Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Enantioselective access to spiro[2,3-dihydrofuran-2,2'-inden-1-ones] via zinc catalyzed [3 + 2] annulation of α-hydroxy-1-indanones with yne-enones

Jiao-Jiao Han, Tao Jiang, Cui Zhang, Dan-Dan Cui, Yuan-Zhao Hua,* Guang-Jian Mei, Min-Can Wang,* and Shi-Kun Jia*

College of Chemistry and Institute of Green Catalysis, Zhengzhou University, Zhengzhou City, Henan 450000, P. R. China

Email: hyzhao@zzu.edu.cn, wangmincan@zzu.edu.cn, jiashikun@zzu.edu.cn

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General Information

All reactions were carried out under an atmosphere of argon using oven-dried glassware. Super dry solvents, metal catalysts, were purchased from chemical companies and used without further treatment. Flash column chromatography was performed using silica gel (300-400 mesh). ^{1}H NMR ,^{13}C NMR, ^{19}F NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 MHz spectrometer; chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (*J*) are given in Hertz. The peak information is described as: s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet. High-resolution mass spectra (HRMS) were obtained using an Agilent LC-MSAD-Trap-XCT instrument using electrospray ionization time-of-flight (ESI-TOF). High performance liquid chromatography (HPLC) was performed on instrument consisted of JASCO model PU-1580 intelligent HPLC pump and JASCO model UV-1575 intelligent UV-vis detector (254 nm) using Daicel Chiralpak IC, ID (4.6 mm × 250 mm) columns. Melting points were determined using YRT-3 melting point apparatus. Optical rotations were measured with Perkin Elmer, model 341 Polarimeter. The instrumentation used for the crystal measurement is Oxford Gemini E X-ray single-crystal diffractometer. α-Hydroxy-1-indanones[1] and yne-enones[2] were synthesized according to the literature.

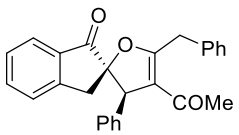
General Procedure for optimization of the reaction conditions

Under a nitrogen atmosphere, a solution of diethylzinc (20 μL, 1.0 M in hexane, 0.02 mmol, 0.2 eq) was added dropwise to a solution of **L** (0.01 mmol, 0.1 eq) in solvent (2 mL). After the mixture was stirred for 30 min at 40 ℃, then, α-hydroxy-1-indanone **1a** (0.1 mmol, 14.8 mg, 1.0 eq), yne-enone **2a** (0.1 mmol, 24.6 mg, 1.0 eq), and additives were added. The reaction mixture was stirred for 48 h at the same temperature. The reaction was quenched with NH_4Cl solution (2 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum ether/ethyl acetate (4/1) to afford the desired product **3a**.

Synthesis of chiral spiro[2,3-dihydrofuran-2,2'-inden-1-ones]

Under a nitrogen atmosphere, a solution of diethylzinc (40 μL, 1.0 M in hexane, 0.04 mmol, 0.2 eq) was added dropwise to a solution of **L1** (0.02 mmol, 14.0 mg, 0.1 eq) in toluene (2 mL). After the mixture was stirred for 30 min at 40 ℃. Then, α-hydroxy-1-indanone **1a** (0.2 mmol, 29.6 mg, 1.0 eq), yne-enone **2a** (0.2 mmol, 49.2 mg, 1.0 eq) and 2-Br-4-ClPhOH (0.04 mmol, 8.28 mg, 0.2 eq) were added. The reaction mixture was stirred for 48 h at 40 ℃. The reaction was quenched with NH_4Cl solution (4 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum ether/ethyl acetate (4/1) to afford the desired product **3a**.

(2*R*,3*R*)-4-acetyl-5-benzyl-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3a):

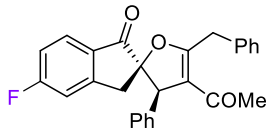


3a

Followed the general procedure, using **1a** (0.2 mmol, 29.6 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.1 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1)

to afforded **3a** as a light yellow oil (54.2 mg, 65% yield, >20:1 dr); $[\alpha]_D^{20}$ = -152.8 (c = 2.0, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.64 (m, 1H), 7.49 – 7.40 (m, 1H), 7.38 – 7.13 (m, 9H), 7.09 -7.02 (m, 1H), 6.90 (s, 2H), 4.48 (s, 1H), 4.12 (dd, *J* = 92.8, 14.2 Hz, 2H), 2.72 (dd, *J* = 96.5, 17.6 Hz, 2H), 1.82 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 194.6, 169.4, 150.7, 139.4, 136.4, 136.0, 133.3, 129.1, 129.0, 128.5, 128.2, 128.0, 126.7, 126.3, 125.3, 116.0, 93.1, 53.8, 36.2, 34.2, 29.8; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{27}H_{22}NaO_3]^+$: 417.1461, found: 417.1462; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 21.87 min and t_{minor} = 10.83 min.

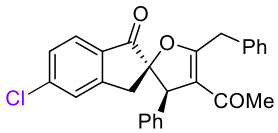
(2*R*,3*R*)-4-acetyl-5-benzyl-5'-fluoro-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3b):



3b

Followed the general procedure, using **1b** (0.2 mmol, 33.4 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.2 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3b** as a light yellow oil (67.9 mg, 78% yield, >20:1 dr); $[\alpha]_D^{20}$ = -133.8 (c = 2.0, DCM, 97% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 1H), 7.43 – 7.37 (m, 2H), 7.35 – 7.27 (m, 5H), 7.26 – 7.21 (m, 1H), 7.12 – 7.06 (m, 1H), 6.99 (s, 2H), 6.86 – 6.79 (m, 1H), 4.57 (s, 1H), 4.20 (dd, *J* = 92.2, 14.4 Hz, 2H), 2.79 (dd, *J* = 94.1, 17.9 Hz, 2H), 1.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.7, 194.6, 169.2, 167.8(d, *J* = 258.7Hz), 153.7 (d, *J* = 10.5 Hz), 139.2, 136.3, 129.6 (d, *J* = 1.8 Hz), 129.2, 129.0, 128.5, 128.1, 127.8 (d, *J* = 10.6 Hz), 126.8, 116.6 (d, *J* = 23.8 Hz), 116.0, 113.2 (d, *J* = 22.6 Hz), 93.1, 53.9, 36.2, 34.2, 29.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -99.7; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{27}H_{21}FNaO_3]^+$: 435.1367, found: 435.1375; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 21.35 min and t_{minor} = 11.26 min.

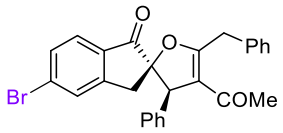
(2*R*,3*R*)-4-acetyl-5-benzyl-5'-chloro-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3c):



3c

Followed the general procedure, using **1c** (0.2 mmol, 36.4 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3c** as a light yellow oil (57.7 mg, 64% yield, >20:1 dr); $[\alpha]_D^{20}$ = -164.6 (c = 1.0, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.35 – 7.29 (m, 4H), 7.29 – 7.21 (m, 2H), 7.16 (s, 1H), 6.99 (s, 2H), 4.56 (s, 1H), 4.20 (dd, *J* = 90.6, 14.3 Hz, 2H), 2.78 (dd, *J* = 95.0, 17.9 Hz, 2H), 1.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.1, 194.6, 169.3, 152.3, 142.6, 139.1, 136.3, 131.7, 129.2, 129.1, 129.0, 128.5, 128.1, 126.8, 126.5, 126.4, 116.0, 93.0, 53.8, 36.0, 34.1, 29.8; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{27}H_{21}ClNaO_3]^+$: 451.1071, found: 451.1078; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 22.86 min and t_{minor} = 11.50 min.

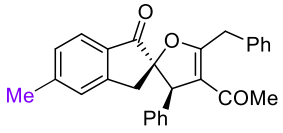
(2*R*,3*R*)-4-acetyl-5-benzyl-5'-bromo-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3d):



3d

Followed the general procedure, using **1d** (0.2 mmol, 45.4 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3d** as a light yellow oil (64.4 mg, 65% yield, >20:1 dr); $[\alpha]_D^{20}$ = -123.4 (c = 2.0, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.27 (m, 6H), 7.26 – 7.22 (m, 1H), 7.05 – 6.92 (m, 2H), 4.55 (s, 1H), 4.19 (dd, *J* = 90.0, 14.3 Hz, 2H), 2.78 (dd, *J* = 94.4, 17.9 Hz, 2H), 1.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.3, 194.6, 169.2, 152.2, 139.1, 136.3, 132.1, 132.0, 131.6, 129.6, 129.2, 129.0, 128.6, 128.1, 126.8, 126.5, 116.0, 92.9, 53.8, 35.9, 34.2, 29.8; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{27}H_{21}BrNaO_3]^+$: 495.0566, found: 495.0569; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 29.59 min and t_{minor} = 14.15 min.

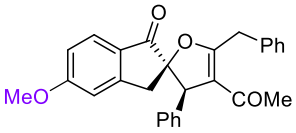
(2*R*,3*R*)-4-acetyl-5-benzyl-5'-methyl-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3e):



3e

Followed the general procedure, using **1e** (0.2 mmol, 32.2 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3e** as a light yellow oil (63.0 mg, 73% yield, >20:1 dr); $[\alpha]_D^{20}$ = -191.3 (c = 2.0, DCM, 94% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.36 – 7.23 (m, 6H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.09 – 6.88 (m, 3H), 4.56 (s, 1H), 4.20 (dd, *J* = 101.6, 14.3 Hz, 2H), 2.75 (dd, *J* = 95.1, 17.7 Hz, 2H), 2.37 (s, 3H), 1.90 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.0, 194.7, 169.4, 151.2, 147.6, 139.5, 136.4, 130.9, 129.5, 129.1, 129.0, 128.5, 127.9, 126.7, 126.6, 125.2, 116.0, 93.3, 53.9, 36.1, 34.2, 29.8, 22.2; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{28}H_{24}NaO_3]^+$: 431.1618, found: 431.1623; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 32.91 min and t_{minor} = 12.82 min.

(2*R*,3*R*)-4-acetyl-5-benzyl-5'-methoxy-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3f):

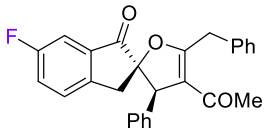


3f

Followed the general procedure, using **1f** (0.2 mmol, 35.4 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3f** as a light yellow oil (57.2 mg, 64% yield, >20:1 dr); $[\alpha]_D^{20}$ = -182.1 (c = 2.0, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.6 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.21 – 7.12 (m, 4H), 7.01 – 6.86 (m, 2H), 6.85 – 6.80 (m, 1H), 6.55 – 6.45 (m, 1H), 4.51 (s, 1H), 4.12 (dd, *J* = 107.5, 14.3 Hz, 2H), 3.72 (s, 3H), 2.67 (dd, *J* = 89.9, 17.8 Hz, 2H), 1.82 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.6, 194.7, 169.4, 166.3, 153.9, 139.6, 136.5, 129.1, 129.0,

128.5, 127.8, 127.1, 126.7, 126.2, 116.2, 116.0, 109.5, 93.4, 55.7, 53.9, 36.4, 34.2, 29.8; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for [$C_{28}H_{24}NaO_4$]$^+$: 447.1567, found: 447.1568; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 61.12 min and t_{minor} = 22.59 min.

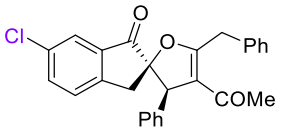
(2*R*,3*R*)-4-acetyl-5-benzyl-6'-fluoro-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3g):



3g

Followed the general procedure, using **1g** (0.2 mmol, 33.0 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3g** as a light yellow oil (60.9 mg, 70% yield, >20:1 dr); $[\alpha]_D^{20}$ = -102.4 (c = 2.0, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 1H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.36 – 7.26 (m, 6H), 7.26 – 7.22 (m, 1H), 7.16 – 7.11 (m, 1H), 7.07 – 6.90 (m, 2H), 4.55 (s, 1H), 4.20 (dd, *J* = 82.3, 14.4 Hz, 2H), 2.77 (dd, *J* = 96.3, 17.4 Hz, 2H), 1.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.7 (d, *J* = 2.7 Hz), 194.6, 169.3, 162.6 (d, *J* = 249.5 Hz), 146.2, 139.1, 136.3, 135.0 (d, *J* = 7.4 Hz), 129.2, 129.0, 128.6, 128.1, 127.8 (d, *J* = 7.8 Hz), 126.8, 123.7 (d, *J* = 23.6 Hz), 116.0, 111.1 (d, *J* = 22.1 Hz), 93.6, 53.8, 35.7, 34.2, 29.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.6; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for [$C_{27}H_{21}FNaO_3$]$^+$: 435.1367, found: 435.1370; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 19.81 min and t_{minor} = 13.21 min.

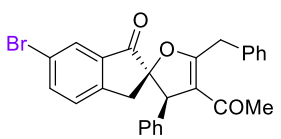
(2*R*,3*R*)-4-acetyl-5-benzyl-6'-chloro-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3h):



3h

Followed the general procedure, using **1h** (0.2 mmol, 36.5 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3h** as a light yellow oil (67.7 mg, 75% yield, >20:1 dr); $[\alpha]_D^{20}$ = -132.2 (c = 3.0, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 1H), 7.53 – 7.48 (m, 1H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.36 – 7.29 (m, 4H), 7.28 – 7.21 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.06 – 6.87 (m, 2H), 4.54 (s, 1H), 4.20 (dd, *J* = 84.0, 14.4 Hz, 2H), 2.77 (dd, *J* = 96.7, 17.7 Hz, 2H), 1.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.3, 194.6, 169.2, 148.8, 139.1, 136.2, 136.0, 134.8, 134.6, 129.2, 129.0, 128.6, 128.1, 127.6, 126.8, 125.0, 116.0, 93.3, 53.8, 35.8, 34.1, 29.8; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for [$C_{27}H_{21}ClNaO_3$]$^+$: 451.1071, found: 451.1078; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 21.44 min and t_{minor} = 12.64 min.

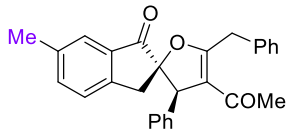
(2*R*,3*R*)-4-acetyl-5-benzyl-6'-bromo-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3i):



3i

Followed the general procedure, using **1i** (0.2 mmol, 45.2 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3i** as a light yellow oil (59.4 mg, 60% yield, >20:1 dr); $[\alpha]_D^{20}$ = -115.7 (c = 2.0, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.86 (m, 1H), 7.68 – 7.61 (m, 1H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.35 – 7.27 (m, 5H), 7.26 – 7.22 (m, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 7.03 – 6.84 (m, 2H), 4.54 (s, 1H), 4.20 (dd, *J* = 84.9, 14.4 Hz, 2H), 2.74 (dd, *J* = 96.3, 17.8 Hz, 2H), 1.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.1, 194.6, 169.2, 149.2, 139.0, 138.8, 136.2, 135.1, 129.2, 129.0, 128.6, 128.1, 128.1, 127.9, 126.8, 122.3, 116.0, 93.2, 53.8, 35.9, 34.1, 29.8; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{27}H_{21}BrNaO_3]^+$: 495.0566, found: 495.0573; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 25.41 min and t_{minor} = 13.54 min.

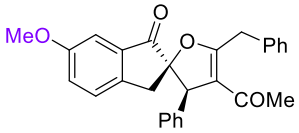
(2*R*,3*R*)-4-acetyl-5-benzyl-6'-methyl-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3j):



3j

Followed the general procedure, using **1j** (0.2 mmol, 32.2 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3j** as a light yellow oil (68.1 mg, 79% yield, >20:1 dr); $[\alpha]_D^{20}$ = -155.3 (c = 1.7, DCM, 99% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.44 – 7.39 (m, 2H), 7.39 – 7.26 (m, 6H), 7.26 – 7.21 (m, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 7.03 – 6.85 (m, 2H), 4.55 (s, 1H), 4.21 (dd, *J* = 95.8, 14.3 Hz, 2H), 2.75 (dd, *J* = 99.5, 17.5 Hz, 2H), 2.39 (s, 3H), 1.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.6, 194.7, 169.5, 148.1, 139.4, 138.3, 137.3, 136.4, 133.4, 129.1, 129.0, 128.5, 127.9, 126.7, 126.0, 125.2, 115.9, 93.5, 53.8, 35.9, 34.2, 29.8, 21.2; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{28}H_{24}NaO_3]^+$: 431.1618, found: 431.1628; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 33.75 min and t_{minor} =12.19 min.

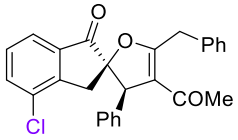
(2*R*,3*R*)-4-acetyl-5-benzyl-6'-methoxy-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3k):



3k

Followed the general procedure, using **1k** (0.2 mmol, 35.4 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3k** as a light yellow oil (58.1 mg, 65% yield, >20:1 dr); $[\alpha]_D^{20}$ = -227.2 (c = 1.0, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.35 – 7.26 (m, 5H), 7.25 – 7.18 (m, 2H), 7.16 – 7.12 (m, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 7.03 – 6.84 (m, 2H), 4.55 (s, 1H), 4.21 (dd, *J* = 86.3, 14.3 Hz, 2H), 3.83 (s, 3H), 2.73 (dd, *J* = 97.8, 17.3 Hz, 2H), 1.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 194.6, 169.5, 159.9, 143.6, 139.4, 136.4, 134.4, 129.1, 129.0, 128.5, 127.9, 127.1, 126.7, 125.4, 115.9, 106.4, 93.8, 55.7, 53.9, 35.6, 34.2, 29.8; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{28}H_{24}NaO_4]^+$: 447.1567, found: 447.1575; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 45.15 min and t_{minor} = 14.44 min.

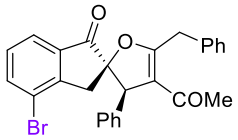
(2*R*,3*R*)-4-acetyl-5-benzyl-4'-chloro-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3l):



3l

Followed the general procedure, using **1l** (0.2 mmol, 36.5 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3l** as a light yellow oil (58.6 mg, 65% yield, >20:1 dr); $[\alpha]_D^{20}$ = -104.0 (c = 2.0, DCM, 99% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.38 – 7.28 (m, 6H), 7.27 – 7.22 (m, 1H), 7.08 – 6.87 (m, 2H), 4.57 (s, 1H), 4.20 (dd, *J* = 85.1, 14.4 Hz, 2H), 2.79 (dd, *J* = 91.4, 18.2 Hz, 2H), 1.93 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.7, 194.6, 169.1, 148.4, 138.9, 136.2, 135.6, 135.2, 132.6, 129.7, 129.3, 129.0, 128.6, 128.2, 126.8, 123.5, 116.0, 92.8, 53.8, 35.2, 34.1, 29.8, 29.7; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{27}H_{21}ClNaO_3]^+$: 451.1071, found: 451.1073; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 21.23 min and t_{minor} =11.20 min.

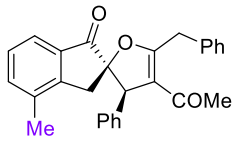
(2*R*,3*R*)-4-acetyl-5-benzyl-4'-bromo-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3m):



3m

Followed the general procedure, using **1m** (0.2 mmol, 45.2 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3m** as a light yellow oil (62.4 mg, 63% yield, >20:1 dr); $[\alpha]_D^{20}$ = -172.2 (c = 2.0, DCM, 99% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 2H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.27 (m, 6H), 7.26 – 7.22 (m, 1H), 7.09 – 6.85 (m, 2H), 4.56 (s, 1H), 4.21 (dd, *J* = 83.0, 14.4 Hz, 2H), 2.74 (dd, *J* = 94.7, 18.1 Hz, 2H), 1.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.9, 194.6, 169.2, 150.4, 138.8, 138.7, 136.2, 135.3, 129.9, 129.3, 129.0, 128.6, 128.2, 126.8, 124.1, 121.8, 116.0, 92.8, 53.8, 37.2, 34.2, 29.8; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{27}H_{21}BrNaO_3]^+$: 495.0566, found: 495.0573; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 22.90 min and t_{minor} =11.81 min.

(2*R*,3*R*)-4-acetyl-5-benzyl-4'-methyl-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3n):

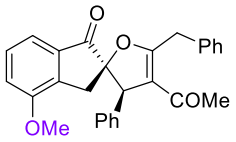


3n

Followed the general procedure, using **1n** (0.2 mmol, 32.2 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3n** as a light yellow oil (58.6 mg, 68% yield, >20:1 dr); $[\alpha]_D^{20}$ = -145.0 (c = 2.0, DCM, 96% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.26 (m, 7H), 7.25 – 7.21 (m, 1H), 7.09 – 6.81 (m, 2H), 4.55 (s, 1H), 4.22 (dd, *J* = 102.9, 14.3 Hz, 2H), 2.67 (dd, *J* = 97.0, 17.5 Hz, 2H), 2.00 (s, 3H), 1.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ

200.9, 194.7, 169.6, 149.6, 139.3, 136.5, 136.4, 135.6, 133.1, 129.1, 129.0, 128.5, 128.3, 128.0, 126.7, 122.7, 115.7, 93.3, 54.0, 34.8, 34.2, 29.8, 17.6; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for [$C_{28}H_{24}NaO_3$]$^+$: 431.1618, found: 431.1626; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 33.90 min and t_{minor} =14.63 min.

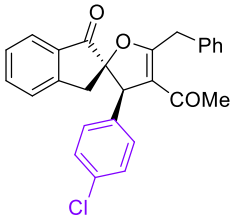
(2*R*,3*R*)-4-acetyl-5-benzyl-4'-methoxy-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3o):



3o

Followed the general procedure, using **1o** (0.2 mmol, 35.4 mg), **2a** (0.2 mmol, 49.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3o** as a light yellow oil (66.2 mg, 74% yield, >20:1 dr); $[\alpha]_D^{20}$ = -283.3 (c = 2.0, DCM, 97% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 3H), 7.37 – 7.26 (m, 6H), 7.25 – 7.20 (m, 1H), 7.08 – 6.95 (m, 3H), 4.59 (s, 1H), 4.18 (dd, *J* = 107.2, 14.3 Hz, 2H), 3.72 (s, 3H), 2.73 (dd, *J* = 80.7, 18.2 Hz, 2H), 1.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.7, 194.7, 169.1, 156.5, 139.8, 139.4, 136.4, 134.6, 129.7, 129.1, 129.0, 128.5, 127.9, 126.7, 116.7, 116.3, 116.3, 92.9, 55.4, 53.6, 34.2, 33.1, 29.8; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for [$C_{28}H_{24}NaO_4$]$^+$: 447.1567, found: 447.1567; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 31.25 min and t_{minor} =14.12 min.

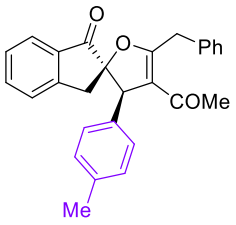
(2*R*,3*R*)-4-acetyl-5-benzyl-3-(4-chlorophenyl)-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3p):



3p

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2b** (0.2 mmol, 56.3 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3p** as a light yellow oil (67.7 mg, 75% yield, >20:1 dr); $[\alpha]_D^{20}$ = -230.0 (c = 2.3, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.46 – 7.37 (m, 3H), 7.37 – 7.30 (m, 2H), 7.29 – 7.22 (m, 3H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.01 – 6.82 (m, 2H), 4.54 (s, 1H), 4.19 (dd, *J* = 88.6, 14.4 Hz, 2H), 2.82 (dd, *J* = 110.0, 17.6 Hz, 2H), 1.95 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.1, 194.1, 169.6, 150.4, 138.0, 136.2, 133.8, 133.2, 129.6, 129.3, 129.0, 128.6, 128.4, 126.8, 126.3, 125.4, 116.1, 92.9, 53.1, 36.1, 34.2, 29.7; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for [$C_{27}H_{21}ClNaO_3$+]$^+$: 451.1071, found: 451.1075; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 22.83 min and t_{minor} =11.71 min.

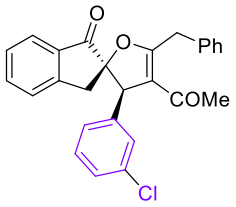
(2*R*,3*R*)-4-acetyl-5-benzyl-3-(*p*-tolyl)-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3q):



3q

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2c** (0.2 mmol, 52.0 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3q** as a light yellow oil (70.7 mg, 82% yield, >20:1 dr); $[\alpha]_D^{20}$ = -254.2 (c = 2.8, DCM, 96% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.44 – 7.35 (m, 3H), 7.34 – 7.28 (m, 2H), 7.24 (d, *J* = 6.3 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.13 – 7.03 (m, 2H), 6.96 – 6.77 (m, 2H), 4.52 (s, 1H), 4.20 (dd, *J* = 91.9, 14.3 Hz, 2H), 2.82 (dd, *J* = 82.4, 17.6 Hz, 2H), 2.32 (s, 3H), 1.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.6, 194.8, 169.3, 150.8, 137.7, 136.5, 136.3, 136.0, 133.3, 129.8, 129.0, 128.5, 128.2, 126.7, 126.3, 125.3, 116.0, 93.2, 53.5, 36.2, 34.2, 29.8, 21.2; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{28}H_{24}NaO_3]^+$: 431.1618, found: 431.1626; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 25.04 min and t_{minor} =12.90 min.

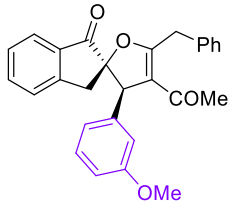
(2*R*,3*R*)-4-acetyl-5-benzyl-3-(3-chlorophenyl)-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3r):



3r

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2d** (0.2 mmol, 56.3 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3r** as a light yellow oil (72.2 mg, 80% yield, >20:1 dr); $[\alpha]_D^{20}$ = -216.6 (c = 4.0, DCM, 96% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.46 – 7.37 (m, 3H), 7.37 – 7.30 (m, 2H), 7.28 – 7.18 (m, 4H), 7.06 – 6.78 (m, 2H), 4.53 (s, 1H), 4.20 (dd, *J* = 91.1, 14.4 Hz, 2H), 2.82 (dd, *J* = 115.3, 17.7 Hz, 2H), 1.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ200.0, 194.0, 169.7, 150.5, 141.7, 136.2, 136.1, 133.1, 130.4, 128.9, 128.6, 128.4, 128.2, 126.9, 126.3, 125.4, 116.0, 92.9, 53.3, 36.2, 34.2, 29.8; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{27}H_{21}ClNaO_3]^+$: 451.1071, found: 451.1072; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 21.49 min and t_{minor} =10.85 min.

(2*R*,3*R*)-4-acetyl-5-benzyl-3-(3-methoxyphenyl)-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3s):

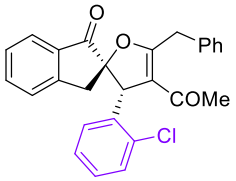


3s

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2e** (0.2 mmol, 55.2 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1)

to afforded **3s** as a light yellow oil (63.5 mg, 71% yield, >20:1 dr); $[\alpha]_D^{20}$ = -265.0 (c = 3.0, DCM, 97% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.48 – 7.35 (m, 3H), 7.35 – 7.27 (m, 2H), 7.27 – 7.16 (m, 3H), 6.83 – 6.76 (m, 1H), 6.75 – 6.26 (m, 2H), 4.52 (s, 1H), 4.20 (dd, *J* = 151.6, 13.3 Hz, 2H), 3.62 (s, 3H), 2.83 (dd, *J* = 89.7, 17.7 Hz, 2H), 1.93 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 194.7, 169.5, 150.9, 141.0, 136.6, 136.0, 133.2, 130.1, 129.1, 128.5, 128.2, 126.7, 126.3, 125.4, 115.7, 93.1, 55.1, 53.7, 36.2, 34.2, 29.8; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{28}H_{24}NaO_4]^+$: 447.1567, found: 447.1574; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 33.41 min and t_{minor} =14.05 min.

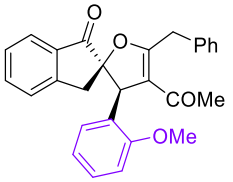
(2*R*,3*R*)-4-acetyl-5-benzyl-3-(2-chlorophenyl)-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3t):



3t

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2f** (0.2 mmol, 56.3 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3t** as a light yellow oil (58.6 mg, 65% yield, 6:1 dr); $[\alpha]_D^{20}$ = -109.8 (c = 3.0, DCM, 89% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.43 – 7.38 (m, 3H), 7.35 – 7.29 (m, 3H), 7.27 – 7.18 (m, 4H), 7.15 – 7.10 (m, 1H), 5.24 (s, 1H), 4.20 (dd, *J* = 97.7, 14.3 Hz, 2H), 2.79 (dd, *J* = 94.9, 17.8 Hz, 2H), 1.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.0, 194.5, 169.8, 150.9, 137.2, 136.3, 136.1, 134.3, 133.1, 129.8, 129.4, 129.1, 129.0, 128.6, 128.2, 127.7, 126.8, 126.2, 125.4, 115.1, 92.6, 49.2, 36.4, 34.2, 29.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{27}H_{21}ClNaO_3]^+$: 451.1071, found: 451.1078; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =15.07 min and t_{minor} =11.42 min.

(2*R*,3*R*)-4-acetyl-5-benzyl-3-(2-methoxyphenyl)-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3u):

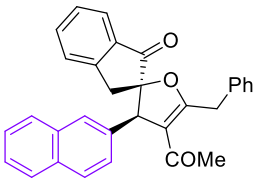


3u

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2g** (0.2 mmol, 55.2 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3u** as a light yellow oil (51.0 mg, 57% yield, >20:1 dr); $[\alpha]_D^{20}$ = -70.6 (c = 2.0, DCM, 89% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.36 (m, 1H), 7.33 – 7.29 (m, 2H), 7.26 – 7.21 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.06 – 7.03 (m, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 5.13 (s, 1H), 4.19 (dd, *J* = 107.2, 14.4 Hz, 2H), 3.24 (s, 3H), 2.75 (dd, *J* = 74.3, 17.7 Hz, 2H), 1.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.3, 195.2, 169.4, 156.9, 151.2, 136.6, 135.6, 133.6, 129.0, 128.9, 128.5, 128.4, 127.8, 127.4, 126.6, 126.0, 125.0, 121.0, 114.2, 110.1, 92.8, 54.6, 46.9, 36.6, 34.2, 29.4; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{28}H_{24}NaO_4]^+$: 447.1567, found: 447.1574; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =27.71 min and

t_{minor} =18.73 min.

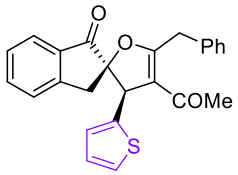
(2*R*,3*R*)-4-acetyl-5-benzyl-3-(naphthalen-2-yl)-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3v):



3v

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2h** (0.2 mmol, 59.2 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3v** as a light yellow oil (68.2 mg, 73% yield, >20:1 dr); $[\alpha]_D^{20}$ = -280.7 (c = 3.0, DCM, 93% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 3H), 7.70 – 7.65 (m, 1H), 7.54 – 7.44 (m, 6H), 7.40 – 7.33 (m, 3H), 7.30 – 7.25 (m, 1H), 7.20 – 6.93 (m, 2H), 4.73 (s, 1H), 4.26 (dd, *J* = 115.1, 14.1 Hz, 2H), 2.82 (dd, *J* = 103.9, 17.7 Hz, 2H), 1.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 194.7, 169.6, 150.8, 136.9, 136.5, 136.1, 133.4, 133.2, 133.0, 129.1, 128.6, 128.3, 127.9, 127.8, 126.8, 126.6, 126.3, 125.4, 116.1, 93.1, 53.9, 36.3, 34.3, 29.9; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{31}H_{24}NaO_3]^+$: 467.1618, found: 467.1616; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =28.91 min and t_{minor} =13.78 min.

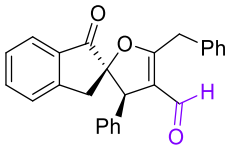
(2*R*,3*R*)-4-acetyl-5-benzyl-3-(thiophen-2-yl)-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3w):



3w

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2i** (0.2 mmol, 50.4 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3w** as a light yellow oil (46.5 mg, 55% yield, 2.5:1 dr); $[\alpha]_D^{20}$ = -206.5 (c = 2.0, DCM, 98%/98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.73 (m, 1H), 7.62 – 7.55 (m, 1H), 7.43 – 7.36 (m, 3H), 7.35 – 7.29 (m, 3H), 7.27 – 7.22 (m, 2H), 6.99 – 6.94 (m, 1H), 6.72 (d, *J* = 3.4 Hz, 1H), 4.82 (s, 1H), 4.47 – 4.31 (m, 1H), 4.14 – 3.95 (m, 1H), 3.05 – 2.98 (m, 1H), 2.91 – 2.82 (m, 1H), 2.01 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.1, 194.3, 169.6, 150.8, 143.9, 136.3, 136.2, 133.2, 129.0, 128.5, 128.3, 127.5, 126.7, 126.4, 126.2, 125.8, 125.4, 116.2, 93.0, 48.7, 35.7, 34.2, 29.5; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{20}NaO_3S]^+$: 423.1025, found: 423.1029; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, major product: t_{major} = 23.17 min and t_{minor} = 12.34 min; minor product: t_{major} = 20.17 min and t_{minor} = 11.43 min.

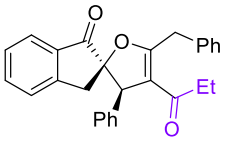
(2*R*,3*R*)-5-benzyl-1'-oxo-3-phenyl-1',3'-dihydro-3*H*-spiro[furan-2,2'-indene]-4-carbaldehyde (3x):



3x

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2j** (0.2 mmol, 46.4 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3x** as a light yellow oil (52.4 mg, 65% yield, >20:1 dr); $[\alpha]_D^{20}$ = -303.0 (c = 2.0, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.41 – 7.34 (m, 5H), 7.31 – 7.28 (m, 1H), 7.26 – 7.22 (m, 3H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.00 – 6.90 (m, 2H), 4.54 (s, 1H), 4.08 (dd, *J* = 35.9, 15.1 Hz, 2H), 2.86 (dd, *J* = 101.7, 17.7 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.1, 184.2, 174.5, 150.6, 138.2, 136.2, 135.0, 133.2, 128.9, 128.8, 128.8, 128.3, 128.1, 127.7, 127.4, 126.3, 125.4, 119.6, 94.4, 51.3, 35.8, 33.2; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{26}H_{20}NaO_3]^+$: 403.1305, found: 403.1308; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =46.57 min and t_{minor} =50.78 min.

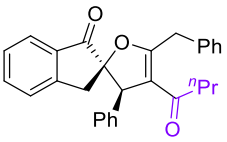
(2*R*,3*R*)-5-benzyl-3-phenyl-4-propionyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3y):



3y

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2k** (0.2 mmol, 52.0 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3y** as a light yellow oil (72.4 mg, 84% yield, 10:1 dr); $[\alpha]_D^{20}$ = -272.1 (c = 2.7, DCM, 99%/92% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.31 – 7.19 (m, 4H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.08 – 6.86 (m, 2H), 4.57 (s, 1H), 4.35 (d, *J* = 14.3 Hz, 1H), 4.08 (d, *J* = 14.3 Hz, 1H), 2.92 (d, *J* = 17.6 Hz, 1H), 2.67 (d, *J* = 17.7 Hz, 1H), 2.47 – 2.32 (m, 1H), 1.98 – 1.84 (m, 1H), 0.89 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 197.5, 168.9, 150.8, 139.5, 136.6, 136.0, 133.3, 129.7, 129.1, 128.5, 128.2, 127.9, 126.6, 126.3, 125.3, 115.6, 93.1, 53.4, 36.2, 34.6, 34.2, 7.6; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{28}H_{24}NaO_3]^+$: 431.1618, found: 431.1621; **HPLC**: Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1 mL/min, λ = 254 nm, major product: t_{major} = 18.90 min and t_{minor} = 23.60 min; minor product: t_{major} = 17.56 min and t_{minor} = 13.62 min.

(2*R*,3*R*)-5-benzyl-4-butyryl-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3z):

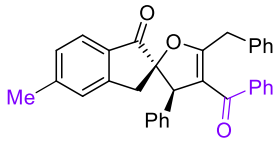


3z

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2l** (0.2 mmol, 54.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3z** as a light yellow oil (67.7 mg, 76% yield, 5:1 dr); $[\alpha]_D^{20}$ = -255.1 (c = 2.0, DCM, 94%/53% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.45 – 7.36 (m, 3H), 7.34 – 7.30 (m, 2H), 7.29 – 7.21 (m, 4H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.10 – 6.84 (m, 2H), 4.58 (s, 1H), 4.33 (d, *J* = 14.3 Hz, 1H), 4.08 (d, *J* = 14.3 Hz, 1H), 2.80 (dd, *J* = 97.3, 17.6 Hz, 2H), 2.41 – 2.26 (m, 1H), 2.00 – 1.84 (m, 1H), 1.58 – 1.33 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.6, 197.1, 168.9, 150.8, 139.5, 136.6, 136.0, 133.3, 129.0, 129.0, 128.7, 128.5, 128.2, 127.9, 126.6, 126.3, 125.3, 115.8, 93.0, 53.5, 43.3, 36.2, 34.2, 17.1, 13.7; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{29}H_{26}NaO_3]^+$: 445.1774, found: 445.1781; **HPLC**: Daicel

Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, major product: t_{major} = 9.34 min and t_{minor} = 7.33 min; minor product: t_{major} = 6.03 min and t_{minor} = 8.75 min.

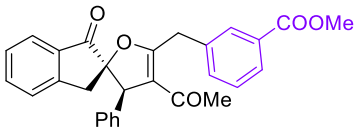
(2*R*,3*R*)-4-benzoyl-5-benzyl-5'-methyl-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3aa):



3aa

Followed the general procedure, using **1e** (0.2 mmol, 32.4 mg), **2m** (0.2 mmol, 61.3 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3aa** as a light yellow oil (65.8 mg, 70% yield, >20:1 dr); $[\alpha]_D^{20}$ = -66.2 (c = 2.0, DCM, 96% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.42 – 7.35 (m, 1H), 7.34 – 7.25 (m, 6H), 7.25 – 7.13 (m, 5H), 6.97 – 6.84 (m, 3H), 4.79 (s, 1H), 3.83 (dd, *J* = 48.3, 14.9 Hz, 2H), 2.83 (dd, *J* = 77.9, 17.7 Hz, 2H), 2.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 192.5, 168.5, 151.5, 147.6, 140.5, 139.0, 136.2, 131.3, 131.1, 129.5, 129.0, 128.7, 128.5, 128.3, 127.9, 127.4, 126.7, 126.7, 125.1, 117.3, 93.2, 55.0, 35.9, 34.4, 22.2; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{33}H_{26}NaO_3]^+$: 493.1774, found: 493.1767; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =14.61 min and t_{minor} =24.32 min.

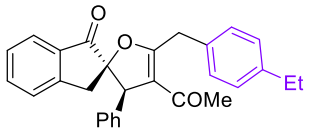
Methyl3-(((2*R*,3*R*)-4-acetyl-1'-oxo-3-phenyl-1',3'-dihydro-3*H*-spiro[furan-2,2'-inden]-5-yl)methyl)benzoate (3ab):



3ab

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2n** (0.2 mmol, 60.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3ab** as a light yellow oil (67.5 mg, 71% yield, >20:1 dr); $[\alpha]_D^{20}$ = -253.5 (c = 3.0, DCM, 96% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.71 – 7.62 (m, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.35 – 7.26 (m, 3H), 7.21 – 7.15 (m, 1H), 7.11 – 6.88 (m, 2H), 4.57 (s, 1H), 4.26 (dd, *J* = 77.0, 14.4 Hz, 2H), 3.91 (s, 3H), 2.82 (dd, *J* = 95.9, 17.6 Hz, 2H), 1.90 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.3, 194.8, 168.6, 167.1, 150.7, 139.2, 136.8, 136.1, 133.6, 133.2, 130.4, 130.1, 129.2, 128.6, 128.3, 128.1, 128.0, 126.3, 125.4, 116.1, 93.2, 53.7, 52.1, 36.2, 33.9, 29.8; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{29}H_{24}NaO_5]^+$: 475.1516, found: 475.1520; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =42.66 min and t_{minor} =25.21 min.

(2*R*,3*R*)-4-acetyl-5-(4-ethylbenzyl)-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3ac):

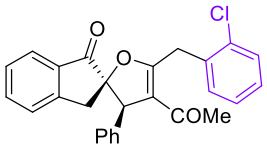


3ac

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2o** (0.2 mmol, 54.8 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1)

to afforded **3ac** as a light yellow oil (73.0 mg, 82% yield, >20:1 dr); $[\alpha]_D^{20}$ = -177.7 (c = 3.0, DCM, 97% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.42 – 7.36 (m, 1H), 7.35 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 7.18 – 7.12 (m, 3H), 7.07 – 6.86 (m, 2H), 4.57 (s, 1H), 4.17 (dd, *J* = 92.4, 14.4 Hz, 2H), 2.81 (dd, *J* = 101.2, 17.8 Hz, 2H), 2.66 – 2.58 (m, 2H), 1.91 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 194.6, 169.7, 150.8, 142.6, 139.4, 136.0, 133.5, 133.3, 129.1, 128.9, 128.2, 128.0, 127.9, 126.3, 125.3, 116.0, 93.1, 53.8, 36.2, 33.8, 29.8, 28.5, 15.6; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{29}H_{26}NaO_3]^+$: 445.1774, found: 445.1783; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =26.14 min and t_{minor} =14.55 min.

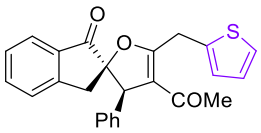
(2*R*,3*R*)-4-acetyl-5-(2-chlorobenzyl)-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3ad):



3ad

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2p** (0.2 mmol, 56.3 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3ad** as a light yellow oil (72.2 mg, 80% yield, >20:1 dr); $[\alpha]_D^{20}$ = -246.2 (c = 3.0, DCM, 95% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.42 – 7.29 (m, 5H), 7.27 – 7.23 (m, 1H), 7.19 – 7.13 (m, 2H), 7.13 – 6.81 (m, 2H), 4.58 (s, 1H), 4.44 – 4.34 (m, 2H), 2.83 (dd, *J* = 93.6, 17.7 Hz, 2H), 1.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.6, 194.5, 168.1, 150.7, 139.3, 136.1, 134.2, 134.0, 133.2, 130.4, 129.3, 129.2, 128.2, 128.1, 128.0, 127.0, 126.3, 125.3, 117.0, 93.2, 53.9, 36.2, 32.1, 29.7; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{27}H_{21}ClNaO_3]^+$: 451.1071, found: 451.1077; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =21.77 min and t_{minor} =11.16 min.

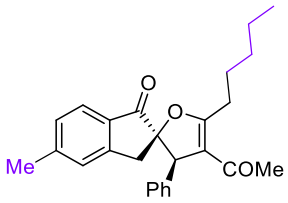
(2*R*,3*R*)-4-acetyl-3-phenyl-5-(thiophen-2-ylmethyl)-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3ae):



3ae

Followed the general procedure, using **1a** (0.2 mmol, 29.4 mg), **2q** (0.2 mmol, 50.4 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3ae** as a light yellow oil (58.4 mg, 69% yield, >20:1 dr); $[\alpha]_D^{20}$ = -285.8 (c = 2.0, DCM, 97% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.42 – 7.38 (m, 1H), 7.35 – 7.26 (m, 3H), 7.20 – 7.16 (m, 2H), 7.13 – 6.97 (m, 3H), 6.96 – 6.93 (m, 1H), 4.58 (s, 1H), 4.38 (dd, *J* = 139.2, 14.9 Hz, 2H), 2.84 (dd, *J* = 109.1, 17.7 Hz, 2H), 1.90 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.4, 194.6, 168.0, 150.8, 139.2, 137.8, 136.1, 133.3, 129.2, 128.3, 128.0, 126.8, 126.3, 126.3, 125.4, 124.4, 115.6, 93.3, 53.7, 36.3, 29.7, 28.7; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{20}NaO_3S]^+$: 423.1025, found: 423.1029; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =30.73 min and t_{minor} =13.43 min.

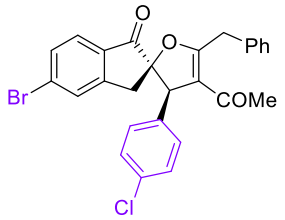
(2*R*,3*R*)-4-acetyl-5'-methyl-5-pentyl-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3af):



3af

Followed the general procedure, using **1e** (0.2 mmol, 32.4 mg), **2r** (0.2 mmol, 45.4 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3af** as a light yellow oil (42.7 mg, 55% yield, >20:1 dr); $[\alpha]_D^{20}$ = -156.8 (c = 2.0, DCM, 96% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.18 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.09 – 6.94 (m, 2H), 6.92 (s, 1H), 4.43 (s, 1H), 2.88 – 2.82 (m, 1H), 2.82 – 2.68 (m, 2H), 2.64 – 2.55 (m, 1H), 2.32 (s, 3H), 1.81 (s, 3H), 1.67 – 1.56 (m, 2H), 1.39 – 1.26 (m, 4H), 0.84 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.0, 193.5, 171.5, 150.2, 146.5, 138.7, 129.9, 128.4, 128.0, 126.7, 125.6, 124.1, 114.4, 92.0, 52.7, 35.1, 30.6, 28.7, 27.3, 25.5, 21.3, 21.2, 13.0; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{26}H_{28}NaO_3]^+$: 411.1931, found: 411.1927; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =20.38 min and t_{minor} = 8.37 min.

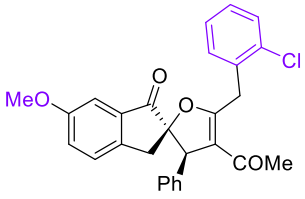
(2*R*,3*R*)-4-acetyl-5-benzyl-5'-bromo-3-(4-chlorophenyl)-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3ag):



3ag

Followed the general procedure, using **1d** (0.2 mmol, 45.2 mg), **2b** (0.2 mmol, 56.4 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3ag** as a light yellow oil (79.4 mg, 75% yield, >20:1 dr); $[\alpha]_D^{20}$ = -147.9 (c = 3.0, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.44 – 7.36 (m, 3H), 7.35 – 7.28 (m, 3H), 7.28 – 7.23 (m, 2H), 6.98 – 6.88 (m, 2H), 4.53 (s, 1H), 4.18 (dd, *J* = 86.3, 14.4 Hz, 2H), 2.79 (dd, *J* = 105.4, 17.9 Hz, 2H), 1.95 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.0, 194.0, 169.4, 151.9, 137.7, 136.0, 134.0, 132.1, 132.0, 131.7, 129.6, 129.5, 128.9, 128.6, 126.9, 126.5, 116.1, 92.6, 53.1, 35.8, 34.2, 29.7; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{27}H_{20}BrClNaO_3]^+$: 529.0177, found: 529.0187; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =31.28 min and t_{minor} =17.28 min.

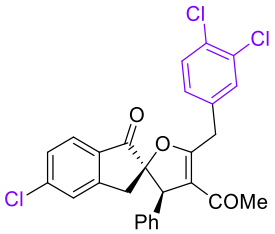
(2*R*,3*R*)-4-acetyl-5-(2-chlorobenzyl)-6'-methoxy-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3ah):



3ah

Followed the general procedure, using **1k** (0.2 mmol, 35.4 mg), **2p** (0.2 mmol, 56.3 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3ah** as a light yellow oil (80.8 mg, 84% yield, >20:1 dr); $[\alpha]_D^{20}$ = -170.2 (c = 3.0, DCM, 92% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 1H), 7.37 – 7.27 (m, 4H), 7.26 – 7.23 (m, 1H), 7.23 – 7.21 (m, 1H), 7.20 – 7.17 (m, 1H), 7.17 – 7.13 (m, 1H), 7.13 – 7.09 (m, 1H), 7.09 – 7.00 (m, 2H), 4.57 (s, 1H), 4.45 – 4.31 (m, 2H), 3.82 (s, 3H), 2.75 (dd, *J* = 93.8, 17.3 Hz, 2H), 1.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.6, 194.5, 168.2, 159.9, 143.6, 139.3, 134.3, 134.2, 134.0, 130.4, 129.3, 129.1, 128.1, 128.0, 127.0, 127.0, 125.4, 116.9, 106.4, 93.9, 55.7, 54.1, 35.5, 32.1, 29.7; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{28}H_{23}ClNaO_4]^+$: 481.1177, found: 481.1181; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =37.74 min and t_{minor} =12.65 min.

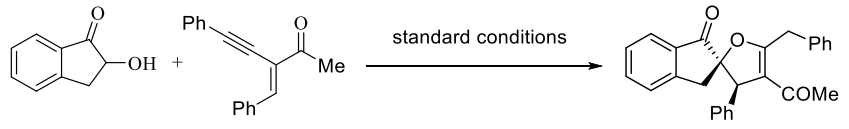
(2*R*,3*R*)-4-acetyl-5'-chloro-5-(3,4-dichlorobenzyl)-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3ai):



3ai

Followed the general procedure, using **1c** (0.2 mmol, 36.5 mg), **2s** (0.2 mmol, 63.4 mg) and **L1** (0.02 mmol, 14.0 mg). Purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afforded **3ai** as a light yellow oil (81.0 mg, 78% yield, >20:1 dr); $[\alpha]_D^{20}$ = -156.7 (c = 3.0, DCM, 99% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.41 – 7.37 (m, 2H), 7.36 – 7.28 (m, 3H), 7.27 – 7.24 (m, 1H), 7.21 – 7.16 (m, 1H), 7.04 – 6.90 (m, 2H), 4.54 (s, 1H), 4.21 – 4.07 (m, 2H), 2.80 (dd, *J* = 92.5, 17.9 Hz, 2H), 1.88 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.9, 194.8, 167.9, 152.0, 142.8, 138.7, 136.5, 132.4, 131.5, 131.0, 130.8, 130.4, 129.4, 129.2, 128.5, 128.3, 126.6, 126.5, 117.0, 116.1, 93.2, 53.7, 35.9, 33.2, 29.8; **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $[C_{27}H_{19}Cl_3NaO_3]^+$: 519.0292, found: 519.0300; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} =14.98 min and t_{minor} =8.89 min.

