Electronic Supplementary Material (ESI) for Chemical Communications

Chincona-based squaramide-catalysed cascade aza-Michael/Michael addition: enantioselective construction of functionalized spirooxindole tetrahydroquinolines

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Supporting Information

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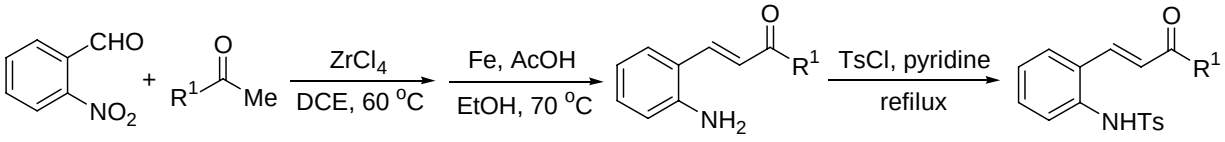
General information

Unless otherwise stated, commercially available compounds were used without further purification. Column chromatography was carried out with silica gel (200–300 mesh). Melting points were measured with a XT-4 melting point apparatus without correction. ^{1}H NMR spectra were recorded with a Varian Mercury-plus 400 MHz spectrometer. Chemical shifts were reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as follows: chemical shift (ppm), and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br s = broad singlet), coupling constant(s) in Hz, integration assignment. ^{13}C NMR spectra were recorded at 100 MHz. Infrared spectra were obtained with a Perkin Elmer Spectrum One spectrometer. The high resolution MS spectra were obtained with ESI ionization using a Bruker APEX IV mass spectrometer. Optical rotations were measured with a Krüss P8000 or WZZ–3 polarimeter at the indicated concentration with unit g/100 mL. The enantiomeric excesses were determined by chiral HPLC using an Agilent 1200 LC instrument with Daicel Chiralcel column AD-H, Daicel Chiralpak column IA, or IB.

Materials

Squaramide catalysts **I**–**VII**,[1] 2-tosylaminoenones **1**,[2] and 3-ylidenoxindoles **2**[3] were prepared according to the reported procedures.



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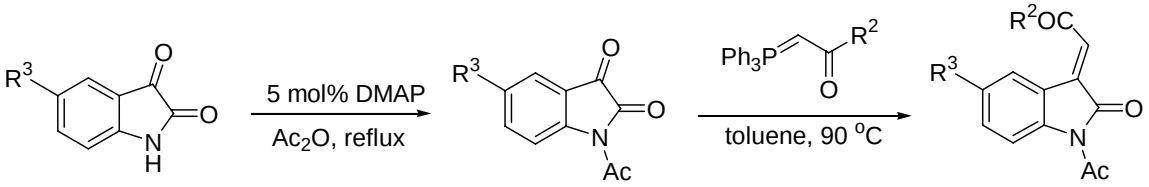
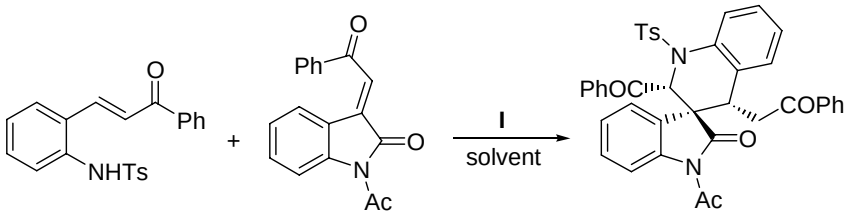


2

Optimization of reaction conditions

Table S1 Optimization of reaction conditions[a]



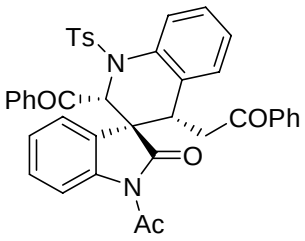
1a **2a** **3aa**

Entry	Solvent	Loading (mol%)	*t* (h)	Yield[b] (%)	dr[c]	ee[d] (%)
1	CH_2Cl_2	5	24	99	> 25:1	88
2	$ClCH_2CH_2Cl$	5	24	99	> 25:1	90
3	$CHCl_3$	5	24	93	> 25:1	86
4	PhMe	5	24	54	> 25:1	87
5	THF	5	24	44	> 25:1	76
6	MeCN	5	24	80	> 25:1	68
7[e]	$ClCH_2CH_2Cl$	5	48	93	> 25:1	90
8[f]	$ClCH_2CH_2Cl$	5	72	91	> 25:1	90
9	$ClCH_2CH_2Cl$	10	12	94	> 25:1	90
10	$ClCH_2CH_2Cl$	2	36	90	> 25:1	89

[a] Reactions were carried out with **1a** (0.11 mmol) and **2a** (0.1 mmol) in the solvent (0.5 mL). [b] Isolated yield. [c] Determined by ^{1}H NMR analysis. [d] Determined by chiral HPLC analysis. [e] 0 °C. [f] -10 °C.

General procedure for the enantioselective cascade aza-Michael/Michael addition

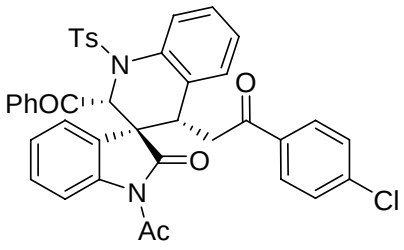
A mixture of 3-ylidenoxindole **2** (0.1 mmol) and squaramide catalyst **I** (3.2 mg, 0.005 mmol, 5 mol%) in dichloroethane (0.5 mL) was stirred at room temperature for 10 min. Then 2-tosylaminoenone **1** (0.11 mmol) was added. After stirring for 12–24 h, the reaction mixture was concentrated and directly purified by silica gel column chromatography to afford the desired adduct **3**.



3aa

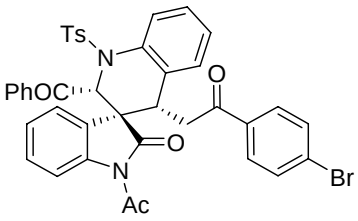
(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-benzoyl-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3aa): The title compound **3aa** was obtained according to the general procedure (66.8 mg, 99% yield). White solid, m.p. 189–191 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): major enantiomer t_R = 17.2 min, minor enantiomer t_R = 16.0 min, 90% ee. $[\alpha]_D^{20}$ +2.2 (*c* 1.11, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* =

8.0 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.55–7.48 (m, 2H), 7.41–7.34 (m, 5H), 7.21–7.11 (m, 6H), 6.77 (t, J = 7.6 Hz, 1H), 6.54 (d, J = 7.6 Hz, 1H), 6.46 (s, 1H), 5.29 (d, J = 7.6 Hz, 1H), 3.15 (dd, J_1 = 10.4 Hz, J_2 = 2.0 Hz, 1H), 2.67 (dd, J_1 = 17.6 Hz, J_2 = 10.4 Hz, 1H), 2.47 (s, 3H), 2.44 (s, 3H), 2.28 (dd, J_1 = 17.6 Hz, J_2 = 2.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 194.8, 177.6, 169.7, 144.5, 139.7, 136.9, 136.1, 135.7, 135.4, 133.5, 132.94, 132.89, 130.0, 129.3, 128.7, 128.6, 128.5, 128.1, 127.8, 127.5, 126.9, 125.9, 125.3, 125.2, 124.2, 115.7, 69.1, 60.2, 40.0, 34.5, 26.6, 21.7 ppm; IR (KBr): ν 3065, 2924, 1747, 1720, 1688, 1598, 1463, 1448, 1370, 1358, 1340, 1295, 1270, 1237, 1167, 1091, 1018, 970, 812, 754, 694, 663, 587, 560 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{40}H_{36}N_3O_6S$ $[M + NH_4]^+$ 686.23193, found 686.23053.



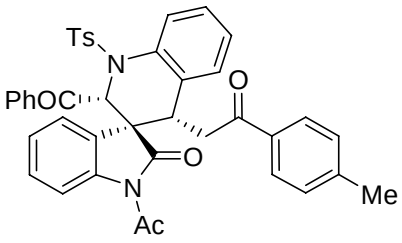
3ba

(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-benzoyl-4'-(2-oxo-1-(4-chlorophenylethyl))-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3ba): The title compound **3ba** was obtained according to the general procedure (70.1 mg, 99% yield). White solid, m.p. 107–110 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 95:5, flow rate 0.8 mL/min, detection at 254 nm): major enantiomer t_R = 92.3 min, minor enantiomer t_R = 100.6 min, 88% ee. $[\alpha]_D^{20}$ –5.1 (*c* 1.17, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.42–7.33 (m, 5H), 7.22–7.12 (m, 6H), 6.77 (t, J = 7.6 Hz, 1H), 6.52 (d, J = 8.0 Hz, 1H), 6.45 (s, 1H), 5.28 (d, J = 7.6 Hz, 1H), 3.14 (d, J = 8.8 Hz, 1H), 2.63 (dd, J_1 = 17.2 Hz, J_2 = 10.8 Hz, 1H), 2.47 (s, 3H), 2.43 (s, 3H), 2.23 (dd, J_1 = 17.2 Hz, J_2 = 2.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 193.8, 177.6, 169.6, 144.5, 140.0, 139.7, 136.9, 136.1, 135.4, 133.9, 133.0, 132.7, 129.9, 129.4, 129.3, 129.0, 128.8, 128.6, 128.1, 127.5, 126.9, 125.8, 125.3, 125.2, 124.0, 115.7, 69.1, 60.2, 39.6, 34.6, 26.6, 21.7 ppm; IR (KBr): ν 3069, 2925, 1746, 1720, 1688, 1589, 1488, 1463, 1368, 1359, 1272, 1237, 1166, 1092, 1010, 970, 811, 757, 690, 658, 586, 560 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{40}H_{35}ClN_3O_6S$ $[M + NH_4]^+$ 720.19296, found 720.19377.



3ca

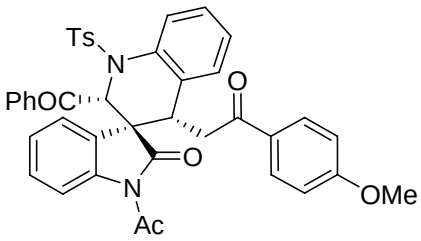
(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-benzoyl-4'-(2-oxo-1-(4-bromophenylethyl))-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3ca): The title compound **3ca** was obtained according to the general procedure (74.2 mg, 99% yield). White solid, m.p. 119–121 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 90:10, flow rate 0.8 mL/min, detection at 254 nm): major enantiomer t_R = 44.1 min, minor enantiomer t_R = 48.7 min, 88% ee. $[\alpha]_D^{20}$ –10.0 (*c* 1.24, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.51–7.48 (m, 5H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.21–7.12 (m, 6H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 6.45 (s, 1H), 5.27 (d, *J* = 7.6 Hz, 1H), 3.14 (d, *J* = 10.0 Hz, 1H), 2.62 (dd, J_1 = 17.2 Hz, J_2 = 10.4 Hz, 1H), 2.47 (s, 3H), 2.43 (s, 3H), 2.23 (d, *J* = 17.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 194.0, 177.6, 169.6, 144.5, 139.6, 136.9, 136.1, 135.4, 134.3, 133.0, 132.6, 131.9, 129.9, 129.40, 129.36, 128.8, 128.7, 128.6, 128.1, 127.5, 126.90. 126.87, 125.8, 125.3, 125.2, 124.0, 115.7, 69.1, 60.2, 39.6, 34.6, 26.6, 21.7 ppm; IR (KBr): ν 3065, 2922, 1746, 1720, 1690, 1598, 1585, 1478, 1463, 1368, 1358, 1339, 1270, 1238, 1167, 1099, 1091, 1008, 970, 812, 756, 697, 658, 585, 560 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{40}H_{35}BrN_3O_6S$ $[M + NH_4]^+$ 764.14245, found 764.14366.



3da

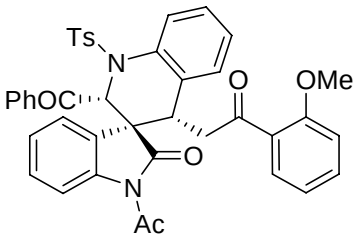
(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-benzoyl-4'-(2-oxo-1-(4-methylphenylethyl))-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (**3da**): The title compound 3da was obtained according to the general procedure (67.8 mg, 99% yield). White solid, m.p. 101–104 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 90:10, flow rate 0.8 mL/min, detection at 254 nm): major enantiomer t_R = 34.3 min, minor enantiomer t_R = 32.2 min, 90% ee. $[\alpha]_D^{20}$ –8.8 (*c* 1.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.41–7.34 (m, 3H), 7.21–7.11 (m, 8H), 6.76 (t, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.46 (s, 1H), 5.29 (d, *J* = 7.6 Hz, 1H), 3.15 (d, *J* = 8.8 Hz, 1H), 2.64 (dd, J_1 = 17.2 Hz, J_2 = 10.4 Hz, 1H), 2.46 (s, 3H), 2.43 (s, 3H), 2.36 (s, 3H), 2.24 (dd, J_1

= 17.2 Hz, J_2 = 2.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 194.4, 177.6, 169.7, 144.44, 144.38, 139.7, 136.9, 136.1, 135.4, 133.2, 133.0, 132.9, 129.9, 129.3, 128.6, 128.4, 128.1, 127.9, 127.5, 126.9, 126.8, 126.0, 125.3, 125.1, 124.2, 115.7, 69.1, 60.2, 39.6, 34.4, 26.5, 21.7, 21.6 ppm; IR (KBr): ν 3065, 2924, 1747, 1721, 1684, 1605, 1487, 1478, 1463, 1370, 1358, 1339, 1294, 1271, 1237, 1167, 1101, 1091, 1017, 970, 811, 758, 692, 659, 584, 560 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{41}H_{38}N_3O_6S$ $[M + NH_4]^+$ 700.24758, found 700.24737.



3ea

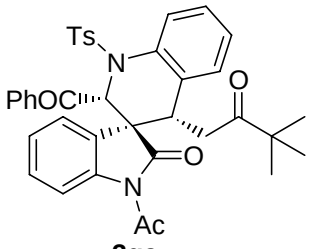
(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-benzoyl-4'-(2-oxo-1-(4-methoxyphenylethyl))-2-oxo-1'- tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3ea): The title compound **3ea** was obtained according to the general procedure (69.3 mg, 99% yield). White solid, m.p. 189–192 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol/ethyl acetate = 85:3:12, flow rate 1.0 mL/min, detection at 254 nm): major enantiomer t_R = 22.6 min, minor enantiomer t_R = 25.3 min, 94% ee. $[\alpha]_D^{20}$ –9.5 (*c* 1.16, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.41–7.34 (m, 3H), 7.21–7.11 (m, 6H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 6.46 (s, 1H), 5.28 (d, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 3.15 (d, *J* = 10.0 Hz, 1H), 2.61 (dd, J_1 = 17.2 Hz, J_2 = 10.8 Hz, 1H), 2.47 (s, 3H), 2.43 (s, 3H), 2.22 (d, *J* = 17.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 193.4, 177.6, 169.7, 163.6, 144.5, 139.7, 136.8, 136.1, 135.4, 133.0, 132.9, 130.1, 129.9, 129.3, 128.7, 128.6, 128.4, 128.1, 127.5, 126.91, 126.86, 126.0, 125.3, 125.1, 124.3, 115.7, 113.7, 69.1, 60.2, 55.4, 39.7, 34.2, 26.6, 21.7 ppm; IR (KBr): ν 3065, 2934, 1747, 1720, 1678, 1600, 1478, 1463, 1368, 1357, 1339, 1263, 1239, 1167, 1101, 1091, 1018, 970, 810, 758, 693, 660, 584, 560 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{41}H_{38}N_3O_7S$ $[M + NH_4]^+$ 716.24250, found 716.24279.



3fa

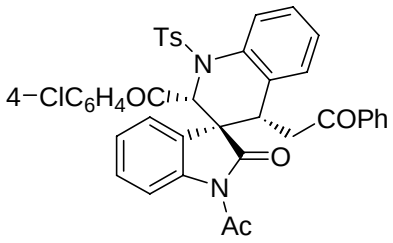
(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-benzoyl-4'-(2-oxo-1-(2-methoxyphenylethyl))-2-oxo-1'-

tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3fa): The title compound **3fa** was obtained according to the general procedure (66.1 mg, 95% yield). White solid, m.p. 213–216 ^{o}C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): major enantiomer t_R = 21.4 min, minor enantiomer t_R = 25.6 min, 92% ee. $[\alpha]_D^{20}$ +35.6 (c 1.10, CH2Cl2). 1H NMR (400 MHz, CDCl3): δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.70–7.74 (m, 3H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.44–7.36 (m, 4H), 7.20–7.08 (m, 6H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.47 (s, 1H), 5.27 (d, *J* = 7.6 Hz, 1H), 3.50 (s, 3H), 3.03 (d, *J* = 10.0 Hz, 1H), 2.63 (dd, J_1 = 18.8 Hz, J_2 = 10.8 Hz, 1H), 2.51 (s, 3H), 2.47–2.43 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1, 177.7, 169.8, 158.6, 144.4, 139.6, 136.9, 136.2, 135.5, 134.2, 133.2, 132.8, 130.5, 130.0, 129.0, 128.6, 128.2, 128.0, 127.6, 127.0, 126.7, 126.4, 126.2, 125.2, 124.9, 124.6, 120.7, 115.2, 111.5, 68.7, 60.3, 54.9, 40.4, 40.0, 26.5, 21.7 ppm; IR (KBr): ν 3065, 2925, 1747, 1719, 1676, 1598, 1485, 1464, 1370, 1357, 1339, 1294, 1272, 1242, 1167, 1099, 1091, 1018, 971, 811, 756, 695, 661, 586, 560 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{41}H_{38}N_3O_7S$ $[M + NH_4]^+$ 716.24250, found 716.24386.



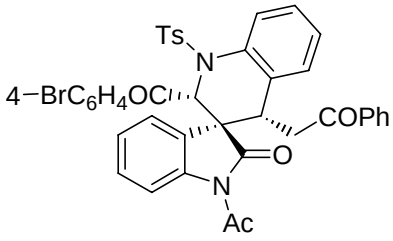
3ga

(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-benzoyl-4'-(2-oxo-1-(3,3-dimethylbutyl))-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3ga): The title compound **3ga** was obtained according to the general procedure (51.3 mg, 79% yield). White solid, m.p. 205–207 ^{o}C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 254 nm): major enantiomer t_R = 12.1 min, minor enantiomer t_R = 14.3 min, 5% ee. $[\alpha]_D^{20}$ +8.6 (*c* 1.28, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.74–7.71 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.40–7.35 (m, 3H), 7.22–7.07 (m, 6H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 6.39 (s, 1H), 5.22 (d, *J* = 7.6 Hz, 1H), 2.79 (d, *J* = 10.0 Hz, 1H), 2.49 (s, 3H), 2.42 (s, 3H), 2.13 (dd, J_1 = 18.4 Hz, J_2 = 10.4 Hz, 1H), 1.88 (dd, J_1 = 18.4 Hz, J_2 = 2.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.4, 196.0, 177.7, 169.5, 144.4, 139.5, 136.8, 136.1, 135.4, 133.2, 132.9, 130.0, 129.2, 128.7, 128.3, 128.1, 127.5, 126.9, 126.8, 125.6, 125.2, 125.1, 124.2, 115.6, 69.1, 60.3, 44.1, 39.1, 32.4, 26.55, 26.46, 21.6 ppm; IR (KBr): ν 3065, 2967, 2931, 1747, 1713, 1599, 1478, 1463, 1370, 1358, 1339, 1294, 1272, 1167, 1101, 1091, 1011, 971, 812, 757, 693, 659, 560 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{38}H_{40}N_3O_6S$ $[M + NH_4]^+$ 666.26323, found 666.26525.



3ab

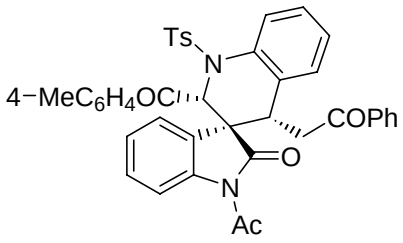
(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-(4-chlorobenzoyl)-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3ab): The title compound **3ab** was obtained according to the general procedure (68.0 mg, 97% yield). White solid, m.p. 206–208 ^{o}C. Enantiomeric excess was determined by HPLC (Daicel Chiralpak IB, *n*-hexane/2-propanol = 90:10, flow rate 0.8 mL/min, detection at 254 nm): major enantiomer t_R = 16.2 min, minor enantiomer t_R = 15.1 min, 91% ee. $[\alpha]_D^{20}$ +40.0 (*c* 1.13, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.55–7.48 (m, 2H), 7.40–7.34 (m, 4H), 7.20–7.12 (m, 6H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.35 (s, 1H), 5.27 (d, *J* = 7.6 Hz, 1H), 3.13 (d, *J* = 9.6 Hz, 1H), 2.68 (dd, J_1 = 17.6 Hz, J_2 = 10.4 Hz, 1H), 2.52 (s, 3H), 2.44 (s, 3H), 2.29 (d, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 194.8, 177.5, 169.6, 144.6, 139.7, 139.4, 136.8, 135.7, 135.1, 134.4, 133.5, 132.8, 130.0, 129.5, 129.1, 128.7, 128.6, 128.5, 128.4, 127.8, 126.94, 126.92, 126.0, 125.23, 125.19, 124.0, 115.9, 69.4, 60.3, 39.5, 34.5, 26.5, 21.7 ppm; IR (KBr): ν 3065, 2922, 1747, 1721, 1689, 1596, 1487, 1463, 1370, 1359, 1339, 1294, 1267, 1234, 1167, 1091, 1018, 1008, 971, 812, 757, 709, 689, 663, 586, 562 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{40}H_{35}ClN_3O_6S$ $[M + NH_4]^+$ 720.19296, found 720.19383.



3ac

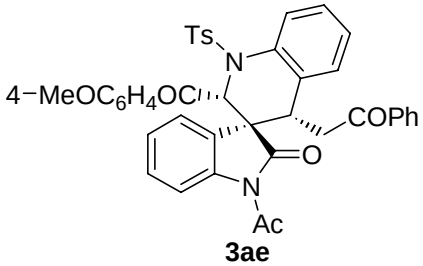
(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-(4-bromobenzoyl)-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3ac): The title compound **3ac** was obtained according to the general procedure (72.2 mg, 97% yield). White solid, m.p. 196–198 ^{o}C. Enantiomeric excess was determined by HPLC (Daicel Chiralpak IB, *n*-hexane/2-propanol = 90:10, flow rate 0.8 mL/min, detection at 254 nm): major enantiomer t_R = 17.0 min, minor enantiomer t_R = 15.8 min, 91% ee. $[\alpha]_D^{20}$ +55.9 (*c* 1.21, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.55–7.48 (m, 2H), 7.40–7.34 (m, 6H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.34 (s, 1H), 5.27 (d, *J* = 8.0

Hz, 1H), 3.12 (d, J = 9.6 Hz, 1H), 2.68 (dd, J_1 = 17.2 Hz, J_2 = 10.4 Hz, 1H), 2.51 (s, 3H), 2.44 (s, 3H), 2.28 (dd, J_1 = 17.2 Hz, J_2 = 2.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 194.8, 177.5, 169.6, 144.7, 139.7, 136.8, 135.7, 135.1, 134.9, 133.5, 132.8, 131.4, 130.0, 129.5, 129.2, 128.7, 128.6, 128.5, 128.0, 127.8, 127.0, 126.9, 126.1, 125.23, 125.21, 124.1, 115.9, 69.4, 60.3, 39.5, 34.5, 26.4, 21.7 ppm; IR (KBr): ν 3069, 2922, 1747, 1721, 1688, 1598, 1585, 1478, 1463, 1368, 1359, 1339, 1294, 1267, 1235, 1167, 1097, 1091, 1072, 1008, 971, 812, 757, 689, 662, 586, 561 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{40}H_{35}BrN_3O_6S$ $[M + NH_4]^+$ 764.14245, found 764.14430.



3ad

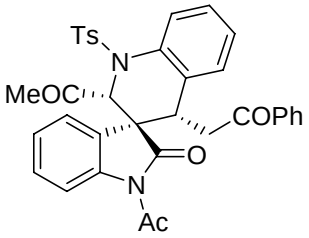
(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-(4-methylbenzoyl)-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3ad): The title compound **3ad** was obtained according to the general procedure (67.7 mg, 99% yield). White solid, m.p. 208–210 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 80:20, flow rate 1.0 mL/min, detection at 254 nm): major enantiomer t_R = 24.6 min, minor enantiomer t_R = 16.3 min, 89% ee. $[\alpha]_D^{20}$ +28.8 (*c* 1.13, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.72 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.54–7.47 (m, 2H), 7.39–7.33 (m, 4H), 7.17–6.97 (m, 6H), 6.75 (t, J = 8.0 Hz, 1H), 6.53 (d, J = 8.0 Hz, 1H), 6.42 (s, 1H), 5.28 (d, J = 7.6 Hz, 1H), 3.14 (d, J = 10.4 Hz, 1H), 2.66 (dd, J_1 = 17.2 Hz, J_2 = 10.4 Hz, 1H), 2.49 (s, 3H), 2.43 (s, 3H), 2.29–2.25 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 194.9, 177.7, 169.7, 144.4, 143.9, 139.7, 136.9, 135.7, 135.4, 133.5, 132.9, 129.9, 129.3, 128.7, 128.6, 128.4, 127.8, 127.7, 126.9, 126.8, 125.9, 125.3, 125.1, 124.3, 115.7, 69.0, 60.3, 39.6, 34.6, 26.5, 21.7, 21.5 ppm; IR (KBr): ν 3043, 2924, 1747, 1721, 1691, 1604, 1488, 1477, 1463, 1368, 1358, 1339, 1294, 1268, 1239, 1167, 1091, 1018, 1007, 813, 781, 756, 689, 662, 586, 559 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{41}H_{38}N_3O_6S$ $[M + NH_4]^+$ 700.24758, found 700.24752.



3ae

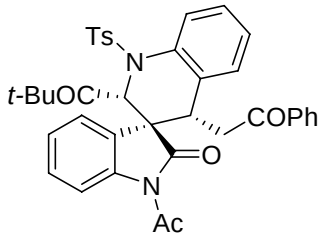
(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-(4-methoxybenzoyl)-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-

tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3ae): The title compound **3ae** was obtained according to the general procedure (65.6 mg, 94% yield). White solid, m.p. 198–200 ^{o}C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): major enantiomer t_R = 62.9 min, minor enantiomer t_R = 32.2 min, 89% ee. $[\alpha]_D^{20}$ +43.7 (*c* 1.09, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.55–7.48 (m, 2H), 7.40–7.33 (m, 4H), 7.21–7.10 (m, 4H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.40 (s, 1H), 5.30 (d, *J* = 8.0 Hz, 1H), 3.77 (s, 3H), 3.16 (d, *J* = 8.8 Hz, 1H), 2.67 (dd, J_1 = 17.6 Hz, J_2 = 10.4 Hz, 1H), 2.54 (s, 3H), 2.43 (s, 3H), 2.28 (dd, J_1 = 17.6 Hz, J_2 = 2.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 194.3, 177.8, 169.8, 163.4, 144.4, 139.6, 137.1, 135.7, 135.5, 133.5, 132.9, 129.9, 129.2, 128.7, 128.6, 128.4, 127.8, 126.9, 126.8, 125.9, 125.3, 125.1, 124.3, 115.6, 113.4, 68.7, 60.5, 55.4, 39.6, 34.7, 26.6, 21.7 ppm; IR (KBr): ν 2928, 2845, 1746, 1721, 1690, 1600, 1510, 1463, 1368, 1356, 1340, 1265, 1243, 1166, 1091, 1017, 971, 756, 689, 662, 586, 560 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{41}H_{38}N_3O_7S$ $[M + NH_4]^+$ 716.24250, found 716.24271.



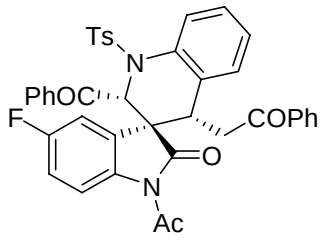
3af

(2'*R*,3'*S*,4'*S*)-1,2'-Diacetyl-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3af): The title compound **3af** was obtained according to the general procedure (58.3 mg, 96% yield). White solid, m.p. 198–201 ^{o}C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): major enantiomer t_R = 9.2 min, minor enantiomer t_R = 7.3 min, 85% ee. $[\alpha]_D^{30}$ –4.6 (*c* 1.45, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8..22 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.56–7.50 (m, 4H), 7.42–7.34 (m, 4H), 7.26–7.19 (m, 2H), 6.73 (t, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 5.25 (s, 1H), 5.21 (d, *J* = 8.0 Hz, 1H), 2.82 (d, *J* = 10.4 Hz, 1H), 2.72 (s, 3H), 2.66 (dd, J_1 = 17.6 Hz, J_2 = 11.2 Hz, 1H), 2.44 (s, 3H), 2.37 (d, *J* = 17.6 Hz, 1H), 2.15 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.8, 194.9, 176.6, 170.7, 145.2, 140.7, 136.4, 135.7, 133.6, 133.54, 133.50, 130.1, 129.7, 128.7, 128.5, 128.0, 127.8, 127.4, 127.1, 126.8, 124.8, 124.7, 122.9, 116.6, 72.6, 59.7, 38.7, 34.7, 28.4, 26.8, 21.7 ppm; IR (KBr): ν 3067, 2925, 1750, 1718, 1689, 1599, 1477, 1463, 1417, 1361, 1337, 1295, 1270, 1232, 1187, 1169, 1014, 925, 916, 813, 759, 690, 663, 585, 568 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{35}H_{30}N_2NaO_6S$ $[M + Na]^+$ 629.17168, found 629.17189.



3ag

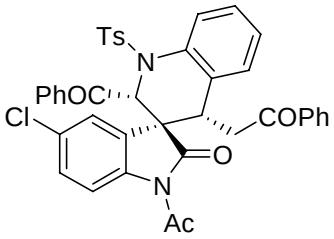
(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-(2,2-dimethylpropionyl)-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3ag): The title compound **3ag** was obtained according to the general procedure (55.4 mg, 85% yield). White solid, m.p. 174–176 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralpak ASH, *n*-hexane/2-propanol = 95:5, flow rate 0.5 mL/min, detection at 254 nm): major enantiomer t_R = 20.1 min, minor enantiomer t_R = 33.4 min, 86% ee. $[\alpha]_D^{30}$ –46.1 (*c* 1.38, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.68–7.63 (m, 4H), 7.56–7.46 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30–7.24 (m, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.03 (s, 1H), 5.52 (d, *J* = 7.6 Hz, 1H), 3.03 (d, *J* = 10.0 Hz, 1H), 2.72 (s, 3H), 2.62 (dd, J_1 = 17.2 Hz, J_2 = 10.4 Hz, 1H), 2.41 (s, 3H), 2.28 (dd, J_1 = 17.6 Hz, J_2 = 2.4 Hz, 1H), 0.85 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.5, 194.7, 178.0, 170.4, 144.4, 139.8, 137.5, 135.8, 135.3, 133.5, 132.9, 129.8, 129.4, 129.1, 128.7, 128.3, 127.8, 127.1, 126.8, 126.7, 125.7, 125.0, 124.6, 116.0, 67.4, 61.1, 44.2, 40.5, 34.2, 26.9, 26.3, 21.7 ppm; IR (KBr): ν 3066, 2961, 2922, 1748, 1718, 1686, 1599, 1479, 1463, 1449, 1369, 1354, 1339, 1294, 1266, 1232, 1167, 1088, 1046, 1015, 976, 812, 758, 689, 664, 585, 561 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{38}H_{40}N_3O_6S$ $[M + NH_4]^+$ 666.26323, found 666.26339.



3ah

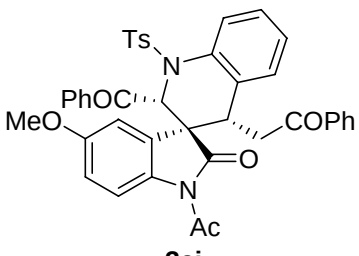
(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-benzoyl-5-fluoro-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3ah): The title compound **3ah** was obtained according to the general procedure (67.8 mg, 99% yield). White solid, m.p. 105–108 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralpak IA, *n*-hexane/2-propanol = 90:10, flow rate 0.8 mL/min, detection at 254 nm): major enantiomer t_R = 24.6 min, minor enantiomer t_R = 21.4 min, 76% ee. $[\alpha]_D^{20}$ +14.7 (*c* 1.13, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.82–7.79 (m, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.56–7.50 (m, 2H), 7.42–7.34 (m, 5H), 7.28–7.16 (m, 5H), 6.84 (dt, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 6.45 (s, 1H), 4.97 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H), 3.18 (d, *J* = 10.4 Hz, 1H), 2.68 (dd, J_1 = 17.2 Hz, J_2 = 10.4 Hz, 1H), 2.45 (s, 3H), 2.44 (s,

3H), 2.25 (dd, J_1 = 17.2 Hz, J_2 = 2.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 194.6, 177.2, 169.4, 158.2, 144.6, 136.8, 136.0, 135.8, 135.6, 135.3, 133.6, 133.2, 132.5, 128.8 (d, $^1J_{CF}$ = 236.9 Hz), 128.9, 128.74, 128.70, 128.2, 127.8, 127.0, 126.9, 126.3, 126.2, 126.0, 117.1 (d, $^3J_{CF}$= 7.9 Hz), 116.1 (d, $^2J_{CF}$ = 22.4 Hz), 112.9 (d, $^2J_{CF}$ = 25.6 Hz), 70.0, 60.4, 39.6, 34.5, 26.4, 21.7 ppm; IR (KBr): ν 3066, 2925, 1751, 1721, 1689, 1598, 1477, 1448, 1370, 1359, 1291, 1251, 1168, 1091, 1011, 970, 813, 759, 738, 695, 666, 581, 565 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{40}H_{35}FN_3O_6S$ $[M + NH_4]^+$ 704.22251, found 704.22153.



3ai

(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-benzoyl-5-chloro-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3ai): The title compound **3ai** was obtained according to the general procedure (69.6 mg, 99% yield). White solid, m.p. 102–105 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralpak IA, *n*-hexane/2-propanol = 95:5, flow rate 0.8 mL/min, detection at 254 nm): major enantiomer t_R = 46.9 min, minor enantiomer t_R = 41.9 min, 89% ee. $[\alpha]_D^{20}$ –10.1 (*c* 1.19, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.56–7.51 (m, 2H), 7.44–7.34 (m, 5H), 7.25–7.17 (m, 5H), 7.12 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.56 (d, *J* = 7.2 Hz, 1H), 6.43 (s, 1H), 5.15 (d, *J* = 2.0 Hz, 1H), 3.17 (d, *J* = 8.8 Hz, 1H), 2.69 (dd, J_1 = 17.6 Hz, J_2 = 2.4 Hz, 1H), 2.46 (s, 3H), 2.44 (s, 3H), 2.25 (dd, J_1 = 17.6 Hz, J_2 = 2.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 194.6, 176.9, 169.5, 144.6, 138.2, 136.8, 136.0, 135.6, 135.3, 133.6, 133.1, 132.5, 130.6, 130.0, 129.4, 128.9, 128.8, 128.7, 128.2, 127.8, 127.7, 127.0, 126.9, 126.1, 126.0, 125.4, 116.9, 69.1, 60.3, 39.6, 34.4, 26.4, 21.7 ppm; IR (KBr): ν 3069, 2925, 1752, 1723, 1689, 1597, 1487, 1468, 1448, 1368, 1359, 1321, 1293, 1258, 1237, 1167, 1104, 1091, 1008, 969, 812, 756, 742, 726, 695, 666, 613, 569 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{40}H_{35}ClN_3O_6S$ $[M + NH_4]^+$ 720.19296, found 720.19306.

