Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Asymmetric synthesis of highly functionlized furanones via direct Michael reactions promoted by a bulky primary amine

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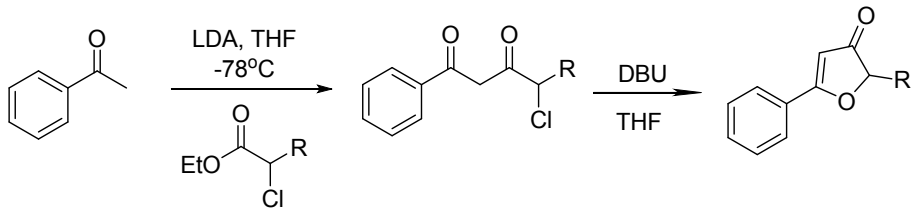
A: General Information and Starting Materials

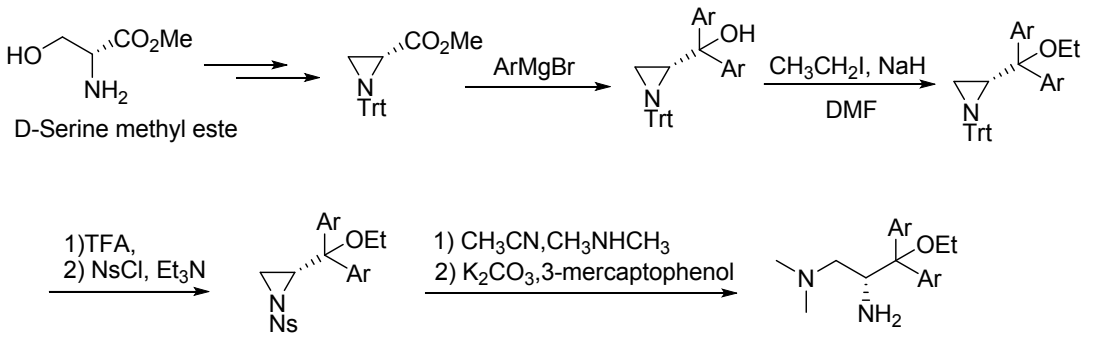
General Information. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AV-400 spectrometer (400 MHz and 100 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26) Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). High resolution mass spectra (EI) were measured on a Waters Micromass GCT spectrometer. High resolution mass spectrometry (ESI) were carried out using a Waters Quatro Macro triple quadrupole mass spectrometer. Optical rotations were measured on an Autopol III automatic polarimeter (Rudolph Research analytical). Melting points were measured on a XT3A apparatus. High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using chiral columns (DAICEL CHIRALPAK IA) as noted.

Starting Materials. All solvents and inorganic reagents were from commercial sources(Adamas-beta®) and used without purification unless otherwise noted. The pronucleophiles 3(2*H*)-furanones were synthesized following the literature procedure.[1]

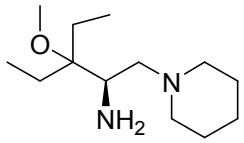


B: Preparation of chiral catalysts

Catalyst **1a** are known compound.[2]
Catalysts **1b**-**1e** were synthesized following the reported procedure.[3]

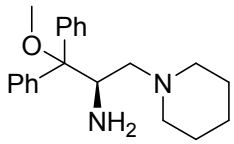


1b: (*R*)-3-ethyl-3-methoxy-1-(piperidin-1-yl)pentan-2-amine



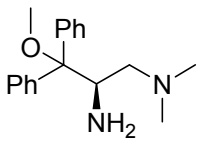
Pale yellow oil; ^{1}H NMR (400MHz, $CDCl_3$): δ 3.24 (s, 3H), 3.06 (dd, *J* = 4.0, 9.2 Hz, 1H), 2.97 (s, 1H), 2.90 (s, 1H), 2.52 (br, 1H), 2.30-2.28 (m, 3H), 1.91 (brs, 3H), 1.66-1.56 (m, 7H), 1.44-1.43 (m, 2H), 0.91 (dt, *J* = 1.6, 7.6 Hz, 6H); ^{13}C NMR (100MHz, $CDCl_3$): δ 79.4, 61.4, 52.3, 49.7, 26.2, 25.2, 24.7, 24.5, 8.6, 8.3. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{13}H_{28}N_2O$) requires m/z 228.2202, found m/z 228.2206.

1c: (*R*)-1-methoxy-1, 1-diphenyl-3-(piperidin-1-yl) propan-2-amine



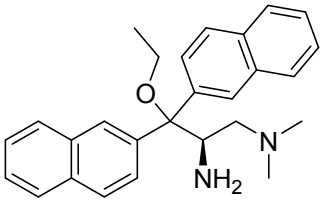
Pale yellow oil; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.47-7.44 (m, 4H), 7.38-7.29 (m, 6H), 4.03 (dd, *J* = 1.6, 10.4 Hz, 1H), 2.99 (s, 3H), 2.56 (dd, *J* = 1.6, 12.4 Hz, 1H), 2.24 (br, 2H), 1.65 (dd, *J* = 10.4, 12.4 Hz, 1H), 1.61-1.49 (m, 6H), 1.45-1.40 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ140.9, 140.3, 129.5, 129.3, 127.6, 127.4, 127.2, 85.4, 62.2, 55.4, 52.3, 51.3, 26.2, 24.5; HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{21}H_{29}N_2O$) requires m/z 325.2280, found m/z 325.2274.

1d: (*R*)-3-methoxy-N^1,N^1-dimethyl-3,3-diphenylpropane-1,2-diamine



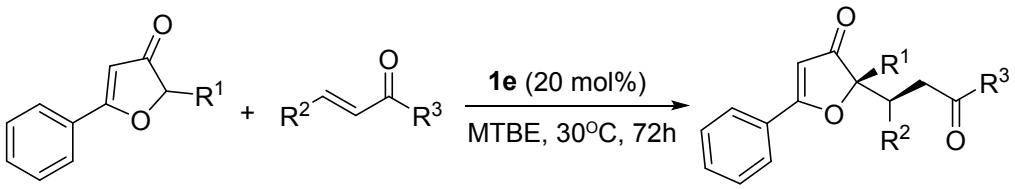
Pale yellow oil; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.45-7.43 (m, 4H), 7.39-7.31 (m, 6H), 3.96 (dd, *J* = 2.0, 10.4 Hz, 1H), 2.97 (s, 3H), 2.48 (dd, *J* = 2.0, 10.4 Hz, 1H), 2.25 (s, 6H), 1.66 (dd, *J* = 10.4, 12.4 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ140.5, 140.1, 129.4, 129.2, 127.7, 127.5, 127.4, 127.3, 85.7, 62.7, 53.3, 51.4, 46.2; HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{18}H_{25}N_2O$) requires m/z 285.1967, found m/z 285.1961.

1e: (*R*)-3-ethoxy-N^1,N^1-dimethyl-3,3-di(naphthalen-2-yl)propane-1,2-diamine



Pale yellow solid; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.11 (s, 1H), 8.02 (s, 1H), 7.88-7.80 (m, 6H), 7.59-7.46 (m, 6H), 4.19-4.15 (m, 1H), 3.23-3.18 (m, 2H), 2.65 (d, *J* = 12.4 Hz, 1H), 2.29 (s, 6H), 1.80 (t, *J* = 11.2 Hz, 1H), 1.20 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 138.8, 138.5, 132.8, 132.7, 132.6, 128.6, 128.5, 128.4, 128.0, 127.5, 127.4, 127.3, 127.1, 126.3, 126.2, 126.1, 126.0, 85.4, 63.0, 59.0, 53.5, 46.3, 15.7; HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{31}N_2O$) requires m/z 399.2436, found m/z 399.2441.

C: General Procedure for Asymmetric Conjugated Addition

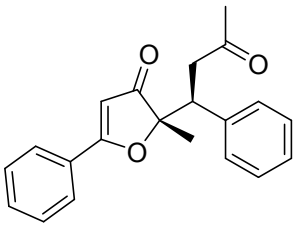


2 **3** **4**

3(2*H*)-furanones **2** (0.20 mmol, 1.0 equiv.) was added to a mixture of catalyst **1e** (0.04 mmol, 0.20 equiv.) and α,β-unsaturated ketones **3** (0.30 mmol, 1.5 equiv.) in MTBE (0.8 mL) at 30℃. The reaction mixture was maintained at this temperature for 3 days and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired addition product. The enantiomeric ratio was determined by HPLC analysis on chiral column.

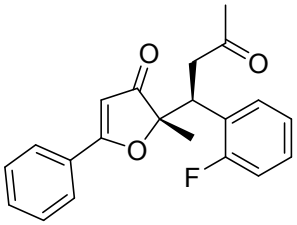
D: Characterization of Conjugated Addition Products

4a: (*S*)-2-methyl-2-((*S*)-3-oxo-1-phenylbutyl)-5-phenylfuran-3(2*H*)-one



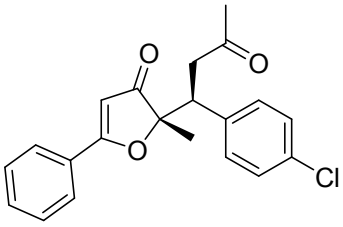
The product was obtained in 99% yield, 63.4 mg, yellow oil. $[\alpha]^{25}_{D}$ 70.3 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.76-7.74 (m, 2H), 7.58-7.54 (m, 1H), 7.50-7.46 (m, 2H), 7.24-7.21 (m, 2H), 7.18-7.14 (m, 3H), 5.72 (s, 1H), 3.80-3.76 (m, 1H), 3.23 (dd, *J* = 4.8, 16.8 Hz, 1H),3.14 (dd, *J* = 9.6, 16.8 Hz, 1H), 2.07 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.1, 205.5, 183.7, 138.1, 132.7, 129.1, 128.9, 128.8, 128.1, 127.3, 127.0, 100.3, 91.6, 45.7, 43.5, 30.3, 20.1; HRMS (EI): exact mass calculated for M^+ ($C_{21}H_{20}O_3$) requires m/z 320.1412, found m/z 320.1414; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 7.7 min (major), 12.6 min (minor), ee 93%.

4b:(*S*)-2-((*S*)-1-(2-fluorophenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



The product was obtained in 98% yield, 66.3 mg, yellow oil. $[\alpha]^{25}_{D}$ 43.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78-7.76 (m, 2H), 7.57-7.53 (m, 1H), 7.49-7.45 (m, 2H), 7.30-7.25 (m, 1H), 7.18-7.13 (m, 1H), 7.00-6.95 (m, 2H), 5.83 (s, 1H), 4.18-4.14 (m, 1H), 3.28 (dd, *J* = 4.8, 17.2 Hz, 1H), 3.11 (dd, *J* = 9.6, 17.6 Hz, 1H), 2.08 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.6, 205.2, 183.8, 162.3, 159.8, 132.8, 130.2, 130.1, 129.0, 128.9, 128.7, 127.1, 125.5, 125.4, 123.8, 123.7, 115.7, 115.5, 99.9, 91.0, 42.6, 38.5, 30.1, 19.7; HRMS (EI): exact mass calculated for M^+ ($C_{21}H_{19}FO_3$) requires m/z 338.1318, found m/z 338.1320; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 8.4 min (major), 17.1 min (minor), ee 85%.

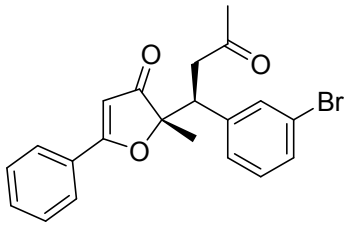
4c: (*S*)-2-((*S*)-1-(4-chlorophenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



The product was obtained in 94% yield, 66.5 mg, white solid. Mp 97-98°C; $[\alpha]^{25}_{D}$ 99.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.76-7.74 (m, 2H), 7.60-7.56 (m, 1H), 7.51-7.48 (m, 2H), 7.17-7.11 (m, 4H), 5.73 (s, 1H), 3.77-3.73 (m, 1H), 3.20 (dd, *J* = 4.8, 16.8 Hz, 1H), 3.10 (dd, *J* = 9.6, 16.8 Hz, 1H), 2.09 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.7, 205.3, 183.7, 136.7, 133.1, 132.9, 130.3, 129.0, 128.6, 128.3, 127.0, 100.4, 91.3, 45.0, 43.3, 30.4, 20.2; HRMS (EI): exact mass calculated for M^+ ($C_{21}H_{19}ClO_3$) requires m/z 354.1023, found m/z 354.1028; The enantiomeric excess

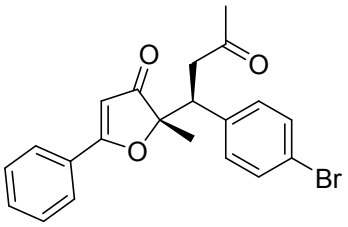
was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 8.7 min (major), 14.2 min (minor), ee 90%.

4d: (*S*)-2-((*S*)-1-(3-bromophenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



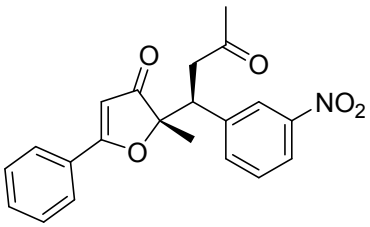
The product was obtained in 98% yield, 78.1 mg, yellow oil. $[\alpha]^{25}_{D}$ 69.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.76-7.74 (m, 2H), 7.58-7.54 (m, 1H), 7.50-7.47 (m, 2H), 7.38-7.37 (m, 1H), 7.28-7.25 (m, 1H), 7.17-7.15 (m, 1H), 7.05-7.01 (m, 1H), 5.73 (s, 1H), 3.76-3.72 (m, 1H), 3.23 (dd, *J* = 4.8, 17.2 Hz, 1H), 3.08 (dd, *J* = 9.6, 17.2 Hz, 1H), 2.10 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.5, 205.1, 183.8, 140.6, 132.8, 131.9, 130.4, 129.6, 129.0, 128.5, 128.0, 127.1, 100.3, 91.1, 45.2, 43.2, 30.4, 19.9; HRMS (EI): exact mass calculated for M^+ ($C_{21}H_{19}BrO_3$) requires m/z 398.0518, found m/z 398.0523; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 8.0 min (major), 10.1 min (minor), ee 90%.

4e: (*S*)-2-((*S*)-1-(4-bromophenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



The product was obtained in 98% yield, 78.1 mg, white solid. Mp 103-104°C; $[\alpha]^{25}_{D}$ 103.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.76-7.74 (m, 2H), 7.58-7.55 (m, 1H), 7.50-7.46 (m, 2H), 7.28-7.26 (m, 2H), 7.11-7.08 (m, 2H), 5.73 (s, 1H), 3.75-3.72 (m, 1H), 3.20 (dd, *J* = 4.8, 17.2 Hz, 1H), 3.09 (dd, *J* = 9.6, 17.2 Hz, 1H), 2.08 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.7, 205.2, 183.7, 137.3, 132.9, 131.2, 130.7, 129.0, 128.6, 127.0, 121.3, 100.4, 91.2, 45.0, 43.3, 30.4, 20.2; HRMS (EI): exact mass calculated for M^+ ($C_{21}H_{19}BrO_3$) requires m/z 398.0518, found m/z 398.0520; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 9.5 min (major), 15.0 min (minor), ee 92%.

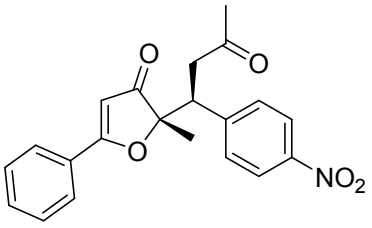
4f: (*S*)-2-methyl-2-((*S*)-1-(3-nitrophenyl)-3-oxobutyl)-5-phenylfuran-3(2*H*)-one



The product was obtained in 97% yield, 70.8 mg, gray solid. Mp 128-129°C; $[\alpha]^{25}_{D}$ 62.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12-8.11 (m, 1H), 8.03-8.00 (m, 1H), 7.77-7.74 (m, 2H), 7.60-7.56 (m, 2H), 7.52-7.48 (m, 2H), 7.40-7.36 (m, 1H), 5.72 (s, 1H), 3.93-3.89 (m, 1H), 3.33 (dd, *J* = 4.4, 18.0 Hz, 1H), 3.21 (dd, *J* = 9.6, 17.6 Hz, 1H), 2.15 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.1, 204.8, 184.0, 140.5, 136.2, 133.1, 129.0, 128.2, 127.0, 123.1, 123.1, 122.4, 100.3, 90.9, 44.9, 43.0, 30.5, 20.1; HRMS (EI):

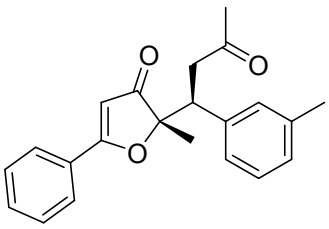
exact mass calculated for M^+ ($C_{21}H_{19}NO_5$) requires m/z 365.1263, found m/z 365.1265; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 13.2 min (major), 16.0 min (minor), ee 90%.

4g: (*S*)-2-methyl-2-((*S*)-1-(4-nitrophenyl)-3-oxobutyl)-5-phenylfuran-3(2*H*)-one



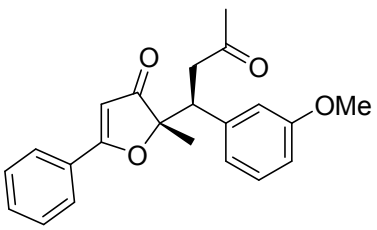
The product was obtained in 97% yield, 70.7 mg, yellow solid. Mp 135-136°C; $[\alpha]^{25}_D$ 106.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.00-7.98 (m, 2H), 7.75-7.73 (m, 2H), 7.59-7.56 (m, 1H), 7.51-7.47 (m, 2H), 7.41-7.39 (m, 2H), 5.72 (s, 1H), 3.90-3.87 (m, 1H), 3.30 (dd, *J* = 4.4, 17.6 Hz, 1H), 3.19 (dd, *J* = 9.6, 17.6 Hz, 1H), 2.12 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.1, 204.7, 183.9, 147.1, 146.1, 133.1, 130.0, 129.1, 128.3, 127.0, 123.2, 100.3, 91.0, 45.2, 43.1, 30.3, 20.3; HRMS (EI): exact mass calculated for M^+ ($C_{21}H_{19}NO_5$) requires m/z 365.1263, found m/z 365.1266; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 13.1 min (major), 19.3 min (minor), ee 90%.

4h: (*S*)-2-methyl-2-((*S*)-3-oxo-1-m-tolylbutyl)-5-phenylfuran-3(2*H*)-one



The product was obtained in 78% yield, 52.1 mg, yellow oil. $[\alpha]^{25}_D$ 61.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77-7.75 (m, 2H), 7.58-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.06-7.00 (m, 3H), 6.95-6.94 (m, 1H), 5.71 (s, 1H), 3.75-3.71 (m, 1H), 3.21 (dd, *J* = 4.8, 17.2 Hz, 1H), 3.12 (dd, *J* = 9.6, 16.8 Hz, 1H), 2.16 (s, 3H), 2.08 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.2, 205.6, 183.7, 137.9, 137.5, 132.6, 129.9, 128.8, 128.0, 127.9, 127.0, 126.1, 100.3, 91.6, 45.7, 43.5, 30.3, 21.3, 20.0; HRMS (EI): exact mass calculated for M^+ ($C_{22}H_{22}O_3$) requires m/z 334.1569, found m/z 334.1568; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 6.3 min (major), 8.6 min (minor), ee 89%.

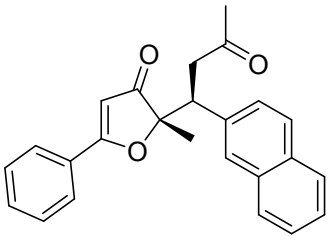
4i:(*S*)-2-((*S*)-1-(3-methoxyphenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



The product was obtained in 79% yield, 55.2 mg, yellow oil. $[\alpha]^{25}_D$ 73.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78-7.77 (m, 2H), 7.59-7.55 (m, 1H), 7.51-7.48 (m, 2H), 7.10-7.06 (m, 1H), 6.83-6.6.77 (m, 2H), 6.70-6.6.69 (m, 1H), 5.75

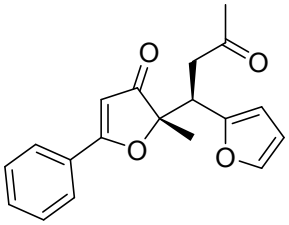
(s, 1H), 3.78-3.74 (m, 1H), 3.63 (s, 1H), 3.21 (dd, J = 4.8, 17.2 Hz, 1H), 3.12 (dd, J = 9.6, 16.8 Hz, 1H), 2.10 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.1, 205.5, 183.6, 159.2, 139.6, 132.7, 129.0, 128.9, 128.8, 127.1, 121.5, 114.4, 113.2, 100.3, 91.5, 55.0, 45.7, 43.5, 30.4, 20.1; HRMS (EI): exact mass calculated for M^+ ($C_{22}H_{22}O_4$) requires m/z 350.1518, found m/z 350.1521; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 8.4 min (major), 11.0 min (minor), ee 85%.

4j: (*S*)-2-methyl-2-((*S*)-1-(naphthalen-2-yl)-3-oxobutyl)-5-phenylfuran-3(2*H*)-one

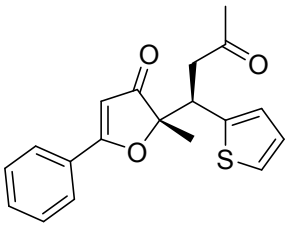


The product was obtained in 95% yield, 70.2 mg, yellow oil solid. $[\alpha]^{25}_D$ 141.1 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77-7.66 (m, 6H), 7.59-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.42-7.39 (m, 3H), 5.70 (s, 1H), 4.00-3.96 (m, 1H), 3.36-3.25 (m, 2H), 2.10 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.1, 205.5, 183.7, 135.8, 133.1, 132.7, 132.6, 128.9, 128.8, 128.1, 127.9, 127.7, 127.5, 127.2, 127.1, 125.9, 127.8, 125.8, 100.4, 91.7, 45.8, 43.6, 30.4, 20.2; HRMS (EI): exact mass calculated for M^+ ($C_{25}H_{22}O_3$) requires m/z 370.1569, found m/z 370.1573; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 10.2 min (major), 15.9 min (minor), ee 90%.

4k: (*S*)-2-((*S*)-1-(furan-2-yl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



The product was obtained in 84% yield, 52.1 mg, yellow oil. $[\alpha]^{25}_D$ 3.9 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81-7.79 (m, 2H), 7.60-7.56 (m, 1H), 7.52-7.48 (m, 2H), 7.28-7.25 (m, 1H), 6.27-6.25 (m, 1H), 6.17-6.16 (m, 1H), 5.88 (s, 1H), 3.89-3.85 (m, 1H), 3.19 (dd, J = 4.8, 17.2 Hz, 1H), 3.11 (dd, J = 9.6, 17.2 Hz, 1H), 2.14 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.7, 205.3, 183.9, 152.1, 141.7, 132.8, 128.9, 127.2, 110.4, 108.1, 99.8, 90.5, 40.9, 39.7, 30.2, 19.3; HRMS (EI): exact mass calculated for M^+ ($C_{19}H_{18}O_4$) requires m/z 310.1205, found m/z 310.1209; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 8.7 min (major), 16.0 min (minor), ee 90%.

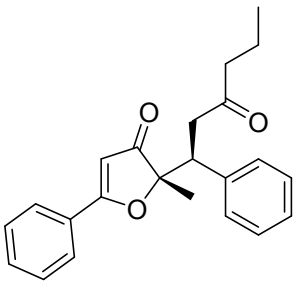


4l: (*S*)-2-methyl-2-((*R*)-3-oxo-1-(thiophen-2-yl)butyl)-5-phenylfuran-3(2*H*)-one

The product was obtained in 87% yield, 56.7 mg, yellow oil.

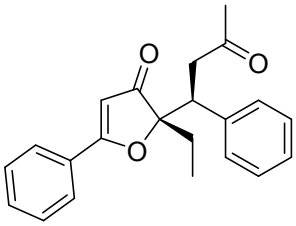
$[\alpha]^{25}_{D}$ 52.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84-7.81 (m, 2H), 7.60-7.57 (m, 1H), 7.53-7.48 (m, 2H), 7.09-7.08 (m, 1H), 6.91-6.90 (m, 1H), 6.86-6.85 (m, 1H), 5.83 (s, 1H), 4.13-4.10 (m, 1H), 3.26 (dd, *J* = 4.4, 17.2 Hz, 1H), 3.10 (dd, *J* = 9.6, 17.2 Hz, 1H), 2.13 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.6, 205.4, 184.1, 140.6, 132.8, 128.9, 128.8, 127.3, 126.9, 126.3, 124.6, 100.3, 91.0, 44.5, 41.2, 30.4, 19.7; HRMS (EI): exact mass calculated for M^+ ($C_{19}H_{18}O_3S$) requires m/z 326.0977, found m/z 326.0981; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 9.8 min (major), 17.5 min (minor), ee 87%.

4m: (*S*)-2-methyl-2-((*S*)-3-oxo-1-phenylhexyl)-5-phenylfuran-3(2*H*)-one



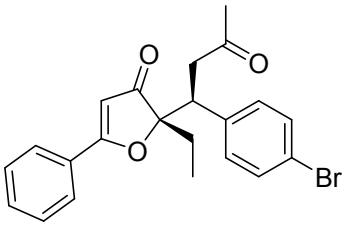
The product was obtained in 72% yield, 50.1 mg, colorless oil. $[\alpha]^{25}_{D}$ 94.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77-7.76 (m, 2H), 7.59-7.55 (m, 1H), 7.51-7.48 (m, 2H), 7.24-7.21 (m, 2H), 7.16-7.14 (m, 3H), 5.72 (s, 1H), 3.82-3.78 (m, 1H), 3.20-3.09 (m, 2H), 2.41-2.24 (m, 2H), 1.54-0.45 (m, 2H), 1.49 (s, 3H), 0.79 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 208.4, 205.6, 183.7, 138.2, 132.7, 129.1, 128.9, 128.8, 128.0, 127.2, 127.0, 100.3, 91.7, 45.7, 45.2, 42.6, 20.2, 17.0, 13.6; HRMS (EI): exact mass calculated for M^+ ($C_{23}H_{24}O_3$) requires m/z 348.1725, found m/z 348.1727; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 7.3 min (major), 10.3 min (minor), ee 85%.

4n: (*S*)-2-ethyl-2-((*S*)-3-oxo-1-phenylbutyl)-5-phenylfuran-3(2*H*)-one



The product was obtained in 90% yield, 60.1 mg, colorless oil. $[\alpha]^{25}_{D}$ 126.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78-7.76 (m, 2H), 7.59-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.25-7.22 (m, 2H), 7.16-7.14 (m, 3H), 5.76 (s, 1H), 3.81-3.77 (m, 1H), 3.19 (dd, *J* = 5.2, 16.8 Hz, 1H), 3.12 (dd, *J* = 9.6, 16.8 Hz, 1H), 2.05 (s, 3H), 1.96 (q, *J* = 7.2 Hz, 2H), 0.81 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.1, 205.1, 184.7, 138.1, 132.7, 129.2, 128.9, 128.7, 128.0, 127.2, 127.0, 102.3, 94.8, 45.8, 43.5, 30.3, 27.2, 7.3; HRMS (EI): exact mass calculated for M^+ ($C_{22}H_{22}O_3$) requires m/z 334.1569, found m/z 334.1566; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 7.0 min (major), 11.0 min (minor), ee 90%.

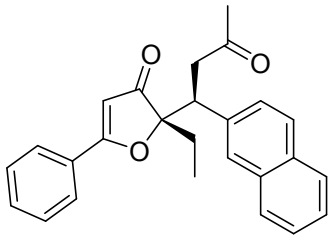
4o: (*S*)-2-((*S*)-1-(4-bromophenyl)-3-oxobutyl)-2-ethyl-5-phenylfuran-3(2*H*)-one



The product was obtained in 99% yield, 81.5 mg, yellow

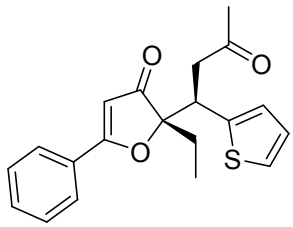
oil. $[\alpha]^{25}_D$ 131.3 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79-7.77 (m, 2H), 7.60-7.56 (m, 1H), 7.52-7.48 (m, 2H), 7.29-7.27 (m, 2H), 7.13-7.11 (m, 2H), 5.79 (s, 1H), 3.77-3.74(m, 1H), 3.17 (dd, *J* = 4.8, 16.8 Hz, 1H), 3.07 (dd, *J* = 9.6, 17.2 Hz, 1H), 2.06 (s, 3H), 1.94 (q, *J* = 7.2 Hz, 2H), 0.81 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.7, 204.8, 184.7, 137.4, 132.9, 131.2, 130.9, 129.0, 128.5, 127.0, 121.3, 102.4, 94.4, 45.1, 43.4, 30.4, 27.4, 7.2; HRMS (EI): exact mass calculated for M^+ ($C_{22}H_{21}BrO_3$) requires m/z 412.0674, found m/z 412.0670;The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 8.9 min (major), 12.1 min (minor), ee 89%.

