Metal-free β, γ- C(sp^3)-H Difunctionalization of Propanols: DMP-iniated Asymmetric Spirocyclopropanation

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Supporting Information

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1. General Information

^{1}H (400MHz) and ^{13}C (101MHz) NMR spectra were recorded on a Bruker Advance 400 spectrometer in $CDCl_3$ using TMS as internal reference. Chemical shifts for ^{1}H NMR spectra are reported in units of parts per million (ppm) downfield from SiMe4 (δ 0.00) and relative to the signal of chloroform (δ 7.26, singlet). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (pentet), m (multiplet), and b (broad). Coupling constants, J, are reported in Hertz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) relative to the signal of chloroform (δ 77.16, triplet).

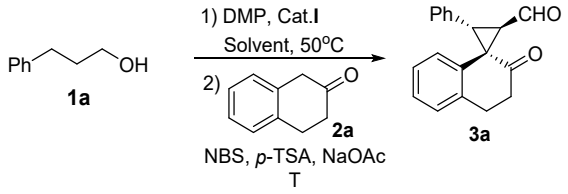
High performance liquid chromatography (HPLC) was performed on Hitachi detectors (λ= 254 nm) using Daicel Chiralpak AD-3 and OD-3 columns. Retention times (tR) and peak areas for HPLC were obtained from reporting integrators.

High resolution mass spectra (HRMS) were recorded under electron impact conditions using a MicroMass GCT CA 055 instrument and recorded on a MicroMass LCTTM spectrometer.

All chemicals were reagent grade and were used as received without further purification. Column chromatography was carried out using 300-400 mesh silica gel.

2. Additional optimization studies [a]

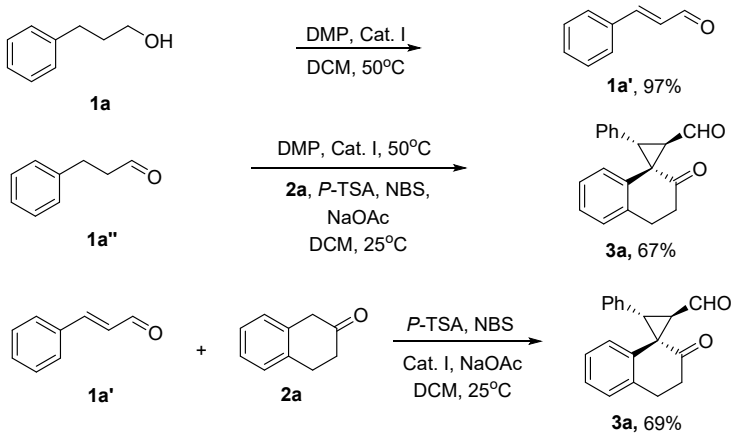
Table S1. Solvent and temperature optimization



entry	T	solvent	t [b] (h)	yield [c] (%)	dr [d] (%)	ee [e] (%)
6	25°C	THF	3	11	ND [f]	ND
7	25°C	$CHCl_3$	3	51	74:26	92
8	25°C	Toluene	3	trace	ND	ND
9	25°C	DMF	3	trace	ND	ND
10	25°C	DCM	3	65	76:24	97
11	0°C	DCM	9	61	75:25	97
13	10°C	DCM	7	60	71:29	97
14	35°C	DCM	3	49	70:30	96

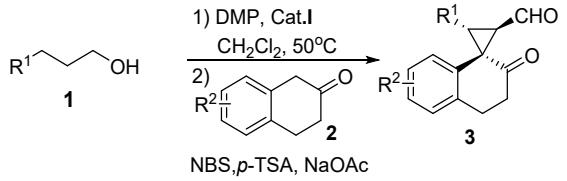
[a] Reaction conditions: **1a** (1.0 mmol, 1.0 equiv.), DMP (1.0 mmol, 1.0 equiv.), catalyst (0.2 mmol, 0.2 equiv.), and 5 mL solvent were stirred at 50 °C for two hours. Then **1b** (1.0 mmol, 1.0 equiv.), *p*-TSA (0.2 mmol, 0.2 equiv.), NBS (1.2 mmol, 1.2 equiv.) were added to the solution sequentially at 25 °C, and NaOAc (4.0 mmol, 4.0 equiv.) were added after half an hour, then the mixture was stirred at showed temperature. [b] The time of second step. [c] Isolated yields. [d] Determined from crude product by ^{1}H NMR. [e] Determined by chiral HPLC analysis. [f] Not determined.

3. Control experiments.



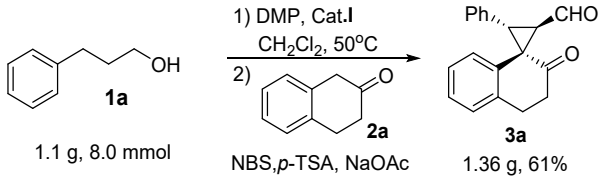
4. Experimental Section

4.1 General Procedure for Synthesis of 3a-3q



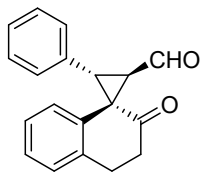
General procedure: **1** (1.0 mmol, 1.0 equiv.), DMP (1.0 mmol, 1.0 equiv.), Cat. **I** (0.2 mmol, 0.2 equiv.), were added to 5 mL CH_2Cl_2 sequentially, stirred at 50°C. When compound **1** was transformed completely in almost two hours, **2** (1.0 mmol, 1.0 equiv.), *p*-TSA (0.2 mmol, 0.2 eqiuv.) and NBS (1.2 mmol, 1.2 equiv.) were added sequentially to the mixture and stirred at 25°C, and NaOAc (4.0 mmol, 4.0 equiv.) were added to the mixture after half an hour. After reaction was completed, the mixture was filtered, concentrated under reduce pressure, keeping the bath temperature under 35°C. The residue was purified by silica gel column chromatography using mixture of petrol ether/ethyl acetate. Racemic samples were obtained with racemic version of Cat**. I** (20 mol %).

4.2 Gram-scale Synthesis of 3a



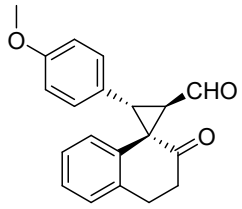
1a (1.10 g, 8.0 mmol), DMP (3.43 g, 8.0 mmol), Cat. **I** (0.53 g, 1.6 mmol), were added to 100 mL CH_2Cl_2 sequentially, stirred at 50°C. When compound **1a** was transformed completely in two hours, **2a** (1.18 g, 8.0 mmol), *p*-TSA (0.28 g, 1.6 mmol) and NBS (1.73 g, 9.6 mmol) were added sequentially to the mixture and stirred at 25°C, and NaOAc (2.65 g, 32.3 mmol) were added to the mixture after half an hour. After reaction was completed, the mixture was filtered, concentrated under reduce pressure, keeping the bath temperature under 35°C. The residue was purified by silica gel column chromatography using mixture of petrol ether/ethyl acetate (10:1, v/v) to obtain **3a** (1.36 g, 61%, 96% ee, 70/30 dr).

4.3 Characterization of the product 3a-3p

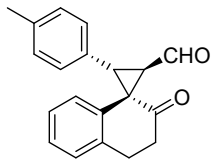


(1*R*,2*R*,3*S*)-2'-oxo-3-phenyl-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-2-carbaldehyde (3a). Yellow oil. Isolated yield: 177 mg, 64%. ee 97%. d.r. 77/23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (d, *J* = 4.9 Hz, 1H), 7.33 – 7.27 (m, 6H), 7.23 (d, *J* = 7.3 Hz, 3H), 3.88 (d, *J* = 7.6 Hz, 1H), 3.64 (dd, *J* = 7.5, 4.9 Hz, 1H), 3.09 (dt, *J* = 15.1, 6.0 Hz, 1H), 3.04 – 2.95 (m, 1H), 2.53 (dt, *J* = 11.1, 9.7, 6.4 Hz, 1H), 2.40 – 2.31 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 197.5, 139.7, 133.6,

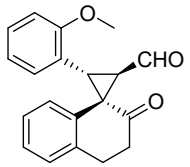
133.0, 128.7(2C), 128.7(2C), 128.2, 127.7, 127.5, 127.0, 125.9, 48.6, 42.1, 39.2, 39.0, 28.0. HRMS (EI) calc. for $C_{19}H_{16}O_2$ [M^+]: 276.1150; found: 276.1155. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 70:25, flow rate 1.0mL / min., λ = 254 nm): tr = 7.20 min. (major), tr = 8.28 min. (minor).



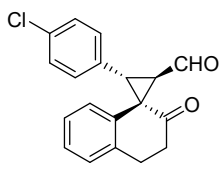
(1*R*,2*R*,3*S*)-3-(4-methoxyphenyl)-2'-oxo-3', 4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-2-carbaldehyde (3b). Yellow oil**.** Isolated yield: 193 mg, 63%. ee 97% d.r. 72/28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (d, J = 5.0 Hz, 1H), 7.27 (s, 2H), 7.26 – 7.24 (m, 1H), 7.16 (dd, J = 10.4, 6.5 Hz, 3H), 6.85 – 6.82 (m, 2H), 3.78 (d, J = 4.7 Hz, 4H), 3.63 (dd, J = 7.6, 5.0 Hz, 1H), 3.13 – 3.05 (m, 1H), 3.02 – 2.94 (m, 1H), 2.50 (dt, J = 16.3, 6.8, 4.6 Hz, 1H), 2.35 (dt, J = 16.5, 9.0, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 197.7, 158.9, 139.7, 133.3, 129.8(2C), 128.2, 127.6, 127.0, 125.9, 125.3, 113.8(2C), 55.2, 48.9, 42.0, 39.1, 39.0, 28.0. HRMS (EI) calc. for $C_{20}H_{18}O_3$ [M^+]: 306.1256; found: 306.1255. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 85:15, flow rate 1.0mL / min., λ = 254 nm): tr = 14.68 min. (major), tr = 20.18 min. (minor).



(1*R*,2*R*,3*S*)-2'-oxo-3-(p-tolyl)-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-2-carbaldehyde (3c). Yellow oil. Isolated yield: 189 mg, 65%. ee 97% d.r. 80/20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (d, J = 4.5 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.07 – 6.99 (m, 2H), 6.91 (d, J = 7.9 Hz, 2H), 6.84 (d, J = 7.6 Hz, 2H), 3.66 (d, J = 7.4 Hz, 1H), 3.30 (dd, J = 7.4, 4.5 Hz, 1H), 3.09 (td, J = 14.2, 4.3 Hz, 1H), 2.95 (dt, J = 14.9, 5.4, 2.7 Hz, 1H), 2.87 (dt, J = 17.2, 4.2, 3.0 Hz, 1H), 2.53 (dt, J = 17.4, 13.5, 5.6 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.6, 198.9, 138.4, 137.4, 131.0, 129.5, 129.0(2C), 128.7(2C), 127.5, 127.1, 126.4, 125.7, 52.2, 42.6, 39.7, 38.5, 27.8, 21.05.HRMS (EI) calc. for $C_{20}H_{18}O_2$ [M^+]: 290.1307; found: 290.1309. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 85:15, flow rate 1.0mL / min., λ = 254 nm): tr = 8.74 min. (major), tr = 10.59 min. (minor).

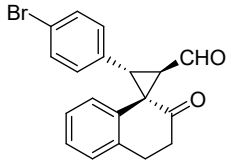


(1*R*,2*R*,3*S*)-3-(2-methoxyphenyl)-2'-oxo-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-2-carbaldehyde (3d). Yellow oil. Isolated yield: 211 mg, 69%. ee >99% d.r. 90/10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (d, J = 4.3 Hz, 1H), 7.10 (dd, J = 13.9, 7.1 Hz, 2H), 7.03 – 6.94 (m, 2H), 6.89 (t, J = 7.6 Hz, 1H), 6.77 (t, J = 7.5 Hz, 1H), 6.65 – 6.58 (m, 2H), 3.74 (d, J = 8.1 Hz, 1H), 3.64 (s, 3H), 3.29 (dd, J = 7.9, 4.4 Hz, 1H), 3.27 – 3.20 (m, 1H), 2.96 – 2.85 (m, 2H), 2.55 (dt, J = 16.6, 13.5, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.2, 199.3, 158.4, 138.3, 131.3, 129.3, 129.1, 127.3, 126.7, 125.9, 124.8, 121.3, 119.9, 109.8, 55.0, 50.8, 39.8, 39.6, 38.9, 27.4. HRMS (EI) calc. for $C_{20}H_{18}O_3$ [M^+]: 306.1256; found: 306.1257. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 85:15, flow rate 1.0mL / min., λ = 254 nm): tr = 12.57 min. (minor), tr = 16.56 min. (major).

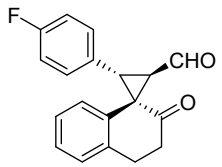


(1*R*,2*S*,3*R*)-2-(4-chlorophenyl)-2'-oxo-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-3-carbaldehyde (3e).

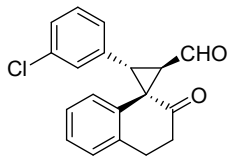
Yellow oil. Isolated yield: 183 mg, 59%. ee 94% d.r. 74/26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (d, J = 4.3 Hz, 1H), 7.16 – 7.07 (m, 4H), 7.04 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 8.2 Hz, 2H), 6.80 (d, J = 7.7 Hz, 1H), 3.65 (d, J = 7.4 Hz, 1H), 3.28 (dd, J = 7.3, 4.4 Hz, 1H), 3.11 – 3.02 (m, 1H), 3.01 – 2.94 (m, 1H), 2.89 (dd, J = 17.3, 3.6 Hz, 1H), 2.60 – 2.48 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 197.0, 139.5, 133.3, 132.6, 132.2, 130.1(2C), 128.5(2C), 128.3, 127.8, 127.0, 125.9, 48.1, 42.6, 39.4, 37.8, 28.0. HRMS (EI) calc. for $C_{19}H_{15}ClO_2$ [M^+]: 310.0761; found: 310.0762. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 85:15, flow rate 1.0mL / min., λ = 254 nm): tr = 7.71 min. (major), tr = 9.33 min. (minor).



(1*R*,2*S*,3*R*)-2-(4-bromophenyl)-2'-oxo-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-3-carbaldehyde (3f). Yellow oil. Isolated yield: 206 mg, 58%. ee 96% d.r. 79/21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (d, J = 4.7 Hz, 1H), 7.43 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 2.7 Hz, 3H), 7.23 (s, 1H), 7.11 (d, J = 8.2 Hz, 2H), 3.87 (d, J = 7.6 Hz, 1H), 3.57 (dd, J = 7.5, 4.7 Hz, 1H), 3.10 – 2.99 (m, 2H), 2.57 (dt, J = 16.3, 5.2 Hz, 1H), 2.44 – 2.34 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 197.0, 139.5, 132.7, 132.5, 131.5(2C), 130.5(2C), 128.3, 127.8, 127.0, 125.9, 121.5, 48.0, 42.6, 39.4, 37.9, 28.0. HRMS (EI) calc. for $C_{19}H_{15}BrO_2$ [M^+]: 354.0255; found: 354.0254. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 85:15, flow rate 1.0mL / min., λ = 254 nm): tr = 9.39 min. (major), tr = 11.25 min. (minor).

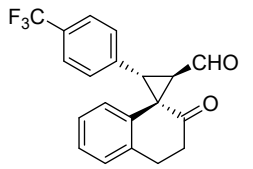


(1*R*,2*S*,3*R*)-2-(4-fluorophenyl)-2'-oxo-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-3-carbaldehyde (3g). Yellow oil. Isolated yield: 176 mg, 60%. ee 95% d.r. 75/25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, J = 4.7 Hz, 1H), 7.28 (d, J = 2.5 Hz, 3H), 7.24 – 7.18 (m, 3H), 7.00 (t, J = 8.5 Hz, 2H), 3.89 (d, J = 7.6 Hz, 1H), 3.59 (dd, J = 7.5, 4.8 Hz, 1H), 3.11 – 2.97 (m, 2H), 2.55 (dt, J = 16.3, 5.2 Hz, 1H), 2.38 (dt, J = 16.0, 9.6, 6.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5, 198.5, 162.1 (d, J = 247.0 Hz), 138.3, 130.7, 130.5 (d, J = 8.2 Hz) (2C), 128.5 (d, J = 3.1 Hz), 127.7, 127.3, 126.5, 125.5, 115.3 (d, J = 21.5 Hz) (2C), 51.6, 41.8, 39.7, 38.5, 27.7. HRMS (EI) calc. for $C_{19}H_{15}FO_2$ [M^+]: 294.1056; found: 294.1057. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 80:20, flow rate 1.0mL / min., λ = 254 nm): tr = 7.50 min. (major), tr = 9.12 min. (minor).

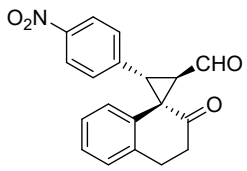


(1*R*,2*S*,3*R*)-2-(3-chlorophenyl)-2'-oxo-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-3-carbaldehyde (3h). Yellow oil. Isolated yield: 193 mg, 62%. ee 95% d.r. 82/18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (d, J = 4.3 Hz, 1H), 7.14 (t, J = 7.2 Hz, 2H), 7.09 – 7.04 (m, 3H), 6.98 (s, 1H), 6.81 (dd, J = 7.5, 2.9 Hz, 2H), 3.65 (d, J = 7.4 Hz, 1H), 3.29 (dd, J = 7.3, 4.3 Hz, 1H), 3.14 – 3.04 (m, 1H), 2.98 (dt, J = 15.1, 5.6, 2.7 Hz, 1H), 2.89 (dt, J = 17.2, 4.1, 3.0 Hz, 1H), 2.55 (dt, J = 17.3, 13.4, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.3, 198.2, 138.4, 134.8, 134.2, 130.4, 129.5, 129.0, 127.9, 127.8, 127.4, 127.0, 126.5, 125.6, 51.6, 41.6, 39.4,

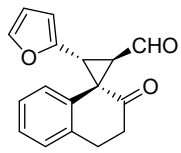
38.5, 27.7. HRMS (EI) calc. for $C_{19}H_{15}FO_2$ [M^+]: 310.0761; found: 310.0760. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 85:15, flow rate 1.0mL / min., λ = 254 nm): tr = 9.18 min. (major), tr =10.66 min. (minor).



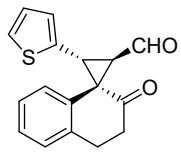
(1*R*,2*R*,3*S*)-2'-oxo-3-(4-(trifluoromethyl)phenyl)-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-2-carbaldehyde (3i). Yellow oil. Isolated yield: 203 mg, 59%. ee 95% d.r. 77/23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (d, J = 4.5 Hz, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.23 – 7.18 (m, 4H), 3.92 (d, J = 7.6 Hz, 1H), 3.51 (dd, J = 7.6, 4.5 Hz, 1H), 2.98 (dd, J = 7.8, 5.2 Hz, 2H), 2.52 (dt, J = 16.3, 4.9 Hz, 1H), 2.33 (dt, J = 16.3, 8.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 196.7, 139.5, 138.0, 132.2, 129.6 (d, J = 32.4 Hz), 129.2(2C), 128.4, 127.9, 127.1, 125.9, 125.3 (d, J = 3.7 Hz) (2C), 121.4 (d, J = 272.0 Hz). 47.7, 43.0, 39.5, 37.4, 27.9. HRMS (EI) calc. for $C_{20}H_{15}F_3O_2$ [M^+]: 344.1024; found: 344.1025. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 85:15, flow rate 1.0mL / min., λ = 254 nm): tr = 8.90 min. (major), tr =9.93 min. (minor).



(1*R*,2*R*,3*S*)-3-(4-nitrophenyl)-2'-oxo-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-2-carbaldehyde (3j). Yellow oil. Isolated yield: 174 mg, 54%. ee 98% d.r. 73/27. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, J = 4.2 Hz, 1H), 8.18 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.31 (s, 4H), 4.09 (d, J = 7.7 Hz, 1H), 3.56 (dd, J = 7.6, 4.2 Hz, 1H), 3.09 – 3.03 (m, 2H), 2.64 (dt, J = 16.3, 4.5 Hz, 1H), 2.48 – 2.38 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 196.1, 147.1, 141.8, 139.4, 131.6, 129.8(2C), 128.5, 128.1, 127.1, 125.8, 123.5(2C), 47.4, 43.6, 39.7, 36.5, 27.9. HRMS (EI) calc. for $C_{19}H_{15}NO_4$ [M^+]: 321.1001; found: 321.1003. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 75:250, flow rate 1.0mL / min., λ = 254 nm): tr = 14.16 min. (major), tr =19.13 min. (minor).

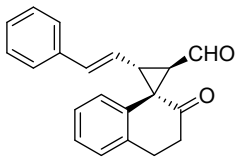


(1*R*,2*R*,3*R*)-3-(furan-2-yl)-2'-oxo-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-2-carbaldehyde (3k). Yellow oil. Isolated yield: 146 mg, 55%. ee 97% d.r. 79/21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (dd, J = 3.1, 1.3 Hz, 1H), 7.26 (d, J = 1.2 Hz, 1H), 7.21 (d, J = 2.2 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.01 (d, J = 7.0 Hz, 1H), 6.26 (dd, J = 3.1, 1.9 Hz, 1H), 6.12 (d, J = 3.2 Hz, 1H), 3.54 – 3.48 (m, 2H), 3.20 – 3.10 (m, 1H), 2.98 – 2.89 (m, 1H), 2.47 – 2.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 196.8, 148.1, 142.4, 140.1, 132.2, 128.2, 127.8, 126.9, 126.0, 110.7, 108.7, 47.9, 40.3, 38.4, 31.2, 27.9. HRMS (EI) calc. for $C_{17}H_{14}O_3$ [M^+]: 266.0943; found: 266.0944. HPLC (Daicel chiralpak OD-3, hexane/i-PrOH = 90:10, flow rate 1.0mL / min., λ = 254 nm): tr = 16.98 min. (minor), tr = 18.66 min. (major).

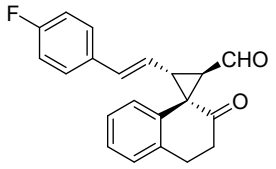


(1*S*,2*R*,3*R*)-2'-oxo-3-(thiophen-2-yl)-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-2-carbaldehyde (3l). Yellow oil. Isolated yield: 164 mg, 58%. ee 97% d.r. 81/19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (dd, *J* = 3.7, 0.8 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.26 – 7.22 (m, 1H), 7.19 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.94 (dd, *J* =

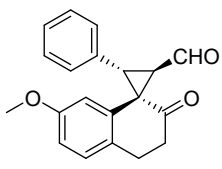
5.1, 3.6 Hz, 1H), 6.88 (d, *J* = 3.5 Hz, 1H), 3.74 (d, *J* = 3.7 Hz, 2H), 3.28 – 3.17 (m, 1H), 3.05 – 2.95 (m, 1H), 2.55 – 2.38 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 196.9, 139.9, 136.4, 132.7, 128.2, 127.8, 127.0(2C), 126.9, 126.0, 125.3, 50.1, 41.9, 38.5, 34.6, 28.1. HRMS (EI) calc. for $C_{17}H_{14}O_2$ [M^+]: 282.0715; found: 282.0716. HPLC (Daicel chiralpak OD-3, hexane/i-PrOH = 90:10, flow rate 1.0mL / min., λ = 254 nm): tr = 26.84 min. (major), tr = 30.84min. (minor).



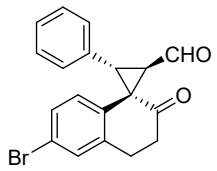
(1*R*,2*R*,3*R*)-2'-oxo-3-((E)-styryl)-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-2-carbaldehyde (3m). Yellow oil. Isolated yield: 151 mg, 50%. ee 95% d.r. 70/30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (d, J = 5.3 Hz, 1H), 7.38 (d, J = 7.6 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.23 (d, J = 5.3 Hz, 3H), 6.75 (d, J = 15.9 Hz, 1H), 6.47 (dd, J = 15.9, 9.0 Hz, 1H), 3.49 – 3.41 (m, 1H), 3.21 (t, J = 6.1 Hz, 1H), 3.05 (dd, J = 8.0, 4.1 Hz, 2H), 2.70 (dt, J = 16.6, 5.0 Hz, 1H), 2.64 – 2.54 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8, 197.0, 139.7, 136.6, 134.2, 132.2, 128.6(2C), 128.2, 127.8, 127.7, 126.9, 126.3(2C), 125.9, 123.6, 47.3, 44.9, 39.5, 37.1, 27.9. HRMS (EI) calc. for $C_{21}H_{18}O_2$ [M^+]: 302.1307; found: 302.1306. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 85:15, flow rate 1.0mL / min., λ = 254 nm): tr = 10.58 min. (major), tr = 11.39min. (minor).



(1*R*,2*R*,3*R*)-2-((E)-4-fluorostyryl)-2'-oxo-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-3-carbaldehyde (3n). Yellow oil. Isolated yield: 157 mg, 49%. ee 94% d.r. 72/28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, J = 5.3 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.27 (d, J = 3.8 Hz, 2H), 7.25 – 7.23 (m, 1H), 6.99 (dd, J = 14.4, 5.8 Hz, 2H), 6.71 (d, J = 15.9 Hz, 1H), 6.42 (dd, J = 15.9, 9.0 Hz, 1H), 3.46 (dd, J = 8.9, 6.9 Hz, 1H), 3.18 (dd, J = 6.8, 5.4 Hz, 1H), 3.05 (dd, J = 8.0, 4.9 Hz, 2H), 2.72 (dt, J = 16.6, 4.9 Hz, 1H), 2.58 (dt, J = 16.5, 8.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.2, 198.1, 162.4 (d, J = 247.9 Hz), 139.0, 133.7, 132.3 (d, J = 3.1 Hz), 131.5, 128.0, 127.7, 127.6(2C), 127.0, 125.1, 122.5, 115.5 (d, J = 21.6 Hz) (2C), 51.4, 41.0, 40.8, 38.3, 27.5. HRMS (EI) calc. for $C_{21}H_{17}FO_2$ [M^+]: 320.1213; found: 320.1212. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 90:10, flow rate 1.0mL / min., λ = 254 nm): tr = 18.10 min. (major), tr = 31.05 min. (minor).



(1*R*,2*R*,3*S*)-7'-methoxy-2'-oxo-3-phenyl-3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalene]-2-carbaldehyde (3o). Yellow oil. Isolated yield: 202 mg, 69%. ee 97% d.r. 83/17. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, J = 4.8 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.24 (dd, J = 13.5, 6.8 Hz, 3H), 7.17 (d, J = 8.2 Hz, 1H), 6.79 (dt, J = 5.7, 2.3 Hz, 2H), 3.88 (d, J = 7.6 Hz, 1H), 3.80 (s, 3H), 3.64 (dd, J = 7.7, 4.8 Hz, 1H), 3.07 – 2.87 (m, 2H), 2.51 (dt, J = 16.1, 5.1 Hz, 1H), 2.34 (ddd, J = 15.9, 9.8, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 197.6, 158.5, 134.3, 133.6, 131.5, 129.2, 128.8(2C), 128.3(2C), 127.5, 112.4(2C), 55.5, 48.4, 42.4, 39.7, 39.2, 27.2. HRMS (EI) calc. for $C_{20}H_{18}O_3$ [M^+]: 306.1256; found: 306.1257. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 80:20, flow rate 1.0mL / min., λ = 254 nm): tr = 10.85 min. (major), tr = 13.70 min. (minor).



(1*R*,2*R*,3*S*)-6'-bromo-2'-oxo-3-phenyl-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalene]-2-carbaldehyde (3p). Yellow oil. Isolated yield: 256 mg, 72%. ee 94% d.r 81/19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (d, J = 4.3 Hz, 1H), 7.43 (s, 1H), 7.39 (dd, J = 8.3, 2.0 Hz, 1H), 7.28 (dd, J = 13.2, 7.4 Hz, 3H), 7.21 (d, J = 6.9 Hz, 2H), 7.08 (d, J = 8.4 Hz, 1H), 3.85 (d, J = 7.7 Hz, 1H), 3.69 (dd, J = 7.7, 4.4 Hz, 1H), 3.09 – 2.91 (m, 2H), 2.51 (ddd, J = 16.4, 6.0, 4.8 Hz, 1H), 2.34 (ddd, J = 9.8, 7.7, 4.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 197.6, 158.5, 134.3, 133.6, 131.5, 129.2, 128.8(2C), 128.3(2C), 127.5(2C), 112.4, 55.5, 48.4, 42.4, 39.7, 39.2, 27.2. HRMS (EI) calc. for $C_{19}H_{15}BrO_2$ [M^+]: 354.0255; found: 354.0252. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 90:10, flow rate 1.0mL / min., λ = 254 nm): tr = 11.80 min. (major), tr = 12.63 min. (minor).

4.4 General Procedure for Synthesis of 5a-5n

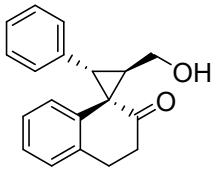
4.4.1 General Procedure for Synthesis of 5a-5d

General procedure: **1** (1.0 mmol, 1.0 equiv.), DMP (1.0 mmol, 1.0 equiv.), Cat. **I** (0.2 mmol, 0.2 equiv.), were added to 5 mL CH_2Cl_2 sequentially, stirred at 50℃. When compound **1** was transformed completely in almost two hours, **2** (1.0 mmol, 1.0 equiv.), *p*-TSA (0.2 mmol, 0.2 eqiuv.) and NBS (1.2 mmol, 1.2 equiv.) were added sequentially to the mixture and stirred at 25°C, and NaOAc (4.0 mmol, 4.0 equiv.) were added to the mixture after half an hour. After the cyclopropylation reaction, the mixture is filtered and the filtrate is concentrated, and 3 mL of MeOH and $NaBH_3CN$ (3.0 equiv.) were added under an ice bath. After reaction was completed, the mixture was filtered, concentrated under reduce pressure, keeping the bath temperature under 35℃. The residue was purified by silica gel column chromatography using mixture of petrol ether/ethyl acetate. Racemic samples were obtained with racemic version of Cat**. I** (20 mol %).

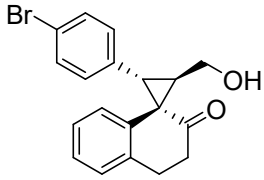
4.4.2 General Procedure for Synthesis of 5e-5n

General procedure: **1** (1.0 mmol, 1.0 equiv.), DMP (1.0 mmol, 1.0 equiv.), Cat. **I** (0.2 mmol, 0.2 equiv.), and 5 mL CH_2Cl_2 were stirred at 50°C for two hours. Then α-bromocarbonyl compounds (1.0 mmol, 1.0 equiv.), and NaOAc (2.0 mmol, 2.0 equiv.) were added to the solution sequentially at 25°C. After the cyclopropylation reaction, the mixture is filtered and the filtrate is concentrated, and 3 mL of MeOH and $NaBH_3CN$ (3.0 equiv.) were added under an ice bath. After reaction was completed, the mixture was filtered, concentrated under reduce pressure, keeping the bath temperature under 35°C. The residue was purified by silica gel column chromatography using mixture of petrol ether/ethyl acetate. Racemic samples were obtained with racemic version of Cat**. I** (20 mol %).

4.5 Characterization of the product 5a-5n

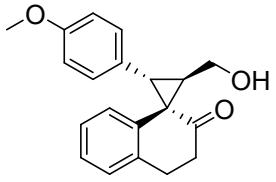


(*1R,2R,3S*)-2-(hydroxymethyl)-3-phenyl-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalen]-2'-one (5a): Isolated yield 167 mg, 60%, ee 97%. d.r. 78/22. White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (qd, *J* = 7.7, 6.4, 3.5 Hz, 9H), 3.95 (dd, *J* = 11.9, 5.6 Hz, 1H), 3.69 – 3.56 (m, 1H), 3.30 (d, *J* = 8.0 Hz, 1H), 3.10 – 2.90 (m, 3H), 2.53 (dt, *J* = 15.7, 4.3 Hz, 1H), 2.37 (ddd, *J* = 15.5, 11.7, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 139.7, 135.9, 134.6, 129.1, 128.2, 128.1, 126.9, 126.8, 126.8, 125.3, 60.8, 43.9, 40.2, 38.8, 38.6, 28.3. HRMS (EI) m/z Calcd for $C_{19}H_{18}O_2$ (M^+): 278.1307; found:278.1299.

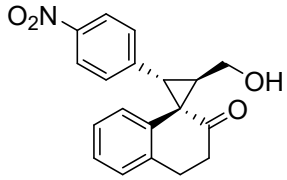


(*1R,2S,3R*)-2-(4-bromophenyl)-3-(hydroxymethyl)-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalen]-2'-one (5b): Isolated yield 193 mg, 54%, ee 92%. d.r. 75/25. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.2 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.12 (d, J = 8.2 Hz, 2H), 3.90 (dd, J = 12.0, 5.7 Hz, 1H), 3.58 (dd,

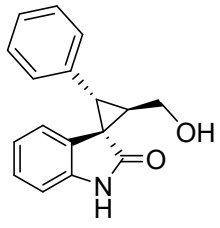
J = 11.8, 9.1 Hz, 1H), 3.26 (d, J = 8.0 Hz, 1H), 3.12 – 3.03 (m, 1H), 2.97 (dt, J = 15.1, 4.7 Hz, 1H), 2.85 (dd, J = 14.2, 8.3 Hz, 1H), 2.55 (dt, J = 15.7, 4.0 Hz, 1H), 2.45 – 2.33 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.9, 139.5, 135.0, 134.0, 131.1(2C), 130.8(2C), 128.2, 126.9, 126.8, 125.2, 120.6, 60.5, 43.6, 40.2, 39.2, 37.4, 28.2. HPLC (Daicel chiralpak AD-3, hexane/i-PrOH = 75:25, flow rate 1.0mL / min., λ = 254 nm): tr = 7.27 min. (major), tr = 11.47 min. (minor). HRMS (EI) m/z calc. for $C_{19}H_{17}BrO_2$ [M^+]: 356.0412; found:356.0407.



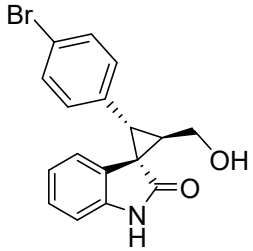
(*1R,2R,3S*)-2-(hydroxymethyl)-3-(4-methoxyphenyl)-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalen]-2'-one (5c): Isolated yield 188 mg, 61%, ee 97% d.r. 72/28. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 7.8, 3.4 Hz, 4H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.98 (dd, *J* = 11.9, 5.6 Hz, 1H), 3.78 (s, 4H), 3.67 (dd, *J* = 11.9, 9.2 Hz, 1H), 3.25 (d, *J* = 8.0 Hz, 1H), 2.99 (dtd, *J* = 28.6, 10.1, 8.5, 5.0 Hz, 3H), 2.53 (dt, *J* = 15.6, 4.4 Hz, 1H), 2.44 – 2.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 158.5, 139.6, 134.8, 130.1, 128.2, 127.7, 126.8, 126.7, 125.2, 113.6, 60.8, 55.3, 43.9, 40.2, 38.7, 28.4. HRMS (EI) m/z calcd for $C_{20}H_{20}O_3$ (M^+): 308.1412; found:308.1402.



(*1R,2R,3S*)-2-(hydroxymethyl)-3-(4-nitrophenyl)-3',4'-dihydro-2'*H*-spiro[cyclopropane-1,1'-naphthalen]-2'-one (5d): Isolated yield 168 mg, 52%, ee 98% d.r. 73/27. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.33 – 7.25 (m, 4H), 3.90 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.56 (dd, *J* = 12.0, 8.9 Hz, 1H), 3.42 (d, *J* = 7.9 Hz, 1H), 3.20 – 3.08 (m, 1H), 3.04 – 2.94 (m, 1H), 2.84 (td, *J* = 8.3, 5.7 Hz, 1H), 2.60 (dt, *J* = 15.9, 3.7 Hz, 1H), 2.48 – 2.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 146.7, 144.5, 139.6, 133.3, 130.0, 128.4, 127.3, 126.9, 125.3, 123.4, 60.3, 43.8, 40.2, 36.2, 28.1, 27.0. HRMS (EI) m/z calcd for $C_{19}H_{17}NO_4$ (M^+): 323.1158; found:323.1149.

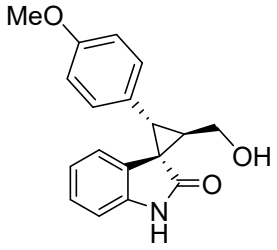


(*1R,2R,3S*)-2-(hydroxymethyl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-one (5e): Isolated yield 191 mg, 72%, ee 99% d.r. 90/10. White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.26 – 7.21 (m, 4H), 7.21 – 7.16 (m, 1H), 7.12 – 7.07 (m, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.96 (q, *J* = 7.1, 5.9 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 4.23 – 4.14 (m, 1H), 3.88 (dd, *J* = 12.0, 8.9 Hz, 1H), 3.28 (s, 1H), 3.09 (d, *J* = 8.5 Hz, 1H), 2.88 (td, *J* = 8.6, 5.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 141.3, 134.3, 129.4, 128.3, 128.1, 127.4, 127.0, 121.9, 120.5, 110.4, 60.5, 42.0, 38.7, 38.0. HPLC: Chiralpak AD-3, *i*-PrOH/hexane = 25/75, flow rate = 1.0 mL/min, λ= 254 nm; t_{major} = 11.5 min and t_{minor} = 10.22 min.

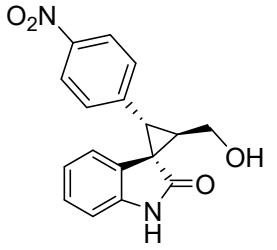


(*1R,2S,3R*)-2-(4-bromophenyl)-3-(hydroxymethyl)spiro[cyclopropane-1,3'-indolin]-2'-one (5f): Isolated yield 255 mg, 74%, ee 97% d.r. 88/12. Light yellow

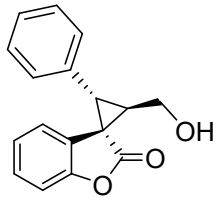
solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.07 (m, 3H), 7.05 – 6.95 (m, 2H), 6.58 (d, *J* = 7.7 Hz, 1H), 4.21 – 4.13 (m, 1H), 3.89 (dd, *J* = 11.8, 9.0 Hz, 1H), 3.16 (s, 1H), 3.03 (d, *J* = 8.4 Hz, 1H), 2.81 (td, *J* = 8.5, 5.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 141.3, 133.4, 131.2, 131.1, 127.9, 127.3, 122.0, 121.3, 120.6, 110.5, 60.23, 41.1, 38.5, 38.0. HPLC: Chiralpak AD-3, *i*-PrOH/hexane = 25/75, flow rate = 1.0 mL/min, λ= 254 nm; t_{major} = 12.62 min and t_{minor} = 13.54 min.



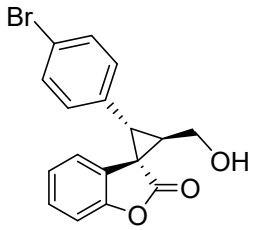
(*1R,2R,3S*)-2-(hydroxymethyl)-3-(4-methoxyphenyl)spiro[cyclopropane-1,3'-indolin]-2'-one (5g): Isolated yield 186 mg, 63%, ee 99% d.r. 80/20. Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.25 – 7.17 (m, 3H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.07 – 7.01 (m, 1H), 6.83 – 6.78 (m, 3H), 4.26 (dt, *J* = 12.3, 5.9 Hz, 1H), 4.01 (ddd, *J* = 12.5, 8.8, 4.8 Hz, 1H), 3.76 (s, 3H), 3.14 (d, *J* = 8.4 Hz, 1H), 2.91 (td, *J* = 8.6, 5.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 158.9, 141.1, 130.4, 127.1, 126.0, 122.1, 120.6, 113.6, 110.1, 60.8, 55.3, 42.0, 38.9, 37.9. HPLC: Chiralpak AD-3, *i*-PrOH/hexane = 25/75, flow rate = 1.0 mL/min, λ= 254 nm; t_{major} = 18.59 min and t_{minor} = 21.37 min.



(*1R,2R,3S*)-2-(hydroxymethyl)-3-(4-nitrophenyl)spiro[cyclopropane-1,3'-indolin]-2'-one (5h): Isolated yield 186 mg, 60%, ee 97% d.r. 85/15. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.12 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 4.27 (dt, *J* = 11.8, 5.8 Hz, 1H), 4.10 – 4.01 (m, 1H), 3.21 (d, *J* = 8.4 Hz, 1H), 2.93 (td, *J* = 8.4, 5.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 147.2, 142.0, 141.2, 130.3, 127.7, 127.3, 123.3, 122.4, 120.9, 110.4, 60.2, 40.6, 38.4, 38.4. HPLC: Chiralpak IC, *i*-PrOH/hexane = 40/60, flow rate = 0.5 mL/min, λ= 254 nm; t_{major} = 15.57 min and t_{minor} = 20.50 min.

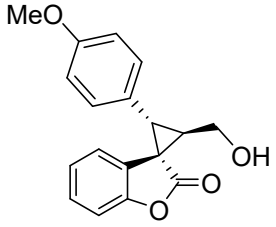


(*2'R,3R,3'S*)-2'-(hydroxymethyl)-3'-phenyl-2*H*-spiro[benzofuran-3,1'-cyclopropan]-2-one (5i): Isolated yield 144 mg, 54%, ee 99% d.r. 72/28. White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 6H), 7.22 – 7.15 (m, 3H), 4.21 (d, *J* = 12.0 Hz, 1H), 4.04 (dd, *J* = 11.9, 8.4 Hz, 1H), 3.27 (d, *J* = 8.6 Hz, 1H), 2.97 (td, *J* = 8.3, 5.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 153.9, 132.9, 129.2, 128.4, 128.0, 126.6, 124.1, 120.9, 111.0, 60.1, 43.0, 39.5, 35.7. HPLC: Chiralpak AD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ= 254 nm; t_{major} = 11.14 min and t_{minor} = 10.65 min. HRMS (EI) m/z calcd for $C_{17}H_{14}O_3$ (M^+): 266.0943; found:266.0937.

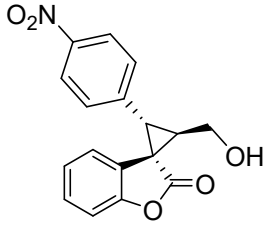


(*2'S,3R,3'R*)-2'-(4-bromophenyl)-3'-(hydroxymethyl)-2*H*-

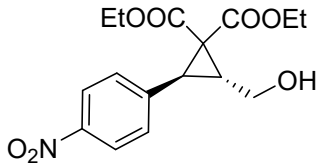
spiro[benzofuran-3,1'-cyclopropan]-2-one (5j): Isolated yield 200 mg, 58%, ee 97% d.r. 85/15. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.33 (ddd, *J* = 8.8, 5.9, 3.2 Hz, 1H), 7.22 – 7.15 (m, 5H), 4.25 – 4.17 (m, 1H), 4.10 – 4.01 (m, 1H), 3.21 (d, *J* = 8.6 Hz, 1H), 2.96 – 2.89 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 154.0, 132.0, 131.5, 130.9, 128.2, 126.2, 124.2, 122.0, 121.0, 111.2, 60.0, 42.1, 39.3, 35.7. HPLC: Chiralpak AD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ= 254 nm; t_{major} = 15.65 min and t_{minor} = 11.45 min. HRMS (EI) m/z calcd for $C_{17}H_{13}BrO_3$ (M^+): 344.0048; found:344.0040.



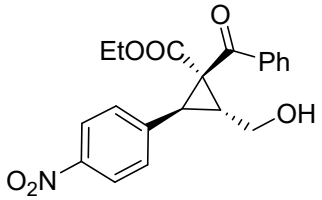
(*2'R,3R,3'S*)-2'-(hydroxymethyl)-3'-(4-methoxyphenyl)-2*H*-spiro[benzofuran-3,1'-cyclopropan]-2-one (5k): Isolated yield 145 mg, 49%, ee 98% d.r. 70/30. Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (ddd, *J* = 8.1, 6.1, 3.0 Hz, 1H), 7.25 – 7.14 (m, 5H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.23 (dd, *J* = 11.4, 4.8 Hz, 1H), 4.06 (dd, *J* = 12.1, 8.2 Hz, 1H), 3.79 (s, 3H), 3.23 (d, *J* = 8.6 Hz, 1H), 2.96 (td, *J* = 8.4, 5.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 159.3, 153.9, 130.3, 127.9, 126.7, 124.8, 124.1, 120.8, 113.8, 111.1, 60.3, 55.4, 42.9, 39.7, 35.7. HPLC: Chiralpak AD-3, *i*-PrOH/hexane = 20/80, flow rate = 1.0 mL/min, λ= 254 nm; t_{major} = 18.08 min and t_{minor} = 16.38 min. HRMS (EI) m/z calcd for $C_{18}H_{16}O_4$ (M^+): 296.1049; found:296.1042.



(*2'R,3R,3'S*)-2'-(hydroxymethyl)-3'-(4-nitrophenyl)-2*H*-spiro[benzofuran-3,1'-cyclopropan]-2-one (5l): Isolated yield 143 mg, 46%, ee 98% d.r. 80/20. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.19 – 7.07 (m, 3H), 4.14 (dd, *J* = 11.2, 4.4 Hz, 1H), 4.03 (dd, *J* = 13.3, 6.9 Hz, 1H), 3.26 (d, *J* = 8.6 Hz, 1H), 2.90 (q, *J* = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 154.0, 147.4, 140.7, 130.3, 128.6, 125.6, 124.4, 121.2, 111.3, 59.6, 41.3, 39.3, 36.2. HPLC: Chiralpak IC, *i*-PrOH/hexane = 15/85, flow rate = 1.0 mL/min, λ= 254 nm; t_{major} = 54.32 min and t_{minor} = 28.94 min. HRMS (EI) m/z calcd for $C_{17}H_{13}NO_5$ (M^+): 311.0794; found:311.0784.



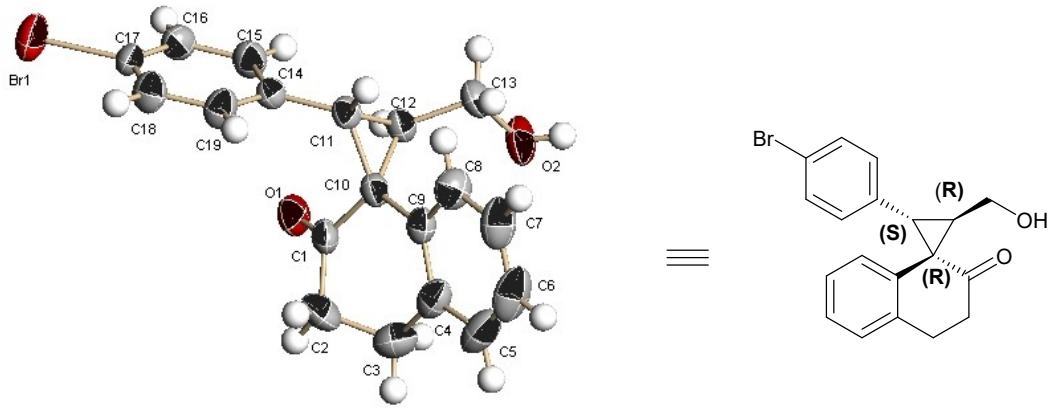
Diethyl (*2R,3S*)-2-(hydroxymethyl)-3-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (5m): Isolated yield 253 mg, 75%, ee 93% d.r. 95/5. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 4.37 – 4.22 (m, 2H), 4.00 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.97 – 3.84 (m, 2H), 3.67 (dd, *J* = 11.9, 8.2 Hz, 1H), 3.22 (d, *J* = 8.0 Hz, 1H), 2.85 (q, *J* = 7.9 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 166.0, 147.0, 141.9, 129.5, 123.2, 62.2, 61.6, 60.2, 42.1, 33.9, 32.2, 13.9, 13.6. HPLC: Chiralpak IC, *i*-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ= 254 nm; t_{major} = 30.98 min and t_{minor} = 29.08 min.



Ethyl (*1S,2R,3S*)-1-benzoyl-2-(hydroxymethyl)-3-(4-nitrophenyl)cyclopropane-1-carboxylate (5n): Isolated yield 225 mg, 61%, ee 92% d.r. 90/10. Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.36 – 7.28 (m, 4H), 4.17 – 3.99 (m, 3H), 3.84 (dd, *J* = 11.4, 8.6 Hz, 1H), 3.59 (d, *J* = 7.9 Hz, 1H), 3.21 (td, *J* = 8.1, 5.9 Hz, 1H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 168.8, 147.1, 141.8, 136.8, 133.4, 128.9, 128.7, 128.1, 123.6, 62.4, 60.0, 47.6, 36.3, 31.7, 13.7. HPLC: Chiralpak IC, *i*-PrOH/hexane = 15/85, flow rate = 1.0 mL/min, λ= 254 nm; t_{major} = 20.95 min and t_{minor} = 17.66 min.

5. X-ray data for compound 5b

The absolute configuration of the products was determined by single crystal X-ray diffraction of **5b**. Crystals of compound **5b** were obtained by slow evaporation of the mixture (methyl tert-butyl ether/chloroform 8:1) at 4 °C.

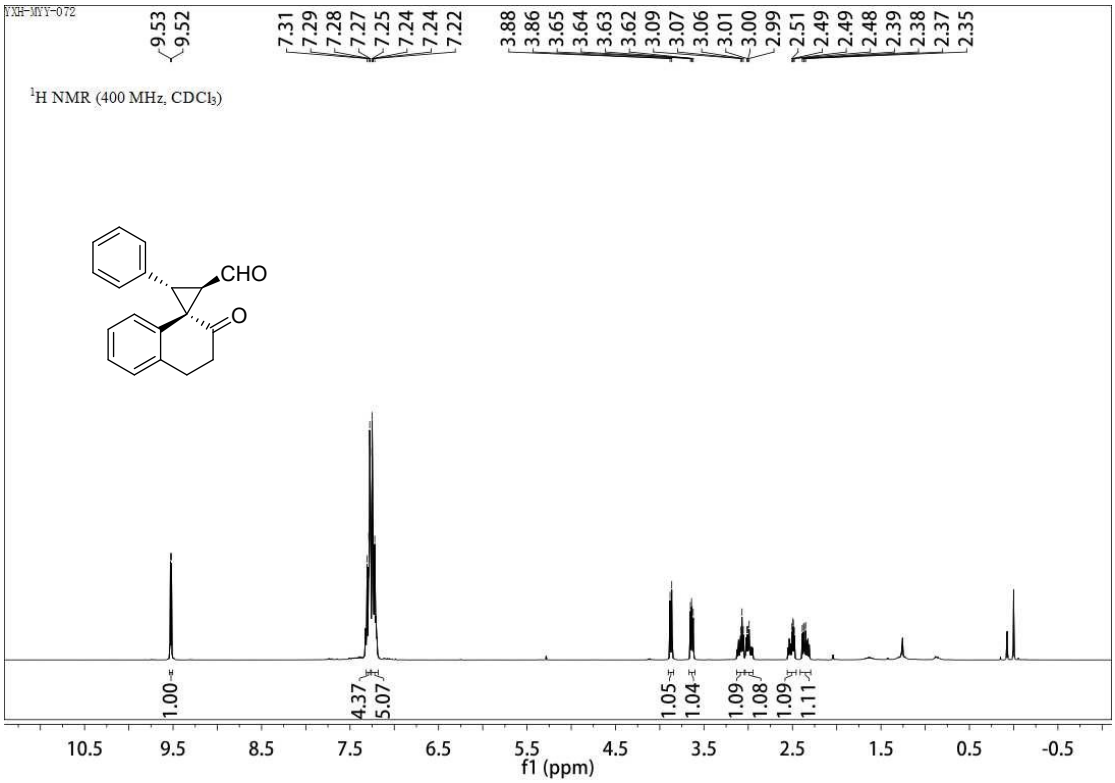


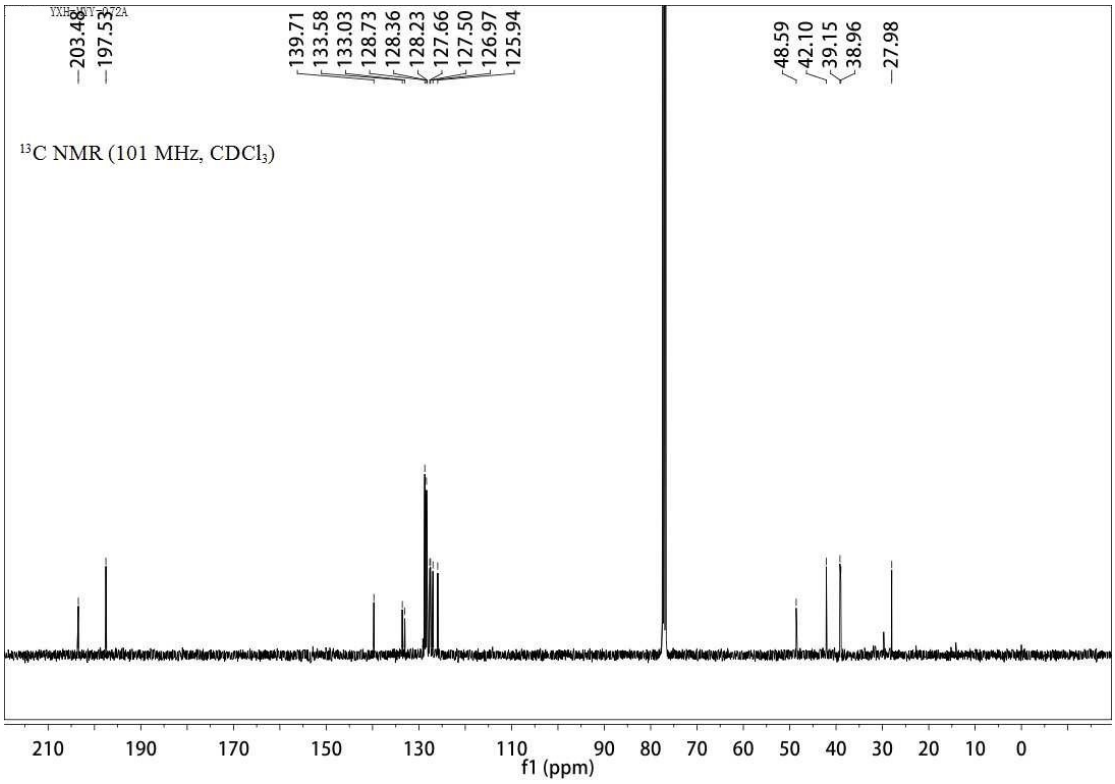
Identification code	cd15018	
Empirical formula	C19 H17 Br O2	
Formula weight	357.23	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.1586(8) Å	α= 90°.
	b = 11.9651(14) Å	β= 90°.
	c = 18.845(2) Å	γ = 90°.
Volume	1614.2(3) $Å^3$	
Z	4	
Density (calculated)	1.470 Mg/m^3	
Absorption coefficient	2.551 mm^{-1}	
F(000)	728	
Crystal size	0.210 x 0.170 x 0.120 mm^3	
Theta range for data collection	2.016 to 25.489°.	
Index ranges	-8<=h<=8, -14<=k<=13, -18<=l<=22	
Reflections collected	9465	
Independent reflections	3005 [R(int) = 0.0622]	

Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.4904
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3005 / 0 / 200
Goodness-of-fit on F^2	1.010
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.0886
R indices (all data)	R1 = 0.0708, wR2 = 0.0981
Absolute structure parameter	0.011(12)
Extinction coefficient	n/a
Largest diff. peak and hole	0.341 and -0.336 e.$Å^{-3}$

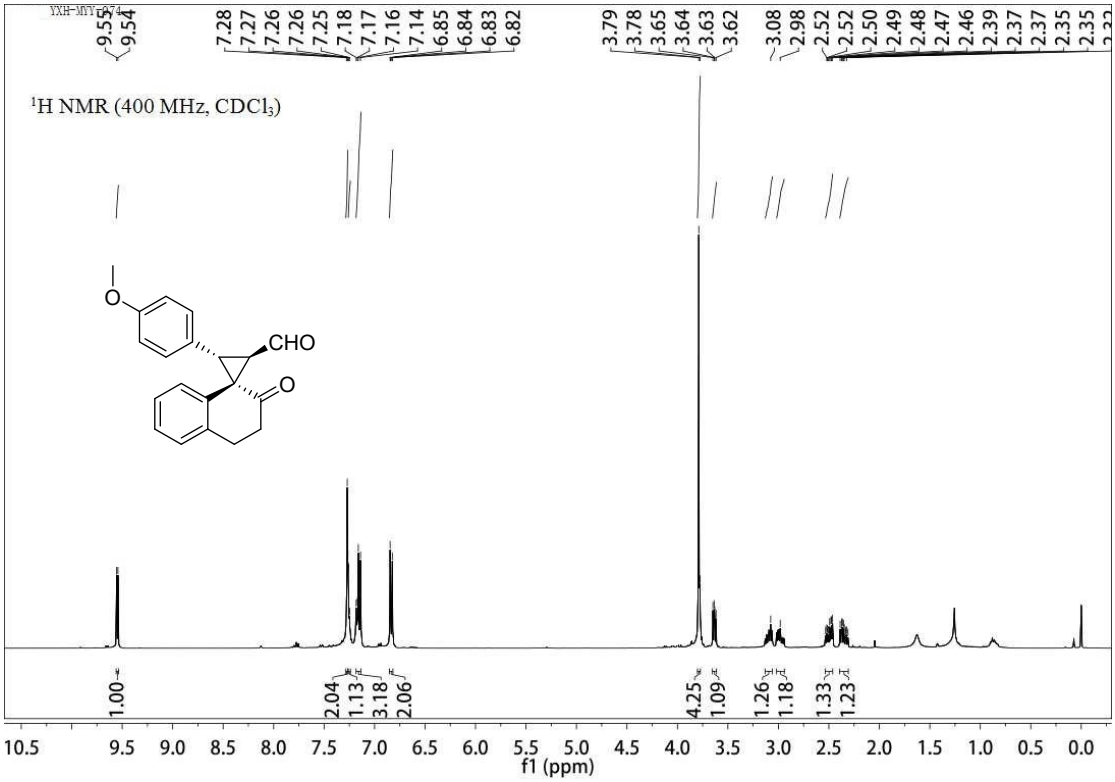
6. NMR spectrum

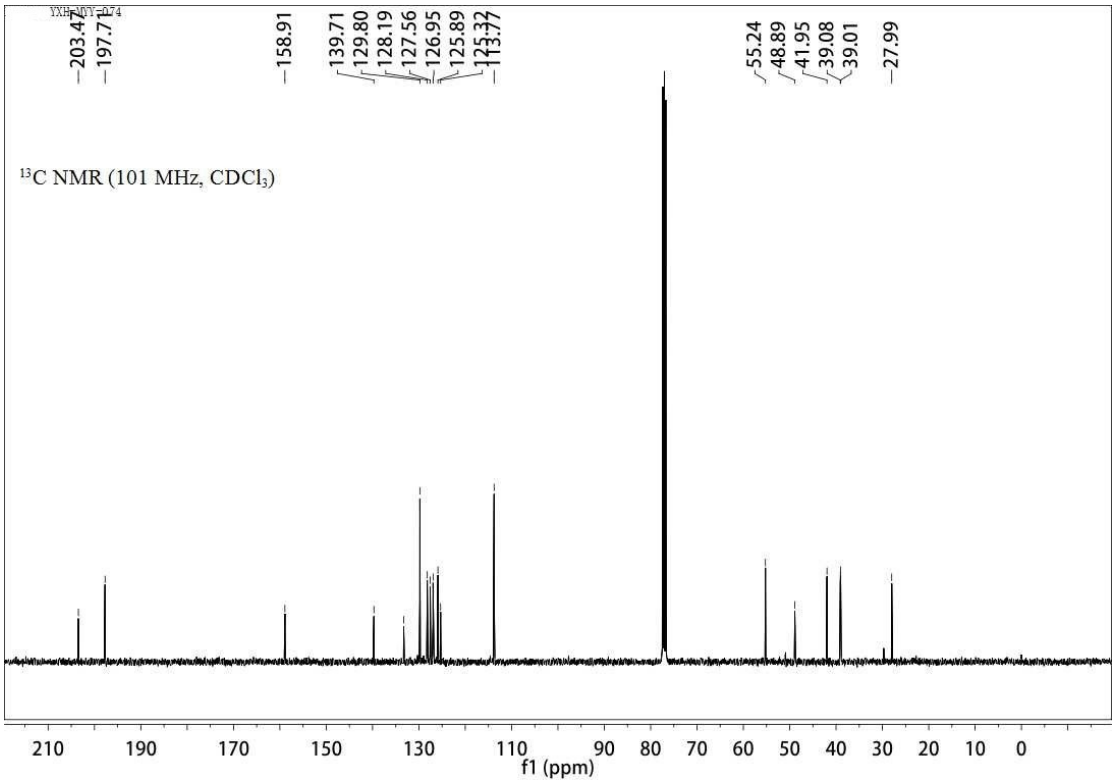
3c



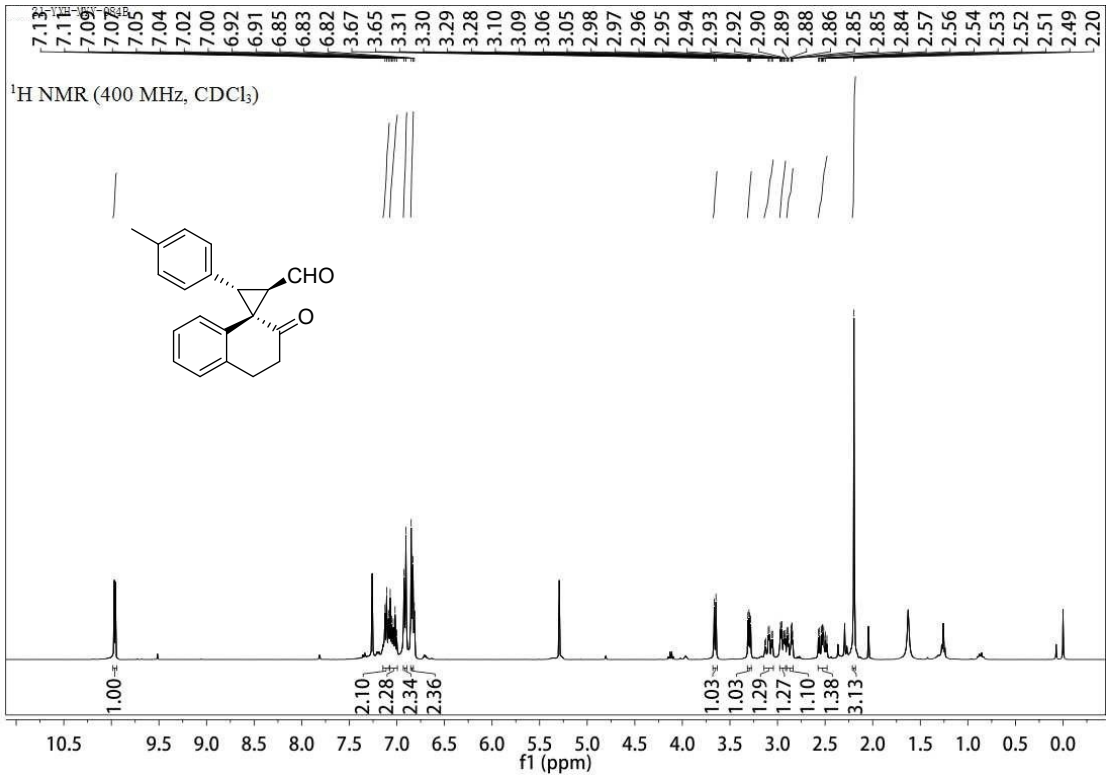


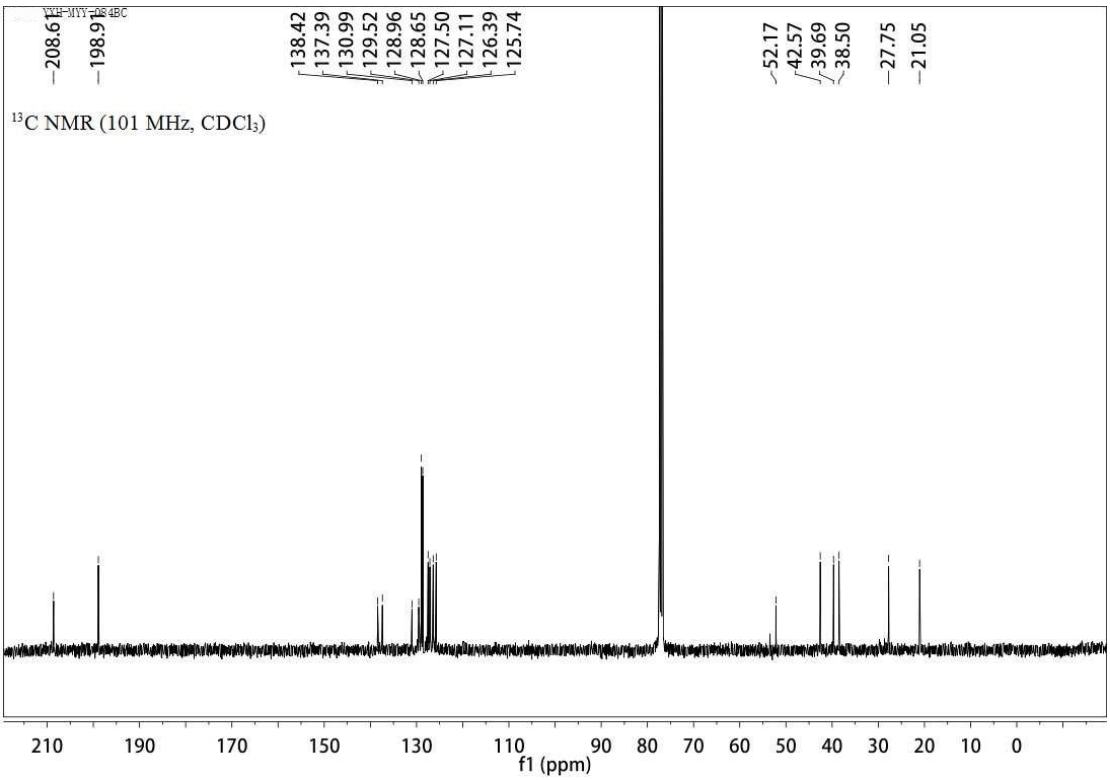
3b



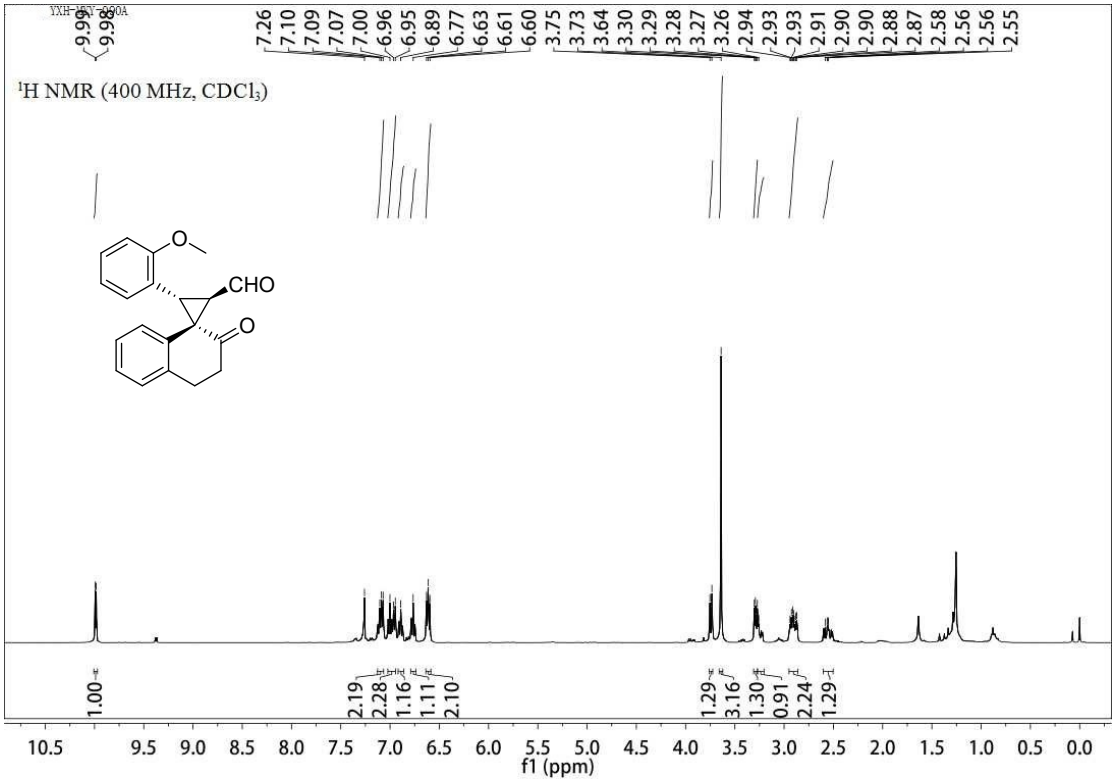


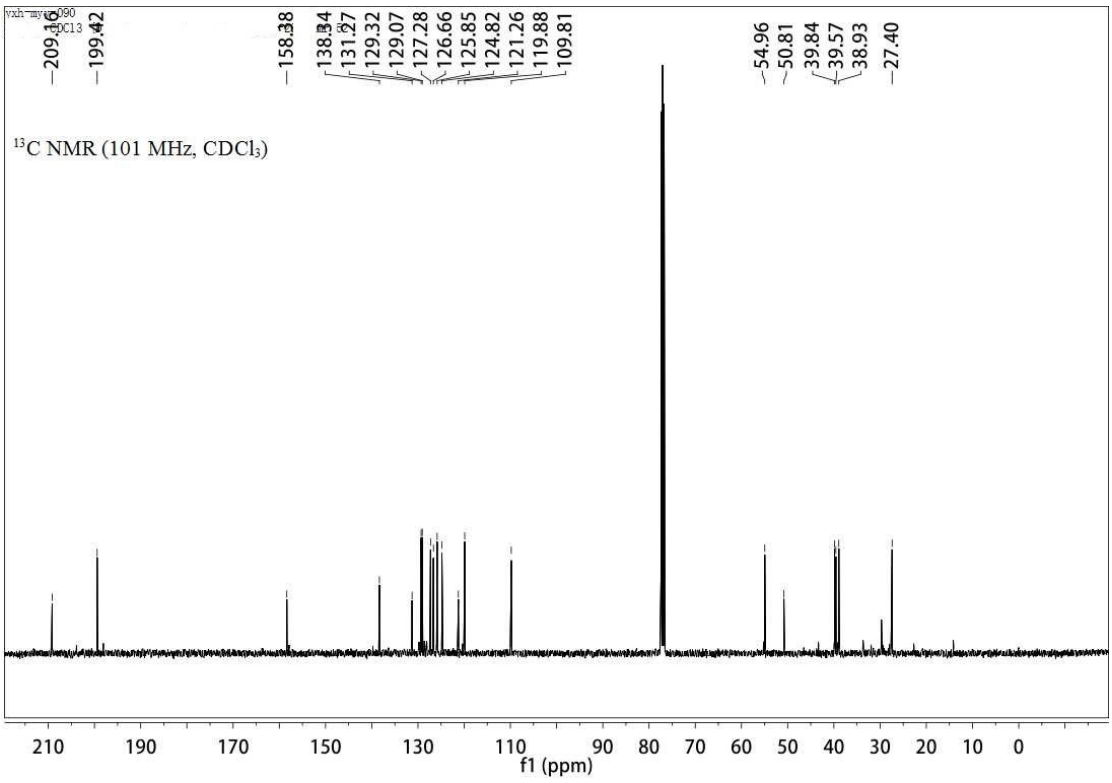
3c


7.15 7.11 7.09 7.07 7.05 7.04 7.02 7.00 6.92 6.91 6.85 6.83 6.82 3.67 3.65 3.31 3.30 3.29 3.28 3.10 3.09 3.06 3.05 2.98 2.97 2.96 2.95 2.94 2.93 2.92 2.90 2.89 2.88 2.86 2.85 2.85 2.84 2.57 2.56 2.54 2.53 2.52 2.51 2.49 2.20
^{1}H NMR (400 MHz, $CDCl_3$)
CHO
O
1.00 2.10 2.28 2.34 2.36 1.03 1.03 1.29 1.27 1.10 1.38 3.13
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

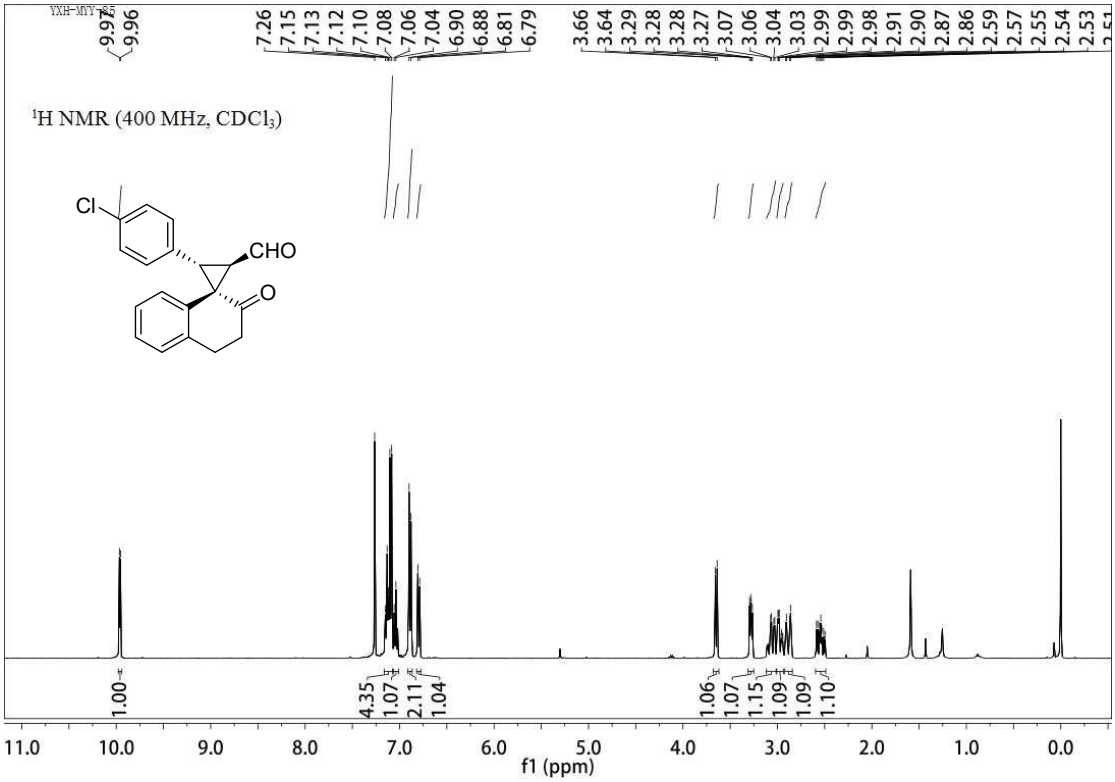

208.61 198.91 138.42 137.39 130.99 129.52 128.96 128.65 127.50 127.11 126.39 125.74 52.17 42.57 39.69 38.50 27.75 21.05
^{13}C NMR (101 MHz, $CDCl_3$)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

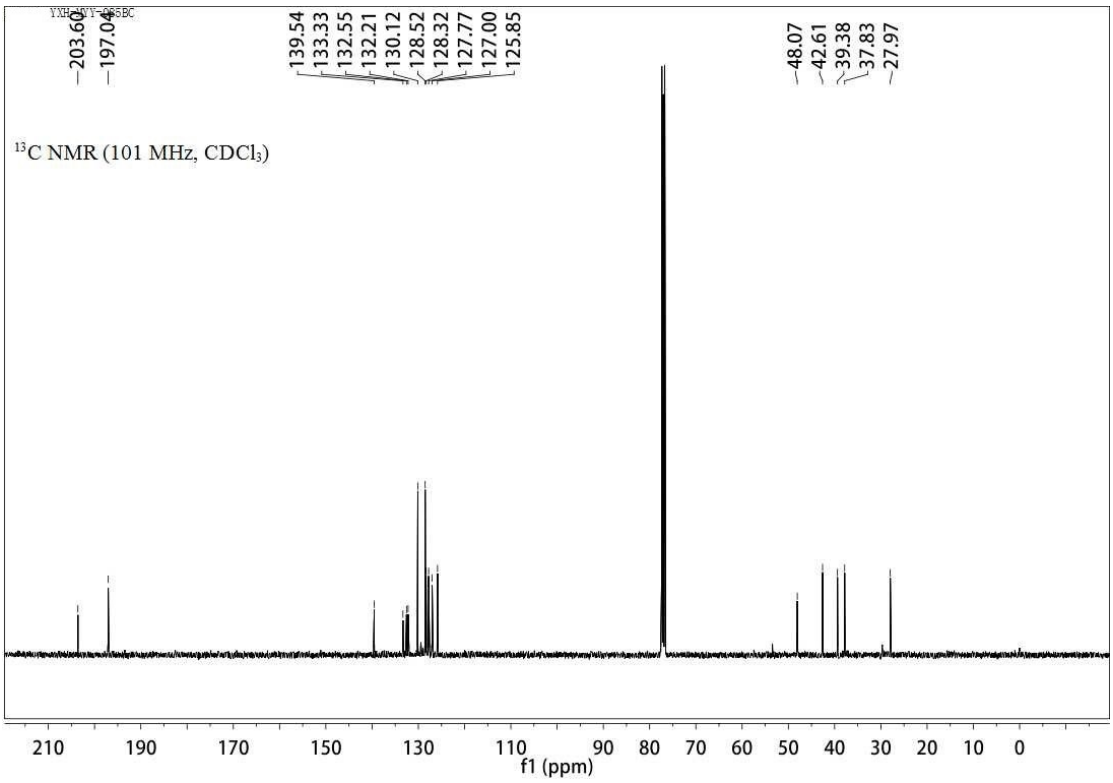
3d



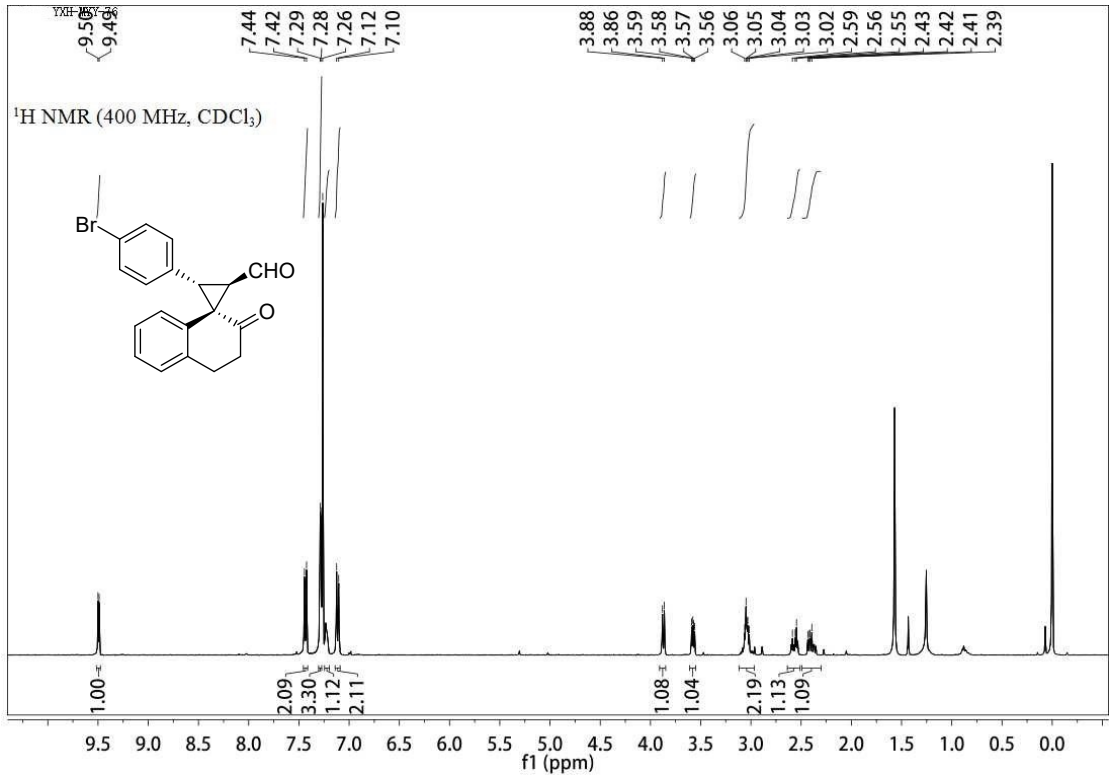


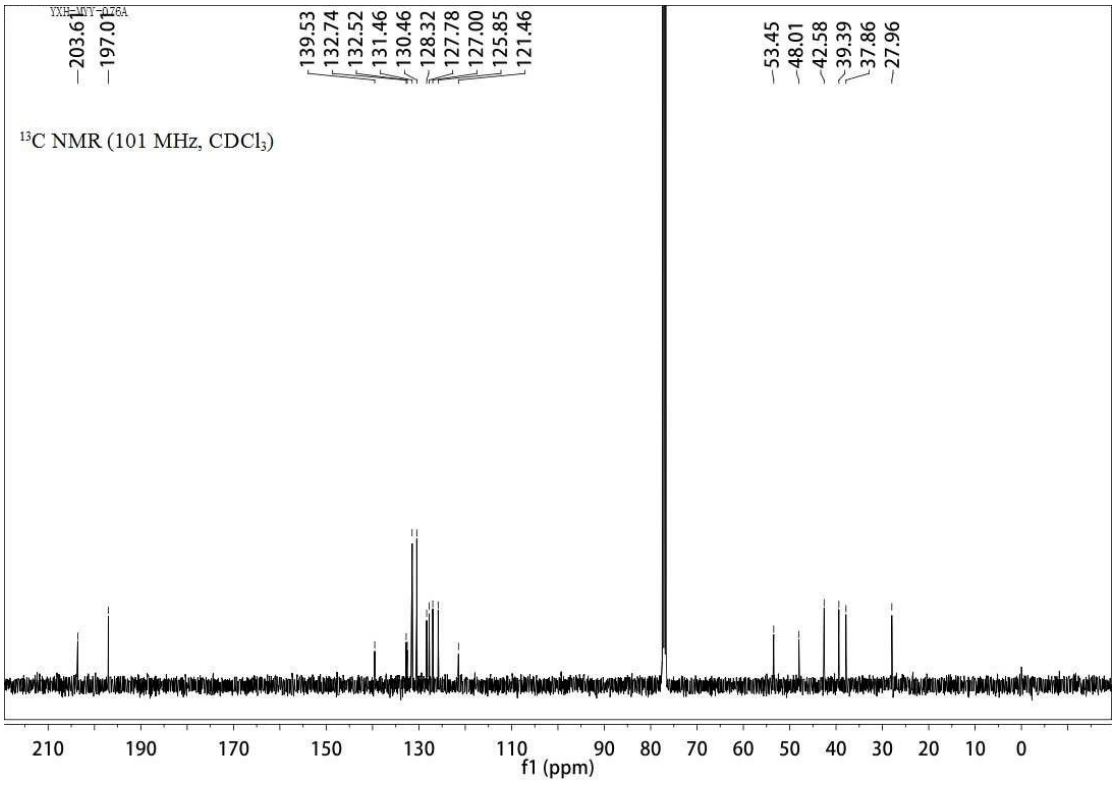
3e



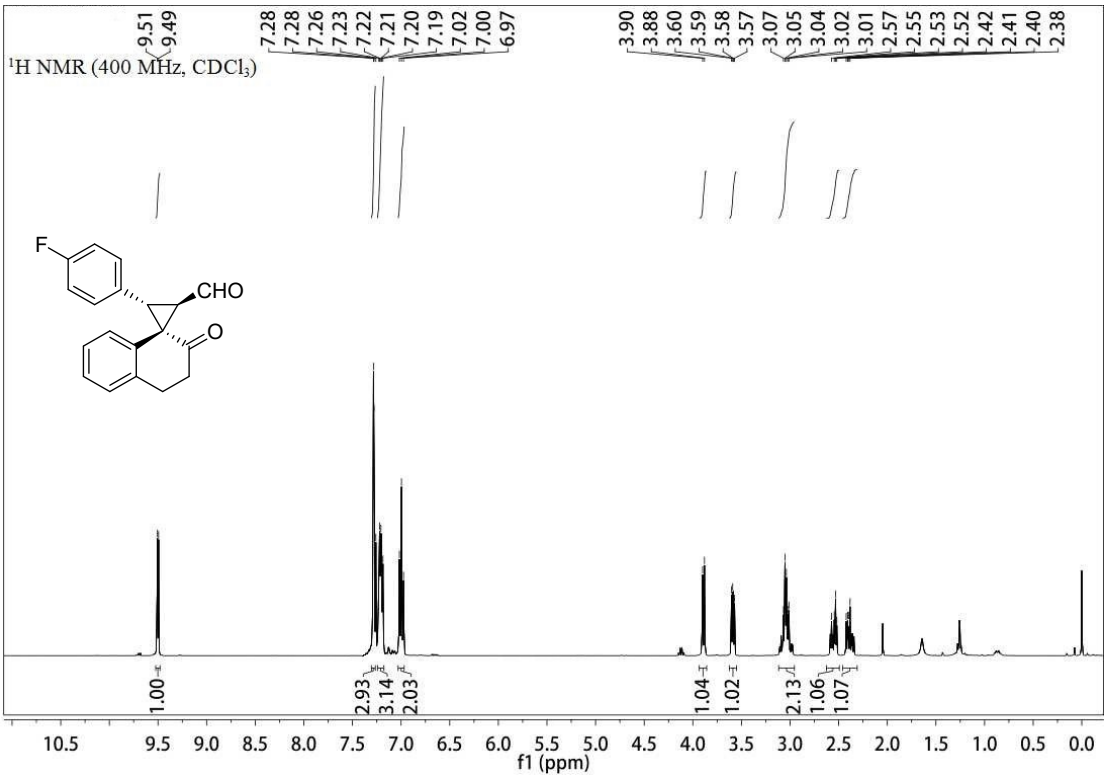


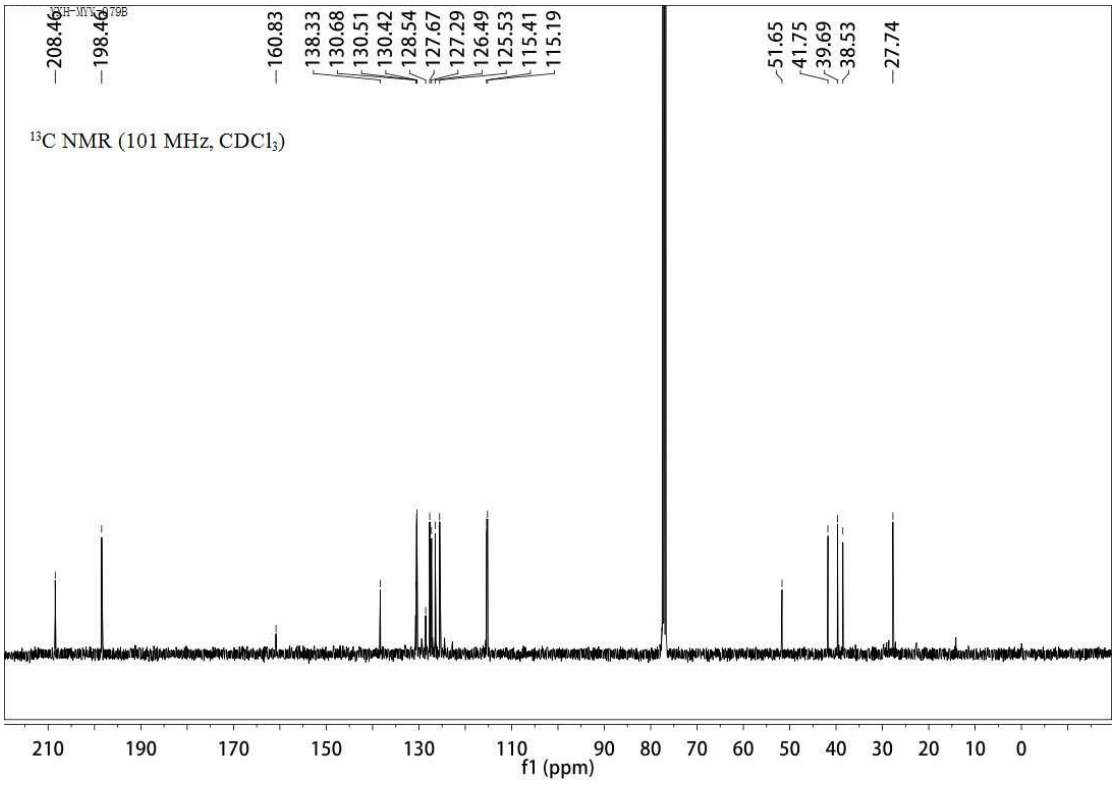
3f


9.50
9.49
7.44
7.42
7.29
7.28
7.26
7.12
7.10
3.88
3.86
3.59
3.58
3.57
3.56
3.06
3.05
3.04
3.03
3.02
2.59
2.56
2.55
2.43
2.42
2.41
2.39
^{1}H NMR (400 MHz, $CDCl_3$)
Br
CHO
O
1.00
2.09
3.30
1.12
2.11
1.08
1.04
2.19
1.13
1.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

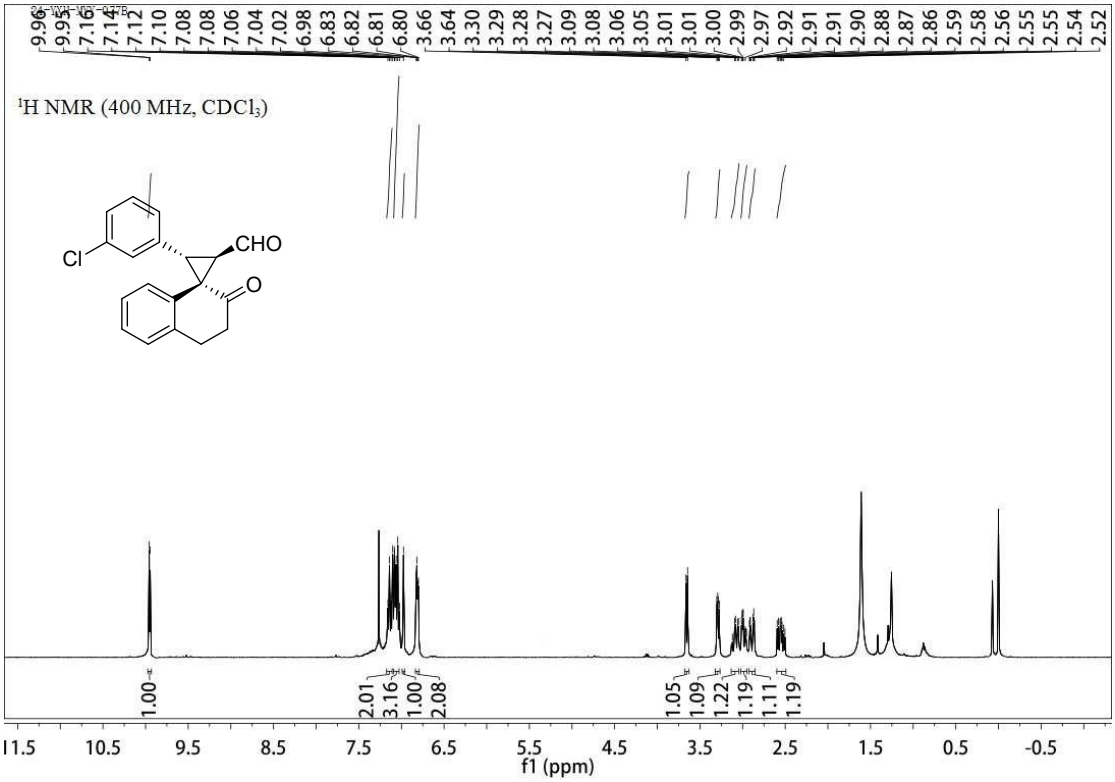

203.67
197.01
139.53
132.74
132.52
131.46
130.46
128.32
127.78
127.00
125.85
121.46
53.45
48.01
42.58
39.39
37.86
27.96
^{13}C NMR (101 MHz, $CDCl_3$)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

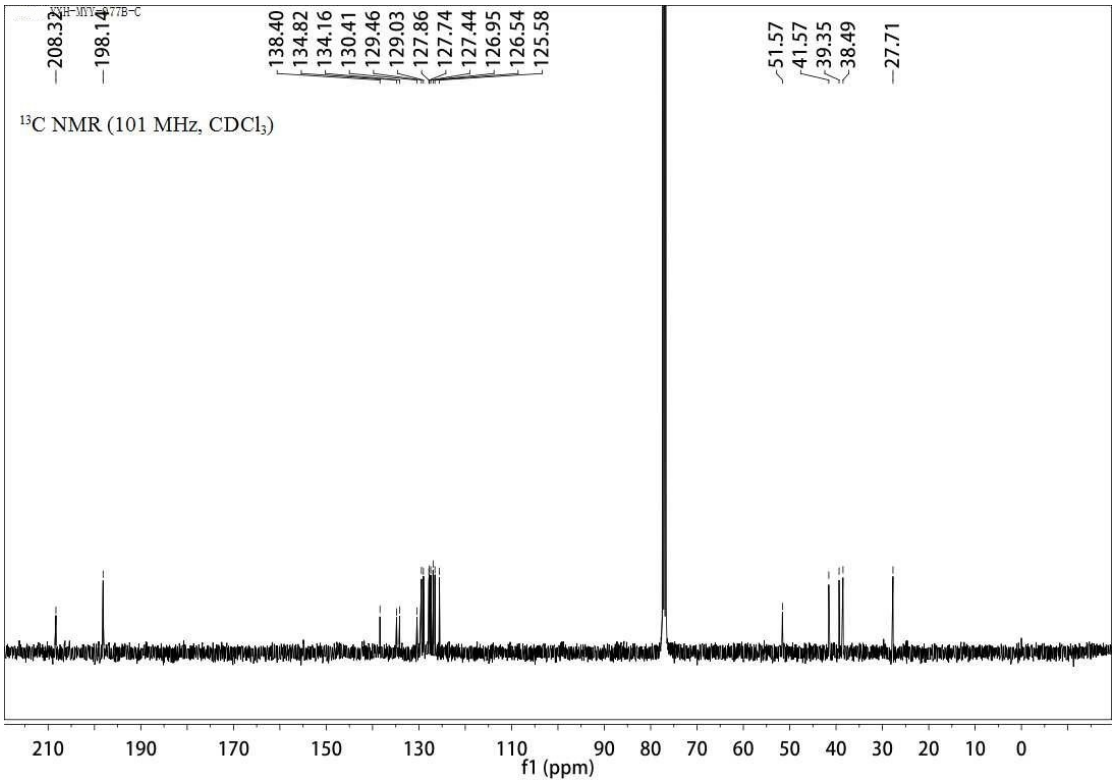
3g


9.51
9.49
7.28
7.28
7.26
7.23
7.22
7.21
7.20
7.19
7.02
7.00
6.97
3.90
3.88
3.60
3.59
3.58
3.57
3.07
3.05
3.04
3.02
3.01
2.57
2.55
2.53
2.52
2.42
2.41
2.40
2.38
^{1}H NMR (400 MHz, $CDCl_3$)
F
CHO
O
1.00
2.93
3.14
2.03
1.04
1.02
2.13
1.06
1.07
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

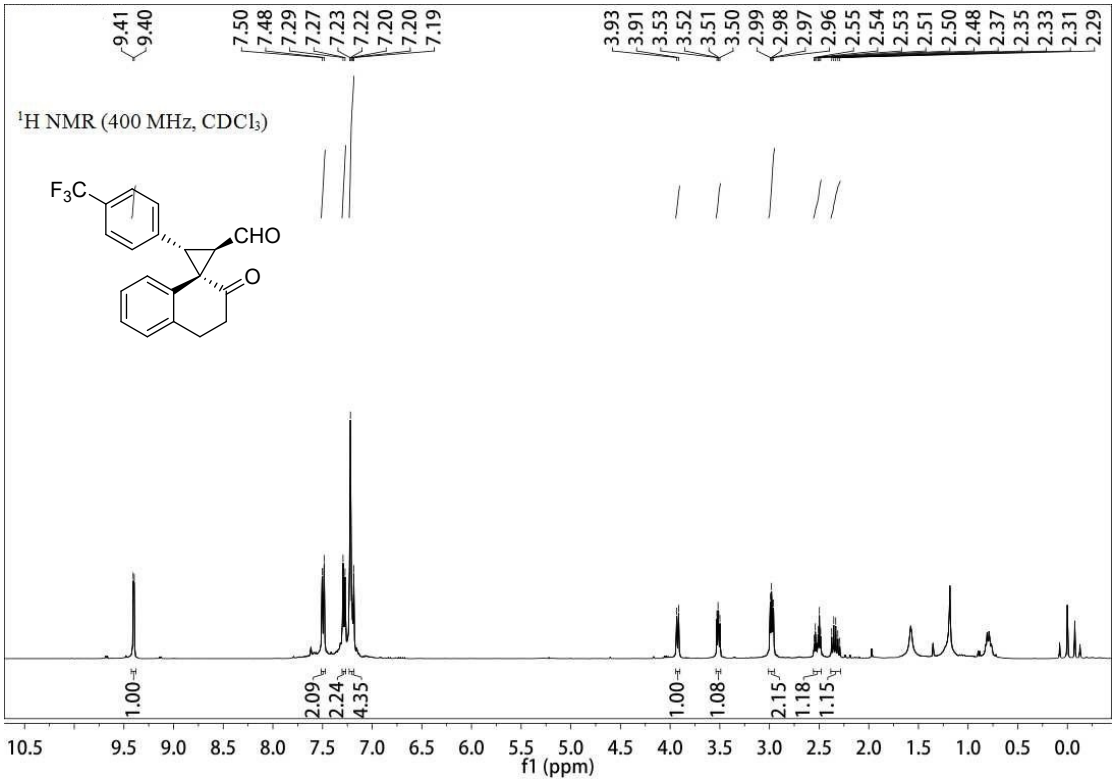

208.46
198.40
160.83
138.33
130.68
130.51
130.42
128.54
127.67
127.29
126.49
125.53
115.41
115.19
51.65
41.75
39.69
38.53
27.74
^{13}C NMR (101 MHz, $CDCl_3$)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

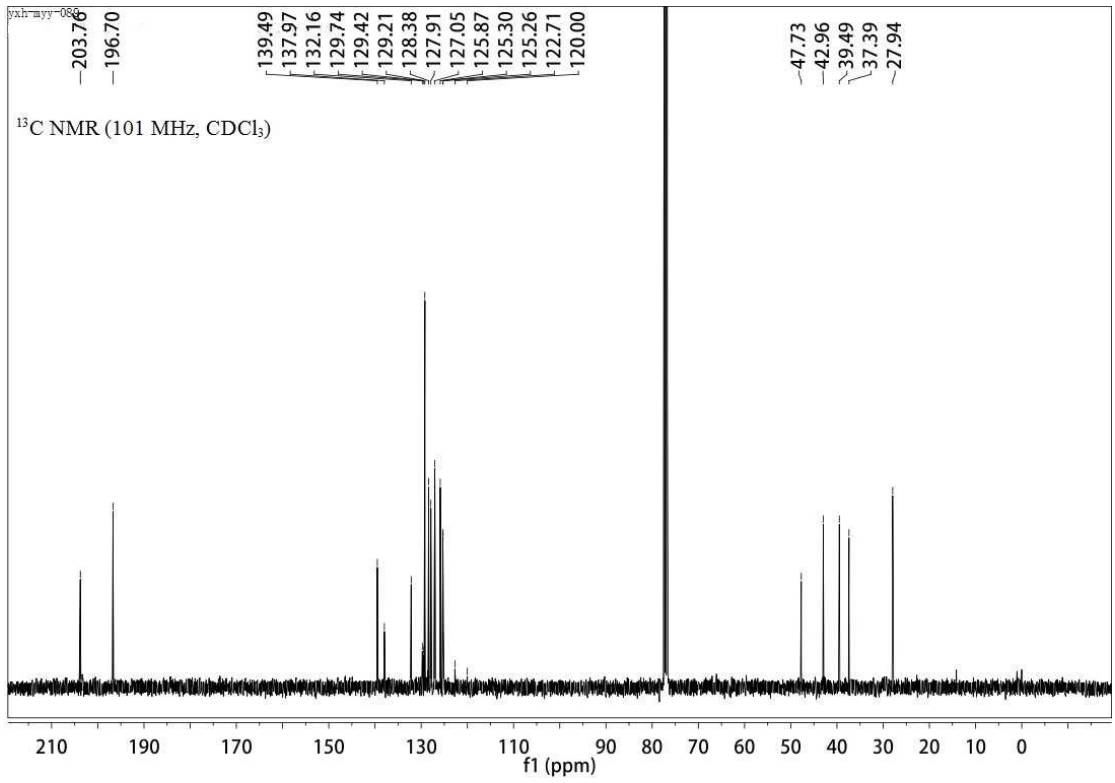
3h


9.96 9.95 7.16 7.14 7.12 7.10 7.08 7.08 7.06 7.04 7.02 6.98 6.83 6.82 6.81 6.80 3.66 3.64 3.30 3.29 3.28 3.27 3.09 3.08 3.06 3.05 3.01 3.01 3.00 2.99 2.97 2.92 2.91 2.91 2.90 2.88 2.87 2.86 2.59 2.58 2.56 2.55 2.55 2.54 2.52
^{1}H NMR (400 MHz, $CDCl_3$)
Cl
CHO
O
1.00 2.01 3.16 1.00 2.08 1.05 1.09 1.22 1.19 1.11 1.19
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)

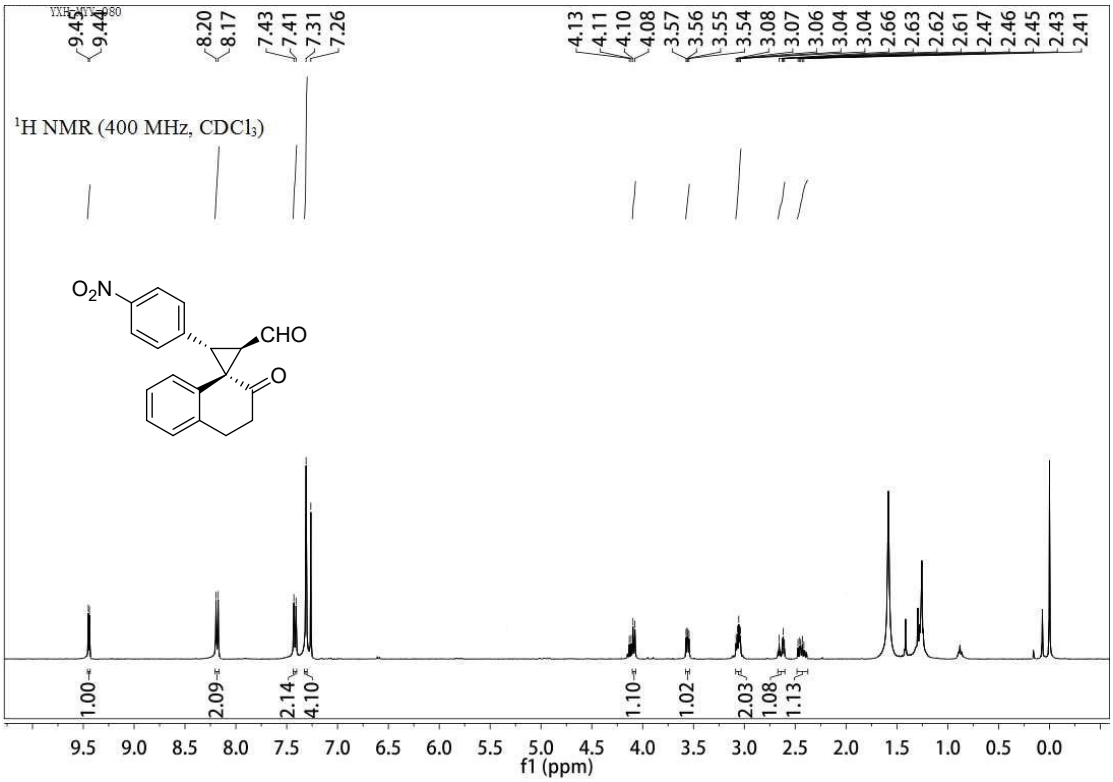

208.32 198.14 138.40 134.82 134.16 130.41 129.46 129.03 127.86 127.74 127.44 126.95 126.54 125.58 51.57 41.57 39.35 38.49 27.71
^{13}C NMR (101 MHz, $CDCl_3$)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

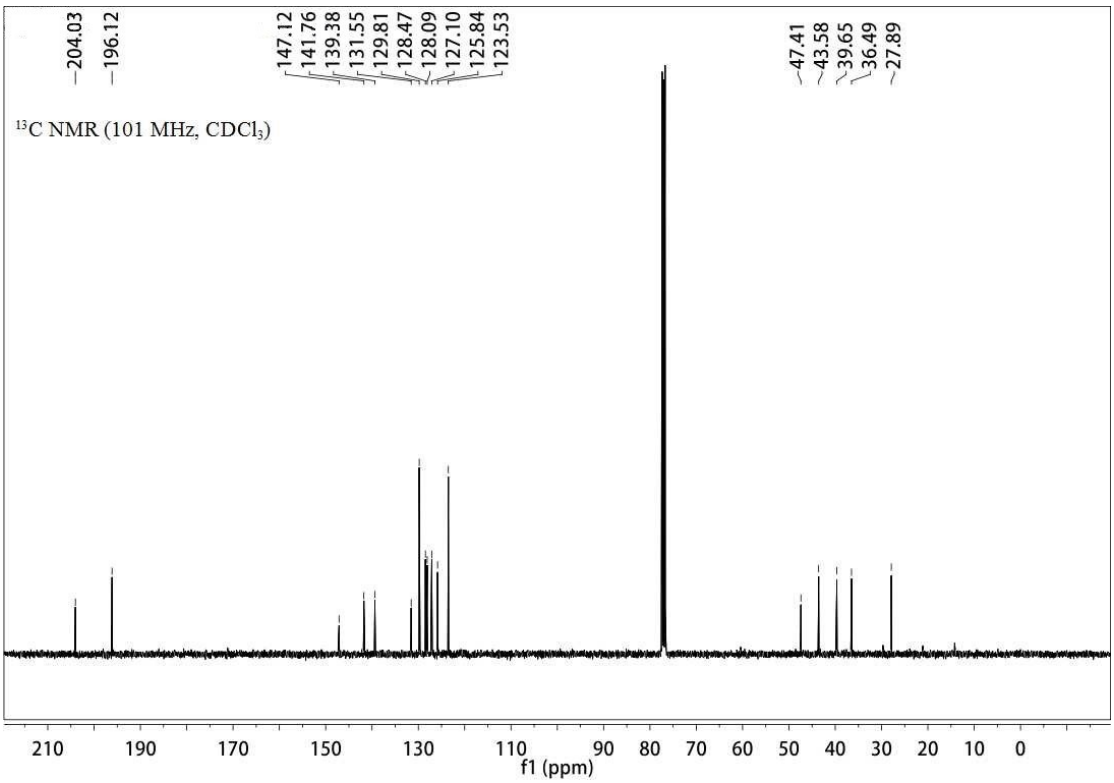
3i


9.41
9.40
7.50
7.48
7.29
7.27
7.23
7.22
7.20
7.20
7.19
3.93
3.91
3.53
3.52
3.51
3.50
2.99
2.98
2.97
2.96
2.55
2.54
2.53
2.51
2.50
2.48
2.37
2.35
2.33
2.31
2.29
^{1}H NMR (400 MHz, $CDCl_3$)
F_3C
CHO
O
1.00
2.09
2.24
4.35
1.00
1.08
2.15
1.18
1.15
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

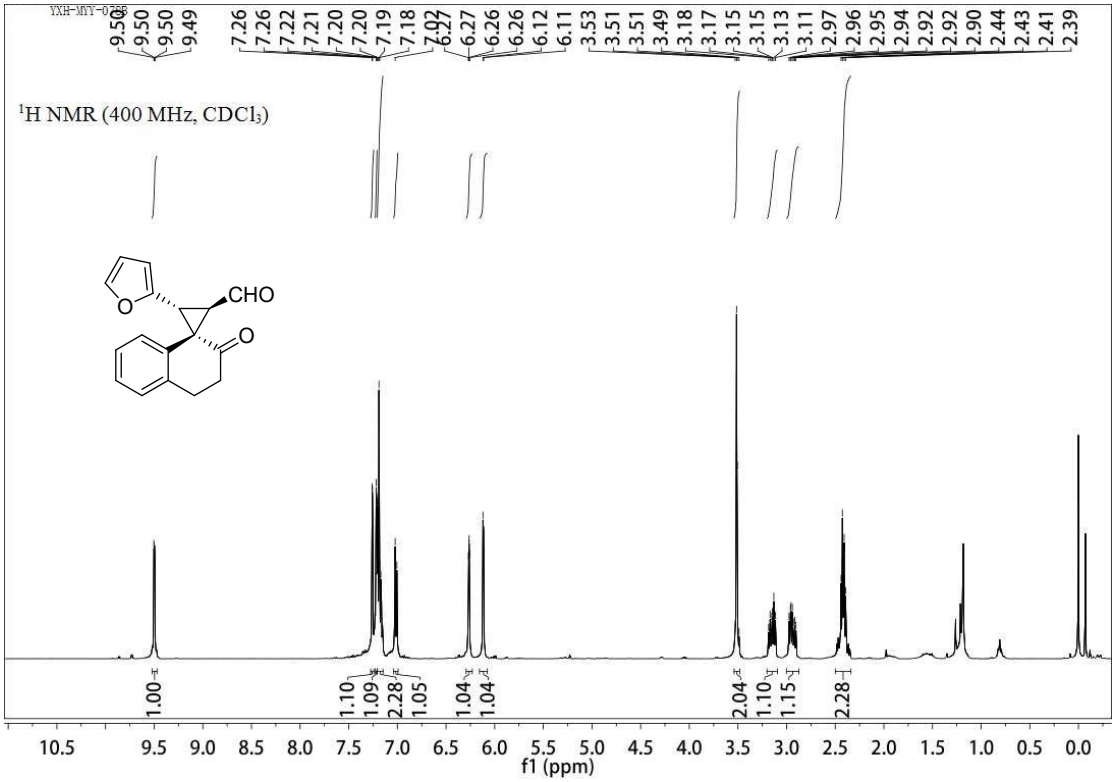

yxh-ayy-08
203.76
196.70
139.49
137.97
132.16
129.74
129.42
129.21
128.38
127.91
127.05
125.87
125.30
125.26
122.71
120.00
47.73
42.96
39.49
37.39
27.94
^{13}C NMR (101 MHz, $CDCl_3$)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

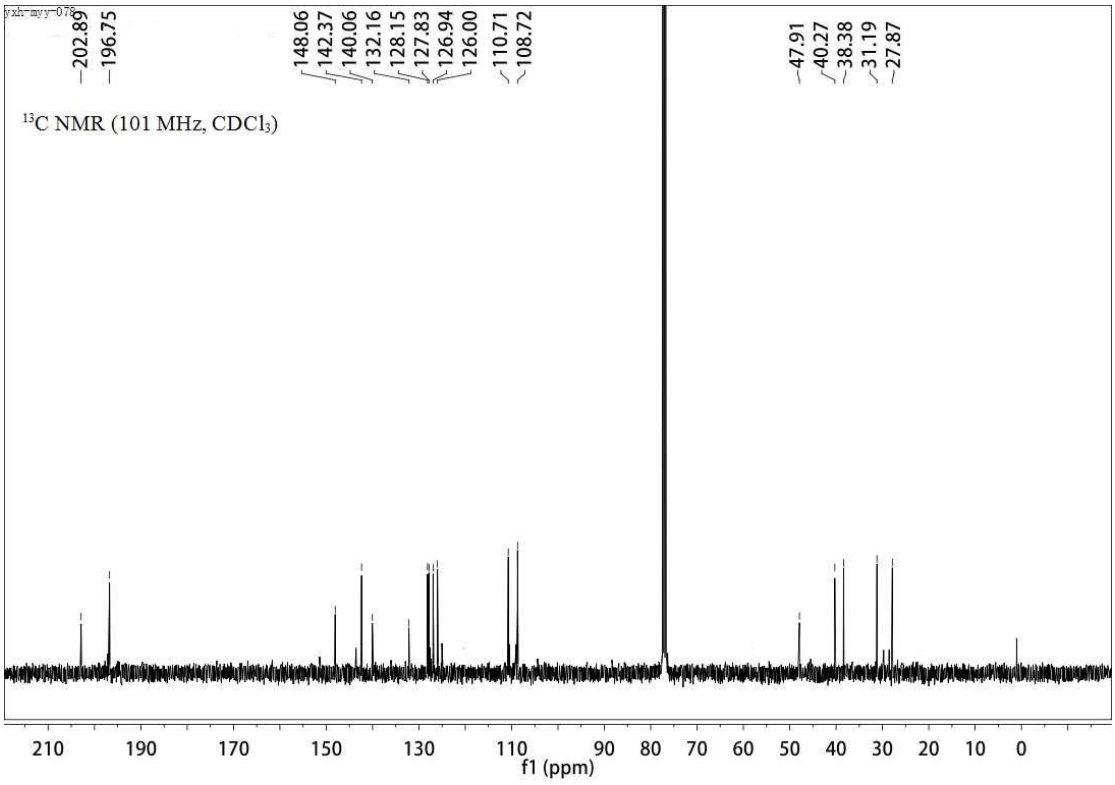
3j


9.45
9.44
8.20
8.17
7.43
7.41
7.31
7.26
4.13
4.11
4.10
4.08
3.57
3.56
3.55
3.54
3.08
3.07
3.06
3.04
3.04
2.66
2.63
2.62
2.61
2.47
2.46
2.45
2.43
2.41
^{1}H NMR (400 MHz, $CDCl_3$)
O_2N
CHO
O
1.00
2.09
2.14
4.10
1.10
1.02
2.03
1.08
1.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

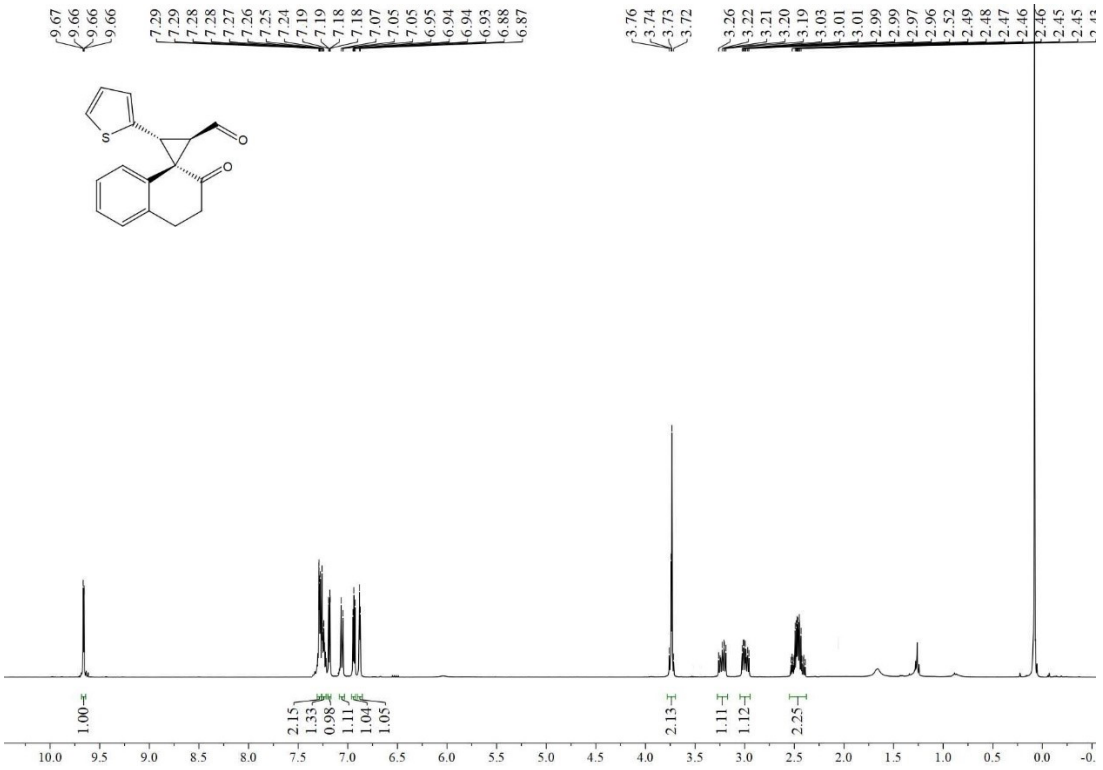

204.03
196.12
147.12
141.76
139.38
131.55
129.81
128.47
128.09
127.10
125.84
123.53
47.41
43.58
39.65
36.49
27.89
^{13}C NMR (101 MHz, $CDCl_3$)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

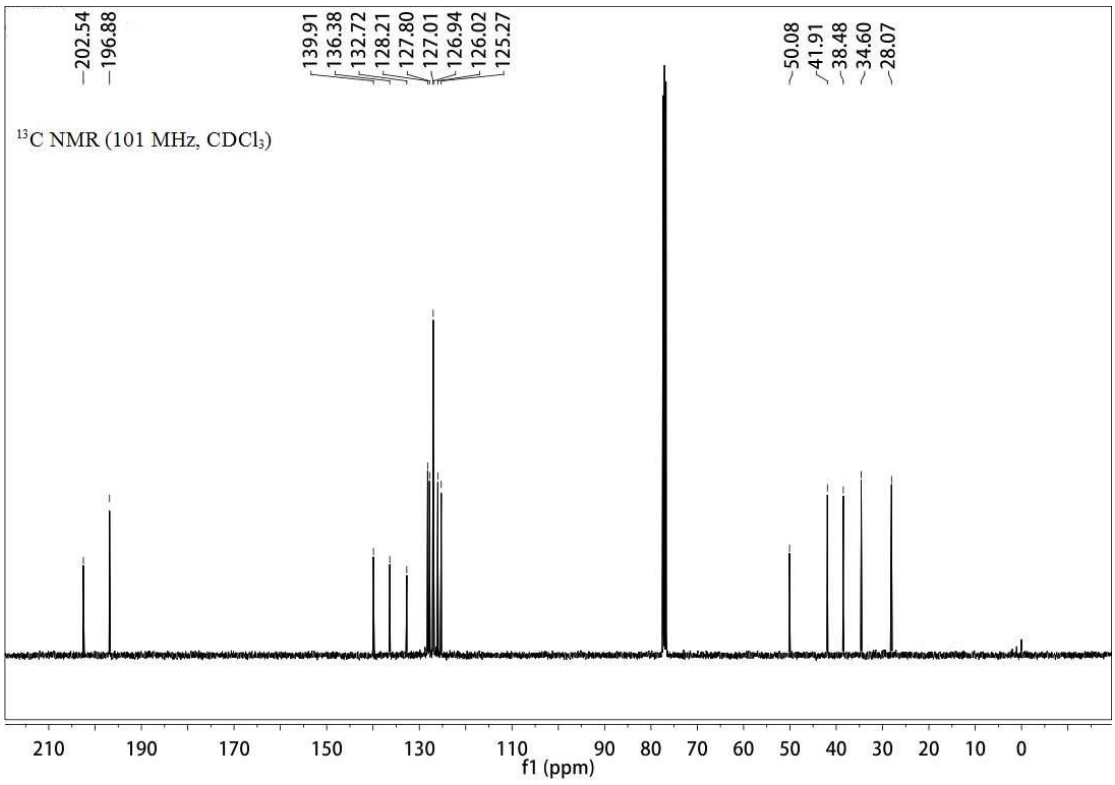
3k


YXH-MYY-0768
9.50
9.50
9.49
7.26
7.26
7.22
7.21
7.20
7.20
7.19
7.18
7.02
6.27
6.26
6.26
6.12
6.11
3.53
3.51
3.51
3.49
3.18
3.17
3.15
3.15
3.13
3.11
2.97
2.96
2.95
2.94
2.92
2.92
2.90
2.44
2.43
2.41
2.39
1H NMR (400 MHz, CDCl3)
CHO
O
O
1.00
1.10
1.09
2.28
1.05
1.04
1.04
2.04
1.10
1.15
2.28
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

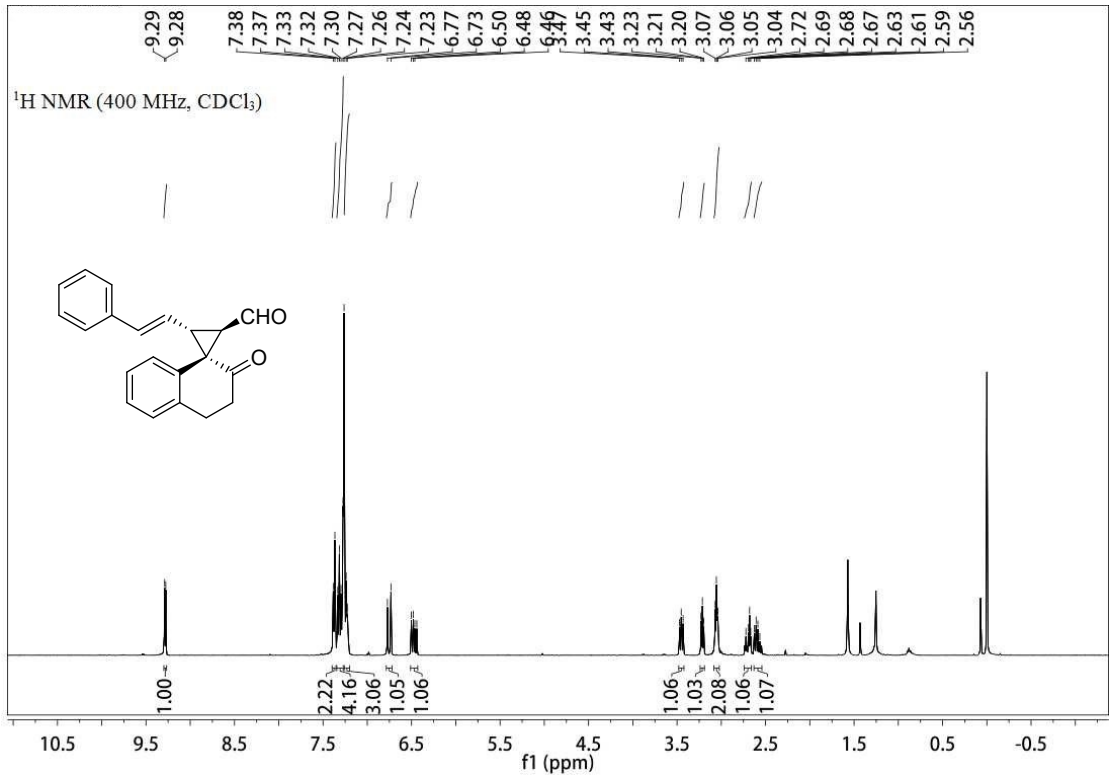

yxh-myy-076
202.89
196.75
148.06
142.37
140.06
132.16
128.15
127.83
126.94
126.00
110.71
108.72
47.91
40.27
38.38
31.19
27.87
13C NMR (101 MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

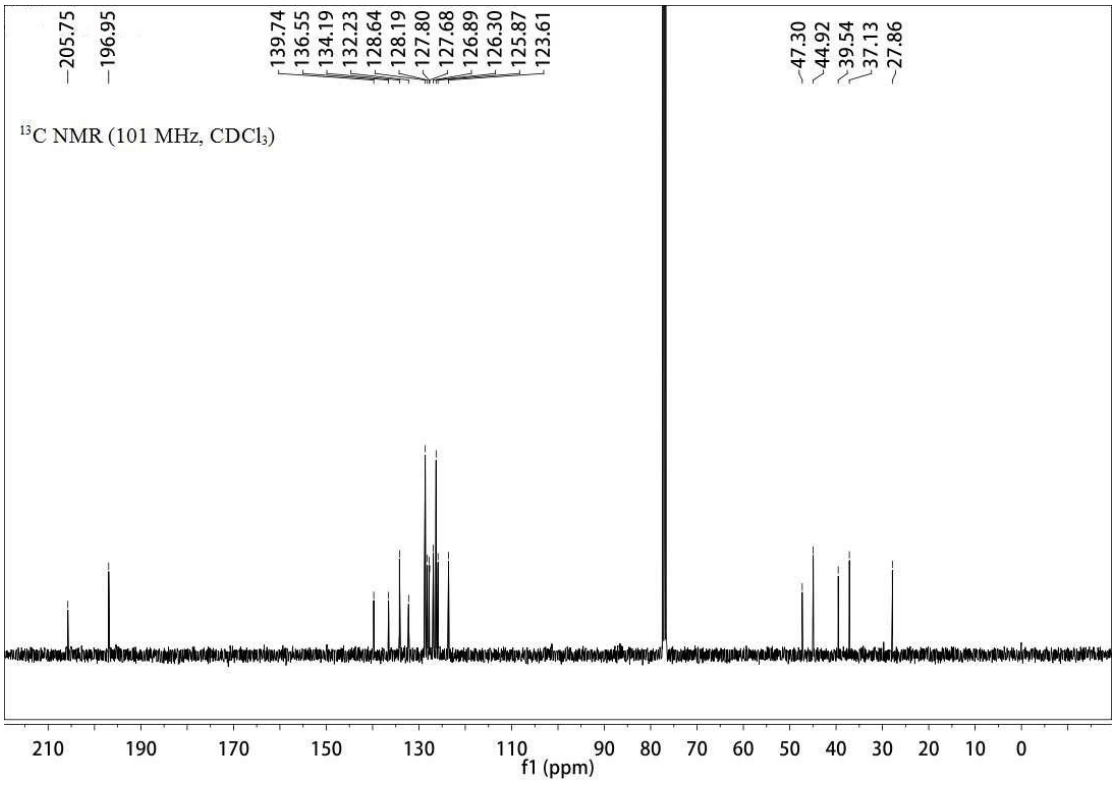
3l


9.67
9.66
9.66
9.66
7.29
7.29
7.28
7.28
7.27
7.26
7.25
7.24
7.19
7.19
7.18
7.18
7.07
7.05
7.05
6.95
6.94
6.94
6.93
6.88
6.87
3.76
3.74
3.73
3.72
3.26
3.22
3.21
3.20
3.19
3.03
3.01
3.01
2.99
2.99
2.97
2.96
2.52
2.49
2.48
2.47
2.46
2.46
2.45
2.45
S
O
O
1.00
2.15
1.33
0.98
1.11
1.04
1.05
2.13
1.11
1.12
2.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

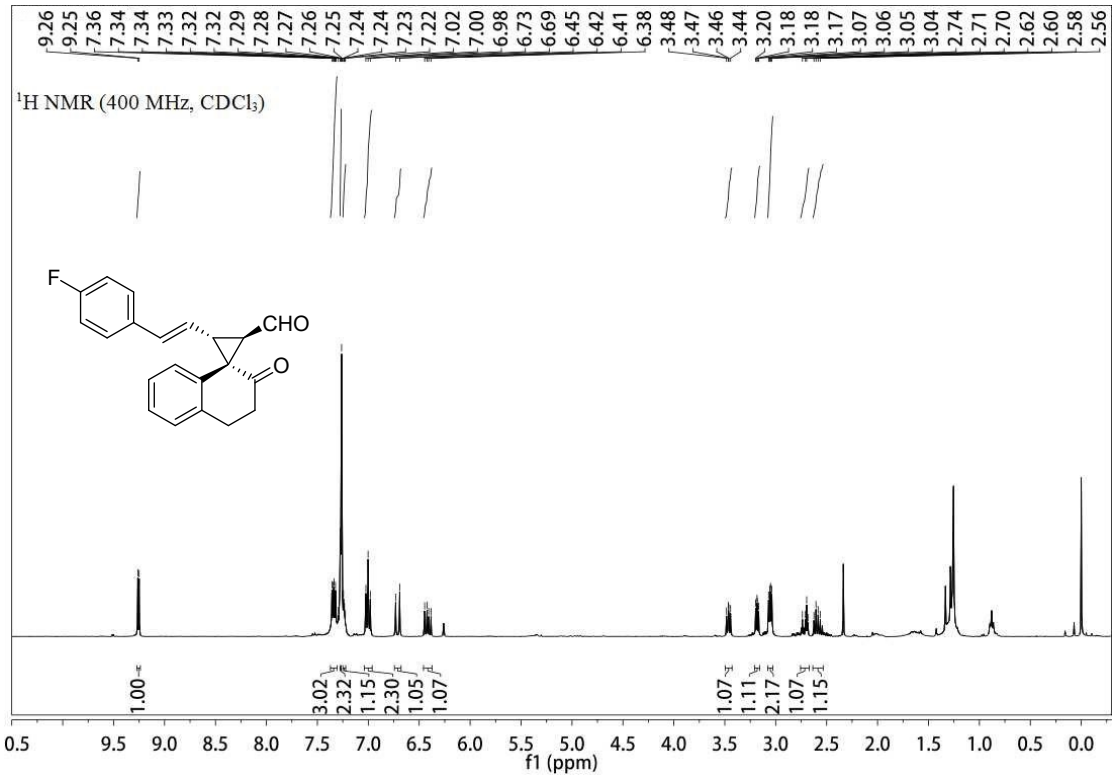

202.54
196.88
139.91
136.38
132.72
128.21
127.80
127.01
126.94
126.02
125.27
50.08
41.91
38.48
34.60
28.07
13C NMR (101 MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

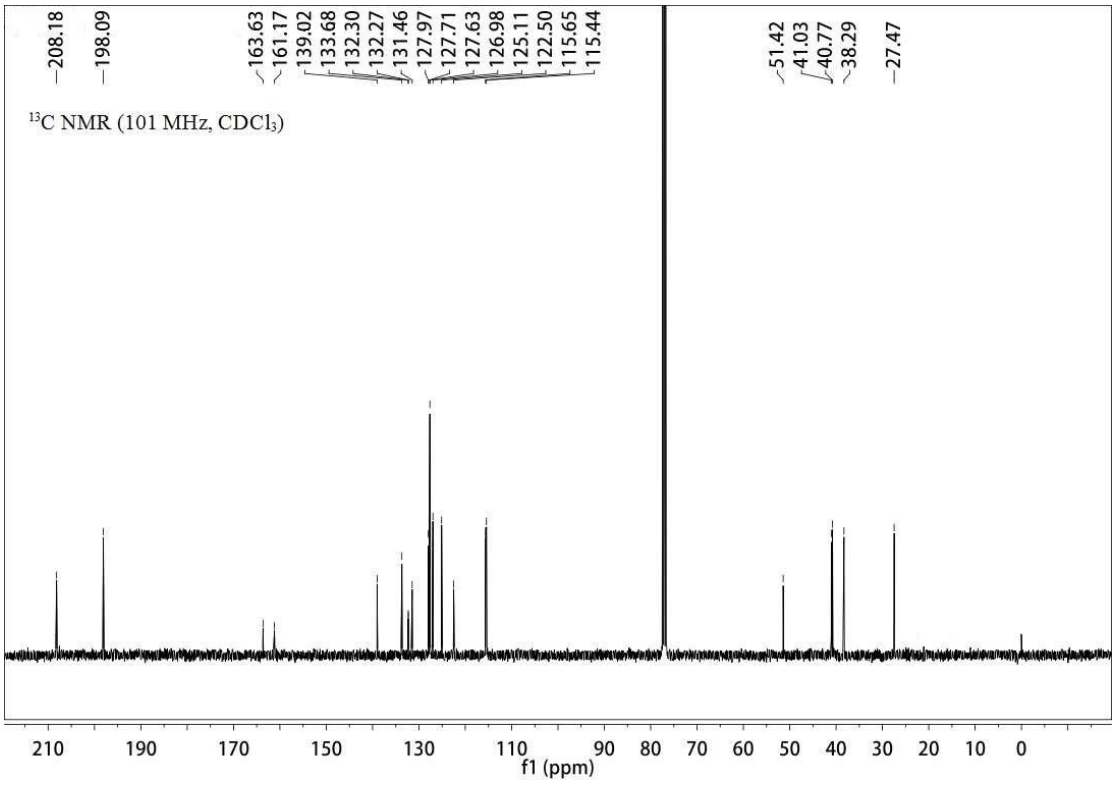
3m


9.29
9.28
7.38
7.37
7.33
7.32
7.30
7.27
7.26
7.24
7.23
6.77
6.73
6.50
6.48
6.46
3.47
3.45
3.43
3.23
3.21
3.20
3.07
3.06
3.05
3.04
2.72
2.69
2.68
2.67
2.63
2.61
2.59
2.56
^{1}H NMR (400 MHz, $CDCl_3$)
CHO
O
1.00
2.22
4.16
3.06
1.05
1.06
1.06
1.03
2.08
1.06
1.07
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

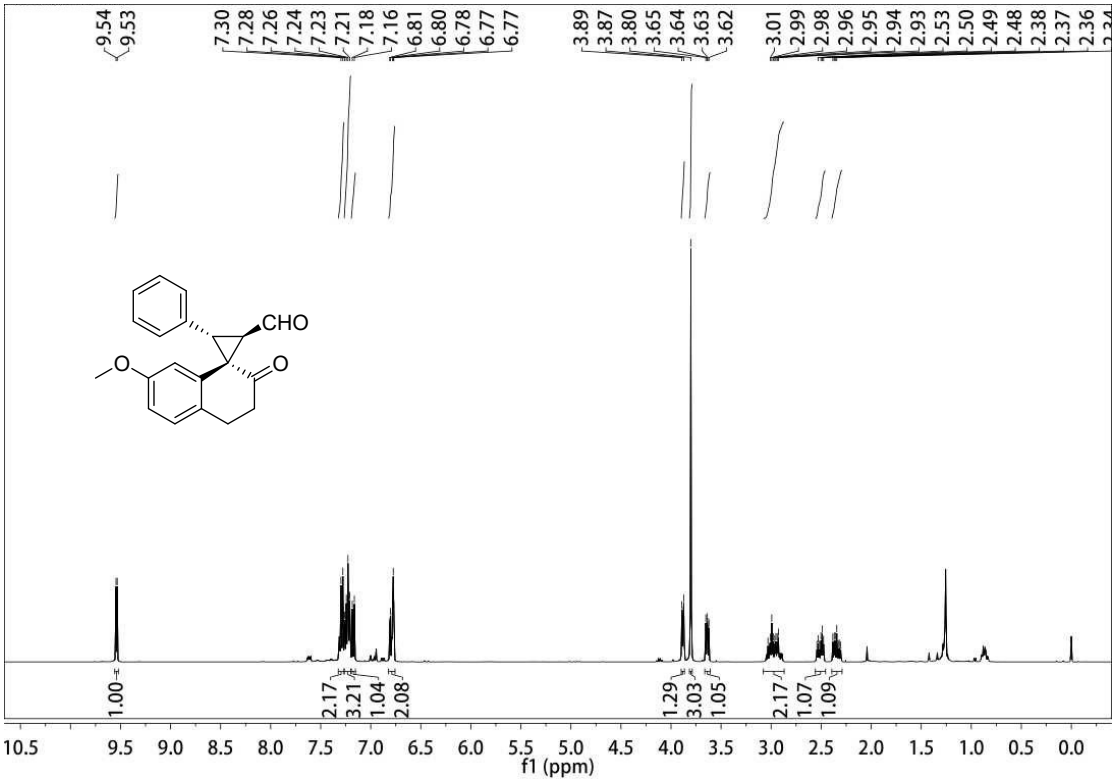

205.75
196.95
139.74
136.55
134.19
132.23
128.64
128.19
127.80
127.68
126.89
126.30
125.87
123.61
47.30
44.92
39.54
37.13
27.86
^{13}C NMR (101 MHz, $CDCl_3$)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3n


9.26
9.25
7.36
7.34
7.34
7.33
7.32
7.32
7.29
7.28
7.27
7.26
7.25
7.24
7.24
7.23
7.22
7.02
7.00
6.98
6.73
6.69
6.45
6.42
6.41
6.38
3.48
3.47
3.46
3.44
3.20
3.18
3.18
3.17
3.07
3.06
3.05
3.04
2.74
2.71
2.70
2.62
2.60
2.58
2.56
^{1}H NMR (400 MHz, CDCl$_3$)
F
CHO
O
1.00
3.02
2.32
1.15
2.30
1.05
1.07
1.07
1.11
2.17
1.07
1.15
0.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


208.18
198.09
163.63
161.17
139.02
133.68
132.30
132.27
131.46
127.97
127.71
127.63
126.98
125.11
122.50
115.65
115.44
51.42
41.03
40.77
38.29
27.47
^{13}C NMR (101 MHz, CDCl$_3$)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3o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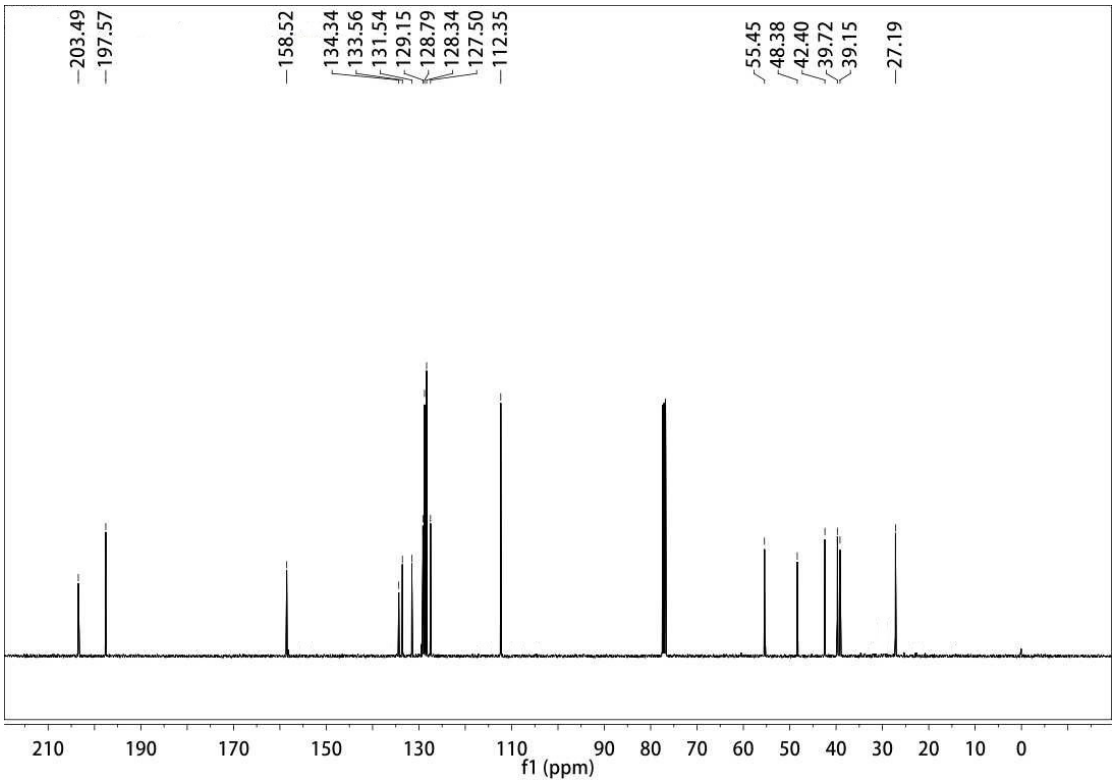
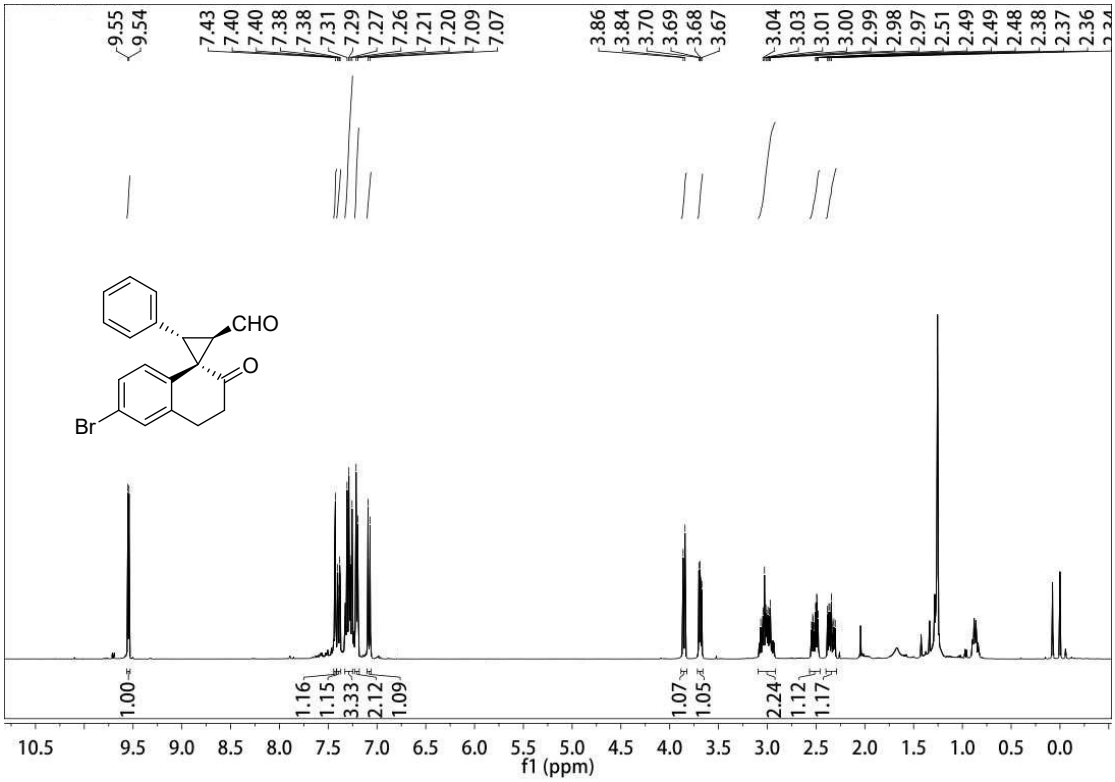
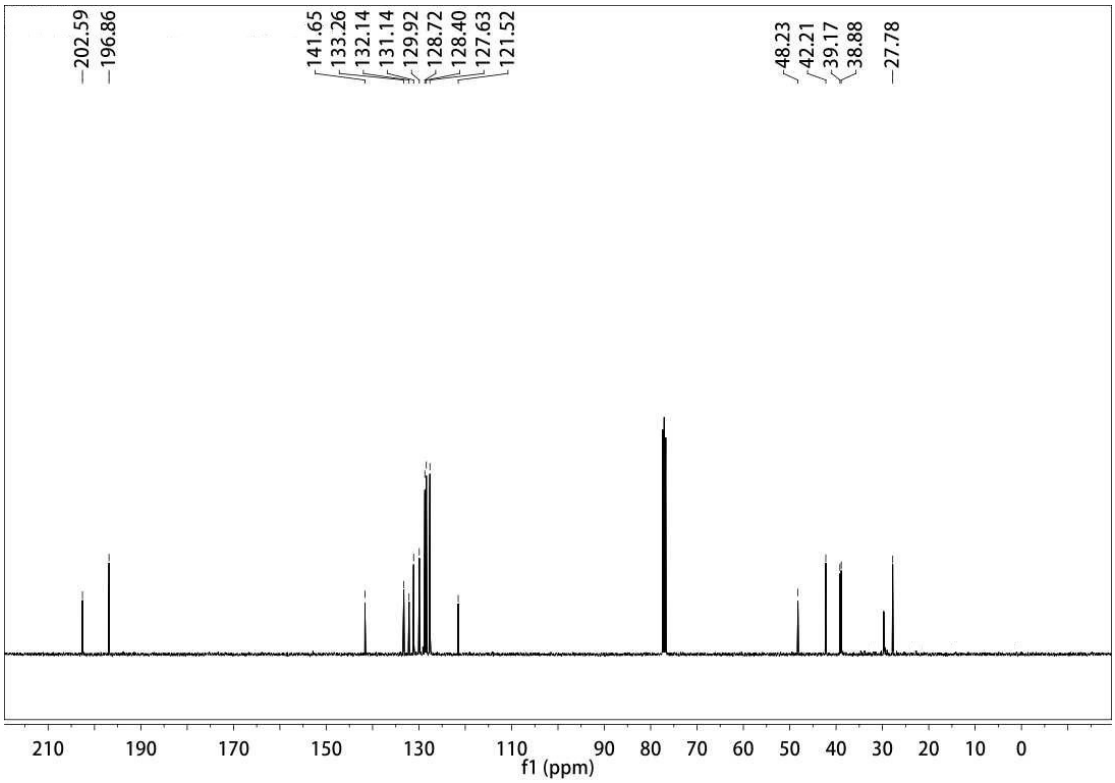
9.53
7.30
7.28
7.26
7.24
7.23
7.21
7.18
7.16
6.81
6.80
6.78
6.77
6.77
3.89
3.87
3.80
3.65
3.64
3.63
3.62
3.01
2.99
2.98
2.96
2.95
2.94
2.93
2.53
2.50
2.49
2.48
2.38
2.37
2.36
CHO
O
O
1.00
2.17
3.21
1.04
2.08
1.29
3.03
1.05
2.17
1.07
1.09
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

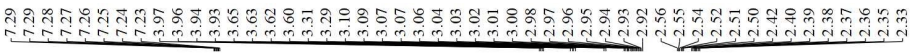

203.49
197.57
158.52
134.34
133.56
131.54
129.15
128.79
128.34
127.50
112.35
55.45
48.38
42.40
39.72
39.15
27.19
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3p


9.55
9.54
7.43
7.40
7.40
7.38
7.38
7.31
7.29
7.27
7.26
7.21
7.20
7.09
7.07
3.86
3.84
3.70
3.69
3.68
3.67
3.04
3.03
3.01
3.00
2.99
2.98
2.97
2.51
2.49
2.49
2.48
2.38
2.37
2.36
CHO
O
Br
1.00
1.16
1.15
3.33
2.12
1.09
1.07
1.05
2.24
1.12
1.17
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


202.59
196.86
141.65
133.26
132.14
131.14
129.92
128.72
128.40
127.63
121.52
48.23
42.21
39.17
38.88
27.78
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5a


7.29
7.29
7.28
7.27
7.26
7.25
7.24
7.23
3.97
3.96
3.94
3.93
3.65
3.63
3.62
3.60
3.31
3.29
3.10
3.09
3.07
3.07
3.06
3.04
3.03
3.02
3.01
3.00
2.98
2.97
2.96
2.95
2.94
2.93
2.92
2.56
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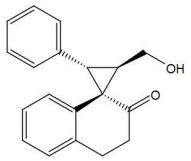
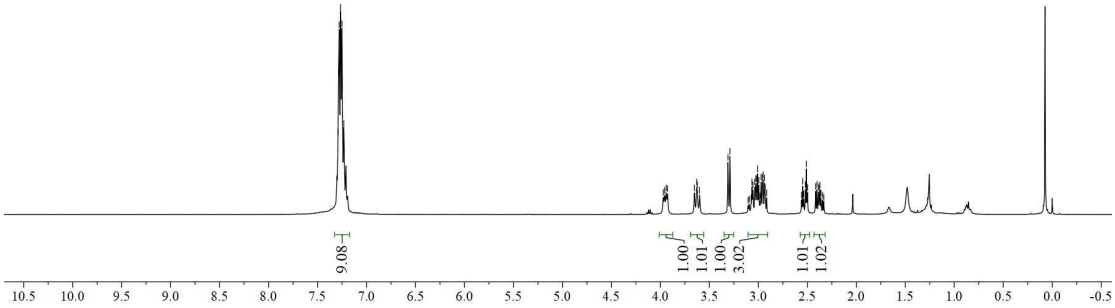
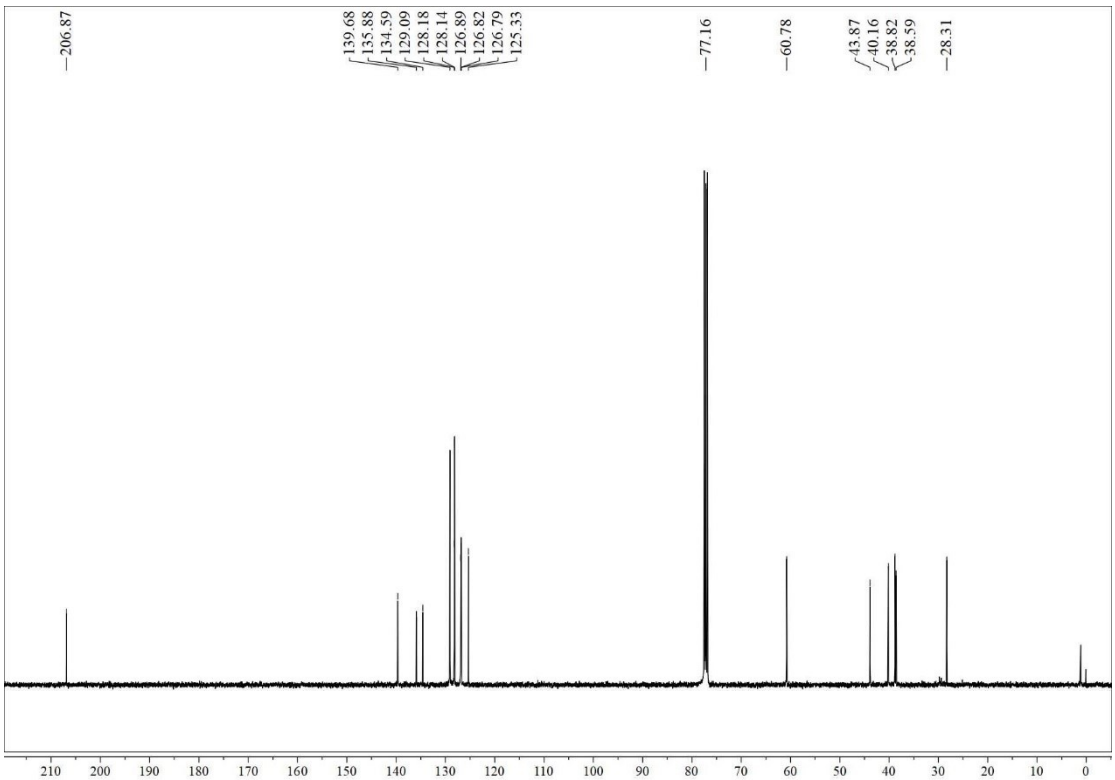
2.39
2.38
2.37
2.36
2.35
2.33


OH
O


9.08
1.00
1.01
1.00
3.02
1.01
1.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


206.87
139.68
135.88
134.59
129.09
128.18
128.14
126.89
126.82
126.79
125.33
77.16
60.78
43.87
40.16
38.82
38.59
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210
200
190
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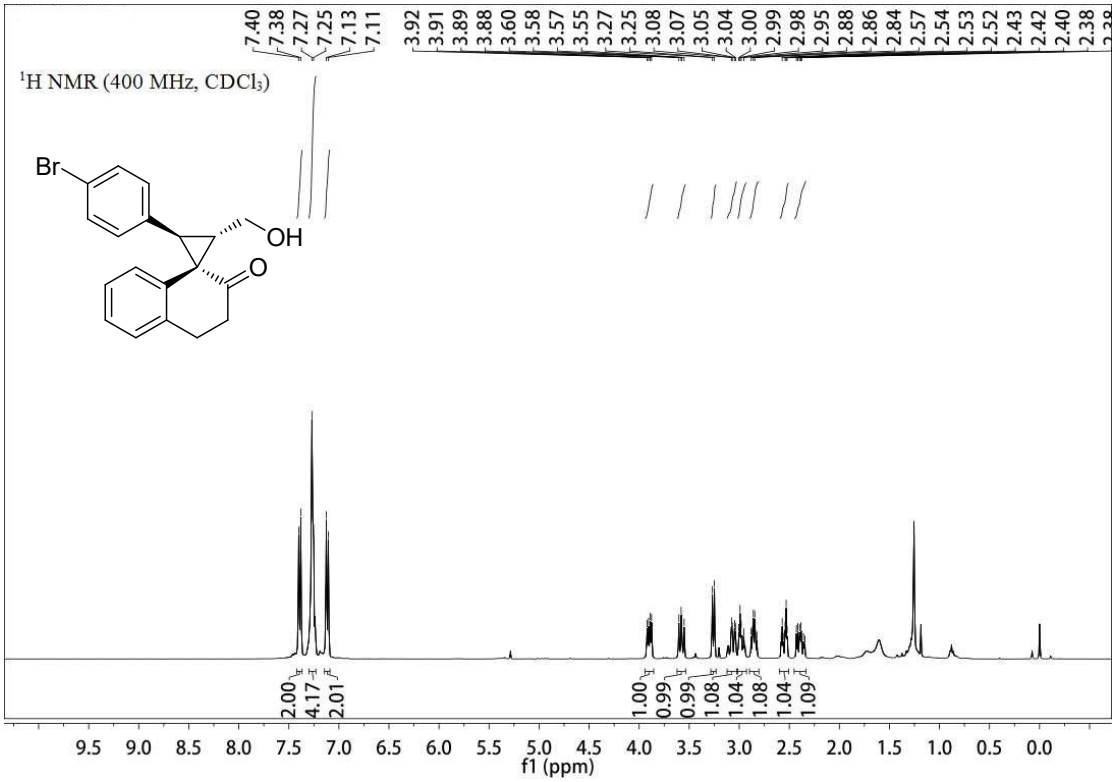
0

5b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3.57
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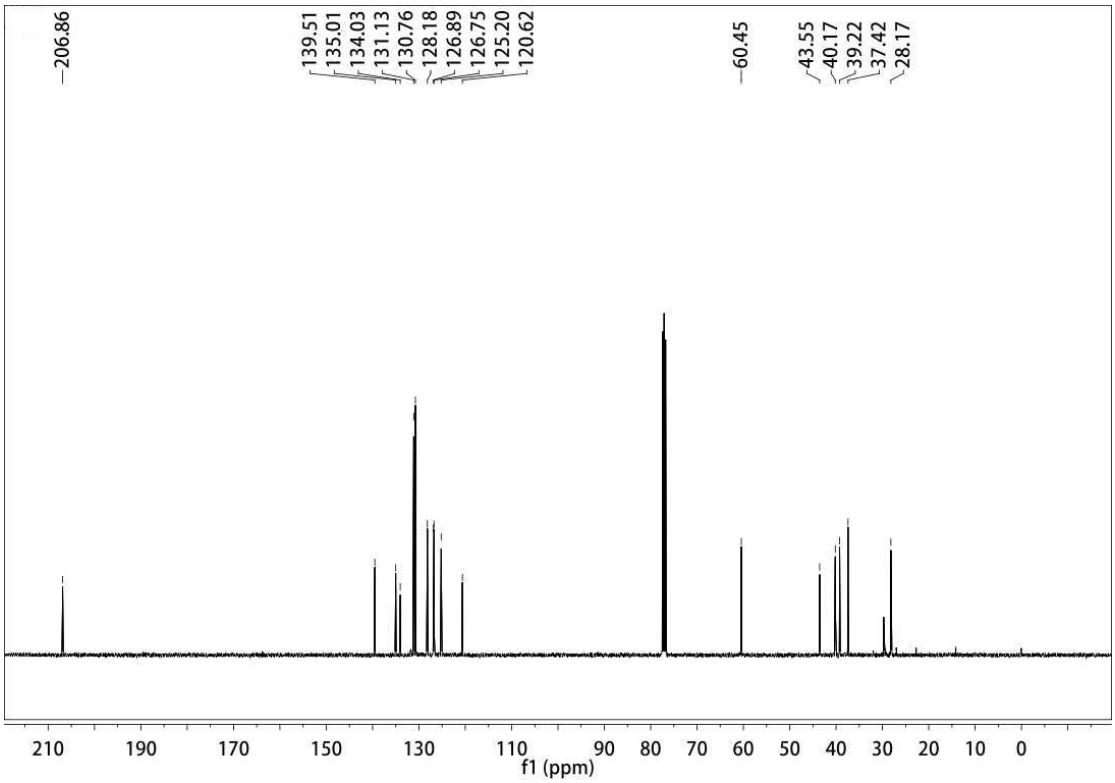
3.27
3.25
3.08
3.07
3.05
3.04
3.00
2.99
2.98
2.95
2.88
2.86
2.84
2.57
2.54
2.53
2.52
2.43
2.42
2.40
2.38
^{1}H NMR (400 MHz, CDCl$_3$)
Br
OH
O
2.00
4.17
2.01
1.00
0.99
0.99
1.08
1.04
1.08
1.04
1.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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139.51
135.01
134.03
131.13
130.76
128.18
126.89
126.75
125.20
120.62
60.45
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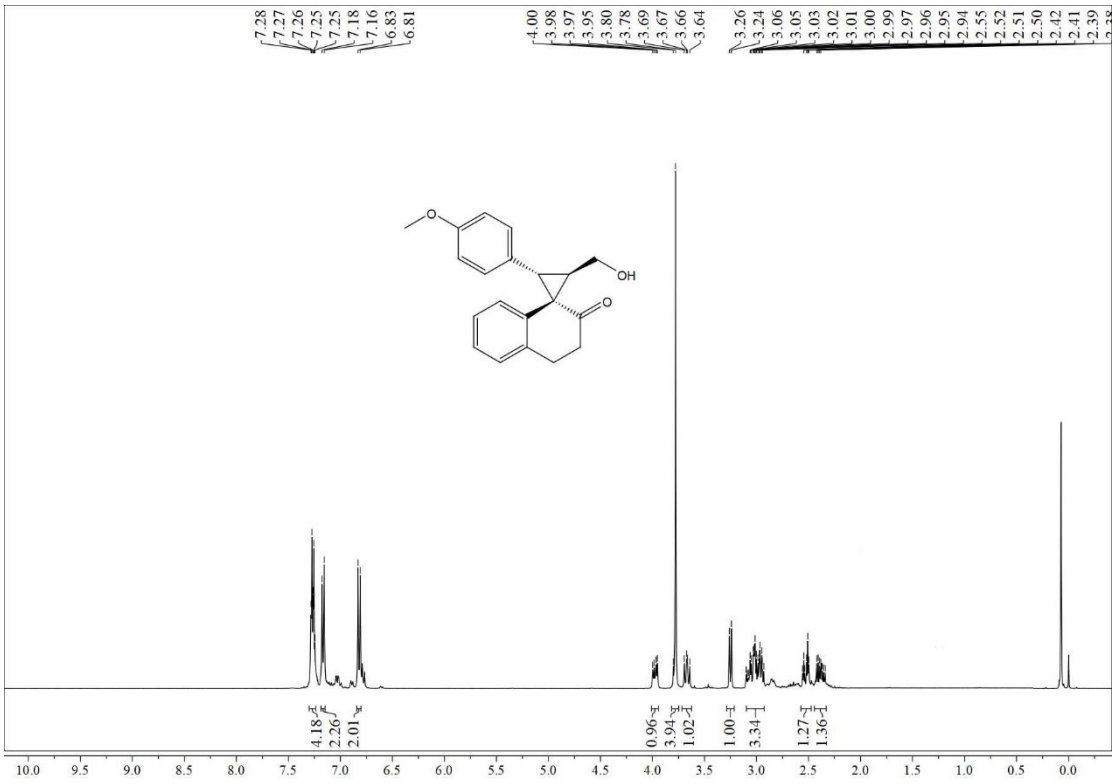
40.17
39.22
37.42
28.17
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5c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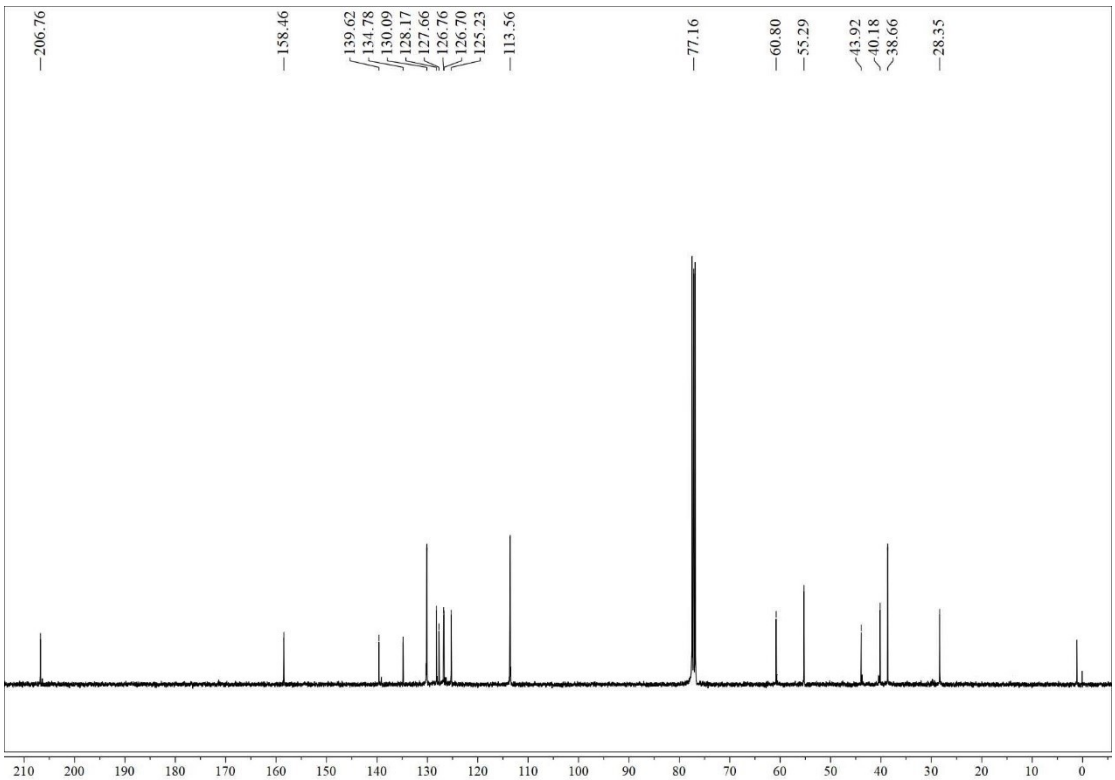
3.78
3.69
3.67
3.66
3.64
3.26
3.24
3.06
3.05
3.03
3.02
3.01
3.00
2.99
2.97
2.96
2.95
2.94
2.55
2.52
2.51
2.50
2.42
2.41
2.39
O
OH
O
4.18
2.26
2.01
0.96
3.94
1.02
1.00
3.34
1.27
1.36
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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127.66
126.76
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125.23
113.56
77.16
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43.92
40.18
38.66
28.35
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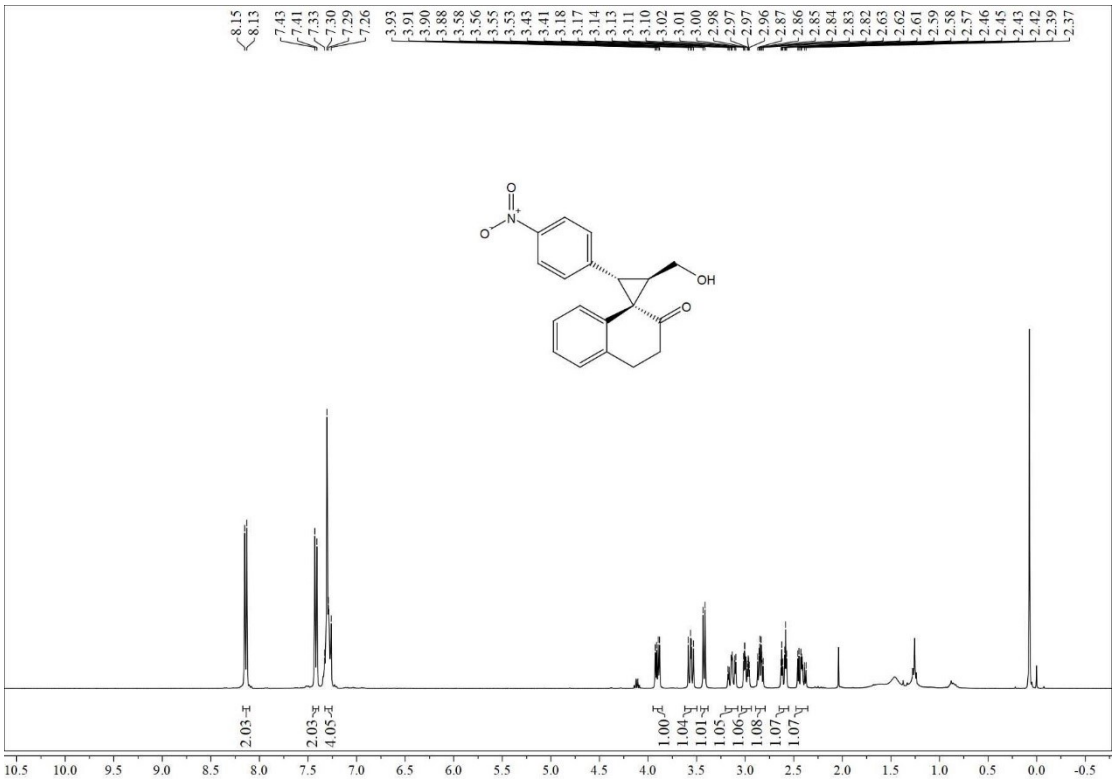
5d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3.56
3.55
3.53
3.43
3.41
3.18
3.17
3.14
3.13
3.11
3.10
3.02
3.01
3.00
2.98
2.97
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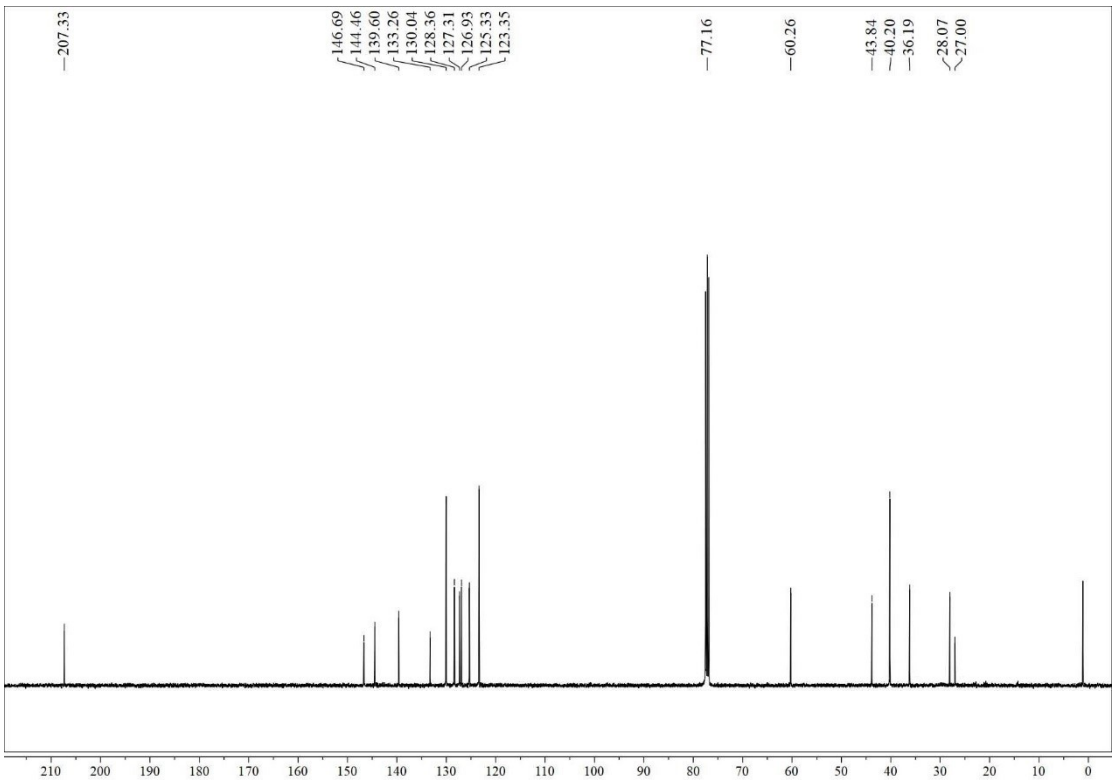
2.82
2.63
2.62
2.61
2.59
2.58
2.57
2.46
2.45
2.43
2.42
2.39
2.37
O
N+
O-
OH
O
2.03
2.03
4.05
1.00
1.04
1.01
1.05
1.06
1.08
1.07
1.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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139.60
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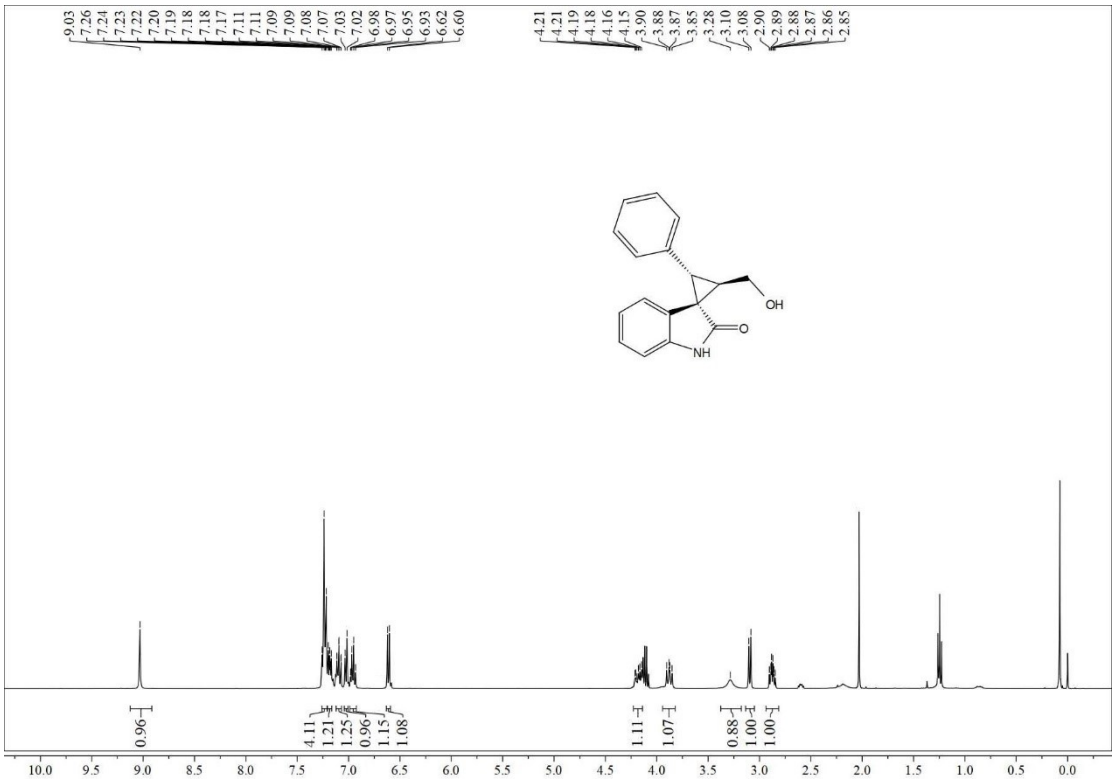
130.04
128.36
127.31
126.93
125.33
123.35
77.16
60.26
43.84
40.20
36.19
28.07
27.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

5e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7.17
7.11
7.11
7.09
7.09
7.08
7.07
7.03
7.02
6.98
6.97
6.95
6.93
6.62
6.60
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4.21
4.19
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4.16
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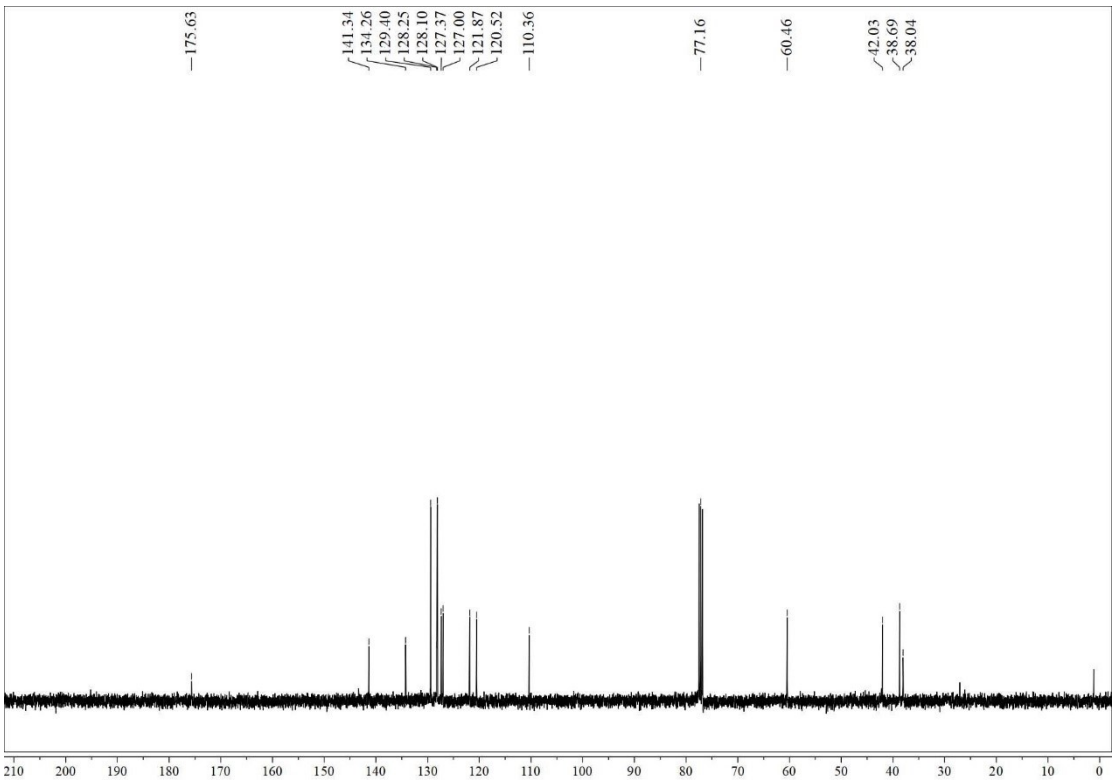
3.85
3.28
3.10
3.08
2.90
2.89
2.88
2.87
2.86
2.85
OH
O
NH
0.96
4.11
1.21
1.25
0.96
1.15
1.08
1.11
1.07
0.88
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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127.00
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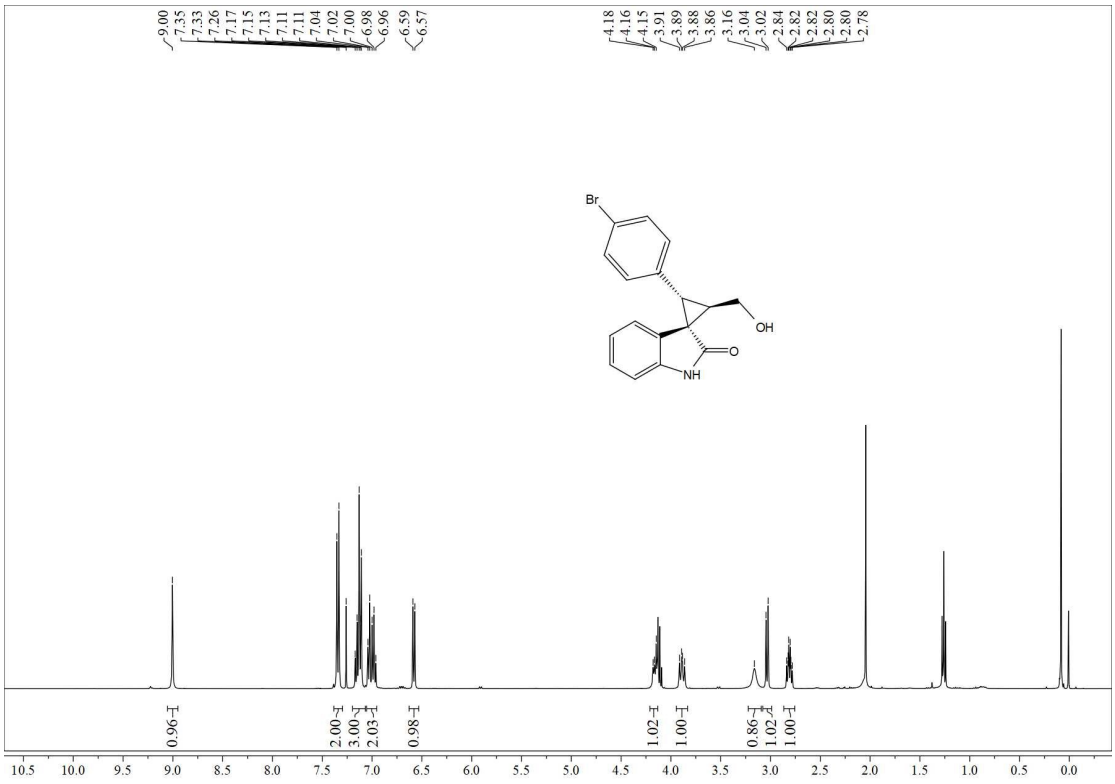
60.46
42.03
38.69
38.04
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

5f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7.35
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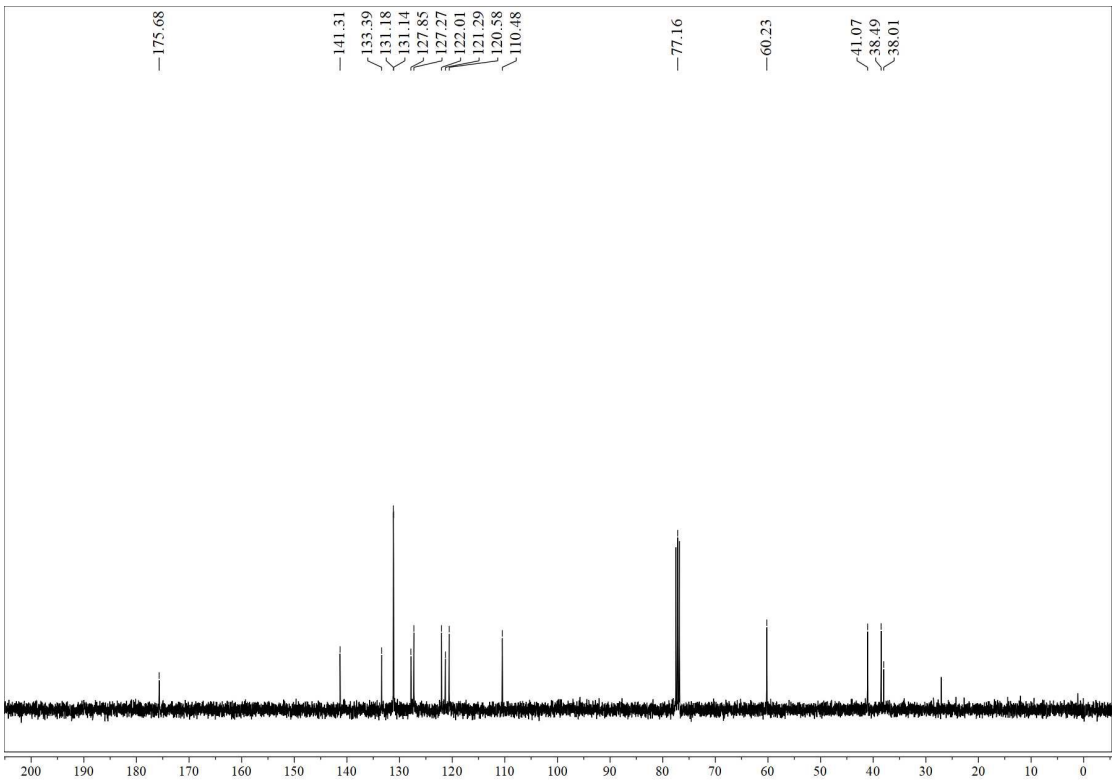
7.17
7.15
7.13
7.11
7.11
7.04
7.02
7.00
6.98
6.96
6.59
6.57
4.18
4.16
4.15
3.91
3.89
3.88
3.86
3.16
3.04
3.02
2.84
2.82
2.82
2.80
2.80
2.78
Br
OH
O
NH
0.96
2.00
3.00
2.03
0.98
1.02
1.00
0.86
1.02
1.00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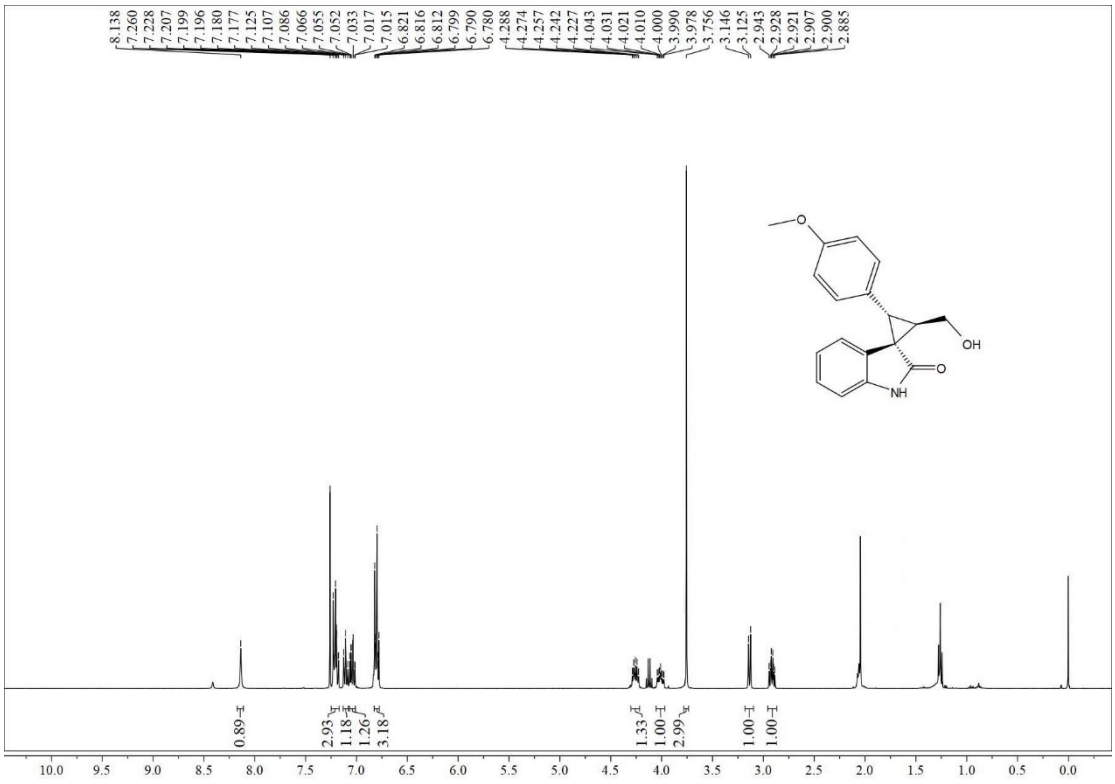
41.07
38.49
38.01

5g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7.066
7.055
7.052
7.033
7.017
7.015
6.821
6.816
6.812
6.799
6.790
6.780
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4.274
4.257
4.242
4.227
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4.031
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4.010
4.000
3.990
3.978
3.756
3.146
3.125
2.943
2.928
2.921
2.907
2.900
2.885
O
OH
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1.26
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1.33
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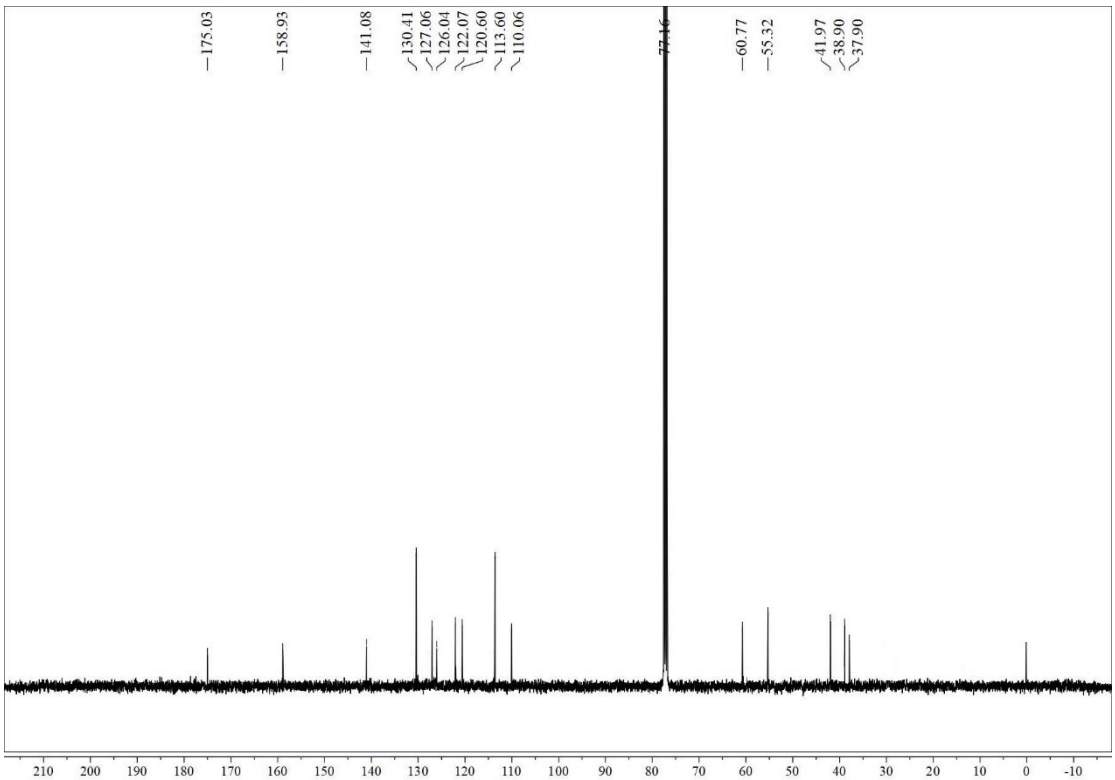
1.00
1.00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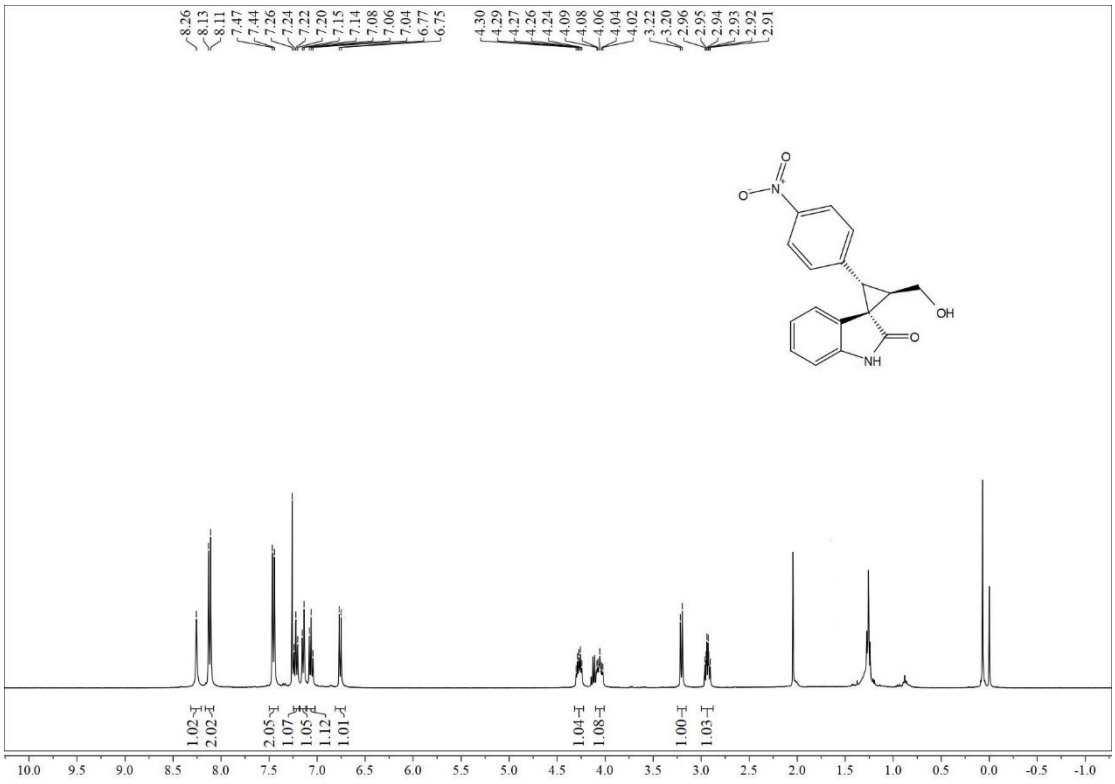
37.90

5h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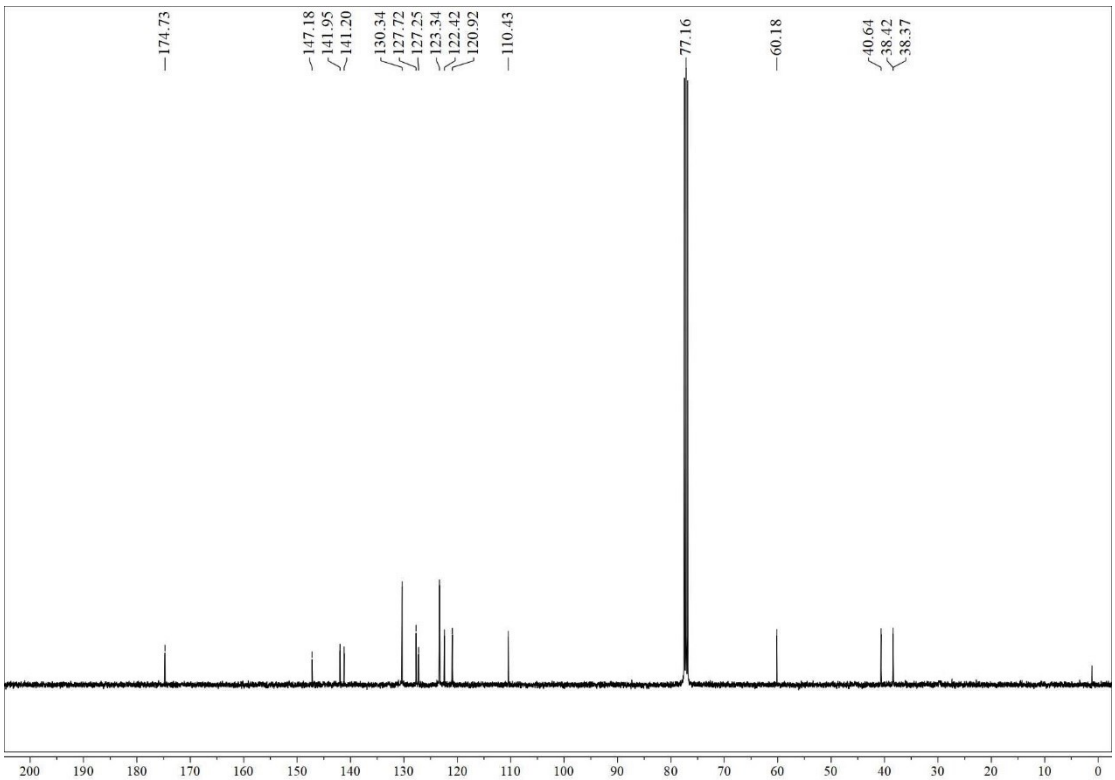
7.06
7.04
6.77
6.75
4.30
4.29
4.27
4.26
4.24
4.09
4.08
4.06
4.04
4.02
3.22
3.20
2.96
2.95
2.94
2.93
2.92
2.91
O
N
O
OH
O
NH
1.02
2.02
2.05
1.07
1.05
1.12
1.01
1.04
1.08
1.00
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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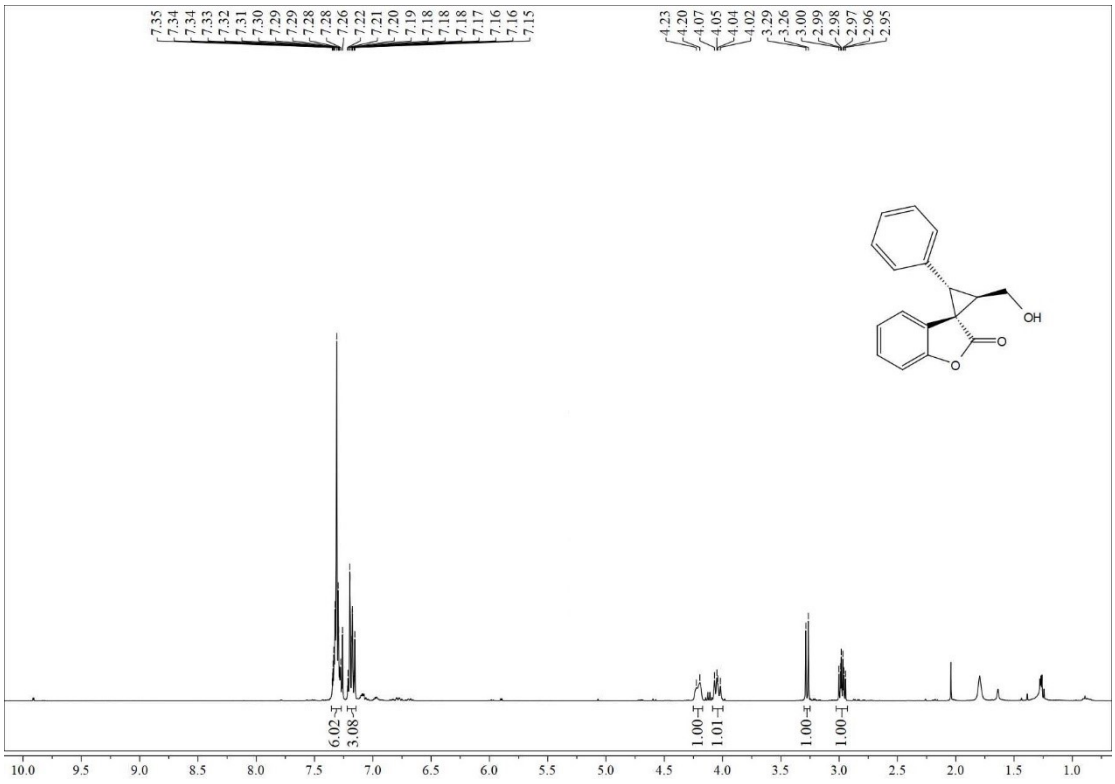
5i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7.21
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7.19
7.18
7.18
7.18
7.17
7.16
7.16
7.15
4.23
4.20
4.07
4.05
4.04
4.02
3.29
3.26
3.00
2.99
2.98
2.97
2.96
2.95
OH
O
O
6.02
3.08
1.00
1.01
1.00
1.00
10.0
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9.0
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7.5
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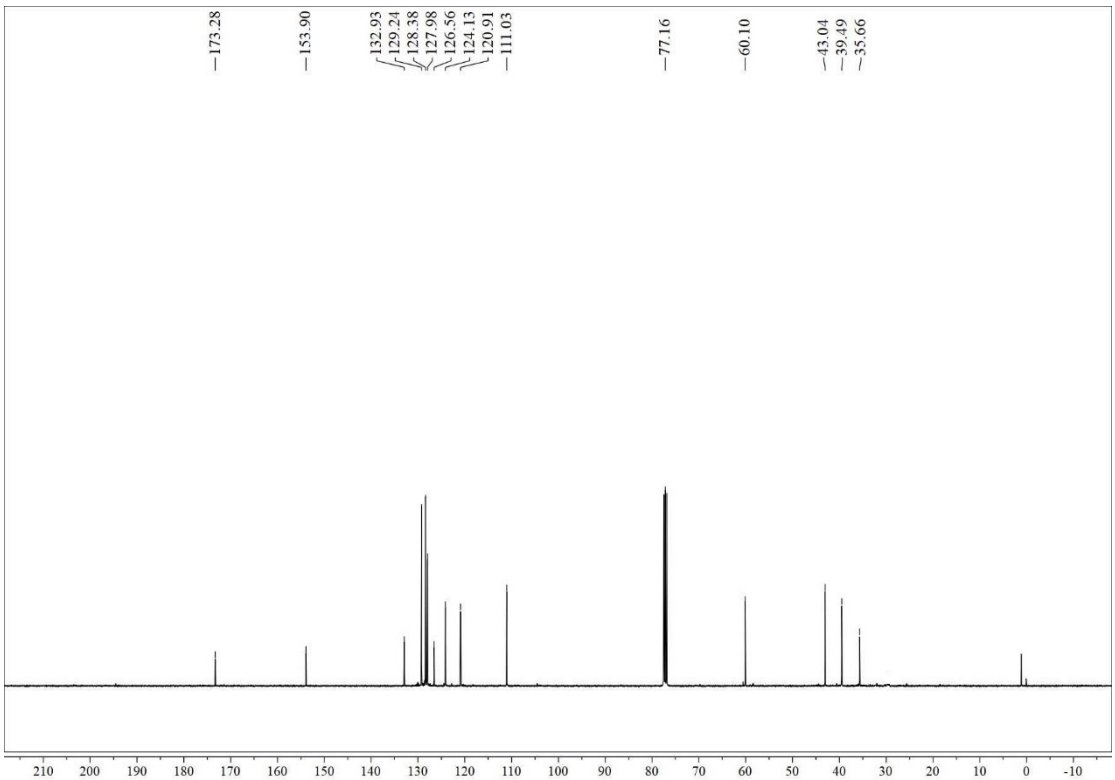
1.0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60.10
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35.66
210
200
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180
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50
40
30
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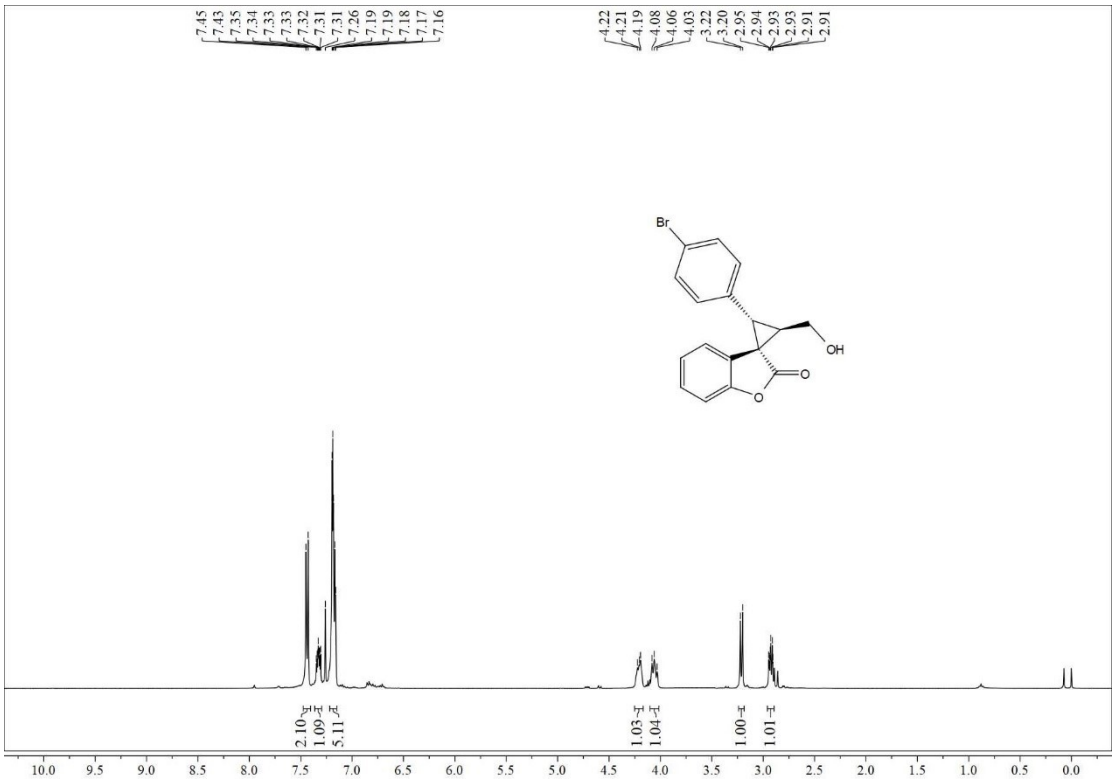
-10

5j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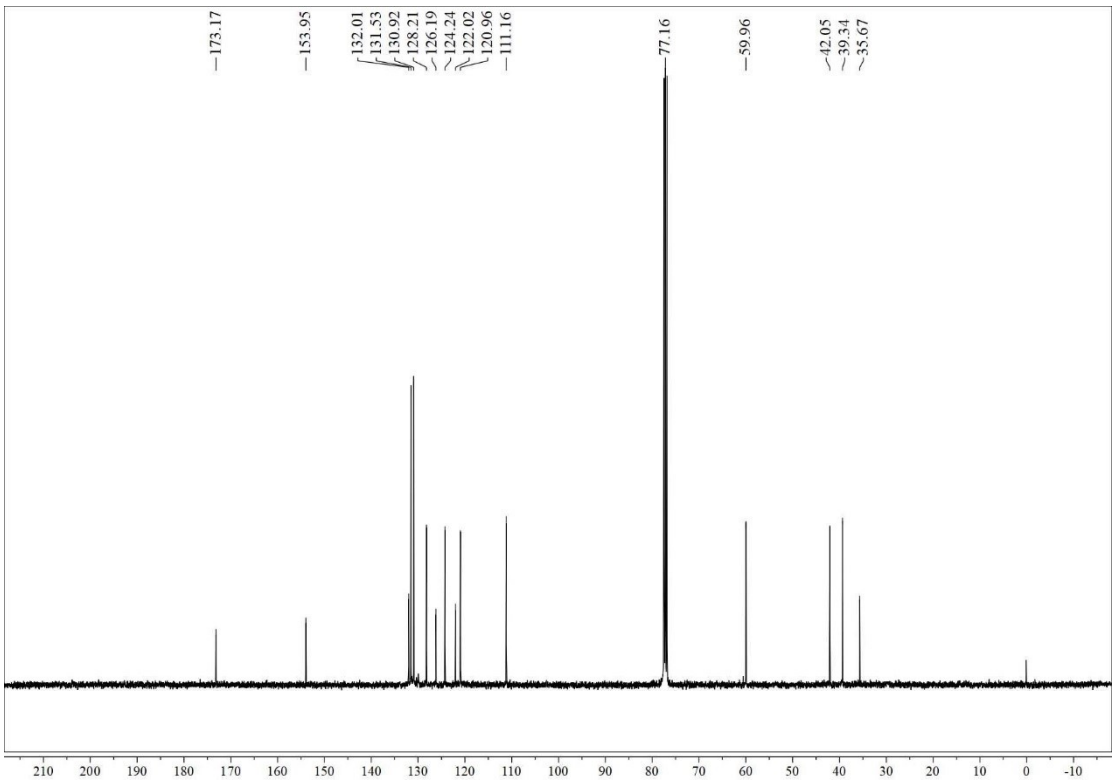
7.18
7.17
7.16
4.22
4.21
4.19
4.08
4.06
4.03
3.22
3.20
2.95
2.94
2.93
2.93
2.91
2.91
Br
OH
O
O
2.10
1.09
5.11
1.03
1.04
1.00
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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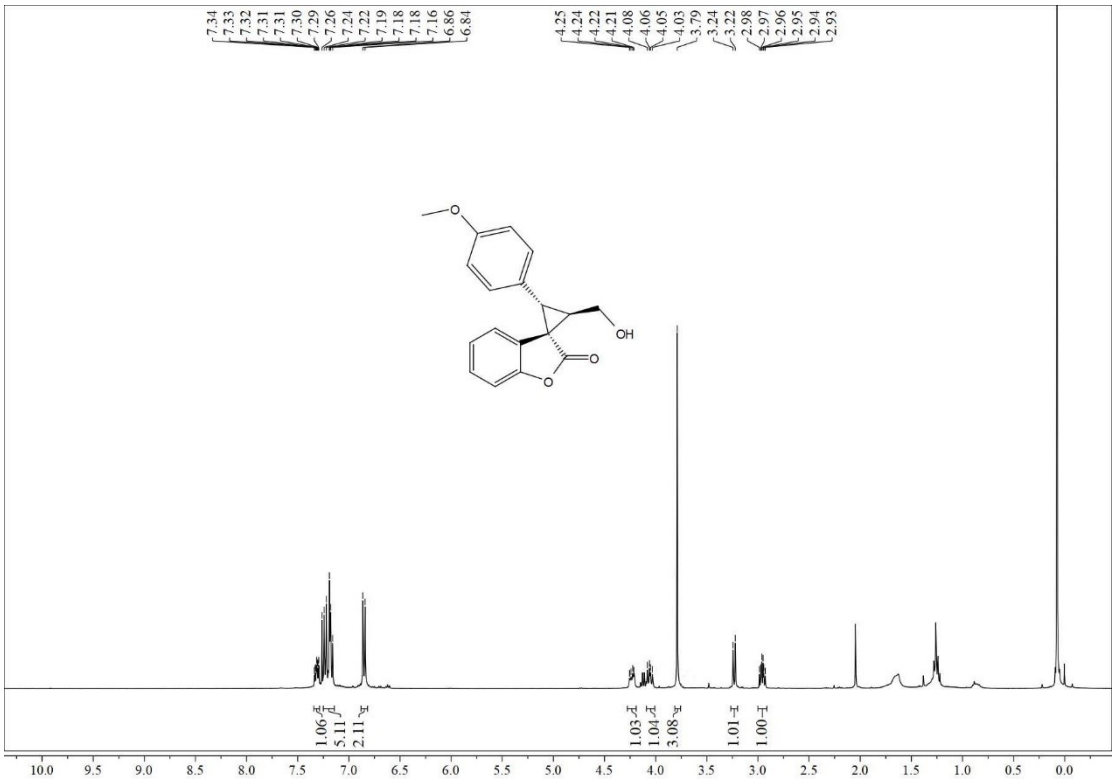
5k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6.84
4.25
4.24
4.22
4.21
4.08
4.06
4.05
4.03
3.79
3.24
3.22
2.98
2.97
2.96
2.95
2.94
2.93
OH
O
O
O
1.06
5.11
2.11
1.03
1.04
3.08
1.01
1.00
10.0
9.5
9.0
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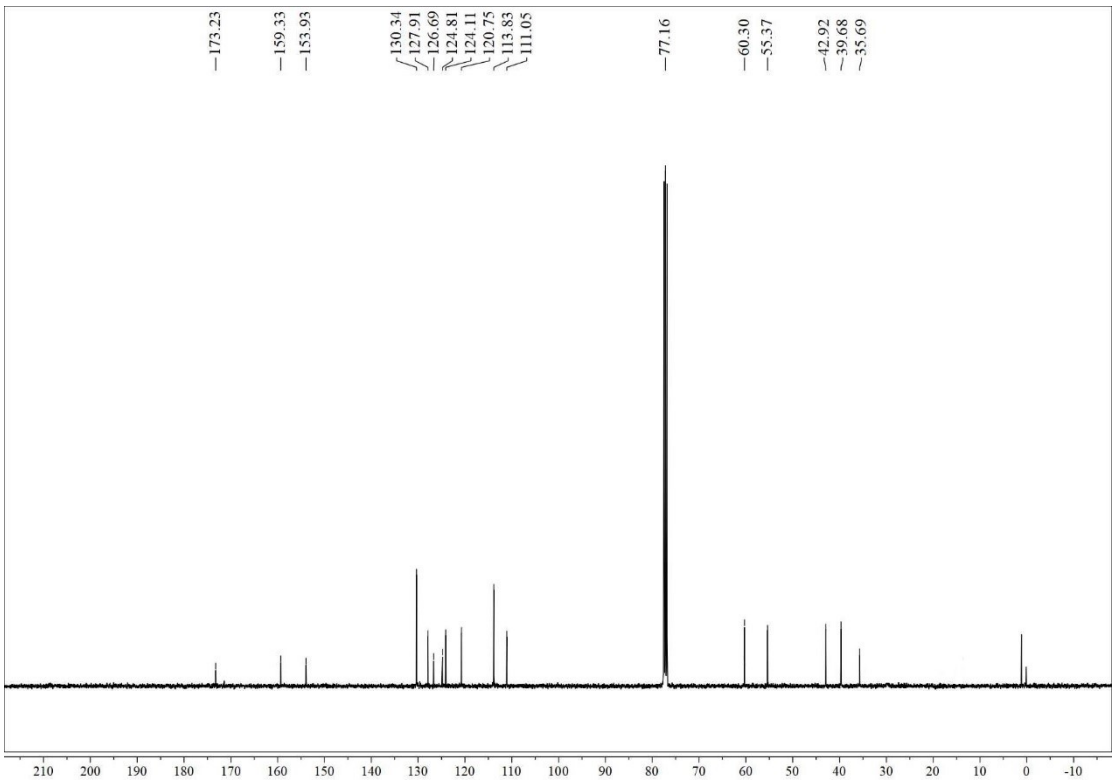
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55.37
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200
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180
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40
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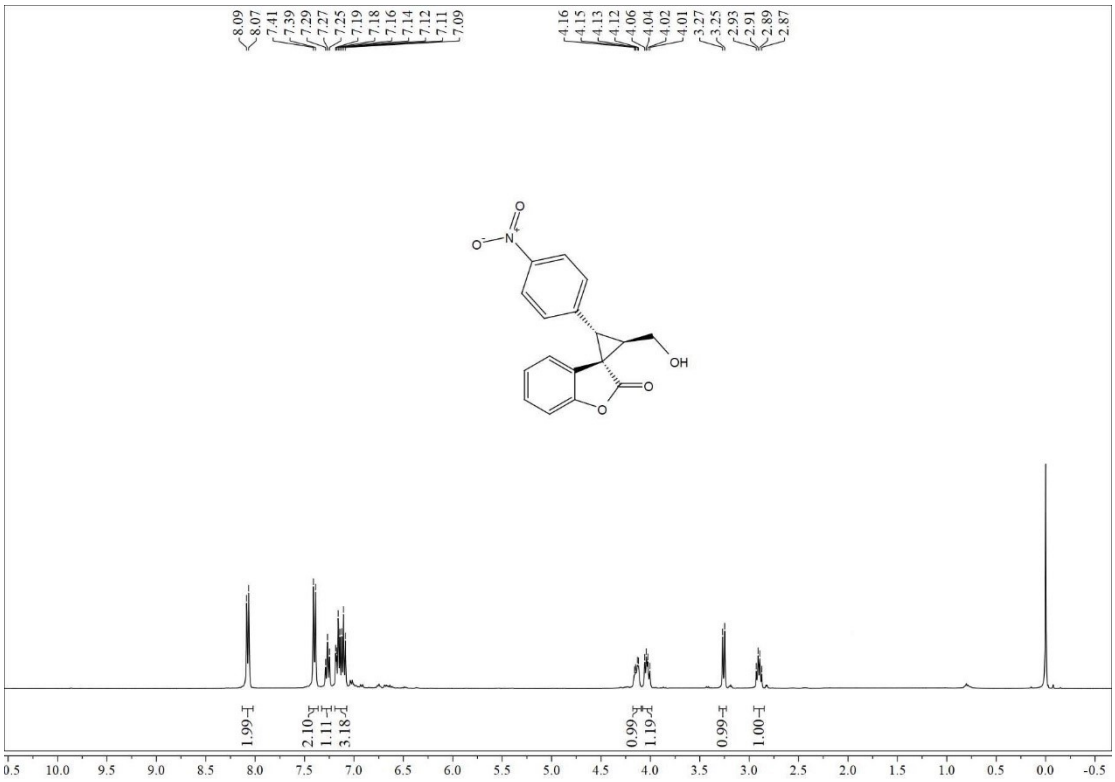
0
-10

5l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7.09
4.16
4.15
4.13
4.12
4.06
4.04
4.02
4.01
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3.25
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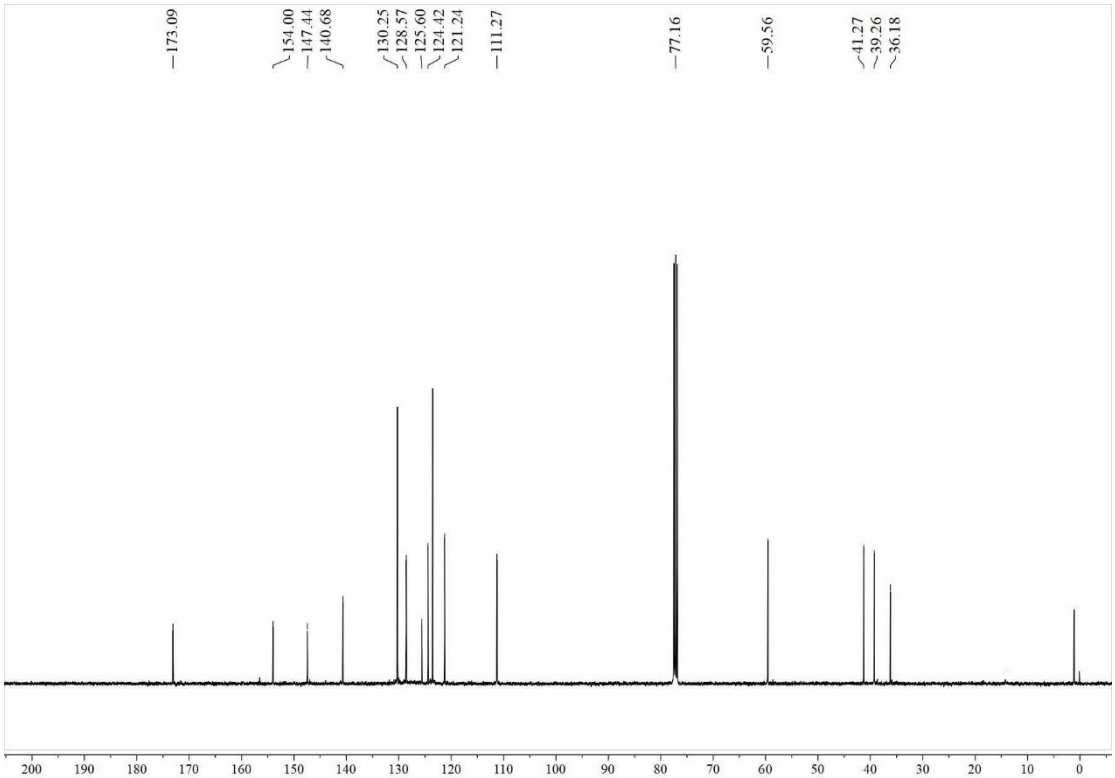
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41.27
39.26
36.18

5m


8.14
8.12
7.41
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7.26
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4.29
4.28
4.27
4.26
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4.23
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4.01
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3.94
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1.32
1.30
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1.95
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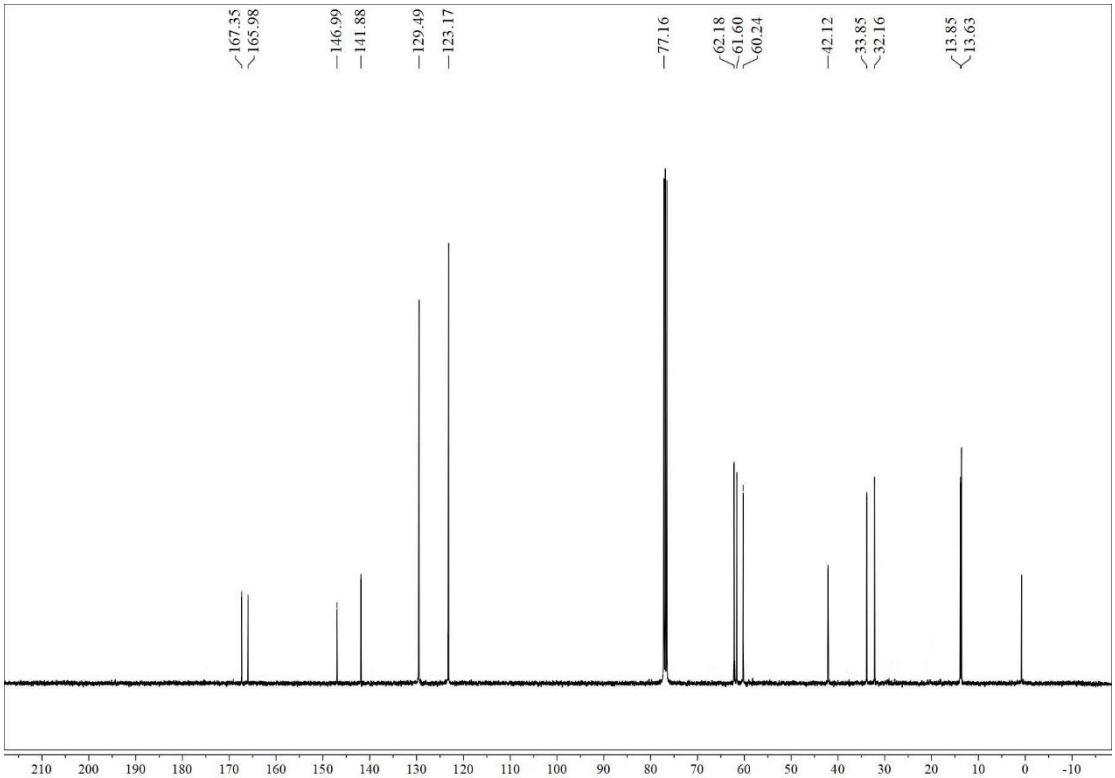
1.09
2.12
1.09
1.01
1.00
2.99
2.99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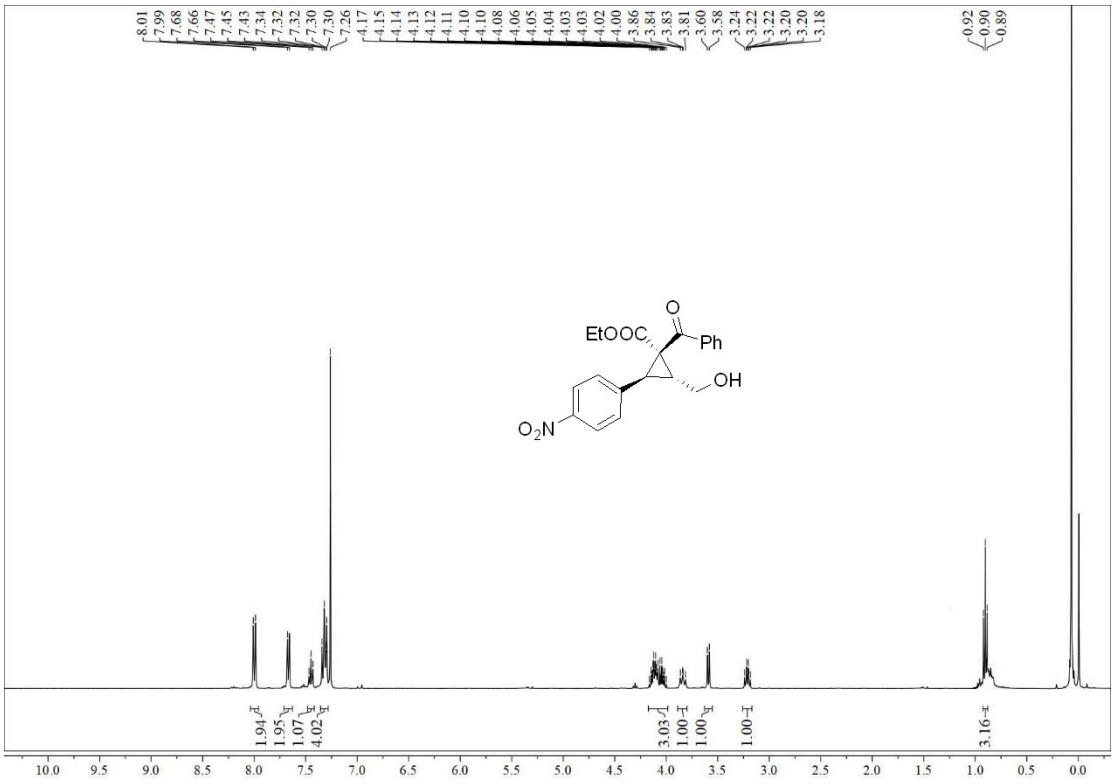
33.85
32.16
13.85
13.63

5n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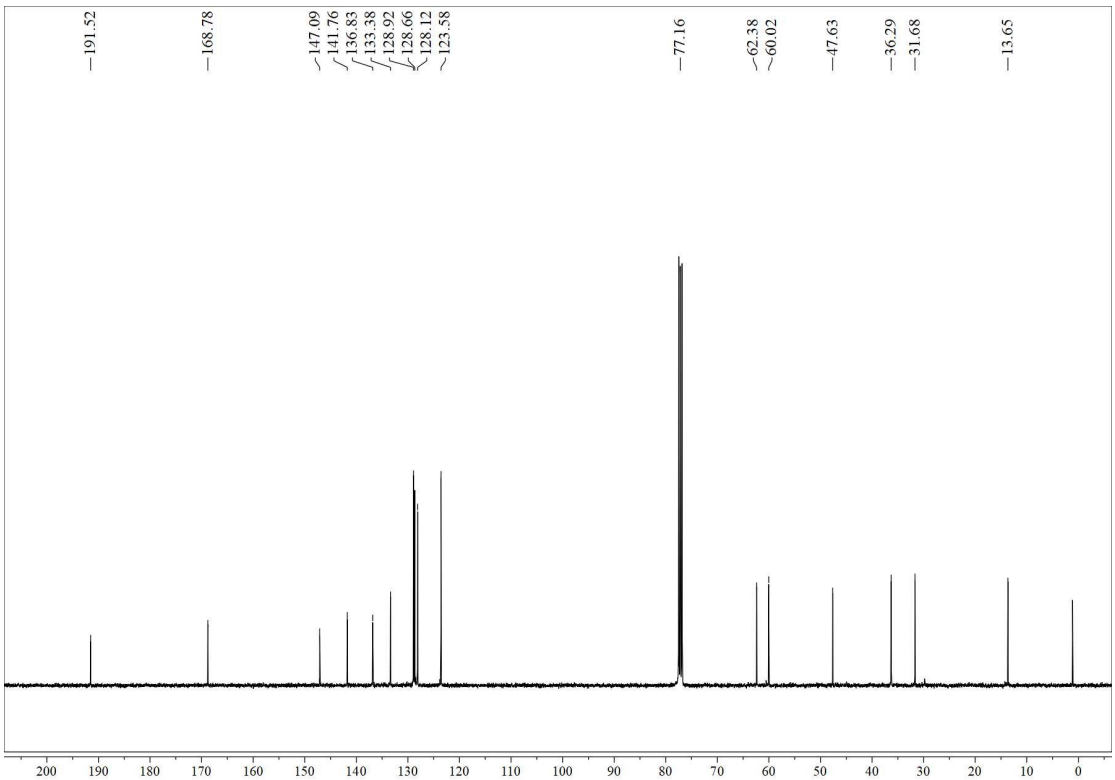
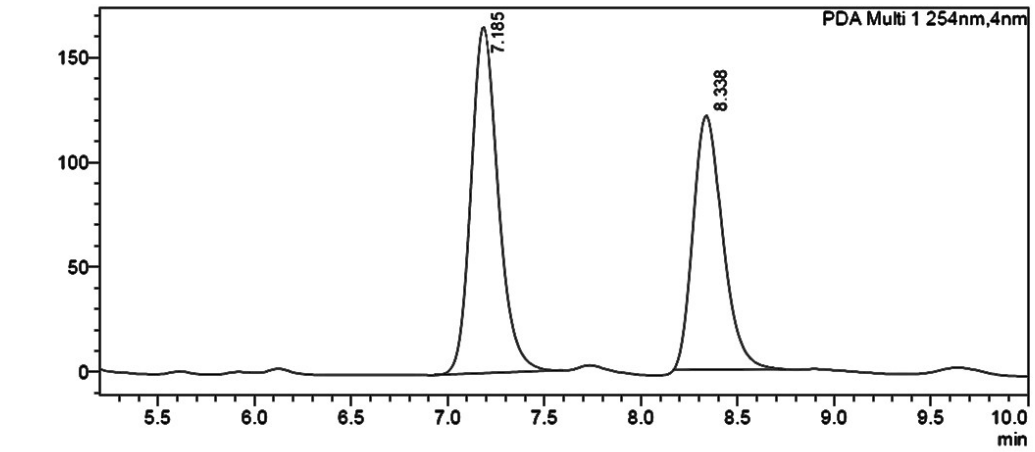
7.47
7.45
7.43
7.34
7.32
7.32
7.30
7.30
7.26
4.17
4.15
4.14
4.13
4.12
4.11
4.10
4.10
4.08
4.06
4.05
4.04
4.03
4.03
4.02
4.00
3.86
3.84
3.83
3.81
3.60
3.58
3.24
3.22
3.22
3.20
3.20
3.18
0.92
0.90
0.89
O
EtOOC
Ph
OH
O2N
1.94
1.95
1.07
4.02
3.03
1.00
1.00
1.00
3.16


191.52
168.78
147.09
141.76
136.83
133.38
128.92
128.66
128.12
123.58
77.16
62.38
60.02
47.63
36.29
31.68
13.65

7. HPLC chromatograms

rac-3a

<Chromatogram>



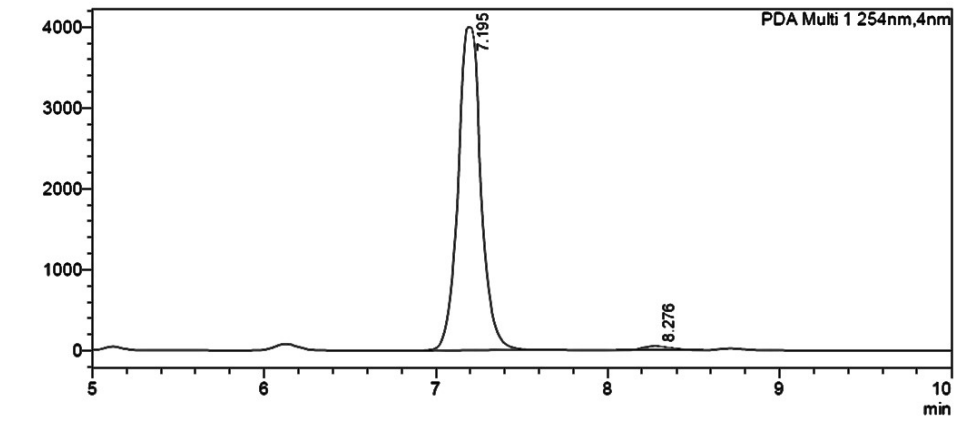
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.185	1625084	164919	55.897	%		RT:7.185
2	8.338	1282224	120903	44.103	%		RT:8.338
Total		2907308	285821				

3a

<Chromatogram>



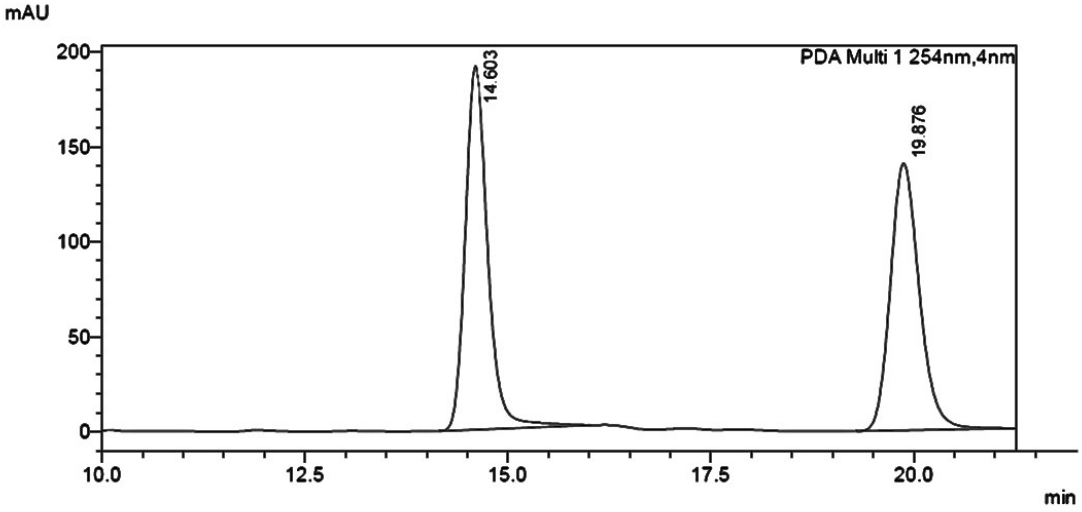
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.195	37094100	3995820	98.368	%		RT:7.195
2	8.276	615583	52842	1.632	%		RT:8.275
Total		37709682	4048663				

rac-3b

<Chromatogram>



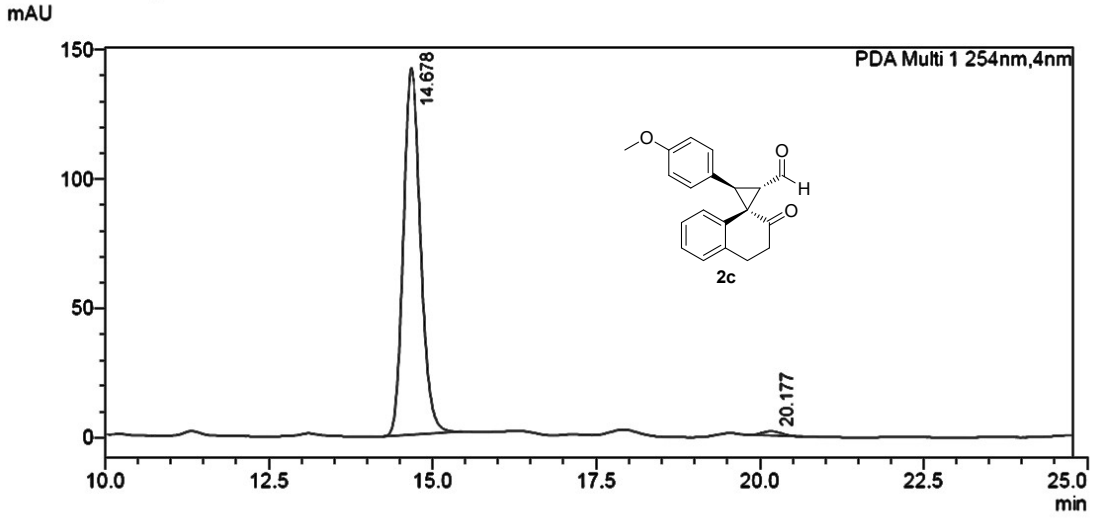
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.603	3660543	191394	51.236	%		RT:14.603
2	19.876	3483894	140499	48.764	%		RT:19.876
Total		7144437	331893				

3b

<Chromatogram>



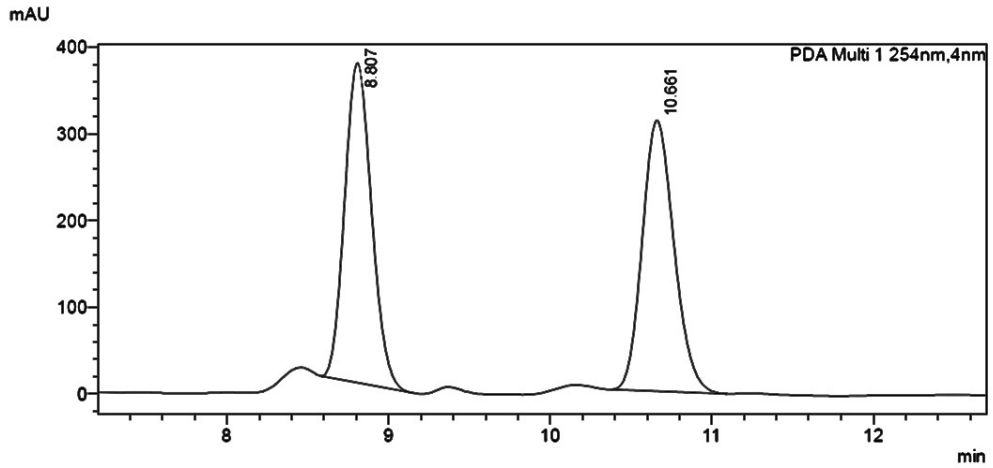
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.678	2576997	141669	98.623	%		RT:14.678
2	20.177	35982	1724	1.377	%		RT:20.177
Total		2612980	143393				

rac-3c

<Chromatogram>



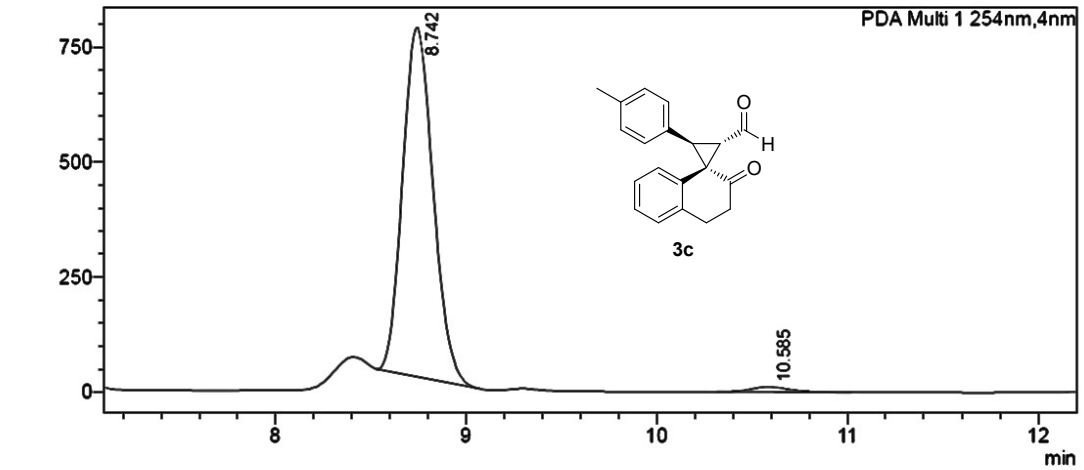
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.807	4269833	369185	49.921	%		RT:8.807
2	10.661	4283354	312346	50.079	%		RT:10.661
Total		8553187	681531				

3c

<Chromatogram>



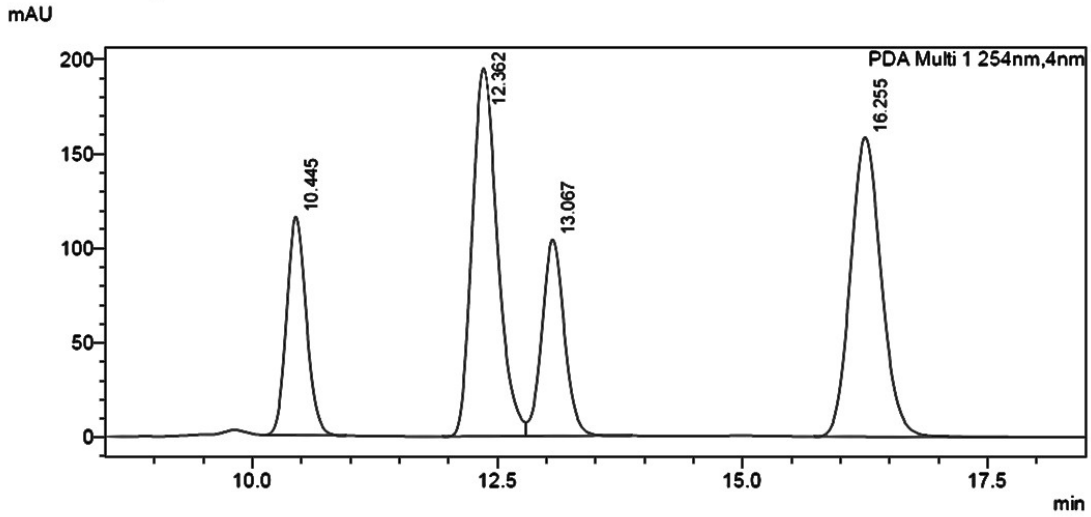
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.742	8443527	758528	98.273	%		RT:8.742
2	10.585	148339	10800	1.727	%		RT:10.585
Total		8591865	769328				

rac-3d

<Chromatogram>



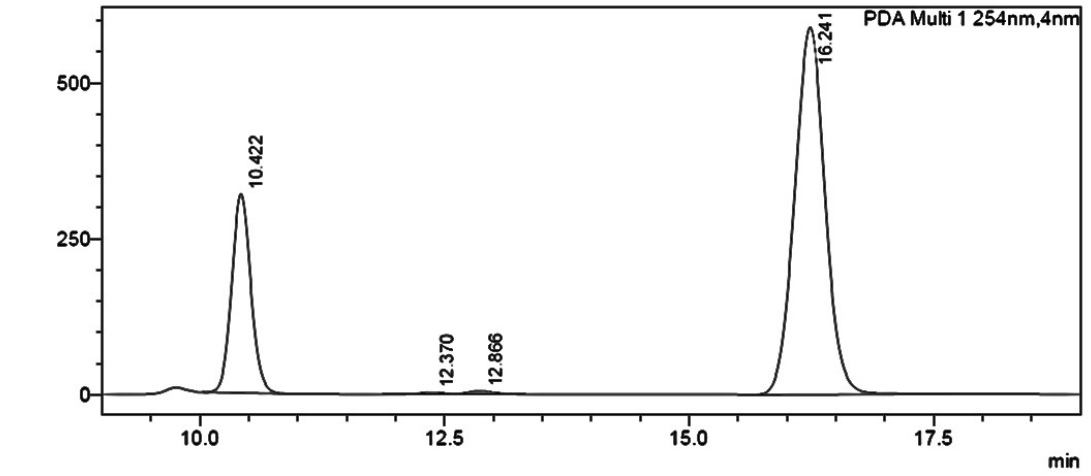
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.445	1612432	115412	15.770	%		RT:10.445
2	12.362	3500279	194781	34.233	%		RT:12.362
3	13.067	1651823	104024	16.155	%	V	RT:13.067
4	16.255	3460361	158392	33.843	%		RT:16.255
Total		10224895	572610				

3d

<Chromatogram>



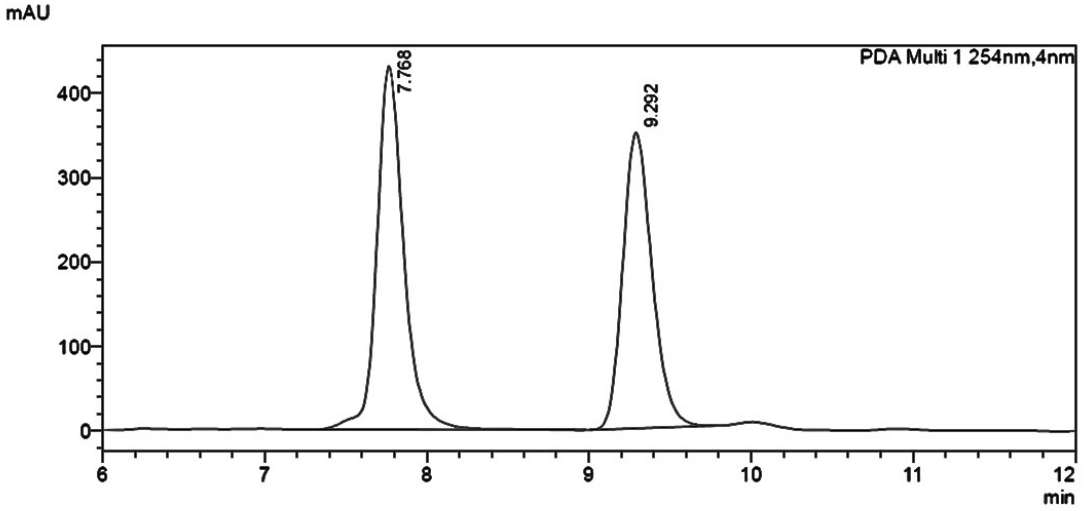
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.422	4353504	319096	25.201	%		RT:10.422
2	12.370	57774	3482	0.334	%		RT:12.370
3	12.866	98875	5078	0.572	%	V	RT:12.866
4	16.241	12765305	588509	73.893	%	S	RT:16.241
Total		17275457	916166				

rac-3e

<Chromatogram>



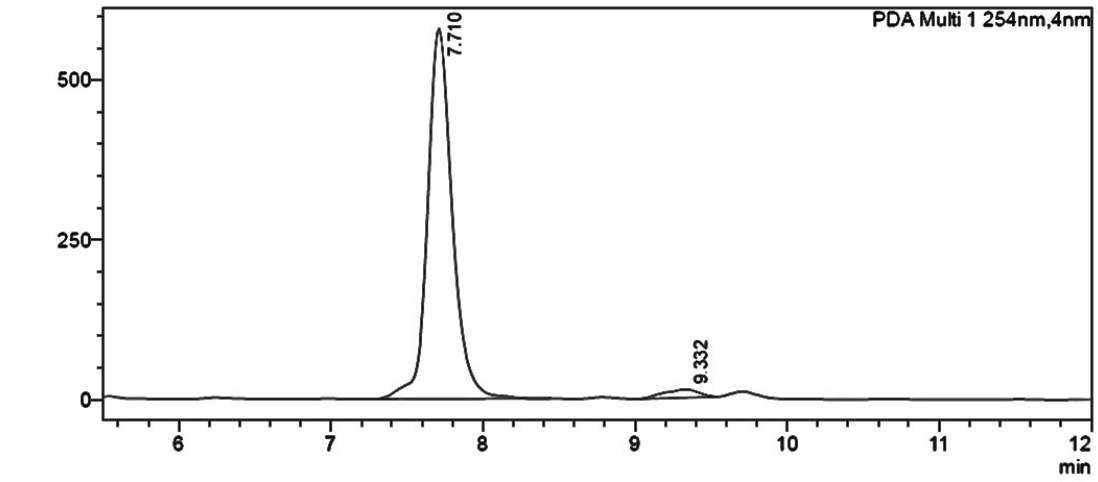
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.768	4993807	430735	53.116	%		RT:7.768
2	9.292	4407810	350532	46.884	%		RT:9.292
Total		9401617	781267				

3e

<Chromatogram>



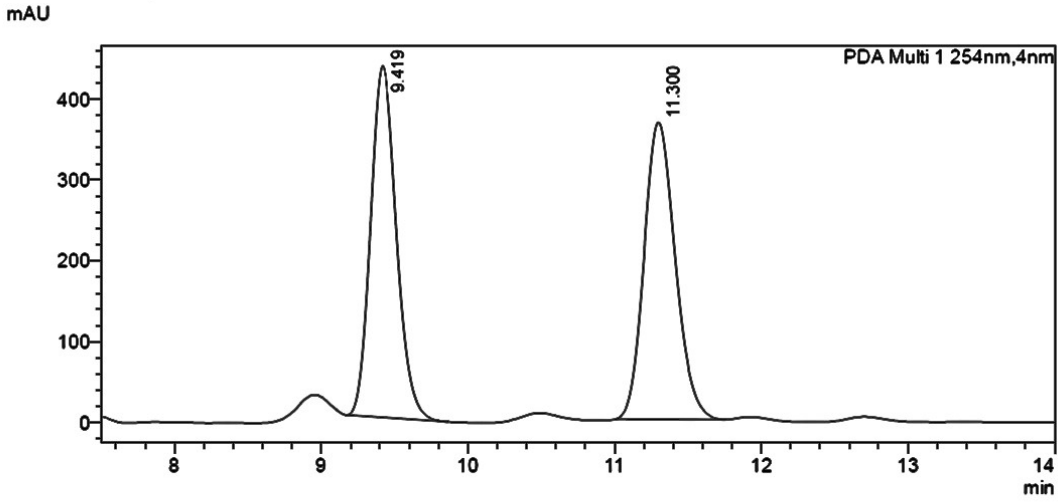
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.710	6509077	578558	96.957	%	S	RT:7.710
2	9.332	204269	12721	3.043	%		RT:9.332
Total		6713346	591278				

Rac-3f

<Chromatogram>



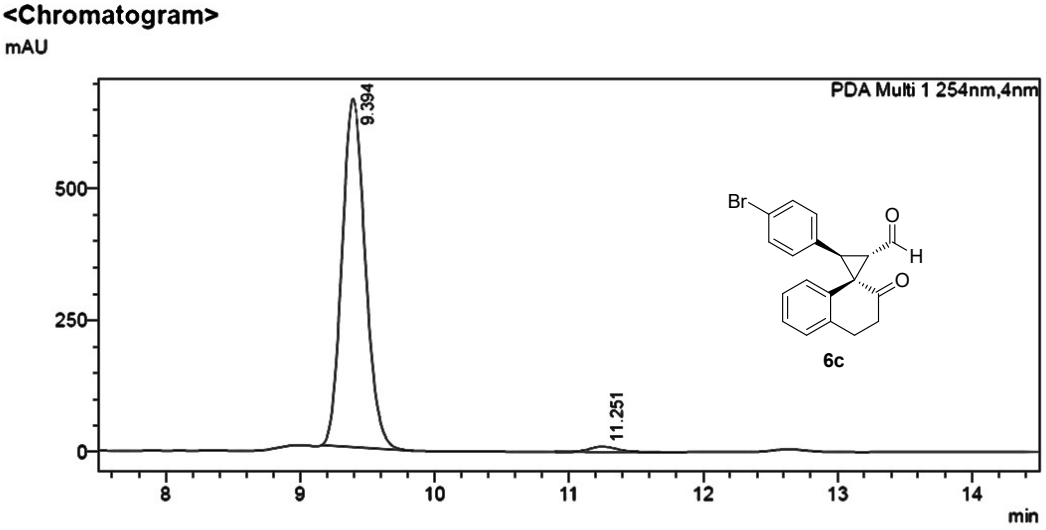
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.419	5297143	434950	49.389	%		RT:9.419
2	11.300	5428298	367273	50.611	%		RT:11.300
Total		10725441	802223				

3f

<Chromatogram>



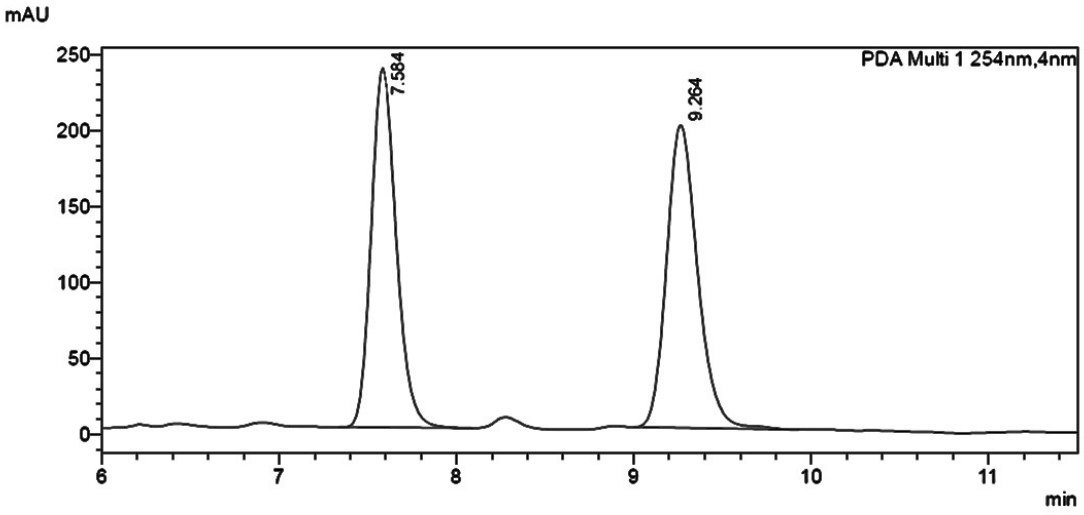
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.394	7936514	662037	98.074	%		RT:9.394
2	11.251	155848	10219	1.926	%		RT:11.251
Total		8092362	672256				

rac-3g

<Chromatogram>



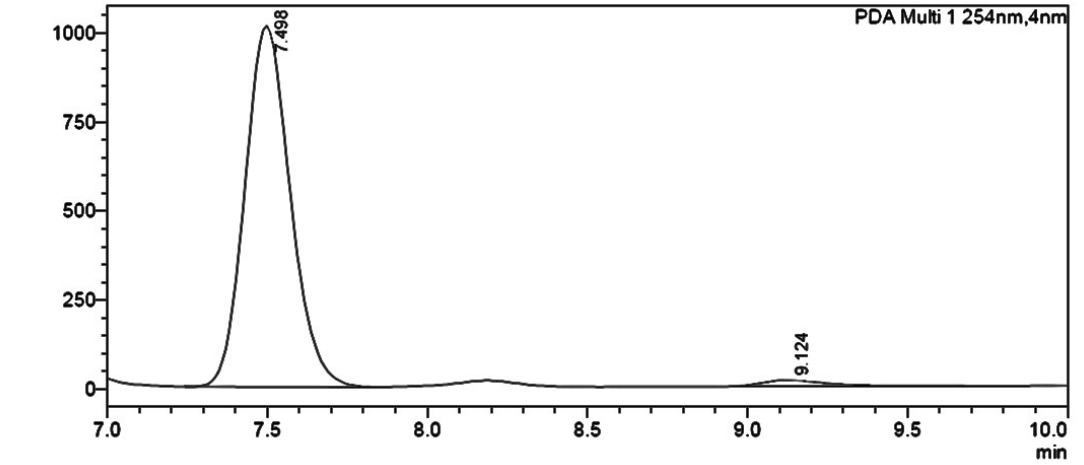
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.584	2325033	236774	48.903	%		RT:7.584
2	9.264	2429382	199376	51.097	%		RT:9.264
Total		4754414	436151				

3g

<Chromatogram>



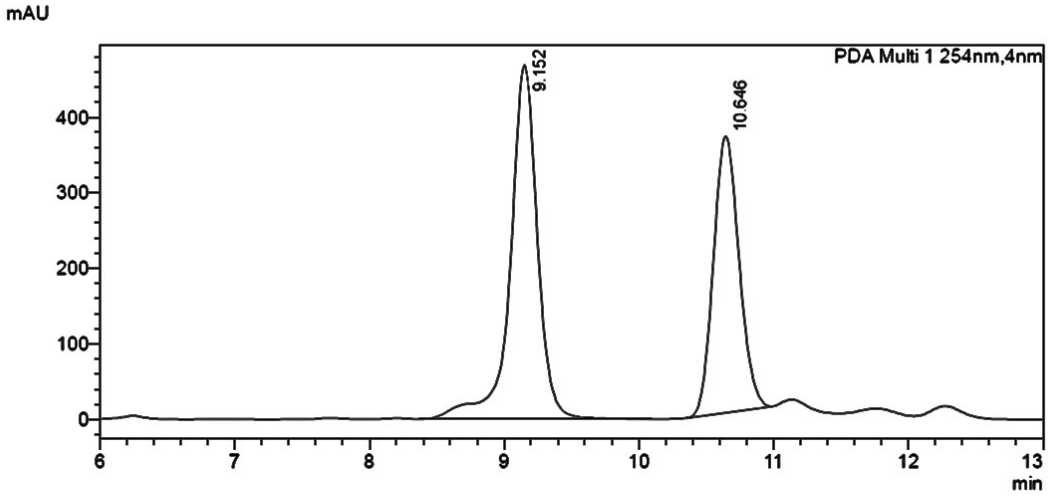
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.498	9968180	1012193	97.591	%		RT:7.498
2	9.124	246061	17216	2.409	%		RT:9.124
Total		10214240	1029410				

rac-3h

<Chromatogram>



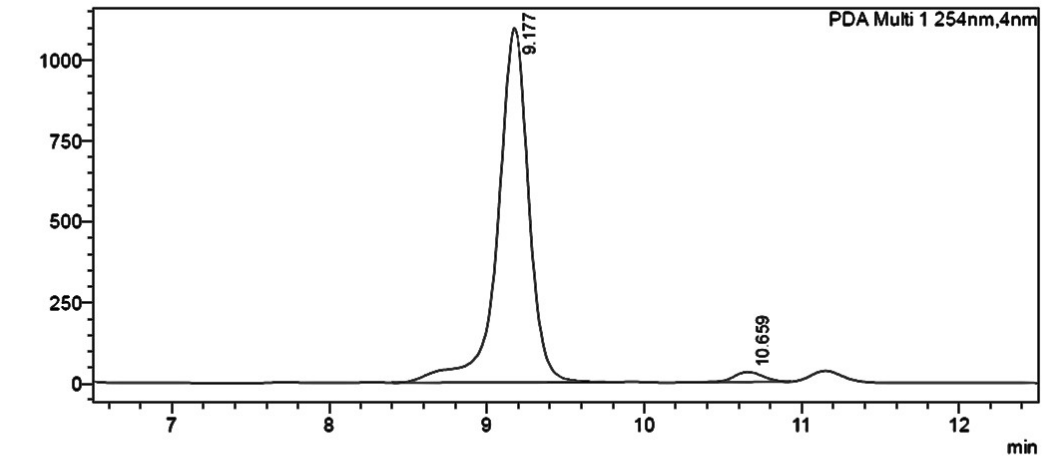
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.152	6603098	468678	57.764	%		RT:9.152
2	10.646	4828084	365765	42.236	%		RT:10.646
Total		11431182	834444				

3h

<Chromatogram>



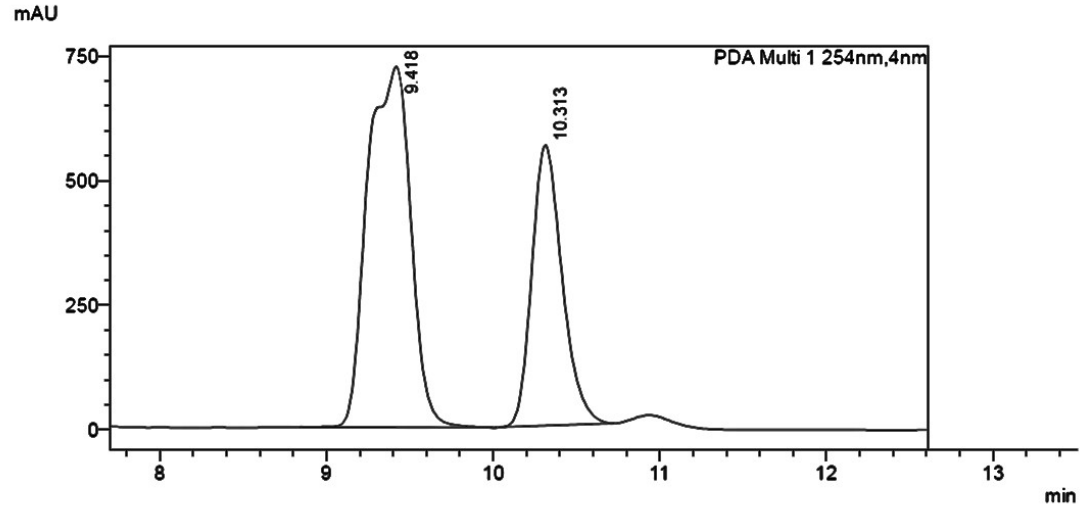
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.177	14962314	1095803	97.454	%		RT:9.177
2	10.659	390816	30577	2.546			
Total		15353130	1126381				

rac-3i

<Chromatogram>



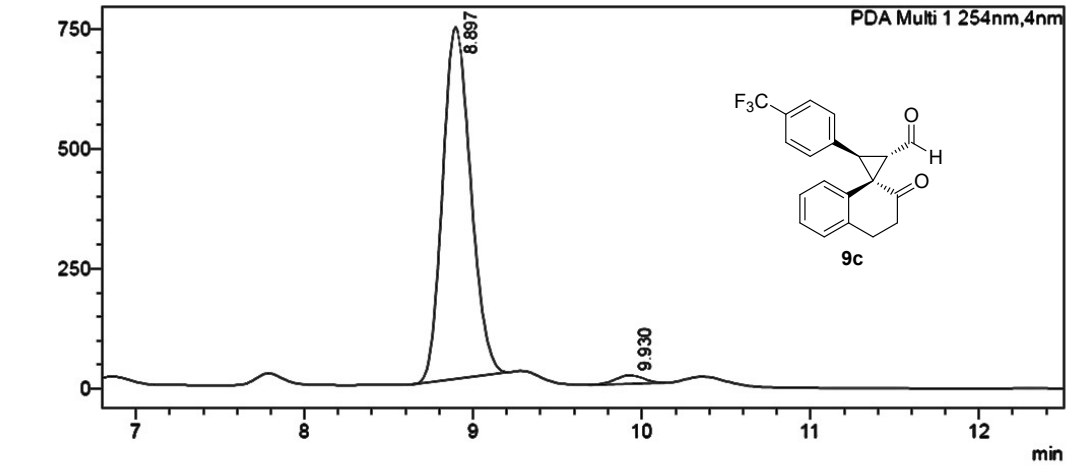
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.418	13034483	724730	64.624	%		RT:9.418
2	10.313	7135196	563522	35.376	%		RT:10.313
Total		20169679	1288253				

3i

<Chromatogram>



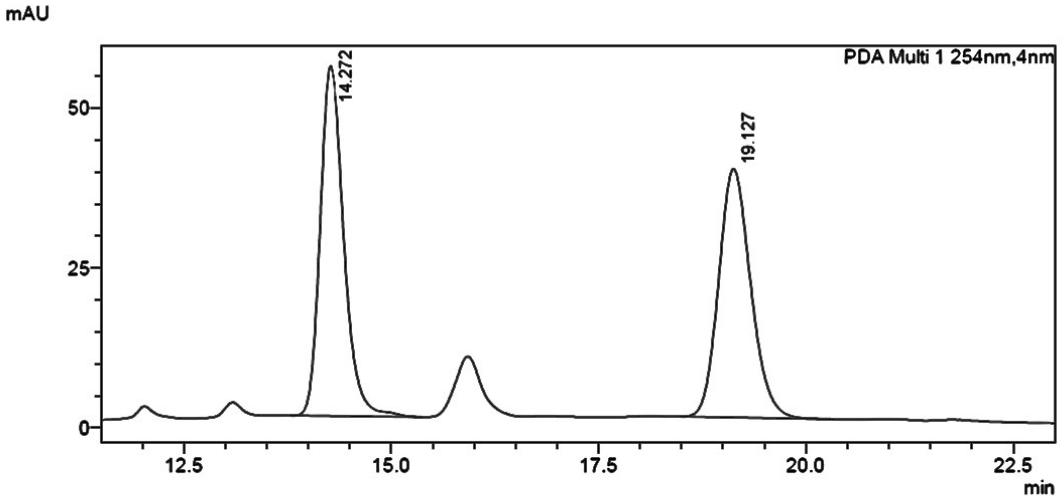
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.897	8514708	733227	97.657	%		RT:8.897
2	9.930	204251	17544	2.343	%		RT:9.930
Total		8718959	750770				

rac-3j

<Chromatogram>



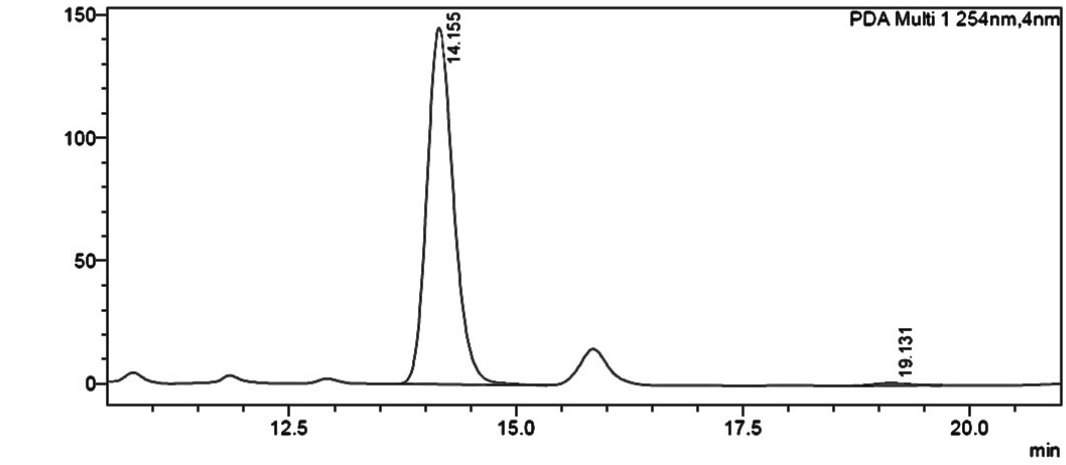
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.272	1078477	54804	50.737	%		RT:14.272
2	19.127	1047140	38916	49.263	%		RT:19.127
Total		2125617	93720				

3j

<Chromatogram>



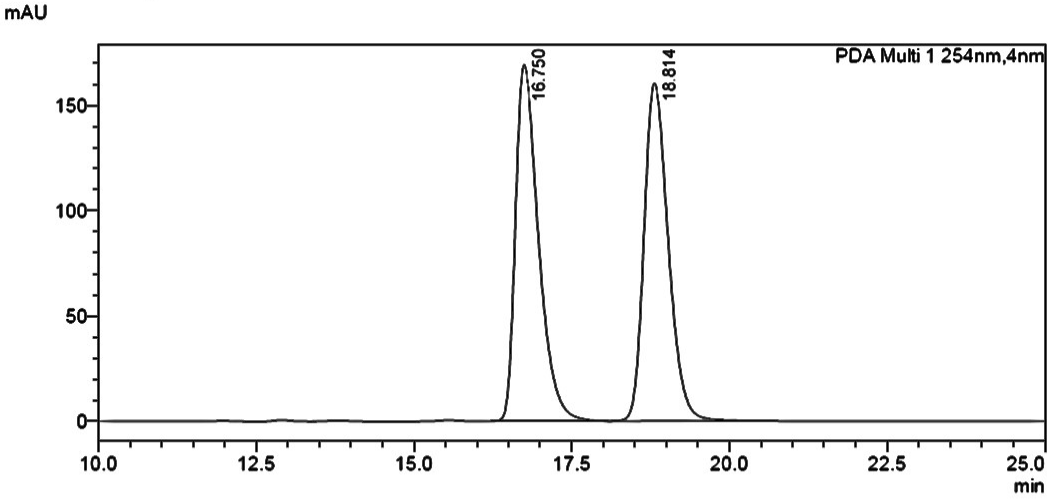
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.155	2952405	145004	99.025	%		RT:14.155
2	19.131	29079	1093	0.975	%		RT:19.131
Total		2981484	146097				

rac-3k

<Chromatogram>



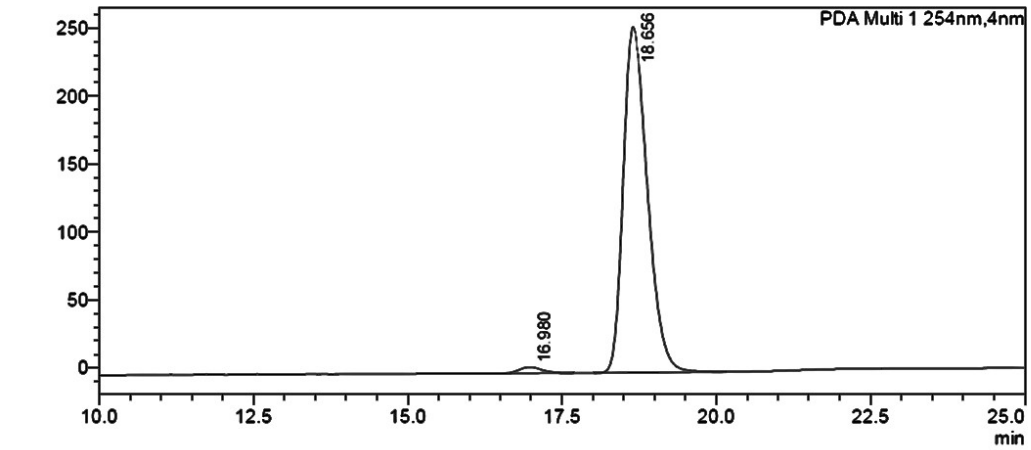
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.750	4285807	169183	50.048	%		RT:16.750
2	18.814	4277580	160308	49.952	%		RT:18.814
Total		8563387	329490				

3k

<Chromatogram>



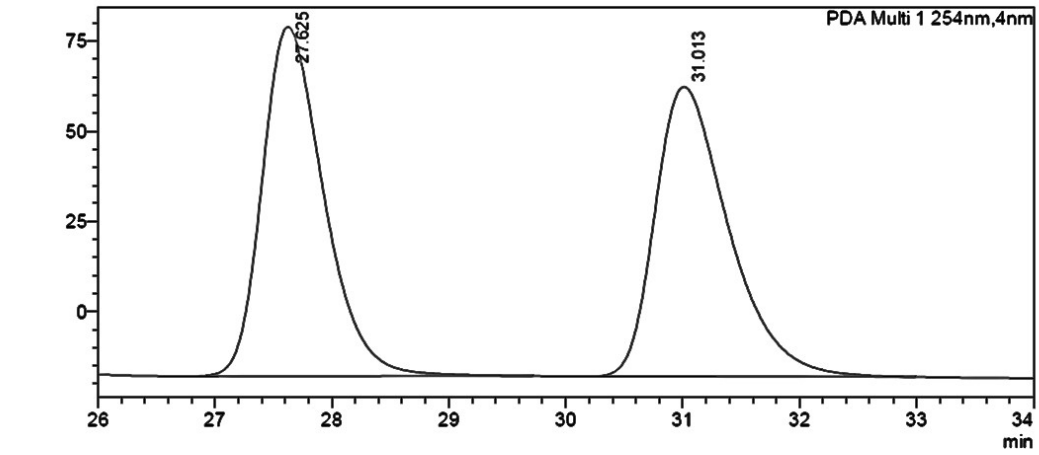
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.980	118008	4587	1.679	%		RT:16.980
2	18.656	6909767	254188	98.321	%		RT:18.656
Total		7027775	258775				

rac-3l

<Chromatogram>



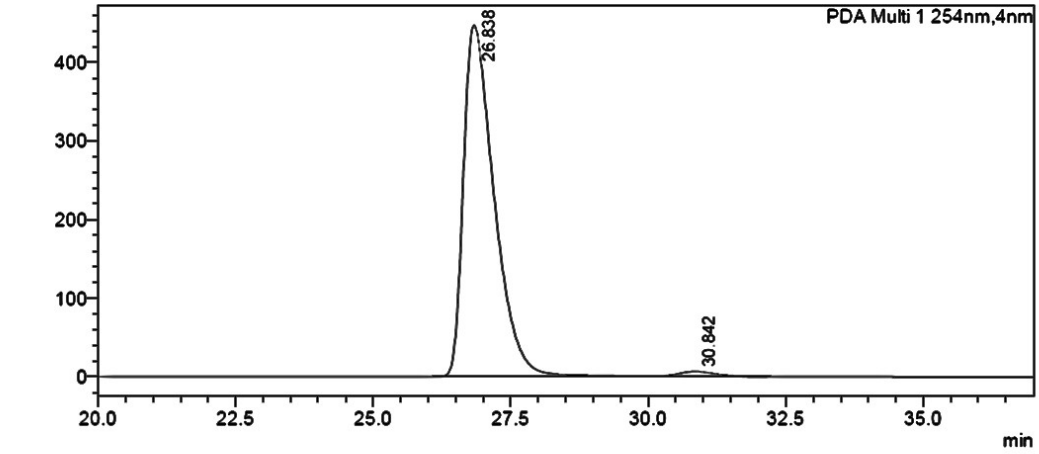
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.625	3547897	96746	50.197	%		RT:27.625
2	31.013	3520068	80267	49.803	%		RT:31.013
Total		7067965	177013				

3l

<Chromatogram>



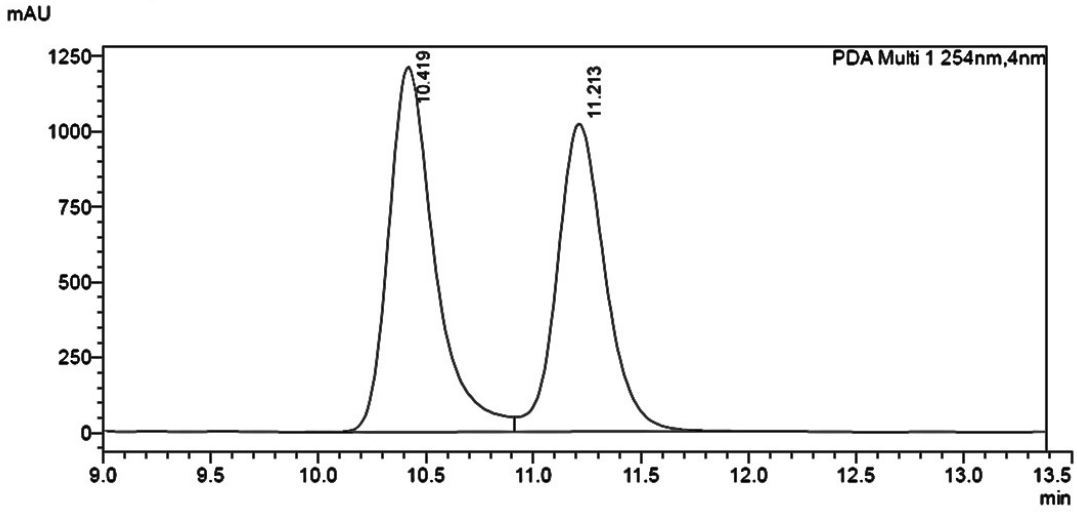
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	26.838	17425730	447587	98.415	%	S	RT:26.838
2	30.842	280669	6185	1.585	%	T	RT:30.842
Total		17706399	453773				

rac-3m

<Chromatogram>



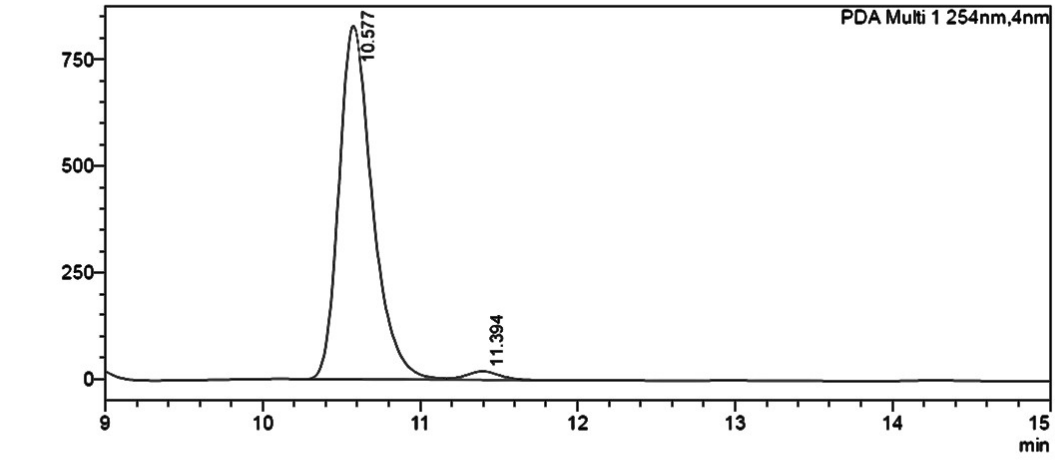
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.419	18025853	1210600	53.367	%		RT:10.419
2	11.213	15751184	1020960	46.633	%	SV	RT:11.213
Total		33777037	2231560				

3m

<Chromatogram>



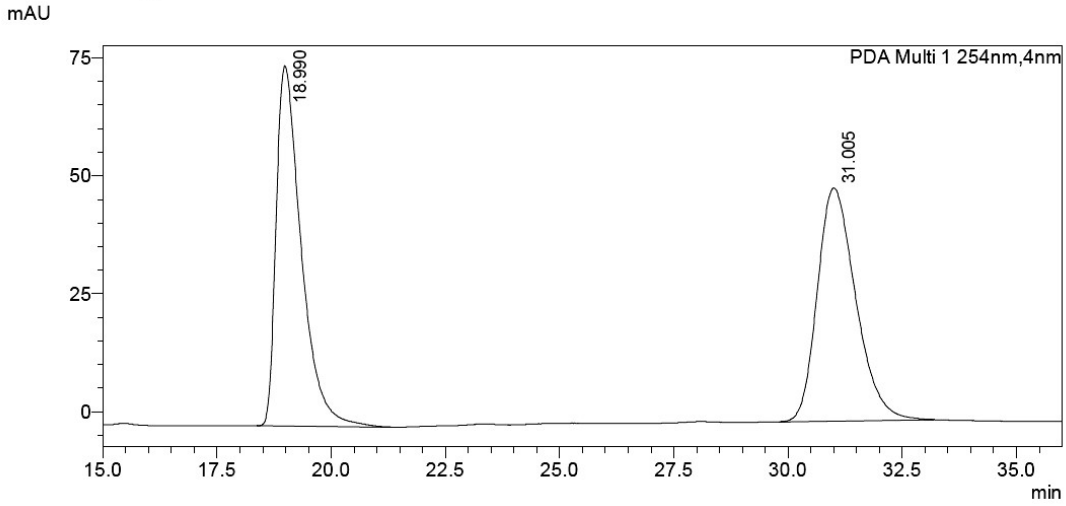
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.577	12206637	828311	97.606	%		RT:10.577
2	11.394	299351	20041	2.394	%	V	RT:11.394
Total		12505988	848352				

rac-3n

<Chromatogram>



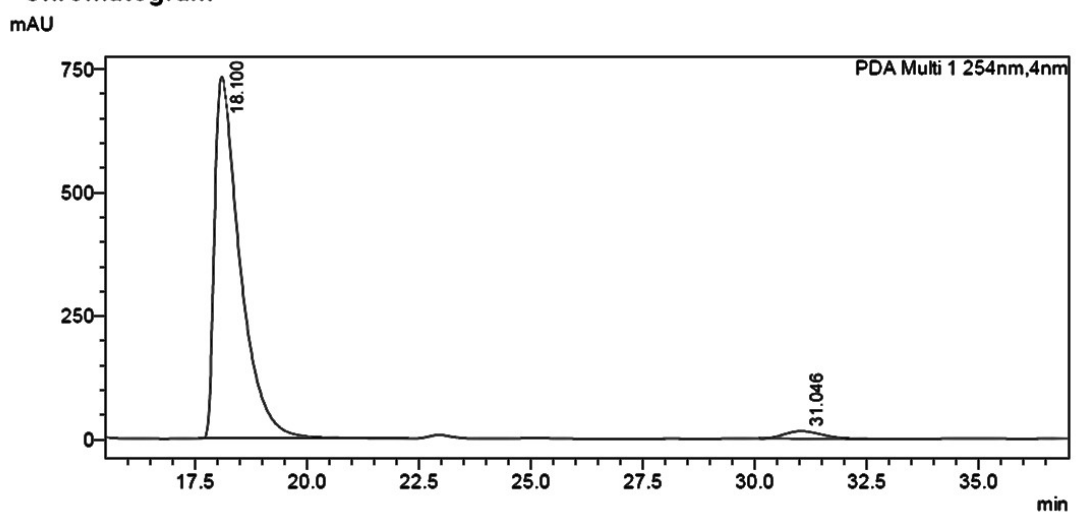
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.990	2915213	76354	50.256	%		RT:18.990
2	31.005	2885569	49403	49.744	%		RT:31.005
Total		5800782	125757				

3n

<Chromatogram>



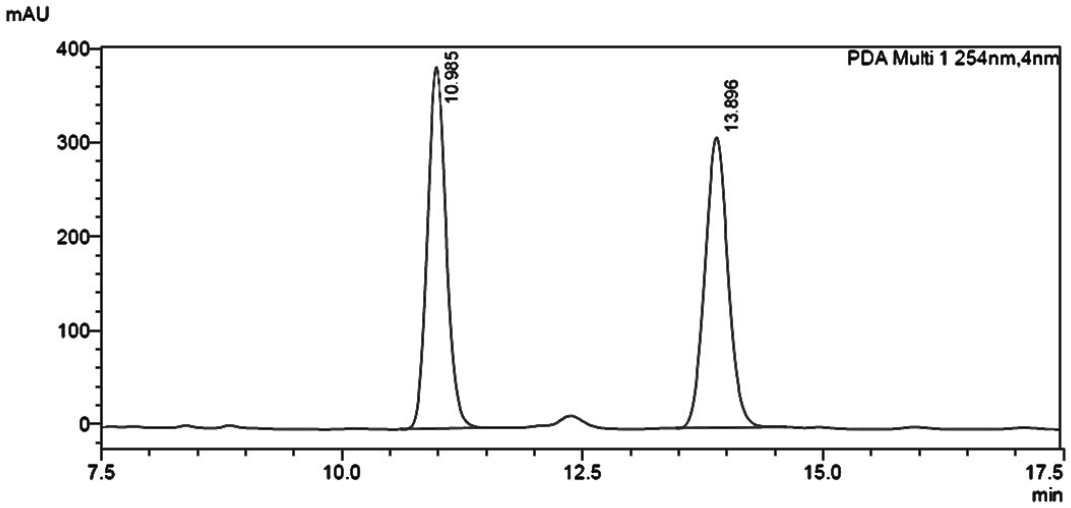
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.100	29132531	732763	97.046	%		RT:18.100
2	31.046	886771	15263	2.954	%		RT:31.046
Total		30019302	748026				

rac-3o

<Chromatogram>



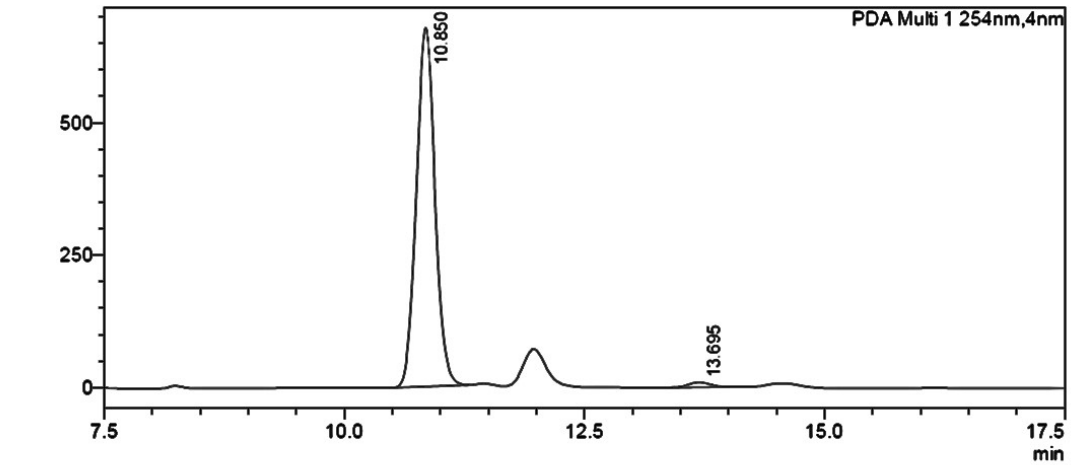
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.985	5206365	385221	50.189	%		RT:10.985
2	13.896	5167179	309139	49.811	%	S	RT:13.896
Total		10373544	694361				

3o

<Chromatogram>



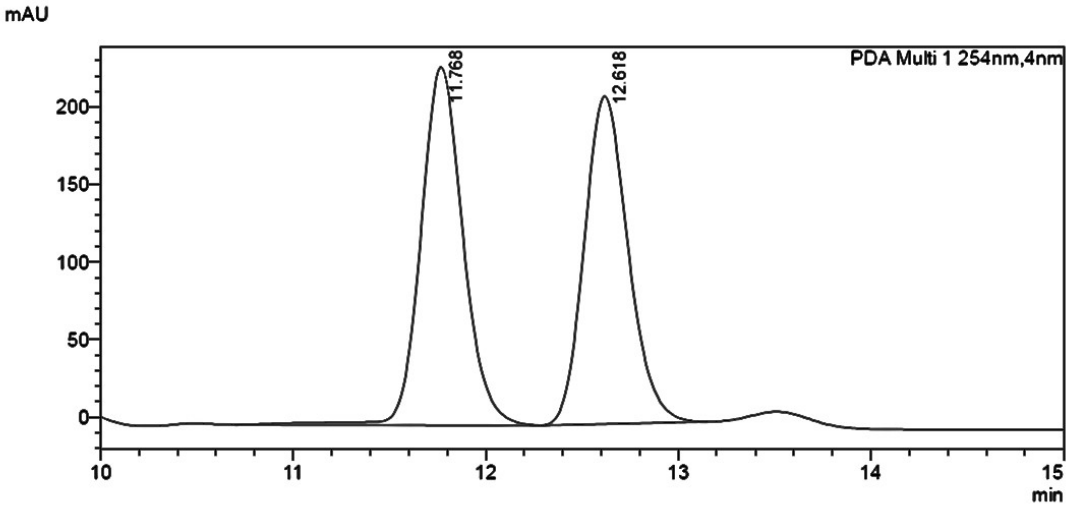
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.850	9148032	676913	98.346	%		RT:10.850
2	13.695	153829	9330	1.654	%		RT:13.695
Total		9301860	686243				

rac-3p

<Chromatogram>



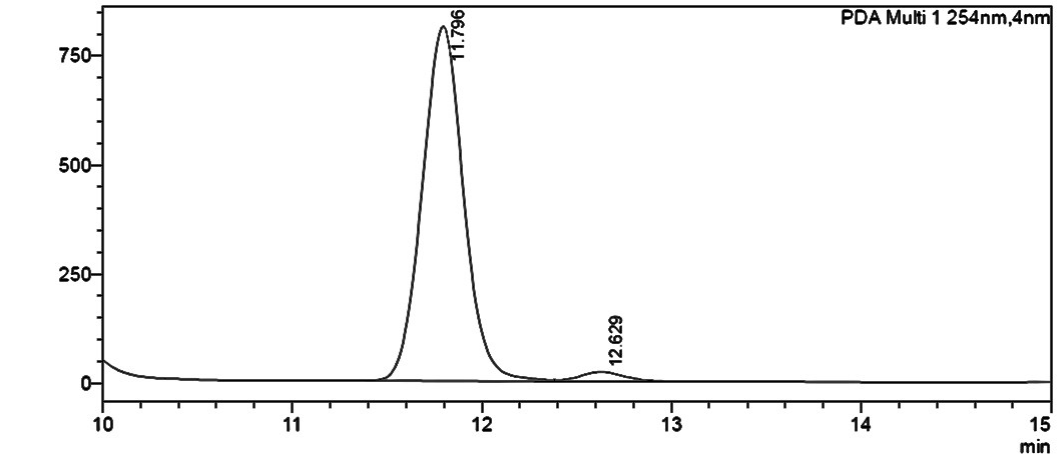
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.768	3520111	230818	51.267	%		RT:11.768
2	12.618	3346083	211529	48.733	%		RT:12.618
Total		6866194	442347				

