Electronic Supplementary Material (ESI) for ChemComm.

Asymmetric synthesis of functionalized tetrahydrofluorenones via an NHC-catalyzed homoenolate Michael addition †

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1. General Methods and Materials

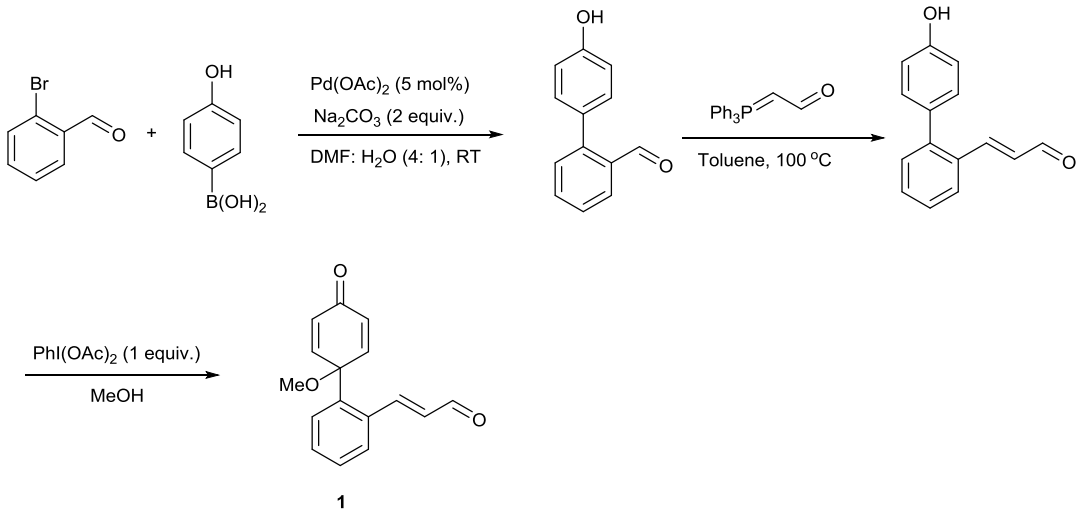
Unless otherwise indicated, all commercially available chemicals were used without purification. All solvents were distilled and purified according to standard procedures. Analytical TLC was visualized with ultraviolet radiation at 254 nm. Optical rotations were measured on a Perkin-Elmer 241 polarimeter and reported as follows: $[\alpha]_D^T$ (concentration (g/100 mL), solvent). High-resolution mass spectra (HRMS) were acquired on a Thermo Fisher Scientific Orbitrap XL spectrometer. IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum 100 using ATR-Unit. ^1H and ^{13}C NMR spectra were recorded at ambient temperature on Varian Innova 400 or Varian 600. Analytical HPLC was performed on a Hewlett-Packard 1100 Series instrument using chiral stationary phases (Daicel IA, Daicel IC).

2. Experimental Procedures

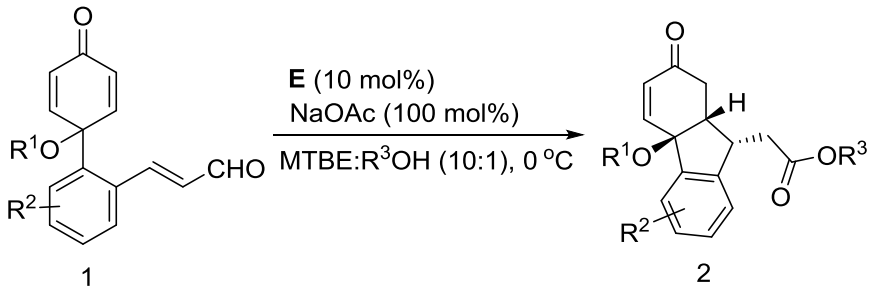
General procedure **I** for the preparation of enal-tethered cyclohexadienones **1**.

A three-step protocol through Suzuki coupling reaction/Wittig reaction/oxidative dearomatization reaction for the synthesis of enal-tethered cyclohexadienones **1** was applied as follows: Substituted 2-bromobenzaldehyde (5 mmol), 4-hydroxyphenylboronic acid (5 mmol) and Na_2CO_3 (10 mmol) were dissolved in 10 mL DMF: H_2O (v/v 2:1), then $Pd(OAc)_2$ (5 mol%) was added and the reaction mixture was stirred at rt until the consumption of starting material. The reaction mixture was extracted with EA (20 mL) three times, washed with sat. NaCl solution and dried over Na_2SO_4. The solvent was removed under vacuum to afford the crude product which was used directly without further purification.

The above-obtained crude product and (triphenylphosphoranylidene)acetaldehyde (5 mmol) was dissolved in 20 mL toluene under argon, then the solution was heated to 100 ^oC for 48 h. The solvent was removed under vacuum, the residue was dissolved in 10 mL methanol and cooled to 0^oC, then $PhI(OAc)_2$ (5 mmol) was added portionwise. The reaction mixture was stirred for further 30 min. The solvent was removed under vacuum, 20 mL water was added. The reaction mixture was extracted with 20 mL EA for three times, washed with sat. NaCl solution, dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash chromatography (pentane: EA 10:1 or DCM: MeOH 500:1) to afford the desired enal-tethered cyclohexadienones **1**.



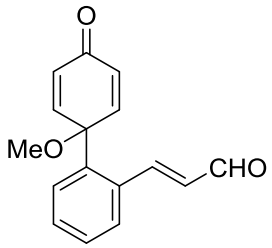
General Procedure **II**: To a dry Schlenk tube equipped with a magnetic stir bar were added enal-tethered cyclohexadienone **1** (0.2 mmol), NHC **E** (10 mol%), NaOAc (0.2 mmol) under Argon, then 2 mL MTBE: ROH (10: 1) was added at 0 °C and the reaction mixture was stirred for further 24 h at 0 °C. The solvent was removed under reduced pressure and the crude residue was purified by flash chromatography (DCM: MeOH = 1000: 1 - 500: 1) to afford **2**.



3. Characterization of Products

The data of major isomers are given as follows:

(*E*)-3-(1'-methoxy-4'-oxo-1',4'-dihydro-[1,1'-biphenyl]-2-yl) acrylaldehyde (1a)



The compound **1a** was obtained (335 mg, 26% yield) over 3 steps according to the general procedure **I**.

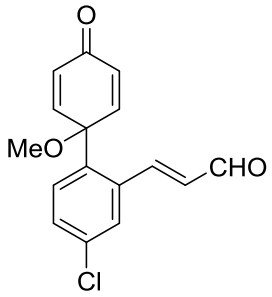
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.66 (d, *J* = 7.8 Hz, 1H), 8.37 (d, *J* = 15.7 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.41 – 7.39 (m, 2H), 6.92 (d, *J* = 10.1 Hz, 2H), 6.50 – 6.45 (m, 3H), 3.39 (s, 3H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.8, 184.9, 152.4, 148.3 (2C), 137.2, 134.1, 130.8, 130.7 (2C), 130.6, 129.4, 129.3, 126.9, 76.5, 52.0.

IR (ATR) 3425, 2927, 2853, 1669, 1459, 1386, 1266, 1166, 1128, 1060, 974, 936, 854, 758 cm^{-1}.

HRMS (ESI) calcd $C_{16}H_{14}O_3Na$ [M + Na] +: calcd 277.0841, found 277.0836.

(*E*)-3-(4-chloro-1'-methoxy-4'-oxo-1',4'-dihydro-[1,1'-biphenyl]-2-yl) acrylaldehyde (1b)



The compound **1b** was obtained (327 mg, 23% yield) over 3 steps according to the general procedure **I**.

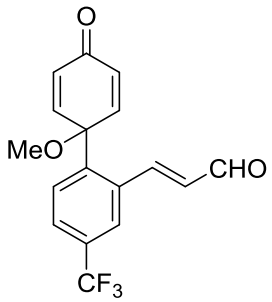
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 7.6 Hz, 1H), 8.20 (d, *J* = 15.8 Hz, 1H), 7.49 – 7.47 (m, 2H), 7.35 – 7.33 (m, 1H), 6.83 – 6.79 (m, 2H), 6.48 – 6.42 (m, 3H), 3.36 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 184.6, 150.3, 147.7 (2C), 135.7, 135.6, 135.2, 131.5, 131.0 (2C), 130.4, 129.0, 128.4, 76.3, 51.9.

IR (ATR) 2939, 2827, 1674, 1628, 1555, 1467, 1387, 1274, 1220, 1114, 1062, 1004, 975, 941, 911, 841, 716 cm^{-1}.

HRMS (ESI) calcd $C_{16}H_{13}O_3ClNa$ [M + Na] +: calcd 311.0451, found 311.0446.

(*E*)-3-(1'-methoxy-4'-oxo-4-(trifluoromethyl)-1',4'-dihydro-[1,1'-biphenyl]-2-yl) acrylaldehyde (1c)



The compound **1c** was obtained (322 mg, 20% yield) over 3 steps according to the general procedure **I**.

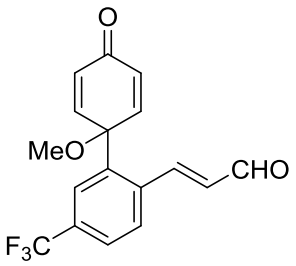
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.65 (d, *J* = 7.6 Hz, 1H), 8.25 (d, *J* = 15.8 Hz, 1H), 7.74 -7.72 (m, 2H), 7.65 – 7.63 (m, 1H), 6.85 – 6.83 (m, 2H), 6.53 – 6.49 (m, 3H), 3.39 (s, 3H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.0, 184.5, 150.2, 147.3 (2C), 140.8, 134.9, 131.8, 131.4 (2C), 127.7, 127.1, 127.0, 126.1, 126.0, 76.4, 52.0.

IR (ATR) 2944, 2160, 1672, 1418, 1330, 1120, 1074, 1007, 958, 908, 840, 755, 704 cm^{-1}.

HRMS (ESI) calcd $C_{17}H_{13}O_3F_3Na$ [M + Na] +: calcd 345.0714, found 345.0707.

(*E*)-3-(1'-methoxy-4'-oxo-5-(trifluoromethyl)-1',4'-dihydro-[1,1'-biphenyl]-2-yl) acrylaldehyde (1d)



The compound **1d** was obtained (290 mg, 18% yield) over 3 steps according to the general procedure **I**.

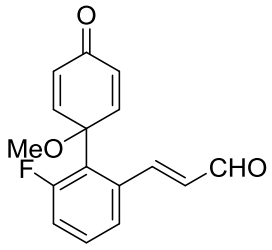
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 7.6 Hz, 1H), 8 .14 (d, *J* = 15.8 Hz, 1H), 7.93 – 7.90 (m, 1H), 7.67 – 7.56 (m, 2H), 7.25-7.24 (m, 1H), 6.84 – 6.82 (m, 2H), 6.54 – 6.50 (m, 2H), 3.38 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 184.5, 149.9, 147.2 (2C), 138.1, 137.3, 132.3, 131.6 (2C), 129.7, 126.0, 125.9, 123.9, 123.8, 75.8, 51.9 ppm.

IR (ATR) 2941, 1673, 1391, 1323, 1161, 1118, 1058, 953, 921, 855, 774, 706, 660 cm^{-1}.

HRMS (ESI) calcd $C_{17}H_{13}O_3F_3Na$ [M + Na] +: calcd 345.0714, found 345.0709.

(*E*)-3-(6-fluoro-1'-methoxy-4'-oxo-1',4'-dihydro-[1,1'-biphenyl]-2-yl) acrylaldehyde (1e)



The compound **1e** was obtained (280 mg, 21% yield) over 3 steps according to the general procedure **I**.

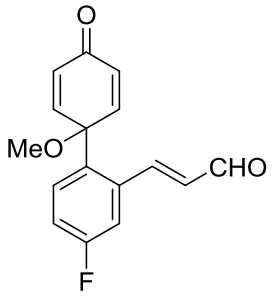
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.73 (d, *J* = 7.8 Hz, 1H), 8.42 (d, *J* = 15.7 Hz, 1H), 7.39-7.31 (m, 1H), 7.27 (d, *J* = 9.0 Hz, 2H), 7.09 – 7.05 (m, 1H), 6.87 – 6.79 (m, 2H), 6.44 (d, *J* = 9.0 Hz, 2H), 3.31 (s, 3H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.6, 185.0, 160.6, 158.9, 153.9, 146.1 (2C), 137.3, 130.3, 130.2 (2C), 126.1, 118.3, 118.2, 74.9, 50.8 ppm.

IR (ATR) 2923, 1665, 1566, 1457, 1391, 1259, 1124, 1060, 968, 918, 852, 782, 707 cm^{-1}.

HRMS (ESI) calcd $C_{16}H_{13}O_3FNa$ [M + Na] +: calcd 295.0746, found 295.0735.

(*E*)-3-(4-fluoro-1'-methoxy-4'-oxo-1',4'-dihydro-[1,1'-biphenyl]-2-yl) acrylaldehyde (1f)



The compound **1f** was obtained (252 mg, 19% yield) over 3 steps according to the general procedure **I**.

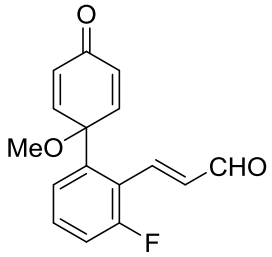
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.66 (d, *J* = 7.6 Hz, 1H), 8.27 (dd, *J* = 15.8, 1.2 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.23 – 7.22 (m, 1H), 7.11 – 7.08 (m, 2H), 6.87 – 6.45 (m, 2H), 6.48 – 6.46 (m, 2H), 3.38 (s, 3H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.2, 184.7, 163.4, 161.7, 150.5, 147.9 (2C), 131.4, 130.9 (2C), 129.1, 128.9, 117.4, 116.0, 76.3, 51.9 ppm.

IR (ATR) 2937, 2832, 1673, 1476, 1390, 1265, 1116, 1064, 973, 838, 767, 707 cm^{-1}.

HRMS (ESI) calcd $C_{16}H_{13}O_3FNa$ [M + Na] +: calcd 295.0746, found 295.0741.

(*E*)-3-(3-fluoro-1'-methoxy-4'-oxo-1',4'-dihydro-[1,1'-biphenyl]-2-yl) acrylaldehyde (1g)



The compound **1g** was obtained (260 mg, 19% yield) over 3 steps according to the general procedure **I**.

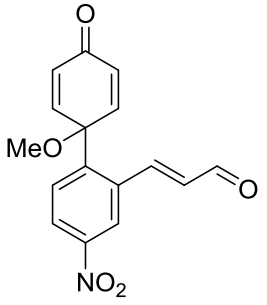
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.96 (d, *J* = 16.3 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.18 – 7.14 (m, 1H), 6.89 – 6.85 (m, 2H), 6.62 (ddd, *J* = 16.3, 7.7, 2.9 Hz, 1H), 6.49 – 6.45 (m, 2H), 3.36 (s, 3H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.9, 184.6, 161.8, 160.2, 147.5 (2C), 144.6, 139.4, 134.8, 131.2, 131.1 (2C), 122.6, 117.1, 76.5, 51.9 ppm.

IR (ATR) 2939, 1669, 1619, 1455, 1390, 1243, 1129, 1058, 970, 880, 792, 714 cm^{-1}.

HRMS (ESI) calcd $C_{16}H_{13}O_3FNa$ [M + Na] +: calcd 295.0746, found 295.0736.

(*E*)-3-(1'-methoxy-4-nitro-4'-oxo-1',4'-dihydro-[1,1'-biphenyl]-2-yl) acrylaldehyde (1h)



The compound **1h** was obtained (240 mg, 16% yield) over 3 steps according to the general procedure **I**.

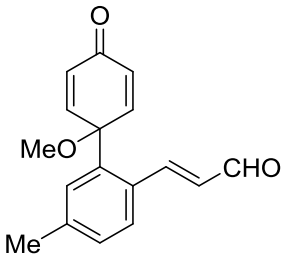
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (d, *J* = 7.5 Hz, 1H), 8.30 (d, *J* = 2.5 Hz, 1H), 8.21 – 8.18 (m, 2H), 7.83 (d, *J* = 8.8 Hz, 1H), 6.83 – 6.80 (m, 2H), 6.56 – 6.51 (m, 3H), 3.39 (s, 3H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 192.7, 184.2, 148.9, 147.9, 146.7 (2C), 143.6, 135.7, 132.4, 131.8 (2C), 128.5, 124.7, 123.9, 76.2, 52.1 ppm.

IR (ATR) 2935, 1675, 1625, 1521, 1464, 1345, 1272, 1117, 1064, 974, 916, 846, 736 cm^{-1}.

HRMS (ESI) calcd $C_{16}H_{13}NO_5Na$ [M + Na] +: calcd 322.0691, found 322.0686.

(*E*)-3-(1'-methoxy-5-methyl-4'-oxo-1',4'-dihydro-[1,1'-biphenyl]-2-yl) acrylaldehyde (1i)



The compound **1i** was obtained (315 mg, 24% yield) over 3 steps according to the general procedure **I**.

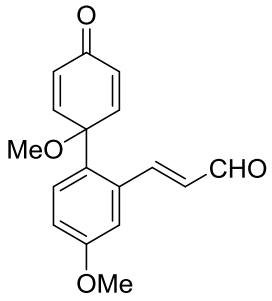
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.63 (d, *J* = 7.9 Hz, 1H), 8.35 (d, *J* = 15.7 Hz, 1H), 7.47 (d, *J* = 7.9 H, 1H), 7.34 – 7.25 (m, 1H), 7.20 - 7.19 (m, 1H), 6.89 – 6.85 (m, 2H), 6.51 – 6.42 (m, 3H), 3.38 (s, 3H), 2.34 (s, 3H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.9, 185.1, 152.4, 148.4 (2C), 141.5, 137.1, 133.4, 130.6 (2C), 130.0, 129.9, 129.3, 127.6, 76.5, 52.0, 21.6 ppm.

IR (ATR) 2925, 2855, 1669, 1617, 1454, 1388, 1274, 1235, 1129, 1062, 970, 919, 866, 820, 704 cm^{-1}.

HRMS (ESI) calcd $C_{17}H_{16}O_3Na$ [M + Na] +: calcd 291.0997, found 291.0992.

(*E*)-3-(1',4-dimethoxy-4'-oxo-1',4'-dihydro-[1,1'-biphenyl]-2-yl) acrylaldehyde (1j)



The compound **1j** was obtained (170 mg, 12% yield) over 3 steps according to the general procedure **I**.

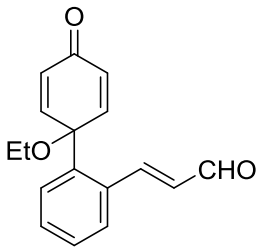
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (d, *J* = 7.7 Hz, 1H), 8.32 (d, *J* = 15.8 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 2.7 Hz, 1H), 6.90-6.83 (m, 3H), 6.46 (dd, *J* = 15.8, 7.7 Hz, 1H), 6.40 (d, *J* = 10.2 Hz, 2H), 3.79 (s, 3H), 3.35 (s, 3H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.5, 184.9, 159.8, 151.9, 148.5 (2C), 135.5, 130.8, 130.4 (2C), 129.3, 128.3, 115.8, 114.5, 76.5, 55.4, 51.9 ppm.

IR (ATR) 2923, 2853, 1664, 1619, 1567, 1459, 1385, 1297, 1262, 1224, 1122, 1051, 975, 921, 853, 812, 706 cm^{-1}.

HRMS (ESI) calcd $C_{17}H_{16}O_4Na$ [M + Na] +: calcd 307.0946, found 307.0942.

(*E*)-3-(1'-ethoxy-4'-oxo-1',4'-dihydro-[1,1'-biphenyl]-2-yl) acrylaldehyde (1k)



The compound **1k** was obtained (163 mg, 15% yield) over 3 steps according to the general procedure **I**.

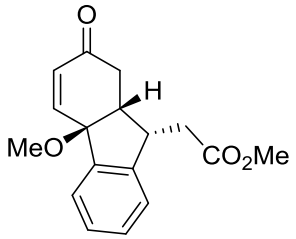
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.65 (dd, *J* = 7.7, 1.5 Hz, 1H), 8.47 (d, *J* = 15.8 Hz, 1H), 7.53-7.52 (m, 1H), 7.47 - 7.45 (m, 1H), 7.37-7.35 (m, 2H), 6.94 (d, *J* = 10.0 Hz, 2H), 6.49 – 6.44 (m, 1H), 6.40 (d, *J* = 10.0 Hz, 2H), 3.57 (q, *J* = 7.0 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.5, 184.9, 152.7, 148.7 (2C), 137.4, 134.2, 130.7 (2C), 130.3, 130.2, 129.4, 129.2, 126.8, 76.7, 60.3, 15.7 ppm.

IR (ATR) 2925, 1669, 1466, 1389, 1280, 1174, 1113, 1059, 970, 896, 854, 759, 686 cm^{-1}.

HRMS (ESI) calcd $C_{17}H_{16}O_3Na$ [M + Na] +: Calcd. 291.0997, found 291.0992.

Methyl 2-((4a*S*,9*S*,9a*R*)-4a-methoxy-2-oxo-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl) acetate (2a)



The compound **2a** was obtained as a colorless oil (47 mg, 83% yield) according to the general procedure **II**, which solidified in the freezer.

$[\alpha]_D^{25}$ = - 21.0 (c 1.0, $CHCl_3$)

dr 16:1, **ee:** 96%, **HPLC:** Chiralpak IA, elute: *n*-Heptan: *i*PrOH = 9:1, detector: 250 nm, flow rate: 0.5mL/min, 30 °C, t_{major} = 21.83 min, t_{minor} = 33.26 min.

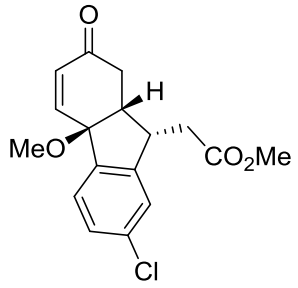
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 1H), 7.30-7.28 (m, 2H), 7.22-7.18 (m, 2H), 6.16 (d, *J* = 10.4 Hz, 1H), 4.05-4.00 (m, 1H), 3.73 (s, 3H), 3.38-3.32 (m, 1H), 3.24 (s, 3H), 2.73 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.54 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.44 (dd, *J* = 16.0, 9.0 Hz, 1H), 1.98 (dd, *J* = 16.0, 11.7 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 172.5, 147.6, 144.8, 140.4, 130.8, 129.7, 127.5, 124.8, 124.3, 83.5, 51.9, 51.8, 46.1, 40.9, 37.1, 33.0 ppm.

IR (KBr) 3453, 2925, 2331, 1730, 1677, 1436, 1374, 1288, 1206, 1162, 1061, 1021, 926, 885, 820, 760 cm^{-1}.

HRMS (ESI) calcd $C_{17}H_{18}O_4Na$ [M + Na] +: 309.1103, found 309.1108.

Methyl 2-((4a*S*,9*S*,9a*R*)-7-chloro-4a-methoxy-2-oxo-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl) acetate (2b)



The compound **2b** was obtained as a yellowlish oil (48 mg, 75% yield) according to the general procedure **II**.

$[\alpha]_D^{25}$ = - 29.6 (c 1.0, $CHCl_3$)

dr: 8:1, **ee:** 93%, **HPLC:** Daicel Chiralpak IC, *n*-heptane/*i*-PrOH 9:1, 0.5 mL/min, t_{major} = 22.6 min, t_{minor} = 42.1 min

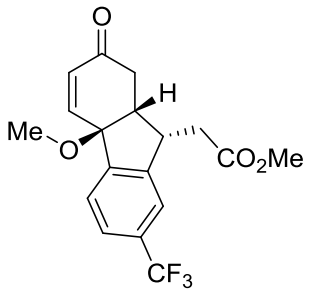
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.27 (m, 1H), 7.23-7.22 (m, 1H), 7.20-7.19 (m, 1H), 7.15 (d, *J* = 10.2 Hz, 1H), 6.18 (dd, *J* = 10.2, 0.8 Hz, 1H), 4.03-4.00 (m, 1H), 3.75 (s, 3H), 3.38-3.34 (m, 1H), 3.24 (s, 3H), 2.70 (dd, *J* = 16.4, 6.9 Hz, 1H), 2.59-2.52 (m, 1H), 2.45 (dd, *J* = 16.4, 8.8 Hz, 1H), 1.98 (dd, *J* = 16.0, 11.3 Hz, 1H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 197.8, 172.2, 146.9, 146.8, 139.1, 135.7, 131.1, 127.9, 125.9, 124.8, 82.9, 52.1, 51.9, 46.2, 40.9, 36.9, 32.8 ppm.

IR (KBr) 3350, 2946, 2088, 1732, 1682, 1592, 1445, 1377, 1259, 1170, 1071, 998, 900, 824, 772, 722, 674 cm^{-1}.

HRMS (ESI) calcd $C_{17}H_{17}O_4ClNa$ [M + Na] +: 343.0713, found 343.0709.

Methyl 2-((4a*S*,9*S*,9a*R*)-4a-methoxy-2-oxo-7-(trifluoromethyl)-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl) acetate (2c)



The compound **2c** was obtained as a yellowlish oil (59 mg, 83% yield) according to the general procedure **II**.

$[\alpha]_D^{25}$ = -27.2 (c 1.0, $CHCl_3$)

dr: 9:1, **ee:** 97% ee, **HPLC:** Daicel Chiralpak IA, *n*-heptane/*i*-PrOH 7:3, 0.7 mL/min, t_{major} = 7.5 min, t_{minor} = 11.1 min

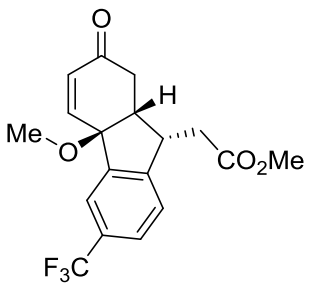
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.50-7.48 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 10.3 Hz, 1H), 6.22 (d, *J* = 10.3 Hz, 1H), 4.09-4.05 (m, 1H), 3.75 (s, 3H), 3.45-3.41 (m, 1H), 3.27 (s, 3H), 2.76 (dd, *J* = 16.4, 7.3 Hz, 1H), 2.58 (dd, *J* = 16.1, 5.8 Hz, 1H), 2.48 (dd, *J* = 16.4, 8.9 Hz, 1H), 1.99 (dd, *J* = 16.1, 11.2 Hz, 1H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 197.6, 172.1, 146.6, 145.7, 144.6, 131.6, 125.2, 125.0, 124.9, 121.5, 121.4, 83.0, 52.1, 52.0, 45.8, 41.0, 36.8, 32.8 ppm.

IR (KBr) 3356, 2945, 2162, 1733, 1684, 1434, 1378, 1324, 1263, 1162, 1125, 1069, 999, 900, 837, 781, 705 cm^{-1}.

HRMS (ESI) calcd $C_{18}H_{17}O_4F_3Na$ [M + Na] +: 377.0977, found 377.0972.

Methyl 2-((4a*S*,9*S*,9a*R*)-4a-methoxy-2-oxo-6-(trifluoromethyl)-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl) acetate (2d)



The compound **2d** was obtained as a yellowlish oil (63 mg, 89% yield) according to the general procedure **II**.

$[\alpha]_D^{25}$ = - 24.3 (c 1.0, $CHCl_3$)

dr: 6:1, **ee:** 95% ee, **HPLC:** Daicel Chiralpak IA, *n*-heptane/*i*-PrOH 7:3, 0.7 mL/min, t_{major} = 8.1 min, t_{minor}= 9.6 min

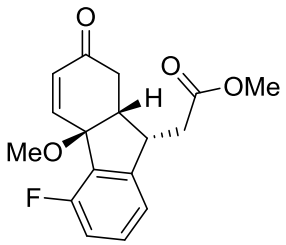
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.55 (s, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 10.4 Hz, 1H), 6.23 (d, *J* = 10.3 Hz, 1H), 4.09-4.06 (m, 1H), 3.75 (s, 3H), 3.44-3.40 (m, 1H), 3.28 (s, 3H), 2.75 (dd, *J* = 16.4, 7.0 Hz, 1H), 2.57 (dd, *J* = 16.4, 5.8 Hz, 1H), 2.48 (dd, *J* = 16.5, 8.7 Hz, 1H), 1.97 (dd, *J* = 16.5, 11.4 Hz, 1H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 197.6, 172.1, 148.8, 146.7, 141.7, 131.8, 126.9, 126.8, 124.9, 121.8, 121.7, 83.1, 52.1, 52.0, 45.9, 41.1, 36.9, 32.8 ppm.