Scale-up reaction



1a
1mmol (0.15 g)

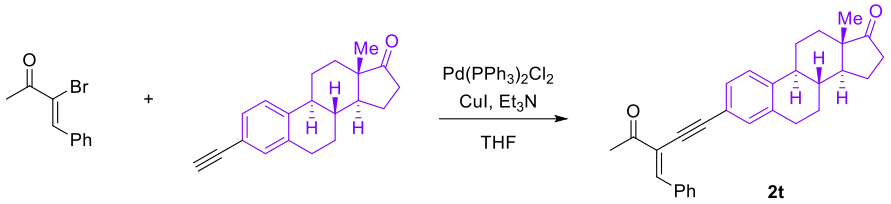
2a
1mmol (0.25 g)

3a
0.29 g,
74% yield, 98% ee, >20:1 dr

Under a nitrogen atmosphere, a solution of diethylzinc (200 μL, 1.0 M in hexane, 0.2 mmol) was added dropwise to a solution of **L1** (0.1 mmol, 70 mg) in toluene (6 mL). After the mixture was stirred for 30 min at 40 ℃. Then, α-hydroxy-1-indanone **1a** (1.0 mmol, 0.15 g), yne-enone **2a** (1.0 mmol, 0.25 g) and 2-Br-4-ClPhOH (0.2 mmol, 41.6 mg) were added. The reaction mixture was stirred for 48 h at 40 ℃. The reaction was quenched with NH_4Cl solution (10 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with brine

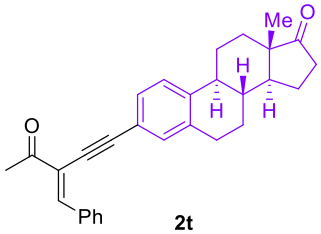
and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum ether/ethyl acetate (5/1) to afford the desired product **3a** (0.29 g) as a yellow oil.

The late-stage functionalization

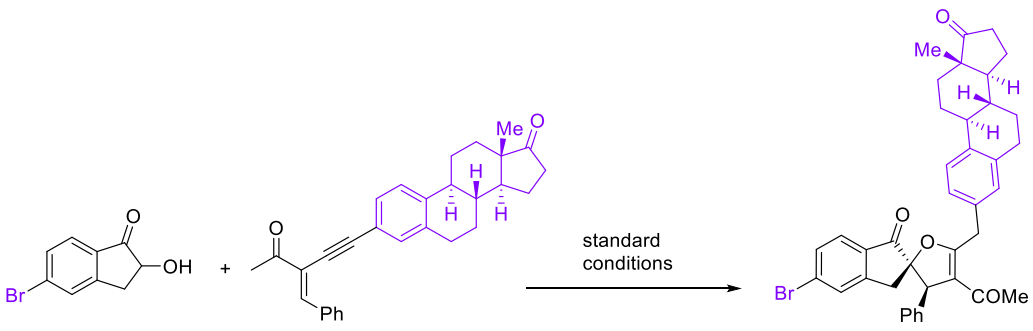


Followed the literature,[2] the α-bromo-α,β-enone was dissolved in anhydrous THF (0.2 M), followed by addition of $Pd(PPh_3)_2Cl_2$ (0.02 equiv.) and CuI (0.04 equiv.). The reaction mixture was cooled to 0 °C and degassed with argon. Alkyne[3] (1.5 equiv.) and Et_3N (3.0 equiv.) was added and the mixture was stirred overnight at ambient temperature. Upon completion, the reaction mixture was diluted with H_2O (40 mL). The aqueous phase was extracted with Et_2O (3 x 40 mL), washed with brine and the combined organic phase was dried over $MgSO_4$. Then, it was filtered and the solvent removed.

(8*R*,9*S*,13*S*,14*S*)-3-(3-((*E*)-benzylidene)-4-oxopent-1-yn-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (2t):



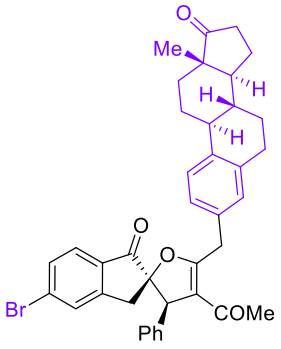
Light yellow solid in 70% isolated yield; **m.p.** = 182.5-183.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 – 8.03 (m, 2H), 7.79 (s, 1H), 7.47 – 7.38 (m, 3H), 7.36 – 7.27 (m, 3H), 2.98 – 2.87 (m, 2H), 2.60 (s, 3H), 2.56 – 2.47 (m, 1H), 2.47 – 2.38 (m, 1H), 2.36 – 2.28 (m, 1H), 2.22 – 2.10 (m, 1H), 2.09 – 1.96 (m, 3H), 1.67 – 1.45 (m, 6H), 0.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.6, 196.3, 142.5, 141.2, 137.0, 134.6, 131.8, 130.7, 130.7, 128.8, 128.6, 125.7, 120.1, 120.1, 99.4, 86.5, 50.5, 47.9, 44.5, 38.0, 35.8, 31.6, 29.2, 28.2, 26.3, 25.6, 21.6, 13.9; **HRMS** (ESI): m/z $[M + H]^+$ calcd for $[C_{30}H_{31}O_2]^+$: 423.2319, found: 423.2321.



Under a nitrogen atmosphere, a solution of diethylzinc (40 μL, 1.0 M in hexane, 0.04 mmol)

was added dropwise to a solution of **L1** (0.02 mmol, 14.0 mg) in toluene (4 mL). After the mixture was stirred for 30 min at 40 ℃. Then, α-hydroxy-1-indanone **1d** (0.2 mmol, 45.2 mg), yne-enone **2t** (0.2 mmol, 84.4 mg) and 2-Br-4-ClPhOH (0.04 mmol, 8.28 mg) were added. The reaction mixture was stirred for 48 h at 40 ℃. The reaction was quenched with NH_4Cl solution (4 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 ×5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure by using a rotary evaporator. The residue was purified by flash chromatography with petroleum ether/ethyl acetate (5/1) to afford the desired product **3aj** as a white solid.

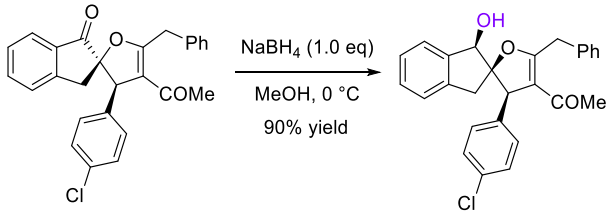
(2*R*,3*R*)-4-acetyl-5'-bromo-5-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)methyl)-3-phenyl-3*H*-spiro[furan-2,2'-inden]-1'(3'*H*)-one (3aj):



3aj

White solid in 80% isolated yield (107.4 mg, >20:1 dr); **m.p.** = 174.6-175.0 ℃; $[\alpha]_D^{20}$ = -38.9 (c = 1.0, DCM, >20:1 de); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.28 (m, 4H), 7.23 (s, 1H), 7.19 – 7.16 (m, 1H), 7.13 (s, 1H), 7.10 – 6.95 (m, 2H), 4.57 (s, 1H), 4.14 (dd, *J* = 48.9, 14.7 Hz, 2H), 2.96 – 2.89 (m, 3H), 2.74 – 2.65 (m, 1H), 2.55 – 2.39 (m, 2H), 2.32 – 2.24 (m, 1H), 2.20 – 1.98 (m, 4H), 1.93 (s, 3H), 1.70 – 1.54 (m, 3H), 1.52 – 1.43 (m, 3H), 0.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 221.0, 199.4, 194.4, 169.2, 152.2, 139.2, 138.1, 136.6, 133.5, 132.2, 132.0, 131.6, 129.6, 129.5, 129.2, 128.1, 126.5, 126.2, 125.6, 116.2, 92.8, 53.8, 50.5, 48.0, 44.4, 38.2, 36.0, 35.9, 33.6, 31.6, 29.8, 29.4, 26.6, 25.7, 21.6, 13.9; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{39}H_{37}BrNaO_4]^+$: 671.1767, found: 671.1776.

Derivatization

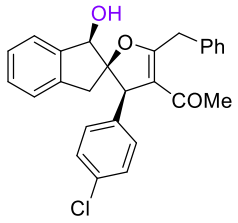


3p
(98% ee, >20:1 dr)

4
(98% ee, >20:1 dr)

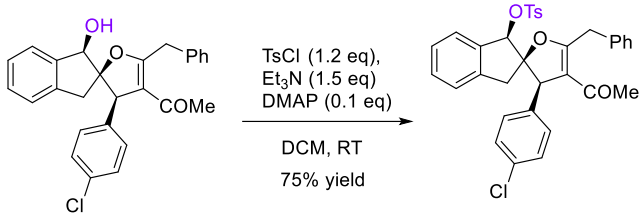
The mixture of **3p** (42.8 mg, 0.1 mmol, 1.0 eq) in MeOH (2 mL) was treated with $NaBH_4$ (3.8 mg, 0.1 mmol, 1.0 eq) at 0 °C. The reaction was allowed to stir at the same temperature for 24 h. Upon completion as shown by TLC, the reaction mixture was washed with brine (2 mL) and extracted using dichloromethane (3 x 2 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography with petroleum ether/ethyl acetate (3/1) to provide the product **4** as a yellow oil.

1-((1'*R*,2*R*,3*R*)-5-benzyl-3-(4-chlorophenyl)-1'-hydroxy-1',3'-dihydro-3*H*-spiro[furan-2,2'-inden]-4-yl)ethan-1-one (4):



4

Light yellow oil in 90% isolated yield (38.8 mg, >20:1 dr); $[\alpha]_D^{20}$ = -40.4 (c = 0.9, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 3H), 7.31 – 7.26 (m, 4H), 7.26 – 7.24 (m, 1H), 7.23 – 7.20 (m, 2H), 7.04 – 6.94 (m, 3H), 4.89 (s, 1H), 4.48 – 4.41 (m, 1H), 4.37 (s, 1H), 3.89 – 3.81 (m, 1H), 2.80 – 2.72 (m, 1H), 2.40 – 2.29 (m, 1H), 1.90 (s, 3H), 1.85 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.8, 169.6, 141.1, 138.9, 138.5, 136.9, 133.6, 129.2, 128.9, 127.4, 127.2, 124.7, 124.4, 115.9, 112.0, 99.1, 82.5, 54.0, 38.3, 34.1, 29.8; **HRMS** (ESI): m/z $[M + H]^+$ calcd for $[C_{27}H_{24}ClO_3]^+$: 431.1408, found: 431.1409; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 9.89 min and t_{minor} = 9.00 min.

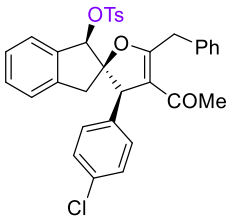


4
(98% ee, >20:1 dr)

5
(98% ee, >20:1 dr)

The mixture of **4** (43.1 mg, 0.1 mmol, 1.0 eq), Et_3N (15.1 mg, 0.15 mmol, 1.2 eq) and DMAP (1.2 mg, 0.12 mmol, 0.1 eq) in DCM (2 mL) was treated with TsCl (22.9 mg, 0.12 mmol, 1.2 eq) at 0 °C. The reaction was allowed to stir at room temperature for 36 h. Upon completion as shown by TLC, the reaction mixture was washed with saturated NH_4Cl (1 mL) and extracted using dichloromethane (3 x 1 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography with petroleum ether/ethyl acetate (3/1) to provide the product **5** as a light yellow oil.

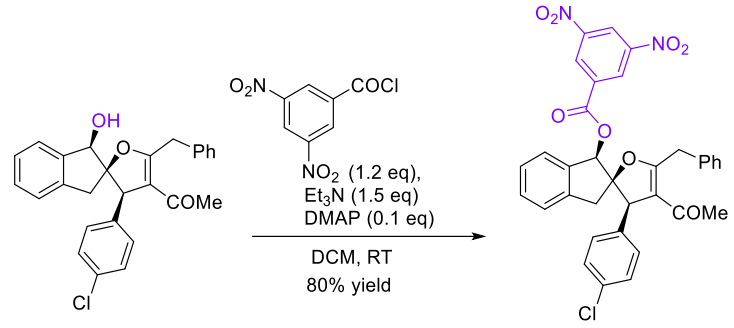
(1'*R*,2*R*,3*R*)-4-acetyl-5-benzyl-3-(4-chlorophenyl)-1',3'-dihydro-3*H*-spiro[furan-2,2'-inden]-1'-yl 4-methylbenzenesulfonate (5):



5

Light yellow oil in 75% isolated yield (45.5 mg, >20:1 dr); $[\alpha]_D^{20}$ = -152.6 (c = 2.0, DCM, 98% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.62 (m, 2H), 7.30 – 7.27 (m, 3H), 7.24 – 7.16 (m, 5H), 7.15 – 7.03 (m, 4H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 2H), 5.79 (s, 1H), 4.37 – 4.26 (m, 1H), 4.06 (s, 1H), 3.58 – 3.49 (m, 1H), 2.84 – 2.73 (m, 1H), 2.39 (s, 3H), 2.34 – 2.27 (m, 1H), 1.81 (s,

3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.1, 170.3, 145.1, 139.7, 137.9, 136.3, 136.2, 133.8, 133.6, 129.9, 129.2, 129.1, 128.5, 127.9, 127.7, 126.8, 125.7, 124.8, 115.5, 96.6, 86.5, 54.3, 37.9, 34.0, 29.6, 21.7; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{34}H_{29}ClNaO_5S]^+$: 607.1316, found: 607.1326; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 18.78 min and t_{minor} = 14.75 min.

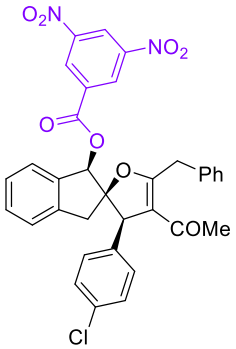


4
(98% ee, >20:1 dr)

6
(97% ee, >20:1 dr)

The mixture of **4** (43.1 mg, 0.1 mmol, 1.0 eq), Et_3N (15.2 mg, 0.15 mmol, 1.2 eq), and DMAP (1.2 mg, 0.12 mmol, 0.1 eq) in DCM (2 mL) was treated with 3,5-dinitrobenzoyl chloride (27.6 mg, 0.12 mmol, 1.2 eq) at 0 °C. The reaction was allowed to stir at room temperature for 24 h. Upon completion as shown by TLC, the reaction mixture was washed with saturated NH_4Cl (1 mL) and extracted using dichloromethane (3 x 1 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography with petroleum ether/ethyl acetate (3/1) to provide the product **6** as a white solid.

(1'*R*,2*R*,3*R*)-4-acetyl-5-benzyl-3-(4-chlorophenyl)-1',3'-dihydro-3*H*-spiro[furan-2,2'-inden]-1'-yl 3,5-dinitrobenzoate (6):



6

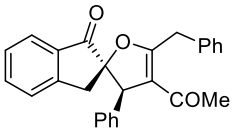
White solid in 80% isolated yield (51.8 mg, >20:1 dr); **m.p.** = 188.1-189.1 °C; $[\alpha]_D^{20}$ = -190.8 (c = 2.3, DCM, 97% ee); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.19 – 9.13 (m, 1H), 8.88 – 8.77 (m, 2H), 7.54 (d, *J* = 6.9 Hz, 1H), 7.48 – 7.21 (m, 5H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.96 – 6.91 (m, 2H), 6.79 – 6.74 (m, 1H), 6.27 (s, 1H), 4.47 – 4.32 (m, 1H), 4.13 (s, 1H), 3.96 – 3.84 (m, 1H), 3.35 – 3.22 (m, 1H), 2.53 – 2.41 (m, 1H), 1.95 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.5, 169.9, 161.9, 148.4, 141.4, 136.8, 136.3, 136.2, 133.9, 133.3, 130.6, 129.4, 128.8, 128.2, 127.9, 127.2, 126.3, 125.1, 122.3, 115.9, 95.2, 81.1, 55.0, 37.0, 34.1, 29.6; **HRMS** (ESI): m/z $[M + Na]^+$ calcd for $[C_{34}H_{25}ClN_2NaO_8]^+$: 647.1192, found: 647.1199; **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1 mL/min, λ = 254 nm, t_{major} = 52.94 min and t_{minor} = 47.56 min.

References

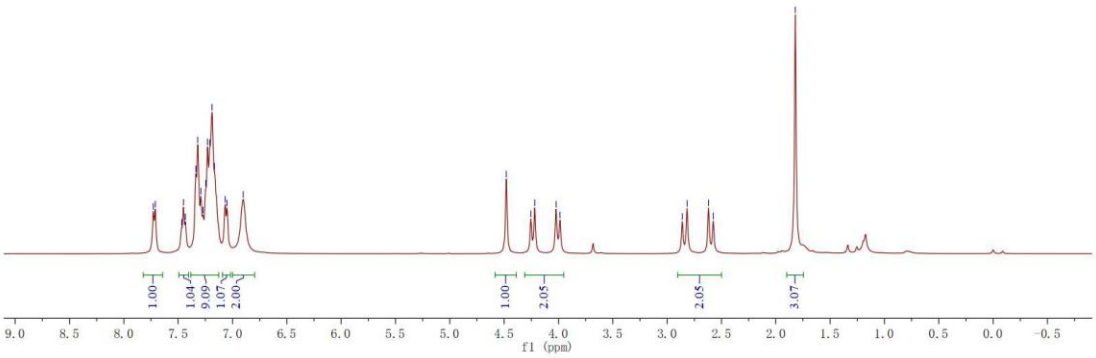
1. Matsuo, K.; Shindo, M. Cu(II)-Catalyzed Acylation by Thiol Esters Under Neutral Conditions: Tandem Acylation-Wittig Reaction Leading to a One-Pot Synthesis of Butenolides. *Org. Lett.,* **2010**, *12*, 5346–5349.
2. Poulsen, P. H.; Li, Y.; Lauridsen, V. H.; Jørgensen, D. K. B.; Palazzo, T. A.; Meazza, M.; Jørgensen, K. A. Organocatalytic Formation of Chiral Trisubstituted Allenes and Chiral Furan Derivatives. *Angew. Chem. Int. Ed.*, **2018**, *57*, 10661–10665.
3. Guo, H. Y., Zhang, S., Yu, X. Q., Feng, X. J., Yamamoto, Y., Bao, M. [3 + 2] Cycloaddition of α-Aryl-α-diazoacetates with Terminal Alkynes via the Cooperative Catalysis of Palladium and Acid. *ACS Catalysis*, **2021**, *11*, 10789-10795.

NMR Spectra of compounds

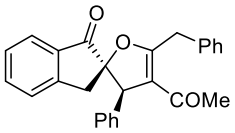
^{1}H NMR (400 MHz, $CDCl_3$)



3a



^{13}C NMR (101 MHz, $CDCl_3$)



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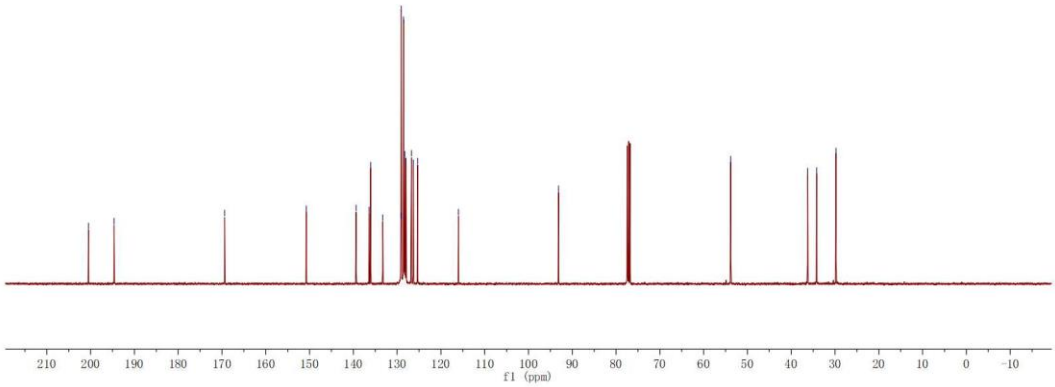
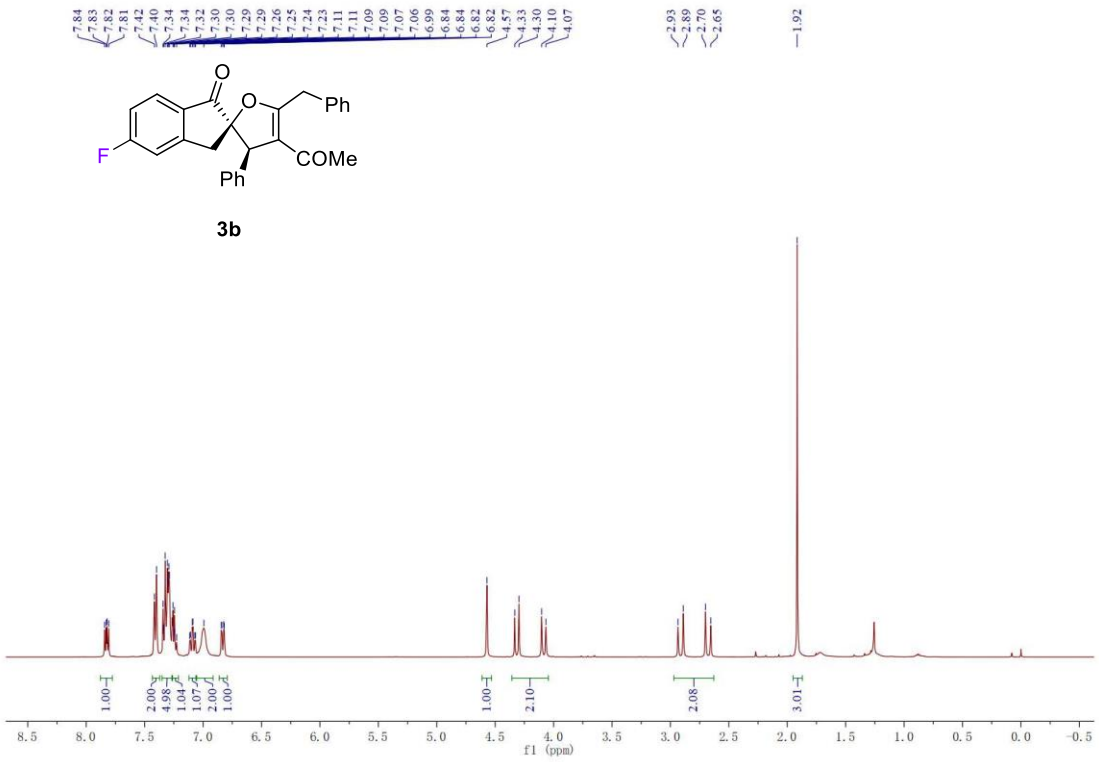
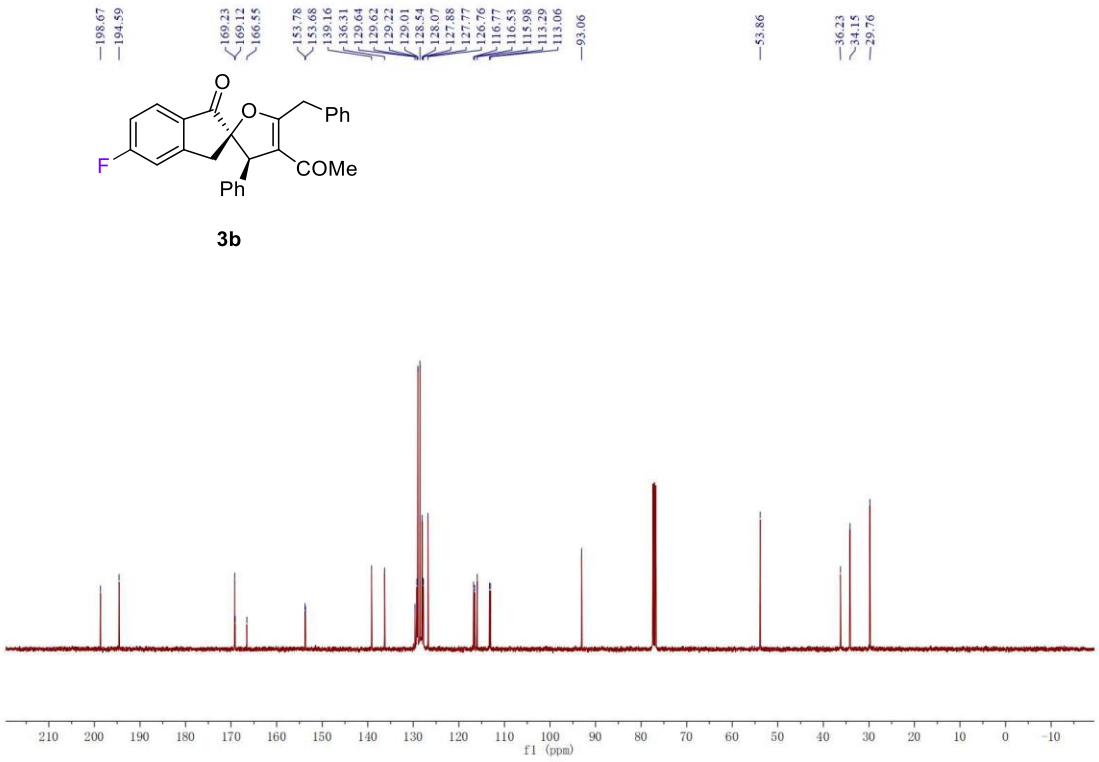


^{1}H NMR (400 MHz, $CDCl_3$)



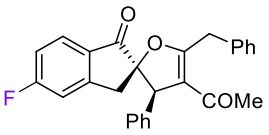
3b

^{13}C NMR (101 MHz, $CDCl_3$)



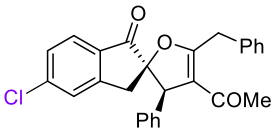
3b

^{19}F NMR (376 MHz, $CDCl_3$)



3b

^{1}H NMR (400 MHz, $CDCl_3$)



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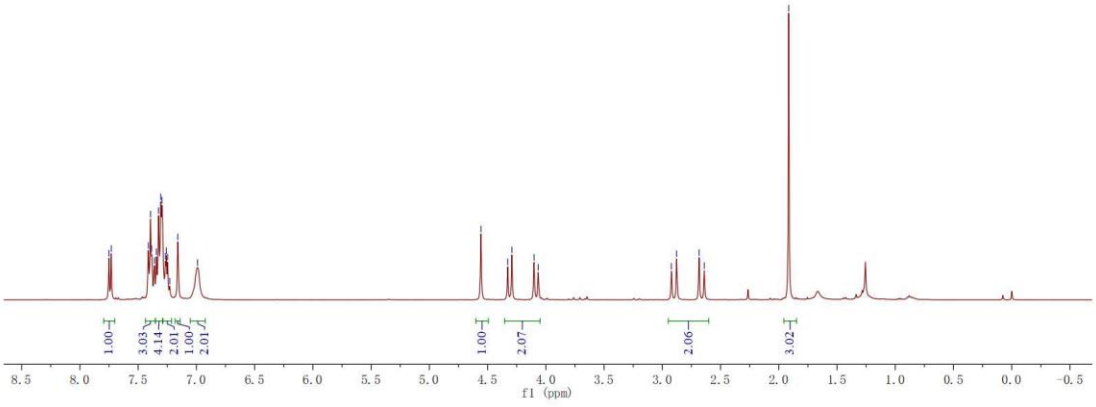

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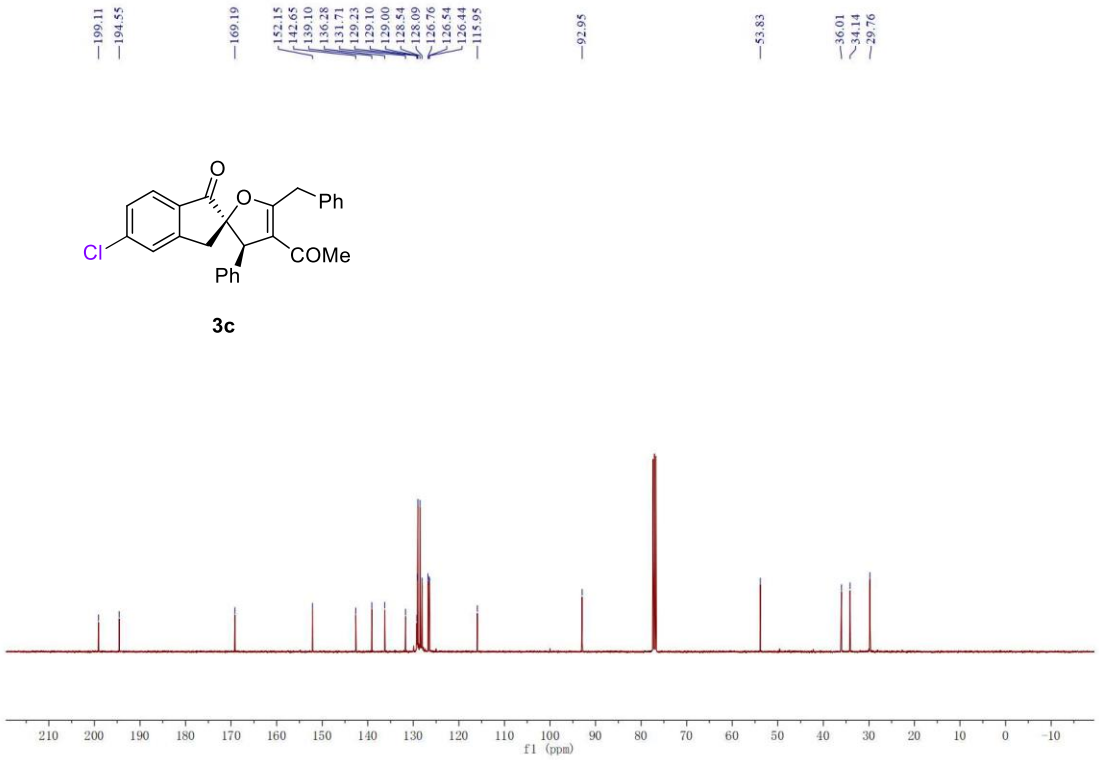

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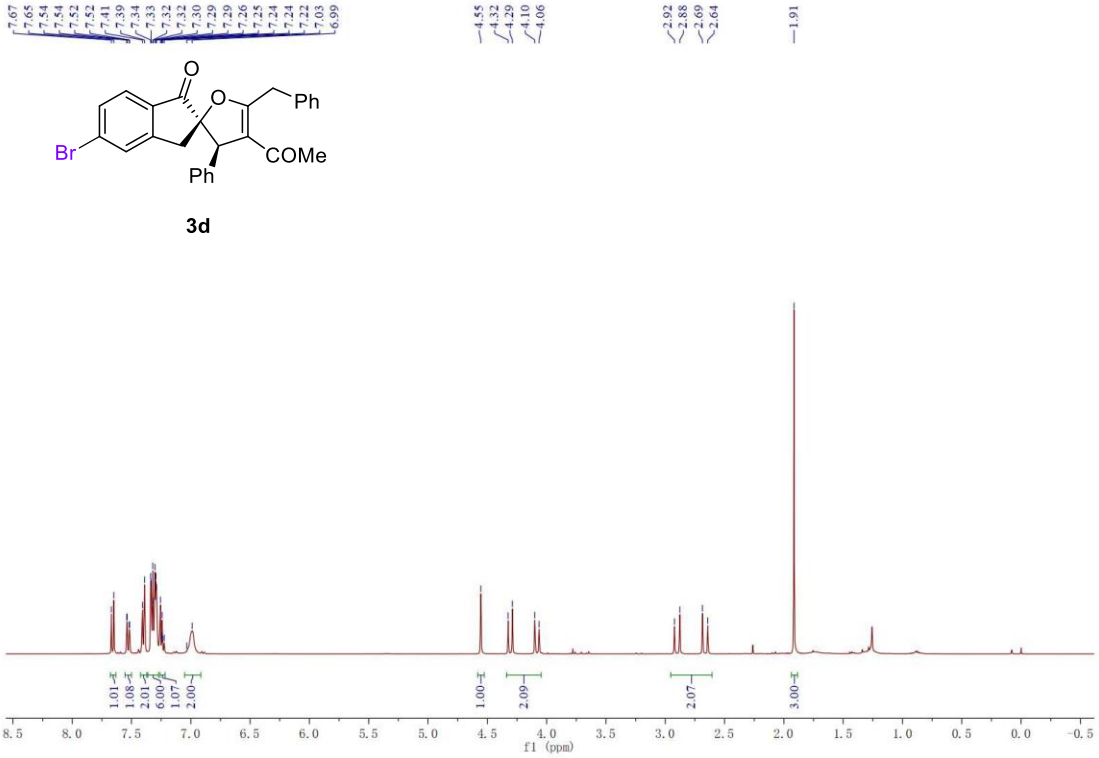

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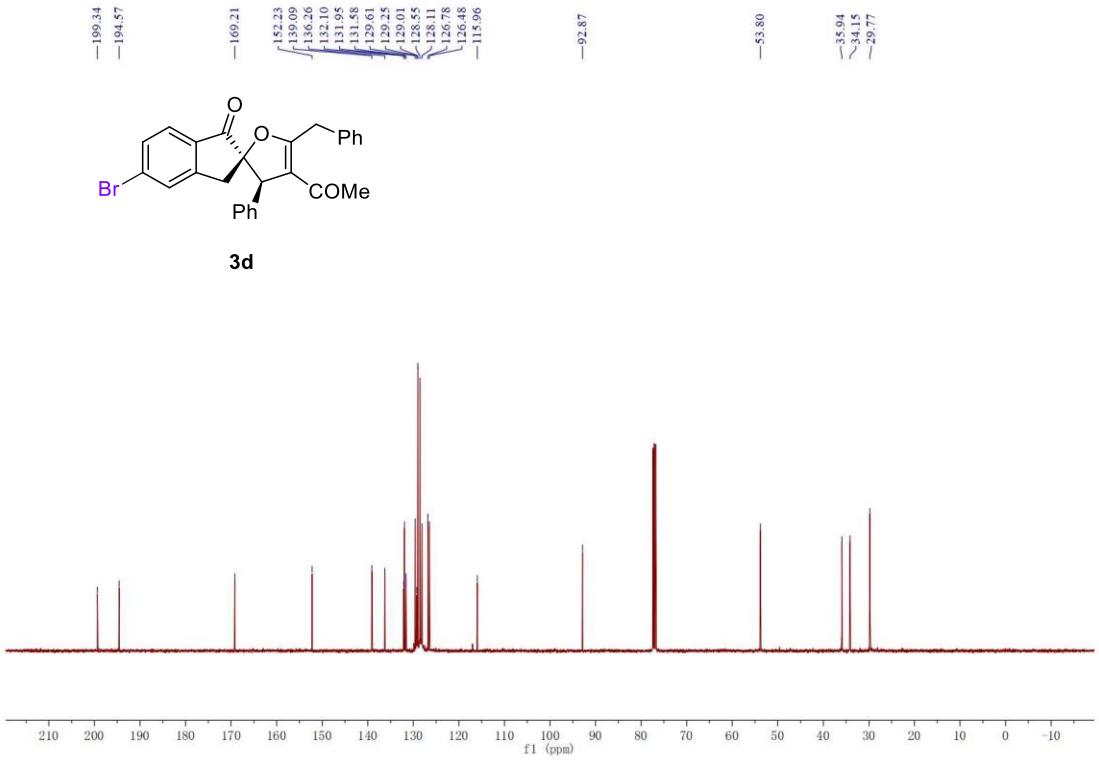

3d

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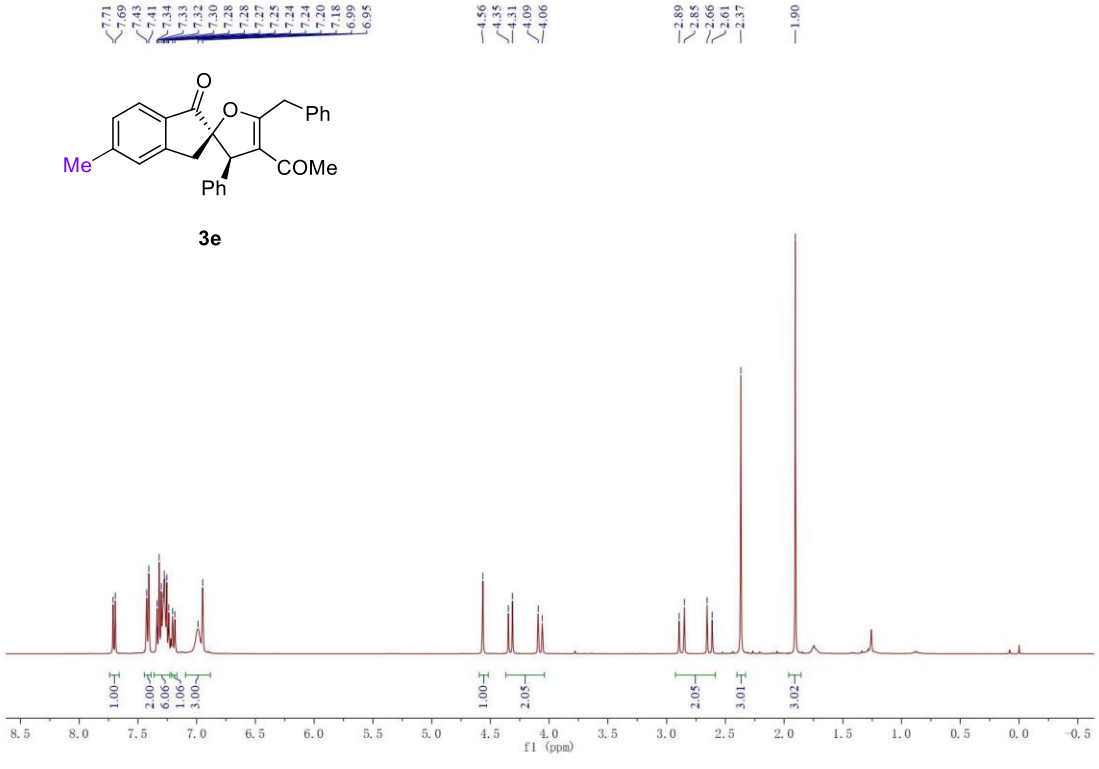

3e

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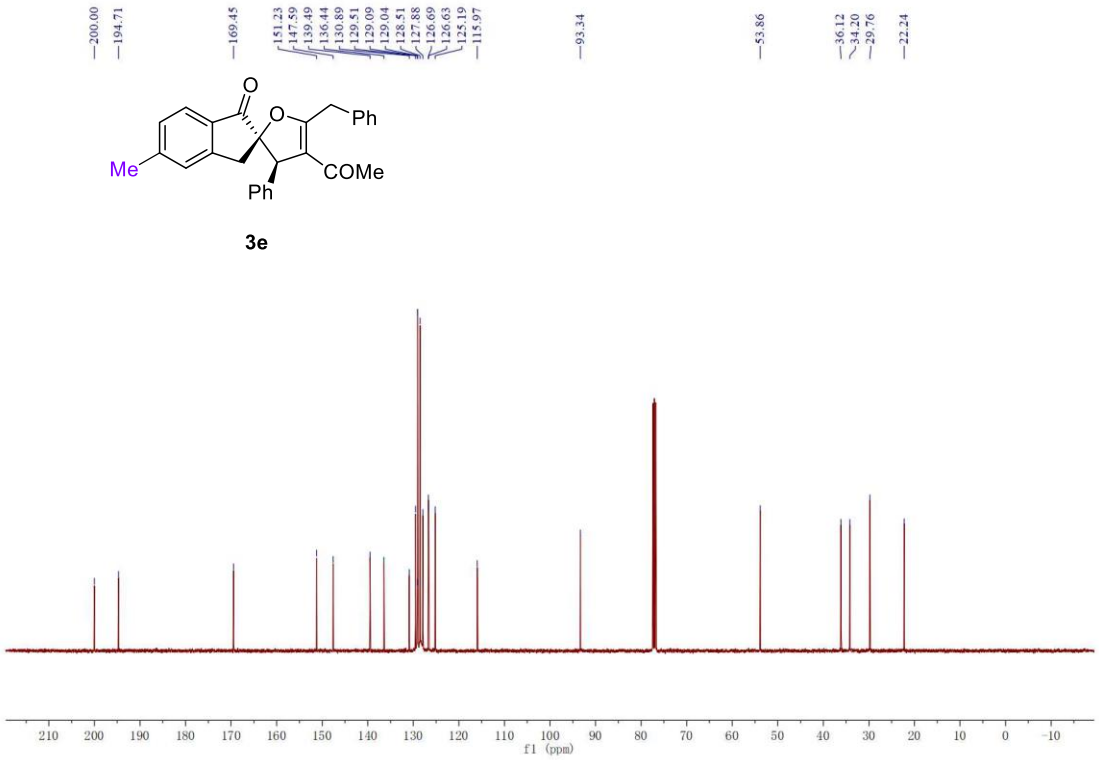

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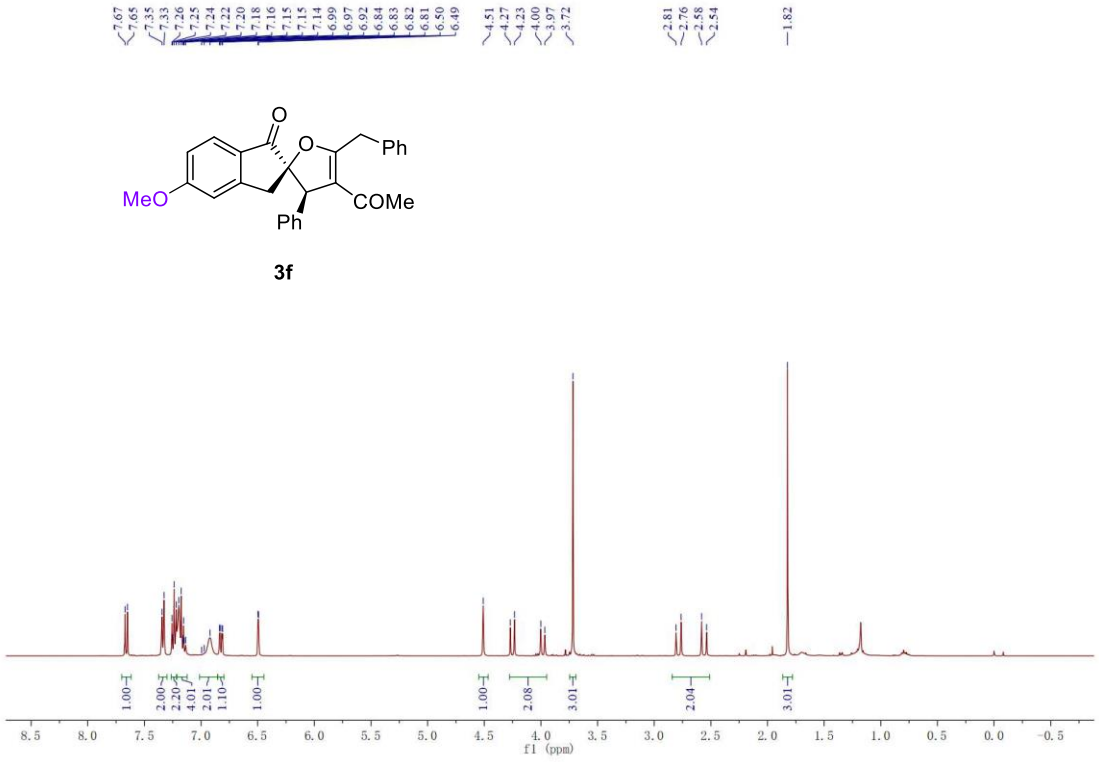

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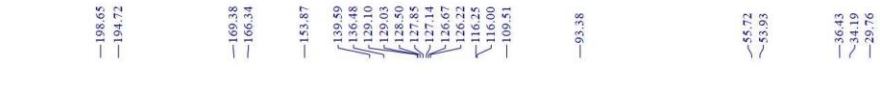

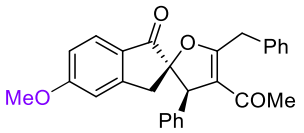

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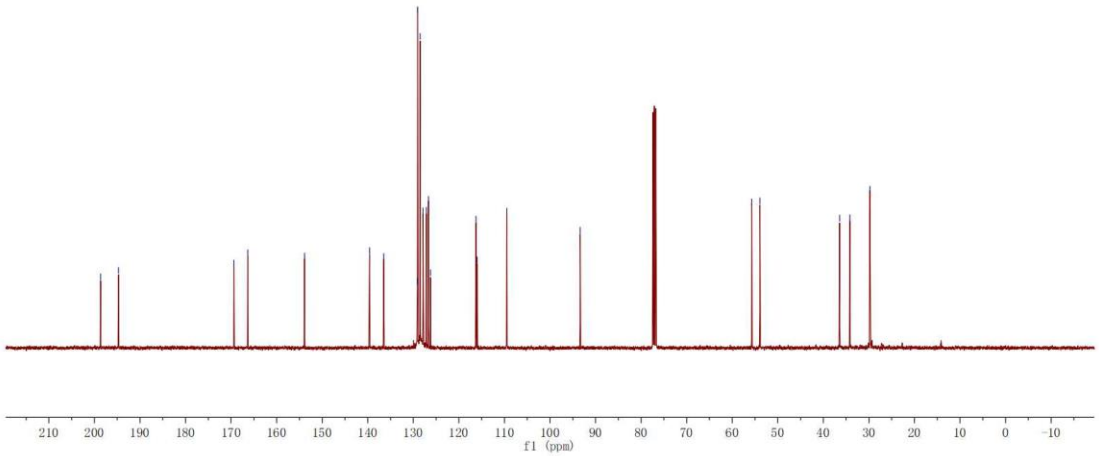

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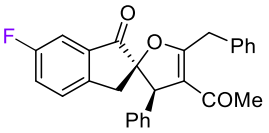

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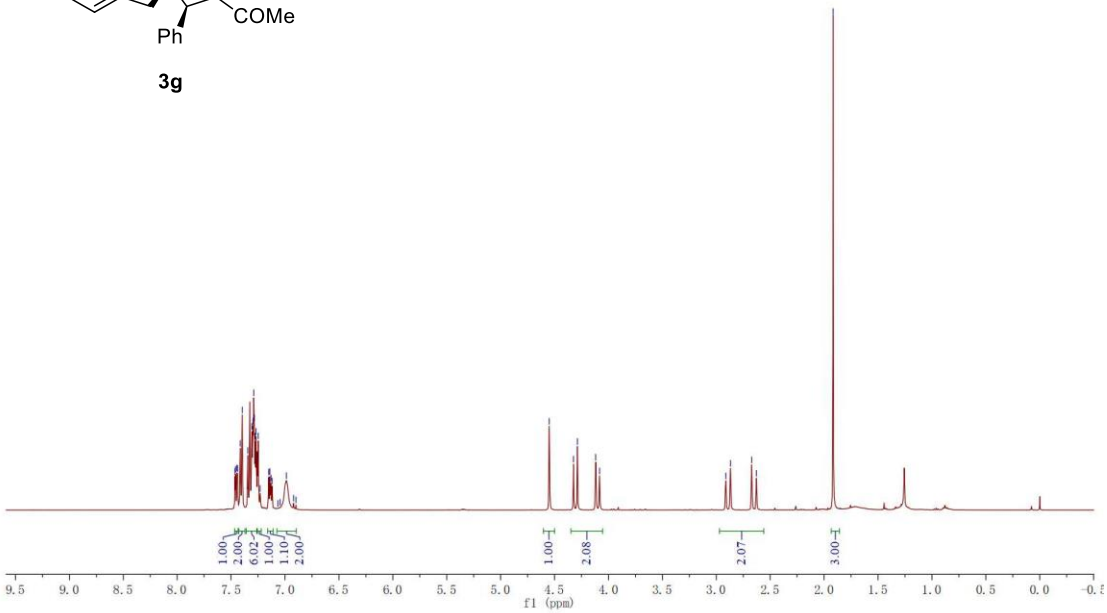
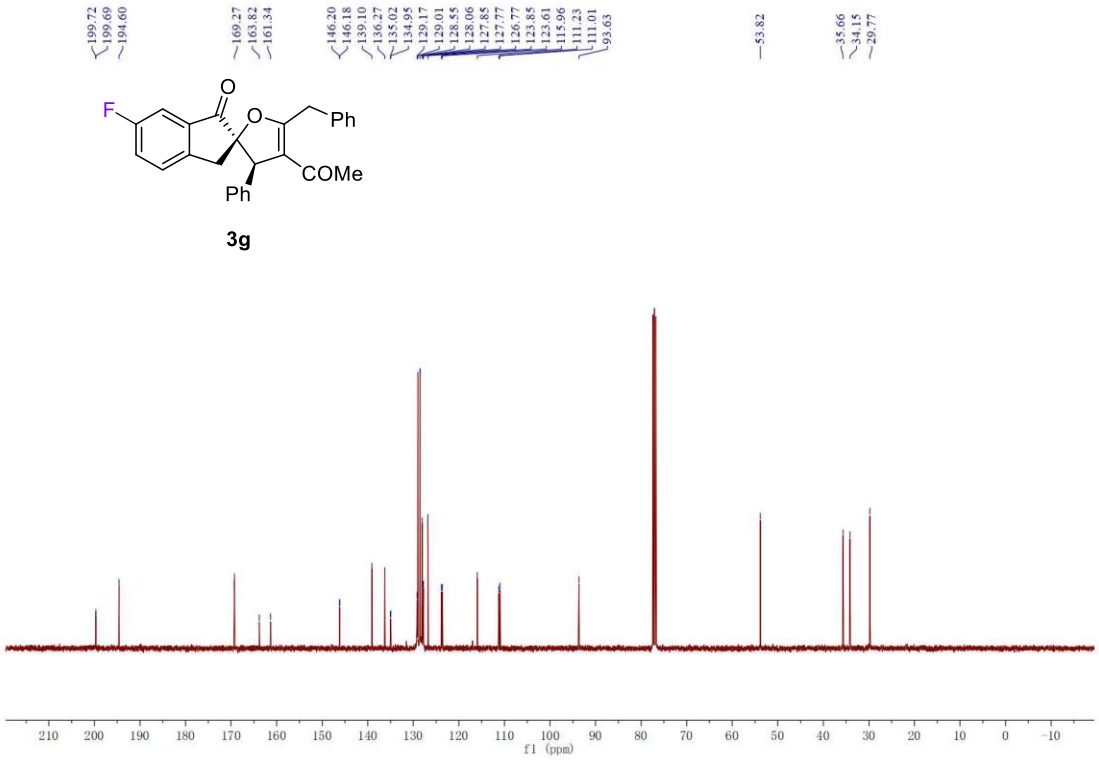


^{13}C NMR (101 MHz, $CDCl_3$)