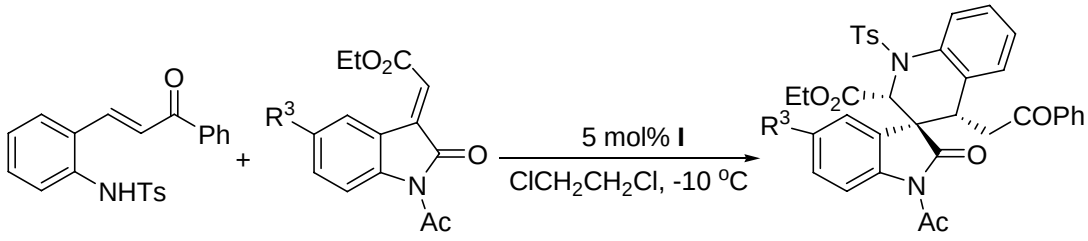


3aj

(2'*R*,3'*S*,4'*S*)-1-Acetyl-2'-benzoyl-5-methoxy-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-

tosyl-spiro[indoline-3,3'-tetrahydroquinoline] (3aj): The title compound **3aj** was obtained according to the general procedure (69.2 mg, 99% yield). White solid, m.p. 94–97 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralpak IA, *n*-hexane/2-propanol = 95:5, flow rate 0.8 mL/min, detection at 254 nm): major enantiomer t_R = 65.1 min, minor enantiomer t_R = 58.3 min, 90% ee. $[\alpha]_D^{20}$ +8.7 (*c* 1.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.74–7.66 (m, 5H), 7.55–7.48 (m, 2H), 7.40–7.34 (m, 5H), 7.24–7.15 (m, 5H), 6.65 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.43 (s, 1H), 4.78 (d, *J* = 2.8 Hz, 1H), 3.32 (s, 3H), 3.15 (dd, J_1 = 10.4 Hz, J_2 = 2.0 Hz, 1H), 2.68 (dd, J_1 = 17.6 Hz, J_2 = 10.4 Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 2.30 (dd, J_1 = 17.6 Hz, J_2 = 2.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 194.9, 177.5, 169.3, 156.5, 144.5, 137.1, 136.2, 135.7, 135.4, 133.5, 133.14, 133.05, 132.9, 130.0, 128.9, 128.7, 128.4, 128.1, 127.8, 127.6, 126.9, 126.8, 126.2, 125.2, 116.8, 115.7, 109.7, 69.2, 60.4, 55.0, 39.6, 34.6, 26.4, 21.7 ppm; IR (KBr): ν 3065, 2925, 1747, 1715, 1689, 1597, 1485, 1448, 1358, 1295, 1256, 1184, 1167, 1099, 1091, 1008, 970, 813, 758, 737, 695, 666, 656, 562 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{41}H_{38}N_3O_7S$ $[M + NH_4]^+$ 716.24250, found 716.24258.

Further investigation of substrate scope



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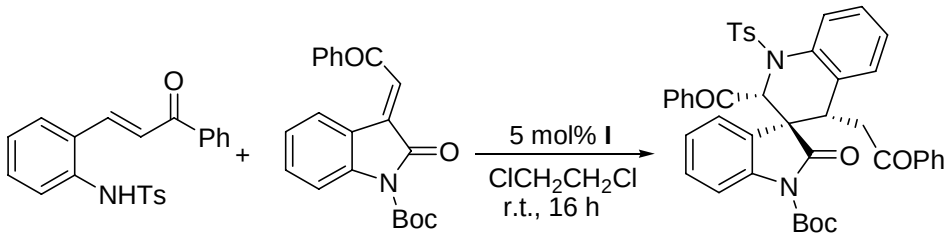
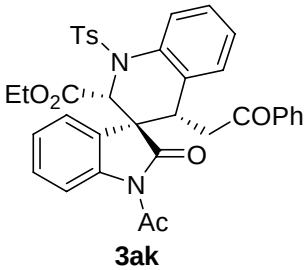


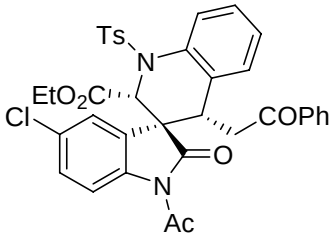
1a **2n** **3an**



3ak

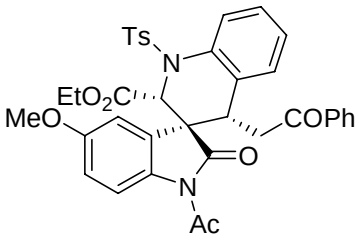
(2'*R*,3'*S*,4'*S*)-2'-Ethyl 1-acetyl-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline]-2'-carboxylate (3ak): The title compound **3ak** was obtained according to the general procedure with −10 °C instead of room temperature (61.6 mg, 97%

yield). White solid, m.p. 196–198 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): major enantiomer t_R = 13.4 min, minor enantiomer t_R = 16.9 min, 84% ee. $[\alpha]_D^{20}$ +3.7 (*c* 1.03, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.48–7.39 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 5.55 (s, 1H), 5.28 (d, *J* = 7.6 Hz, 1H), 3.74–3.66 (m, 1H), 3.60–3.52 (m, 1H), 2.98 (d, *J* = 8.8 Hz, 1H), 2.75–2.68 (m, 4H), 2.42–2.37 (m, 4H), 0.70 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 177.2, 170.6, 167.6, 144.6, 140.4, 136.3, 135.7, 134.8, 133.5, 132.9, 129.9, 129.6, 128.7, 128.45, 128.42, 127.8, 127.0, 126.9, 126.1, 125.0, 124.8, 124.1, 116.0, 66.1, 61.5, 60.0, 39.1, 34.6, 26.8, 21.7, 13.2 ppm; IR (KBr): ν 3065, 2978, 2926, 1756, 1721, 1688, 1599, 1478, 1463, 1368, 1362, 1340, 1299, 1270, 1243, 1186, 1168, 1102, 1095, 1018, 1009, 810, 758, 690, 662, 586, 560 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{36}H_{36}N_3O_7S$ $[M + NH_4]^+$ 654.22685, found 654.22775.



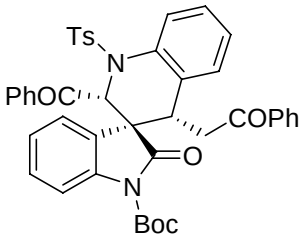
3al

(2'*R*,3'*S*,4'*S*)-2'-Ethyl 1-acetyl-5-chloro-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-tosyl-spiro [indoline-3,3'-tetrahydroquinoline]-2'-carboxylate (3al): The title compound **3al** was obtained according to the general procedure with –10 °C instead of room temperature (66.8 mg, 99% yield). White solid, m.p. 187–189 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 80:20, flow rate 1.0 mL/min, detection at 254 nm): major enantiomer t_R = 10.3 min, minor enantiomer t_R = 8.9 min, 78% ee. $[\alpha]_D^{20}$ –37.1 (*c* 1.11, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.62–7.55 (m, 3H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.24–7.17 (m, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 5.54 (s, 1H), 5.14 (s, 1H), 3.82–3.64 (m, 2H), 3.00 (d, *J* = 10.8 Hz, 1H), 2.77–2.70 (m, 4H), 2.43 (s, 3H), 2.37 (d, *J* = 17.2 Hz, 1H), 0.77 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.7, 176.6, 170.6, 167.6, 144.9, 139.1, 136.3, 135.7, 134.8, 133.8, 132.7, 130.6, 130.2, 129.7, 128.9, 128.8, 128.0, 127.3, 127.0, 126.9, 126.3, 124.6, 117.4, 109.8, 66.2, 61.9, 60.2, 39.2, 34.6, 26.9, 21.9, 13.5 ppm; IR (KBr): ν 3069, 2980, 2927, 1759, 1723, 1688, 1598, 1487, 1469, 1368, 1323, 1295, 1258, 1241, 1187, 1168, 1106, 1092, 1009, 809, 754, 726, 690, 662, 613, 570 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{36}H_{35}ClN_3O_7S$ $[M + NH_4]^+$ 688.18788, found 688.18777.



3am

(2'*R*,3'*S*,4'*S*)-2'-Ethyl 1-acetyl-5-methoxy-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-tosyl-spiro[indoline-3,3'-tetrahydroquinoline]-2'-carboxylate (3am): The title compound **3am** was obtained according to the general procedure with −10 °C instead of room temperature (65.2 mg, 98% yield). White solid, m.p. 99–102 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): major enantiomer t_R = 16.1 min, minor enantiomer t_R = 18.1 min, 84% ee. $[\alpha]_D^{20}$ −15.2 (*c* 1.09, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.63–7.54 (m, 3H), 7.49–7.40 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.76 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 5.53 (s, 1H), 4.80 (s, 1H), 3.80–3.72 (m, 1H), 3.66–3.58 (m, 1H), 3.32 (s, 3H), 2.97 (d, *J* = 10.0 Hz, 1H), 2.77–2.69 (m, 4H), 2.43–2.39 (m, 4H), 0.74 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 177.0, 170.2, 167.5, 156.3, 144.6, 136.4, 135.7, 134.8, 133.64, 133.56, 133.1, 130.0, 128.7, 128.6, 128.3, 127.8, 127.0, 126.9, 126.4, 125.9, 117.1, 115.4, 109.0, 66.0, 61.5, 60.1, 54.9, 39.1, 34.6, 26.6, 21.7, 13.3 ppm; IR (KBr): ν 3065, 2939, 1755, 1716, 1689, 1597, 1485, 1450, 1361, 1297, 1257, 1185, 1169, 1103, 1095, 1034, 1008, 812, 755, 742, 691, 662, 617, 579 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{37}H_{38}N_3O_8S$ $[M + NH_4]^+$ 684.23741, found 684.23865.



3an

(2'*R*,3'*S*,4'*S*)-1-*tert*-Butyl 2'-benzoyl-4'-(2-oxo-1-phenylethyl)-2-oxo-1'-tosyl-spiro-[indoline-3,3'-tetrahydroquinoline]-1-carboxylate (3an): The title compound **3an** was obtained according to the general procedure (72.0 mg, 99% yield). White solid, m.p. 108–111 °C. Enantiomeric excess was determined by HPLC (Daicel Chiralcel AD-H, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): major enantiomer t_R = 22.3 min, minor enantiomer t_R = 14.4 min, 53% ee. $[\alpha]_D^{20}$ +4.7 (*c* 1.20, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.54–7.46 (m, 2H), 7.40–7.28 (m, 6H), 7.22–7.06 (m, 6H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 6.51 (s, 1H), 5.27 (d, *J* = 7.6 Hz, 1H), 3.12 (d, *J* = 9.6 Hz, 1H), 2.60

(dd, J_1 = 17.2 Hz, J_2 = 10.8 Hz, 1H), 2.41–2.36 (m, 4H), 1.57 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8, 195.1, 175.6, 147.7, 144.2, 139.2, 136.9, 135.9, 135.6, 133.3, 133.2, 132.6, 129.9, 129.1, 128.9, 128.5, 128.3, 128.2, 127.8, 127.6, 126.9, 126.8, 126.0, 125.5, 124.4, 124.0, 114.0, 85.1, 68.8, 60.2, 39.5, 34.7, 27.9, 21.6 ppm; IR (KBr): ν 3060, 2980, 2931, 1790, 1754, 1740, 1708, 1691, 1598, 1479, 1464, 1448, 1357, 1298, 1239, 1167, 1150, 1093, 971, 753, 694, 664, 561 cm^{-1}; HRMS (ESI): m/z calcd. for $C_{43}H_{42}N_3O_7S$ $[M + NH_4]^+$ 744.27380, found 744.27502.

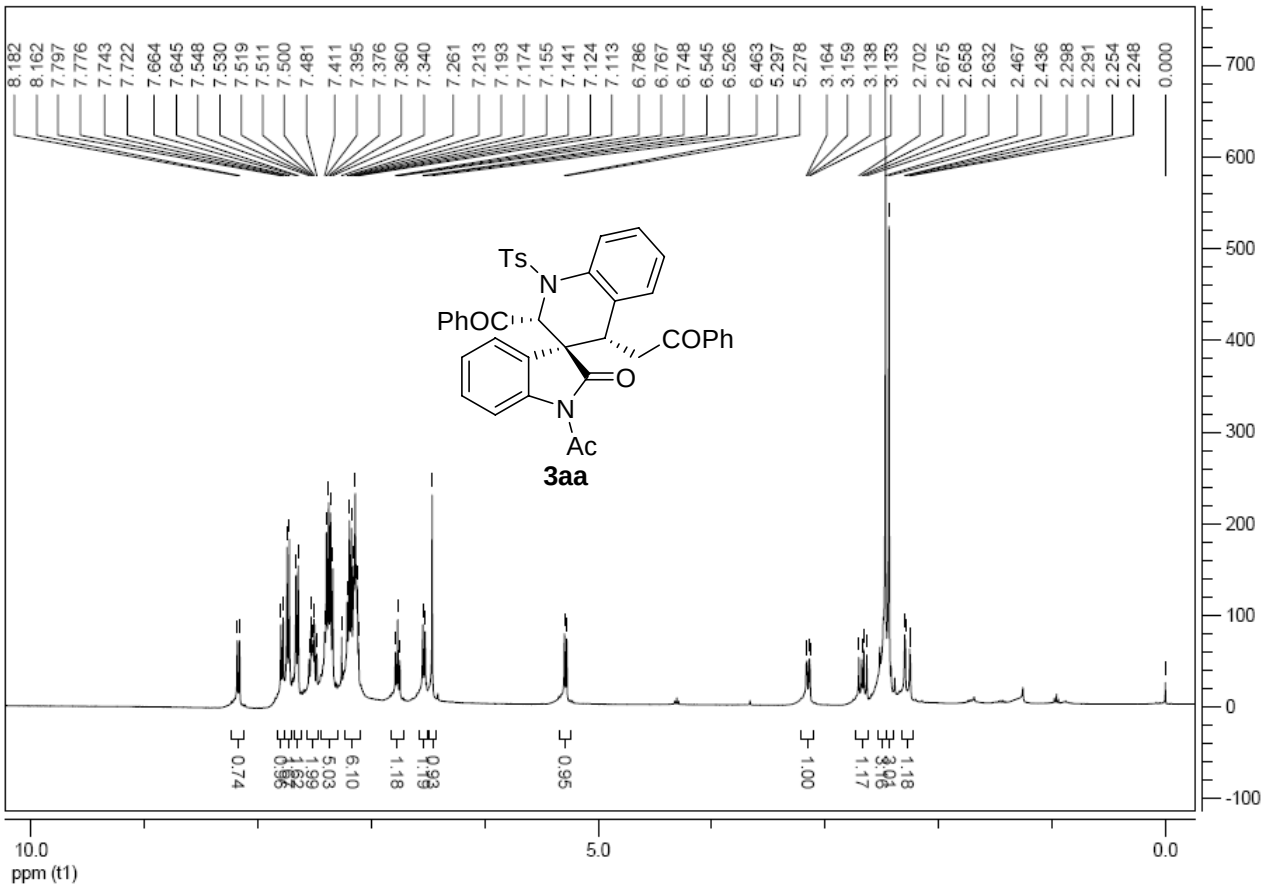
References

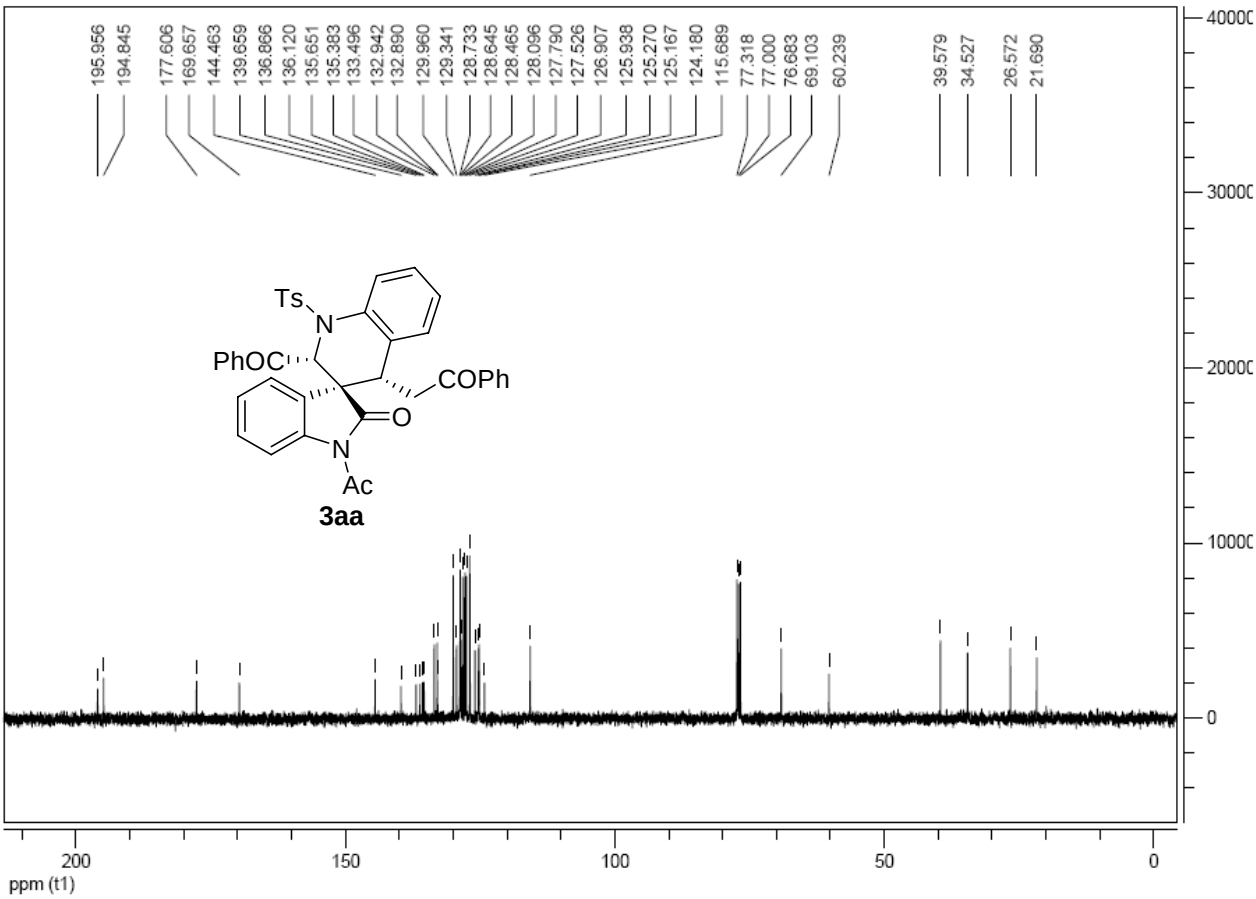
1 (*a*) W. Yang and D.-M. Du, *Org. Lett.*, 2010, **12**, 5450; (*b*) W. Yang and D.-M. Du, *Adv. Synth. Catal.*, 2011, **353**, 1241; (*c*) J. W. Lee, T. H. Ryu, J. S. Oh, H. Y. Bae, H. B. Jang and C. E. Song, *Chem. Commun.*, 2009, 7224.

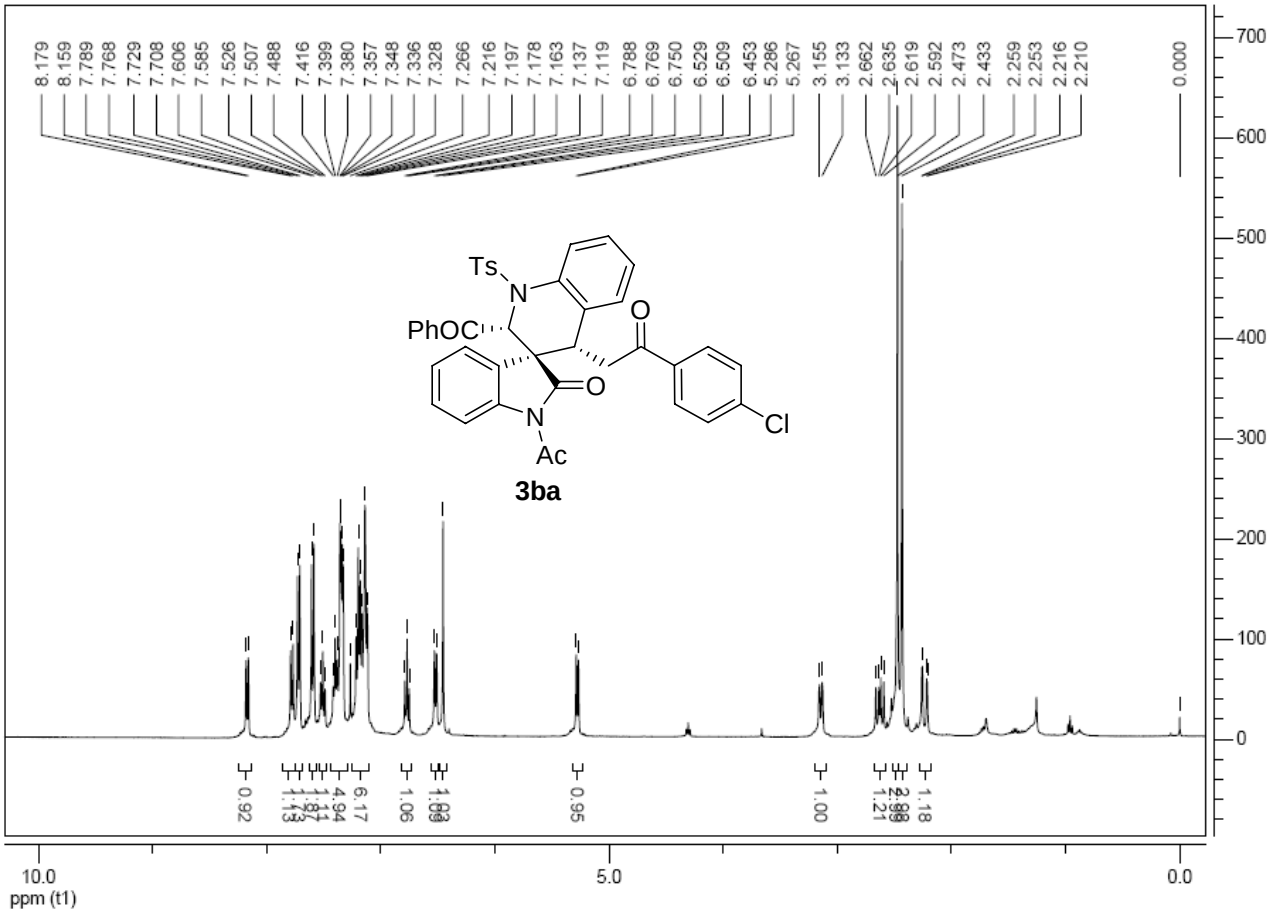
2 (*a*) A. Patti and S. Pedotti, *Tetrahedron*, 2010, **66**, 5607; (*b*) W. R. Bowman, A. J. Fletcher, J. M. Pedersen, P. J. Lovell, M. R. J. Elsegood, E. H. Lopez, V. Mckee and G. B. S. Potts, *Tetrahedron*, 2007, **63**, 191; (*c*) A. Gonzalez-Gomez, G. Dominguez and J. Perez-Castells, *Eur. J. Org. Chem.*, 2009, 5057.