IR (KBr) 3357, 2946, 2161, 1734, 1684, 1623, 1435, 1329, 1273, 1160, 1121, 1072, 1004, 896, 839, 786, 709, 663 cm^{-1}.

HRMS (ESI) calcd $C_{18}H_{17}O_4F_3Na$ [M + Na] +: 377.0977, found 377.0978.

Methyl 2-((4a*S*,9*S*,9a*R*)-5-fluoro-4a-methoxy-2-oxo-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl) acetate (2e)



The compound **2e** was obtained as a yellowlish oil (50 mg, 82% yield) according to the general procedure **II**.

$[\alpha]_D^{25}$ = - 53.5 (c 1.0, $CHCl_3$)

dr: 4:1, **ee:** 92% ee, **HPLC:** Daicel Chiralpak IA, *n*-heptane/*i*-PrOH 7:3, 0.7 mL/min, t_{major} = 8.2 min, t_{minor} = 10.6 min

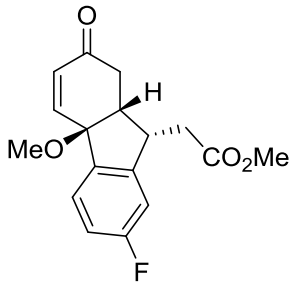
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 10.4, 3.9 Hz, 1H), 7.35-7.31 (m, 1H), 7.00-6.95 (m, 2H), 6.15 (d, *J* = 10.3 Hz, 1H), 4.09-4.05 (m, 1H), 3.74 (s, 3H), 3.28 (s, 3H), 2.81-2.75 (m, 2H), 2.52-2.43 (m, 2H), 1.92 (dd, *J* = 15.9, 12.7 Hz, 1H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 198.0, 172.2, 161.1, 148.4, 146.7, 131.9, 130.1, 125.9, 120.0, 114.9, 83.6, 52.0, 51.9, 48.4, 41.3, 36.9, 32.6 ppm.

IR (KBr) 3354, 2924, 2327, 2099, 1916, 1733, 1682, 1586, 1466, 1373, 1236, 1171, 1074, 994, 894, 844, 788, 741 cm^{-1}.

HRMS (ESI) calcd $C_{17}H_{17}O_4FNa$ [M + Na] +: 327.1009, found 327.1010

Methyl 2-((4a*S*,9*S*,9a*R*)-7-fluoro-4a-methoxy-2-oxo-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl) acetate (2f)



The compound **2f** was obtained as a yellowlish oil (41mg, 68% yield) according to the general procedure **II**.

$[\alpha]_D^{25}$ = - 31.2 (c 1.0, $CHCl_3$)

dr: 9:1, **ee:** 96% ee, **HPLC:** Daicel Chiralpak IA, *n*-heptane/*i*-PrOH 7:3, 0.7 mL/min, t_{major} = 8.4 min, t_{minor} = 11.5 min

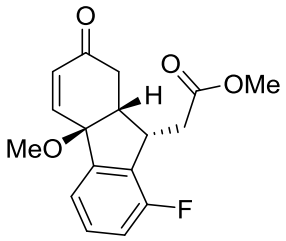
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.24 (m, 1H), 7.16 (d, *J* = 10.3 Hz, 1H), 7.01-6.96 (m, 1H), 7.00-6.97 (m, 1H), 6.18 (dd, *J* = 10.3, 0.8 Hz, 1H), 4.05-3.99 (m, 1H), 3.75 (s, 3H), 3.40-3.35 (m, 1H), 3.25 (s, 3H), 2.68 (dd, *J* = 16.4, 7.0 Hz, 1H), 2.58-2.53 (m, 1H), 2.46 (dd, *J* = 16.4, 8.7 Hz, 1H), 1.99 (dd, *J* = 16.0, 11.3 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 197.9, 172.2, 164.7, 147.5, 147.2, 136.3, 130.9, 126.2, 114.8, 111.9, 82.9, 52.1, 51.9, 46.4, 40.9, 37.1, 32.9 ppm.

IR (KBr) 3355, 2947, 2160, 1733, 1682, 1599, 1479, 1438, 1374, 1260, 1171, 1071, 998, 896, 824, 777, 691 cm^{-1}.

HRMS (ESI) calcd $C_{17}H_{17}O_4FNa$ [M + Na] +: 327.1009, found 327.1006

Methyl 2-((4a*S*,9*S*,9a*R*)-8-fluoro-4a-methoxy-2-oxo-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl) acetate (2g)



The compound **2g** was obtained as a yellowlish oil (44 mg, 72% yield) according to the general procedure **II**.

$[\alpha]_D^{25}$ = - 20.6 (c 1.0, $CHCl_3$)

dr: 20:1, **ee:** 95% ee, **HPLC:** Daicel Chiralpak IA, *n*-heptane/*i*-PrOH 7:3, 0.7 mL/min, t_{major} = 7.7 min, t_{minor} = 10.1 min

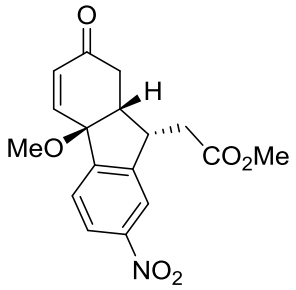
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (td, *J* = 7.8, 4.8 Hz, 1H), 7.13 (d, *J* = 10.3 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.19 (d, *J* = 10.3 Hz, 1H), 4.22-4.19 (m, 1H), 3.74 (s, 3H), 3.41-3.37 (m, 1H), 3.26 (s, 3H), 3.05 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.58 (dd, *J* = 16.2, 6.0 Hz, 1H), 2.48 (dd, *J* = 16.8, 10.7 Hz, 1H), 2.13 (dd, *J* = 16.2, 10.7 Hz, 1H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 197.9, 172.3, 161.2, 147.1, 144.1, 131.1, 129.7, 129.6, 120.6, 116.9, 83.6, 52.0, 51.9, 45.4, 39.9, 36.9, 32.5 ppm.

IR (KBr) 3347, 2930, 2154, 1726, 1677, 1586, 1471, 1438, 1369, 1304, 1234, 1160, 1063, 983, 871, 795, 731 cm^{-1}.

HRMS (ESI) calcd $C_{17}H_{17}O_4FNa$ [M + Na] +: 327.1009, found 327.1003.

Methyl 2-((4a*S*,9*S*,9a*R*)-4a-methoxy-7-nitro-2-oxo-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl) acetate (2h)



The compound **2h** was obtained as a yellowlish oil (64 mg, 95% yield) according to the general procedure **II**.

$[\alpha]_D^{25}$ = - 34.0 (c 1.0, $CHCl_3$)

dr: 6:1**, ee:** 97% ee, **HPLC:** Daicel Chiralpak IA, *n*-heptane/*i*-PrOH 7:3, 0.7 mL/min, t_{major} = 12.9 min, t_{minor} = 21.7 min

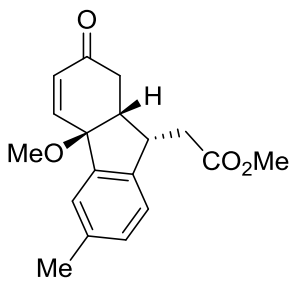
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 – 8.19 (m, 1H), 8.10-8.09 (m, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.17 (d, *J* = 10.3 Hz, 1H), 6.25 (d, *J* = 10.3 Hz, 1H), 4.12-4.08 (m, 1H), 3.77 (s, 3H), 3.49-3.45 (m, 1H), 3.30 (s, 3H), 2.79 (dd, *J* = 16.5, 7.0 Hz, 1H), 2.59 (dd, *J* = 16.2, 6.0 Hz, 1H), 2.52 (dd, *J* = 16.5, 8.8 Hz, 1H), 1.98 (dd, *J* = 16.2, 11.2 Hz, 1H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 197.1, 171.9, 149.2, 147.6, 146.7, 146.1, 132.2, 125.5, 123.5, 119.9, 82.8, 52.2, 52.1, 45.9, 40.9, 36.7, 32.7 ppm.

IR (KBr) 3354, 2946, 2161, 1732, 1683, 1524, 1440, 1344, 1264, 1168, 1070, 998, 897, 839, 740, 670 cm^{-1}.

HRMS (ESI) calcd $C_{17}H_{17}NO_6Na$ [M + Na] +: 354.0954, found 354.0948.

Methyl 2-((4a*S*,9*S*,9a*R*)-4a-methoxy-6-methyl-2-oxo-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl) acetate (2i)



The compound **2i** was obtained as a yellowlish oil (45 mg, 75% yield) according to the general procedure **II**.

$[\alpha]_D^{25}$ = -27.8 (c 1.0, $CHCl_3$)

dr: 6:1, **ee:** 87% ee, **HPLC:** Daicel Chiralpak IA, elute: *n*-heptane/*i*-PrOH 7:3, 0.7 mL/min, t_{major} = 7.9 min, t_{minor} = 9.5 min

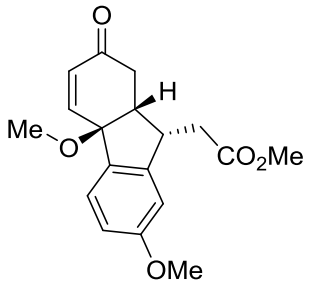
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (d, *J* = 10.4 Hz, 1H), 7.18-7.16 (m, 1H), 7.12-7.09 (m, 2H), 6.18 (d, *J* = 10.4 Hz, 1H), 4.01-3.97 (m, 1H), 3.75 (s, 3H), 3.38-3.34 (m, 1H), 3.27 (s, 3H), 2.72 (dd, *J* = 16.3, 6.8 Hz, 1H), 2.56 (dd, *J* = 16.0, 5.7 Hz, 1H), 2.43 (dd, *J* = 16.3, 9.0 Hz, 1H), 2.37 (s, 3H), 2.02 (dd, *J* = 16.0, 11.3 Hz, 1H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 198.4, 172.5, 147.9, 141.8, 140.6, 137.5, 130.9, 130.5, 125.3, 124.0, 83.5, 52.0, 51.9, 45.9, 40.7, 37.2, 33.2, 21.3 ppm.

IR (KBr) 3335, 2929, 2149, 1725, 1673, 1436, 1381, 1269, 1190, 1067, 996, 895, 824, 741, 691 cm^{-1}.

HRMS (ESI) calcd $C_{18}H_{20}O_4Na$ [M + Na] +: 323.1259, found 323.1267.

Methyl 2-((4a*S*,9*S*,9a*R*)-4a,7-dimethoxy-2-oxo-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl) acetate (2j)



The compound **2j** was obtained as a yellowlish oil (54 mg, 87% yield) according to the general procedure **II**.

$[\alpha]_D^{25}$ = - 41.5 (c 1.0, $CHCl_3$)

dr: 7:1**, ee:** 90% ee, **HPLC:** Daicel Chiralpak IA, elute: *n*-heptane/*i*-PrOH 7:3, 0.7 mL/min, t_{major} = 9.8 min, t_{minor} = 13.5 min

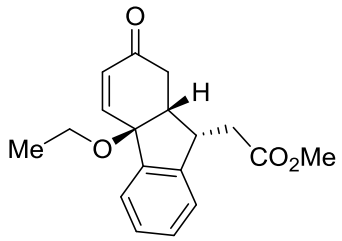
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22-7.17 (m, 2H), 6.83-6.81 (m, 1H), 6.74-6.73 (m, 1H), 6.16-6.14 (m, 1H), 4.02-3.98 (m, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.36-3.32 (m, 1H), 3.23 (s, 3H), 2.71 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.55 (dd, *J* = 16.0, 5.7 Hz, 1H), 2.46-2.42 (m, 1H), 2.03-1.98 (m, 1H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 198.4, 172.5, 161.1, 147.7, 146.8, 132.5, 130.4, 125.8, 113.0, 110.0, 83.1, 55.5, 51.9, 51.7, 46.5, 40.9, 37.2, 33.0 ppm.

IR (KBr) 3349, 2942, 2322, 2155, 1912, 1732, 1679, 1603, 1447, 1374, 1321, 1251, 1165, 1070, 895, 819, 733, 690 cm^{-1}.

HRMS (ESI) calcd $C_{18}H_{20}O_5Na$ [M + Na] +: 339.1208, found 339.1209.

Methyl 2-((4a*S*,9*S*,9a*R*)-4a-ethoxy-2-oxo-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl)-acetate (2k)



The compound **2k** was obtained as a yellowlish oil (51 mg, 85% yield) according to the general procedure **II**.

$[\alpha]_D^{25}$ = - 14.9 (c 1.0, $CHCl_3$)

dr: 9:1, **ee:** 97% ee, **HPLC:** Daicel Chiralpak IA, elute: *n*-heptane/*i*-PrOH 7:3, 0.7 mL/min, t_{major} = 7.1 min, t_{minor} = 8.9 min

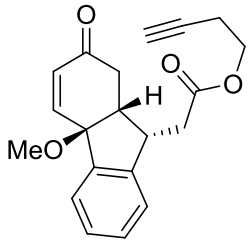
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.33 (m, 1H), 7.31-7.29 (m, 2H), 7.21 -7.19 (m, 2H), 6.14 (d, *J* = 10.3Hz, 1H), 4.07-4.03 (m, 1H), 3.74 (s, 3H), 3.55-3.50 (m, 1H), 3.38-3.33 (m, 2H), 2.73 (dd, *J* = 16.0, 6.9 Hz, 1H), 2.59-2.51 (m, 1H), 2.49-2.41 (m, 1H), 1.99 (dd, *J* = 16.0, 11.1 Hz, 1H), 1.14 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 198.4, 172.6, 148.3, 144.8, 140.9, 130.4, 129.6, 127.6, 124.8, 124.3, 83.3, 59.8, 51.9, 46.7, 41.0, 37.1, 33.1, 15.9.

IR (KBr) 3452, 2925, 2151, 1730, 1677, 1437, 1374, 1288, 1206, 1162, 1114, 1061, 991, 926, 886, 819, 763 cm^{-1}.

HRMS (ESI) calcd $C_{18}H_{20}O_4Na$ [M + Na] +: 323.1259, found 323.1254.

But-3-yn-1-yl 2-((4a*S*,9*S*,9a*R*)-4a-methoxy-2-oxo-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl) acetate (2l)



The compound **2l** was obtained as a yellowlish oil (30 mg, 47% yield) according to the general procedure **II**.

$[\alpha]_D^{25}$ = - 31.7 (c 1.0, $CHCl_3$)

dr: 8:1, **ee:** 96% ee, **HPLC:** Daicel Chiralpak IA, elute: *n*-heptane/*i*-PrOH 7:3, 0.7 mL/min, t_{major} = 11.0 min, t_{minor} = 12.6 min

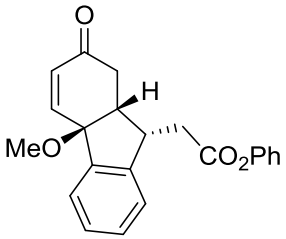
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 1H), 7.29 (d, *J* = 4.2 Hz, 2H), 7.24-7.21 (m 2H), 6.17 (d, *J* = 10.3 Hz, 1H), 4.26 (t, *J* = 6.6 Hz, 2H), 4.09-3.97 (m, 1H), 3.42-3.35 (m, 1H), 3.25 (s, 3H), 2.81-2.75 (m, 1H), 2.60-2.53 (m, 3H), 2.46 (dd, *J* = 16.3, 9.2 Hz, 1H), 2.02-1.94 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 171.8, 147.6, 144.7, 140.4, 130.9, 129.7, 127.6, 124.8, 124.3, 83.5, 79.9, 70.2, 62.4, 51.9, 46.1, 40.9, 37.1, 33.1, 19.0 ppm.

IR (KBr) 3286, 2928, 2158, 1732, 1680, 1461, 1387, 1281, 1161, 1070, 1004, 901, 761, 699 cm^{-1}.

HRMS (ESI) calcd $C_{20}H_{20}O_4Na$ [M + Na] +: 347.1259, found 347.1254.

Phenyl 2-((4a*S*,9*S*,9a*R*)-4a-methoxy-2-oxo-2,4a,9,9a-tetrahydro-1H-fluoren-9-yl) acetate (2m)



The compound **2m** was obtained as a yellowlish oil (46 mg, 66% yield) according to the general procedure **II**.

$[\alpha]_D^{25}$ = - 36.2 (c 1.0, $CHCl_3$)

dr: 12:1, **ee:** 96% ee, **HPLC:** Daicel Chiralpak IA, elute: *n*-heptane/*i*-PrOH 7:3, 0.7 mL/min, t_{major} = 10.2 min, t_{minor} = 14.2 min

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42-7.39 (m, 3H), 7.35-7.32 (m, 3H), 7.27-7.25 (m, 1H), 7.22 (d, *J* = 10.3 Hz, 1H), 7.14-7.12 (m, 2H), 6.22 (d, *J* = 10.3 Hz, 1H), 4.18-4.14 (m, 1H), 3.47-3.43 (m, 1H), 3.28 (s, 3H), 2.98 (dd, *J* = 16.6, 7.0 Hz, 1H), 2.74-2.66 (m, 2H), 2.13 (dd, *J* = 16.6, 10.8 Hz, 1H) ppm.

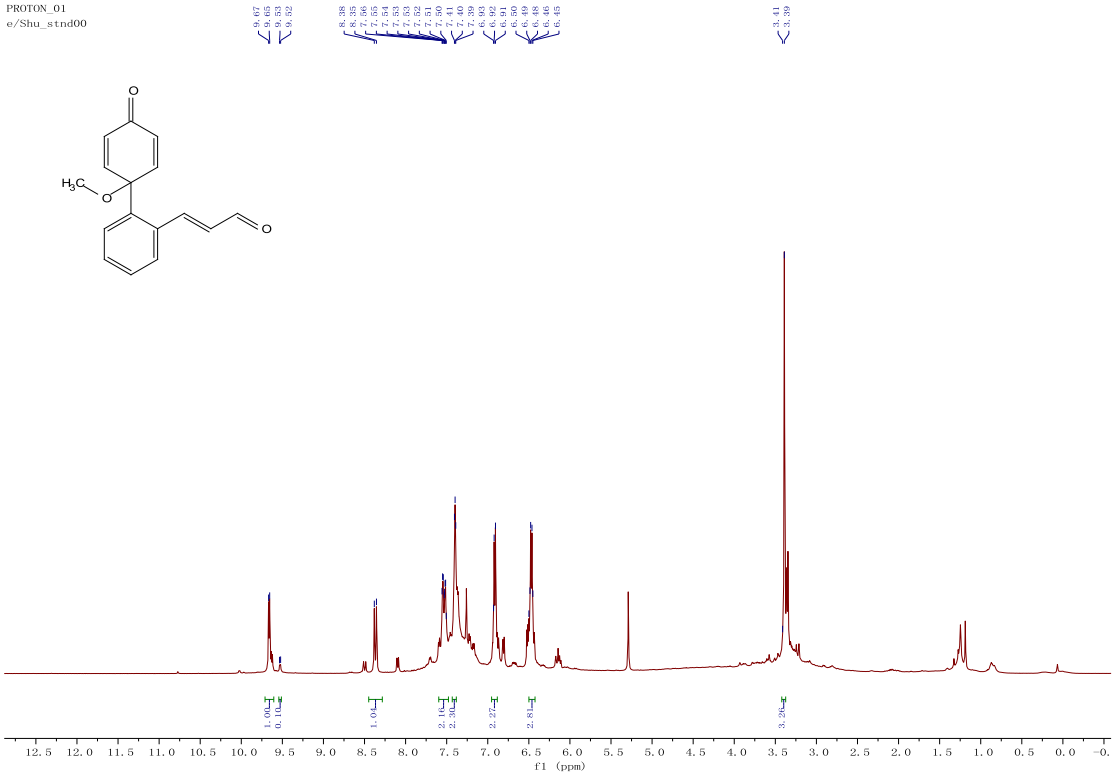
^{13}C NMR (150 MHz, $CDCl_3$) δ 198.1, 170.8, 150.4, 147.7, 144.6, 140.6, 130.9, 129.8, 129.5 (2C), 127.8, 126.1, 124.9, 124.4, 121.5 (2C), 83.5, 51.9, 45.7, 41.1, 37.1, 33.6 ppm.

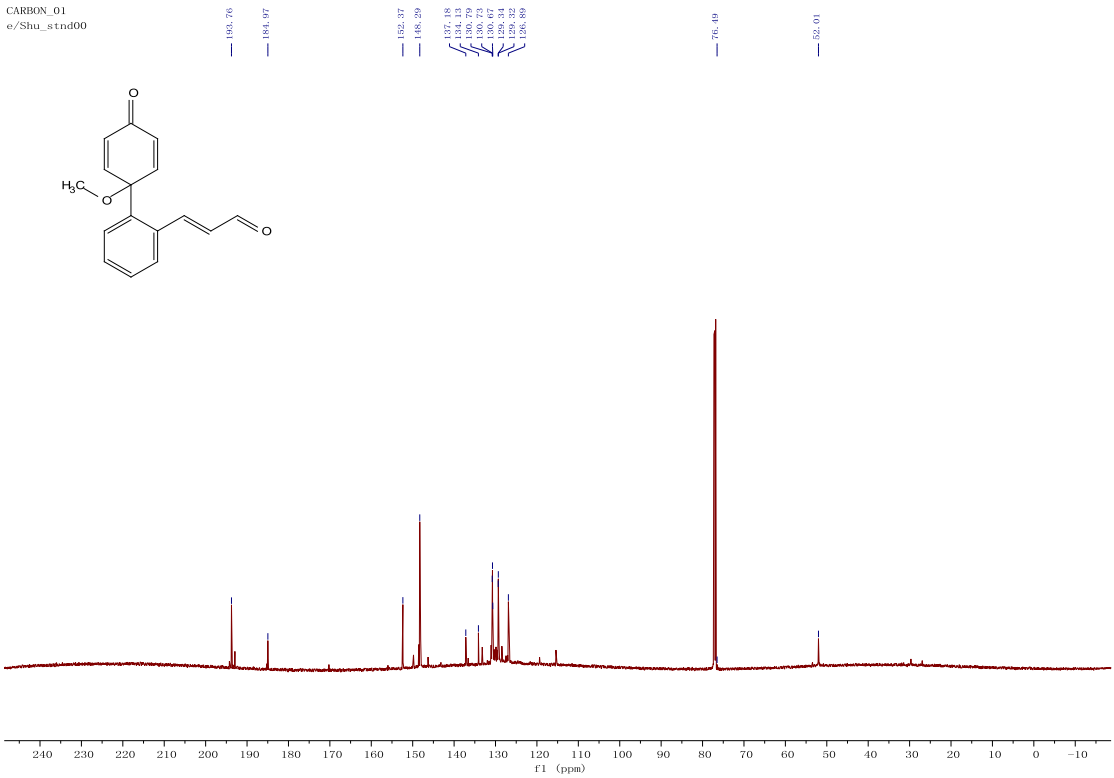
IR (KBr) 3351, 3040, 2925, 2856, 2156, 1752, 1679, 1592, 1485, 1375, 1282, 1191, 1134, 1070, 901, 811, 757, 694 cm^{-1}.

HRMS (ESI) calcd $C_{22}H_{20}O_4Na$ [M + Na] +: 371.1259, found 371.1254.

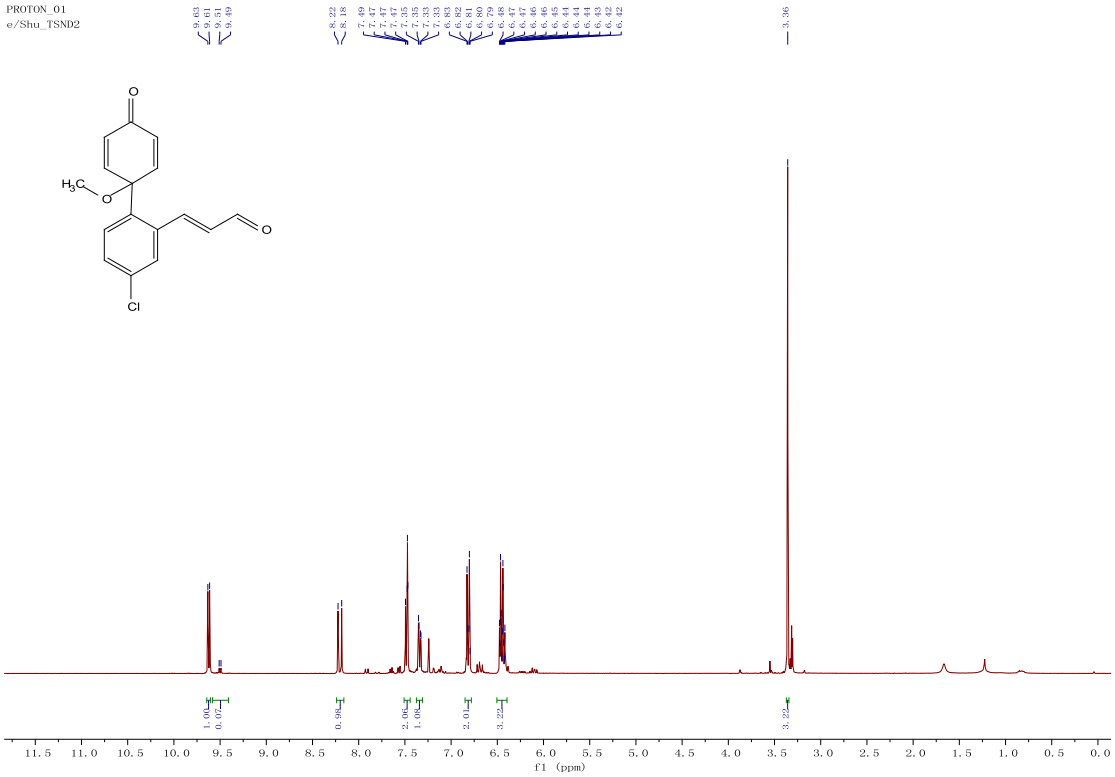
4. Copies of NMR Spectra

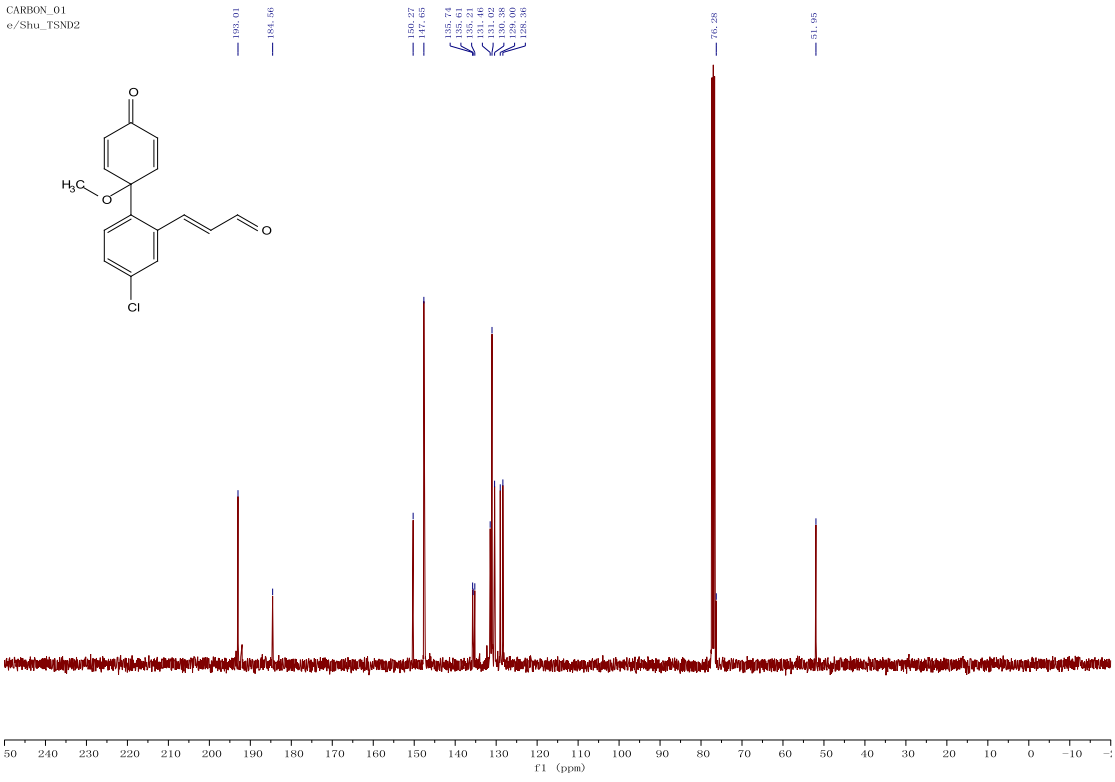
^{1}HNMR and ^{13}C NMR of **1a** (E/Z 10:1)



