Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Highly Enantioselective Addition of Sulfur-Containing Heterocycles to Isatin-Derived Ketimines

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Content

1 General information

Chemicals and solvents were either purchased from commercial suppliers in p.a. purity or purified by standard method. Reactions were monitored by thin-layer chromatography (TLC), silica plates Merck 60 F 254 were used. Compounds were detected by irradiation with UV light and subsequently plates visualized by treatment detection reagent AMC or ninhydrin or vanillin or $KMnO_4$ followed by heating. The detection reagent AMC was prepared from phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), conc. H_2SO_4 (60 ml) and H_2O (940 ml). The detection solution of ninhydrin was prepared from ninhydrin (1.5 g) in 100 ml of *n*-butanol and then was added acetic acid (3 ml). The solution of vanilline was prepared from vanilline (15 g) in ethanol (250 ml) and conc. sulfuric acid (2.5 ml). Column chromatography was performed by using silica gel Fluka (40-63 μm). The solvents for column chromatography separation were purified by distillation. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded with Varian UNITY INOVA 300, Bruker AVANCE III 400 and Bruker AVANCE III 600. Chemical shifts are given in ppm relative to $CDCl_3$, and coupling constants *J* are given in Hz. The NMR spectra were recorded in $CDCl_3$ as solvent at room temperature, TMS served as internal standard (δ = 0.0 ppm) for ^{1}H NMR, $CDCl_3$ was used as internal standard (δ = 77.0 ppm) for ^{13}C NMR, and TFA was used as external standard for ^{19}F NMR. High-resolution mass spectra were recorded with a LCQ Fleet spectrometer. Chiral HPLC was carried out by using a Shimadzu chromatograph with SPD-M20A spectrophotometric detector. Chiral column Daicel Chiralpak AD was used for separation of enantiomers. Specific optical rotations were measured on AU-Tomatica polarimeter, Autopol III and as solvent was used $CHCl_3$. Specific optical rotations are given in concentrations *c* [g/100 mL]. Infrared spectroscopy spectra were measured on a Nicolet Avatar 370 FTIR. The method used for measuring was a diffuse reflectance (DRIFT) in KBr. IR absorptions are given in wavenumbers as cm^{-1}.

2 Preparation of starting material

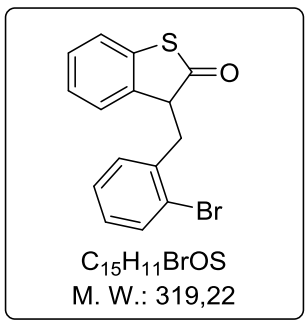
Ketimines **1a-m** were prepared by published literature[1]. Benzothiophenones **2a,f,g,h,** were prepare by published literature[2]. Derivative of rhodanine **4** was synthetized by according literature[3]. Derivative of thiohydantoin **5** was prepared by following procedure[4].

2.1 General procedure for benzo[*b*]thiophen-2(3*H*)-ones 2b,c,d,e,i

According modified procedure[2] to the solution of benzo[b]thiophen-2(3H)-one (1.67 mmol, 1 equiv.) in toluene (7 mL) were added corresponding benzaldehyde (2 equiv., 3.33 mmol), morpholine (0.17 mmol, 0.1 equiv.), and acetic acid (0.17 mmol, 0.1 equiv.) and reaction mixture was refluxed with stirring until full conversion (TLC monitoring). After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel with the aid of EtOAc, and then concentrated. The resulting residue was dissolved in EtOAc (7 mL), and the flask was degassed by alternating vacuum evacuation/Ar backfill. After successive addition of 10% Pd/C (100 mg) at 0 °C, the reaction flask was evacuated again and refilled with H_2 three times. The resulting suspension was stirred for 12 h at room temperature. After flushing the remaining H_2 out with Ar, the mixture was filtered to remove Pd/C. The filtrate was evaporated and the residue was then loaded on silica and afforded the resulting product as described below.

2.2 Characterization data for new compounds 2b,c,d,e,i

3-(2-Bromobenzyl)benzo[*b*]thiophen-2(3*H*)-one (2b)

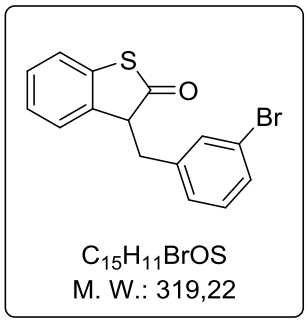


$C_{15}H_{11}BrOS$
M. W.: 319,22

Product **2b** was obtained as oil in 40% yield (205 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.60 (dd, *J* = 7.9 Hz, *J'* = 1.3 Hz, 1H), 7.36 (dd, *J* = 7.5 Hz, *J'* = 0.8 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.19 – 7.06 (m, 3H), 6.77 (d, *J* = 7.7 Hz, 1H), 4.31 – 4.19 (m, 1H), 3.48 (dd, *J* = 13.9 Hz, *J'* = 6.6 Hz, 1H), 3.17 (dd, *J* = 13.9 Hz, *J'* = 8.4 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 204.9, 136.5, 136.0, 135.6, 133.1, 132.3, 128.8, 128.4, 127.3, 125.8, 125.5, 124.9, 122.9, 56.0, 39.7 ppm. **IR** (KBr):

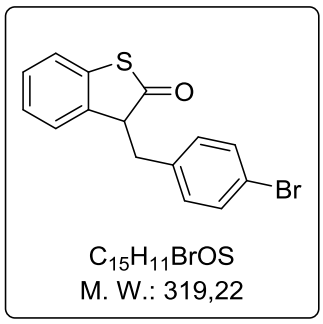
ν/cm^{-1} = 3402, 3067, 3010, 2962, 2929, 2854, 1799, 1700, 1592, 1464, 1449, 1281, 1251, 1159, 1129, 1090. **HRMS** (ESI) m/z calcd for $C_{15}H_{11}OSBr$ $[M]^+$ = 317.9714, found: 317.9712.

3-(3-Bromobenzyl)benzo[*b*]thiophen-2(3*H*)-one (2c)



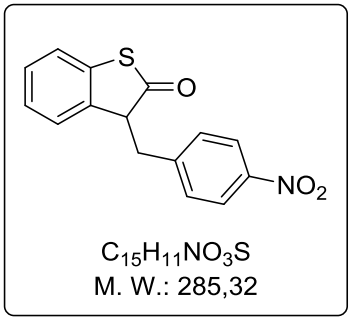
Product **2c** was obtained as oil in 41% yield (217 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36 – 7.31 (m, 1H), 7.31 – 7.25 (m, 2H), 7.21 (t, *J* = 1.7 Hz, 1H), 7.20 – 7.14 (m, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 7.02 – 6.94 (m, 2H), 4.07 (ddd, *J* = 7.4 Hz, *J'* = 4.9 Hz, *J''* = 0.8 Hz, 1H), 3.37 (dd, *J* = 13.9 Hz, *J'* = 4.9 Hz, 1H), 3.16 (dd, *J* = 13.9 Hz, *J'* = 7.4 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 205.5, 138.8, 135.9, 135.5, 132.5, 130.0, 129.8, 128.6, 128.1, 126.0, 125.2, 123.1, 122.3, 57.8, 38.2 ppm. **IR** (KBr): ν/cm^{-1} = 3396, 3058, 3013, 2929, 2851, 1706, 1682, 1595, 1565, 1467, 1428, 1278, 1213, 1171, 1132, 1090. **HRMS** (ESI) m/z calcd for $C_{15}H_{11}OSBr$ $[M]^+$ = 317.9714, found: 317.9714.

3-(4-Bromobenzyl)benzo[*b*]thiophen-2(3*H*)-one (2d)



Product **2d** was obtained as oil in 36% yield (190 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.35 – 7.30 (m, 2H), 7.29 – 7.24 (m, 2H), 7.20 – 7.13 (m, 1H), 7.00 (dd, *J* = 7.6 Hz, *J'* = 0.9 Hz, 1H), 6.94 – 6.89 (m, 2H), 4.06 (ddd, *J* = 7.1 Hz, *J'* = 4.8 Hz, *J''* = 0.8 Hz, 1H), 3.34 (dd, *J* = 13.9 Hz, *J'* = 4.9 Hz, 1H), 3.19 (dd, *J* = 13.9 Hz, *J'* = 7.1 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 205.6, 136.0, 135.5, 135.3, 131.3 (2C), 131.2 (2C), 128.5, 125.9, 125.1, 123.0, 120.9, 57.8, 37.9 ppm. **IR** (KBr): ν/cm^{-1} = 3509, 3390, 3064, 2929, 2857, 1900, 1685, 1592, 1413, 1278, 1204, 1183, 1090, 1072. **HRMS** (ESI) m/z calcd for $C_{15}H_{11}OSBr$ $[M]^+$ = 317.9714, found: 317.9721.

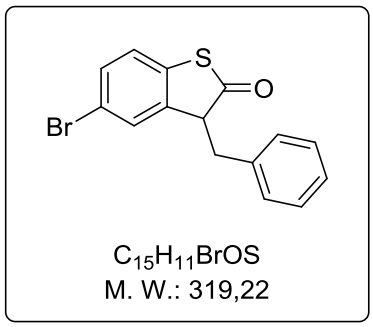
3-(4-Nitrobenzyl)benzo[*b*]thiophen-2(3*H*)-one (2e)



$C_{15}H_{11}NO_3S$
M. W.: 285,32

Product **2e** was obtained as oil in 35% yield (167 mg).**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1H NMR (400 MHz, CDCl3) δ = 8.09 – 8.01 (m, 2H), 7.33 – 7.17 (m, 5H), 7.14 – 7.09 (m, 1H), 4.17 (t, *J* = 5.8 Hz, 1H), 3.49 – 3.39 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 205.2, 146.9, 143.9, 135.9, 134.9, 130.3 (2C), 128.8, 126.2, 124.9, 123.4 (2C), 123.2, 57.4, 38.0 ppm. **IR** (KBr): ν/cm^{-1} = 3396, 3111, 3079, 3064, 2962, 2935, 2887, 2842, 1700, 1604, 1341, 1308, 1180, 1108. **HRMS** (ESI) m/z calcd for $C_{15}H_{11}NO_3S$ $[M]^+$ = 285.0460, found: 285.0459.

3-Benzyl-5-bromobenzo[*b*]thiophen-2(3*H*)-one (2i)

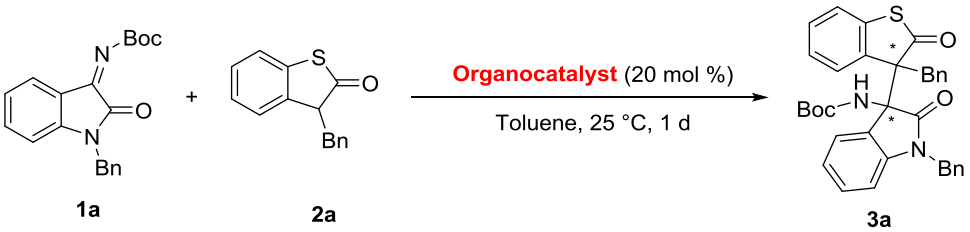


$C_{15}H_{11}BrOS$
M. W.: 319,22

Product **2i** was obtained as oil in 64% yield (340 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.43 – 7.37 (m, 1H), 7.32 – 7.21 (m, 3H), 7.16 (d, *J* = 8.3 Hz, 1H), 7.11 – 7.06 (m, 2H), 7.03 (dd, *J* = 1.9, *J'* = 1.0 Hz, 1H), 4.07 (dd, J = 7.6, *J'* = 4.9 Hz, 1H), 3.42 (dd, *J* = 13.8, *J'* = 4.8 Hz, 1H), 3.18 (dd, *J* = 13.8, *J'* = 7.7 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 204.53, 137.83, 135.94, 134.92, 131.39, 129.46, 128.47, 128.43, 127.10, 124.14, 119.37, 58.12, 38.64 ppm. **IR** (KBr): ν/cm^{-1} = 3405, 3088, 3064, 3034, 2926, 2854, 2340, 1879, 1682, 1601, 1440, 1404, 1263, 1183, 1171, 1144, 1090. **HRMS** (ESI) m/z calcd for $C_{15}H_{11}OSBr$ $[M]^+$ = 317.9714, found: 317.9713.

3 Screening and Optimization Studies

Table 1: Catalyst screening



1a 2a 3a

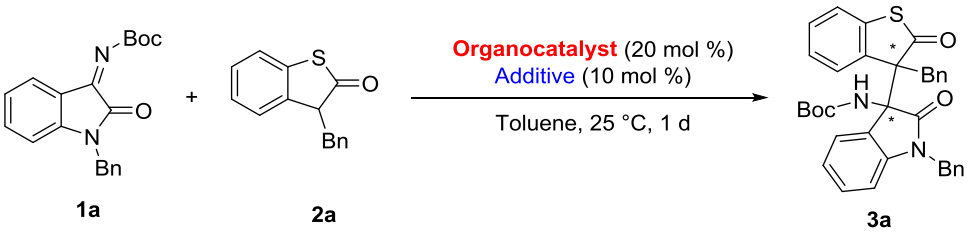
Entry	Organocatalyst	Yield (%)	*dr*	*ee* (%)
1	-	n.r.	-	-
2	QN **B**	79	20:1	24
3	CN **A**	92	20:1	41
4	QD **D**	75	20:1	18
5	CD **C**	88	20:1	22
6	Soós epi-CD **F**	51	20:1	80
7	Rawal epi-CN **G**	66	20:1	37
8	Takemoto **E**	53	20:1	82
9	$(DHQD)_2AQN$ **H**	65	20:1	31
10	CPA **J**	26	20:1	25
11	β-ICP **I**	40	20:1	11
12	Soós epi-CN **K**	44	20:1	72
13	Soós epi-QD **L**	49	20:1	73
14	Soós epi-QN **M**	45	20:1	66

CN = cinchonin; CD = cinchonidin, QN = chinin; QD = chinidin

CPA = chiral phosphoric acid (BINOL)

β-ICP = β-isocupreidin

Table 2: Additive screening

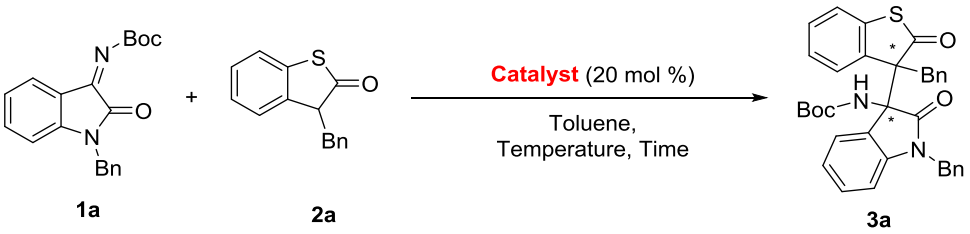


1a 2a 3a

Entry	Organoatalyst	Additive	2 (equiv.)	Yield (%)	*dr*	*ee* (%)
1	**F**	-	1.5	73	20:1	84
2	**F**	PhCOOH	1.5	63	20:1	76
3	**F**	2,4-DNBA	1.5	64	20:1	77
4	**F**	$Yb(OTf)_3$	1.5	59	20:1	81

2,4-DNBA = 2,4-dinitrobenzoic acid

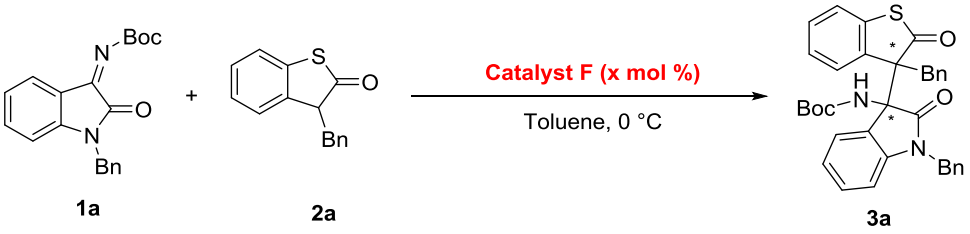
Table 3: Temperature and reaction time screening



1a 2a 3a

Entry	Catalyst	Temperature(°C)	Time (h)	Yield (%)	*dr*	*ee* (%)
1	**E**	0	2	53	20:1	81
2	**F**	0	2	64	20:1	85
3	CN	0	2	71	20:1	41
4	**E**	-50	2	49	20:1	83
5	**F**	-50	2	67	20:1	87
6	CN	-50	2	86	20:1	70
7	**E**	-78	4	45	20:1	22
8	**F**	-78	4	54	20:1	70
9	CN	-78	4	69	20:1	36

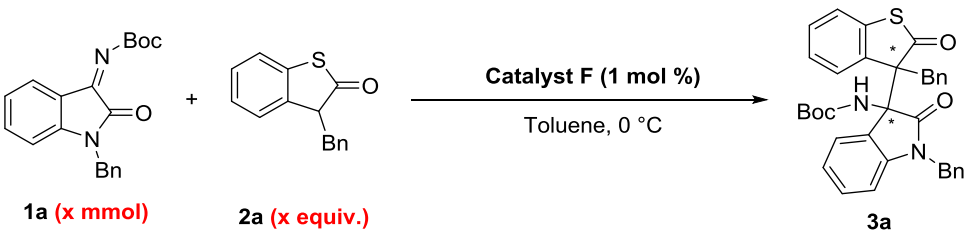
Table 4: Reducing the amount of catalyst



1a 2a 3a

Entry	Cat. (mol%)	Time (h)	Yield (%)	*dr*	*ee* (%)
1	20	2	64	20:1	85
2	10	3	69	20:1	87
3	5	3	68	20:1	87
4	2,5	3	67	20:1	87
5	1,0	4	68	20:1	89
6	0,5	4	62	20:1	83

Table 5: Concentration screening of **1a** and influence amount of **2a**

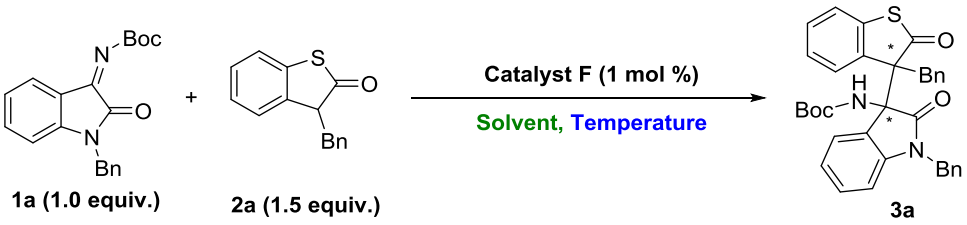


1a (x mmol) **2a** (x equiv.) **3a**

Entry	2a (equiv.)	Time (h)	Yield (%)	*dr*	*ee* (%)
1	1,0	4	68	20:1	89
2	1,2	5	62	20:1	91
3	1,5	5	80	20:1	92

Entry	conc. 1a (mmol)	Time (h)	Yield (%)	*dr*	*ee* (%)
1	0,2	5	78	20:1	90
2	0,1	5	80	20:1	92
3	0,05	7	77	20:1	91
4	0,02	7	79	20:1	91

Table 6: Solvent screening



Entry	Solvent	Temperature (°C)	Time (h)	Yield (%)	*dr*	*ee* (%)
1	toluene	0	5	80	20:1	92
2	$CHCl_3$	0	5	78	20:1	85
3	THF	0	5	76	20:1	27
4	MTBE	0	5	76	20:1	72
5	CH_2Cl_2	0	5	61	20:1	61
6	CH_3CN	0	5	53	20:1	59
7	MeOH	0	5	77	20:1	31
8	DMF	0	6	48	20:1	23
9	toluene	- 25	8	81	20:1	93
10	$CHCl_3$	- 25	8	73	20:1	93
11	THF	- 25	8	29	20:1	41
12	MTBE	- 25	8	69	20:1	88
13	MeOH	- 25	8	95	20:1	35

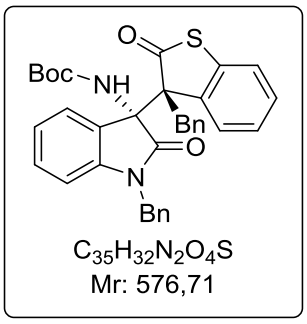
4 The Enantioselective Addition of α-Substituted Benzo[b]thiofen-2(3H)-ones to Isatine-Derived Ketimines

4.1 General procedure

In a Schlenk flask, Benzo[b]thiophen-2(3H)-ones **2a-h** (0.15 mmol, 1.5 equiv.) and chiral catalyst Soós's with CD (0.001 mmol, 1 mol%) were placed. After an injection of toluene (0.5 mL) reaction mixture was cold to -25 °C. Then ketamine **1a-k** (0.10 mmol, 1.0 equiv.) was added in 0.5 mL of toluene at -25 °C. After that the mixture was stirred until complete disappearance of the ketamine (monitored by TLC and ^{1}H NMR), the mixture was purified by flash chromatography (silica gel, hexane/ethyl acetate) and afforded the resulting product as described below.

4.2 Characterization data for new compounds 3a-u

***tert*-Butyl ((*R*)-*N*-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3a)**

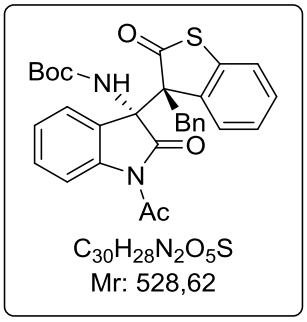


Adduct **3a** was prepared from 33.6 mg (0.10 mmol, 1.0 equiv) ketimine **1a** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2a** 36.0 mg (0.15 mmol, 1.5 equiv). Product **3a** was obtained as light yellow foam in 82% yield (47.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 7.2 Hz, 1H), 7.44 (s, 1H), 7.32 (td, *J* = 7.8 Hz, *J'* = 1.2 Hz, 1H), 7.23 – 7.03 (m, 7H), 7.02 – 6.95 (m, 2H), 6.79 (td, *J* = 7.8 Hz, *J'* = 1.2 Hz, 1H), 6.72 – 6.68 (m, 2H), 6.67 – 6.63 (m, 2H), 6.56 (d, *J* = 7.7 Hz, 1H), 5.91 (d, *J* = 7.8 Hz, 1H), 4.75 (d, *J* = 15.8 Hz, 1H), 4.32 (d, *J* = 15.8 Hz, 1H), 3.87 (d, *J* = 12.8 Hz, 1H), 3.43 (d, *J* = 12.8 Hz, 1H), 1.31 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.8, 174.7, 154.5, 144.7, 137.0, 135.3, 133.8, 133.2, 130.5 (2C), 129.9, 129.4, 128.5 (2C), 127.8 (2C), 127.1, 127.0 (2C), 126.9, 126.9, 126.3, 125.4, 124.7, 122.8, 122.4, 109.6, 80.5, 67.8, 64.5, 44.3, 40.1, 28.1 (3C) ppm. **[α]**$_D^{rt}$ = +121.6 ° (c = 0.51 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3360, 3064, 3031, 2977, 2923, 2851, 1718, 1685, 1613, 1494, 1464, 1362, 1278, 1257, 1165, 1105. **HRMS** (ESI) m/z calcd for $C_{35}H_{32}N_2O_4S$ $[M + Na]^+$ = 599.1975,

found: 599.1984. **HPLC analysis** *ee* = 93 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 7.141 min, t_{major} = 29.166 min.

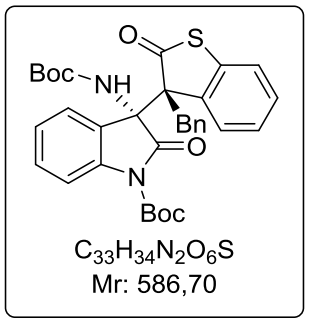
tert-Butyl ((_R_)-_N_-1-acetyl-3-((_R_)-3-benzyl-2-oxo-2,3-dihydrobenzo[_b_]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3b)



Adduct **3b** was prepared from 28.8 mg (0.10 mmol, 1.0 equiv) ketimine **1b** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2a** 36.0 mg (0.15 mmol, 1.5 equiv). Product **3b** was obtained as light yellow foam in 75% yield (39.6 mg). Product **3b** was obtained as mixture of diastereoisomers, *dr* = 12:1.

Major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.51 (td, *J* = 8.0 Hz, *J'* = 1.3 Hz, 1H), 7.37 (td, *J* = 7.5 Hz, *J'* = 0.9 Hz, 1H), 7.32 (s, 1H), 7.21 (td, *J* = 7.7 Hz, *J'* = 1.1 Hz, 1H), 7.15 – 7.04 (m, 2H), 7.03 – 6.96 (m, 2H), 6.93 (td, *J* = 7.7 Hz, *J'* = 1.2 Hz, 1H), 6.67 (d, *J* = 7.2 Hz, 2H), 5.97 (d, *J* = 7.8 Hz, 1H), 3.74 (d, *J* = 12.9 Hz, 1H), 3.37 (d, *J* = 12.9 Hz, 1H), 2.16 (s, 3H), 1.28 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.0, 175.4, 169.4, 141.6, 136.3, 132.9, 132.7, 130.5, 130.5 (2C), 130.3, 130.0, 127.9 (2C), 127.9, 127.1, 126.1, 125.7, 125.0, 124.4, 122.6, 116.9, 81.2, 68.4, 65.0, 39.2, 28.0 (3C), 25.5 ppm. **Mixture of diastereoisomers: $[\alpha]_D^{rt}$** = +40.0 ° (c = 055 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3372, 3061, 3034, 2980, 2929, 2848, 1772, 1688, 1604, 1473, 1371, 1335, 1305, 1278, 1248, 1168, 1105. **HRMS** (ESI) m/z calcd for $C_{35}H_{32}N_2O_4S$ $[M + Na]^+$ = 551.1611, found: 551.1608. **HPLC analysis:** major diastereoisomer: *ee* = 72 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 6.716 min, t_{major} = 20.412 min, minor diastereoisomer: *ee* = 69 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 7.961 min, t_{major} = 10.864 min.

***tert*-Butyl 3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-3-((*R*)-(*tert*-butoxycarbonyl)amino)-2-oxoindolin-*N*-1-carboxylate (3c)**

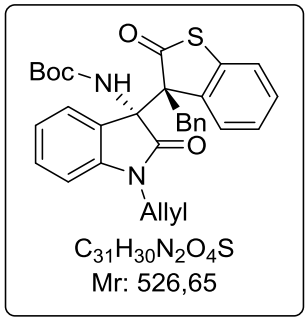


$C_{33}H_{34}N_2O_6S$
Mr: 586,70

Adduct **3c** was prepared from 34.6 mg (0.10 mmol, 1.0 equiv) ketimine **1c** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2a** 36.0 mg (0.15 mmol, 1.5 equiv). Product **3c** was obtained as light yellow foam in 98% yield (57.2 mg). Product **3c** was obtained as mixture of diastereoisomers, *dr* = 2:1.

Major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 – 7.44 (m, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.22 (m, 2H), 7.14 – 6.88 (m, 7H), 6.81 – 6.72 (m, 2H), 6.67 (d, *J* = 7.1 Hz, 1H), 3.91 (d, *J* = 13.9 Hz, 1H), 3.74 (d, *J* = 13.8 Hz, 1H) 1.69 (s, 9H), 1.37 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 209.7, 172.3, 154.2, 148.4, 141.2, 139.0, 134.0, 133.0, 130.4 (2C), 129.6, 129.3, 127.7 (2C), 126.6, 125.8, 125.3, 124.1, 123.7, 122.5, 122.4, 115.3, 84.3, 83.4, 67.0, 64.9, 36.7, 28.1 (3C), 27.7 (3C) ppm. **Minor diastereoisomer: ^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.35 – 7.22 (m, 2H), 7.18 (td, *J* = 7.7 Hz, *J'* = 1.1 Hz, 1H), 7.14 – 6.88 (m, 5H), 6.81 – 6.72 (m, 2H), 5.95 (d, *J* = 7.8 Hz, 1H), 3.72 (d, *J* = 12.9 Hz, 1H), 3.33 (d, *J* = 12.9 Hz, 1H), 1.27 (s, 9H), 1.09 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.0, 171.3, 153.9, 147.9, 136.5, 135.4, 133.2, 132.7, 130.4 (2C), 130.0, 129.5, 127.8 (2C), 126.9, 126.0, 125.5, 125.2, 124.4, 123.0, 122.6, 114.3, 80.9, 80.6, 68.3, 64.7, 38.9, 28.0 (3C), 27.7 (3C) ppm. **Mixture of diastereoisomers: $[\alpha]_D^{rt}$** = +56.0 ° (c = 0.63 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3381, 2980, 2929, 1802, 1778, 1724, 1679, 1607, 1482, 1470, 1371, 1347, 1293, 1248, 1147, 1099. **HRMS** (ESI) m/z calcd for $C_{35}H_{32}N_2O_4S$ $[M + Na]^+$ = 609.2030, found: 609.2028. **HPLC analysis:** major diastereoisomer: *ee* = 86 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 95:5, 15 °C, 1.0 mL/min, λ = 190 nm, retention time: t_{major} = 97.728 min, t_{minor} = 33.596 min, minor diastereoisomer: *ee* = 82 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 95:5, 15 °C, 1.0 mL/min, λ = 190 nm, retention time: t_{major} = 46.907 min, t_{minor} = 30.019 min.

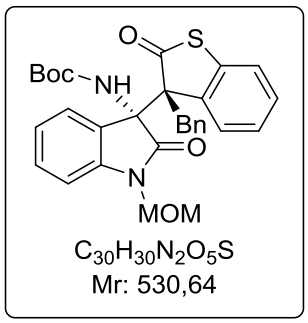
***tert*-Butyl ((*R*)-*N*-1-allyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3d)**



Adduct **3d** was prepared from 28.6 mg (0.10 mmol, 1.0 equiv) ketimine **1d** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2a** 36.0 mg (0.15 mmol, 1.5 equiv). Product **3d** was obtained as light yellow foam in 81% yield (41.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (d, *J* = 7.3 Hz, 1H), 7.41 (td, *J* = 7.8 Hz, *J'* = 1.2 Hz, 1H), 7.32 (s, 1H), 7.23 – 7.15 (m, 2H), 7.09 – 7.02 (m, 2H), 7.01 – 6.95 (m, 2H), 6.85 (td, *J* = 7.7 Hz, *J'* = 1.2 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.69 – 6.64 (m, 2H), 5.89 (d, *J* = 7.8 Hz, 1H), 4.97 – 4.79 (m, 3H), 4.20 (dd, *J* = 16.2 Hz, *J'* = 3.0 Hz, 1H), 3.82 (d, *J* = 12.9 Hz, 1H), 3.67 (dd, *J* = 15.9 Hz, *J'* = 4.9 Hz, 1H), 3.39 (d, *J* = 12.9 Hz, 1H), 1.29 (s, 9H) ppm. **^{13}C NMR** (101 MHz, CDCl3) δ = 208.7, 173.7, 154.3, 144.4, 137.0, 133.8, 133.3, 131.3, 130.5 (2C), 129.8, 129.2, 127.8 (2C), 126.9, 126.6, 126.2, 125.2, 124.7, 122.8, 122.3, 117.6, 109.3, 80.5, 68.0, 64.6, 42.5, 39.7, 28.1 (3C) ppm. **[α]**$_D^{rt}$ = +114.0 ° (c = 0.61 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3363, 3064, 3031, 3010, 2977, 2920, 2854, 1718, 1682, 1616, 1488, 1470, 1359, 1275, 1254, 1162, 1102. **HRMS** (ESI) m/z calcd for $C_{35}H_{32}N_2O_4S$ [M + Na]$^+$ = 549.1818, found: 549.1820. **HPLC analysis** *ee* = 95 %, (Daicel Chiracel) AD culumn, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 5.380 min, t_{major} = 11.261 min.

***tert*-Butyl (3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)- (*R*)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3e)**

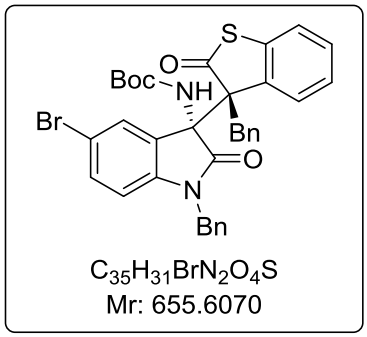


Adduct **3e** was prepared from 29.0 mg (0.10 mmol, 1.0 equiv) ketimine **1e** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2a** 36.0 mg (0.15 mmol, 1.5 equiv). Product **3e** was obtained as light yellow foam in 82% yield (43.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 7.4 Hz, 1H), 7.46 (td, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.42 (s, 1H), 7.29 – 7.22 (m, 1H), 7.16 (td, *J* = 7.7 Hz, 1.2 Hz, 1H), 7.09 – 7.03 (m, 2H), 7.02 – 6.87 (m, 4H), 6.72 – 6.59 (m, 2H), 5.94 (d, *J* = 7.8 Hz, 1H), 4.70 (s, 2H), 3.82 (d, *J* = 12.8 Hz, 1H), 3.41 (d, *J* = 12.8 Hz, 1H), 2.77 (s, 3H), 1.30 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.7, 175.0, 154.4, 143.8, 136.9, 133.8, 133.1, 130.5 (2C), 130.2, 129.5, 127.8 (2C), 127.0, 126.3, 126.2, 125.3, 124.8, 122.9, 122.7,

110.0, 80.6, 71.7, 68.2, 64.4, 55.9, 39.9, 28.1 (3C) ppm. **[α]**$_D^{rt}$ = +96.6 ° (c = 0.60 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3357, 3064, 3031, 2980, 2929, 1718, 1691, 1616, 1491, 1461, 1350, 1278, 1245, 1165, 1120. **HRMS** (ESI) m/z calcd for $C_{35}H_{32}N_2O_4S$ [M + Na]$^+$ = 553.1768, found: 553.1765. **HPLC analysis** *ee* = 95 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 5.149 min, t_{major} = 9.379 min.

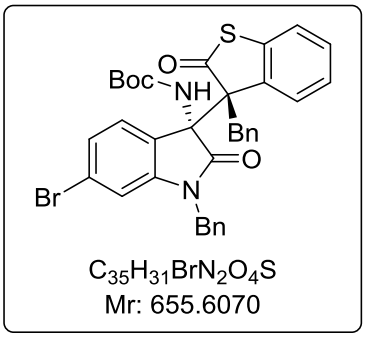
***tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-5-bromo-2-oxoindolin-3-yl)carbamate (3h)**



Adduct **3h** was prepared from 39.4 mg (0.10 mmol, 1.0 equiv) ketimine **1h** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2a** 36.0 mg (0.15 mmol, 1.5 equiv). Product **3h** was obtained as light yellow foam in 63% yield (41.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 16.8 Hz, 1H), 7.43 (dd, J = 8.4 Hz, *J'* = 1.9 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.20 – 7.04 (m, 5H), 7.00 (m, 2H), 6.87 (td, *J* = 7.8 Hz, *J'* = 1.0 Hz, 1H), 6.74 – 6.60 (m, 4H), 6.43 (d, *J* = 8.3 Hz, 1H), 6.04 (d, *J* = 7.7 Hz, 1H), 4.68 (d, *J* = 15.9 Hz, 1H), 4.34 (d, *J* = 15.8 Hz, 1H), 3.82 (d, *J* = 12.8 Hz, 1H), 3.38 (d, *J* = 12.8 Hz, 1H), 1.35 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 208.3, 174.3, 154.5, 143.8, 137.0, 134.8, 133.5, 132.9, 132.7, 130.5 (2C), 129.6, 129.0, 128.6 (2C), 127.9 (2C), 127.7, 127.3, 127.06, 127.0 (2C), 126.1, 125.5, 123.0, 115.1, 111.0, 80.9, 67.7, 64.2, 44.4, 40.0, 28.2 (3C) ppm. **[α]**$_D^{rt}$ = +129.5 ° (c = 0.56 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3360, 3064, 3028, 2980, 2926, 2857, 1724, 1685, 1610, 1479, 1452, 1425, 1344, 1278, 1254, 1162, 1114. **HRMS** (ESI) m/z calcd for $C_{35}H_{32}N_2O_4NaS$ [M + Na]$^+$ = 677.1080, found: 677.1080. **HPLC analysis** *ee* = 90 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 5.775 min, t_{major} = 17.036 min.

***tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-6-bromo-2-oxoindolin-3-yl)carbamate (3i)**

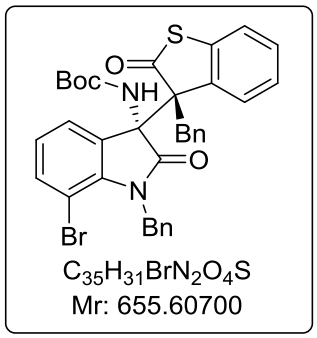


$C_{35}H_{31}BrN_2O_4S$
Mr: 655.6070

Adduct **3i** was prepared from 39.4 mg (0.10 mmol, 1.0 equiv) ketimine **1i** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2a** 36.0 mg (0.15 mmol, 1.5 equiv). Product **3i** was obtained as light yellow foam in 46% yield (30.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (d, *J* = 5.6 Hz, 1H), 7.41 (s, 1H), 7.32 (dd, *J* = 7.9 Hz, *J'* = 1.6 Hz, 1H), 7.22 (td, *J* = 7.7 Hz, *J'* = 1.2 Hz, 1H), 7.18 – 7.02 (m, 5H), 6.98 (t, *J* = 7.4 Hz, 2H), 6.88 (td, *J* = 7.8 Hz, *J'* = 1.1 Hz, 1H), 6.72 – 6.58 (m, 5H), 6.05 (d, *J* = 7.8 Hz, 1H), 4.71 (d, *J* = 15.9 Hz, 1H), 4.29 (d, *J* = 15.9 Hz, 1H), 3.82 (d, *J* = 12.8 Hz, 1H), 3.35 (d, *J* = 12.8 Hz, 1H), 1.33 (s, 9H). ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.5, 174.7, 154.5, 146.1, 136.9, 134.7, 133.5, 132.9, 130.5 (2C), 129.6, 128.7 (2C), 127.9 (2C), 127.3, 127.0, 126.9 (2C), 126.1, 125.9, 125.8, 125.6, 125.4, 123.6, 123.0, 112.9, 80.8, 67.5, 64.2, 44.4, 40.0, 28.2 (3C) ppm. $[\alpha]_D^{rt}$ = +136.9 ° (c = 0.84 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3357, 3064, 3034, 2980, 2932, 2857, 1715, 1685, 1601, 1488, 1452, 1434, 1368, 1350, 1281, 1257, 1165, 1102. **HRMS** (ESI) m/z calcd for $C_{35}H_{31}O_4N_2BrNaS$ [M + Na]$^+$ = 677.1080, found: 677.1082. **HPLC analysis** *ee* = 91 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 5.330 min, t_{major} = 15.654 min.

***tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-7-bromo-2-oxoindolin-3-yl)carbamate (3j)**



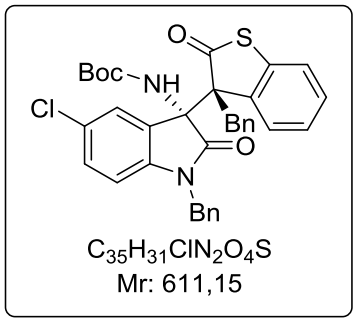
$C_{35}H_{31}BrN_2O_4S$
Mr: 655.60700

Adduct **3j** was prepared from 39.4 mg (0.10 mmol, 1.0 equiv) ketimine **1j** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2a** 36.0 mg (0.15 mmol, 1.5 equiv). Product **3j** was obtained as light yellow foam in 67% yield (43.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 – 7.50 (m, 2H), 7.43 (s, 1H), 7.29 (td, *J* = 7.7 Hz, 1.2 Hz, 1H), 7.15 – 7.04 (m, 6H), 7.04 – 6.96 (m, 3H), 6.77 – 6.69 (m, 2H), 6.68 – 6.61 (m, 2H), 5.95 (d, *J* = 7.8 Hz, 1H), 4.98 – 4.80 (m, 2H), 3.81 (d, *J* = 12.8 Hz, 1H), 3.35 (d, *J* = 12.8 Hz, 1H), 1.36 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.4, 175.7, 154.6, 142.3, 137.1, 137.0, 135.7, 133.4, 133.0, 130.5 (2C), 130.3, 129.8, 128.1 (2C), 127.9 (2C), 127.0, 126.4, 126.1 (2C), 126.0, 125.4, 123.6, 123.4,

123.0, 103.1, 80.9, 67.3, 64.5, 45.3, 39.6, 28.1 (3C) ppm. $[\alpha]_D^{rt}$ = +66.3 ° (c = 0.95 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3375, 3354, 3067, 3031, 2974, 2929, 1736, 1718, 1682, 1607, 1583, 1494, 1452, 1392, 1371, 1356, 1275, 1257, 1219, 1168, 1114. **HRMS** (ESI) m/z calcd for $C_{35}H_{31}O_4N_2BrNaS$ $[M + Na]^+$ = 677.1080, found: 677.1083. **HPLC analysis** *ee* = 89 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 6.433 min, t_{major} = 22.043 min.