3 B. Tan, X. Zeng, W. W. Y. Leong, Z. Shi, C. F. Barbas III and G. Zhong, *Chem. Eur. J.*, 2012, **18**, 63.

Copies of ^{1}H and ^{13}C NMR spectra of new compounds



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7.163
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6.769
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2.619
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Ac
Cl
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1.97
4.94
6.17
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0.95
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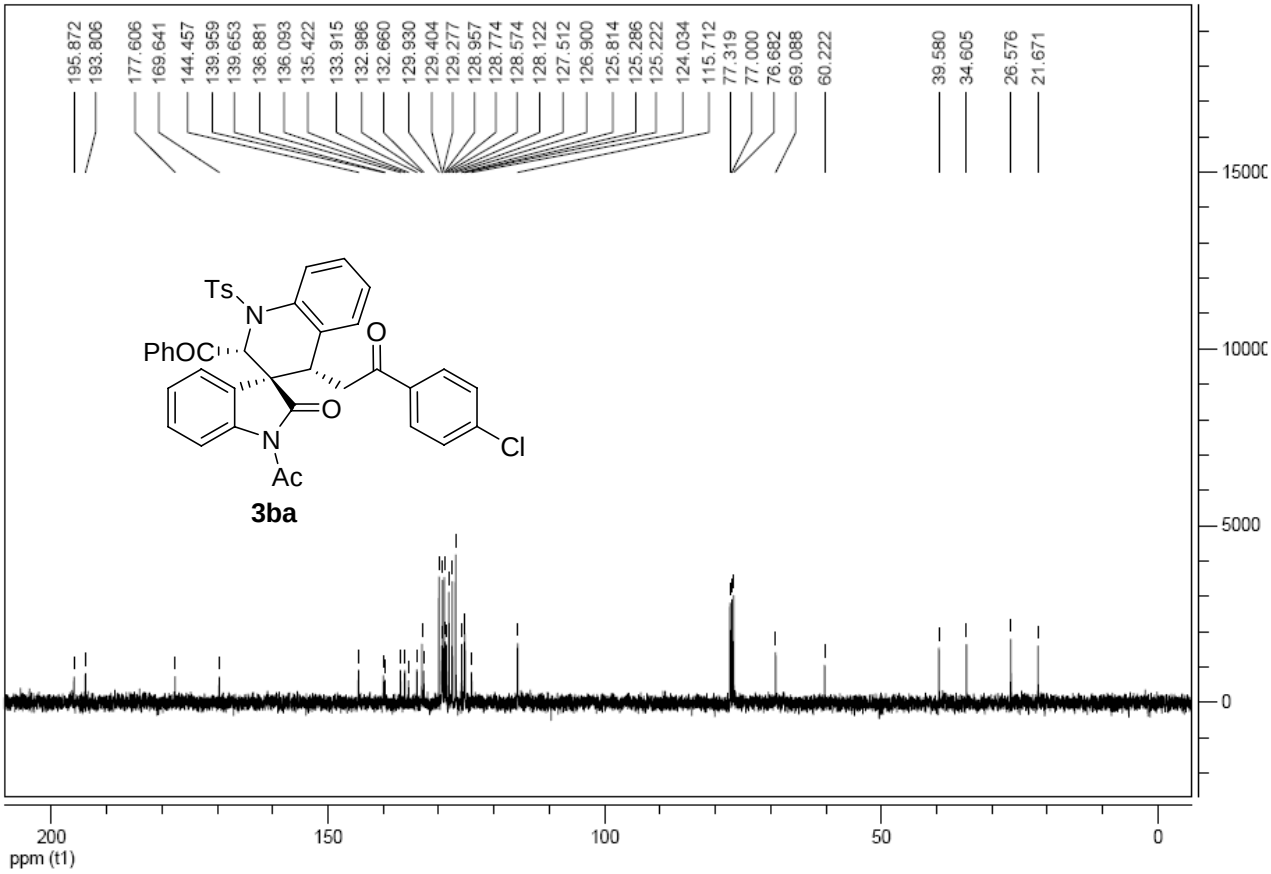
ppm (t1)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125.286
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Ts
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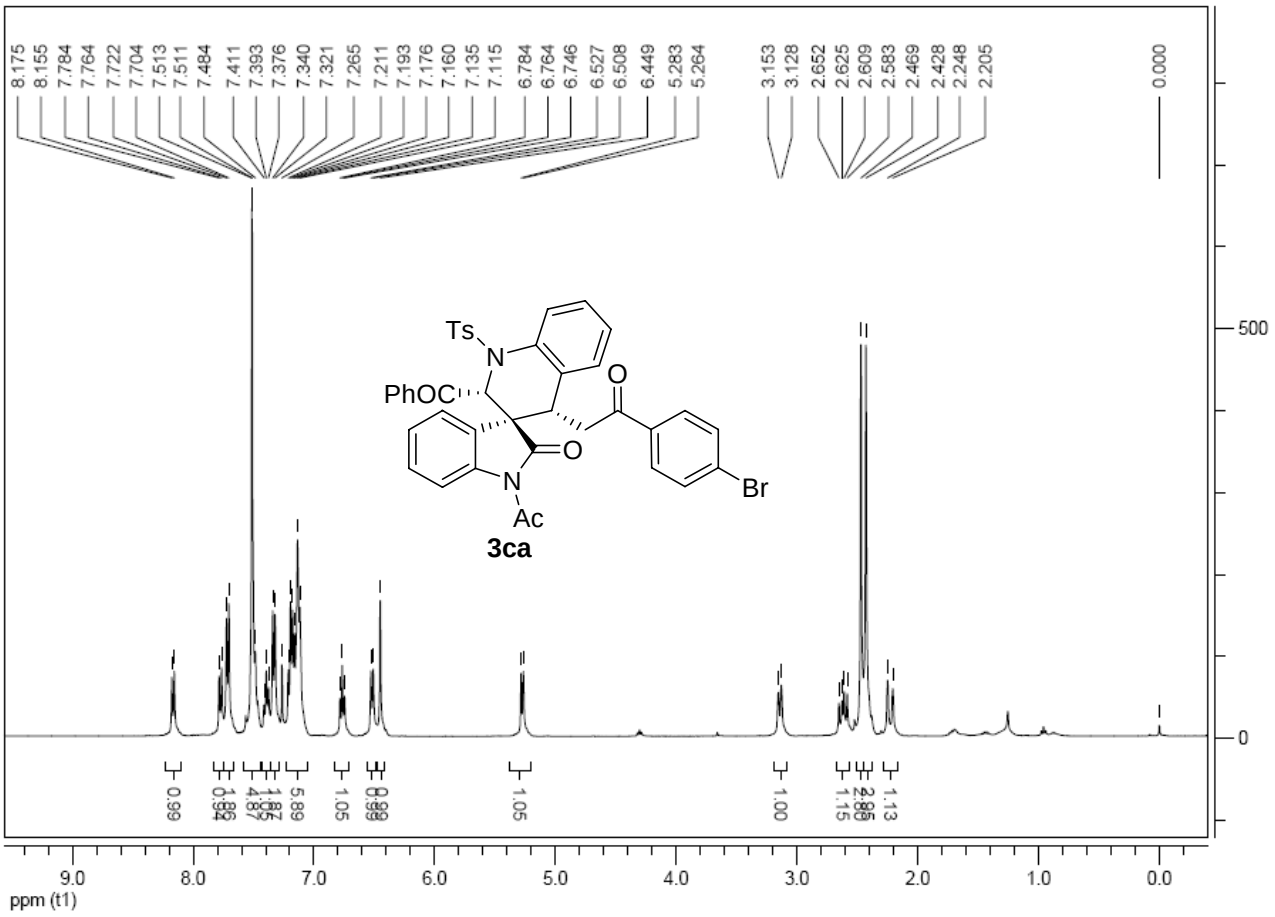
ppm (t1)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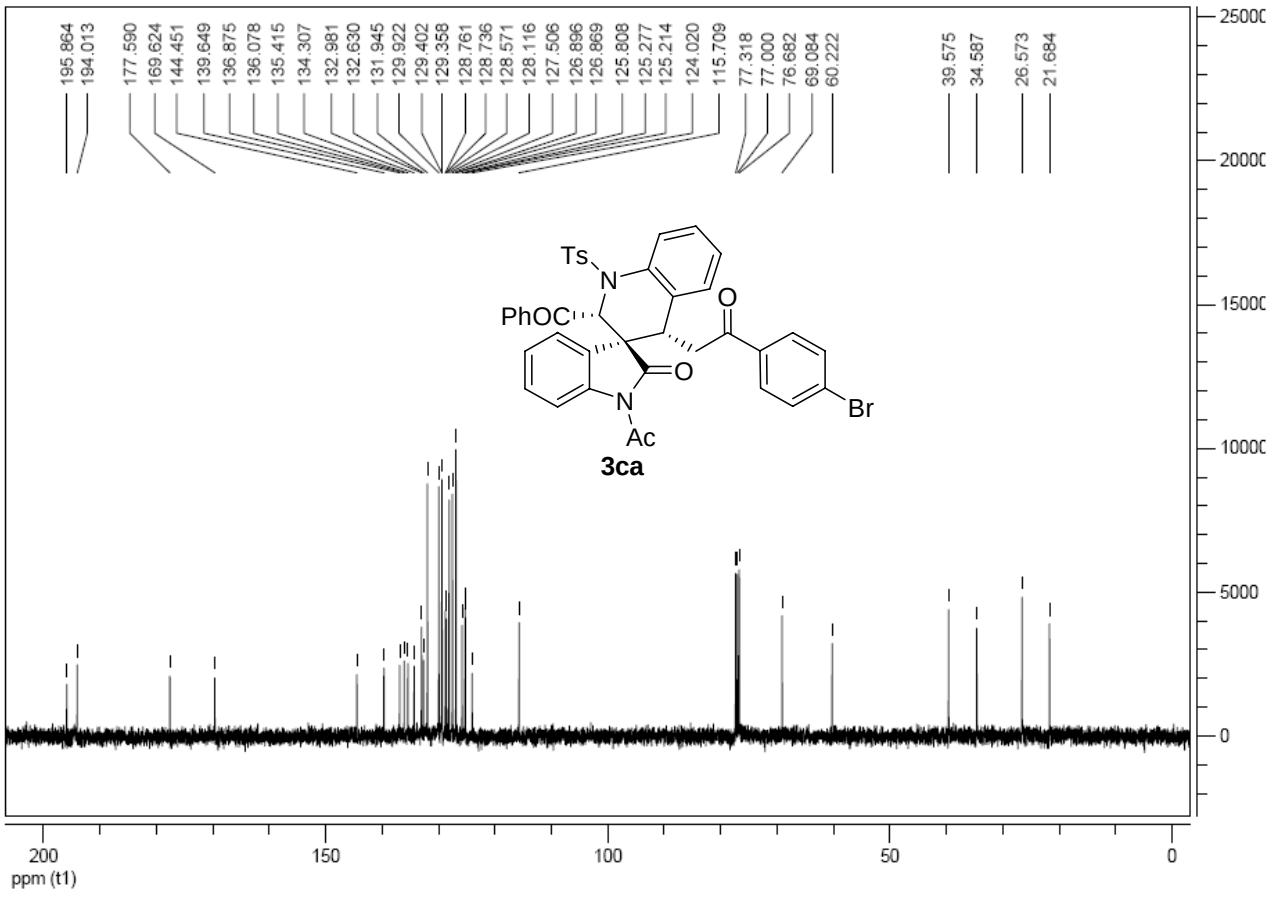
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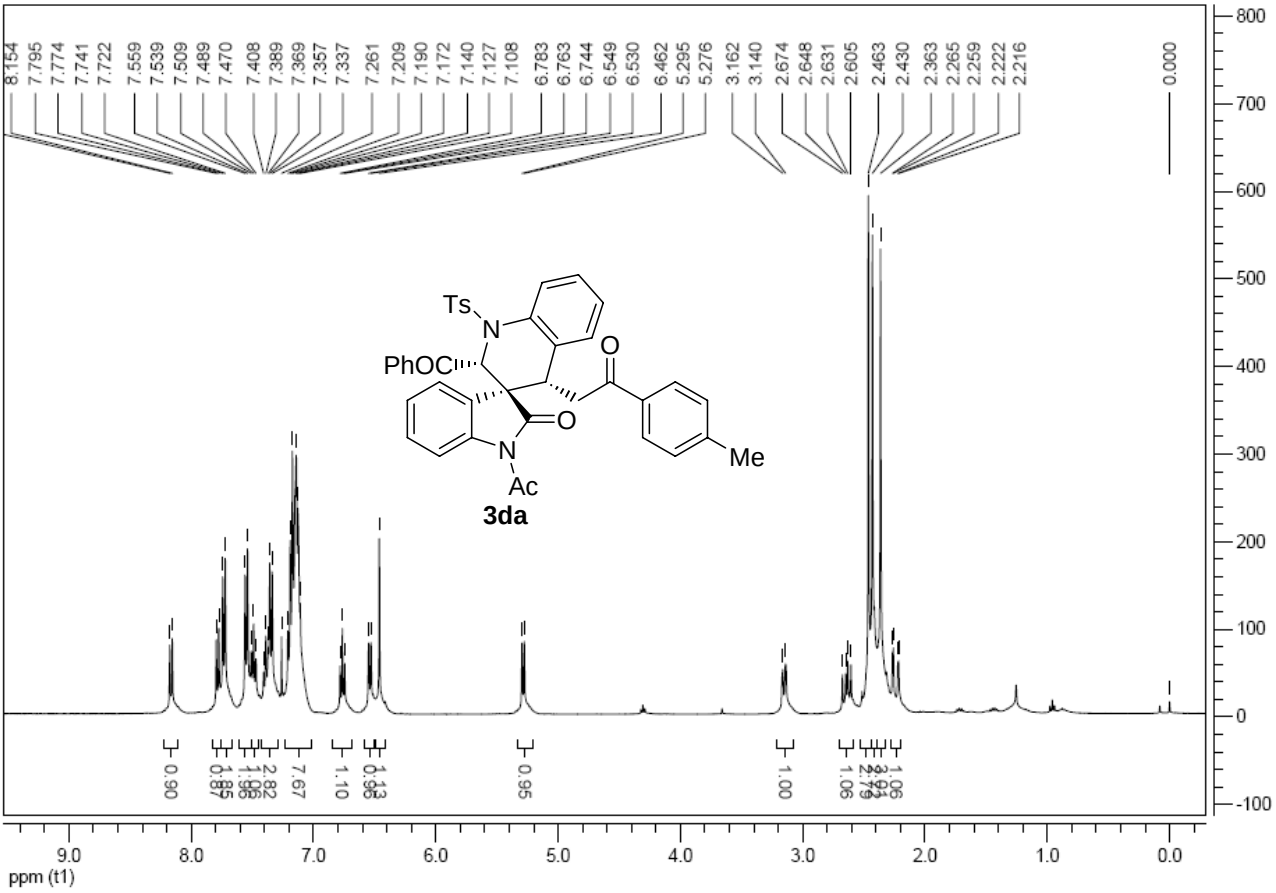
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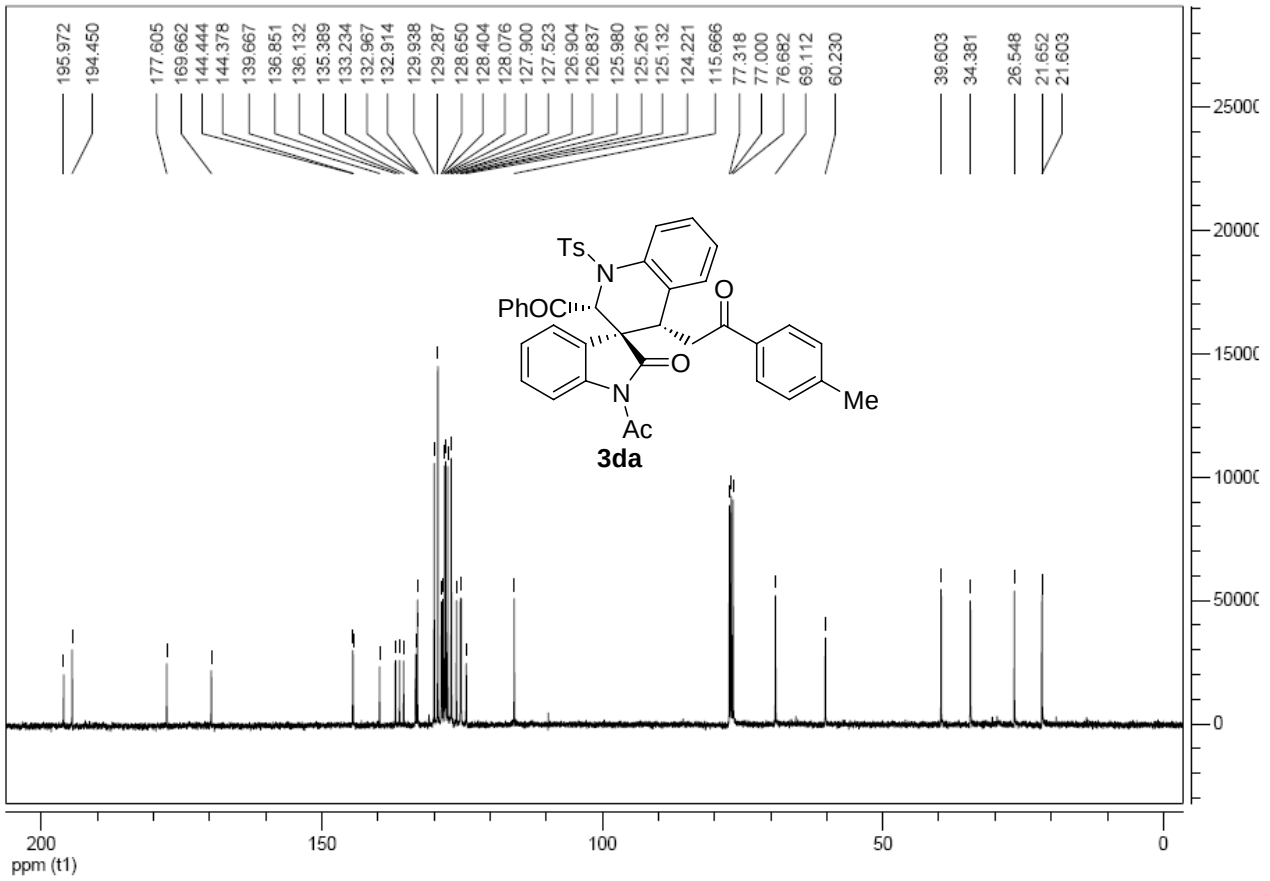
ppm (t1)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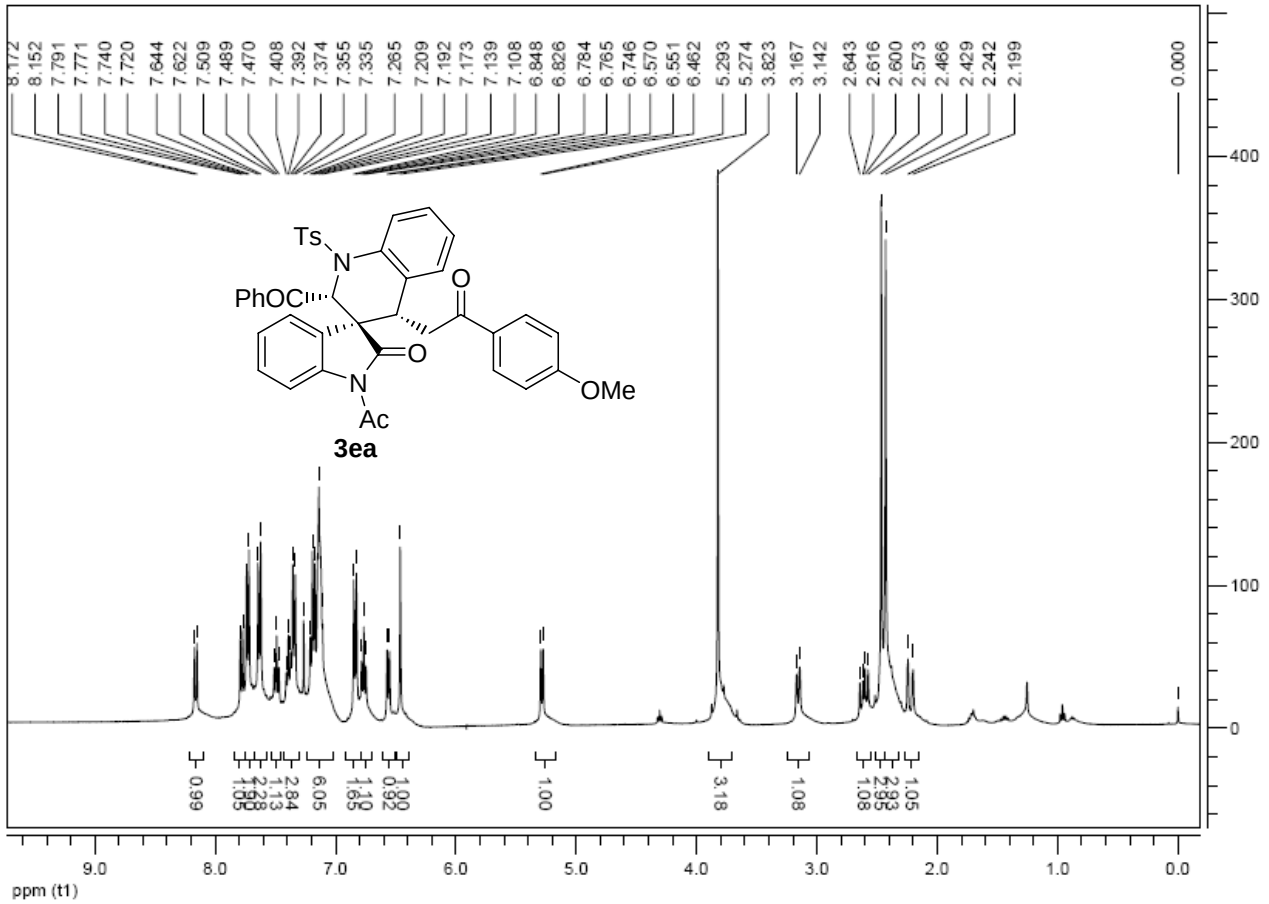
ppm (t1)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7.139
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6.746
6.570
6.551
6.462
5.293
5.274
3.823
3.167
3.142
2.643
2.616
2.600
2.573
2.466
2.429
2.242
2.199
0.000
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N
PhOC
O
O
N
Ac
OMe
3ea
0.99
1.05
1.13
2.84
6.05
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1.00
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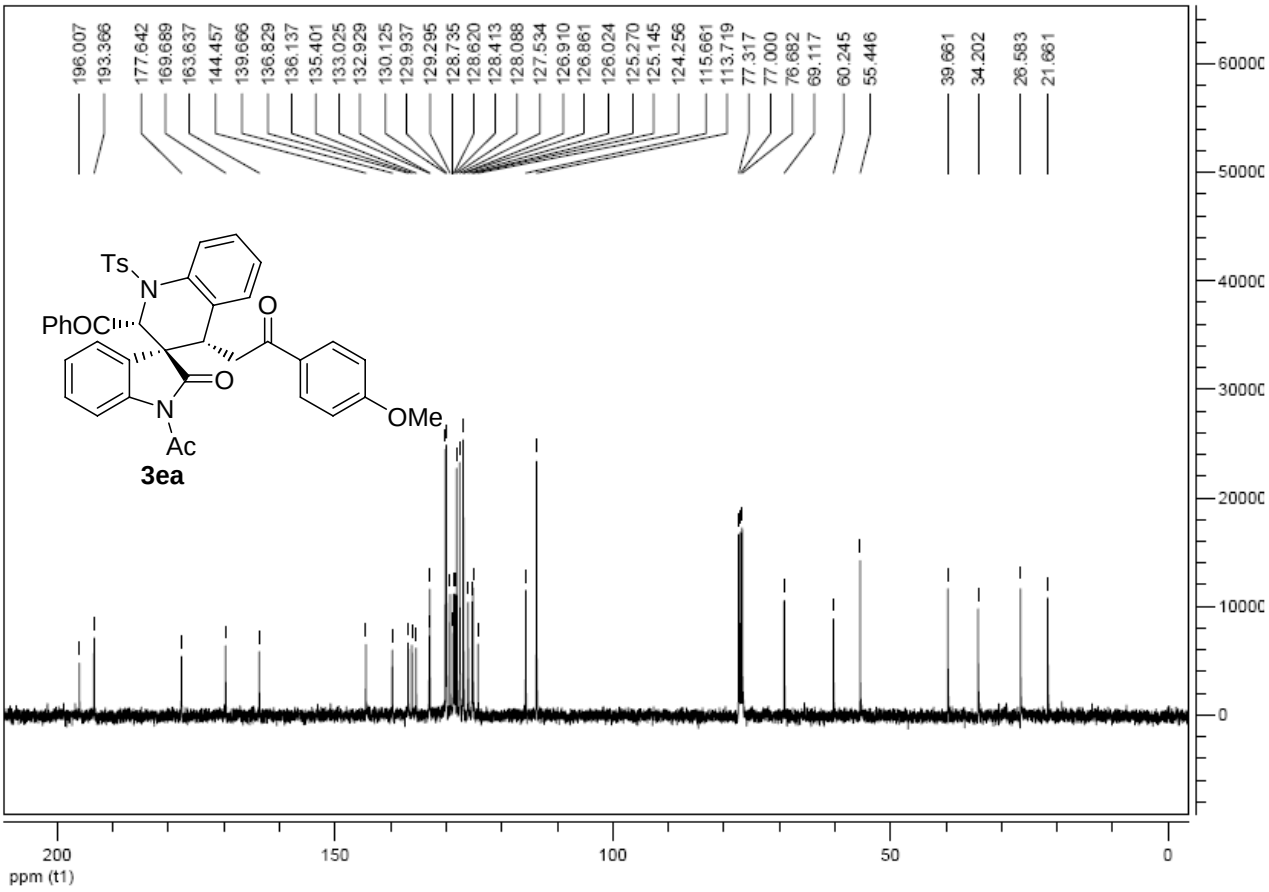
1.08
1.08
2.95
2.83
1.05
ppm (t1)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136.829
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135.401
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132.929
130.125
129.937
129.295
128.735
128.620
128.413
128.088
127.534
126.910
126.861
126.024
125.270
125.145
124.256
115.661
113.719
77.317
77.000
76.682
69.117
60.245
55.446
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26.583
21.661
Ts
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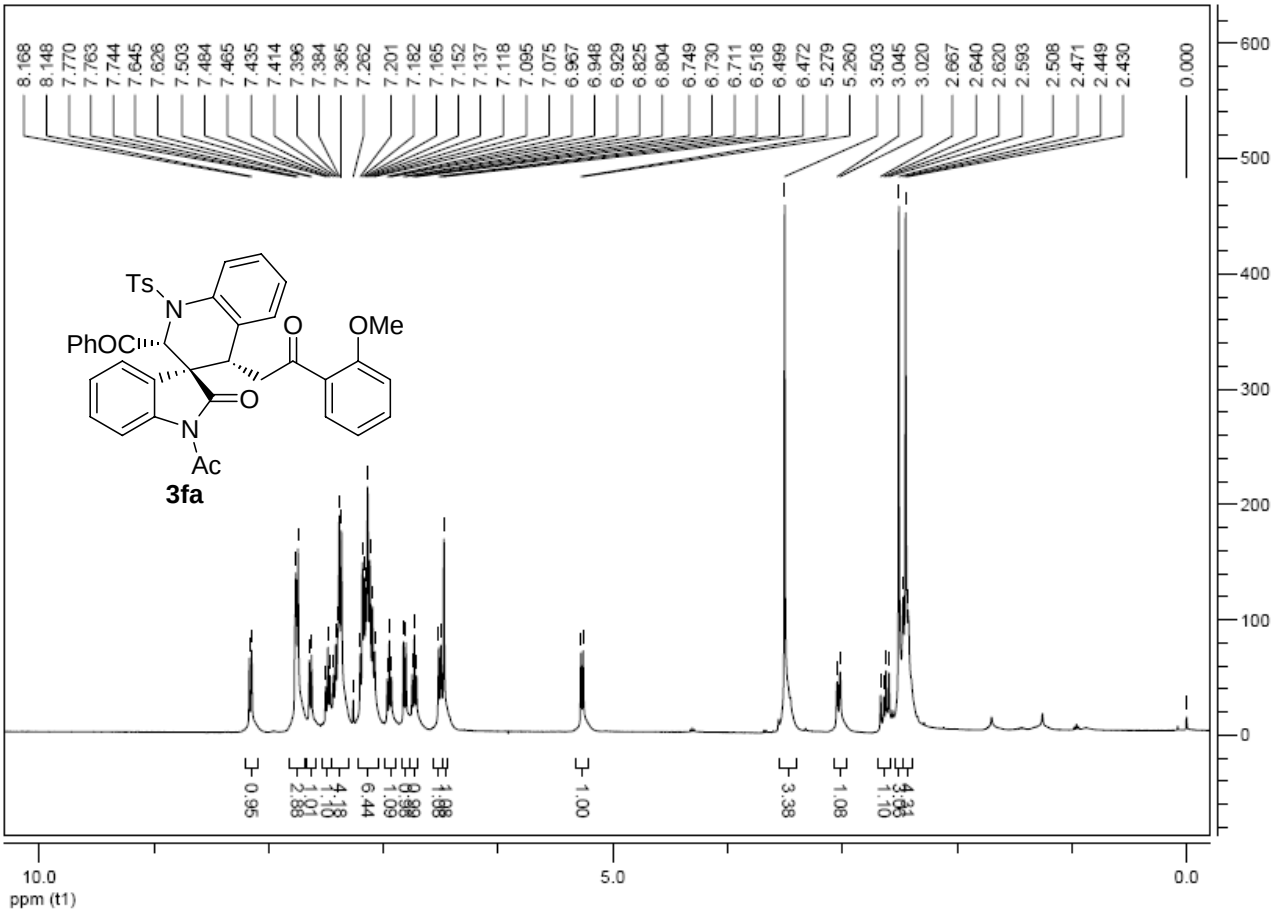
PhOC
O
O
N
Ac
OMe
3ea
ppm (t1)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7.503
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7.465
7.435
7.414
7.396
7.384
7.365
7.262
7.201
7.182
7.165
7.152
7.137
7.118
7.095
7.075
6.967
6.948
6.929
6.825
6.804
6.749
6.730
6.711
6.518
6.499
6.472
5.279
5.260
3.503
3.045
3.020
2.667
2.640
2.620
2.593
2.508
2.471
2.449
2.430
0.000
Ts
N
PhOC
O
OMe
O
N
Ac
3fa
0.95
2.88
1.01
1.18
4.10
6.44
1.09
0.98
0.98
1.88
1.00
3.38
1.08
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4.24
600
500
400
300
200
100
0
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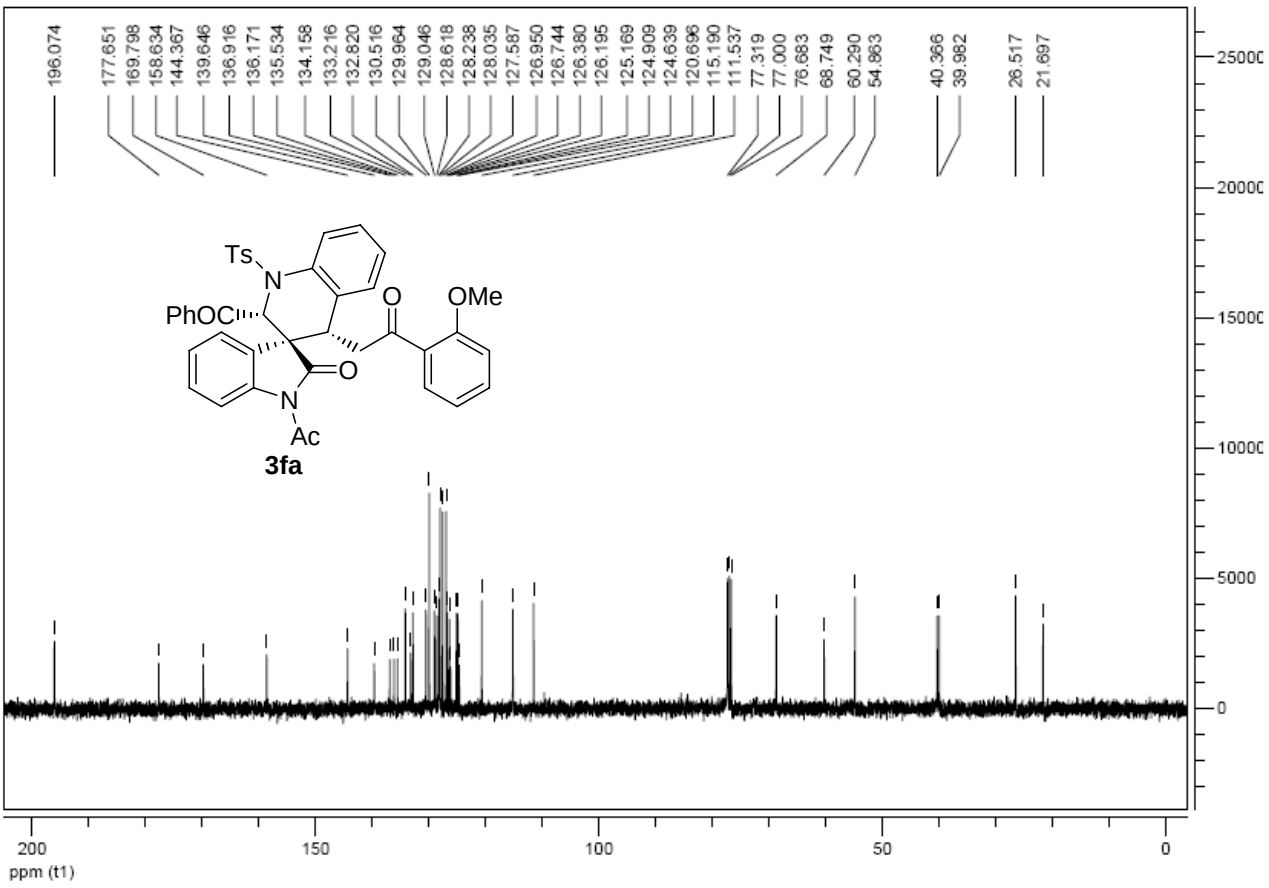
ppm (t1)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128.238
128.035
127.587
126.950
126.744
126.380
126.195
125.169
124.909
124.639
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77.319
77.000
76.683
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40.366
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26.517
21.697
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N
PhOC
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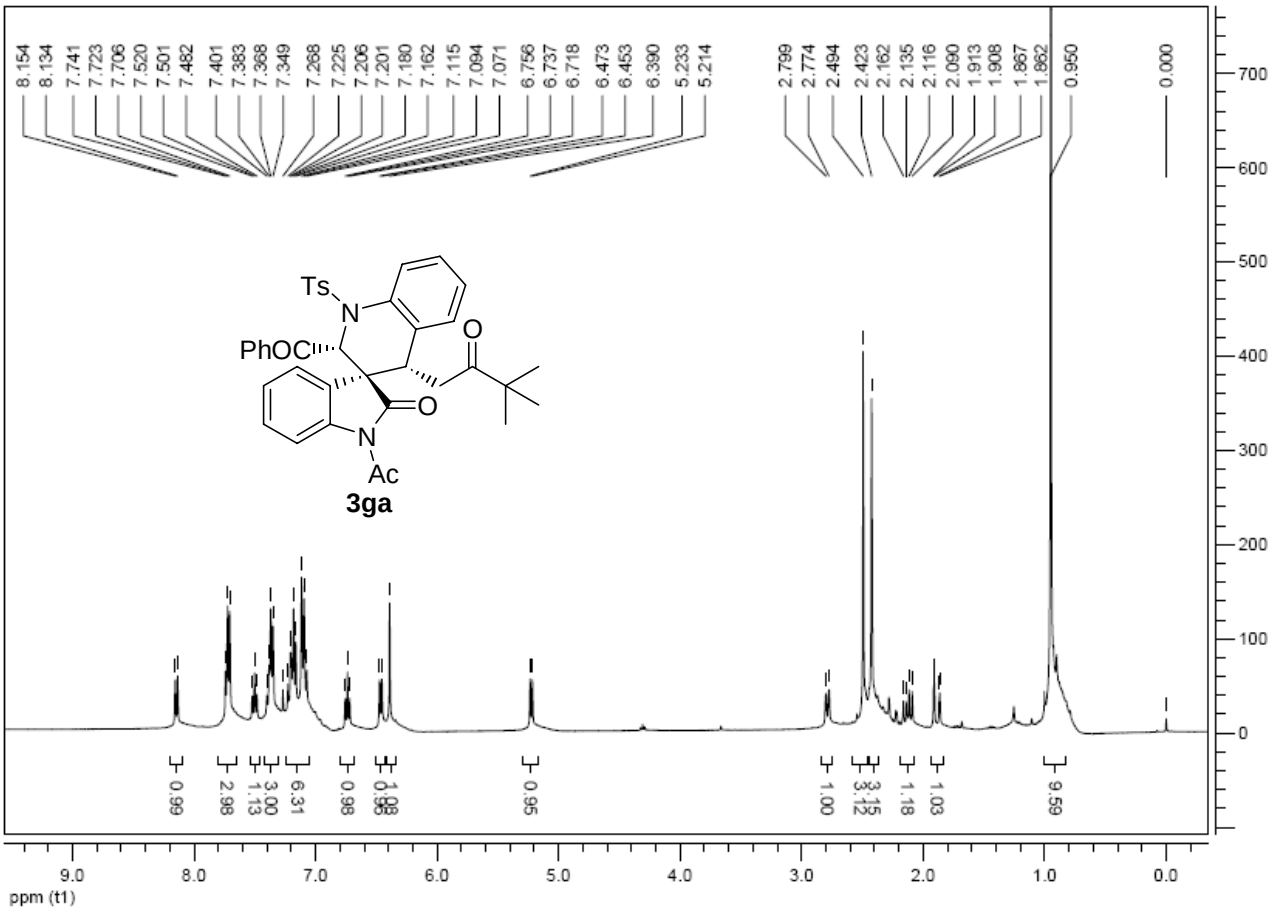
ppm (t1)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7.520
7.501
7.482
7.401
7.383
7.368
7.349
7.268
7.225
7.206
7.201
7.180
7.162
7.115
7.094
7.071
6.756
6.737
6.718
6.473
6.453
6.390
5.233
5.214
2.799
2.774
2.494
2.423
2.162
2.135
2.116
2.090
1.913
1.908
1.867
1.862
0.950
0.000
Ts
N
PhOC
O
O
N
Ac
3ga
0.99
2.98
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1.18
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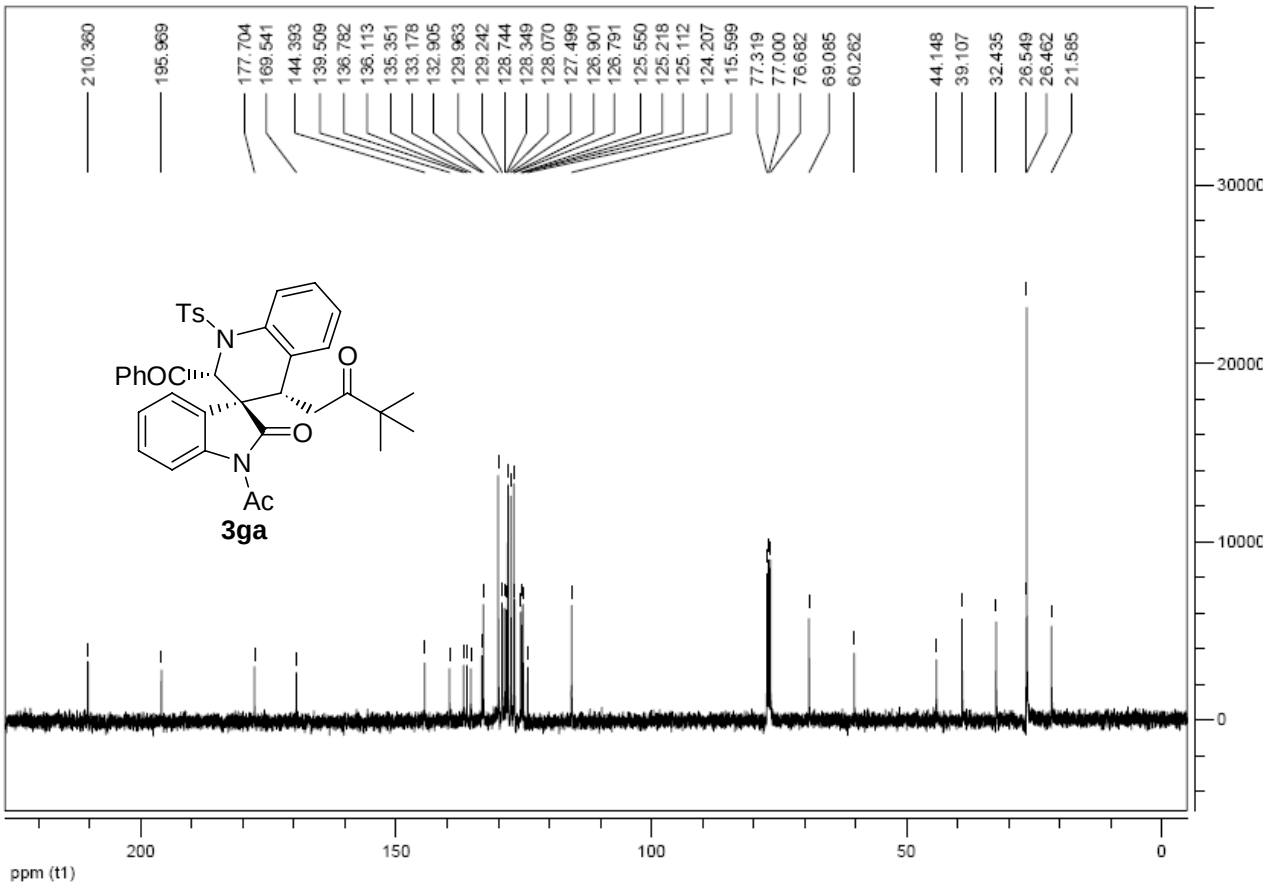
ppm (t1)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128.349
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127.499
126.901
126.791
125.550
125.218
125.112
124.207
115.599
77.319
77.000
76.682
69.085
60.262
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26.549
26.462
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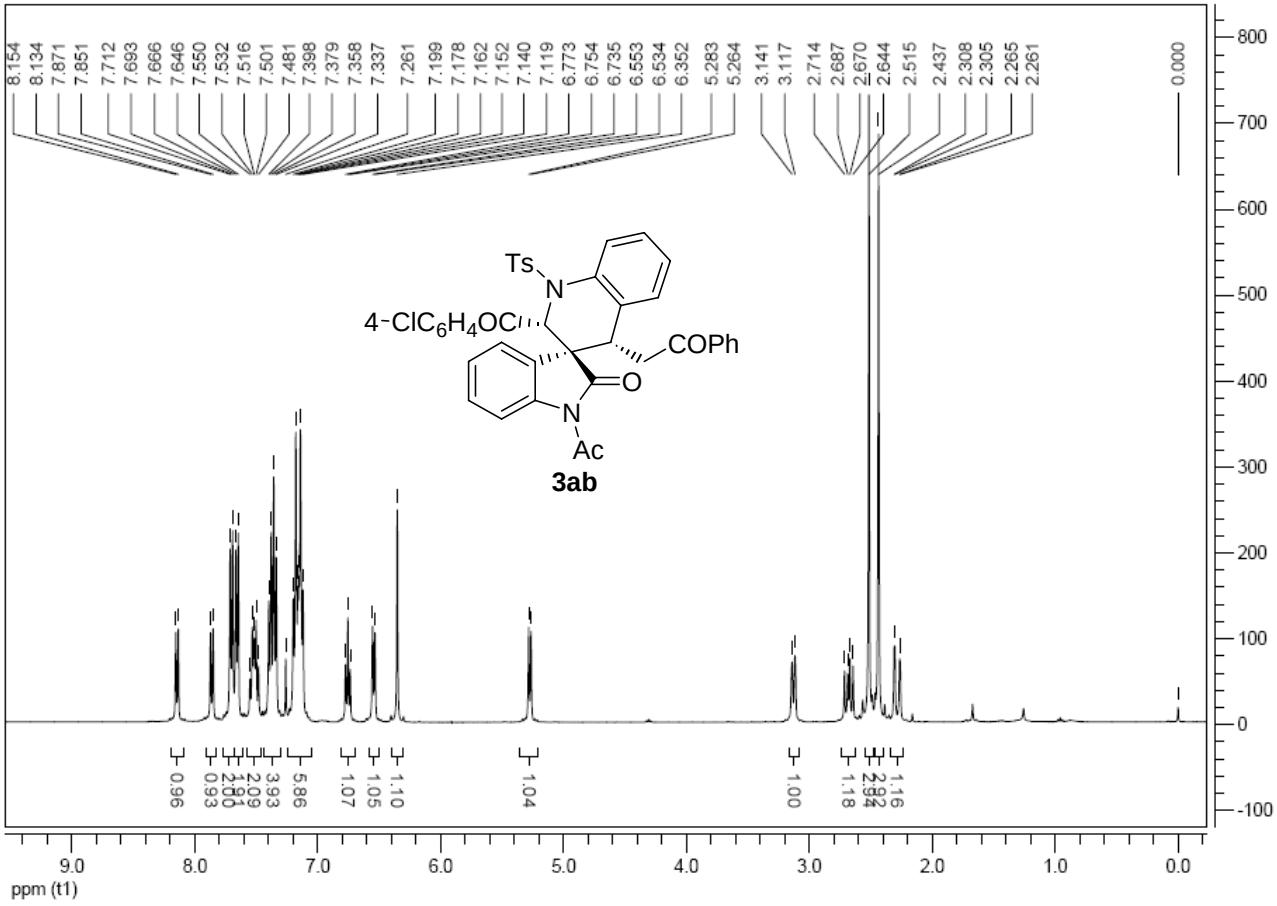
PhOC
O
O
N
Ac
3ga
ppm (t1)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7.646
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7.532
7.516
7.501
7.481
7.398
7.379
7.358
7.337
7.261
7.199
7.178
7.162
7.152
7.140
7.119
6.773
6.754
6.735
6.553
6.534
6.352
5.283
5.264
3.141
3.117
2.714
2.687
2.670
2.644
2.515
2.437
2.308
2.305
2.265
2.261
0.000
Ts
N
4-ClC6H4OC
COPh
O
N
Ac
3ab
0.96
0.93
2.00
2.13
2.09
3.93
5.86
1.07
1.05
1.10
1.04
1.00
1.18
2.94
2.92
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2.0
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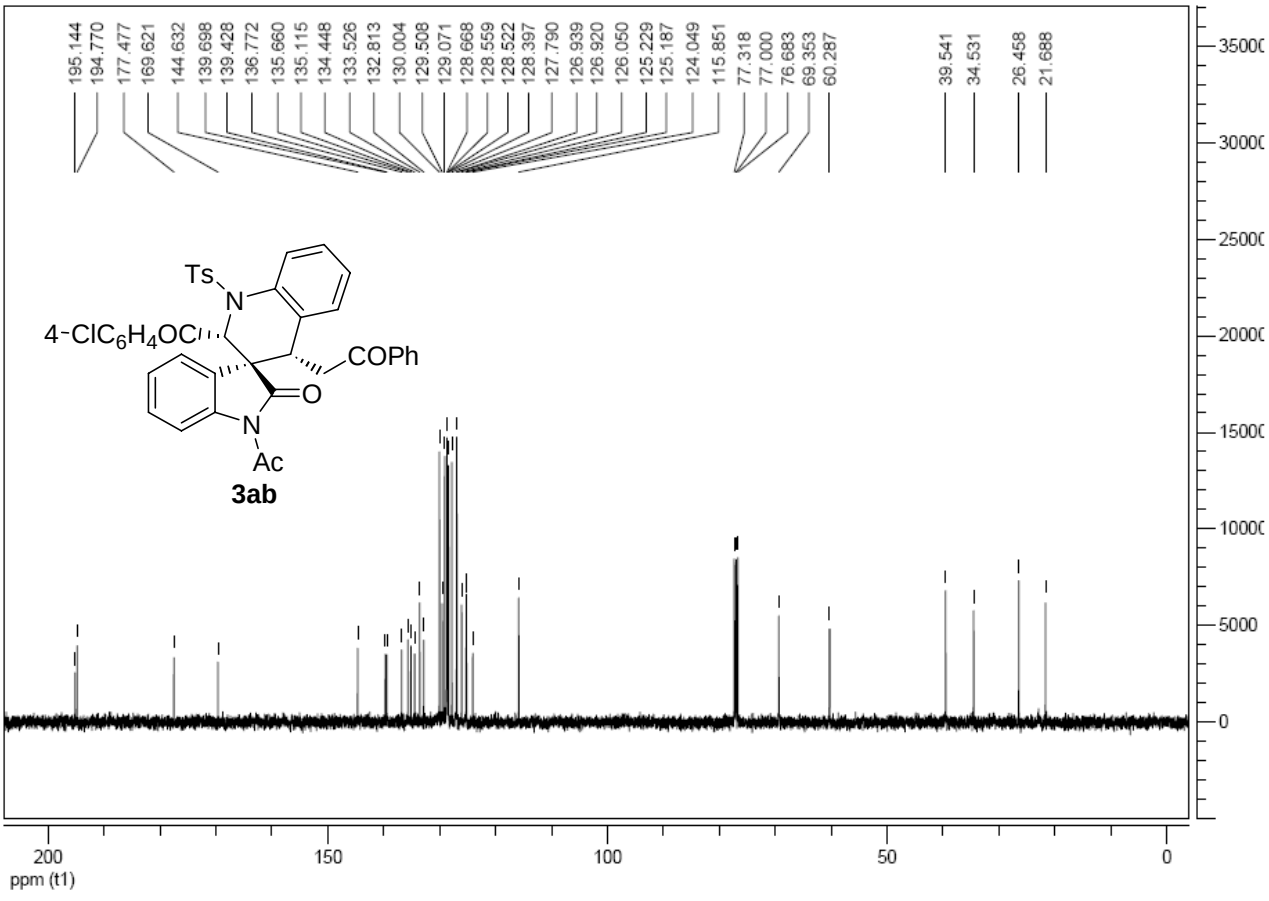
0.0
ppm (t1)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130.004
129.508
129.071
128.668
128.559
128.522
128.397
127.790
126.939
126.920
126.050
125.229
125.187
124.049
115.851
77.318
77.000
76.683
69.353
60.287
39.541
34.531
26.458
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4-ClC6H4OC
COPh
O
N
Ac
3ab
200
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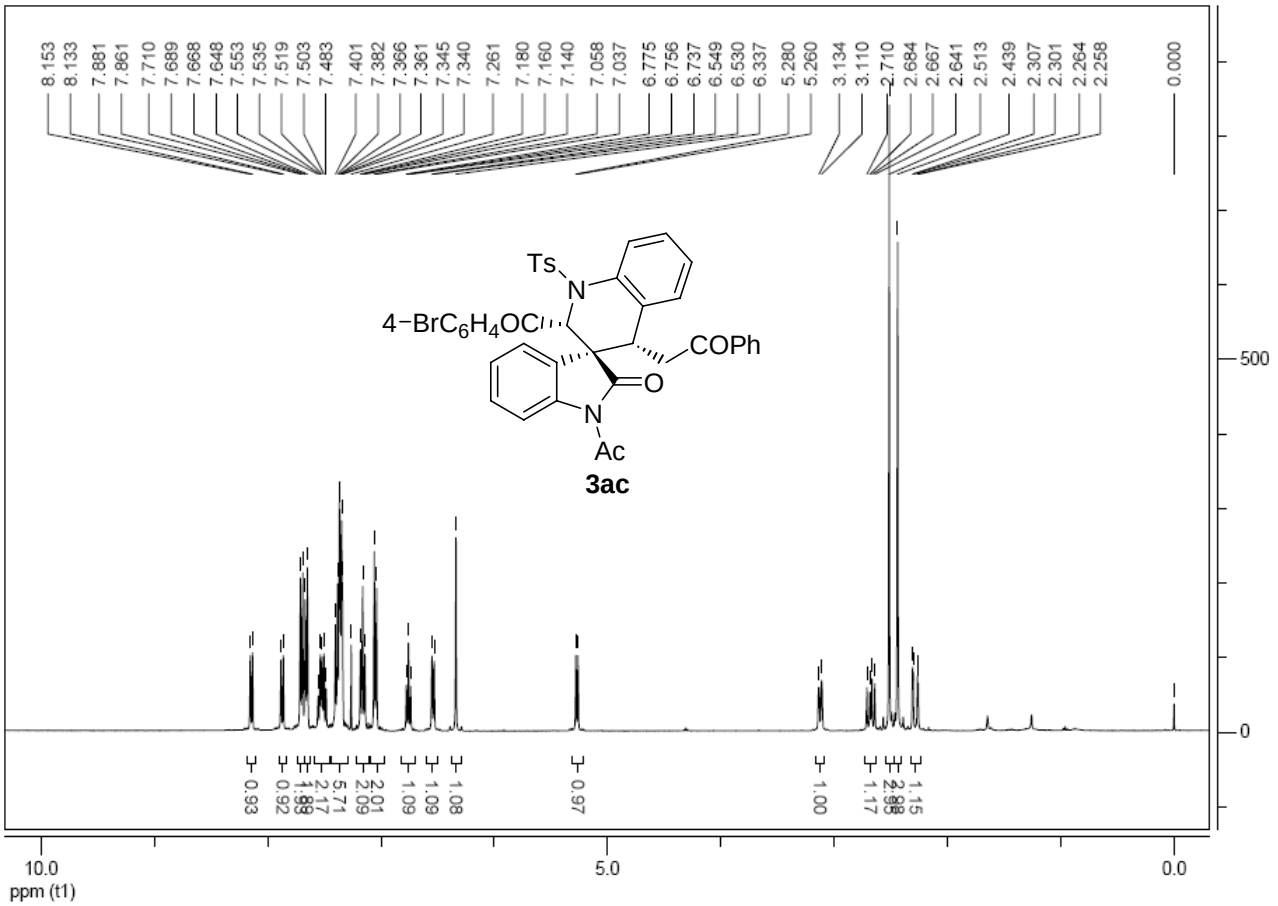
100
50
0
ppm (t1)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7.710
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7.553
7.535
7.519
7.503
7.483
7.401
7.382
7.366
7.361
7.345
7.340
7.261
7.180
7.160
7.140
7.058
7.037
6.775
6.756
6.737
6.549
6.530
6.337
5.280
5.260
3.134
3.110
2.710
2.684
2.667
2.641
2.513
2.439
2.307
2.301
2.264
2.258
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Ts
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4−BrC6H4OC
COPh
O
N
Ac
3ac
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0.92
1.98
1.88
1.17
5.71
2.09
2.01
1.09
1.09
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1.17
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2.98
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0
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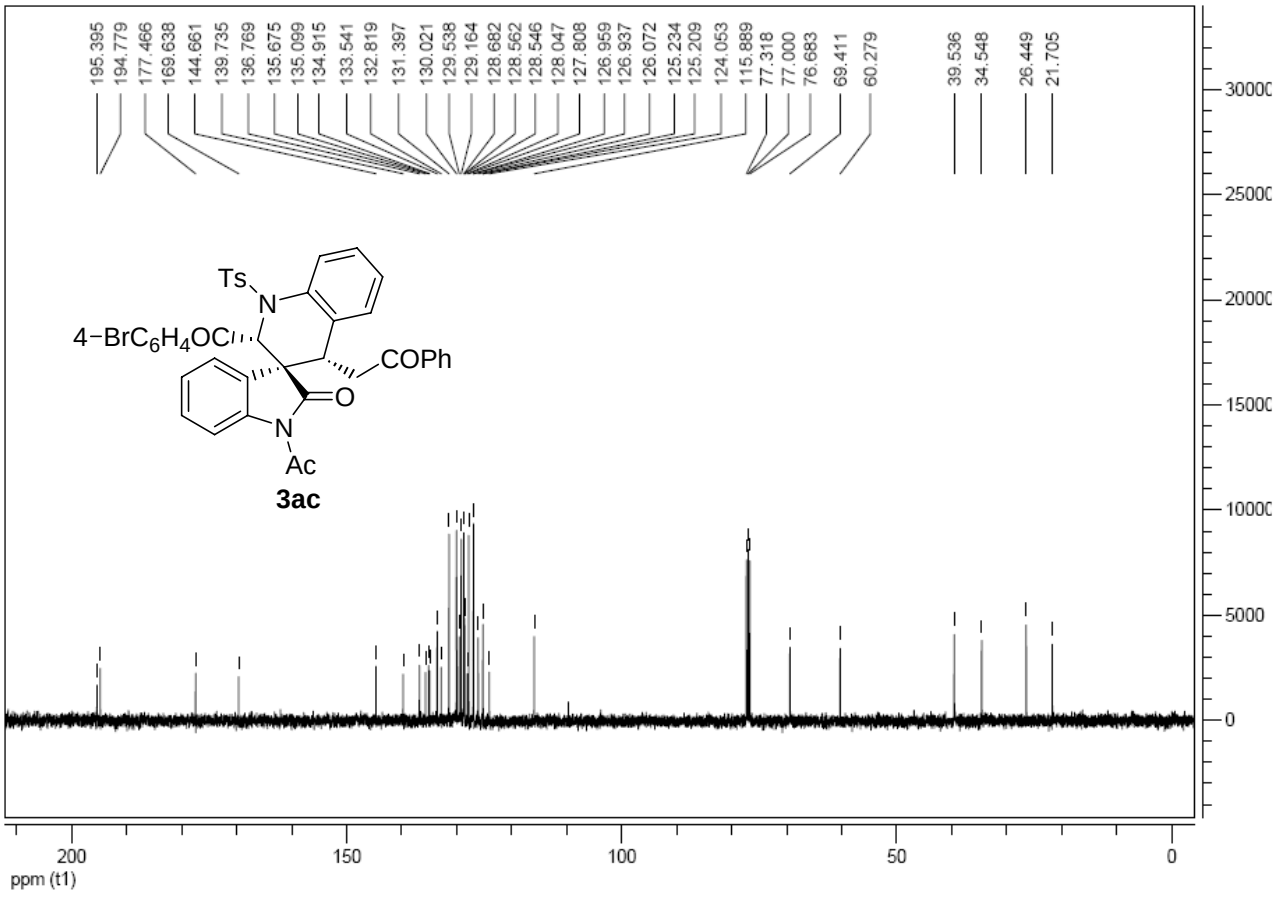
ppm (t1)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125.234
125.209
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77.000
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69.411
60.279
39.536
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26.449
21.705
Ts
N
4−BrC6H4OC
COPh
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Ac
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100
50
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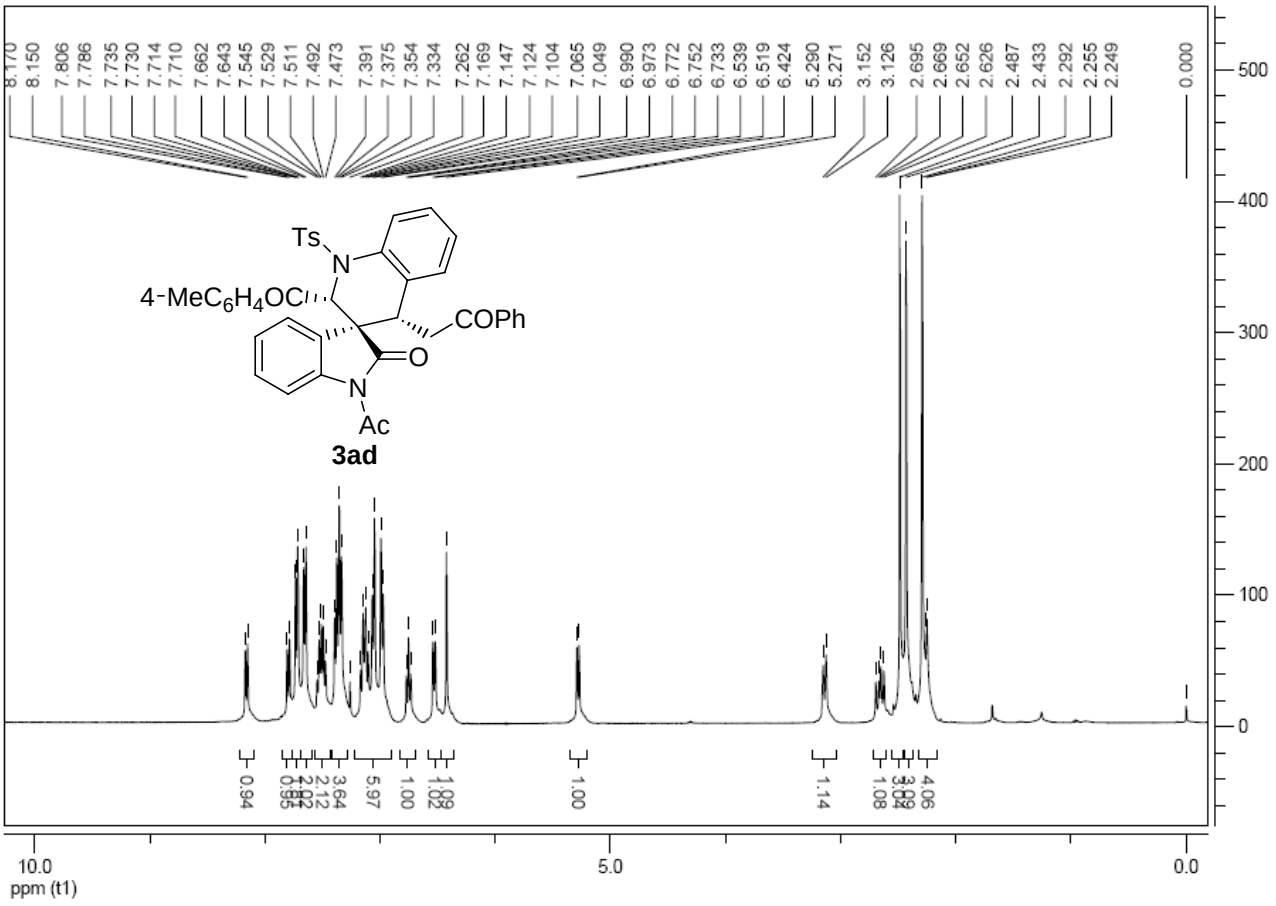
ppm (t1)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7.730
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7.710
7.662
7.643
7.545
7.529
7.511
7.492
7.473
7.391
7.375
7.354
7.334
7.262
7.169
7.147
7.124
7.104
7.065
7.049
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6.973
6.772
6.752
6.733
6.539
6.519
6.424
5.290
5.271
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3.126
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2.669
2.652
2.626
2.487
2.433
2.292
2.255
2.249
0.000
Ts
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4-MeC6H4OC
COPh
O
N
Ac
3ad
0.94
0.96
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2.12
3.64
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1.00
1.02
1.00
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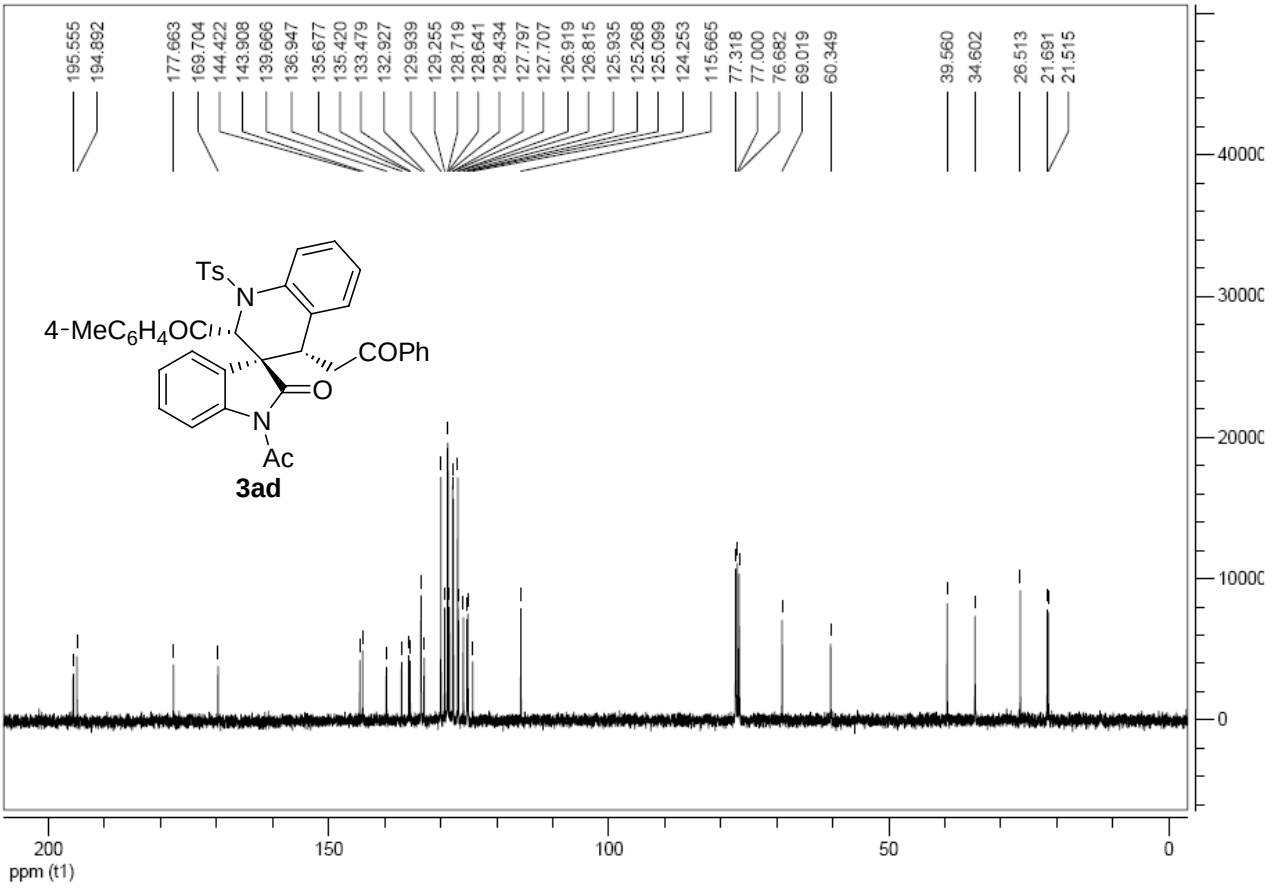
ppm (t1)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127.797
127.707
126.919
126.815
125.935
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125.099
124.253
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77.000
76.682
69.019
60.349
39.560
34.602
26.513
21.691
21.515
Ts
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COPh
O
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Ac