4p: (*S*)-2-ethyl-2-((*S*)-1-(naphthalen-2-yl)-3-oxobutyl)-5-phenylfuran-3(2*H*)-one



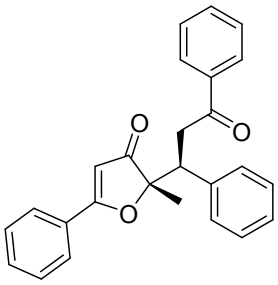
The product was obtained in 96% yield, 73.7 mg, yellow oil. $[\alpha]^{25}_D$ 186.5 (c 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80-7.78 (m, 2H), 7.76-7.74 (m, 2H), 7.71-7.67 (m, 2H), 7.59-7.56 (m, 1H), 7.51-7.48 (m, 2H), 7.45-7.40 (m, 3H), 5.76 (s, 1H), 4.03-3.99 (m, 1H), 3.30-3.27 (m, 2H), 2.08 (s, 3H), 2.05 (q, *J* = 7.2 Hz, 2H), 0.86 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.1, 205.0, 184.7, 135.9, 133.1, 132.7, 132.6, 128.9, 128.7, 128.3, 128.0, 127.6, 127.5, 127.4, 127.0, 125.9, 125.8, 102.4, 94.9, 46.0, 43.7, 30.4, 27.3, 7.3; HRMS (EI): exact mass calculated for M^+ ($C_{26}H_{24}O_3$) requires m/z 384.1725, found m/z 384.1728; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 9.9 min (major), 13.8 min (minor), ee 90%.

4q: (*S*)-2-ethyl-2-((*R*)-3-oxo-1-(thiophen-2-yl)butyl)-5-phenylfuran-3(2*H*)-one



The product was obtained in 96% yield, 65.2 mg, yellow oil. $[\alpha]^{25}_D$ 91.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84-7.82 (m, 2H), 7.59-7.56 (m, 1H), 7.52-7.48 (m, 2H), 7.07-7.06 (m, 1H), 6.90-6.89 (m, 1H), 6.84-6.82 (m, 1H), 5.86 (s, 1H), 4.14-4.10 (m, 1H), 3.21 (dd, *J* = 4.4, 16.8 Hz, 1H), 3.07 (dd, *J* = 9.6, 16.8 Hz, 1H), 2.10 (s, 3H), 1.96 (q, *J* = 7.2 Hz, 2H), 0.82 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.6, 204.8, 185.0, 140.8, 132.8, 128.9, 128.7, 127.2, 126.9, 126.3, 124.6, 102.2, 94.1, 44.5, 41.2, 30.4, 26.8, 7.3; HRMS (EI): exact mass calculated for M^+ ($C_{20}H_{20}O_3S$) requires m/z 340.1133, found m/z 340.1130; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 8.7 min (major), 14.3 min (minor), ee 87%.

5: (*S*)-2-methyl-2-((*S*)-3-oxo-1,3-diphenylpropyl)-5-phenylfuran-3(2*H*)-one



The product was obtained in 56% yield, 42.7 mg, colorless oil(79:21 dr, 8/0 ee). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.05-8.03 (m, 2H), 7.93-7.91 (m, 2H), 7.85-7.83 (m, 2H), 7.70-7.68 (m, 2H), 7.46-7.38 (m, 5H), 7.19-7.17 (m, 1H), 7.04-7.03 (m, 1H), 5.67 (s, 1H), 3.95-3.92 (m, 1H), 3.67-3.63 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.1, 197.7, 183.8, 138.4, 136.9, 135.2, 133.6, 133.1, 132.7, 132.7, 129.1, 128.9, 128.7, 128.5, 128.2, 128.1, 127.8, 127.2, 127.1, 100.4, 93.9, 92.0, 45.8, 38.6, 25.1, 20.4;; HRMS (EI): exact mass calculated for M^+ ($C_{26}H_{22}O_3$) requires m/z 382.1569, found m/z 382.1574; The enantiomeric excess was determined by HPLC. [IA column, 254 nm, *n*-Hexane: IPA = 5:1, 1.0 mL/min]: 8.7 min (major), 14.3 min (minor), ee 8%.

E: References

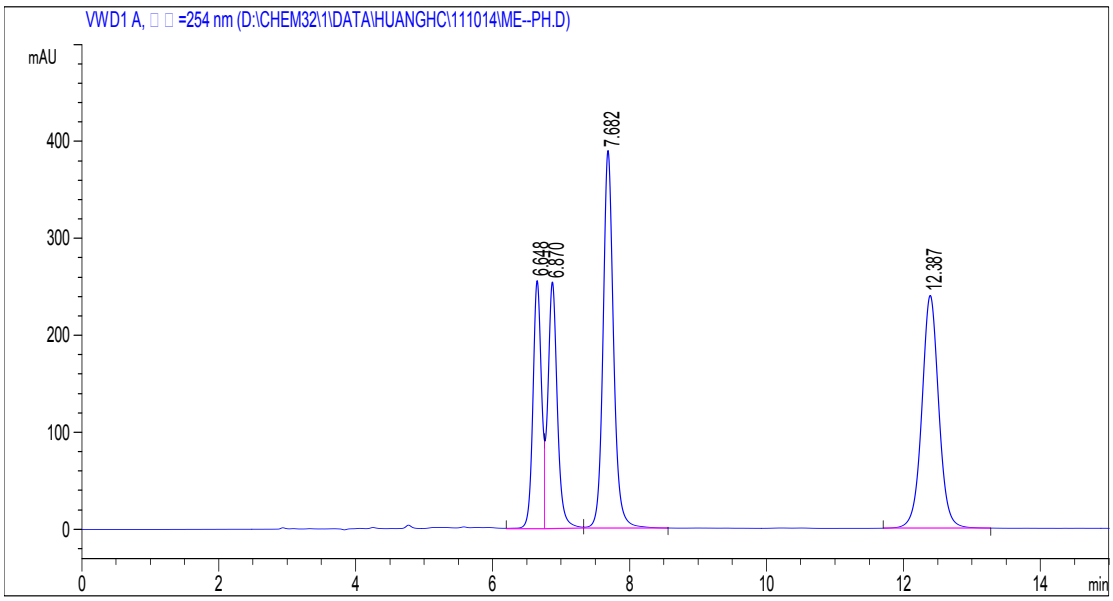
[1] a) Li, Z.; Nakashige, M.; William, W. J. *J. Am. Chem. Soc.* **2011**, *133*, 6553-6556; b) Mukerji, S. K.; Sharma, K. K.; Torssell, K. B. G.. *Tetrahedron* 1983, 39, 2231–2235; c) Winkler, J. D.; Oh, K.; Asselin, S. M. *Org. Lett.* 2005, 7, 387–389.

[2] Gao, Y.; Ren, Q.; Wang, L.; Wang, J. *Chem. Eur. J.* **2010**, *16*, 13068-13071.

[3] Yu, F.; Hu, H.; Gu, X.; Ye, J. *Org. Lett.* **2012**, *14*, 2038–2041.

F: HPLC Charts of Asymmetric Addition Products

4a:(*S*)-2-methyl-2-((*S*)-3-oxo-1-phenylbutyl)-5-phenylfuran-3(2*H*)-one



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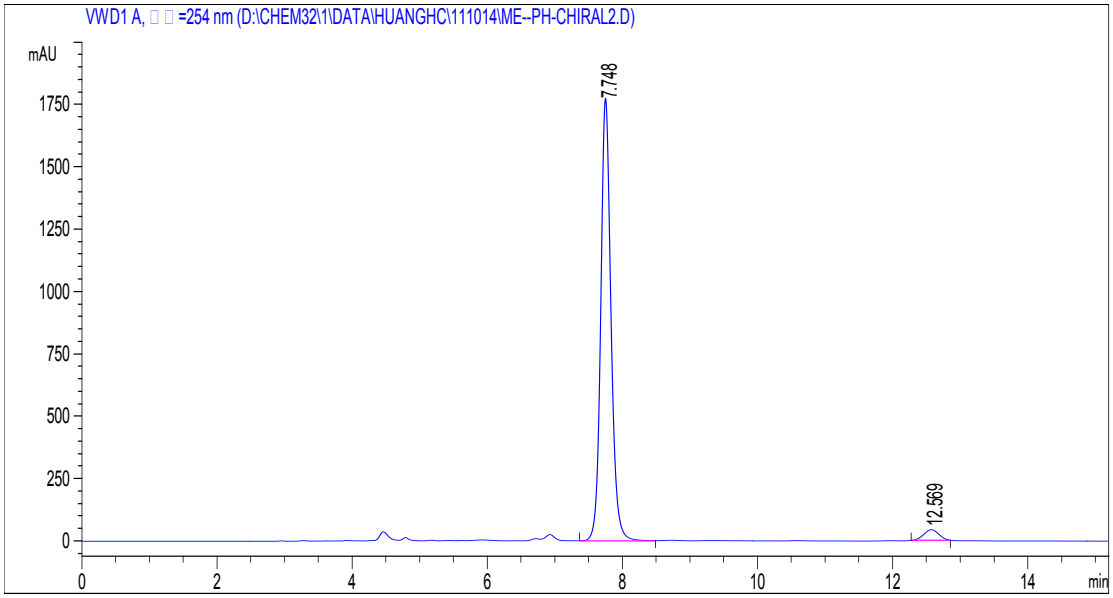
2	6.87	2344.8	255.3	0.1531	0.797	18.116
3	7.682	4163.4	389.8	0.161	0.844	32.167
4	12.387	4117	240.2	0.2611	0.945	31.808



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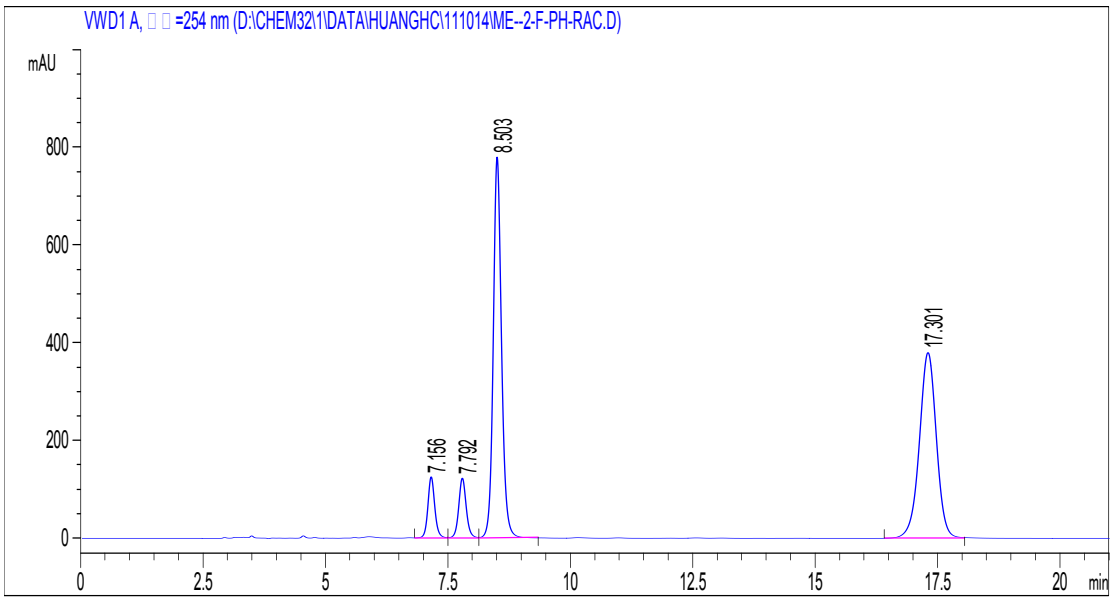
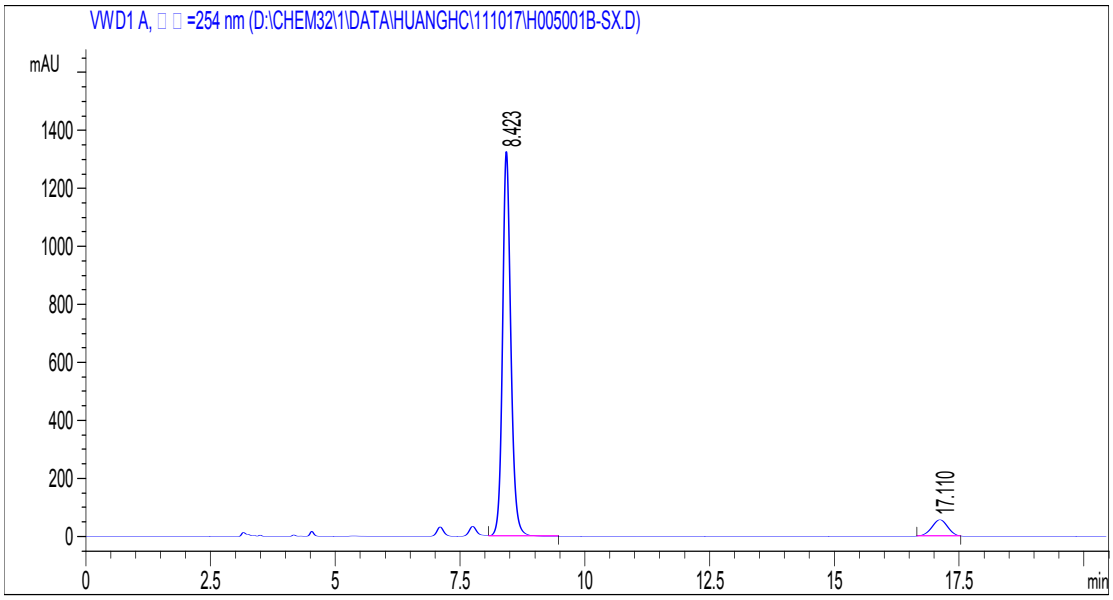
1	7.748	18697.4	1775.3	0.1755	0.847	96.651
2	12.569	648	42.4	0.2545	0.989	3.349

4b:(*S*)-2-((*S*)-1-(2-fluorophenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



#	Time	Area	Height	Width	Symmetry	Area %
1	7.156	1243.1	125.7	0.1503	0.881	5.952
2	7.792	1321.1	122.9	0.1633	0.899	6.325
3	8.503	9142.5	779.6	0.179	0.846	43.776
4	17.301	9178	380.1	0.4025	1.015	43.946



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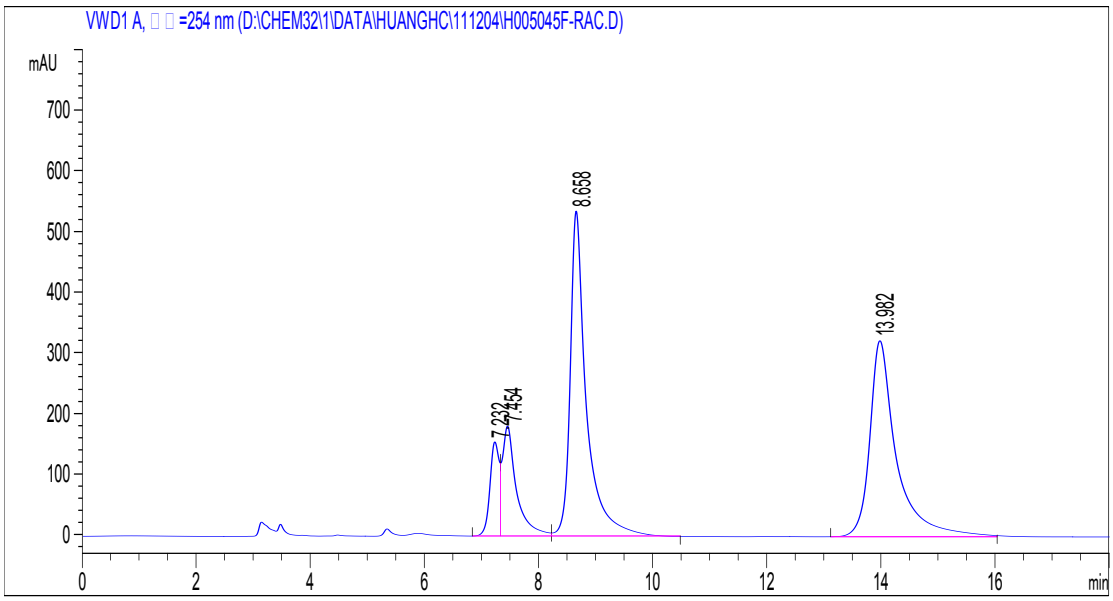
4c: (*S*)-2-((*S*)-1-(4-chlorophenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



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1	7.232	1778.9	155.9	0.1695	1.189	6.839
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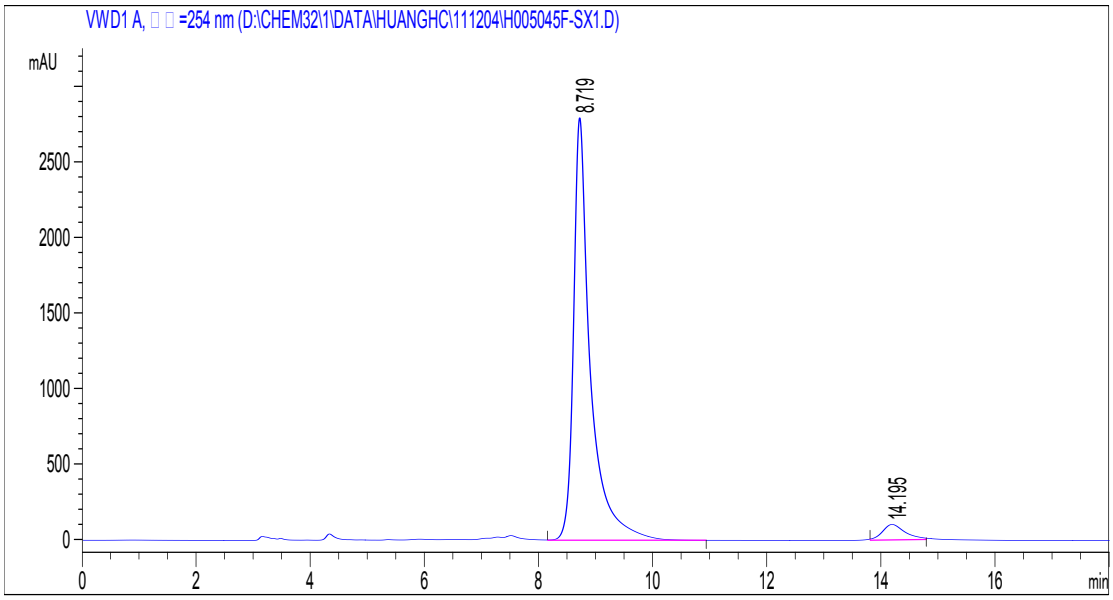
3	8.658	10587.2	536.2	0.2799	0.538	40.704
4	13.982	10490.8	323.1	0.5411	0.589	40.334



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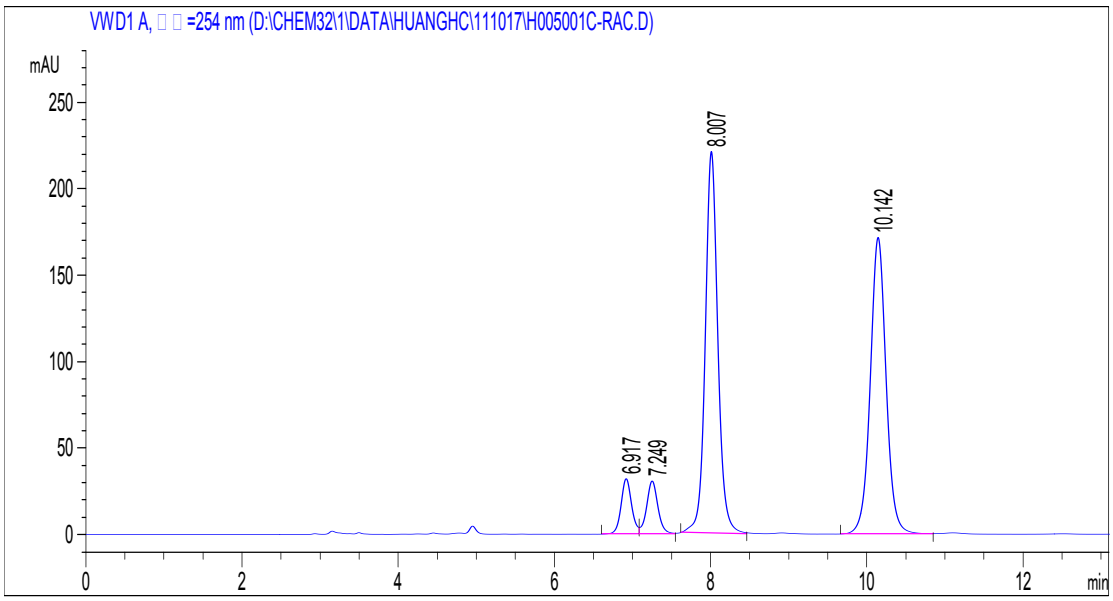
4d: (*S*)-2-((*S*)-1-(3-bromophenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



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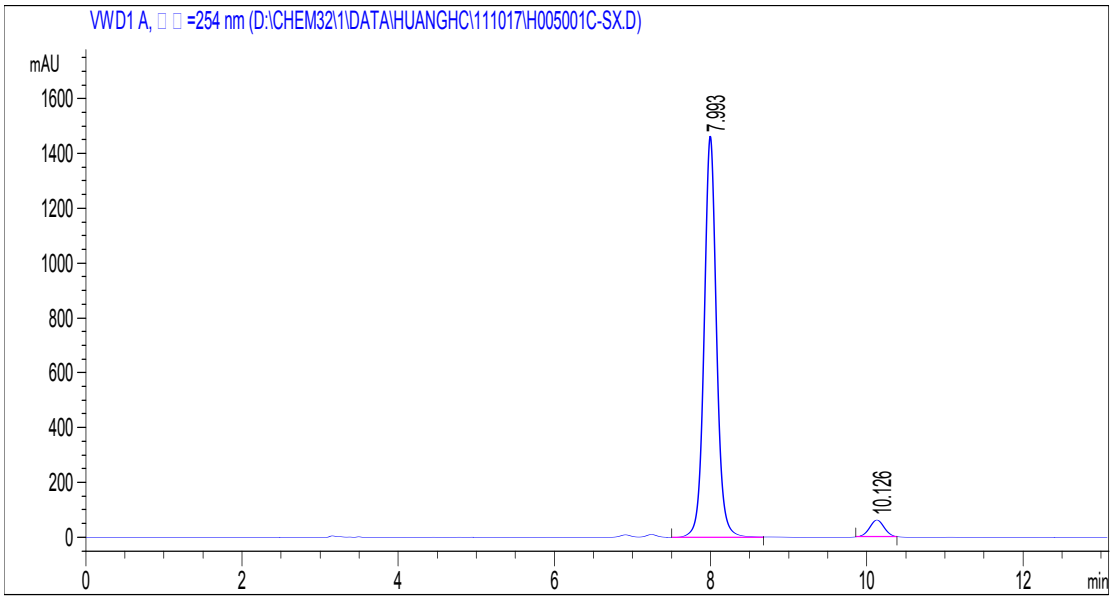
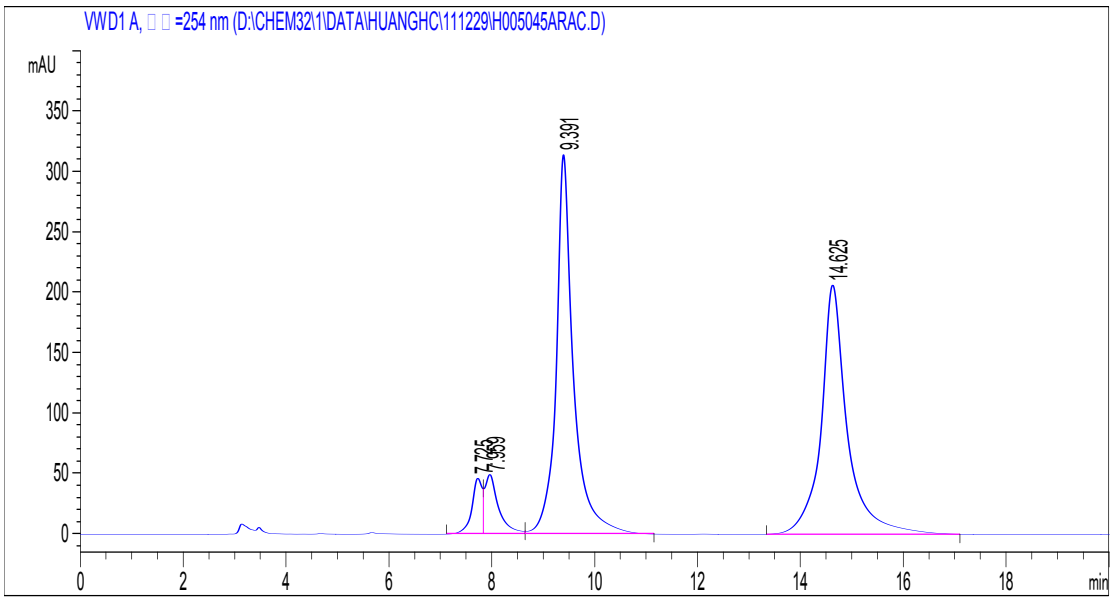
3	8.007	2462.3	221.3	0.1855	0.895	44.796
4	10.142	2421.6	171.5	0.2157	0.94	44.055

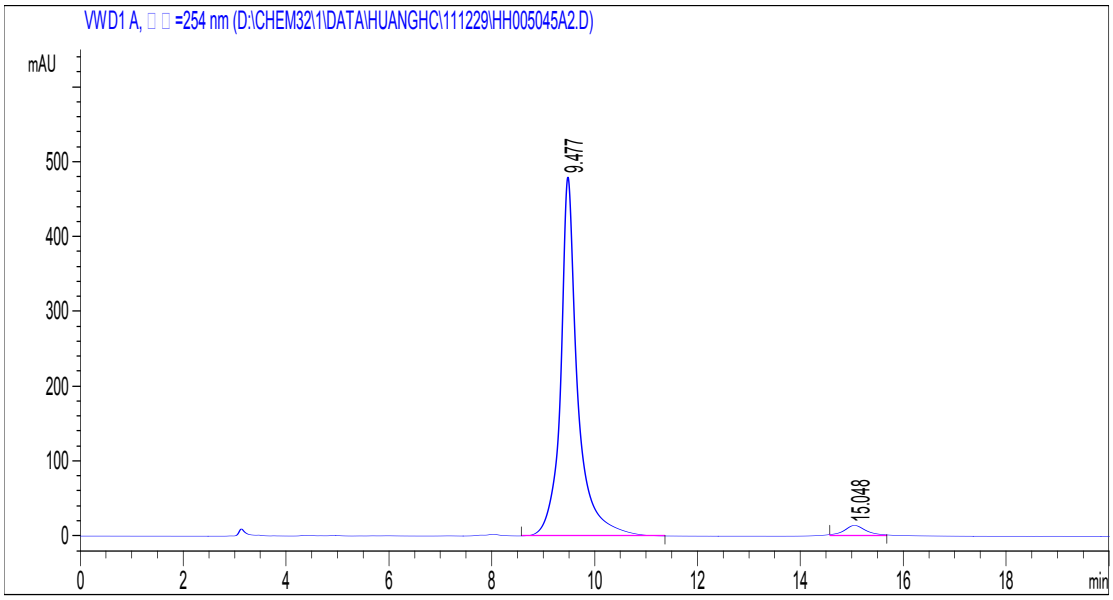


#	Time	Area	Height	Width	Symmetry	Area %
1	7.993	16130.4	1464.2	0.1678	0.934	95.317
2	10.126	792.6	61.2	0.216	0.979	4.683

4e: (*S*)-2-((*S*)-1-(4-bromophenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one

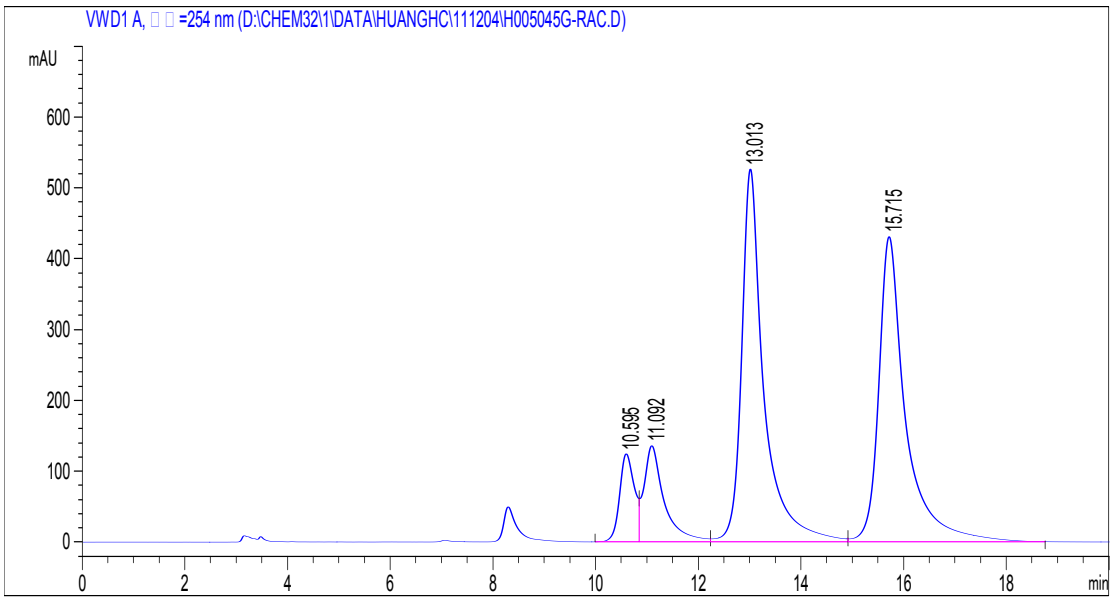


#	Time	Area	Height	Width	Symmetry	Area %
1	7.725	656.1	46.3	0.206	1.459	4.036
2	7.959	920	49.5	0.2593	0.49	5.659
3	9.391	7345.8	314.2	0.3267	0.702	45.188
4	14.625	7334.2	206.4	0.4989	0.759	45.117

