Supporting Information

Diastereoselective Formal [3 + 3] Cycloaddition of Isatin-Based α-(Trifluoromethyl)imines with *N*, *N*'-Dialkyloxyureas

Hong-Wu Zhao,*[a] Jia-Ming Guo,[a] Li-Ru Wang,[a] Wan-Qiu Ding,[a] Zhe Tang,[a] Xiu-Qing Song,[a] Hui-Hui Wu,[a] Xiao-Zu Fan,[a] Xiao-Fan Bi[a]

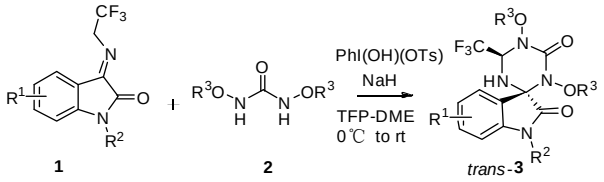
Beijing Key Laboratory of Environmental and Viral Oncology, College of Life Science and Bio-engineering, Beijing University of Technology, Beijing 100124,
P.R. China; *Phone: 86-10-6739-6211; Fax: 86-10-6739-6211; Email: hwzhao@bjut.edu.cn*

Table of Contents

1. General information

Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on 400 MHz instrument (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) and calibrated using tetramethylsilane (TMS) as internal reference. High resolution mass spectra (HRMS) were recorded under electrospray ionization (ESI) conditions. The melting point of compounds was determined by a melting point instrument. Flash column chromatography was performed on silica gel (0.035–0.070 mm) using compressed air. Thin layer chromatography (TLC) was carried out on 0.25 mm SDS silica gel coated glass plates (60F254). Eluted plates were visualized using a 254 nm UV lamp. Unless otherwise indicated, all reagents were commercially available and used without further purification. All solvents were distilled from the appropriate drying agents immediately before using. HPLC analysis was performed on Waters equipment using Chiralpak AD-H (25 cm × 0.46 cm) and OD-H (25 cm × 0.46 cm) columns. Substituted isatin-based α-(trifluoromethyl)imines (**1a**–**1q**) were prepared according to literature procedures,[1] *N, N′*-dialkyloxyureas (**2a**–**2e**) were synthesized according to the reported procedures.[2]

2. General procedure for synthesis of compounds *trans*-3

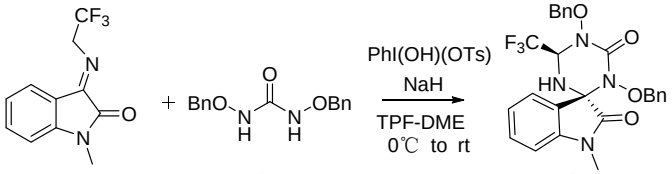


At 0 °C, to a well-stirred solution of NaH (0.3 mmol，3.0 equiv.) in TFP (0.5 mL) was added a mixture of isatin-based α-(trifluoromethyl)imines **1** (0.2 mmol, 2.0 equiv.) and *N*, *N*'-dialkyloxyureas **2** (0.1 mmol, 1.0 equiv.) in DME (0.5 mL) slowly. Then, oxidant PhI(OH)(OTs) (0.2 mmol, 2.0 equiv.) in DME (1.5 mL) was added dropwise over 1 min. After addition, the resultant reaction mixture was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and the crude products were purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford products *trans*-**3** (50–81% yields).

3. Screening of the ratio of 1a/2a/PhI(OH)(OTs)/NaH

At 0 °C, to a well-stirred solution of NaH in TFP (0.5 mL) was added a mixture of isatin-based α-(trifluoromethyl)imines **1a** and *N*, *N*'-dialkyloxyureas **2a** in DME (0.5 mL) slowly. Then, oxidant PhI(OH)(OTs) in DME (1.5 mL) was added dropwise over 1 min. After addition, the resultant reaction mixture was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and the crude products were purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford products *trans*-**3aa** (15–44% yields).

Table S1 Screening of the ratio of **1a**/**2a**/PhI(OH)(OTs)/NaH[a]



1a **2a** *trans*-**3aa**

Entry	(**1a**/**2a**/PhI(OH)(OTs)/NaH) (mmol/mmol/mmol/mmol)	Time (h)	Yield[b](%)	dr[c]
1	0.1:0.1:0.2:0.3	18	15	>99:1
2	0.15:0.1:0.2:0.3	18	23	>99:1
3	0.2:0.1:0.2:0.3	18	55	>99:1
4	0.1:0.2:0.2:0.3	18	44	>99:1
5	0.1:0.3:0.2:0.3	18	43	>99:1
6	0.1:0.3:0.2:0.3	36	44	>99:1
7	0.2:0.1:0.1:0.3	18	26	>99:1
8	0.2:0.1:0.3:0.3	18	30	>99:1
9	0.2:0.1:0.2:0.1	18	29	>99:1
10	0.2:0.1:0.2:0.2	18	27	>99:1
11	0.2:0.1:0.2:0.4	18	18	>99:1

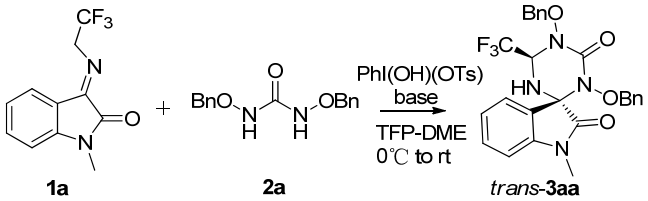
[a] Unless otherwise noted, all reactions were conducted by adding PhI(OH)(OTs) in DME (1.5 mL) to a stirred solution of NaH, isatin-based α-(trifluoromethyl)imine **1a** and *N*, *N'*-dialkyloxyurea **2a** in TFP (0.5 mL) over 30 min at 0 ℃. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

We explored the effect of the ratio of **1a**/**2a**/PhI(OH)(OTs)/NaH on the [3 + 3] cycloaddition between **1a** and **2a** as summarized in Table S2. Apparently, the tested ratios affected the chemical yield of **3aa** significantly, and generally delivered *trans*-**3aa** in > 20:1 dr. Initially, by keeping the ratio of PhI(OH)(OTs)/NaH as 0.2:0.3 (mmol/mmol), we optimized the ratio of **1a**/**2a** and found that the ratio of 0.2:0.1 gave cycloadduct **3aa** in the highest chemical yield (entries 1–5). Meanwhile, the prolonged reaction time did not improve the chemical yield greatly (entries 5 vs. 6). Finally, by using **1a**/**2a** in the ratio of 0.2:0.1, we screened the different ratios of PhI(OH)(OTs)/NaH. Unfortunately, in all these cases, the chemical yield remained quite low (entries 7–11). Currently, we finalized the optimal ratio of **1a**/**2a**/PhI(OH)(OTs)/NaH as 0.2:0.1:0.2:0.3 (entry 3).

4. Screening of bases

At 0 °C, to a well-stirred solution of base (0.3 mmol，3.0 equiv.) in TFP (0.5 mL) was added a mixture of isatin-based α-(trifluoromethyl)imines **1a** (0.1 mmol, 1.0 equiv.) and *N*, *N*'-dialkyloxyureas **2a** (0.2 mmol, 2.0 equiv.) in DME (0.5 mL) slowly. Then, oxidant PhI(OH)(OTs) (0.2 mmol, 2.0 equiv.) in DME (1.5 mL) was added dropwise over 30 min. After addition, the resultant reaction mixture was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and the crude products were purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford products *trans*-**3aa** (trace–33% yields).

Table S2 Screening of bases[a]



Entry	Base	Time (h)	Yield[b] (%)	dr[c]
1	Et_3N	18	trace	–
2	DIPEA	18	trace	–
3	DABCO	18	33	>99:1
4	DMAP	18	trace	–
5	K_2CO_3	18	trace	–
6	Cs_2CO_3	18	trace	–
7[d]	Cs_2CO_3	18	trace	–

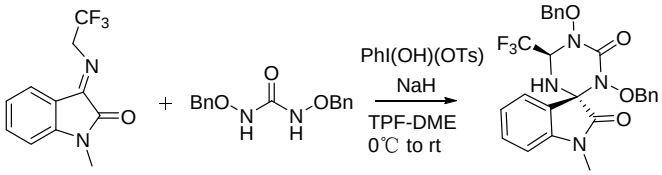
[a] Unless otherwise noted, all reactions were conducted by adding PhI(OH)(OTs) (0.2 mmol, 2.0 equiv.) in DME (1.5 mL) to a stirred solution of base (0.3 mmol, 3.0 equiv.), isatin-based α-(trifluoromethyl)imine **1a** (0.1 mmol, 1.0 equiv.) and *N, N'* -dialkyloxyurea **2a** (0.2 mmol, 2.0 equiv.) in TFP (0.5 mL) over 30 min at 0 ℃. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] the reactions were conducted by adding PhI(OH)(OTs) (0.2 mmol, 2.0 equiv.) in MeCN (1.5 mL) to a stirred solution of Cs_2CO_3 (0.3 mmol, 3.0 equiv.), isatin-based α-(trifluoromethyl)imine **1a** (0.1 mmol, 1.0 equiv.) and *N, N'* -dialkyloxyurea **2a** (0.2 mmol, 2.0 equiv.) in MeCN (0.5 mL) over 30 min at 0 ℃.

We examined the base effect on the [3 + 3] cycloaddition between **1a** and **2a** as shown in Table S1. Concerning the bases such as Et_3N, DIPEA, DMAP, K_2CO_3 and Cs_2CO_3, they furnished product **3aa** only in a trace amount (entries 1–2 & 4–7). In the case of DABCO, it gave **3aa** in 33% chemical yield (entry 3).

5. Screening of the addition time of PhI(OH)(OTs)

At 0 °C, to a well-stirred solution of NaH (0.3 mmol，3.0 equiv.) in TFP (0.5 mL) was added a mixture of isatin-based α-(trifluoromethyl)imine **1a** (0.2 mmol, 2.0 equiv.) and *N*, *N*'-dialkyloxyurea **2a** (0.1 mmol, 1.0 equiv.) in DME (0.5 mL) slowly. Then, oxidant PhI(OH)(OTs) (0.2 mmol, 2.0 equiv.) in DME (1.5 mL) was added over the indicated time. After addition, the resultant reaction mixture was stirred at room temperature. The reaction mixture was concentrated under reduced pressure and the crude products were purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford products *trans*-**3aa** (46–65% yields).

Table S3 Screening of the addition time of PhI(OH)(OTs)[a]



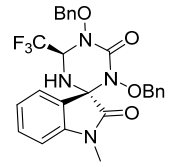
1a **2a** *trans*-**3aa**

Entry	Addition time of PhI(OH)(OTs) (min)	Time(h)	Yield[b](%)	dr[c]
1	180	18	50	>99:1
2	60	18	46	>99:1
3	30	18	55	>99:1
4	1	2	65	>99:1

[a] Unless otherwise noted, all reactions were conducted by adding PhI(OH)(OTs) (0.2 mmol, 2.0 equiv.) in DME (1.5 mL) to a stirred solution of the NaH (0.3 mmol, 3.0 equiv.), isatin-based α-(trifluoromethyl)imine **1a** (0.2 mmol, 2.0 equiv.) and *N*, *N'*-dialkyloxyurea **2a** (0.1 mmol, 1.0 equiv.) in TFP (0.5 mL) at 0 ℃. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

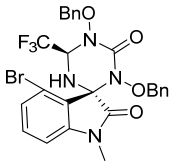
6. Characterization of compounds *trans*-3

1',5'-bis(benzyloxy)-1-methyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]triazinane]-2,6'-dione (*trans*-3aa):



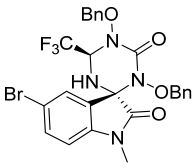
White solid, yield: 33.3 mg, 65%; M.P. = 176.2 – 177.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.49 (m, 3H), 7.42 – 7.35 (m, 4H), 7.26 – 7.22 (m, 1H), 7.21 – 7.16 (m, 3H), 6.93 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 6.8 Hz, 2H), 5.62 – 5.56 (m, 1H), 5.34 (d, J = 8.8 Hz, 1H), 5.03 – 4.97 (m, 2H), 4.49 (d, J = 9.6 Hz, 1H), 3.18 (s, 3H), 3.14 (d, J = 12.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 161.9, 144.4, 134.9, 134.5, 131.7, 129.7, 129.4, 128.7, 128.5, 128.4, 128.2, 124.4, 123.5, 123.1, 122.5 (q, $J_{C,F}$ = 280.0 Hz), 109.4, 78.8, 77.9, 75.7, 68.3 (q, $J_{C,F}$ = 32.0 Hz), 26.4 ppm; HRMS (ESI) calculated for $C_{26}H_{23}F_3N_4O_4$ $[M + H]^+$: 513.1744, found 513.1730. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 6.145 min, t_R (major) = 16.011 min.

1',5'-bis(benzyloxy)-4-bromo-1-methyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]tria-zinane]-2,6'-dione (*trans*-3ba):



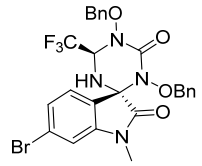
White solid, yield: 29.5 mg, 50%; M.P. = 184.8 – 186.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.53 (m, 2H), 7.42 – 7.36 (m, 4H), 7.32 – 7.30 (m, 1H), 7.24 – 7.15 (m, 3H), 6.88 – 6.85 (m, 3H), 5.60 – 5.56 (m, 1H), 5.35 (d, J = 8.8 Hz, 1H), 5.12 (d, J = 9.6 Hz, 1H), 4.98 (d, J = 8.8 Hz, 1H), 4.62 (d, J = 9.6 Hz, 1H), 4.17 (d, J = 12.4 Hz, 1H), 3.15 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 161.6, 146.8, 134.9, 134.7, 133.0, 129.6, 129.0, 128.6, 128.4, 128.3, 128.2, 127.2, 122.5 (q, $J_{C,F}$ = 280.0 Hz), 122.1, 118.8, 108.5, 78.6, 78.0, 76.6, 67.9 (q, $J_{C,F}$ = 32.0 Hz), 26.6 ppm; HRMS (ESI) calculated for $C_{26}H_{22}BrF_3N_4O_4$ $[M + H]^+$: 591.0849, found 591.0833. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 6.505 min, t_R (major) = 9.824 min.

1',5'-bis(benzyloxy)-5-bromo-1-methyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]tria-zinane]-2,6'-dione (*trans*-3ca):



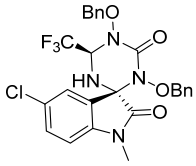
White solid, yield: 47.2 mg, 80%; M.P. = 205.9 – 207.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.54 (m, 3H), 7.43 – 7.38 (m, 4H), 7.30 – 7.28 (m, 1H), 7.25 – 7.21 (m, 2H), 6.95 – 6.93 (m, 2H), 6.78 (d, J = 8.4 Hz, 1H), 5.58 – 5.53 (m, 1H), 5.33 (d, J = 8.8 Hz, 1H), 5.02 (d, J = 10.0 Hz, 1H), 4.99 (d, J = 8.8 Hz, 1H), 4.59 (d, J = 10.0 Hz, 1H), 3.14 (s, 3H), 3.12 (d, J = 12.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 161.7, 143.4, 134.7, 134.4, 129.7, 129.4, 128.8, 128.7, 128.4, 128.3, 127.9, 126.4, 126.2, 122.3 (q, $J_{C,F}$ = 280.0 Hz), 115.9, 110.8, 78.8, 78.0, 75.5, 68.2 (q, $J_{C,F}$ = 32.0 Hz), 26.6 ppm; HRMS (ESI) calculated for $C_{26}H_{22}BrF_3N_4O_4$ $[M + H]^+$: 591.0849, found 591.0846. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 5.900 min, t_R (major) = 17.709 min.

1',5'-bis(benzyloxy)-6-bromo-1-methyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]tria-zinane]-2,6'-dione (*trans*-3da):



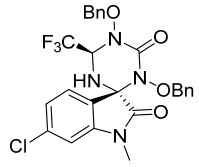
White solid, yield: 41.8 mg, 71%; M.P. = 151.5 – 152.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.53 (m, 2H), 7.43 – 7.37 (m, 3H), 7.29 – 7.20 (m, 4H), 7.15 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 1.2 Hz, 1H), 6.92 – 6.89 (m, 2H), 5.57 – 5.51 (m, 1H), 5.32 (d, J = 8.8 Hz, 1H), 5.02 – 4.96 (m, 2H), 4.53 (d, J = 10.0 Hz, 1H), 3.16 (s, 3H), 3.12 (d, J = 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 161.7, 145.6, 134.7, 134.6, 129.6, 129.3, 128.7, 128.6, 128.4, 128.3, 126.2, 125.4, 124.1, 123.4, 122.3 (q, $J_{C,F}$ = 280.0 Hz), 112.8, 78.8, 77.9, 75.3, 68.2 (q, $J_{C,F}$ = 32.0 Hz), 26.7 ppm; HRMS (ESI) calculated for $C_{26}H_{22}BrF_3N_4O_4$ $[M + H]^+$: 591.0849, found 591.0833. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 6.145 min, t_R (major) = 11.851 min.

1',5'-bis(benzyloxy)-5-chloro-1-methyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]tria-zinane]-2,6'-dione (*trans*-3ea):



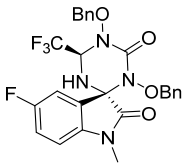
White solid, yield: 37.1 mg, 68%; M.P. = 185.9 – 187.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.54 (m, 2H), 7.45 – 7.37 (m, 4H), 7.31 – 7.27 (m, 1H), 7.24 – 7.21 (m, 3H), 6.94 – 6.92 (m, 2H), 6.83 (d, J = 8.0 Hz, 1H), 5.57 – 5.53 (m, 1H), 5.33 (d, J = 8.8 Hz, 1H), 5.03 – 5.98 (m, 2H), 4.59 (d, J = 10.0 Hz, 1H), 3.16 (s, 3H), 3.10 (d, J = 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.88, 161.79, 142.90, 134.67, 134.42, 131.46, 129.65, 129.38, 128.81, 128.77, 128.70, 128.43, 128.24, 126.00, 123.50, 122.31 (q, $J_{C,F}$ = 280.0 Hz), 110.29, 78.72, 77.93, 75.50, 68.16 (q, $J_{C,F}$ = 32.0 Hz), 26.61 ppm; HRMS (ESI) calculated for $C_{26}H_{22}ClF_3N_4O_4$ $[M + H]^+$: 547.1354, found 547.1352. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 5.481 min, t_R (major) = 15.266 min.

1',5'-bis(benzyloxy)-6-chloro-1-methyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]tria-zinane]-2,6'-dione (*trans*-3fa):



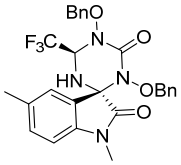
White solid, yield: 39.8 mg, 73%; M.P. = 157.9 – 158.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.53 (m, 2H), 7.43 – 7.37 (m, 3H), 7.30 – 7.26 (m, 1H), 7.24 – 7.19 (m, 3H), 7.09 (dd, J = 8.0, 1.6 Hz, 1H), 6.92 – 6.90 (m, 3H), 5.56 – 5.51 (m, 1H), 5.31 (d, J = 8.4 Hz, 1H), 5.00 (d, J = 10.0 Hz, 1H), 4.97 (d, J = 8.8 Hz, 1H), 4.53 (d, J = 10.0 Hz, 1H), 3.17 (s, 3H), 3.08 (d, J = 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 161.7, 145.5, 137.5, 134.7, 134.6, 129.6, 129.3, 128.7, 128.6, 128.4, 128.3, 124.0, 123.2, 122.8, 122.4 (q, $J_{C,F}$ = 280.0 Hz), 110.0, 78.8, 77.9, 75.3, 68.2 (q, $J_{C,F}$ = 32.0 Hz), 26.6 ppm; HRMS (ESI) calculated for $C_{26}H_{22}ClF_3N_4O_4$ $[M + H]^+$: 547.1354, found 547.1338. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 6.141 min, t_R (major) = 11.986 min.