3ad
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30000
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0
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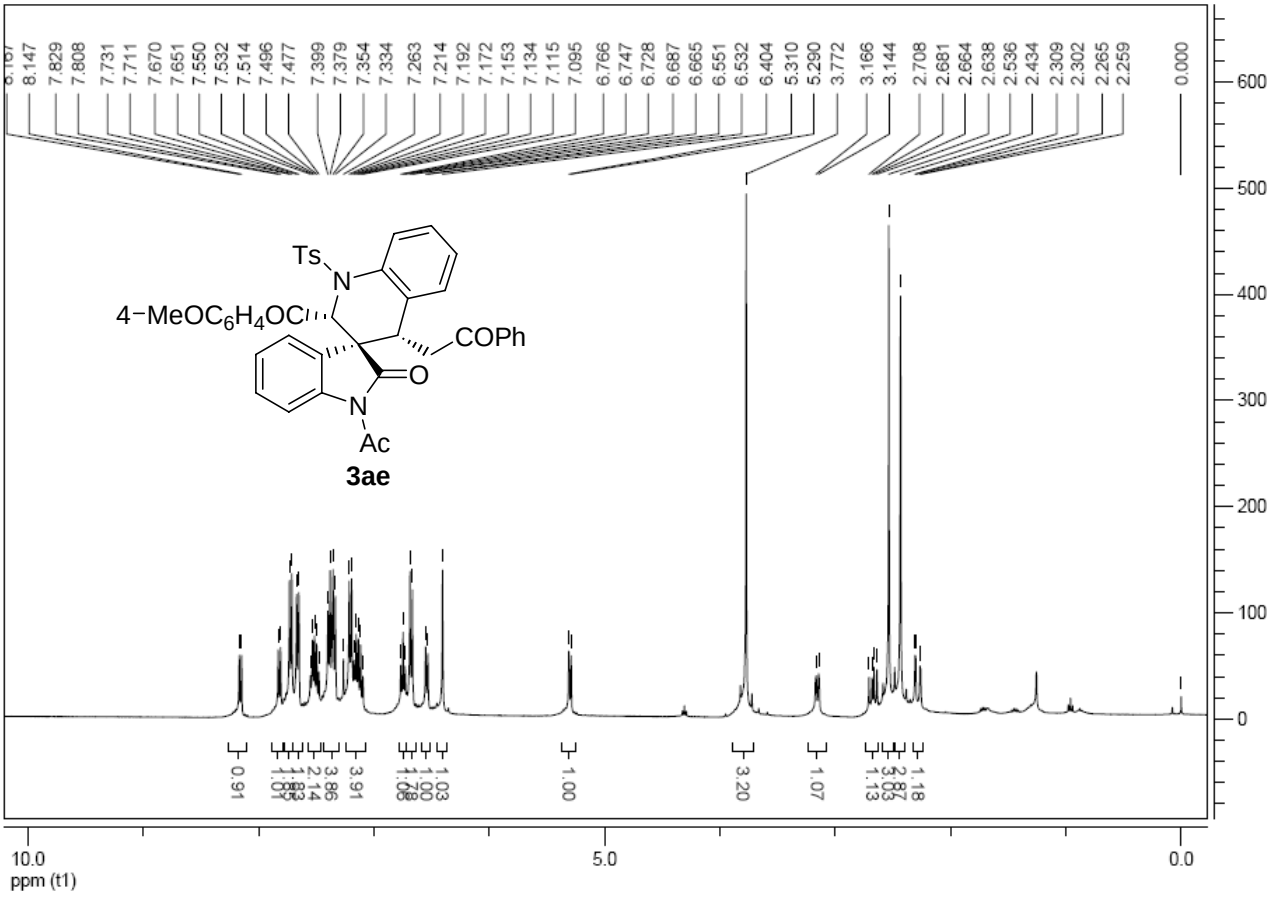
150
100
50
0
ppm (t1)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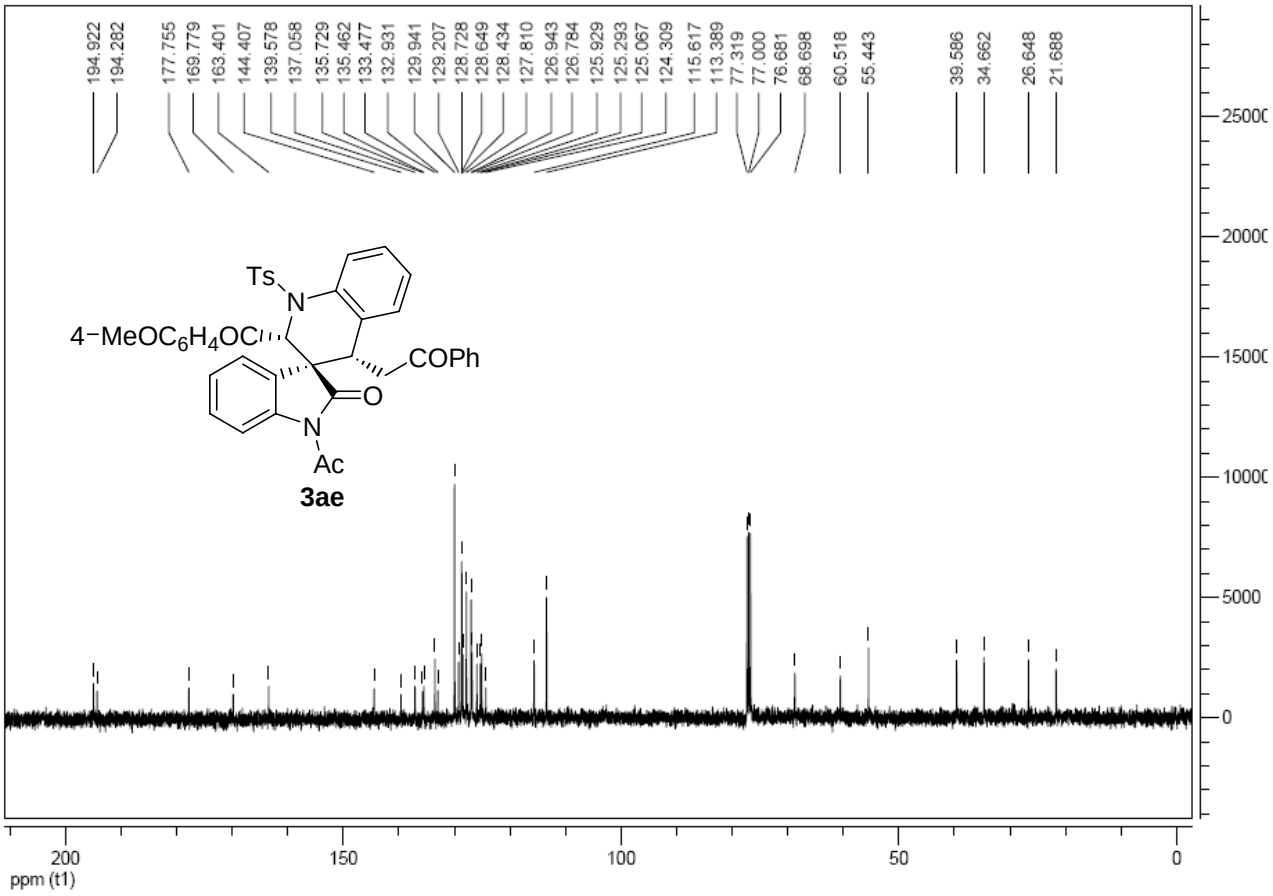
COPh
O
N
Ac
3ae
ppm (t1)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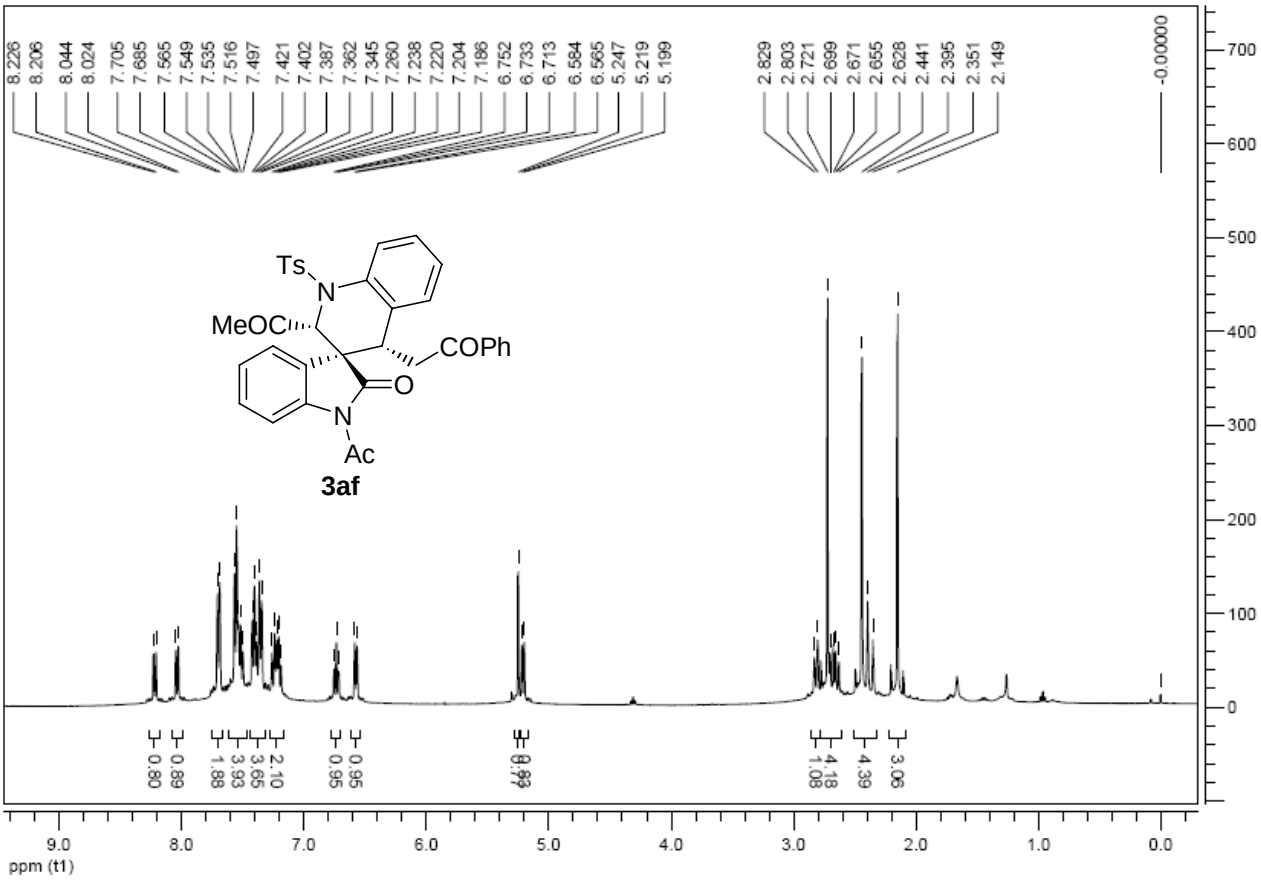
COPh
O
N
Ac
3ae
ppm (t1)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7.260
7.238
7.220
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6.565
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5.219
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2.149
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COPh
O
N
Ac
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0.96
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1.08
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2.0
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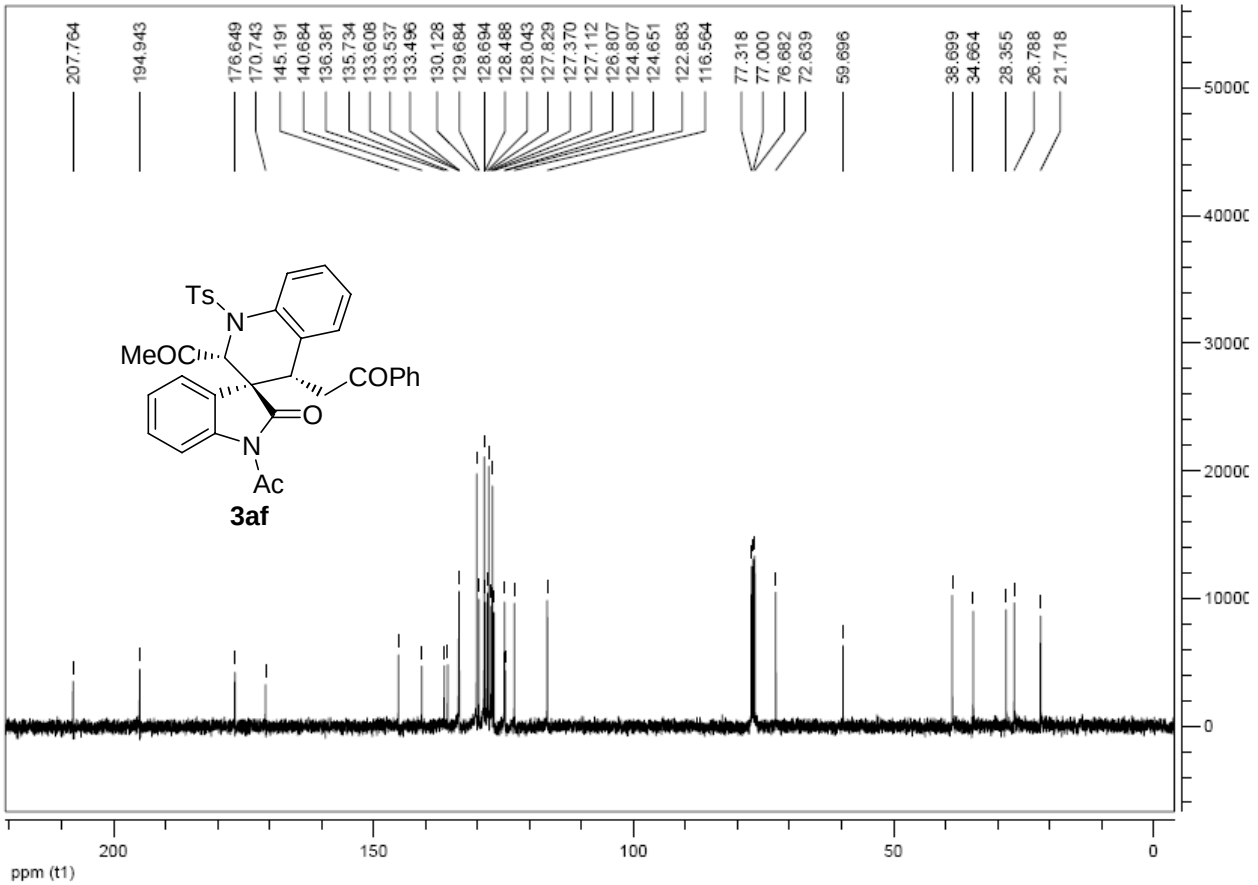
ppm (t1)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72.639
59.696
38.699
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28.355
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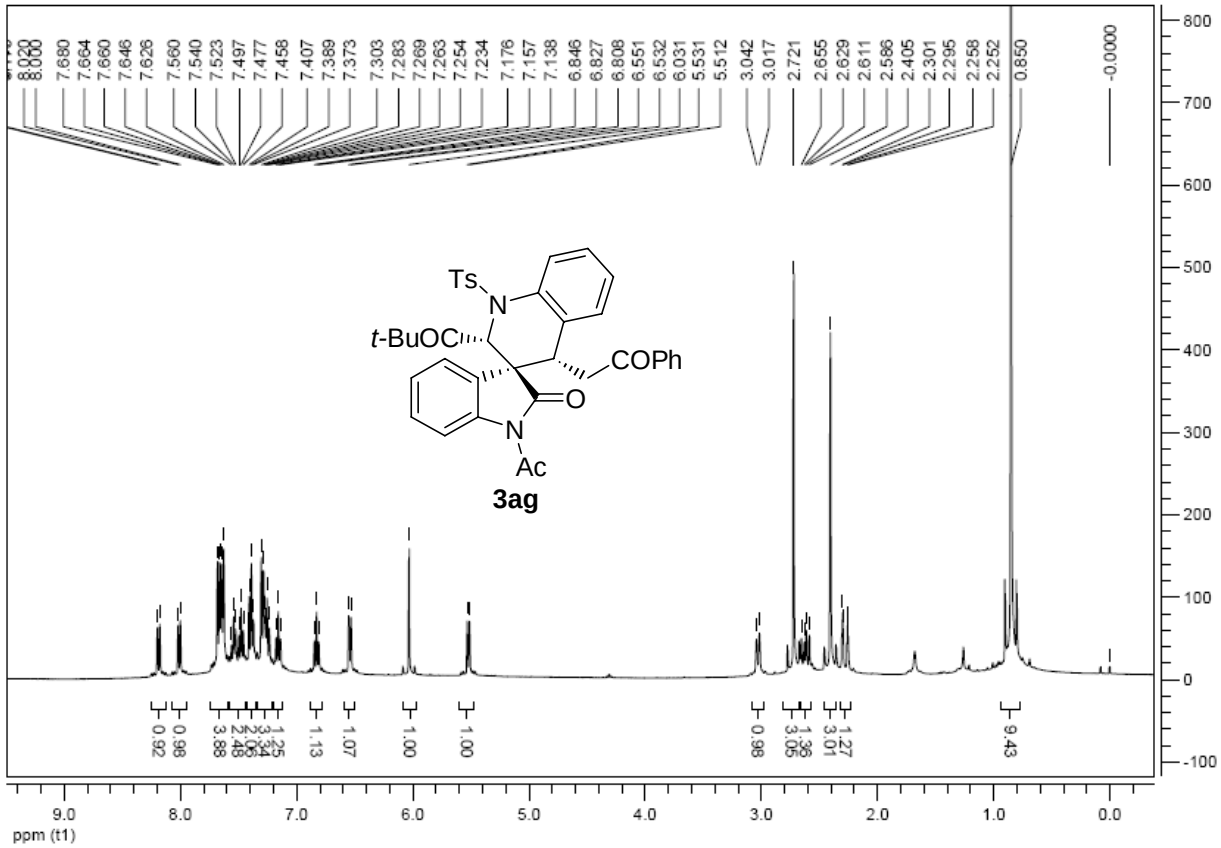
ppm (t1)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O
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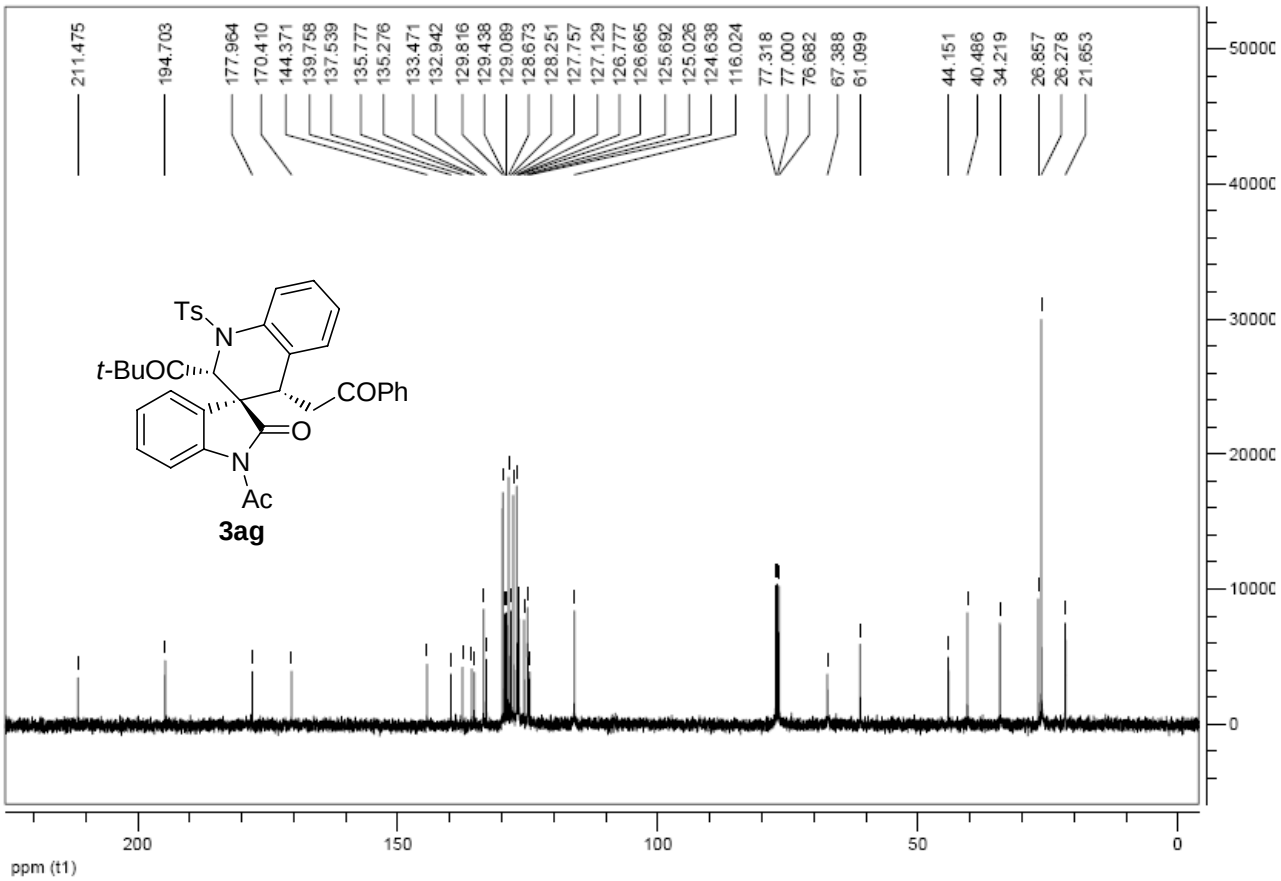
Ac
3ag
ppm (t1)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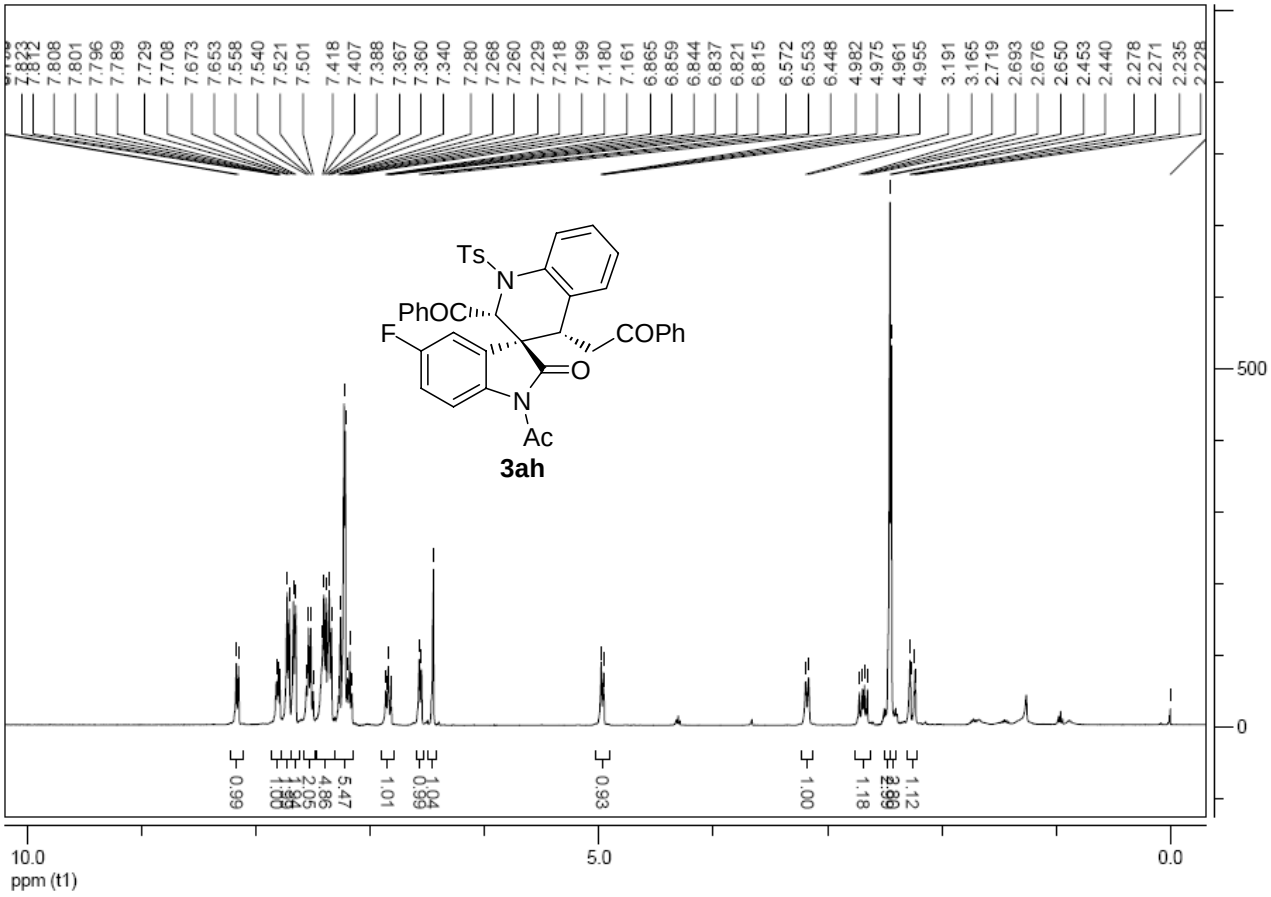
t-BuOC
COPh
O
N
Ac
3ag
ppm (t1)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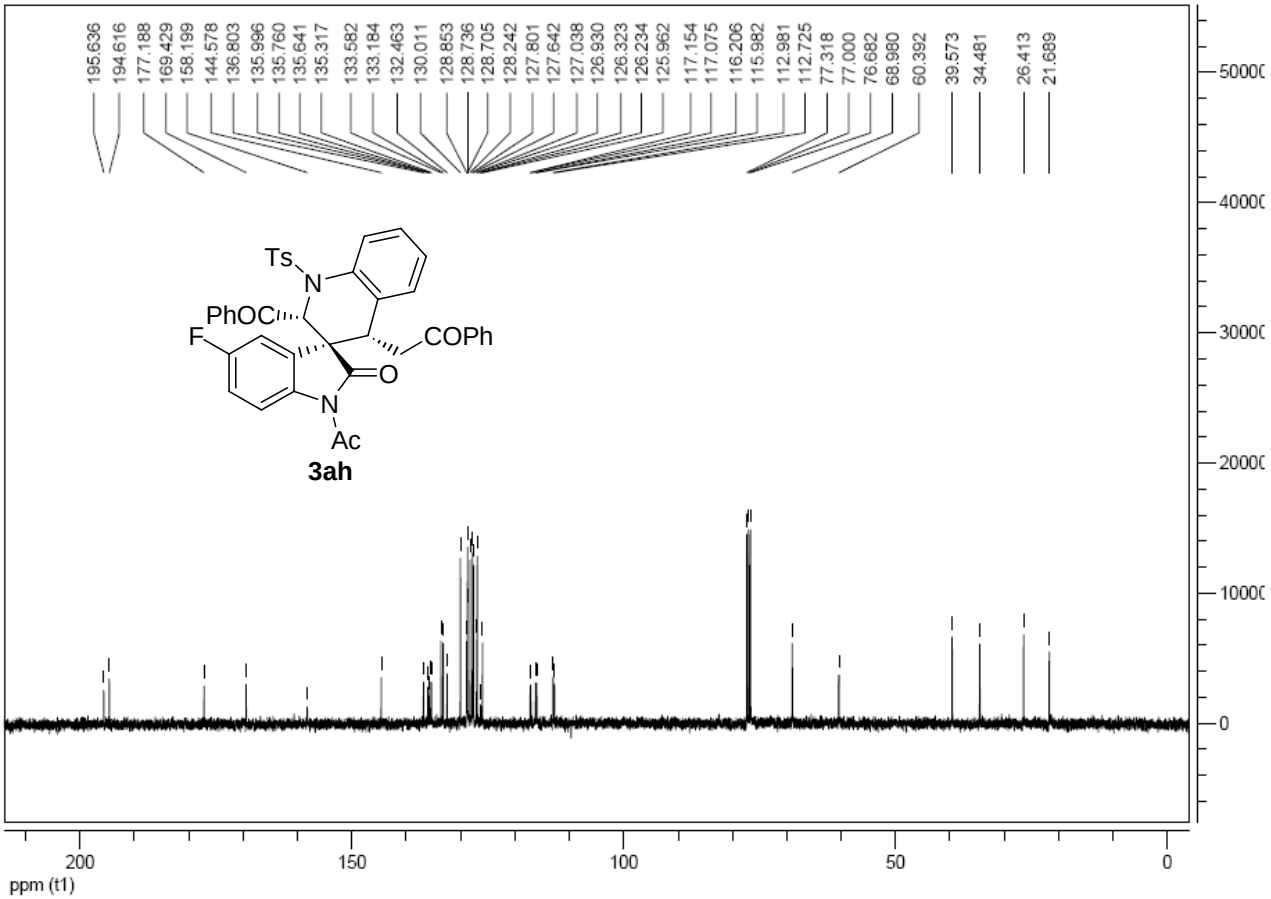
F
COPh
O
N
Ac
3ah
ppm (t1)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PhOC
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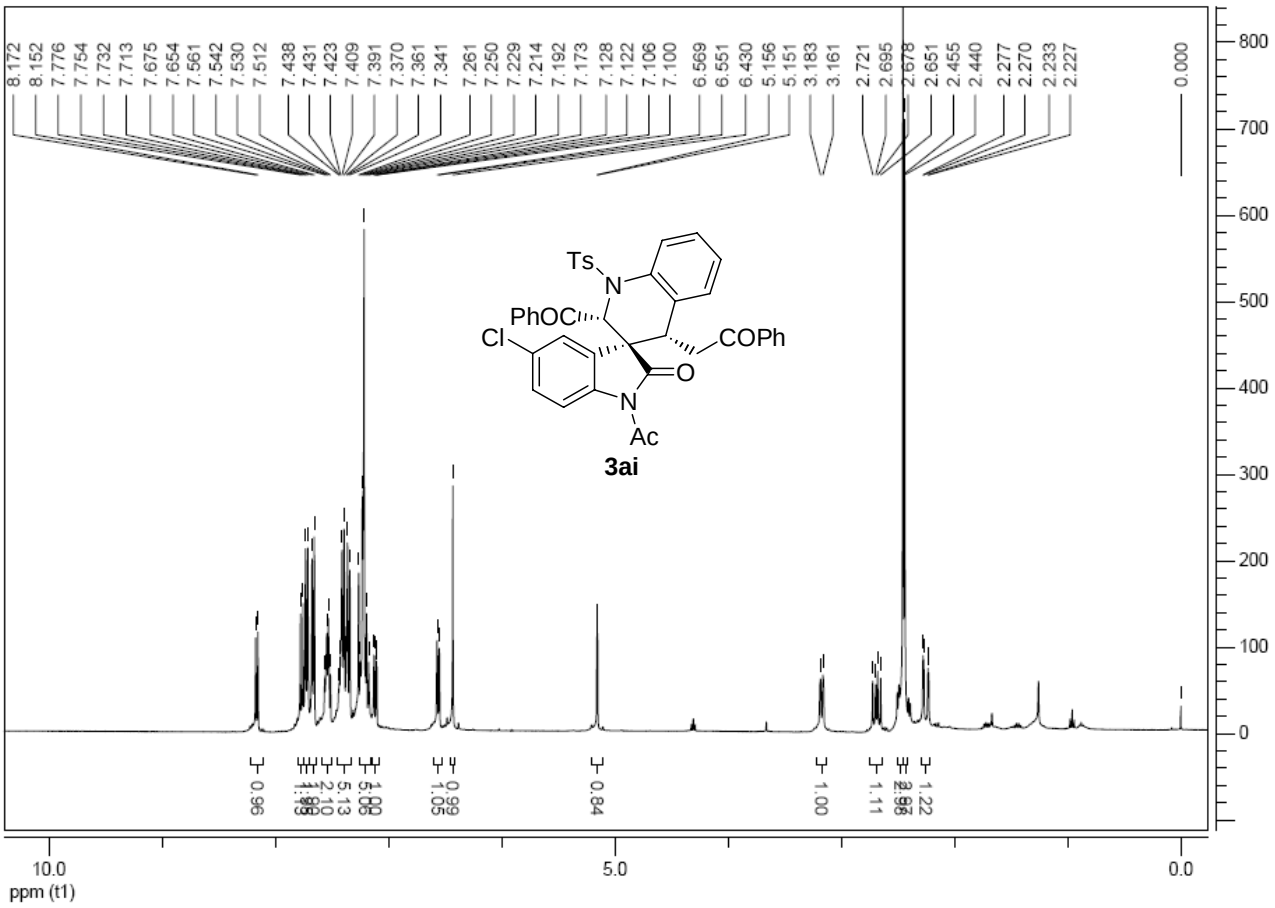
COPh
O
N
Ac
3ah
ppm (t1)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7.431
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7.250
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7.192
7.173
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7.100
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6.551
6.430
5.156
5.151
3.183
3.161
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2.270
2.233
2.227
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Ts
N
PhOC
Cl
COPh
O
N
Ac
3ai
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2.10
5.13
5.06
1.00
0.99
0.84
1.00
1.11
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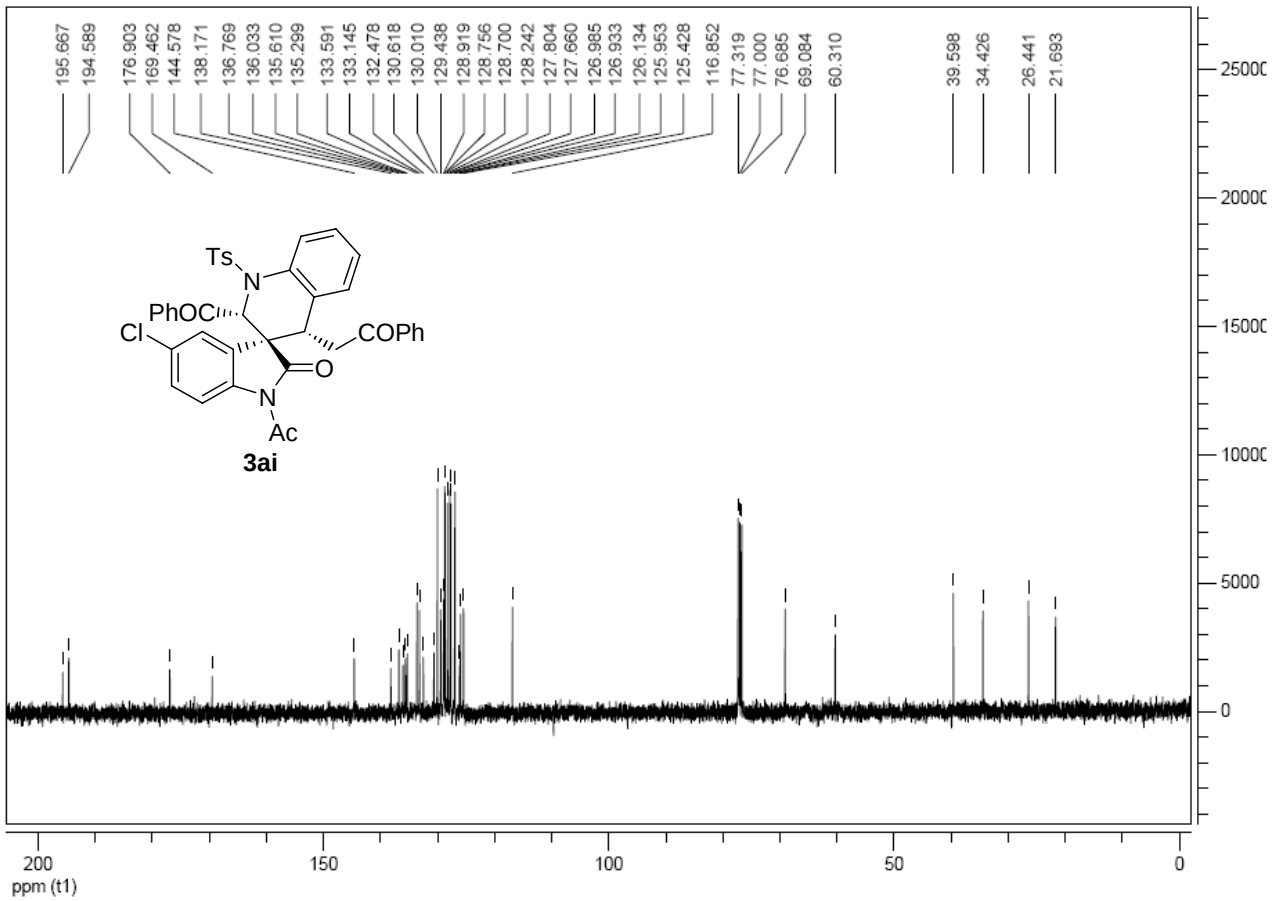
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136.033
135.610
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130.618
130.010
129.438
128.919
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128.242
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125.428
116.852
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77.000
76.685
69.084
60.310
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34.426
26.441
21.693
Ts
N
PhOC
Cl
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O
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Ac
3ai
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10000
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150
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50
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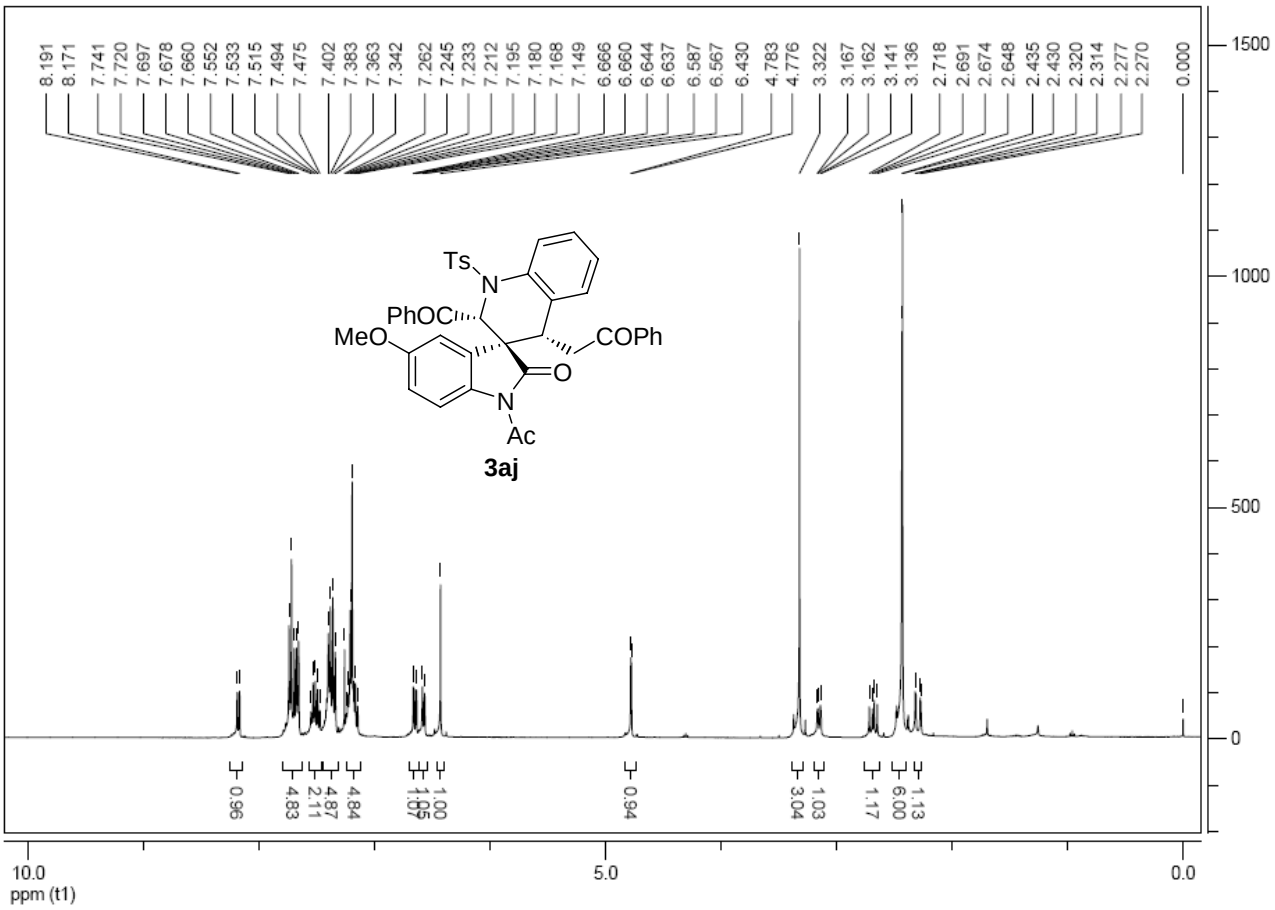
ppm (t1)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6.637
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6.567
6.430
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2.314
2.277
2.270
0.000
Ts
N
PhOC
MeO
COPh
O
N
Ac
3aj
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2.11
4.87
4.84
1.87
1.95
1.00
0.94
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6.00
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1000
500
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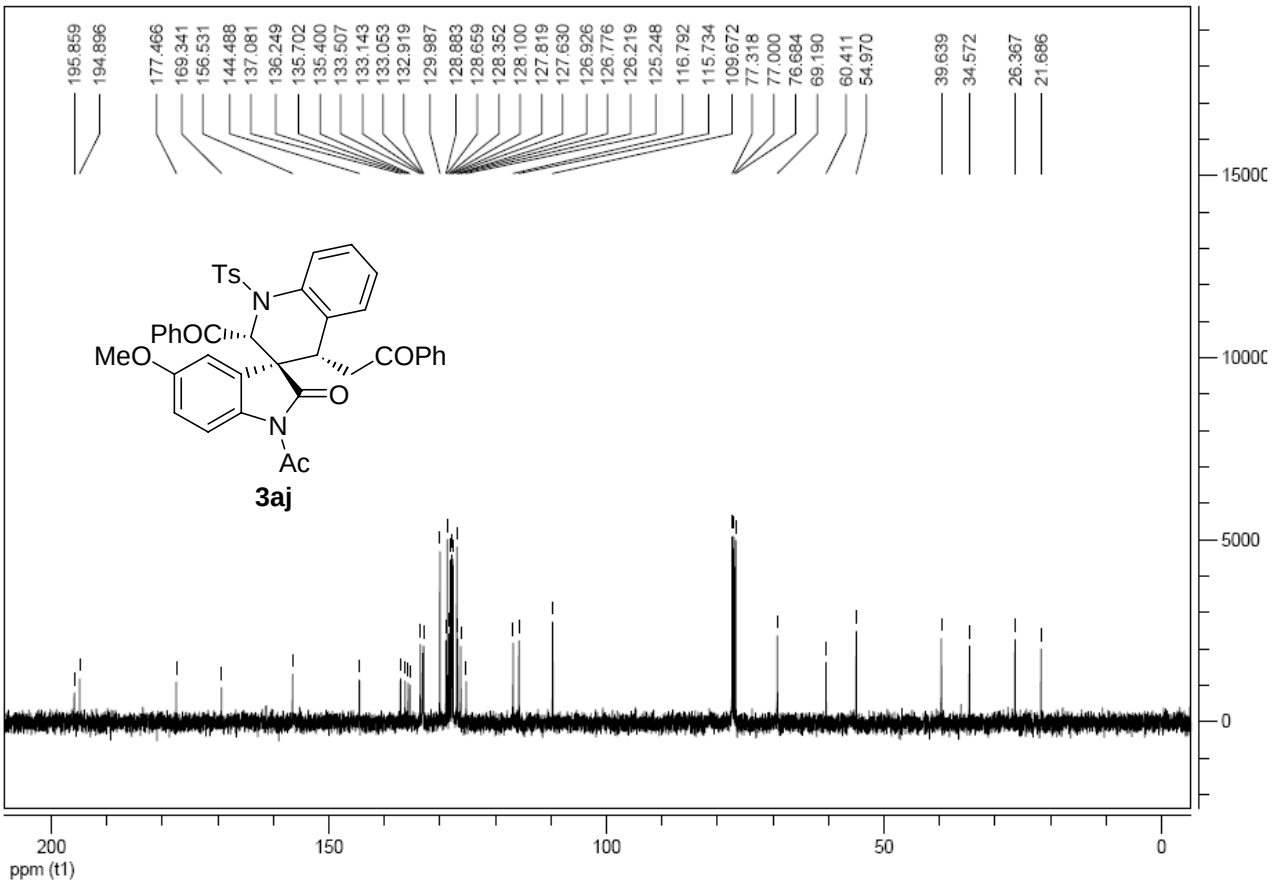
ppm (t1)
5.0
0.0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128.659
128.352
128.100
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127.630
126.926
126.776
126.219
125.248
116.792
115.734
109.672
77.318
77.000
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69.190
60.411
54.970
39.639
34.572
26.367
21.686
Ts
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PhOC
MeO
COPh
O
N
Ac
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0
200
ppm (t1)
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100
50
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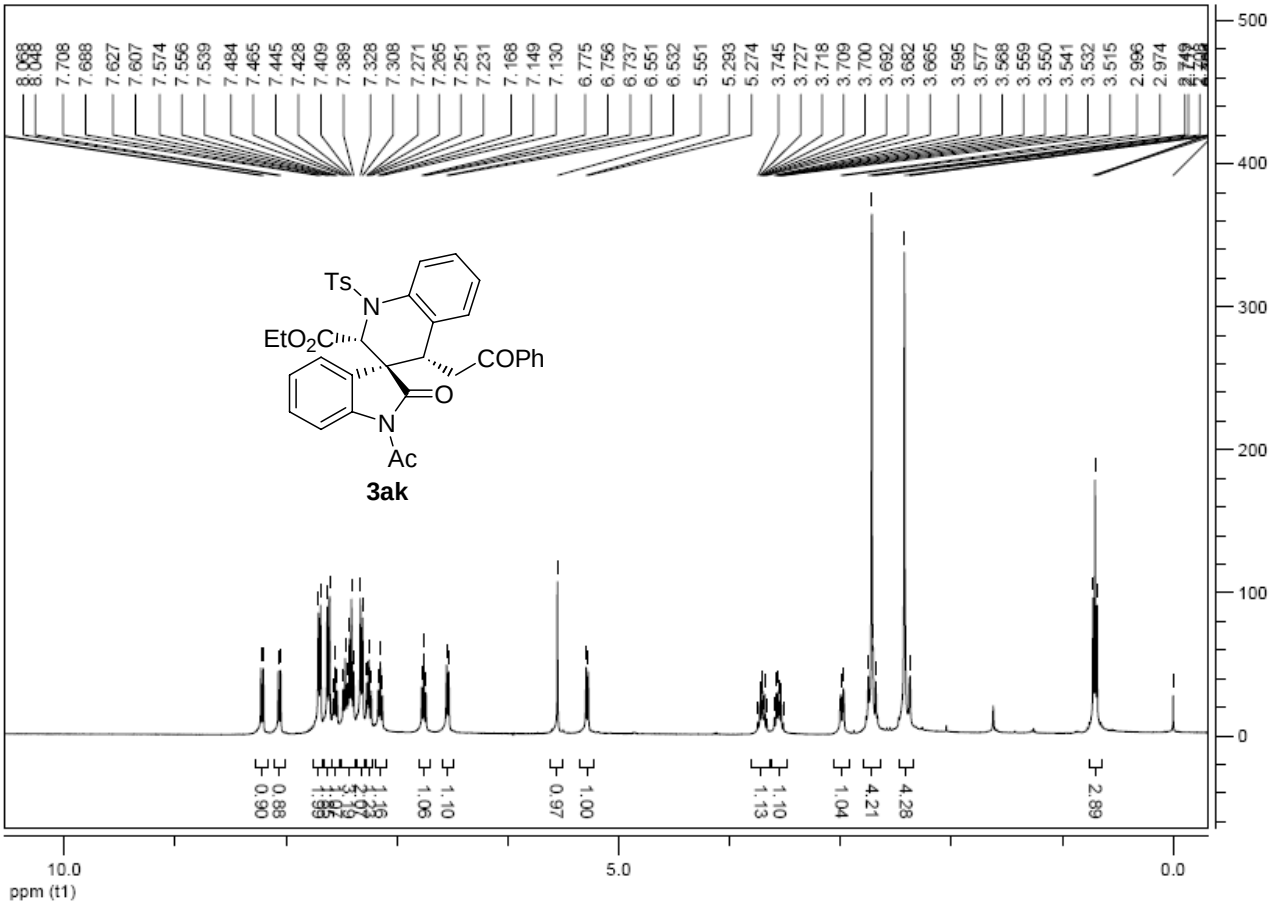
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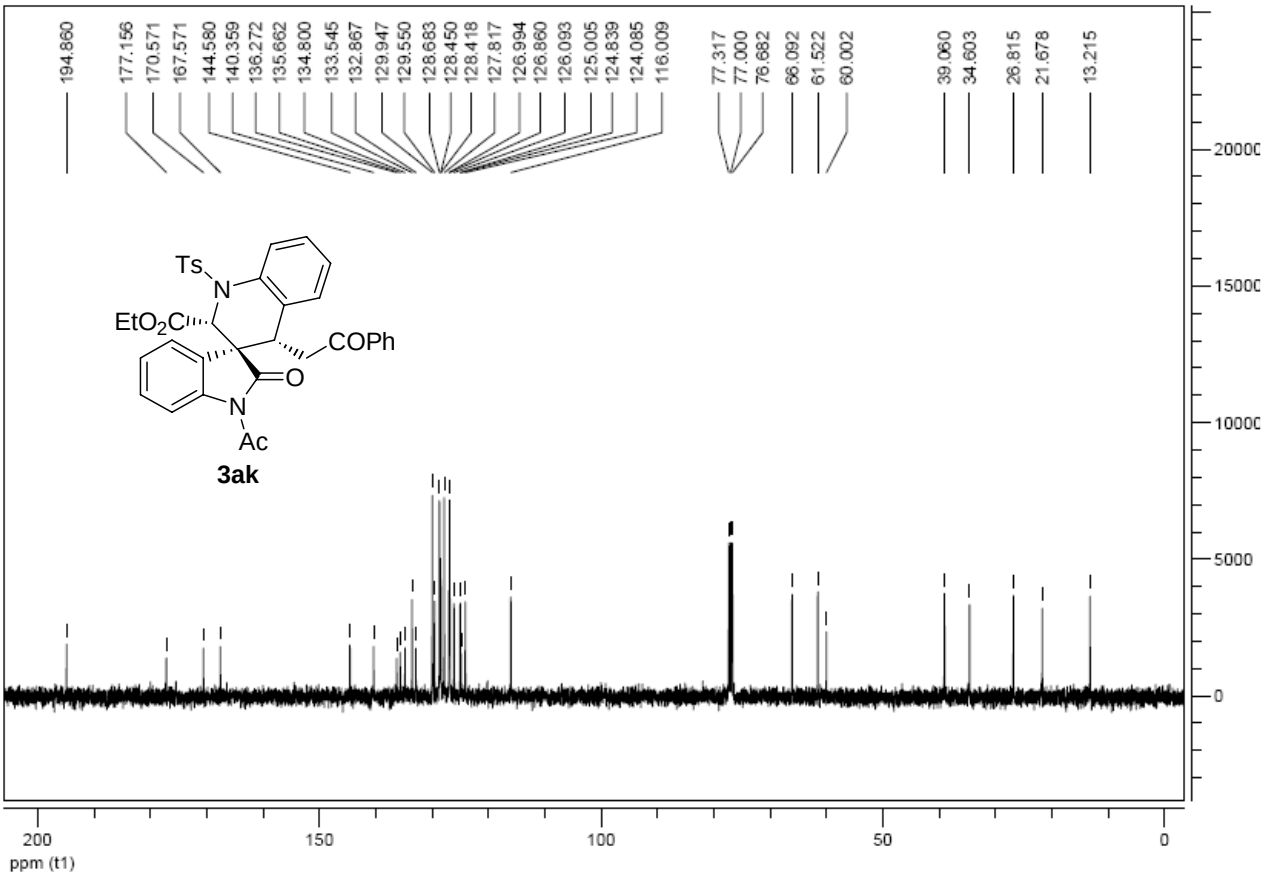
N
EtO2C
COPh
O
N
Ac
3ak
ppm (t1)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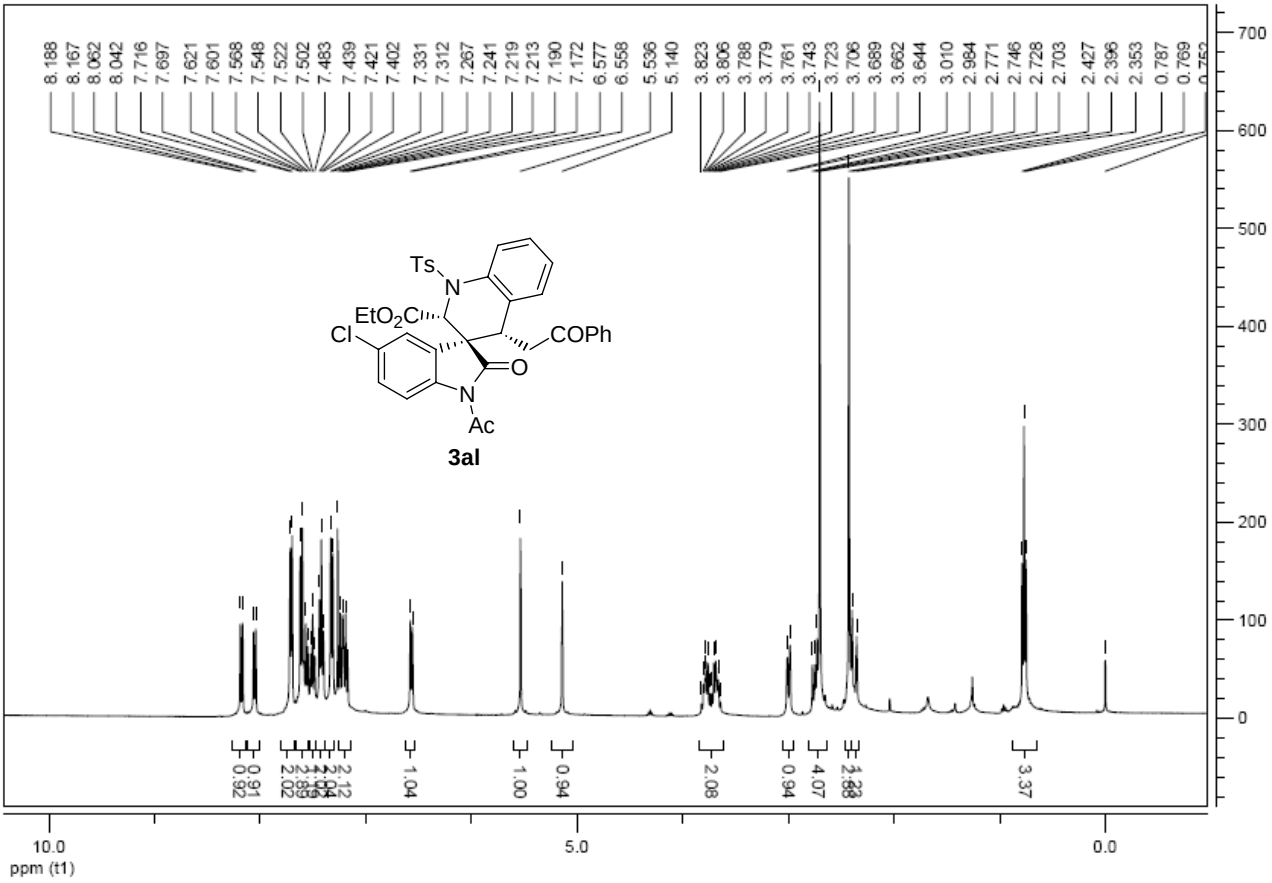
EtO2C
COPh
O
N
Ac
3ak
ppm (t1)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7.312
7.267
7.241
7.219
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7.190
7.172
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6.558
5.536
5.140
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2.746
2.728
2.703
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2.396
2.353
0.787
0.769
Ts
N
EtO2C
Cl
COPh
O
N
Ac
3al
0.92
0.91
2.02
1.04
1.00
0.94
2.08
0.94
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600
500
400
300
200
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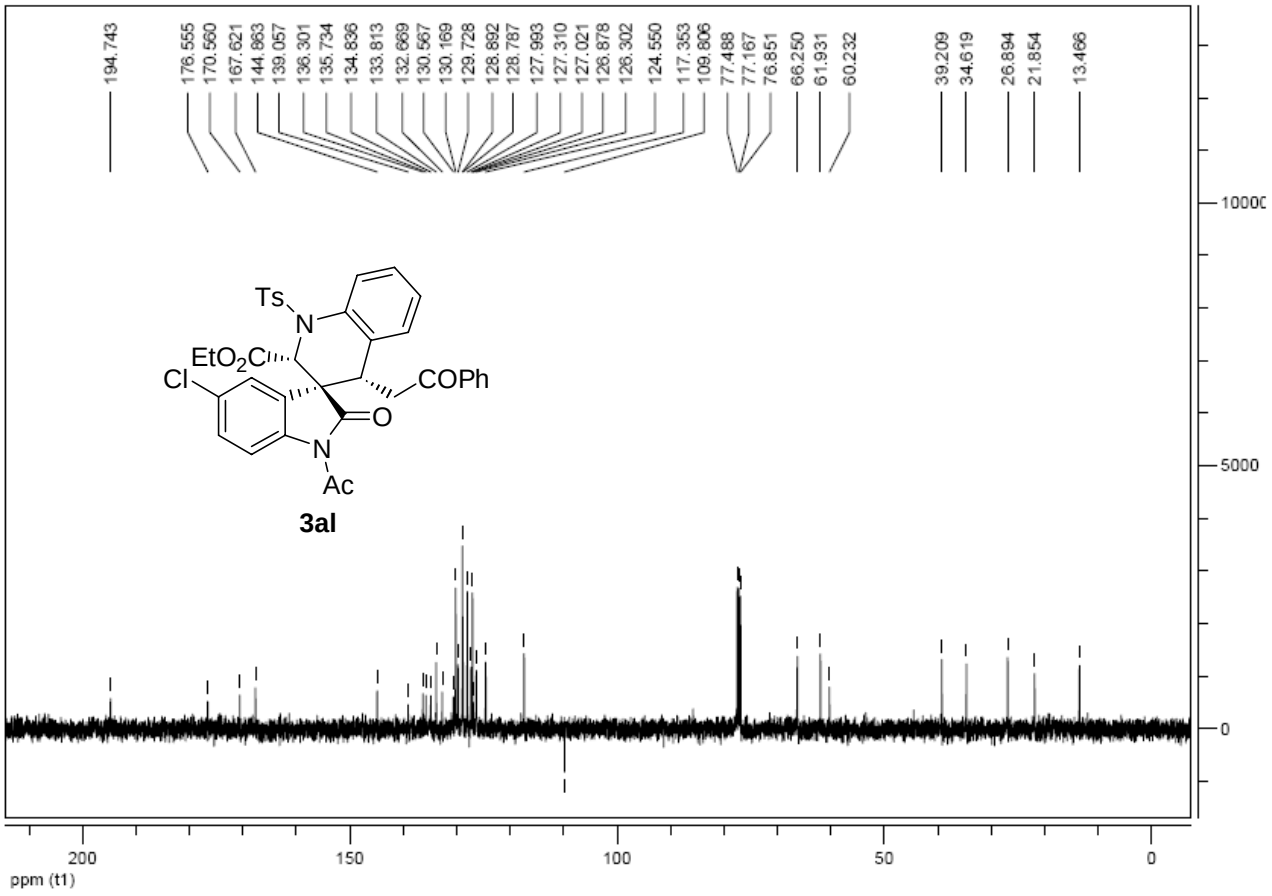
0
10.0
5.0
0.0
ppm (t1)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60.232
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13.466
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Cl
COPh
O
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Ac
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50
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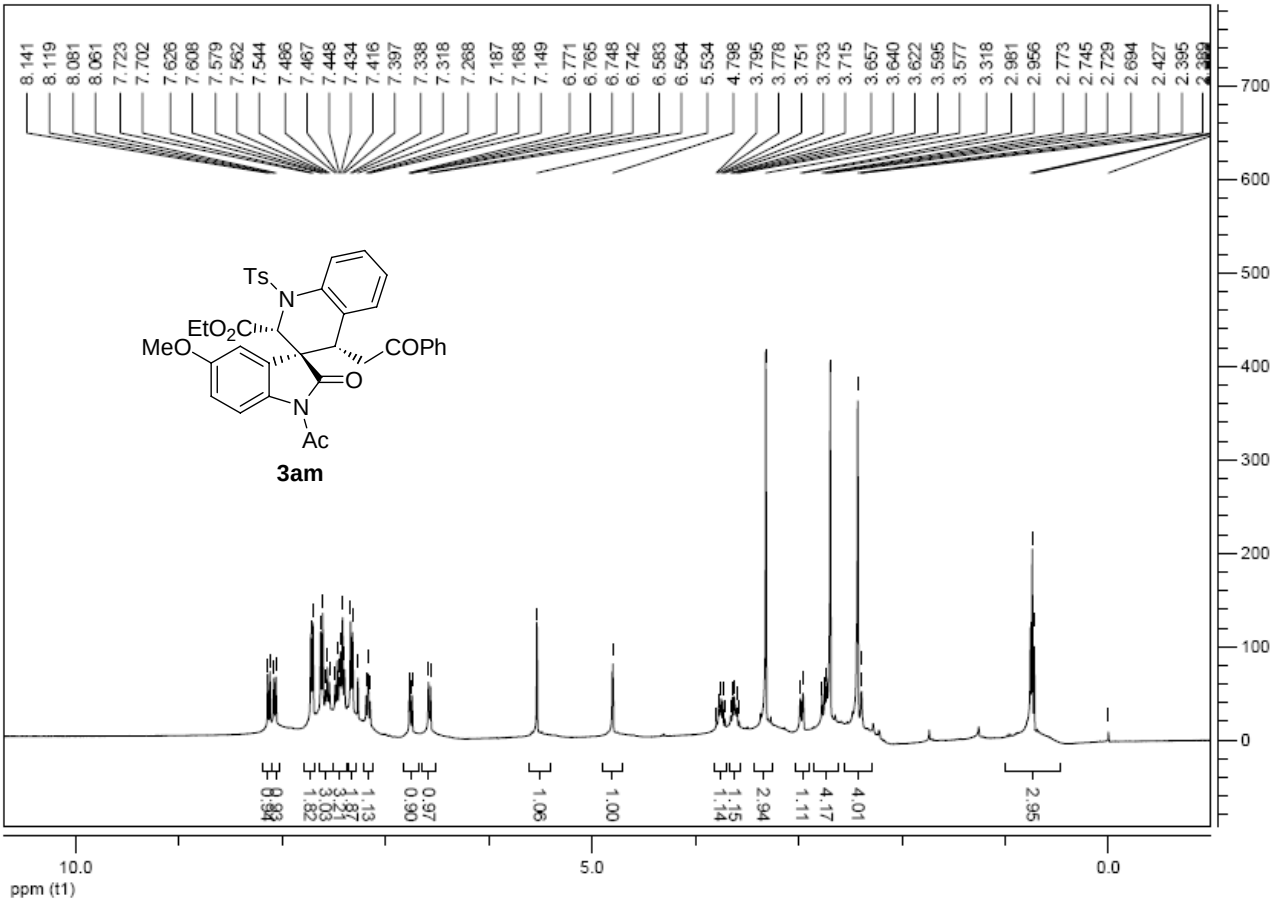
ppm (t1)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3.595
3.577
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2.981
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2.773
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Ts
N
EtO2C
MeO
COPh
O
N
Ac
3am
0.98
1.82
3.03
3.21
1.87
1.13
0.90
0.97
1.06
1.00
1.15
2.94
1.11
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400
300
200
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0
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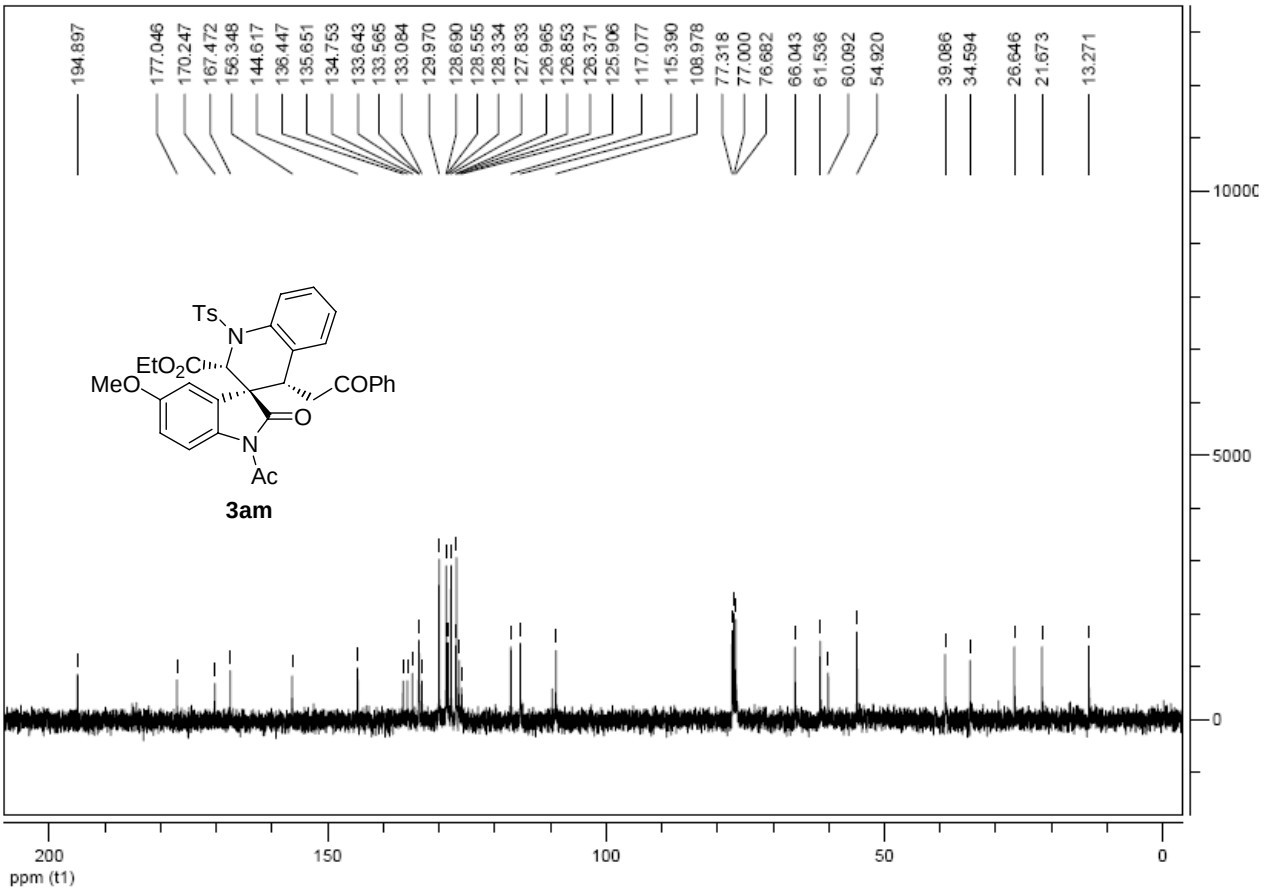
0.0
ppm (t1)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Ts
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EtO2C
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COPh
O
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0
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150
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50
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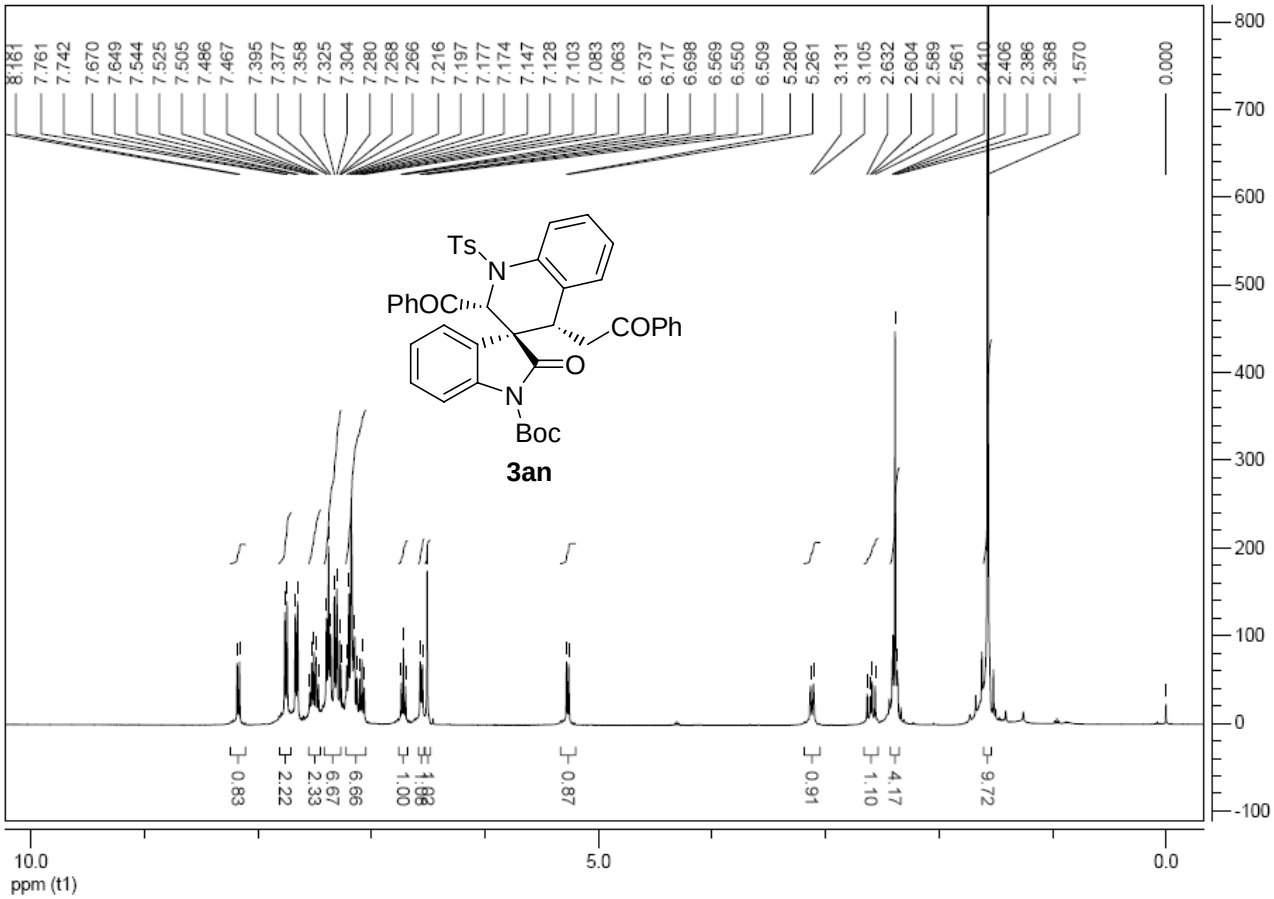
ppm (t1)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7.266
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7.197
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7.174
7.147
7.128
7.103
7.083
7.063
6.737
6.717
6.698
6.569
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6.509
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5.261
3.131
3.105
2.632
2.604
2.589
2.561
2.410
2.406
2.386
2.368
1.570
0.000
Ts
N
PhOC
COPh
O
N
Boc
3an
0.83
2.22
2.33
6.67
6.66
1.00
1.08
0.87
0.91
1.10
4.17
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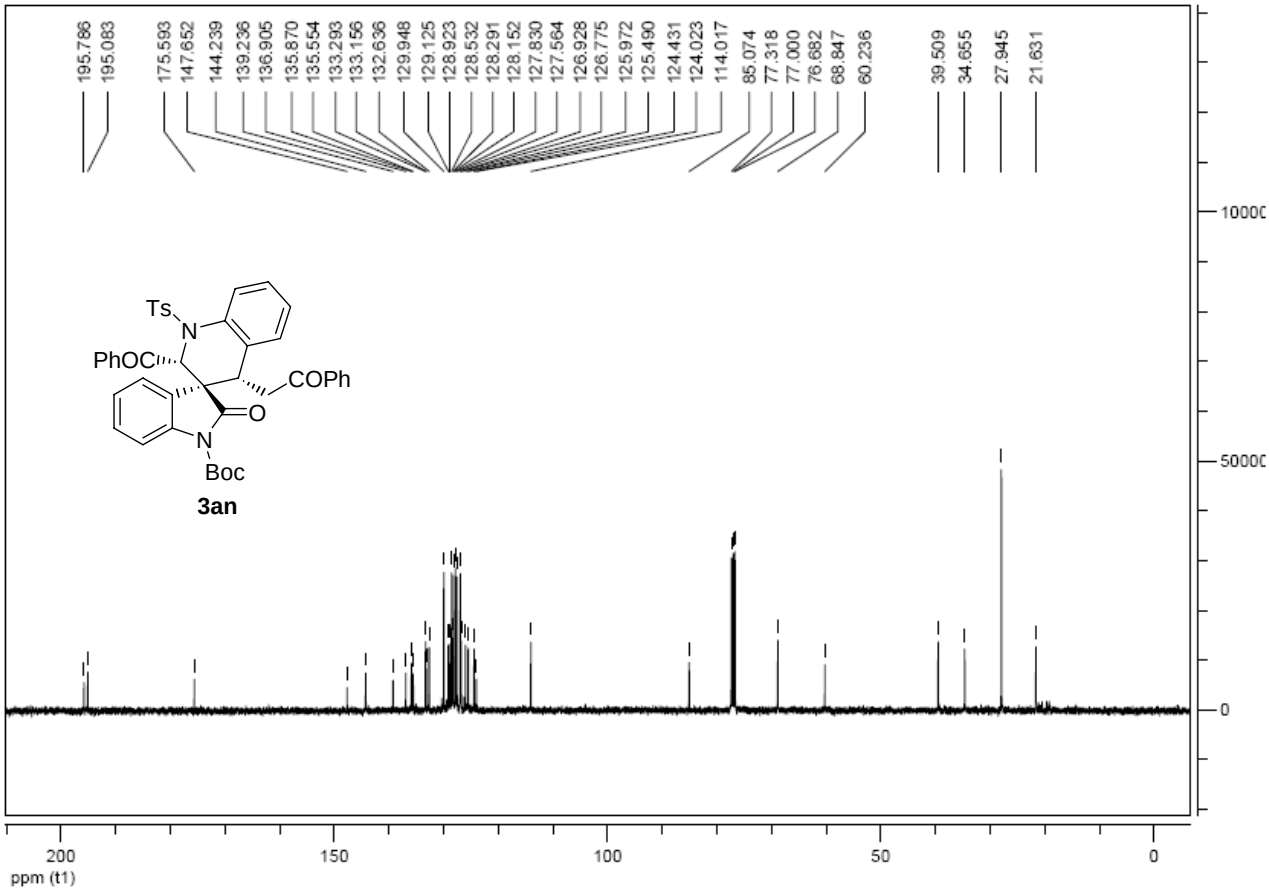
700
600
500
400
300
200
100
0
-100
10.0
5.0
0.0
ppm (t1)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125.490
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114.017
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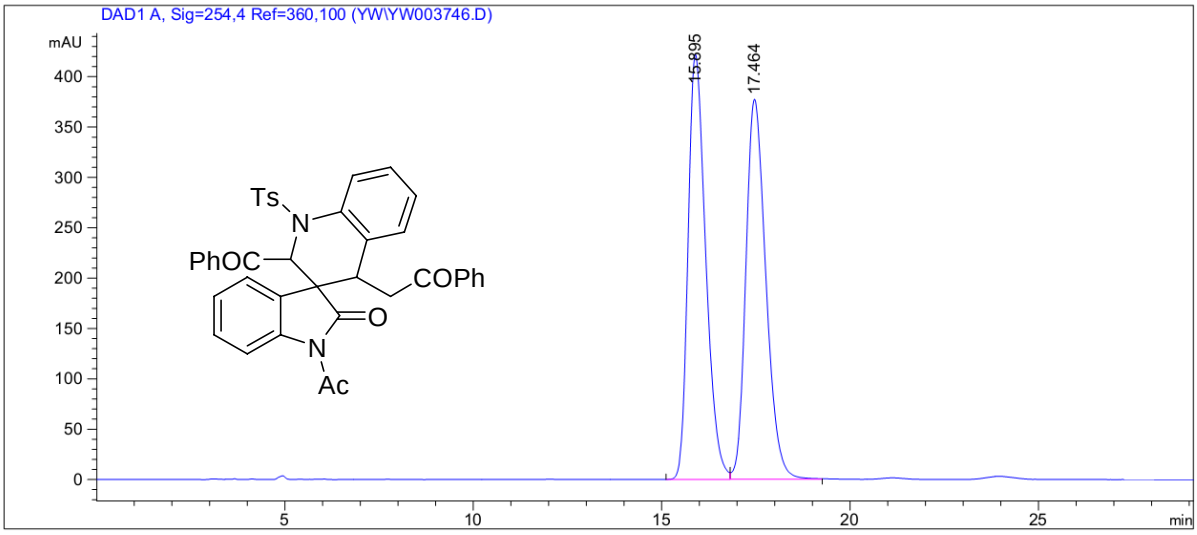
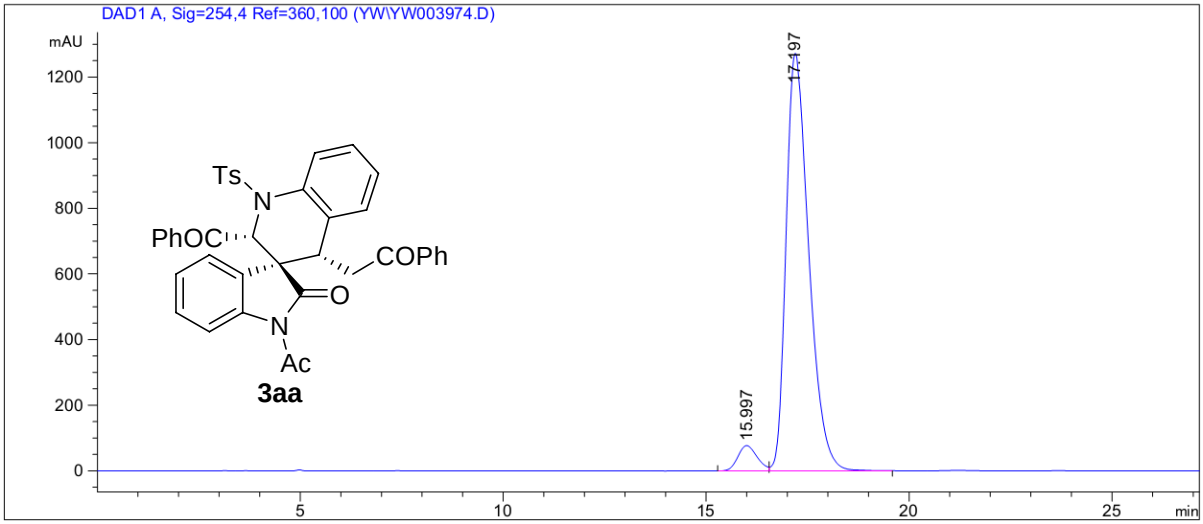
77.000
76.682
68.847
60.236
39.509
34.655
27.945
21.631
Ts
N
PhOC
COPh
O
N
Boc
3an
10000
50000
0
200
150
100
50
0
ppm (t1)