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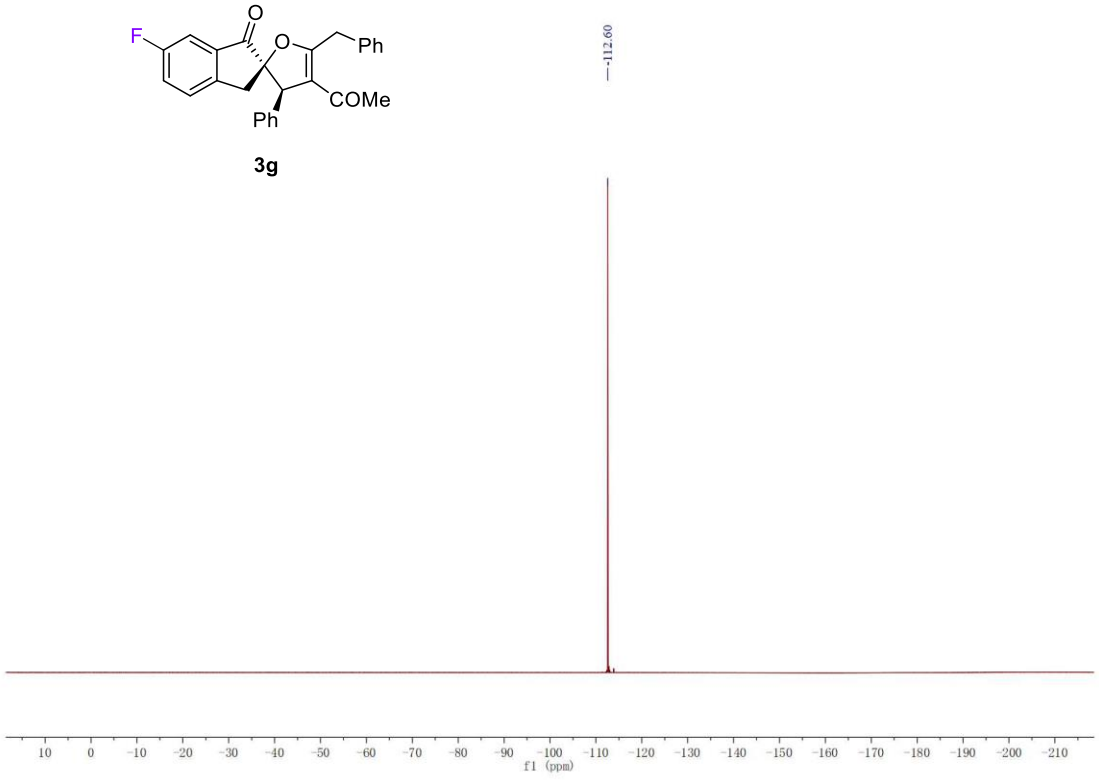
^{19}F NMR (376 MHz, $CDCl_3$)



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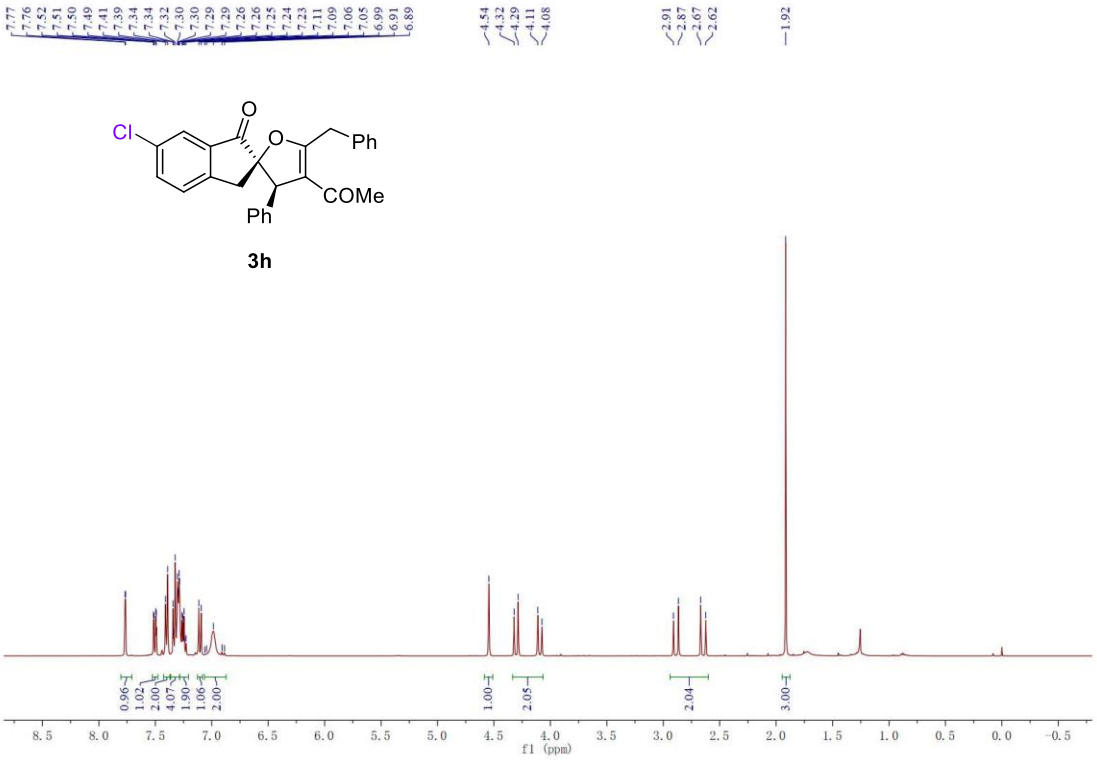

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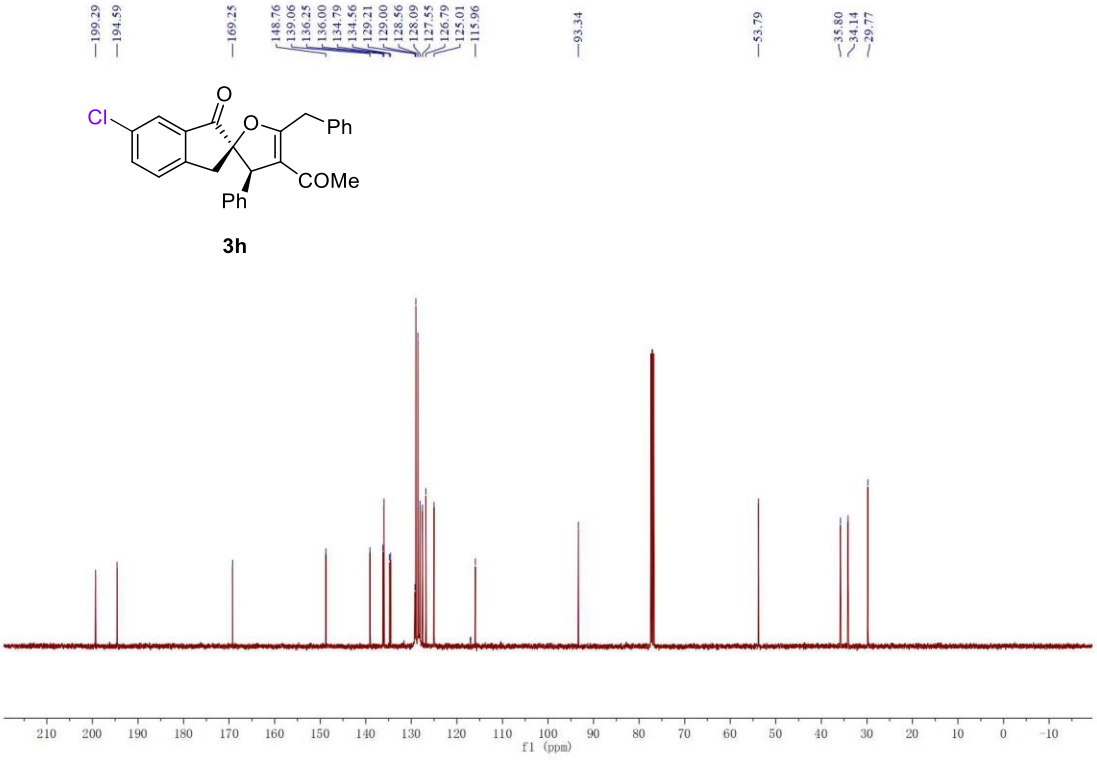

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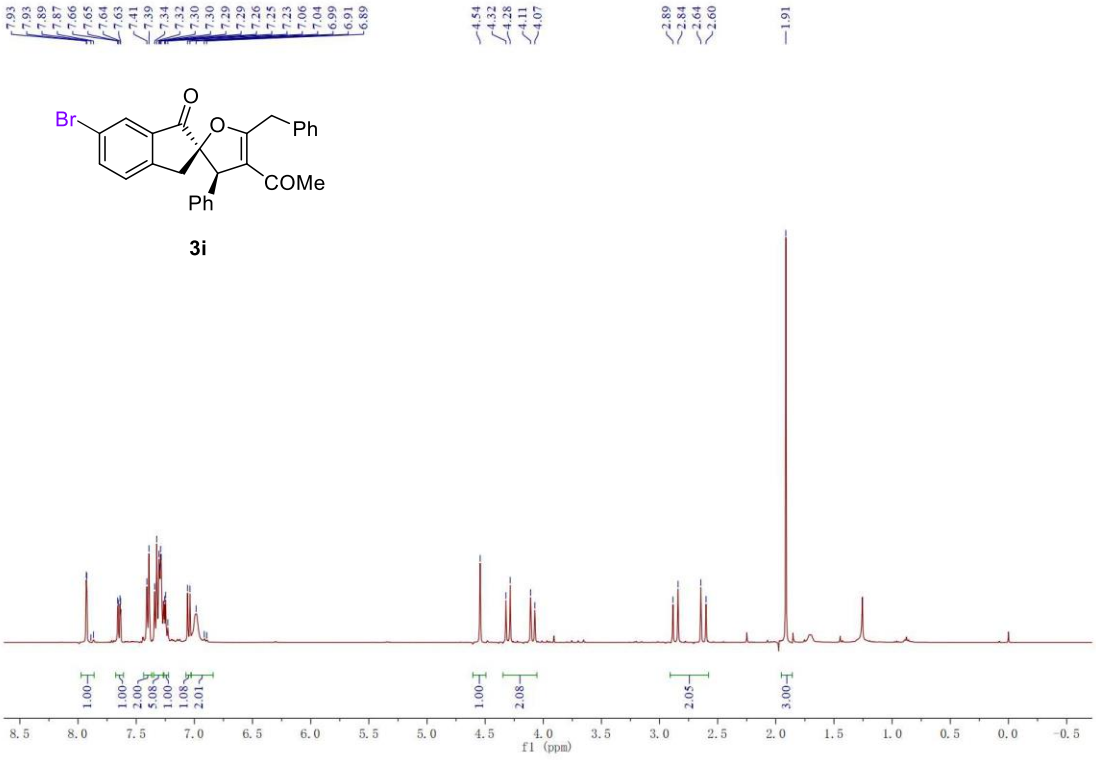

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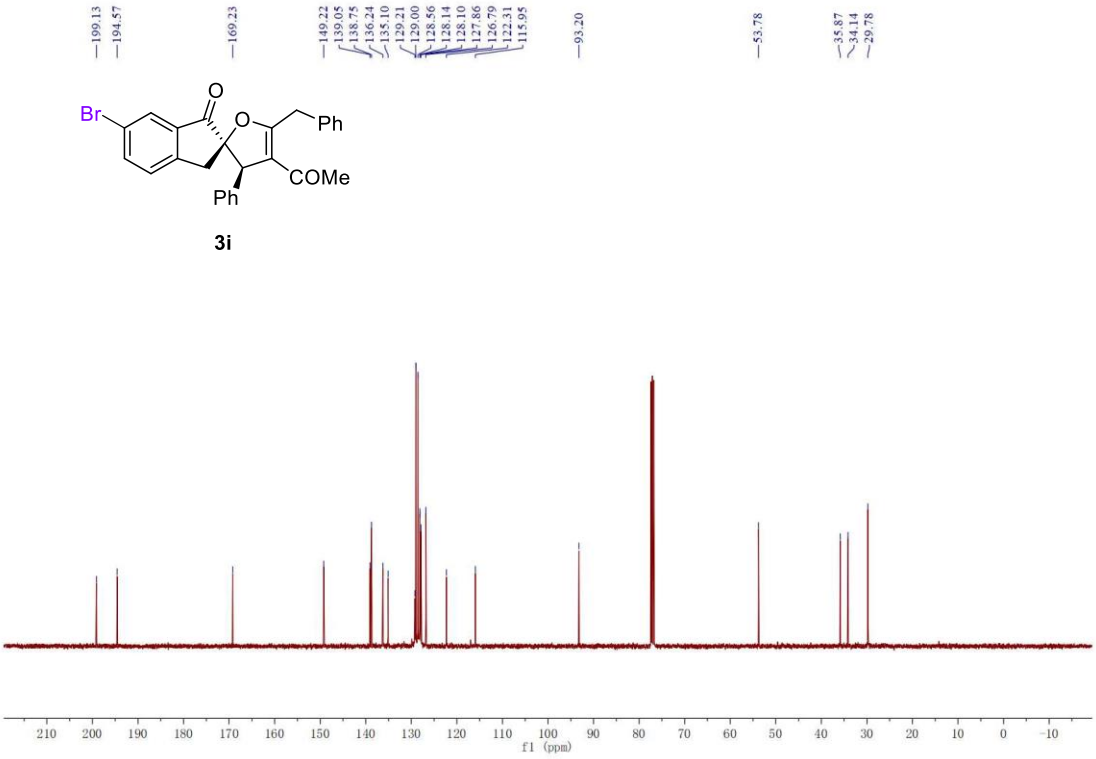

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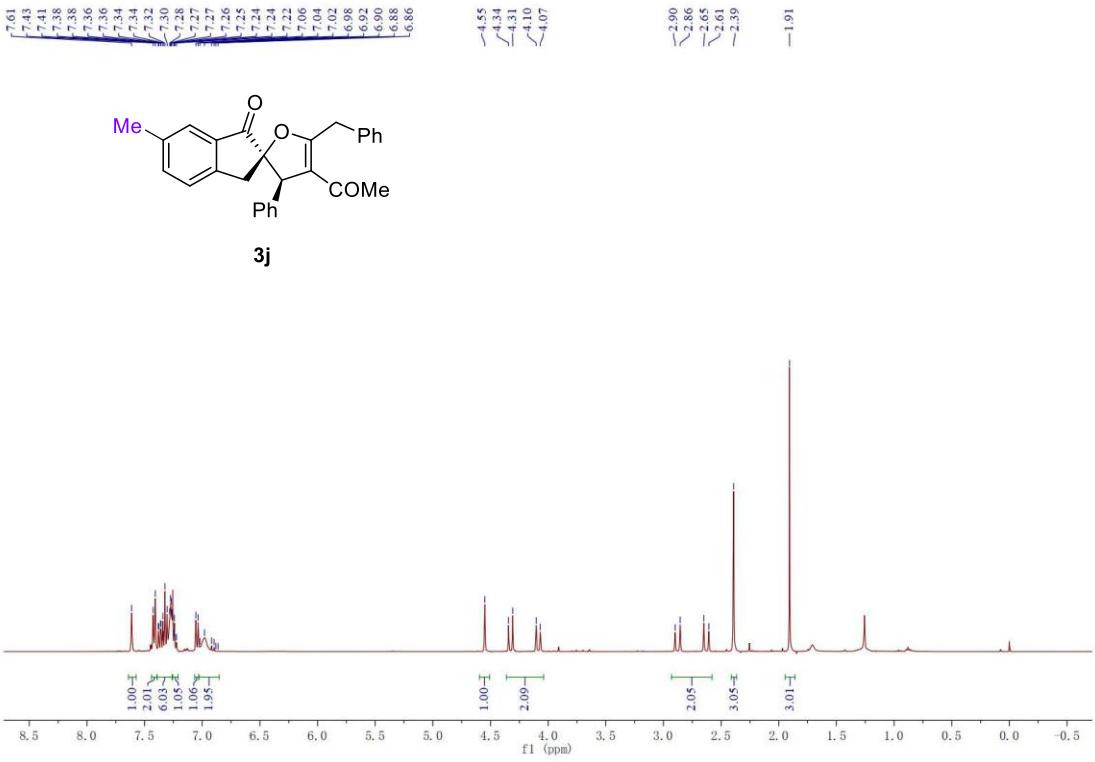

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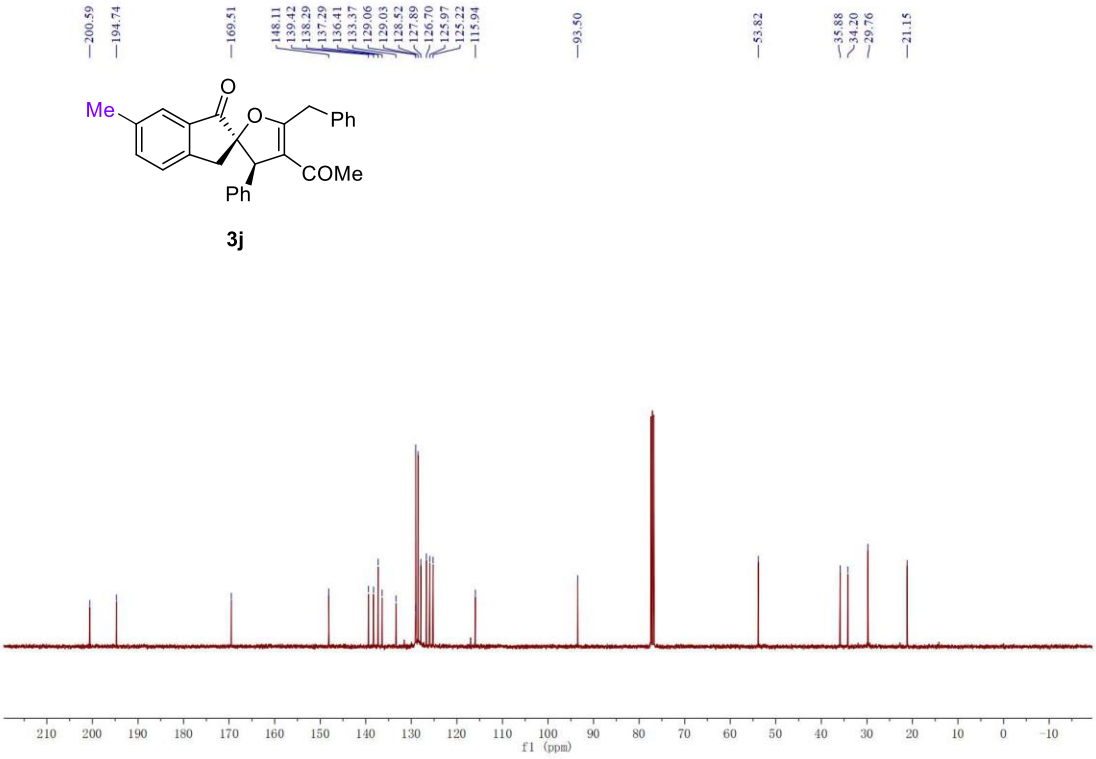

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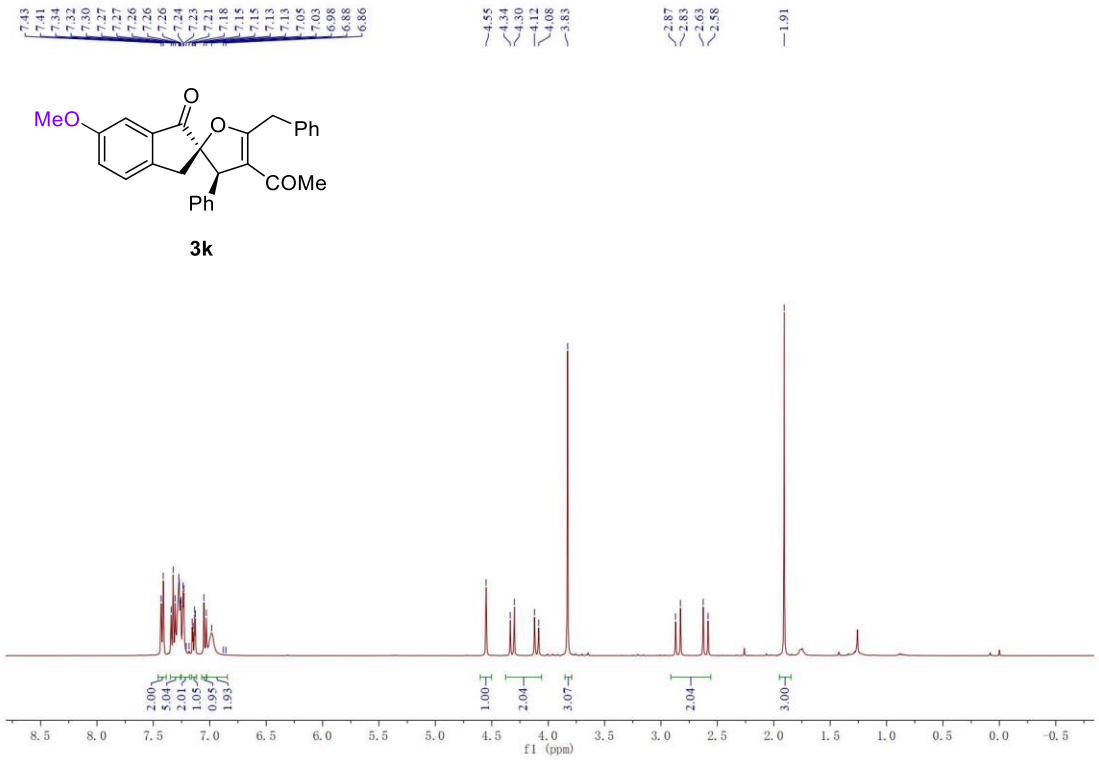

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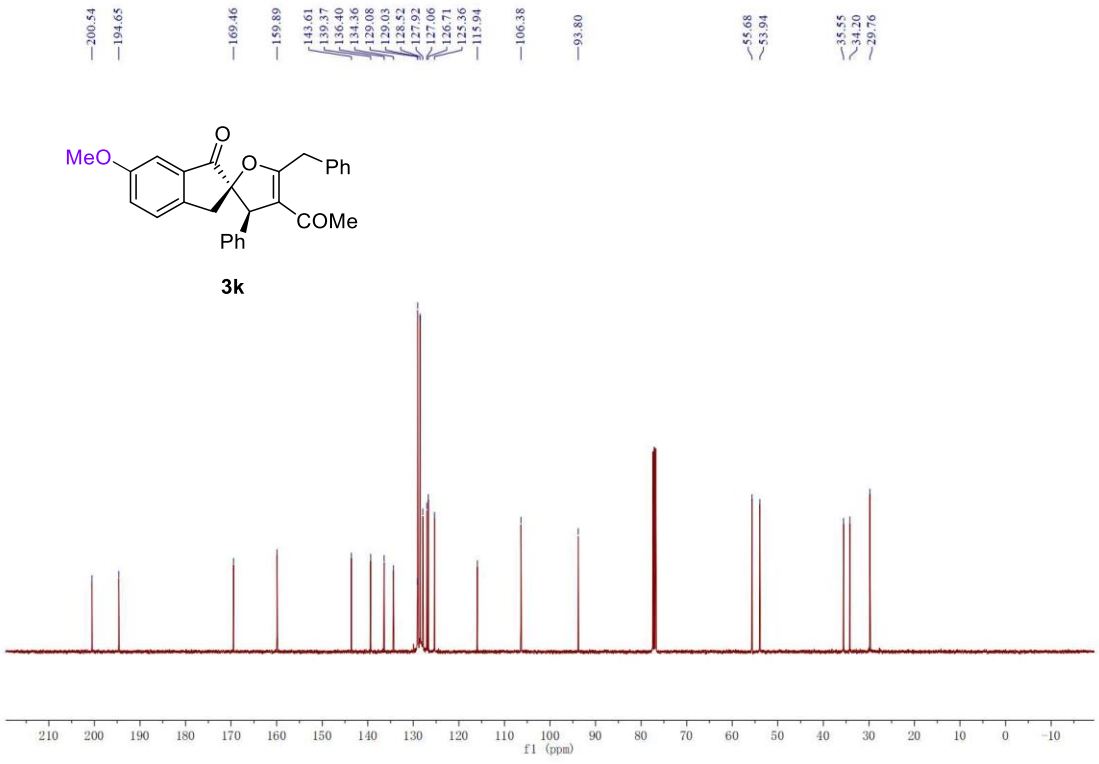

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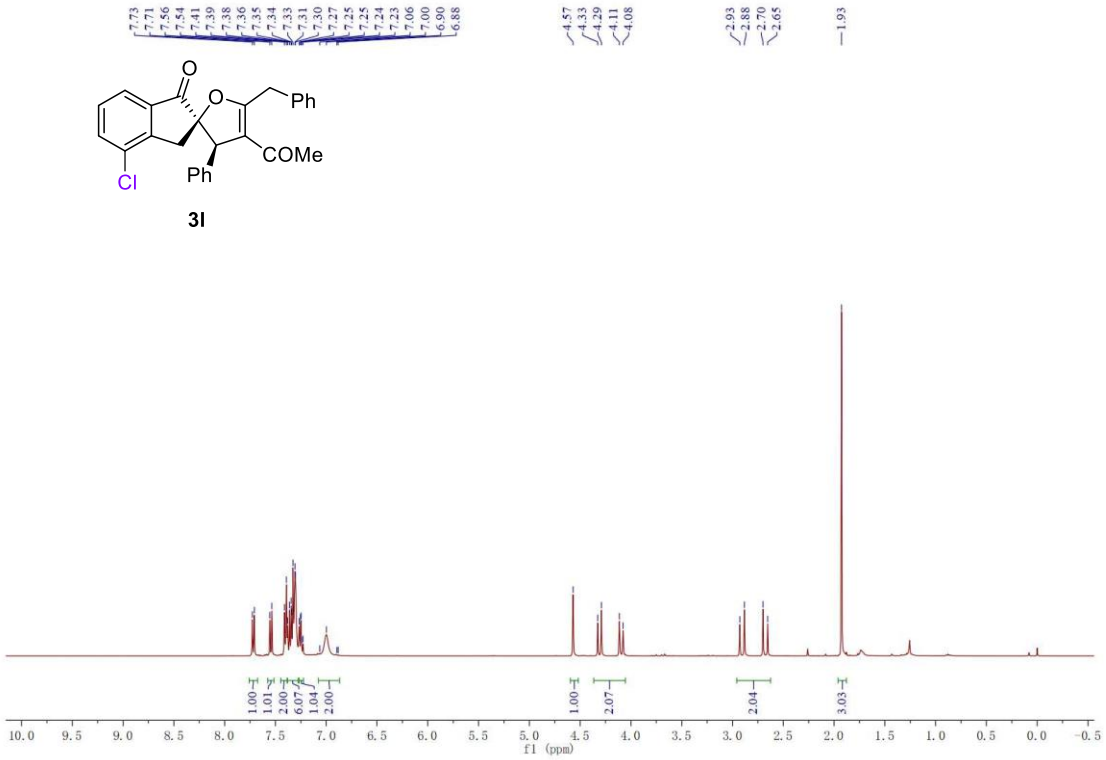

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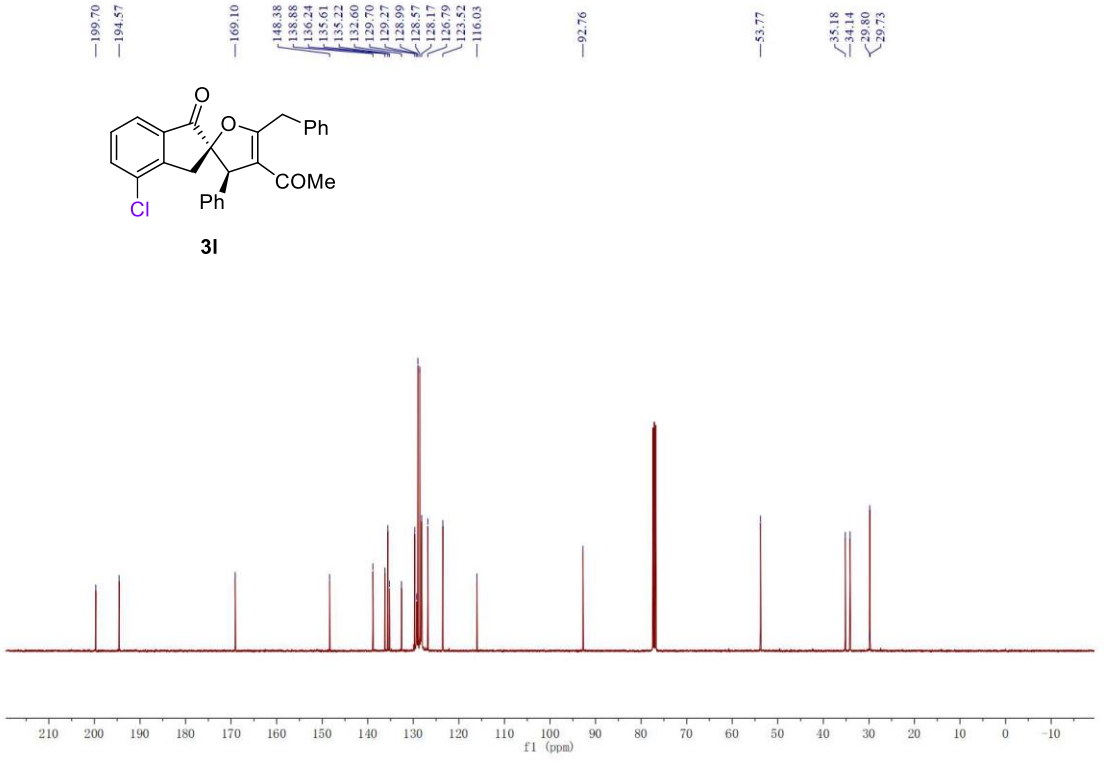

3l

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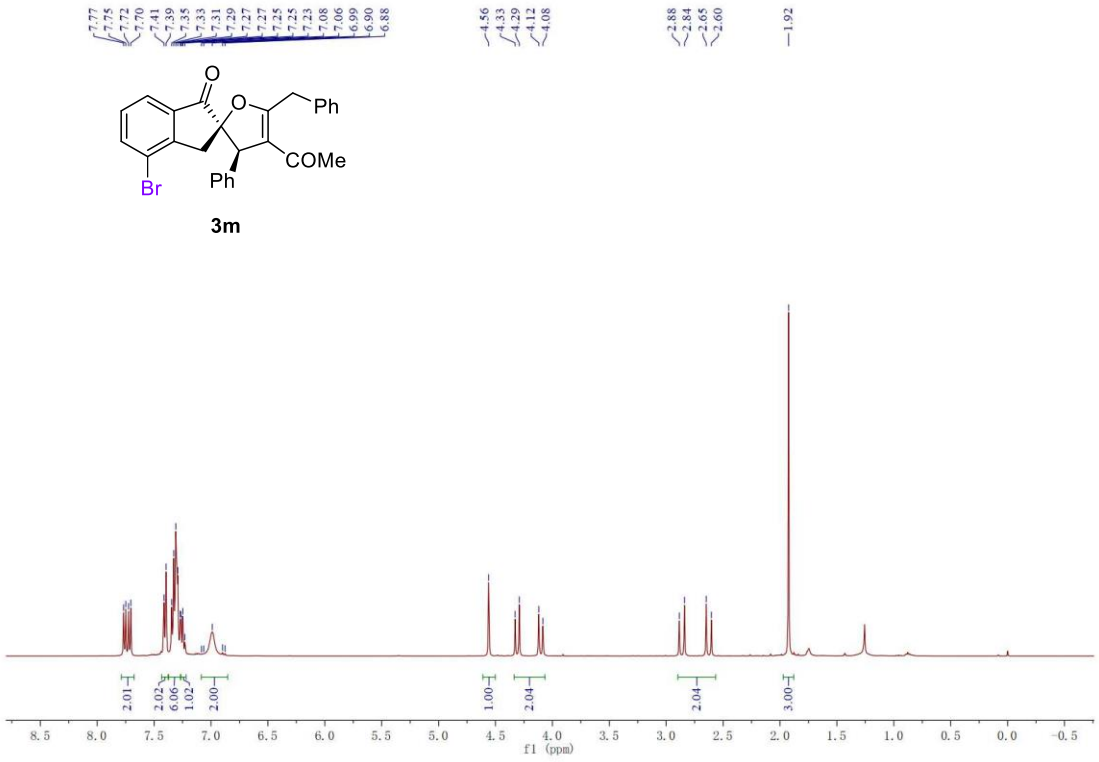

3m

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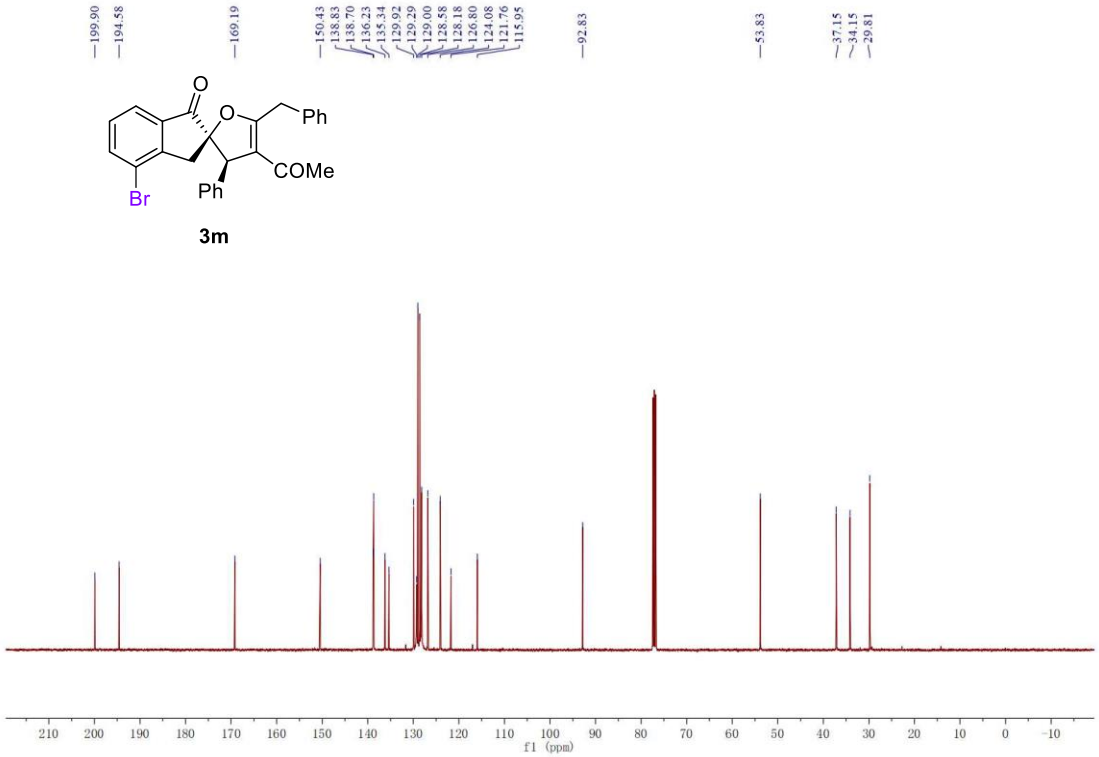

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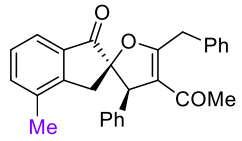
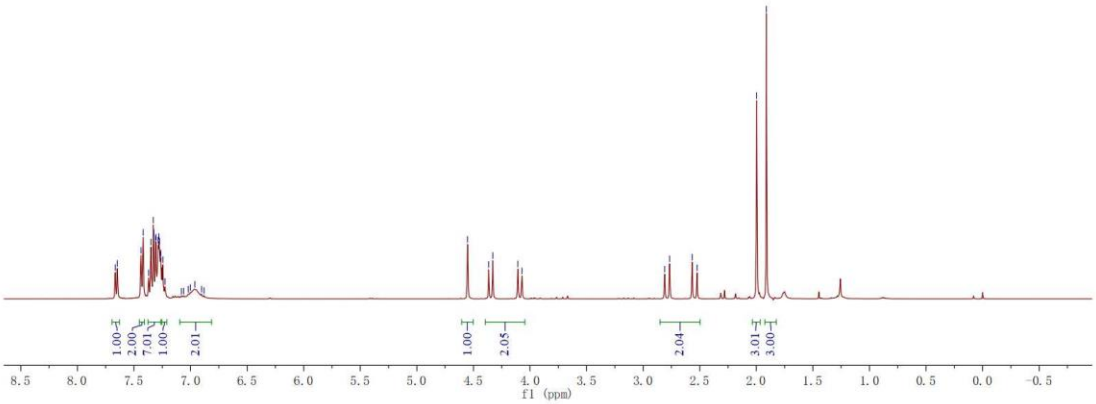
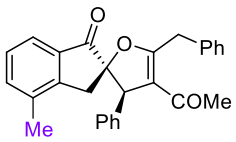


3n



^{13}C NMR (101 MHz, $CDCl_3$)



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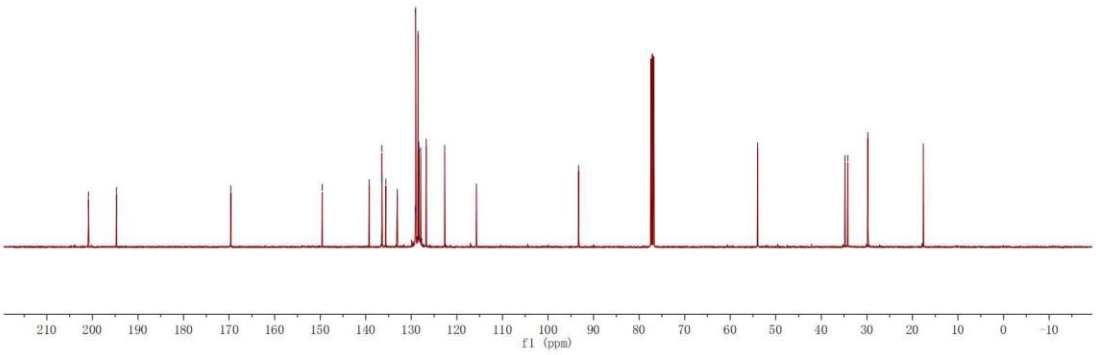

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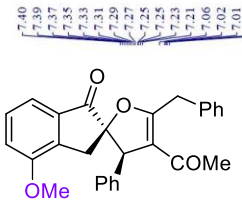
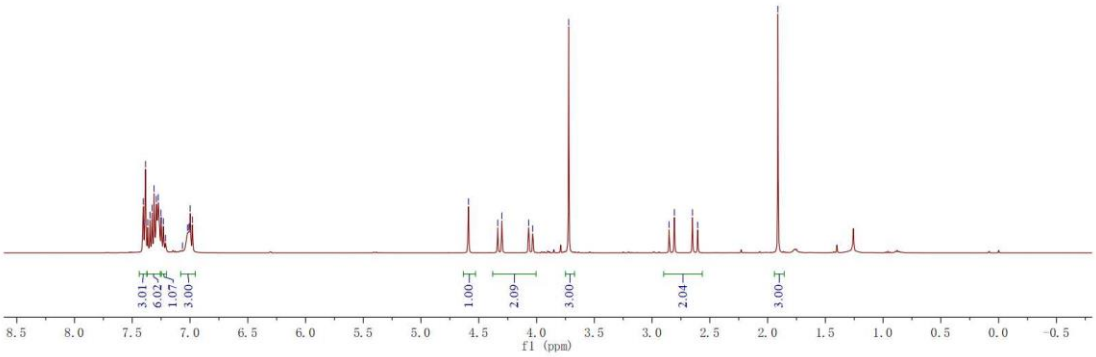


3o



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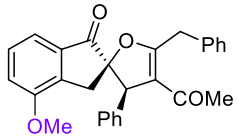
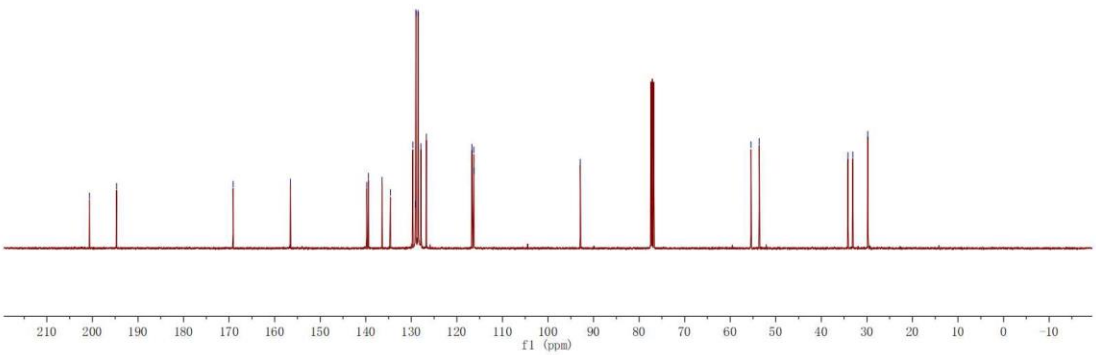


3o



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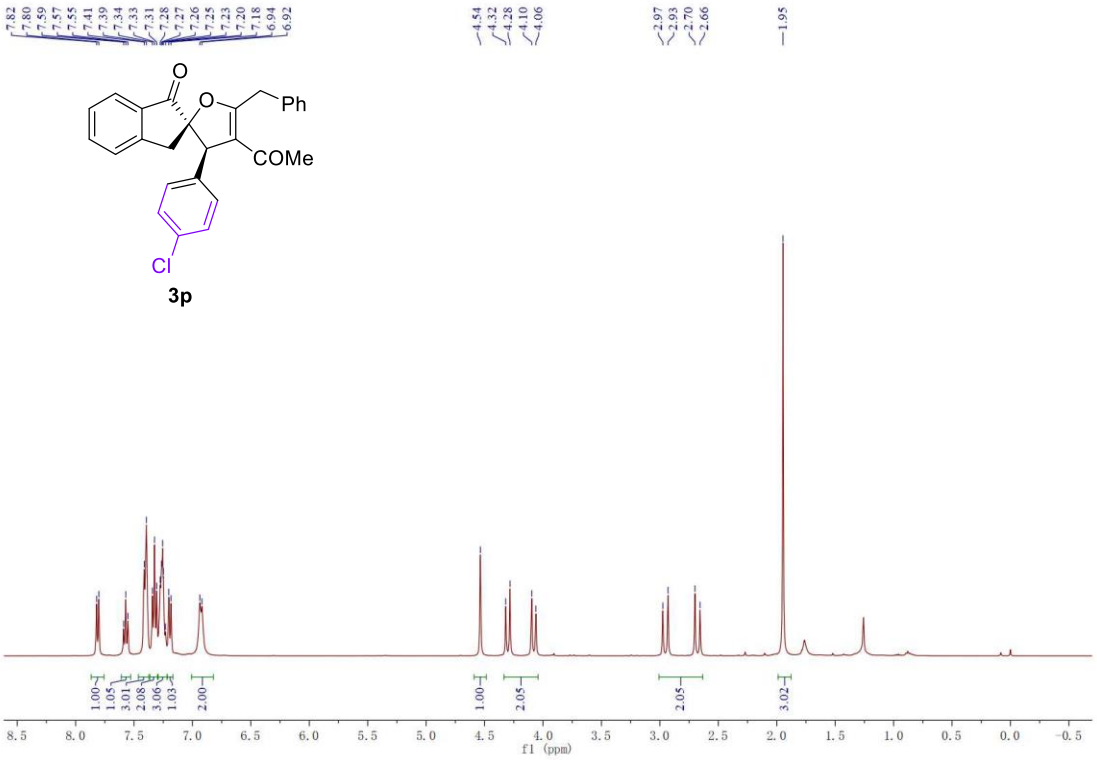
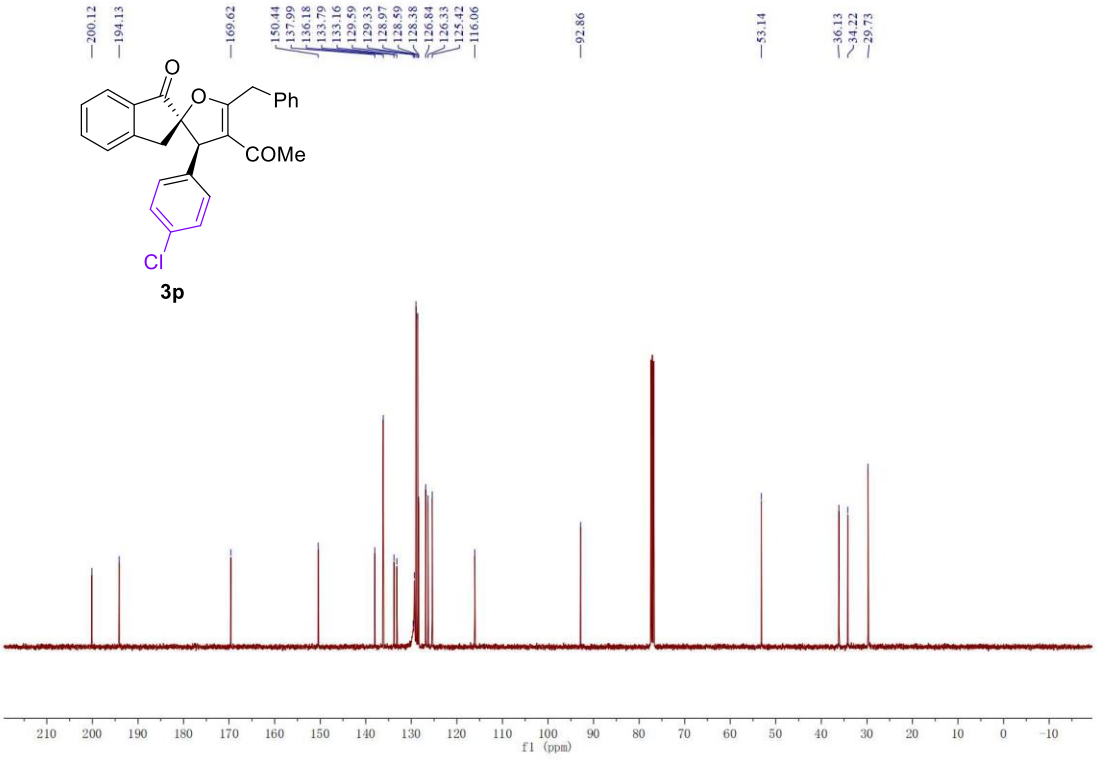
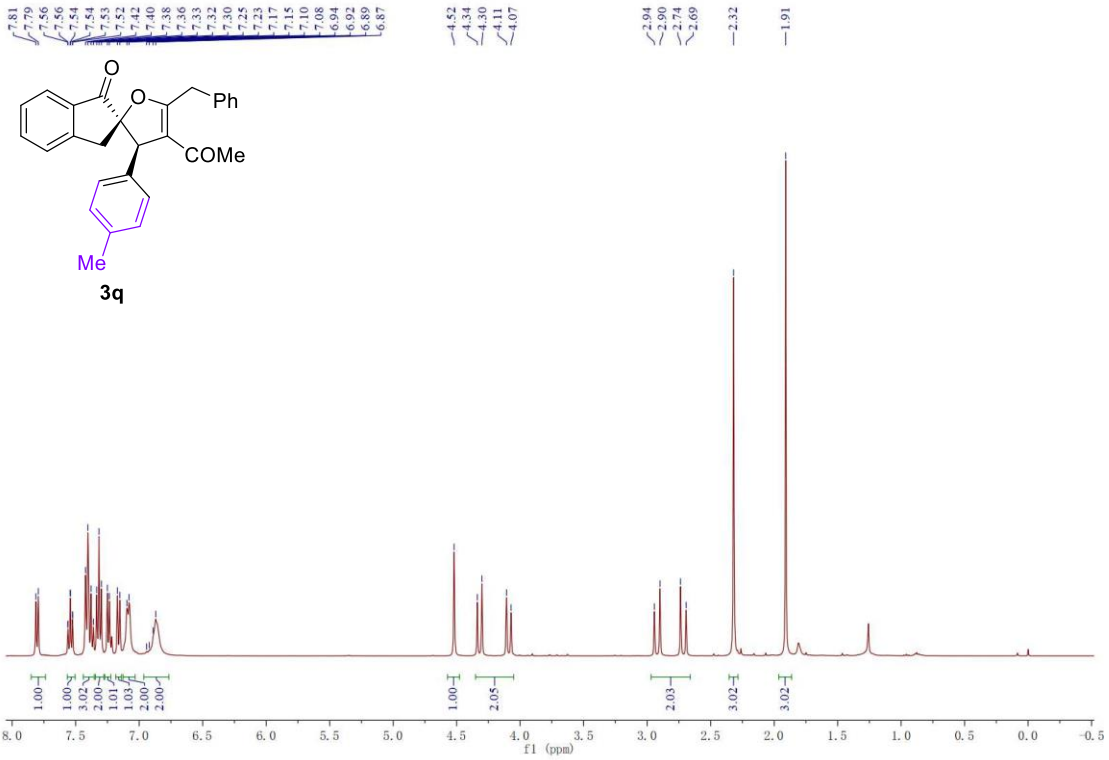


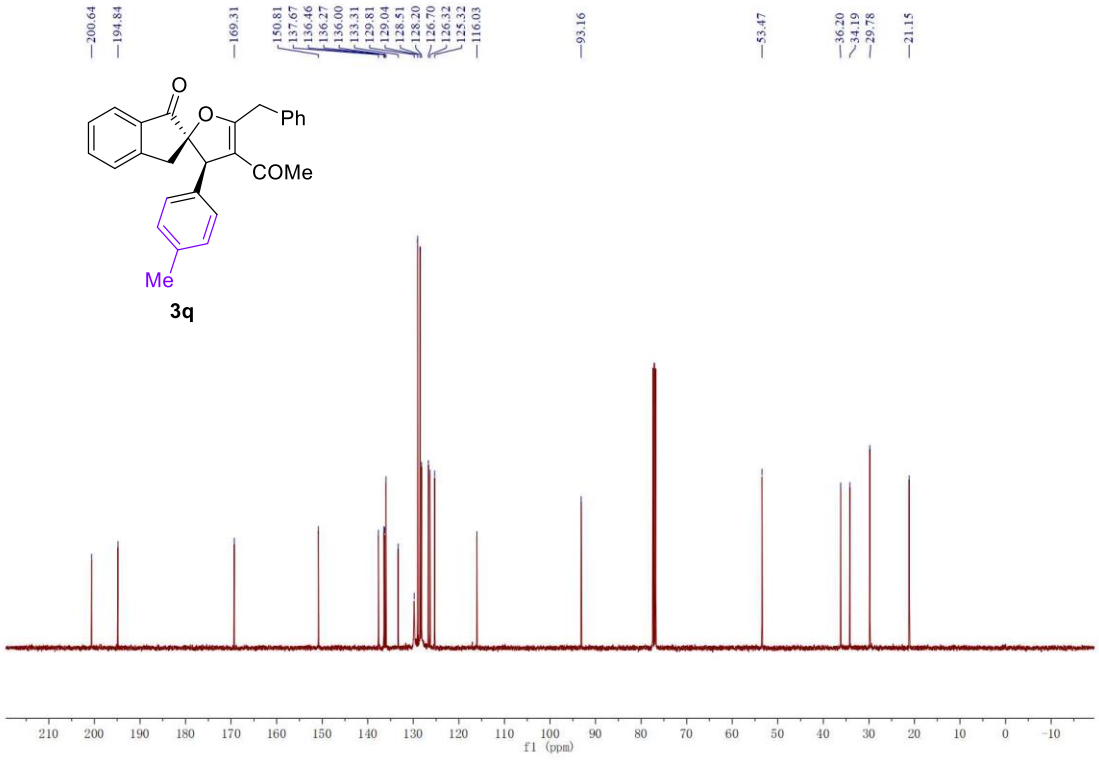
^{13}C NMR (101 MHz, $CDCl_3$)