1',5'-bis(benzyloxy)-5-fluoro-1-methyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]triaz-inane]-2,6'-dione (*trans*-3ga):



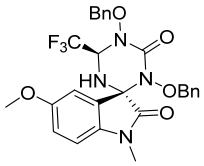
White solid, yield: 29.1 mg, 55%; M.P. = 164.7 – 166.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.53 (m, 2H), 7.42 – 7.37 (m, 3H), 7.27 – 7.26 (m, 1H), 7.23 – 7.14 (m, 3H), 6.97 (dd, J = 7.2, 2.8 Hz, 1H), 6.94 – 6.91 (m, 2H), 6.84 (dd, J = 8.4, 3.6 Hz, 1H), 5.58 – 5.53 (m, 1H), 5.32 (d, J = 8.4 Hz, 1H), 5.01 – 4.97 (m, 2H), 4.59 (d, J = 10.0 Hz, 1H), 3.17 (s, 3H), 3.07 (d, J = 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 161.8, 159.2 (d, $J_{C,F}$ =242.0 Hz), 140.3 (d, $J_{C,F}$ =3.0 Hz), 134.7, 134.5, 129.6, 129.4, 128.7 (d, $J_{C,F}$ =2.0 Hz), 128.4, 128.2, 125.8 (d, $J_{C,F}$ =8.0 Hz), 122.3 (q, $J_{C,F}$ = 280.0 Hz), 117.8 (d, $J_{C,F}$ =23.0 Hz), 111.4 (d, $J_{C,F}$ =24.0 Hz), 110.0, 109.9, 78.6, 77.9, 75.6, 68.2 (q, $J_{C,F}$ = 32.0 Hz), 26.7 ppm; HRMS (ESI) calculated for $C_{26}H_{22}F_4N_4O_4$ $[M + H]^+$: 531.1650, found 531.1639. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 5.828 min, t_R (major) = 15.268 min.

1',5'-bis(benzyloxy)-1,5-dimethyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]triazinan-e]-2,6'-dione (*trans*-3ha):



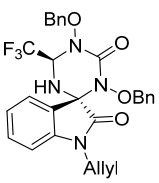
White solid, yield: 34.7 mg, 66%; M.P. = 187.6 – 188.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.54 (m, 2H), 7.42 – 7.36 (m, 3H), 7.30 – 7.23 (m, 2H), 7.21 – 7.16 (m, 3H), 6.87 – 6.84 (m, 2H), 6.82 (d, J = 8.0 Hz, 1H), 5.63 – 5.59 (m, 1H), 5.34 (d, J = 8.8 Hz, 1H), 5.02 (d, J = 5.6 Hz, 1H), 4.99 (d, J = 4.4 Hz, 1H), 4.54 (d, J = 9.6 Hz, 1H), 3.15 – 3.12 (m, 4H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 161.9, 142.1, 134.9, 134.6, 133.1, 131.8, 129.6, 129.3, 128.6, 128.5, 128.4 128.1, 124.5, 123.6, 122.4 (q, $J_{C,F}$ = 280.0 Hz), 109.1, 78.7, 77.8, 75.7, 68.2 (q, $J_{C,F}$ = 32.0 Hz), 26.5, 21.1 ppm; HRMS (ESI) calculated for $C_{27}H_{25}F_3N_4O_4$ $[M + H]^+$: 527.1901, found 527.1888. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 5.147 min, t_R (major) = 16.877 min.

1',5'-bis(benzyloxy)-5-methoxy-1-methyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]tr-iazinane]-2,6'-dione (*trans*-3ia):



White solid, yield: 28.1 mg, 52%; M.P. = 189.1 – 190.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.53 (m, 2H), 7.42 – 7.36 (m, 3H), 7.25 – 7.16 (m, 3H), 7.02 – 6.98 (m, 2H), 6.89 – 6.86 (m, 2H), 6.84 (dd, J =7.6, 1.6 Hz, 1H), 5.62 – 5.57 (m, 1H), 5.32 (d, J = 8.8 Hz, 1H), 5.02 (d, J = 9.6 Hz, 1H), 4.98 (d, J = 8.8 Hz, 1H), 4.55 (d, J = 10.0 Hz, 1H), 3.84 (s, 3H), 3.16 (s, 3H), 3.09 (d, J=12.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 161.9, 156.6, 137.7, 134.8, 134.6, 129.6, 129.2, 128.6, 128.4, 128.3, 128.1, 125.6, 121.4 (q, $J_{C,F}$ = 280.0 Hz), 115.7, 110.5, 109.9, 78.7, 77.8, 75.8, 68.3 (q, $J_{C,F}$ = 32.0 Hz), 56.0, 26.6 ppm; HRMS (ESI) calculated for $C_{27}H_{25}F_3N_4O_5$ $[M + H]^+$: 543.1850, found 543.1846. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 12.844 min, t_R (major) = 26.065 min.

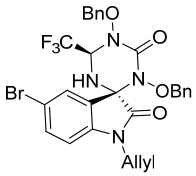
1-allyl-1',5'-bis(benzyloxy)-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]triazinane]-2,6'-dione (*trans*-3ja):



Colorless transparent semisolid, yield: 41.9 mg, 78%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.54 (m, 2H), 7.50 – 7.46 (m, 2H), 7.42 – 7.37 (m, 3H), 7.24 – 7.21 (m, 2H),

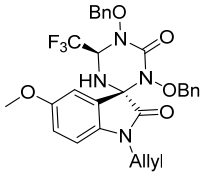
7.16 – 7.14 (m, 2H), 6.90 (d, J = 7.6 Hz, 1H), 6.79 – 6.77 (m, 2H), 5.68 – 5.60 (m, 2H), 5.34 (d, J = 8.8 Hz, 1H), 5.06 (d, J = 9.2 Hz, 1H), 5.01 (s, 1H), 4.98 – 4.94 (m, 2H), 4.46 – 4.40 (m, 2H), 4.16 – 4.10 (m, 1H), 3.19 (d, J = 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 161.9, 143.7, 134.8, 134.3, 131.5, 129.7, 129.6, 129.4, 128.6, 128.5, 128.4, 128.1, 124.6, 123.3, 122.9, 122.4 (q, $J_{C,F}$ = 280.0 Hz), 117.7, 110.4, 78.9, 77.8, 75.6, 68.2 (q, $J_{C,F}$ = 32.0 Hz), 42.3 ppm; HRMS (ESI) calculated for $C_{28}H_{25}F_3N_4O_4$ [M + H]$^+$: 539.1901, found 539.1896. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 5.366 min, t_R (major) = 19.029 min.

1-allyl-1',5'-bis(benzyloxy)-5-bromo-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]triazin-ane]-2,6'-dione (*trans*-3ka):



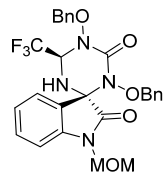
White semisolid, yield: 49.7 mg, 81%; M.P. = 56.4 – 57.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.54 (m, 3H), 7.48 (d, J = 2.0 Hz, 1H), 7.20 – 7.37 (m, 4H), 7.27 – 7.19 (m, 2H), 6.89 – 6.87 (m, 2H), 6.75 (d, J = 8.4 Hz, 1H), 5.58 – 5.54 (m, 2H), 5.32 (d, J = 8.4 Hz, 1H), 5.07 (d, J = 9.6 Hz, 1H), 5.01 – 4.97 (m, 3H), 4.53 (d, J =9.6 Hz, 1H), 4.40 – 4.39 (m, 1H), 4.14 – 4.12 (m, 1H), 3.11 (d, J =12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 161.8, 142.6, 134.7, 134.3, 134.2, 129.6, 129.4, 129.2, 128.8, 128.7, 128.4, 128.2, 126.5, 126.3, 122.3 (q, $J_{C,F}$ = 280.0 Hz), 118.0, 115.8, 111.9, 79.0, 78.0, 75.5, 68.2 (q, $J_{C,F}$ = 32.0 Hz), 42.4 ppm; HRMS (ESI) calculated for $C_{28}H_{24}BrF_3N_4O_4$ [M + H]$^+$: 617.1006, found 617.0992. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 5.102 min, t_R (major) = 22.363 min.

1-allyl-1',5'-bis(benzyloxy)-5-methoxy-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]triaz-inane]-2,6'-dione (*trans*-3la):



Colorless transparent semisolid, yield: 42.6 mg, 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.53 (m, 2H), 7.41 – 7.36 (m, 3H), 7.24 – 7.22 (m, 1H), 7.19 – 7.15 (m, 2H), 7.04 (d, J = 2.4 Hz, 1H), 6.98 (dd, J = 8.4, 2.4 Hz, 1H), 6.84 – 6.80 (m, 3H), 5.64 – 5.59 (m, 2H), 5.32 (d, J = 8.8 Hz, 1H), 5.07 – 4.97 (m, 4H), 4.51 (d, J =9.2 Hz, 1H), 4.40 – 4.39 (m, 1H), 4.14 – 4.10 (m, 1H), 3.85 (s, 3H), 3.11 (d, J =12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 161.9, 156.5, 136.8, 134.8, 134.4, 130.0, 129.6, 129.4, 128.6, 128.5, 128.4, 128.1, 125.6, 122.4 (q, $J_{C,F}$ = 280.0 Hz), 117.7, 115.7, 111.0, 110.3, 78.8, 77.8, 75.8, 68.2 (q, $J_{C,F}$ = 32.0 Hz), 56.0, 42.4 ppm; HRMS (ESI) calculated for $C_{29}H_{27}F_3N_4O_5$ [M + H]$^+$: 569.2006, found 569.1991. HPLC separation (Chiralpak OD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 6.358 min, t_R (major) = 7.149 min.

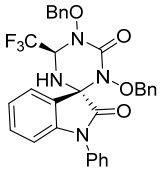
1',5'-bis(benzyloxy)-1-(methoxymethyl)-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]tri-azinane]-2,6'-dione (*trans*-3ma):



White solid, yield: 36.3 mg, 67%; M.P. = 141.0 – 142.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.51 (m, 4H), 7.41 – 7.38 (m, 3H), 7.29 – 7.27 (m, 1H), 7.26 – 7.21 (m, 1H), 7.18 – 7.14 (m, 3H), 6.76 – 6.74 (m, 2H), 5.57 – 5.34 (m, 1H), 5.33 (d, J = 8.0 Hz, 1H), 5.15 (d, J = 11.2 Hz, 1H), 5.06 (d, J = 9.2 Hz, 1H), 5.02 (d, J = 11.2 Hz, 1H), 4.98 (d, J = 8.4 Hz, 1H), 4.41 (d, J = 8.8 Hz, 1H), 3.17 (d, J = 12.0 Hz, 1H), 2.92

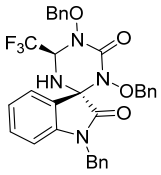
(s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 161.9, 142.7, 134.7, 134.1, 131.7, 129.7, 129.4, 128.7, 128.6, 128.4, 128.2, 124.2, 123.9, 122.9, 122.3 (q, $J_{C,F}$ = 280.0 Hz), 111.2, 79.0, 77.9, 76.0, 71.3, 68.3 (q, $J_{C,F}$ = 32.0 Hz), 55.9 ppm; HRMS (ESI) calculated for $C_{27}H_{25}F_3N_4O_5$ $[M + H]^+$: 543.1850, found 543.1830. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 5.132 min, t_R (major) = 8.517 min.

1',5'-bis(benzyloxy)-1-phenyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]triazinane]-2,6'-dione (*trans*-3na):



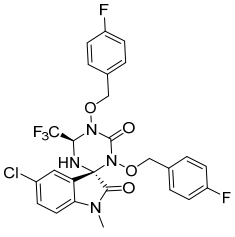
White solid, yield: 39.0 mg, 68%; M.P. = 68.2 – 69.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.52 (m, 3H), 7.49 – 7.45 (m, 3H), 7.43 – 7.35 (m, 4H), 7.29 – 7.22 (m, 4H), 7.20 – 7.17 (m, 2H), 6.91 (d, J = 8.0 Hz, 1H), 6.85 – 6.83 (m, 2H), 5.66 – 5.61 (m, 1H), 5.32 (d, J = 8.4 Hz, 1H), 5.09 (d, J = 9.2 Hz, 1H), 5.00 (d, J = 8.4 Hz, 1H), 4.51 (d, J = 9.6 Hz, 1H), 3.22 (d, J = 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 166.7, 144.8, 134.8, 134.5, 133.3, 131.6, 129.7, 129.6, 129.2, 128.7, 128.6, 128.5, 128.4, 128.2, 126.4, 124.4, 123.8, 123.2, 122.4 (q, $J_{C,F}$ = 280.0 Hz), 110.7, 78.9, 77.7, 75.7, 68.2 (q, $J_{C,F}$ = 32.0 Hz) ppm; HRMS (ESI) calculated for $C_{31}H_{25}F_3N_4O_4$ $[M + H]^+$: 575.1901, found 575.1891. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 5.717 min, t_R (major) = 7.440 min.

1-benzyl-1',5'-bis(benzyloxy)-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]triazinane]-2,6'-dione (*trans*-3oa):



White solid, yield: 41.1 mg, 70%; M.P. = 97.7 – 98.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.56 (m, 2H), 7.52 (d, J = 6.8 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.26 – 7.24 (m, 1H), 7.21 – 7.17 (m, 1H), 7.16 – 7.11 (m, 3H), 7.06 (d, J = 7.6 Hz, 2H), 6.98 – 6.94 (m, 2H), 6.78 – 6.76 (m, 2H), 6.71 (d, J = 7.6 Hz, 1H), 5.70 – 5.65 (m, 1H), 5.37 (d, J = 8.8 Hz, 1H), 5.24 (d, J = 16.0 Hz, 1H), 5.11 (d, J = 8.8 Hz, 1H), 5.02 (d, J = 8.8 Hz, 1H), 4.55 (d, J = 16.0 Hz, 1H), 4.45 (d, J = 9.2 Hz, 1H), 3.26 (d, J = 12.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 162.0, 143.6, 134.8, 134.2, 134.0, 131.5, 129.7, 129.5, 128.7, 128.6, 128.5, 128.4, 128.3, 127.5, 126.7, 124.6, 123.4, 122.9,122.4 (q, $J_{C,F}$ = 280.0 Hz), 110.7, 79.0, 77.9, 75.6, 68.2 (q, $J_{C,F}$ = 32.0 Hz), 43.9 ppm; HRMS (ESI) calculated for $C_{32}H_{27}F_3N_4O_4$ $[M + H]^+$: 589.2057, found 589.2044. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 8.322 min, t_R (major) = 22.662 min.

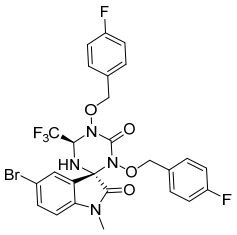
5-chloro-1',5'-bis((4-fluorobenzyl)oxy)-1-methyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]triazinane]-2,6'-dione (*trans*-3eb):



White solid, yield: 36.6 mg, 63%; M.P. = 72.9 – 73.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.50 (m, 2H), 7.45 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.19 (d, J = 2.0 Hz, 1H), 7.08 (t, J = 8.8 Hz, 2H), 6.92 – 6.90 (m, 4H), 6.84 (d, J = 8.4 Hz, 1H), 5.54–5.49 (m, 1H), 5.25 (d, J = 8.8 Hz, 1H), 4.96 – 4.92 (m, 2H), 4.55 (d, J = 10.4 Hz, 1H), 3.18 (s, 3H), 3.06 (d, J = 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 163.1 (d, $J_{C,F}$ = 245.0 Hz), 163.0 (d, $J_{C,F}$ = 246.0 Hz), 161.8, 142.9, 131.6 (d, $J_{C,F}$ = 9.0 Hz), 131.4, 131.3 (d, $J_{C,F}$ = 8.0 Hz), 130.5 (d, $J_{C,F}$ = 3.0 Hz), 130.4 (d, $J_{C,F}$ = 3.0 Hz), 128.9, 125.9, 123.5, 122.2 (q, $J_{C,F}$ = 280.0 Hz), 115.4 (d, $J_{C,F}$ = 8.0 Hz), 115.2 (d, $J_{C,F}$ = 8.0 Hz), 110.3, 77.8, 76.9, 75.5, 68.2 (q, $J_{C,F}$ = 32.0 Hz), 26.7 ppm; HRMS (ESI) calculated for

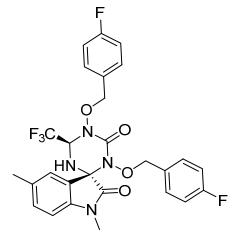
$C_{26}H_{20}ClF_5N_4O_4$ [M + H]$^+$: 583.1166, found 583.1153. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 5.893 min, t_R (major) = 16.830 min.

5-bromo-1',5'-bis((4-fluorobenzyl)oxy)-1-methyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]triazinane]-2,6'-dione (*trans*-3cb):



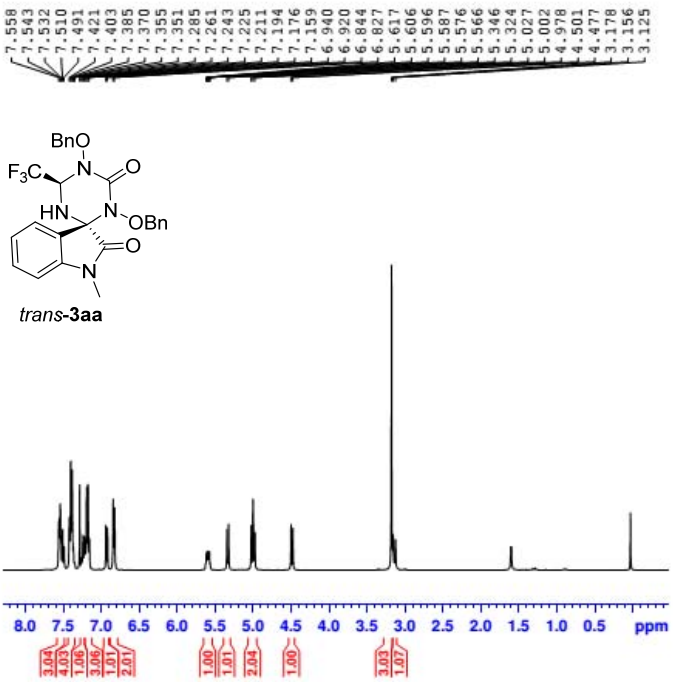
White solid, yield: 43.9 mg, 70%; M.P. = 62.0 – 63.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, J = 8.4, 2.0 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.35 (d, J = 2.0 Hz, 1H), 7.10 – 7.06 (m, 2H), 6.92 – 6.90 (m, 4H), 6.80 (d, J = 8.4 Hz, 1H), 5.54 – 5.48 (m, 1H), 5.25 (d, J = 9.2 Hz, 1H), 4.96 – 4.92 (m, 2H), 4.55 (d, J = 10.0 Hz, 1H), 3.17 (s, 3H), 3.05 (d, J = 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 163.0 (d, $J_{C,F}$ = 245.0 Hz), 162.9 (d, $J_{C,F}$ = 296.0 Hz), 161.8, 143.4, 134.4,131.6 (d, $J_{C,F}$ = 8.0 Hz), 131.3 (d, $J_{C,F}$ = 8.0 Hz), 130.5 (d, $J_{C,F}$ = 3.0 Hz), 130.3 (d, $J_{C,F}$ = 3.0 Hz), 126.3, 126.2, 122.2 (q, $J_{C,F}$ = 280.0 Hz), 115.9, 115.4 (d, $J_{C,F}$ = 5.0 Hz), 115.2 (d, $J_{C,F}$ = 5.0 Hz), 110.7, 77.8, 76.9, 75.5, 68.2 (q, $J_{C,F}$ = 32.0 Hz), 26.6 ppm; HRMS (ESI) calculated for $C_{26}H_{20}BrF_5N_4O_4$ [M + H]$^+$: 627.0661, found 627.0646. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 6.305 min, t_R (major) = 19.609 min.