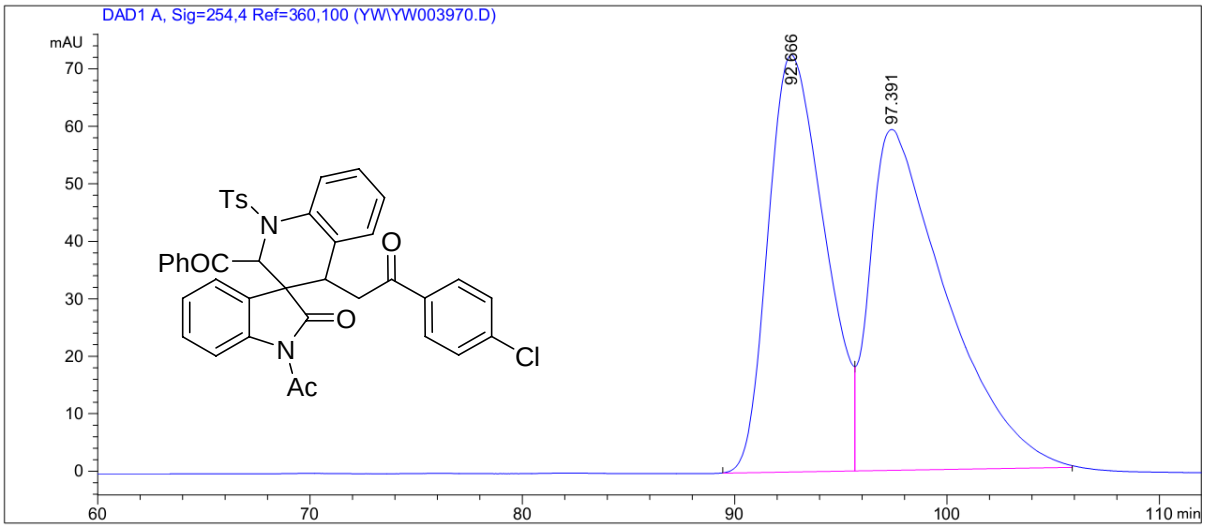
Copies of HPLC profiles of Michael addition products



