Formal Metal-Free γ-Arylation of 1,3-Dicarbonyl Compounds via an Isomerisation/1,4-Addition/[3,3]-Sigmatropic Rearrangement Sequence

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1. General Information

All reagents were used as received from commercial source unless specified otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300 or 400 spectrometer at the ambient temperature in $CDCl_3$. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, m = multiplet. High-resolution mass spectra (HRMS) was carried out by LC/MSD TOF using a column of C18 (rapid resolution, 3.5 μm, 2.1 mm × 30 mm) at a flow of 0.40 mL/min. Column chromatography was performed using 160-200 mesh silica gel. Aryl sulfoxides are commercially available.

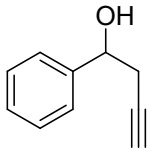
2. Experimental Procedures and Spectroscopic Data

① General Procedure for γ-Arylation of 1,3-Dicarbonyl Compounds and Analytical Data

Step 1: Synthesis of homopropargyl alcohols

The starting materials homopropargyl alcohols were synthesized following the known procedure.[1]

To a stirred suspension of the corresponding aldehyde (1 equiv.), propargyl bromide (2.0 equiv.; 80% in toluene) and zinc dust (5.0 equiv.) in THF at 0 °C was added to a saturated aqueous NH_4Cl solution dropwise. The mixture was allowed to warm up to room temperature and was stirred until full conversion was detected by TLC. The mixture was filtered over celite and the filter cake rinsed with CH_2Cl_2. The combined filtrates were washed with a saturated aqueous NH_4Cl solution and distilled water. After drying over $MgSO_4$, filtration and evaporation of the solvent in vacuo gave the crude product which was purified by flash column chromatography. For example, 1-phenylbut-3-yn-1-ol[1]



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 5H), 4.88 (dt, *J* = 9.4, 4.4 Hz, 1H), 2.64 (d, *J* = 3.7 Hz, 2H), 2.44 (s, 1H), 2.08 (s, 1H).

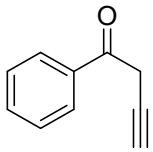
^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 128.5, 128.0, 125.7, 80.6, 72.3, 71.0, 29.4.

Step 2: General procedure for synthesis of 1,3-dicarbonyl compounds

The Dess-Martin periodinane reagent (1.2 equiv.) as a solid was added to a solution of the corresponding homopropargyl alcohol (0.2 mmol) dissolved in CH_2Cl_2 (2 mL) at 0 °C. The solution was warmed up to room temperature and monitored by TLC (usually a fast reaction with reaction times < 1 h). Upon full conversion, the hexane was added into the reaction solution, and cooled to -78 °C for 30 min. After filtration and evaporation of the solvent under reduced pressure at low temperature (< 30 °C), the

crude material can be directly used in the next chemical reaction without further purification.

1-phenylbut-3-yn-1-one (**2a**)



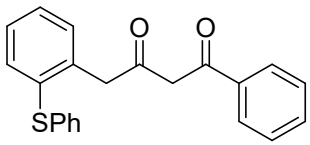
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 6.7 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 2H), 2.32 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 135.7, 134.2, 129.2, 129.0, 79.8, 74.1, 31.0.

HRMS (ESI-TOF): Calculated for $C_{10}H_9O^+$, $[M+H]^+$ 145.0648, Found 145.0646.

The TfOH (0.2 equiv.) as a catalyst was added to a solution of the above crude material **2a** and aryl sulfoxide **1a** (1.1 equiv.) in EtOAc (1 mL). The solution was stirred under air atmosphere at specified temperature, and monitored by TLC. After completion, the mixture was then quenched with saturated aqueous $NaHCO_3$, and extracted with EtOAc (3 x 5 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the products **3**.

1-phenyl-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3a**)



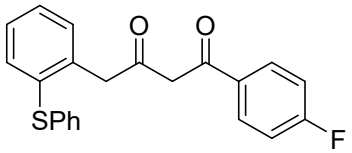
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 63.7 mg (92%).

^{1}H NMR (300 MHz, $CDCl_3$) enol δ 15.93 (s, 1H), 7.78 – 7.70 (m, 2H), 7.53 – 7.32 (m, 6H), 7.27 – 7.14 (m, 6H), 6.05 (s, 1H), 3.98 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) enol δ 195.3, 181.9, 137.6, 136.4, 134.5, 134.4, 134.2, 132.2, 131.3, 129.3, 129.1, 128.6, 128.5, 128.3, 126.9, 126.4, 96.5, 44.4.

HRMS (ESI-TOF): Calculated for $C_{22}H_{19}O_2S^+$, $[M+H]^+$ 347.1100, Found 347.1094.

1-(4-fluorophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3b**)



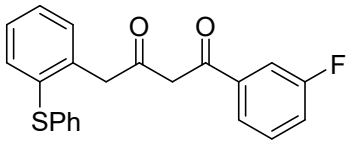
The product was obtained as a colorless oil after chromatography (n-hexane/EtOAc = 15:1), 64.0 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.89 (s, 1H), 7.68 – 7.65 (m, 2H), 7.37 – 7.32 (m, 2H), 7.28 – 7.24 (m, 1H), 7.23 – 7.16 (m, 2H), 7.16 – 7.12 (m, 2H), 7.11 – 7.10 (m, 1H), 7.09 – 7.06 (m, 1H), 7.00 (td, *J* = 8.6, 1.6 Hz, 2H), 5.91 (s, 1H), 3.89 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 194.5, 181.4, 165.2 (d, *J* = 252.0 Hz), 137.5, 136.4, 134.6, 134.1, 131.3, 130.8 (d, *J* = 3.0 Hz), 129.4 (d, *J* = 9.0 Hz), 129.2 (d, *J* = 12.9 Hz), 129.2, 128.6, 128.3, 126.4, 115.6 (d, *J* = 21.7 Hz), 96.2, 44.2.

HRMS (ESI-TOF): Calculated for $C_{22}H_{18}FO_2S^+$, $[M+H]^+$ 365.1006, Found 365.1000.

1-(3-fluorophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3c**)



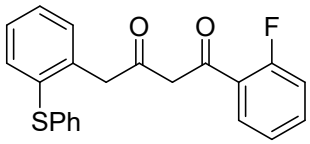
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 62.1 mg (85%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.69 (s, 1H), 7.40 (d, *J* = 9.8 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 6.7 Hz, 1H), 5.87 (s, 1H), 3.89 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 194.6, 178.3, 157.0 (d, *J* = 250.0 Hz), 136.3, 135.4, 134.0 (d, *J* = 6.0 Hz), 133.7, 133.0, 130.3, 129.7, 128.1, 127.6 (d, *J* = 25.9 Hz), 125.5, 124.0 (d, *J* = 18.0 Hz), 122.2 (d, *J* = 4.0 Hz), 113.9 (d, *J* = 22.0 Hz), 95.6, 43.4.

HRMS (ESI-TOF): Calculated for $C_{22}H_{18}FO_2S^+$, $[M+H]^+$ 365.1006, Found 365.1000.

1-(2-fluorophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3d**)



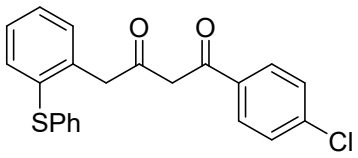
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 60.4 mg (83%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.75 (s, 1H), 7.84 – 7.75 (m, 1H), 7.40 – 7.36 (m, 2H), 7.32 – 7.30 (m, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.22 – 7.21 (m, 1H), 7.20 – 7.19 (m, 2H), 7.16 – 7.15 (m, 1H), 7.13 – 7.11 (m, 2H), 7.08 – 7.06 (m, 1H), 7.05 – 6.99 (m, 1H), 6.13 (s, 1H), 3.90 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 196.4, 177.0, 161.0 (d, *J* = 254.0 Hz), 137.4, 136.4, 134.5, 134.4, 133.3 (d, *J* = 9.3 Hz), 131.3, 129.9 (d, *J* = 2.0 Hz), 129.4, 129.1, 128.4 (d, *J* = 18.0 Hz), 126.4, 124.4 (d, *J* = 3.5 Hz), 122.8 (d, *J* = 10.3 Hz), 116.5 (d, *J* = 23.0 Hz), 101.3 (d, *J* = 13.6 Hz), 77.2, 44.7.

HRMS (ESI-TOF): Calculated for $C_{22}H_{18}FO_2S^+$, $[M+H]^+$ 365.1006, Found 365.1000.

1-(4-chlorophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3e**)



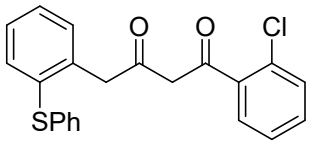
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 67.6 mg (89%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.46 (s, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 2H), 7.19 (q, *J* = 6.7, 6.1 Hz, 3H), 7.11 (d, *J* = 10.8 Hz, 2H), 7.09 – 7.04 (m, 3H), 7.03 (d, *J* = 6.8 Hz, 1H), 5.83 (s, 1H), 3.84 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 193.3, 181.7, 136.1, 135.3, 133.9, 133.4, 133.3, 130.8, 130.5, 130.3, 129.6, 129.1, 128.4, 128.1, 127.5, 127.3, 125.8, 125.5, 100.7, 43.0.

HRMS (ESI-TOF): Calculated for $C_{22}H_{18}ClO_2S^+$, $[M+H]^+$ 381.0711, Found 381.0707.

1-(2-chlorophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3f**)



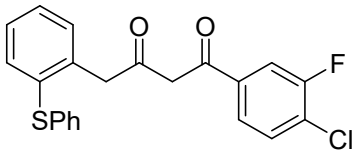
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 60.8 mg (80%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.47 (s, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.17 – 7.12 (m, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.07 – 7.01 (m, 3H), 5.83 (s, 1H), 3.84 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 193.3, 181.7, 136.1, 135.2, 133.9, 133.4, 133.3, 130.8, 130.5, 130.3, 129.6, 129.1, 128.4, 128.1, 127.5, 127.3, 125.8, 125.5, 100.6, 43.0.

HRMS (ESI-TOF): Calculated for $C_{22}H_{18}ClO_2S^+$, $[M+H]^+$ 381.0711, Found 381.0706.

1-(4-chloro-3-fluorophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3g**)



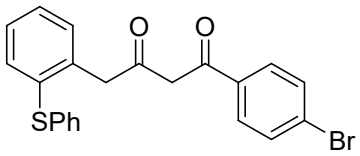
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 73.2 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.69 (s, 1H), 7.41 – 7.35 (m, 2H), 7.32 – 7.29 (m, 3H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.04 – 7.02 (m, 1H), 5.87 (s, 1H), 3.89 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 195.6, 179.2, 158.0 (d, *J* = 248.0 Hz), 137.3, 136.4, 135.0 (d, *J* = 7.0 Hz), 134.7, 134.0, 131.3, 130.7, 129.2, 129.1 (d, *J* = 1.5 Hz), 128.5 (d, *J* = 26.1 Hz), 126.5, 125.1 (d, *J* = 17.8 Hz) , 123.1 (d, *J* = 3.7 Hz), 114.9 (d, *J* = 22.4 Hz), 96.6, 44.4.

HRMS (ESI-TOF): Calculated for $C_{22}H_{17}ClFO_2S^+$, $[M+H]^+$ 399.0616, Found 399.0610.

1-(4-bromophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3h**)



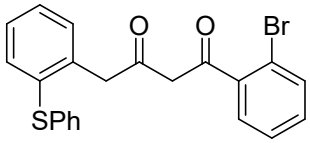
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 76.3 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.78 (s, 1H), 7.53 – 7.44 (m, 4H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.15 – 7.13 (m, 1H), 7.11 – 7.07 (m, 2H), 5.93 (s, 1H), 3.91 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 194.4, 179.7, 136.4, 135.4, 133.7, 133.1, 132.4, 130.8, 130.3, 128.2, 128.1, 127.6, 127.4, 127.4, 126.0, 125.5, 95.4, 43.5.

HRMS (ESI-TOF): Calculated for $C_{22}H_{18}BrO_2S^+$, $[M+H]^+$ 425.0205, Found 425.0200.

1-(2-bromophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3i**)



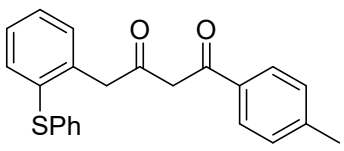
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 68.7 mg (81％).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.38 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.25 – 7.23 (m, 2H), 7.18 – 7.15 (m, 2H), 7.14 – 7.12 (m, 2H), 7.10 – 7.06 (m, 3H), 5.75 (s, 1H), 3.86 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 192.7, 183.6, 136.2, 136.1, 135.3, 133.4, 133.3, 132.8, 130.5, 130.3, 129.0, 128.4, 128.1, 127.5, 127.4, 126.3, 125.5, 119.2, 100.5, 42.9.

HRMS (ESI-TOF): Calculated for $C_{22}H_{18}BrO_2S^+$, $[M+H]^+$ 425.0205, Found 425.0204.

4-(2-(phenylthio)phenyl)-1-(p-tolyl)butane-1,3-dione (**3j**)



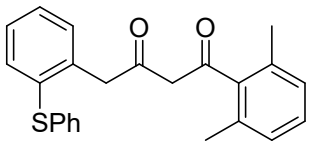
The product was obtained as a colorless oil after chromatography (n-hexane/EtOAc = 15:1), 67.0 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.94 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.20 – 7.14 (m, 3H), 7.12 (d, *J* = 7.0 Hz, 4H), 7.09 – 7.06 (m, 1H), 5.94 (s, 1H), 3.88 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 194.7, 182.3, 143.1, 137.7, 136.5, 134.6, 134.3, 131.8, 131.3, 129.4, 129.3, 129.2, 128.6, 128.3, 127.1, 126.5, 96.2, 44.4, 21.7.

HRMS (ESI-TOF): Calculated for $C_{23}H_{21}O_2S^+$, $[M+H]^+$ 361.1257, Found 361.1250.

1-(2,6-dimethylphenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3k**)



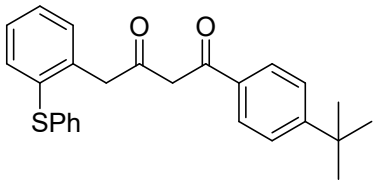
The product was obtained as a colorless oil after chromatography (n-hexane/EtOAc = 20:1), 65.1 mg (87%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.49 (s, 1H), 7.36 (td, *J* = 7.5, 1.6 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.26 – 7.22 (m, 3H), 7.19 – 7.16 (m, 3H), 7.15 – 7.13 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 2H), 5.49 (s, 1H), 3.92 (s, 2H), 2.24 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 195.8, 186.4, 137.1, 136.4, 136.1, 134.9, 134.7, 134.1, 131.3, 129.7, 129.2, 129.0, 128.4, 127.6, 126.6, 102.5, 44.6, 19.7.

HRMS (ESI-TOF): Calculated for $C_{24}H_{23}O_2S^+$, $[M+H]^+$ 375.1413, Found 375.1410.

1-(4-(tert-butyl)phenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3l**)



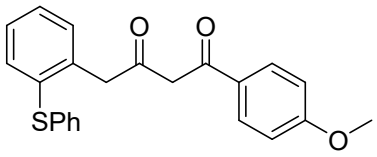
The product was obtained as a colorless oil after chromatography (n-hexane/EtOAc = 15:1), 72.4 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.90 (s, 1H), 7.78 – 7.65 (m, 1H), 7.65 – 7.55 (m, 2H), 7.40 – 7.35 (m, 1H), 7.34 – 7.33 (m, 3H), 7.23 (s, 1H), 7.17 – 7.13 (m, 2H), 7.13 – 7.08 (m, 3H), 5.95 (s, 1H), 3.87 (s, 2H), 1.23 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 193.7, 181.1, 155.0, 136.6, 135.4, 133.4, 133.3, 130.7, 130.2, 128.4, 128.1, 127.5, 127.2, 125.9, 125.8, 125.4, 124.6, 124.5, 95.2, 43.3, 34.0, 30.1.

HRMS (ESI-TOF): Calculated for $C_{26}H_{27}O_2S^+$, $[M+H]^+$ 403.1726, Found 403.1720.

1-(4-methoxyphenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3m**)



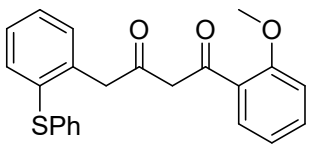
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 10:1), 70.7 mg (94%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 16.07 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.16 – 7.15 (m, 1H), 7.13 – 7.11 (m, 2H), 7.09 – 7.05 (m, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 5.90 (s, 1H), 3.87 (s, 2H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 193.3, 182.8, 163.1, 137.8, 136.6, 134.5, 134.2, 131.3, 129.4, 129.2, 129.1, 128.6, 128.3, 127.1, 126.5, 113.9, 95.7, 55.5, 44.0.

HRMS (ESI-TOF): Calculated for $C_{23}H_{21}O_3S^+$, $[M+H]^+$ 377.1206, Found 377.1200.

1-(2-methoxyphenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3n**)



The product was obtained as a colorless oil after chromatography (n-hexane/EtOAc = 10:1), 66.9 mg (89%).

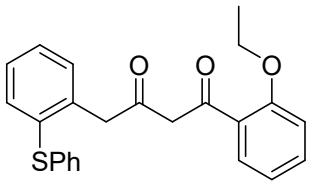
^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.91 (s, 1H), 7.84 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.31 (td, *J* = 7.4, 1.5 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.24 – 7.21 (m, 2H),

7.20 – 7.19 (m, 2H), 7.16 – 7.12 (m, 1H), 7.01 – 6.97 (m, 1H), 6.89 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.38 (s, 1H), 3.95 (s, 2H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 195.9, 179.7, 158.5, 137.9, 136.5, 134.7, 134.3, 133.0, 131.4, 130.2, 129.6, 129.1, 128.4, 128.2, 126.5, 123.6, 120.7, 111.6, 101.7, 55.5, 44.7.

HRMS (ESI-TOF): Calculated for $C_{23}H_{21}O_3S^+$, $[M+H]^+$ 377.1206, Found 377.1200.

1-(2-ethoxyphenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3o**)



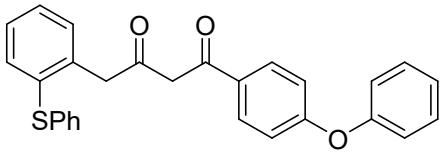
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 70.2 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 16.05 (s, 1H), 7.81 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.31 – 7.29 (m, 3H), 7.23 (td, *J* = 7.4, 1.5 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.14 – 7.13 (m, 1H), 7.12 – 7.11 (m, 2H), 7.08 – 7.04 (m, 1H), 6.93 – 6.88 (m, 1H), 6.79 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.37 (s, 1H), 3.92 (q, *J* = 7.0 Hz, 2H), 3.87 (s, 2H), 1.19 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 194.9, 178.9, 156.9, 136.7, 135.4, 133.7, 133.2, 131.9, 130.3, 129.2, 128.6, 128.1, 127.4, 127.1, 125.5, 122.5, 119.5, 111.3, 100.5, 63.1, 43.8, 13.6.

HRMS (ESI-TOF): Calculated for $C_{24}H_{23}O_3S^+$, $[M+H]^+$ 391.1362, Found 391.1360.

1-(4-phenoxyphenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3p**)



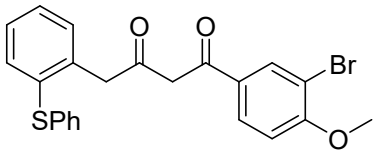
The product was obtained as a colorless oil after chromatography (n-hexane/EtOAc = 15:1), 80.6 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.98 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.13 – 7.09 (m, 3H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 5.91 (s, 1H), 3.88 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 192.9, 181.1, 160.3, 154.0, 136.7, 135.4, 133.5, 133.2, 130.2, 129.0, 128.3, 128.1, 128.1, 127.9, 127.5, 127.3, 125.4, 123.4, 119.0, 116.5, 94.9, 43.1.

HRMS (ESI-TOF): Calculated for $C_{28}H_{23}O_3S^+$, $[M+H]^+$ 439.1362, Found 439.1363.

1-(3-bromo-4-methoxyphenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3q**)



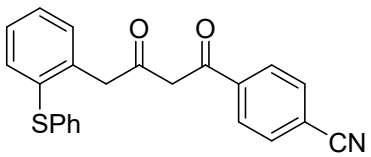
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 79.9 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.99 (s, 1H), 7.95 (d, *J* = 2.1 Hz, 1H), 7.70 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.36 – 7.32 (m, 1H), 7.29 – 7.25 (m, 1H), 7.23 – 7.21 (m, 2H), 7.20 – 7.13 (m, 3H), 6.89 (d, *J* = 8.6 Hz, 1H), 5.94 (s, 1H), 3.96 (s, 2H), 3.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 193.6, 181.3, 159.0, 137.7, 136.5, 134.7, 134.2, 132.3, 131.3, 129.4, 129.2, 128.7, 128.4, 128.0, 126.5, 111.9, 111.3, 95.9, 56.5, 44.0.

HRMS (ESI-TOF): Calculated for $C_{23}H_{20}BrO_3S^+$, $[M+H]^+$ 455.0311, Found 455.0307.

4-(3-oxo-4-(2-(phenylthio)phenyl)butanoyl)benzonitrile (**3r**)



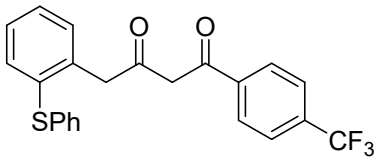
The product was obtained as a colorless oil after chromatography (n-hexane/EtOAc = 15:1), 52.7 mg (71%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.58 (s, 1H), 7.75 – 7.69 (m, 2H), 7.64 – 7.59 (m, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.26 (m, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.16 – 7.11 (m, 2H), 7.11 – 7.05 (m, 3H), 5.98 (s, 1H), 3.94 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 196.2, 177.0, 137.3, 136.1, 135.3, 133.8, 133.0, 131.3, 130.4, 128.2, 128.1, 127.8, 127.5, 126.3, 125.5, 117.1, 114.2, 96.5, 44.0.

HRMS (ESI-TOF): Calculated for $C_{23}H_{18}NO_2S^+$, $[M+H]^+$ 372.1053, Found 372.1041.

4-(2-(phenylthio)phenyl)-1-(4-(trifluoromethyl)phenyl)butane-1,3-dione (**3s**)



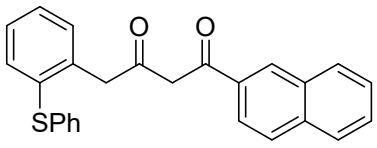
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 63.8 mg (77%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.65 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.39 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.33 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.28 (td, *J* = 7.4, 1.5 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.17 – 7.13 (m, 2H), 7.12 – 7.09 (m, 2H), 7.09 – 7.03 (m, 1H), 5.99 (s, 1H), 3.94 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 196.6, 179.3, 137.6, 137.3, 136.4, 134.7, 134.1, 133.4 (q, *J* = 33.0 Hz), 131.3, 129.1, 129.1, 128.7, 128.4, 127.2, 126.5, 125.5 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 271.0 Hz), 97.22, 44.77.

HRMS (ESI-TOF): Calculated for $C_{23}H_{18}F_3O_2S^+$, $[M+H]^+$ 415.0974, Found 415.0970.

1-(naphthalen-2-yl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3t**)



The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 55.4 mg (70%).

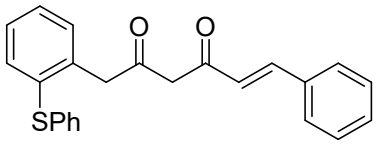
^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.87 (s, 1H), 8.33 – 8.27 (m, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.80 – 7.78 (m, 1H), 7.51 – 7.50 (m, 1H), 7.46 – 7.42 (m, 2H), 7.37 – 7.34 (m,

2H), 7.26 (t, J = 7.5 Hz, 1H), 7.22 – 7.16 (m, 2H), 7.15 – 7.13 (m, 1H), 7.12 – 7.10 (m, 3H), 7.09 – 7.04 (m, 1H), 5.82 (s, 1H), 3.92 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 193.0, 185.6, 136.4, 135.3, 133.5, 133.3, 132.8, 132.7, 130.6, 130.4, 129.0, 128.4, 128.1, 127.5, 127.4, 127.3, 126.1, 125.9, 125.5, 125.3, 124.5, 123.7, 100.6, 43.1.

HRMS (ESI-TOF): Calculated for $C_{26}H_{21}O_2S^+$, $[M+H]^+$ 397.1257, Found 397.1248.

(*E*)-6-phenyl-1-(2-(phenylthio)phenyl)hex-5-ene-2,4-dione (**3u**)



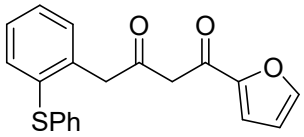
The product was obtained as a colorless oil after chromatography (n-hexane/EtOAc = 15:1), 62.5 mg (84%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 14.96 (s, 1H), 7.50 – 7.41 (m, 3H), 7.36 (d, J = 7.6 Hz, 1H), 7.32 – 7.29 (m, 3H), 7.26 – 7.24 (m, 1H), 7.20 – 7.16 (m, 4H), 7.14 – 7.10 (m, 3H), 6.27 (dd, J = 15.7, 1.8 Hz, 1H), 5.42 (s, 1H), 3.86 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 197.8, 174.8, 138.5, 136.5, 135.4, 134.0, 133.5, 133.3, 130.3, 128.8, 128.5, 128.1, 127.8, 127.5, 127.3, 126.9, 125.5, 121.5, 99.9, 44.6.

HRMS (ESI-TOF): Calculated for $C_{24}H_{21}O_2S^+$, $[M+H]^+$ 373.1257, Found 373.1253.

1-(furan-2-yl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3v**)



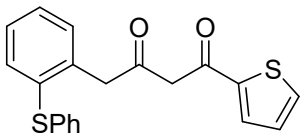
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 61.2 mg (91%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.34 (s, 1H), 7.47 – 7.45 (m, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.31 (d, J = 7.5 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.21 – 7.15 (m, 2H), 7.14 – 7.13 (m, 2H), 7.10 – 7.09 (m, 1H), 7.07 – 7.05 (m, 1H), 7.01 – 6.97 (m, 1H), 6.43 (dd, J = 3.2, 1.6 Hz, 1H), 5.86 (s, 1H), 3.85 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 190.4, 173.7, 149.0, 144.9, 130.2, 128.5, 128.1, 127.5, 127.3, 125.5, 114.6, 111.4, 95.0, 42.2.

HRMS (ESI-TOF): Calculated for $C_{20}H_{17}O_3S^+$, $[M+H]^+$ 337.0893, Found 337.0869.

4-(2-(phenylthio)phenyl)-1-(thiophen-2-yl)butane-1,3-dione (**3w**)



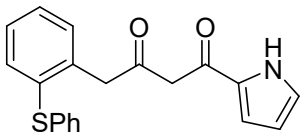
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 66.9 mg (95%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.60 (s, 1H), 7.57 – 7.52 (m, 2H), 7.44 – 7.39 (m, 2H), 7.35 – 7.31 (m, 1H), 7.30 – 7.26 (m, 1H), 7.25 – 7.22 (m, 2H), 7.20 – 7.19 (m, 2H), 7.16 – 7.13 (m, 1H), 7.09 – 7.06 (m, 1H), 5.88 (s, 1H), 3.91 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 189.0, 180.7, 141.2, 137.6, 136.4, 134.5, 134.4, 132.4, 131.2, 130.3, 129.5, 129.2, 128.6, 128.4, 128.2, 126.5, 96.5, 42.5.

HRMS (ESI-TOF): Calculated for $C_{20}H_{17}O_2S_2^+$, $[M+H]^+$ 353.0664, Found 353.0660.

4-(2-(phenylthio)phenyl)-1-(1*H*-pyrrol-2-yl)butane-1,3-dione (**3x**)



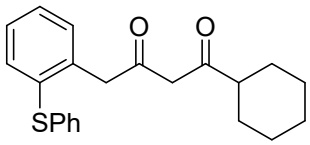
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 61.0 mg (91%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.53 (s, 1H), 7.50 – 7.43 (m, 2H), 7.34 (ddd, *J* = 9.4, 7.6, 1.6 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.20 – 7.19(m, 1H), 7.16 – 7.13 (m, 2H), 7.12 – 7.11 (m, 1H), 7.11 – 7.09 (m, 1H), 7.08 – 7.04 (m, 1H), 7.01 – 6.99 (m, 1H), 5.80 (s, 1H), 3.84 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 187.9, 179.6, 140.1, 136.5, 135.4, 133.5, 133.3, 131.3, 130.2, 129.2, 128.4, 128.1, 127.5, 127.3, 127.1, 125.5, 95.4, 41.4.

HRMS (ESI-TOF): Calculated for $C_{20}H_{18}NO_2S^+$, $[M+H]^+$ 336.1053, Found 336.1050.

1-cyclohexyl-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3y**)



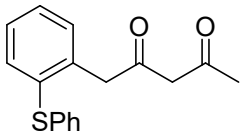
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 64.1 mg (91%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.36 (s, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.18 – 7.14(m, 3H), 7.11 – 7.06 (m, 3H), 5.28 (s, 1H), 3.76 (s, 2H), 2.00 – 1.97 (m, 1H), 1.59 – 1.58 (m, 4H), 1.25 – 1.06 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 194.8, 192.7, 136.7, 135.6, 133.5, 133.2, 130.2, 128.3, 128.08, 127.5, 127.2, 125.4, 96.7, 44.9, 42.8, 28.4, 24.7, 24.7.

HRMS (ESI-TOF): Calculated for $C_{22}H_{25}O_2S^+$, $[M+H]^+$ 353.1570, Found 353.1567.

1-(2-(phenylthio)phenyl)pentane-2,4-dione (**3z**)



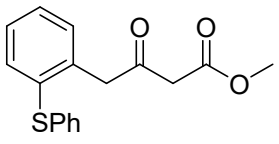
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 10:1), 50.0 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.32 (s, 1H), 7.40 (d, *J* = 7.6, 1H), 7.34 – 7.28 (m, 2H), 7.26 – 7.22 (m, 3H), 7.18 – 7.15 (m, 3H), 5.32 (s, 1H), 3.82 (s, 2H), 1.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 192.7, 189.7, 137.4, 136.4, 134.4, 134.2, 131.2, 129.4, 129.0, 128.4, 128.2, 126.4, 100.0, 43.5, 24.3.

HRMS (ESI-TOF): Calculated for $C_{17}H_{17}O_2S^+$, $[M+H]^+$ 285.0944, Found 285.0940.

methyl 3-oxo-4-(2-(phenylthio)phenyl)butanoate (**3a'**)



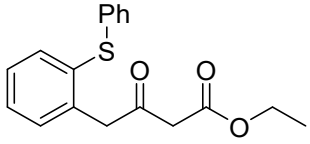
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 10:1), 50.4 mg (84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.4, 2.1 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.19 – 7.18 (m, 3H), 7.14 (dd, *J* = 6.3, 1.9 Hz, 1H), 7.11 – 7.07 (m, 2H), 3.95 (s, 2H), 3.63 (s, 3H), 3.39 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 166.5, 135.1, 135.1, 133.4, 133.2, 130.5, 128.7, 128.4, 128.2, 127.6, 125.6, 51.3, 47.6, 47.1.

HRMS (ESI-TOF): Calculated for $C_{17}H_{17}O_3S^+$, $[M+H]^+$ 301.0893, Found 301.0897.

ethyl 3-oxo-4-(2-(phenylthio)phenyl)butanoate (**3b'**)



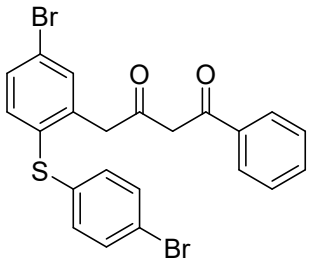
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 10:1), 54.0 mg (86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 1H), 7.30 – 7.22 (m, 5H), 7.22 – 7.13 (m, 3H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 2H), 3.44 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 167.0, 136.2, 136.1, 134.3, 134.2, 131.5, 129.4, 129.2, 128.5, 128.5, 126.6, 61.3, 48.8, 48.1, 14.1.

HRMS (ESI-TOF): Calculated for $C_{18}H_{19}O_3S^+$, $[M+H]^+$ 315.1049, Found 315.1050.

4-(5-bromo-2-((4-bromophenyl)thio)phenyl)-1-phenylbutane-1,3-dione (**3d'**)



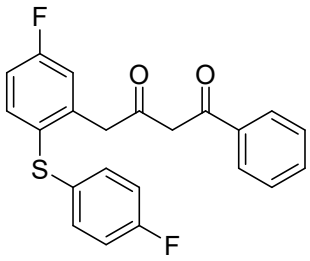
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 84.3 mg (84%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.82 (s, 1H), 7.80 – 7.71 (m, 2H), 7.56 (d, *J* = 2.2 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.45 – 7.39 (m, 3H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.05 – 6.99 (m, 2H), 6.04 (s, 1H), 3.91 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 194.2, 181.8, 139.6, 135.9 135.2 134.2, 134.1, 132.9 132.4, 132.3, 131.6 130.8 128.6, 127.0 123.0 120.7, 96.4, 44.3

HRMS (ESI-TOF): Calculated for $C_{20}H_{16}O_3S^+$, $[M+H]^+$ 502.9311, Found 502.9307.

4-(5-fluoro-2-((4-fluorophenyl)thio)phenyl)-1-phenylbutane-1,3-dione (**3e'**)



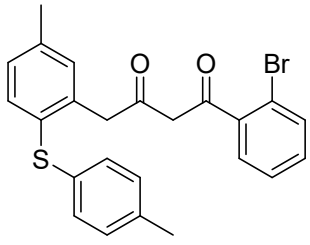
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 65.7 mg (86%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.84 (s, 1H), 7.78 – 7.72 (m, 2H), 7.54 – 7.47 (m, 1H), 7.45 – 7.39 (m, 3H), 7.16 – 7.09 (m, 3H), 6.99 (td, *J* = 8.3, 2.8 Hz, 1H), 6.94 – 6.88 (m, 2H), 6.02 (s, 1H), 3.95 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 194.4, 181.9, 162.7 (d, *J* = 248.7 Hz), 161.7 (d, *J* = 246.0 Hz), 140.1 (d, *J* = 8.0 Hz), 136.6 (d, *J* = 8.8 Hz), 134.2, 132.4, 131.1 (d, *J* = 8.0 Hz), 128.6, 127.0, 126.9, 118.3 (d, *J* = 22.0 Hz), 116.3 (d, *J* = 22.0 Hz), 115.6 (d, *J* = 22.0 Hz), 96.4, 44.5, 44.5.