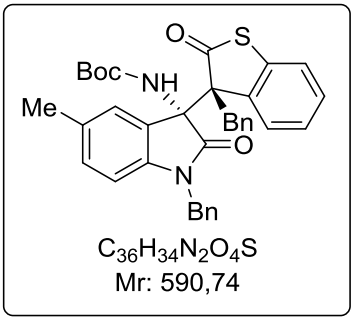
tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-5-chloro-2-oxoindolin-3-yl)carbamate (3k)



Adduct **3k** was prepared from 37.1 mg (0.10 mmol, 1.0 equiv) ketimine **1k** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2a** 36.0 mg (0.15 mmol, 1.5 equiv). Product **3k** was obtained as light yellow foam in 67% yield (41.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (s, 1H), 7.44 (s, 1H), 7.28 (dd, *J* = 8.4 Hz, *J'* = 2.1 Hz, 1H), 7.23 (td, *J* = 7.7 Hz, *J'* = 0.8 Hz, 1H), 7.20 – 7.04 (m, 5H), 7.00 (t, *J* = 7.5 Hz, 2H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.70 (d, *J* = 7.0 Hz, 2H), 6.66 (d, *J* = 7.4 Hz, 2H), 6.47 (d, *J* = 8.4 Hz, 1H), 6.04 (d, *J* = 7.8 Hz, 1H), 4.68 (d, *J* = 15.9 Hz, 1H), 4.34 (d, *J* = 15.8 Hz, 1H), 3.83 (d, *J* = 12.8 Hz, 1H), 3.38 (d, *J* = 12.8 Hz, 1H), 1.35 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 208.4, 174.4, 154.5, 143.3, 137.0, 134.8, 133.5, 132.9, 130.5 (2C), 129.8, 129.7, 129.6, 128.6 (2C), 127.9, 127.9 (2C), 127.3, 127.1, 126.9 (2C), 126.1, 125.5, 125.0, 123.0, 110.5, 80.9, 67.8, 64.2, 44.4, 40.0, 28.2 (3C) ppm. $[\alpha]_D^{rt}$ = +119.7 ° (c = 0.64 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3360, 3067, 3037, 2974, 2923, 2851, 1727, 1682, 1610, 1482, 1455, 1428, 1365, 1281, 1257, 1162, 1096. **HRMS** (ESI) m/z calcd for $C_{35}H_{32}N_2O_4S$ $[M + Na]^+$ = 633.1585, found: 633.1586. **HPLC analysis** *ee* = 89 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 5.718 min, t_{major} = 17.727 min.

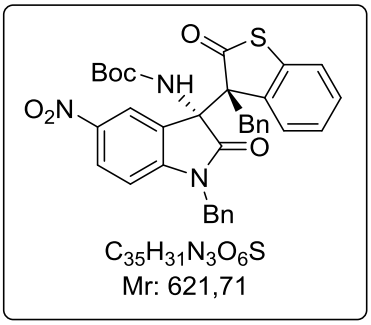
***tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl) 5-methyl-2-oxoindolin-3-yl)carbamate (3l)**



Adduct **3l** was prepared from 35.0 mg (0.10 mmol, 1.0 equiv) ketimine **1l** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2a** 36.0 mg (0.15 mmol, 1.5 equiv). Product **3l** was obtained as light yellow foam in 78% yield (45.8mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.41 (d, J = 16.2 Hz, 2H), 7.19 (td, *J* = 7.7 Hz, *J'* = 1.2 Hz, 1H), 7.16 – 7.04 (m, 6H), 7.02 – 6.96 (m, 2H), 6.81 (td, *J* = 7.8 Hz, *J'* = 1.2 Hz, 1H), 6.71 (d, *J* = 6.5 Hz, 2H), 6.66 (d, *J* = 7.1 Hz, 2H), 6.44 (d, *J* = 8.0 Hz, 1H), 5.94 (d, *J* = 7.8 Hz, 1H), 4.67 (d, *J* = 15.8 Hz, 1H), 4.32 (d, *J* = 15.8 Hz, 1H), 3.84 (d, *J* = 12.8 Hz, 1H), 3.43 (d, *J* = 12.8 Hz, 1H), 2.42 (s, 3H), 1.32 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.9, 174.6, 154.5, 142.3, 137.0, 135.4, 133.9, 133.3, 131.9, 130.5 (2C), 130.3, 129.4, 128.5 (2C), 127.8 (2C), 127.1, 127.0 (2C), 126.9, 126.8, 126.4, 125.5, 125.3, 122.8, 109.4, 80.5, 67.9, 64.5, 44.3, 40.1, 28.2 (3C), 21.4 ppm. **[α]**$_D^{rt}$ = +121.4 ° (c = 0.56 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3360, 3067, 3034, 2980, 2923, 2851, 1718, 1688, 1622, 1601, 1500, 1452, 1371, 1281, 1245, 1159, 1099. **HRMS** (ESI) m/z calcd for $C_{35}H_{32}N_2O_4S$ [M + Na]$^+$ = 613.2131, found: 613.2137. **HPLC analysis** *ee* = 95 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 5.376 min, t_{major} = 21.0305 min.

***tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-5-nitro-2-oxoindolin-3-yl)carbamate (3m)**

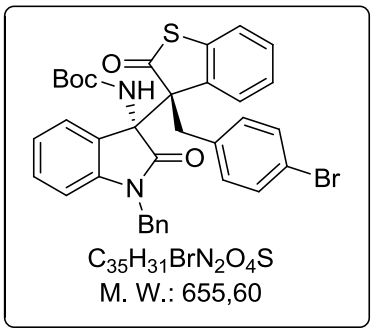


Adduct **3m** was prepared from 38.1 mg (0.10 mmol, 1.0 equiv) ketimine **1m** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2a** 36.0 mg (0.15 mmol, 1.5 equiv). Product **3m** was obtained as light yellow foam in 98 % yield (61.6 mg). Product **3m** was obtained as mixture of diastereoisomers, *dr* = 2:1.

Major diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ = δ 8.15 (d, *J* = 2.2 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.50 (s, 1H), 7.46 (d, *J* = 6.7 Hz, 2H), 7.41 – 7.30 (m, 2H), 7.29 – 7.11 (m, 3H), 7.11 – 6.96 (m, 3H), 6.82 – 6.72 (m, 3H), 6.71 – 6.62 (m, 1H), 6.40 (d, *J* = 8.1 Hz, 1H), 5.32 (d, *J* = 15.4 Hz, 1H), 4.62 (d, *J* = 15.5 Hz, 1H), 4.03 (d, *J* = 13.9 Hz, 1H), 3.78 (d, *J* = 13.9 Hz, 1H), 1.41 (s, 9H) ppm. **^{13}C NMR** (600 MHz, $CDCl_3$) δ =

209.1, 173.6, 153.8, 148.3, 142.7, 135.2, 134.1, 134.0, 132.4, 130.5 (3C), 129.4, 128.8 (2C), 128.0, 127.8 (3C), 126.9, 126.8, 126.3, 125.9, 125.5, 122.7, 118.4, 108.0, 81.2, 66.1, 64.3, 44.8, 36.6, 28.2 (3C) ppm. **Minor diastereoisomer:** **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.42 (s, 1H), 8.27 (dd, *J* = 8.7 Hz, *J'* = 2.2 Hz, 1H), 7.41 – 7.30 (m, 2H), 7.29 – 7.11 (m, 3H), 7.11 – 6.96 (m, 4H), 6.96 – 6.85 (m, 2H), 6.82 – 6.72 (m, 3H), 6.71 – 6.62 (m, 1H), 6.09 (s, 1H), 4.72 (d, *J* = 15.9 Hz, 1H), 4.47 (d, *J* = 15.9 Hz, 1H), 3.92 (d, *J* = 12.8 Hz, 1H), 3.40 (d, *J* = 12.8 Hz, 1H), 1.37 (s, 9H) ppm. **^{13}C NMR** (600 MHz, $CDCl_3$) δ = 207.8, 175.1, 154.6, 150.2, 143.1, 137.0, 133.7, 133.0, 132.8, 130.4 (3C), 129.9, 128.7 (2C), 127.9 (3C), 127.7, 127.6, 127.1, 126.8, 125.7, 125.6, 123.3, 120.0, 109.1, 81.3, 67.2, 64.1, 44.6, 39.9, 28.1 (3C) ppm. **Mixture of diastereoisomers:** **$[\alpha]_D^{rt}$** = +51.2 ° (c = 0.63 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3384, 3067, 3034, 2974, 2932, 1736, 1718, 1685, 1613, 1601, 1521, 1488, 1452, 1392, 1368, 1335, 1275, 1251, 1162, 1102. **HRMS** (ESI) m/z calcd for $C_{35}H_{32}N_2O_4S$ $[M + Na]^+$ = 644.1825, found: 644.1831. **HPLC analysis:** major diastereoisomer: *ee* = 23 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 250 nm, retention time: t_{major} = 10.589 min, t_{minor} = 13.466 min. *ee* = 17 %, minor diastereoisomer: *ee* = 99 % (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 250 nm, retention time: t_{major} = 18.539 min, t_{minor} = 28.616 min.

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(4-bromobenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3n)



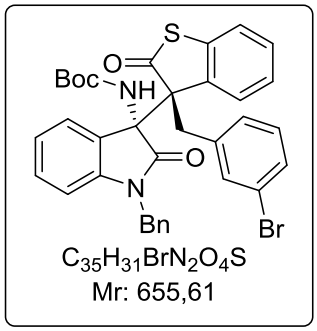
$C_{35}H_{31}BrN_2O_4S$
M. W.: 655,60

Adduct **3n** was prepared from 33.6 mg (0.10 mmol, 1.0 equiv) ketimine **1a** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2d** 47.9 mg (0.15 mmol, 1.5 equiv). Product **3n** was obtained as light yellow foam in 80% yield (52,5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (d, *J* = 7.3 Hz, 1H), 7.38 (s, 1H), 7.32 (td, *J* = 7.8 Hz, *J'* = 1.0 Hz, 1H), 7.24 – 7.07 (m, 8H), 6.79 (td, *J* = 7.9 Hz, *J'* = 1.0 Hz, 1H), 6.69 (d, *J* = 6.9 Hz, 2H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 2H), 5.88 (d, *J* = 7.8 Hz, 1H), 4.74 (d, *J* = 15.8 Hz, 1H), 4.32 (d, *J* = 15.8 Hz, 1H), 3.82 (d, *J* = 12.9 Hz, 1H), 3.36 (d, *J* = 12.9 Hz, 1H), 1.30 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.7, 174.6, 154.4, 144.7, 136.9, 135.2, 133.4, 132.3, 132.1 (2C), 130.9 (2C), 130.0, 129.6, 128.5 (2C), 127.1, 127.0 (2C), 126.7, 126.1, 125.5, 124.6, 123.0, 122.4, 121.3, 109.7, 80.6, 67.7, 64.3, 44.3, 39.4, 28.1 (3C) ppm. **$[\alpha]_D^{rt}$** = +100.4 ° (c = 1.23 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3381, 3061, 3028, 3010, 2977, 2929, 1721, 1685, 1613, 1491, 1467, 1371,

1275, 1251, 1159, 1102. **HRMS** (ESI) m/z calcd for $C_{35}H_{31}O_4N_2BrNaS$ $[M + Na]^+$ = 677.1080, found: 677.1082. **HPLC analysis** *ee* = 92 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 8.235 min, t_{major} = 48.960 min.

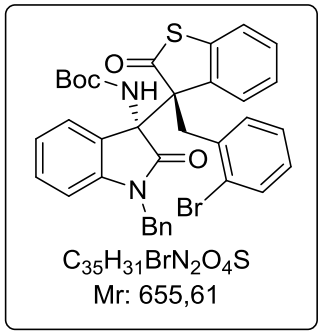
tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(3-bromobenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3o)



Adduct **3o** was prepared from 33.6 mg (0.10 mmol, 1.0 equiv) ketimine **1a** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2c** 47.9 mg (0.15 mmol, 1.5 equiv). Product **3o** was obtained as light yellow foam in 81 % yield (53.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 7.3 Hz, 1H), 7.40 (s, 1H), 7.34 (td, *J* = 7.8 Hz, *J'*= 1.2 Hz, 1H), 7.27 – 7.10 (m, 7H), 6.90 (t, *J* = 7.9 Hz, 1H), 6.84 (td, *J* = 7.8 Hz, *J'*= 1.2 Hz, 1H), 6.76 – 6.66 (m, 4H), 6.59 (d, *J* = 7.7 Hz, 1H), 5.91 (d, *J* = 7.8 Hz, 1H), 4.77 (d, *J* = 15.8 Hz, 1H), 4.34 (d, *J* = 15.8 Hz, 1H), 3.84 (d, *J* = 12.9 Hz, 1H), 3.40 (d, *J* = 12.9 Hz, 1H), 1.32 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.6, 174.6, 154.4, 144.7, 136.9, 135.6, 135.2, 133.4, 133.3, 130.1, 130.0, 129.7, 129.3, 129.2, 128.5 (2C), 127.1, 127.0 (2C), 126.7, 126.2, 125.6, 124.6, 123.0, 122.5, 121.7, 109.7, 80.6, 67.7, 64.3, 44.3, 39.6, 28.1 (3C) ppm. **[α]**$_D^{rt}$ = +108.1 ° (c = 1.18 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3363, 3067, 3028, 3004, 2977, 2929, 2854, 1718, 1688, 1613, 1568, 1488, 1470, 1365, 1281, 1251, 1180, 1162, 1102. **HRMS** (ESI) m/z calcd for $C_{35}H_{31}O_4N_2BrNaS$ $[M + Na]^+$ = 677.1080, found: 677.1081. **HPLC analysis** *ee* = 92 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 8.117 min, t_{major} = 42.897 min.

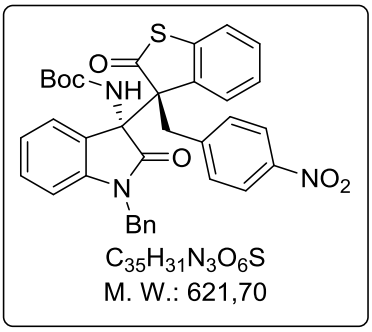
tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(2-bromobenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3p)



Adduct **3p** was prepared from 33.6 mg (0.10 mmol, 1.0 equiv) ketimine **1a** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2b** 47.9 mg (0.15 mmol, 1.5 equiv). Product **3p** was obtained as light yellow foam in 43 % yield (28,0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 7.3 Hz, 1H), 7.40 – 7.28 (m, 3H), 7.24 – 7.07 (m, 6H), 6.95 – 6.87 (m, 2H), 6.77 – 6.63 (m, 4H), 6.54 (d, *J* = 7.7 Hz, 1H), 6.01 (d, *J* = 7.8 Hz, 1H), 4.72 (d, *J* = 15.8 Hz, 1H), 4.33 (d, *J* = 15.8 Hz, 1H), 4.19 (d, *J* = 13.9 Hz, 1H), 3.85 (d, *J* = 14.0 Hz, 1H), 1.30 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.4, 174.5, 154.4, 144.7, 136.4, 135.3, 133.9, 133.4, 133.1, 130.0, 129.9, 129.5, 128.6, 128.5 (3C), 127.1, 127.0 (2C), 126.8, 126.7, 126.1, 125.3, 124.9, 122.6, 122.5, 109.5, 80.5, 68.2, 64.5, 44.3, 38.5, 28.1 (3C) ppm. **[α]**$_D^{rt}$ = +56.7 ° (c = 0.67 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3366, 3064, 3007, 2983, 2926, 2857, 1718, 1691, 1610, 1491, 1464, 1371, 1278, 1251, 1165, 1102. **HRMS** (ESI) m/z calcd for $C_{35}H_{31}O_4N_2BrNaS$ $[M + Na]^+$ = 677.1080, found: 677.1078. **HPLC analysis** *ee* = 80 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 210 nm, retention time: t_{major} = 17.036 min, t_{minor} = 5.775 min.

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(4-nitrobenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3q)

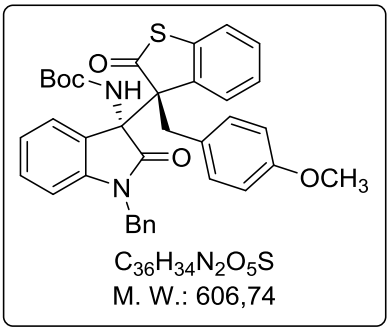


Adduct **3q** was prepared from 33.6 mg (0.10 mmol, 1.0 equiv) ketimine **1a** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2e** 43.0 mg (0.15 mmol, 1.5 equiv). Product **3q** was obtained as light yellow foam in 91% yield (56.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 – 7.82 (m, 2H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.25 – 7.08 (m, 6H), 6.87 – 6.79 (m, 3H), 6.71 (d, *J* = 6.9 Hz, 2H), 6.59 (d, *J* = 7.8 Hz, 1H), 5.92 (d, *J* = 7.8 Hz, 1H), 4.74 (d, *J* = 15.8 Hz, 1H), 4.33 (d, *J* = 15.8 Hz, 1H), 3.97 (d, *J* = 12.7 Hz, 1H), 3.50 (d, *J* = 12.7 Hz, 1H), 1.30 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.3, 174.4, 154.4, 147.0, 144.7, 141.1, 136.6, 135.1, 133.0, 131.3 (2C), 130.2, 129.9, 128.5 (2C), 127.2, 127.0 (2C), 126.5, 126.1, 125.7, 124.5, 123.2, 122.9 (2C), 122.5, 109.8, 80.7, 67.7, 64.3, 44.3, 39.7, 28.1 (3C) ppm. **[α]**$_D^{rt}$ = + 145.9 ° (c = 0.98 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3360, 3061, 3007, 2980, 2929, 2851, 1721, 1688, 1607, 1521, 1491, 1344, 1281, 1260, 1165, 1105. **HRMS** (ESI) m/z calcd

for $C_{35}H_{31}O_6N_3NaS$ $[M + Na]^+$ = 644.1826, found: 644.1822. **HPLC analysis** *ee* = 93 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 207 nm, retention time: t_{minor} = 10.458 min, t_{major} = 13.636 min.

***tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(4-methoxybenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3r)**

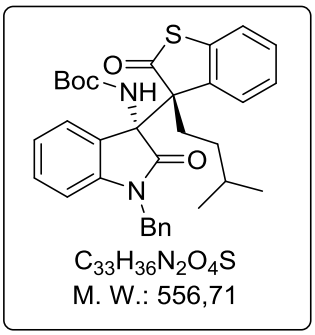


$C_{36}H_{34}N_2O_5S$
M. W.: 606,74

Adduct **3r** was prepared from 33.6 mg (0.10 mmol, 1.0 equiv) ketimine **1a** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2f** 40.6 mg (0.15 mmol, 1.5 equiv). Product **3r** was obtained as light yellow foam in 66 % yield (39.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, J = 7.2 Hz, 1H), 7.43 (s, 1H), 7.31 (td, *J* = 7.7 Hz, *J'* = 1.2 Hz, 1H), 7.23 – 7.07 (m, 6H), 6.79 (td, *J* = 7.8 Hz, *J'* = 1.2 Hz, 1H), 6.69 (d, *J* = 6.7 Hz, 2H), 6.61 – 6.48 (m, 5H), 5.90 (d, *J* = 7.8 Hz, 1H), 4.75 (d, *J* = 15.8 Hz, 1H), 4.31 (d, *J* = 15.8 Hz, 1H), 3.82 (d, J = 13.0 Hz, 1H), 3.67 (s, 3H), 3.37 (d, *J* = 13.0 Hz, 1H), 1.30 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 209.0, 174.8, 158.4, 154.5, 144.7, 137.0, 135.3, 133.9, 131.5 (2C), 129.9, 129.3, 128.5 (2C), 127.1, 127.0 (2C), 126.9, 126.2, 125.3, 125.0, 124.7, 122.9, 122.4, 113.2 (2C), 109.6, 80.4, 67.7, 64.5, 55.0, 44.3, 39.2, 28.1 (3C) ppm. **[α]**$_D^{rt}$ = +135.6 ° (c = 0.73 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3366, 3064, 3031, 3007, 2977, 2929, 2842, 1721, 1679, 1616, 1515, 1371, 1353, 1254, 1183, 1168, 1102, 1036, 1012. **HRMS** (ESI) m/z calcd for C36 H34 O5 N2 Na S $[M + Na]^+$ = 629.2081, found: 629.2077. **HPLC analysis** *ee* = 96 %, (Daicel Chiracel) ODH column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 190 nm, retention time: t_{minor} = 9.598 min, t_{major} = 12.031 min.

***tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-isopentyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3s)**



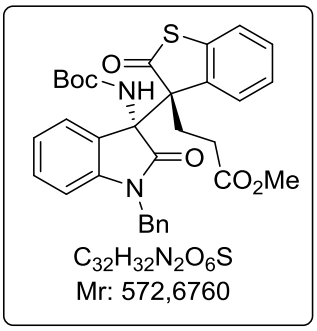
$C_{33}H_{36}N_2O_4S$
M. W.: 556,71

Adduct **3s** was prepared from 33.6 mg (0.10 mmol, 1.0 equiv) ketimine **1a** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2g** 33.0 mg (0.15 mmol, 1.5 equiv). Product **3s** was obtained as light yellow foam in 57% yield (31.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 7.3 Hz, 1H), 7.31 (dd, *J* = 7.8 Hz, *J'*= 1.0 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.19 – 7.08 (m, 4H), 7.05 (s, 1H), 6.74 (td, *J* = 7.7 Hz, *J'*= 1.2 Hz, 1H), 6.69 (d, *J* = 6.5 Hz, 2H), 6.48 (d, *J* = 7.7 Hz, 1H), 5.69 (d, *J* = 7.8 Hz, 1H), 4.71 (d, *J* = 15.8 Hz, 1H), 4.30 (d, *J* = 15.8 Hz, 1H), 2.53 (td, *J* = 12.6 Hz, *J'*= 4.4 Hz, 1H), 2.13 (td, *J* = 12.7 Hz, *J'*= 4.0 Hz, 1H), 1.50 – 1.36 (m, 1H), 1.27 (s, 9H), 1.13 – 0.98 (m, 1H), 0.81 (d, *J* = 6.6 Hz, 3H), 0.72 (d, *J* = 6.6 Hz, 3H), 0.48 – 0.35 (m, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 209.3, 174.8, 154.4, 144.6, 136.7, 135.3, 134.5,

129.7, 129.2, 128.5 (3C), 127.1, 127.0 (2C), 125.7, 125.3, 124.6, 122.9, 122.2, 109.4, 80.4, 68.0, 63.6, 44.3, 32.4, 31.8, 28.2, 28.1 (3C), 22.41, 22.13 ppm. $[\alpha]_D^{rt}$ = +29,5 ° (c = 0,62 in $CHCl_3$). **IR** (KBr): ν = 3369, 3061, 2956, 2929, 2869, 1721, 1679, 1613, 1488, 1467, 1365, 1272, 1254, 1165, 1099 cm^{-1}. **HRMS** (ESI) m/z calcd for $C_{33}H_{36}N_2O_4NaS$ $[M + Na]^+$ = 579.2288, found: 579.2289. **HPLC analysis** *ee* = 91 %, (Daicel Chiracel) AD column, heptan/*iso*-propanol, 80:20, 1.0 mL/min, λ = 207 nm, retention time: t_{minor} = 4.715 min, t_{major} = 13.491 min.

Methyl 3-(3-(1-benzyl-3-((*tert*-butoxycarbonyl)amino)-2-oxoindolin-3-yl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)propanoate (3t)

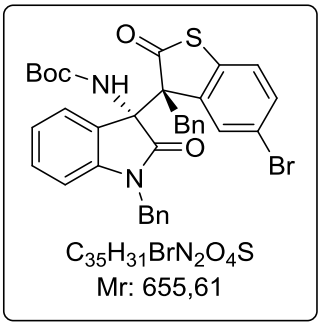


Adduct **3t** was prepared from 33.6 mg (0.10 mmol, 1.0 equiv) ketimine **1a** and Benzo[b]thiophen-2(3H)-one **2h** 35.4 mg (0.15 mmol, 1.5 equiv). Product **3t** was obtained as light yellow foam in 98% yield (56.1 mg). Product **3t** was obtained as mixture of diastereoisomers, *dr* = 3:2.

Major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 – 7.35 (m, 2H), 7.35 – 7.19 (m, 3H), 7.18 – 6.90 (m, 4H), 6.74 (tt, *J* = 6.4 Hz, *J'*= 3.2 Hz, 1H), 6.68 (d, *J* = 6.7 Hz, 2H), 6.49 (d, *J* = 7.7 Hz, 1H), 5.72 (d, *J* = 7.8 Hz, 1H), 4.71 (d, *J* = 15.9 Hz, 1H), 4.30 (d, *J* = 15.9 Hz, 1H), 3.55 (s, 3H), 2.87 (ddd, *J* = 13.2 Hz, *J'*= 12.1 Hz, *J''* = 4.8 Hz, 1H), 2.60 – 2.44 (m, 1H), 2.27 – 2.11 (m, 1H), 1.61 (ddd, *J* = 16.4 Hz, *J'*= 11.9 Hz, *J''* = 4.7 Hz, 1H), 1.24 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 209.0, 174.5, 172.5, 154.2, 144.5, 136.5, 135.3, 135.2, 133.2, 129.9, 129.7, 128.5 (3C), 126.9 (2C), 126.0, 125.7, 125.2, 124.8, 123.1, 109.5, 80.9, 67.8, 62.9, 51.8, 44.3, 29.4, 28.1 (4C) ppm. **Minor diastereoisomer: ^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.53 (d, *J* = 7.2 Hz, 2H), 7.35 – 7.19 (m, 3H), 7.18 – 6.91 (m, 4H), 6.83 (t, *J* = 7.5 Hz, 2H), 6.71 – 6.64 (m, 2H), 6.33 (s, 1H), 5.05 (s, 1H), 4.60 (s, 1H), 3.56 (s, 3H), 3.22 (td, *J* = 14.2 Hz, *J'*= 5.0 Hz, 1H), 2.81 – 2.67 (m, 1H), 2.07 – 1.91 (m, 1H), 1.74 – 1.66 (m, 1H), 1.33 (t, *J* = 17.0 Hz, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 208.6, 173.1, 172.3, 153.6, 142.6, 135.0, 133.1, 129.3, 129.3, 128.6 (3C), 128.1, 127.5, 127.1 (2C), 126.4, 126.1, 122.9, 122.6, 121.9, 108.3, 80.4, 64.9, 64.4, 51.7, 44.6, 29.5, 28.2 (3C), 26.4 ppm. **Mixture of diastereoizomers:** $[\alpha]_D^{rt}$ = -102.8 ° (c = 0.53 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3393, 3372, 3064, 3013, 2983, 2950, 2926, 1987, 1721, 1685, 1613, 1488, 1365, 1272, 1254, 1171. **HRMS** (ESI) m/z calcd for $C_{32}H_{32}O_6N_2NaS$ $[M + Na]^+$ = 595.1873, found: 595.1853. **HPLC analysis:** major diastereoisomer: *ee* = 91 %, (Daicel Chiracel) AD column, heptane/*iso*-

propanol, 80:20, 1.0 mL/min, λ = 210 nm, retention time: t_{minor} = 8.767 min, t_{major} = 41.500 min, minor diastereoisomer: *ee* = 77 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 210 nm, retention time: t_{minor} = 16.153 min, t_{major} = 23.590 min.

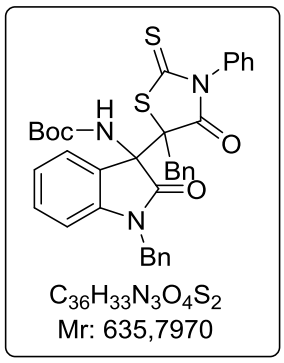
tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-5-bromo-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3u)



Adduct **3u** was prepared from 33.6 mg (0.10 mmol, 1.0 equiv) ketimine **1a** and derivative of benzo[*b*]thiophen-2(3*H*)-one **2i** 33.0 mg (0.15 mmol, 1.5 equiv). Product **3u** was obtained as light yellow foam in 74 % yield (48.4 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 7.0 Hz, 1H), 7.40 (td, *J* = 7.8 Hz, *J'*= 1.1 Hz, 1H), 7.33 (s, 1H), 7.26 – 7.14 (m, 5H), 7.12 – 7.05 (m, 1H), 7.05 – 6.99 (m, 2H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.84 – 6.79 (m, 2H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.69 – 6.65 (m, 2H), 5.86 (d, *J* = 1.8 Hz, 1H), 4.76 (d, *J* = 15.6 Hz, 1H), 4.33 (d, *J* = 15.6 Hz, 1H), 3.84 (d, *J* = 12.9 Hz, 1H), 3.36 (d, *J* = 12.9 Hz, 1H), 1.31 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 207.73, 174.36, 154.41, 144.48, 135.72, 135.55, 135.16, 132.78, 132.30, 130.44 (2C), 130.19, 129.30, 128.62 (2C), 127.96 (2C), 127.29, 127.15 (2C), 127.10, 126.32, 124.59, 123.76, 122.66, 119.01, 109.62, 80.66, 67.66, 64.76, 44.32, 39.91, 28.09 (3C) ppm. $[\alpha]_D^{rt}$ = +83.5 ° (c = 1.06 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3363, 3067, 3031, 2977, 2929, 2866, 1724, 1685, 1616, 1491, 1473, 1452, 1368, 1272, 1257, 1162, 1099, 1075, 1030, 1006. **HRMS** (ESI) m/z calcd for C35 H31 O4 N2 Br Na S $[M + Na]^+$ = 677.1080, found: 677.1075. **HPLC analysis** *ee* = 89 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 80:20, 1.0 mL/min, λ = 210 nm, retention time: t_{minor} = 5.878 min, t_{major} = 19.645 min.

***tert*-butyl (1-benzyl-3-(5-benzyl-4-oxo-3-phenyl-2-thioxothiazolidin-5-yl)-2-oxoindolin-3-yl)carbamate (6a')**



$C_{36}H_{33}N_3O_4S_2$
Mr: 635,7970

Adduct **6a** was prepared from 33.6 mg (0.10 mmol, 1.0 equiv) ketimine **1a** and derivative of *N*-phenylrhodanine **4** 29.9 mg (0.10 mmol, 1.5 equiv). Product **3u** was obtained as light yellow foam in 32 % yield (48.4 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 7.0 Hz, 1H), 7.46 – 7.39 (m, 6H), 7.39 – 7.23 (m, 11H), 7.14 (td, *J* = 7.6, 0.7 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.13 (d, *J* = 15.6 Hz, 1H), 4.80 (d, *J* = 15.6 Hz, 1H), 4.09 (d, *J* = 13.5 Hz, 1H), 3.47 (d, *J* = 13.5 Hz, 1H), 1.30 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 197.3, 175.7, 174.4, 154.2, 144.0, 135.1, 134.8, 132.1 (3C), 131.5, 130.5, 129.7, 129.4, 128.8 (3C), 128.3 (3C), 128.1, 127.8 (2C), 127.7, 126.1, 125.0, 122.9, 80.9, 77.2, 66.8, 66.5, 44.7, 38.4, 28.0 (3C) ppm. **[α]**$_D^{rt}$ = +34.8 ° (c = 0.94 in $CHCl_3$). **IR** (KBr): ν/cm^{-1} = 3358, 3031, 2983, 2932, 1700, 1610, 1491, 1353, 1248, 1162, 1078, 1027. **HRMS** (ESI) m/z calcd for $C_{36}H_{33}N_3O_4S_2$ $[M + Na]^+$ = 658.1805, found: 658.1782. **HPLC analysis** *ee* = 34 %, (Daicel Chiracel) AD column, heptane/*iso*-propanol, 90:10, 1.0 mL/min, λ = 211 nm, retention time: t_{major} = 17.8 min, t_{minor} = 23.1 min.

5 Determination of absolute configuration of 3n

Crystallographic data for **3n** was collected on Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube MoKα (λ= 0.71073) at a temperature of 120(2) K. The structure was solved by direct methods (XT)[i] and refined by full matrix least squares based on F^2 (SHELXL2018)[ii]. The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors either $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or $H_{iso}(H) = 1.5\ U_{eq}$ (pivot atom) for methyl moiety. The absolute structure determination was based on anomalous dispersion.

Crystal data for **3n**: $C_{35}H_{31}BrN_2O_4S$, M_r = 655.59; Orthorhombic, $P\ 2_1\ 2_1\ 2_1$ (No 19), a = 7.2208 (4) Å, b = 16.3286 (9) Å, c = 27.1076 (12) Å , V = 3196.1 (3) Å^3, Z = 4, D_x = 1.362 Mg m^{-3}, colorless prism of dimensions 0.31 × 0.09 × 0.07 mm, numerical absorption correction (μ = 1.39 mm^{-1}) T_{min} = 0.74, T_{max} = 0.91; a total of 32635 measured reflections (θ_{max}= 26.˚), from which 6251 were unique (R_{int} = 0.064) and 5023 observed according to the $I > 2\sigma(I)$ criterion. The refinement converged (Δ/σ_{max}= 0.001) to R = 0.036 for observed reflections and w$R(F^2)$ = 0.072, GOF = 1.04 for 392 parameters and all 6251 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.29, $\Delta\rho_{min}$ -0.40 e.Å^{-3}). Absolute structure parameter (Flack[iii]) -0.002(4).

X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under deposition number CCDC 1852707 for **3n**, respectively and can be obtained free of charge from the Centre via its website (www.ccdc.cam.ac.uk/getstructures).

i SHELXT: Sheldrick, G.M. (2015). *Acta Cryst*. **A71**, 3-8.

ii SHELXL: Sheldrick, G.M. (2015). *Acta Cryst.* **C71**, 3-8.

iii Parsons,S., Flack, H.D. and Wagner, T. (2013) *Acta Cryst*. **B69**, 249-259.

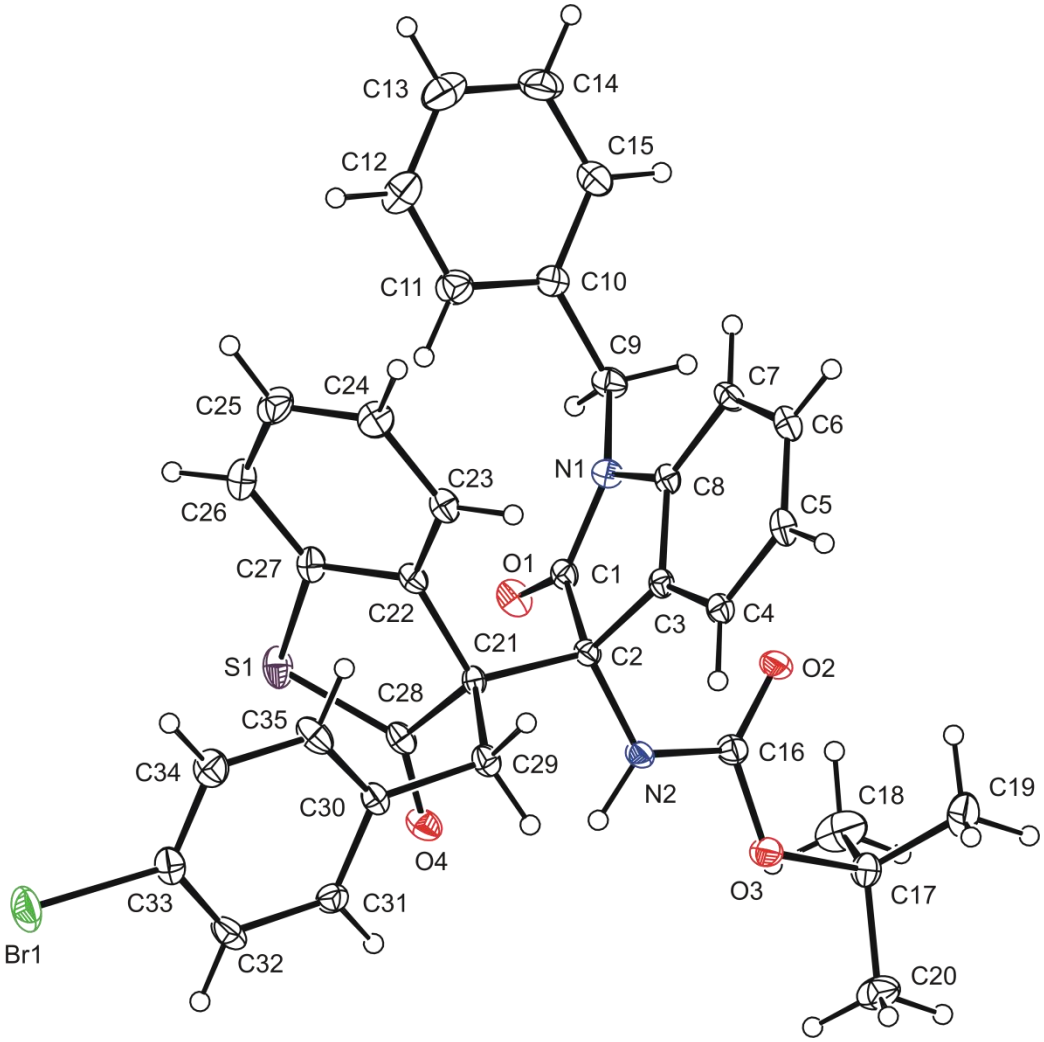


Figure 1. View on molecule of **3n**, displaying *R*,*R* configuration on C2, C21 respectively. The displacement ellipsoids at 30% probability level.

Computing details

Data collection: Bruker Instrument Service vV6.2.6; cell refinement: *SAINT* V8.38A (Bruker AXS Inc., 2017); data reduction: *SAINT* V8.38A (Bruker AXS Inc., 2017); program(s) used to solve structure: SHELXT 2014/5 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2018*/1 (Sheldrick, 2018).