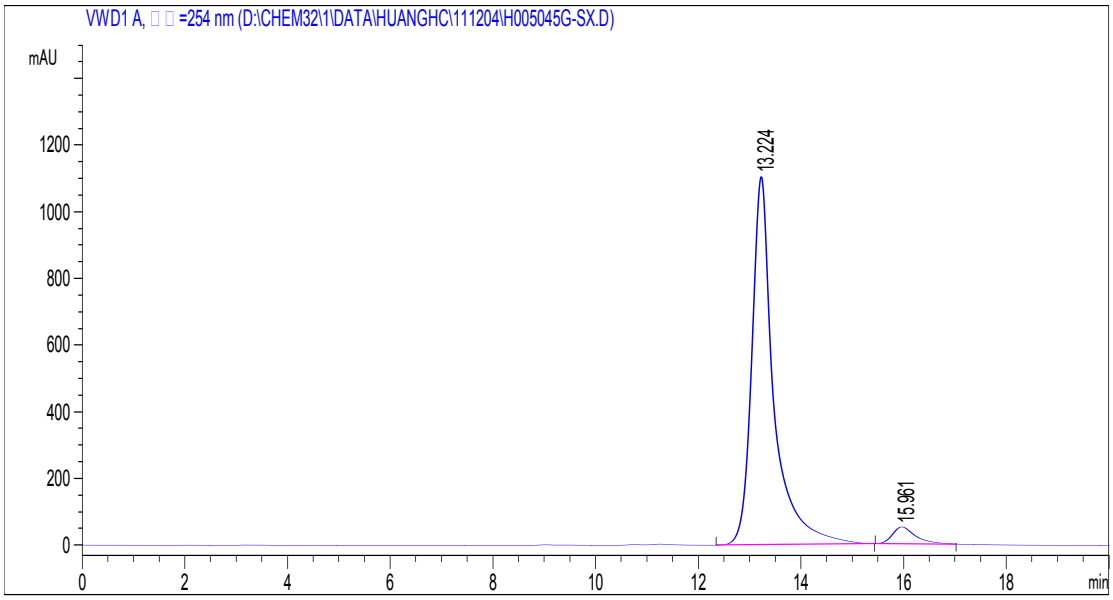


#	Time	Area	Height	Width	Symmetry	Area %
1	9.477	11018.2	480	0.3232	0.721	96.159
2	15.048	440.1	14.2	0.5177	0.857	3.841

4f: (*S*)-2-methyl-2-((*S*)-1-(3-nitrophenyl)-3-oxobutyl)-5-phenylfuran-3(2*H*)-one

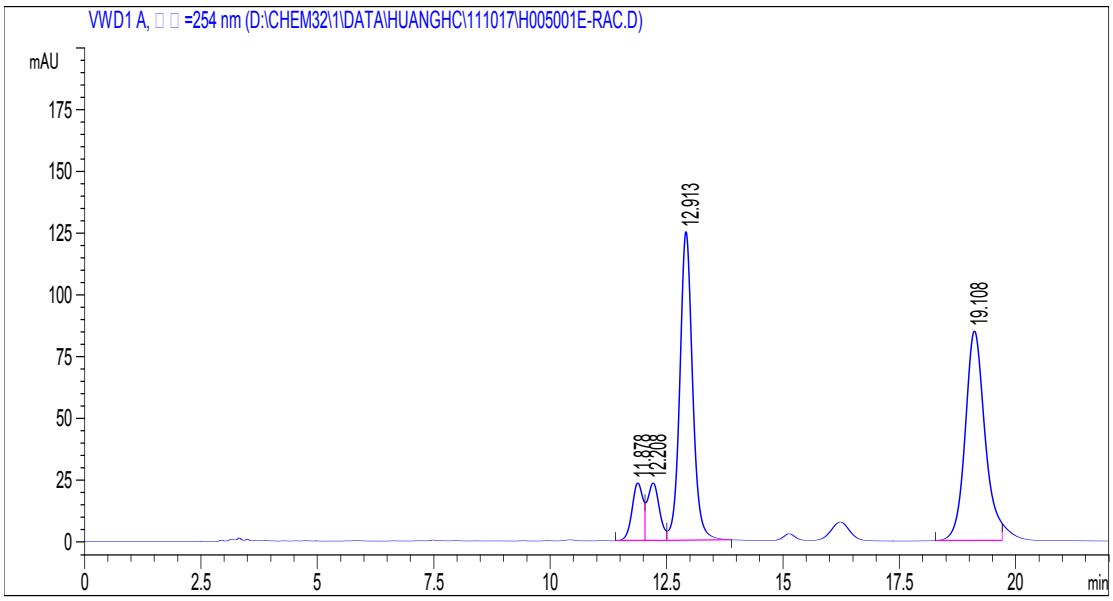


#	Time	Area	Height	Width	Symmetry	Area %
1	10.595	2508.6	124.4	0.2993	0.807	6.653
2	11.092	3697.1	135.8	0.3831	0.56	9.804
3	13.013	15848.6	526.4	0.4284	0.6	42.029
4	15.715	15654.3	430.8	0.52	0.577	41.514

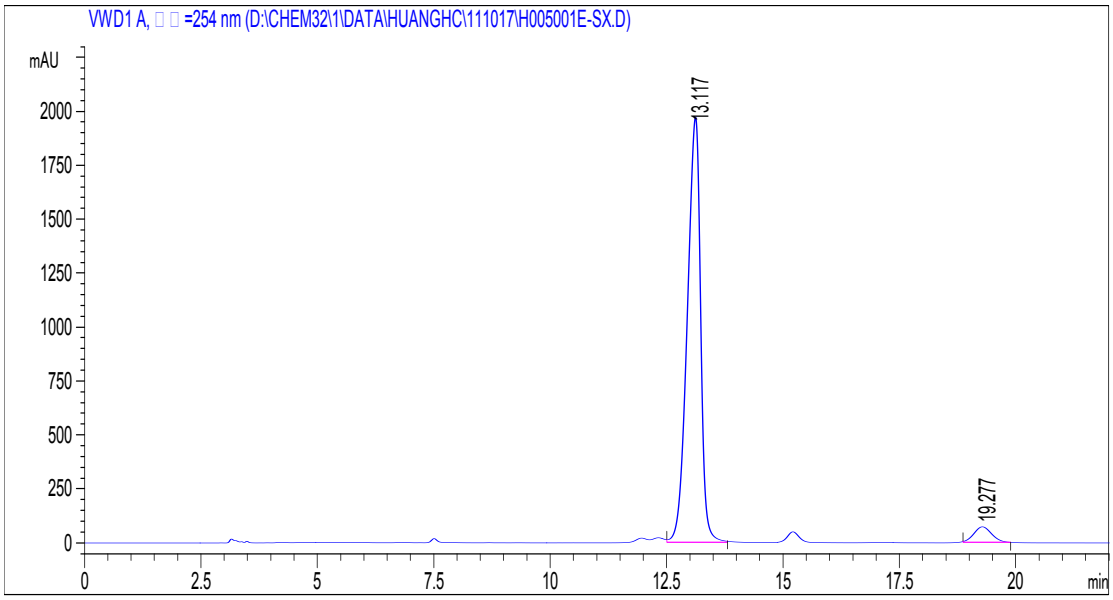


#	Time	Area	Height	Width	Symmetry	Area %
1	13.224	33000.5	1105.2	0.4976	0.708	95.137
2	15.961	1687	51.8	0.5433	0.646	4.863

4g: (*S*)-2-methyl-2-((*S*)-1-(4-nitrophenyl)-3-oxobutyl)-5-phenylfuran-3(2*H*)-one

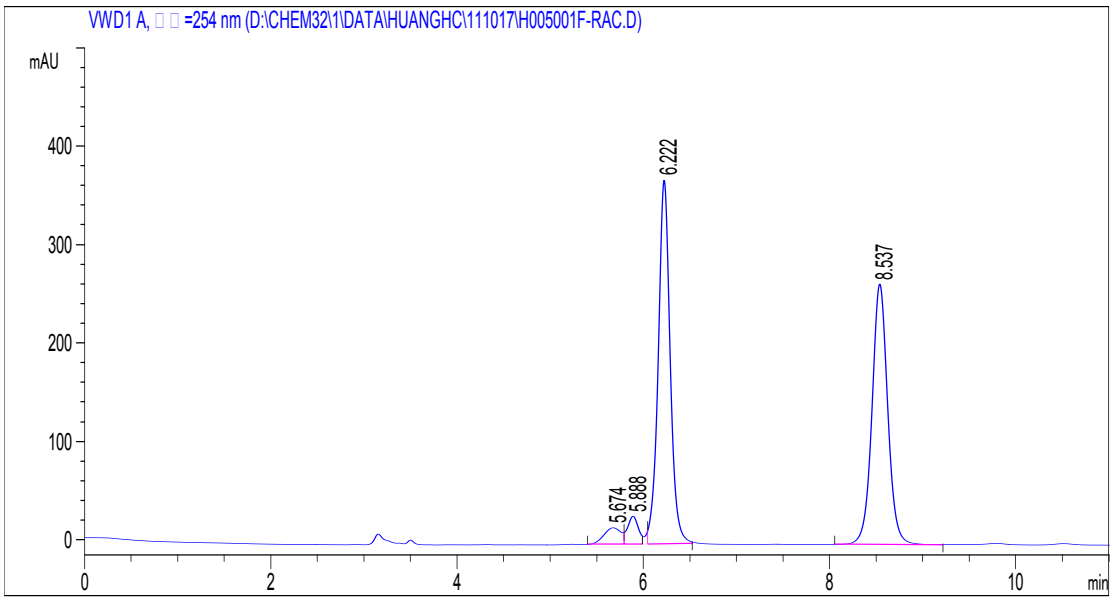


#	Time	Area	Height	Width	Symmetry	Area %
1	11.878	389.1	23.4	0.2496	1.099	6.862
2	12.208	414	23.4	0.2651	0.827	7.301
3	12.913	2377.6	124.8	0.2892	0.89	41.926
4	19.108	2490.2	84.8	0.4893	0.859	43.911

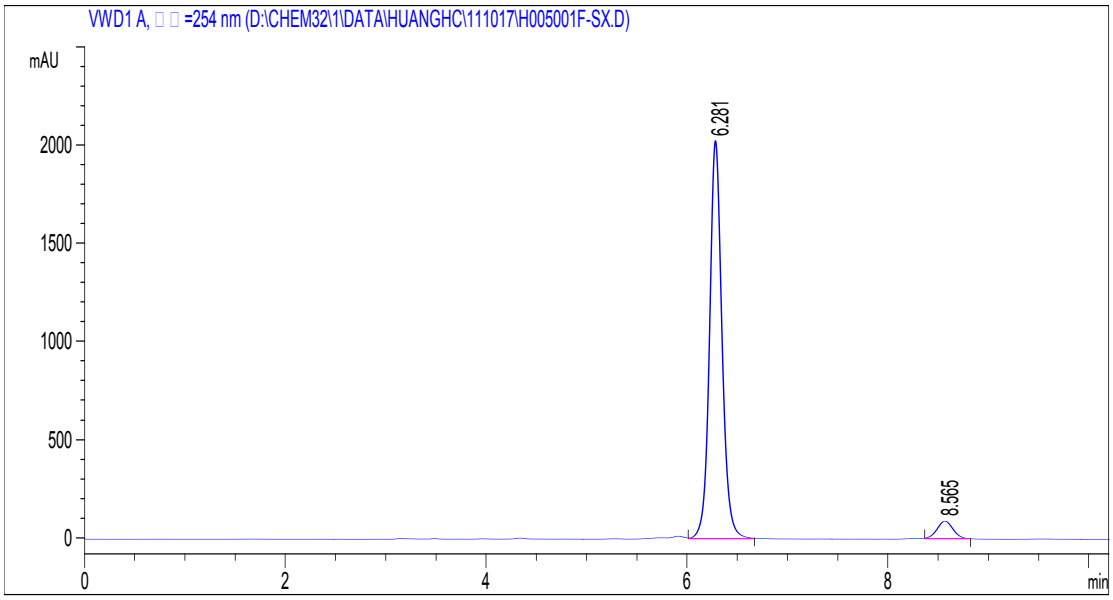


#	Time	Area	Height	Width	Symmetry	Area %
1	13.117	39308.2	1973.7	0.3319	1.518	95.031
2	19.277	2055.5	74.4	0.4603	0.884	4.969

4h: (*S*)-2-methyl-2-((*S*)-3-oxo-1-m-tolylbutyl)-5-phenylfuran-3(2*H*)-one

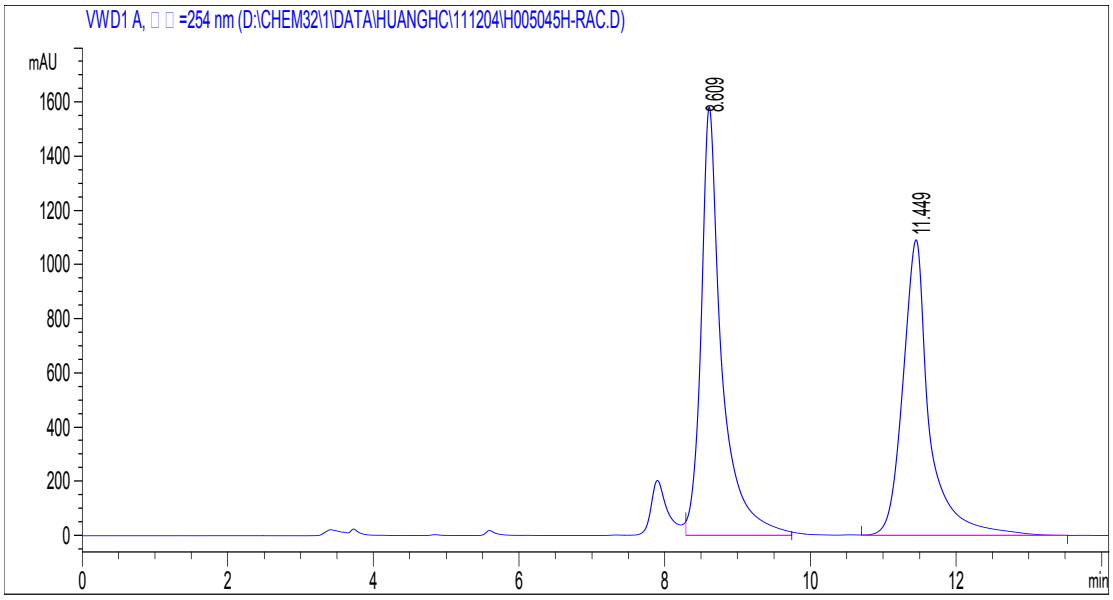


#	Time	Area	Height	Width	Symmetry	Area %
1	5.674	217.5	17.2	0.1943	1.347	3.155
2	5.888	247.5	28.9	0.1261	1.02	3.591
3	6.222	3308.8	370.2	0.149	0.954	48.005
4	8.537	3118.9	264.8	0.1796	0.94	45.249

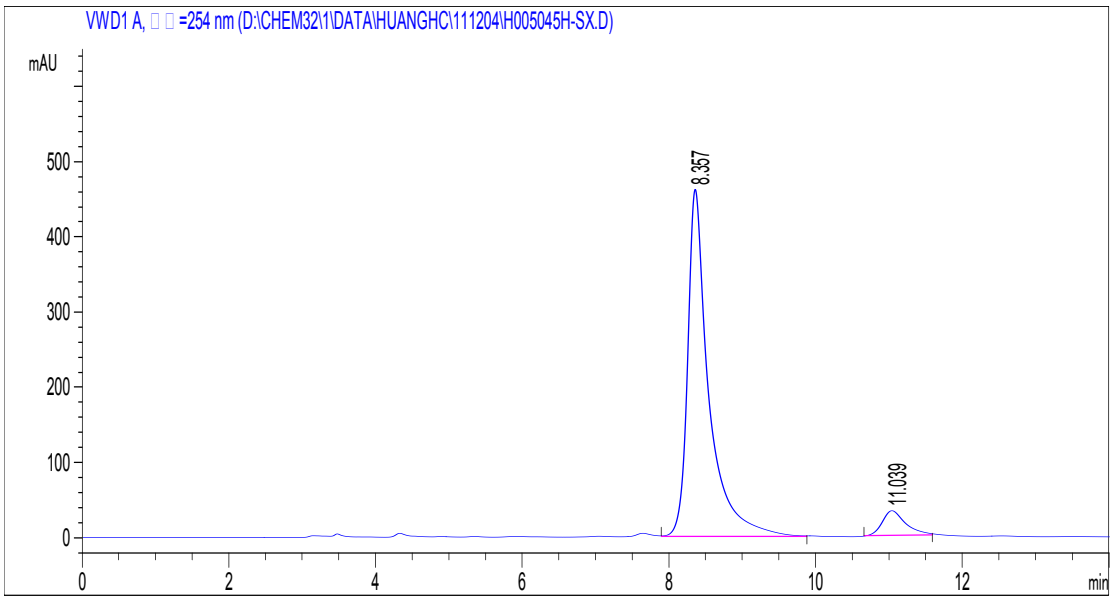


#	Time	Area	Height	Width	Symmetry	Area %
1	6.281	17492.4	2029	0.1437	0.881	94.559
2	8.565	1006.5	90.1	0.1861	0.957	5.441

4i:(*S*)-2-((*S*)-1-(3-methoxyphenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one

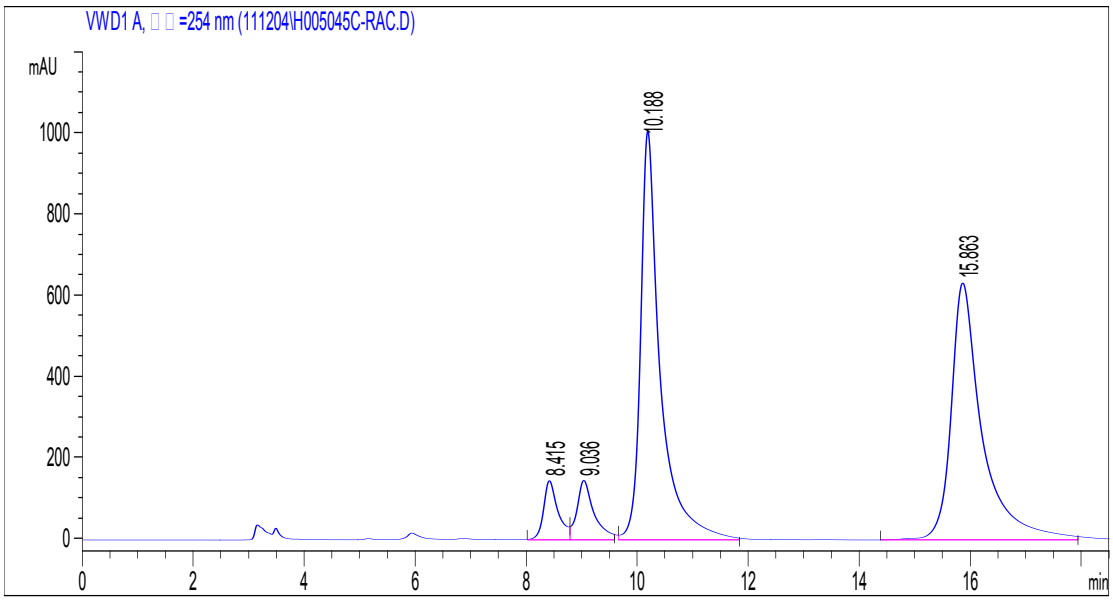


#	Time	Area	Height	Width	Symmetry	Area %
1	8.609	29960.7	1583.5	0.3278	0.623	50.898
2	11.449	28903.2	1093.3	0.3655	0.87	49.102

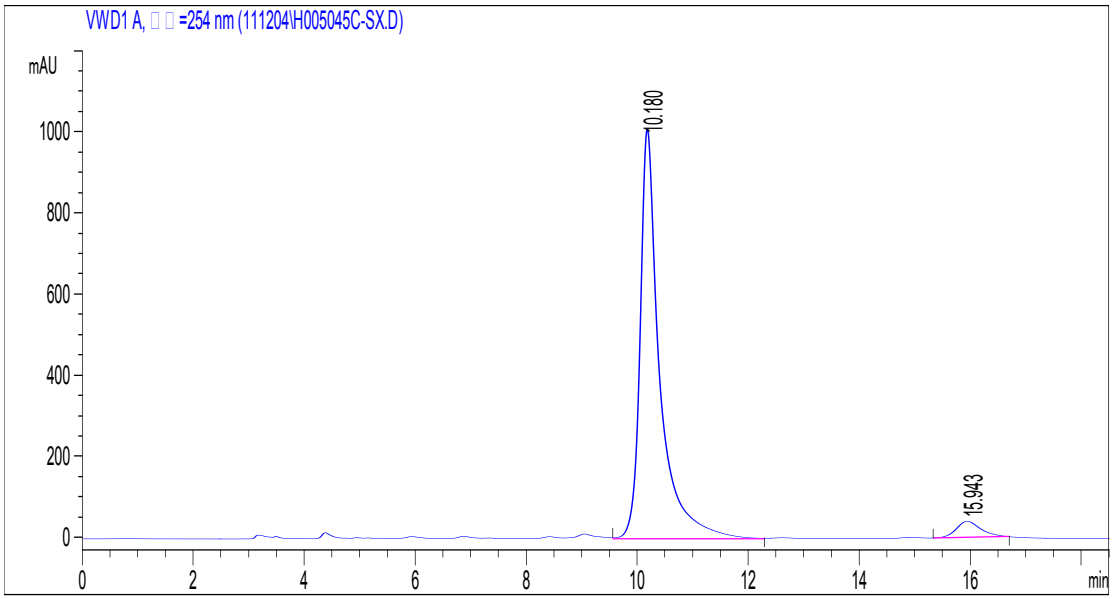


#	Time	Area	Height	Width	Symmetry	Area %
1	8.357	9293	462.2	0.2856	0.512	92.573
2	11.039	745.6	33.2	0.3745	0.67	7.427

4j: (*S*)-2-methyl-2-((*S*)-1-(naphthalen-2-yl)-3-oxobutyl)-5-phenylfuran-3(2*H*)-one

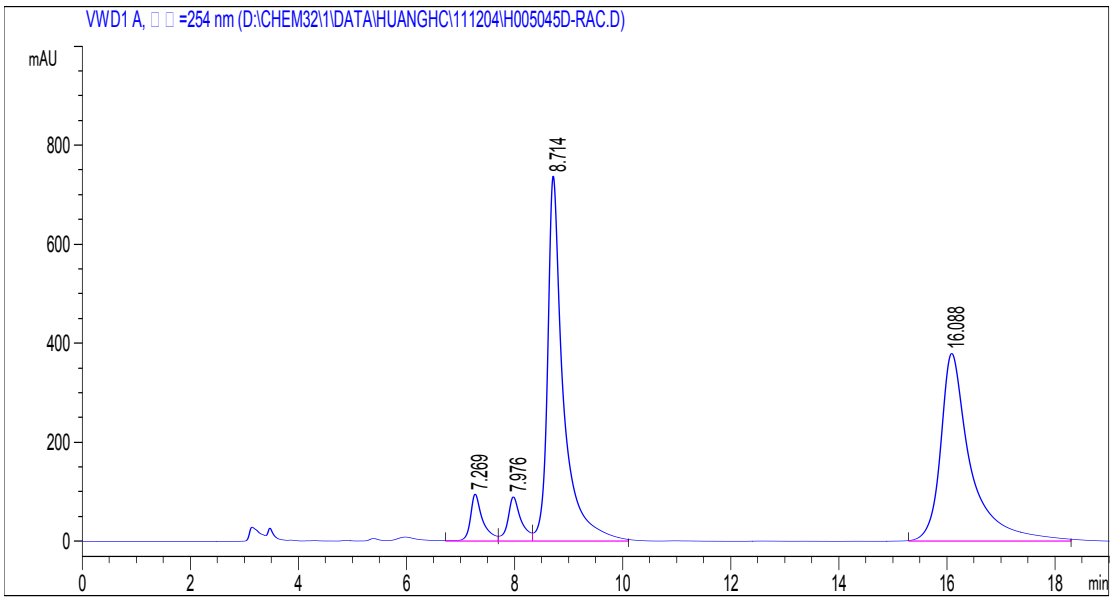


#	Time	Area	Height	Width	Symmetry	Area %
1	8.415	2679.9	146.1	0.3056	0	4.842
2	9.036	3112.6	146.9	0.3533	0.64	5.624
3	10.188	24922.8	1008	0.4121	0.558	45.028
4	15.863	24634.4	633.8	0.6478	0.58	44.507

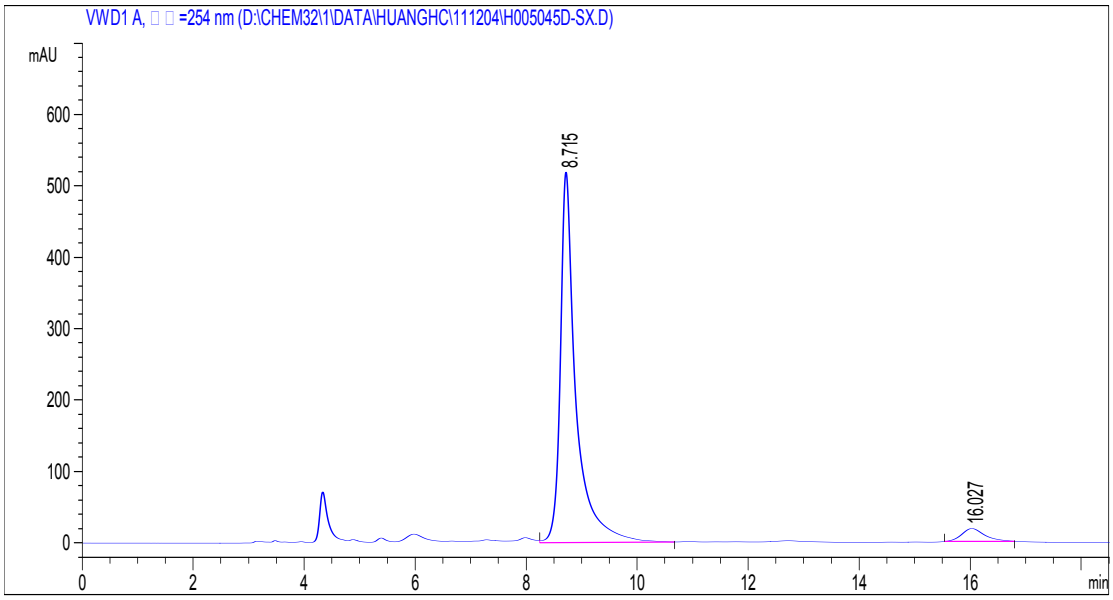


#	Time	Area	Height	Width	Symmetry	Area %
1	10.18	24789.4	1010.7	0.3488	0.53	95.182
2	15.943	1254.9	40	0.5231	0.784	4.818

4k: (*S*)-2-((*S*)-1-(furan-2-yl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one

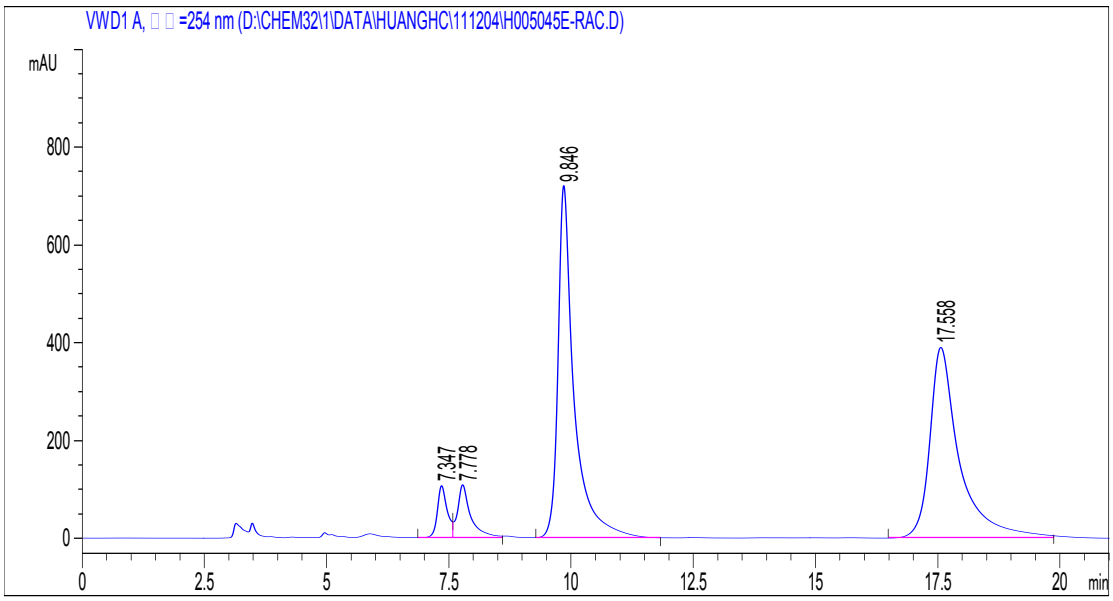


#	Time	Area	Height	Width	Symmetry	Area %
1	7.269	1544.9	95.5	0.2295	0.614	4.721
2	7.976	1543.7	89.9	0.2455	0.686	4.717
3	8.714	14958.1	737.9	0.3379	0.538	45.707
4	16.088	14679.2	379.4	0.6449	0.567	44.855