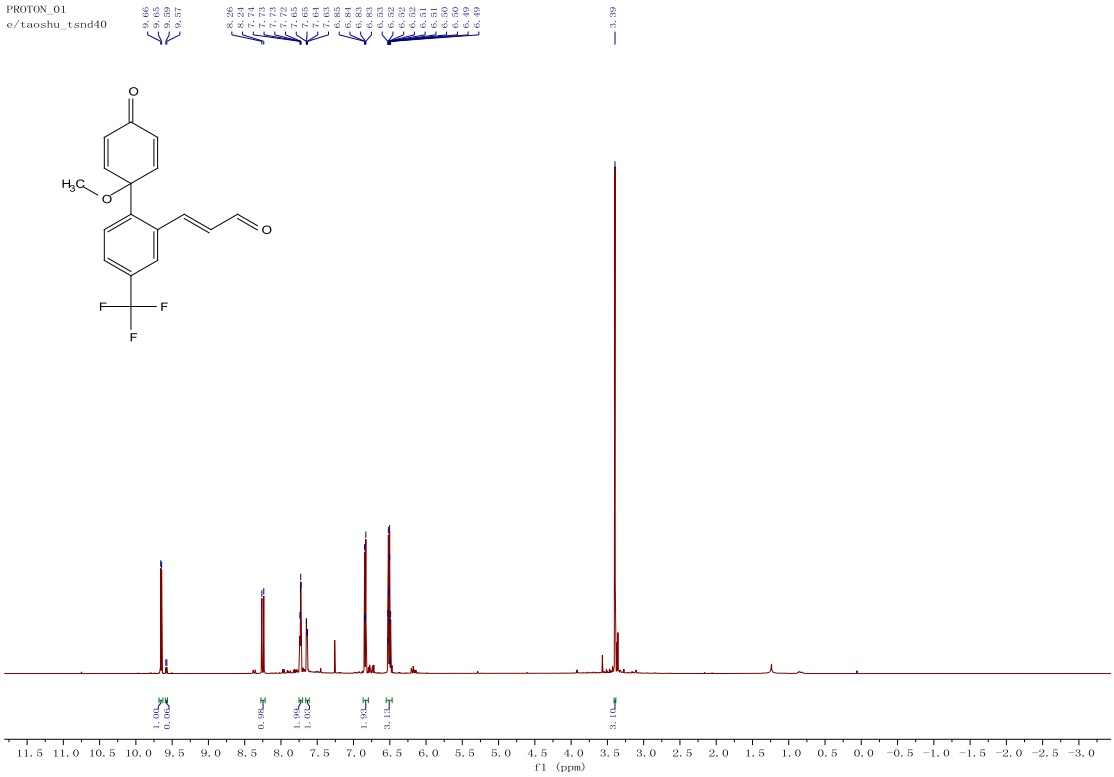


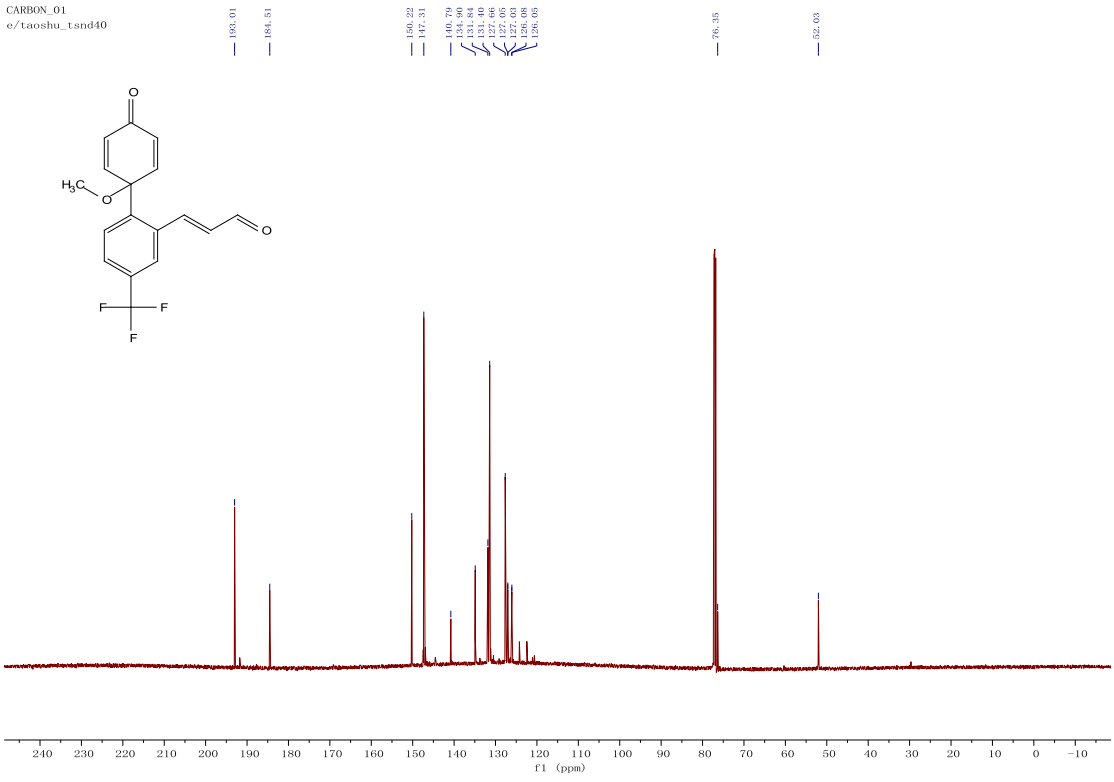
^{1}HNMR and ^{13}C NMR of **1b** (E/Z 14:1)



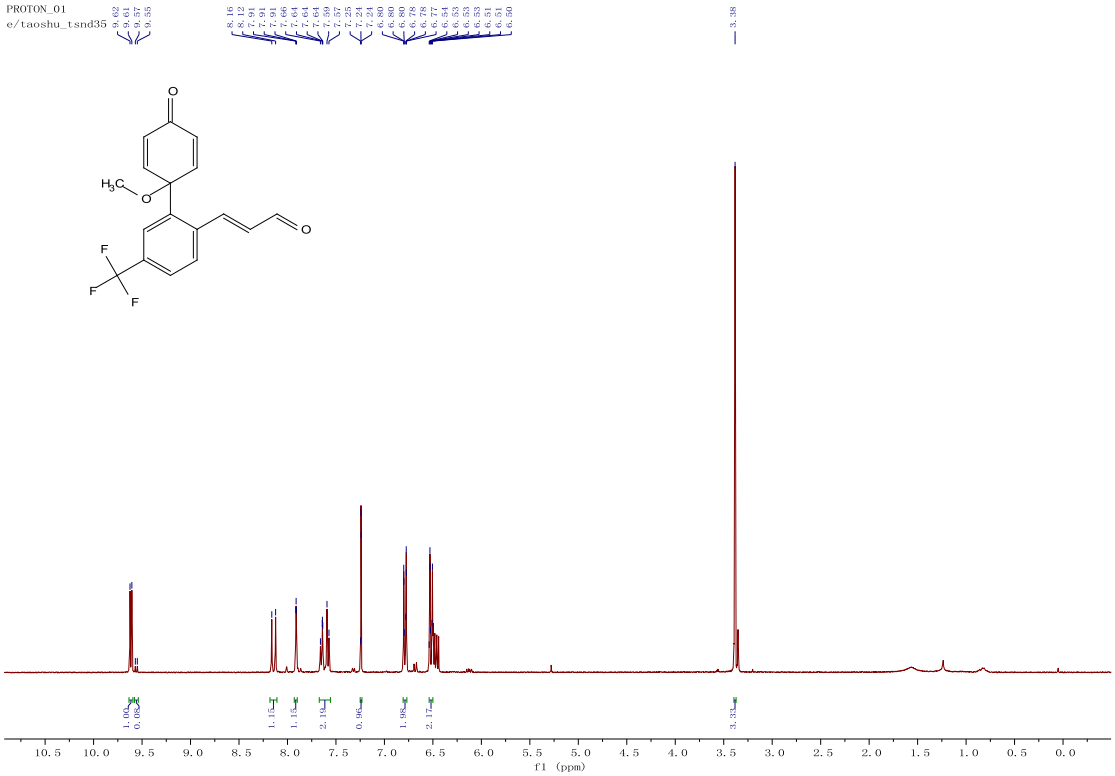


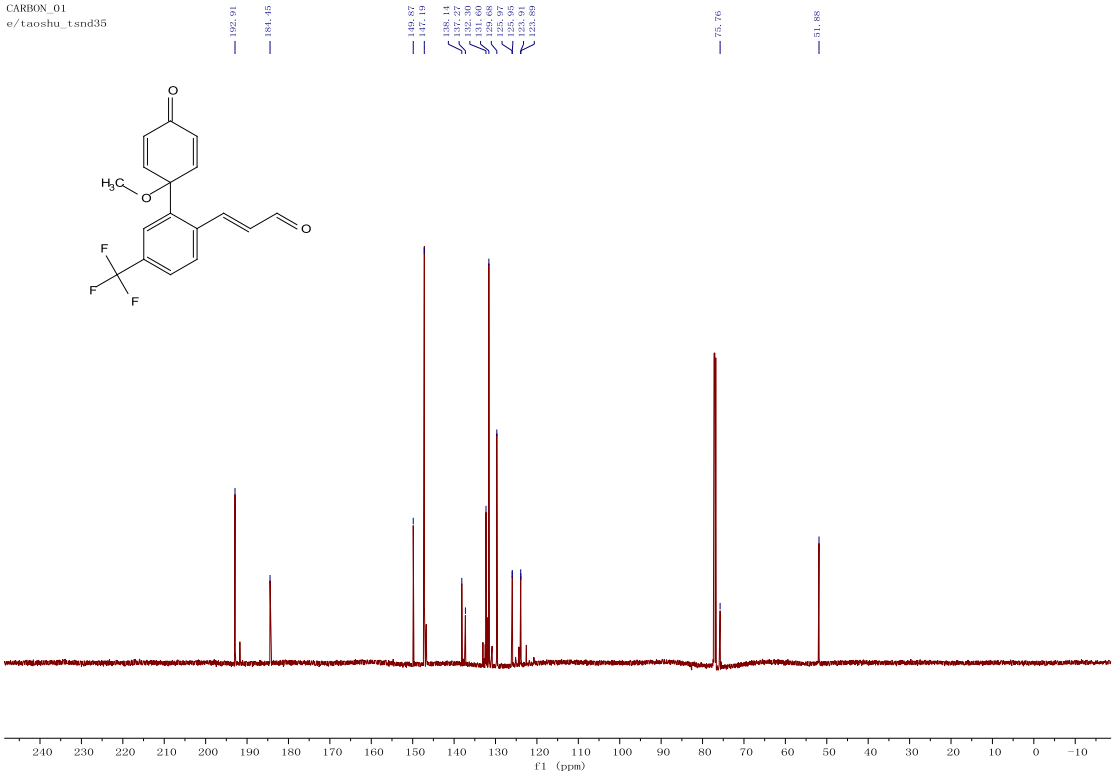
^{1}HNMR and ^{13}C NMR of **1c** (E/Z 17:1)



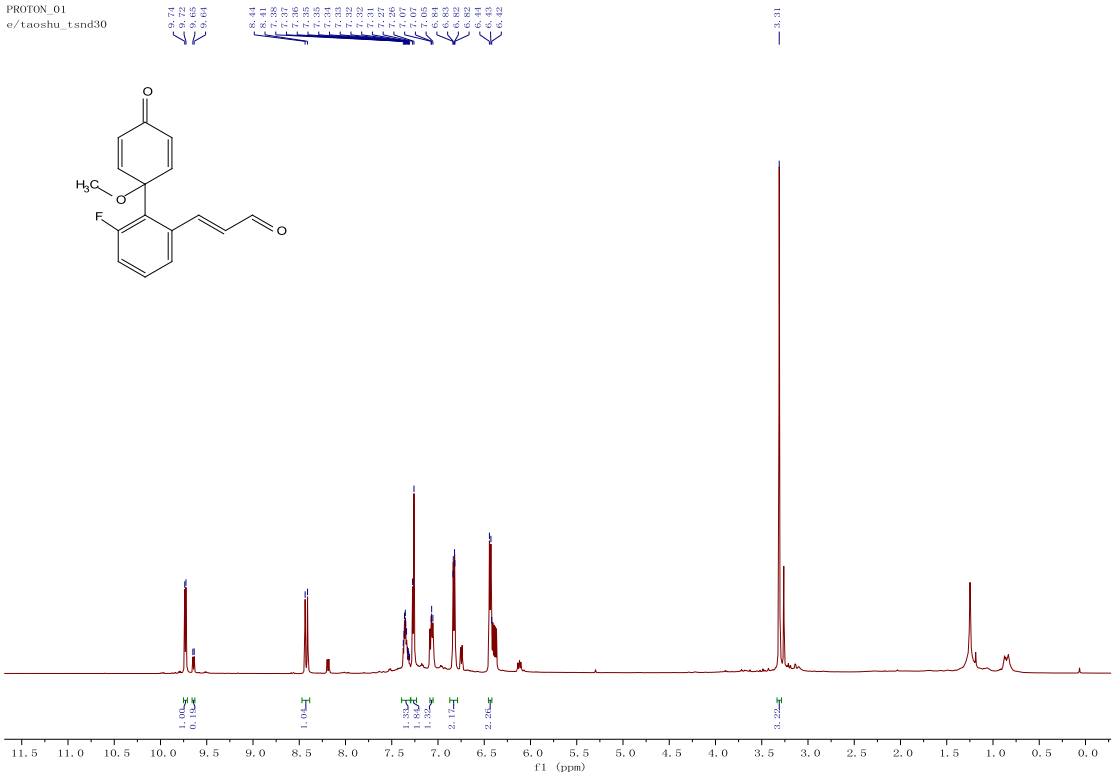


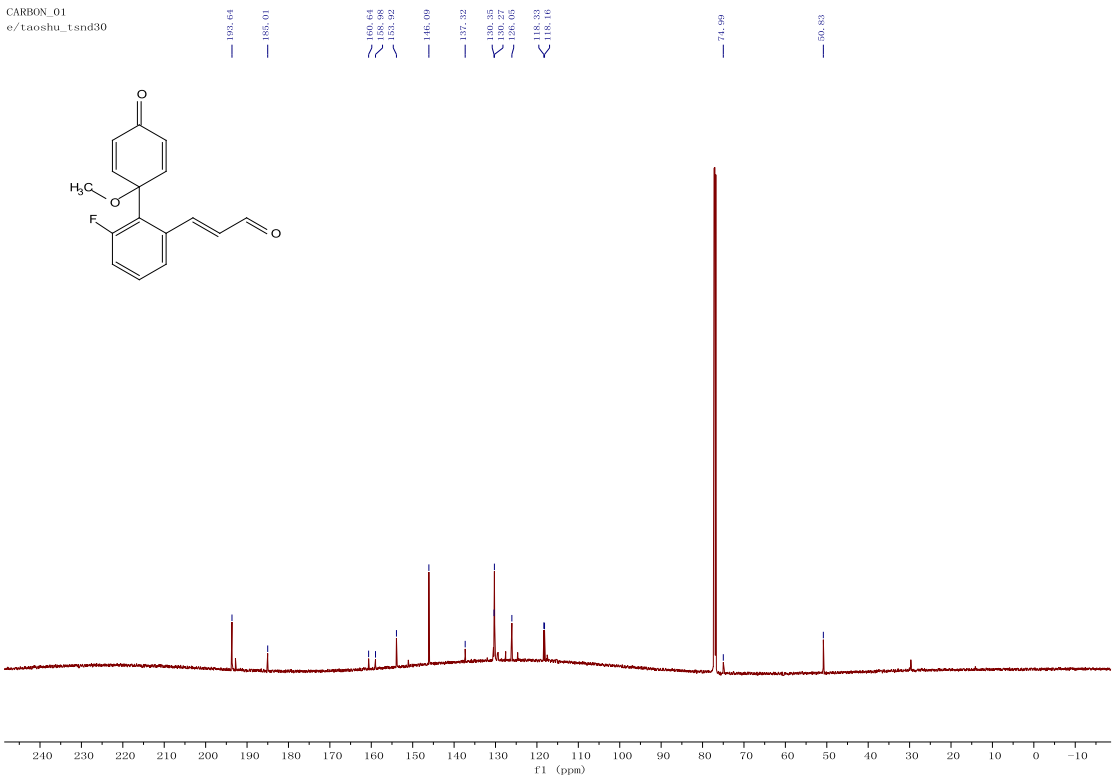
^{1}HNMR and ^{13}C NMR of **1d** (E/Z 13:1)



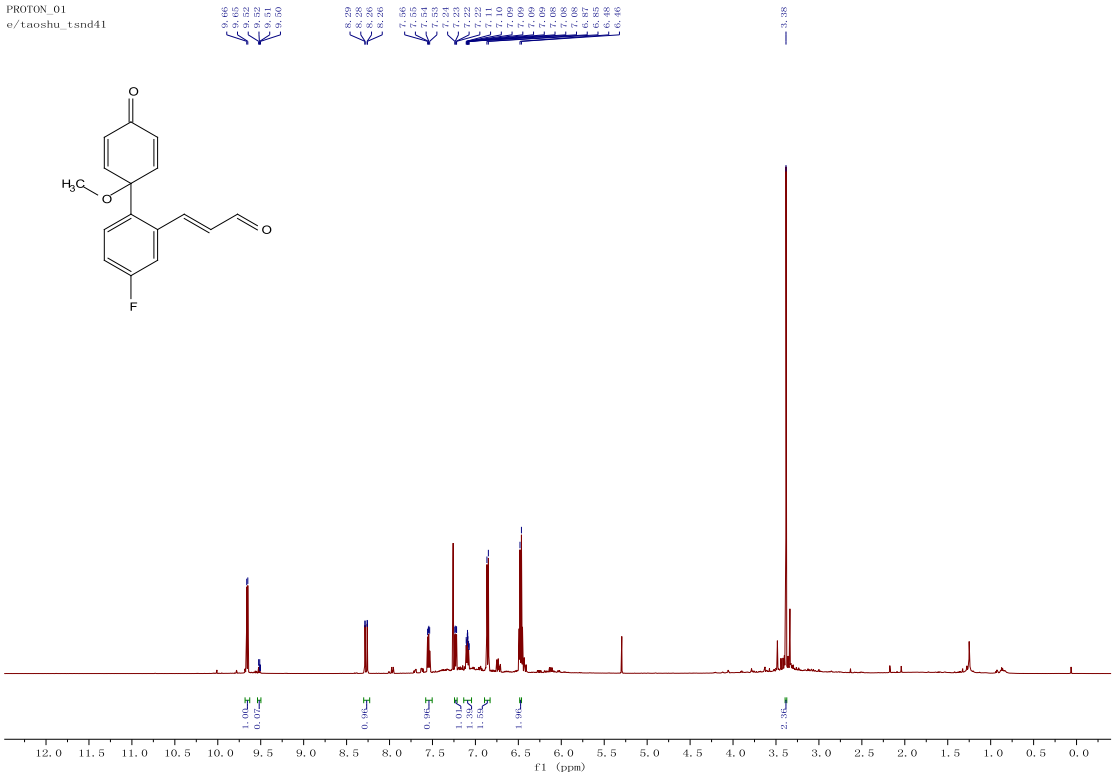


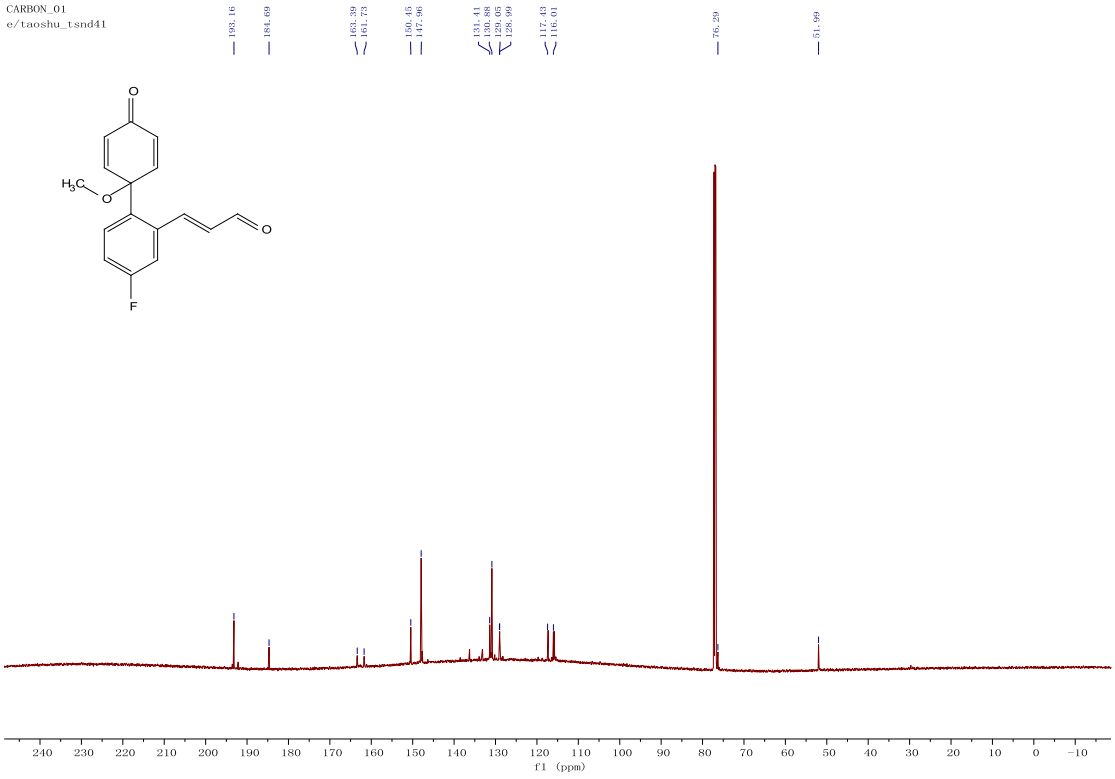
^{1}HNMR and ^{13}C NMR of **1e** (E/Z 5:1)



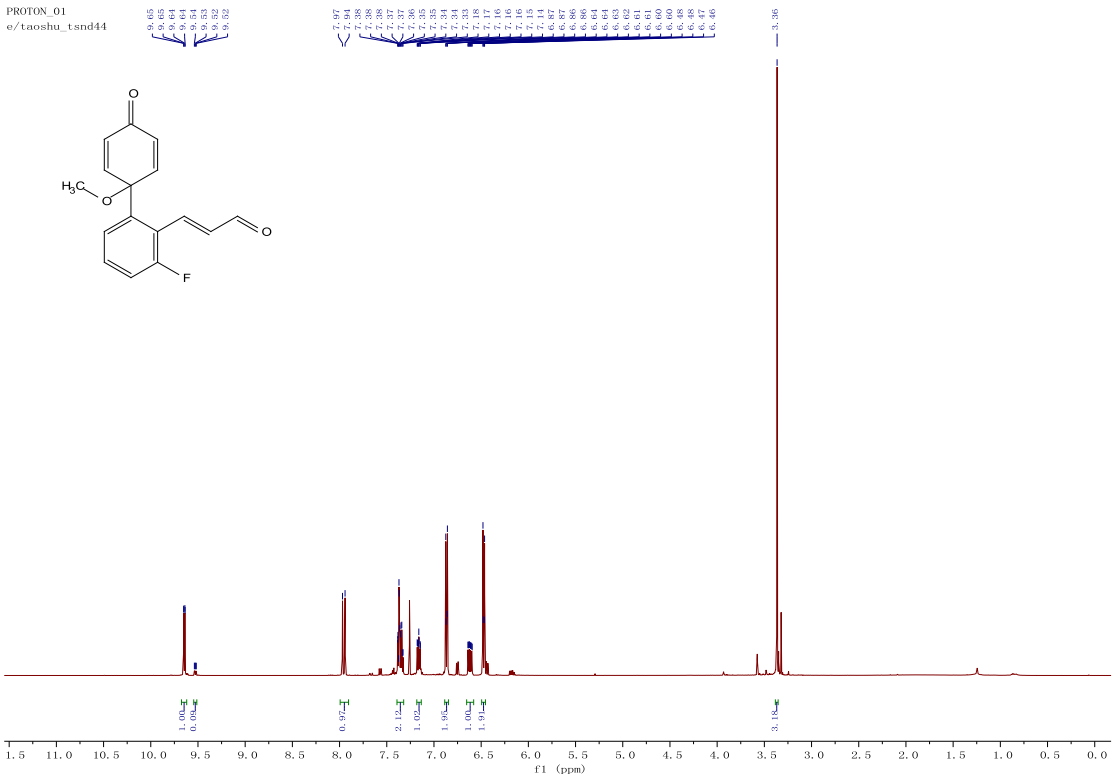


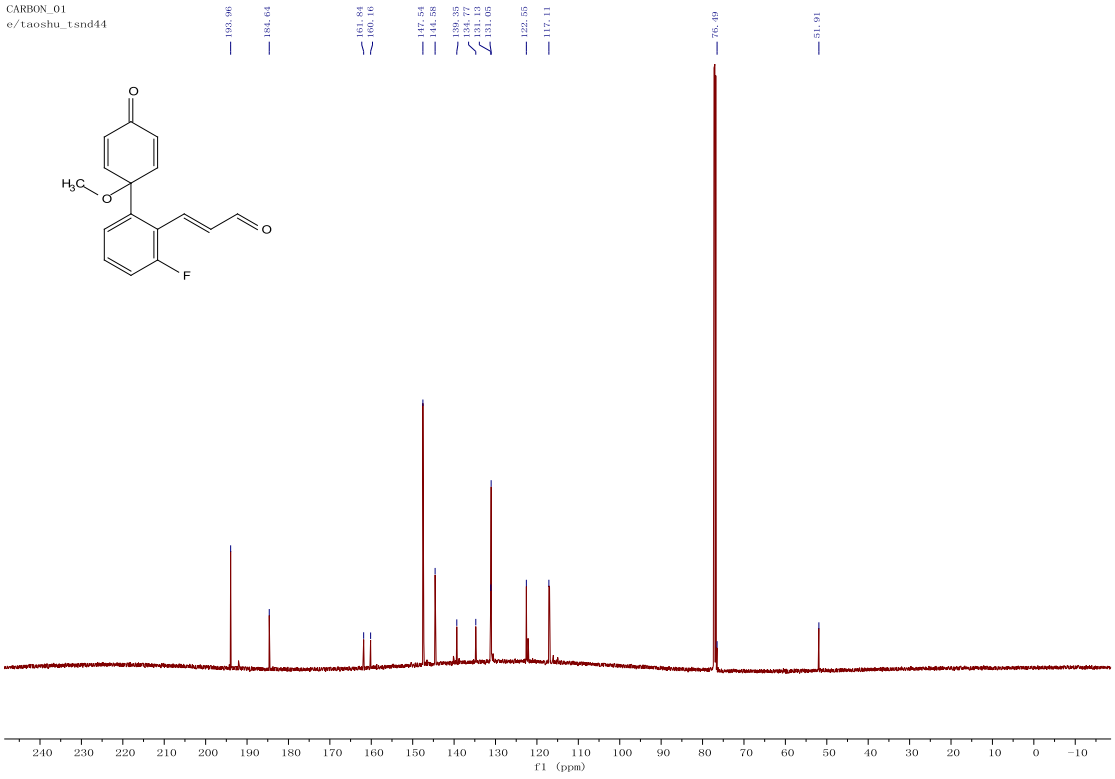
^{1}HNMR and ^{13}C NMR of **1f** (E/Z 14:1)