HRMS (ESI-TOF): Calculated for $C_{22}H_{17}F_2O_2S^+$, $[M+H]^+$ 383.0912, Found 383.0910.

1-(2-bromophenyl)-4-(5-methyl-2-(*p*-tolylthio)phenyl)butane-1,3-dione (**3f'**)



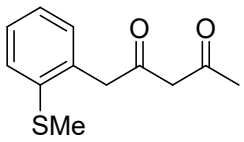
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 80.0 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.39 (s, 1H), 7.48 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.30 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.21 (dd, *J* = 7.6, 5.4 Hz, 2H), 7.13 (td, *J* = 7.6, 1.8 Hz, 1H), 7.09 (d, *J* = 2.0 Hz, 1H), 7.00 – 6.88 (m, 5H), 5.75 (s, 1H), 3.81 (s, 2H), 2.24 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 194.1, 184.4, 138.5, 137.2, 137.0, 136.2, 134.5, 133.8, 133.1, 132.0, 131.5, 131.2, 130.0, 129.8, 129.3, 129.1, 127.2, 120.2, 101.5, 43.8, 21.1, 20.9.

HRMS (ESI-TOF): Calculated for $C_{24}H_{22}BrO_2S^+$, $[M+H]^+$ 453.0518, Found 453.0515.

1-(2-(methylthio)phenyl)pentane-2,4-dione (**3g'**)



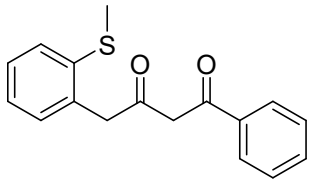
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 40.4 mg (91%).

^{1}H NMR (400 MHz, $CDCl_3$) enol δ 15.40 (s, 1H), 7.29 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 7.18 – 7.13 (m, 1H), 5.41 (s, 1H), 3.76 (s, 2H), 2.45 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 193.0, 189.8, 138.1, 133.5, 130.6, 127.9, 126.6, 125.4 99.8, 43.2, 24.4, 16.3.

HRMS (ESI-TOF): Calculated for $C_{12}H_{15}O_2S^+$, $[M+H]^+$ 223.0787, Found 223.0780.

4-(2-(methylthio)phenyl)-1-phenylbutane-1,3-dione (**3h'**)



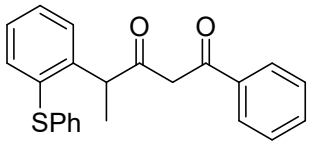
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 50.6 mg (89%).

^{1}H NMR (300 MHz, $CDCl_3$) enol δ 16.01 (s, 1H), 7.88 – 7.83 (m, 2H), 7.57 – 7.51 (m, 1H), 7.48 – 7.43 (m, 2H), 7.36 – 7.31 (m, 3H), 7.26 – 7.23 (m, 1H), 6.14 (s, 1H), 3.91 (s, 2H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) enol δ 195.4, 182.1, 138.2, 134.6, 133.7, 132.2, 130.6, 128.6, 128.6, 128.5, 128.0, 127.0, 126.8, 125.5, 96.3, 44.1, 16.4.

HRMS (ESI-TOF): Calculated for $C_{17}H_{17}O_2S^+$, $[M+H]^+$ 285.0944, Found 285.0940.

1-phenyl-4-(2-(phenylthio)phenyl)pentane-1,3-dione (**3i'**)



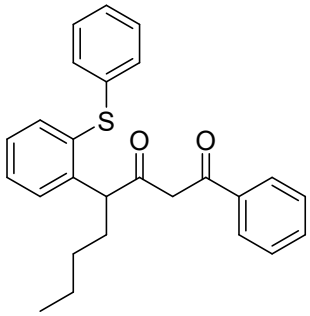
The product was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 62.6 mg (87%).

^{1}H NMR (300 MHz, $CDCl_3$) enol δ 15.81 (s, 1H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 8.9 Hz, 3H), 7.37 (d, *J* = 7.6 Hz, 3H), 7.29 – 7.14 (m, 6H), 5.93 (s, 1H), 4.62 (q, *J* = 6.9 Hz, 1H), 1.46 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) enol δ 200.5, 180.1, 144.5, 137.5, 135.7, 134.4, 133.0, 132.3, 129.9, 129.6, 129.5, 129.1, 128.8, 128.3, 127.1, 126.6, 96.8, 46.7.

HRMS (ESI-TOF): Calculated for $C_{23}H_{21}O_2S^+$, $[M+H]^+$ 361.1257, Found 361.1249.

1-phenyl-4-(2-(phenylthio)phenyl)octane-1,3-dione (**3j'**)



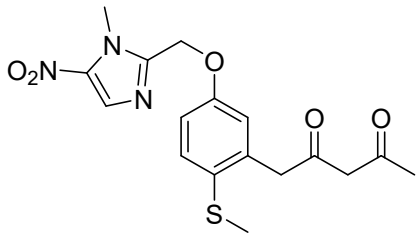
The product was obtained as a colorless oil after chromatography (n-hexane/EtOAc = 15:1), 72.4 mg (90%).

^{1}H NMR (300 MHz, $CDCl_3$) enol δ 15.96 (s, 1H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.40 (m, 3H), 7.40 – 7.30 (m, 3H), 7.25 – 7.10(m, 6H), 5.94 (s, 1H), 4.53 (t, *J* = 7.5 Hz, 1H), 2.14 (d, *J* = 10.8 Hz, 1H), 1.73 (q, *J* = 7.1 Hz, 1H), 1.39 – 1.10 (m, 4H), 0.84 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) enol δ 199.1, 180.2, 143.0, 137.3, 135.5, 134.1, 132.9, 132.0, 129.2, 129.1, 128.6, 128.5, 128.4, 127.8, 126.8, 126.1, 97.2, 51.8, 32.5, 29.8, 22.6, 13.9.

HRMS (ESI-TOF): Calculated for $C_{26}H_{27}O_2S^+$, $[M+H]^+$ 403.1726, Found 403.1719.

1-(5-((1-methyl-5-nitro-1*H*-imidazol-2-yl)methoxy)-2-(methylthio)phenyl)pentane-2,4-dione (**3k'**)



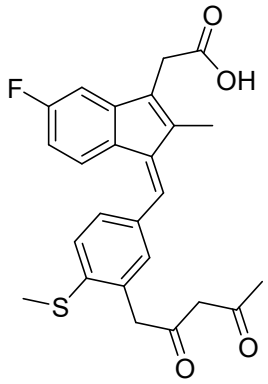
The product was obtained as a colorless oil after chromatography (n-hexane/actone = 3:1), 64.8 mg (86%).

^{1}H NMR (300 MHz, $CDCl_3$) enol δ 15.34 (s, 1H), 7.97 (s, 1H), 7.35 – 7.30 (m, 1H), 7.07 – 6.92 (m, 2H), 5.45 (s, 1H), 5.20 (s, 2H), 4.06 (s, 3H), 3.79 (s, 2H), 2.39 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) enol δ 192.9, 189.5, 155.9, 147.2, 136.8, 131.6, 130.9, 130.6, 117.2, 114.3, 99.9, 62.7, 43.5, 33.9, 24.3, 18.1.

HRMS (ESI-TOF): Calculated for $C_{17}H_{20}N_3O_5S^+$, $[M+H]^+$ 378.1118, Found 378.1112.

(Z)-2-(1-(3-(2,4-dioxopentyl)-4-(methylthio)benzylidene)-5-fluoro-2-methyl-1*H*-inden-3-yl)acetic acid (**3l'**)



The product was obtained as a yellow solid after chromatography (DCM/MeOH = 30:1), 78.8 mg (90%).

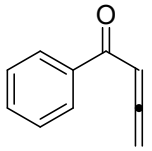
^{1}H NMR (300 MHz, $CDCl_3$) enol δ 15.38 (s, 1H), 7.46 – 7.41 (m, 1H), 7.40 – 7.34 (m, 2H), 7.30 (s, 1H), 7.28 – 7.25 (m, 1H), 7.14 (s, 1H), 6.87 (d, J = 9.0 Hz, 1H), 6.62 – 6.52 (m, 1H), 5.49 (s, 1H), 3.76 (s, 2H), 3.59 (s, 2H), 2.53 (s, 3H), 2.19 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) enol δ 192.5, 190.0, 175.6, 163.1 (d, J = 244.5 Hz), 146.2 (d, J = 8.3 Hz), 140.2, 138.8, 133.1, 131.6, 130.1, 129.8, 129.6, 129.2, 128.9, 125.7, 123.8 (d, J = 9.0 Hz), 110.7 (d, J = 22.5 Hz), 105.8 (d, J = 23.3 Hz), 100.0, 43.0, 31.3, 24.5, 15.9, 10.6.

HRMS (ESI-TOF): Calculated for $C_{25}H_{24}FO_4S^+$, $[M+H]^+$ 439.1374, Found 439.1370.

② **Synthesis of the Conjugated Allenone (4)**

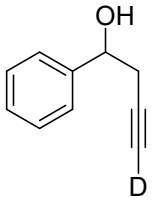
4 was prepared according to the previously reported method.[2]



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.83 (m, 2H), 7.63 – 7.51 (m, 1H), 7.51 – 7.39 (m, 2H), 6.50 – 6.40 (m, 1H), 5.30 – 5.23 (m, 2H).

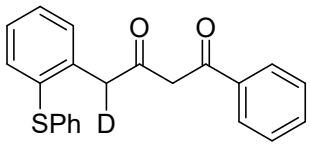
^{13}C NMR (75 MHz, $CDCl_3$) δ 217.1, 191.1, 137.4, 132.8, 128.7, 128.3, 93.2, 79.3.

③ **Synthesis of 1-phenyl-4-(2-(phenylthio)phenyl)butane-1,3-dione-4-*d* (6)**



1-Phenylbut-3-yn-4-*d*-1-ol was prepared according to the previously reported method.[3]

1-phenyl-4-(2-(phenylthio)phenyl)butane-1,3-dione-4-*d* (**6**)



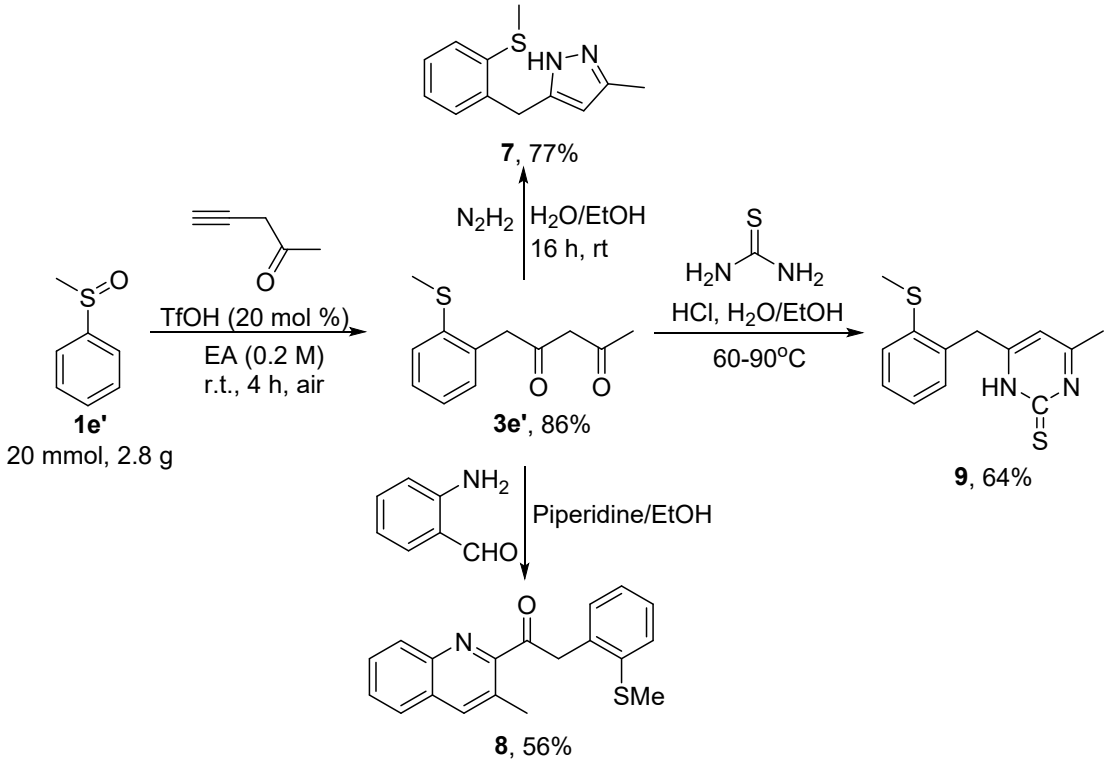
The product **6** was obtained as a light-yellow oil after chromatography (n-hexane/EtOAc = 15:1), 61.8 mg (89%).

^{1}H NMR (300 MHz, $CDCl_3$) enol δ 15.95 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.31 (m, 6H), 7.30 – 7.14 (m, 6H), 6.04 (d, *J* = 2.7 Hz, 1H), 3.95 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) enol δ 195.2, 181.9, 137.5, 136.4, 134.5, 134.4, 134.1, 132.2, 131.2, 129.3, 129.1, 128.6, 128.5, 128.3, 126.9, 126.4, 96.5, 44.1 (t, *J* = 19.5 Hz).

HRMS (ESI-TOF): Calculated for $C_{22}H_{18}DO_2S^+$, $[M+H]^+$ 348.1163, Found 348.1160.

④ **Gram-Scale Synthesis and Further Applications**



Synthesis of 3-methyl-5-(2-(methylthio)benzyl)-1*H*-pyrazole (**7**)

This pyrazole was obtained in 77% yield by the reaction of **3g'** with hydrazine hydrate.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.34 – 6.97 (m, 4H), 5.83 (s, 1H), 4.03 (s, 2H), 2.43 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 144.3, 137.3, 137.0, 129.5, 127.3, 125.8, 125.2, 104.2, 76.6, 31.2, 15.9, 12.2.

HRMS (ESI-TOF): Calculated for $C_{12}H_{15}N_2S^+$, $[M+H]^+$ 219.0950, Found 219.0945.

Synthesis of 1-(3-methylquinolin-2-yl)-2-(2-(methylthio)phenyl)ethan-1-one (**8**)

A mixture of 0.12 g of 2-aminobenzaldehyde, and 0.44 g of **3g'**, and 25 μL of piperidine in 1 mL of ethanol was heated under reflux on an oil bath for 3 hour. The reaction mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the products **8** in 56% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (d, J = 5.6 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.89 – 7.71 (m, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.35 – 7.12 (m, 4H), 4.45 (s, 2H), 2.88 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 157.6, 148.1, 137.7, 137.2, 133.4, 131.5, 131.1, 130.7, 128.5, 128.3, 128.1, 127.3, 126.5, 125.6, 125.4, 46.4, 25.2, 16.6.

HRMS (ESI-TOF): Calculated for $C_{19}H_{18}NOS^+$, $[M+H]^+$ 308.1104, Found 308.1100.

Synthesis of 4-methyl-6-(2-(methylthio)benzyl)pyrimidine-2(1*H*)-thione (**9**)

The mixture of 0.22 g of **3g'** (1.0 mmol) and thiourea (1.0 mmol) in the presence of 0.35 mL of conc. HCl in 3.0 mL of ethanol was refluxed for 6 h. Then the whole was neutralized with 10% NaOH and extracted with dichloromethane. The crude product was purified by column chromatography on silica gel to provide 167 mg of **9** (64%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.13 (m, 4H), 6.29 (s, 1H), 4.14 (s, 2H), 2.44 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 179.5, 169.2, 164.1, 138.1, 133.6, 130.8, 128.3, 126.4, 125.6, 111.2, 40.5, 21.7, 16.1.

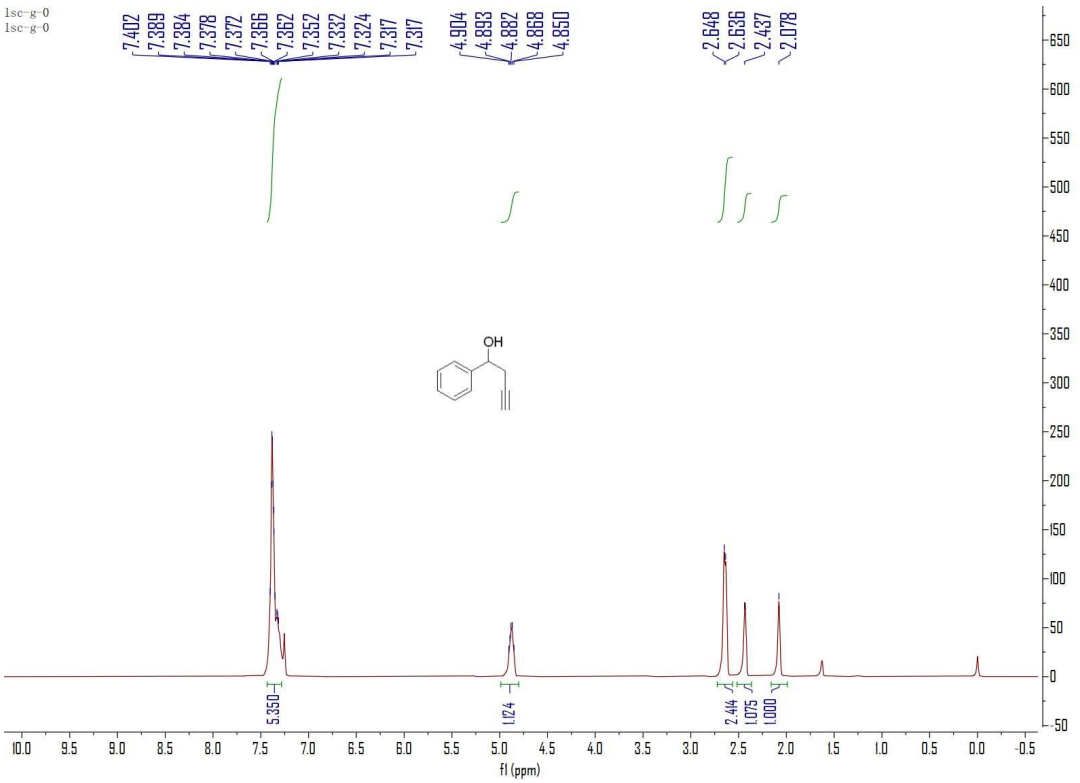
HRMS (ESI-TOF): Calculated for $C_{13}H_{15}N_2S_2^+$, $[M+H]^+$ 263.0671, Found 263.0666.

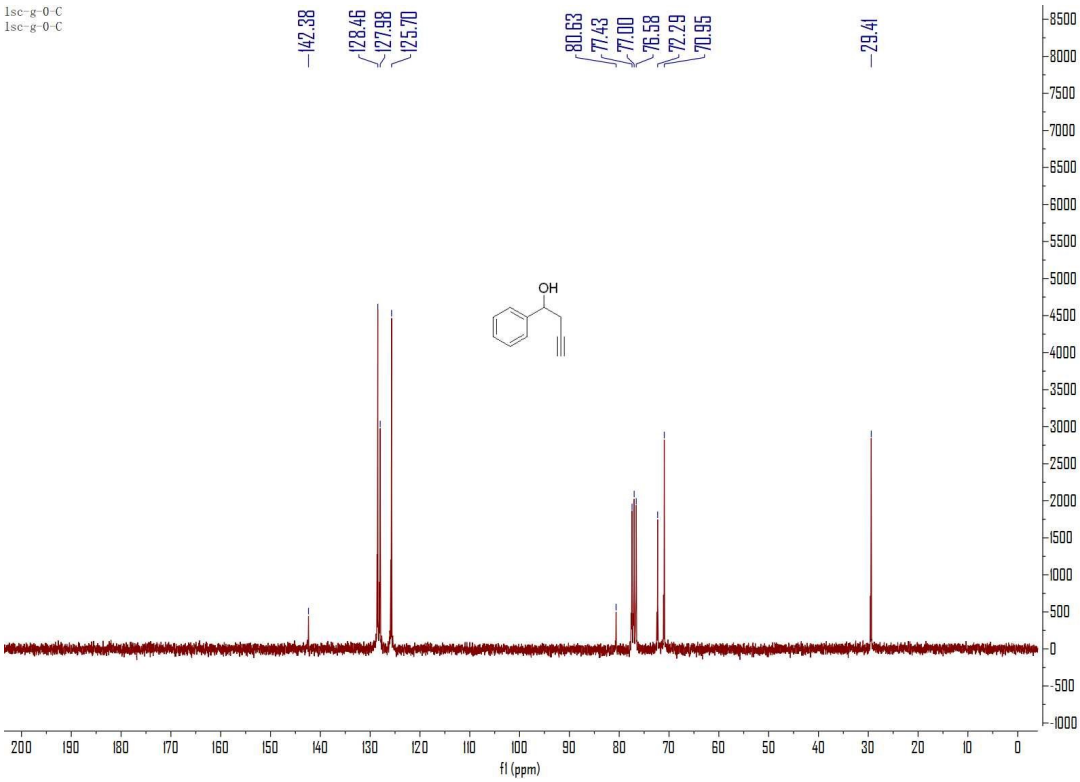
References

1. A. M. Sherwood, S. E. Williamson, S. N. Johnson, A. Yilmaz, V. W. Day and T. E. Prisinzano, *J. Org. Chem.* **2018**, *83*, 980 – 992.
2. L. Zorba, M. Kidonakis, I. Saridakis and M. Stratakis, *Org. Lett.* **2019**, *21*, 5552 – 5555.
3. A. C. Hunter, S. C. Schlitzer, J. C. Stevens, B. Almutwalli and I. Sharma, *J. Org. Chem.* **2018**, *83*, 2744 – 2752.
4. A. L. Rheingold, L. N. Zakharov and S. Trofimenko, *Inorg. Chem.* **2003**, *42*, 827 – 833.

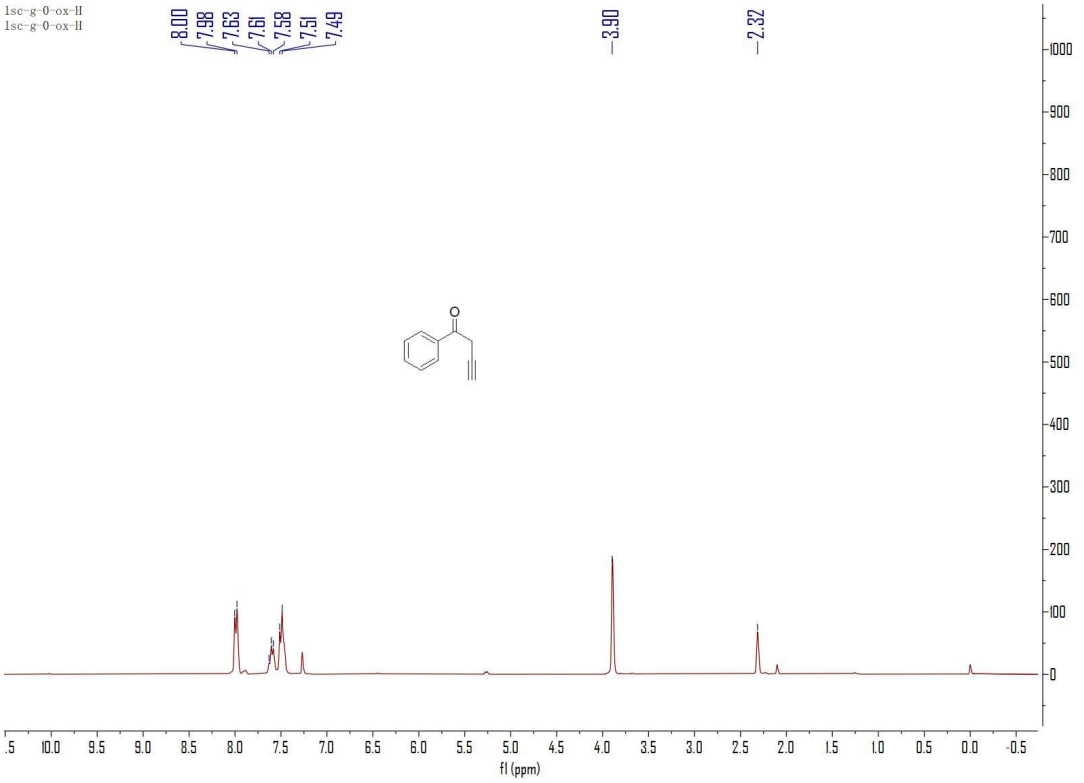
^{1}H NMR and ^{13}C NMR Spectra

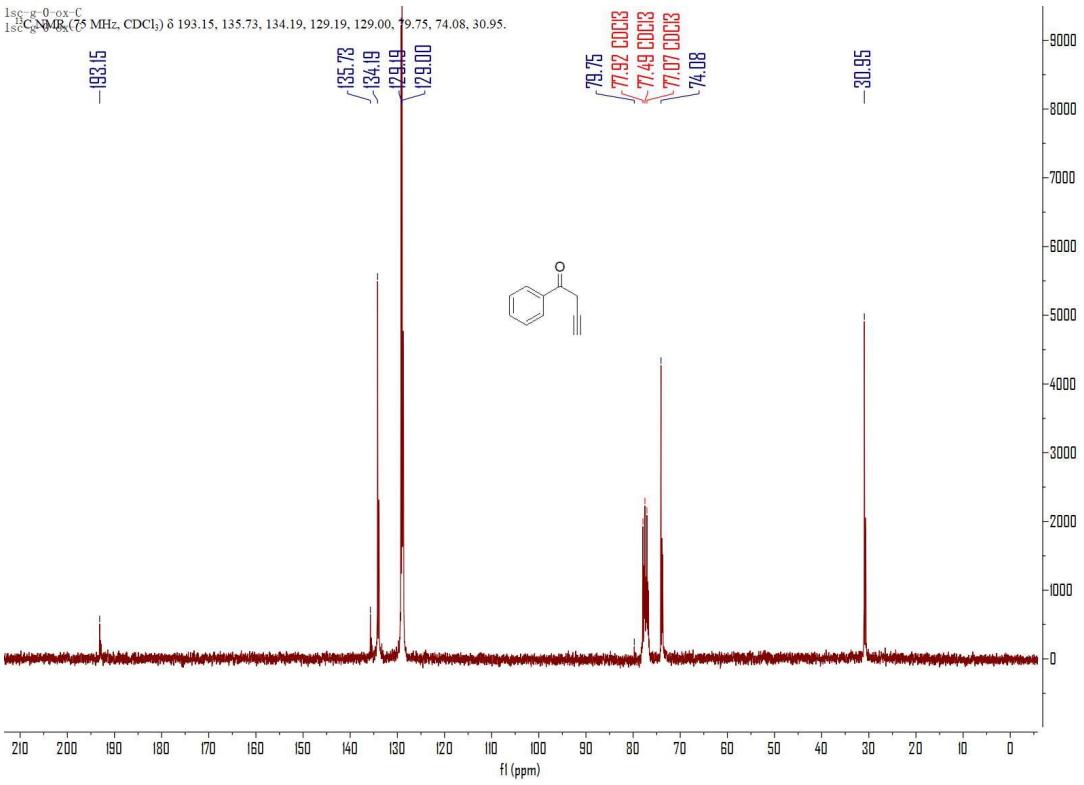
1-phenylbut-3-yn-1-ol



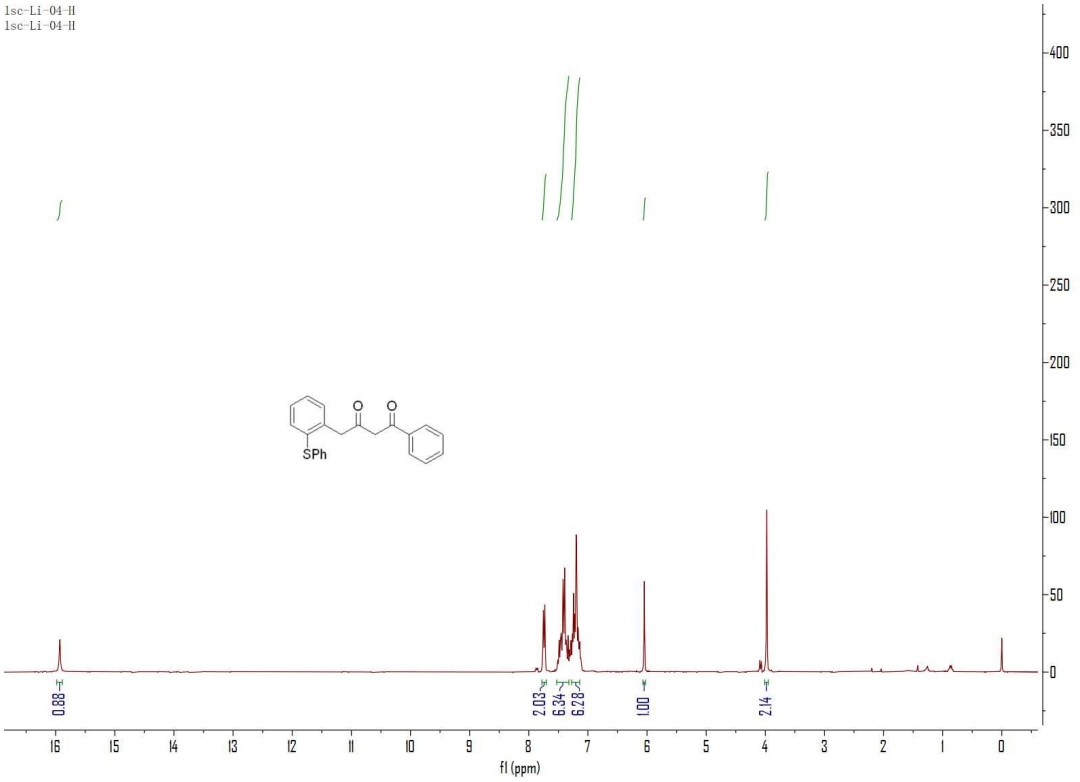


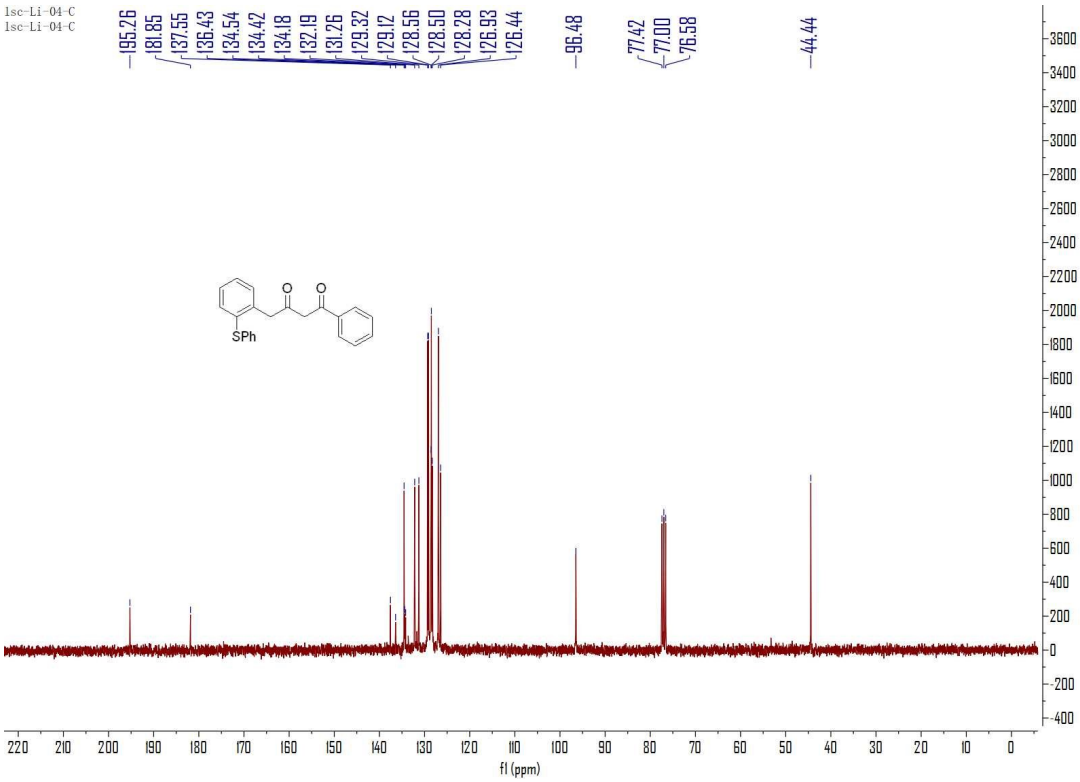
1-phenylbut-3-yn-1-one (**2a**)