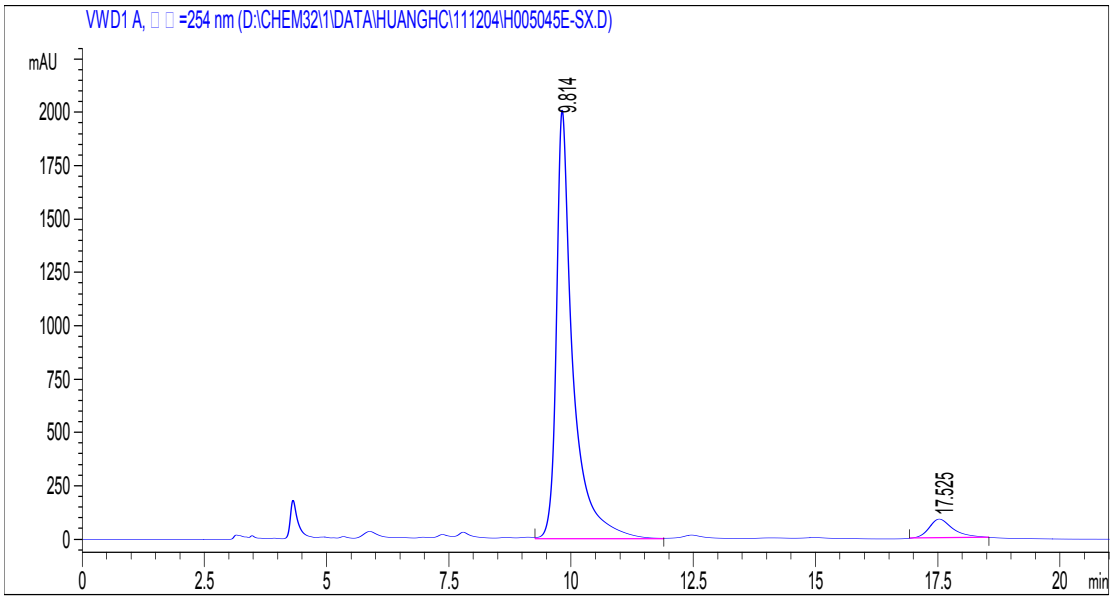


#	Time	Area	Height	Width	Symmetry	Area %
1	8.715	10190.4	519.5	0.2769	0.514	95.043
2	16.027	531.5	18.2	0.487	0.757	4.957

4l: (*S*)-2-methyl-2-((*R*)-3-oxo-1-(thiophen-2-yl)butyl)-5-phenylfuran-3(2*H*)-one

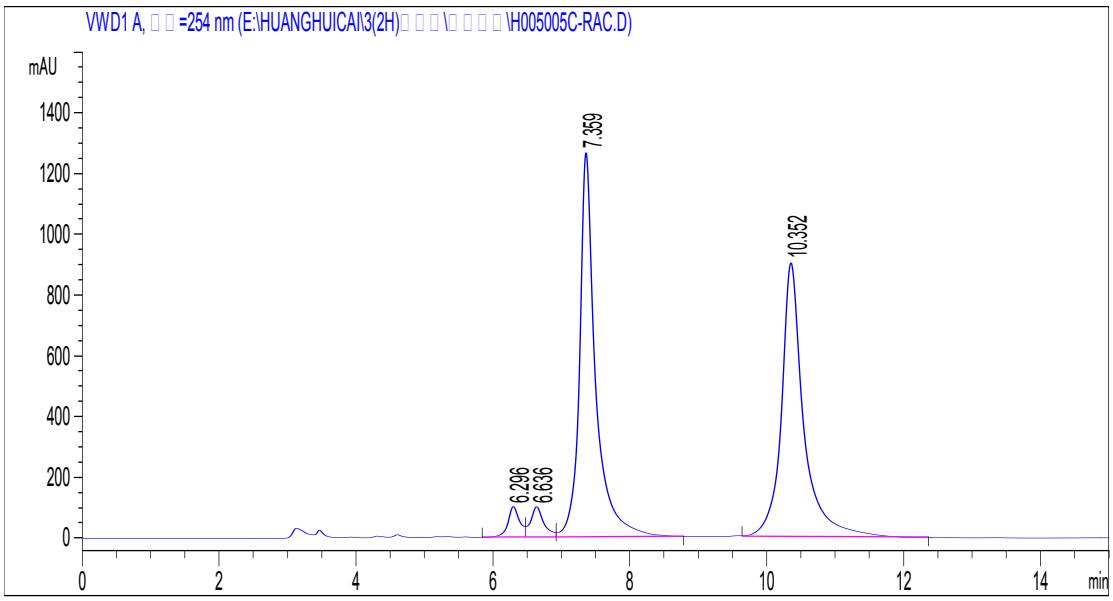


#	Time	Area	Height	Width	Symmetry	Area %
1	7.347	1508.8	106.4	0.2063	0.711	4.145
2	7.778	2006.1	108.3	0.2598	0.564	5.511
3	9.846	16398.4	719.7	0.3226	0.512	45.050
4	17.558	16487	390.1	0.7044	0.571	45.294

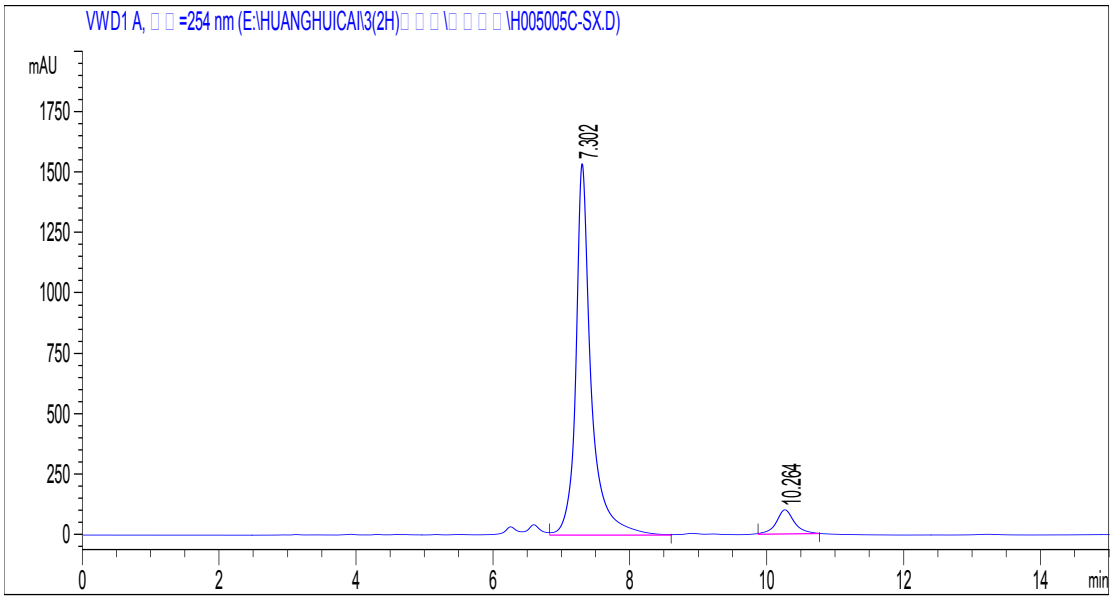


#	Time	Area	Height	Width	Symmetry	Area %
1	9.814	47427.1	2011	0.3334	0.496	93.834
2	17.525	3116.3	89.2	0.5821	0.711	6.166

4m: (*S*)-2-methyl-2-((*S*)-3-oxo-1-phenylhexyl)-5-phenylfuran-3(2*H*)-one

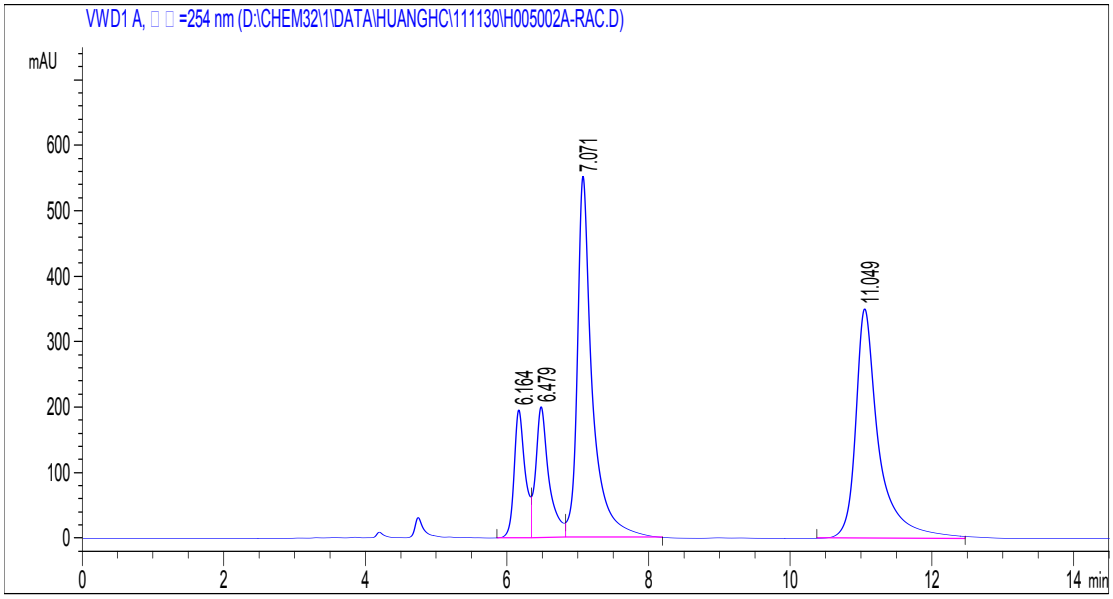


#	Time	Area	Height	Width	Symmetry	Area %
1	6.296	1225	101.4	0.1744	0.863	2.803
2	6.636	1359.7	100.7	0.1925	0.774	3.111
3	7.359	20525.6	1264.6	0.2287	0.636	46.969
4	10.352	20590	902.6	0.3258	0.703	47.116

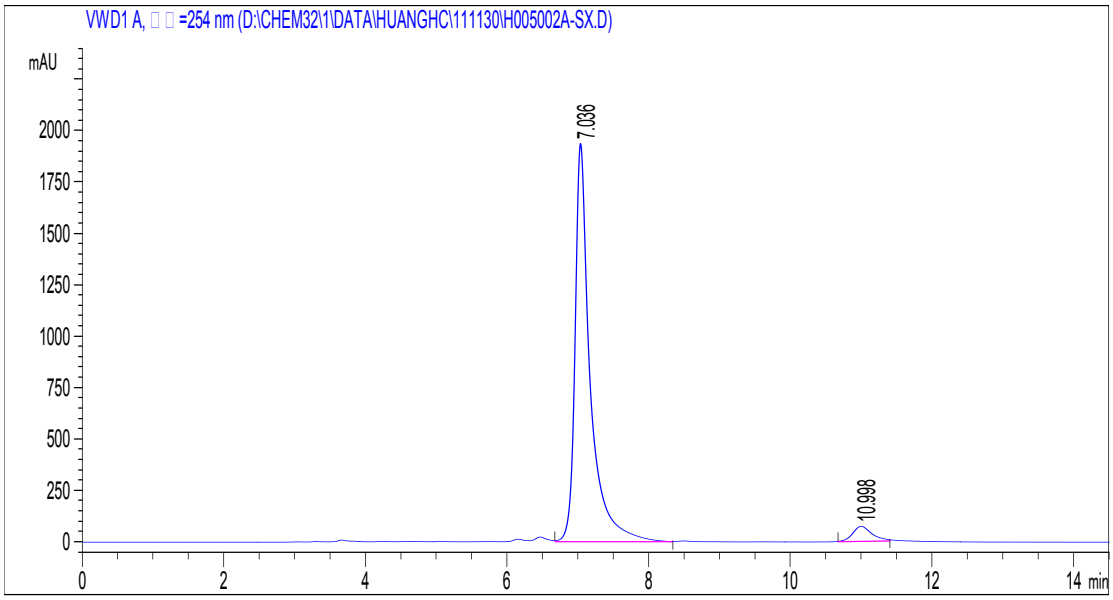


#	Time	Area	Height	Width	Symmetry	Area %
1	7.302	23827.8	1536.2	0.2217	0.659	92.556
2	10.264	1916.5	101.2	0.3155	0.879	7.444

4n: (*S*)-2-ethyl-2-((*S*)-3-oxo-1-phenylbutyl)-5-phenylfuran-3(2*H*)-one

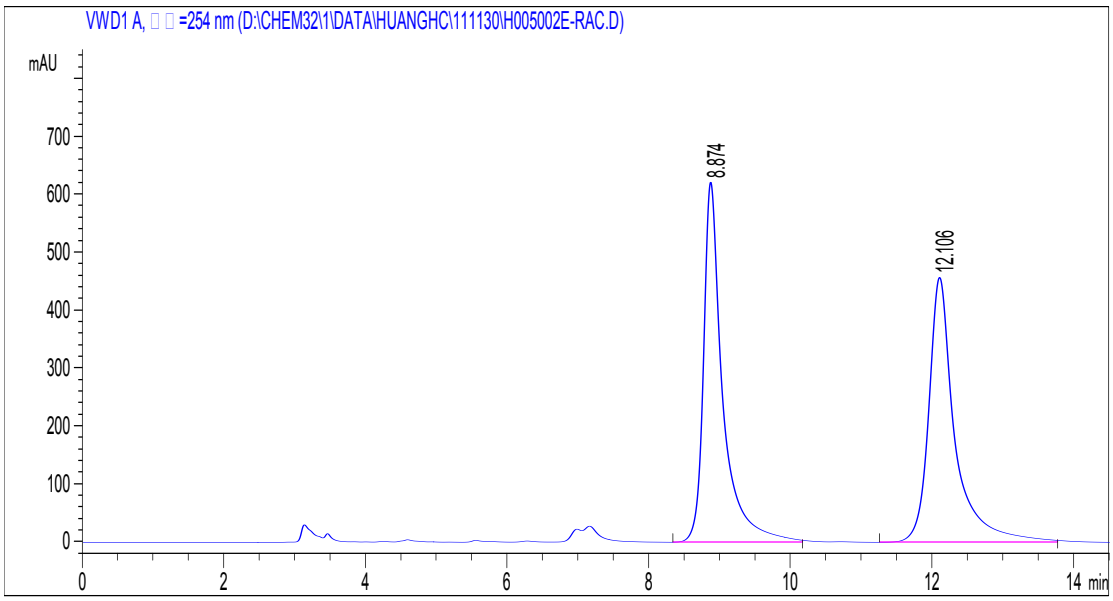


#	Time	Area	Height	Width	Symmetry	Area %
1	6.164	2149	195.7	0.183	0	10.335
2	6.479	2582.2	200.4	0.2148	0	12.418
3	7.071	8102.8	552.7	0.2443	0.586	38.967
4	11.049	7960.1	351.1	0.3779	0.611	38.281

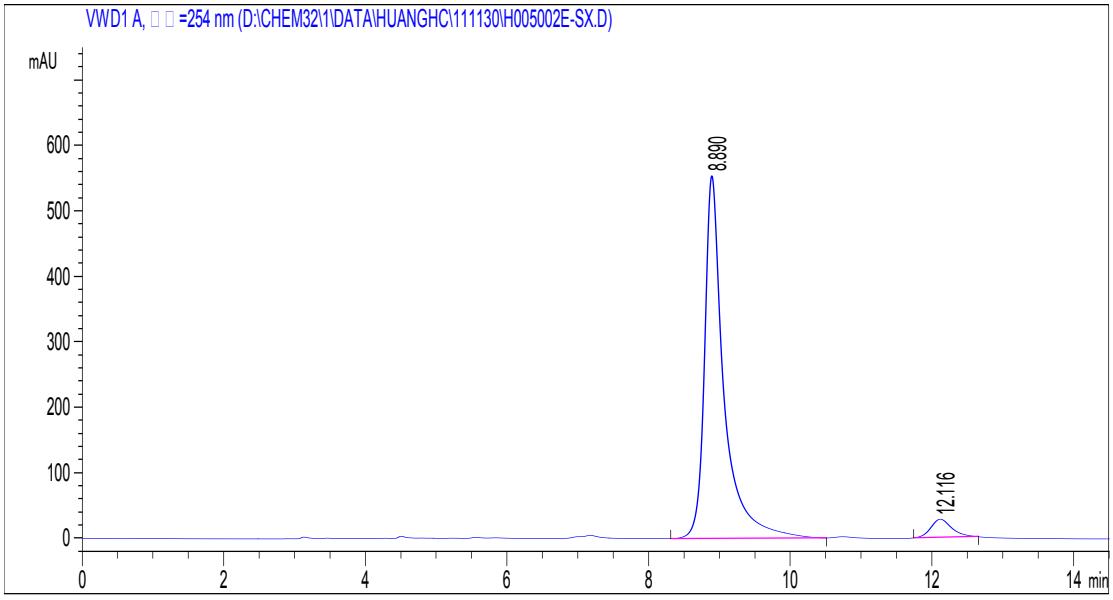


#	Time	Area	Height	Width	Symmetry	Area %
1	7.036	28892.2	1938.8	0.2117	0.519	95.120
2	10.998	1482.3	75.2	0.3286	0.742	4.880

4o: (*S*)-2-((*S*)-1-(4-bromophenyl)-3-oxobutyl)-2-ethyl-5-phenylfuran-3(2*H*)-one

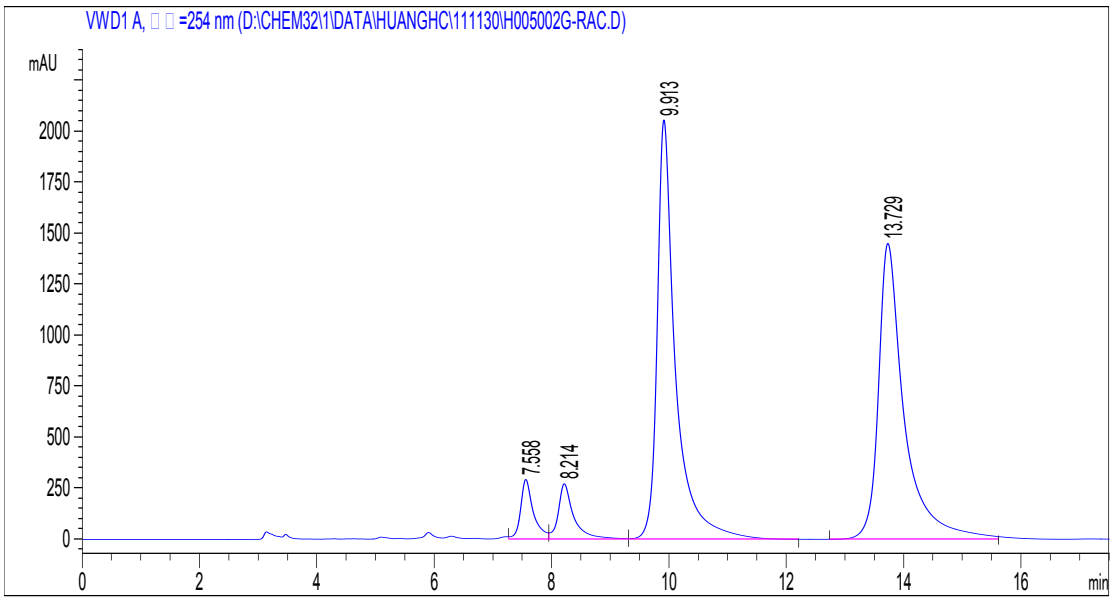


#	Time	Area	Height	Width	Symmetry	Area %
1	8.874	11728.4	622	0.3142	0.57	50.011
2	12.106	11723.1	457.5	0.4271	0.67	49.989

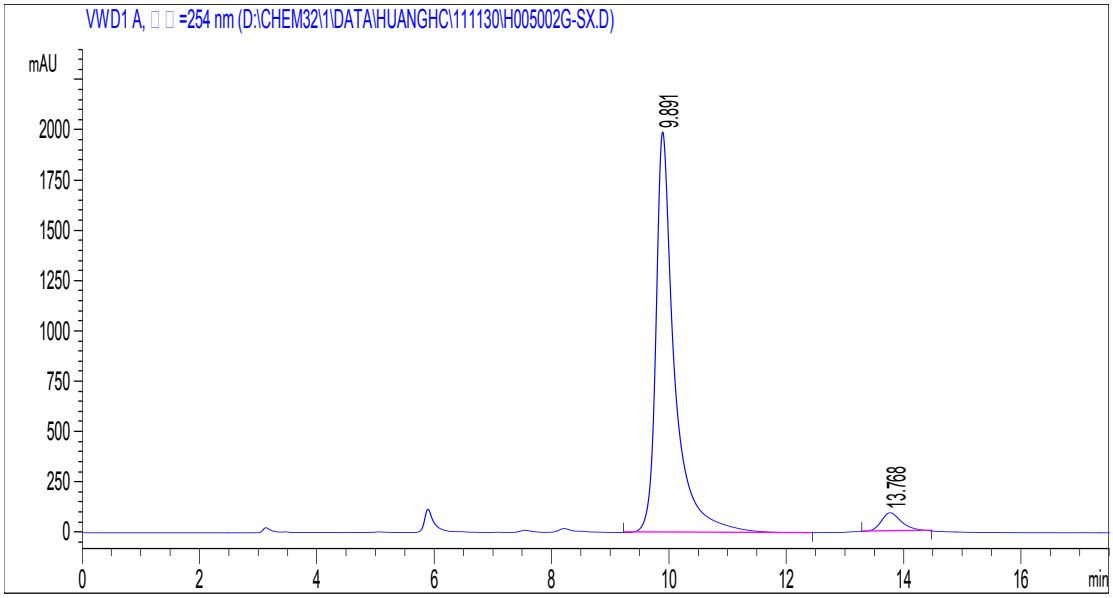


#	Time	Area	Height	Width	Symmetry	Area %
1	8.89	10644.8	555.2	0.3196	0.573	94.683
2	12.116	597.7	28.3	0.3522	0.793	5.317

4p: (*S*)-2-ethyl-2-((*S*)-1-(naphthalen-2-yl)-3-oxobutyl)-5-phenylfuran-3(2*H*)-one

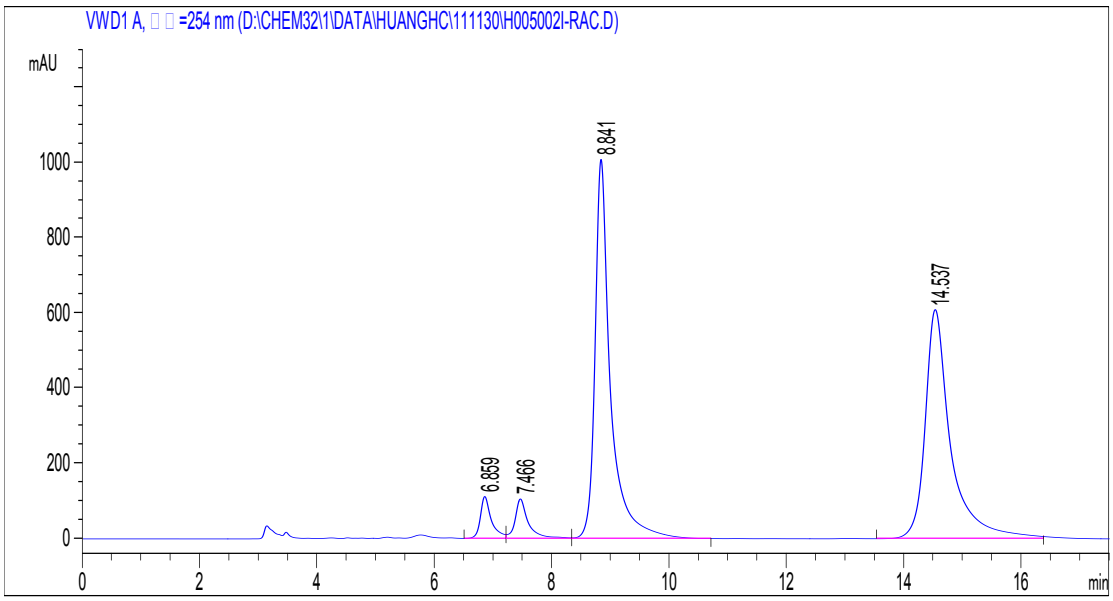


#	Time	Area	Height	Width	Symmetry	Area %
1	7.558	4485.1	293.8	0.2203	0.647	4.547
2	8.214	5068.7	272.6	0.2636	0.572	5.138
3	9.913	44645.4	2056.6	0.3101	0.531	45.259
4	13.729	44444.6	1451.2	0.5104	0.555	45.056

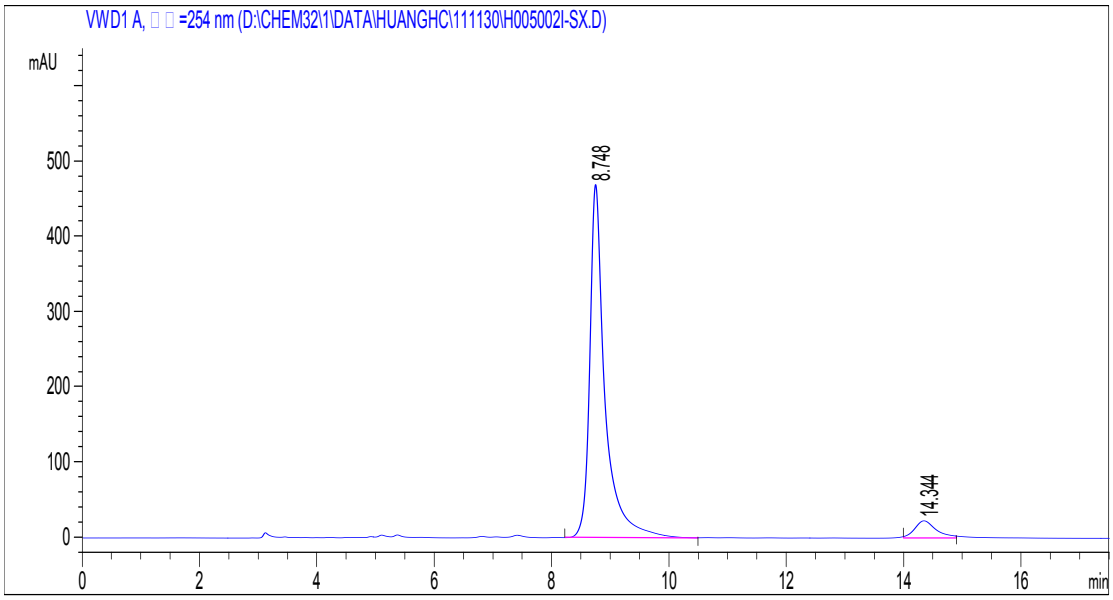


#	Time	Area	Height	Width	Symmetry	Area %
1	9.891	43627.2	1991.6	0.3138	0.528	94.983
2	13.768	2304.2	92.8	0.4138	0.753	5.017

4q: (*S*)-2-ethyl-2-((*R*)-3-oxo-1-(thiophen-2-yl)butyl)-5-phenylfuran-3(2*H*)-one

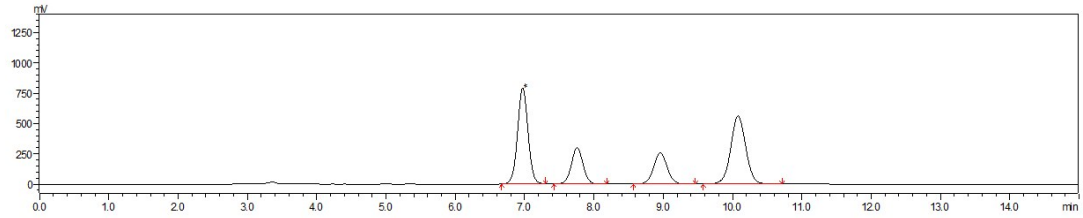


#	Time	Area	Height	Width	Symmetry	Area %
1	6.859	1495	112.4	0.1915	0.628	3.721
2	7.466	1697.3	106	0.2262	0.592	4.225
3	8.841	18469.9	1009.1	0.2616	0.576	45.974
4	14.537	18512.1	609.9	0.5059	0.622	46.079

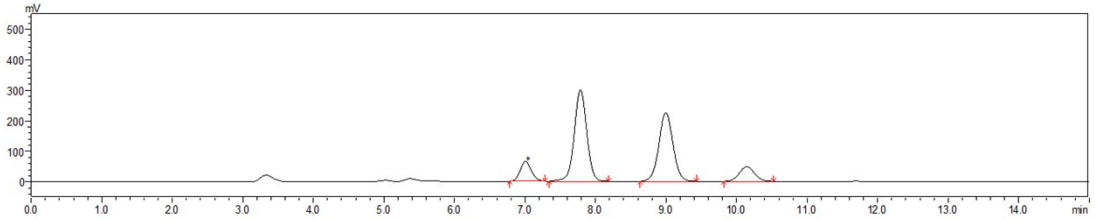


#	Time	Area	Height	Width	Symmetry	Area %
1	8.748	8479	470.1	0.2585	0.565	93.529
2	14.344	586.6	22.9	0.4262	0.733	6.471

5: (*S*)-2-methyl-2-((*S*)-3-oxo-1,3-diphenylpropyl)-5-phenylfuran-3(2*H*)-one



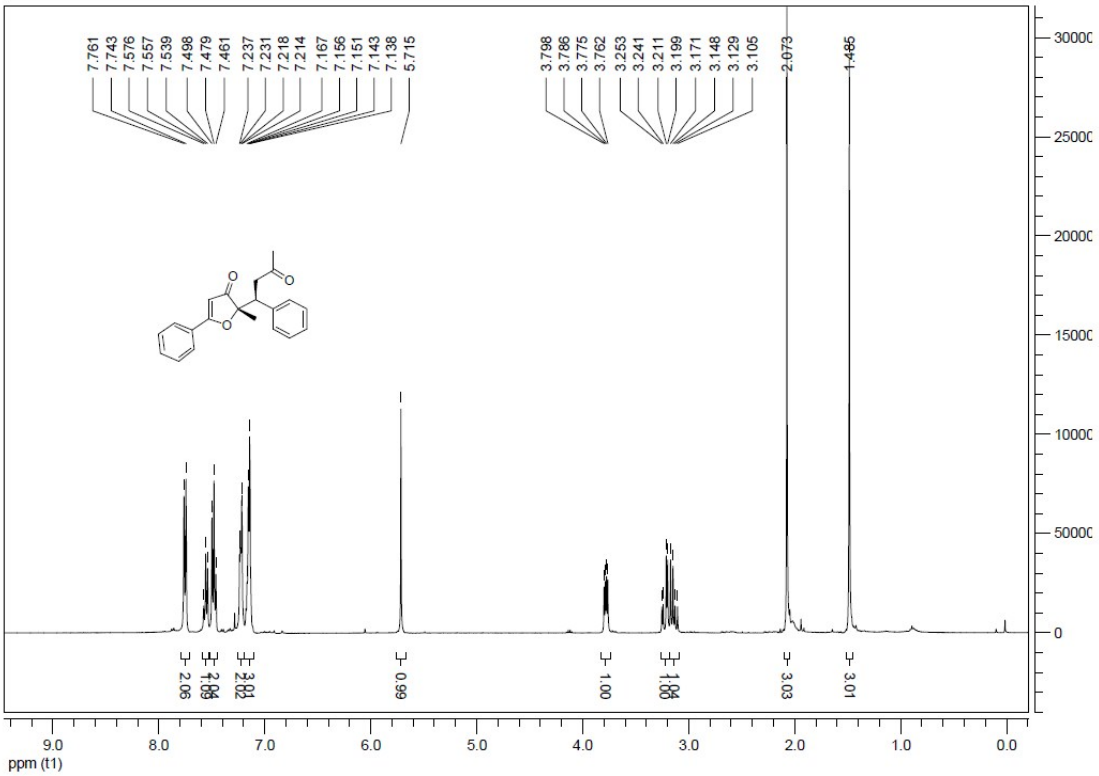
#	Time	Area	Height	Area %
1	6.971	8315867	789963	34.864
2	7.757	3511879	300854	14.723
3	8.956	3526795	259278	14.786
4	10.078	8497895	560995	35.627