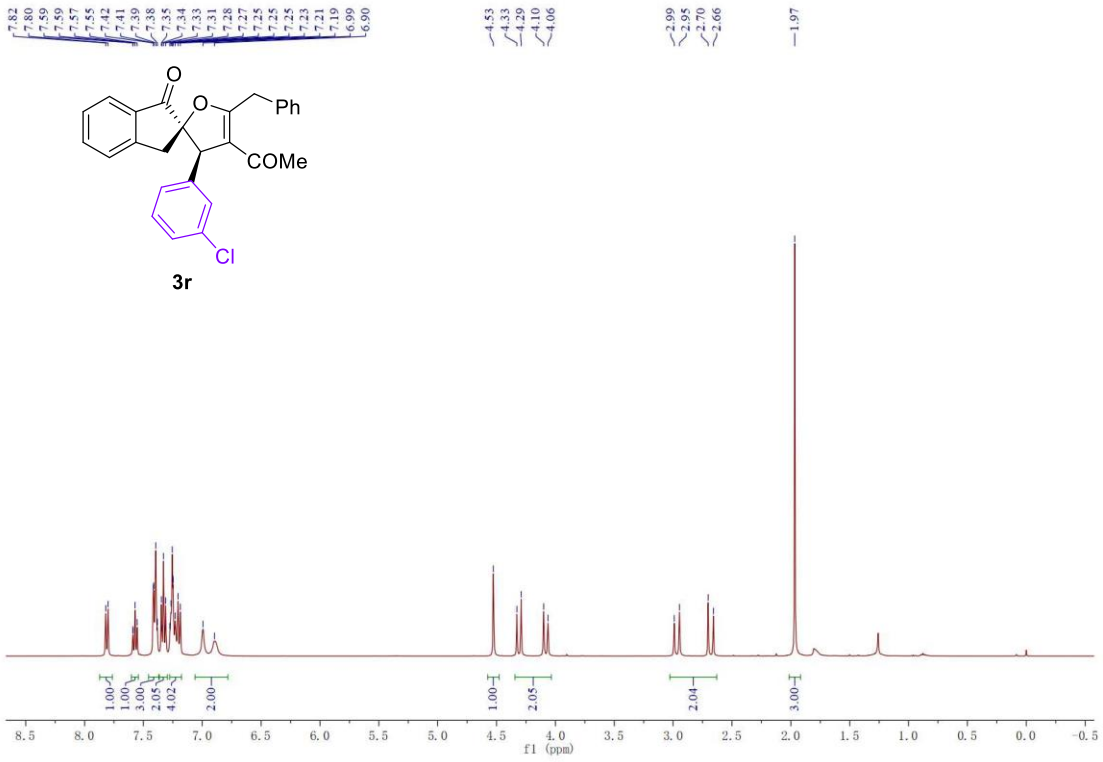
^{1}H NMR (400 MHz, $CDCl_3$)



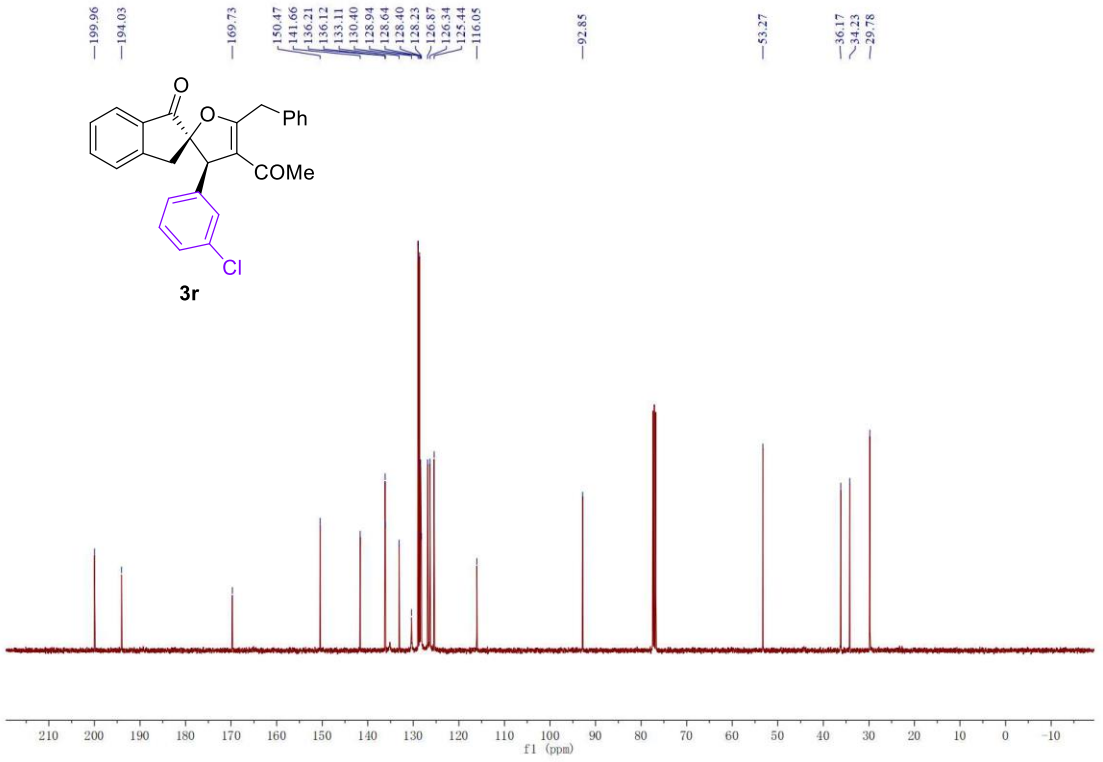
^{13}C NMR (101 MHz, $CDCl_3$)



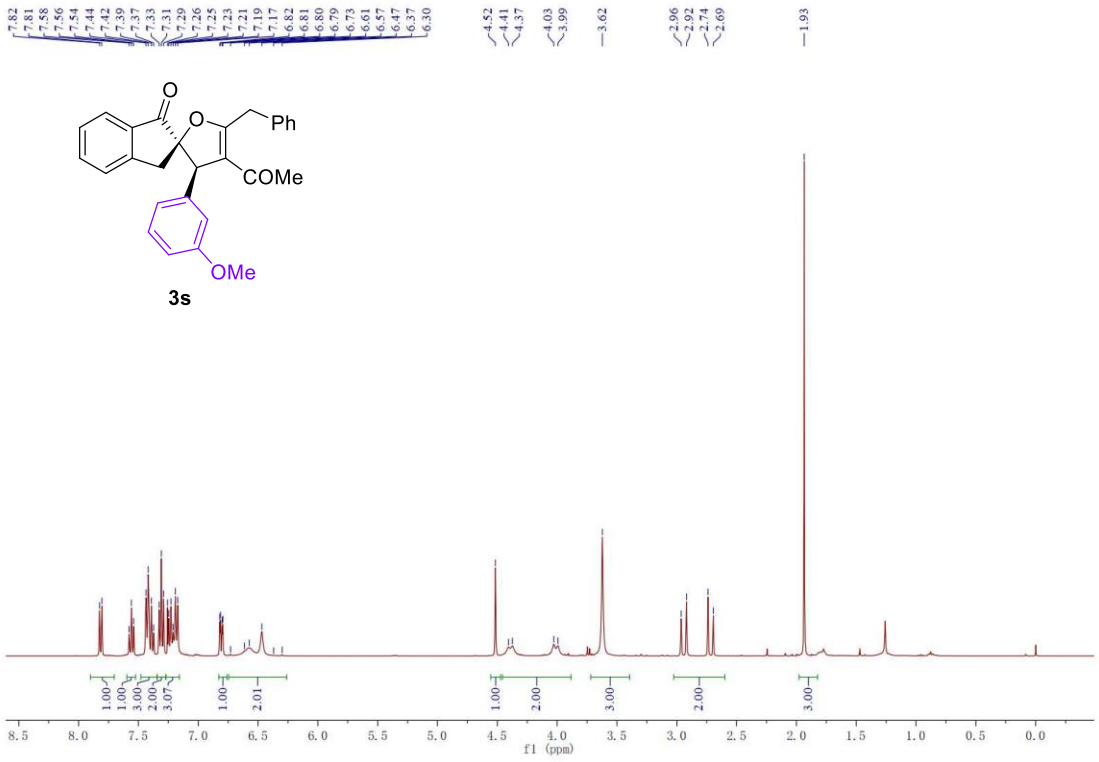
^{1}H NMR (400 MHz, $CDCl_3$)



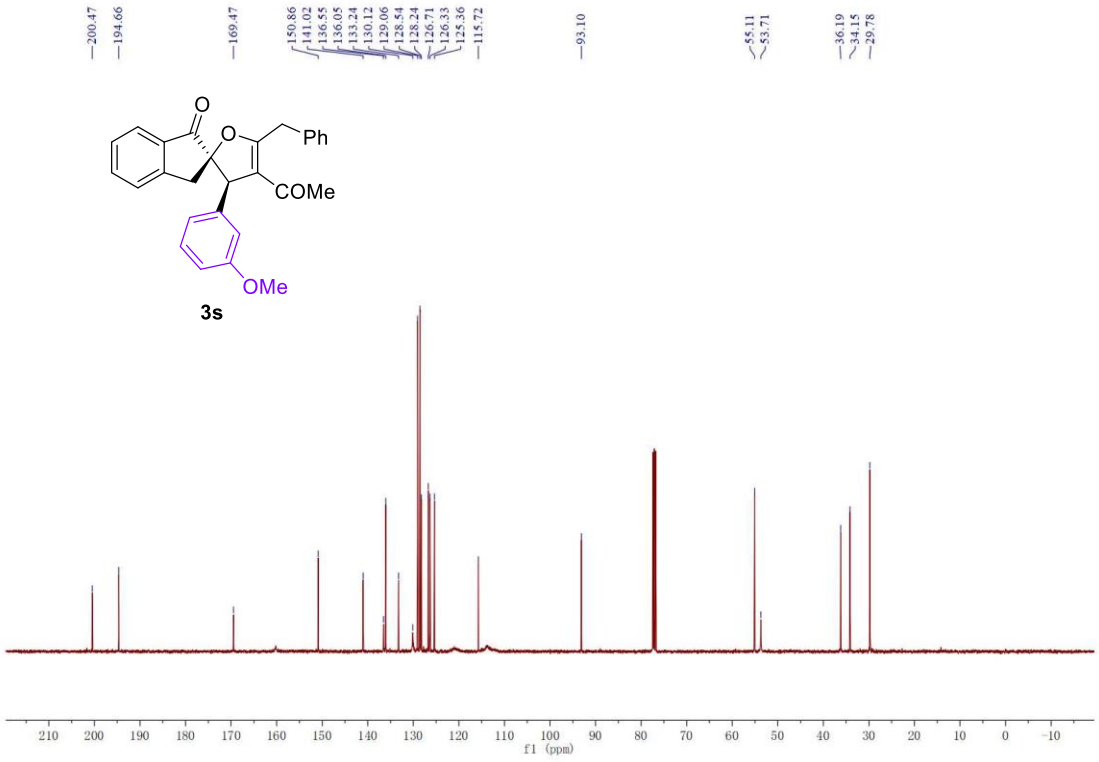
^{13}C NMR (101 MHz, $CDCl_3$)



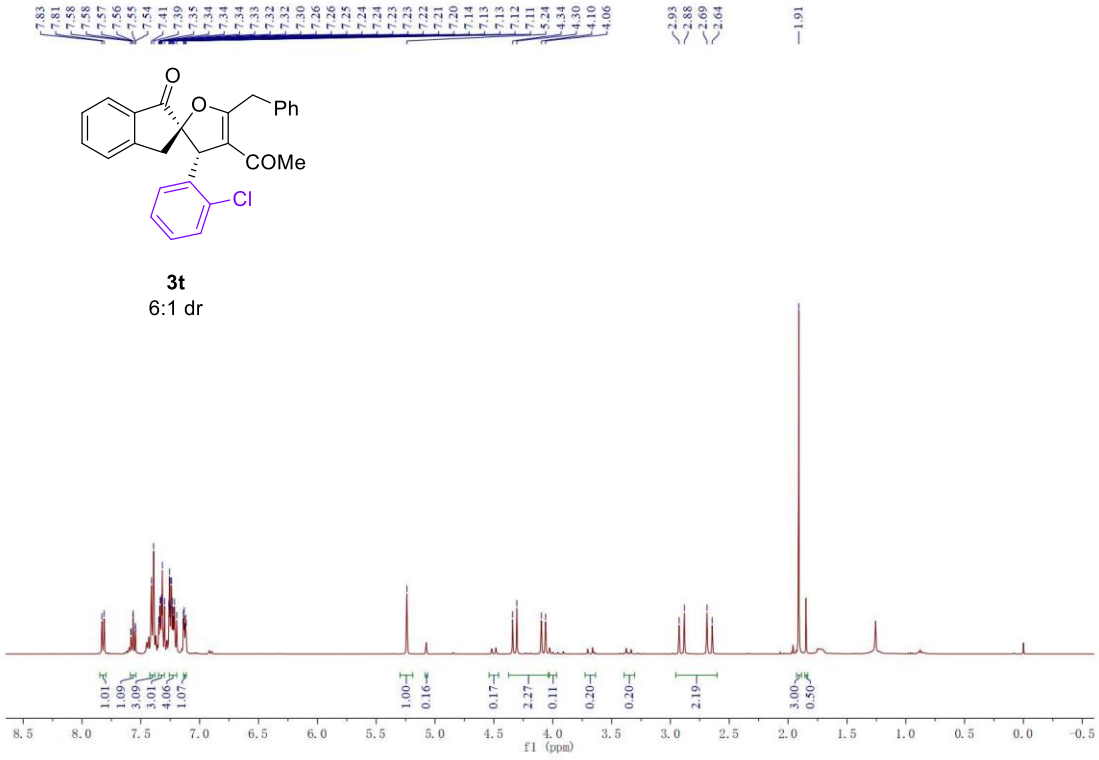
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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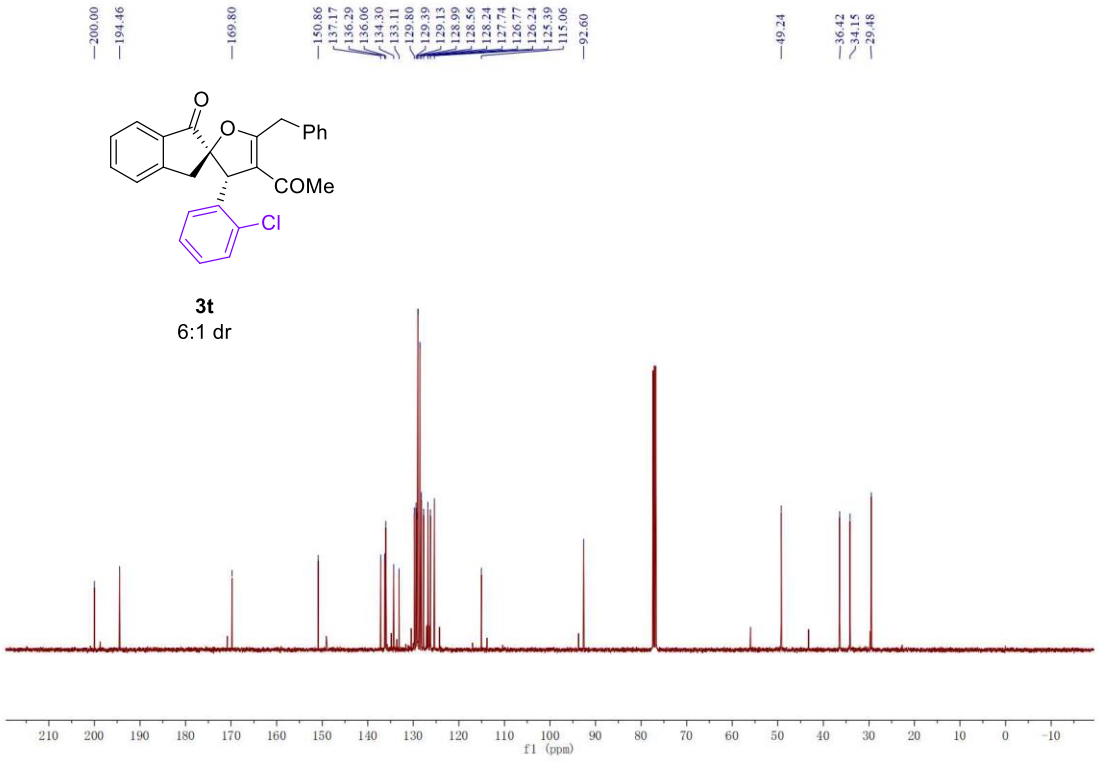

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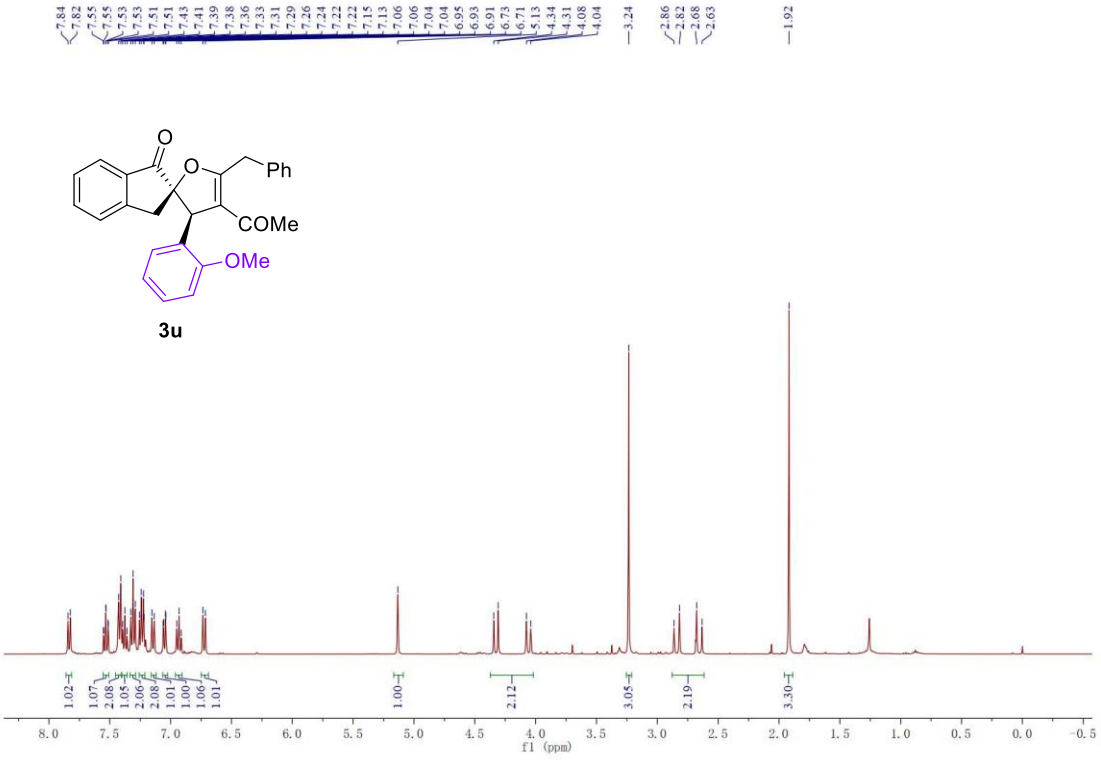

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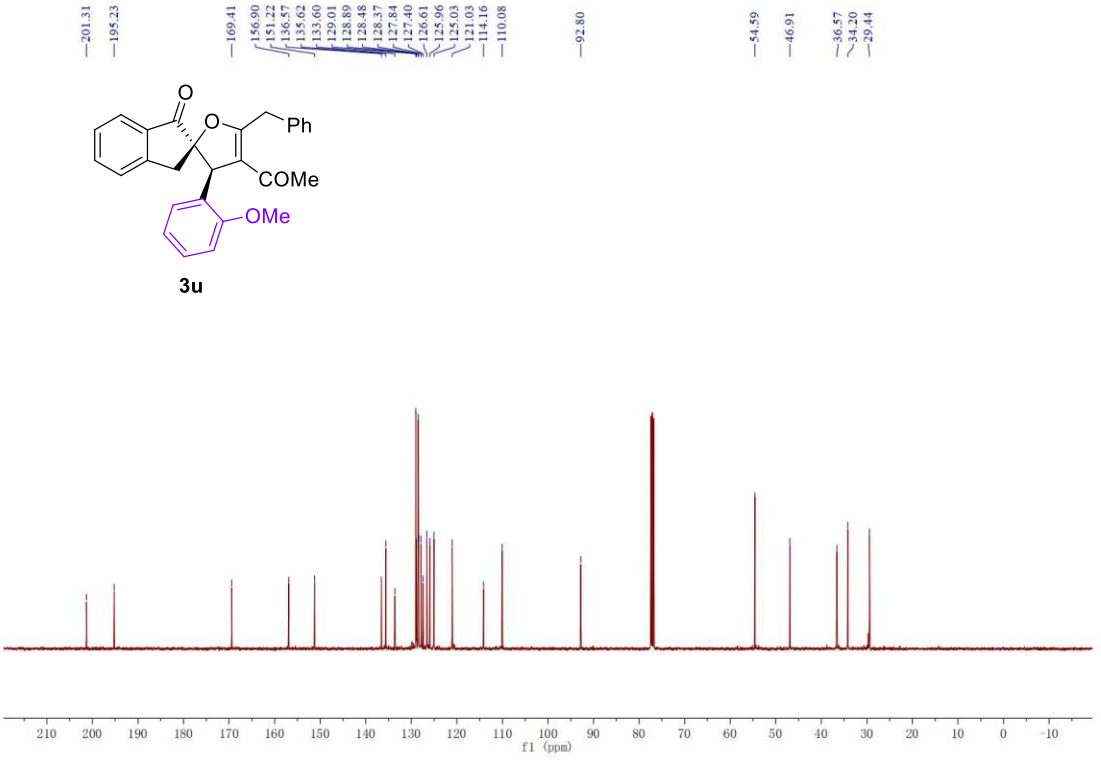

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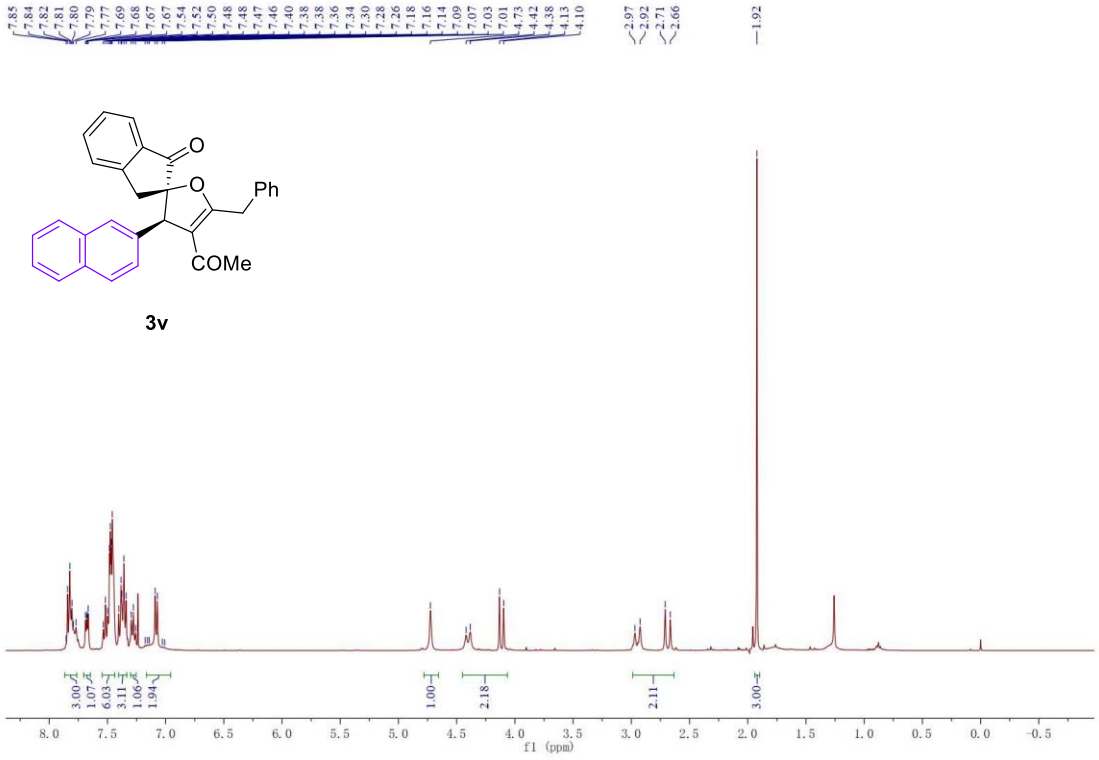
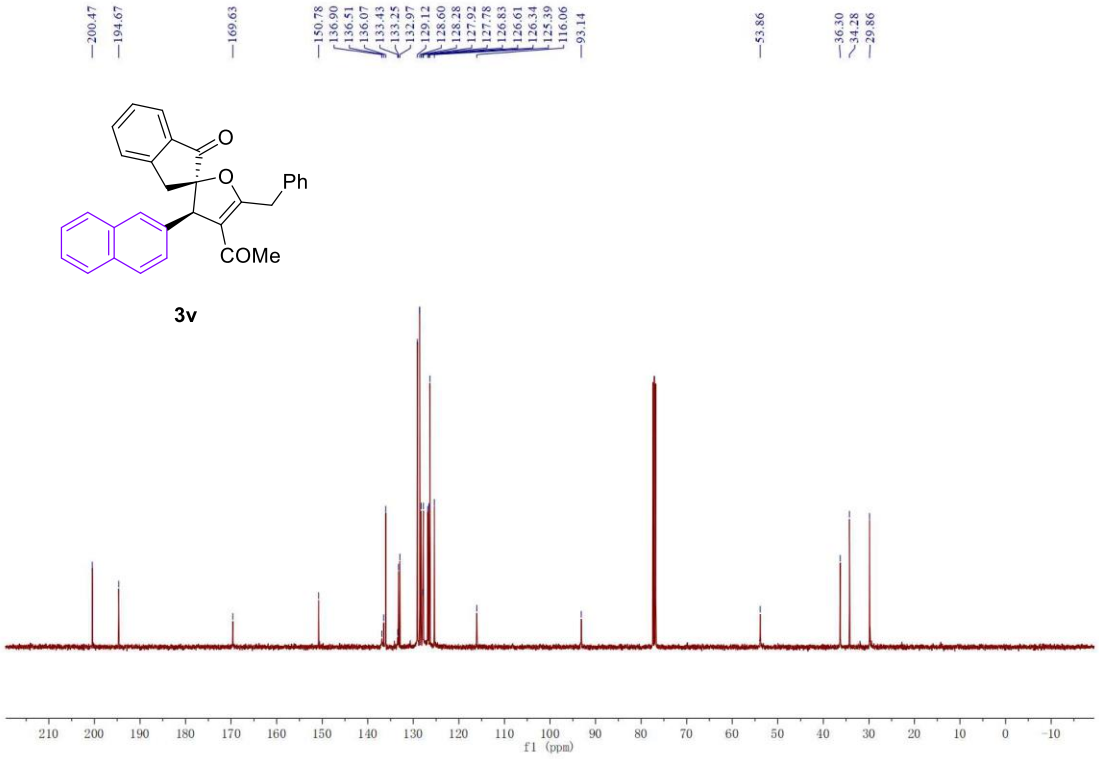


^{13}C NMR (101 MHz, $CDCl_3$)



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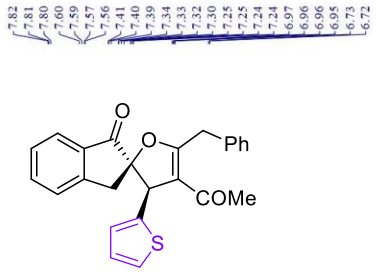
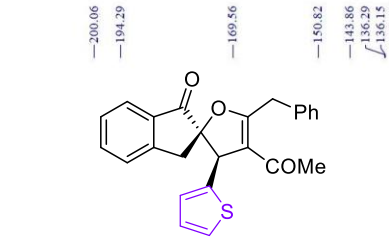


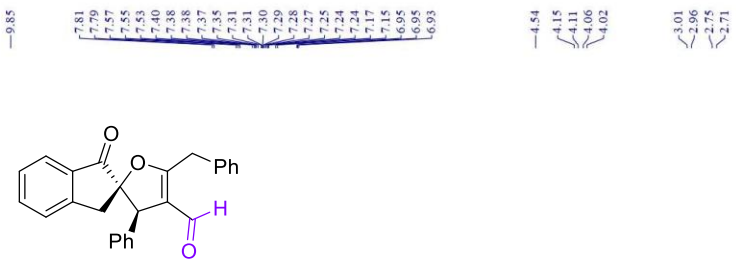
3w
2.5:1 dr

^{13}C NMR (101 MHz, $CDCl_3$)

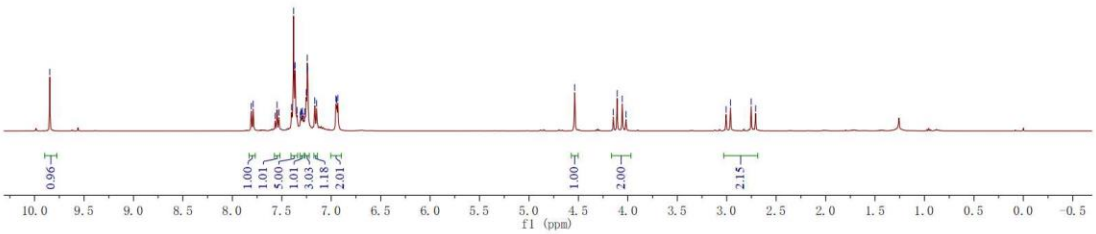


3w
2.5:1 dr

^{1}H NMR (400 MHz, $CDCl_3$)

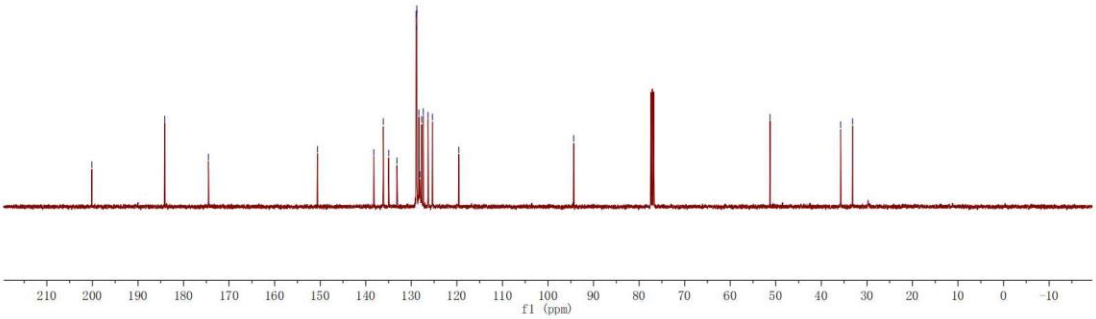


3x

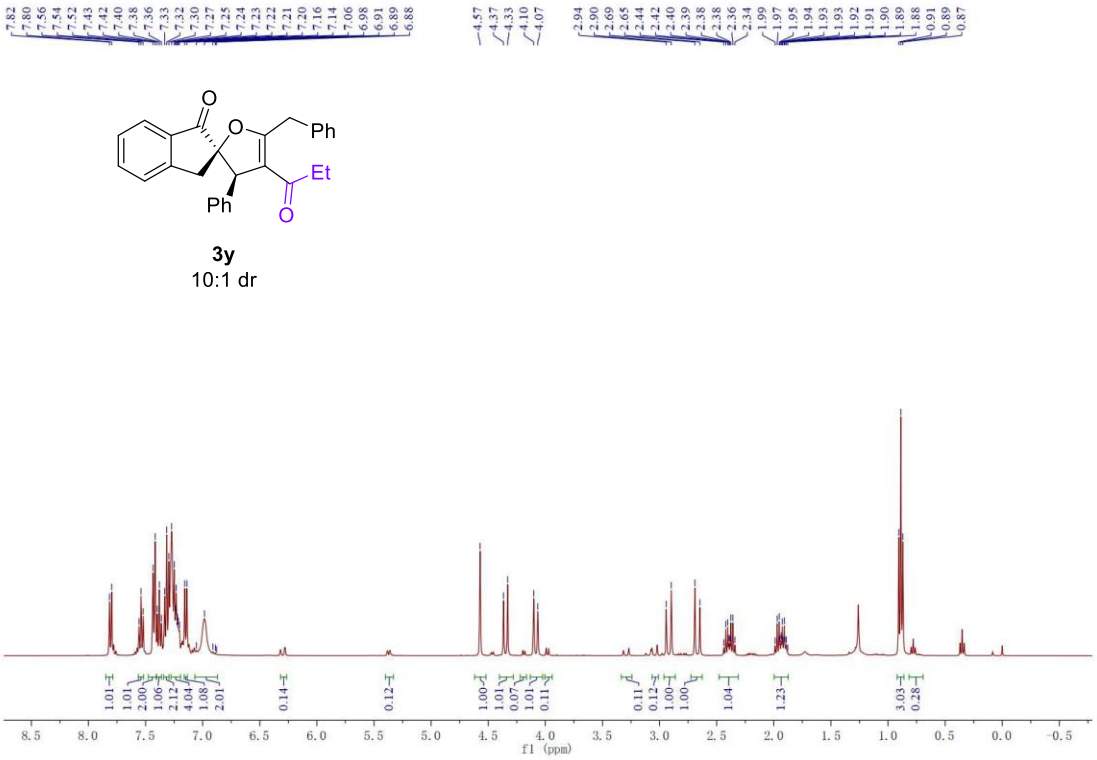


^{13}C NMR (101 MHz, $CDCl_3$)

3x

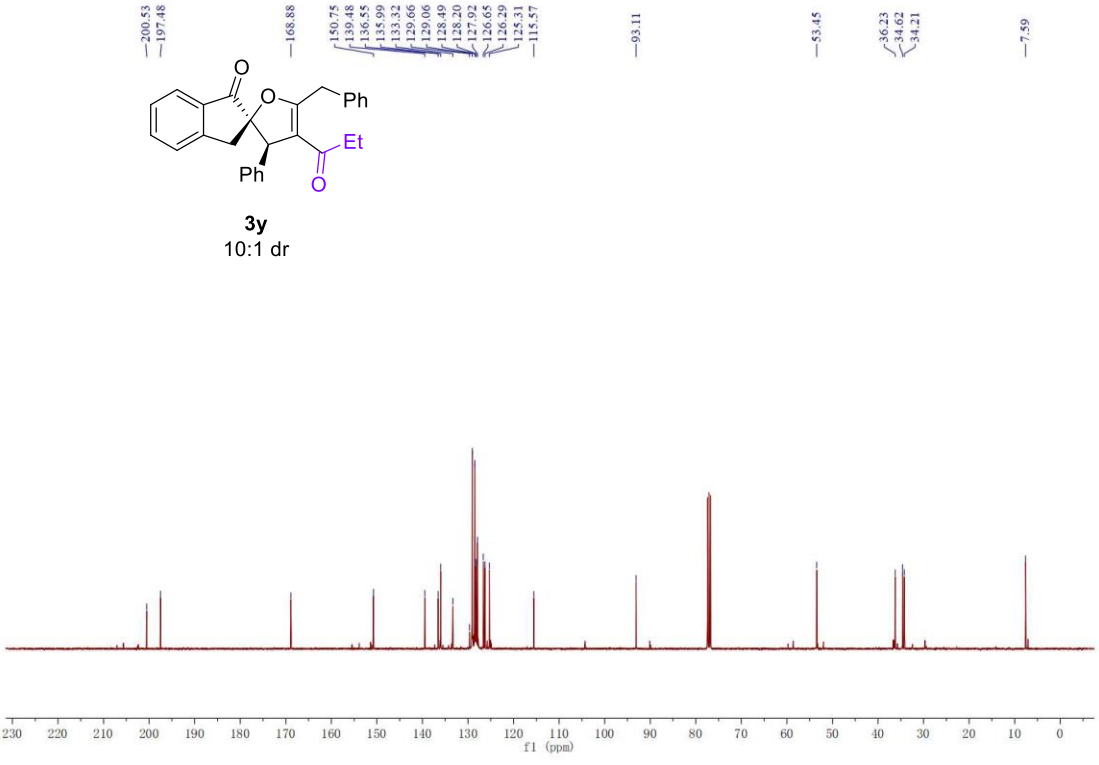


^{1}H NMR (400 MHz, $CDCl_3$)



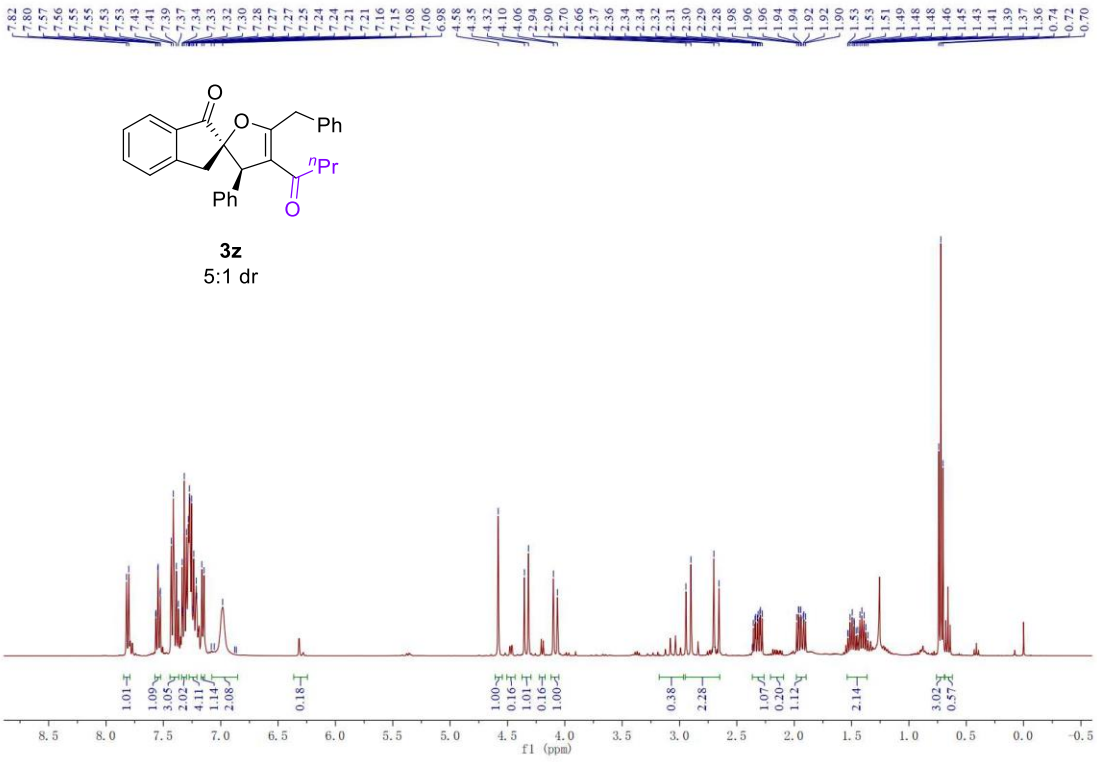
3y
10:1 dr

^{13}C NMR (101 MHz, $CDCl_3$)



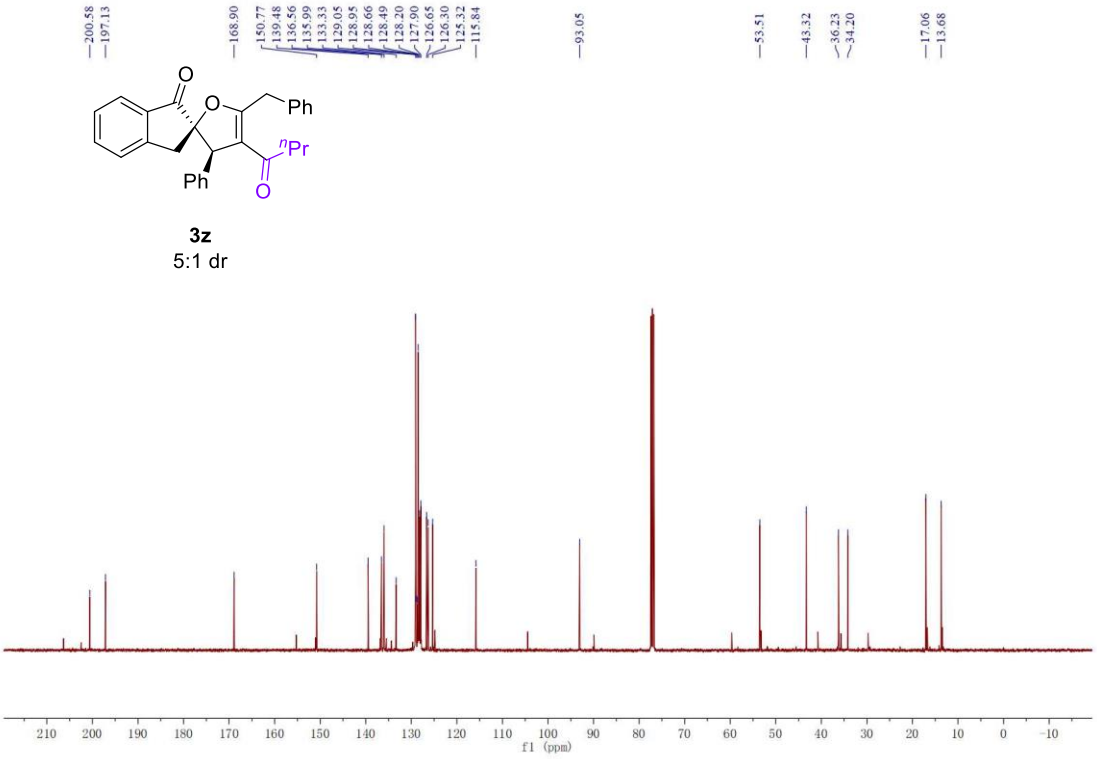
3y
10:1 dr

^{1}H NMR (400 MHz, $CDCl_3$)



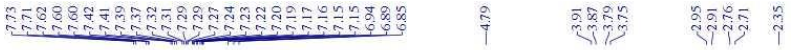
3z
5:1 dr

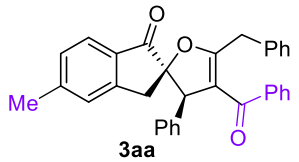
^{13}C NMR (101 MHz, $CDCl_3$)

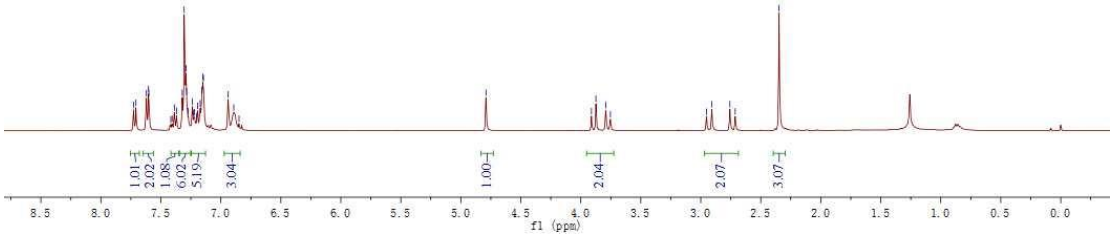


3z
5:1 dr

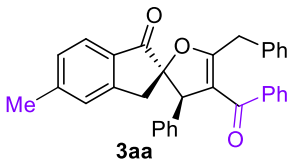
^{1}H NMR (400 MHz, $CDCl_3$)

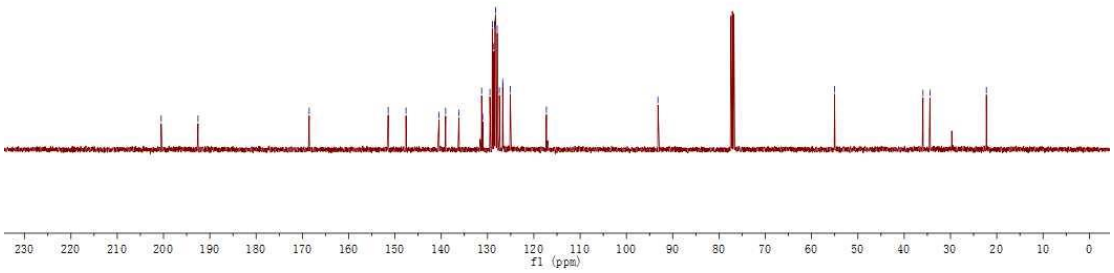




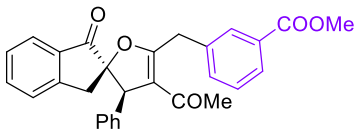


^{13}C NMR (101 MHz, $CDCl_3$)





^{1}H NMR (400 MHz, $CDCl_3$)



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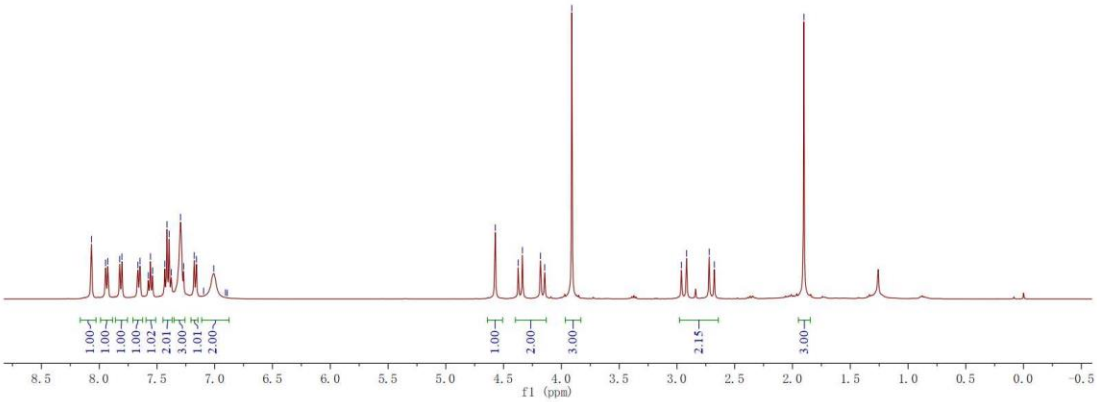
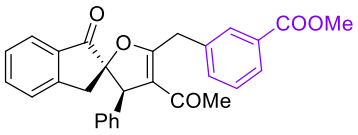
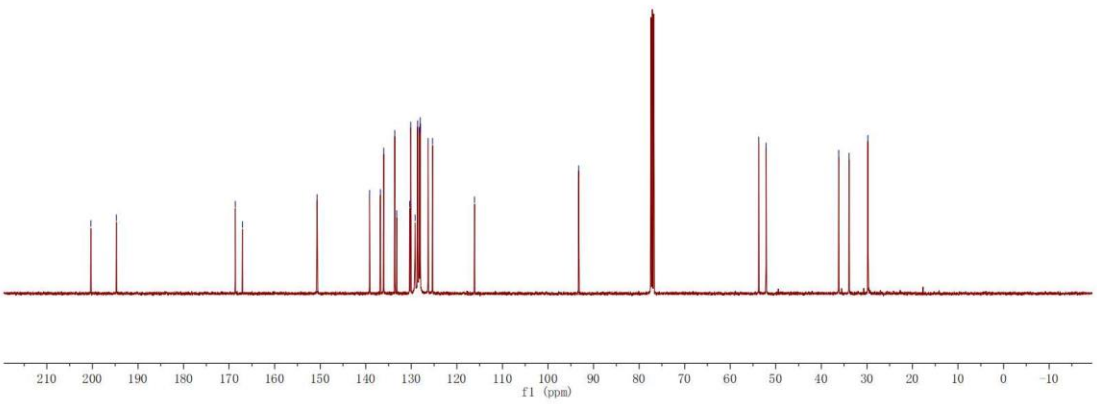


