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Organocatalytic Asymmetric Synthesis of Highly Functionalized Spiro-Thiazolone-Cyclopropane-Oxindoles Bearing Two Vicinal Spiro Quaternary Centers

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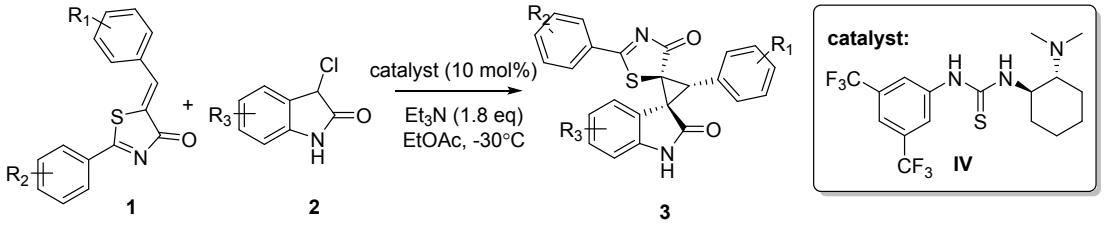
General Information

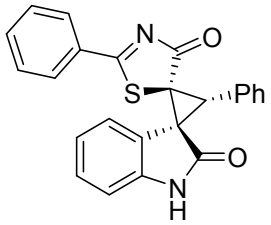
All reagents and solvents were reagent grade or were purified by standard methods before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE300 or AVANCE400 or AVANCE600 spectrometer (Bruker Company, Germany), using TMS as an internal standard and $CDCl_3$, CD_3OD or DMSO-d_6 as solvent. Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (double of doublet) or m (multiplets). Chemical shifts (δ values) and coupling constants (J values) are given in ppm and Hz, respectively. High resolution mass spectrometry (HRMS) was recorded on an Agilent 6538 UHD Accurate-Mass Q-TOF LC/MS spectrometer. TLC analysis was carried out on silica gel plates GF254 (Qindao Haiyang Chemical, China). Silica gel column chromatography was performed with Silica gel 60G (Qindao Haiyang Chemical, China). Enantioselectivities were determined by High performance liquid chromatography (HPLC) analysis employing a Daicel Chiralpak AD, OD or OZ. Optical rotations were measured on a Perkin-Elmer 343 polarimeter (c given in g/100 mL) with instruments operating at λ = 589 nm, corresponding to the sodium D line at 25°C. Absolute configuration of the products was determined by X-ray.

General procedure for the organocatalytic Michael-Alkylation cascade reaction



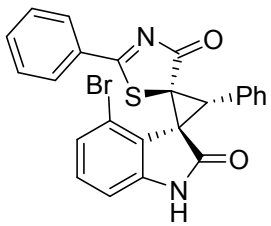
A solution of catalyst (10 mol %) and Et_3N (0.18 mmol, 1.8 eq), substrate **1** (0.10 mmol) and **2** (0.12 mmol, 1.2 eq) in EtOAc (2.0 mL) was stirred at -30°C for 12 h. After reaction, the solvent was evaporated and the crude product was purified using flash column chromatography (silica gel, DCM) to afford the desired product **3**. For the preparation of racemic **3**, racemic catalyst **IV** (*er* = 44 : 56) was used.

Characterization of products 3



3a

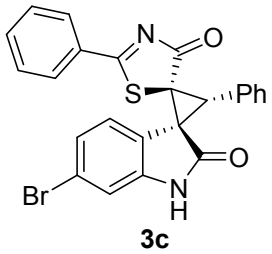
(2'S,3R,3'R)-2'',3'-diphenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3a**). Faint yellow solid (30 mg), yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34 (s, 1H), 6.93 (d, J = 7.7 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 7.27-7.32 (m, 3H), 7.35 (br, 3H), 7.52 (t, J = 7.6 Hz, 2H), 7.68 (t, J = 7.3 Hz, 1H), 8.10 (d, J = 7.7 Hz, 1H), 8.17 (d, J = 8.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.28, 45.91, 56.76, 109.78, 122.76, 124.62, 125.67, 128.20, 128.33, 128.58, 128.76, 129.06, 129.46, 131.23, 132.26, 135.12, 140.62, 171.73, 187.41, 195.42. HRMS (ESI+) m/z calculated for $C_{24}H_{16}KN_2O_2S$ (M+K): 435.0570, found 435.0568. HPLC (Chiralpak OD, 0.46 cm I.D. ×25 cm L ×5 um, 25^{o}C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 10.88 min, t_{minor} = 20.63 min, *ee* = 93%; $[\alpha]^{25}{}_{D}$ = -68.1 (c = 0.15 in DCM).



3b

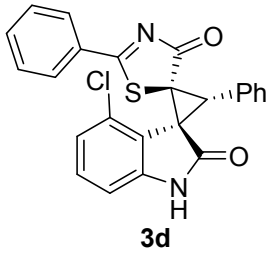
(2'S,3R,3'R)-4-bromo-2'',3'-diphenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3b**). Faint yellow solid (39 mg), yield 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (s, 1H), 6.66 (d, J = 7.6 Hz, 1H), 7.08 (t, J = 8.0 Hz, 1H), 7.31-7.39 (m, 6H), 7.46 (t, J = 7.8 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 8.06 (t, J = 7.4 Hz, 2H), 8.67 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.70, 48.88, 60.19, 109.35, 120.46, 121.90, 128.14, 128.23, 128.45, 128.67, 129.03, 129.65, 129.99, 130.87, 132.12, 135.07, 143.17, 172.57, 186.57, 193.73. HRMS (ESI+) m/z calculated for $C_{24}H_{15}BrKN_2O_2S$ (M+K): 512.9675, found 512.9669. HPLC (Chiralpak OD, 0.46 cm

I.D. ×25 cm L ×5 um, 25°C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 12.55 min, t_{minor} = 16.38 min, *ee* = 80%; $[\alpha]^{25}{}_{D}$ = 129.8 (c = 0.19 in DCM).



3c

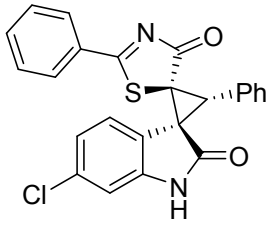
(2'S,3R,3'R)-6-bromo-2'',3'-diphenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3c**). Faint yellow solid (37 mg), yield 78%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.30 (s, 1H), 7.06 (s, 1H), 7.25-7.27 (m, 2H), 7.28 (d, J = 8.2 Hz, 1H), 7.34-7.36 (br, 3H), 7.50-7.54 (m, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 8.15 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 43.44, 45.78, 56.96, 113.51, 122.67, 123.68, 125.82, 127.06, 128.49, 128.58, 128.76, 129.28, 129.50, 131.06, 132.28, 135.44, 142.05, 172.10, 187.47, 195.69. HRMS (ESI+) m/z calculated for $C_{24}H_{16}BrN_2O_2S$ (M+H): 475.0116, found 475.0105. HPLC (Chiralpak OZ, 0.46 cm I.D. ×25 cm L ×5 um, 25°C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 9.83 min, t_{minor} = 19.03 min, *ee* = 86%; $[\alpha]^{25}{}_{D}$ = -55.6 (c = 0.23 in DCM).



3d

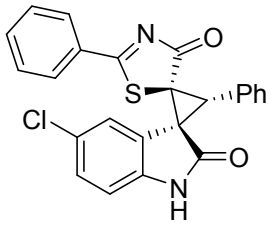
(2'S,3R,3'R)-4-chloro-2'',3'-diphenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3d**). Faint yellow solid (37 mg), yield 86%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.52 (s, 1H), 6.54 (d, J = 7.2 Hz, 1H), 7.11-7.15 (m, 2H), 7.22 (t, J = 7.9 Hz, 1H), 7.32-7.39 (m, 5H), 7.45 (t, J = 7.6 Hz, 2H), 7.62 (t, J = 7.1 Hz, 1H), 8.05 (d, J = 8.2 Hz, 2H), 8.79 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 38.87, 48.07, 59.98, 108.85, 119.13, 125.33, 128.22, 128.43, 129.02, 129.70, 129.88, 130.95,

132.08, 133.67, 135.05, 143.08, 172.60, 186.40, 193.65. HRMS (ESI+) m/z calculated for $C_{24}H_{16}ClN_2O_2S$ (M+H): 431.0621, found 431.0608. HPLC (Chiralpak OD, 0.46 cm I.D. ×25 cm L ×5 um, 25°C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 11.72 min, t_{minor} = 17.15 min, *ee* = 73%; $[\alpha]^{25}{}_{D}$ = 104.9 (c = 0.29 in DCM).



3e

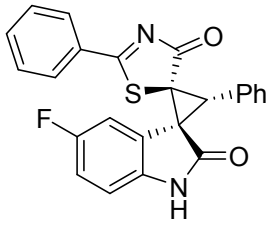
(2'S,3R,3'R)-6-chloro-2'',3'-diphenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3e**). Faint yellow solid (30 mg), yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (s, 1H), 6.91 (s, 1H), 7.14 (d, J = 8.3 Hz, 1H), 7.27 (br, 1H), 7.36-7.38 (m, 3H), 7.51 (t, J = 7.8 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 8.14 (d, J = 7.8 Hz, 2H), 8.73 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.31, 45.61, 56.84, 110.62, 122.74, 122.99, 126.61, 128.35, 128.44, 128.60, 129.13, 129.38, 130.95, 132.12, 134.68, 135.29, 141.78, 172.15, 187.35, 195.55. HRMS (ESI+) m/z calculated for $C_{24}H_{16}ClN_2O_2S$ (M+H): 431.0621, found 431.0623. HPLC (Chiralpak OD, 0.46 cm I.D. ×25 cm L ×5 um, 25°C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 12.50 min, t_{minor} = 21.57 min, *ee* = 87%; $[\alpha]^{25}{}_{D}$ = -65.2 (c = 0.25 in DCM).



3f

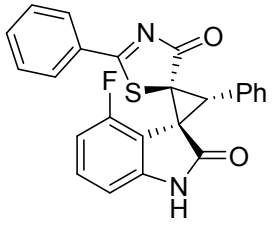
(2'S,3R,3'R)-5-chloro-2'',3'-diphenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3f**). Faint yellow solid (33 mg), yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (s, 1H), 6.61 (d, J = 8.2 Hz, 1H), 7.23-7.28 (m, 2H), 7.36 (br, 3H), 7.48 (t, J = 7.4 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 8.08-8.11 (m, 3H), 9.03 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 43.44, 45.68, 56.88, 111.05, 125.84, 126.20, 128.26, 128.36, 128.39, 128.57, 128.71, 129.10, 129.46, 130.97, 132.08, 135.30, 139.40, 171.89, 187.21, 195.47. HRMS (ESI+) m/z calculated for $C_{24}H_{16}ClN_2O_2S$ (M+H): 431.0621, found 431.0617. HPLC (Chiralpak OD, 0.46 cm I.D. ×25 cm L ×5 um, 25°C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 12.02 min, t_{minor} = 18.32 min, *ee* = 90%; $[\alpha]^{25}{}_{D}$ = 35.6 (c = 0.19 in DCM).



3g

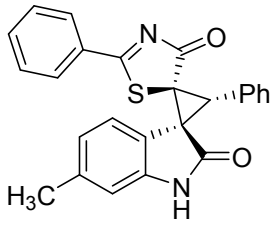
(2'S,3R,3'R)-5-fluoro-2'',3'-diphenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3g**). Faint yellow solid (30 mg), yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29 (s, 1H), 6.85 (br, 1H), 7.04 (t, J = 8.4 Hz, 1H), 7.35 (br, 2H), 7.53 (t, J = 7.4 Hz, 2H), 7.69 (t, J = 7.3 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 7.5 Hz, 1H), 8.25 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.65, 45.84, 56.81, 110.15, 110.23, 113.70, 113.97, 115.13, 115.36, 126.13, 126.23, 128.23, 128.33, 128.39, 128.44, 128.64, 129.12, 129.40, 130.18, 130.92, 132.16, 135.10, 135.29, 136.57, 157.77, 160.16, 171.68, 187.35, 195.66. HRMS (ESI+) m/z calculated for $C_{24}H_{16}FN_2O_2S$ (M+H): 415.0917, found 415.0915. HPLC (Chiralpak OD, 0.46 cm I.D. ×25 cm L ×5 um, 25°C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 11.48 min, t_{minor} = 17.95 min, *ee* = 83%; $[\alpha]^{25}{}_{D}$ = -80.1 (c = 0.21 in DCM).



3h

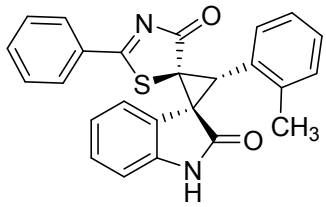
(2'S,3R,3'R)-4-fluoro-2'',3'-diphenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3h**). Faint yellow solid (33 mg), yield 80%. ^{1}H NMR

(600 MHz, $CDCl_3$) δ 4.87 (s, 1H), 6.51 (d, J = 7.7 Hz, 1H), 6.85 (t, J = 9.3 Hz, 1H), 7.19-7.23 (m, 1H), 7.29-7.30 (m, 2H), 7.36 (br, 3H), 7.46 (t, J = 7.8 Hz, 2H), 7.63 (t, J = 7.4 HZ, 1H), 8.07 (d, J = 7.5 Hz, 2H), 8.79 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 39.29, 46.20, 58.46, 106.48, 109.88, 111.19, 111.34, 128.40, 128.62, 129.17, 129.88, 130.87, 130.95, 132.28, 135.20, 143.12, 143.16, 158.92, 172.38, 186.45, 194.07. HRMS (ESI+) m/z calculated for $C_{24}H_{16}FN_2O_2S$ (M+H): 415.0917, found 415.0913. HPLC (Chiralpak OD, 0.46 cm I.D. ×25 cm L ×5 um, 25°C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 11.96 min, t_{minor} = 21.03 min, *ee* = 86%; $[\alpha]^{25}{}_D$ = 14.8 (c = 0.24 in DCM).



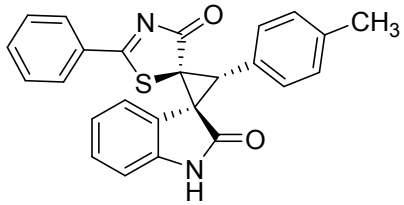
3i

(2'S,3R,3'R)-6-methyl-2'',3'-diphenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3i**). Faint yellow solid (25 mg), yield 60%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 4.27 (s, 1H), 6.71 (s, 1H), 6.94 (d, J = 7.9 Hz, 1H), 7.27 (br, 1H), 7.33-7.35 (br, 3H), 7.48 (t, J = 7.8 Hz, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 7.4 Hz, 2H), 8.52 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.81, 43.30, 46.16, 56.72, 110.96, 121.78, 123.48, 125.46, 128.22, 128.44, 128.66, 129.17, 129.60, 131.55, 132.43, 135.17, 139.27, 141.00, 172.56, 187.65, 195.45. HRMS (ESI+) m/z calculated for $C_{25}H_{19}N_2O_2S$ (M+H): 411.1167, found 411.1163. HPLC (Chiralpak OZ, 0.46 cm I.D. ×25 cm L ×5 um, 25°C, *i*-propanol/hexane = 10: 90, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 10.74 min, t_{minor} = 30.25 min, *ee* = 89%; $[\alpha]^{25}{}_D$ = -64.7 (c = 0.23 in DCM).



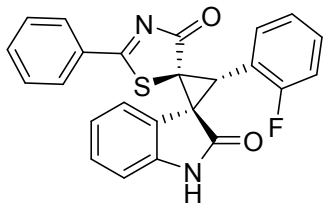
3j

(2'S,3R,3'R)-2''-phenyl-3'-(o-tolyl)-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3j**). Faint yellow solid (25 mg), yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (s, 3H), 4.18 (s, 1H), 6.96 (d, J = 7.7 Hz, 1H), 7.16-7.22 (m, 3H), 7.34 (t, J = 7.6 Hz, 2H), 7.53 (t, J = 7.6 Hz, 2H), 7.69 (t, J = 7.5 Hz, 2H), 7.80 (s, 1H), 8.11 (d, J = 7.6 Hz, 1H), 8.17 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.61, 42.86, 46.19, 56.91, 109.97, 122.83, 124.49, 125.48, 125.54, 128.36, 128.56, 128.75, 129.06, 129.40, 129.79, 130.35, 132.23, 135.13, 137.73, 140.71, 172.31, 187.33, 195.54. HRMS (ESI+) m/z calculated for $C_{25}H_{19}N_2O_2S$ (M+H): 411.1167, found 411.1160. HPLC (Chiralpak OD, 0.46 cm I.D. ×25 cm L ×5 um, 25^{o}C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 9.43 min, t_{minor} = 35.79 min, *ee* = 93%; $[\alpha]^{25}{}_{D}$ = -74.3 (c = 0.23 in DCM).



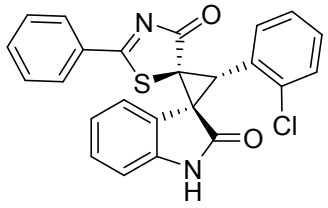
3k

(2'S,3R,3'R)-2''-phenyl-3'-(p-tolyl)-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3k**). Faint yellow solid (25 mg), yield 62%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H), 4.29 (s, 1H), 6.78 (d, J = 7.6 Hz, 1H), 7.11-7.15 (m, 5H), 7.25 (br, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 8.06-8.12 (m, 3H), 8.77 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.39, 43.32, 46.15, 56.98, 110.13, 122.77, 124.83, 125.67, 128.32, 128.65, 128.75, 129.15, 129.19, 129.46, 132.36, 135.19, 138.07, 140.94, 172.32, 187.60, 195.48. HRMS (ESI+) m/z calculated for $C_{25}H_{19}N_2O_2S$ (M+H): 411.1167, found 411.1160. HPLC (Chiralpak OD, 0.46 cm I.D. ×25 cm L ×5 um, 25^{o}C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 9.14 min, t_{minor} = 20.64 min, *ee* = 91%; $[\alpha]^{25}{}_{D}$ = -64.3 (c = 0.14 in DCM).



3l

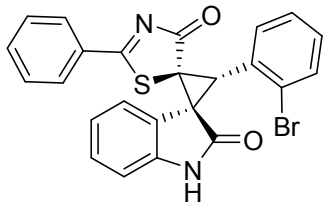
(2'S,3R,3'R)-3'-(2-fluorophenyl)-2''-phenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3l**). Faint yellow solid (26 mg), yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (s, 1H), 6.95 (d, J = 7.7 Hz, 1H), 7.05 (t, J = 8.7 Hz, 1H), 7.18 (t, J = 7.6 Hz, 2H), 7.32-7.38 (m, 3H), 7.53 (t, J = 7.6 Hz, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.87 (s, 1H), 8.11 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.87, 45.52, 55.92, 109.95, 110.02, 115.53, 115.68, 118.76, 118.85, 122.56, 122.90, 124.10, 124.42, 125.80, 128.58, 128.72, 128.95, 129.19, 130.22, 130.27, 131.38, 132.38, 135.01, 135.26, 140.97, 160.63, 162.28, 172.21, 187.41, 195.60. HRMS (ESI+) m/z calculated for $C_{24}H_{16}FN_2O_2S$ (M+H): 415.0917, found 415.0915. HPLC (Chiralpak OD, 0.46 cm I.D. ×25 cm L ×5 um, 25^{o}C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 12.27 min, t_{minor} = 23.76 min, *ee* = 82%; $[\alpha]^{25}{}_D$ = -49.7 (c = 0.18 in DCM).



3m

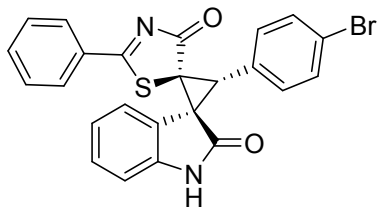
(2'S,3R,3'S)-3'-(2-chlorophenyl)-2''-phenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3m**). Faint yellow solid (30 mg), yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (s, 1H), 6.95 (d, J = 7.8 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.31-7.35 (m, 3H), 7.39 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.84 (br, 1H), 8.11 (d, J = 7.6 Hz, 2H), 8.17 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.79, 46.28, 56.41, 109.82, 122.80, 124.39, 125.64, 126.46, 128.44, 128.59, 128.77, 129.02, 129.07, 129.48, 129.57, 131.03, 132.22, 135.15, 135.34, 140.88, 172.14, 187.18, 195.48.

HRMS (ESI+) m/z calculated for $C_{24}H_{16}ClN_2O_2S$ (M+H): 431.0621, found 431.0614. HPLC (Chiralpak OZ, 0.46 cm I.D. ×25 cm L ×5 um, 25°C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 9.31 min, t_{minor} = 18.37 min, *ee* = 79%; $[\alpha]^{25}{}_{D}$ = -70.4 (c = 0.25 in DCM).



3n

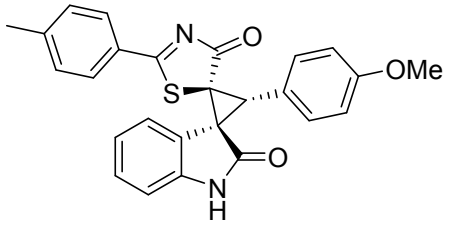
(2'S,3R,3'S)-3'-(2-bromophenyl)-2''-phenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3n**). Faint yellow solid (32 mg), yield 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (s, 1H), 6.90 (d, J = 7.7 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 7.30-7.35 (m, 2H), 7.44 (d, J = 7.5 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.58 (d, J = 7.9 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 8.11 (d, J = 7.7 Hz, 1H), 8.14 (d, J = 7.6 Hz, 2H), 8.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.91, 46.53, 56.78, 77.23, 109.83, 122.79, 124.45, 125.50, 125.69, 126.96, 128.58, 128.76, 129.07, 129.74, 131.21, 131.35, 132.23, 132.83, 135.14, 140.92, 172.13, 187.12, 195.47. HRMS (ESI+) m/z calculated for $C_{24}H_{16}BrN_2O_2S$ (M+H): 475.0116, found 475.0107. HPLC (Chiralpak OD, 0.46 cm I.D. ×25 cm L ×5 um, 25°C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 12.46 min, t_{minor} = 38.62 min, *ee* = 74%; $[\alpha]^{25}{}_{D}$ = -49.8 (c = 0.15 in DCM).



3o

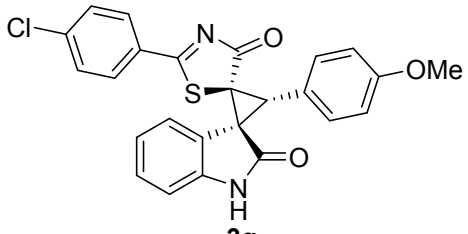
(2'S,3R,3'R)-3'-(4-bromophenyl)-2''-phenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**3o**). Faint yellow solid (33 mg), yield 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (s, 1H), 6.95 (d, J = 7.8 Hz, 1H), 7.16-7.20 (m, 3H), 7.35 (t, J = 7.7 Hz, 1H), 7.47-7.55 (m, 4H), 7.67 (t, J = 7.6 Hz, 1H), 8.05 (s, 1H),

8.09 (d, J = 7.7 Hz, 1H), 8.15 (d, J = 7.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.40, 45.72, 56.46, 109.86, 122.40, 122.88, 124.31, 125.70, 128.61, 128.95, 129.11, 130.30, 131.14, 131.56, 132.15, 135.26, 140.56, 171.55, 187.18, 195.36. HRMS (ESI+) m/z calculated for $C_{24}H_{16}BrN_2O_2S$ (M+H): 475.0116, found 475.0106. HPLC (Chiralpak OD, 0.46 cm I.D. ×25 cm L ×5 um, 25°C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 11.27 min, t_{minor} = 21.89 min, *ee* = 90%; $[\alpha]^{25}{}_D$ = -62.3 (c = 0.13 in DCM).



3p

(2'S,3R,3'R)-3'-(4-methoxyphenyl)-2''-(p-tolyl)-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione **(3p).** Faint yellow solid (38 mg), yield 86%. ^{1}H NMR (600MHz， CD_3OD) *δ*: 2.44 (s, 3H), 3.77 (s, 3H), 4.19 (s, 1H), 6.85-6.88 (m, 2H), 6.99 (d, *J* = 7.83, 1H), 7.07-7.11 (m, 1H), 7.13-7.16 (m, 2H), 7.29-7.33 (m, 1H), 7.36-7.40 (m, 2H), 7.98 (d, *J* = 7.36 Hz, 1H), 8.00-8.02 (m, 2H). ^{13}C NMR (150 MHz, CD_3OD) *δ*: 20.47, 42.75, 54.32, 56.55, 109.68, 113.35, 121.69, 123.33, 124.62, 124.91, 128.10, 128.47, 129.55, 129.66, 130.30, 141.93, 146.94, 159.49, 172.18, 187.60, 195.66. HRMS (ESI+) m/z calcd for $C_{26}H_{21}N_2O_3S$ (M + H): 441.1267; found 441.1272. HPLC (Chiralcel OZ, 0.46 mm I.D. ×250 mm L ×5 um, 25°C, *i*-propanol/hexane = 50: 50, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 9.29 min, t_{minor} = 49.32 min, *ee* = 73%; $[\alpha]^{25}{}_D$ = -42.9 (c = 0.10 in DCM).

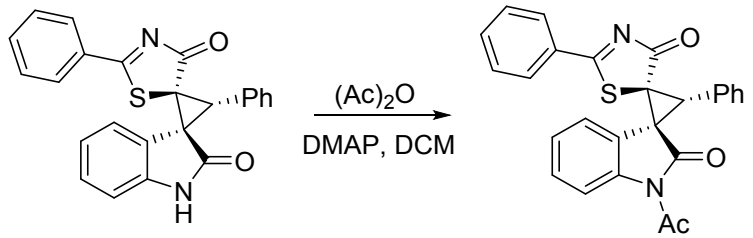


3q

(2'S,3R,3'R)-2''-(4-chlorophenyl)-3'-(4-methoxyphenyl)-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione **(3q).** Faint yellow solid (37 mg), yield 80%.

^{1}H NMR (600MHz, DMSO-d_6) δ: 3.74 (s, 3H), 4.17 (s, 1H), 6.86 (d, J = 8.46 Hz, 2H), 6.96 (d, J = 7.68 Hz, 1H), 7.06 (t, J = 7.45 Hz, 1H), 7.16 (d, J = 8.23 Hz, 2H), 7.30 (t, J = 7.68 Hz, 1H), 7.68 (d, J = 8.39 Hz, 2H), 7.87 (d, J = 7.66 Hz, 1H), 8.11 (d, J = 8.29 Hz, 2H), 10.97 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 42.61, 46.18, 55.55, 57.39, 110.29, 113.95, 121.74, 123.84, 124.78, 125.41, 129.12, 130.08, 130.31, 130.74, 131.12, 140.53, 142.77, 159.21, 171.44, 187.16, 193.82. HRMS (ESI+) m/z calcd for $C_{25}H_{18}ClN_2O_3S$ (M + H): 461.0721; found 461.0724. HPLC (Chiralpak AD, 4.6 mm I.D. ×250 mm L ×5 um, 25^{o}C, *i*-propanol/hexane = 20: 80, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 59.06 min, t_{minor} = 20.58 min, *ee* = 80%; $[\alpha]^{25}{}_{D}$ = -32.7 (c = 0.10 in DCM).