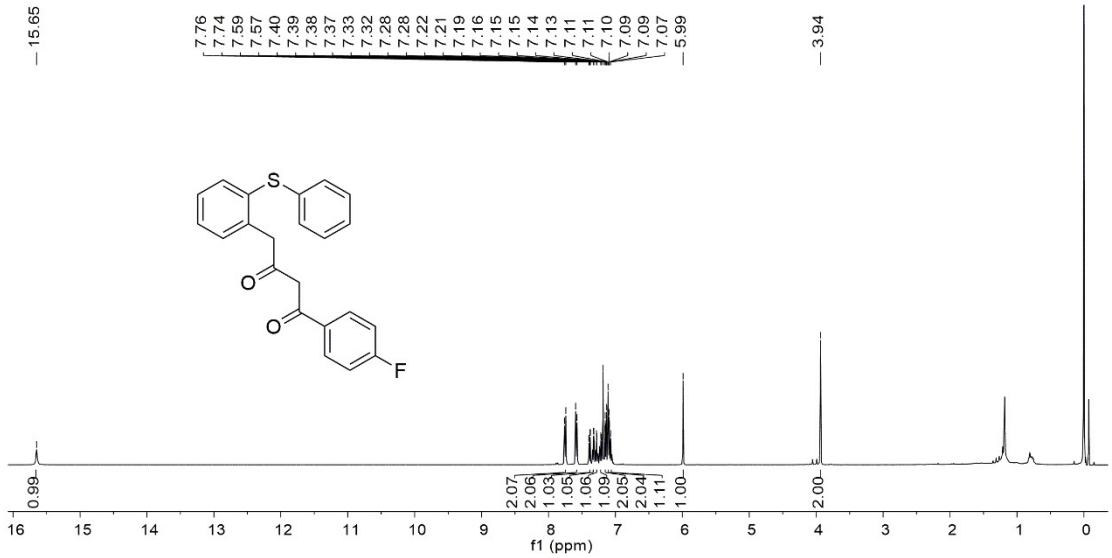


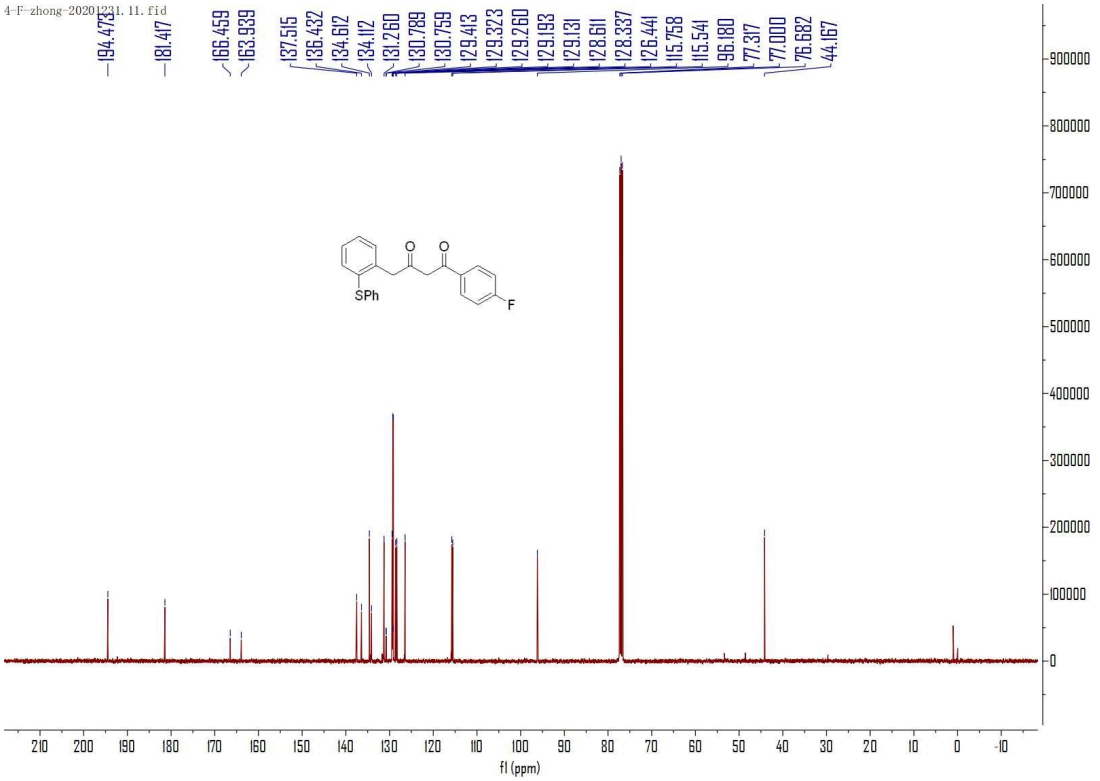
1-phenyl-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3a**)



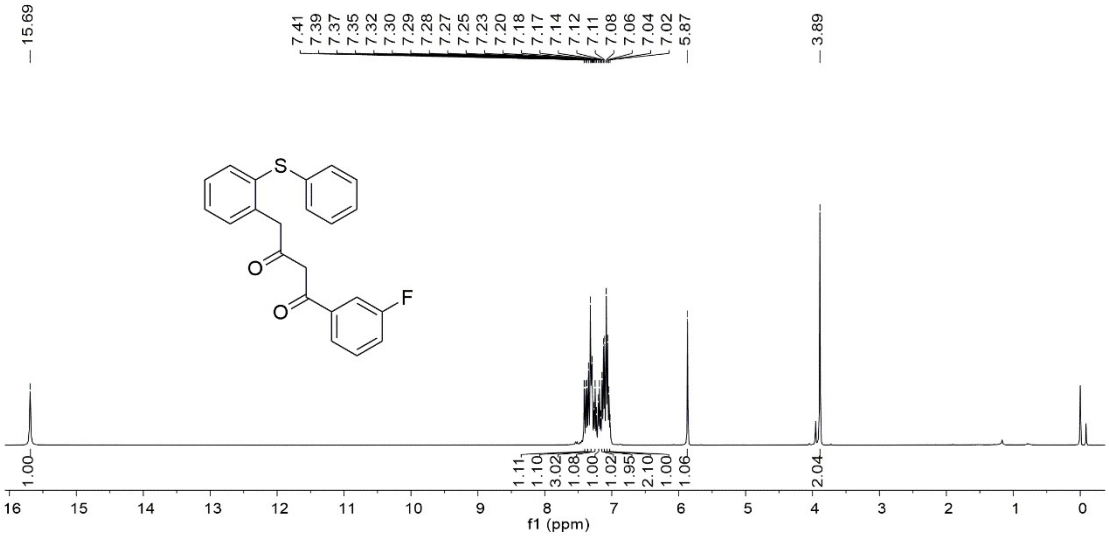


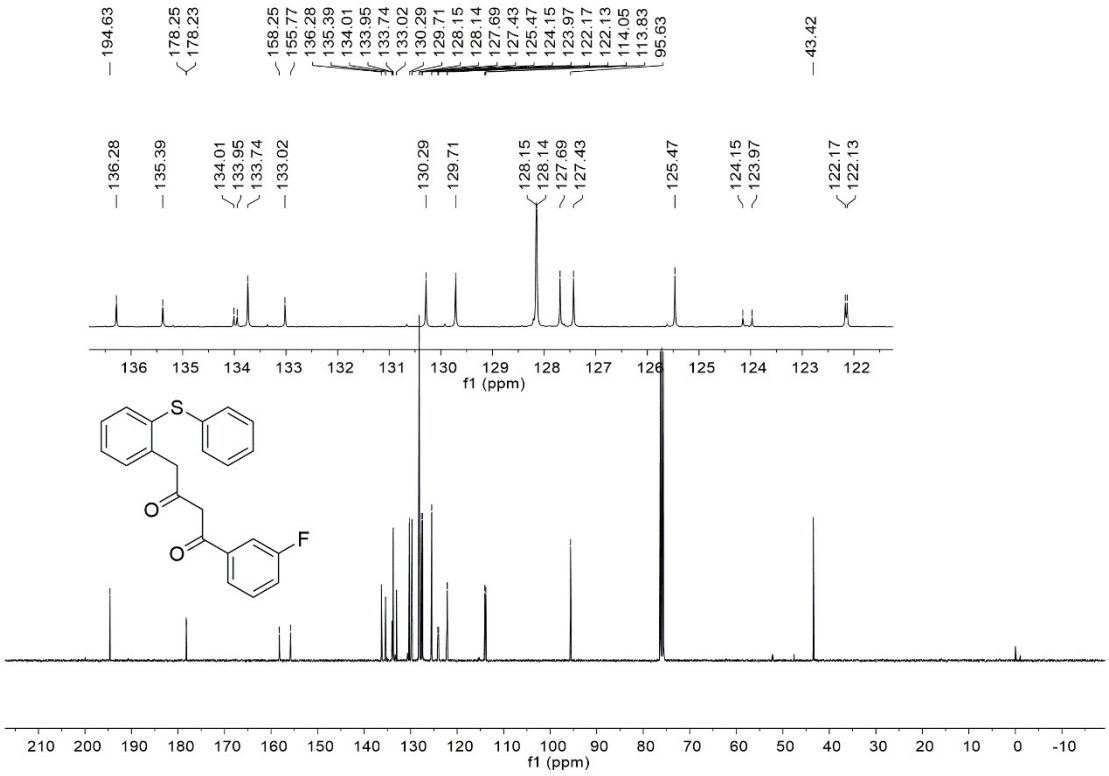
1-(4-fluorophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3b**)



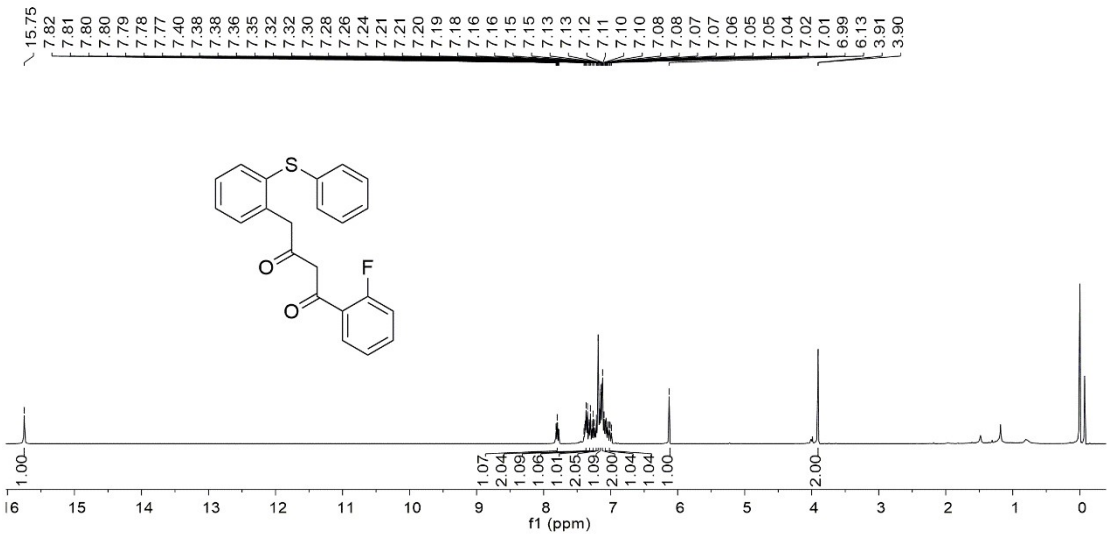


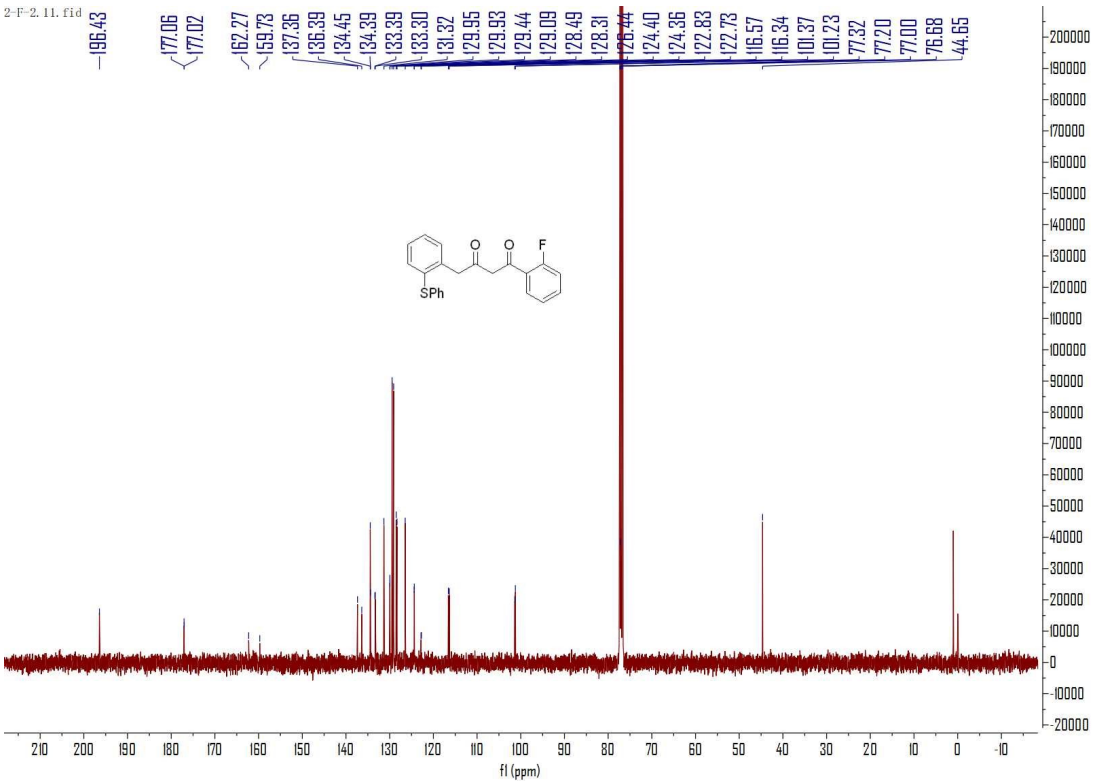
1-(3-fluorophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3c**)



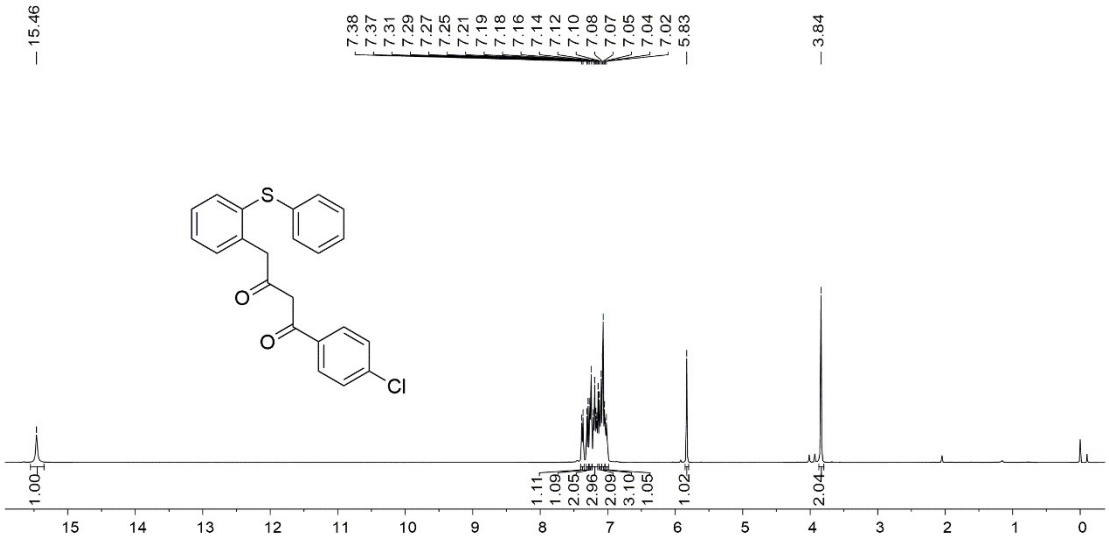


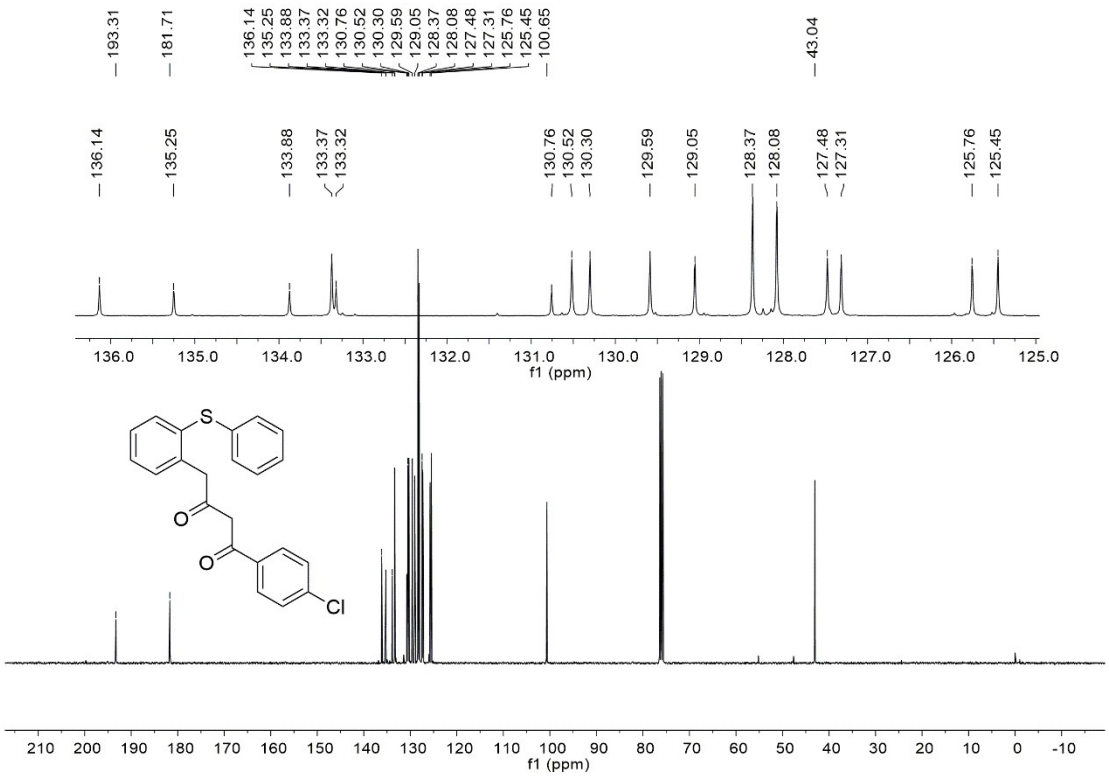
1-(2-fluorophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3d**)



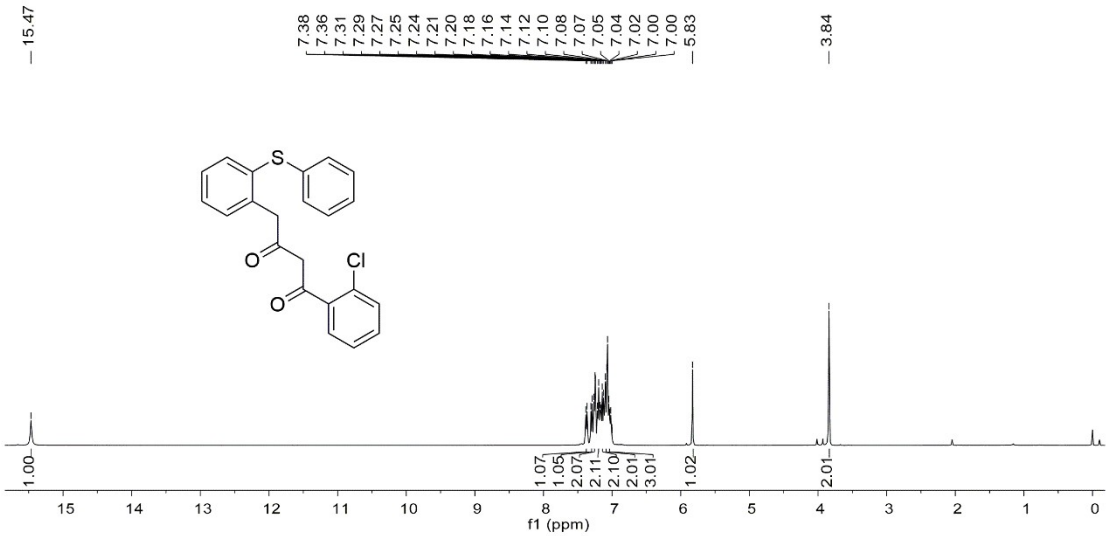


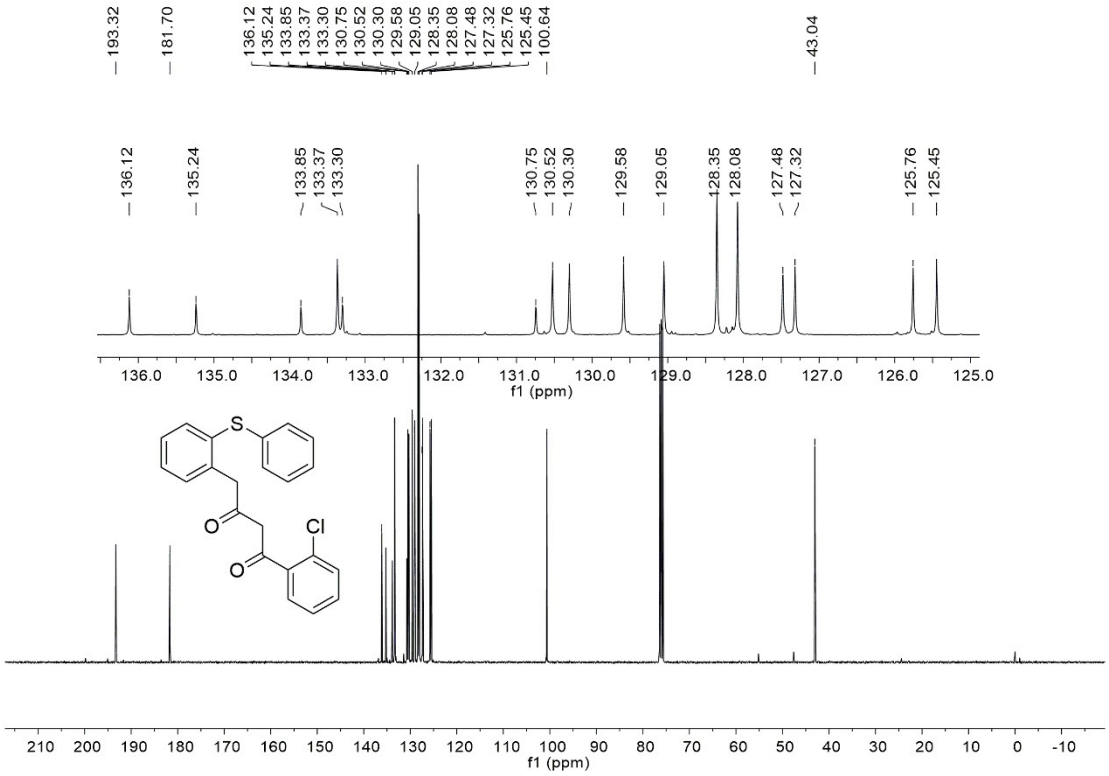
1-(4-chlorophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3e**)



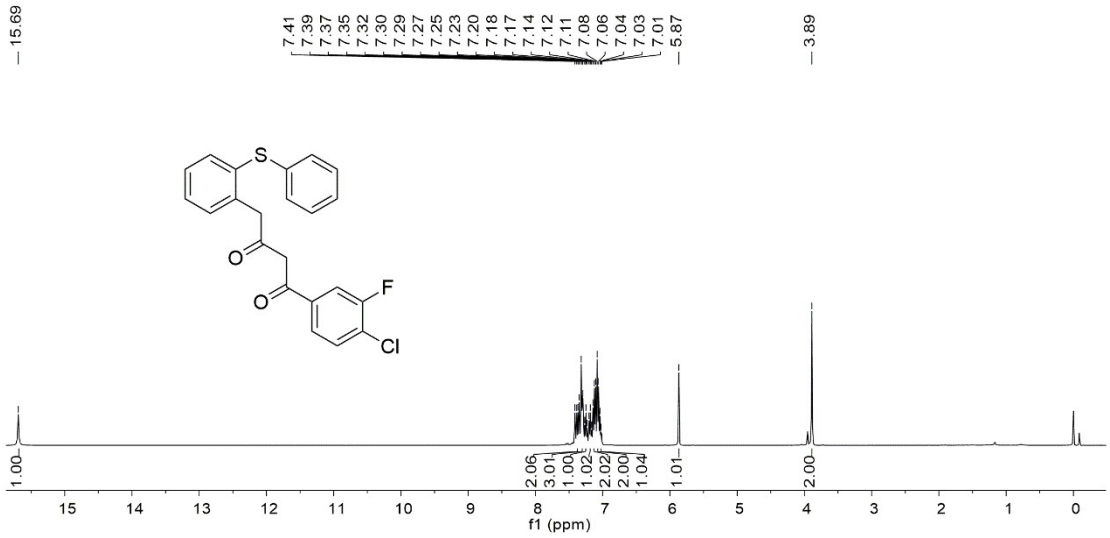


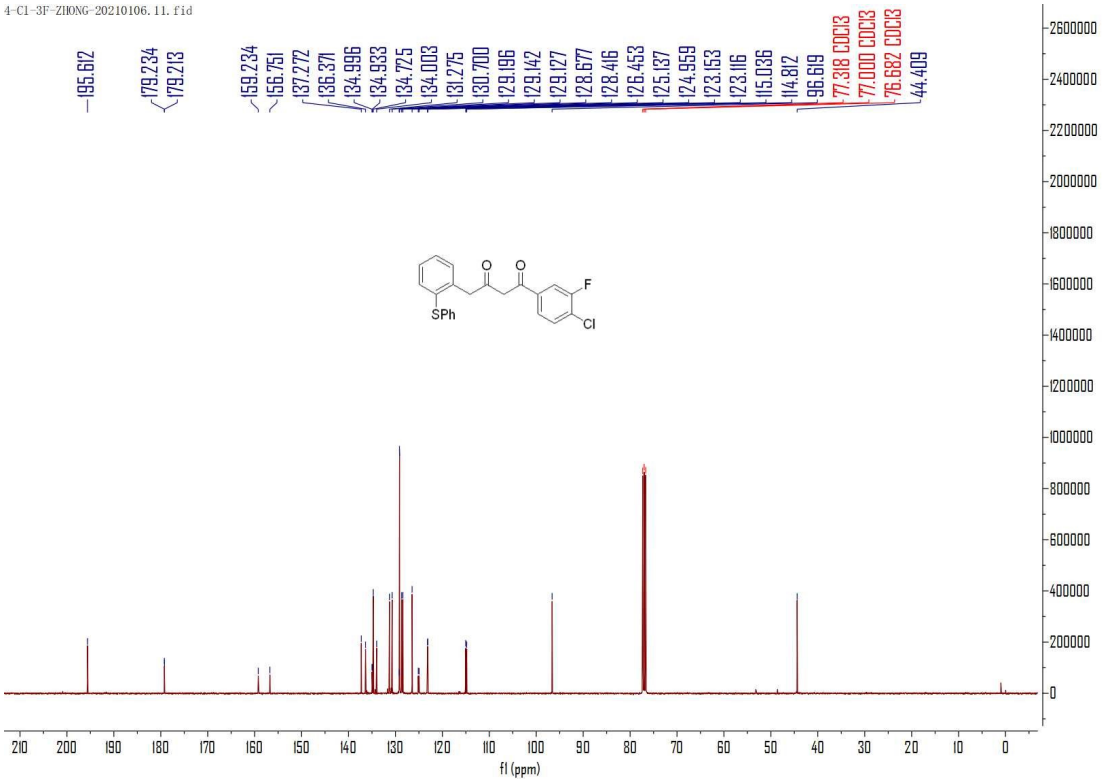
1-(2-chlorophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3f**)



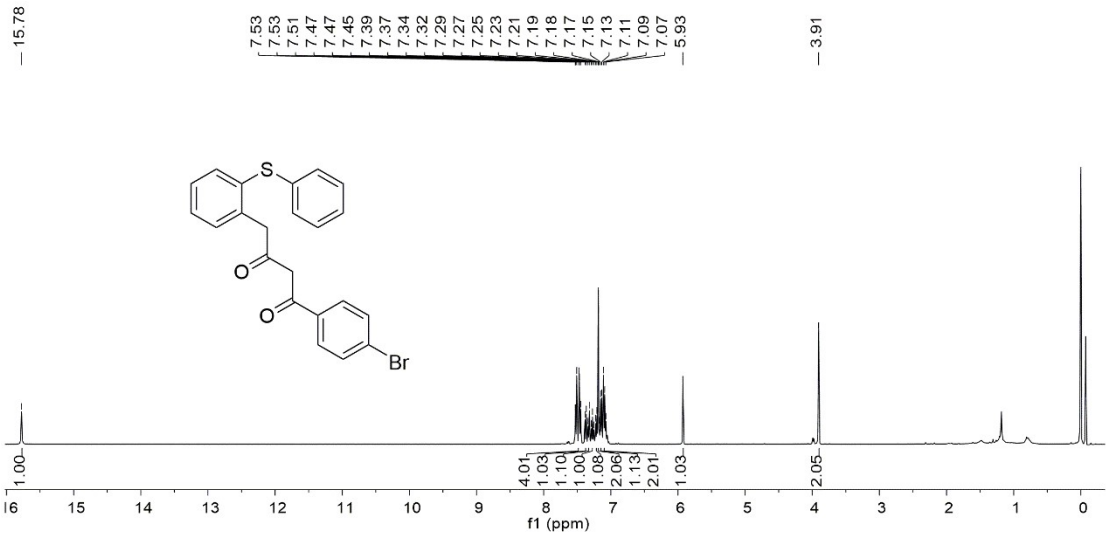


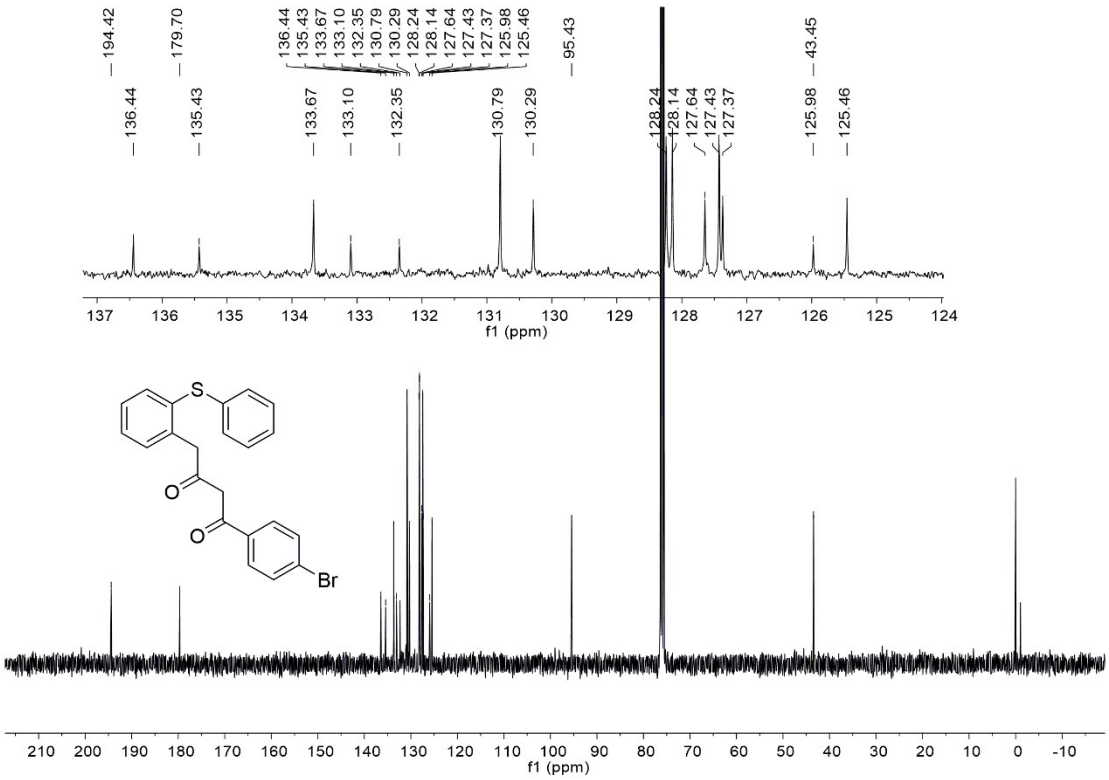
1-(4-chloro-3-fluorophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3g**)