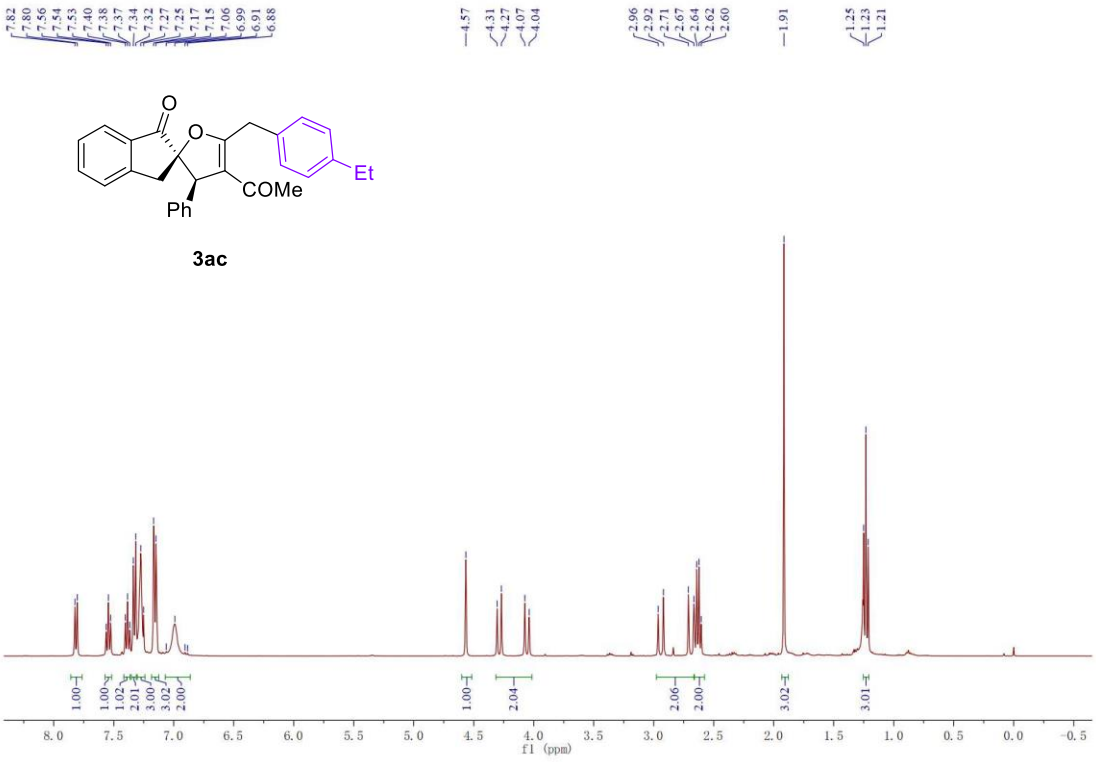
^{13}C NMR (101 MHz, $CDCl_3$)



3ab

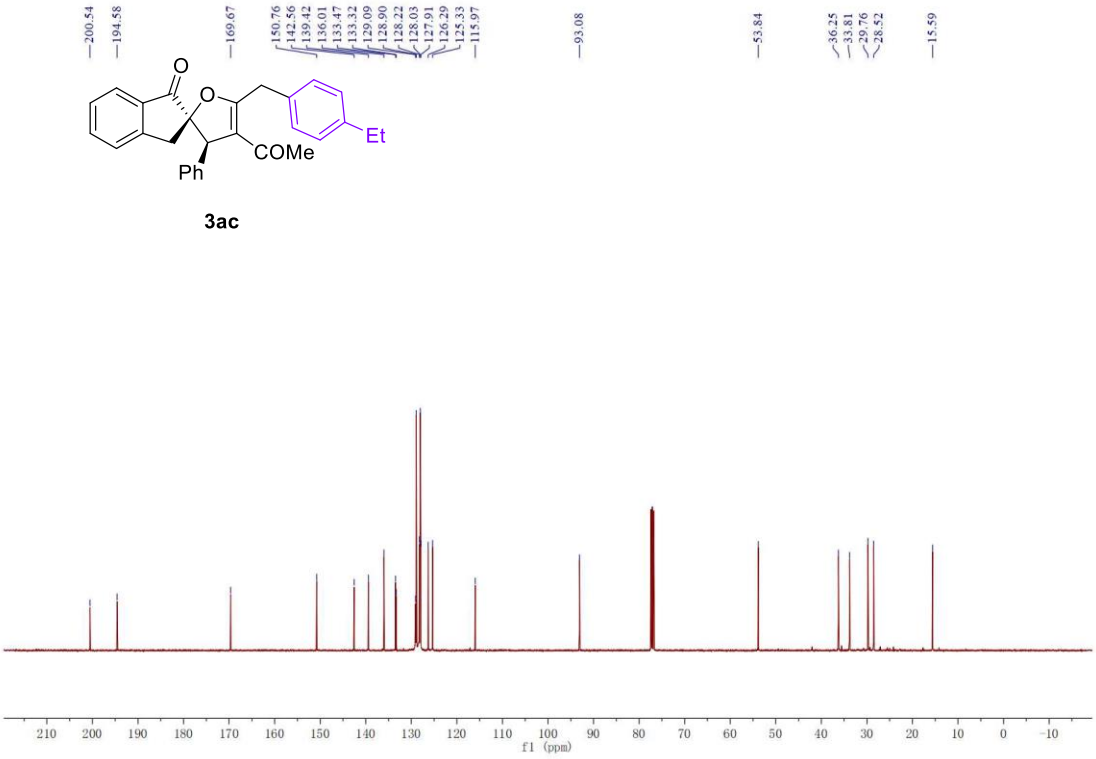


^{1}H NMR (400 MHz, $CDCl_3$)



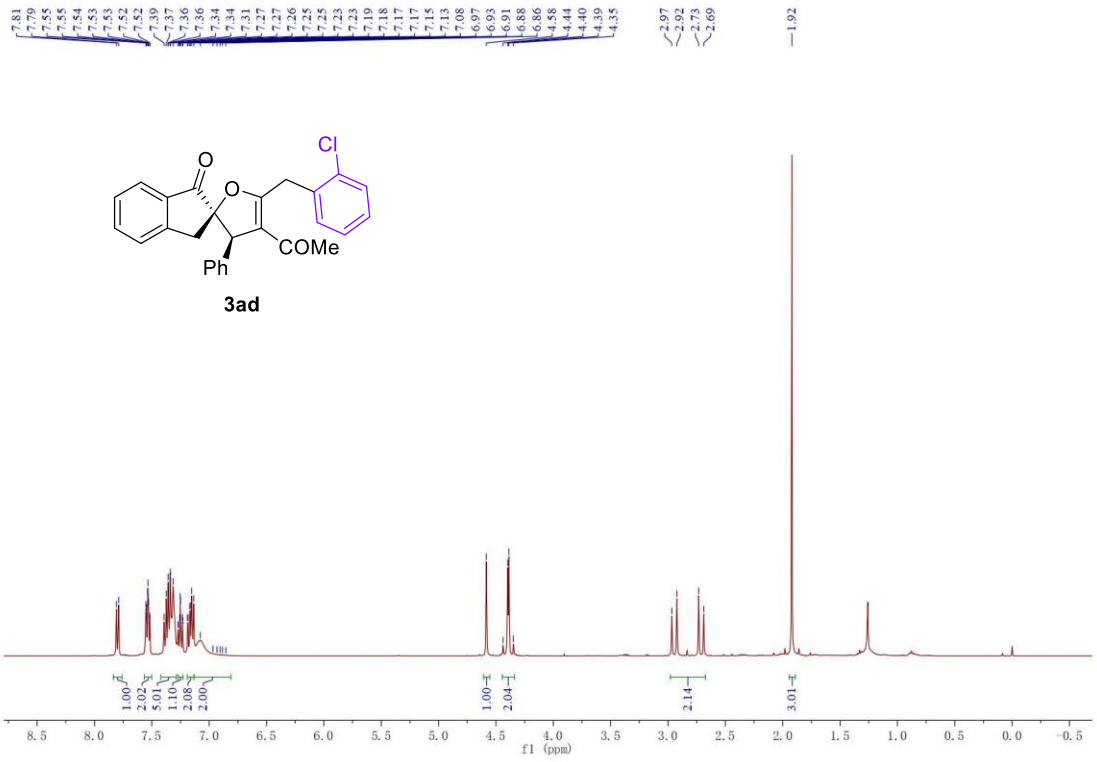
3ac

^{13}C NMR (101 MHz, $CDCl_3$)

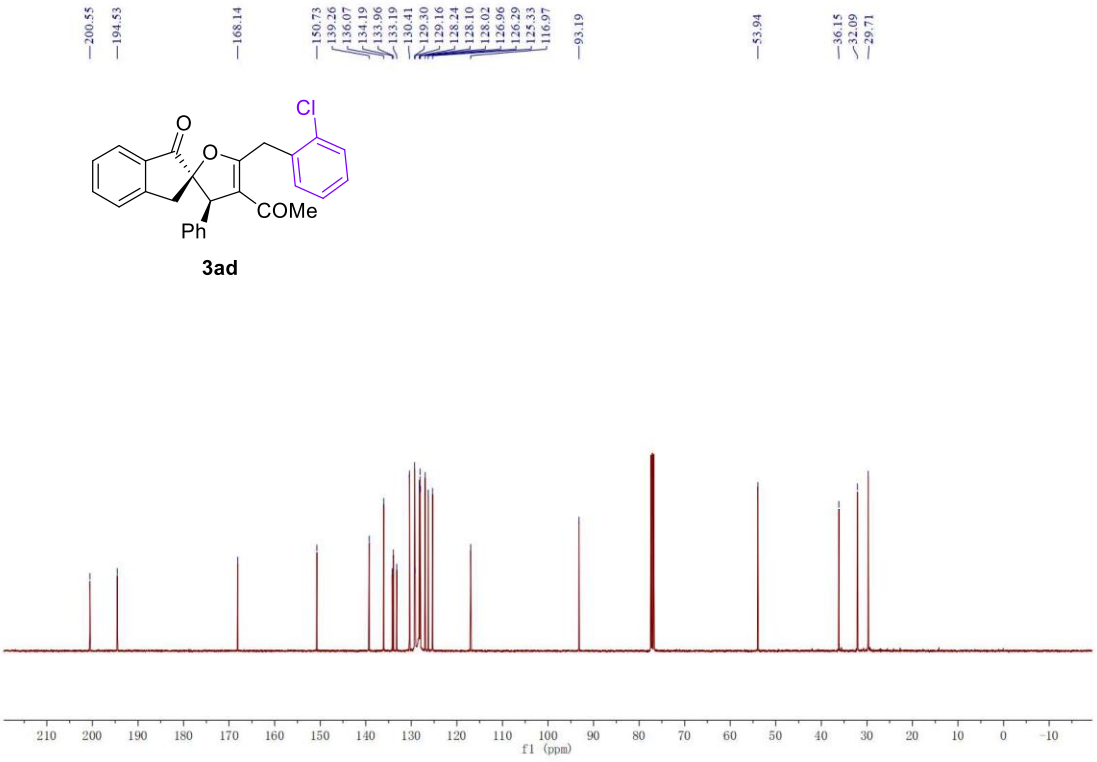


3ac

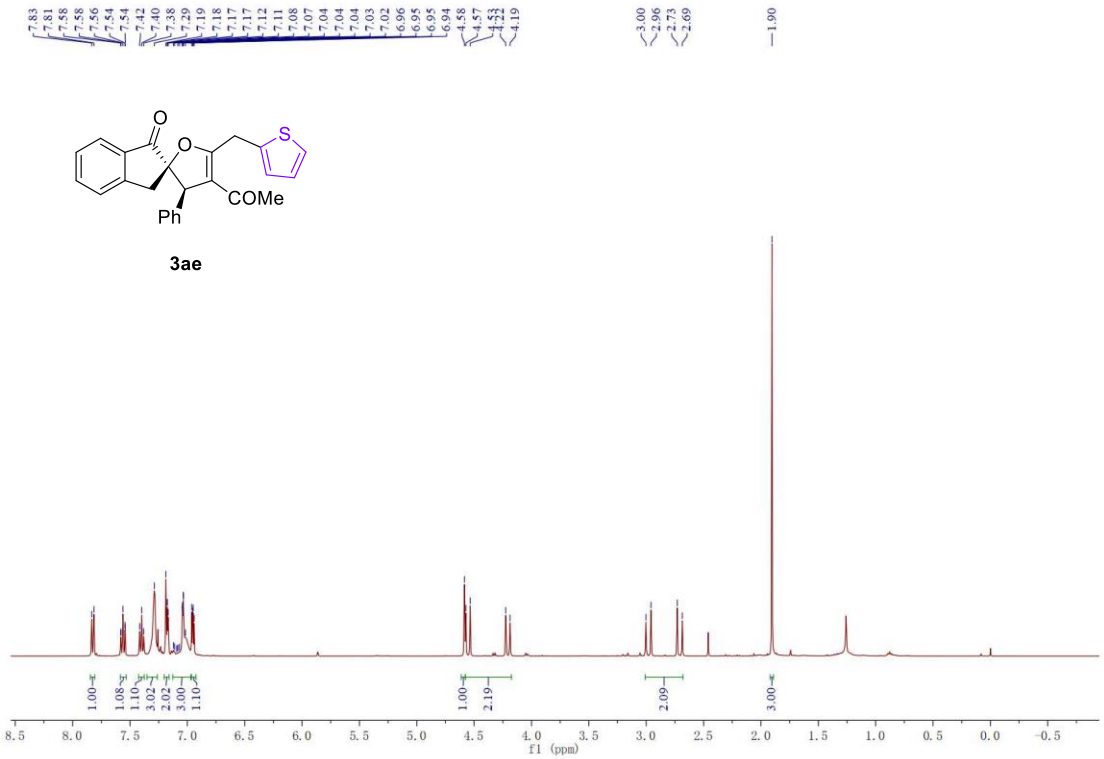
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

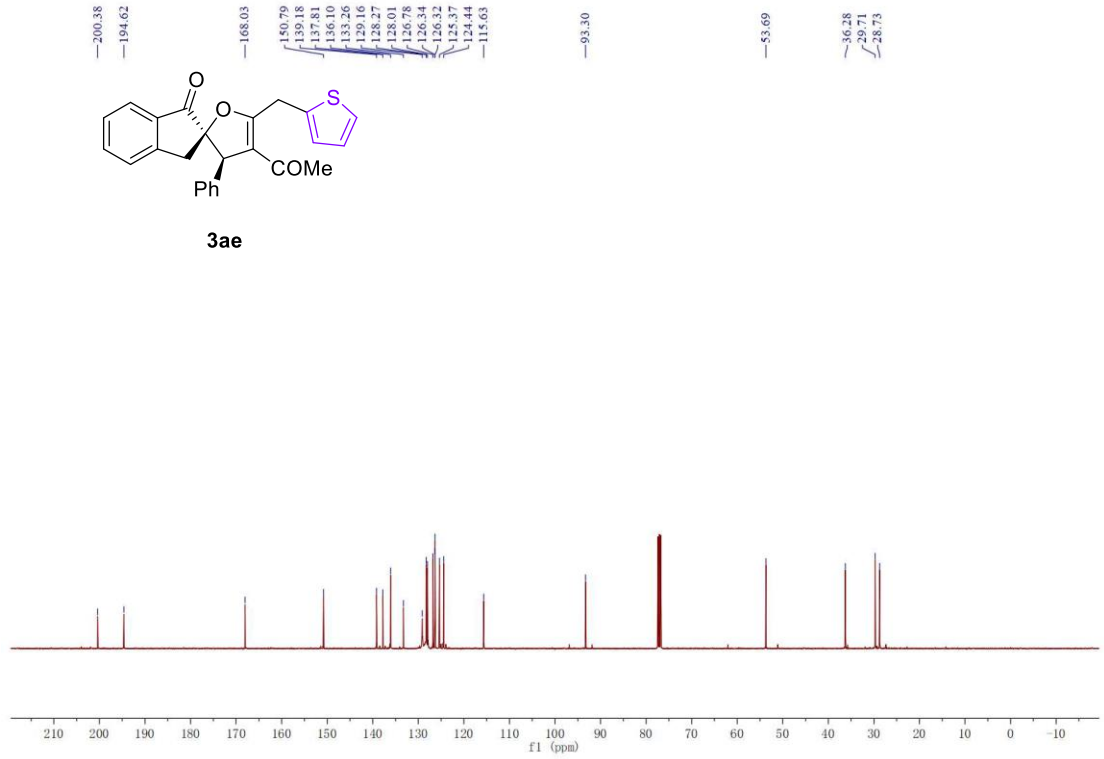


^{1}H NMR (400 MHz, $CDCl_3$)



3ae

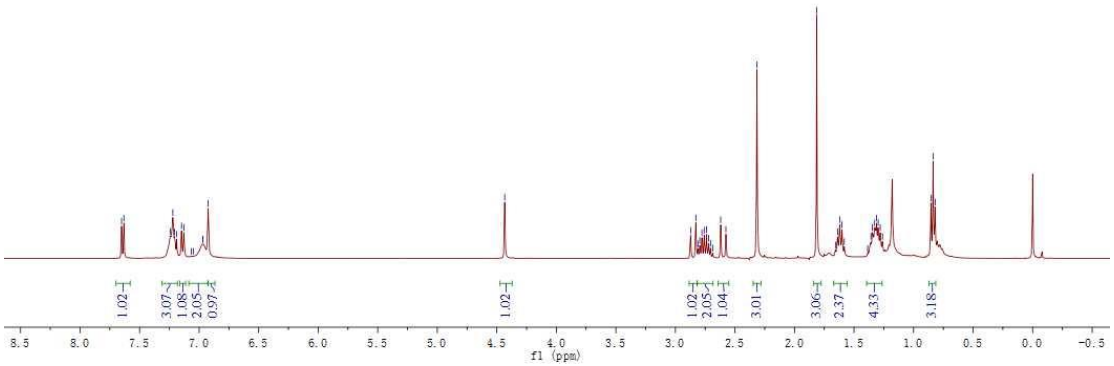
^{13}C NMR (101 MHz, $CDCl_3$)



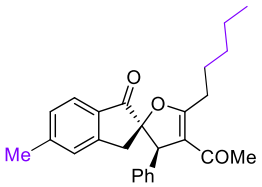
3ae

^{1}H NMR (400 MHz, $CDCl_3$)

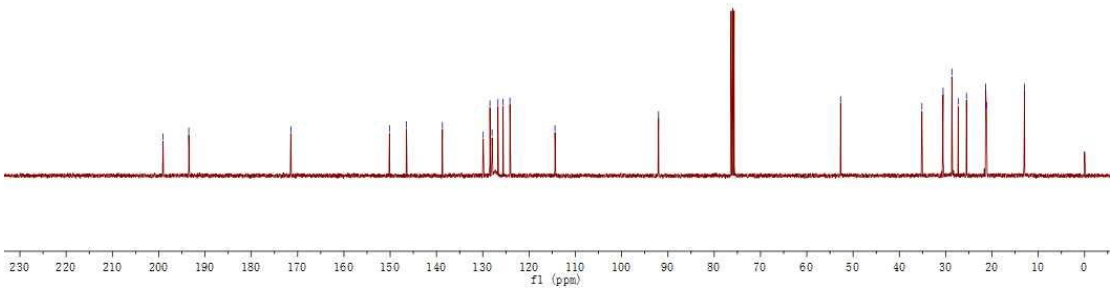
3af



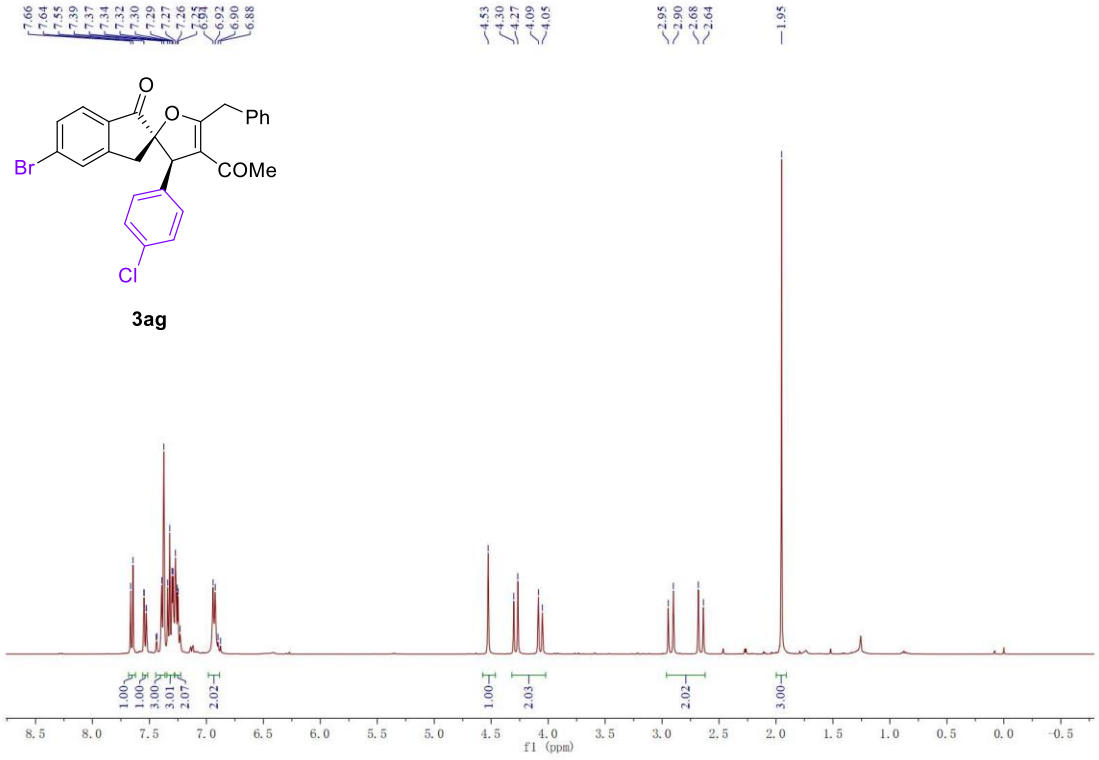
^{13}C NMR (101 MHz, $CDCl_3$)



3af

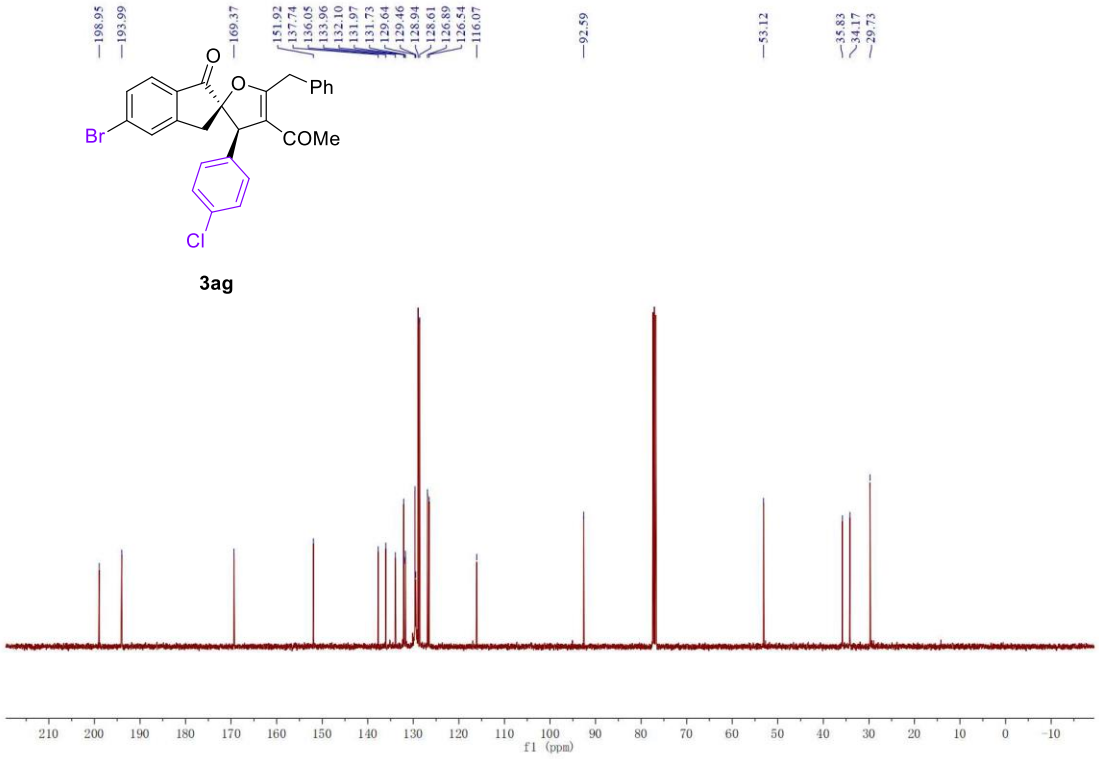


^{1}H NMR (400 MHz, $CDCl_3$)



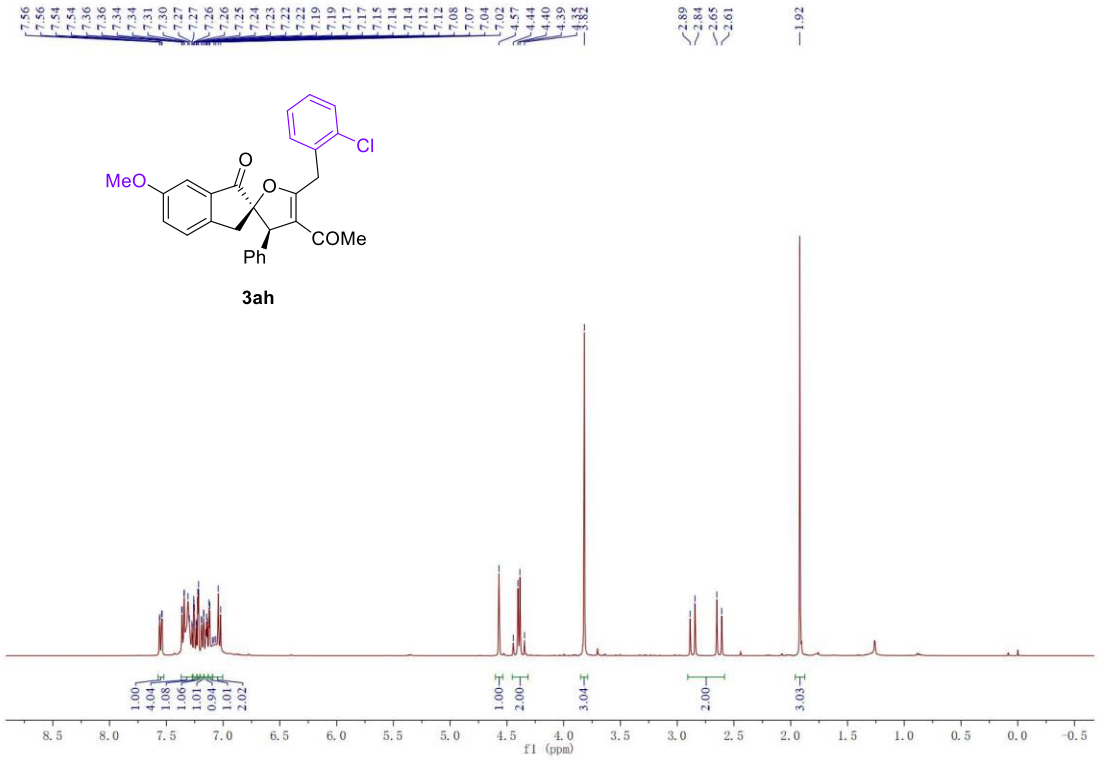
3ag

^{13}C NMR (101 MHz, $CDCl_3$)

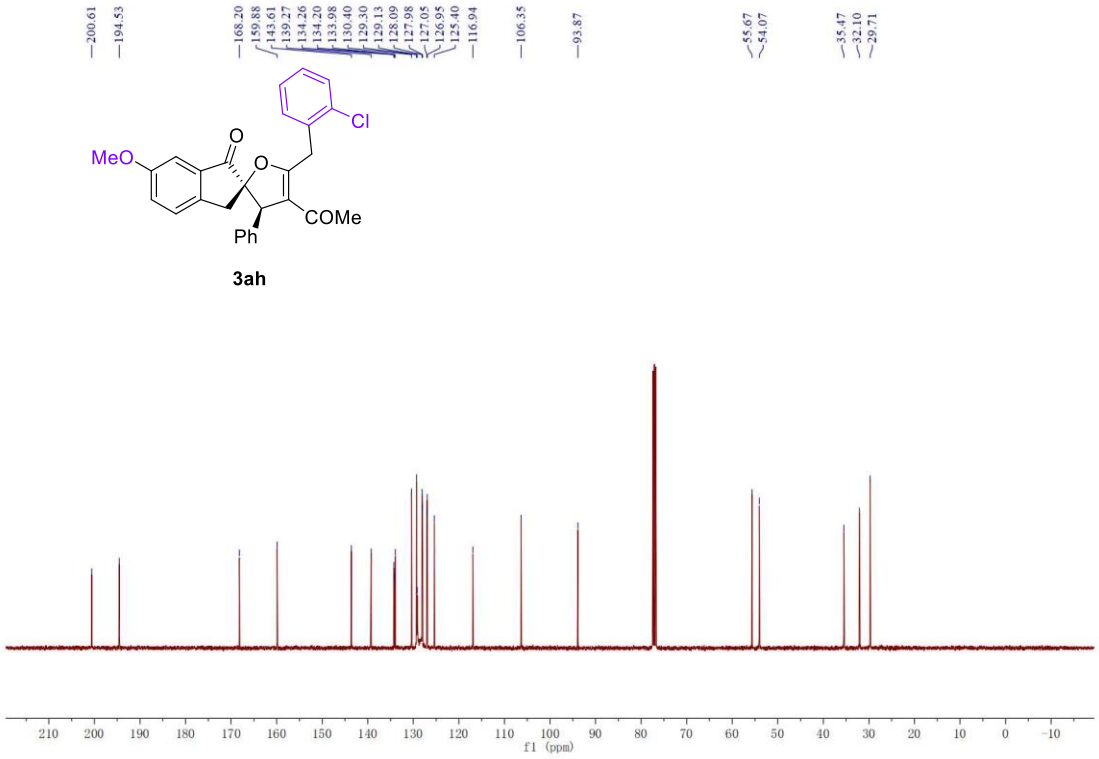


3ag

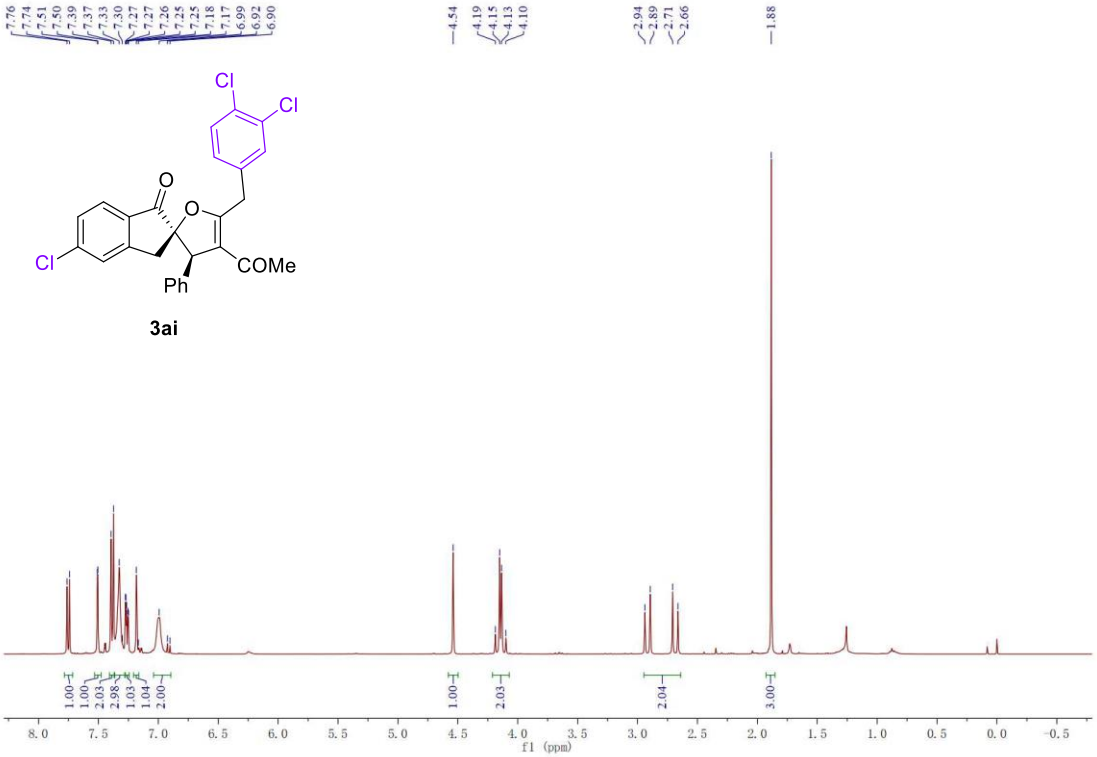
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

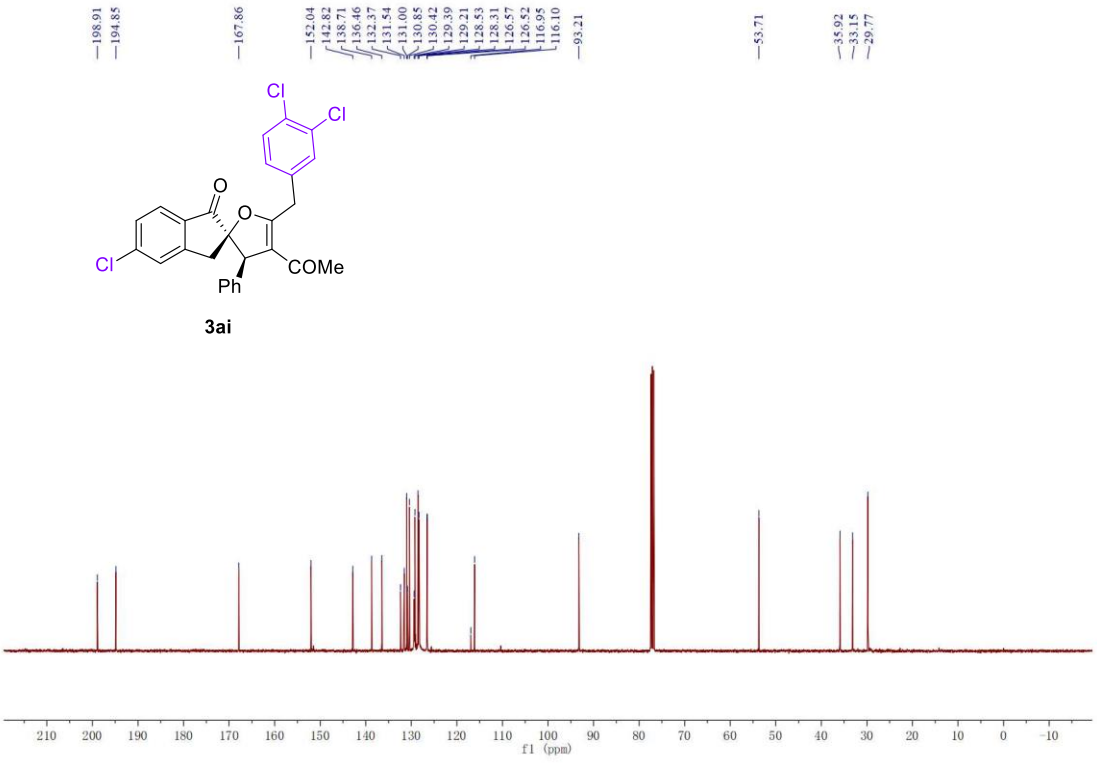


^{1}H NMR (400 MHz, $CDCl_3$)



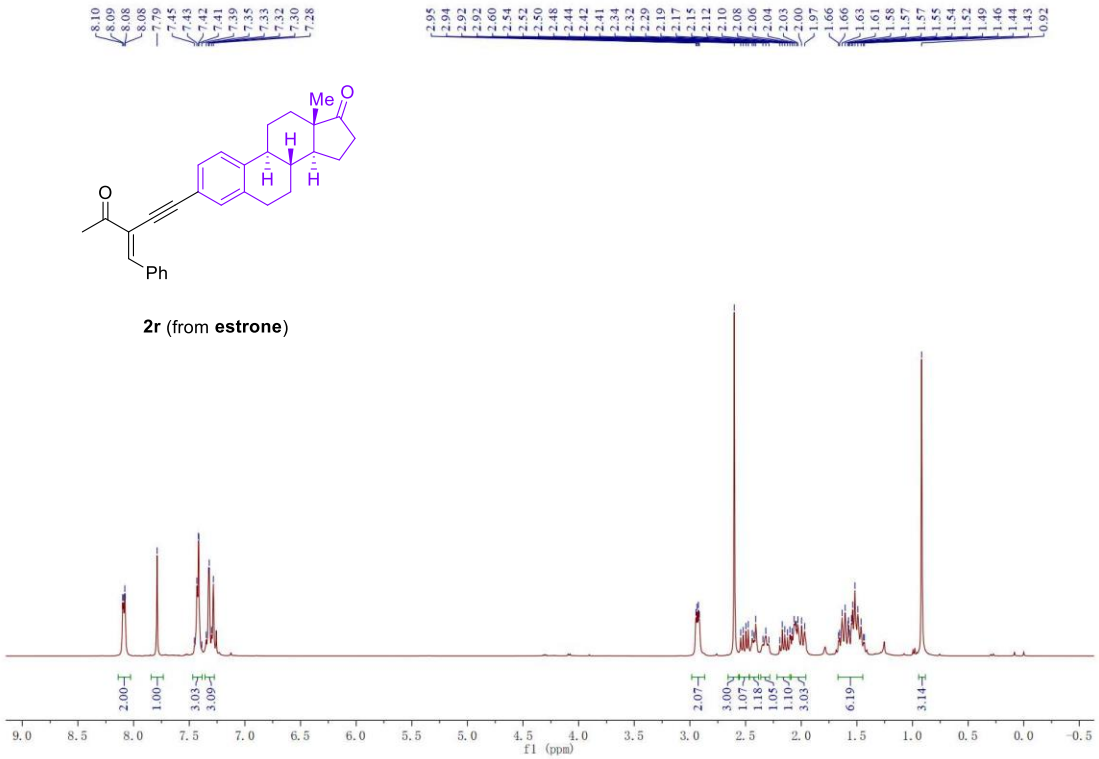
3ai

^{13}C NMR (101 MHz, $CDCl_3$)



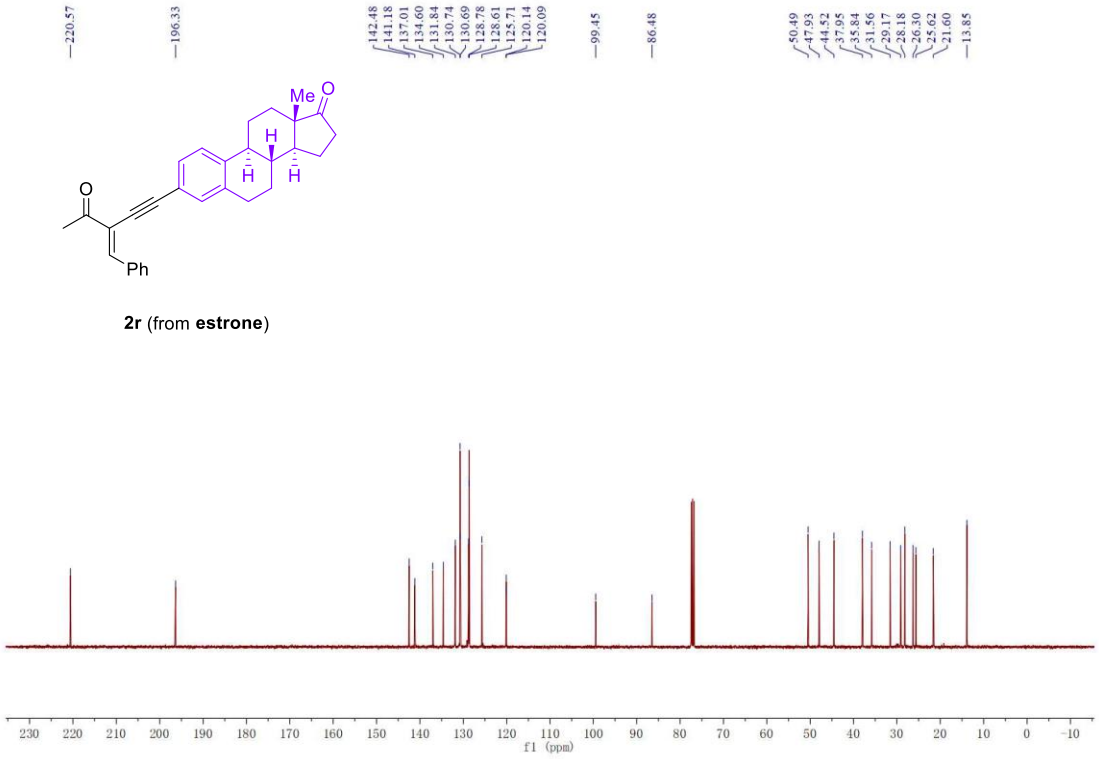
3ai

^{1}H NMR (400 MHz, $CDCl_3$)



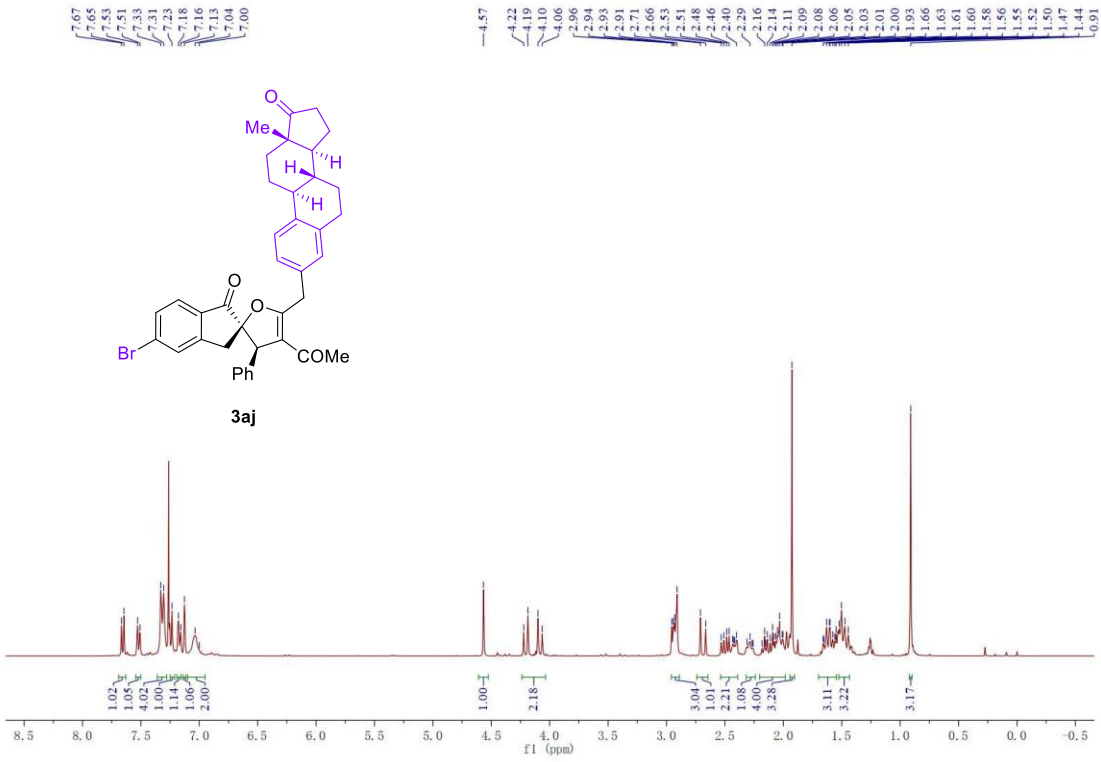
2r (from **estrone**)

^{13}C NMR (101 MHz, $CDCl_3$)

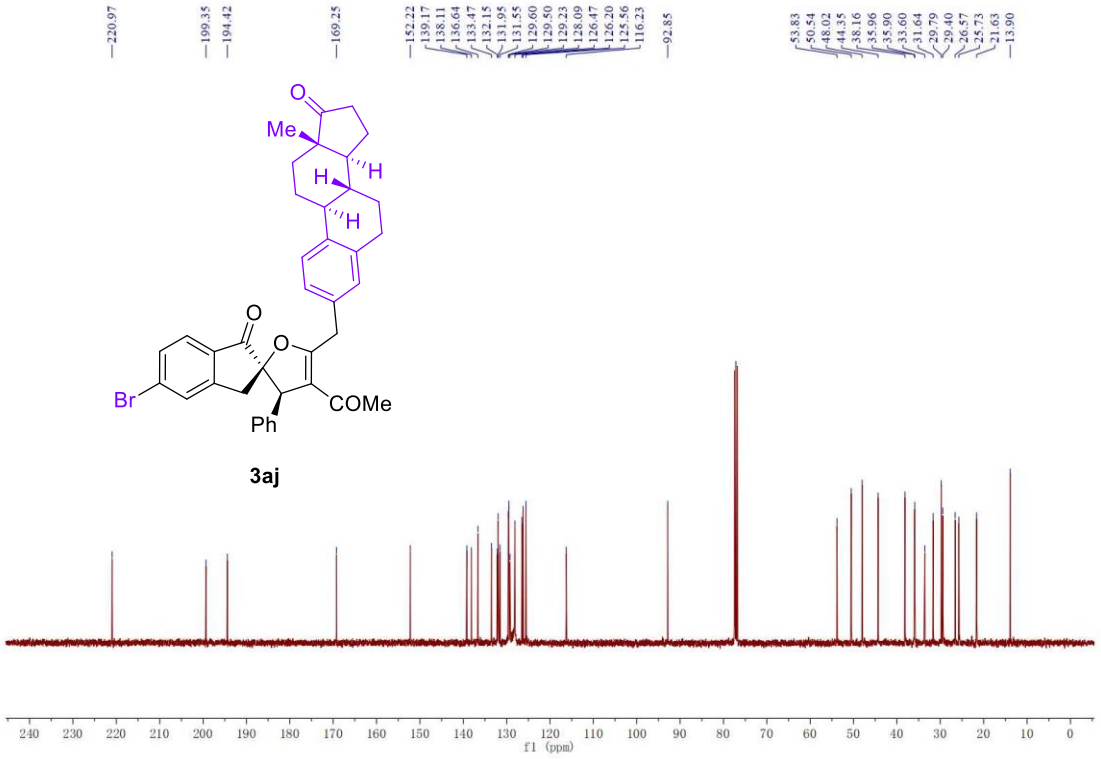


2r (from **estrone**)

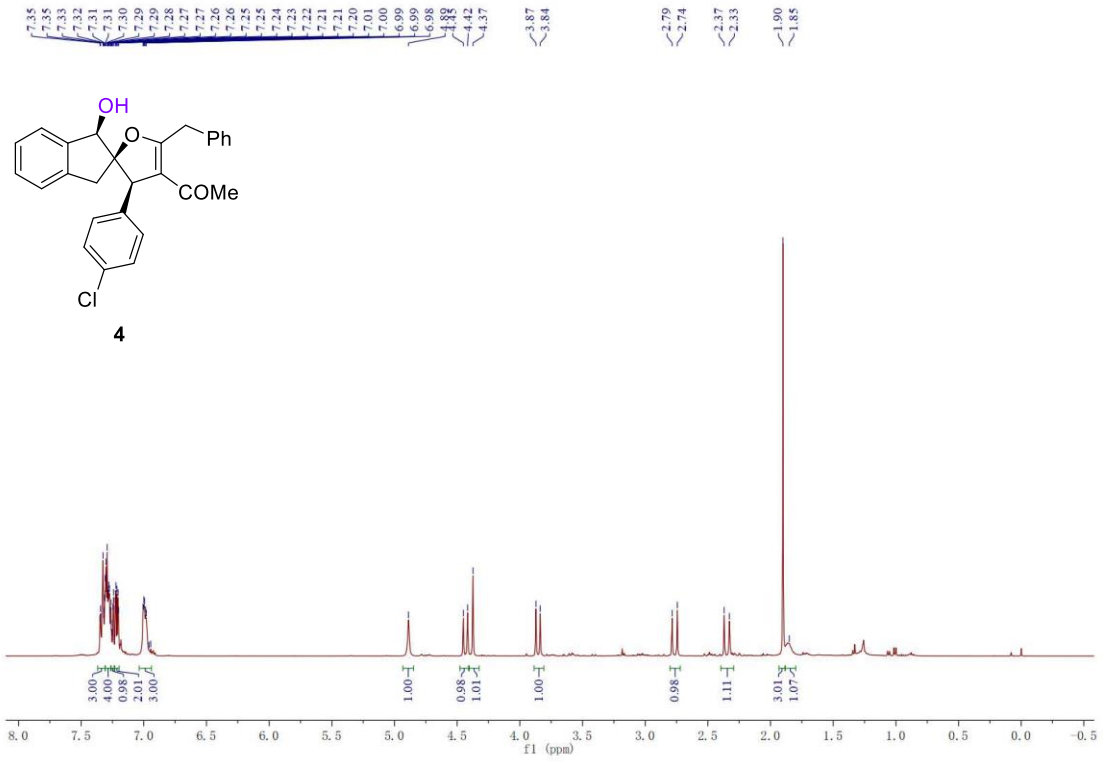
^{1}H NMR (400 MHz, $CDCl_3$)



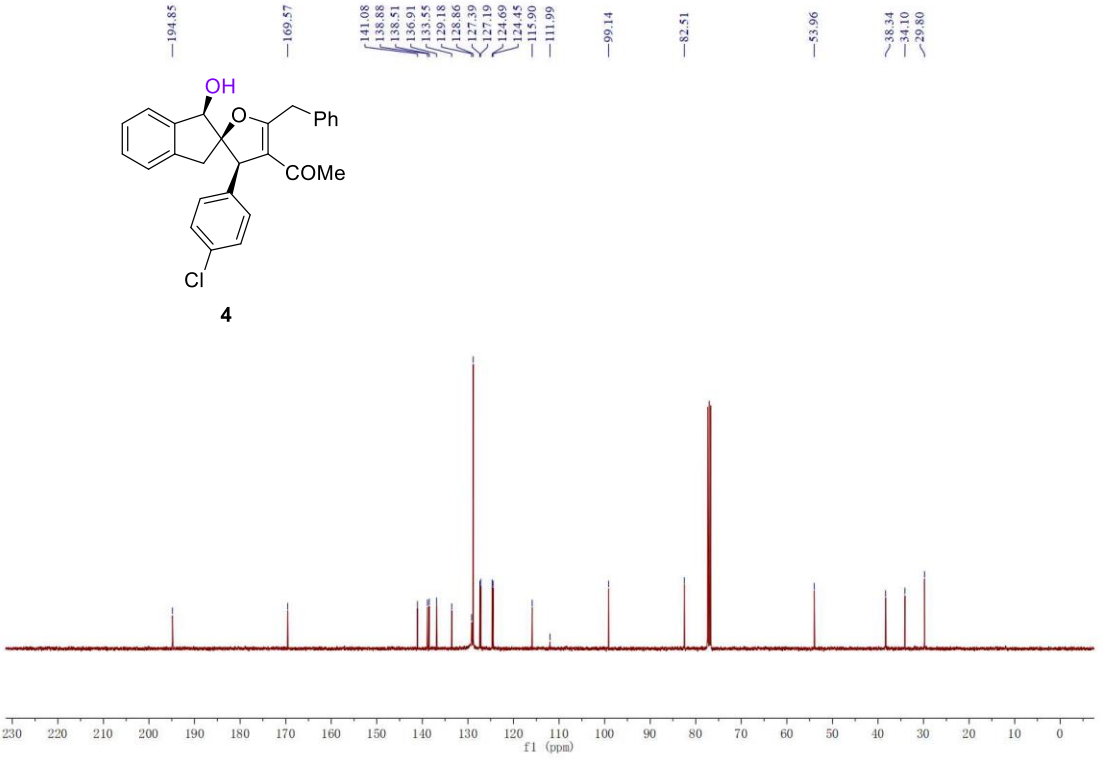
^{13}C NMR (101 MHz, $CDCl_3$)