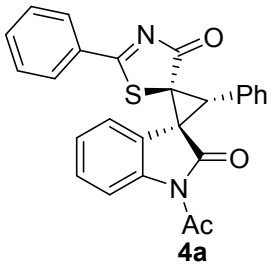
Synthetic Elaboration of Michael-Alkylation Adduct 3a



3a **4a**

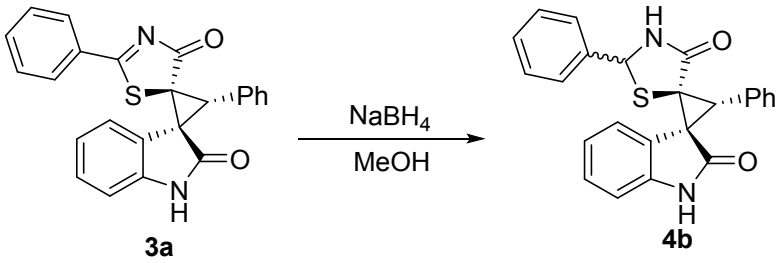
yield: 96%

To a solution of **3a** (10 mg, 0.025 mmol) in DCM (2 mL), $(Ac)_2O$ (3.8 mg, 0.038 mmol) and DMAP (1 mg) were added and the mixture was stirred at room temperature for overnight. After reaction, the solvent was evaporated and the crude product was purified using flash column chromatography (silica gel, DCM) to afford the desired product **4a**.

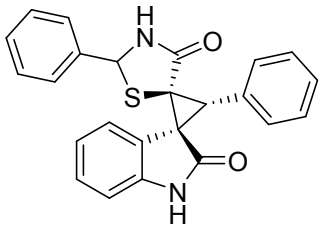


4a

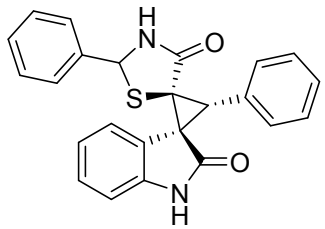
(2'S,3R,3'R)-1-acetyl-2'',3'-diphenyl-4''H-dispiro[indoline-3,1'-cyclopropane-2',5''-thiazole]-2,4''-dione (**4a**). Faint yellow solid (10.6 mg), yield 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 3H), 4.41 (s, 1H), 7.33-7.43 (m, 4H), 7.45 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 8.16 (t, J = 7.8 Hz, 2H), 8.17 (d, J = 7.4 Hz, 1H), 8.35 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.96, 43.39, 46.29, 58.06, 116.22, 123.25, 124.68, 125.29, 128.43, 128.50, 128.64, 129.17, 129.27, 130.75, 132.06, 135.37, 140.14, 170.45, 171.30, 186.22, 194.76. HRMS (ESI+) m/z calculated for $C_{26}H_{19}N_2O_3S$ (M+H): 439.1116, found 439.1113. HPLC (Chiralcel OZ, 0.46 mm I.D. ×250 mm L ×5 um, 25^{o}C, *i*-propanol/hexane = 30: 70, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 13.02 min, t_{minor} = 4.31 min, *ee* = 92%; $[\alpha]^{25}{}_D$ = -147 (c = 0.2 in DCM).



A solution of compound **3a** (0.10 mmol) in MeOH (2.0 mL) was stirred at 0°C for 10 min, followed by the addition of $NaBH_4$ (0.20 mmol, 2.0 eq) in portions. Then the mixture was stirred at room temperature for 2 h. The reaction was quenched by the addition of H_2O (2.0 mL) and the extracted with EtOAc (3 mL × 3). The organic phases were collected and then dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (silica gel, PE: EA = 4: 1) to afford compound **4b-1** (major) and **4b-2** (minor) (32 mg, yield 80%, *dr* = 1.8:1) as a white solid.

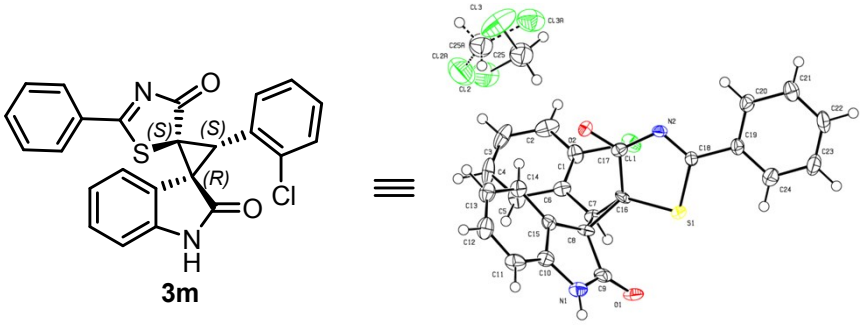


(2'S,3R,3'R)-2'',3'-diphenyldispiro[indoline-3,1'-cyclopropane-2',5''-thiazolidine]-2,4''-dione **(4b-1).** ^{1}H NMR (600MHz, DMSO-d_6) δ: 4.01 (s, 1H), 5.85 (s, 1H), 6.94 (d, J = 7.39 Hz, 1H), 6.97-7.01 (m, 1H), 7.02 (d, J = 7.39 Hz, 2H), 7.15-7.20 (m, 4H), 7.20-7.30 (m, 5H), 7.74 (d, J =7.73 Hz, 1H), 9.38 (s, 1H), 10.52 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 37.32, 43.11, 51.77, 55.68, 109.48, 121.08, 124.94, 125.97, 126.24, 127.47, 127.94, 128.30, 128.57, 128.95, 129.91, 142.47, 142.81, 170.73, 170.89. HRMS (ESI positive) m/z calcd for $C_{24}H_{29}N_2O_3S$ (M + H): 399.1162; found 399.1159. HPLC (Chiralcel OZ, 0.46 mm I.D. ×250 mm L ×5 um, 25^{o}C, *i*-propanol/hexane = 15: 85, flow rate 0.4 mL/min, λ = 254 nm): t_{major} = 32.82 min, t_{minor} = 27.27 min, *ee* = 84%; $[\alpha]^{25}{}_D$ = -34.5 (c = 0.15 in DCM).



(2'S,3R,3'R)-2'',3'-diphenyldispiro[indoline-3,1'-cyclopropane-2',5''-thiazolidine]-2,4''-dione **(4b-2).** ^{1}H NMR (600MHz, DMSO-d_6) δ: 4.01 (s, 1H), 5.77 (s, 1H), 6.93 (d, J = 7.84 Hz, 1H), 6.96 (t, J = 7.70 Hz, 1H), 7.09-7.11 (m, 2H), 7.20-7.25 (m, 4H), 7.37-7.40 (m, 1H), 7.44 (t, J = 7.45 Hz, 2H), 7.49-7.52 (m, 1H), 7.67 (d, J = 7.45 Hz, 1H), 9.43 (s, 1H), 10.68 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 37.99, 42.81, 53.76, 56.30, 109.60, 121.11, 125.30, 126.51, 127.14, 127.41, 127.86, 128.25, 129.16, 129.27, 129.91, 132.20, 141.17, 142.75, 170.70, 171.25. HRMS (ESI positive) m/z calcd for $C_{24}H_{29}N_2O_3S$ (M + H): 399.1162; found 399.1162. HPLC (Chiralpak OZ, 0.46 cm I.D. ×25 cm L ×5 um, 25^{o}C, *i*-propanol/hexane = 10: 90, flow rate 0.6 mL/min, λ = 254 nm): t_{major} = 16.57 min, t_{minor} = 33.62 min, *ee* = 79%; $[\alpha]^{25}{}_{D}$ = -78.2 (c = 0.15 in DCM).

X-ray structure of compound 3m



3m

ORTEP drawing of compound **3m**. Ellipsoids are shown at the 50% probability level.

Bond precision: C-C = 0.0098 A Wavelength=1.54184

Cell: a=13.0109(8) b=11.5329(5) c=16.1284(9)
alpha=90 beta=109.629(6) gamma=90

Temperature: 150 K

	Calculated	Reported
Volume	2279.5(2)	2279.5(2)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C24 H15 Cl N2 O2 S, C H2 Cl2	?
Sum formula	C25 H17 Cl3 N2 O2 S	C25 H17 Cl3 N2 O2 S
Mr	515.82	515.81
Dx,g cm-3	1.503	1.503
Z	4	4
Mu (mm-1)	4.721	4.721
F000	1056.0	1056.0
F000'	1064.09	
h,k,lmax	15,13,19	15,13,19
Nref	3987	3976
Tmin,Tmax	0.492,0.470	
Tmin'	0.372	

Correction method= Not given

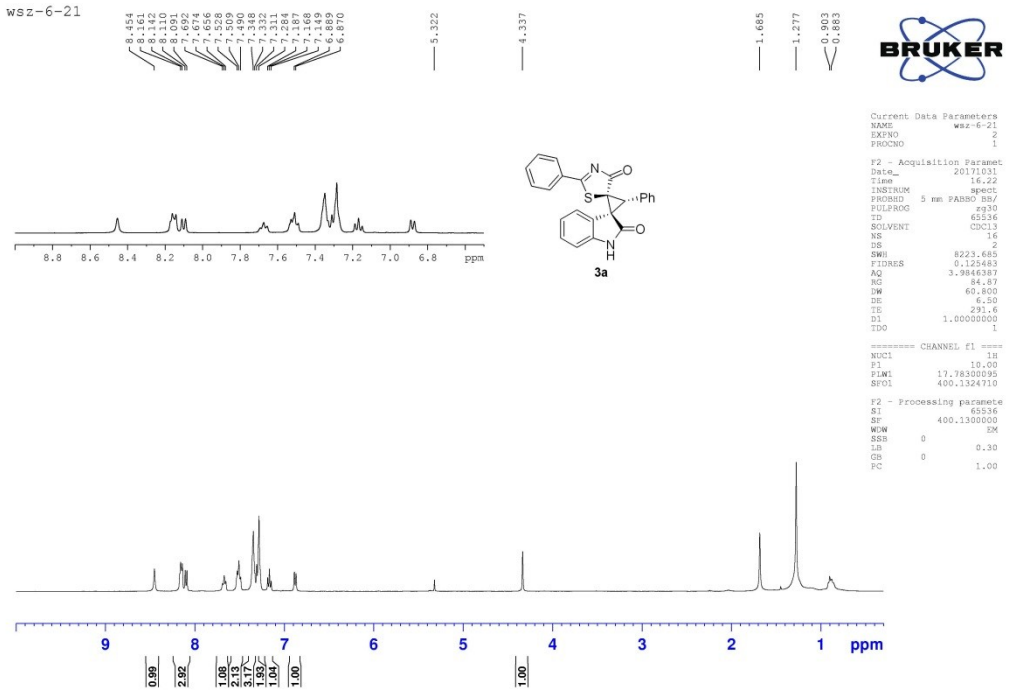
Data completeness= 0.997 Theta(max)= 65.999

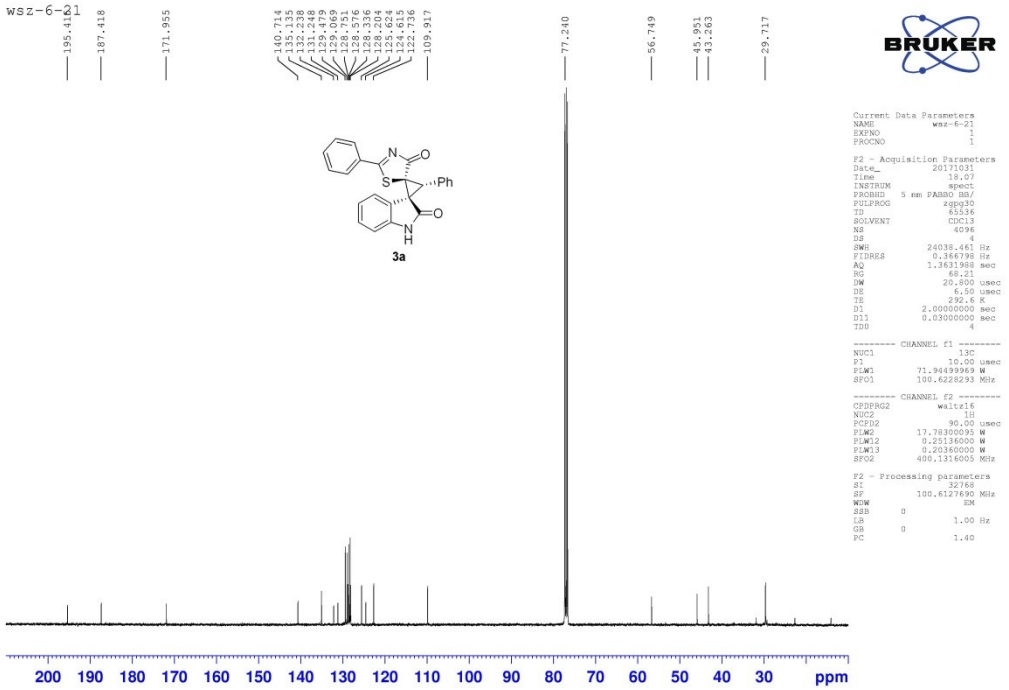
R(reflections)= 0.1264(3460) wR2(reflections)= 0.3380(3976)

S = 1.073 Npar= 320

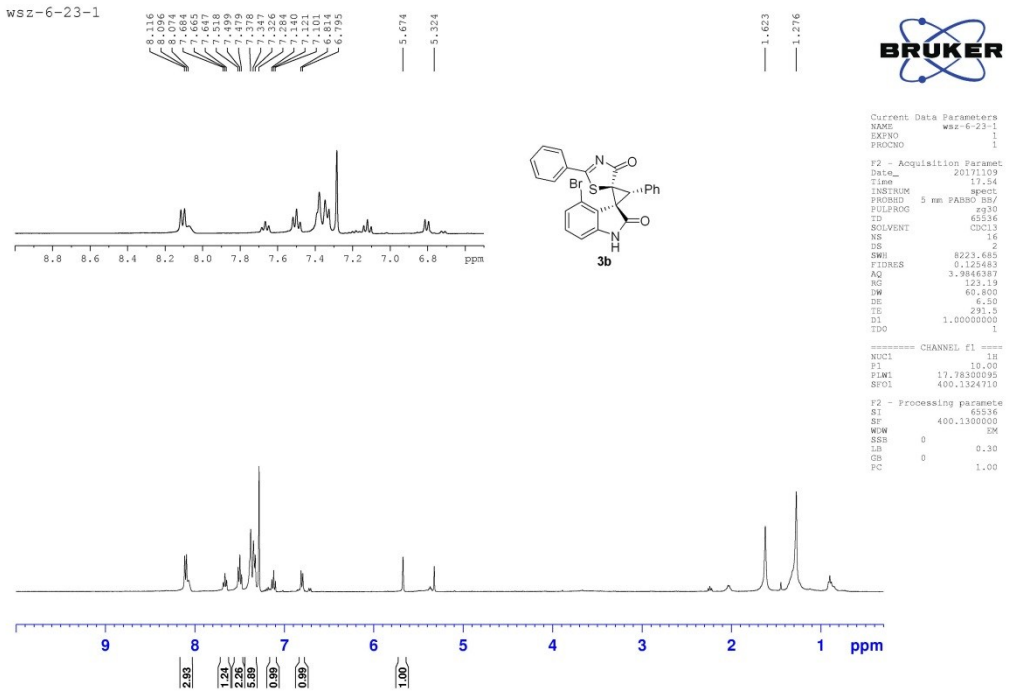
NMR Spectra and HPLC Profile

Compound 3a





Compound 3b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7.101
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5.324
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BRUKER
Current Data Parameters
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Date_ 20171109
Time 17.54
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DS 2
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AQ 3.9846387
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DE 6.50
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D1 1.00000000
TDO 1
======== CHANNEL f1 ====
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P1 10.00
PLW1 17.78300095
SFO1 400.1324710
F2 - Processing paramete
SI 65536
SF 400.1300000
WDW EM
SSB 0
LB 0.30
GB 0
PC 1.00
Br
S
N
O
Ph
N
H
3b
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm
9 8 7 6 5 4 3 2 1 ppm
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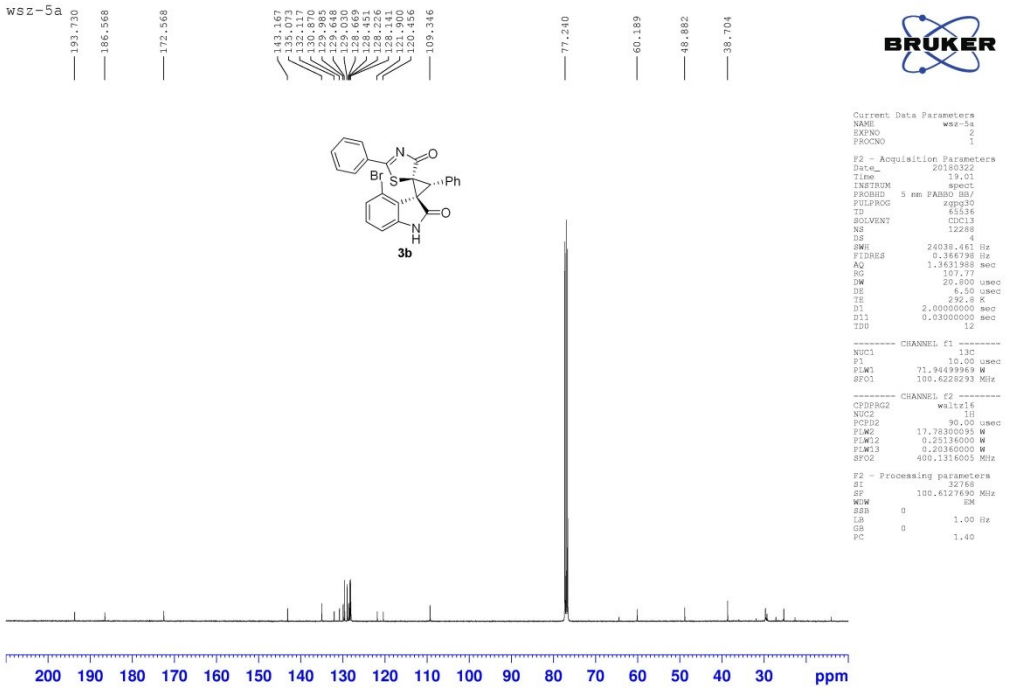
1.24
2.26
5.89
0.99
0.99
1.00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======== CHANNEL f2 ========
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NUC2 1H
PCPD2 90.00 usec
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PLW12 0.25136000 W
PLW13 0.20360000 W
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3b
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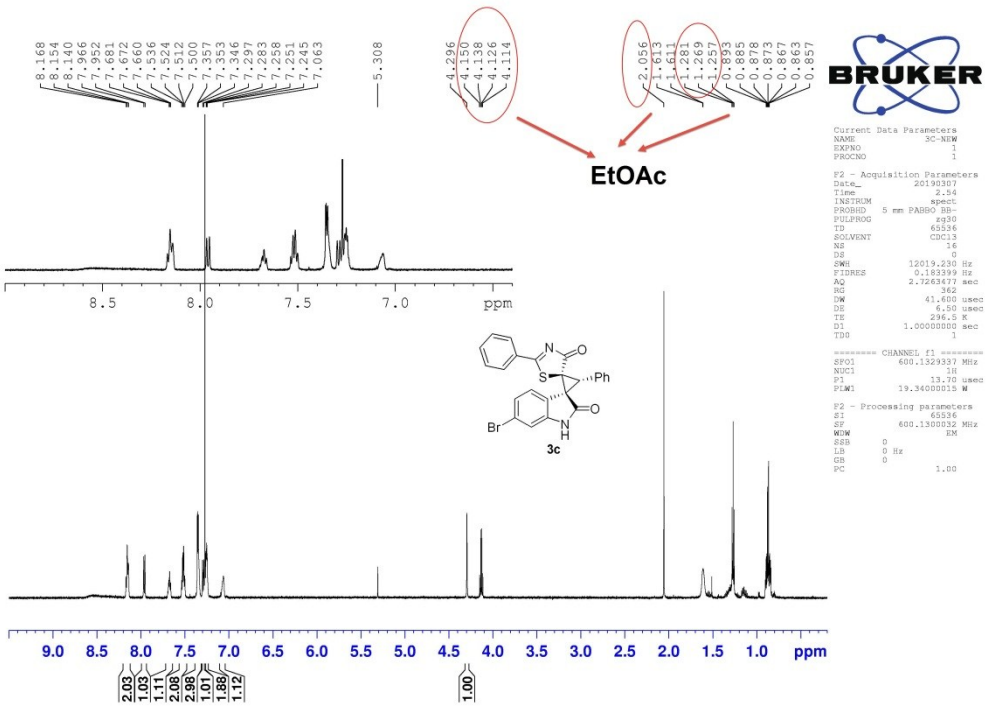
Compound 3c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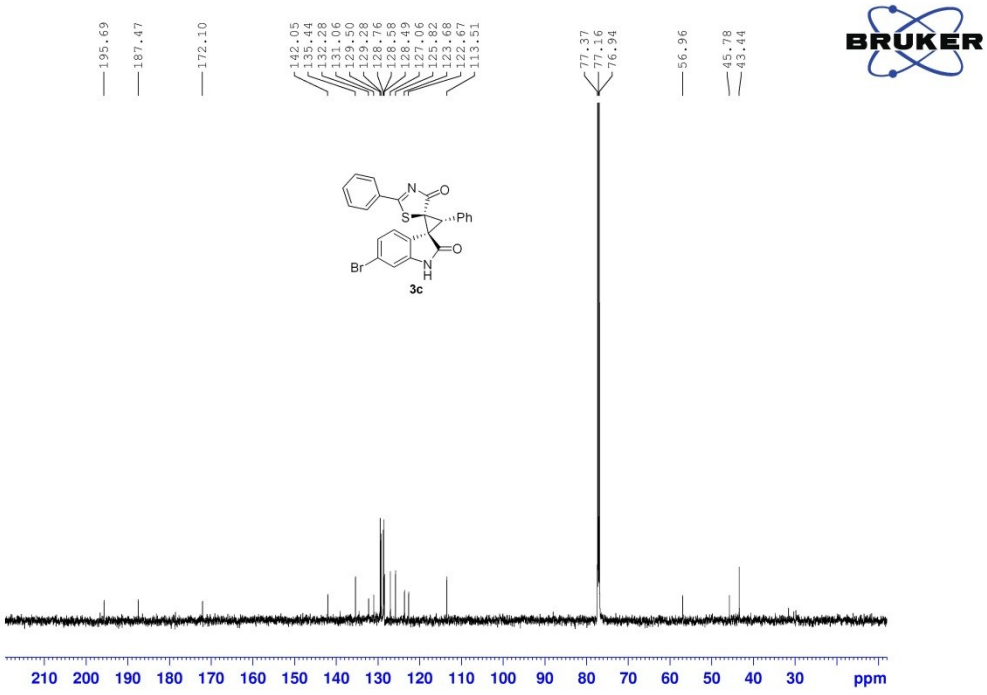
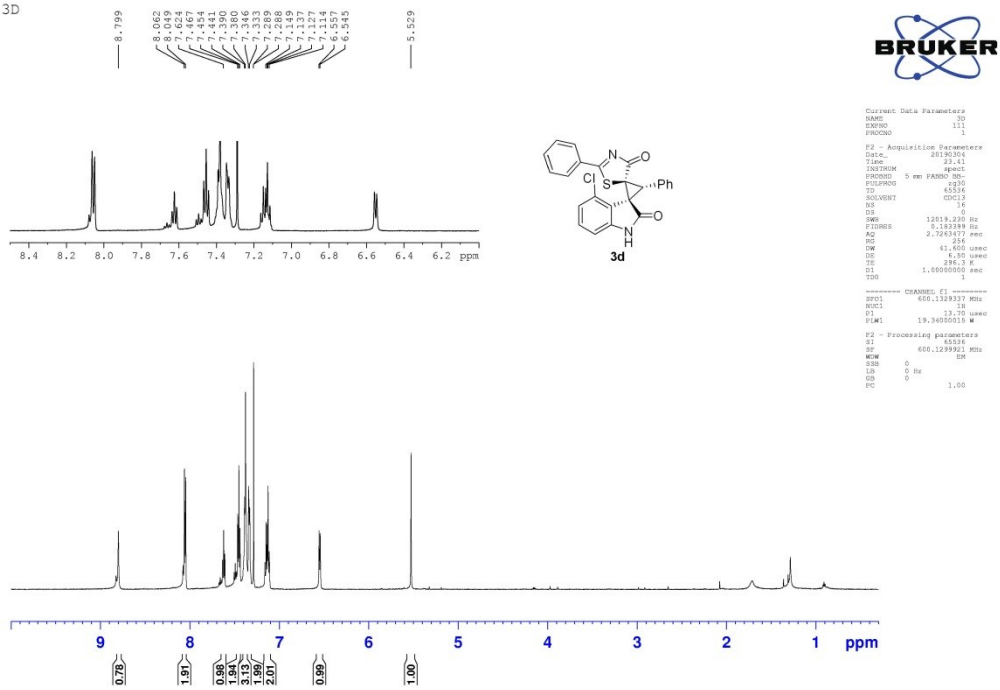
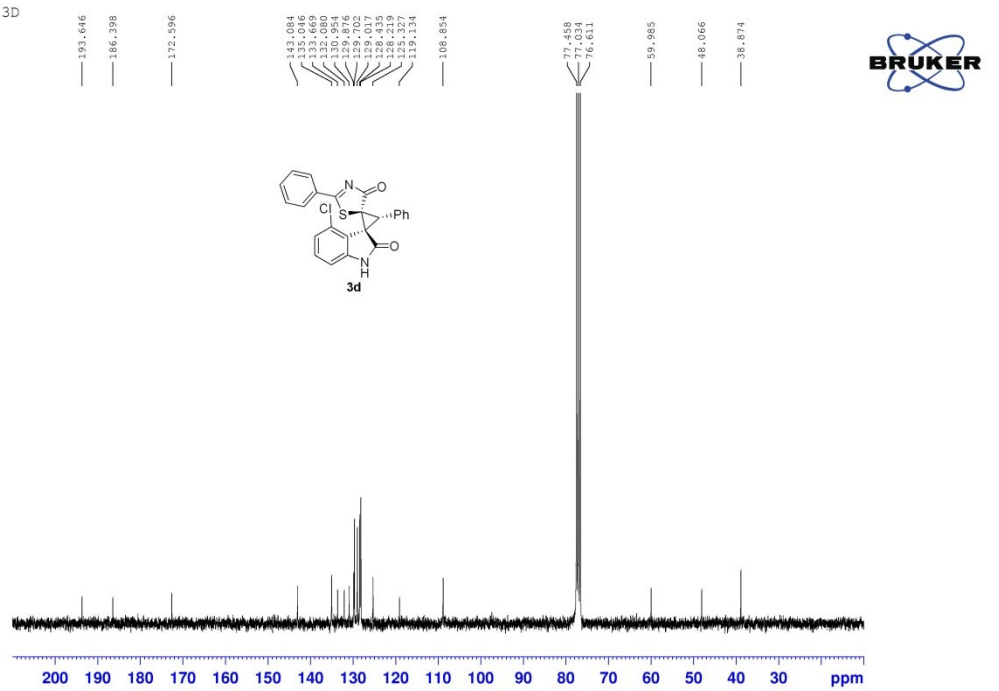
Br
3c
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.03 1.03 1.11 2.09 2.98 1.01 1.88 1.12
1.00