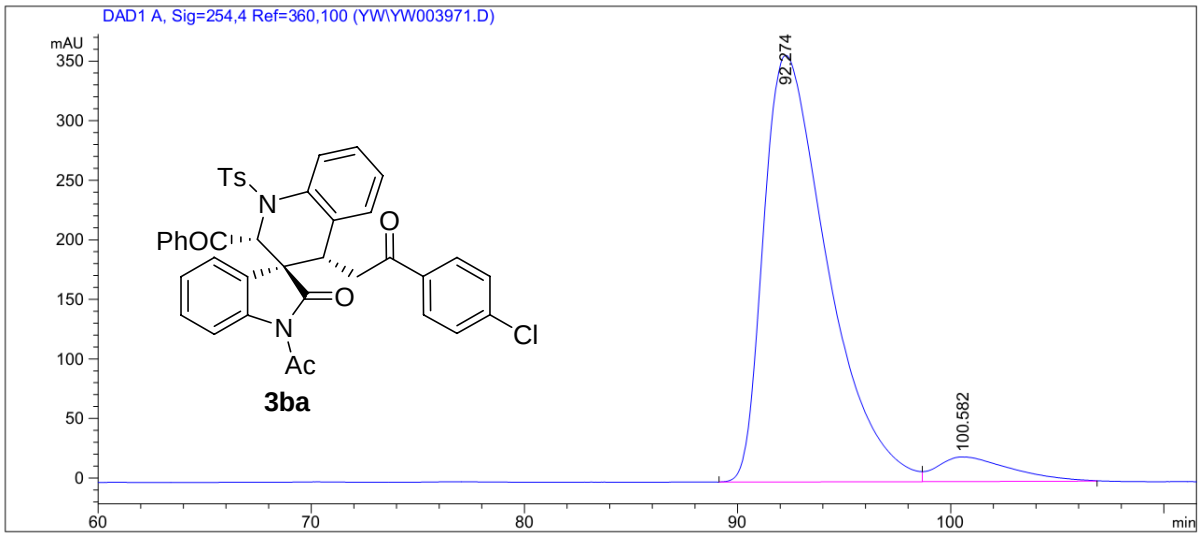
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.895	BV	0.5007	1.37655e4	421.87726	49.7440
2	17.464	VB	0.5701	1.39072e4	377.25092	50.2560



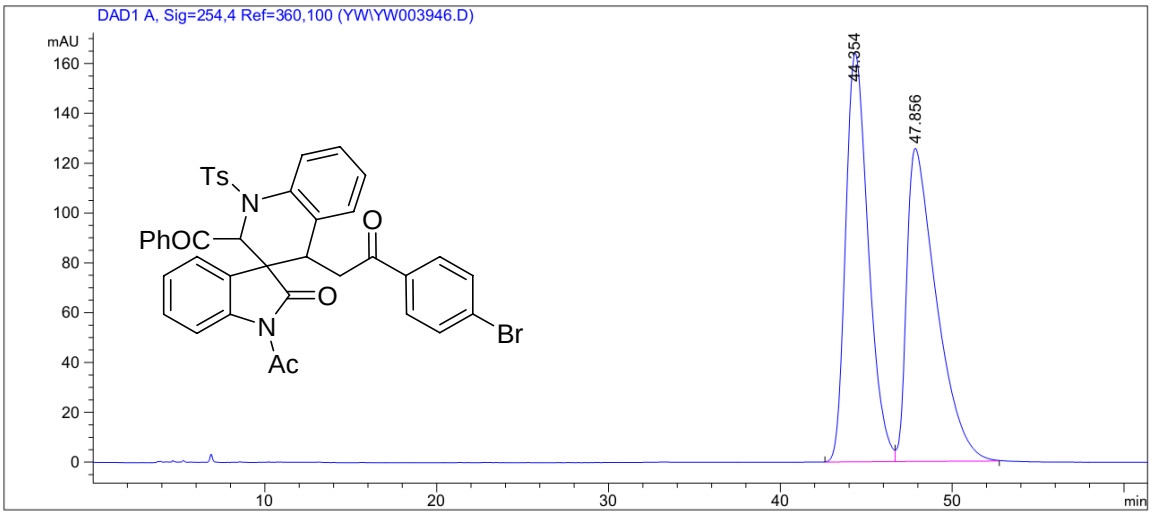
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.997	BV	0.5131	2548.03979	77.18757	4.9012
2	17.197	VB	0.5972	4.94400e4	1272.77136	95.0988



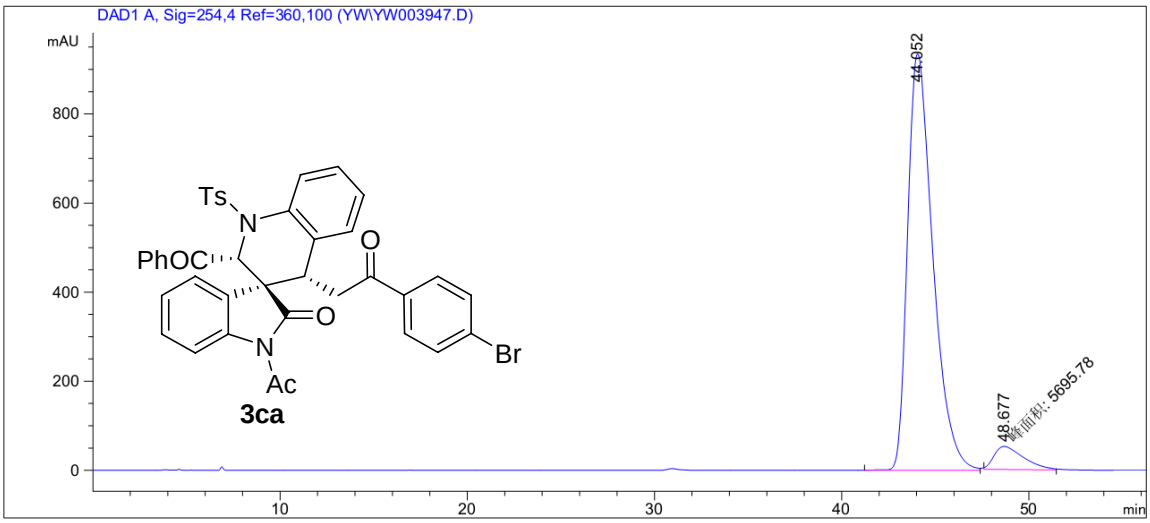
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	92.666	BV	2.6884	1.34464e4	72.61513	47.3652
2	97.391	VB	3.3399	1.49424e4	59.29647	52.6348



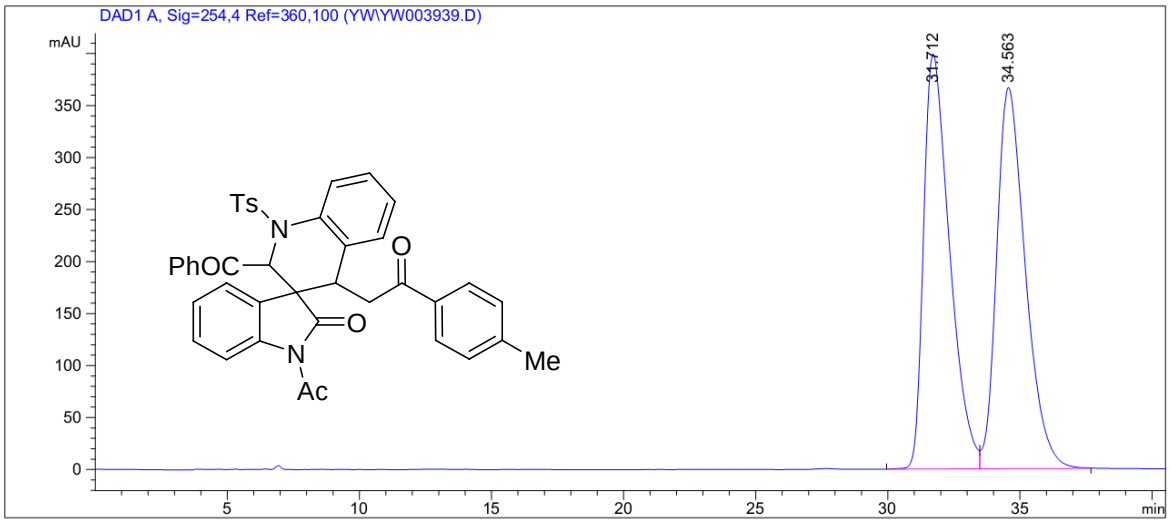
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	92.274	BV	3.0036	7.44849e4	357.96228	93.7944
2	100.582	VB	2.8580	4928.04785	20.51919	6.2056



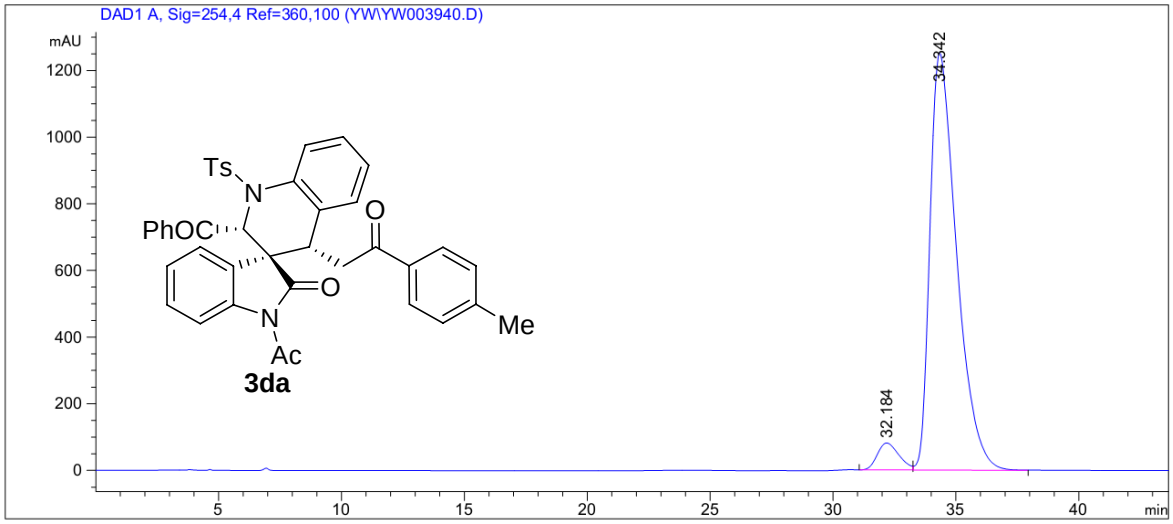
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.354	BV	1.4145	1.50995e4	163.94212	49.8650
2	47.856	VB	1.7892	1.51812e4	125.68217	50.1350