1',5'-bis((4-fluorobenzyl)oxy)-1,5-dimethyl-4'-(trifluoromethyl)spiro[indoline-3,2'-[1,3,5]triazinane]-2,6'-dione (*trans*-3hb):

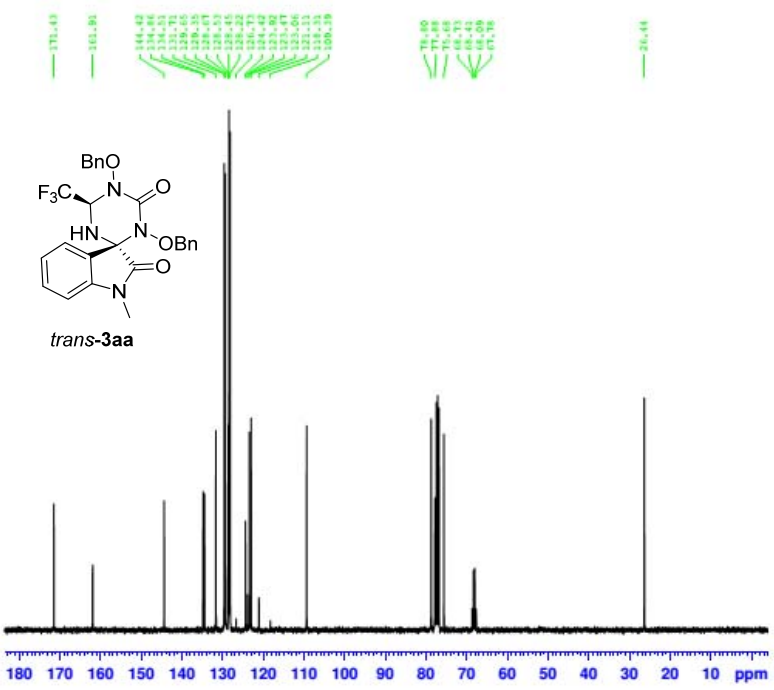


White solid, yield: 32.5 mg, 58%; M.P. = 70.3 – 71.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.50 (m, 2H), 7.31 – 7.30 (m, 1H), 7.15 – 7.14 (m, 1H), 7.10 – 7.05 (m, 2H), 6.89 – 6.79 (m, 5H), 5.58 – 5.54 (m, 1H), 5.26 (d, J = 8.8 Hz, 1H), 4.95 – 4.93 (m, 2H), 4.49 (d, J = 10.0 Hz, 1H), 3.16 (s, 3H), 3.08 (d, J = 12.0 Hz, 1H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 163.0 (d, $J_{C,F}$ = 246.0 Hz), 162.8 (d, $J_{C,F}$ = 246.0 Hz), 162.0, 142.1, 133.2, 131.8, 131.5 (d, $J_{C,F}$ = 8.0 Hz), 131.2 (d, $J_{C,F}$ = 8.0 Hz), 130.7 (d, $J_{C,F}$ = 4.0 Hz), 130.5 (d, $J_{C,F}$ = 4.0 Hz), 124.4, 123.5, 122.4 (q, $J_{C,F}$ = 280.0 Hz), 115.3 (d, $J_{C,F}$ = 22.0 Hz), 115.1 (d, $J_{C,F}$ = 21.0 Hz), 109.1, 77.8, 77.0, 75.7, 68.2 (q, $J_{C,F}$ = 32.0 Hz), 26.5, 21.1 ppm; HRMS (ESI) calculated for $C_{27}H_{23}F_5N_4O_4$ [M + H]$^+$: 563.1712, found 563.1702. HPLC separation (Chiralpak AD-H column, solvent: hexane/ethanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm): retention times t_R (minor) = 5.624 min, t_R (major) = 22.851 min.

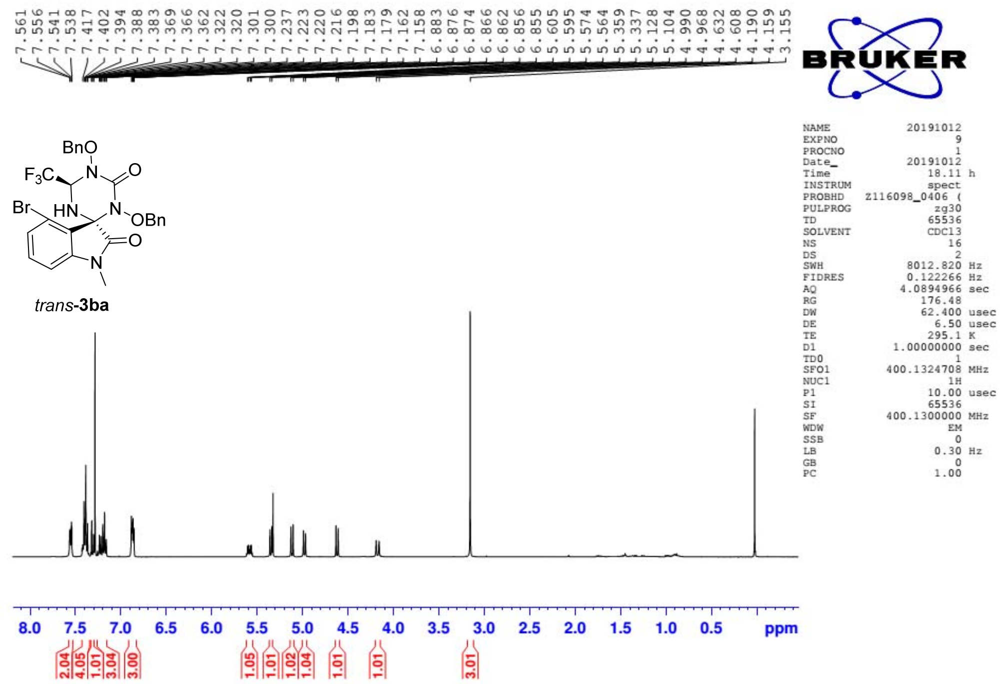
7. ^{1}H and ^{13}C NMR spectra of compounds *trans*-3

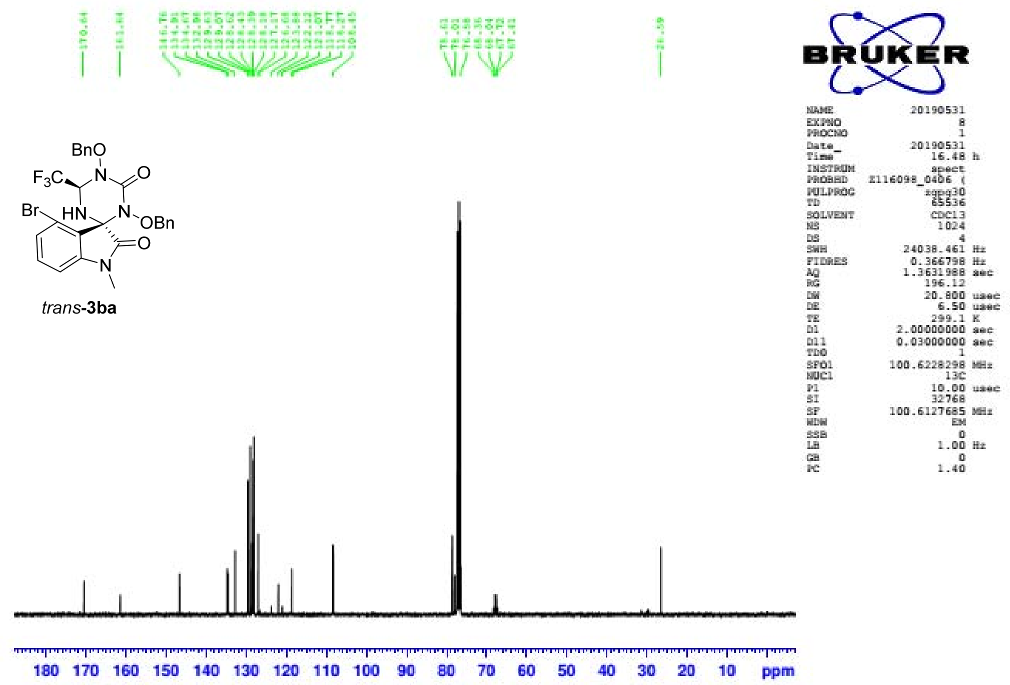


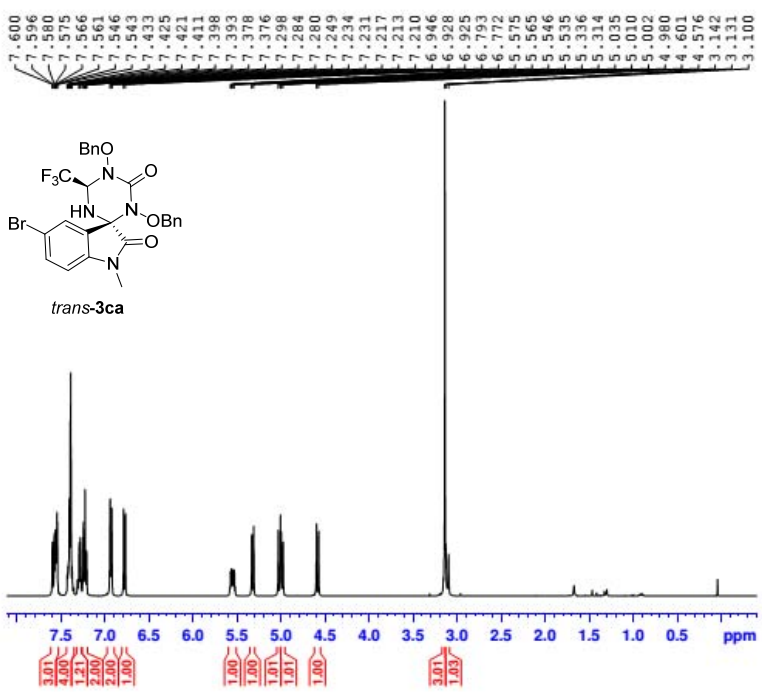

```
NAME                20190611
EXPNO                      1
PROCNO                     1
Date_            20190611
Time                  9.11 h
INSTRUM                spect
PROBHD    2116098_0406 (
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894966 sec
RG                    141.68
DW                    62.400 usec
DE                     6.50 usec
TE                    298.5 K
D1                 1.00000000 sec
TD0                        1
SFO1             400.1324708 MHz
NUC1                      1H
P1                    10.00 usec
SI                     65536
SF               400.1300000 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                      1.00
```



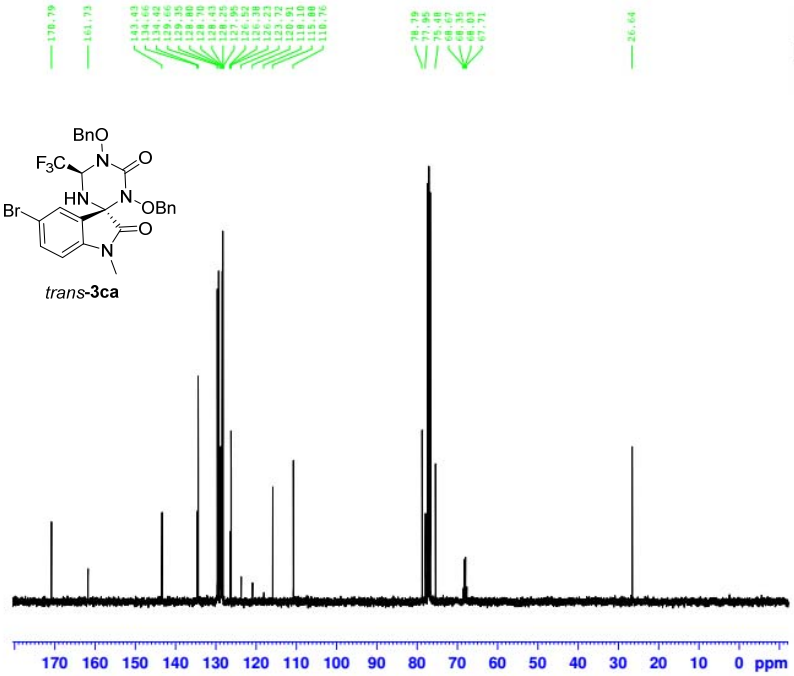

```
NAME                20190610
EXPNO                     12
PROCNO                     1
Date_            20190610
Time                 12.18 h
INSTRUM                spect
PROBHD    2116098_0406 (
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       256
DS                         4
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631988 sec
RG                    196.12
DW                    20.800 usec
DE                     6.50 usec
TE                    298.9 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1
SFO1             100.6228298 MHz
NUC1                      13C
P1                    10.00 usec
SI                     32768
SF               100.6127685 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                      1.40
```


BnO
F3C
HN
N
O
Br
OBn
trans-3ba
BRUKER
ppm

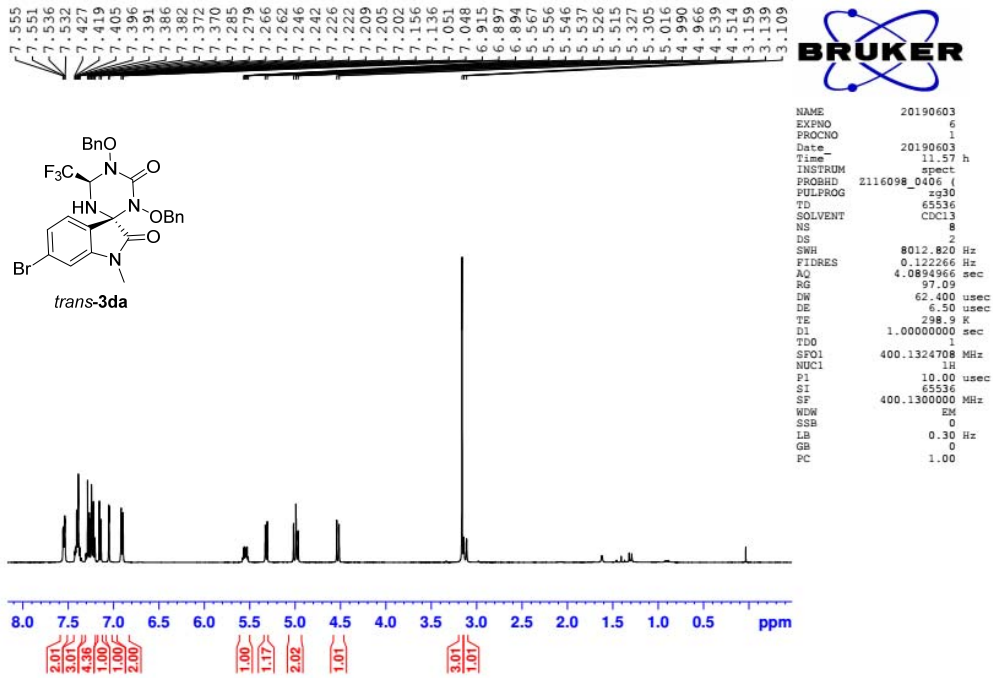

BnO
F3C
HN
N
O
Br
OBn
trans-3ba
BRUKER
ppm

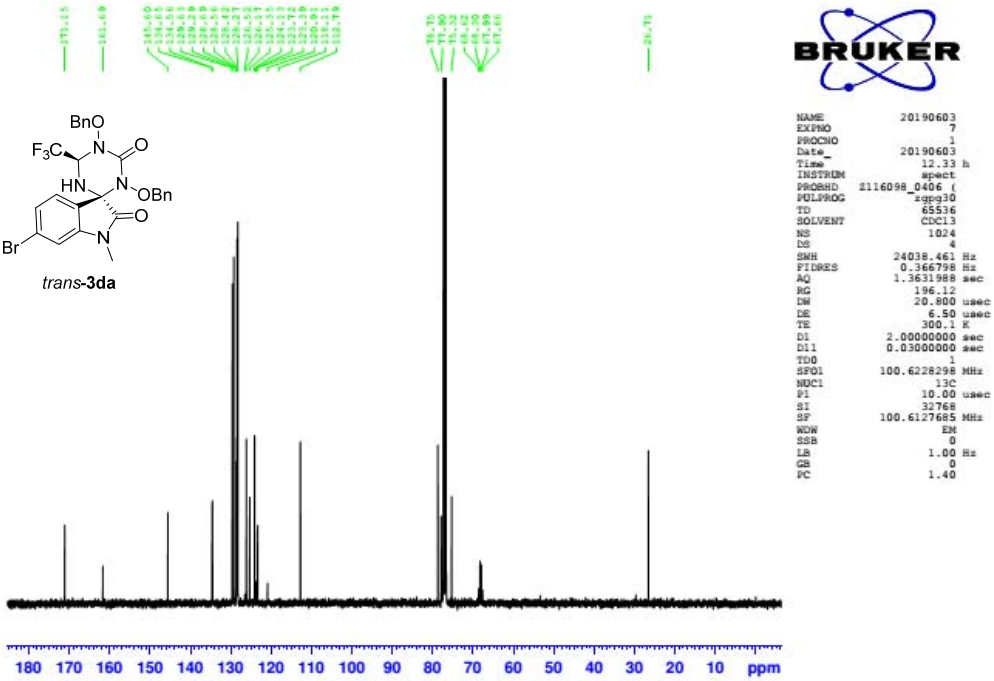


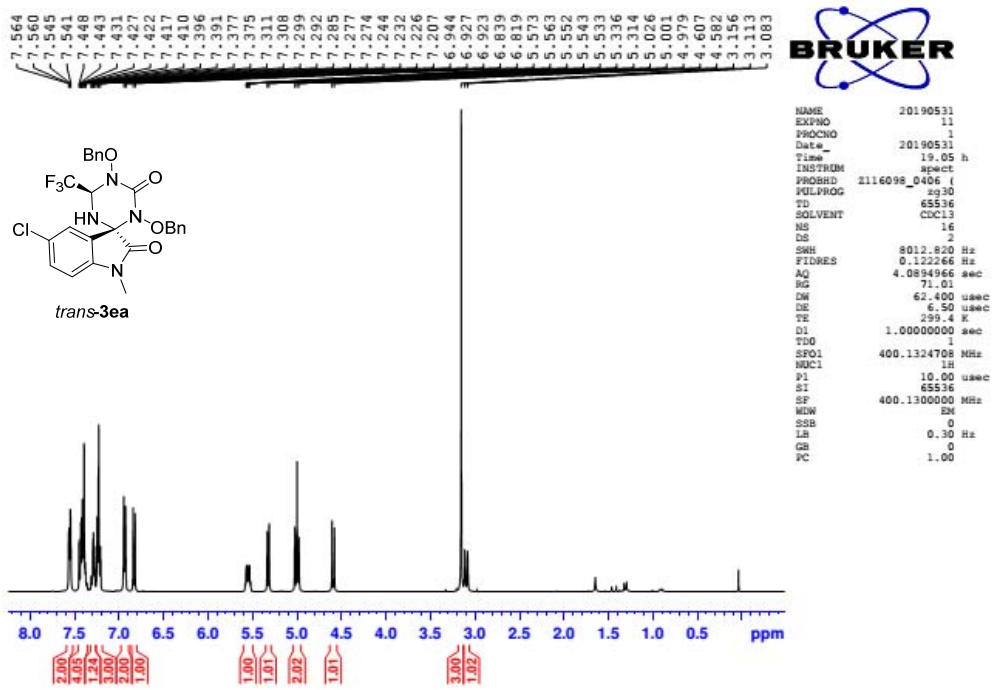
```
NAME                20190531
EXPNO                      1
PROCNO                     1
Date_               20190531
Time                   14.44 h
INSTRUM                spect
PROBHD     Z116098_0406 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        16
DS                         2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                  4.0894966 sec
RG                     63.47
DW                    62.400 usec
DE                     6.50 usec
TE                    298.5 K
D1                  1.00000000 sec
TD0                        1
SFO1              400.1324708 MHz
NUC1                       1H
P1                    10.00 usec
SI                    65536
SF                400.1300000 MHz
WDW                       EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                     1.00
```

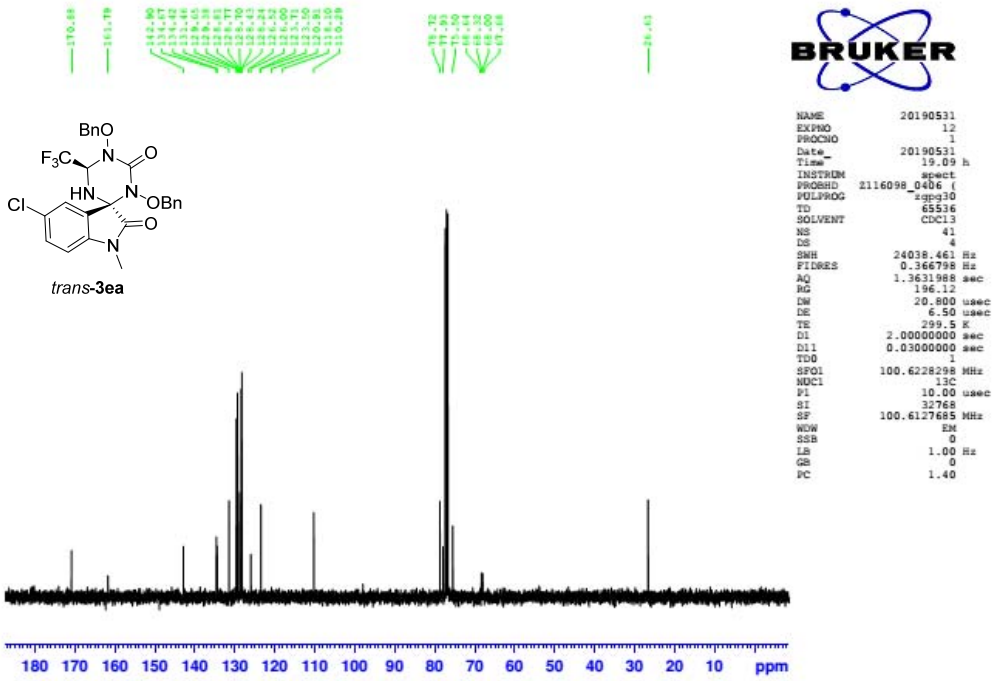


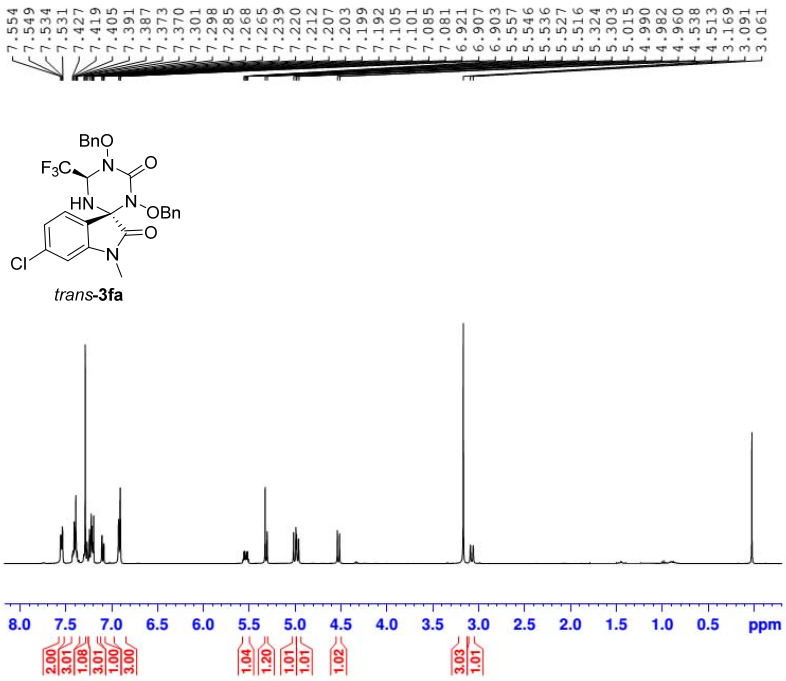
```
NAME                20190531
EXPNO                      2
PROCNO                     1
Date_               20190531
Time                   14.46 h
INSTRUM                spect
PROBHD     Z116098_0406 (
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       266
DS                         4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                    196.12
DW                    20.800 usec
DE                     6.50 usec
TE                    298.7 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                        1
SFO1              100.6228298 MHz
NUC1                       13C
P1                    10.00 usec
SI                    32768
SF                100.6127685 MHz
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                     1.40
```