3a (fm309)

Crystal data

$C_{35}H_{31}BrN_2O_4S$	D_x = 1.362 Mg m^{-3}
M_r = 655.59	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 7766 reflections
a = 7.2208 (4) Å	θ = 2.5–25.9°
b = 16.3286 (9) Å	μ = 1.39 mm^{-1}
c = 27.1076 (12) Å	T = 150 K
V = 3196.1 (3) Å^3	Prism, colourless
Z = 4	0.31 × 0.09 × 0.07 mm
F(000) = 1352	

Data collection

Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS diffractometer	6251 independent reflections
Radiation source: IμS micro-focus sealed tube	5023 reflections with $I > 2\sigma(I)$
Quazar Mo multilayer optic monochromator	R_{int} = 0.064
ϕ and ω scans	θ_{max} = 26.0°, θ_{min} = 2.5°
Absorption correction: numerical Mu From Formula *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction	h = -8→8
T_{min} = 0.74, T_{max} = 0.91	k = -19→20
32635 measured reflections	l = -33→33

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2 + 1.1717P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.036	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.072	$\Delta\rangle_{max}$ = 0.29 e Å^{-3}
S = 1.04	$\Delta\rangle_{min}$ = -0.40 e Å^{-3}
6251 reflections	Extinction correction: *SHELXL2018*/1 (Sheldrick 2018), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
392 parameters	Extinction coefficient: 0.0036 (4)
0 restraints	Absolute structure: Flack x determined using 1839 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Hydrogen site location: mixed	Absolute structure parameter: -0.002 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	1.03963 (7)	0.26127 (3)	0.05528 (2)	0.04551 (16)
S1	0.48421 (13)	0.20397 (6)	0.22350 (3)	0.0307 (2)
O1	0.3206 (3)	0.24578 (18)	0.33765 (9)	0.0283 (6)
O2	0.4674 (4)	0.37889 (15)	0.42406 (8)	0.0293 (6)
O3	0.4726 (4)	0.49856 (15)	0.38047 (9)	0.0286 (6)
O4	0.4790 (4)	0.35933 (16)	0.24899 (9)	0.0294 (6)
N1	0.5211 (4)	0.19183 (17)	0.39534 (10)	0.0200 (6)
N2	0.5906 (4)	0.38680 (19)	0.34690 (10)	0.0224 (7)
H2	0.574951	0.415778	0.316834	0.027*
C1	0.4699 (5)	0.2443 (2)	0.35826 (10)	0.0204 (8)
C2	0.6383 (5)	0.3000 (2)	0.34608 (12)	0.0188 (8)
C3	0.7718 (5)	0.2773 (2)	0.38647 (12)	0.0187 (8)
C4	0.9396 (5)	0.3109 (2)	0.39969 (12)	0.0227 (8)
H4	0.989001	0.356219	0.382062	0.027*
C5	1.0357 (5)	0.2772 (2)	0.43948 (11)	0.0253 (8)
H5	1.152094	0.299321	0.448868	0.030*
C6	0.9631 (5)	0.2121 (2)	0.46519 (12)	0.0257 (9)
H6	1.030515	0.189973	0.492166	0.031*
C7	0.7924 (5)	0.1778 (2)	0.45254 (12)	0.0232 (9)
H7	0.742579	0.132654	0.470210	0.028*
C8	0.6988 (4)	0.2125 (2)	0.41305 (12)	0.0182 (8)
C9	0.3946 (5)	0.1357 (2)	0.41913 (14)	0.0260 (9)
H9A	0.270821	0.141656	0.403821	0.031*
H9B	0.383072	0.151161	0.454314	0.031*
C10	0.4529 (5)	0.0470 (2)	0.41599 (13)	0.0248 (8)
C11	0.5302 (6)	0.0148 (2)	0.37331 (14)	0.0335 (10)
H11	0.550598	0.049394	0.345646	0.040*

C12	0.5781 (6)	-0.0675 (3)	0.37072 (17)	0.0426 (12)
H12	0.633051	-0.088541	0.341508	0.051*
C13	0.5468 (7)	-0.1183 (3)	0.40985 (18)	0.0451 (11)
H13	0.577000	-0.174801	0.407738	0.054*
C14	0.4714 (7)	-0.0869 (3)	0.45221 (16)	0.0479 (12)
H14	0.451873	-0.121838	0.479728	0.057*
C15	0.4232 (6)	-0.0047 (3)	0.45553 (14)	0.0380 (11)
H15	0.369661	0.015989	0.485027	0.046*
C16	0.5048 (5)	0.4184 (2)	0.38746 (13)	0.0243 (9)
C17	0.3793 (6)	0.5479 (3)	0.41937 (14)	0.0313 (10)
C18	0.1789 (6)	0.5184 (3)	0.42345 (19)	0.0518 (14)
H18A	0.108870	0.555823	0.444658	0.078*
H18B	0.176775	0.463239	0.437736	0.078*
H18C	0.122606	0.517065	0.390557	0.078*
C19	0.4814 (9)	0.5434 (3)	0.46693 (15)	0.0592 (16)
H19A	0.426627	0.581885	0.490512	0.089*
H19B	0.611651	0.557627	0.461483	0.089*
H19C	0.473224	0.487629	0.480133	0.089*
C20	0.3869 (6)	0.6330 (3)	0.39817 (16)	0.0405 (11)
H20A	0.327416	0.671375	0.421003	0.061*
H20B	0.321862	0.634001	0.366447	0.061*
H20C	0.516386	0.649011	0.393254	0.061*
C21	0.7078 (4)	0.2768 (2)	0.29274 (12)	0.0171 (8)
C22	0.7556 (5)	0.1867 (2)	0.28855 (12)	0.0202 (8)
C23	0.8995 (5)	0.1465 (2)	0.31224 (13)	0.0240 (9)
H23	0.974434	0.174845	0.335463	0.029*
C24	0.9334 (6)	0.0645 (3)	0.30176 (14)	0.0317 (10)
H24	1.031313	0.036835	0.318225	0.038*
C25	0.8266 (6)	0.0224 (3)	0.26771 (15)	0.0344 (11)
H25	0.850005	-0.033853	0.261449	0.041*
C26	0.6856 (6)	0.0625 (3)	0.24276 (14)	0.0321 (10)
H26	0.614101	0.034571	0.218614	0.039*
C27	0.6509 (5)	0.1441 (2)	0.25372 (13)	0.0237 (9)
C28	0.5472 (5)	0.2928 (2)	0.25610 (12)	0.0224 (8)
C29	0.8757 (5)	0.3297 (2)	0.27584 (12)	0.0234 (9)
H29A	0.846121	0.388348	0.280569	0.028*
H29B	0.984538	0.316484	0.296583	0.028*
C30	0.9234 (5)	0.3145 (2)	0.22186 (12)	0.0216 (8)
C31	0.8558 (5)	0.3666 (2)	0.18551	0.0252 (9)

			(13)	
H31	0.783370	0.412705	0.194683	0.030*
C32	0.8928 (5)	0.3521 (3)	0.13572 (13)	0.0308 (10)
H32	0.847381	0.388038	0.110980	0.037*
C33	0.9966 (5)	0.2845 (2)	0.12328 (12)	0.0278 (9)
C34	1.0666 (5)	0.2330 (3)	0.15833 (13)	0.0326 (10)
H34	1.138786	0.186873	0.149005	0.039*
C35	1.0311 (5)	0.2489 (3)	0.20778 (12)	0.0299 (9)
H35	1.081929	0.213889	0.232294	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0599 (3)	0.0561 (3)	0.02054 (18)	-0.0196 (2)	0.0088 (2)	-0.00610 (19)
S1	0.0226 (5)	0.0426 (6)	0.0269 (5)	0.0021 (5)	-0.0075 (4)	-0.0079 (4)
O1	0.0170 (12)	0.0404 (19)	0.0275 (13)	0.0011 (12)	-0.0016 (11)	0.0024 (13)
O2	0.0425 (16)	0.0246 (15)	0.0208 (12)	0.0045 (14)	0.0064 (13)	0.0045 (11)
O3	0.0389 (16)	0.0221 (15)	0.0246 (12)	0.0080 (14)	0.0104 (13)	0.0015 (10)
O4	0.0294 (14)	0.0336 (17)	0.0252 (12)	0.0070 (13)	-0.0009 (13)	0.0065 (12)
N1	0.0151 (14)	0.0226 (17)	0.0224 (14)	-0.0006 (14)	0.0032 (13)	0.0025 (12)
N2	0.0299 (18)	0.0211 (19)	0.0163 (14)	0.0059 (14)	0.0042 (13)	0.0023 (13)
C1	0.0199 (18)	0.024 (2)	0.0173 (15)	0.0014 (18)	0.0049 (15)	-0.0012 (15)
C2	0.0194 (17)	0.020 (2)	0.0166 (17)	0.0026 (16)	0.0000 (15)	0.0012 (16)
C3	0.0186 (17)	0.021 (2)	0.0166 (16)	0.0027 (16)	0.0014 (15)	-0.0025 (15)
C4	0.0255 (19)	0.024 (2)	0.0188 (17)	-0.0004 (18)	0.0026 (16)	-0.0011 (15)
C5	0.0210 (17)	0.036 (2)	0.0190 (16)	0.0001 (18)	-0.0016 (17)	-0.0044 (16)
C6	0.0254 (18)	0.034 (2)	0.0179 (16)	0.0047 (19)	-0.0009 (17)	-0.0013 (16)
C7	0.0264 (19)	0.027 (2)	0.0164 (18)	0.0069 (16)	0.0033 (16)	0.0040 (16)
C8	0.0154 (17)	0.023 (2)	0.0162 (17)	0.0032 (15)	0.0037 (15)	-0.0021 (15)
C9	0.023 (2)	0.029 (3)	0.026 (2)	0.0000 (17)	0.0069 (17)	0.0049 (17)
C10	0.0210 (18)	0.026 (2)	0.0275 (18)	-0.0029 (18)	-0.0034 (18)	0.0029 (16)
C11	0.035 (2)	0.031 (3)	0.035 (2)	-0.001 (2)	0.006 (2)	0.0019 (17)
C12	0.042 (3)	0.033 (3)	0.052 (3)	-0.003 (2)	0.006 (2)	-0.010 (2)
C13	0.043	0.027	0.065	0.001	-	-

	(3)	(3)	(3)	(2)	0.013 (3)	0.002 (2)
C14	0.062 (3)	0.035 (3)	0.046 (3)	-0.006 (2)	-0.021 (3)	0.016 (2)
C15	0.050 (3)	0.038 (3)	0.026 (2)	-0.005 (2)	-0.004 (2)	0.0055 (18)
C16	0.025 (2)	0.024 (2)	0.0237 (18)	0.0053 (17)	-0.0013 (17)	0.0009 (16)
C17	0.044 (2)	0.027 (3)	0.0230 (19)	0.007 (2)	0.0100 (19)	-0.0046 (18)
C18	0.050 (3)	0.038 (3)	0.067 (3)	0.005 (2)	0.032 (3)	0.002 (2)
C19	0.100 (5)	0.041 (3)	0.037 (2)	0.011 (3)	-0.013 (3)	-0.014 (2)
C20	0.048 (3)	0.026 (3)	0.048 (3)	0.007 (2)	0.014 (2)	0.002 (2)
C21	0.0143 (16)	0.022 (2)	0.0149 (16)	0.0004 (15)	-0.0011 (14)	-0.0022 (15)
C22	0.0167 (17)	0.027 (2)	0.0165 (18)	0.0029 (16)	0.0056 (15)	0.0020 (16)
C23	0.0196 (19)	0.032 (3)	0.0206 (18)	0.0037 (17)	0.0015 (16)	-0.0005 (17)
C24	0.028 (2)	0.033 (3)	0.034 (2)	0.0112 (19)	0.0016 (19)	-0.0015 (18)
C25	0.038 (2)	0.027 (3)	0.039 (2)	0.0080 (19)	0.006 (2)	-0.007 (2)
C26	0.031 (2)	0.037 (3)	0.028 (2)	-0.0031 (19)	0.0005 (18)	-0.0103 (19)
C27	0.0184 (18)	0.031 (3)	0.0221 (18)	-0.0020 (16)	0.0031 (16)	-0.0041 (18)
C28	0.0176 (16)	0.032 (2)	0.0173 (16)	-0.0010 (18)	0.0033 (16)	0.0025 (15)
C29	0.0215 (18)	0.029 (2)	0.0197 (18)	-0.0030 (16)	-0.0013 (16)	0.0006 (17)
C30	0.0174 (18)	0.030 (2)	0.0173 (17)	-0.0070 (16)	-0.0009 (15)	0.0013 (16)
C31	0.028 (2)	0.021 (2)	0.027 (2)	-0.0034 (17)	0.0022 (17)	0.0008 (17)
C32	0.032 (2)	0.040 (3)	0.0208 (19)	-0.010 (2)	-0.0016 (17)	0.0100 (18)
C33	0.023 (2)	0.037 (3)	0.0230 (18)	-0.0100 (18)	0.0039 (16)	-0.0023 (16)
C34	0.031 (2)	0.036 (3)	0.0311 (19)	0.001 (2)	0.0083 (18)	-0.0029 (19)
C35	0.0212 (17)	0.046 (3)	0.0226 (16)	0.005 (2)	0.0042 (16)	0.0074 (18)

Geometric parameters (Å, º)

Br1—C33	1.907 (3)	C15—H15	0.9500
S1—C27	1.753 (4)	C17—C19	1.487 (6)
S1—C28	1.758 (4)	C17—C20	1.504 (6)
O1—C1	1.215 (4)	C17—C18	1.530 (6)
O2—C16	1.214 (4)	C18—H18A	0.9800
O3—C16	1.343 (4)	C18—H18B	0.9800
O3—C17	1.489 (4)	C18—H18C	0.9800
O4—C28	1.209 (4)	C19—H19A	0.9800
N1—C1	1.371 (4)	C19—H19B	0.9800
N1—C8	1.411 (4)	C19—H19C	0.9800

N1—C9	1.446 (4)	C20—H20A	0.9800
N2—C16	1.364 (4)	C20—H20B	0.9800
N2—C2	1.459 (5)	C20—H20C	0.9800
N2—H2	0.9491	C21—C22	1.515 (5)
C1—C2	1.554 (5)	C21—C28	1.549 (5)
C2—C3	1.505 (5)	C21—C29	1.557 (5)
C2—C21	1.576 (5)	C22—C23	1.387 (5)
C3—C4	1.378 (5)	C22—C27	1.395 (5)
C3—C8	1.383 (5)	C23—C24	1.392 (5)
C4—C5	1.396 (5)	C23—H23	0.9500
C4—H4	0.9500	C24—C25	1.385 (6)
C5—C6	1.374 (5)	C24—H24	0.9500
C5—H5	0.9500	C25—C26	1.386 (6)
C6—C7	1.396 (5)	C25—H25	0.9500
C6—H6	0.9500	C26—C27	1.389 (6)
C7—C8	1.387 (5)	C26—H26	0.9500
C7—H7	0.9500	C29—C30	1.524 (5)
C9—C10	1.512 (5)	C29—H29A	0.9900
C9—H9A	0.9900	C29—H29B	0.9900
C9—H9B	0.9900	C30—C35	1.378 (5)
C10—C15	1.380 (5)	C30—C31	1.390 (5)
C10—C11	1.388 (5)	C31—C32	1.396 (5)
C11—C12	1.389 (6)	C31—H31	0.9500
C11—H11	0.9500	C32—C33	1.376 (6)
C12—C13	1.366 (6)	C32—H32	0.9500
C12—H12	0.9500	C33—C34	1.366 (5)
C13—C14	1.370 (6)	C34—C35	1.389 (5)
C13—H13	0.9500	C34—H34	0.9500
C14—C15	1.390 (6)	C35—H35	0.9500
C14—H14	0.9500		
C27—S1—C28	92.69 (18)	C17—C18—H18B	109.5
C16—O3—C17	120.4 (3)	H18A—C18—H18B	109.5
C1—N1—C8	110.2 (3)	C17—C18—H18C	109.5
C1—N1—C9	123.5 (3)	H18A—C18—H18C	109.5
C8—N1—C9	125.1 (3)	H18B—C18—H18C	109.5
C16—N2—C2	119.1 (3)	C17—C19—H19A	109.5
C16—N2—H2	116.7	C17—C19—H19B	109.5
C2—N2—H2	120.0	H19A—C19—H19B	109.5
O1—C1—N1	126.1 (3)	C17—C19—H19C	109.5
O1—C1—C2	125.8 (3)	H19A—C19—H19C	109.5
N1—C1—C2	108.1 (3)	H19B—C19—H19C	109.5
N2—C2—C3	112.3 (3)	C17—C20—H20A	109.5
N2—C2—C1	112.4 (3)	C17—C20—H20B	109.5

C3—C2—C1	101.7 (3)	H20A—C20—H20B	109.5
N2—C2—C21	108.8 (3)	C17—C20—H20C	109.5
C3—C2—C21	113.9 (3)	H20A—C20—H20C	109.5
C1—C2—C21	107.7 (3)	H20B—C20—H20C	109.5
C4—C3—C8	120.3 (3)	C22—C21—C28	106.6 (3)
C4—C3—C2	130.8 (3)	C22—C21—C29	109.8 (3)
C8—C3—C2	108.9 (3)	C28—C21—C29	107.5 (3)
C3—C4—C5	118.7 (3)	C22—C21—C2	112.0 (3)
C3—C4—H4	120.6	C28—C21—C2	108.0 (3)
C5—C4—H4	120.6	C29—C21—C2	112.6 (3)
C6—C5—C4	120.5 (3)	C23—C22—C27	118.9 (4)
C6—C5—H5	119.7	C23—C22—C21	126.5 (3)
C4—C5—H5	119.7	C27—C22—C21	114.3 (3)
C5—C6—C7	121.5 (3)	C22—C23—C24	119.5 (4)
C5—C6—H6	119.3	C22—C23—H23	120.2
C7—C6—H6	119.3	C24—C23—H23	120.2
C8—C7—C6	117.1 (3)	C25—C24—C23	121.0 (4)
C8—C7—H7	121.5	C25—C24—H24	119.5
C6—C7—H7	121.5	C23—C24—H24	119.5
C3—C8—C7	121.9 (3)	C24—C25—C26	120.1 (4)
C3—C8—N1	110.6 (3)	C24—C25—H25	120.0
C7—C8—N1	127.4 (3)	C26—C25—H25	120.0
N1—C9—C10	114.0 (3)	C25—C26—C27	118.7 (4)
N1—C9—H9A	108.8	C25—C26—H26	120.6
C10—C9—H9A	108.8	C27—C26—H26	120.6
N1—C9—H9B	108.8	C26—C27—C22	121.7 (3)
C10—C9—H9B	108.8	C26—C27—S1	124.0 (3)
H9A—C9—H9B	107.7	C22—C27—S1	114.2 (3)
C15—C10—C11	118.6 (4)	O4—C28—C21	123.9 (3)
C15—C10—C9	119.9 (3)	O4—C28—S1	123.8 (3)
C11—C10—C9	121.4 (3)	C21—C28—S1	112.2 (3)
C10—C11—	120.5 (4)	C30—C29—	111.6 (3)

C12		C21	
C10—C11—H11	119.7	C30—C29—H29A	109.3
C12—C11—H11	119.7	C21—C29—H29A	109.3
C13—C12—C11	120.5 (4)	C30—C29—H29B	109.3
C13—C12—H12	119.8	C21—C29—H29B	109.3
C11—C12—H12	119.8	H29A—C29—H29B	108.0
C12—C13—C14	119.3 (4)	C35—C30—C31	118.5 (3)
C12—C13—H13	120.4	C35—C30—C29	121.3 (3)
C14—C13—H13	120.4	C31—C30—C29	120.1 (3)
C13—C14—C15	121.0 (4)	C30—C31—C32	120.9 (4)
C13—C14—H14	119.5	C30—C31—H31	119.5
C15—C14—H14	119.5	C32—C31—H31	119.5
C10—C15—C14	120.0 (4)	C33—C32—C31	118.5 (4)
C10—C15—H15	120.0	C33—C32—H32	120.7
C14—C15—H15	120.0	C31—C32—H32	120.7
O2—C16—O3	126.5 (3)	C34—C33—C32	121.7 (3)
O2—C16—N2	124.0 (3)	C34—C33—Br1	119.3 (3)
O3—C16—N2	109.5 (3)	C32—C33—Br1	119.0 (3)
C19—C17—O3	111.3 (3)	C33—C34—C35	119.2 (4)
C19—C17—C20	111.1 (4)	C33—C34—H34	120.4
O3—C17—C20	102.3 (3)	C35—C34—H34	120.4
C19—C17—C18	113.0 (4)	C30—C35—C34	121.1 (3)
O3—C17—C18	108.0 (3)	C30—C35—H35	119.4
C20—C17—C18	110.7 (4)	C34—C35—H35	119.4
C17—C18—H18A	109.5		

6 Literature

[1] Urban, M.; Franc, M.; Hofmanová, M.; Veselý, J. *Org. Biomol. Chem.* **2017**, *15*, 9077.

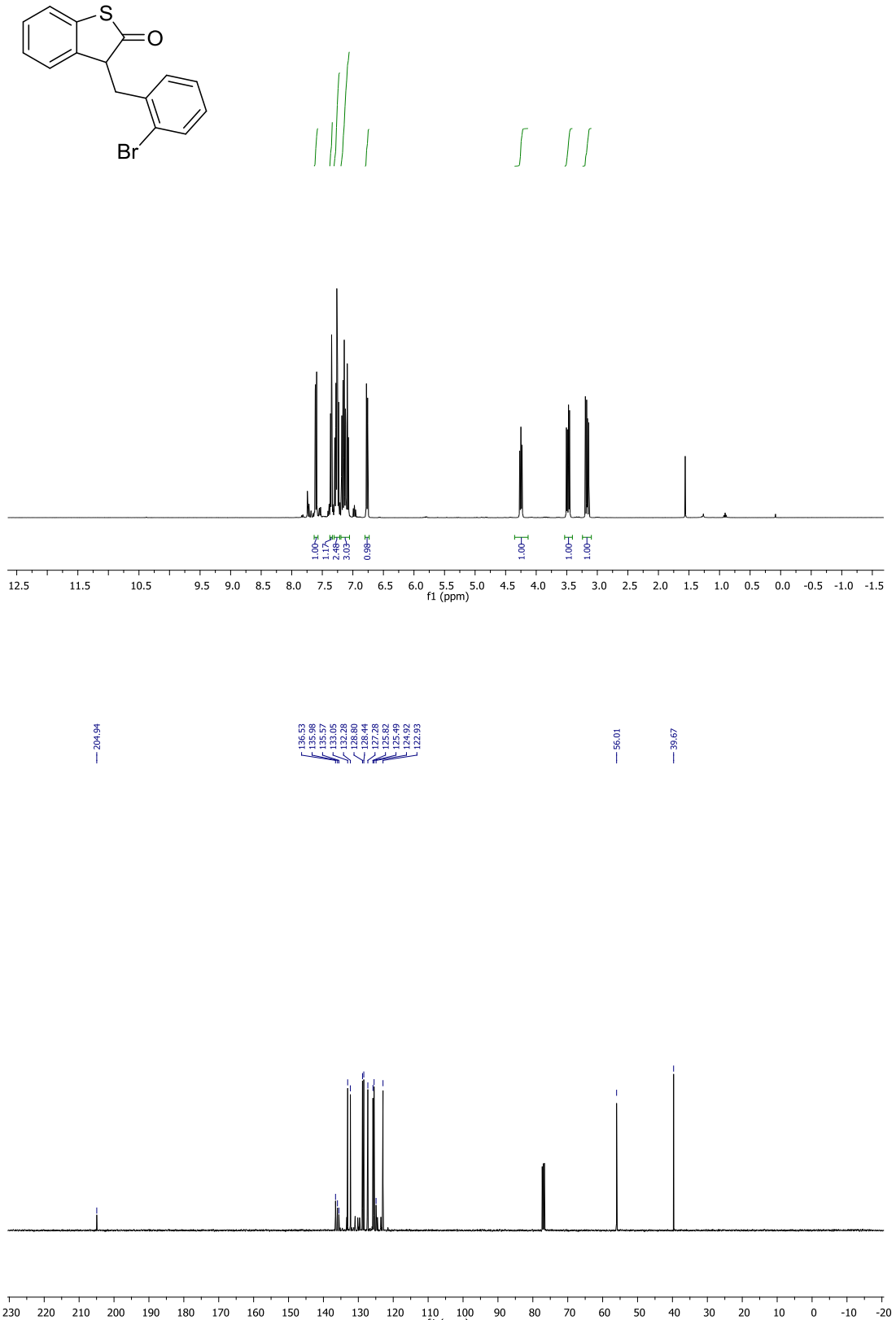
[2] Ohmatsu, Kohsuke et al *Chem. Sci.* **2014**, *5*, 3645.

[3] a) Giles, R. G.; Lewis, N. J.; Quick, J. K.; Sasse, M. J.; Urquhart, M. W. J.; Youssef, L. *Tetrahedron*, **2000**, *56*, 4531. b) Kamlar, M.; Císařová, I.; Veselý, J. *Org. Biomol. Chem.* **2015**, *13*, 2884.

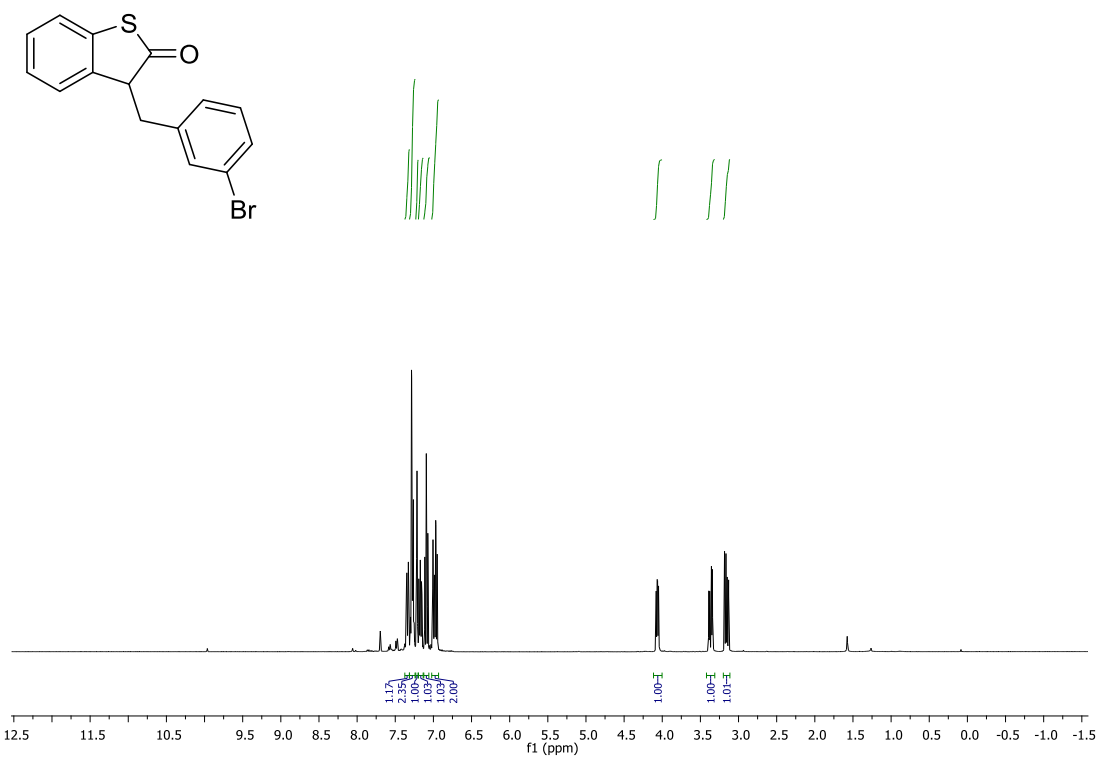
[4] a) Cao, S; Zhu, L.; Zhao, Ch.; Tang, X.; Sun, H.; Feng, X.; Quian, X. *Monatsh Chem*, **2008**, 139, 923. b) *Indian J. Chem., Sec. B*, **2000**, *39B*, 853.

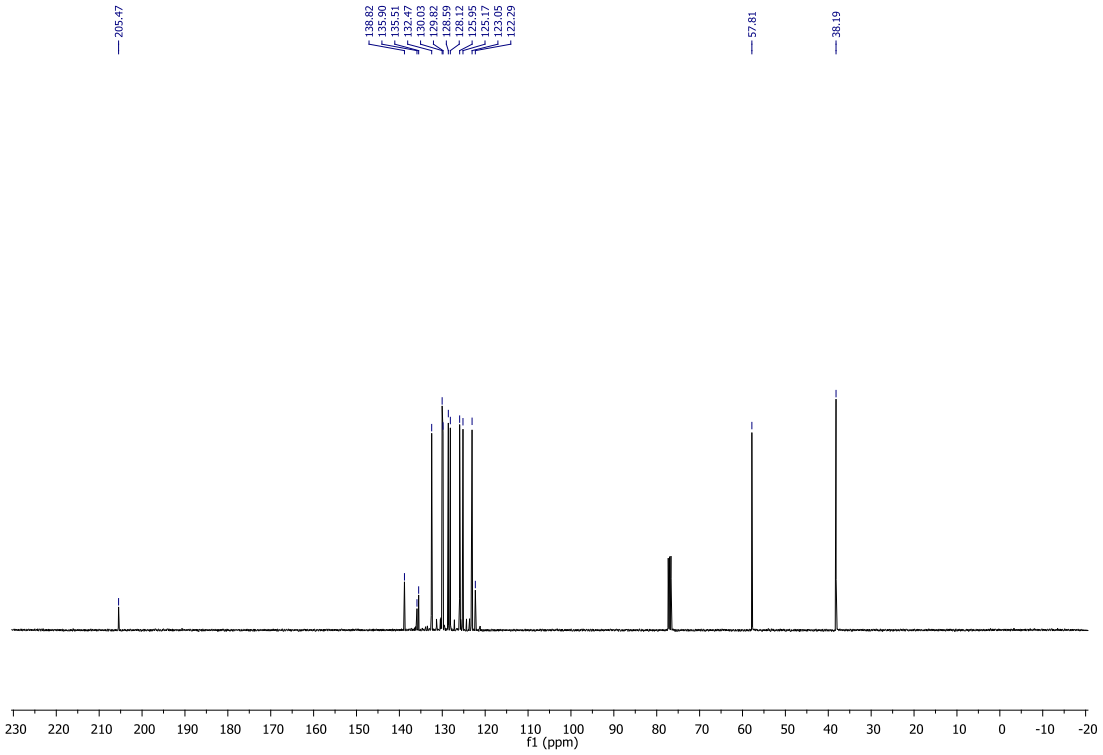
7 NMR Spectra of Compounds

2b 3-(2-Bromobenzyl)benzo[*b*]thiophen-2(3*H*)-on

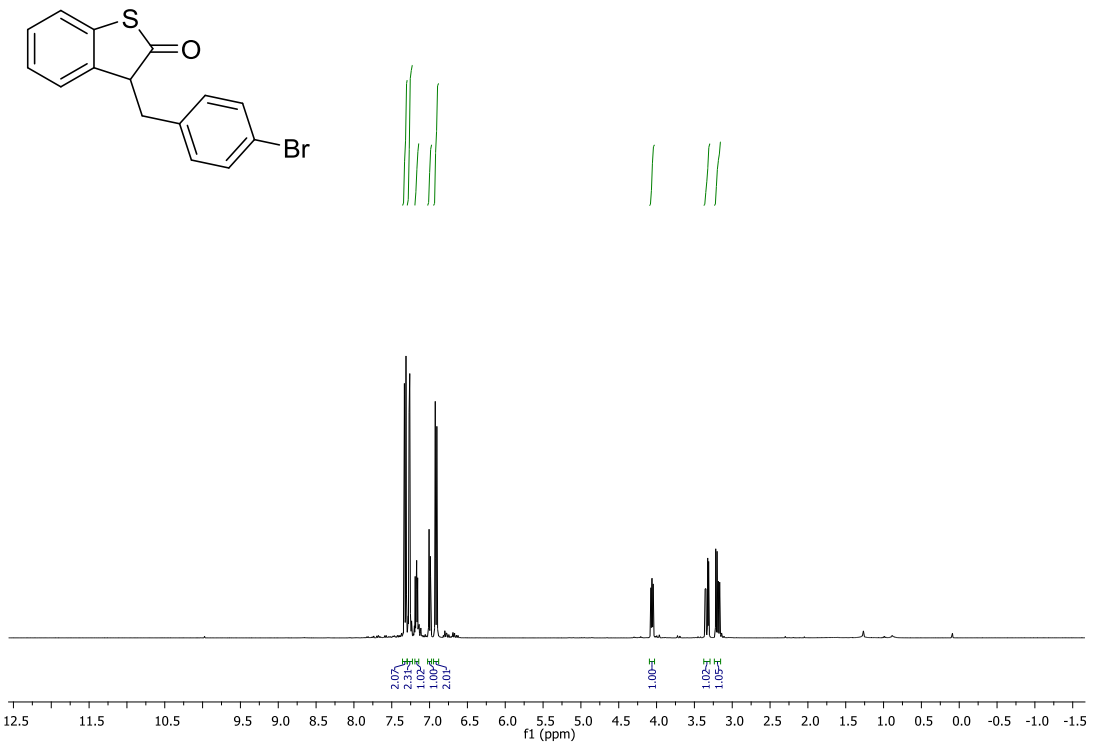


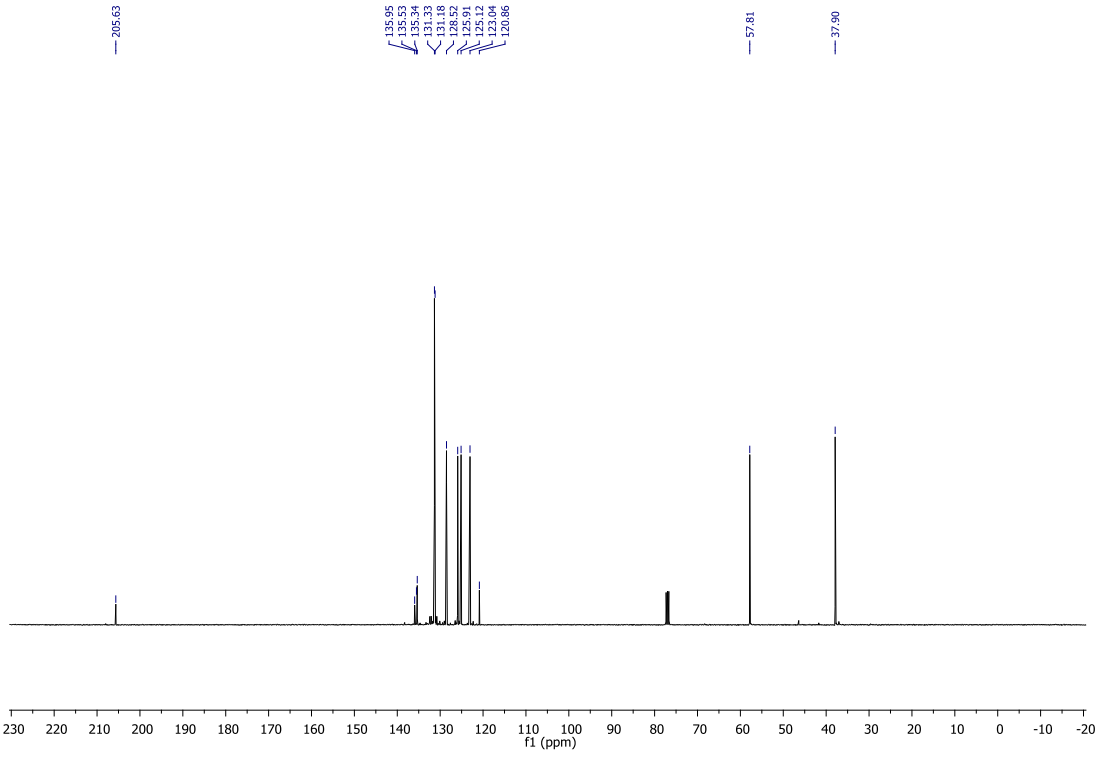
2c 3-(3-Bromobenzyl)benzo[*b*]thiophen-2(3*H*)-one



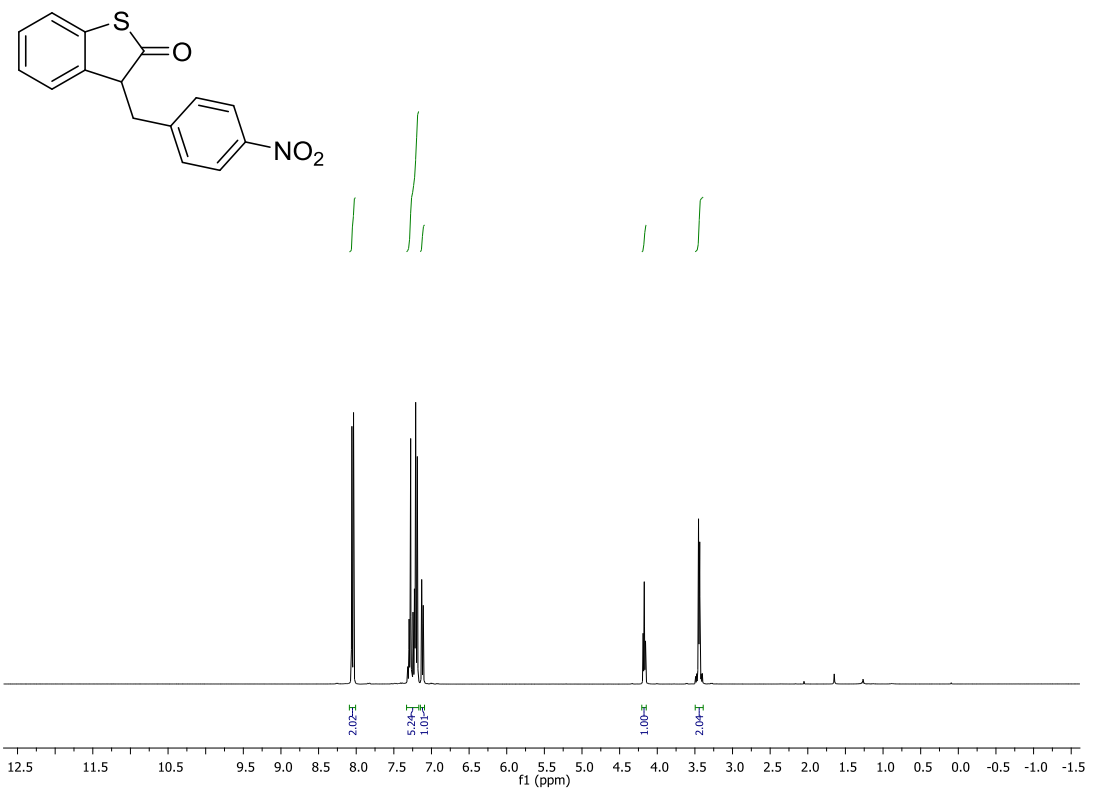


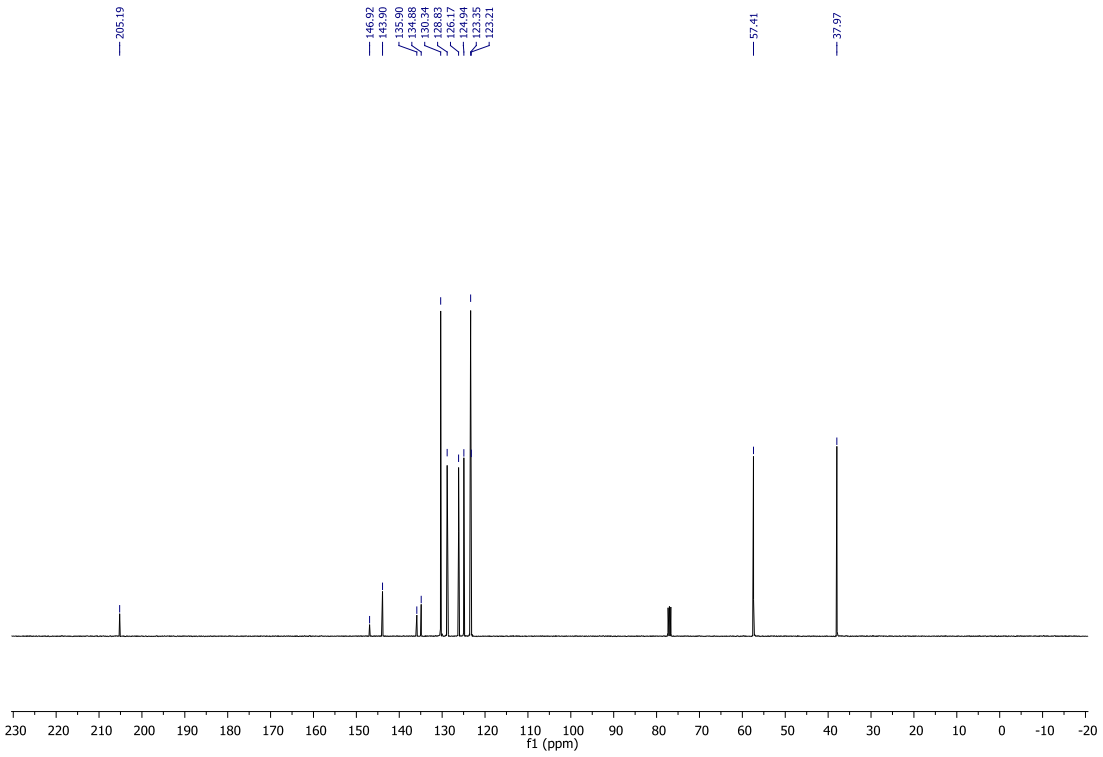
2d 3-(4-Bromobenzyl)benzo[*b*]thiophen-2(3*H*)-one