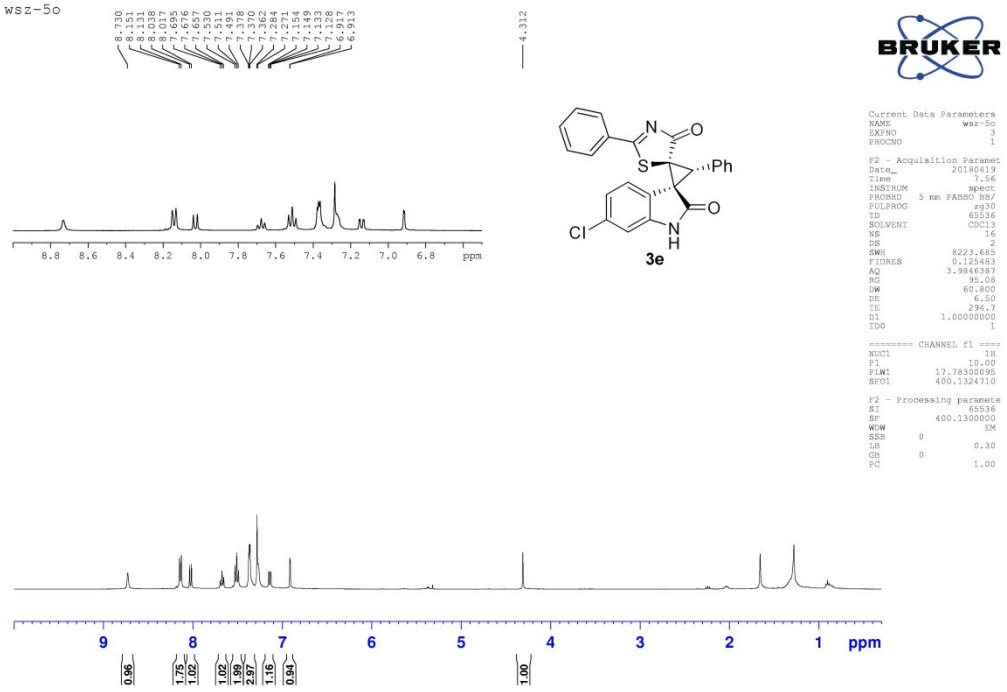

195.69
187.47
172.10
142.05
135.44
132.28
131.06
129.50
129.28
128.76
128.58
128.49
127.06
125.82
123.68
122.67
113.51
77.37
77.16
76.94
56.96
45.78
43.44
BRUKER
Ph
Br
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

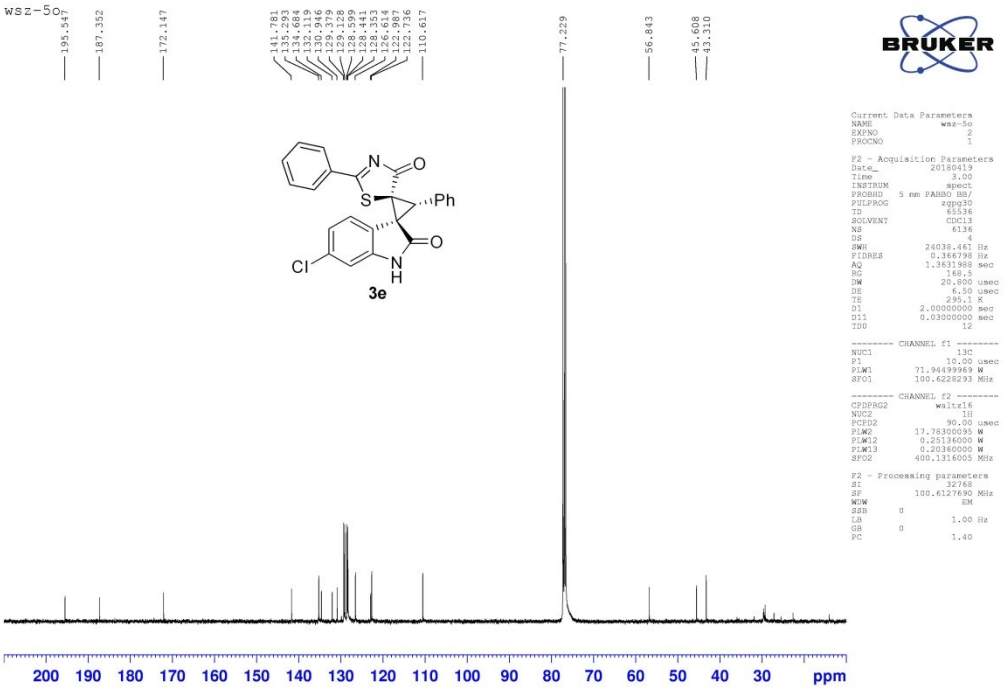
Compound 3d


3D
8.799
8.062
8.059
8.054
7.467
7.454
7.441
7.380
7.380
7.346
7.333
7.289
7.288
7.149
7.137
7.127
7.114
7.057
6.545
5.529
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 ppm
3d
BRUKER
Current Data Parameters
NAME 3D
EXPNO 111
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190304
Time 23.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 406
DW 41.600 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 600.1329937 MHz
NUC1 1H
P1 13.70 usec
PLW1 19.34000015 W
F2 - Processing parameters
SI 65536
SF 600.1299921 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
9 8 7 6 5 4 3 2 1 ppm
0.78 1.91 0.98 1.94 3.13 1.99 2.01 0.99 1.00

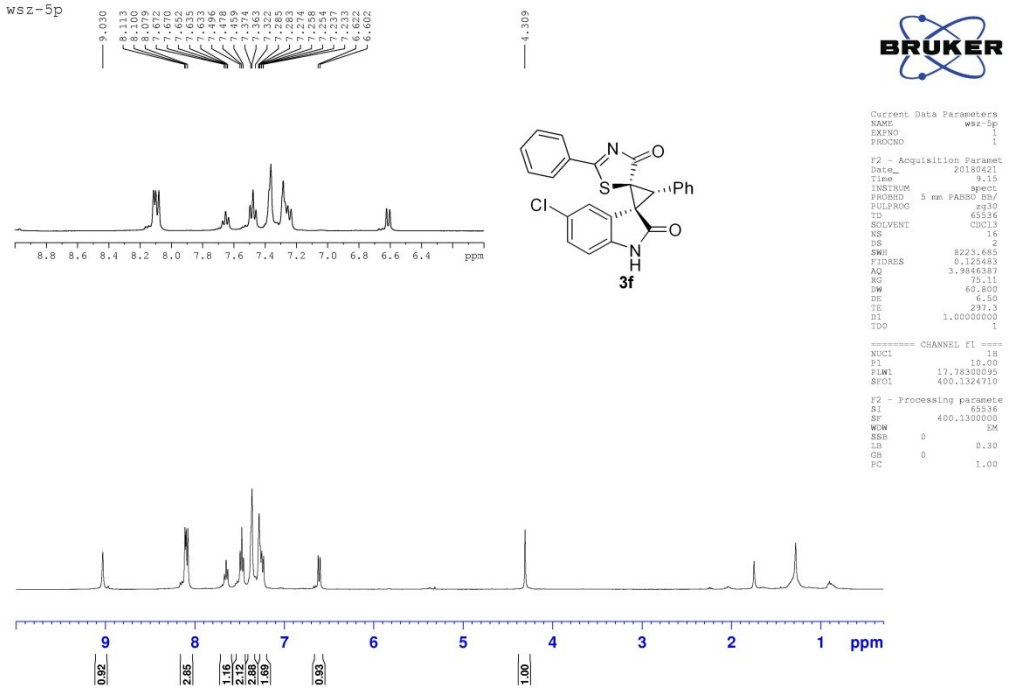

3D
193.646
186.398
172.596
143.084
135.046
133.669
132.080
130.854
129.876
129.702
129.017
128.435
128.219
125.327
119.134
108.854
77.458
77.034
76.611
59.985
48.066
38.874
3d
BRUKER
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

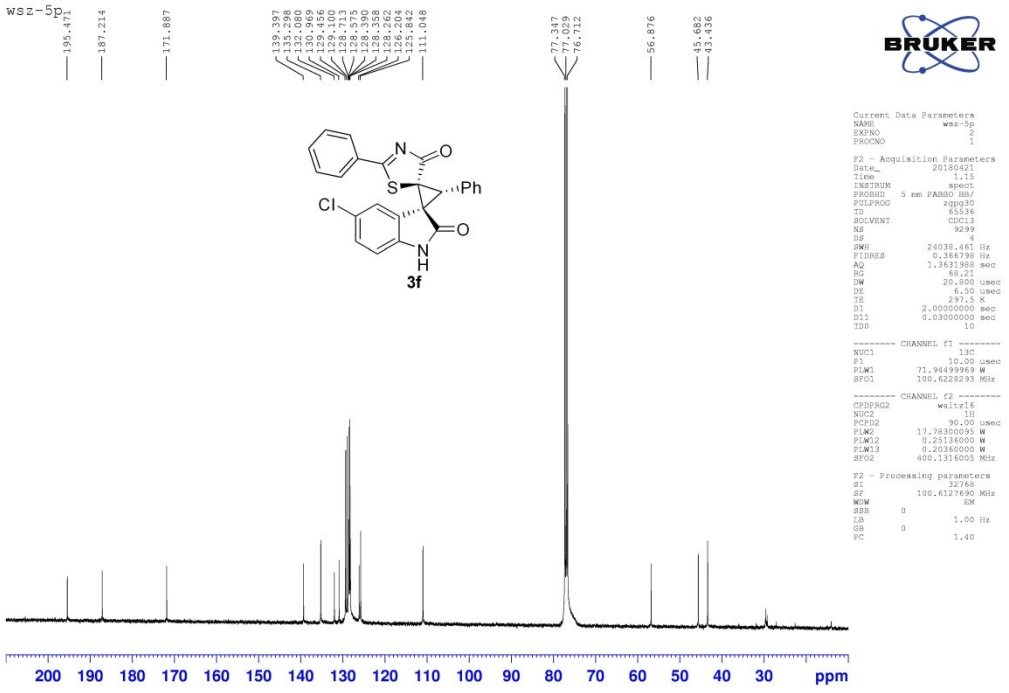
Compound 3e


wsz-5o
8.730
8.151
8.131
8.038
8.017
7.695
7.676
7.667
7.530
7.511
7.491
7.378
7.370
7.362
7.284
7.271
7.164
7.149
7.133
7.128
6.917
6.913
4.312
3e
Current Data Parameters
NAME wsz-5o
EXPNO 3
PROCNO 1
F2 - Acquisition Paramet
Date_ 20180419
Time 7.56
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685
FIDRES 0.125483
AQ 3.9846387
RG 95.08
DW 60.800
DE 6.50
TE 294.7
D1 1.00000000
TD0 1
======== CHANNEL f1 ====
NUC1 1H
P1 10.00
PLW1 17.78300095
SFO1 400.1324710
F2 - Processing paramete
SI 65536
SF 400.1300000
WDW EM
SSB 0
LB 0.30
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
0.96
1.75
1.02
1.02
1.99
2.97
1.16
0.94
1.00

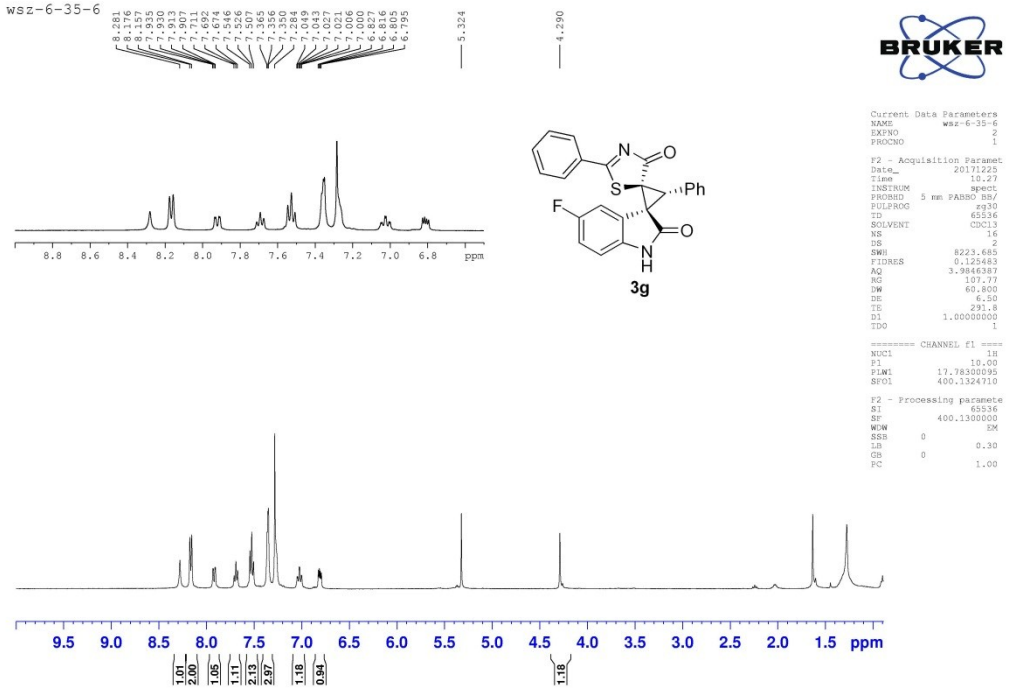

wsz-5o
195.547
187.352
172.147
141.781
135.293
134.284
132.119
130.946
129.379
129.128
128.569
128.441
128.353
126.614
122.987
122.736
110.617
77.229
56.843
45.608
43.310
3e
Current Data Parameters
NAME wsz-5o
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180419
Time 3.00
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 6136
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 168.5
DW 20.800 usec
DE 6.50 usec
TE 295.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 12
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 71.94499969 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 17.78300095 W
PLW12 0.25136000 W
PLW13 0.20360000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

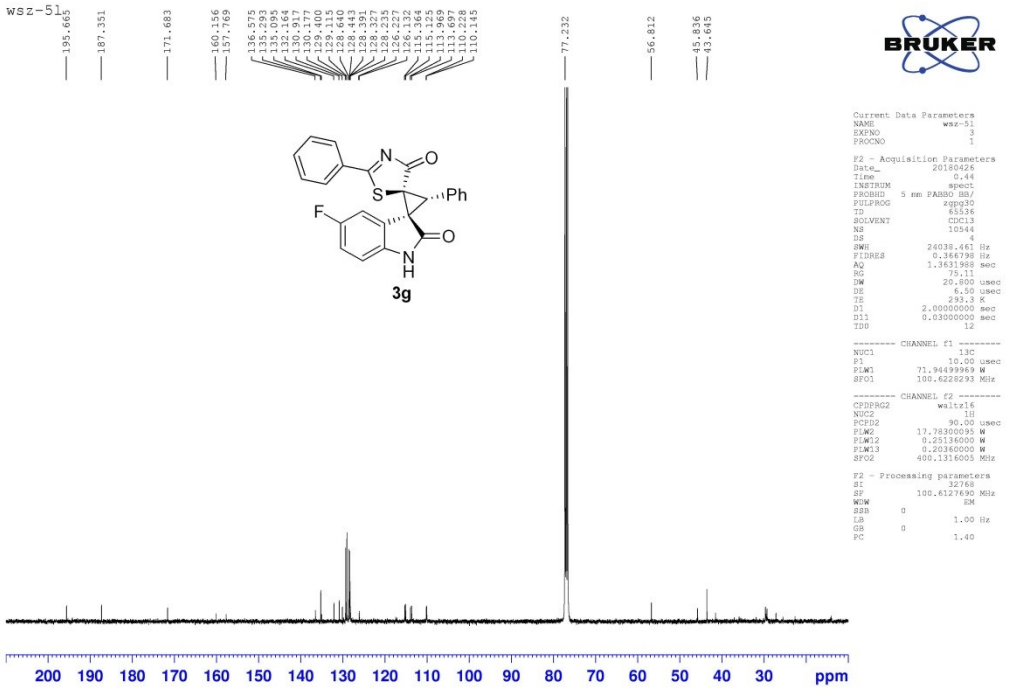
Compound 3f


wsz-5p
9.030
8.113
8.100
8.079
8.072
7.670
7.652
7.635
7.493
7.486
7.478
7.459
7.374
7.363
7.322
7.285
7.283
7.274
7.258
7.254
7.237
7.233
6.622
6.602
4.309
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 ppm
Cl
Ph
3f
BRUKER
Current Data Parameters
NAME wsz-5p
EXPNO 1
PROCNO 1
F2 - Acquisition Paramet
Date_ 20180421
Time 9.15
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685
FIDRES 0.125483
AQ 3.9846387
RG 75.11
DW 60.800
DE 6.50
TE 297.3
D1 1.00000000
TD0 1
======== CHANNEL f1 ====
NUC1 1H
P1 10.00
PLW1 17.78300095
SFO1 400.1324710
F2 - Processing paramete
SI 65536
SF 400.1300000
WDW EM
SSB 0
LB 0.30
GB 0
PC 1.00
9 8 7 6 5 4 3 2 1 ppm
0.92 2.85 1.16 2.12 2.88 1.69 0.93 1.00

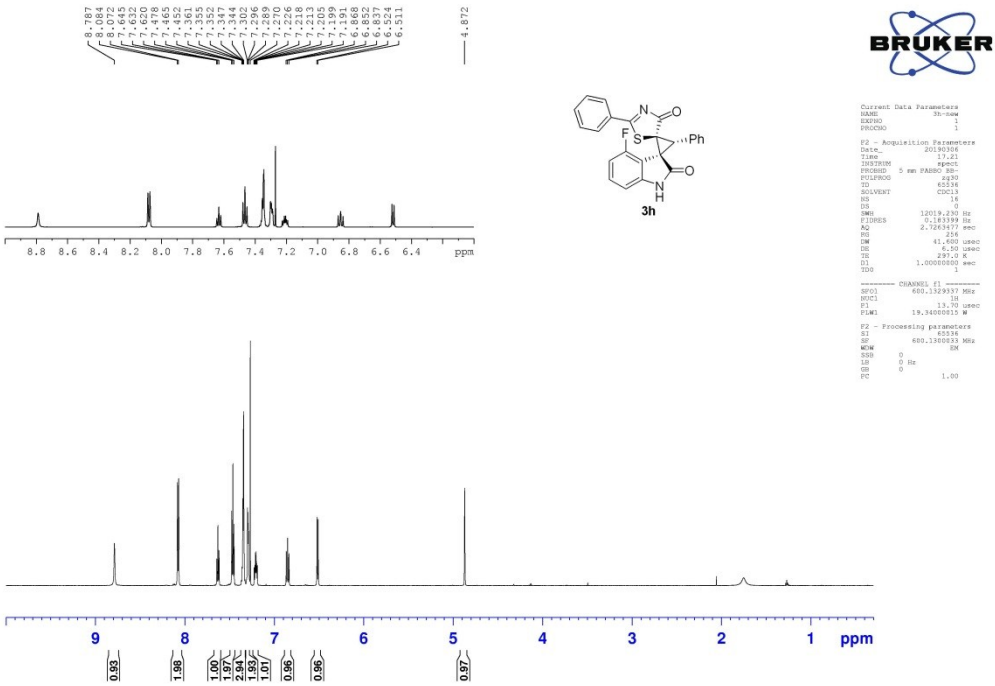

wsz-5p
195.471
187.214
171.887
139.397
135.298
132.880
130.969
129.456
129.100
128.713
128.575
128.390
128.358
128.262
126.204
125.682
111.048
77.347
77.029
76.712
56.876
45.682
43.436
Cl
Ph
3f
BRUKER
Current Data Parameters
NAME wsz-5p
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180421
Time 1.15
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 9299
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 68.21
DW 20.800 usec
DE 6.50 usec
TE 297.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 10
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 71.94499969 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 17.78300095 W
PLW12 0.25136000 W
PLW13 0.20360000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

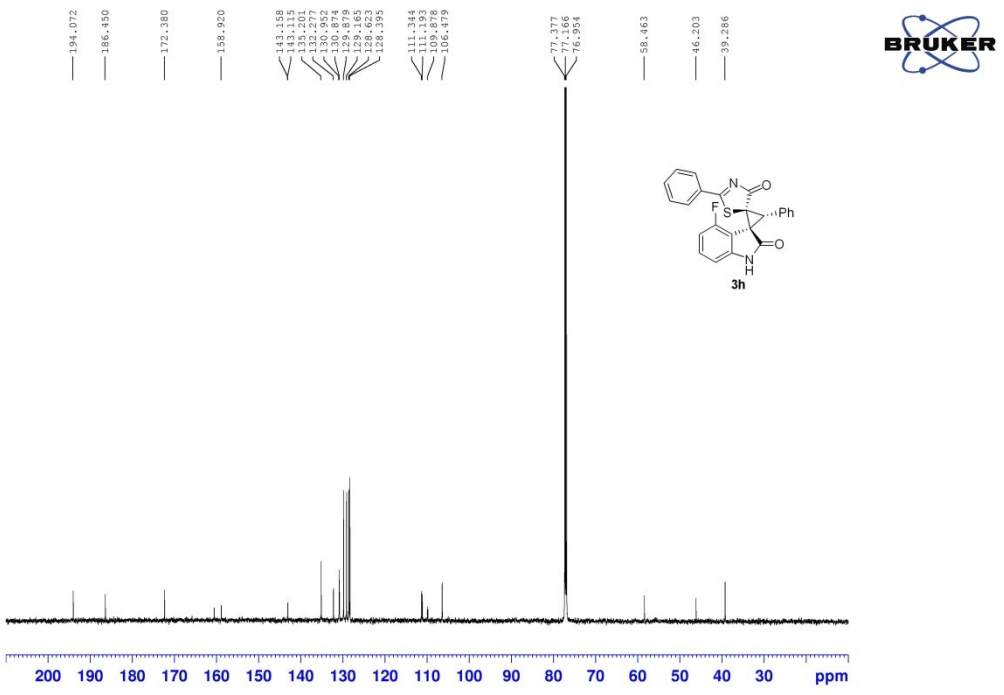
Compound 3g



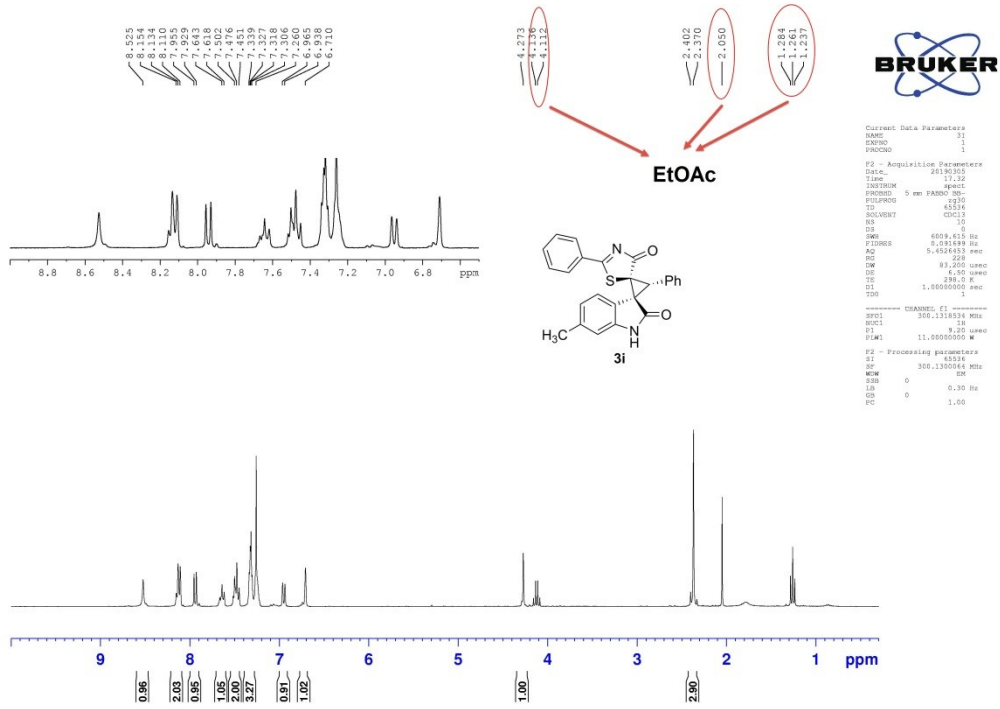


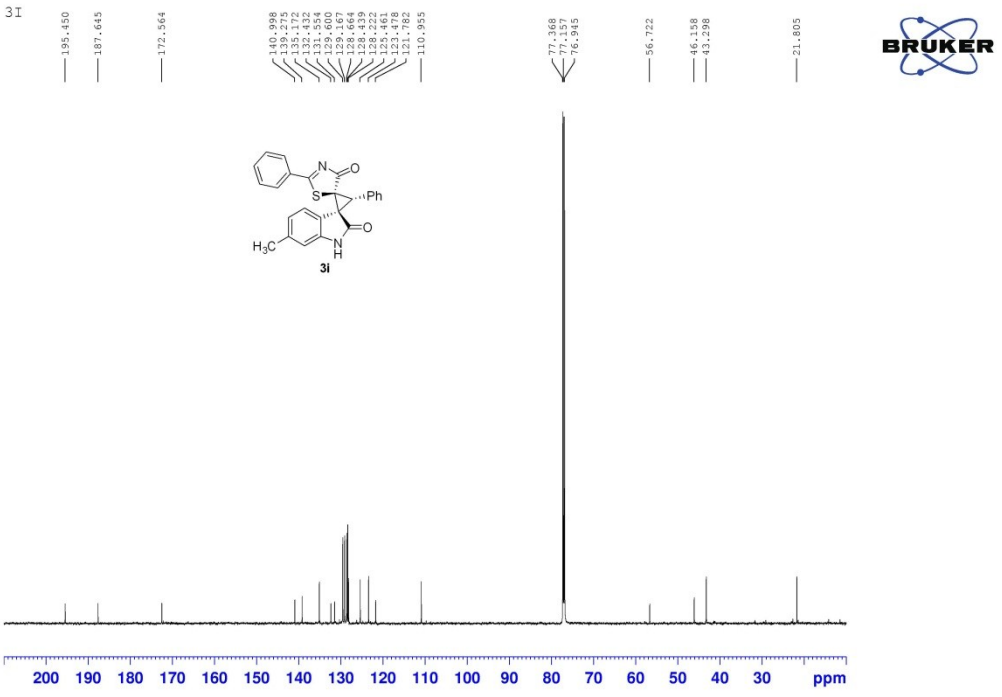
Compound 3h


8.787
8.084
8.072
7.645
7.622
7.620
7.478
7.465
7.452
7.351
7.355
7.352
7.347
7.344
7.302
7.296
7.289
7.270
7.226
7.218
7.213
7.205
7.199
7.191
6.868
6.852
6.837
6.524
6.511
4.872
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 ppm
3h
BRUKER
Current Data Parameters
NAME 3h-new
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190306
Time 17.21
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 256
DW 41.600 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
SFO1 600.1329337 MHz
NUC1 1H
P1 13.70 usec
PLW1 19.34000015 W
F2 - Processing parameters
SI 65536
SF 600.1300033 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
9 8 7 6 5 4 3 2 1 ppm
0.93 1.98 1.00 1.97 2.94 1.93 1.01 0.96 0.96 0.97

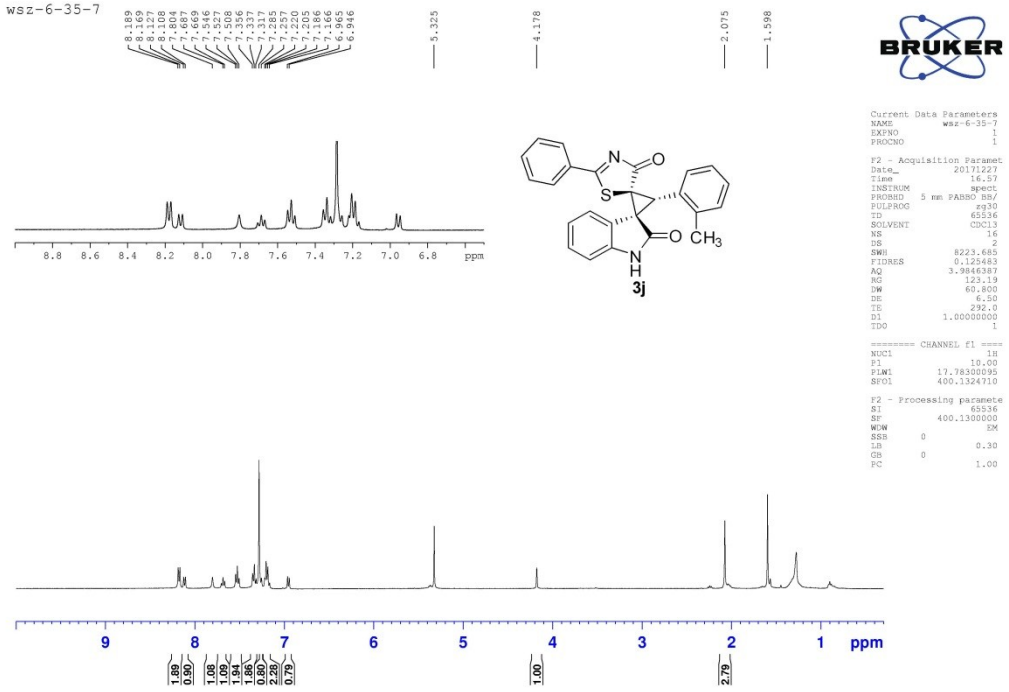

194.072
186.450
172.380
158.920
143.158
143.115
135.201
132.377
130.952
130.874
129.879
129.165
128.653
128.395
111.344
111.193
109.878
106.479
77.377
77.166
76.954
58.463
46.203
39.286
3h
BRUKER
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