7.555
7.551
7.536
7.532
7.427
7.419
7.405
7.396
7.391
7.386
7.382
7.372
7.370
7.285
7.279
7.266
7.262
7.246
7.242
7.226
7.222
7.209
7.205
7.202
7.156
7.136
7.051
7.048
6.915
6.897
6.894
5.567
5.556
5.546
5.537
5.526
5.515
5.327
5.305
5.016
4.990
4.966
4.539
4.514
3.159
3.139
3.109
BnO
F3C
HN
OBn
Br
trans-3da
BRUKER
NAME 20190603
EXPNO 6
PROCNO 1
Date_ 20190603
Time 11.57 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 97.09
DW 62.400 usec
DE 6.50 usec
TE 298.9 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.01 3.01 4.36 1.00 1.00 2.00 1.00 1.17 2.02 1.01 3.01 1.01


BnO
F3C
HN
OBn
Br
trans-3da
BRUKER
NAME 20190603
EXPNO 7
PROCNO 1
Date_ 20190603
Time 12.33 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 196.12
DW 20.800 usec
DE 6.50 usec
TE 300.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

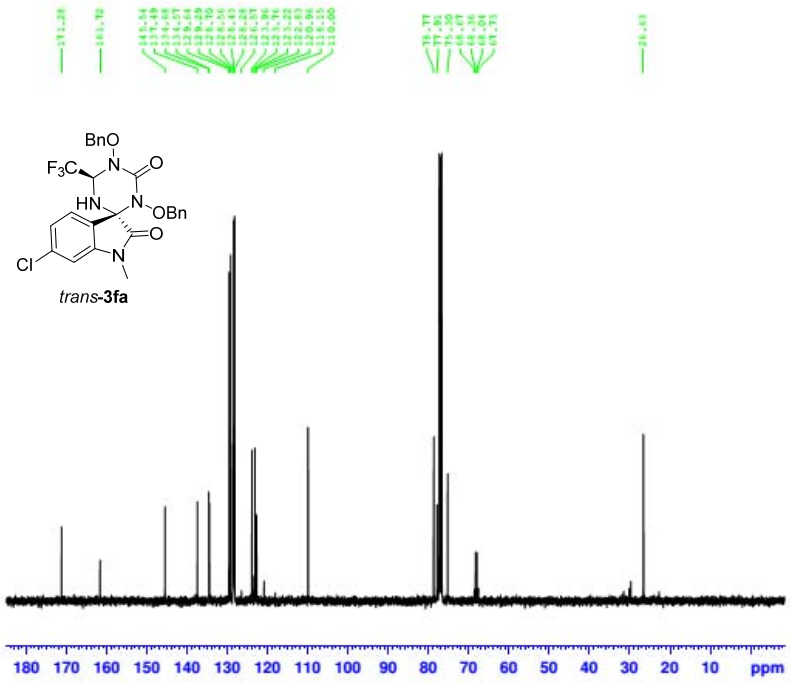

7.564
7.560
7.545
7.541
7.448
7.443
7.431
7.427
7.422
7.417
7.410
7.396
7.391
7.377
7.375
7.311
7.308
7.299
7.292
7.285
7.277
7.274
7.244
7.232
7.226
7.207
6.944
6.927
6.923
6.839
6.819
5.573
5.563
5.552
5.543
5.533
5.336
5.314
5.026
5.001
4.979
4.607
4.582
3.156
3.113
3.083
BRUKER
BnO
F3C
N
O
HN
N
OBn
Cl
O
N
trans-3ea
NAME 20190531
EXPNO 11
PROCNO 1
Date_ 20190531
Time 19.05 h
INSTRUM spect
PROBHD 2116098_0406 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 71.01
DW 62.400 usec
DE 6.50 usec
TE 299.4 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
4.05
1.24
3.00
2.00
1.00
1.00
1.01
2.02
1.01
3.00
1.02


BRUKER
BnO
F3C
N
O
HN
N
OBn
Cl
O
N
trans-3ea
NAME 20190531
EXPNO 12
PROCNO 1
Date_ 20190531
Time 19.09 h
INSTRUM spect
PROBHD 2116098_0406 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 41
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 196.12
DW 20.800 usec
DE 6.50 usec
TE 299.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



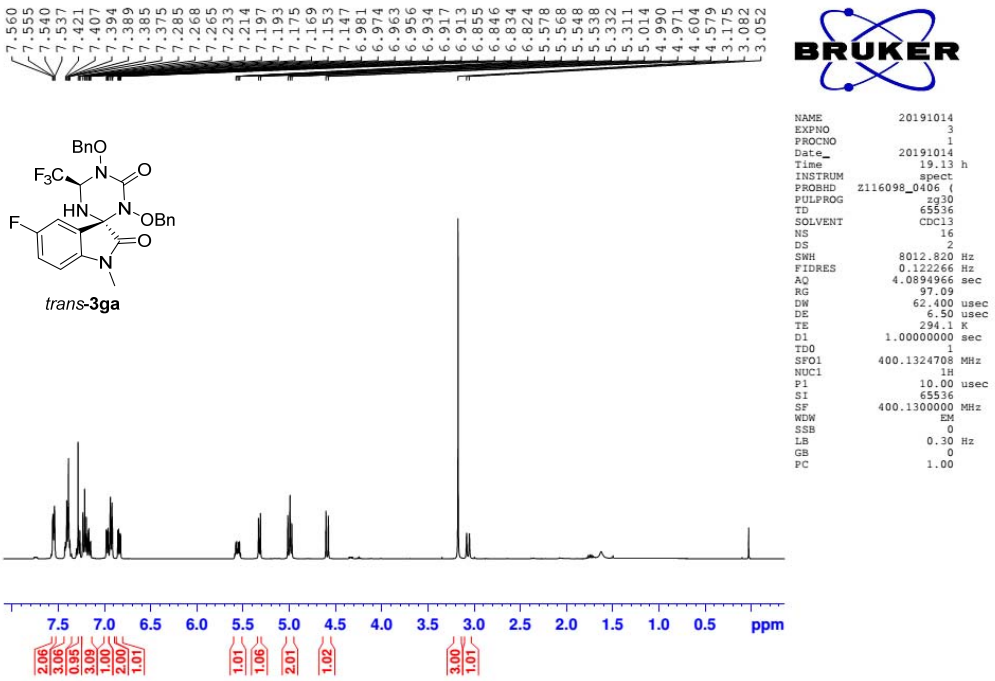
BRUKER

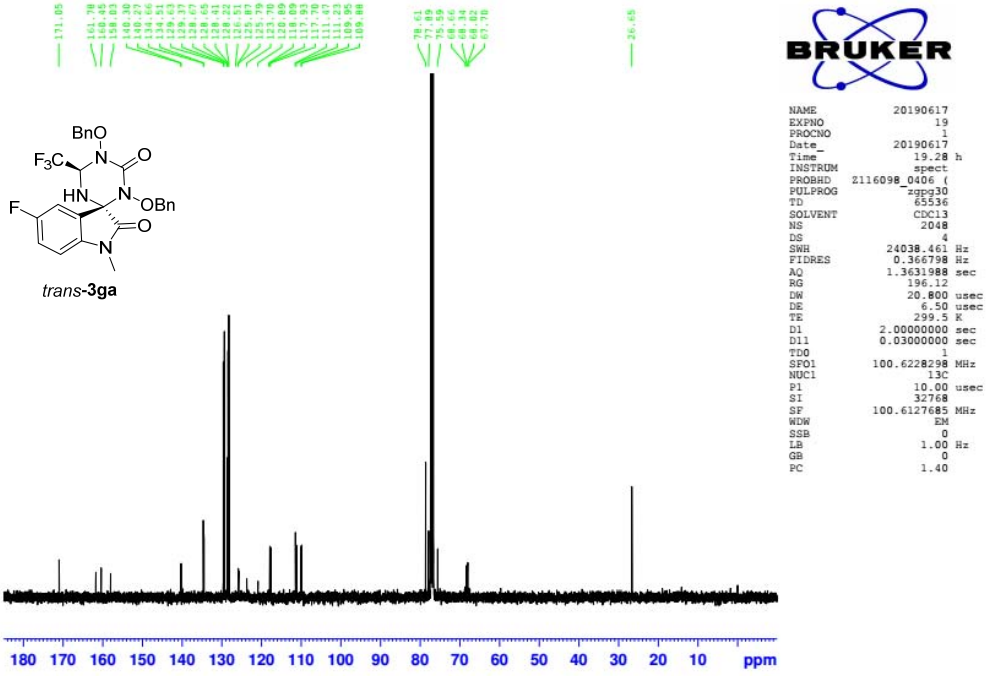
```
NAME                20191012
EXPNO                      6
PROCNO                     1
Date_               20191012
Time                   17.57 h
INSTRUM                spect
PROBHD     Z116098_0406 (
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                  4.0894966 sec
RG                     176.48
DW                     62.400 usec
DE                      6.50 usec
TE                     295.2 K
D1                  1.00000000 sec
TD0                        1
SFO1               400.1324708 MHz
NUC1                       1H
P1                     10.00 usec
SI                     65536
SF                 400.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

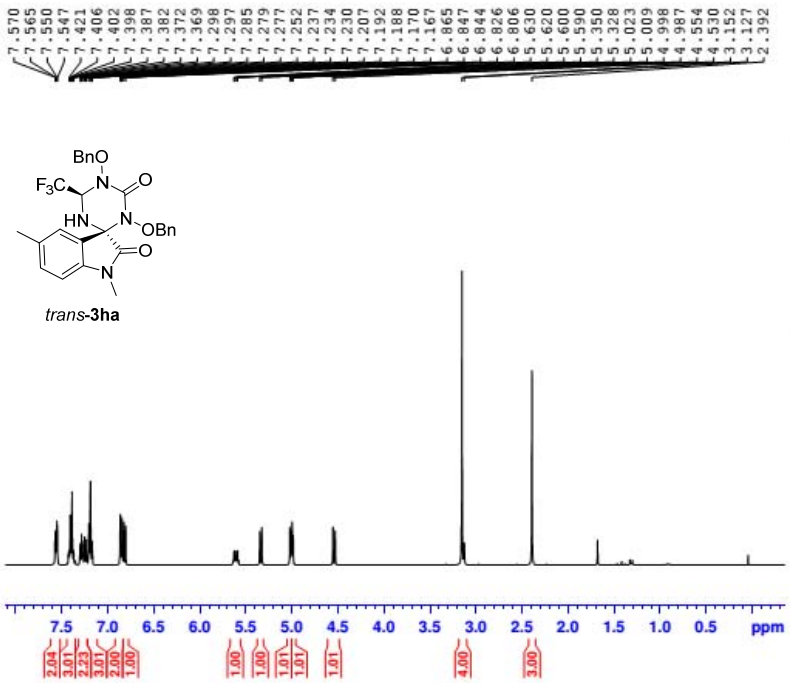


BRUKER

```
NAME                20190603
EXPNO                     11
PROCNO                     1
Date_               20190603
Time                   14.10 h
INSTRUM                spect
PROBHD     Z116098_0406 (
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       398
DS                         4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                     196.12
DW                     20.800 usec
DE                      6.50 usec
TE                     300.3 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                        1
SFO1               100.6228298 MHz
NUC1                       13C
P1                     10.00 usec
SI                     32768
SF                 100.6127685 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

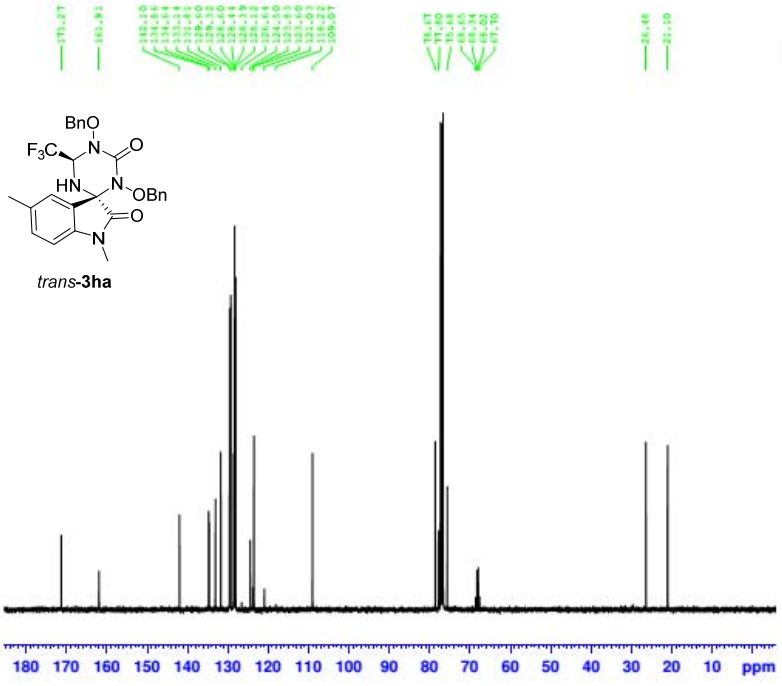

7.560
7.555
7.540
7.537
7.421
7.407
7.394
7.389
7.385
7.375
7.285
7.268
7.265
7.233
7.214
7.197
7.193
7.175
7.169
7.153
7.147
6.981
6.974
6.963
6.956
6.934
6.917
6.913
6.855
6.846
6.834
6.824
5.578
5.568
5.548
5.538
5.332
5.311
5.014
4.990
4.971
4.604
4.579
3.175
3.082
3.052
BnO
F3C
HN
OBn
F
trans-3ga
NAME 20191014
EXPNO 3
PROCNO 1
Date_ 20191014
Time 19.13 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 97.09
DW 62.400 usec
DE 6.50 usec
TE 294.1 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.06 3.06 0.85 3.09 1.00 2.00 1.01 1.01 1.06 2.01 1.02 3.00 1.01


171.85
161.78
159.45
159.03
140.30
140.27
134.66
134.51
129.43
129.37
128.67
128.65
128.41
128.22
126.51
125.87
125.79
123.70
123.69
118.09
117.93
117.70
117.67
111.23
109.95
109.88
78.61
77.89
75.59
68.66
68.34
68.02
67.70
26.65
BnO
F3C
HN
OBn
F
trans-3ga
NAME 20190617
EXPNO 19
PROCNO 1
Date_ 20190617
Time 19.28 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 196.12
DW 20.800 usec
DE 6.50 usec
TE 299.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



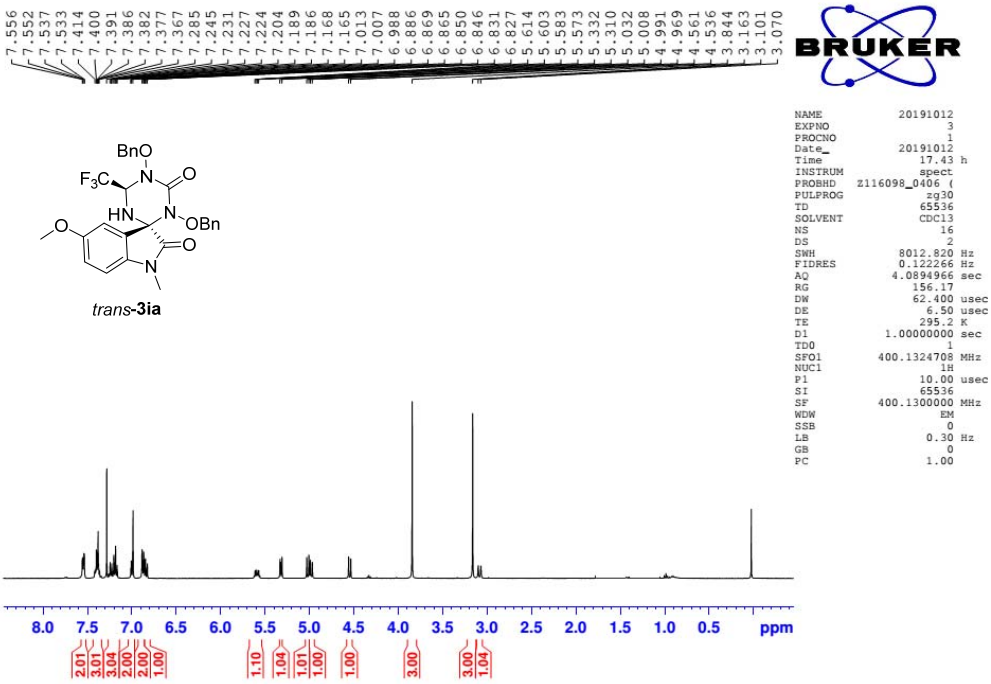
BRUKER

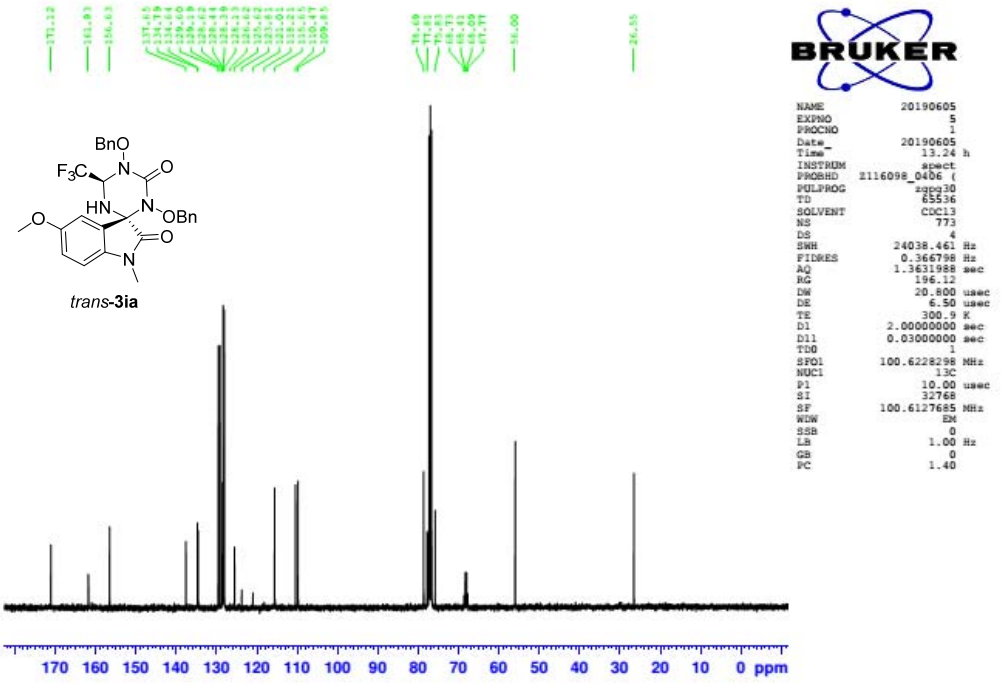
```
NAME                20190603
EXPNO                      8
PROCNO                     1
Date_               20190603
Time                  13.05 h
INSTRUM                apect
PROBHD    Z116098_0406 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894966 sec
RG                    63.47
DW                   62.400 usec
DE                    6.50 usec
TE                   299.1 K
D1                1.00000000 sec
TD0                       1
SFO1           400.1324708 MHz
NUC1                    1H
P1                   10.00 usec
SI                    65536
SF             400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

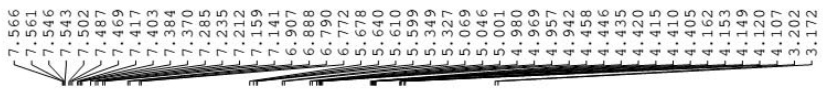


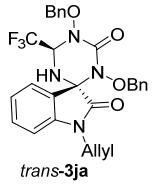
BRUKER

```
NAME                20190603
EXPNO                      9
PROCNO                     1
Date_               20190603
Time                  13.45 h
INSTRUM                apect
PROBHD    Z116098_0406 (
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      701
DS                        4
SWH               24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                   196.12
DW                   20.800 usec
DE                    6.50 usec
TE                   300.4 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1
SFO1           100.6228298 MHz
NUC1                    13C
P1                   10.00 usec
SI                    32768
SF             100.6127685 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```


7.556
7.552
7.537
7.533
7.414
7.400
7.391
7.386
7.382
7.377
7.367
7.285
7.245
7.231
7.227
7.224
7.204
7.189
7.186
7.168
7.165
7.013
7.007
6.988
6.886
6.869
6.865
6.850
6.846
6.831
6.827
5.614
5.603
5.583
5.573
5.332
5.310
5.032
5.008
4.991
4.969
4.561
4.536
3.844
3.163
3.101
3.070
BRUKER
BnO
F3C
N
O
HN
N
OBn
O
O
N
trans-3ia
NAME 20191012
EXPNO 3
PROCNO 1
Date_ 20191012
Time 17.43 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 156.17
DW 62.400 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.01 3.01 3.04 2.00 2.00 1.00 1.10 1.04 1.01 1.00 1.00 3.00 3.00 1.04

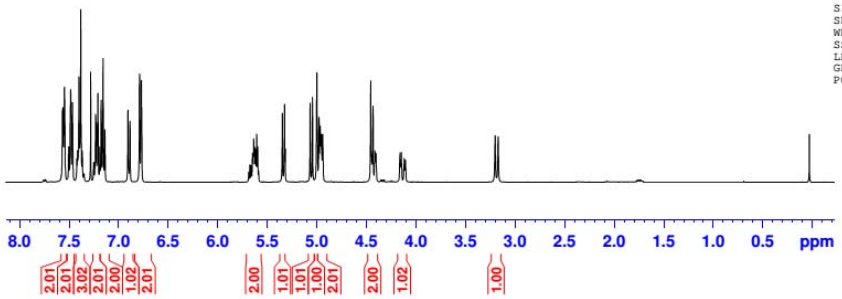

BRUKER
BnO
F3C
N
O
HN
N
OBn
O
O
N
trans-3ia
NAME 20190605
EXPNO 5
PROCNO 1
Date_ 20190605
Time 13.24 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 773
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 196.12
DW 20.800 usec
DE 6.50 usec
TE 300.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

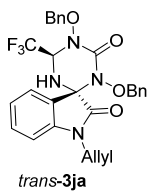




trans-**3ja**

```
NAME            20191012
EXPNO                7
PROCNO               1
Date_           20191012
Time               18.02 h
INSTRUM            spect
PROBHD   Z116098_0406 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                  87.14
DW                 62.400 usec
DE                  6.50 usec
TE                295.1 K
D1             1.00000000 sec
TD0                    1
SFO1          400.1324708 MHz
NUC1                  1H
P1                 10.00 usec
SI                 65536
SF            400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

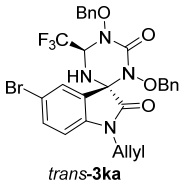




trans-**3ja**

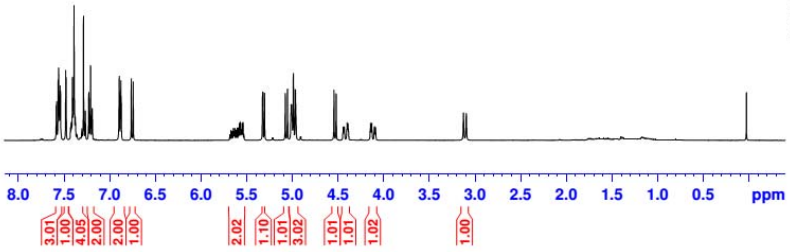
```
NAME            20190531
EXPNO                10
PROCNO                1
Date_           20190531
Time               18.02 h
INSTRUM            spect
PROBHD   Z116098_0406 (
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES             0.366798 Hz
AQ              1.3631988 sec
RG                 196.12
DW                 20.800 usec
DE                  6.50 usec
TE                299.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1          100.6228298 MHz
NUC1                  13C
P1                 10.00 usec
SI                 32768
SF            100.6127685 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

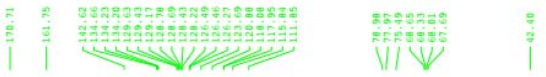
BRUKER



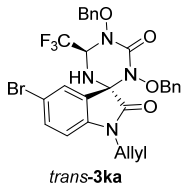
trans-**3ka**

```
NAME            20191012
EXPNO                8
PROCNO               1
Date_           20191012
Time               18.06 h
INSTRUM            spect
PROBHD   Z116098_0406 (
PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                 97.09
DW                 62.400 usec
DE                  6.50 usec
TE                295.2 K
D1             1.00000000 sec
TD0                    1
SFO1          400.1324708 MHz
NUC1                  1H
P1                 10.00 usec
SI                 65536
SF            400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



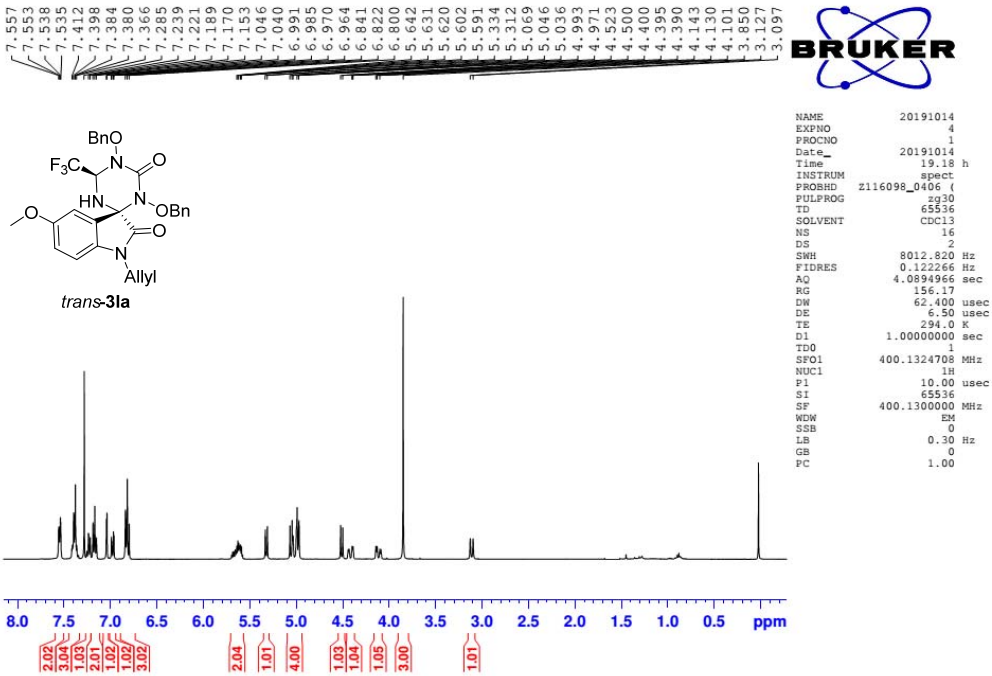


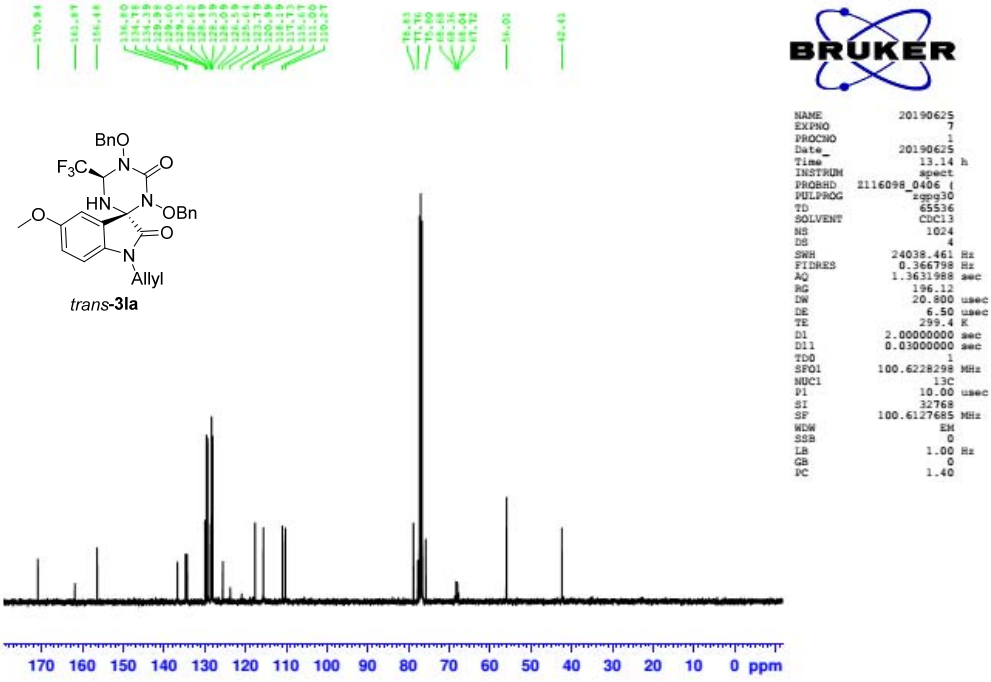
BRUKER

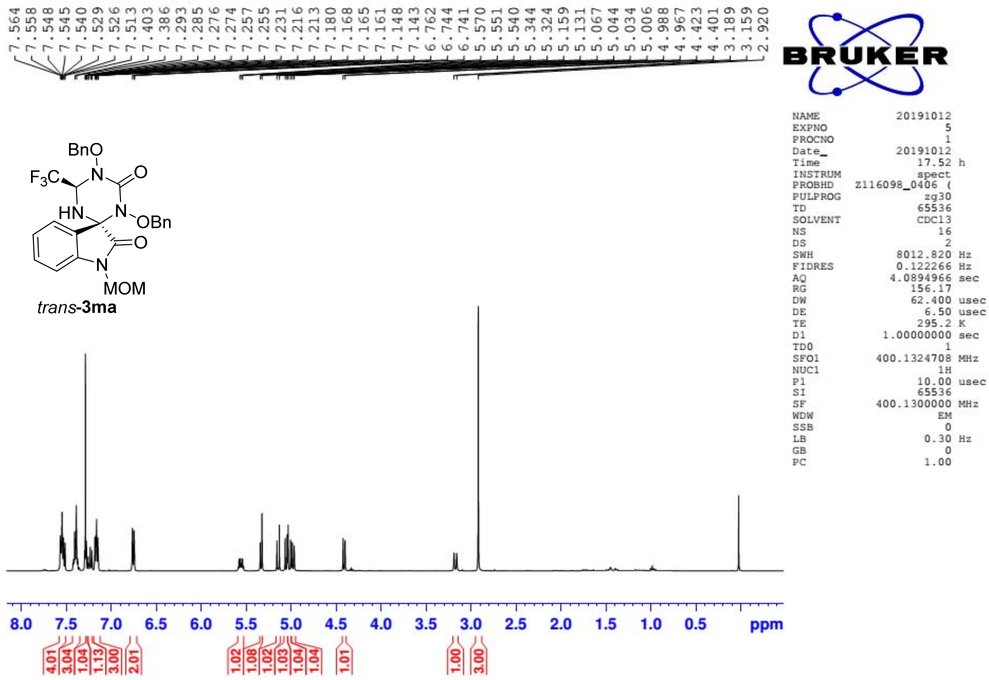


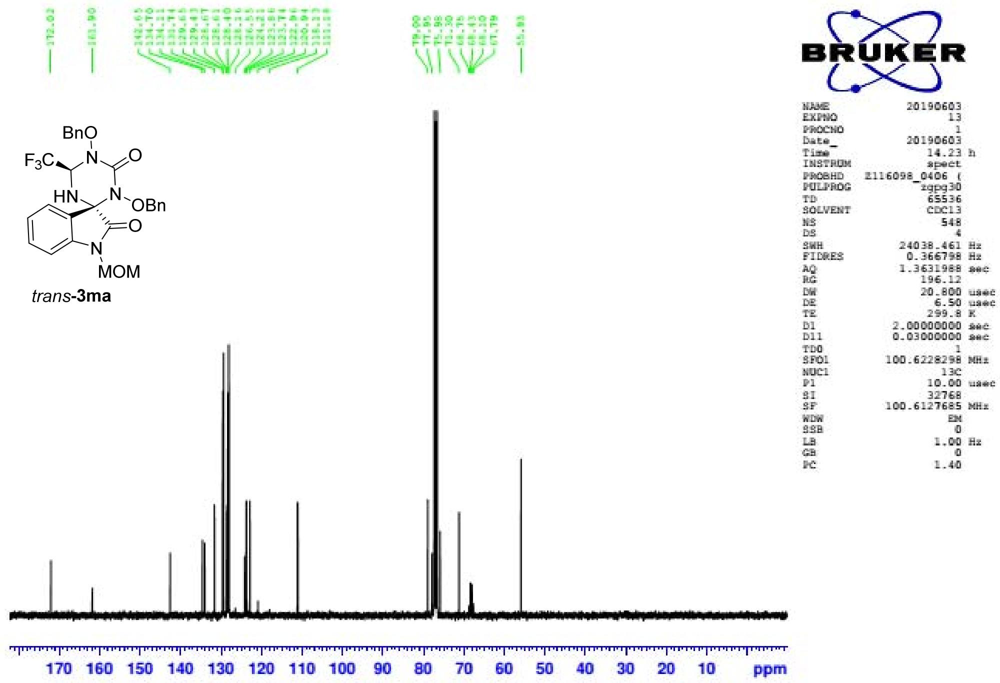
trans-**3ka**

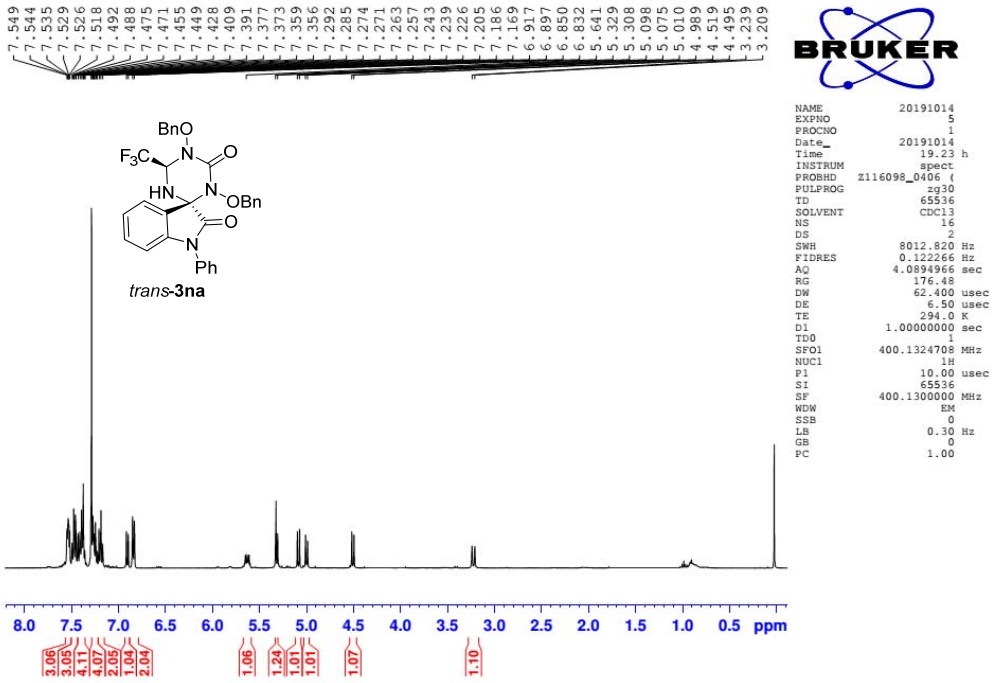
```
NAME            20190612
EXPNO                8
PROCNO               1
Date_           20190612
Time               14.32 h
INSTRUM            spect
PROBHD   Z116098_0406 (
PULPROG          zgpg30
TD                 65536
SOLVENT            CDC13
NS                   779
DS                     4
SWH            24038.461 Hz
FIDRES             0.366798 Hz
AQ              1.3631988 sec
RG                 196.12
DW                 20.800 usec
DE                  6.50 usec
TE                299.5 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1          100.6228298 MHz
NUC1                  13C
P1                 10.00 usec
SI                 32768
SF            100.6127685 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

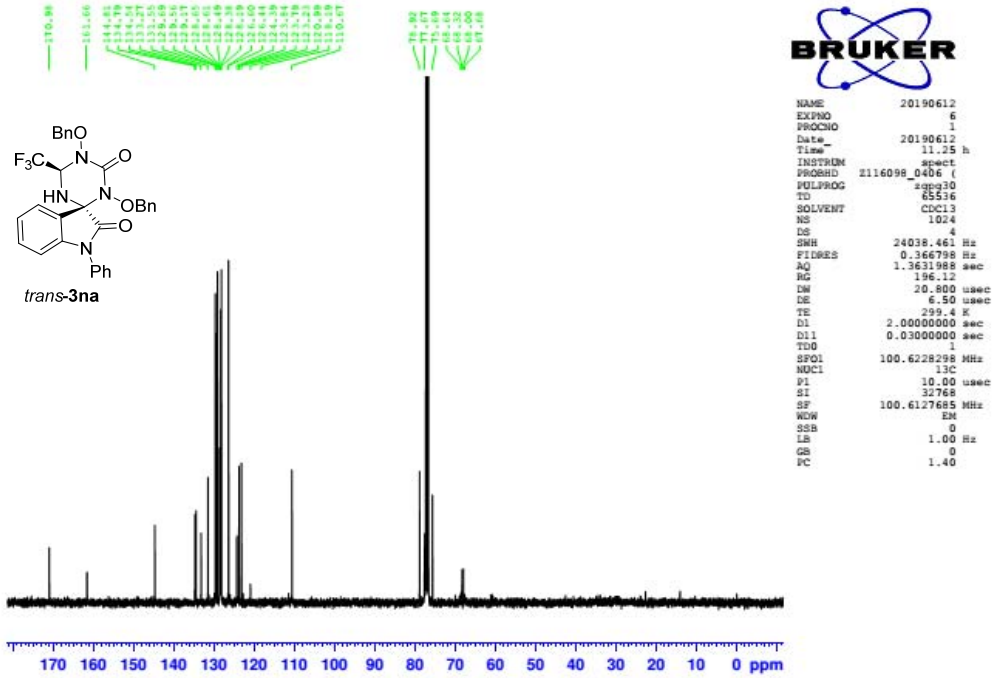

7.557
7.553
7.538
7.535
7.412
7.398
7.384
7.380
7.366
7.285
7.239
7.221
7.189
7.170
7.153
7.046
7.040
6.991
6.985
6.970
6.964
6.841
6.822
6.800
5.642
5.631
5.620
5.602
5.591
5.334
5.312
5.069
5.046
5.036
4.993
4.971
4.523
4.500
4.400
4.395
4.390
4.143
4.130
4.101
3.850
3.127
3.097
BnO
F3C
N
O
HN
N
OBn
O
O
N
Allyl
trans-3la
NAME 20191014
EXPNO 4
PROCNO 1
Date_ 20191014
Time 19.18 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 156.17
DW 62.400 usec
DE 6.50 usec
TE 294.0 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.02 3.04 1.03 2.01 1.02 1.02 3.02 2.04 1.01 4.00 1.03 1.04 1.05 3.00 1.01

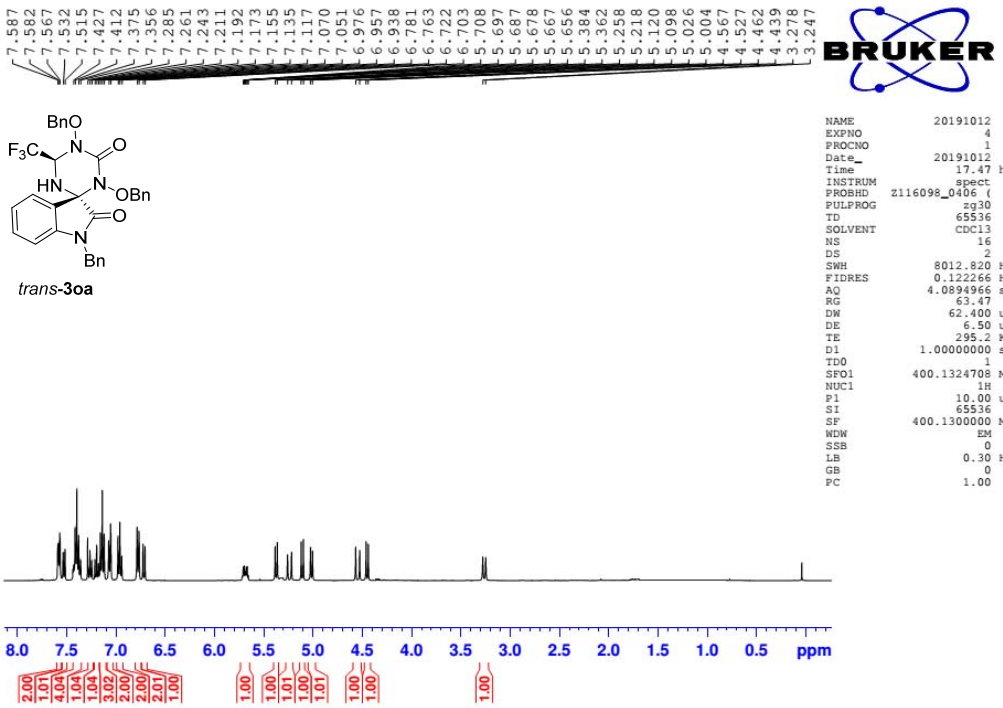

170.94
161.87
156.48
134.76
134.39
134.32
129.40
129.31
128.62
128.39
128.19
128.09
126.59
125.44
125.39
123.39
118.19
117.73
115.87
115.80
110.87
78.83
77.76
75.80
68.58
68.56
68.04
67.72
54.01
42.41
BnO
F3C
N
O
HN
N
OBn
O
O
N
Allyl
trans-3la
NAME 20190625
EXPNO 7
PROCNO 1
Date_ 20190625
Time 13.14 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 196.12
DW 20.800 usec
DE 6.50 usec
TE 299.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

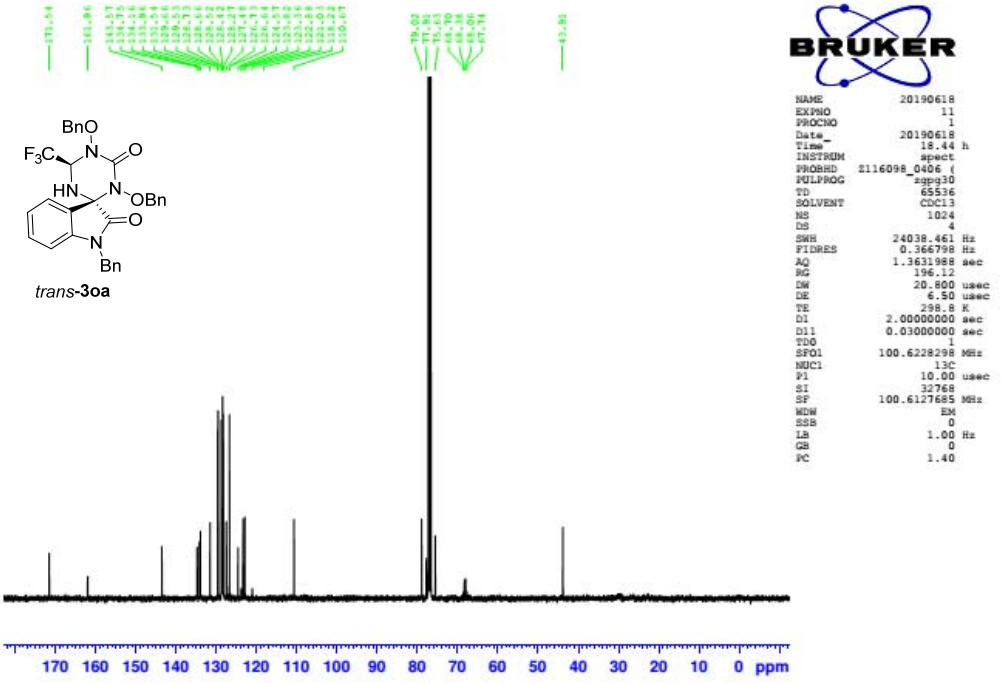

BnO
F3C
N
O
HN
N
OBn
O
N
MOM
trans-3ma
BRUKER
NAME 20191012
EXPNO 5
PROCNO 1
Date_ 20191012
Time 17.52 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 156.17
DW 62.400 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

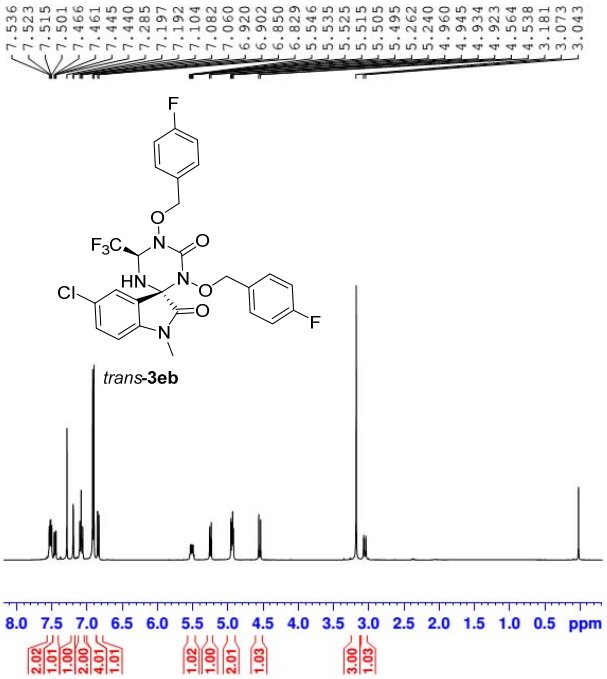

BnO
F3C
N
O
HN
N
OBn
O
N
MOM
trans-3ma
BRUKER
NAME 20190603
EXPNO 13
PROCNO 1
Date_ 20190603
Time 14.23 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 548
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 196.12
DW 20.800 usec
DE 6.50 usec
TE 299.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
ppm


7.549
7.544
7.535
7.529
7.526
7.518
7.492
7.488
7.475
7.471
7.455
7.449
7.428
7.409
7.391
7.377
7.373
7.359
7.356
7.292
7.285
7.274
7.271
7.263
7.257
7.243
7.239
7.226
7.205
7.186
7.169
6.917
6.897
6.850
6.832
5.641
5.329
5.308
5.098
5.075
5.010
4.989
4.519
4.495
3.239
3.209
BnO
F3C
HN
OBn
Ph
trans-3na
BRUKER
NAME 20191014
EXPNO 5
PROCNO 1
Date_ 20191014
Time 19.23 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 176.48
DW 62.400 usec
DE 6.50 usec
TE 294.0 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.06 3.05 4.11 4.07 2.05 1.04 2.04 1.06 1.24 1.01 1.01 1.07 1.10

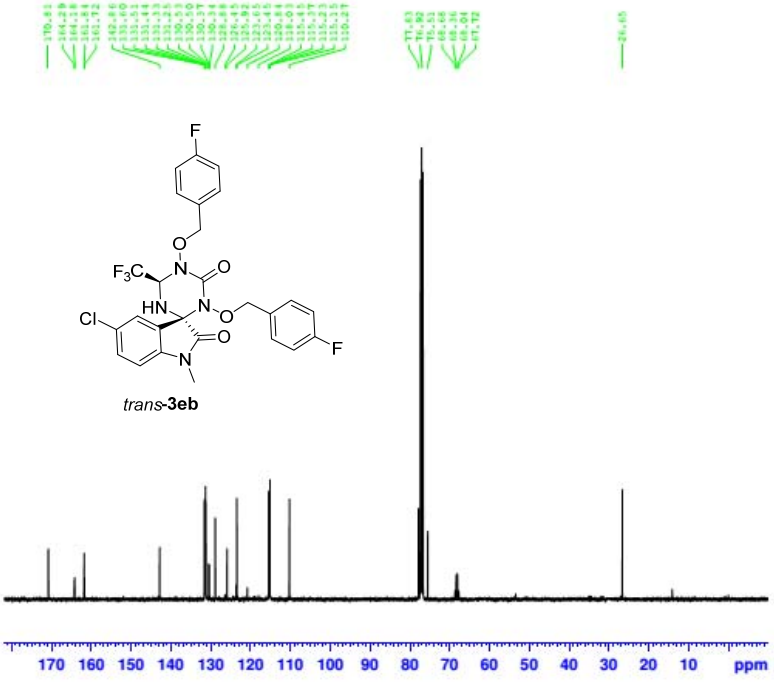

BnO
F3C
HN
OBn
Ph
trans-3na
BRUKER
NAME 20190612
EXPNO 6
PROCNO 1
Date_ 20190612
Time 11.25 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 196.12
DW 20.800 usec
DE 6.50 usec
TE 299.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.587
7.582
7.567
7.532
7.515
7.427
7.412
7.375
7.356
7.285
7.261
7.243
7.211
7.192
7.173
7.155
7.135
7.117
7.070
7.051
6.976
6.957
6.938
6.781
6.763
6.722
6.703
6.708
5.697
5.687
5.678
5.667
5.656
5.384
5.362
5.258
5.218
5.120
5.098
5.026
5.004
4.567
4.527
4.462
4.439
3.278
3.247
BRUKER
BnO
F3C
N
O
HN
N
OBn
O
N
Bn
trans-3oa
NAME 20191012
EXPNO 4
PROCNO 1
Date_ 20191012
Time 17.47 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 63.47
DW 62.400 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00 1.01 4.04 1.04 1.04 3.02 2.00 2.00 2.01 1.00
1.00 1.00 1.01 1.00 1.01
1.00 1.00
1.00

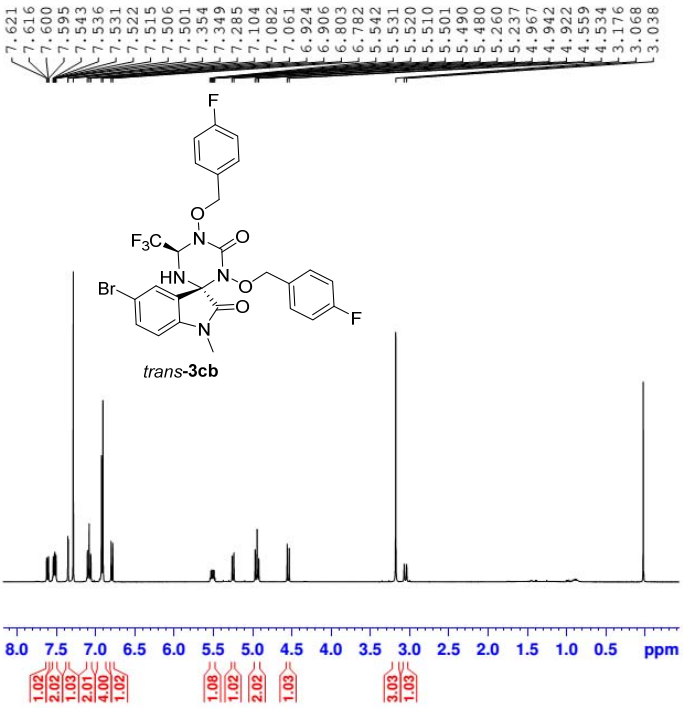

BRUKER
BnO
F3C
N
O
HN
N
OBn
O
N
Bn
trans-3oa
NAME 20190618
EXPNO 11
PROCNO 1
Date_ 20190618
Time 18.44 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 196.12
DW 20.800 usec
DE 6.50 usec
TE 298.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

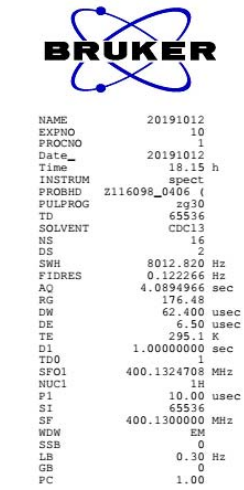


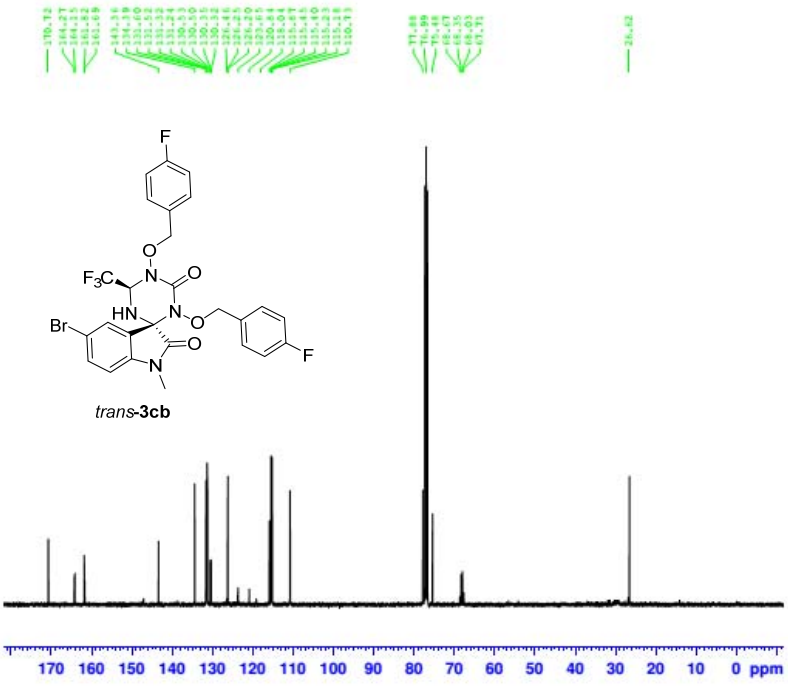
```
NAME                20191014
EXPNO                      7
PROCNO                     1
Date_               20191014
Time                  19.32 h
INSTRUM                spect
PROBHD    Z116098_0406 (
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES            0.122266 Hz
AQ                4.0894966 sec
RG                    141.68
DW                    62.400 usec
DE                     6.50 usec
TE                    294.0 K
D1                1.00000000 sec
TD0                        1
SFO1           400.1324708 MHz
NUC1                      1H
P1                    10.00 usec
SI                     65536
SF             400.1300000 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                    1.00
```



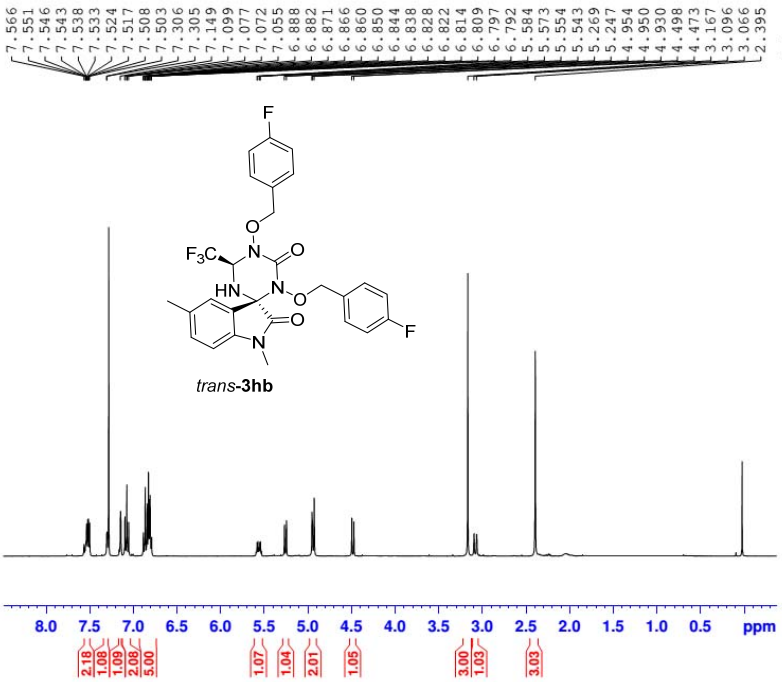
```
NAME                20190617
EXPNO                     15
PROCNO                     1
Date_               20190617
Time                  13.35 h
INSTRUM                spect
PROBHD    Z116098_0406 (
PULPROG             zgpg30
TD                     65536
SOLVENT              CDCl3
NS                       990
DS                         4
SWH               24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                    196.12
DW                    20.800 usec
DE                     6.50 usec
TE                    299.7 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1
SFO1           100.6228298 MHz
NUC1                      13C
P1                    10.00 usec
SI                     32768
SF             100.6127685 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                    1.40
```


7.621
7.616
7.600
7.595
7.543
7.536
7.531
7.522
7.515
7.506
7.501
7.354
7.349
7.285
7.104
7.082
7.061
6.924
6.906
6.803
6.782
5.542
5.531
5.520
5.510
5.501
5.490
5.480
5.260
5.237
4.967
4.942
4.922
4.559
4.534
3.176
3.068
3.038
F
O
F3C
N
O
HN
N
O
Br
O
F
N
trans-3cb
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.02
2.02
1.03
2.01
4.00
1.02
1.08
1.02
2.02
1.03
3.03
1.03

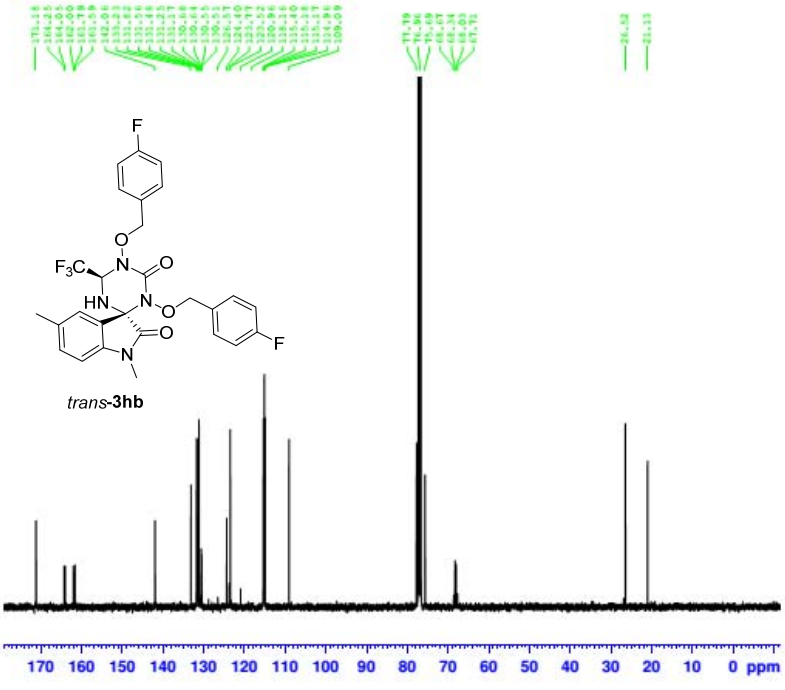

BRUKER
NAME 20191012
EXPNO 10
PROCNO 1
Date_ 20191012
Time 18.15 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 176.48
DW 62.400 usec
DE 6.50 usec
TE 295.1 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


F
O
F3C
N
O
HN
N
O
Br
O
F
N
trans-3cb
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


BRUKER
NAME 20190625
EXPNO 5
PROCNO 1
Date_ 20190625
Time 12.02 h
INSTRUM spect
PROBHD Z116098_0406 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 196.12
DW 20.800 usec
DE 6.50 usec
TE 298.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

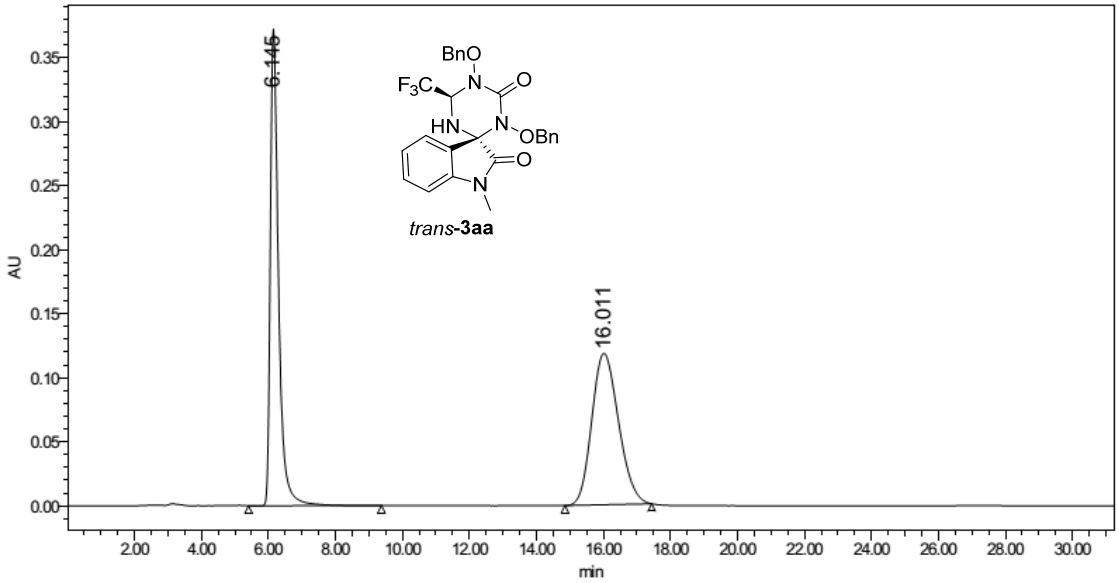



```
NAME            20191014
EXPNO                  6
PROCNO                 1
Date_           20191014
Time               19.27 h
INSTRUM             spect
PROBHD   Z116098_0406 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                141.68
DW                62.400 usec
DE                 6.50 usec
TE                294.0 K
D1             1.00000000 sec
TD0                    1
SFO1          400.1324708 MHz
NUC1                  1H
P1                10.00 usec
SI                 65536
SF            400.1300000 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```



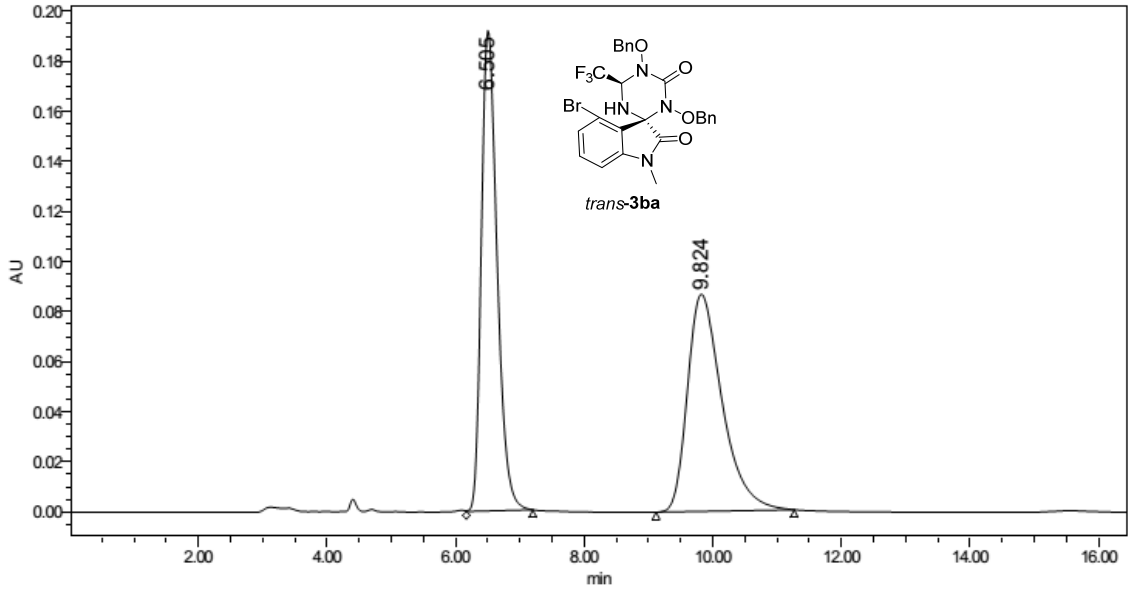

```
NAME            20190617
EXPNO                 17
PROCNO                 1
Date_           20190617
Time               13.45 h
INSTRUM             spect
PROBHD   Z116098_0406 (
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES             0.366798 Hz
AQ              1.3631988 sec
RG                196.12
DW                20.800 usec
DE                 6.50 usec
TE                298.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1          100.6228298 MHz
NUC1                  13C
P1                10.00 usec
SI                 32768
SF            100.6127685 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

8. Copies of chiral HPLC spectra of compounds *trans*-3



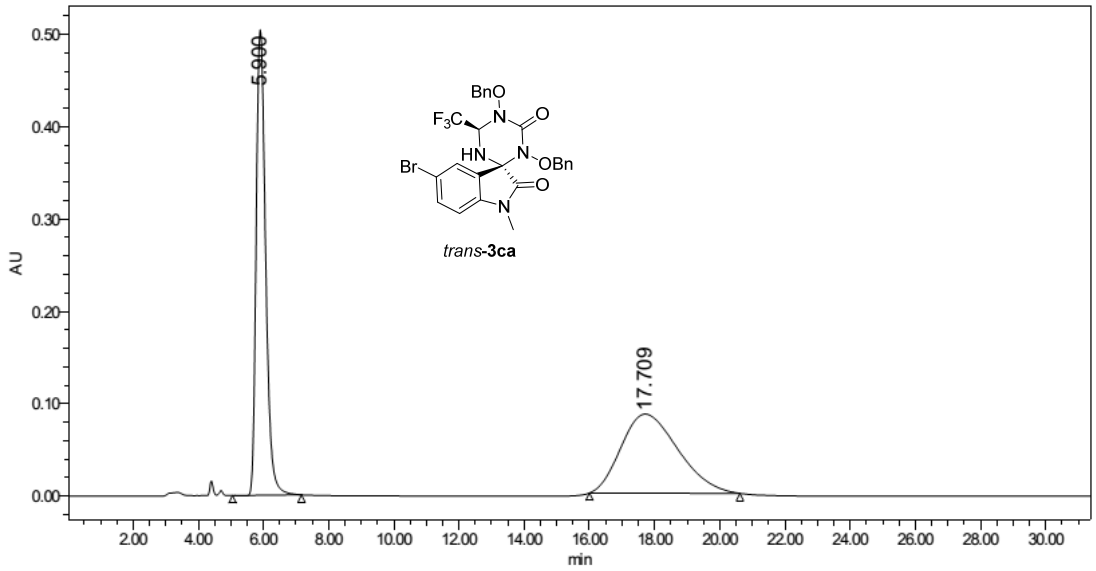
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	6.145	6378349	49.26	372915
2	16.011	6569801	50.74	118328



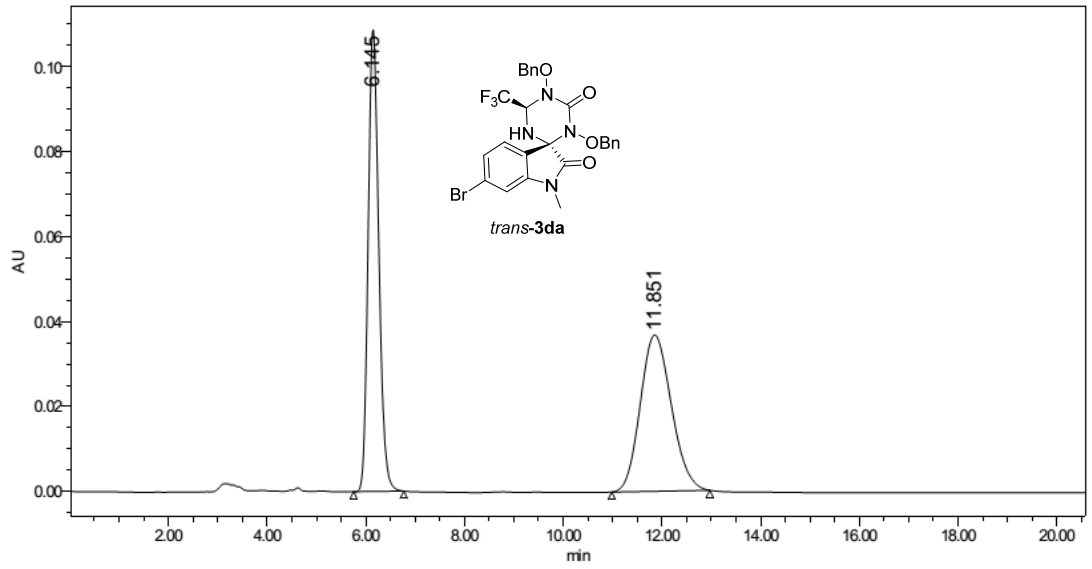
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	6.505	3252896	50.04	192136
2	9.824	3247418	49.96	86791



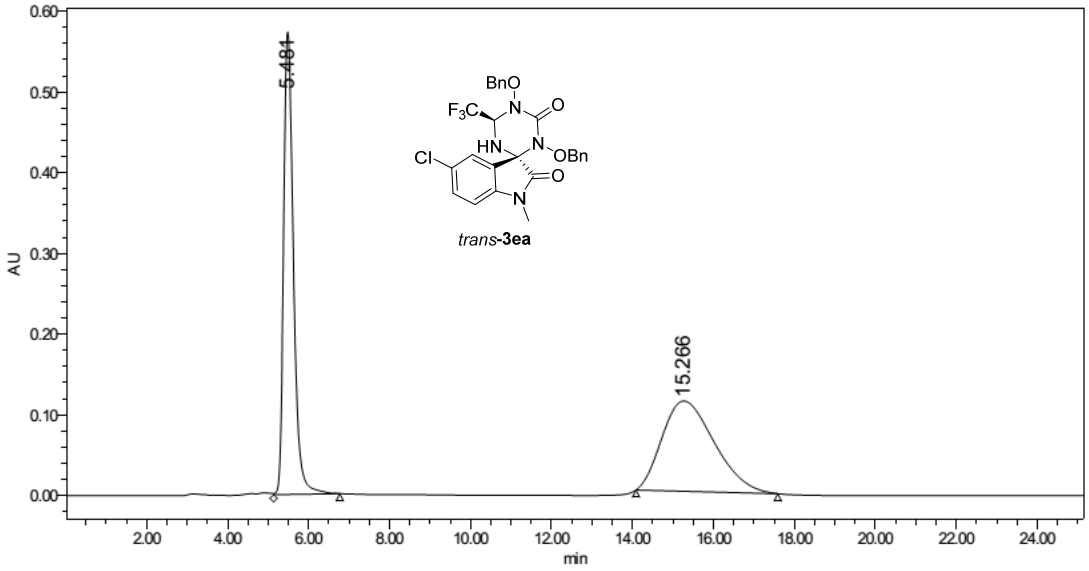
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	5.900	10124105	49.37	503934
2	17.709	10381129	50.63	85601



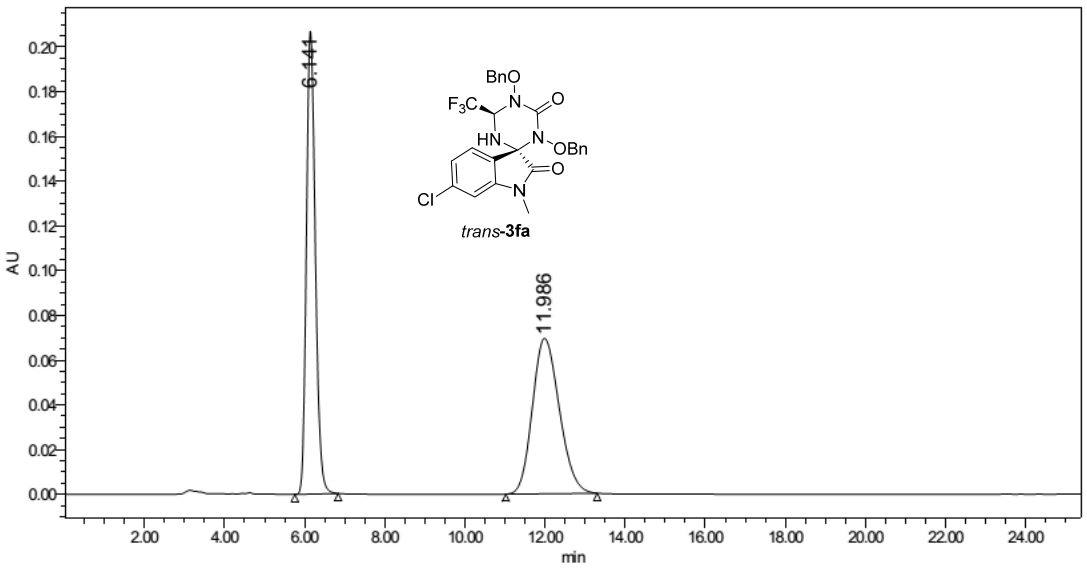
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	6.145	1629599	50.26	108845
2	11.851	1612803	49.74	36814



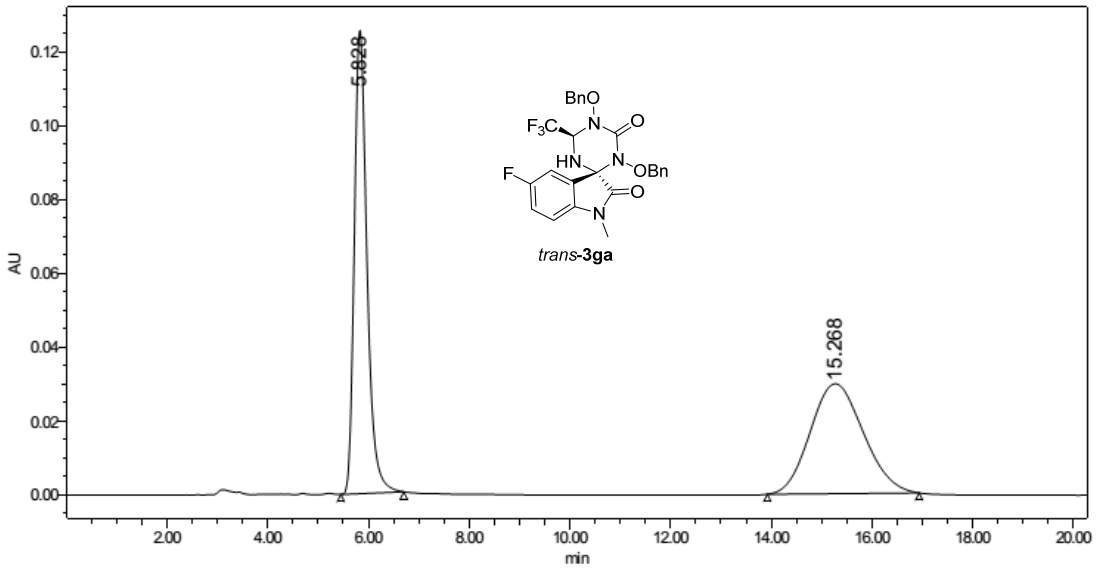
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	5.481	9669617	49.08	573248
2	15.266	10031076	50.92	111866



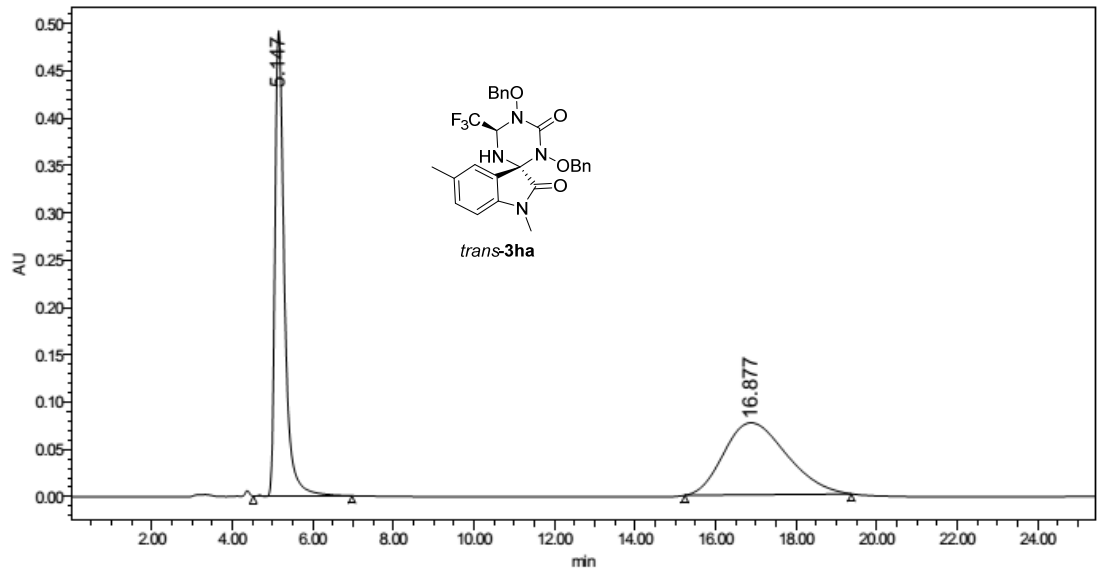
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	6.141	3194481	49.62	207519
2	11.986	3242855	50.38	69514



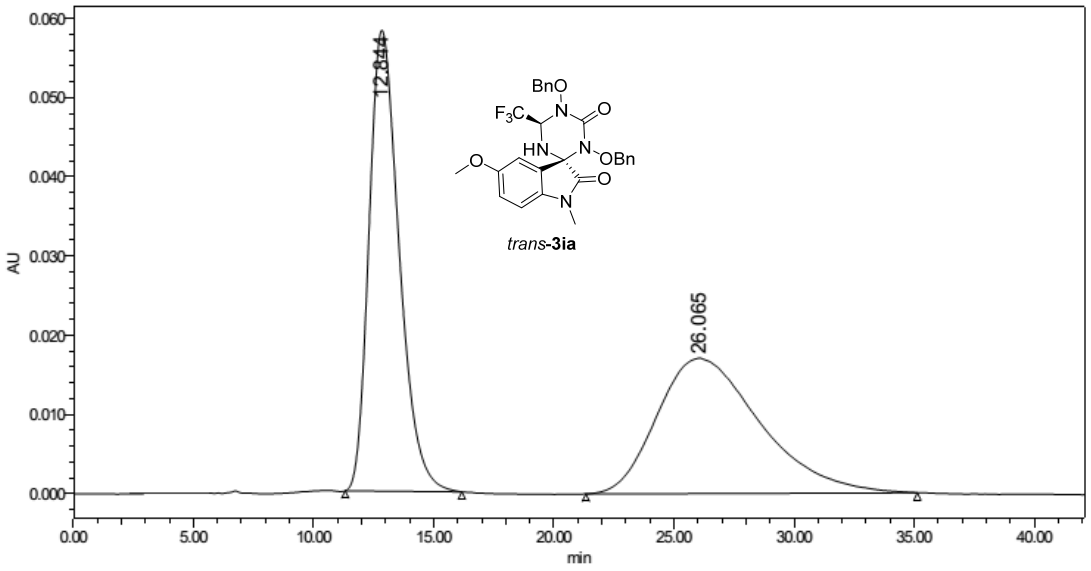
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	5.828	2180863	50.00	125650
2	15.268	2181089	50.00	29766



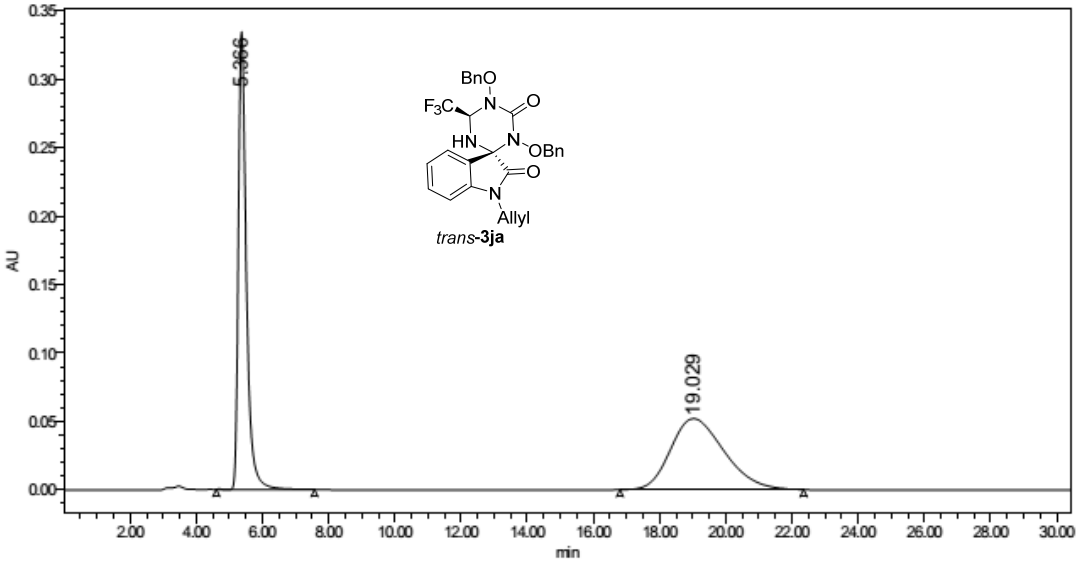
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	5.147	8032637	49.21	492457
2	16.877	8289598	50.79	76196