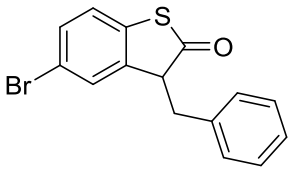


2e 3-(4-Nitrobenzyl)benzo[*b*]thiophen-2(3*H*)-one





2i 3-Benzyl-5-bromobenzo[*b*]thiophen-2(3*H*)-one


S
O
Br

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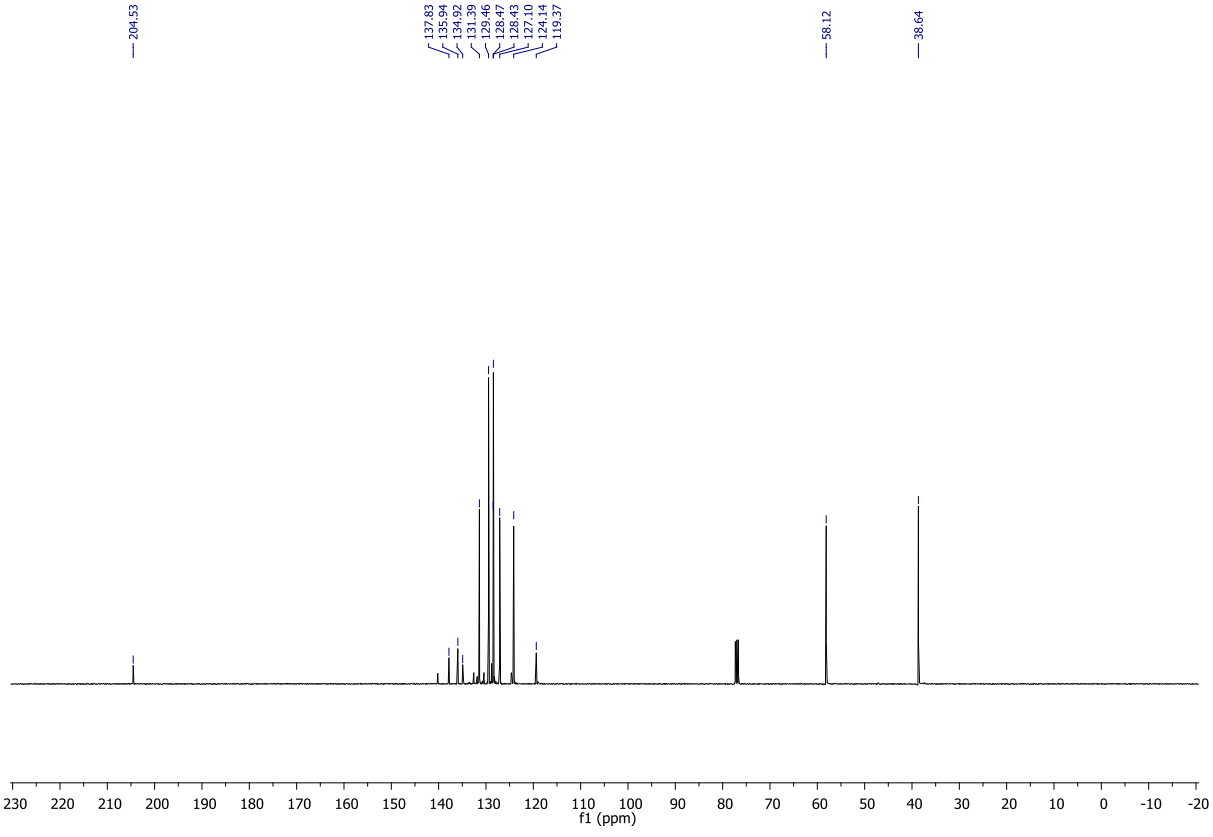
3.28
1.00
2.04
1.00
1.00
1.01
1.03
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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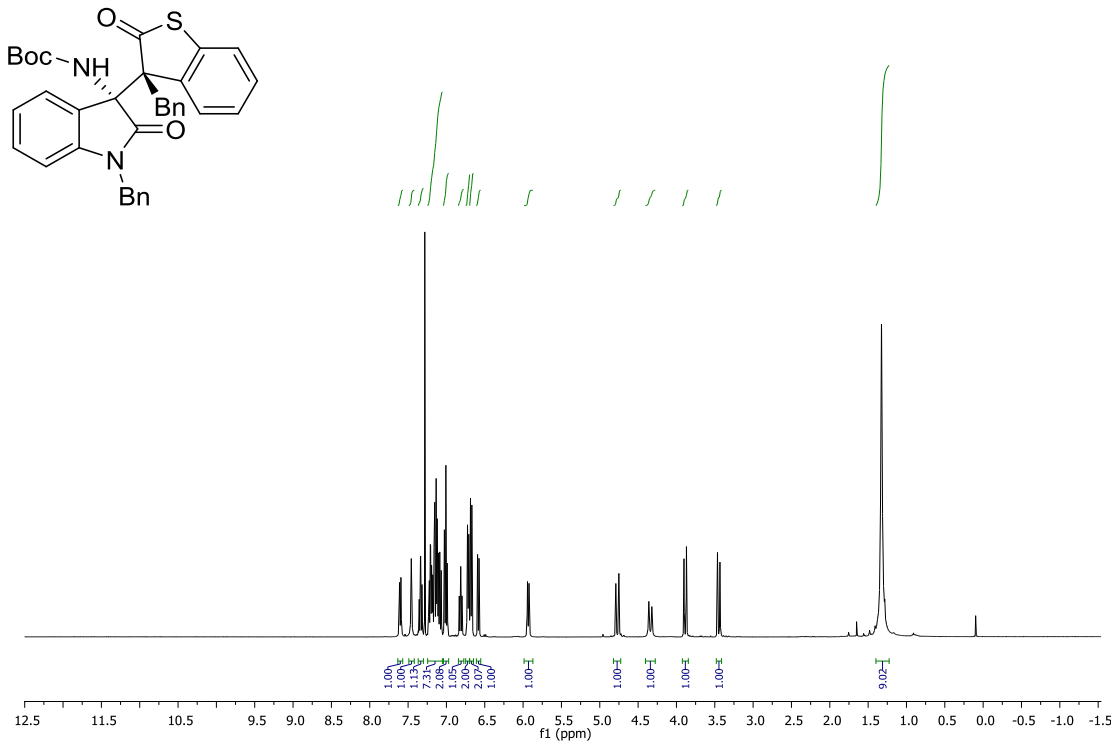
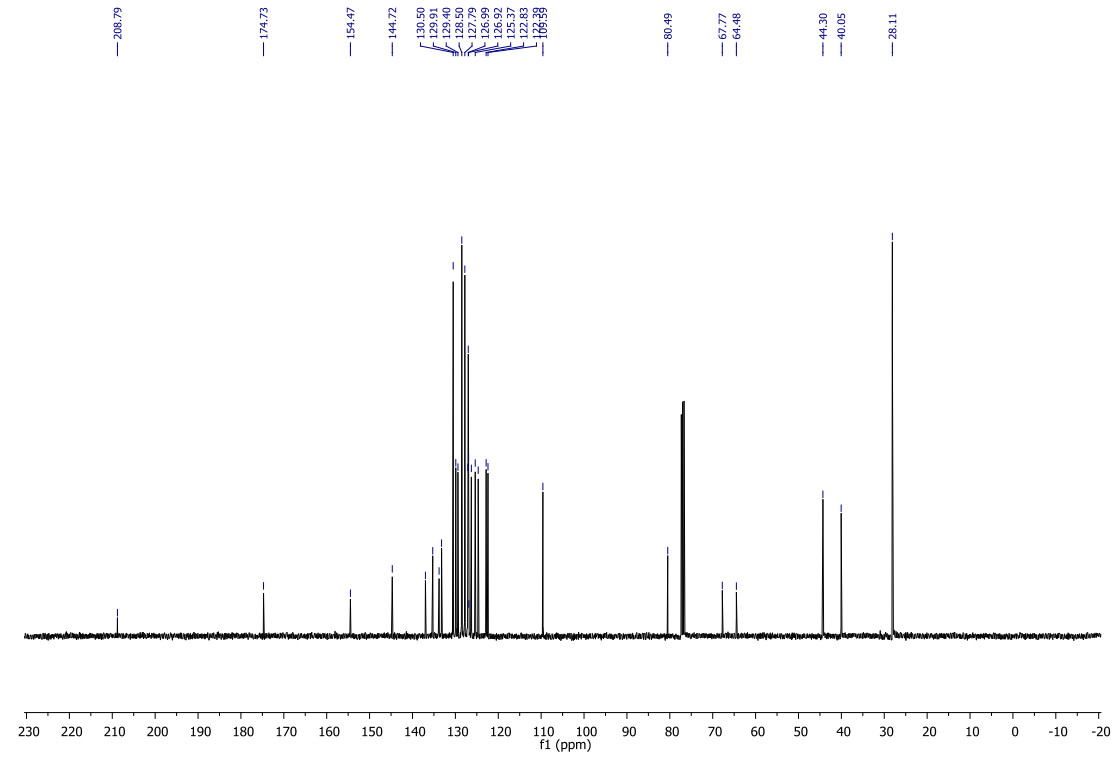
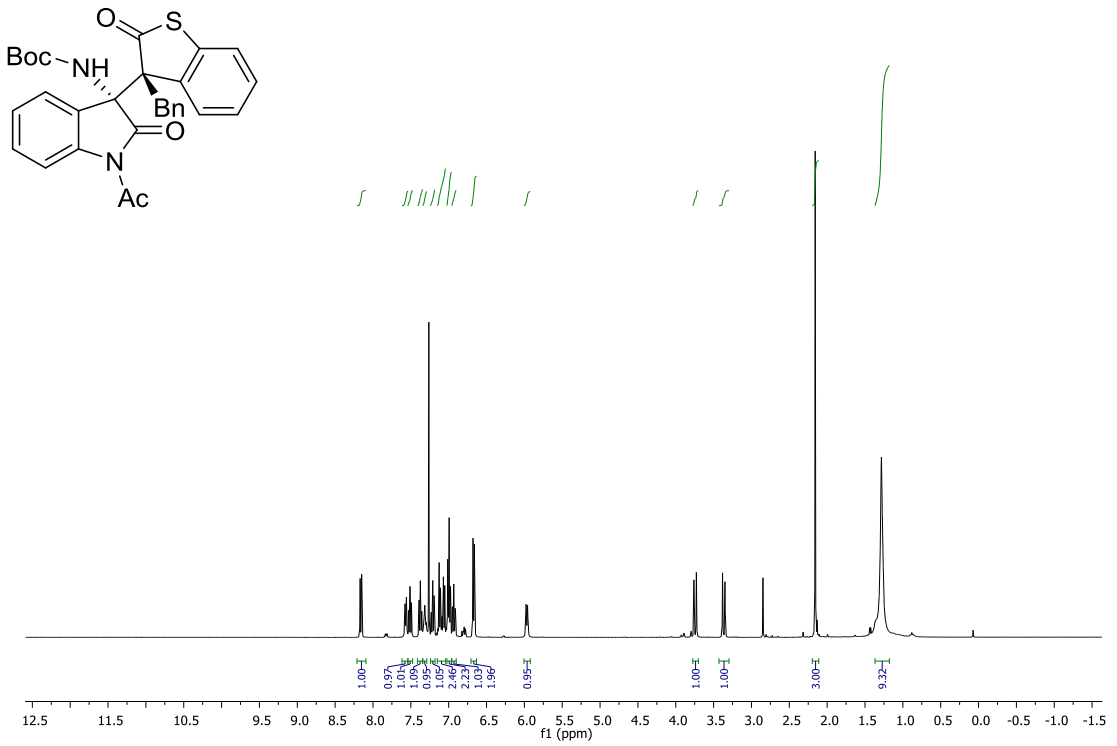
135.94
134.92
131.39
129.46
128.47
128.43
127.10
124.14
119.37
58.12
38.64
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

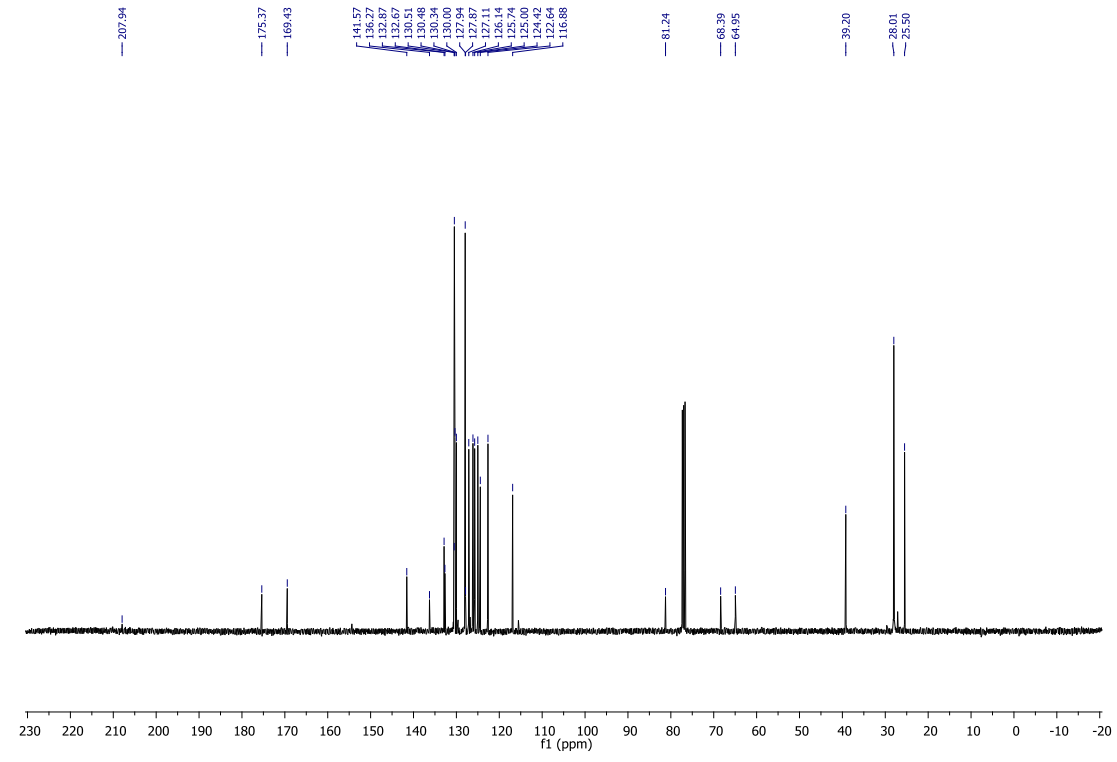
3a *tert*-Butyl ((*R*)-*N*-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate



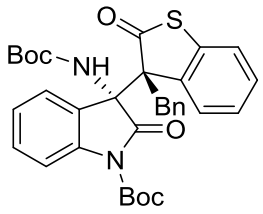


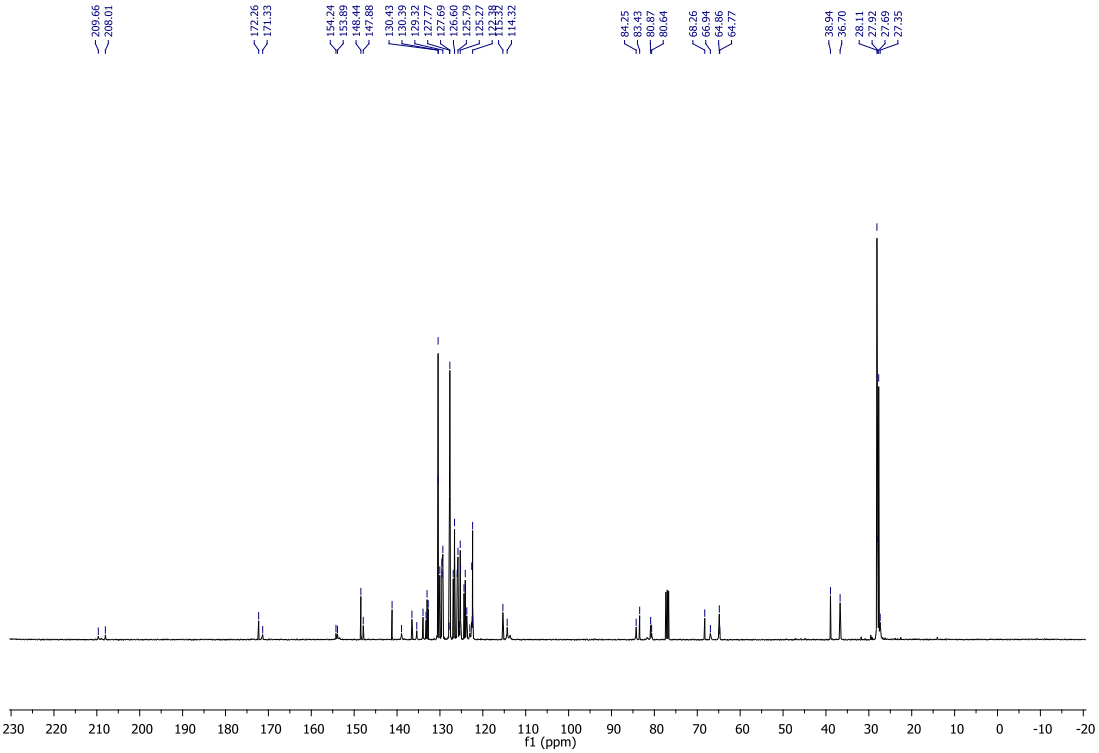
3b *tert*-Butyl ((*R*)-*N*-1-acetyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate



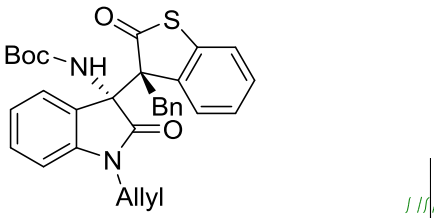


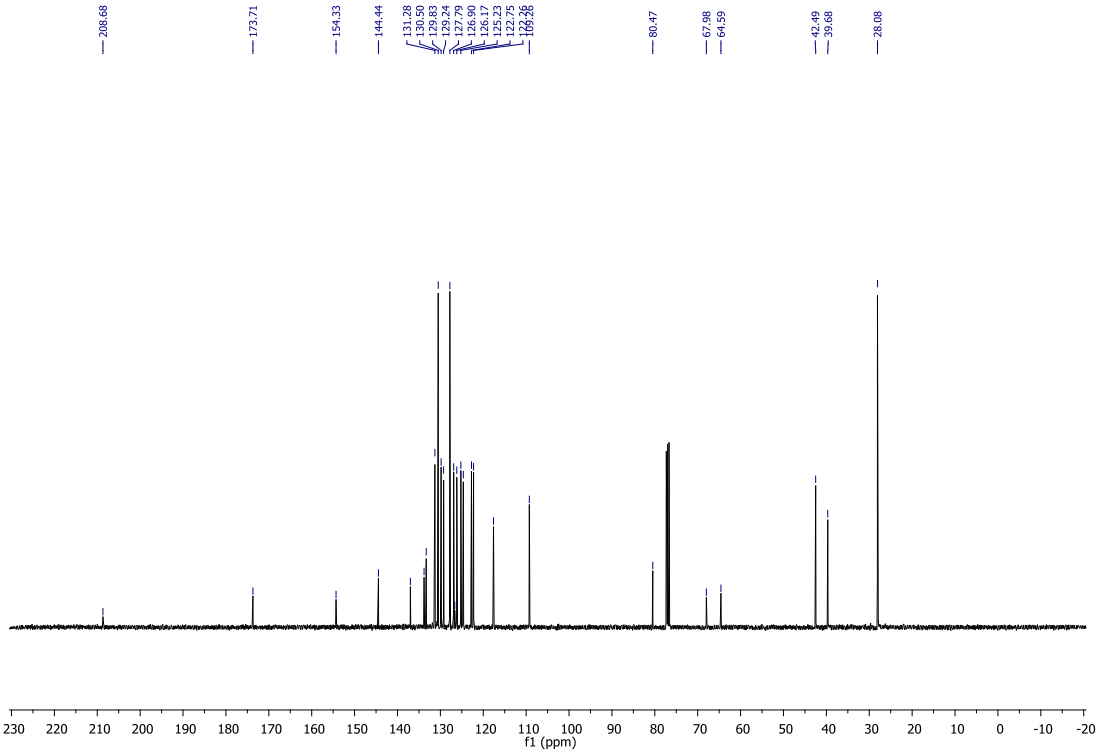
3c *tert*-Butyl 3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-3-((*R*)-(*tert*-butoxycarbonyl)amino)-2-oxoindolin-*N*-1-carboxylate



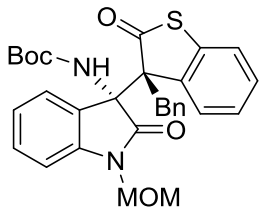


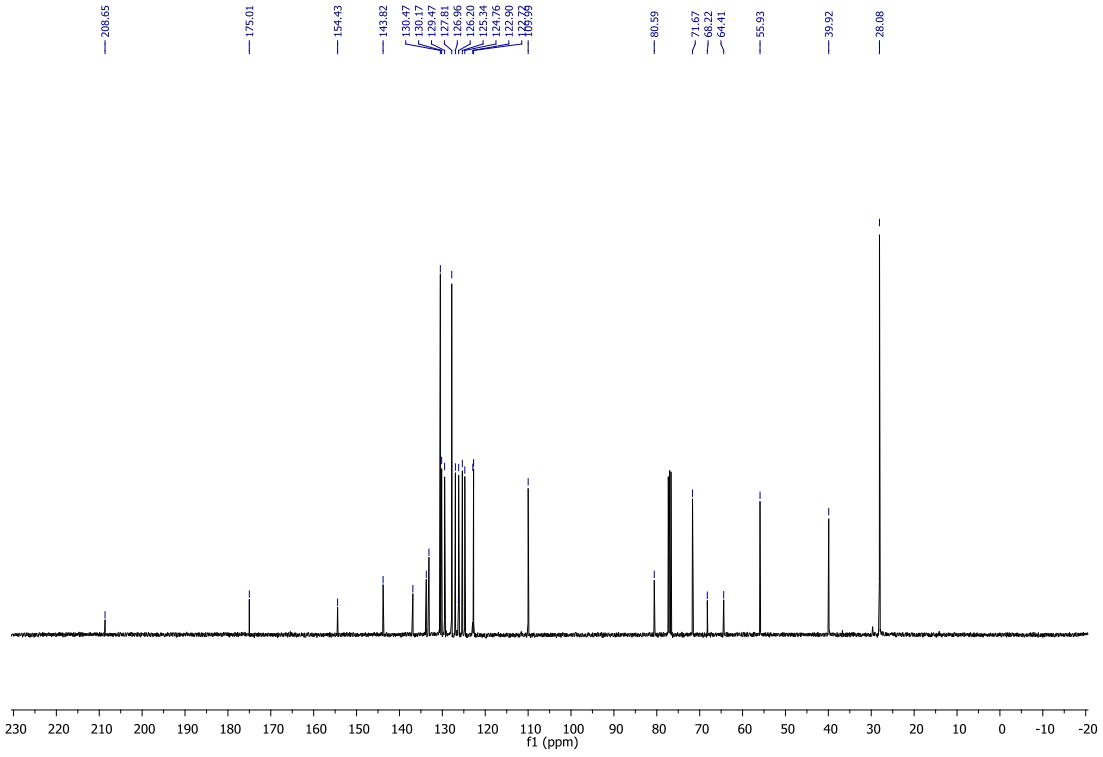
3d *tert*-Butyl ((*R*)-*N*-1-allyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate



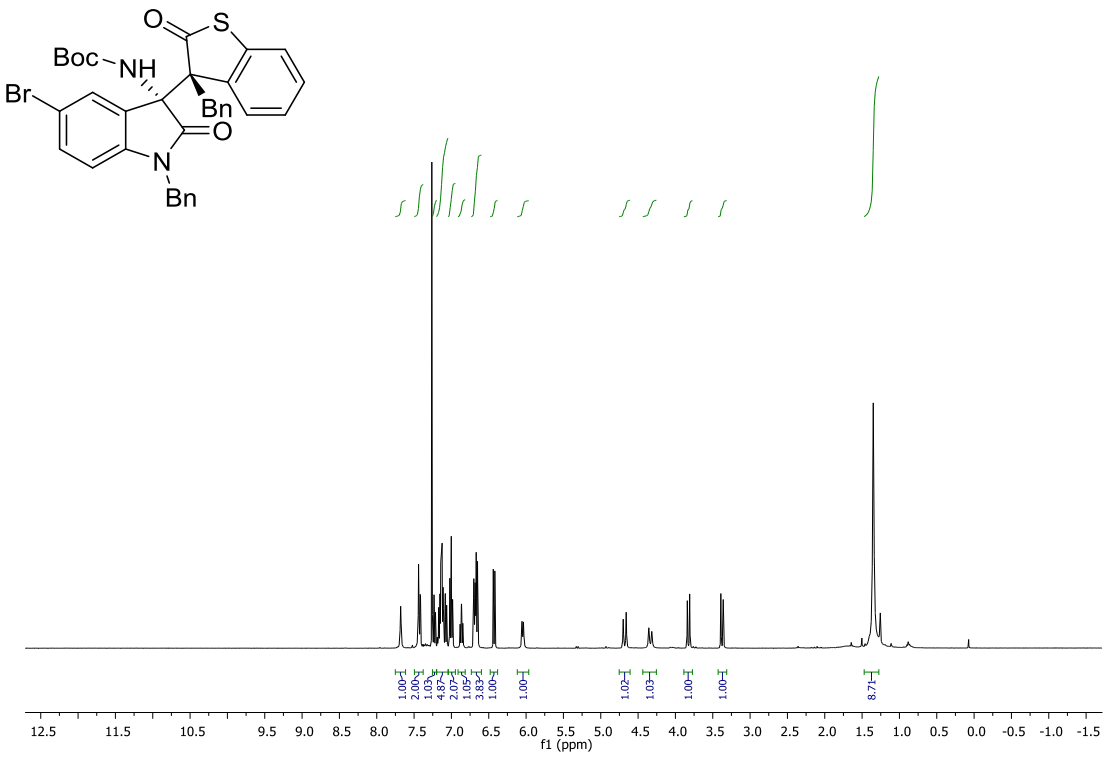


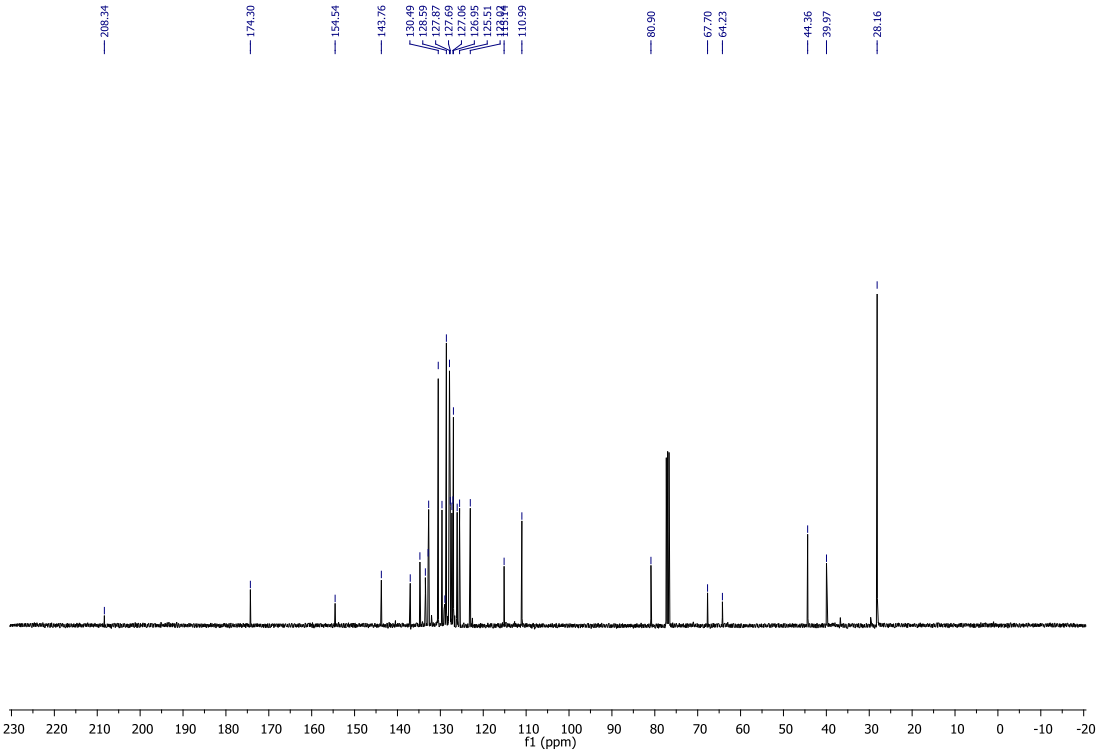
3e *tert*-Butyl (3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)- (*R*)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate



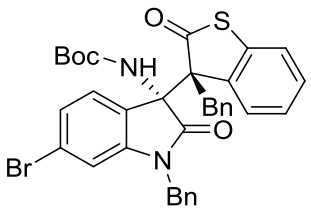


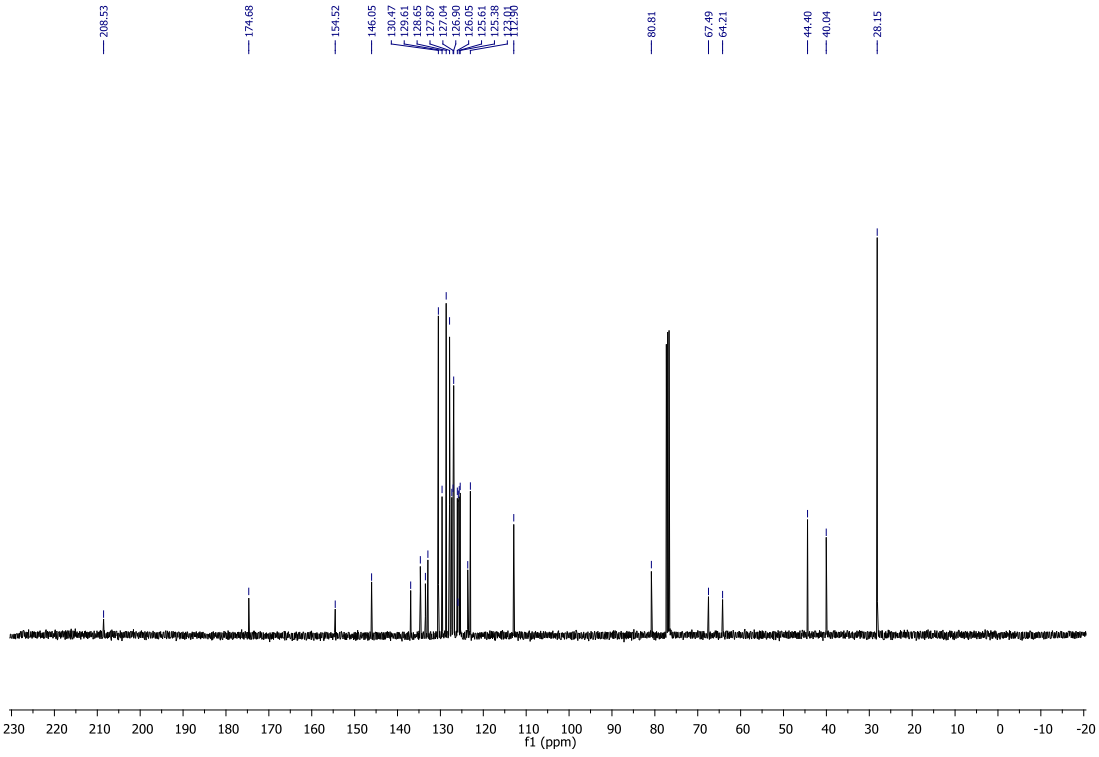
3h *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-5-bromo-2-oxoindolin-3-yl)carbamate



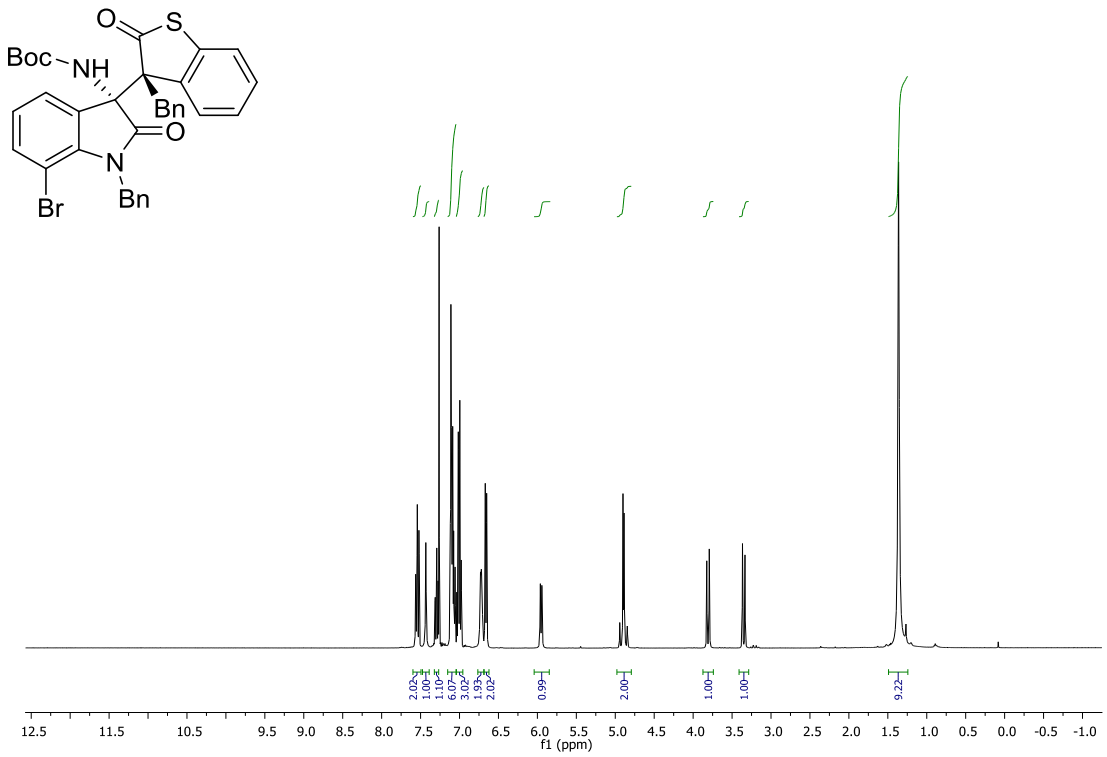


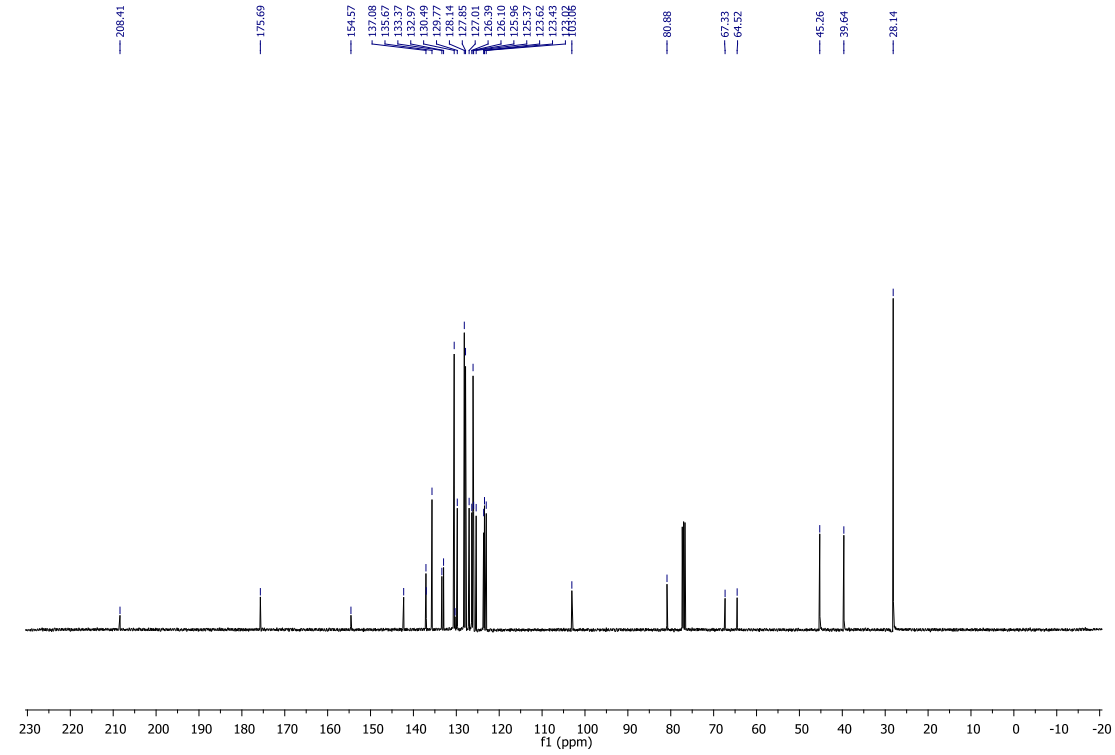
3i *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-6-bromo-2-oxoindolin-3-yl)carbamate



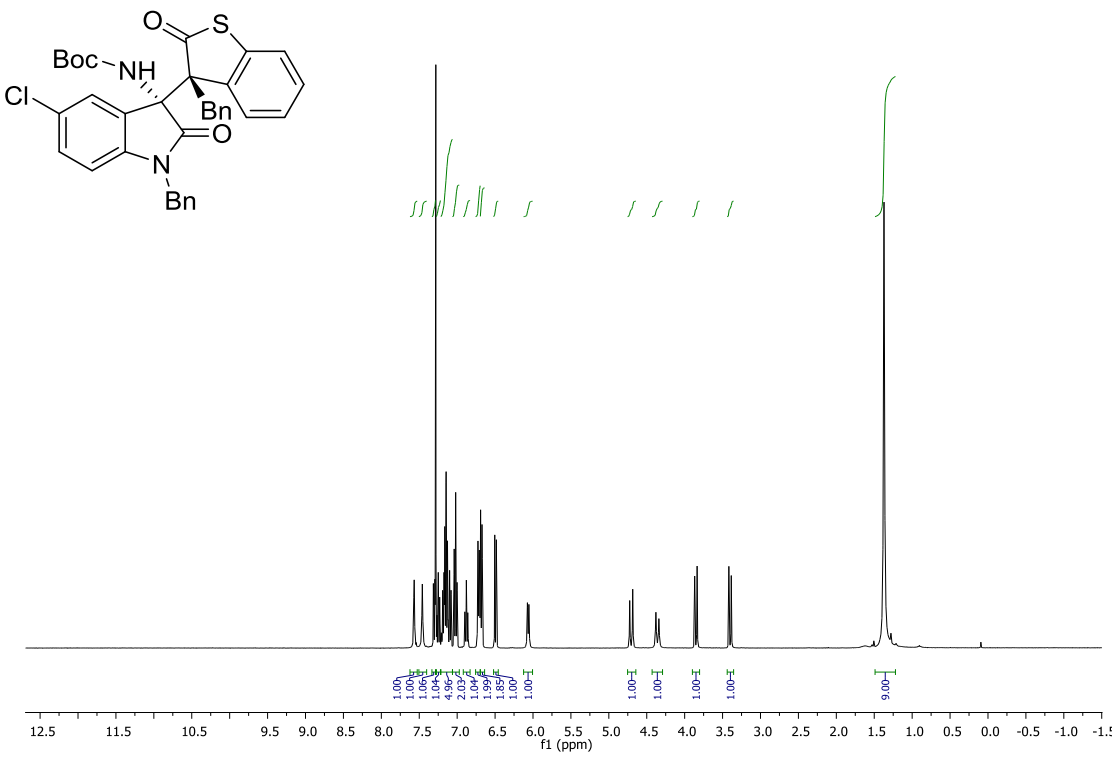


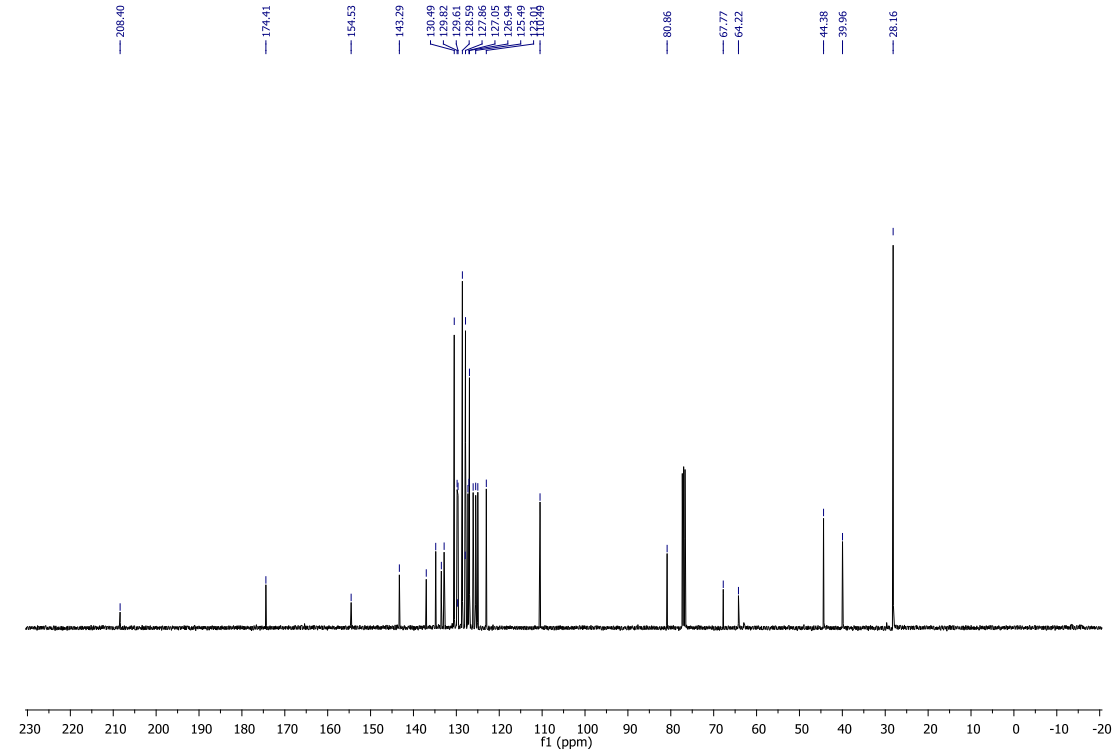
3j *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-7-bromo-2-oxoindolin-3-yl)carbamate