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.052	BV	1.4287	8.75600e4	934.88824	93.8923
2	48.677	MM	1.8337	5695.78125	51.76985	6.1077



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.712	BV	1.0379	2.72846e4	398.96933	49.5799
2	34.563	VB	1.1631	2.77469e4	366.57468	50.4201



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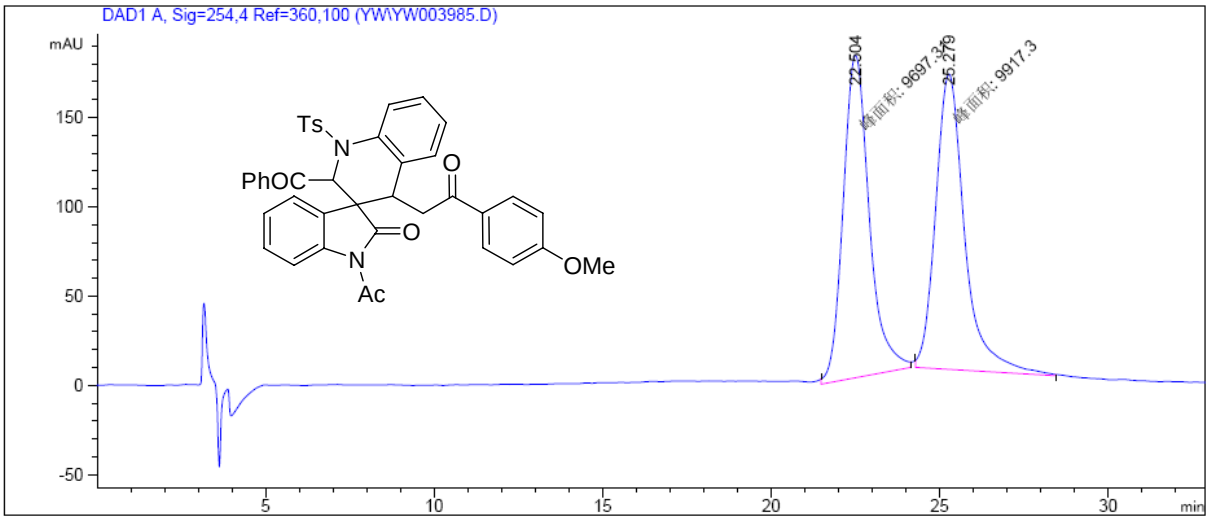
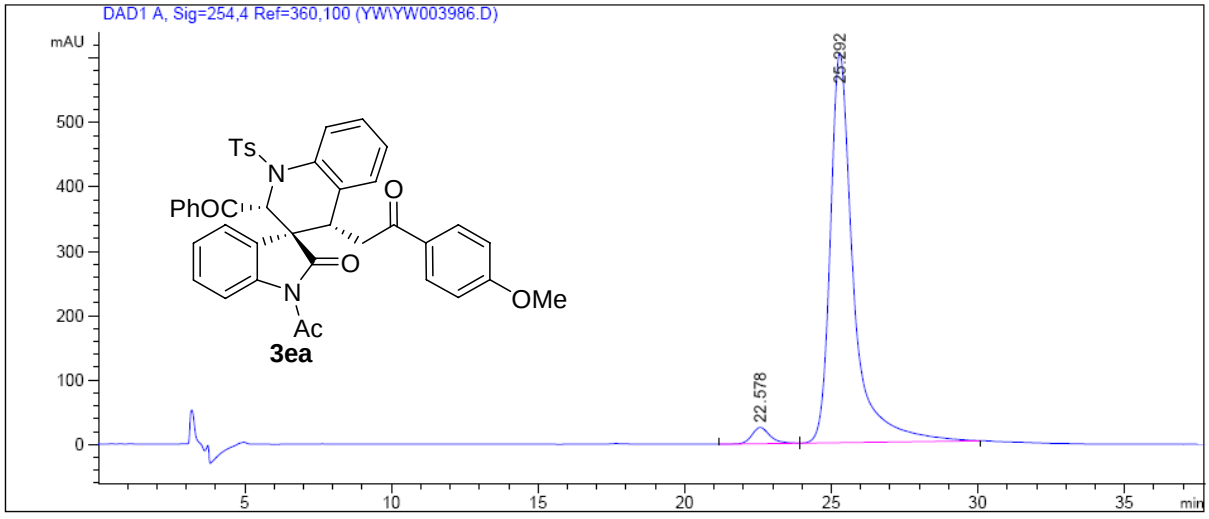
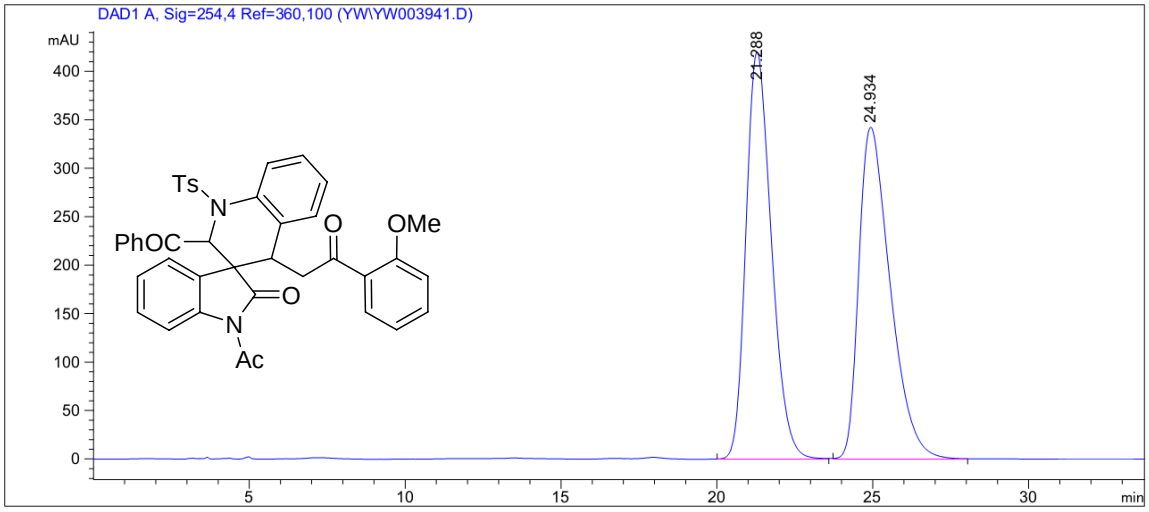
1	32.184	BV X	0.9599	4934.57861	80.86377	4.9776
2	34.342	VB X	1.1624	9.42002e4	1251.11340	95.0224



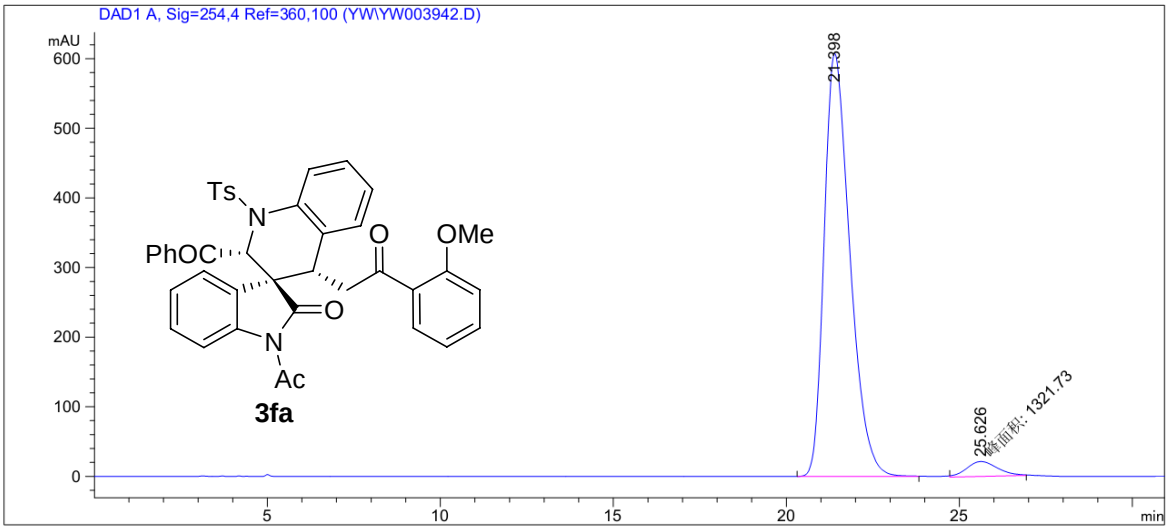
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.504	MM	0.8947	9697.31055	180.63661	49.4392
2	25.279	MM	1.0001	9917.29688	165.27892	50.5608



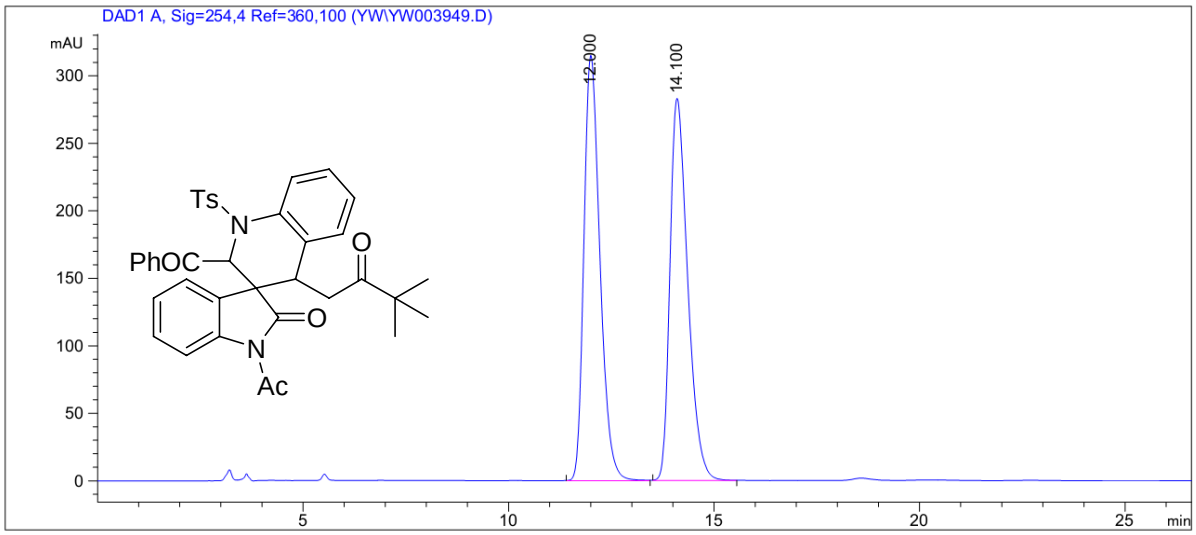
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.578	BV	0.6488	1079.97546	25.35988	3.1425
2	25.292	VB	0.8134	3.32866e4	605.43640	96.8575



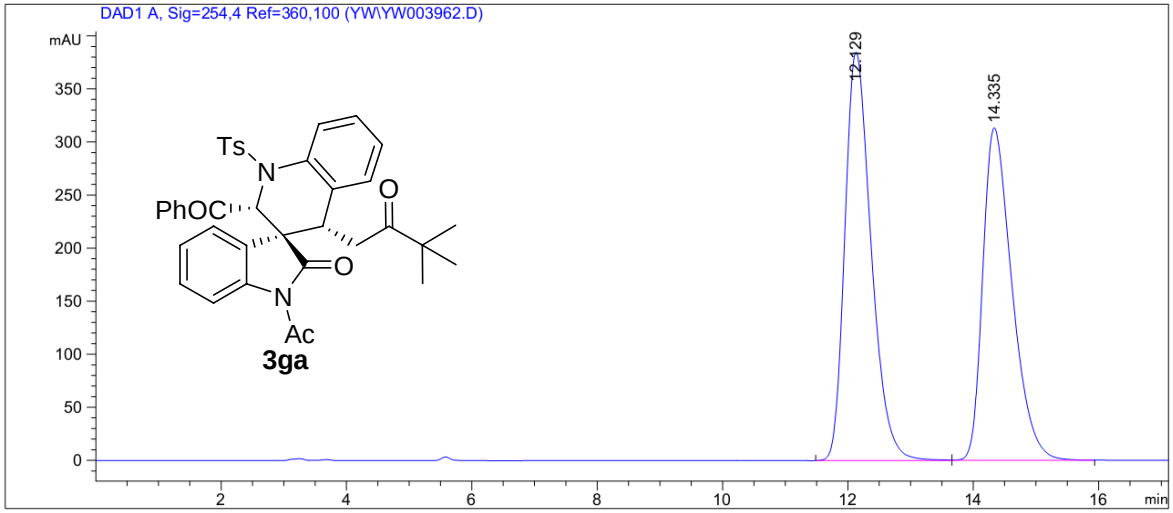
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.288	BB	0.8826	2.38622e4	420.17181	49.9265
2	24.934	BB	1.0677	2.39325e4	342.30020	50.0735



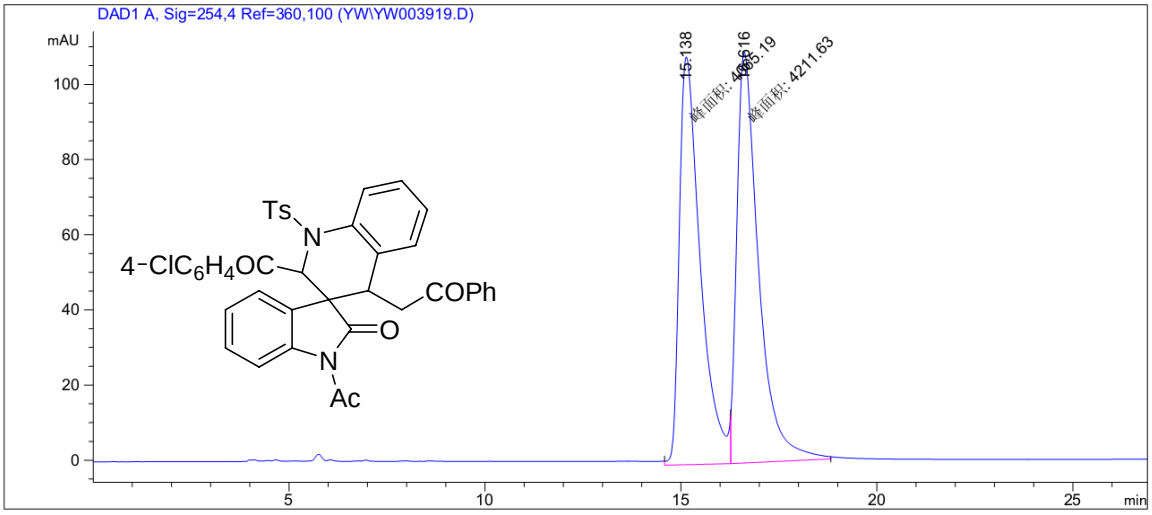
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.398	BB	0.7954	3.14152e4	607.42603	95.9626
2	25.626	MM	1.0308	1321.73438	21.36987	4.0374



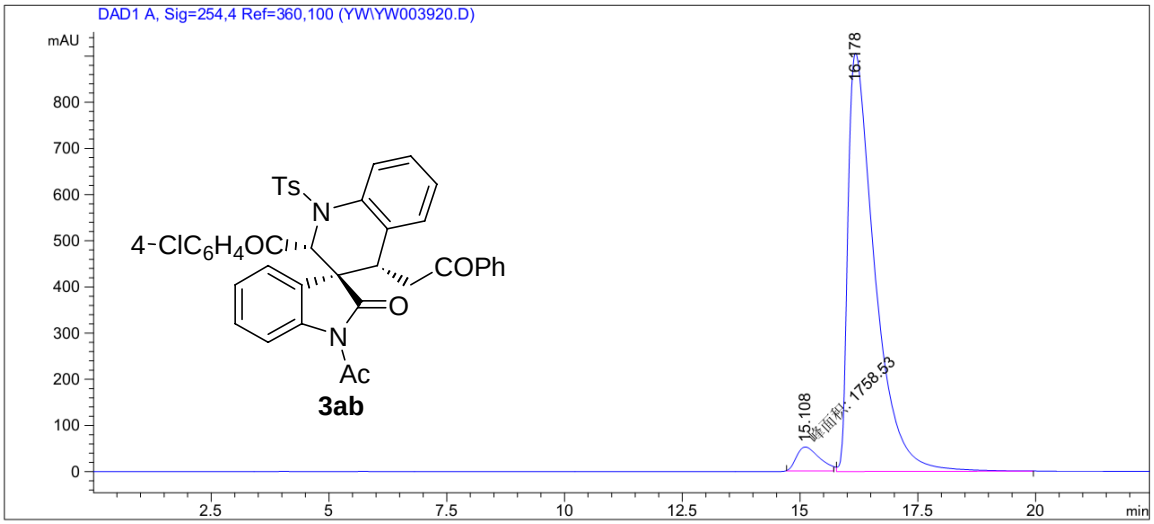
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.000	BB	0.4158	8526.93359	314.98444	50.1114
2	14.100	BB	0.4618	8489.01270	283.09863	49.8886



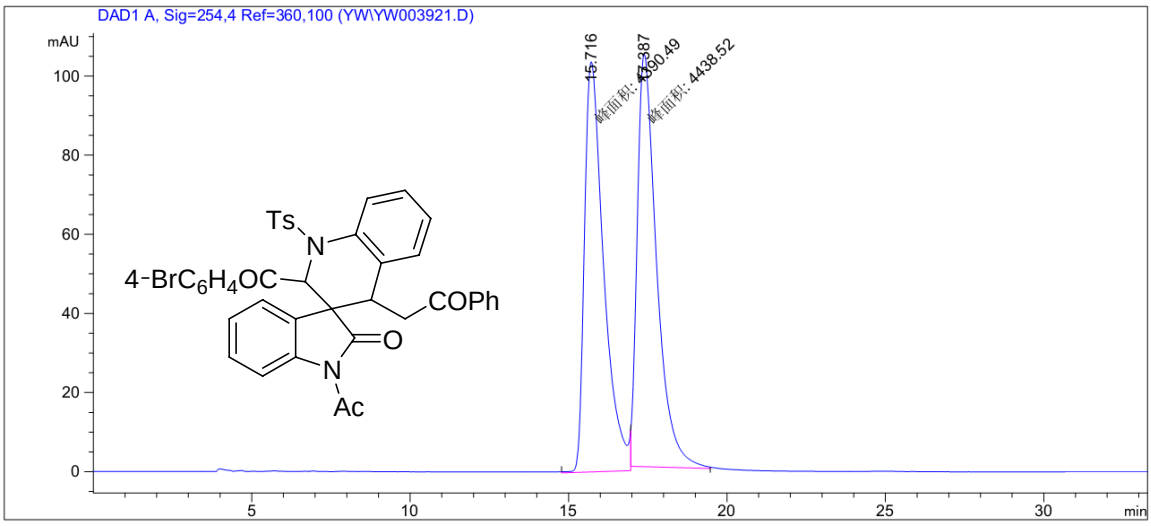
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.129	BV	0.4521	1.12192e4	384.85855	52.4968
2	14.335	VB	0.4941	1.01521e4	313.28442	47.5032



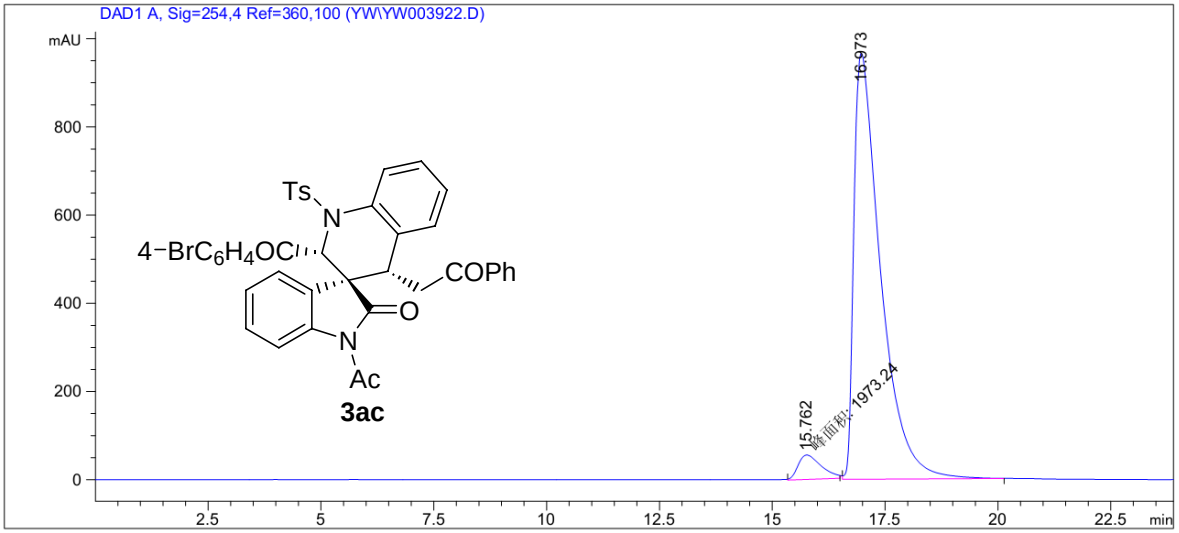
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.138	MM	0.6246	4065.19165	108.47662	49.1154
2	16.616	MM	0.6420	4211.63037	109.34003	50.8846



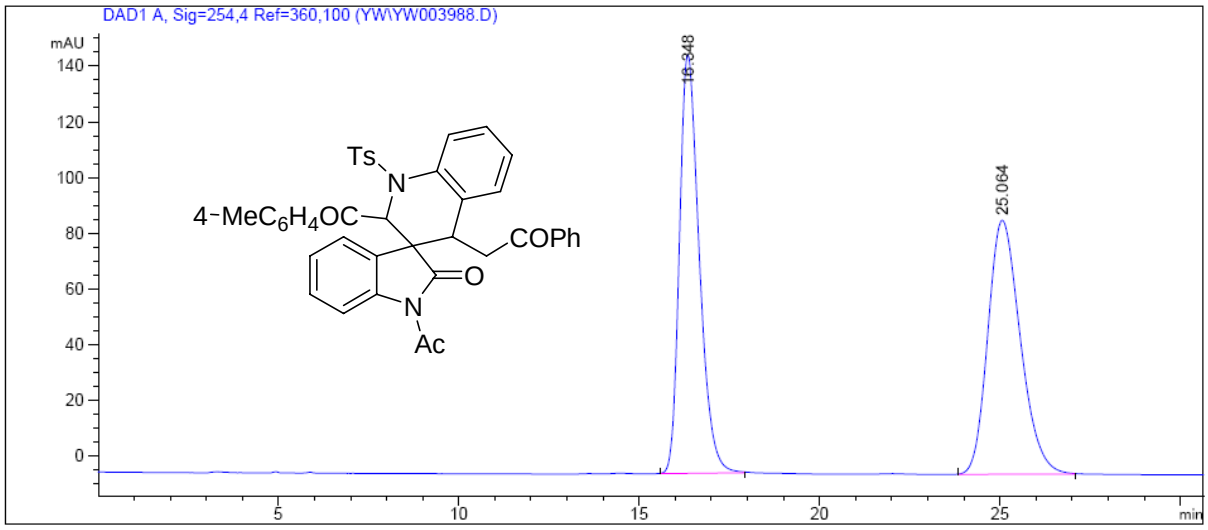
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.108	MM	0.5609	1758.53027	52.25431	4.6900
2	16.178	VB	0.5882	3.57369e4	905.97827	95.3100



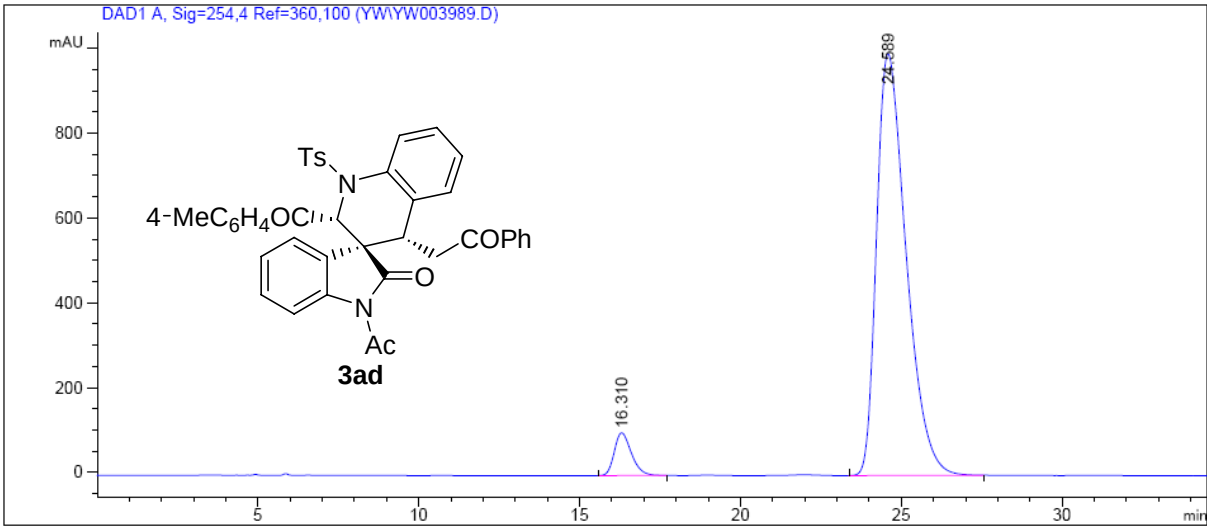
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.716	MM	0.7057	4390.48877	103.68638	49.7280
2	17.387	MM	0.7094	4438.52441	104.27663	50.2720



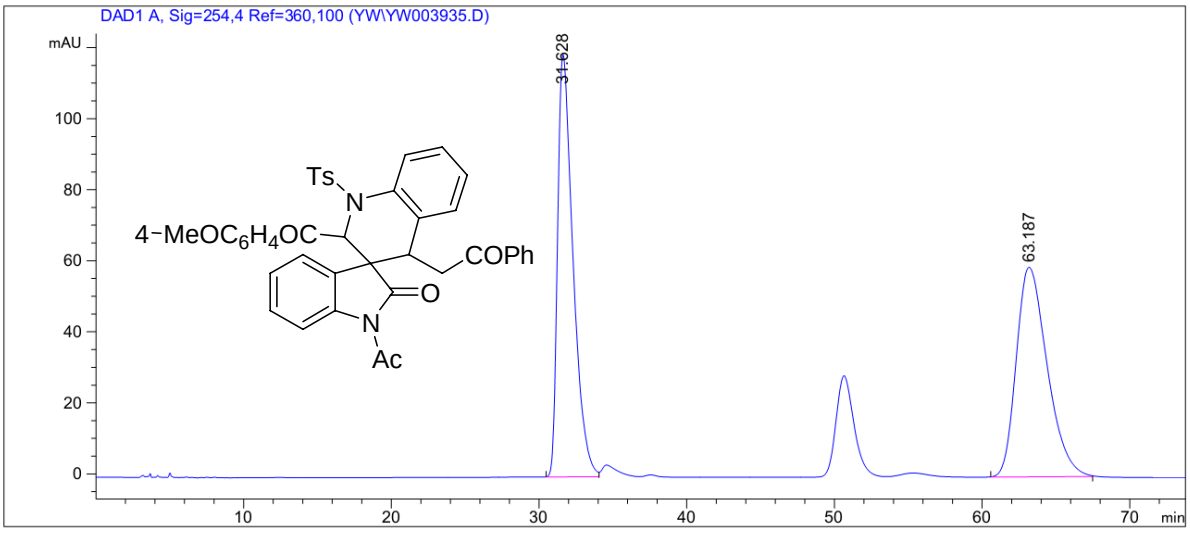
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.762	MM	0.5930	1973.24487	55.45978	4.7234
2	16.973	VB	0.6086	3.98029e4	966.15192	95.2766



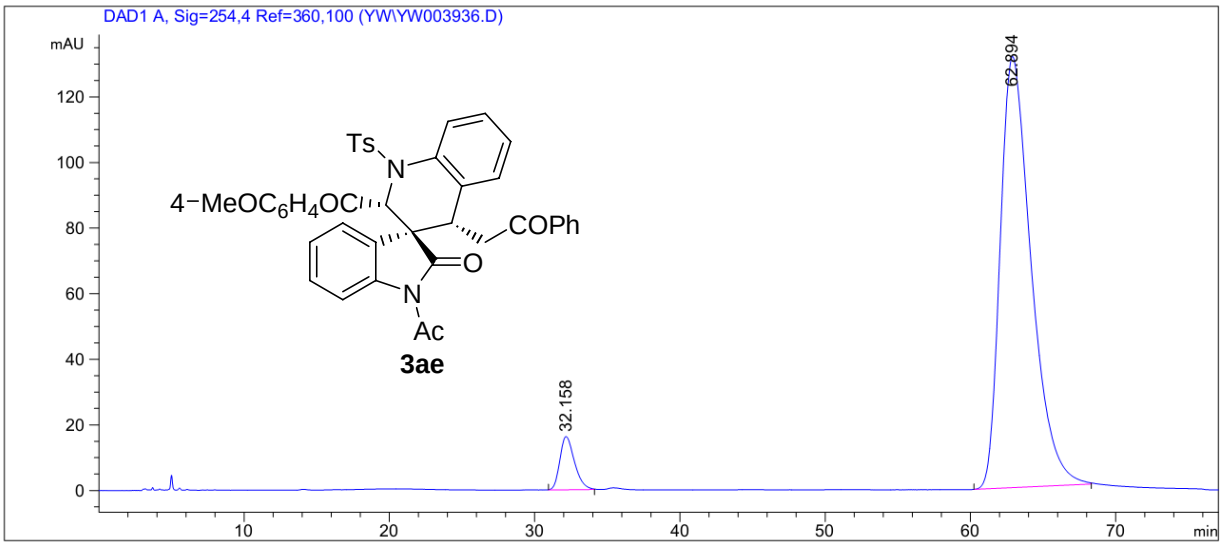
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.348	BB	0.5823	5727.19434	150.38698	50.0748
2	25.064	BB	0.9643	5710.07666	91.21992	49.9252



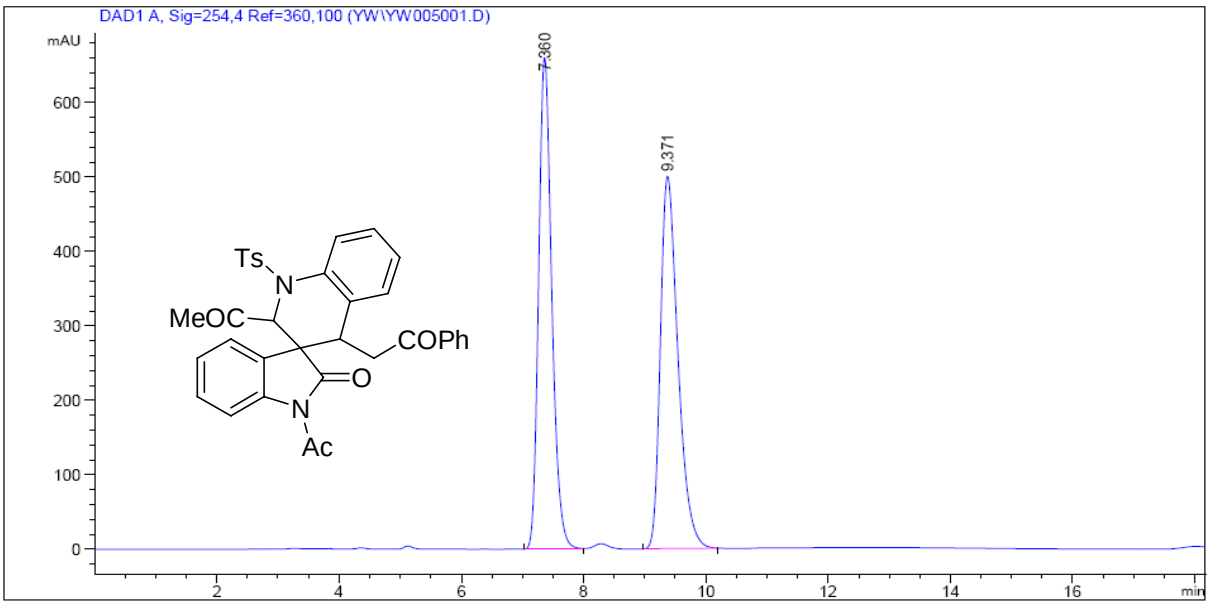
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.310	BB	0.5683	3734.47900	100.77486	5.5483
2	24.589	BB	0.9798	6.35745e4	994.54407	94.4517



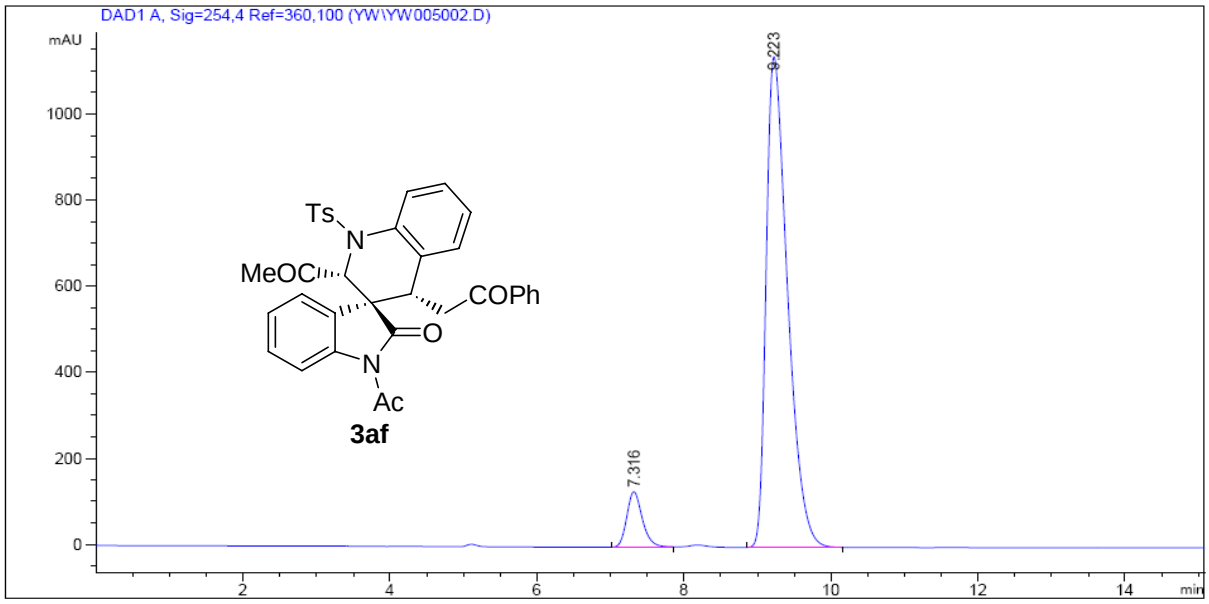
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.628	BV	1.0895	8607.57422	118.77785	50.0997
2	63.187	BB	2.1671	8573.29980	59.00547	49.9003