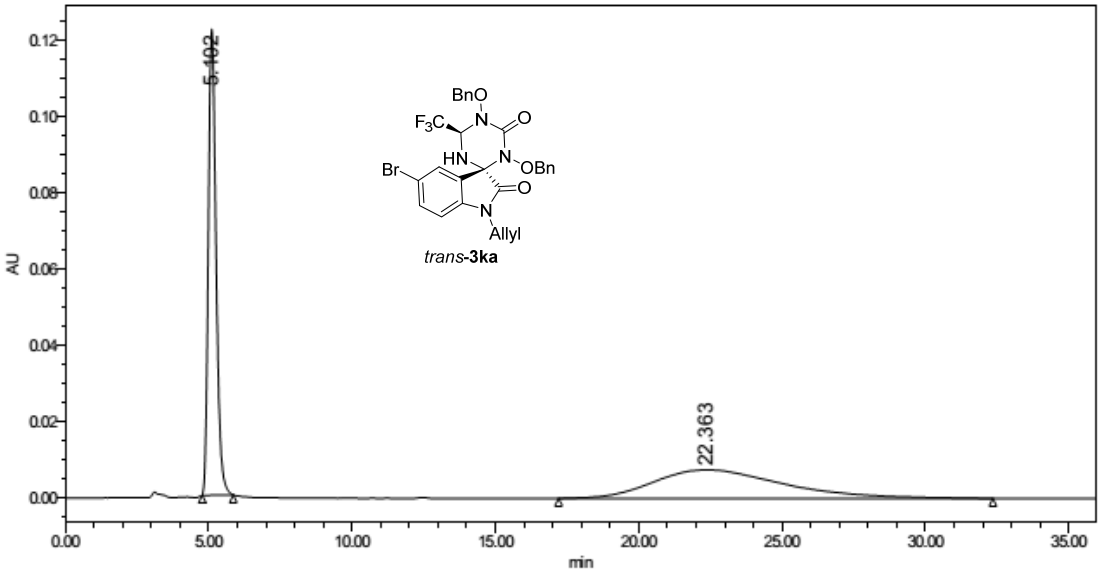
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	12.844	5073460	49.86	58197
2	26.065	5102193	50.14	17110



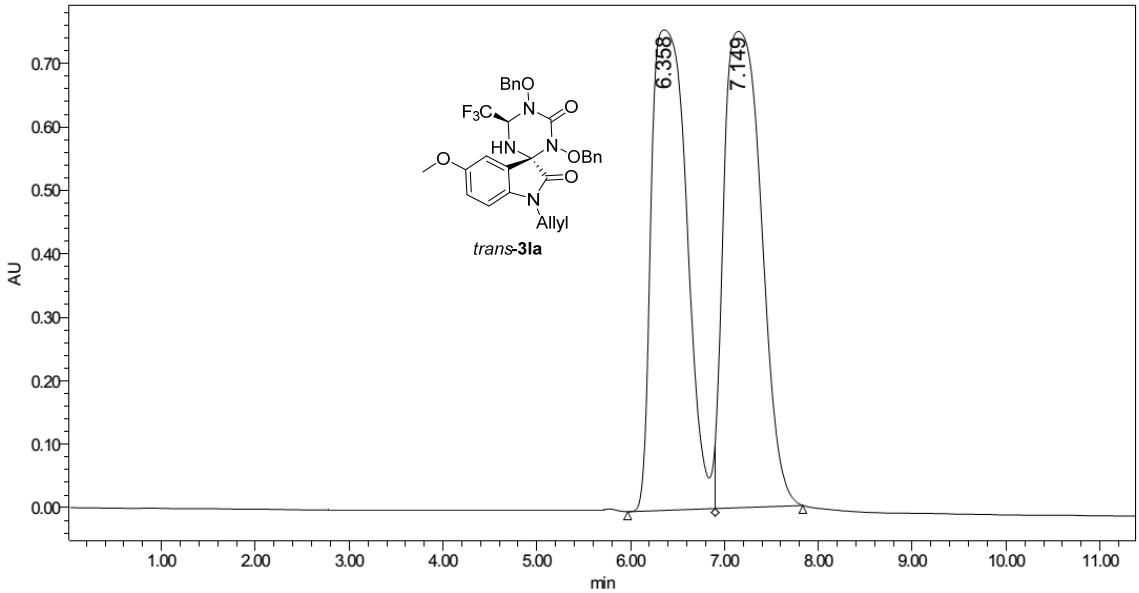
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	5.366	5627363	49.02	334468
2	19.029	5853036	50.98	51899



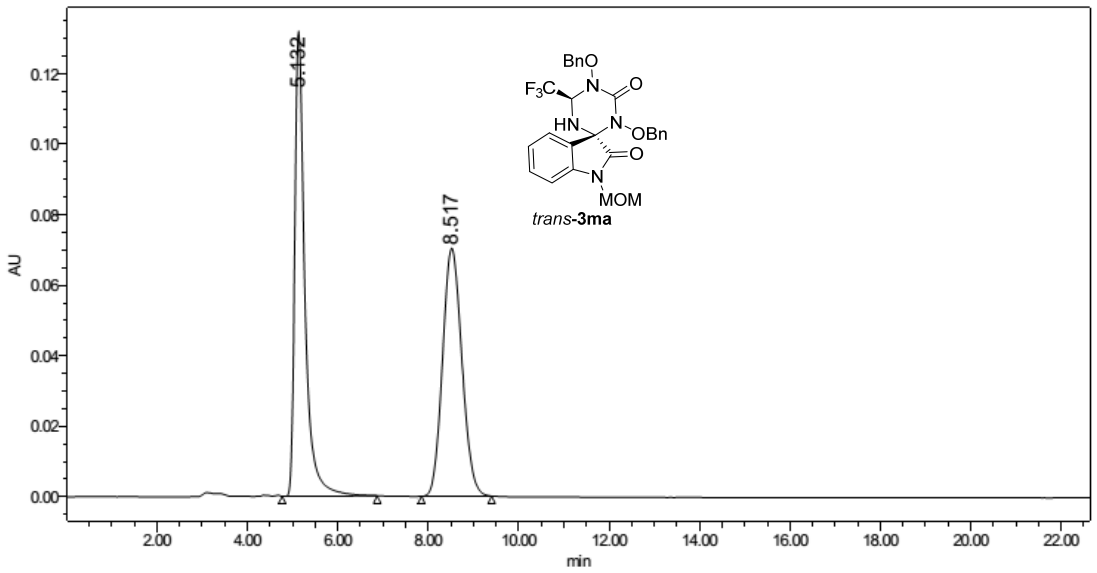
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	5.102	2278160	49.40	122188
2	22.363	2333877	50.60	7473



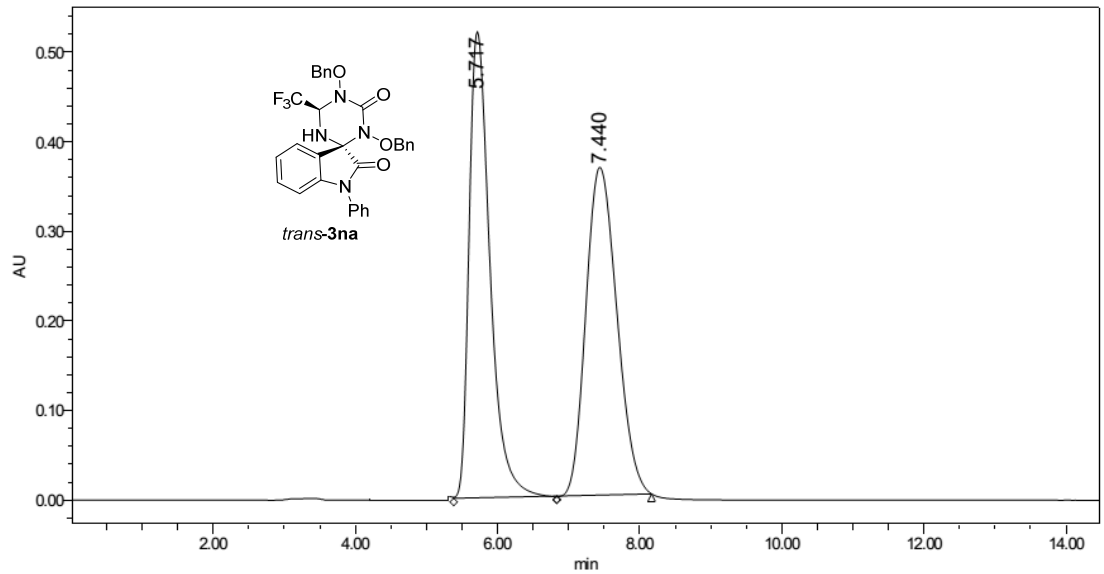
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	6.358	19919519	48.93	757421
2	7.149	20794850	51.07	750494



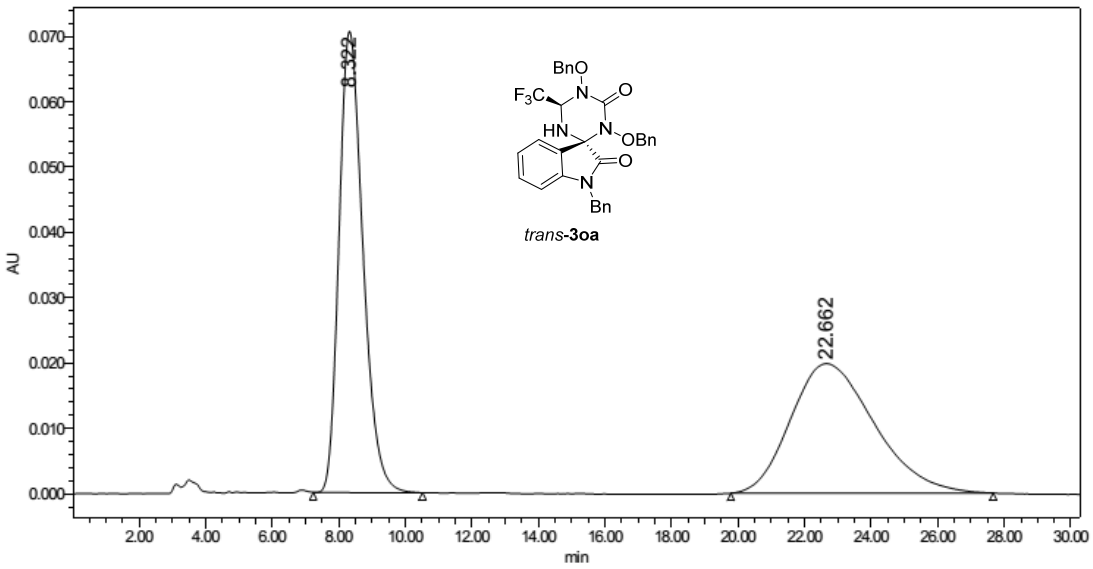
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	5.132	2055873	49.57	131951
2	8.517	2091959	50.43	70398



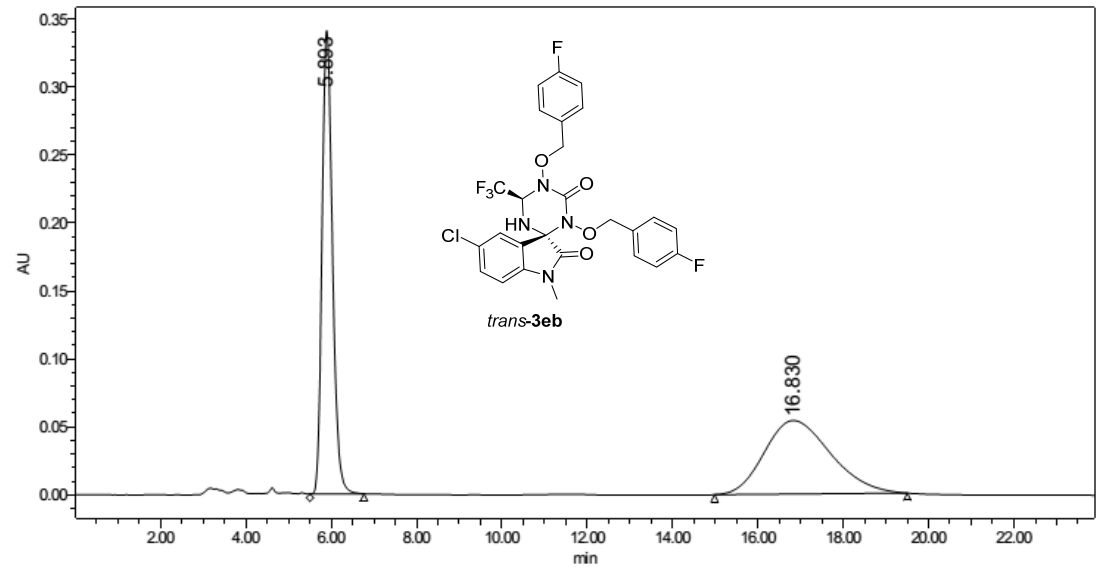
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	5.717	10577915	48.90	520646
2	7.440	11053306	51.10	365973



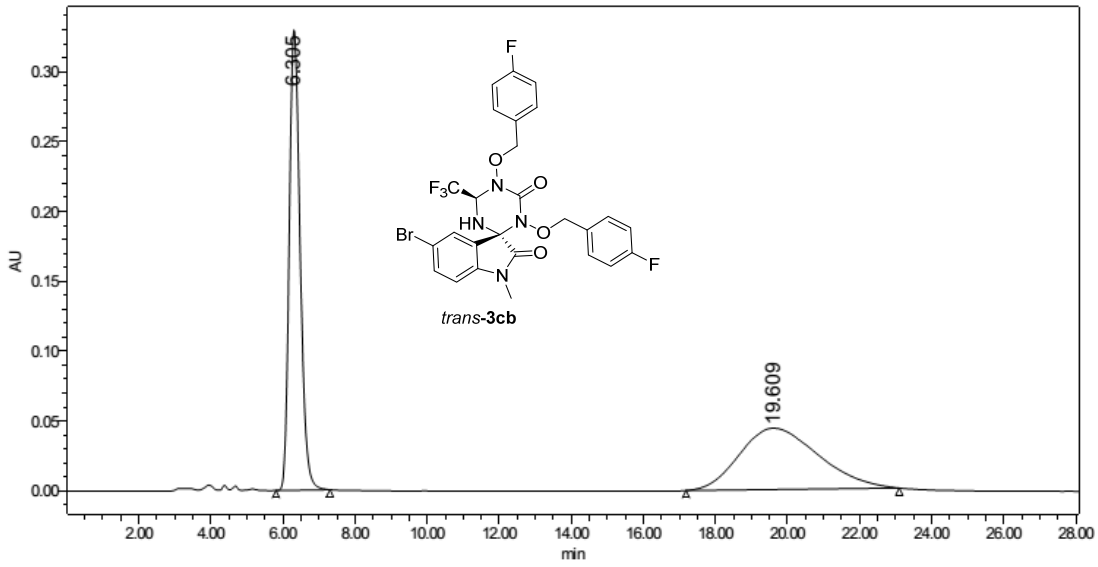
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	8.322	3518651	50.38	70592
2	22.662	3466017	49.62	19841



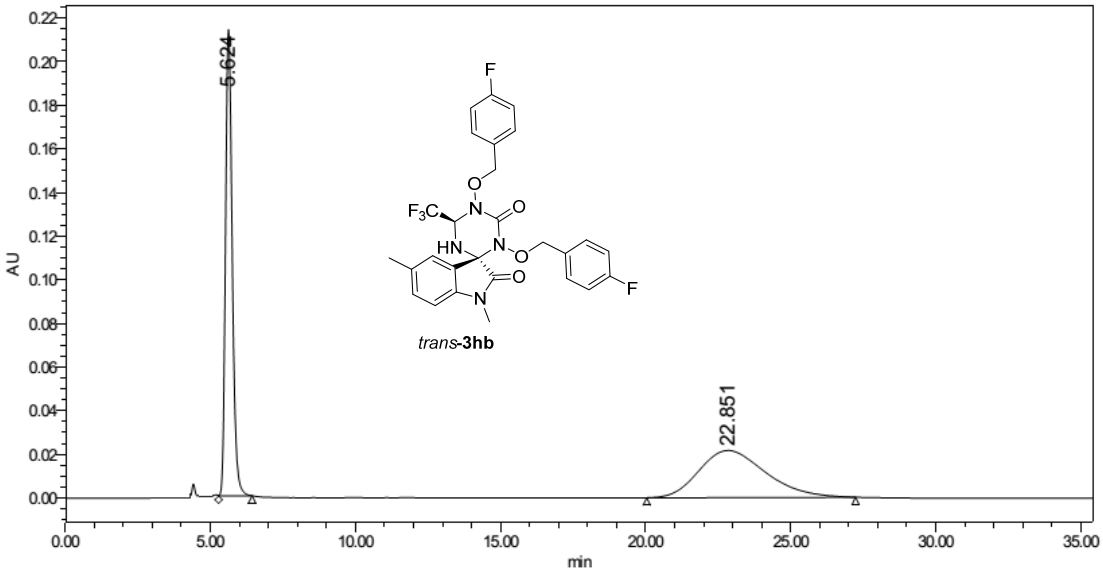
<Column Performance Report>

entry	R.T	Area	%Area	Height
1	5.893	5777365	49.64	341575
2	16.830	5860462	50.36	54165



<Column Performance Report>

entry	R.T	Area	%Area	Height
1	6.305	6898638	50.69	329715
2	19.609	6711614	49.31	43934



<Column Performance Report>

entry	R.T	Area	%Area	Height
1	5.624	3450658	49.99	214192
2	22.851	3452080	50.01	21576

9. X-Ray crystal data of compound *trans*-3ba

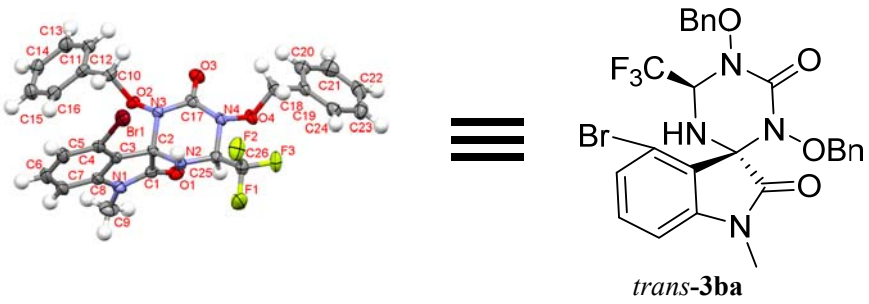


Fig. 1 X-ray single crystal structure of *trans*-**3ba** (with thermal ellipsoils shown at the 50% probability level)

Identification code	*trans*-**3ba**
Empirical formula	$C_{26}H_{22}BrF_3N_4O_4$
Formula weight	591.38
Temperature/K	133.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.2204(18)
b/Å	24.665(5)
c/Å	11.584(2)
α/°	90
β/°	105.11(3)
γ/°	90
Volume/Å^3	2543.4(9)
Z	4
ρ_{calc}g/cm^3	1.544

μ/mm-1	1.679
F(000)	1200.0
Crystal size/mm^3	0.2 × 0.18 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.302 to 55.776
Index ranges	-11 ≤ h ≤ 12, -32 ≤ k ≤ 32, -15 ≤ l ≤ 15
Reflections collected	25176
Independent reflections	6038 [R_{int} = 0.0641, R_{sigma} = 0.0570]
Data/restraints/parameters	6038/1/348
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0556, wR_2 = 0.1249
Final R indexes [all data]	R_1 = 0.0779, wR_2 = 0.1370
Largest diff. peak/hole / e $Å^{-3}$	0.67/-0.58

10. References

1. For selected examples, see: (a) Y. You, W. Y. Lu, Z. H. Wang, Y. Z. Chen, X. Y. Xu, X. M. Zhang and W. C. Yuan, *Org. Lett.*, 2018, **20**, 4453. (b) X. Li, J. Su, Z. Liu, Y. Zhu, Z. Dong, S. Qiu, J. Wang, L. Lin, Z. Shen, W. Yan, K. Wang and R. Wang, *Org. Lett.*, 2016, **18**, 956.
2. For selected examples, see: (a) D. Anumandla, A. Acharya and C. S. Jeffrey, *Org. Lett.*, 2016, **18**, 476. (b) D. Anumandla, R. Littlefield and C. S. Jeffrey, *Org. Lett.*, 2014, **16**, 5112.