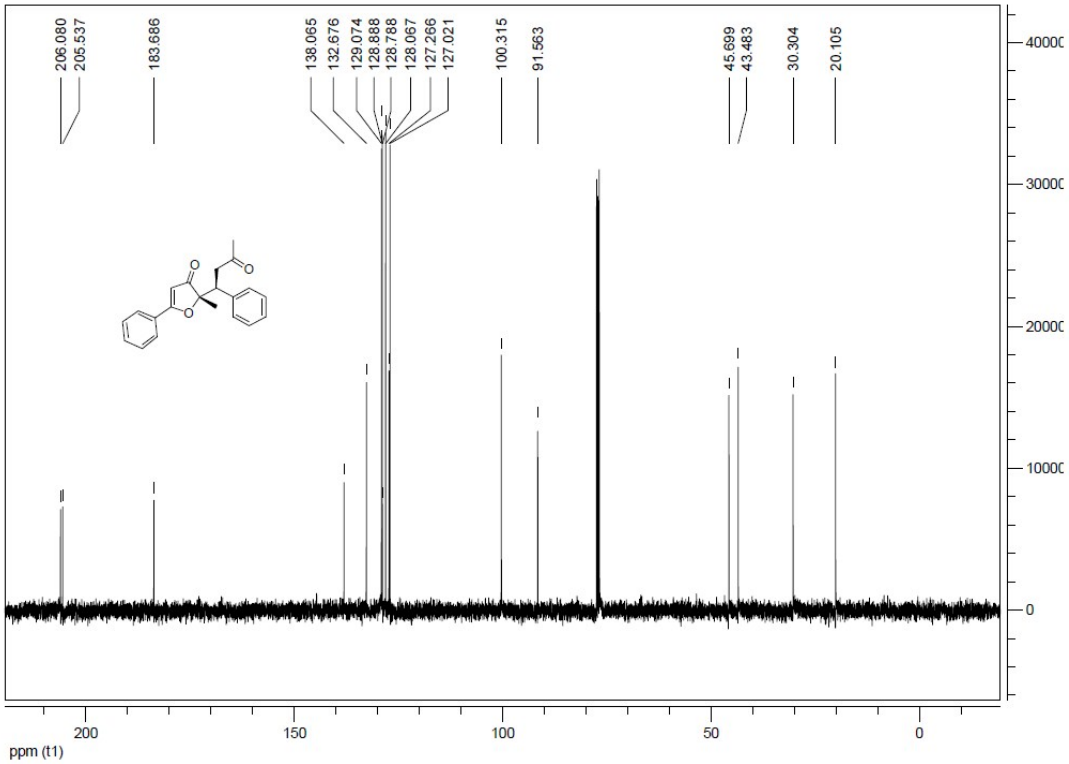


#	Time	Area	Height	Area %
1	7.007	722395	65404	8.680
2	7.787	3713056	299237	44.616
3	8.997	3144677	225468	37.787
4	10.145	742074	48601	8.917

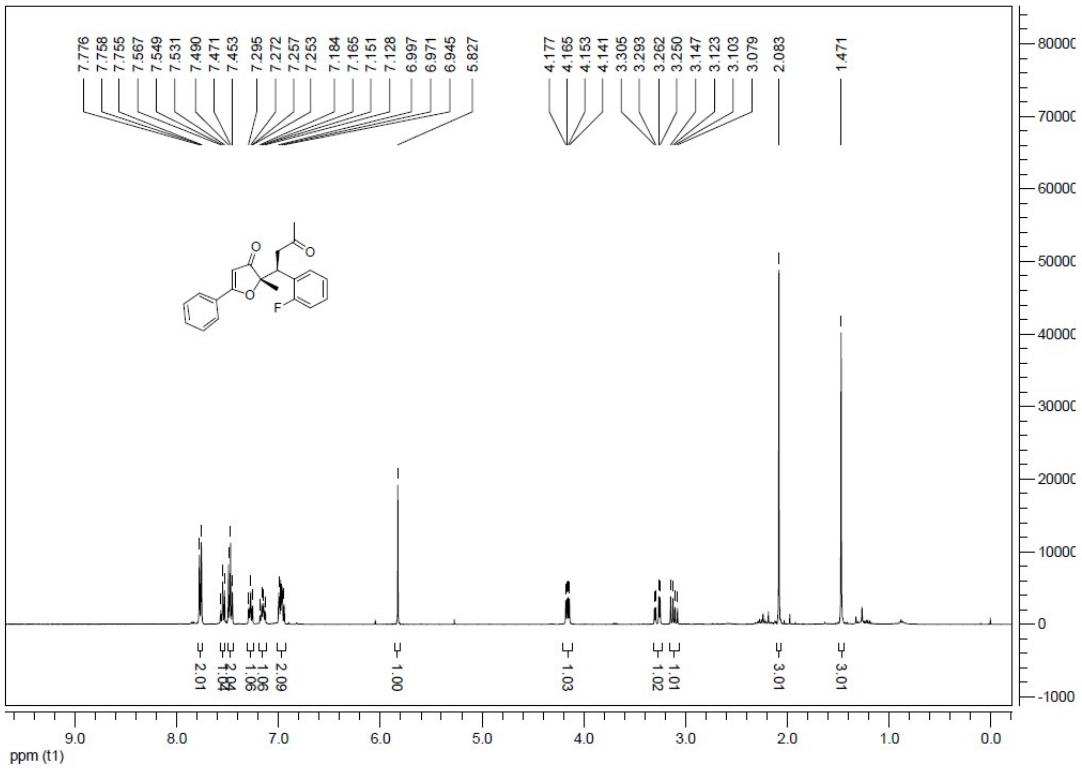
G: NMR Spectra of Asymmetric Addition Products

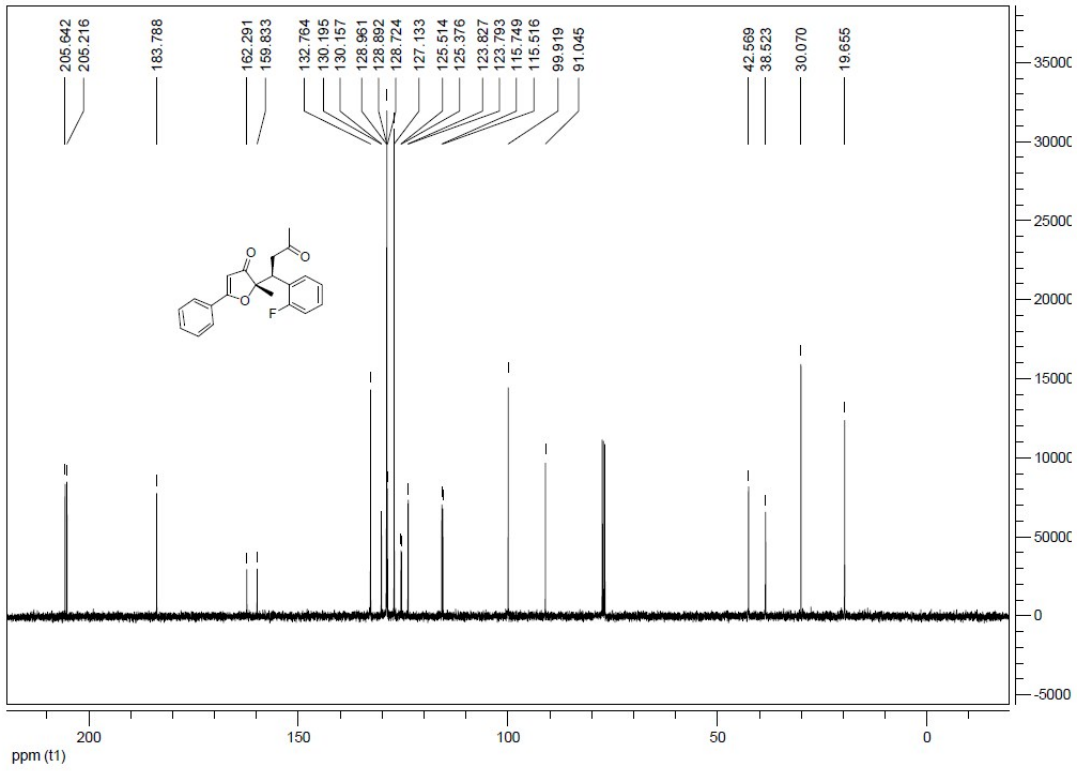
4a: (*S*)-2-methyl-2-((*S*)-3-oxo-1-phenylbutyl)-5-phenylfuran-3(2*H*)-one



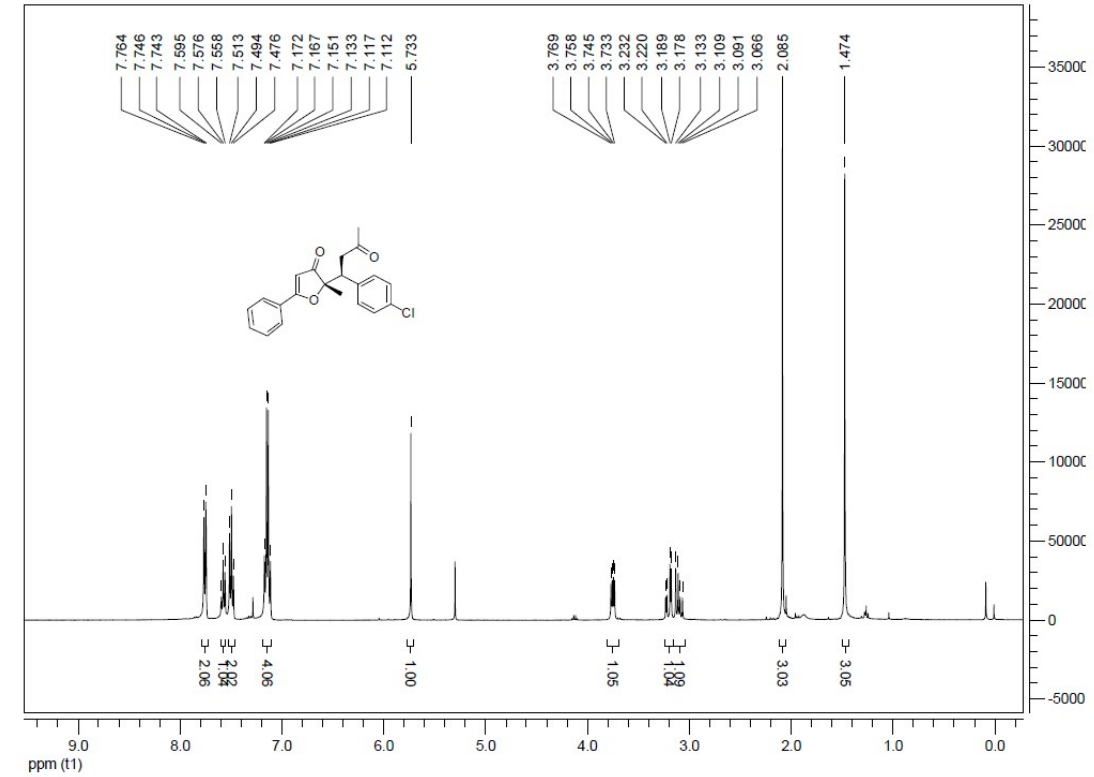


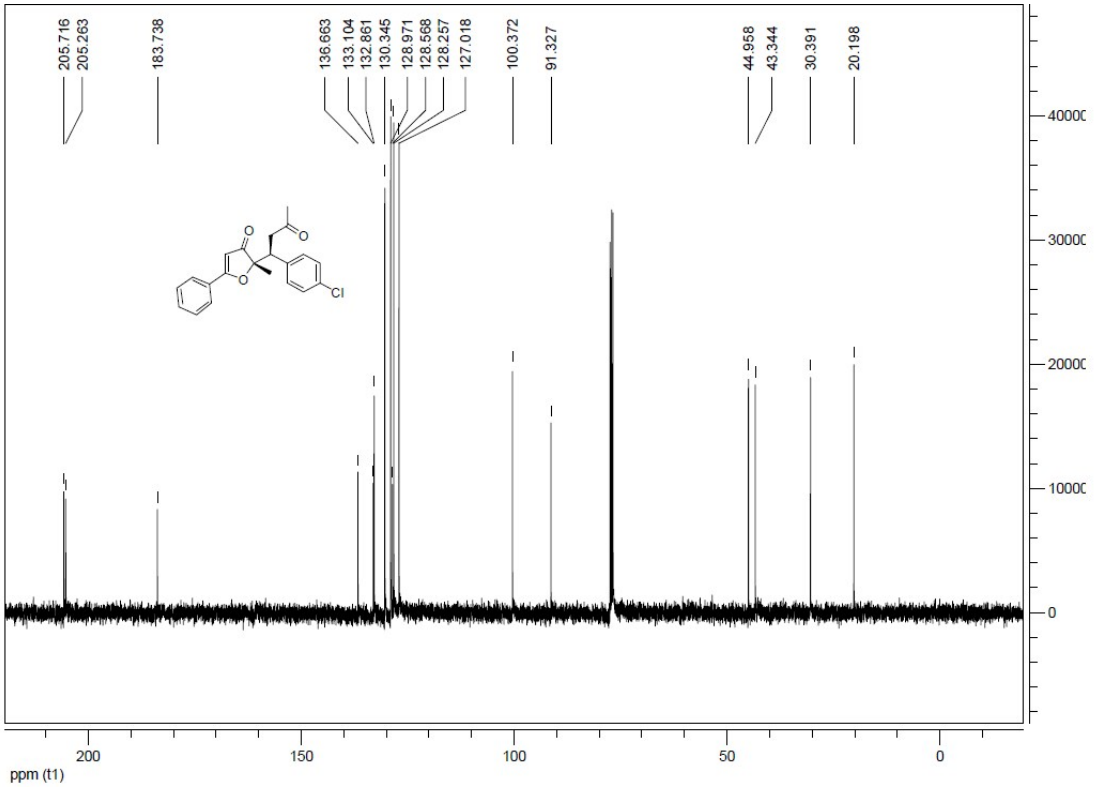
4b:(*S*)-2-((*S*)-1-(2-fluorophenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



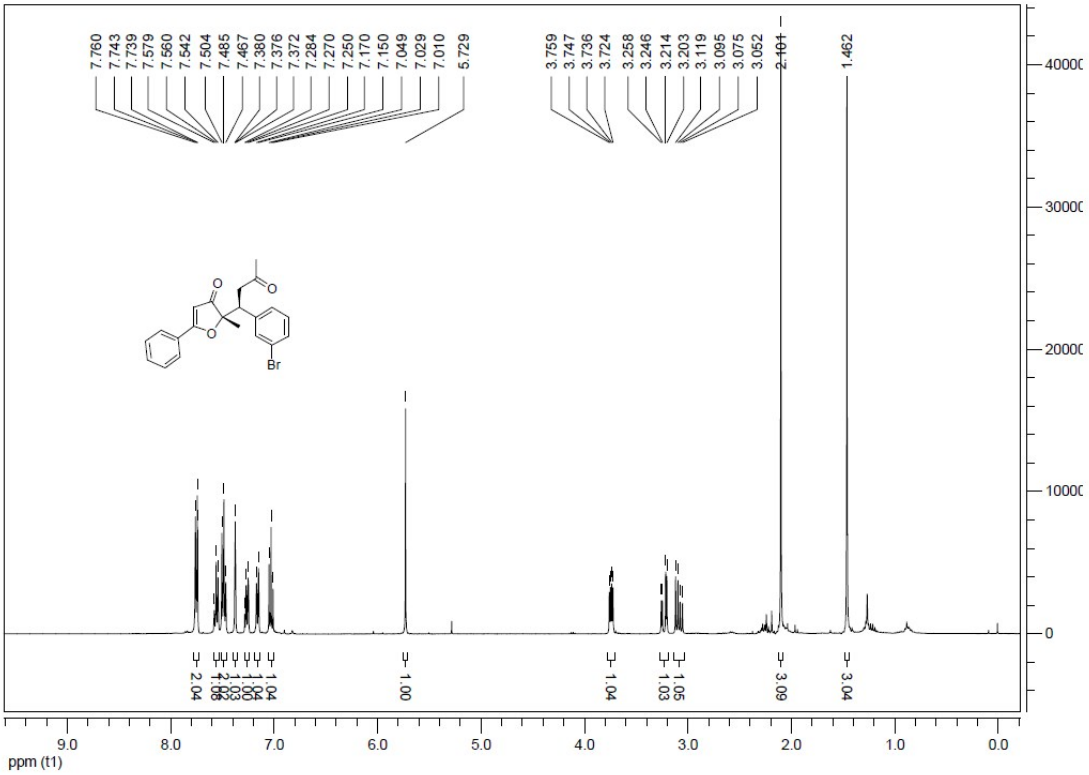


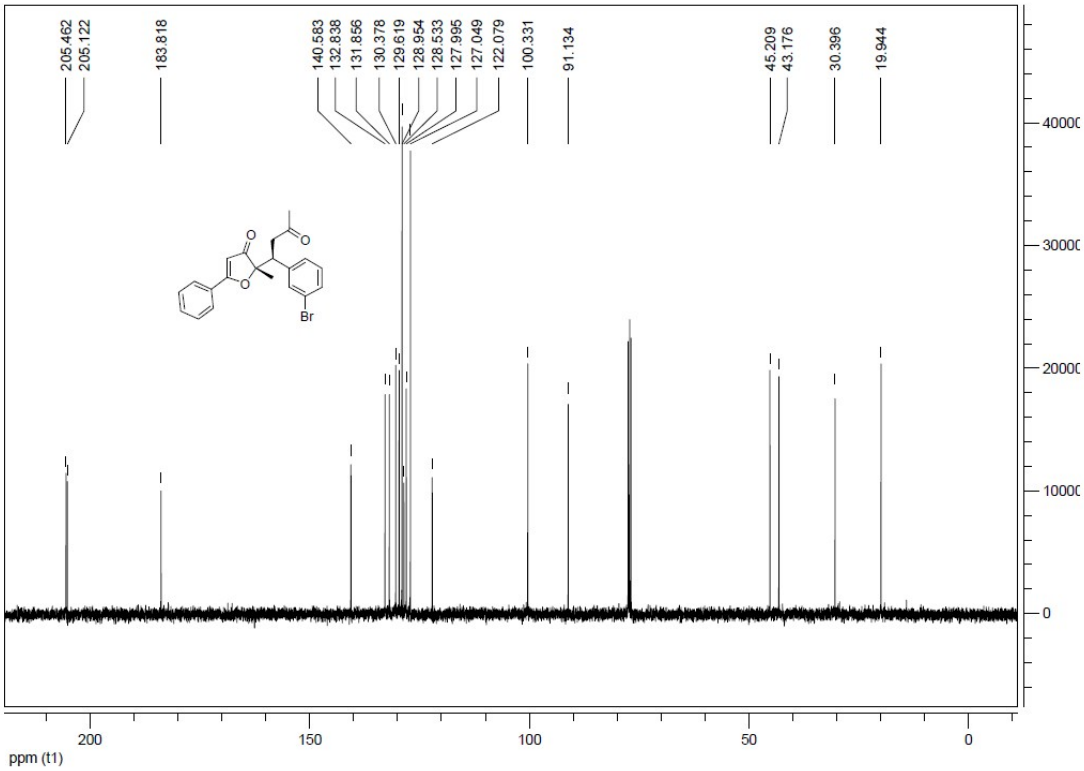
4c: (*S*)-2-((*S*)-1-(4-chlorophenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



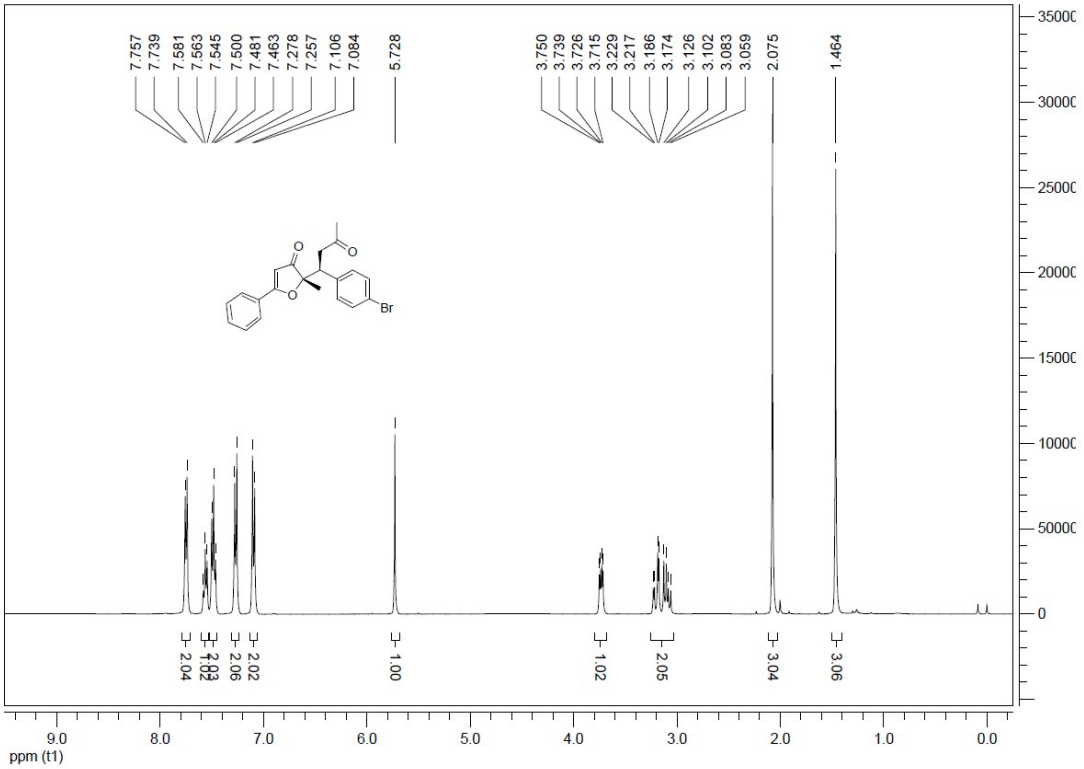


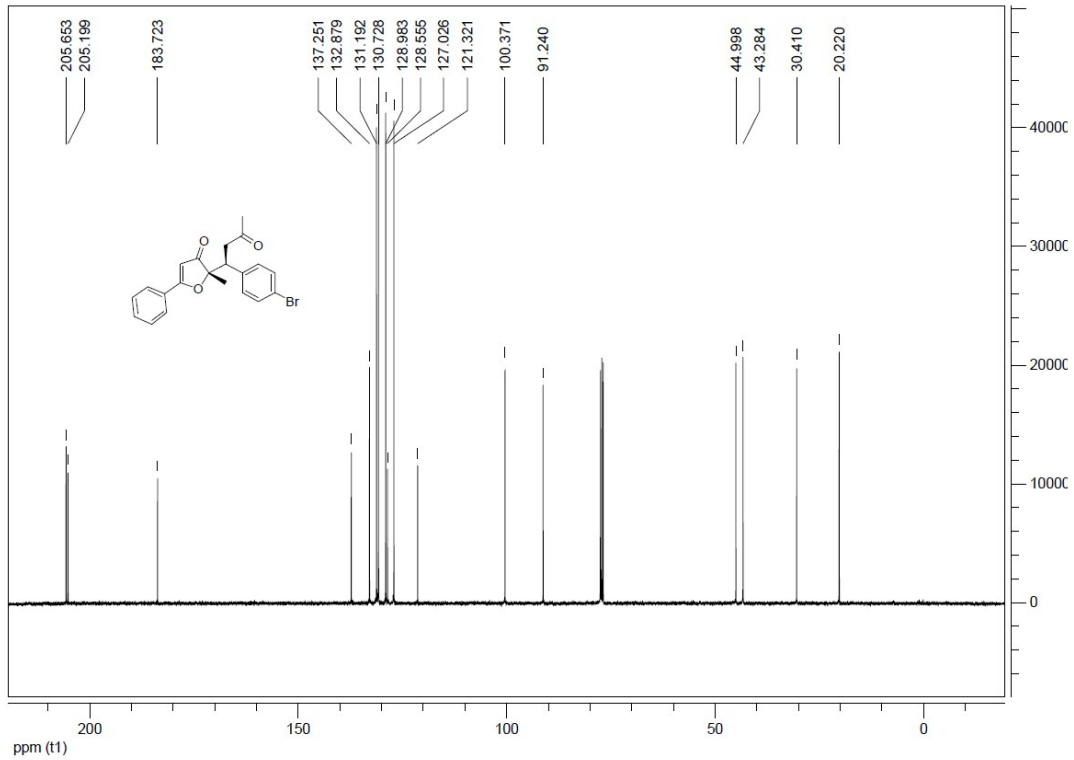
4d: (*S*)-2-((*S*)-1-(3-bromophenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



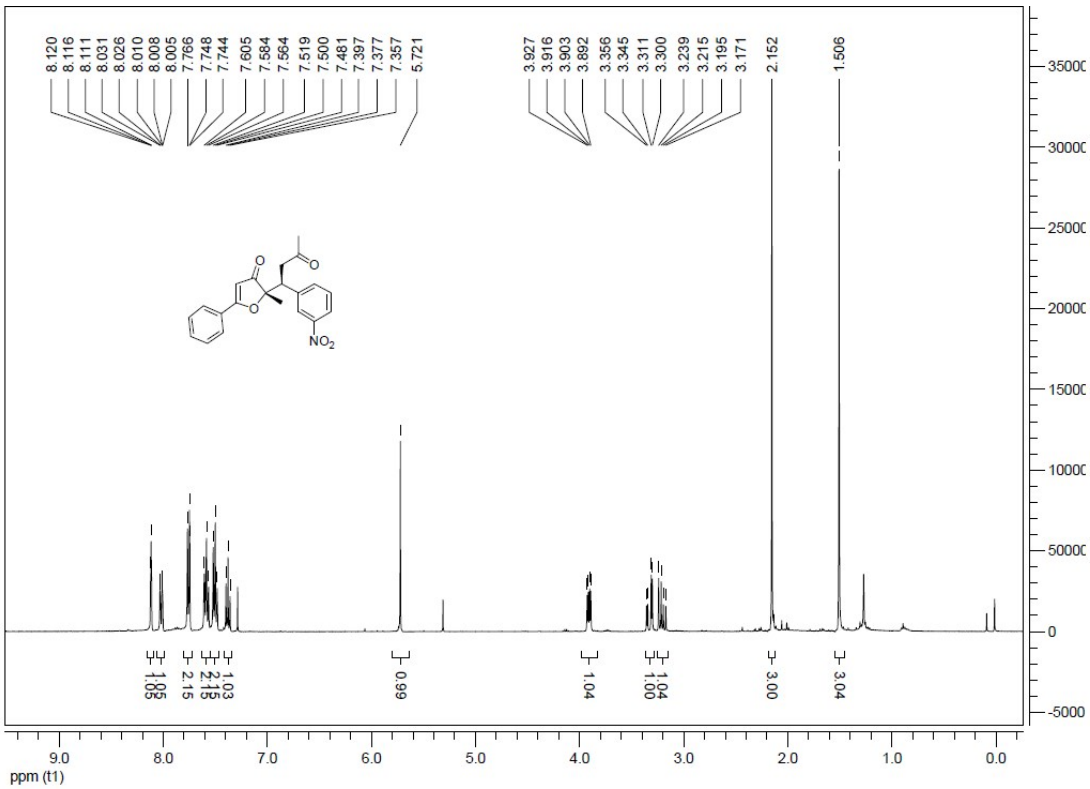


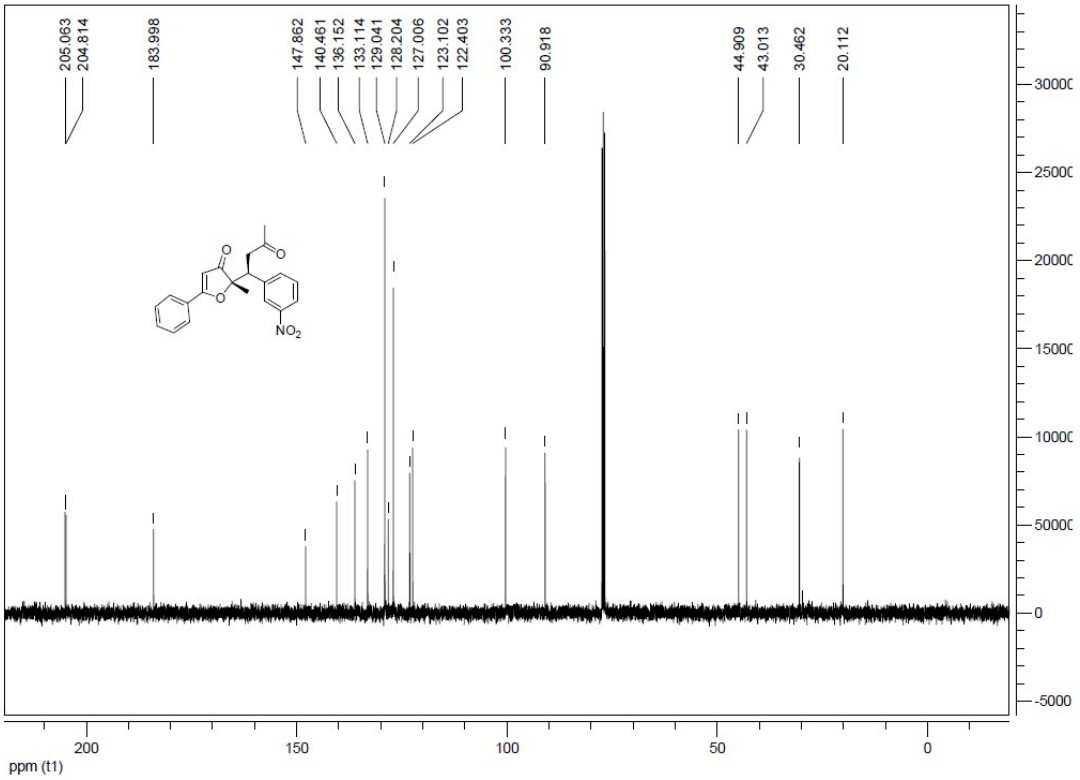
4e: (*S*)-2-((*S*)-1-(4-bromophenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