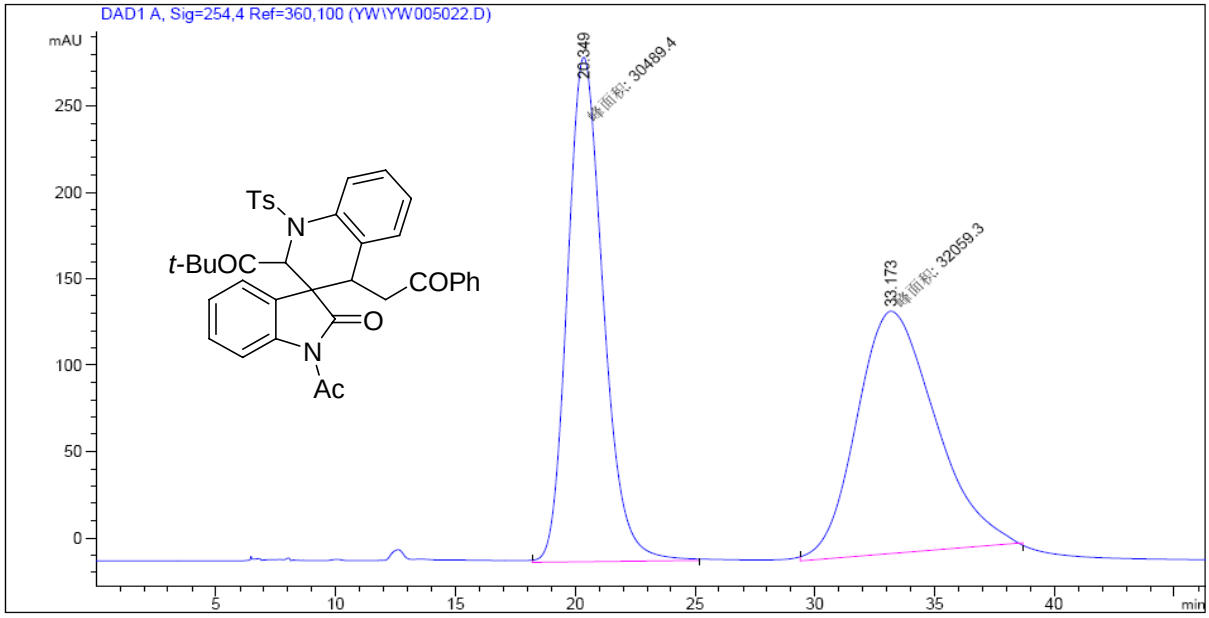
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.158	BB	1.0606	1140.77759	16.21844	5.5438
2	62.894	BB	2.2248	1.94369e4	131.47235	94.4562



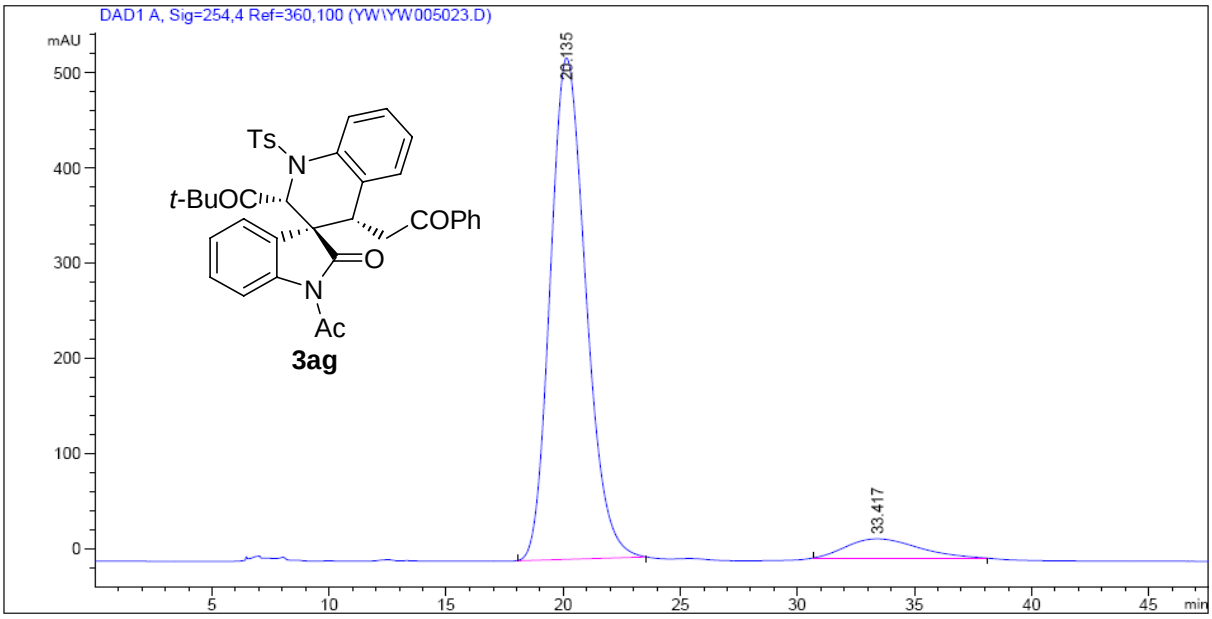
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.360	BB	0.2287	9895.47949	660.79425	49.7235
2	9.371	BB	0.3051	1.00055e4	500.67511	50.2765



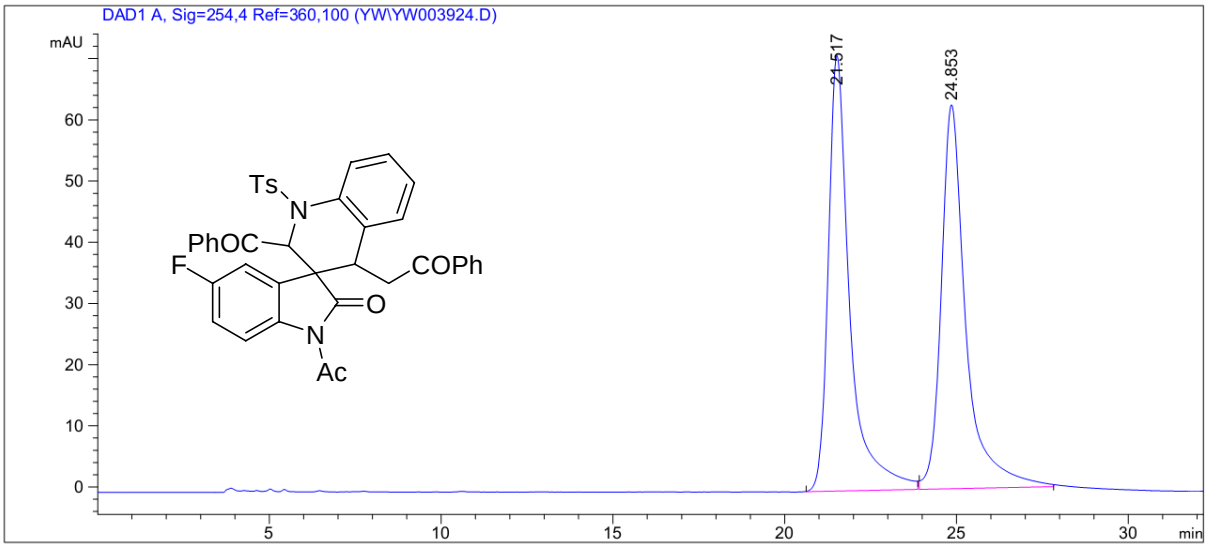
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.316	BB	0.2267	1911.90051	129.12350	7.6631
2	9.223	BB	0.3078	2.30375e4	1139.59424	92.3369



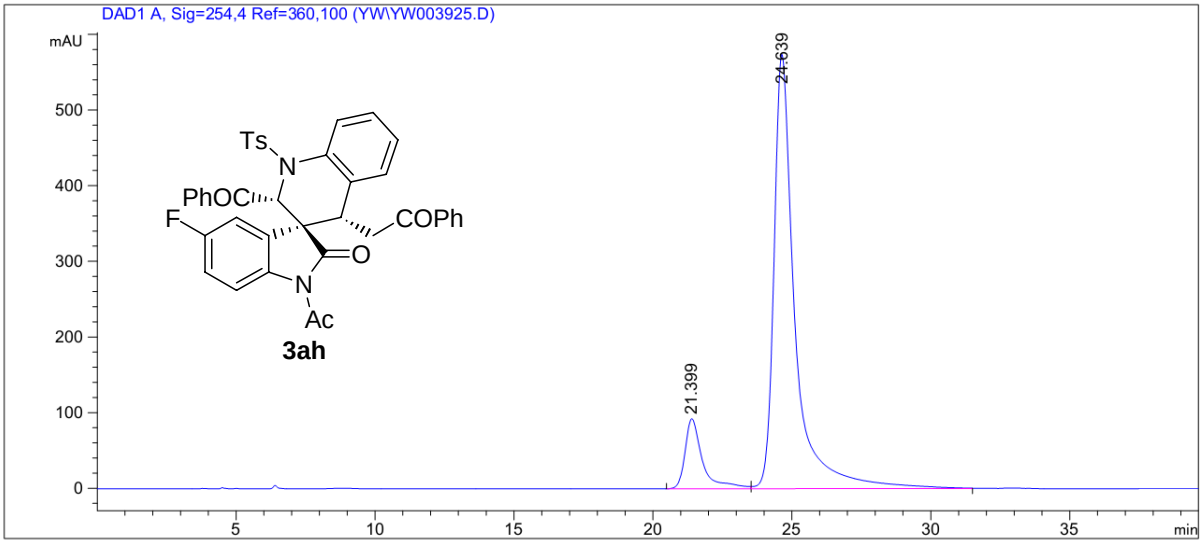
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.349	MM	1.7401	3.04894e4	292.03174	48.7450
2	33.173	MM	3.8079	3.20593e4	140.32043	51.2550



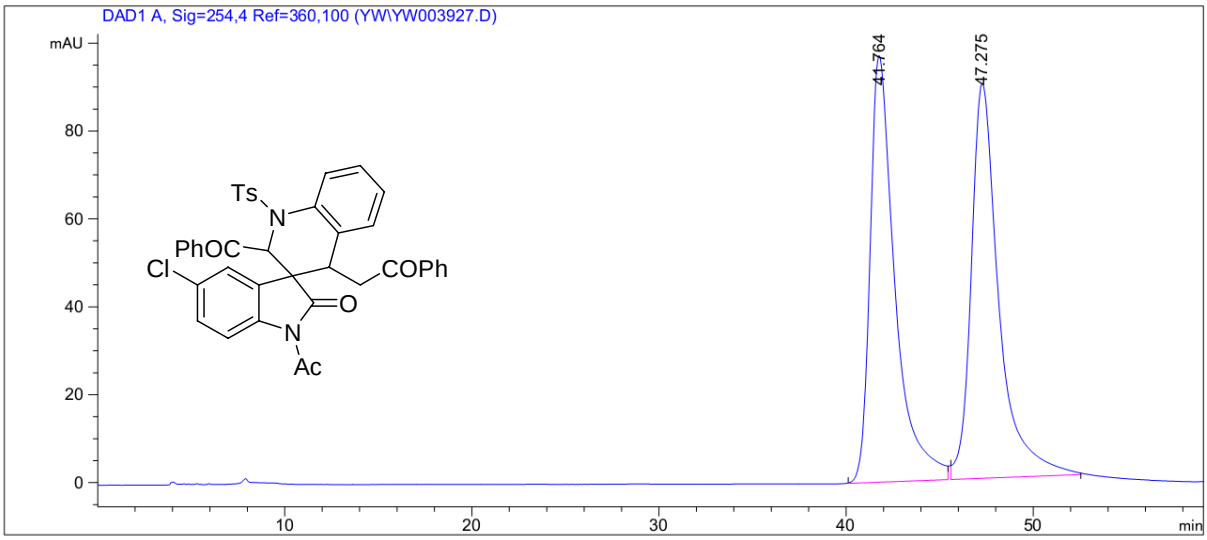
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.135	BB	1.6335	5.57027e4	526.82861	92.7600
2	33.417	BB	2.5203	4347.64063	20.20577	7.2400



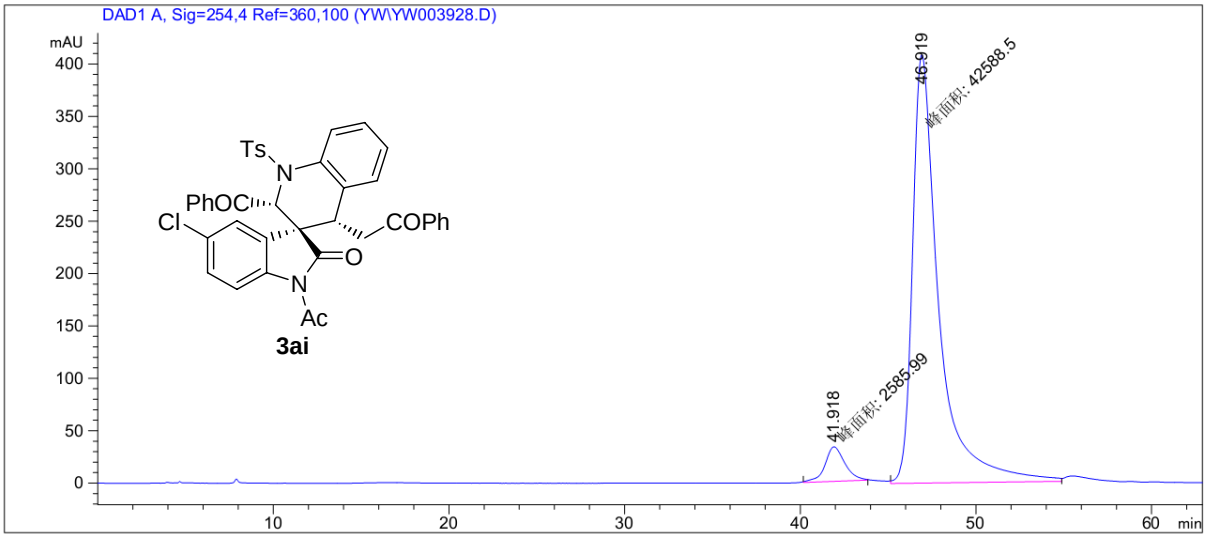
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.517	BB	0.6395	3095.76831	71.16900	49.7743
2	24.853	BB	0.7332	3123.84155	62.70801	50.2257



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.399	BV	0.6392	4058.64941	92.62091	11.8605
2	24.639	VB	0.7648	3.01612e4	574.21545	88.1395

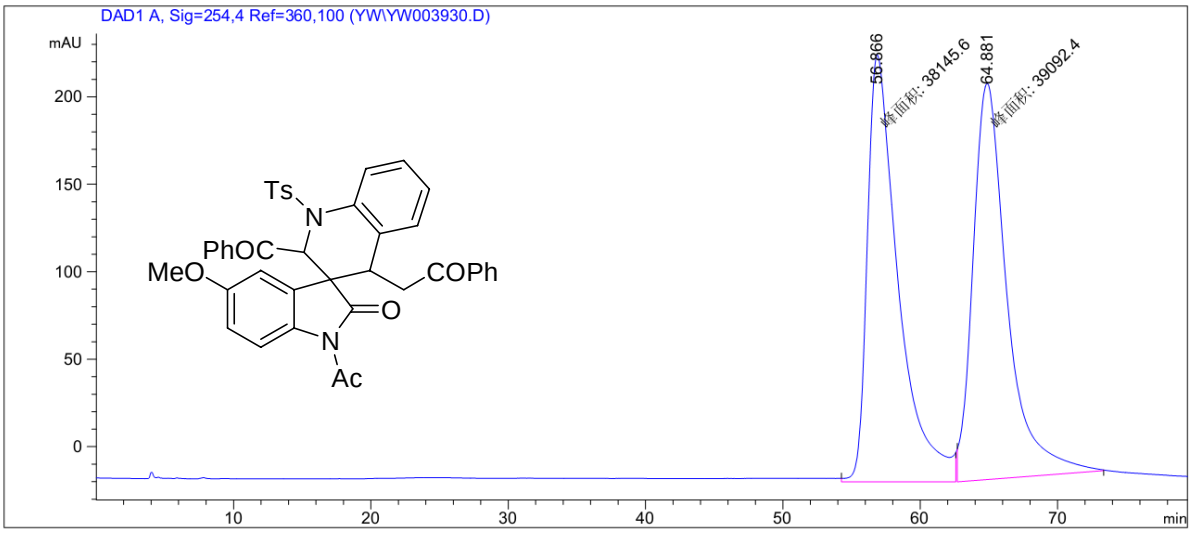


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.764	BB	1.3614	8964.02148	97.06768	49.3125
2	47.275	BB	1.5082	9213.97266	89.86597	50.6875

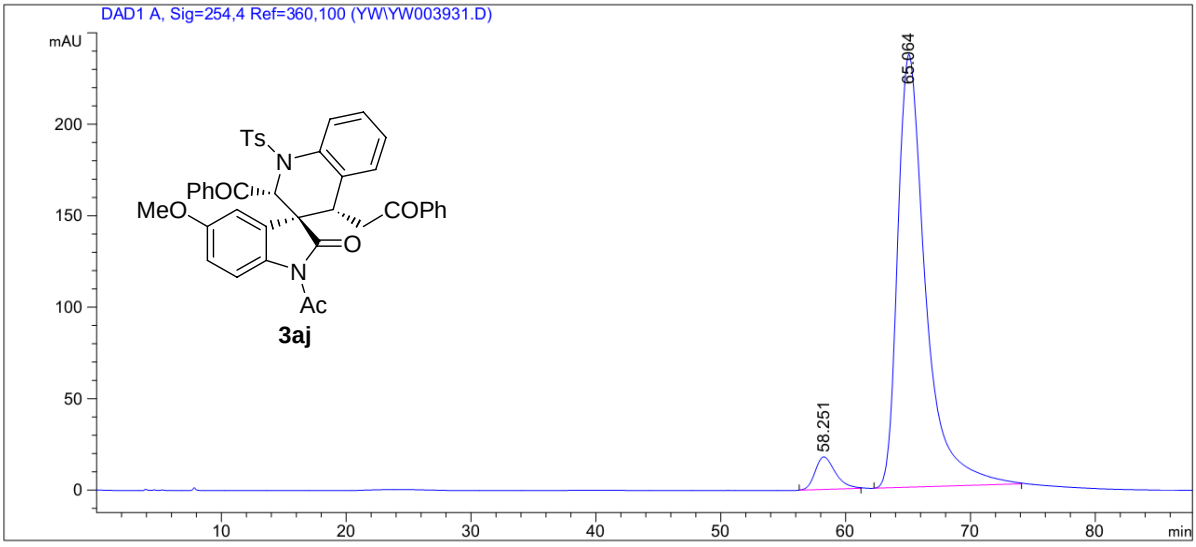


3ai

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.918	MM	1.3084	2585.98999	32.94071	5.7244
2	46.919	MM	1.7352	4.25885e4	409.07346	94.2756

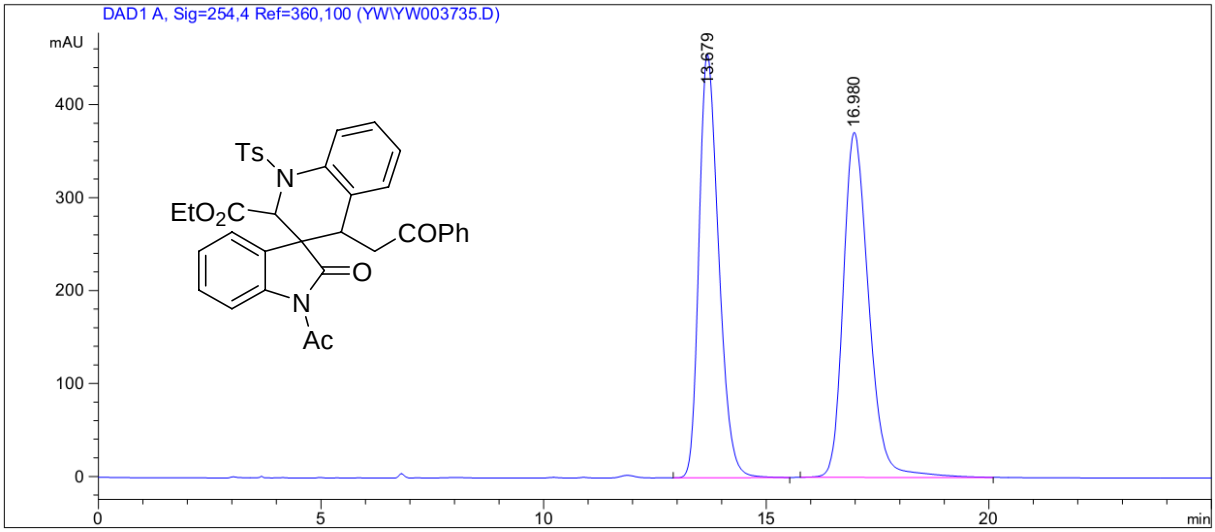


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	56.866	MM	2.6049	3.81456e4	244.05865	49.3871
2	64.881	MM	2.8785	3.90924e4	226.35028	50.6129

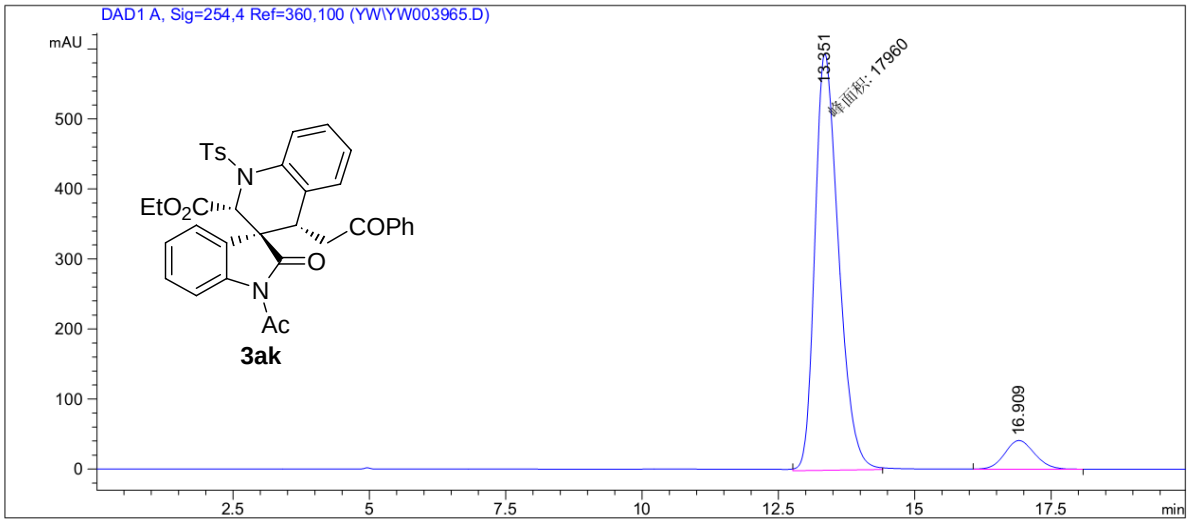


3aj

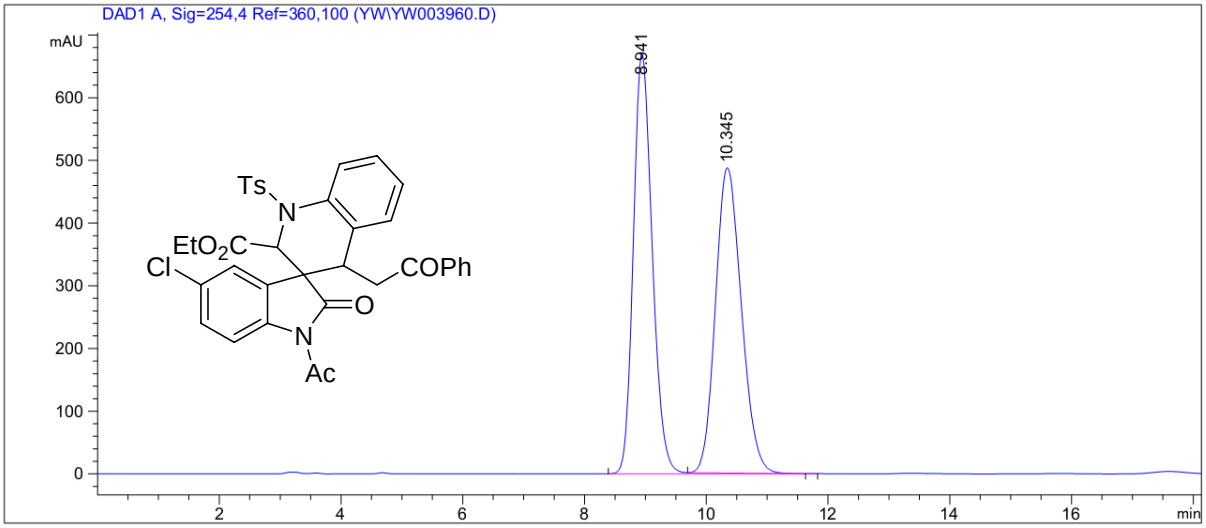
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	58.251	BB	1.6868	2001.29041	17.81259	5.1539
2	65.064	BB	2.3563	3.68297e4	236.57355	94.8461



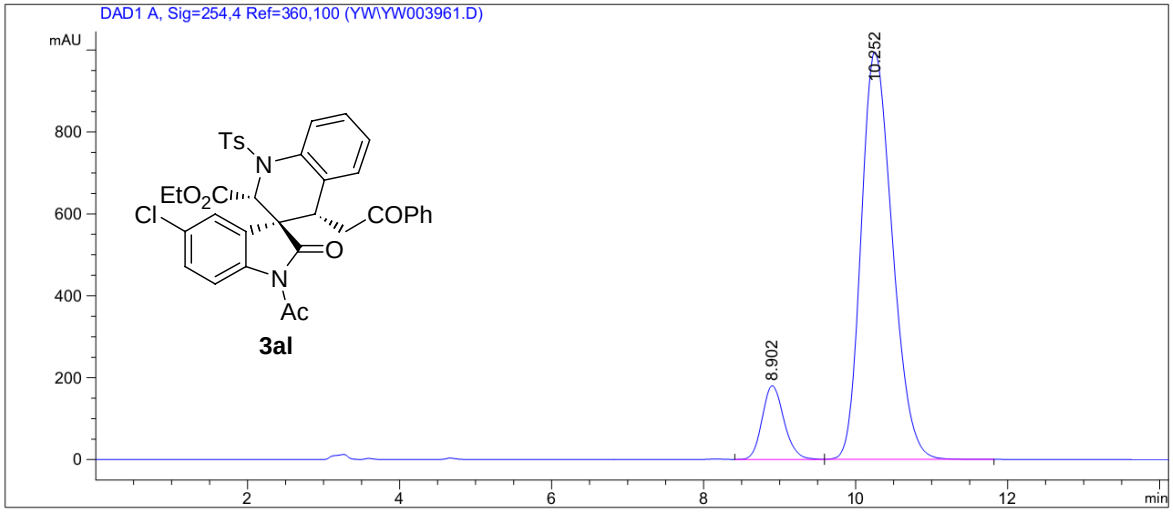
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.679	VB T	0.4735	1.39683e4	455.86218	48.6011
2	16.980	BB	0.6123	1.47724e4	371.18472	51.3989



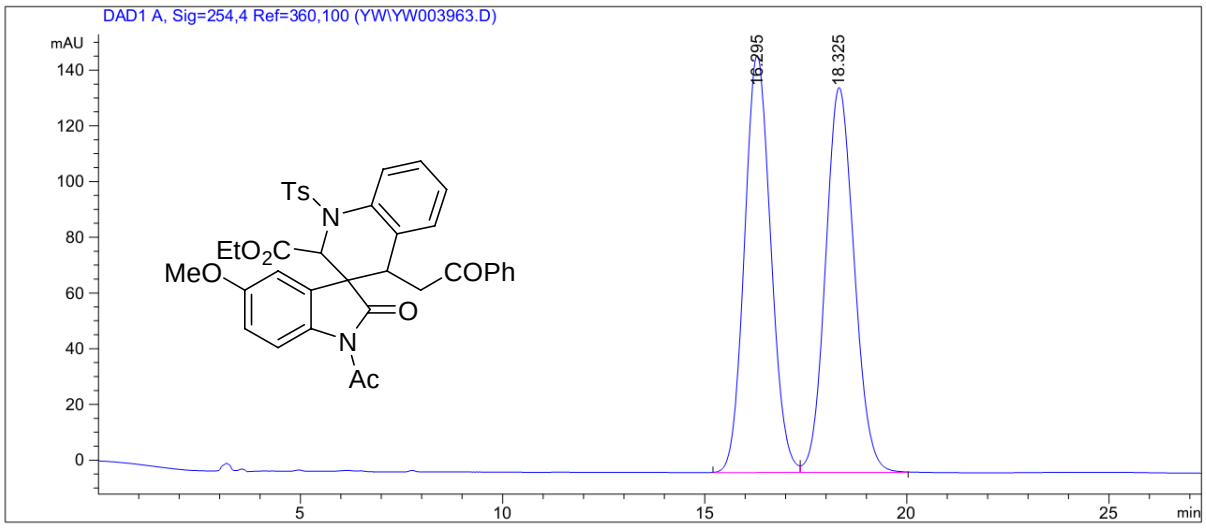
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.351	MM	0.5034	1.79600e4	594.65936	91.9922
2	16.909	BB	0.5925	1563.38684	41.03148	8.0078



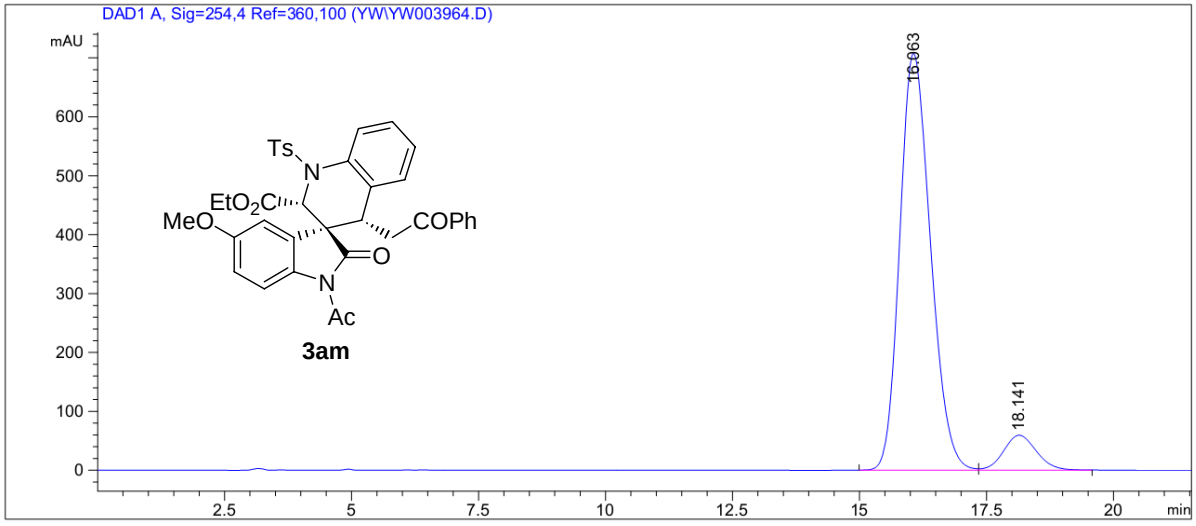
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.941	BB S	0.3325	1.44919e4	669.60480	50.1964
2	10.345	BB T	0.4604	1.43785e4	487.04489	49.8036



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.902	BV	0.3089	3594.08862	180.06804	11.2523
2	10.252	VB S	0.4405	2.83467e4	994.63623	88.7477

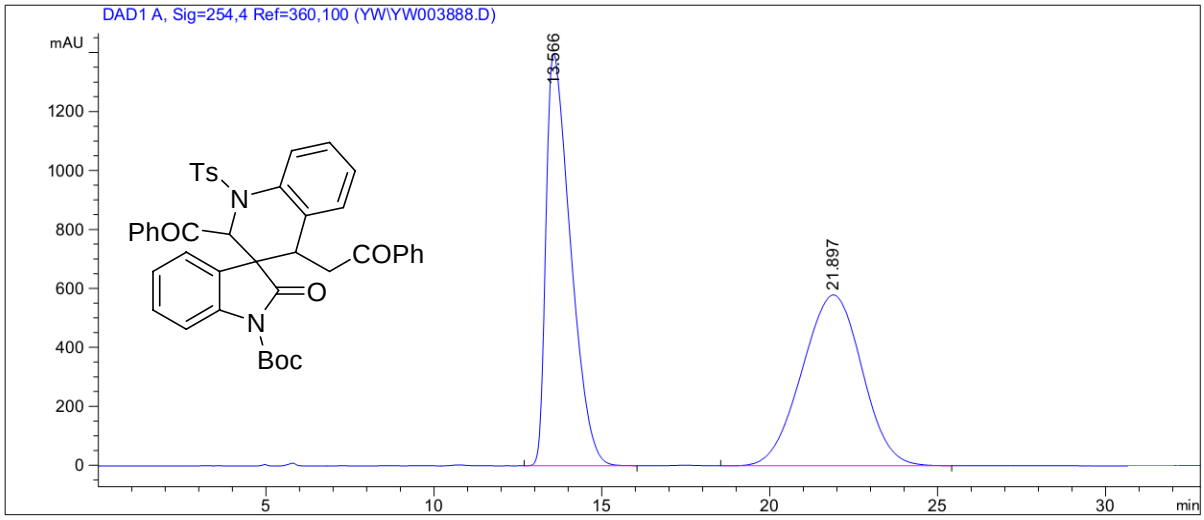


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.295	BV	0.6998	6773.83105	149.72369	49.9060
2	18.325	VB	0.7660	6799.33936	138.19928	50.0940

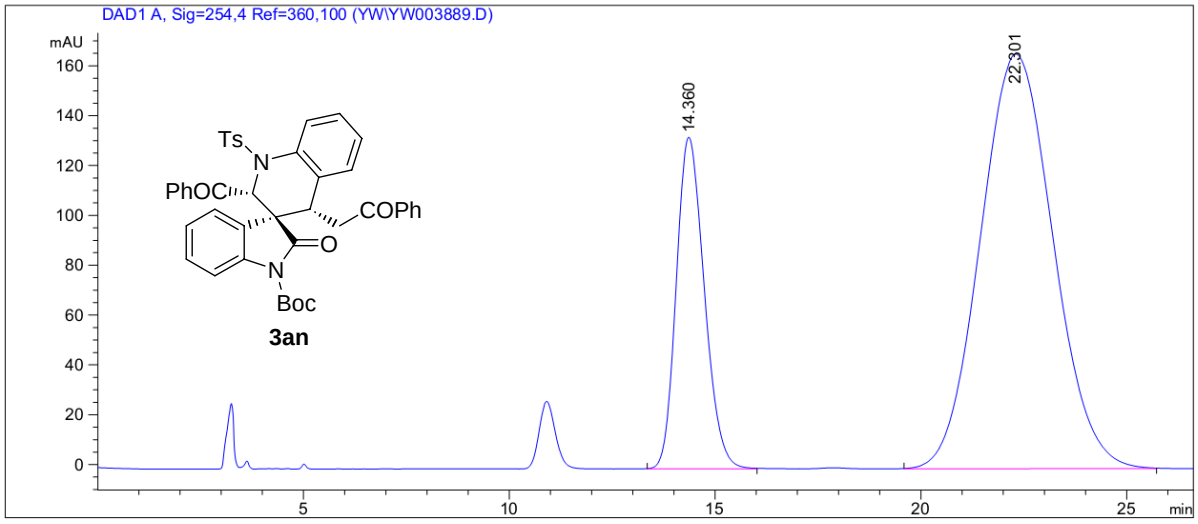


3am

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.063	BV	0.6546	2.97510e4	707.52301	91.7667
2	18.141	VB	0.6964	2669.26172	59.38599	8.2333



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.566	BB	0.7778	7.11002e4	1396.82397	49.6666
2	21.897	VB	1.9146	7.20549e4	579.52600	50.3334



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.360	BB	0.7356	6289.84912	133.02866	23.5948
2	22.301	BB	1.9197	2.03680e4	166.44524	76.4052