3p

<Chromatogram>



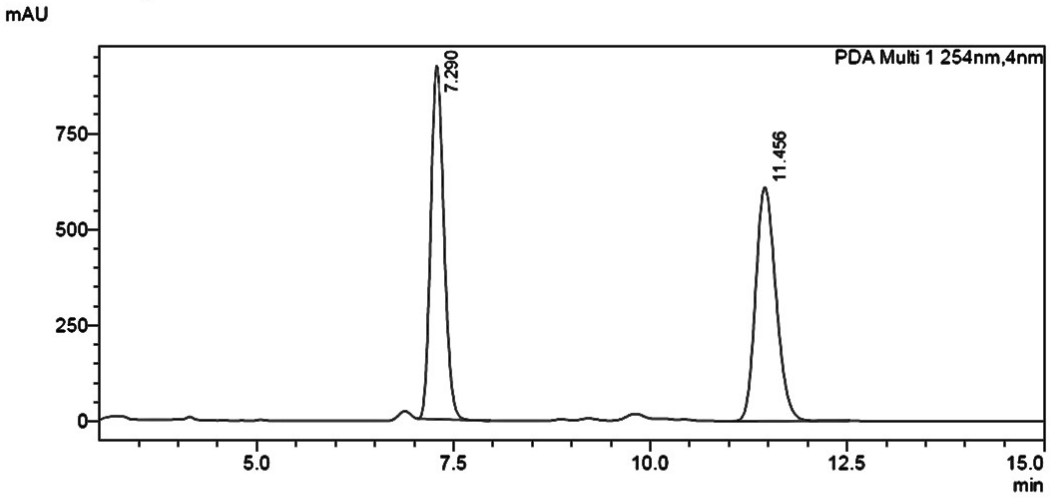
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.796	12329819	813070	97.215	%		RT:11.796
2	12.629	353163	21619	2.785	%	V	RT:12.629
Total		12682982	834688				

rac-5b

<Chromatogram>



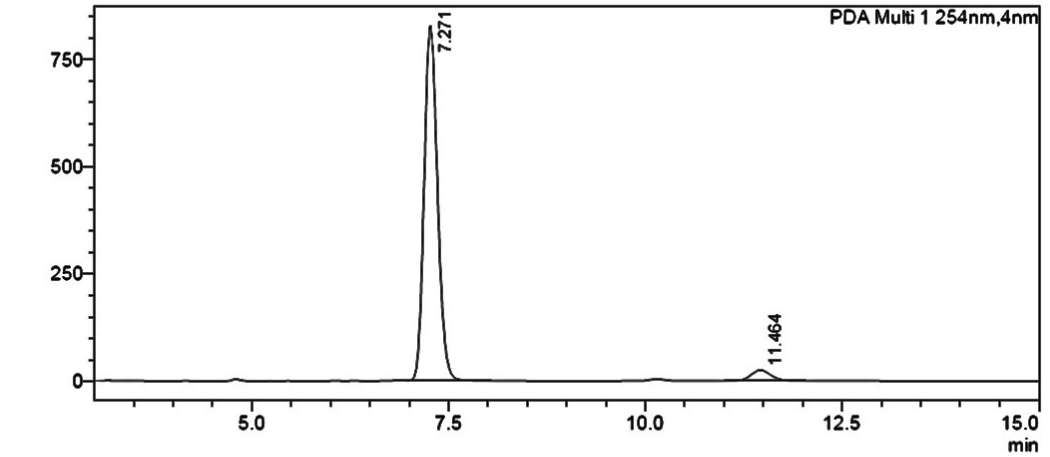
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.290	10762087	921770	49.544	%		RT:7.290
2	11.456	10960045	610485	50.456	%		RT:11.456
Total		21722131	1532256				

5b

<Chromatogram>



<Peak Table>

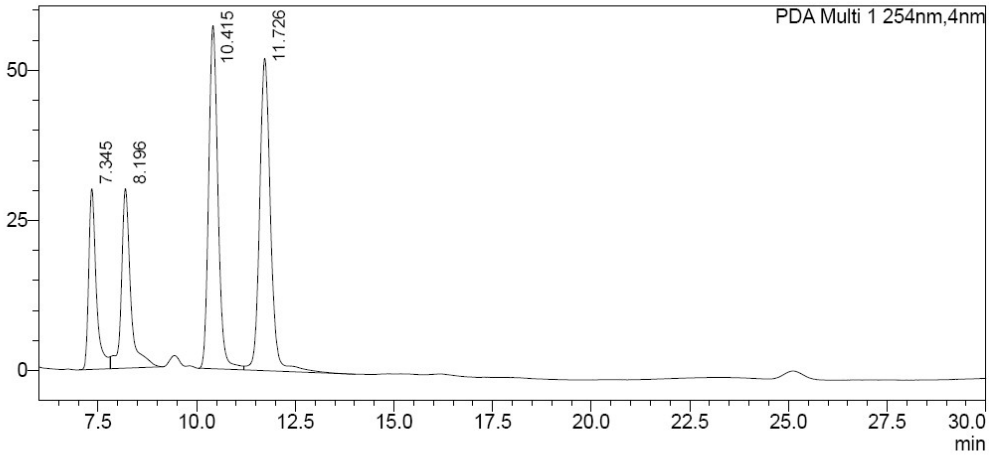
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.271	9785529	826059	95.673	%		RT:7.271
2	11.464	442615	24978	4.327	%		RT:11.464
Total		10228144	851037				

rac-5e

<Chromatogram>

mAU



<Peak Table>

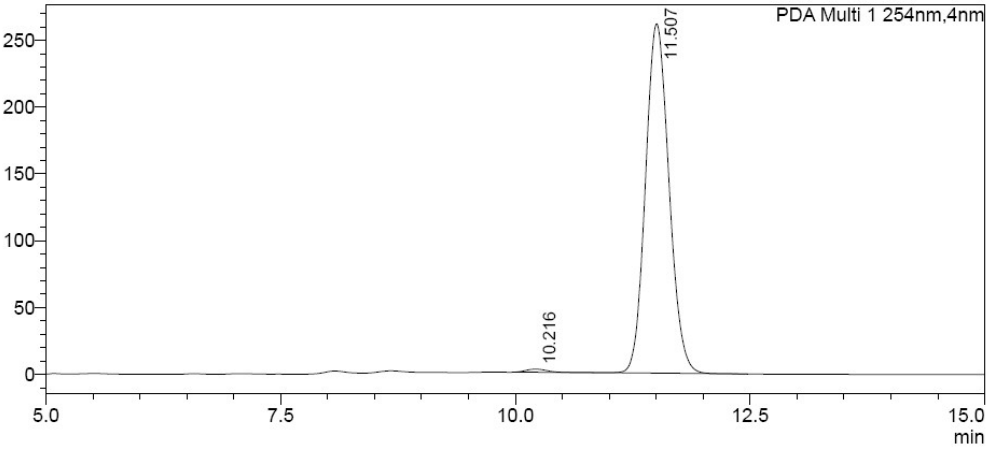
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.345	403361	29024	14.229	%		RT:7.345
2	8.196	487221	27549	17.188	%	V	RT:8.196
3	10.415	937410	56074	33.069	%		RT:10.415
4	11.726	1006736	50349	35.514	%	V	RT:11.726
Total		2834728	162996				

5e

<Chromatogram>

mAU



<Peak Table>

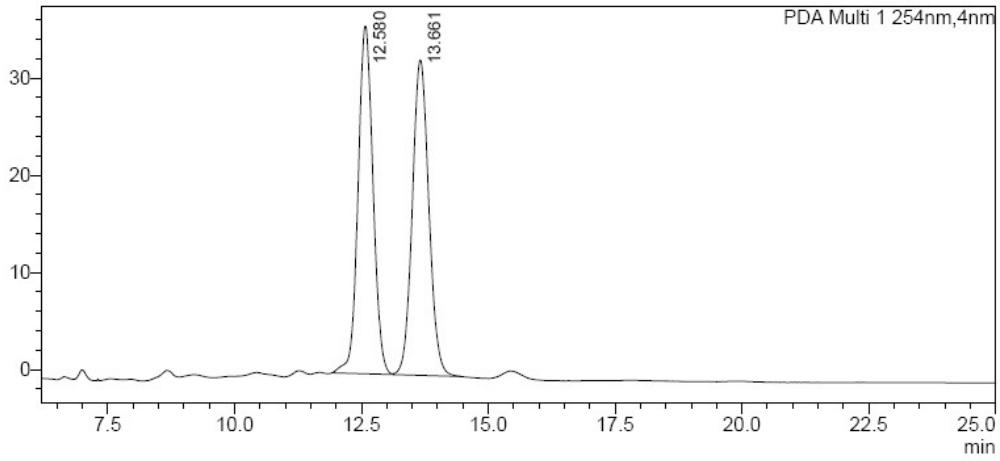
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.216	35215	2293	0.767	%		RT:10.216
2	11.507	4557478	245257	99.233	%		RT:11.507
Total		4592693	247550				

rac-5f

<Chromatogram>

mAU



<Peak Table>

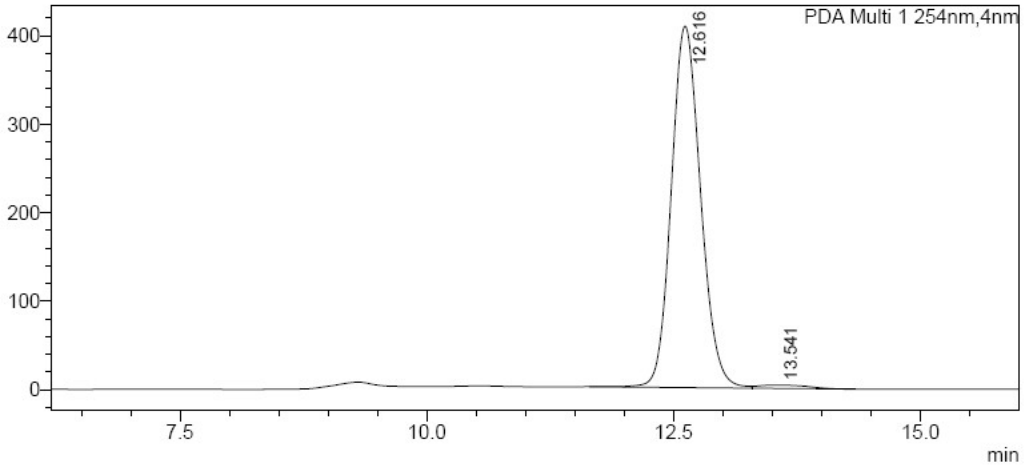
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.580	735032	35291	49.989	%		RT:12.580
2	13.661	735362	31502	50.011	%	V	RT:13.661
Total		1470394	66793				

5f

<Chromatogram>

mAU



<Peak Table>

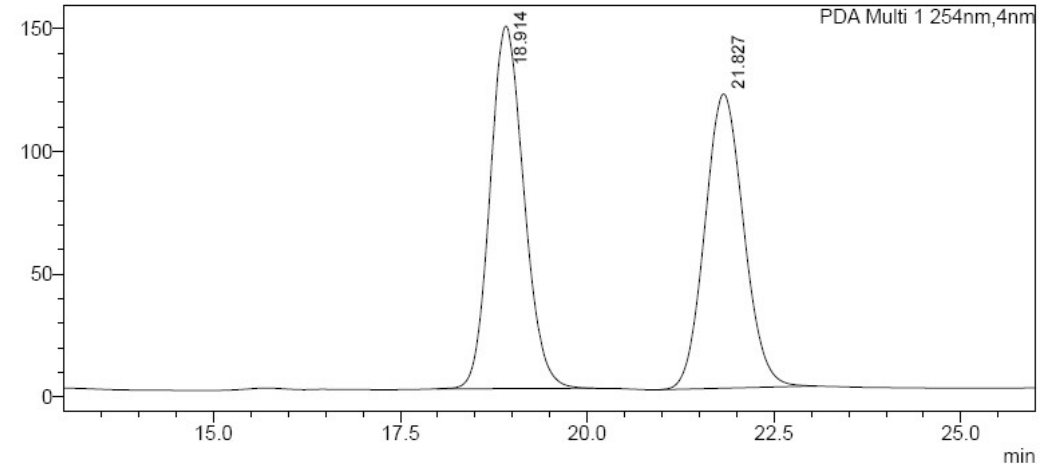
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.616	8434867	393842	98.515	%		RT:12.616
2	13.541	127116	3757	1.485	%	V	RT:13.541
Total		8561984	397600				

rac-5g

<Chromatogram>

mAU



<Peak Table>

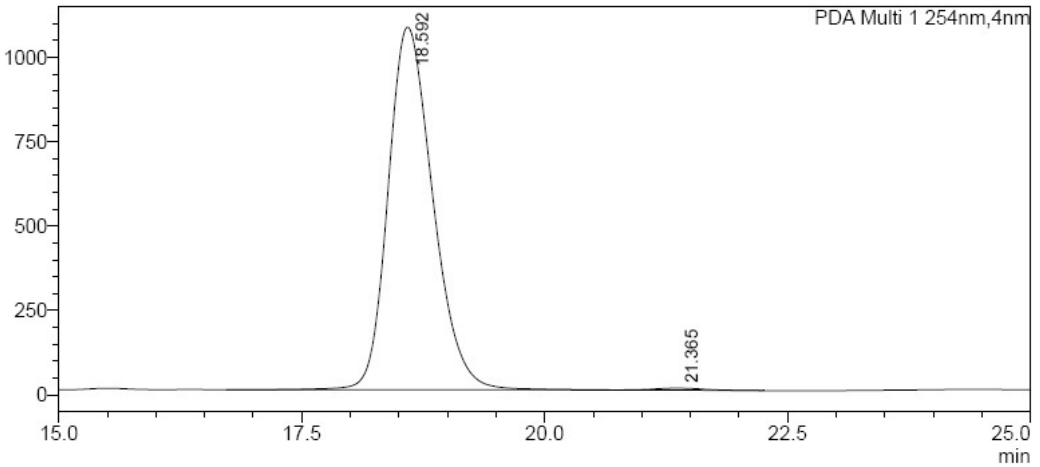
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.914	4664434	146221	51.770	%		RT:18.914
2	21.827	4345566	119039	48.230	%		RT:21.827
Total		9010001	265260				

5g

<Chromatogram>

mAU

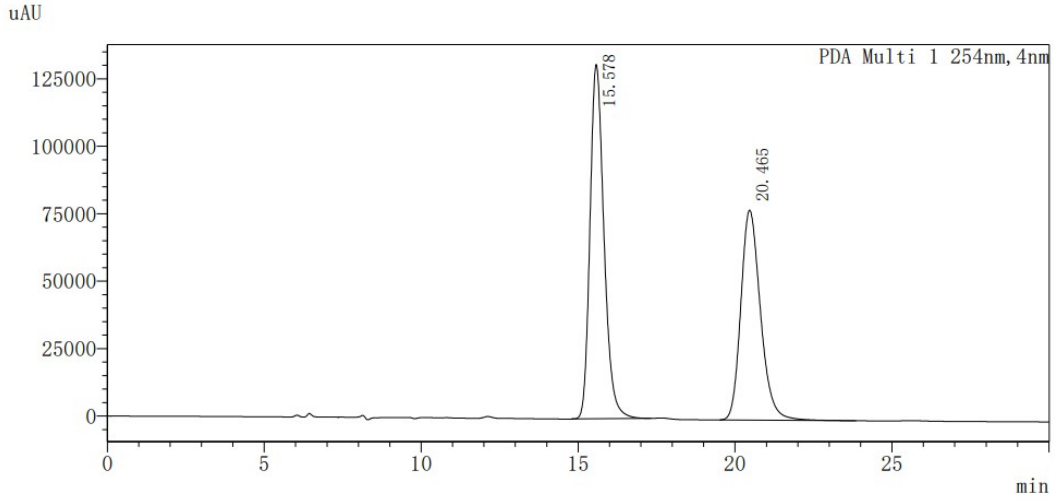


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.592	34484052	1055738	99.434	%		RT:18.592
2	21.365	196233	5847	0.566	%		RT:21.365
Total		34680285	1061586				

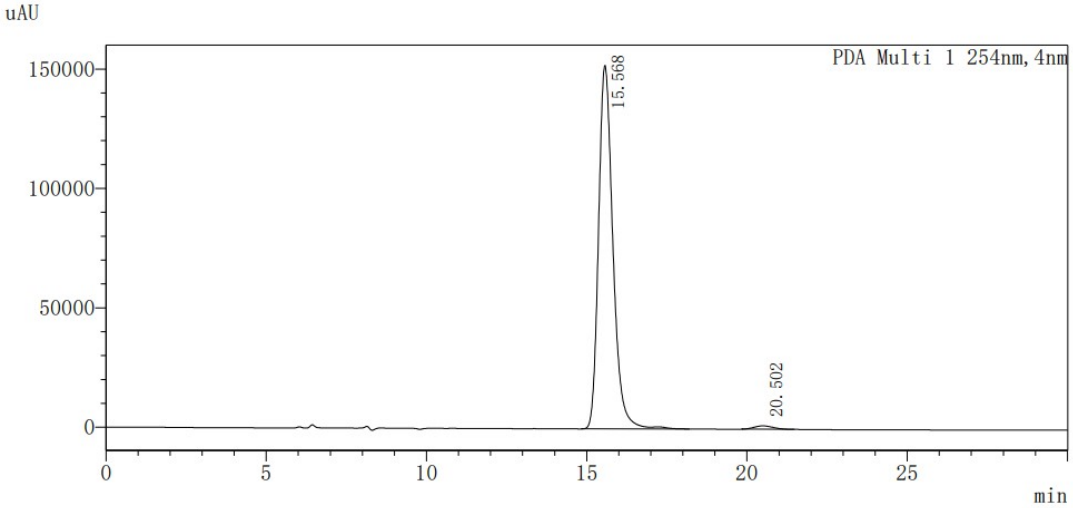
rac-5h



PDA Ch1 254nm

#	[min]	[uAU*s]	[uAU]	%
1	15.578	4071795	131287	54.620
2	20.465	3383014	77831	45.380
总计		7454809	209118	100.000

5h

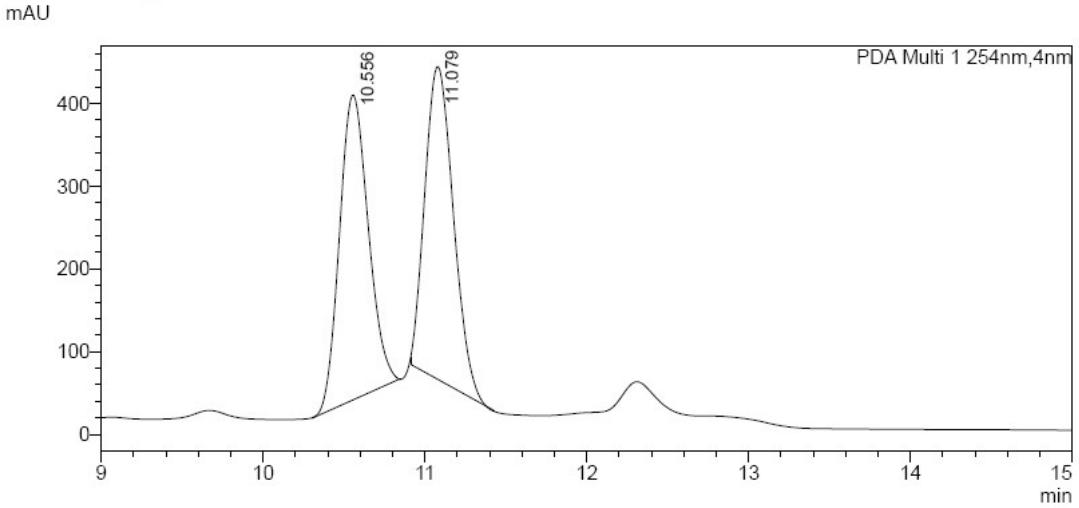


PDA Ch1 254nm

#	[min]	[uAU*s]	[uAU]	%
1	15.568	4739680	152193	98.776
2	20.502	58743	1425	1.224
总计		4798423	153619	100.000

rac-5i

<Chromatogram>



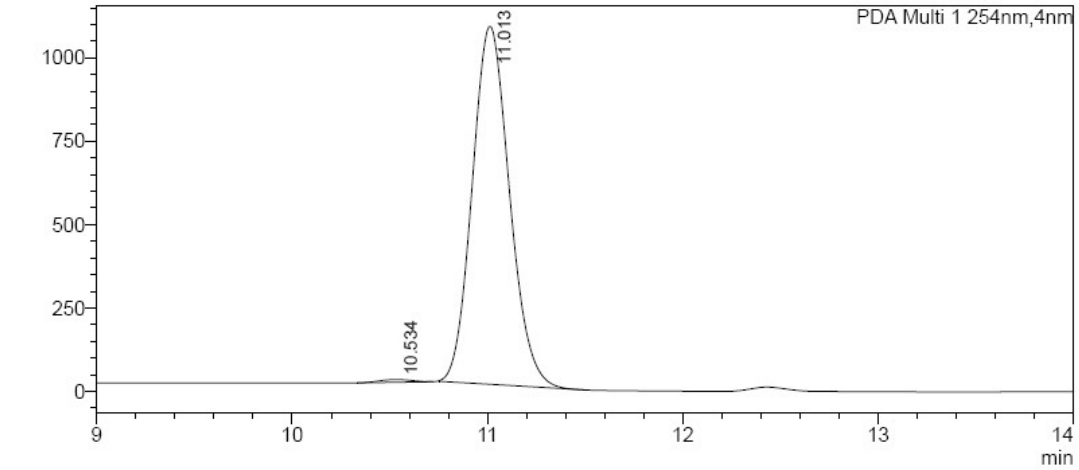
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.556	4578091	365757	49.820	%		RT:10.556
2	11.079	4611189	371061	50.180	%		RT:11.079
Total		9189280	736818				

5i

<Chromatogram>



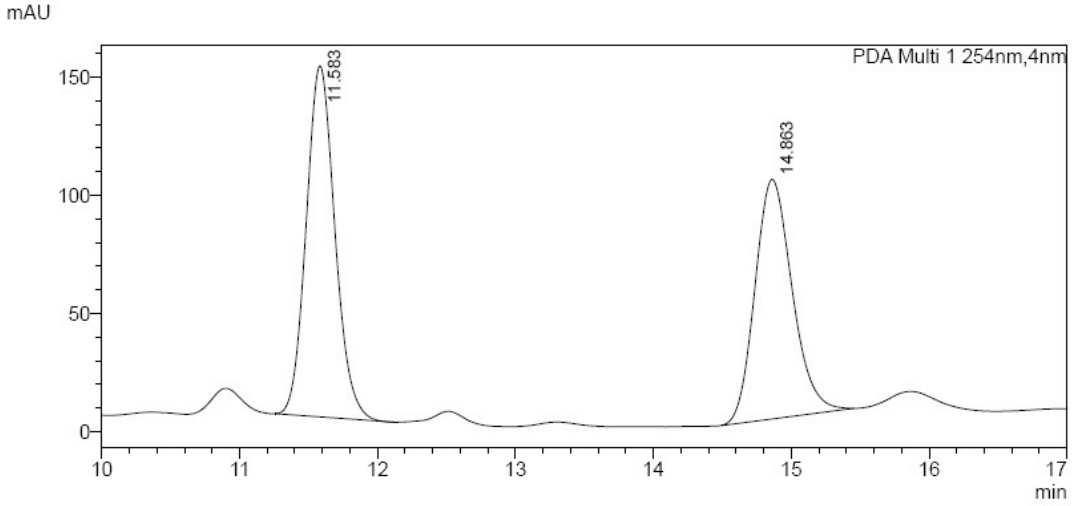
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.534	94745	8200	0.661	%		RT:10.534
2	11.013	14230158	1051206	99.339	%		RT:11.013
Total		14324903	1059406				

rac-5j

<Chromatogram>



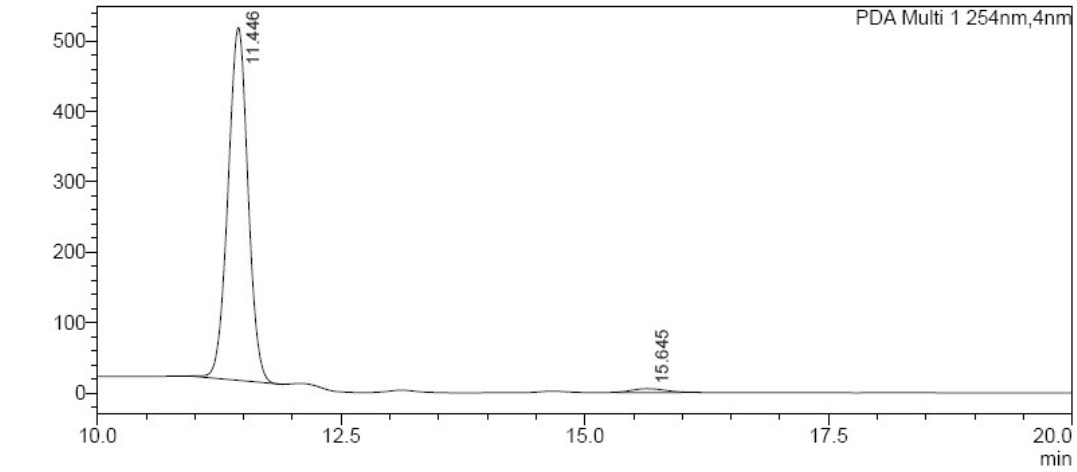
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.583	2150179	147083	53.040	%		RT:11.583
2	14.863	1903673	101001	46.960	%		RT:14.863
Total		4053852	248085				

5j

<Chromatogram>



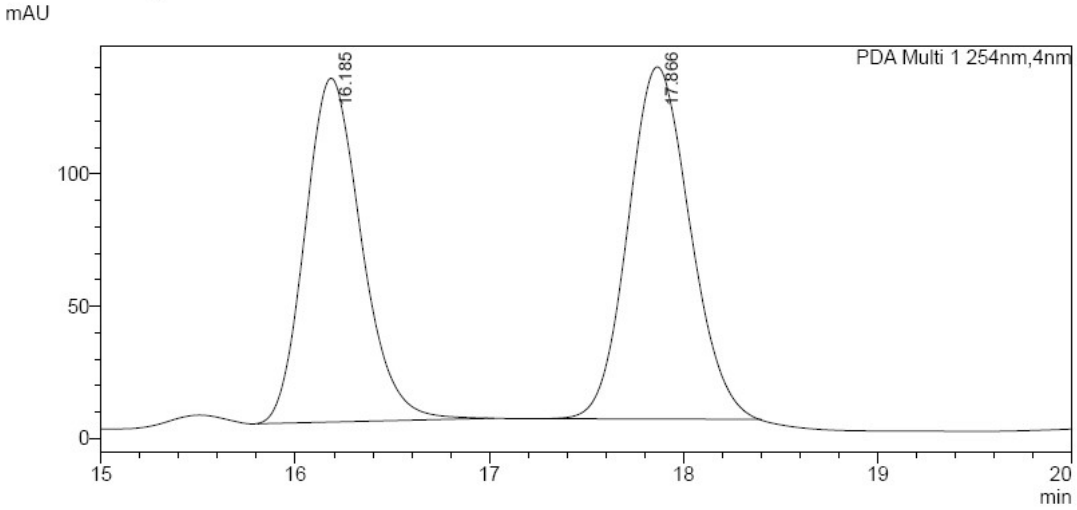
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.446	7155167	499622	98.252	%		RT:11.445
2	15.645	127329	5332	1.748	%	V	RT:15.645
Total		7282496	504954				

rac-5k

<Chromatogram>



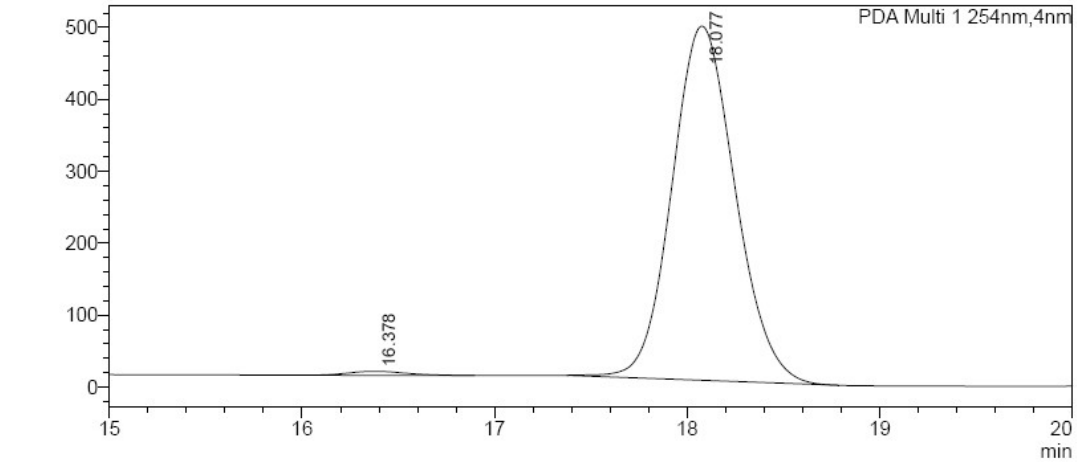
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.185	2628940	129634	47.072	%		RT:16.185
2	17.866	2956019	132454	52.928	%		RT:17.866
Total		5584959	262088				

5k

<Chromatogram>

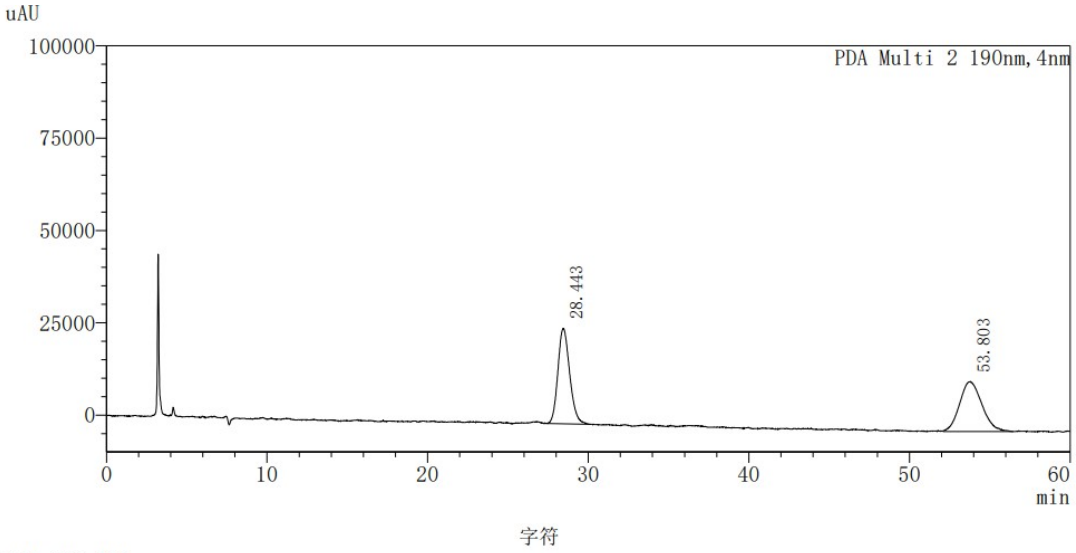


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.378	111926	5524	0.984	%		RT:16.378
2	18.077	11259083	491105	99.016	%		RT:18.077
Total		11371009	496629				

rac-5l

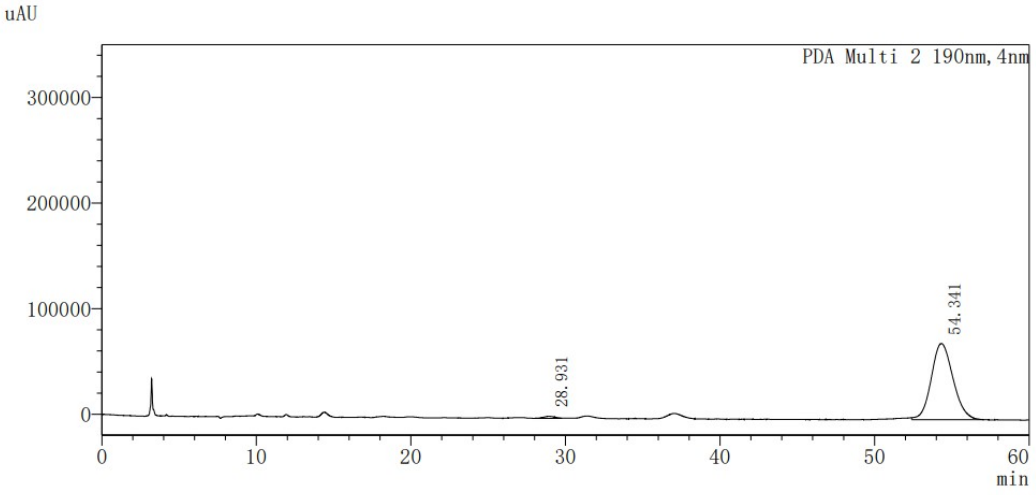


字符

PDA Ch2 190nm

#	[min]	[uAU*s]	[uAU]	%
1	28.443	1320307	25830	50.267
2	53.803	1306277	13471	49.733
总计		2626584	39301	100.000

5l



字符

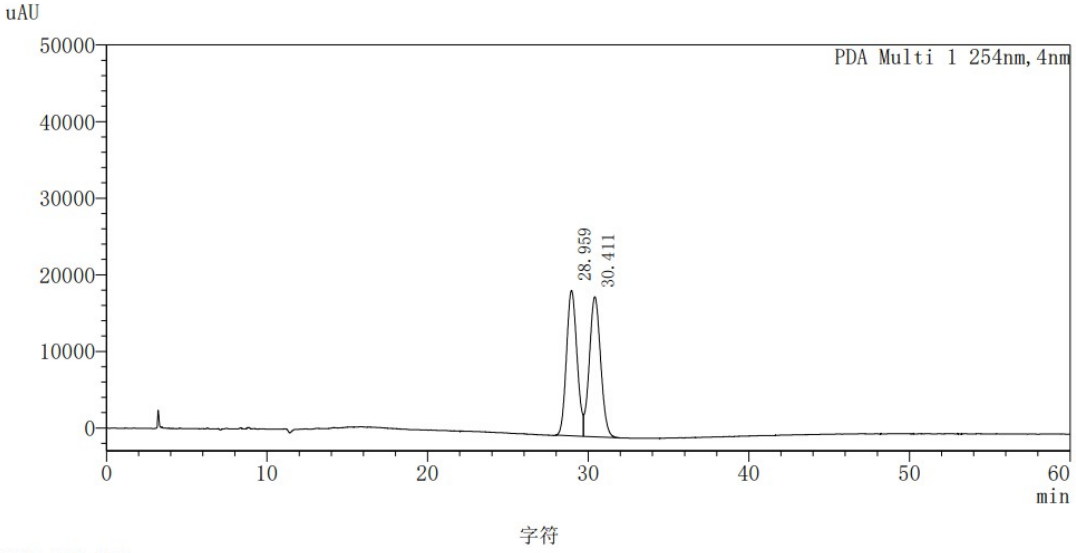
PDA Ch1 254nm

#	[min]	[uAU*s]	[uAU]	%
1	28.944	28751	658	0.894
2	54.320	3187363	30392	99.106
总计		3216114	31050	100.000

PDA Ch2 190nm

#	[min]	[uAU*s]	[uAU]	%
1	28.931	107179	1983	1.493
2	54.341	7070651	72121	98.507
总计		7177830	74104	100.000

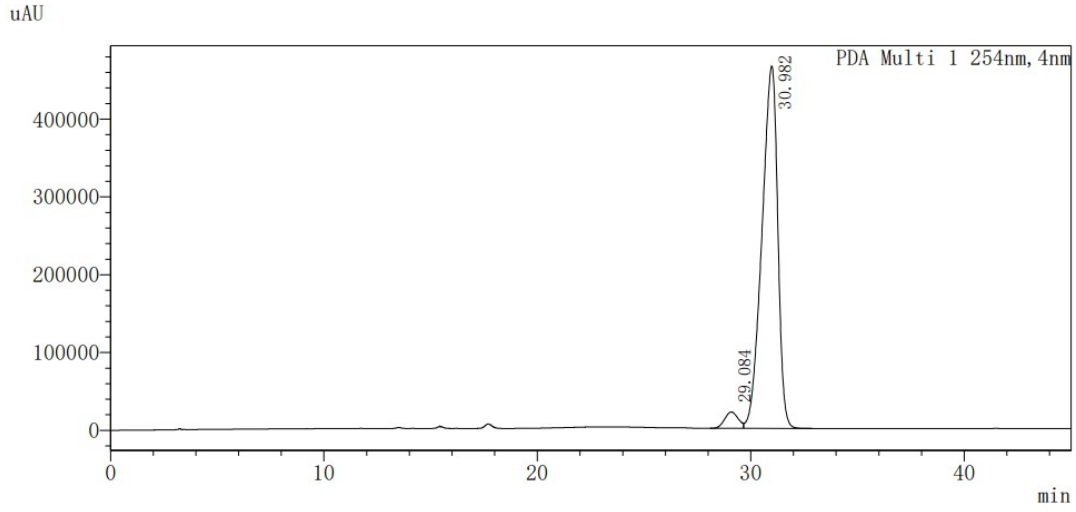
rac-5m



PDA Ch1 254nm

#	[min]	[uAU*s]	[uAU]	%
1	28.959	866461	18976	49.195
2	30.411	894808	18279	50.805
总计		1761269	37255	100.000

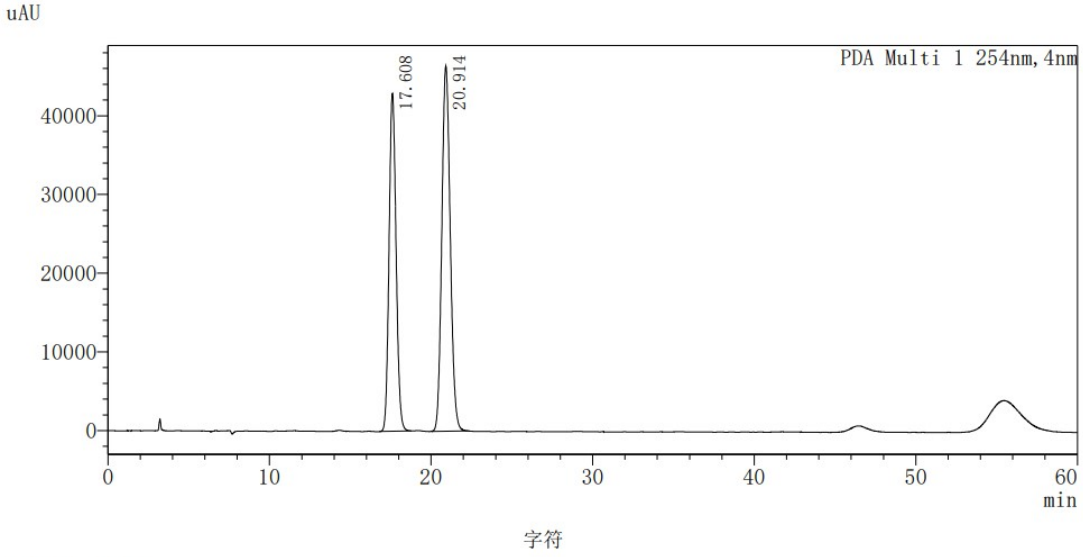
5m



PDA Ch1 254nm

#	[min]	[uAU*s]	[uAU]	%
1	29.084	936511	21125	3.754
2	30.982	24009794	465706	96.246
总计		24946305	486832	100.000

rac-5n

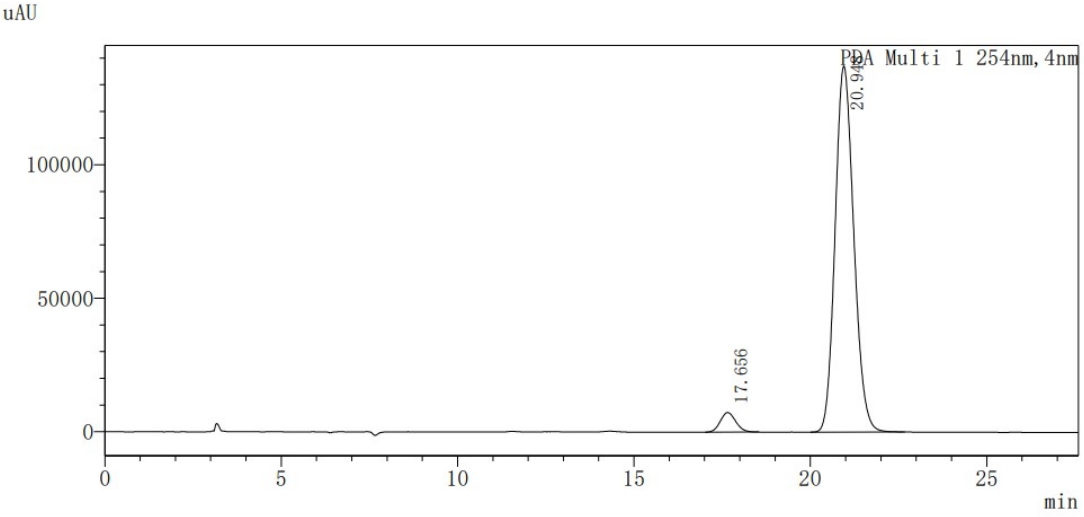


字符

PDA Ch1 254nm

#	[min]	[uAU*s]	[uAU]	%
1	17.608	1295050	42943	43.467
2	20.914	1684322	46381	56.533
总计		2979372	89324	100.000

5n



字符

PDA Ch1 254nm

#	[min]	[uAU*s]	[uAU]	%
1	17.656	223413	7333	4.234
2	20.948	5052817	137107	95.766
总计		5276231	144440	100.000