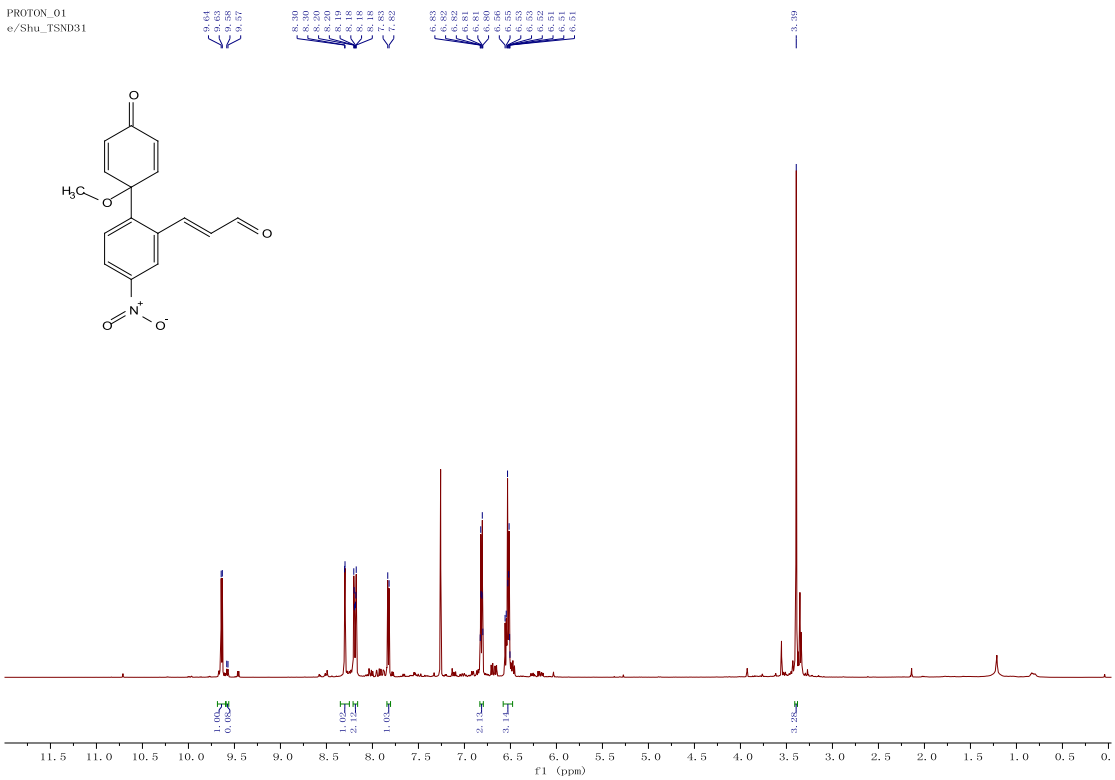


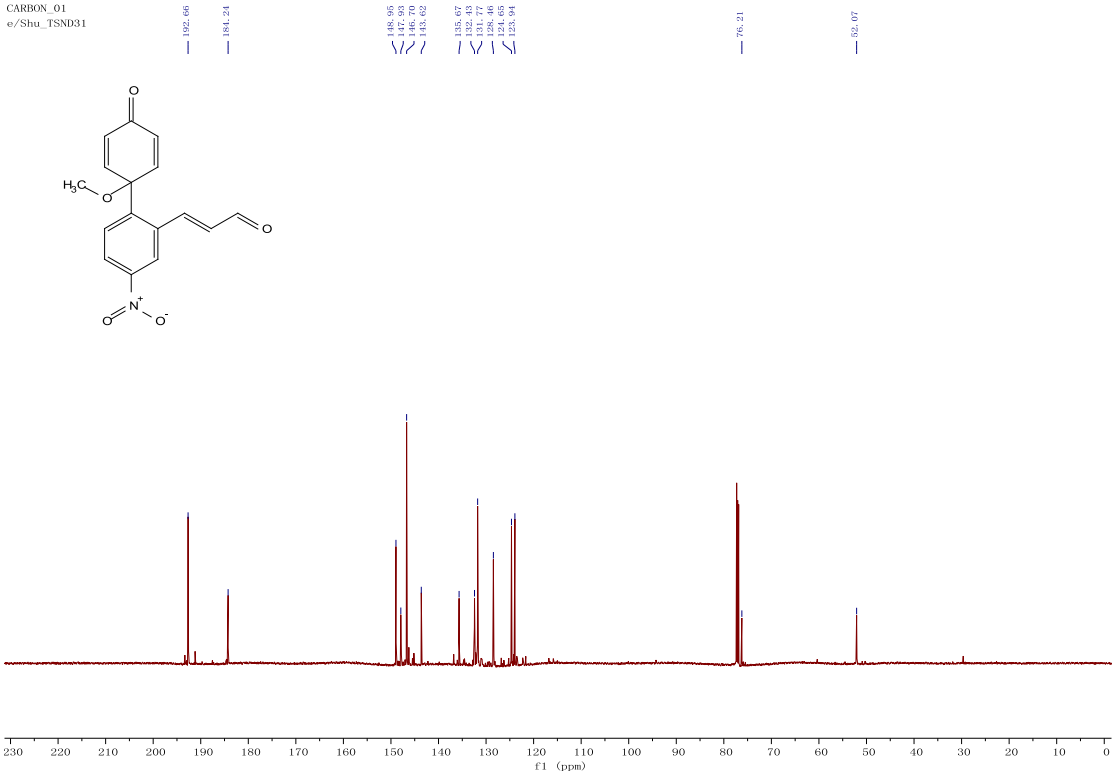
^{1}HNMR and ^{13}C NMR of **1g** (E/Z 11:1)



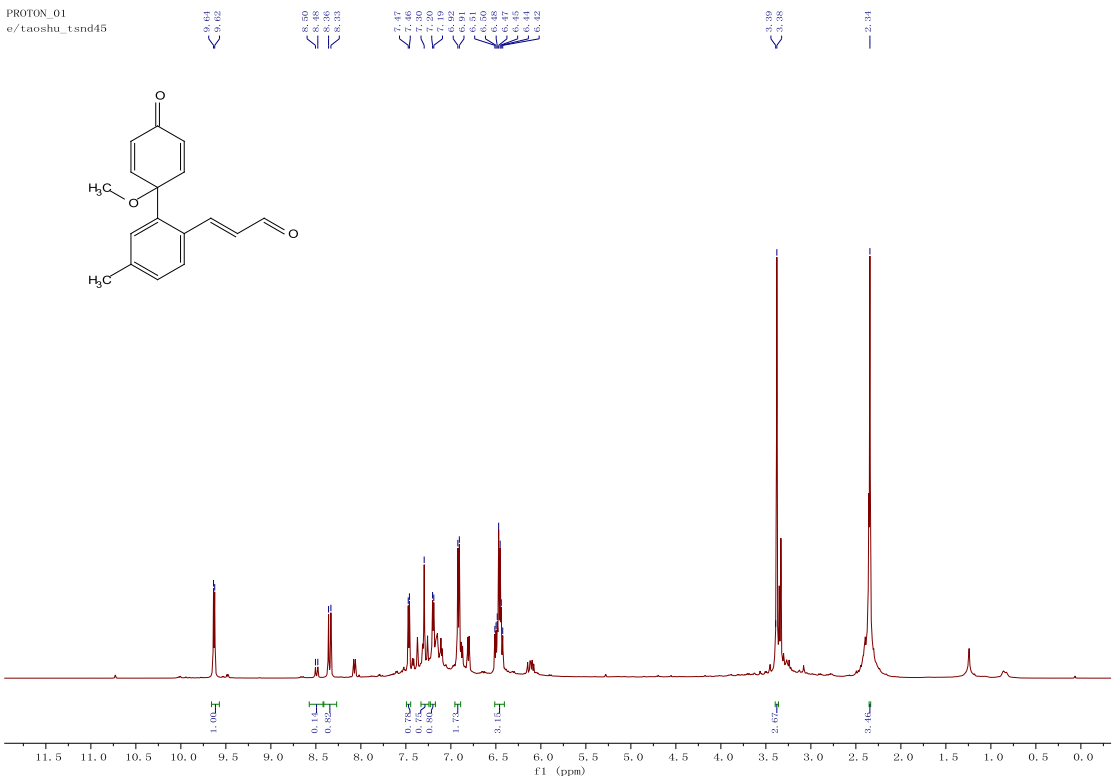


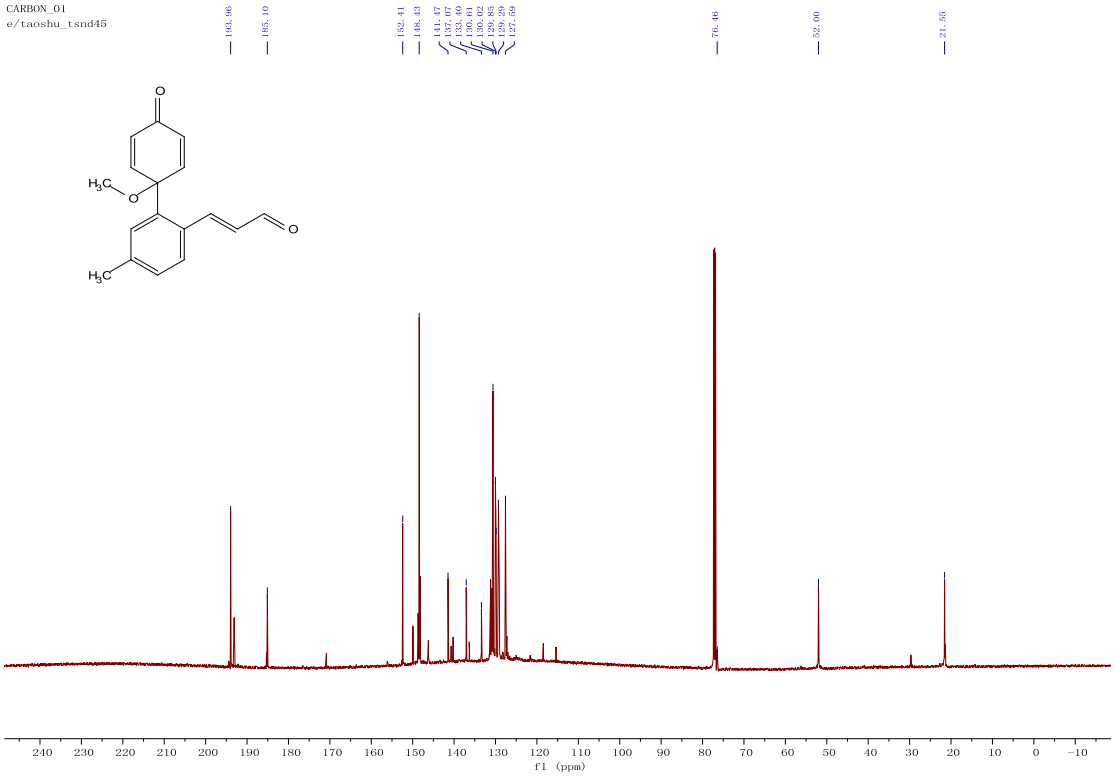
^{1}HNMR and ^{13}C NMR of **1h** (E/Z 12:1)



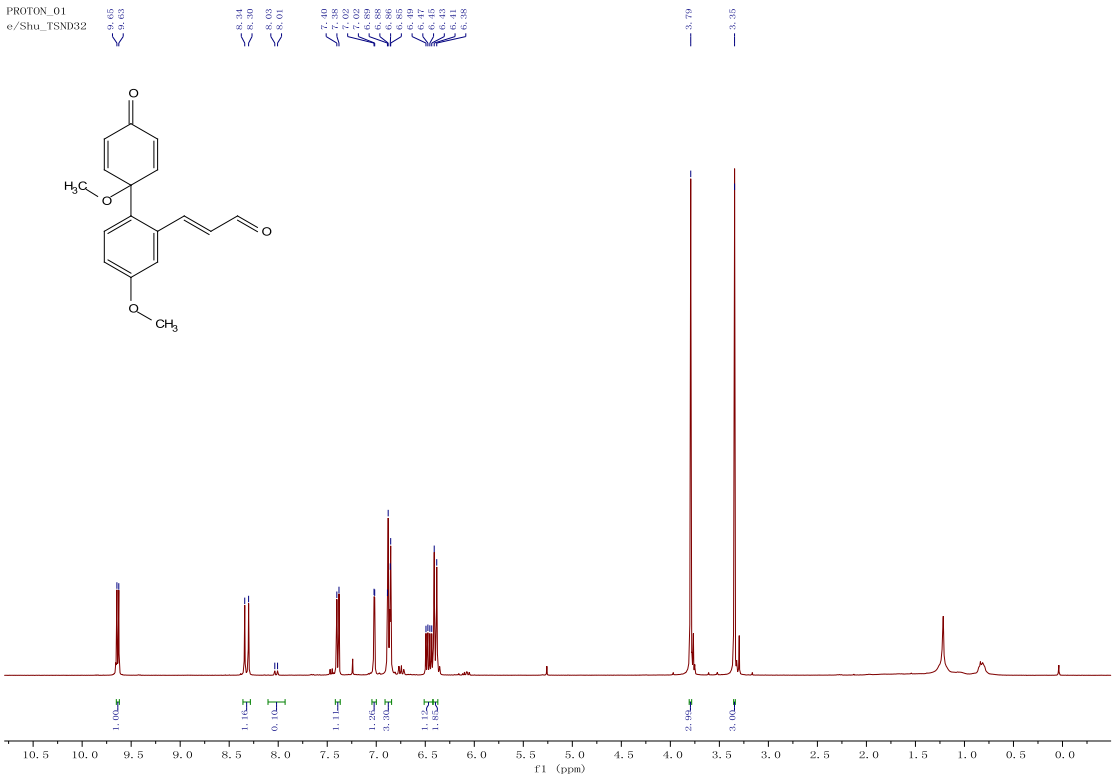


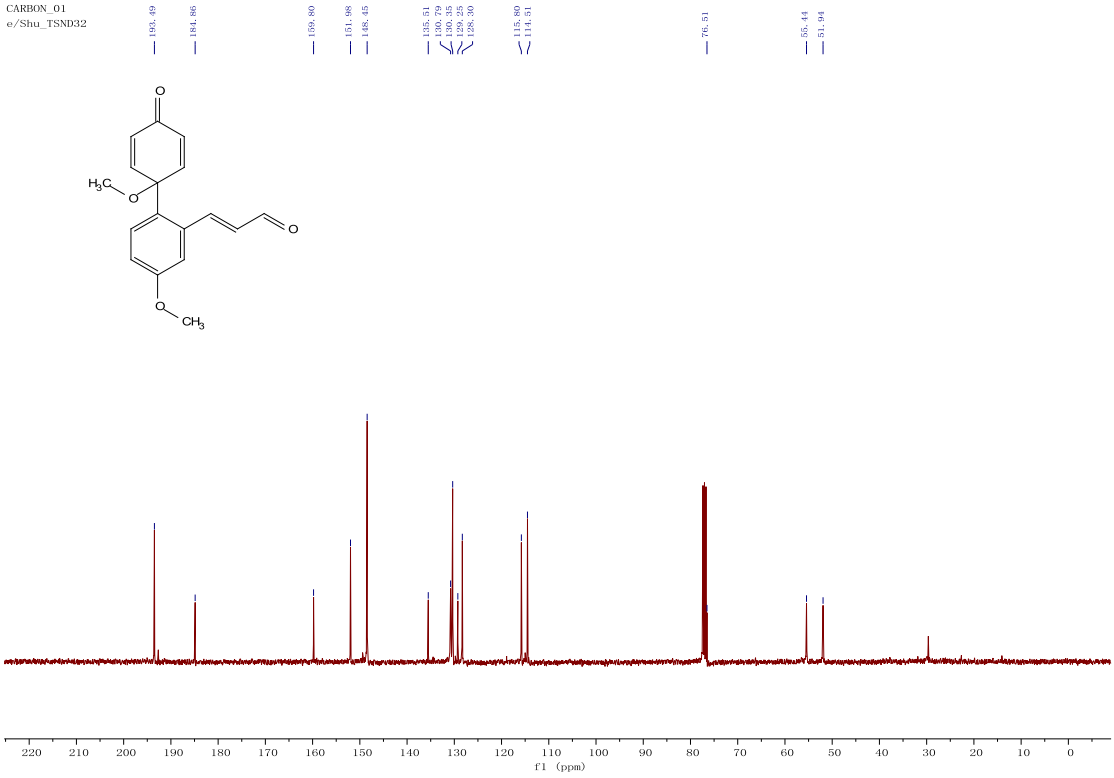
^{1}HNMR and ^{13}C NMR of **1i** (E/Z 6:1)



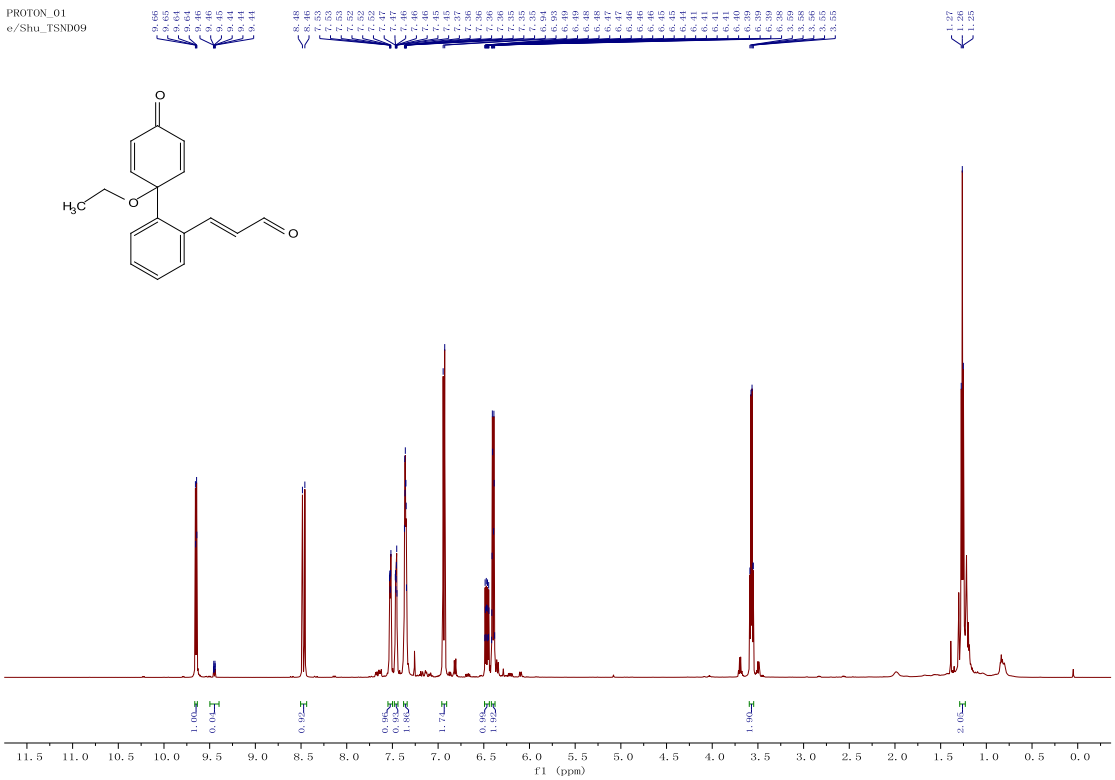


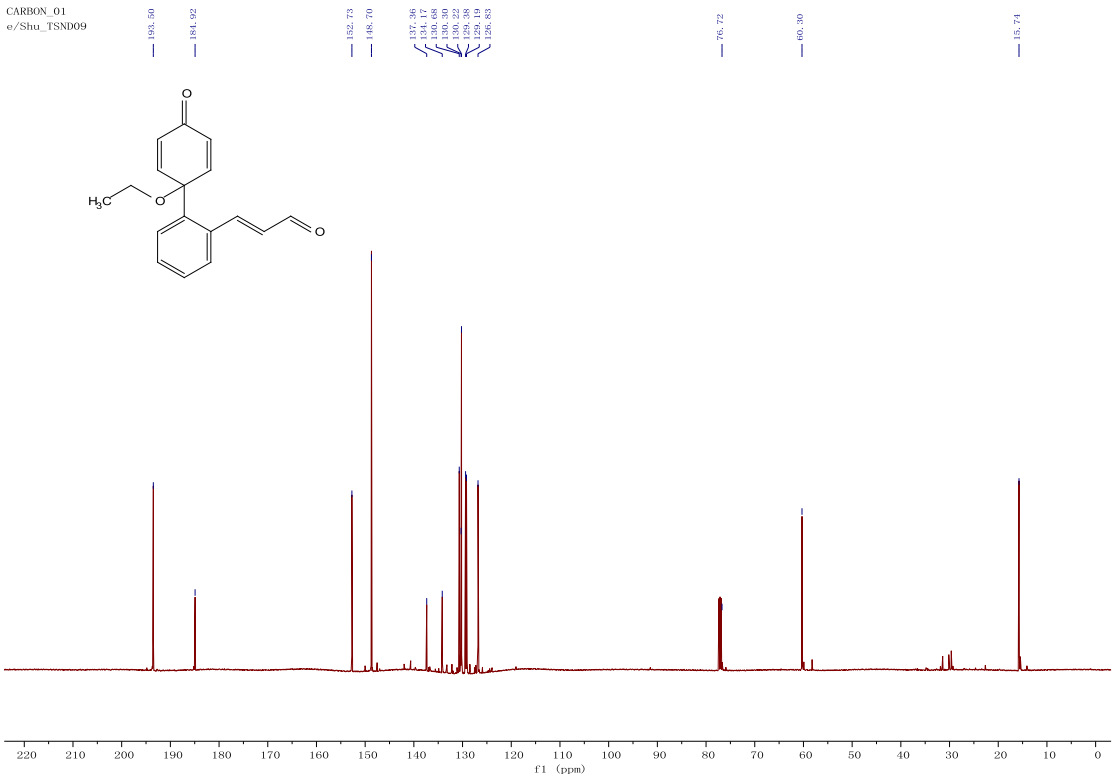
^{1}HNMR and ^{13}C NMR of **1j** (E/Z 12:1)



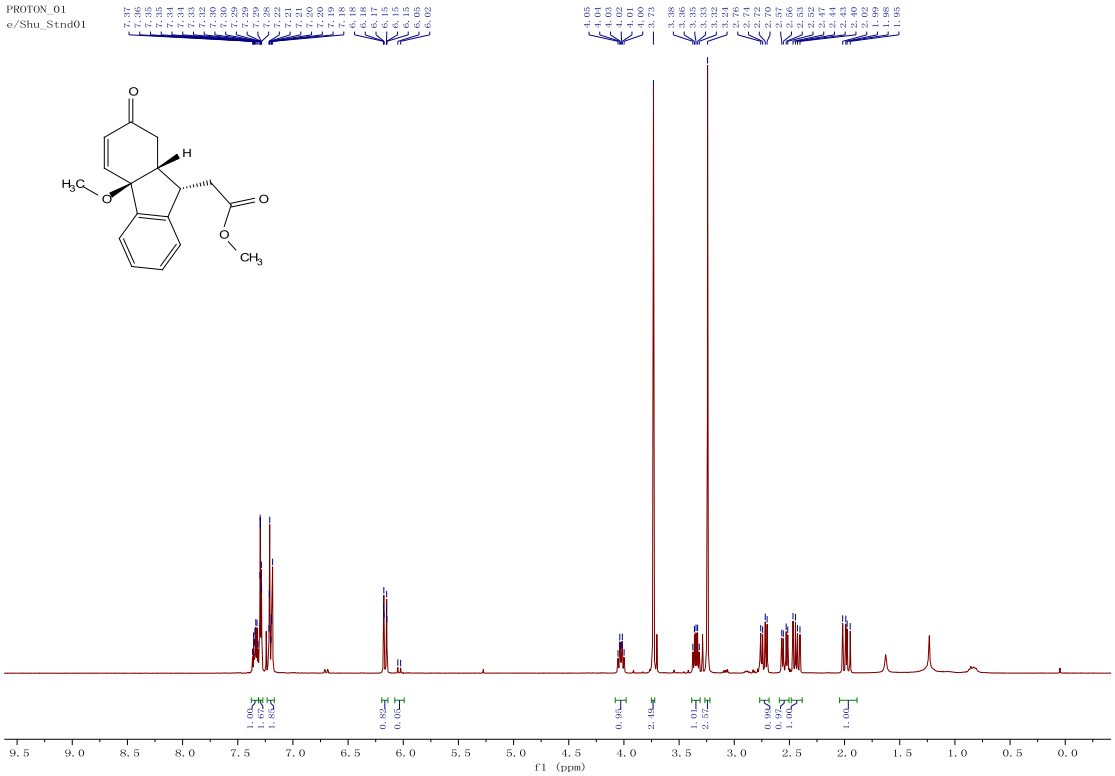


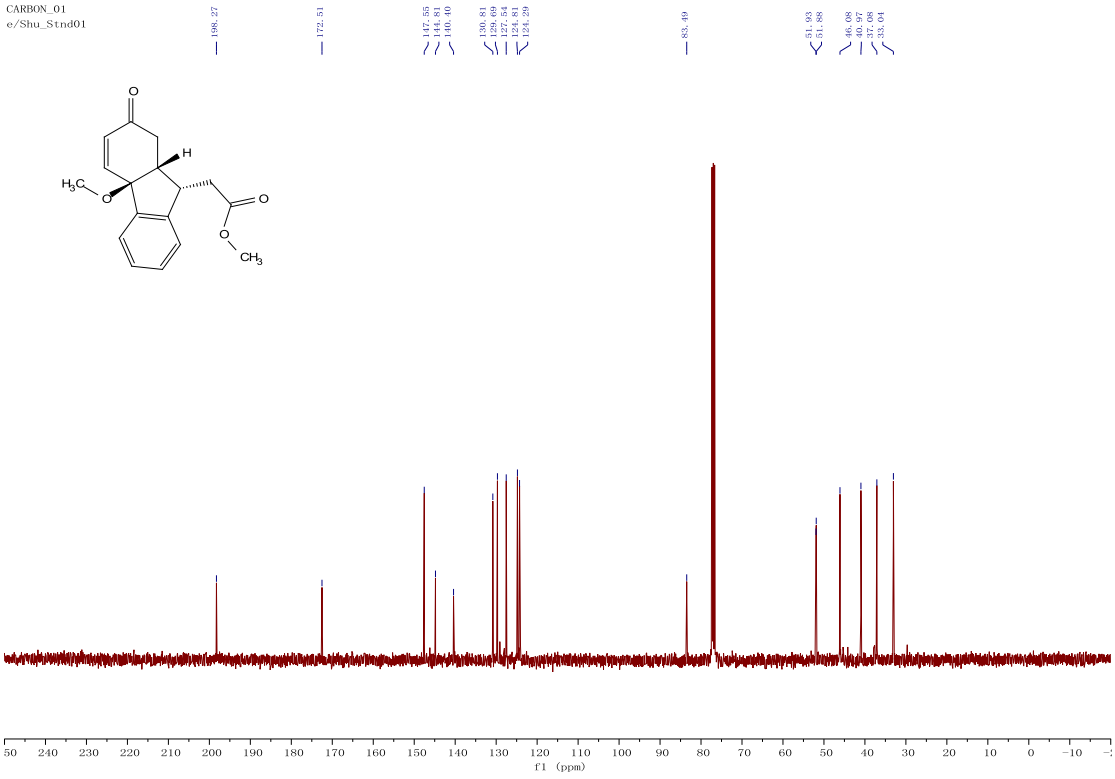
^{1}HNMR and ^{13}C NMR of **1k** (E/Z 25:1)