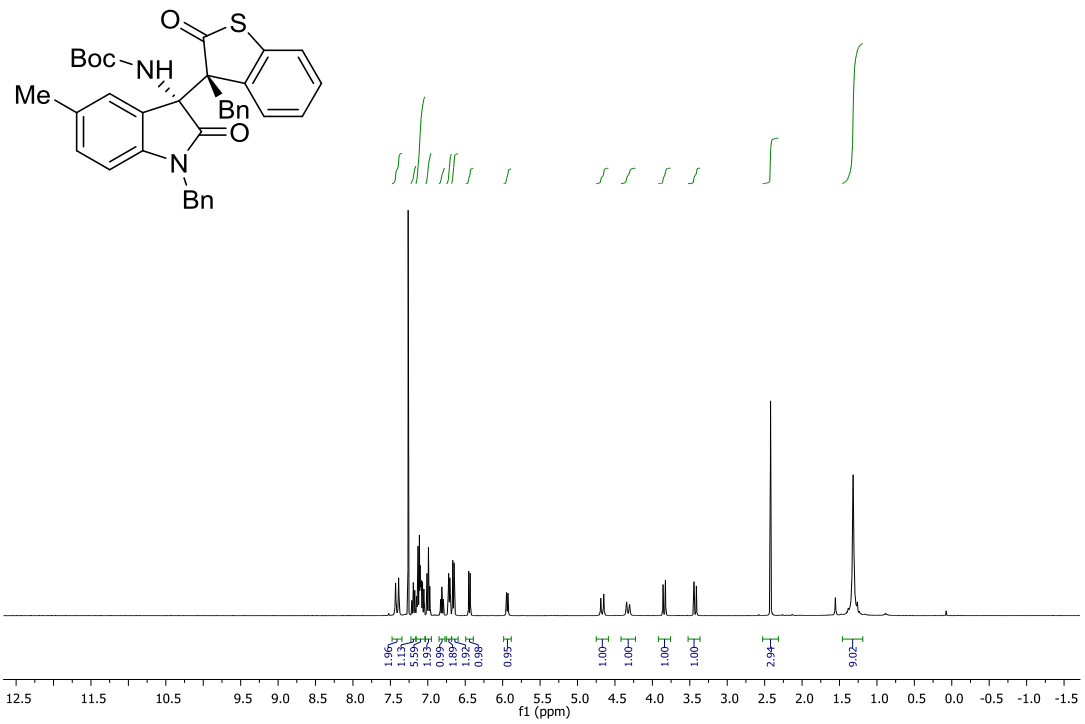


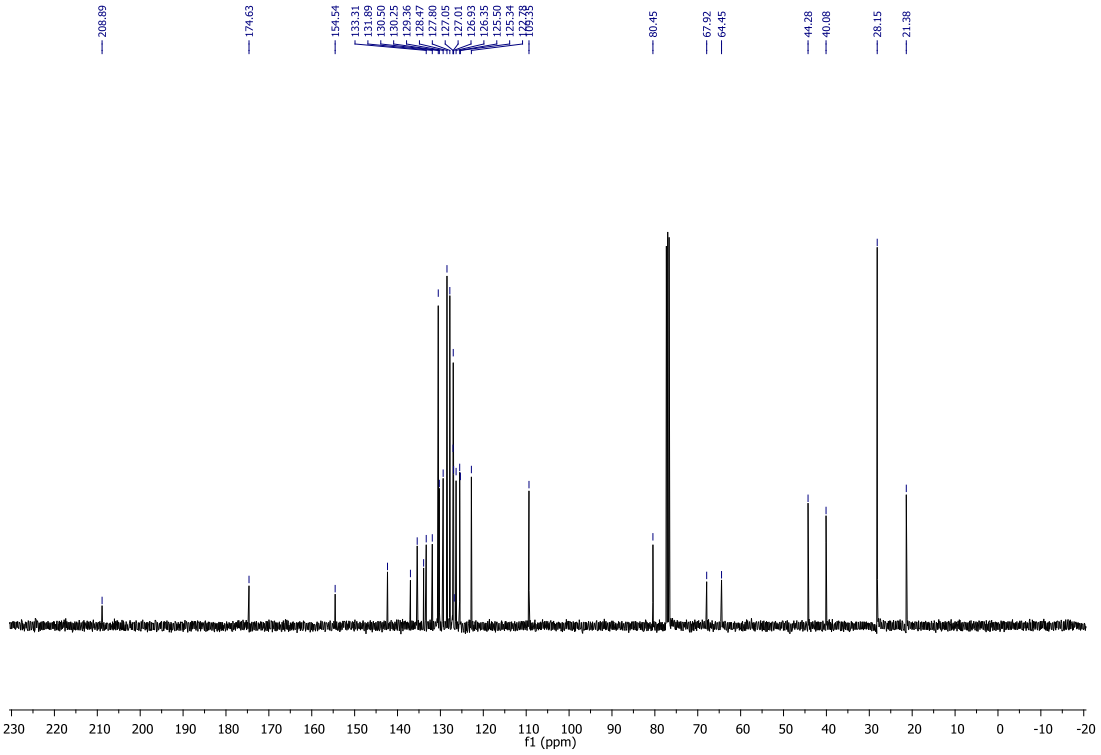
3k *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-5-chloro-2-oxoindolin-3-yl)carbamate



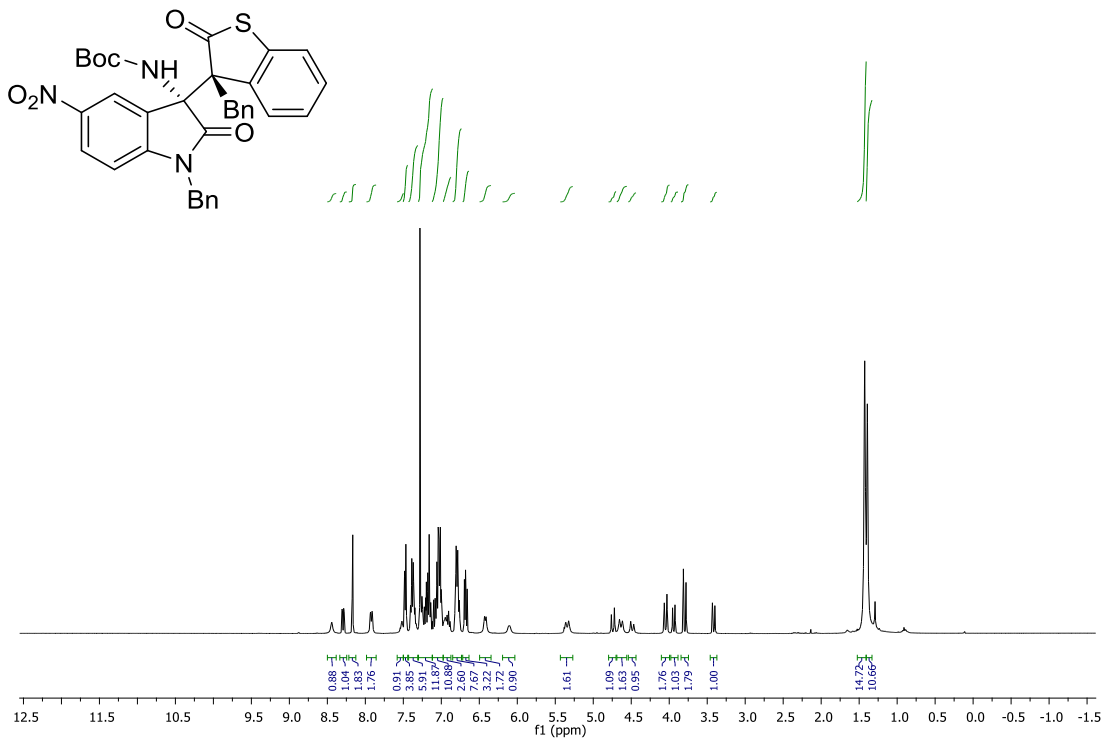


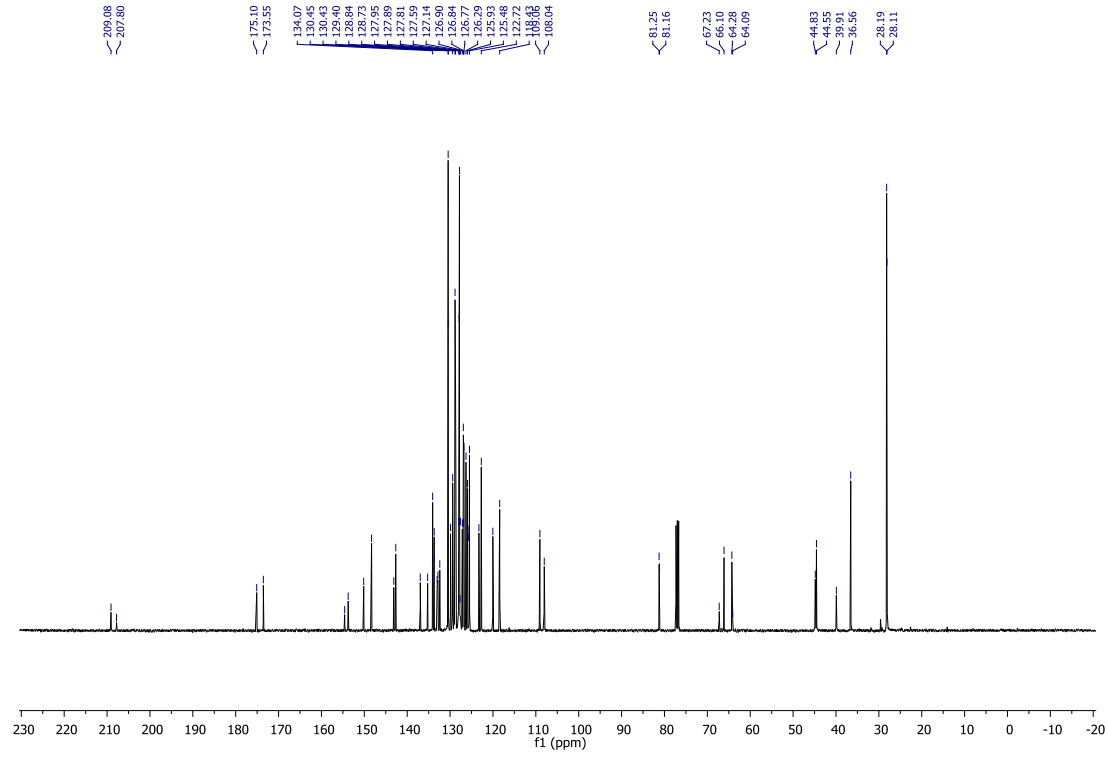
3l *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl) 5-methyl-2-oxoindolin-3-yl)carbamate



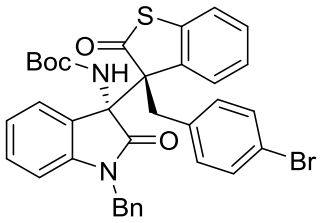


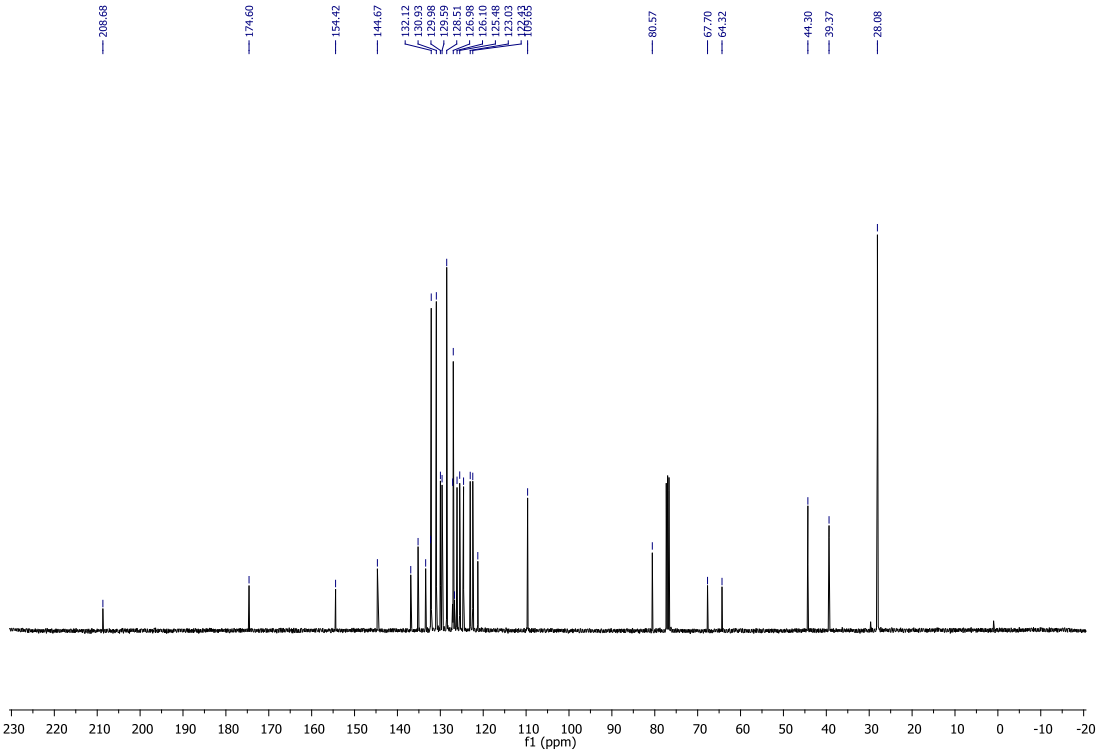
3m *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-5-nitro-2-oxoindolin-3-yl)carbamate



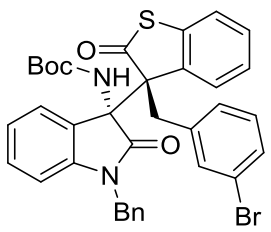


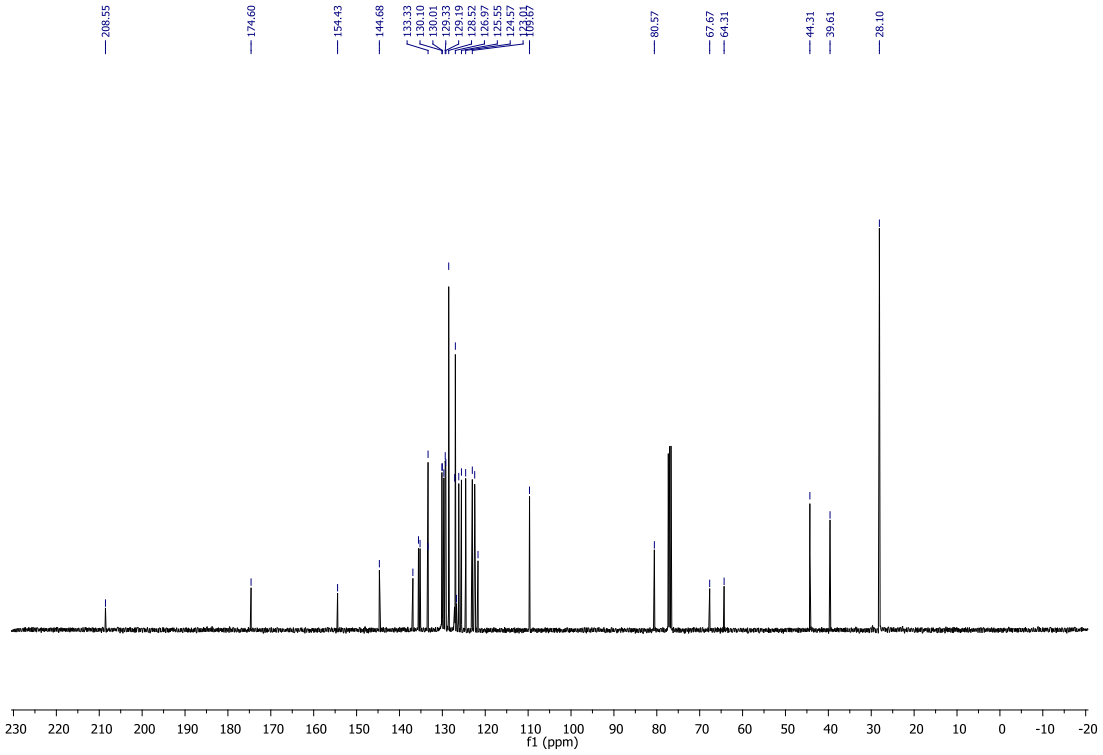
3n *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(4-bromobenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate



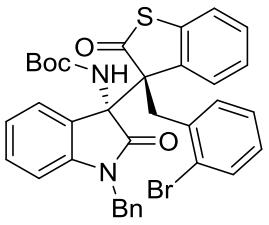


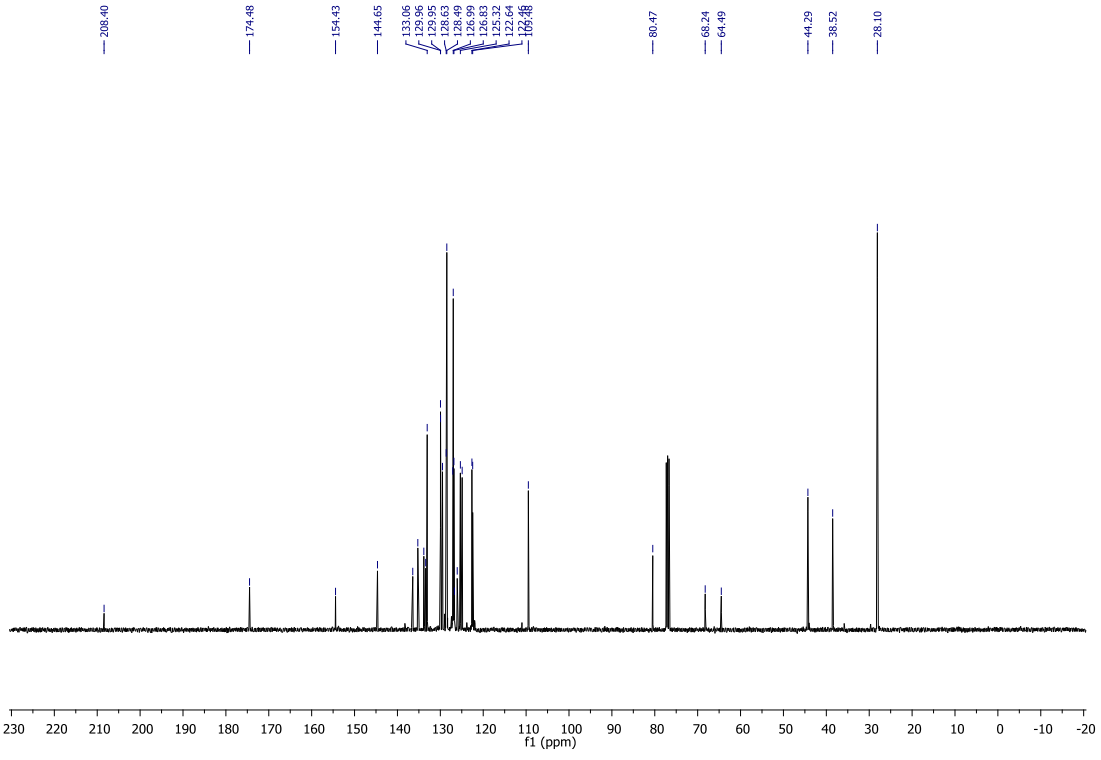
3o *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(3-bromobenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate



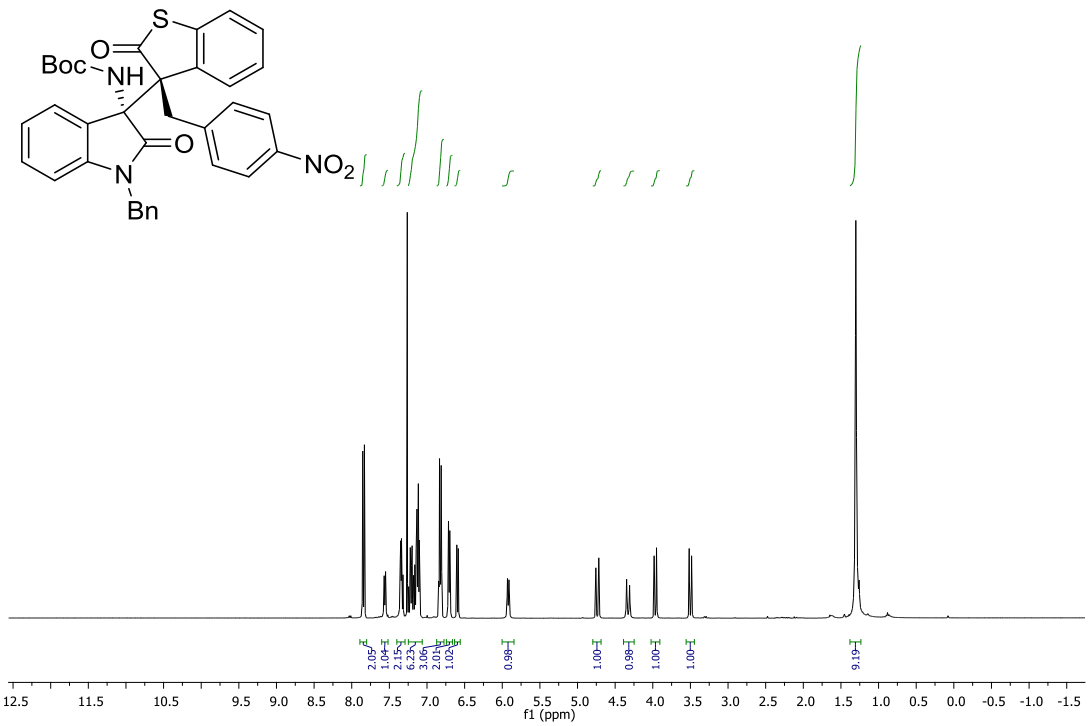


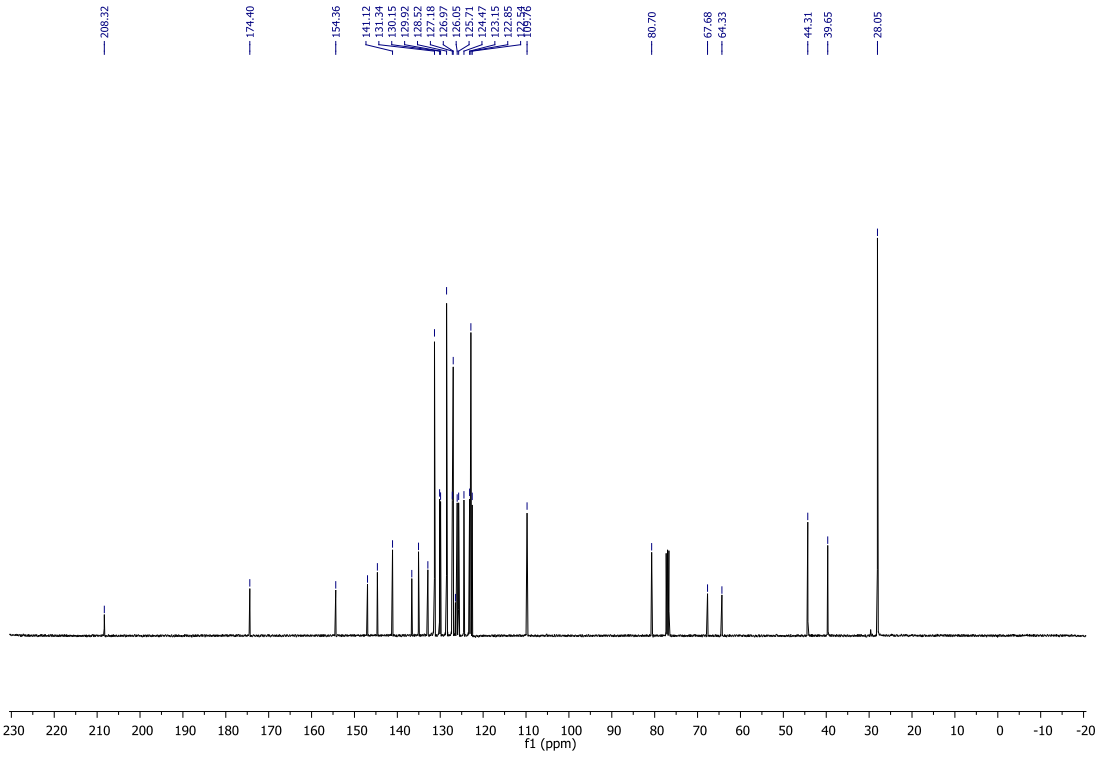
3p *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(2-bromobenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate



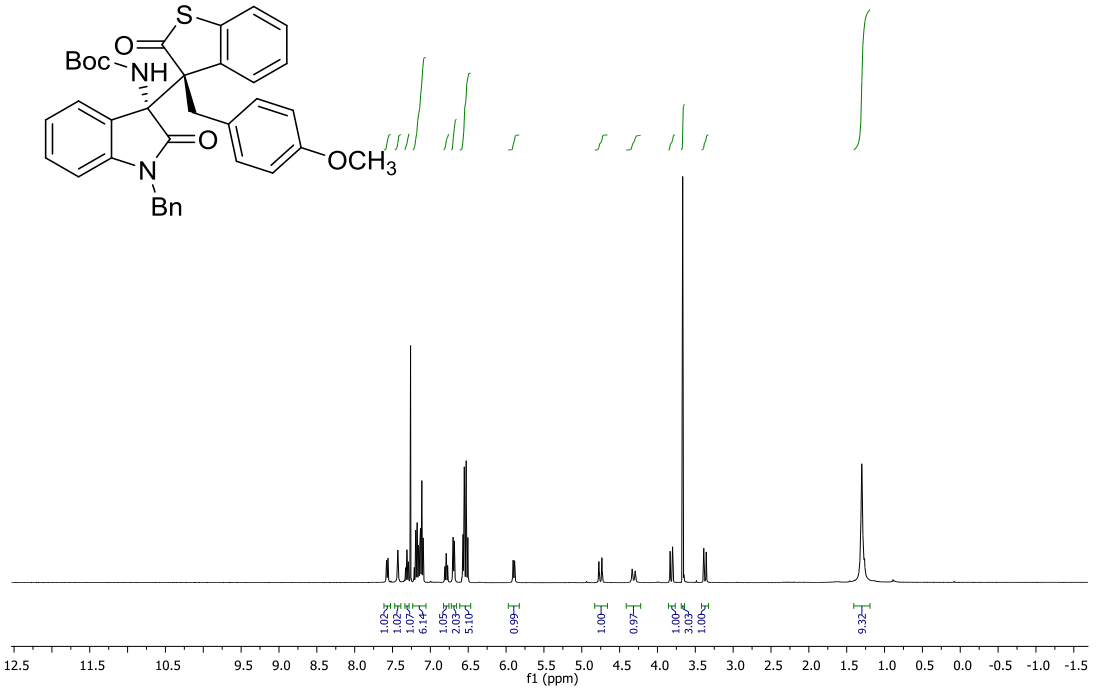


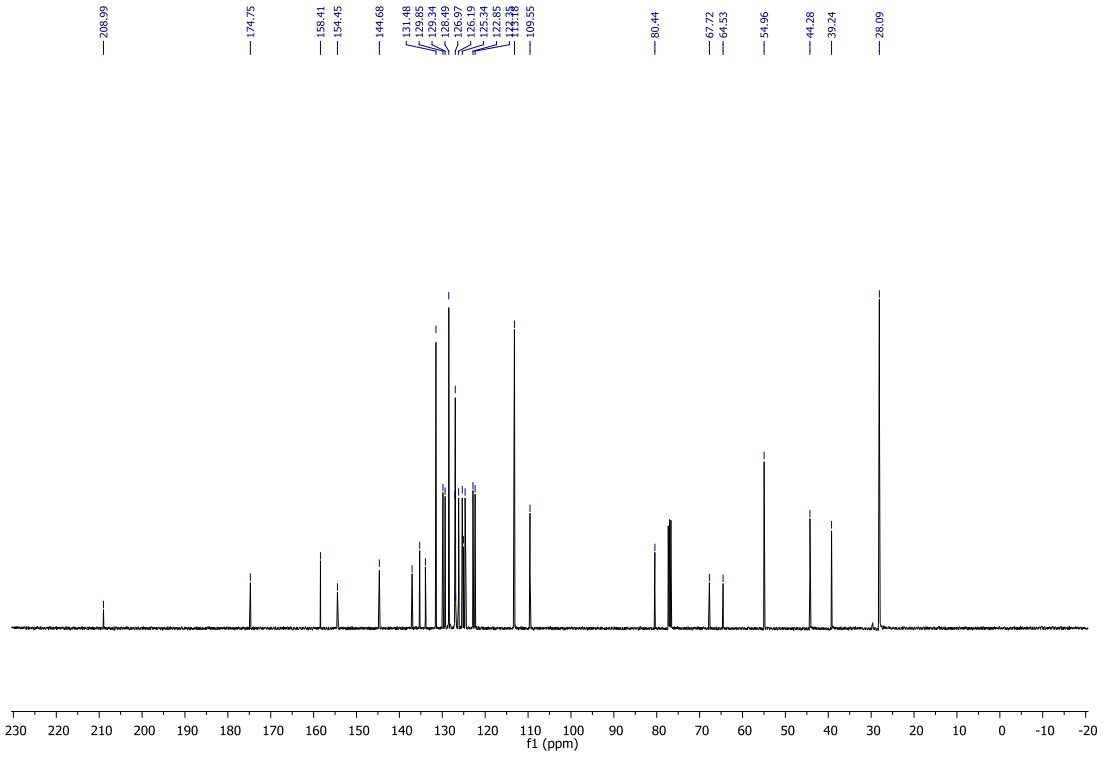
3q *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(4-nitrobenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate



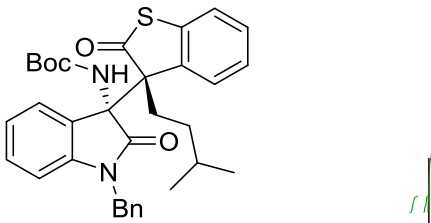


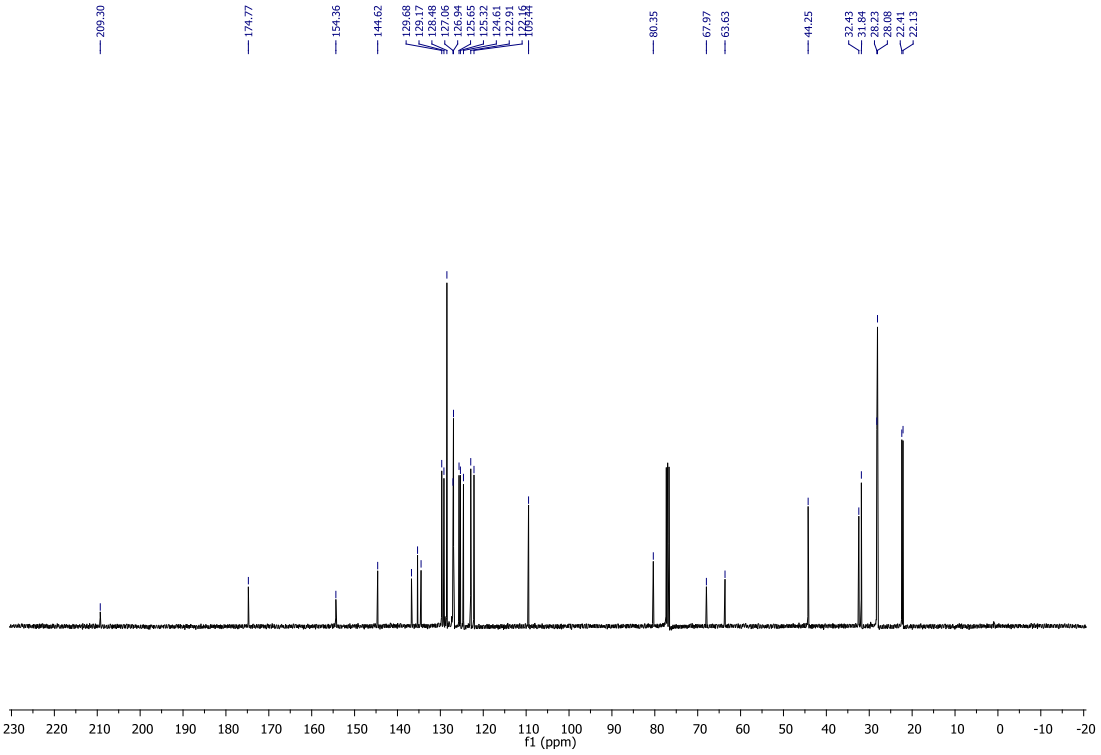
3r *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(4-methoxybenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate



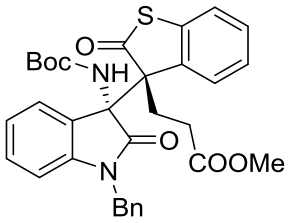


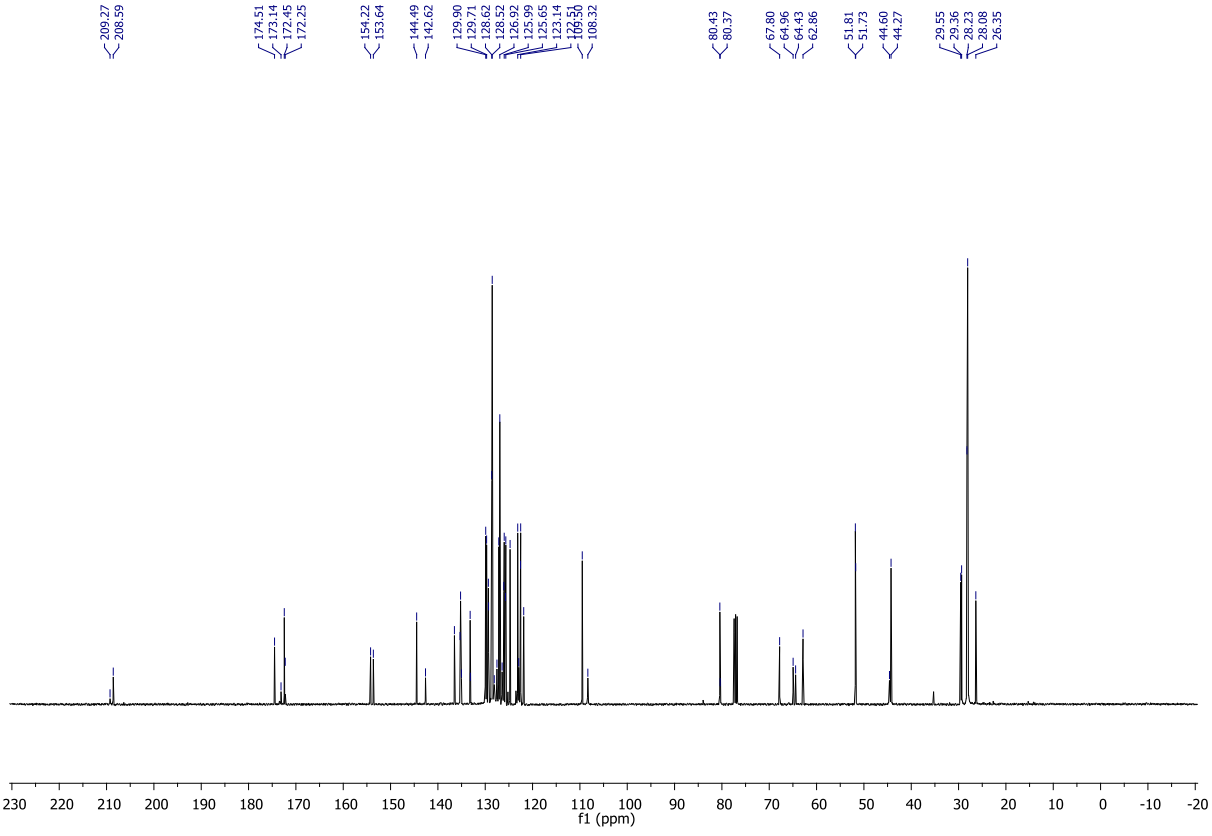
3s *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-isopentyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate



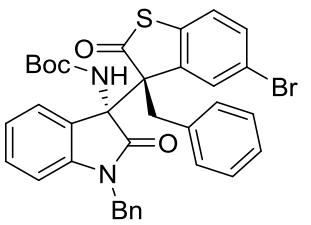


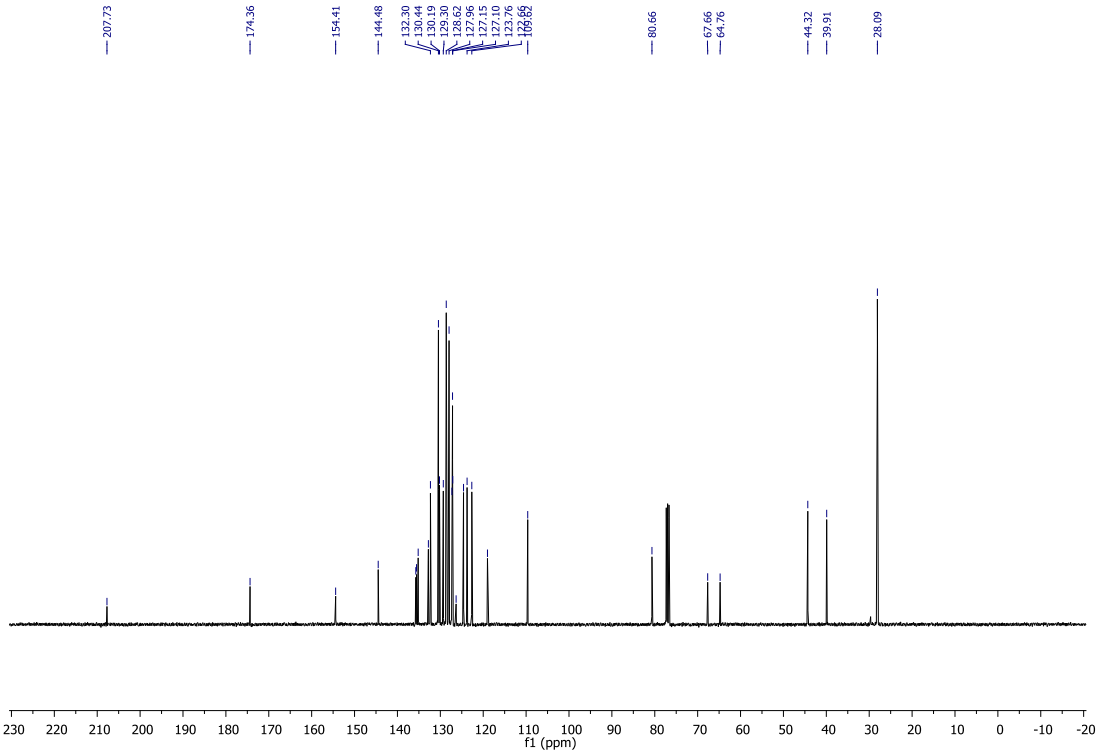
3t Methyl 3-(3-(1-benzyl-3-((*tert*-butoxycarbonyl)amino)-2-oxoindolin-3-yl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)propanoate



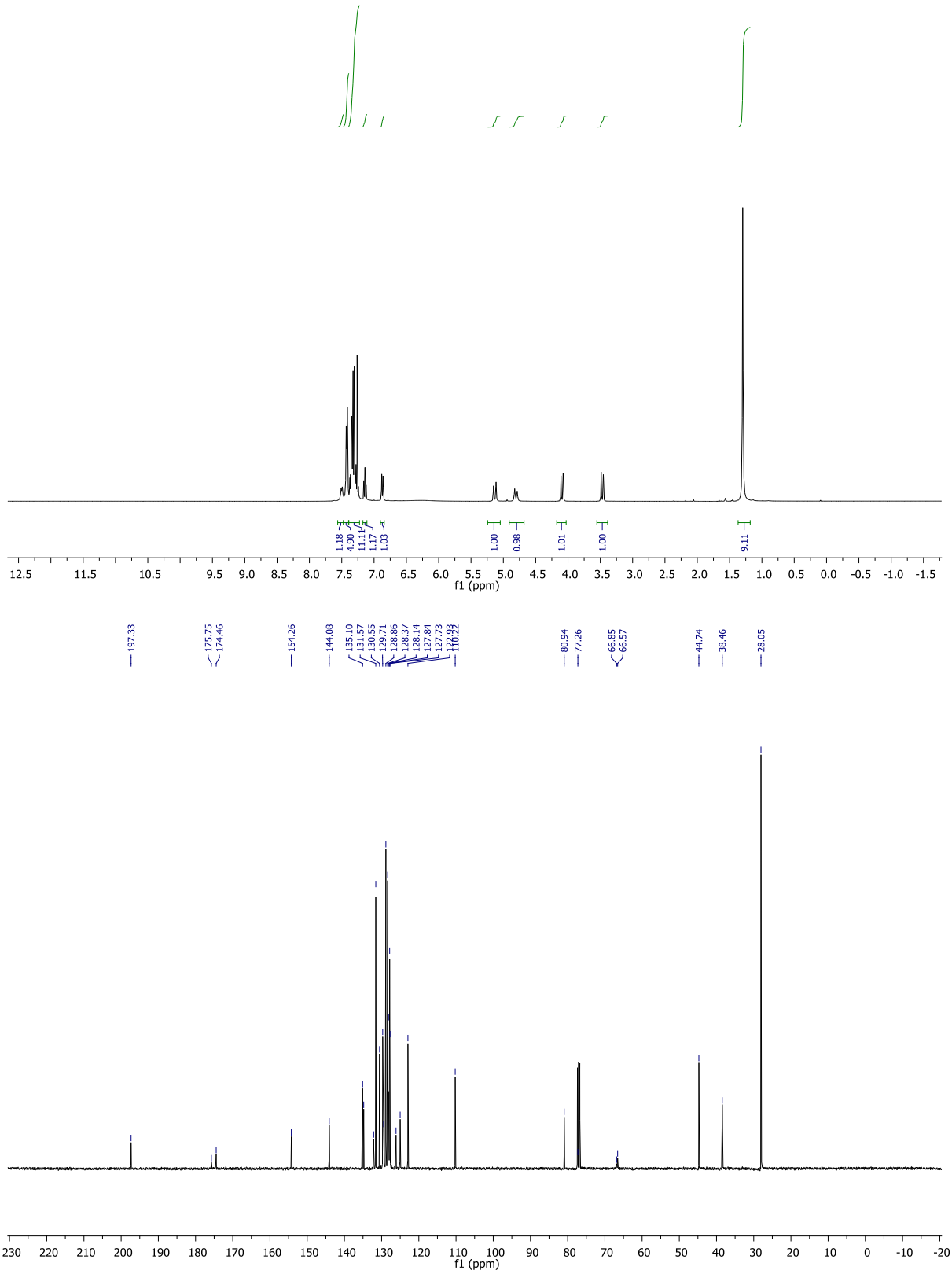


3u *tert*-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-5-bromo-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate





(6a‘) *tert*-butyl (1-benzyl-3-(5-benzyl-4-oxo-3-phenyl-2-thioxothiazolidin-5-yl)-2-oxoindolin-3-yl)carbamate

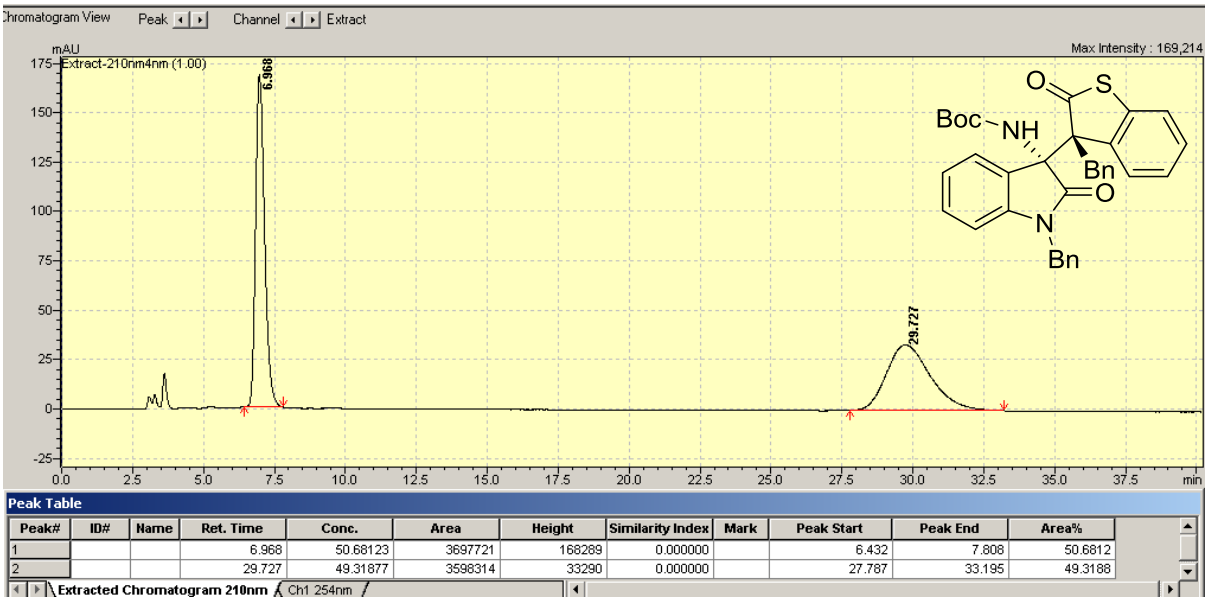


8 HPLC Analysis of Compounds

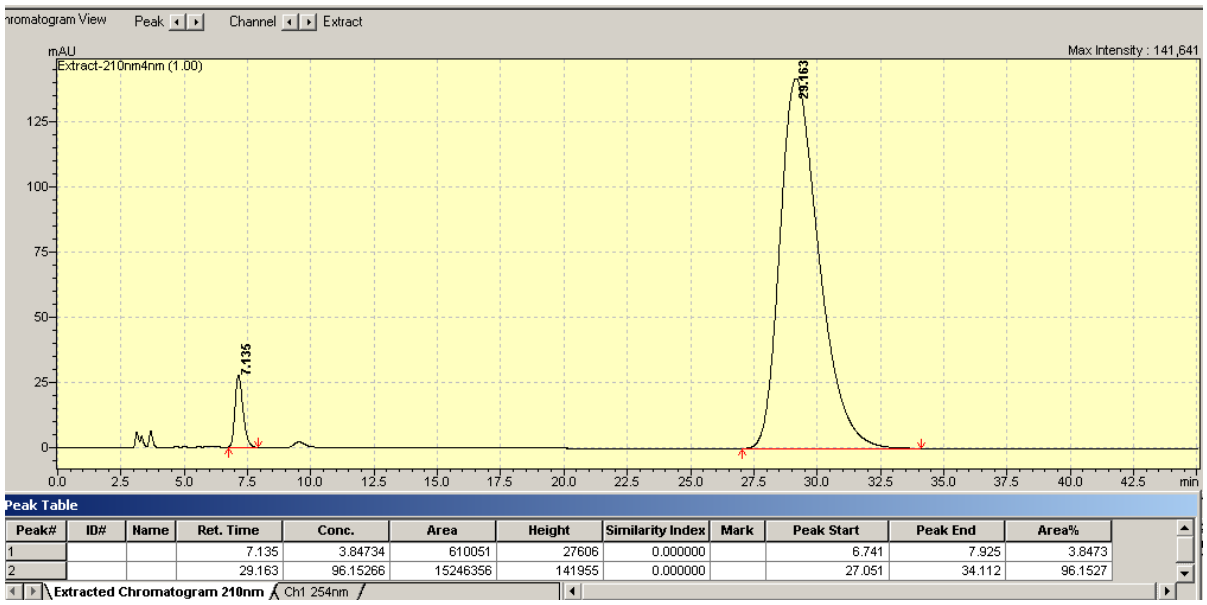
tert-Butyl ((*R*)-*N*-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3a)

HPLC **3a**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate



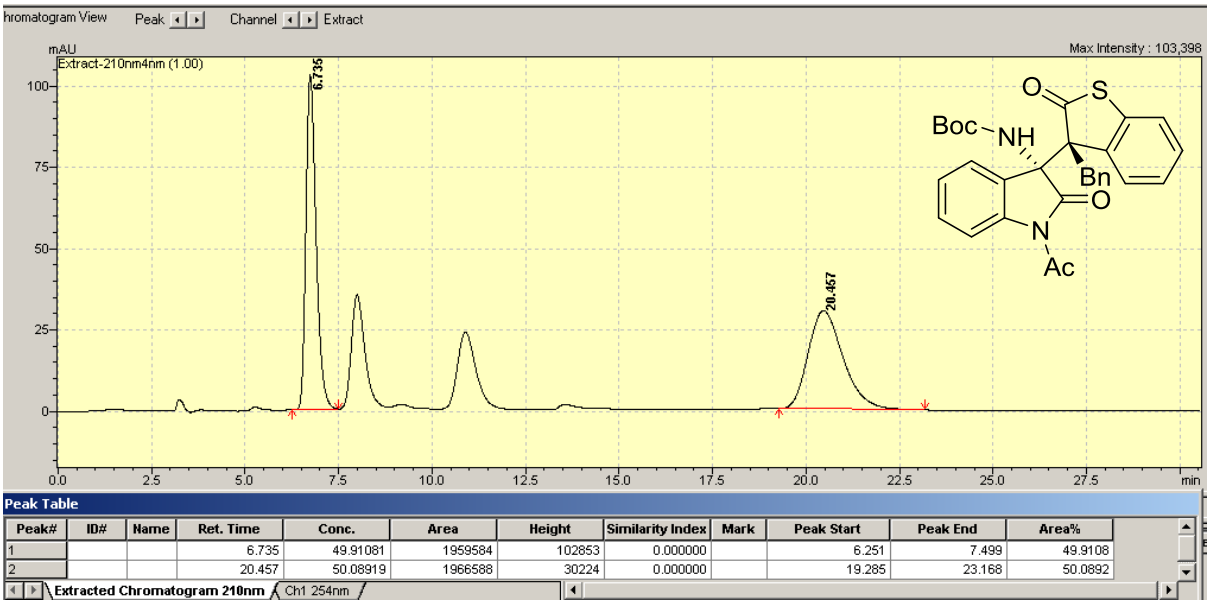
Chiral *ee* = 92 %



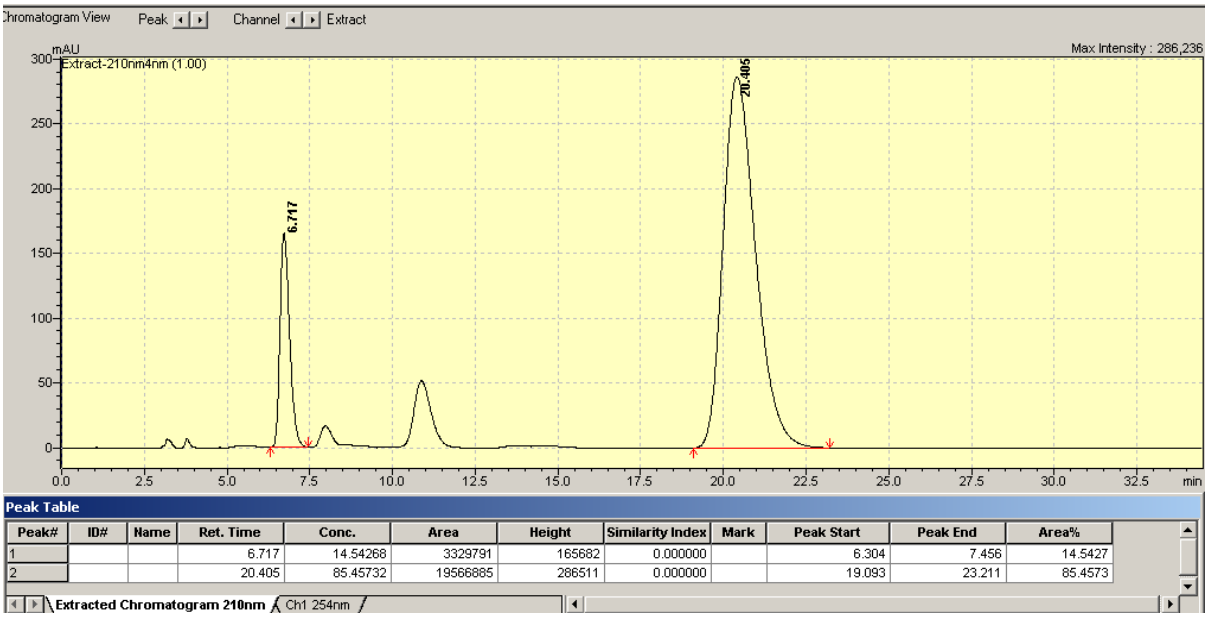
tert-Butyl ((_R_)-1-acetyl-3-((_R_)-3-benzyl-2-oxo-2,3-dihydrobenzo[_b_]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3b) – major diastereoisomer

HPLC **3b**: Chiral column AD, *n*-heptane/isopropanol (90:10), 1.0 mL, 210 nm, 25 °C

Racemate



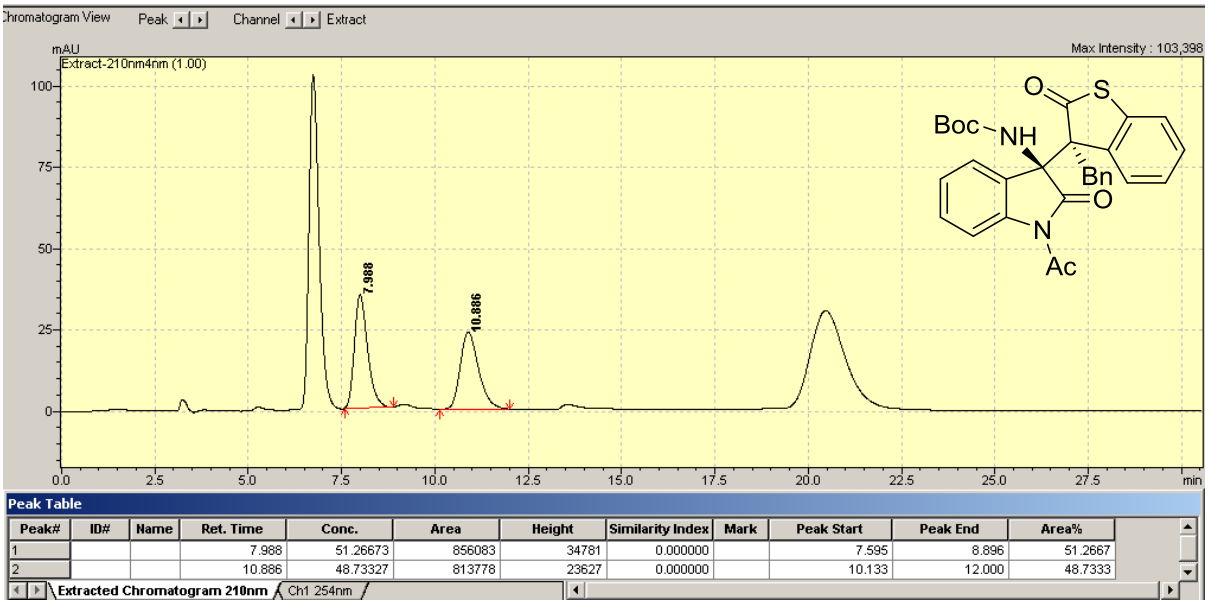
Chiral *ee* = 71 %



***tert*-Butyl ((*S*)-1-acetyl-3-((*S*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3b‘) - minor diastereoisomer**

HPLC **3b‘**: Chiral column AD, *n*-heptane/isopropanol (90:10), 1.0 mL, 210 nm, 25 °C

Racemate

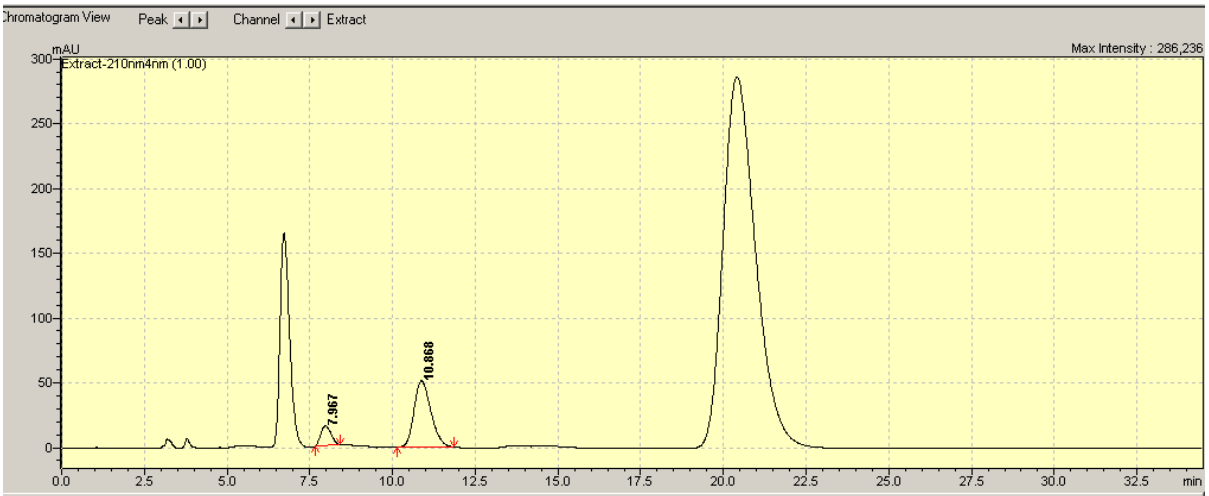


Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			7.988	51.26673	856083	34781	0.000000		7.595	8.896	51.2667
2			10.886	48.73327	813778	23627	0.000000		10.133	12.000	48.7333

Extracted Chromatogram 210nm | Ch1 254nm

Chiral *ee* = 69 %



Peak Table

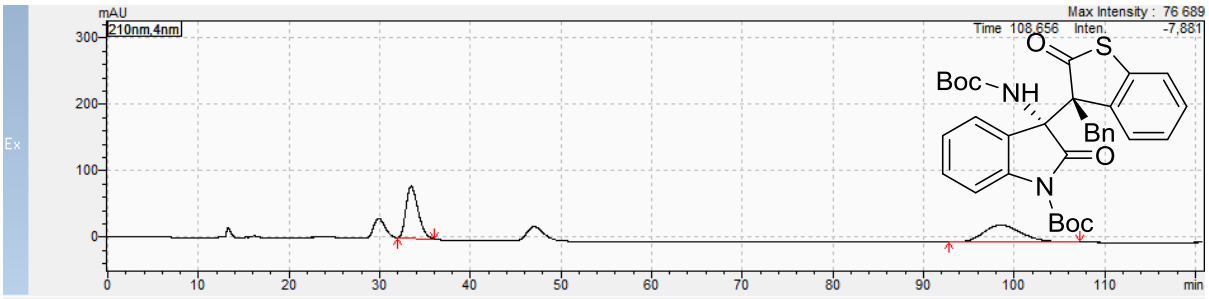
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			7.967	15.54646	333334	15378	0.000000		7.669	8.416	15.5465
2			10.868	84.45354	1810782	51153	0.000000		10.144	11.861	84.4535

Extracted Chromatogram 210nm | Ch1 254nm

***tert*-Butyl 3-(3-benzyl-2-oxo-2,3-dihydrobenzo[b]thiophen-3-yl)-3-((*tert*-butoxycarbonyl)amino)-2-oxoindolin-*N*-1-carboxylate (3c) – major diastereoisomer**

HPLC **3c**: Chiral column AD, *n*-heptane/isopropanol (95:5), 0.25 mL, 210 nm, 15 °C

Racemate

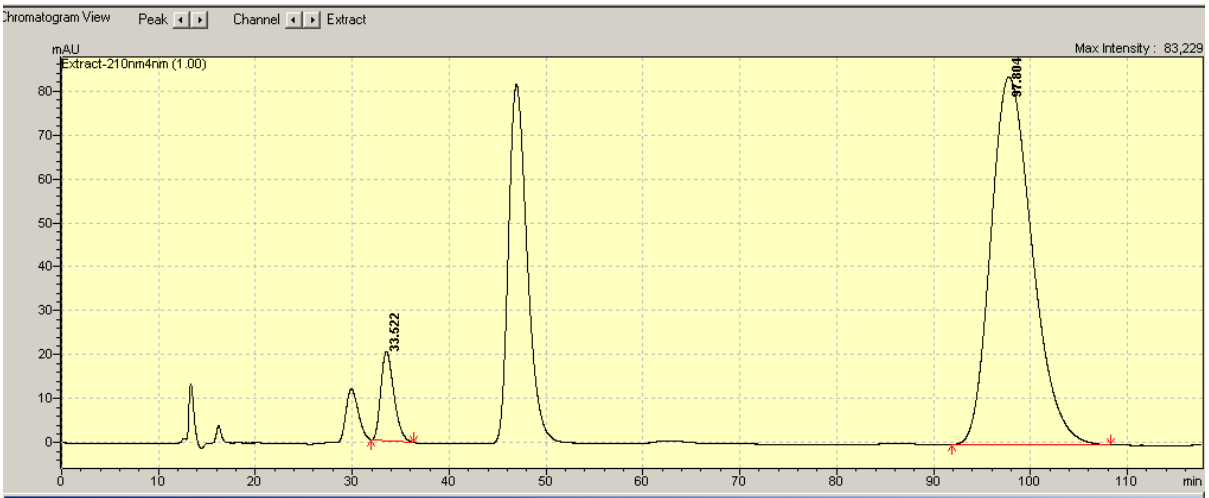


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	33,463	48,81539	7314371	78493	0,000000	M	31,957	36,032	48,815
2	98,520	51,18461	7669368	25953	0,000000	M	92,747	107,296	51,185

Chiral *ee* = 86 %



Peak Table

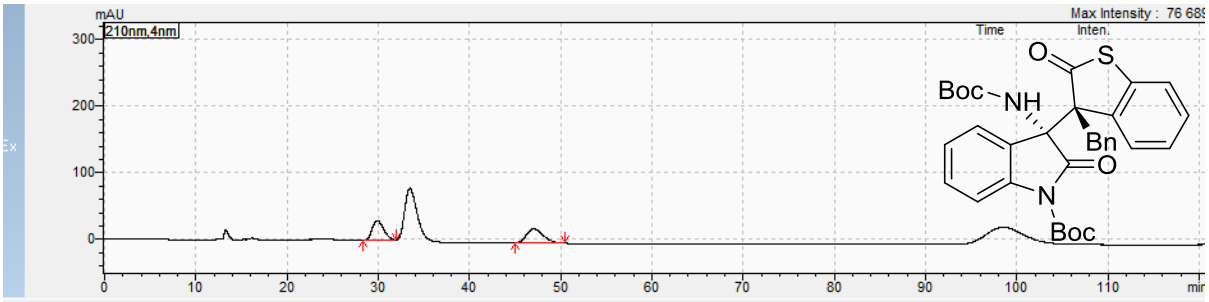
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			33.522	7.12287	1904161	20263	0.000000		31.989	36.363	7.1229
2			97.804	92.87713	24828883	83683	0.000000		91.893	108.288	92.8771

Extracted Chromatogram 210nm | Ch1 254nm

***tert*-Butyl 3-(3-benzyl-2-oxo-2,3-dihydrobenzo[b]thiophen-3-yl)-3-((*tert*-butoxycarbonyl)amino)-2-oxoindolin-*N*-1-carboxylate (3c‘) – minor diastereoisomer**

HPLC **3c‘**: Chiral column AD, *n*-heptane/isopropanol (95:5), 0.25 mL, 210 nm, 15 °C

Racemate

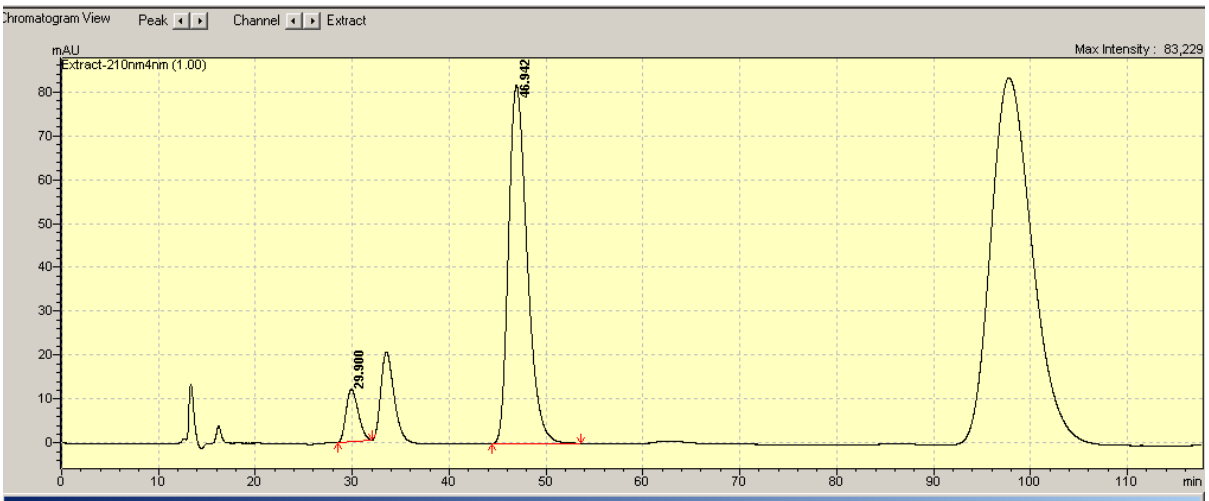


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	29,871	48,23362	2607036	29853	0,000000	M	28,373	31,957	48,234
2	47,024	51,76638	2797983	21496	0,000000	M	45,003	50,475	51,766

Chiral *ee* = 82 %



Peak Table

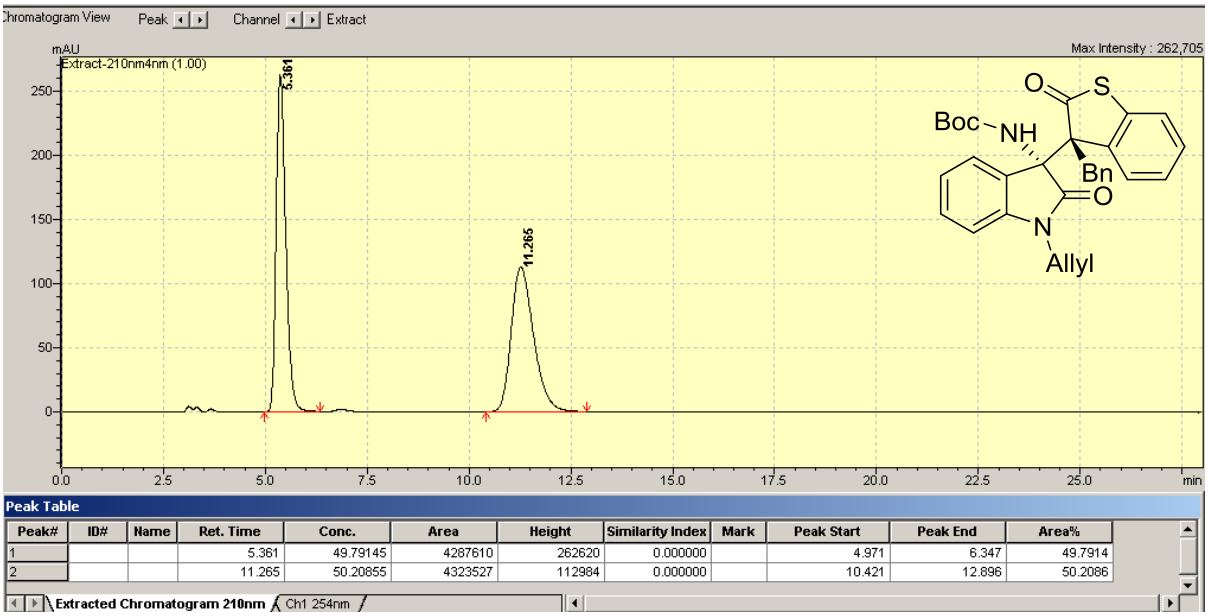
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			29.900	8.73598	1044296	11903	0.000000		28.512	32.053	8.7360
2			46.942	91.26402	10909663	81595	0.000000		44.416	53.589	91.2640

Extracted Chromatogram 210nm | Ch1 254nm

***tert*-Butyl ((*R*)-*N*-1-allyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3d)**

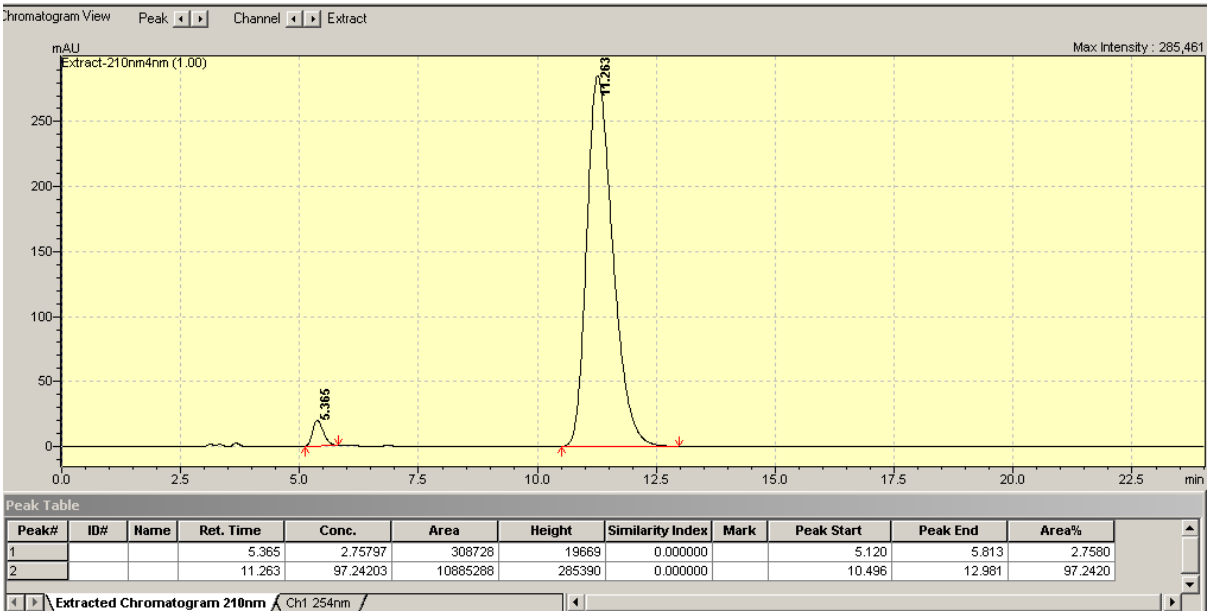
HPLC **3d**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate



Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			5.361	49.79145	4287610	262620	0.000000		4.971	6.347	49.7914
2			11.265	50.20855	4323527	112984	0.000000		10.421	12.896	50.2086

Chiral *ee* = 94 %

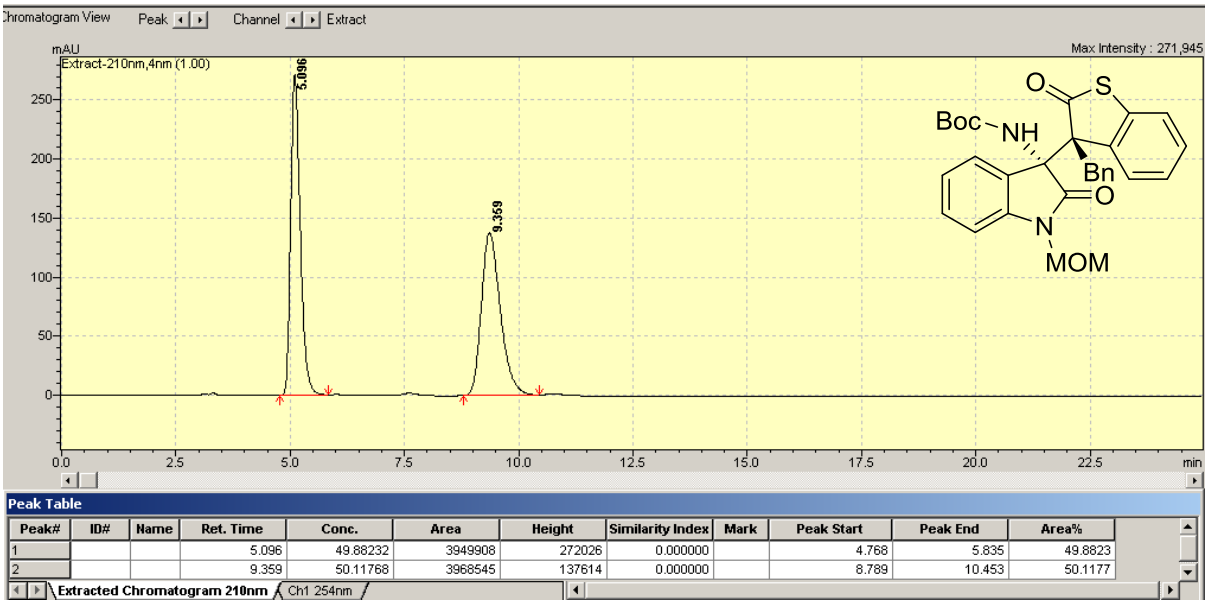


Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			5.365	2.75797	308728	19669	0.000000		5.120	5.813	2.7580
2			11.263	97.24203	10885288	285390	0.000000		10.496	12.981	97.2420

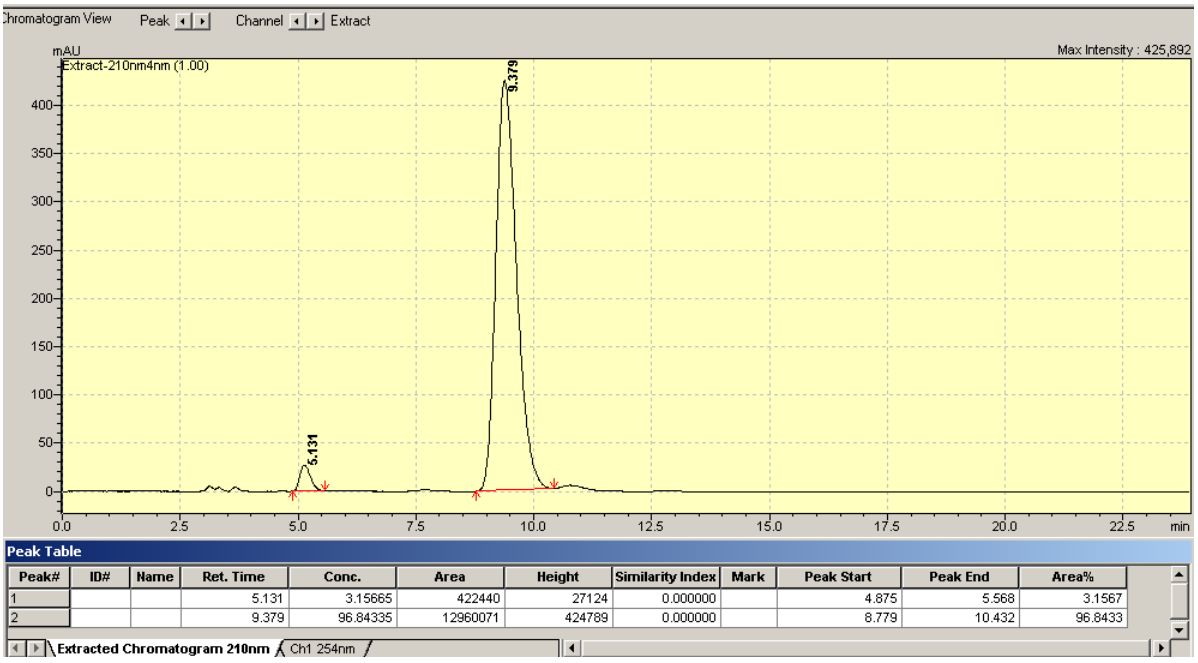
tert-Butyl ((*R*)-3-(3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)- (*R*)-1-(methoxymethyl)-2-oxoindolin-3-yl)carbamate (3e)

HPLC **3e**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate



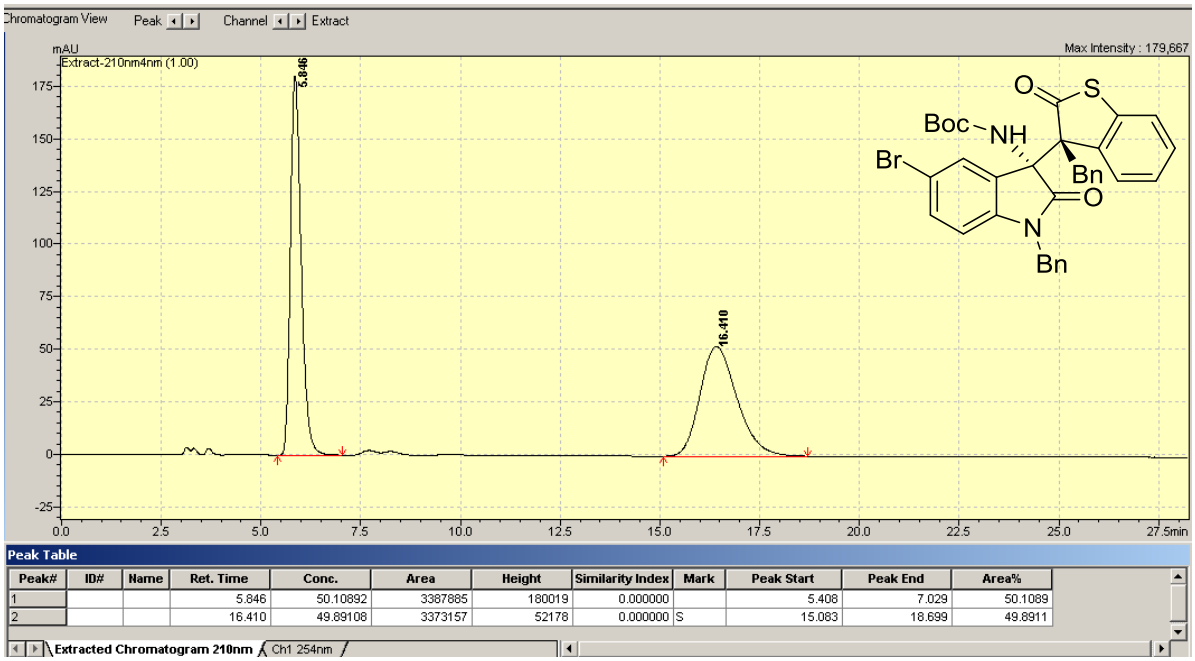
Chiral *ee* = 94 %



tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-5-bromo-2-oxoindolin-3-yl)carbamate (3h)

HPLC **3h**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate

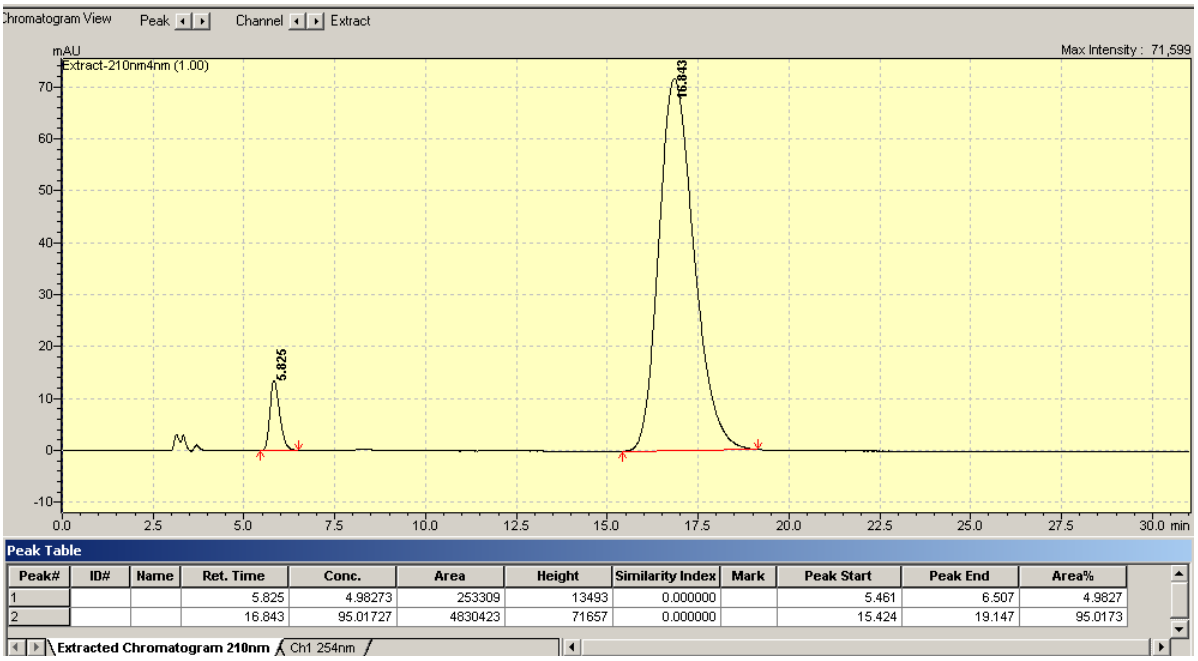


Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			5.846	50.10892	3387885	180019	0.000000		5.408	7.029	50.1089
2			16.410	49.89108	3373157	52178	0.000000	S	15.083	18.699	49.8911

Extracted Chromatogram 210nm | Ch1 254nm

Chiral *ee* = 90 %



Peak Table

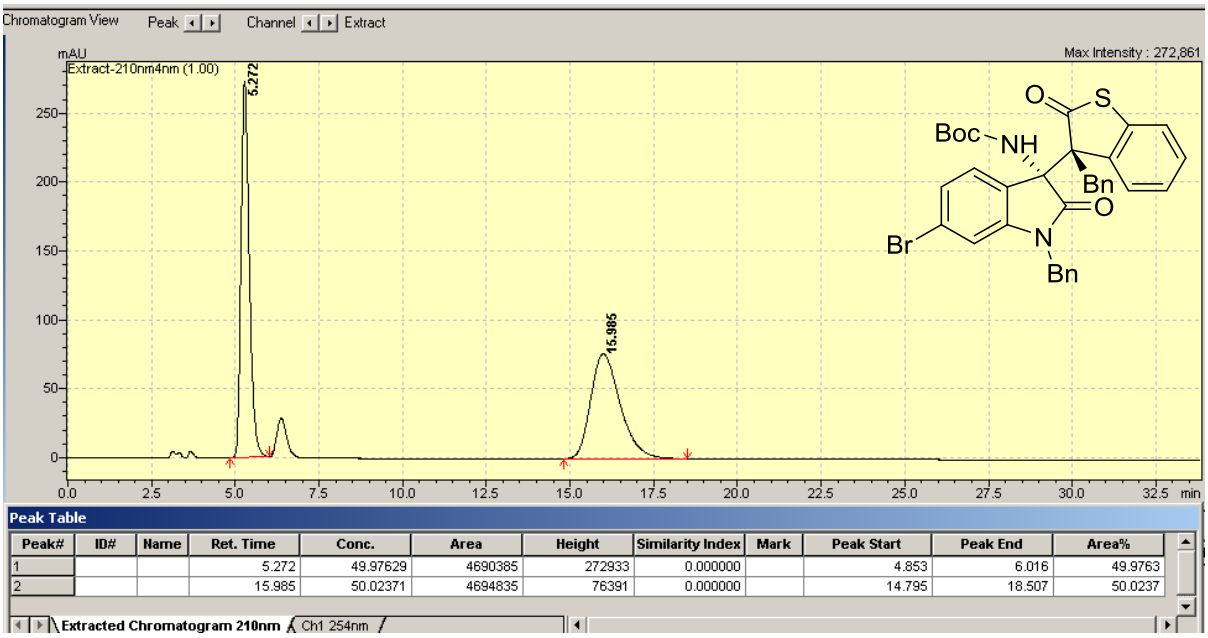
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			5.825	4.98273	253309	13493	0.000000		5.461	6.507	4.9827
2			16.843	95.01727	4830423	71657	0.000000		15.424	19.147	95.0173

Extracted Chromatogram 210nm | Ch1 254nm

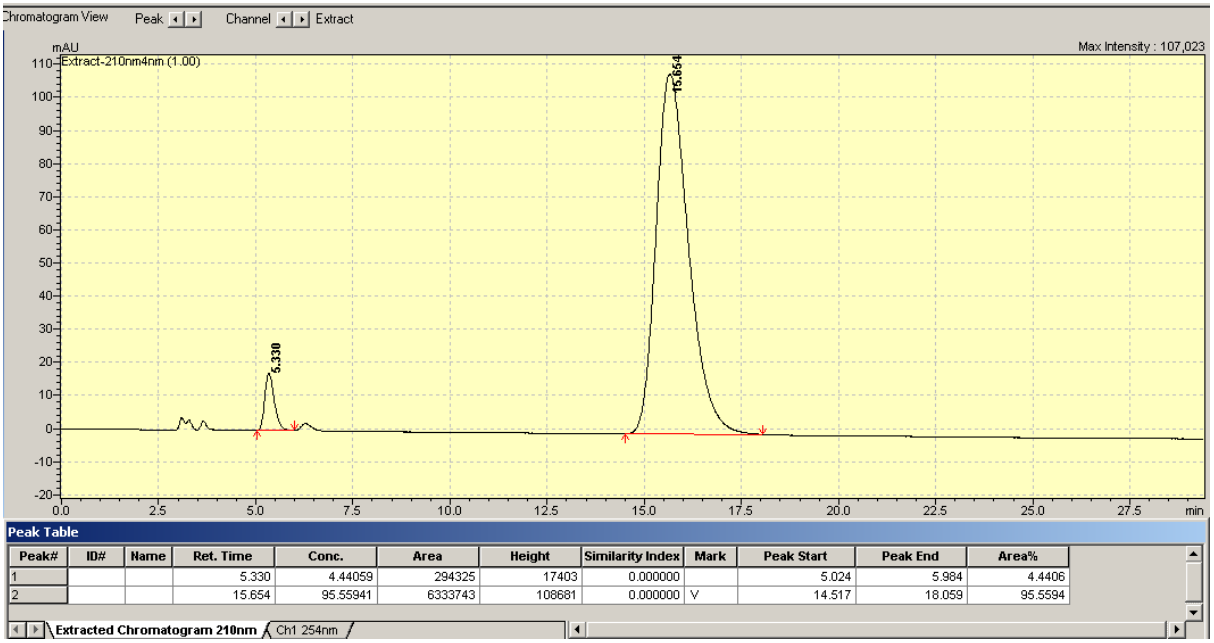
tert-Butyl ((*R*)-1-benzyl-3-((*R*)3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-6-bromo-2-oxoindolin-3-yl)carbamate (3i)

HPLC **3i**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate



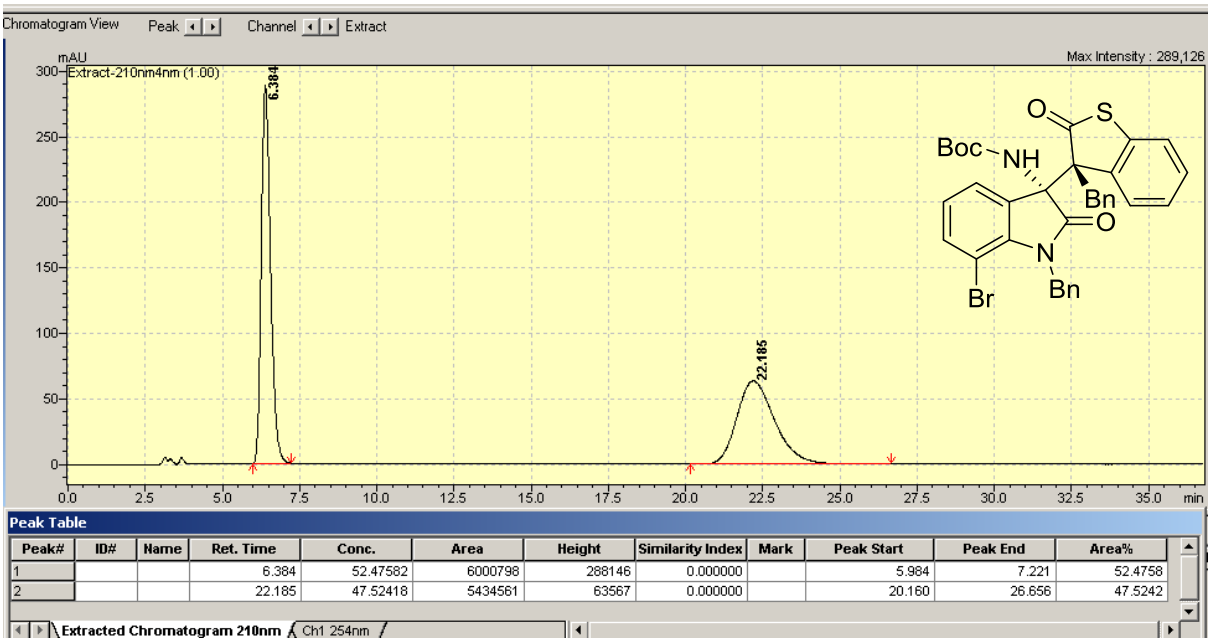
Chiral *ee* = 91 %



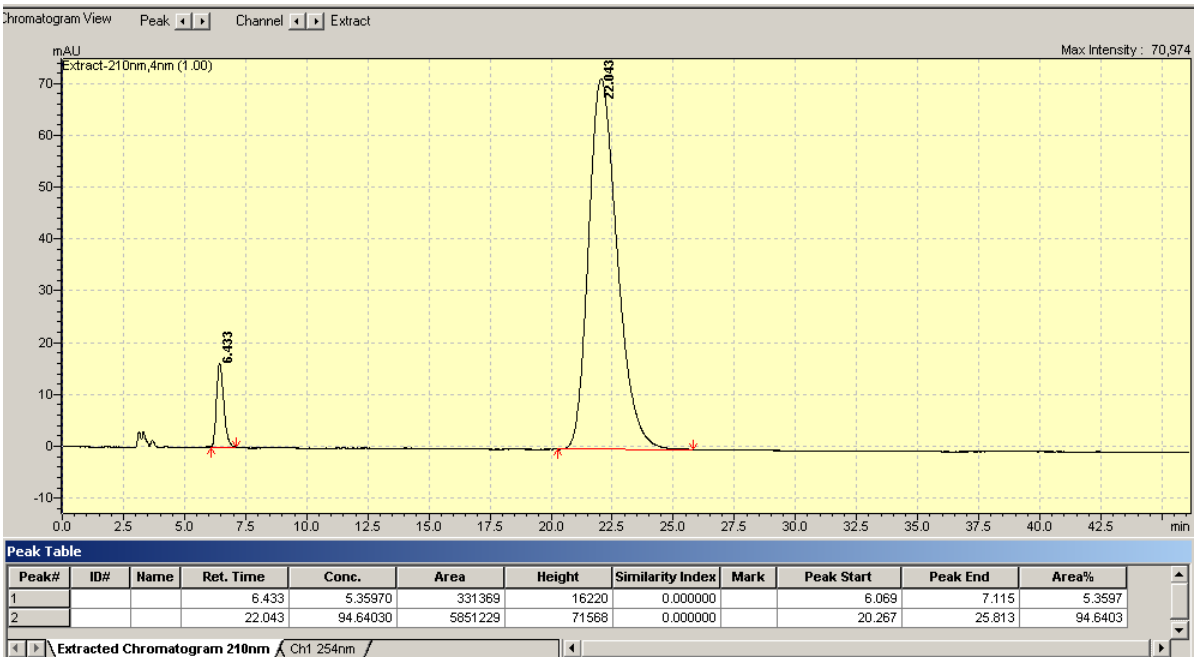
tert-Butyl ((*R*)-1-benzyl-3-((*R*)3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-7-bromo-2-oxoindolin-3-yl)carbamate (3j)

HPLC **3j**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate



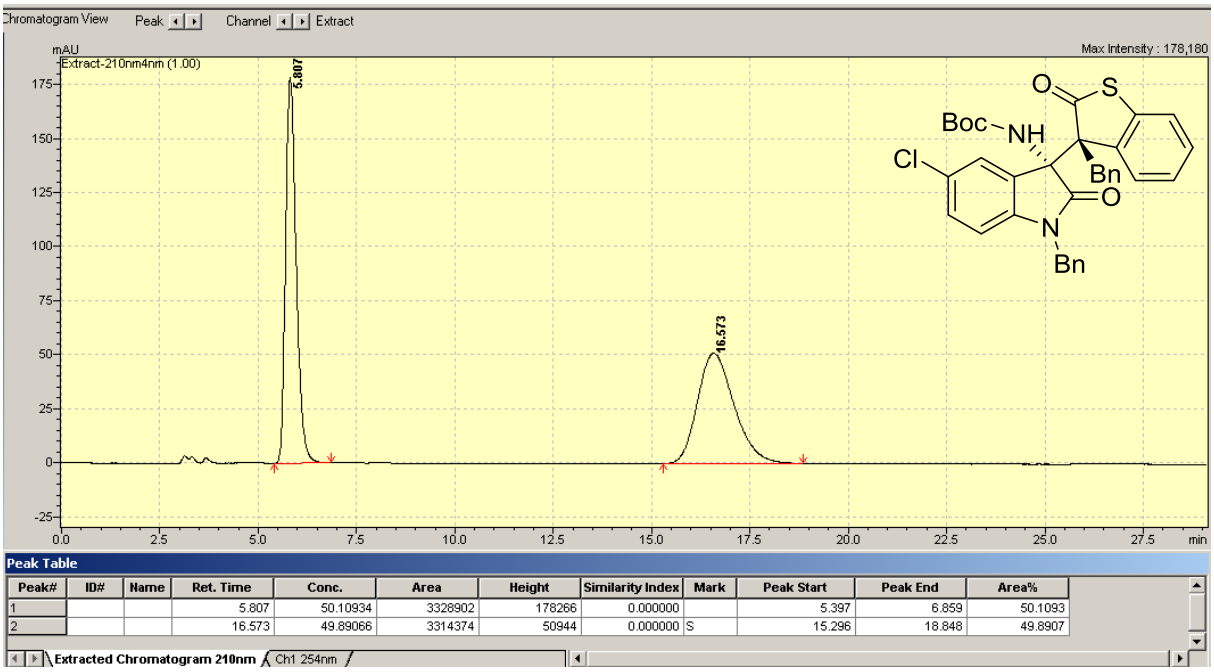
Chiral *ee* = 89 %



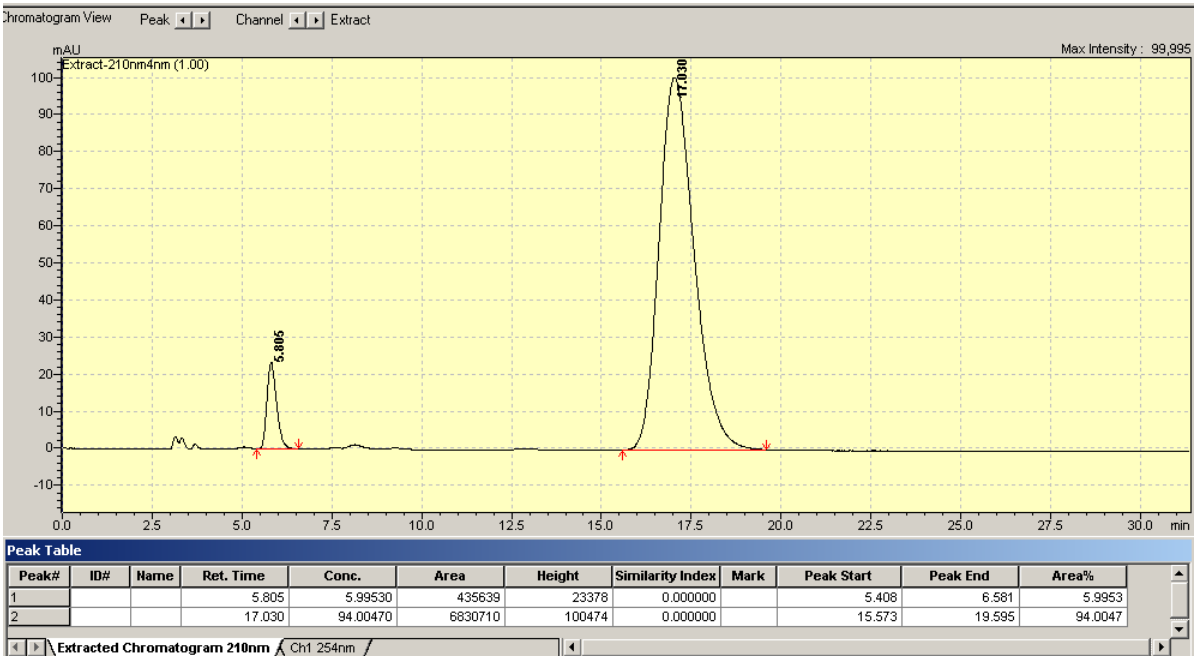
tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-5-chloro-2-oxoindolin-3-yl)carbamate (3k)

HPLC **3k**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate



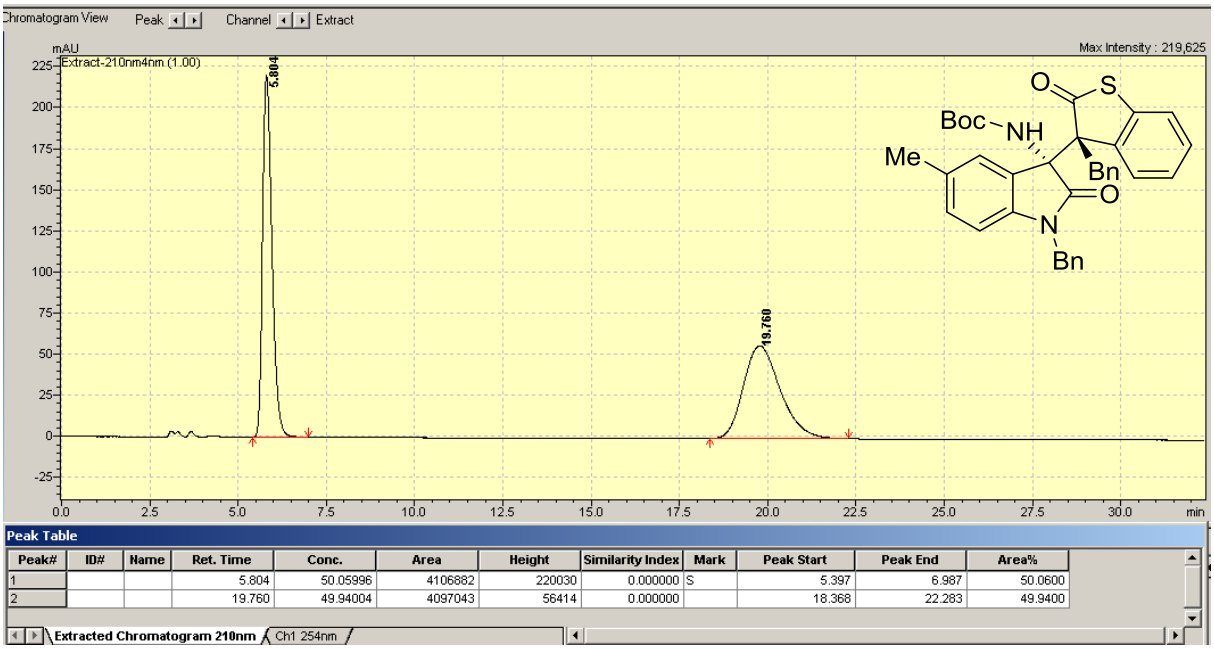
Chiral *ee* = 88 %



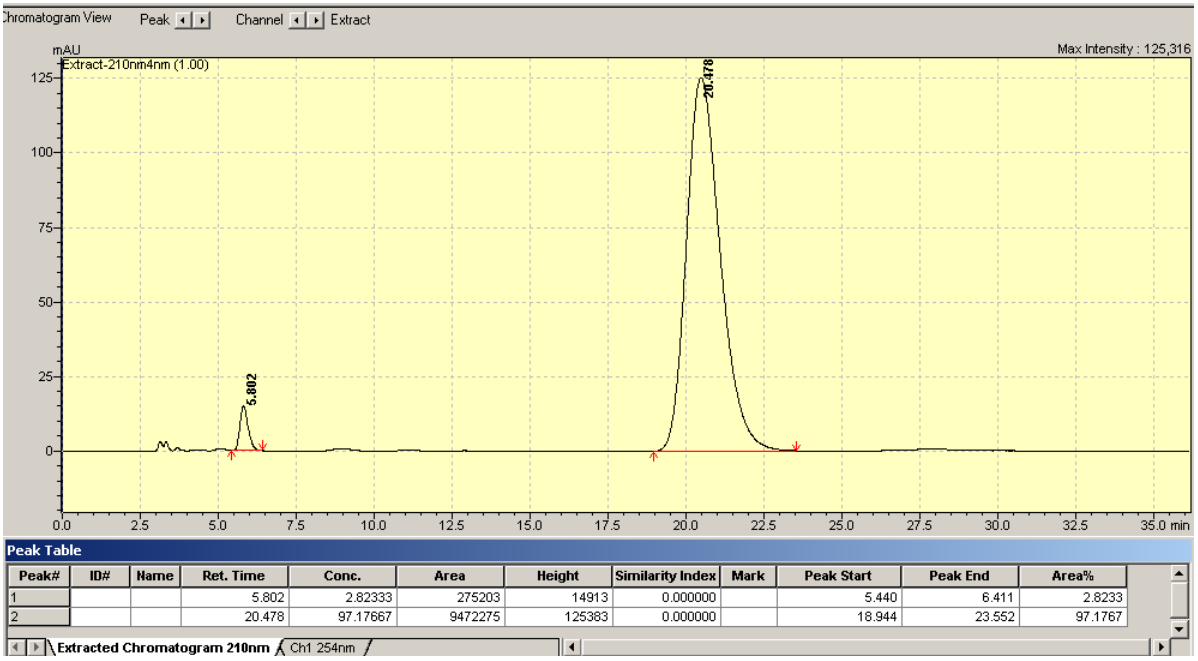
tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl) 5-methyl-2-oxoindolin-3-yl)carbamate (3l)

HPLC **3l**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate



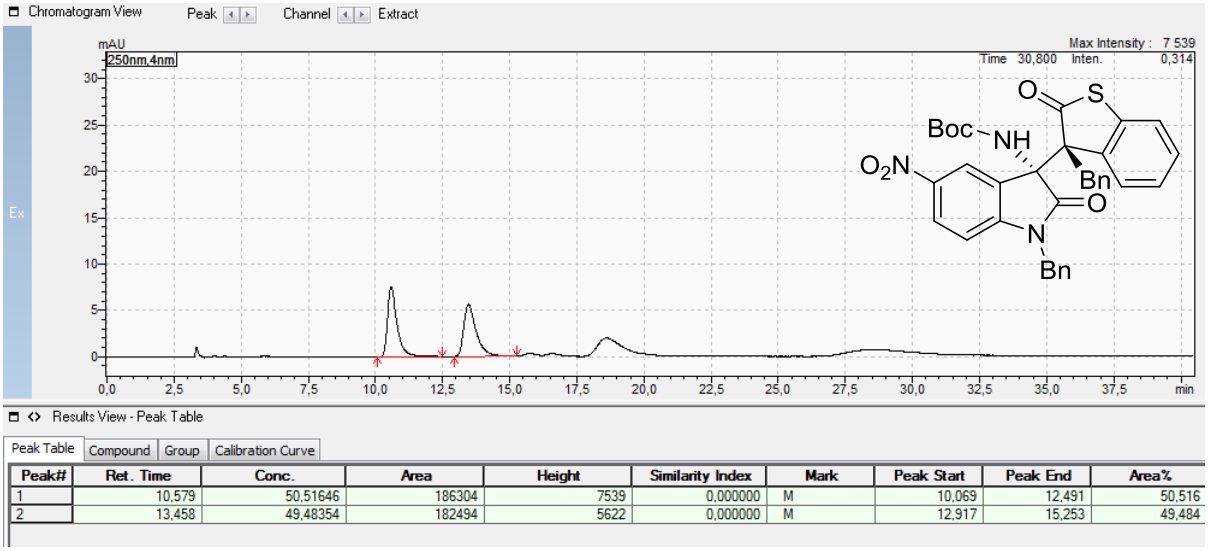
Chiral *ee* = 94 %



tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-5-nitro-2-oxoindolin-3-yl)carbamate (3m) – major diastereoizomer

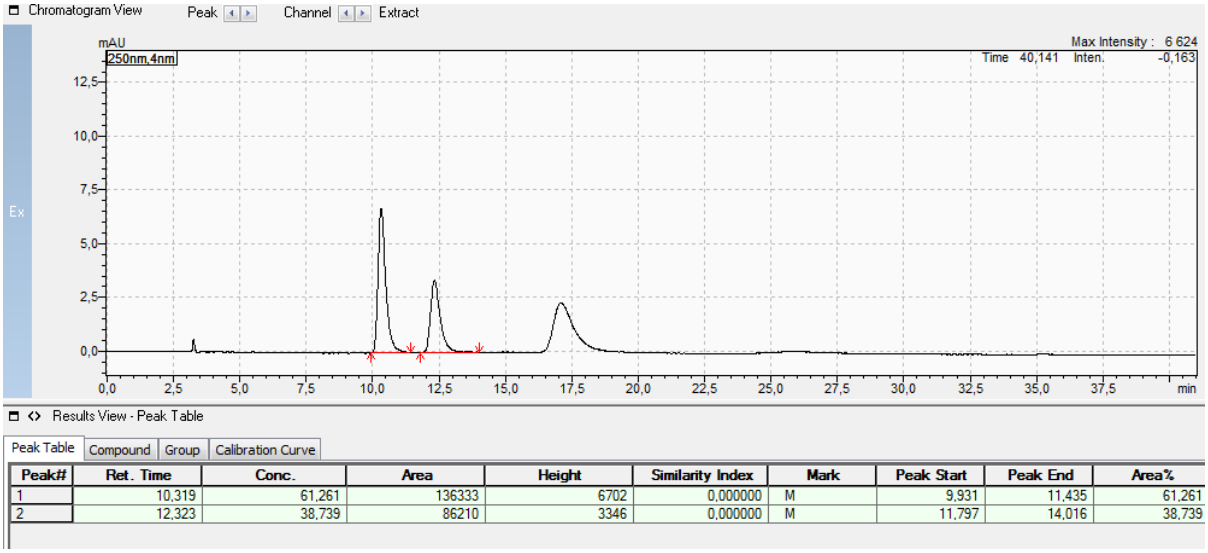
HPLC **3m**: Chiral column IB, *n*-heptane/isopropanol (95:5), 1.0 mL, 250 nm, 25 °C

Racemate



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,579	50,51646	186304	7539	0,000000	M	10,069	12,491	50,516
2	13,458	49,48354	182494	5622	0,000000	M	12,917	15,253	49,484

Chiral *ee* = 23 %

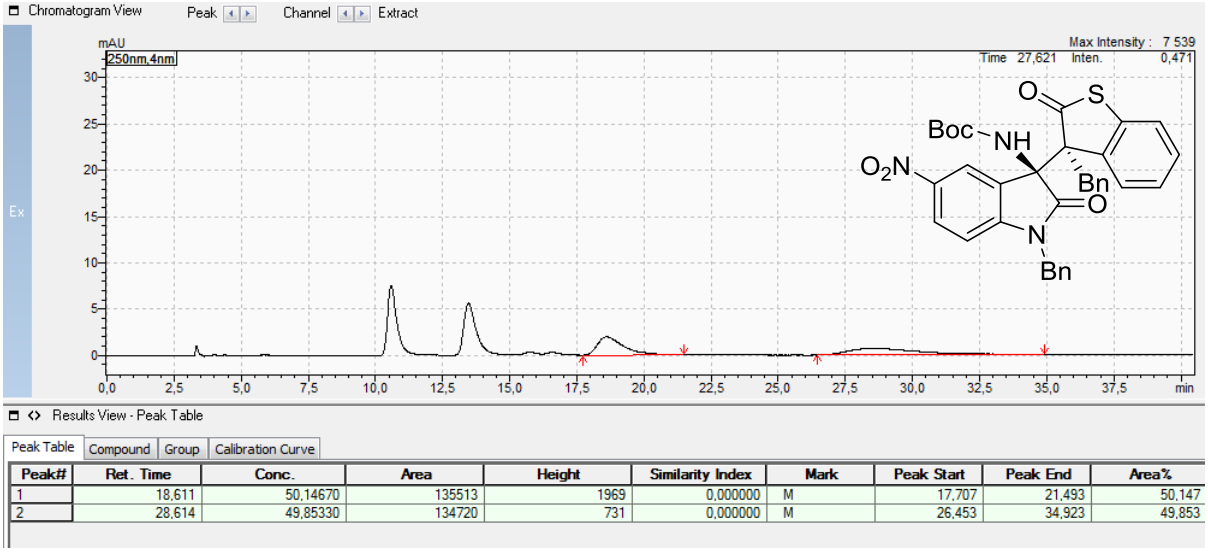


Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,319	61,261	136333	6702	0,000000	M	9,931	11,435	61,261
2	12,323	38,739	86210	3346	0,000000	M	11,797	14,016	38,739

tert-Butyl ((*S*)-1-benzyl-3-((*S*)-3-benzyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-5-nitro-2-oxoindolin-3-yl)carbamate (3m‘) – minor diastereoizomer

HPLC **3m‘**: Chiral column IB, *n*-heptane/isopropanol (95:5), 1.0 mL, 250 nm, 25 °C

Racemate

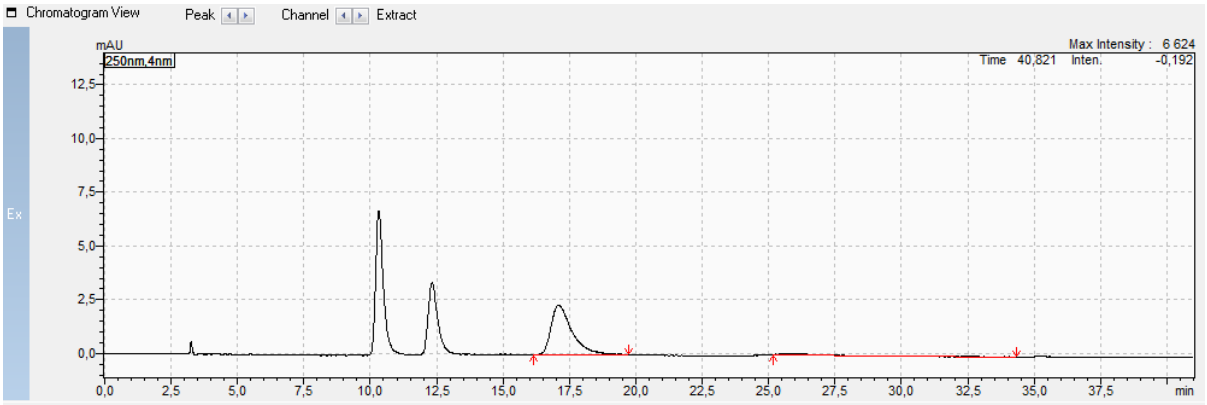


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	18,611	50,14670	135513	1969	0,000000	M	17,707	21,493	50,147
2	28,614	49,85330	134720	731	0,000000	M	26,453	34,923	49,853

Chiral *ee* = 99 %



Results View - Peak Table

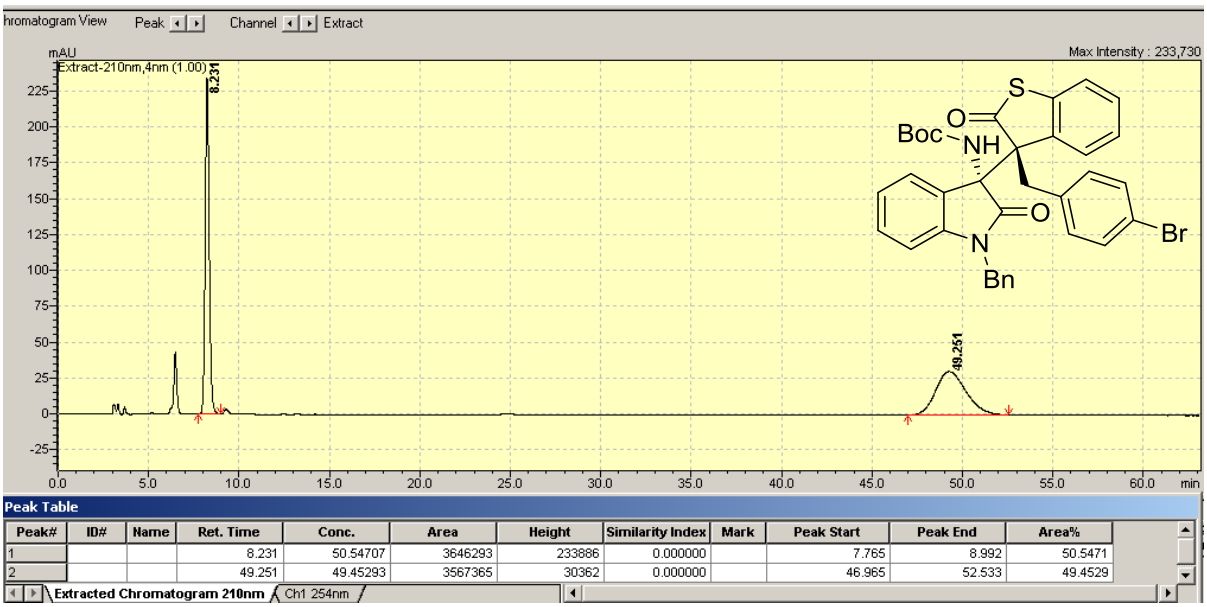
Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	17,071	99,599	125948	2321	0,000000	M	16,149	19,733	99,599
2	26,038	0,401	507	55	0,000000	M	25,173	34,336	0,401

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(4-bromobenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3n)

HPLC **3n**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate

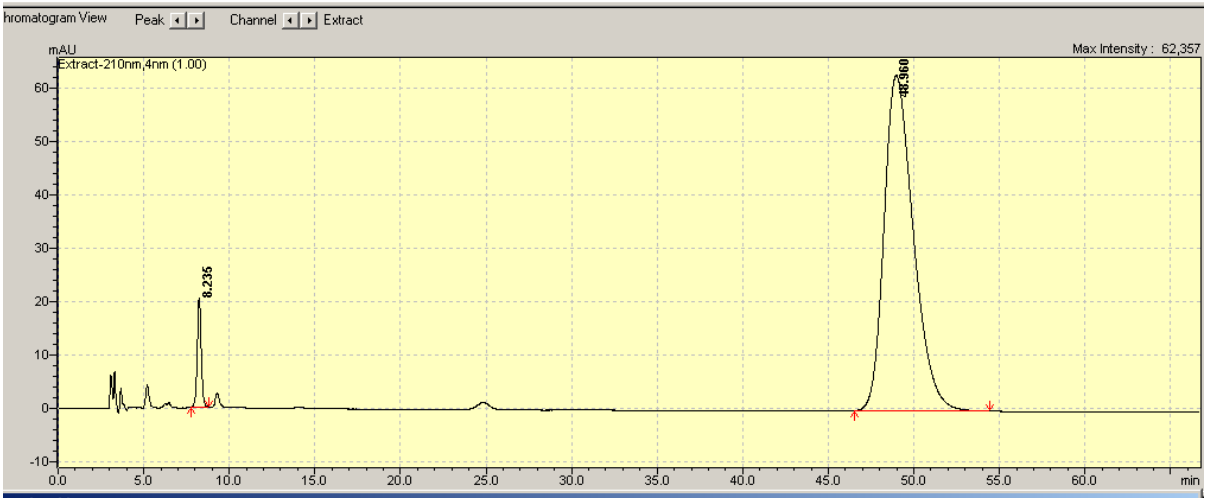


Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.231	50.54707	3646293	233886	0.000000		7.765	8.992	50.5471
2			49.251	49.45293	3567365	30362	0.000000		46.965	52.533	49.4529

Extracted Chromatogram 210nm | Ch1 254nm

Chiral *ee* = 92 %



Peak Table

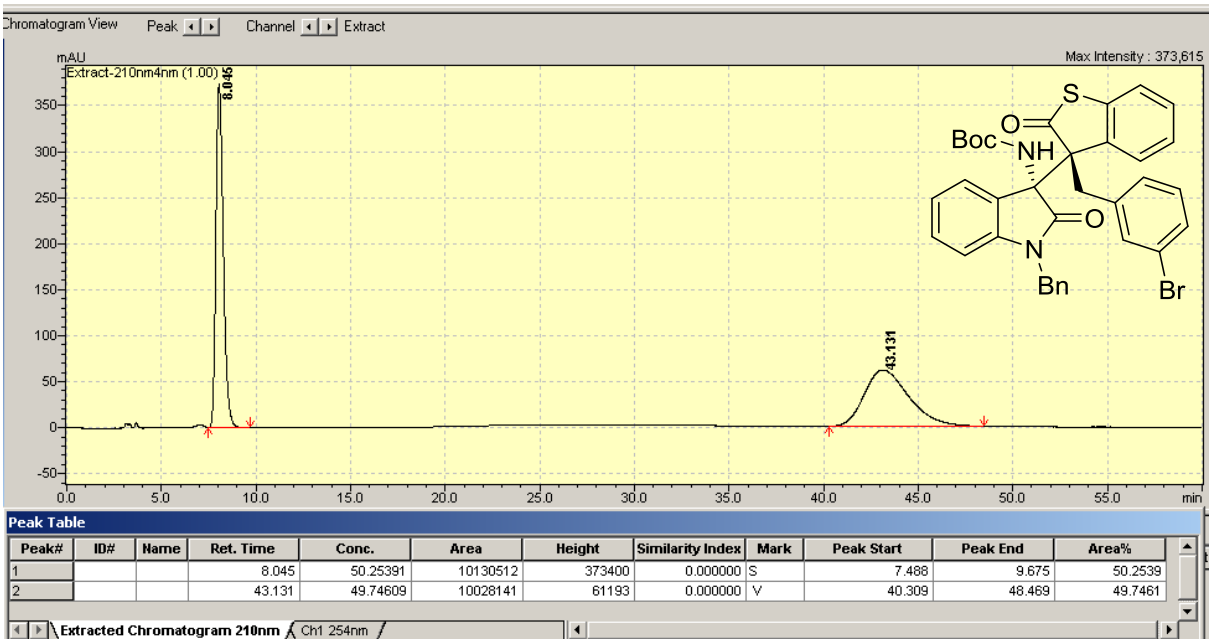
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.235	4.18932	328223	20383	0.000000		7.797	8.832	4.1893
2			48.960	95.81068	7506530	62846	0.000000		46.528	54.443	95.8107