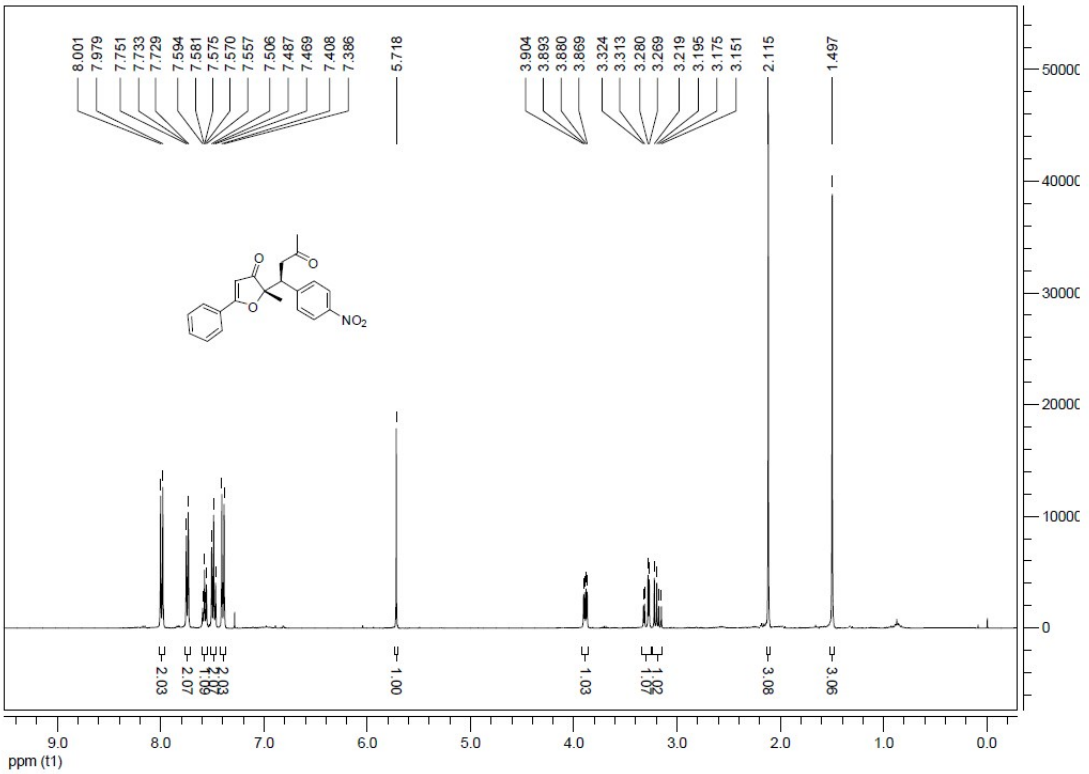


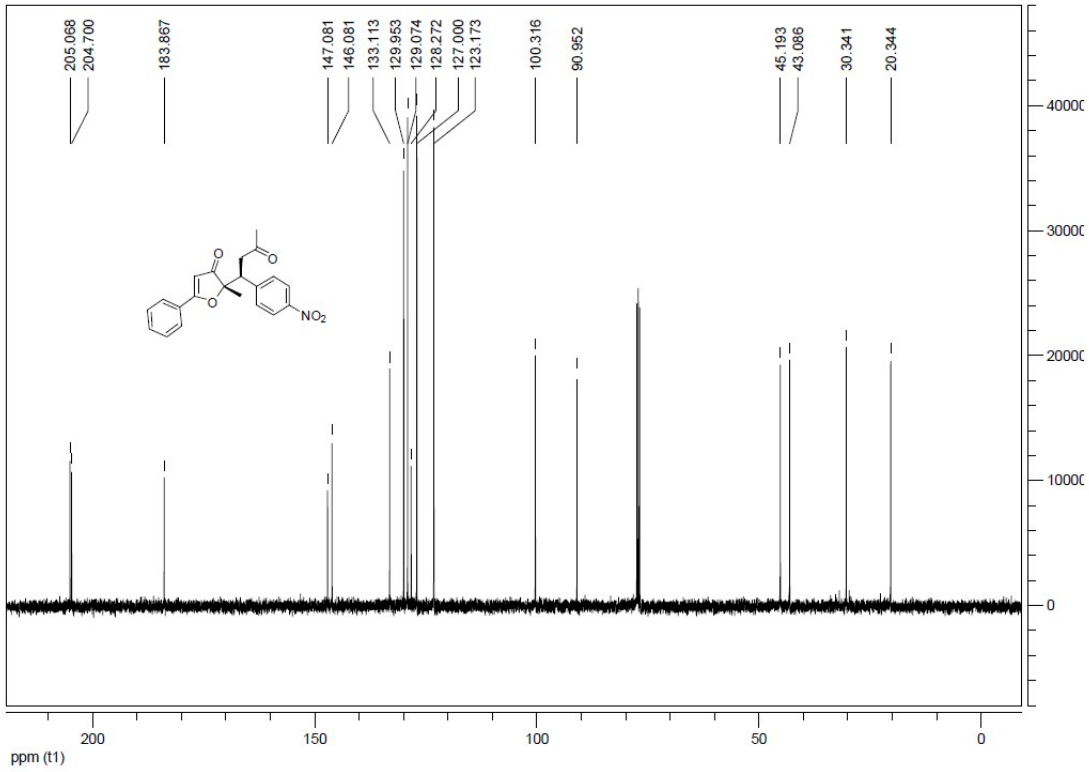
4f: (*S*)-2-methyl-2-((*S*)-1-(3-nitrophenyl)-3-oxobutyl)-5-phenylfuran-3(2*H*)-one



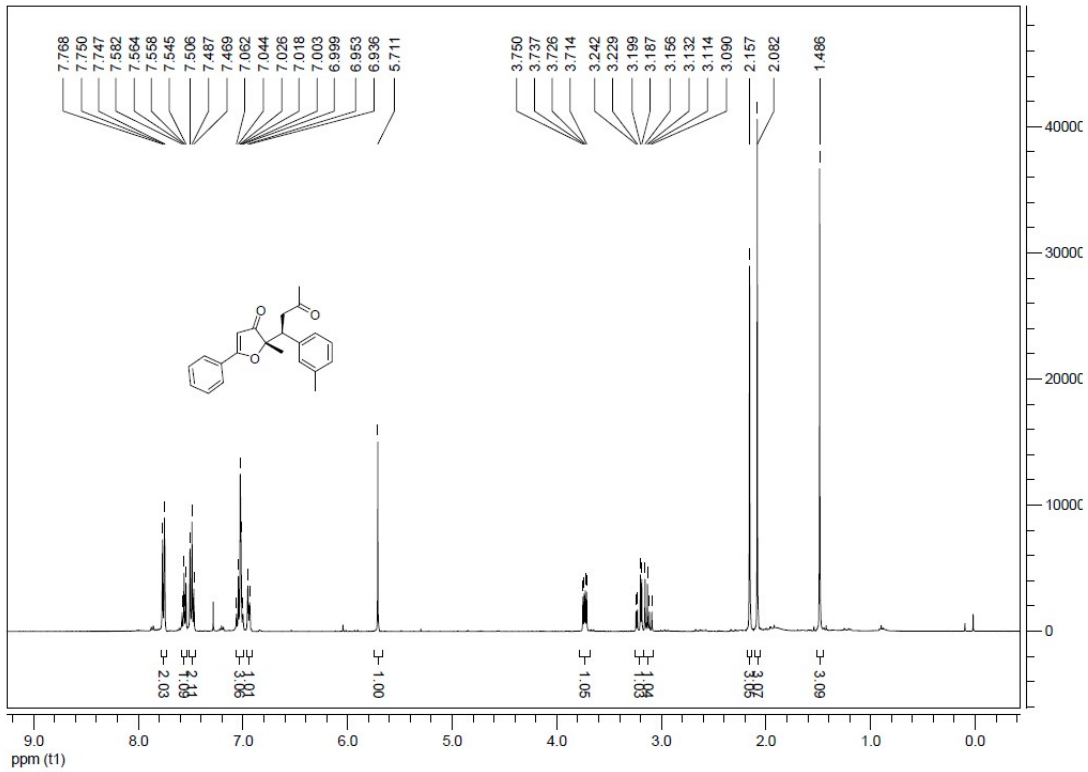


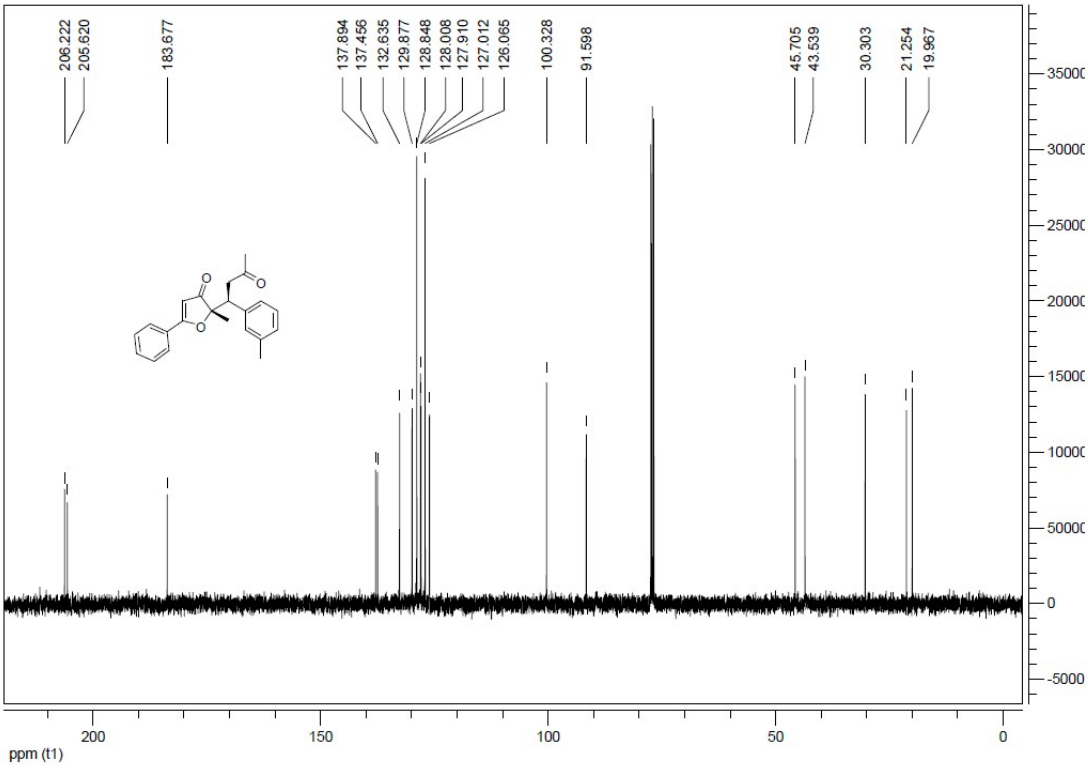
4g: (*S*)-2-methyl-2-((*S*)-1-(4-nitrophenyl)-3-oxobutyl)-5-phenylfuran-3(2*H*)-one



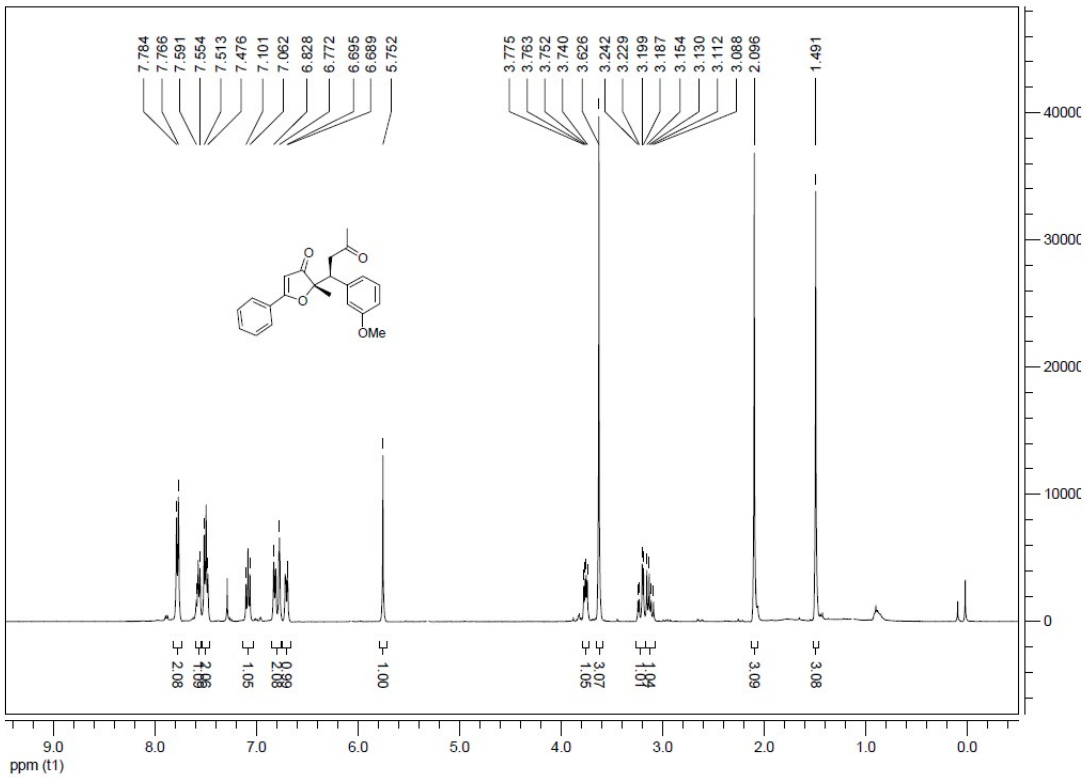


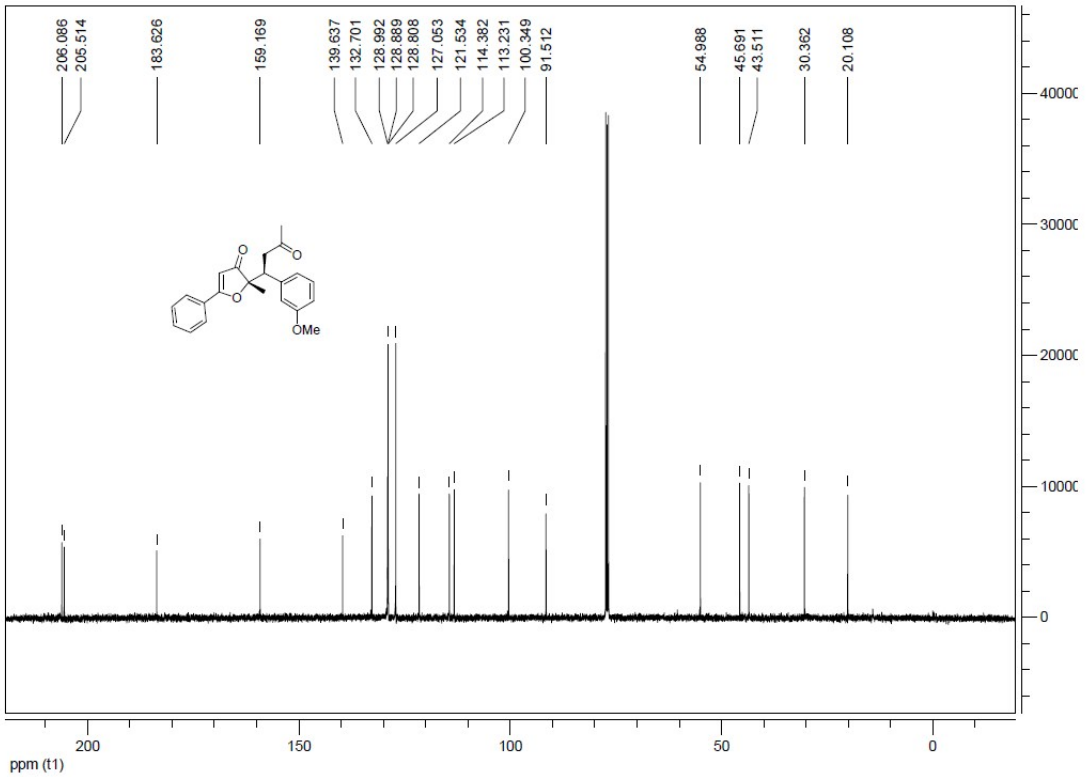
4h: (*S*)-2-methyl-2-((*S*)-3-oxo-1-m-tolylbutyl)-5-phenylfuran-3(2*H*)-one



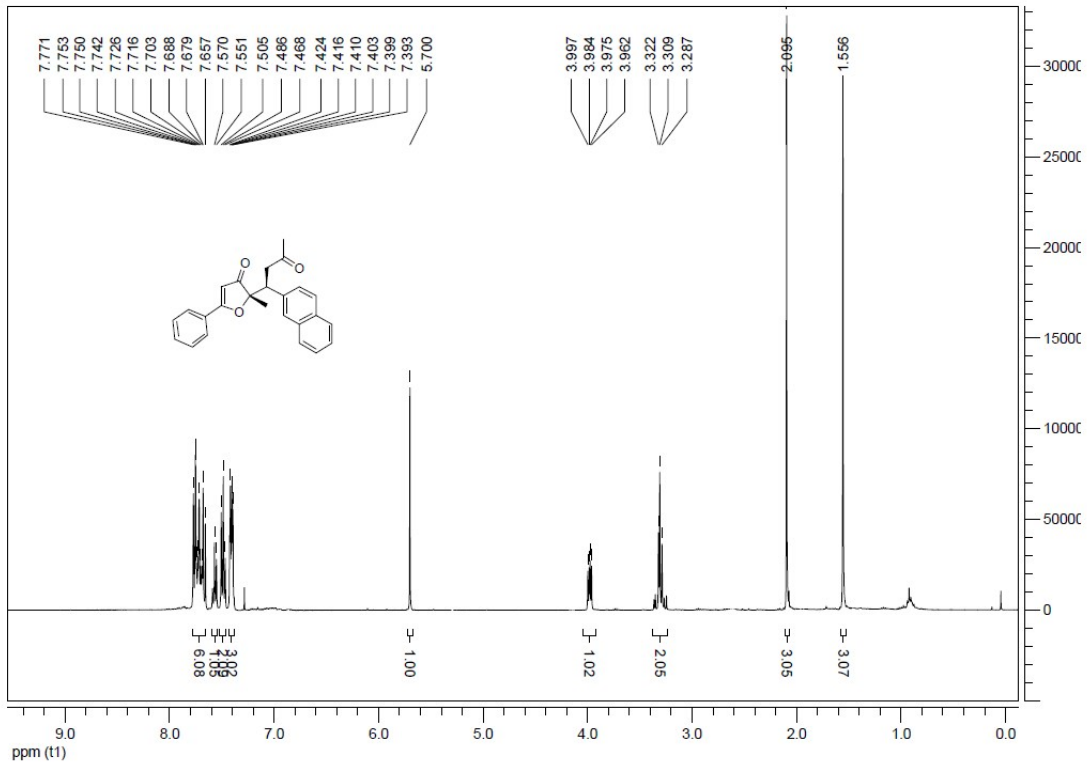


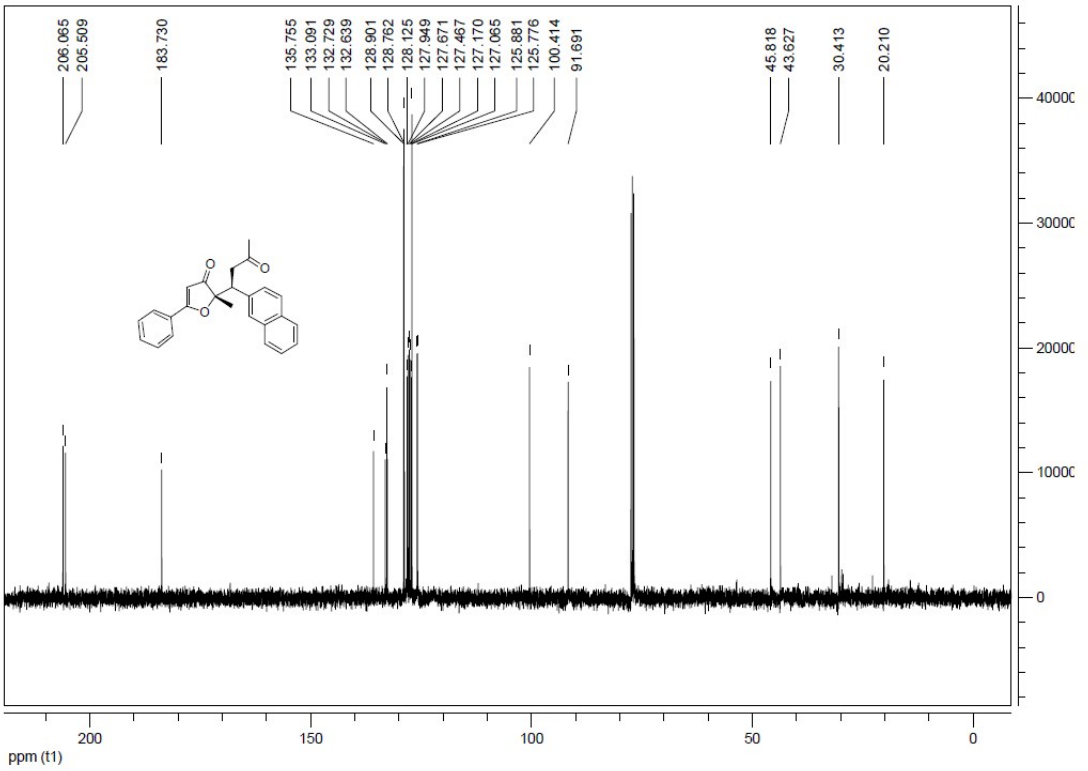
4i:(*S*)-2-((*S*)-1-(3-methoxyphenyl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



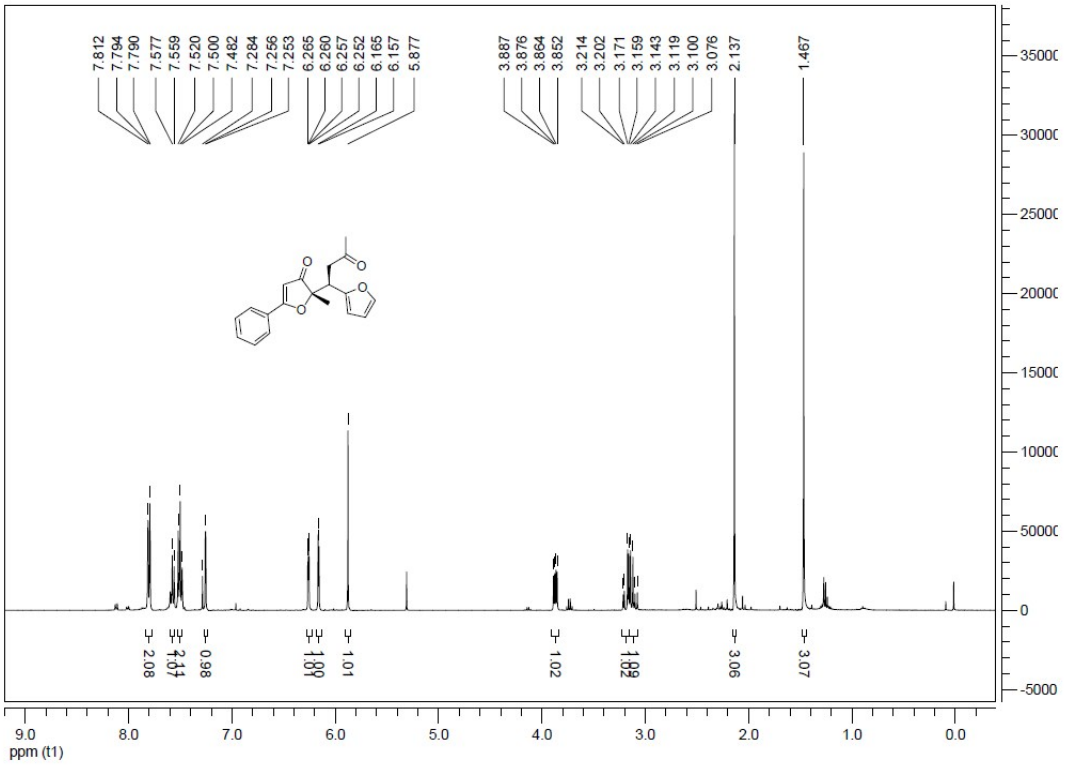


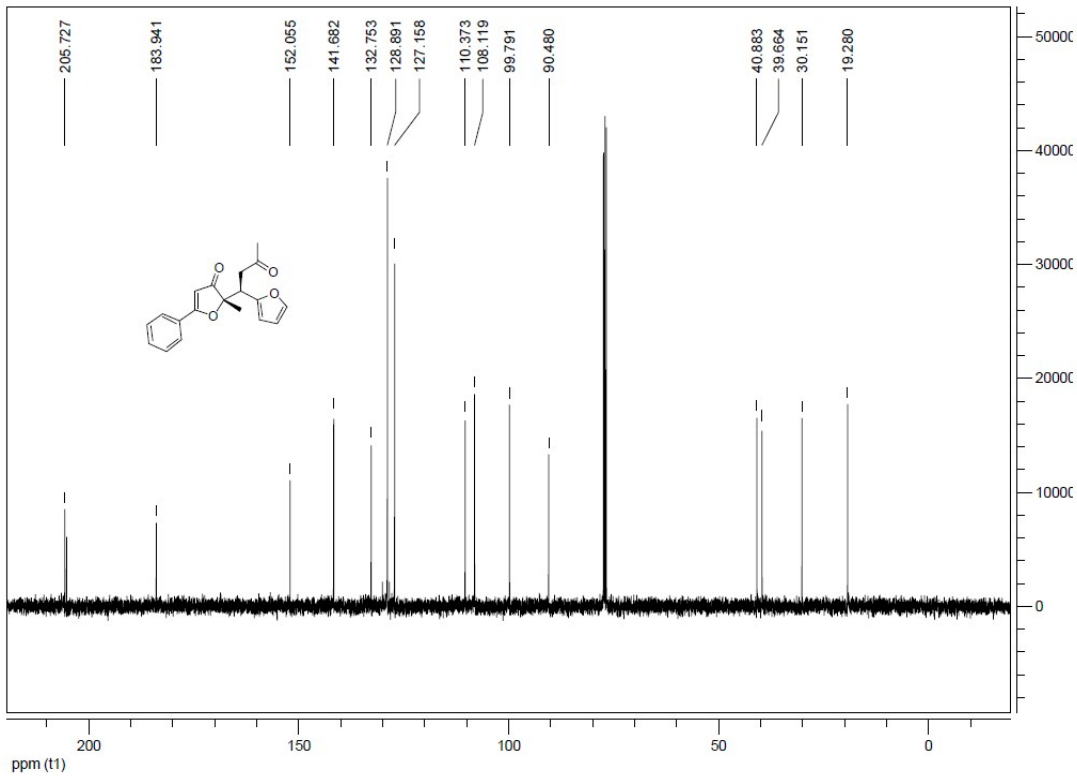
4j: (*S*)-2-methyl-2-((*S*)-1-(naphthalen-2-yl)-3-oxobutyl)-5-phenylfuran-3(2*H*)-one