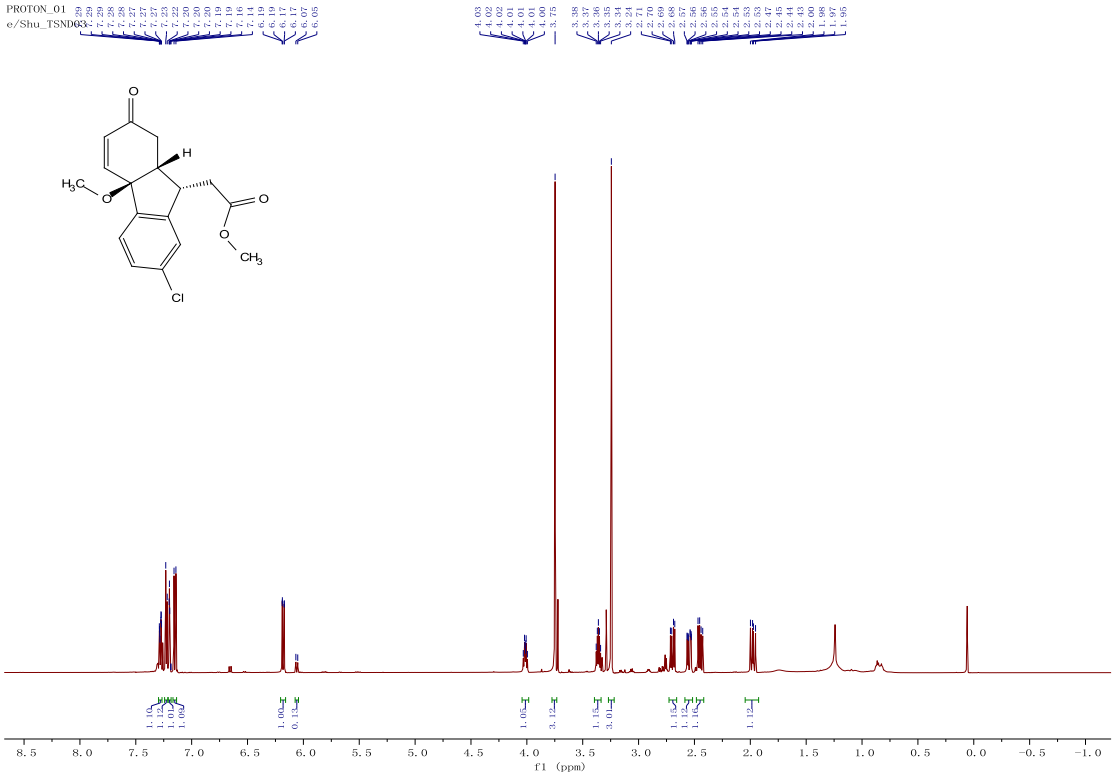


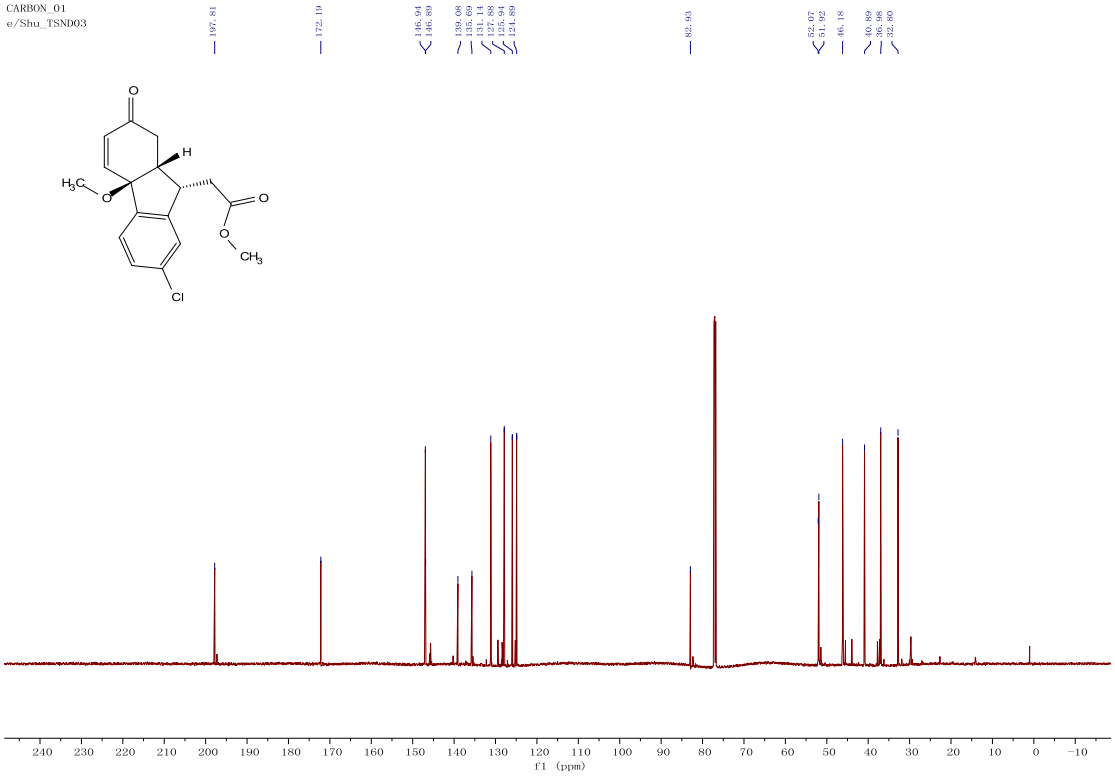
^{1}HNMR and ^{13}C NMR of **2a** (dr 16:1)



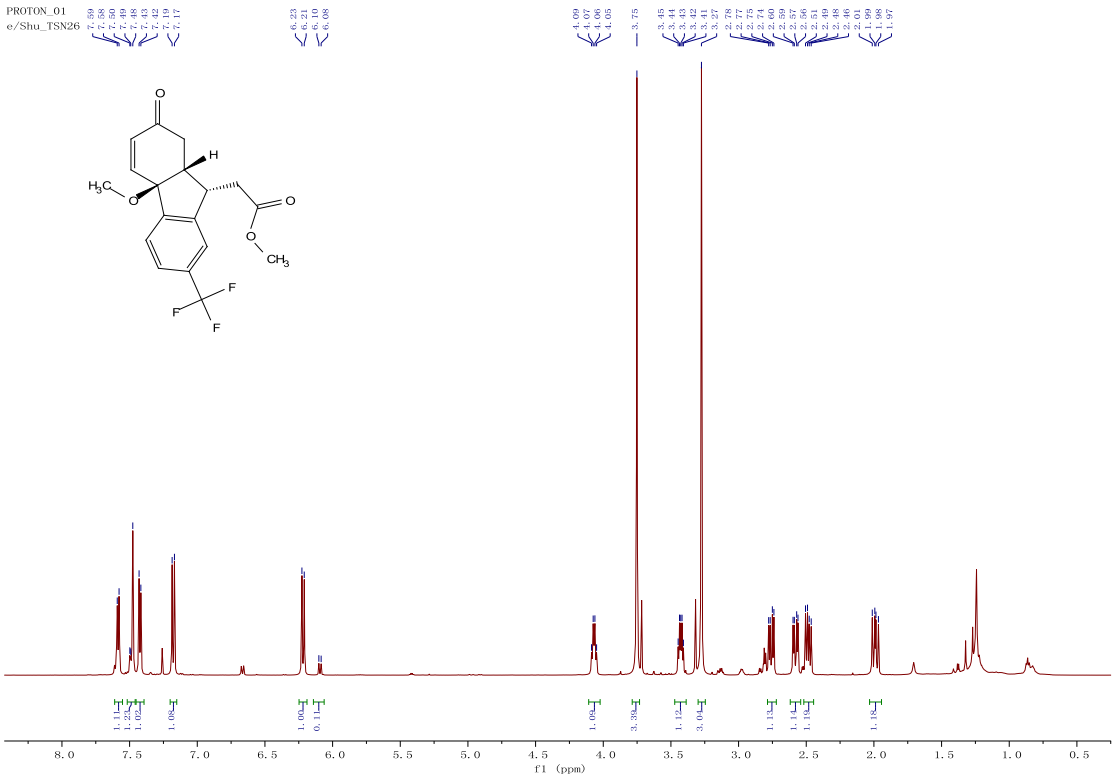


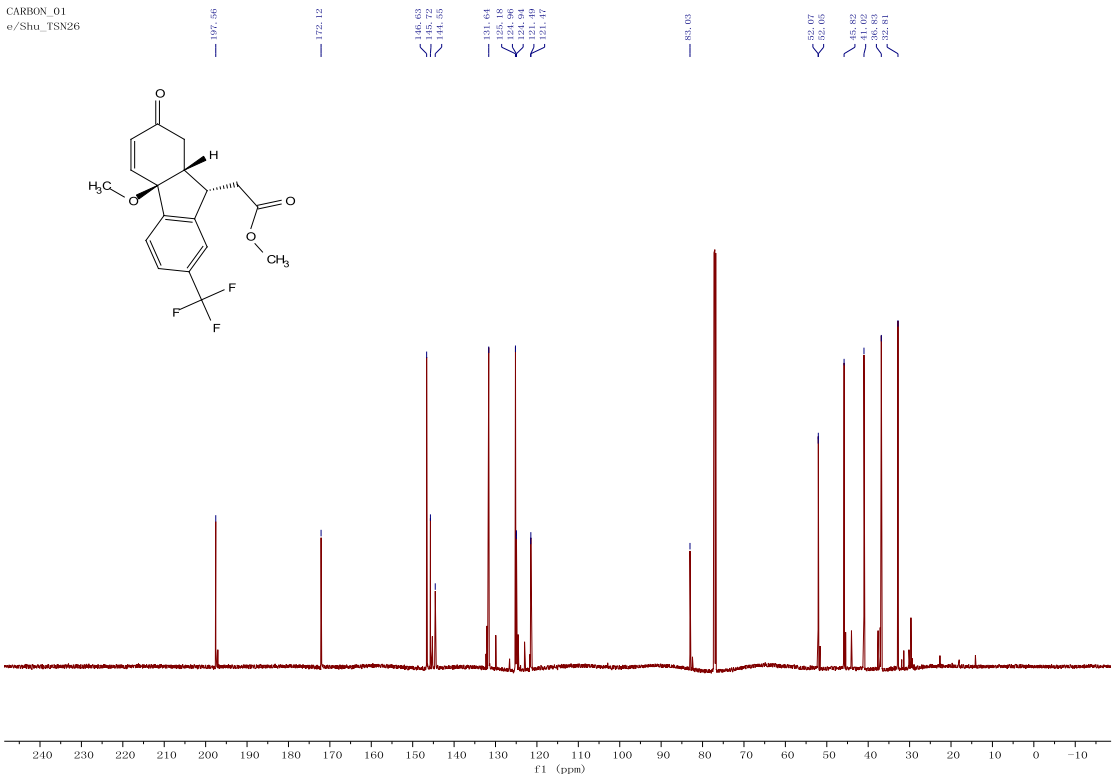
^{1}HNMR and ^{13}C NMR of **2b** (dr 8:1)



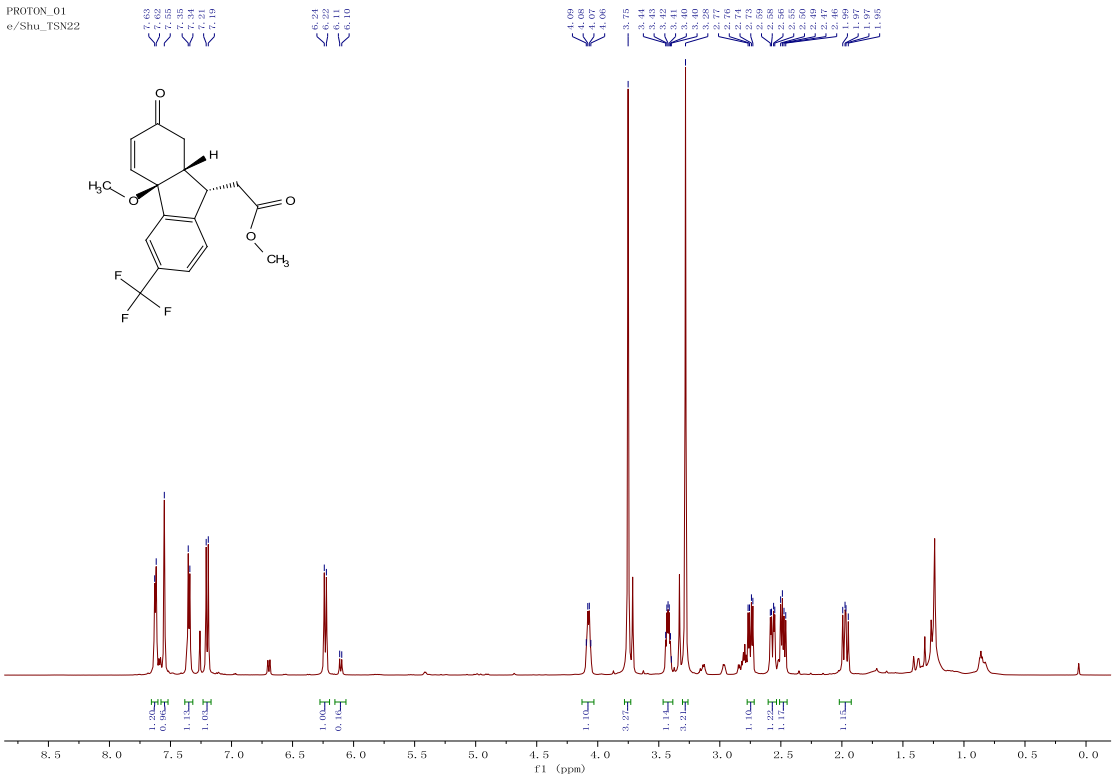


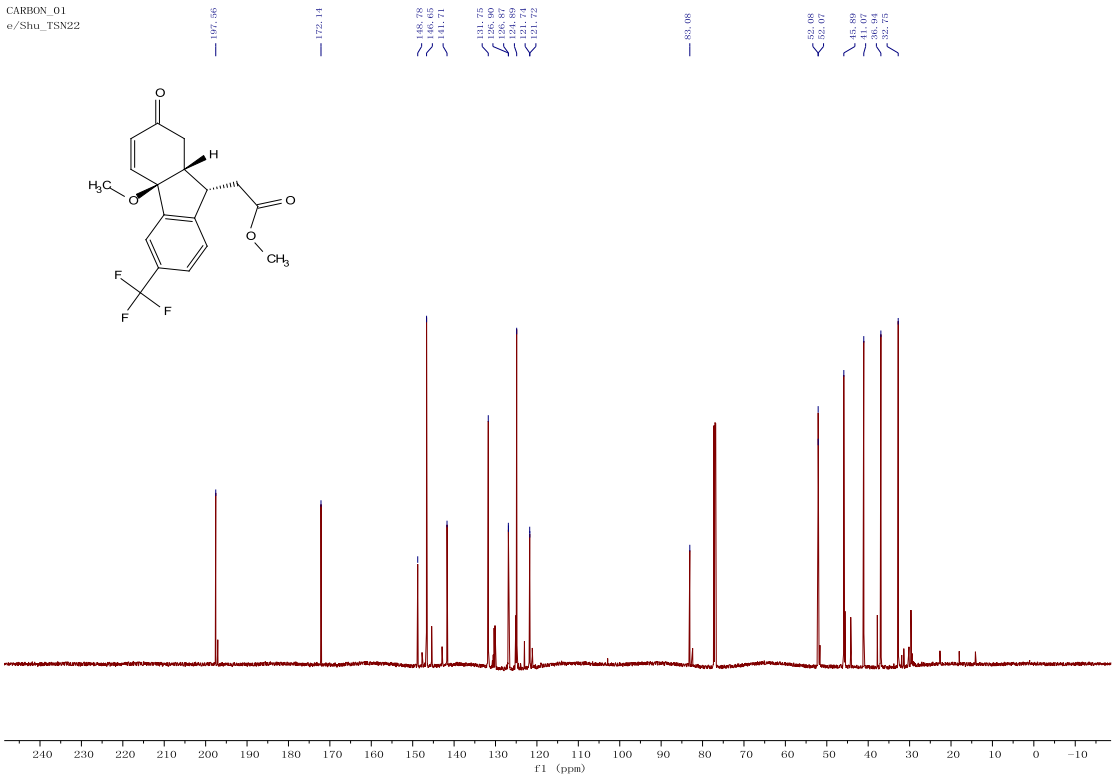
^{1}HNMR and ^{13}C NMR of **2c** (dr 9:1)



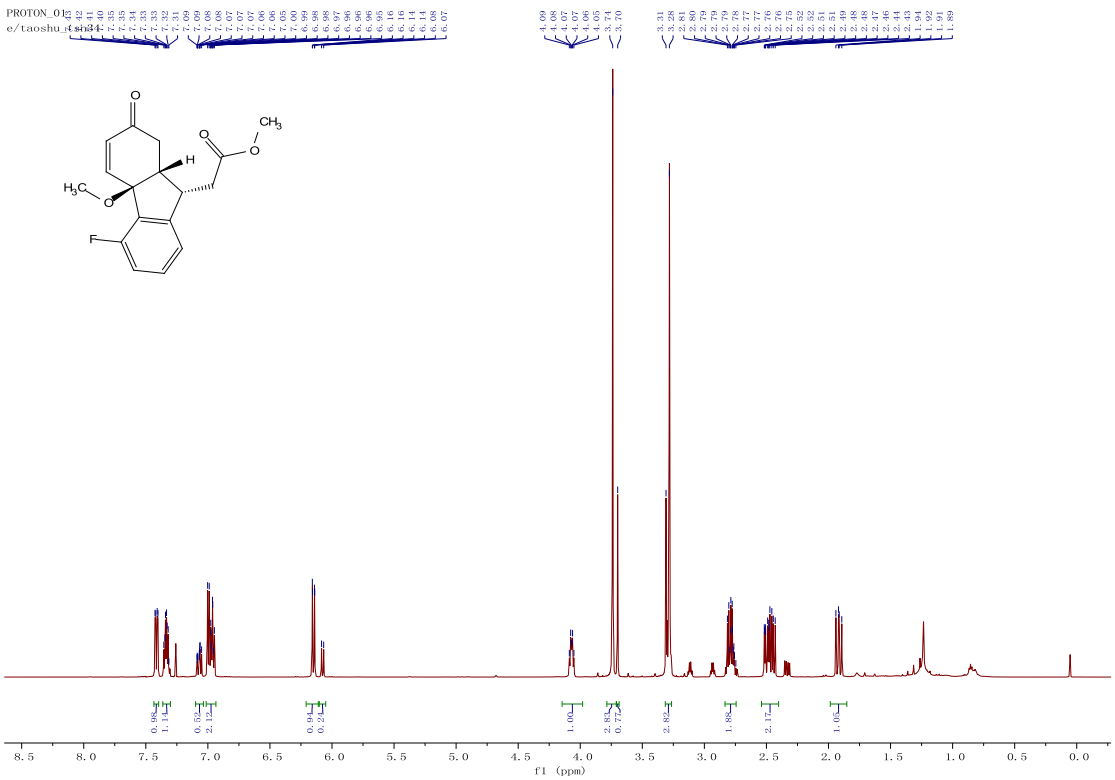


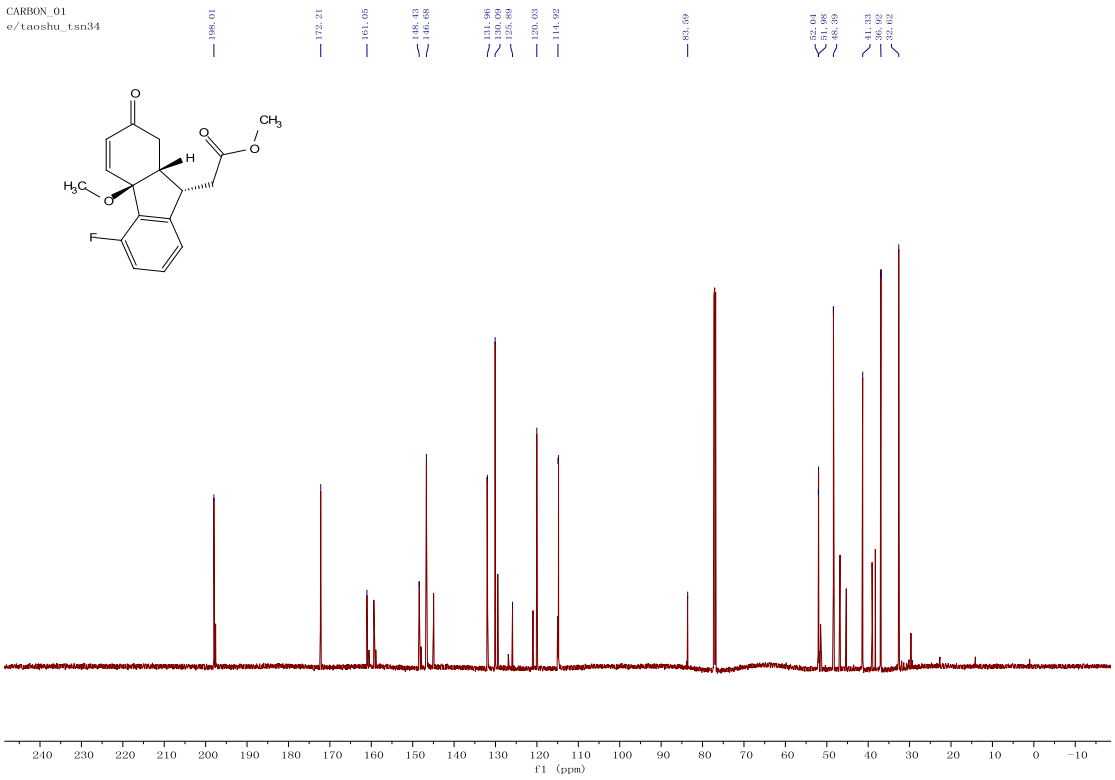
^{1}HNMR and ^{13}C NMR of **2d** (dr 6:1)



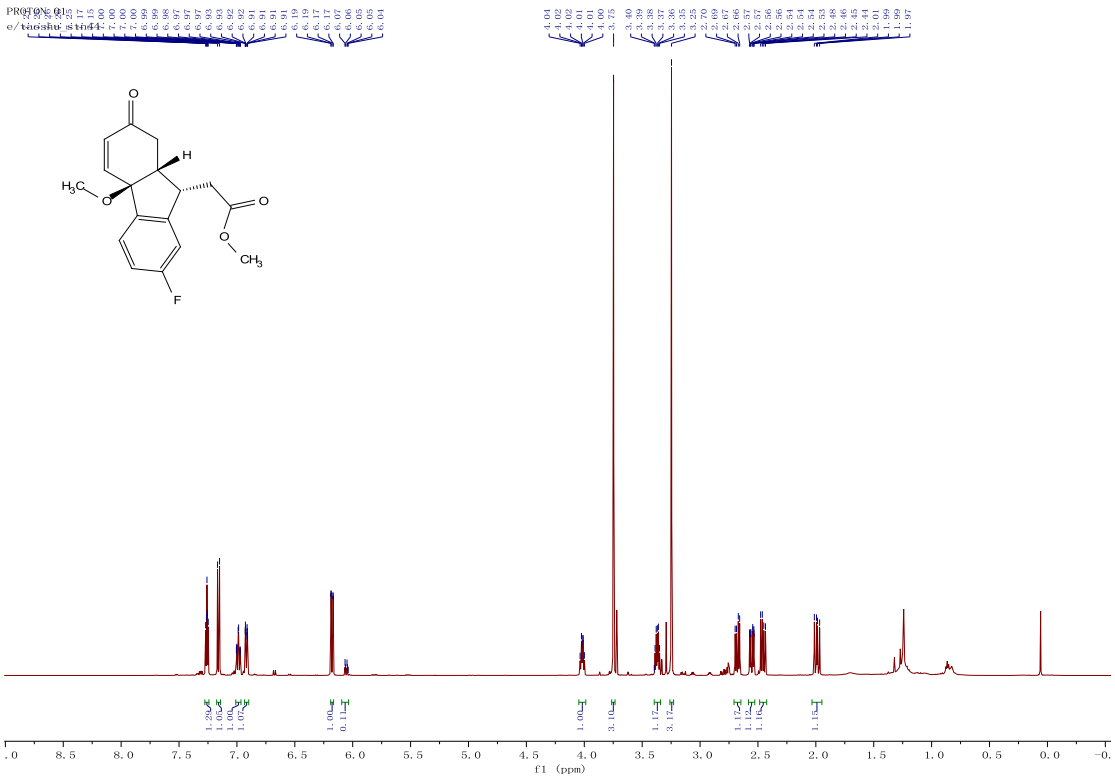


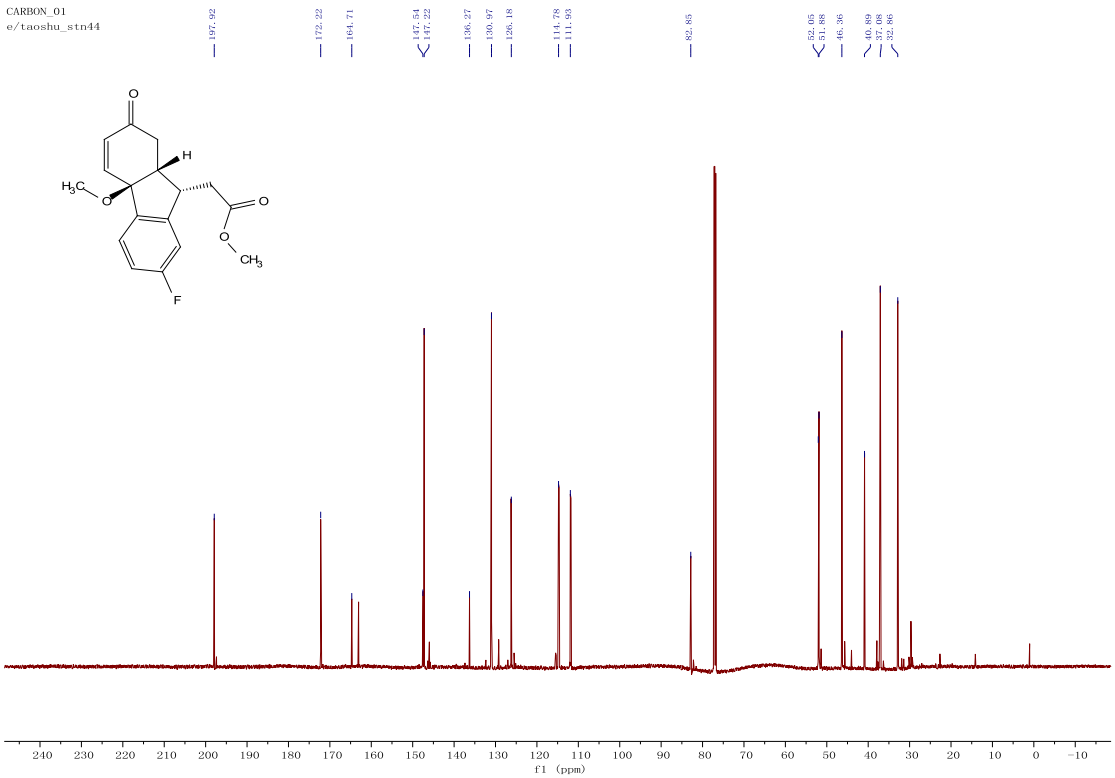
^{1}HNMR and ^{13}C NMR of **2e** (dr 4:1)