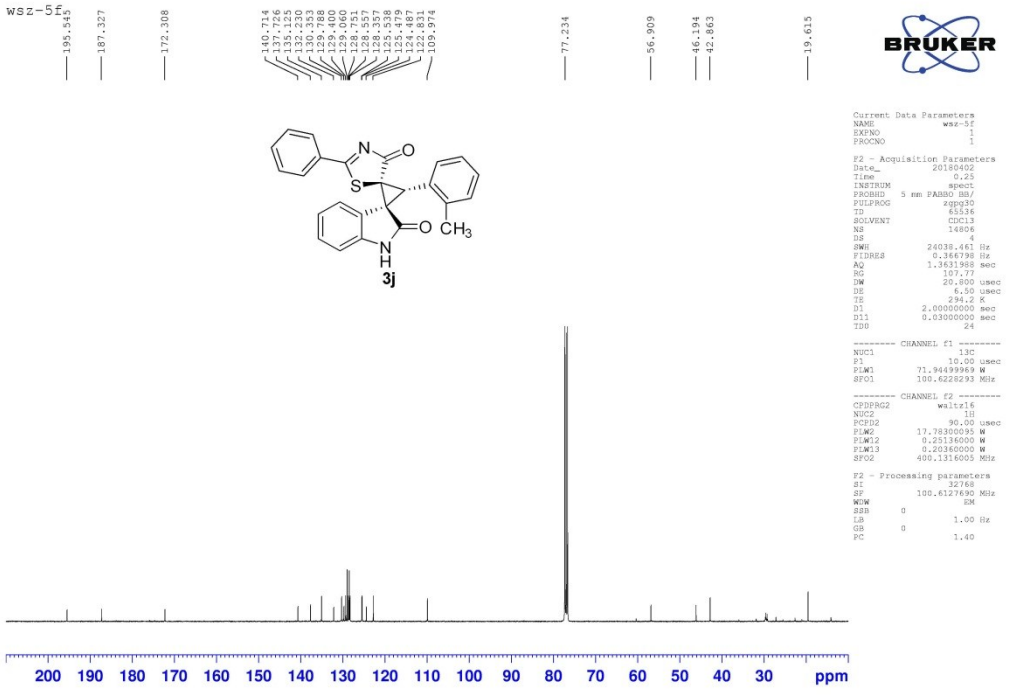
Compound 3i


8.525
8.134
8.114
8.110
7.955
7.929
7.643
7.618
7.502
7.476
7.451
7.329
7.327
7.318
7.306
7.260
6.965
6.938
6.710
4.273
4.136
4.112
2.402
2.370
2.050
1.284
1.261
1.237
EtOAc
Ph
H3C
3i
9
8
7
6
5
4
3
2
1
ppm
0.96
2.03
0.95
1.05
2.00
3.27
0.91
1.02
1.00
2.90

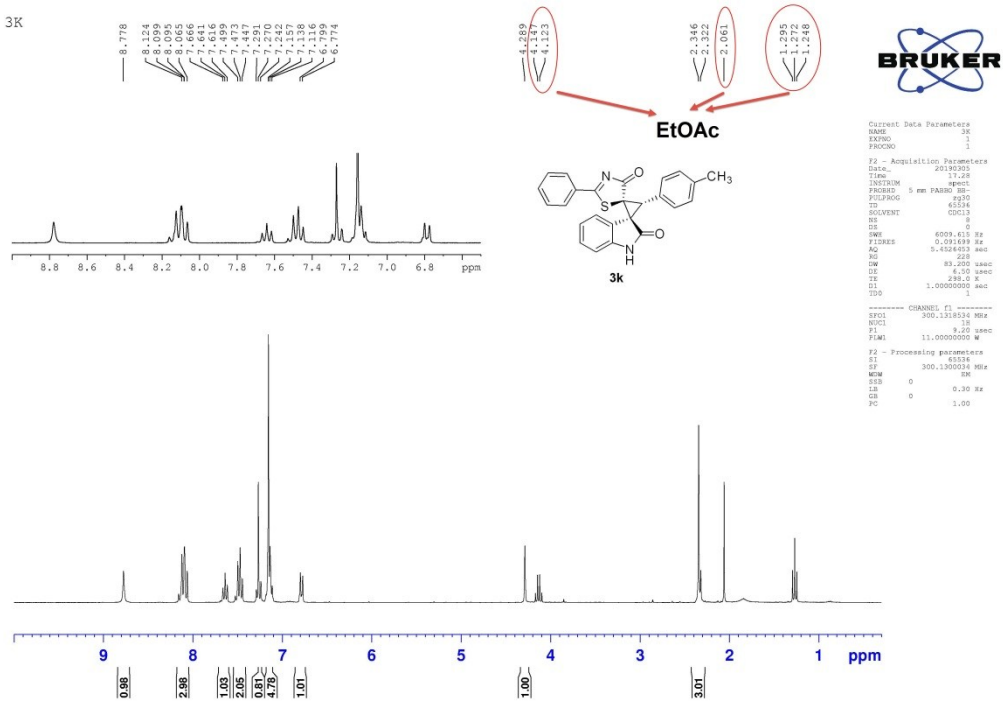

3I
195.450
187.645
172.564
140.998
139.275
135.172
132.432
131.554
129.600
129.167
129.164
128.439
128.222
125.461
124.178
121.382
110.955
77.368
77.157
76.945
56.722
46.158
43.298
21.805
Ph
H3C
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

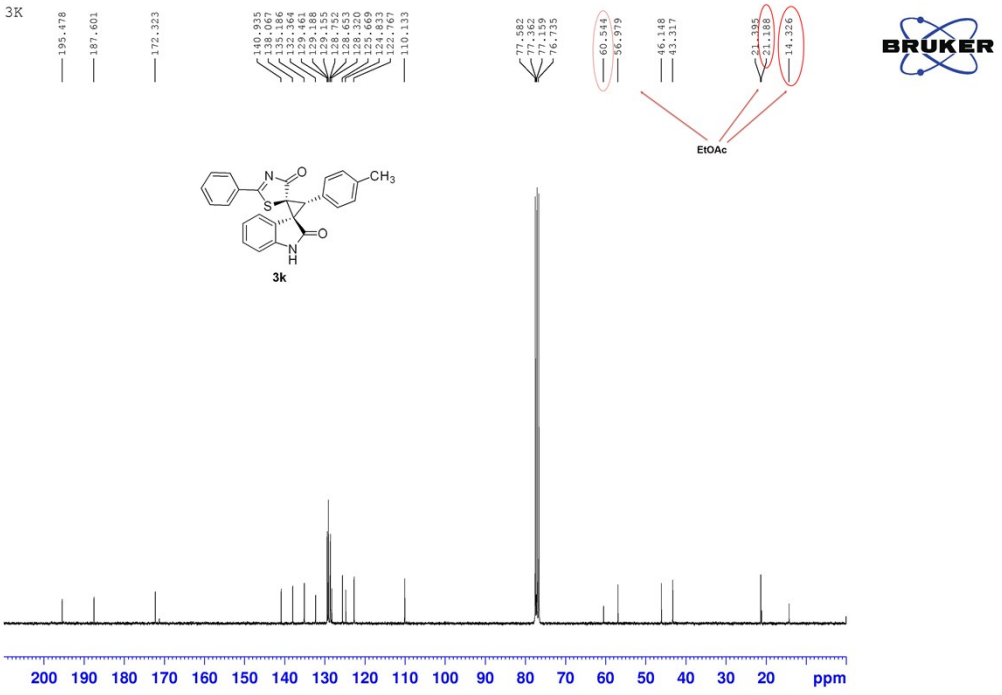
Compound 3j


wsz-6-35-7
8.189
8.169
8.127
8.108
7.804
7.667
7.669
7.546
7.527
7.388
7.356
7.337
7.317
7.285
7.257
7.220
7.205
7.186
7.166
7.065
6.946
5.325
4.178
2.075
1.598
BRUKER
Current Data Parameters
NAME wsz-6-35-7
EXPNO 1
PROCNO 1
F2 - Acquisition Paramet
Date_ 20171227
Time 16.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685
FIDRES 0.125483
AQ 3.9846387
RG 123.19
DW 60.800
DE 6.50
TE 292.0
D1 1.00000000
TD0 1
======== CHANNEL f1 ====
NUC1 1H
P1 10.00
PLW1 17.78300095
SFO1 400.1324710
F2 - Processing paramete
SI 65536
SF 400.1300000
WDW EM
SSB 0
LB 0.30
GB 0
PC 1.00
O
N
S
O
O CH3
N
H
3j
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm
9 8 7 6 5 4 3 2 1 ppm
1.89
0.90
1.08
1.09
1.94
1.86
0.80
2.28
0.79
1.00
2.79

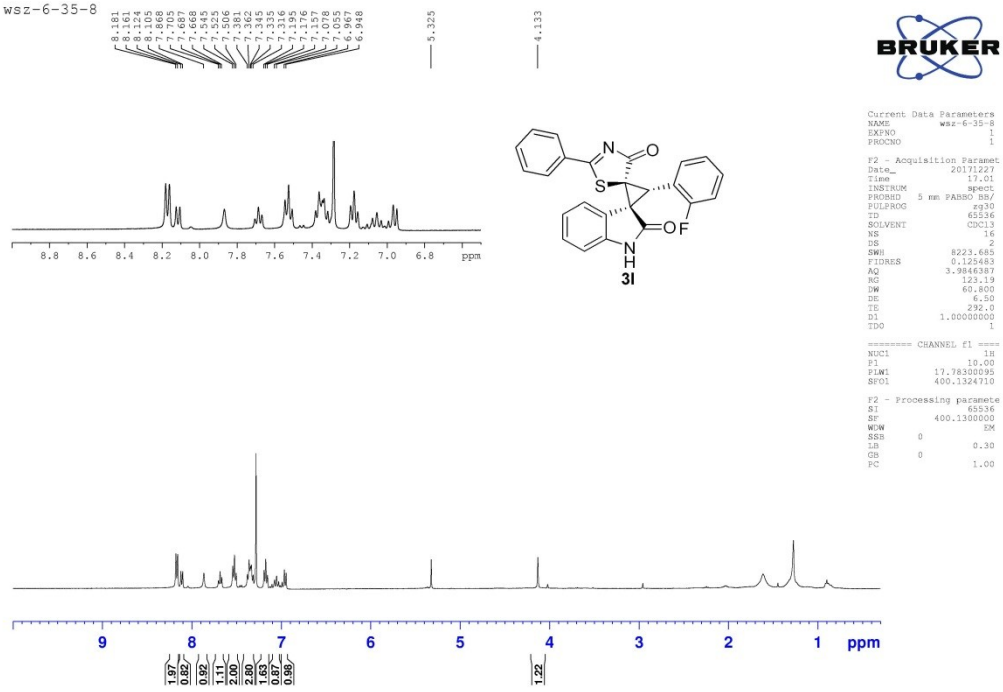

wsz-5f
195.545
187.327
172.308
140.714
137.726
135.125
132.230
130.353
129.788
129.400
129.060
128.751
128.557
128.357
125.538
125.479
124.887
122.831
109.974
77.234
56.909
46.194
42.863
19.615
BRUKER
Current Data Parameters
NAME wsz-5f
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180402
Time 0.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 14806
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 107.77
DW 20.800 usec
DE 6.50 usec
TE 294.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 24
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 71.94499969 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 17.78300095 W
PLW12 0.25136000 W
PLW13 0.20360000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
N
S
O
O CH3
N
H
3j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

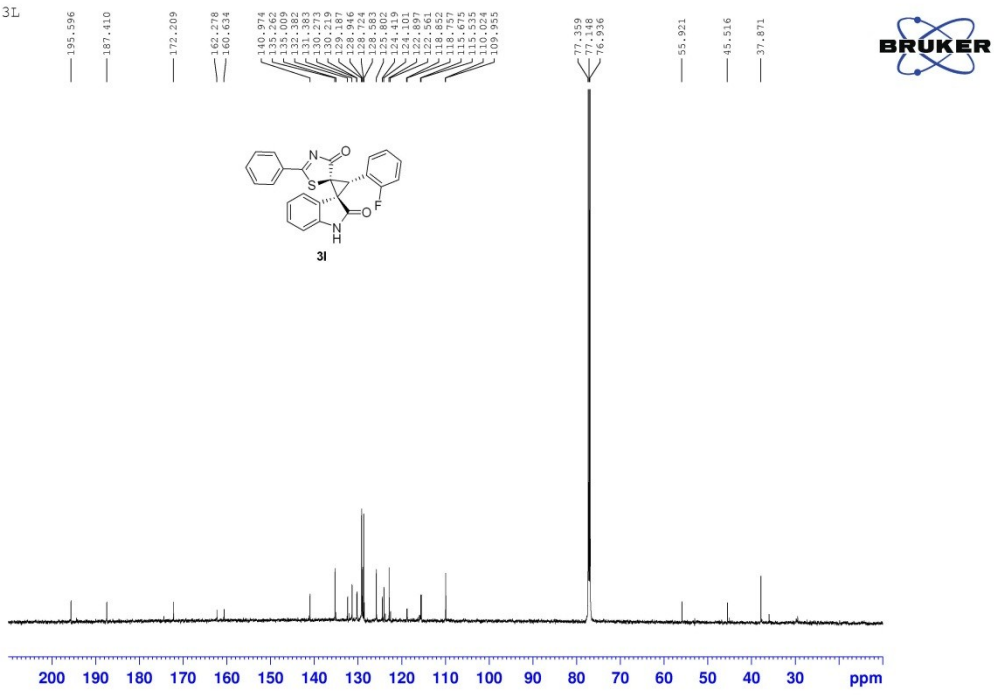
Compound 3k



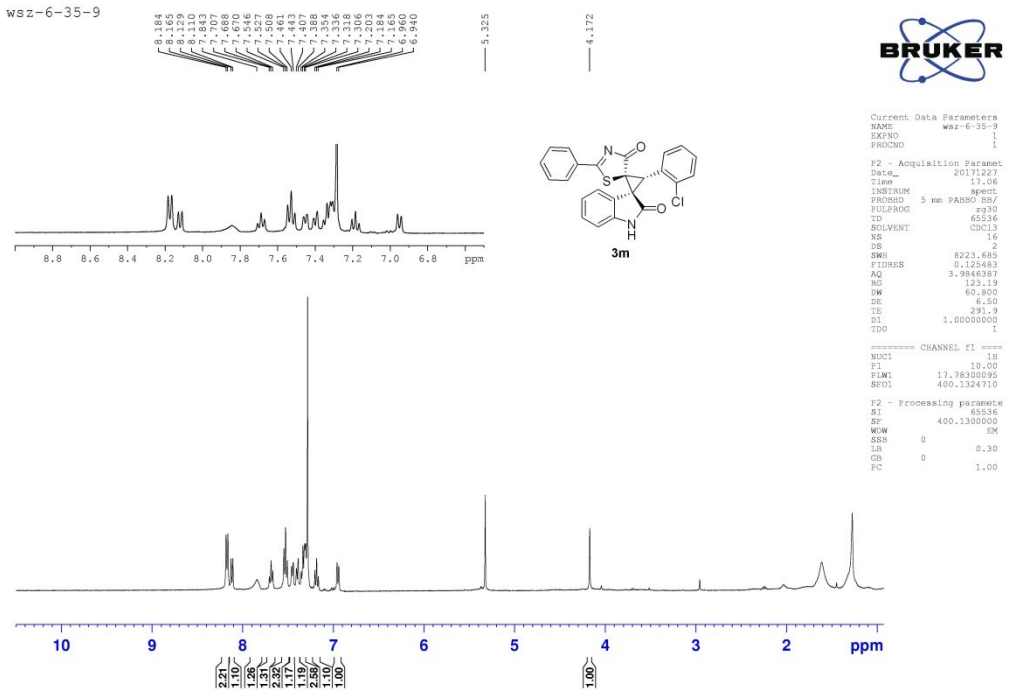


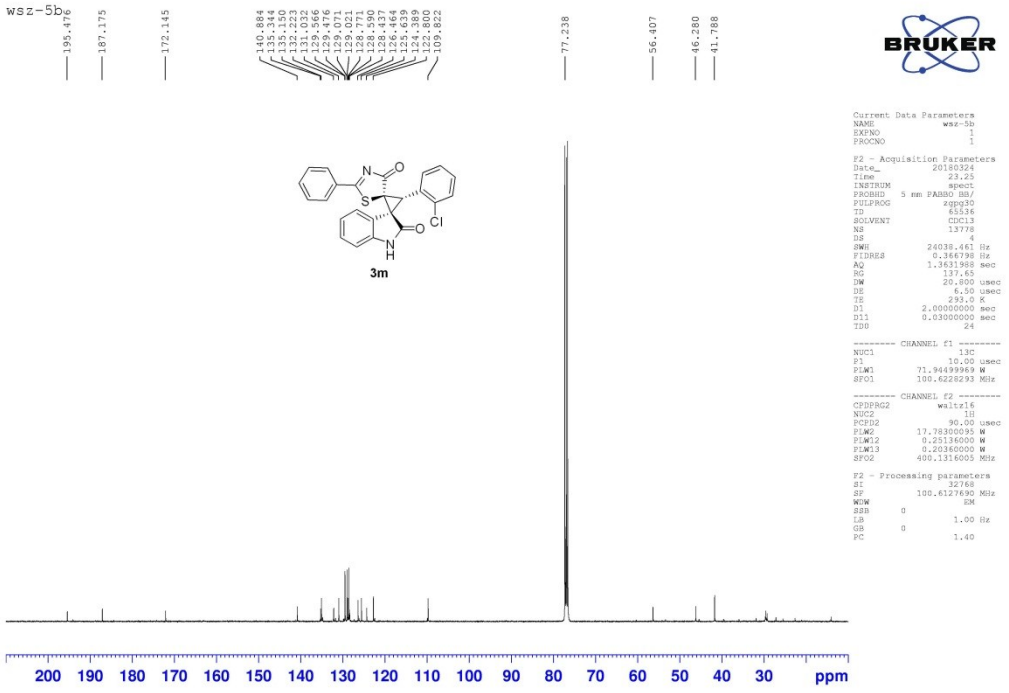
Compound 3l


wsz-6-35-8
8.181
8.151
8.124
8.105
7.868
7.765
7.687
7.668
7.545
7.525
7.506
7.381
7.362
7.345
7.335
7.316
7.195
7.176
7.157
7.078
7.055
6.967
6.948
5.325
4.133
BRUKER
Current Data Parameters
NAME wsz-6-35-8
EXPNO 1
PROCNO 1
F2 - Acquisition Paramet
Date_ 20171227
Time 17.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685
FIDRES 0.125483
AQ 3.9846387
RG 123.19
DW 60.800
DE 6.50
TE 292.0
D1 1.00000000
TD0 1
======== CHANNEL f1 ====
NUC1 1H
P1 10.00
PLW1 17.78300095
SFO1 400.1324710
F2 - Processing paramete
SI 65536
SF 400.1300000
WDW EM
SSB 0
LB 0.30
GB 0
PC 1.00
O
N
S
O
F
N
H
3l
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm
9 8 7 6 5 4 3 2 1 ppm
1.97
0.82
0.92
1.11
2.00
2.80
1.63
0.87
0.98
1.22

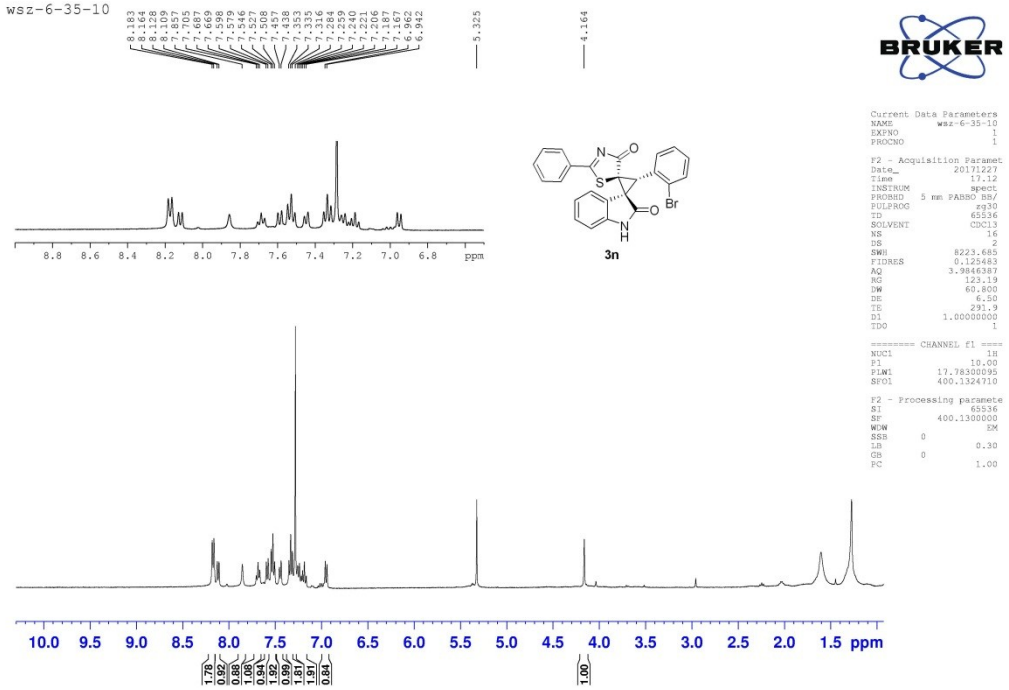

3L
195.596
187.410
172.209
162.278
160.634
140.974
135.262
135.009
132.382
131.383
130.273
130.219
129.187
128.946
128.724
128.583
125.802
124.419
124.101
122.497
122.561
118.852
118.757
115.675
115.535
110.024
109.955
77.359
77.148
76.936
55.921
45.516
37.871
BRUKER
O
N
S
O
F
N
H
3l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

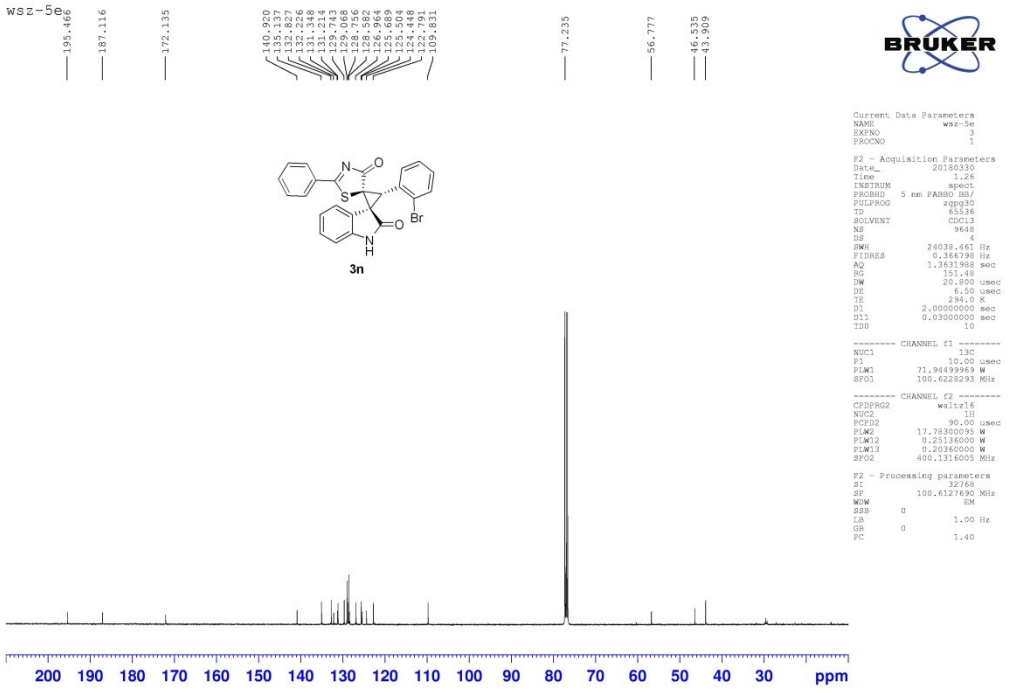
Compound 3m



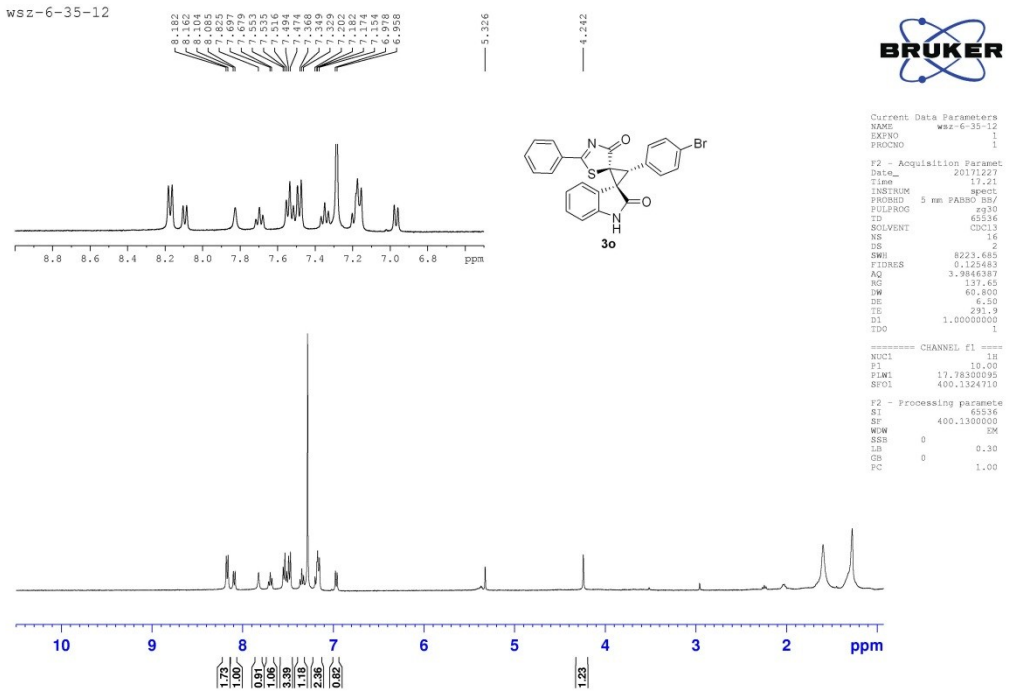


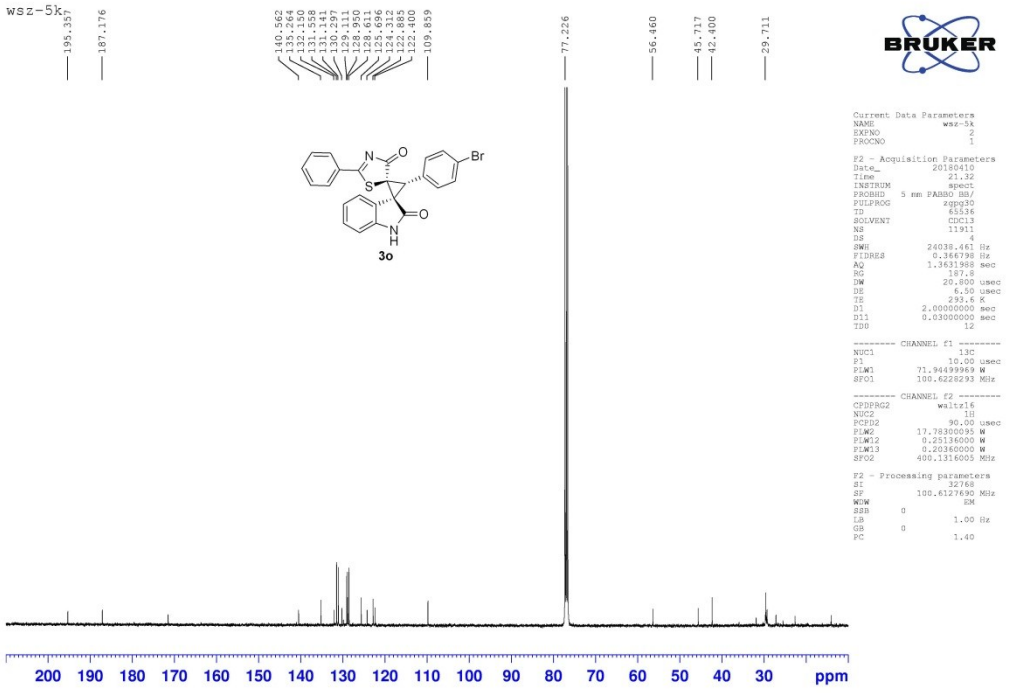
Compound 3n


wsz-6-35-10
3n
Current Data Parameters
NAME wsz-6-35-10
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171227
Time 17.12
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685
FIDRES 0.125483
AQ 3.9846387
RG 123.19
DW 60.800
DE 6.50
TE 291.9
D1 1.00000000
TD0 1
======== CHANNEL f1 ====
NUC1 1H
P1 10.00
PLW1 17.78300095
SFO1 400.1324710
F2 - Processing parameters
SI 65536
SF 400.1300000
WDW EM
SSB 0
LB 0.30
GB 0
PC 1.00

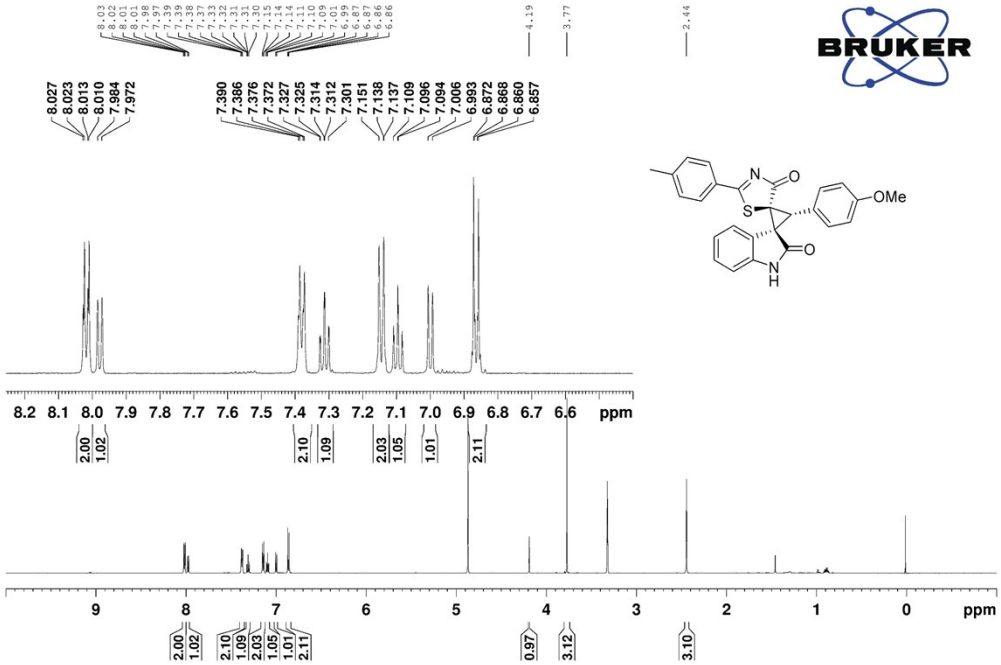

wsz-5e
3n
Current Data Parameters
NAME wsz-5e
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180330
Time 1.26
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 9648
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 151.46
DW 20.800 usec
DE 6.50 usec
TE 294.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 10
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 71.94499969 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 17.78300095 W
PLW12 0.25136000 W
PLW13 0.20360000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

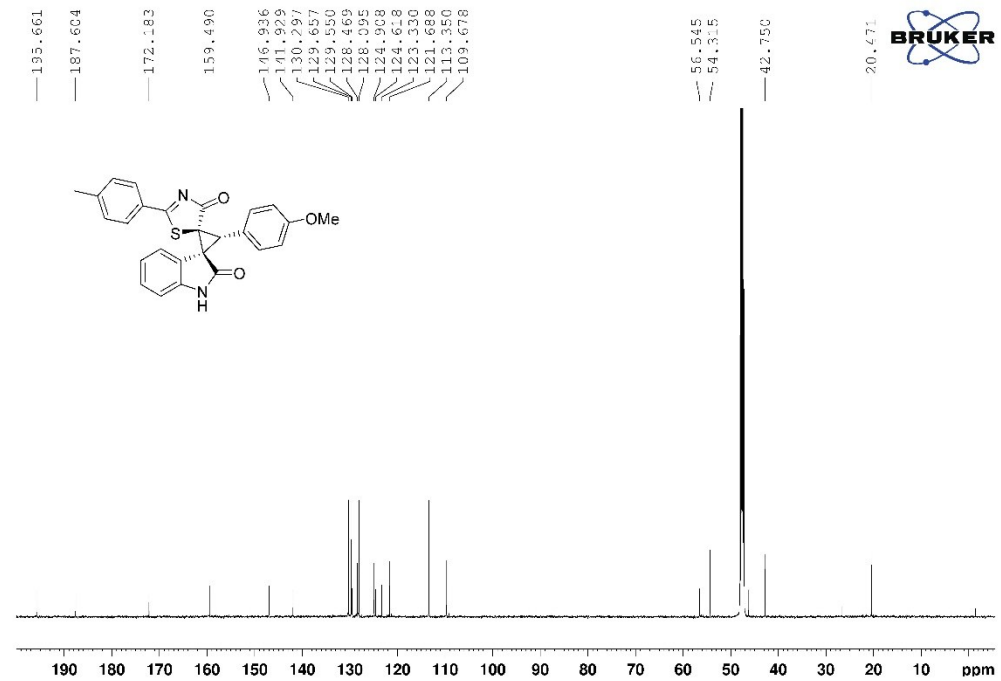
Compound 3o


wsz-6-35-12
8.182
8.162
8.104
8.085
7.825
7.697
7.679
7.553
7.535
7.516
7.494
7.474
7.368
7.349
7.329
7.202
7.182
7.174
7.154
6.978
6.958
5.326
4.242
Br
O
N
S
O
N
H
3o
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm
Current Data Parameters
NAME wsz-6-35-12
EXPNO 1
PROCNO 1
F2 - Acquisition Paramet
Date_ 20171227
Time 17.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685
FIDRES 0.125483
AQ 3.9846387
RG 137.65
DW 60.800
DE 6.50
TE 291.9
D1 1.00000000
TD0 1
======== CHANNEL f1 ====
NUC1 1H
P1 10.00
PLW1 17.78300095
SFO1 400.1324710
F2 - Processing paramete
SI 65536
SF 400.1300000
WDW EM
SSB 0
LB 0.30
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 ppm
1.73
1.00
0.91
1.06
3.39
1.16
2.36
0.82
1.23

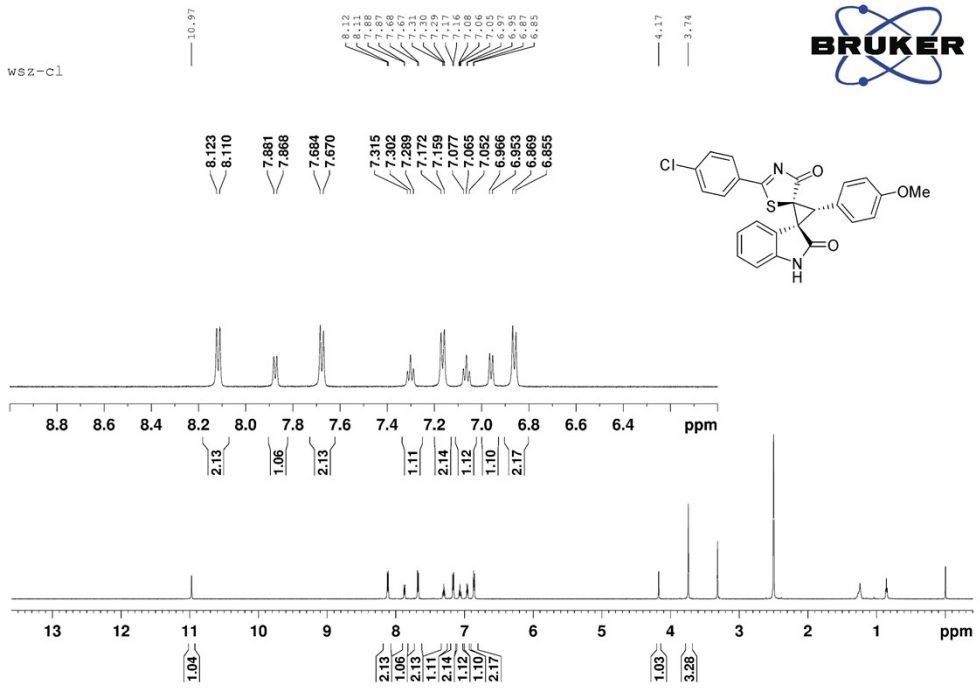

wsz-5k
195.357
187.176
140.562
135.264
132.150
131.558
131.141
130.297
129.111
128.950
128.611
125.696
124.312
122.885
122.400
109.859
77.226
56.460
45.717
42.400
29.711
Br
O
N
S
O
N
H
3o
Current Data Parameters
NAME wsz-5k
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180410
Time 21.32
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 11911
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 187.6
DW 20.800 usec
DE 6.50 usec
TE 293.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 12
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 71.94499969 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 17.78300095 W
PLW12 0.25136000 W
PLW13 0.20360000 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

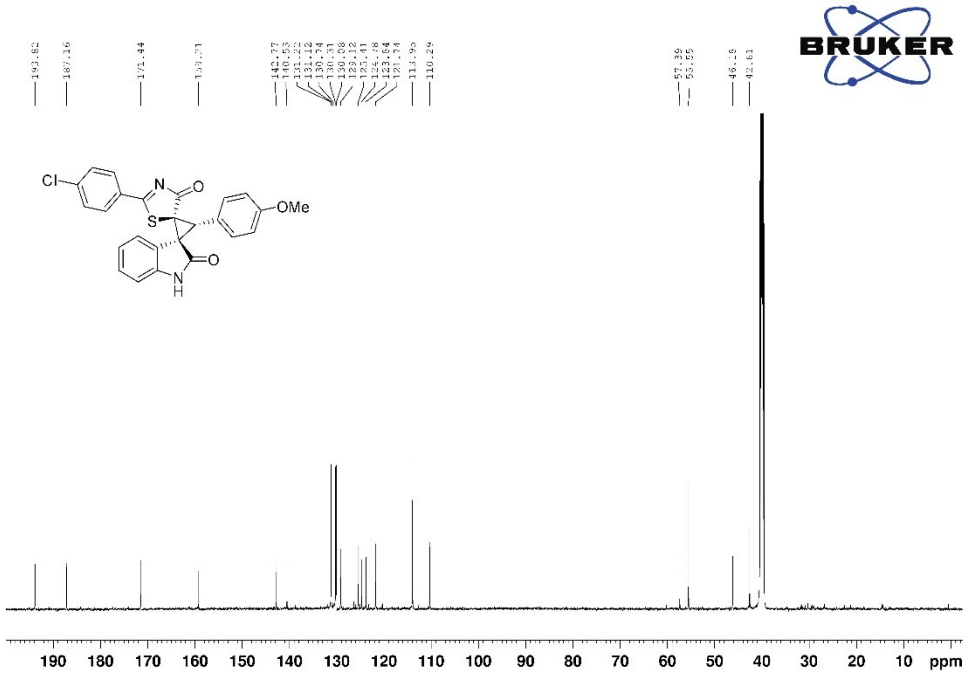
Compound 3p



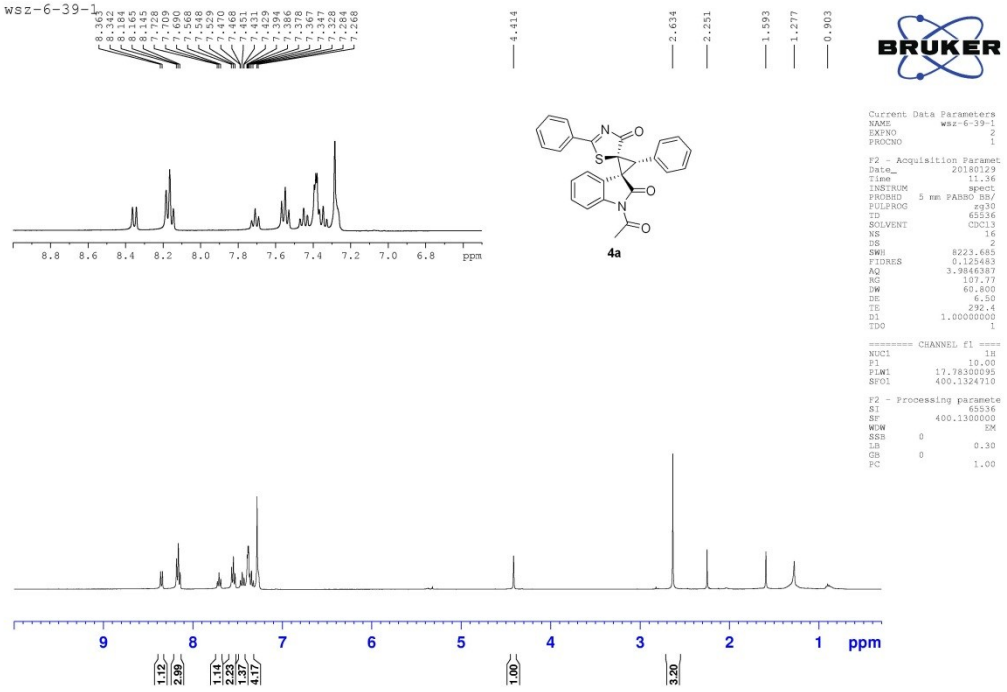


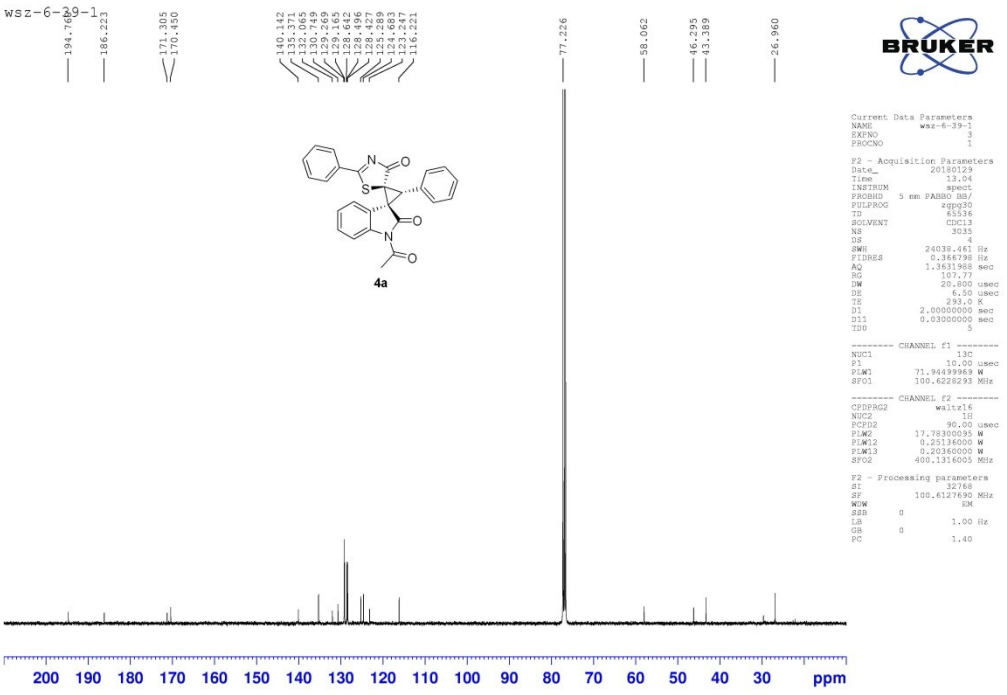
Compound 3q


wsz-cl
10.97
8.123
8.110
7.881
7.868
7.684
7.670
7.315
7.302
7.289
7.172
7.159
7.077
7.065
7.052
6.966
6.953
6.869
6.855
4.17
3.74
Cl
N
O
S
OMe
O
N
H
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 ppm
2.13 1.06 2.13 1.11 2.14 1.12 1.10 2.17
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.04 2.13 1.06 2.13 1.11 2.14 1.12 1.10 2.17 1.03 3.28

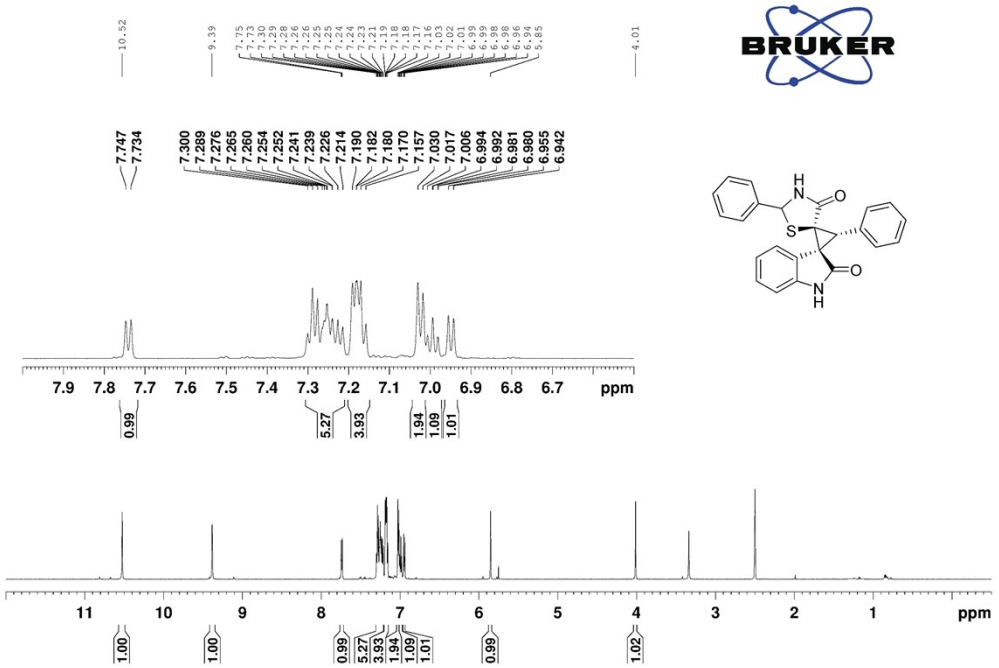

193.82
187.16
171.44
158.71
142.77
140.53
131.22
131.12
130.74
130.31
130.08
129.12
125.41
124.78
123.64
121.74
113.95
110.29
57.29
55.55
46.26
42.61
Cl
N
O
S
OMe
O
N
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

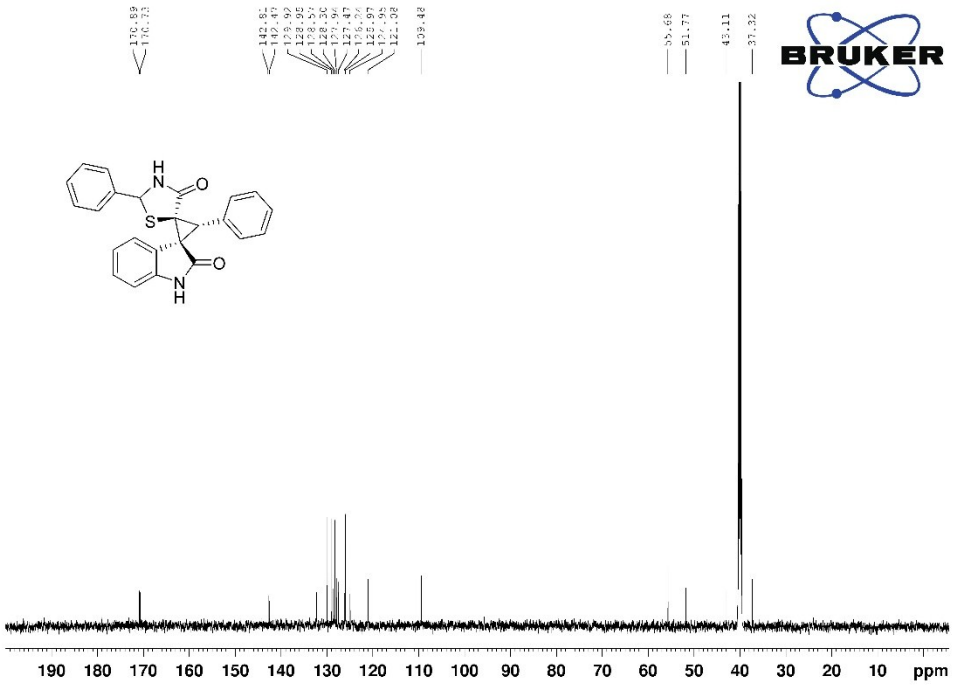
Compound 4a



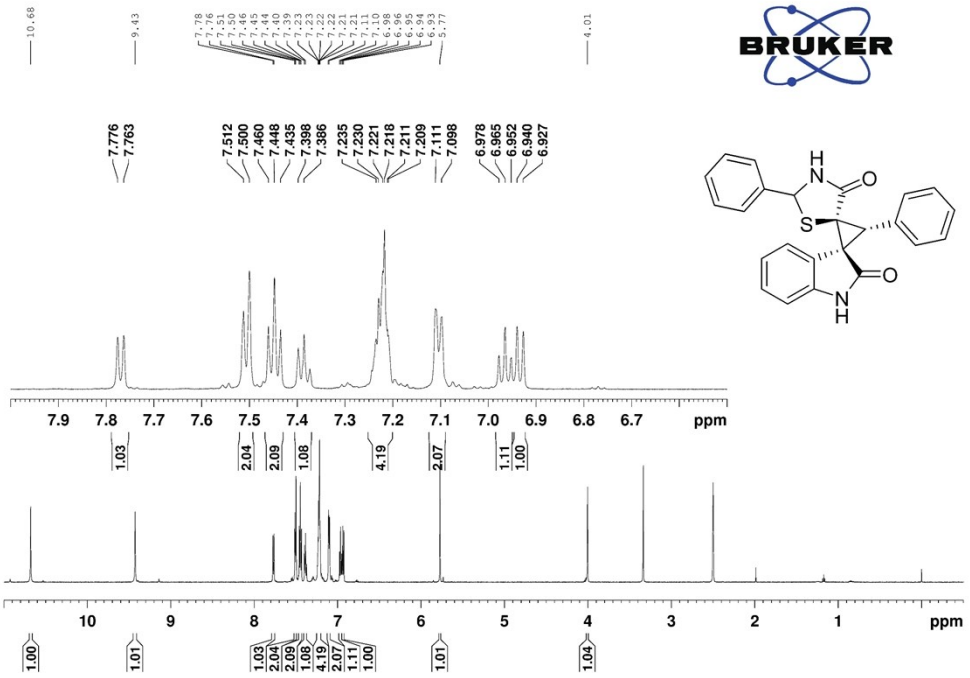


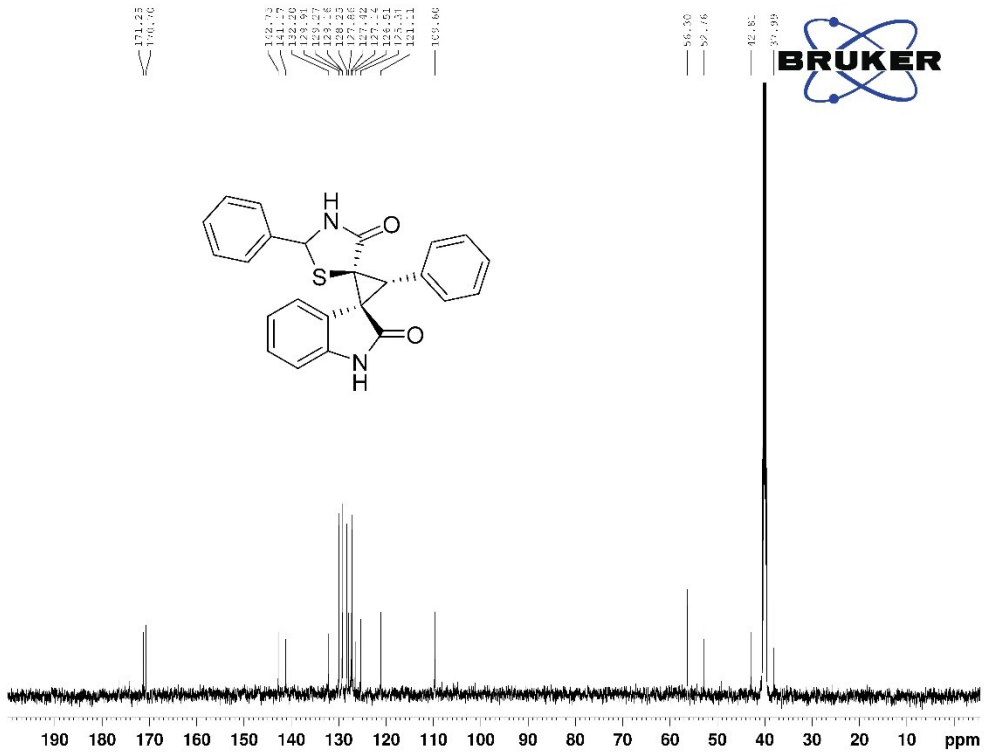
Compound 4b (major)



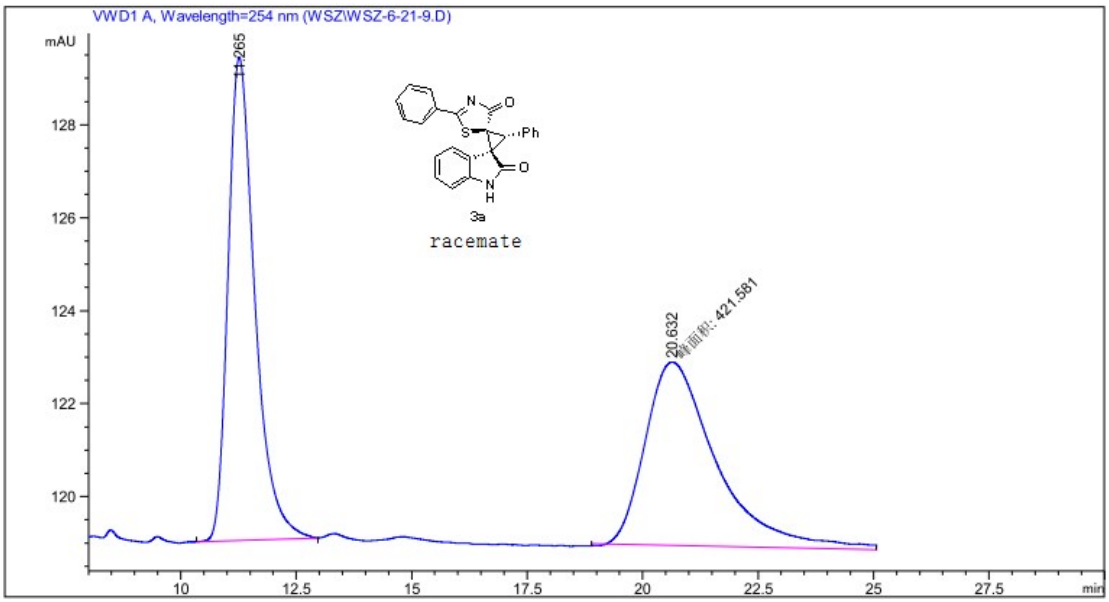


Compound 4b (minor)

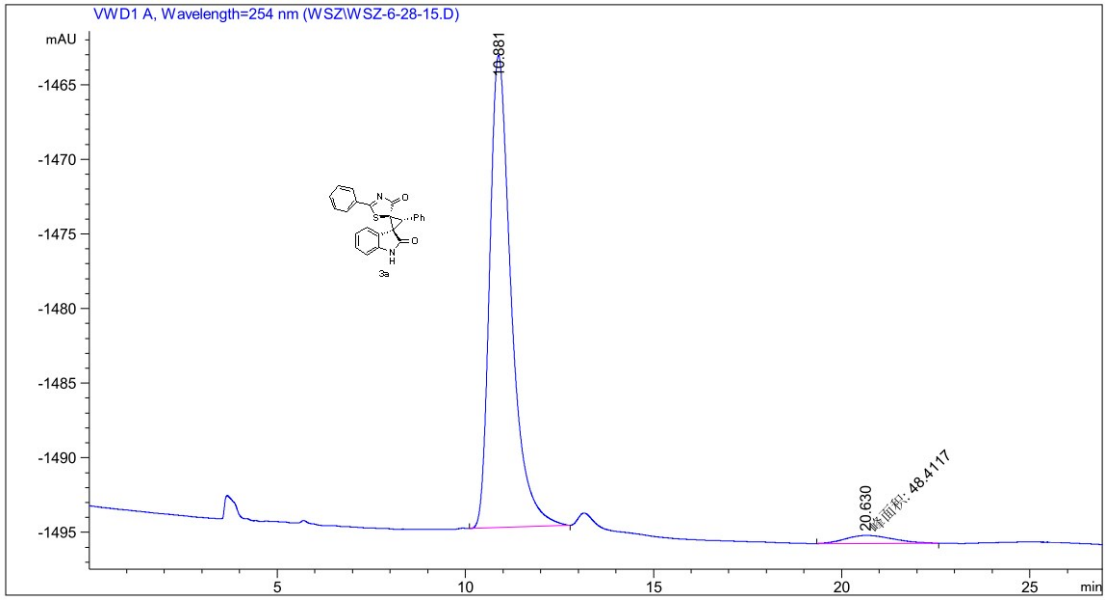




Compound 3a

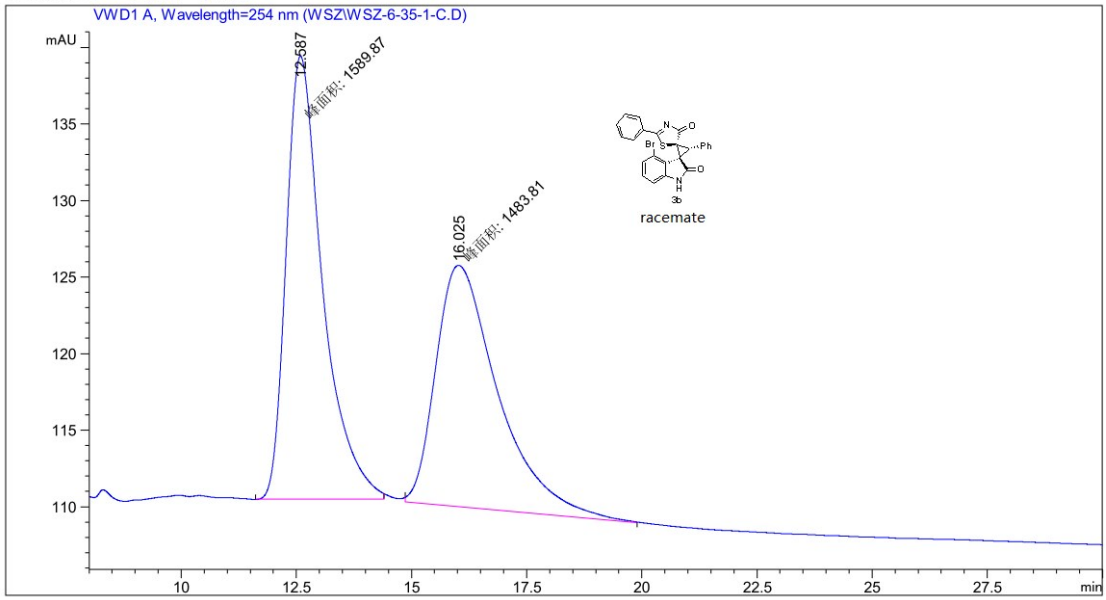


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.265	BB	0.6055	420.21222	10.39806	49.9187
2	20.632	MM	1.7810	421.58066	3.94527	50.0813

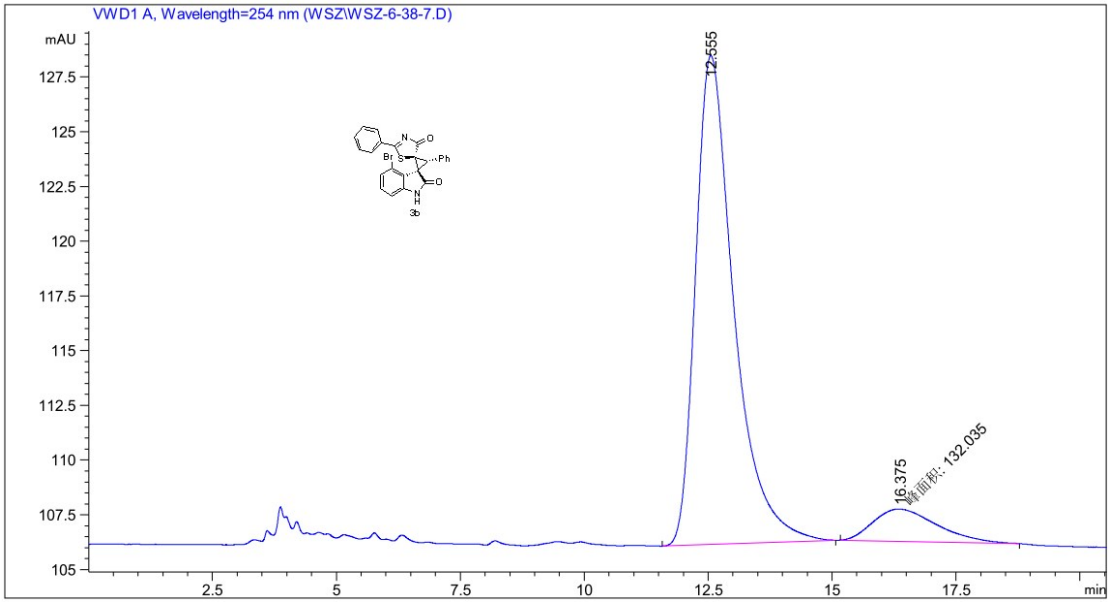


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.881	BB	0.6017	1260.66394	31.65170	96.3018
2	20.630	MM	1.4799	48.41169	5.45224e-1	3.6982

Compound 3b

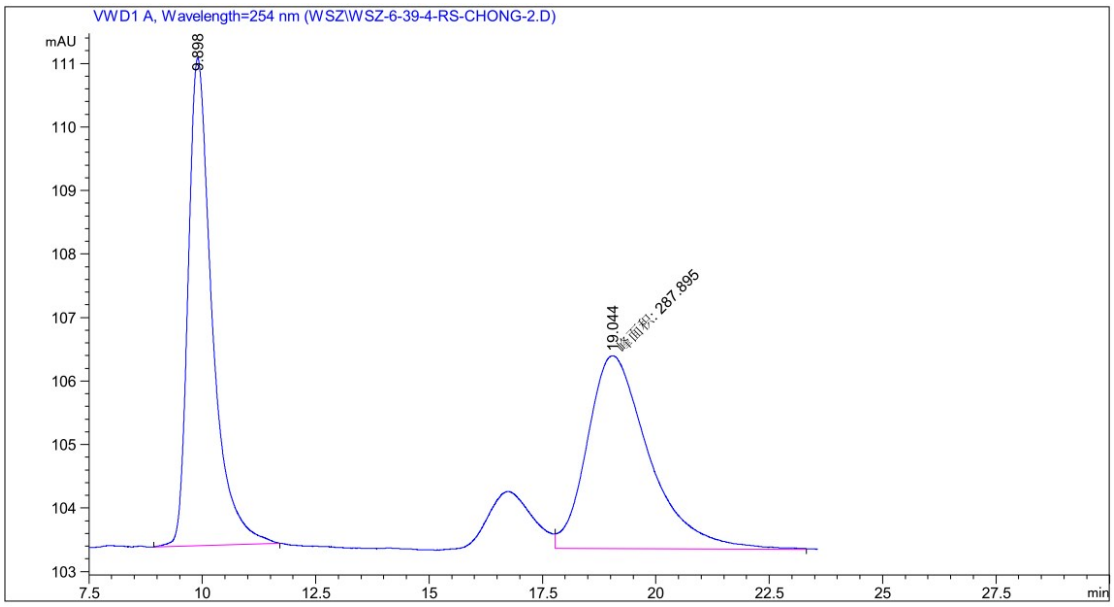


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.587	MM	0.9161	1589.87354	28.92599	51.7253
2	16.025	MM	1.5689	1483.81079	15.76244	48.2747

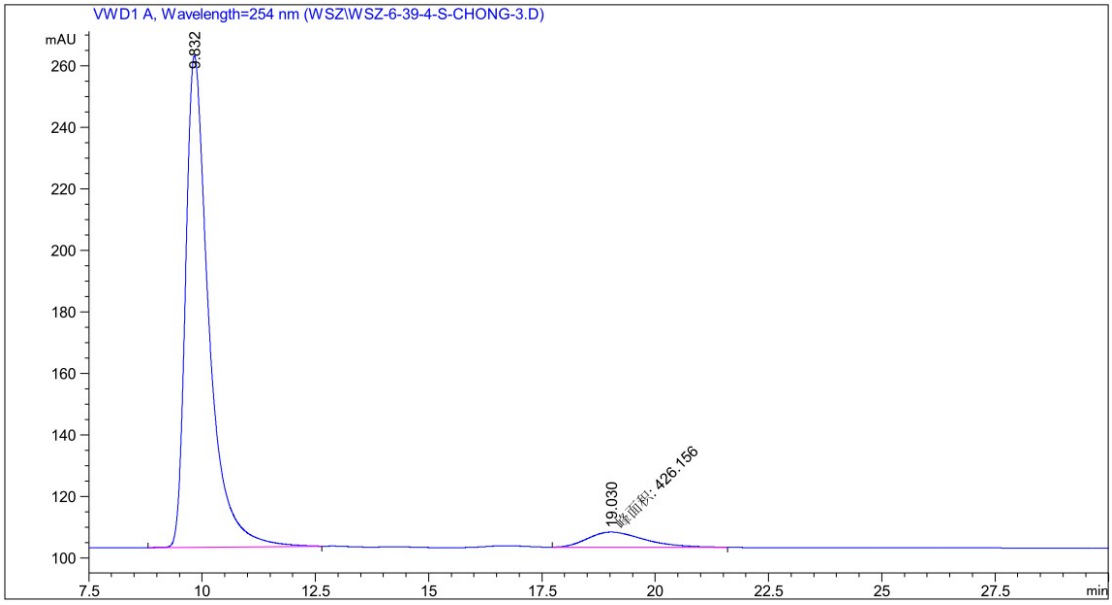


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.555	BB	0.8083	1203.09009	22.33871	90.1107
2	16.375	MM	1.4955	132.03458	1.47146	9.8893

Compound 3c

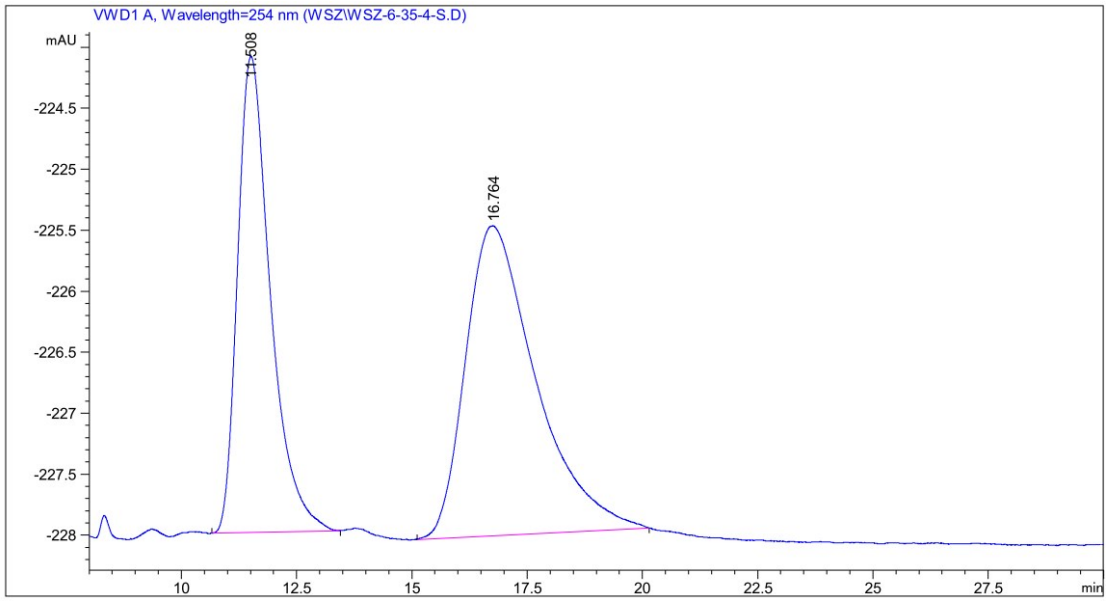


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.898	BB	0.5464	282.06900	7.68214	49.4889
2	19.044	MM	1.5787	287.89496	3.03933	50.5111

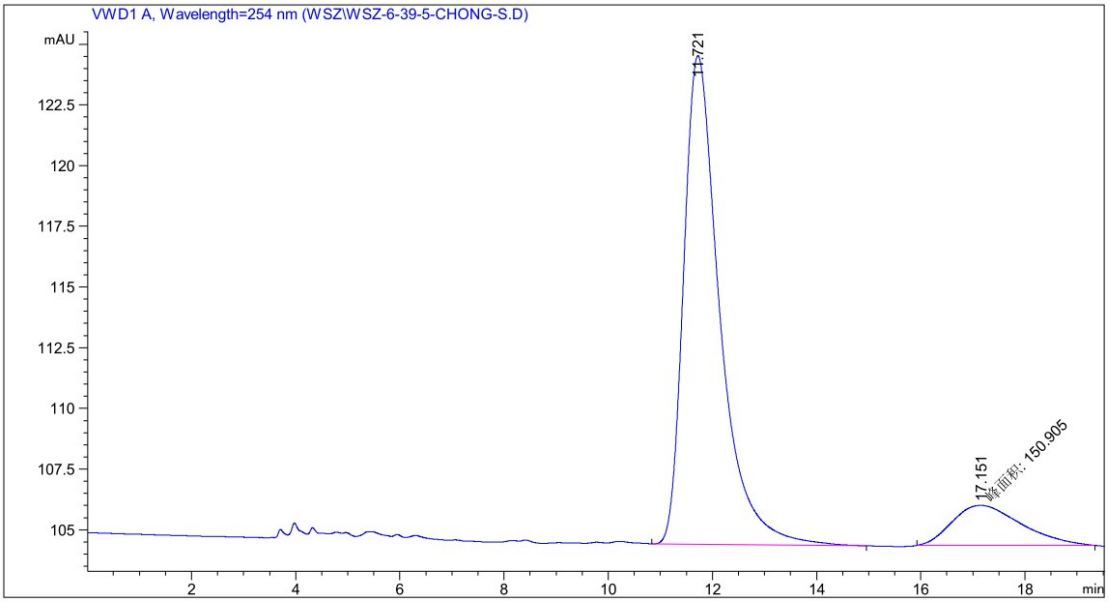


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.832	BB	0.5293	5674.71875	159.81288	93.0148
2	19.030	MM	1.4429	426.15601	4.92243	6.9852

Compound 3d

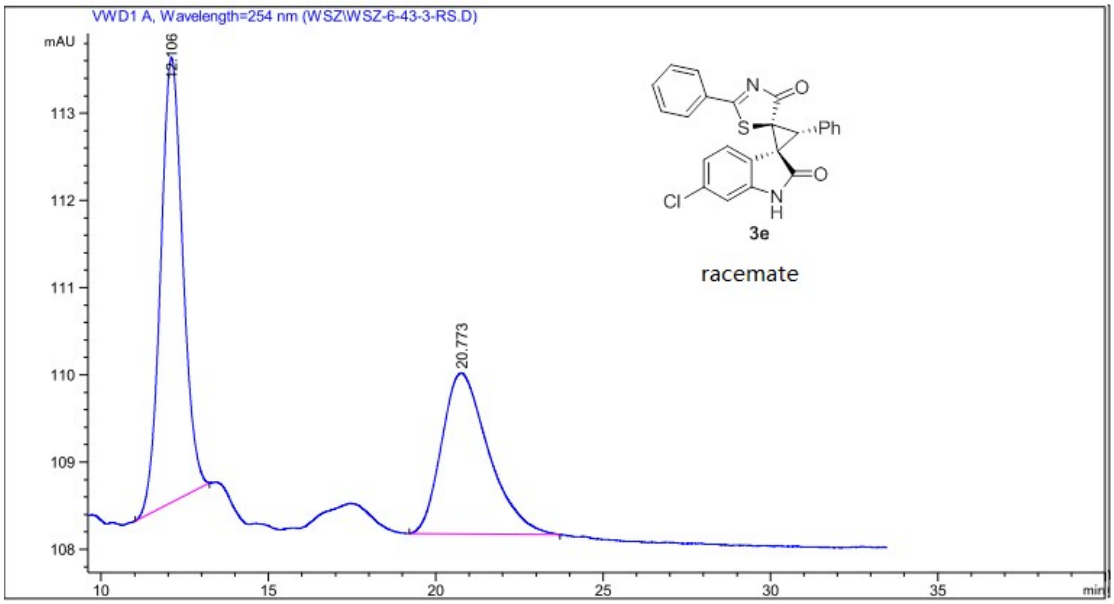


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.508	BB	0.7232	193.44489	3.90305	41.8192
2	16.764	BB	1.2486	269.12982	2.54125	58.1808

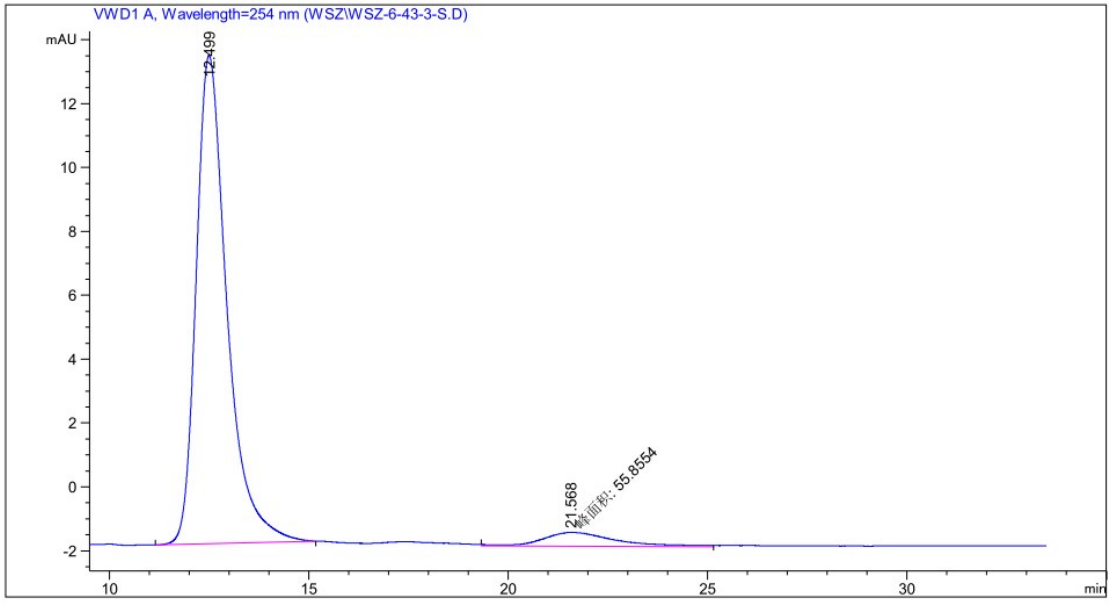


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.721	BB	0.7250	969.47461	20.12532	86.5309
2	17.151	MM	1.5267	150.90471	1.64741	13.4691

Compound 3e

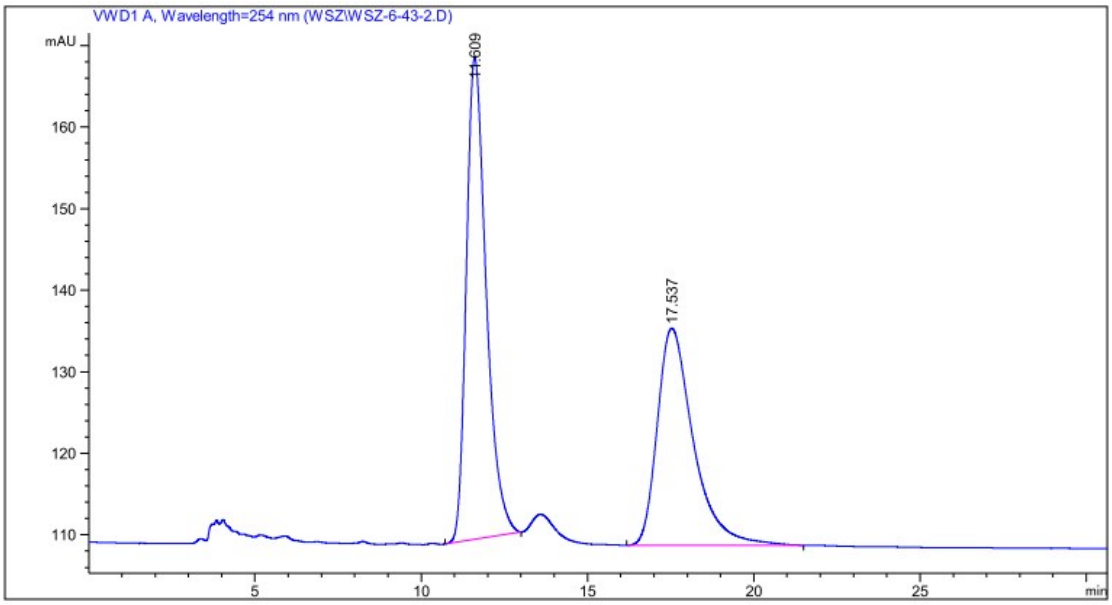


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.106	BB	0.6933	234.42122	5.09945	56.5883
2	20.773	BB	1.1530	179.83617	1.84694	43.4117

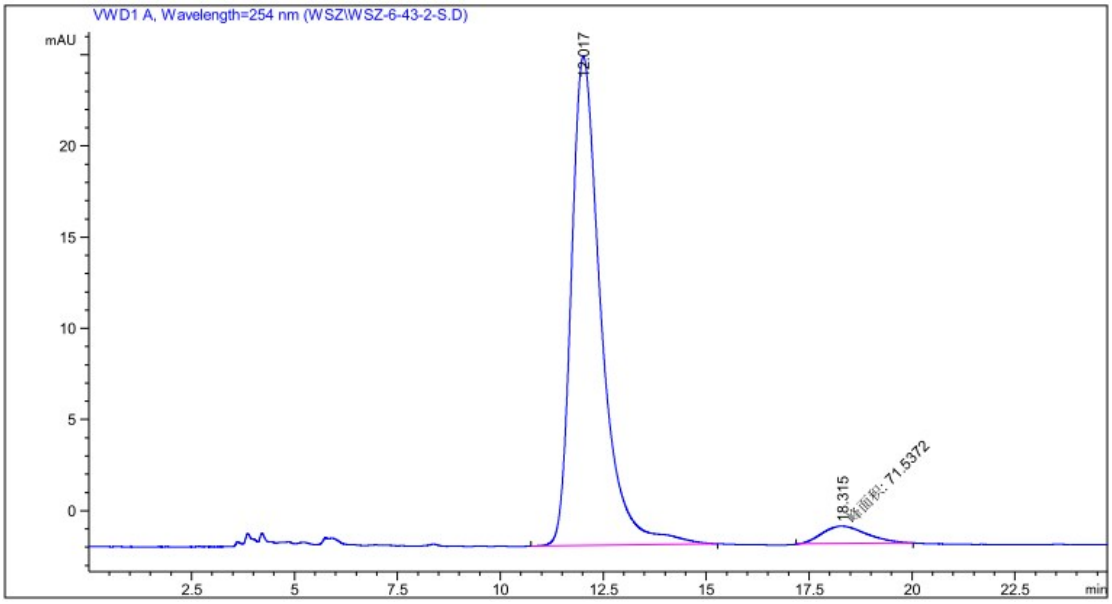


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.499	BB	0.8087	822.41742	15.28688	93.6403
2	21.568	MM	2.1424	55.85537	4.34525e-1	6.3597

Compound 3f

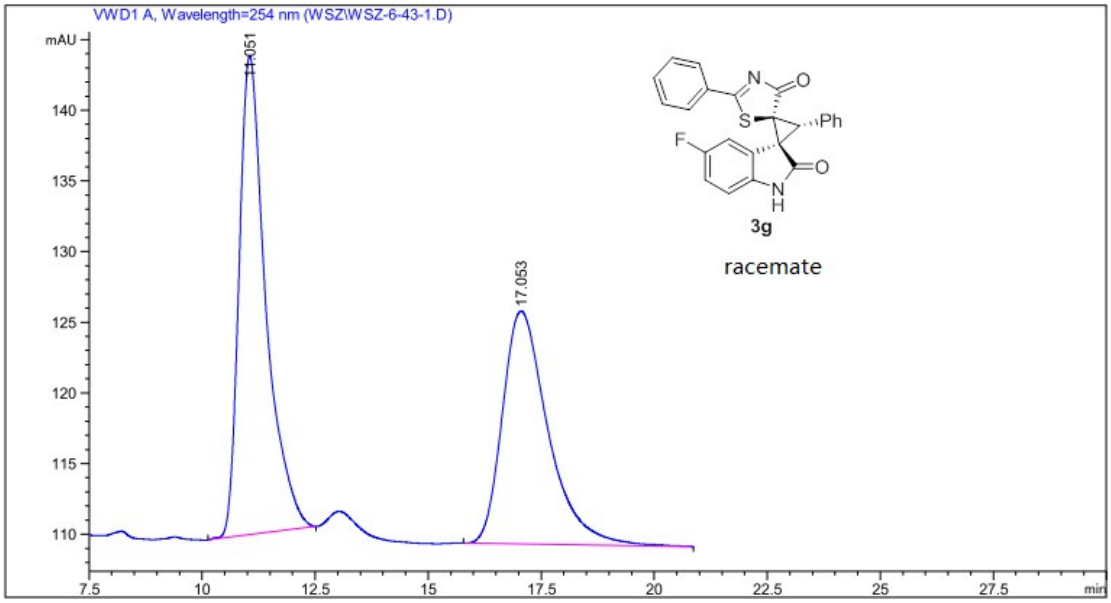


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.609	BB	0.6341	2457.73022	59.11368	55.0417
2	17.537	BB	1.1113	2007.48730	26.63530	44.9583

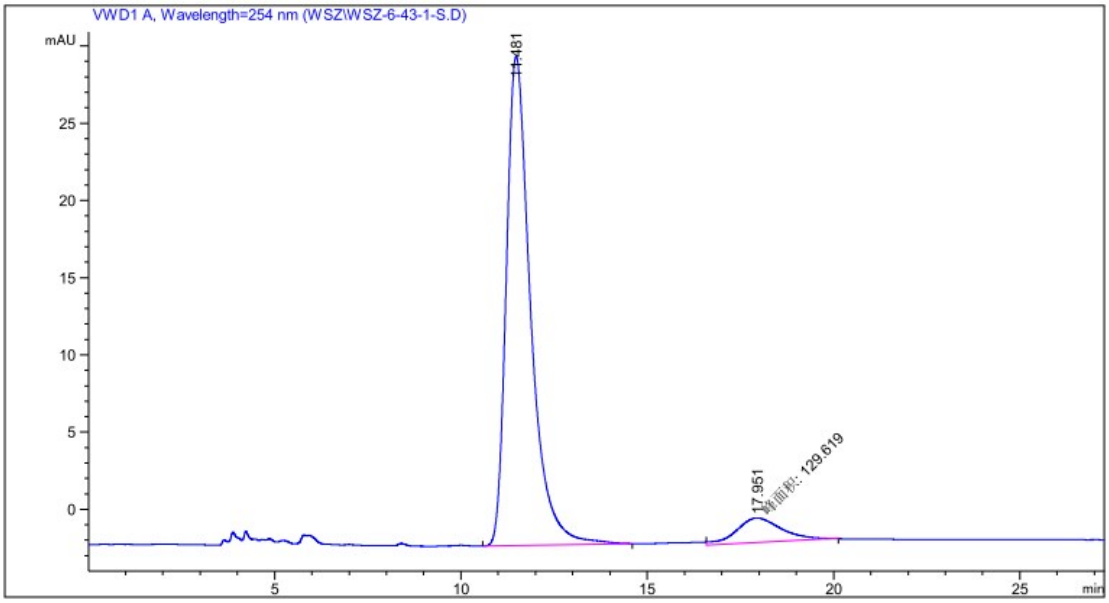


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.017	BB	0.7543	1343.23877	26.82208	94.9436
2	18.315	MM	1.2534	71.53716	9.51210e-1	5.0564

Compound 3g

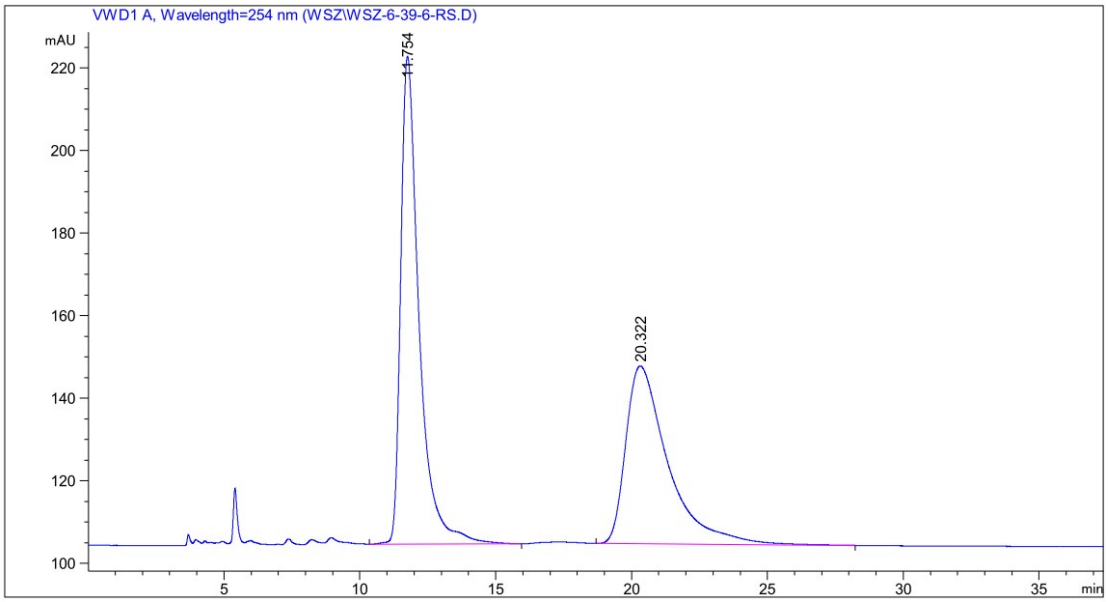


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.051	BB	0.6132	1394.07715	33.86860	54.6502
2	17.053	BBA	1.0329	1156.83069	16.48169	45.3498

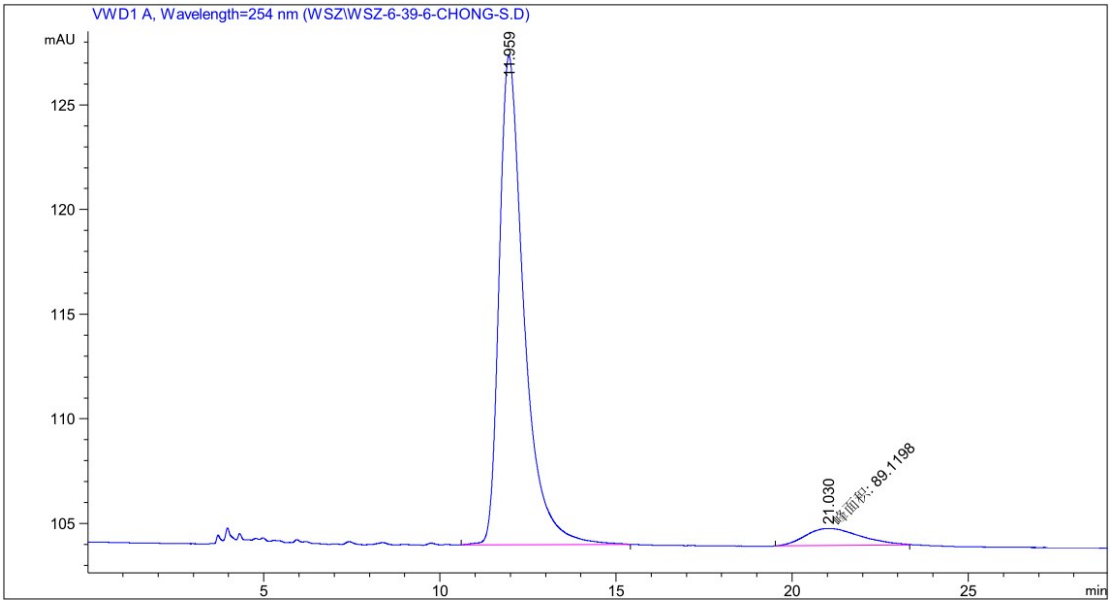


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.481	BB	0.6849	1436.49634	31.68570	91.7235
2	17.951	MM	1.3770	129.61882	1.56888	8.2765

Compound 3h

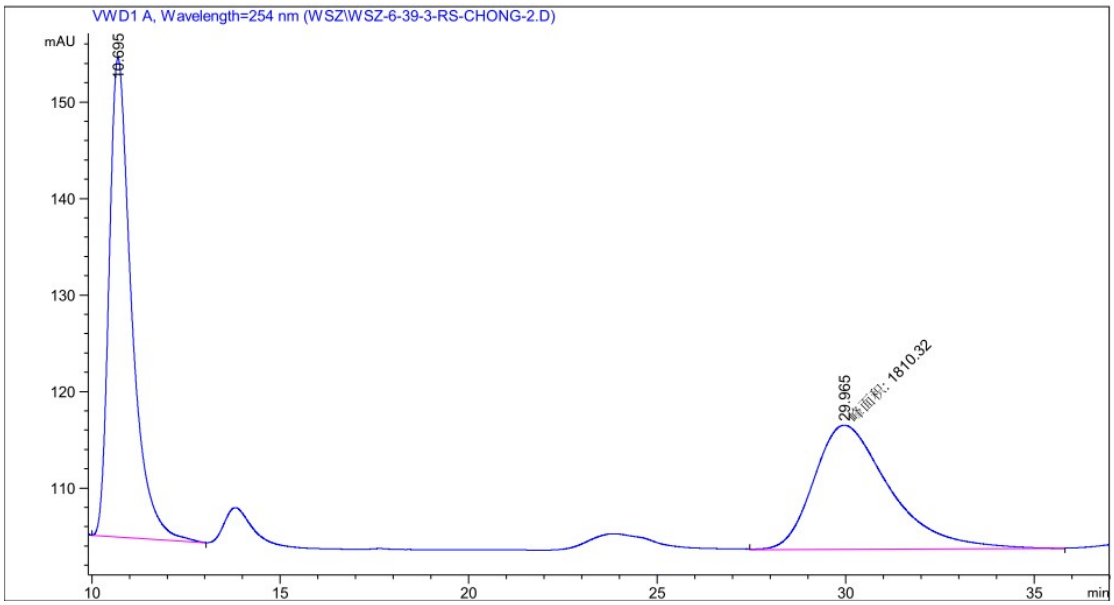


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.754	BB	0.7006	5565.58838	118.13480	54.4242
2	20.322	BB	1.5740	4660.72559	43.08551	45.5758

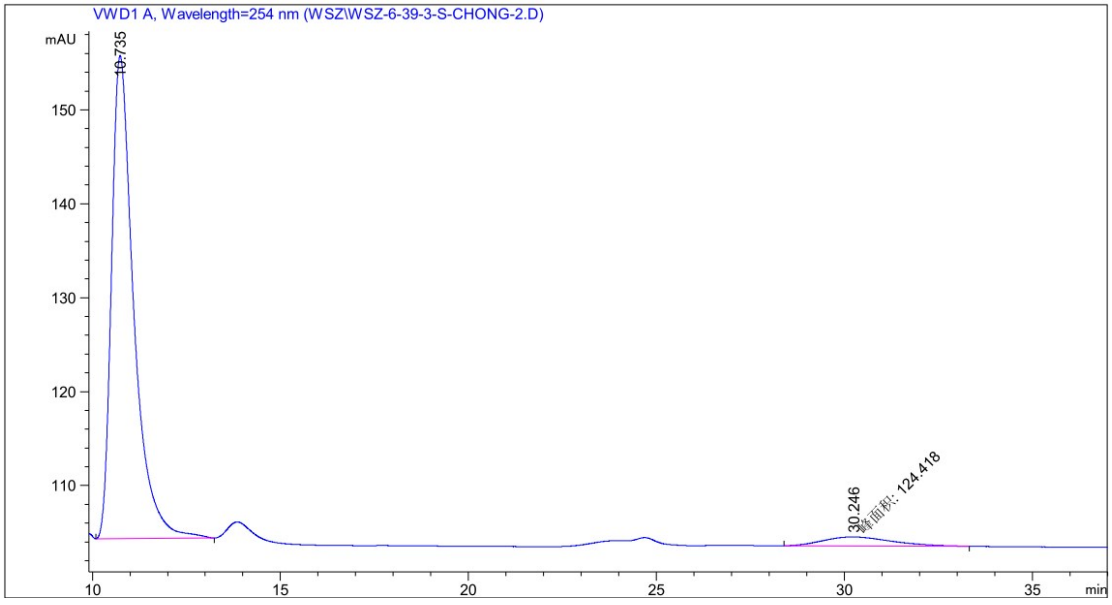


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.959	BB	0.7346	1148.93469	23.36784	92.8016
2	21.030	MM	1.8148	89.11977	8.18460e-1	7.1984

Compound 3i

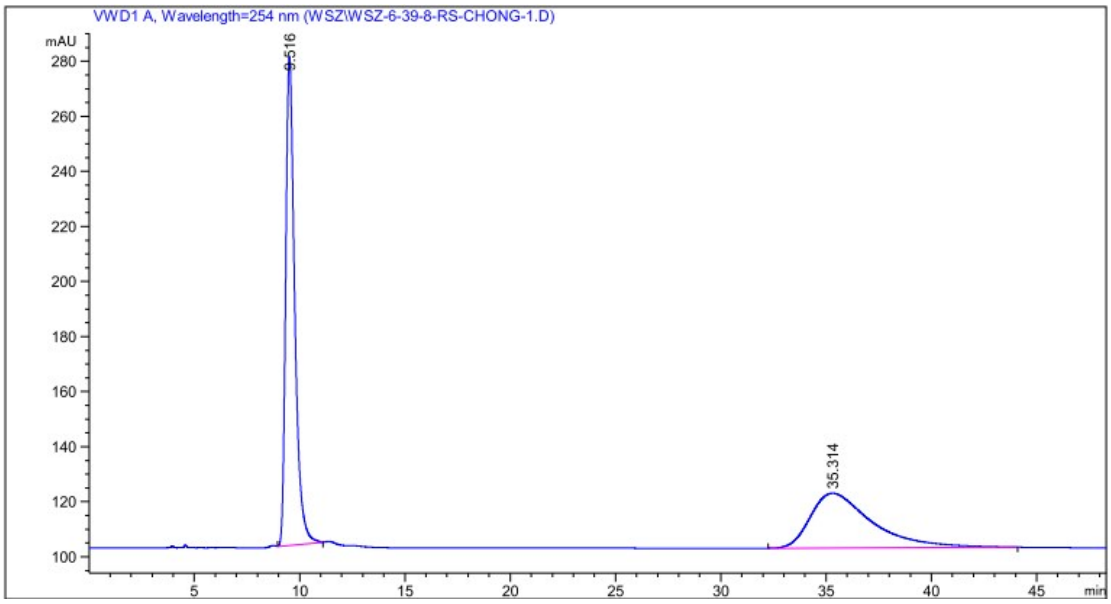


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.695	BB	0.6192	2052.77319	49.66376	53.1380
2	29.965	MM	2.3429	1810.32153	12.87823	46.8620

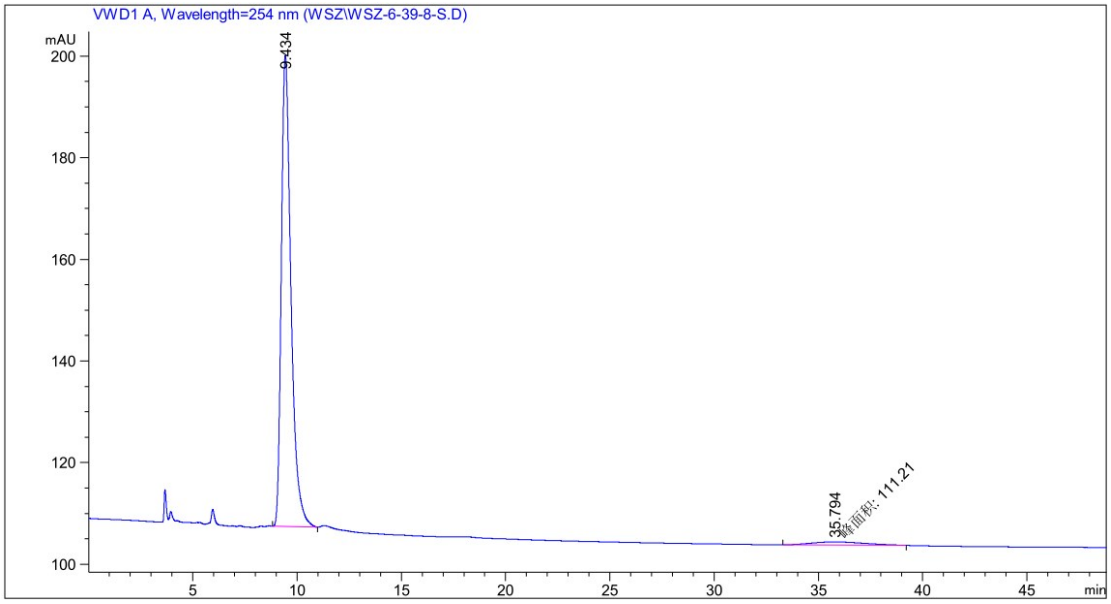


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.735	BB	0.6140	2112.05786	51.43814	94.4369
2	30.246	MM	2.1410	124.41755	9.68518e-1	5.5631

Compound 3j

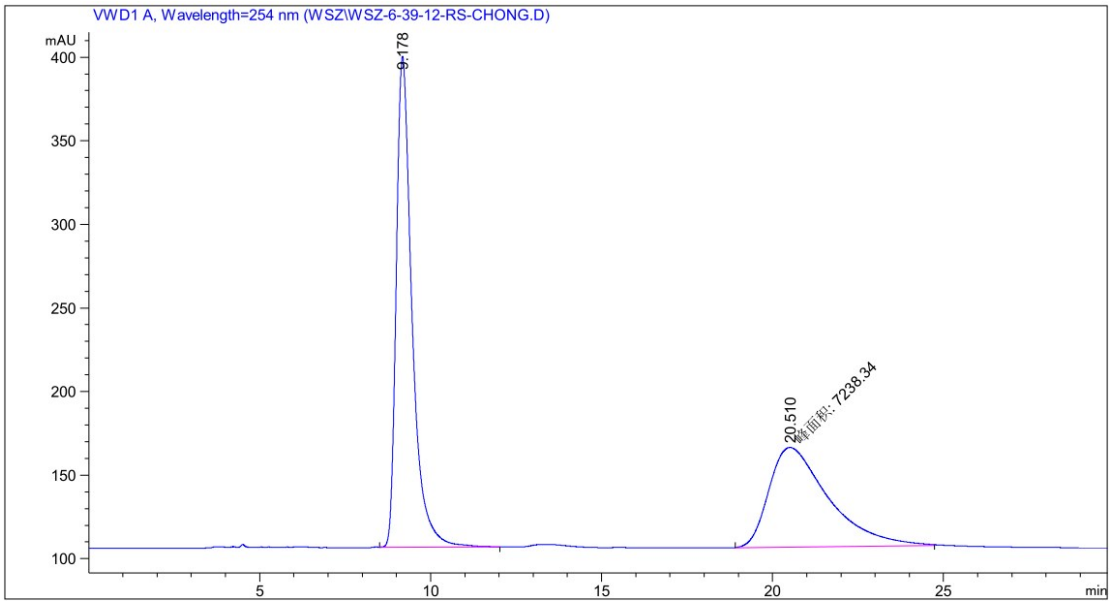


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.516	VB	0.4515	5279.71826	177.24985	56.6623
2	35.314	BB	2.5963	4038.14331	19.90141	43.3377

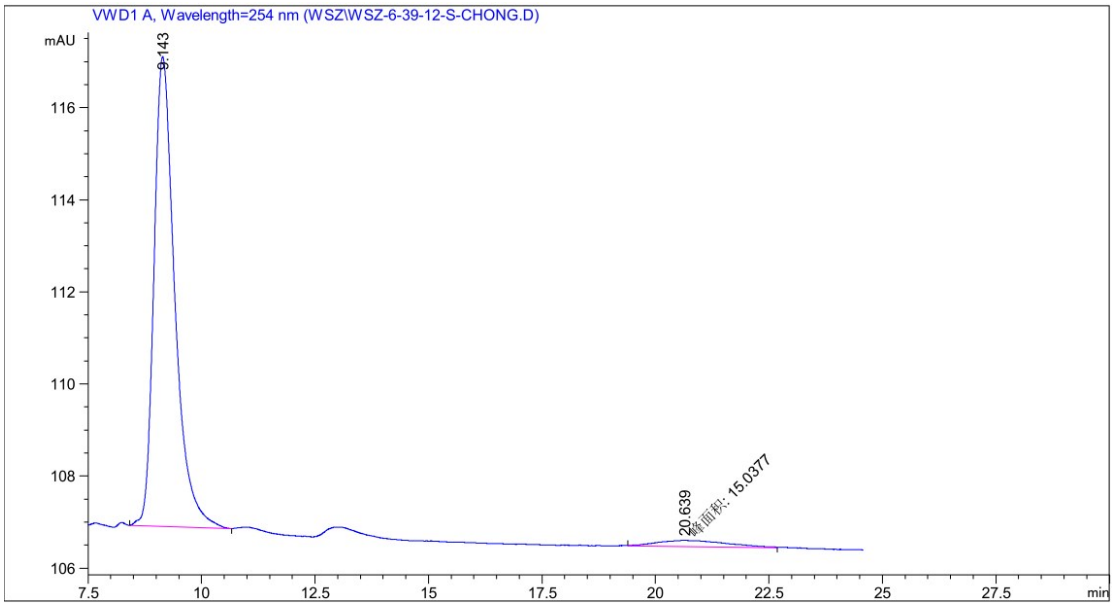


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.434	BB	0.4903	2996.54419	92.64890	96.4215
2	35.794	MM	2.9954	111.20969	6.18774e-1	3.5785

Compound 3k

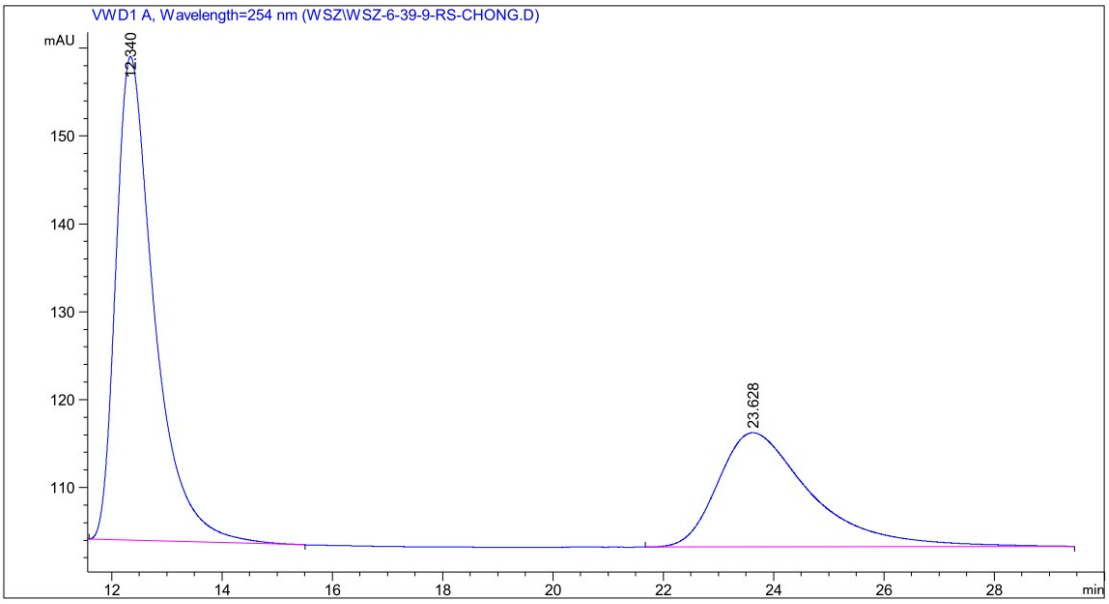


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.178	BB	0.4806	9395.75781	293.43427	56.4849
2	20.510	MM	2.0206	7238.34033	59.70565	43.5151

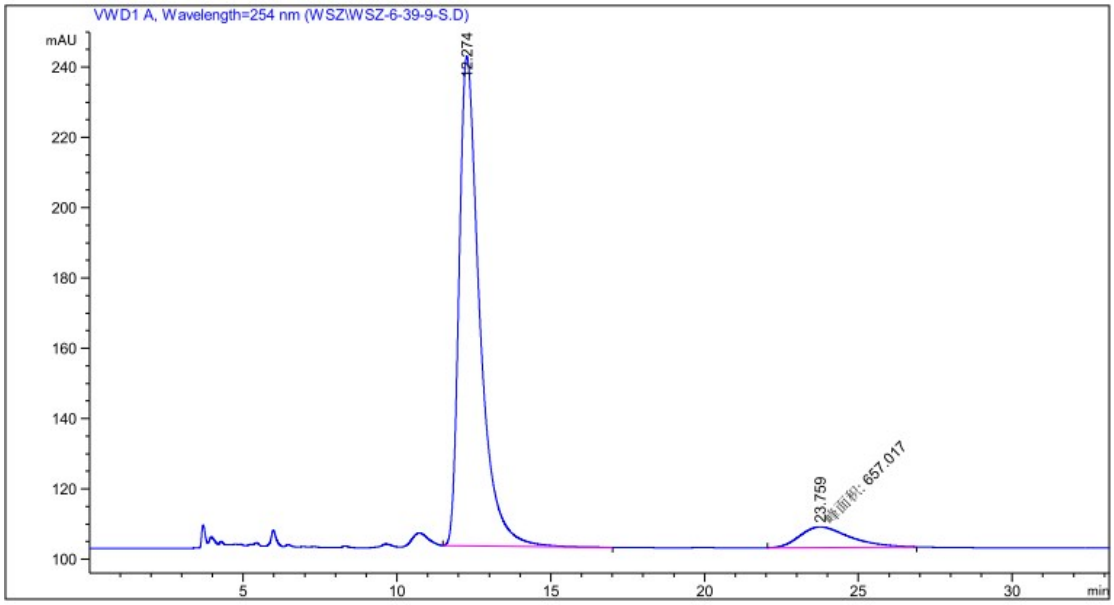


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.143	BB	0.4796	324.77539	10.19748	95.5747
2	20.639	MM	1.8311	15.03765	1.36872e-1	4.4253

Compound 3l

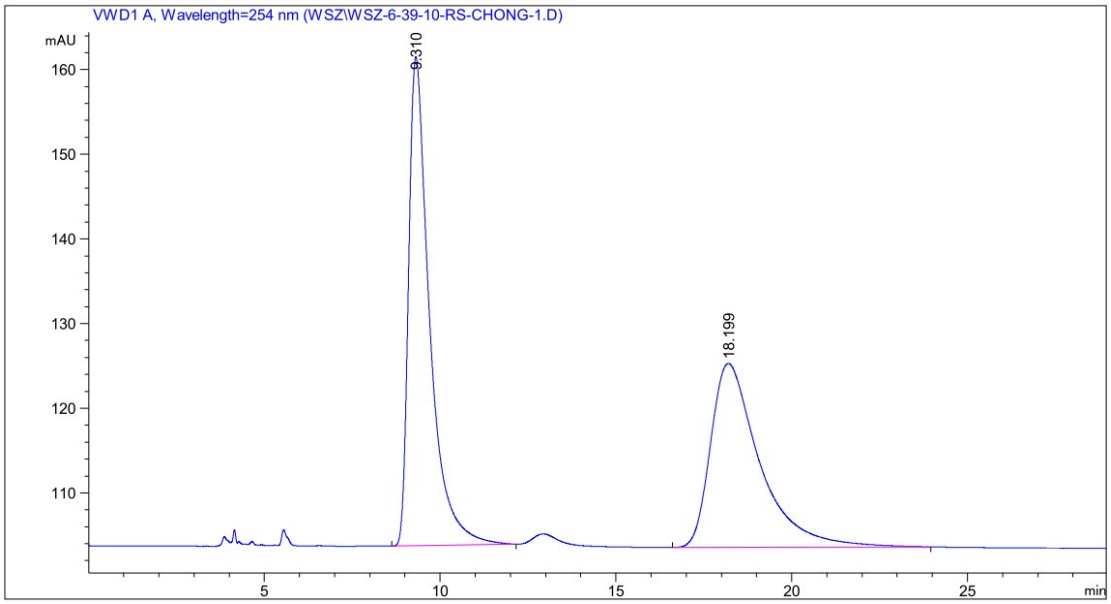


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.340	BB	0.7227	2664.28516	55.03978	63.6416
2	23.628	BBA	1.5976	1522.10522	12.99458	36.3584