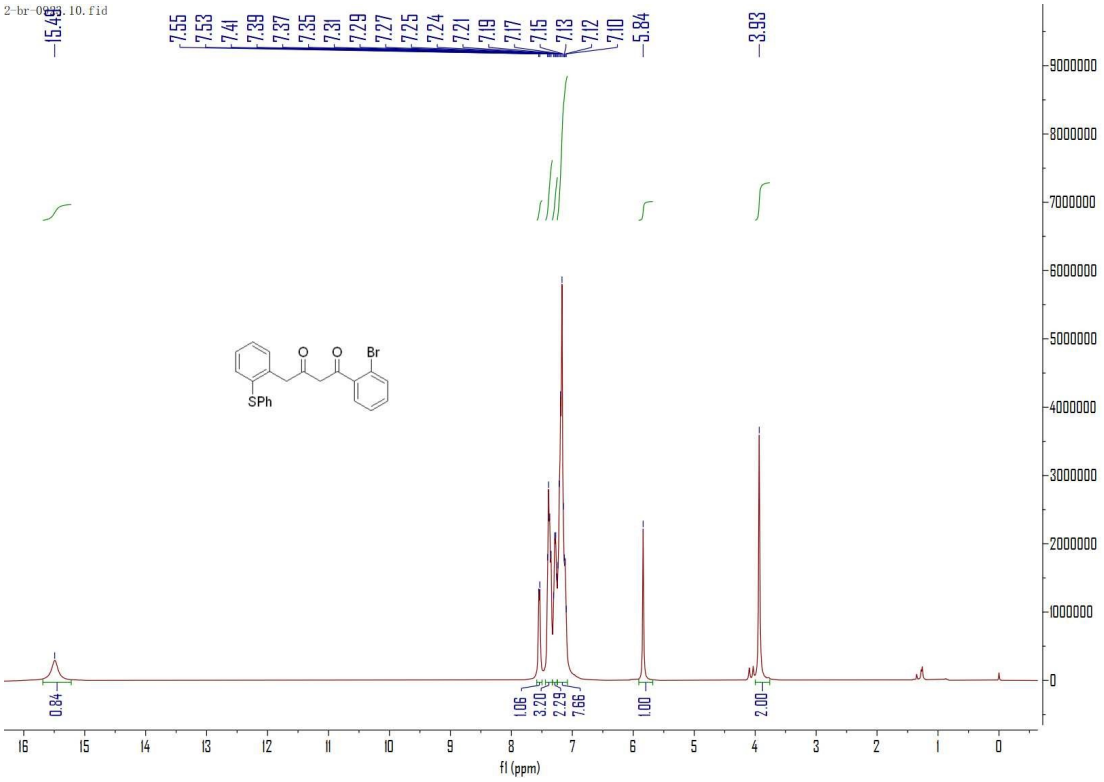


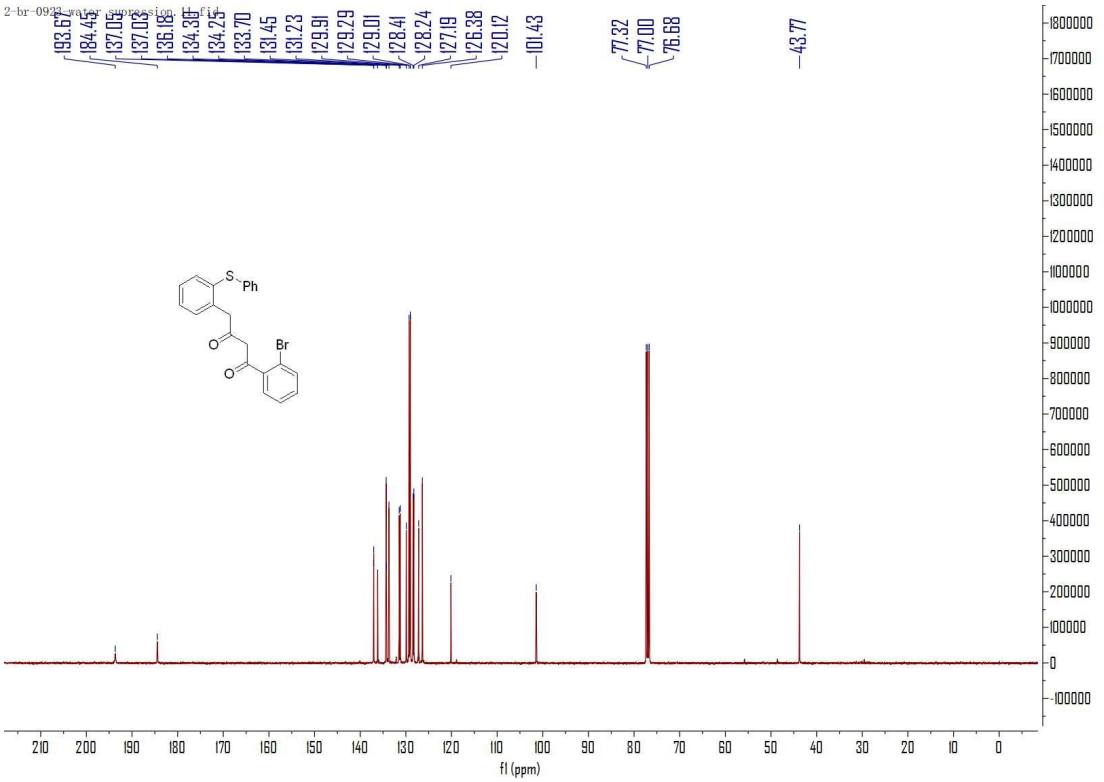
1-(4-bromophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3h**)



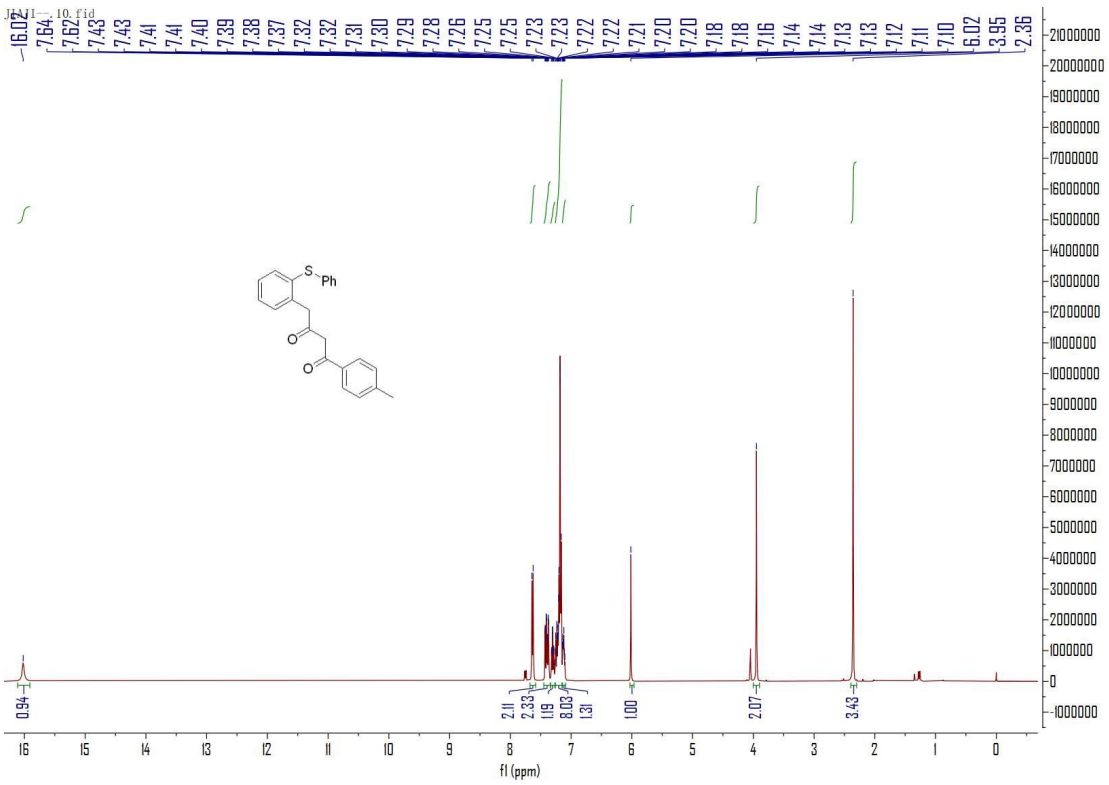


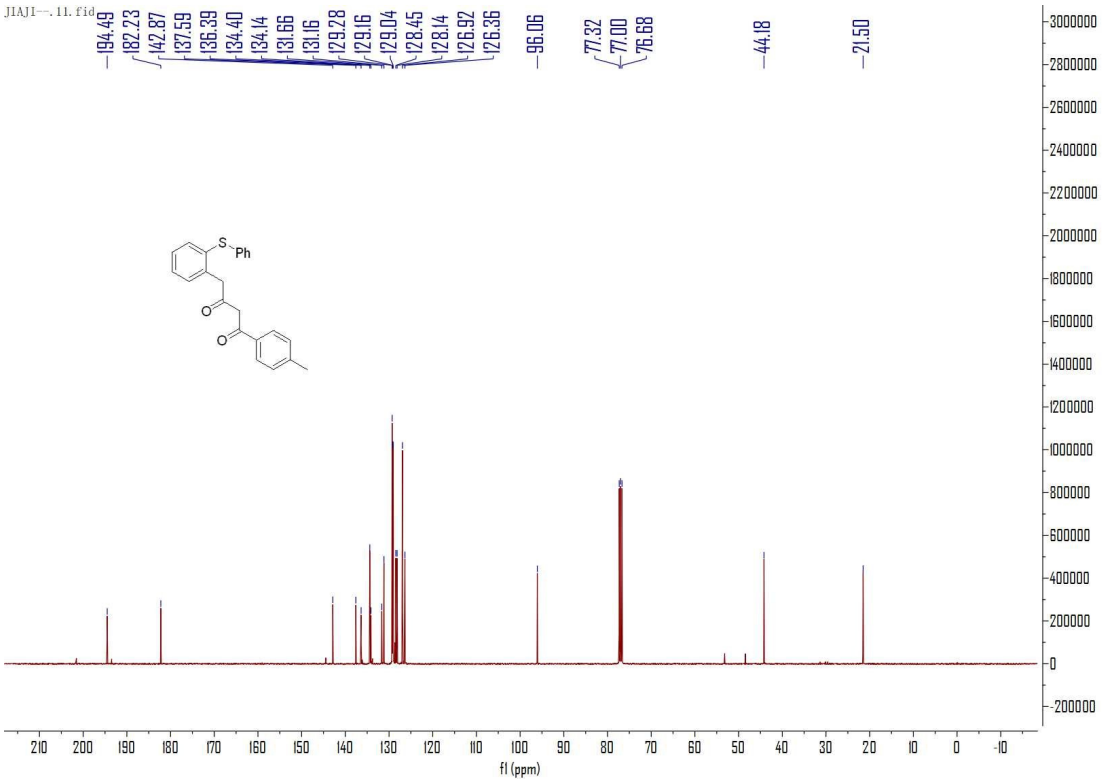
1-(2-bromophenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3i**)



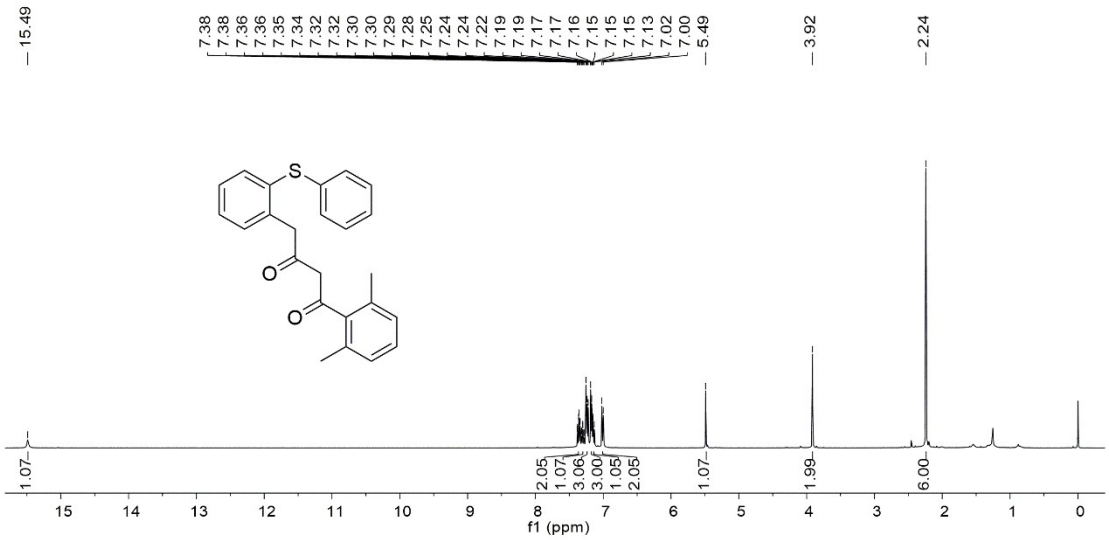


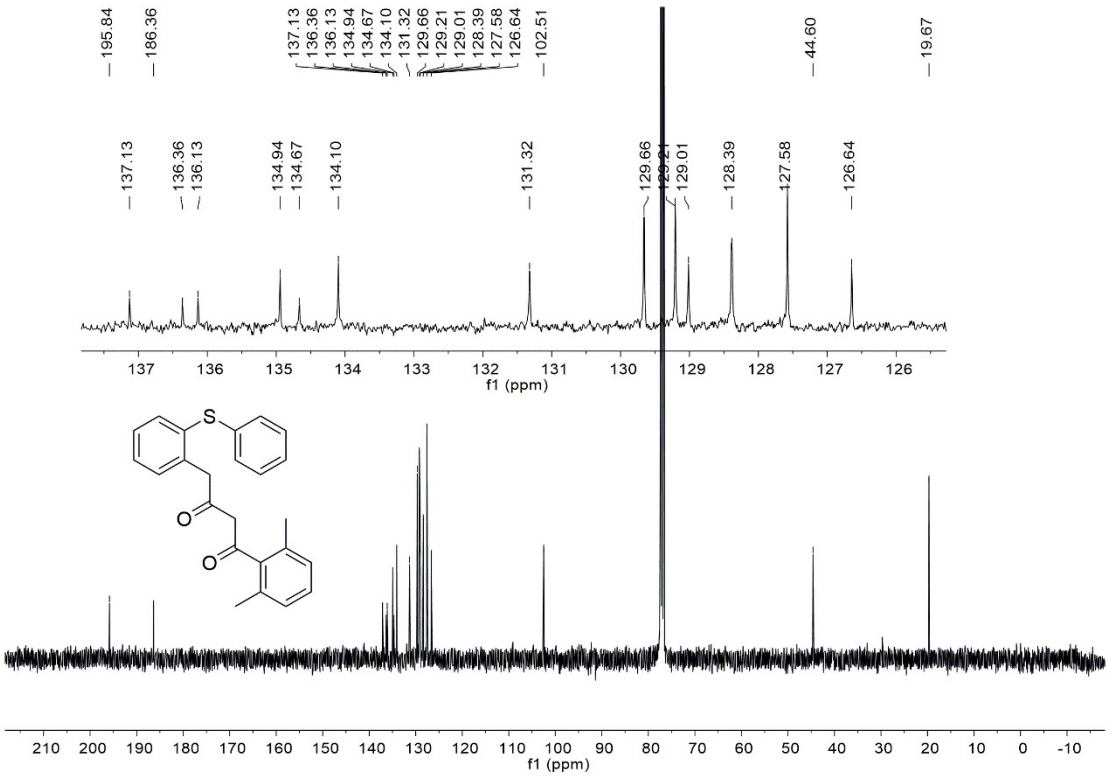
4-(2-(phenylthio)phenyl)-1-(p-tolyl)butane-1,3-dione (**3j**)



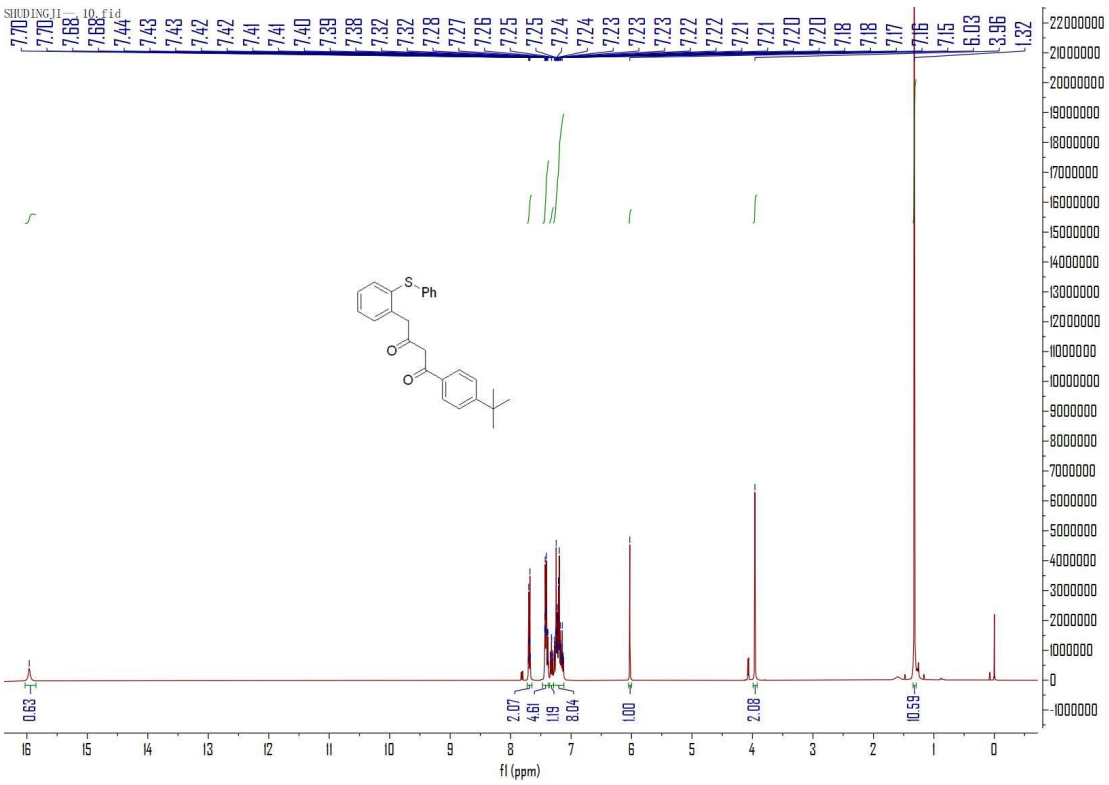


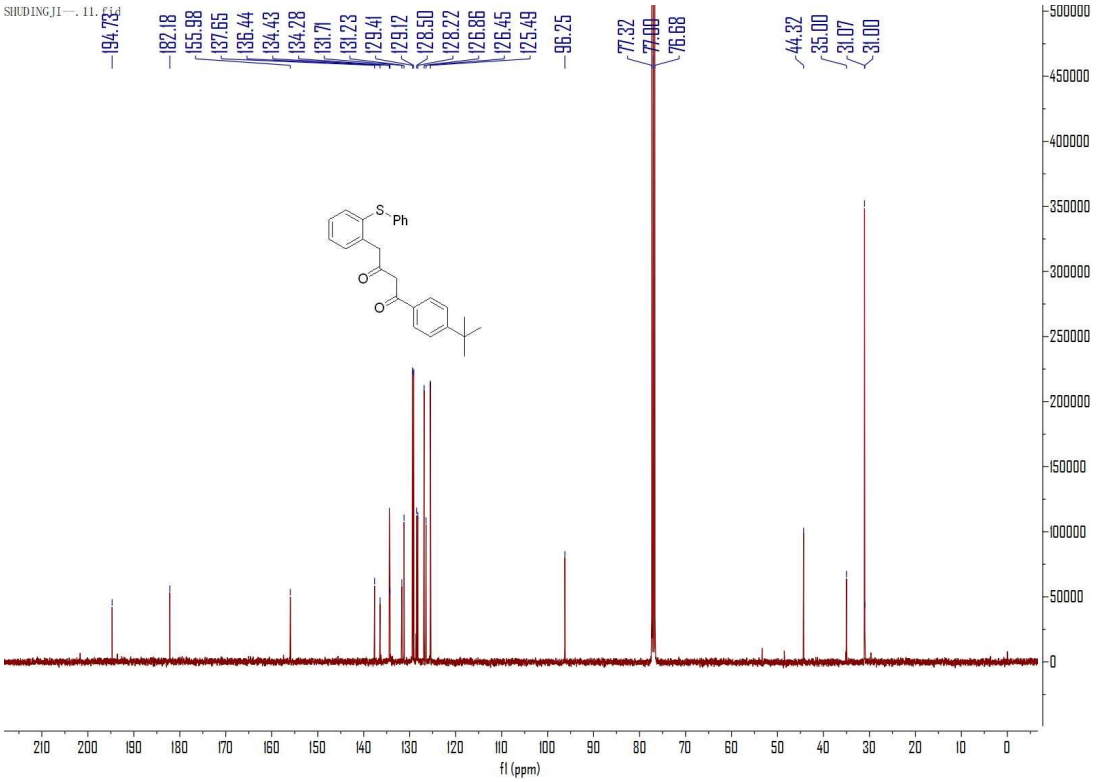
1-(2,6-dimethylphenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3k**)



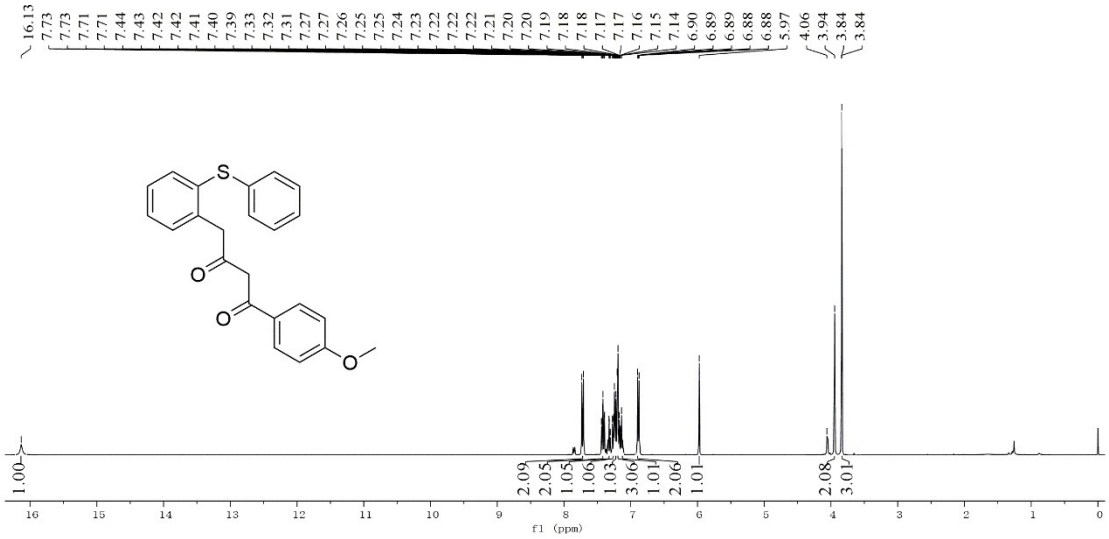


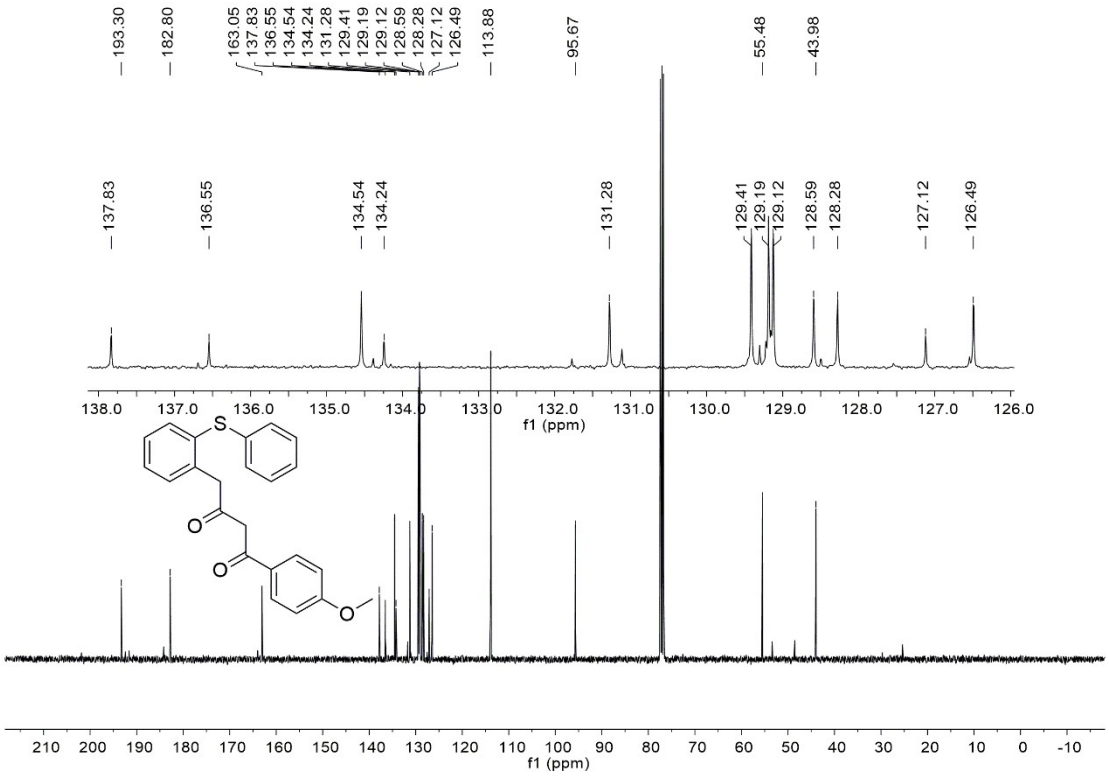
1-(4-(tert-butyl)phenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3l**)



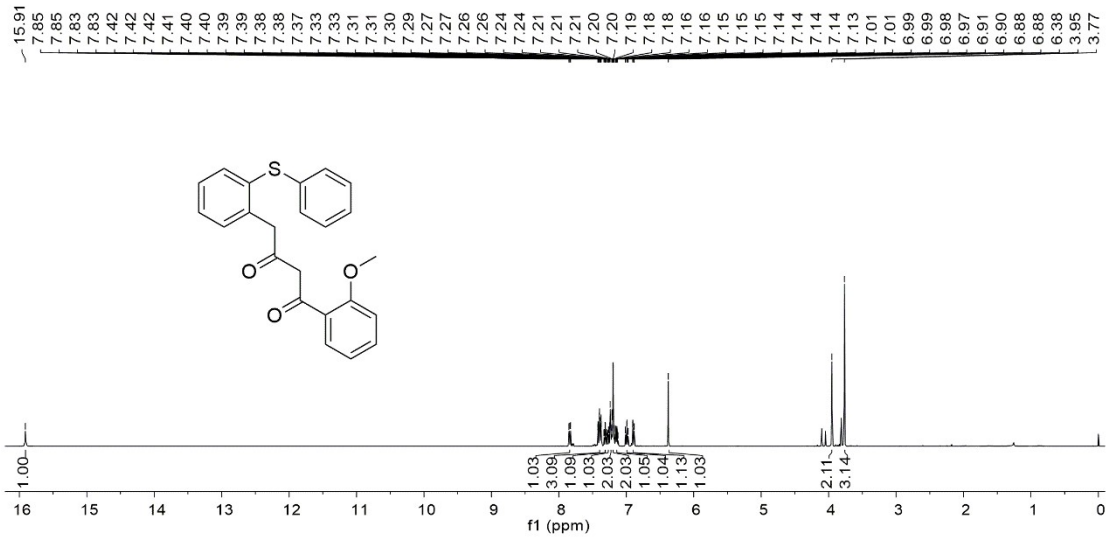


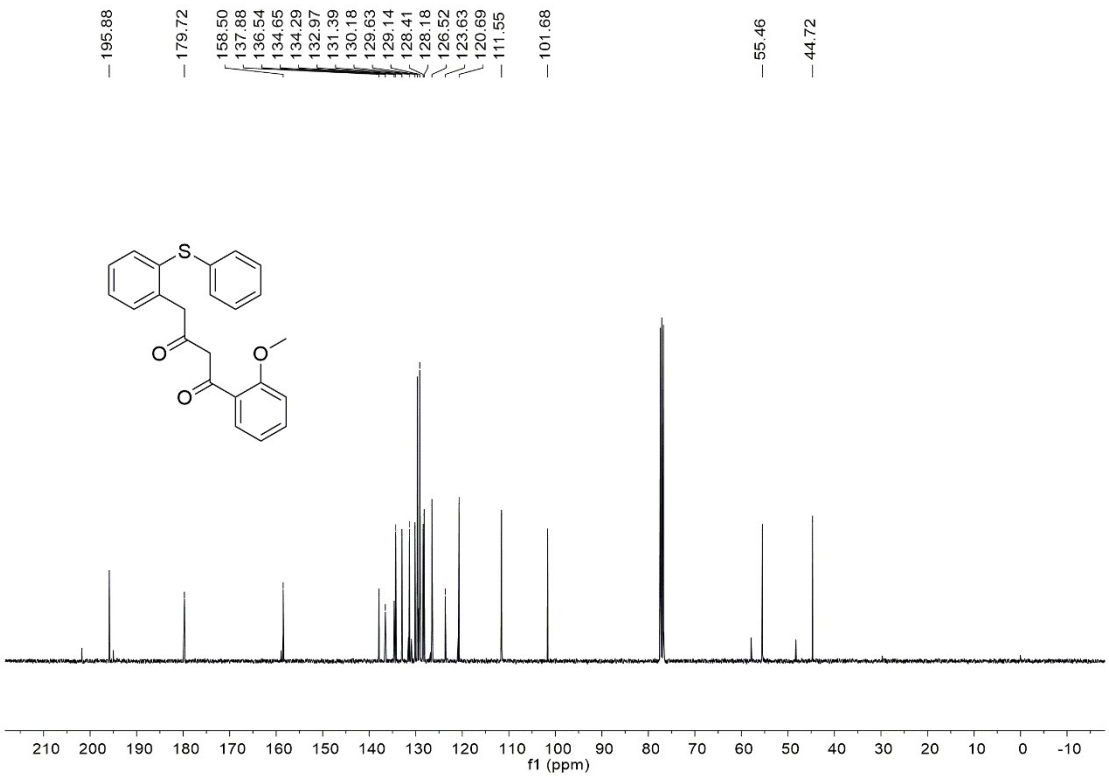
1-(4-methoxyphenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3m**)



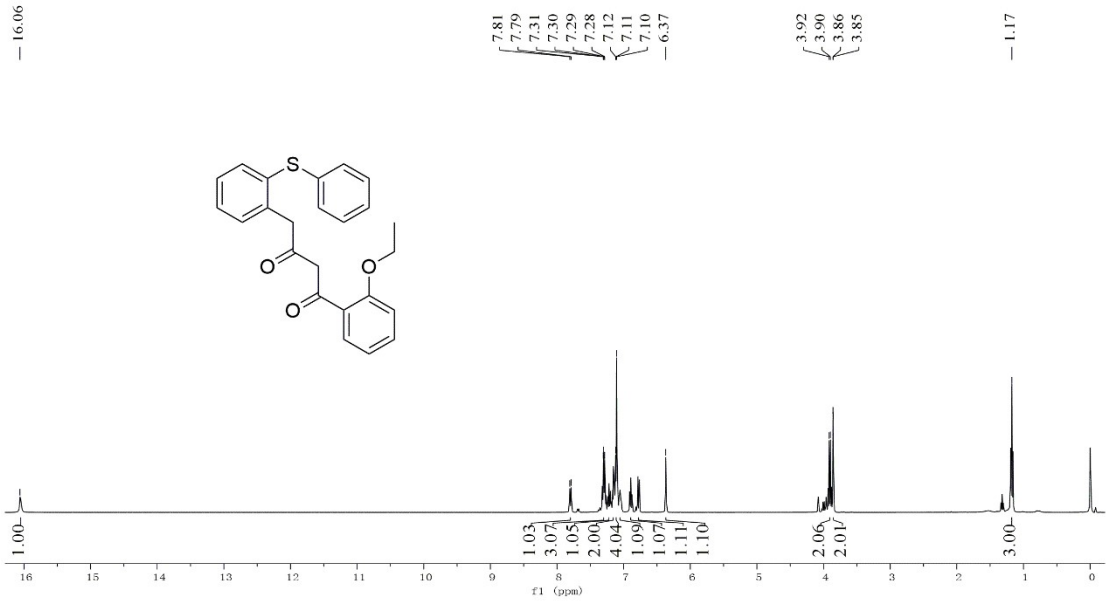


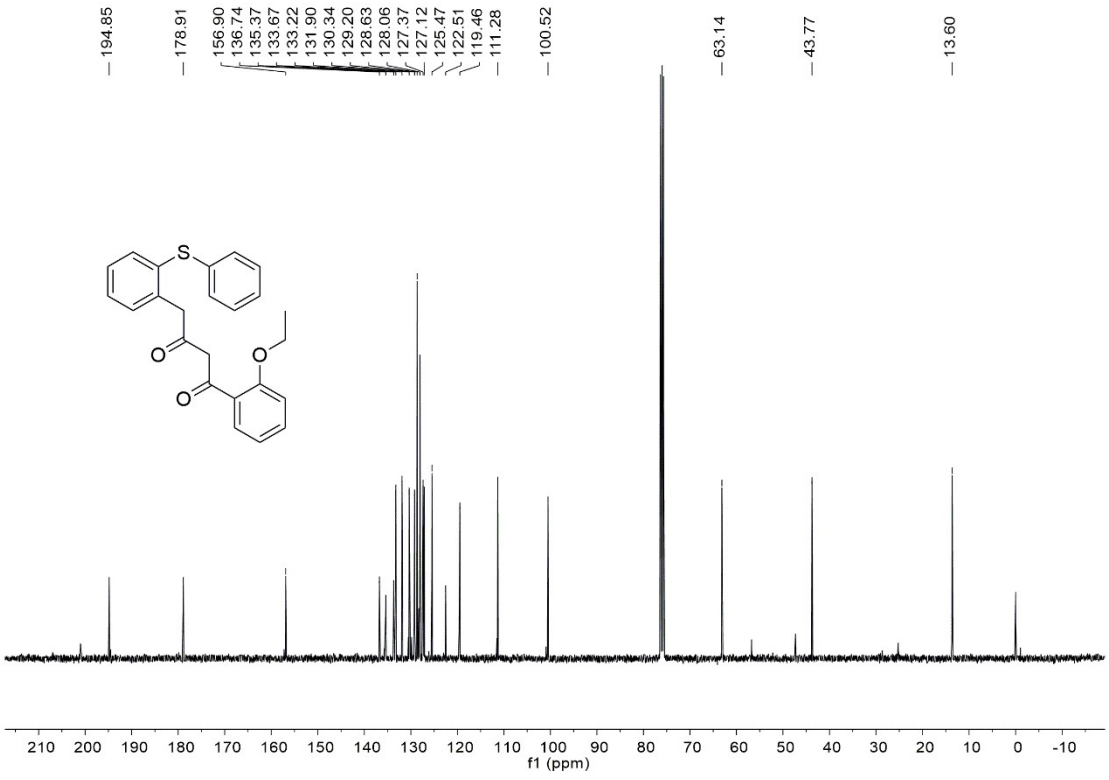
1-(2-methoxyphenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3n**)