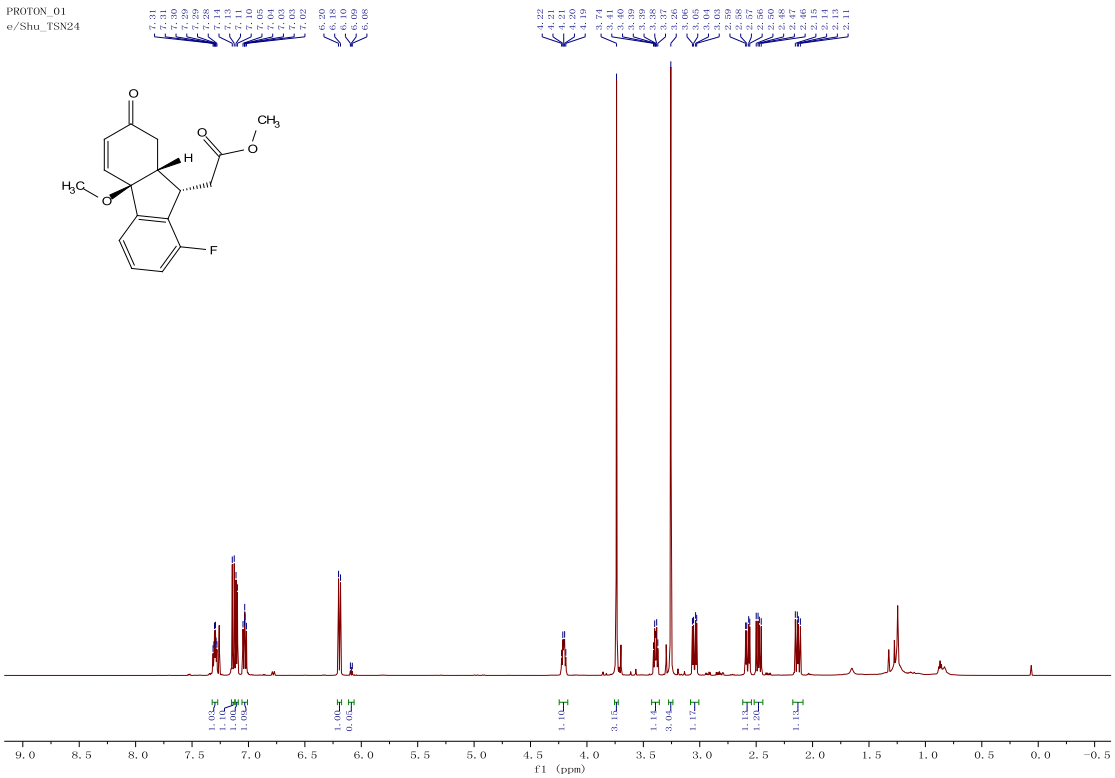


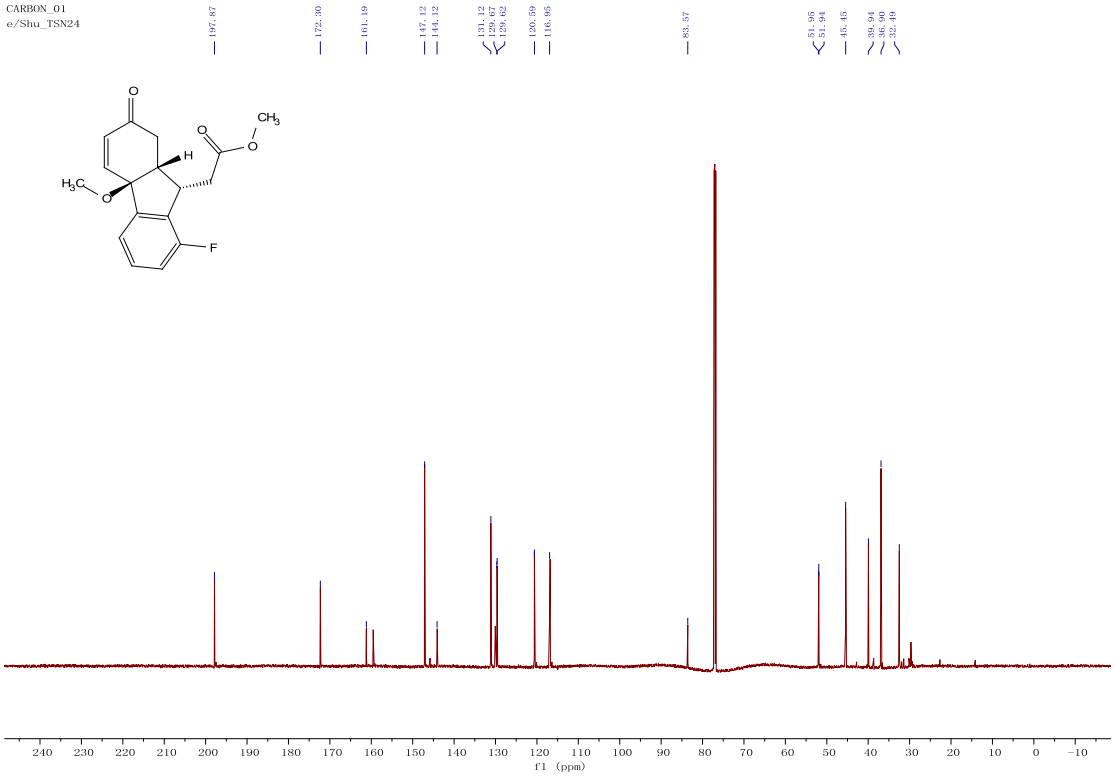
^{1}HNMR and ^{13}C NMR of **2f** (dr 9:1)



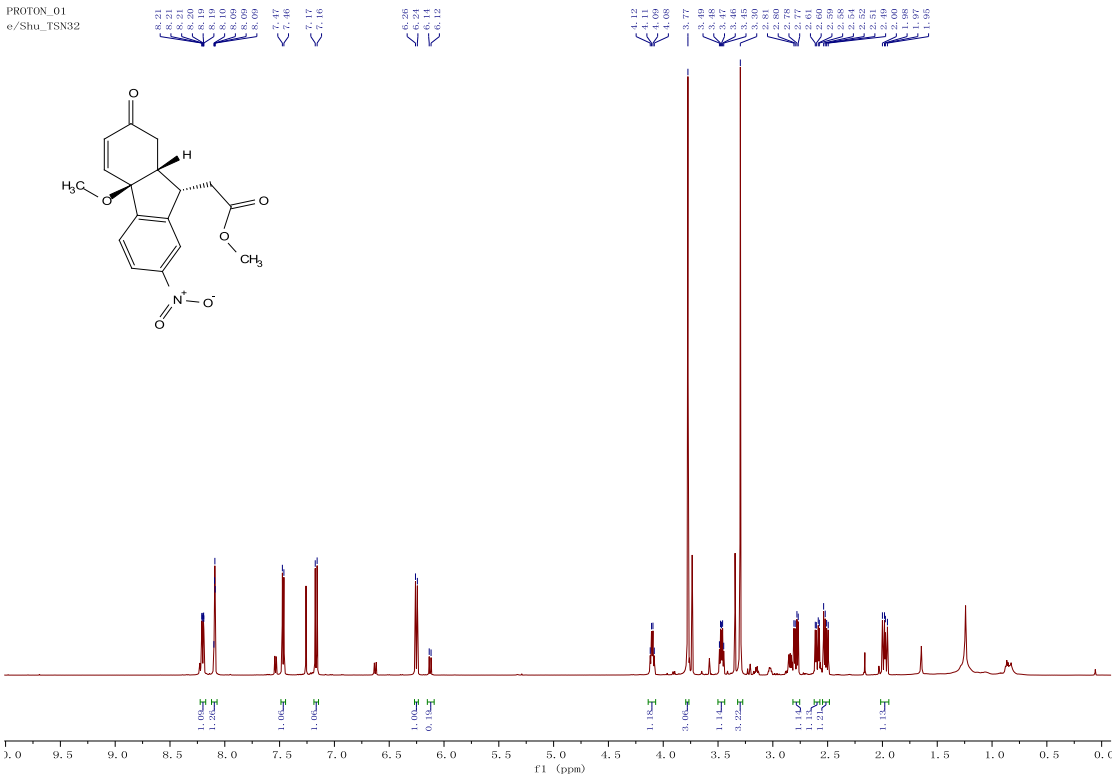


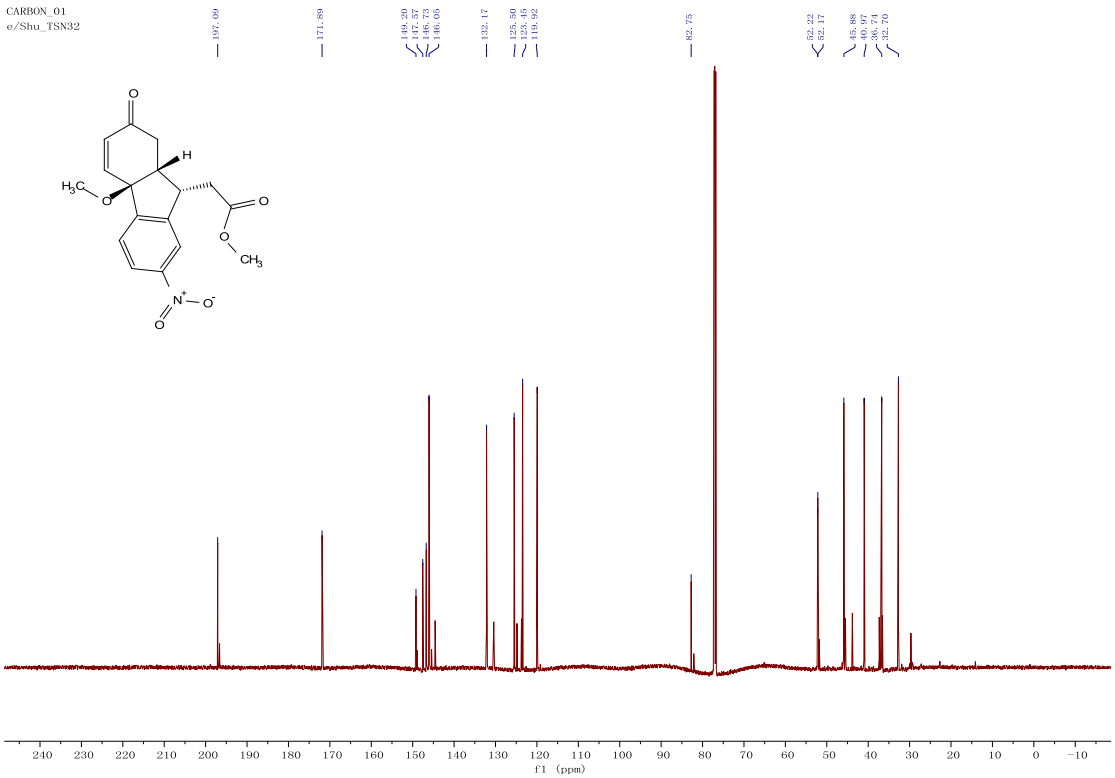
^{1}HNMR and ^{13}C NMR of **2g** (dr 20:1)



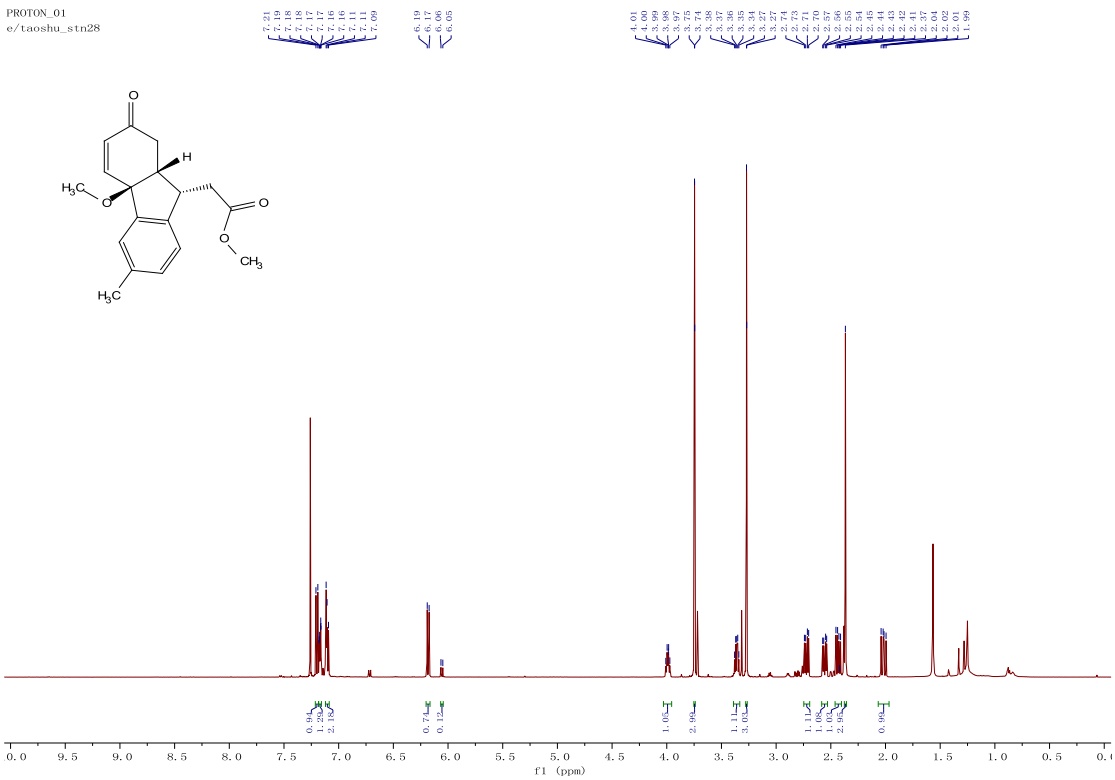


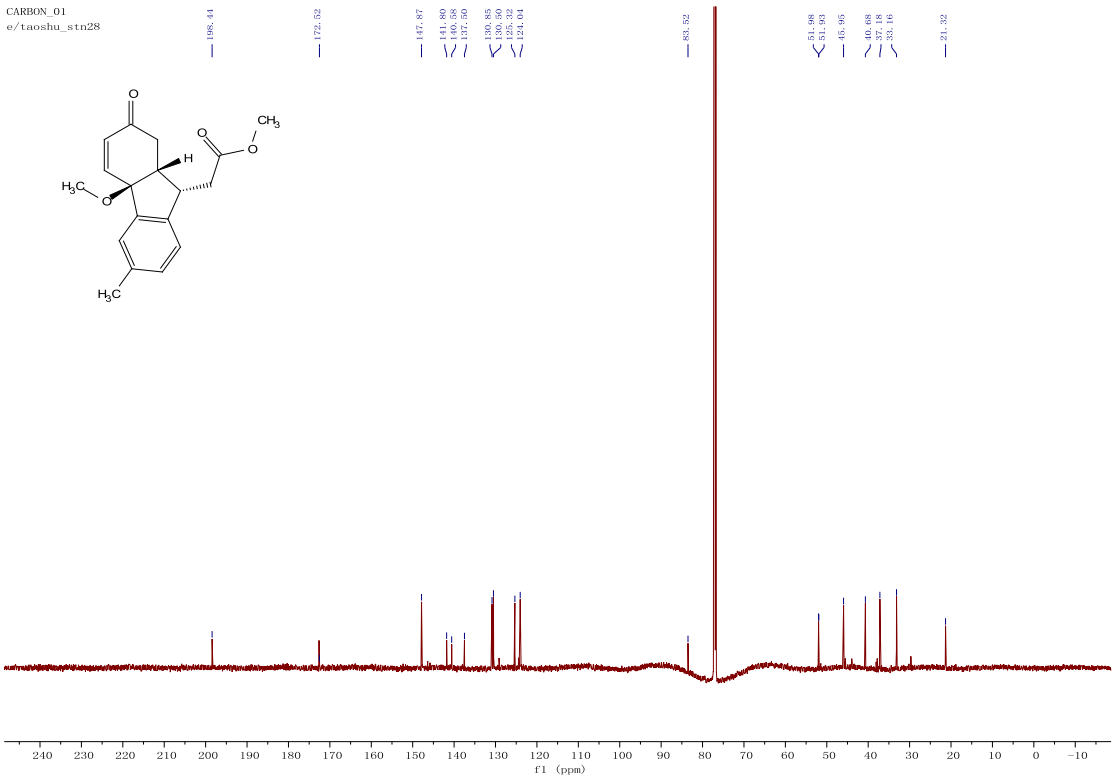
^{1}HNMR and ^{13}C NMR of **2h** (dr 6:1)



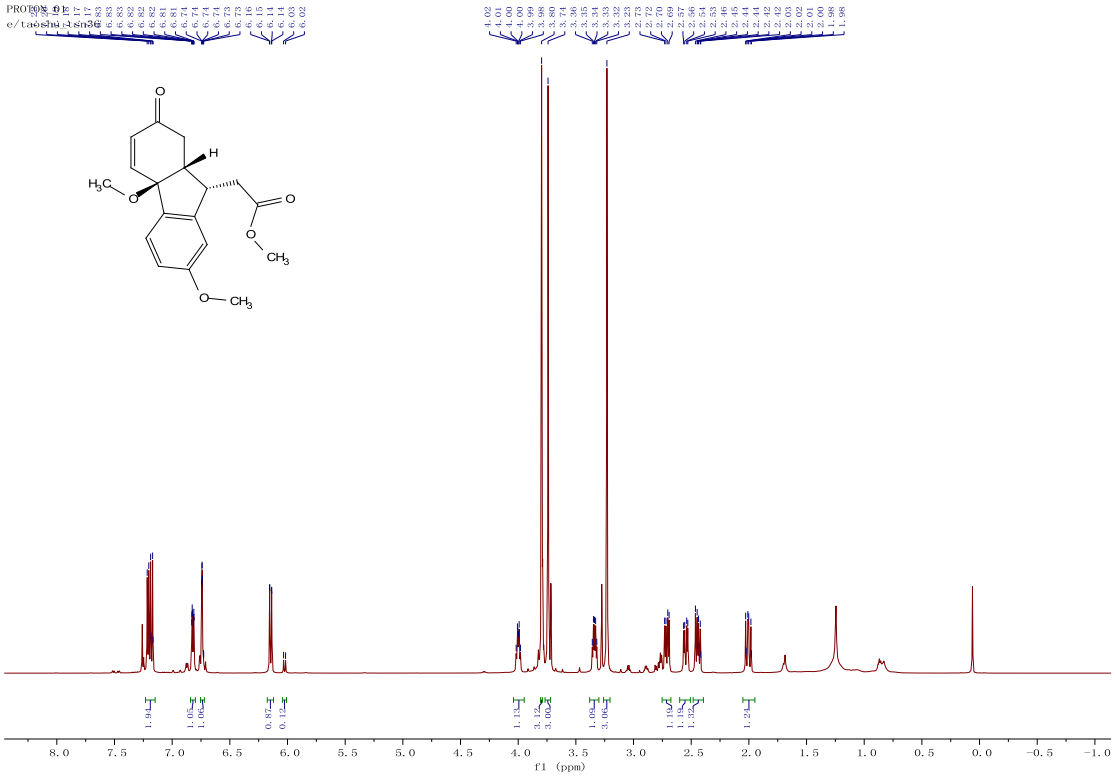


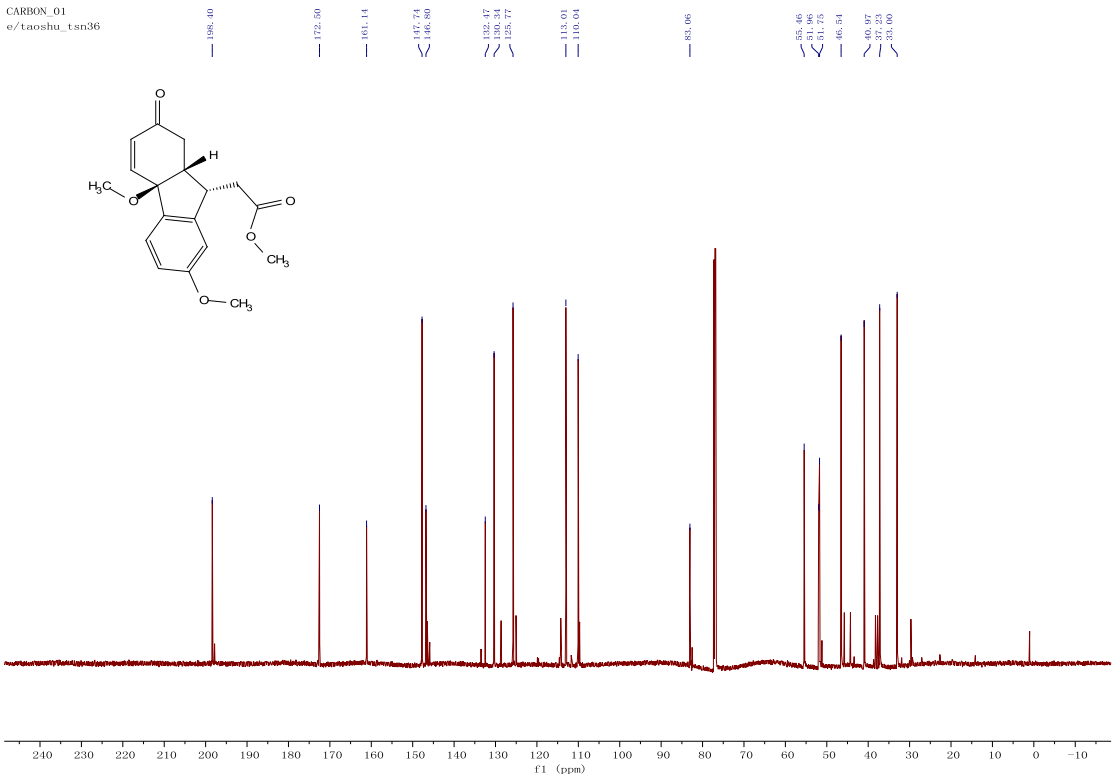
^{1}HNMR and ^{13}C NMR of **2i** (dr 6:1)



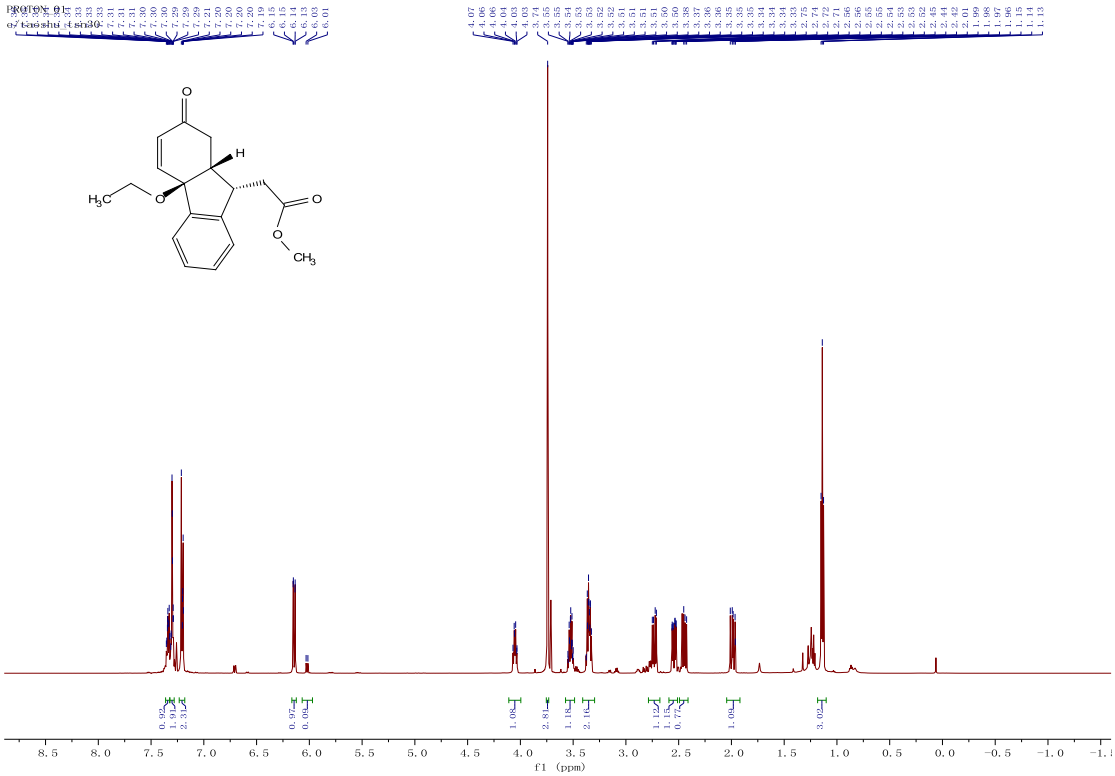


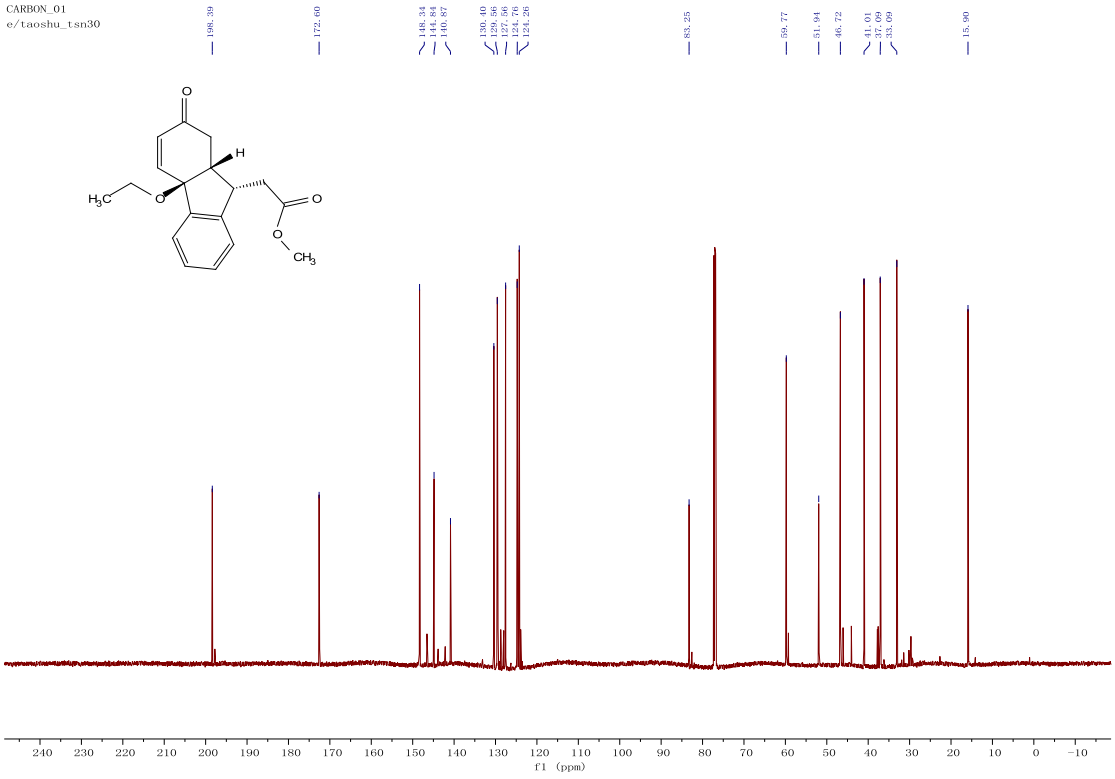
^{1}HNMR and ^{13}C NMR of **2j** (dr 7:1)



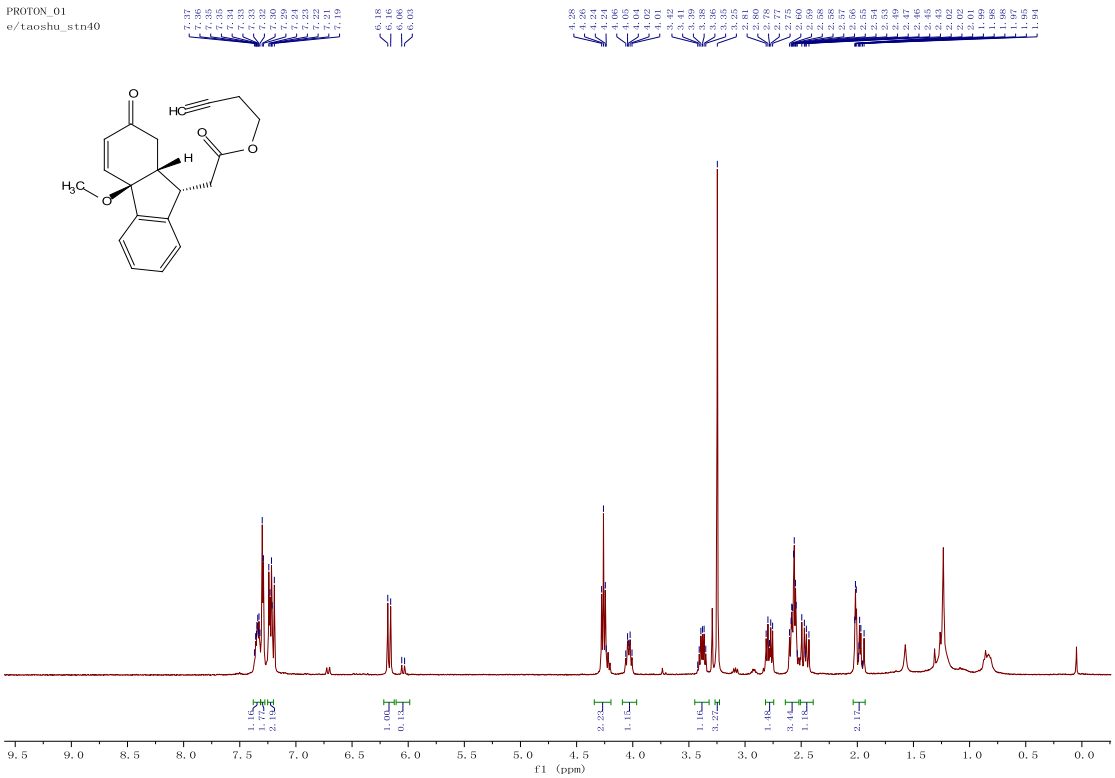


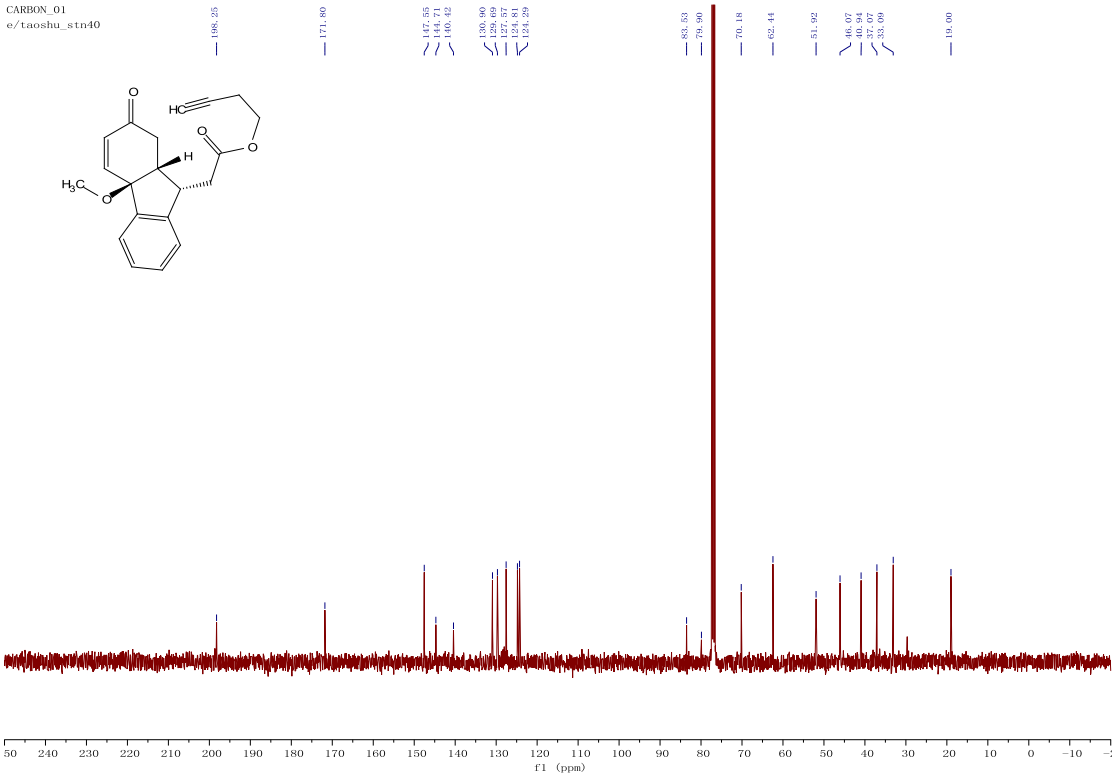
^{1}HNMR and ^{13}C NMR of **2k** (dr 9:1)



