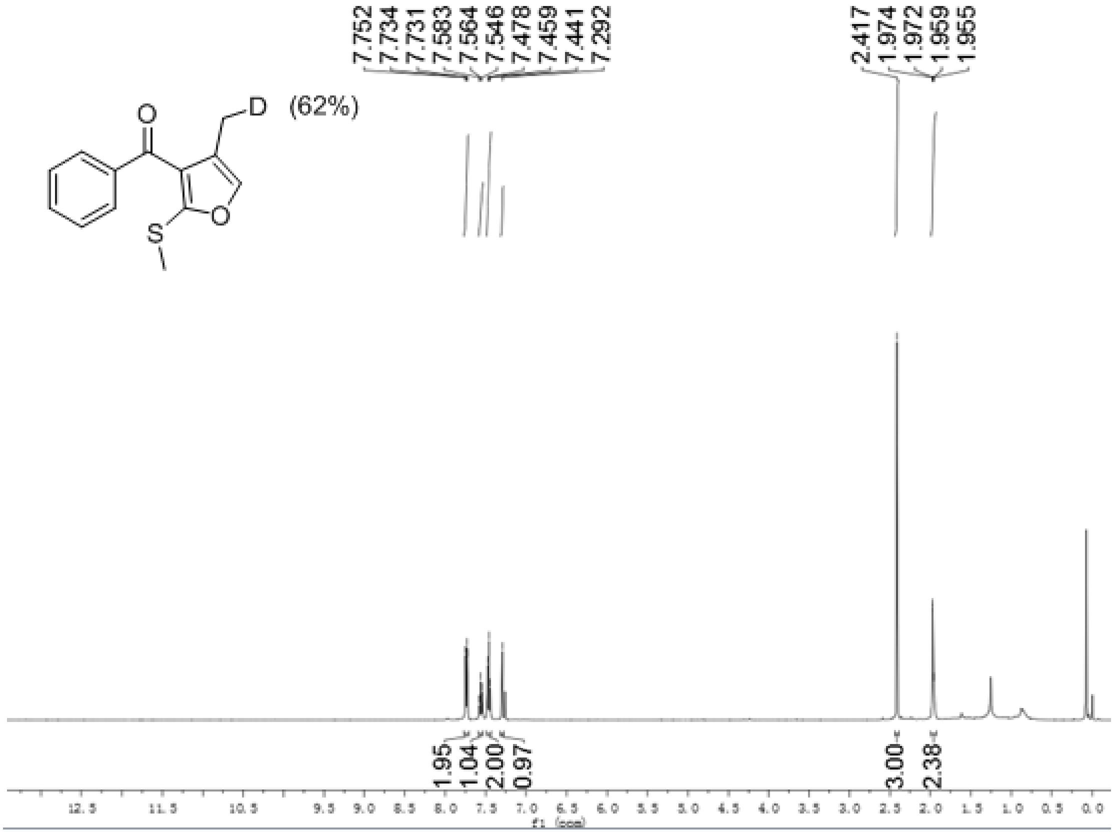


Figure S80. ^{1}H NMR spectra of 3-benzoyl-4-methyl-2-methylthio-furan-*d*1 (**2aa-*d***) in CDCl$_3$.

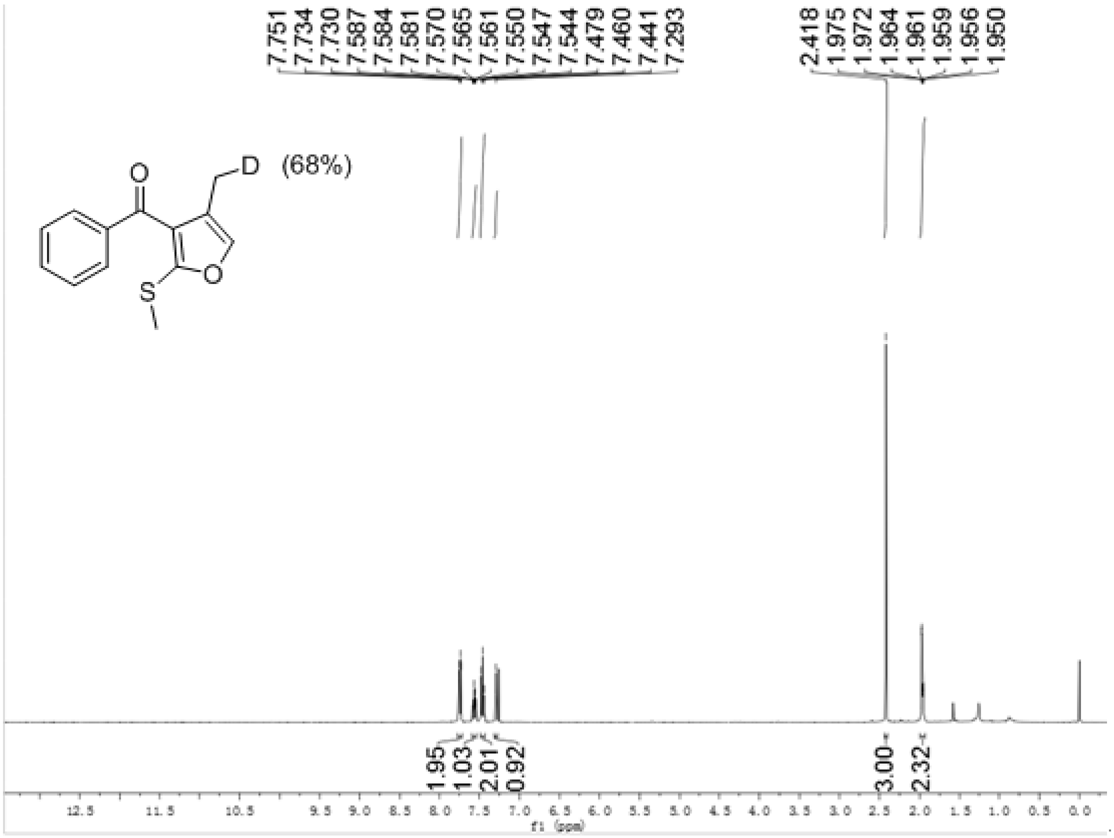


Figure S81. ^{1}H NMR spectra of 3-benzoyl-4-methyl-2-methylthio-furan-*d*1 (**2ab-*d***) in CDCl$_3$.

4. References

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