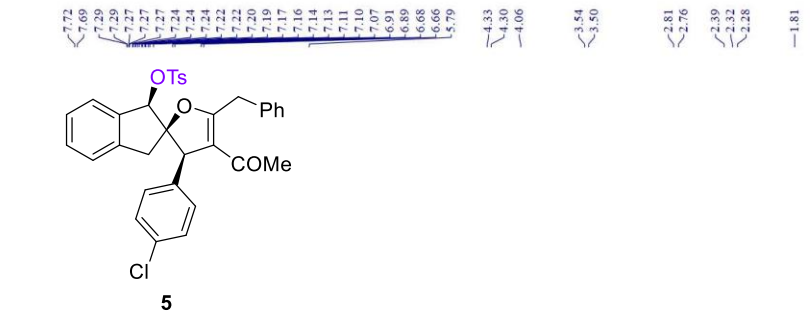
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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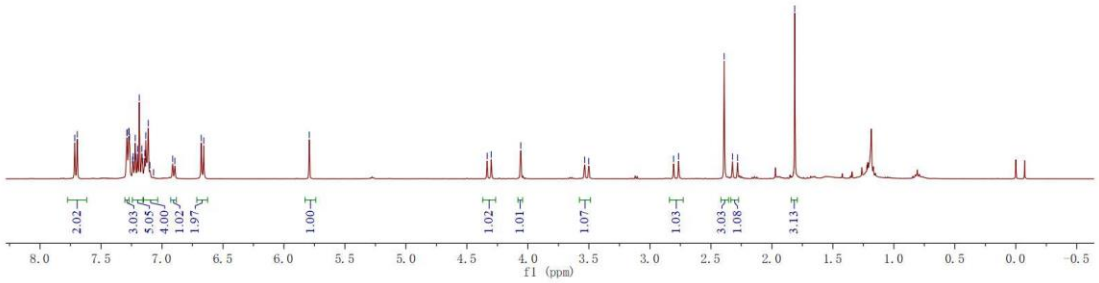
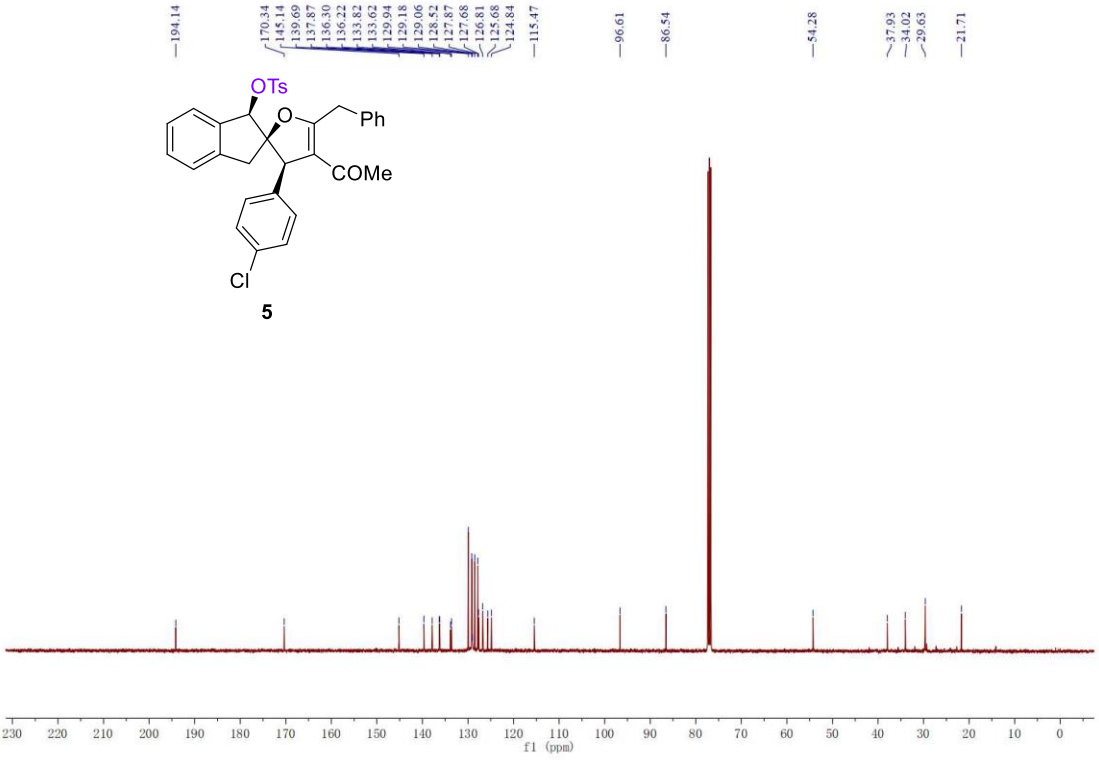
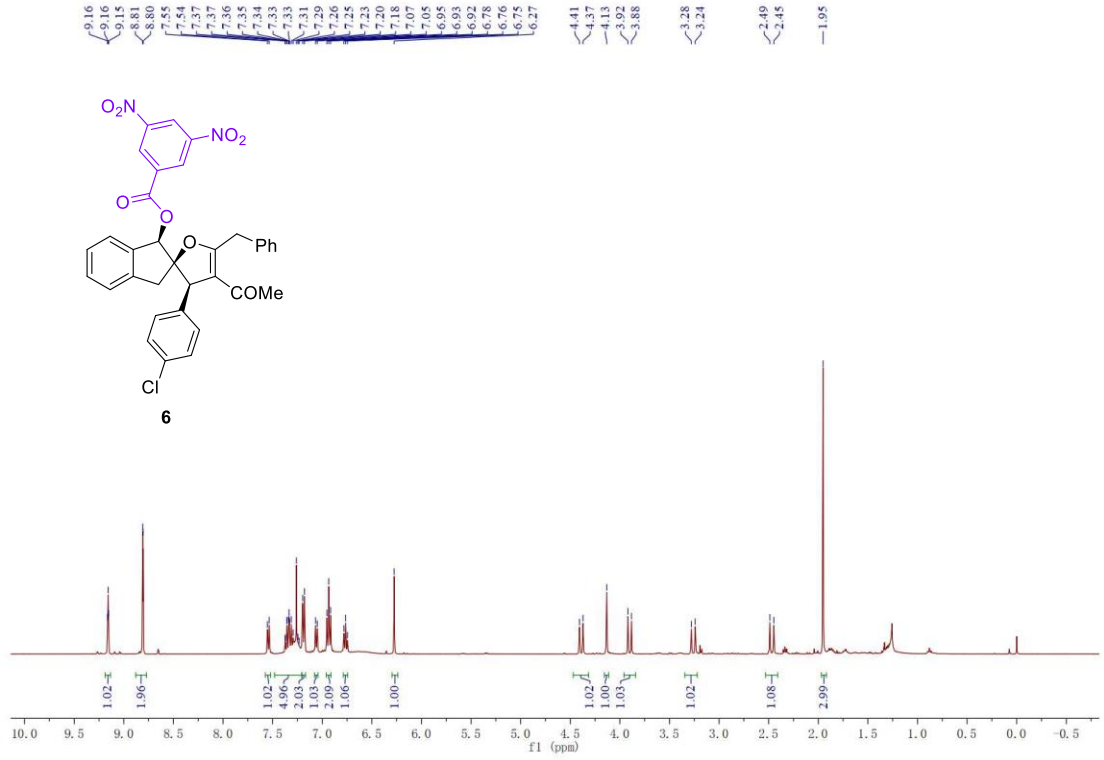


^{13}C NMR (101 MHz, $CDCl_3$)

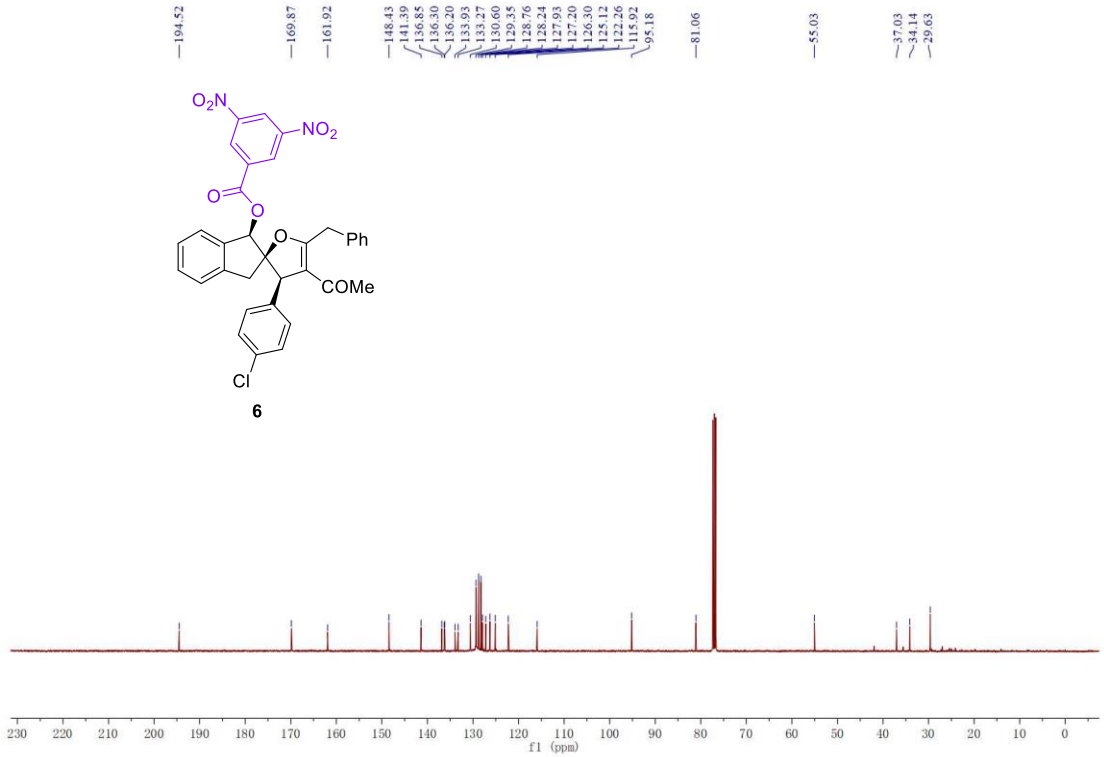


5

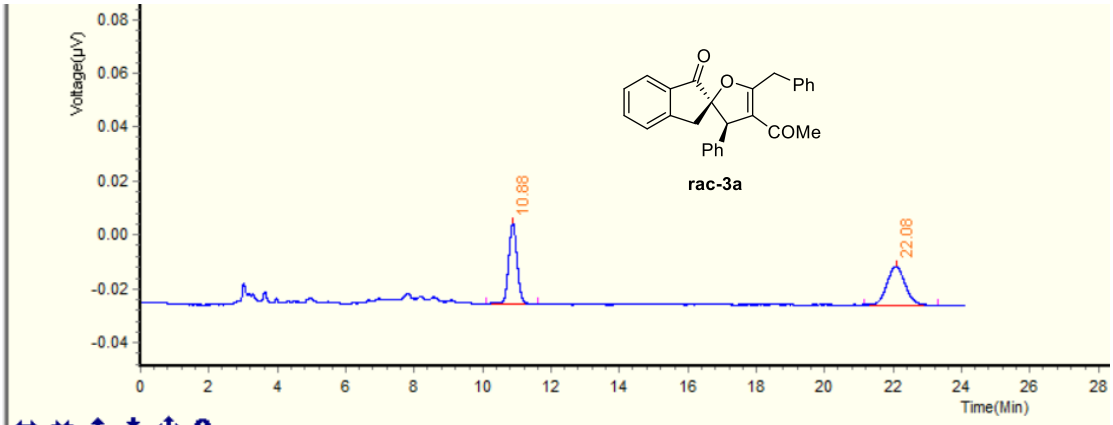
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

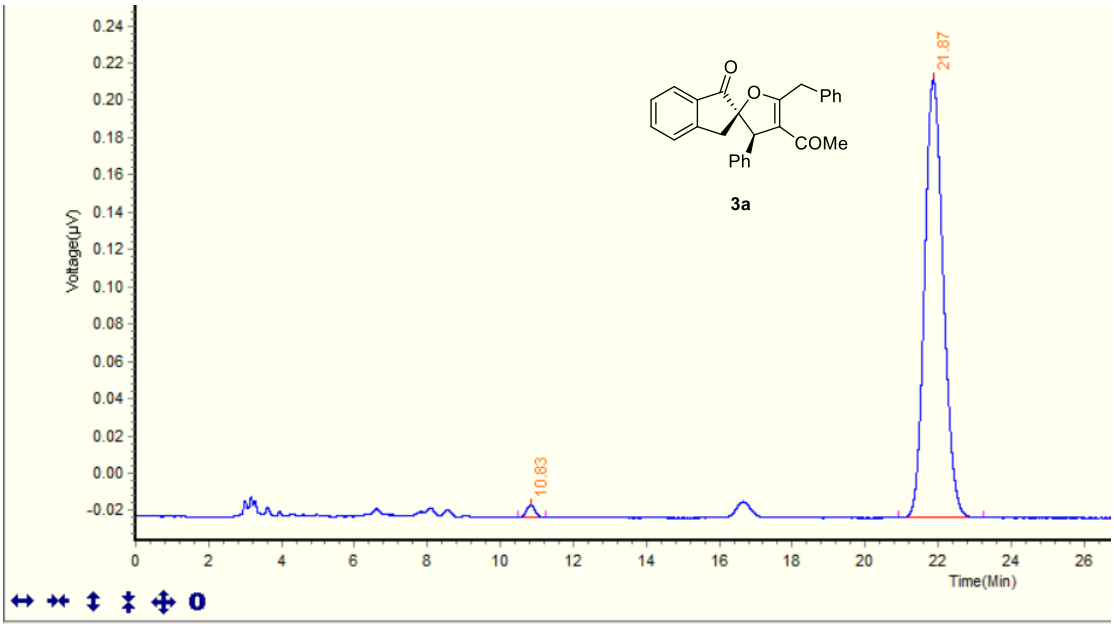


HPLC spectra of compounds



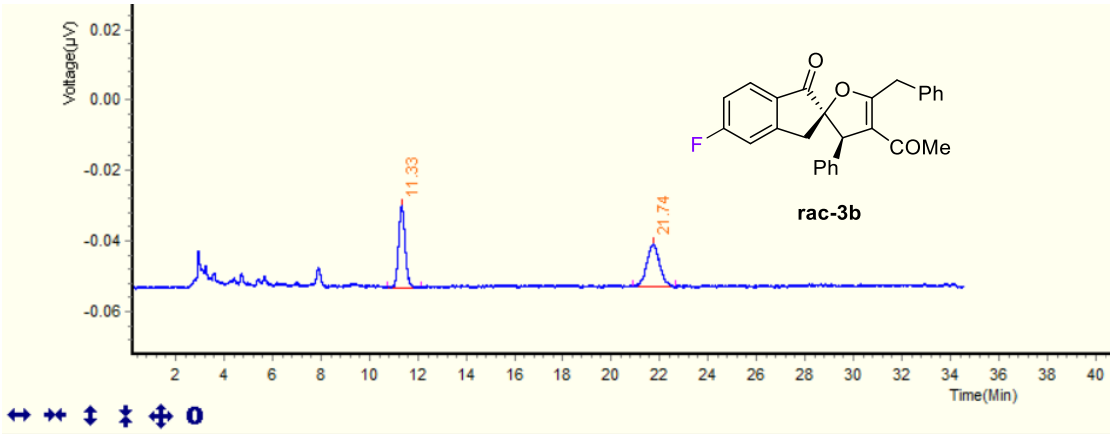
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	10.88	257593	14962	49.95%	1.511	BB
2	22.08	258137	7153	50.05%	2.158	BB
Total		515,730	22,115	100.00%		



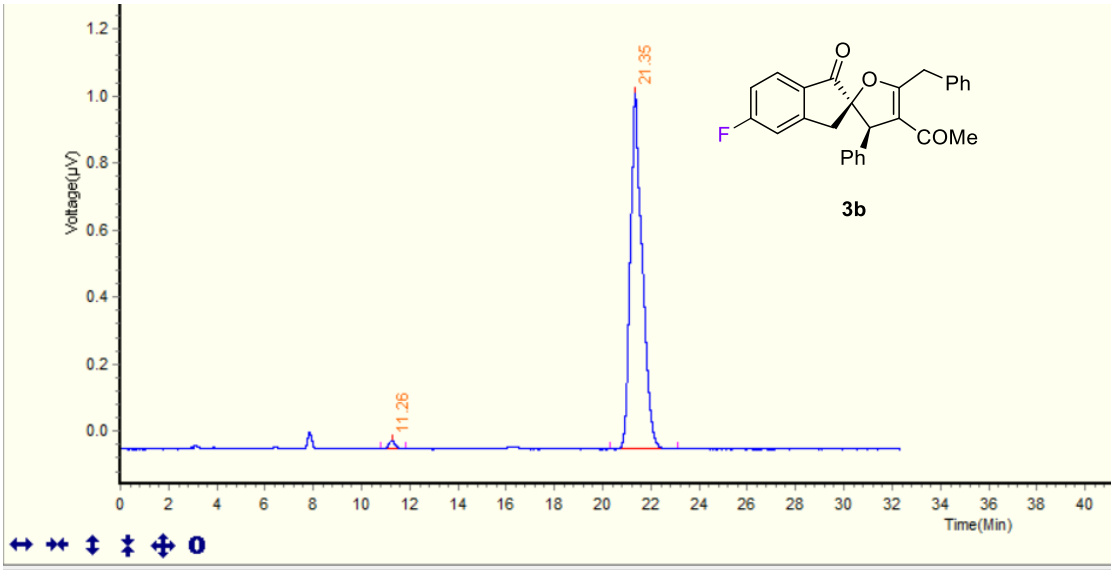
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	10.83	53590	3263	1.26%	0.753	BB
2	21.87	4183846	117487	98.74%	2.342	BB
Total		4,237,436	120,750	100.00%		



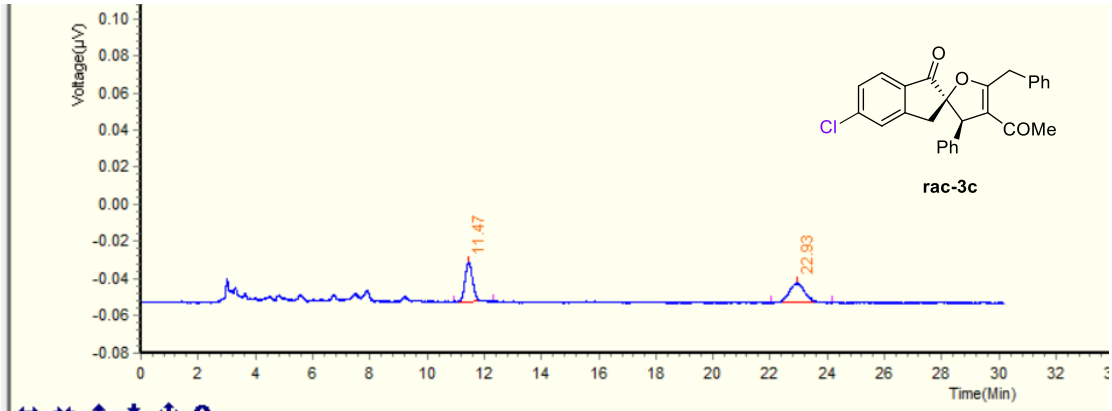
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.33	220670	11694	49.97%	1.403	BB
2	21.74	220955	6073	50.03%	1.731	BB
Total		441,625	17,767	100.00%		



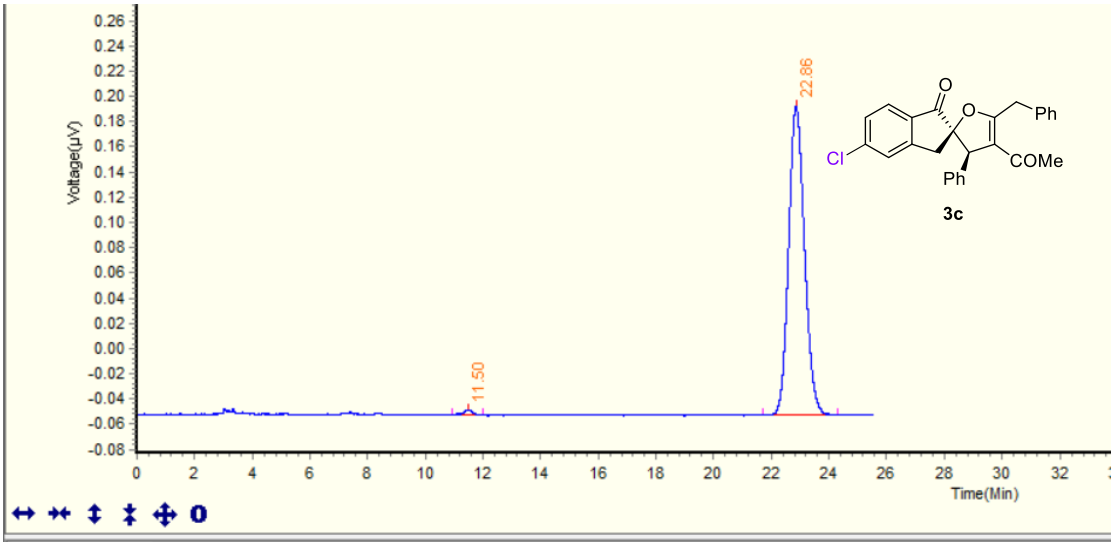
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.26	239300	12591	1.31%	1.031	BB
2	21.35	18089617	530716	98.69%	2.825	BB
Total		18,328,917	543,307	100.00%		



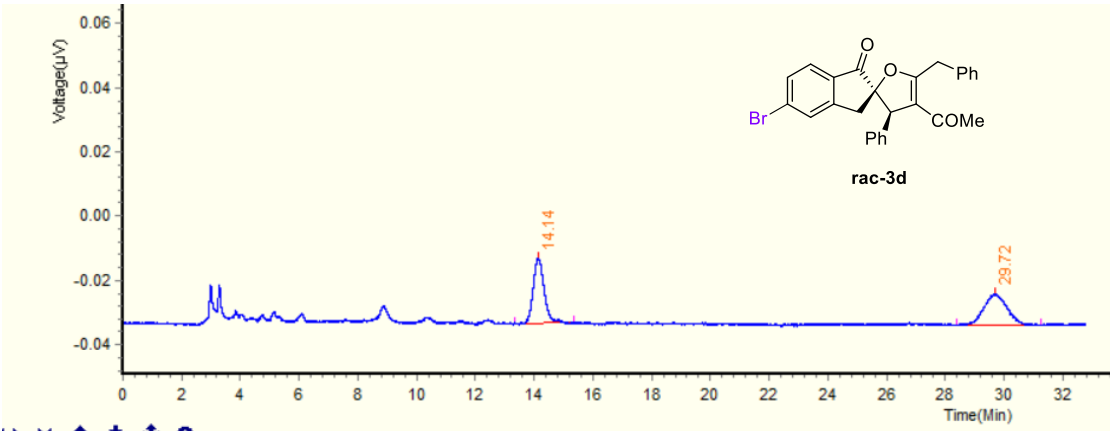
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.47	196105	10615	50.06%	1.344	BB
2	22.93	195646	5122	49.94%	2.095	BB
Total		391,751	15,737	100.00%		



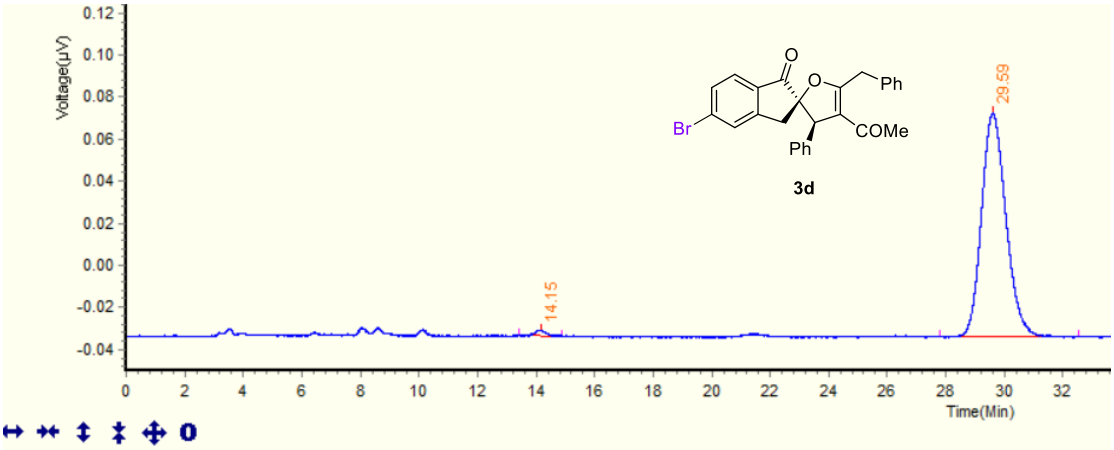
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.50	41528	2066	0.88%	1.058	BB
2	22.86	4657260	122118	99.12%	2.593	BB
Total		4,698,788	124,184	100.00%		



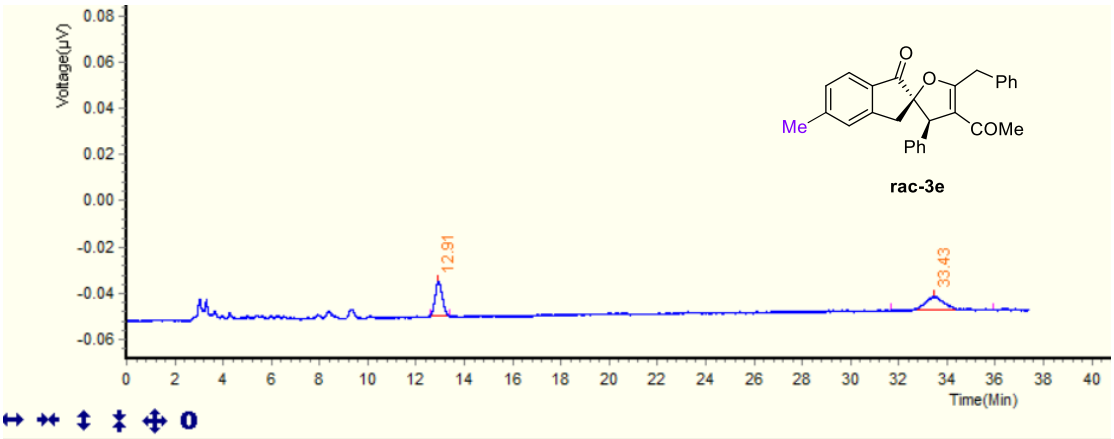
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.14	262778	10139	49.99%	2.038	BB
2	29.72	262836	4767	50.01%	2.887	BB
Total		525,614	14,906	100.00%		



Integration Result | Calculation Result | TimeTable

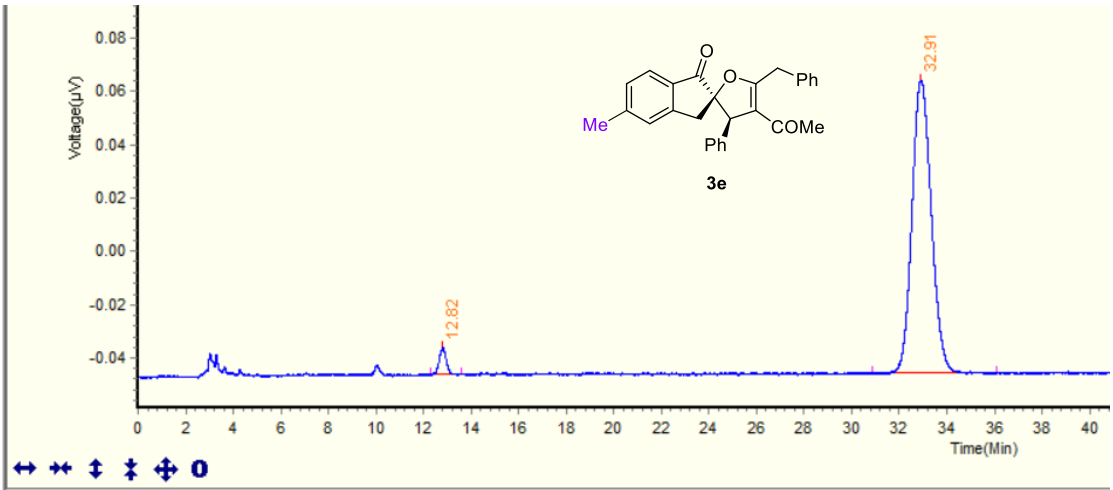
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.15	31829	1397	1.03%	1.423	BB
2	29.59	3066218	53087	98.97%	4.752	BB
Total		3,098,047	54,484	100.00%		



rac-3e

Integration Result | Calculation Result | TimeTable

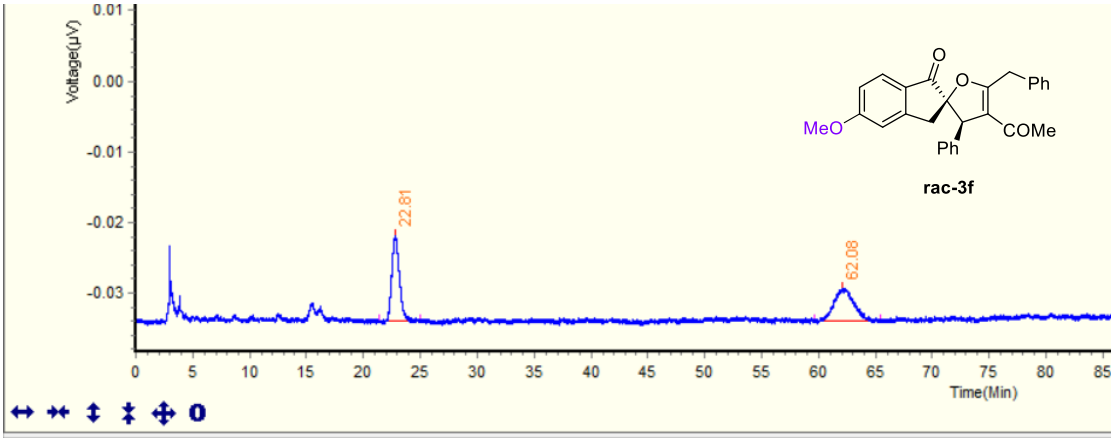
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	12.91	154095	7554	50.01%	0.807	BB
2	33.43	154013	2885	49.99%	4.224	BB
Total		308,108	10,439	100.00%		



3e

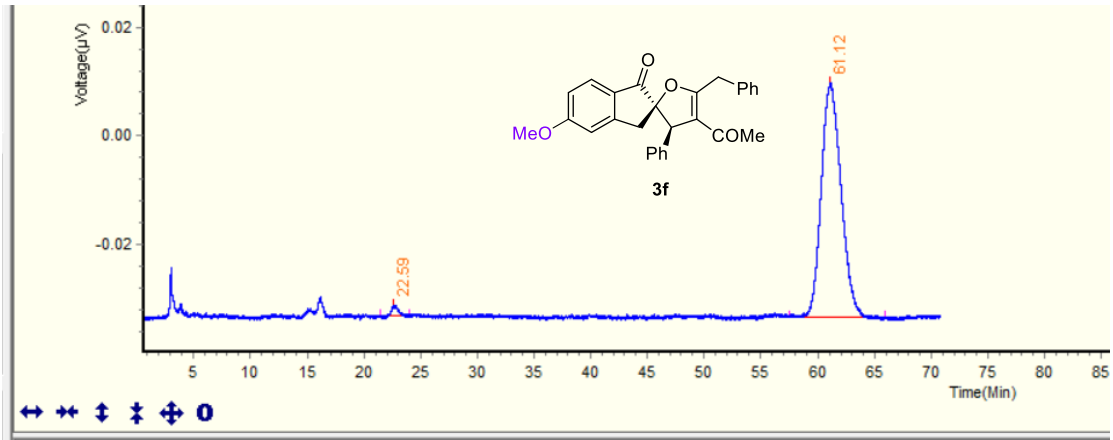
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	12.82	98944	4906	3.10%	1.295	BB
2	32.91	3097432	54892	96.90%	5.237	BB
Total		3,196,376	59,798	100.00%		



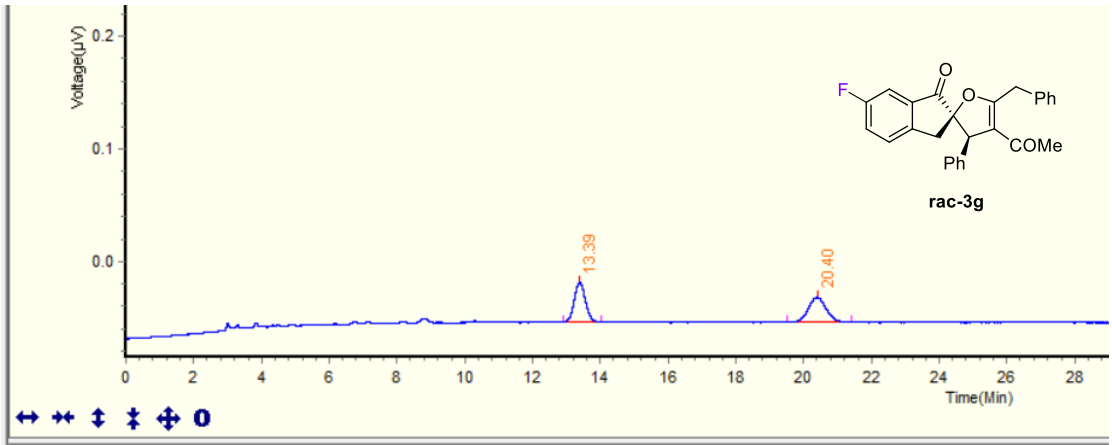
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	22.81	278757	6069	49.92%	3.577	BB
2	62.08	279654	2305	50.08%	5.903	BB
Total		558,411	8,374	100.00%		



Integration Result | Calculation Result | TimeTable

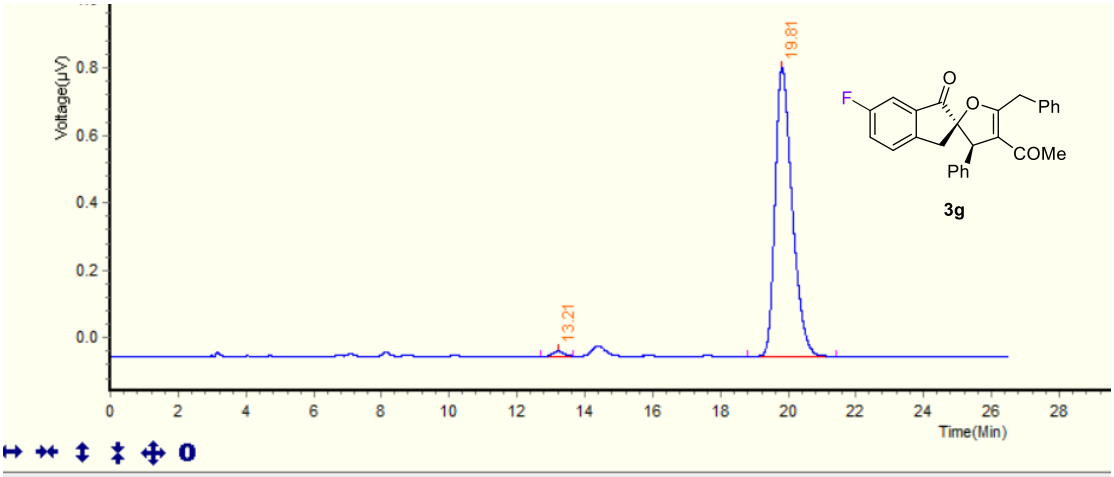
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	22.59	31353	925	1.19%	2.565	BB
2	61.12	2612968	21592	98.81%	8.501	BB
Total		2,644,321	22,517	100.00%		



rac-3g

Integration Result | Calculation Result | TimeTable

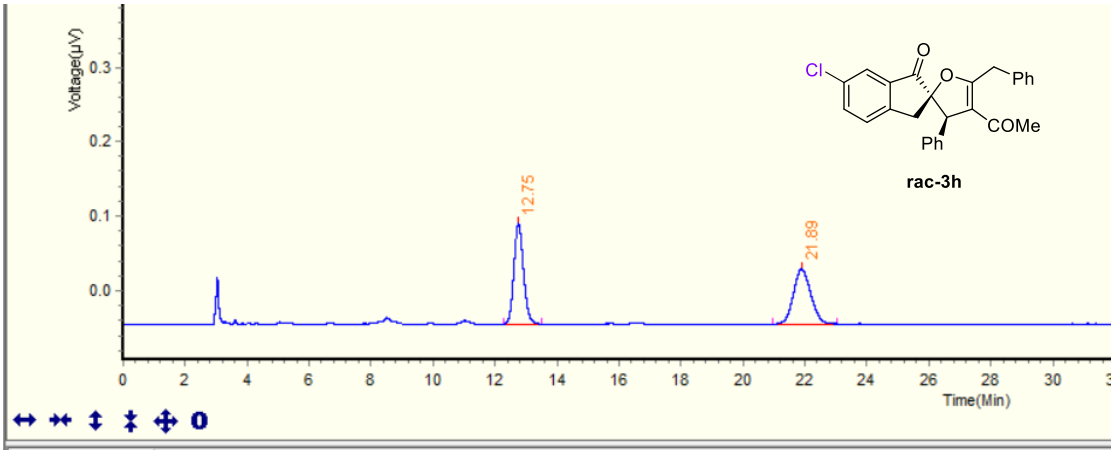
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	13.39	402845	17586	50.04%	1.143	BB
2	20.40	402267	11076	49.96%	1.896	BB
Total		805,112	28,662	100.00%		



3g

Integration Result | Calculation Result | TimeTable

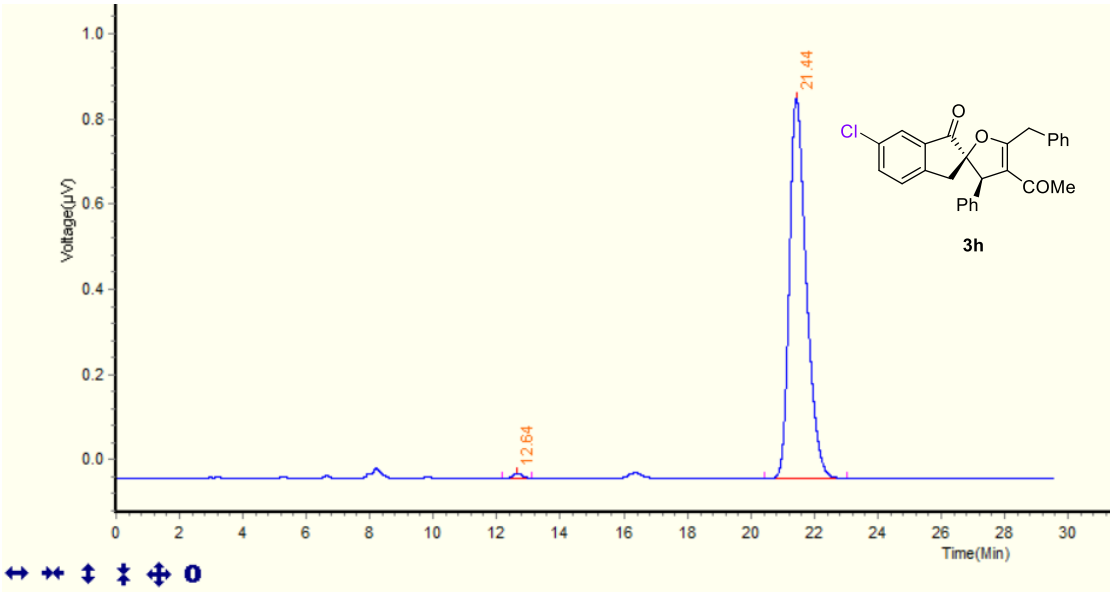
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	13.21	160698	7367	1.07%	0.98	BB
2	19.81	14904369	426949	98.93%	2.612	BB
Total		15,065,067	434,316	100.00%		



rac-3h

Integration Result | Calculation Result | TimeTable

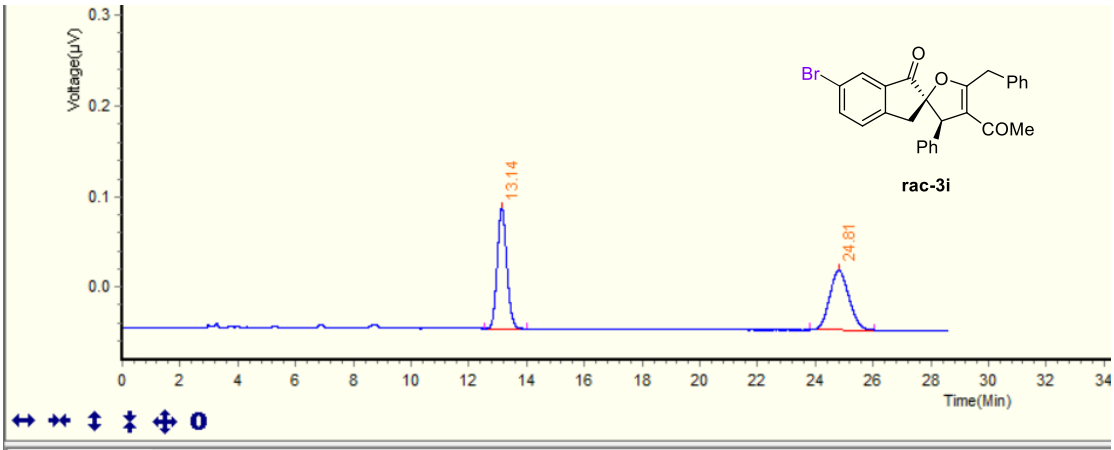
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	12.75	1440607	67495	50.09%	1.225	BB
2	21.89	1435399	36963	49.91%	2.105	BB
Total		2,876,006	104,458	100.00%		



3h

Integration Result | Calculation Result | TimeTable

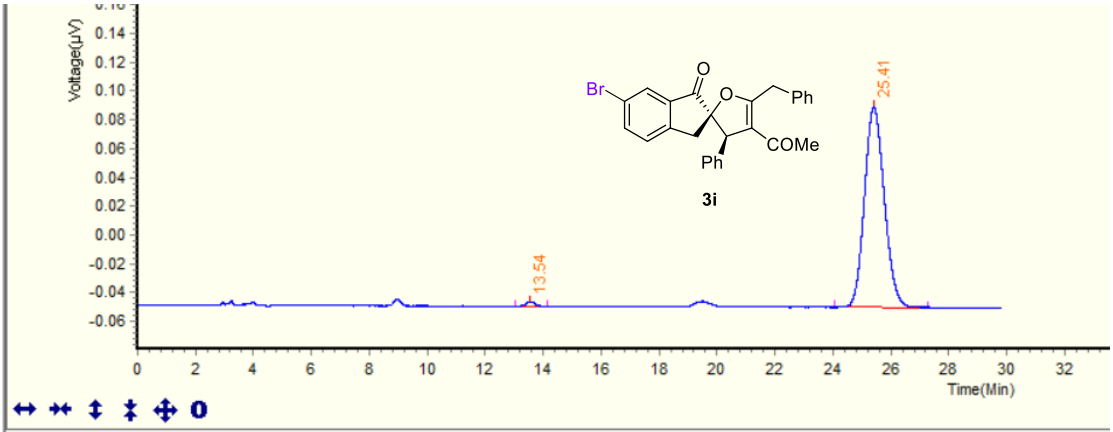
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	12.64	119243	5802	0.72%	0.943	BB
2	21.44	16498025	446210	99.28%	2.583	BB
Total		16,617,268	452,012	100.00%		



rac-3i

Integration Result | Calculation Result | TimeTable

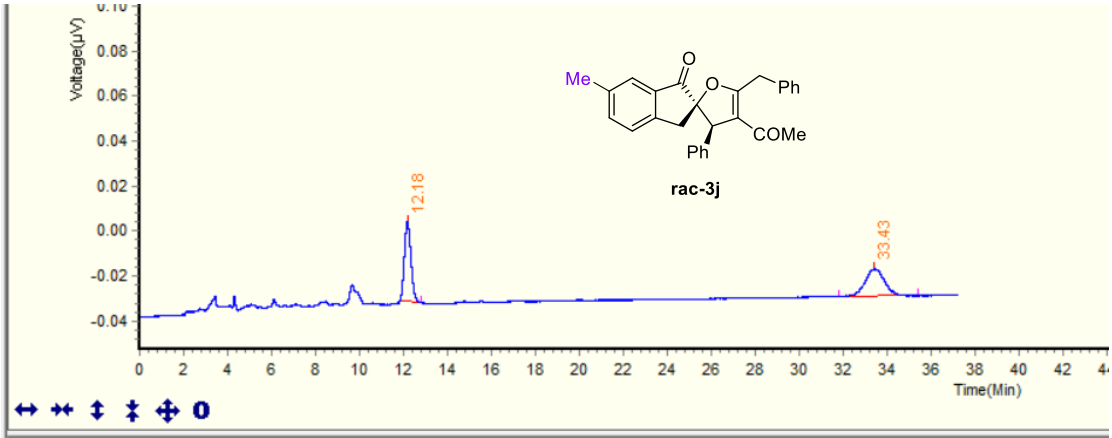
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	13.14	1539873	66719	50.05%	1.474	BB
2	24.81	1536513	33017	49.95%	2.241	BB
Total		3,076,386	99,736	100.00%		



3i

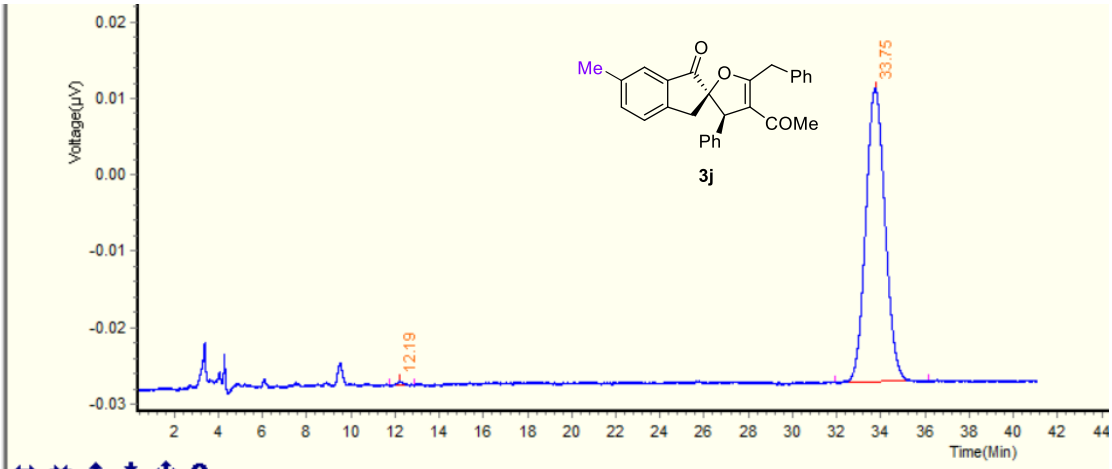
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	13.54	37209	1544	1.11%	1.113	BB
2	25.41	3312631	69577	98.89%	3.183	BB
Total		3,349,840	71,121	100.00%		



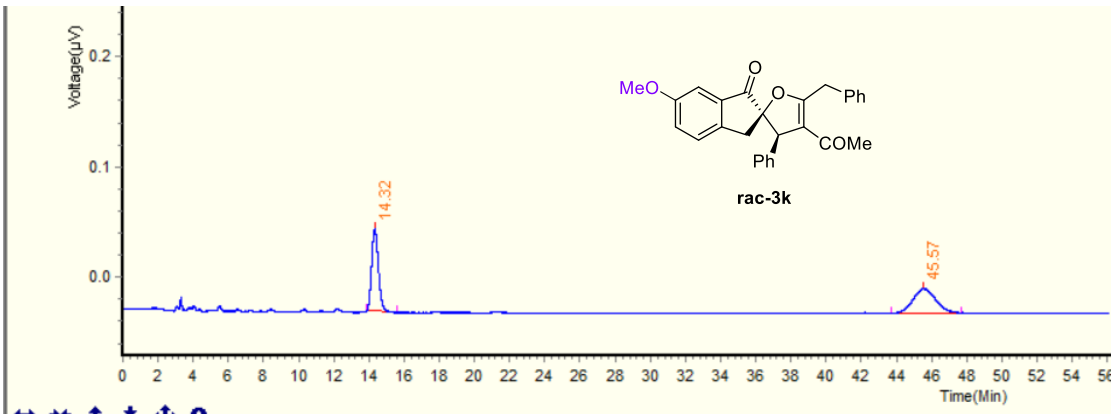
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	12.18	366719	17736	50.17%	0.927	BB
2	33.43	364258	5990	49.83%	3.589	BB
Total		730,977	23,726	100.00%		



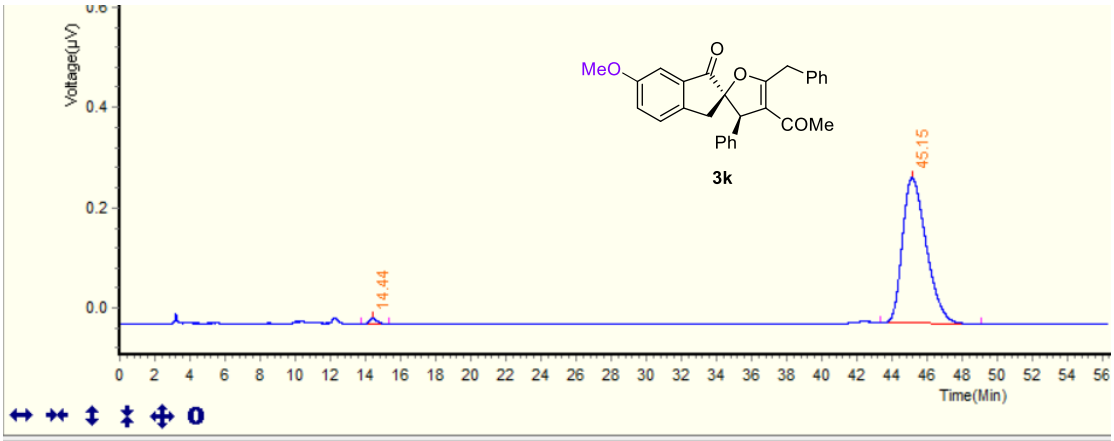
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	12.19	2769	241	0.24%	1.155	BB
2	33.75	1165557	19232	99.76%	4.233	BB
Total		1,168,326	19,473	100.00%		



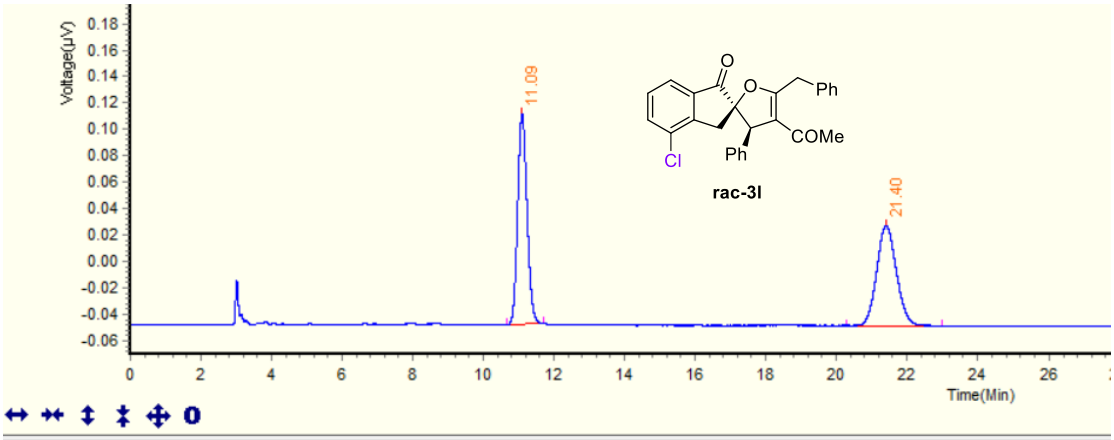
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.32	981253	36892	49.95%	1.743	BB
2	45.57	983053	11050	50.05%	3.95	BB
Total		1,964,306	47,942	100.00%		



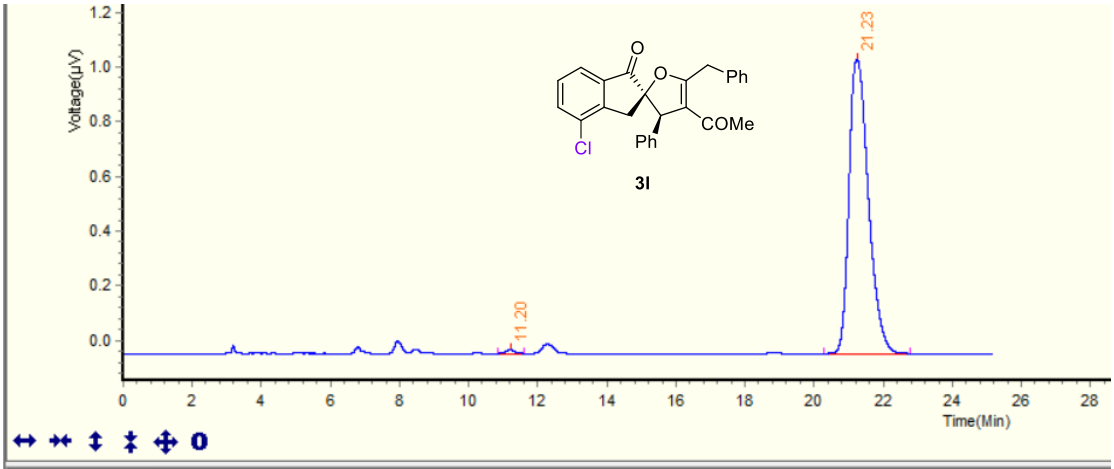
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.44	156364	5592	1.12%	1.634	BB
2	45.15	13760880	145949	98.88%	5.778	BB
Total		13,917,244	151,541	100.00%		



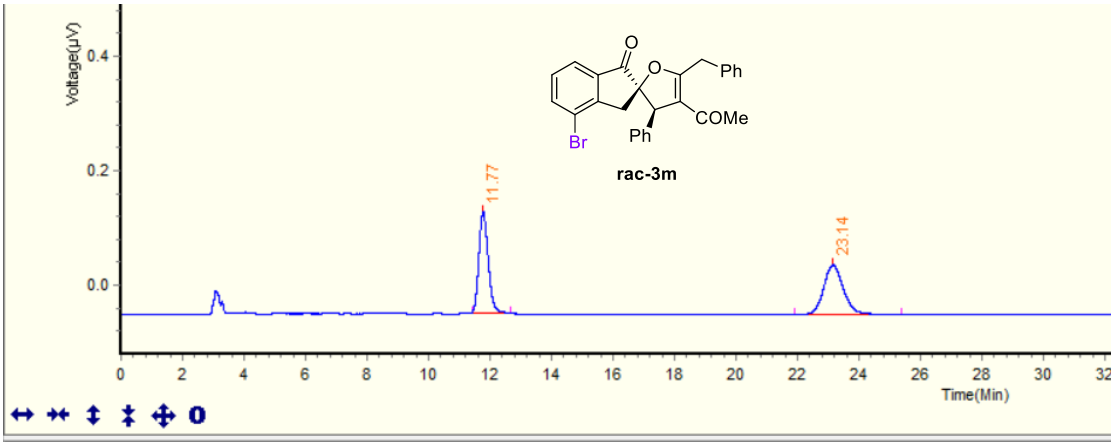
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.09	1471510	79699	50.23%	1.041	BB
2	21.40	1458291	37894	49.77%	2.718	BB
Total		2,929,801	117,593	100.00%		



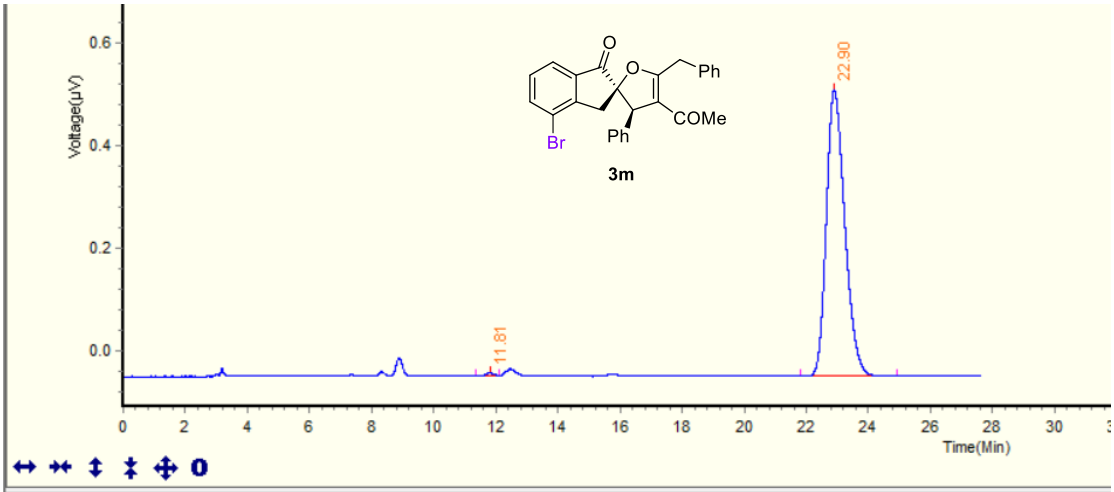
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.20	121050	6720	0.57%	0.75	BB
2	21.23	21024995	539365	99.43%	2.509	BB
Total		21,146,045	546,085	100.00%		



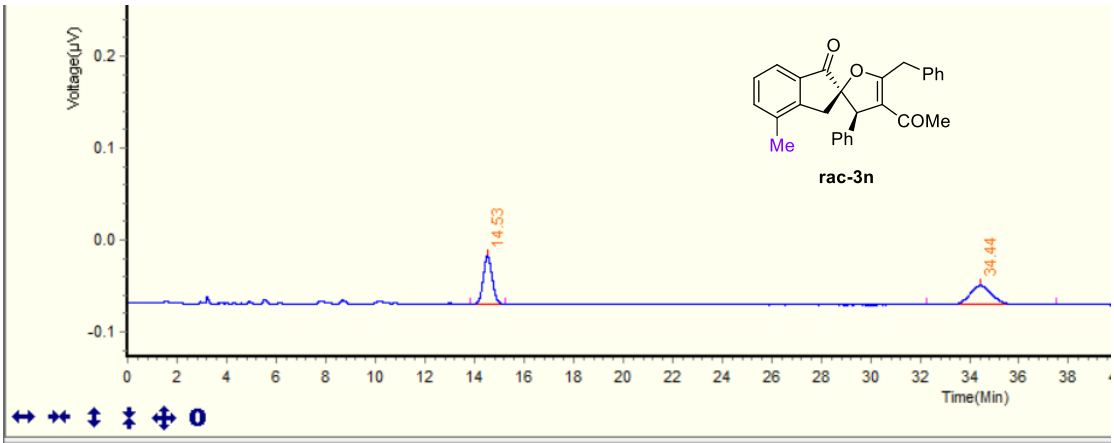
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.77	1852573	87858	50.03%	1.28	BB
2	23.14	1850626	42703	49.97%	3.48	BB
Total		3,703,199	130,561	100.00%		



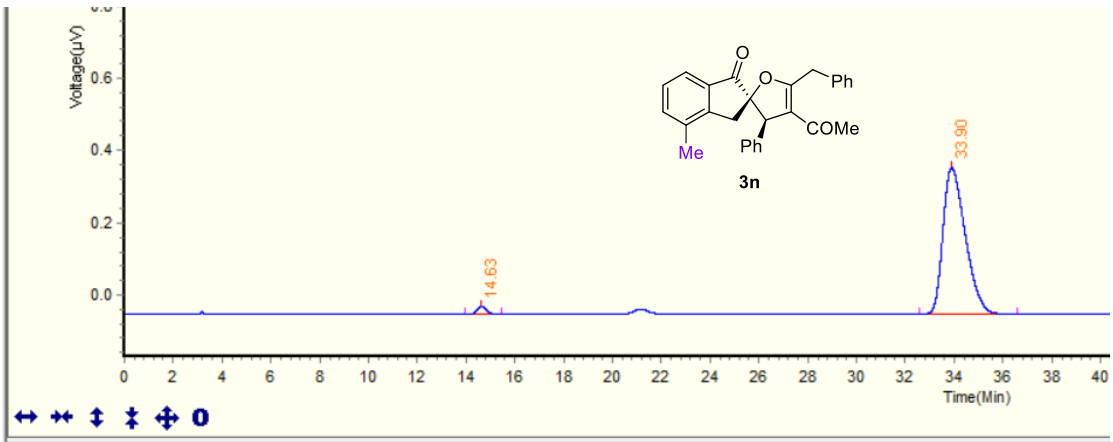
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.81	47741	2775	0.41%	0.774	BB
2	22.90	11499151	278304	99.59%	3.094	BB
Total		11,546,892	281,079	100.00%		



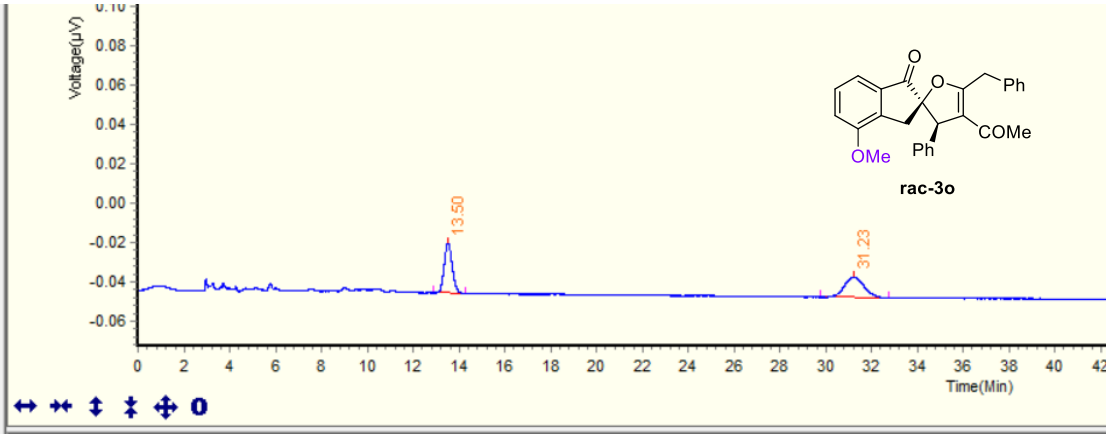
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.53	659833	26127	50.29%	1.381	BB
2	34.44	652142	10400	49.71%	5.228	BB
Total		1,311,975	36,527	100.00%		



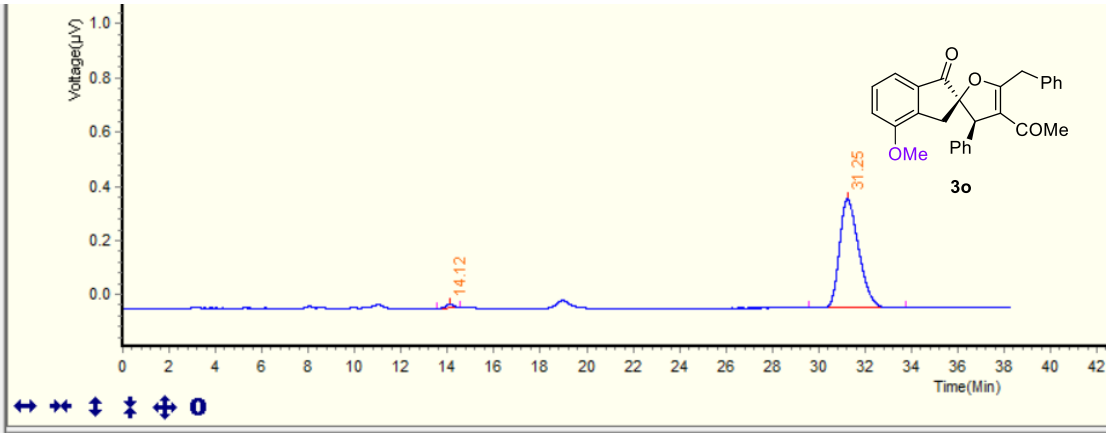
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.63	265141	10479	2.02%	1.51	BB
2	33.90	12881036	202621	97.98%	4.027	BB
Total		13,146,177	213,100	100.00%		



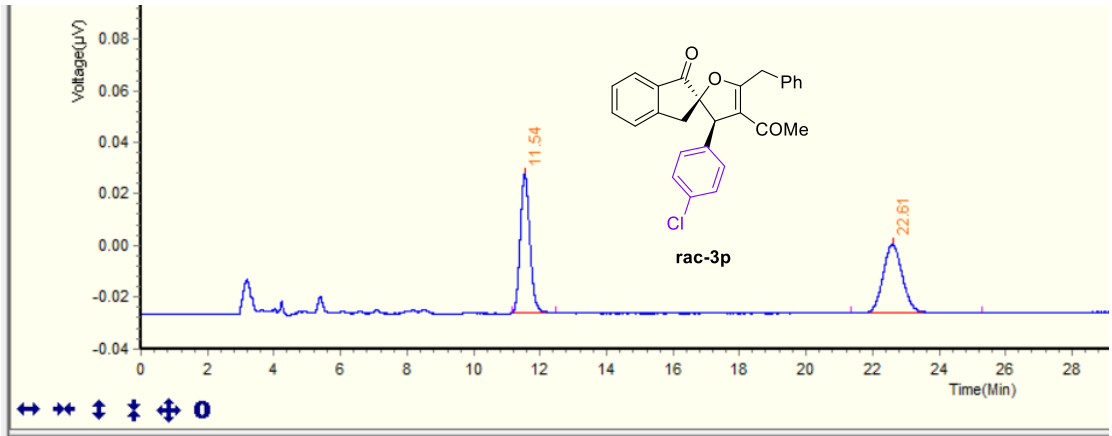
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	13.50	306116	12593	50.10%	1.41	BB
2	31.23	304834	5202	49.90%	2.997	BB
Total		610,950	17,795	100.00%		



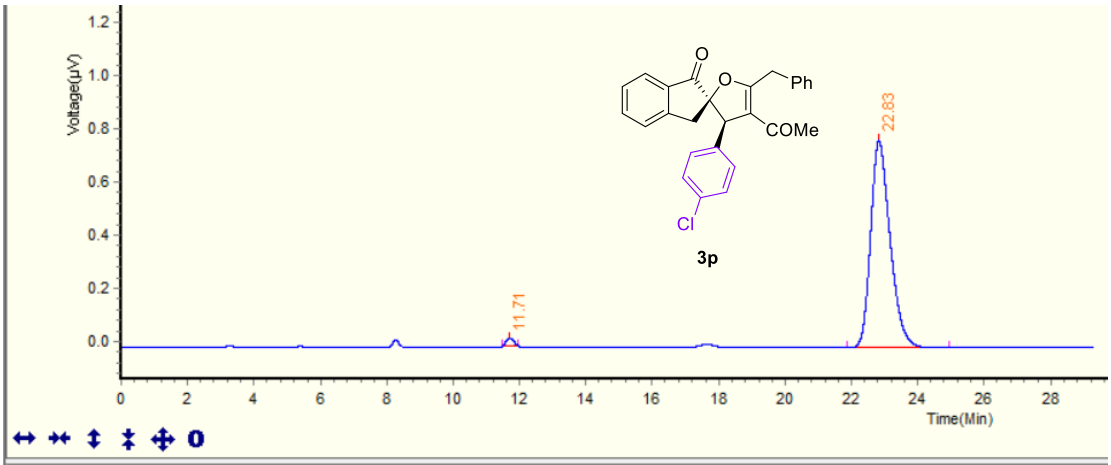
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.12	150307	6598	1.28%	1.032	BB
2	31.25	11564114	200611	98.72%	4.168	BB
Total		11,714,421	207,209	100.00%		



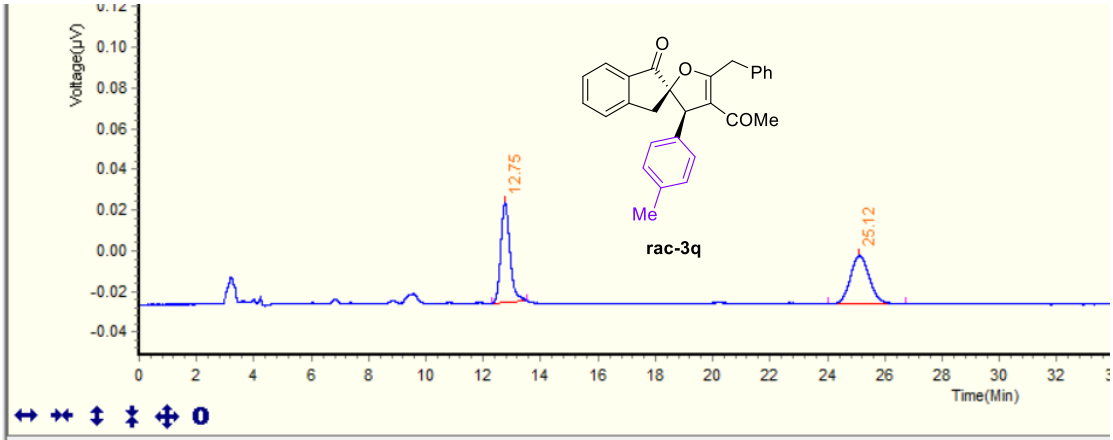
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.54	542477	26852	50.06%	1.329	BB
2	22.61	541238	13340	49.94%	3.937	BB
Total		1,083,715	40,192	100.00%		



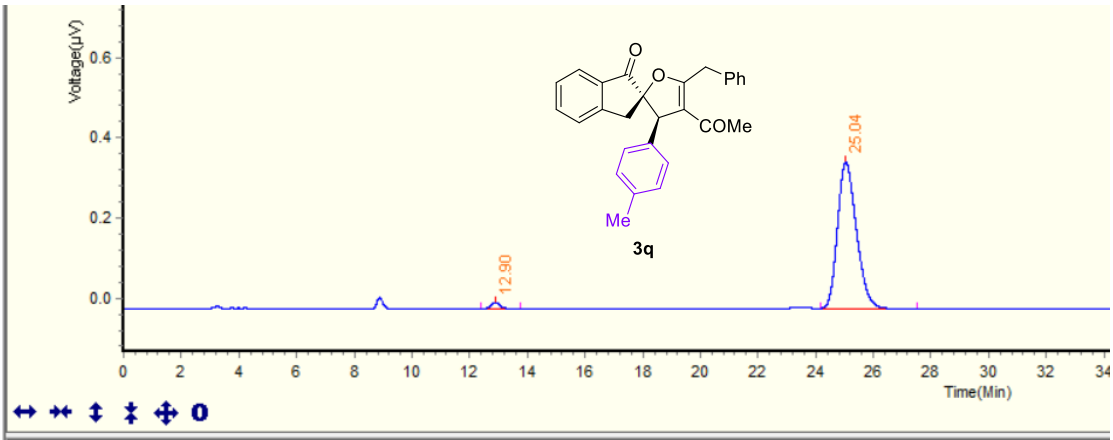
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.71	207007	13561	1.29%	0.453	BB
2	22.83	15881611	390377	98.71%	3.098	BB
Total		16,088,618	403,938	100.00%		



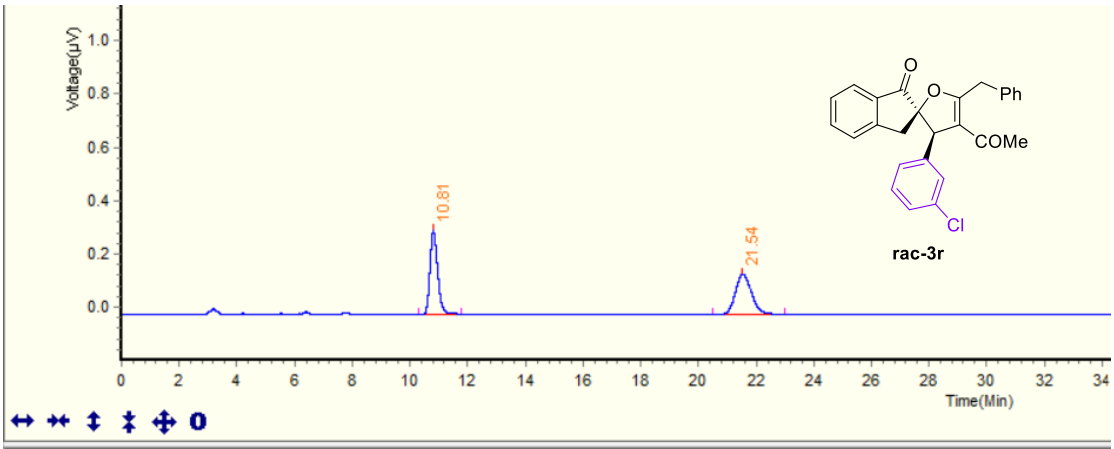
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	12.75	541720	24334	49.91%	1.192	BB
2	25.12	543697	11899	50.09%	2.711	BB
Total		1,085,417	36,233	100.00%		



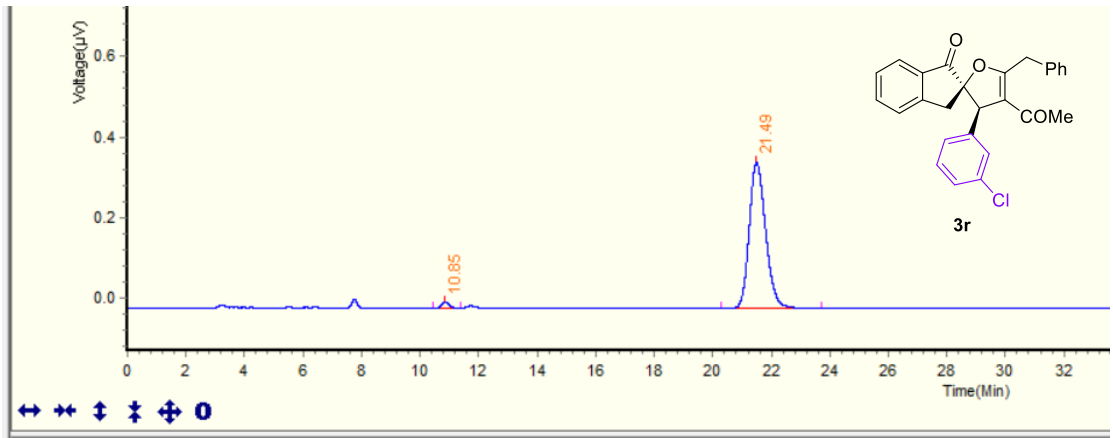
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	12.90	175045	7792	2.07%	1.352	BB
2	25.04	8285545	182011	97.93%	3.343	BB
Total		8,460,590	189,803	100.00%		



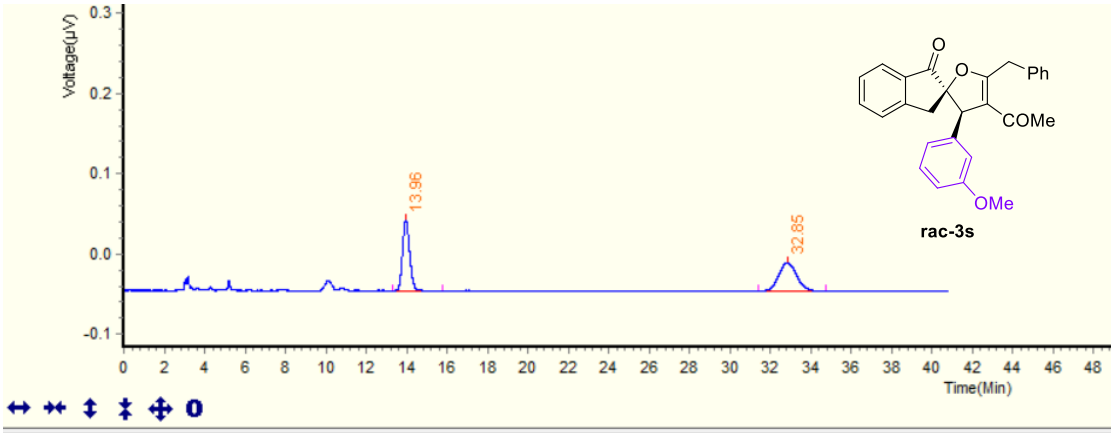
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	10.81	2886546	155534	49.90%	1.5	BB
2	21.54	2898264	74856	50.10%	2.514	BB
Total		5,784,810	230,390	100.00%		



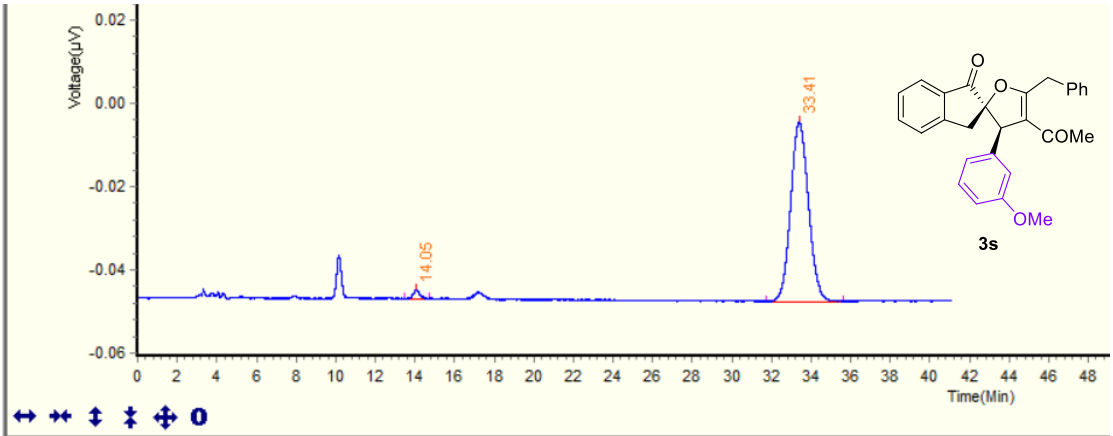
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	10.85	128435	7180	1.79%	0.961	BB
2	21.49	7065504	181373	98.21%	3.385	BB
Total		7,193,939	188,553	100.00%		



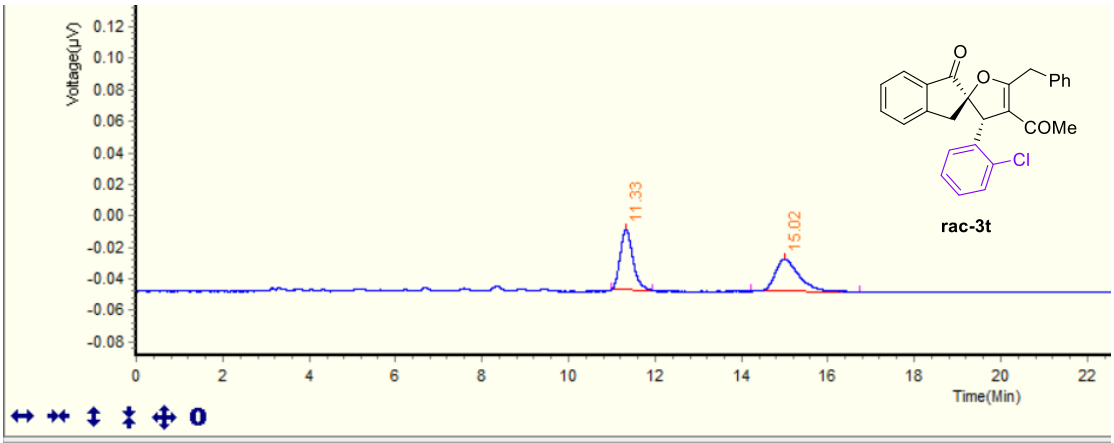
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	13.96	1080035	44070	50.02%	2.452	BB
2	32.85	1078995	17732	49.98%	3.342	BB
Total		2,159,030	61,802	100.00%		



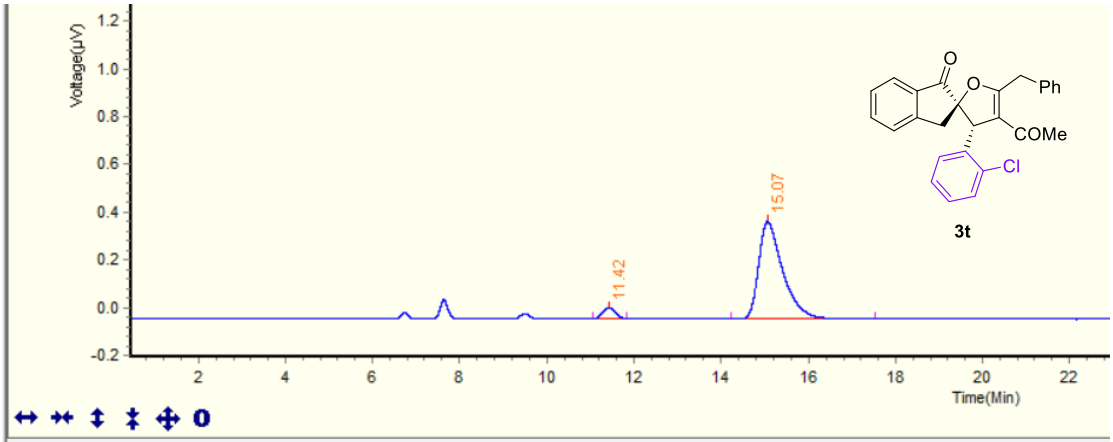
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.05	23093	970	1.68%	1.278	BB
2	33.41	1349573	21580	98.32%	3.962	BB
Total		1,372,666	22,550	100.00%		



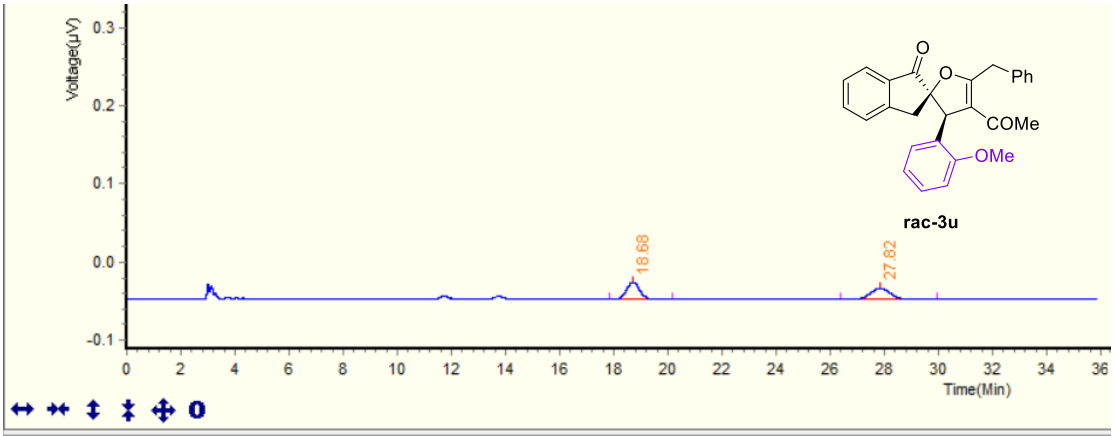
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.33	393574	19170	49.97%	0.953	BB
2	15.02	394087	10247	50.03%	2.524	BB
Total		787,661	29,417	100.00%		



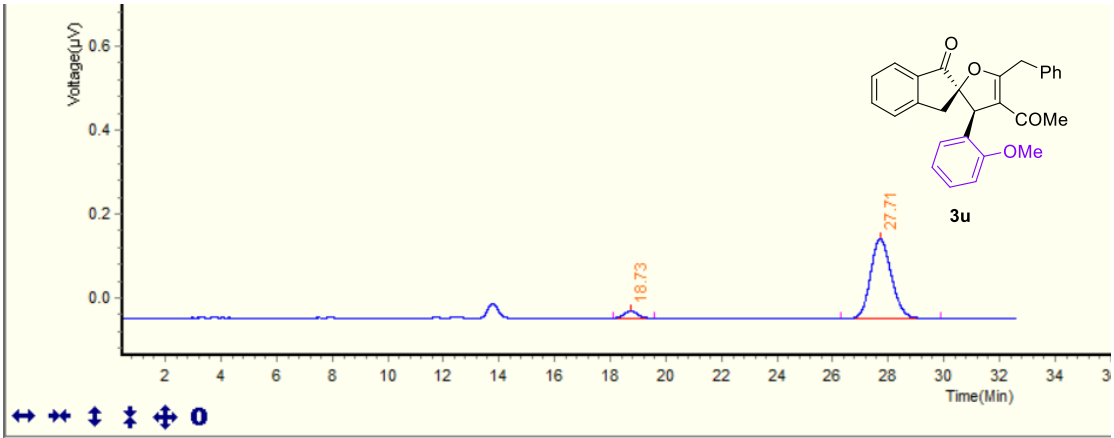
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.42	461580	23072	5.54%	0.791	BB
2	15.07	7875319	204135	94.46%	3.305	BB
Total		8,336,899	227,207	100.00%		



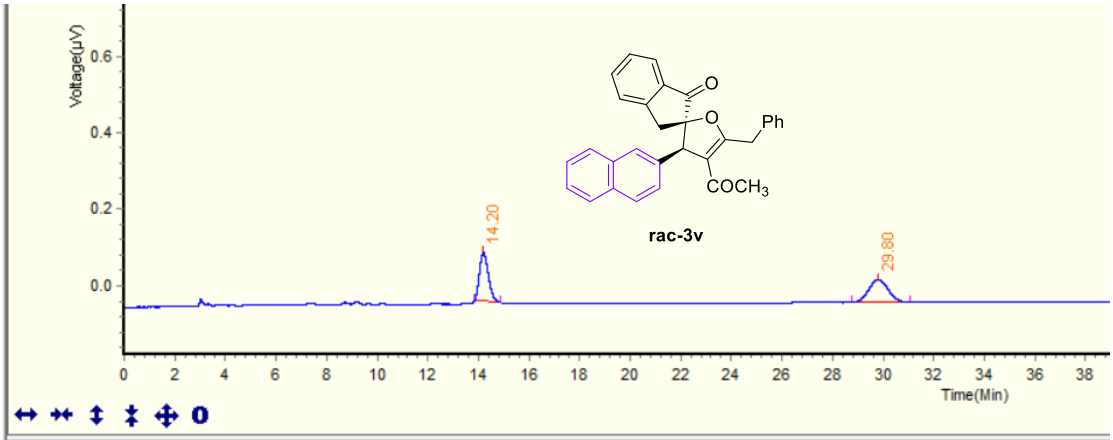
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	18.68	367643	10976	49.88%	2.302	BB
2	27.82	369367	7085	50.12%	3.563	BB
Total		737,010	18,061	100.00%		



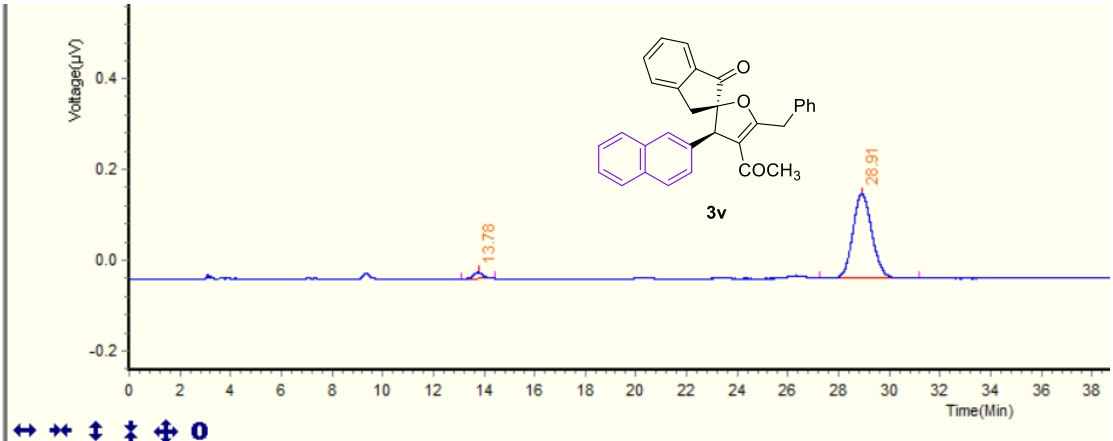
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	18.73	285124	8623	5.52%	1.488	BB
2	27.71	4884598	94837	94.48%	3.584	BB
Total		5,169,722	103,460	100.00%		



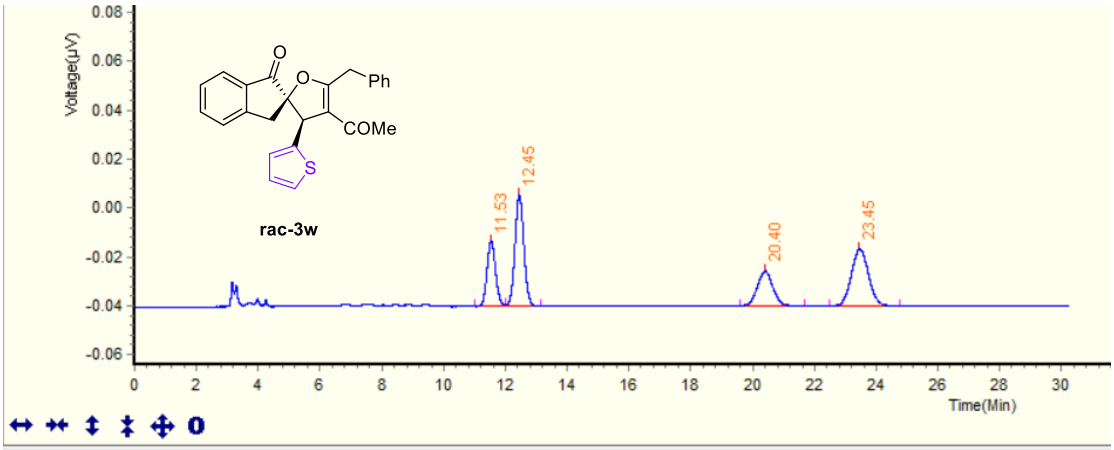
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.20	1579784	64265	49.87%	1.039	BB
2	29.80	1587824	29639	50.13%	2.314	BB
Total		3,167,608	93,904	100.00%		



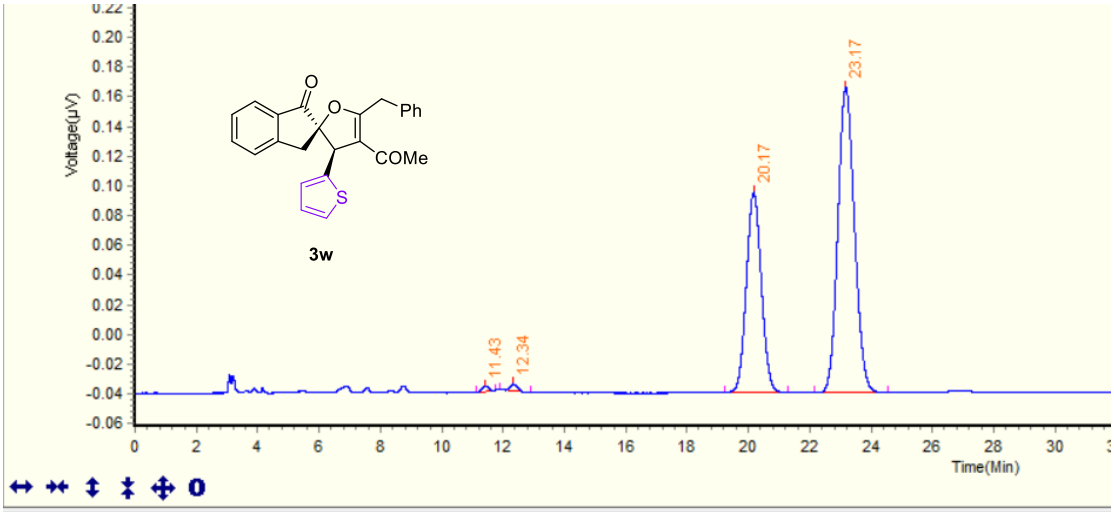
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	13.78	172896	6598	3.42%	1.33	BB
2	28.91	4884591	93297	96.58%	3.909	BB
Total		5,057,487	99,895	100.00%		



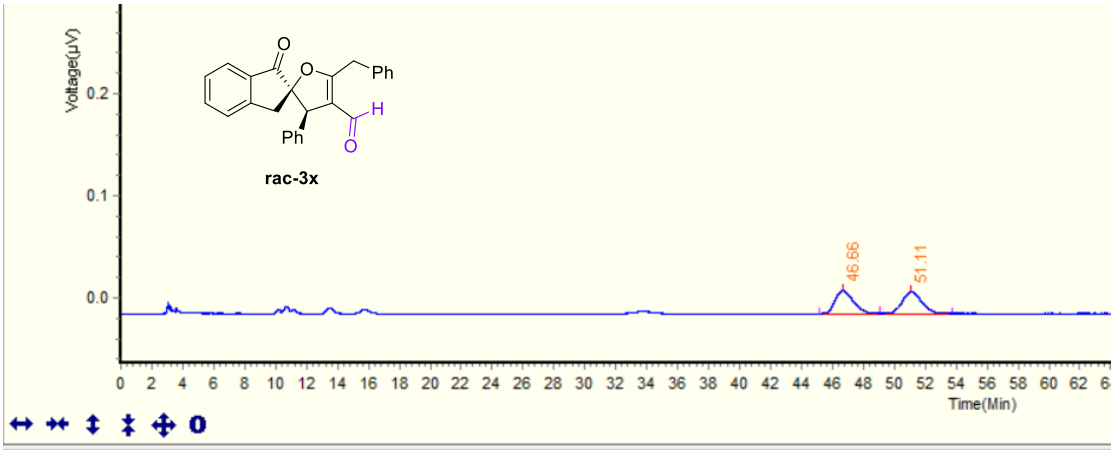
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.53	257930	13342	18.39%	0.97	BV
2	12.45	454544	22700	32.41%	1.158	VB
3	20.40	245979	7075	17.54%	2.129	BB
4	23.45	444196	11574	31.67%	2.255	BB
Total		1,402,649	54,691	100.00%		



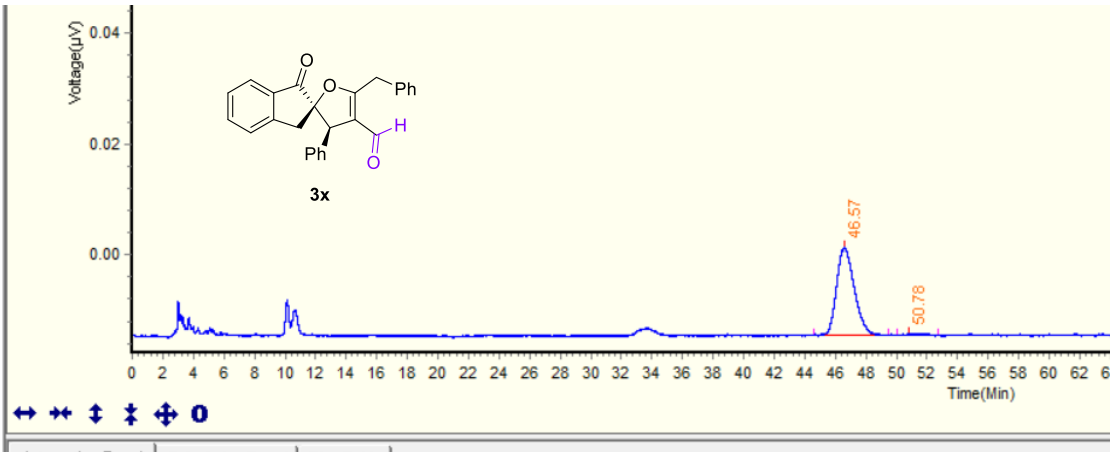
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.43	26360	1721	0.42%	0.639	BB
2	12.34	31468	2198	0.51%	0.998	BB
3	20.17	2280065	67260	36.75%	2.078	BB
4	23.17	3866186	102814	62.32%	2.438	BB
Total		6,204,079	173,993	100.00%		



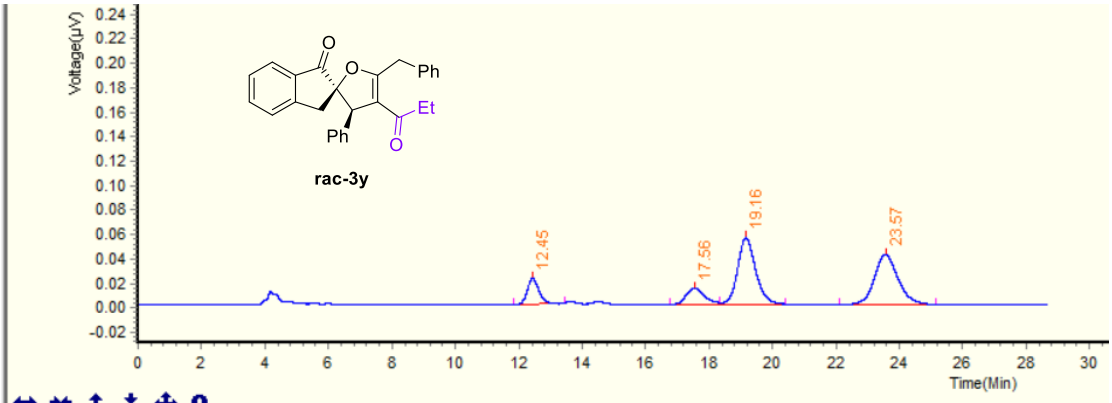
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	46.66	901086	11147	49.56%	3.845	BV
2	51.11	917132	10469	50.44%	4.72	VB
Total		1,818,218	21,616	100.00%		



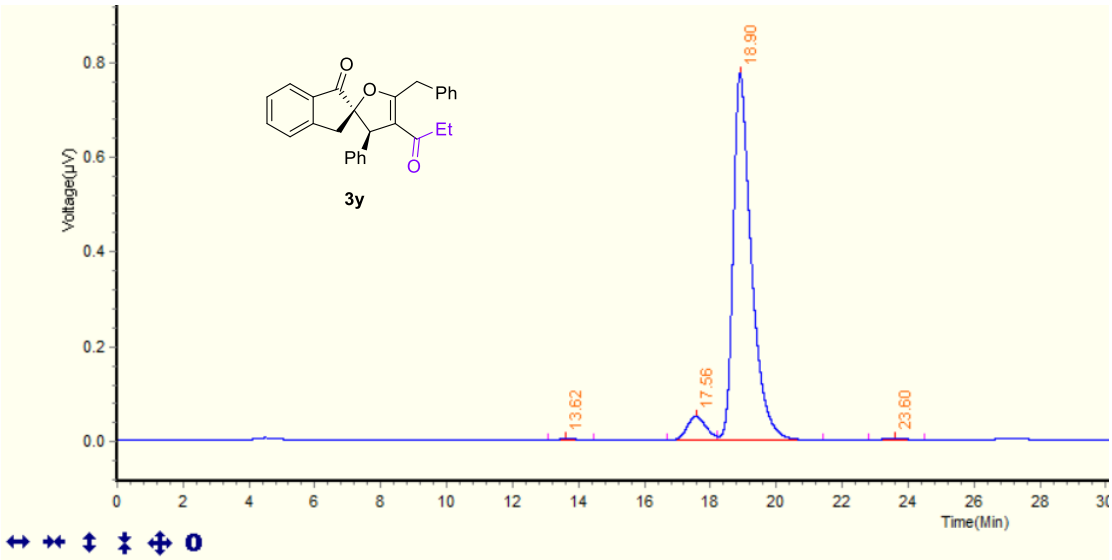
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	46.57	633753	7880	98.77%	4.893	BB
2	50.78	7860	150	1.23%	2.681	BB
Total		641,613	8,030	100.00%		