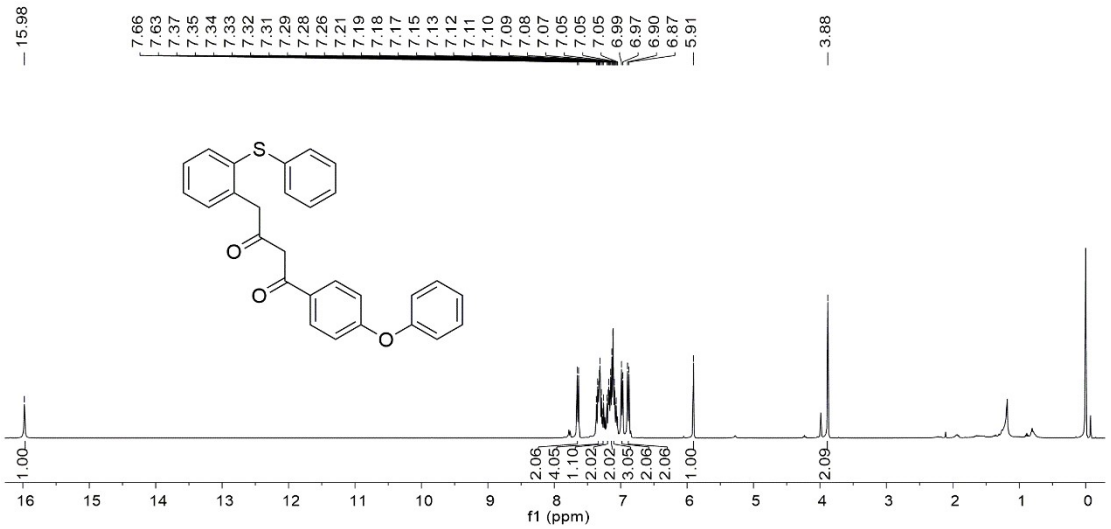


1-(2-ethoxyphenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3o**)





1-(4-phenoxyphenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3p**)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7.11
7.10
7.09
7.08
7.07
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6.90
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5.91
3.88
S
O
O
O
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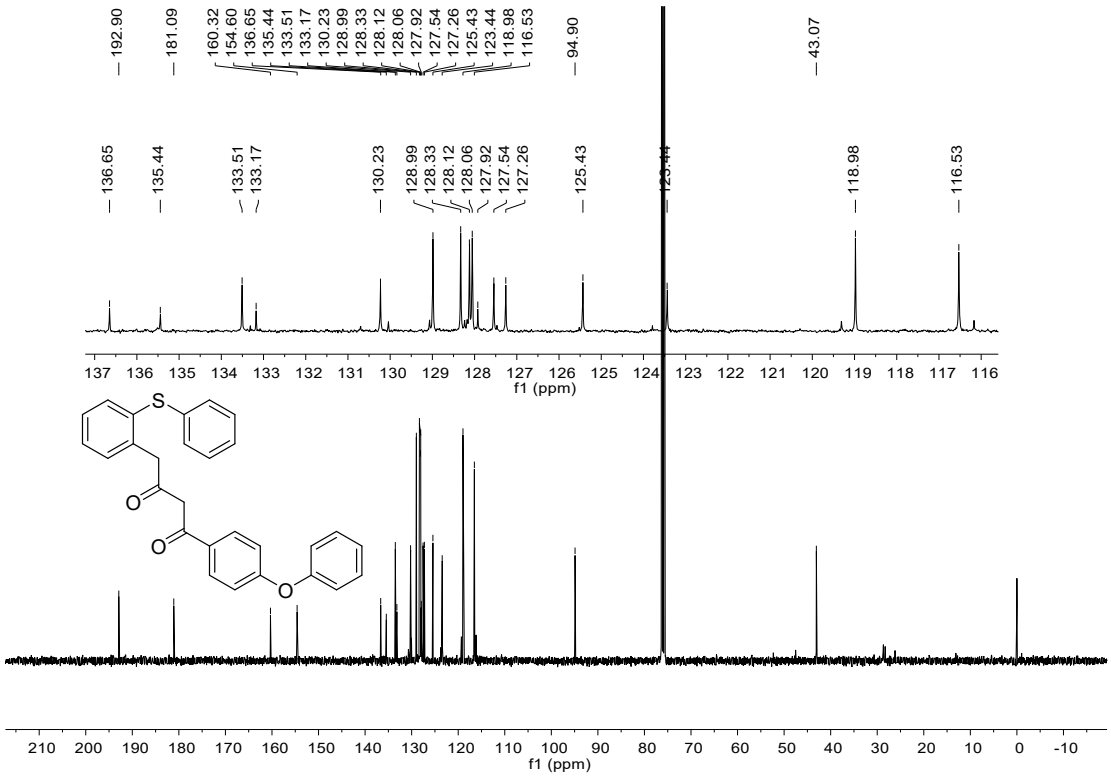
2.06
2.06
1.00
2.09
f1 (ppm)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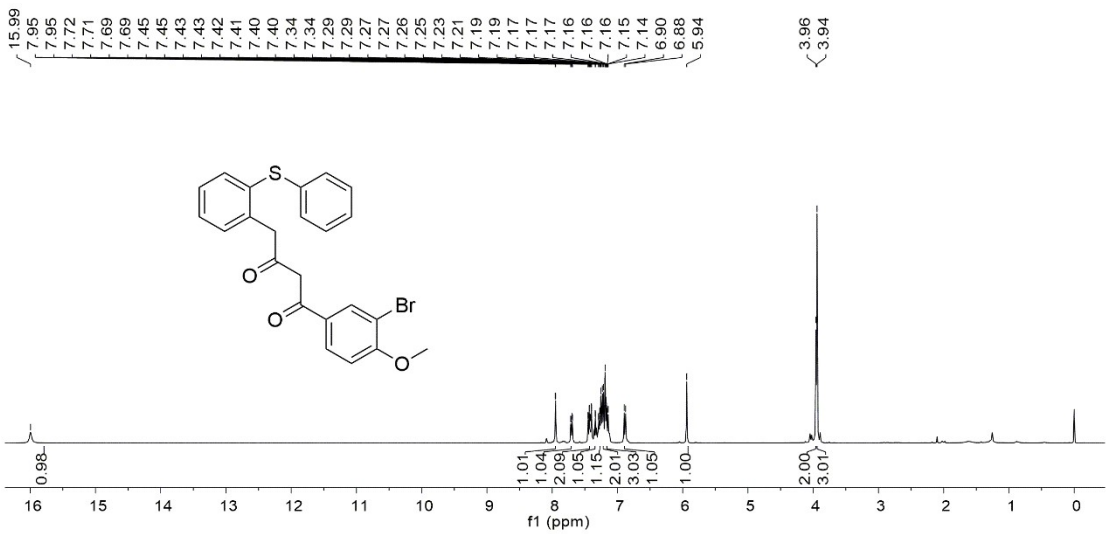
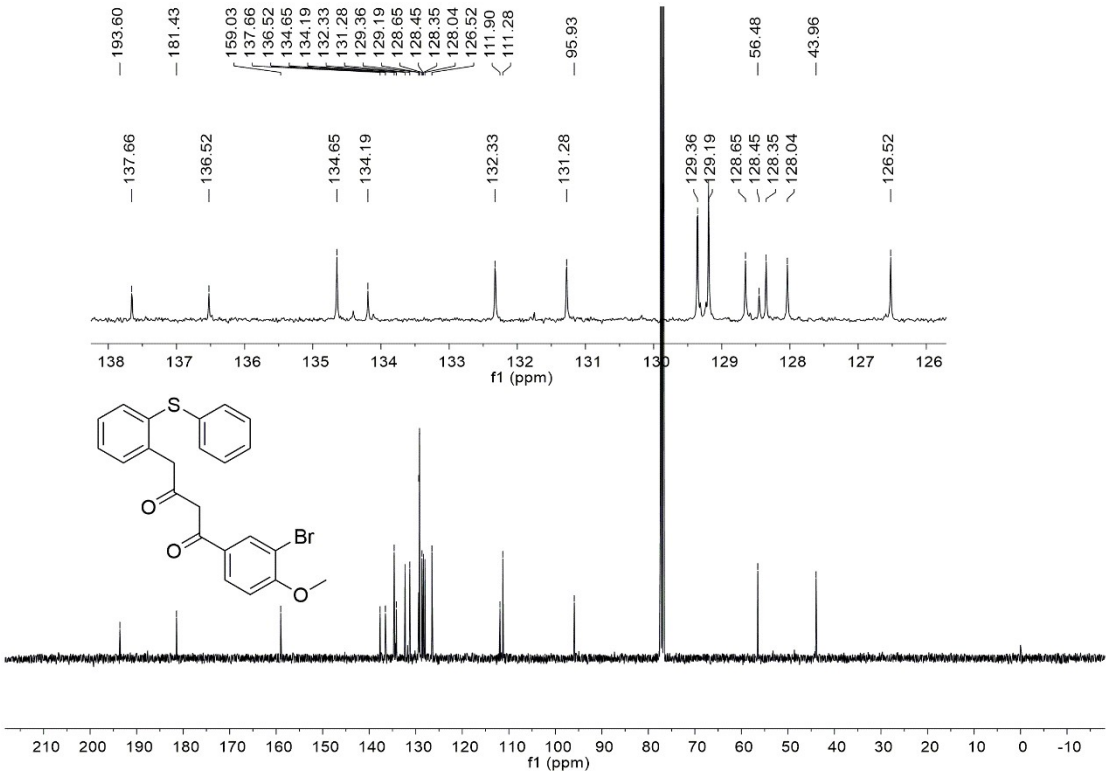
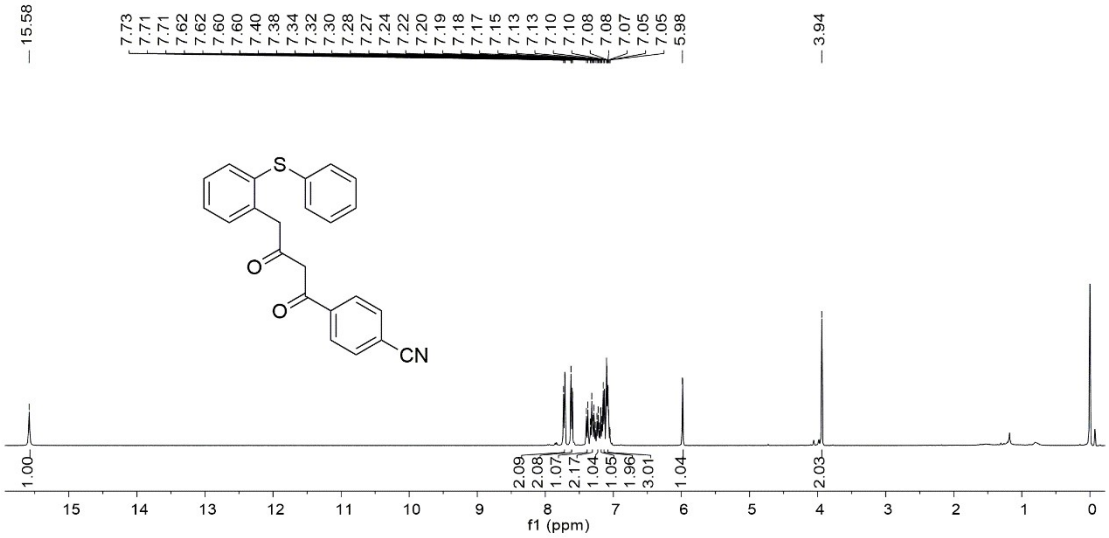
127.26
125.43
123.44
118.98
116.53
94.90
43.07
f1 (ppm)
S
O
O
O
f1 (ppm)

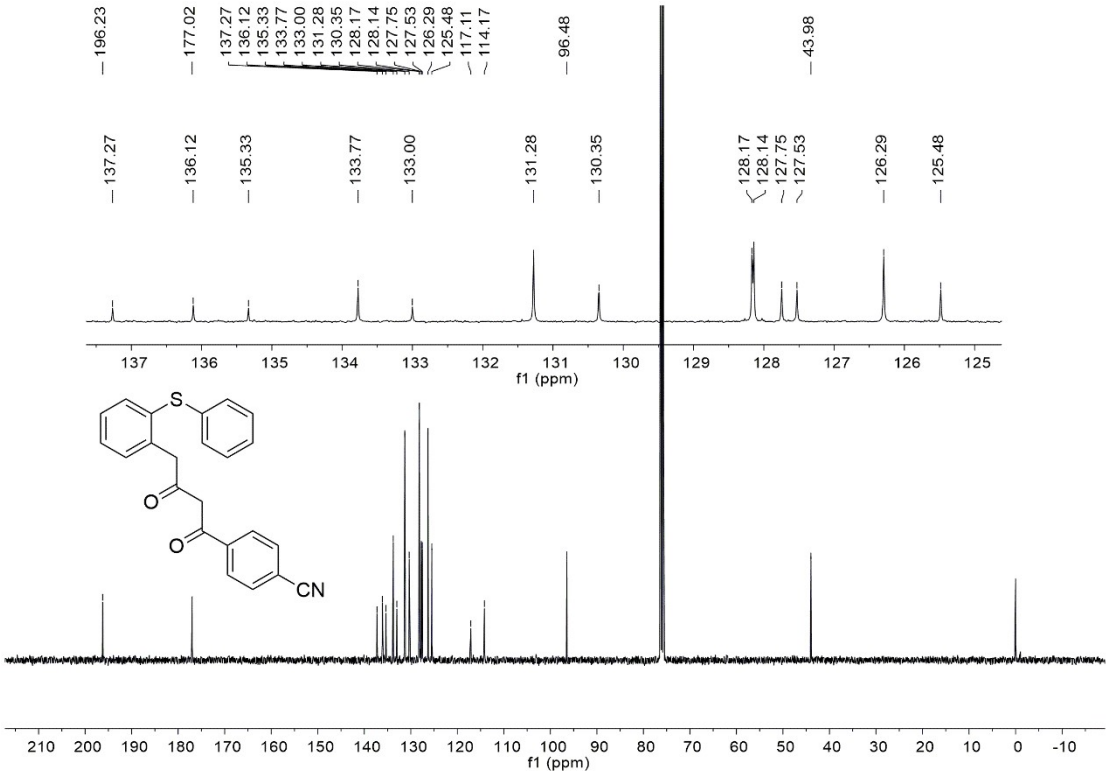
1-(3-bromo-4-methoxyphenyl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3q**)



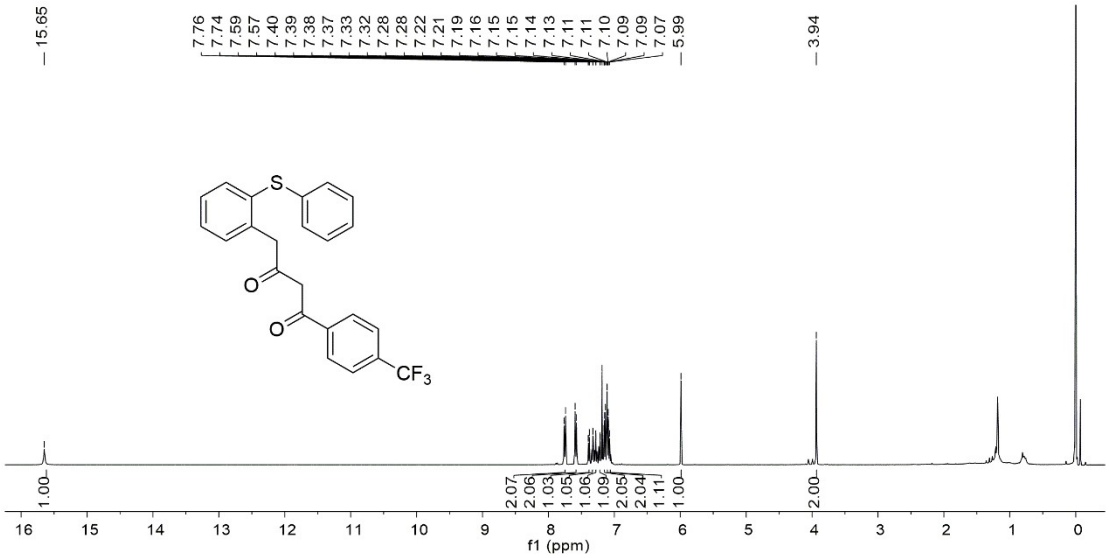


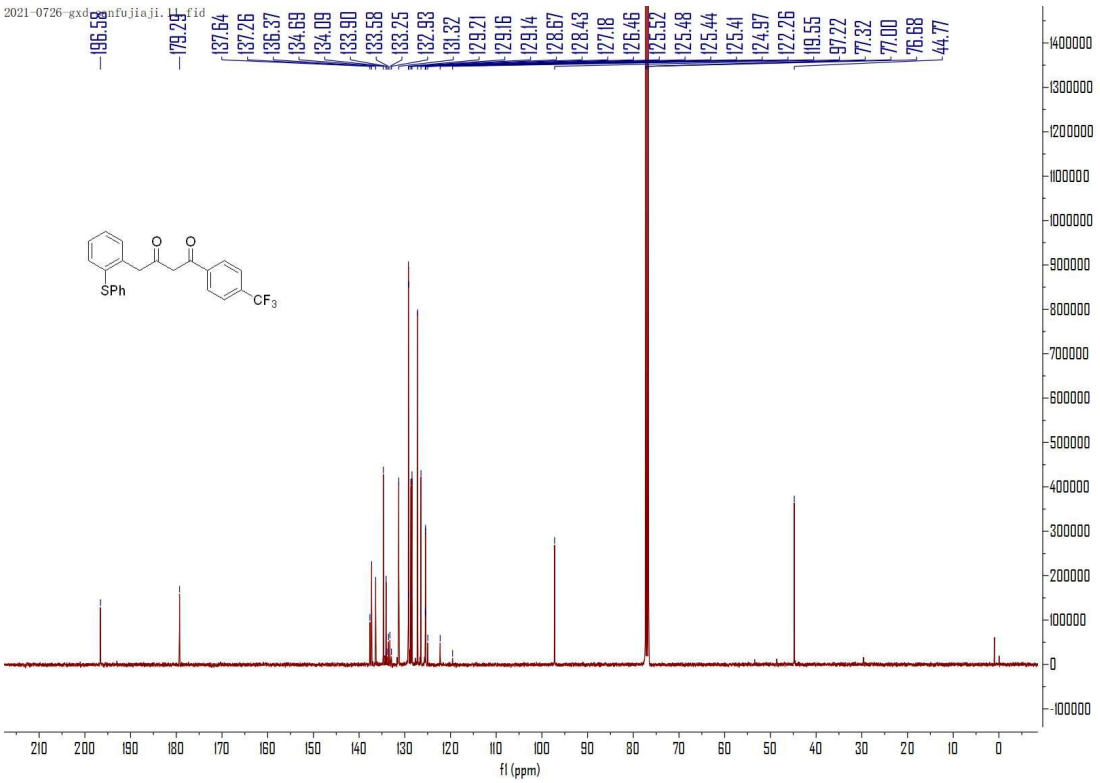
4-(3-oxo-4-(2-(phenylthio)phenyl)butanoyl)benzonitrile (**3r**)



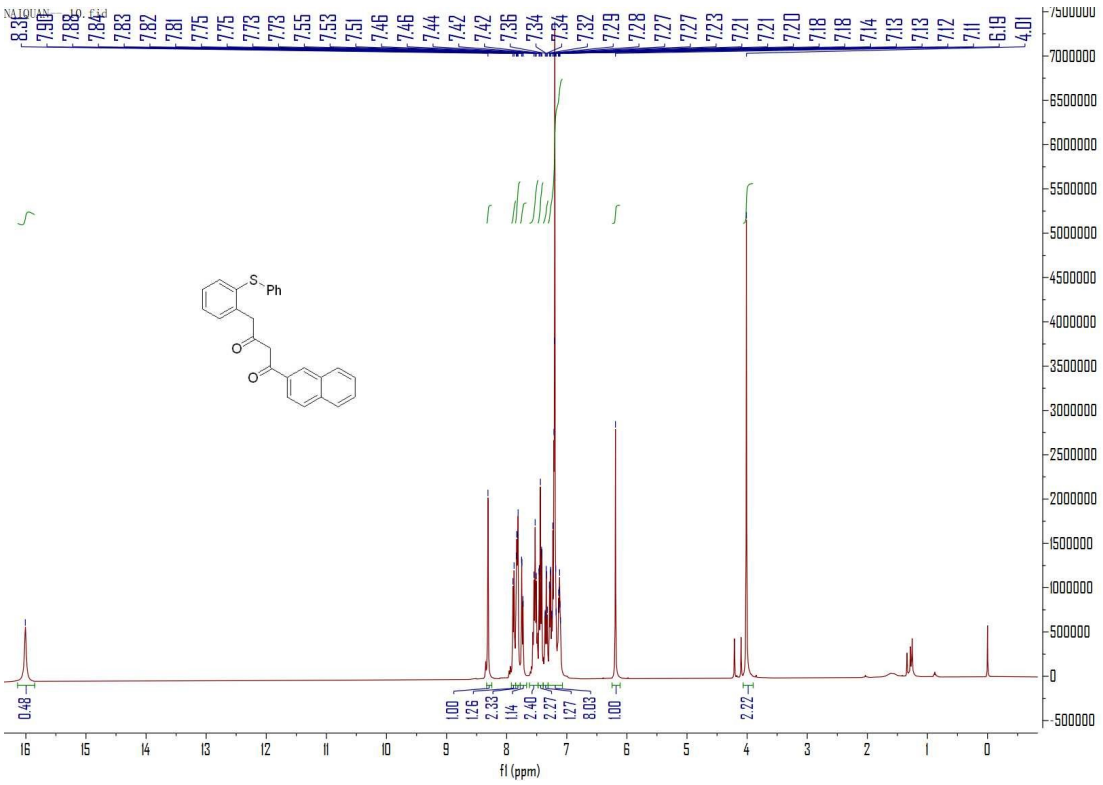


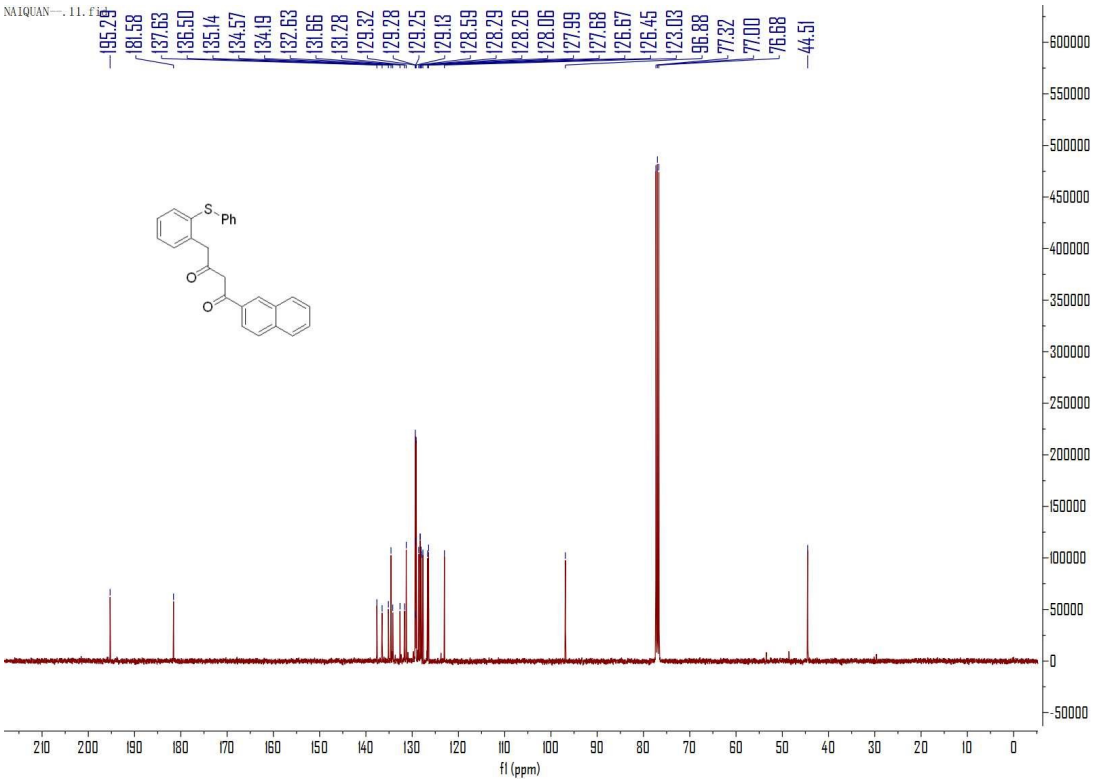
4-(2-(phenylthio)phenyl)-1-(4-(trifluoromethyl)phenyl)butane-1,3-dione (**3s**)



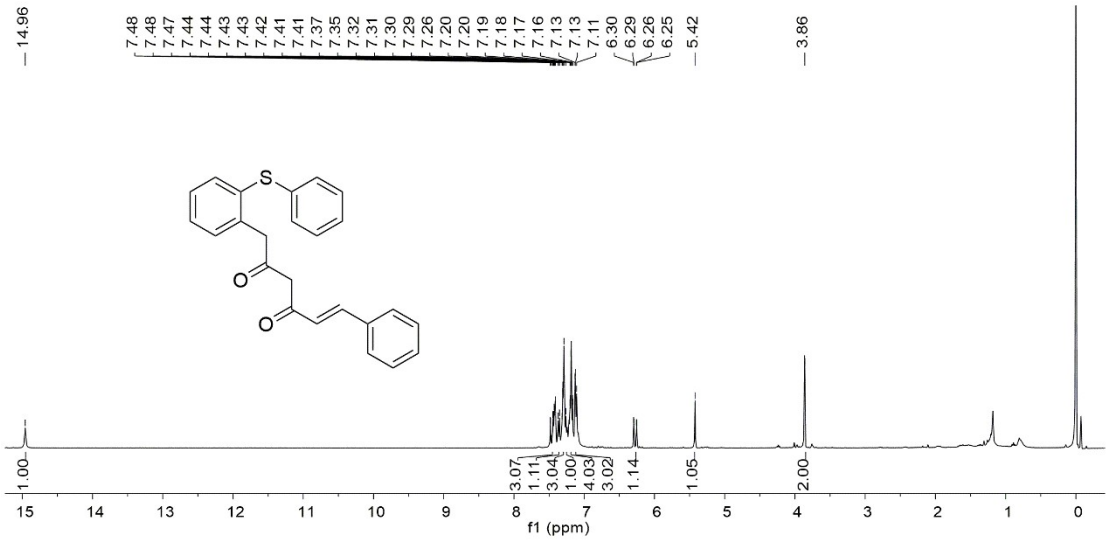


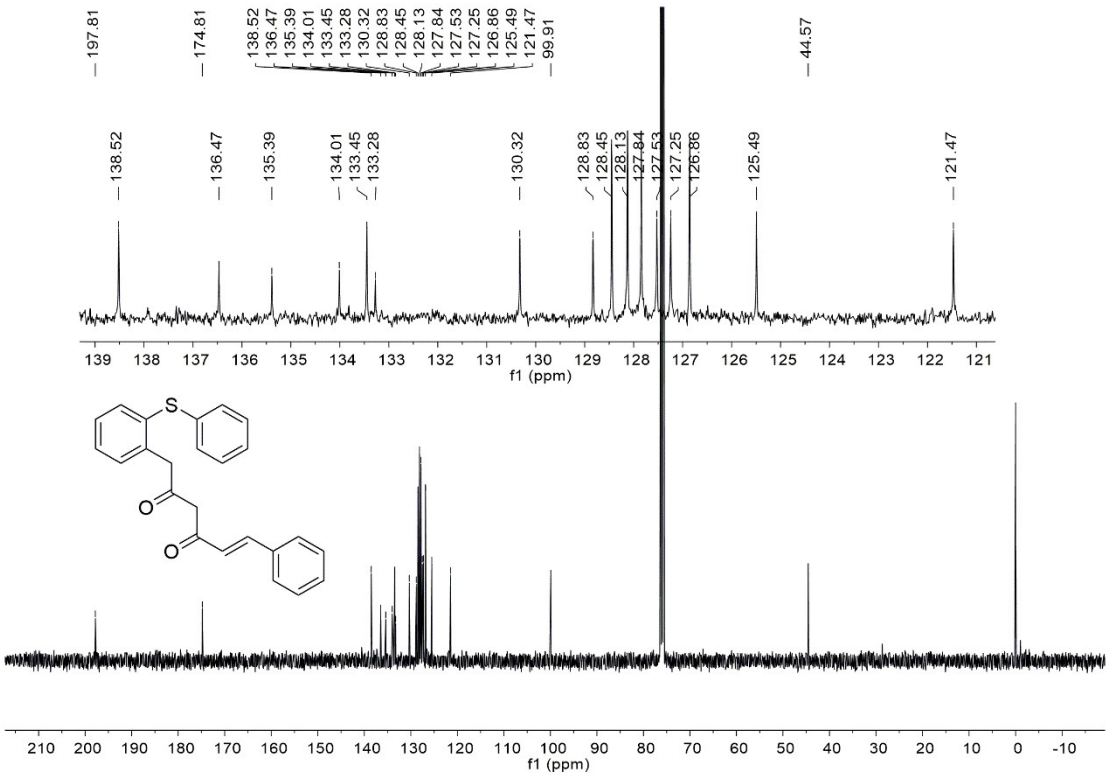
1-(naphthalen-2-yl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3t**)



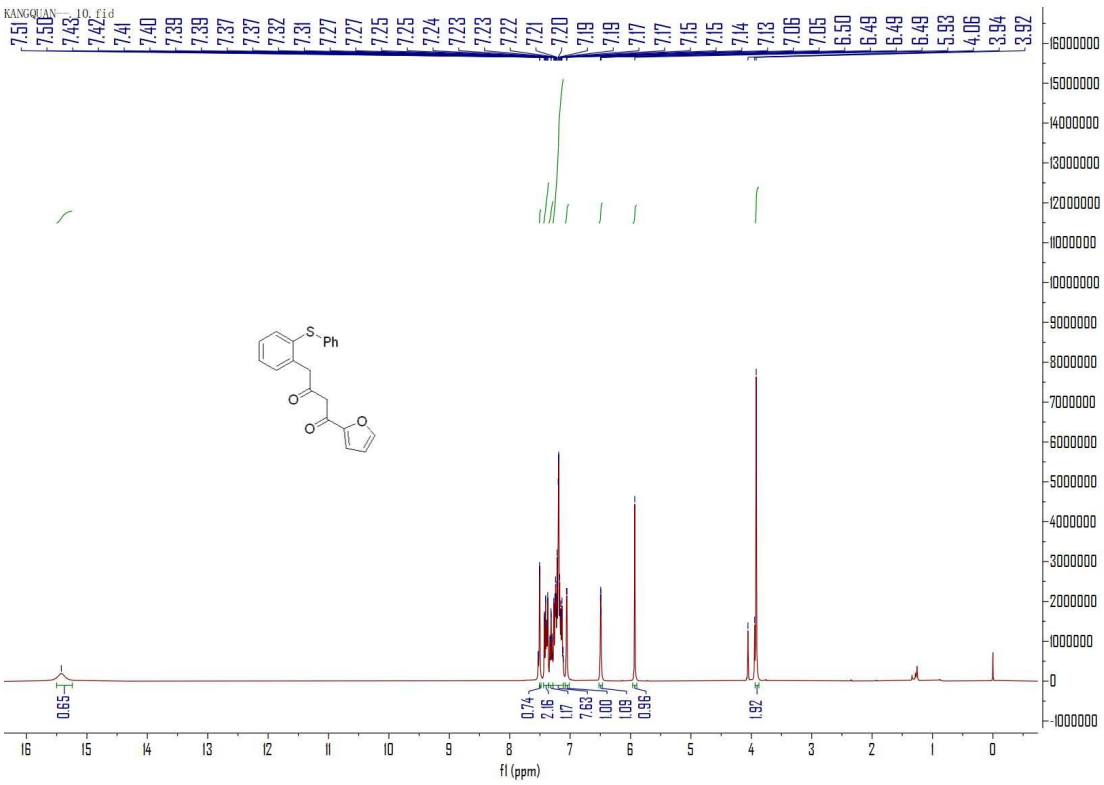


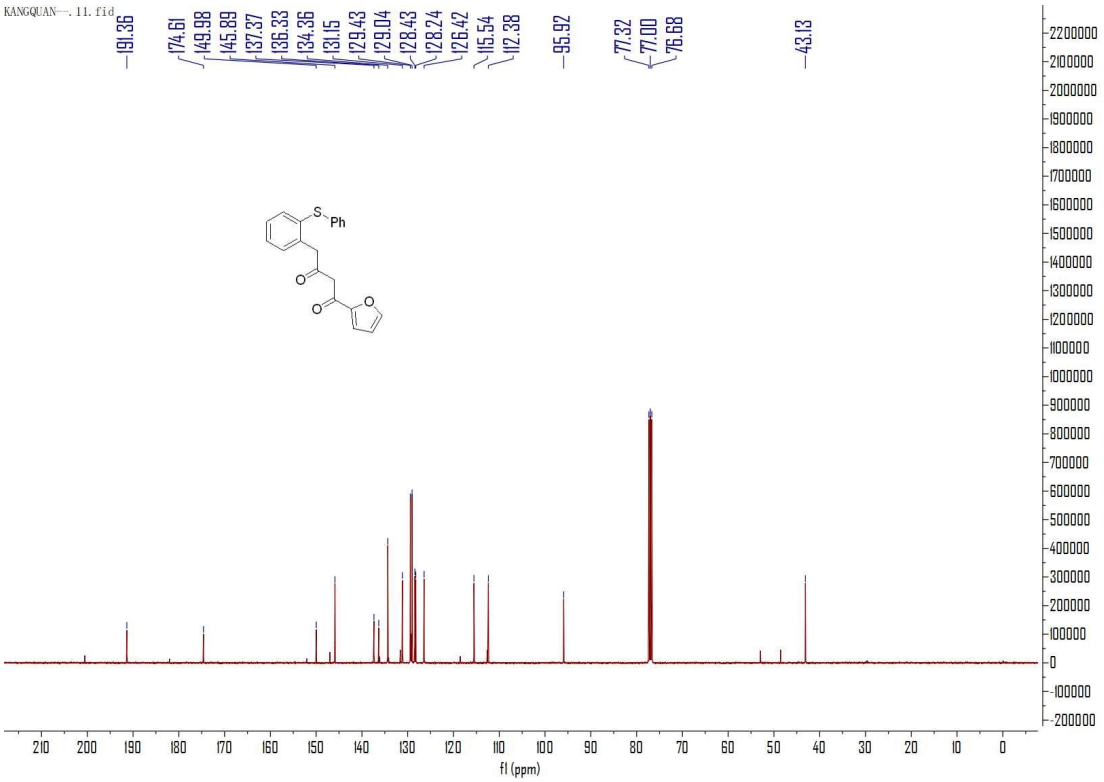
(*E*)-6-phenyl-1-(2-(phenylthio)phenyl)hex-5-ene-2,4-dione (**3u**)