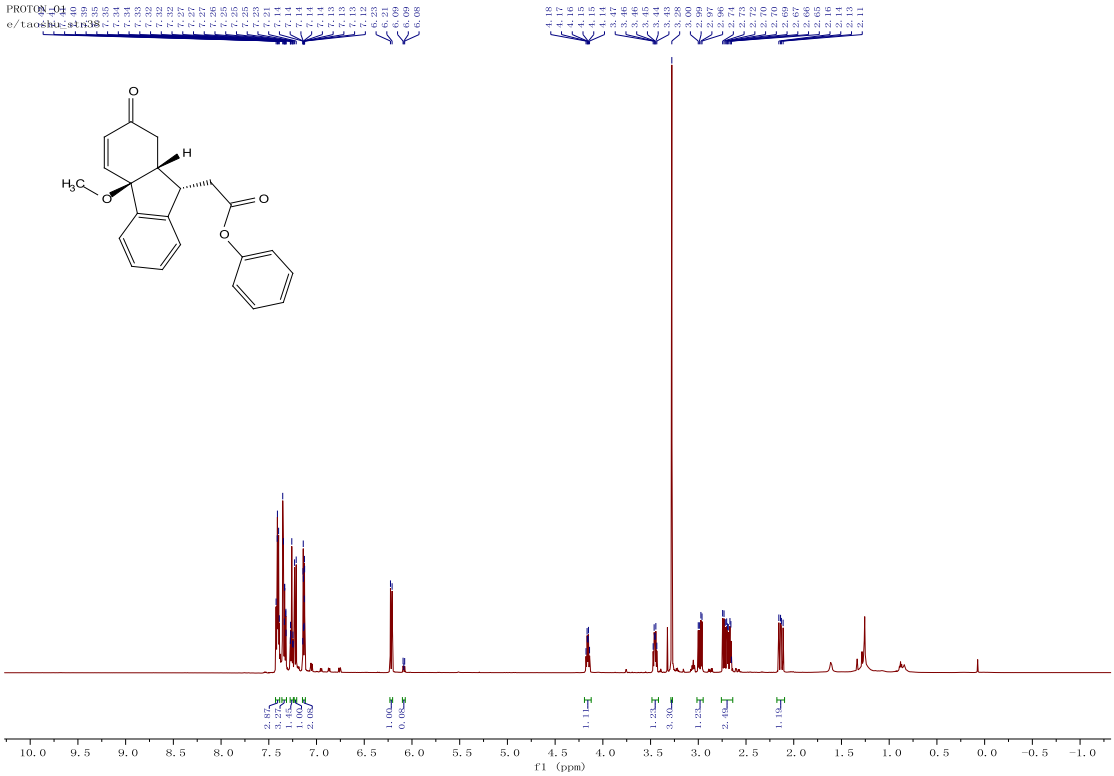


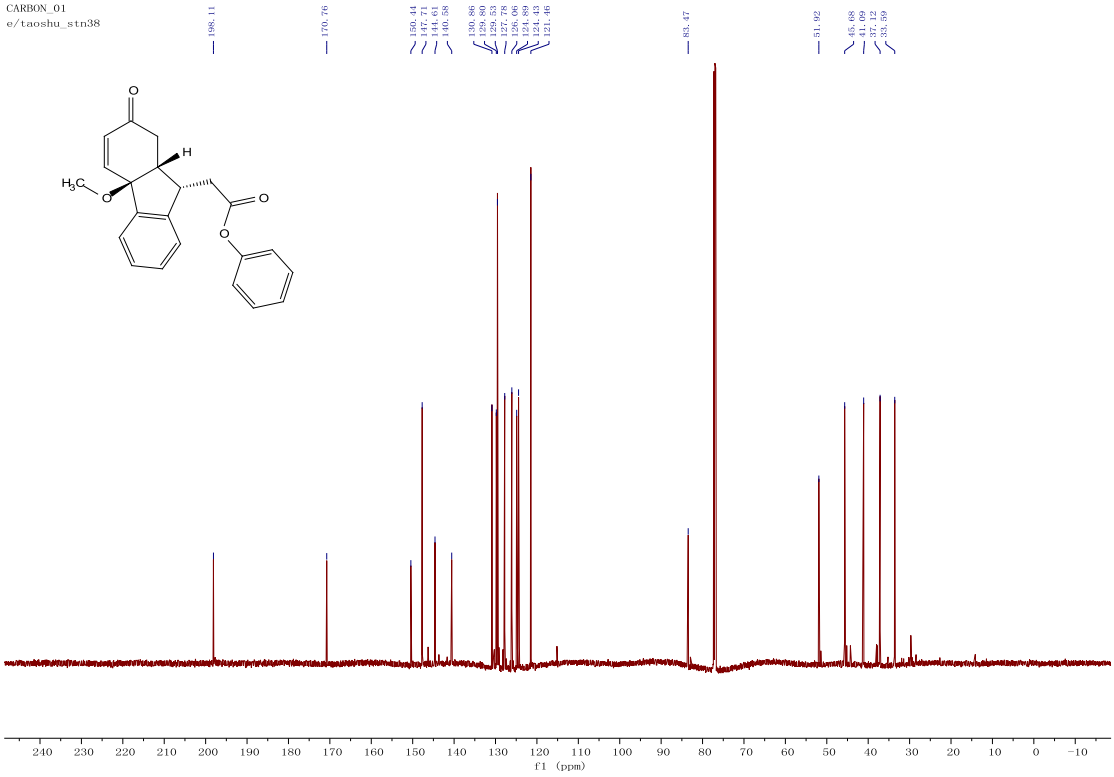
^{1}HNMR and ^{13}C NMR of **2l** (dr 8:1)





^{1}HNMR and ^{13}C NMR of **2m** (dr 12:1)





5. Copies of HPLC data

Mixture of diastereomers

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: **STN01**

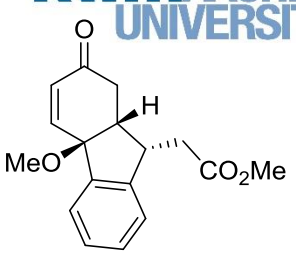
Data file: C:\SNOOPY\ST\STN01RIA.D

Description: Mobile phase: n-Heptane/iPrOH 9:1;
The sample is solved in DCM/MP

Injection date: 8/30/2017 4:35:30 PM

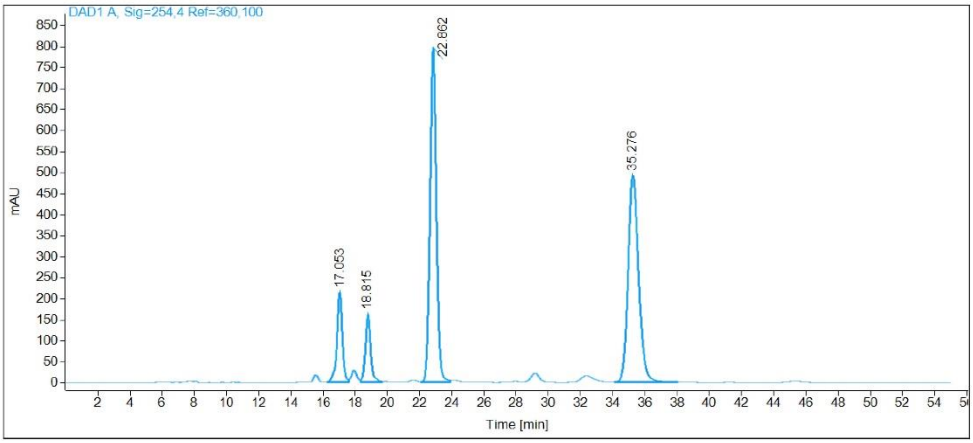
Acq. Analysis method: CHIRALPAK-IA.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036



rac-**2a**

Pressure at start: 24 bar **Start flow:** 0.500 ml/min **Column oven:** 29.98 °C



Name STN01

RT [min]	Type	Area%	Area	Height	Width [min]
17.05	BV	9.21	4850.54	212.82	0.34
18.82	VB	6.83	3596.26	159.29	0.34
22.86	VV	41.76	21990.23	796.97	0.42
35.28	VB	42.20	22218.55	491.64	0.69
	Sum	100.00	52655.57		

Agilent 1260 Infinity **Page 1**

AK Prof. Enders - Analytiklabor 4.04

RWTH AACHEN UNIVERSITY

Sample name: **STN18**

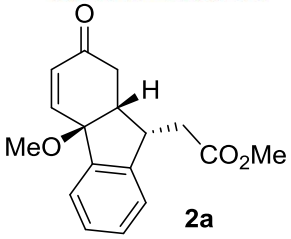
Data file: C:\SNOOPY\ST\STN18.D

Description: Mobile phase: n-Heptane/iPrOH 9:1;
The sample is solved in DCM/MP

Injection date: 10/6/2017 2:34:23 PM

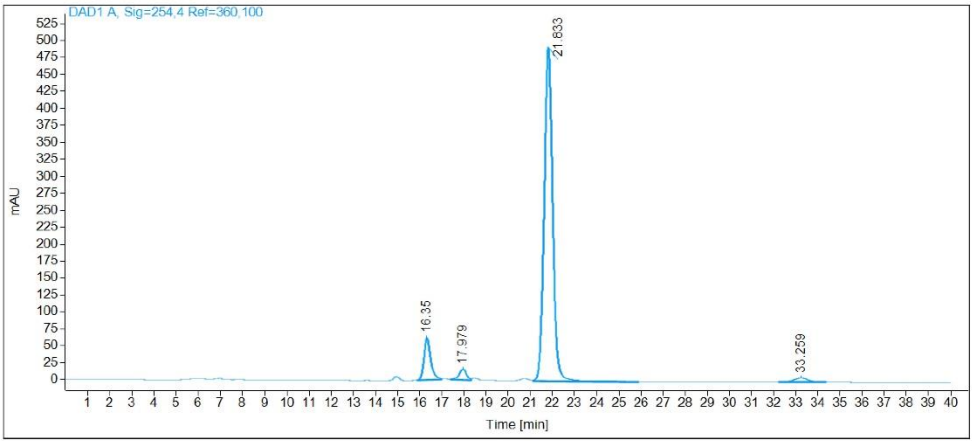
Acq. Analysis method: CHIRALPAK-IA.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036



2a

Pressure at start: 24 bar **Start flow:** 0.500 ml/min **Column oven:** 30.01 °C



Name STN18

RT [min]	Type	Area%	Area	Height	Width [min]
16.35	BV	8.91	1343.54	62.56	0.32
17.98	BV	2.46	371.57	16.18	0.34
21.83	VB	86.92	13111.51	492.96	0.41
33.26	BB	1.71	258.33	6.20	0.60
	Sum	100.00	15084.95		

AK Prof. Enders - Analytiklabor 4.04

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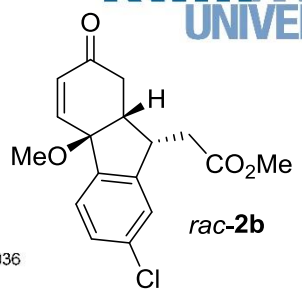
Sample name: **STN20 rac**

Data file: C:\SNOOPY\ST\STN20RIA.D
Description: Mobile phase: n-Heptane/iPrOH 9:1;
The sample is solved in DCM/MP

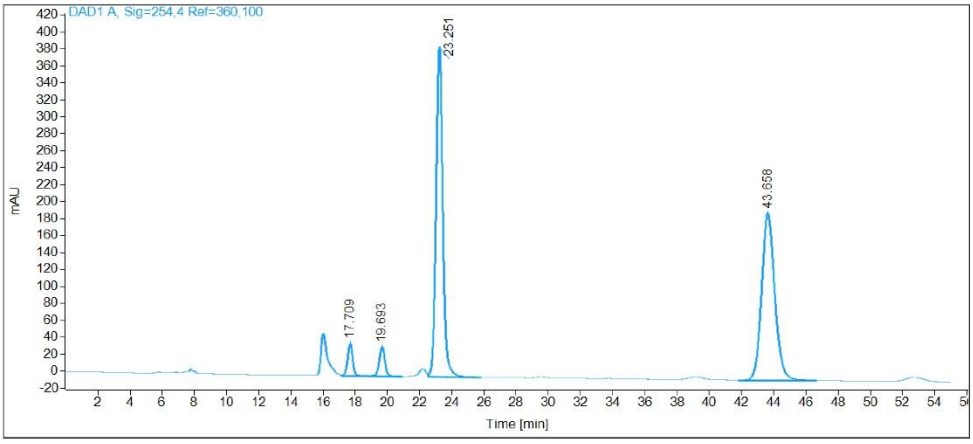
Injection date: 10/20/2017 3:17:23 PM
Acq. Analysis method: CHIRALPAK-IA.M

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036



rac-**2b**

Pressure at start: 25 bar **Start flow:** 0.500 ml/min **Column oven:** 29.99 °C



Name STN20 rac

RT [min]	Type	Area%	Area	Height	Width [min]
17.71	VB	3.33	800.24	37.66	0.32
19.69	BB	3.43	824.76	33.91	0.37
23.25	VB	46.94	11293.79	389.23	0.44
43.66	BB	46.30	11138.85	197.18	0.86
	Sum	100.00	24057.64		

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Sample name: STN21

Data file: C:\SNOOPY\ST\STN21.D

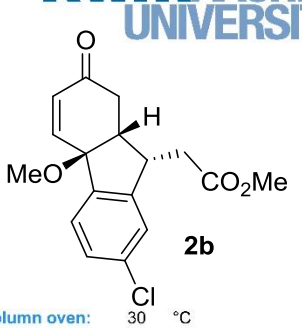
Description: Mobile phase: n-Heptane/iPrOH 9:1;
The sample is solved in DCM/MP

Injection date: 10/23/2017 5:09:49 PM

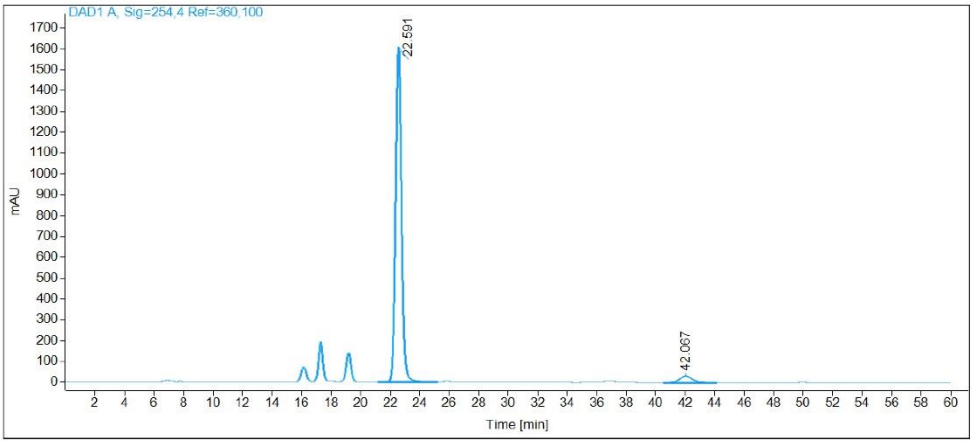
Acq. Analysis method: CHIRALPAK-IA.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 25 bar **Start flow:** 0.500 ml/min **Column oven:** 30 °C



2b



Name STN21

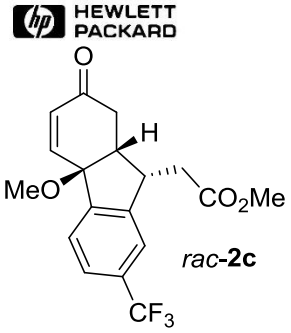
RT [min]	Type	Area%	Area	Height	Width [min]
22.59	BV	96.36	45164.55	1609.24	0.43
42.07	BB	3.64	1703.94	31.32	0.82
	Sum	100.00	46868.49		

Sample Name: STN25 rac
Data file: D:\GONZO\ST\STN25RIA.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

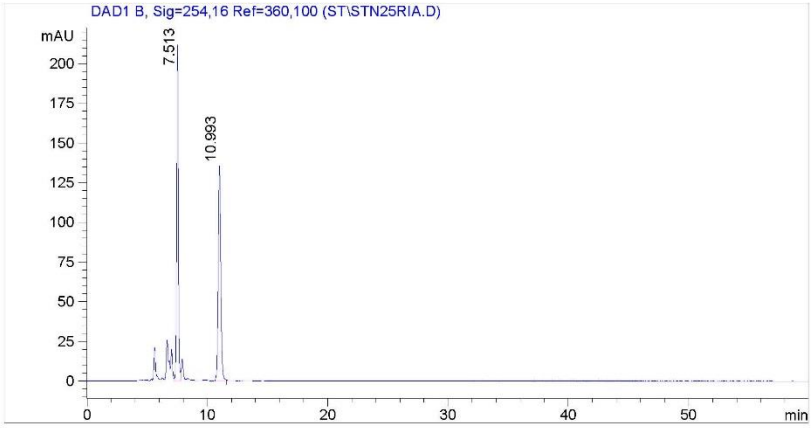
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 21:48:46
Injektion Date: 15.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.7	41.4
Flow in ml/min:	0.70	0.70



rac-**2c**



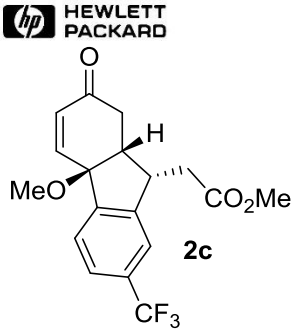
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.51	0.15	211.80	2015.74	50.07
2	10.99	0.22	135.64	2009.76	49.93
Total				4025.50	100.00

Sample Name: STN26
Data file: D:\GONZO\ST\STN26.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

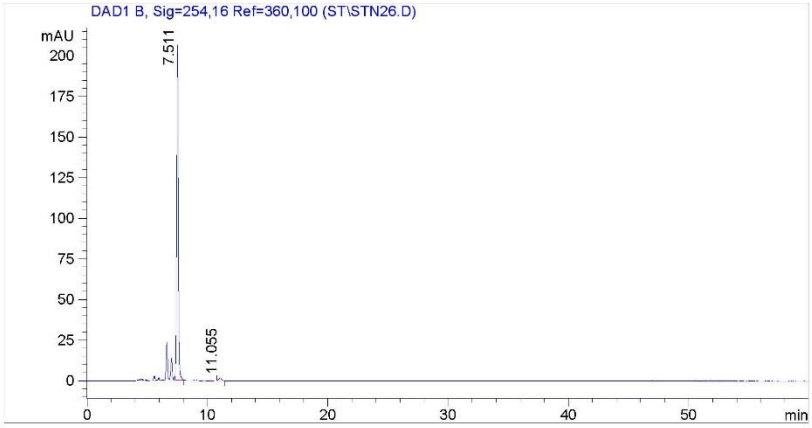
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 22:49:58
Injektion Date: 15.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	41.0	41.5
Flow in ml/min:	0.70	0.70



2c



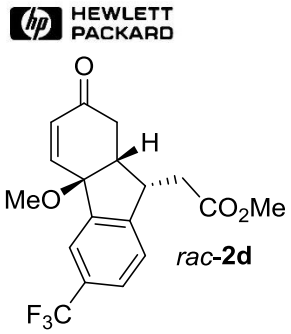
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.51	0.14	206.68	1962.72	98.65
2	11.05	0.22	1.80	26.87	1.35
Total				1989.60	100.00

Sample Name: STN21 rac
Data file: D:\GONZO\ST\STN21RIA.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

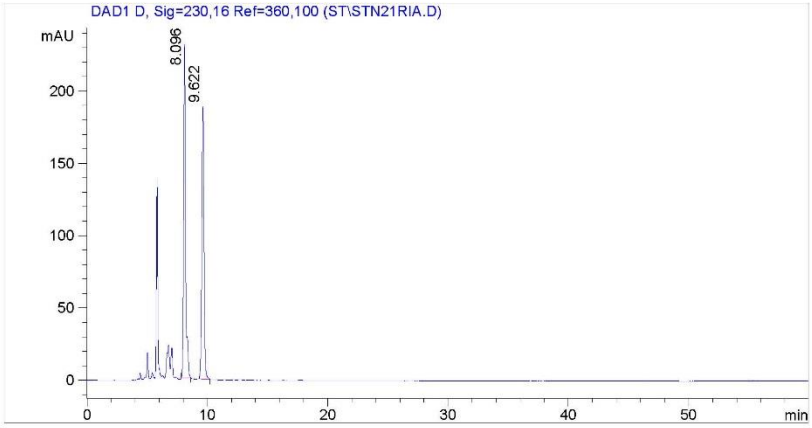
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 17:43:54
Injektion Date: 15.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.8	41.2
Flow in ml/min:	0.70	0.70



rac-**2d**



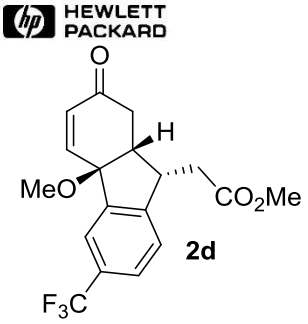
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.10	0.19	230.80	2589.66	52.36
2	9.62	0.19	188.40	2356.55	47.64
Total				4946.21	100.00

Sample Name: STN22
Data file: D:\GONZO\ST\STN22.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

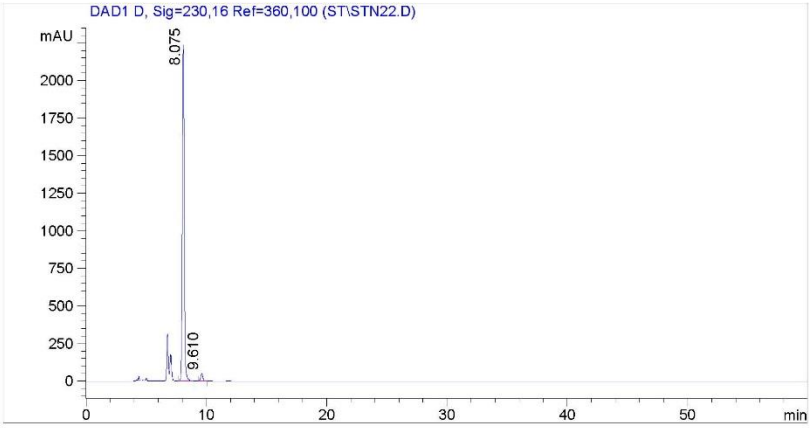
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 18:45:07
Injektion Date: 15.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.4	41.0
Flow in ml/min:	0.70	0.70



2d



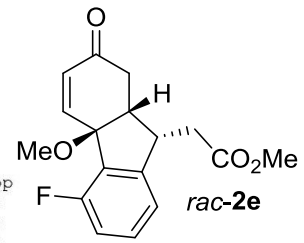
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.08	0.18	2238.02	25272.36	97.52
2	9.61	0.20	49.63	641.70	2.48
Total				25914.06	100.00

Sample Name: TSN33 rac
Data file: D:\GONZO\ST\TSN33RIA.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

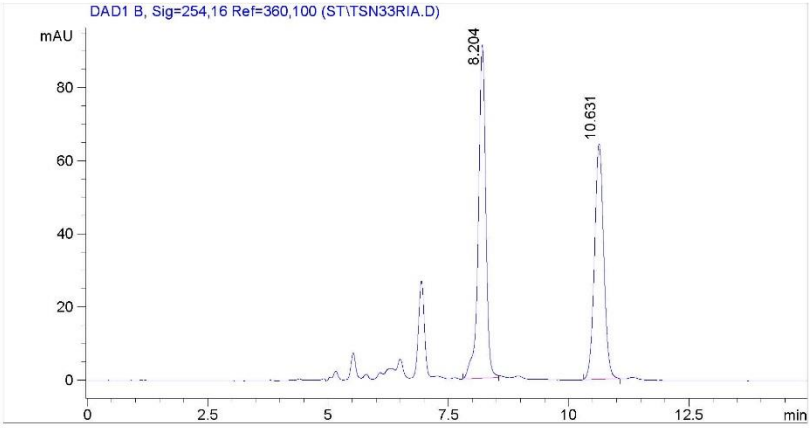
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 14:49:45
Injektion Date: 18.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.9	41.2
Flow in ml/min:	0.70	0.70



rac-**2e**



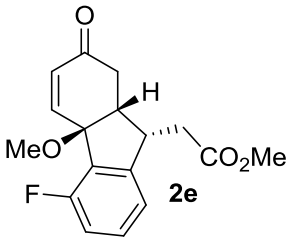
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.20	0.16	91.19	969.35	53.15
2	10.63	0.20	64.40	854.55	46.85
Total				1823.90	100.00

Sample Name: TSN34
Data file: D:\GONZO\ST\TSN34.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

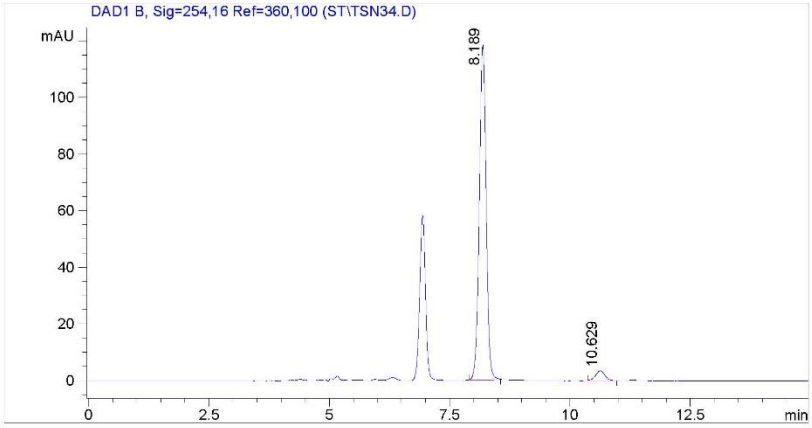
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 15:35:11
Injektion Date: 18.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	41.0	41.3
Flow in ml/min:	0.70	0.70



2e



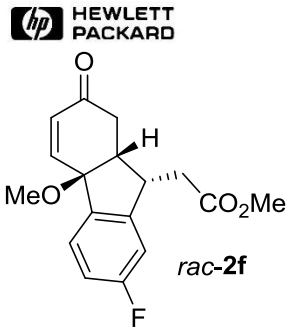
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.19	0.15	118.45	1166.07	96.20
2	10.63	0.19	3.50	46.12	3.80
Total				1212.19	100.00

Sample Name: TSN43 rac
Data file: D:\GONZO\ST\TSN43RIA.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

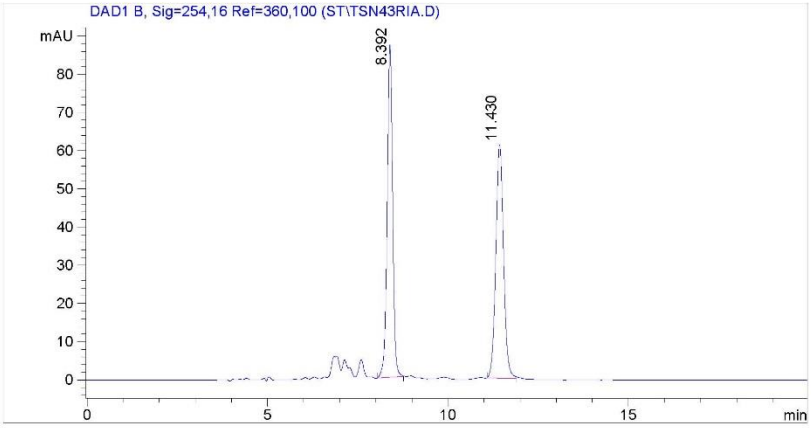
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 16:20:29
Injektion Date: 30.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.5	41.3
Flow in ml/min:	0.70	0.70



rac-**2f**



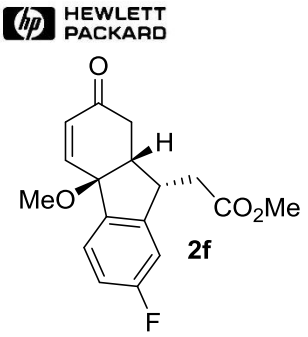
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.39	0.16	87.08	911.80	50.14
2	11.43	0.23	61.14	906.71	49.86
Total				1818.51	100.00

Sample Name: TSn44
Data file: D:\GONZO\ST\TSN44.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

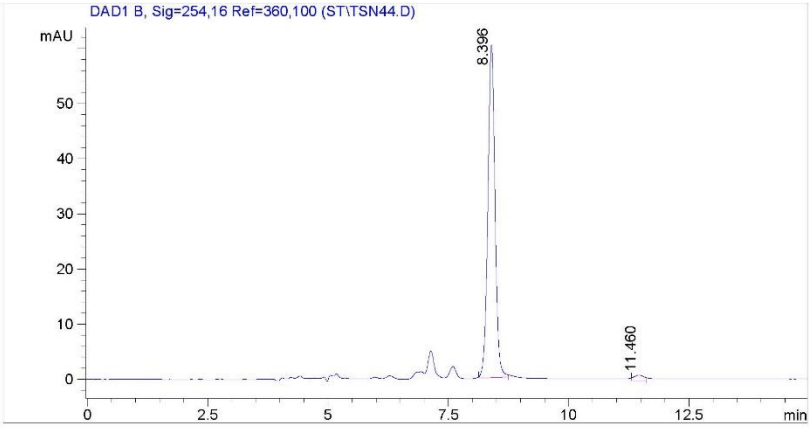
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 16:58:44
Injektion Date: 30.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.6	41.3
Flow in ml/min:	0.70	0.70



2f



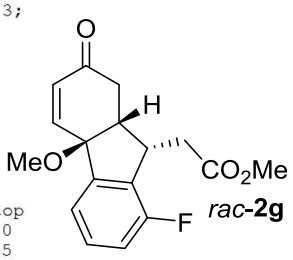
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.40	0.16	60.37	623.03	97.81
2	11.46	0.25	0.93	13.93	2.19
Total				636.96	100.00

Sample Name: STN23 rac
Data file: D:\GONZO\ST\STN23RIA.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

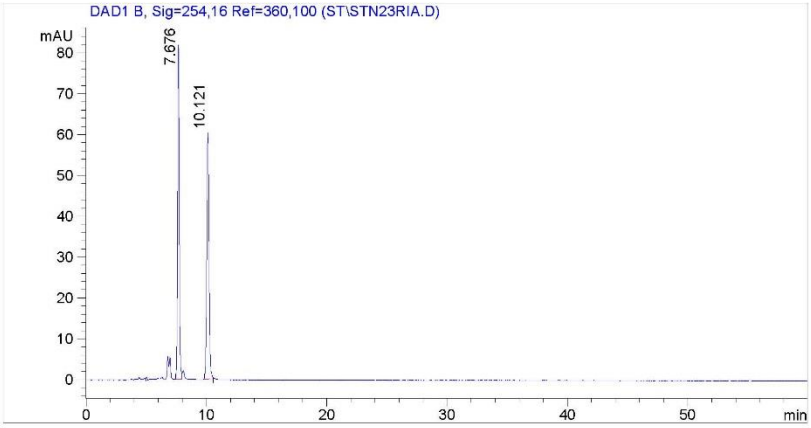
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 19:46:21
Injektion Date: 15.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	41.1	41.5
Flow in ml/min:	0.70	0.70



rac-**2g**



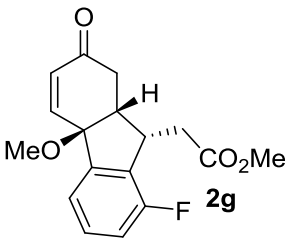
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.68	0.14	81.90	777.50	50.10
2	10.12	0.20	60.30	774.53	49.90
Total				1552.03	100.00

Sample Name: STN24
Data file: D:\GONZO\ST\STN24.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

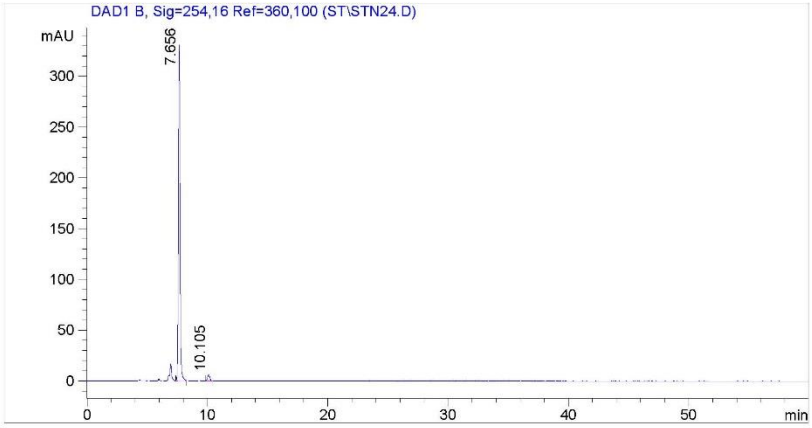
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 20:47:33
Injektion Date: 15.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	41.0	41.1
Flow in ml/min:	0.70	0.70



2g



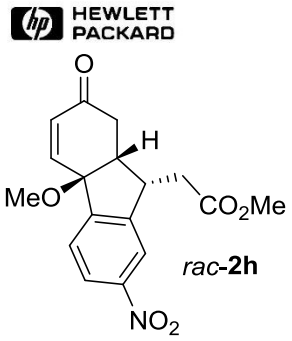
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.66	0.15	330.75	3150.44	97.53
2	10.10	0.20	5.98	79.67	2.47
Total				3230.10	100.00

Sample Name: TSN31 rac
Data file: D:\GONZO\ST\TSN31RIA.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

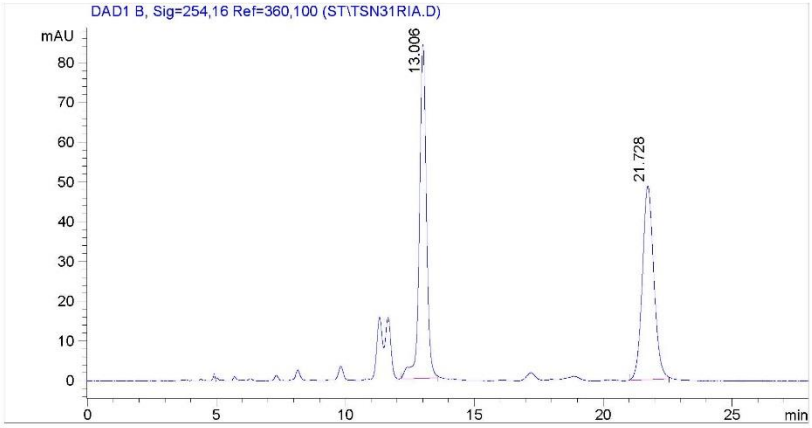
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 14:20:33
Injektion Date: 18.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	41.1	40.8
Flow in ml/min:	0.70	0.70



rac-**2h**



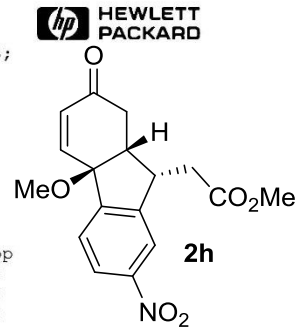
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	13.01	0.28	83.95	1584.50	51.26
2	21.73	0.47	48.72	1506.87	48.74
Total				3091.37	100.00

Sample Name: TSN32
Data file: D:\GONZO\ST\TSN32.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

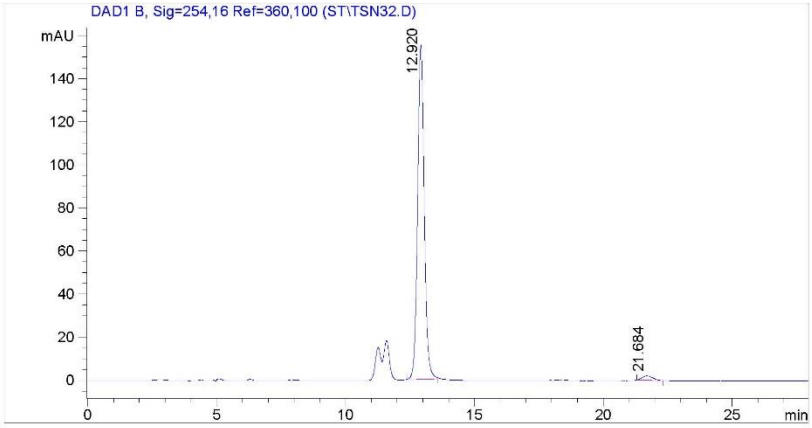
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 15:05:59
Injektion Date: 18.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.6	41.3
Flow in ml/min:	0.70	0.70



2h



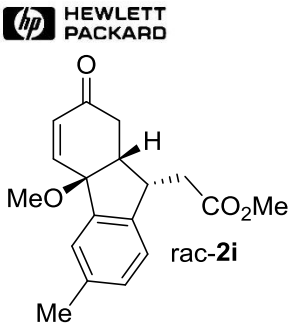
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	12.92	0.27	155.29	2776.40	97.93
2	21.68	0.35	2.05	58.65	2.07
Total				2835.05	100.00

Sample Name: TSN27 rac
Data file: D:\GONZO\ST\TSN27RIA.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

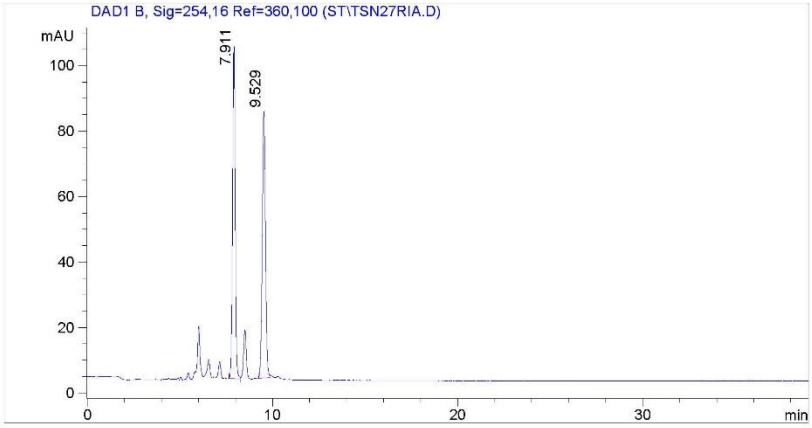
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 14:18:29
Injektion Date: 17.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.8	41.0
Flow in ml/min:	0.70	0.70



rac-**2i**



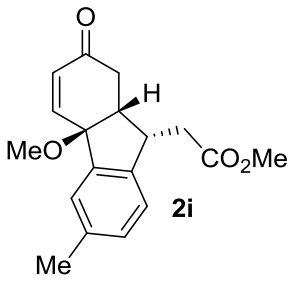
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.91	0.15	101.97	995.09	50.30
2	9.53	0.19	81.47	983.12	49.70
Total				1978.21	100.00

Sample Name: TSN28
Data file: D:\GONZO\ST\TSN28.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

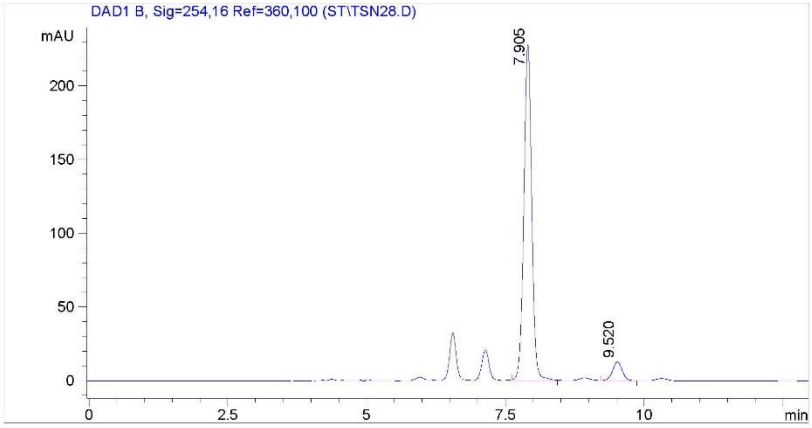
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 15:12:59
Injektion Date: 17.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.6	41.0
Flow in ml/min:	0.70	0.70



2i



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.90	0.15	227.95	2247.57	93.52
2	9.52	0.19	12.73	155.70	6.48
Total				2403.27	100.00

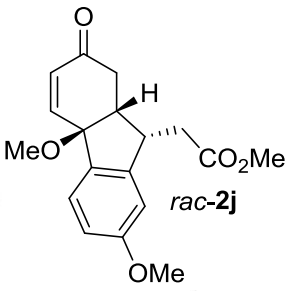
HEWLETT PACKARD

Sample Name: TSN35 rac
Data file: D:\GONZO\ST\TSN35RIA.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

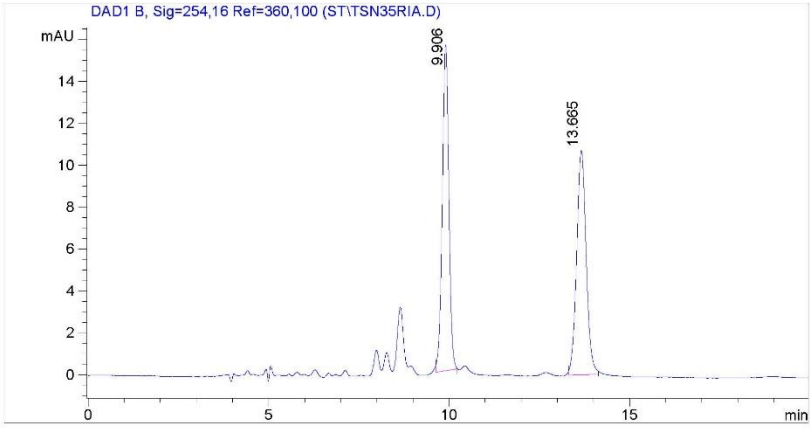
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 13:25:40
Injektion Date: 30.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.5	41.3
Flow in ml/min:	0.70	0.70



rac-**2j**



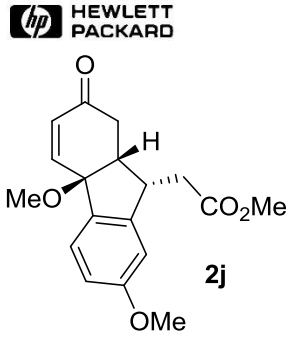
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.91	0.19	15.57	194.88	49.89
2	13.67	0.28	10.72	195.73	50.11
Total				390.61	100.00

Sample Name: TSN36
Data file: D:\GONZO\ST\TSN36.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

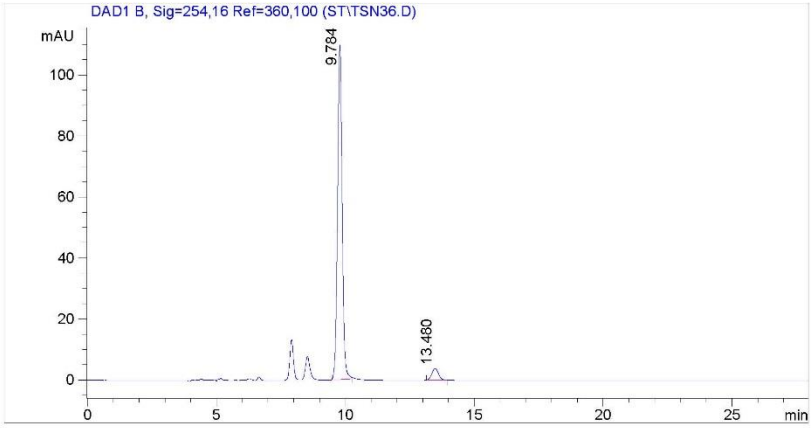
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 14:13:12
Injektion Date: 30.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.7	41.2
Flow in ml/min:	0.70	0.70



2j



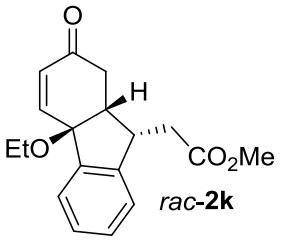
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.78	0.19	109.82	1368.18	95.11
2	13.48	0.28	3.90	70.40	4.89
Total				1438.58	100.00

Sample Name: TSN29 rac
Data file: D:\GONZO\ST\TSN29RIA.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

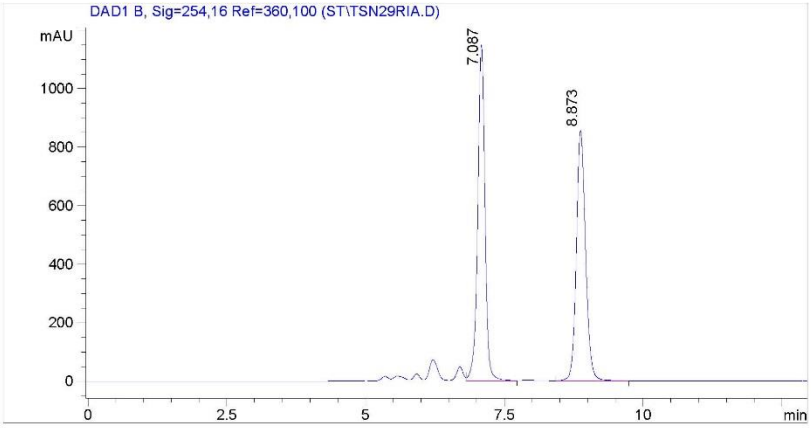
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 14:58:43
Injektion Date: 17.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.5	41.4
Flow in ml/min:	0.70	0.70



rac-**2k**



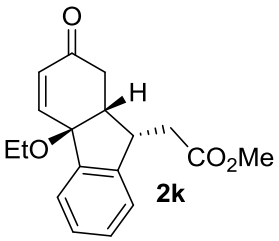
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.09	0.14	1149.73	10427.11	51.27
2	8.87	0.17	856.47	9908.66	48.73
Total				20335.78	100.00

Sample Name: TSN30
Data file: D:\GONZO\ST\TSN30.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

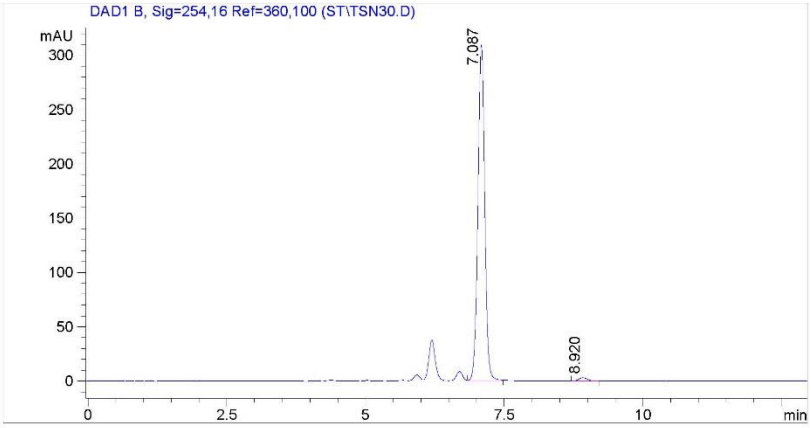
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 15:27:14
Injektion Date: 17.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	41.0	41.1
Flow in ml/min:	0.70	0.70



2k



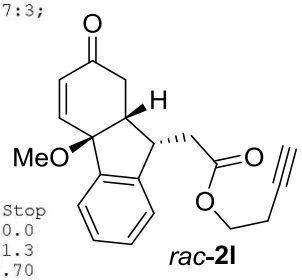
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.09	0.13	309.83	2639.72	98.74
2	8.92	0.17	3.06	33.66	1.26
Total				2673.38	100.00

Sample Name: TSN39 rac
Data file: D:\GONZO\ST\TSN39RIA.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

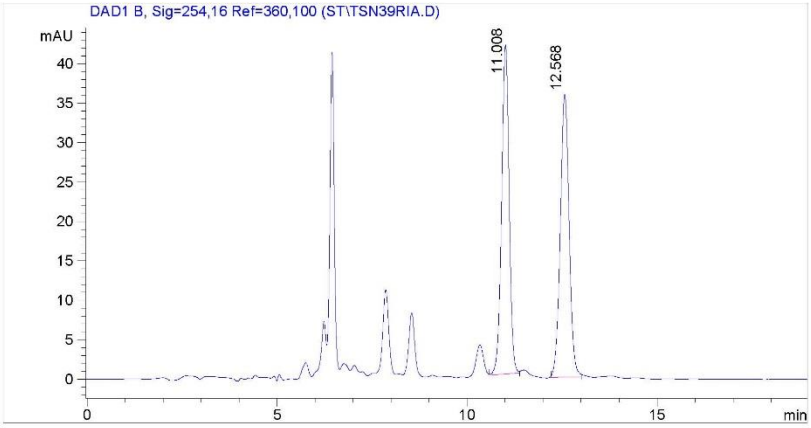
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 15:33:50
Injektion Date: 30.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	41.0	41.3
Flow in ml/min:	0.70	0.70



rac-**2l**



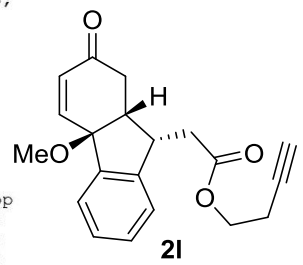
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	11.01	0.21	41.79	577.55	49.94
2	12.57	0.25	35.88	578.94	50.06
Total				1156.49	100.00

Sample Name: TSN40
Data file: D:\GONZO\ST\TSN40.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

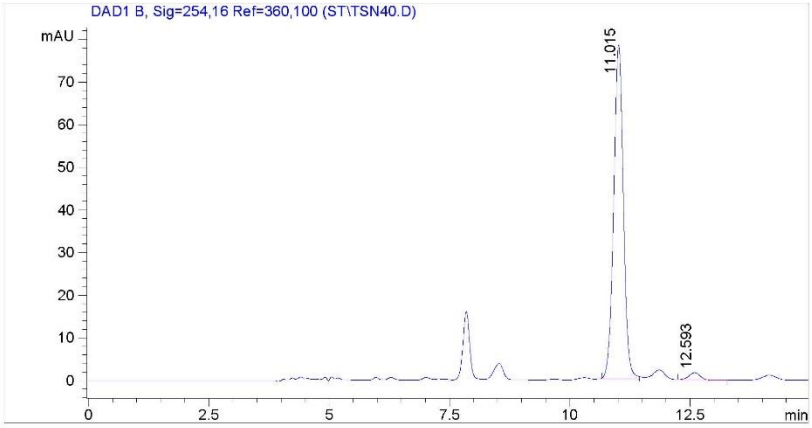
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 16:41:41
Injektion Date: 30.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.7	40.8
Flow in ml/min:	0.70	0.70



2l



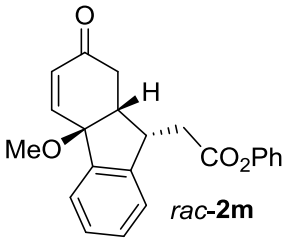
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	11.01	0.21	78.37	1094.86	97.72
2	12.59	0.24	1.66	25.53	2.28
Total				1120.39	100.00

Sample Name: TSN37 rac
Data file: D:\GONZO\ST\TSN37RIA.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

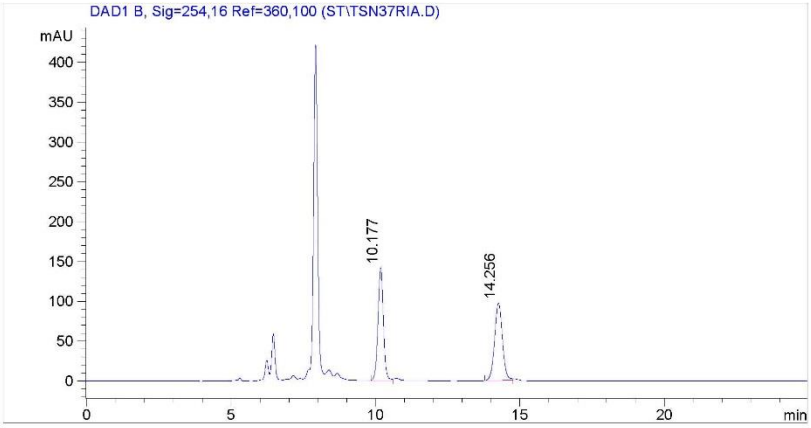
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 13:46:54
Injektion Date: 30.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.8	40.7
Flow in ml/min:	0.70	0.70



rac-**2m**



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	10.18	0.20	141.52	1829.91	50.15
2	14.26	0.29	97.27	1818.62	49.85
Total				3648.53	100.00

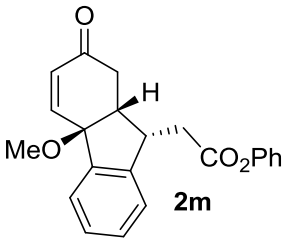
HEWLETT PACKARD

Sample Name: TSN38
Data file: D:\GONZO\ST\TSN38.D
Sample Info: Mobile phase: n-Heptan/iPrOH 7:3;
The sample is solved in MP

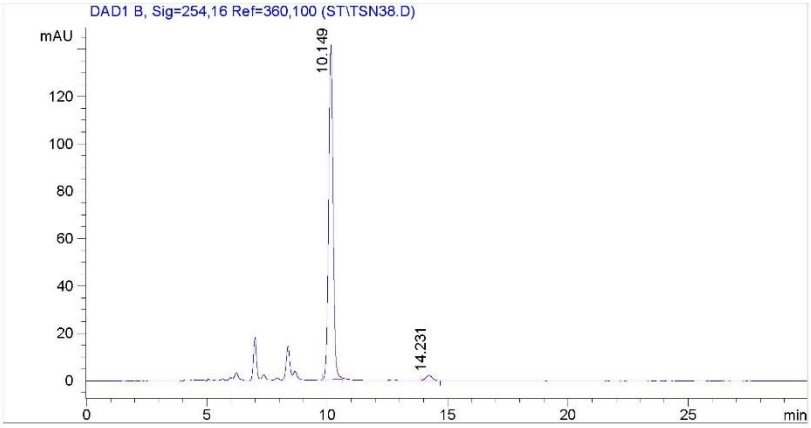
Methode file: IA.M
Column-info: Chiralpak IA (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 14:42:24
Injektion Date: 30.01.2018

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	40.8	41.4
Flow in ml/min:	0.70	0.70



2m



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	10.15	0.20	141.33	1822.05	97.80
2	14.23	0.28	2.20	40.90	2.20
Total				1862.95	100.00