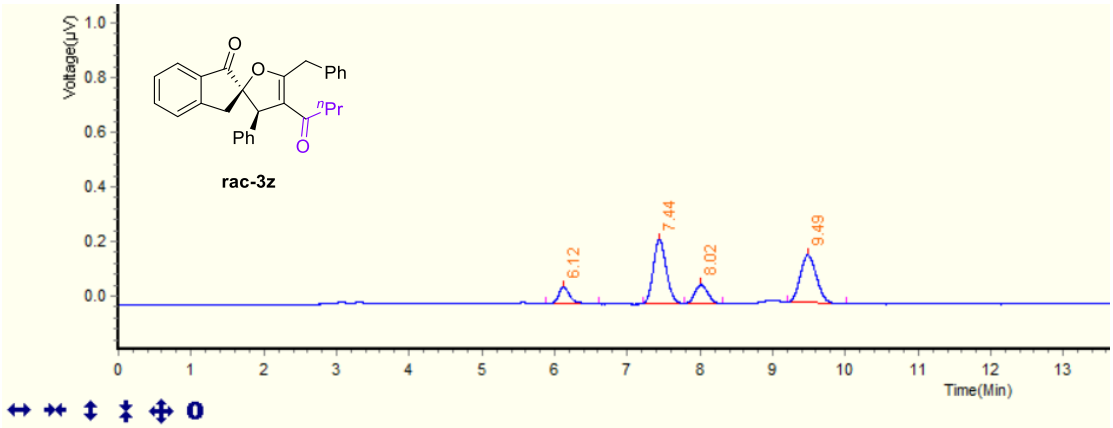
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	12.45	250716	10326	9.49%	1.635	BB
2	17.56	265743	6564	10.06%	1.545	BV
3	19.16	1071575	27108	40.58%	2.111	VB
4	23.57	1052665	20346	39.86%	3.063	BB
Total		2,640,699	64,344	100.00%		



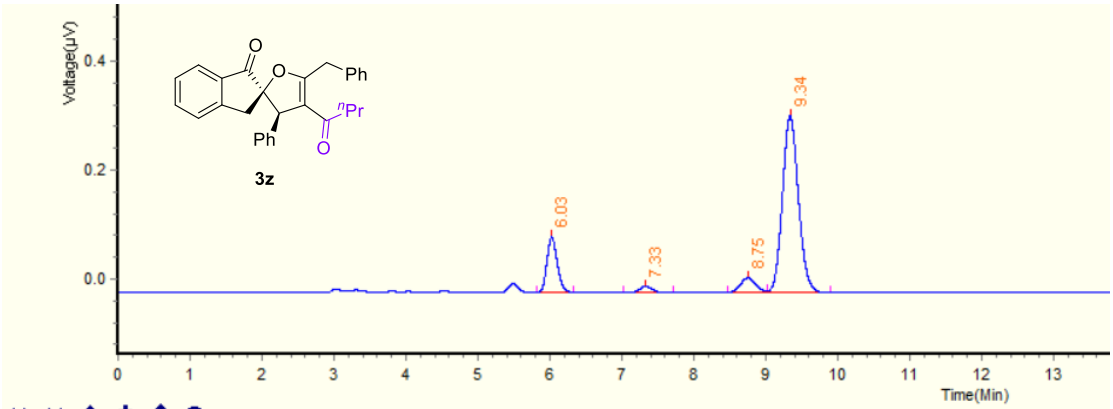
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	13.62	42240	1518	0.27%	1.388	BB
2	17.56	1000482	25233	6.29%	1.537	BV
3	18.90	14809820	388143	93.04%	3.187	VB
4	23.60	64736	1440	0.41%	1.688	BB
Total		15,917,278	416,334	100.00%		



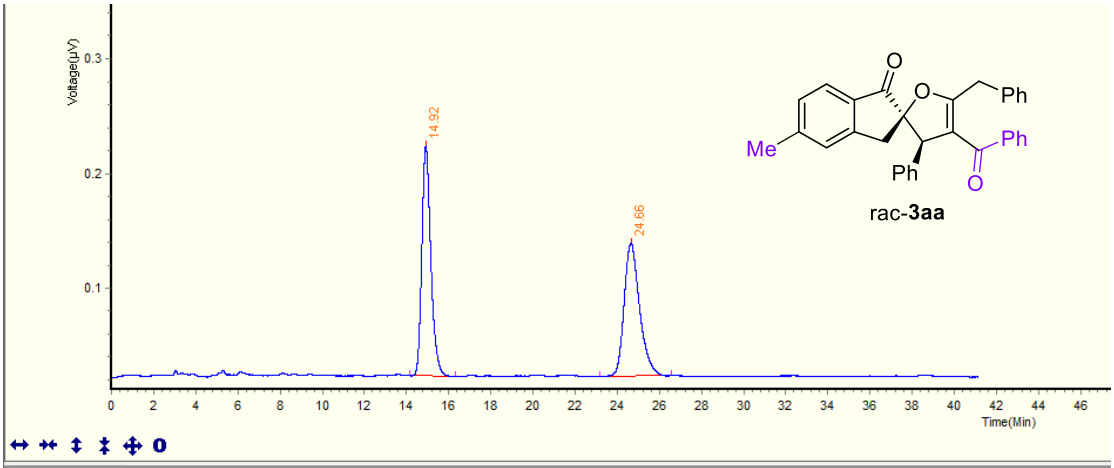
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	6.12	329937	31367	9.26%	0.733	BB
2	7.44	1454221	117280	40.79%	0.572	BV
3	8.02	438833	34450	12.31%	0.537	VB
4	9.49	1341948	87119	37.64%	0.823	BB
Total		3,564,939	270,216	100.00%		



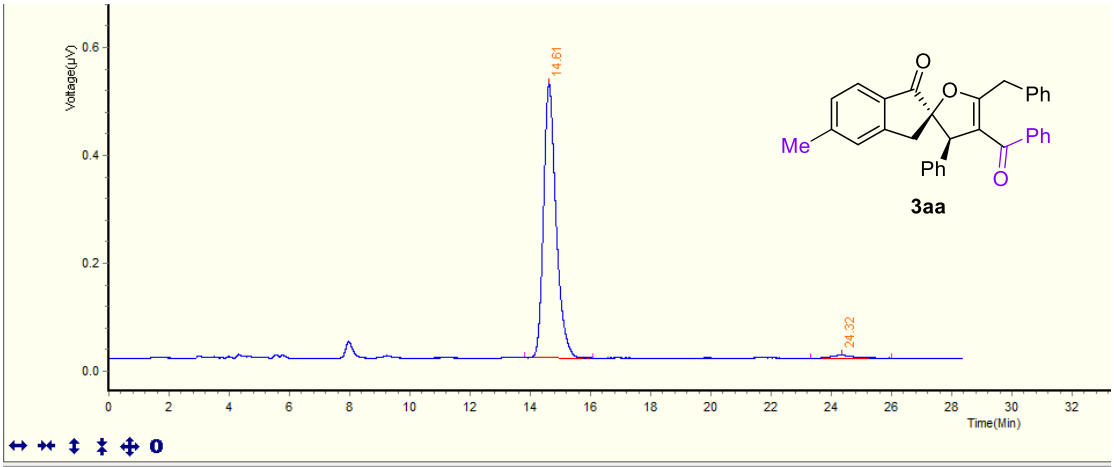
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	6.03	508334	50982	15.49%	0.511	BB
2	7.33	67583	5414	2.06%	0.7	BB
3	8.75	200963	13468	6.13%	0.551	BV
4	9.34	2504123	162470	76.32%	0.877	VB
Total		3,281,003	232,334	100.00%		



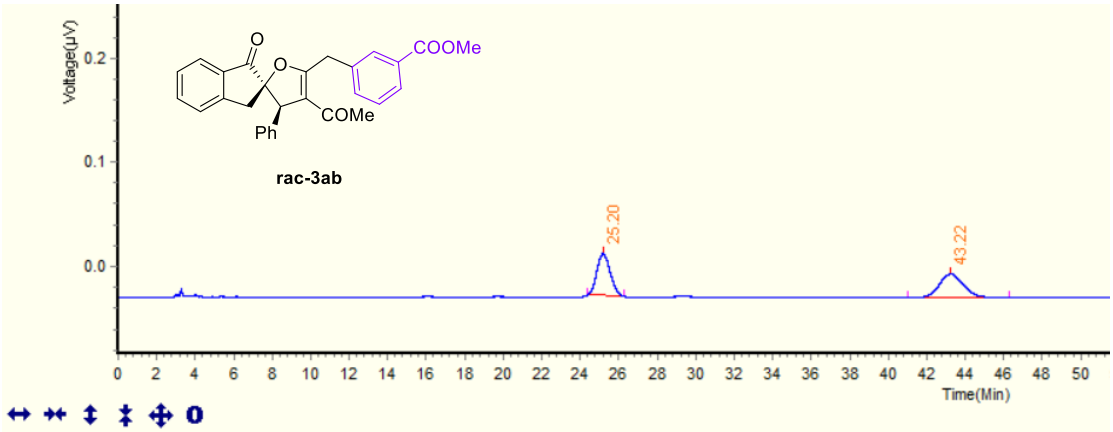
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.92	2971095	100200	50.08%	2.147	BB
2	24.66	2961726	57880	49.92%	3.423	BB
Total		5,932,821	158,080	100.00%		



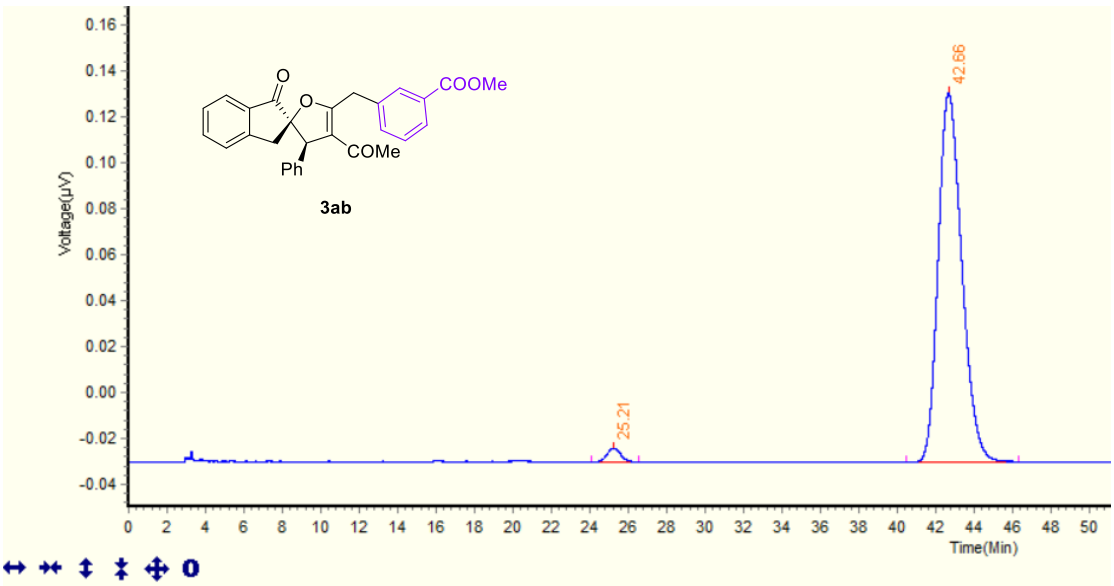
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.61	7325580	253978	98.25%	2.26	BB
2	24.32	130768	2597	1.75%	2.676	BB
Total		7,456,348	256,575	100.00%		



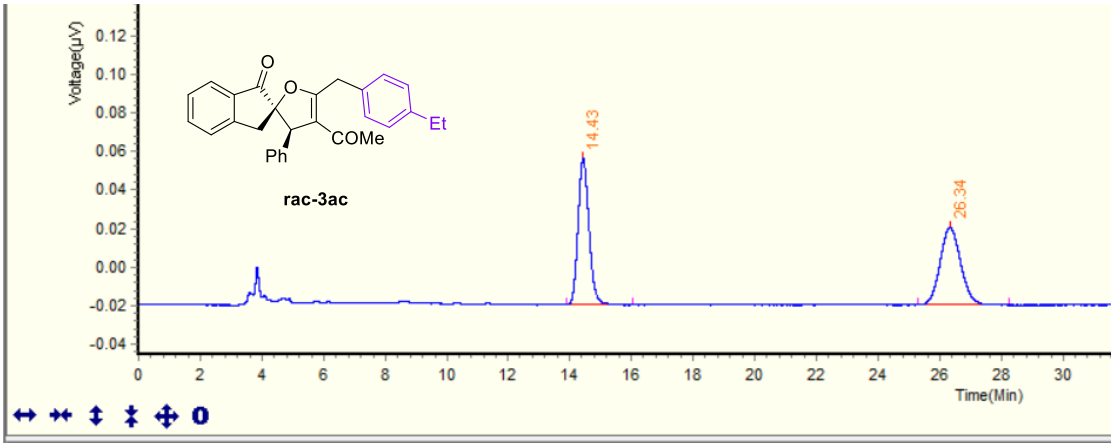
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	25.20	972822	20075	50.08%	1.889	BB
2	43.22	969802	11280	49.92%	5.289	BB
Total		1,942,624	31,355	100.00%		



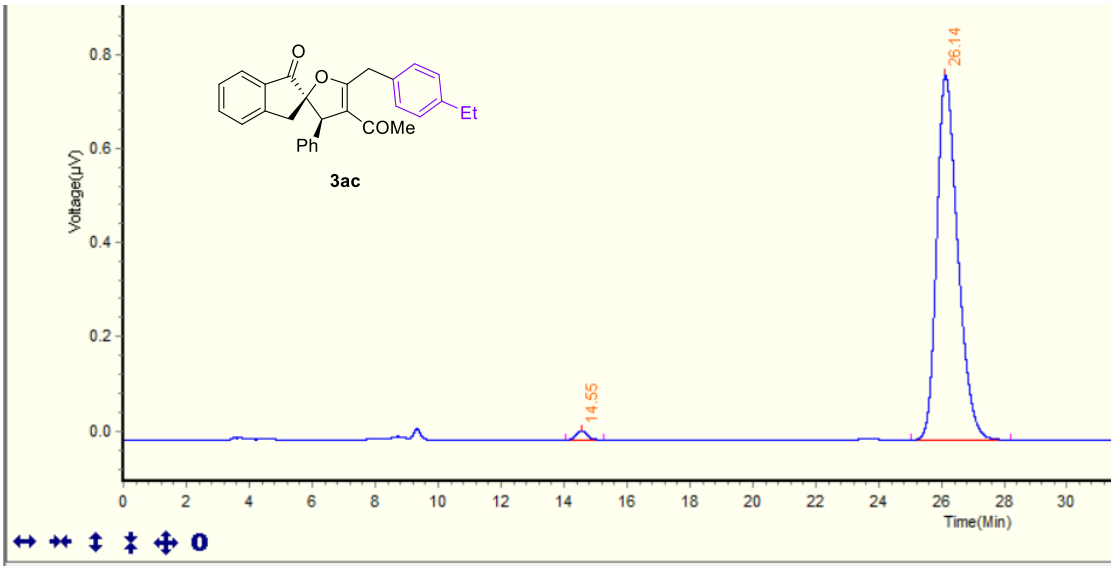
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	25.21	145874	3006	2.09%	2.458	BB
2	42.66	6841055	80231	97.91%	5.875	BB
Total		6,986,929	83,237	100.00%		



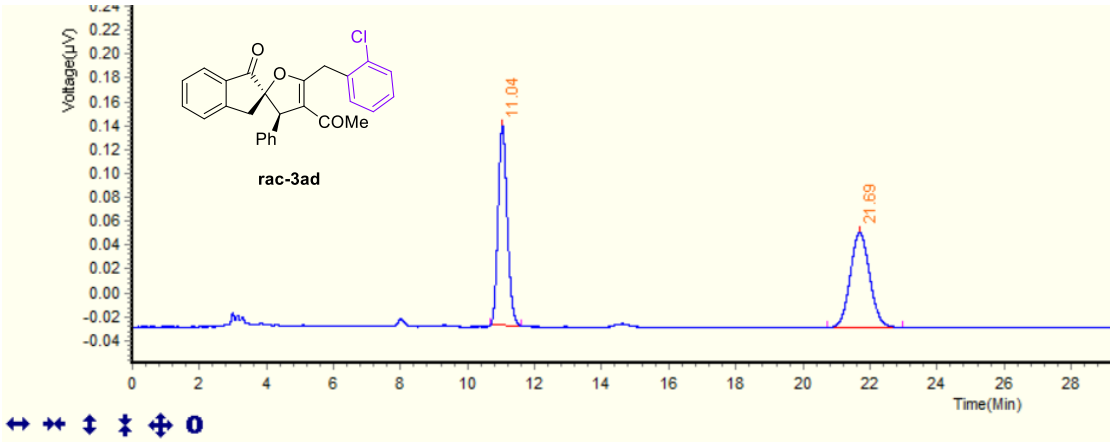
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.43	930380	37869	49.96%	2.136	BB
2	26.34	931785	20043	50.04%	2.947	BB
Total		1,862,165	57,912	100.00%		



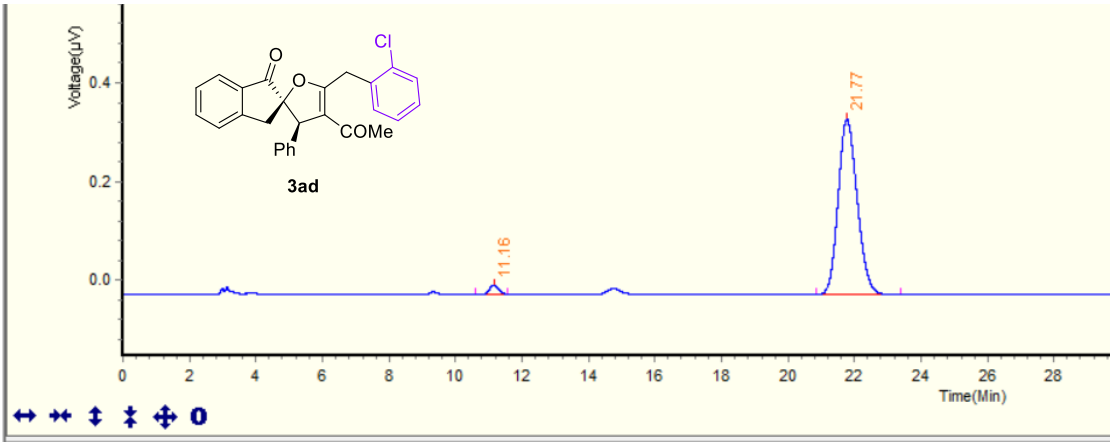
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.55	244335	9767	1.34%	1.196	BB
2	26.14	17990143	387969	98.66%	3.2	BB
Total		18,234,478	397,736	100.00%		



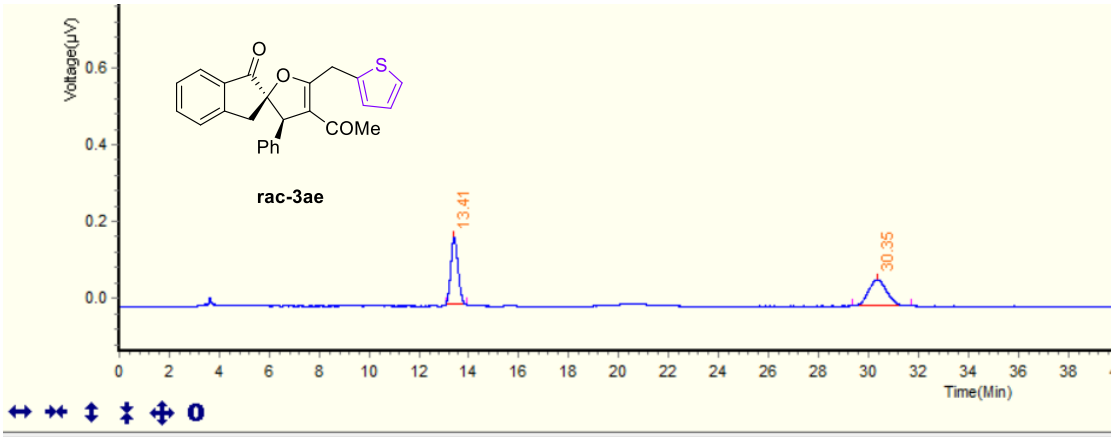
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.04	1591856	83551	50.16%	0.938	BB
2	21.69	1581675	39498	49.84%	2.243	BB
Total		3,173,531	123,049	100.00%		



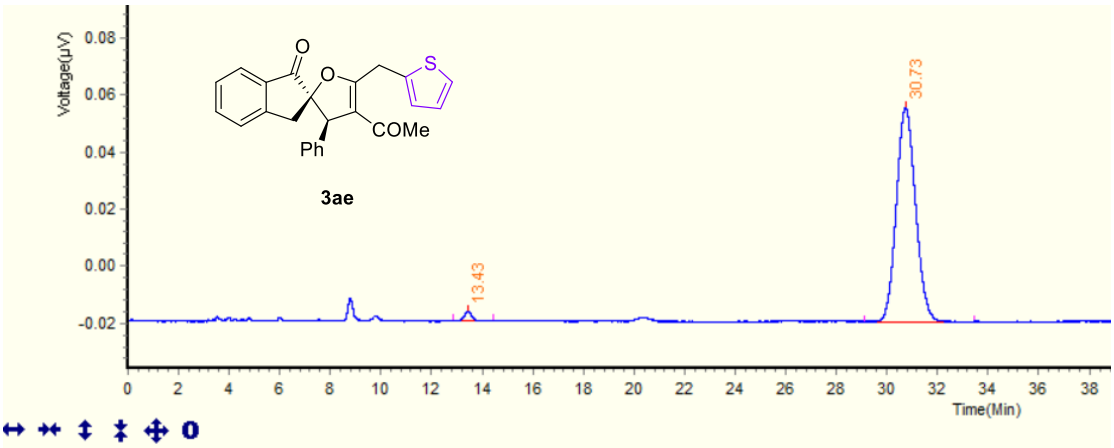
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	11.16	168390	8756	2.33%	0.972	BB
2	21.77	7053813	177199	97.67%	2.518	BB
Total		7,222,203	185,955	100.00%		



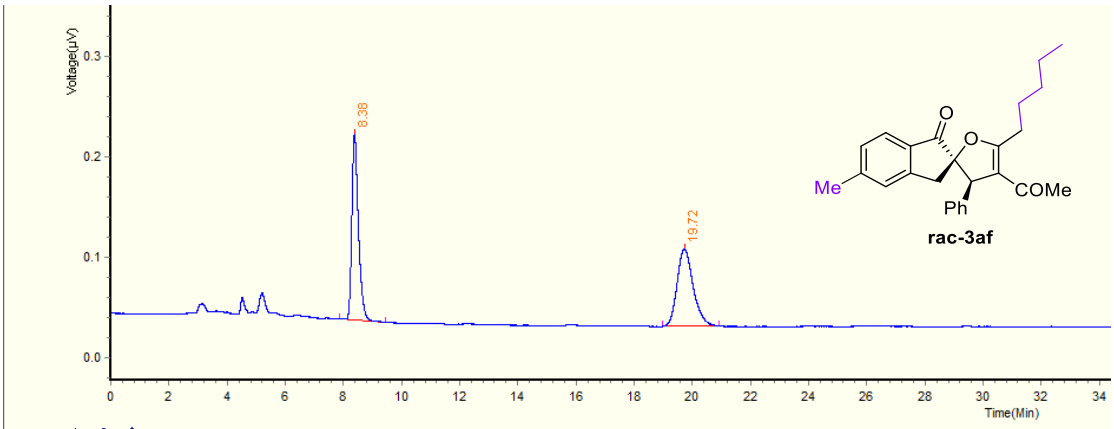
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	13.41	1743649	86542	50.05%	0.826	BB
2	30.35	1740160	33844	49.95%	2.355	BB
Total		3,483,809	120,386	100.00%		



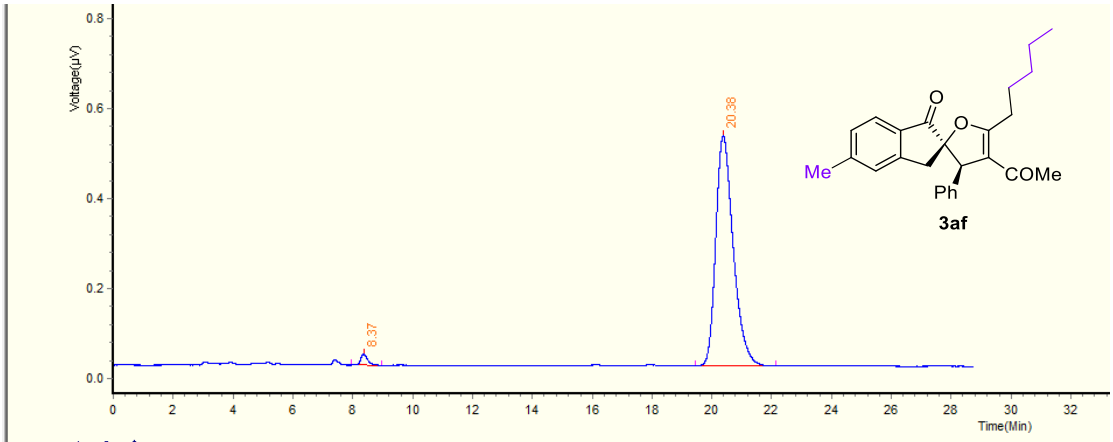
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	13.43	32119	1677	1.60%	1.548	BB
2	30.73	1979628	37501	98.40%	4.361	BB
Total		2,011,747	39,178	100.00%		



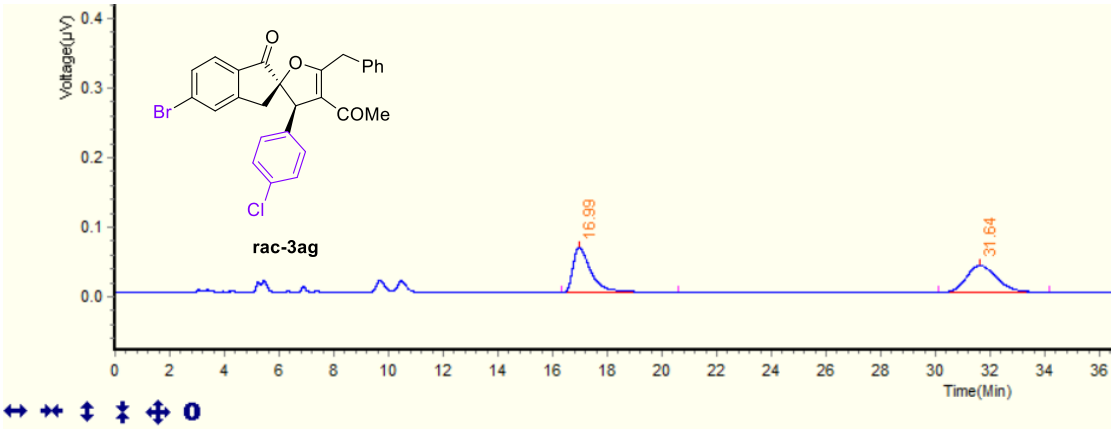
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	8.38	1449654	92504	49.64%	1.581	BB
2	19.72	1470668	38500	50.36%	1.946	BB
Total		2,920,322	131,004	100.00%		



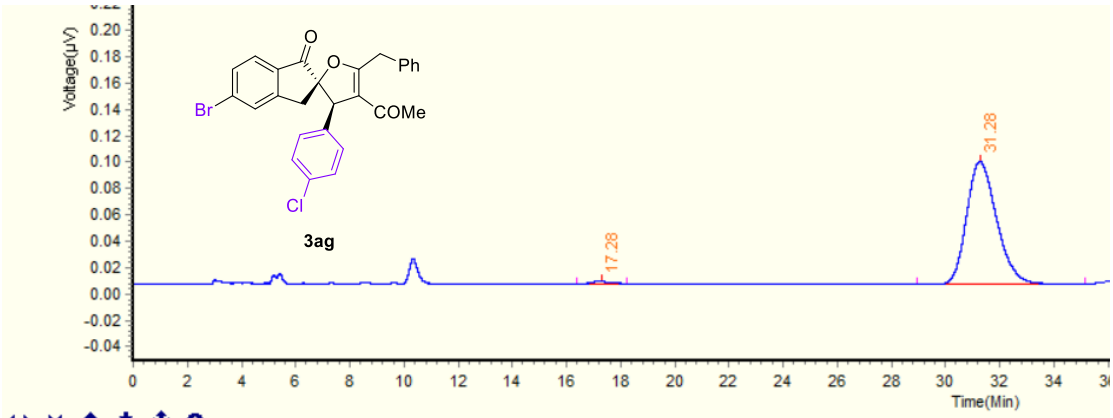
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	8.37	197552	12243	1.88%	1.015	BB
2	20.38	10329043	254947	98.12%	2.661	BB
Total		10,526,595	267,190	100.00%		



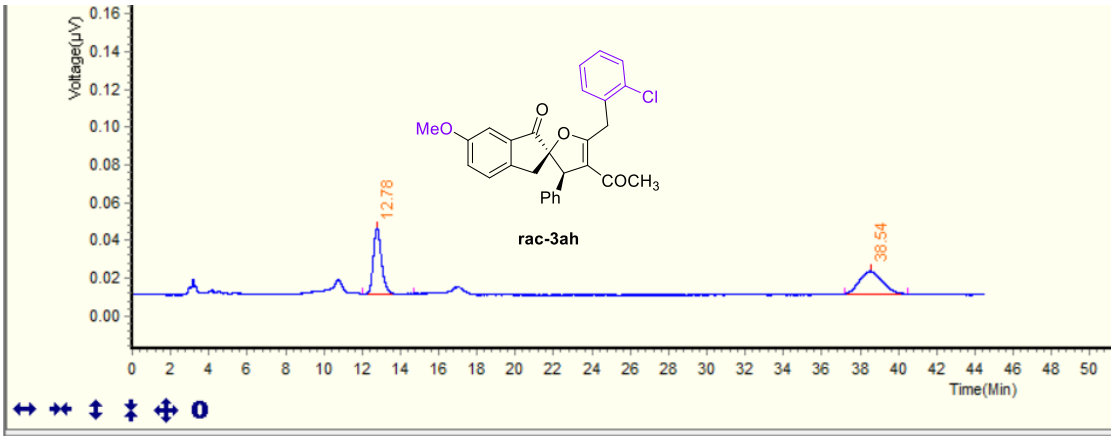
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	16.99	1463563	32212	49.96%	4.265	BB
2	31.64	1465654	19035	50.04%	4.069	BB
Total		2,929,217	51,247	100.00%		



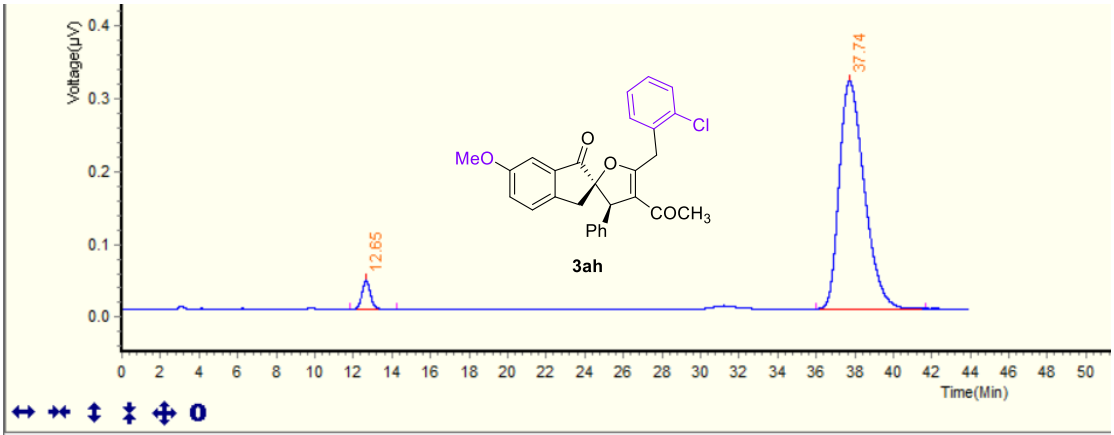
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	17.28	40779	907	1.13%	1.807	BB
2	31.28	3571309	46553	98.87%	6.191	BB
Total		3,612,088	47,460	100.00%		



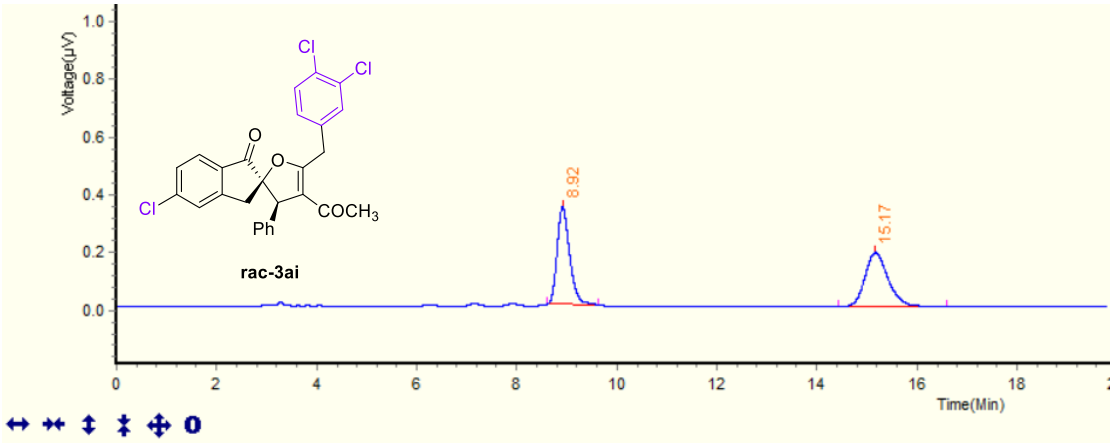
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	12.78	509479	17488	50.09%	2.682	BB
2	38.54	507749	6052	49.91%	3.328	BB
Total		1,017,228	23,540	100.00%		



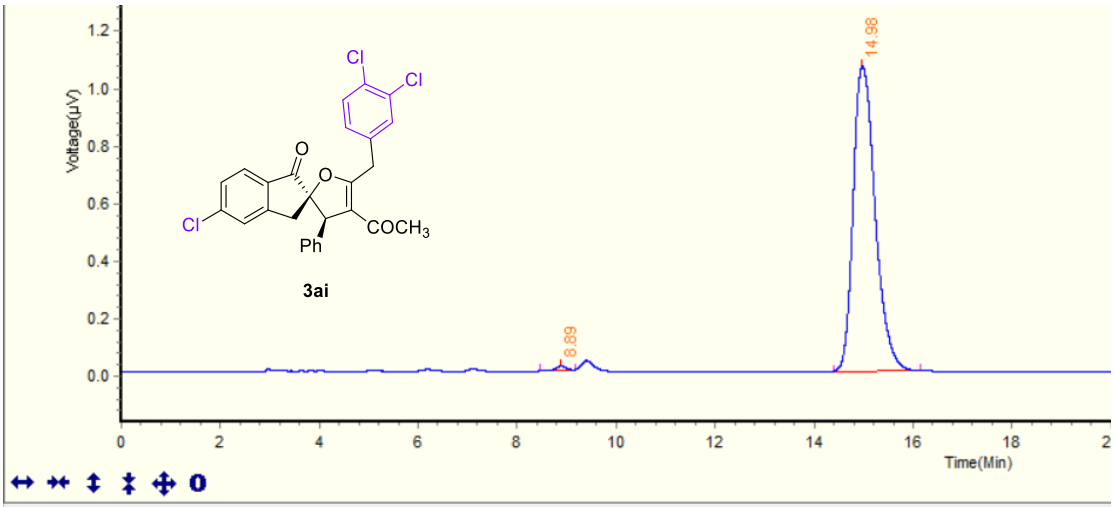
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	12.65	611077	19836	4.15%	2.404	BB
2	37.74	14128473	156344	95.85%	5.669	BB
Total		14,739,550	176,180	100.00%		



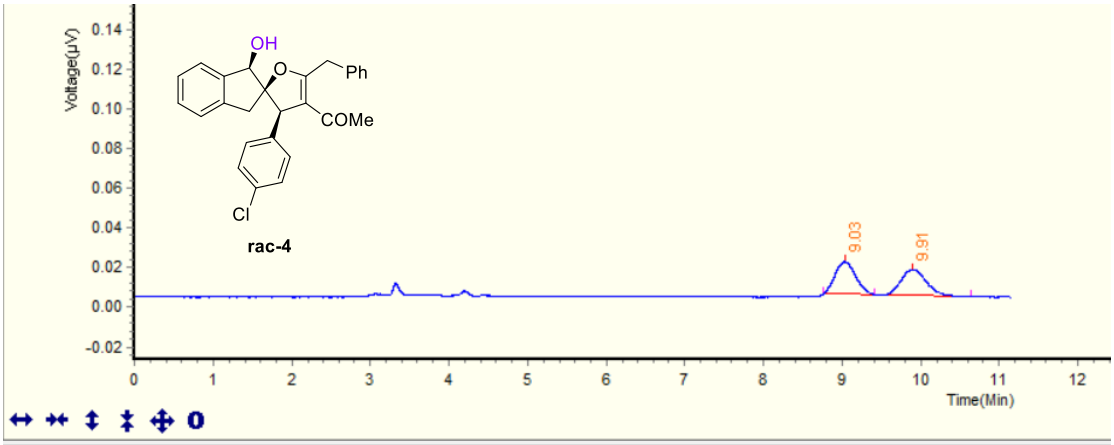
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	8.92	2937738	168189	50.02%	1.042	BB
2	15.17	2935047	92618	49.98%	2.186	BB
Total		5,872,785	260,807	100.00%		



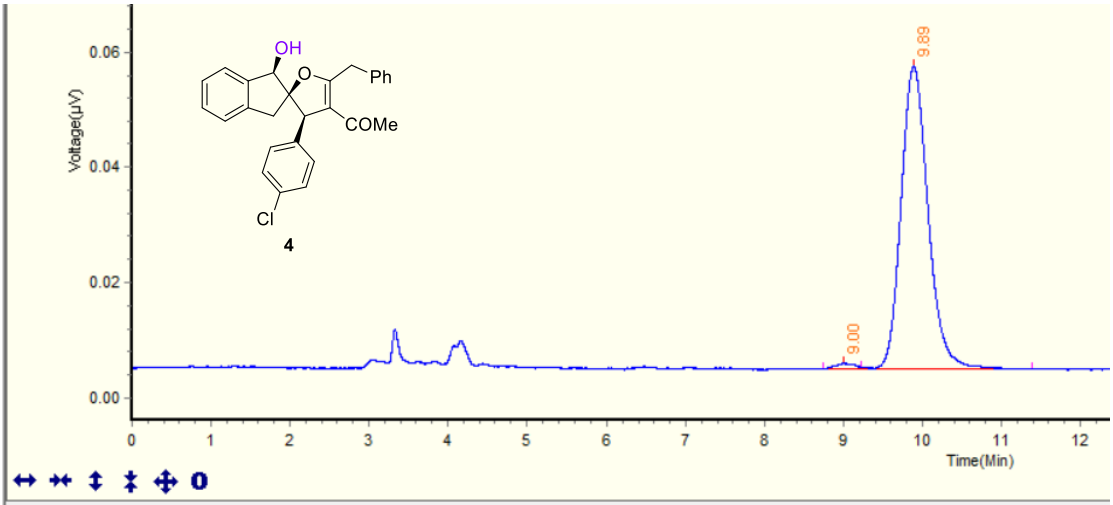
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	8.89	83982	6563	0.51%	0.712	BB
2	14.98	16402485	530765	99.49%	1.753	BB
Total		16,486,467	537,328	100.00%		



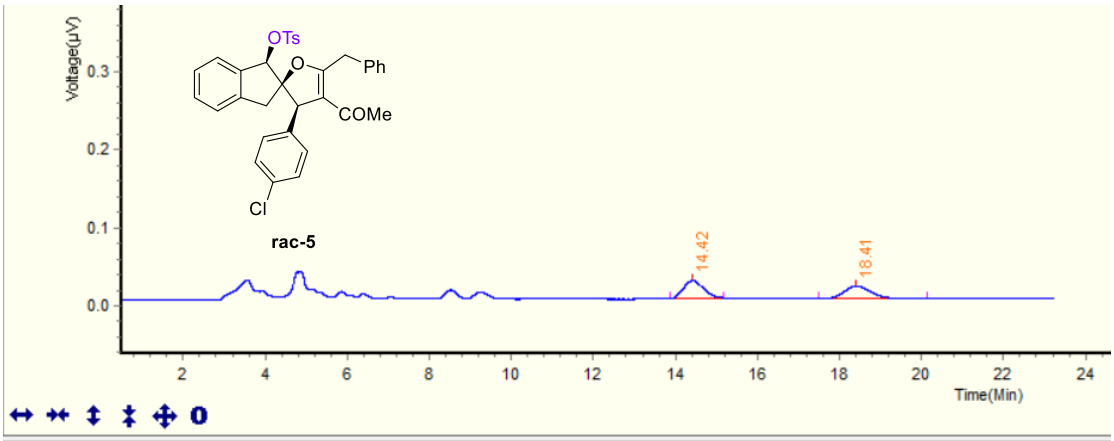
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	9.03	152518	8291	50.28%	0.658	BV
2	9.91	150849	6644	49.72%	1.223	VB
Total		303,367	14,935	100.00%		



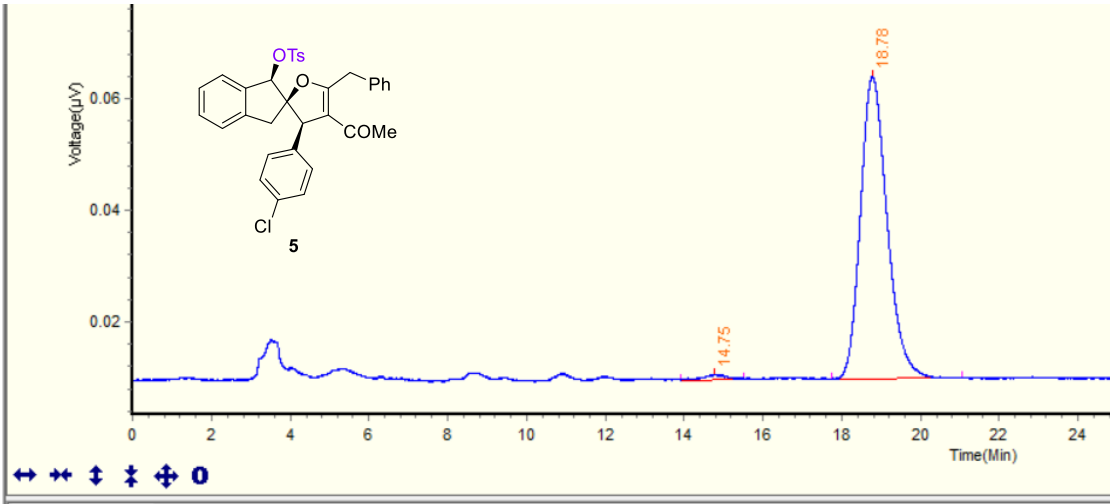
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	9.00	7152	472	1.15%	0.491	BV
2	9.89	617248	26184	98.85%	2.148	VB
Total		624,400	26,656	100.00%		



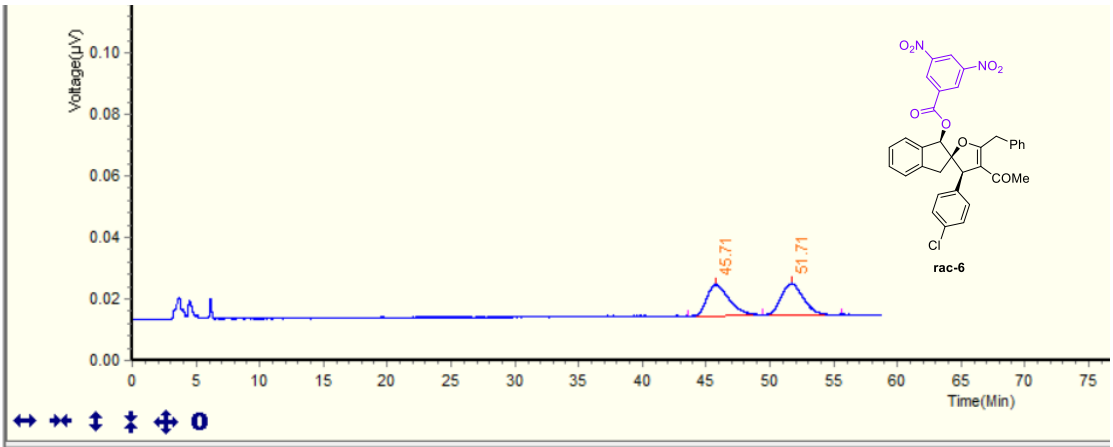
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.42	380746	11185	50.15%	1.319	BB
2	18.41	378500	8274	49.85%	2.638	BB
Total		759,246	19,459	100.00%		



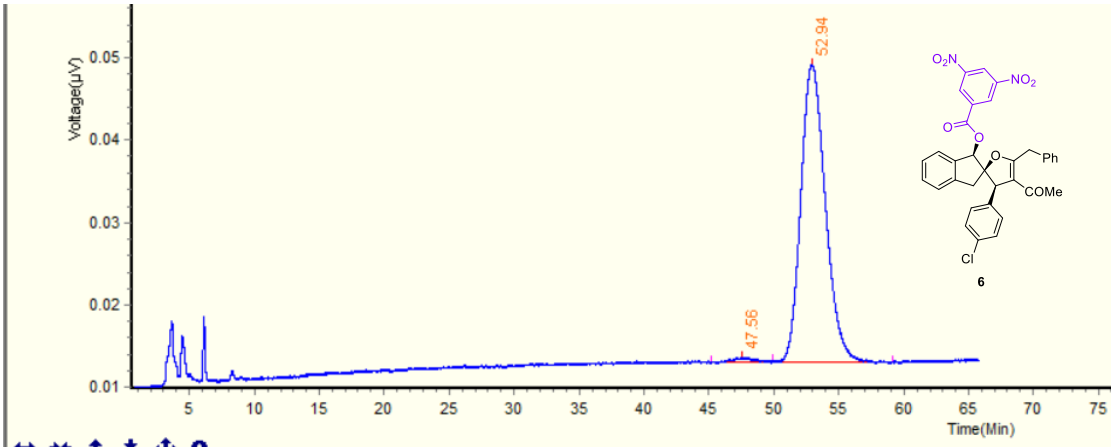
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	14.75	15380	393	1.20%	1.602	BB
2	18.78	1270326	27059	98.80%	3.308	BB
Total		1,285,706	27,452	100.00%		



Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	45.71	615375	5091	50.24%	5.83	BB
2	51.71	609540	5125	49.76%	6.134	BB
Total		1,224,915	10,216	100.00%		



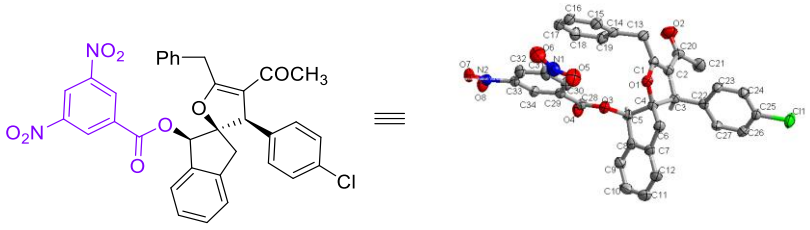
Integration Result | Calculation Result | TimeTable

No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width	
1	47.56	33492	290	1.39%	4.706	BV
2	52.94	2373658	18063	98.61%	9.208	VB
Total		2,407,150	18,353	100.00%		

Single-crystal X-ray diffraction of 6 (CCDC 2247366)

X-ray analysis was carried out using the single crystal which was grown in Hexane/acetone.

The instrumentation used for the crystal measurement is Oxford Gemini E X-ray single-crystal diffractometer (ellipsoid contour at 30% probability level).



6

Datablock: 20230229

Bond precision: C-C = 0.0059 A Wavelength=1.54184

Cell: a=15.7718(3) b=14.18227(19) c=16.7062(3)
alpha=90 beta=115.571(2) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	3370.82(11)	3370.80(11)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C34 H25 Cl N2 O8 [+ solvent]	1(C34 H25 Cl N2 O8)
Sum formula	C34 H25 Cl N2 O8 [+ solvent]	C34 H25 Cl N2 O8
Mr	625.01	625.01
Dx,g cm-3	1.232	1.232
Z	4	4
Mu (mm-1)	1.435	1.435
F000	1296.0	1296.0
F000'	1301.58	
h,k,lmax	19,17,20	19,17,20
Nref	13011[6787]	12736
Tmin,Tmax	0.799,0.866	0.915,1.000
Tmin'	0.795	

Correction method= # Reported T Limits: Tmin=0.915 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.88/0.98 Theta(max)= 70.964

R(reflections)= 0.0477(10785) wR2(reflections)= 0.1358(12736)

S = 1.028 Npar= 807

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT234_ALERT_4_C Large Hirshfeld Difference C10      --C11      .       0.16 Ang.
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C25' Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C20 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C25 Check
PLAT334_ALERT_2_C Small <C-C> Benzene Dist.   C22      -C27      .       1.37 Ang.
PLAT334_ALERT_2_C Small <C-C> Benzene Dist.   C29      -C34      .       1.37 Ang.
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00588 Ang.
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Alert level G

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PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         13 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         13 Report
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records         13 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          8 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records          3 Report
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        293 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )        22% Note
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  2  )         7% Note
PLAT398_ALERT_2_G Deviating  C-O-C   Angle From 120 for O1'      .      106.6 Degree
PLAT398_ALERT_2_G Deviating  C-O-C   Angle From 120 for O1       .      107.1 Degree
PLAT431_ALERT_2_G Short Inter HL..A Contact  C11'     ..O7'      .       3.14 Ang.
                                                  x,y,1+z  =      1_556 Check
PLAT606_ALERT_4_G Solvent Accessible VOID(S) in Structure ........          ! Info
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          7 Note
PLAT721_ALERT_1_G Bond    Calc     0.96000, Rep     0.97000 Dev...       0.01 Ang.
          C1A      -H1AA           1_555   1_555 ........     #   80 Check
PLAT791_ALERT_4_G Model has Chirality at C3          (Sohnke SpGr)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C3'         (Sohnke SpGr)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C4          (Sohnke SpGr)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C4'         (Sohnke SpGr)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C5          (Sohnke SpGr)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C5'         (Sohnke SpGr)          R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        87 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        51 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........       4.0 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         0 Info
```

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
7 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
26 **ALERT level G** = General information/check it is not something unexpected

```
  3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 11 ALERT type 2 Indicator that the structure model may be wrong or deficient
  6 ALERT type 3 Indicator that the structure quality may be low
 13 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 28/11/2022; check.def file version of 28/11/2022