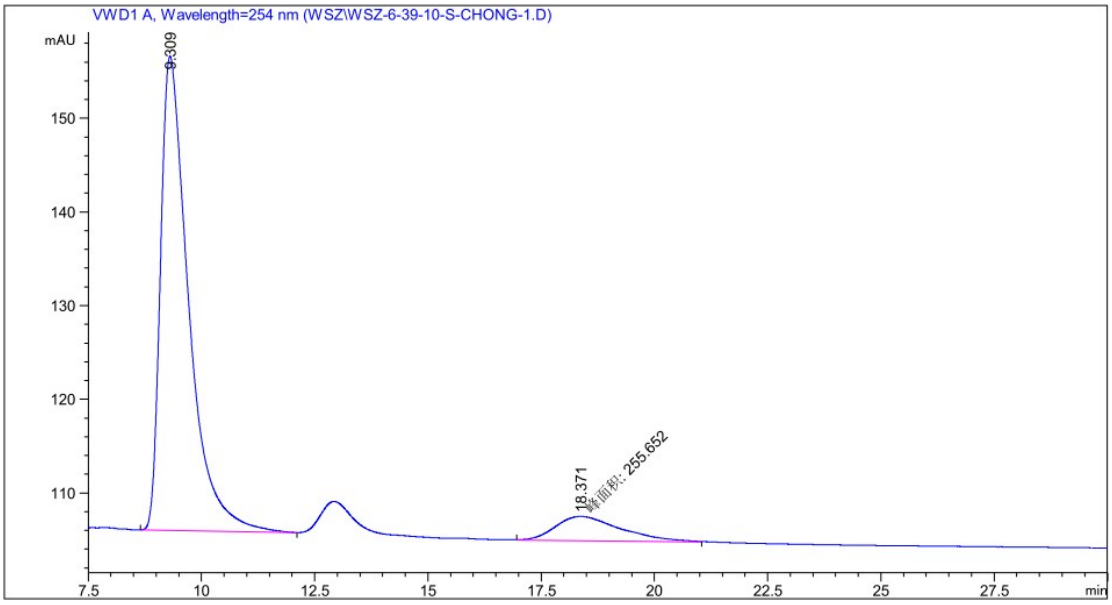


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.274	BB	0.6943	6460.10156	139.22293	90.7685
2	23.759	MM	1.8752	657.01715	5.83939	9.2315

Compound 3m

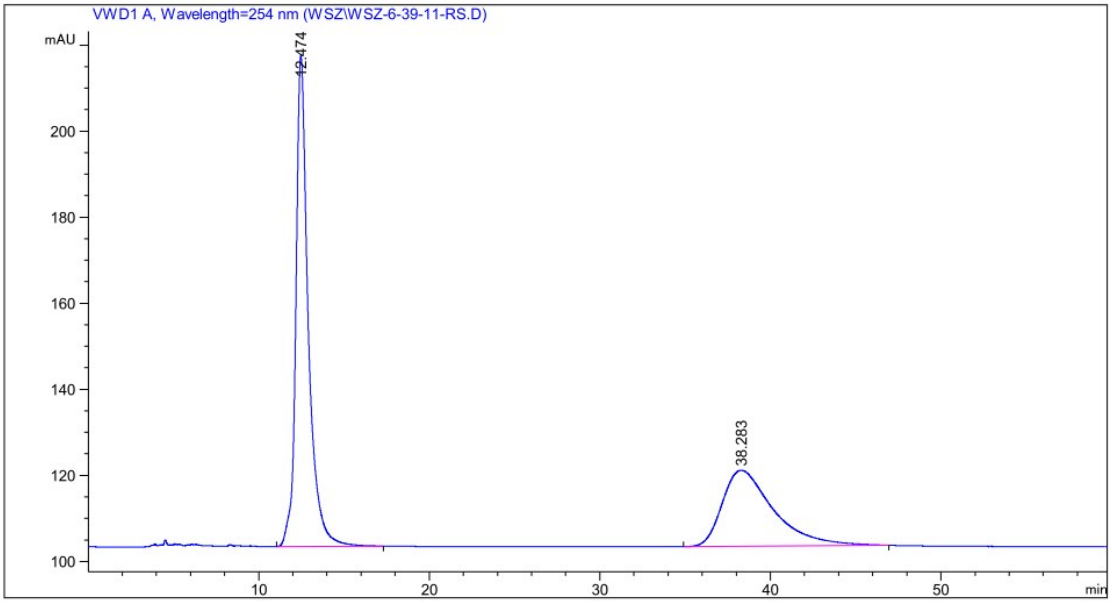


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.310	BB	0.6071	2387.91724	57.78387	53.0933
2	18.199	BB	1.4093	2109.66943	21.73743	46.9067

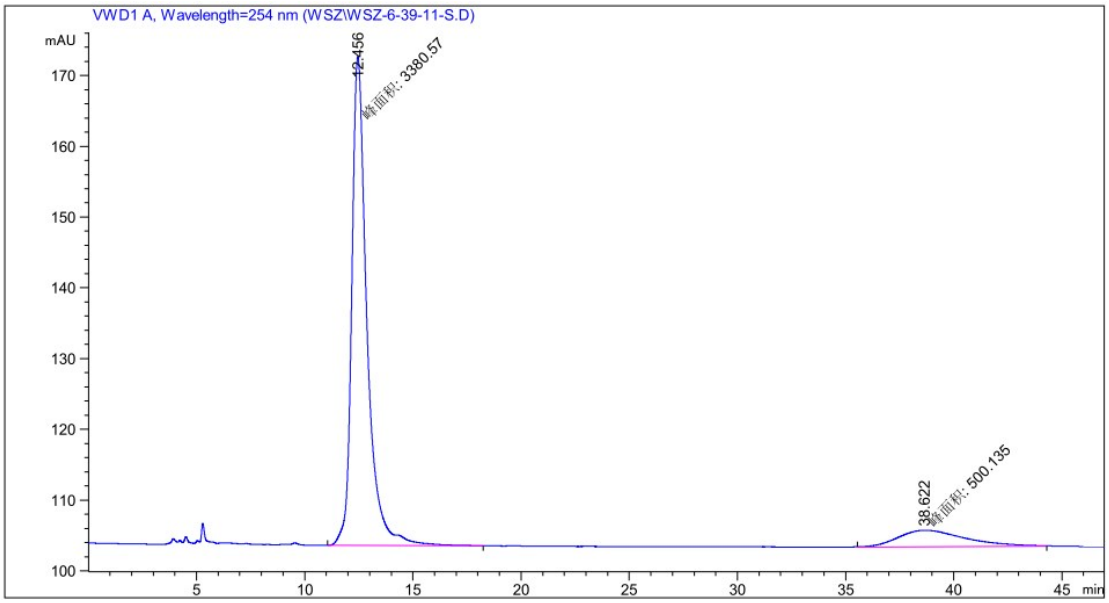


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.309	BB	0.6497	2175.98438	50.59925	89.4864
2	18.371	MM	1.6515	255.65184	2.58002	10.5136

Compound 3n

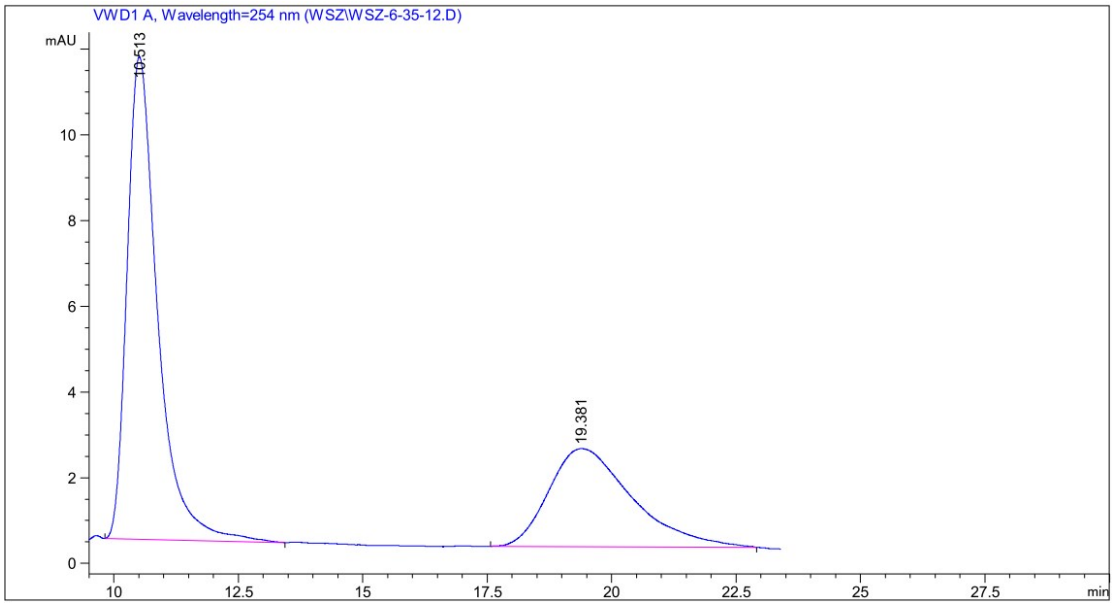


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.474	BB	0.7416	5764.56104	114.06396	61.0198
2	38.283	BB	2.4605	3682.46973	17.68326	38.9802

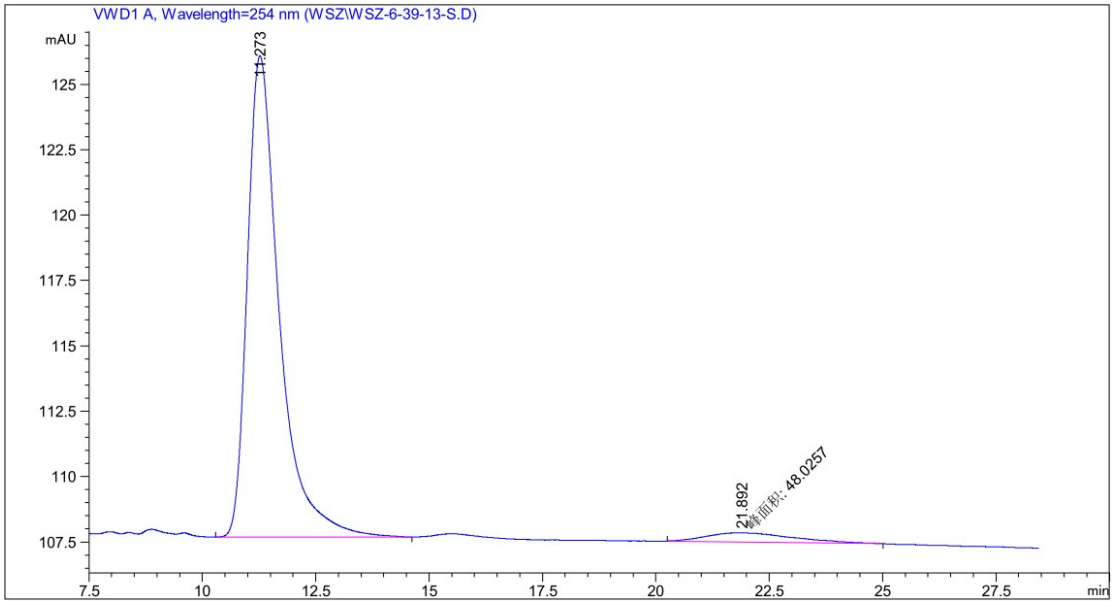


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.456	MM	0.8157	3380.57349	69.07710	87.1123
2	38.622	MM	3.5842	500.13513	2.32565	12.8877

Compound 3o

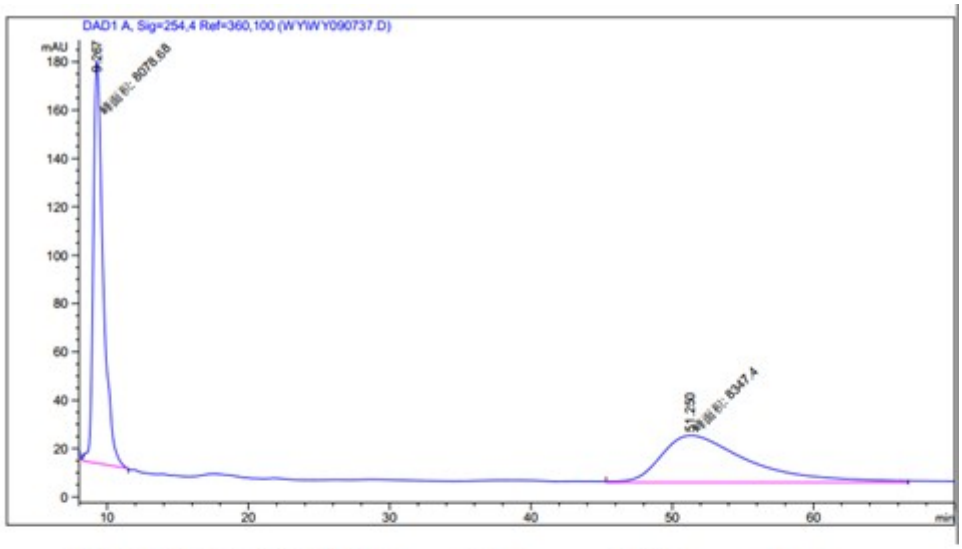


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.513	BB	0.6427	481.39719	11.26151	64.3905
2	19.381	BB	1.3723	266.22421	2.28667	35.6095

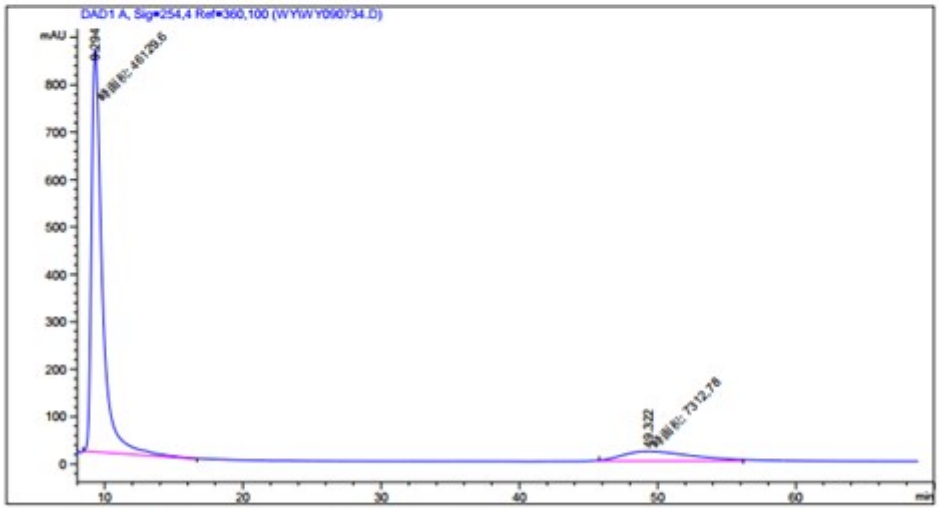


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.273	BB	0.7265	901.66608	18.40811	94.9430
2	21.892	MM	2.2467	48.02568	3.56272e-1	5.0570

Compound 3p

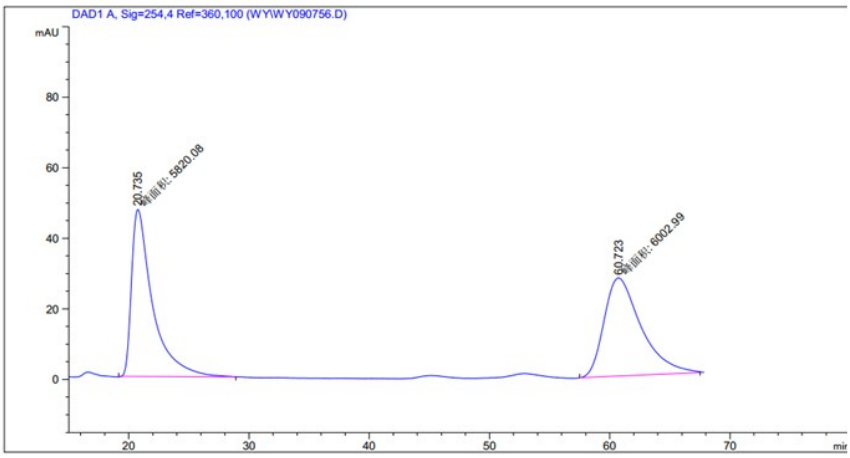


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.267	MM	0.8088	8078.68262	166.46893	49.1820
2	51.250	MM	7.1616	8347.40430	19.42635	50.8180

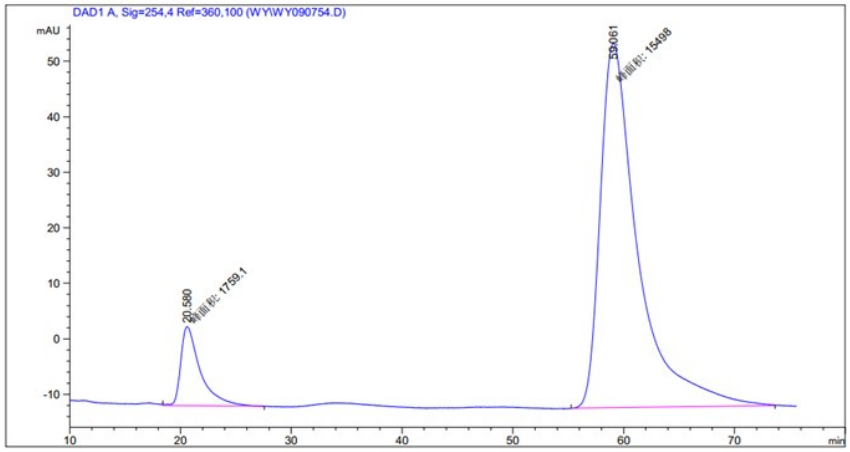


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.294	MM	0.9055	4.61296e4	849.02722	86.3165
2	49.322	MM	5.8421	7312.77832	20.86219	13.6835
总量：				5.34423e4	869.88941	

Compound 3q

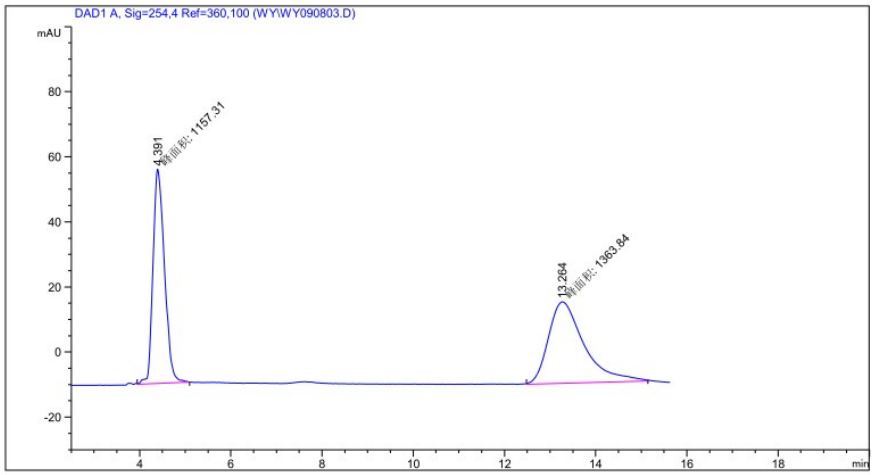


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.735	MM	2.0461	5820.07715	47.40845	49.2265
2	60.723	MM	3.5862	6002.98633	27.89836	50.7735

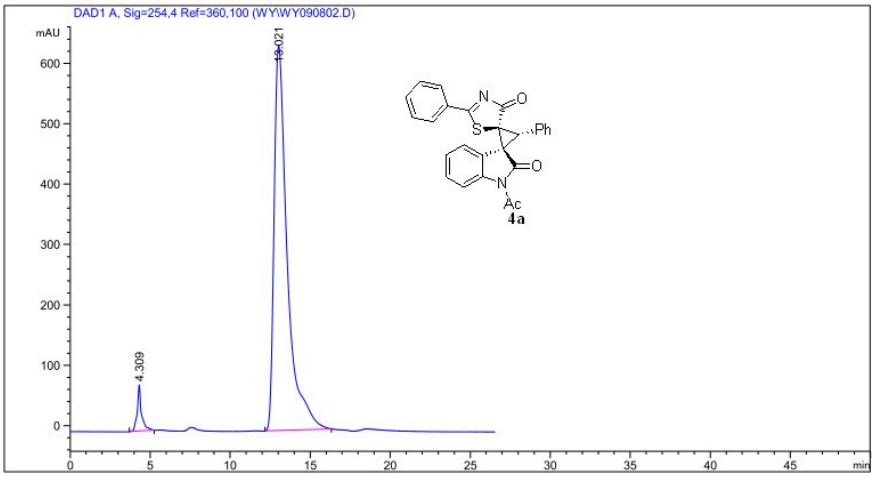


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.580	MM	2.0588	1759.10132	14.24020	10.1935
2	59.061	MM	3.9318	1.54980e4	65.69576	89.8065

Compound 4a

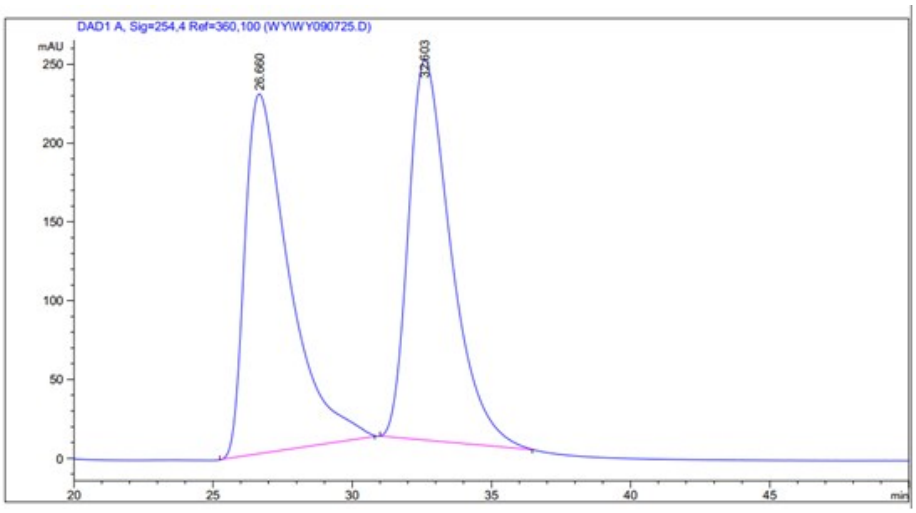


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.391	MM	0.2928	1157.30786	65.87556	45.9040
2	13.264	MM	0.9056	1363.84229	25.09993	54.0960

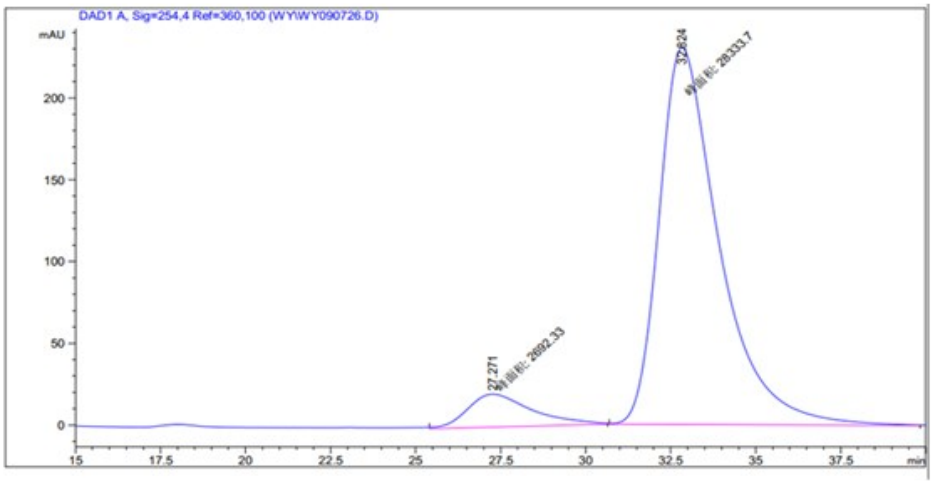


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.309	BB	0.2570	1436.48645	76.50902	3.7917
2	13.021	BB	0.8374	3.64488e4	637.14551	96.2083

Compound 4b (major)

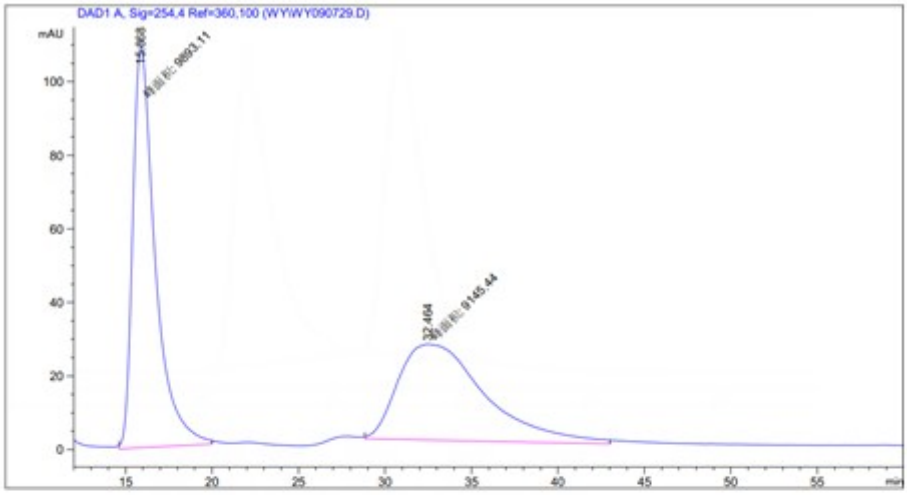


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.660	BB	1.4699	2.52583e4	228.44777	49.6041
2	32.603	BB	1.4968	2.56615e4	241.28918	50.3959

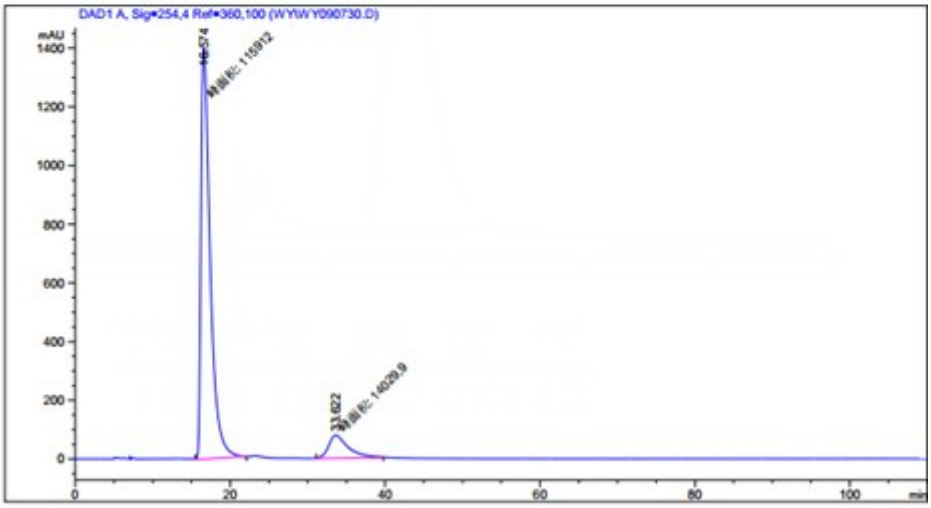


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.271	MM	2.2190	2692.32910	20.22142	8.6776
2	32.824	MM	2.0497	2.83337e4	230.39233	91.3224

Compound 4b (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.868	MM	1.5126	9893.10938	109.00809	51.9636
2	32.464	MM	5.8439	9145.43848	26.08268	48.0364
总量：				1.90385e4	135.09077	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.574	MM	1.3795	1.15912e5	1400.39795	89.2029
2	33.622	MM	2.9799	1.40299e4	78.46845	10.7971