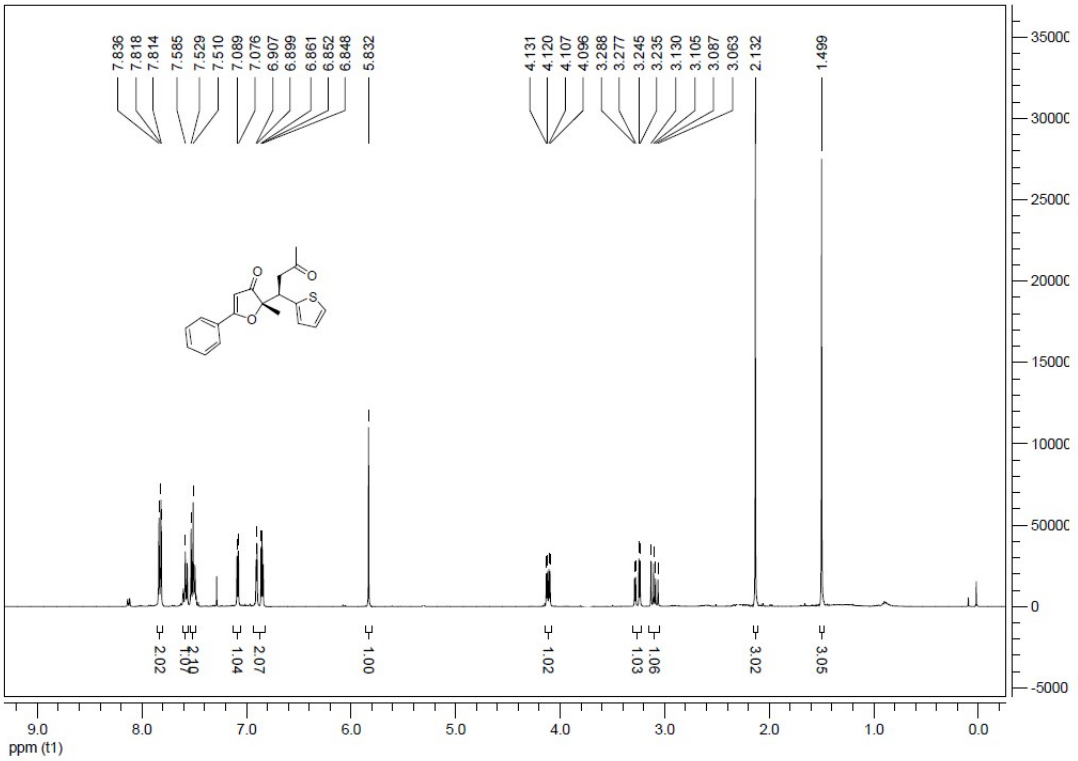


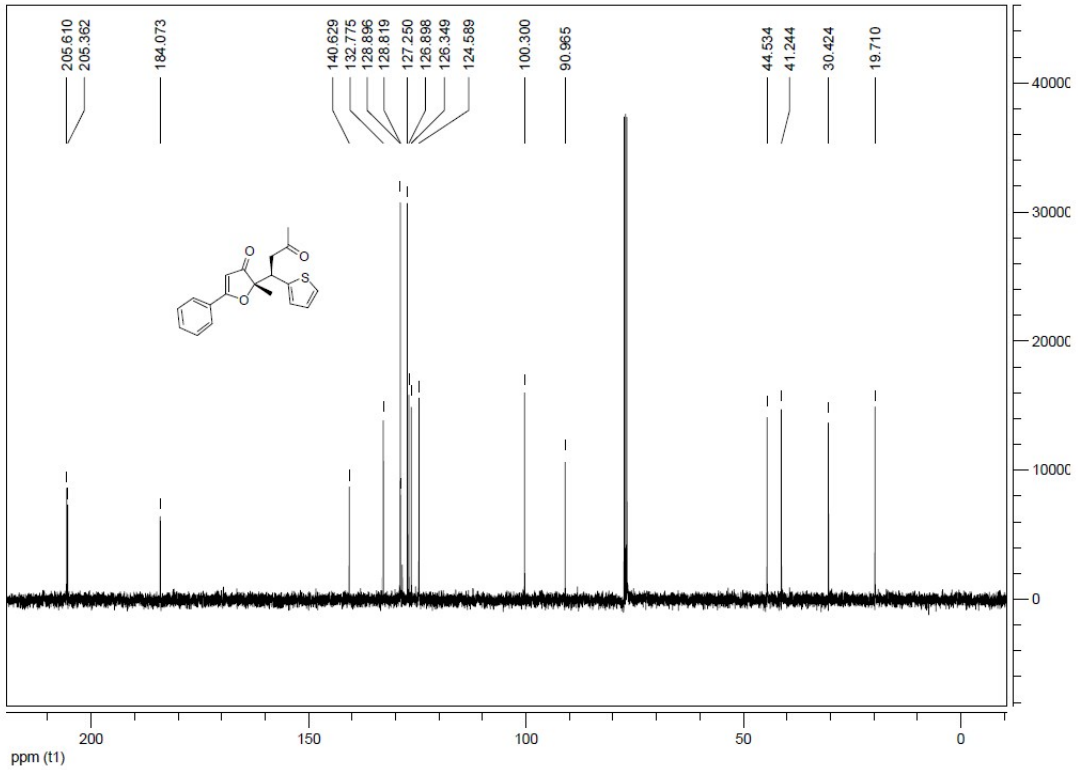
4k: (*S*)-2-((*S*)-1-(furan-2-yl)-3-oxobutyl)-2-methyl-5-phenylfuran-3(2*H*)-one



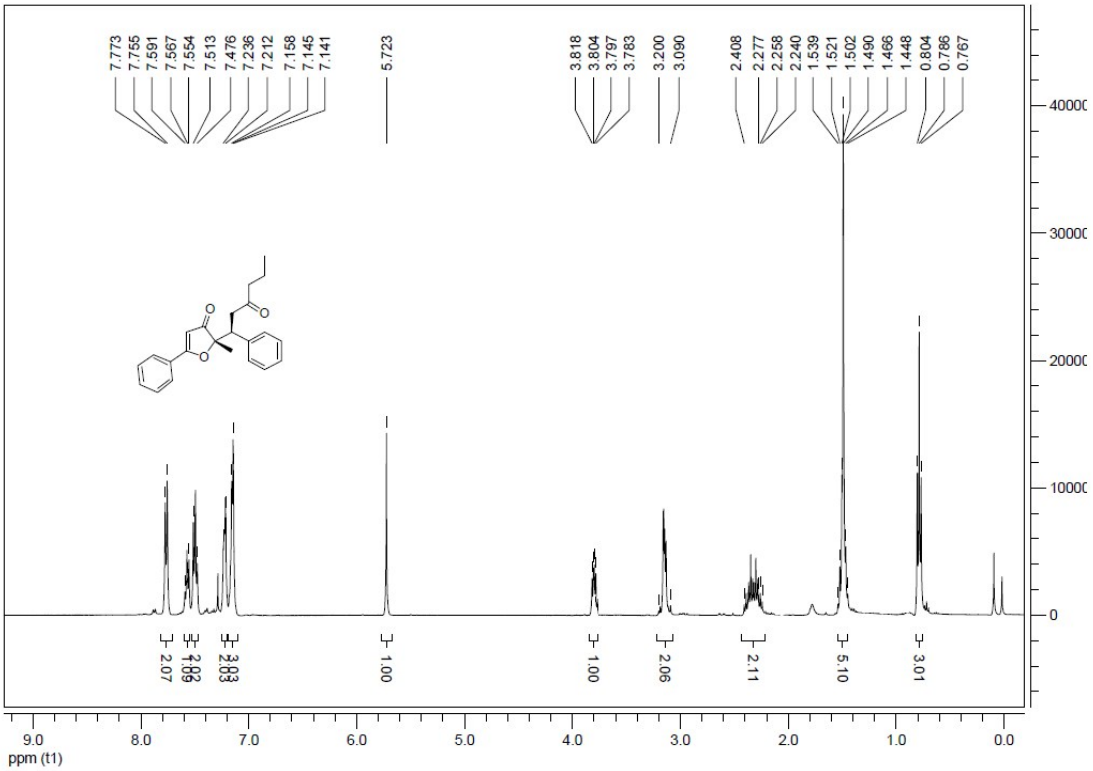


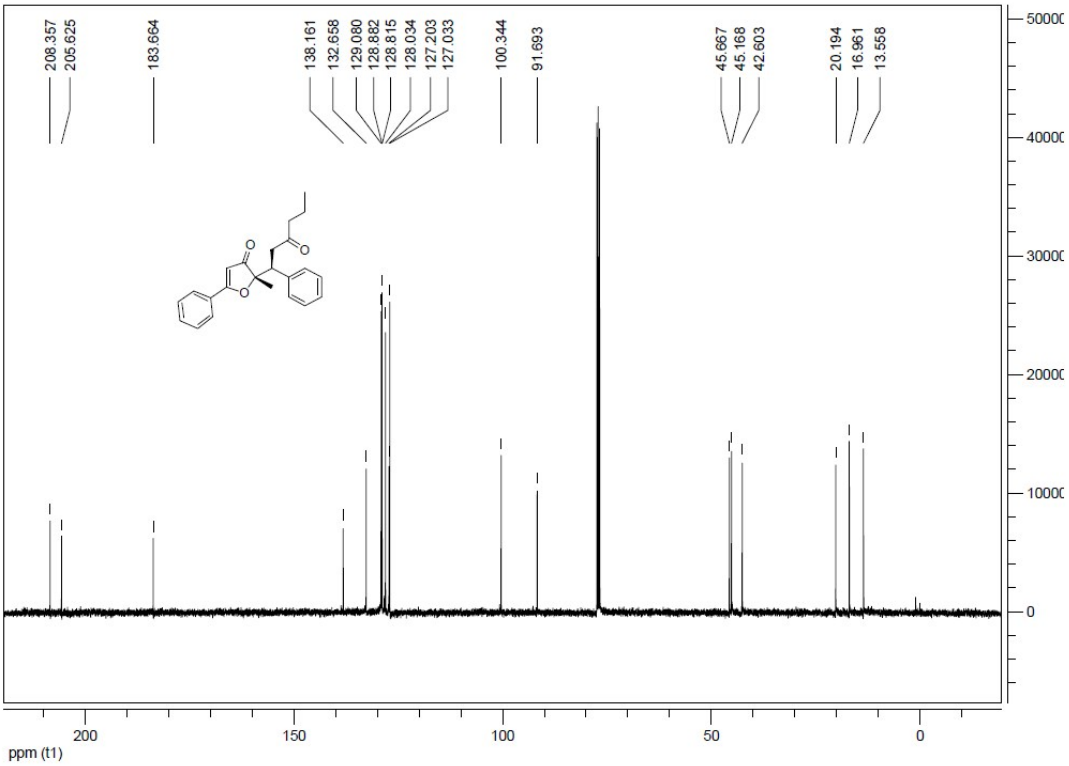
4l: (*S*)-2-methyl-2-((*R*)-3-oxo-1-(thiophen-2-yl)butyl)-5-phenylfuran-3(2*H*)-one



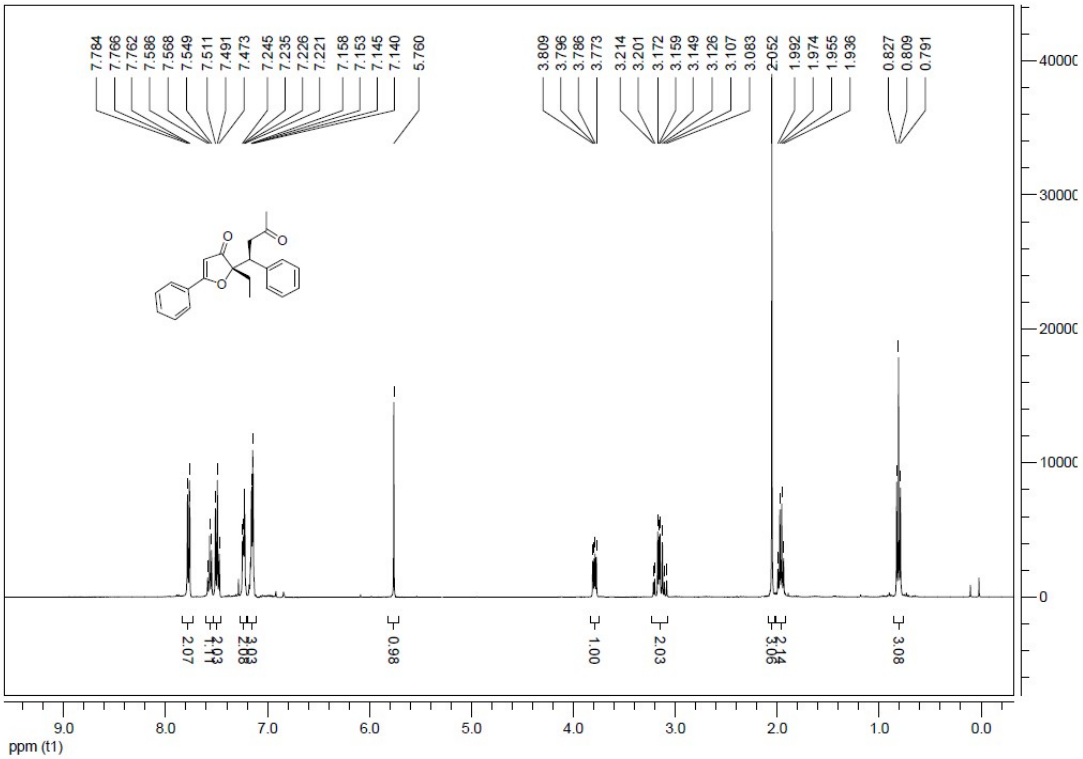


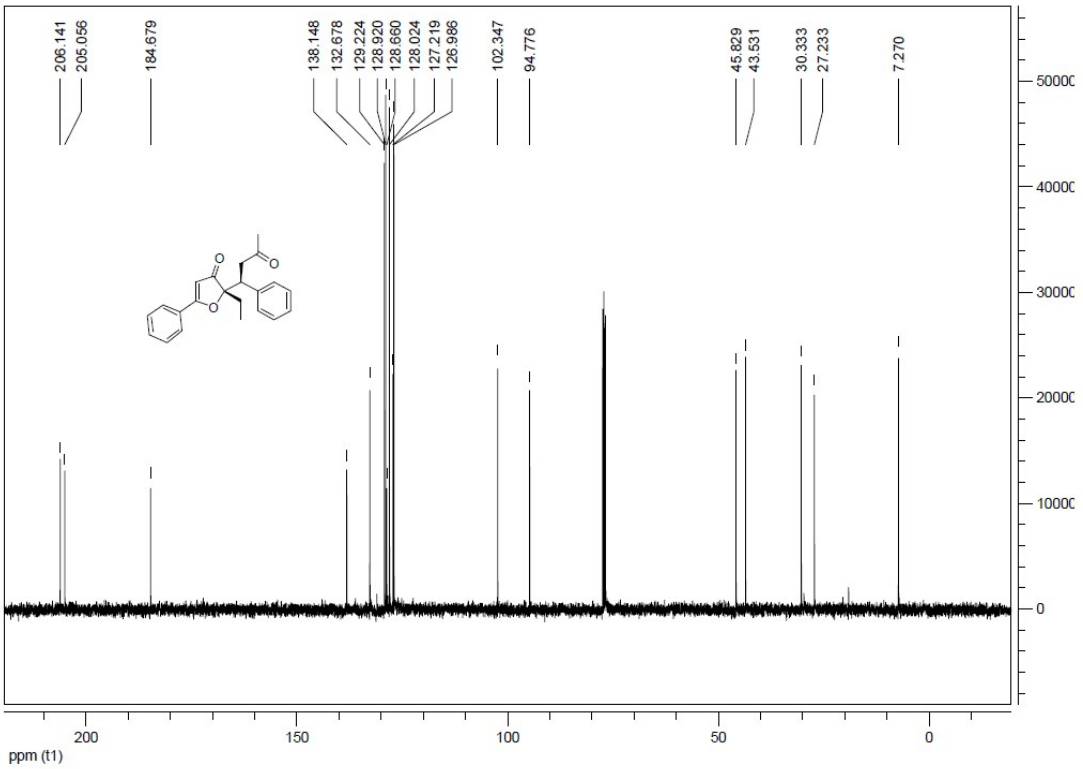
4m: (*S*)-2-methyl-2-((*S*)-3-oxo-1-phenylhexyl)-5-phenylfuran-3(2*H*)-one



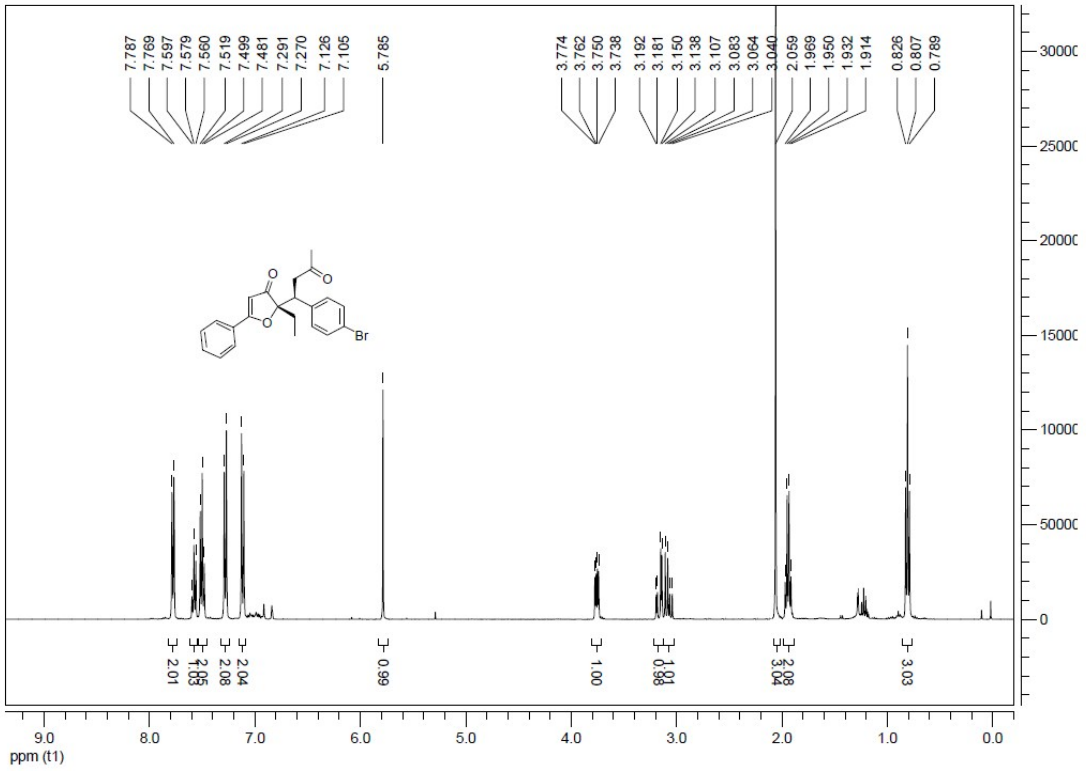


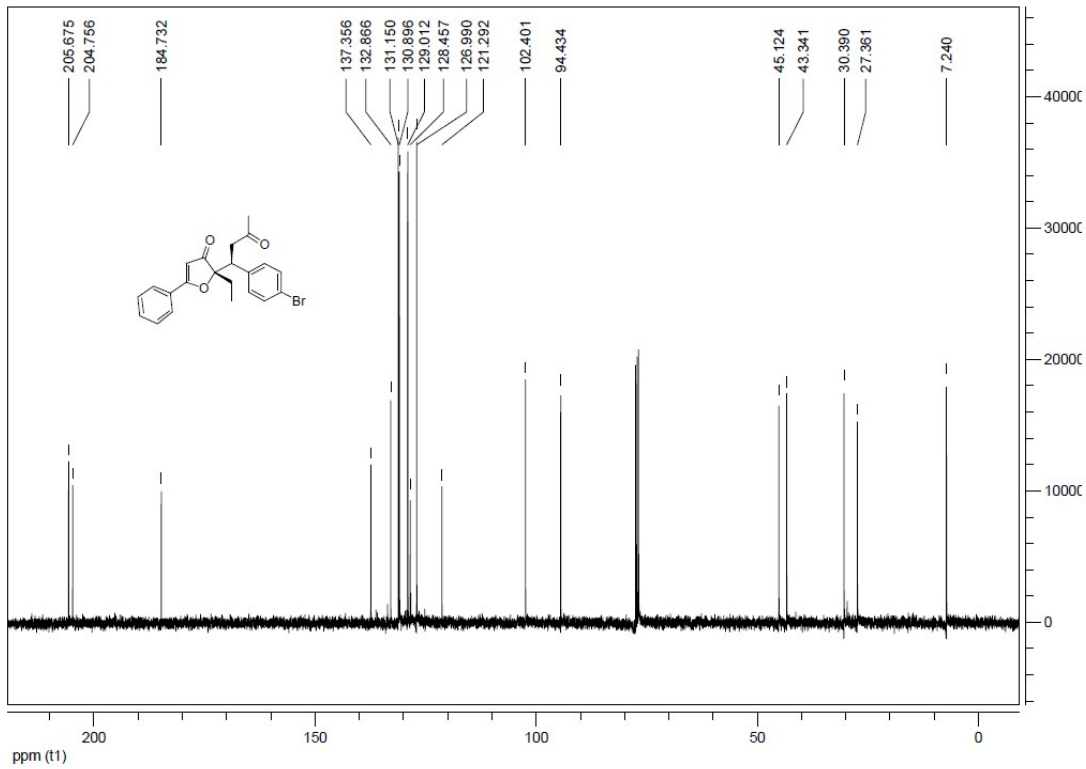
4n: (*S*)-2-ethyl-2-((*S*)-3-oxo-1-phenylbutyl)-5-phenylfuran-3(2*H*)-one



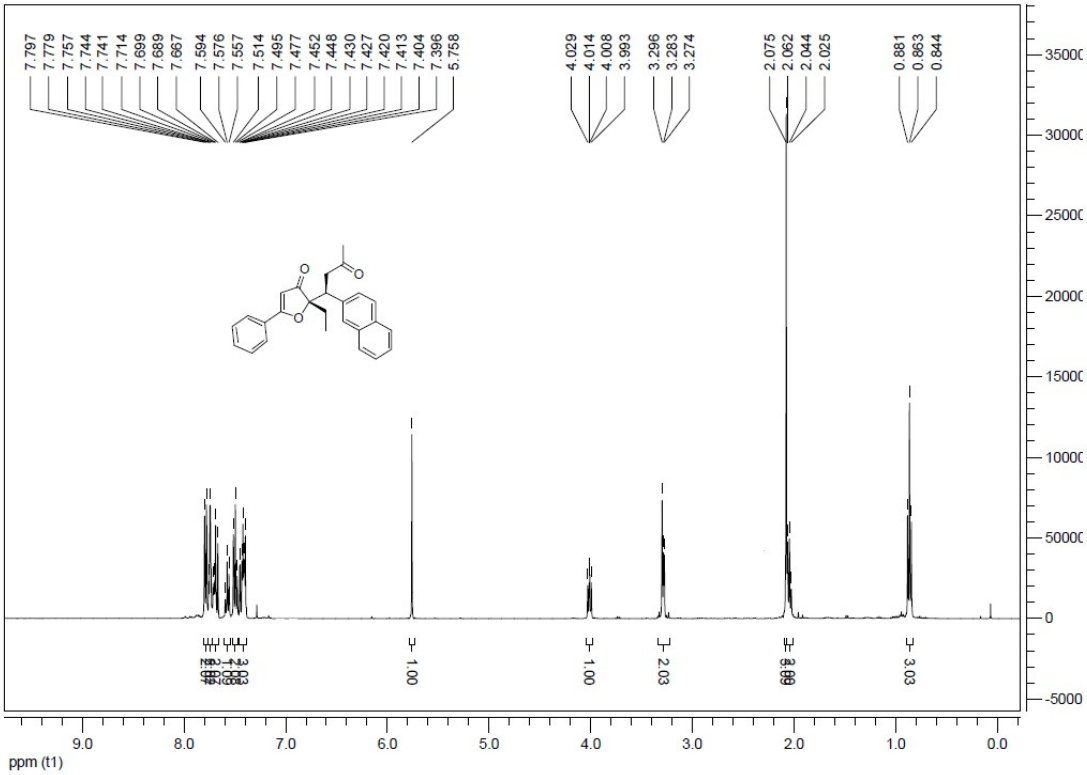


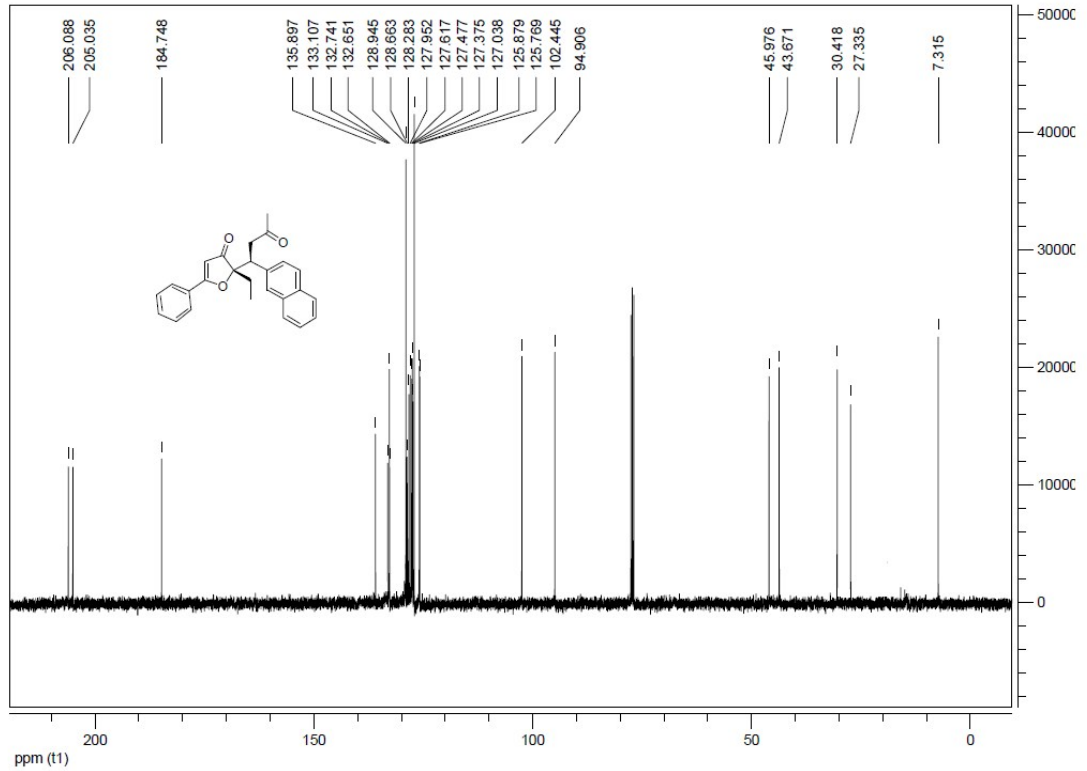
4o: (*S*)-2-((*S*)-1-(4-bromophenyl)-3-oxobutyl)-2-ethyl-5-phenylfuran-3(2*H*)-one



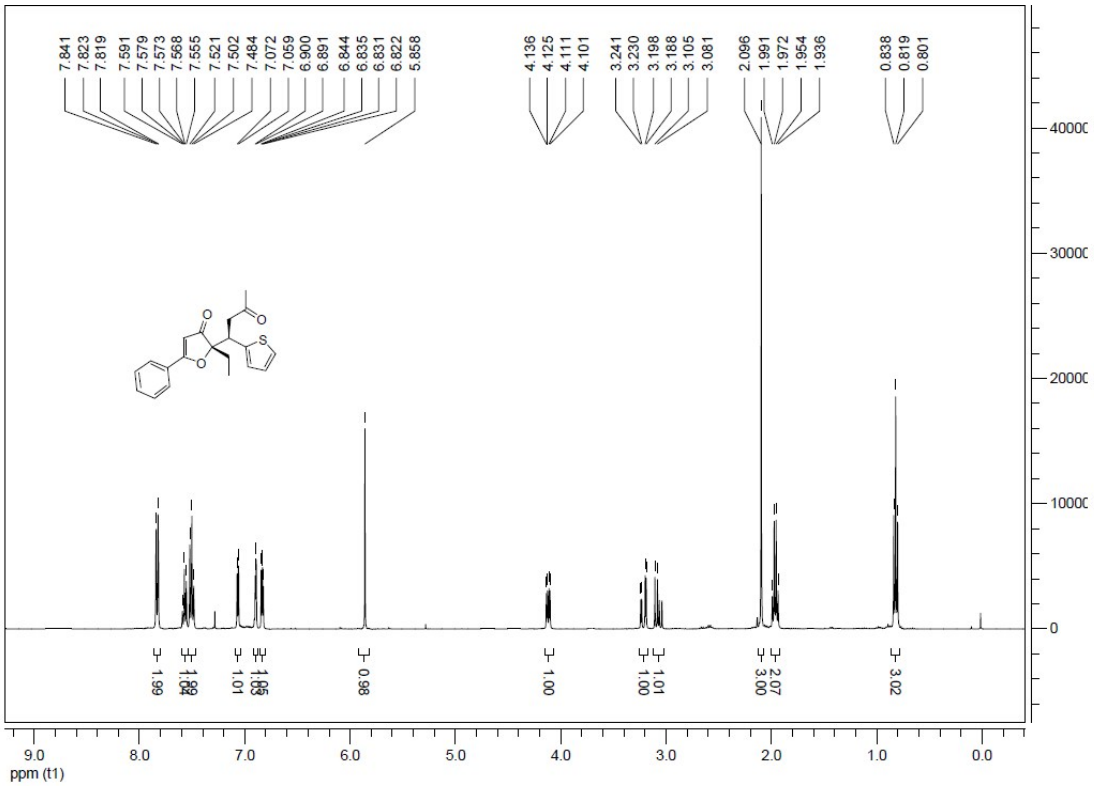


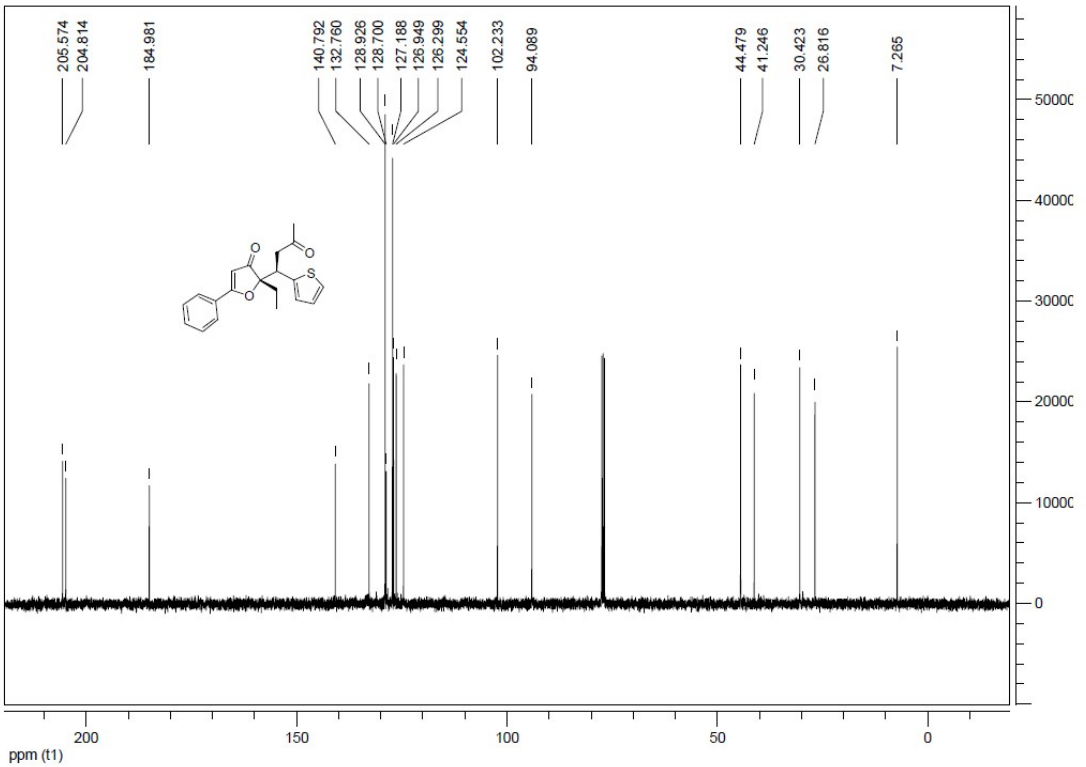
4p: (*S*)-2-ethyl-2-((*S*)-1-(naphthalen-2-yl)-3-oxobutyl)-5-phenylfuran-3(2*H*)-one