Extracted Chromatogram 210nm | Ch1 254nm

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(3-bromobenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3o)

HPLC **3o**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate

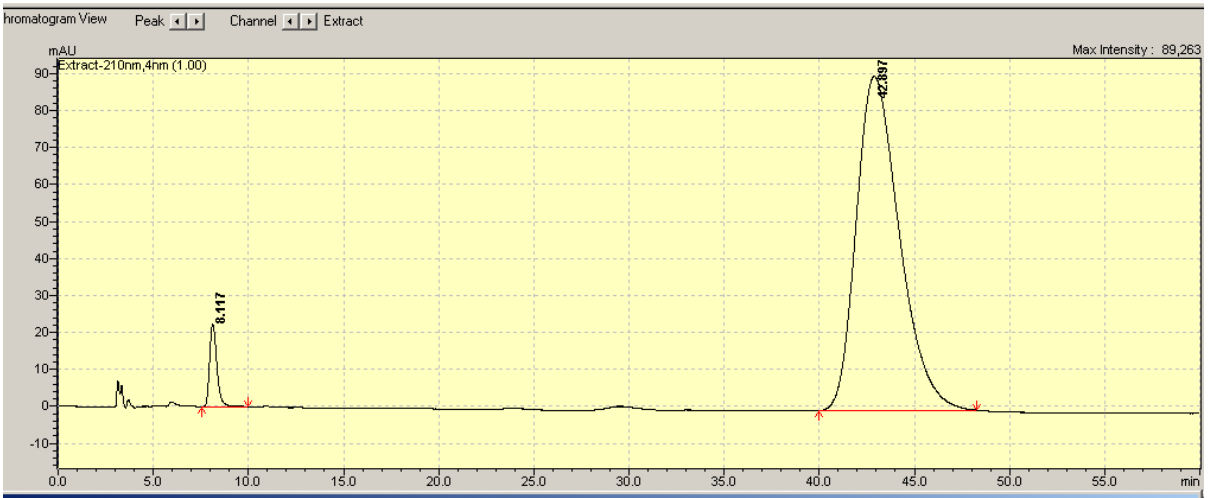


Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.045	50.25391	10130512	373400	0.000000	S	7.488	9.675	50.2539
2			43.131	49.74609	10028141	61193	0.000000	V	40.309	48.469	49.7461

Extracted Chromatogram 210nm | Ch1 254nm

Chiral *ee* = 92 %



Peak Table

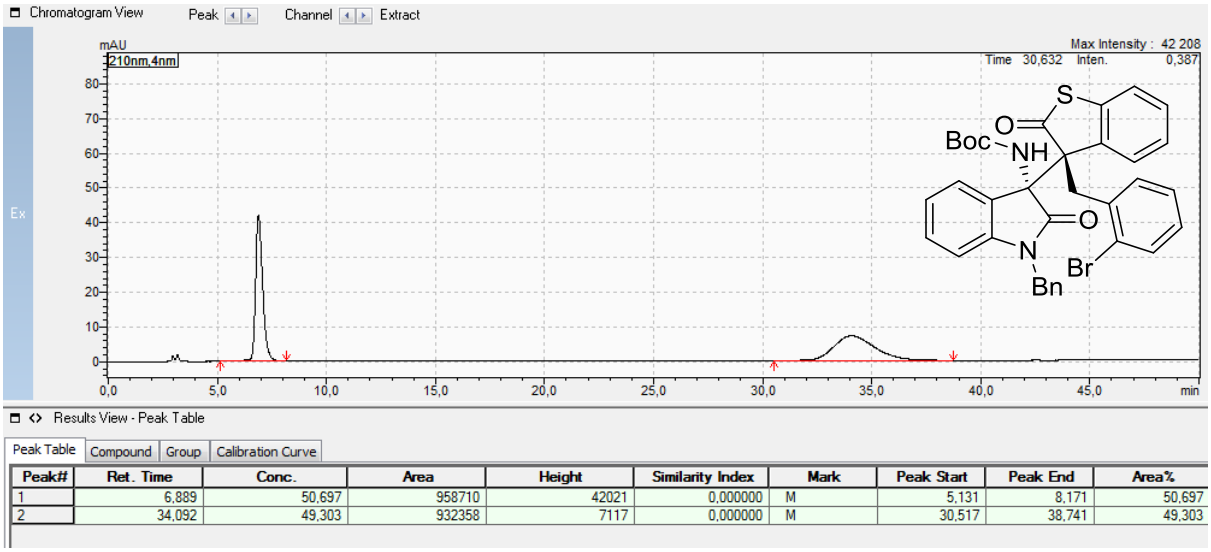
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			8.117	4.12617	614939	22531	0.000000		7.563	10.005	4.1262
2			42.897	95.87383	14288436	90396	0.000000	S	39.968	48.299	95.8738

Extracted Chromatogram 210nm | Ch1 254nm

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(3-bromobenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3p)

HPLC **3p**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate

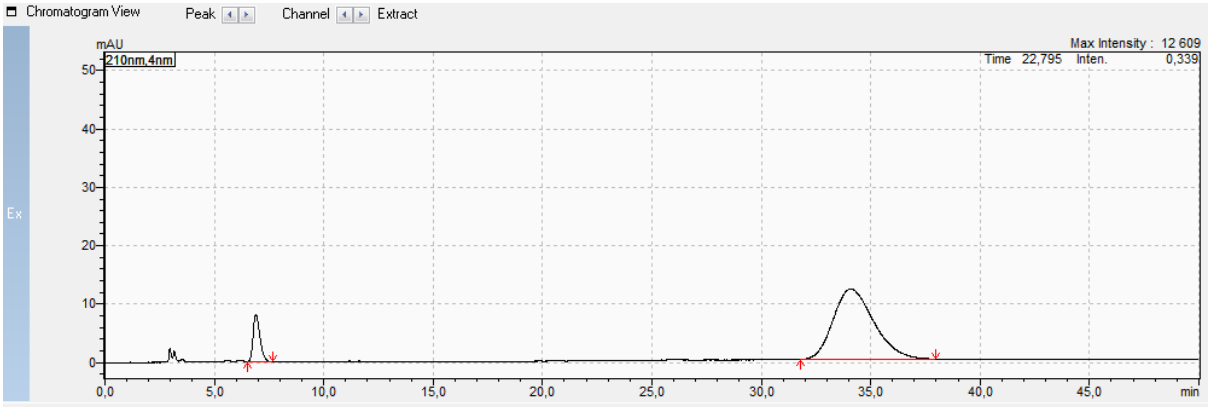


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,889	50,697	958710	42021	0,000000	M	5,131	8,171	50,697
2	34,092	49,303	932358	7117	0,000000	M	30,517	38,741	49,303

Chiral *ee* = 80 %



Results View - Peak Table

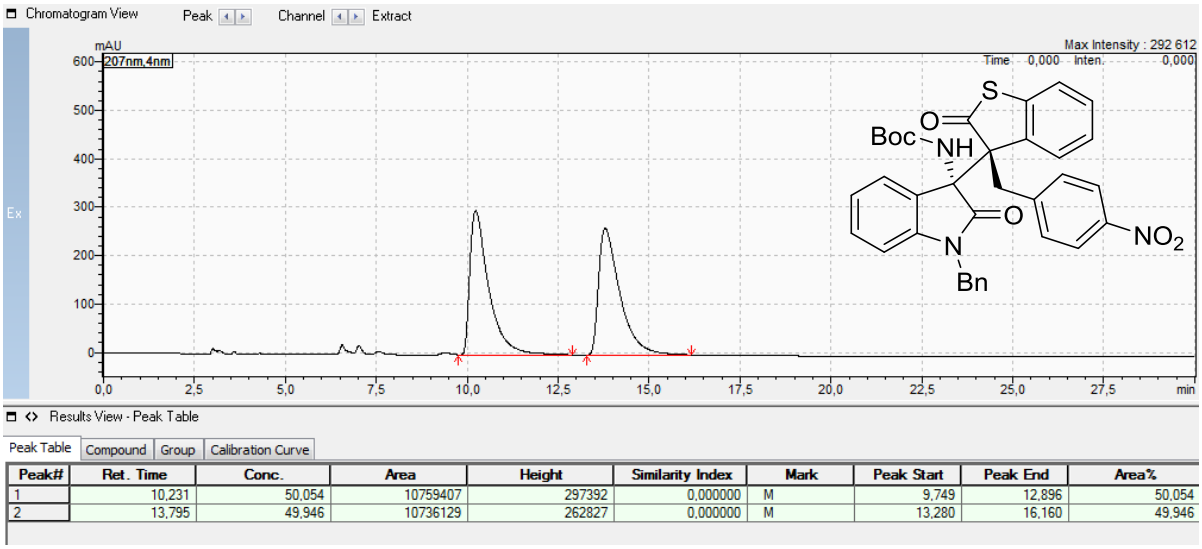
Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,900	10,109	174572	7968	0,000000	M	6,517	7,669	10,109
2	34,112	89,891	1552246	12041	0,000000	M	31,787	37,973	89,891

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(4-nitrobenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3q)

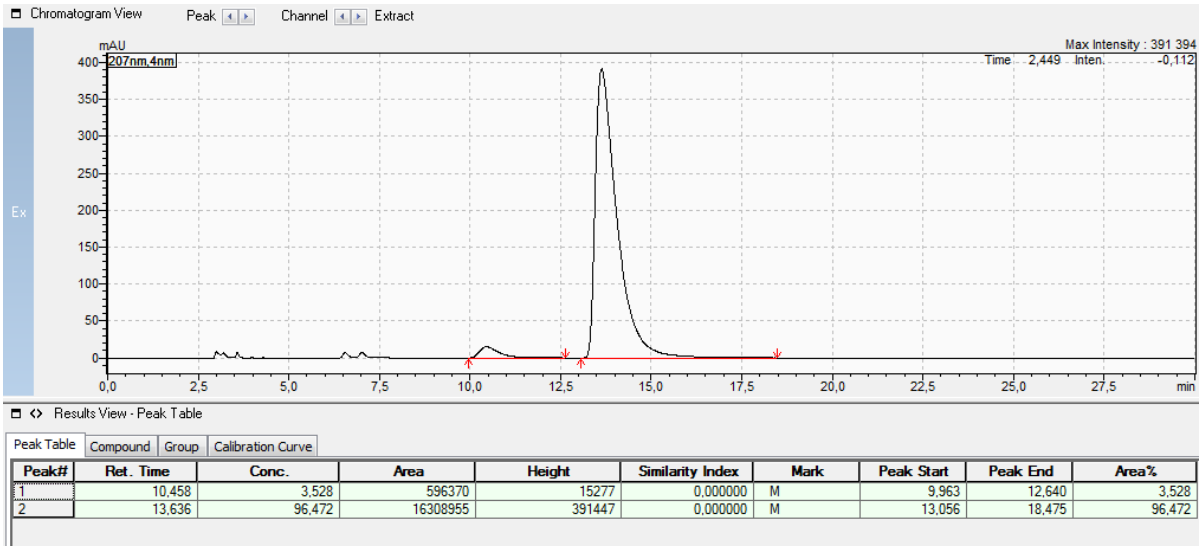
HPLC **3q**: Chiral column IB, *n*-heptane/isopropanol (80:20), 1.0 mL, 207 nm, 25 °C

Racemate



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,231	50,054	10759407	297392	0,000000	M	9,749	12,896	50,054
2	13,795	49,946	10736129	262827	0,000000	M	13,280	16,160	49,946

Chiral *ee* = 93 %

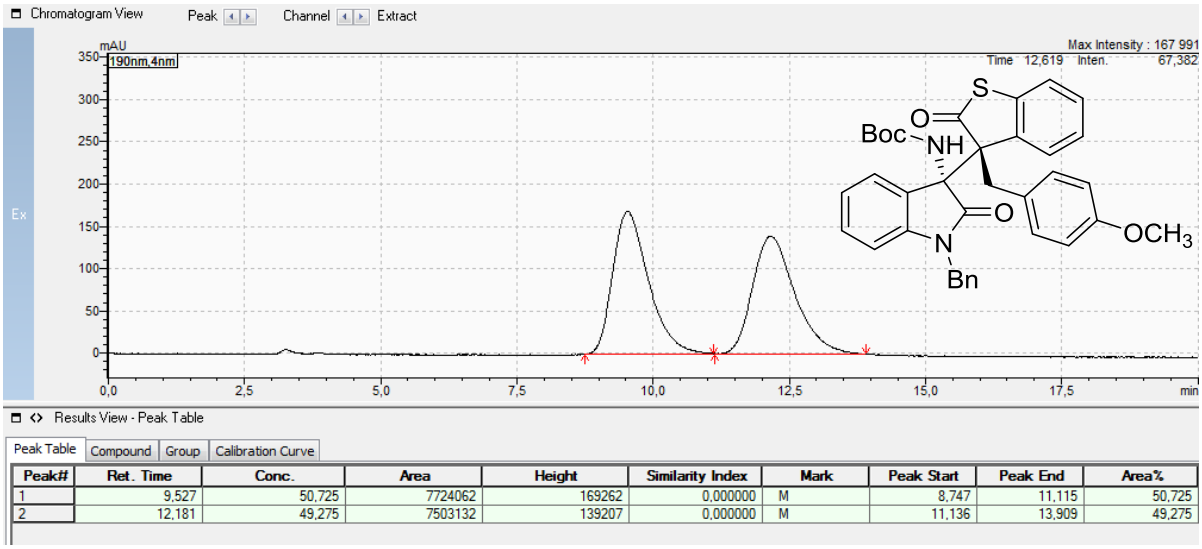


Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,458	3,528	596370	15277	0,000000	M	9,963	12,640	3,528
2	13,636	96,472	16308955	391447	0,000000	M	13,056	18,475	96,472

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-(4-methoxybenzyl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3r)

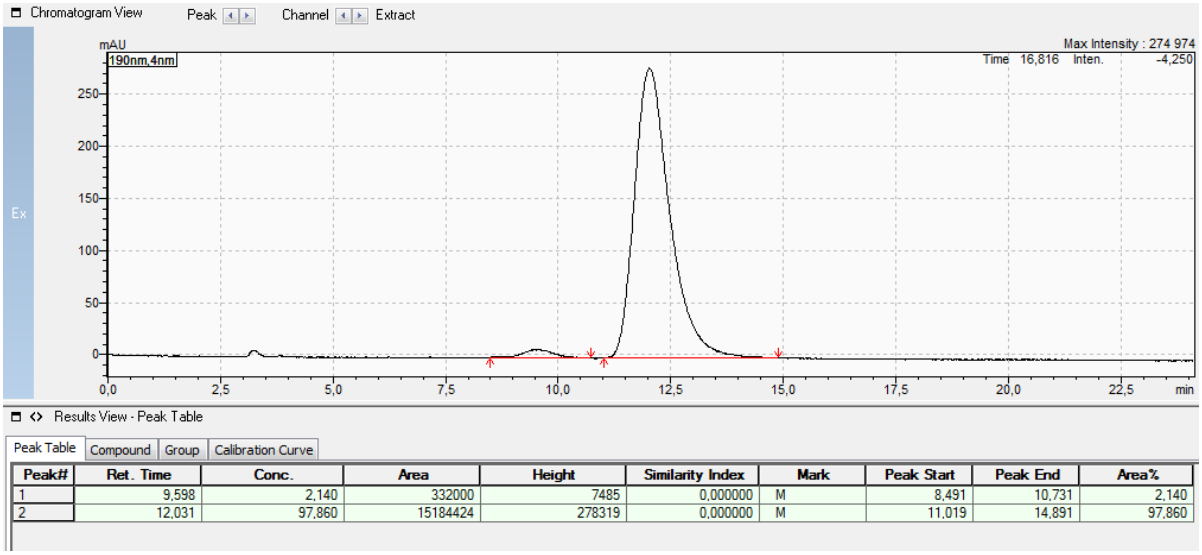
HPLC **3r**: Chiral column ODH, *n*-heptane/isopropanol (90:10), 1.0 mL, 190 nm, 25 °C

Racemate



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	9,527	50,725	7724062	169262	0,000000	M	8,747	11,115	50,725
2	12,181	49,275	7503132	139207	0,000000	M	11,136	13,909	49,275

Chiral *ee* = 96 %

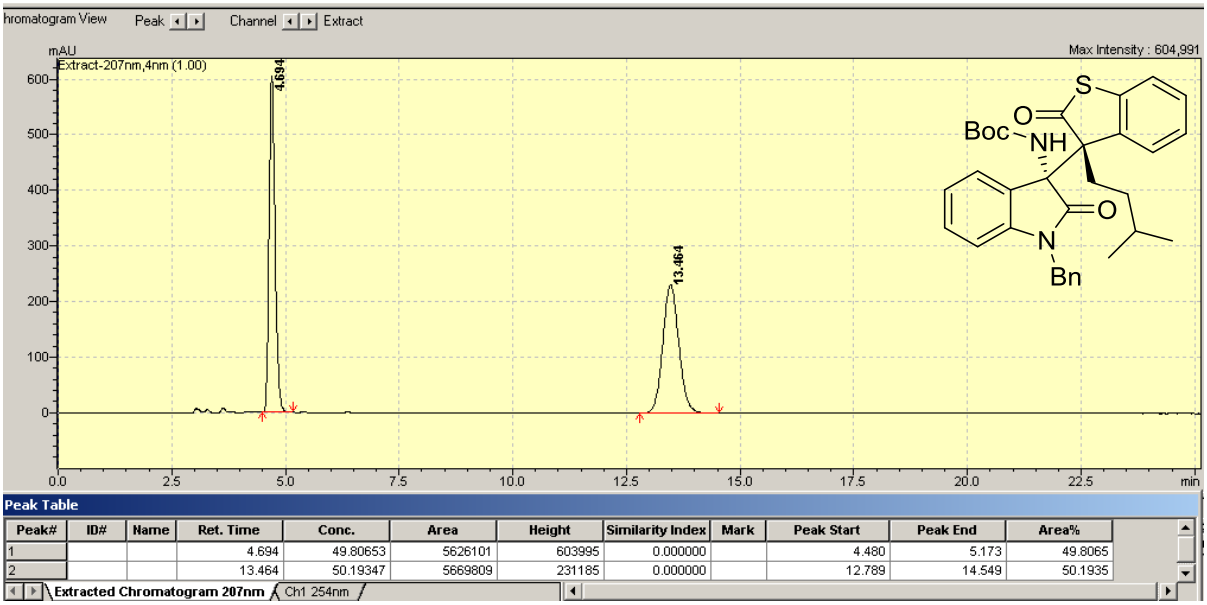


Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	9,598	2,140	332000	7485	0,000000	M	8,491	10,731	2,140
2	12,031	97,860	15184424	278319	0,000000	M	11,019	14,891	97,860

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-isopentyl-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3s)

HPLC **3s**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 207 nm, 25 °C

Racemate

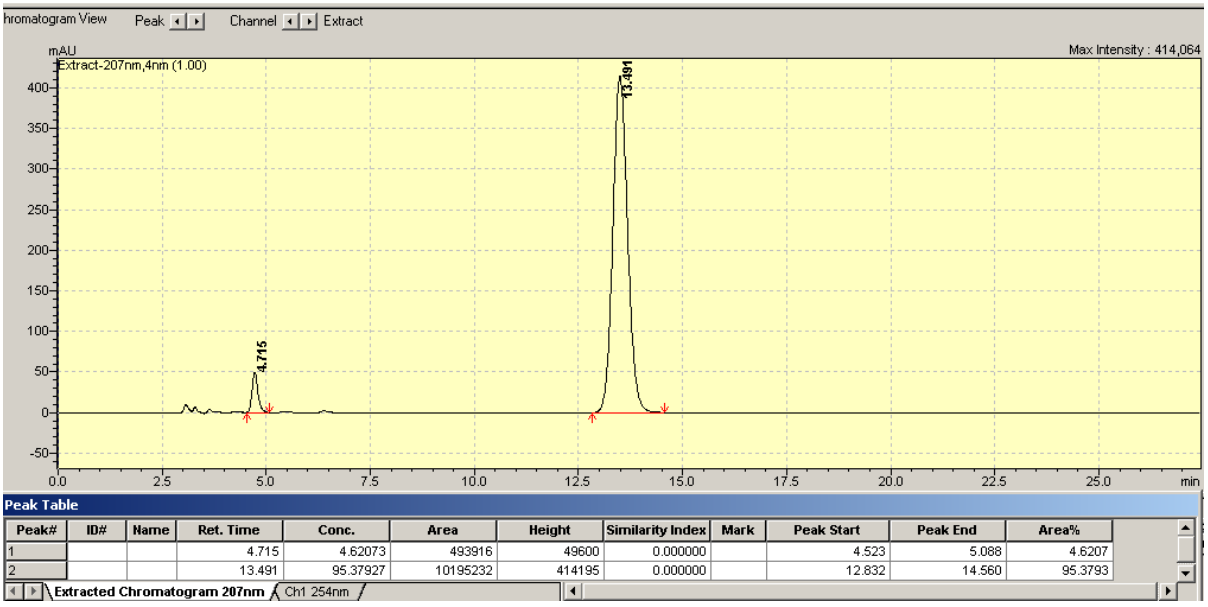


Peak Table

Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			4.694	49.80653	5626101	603995	0.000000		4.480	5.173	49.8065
2			13.464	50.19347	5669809	231185	0.000000		12.789	14.549	50.1935

Extracted Chromatogram 207nm | Ch1 254nm

Chiral *ee* = 91 %



Peak Table

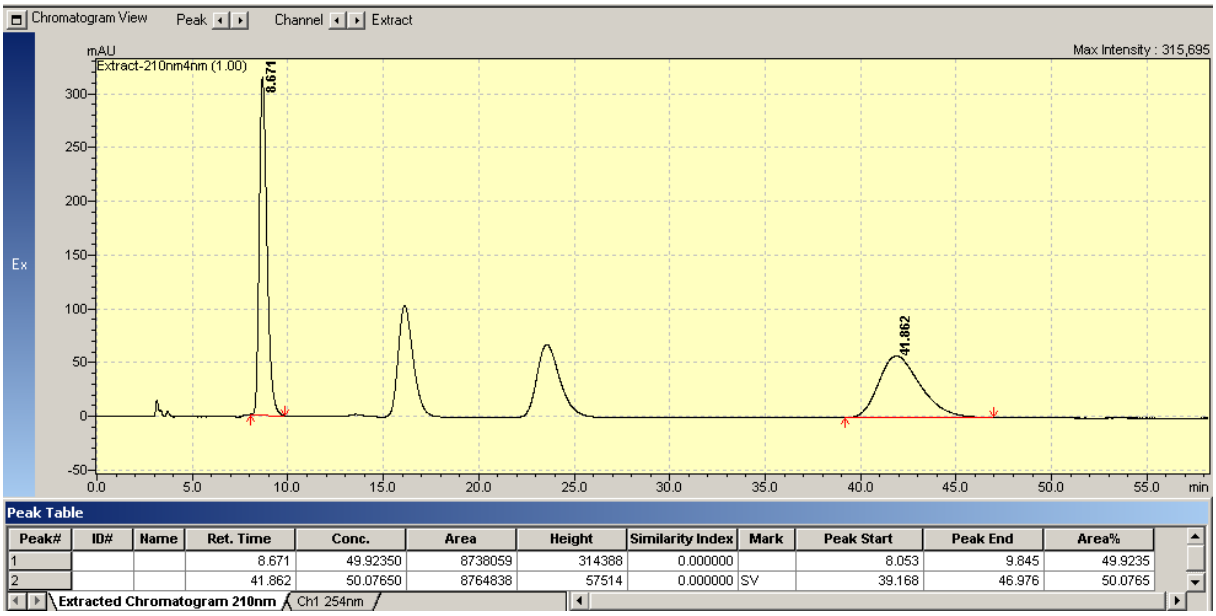
Peak#	ID#	Name	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1			4.715	4.62073	493916	49600	0.000000		4.523	5.088	4.6207
2			13.491	95.37927	10195232	414195	0.000000		12.832	14.560	95.3793

Extracted Chromatogram 207nm | Ch1 254nm

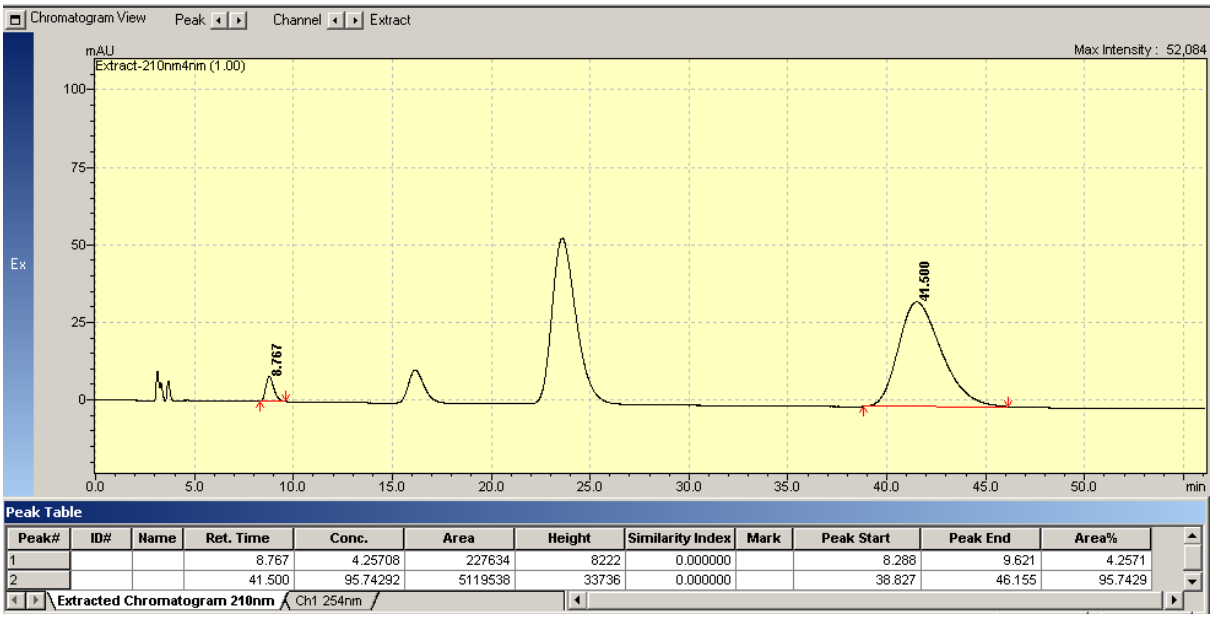
Methyl 3-(3-(1-benzyl-3-((*tert*-butoxycarbonyl)amino)-2-oxoindolin-3-yl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)propanoate (3t) – major diastereoizomer

HPLC 3t: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate



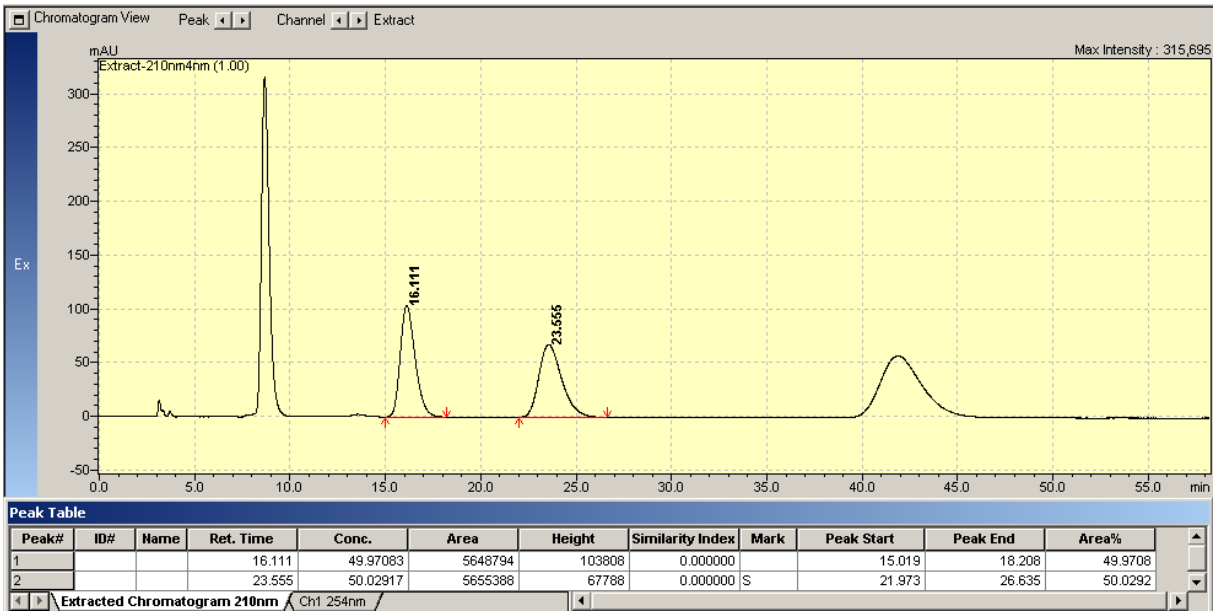
Chiral *ee* = 91 %



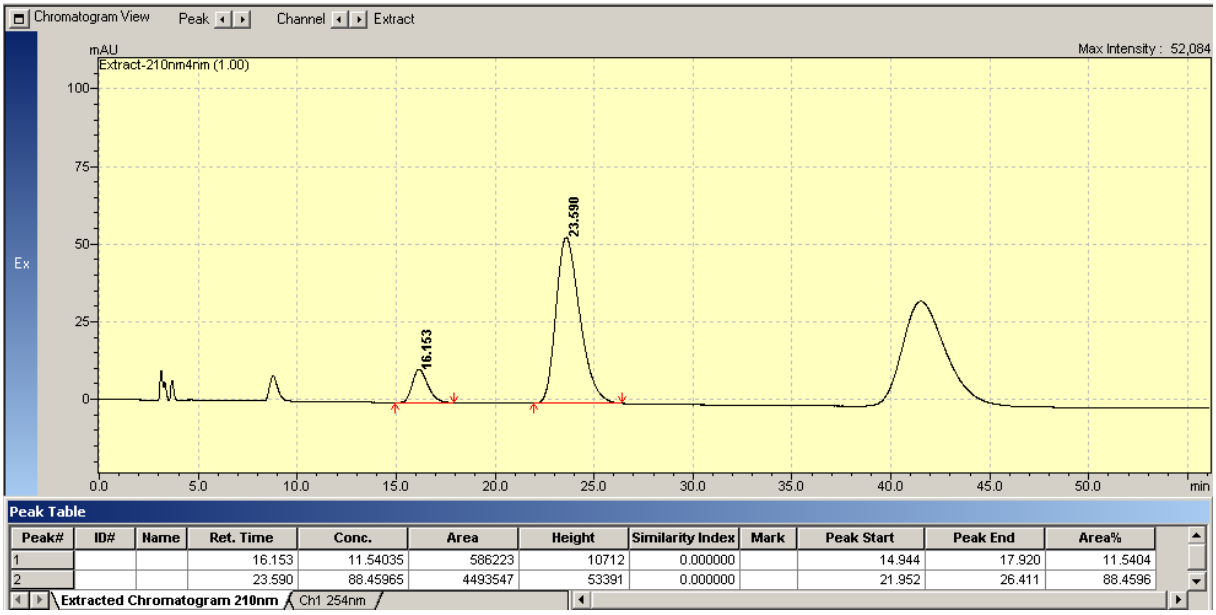
Methyl 3-(3-(1-benzyl-3-((*tert*-butoxycarbonyl)amino)-2-oxoindolin-3-yl)-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)propanoate (3t‘) - minor diastereoizomer

HPLC **3t‘**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate



Chiral *ee* = 77 %

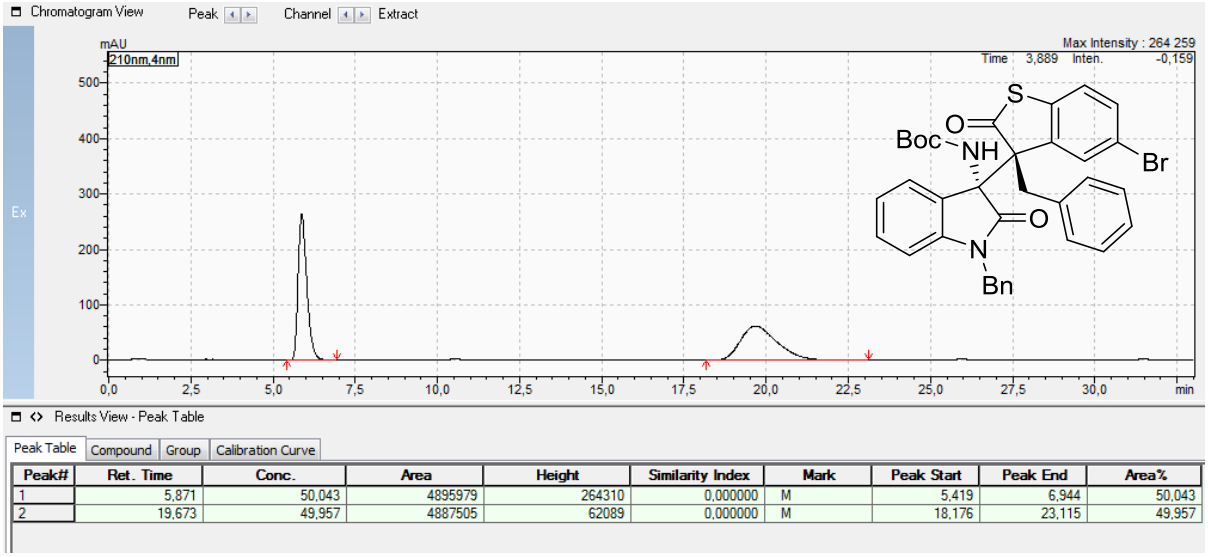


..

tert-Butyl ((*R*)-1-benzyl-3-((*R*)-3-benzyl-5-bromo-2-oxo-2,3-dihydrobenzo[*b*]thiophen-3-yl)-2-oxoindolin-3-yl)carbamate (3u)

HPLC **3u**: Chiral column AD, *n*-heptane/isopropanol (80:20), 1.0 mL, 210 nm, 25 °C

Racemate

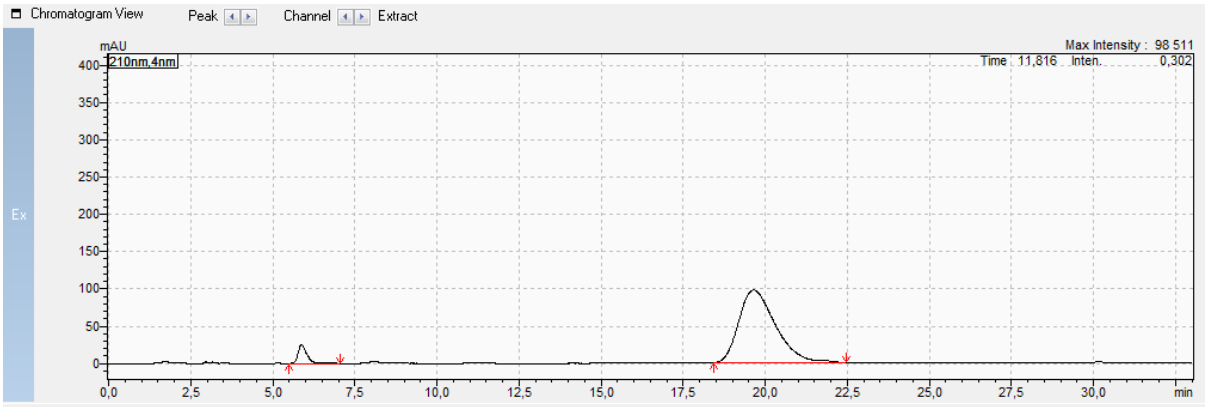


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,871	50,043	4895979	264310	0,000000	M	5,419	6,944	50,043
2	19,673	49,957	4887505	62089	0,000000	M	18,176	23,115	49,957

Chiral *ee* = 89 %



Results View - Peak Table

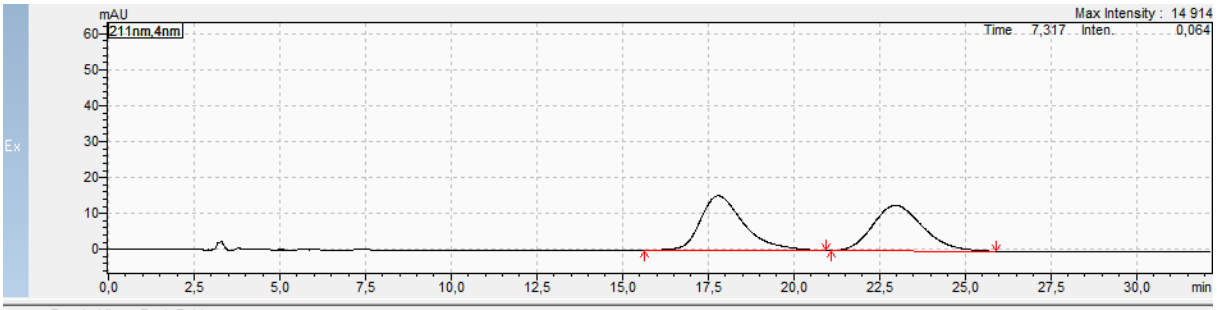
Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,878	5,686	457436	24600	0,000000	M	5,493	7,051	5,686
2	19,645	94,314	7587930	97344	0,000000	M	18,432	22,464	94,314

***tert*-butyl (1-benzyl-3-(5-benzyl-4-oxo-3-phenyl-2-thioxothiazolidin-5-yl)-2-oxoindolin-3-yl)carbamate (6a')**

HPLC **6a'**: Chiral column AD, *n*-heptane/isopropanol (90:10), 1.0 mL, 211 nm, 25 °C

Racemate

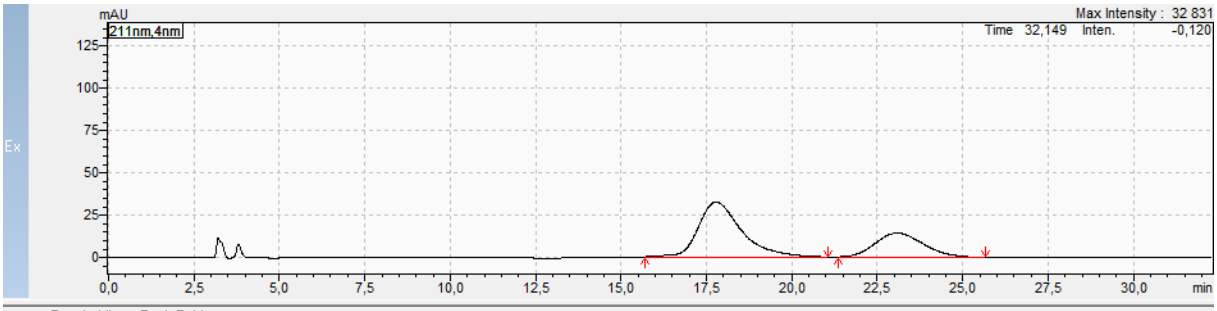


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	17,795	51,46087	1366484	15360	0,000000		15,659	20,949	51,461
2	22,961	48,53913	1288901	12715	0,000000		21,077	25,899	48,539

Chiral *ee* = 34 %



Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	17,775	67,29155	2860962	32443	0,000000		15,691	21,056	67,292
2	23,085	32,70845	1390630	14179	0,000000		21,344	25,675	32,708