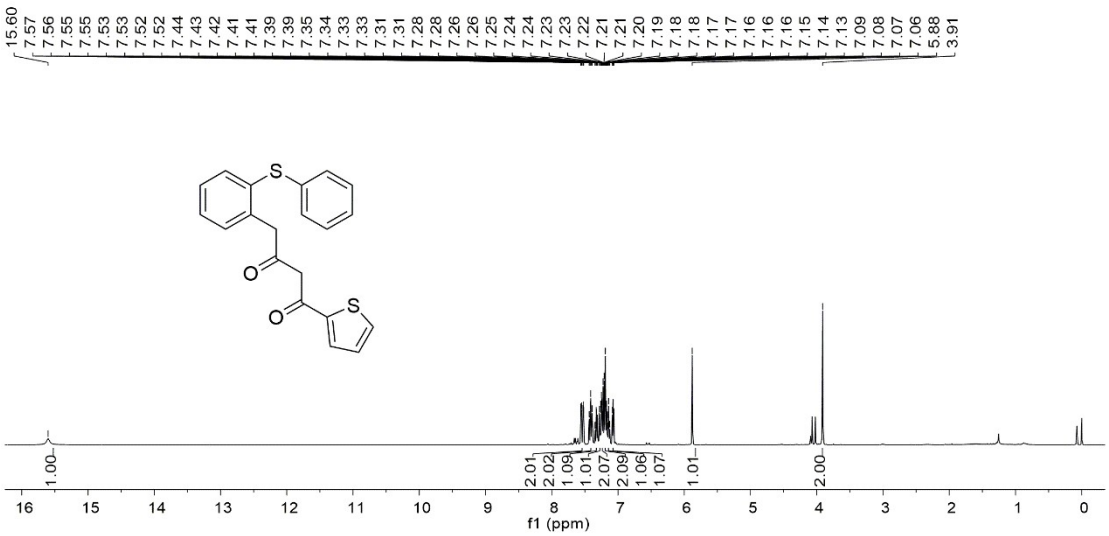


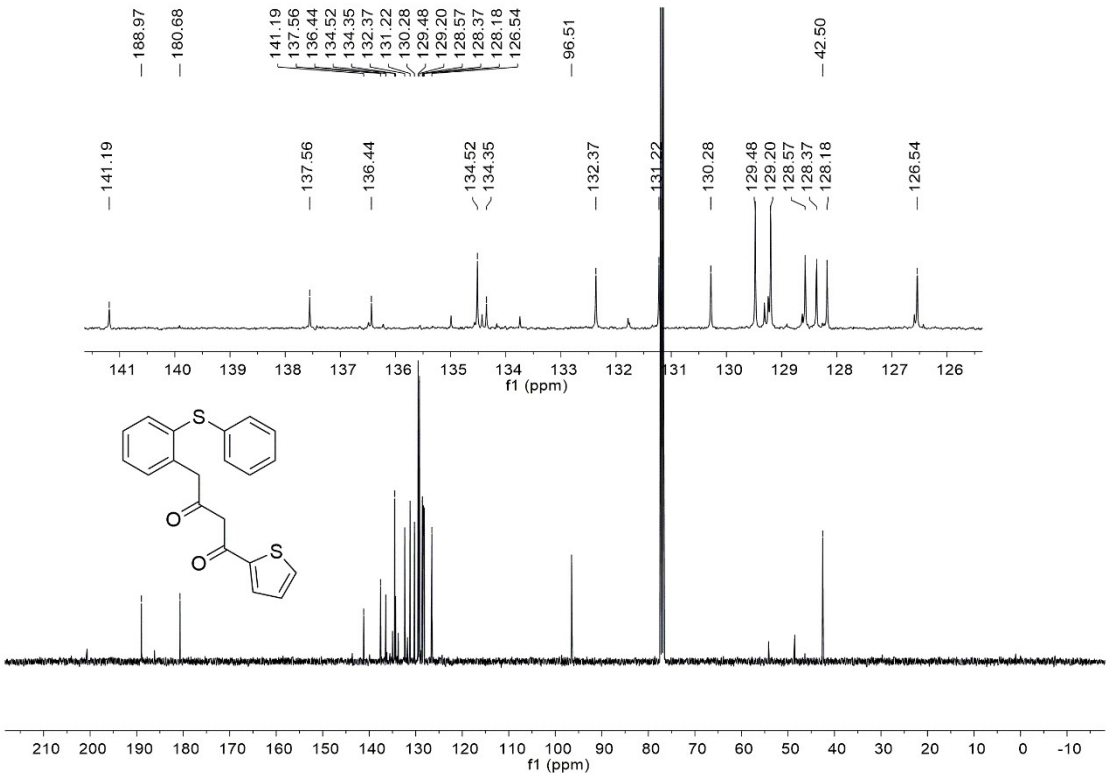
1-(furan-2-yl)-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3v**)



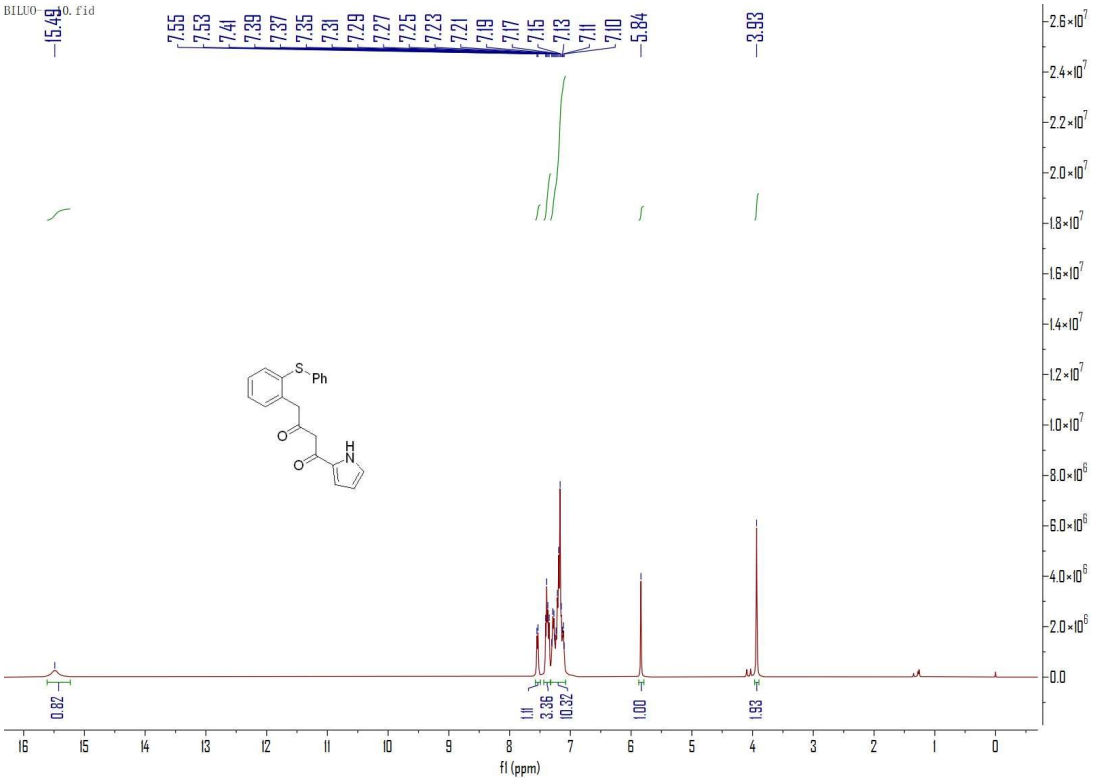


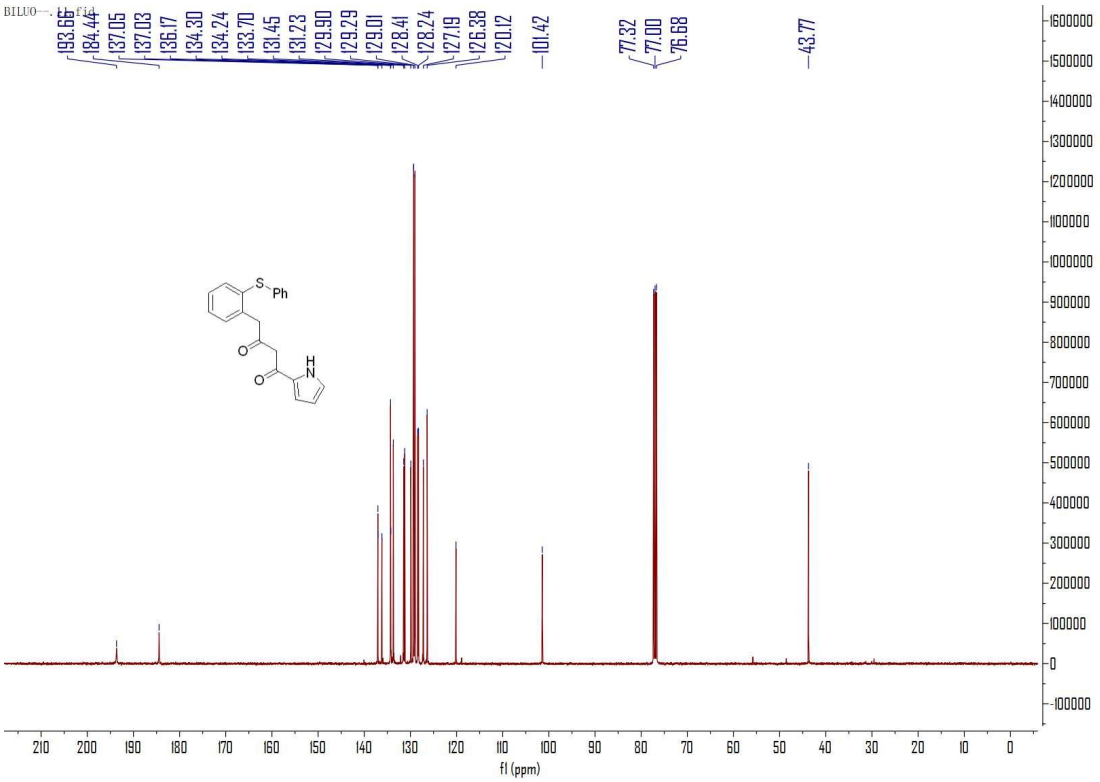
4-(2-(phenylthio)phenyl)-1-(thiophen-2-yl)butane-1,3-dione (**3w**)



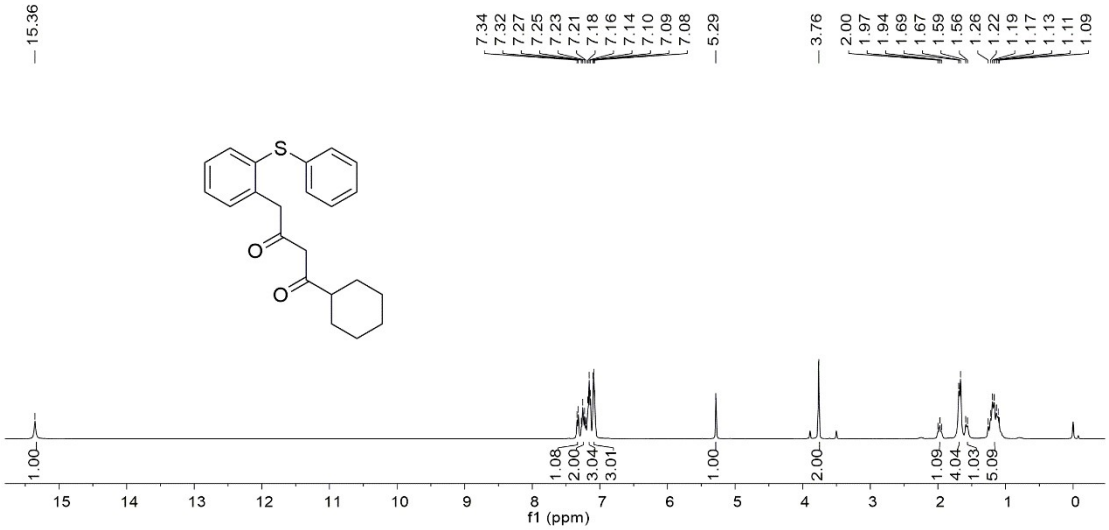


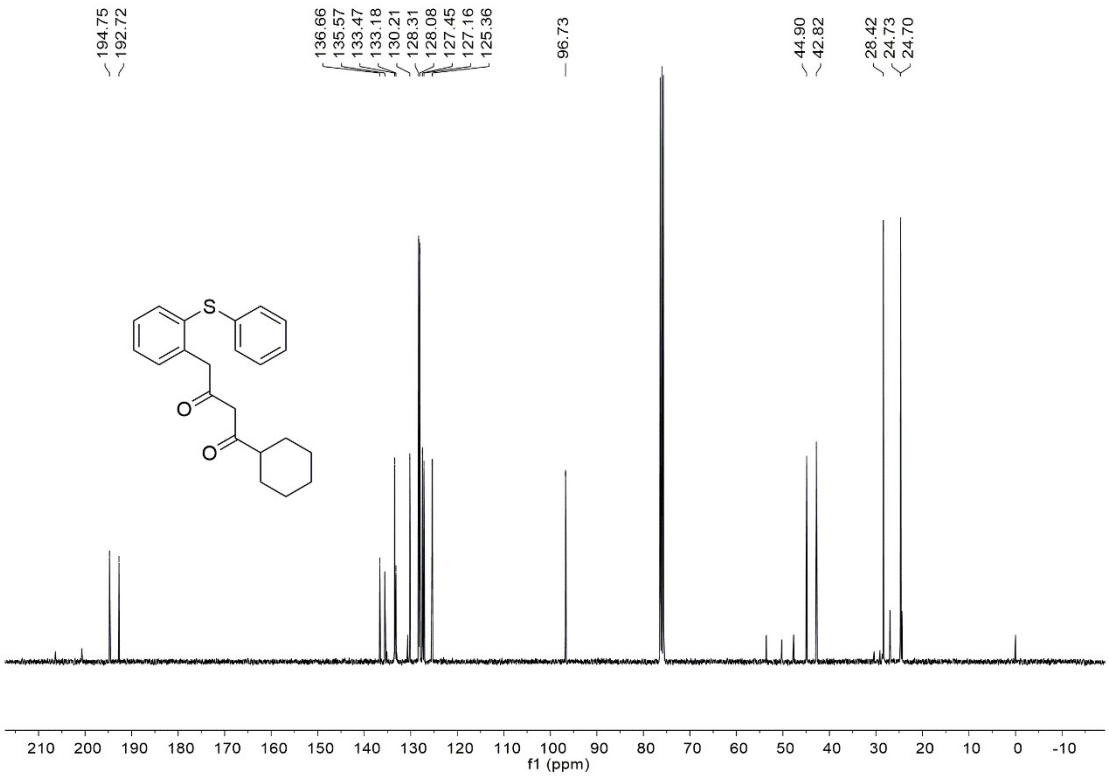
4-(2-(phenylthio)phenyl)-1-(1*H*-pyrrol-2-yl)butane-1,3-dione (**3x**)



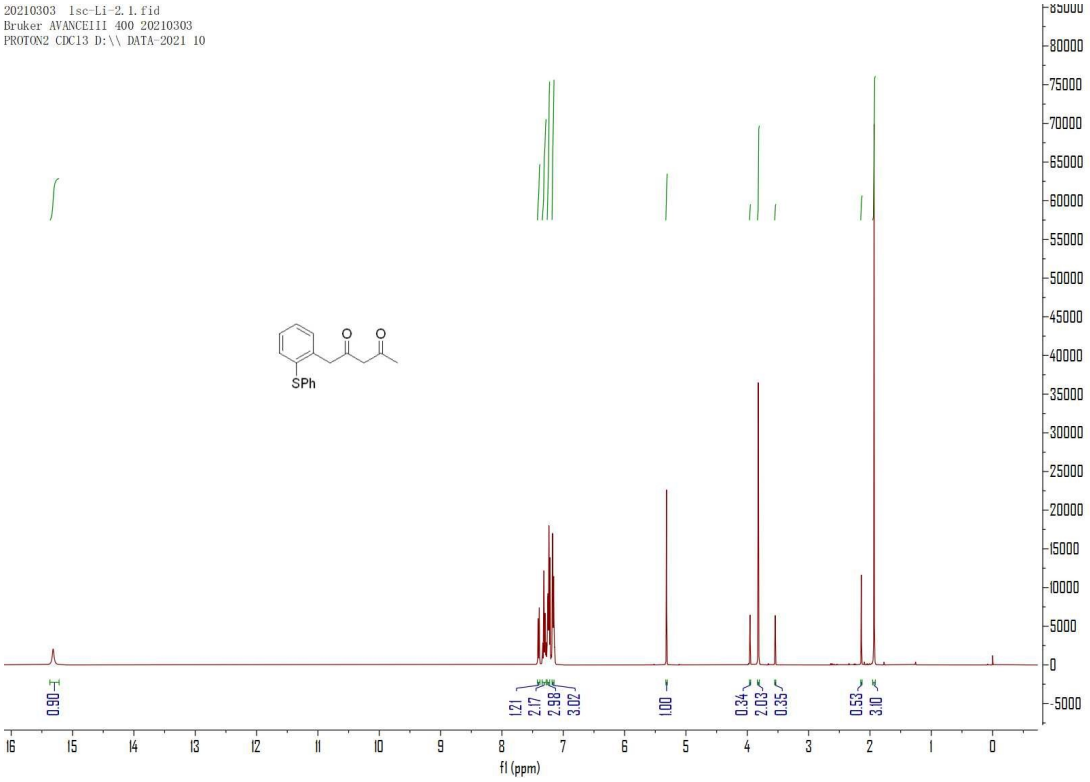


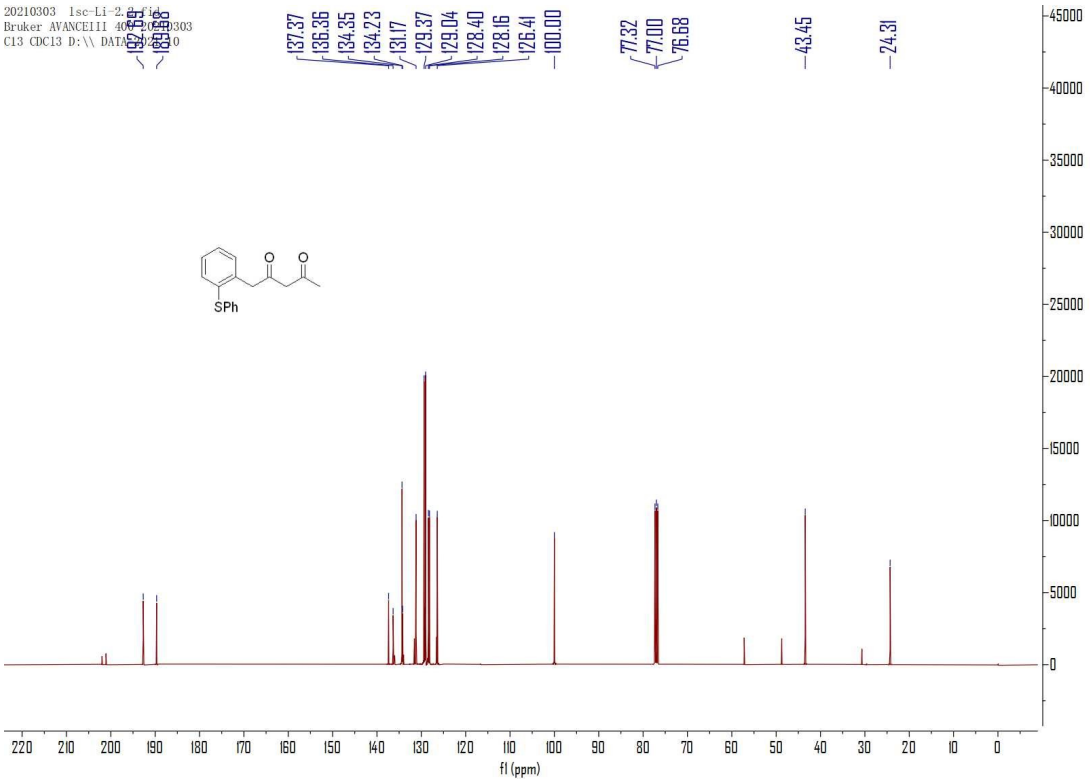
1-cyclohexyl-4-(2-(phenylthio)phenyl)butane-1,3-dione (**3y**)



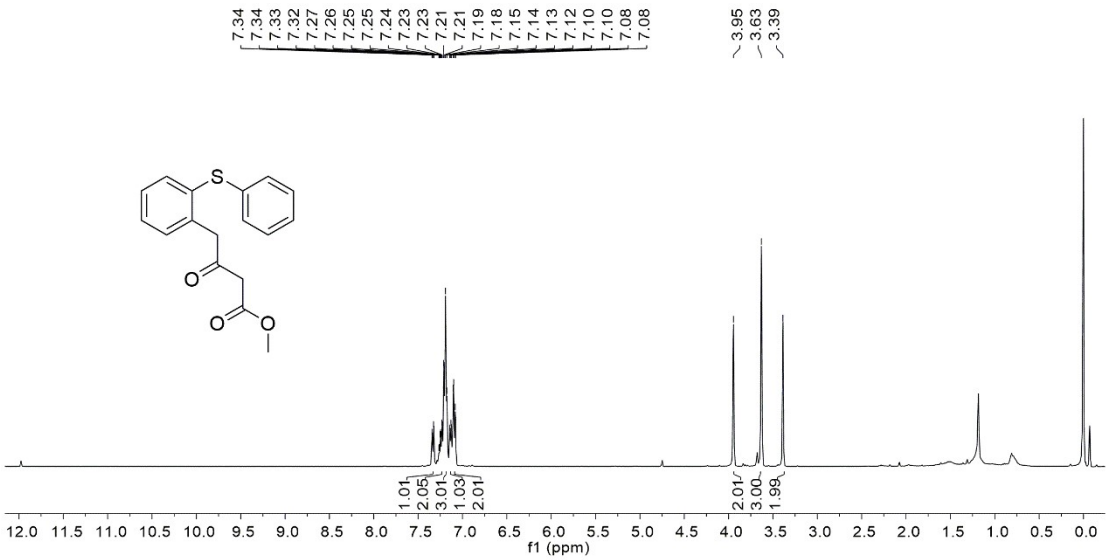


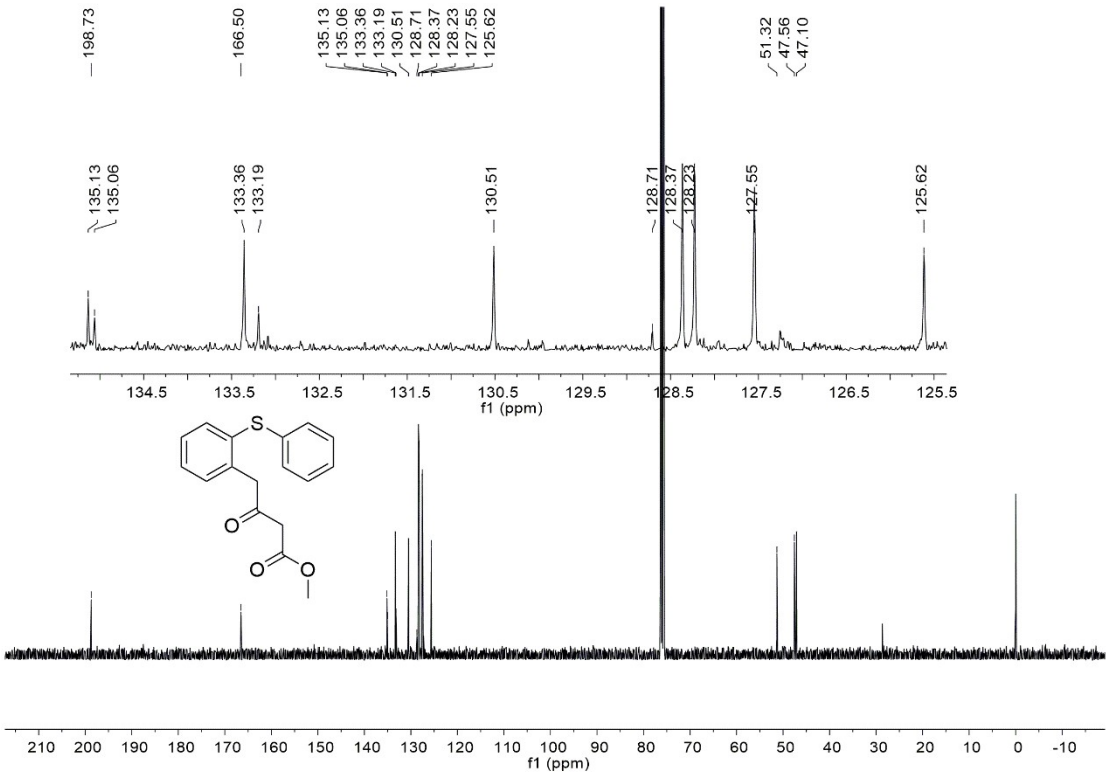
1-(2-(phenylthio)phenyl)pentane-2,4-dione (**3z**)



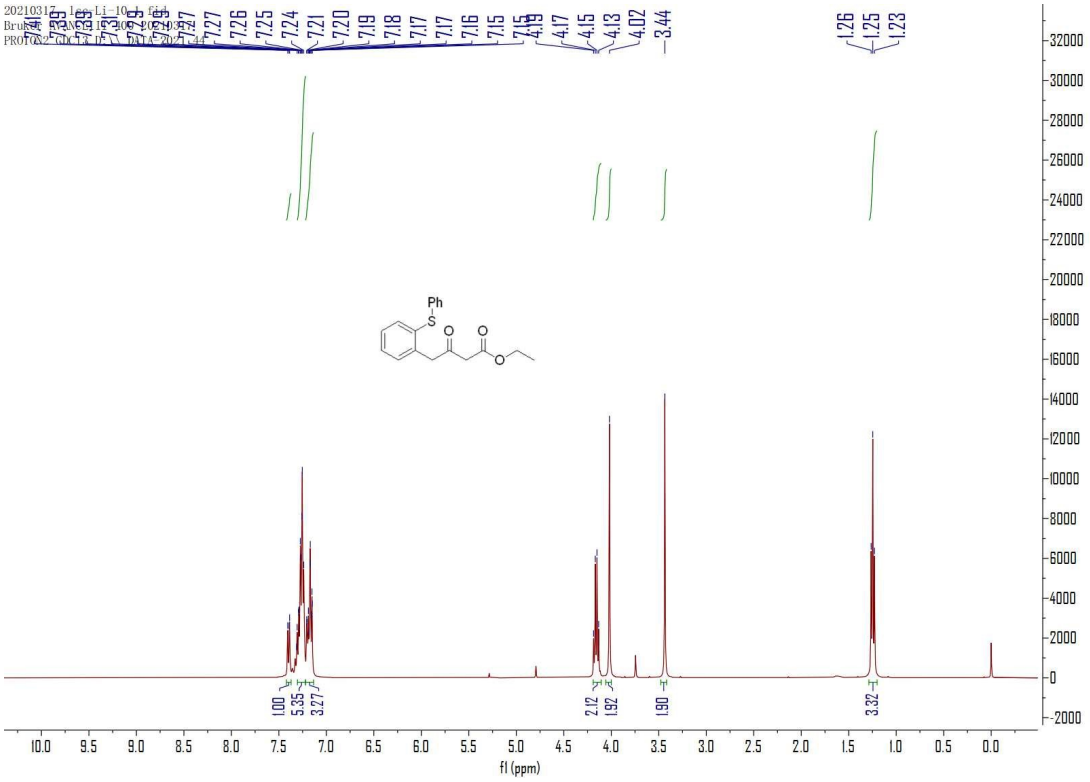


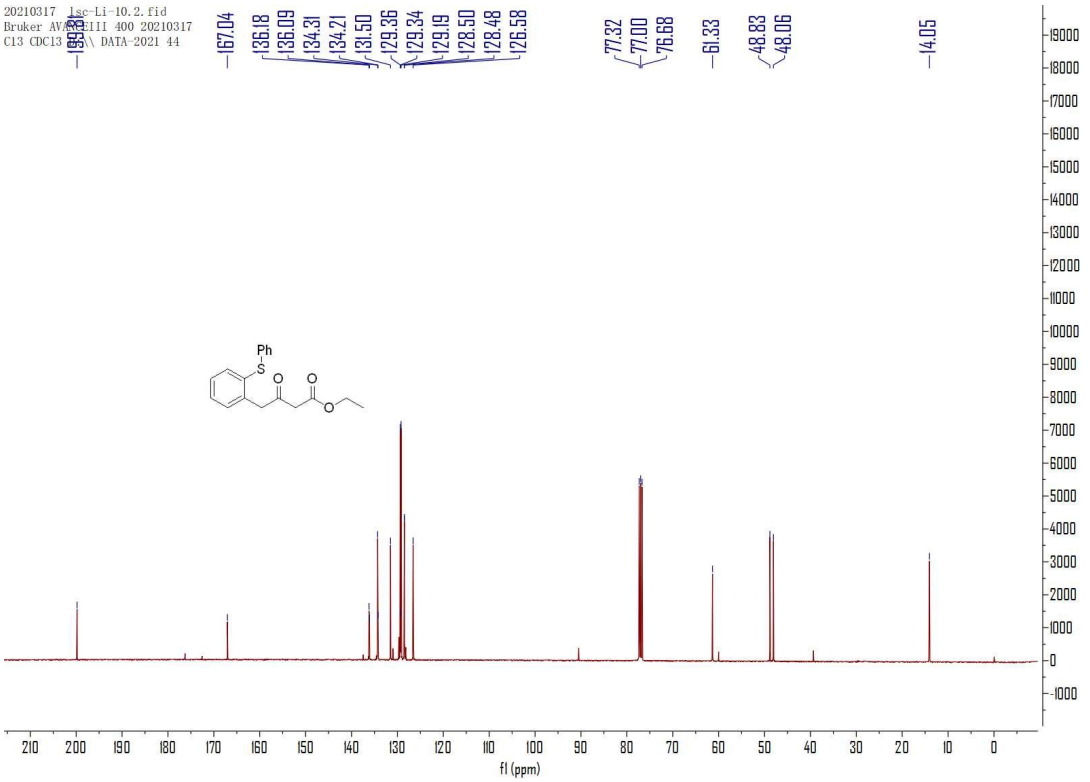
methyl 3-oxo-4-(2-(phenylthio)phenyl)butanoate (**3a'**)



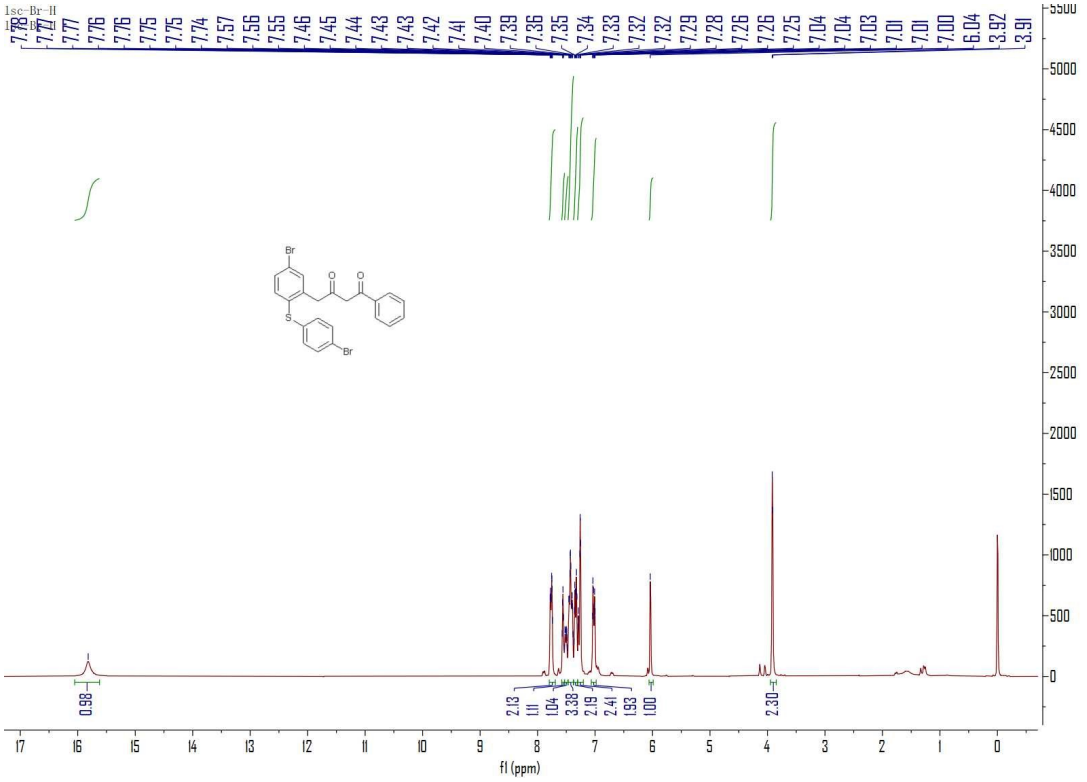


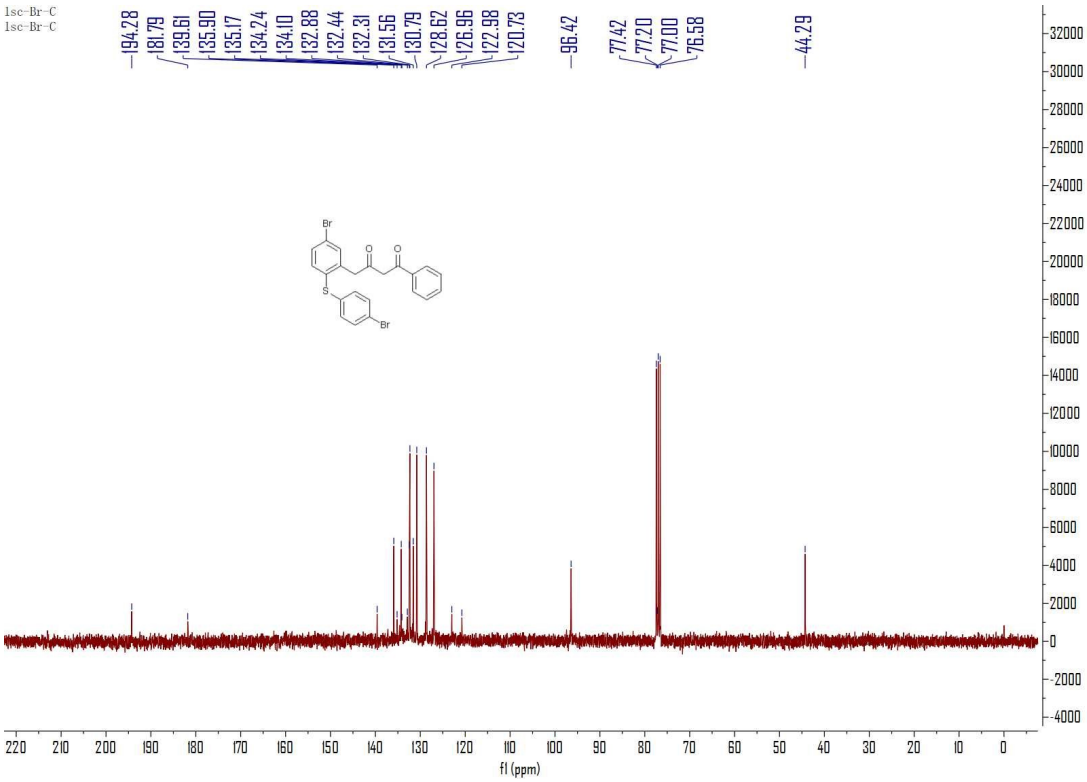
ethyl 3-oxo-4-(2-(phenylthio)phenyl)butanoate (**3b'**)



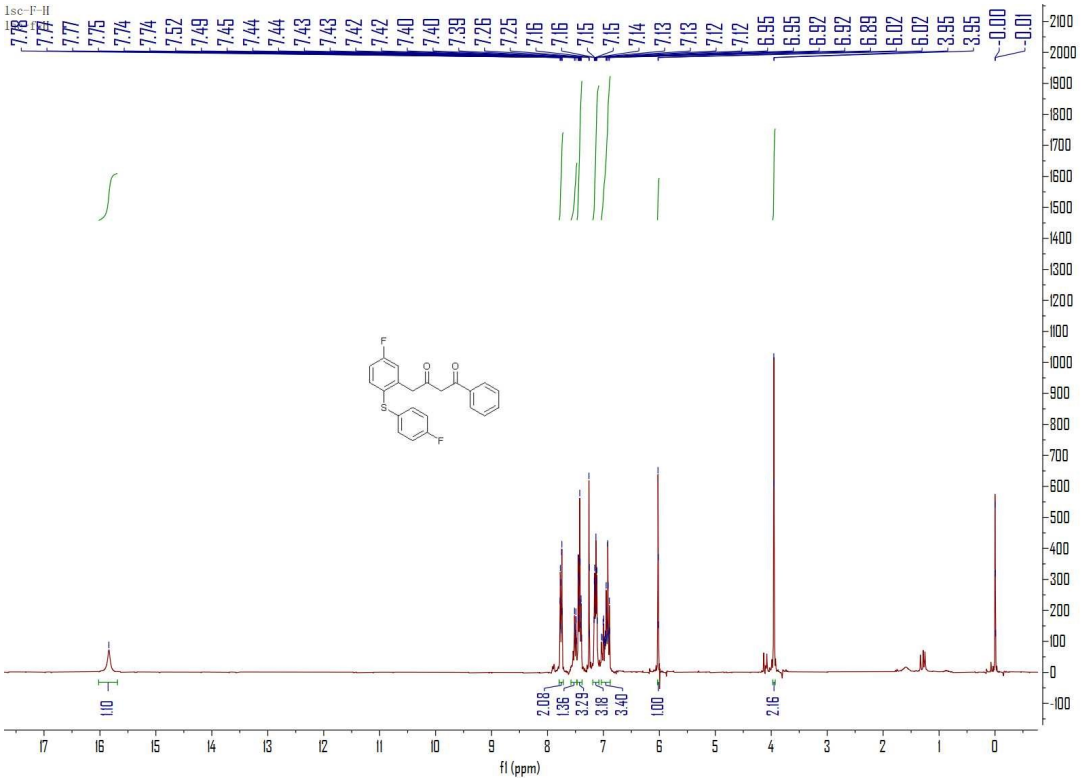


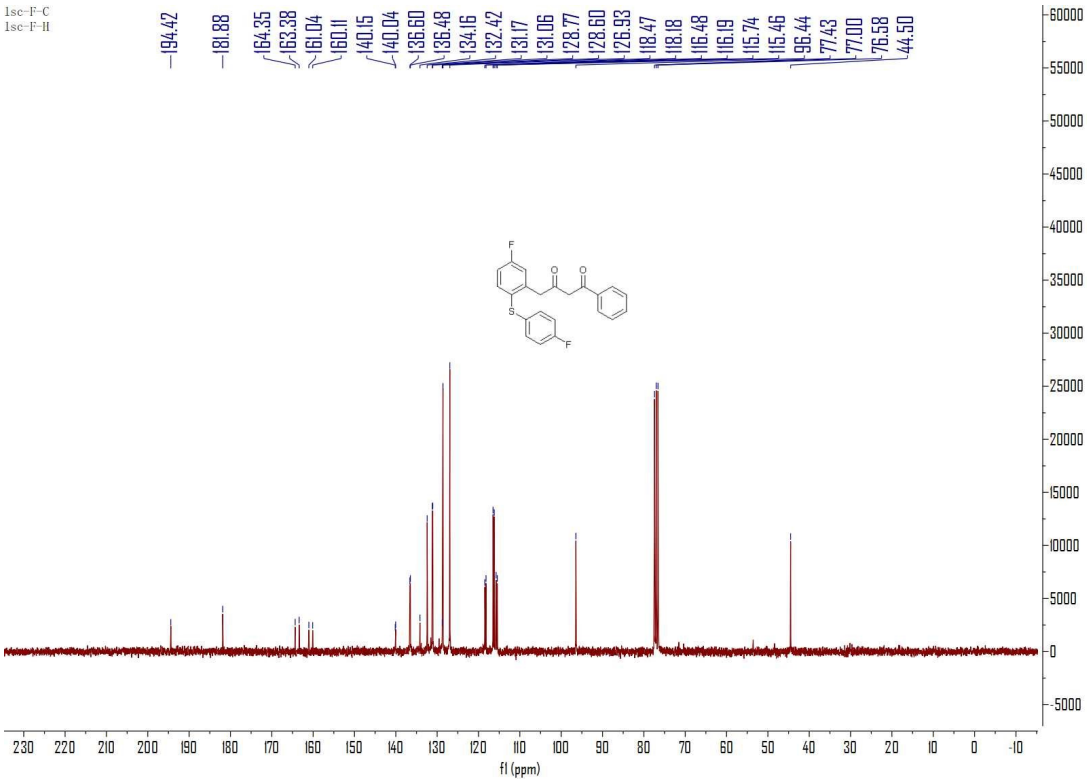
4-(5-bromo-2-((4-bromophenyl)thio)phenyl)-1-phenylbutane-1,3-dione (**3d'**)



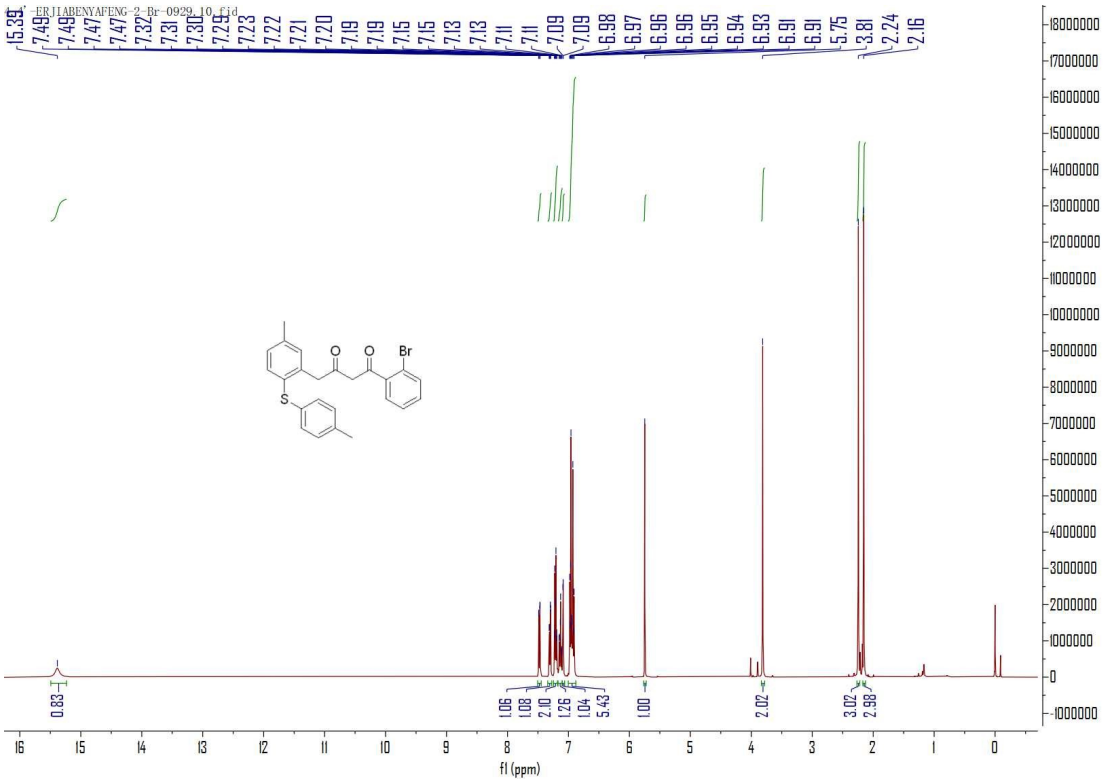


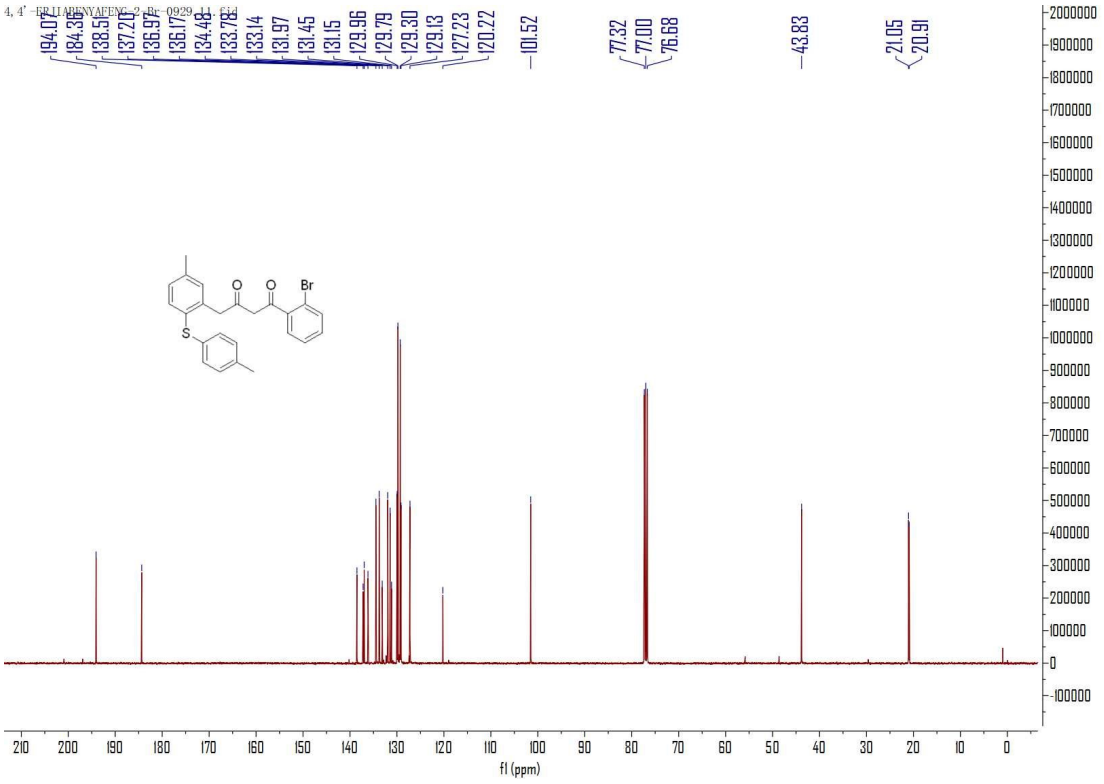
4-(5-fluoro-2-((4-fluorophenyl)thio)phenyl)-1-phenylbutane-1,3-dione (**3e'**)



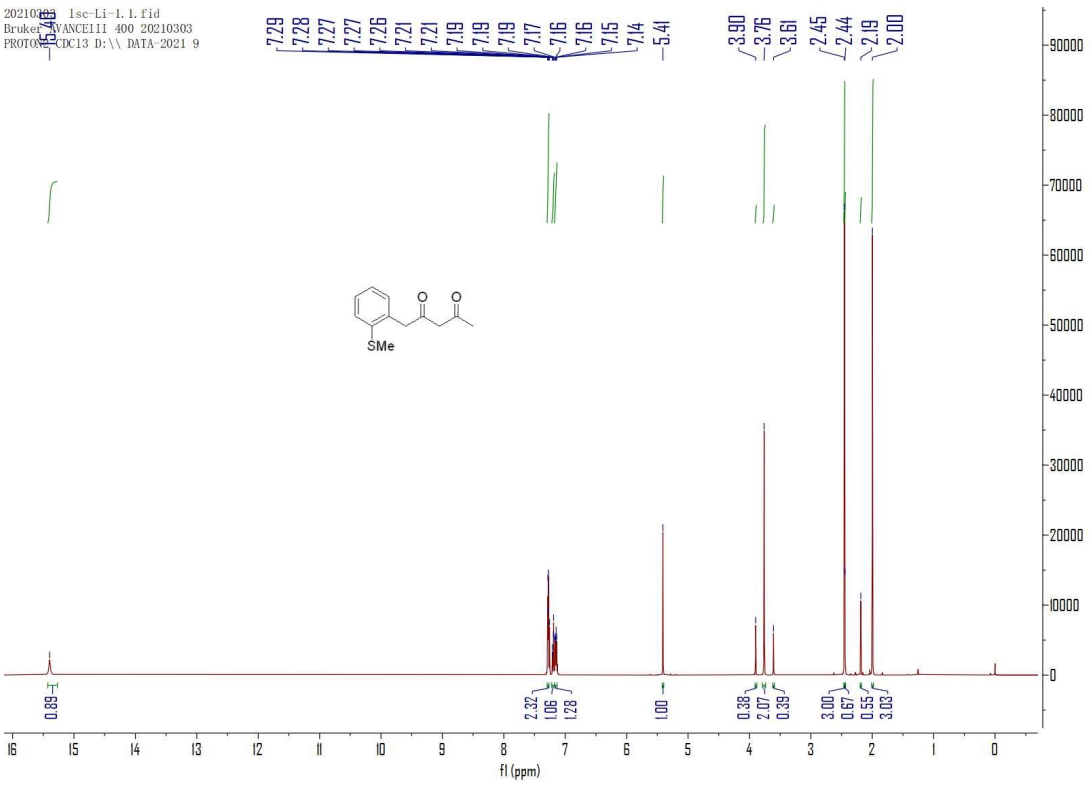


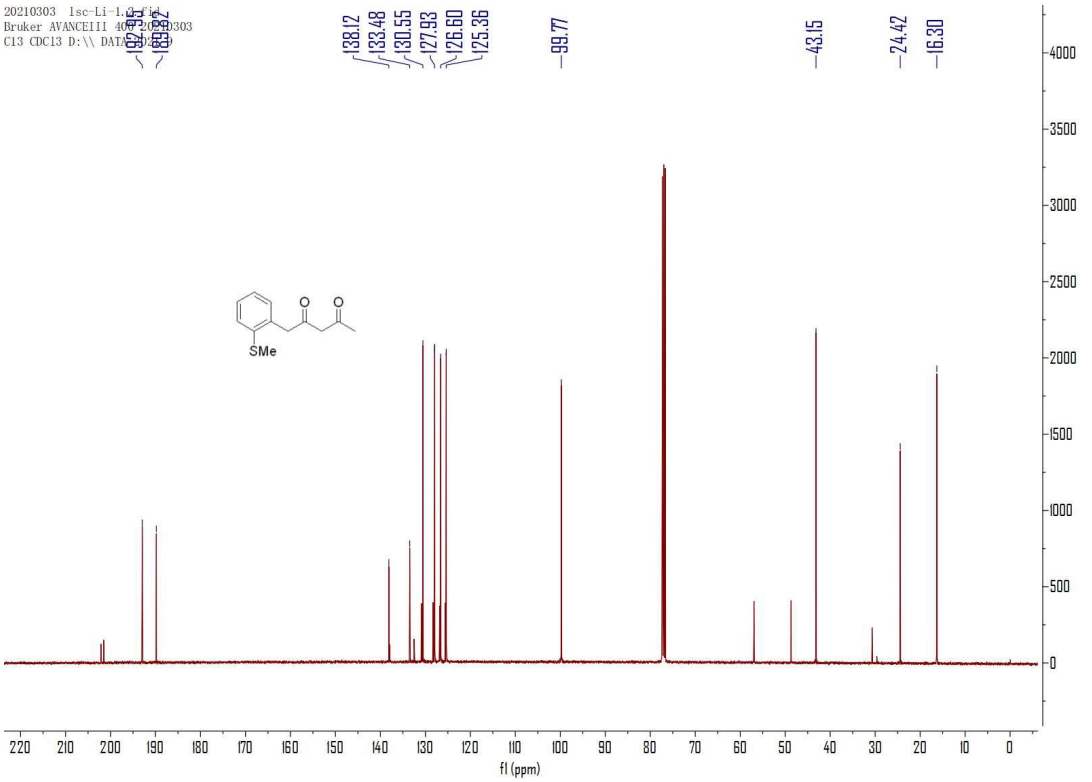
1-(2-bromophenyl)-4-(5-methyl-2-(*p*-tolylthio)phenyl)butane-1,3-dione (**3f'**)



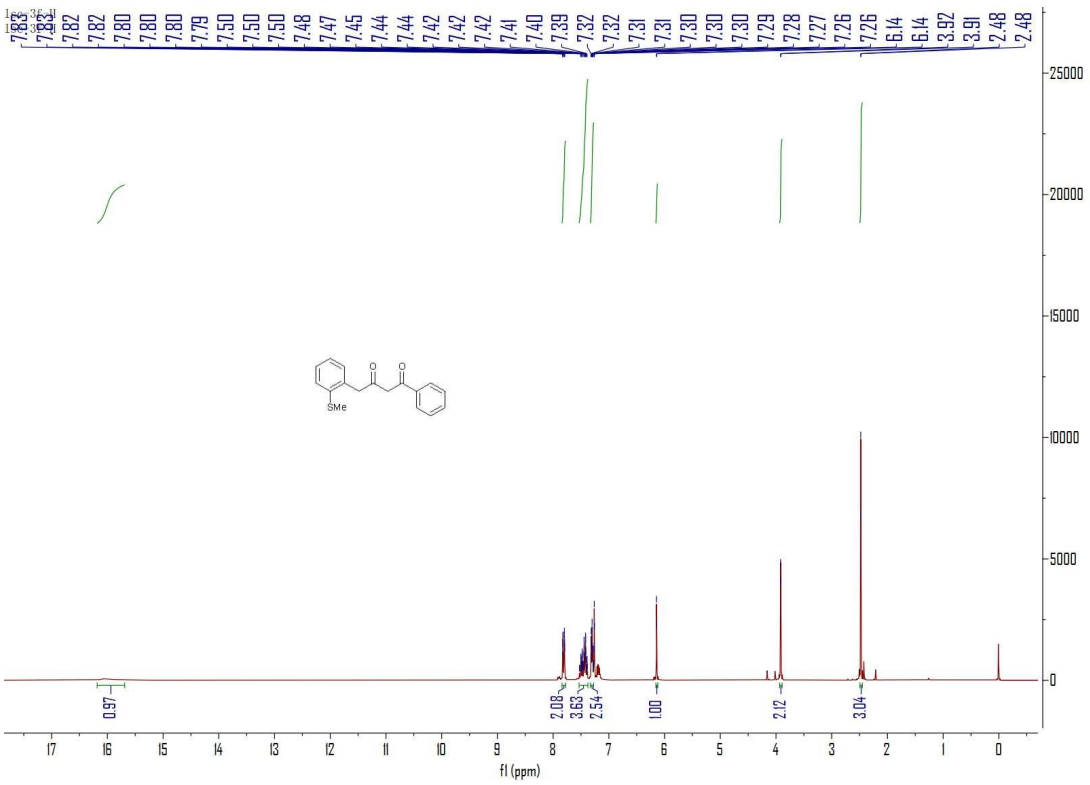


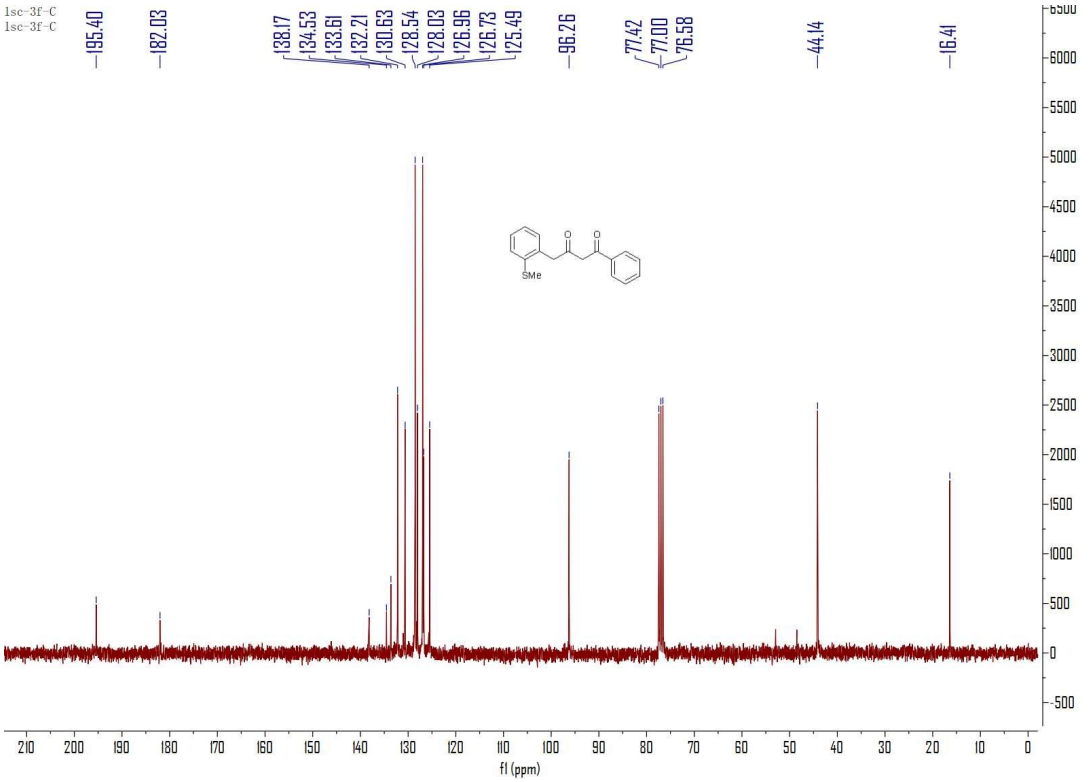
1-(2-(methylthio)phenyl)pentane-2,4-dione (**3g'**)



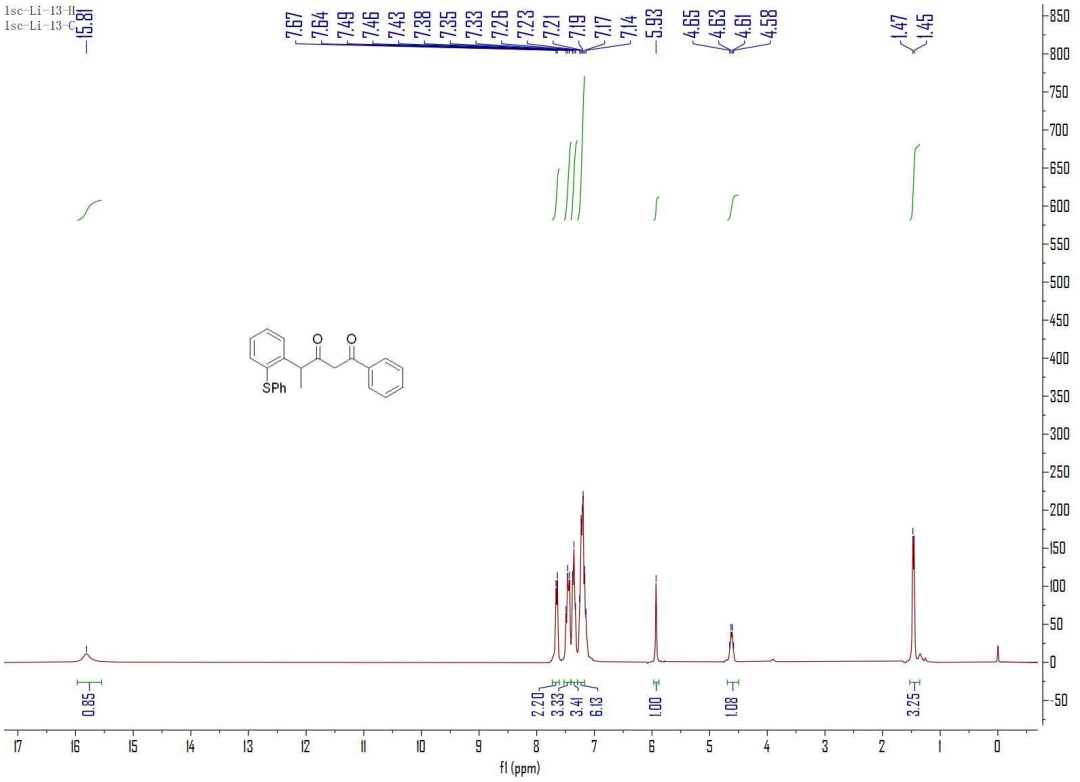


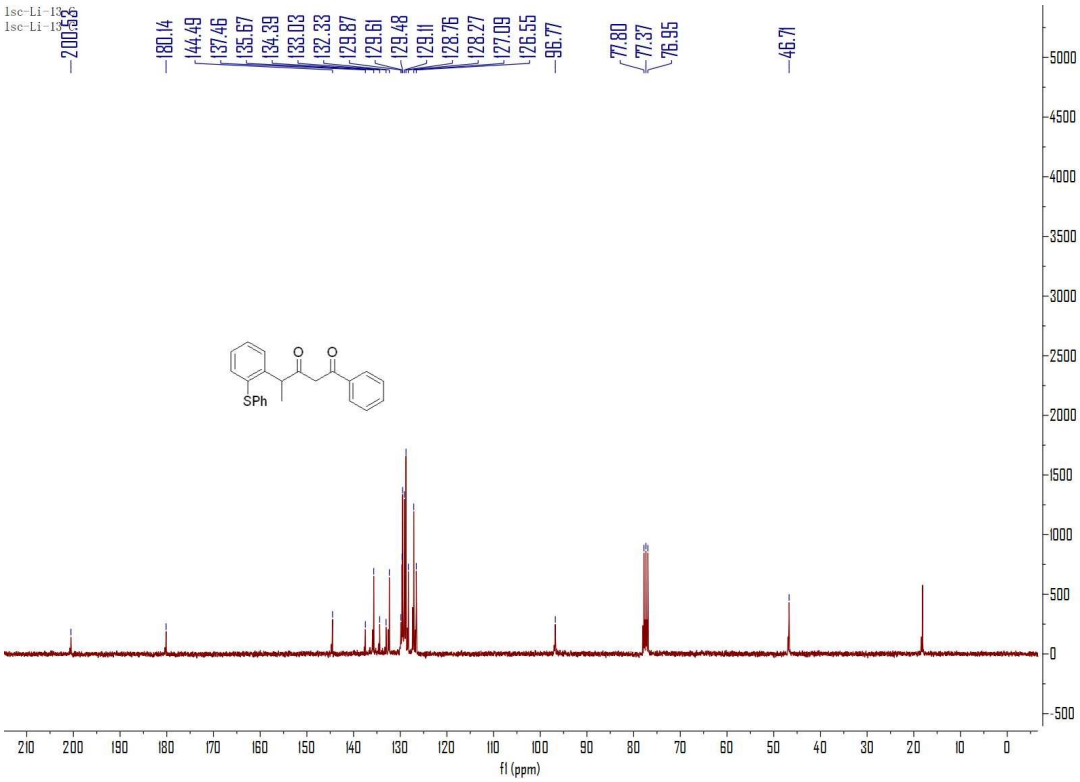
4-(2-(methylthio)phenyl)-1-phenylbutane-1,3-dione (**3h'**)



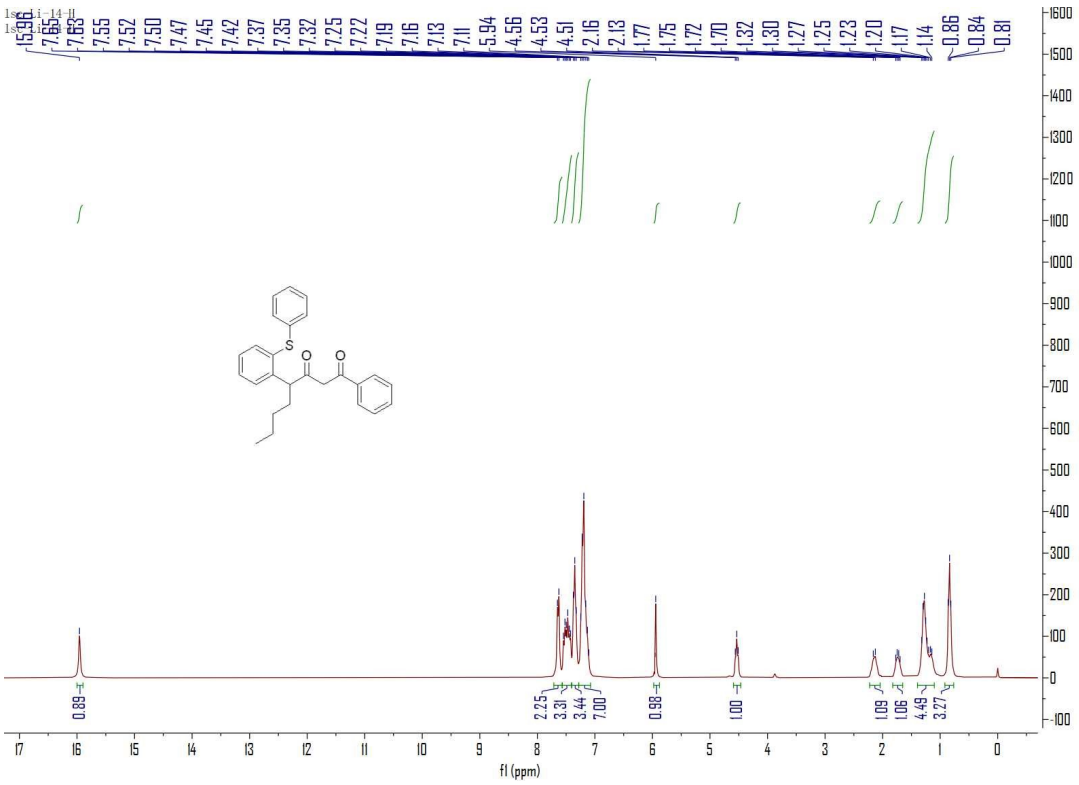


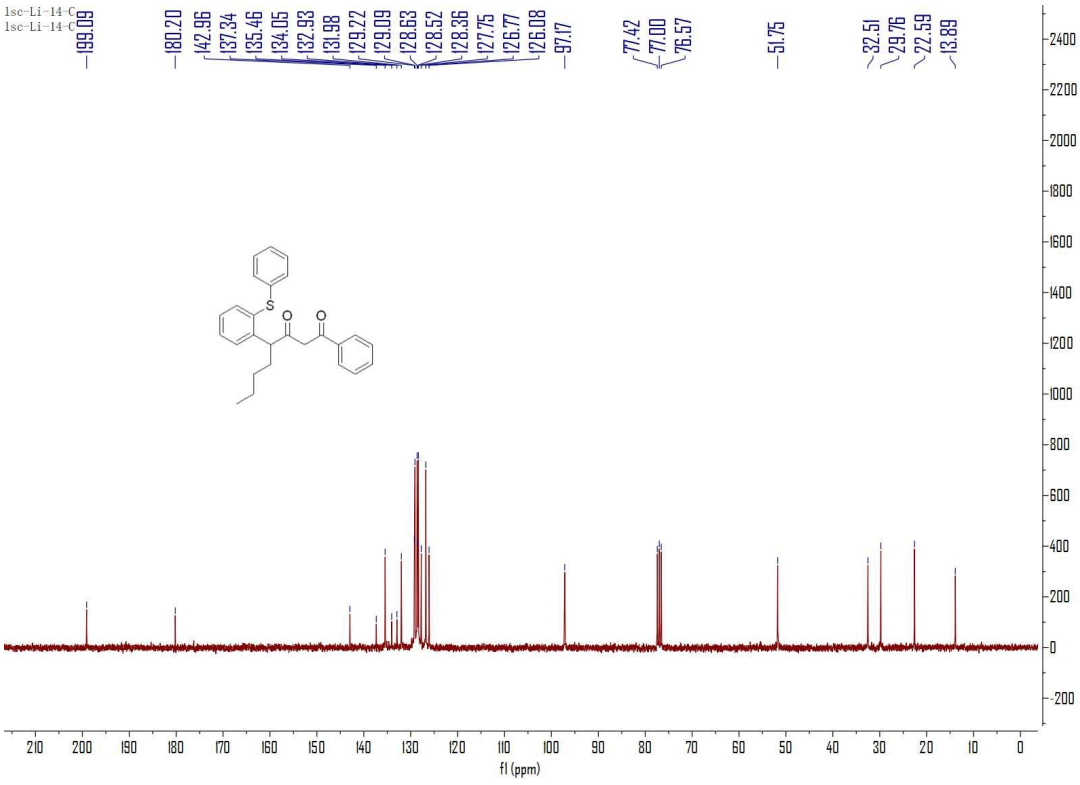
1-phenyl-4-(2-(phenylthio)phenyl)pentane-1,3-dione (**3i'**)



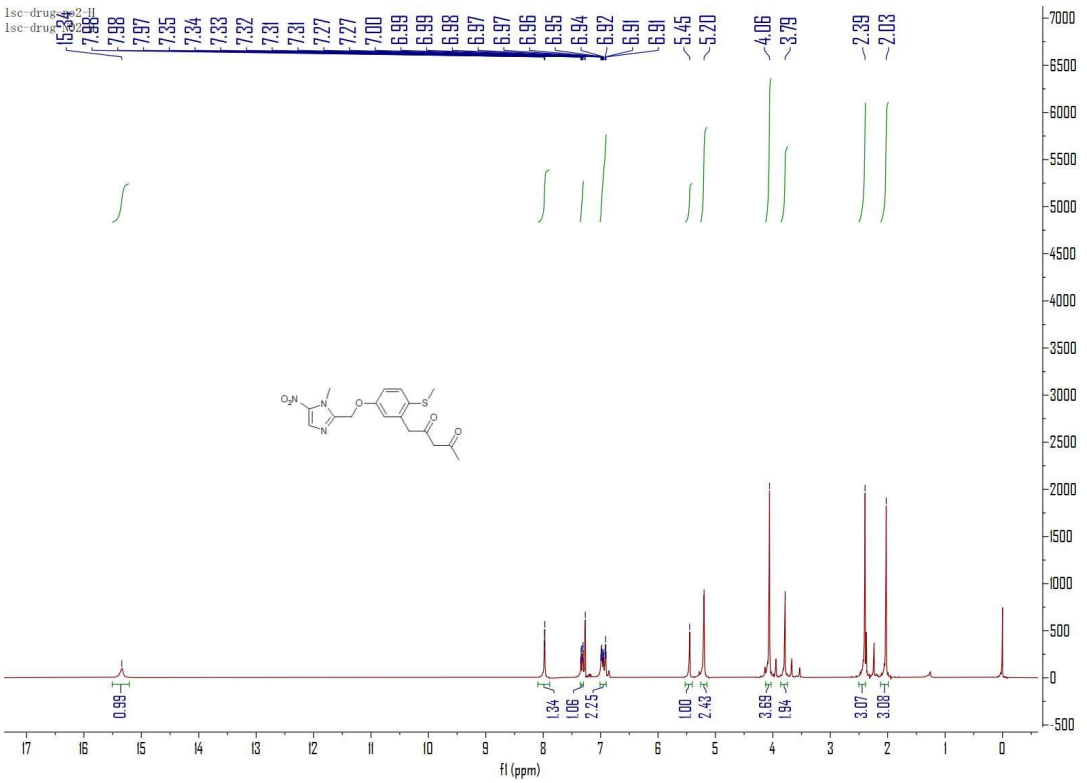


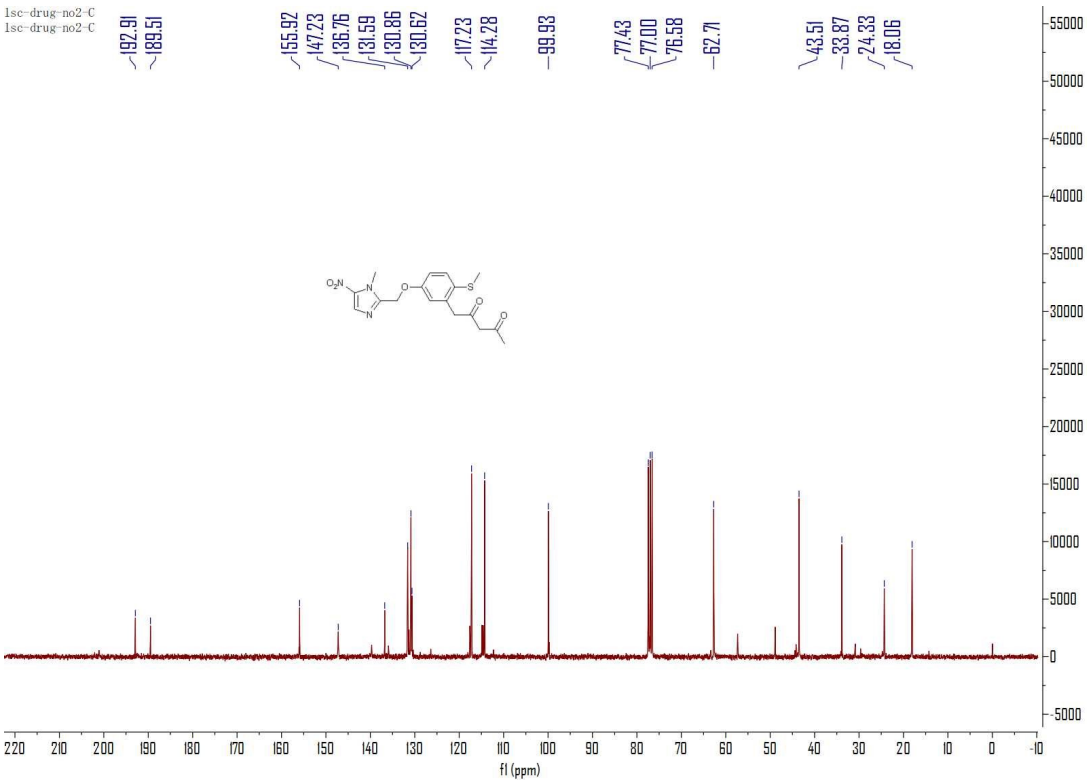
1-phenyl-4-(2-(phenylthio)phenyl)octane-1,3-dione (**3j'**)



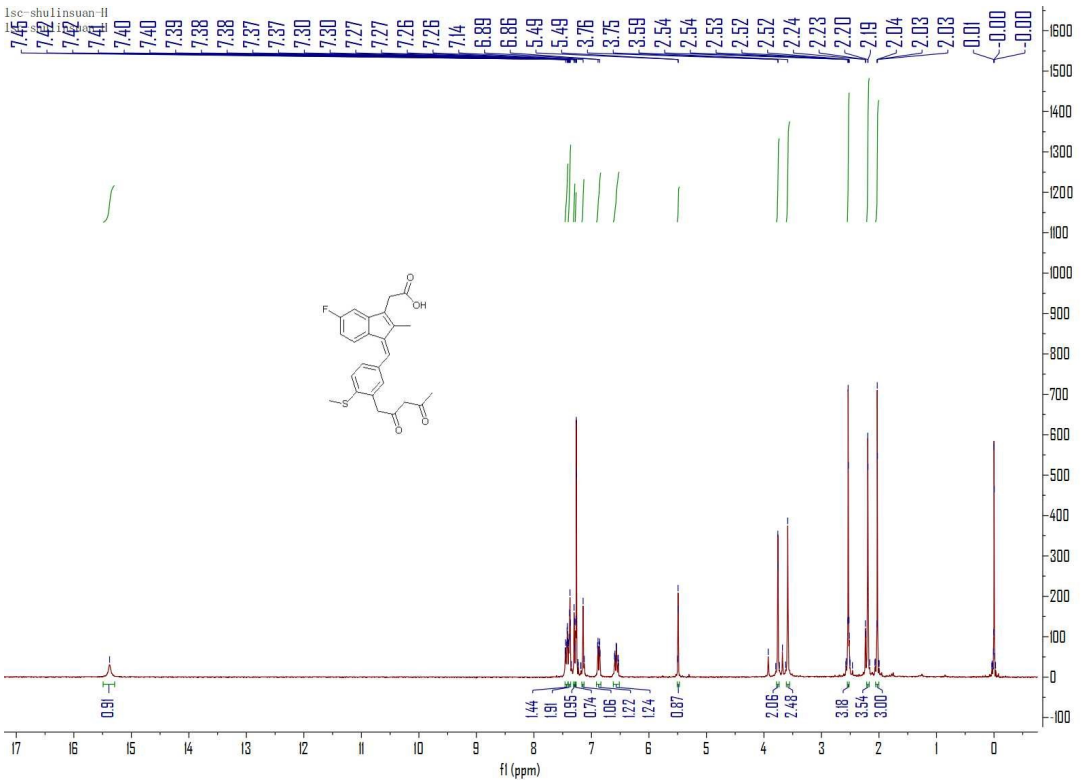


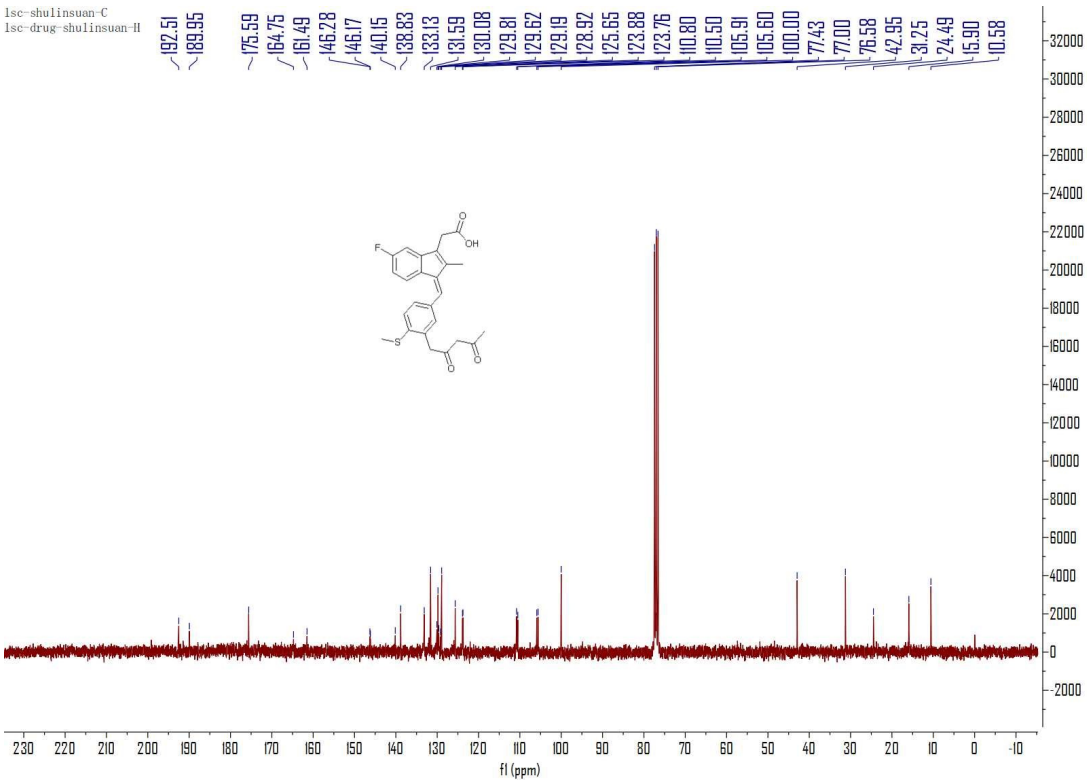
1-(5-((1-methyl-5-nitro-1*H*-imidazol-2-yl)methoxy)-2-(methylthio)phenyl)pentane-2,4-dione (**3k'**)



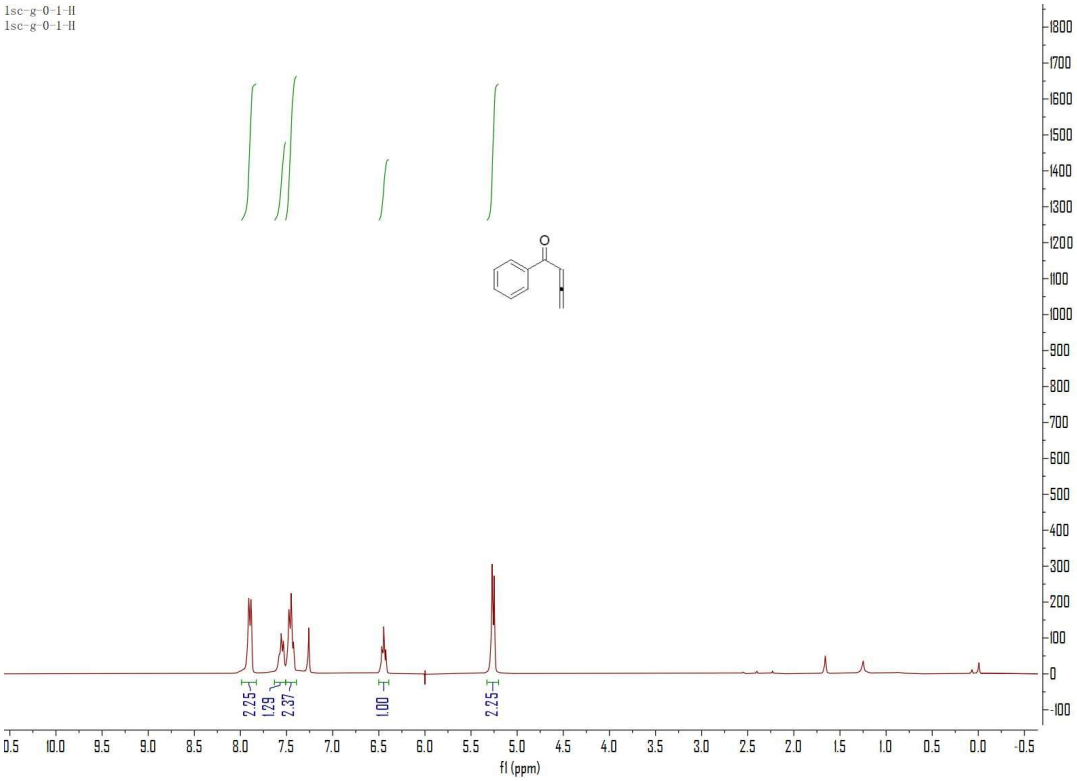


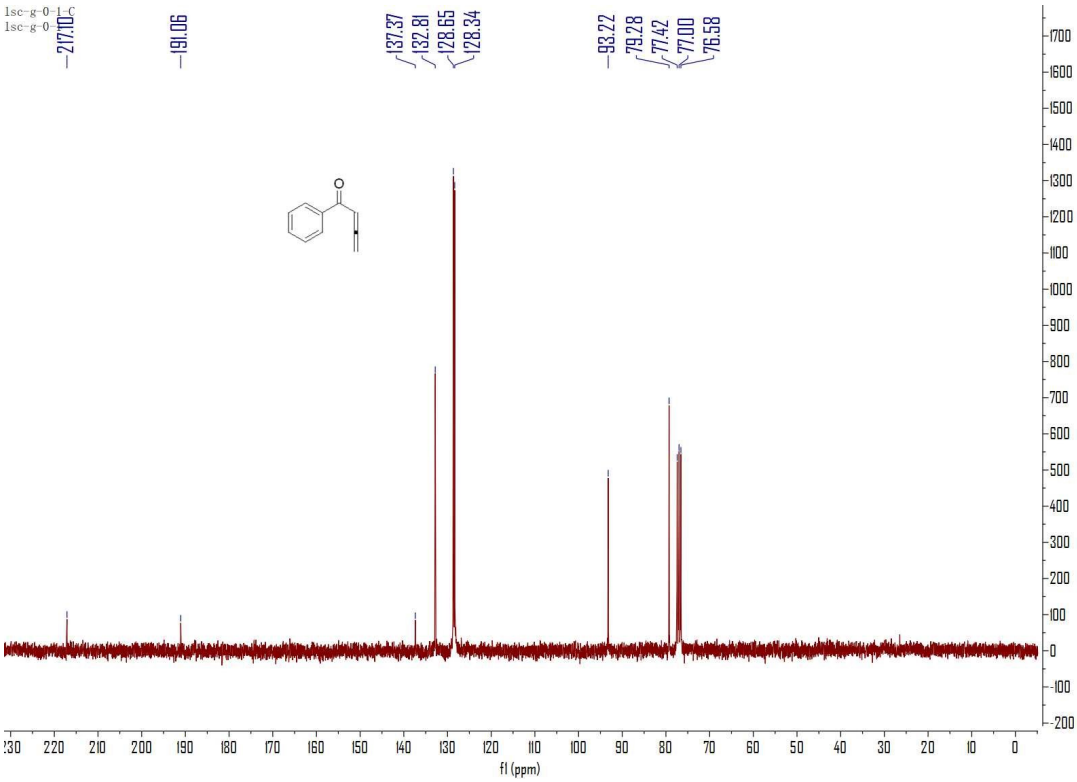
(Z)-2-(1-(3-(2,4-dioxopentyl)-4-(methylthio)benzylidene)-5-fluoro-2-methyl-1*H*-inden-3-yl)acetic acid (**3l'**)



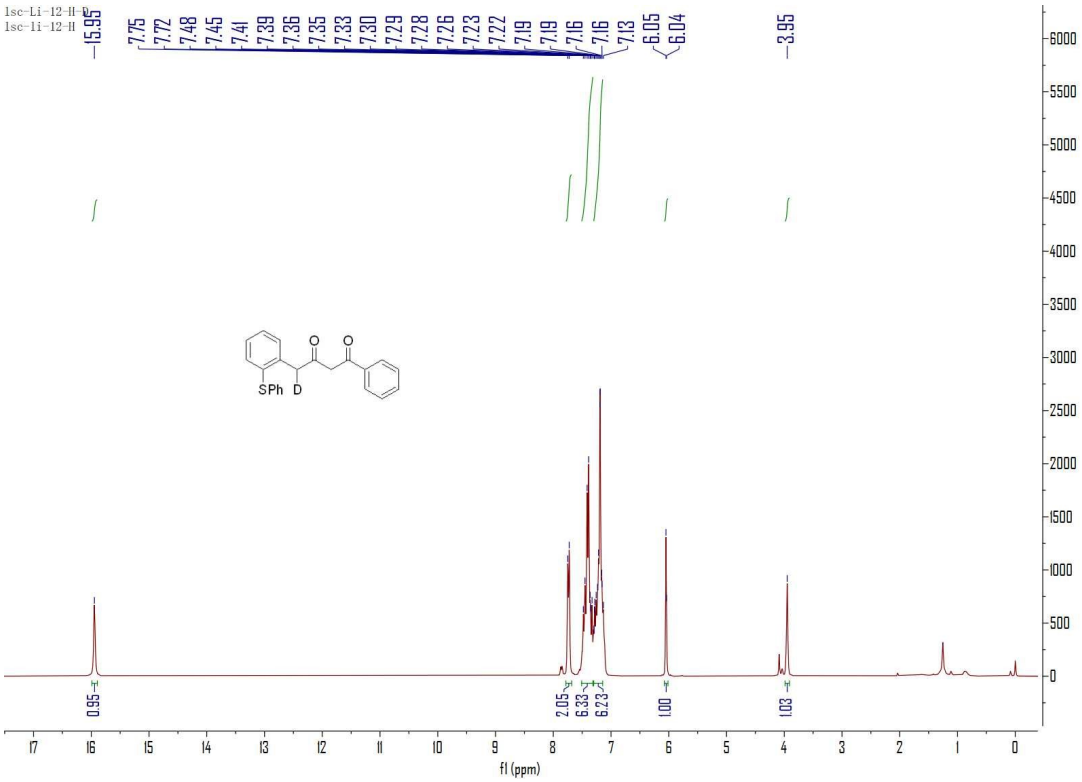


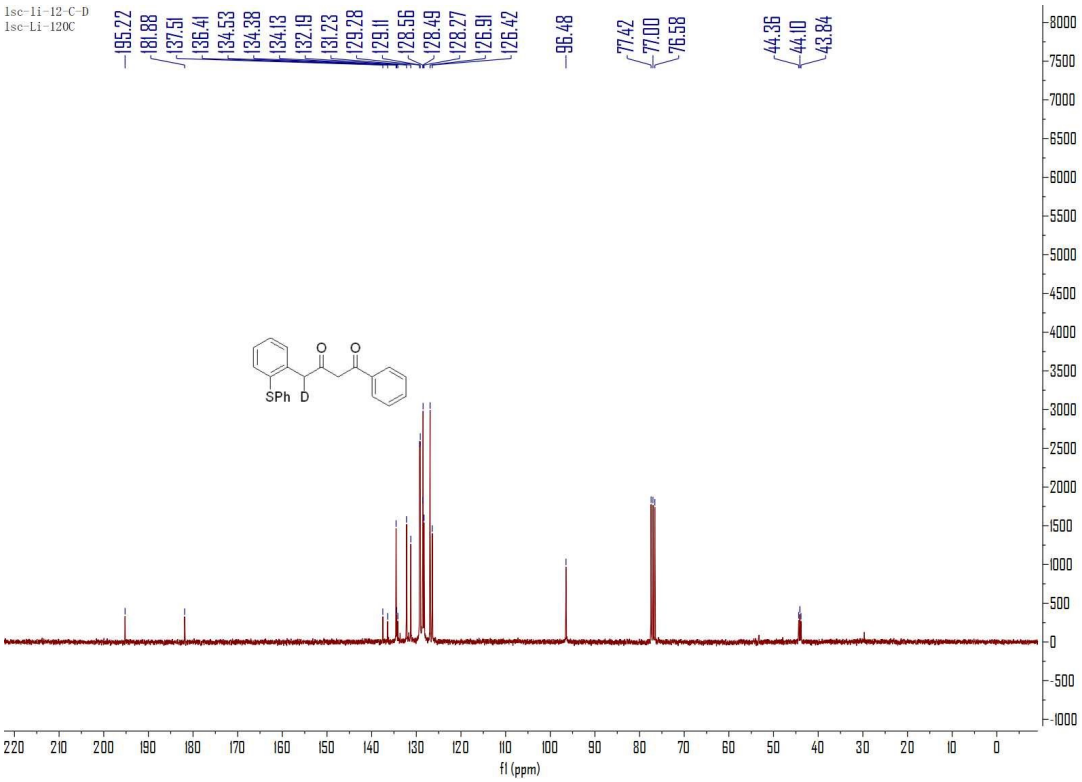
conjugated allenone **4**



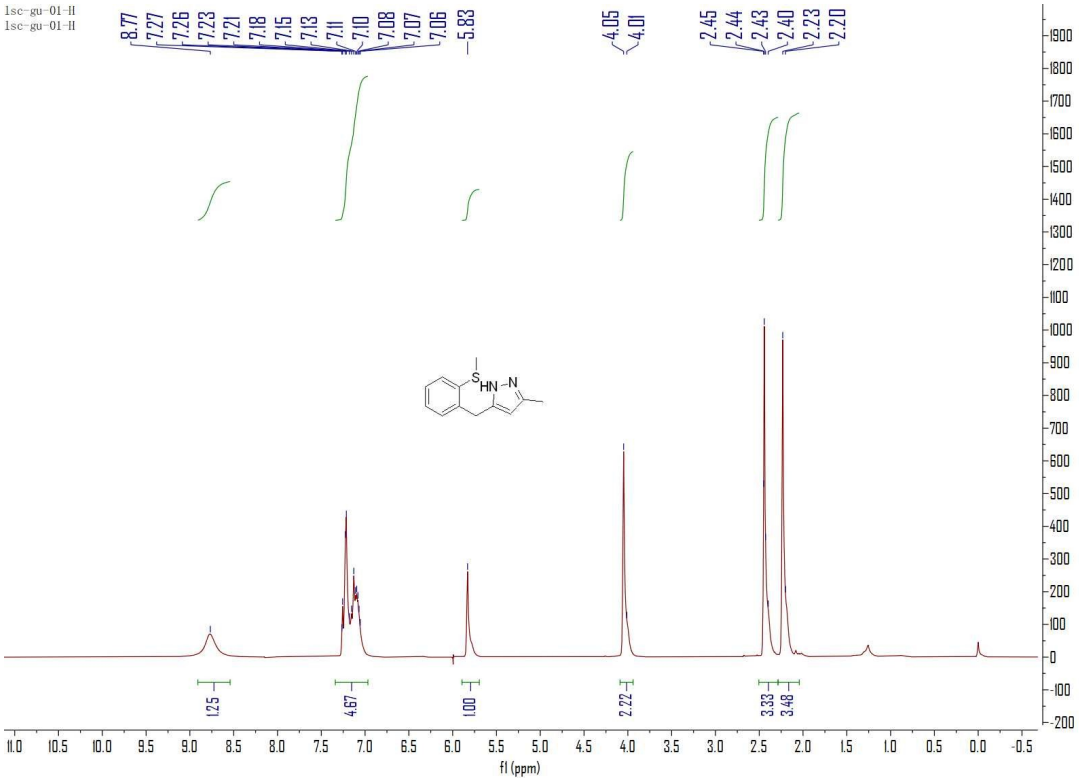


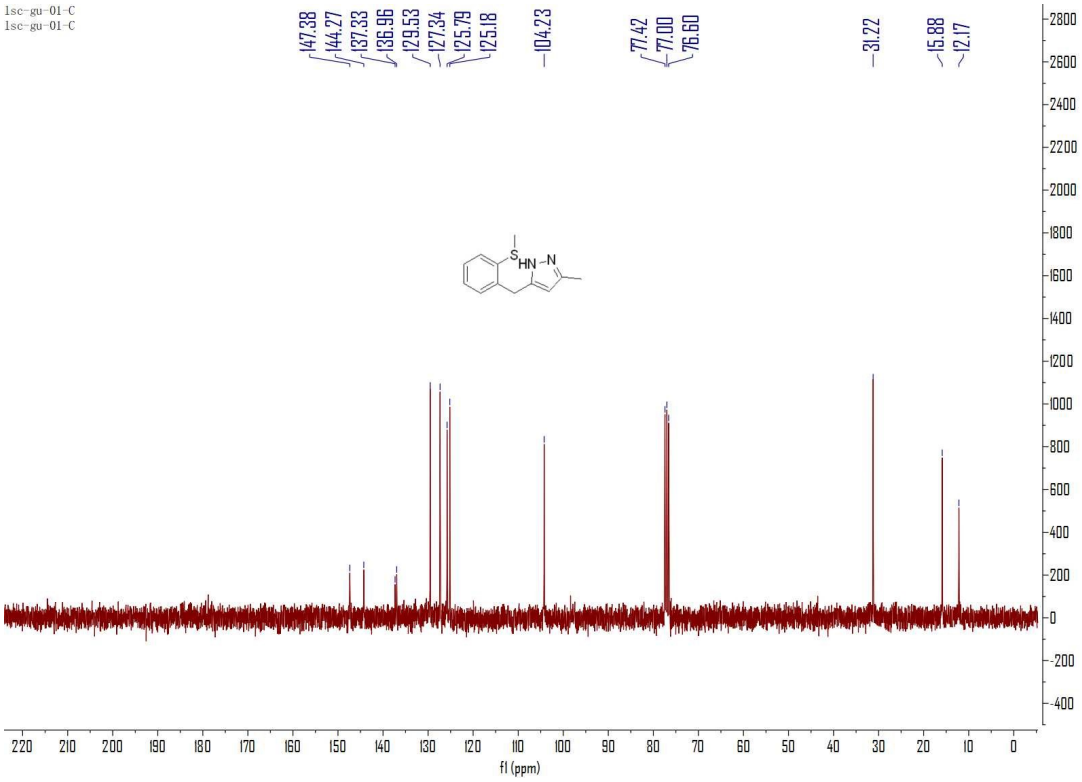
1-phenyl-4-(2-(phenylthio)phenyl)butane-1,3-dione-4-*d* (**6**)



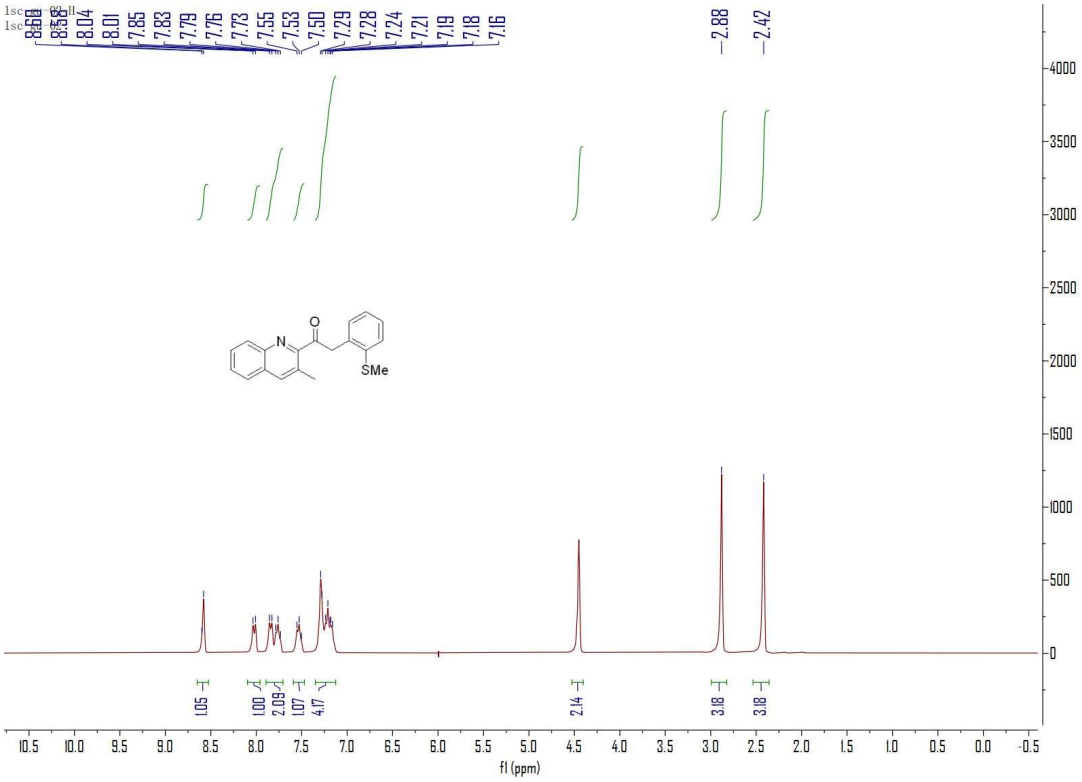


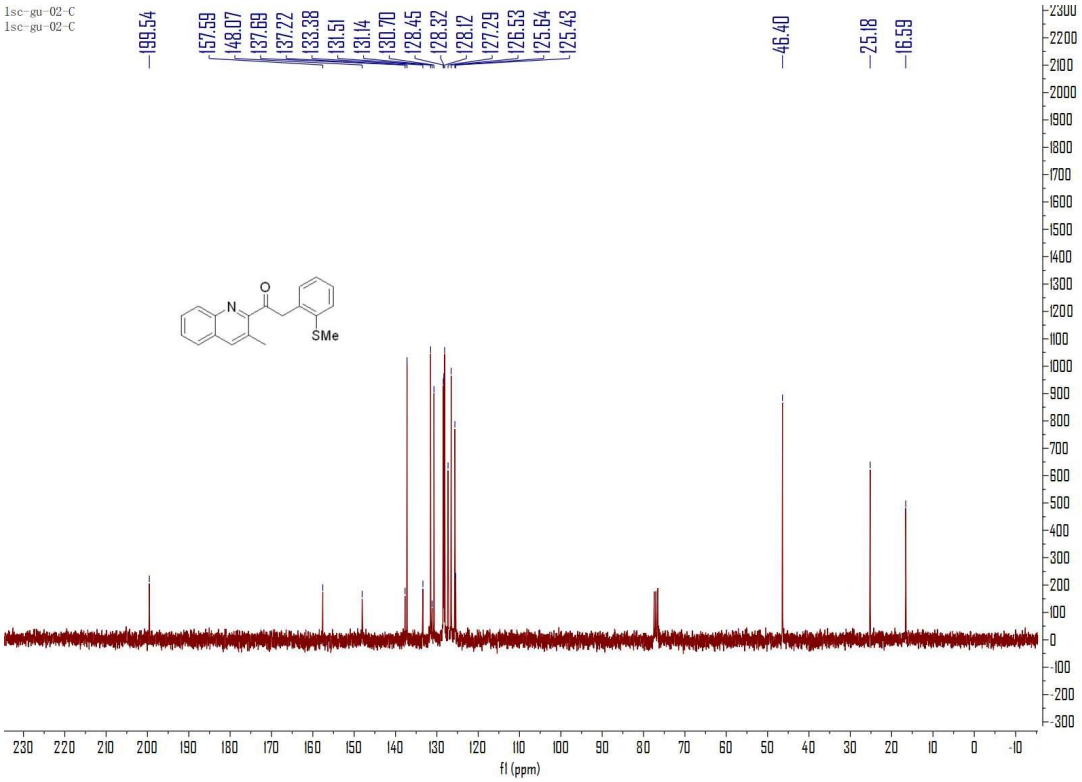
3-methyl-5-(2-(methylthio)benzyl)-1*H*-pyrazole (**7**)





1-(3-methylquinolin-2-yl)-2-(2-(methylthio)phenyl)ethan-1-one (**8**)





4-methyl-6-(2-(methylthio)benzyl)pyrimidine-2(1*H*)-thione (**9**)