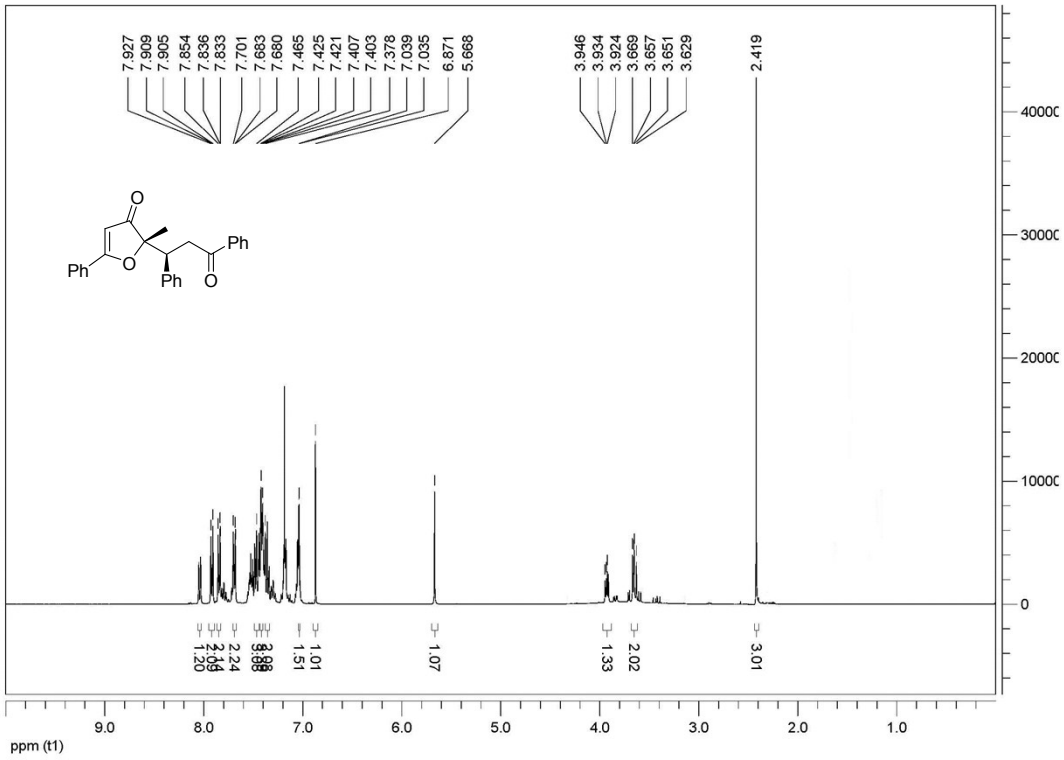


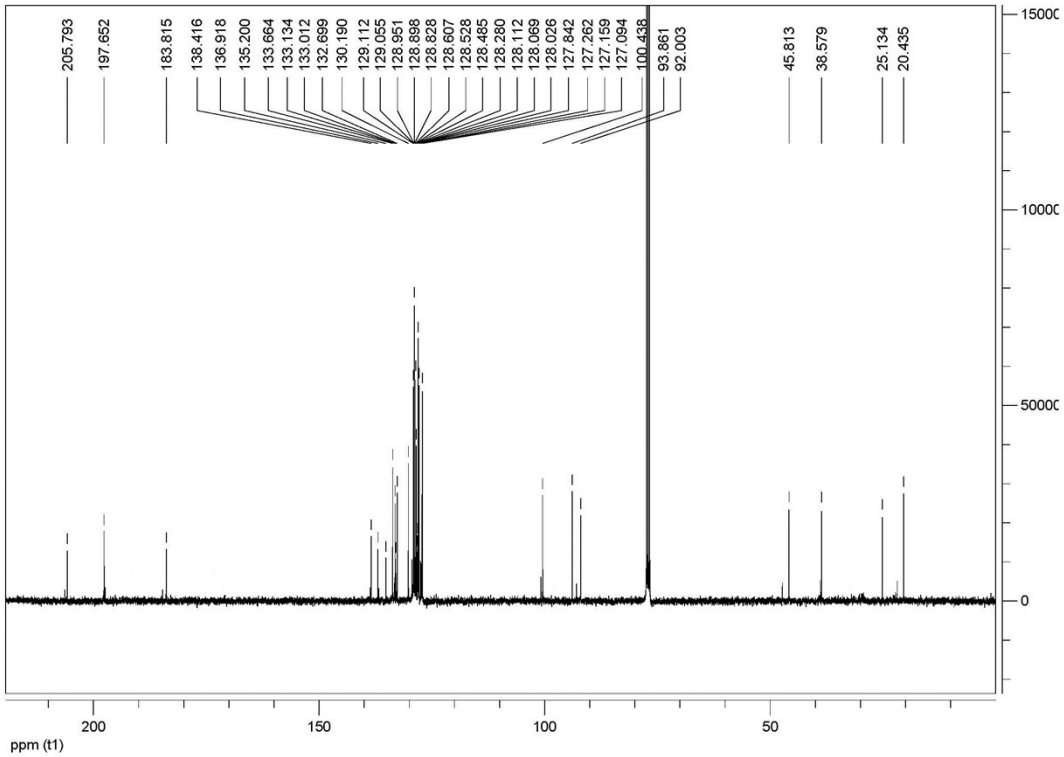
4q: (*S*)-2-ethyl-2-((*R*)-3-oxo-1-(thiophen-2-yl)butyl)-5-phenylfuran-3(2*H*)-one



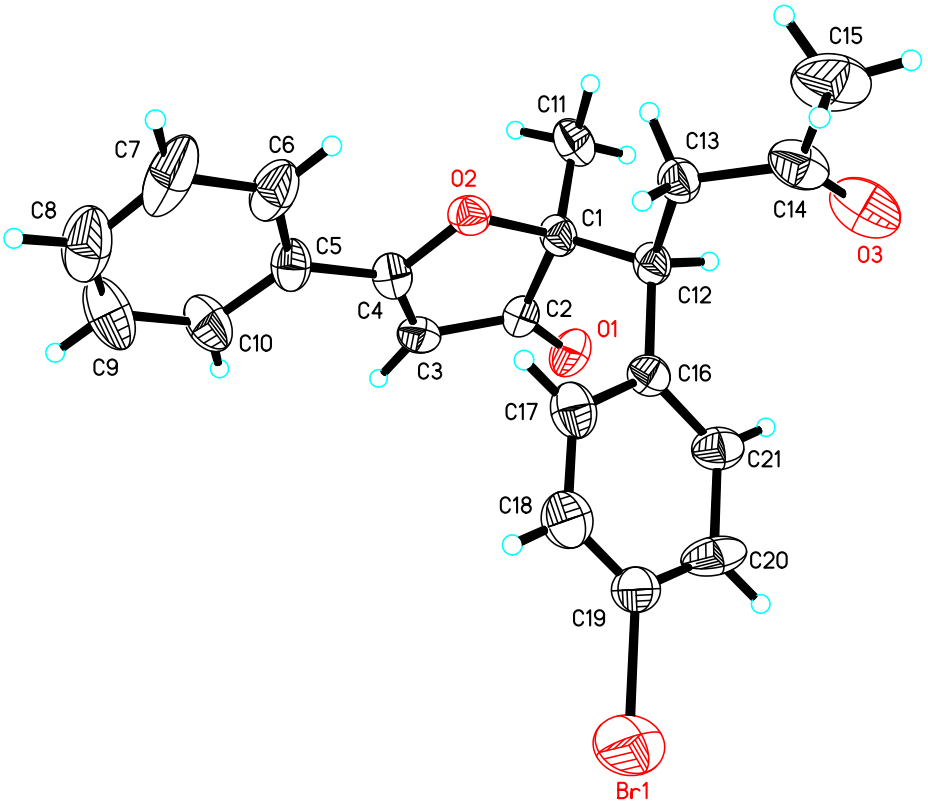


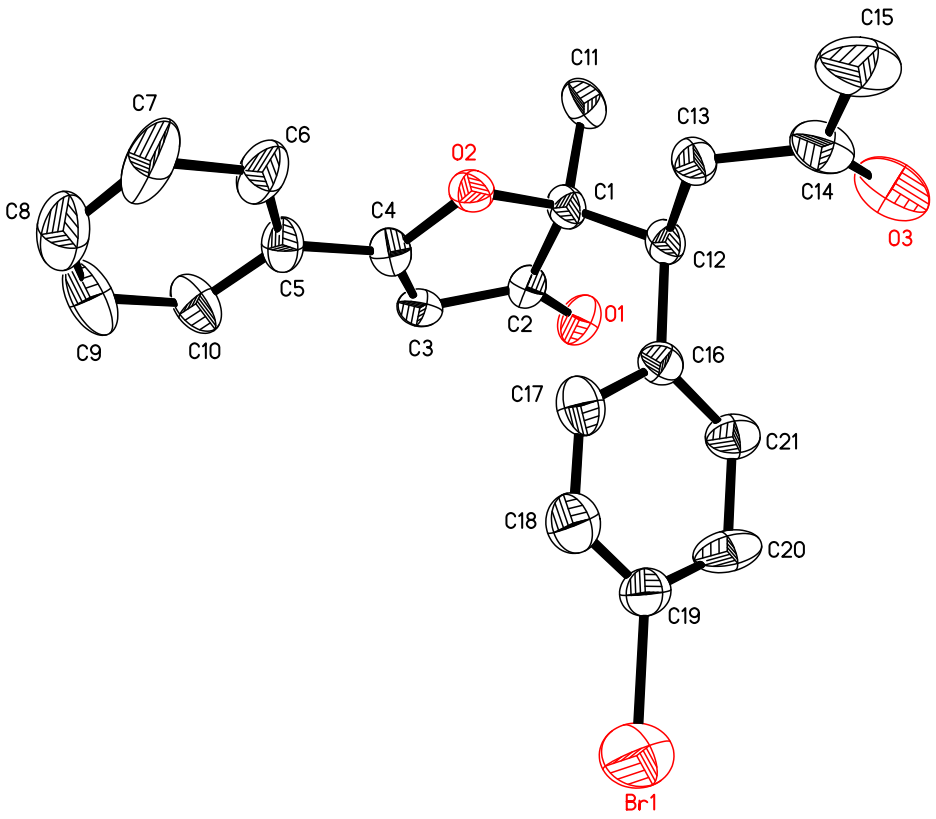
5: (*S*)-2-methyl-2-((*S*)-3-oxo-1,3-diphenylpropyl)-5-phenylfuran-3(2*H*)-one





H: Crystallographic Information for Product 4e




C15
C11
C7
C6
C13
O2
C1
C14
C8
C4
O3
C12
C5
C2
O1
C9
C10
C3
C16
C17
C21
C18
C20
C19
Br1

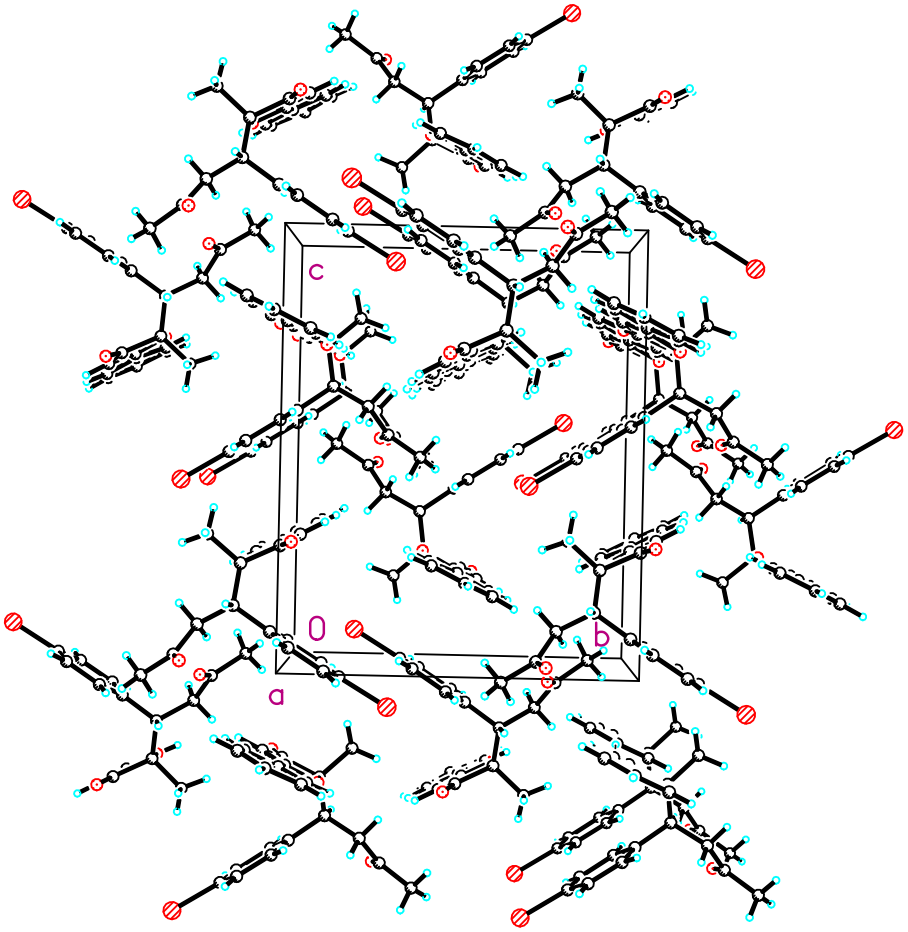

c
0
b
a

Table 1. Crystal data and structure refinement for **4e**.

Identification code	**4e**
Empirical formula	$C_{21}H_{19}BrO_3$
Formula weight	399.27
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 10.687(8) Å $\alpha = 90^o$
	b = 12.035(9) Å $\beta = 90^o$
	c = 14.902(11) Å $\gamma = 90^o$
Volume	1917(2) $Å^3$
Z	4
Calculated density	1.384 Mg/m^3
Absorption coefficient	2.160 mm^{-1}
F(000)	816
Crystal size	0.321 × 0.225 × 0.197 mm^3
θ range for data collection	2.18 to 25.49°
Limiting indices	-12⩽h⩽12, -14⩽k⩽7, -15⩽l⩽18
Reflections collected / unique	9193 / 3560 [R_{int} = 0.0692]
Completeness to θ = 25.49°	100.0 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.0895
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3560 / 1 / 229
Goodness-of-fit on F^2	1.008
Final R indices [I>2σ (I)]	R_1 = 0.0517, wR_2 = 0.1255
R indices (all data)	R_1 = 0.0873, wR_2 = 0.1398
Absolute structure parameter	-0.006(13)
Extinction coefficient	0.042(3)
Largest diff. peak and hole	0.526 and -0.560 e.Å^{-3}

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for **4e**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Br(1)	8994(1)	13054(1)	-761(1)	121(1)
O(1)	10324(3)	10361(3)	2937(2)	74(1)
O(2)	7610(2)	8884(2)	2388(2)	50(1)
O(3)	10869(4)	7404(3)	289(3)	96(1)
C(1)	8979(3)	8902(3)	2406(3)	46(1)

C(2)	9264(4)	10007(4)	2824(3)	54(1)
C(3)	8100(4)	10506(4)	3063(3)	57(1)
C(4)	7201(4)	9818(4)	2798(3)	51(1)
C(5)	5849(4)	9926(4)	2863(3)	57(1)
C(6)	5093(4)	9100(6)	2576(4)	82(2)
C(7)	3805(5)	9186(8)	2645(5)	119(3)
C(8)	3308(6)	10152(8)	3023(5)	107(2)
C(9)	4060(6)	10950(7)	3337(5)	108(2)
C(10)	5313(5)	10848(5)	3259(4)	85(2)
C(11)	9412(5)	7995(4)	3058(3)	66(1)
C(12)	9477(3)	8750(3)	1471(3)	46(1)
C(13)	8925(4)	7722(3)	1010(3)	53(1)
C(14)	9776(7)	7152(4)	364(3)	74(2)
C(15)	9186(8)	6205(5)	-144(4)	112(2)
C(16)	9343(4)	9776(3)	891(3)	48(1)
C(17)	8192(5)	10197(4)	654(3)	66(1)
C(18)	8087(6)	11161(5)	159(4)	79(2)
C(19)	9115(7)	11699(4)	-99(3)	75(1)
C(20)	10291(6)	11310(4)	85(3)	72(1)
C(21)	10393(5)	10336(4)	598(3)	63(1)

Table 3. Bond lengths [Å] and angles [°] for **4e**.

Br(1)-C(19)	1.911(5)	O(1)-C(2)	1.221(5)
O(2)-C(4)	1.352(5)	O(2)-C(1)	1.463(5)
O(3)-C(14)	1.212(7)	C(1)-C(2)	1.500(6)
C(1)-C(12)	1.503(6)	C(1)-C(11)	1.533(6)
C(2)-C(3)	1.427(6)	C(3)-C(4)	1.328(6)
C(3)-H(3)	0.9300	C(4)-C(5)	1.455(6)
C(5)-C(6)	1.351(7)	C(5)-C(10)	1.380(7)
C(6)-C(7)	1.384(8)	C(6)-H(6)	0.9300
C(7)-C(8)	1.397(10)	C(7)-H(7)	0.9300
C(8)-C(9)	1.337(10)	C(8)-H(8)	0.9300
C(9)-C(10)	1.350(8)	C(9)-H(9)	0.9300
C(10)-H(10)	0.9300	C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600	C(11)-H(11C)	0.9600
C(12)-C(16)	1.514(6)	C(12)-C(13)	1.533(6)
C(12)-H(12)	0.9800	C(13)-C(14)	1.490(7)
C(13)-H(13A)	0.9700	C(13)-H(13B)	0.9700
C(14)-C(15)	1.506(8)	C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600	C(15)-H(15C)	0.9600
C(16)-C(17)	1.376(6)	C(16)-C(21)	1.380(6)
C(17)-C(18)	1.379(7)	C(17)-H(17)	0.9300

C(18)-C(19)	1.332(8)	C(18)-H(18)	0.9300
C(19)-C(20)	1.368(8)	C(20)-C(21)	1.404(7)
C(20)-H(20)	0.9300	C(21)-H(21)	0.9300
C(4)-O(2)-C(1)	107.6(3)	O(2)-C(1)-C(2)	102.9(3)
O(2)-C(1)-C(12)	109.6(3)	C(2)-C(1)-C(12)	114.9(3)
O(2)-C(1)-C(11)	107.6(3)	C(2)-C(1)-C(11)	107.9(3)
C(12)-C(1)-C(11)	113.2(3)	O(1)-C(2)-C(3)	128. 9(4)
O(1)-C(2)-C(1)	123.7(4)	C(3)-C(2)-C(1)	107.4(3)
C(4)-C(3)-C(2)	107.1(4)	C(4)-C(3)-H(3)	126.4
C(2)-C(3)-H(3)	126.4	C(3)-C(4)-O(2)	114.8(4)
C(3)-C(4)-C(5)	130.0(4)	O(2)-C(4)-C(5)	115.2(4)
C(6)-C(5)-C(10)	118.6(4)	C(6)-C(5)-C(4)	120.5(4)
C(10)-C(5)-C(4)	120.8(5)	C(5)-C(6)-C(7)	121.0(6)
C(5)-C(6)-H(6)	119.5	C(7)-C(6)-H(6)	119.5
C(6)-C(7)-C(8)	118.1(7)	C(6)-C(7)-H(7)	121.0
C(8)-C(7)-H(7)	121.0	C(9)-C(8)-C(7)	120.7(6)
C(9)-C(8)-H(8)	119.7	C(7)-C(8)-H(8)	119.7
C(8)-C(9)-C(10)	120.0(7)	C(8)-C(9)-H(9)	120.0
C(10)-C(9)-H(9)	120.0	C(9)-C(10)-C(5)	121.4(7)
C(9)-C(10)-H(10)	119.3	C(5)-C(10)-H(10)	119.3
C(1)-C(11)-H(11A)	109.5	C(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5	C(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5	H(11B)-C(11)-H(11C)	109.5
C(1)-C(12)-C(16)	113.3(3)	C(1)-C(12)-C(13)	112.2(3)
C(16)-C(12)-C(13)	111.5(3)	C(1)-C(12)-H(12)	106.4
C(16)-C(12)-H(12)	106.4	C(13)-C(12)-H(12)	106.4
C(14)-C(13)-C(12)	115.2(4)	C(14)-C(13)-H(13A)	108.5
C(12)-C(13)-H(13A)	108.5	C(14)-C(13)-H(13B)	108.5
C(12)-C(13)-H(13B)	108.5	H(13A)-C(13)-H(13B)	107.5
O(3)-C(14)-C(13)	122.2(5)	O(3)-C(14)-C(15)	123.1(6)
C(13)-C(14)-C(15)	114.7(5)	C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	C(17)-C(16)-C(21)	117.7(4)
C(17)-C(16)-C(12)	122.1(4)	C(21)-C(16)-C(12)	120.1(4)
C(16)-C(17)-C(18)	121.3(5)	C(16)-C(17)-H(17)	119.3
C(18)-C(17)-H(17)	119.3	C(19)-C(18)-C(17)	119.8(5)
C(19)-C(18)-H(18)	120.1	C(17)-C(18)-H(18)	120.1
C(18)-C(19)-C(20)	122.2(5)	C(18)-C(19)-Br(1)	120.5(5)
C(20)-C(19)-Br(1)	117.3 (5)	C(19)-C(20)-C(21)	117.8(5)
C(19)-C(20)-H(20)	121.1	C(21)-C(20)-H(20)	121.1
C(16)-C(21)-C(20)	121.1(5)	C(16)-C(21)-H(21)	119.4

C(20)-C(21)-H(21)	119.4

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **4e**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	201(1)	65(1)	98(1)	29(1)	-22(1)	-10(1)
O(1)	47(2)	83(2)	91(3)	-6(2)	-14(2)	-10(2)
O(2)	45(2)	46(2)	58(2)	-4(1)	5(1)	0(1)
O(3)	94(3)	83(3)	112(3)	0(2)	53(2)	20(3)
C(1)	34(2)	48(2)	57(2)	4(2)	3(2)	3(2)
C(2)	50(3)	56(3)	54(3)	-1(2)	-11(2)	0(2)
C(3)	60(3)	48(3)	63(3)	-13(2)	-1(2)	5(2)
C(4)	48(2)	60(3)	44(2)	4(2)	4(2)	7(2)
C(5)	45(2)	79(3)	47(2)	3(2)	2(2)	8(3)
C(6)	46(3)	123(5)	78(4)	-30(4)	0(3)	2(3)
C(7)	57(3)	207(9)	94(5)	-39(5)	-11(3)	-7(5)
C(8)	62(3)	168(7)	89(5)	-19(5)	0(3)	24(5)
C(9)	75(4)	125(6)	123(5)	10(5)	27(4)	48(5)
C(10)	67(3)	84(4)	103(4)	-2(3)	13(3)	29(3)
C(11)	74(3)	58(3)	65(3)	12(2)	-3(2)	16(2)
C(12)	32(2)	49(2)	57(3)	2(2)	2(2)	3(2)
C(13)	48(2)	51(2)	59(3)	3(2)	-1(2)	4(2)
C(14)	113(5)	55(3)	54(3)	6(2)	17(3)	6(3)
C(15)	171(7)	87(4)	78(4)	-28(3)	17(4)	4(5)
C(16)	51(2)	47(2)	47(2)	1(2)	3(2)	2(2)
C(17)	62(3)	72(3)	65(3)	17(3)	1(3)	6(3)
C(18)	102(4)	70(4)	65(3)	19(3)	-11(3)	5(3)
C(19)	128(4)	49(3)	49(3)	4(2)	-20(3)	-5(3)
C(20)	100(3)	51(3)	64(3)	-2(2)	4(3)	-27(2)
C(21)	74(3)	52(3)	62(3)	1(2)	5(2)	-11(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **4e**.

	x	y	z	U(eq)
H(3)	7991	11185	3351	68
H(6)	5444	8462	2329	99
H(7)	3286	8617	2446	143
H(8)	2445	10242	3056	128
H(9)	3720	11576	3610	129
H(10)	5827	11411	3476	102

H(11A)	9057	8129	3640	99
H(11B)	10308	8004	3099	99
H(11C)	9141	7282	2842	99
H(12)	10377	8613	1531	55
H(13A)	8682	7192	1469	63
H(13B)	8173	7942	693	63
H(15A)	8651	6495	-605	168
H(15B)	8703	5758	262	168
H(15C)	9830	5758	-412	168
H(17)	7471	9825	832	80
H(18)	7302	11434	7	95
H(20)	10998	11678	-124	86
H(21)	11182	10065	744	75

Table 6. Torsion angles [°] for **4e**.

C(4)-O(2)-C(1)-C(2)	-3.8(4)	C(4)-O(2)-C(1)-C(12)	-126.5(3)
C(4)-O(2)-C(1)-C(11)	110.1(4)	O(2)-C(1)-C(2)-O(1)	-177.9(4)
C(12)-C(1)-C(2)-O(1)	-58.8(6)	C(11)-C(1)-C(2)-O(1)	68.5(5)
O(2)-C(1)-C(2)-C(3)	3.5(4)	C(12)-C(1)-C(2)-C(3)	122.6(4)
C(11)-C(1)-C(2)-C(3)	-110.1(4)	O(1)-C(2)-C(3)-C(4)	179.4(5)
C(1)-C(2)-C(3)-C(4)	-2.0(5)	C(2)-C(3)-C(4)-O(2)	-0.5(5)
C(2)-C(3)-C(4)-C(5)	-178.9(4)	C(1)-O(2)-C(4)-C(3)	2.9(5)
C(1)-O(2)-C(4)-C(5)	-178.5(4)	C(3)-C(4)-C(5)-C(6)	-177.6(5)
O(2)-C(4)-C(5)-C(6)	4.0(6)	C(3)-C(4)-C(5)-C(10)	-0.9(8)
O(2)-C(4)-C(5)-C(10)	-179.3(4)	C(10)-C(5)-C(6)-C(7)	2.3(9)
C(4)-C(5)-C(6)-C(7)	179.1(6)	C(5)-C(6)-C(7)-C(8)	-0.2(10)
C(6)-C(7)-C(8)-C(9)	-2.4(11)	C(7)-C(8)-C(9)-C(10)	2.7(11)
C(8)-C(9)-C(10)-C(5)	-0.5(11)	C(6)-C(5)-C(10)-C(9)	-2.0(9)
C(4)-C(5)-C(10)-C(9)	-178.9(5)	O(2)-C(1)-C(12)-C(16)	74.8(4)
C(2)-C(1)-C(12)-C(16)	-40.5(4)	C(11)-C(1)-C(12)-C(16)	-165.0(3)
O(2)-C(1)-C(12)-C(13)	-52.5(4)	C(2)-C(1)-C(12)-C(13)	-167.8(3)
C(11)-C(1)-C(12)-C(13)	67.7(4)	C(1)-C(12)-C(13)-C(14)	-147.9(4)
C(16)-C(12)-C(13)-C(14)	83.8(4)	C(12)-C(13)-C(14)-O(3)	8.4(7)
C(12)-C(13)-C(14)-C(15)	-174.9(4)	C(1)-C(12)-C(16)-C(17)	-64.5(6)
C(13)-C(12)-C(16)-C(17)	63.2(6)	C(1)-C(12)-C(16)-C(21)	114.0(4)
C(13)-C(12)-C(16)-C(21)	-118.3(4)	C(21)-C(16)-C(17)-C(18)	-1.5(7)
C(12)-C(16)-C(17)-C(18)	177.1(4)	C(16)-C(17)-C(18)-C(19)	0.1(8)
C(17)-C(18)-C(19)-C(20)	2.2(8)	C(17)-C(18)-C(19)-Br(1)	-178.5(4)
C(18)-C(19)-C(20)-C(21)	-2.9(8)	Br(1)-C(19)-C(20)-C(21)	177.7(3)
C(17)-C(16)-C(21)-C(20)	0.7(7)	C(12)-C(16)-C(21)-C(20)	-177.9(4)
C(19)-C(20)-C(21)-C(16)	1.5(7)		

Symmetry transformations used to generate equivalent atoms: