Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

A Formal [4+2] Cycloaddition of Sulfur-Containing Alkylidene Heterocycles with Allenic Compounds

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Electronic Supplementary Information

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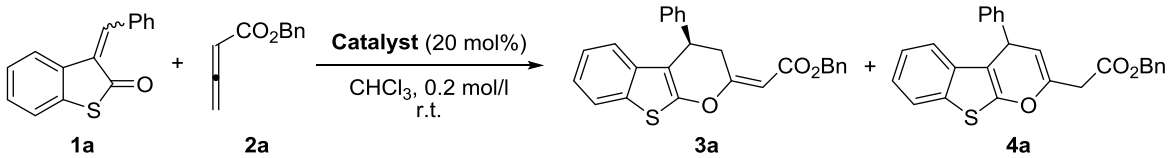
General

Chemicals and solvents were either purchased puriss *p.A.* from commercial suppliers or purified by standard techniques. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of phosphomolybdic acid (AMC) or vaniline followed by heating. The solution of 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 solution of vanilline was prepared from vanilline (15 g) in ethanol (250 ml) and conc. sulfuric acid (2.5 ml). Column chromatography was performed using silica gel Fluka (40-63 μm). ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded with Bruker AVANCE III 400. Chemical shifts for protons are given in δ and are referenced to residual protium in the NMR solvent (Chloroform-*d*: δ = 7.26 ppm). Chemical shifts for carbon are referenced to the carbon in NMR solvent (Chloroform-*d*: δ = 77.0 ppm). The coupling constants *J* are given in Hz. Chiral HPLC was carried out using a LC20AD Shimadzu liquid chromatograph with SPD-M20A diode array detector with columns Daicel Chiralpak® IA, Daicel Chiralpak® IB, Daicel Chiralpak® AD, Daicel Chiralpak® ODH. Optical rotations were measured on AU-Tomatica polarimeter, Autopol III. Specific optical rotations are given in concentrations *c* [g/100 ml]. IR DRIFT spectras were recorded with Nicolet AVATAR 370 FT-IR in cm^{-1}. High-resolution mass spectras were recorded with a LCQ Fleet spectrometer.

Optimization of reaction conditions for cycloaddition reaction

Table S1. Catalyst screening.



1a 1.0 eq. **2a** 1.2 eq. **3a** **4a**

Entry	Catalyst	Time (h)	Convers.[a] (%)	3a/4a[a]	Yield[b] (%)	*ee* (%)[c]
1	none	120	0	n.d.	n.d.	n.d.
2	2,4-DNBA	120	0	n.d.	n.d.	n.d.
3	DABCO	15	100	7:1	98	-
4	PPh_3	120	70	n.d.	n.d.[d]	n.d.
5	β-ICD	15	100	>20:1	94	48
6	QN	15[e]	84	>20:1	49	-64
7	QD	15	100	20:1	83	73
8[e]	QD	40	100	20:1	70	71
9	CD	48	89	20:1	67	-16
10	CN	65	76	15:1	72	39
11	TMS-QD	15	100	>20:1	91	66
12	Bz-QD	18	55	20:1	52	52
13	$(DHQD)_2AQN$	15[e]	100	>20:1	83	63
14	$(DHQ)_2AQN$	15	100	20:1	83	-53
15	$(DHQD)_2Phal$	65	73	8:1	47	64
16	$(DHQ)_2Phal$	48	70	20:1	39	-5
17	$(DHQD)_2Pyr$	15	90	11:1	43	71
18	$(DHQ)_2Pyr$	15	100	20:1	86	-68
19	C1	120	0	n.d.	n.d.	n.d.
20	C2	120	0	n.d.	n.d.	n.d.
21	(*R*,*R*)-TUC	120	0	n.d.	n.d.	n.d.

[a] Determined by ^1H NMR of crude reaction mixture. [b] Isolated yield after column chromatography. [c] Determined by HPLC with IB chiral column. [d] Different product was observed. [e] Reaction was performed at -20 °C.
2,4-DNBA = 2,4-dinitrobenzoic acid

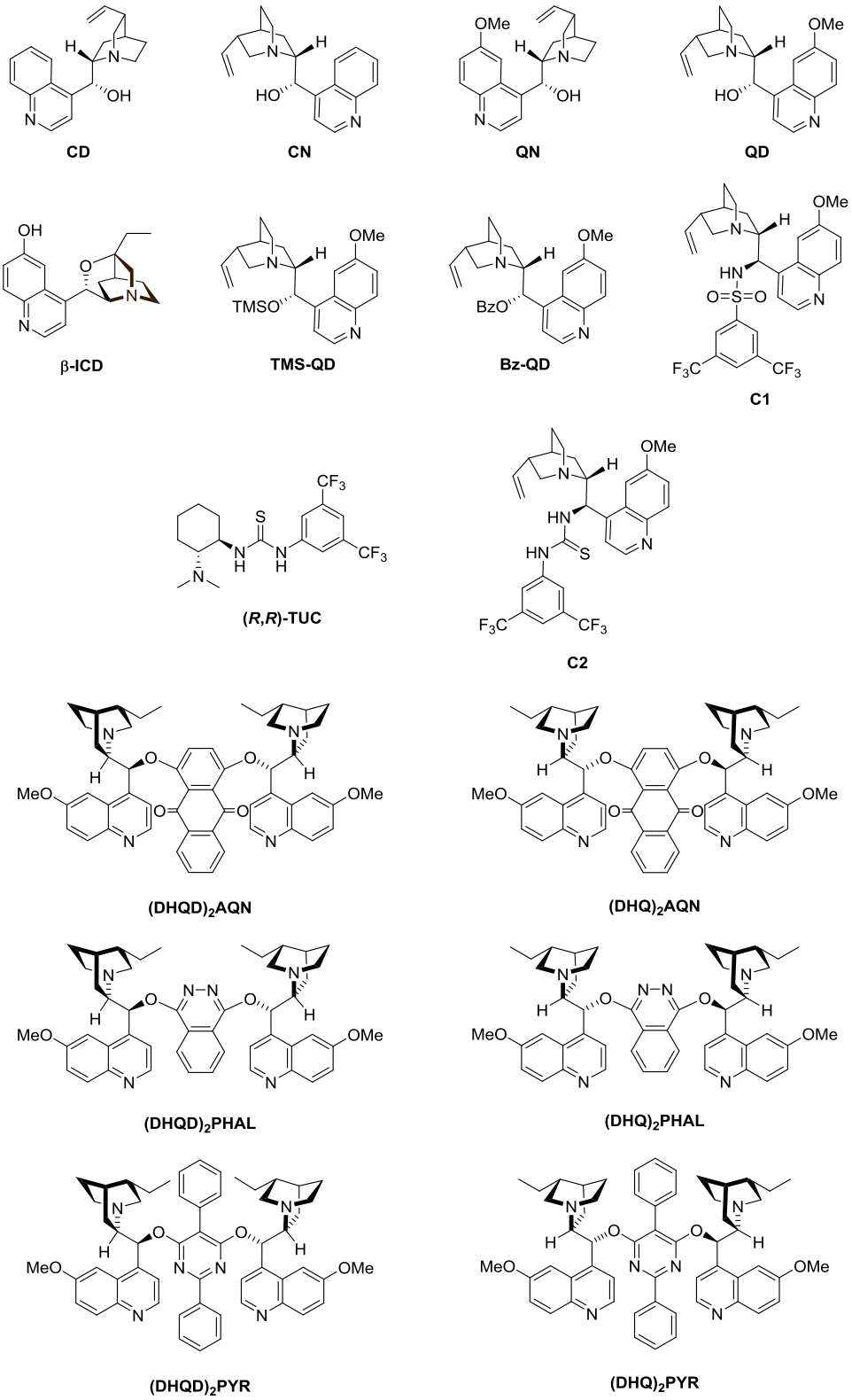
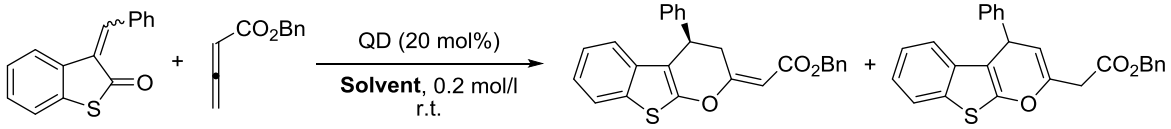


Figure S1. Structures of catalysts screened.

Table S2. Solvent screening.

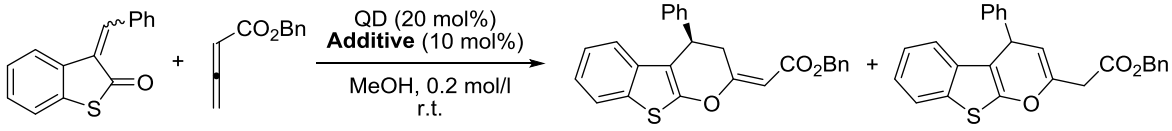


1a 1.0 eq. **2a** 1.2 eq. **3a** **4a**

Entry	Solvent	Time (h)	Convers.[a] (%)	3a/4a[a]	Yield[b] (%)	*ee* (%)[c]
1	$CHCl_3$	15	100	20:1	83	73
2	DCM	15	100	19:1	86	78
3	DCE	15	90	17:1	73	82
4	MTBE	15	95	19:1	98[d]	74
5	THF	15	100	19:1	90	78
6	EtOAc	15	100	12:1	93	83
7	MeCN	15	91	12:1	72	85
8	acetone	15	100	9:1	80	86
9	benzene	15	100	20:1	93	79
10	toluene	40	90	>20:1	95	75
11	DMF	15	100	4:1	62	86
12	DMSO	15	100	5:1	41	73
13	MeOH	15	100	>20:1	82[d]	89
14	EtOH	15	100	>20:1	75[d]	83
15	2,2,2-trifluoroethanol	120	50	n.d.	n.d.	n.d.
16	*i*-PrOH	15	100	>20:1	77[d]	67
17	PrOH	15	100	>20:1	79[d]	80
18	Diethylene glycol	15	95	7:1	71[d]	85

[a] Determined by ^{1}H NMR of crude reaction mixture. [b] Isolated yield after column chromatography. [c] Determined by HPLC with IB chiral column. [d] Product precipitated from reaction mixture.

Table S3. Additive screening.

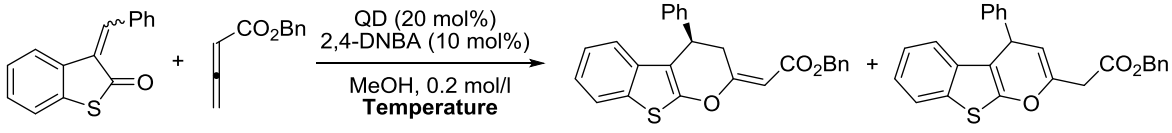


1a 1.0 eq. **2a** 1.2 eq. **3a** **4a**

Entry	Additive	Time (h)	Convers.[a] (%)	3a/4a[a]	Yield[b] (%)	*ee* (%)[c]
1	none	15	100	>20:1	82[d]	89
2	PhCOOH	15	90	>20:1	77[d]	89
3	*p*-TsOH	15	92	>20:1	78[d]	84
4	2,4-DNBA	15	97	>20:1	92[d]	90
5	PhOH	15	100	17:1	75	85
6	4-NO_2PhOH	15	95	19:1	89[d]	89.5
7	(*S*)-CSA	15	94	>20:1	77[d]	84
8	(*R*)-BNPPA	15	100	19:1	71[d]	88
9[e]	2,4-DNBA	20	87	>20:1	88	74

[a] Determined by ^{1}H NMR of crude reaction mixture. [b] Isolated yield after column chromtography. [c] Determined by HPLC with IB chiral column. [d] Product precipitated from reaction mixture. [e] Reaction was perfomed in DCM. (*S*)-CSA = (1*S*)-(+)-Camphorsulfonic acid , (*R*)-BNPPA = (*R*)-(-)-1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate

Table S4. Temperature screening.

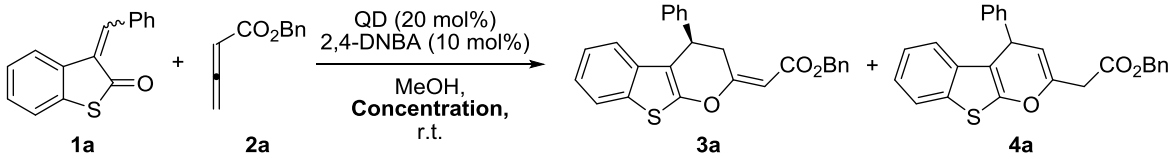


1a 1.0 eq. **2a** 1.2 eq. **3a** **4a**

Entry	Temperature	Time (h)	Convers.[a] (%)	3a/4a[a]	Yield[b] (%)	*ee* (%)[c]
1	r.t.	15	100	>20:1	92[d]	90
2	0 °C	72	96	19:1	75[d]	88
3	-20 °C	120	62	8:1	55[d]	85
4	40 °C	5	85	20:1	90[d]	86
5	60 °C	5	85	5:1	56	66

[a] Determined by ^{1}H NMR of crude reaction mixture. [b] Isolated yield after column chromtography. [c] Determined by HPLC with IB chiral column. [d] Product precipitated from reaction mixture.

Table S5. Concentration screening.

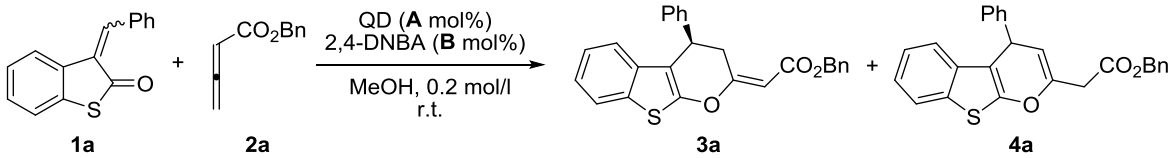


1a 1.0 eq. **2a** 1.2 eq. **3a** **4a**

Entry	Concentration	Time (h)	Convers.[a] (%)	3a/4a[a]	Yield[b] (%)	*ee* (%)[c]
1	0.2 mol/l	15	100	>20:1	92[d]	90
2	0.1 mol/l	15	92	20:1	78[d]	89
3	0.05 mol/l	48	87	10:1	69	90
4	0.4 mol/l	15	100	>20:1	86[d]	86
5	0.8 mol/l	15	100	20:1	93[d]	88

[a] Determined by ^{1}H NMR of crude reaction mixture. [b] Isolated yield after column chromtography. [c] Determined by HPLC with IB chiral column. [d] Product precipitated from reaction mixture.

Table S6. Catalyst and additive loading screening.



1a 1.0 eq. **2a** 1.2 eq. **3a** **4a**

Entry	A	B	Time (h)	Convers.[a] (%)	3a/4a[a]	Yield[b] (%)	*ee* (%)[c]
1	20	10	15	97	>20:1	92[d]	90
2	20	20	48	89	>20:1	75[d]	89
3	20	50	120	0	n.d.	n.d.	n.d.
4	20	100	120	100	n.d.	n.d.	n.d.
5	10	5	40	98	>20:1	90[d]	84
6	5	2.5	72	92	>20:1	75[d]	86
7	5	0	15	100	>20:1	72[d]	82

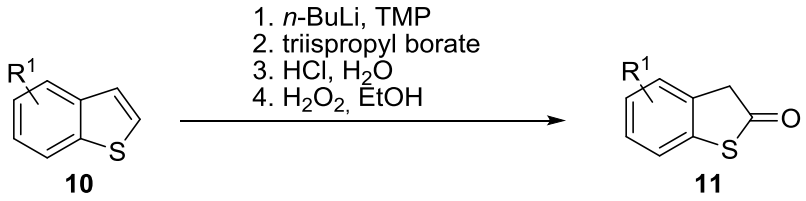
[a] Determined by ^{1}H NMR of crude reaction mixture. [b] Isolated yield after column chromtography. [c] Determined by HPLC with IB chiral column. [d] Product precipitated from reaction mixture.

Starting material

Preparation of allenoates and selected alkylidenes

Allenoates **2a** and **2b** were prepared according to previously reported procedures.[1] Corresponding allenic ketone **2c** was prepared according to previously reported procedure.[2] (*Z*)-2-benzylidenebenzo[*b*]thiophen-3(2*H*)-one (**5a**) was prepared by Wittig reaction from thioisatine.[3] Thiazolone alkylidene **5b** was prepared according to previously reported procedure.[4] Thiazolone alkylidene **5c** was prepared according to previously reported procedure.[5]

Preparation of benzothiophen-2-ones



To a stirred solution of 2,2,6,6-tetramethylpiperidine (0.52 ml, 3.05 mmol, 1.3 eq.) in anhydrous THF (3 ml) was *n*-BuLi (1.13 ml, 2.81 mmol, 1.2 eq., 2.5M solution in hexanes) added dropwise (during 3 minutes) at -78 °C under argon atmosphere. Reaction was stirred for 15 min at the same temperature. Light yellow solution was slowly cannulated to a stirred solution of corresponding thiophene **10** (2.34 mmol, 1.0 eq.) in anhydrous THF (7 ml) under Ar atmosphere. Resulting reaction mixture was stirred at the same temperature for 1.5 h. Then triisopropyl borate (0.87 ml, 3.74 mmol, 1.6 eq.) was added dropwise. Reaction mixture was stirred for 30 min at -78 °C, then 1 h at room temperature. Reaction was quenched with HCl (10 ml, 1M). Resulting suspension was stirred for 15 min at room temperature. Mixture was diluted with Et_2O (30 ml). Organic phase was separated and water phase was washed with Et_2O (2 × 30 ml). Collected organic phases were washed with solution of NaOH (2 × 25 ml, 1M). Collected alkaline solutions were neutralized and acidified to pH ~ 2 with hydrochloric acid (36%). Resulting suspension was washed with Et_2O (3 × 30 ml). Collected org. phases were extracted with brine (1 × 20 ml) and dried under anhydrous $MgSO_4$. Mixture was filtered and solvents were evaporated *in vacuo* to give crude boronic acid, which was used directly in next step.

Following the reported procedure,[6] to a solution of crude boronic acid (2.3 mmol) in EtOH (4.0 ml) was H_2O_2 (30%, 1.0 eq.) added dropwise. Reaction was stirred overnight at room temperature. Then solvent was carefully evaporated on rotavap. Residue was suspended in water (20 ml). This mixture was washed with EtOAc (3 × 30 ml). Collected organic phases were washed with brine (1 × 30 ml) and dried under anhydrous $MgSO_4$. Mixture was filtered and solvents were evaporated *in vacuo.* Crude product was purified by flash chromatography (Hex/EtOAc) affording desired products.

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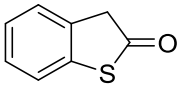
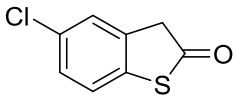
[1] a) J.Bang, H. Kim, J. Kim, and Ch. Yu, *Org. Lett.*, 2015, **17**, 1573; b) L. Rout and A. M. Harned, *Chem. Eur. J.*, 2009, **15**, 12926.
[2] L. Yang, D. Mario and B. Marco, *Synthesis*, 2018, **50**, 3187.
[3] Y. Takeuchi, T. Choshi, H. Tomozane, H. Yoshida, M.Yamato, *Chem. Pharm. Bull.*, 1990, **38**, 2265.
[4] L. Lin, Y. Yang, M. Wang, L. Lai, Y. Guoa and R. Wang, *Chem. Commun.*, 2015, **51**, 8134.
[5] I. Arenal, M. Bernabé, O. Cuevas, E. Fernández Alvarez, *Tetrahedron*, 1983, **39**, 1387.
[6] P. S.Banerjee, E. S.Zuniga,I. Ojima and I. S.Carrico, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 4985.

Benzo[*b*]thiophen-2(3*H*)-one (11a)



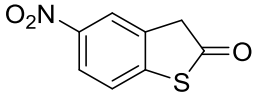
The title compound was synthesized according to general procedure. Known compound,[6] light brown solid, yield = 95 % (for last step – commercially available boronic acid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38 – 7.15 (m, 4H), 3.96 (s, 2H) ppm.

5-Chlorobenzo[*b*]thiophen-2(3*H*)-one (11b)



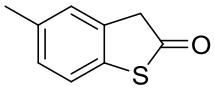
The title compound was synthesized according to general procedure. White solid, yield = 71 % (over four steps); **m.p**. = 112.7 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.33 – 7.26 (m, 3H), 3.97 (s, 2H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 201.7, 135.4, 133.6, 132.1, 128.6, 125.1, 124.0, 47.2 ppm; **IR** (KBr): ν = 3428, 3117, 3079, 3022, 2941, 2908, 2095, 2029, 1891, 1853, 1814, 1760, 1700, 1688, 1628, 1592, 1559, 1461, 1443, 1416, 1974, 1275, 1228, 1195, 1132, 1087, 1021, 1006, 911 cm^{-1}, **HRMS** (EI) *m*/*z*: calcd. for C_8H_5OSCl [M]: 183.9750, found: 183.9749.

5-Nitrobenzo[*b*]thiophen-2(3*H*)-one (11c)



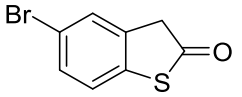
The title compound was synthesized according to general procedure. Light orange solid; yield = 38 % (over four steps); **m.p**. = 125.4 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 8.33 – 8.13 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 4.10 (s, 2H) ppm, **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 199.8, 146.4, 145.9, 133.2, 123.8, 123.4, 119.8, 46.9. ppm; **IR** (KBr): ν = 3422, 3094, 3073, 3043, 3025, 2989, 2938, 2911, 2848, 2830, 2738, 2627, 2531, 2026, 1927, 1862, 1718, 1688, 1637, 1598, 1574, 1527, 1512, 1464, 1422, 1341, 1311, 1272, 1228, 1198, 1141, 1078, 1039, 1018, 934, 920, 836, 812 cm^{-1}; **HRMS** (EI) *m*/*z*: calcd. for $C_8H_5NO_3S$ [M]: 194.9990, found: 194.9993.

5-Methylbenzo[*b*]thiophen-2(3*H*)-one (11d)



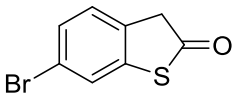
The title compound was synthesized according to general procedure. Known compound,[7] white solid, yield 76% (over four steps), **m.p**. = 75.6 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.24-7.20 (m, 2H), 7.17 – 7.06 (m, 2H), 3.93 (s, 2H), 2.34 (s, 3H) ppm.

5-Bromobenzo[*b*]thiophen-2(3*H*)-one (11e)



The title compound was synthesized according to general procedure. Light yellow solid, yield = 69 % (over four steps), **m.p**. = 125.4 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.52 – 7.37 (m, 2H), 7.26 – 7.20 (m, 1H), 3.98 (s, 2H) ppm, **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 201.5, 136.0, 133.9, 131.4, 127.9, 124.3, 119.7, 47.1 ppm; **IR** (KBr): ν = 3419, 3411, 3114, 3073, 2938, 2902, 2152, 2110, 2077, 2038, 1903, 1814, 1715, 1649, 1622, 1556, 1497, 1461, 1440, 1410, 1374, 1281, 1261, 1228, 1195, 1141, 1096, 1018, 824 cm^{-1}; **HRMS** (EI) *m*/*z*: calcd. for C_8H_5OSBr [M]:, found: 227.9244.

6-Bromobenzo[*b*]thiophen-2(3*H*)-one (11f)

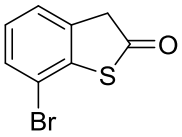


The title compound was synthesized according to general procedure. White solid, yield = 65 % (over four steps), **m.p**. = 90.0 °C, **^{1}H NMR** (400 MHz, Chloroform-*d*): δ =7.48 (d, *J* = 1.9 Hz, 1H), 7.34 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.15 (dt, *J* = 8.1, 1.2 Hz, 1H), 3.91 (s, 2H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 201.6, 139.0, 130.8, 129.2, 125.9, 125.7, 121.8, 46.7 ppm; **IR** (KBr): ν = 3390, 3073, 3061, 2938, 2914, 1885, 1844, 1709, 1664, 1598, 1559, 1518, 1461, 1392, 1362, 1305, 1257,

[7] V. Valenta, J. Jílek, J. Pomykáček, A. Dlabač, M. Valchář, J. Metyš and M. Protiva *Collect. Czech. Chem. Commun.*, 1979, **44**, 2677.

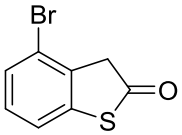
1237, 1189, 1135, 1108, 1090, 1063, 1024, 1003 cm^{-1}; **HRMS** (EI) *m*/*z*: calcd. for C_8H_5OSBr [M]: 227.9244, found: 227.9248.

7-Bromobenzo[*b*]thiophen-2(3*H*)-one (11g)



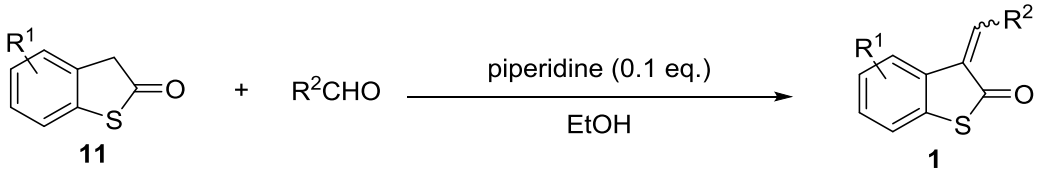
The title compound was synthesized according to general procedure. White solid, yield = 71 % (over four steps), **m.p**. = 99.7 °C, **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.44 (dq, *J* = 8.1, 1.0 Hz, 1H), 7.22 (dq, *J* = 7.6, 1.2 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 4.10 (s, 2H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 200.4, 139.5, 133.6, 131.4, 127.3, 123.1, 116.5, 49.3 ppm; **IR** (KBr): *v* = 3405, 3396, 3114, 3061, 3028, 2926, 2902, 2086, 2044, 1945, 1888, 1847, 1808, 1790, 1721, 1712, 1676, 1589, 1553, 1455, 1419, 1380, 1368, 1311, 1269, 1183, 1162, 1141, 1111, 1066, 1024, 979, 887, 770 cm^{-1}; **HRMS** (EI) *m*/*z*: calcd. for C_8H_5OSBr [M]: 227.9244, found: 227.9247.

4-Bromobenzo[*b*]thiophen-2(3*H*)-one (11h)



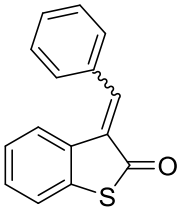
The title compound was synthesized according to general procedure. White solid, yield = 83 % (over four steps), **m.p**. = 66.7 °C, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.38 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.28 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.18 (tt, *J* = 7.9, 1.0 Hz, 1H), 3.97 (s, 2H) ppm, **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 199.9, 138.2, 132.7, 129.7, 129.5, 121.8, 119.8, 49.4 ppm; **IR** (KBr): *v* = 3415, 3408, 3079, 2926, 2896, 1716, 1670, 1586, 1574, 1556, 1452, 1431, 1377, 1302, 1248, 1219, 1177, 1069, 1027 cm^{-1}, **HRMS** (EI) *m*/*z*: calcd. for C_8H_5OSBr [M]: 227.9244, found: 227.9248.

Preparation of 3-alkylidenebenzothiophenones



Following the reported procedure[8] in a round-bottom flask benzothiophen-2-one **11** (2.0 mmol, 1 eq.) and corresponding aldehyde (2.1 mmol, 1.05 eq.) was dissolved in 96% EtOH (3.5 ml, 0.55M), then piperidine (0.02 ml, 0.2 mmol, 0.1 eq.) was added. Reaction mixture was left to stirr overnight at room temperature. After consumption of benzothiophen-2-one (monitored by TLC) the reaction mixture was evaporated and purified by flash column chromatography on silicagel (Hex/EtOAc or Hex/toluene mixtures) or precipitated product was filtered over sintered funnel, washed with small amount of 96% EtOH and recrystallized from boiling 96 % EtOH affording desired products.

3-Benzylidenebenzo[*b*]thiophen-2(3*H*)-one (1a)

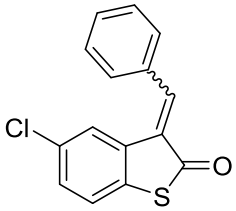


The title compound was synthesized according to general procedure. Mixture of *E*/*Z* isomers (**1a(*E*)/1a(*Z*)** = 5/1), yellow semi-solid, yield = 78 %, pure *E* isomer **1a(E)**, yield = 12 %; **^{1}H NMR** (400 MHz, Chloroform-*d*): [isomer **1a(*E*)** − H′; isomer **1a(*Z*) –** H]: δ 7.97 – 7.95 (m, 2H), 7.81 (s, 1H‘), 7.59 – 7.56 (m, 3H‘+2H, *overlapped*), 7.49 – 7.43 (m, 3H‘+3H, *overlapped*), 7.36 – 7.34 (m, 1H‘), 7.33 – 7.32 (m, 2H), 7.26 (t, *J* = 7.7 Hz, 1H‘+1H, *overlapped*), 7.02 – 6.98 (m, 1H‘) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): [isomer **1a(*E*)** − C′; isomer **1a(*Z*) –** C]: δ = δ 194.6 (1C‘), 192.2 (1C), 138.7 (1C), 138.4 (1C‘), 135.9

[8] R. A. Conley and N. D. Heindel, *J. Org. Chem.*, 1976, **41**, 3743.

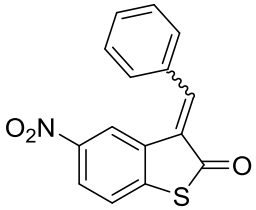
(1C‘), 134.9 (1C), 134.3 (1C‘), 133.7 (1C‘), 133.2 (1C), 133.0 (1C), 131.7 (1C), 131.6 (2C), 131.0 (1C), 130.1 (1C‘), 129.9 (1C‘), 129.8 (1C‘), 129.3 (1C), 128.8 (2C‘), 128.8 (2C‘), 128.1 (2C), 125.8 (1C), 125.5 (1C‘), 124.2 (1C‘), 123.5 (1C‘), 123.2 (1C), 121.0 (1C) ppm; **IR** (KBr): *ν* = 3067, 3019, 2657, 2110, 1951, 1918, 1888, 1811, 1778, 1754, 1688, 1667, 1604, 1497, 1443, 1368, 1275, 1222, 1210, 1180, 1075, 1054, 1024, 1003, 937, 905, 878, 845, 800, 764, 726, 698, 606, 564 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{10}H_{15}NaOS^+$ $[M+Na]^+$ = 261.0345, found = 261.0346.

3-Benzylidene-5-chlorobenzo[*b*]thiophen-2(3*H*)-one (1b)



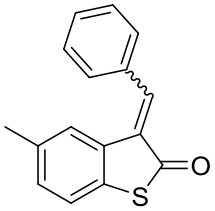
The title compound was synthesized according to general procedure. Inseparable mixture of *E*/*Z* isomers (**1b(*E*)/1b(*Z*)** = 2.2/1), yellow solid, yield = 84 %; **m.p**. = 71.9 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): [isomer **1b(*E*)** − H′; isomer **1b(*Z*) –** H]: δ = 8.07 – 7.94 (m, 2H), 7.86 (d, *J* = 2.6 Hz, 1H´), 7.61 – 7.40 (m, 6H´+ 5H, *overlapped*), 7.33 – 7.20 (m, 2H + 2H´, *overlapped*) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): [isomer **1b(*E*)** − C′; isomer **1b(*Z*) –** C]: δ = 193.8 (1C´), 192.1 (1C, *from 2D experiments*), 140.2 (2C´ + 1C, *overlapped*), 134.2 (1C´ + 1C), *overlapped*), 133.7 (1C´) 133.1 (1C), 132.9, (1C), 131.9 (1C´+ 1C, *overlapped*), 131.6 (1C´), 131.5 (1C), 131.4 (1C´), 130.4 (2C), 129.9 (2C), 129.2 (2C´), 129.1 (1C), 128.8 (2C´), 128.3 (1C´), 124.4 (1C), 124.2 (1C´), 124.2 (1C), 121.2 (1C´) ppm; **IR** (KBr): *ν* = 3363, 3058, 3025, 2995, 1972, 1879, 1694, 1676, 1604, 1583, 1556, 1494, 1446, 1419, 1377, 1326, 1287, 1260, 1242, 1198, 1168, 1090, 1078, 1051, 1030, 1018 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{15}H_9FClNaOS$ $[M+Na]^+$: 294.9954, found: 294.9955.

3-Benzylidene-5-nitrobenzo[*b*]thiophen-2(3*H*)-one (1c)



The title compound was synthesized according to general procedure. Inseparable mixture of *E*/*Z* isomers (**1c(*E*)/1c(*Z*)** = 2.2/1), yellow solid, yield = 63 %; **m.p**. = 145.9 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): [isomer **1c(*E*)** − H′; isomer **1c(*Z*) –** H]: δ = 8.52 (d, *J* = 2.3 Hz, 1H´), 8.46 (d, *J* = 2.2 Hz, 1H), 8.21 (dd, *J* = 8.6, 2.2 Hz, 1H), 8.15 (dd, *J* = 8.6, 2.3 Hz, 1H´), 8.08 – 8.03 (m, 2H, *overlapped*), 8.01 (s, 1H´), 7.79 (s, 1H), 7.63 – 7.44 (m, 6H´ + 4H, *overlapped*) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): [isomer **1c(*E*)** − C′; isomer **1c(*Z*) –** C]: δ = 192.3 (1C´), 190.0 (1C, *from 2D experiments*), 146.0 (1C), 140.0 (1C´), 142.9 (1C), 142.5 (2C´, *overlapped*), 134.2 (1C), 133.0 (1C´), 132.4 (1C´ + 2C, *overlapped*), 131.9 (1C´), 131.2 (2C), 130.8 (1C´), 129.3 (2C´), 129.0 (2C´), 128.9 (2C), 128.5 (1C), 124.4 (1C´), 123.7 (1C´ + 1C, *overlapped*), 123.6 (1C), 118.8 (1C´), 115.9 (1C) ppm; **IR** (KBr): *ν* = 3405, 3108, 3085, 3058, 2935, 2914, 2851, 1969, 1915, 1793, 1715, 1679, 1604, 1574, 1521, 1491, 1449, 1338, 1263, 1242, 1263, 1242, 1189, 1171, 1138, 1105, 1084, 1060, 1036, 1018, 1000 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{15}H_9NNaO_3S$ $[M+Na]^+$: 306.0196, found: 306.0195.

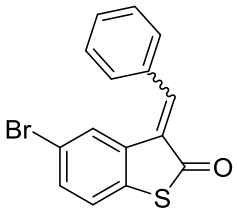
3-Benzylidene-5-methylbenzo[*b*]thiophen-2(3*H*)-one (1d)



The title compound was synthesized according to general procedure. Inseparable mixture of *E*/*Z* isomers (**1d(*E*)/1d(*Z*)** = 2.8/1), orange oil, yield = 74 %; **^{1}H-NMR** (400 MHz, Chloroform-*d*): [isomer **1d(*E*)** − H′; isomer **1d(*Z*) –** H]: δ = 7.99 – 7.94 (m, 2H), 7.78 (s, 1H´), 7.64 – 7.38 (m, 7H + 7H´, *overlapped*), 7.23 (t, *J* = 8.4 Hz, 1H´), 7.15 (ddd, *J* = 7.9, 1.6, 0.7 Hz, 1H), 7.09 (ddd, *J* = 8.0, 1.8, 0.9 Hz, 1H´), 2.41 (s, 3H), 2.16 (s, 3H´) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*) [isomer **1d(*E*)** − C′; isomer **1d(*Z*) –** C: δ = 195.2 (1C´), 192.7 (1C, *from 2D experiments*), 138.3 (1C), 138.1 (2C´), 135.3 (2C), 134.4 (1C´), 133.9 (1C), 133.3 (1C´), 132.5 (1C´), 131.6 (2C), 130.9 (2C´ + 1C, *overlapped*), 130.3 (2C),

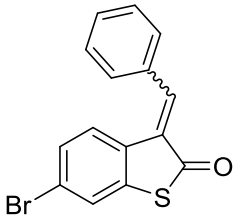
130.1 (1C), 129.8 (2C′), 129.6 (1C), 128.9 (3C′) , 128.2 (1C), 125.0 (1C′), 123.2 (1C′), 122.9 (1C), 121.7 (1C), 21.4 (1C), 21.3 (1C′) ppm; **IR** (KBr): ν = 3551, 3258, 3064, 2863, 2591, 1820, 1658, 1604, 1248, 1210, 1180, 1156, 10877, 1066, 1033, 1000, 943 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{16}H_{13}OS$ $[M+H]^+$: 253.0680, found: 253.0682.

3-Benzylidene-5-bromobenzo[*b*]thiophen-2(3*H*)-one (1e)



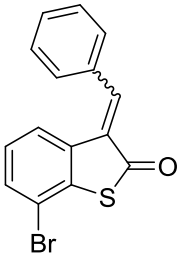
The title compound was synthesized according to general procedure. Inseparable mixture of *E*/*Z* isomers (**1e(*E*)/1e(*Z*)** = 2.0/1); yellow solid; yield = 82 %; **m.p**. = 101.6 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): [isomer **1e(*E*)** − H′; isomer **1e(*Z*) –** H]: δ = 8.01 – 7.94 (m, 2H), 7.86 (s, 1H′), 7.73 (d, *J* = 2.0 Hz, 1H′), 7.71 (s, 1H), 7.60 – 7.33 (m, 6H′ + 5H, *overlapped*), 7.25 – 7.15 (m, 1H′ + 1H, *overlapped*) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): [isomer **1e(*E*)** − C′; isomer **1e(*Z*) –** C]: δ =193.6 (1C′), 192.3 (1C, *only from 2D*), 140.2 (2C′ + 1C, *overlapped*), 134.8 (1C′+ 1C, *overlapped*), 133.6 (1C′), 132.7 (1C), 132.6 (1C′), 132.0 (1C′), 131.9 (1C), 131.8 (1C′), 131.6 (1C), 130.5 (2C), 129.0 (2C), 128.9 (2C′ + 1C, *overlapped*), 128.3 (2C′), 127.1 (1C′), 124.7 (2C′), 124.5 (1C), 124.1 (1C′), 119.6 (1C) ,119.2 (1C′) ppm; **IR** (KBr): ν = 3440, 3366, 3082, 3064, 3049, 3022, 3001, 2929, 1963, 1906, 1891, 1688, 1601, 1574, 1553, 1491, 1449, 1440, 1416, 1353, 1314, 1281, 1263, 1242, 1168, 1078, 1048, 1015 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{15}H_9BrNaOS$ $[M+Na]^+$: 338.9445, found: 338.9450.

3-Benzylidene-6-bromobenzo[*b*]thiophen-2(3*H*)-one (1f)



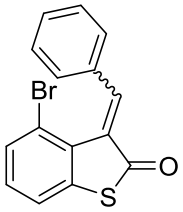
The title compound was synthesized according to general procedure. Inseparable mixture of *E*/*Z* isomers (**1f(*E*)/1f(*Z*)** = 5.8/1), yellow solid, yield = 94 %; **m.p**. = 101.6 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): [isomer **1f(*E*)** − H′; isomer **1f(*Z*) –** H]: δ = 8.00 – 7.89 (m, 2H), 7.84 (s, 1H′), 7.58 (s, 1H) 7.57 – 7.41 (m, 7H′ + 5H, *overlapped*), 7.38 (dd, *J* = 8.4, 1.8 Hz, 1H) 7.12 (dd, *J* = 8.5, 2.0 Hz, 1H′) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): [isomer **1f(*E*)** − C′; isomer **1f(*Z*) –** C]: δ = 193.49, 139.47, 139.2, 137.8, 134.0, 132.8, 131.7, 131.4, 130.1, 129.0, 128.9, 128.8, 128.7, 128.2, 126.2, 125.9, 125.2, 123.6, 122.1 ppm; **IR** (KBr): ν = 3333, 3079, 3058, 3043, 3022, 2932, 1975, 1957, 1888, 1811, 1700, 1676, 1598, 1494, 1464, 1446, 1401, 1317, 1242, 1198, 1171, 1138, 1093, 1054, 1030, 1009, 997 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{15}H_9BrNaOS$ $[M+Na]^+$: 338.9446, found: 338.9445.

3-Benzylidene-7-bromobenzo[*b*]thiophen-2(3*H*)-one (1g)



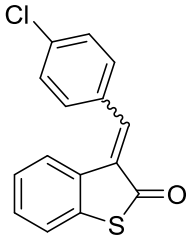
The title compound was synthesized according to general procedure. Inseparable mixture of *E*/*Z* isomers (**1g(*E*)/1g(*Z*)** = 4.5/1), yellow solid, yield = 61 %; **m.p.** = 102.5 °C; **^{1}H-NMR** (400 MHz, Chloroform-*d*): [isomer **1g(*E*)** − H′; isomer **1g(*Z*) –** H]: δ = 8.03 – 7.96 (m, 2H), 7.86 (s, 1H′), 7.62 – 7.39 (m, 7H′ + 6H, *overlapped*), 7.19 (t, *J* = 7.9 Hz, 1H), 6.92 (t, *J* = 8.0 Hz, 1H′) ppm; **^{13}C-NMR** (101 MHz, Chloroform-*d*): [isomer **1g(*E*)** − C′; isomer **1g(*Z*) –** C]: δ = 192.9 (1C′), 190.6 (1C, *from 2D experiments)*, 140.7 (2C), 140.4 (2C′), 138.3 (1C′ + 2C, *overlapped*), 134.7 (1C′), 133.8 (1C), 132.6 (1C′), 131.9 (2C), 131.8 (1C′), 131.5 (1C), 130.1 (2C), 128.9 (4C′), 128.3 (2C), 127.0 (1C), 126.7 (1C′), 122.5 (1C′), 119.3 (1C), 117.3 (1C′) ppm; **IR** (KBr): ν = 3082, 3052, 3028, 2956, 2923, 2893, 2872, 1694, 1646, 1604, 1580, 1530, 1500, 1458, 1410, 1377, 1356, 1344, 1305, 1263, 1228, 1195, 1171, 1138, 1108, 1084, 1051, 1024, 982, 964 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{15}H_9BrNaOS$ $[M+Na]^+$: 338.9448, found: 338.9445.

3-Benzylidene-4-bromobenzo[*b*]thiophen-2(3*H*)-one



The title compound was not possible isolate in pure form due to instability on silica gel or Al_2O_3. During purification on silica gel chromatography decomposition of product to starting benzothiophenone was observed.

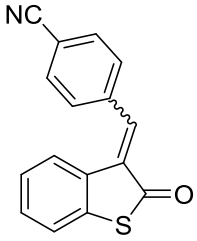
3-(4-Chlorobenzylidene)benzo[*b*]thiophen-2(3*H*)-one (1h)



The title compound was synthesized according to general procedure and purified by crystallization.

Mixture of *E*/*Z* isomers (**1h(*E*)/1h(*Z*)** = 6.5/1), yellow solid, yield = 68 %; **m.p.** = 121 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): [isomer **1h(*E*)** − H′; isomer **1h(*Z*) –** H]: δ = 7.91 (d, *J* = 8.6 Hz, 2H), 7.71 (s, 1H‘), 7.56 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 1H‘), 7.51 (d, *J* = 8.6 Hz, 2H‘), 7.44 (d, *J* = 8.3 Hz, 2H‘), 7.41 − 7.33 (m, 4H+1H‘), 7.28 (t, *J* = 7.5 Hz, 1H+1H‘), 7.02 (t, *J* = 7.7 Hz, 1H‘) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): [isomer **1h(*E*)** − C′; isomer **1h(*Z*) –** C]: δ = δ 194.4 (1C‘), 192.4 (1C), 136.9 (1C), 136.7 (1C‘), 136.1 (1C‘), 135.8 (1C‘), 135.0 (1C), 134.1 (1C‘), 132.9 (2C), 132.8 (1C), 132.7 (1C‘), 132.2 (1C), 131.6 (1C), 130.2 (2C‘), 130.2 (1C‘), 129.8 (1C‘), 129.5 (1C), 129.2 (2C‘), 128.4 (2C), 125.9 (1C), 125.6 (1C‘), 124.2 (1C‘), 123.6 (1C‘), 123.2 (1C), 121.0 (1C) (*one qC is missing*) ppm; **IR** (KBr): *ν* = 3064, 1688, 1607, 1589, 1491, 1404, 1278, 1171, 1156, 1096, 1072, 1054, 1030, 1015, 920, 830 cm^{-1}; **HRMS** (ESI) *m*/*z*: calcd for $C_{15}H_9ClNaOS^+$ $[M+Na]^+$ = 294.9955, found = 294.9952.

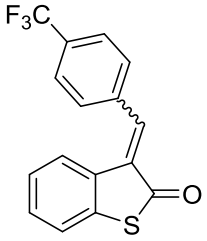
4-((2-Oxobenzo[*b*]thiophen-3(2*H*)-ylidene)methyl)benzonitrile (1i)



The title compound was synthesized according to general procedure and purified by crystallization.

Mixture of *E*/*Z* isomers (**1i(*E*)/1i(*Z*)** = 25/1) – slow isomerisation in $CDCl_3$ solution occurred, yellow solid, yield = 46 %; **m.p.** = 163 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): [isomer **1i(*E*)** − H′; isomer **1i(*Z*) –** H]: *δ* = 7.95 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H‘), 7.73 (s, 1H‘), 7.70 (d, *J* = 8.3 Hz, 2H, *overlapped*), 7.68 (d, *J* = 8.0 Hz, 2H‘), 7.61 (d, *J* = 7.7 Hz, 1H), 7.55 (s, 1H), 7.41 – 7.31 (m, 3H+3H‘, *overlapped*), 7.04 (td, *J* = 7.8, 1.2 Hz, 1H‘) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): [determined only isomer **1i(*E*)** − C′]: *δ* = 194.0, 139.3, 134.9, 134.9, 132.7 (2C‘), 131.7, 131.3, 130.8, 129.3 (2C), 125.8, 124.4, 123.8, 118.2, 113.1 ppm; **IR** (KBr): *ν* = 3357, 3049, 2956, 2226, 1796, 1682, 1613, 1278, 1162, 1057, 1024, 923, 845 cm^{-1}; **HRMS** (ESI) *m*/*z*: calcd for $C_{16}H_9NNaOS^+$ $[M+Na]^+$ = 286.0297, found = 286.0298.

3-(4-(Trifluoromethyl)benzylidene)benzo[*b*]thiophen-2(3*H*)-one (1j)

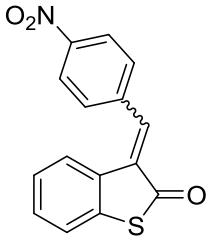


The title compound was synthesized according to general procedure and purified by crystallization.

Mixture of *E*/*Z* isomers (**1j(*E*)/1j(*Z*)** = 12.5/1), yellow solid, yield = 55 %; **m.p.** = 118 °C; **^{1}H NMR** (600 MHz, Chloroform-*d*): [isomer **1j(*E*)** − H′; isomer **1j(*Z*) –** H]: *δ* = 7.96 (d, *J* = 8.1 Hz, 2H‘), 7.76 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H’), 7.57 (s, 1H’), 7.41 – 7.37 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H) ppm. **^{13}C NMR** (151 MHz, Chloroform-*d*): [isomer **1j(*E*)** − C′; isomer **1j(*Z*) –** C]: *δ* = 194.2 (1C’), 192.2 (1C), 138.2 (1C’), 136.5 (1C), 136.3 (1C’), 135.8 (1C), 135.8 (1C’), 135.3 (1C), 135.1 (1C’), 133.7 (1C), 132.2 (1C), 131.8 (q, ^2J = 33.2 Hz, 1C), 131.4 (q, *J* = 33.2 Hz, 1C‘), 131.2 (1C), 130.5 (1C‘), 130.1 (1C), 129.5 (1C‘), 129.0 (2C+2C‘, *overlapped*), 126.1 (1C), 125.9 (q,

^4J = 3.6 Hz, 2C‘), 125.8 (1C‘), 125.0 (q, J = 3.6 Hz, 2C), 124.4 (1C‘), 123.8 (q, J = 271.8 Hz, 1C), 123.8 (q, J = 271.8 Hz, 1C’), 123.7 (1C‘), 123.4 (1C), 121.4 (1C) ppm; **^{19}F NMR** (376 MHz, Chloroform-*d*): [isomer **1j(*E*)** – F′; isomer **1j(*Z*) –** F]: δ = -62.83 (s, 3F‘), -62.95 (s, 3F) ppm; **IR** (KBr): ν = 3079, 1691, 1610, 1449, 1416, 1326, 1296, 1275, 1171, 1123, 1111, 1066, 1054, 1015, 926 cm^{-1}; **HRMS** (ESI) *m/z*: calcd for $C_{16}H_9F_3NaOS^+$ $[M+Na]^+$ = 329.0218, found = 329.0217.

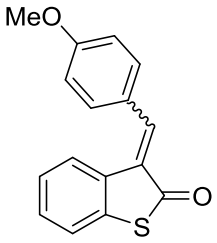
3-(4-Nitrobenzylidene)benzo[*b*]thiophen-2(3*H*)-one (1k)



The title compound was synthesized according to general procedure and purified by crystallization.

Mixture of *E*/*Z* isomers (**1k(*E*)/1k(*Z*)** = 4/1; orange powder, yield = 88 %; **m.p.** = 149 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): [isomer **1k(*E*)** − H′; isomer **1k(*Z*) –** H]: δ = 8.33 (d, J = 8.7 Hz, 2H’), 8.25 (d, J = 8.9 Hz, 2H), 7.96 (d, J = 8.7 Hz, 2H), 7.73 (s, 1H’), 7.72 (d, J = 8.9 Hz, 2H’), 7.60 (d, J = 7.8 Hz, 1H), 7.57 (s, 1H), 7.39 – 7.30 (m, 3H’+ 3H, *overlapped*), 7.02 (t, J = 7.7 Hz, 1H’) ppm; **^{13}C NMR** (151 MHz, Chloroform-*d*): [isomer **1k(*E*)** − C′; isomer **1k(*Z*) –** C]: δ = 193.9 (1C‘), 192.3 (1C), 148.2 (1C), 148.1 (1C‘), 141.3 (1C‘), 139.4 (1C), 136.6 (1C‘), 135.9 (1C‘), 135.6 (1C), 134.8 (1C), 134.4 (1C‘), 134.2 (1C‘), 131.8 (1C), 131.6 (2C), 130.9 (1C‘), 130.5 (1C), 129.6 (2C‘), 129.1 (1C), 126.2 (1C), 125.9 (1C‘), 124.5 (1C‘), 124.2 (2C‘), 123.9 (1C‘), 123.5 (1C), 123.2 (2C), 121.6 (1C) ppm; **IR** (KBr): ν = 3372, 3106, 2839, 2457, 1691, 1592, 1518, 1341, 1296, 1272, 1171, 1111, 1069, 1054, 1018, 920 cm^{-1}; **HRMS** (ESI) *m/z*: calcd for $C_{15}H_9NNaO_3S^+$ $[M+Na]^+$ = 306.0195, found = 306.0197.

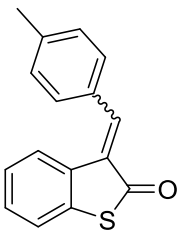
3-(4-Methoxybenzylidene)benzo[b]thiophen-2(3*H*)-one (1l)



The title compound was synthesized according to general procedure and purified by column chromatography.

Mixture of *E*/*Z* isomers (**1l(*E*)/1l(*Z*)** = 2.2/1), red-orange oil, yield = 95 %; **^{1}H NMR** (400 MHz, Chloroform-*d*): [isomer **1l(*E*)** − H′; isomer **1l(*Z*) –** H]: δ = 8.11 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 7.0 Hz, 1H‘), 7.75 (s, 1H‘), 7.60 (d, J = 8.9 Hz, 2H‘), 7.55 (d, J = 7.3 Hz, 1H), 7.52 (s, 1H), 7.36 (d, J = 7.8 Hz, 1H‘), 7.33 – 7.23 (m, 3H+1H‘), 7.04 (td, J = 7.9, 1.3 Hz, 1H‘), 6.98 – 6.94 (m, 2H+2H‘), 3.89 (s, 3H‘), 3.88 (s, 3H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): [isomer **1l(*E*)** − C′; isomer **1l(*Z*) –** C]: δ = 194.8 (1C‘), 192.5 (1C), 162.3 (1C), 161.2 (1C‘), 139.0 (1C), 138.9 (1C‘), 135.7 (1C‘), 134.6 (2C), 134.5 (1C), 133.8 (1C), 132.0 (1C‘), 131.3 (2C‘), 130.5 (1C‘), 129.5 (1C‘), 129.3 (1C), 128.5 (1C), 126.3 (1C‘), 126.2 (1C), 125.7 (1C), 125.4 (1C‘), 123.7 (1C‘), 123.4 (1C‘), 123.0 (1C), 120.5 (1C), 114.2 (2C‘), 113.7 (1C), 55.44 (1C), 55.41 (1C‘) ppm; **IR** (KBr): ν = 3064, 2836, 1685, 1601, 1512, 1443, 1260, 1180, 1069, 1054, 1030, 1003, 920 cm^{-1}; **HRMS** (ESI) *m/z*: calcd for $C_{16}H_{12}NaO_2S^+$ $[M+Na]^+$ = 291.0450, found = 291.0450.

3-(4-Methylbenzylidene)benzo[*b*]thiophen-2(3*H*)-one (1m)

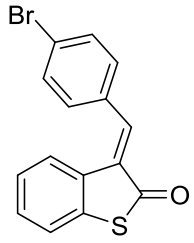


The title compound was synthesized according to general procedure and purified by column chromatography.

Mixture of *E*/*Z* isomers (**1m(*E*)/1m(*Z*)** = 4/1), yellow oil, yield = 80 %; **^{1}H NMR** (400 MHz, Chloroform-*d*): [isomer **1m(*E*)** − H′; isomer **1m(*Z*) –** H]: δ = 7.92 (d, J = 8.2 Hz, 2H), 7.79 (s, 1H‘), 7.70 (d, J = 8.0 Hz, 1H‘), 7.58 − 7.56 (m, 2H), 7.50 (d, J = 8.0 Hz, 2H‘), 7.35 (d, J = 7.8 Hz, 1H‘), 7.34 − 7.30 (m, 2H), 7.27 − 7.24 (m, 3H+3H‘), 7.02 (td, J = 7.9, 1.2 Hz, 1H‘), 2.43 (s, 3H‘), 2.42 (s, 3H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): [isomer **1m(*E*)** − C′; isomer **1m(*Z*) –** C]: δ = 194.7 (1C‘), 192.3 (1C), 142.0 (1C), 140.4 (1C‘), 139.1 (1C), 138.9 (1C‘), 135.8 (1C‘),

134.7 (1C), 133.4 (1C), 133.0 (1C‘), 132.0 (2C), 131.3 (1C‘), 130.8 (1C), 130.5 (1C), 130.3 (1C‘), 129.7 (1C‘), 129.5 (2C‘), 129.1 (2C‘), 128.96 (1C), 128.95 (1C), 125.7 (1C), 125.4 (1C‘), 124.1 (1C‘), 123.4 (1C‘), 123.1 (1C), 120.8 (1C), 21.7 (1C), 21.6 (1C‘) ppm; **IR** (KBr): ν = 3058, 2923, 1688, 1601, 1446, 1380, 1275, 1186, 1162, 1066, 1054, 1027, 1003, 923, 815 cm^{-1}. **HRMS** (ESI) *m*/*z*: calcd for $C_{16}H_{12}NaOS^+$ $[M+Na]^+$ = 275.0501, found = 275.0501.

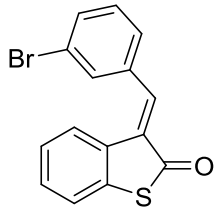
3-(4-Bromobenzylidene)benzo[*b*]thiophen-2(3*H*)-one (1n)



The title compound was synthesized according to general procedure and purified by crystallization.

E isomer, yellow needles, yield = 69 %; **m.p.** = 146 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.69 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.28 (td, *J* = 7.5, 1.1 Hz, 1H), 7.02 (td, *J* = 7.9, 1.3 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 194.4, 136.7, 136.1, 134.1, 132.2 (3C), 130.4 (2C), 130.2, 129.8, 125.6, 124.2, 124.0, 123.6 ppm; **IR** (KBr): ν = 3085, 1685, 1604, 1580, 1491, 1395, 1275, 1168, 1108, 1072, 1012, 920, 827 cm^{-1}; **HRMS** (ESI) *m*/*z*: calcd for $C_{15}H_9BrNaOS^+$ $[M+Na]^+$ = 338.9450, found = 338.9441.

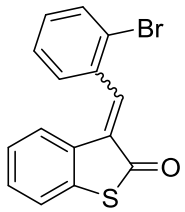
3-(3-Bromobenzylidene)benzo[*b*]thiophen-2(3*H*)-one (1o)



The title compound was synthesized according to general procedure and purified by crystallization.

E isomer, yellow needles, yield = 48 %; **m.p.** = 98 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.70 (s, 2H, *overlapped*), 7.57 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.29 (td, *J* = 7.6, 1.2 Hz, 1H), 7.03 (td, *J* = 7.9, 1.3 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 194.3, 136.5, 136.2, 136.0, 134.7, 132.6, 131.4, 130.5, 130.3, 129.6, 127.2, 125.7, 124.4, 123.6, 123.0 ppm; **IR** (KBr): ν = 3061, 1688, 1604, 1556, 1452, 1365, 1269, 1180, 1072, 1054, 1003, 929 cm^{-1}; **HRMS** (ESI) *m*/*z*: calcd for $C_{15}H_{10}BrOS^+$ $[M+H]^+$ = 316.9630, found = 316.9640.

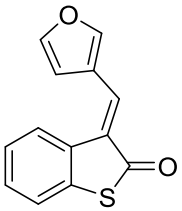
3-(2-Bromobenzylidene)benzo[*b*]thiophen-2(3*H*)-one (1p)



The title compound was synthesized according to general procedure and purified by crystallization.

Mixture of *E*/*Z* isomers (**1p(*E*)/1p(*Z*)** = 6.5/1), yellow solid, yield = 68 %; **m.p.** = 121 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): [isomer **1p(*E*)** − H′; isomer **1p(*Z*) –** H]: δ = 7.82 (d, *J* = 7.7 Hz, 1H), 7.74 – 7.71 (m, 2H‘), 7.68 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.54 – 7.52 (m, 1H‘), 7.40 – 7.25 (m, 5H+4H‘, *overlapped*), 7.21 (d, *J* = 7.8 Hz, 1H‘), 6.97 (t, *J* = 7.7 Hz, 1H‘) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): [isomer **1p(*E*)** − C′; isomer **1p(*Z*) –** C]: δ = 194.0 (1C‘), 191.9 (1C), 136.6 (1C‘), 136.2 (1C), 136.1 (1C‘), 135.2 (1C‘), 134.6 (1C), 133.5 (1C), 133.3 (1C‘), 132.4 (1C), 131.9 (1C), 131.3 (1C), 130.9 (1C‘), 130.3 (1C), 130.2 (1C‘), 129.9 (1C‘), 129.7 (1C‘), 129.6 (1C‘), 127.5 (1C‘), 126.6 (1C), 126.1 (1C), 125.7 (1C‘), 124.7 (1C), 124.5 (1C‘), 123.6 (1C‘), 123.5 (1C‘), 123.3 (1C), 121.6 (1C), (*two qC are missing*) ppm; **IR** (KBr): ν = 3058, 1691, 1607, 1583, 1446, 1281, 1174, 1135, 1054, 1030, 923, 881 cm^{-1}; **HRMS** (ESI) *m*/*z*: calcd for $C_{16}H_{13}BrNaO_2S^+$ $[M+Na]^+$ = 370.9712, found = 370.9713.

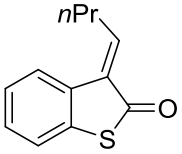
3-(Furan-3-ylmethylene)benzo[*b*]thiophen-2(3*H*)-one (1q)



The title compound was synthesized according to general procedure and purified by column chromatography.

E isomer, yellow powder, yield = 41 %; **m.p.** = 103 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 8.27 (d, *J* = 3.7 Hz, 1H), 7.67 (d, *J* = 1.7 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.47 (s, 1H), 7.37 – 7.21 (m, 3H), 6.65 (dd, *J* = 3.7, 1.2 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): *δ* = 191.9, 151.2, 146.7, 134.8, 132.9, 128.8, 127.1, 125.7, 123.2, 122.8, 120.9, 120.4, 114.0 ppm; **IR** (KBr): *v* = 3357, 3120, 3055, 3016, 2092, 2074, 1942, 1912, 1850, 1772, 1685, 1604, 1586, 1536, 1473, 1449, 1395, 1341, 1302, 1290, 1219, 1159, 1129, 1093, 1048, 1033, 931, 890, 863, 824, 746, 722, 701, 680, 612, 588 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{13}H_9O_2S^+$ $[M+H]^+$ = 229.0318, found = 229.0316.

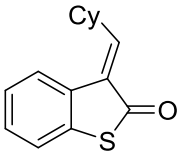
(*E*)-3-Butylidenebenzo[*b*]thiophen-2(3*H*)-one (1r)



The title compound was synthesized according to general procedure and purified by column chromatography.

E isomer, brownish solid, yield = 35 %; **m.p.** = 85.0 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): *δ* = 7.67 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.33 – 7.24 (m, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 2.67 (q, *J* = 7.4 Hz, 2H), 1.72 (h, *J* = 7.4 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): *δ* = 194.1, 144.1, 135.5, 134.3, 131.3, 129.0, 126.0, 125.0, 123.5, 31.4, 22.1, 14.0 ppm; **IR** (KBr): *v* = 3058, 2866, 1694, 1625, 1583, 1467, 1446, 1374, 1347, 1293, 1254, 1186, 1132, 1105, 1042, 1024, 914, 851 cm^{-1}; **HRMS** (ESI) *m*/*z*: calcd for $C_{12}H_{12}ONaS^+$ $[M+Na]^+$ = 227.0501, found = 227.0502.

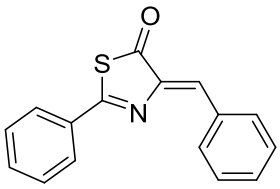
(*E*)-3-(cyclohexylmethylene)benzo[*b*]thiophen-2(3*H*)-one (1s)



The title compound was synthesized according to general procedure and purified by column chromatography.

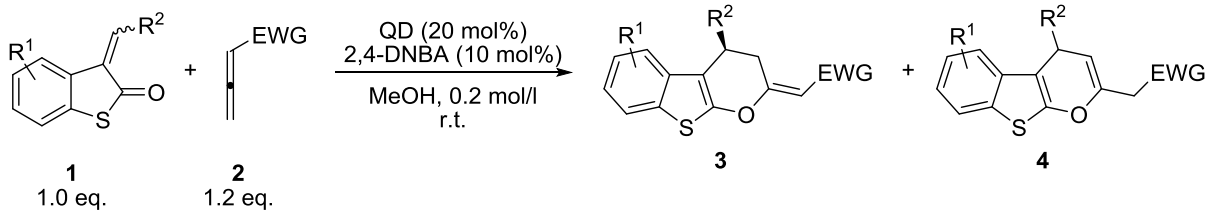
E isomer, yellow oil, yield = 33 %; **^{1}H NMR** (400 MHz, Chloroform-*d*): *δ* = 7.49 – 7.39 (m, 1H), 7.33 – 7.17 (m, 3H), 6.74 (d, *J* = 9.8 Hz, 1H), 3.63 (tdt, *J* = 11.1, 9.8, 3.5 Hz, 1H), 1.86 – 1.66 (m, 5H), 1.49 – 1.34 (m, 2H), 1.33 – 1.13 (m, 3H). ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): *δ* = 193.5, 149.8, 134.3, 132.0, 131.3, 128.8, 125.7, 123.1, 120.5, 36.3, 32.1, 25.8, 25.4 ppm; **IR** (KBr): *v* = 3933, 3892, 3886, 3874, 3644, 3621, 3616, 3780, 3771, 3760, 3752, 3736, 3726, 3712, 3676, 3650, 3629, 3361, 3297, 3297, 3138, 3063, 3028, 2992, 2925, 2850, 2790, 2656, 2365, 2254, 1938, 1905, 1870, 1830, 1783, 1689, 1614, 1588, 1572, 1550, 1508, 1462, 1449, 1364, 1344, 1314, 1290, 1262, 1239, 1216, 1178, 1160, 1131, 1109, 1071, 1029, 1004, 952, 930, 922, 906, 877, 755, 726, 711, 692, 674, 589 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd for $C_{15}H_{17}OS^+$ $[M+H]^+$ = 245.0995, found = 245.0995.

(Z)-4-Benzylidene-2-phenylthiazol-5(4H)-one (5c)



The title compound was synthesized according to reported procedure.[5] Yellow solid, yield = 52 %; **m.p.** = 132 °C, (lit,[5] m. p. = 132°C); **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 8.29 – 8.27 (m, 2H), 8.05 – 8.02 (m, 2H), 7.61 – 7.45 (m, 6H), 7.26 (s, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 194.7, 166.8, 146.2, 133.7, 133.4, 133.2 (2C), 132.7, 131.3, 131.3, 129.0 (2C), 128.9 (2C), 128.3 (2C) ppm; **IR** (KBr): *v* = 3360, 3064, 3022, 1972, 1796, 1694, 1613, 1571, 1512, 1485, 1440, 1314, 1257, 1141, 1030, 1003, 982, 934, 746 cm^{-1}; **HRMS** (ESI+) m/z calcd for $C_{17}H_{15}NNaO_2S^+$ $[M+Na]^+$ = 320.0716, found = 320.0721.

General procedure for formal cycloaddition reaction



1 1.0 eq. **2** 1.2 eq. **3** **4**

To a solution of corresponding allenic compound **2** (0.12 mmol, 1.2 eq.) in MeOH (0.5 ml) was quinidine (6.5 mg, 0.02 mmol, 0.2 eq.) added in one portion. The mixture was stirred for 10 minutes at room temperature. Then corresponding alkylidene compound **1** (0.1 mmol, 1.0 eq.) and 2,4-DNBA (2.1 mg, 0.01 mmol, 0.1 eq.) were added to the reaction mixture. The reaction was stirred for the indicated time.

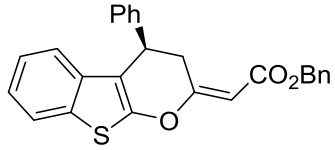
Method A:

After the reaction was completed the solvent was evaporated. Crude product was purified by column chromatography (Hex/EtOAc mixtures).

Method B:

After the reaction was completed the precipitate was filtered and washed with minimal amount of cold MeOH.

Benzyl (*R*,*E*)-2-(4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-b]pyran-2-ylidene)acetate (3a)



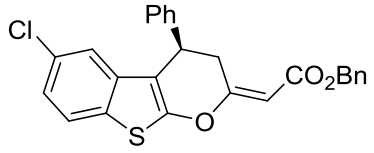
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a white solid, **3a**/**4a** ≥ 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 50:1), *ee* = 90 %; yield **3a** = 92 %; $[\alpha]_D^{20}$ = -15.4 (*c* = 0.6, $CHCl_3$).

Method B: *ee* = 99 %; yield **3a** = 73 %; $[\alpha]_D^{20}$ = -17.7 (*c* = 0.5, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 207 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 5.8 min (major enan.), t_R = 10.0 min (minor enan.), **m.p.** = 113.6 °C, **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.80 – 7.64 (m, 1H), 7.44 – 7.12 (m, 13H), 5.84 (d, *J* = 1.5 Hz, 1H), 5.11 (q, *J* = 12.5 Hz, 2H), 4.38 (dd, *J* = 6.5, 4.3 Hz, 1H), 4.10 (dd, *J* = 15.5, 4.3 Hz, 1H), 3.36 (ddd, *J* = 15.4, 6.6, 1.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.3, 165.9, 153.5, 141.4, 136.2, 136.0, 131.6, 128.7 (2C), 128.5 (2C), 128.1, 128.0 (2C), 127.4 (2C), 127.1, 124.8, 123.4, 122.4, 120.8, 112.3, 101.7, 65.8, 36.0, 31.1 ppm; **IR** (KBr): *v* = 3067, 3034, 2959, 2887, 2836, 1945, 1900, 1870, 1820, 1787, 1703, 1655, 1598, 1586, 1548, 1497, 1470, 1452, 1434, 1389, 1356, 1306, 1266, 1248, 1228, 1207, 1195, 1174, 1102, 1016, 1063, 1018, 988 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{20}NaO_3S^+$ $[M+Na]^+$: 435.1025, found: 435.1024.

Benzyl (*R*,*E*)-2-(6-chloro-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3b)



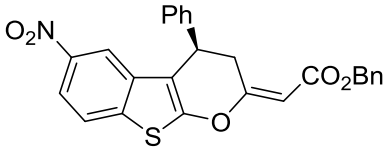
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a white solid, **3b**/**4b** ≥ 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 25:1), *ee* = 86 %; yield **3b** = 82 %; $[\alpha]_D^{20}$ = 28.6 (*c* = 0.9, $CHCl_3$).

Method B: *ee* = 89 %, yield **3b** = 80 %, $[\alpha]_D^{20}$ = 29.3 (*c* = 1.1, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IA column (mobile phase: *n*-heptane/propan-2-ol – 97:3, λ = 232 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 10.0 min (minor. enan.), t_R = 10.7 min (major. enan.); **m.p.** = 104.3 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.59 (d, *J* = 8.5 Hz, 1H), 7.39 – 7.21 (m, 8H), 7.21 – 7.07 (m, 4H), 5.83 (d, *J* = 1.5 Hz, 1H), 5.09 (q, *J* = 12.5 Hz, 2H), 4.33 (dd, *J* = 6.5, 4.0 Hz, 1H), 4.10 (dd, *J* = 15.4, 4.1 Hz, 1H), 3.30 (ddd, *J* = 15.4, 6.5, 1.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 166.1, 165.4, 155.0, 140.9, 137.5, 136.0, 131.1, 129.6, 128.8 (2C), 128.5 (2C), 128.1 (2C), 128.0, 127.3 (2C), 127.3, 123.8, 123.5, 120.5, 112.0, 102.2, 65.9, 35.9, 31.0 ppm; **IR** (KBr): *v* = 3082, 3064, 3025, 3004, 2989, 2941, 2923, 2869, 2851, 1957, 1870, 1817, 1709, 1649, 1595, 1577, 1545, 1500, 1449, 1428, 1380, 1353, 1329, 1308, 1293, 1260, 1222, 1204, 1168, 1102, 1078, 1027, 994, 967, 863 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{19}ClNaO_3S$ $[M+Na]^+$: 469.0628, found: 469.0636.

Benzyl (*R*,*E*)-2-(6-nitro-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3c)



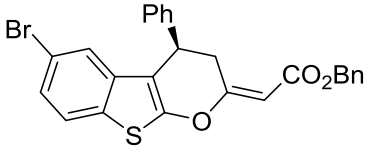
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a white solid, **3c**/**4c** ≥ 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 7:1), *ee* = 80 %; yield **3c** = 72 %; $[\alpha]_D^{20}$ = 52.2 (*c* = 1.4, $CHCl_3$).

Method B: *ee* = 80 %; yield **3c** = 65 %; $[\alpha]_D^{20}$ = 48.1 (*c* = 0.5, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 280 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 10.2 min (major enan.), t_R = 10.9 min (minor enan.); **m.p.** = 98.8 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 8.06 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.98 (d, *J* = 2.2 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.40 – 7.26 (m, 8H), 7.21 – 7.14 (m, 2H), 5.87 (d, *J* = 1.4 Hz, 1H), 5.10 (q, *J* = 12.4 Hz, 2H), 4.43 (dd, *J* = 6.5, 4.4 Hz, 1H), 4.08 (dd, *J* = 15.5, 4.4 Hz, 1H), 3.39 (ddd, *J* = 15.4, 6.5, 1.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 165.9, 164.9, 156.0, 145.8, 140.4, 137.7, 136.5, 135.8, 129.0 (2C), 128.5 (2C), 128.2, 128.0 (2C), 127.6, 127.3 (2C), 123.0, 117.9, 116.1, 113.1, 102.8, 66.0, 36.1, 30.9 ppm; **IR** (KBr): *v* = 3091, 3061, 3034, 2956, 2929, 2854, 1709, 1658, 1613, 1580, 1518, 1494, 1449, 1383, 1338, 1251, 1216, 1198, 1165, 1099, 1084, 1057, 1027, 991 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{19}NNaO_5S$ $[M+Na]^+$: 480.0871, found: 480.0876.

Benzyl (*R*,*E*)-2-(6-bromo-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3e)



The title compound was synthesized according to general procedure (reaction time: 24 hours), affording the title compound as a white solid, **3e**/**4e** = 15:1.

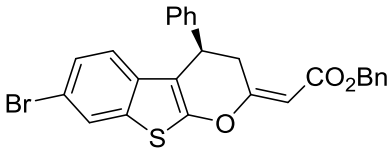
Method A: Crude product was purified by column chromatography (hexane/EtOAc = 15:1), *ee* = 89 %; yield **3e** = 87 %; $[\alpha]_D^{20}$ = 43.7 (*c* = 1.0, $CHCl_3$).

Method B: *ee* = 90 %; yield **3e** = 88 %; $[\alpha]_D^{20}$ = 45.4 (*c* = 0.8, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IA column (mobile phase: *n*-heptane/propan-2-ol – 97:3, λ = 234 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 10.5 min (minor enan.), t_R = 11.4 min (major enan.); **m.p.** = 116.9 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.53 (d, *J* = 8.5 Hz, 1H), 7.39 – 7.22 (m, 10H), 7.18 – 7.13 (m, 2H), 5.82 (d, *J* = 1.5 Hz, 1H), 5.09 (q, *J* = 12.5 Hz, 2H), 4.33 (dd, *J* = 6.5, 3.9 Hz, 1H), 4.12 (dd, *J* = 15.4, 4.0 Hz, 1H), 3.28 (ddd, *J* = 15.4, 6.5, 1.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*):

δ = 166.1, 165.5, 154.8, 140.8, 137.8, 136.0, 130.1, 128.8 (2C), 128.5 (2C), 128.1, 128.0 (2C), 127.3 (3C), 126.5, 123.8, 123.5, 118.9, 111.9, 102.2, 65.9, 35.9, 31.0 ppm; **IR** (KBr): ν = 3088, 3064, 3031, 2932, 2881, 2851, 1876, 1715, 1697, 1649, 1595, 1577, 1500, 1440, 1416, 1380, 1362, 1332, 1308, 1257, 1222, 1198, 1162, 1111, 1066, 1021 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{19}BrNaO_3S$ $[M+Na]^+$: 513.0127, found: 513.0130.

Benzyl (*R*,*E*)-2-(7-bromo-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3f)



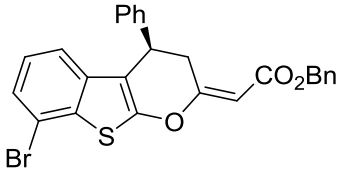
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a white solid; **3f**/**4f** ≥ 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 25:1); *ee* = 83 %; yield **3f** = 86 %; $[\alpha]_D^{20}$ = -8.9 (*c* = 0.8, $CHCl_3$).

Method B: *ee* = 87 %; yield **3f** = 82 %; $[\alpha]_D^{20}$ = -10.0 (*c* = 1.1, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IA column (mobile phase: *n*-heptane/propan-2-ol – 97:3, λ = 206 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 10.1 min (minor. enan.), t_R = 11.0 min (major. enan.); **m.p.** = 136.1 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.83 (d, *J* = 1.8 Hz, 1H), 7.41 – 7.29 (m, 7H), 7.28 – 7.23 (m, 1H), 7.23 – 7.09 (m, 2H), 6.97 (d, *J* = 8.5 Hz, 1H), 5.84 (d, *J* = 1.3 Hz, 1H), 5.12 (q, *J* = 12.5 Hz, 2H), 4.34 (dd, *J* = 6.5, 4.7 Hz, 1H), 4.01 (dd, *J* = 15.5, 4.7 Hz, 1H), 3.43 (ddd, *J* = 15.5, 6.5, 1.5 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.2, 165.5, 153.9, 141.1, 136.0, 135.1, 133.0, 128.8 (2C), 128.6 (2C), 128.2 (2C), 128.1 (2C), 127.4 (2C), 127.3, 124.9, 122.1, 116.6, 112.1, 102.1, 65.9, 36.2, 31.2 ppm; **IR** (KBr): ν = 3082, 3067, 3028, 3010, 2941, 2929, 2893, 2884, 2851, 1703, 1655, 1598, 1577, 1539, 1491, 1458, 1422, 1380, 1362, 1299, 1263, 1245, 1213, 1192, 1168, 1135, 1099, 1054, 1030, 991 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{19}BrNaO_3S$ $[M+Na]^+$: 513.0121, found: 513.0131.

Benzyl (*R*,*E*)-2-(8-bromo-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3g)



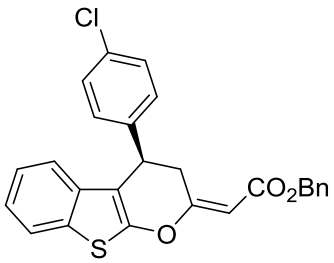
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a white solid, **3g**/**4g** ≥ 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 25:1), *ee* = 87 %; yield **3g** = 78 %; $[\alpha]_D^{20}$ = -43.5 (*c* = 0.9, $CHCl_3$).

Method B: *ee* = 90 %; yield **3g** = 83 %; $[\alpha]_D^{20}$ = -45.0 (*c* = 1.2, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IA column (mobile phase: *n*-heptane/propan-2-ol – 97:3, λ = 206 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 8.0 min (minor enan.), t_R = 8.8 min (major enan.), **m.p.** = 123.8 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.40 – 7.33 (m, 5H), 7.33 – 7.29 (m, 3H), 7.28 – 7.22 (m, 1H), 7.21 – 7.15 (m, 2H), 7.13 – 7.08 (m, 2H), 5.87 (d, *J* = 1.4 Hz, 1H), 5.12 (q, *J* = 12.5 Hz, 2H), 4.36 (dd, *J* = 6.5, 4.5 Hz, 1H), 4.06 (dd, *J* = 15.5, 4.5 Hz, 1H), 3.40 (ddd, *J* = 15.4, 6.5, 1.5 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.2, 165.4, 154.3, 141.1, 137.4, 136.0, 133.6, 128.8 (2C), 128.5 (2C), 128.1, 128.0 (2C), 127.4 (2C), 127.3, 126.2 (2C), 119.7, 115.8, 113.4, 102.2, 65.9, 36.4, 31.1 ppm; **IR** (KBr): ν = 3028, 2956, 1694, 1646, 1604, 1580, 1539, 1497, 1458, 1410, 1383, 1356, 1311, 1257, 1228, 1195, 1171, 1141, 1114, 1045, 1024, 961 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{19}BrNaO_3S$ $[M+Na]^+$: 513.0121, found: 513.0131.

Benzyl (*R*,*E*)-2-(4-(4-chlorophenyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3h)



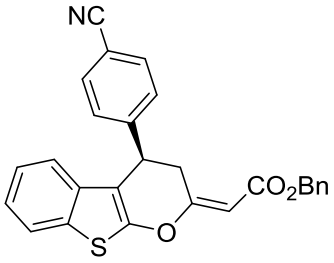
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a white solid, **3h**/**4h** > 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 50:1), *ee* = 88 %; yield **3h** = 82 %; $[\alpha]_D^{20}$ = -12.5 (*c* = 0.8, $CHCl_3$).

Method B: *ee* = 93 %; yield **3h** = 63 %; $[\alpha]_D^{20}$ = -14.7 (*c* = 0.9, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 254 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 6.5 min (minor enan.), t_R = 14.0 min (major enan.), **m.p.** = 122.0 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.70 (dd, *J* = 5.9, 3.1 Hz, 1H), 7.39 – 7.29 (m, 5H), 7.25 – 7.21 (m, 4H), 7.17 – 7.14 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.83 (s, 1H), 5.12 – 5.07 (m, 2H), 4.35 (dd, *J* = 6.3, 3.8 Hz, 1H), 4.13 (dd, *J* = 15.4, 3.8 Hz, 1H), 3.27 (dd, *J* = 15.9, 7.1 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.2, 165.4, 153.8, 139.9, 136.0, 132.9, 131.7, 128.9 (2C), 128.8 (2C), 128.6 (2C), 128.2, 128.1 (2C), 124.9, 123.7, 122.6, 120.6, 111.7, 102.1, 65.9, 35.4, 30.9 ppm; **IR** (KBr): ν = 1700, 1646, 1595, 1580, 1551, 1491, 1461, 1431, 1383, 1350, 1311, 1269, 1204, 1156, 1108, 1021, 955, 920, 860, 758, 740 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{19}NaO_3ClS^+$ $[M+Na]^+$: 469.0636, found: 469.0631.

Benzyl (*R*,*E*)-2-(4-(4-cyanophenyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3i)



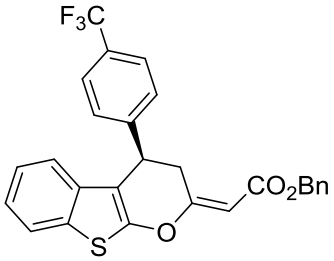
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a yellowish solid, **3i**/**4i** > 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 50:1), *ee* = 80 %; yield **3x** = 90 %; $[\alpha]_D^{20}$ = -15.1 (*c* = 0.3, $CHCl_3$).

Method B: *ee* = 78 %; yield **3x** = 37 %; $[\alpha]_D^{20}$ = -10.0 (*c* = 0.5, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 80:20, λ = 254 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 10.3 min (minor enan.), t_R = 25.4 min (major enan.), **m.p.** = 118.3 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.81 – 7.69 (m, 1H), 7.61 – 7.49 (m, 2H), 7.38 (qd, *J* = 4.2, 2.0 Hz, 3H), 7.34 – 7.29 (m, 4H), 7.28 – 7.22 (m, 2H), 7.21 – 7.07 (m, 1H), 5.86 (d, *J* = 1.6 Hz, 1H), 5.20 – 5.02 (m, 2H), 4.45 (dd, *J* = 6.6, 3.5 Hz, 1H), 4.23 (dd, *J* = 15.4, 3.6 Hz, 1H), 3.28 (ddd, *J* = 15.3, 6.6, 1.7 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.1, 164.7, 154.3, 146.8, 135.9, 135.7, 132.6 (2C), 131.7, 128.6 (2C), 128.3 (3C), 128.1 (2C), 125.1, 123.9, 122.7, 120.3, 118.7, 111.2, 110.8, 102.6, 66.0, 36.0, 30.4 ppm; **IR** (KBr): ν = 2223, 1709, 1652, 1607, 1583, 1500, 1467, 1434, 1380, 1353, 1302, 1269, 1210, 1159, 1090, 1078, 1018, 985, 851, 764, 734, 698 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{27}H_{20}O_3NS^+$ $[M+H]^+$: 438.1158, found: 438.1154.

Benzyl (*R*,*E*)-2-(4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3j)



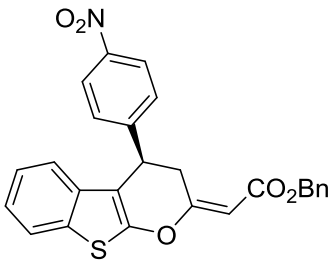
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a transparent oil, **3j**/**4j** = 15:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 50:1), *ee* = 84 %; yield **3j** = 80 %; $[\alpha]_D^{20}$ = -4.4 (*c* = 1.2, $CHCl_3$).

Method B: *ee* = 75 %; yield **3j** = 53 %; $[\alpha]_D^{20}$ = -2.1 (*c* = 1.0, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 254 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 7.0 min (minor enan.), t_R = 17.8 min (major enan.); **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.80 – 7.68 (m, 1H), 7.60 – 7.49 (m, 2H), 7.41 – 7.27 (m, 7H), 7.24 (q, *J* = 4.0, 3.5 Hz, 2H), 7.20 – 7.07 (m, 1H), 5.85 (d, *J* = 1.5 Hz, 1H), 5.21 – 5.00 (m, 2H), 4.44 (dd, *J* = 6.6, 3.7 Hz, 1H), 4.21 (dd, *J* = 15.4, 3.7 Hz, 1H), 3.29 (ddd, *J* = 15.4, 6.7, 1.7 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.2, 165.1, 154.1, 145.5, 135.9 (2C), 131.7, 129.4 (q, *J* = 32.5 Hz), 128.6 (2C), 128.2, 128.1 (2C), 127.8 (2C), 125.8 (q, *J* = 3.8 Hz, 2C), 125.0, 123.8 (q, *J* = 272.2 Hz) 123.8, 122.6, 120.5, 111.3, 102.3, 66.0, 35.8, 30.7 ppm; **^{19}F NMR** (376 MHz, Chloroform-*d*): δ = -62.40 ppm; **IR** (KBr): ν = 3067, 3034, 2956, 1712, 1655, 1622, 1586, 1556, 1494, 1467, 1440, 1416, 1383, 1356, 1323, 1269, 1198, 1162, 1105, 1069, 1015, 988, 845, 761, 731, 701, 609 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{27}H_{20}O_3F_3S^+$ $[M+H]^+$: 481.1080, found: 481.1076.

Benzyl (*R*,*E*)-2-(4-(4-nitrophenyl)-3,4-dihydro-2H-benzo[4,5]thieno[2,3-b]pyran-2-ylidene)acetate (3k)



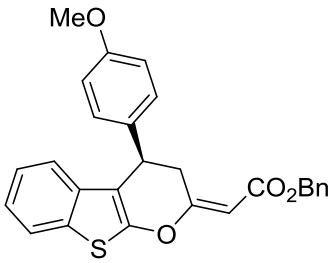
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a yellow solid, **3k**/**4k** = 17:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 20:1), *ee* = 75 %; yield **3k** = 72 %; $[\alpha]_D^{20}$ = -12.8 (*c* = 0.6, $CHCl_3$).

Method B: *ee* = 73 %; yield **3k** = 73 %; $[\alpha]_D^{20}$ = -13.6 (*c* = 0.3, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 80:20, λ = 254 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 9.8 min (minor enan.), t_R = 24.2 min (major enan.), **m.p.** = 114 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 8.11 (d, *J* = 8.8 Hz, 2H), 7.73 – 7.70 (m, 1H), 7.34 – 7.32 (m, 5H), 7.28 – 7.24 (m, 4H), 7.14 – 7.12 (m, 1H), 5.84 (d, *J* = 1.5 Hz, 1H), 5.14 – 5.03 (m, 2H), 4.49 (dd, *J* = 6.7, 3.5 Hz, 1H), 4.24 (dd, *J* = 15.3, 3.5 Hz, 1H), 3.27 (ddd, *J* = 15.4, 6.7, 1.7 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.1, 164.5, 154.4, 148.8, 147.1, 135.8, 135.7, 131.6, 128.5 (2C), 128.3 (2C), 128.3, 128.1 (2C), 125.1, 124.0 (2C), 123.9, 122.7, 120.2, 110.7, 102.7, 66.0, 35.7, 30.4 ppm; **IR** (KBr): ν = 1712, 1655, 1601, 1583, 1524, 1467, 1437, 1386, 1350, 1299, 1269, 1204, 1159, 1102, 1021, 988, 964, 857, 752, 731, 701 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{19}NaO_5NS^+$ $[M+Na]^+$: 480.0876, found: 480.0871.

Benzyl (*R*,*E*)-2-(4-(4-methoxyphenyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3l)



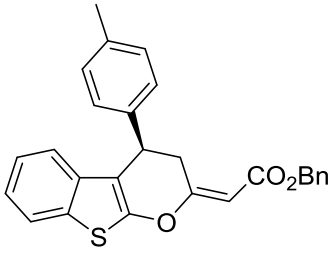
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a white solid, **3l**/**4l** > 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 50:1), *ee* = 85 %; yield **3l** = 90 %; $[\alpha]_D^{20}$ = -20.9 (*c* = 0.4, $CHCl_3$).

Method B: *ee* = 85%; yield **3l** = 62 %; $[\alpha]_D^{20}$ = -17.3 (*c* = 0.7, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 254 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 7.1 min (minor enan.), t_R = 10.8 min (major enan.), **m.p.** = 143 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.70 – 7.66 (m, 1H), 7.37 – 7.28 (m, 5H), 7.23 – 7.18 (m, 2H), 7.17 – 7.14 (m, 1H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 5.80 (d, *J* = 1.4 Hz, 1H), 5.10 (q, *J* = 12.5 Hz, 2H), 4.32 (dd, *J* = 6.5, 4.1 Hz, 1H), 4.06 (dd, *J* = 15.4, 4.2 Hz, 1H), 3.76 (s, 3H), 3.30 (ddd, *J* = 15.4, 6.5, 1.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.3, 166.1, 158.6, 153.4, 136.3, 136.1, 133.5, 131.6, 128.5 (2C), 128.4 (2C), 128.1, 128.0 (2C), 124.8, 123.4, 122.4, 120.9, 114.0 (2C), 112.6, 101.7, 65.8, 55.2, 35.3, 31.3 ppm; **IR** (KBr): ν = 3061, 3040, 2998, 2950, 2929, 2899, 2642, 1709, 1655, 1613, 1583, 1548, 1509, 1461, 1440, 1386, 1356, 1302, 1254, 1216, 1156, 1105, 1078, 1036, 1027, 985, 848, 836, 758, 737, 695 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{27}H_{22}NaO_4S^+$ $[M+Na]^+$: 465.1131, found: 465.1129.

Benzyl (*R*,*E*)-2-(4-(*p*-tolyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3m)



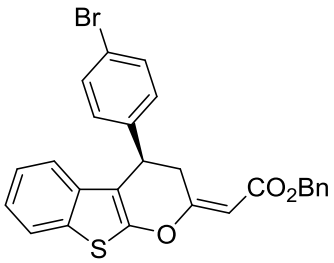
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a brownish solid, **3m**/**4m** > 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 50:1), *ee* = 89 %; yield **3m** = 95 %; $[\alpha]_D^{20}$ = -26.8 (*c* = 0.5, $CHCl_3$).

Method B: *ee* = 89 %; yield **3m** = 77 %; $[\alpha]_D^{20}$ = -17.7 (*c* = 1.6, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 254 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 5.5 min (minor enan.), t_R = 8.9 min (major enan.), **m.p.** = 119 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.68 (dq, *J* = 5.9, 3.5 Hz, 1H), 7.41 – 7.28 (m, 5H), 7.24 – 7.11 (m, 3H), 7.06 (s, 4H), 5.81 (d, *J* = 1.5 Hz, 1H), 5.18 – 5.04 (m, 2H), 4.33 (dd, *J* = 6.5, 4.2 Hz, 1H), 4.07 (dd, *J* = 15.4, 4.2 Hz, 1H), 3.31 (ddd, *J* = 15.4, 6.5, 1.6 Hz, 1H), 2.30 (s, 3H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.3, 166.0, 153.3, 138.4, 136.6, 136.3, 136.1, 131.6, 129.4 (2C), 128.5 (2C), 128.1 (2C), 128.0, 127.2 (2C), 124.7, 123.4, 122.4, 120.9, 112.5, 101.6, 65.8, 35.6, 31.2, 21.1 ppm; **IR** (KBr): ν = 3052, 3025, 2917, 1712, 1652, 1571, 1545, 1515, 1461, 1437, 1380, 1347, 1266, 1204, 1165, 1102, 1075, 1024, 976, 929, 866, 848, 740, 725 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{27}H_{22}NaO_3S^+$ $[M+Na]^+$: 449.1182, found: 449.1178.

Benzyl (*R*,*E*)-2-(4-(4-bromophenyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3n)



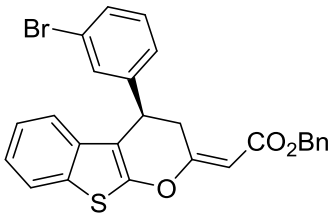
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a yellowish solid, **3n**/**4n** > 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 50:1), *ee* = 86 %; yield **3n** = 86 %; $[\alpha]_D^{20}$ = -9.5 (*c* = 0.6, $CHCl_3$).

Method B: *ee* = 90 %; yield **3n** = 53 %; $[\alpha]_D^{20}$ = -12.0 (*c* = 0.8, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 254 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 7.2 min (minor enan.), t_R = 15.2 min (major enan.), **m.p.** = 126.8 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.71 – 7.67 (m, 1H), 7.39 – 7.28 (m, 7H), 7.24 – 7.22 (m, 2H), 7.15 – 7.13 (m, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 5.82 (d, *J* = 1.6 Hz, 1H), 5.14 – 5.06 (m, 2H), 4.33 (dd, *J* = 6.5, 3.8 Hz, 1H), 4.12 (dd, *J* = 15.4, 3.8 Hz, 1H), 3.26 (ddd, *J* = 15.4, 6.6, 1.7 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.2, 165.3, 153.8, 140.4, 136.0 (2C), 131.8 (2C), 131.6, 129.1 (2C), 128.6 (2C), 128.2, 128.0 (2C), 124.9, 123.6, 122.5, 121.0, 120.6, 111.6, 102.1, 65.9, 35.5, 30.8 ppm; **IR** (KBr): *v* = 3064, 3031, 2926, 2893, 2857, 1948, 1903, 1867, 1826, 1784, 1691, 1646, 1604, 1580, 1491, 1461, 1431, 1377, 1347, 1311, 1269, 1237, 1204, 1162, 1111, 1078, 1024, 1009, 952, 920, 869, 851, 812, 764, 740, 692 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{20}BrO_3S^+$ $[M+H]^+$: 491.0311, found: 491.0306.

Benzyl (*R*,*E*)-2-(4-(3-bromophenyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3o)



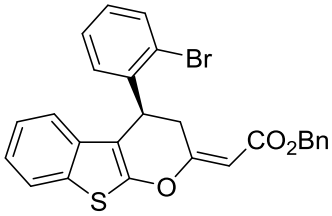
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a yellow solid, **3o**/**4o** > 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 50:1), *ee* = 85 %; yield **3o** = 94 %; $[\alpha]_D^{20}$ = -26.3 (*c* = 0.5, $CHCl_3$).

Method B: *ee* = 86 %; yield **3o** = 63 %; $[\alpha]_D^{20}$ = -23.5 (*c* = 1.5, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 80:20, λ = 254 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 6.2 min (minor enan.), t_R = 12.4 min (major enan.), **m.p.** = 132 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.71 – 7.69 (m, 1H), 7.39 – 7.30 (m, 7H), 7.25 – 7.22 (m, 2H), 7.16 – 7.09 (m, 3H), 5.85 (d, *J* = 1.5 Hz, 1H), 5.16 – 5.08 (m, 2H), 4.33 (dd, *J* = 6.6, 4.0 Hz, 1H), 4.08 (dd, *J* = 15.5, 4.0 Hz, 1H), 3.31 (ddd, *J* = 15.5, 6.6, 1.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.16, 165.14, 153.90, 143.81, 135.95, 135.89, 131.59, 130.42, 130.35, 130.29, 128.52 (2C), 128.11, 128.01 (2C), 126.06, 124.90, 123.62, 122.75, 122.50, 120.62, 111.37, 102.14, 65.91, 35.70, 30.89 ppm; **IR** (KBr): *v* = 3061, 3034, 2950, 2932, 1712, 1658, 1586, 1464, 1434, 1386, 1356, 1299, 1266, 1216, 1156, 1102, 1072, 1021, 997, 929, 851, 788, 755, 734, 692 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{20}BrO_3S^+$ $[M+H]^+$: 491.0311, found: 491.0303.

Benzyl (*R*,*E*)-2-(4-(2-bromophenyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3p)



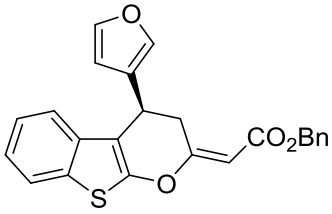
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a white wax, **3p**/**4p** = 6:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 50:1), *ee* = 89 %; yield **3p** = 58 %; $[\alpha]_D^{20}$ = -11.0 (*c* = 0.3, $CHCl_3$).

Method B: *ee* = 88 %; yield **3p** = 42 %; $[\alpha]_D^{20}$ = -13.5 (*c* = 1.1, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IA column (mobile phase: *n*-heptane/propan-2-ol – 97:3, λ = 254 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 6.1 min (major enan.), t_R = 7.7 min (minor enan.); **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.71 – 7.67 (m, 1H), 7.63 – 7.61 (m, 1H), 7.36 – 7.31 (m, 3H), 7.28 – 7.26 (m, 2H), 7.23 – 7.21 (m, 2H), 7.16 – 7.14 (m, 1H), 7.11 – 7.06 (m, 2H), 6.85 – 6.82 (m, 1H), 5.83 (d, *J* = 1.6 Hz, 1H), 5.13 – 5.02 (m, 2H), 4.89 (dd, *J* = 6.9, 3.3 Hz, 1H), 4.18 (dd, *J* = 15.5, 3.2 Hz, 1H), 3.21 (ddd, *J* = 15.5, 6.9, 1.7 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.0, 165.0, 154.3, 140.0, 136.0, 135.8, 133.2, 131.6, 128.9, 128.7, 128.5 (2C), 128.1, 128.0 (2C), 127.7, 124.9, 123.7, 123.7, 122.4, 120.7, 111.4, 102.6, 65.9, 35.2, 29.4 ppm; **IR** (KBr): *v* = 3072, 3032, 2962, 2937, 2890, 1692, 1649, 1574, 1494, 1462, 1437, 1383, 1352, 1312, 1278, 1208, 1154, 1112, 1075, 1029, 1002, 957, 926, 856, 761, 743, 695 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{20}BrO_3S^+$ $[M+H]^+$: 491.0311, found: 491.0304.

Benzyl (*R*,*E*)-2-(4-(furan-3-yl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3q)



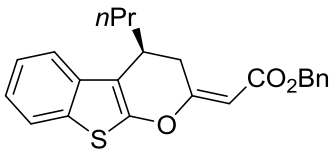
The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a yellow oil, **3q**/**4q** > 20:1 (Slow decomposition of product was observed by staying longer time into $CDCl_3$ – see carbon spectra).

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 50:1), *ee* = 66 %; yield **3q** = 82 %; $[\alpha]_D^{20}$ = 19.6 (*c* = 1.1, $CHCl_3$).

Method B: *ee* = 66 %; yield **3q** = 46 %; $[\alpha]_D^{20}$ = 15.3 (*c* = 0.7, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 254 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 6.3 min (minor enan.), t_R = 10.6 min (major enan.); **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.69 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.43 – 7.21 (m, 8H), 6.24 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.03 (d, *J* = 3.2 Hz, 1H), 5.86 (d, *J* = 1.6 Hz, 1H), 5.28 – 5.10 (m, 2H), 4.47 (dt, *J* = 11.7, 3.4 Hz, 2H), 3.10 (ddd, *J* = 16.1, 7.0, 1.7 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.5, 165.8, 153.9, 153.5, 142.1, 136.2, 136.1, 131.5, 128.6 (2C), 128.2, 128.1 (2C), 125.0, 123.6, 122.4, 120.63, 110.5, 110.2, 106.3, 101.9, 66.0, 29.6, 27.5 ppm; **IR** (KBr): *v* = 3061, 3031, 2959, 2929, 1712, 1661, 1601, 1586, 1553, 1503, 1467, 1437, 1383, 1350, 1308, 1269, 1210, 1171, 1156, 1144, 1105, 1021, 994, 958, 931, 917, 887, 854, 812, 761, 737, 701 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{24}H_{18}NaO_4S^+$ $[M+Na]^+$: 425.0818, found: 425.0813.

Benzyl (*S*,*E*)-2-(4-propyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3r)

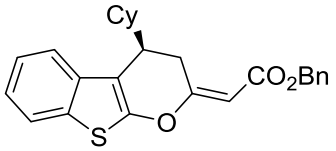


The title compound was synthesized according to general procedure (reaction time: 15 hours), affording the title compound as a yellowish oil, **3r**/**4r** = 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 100:1), *ee* = 89 %; yield **3r** = 36 %; $[\alpha]_D^{20}$ = 121.8 (*c* = 0.4, $CHCl_3$).

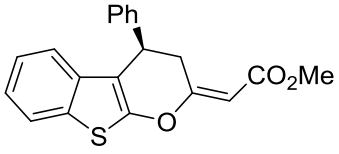
Method B: No precipitate was observed.
Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 254 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 4.6 min (minor enan.), t_R = 5.9 min (major enan.); **^{1}H NMR** (300 MHz, Chloroform-*d*): δ = 7.68 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.33 (m, 6H), 7.24 – 7.21 (m, 1H), 5.85 (s, 1H), 5.26 – 5.15 (m, 2H), 4.32 (d, *J* = 15.5 Hz, 1H), 3.20 – 3.13 (m, 1H), 2.59 (dd, *J* = 15.4, 6.1 Hz, 1H), 1.62 – 1.40 (m, 4H), 0.91 (t, *J* = 6.7 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 167.3, 166.8, 152.0, 136.5, 136.2, 131.7, 128.6 (2C), 128.14, 128.13 (2C), 124.7, 123.2, 122.5, 120.1, 115.2, 101.4, 65.9, 36.8, 29.7, 27.2, 20.6, 14.1 ppm; **IR** (KBr): *v* = 3082, 3063, 3051, 2953, 2871, 1712, 1643, 1602, 1588, 1547, 1501, 1467, 1422, 1365, 1315, 1288, 1278, 1203, 1186, 1175, 1155, 1124, 1069, 1056, 1024, 1007 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{23}H_{22}NaO_3S^+$ $[M+H]^+$: 379.1362, found: 379.1361.

Benzyl (*R*,*E*)-2-(4-cyclohexyl-3,4-dihydro-2H-benzo[4,5]thieno[2,3-b]pyran-2-ylidene)acetate (3s)



The title compound was synthesized according to general procedure (reaction time: 20 hours), affording the title compound as a colorless oil, **3s**/**4s** = 20:1.
Method A: Crude product was purified by column chromatography (hexane/toluene = 3:1), *ee* = 89 %; yield **3s** = 61 %; $[\alpha]_D^{20}$ = 81.6 (*c* = 0.8, $CHCl_3$).
Method B: No precipitate was observed.
Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IA column (mobile phase: *n*-heptane/propan-2-ol – 97:3, λ = 293 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 5.0 min (major enan.), t_R = 5.9 min (minor enan.); **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.70 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.55 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.46 – 7.33 (m, 6H), 7.27 – 7.23 (m, 1H), 5.81 (d, *J* = 2.0 Hz, 1H), 5.33 – 5.16 (m, 2H), 4.51 (dd, *J* = 16.0, 1.8 Hz, 1H), 2.97 (td, *J* = 6.7, 1.8 Hz, 1H), 2.49 (ddd, *J* = 16.1, 6.3, 2.2 Hz, 1H), 1.86 – 1.77 (m, 1H), 1.76 – 1.67 (m, 2H), 1.67 – 1.60 (m, 2H), 1.52 (ddd, *J* = 11.1, 7.4, 3.4 Hz, 1H), 1.27 – 0.95 (m, 5H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 168.4, 166.8, 152.2, 137.1, 136.3, 131.7, 128.5 (2C), 128.1 (3C), 124.6, 123.2, 122.4, 120.9, 114.5, 100.2, 65.8, 42.5, 35.7 (2C), 30.4, 26.4 (2C), 26.3, 25.4 ppm; **IR** (KBr): *v* = 3893, 3858, 3827, 3610, 3790, 3739, 3727, 3704, 3682, 3663, 3534, 3088, 3064, 3032, 2925, 2851, 2793, 2670, 2359, 23359, 2176, 1948, 1895, 1863, 1813, 1775, 1709, 1654, 1648, 1598, 1580, 1549, 1512, 1496, 1464, 1449, 1435, 1386, 1354, 1314, 1271, 1253, 1237, 1212, 1185, 1173, 1155, 1111, 1075, 1020, 1003, 995, 958, 930, 846, 820, 788, 755, 728, 695 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{27}O_3S^+$ $[M+H]^+$: 419.1678, found: 419.1676.

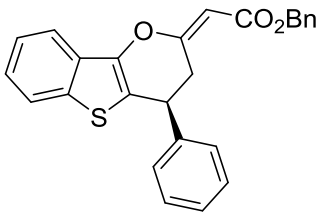
Methyl (*R*,*E*)-2-(4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3t)



The title compound was synthesized according to general procedure (reaction time: 40 hours), affording the title compound as a white solid; **3s**/**4s** ≥ 20:1.
Method A: Crude product was purified by column chromatography (hexane/EtOAc = 25:1), *ee* = 89 %; yield **3s** = 83 %; $[\alpha]_D^{20}$ = -26.0 (*c* = 1.0, $CHCl_3$).
Method B: *ee* = 98 %; yield **3s** = 62 %; $[\alpha]_D^{20}$ = -45.5 (*c* = 0.5, $CHCl_3$).
Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 206 nm, *V* = 1.0 ml/min, *t* = 25 °C), t_R = 5.0 min (minor. enan.), t_R = 9.1 min (major enan.); **m.p.** = 131.6 °C; **^{1}H NMR** (400 MHz,

Chloroform-*d*): δ = 7.73 – 7.66 (m, 1H), 7.34 – 7.23 (m, 3H), 7.23 – 7.18 (m, 4H), 7.17 – 7.12 (m, 1H), 5.77 (d, *J* = 1.5 Hz, 1H), 4.37 (dd, *J* = 6.6, 4.3 Hz, 1H), 4.08 (dd, *J* = 15.5, 4.3 Hz, 1H), 3.65 (s, 3H), 3.35 (ddd, *J* = 15.5, 6.6, 1.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.9, 165.6, 153.5, 141.4, 136.2, 131.6, 128.7 (2C), 127.4, 127.1 (2C), 124.8, 123.4, 122.4, 120.8, 112.3, 101.5, 51.2, 36.0, 31.0 ppm; **IR** (KBr): *v* = 3070, 3061, 3028, 3016, 2995, 2950, 2884, 2833, 1709, 1640, 1601, 1574, 1548, 1500, 1464, 1434, 1356, 1317, 1287, 1269, 1201, 1180, 1156, 1114, 1069, 1024, 1009 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{20}H_{16}NaO_3S$ $[M+Na]^+$: 359.0709, found: 359.0712.

Benzyl (*S*,*E*)-2-(4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[3,2-*b*]pyran-2-ylidene)acetate (6a)



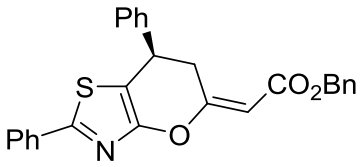
The title compound was synthesized according to general procedure (reaction time: 48 hours), affording the title compound as a yellowish wax, **6a**/**7a** > 20:1 (*Note:* Slow decomposition of product was observed by staying longer time into $CDCl_3$ – see carbon spectra).

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 70:1), *ee* = 98 %; yield **6a** = 52 %; $[\alpha]_D^{20}$ = -108.5 (*c* = 0.5, $CHCl_3$).

Method B: *ee* = 98 %; yield **6a** = 49 %; $[\alpha]_D^{20}$ = -103.8 (*c* = 0.3, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 254 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 6.2 min (major enan.), t_R = 7.2 min (minor enan.); **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.37 – 7.29 (m, 10H), 7.28 – 7.25 (m, 1H), 5.89 (s, 1H), 5.17 – 5.10 (m, 2H), 4.34 (dd, *J* = 7.5, 5.9 Hz, 1H), 3.87 (ddd, *J* = 15.4, 5.9, 1.0 Hz, 1H), 3.66 (ddd, *J* = 15.3, 7.5, 1.0 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.8, 166.0, 141.6, 136.4, 136.2, 130.1, 129.1, 128.7 (2C), 128.5 (2C), 128.1, 128.0 (2C), 127.5 (2C), 127.5, 125.1, 124.4, 122.8, 119.8, 117.8, 100.4, 65.7, 37.6, 31.9 ppm; **IR** (KBr): *v* = 3064, 3031, 2950, 2929, 2854, 1706, 1646, 1589, 1548, 1500, 1437, 1374, 1353, 1296, 1263, 1216, 1174, 1123, 1081, 1060, 1027, 970, 920, 845, 755, 728, 695, 674 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{21}O_3S$ $[M+H]^+$: 413.1206, found: 413.1202.

Benzyl (*R*,*E*)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)acetate (6b)



The title compound was synthesized according to general procedure (reaction time: 24 hours), affording the title compound as a white solid; crystals suitable for X-ray analysis were grown from boiling h *n*-heptane/*i*-PrOH mixture (9:1), **6b**/**7b** ≥ 20:1;.

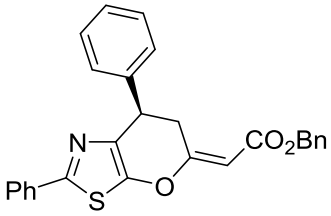
Method A: Crude product was purified by column chromatography (hexane/EtOAc = 10:1), *ee* = 98 %; yield **6b** = 66 %; $[\alpha]_D^{20}$ = -45.2 (*c* = 1.1, $CHCl_3$).

Method B: *ee* = 99 %; yield **6b** = 68 %; $[\alpha]_D^{20}$ = -47.3 (*c* = 0.7, $CHCl_3$).

Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 80:20, λ = 208 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 8.7 min (major enan.), t_R = 10.9 min (minor enan.); **m.p.** = 134.4 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.96 – 7.82 (m, 2H), 7.46 – 7.22 (m, 14H), 5.89 (d, *J* = 0.8 Hz, 1H), 5.13 (d, *J* = 2.8 Hz, 2H), 4.31 (dd, *J* = 8.0, 5.8 Hz, 1H), 3.93 (ddd, *J* = 15.3, 5.8, 0.8 Hz, 1H), 3.48 (ddd, *J* = 15.3, 8.1, 1.1 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.6, 165.3, 164.3, 156.1, 141.7, 136.0, 133.0, 130.4, 128.9 (4C), 128.5 (2C), 128.1 (2C), 127.7, 127.2 (2C), 125.7 (2C), 109.3, 101.5, 65.8, 36.6, 31.8 ppm; **IR** (KBr): *v* = 3088, 3061, 3022, 2929, 2857,

1700, 1655, 1601, 1559, 1494, 1455, 1431, 1359, 1332, 1305, 1269, 1234, 1186, 1168, 1123, 1075, 1057, 1036, 1021 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{27}H_{21}NNaO_3S$ $[M+Na]^+$: 462.1129, found: 462.1134.

Benzyl (*R*,*E*)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[3,2-*d*]thiazol-5-ylidene)acetate (6c)



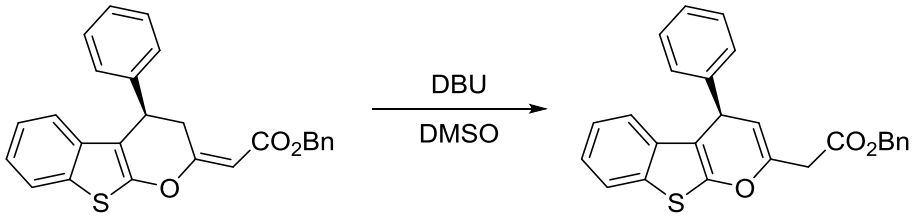
The title compound was synthesized according to general procedure (reaction time: 10 hours), affording the title compound as a white solid; **6c**/**7c** > 20:1.

Method A: Crude product was purified by column chromatography (hexane/EtOAc = 50:1), *ee* = 87 %; yield **6c** = 92 %; $[\alpha]_D^{20}$ = 5.3 (*c* = 0.8, $CHCl_3$).

Method B: *ee* = 98 %; yield **6c** = 42 %; $[\alpha]_D^{20}$ = 7.7 (*c* = 0.3, $CHCl_3$). Enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 80:20, λ = 210 nm, *V* = 1.0 ml/min, *t* = 25 °C), t_R = 5.9 min (minor. enan.), t_R = 29.2 min (major enan.); **m.p.** = 127 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.87 – 7.75 (m, 2H), 7.43 – 7.27 (m, 10H), 7.26 – 7.20 (m, 3H), 5.82 (d, *J* = 1.4 Hz, 1H), 5.22 – 5.07 (m, 2H), 4.45 (dd, *J* = 6.4, 4.2 Hz, 1H), 4.18 (dd, *J* = 15.6, 4.3 Hz, 1H), 3.33 (ddd, *J* = 15.7, 6.5, 1.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 166.2, 165.5, 155.5, 149.4, 141.0, 136.0, 135.6, 133.6, 129.7 , 128.9 (2C), 128.6 (2C), 128.5 (2C), 128.1 (3C), 127.4 (2C), 127.0, 125.8 (2C), 101.9, 65.9, 37.9, 30.5 ppm; **IR** (KBr): ν = 3028, 3004, 2956, 2893, 2854, 1715, 1655, 1559, 1491, 1467, 1452, 1383, 1347, 1242, 1159, 1099, 1024, 994, 961, 943, 920, 857, 764, 746, 701 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{27}H_{22}O_3NS^+$ $[M+H]^+$: 440.1315, found: 440.1307.

Further transformations

Benzyl (*R*)-2-(4-phenyl-4*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-yl)acetate (4a)



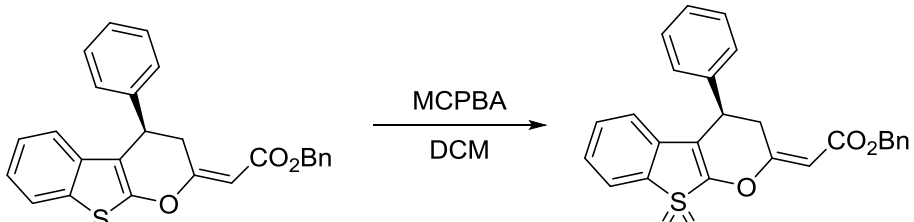
3a
99 % *ee*

4a

To a stirred solution of **3a** (41.3 mg, 0.10 mmol, 1.0 eq.) in DMSO (5 ml) DBU (18 µl, 0.12 mmol, 1.2 eq.) was added in one portion at room temperature. At same temperature reaction was stirred for 24 h. Mixture was diluted with brine (20 ml) and this solution was washed with EtOAc (4 × 10 ml). Organic phase was dried under anhydrous $MgSO_4$. Mixture was filtered and solvents were evaporated *in vacuo*. Crude product was purified by column chromatography (hex / EtOAc = 15:1), affording the title compound as yellow oil.

Yield **4a** = 77 %; *ee* = 99 %; the enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 284 nm, V = 1.0 ml/min, t = 25 °C) t_R = 7.1 min (minor enan.), t_R = 9.7 min (major enan.), $[\alpha]_D^{20}$ = 142.6 (c = 0.9, $CHCl_3$); **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.71 – 7.64 (m, 1H), 7.41 – 7.33 (m, 5H), 7.33 – 7.29 (m, 4H), 7.26 – 7.10 (m, 4H), 5.22 (d, J = 3.1 Hz, 2H), 5.17 – 5.10 (m, 1H), 4.87 (d, J = 3.8 Hz, 1H), 3.36 (s, 2H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 169.0, 143.9, 143.8, 136.4, 135.6, 131.8, 128.7 (2C), 128.6 (2C), 128.3, 128.1 (2C), 128.0 (2C), 126.9, 124.5, 123.3 (2C), 122.1, 121.3, 109.4, 106.0, 66.9, 39.2, 39.1 ppm; **IR** (KBr): ν = 3402, 3064, 3055, 3028, 3004, 2956, 2926, 2851, 1736, 1724, 1694, 1655, 1598, 1589, 1551, 1497, 1437, 1380, 1311, 1257, 1216, 1159, 1072, 1030 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{20}NaO_3S$ $[M+Na]^+$: 435.1021, found: 435.1025.

Benzyl (*R*,*E*)-2-(9,9-dioxido-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-b]pyran-2-ylidene)acetate (8)



3a
99 % *ee*

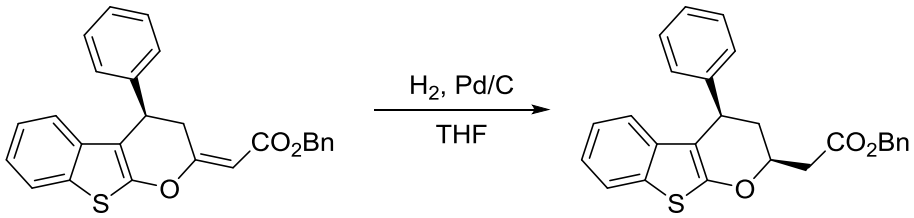
8

To a stirred solution of **3a** (82.6 mg, 0.20 mmol, 1.0 eq.) in DCM (4 ml) MCPBA (40 % w/w) (190 mg, 0.44 mmol, 2.2 eq.) was added in one portion at room temperature. At same temperature reaction was stirred for 24 h. Solution was washed with sat. solution of $NaHCO_3$ (2 × 2 ml) and brine (2 ml). Organic phase was dried under anhydrous $MgSO_4$. Mixture was filtered and solvents were evaporated *in vacuo*. Crude product was purified by column chromatography (Hex / EtOAc = 3:1), affording the title compound as yellow solid.

Yield **8** = 82 %; *ee* = 99 %; the enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 60:40,

λ = 254 nm, V = 1.0 ml/min, t = 25 °C) t_R = 8.1 min (minor enan.), t_R = 14.3 min (major enan.), $[\alpha]_D^{20}$ = -78.9 (c = 1.0, $CHCl_3$); **m.p.** = 174.5 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.64 (dd, J = 5.6, 3.0 Hz, 1H), 7.37 – 7.28 (m, 10H), 7.23 – 7.21 (m, 2H), 6.85 (dd, J = 5.7, 3.0 Hz, 1H), 5.99 (d, J = 1.4 Hz, 1H), 5.09 (q, J = 12.4 Hz, 2H), 4.13 (dd, J = 6.7, 4.2 Hz, 1H), 3.94 (dd, J = 15.7, 4.3 Hz, 1H), 3.34 (ddd, J = 15.7, 6.6, 1.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 165.5, 162.9, 148.9, 138.6, 135.6, 133.8, 132.6, 129.4, 129.24 (2C), 128.6, 128.5 (2C), 128.2, 128.02, 127.99 (2C), 127.3 (2C), 121.8, 121.2, 114.7, 104.8, 66.2, 35.1, 30.6 ppm; **IR** (KBr): ν = 3070, 3037, 2666, 2612, 2558, 1718, 1652, 1589, 1580, 1500, 1467, 1449, 1425, 1383, 1350, 1311, 1284, 1266, 1213, 1156, 1096, 1042, 1018, 982, 937, 851, 767, 752, 734, 707, 659 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for for $C_{26}H_{21}NaO_3S^+$ $[M+H]^+$: 445.1104, found: 445.1104.

Benzyl 2-((2*S*,4*R*)-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-yl)acetateacetate (9)



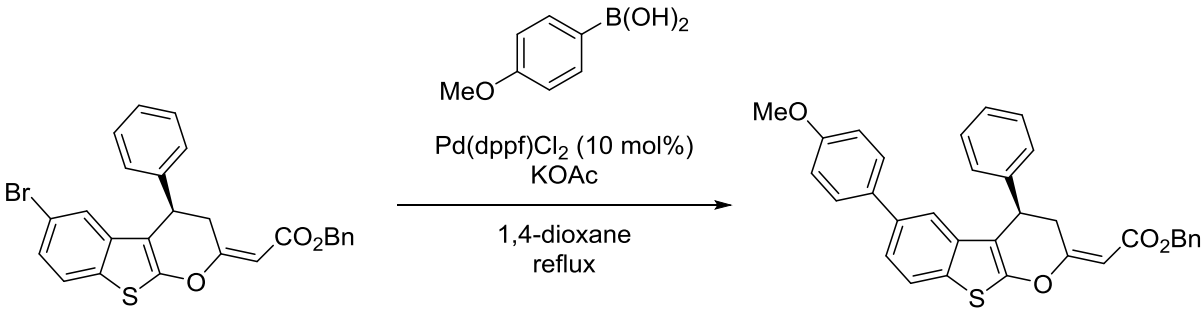
3a
99 % *ee*

9

Solution of **3a** (100 mg, 0.24 mmol, 1.0 eq.) in dry THF (5.0 ml) was degassed (flask was evacuated and refilled with Ar three times) and Pd/C (10%, 25.4 mg, 0.1 eq.) was added. The reaction flask was evacuated again and refilled with H_2 three times. The resulting suspension was stirred 4.5 hrs at 35 °C. (*Note:* Longer reaction time caused debenzylation). The reaction mixture was filtered through short pad of Celite (washed by EtOAc), solvents were evaporated and the residue was purified by column chromatography (hex / EtOAc = 12:1).

Yield **9** = 52 %; *ee* = 99 %; the enantiomeric excess of product was determined by HPLC using chiral HPLC with an IB column (mobile phase: *n*-heptane/propan-2-ol – 90:10, λ = 207 nm, V = 1.0 ml/min, t = 25 °C) t_R = 9.2 min (minor enan.), t_R = 20.0 min (major enan.), $[\alpha]_D^{20}$ = 110.7 (c = 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.60 (dd, J = 7.9, 1.1 Hz, 1H), 7.44 – 7.32 (m, 3H), 7.32 – 7.15 (m, 7H), 7.09 (td, J = 7.6, 1.2 Hz, 1H), 6.99 (td, J = 7.8, 1.1 Hz, 1H), 6.62 (dd, J = 8.0, 1.2 Hz, 1H), 5.20 (s, 2H), 4.77 (dddd, J = 11.3, 7.5, 6.0, 1.7 Hz, 1H), 4.23 (dd, J = 10.9, 6.5 Hz, 1H), 2.94 (dd, J = 15.9, 7.2 Hz, 1H), 2.72 (dd, J = 15.8, 6.0 Hz, 1H), 2.47 (ddd, J = 13.9, 6.5, 1.7 Hz, 1H), 1.95 (dt, J = 14.0, 11.1 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 169.9, 158.6, 143.1, 137.2, 135.6, 131.3, 128.8 (2C), 128.6 (2C), 128.4, 128.2 (2C), 127.7 (2C), 126.8, 124.0, 122.4, 122.1, 121.7, 110.6, 76.3, 66.7, 40.1, 39.8, 39.6 ppm; **IR** (KBr): ν = 3933, 3892, 3886, 3881, 3871, 3639, 3821, 3807, 3736, 3712, 3690, 3656, 3650, 3638, 3630, 3620, 3063, 3030, 2951, 2922, 2865, 2360, 2343, 2250, 1949, 1611, 1740, 1736, 1689, 1647, 1637, 1596, 1572, 1550, 1493, 1462, 1455, 1438, 1399, 1376, 1352, 1341, 1307, 1283, 1241, 1210, 1156, 1103, 1073, 1030, 1022, 980, 940, 909, 846, 756, 734, 699 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{26}H_{23}O_3S^+$ $[M+H]^+$: 415.1362, found: 415.1365.

Benzyl (*R*,*E*)-2-(6-(4-methoxyphenyl)-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (10)



3e
90 % *ee*

10

To a stirred suspension of **3e** (19.5 mg, 0.04 mmol, 1.0 eq.), boronic acid (7.4 mg, 0.05 mmol, 1.2 eq.) and KOAc (15.7 mg, 0.16 mmol, 4.0 eq.) in anhydrous and deggased 1,4-dioxane (0.4 ml) was $Pd(dppf)Cl_2$ (2.9 mg, 0.004 mmol, 0.1 eq.) added in one portion. Reaction mixture was stirred under Ar atmosphere at 105 °C for 24 h. Resulting suspension was filtered through short pad of silica gel (hex / EtOAc – 7:1). Solvents were evaporated *in vacuo.* Crude product was purified by column chromatography (hex / EtOAc = 15:1), affording the title compound as white solid. (*Note:* The title compound readily crystallized from boiling hept / *i*-PrOH – 9:1)

Yield **10** = 48 %; *ee* = 90 %; the enantiomeric excess of product was determined by HPLC using chiral HPLC with an IA column (mobile phase: *n*-heptane/propan-2-ol – 97:3, λ = 256 nm, *V* = 1.0 ml/min, *t* = 25 °C) t_R = 18.6 min (major enan.), t_R = 9.7 min (minor enan.); **m.p.** = 172.7 °C; $[\alpha]_D^{20}$ = 122.6 (*c* = 0.3, $CHCl_3$); **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 7.73 (dd, *J* = 8.3, 0.6 Hz, 1H), 7.43 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.41 – 7.19 (m, 13H), 6.94 (d, *J* = 8.7 Hz, 2H), 5.84 (d, *J* = 1.4 Hz, 1H), 5.12 (q, *J* = 12.5 Hz, 2H), 4.43 (dd, *J* = 6.4, 4.4 Hz, 1H), 4.11 (dd, *J* = 15.4, 4.5 Hz, 1H), 3.85 (s, 3H), 3.40 (ddd, *J* = 15.4, 6.5, 1.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 166.3, 165.9, 159.1, 154.0, 141.3, 137.9, 136.7, 136.1, 133.7, 130.1, 128.7 (2C), 128.5 (2C), 128.2 (2C), 128.1, 128.0 (2C), 127.5 (2C), 127.1, 122.7, 122.6, 118.9, 114.2 (2C), 112.5, 101.7, 65.8, 55.3, 36.1, 31.1 ppm; **IR** (KBr): *v* = 3025, 2962, 2932, 2839, 1715, 1658, 1610, 1589, 1539, 1494, 1449, 1356, 1299, 1272, 1254, 1210, 1186, 1156, 1096, 1039, 1024, 988, 961 cm^{-1}; **HRMS** (ESI+) *m*/*z*: calcd. for $C_{33}H_{26}NaO_4S$ $[M+Na]^+$: 541.1439, found: 541.1444.

Crystallographic data for 3a and 6b

Crystallographic data for **3a** and **6b** were collected on Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube either of MoKα (λ= 0.71073) (**3a**) or Cu Kα (λ= 1.54178 Å) (**6b**) at a temperature of 120(2) K. The structures were solved by direct methods (XT[39a])[9] and refined by full matrix least squares based on F^2 (SHELXL2018[39b]).[10] The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom). The absolute structure determination was based on anomalous dispersion of sulphur atom[40].

Crystal data for **3a**: $C_{26}H_{20}O_3S$, M_r = 412.48; Orthorhombic, *P* 2_1 2_1 2_1 (No 19), *a* = 7.9759 (4) Å, *b* = 16.1628 (8) Å, *c* = 31.7213 (15) Å , *V* = 4089.3 (3) Å^3, Z = 8, D_x = 1.340 Mg m^{-3}, light yellow bar of dimensions 0.37 × 0.20 × 0.11 mm, multi-scan absorption correction (μ = 0.18 mm^{-1}) T_{min} = 0.91, T_{max} = 0.98; a total of 33870 measured reflections (θ_{max}= 27.6˚), from which 9441 were unique (R_{int} = 0.031) and 8559 observed according to the $I > 2\sigma(I)$ criterion. The refinement converged (Δ/σ_{max}= 0.001) to *R* = 0.038 for observed reflections and w$R(F^2)$ = 0.089, *GOF* = 1.09 for 541 parameters and all 9441 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.28, $\Delta\rho_{min}$ -0.30 e.Å^{-3}). Absolute structure parameter (Flack[40]) -0.02(2).

Crystal data for **6b**: $C_{27}H_{21}NO_3S$, M_r = 439.51; Orthorhombic, *P* 2_1 2_1 2_1 (No 19), *a* = 5.7472 (2) Å, *b* = 16.9120 (6) Å, *c* = 22.0104 (8) Å, *V* = 2139.34 (13) Å^3, Z = 4, D_x = 1.365 Mg m^{-3}, colourless bar of dimensions 0.40 × 0.06 × 0.05 mm, multi-scan absorption correction (μ = 1.59 mm^{-1}) T_{min} = 0.77, T_{max} = 0.93; a total of 14933 measured reflections (θ_{max}= 66.6˚), from which 3770 were unique (R_{int} = 0.026) and 3662 observed according to the $I > 2\sigma(I)$ criterion. The refinement converged (Δ/σ_{max}= 0.001) to *R* = 0.026 for observed reflections and w$R(F^2)$ = 0.063, *GOF* = 1.08 for 289 parameters and all 3770 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.13, $\Delta\rho_{min}$ -0.24 e.Å^{-3}). Absolute structure parameter (Flack[40]) -0.008(5).

[9] a) SHELXT: G. M. Sheldrick, *Acta Cryst*., 2015, **A71**, 3; b) SHELXL: G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.
[10] S. Parsons, H. D. Flack and T. Wagner, *Acta Cryst*., 2013, **B69**, 249.

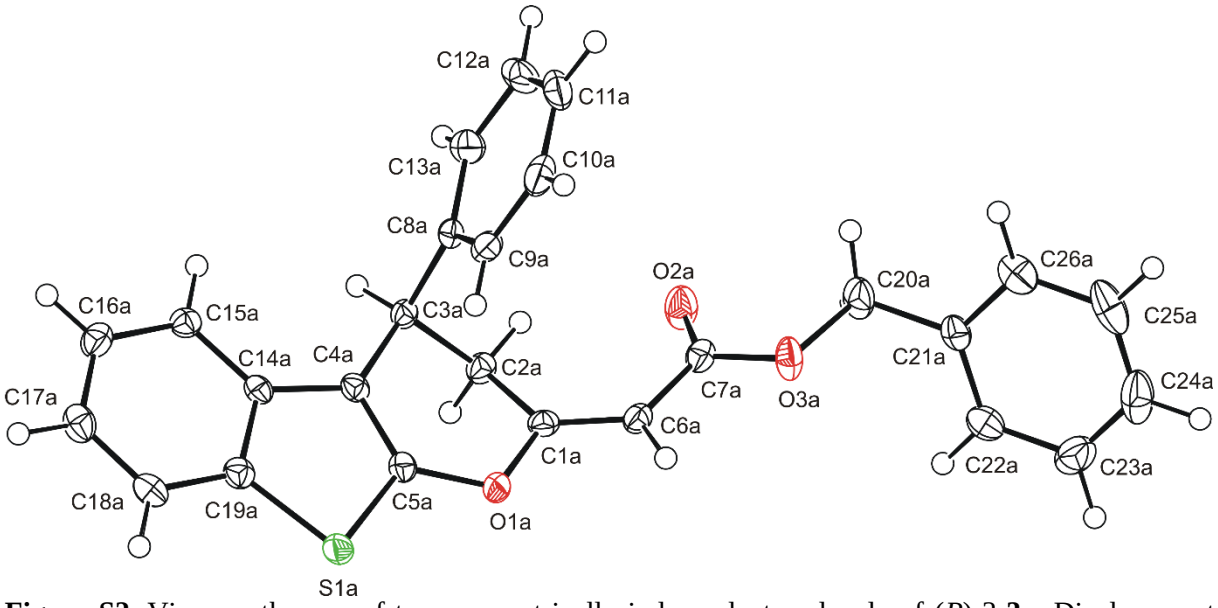


Figure S2. View on the one of two symmetrically independent molecule of (*R*)-3-**3a**. Displacement ellipsoids are drawn on 50% probability level. The most important difference between A and B molecules is in the conformation of pyrane rings.

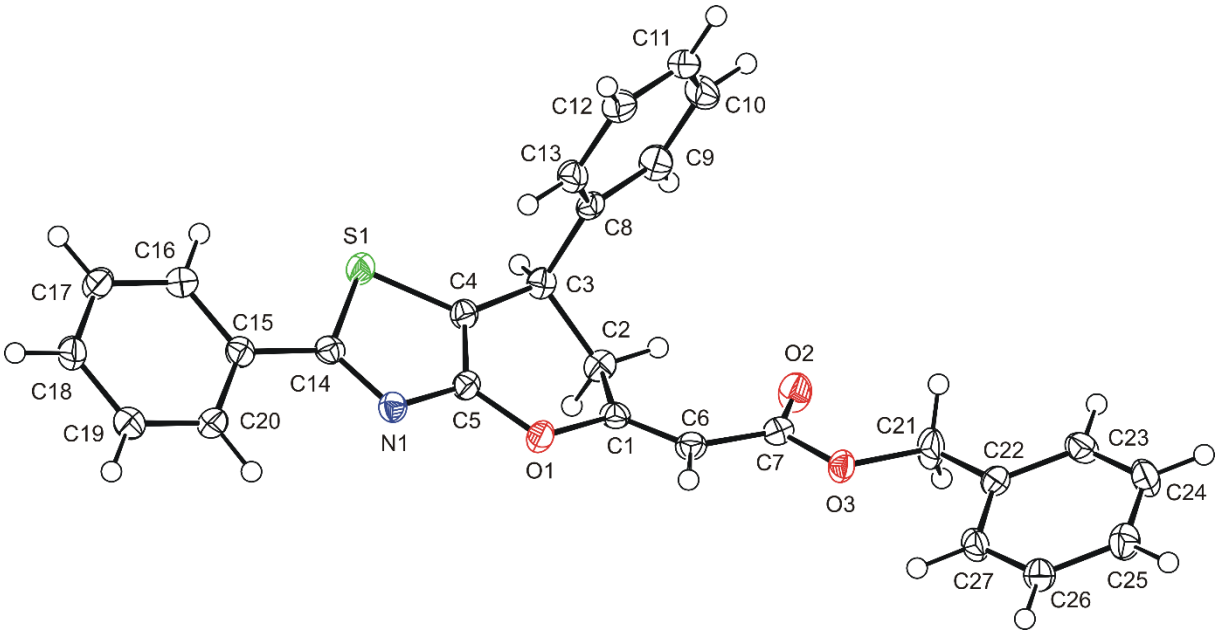


Figure S3. View on molecule of (*R*)-3-6b. Displacement ellipsoids are drawn on 50% probability level.

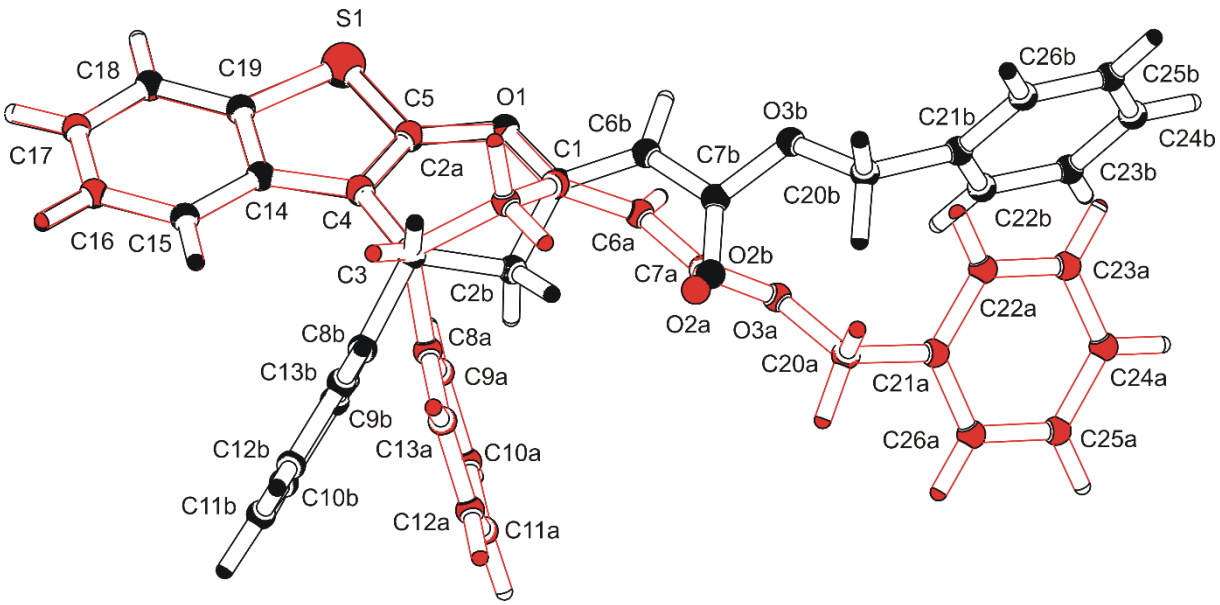
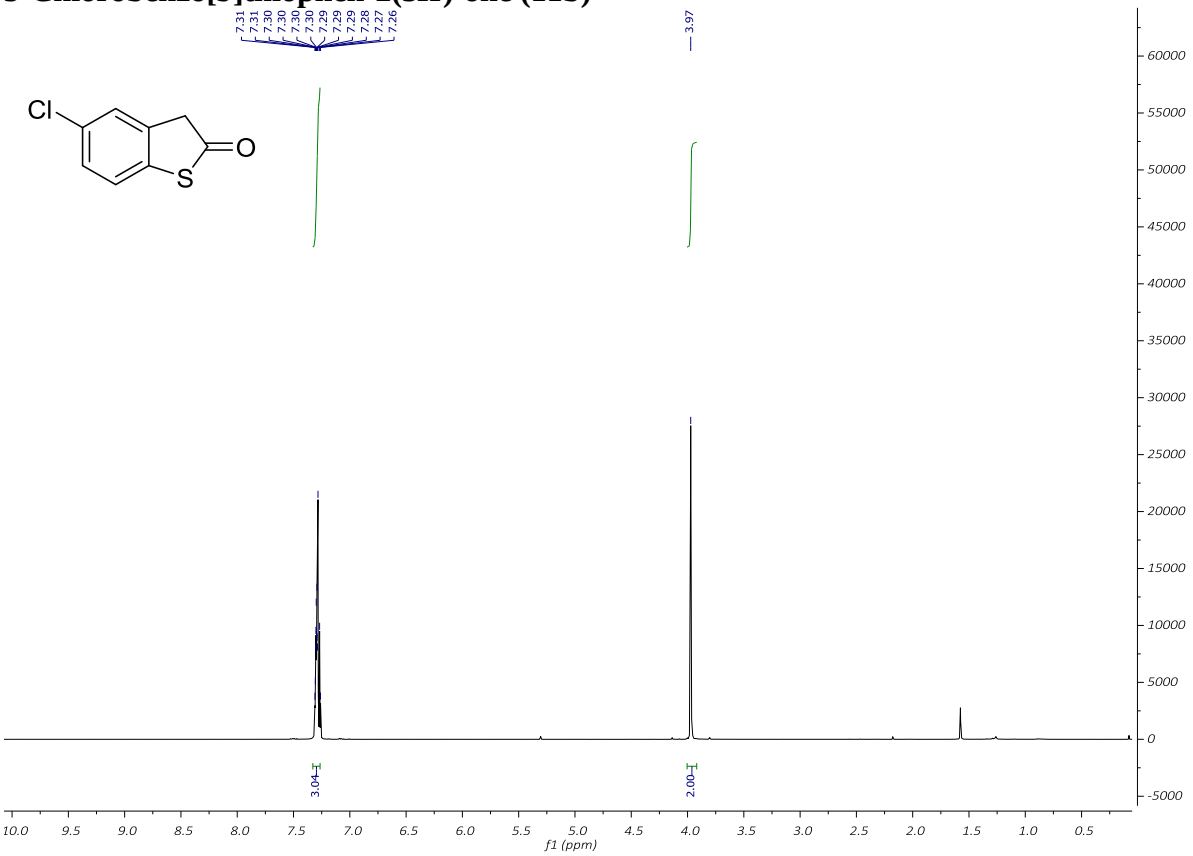


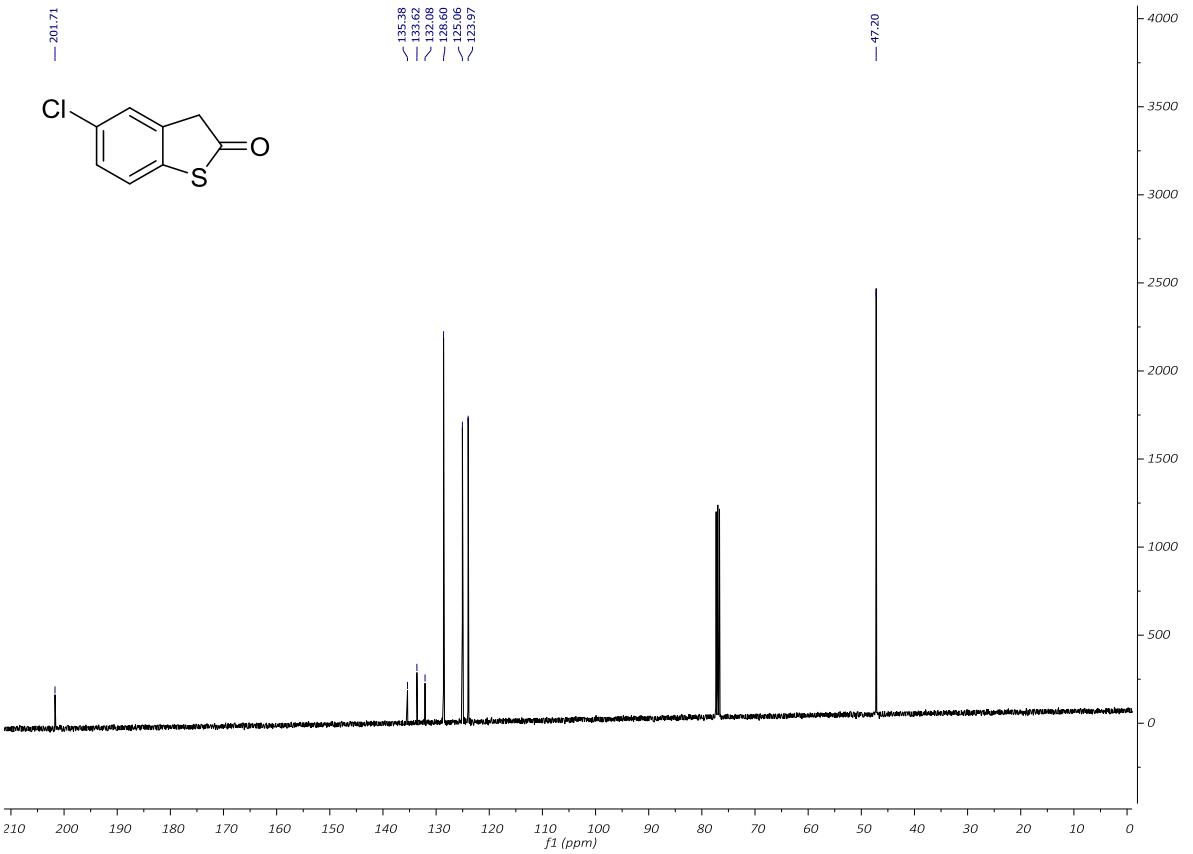
Figure S4. View on the two overlapping molecules of **3a**. The fit as based on atoms S1, C4, C5, C14, C15, C16, C17, C18, C19.

X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under deposition number CCDC 1916993 and CCDC 1916994 for **3a** and **6b**, respectively and can be obtained free of charge from the Centre via its website (www.ccdc.cam.ac.uk/getstructures).

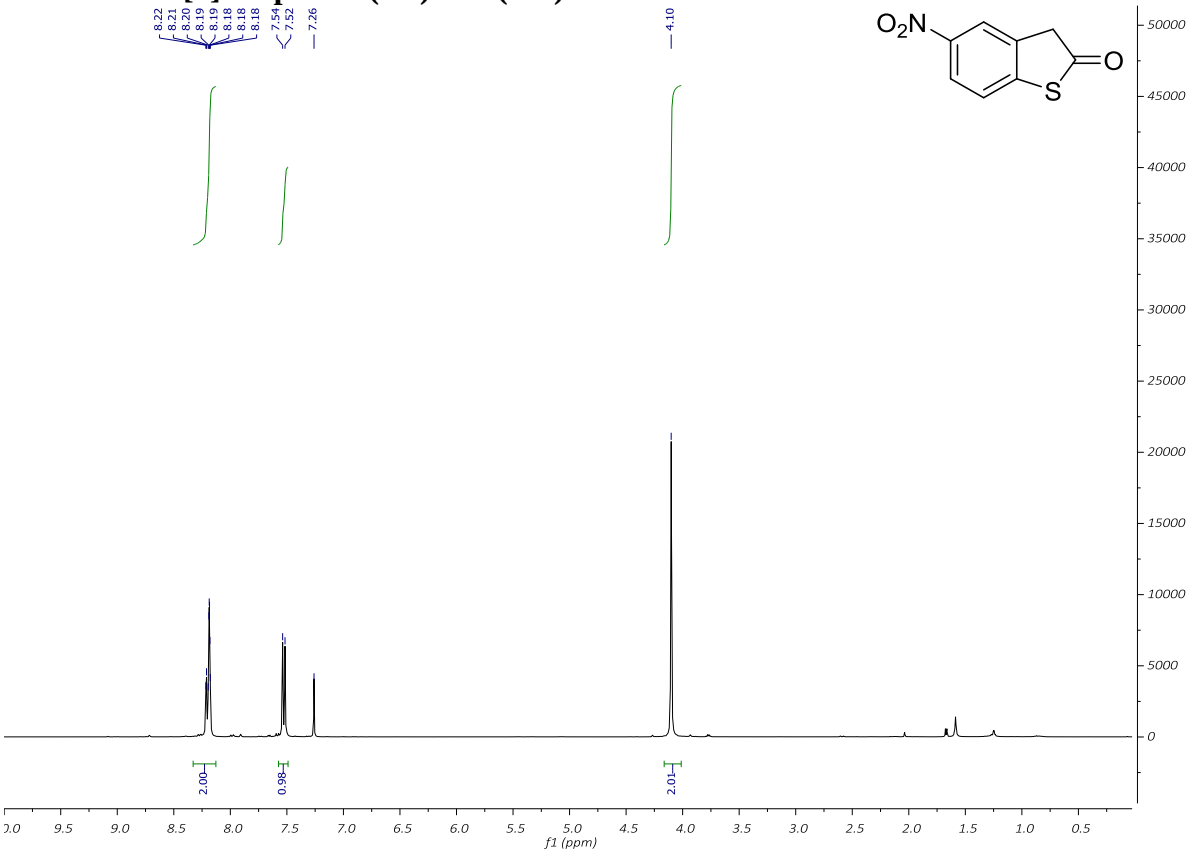
NMR spectra

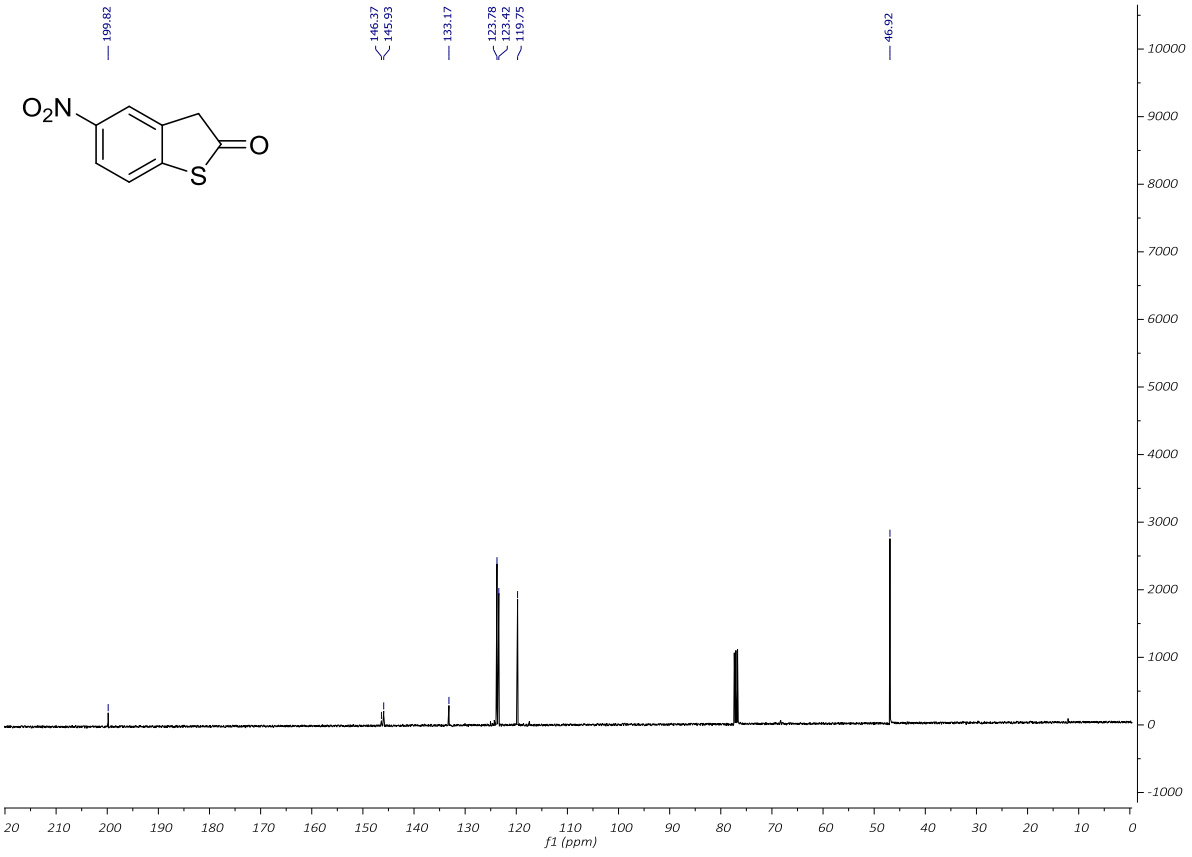
5-Chlorobenzo[*b*]thiophen-2(3*H*)-one (11b)



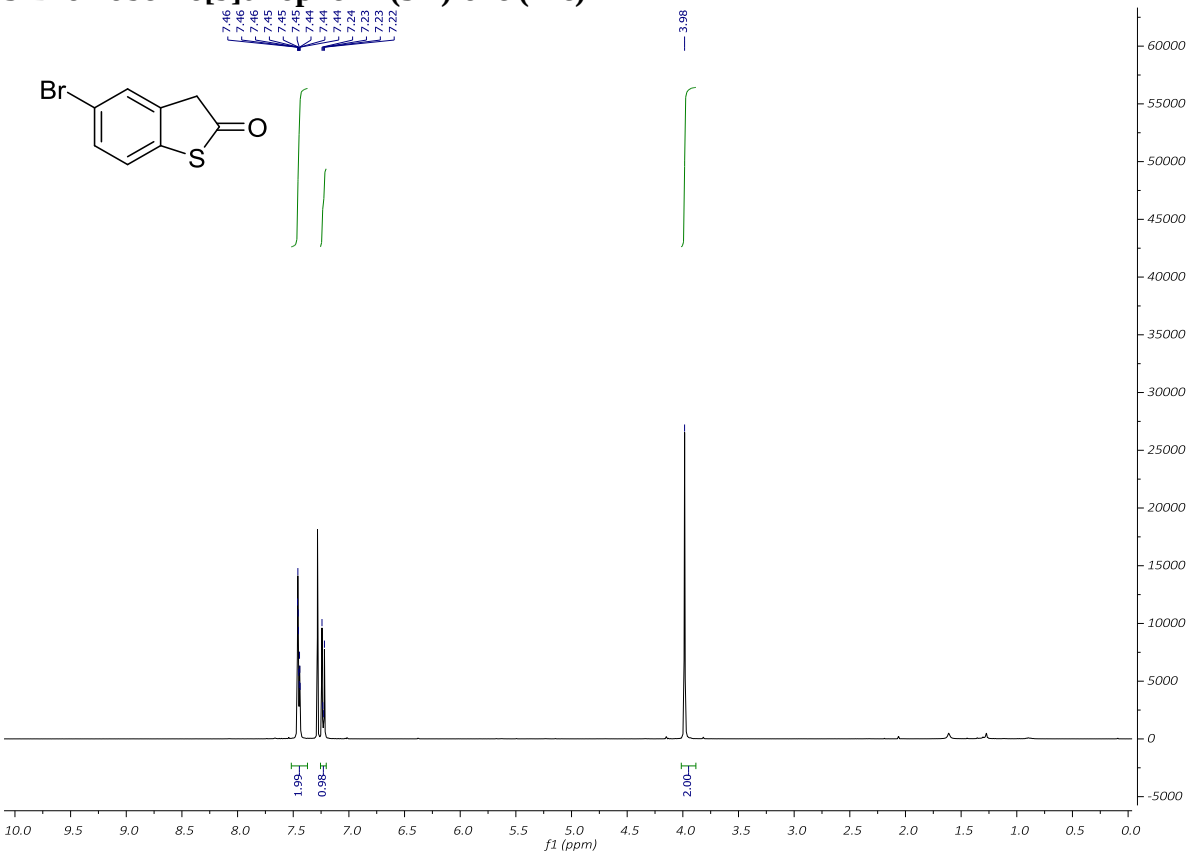


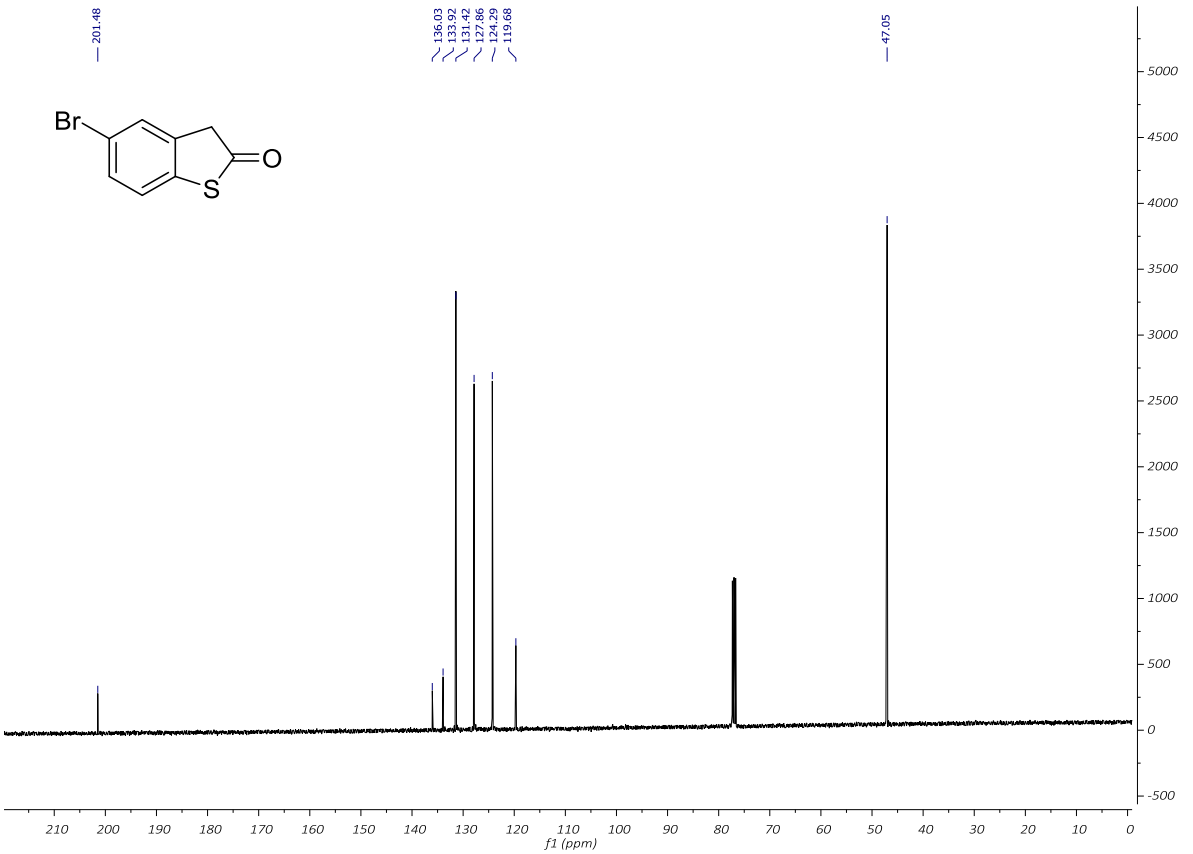
5-Nitrobenzo[*b*]thiophen-2(3*H*)-one (11c)



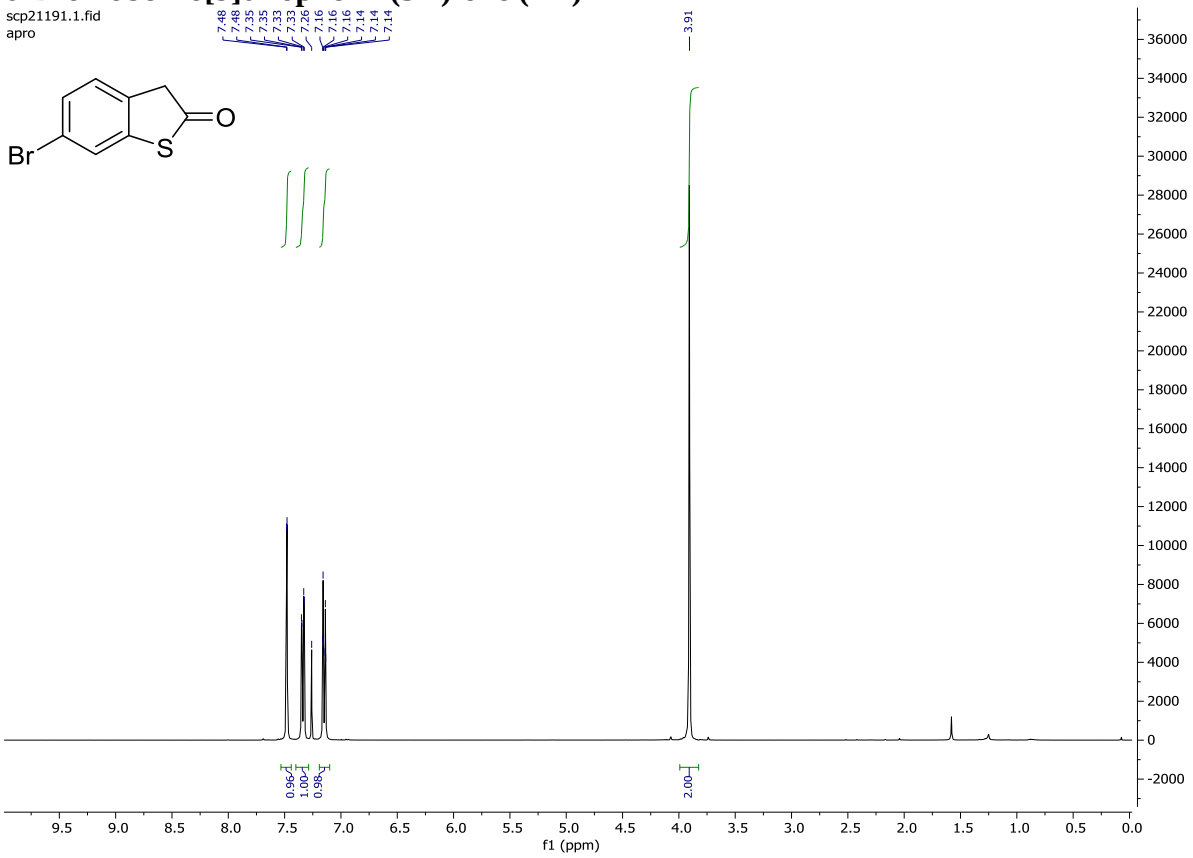


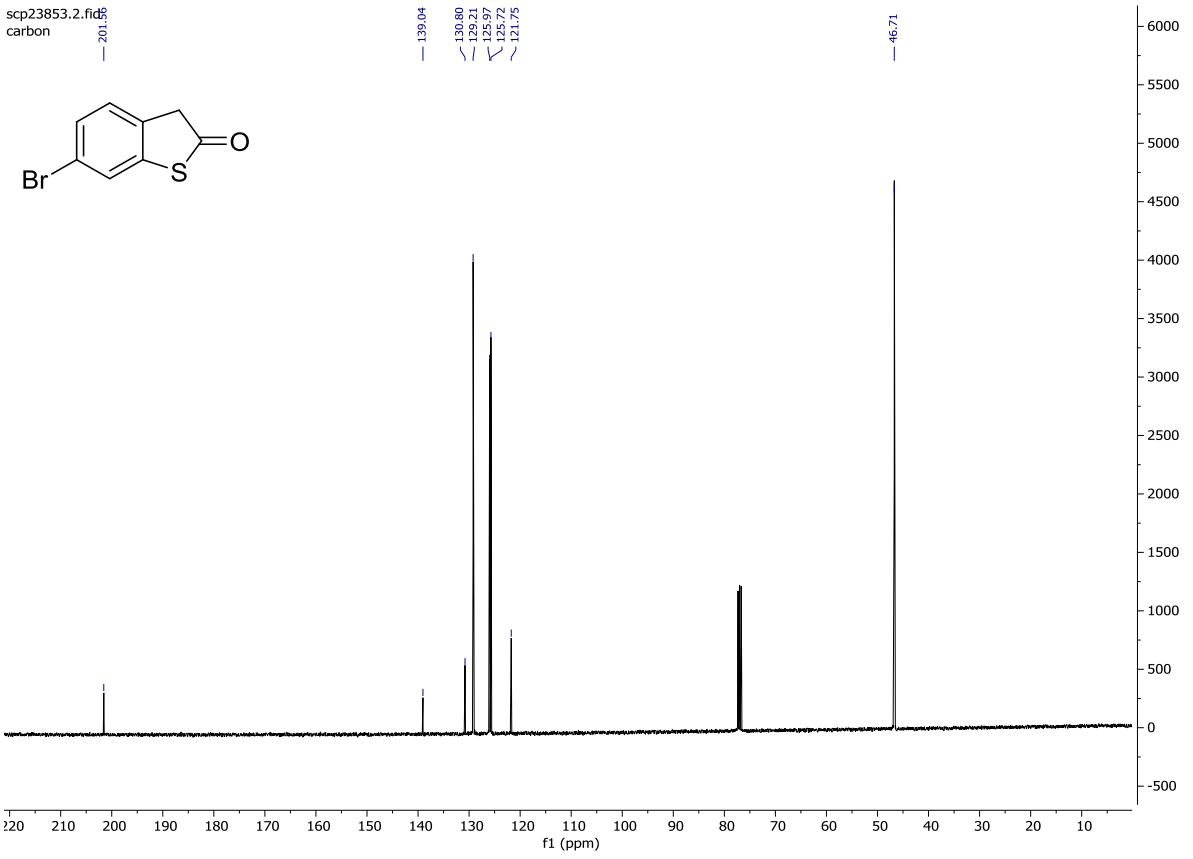
5-Bromobenzo[*b*]thiophen-2(3*H*)-one (11e)



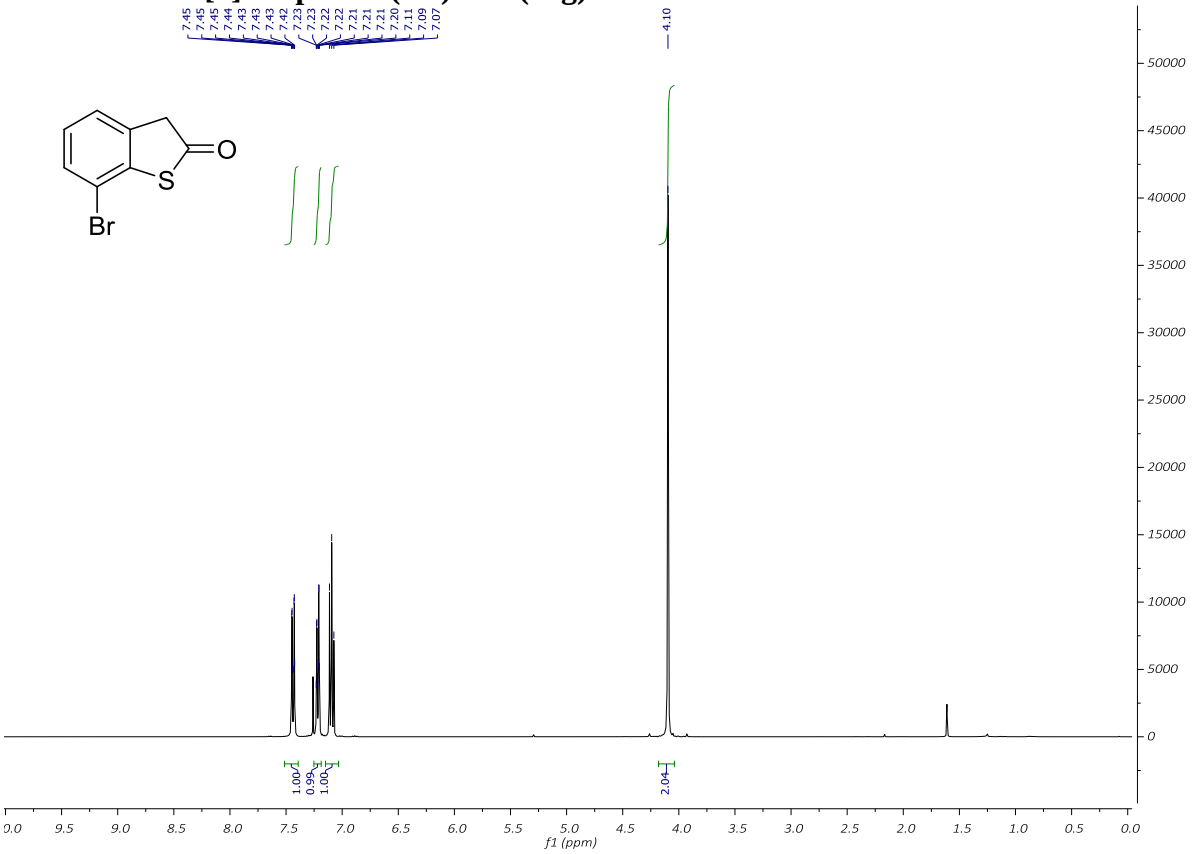


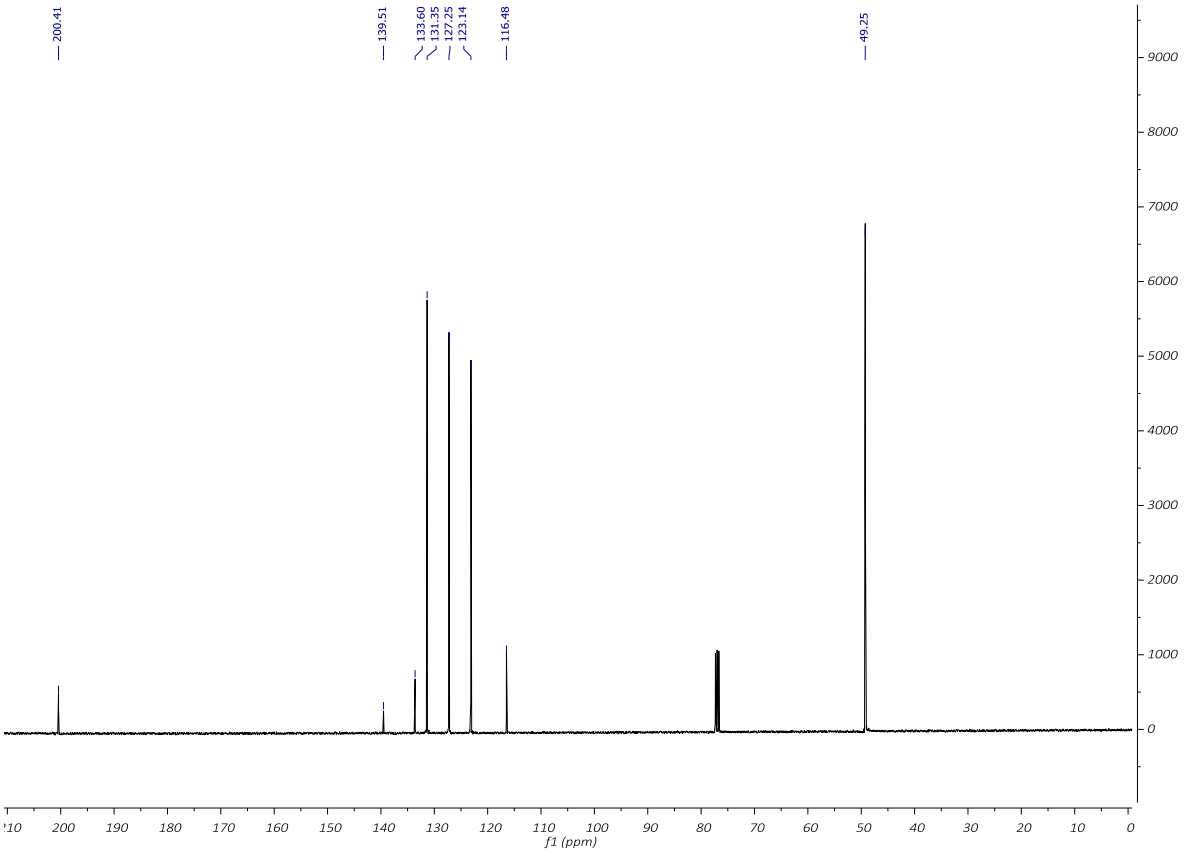
6-Bromobenzo[*b*]thiophen-2(3*H*)-one (11f)



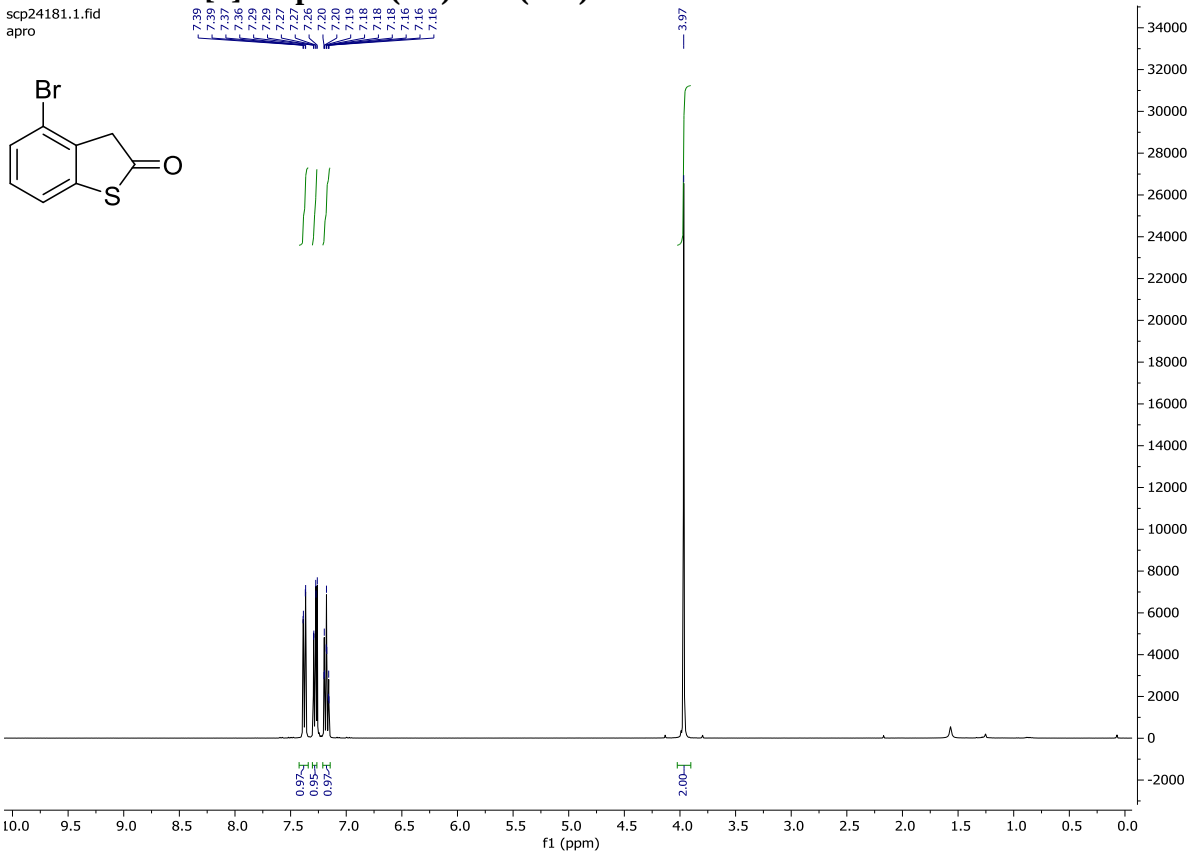


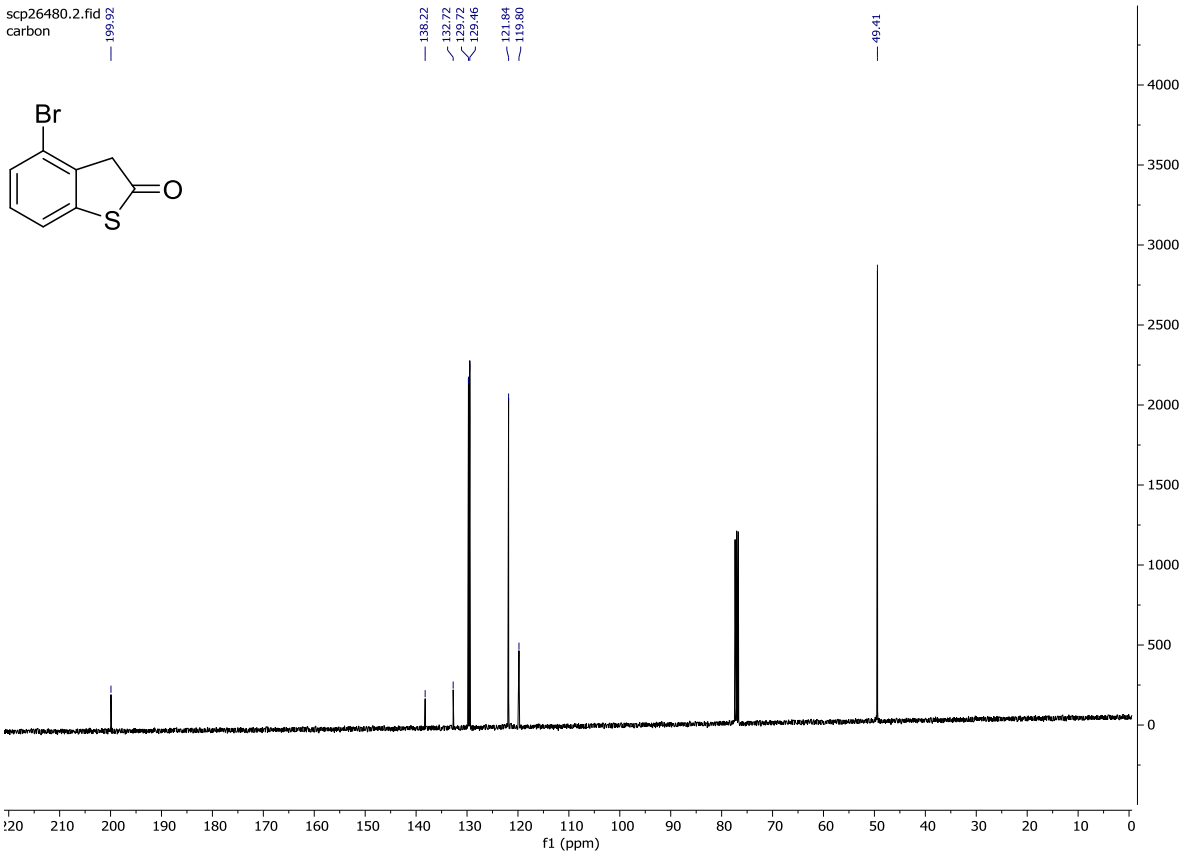
7-Bromobenzo[*b*]thiophen-2(3*H*)-one (11g)



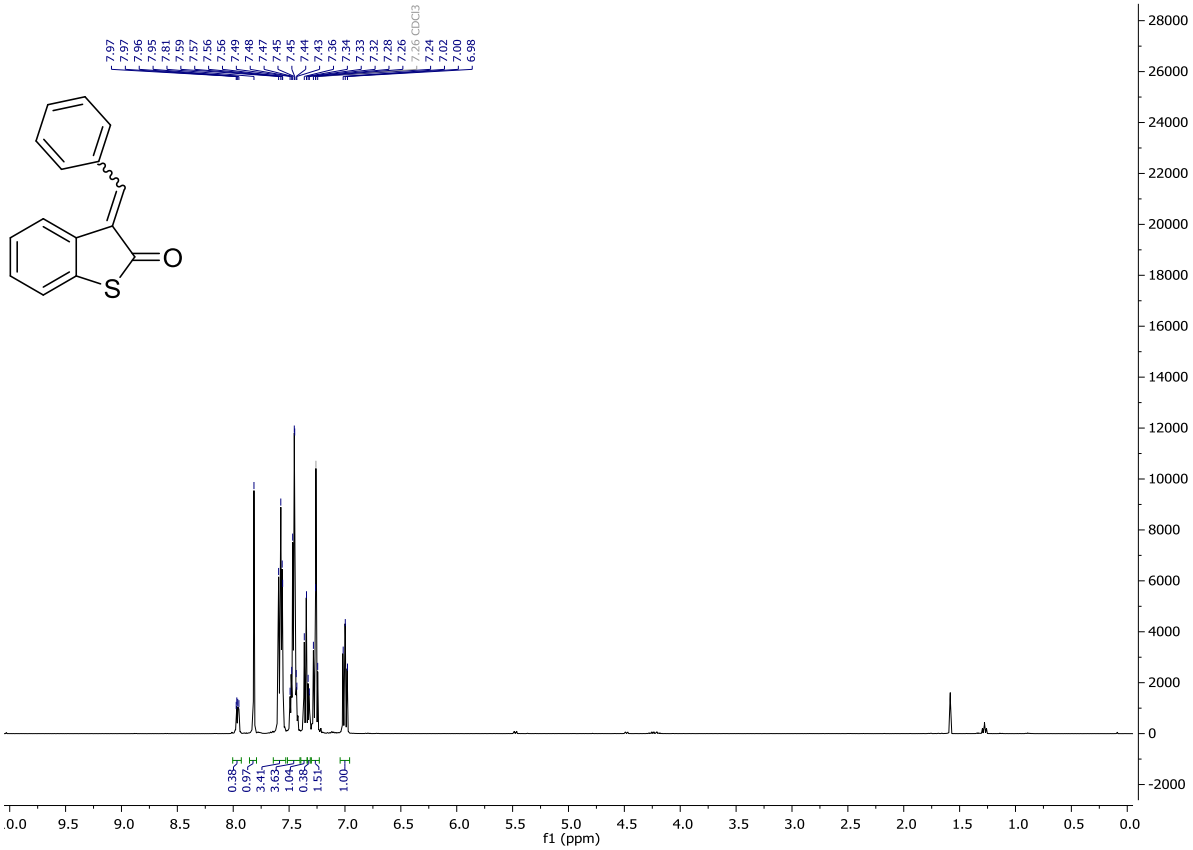


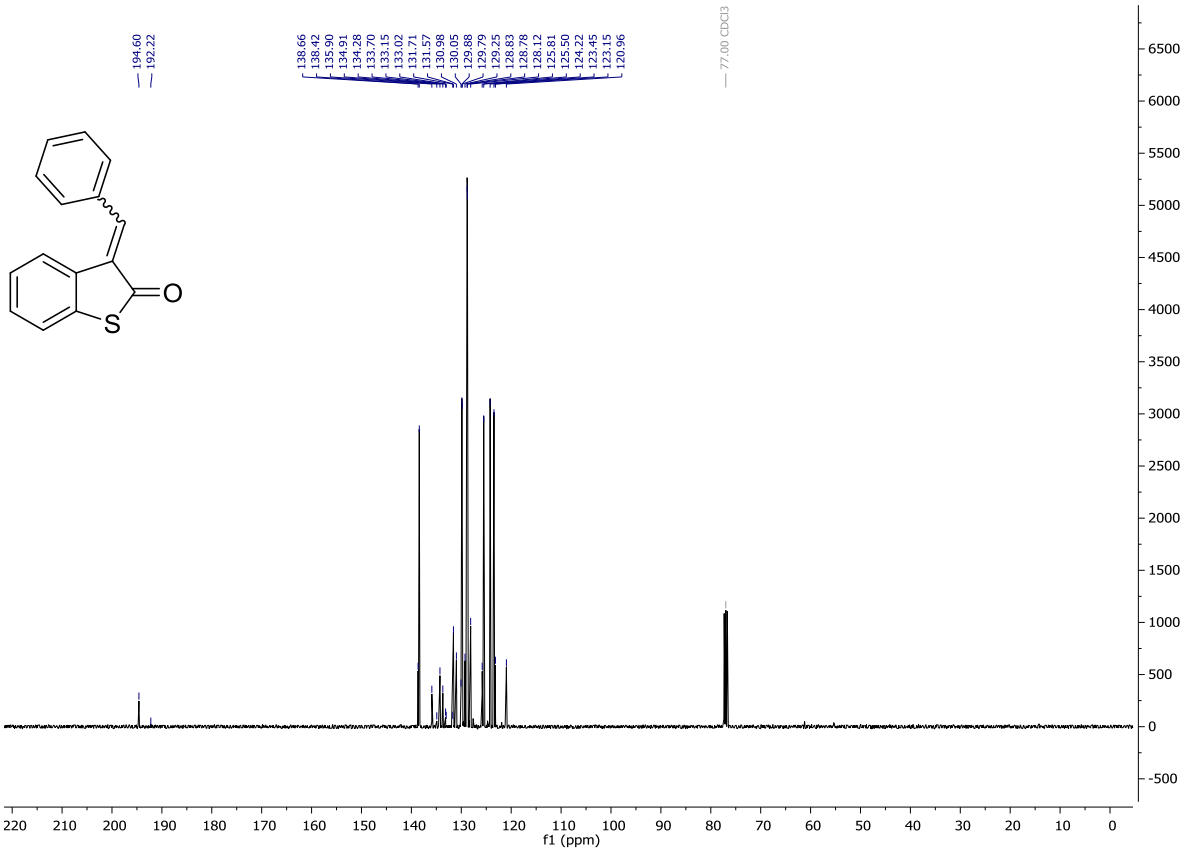
4-Bromobenzo[*b*]thiophen-2(3*H*)-one (11h)



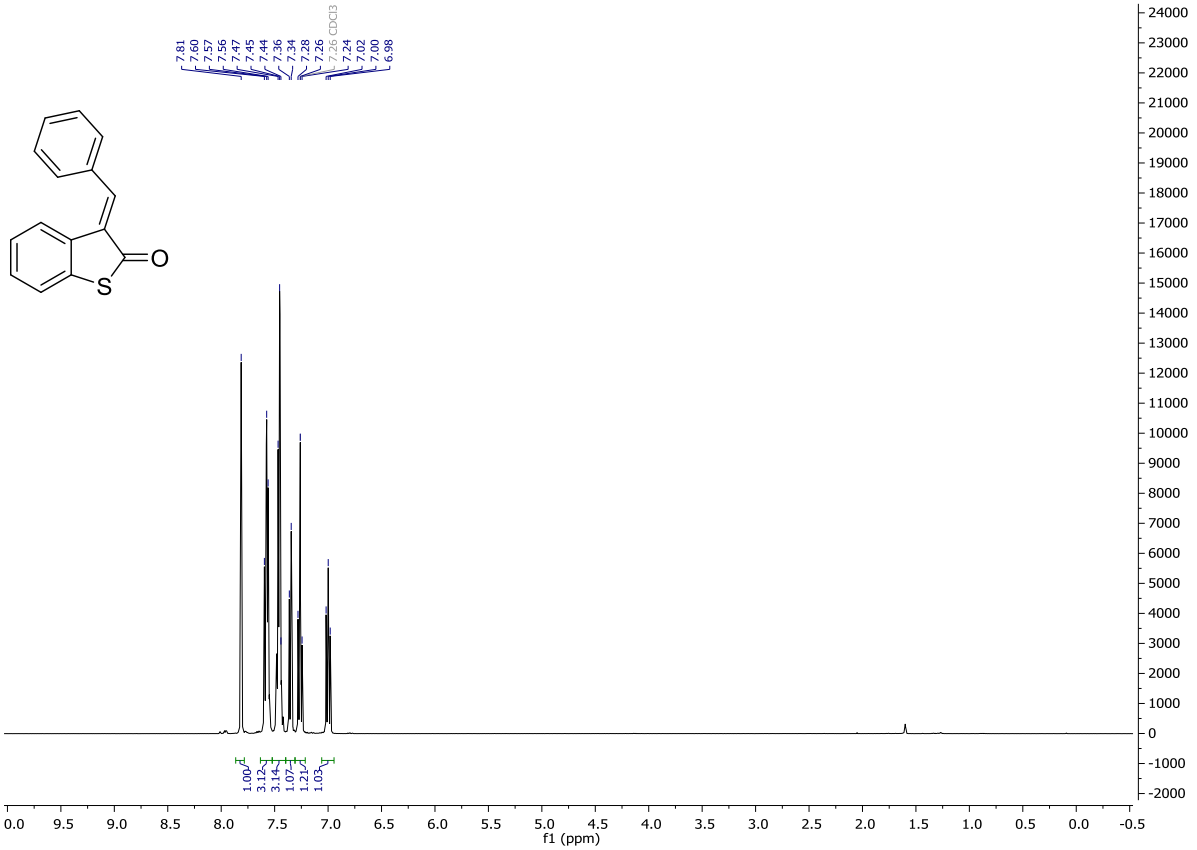


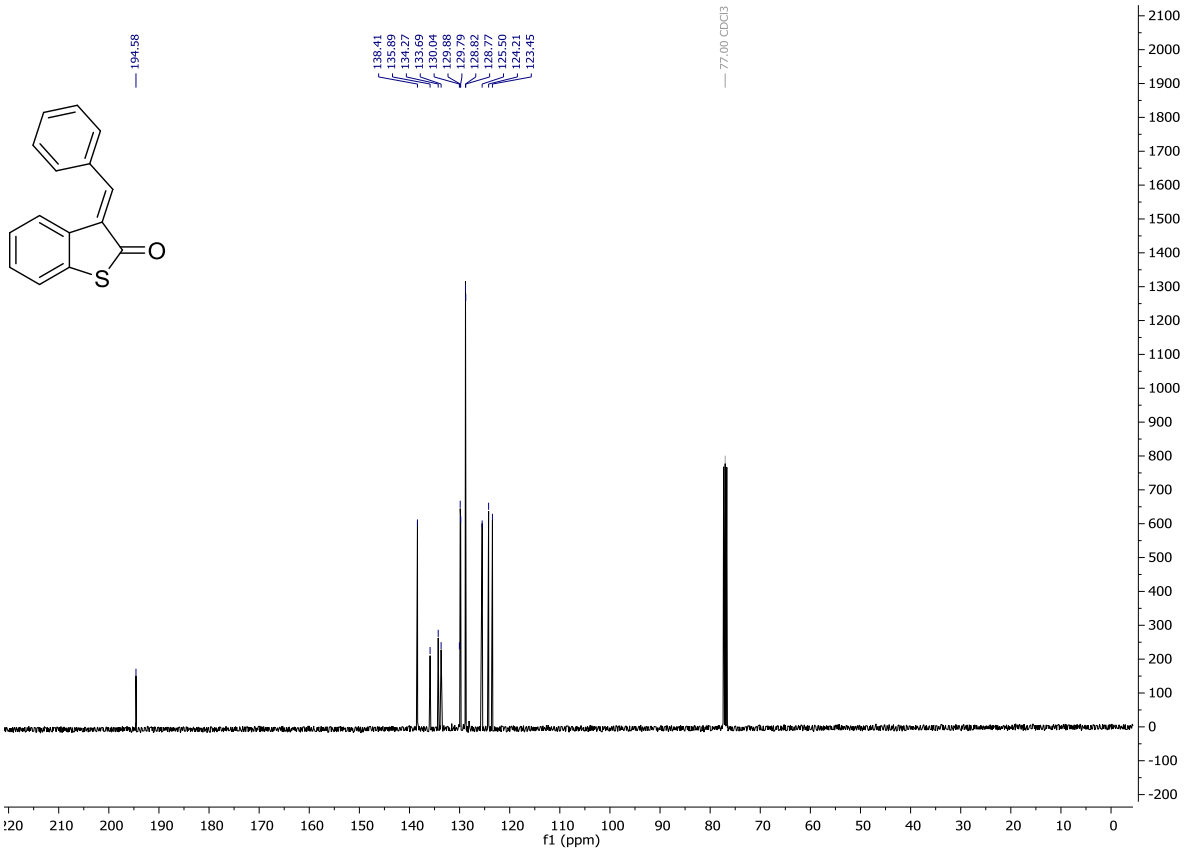
3-Benzylidenebenzo[*b*]thiophen-2(3*H*)-one (1a) – mixture of *E*/*Z* isomers



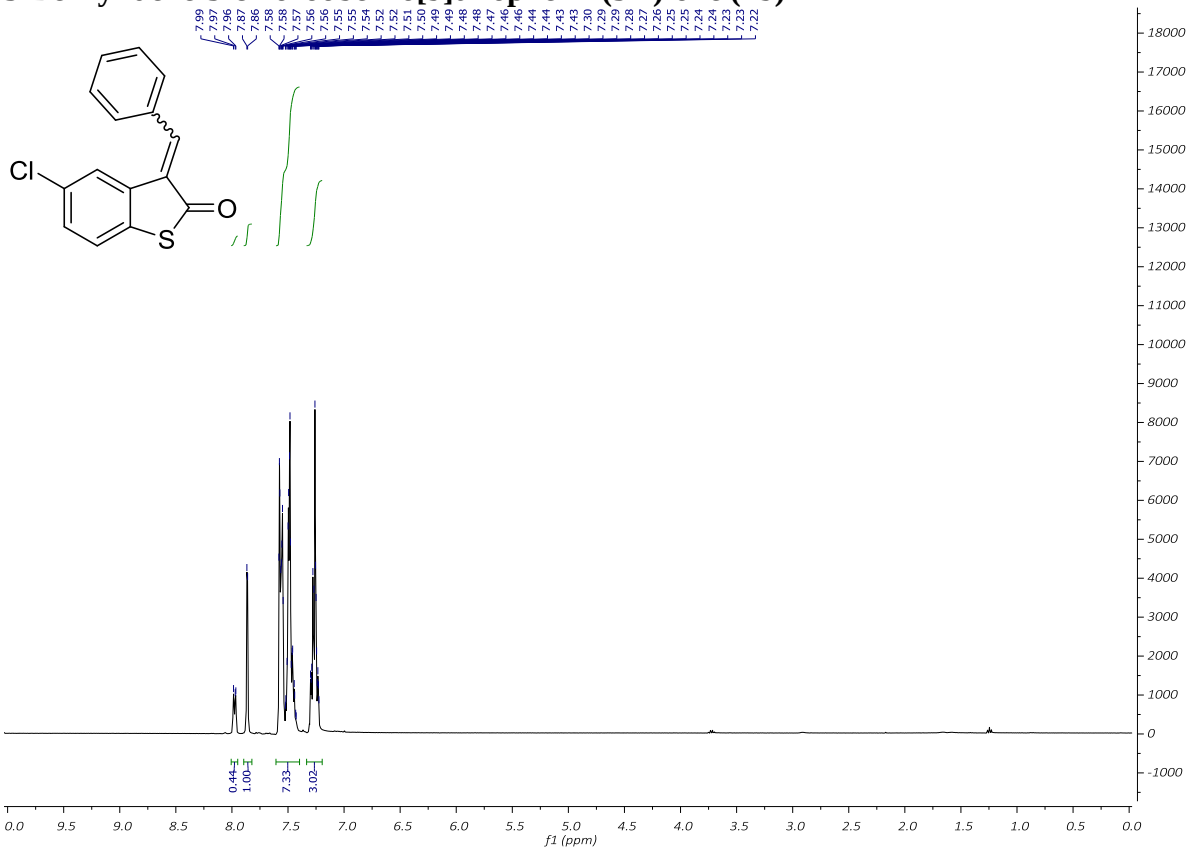


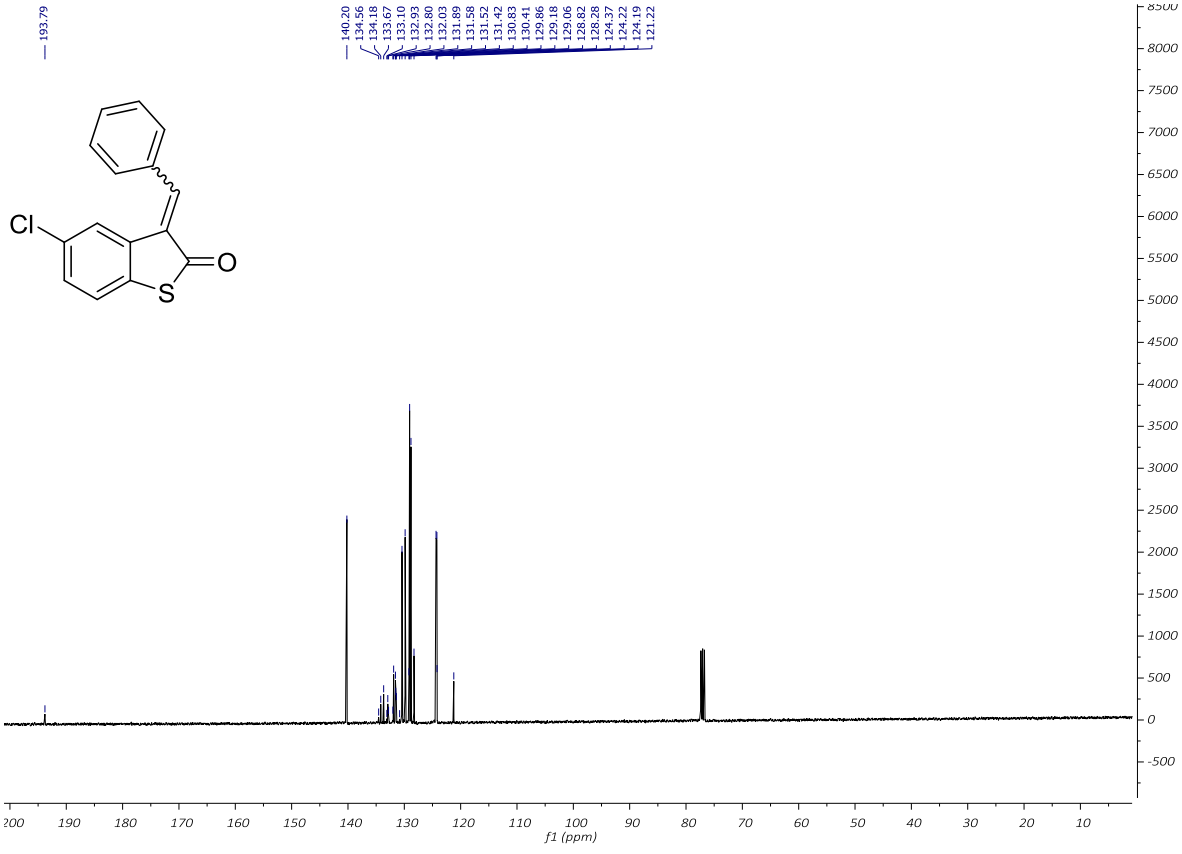
(*E*)-3-Benzylidenebenzo[*b*]thiophen-2(3*H*)-one (1a) – pure *E* isomer



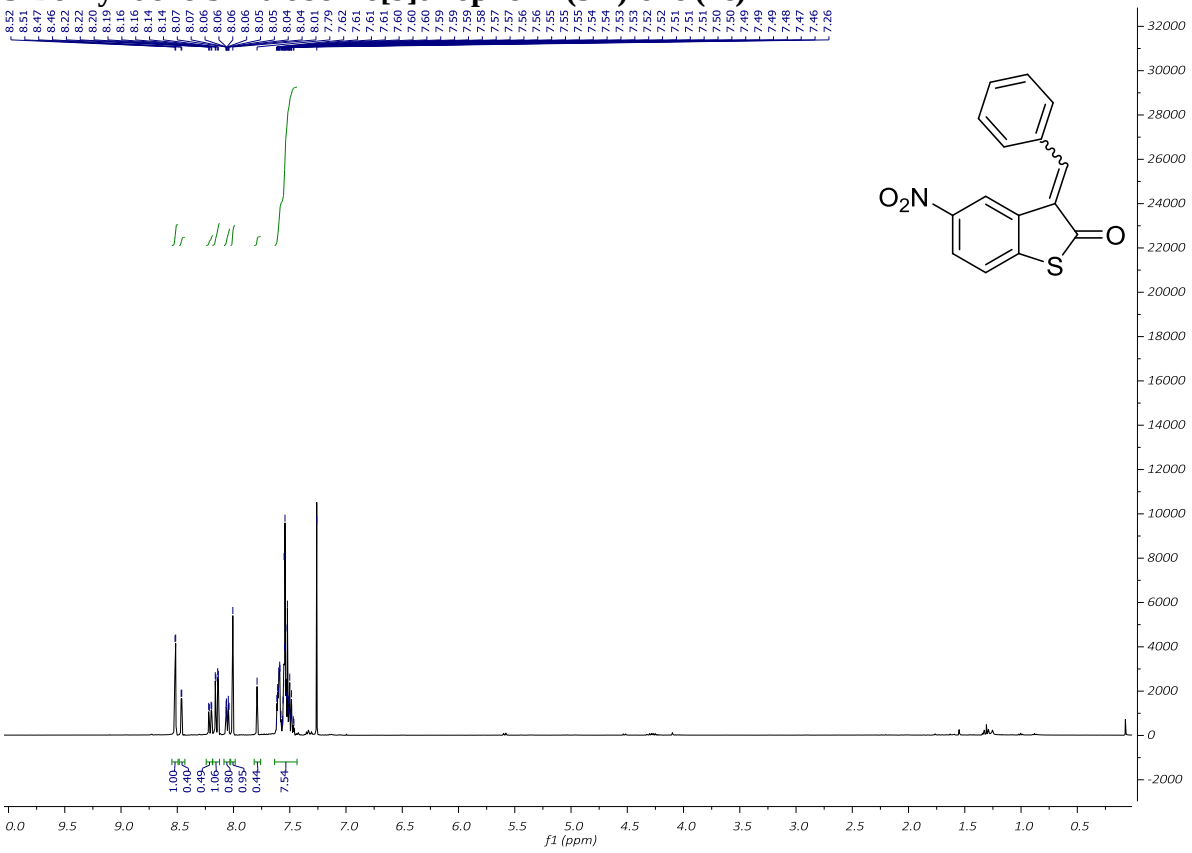


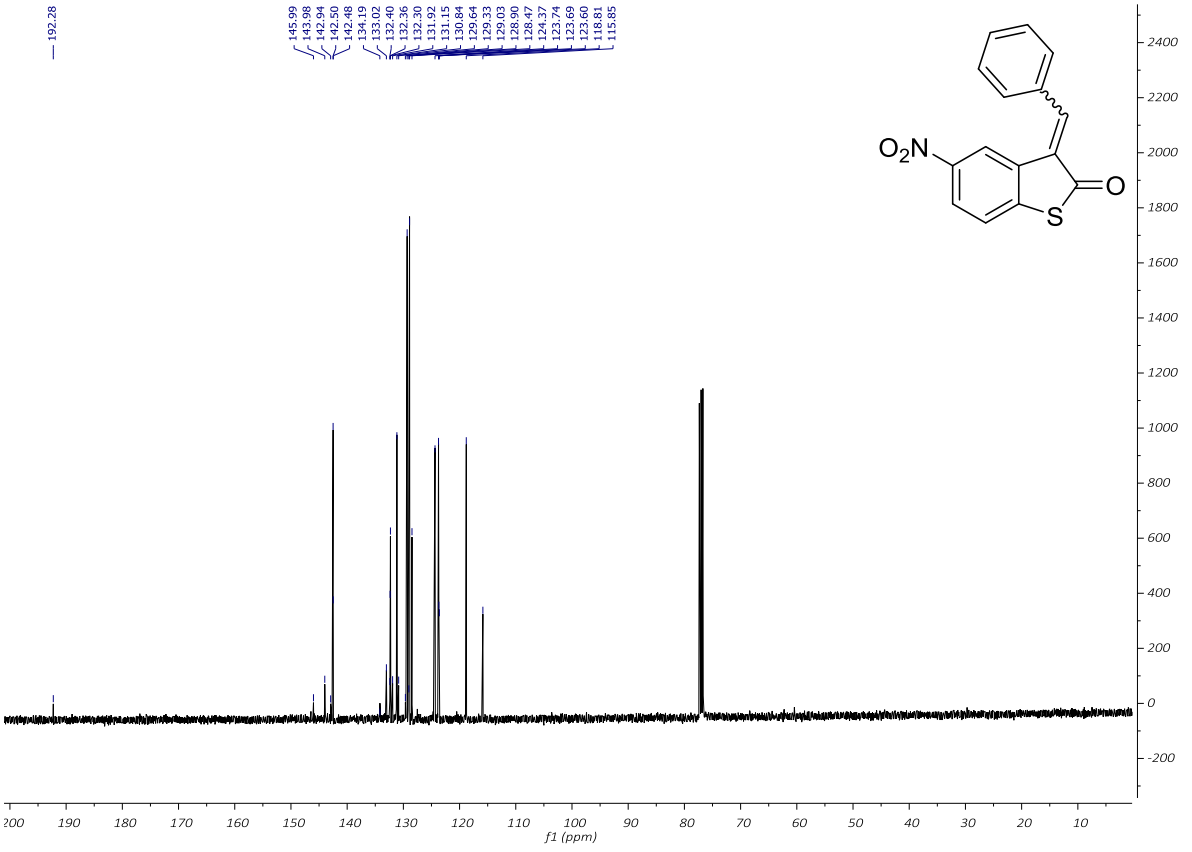
3-Benzylidene-5-chloroobenzo[*b*]thiophen-2(3*H*)-one (1b)



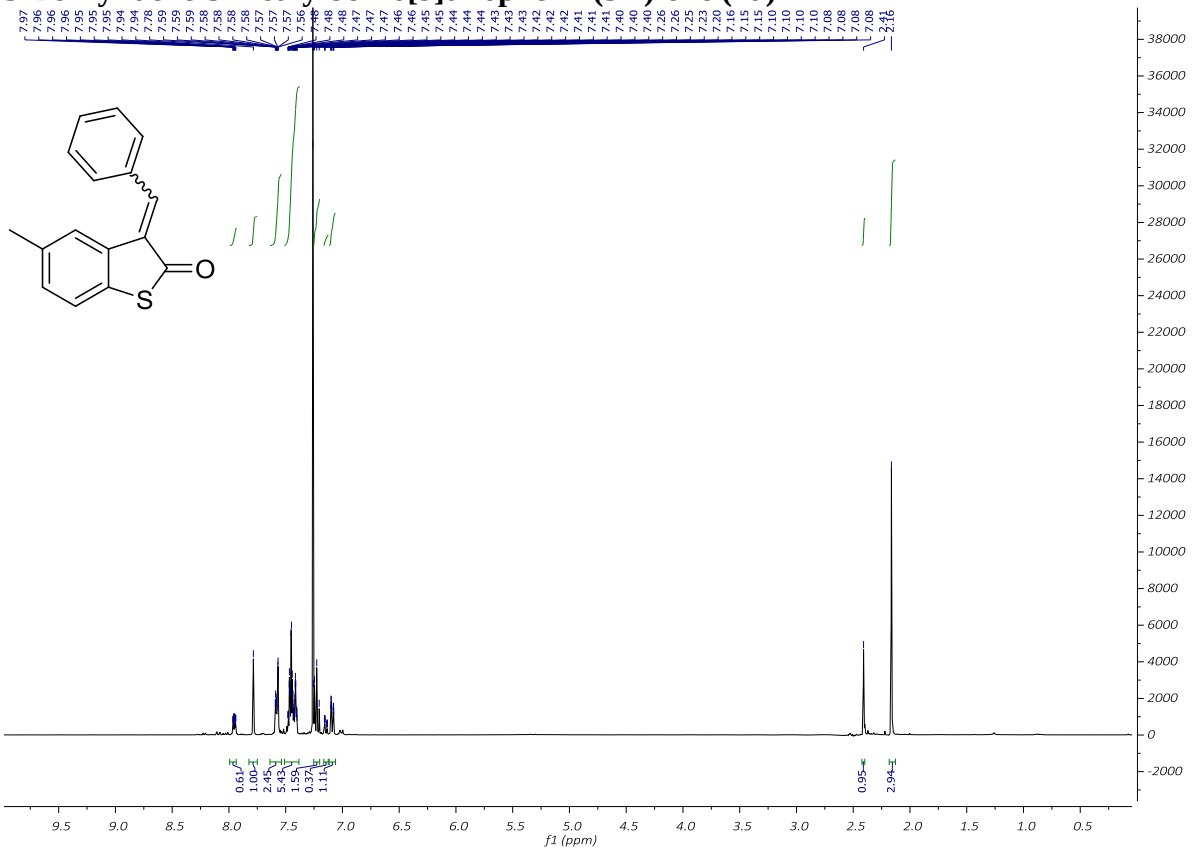


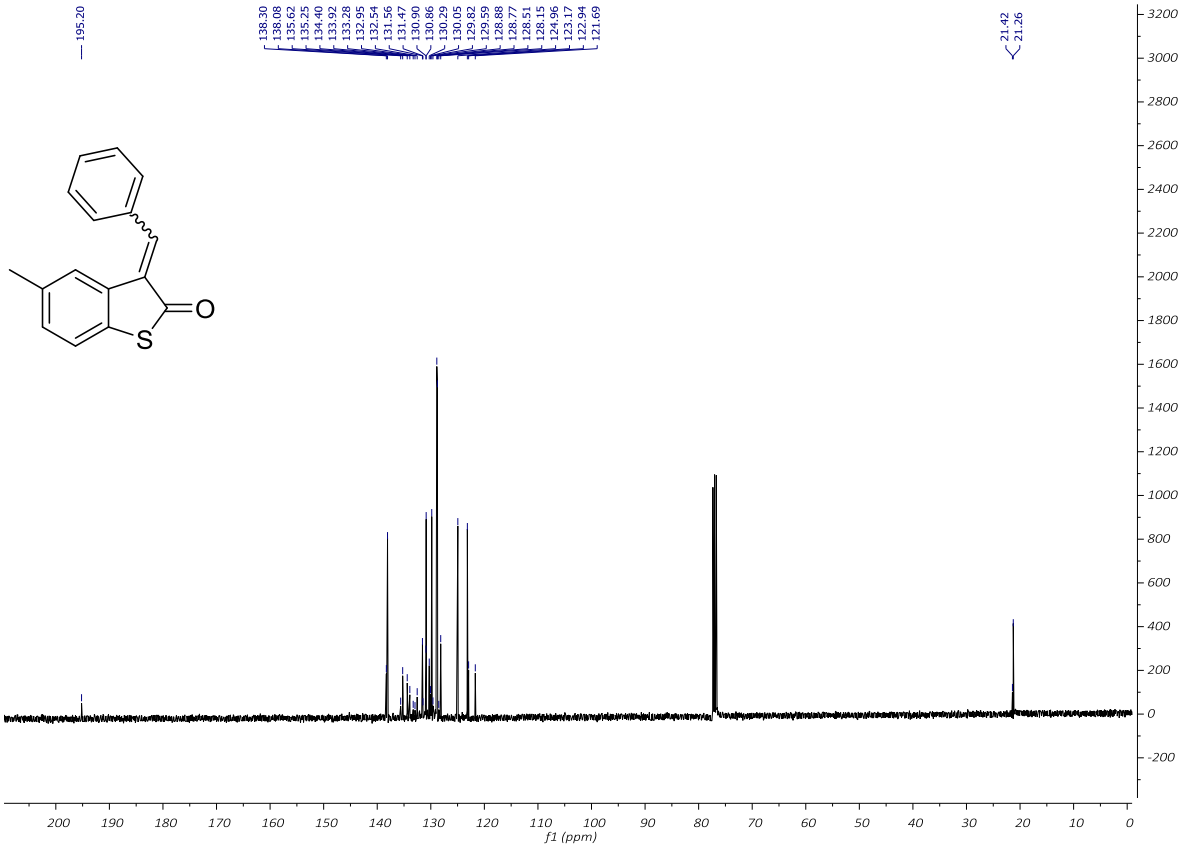
3-Benzylidene-5-nitrobenzo[*b*]thiophen-2(3*H*)-one (1c)



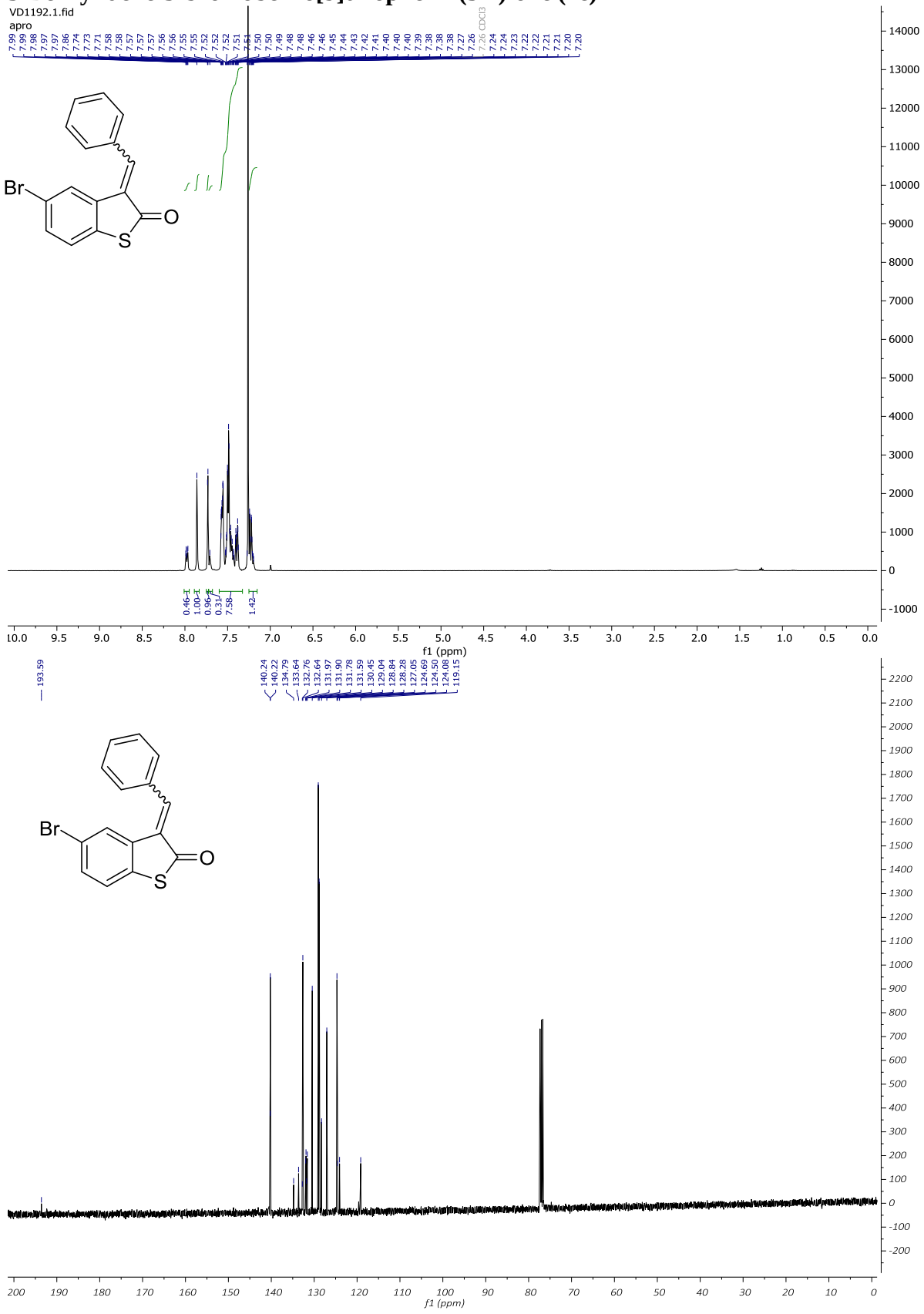


3-Benzylidene-5-methylbenzo[*b*]thiophen-2(3*H*)-one (1d)

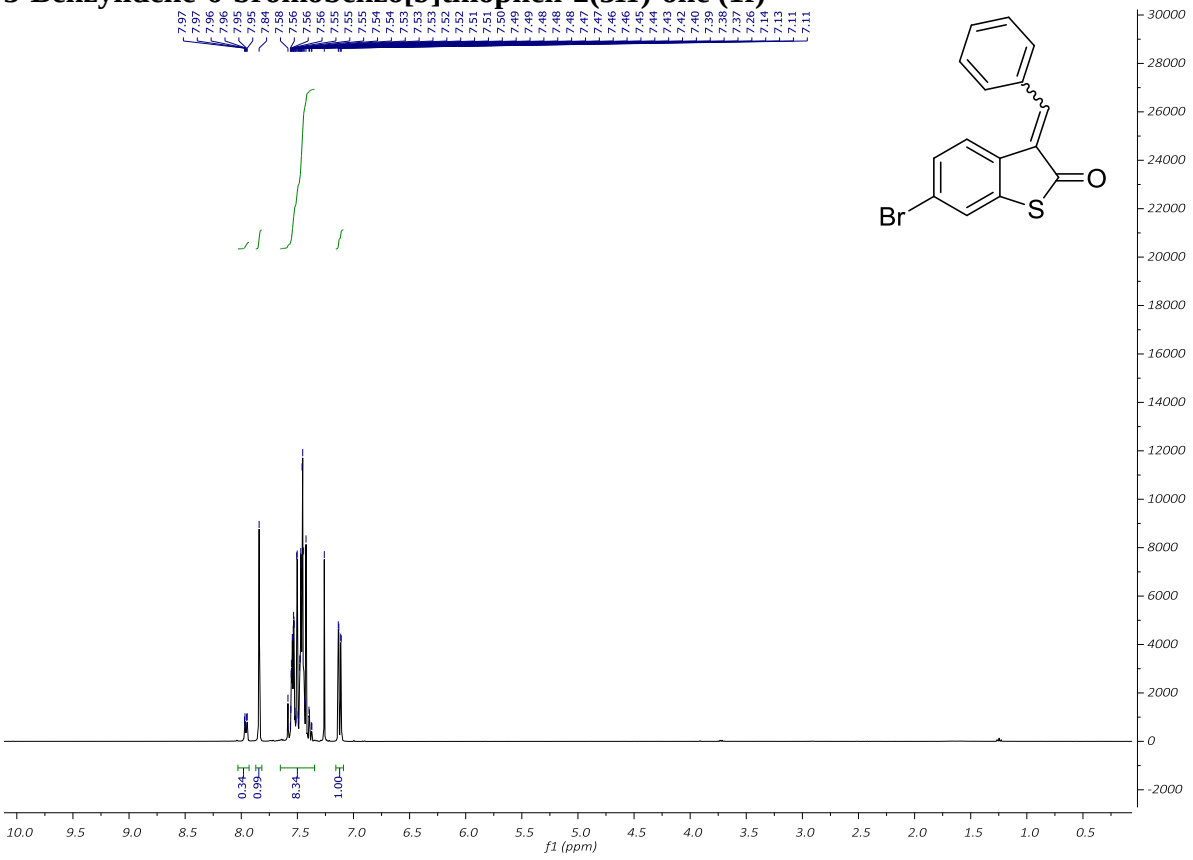


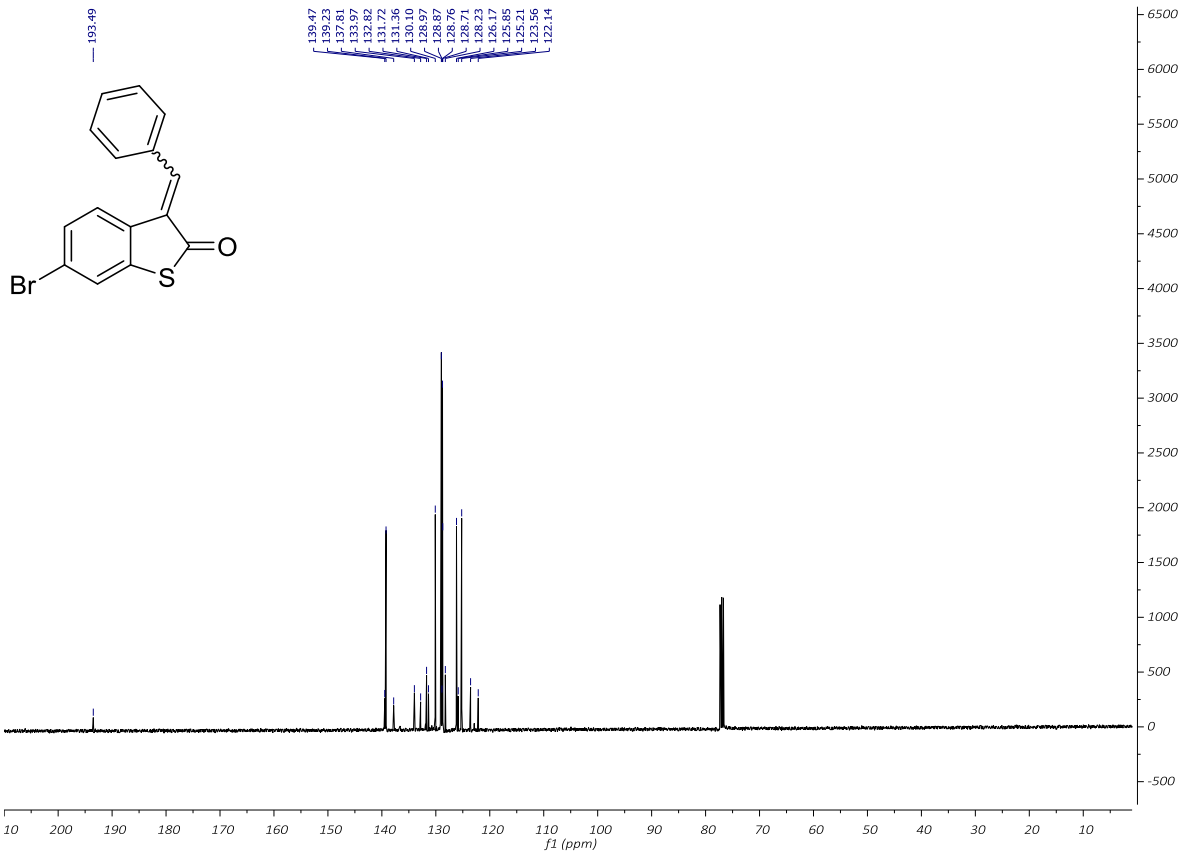


3-Benzylidene-5-bromobenzo[*b*]thiophen-2(3*H*)-one (1e)

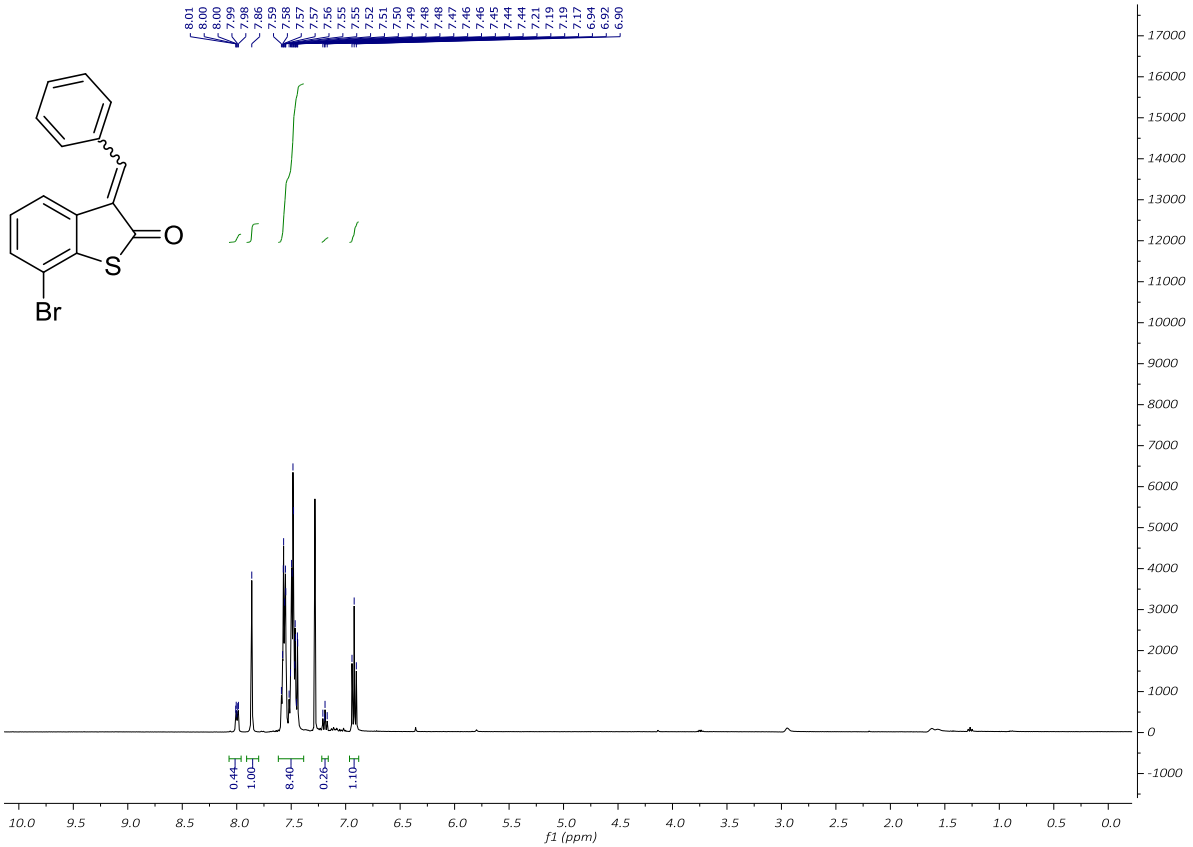


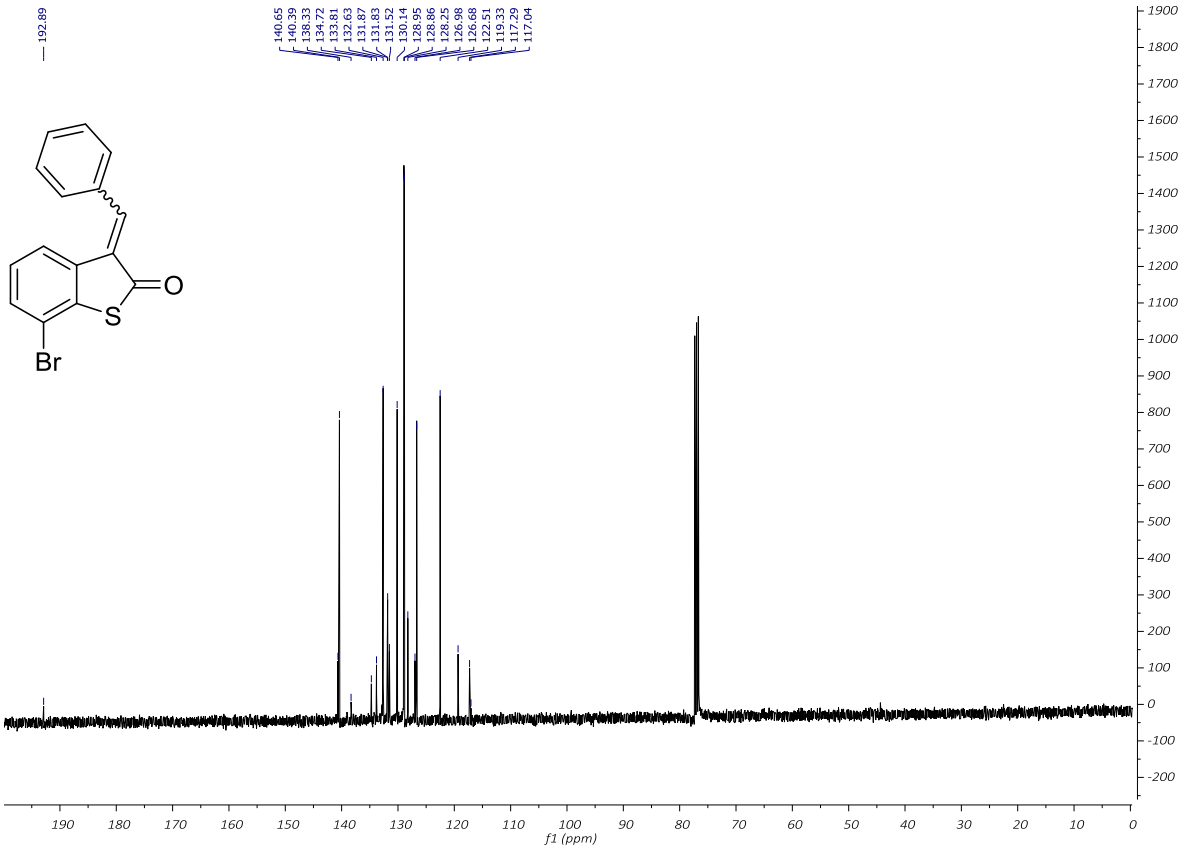
3-Benzylidene-6-bromobenzo[*b*]thiophen-2(3*H*)-one (1f)



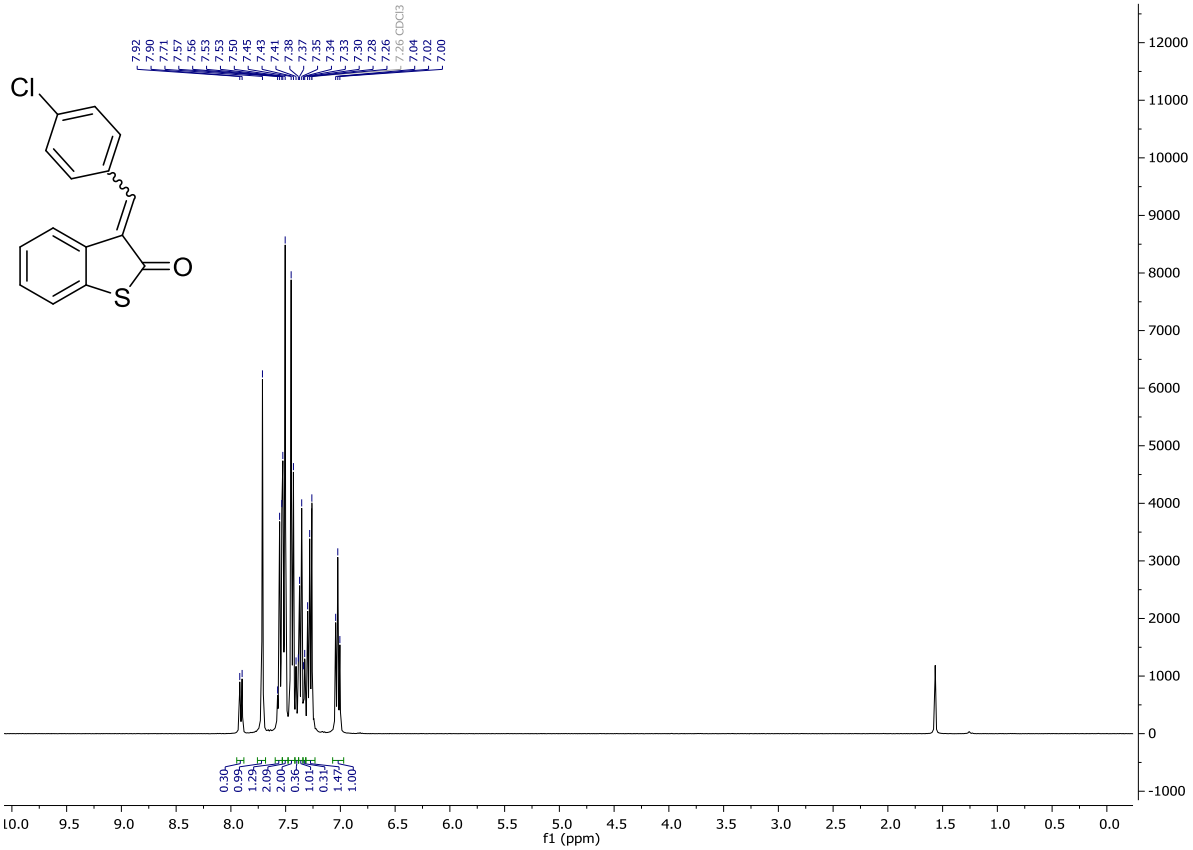


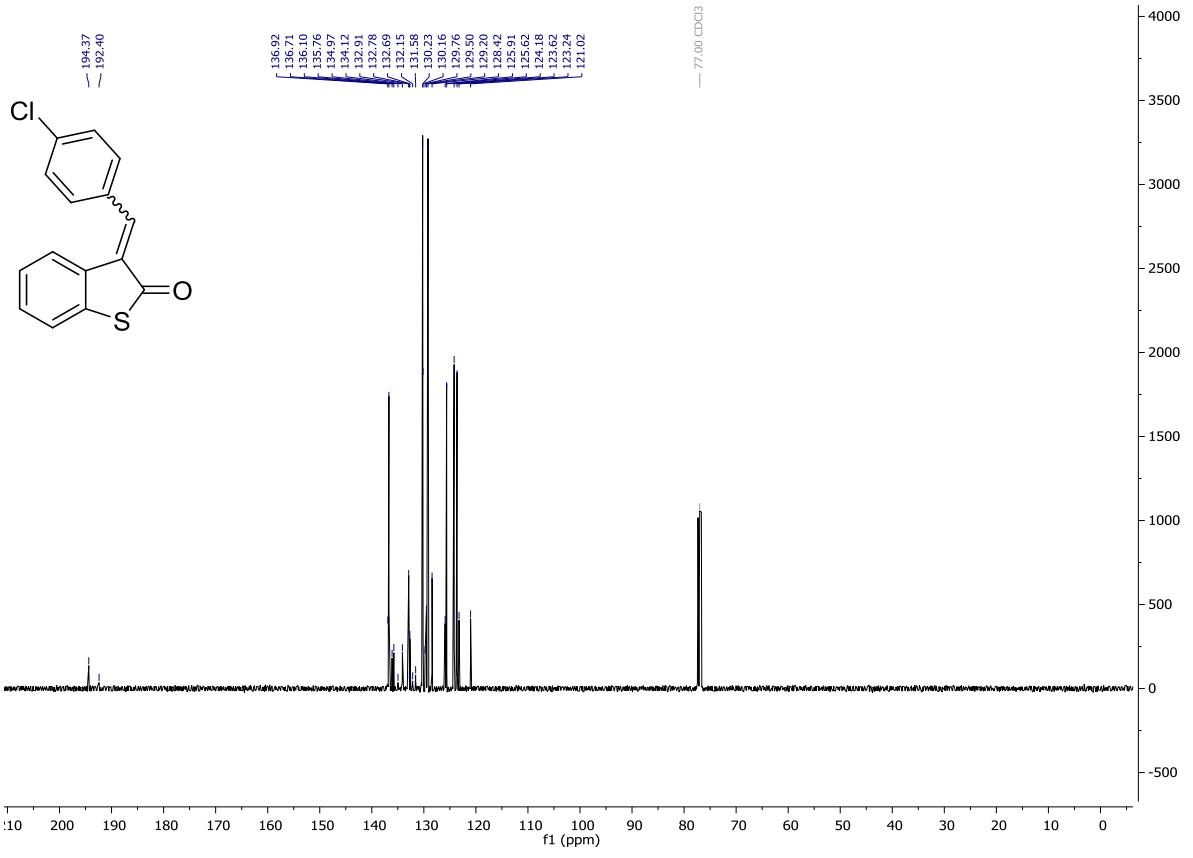
3-Benzylidene-7-bromobenzo[*b*]thiophen-2(3*H*)-one (1g)



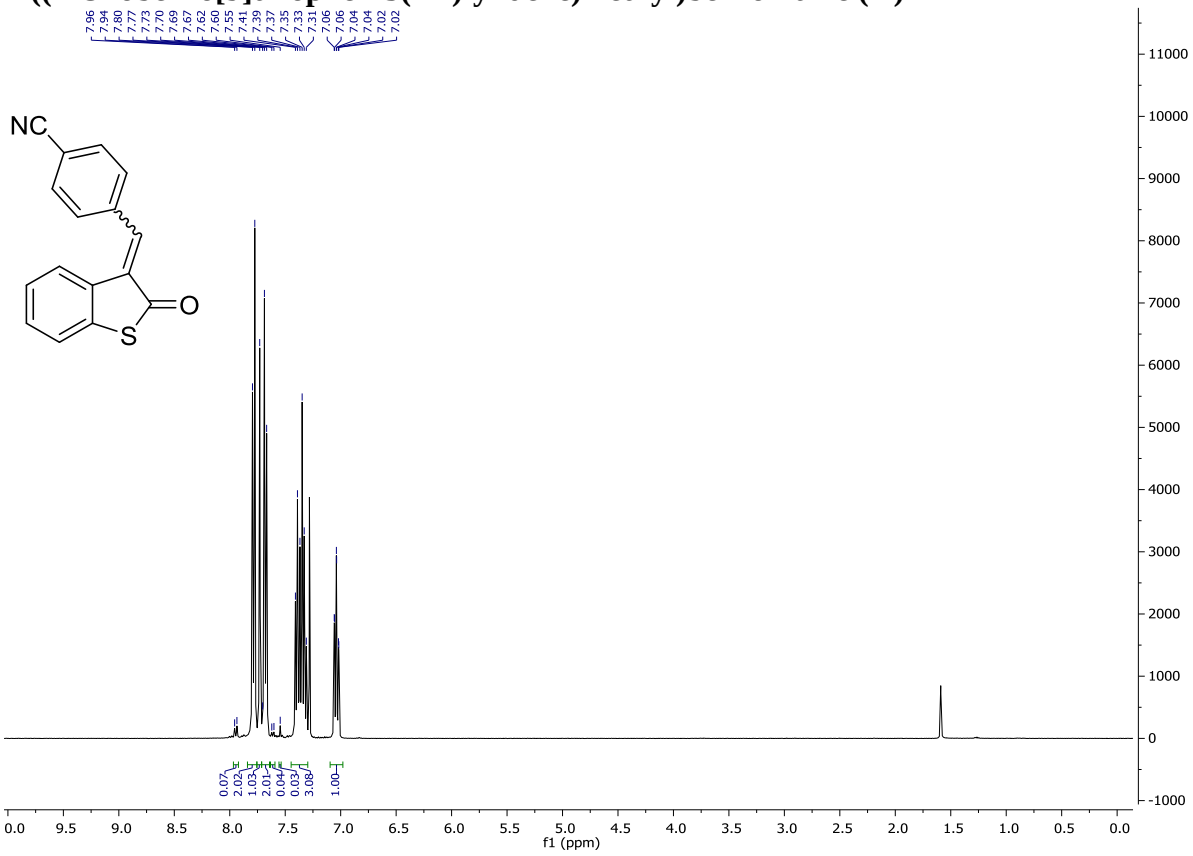


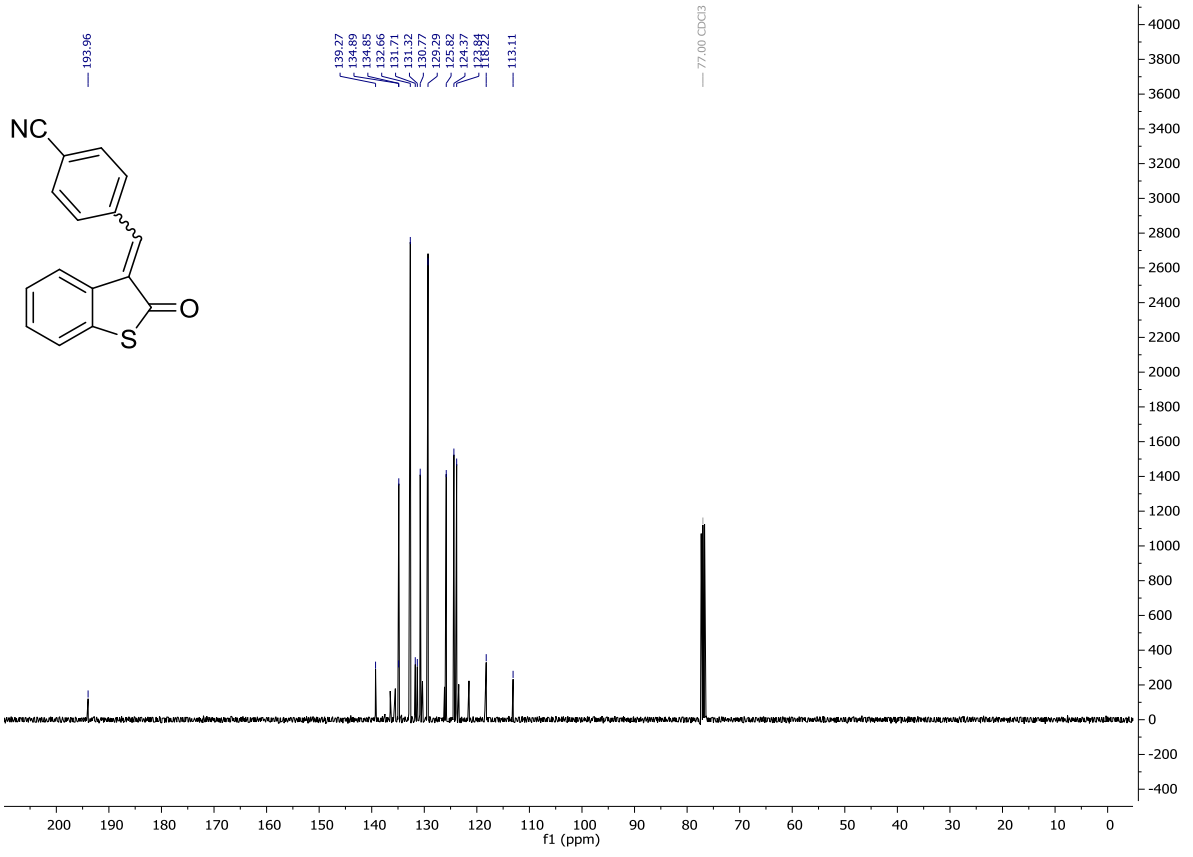
3-(4-Chlorobenzylidene)benzo[*b*]thiophen-2(3H)-one (1h)



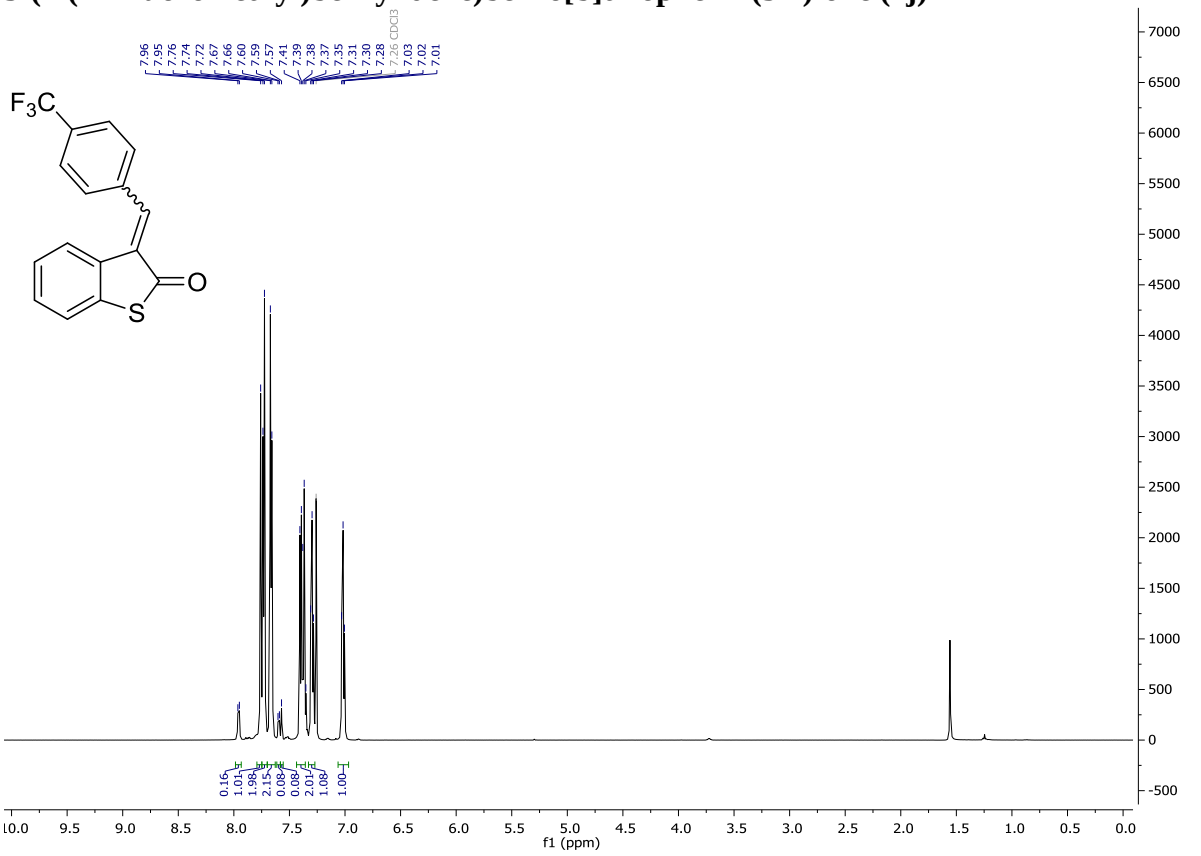


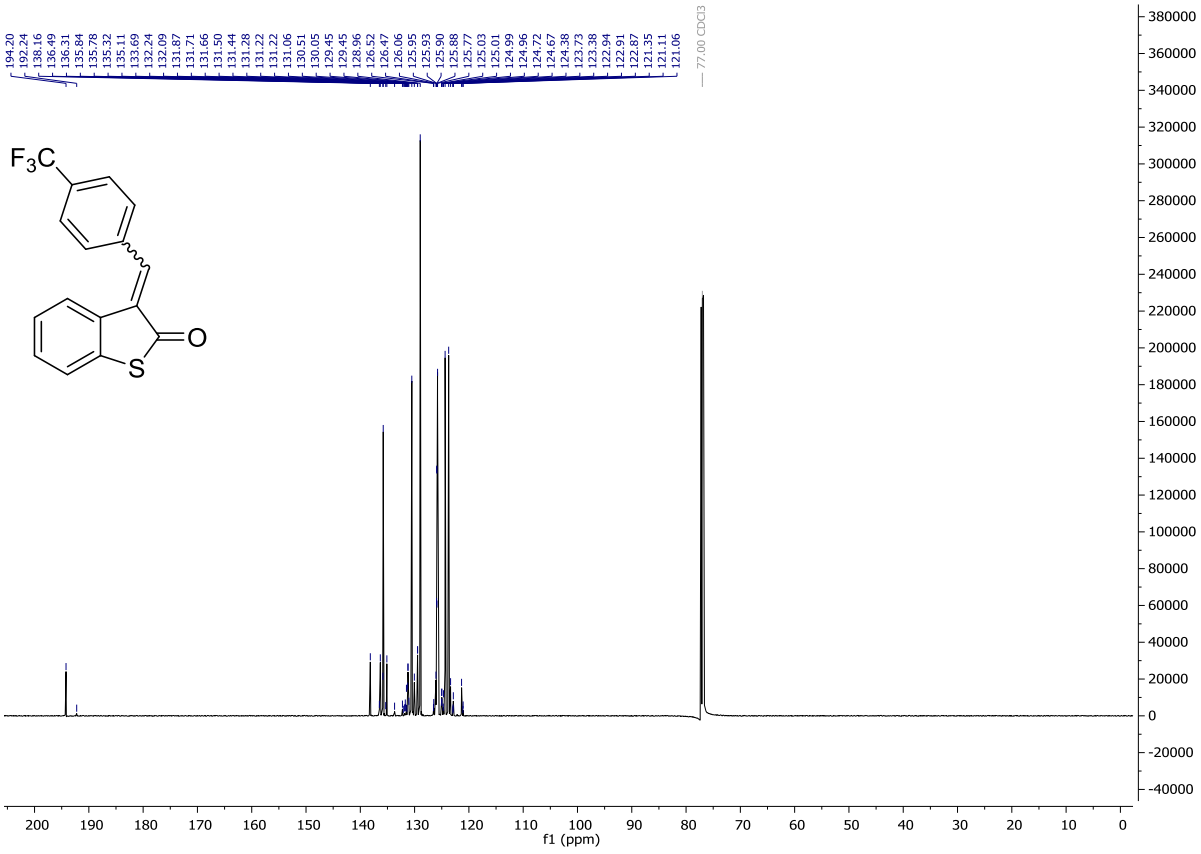
4-((2-Oxobenzo[*b*]thiophen-3(2*H*)-ylidene)methyl)benzonitrile (1i)

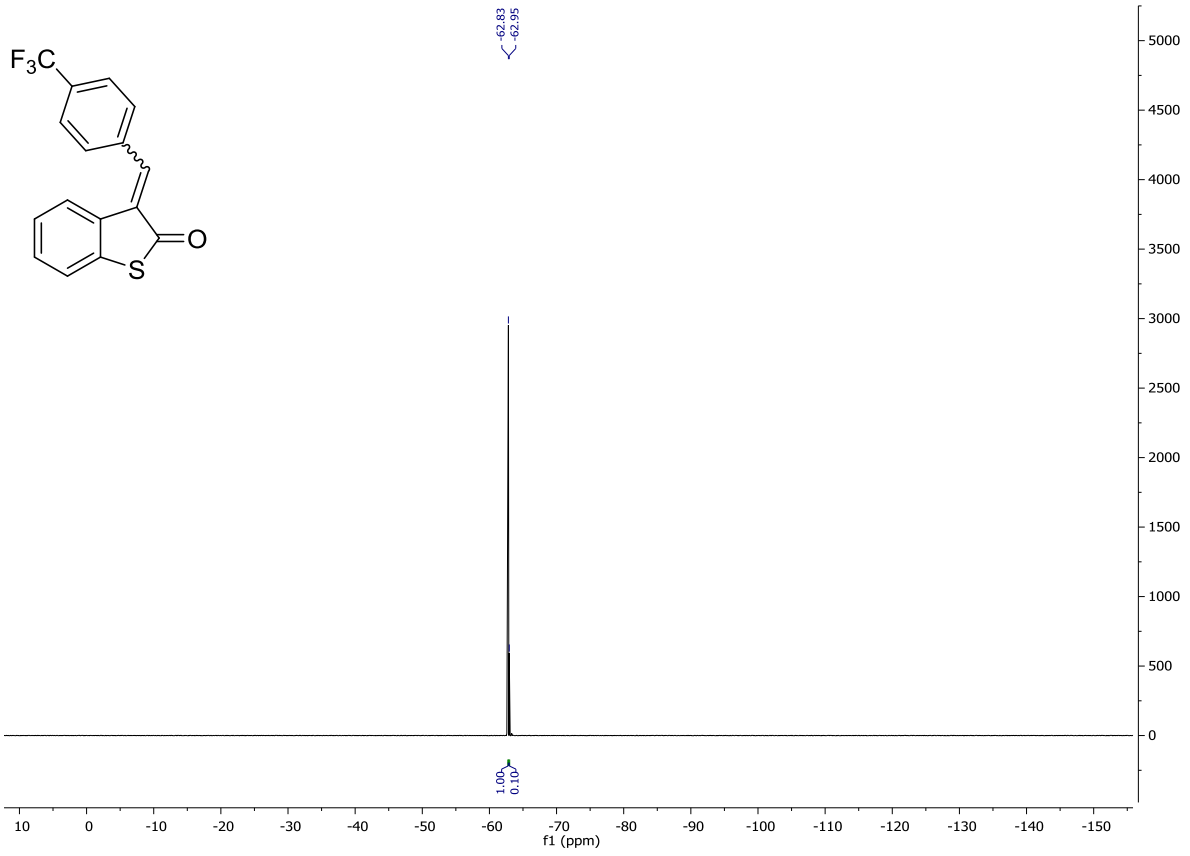




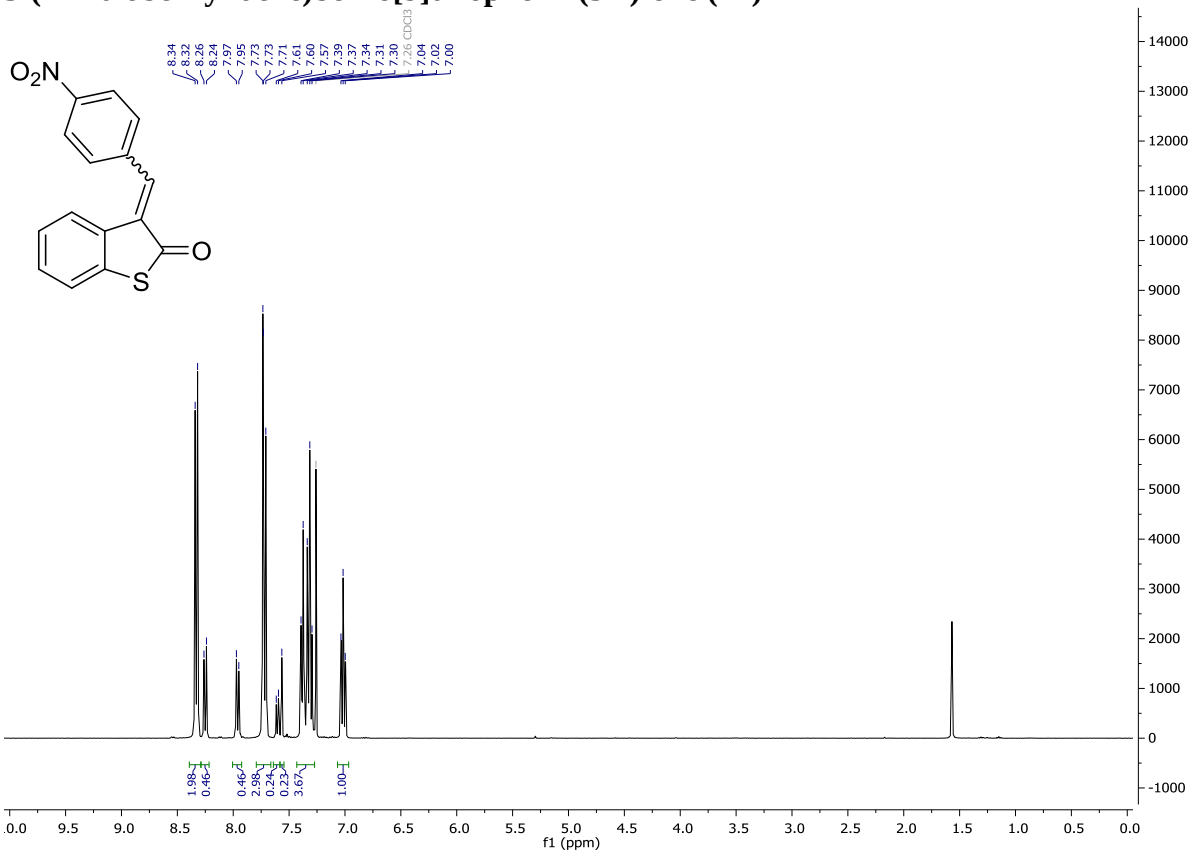
3-(4-(Trifluoromethyl)benzylidene)benzo[b]thiophen-2(3H)-one (1j)

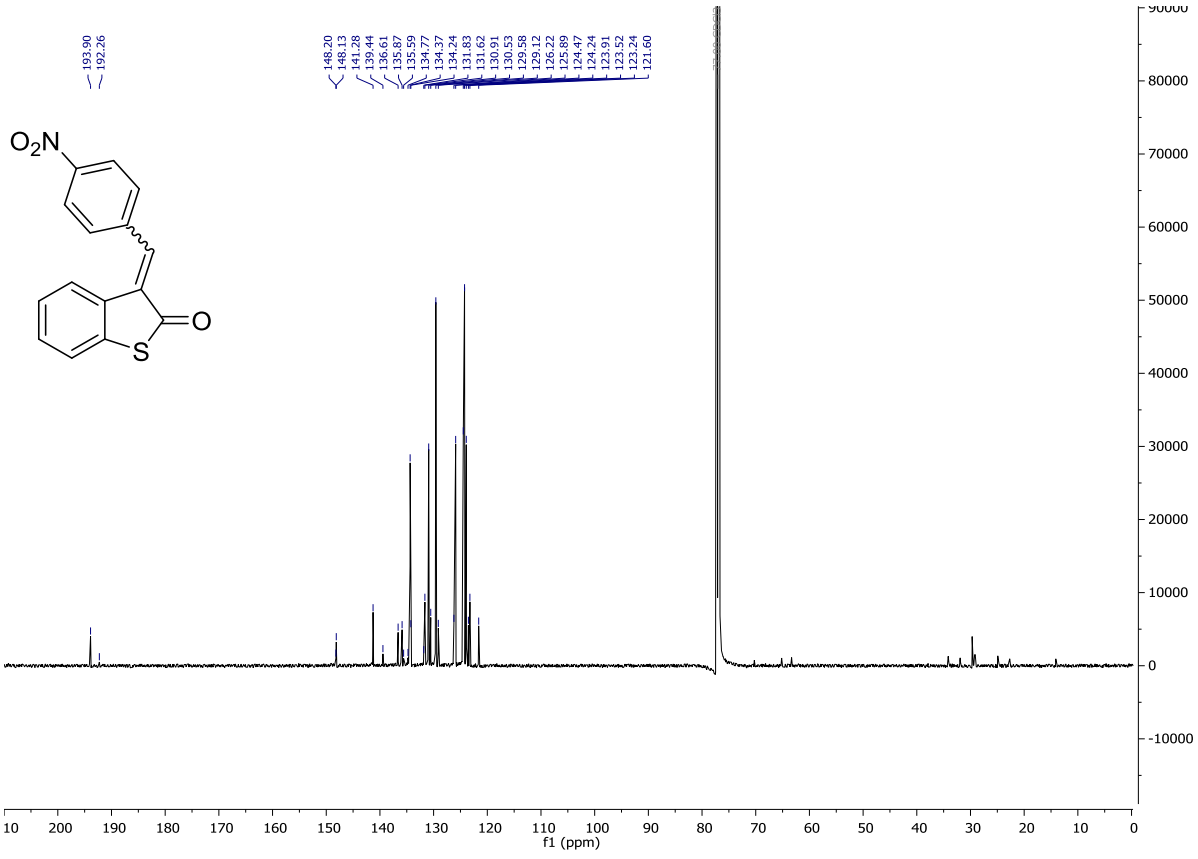




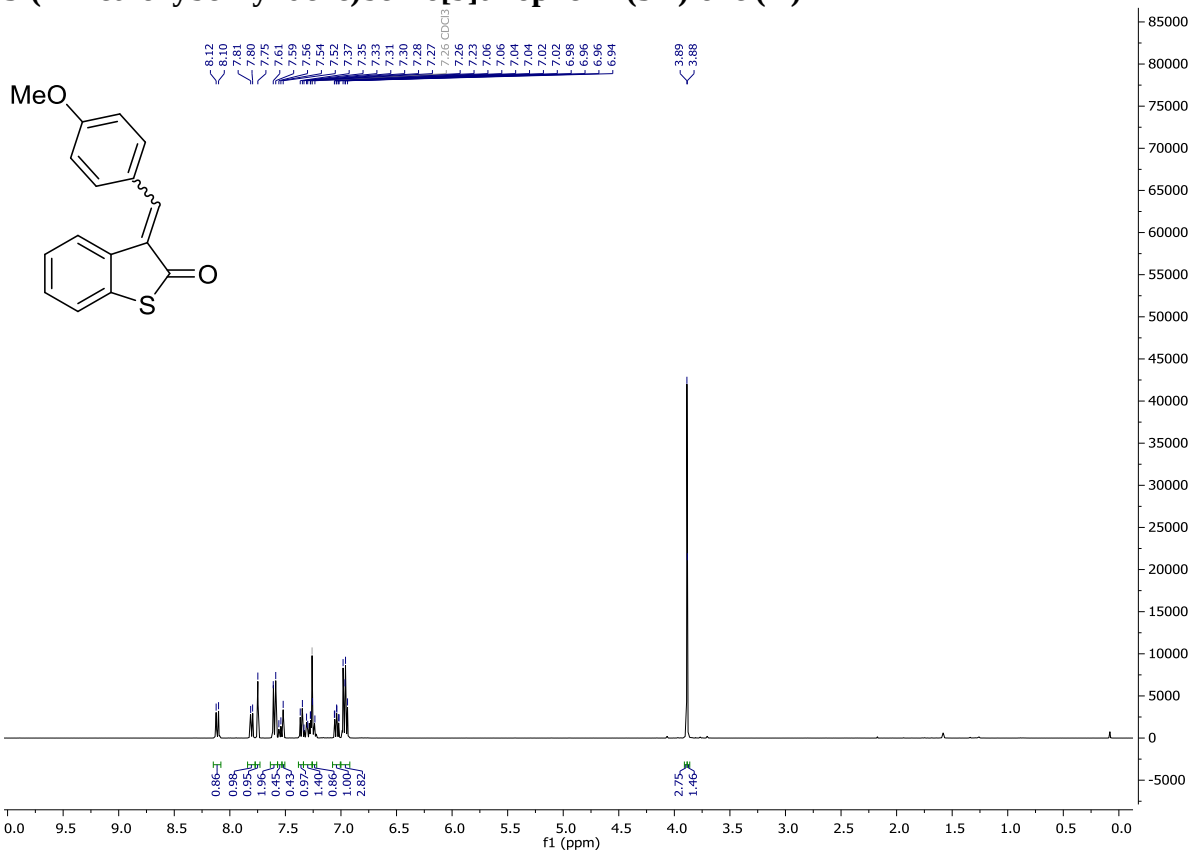

F3C
O
S
-62.83
-62.95
1.00
0.10
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

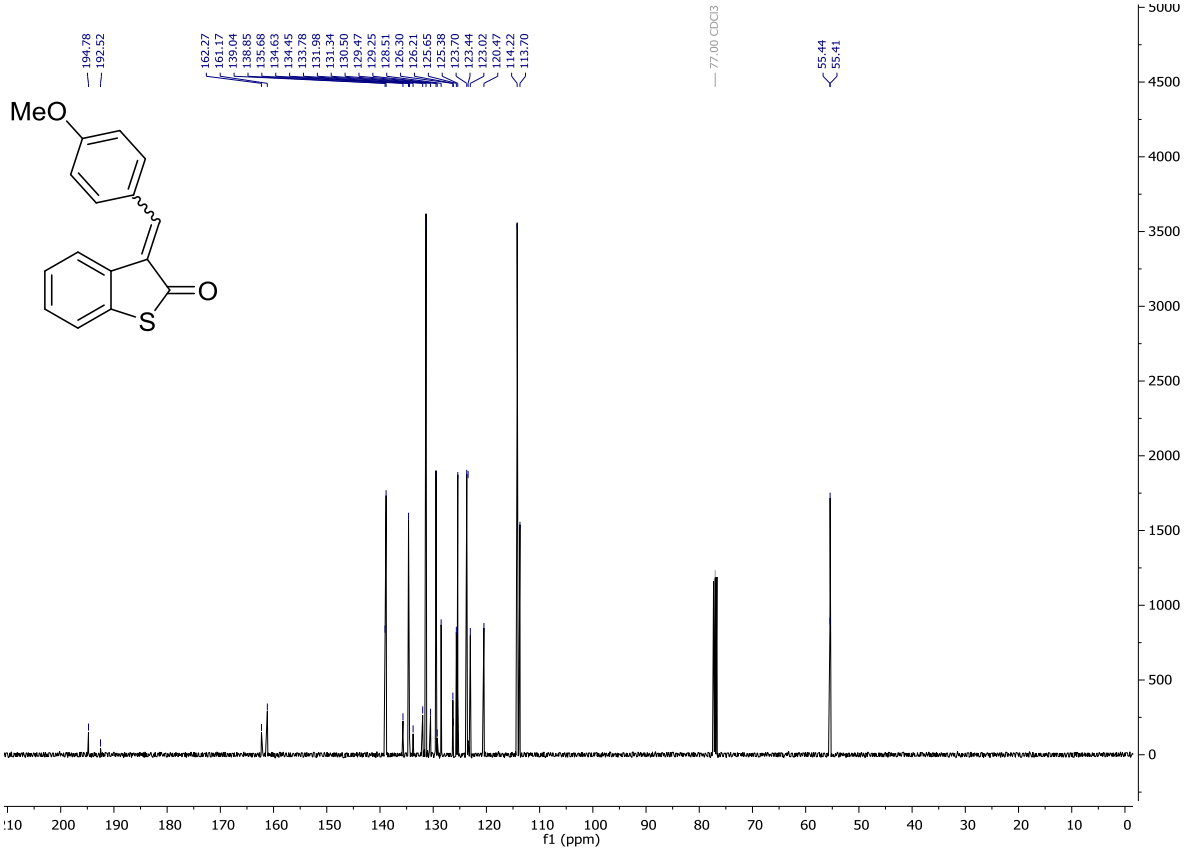
3-(4-Nitrobenzylidene)benzo[*b*]thiophen-2(3*H*)-one (1k)



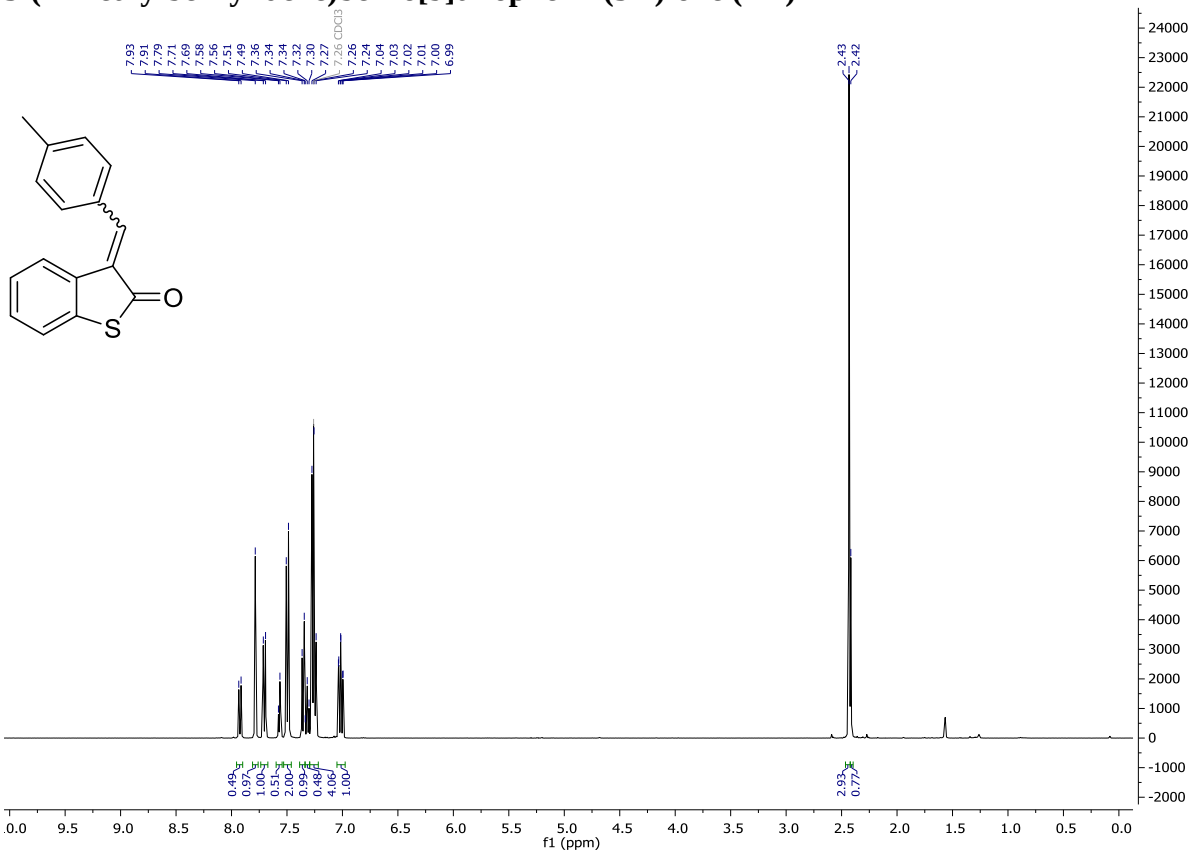


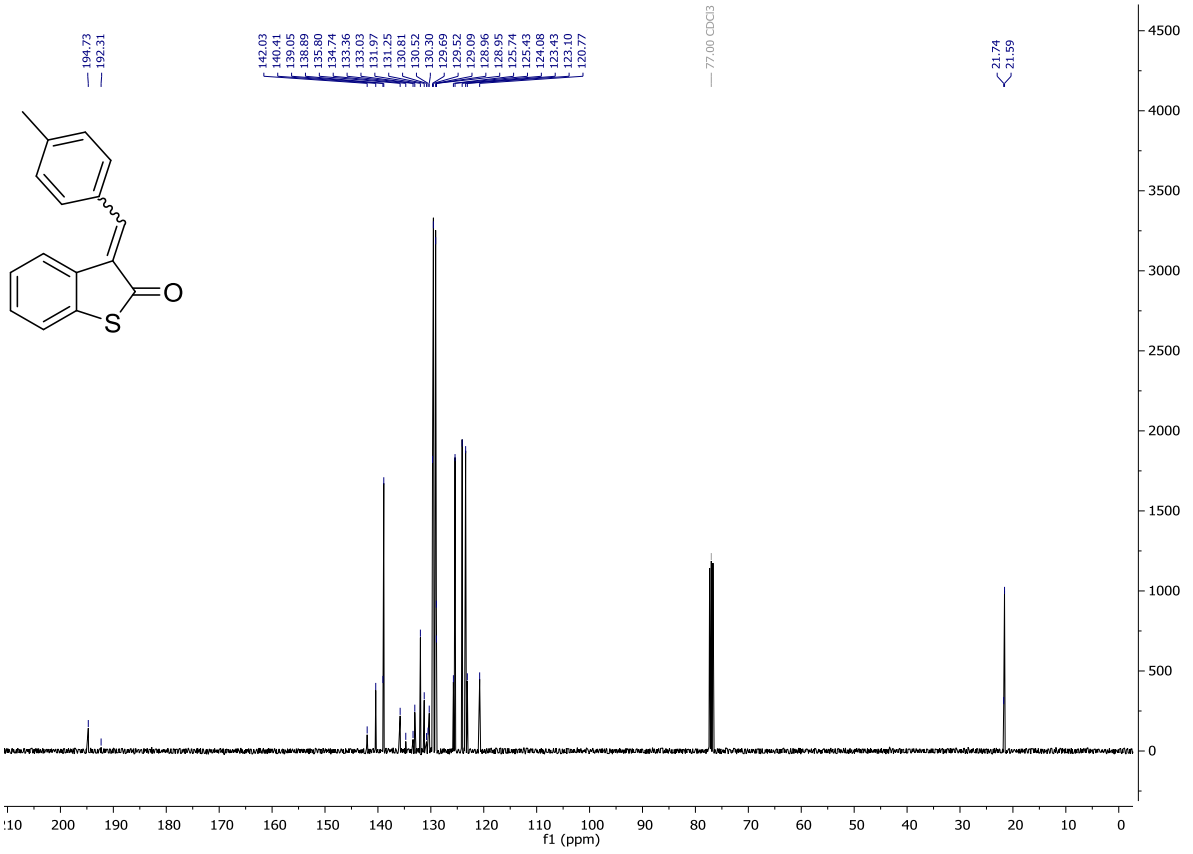
3-(4-Methoxybenzylidene)benzo[*b*]thiophen-2(3*H*)-one (1l)



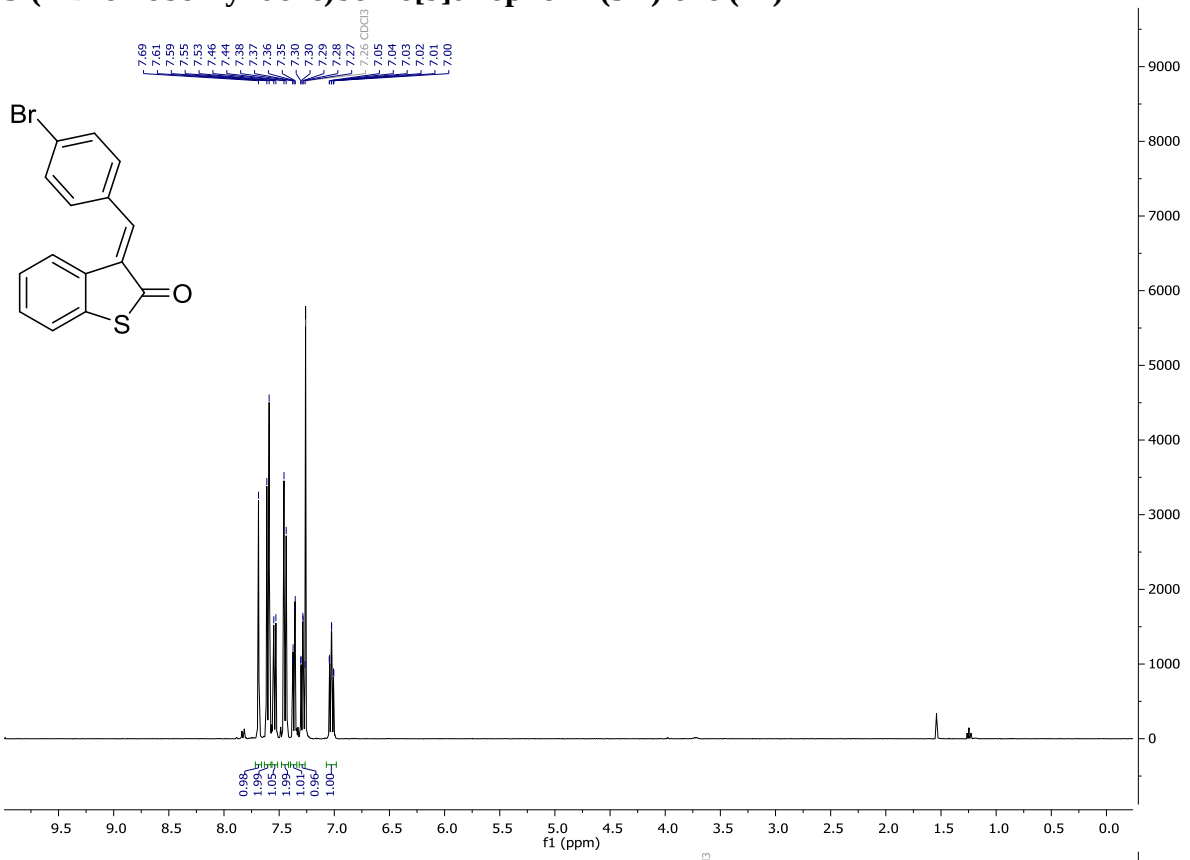


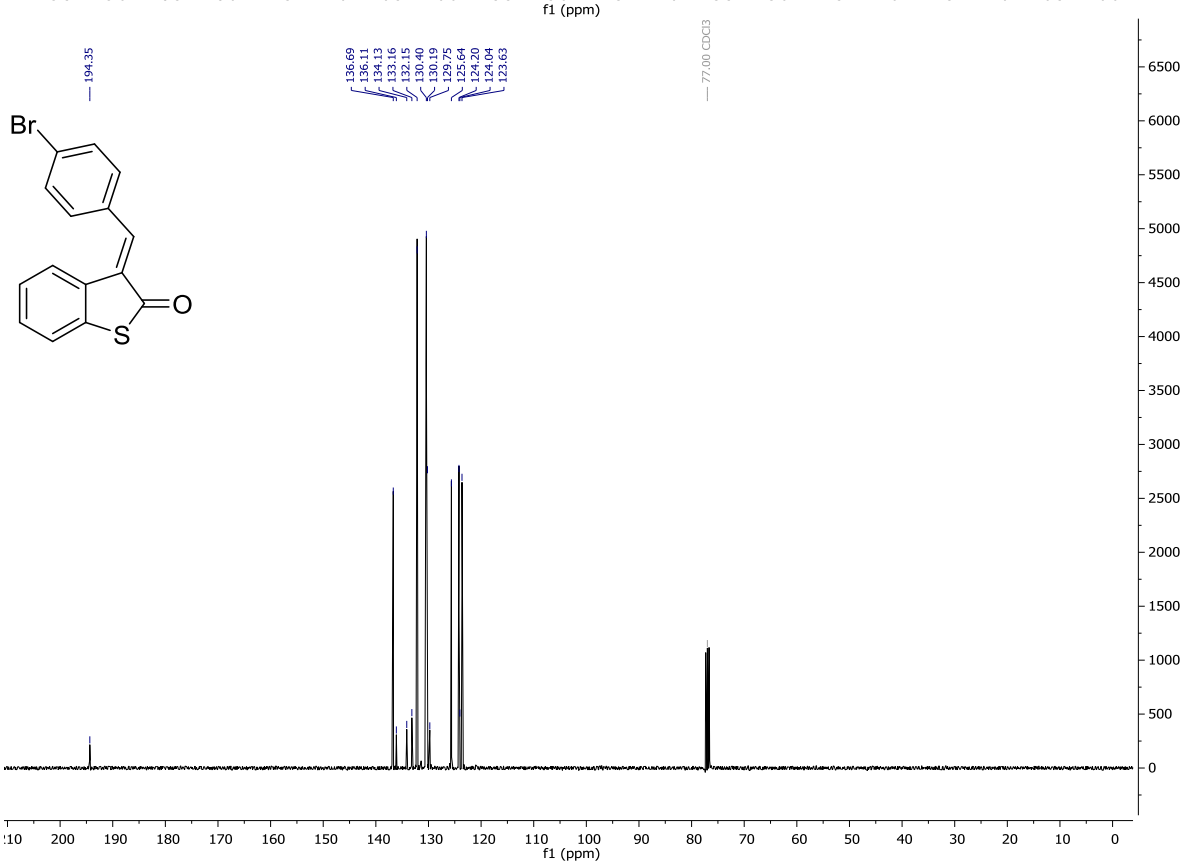
3-(4-Methylbenzylidene)benzo[*b*]thiophen-2(3H)-one (1m)



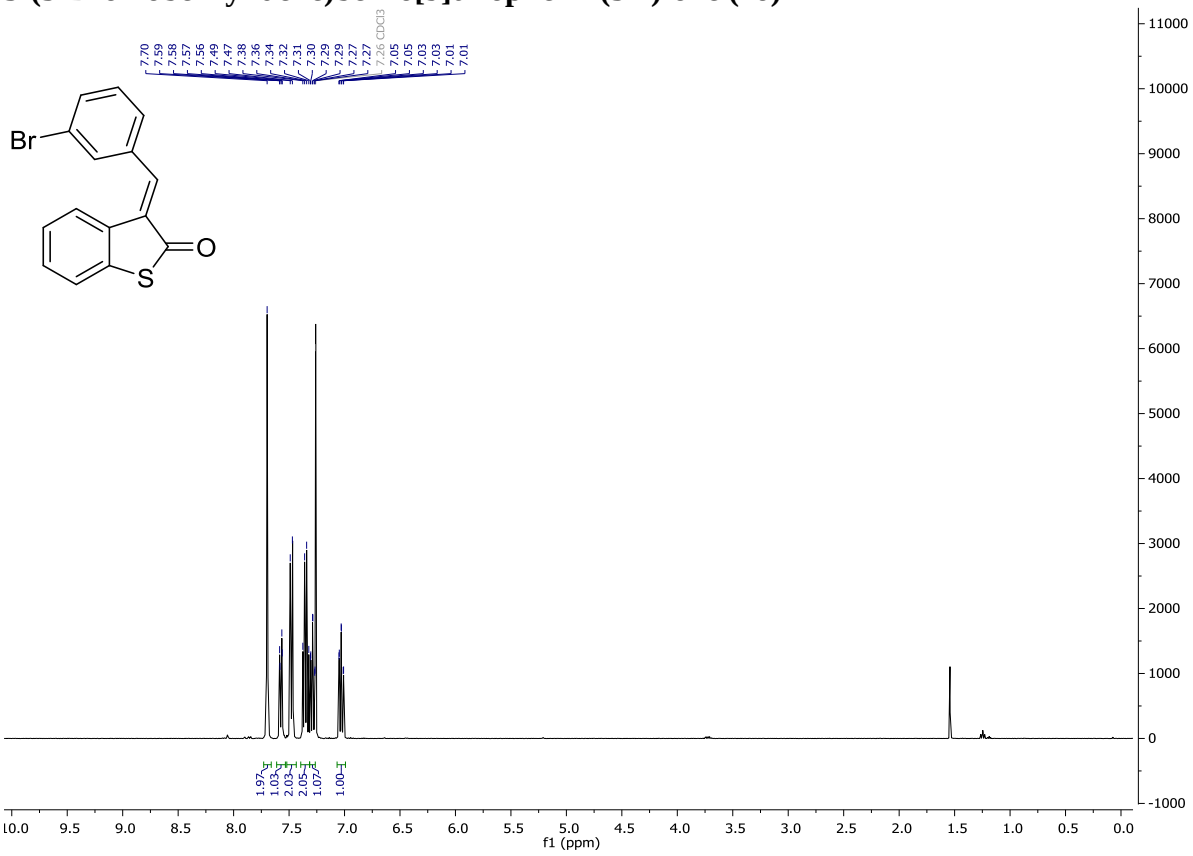


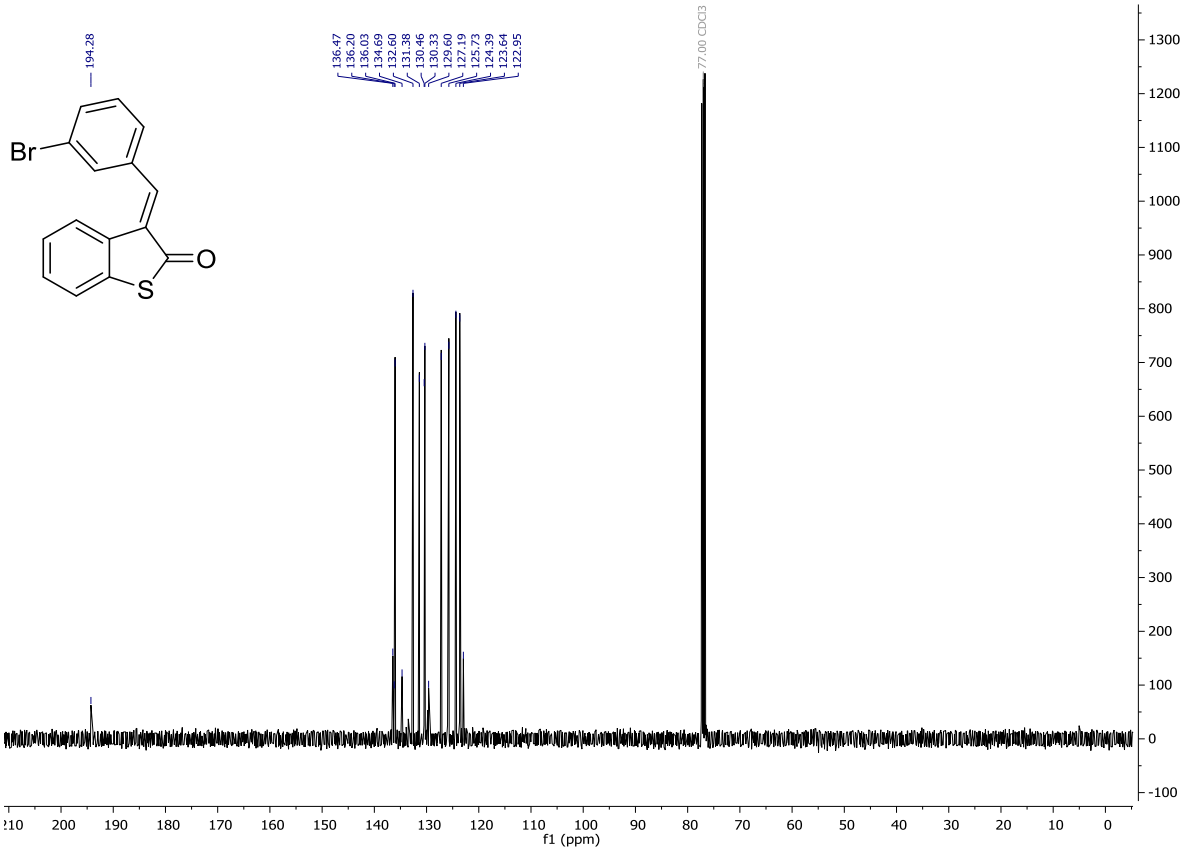
3-(4-Bromobenzylidene)benzo[*b*]thiophen-2(3*H*)-one (1n)



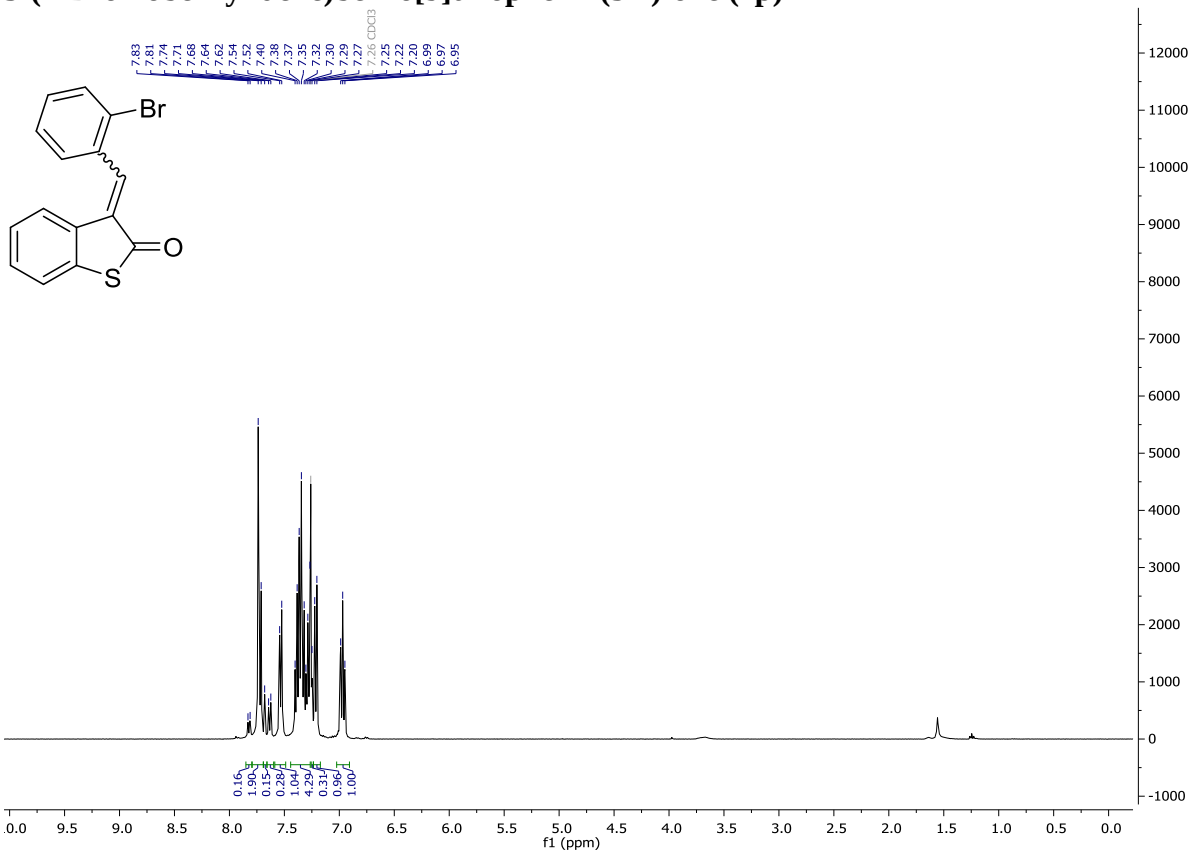


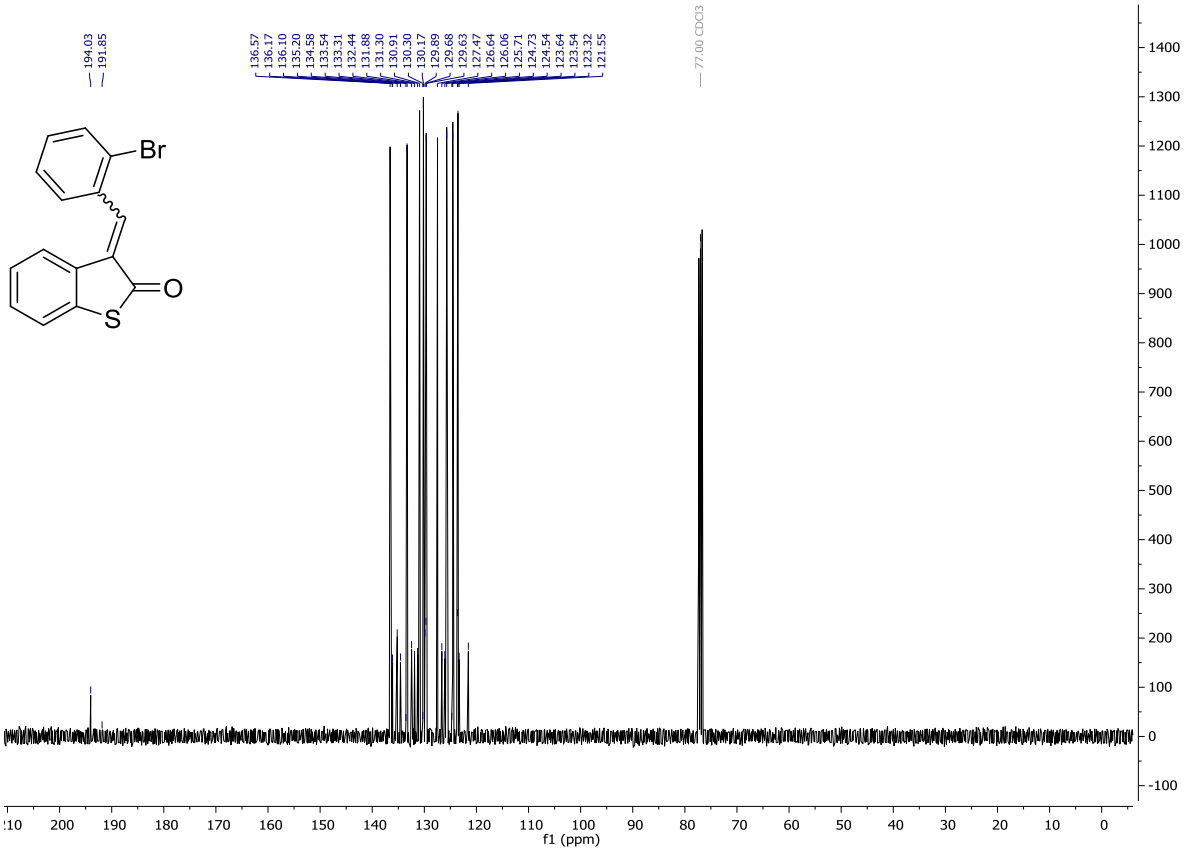
3-(3-Bromobenzylidene)benzo[*b*]thiophen-2(3*H*)-one (1o)



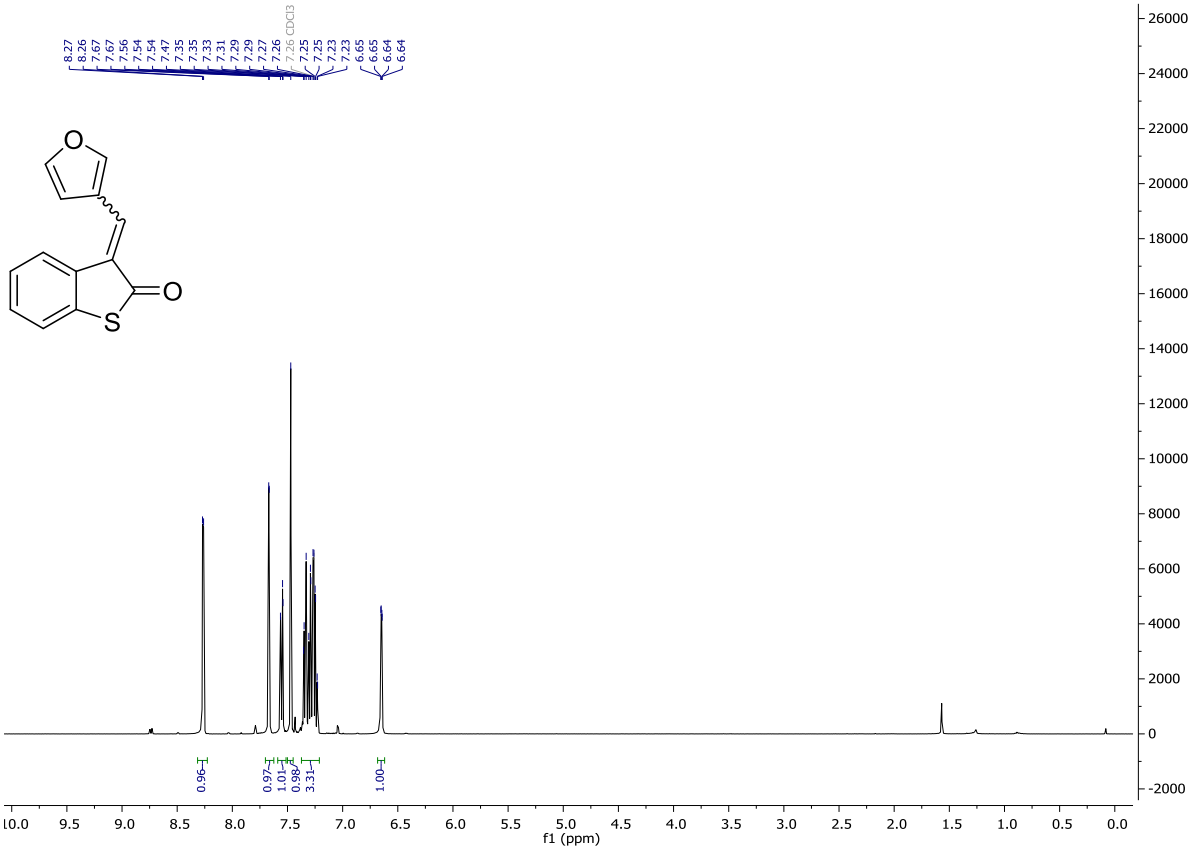


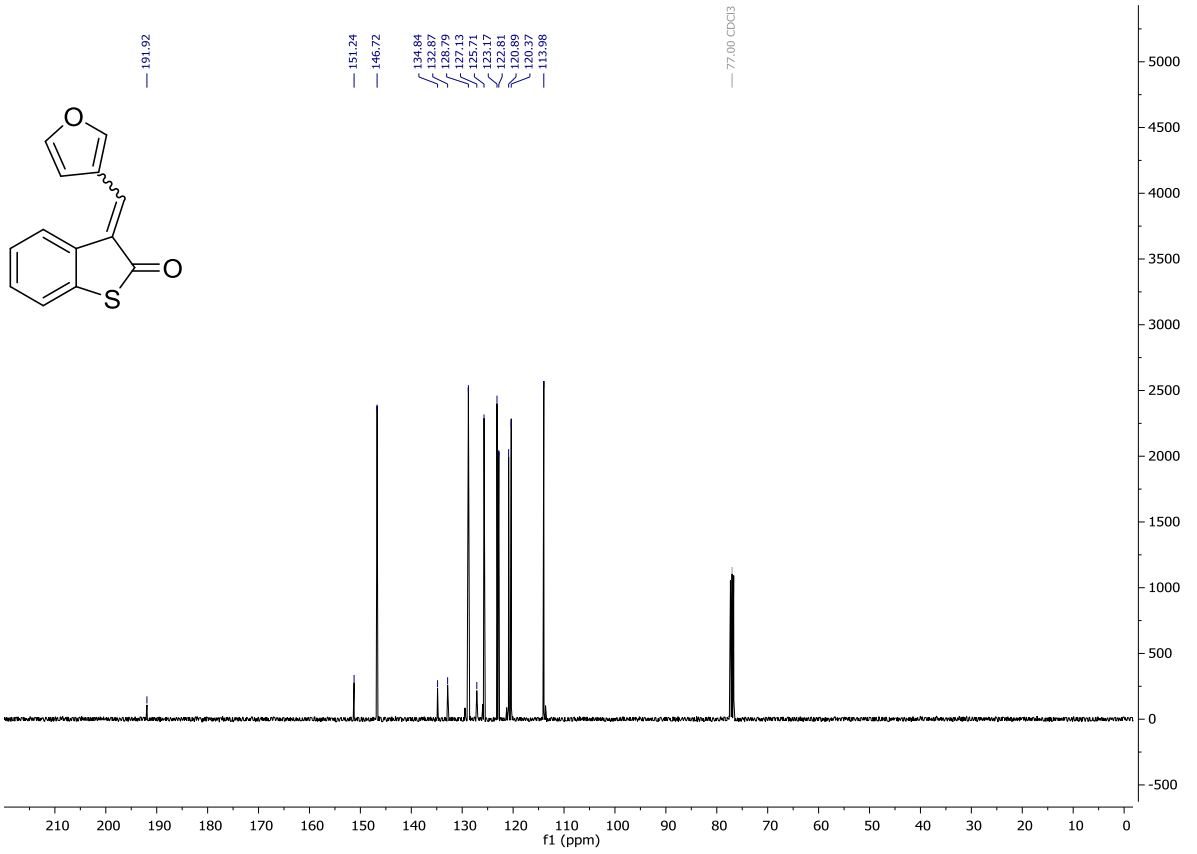
3-(2-Bromobenzylidene)benzo[*b*]thiophen-2(3*H*)-one (1p)



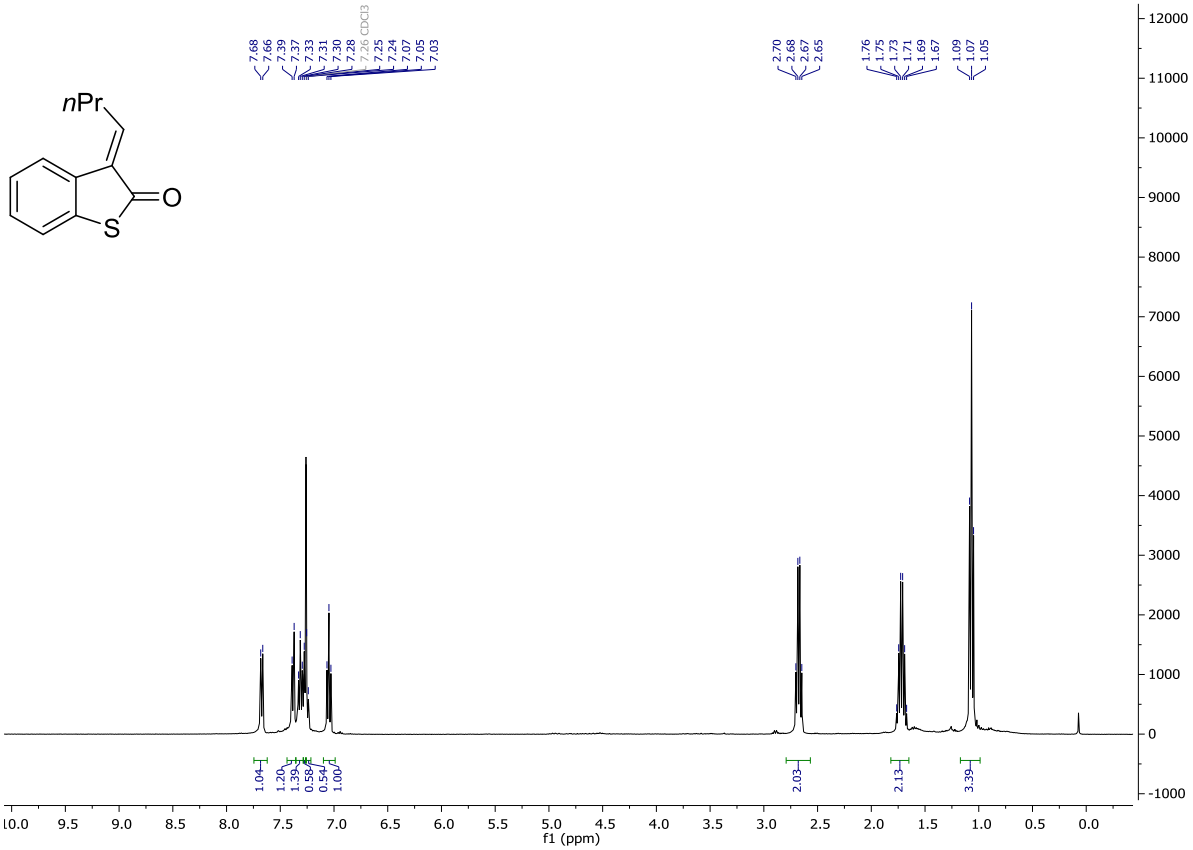


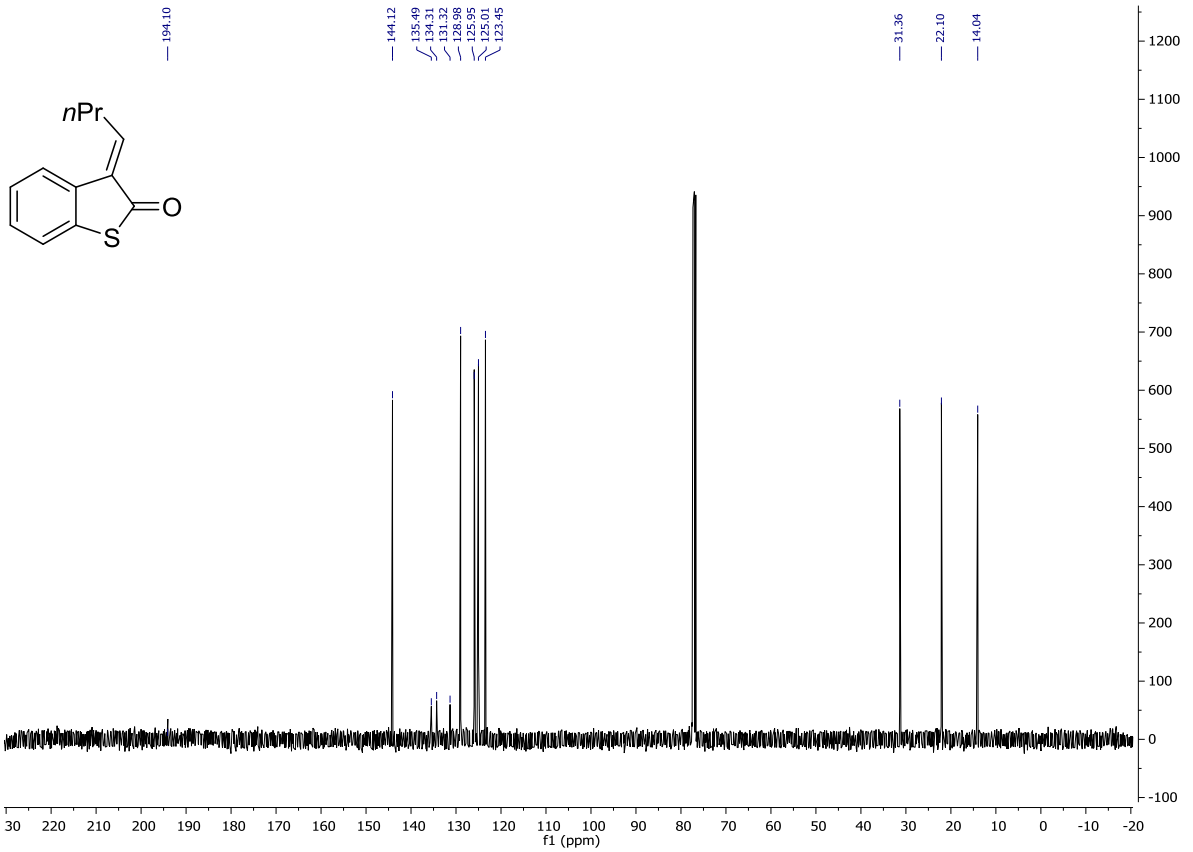
3-(Furan-3-ylmethylene)benzo[*b*]thiophen-2(3*H*)-one (1q)



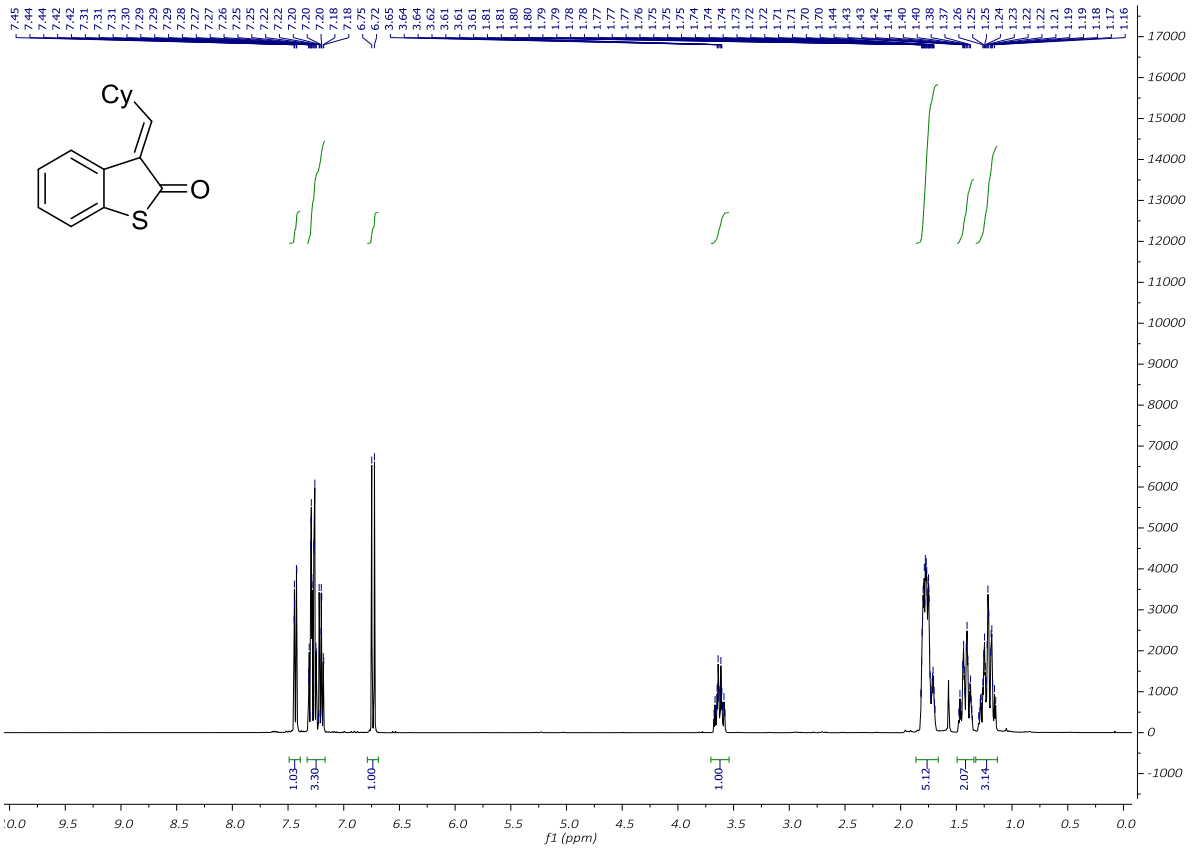


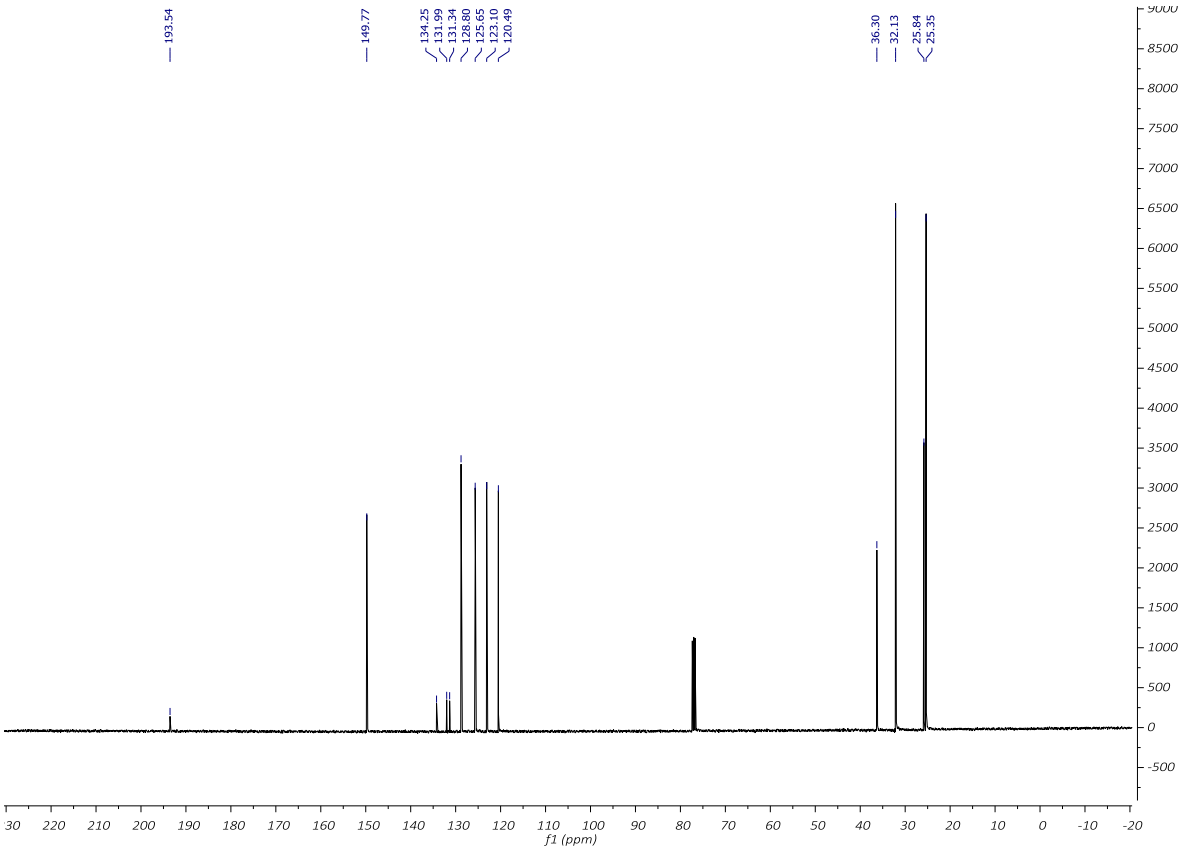
(*E*)-3-Butylidenebenzo[*b*]thiophen-2(3*H*)-one (1r)



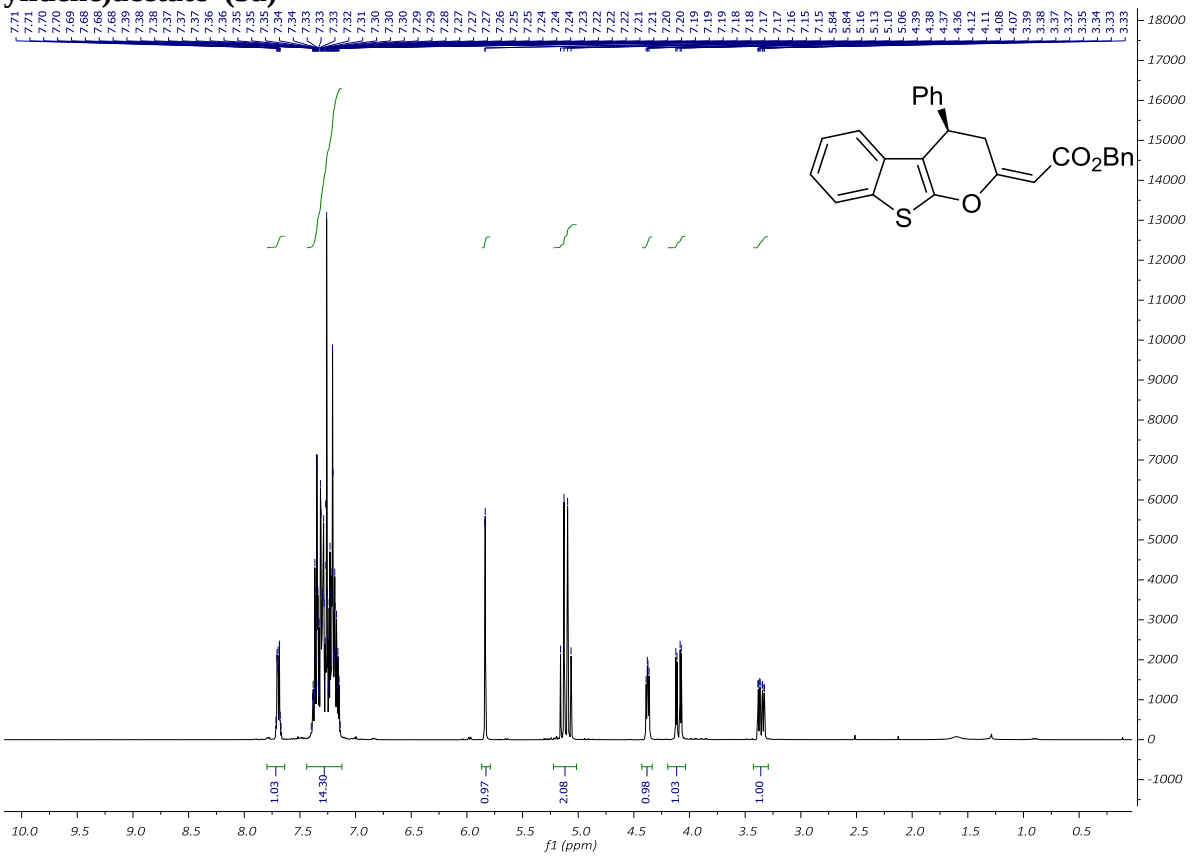


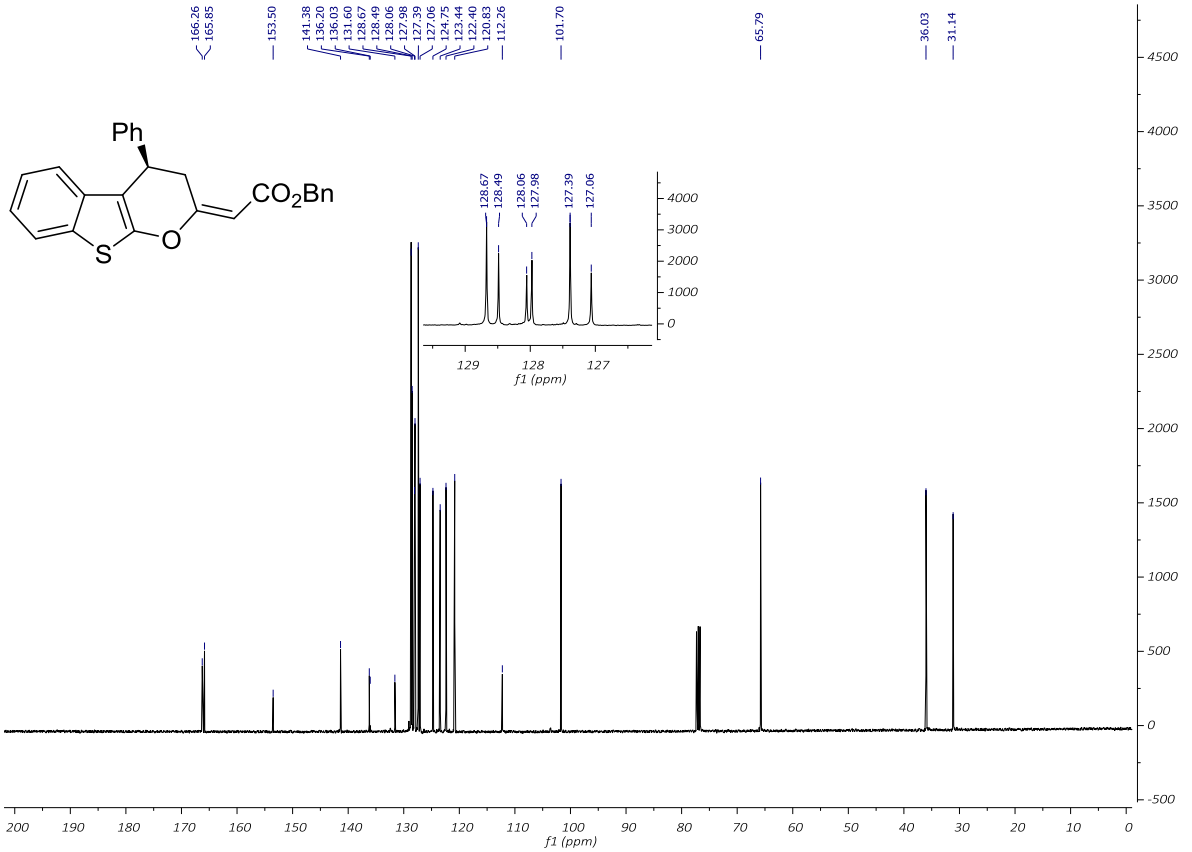
(*E*)-3-(cyclohexylmethylene)benzo[*b*]thiophen-2(3*H*)-one (1s)



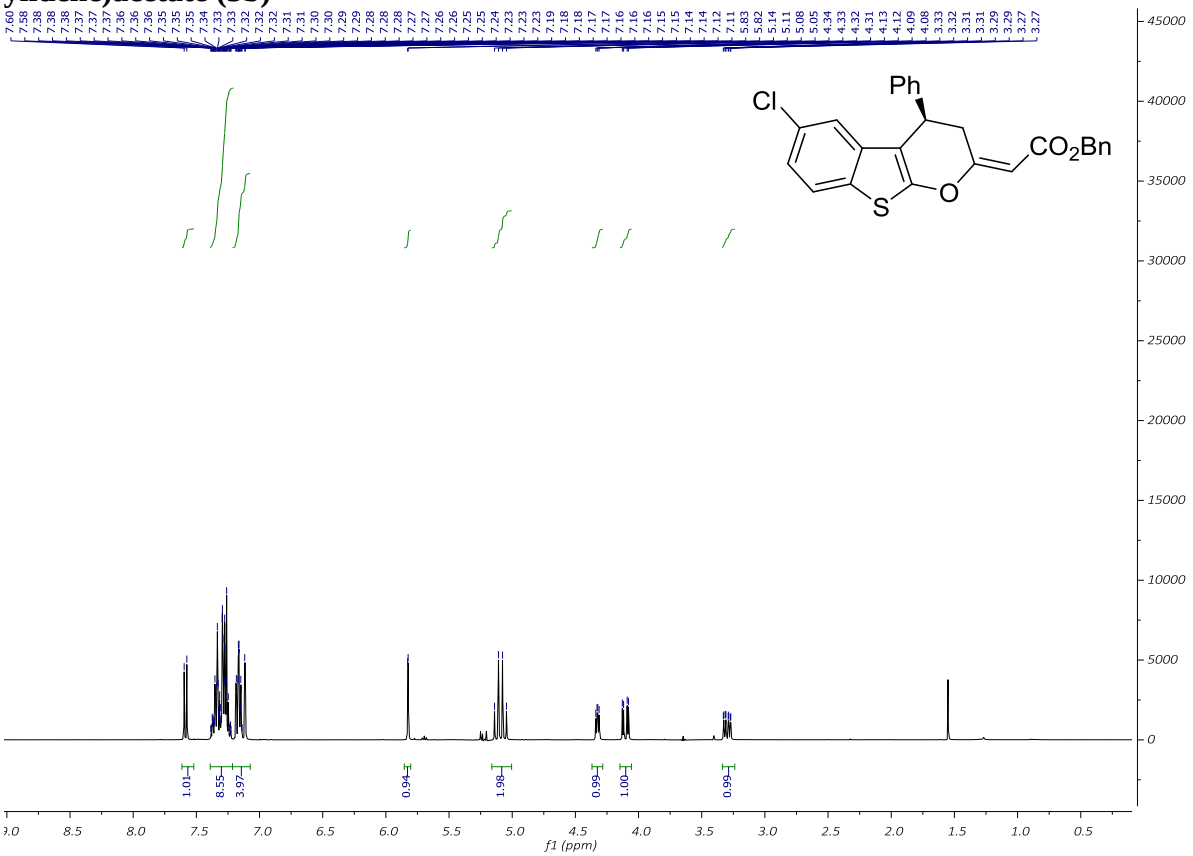


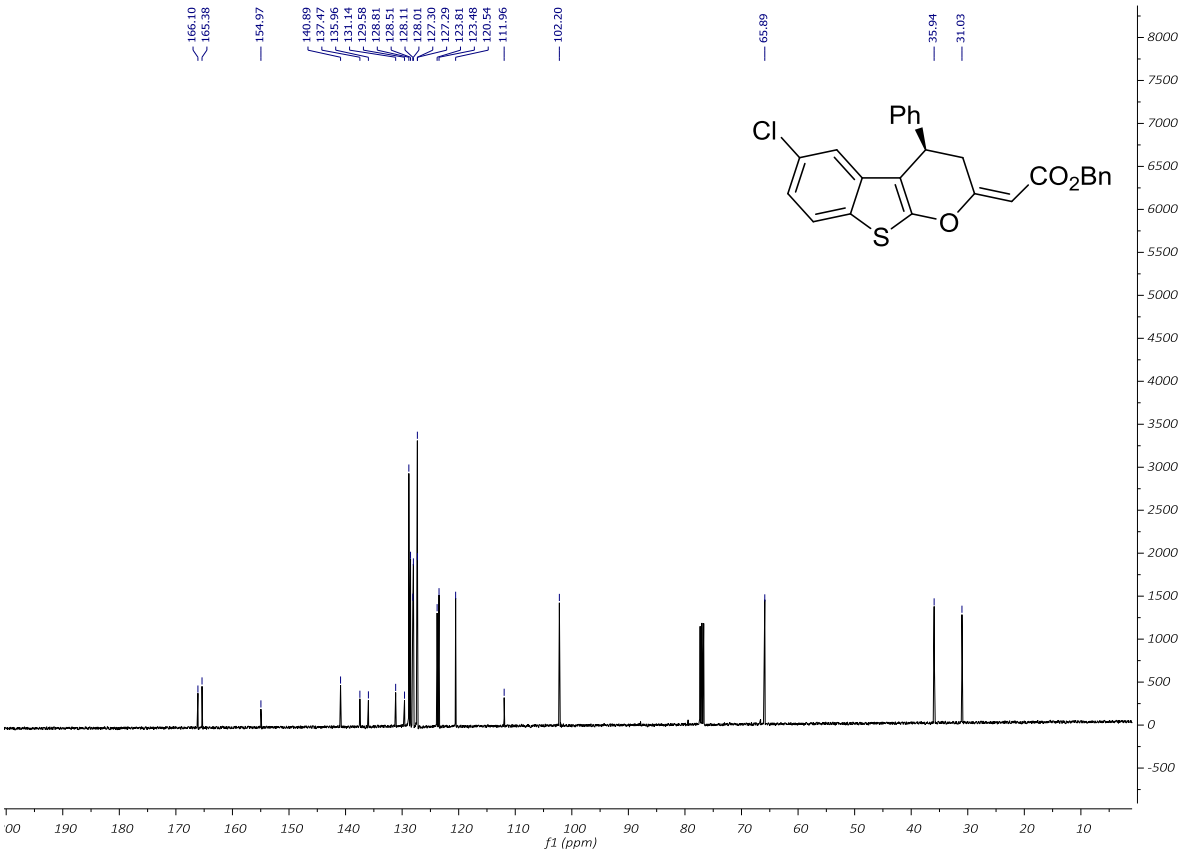
Benzyl (*R*,*E*)-2-(4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3a)



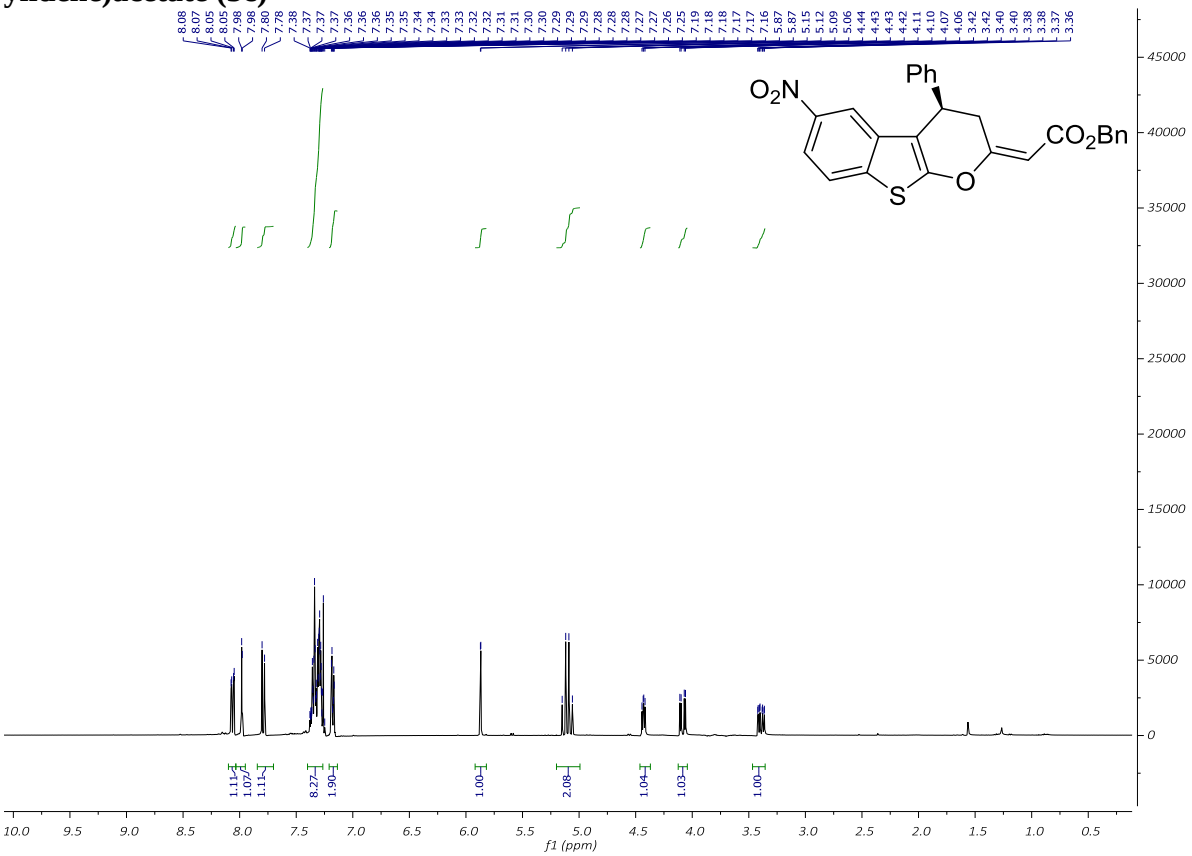


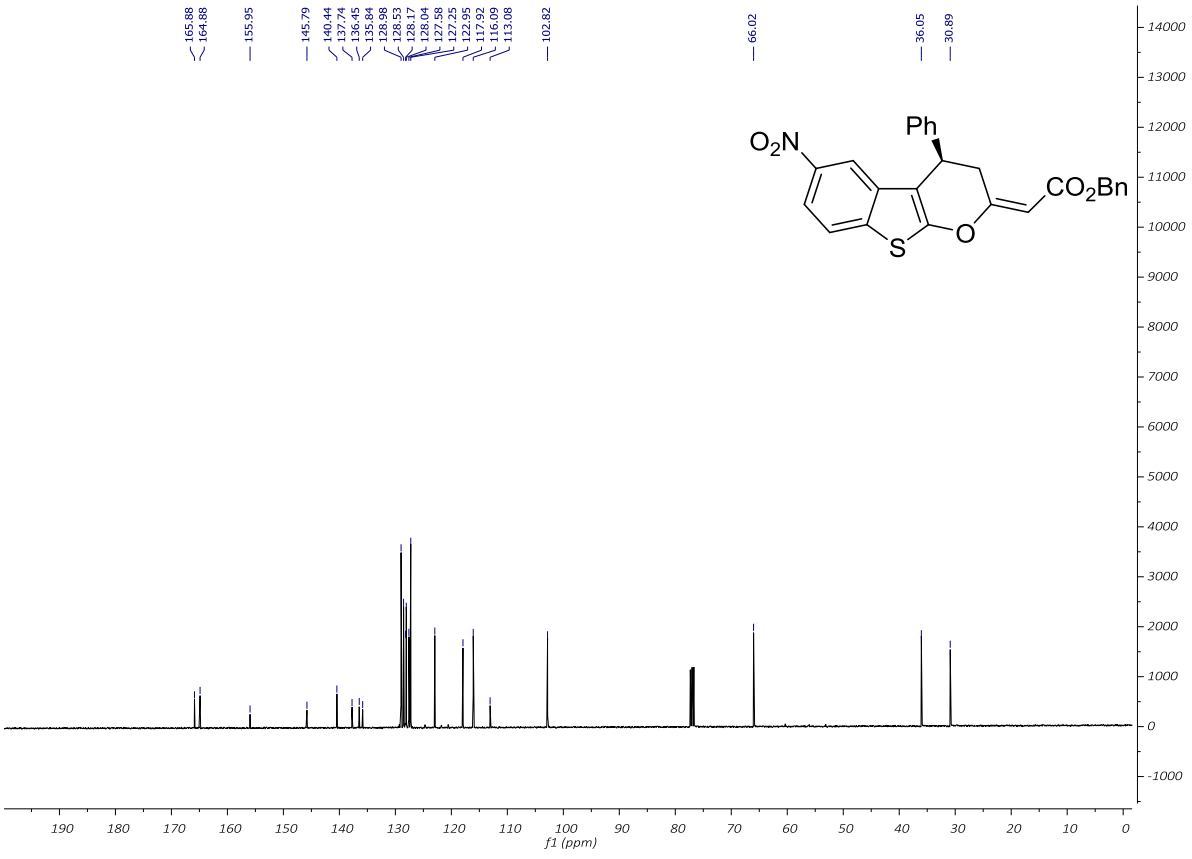
Benzyl (*R*,*E*)-2-(5-chloro-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3b)



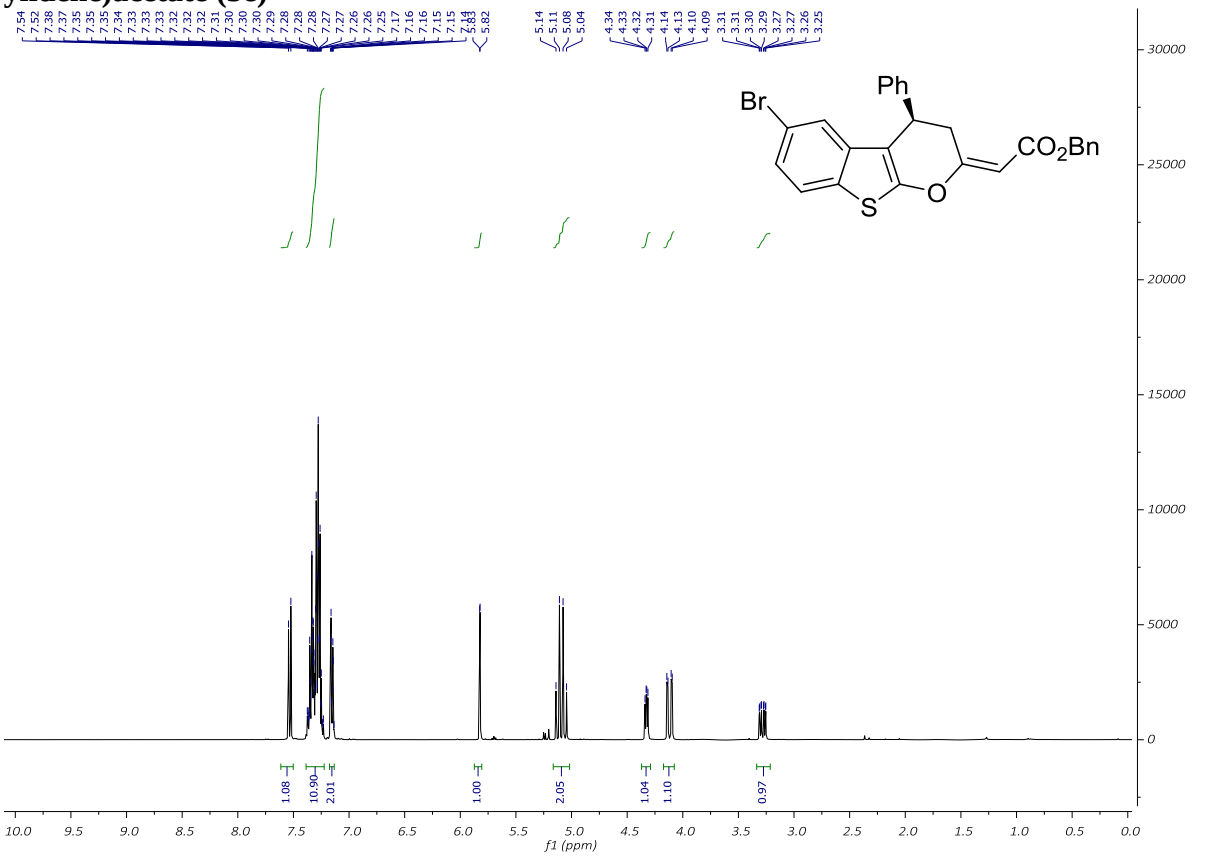


Benzyl (*R*,*E*)-2-(5-nitro-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3c)





Benzyl (*R*,*E*)-2-(6-bromo-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3e)



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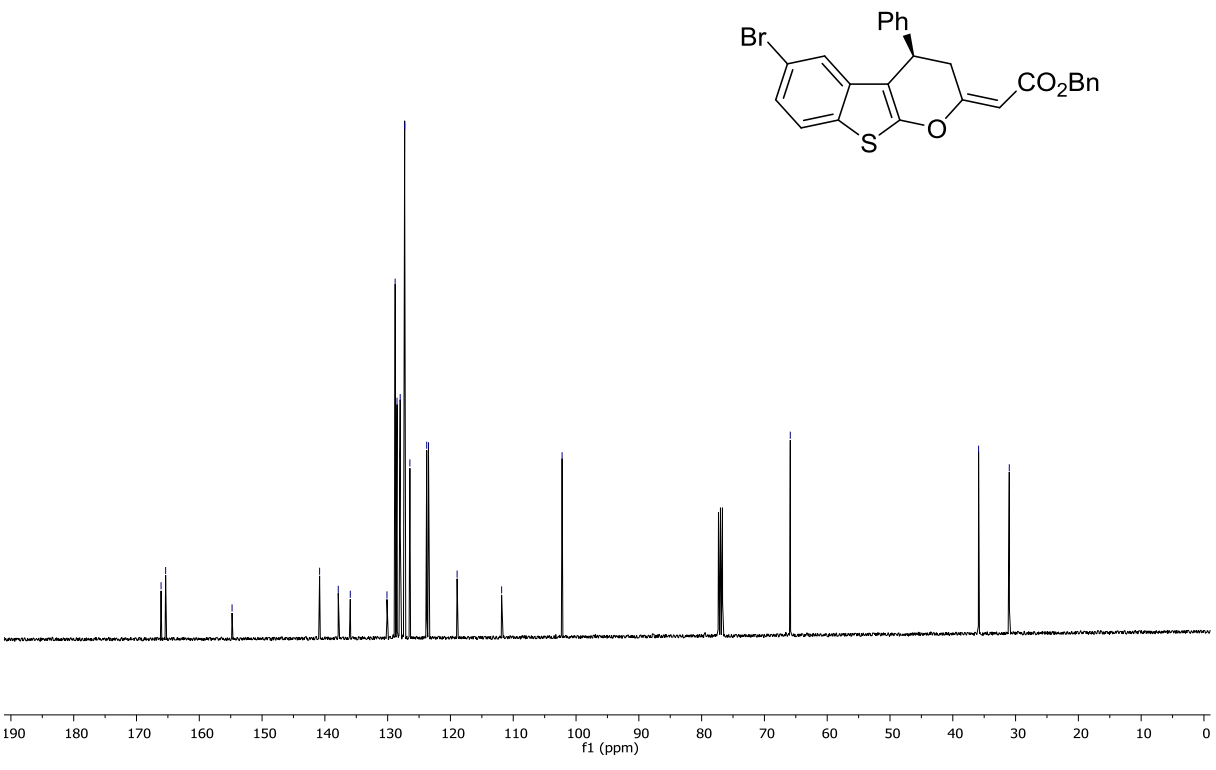
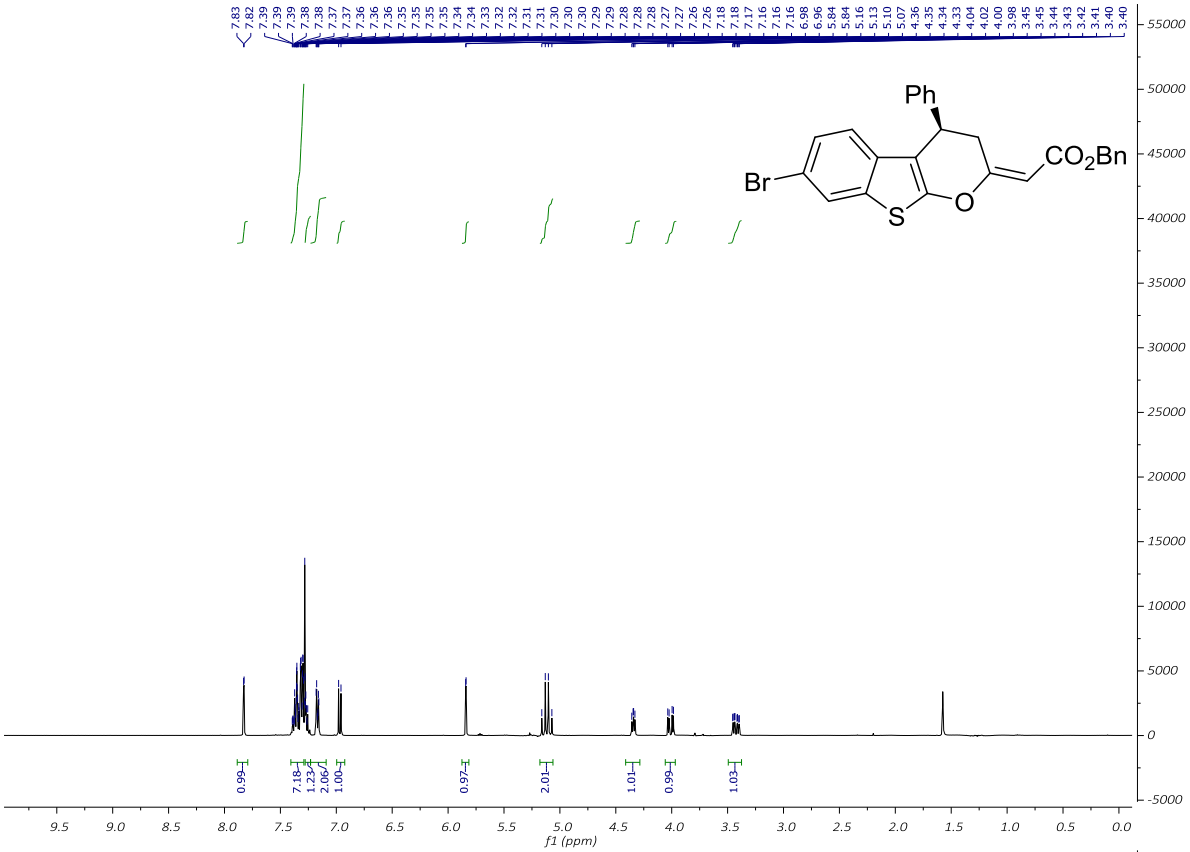
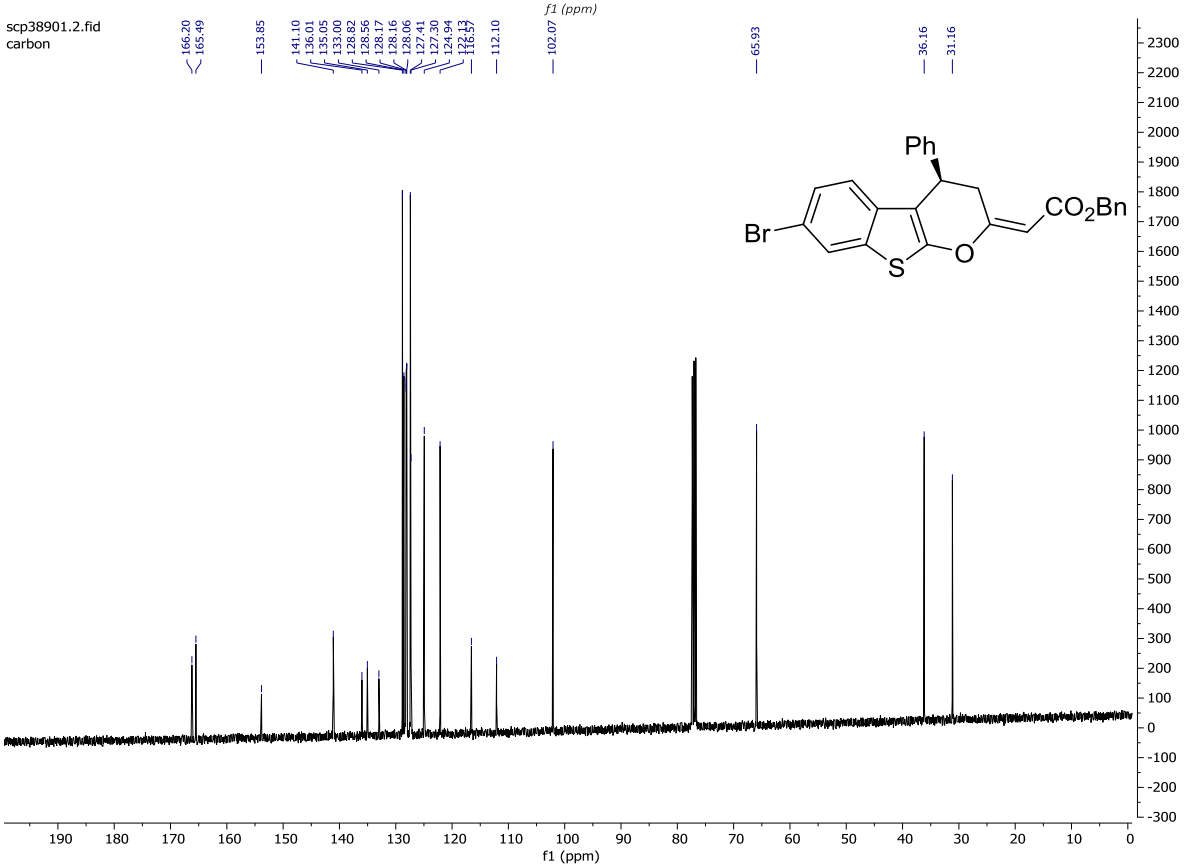
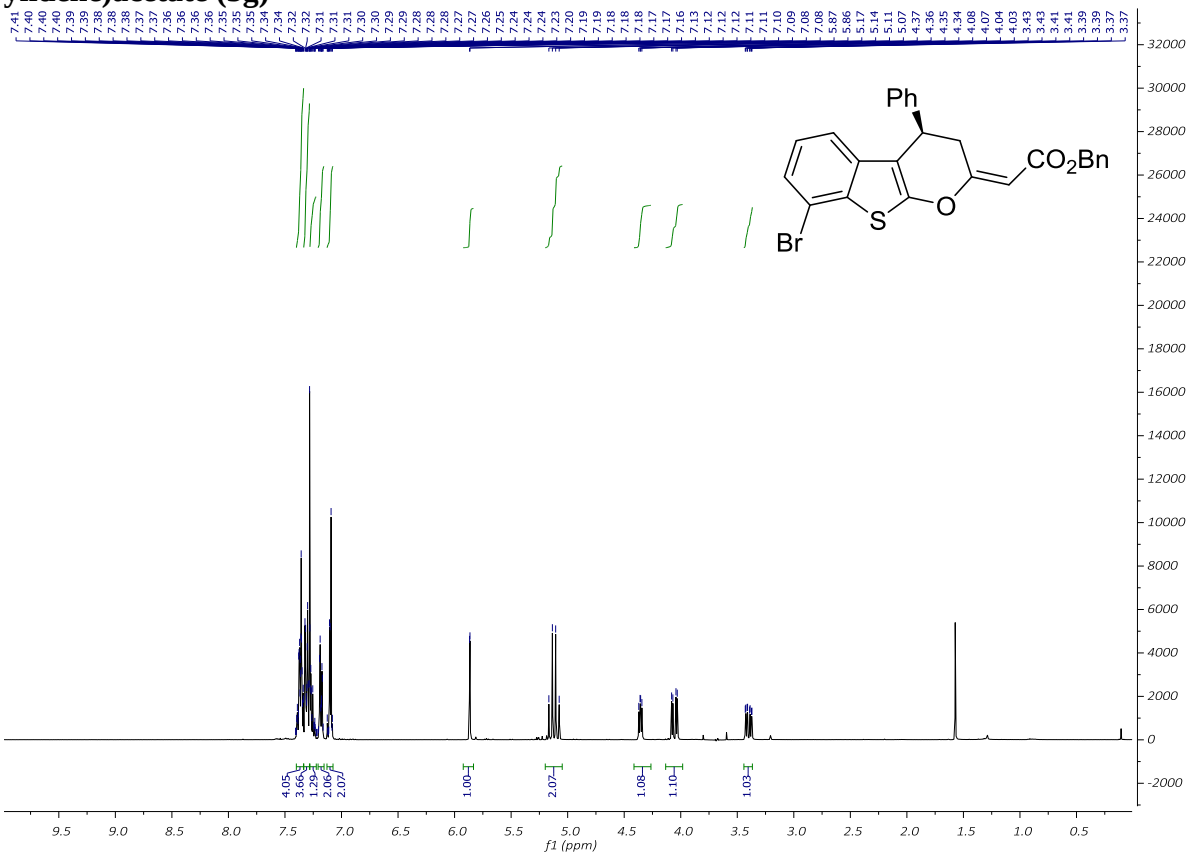


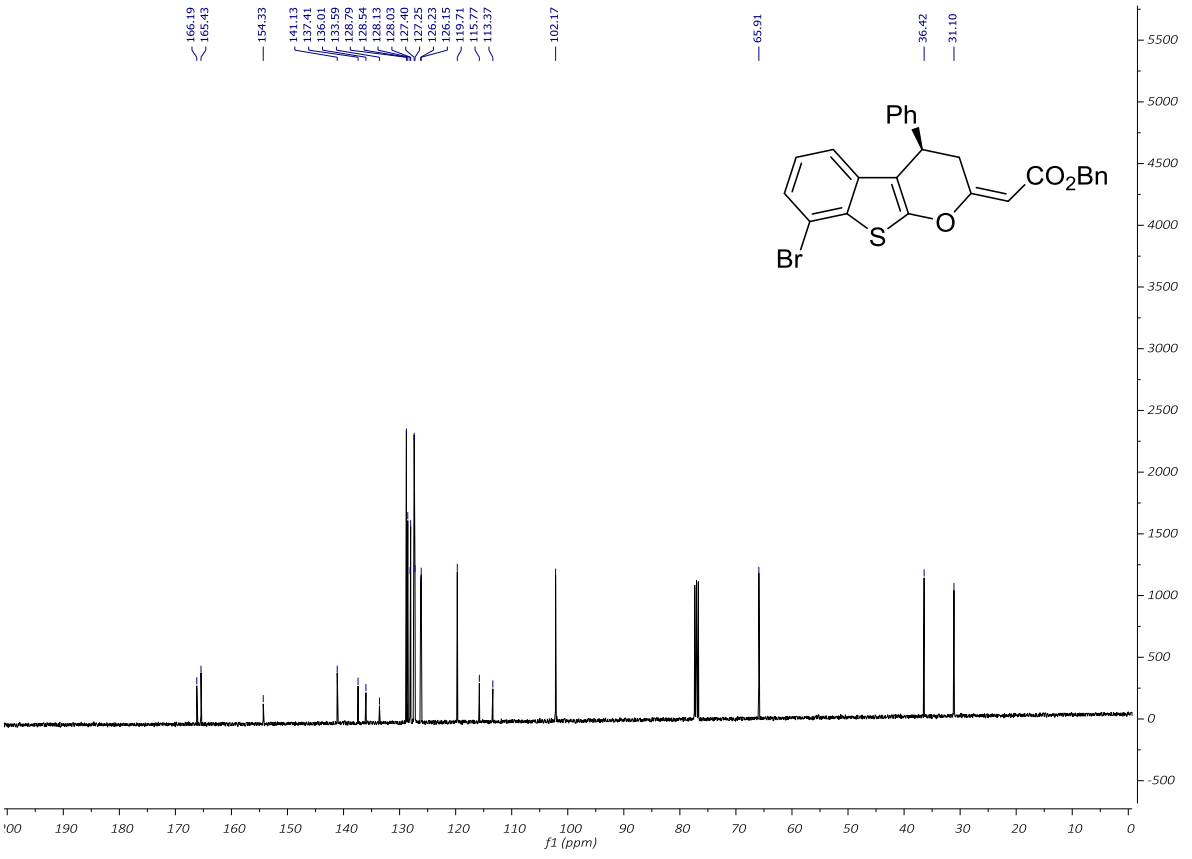
Benzyl (*R*,*E*)-2-(7-bromo-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3f)



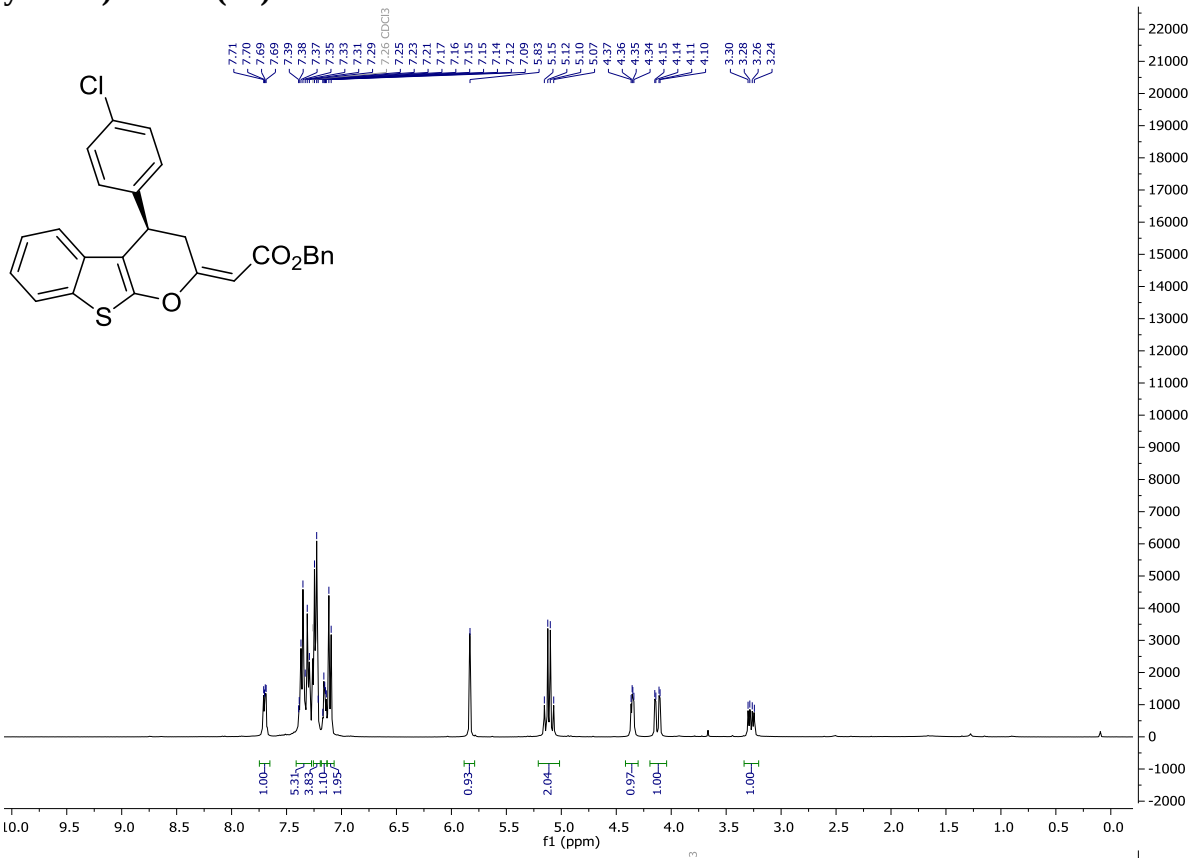


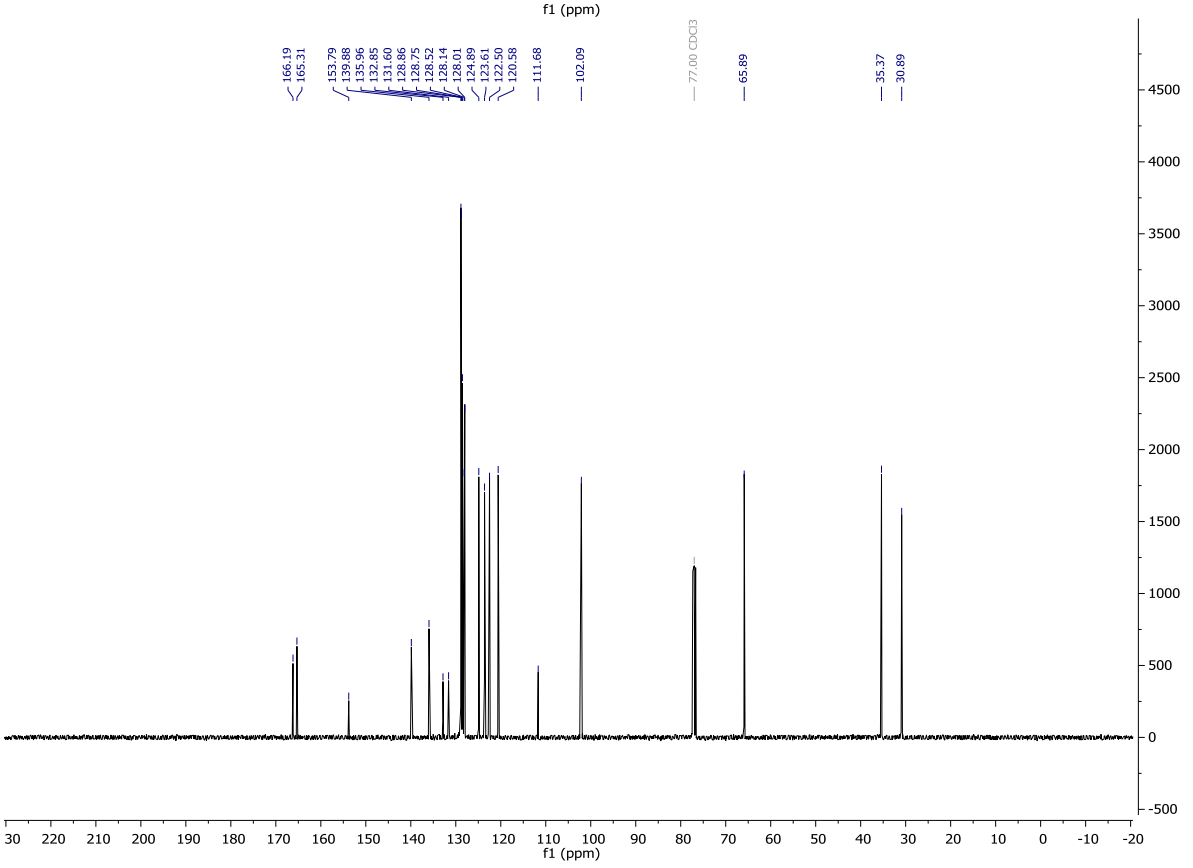
Benzyl (*R*,*E*)-2-(8-bromo-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3g)



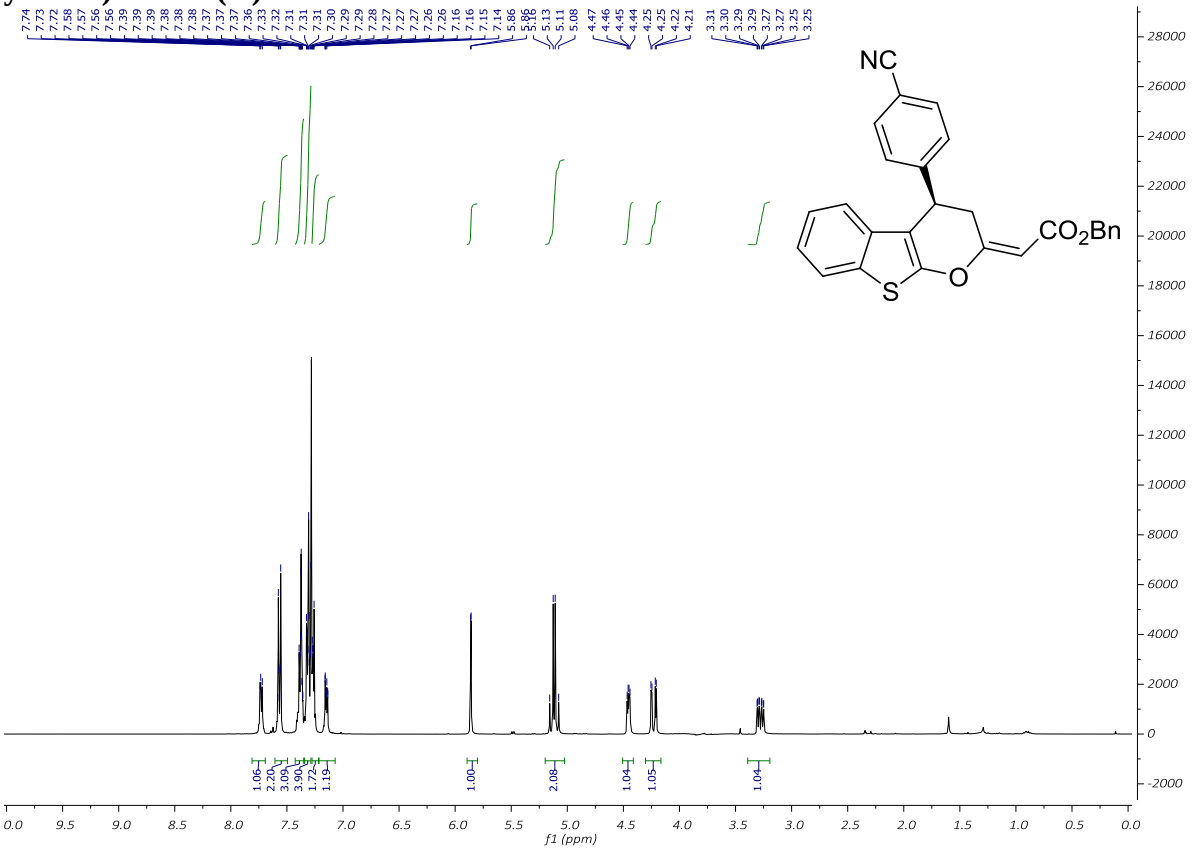


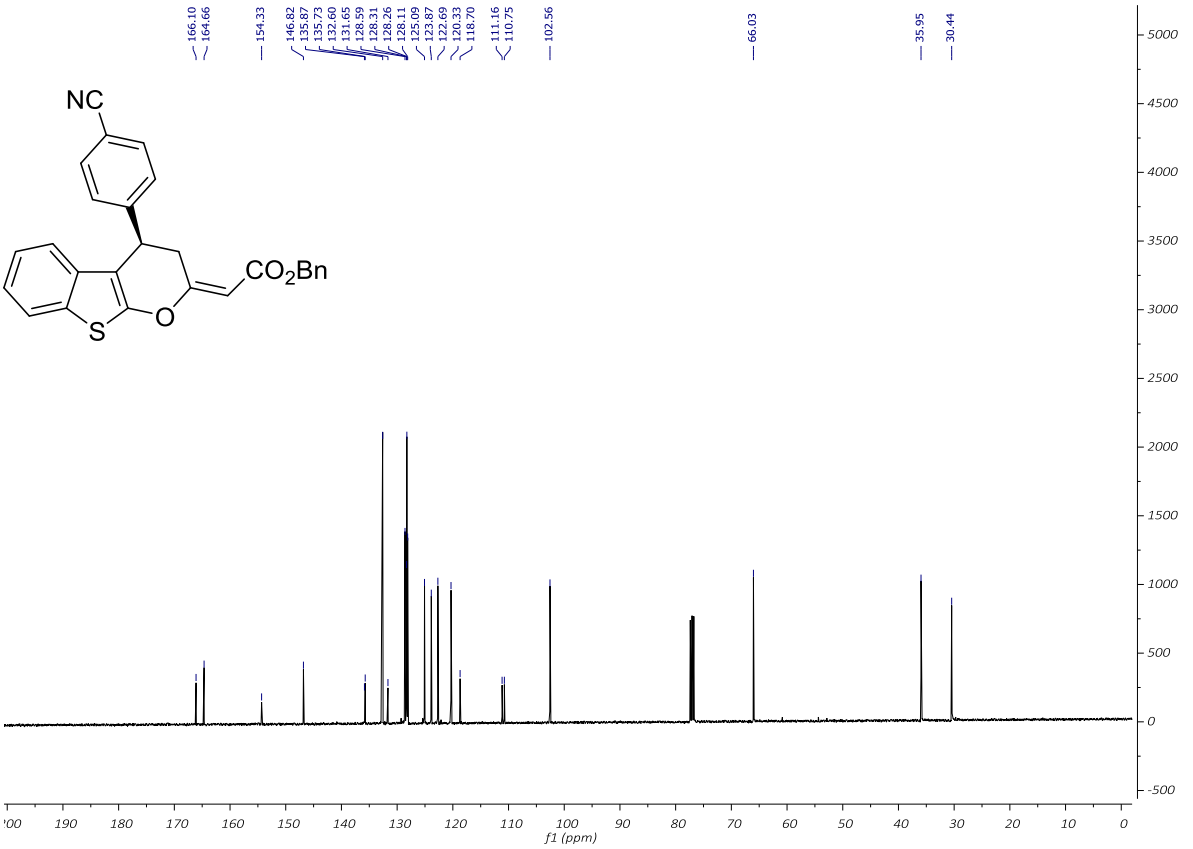
Benzyl (*R*,*E*)-2-(4-(4-chlorophenyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3h)



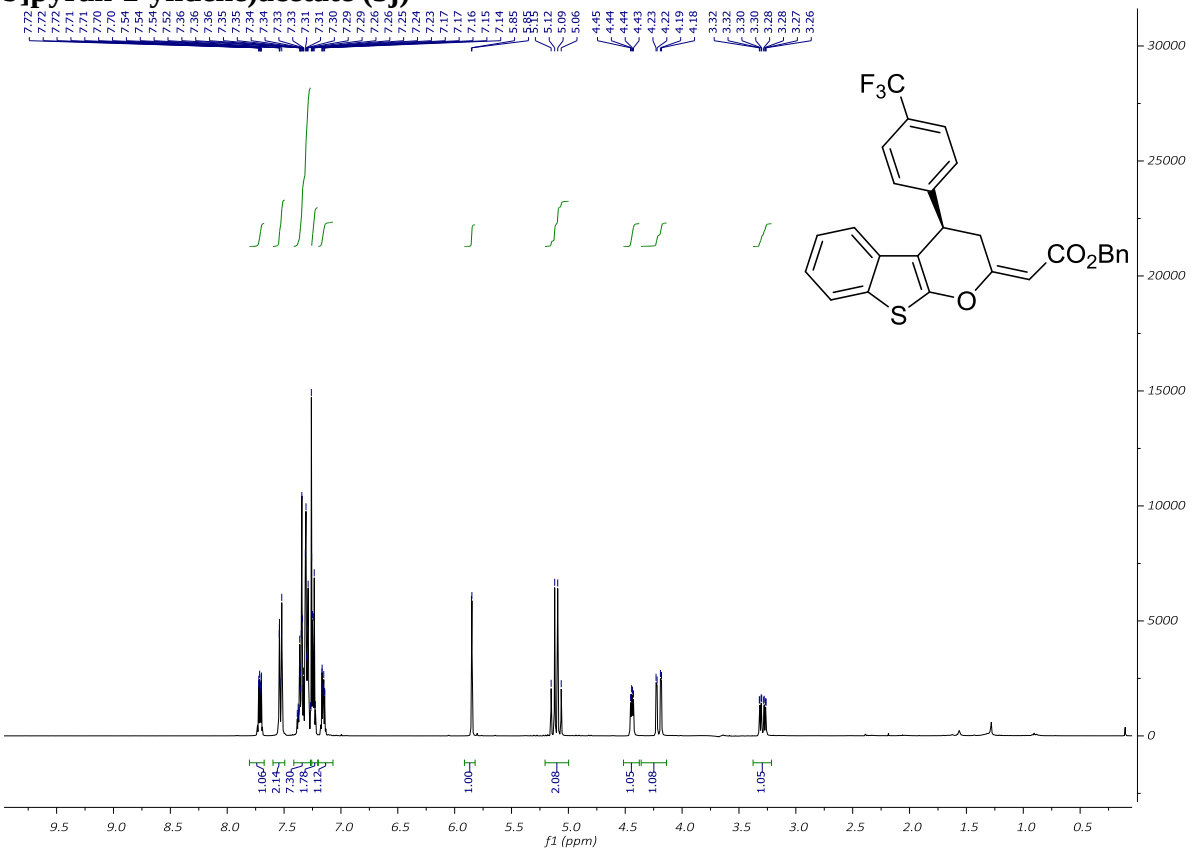


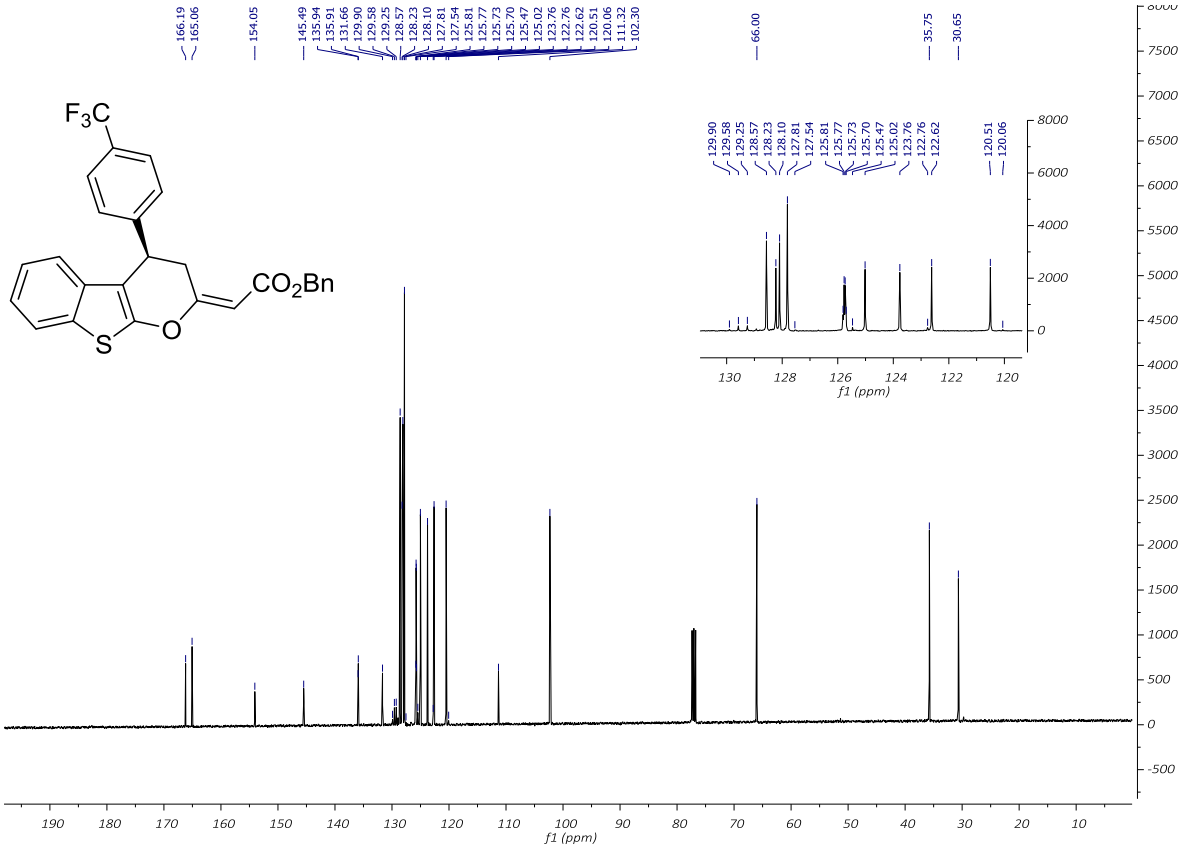
Benzyl (*R*,*E*)-2-(4-(4-cyanophenyl)-3,4-dihydro-2H-benzo[4,5]thieno[2,3-b]pyran-2-ylidene)acetate (3i)





Benzyl (*R*,*E*)-2-(4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3j)






F3C
CO2Bn
S
O
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25000
24000
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17000
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11000
10000
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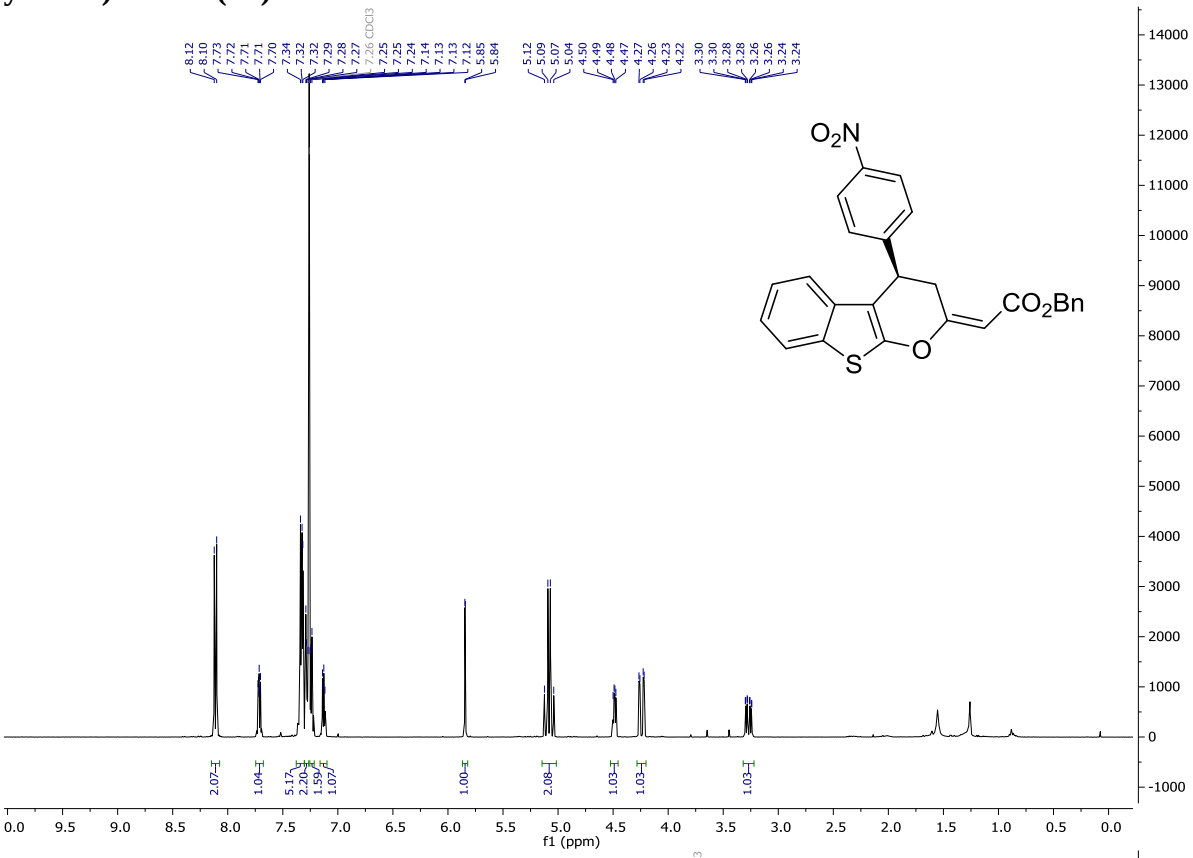
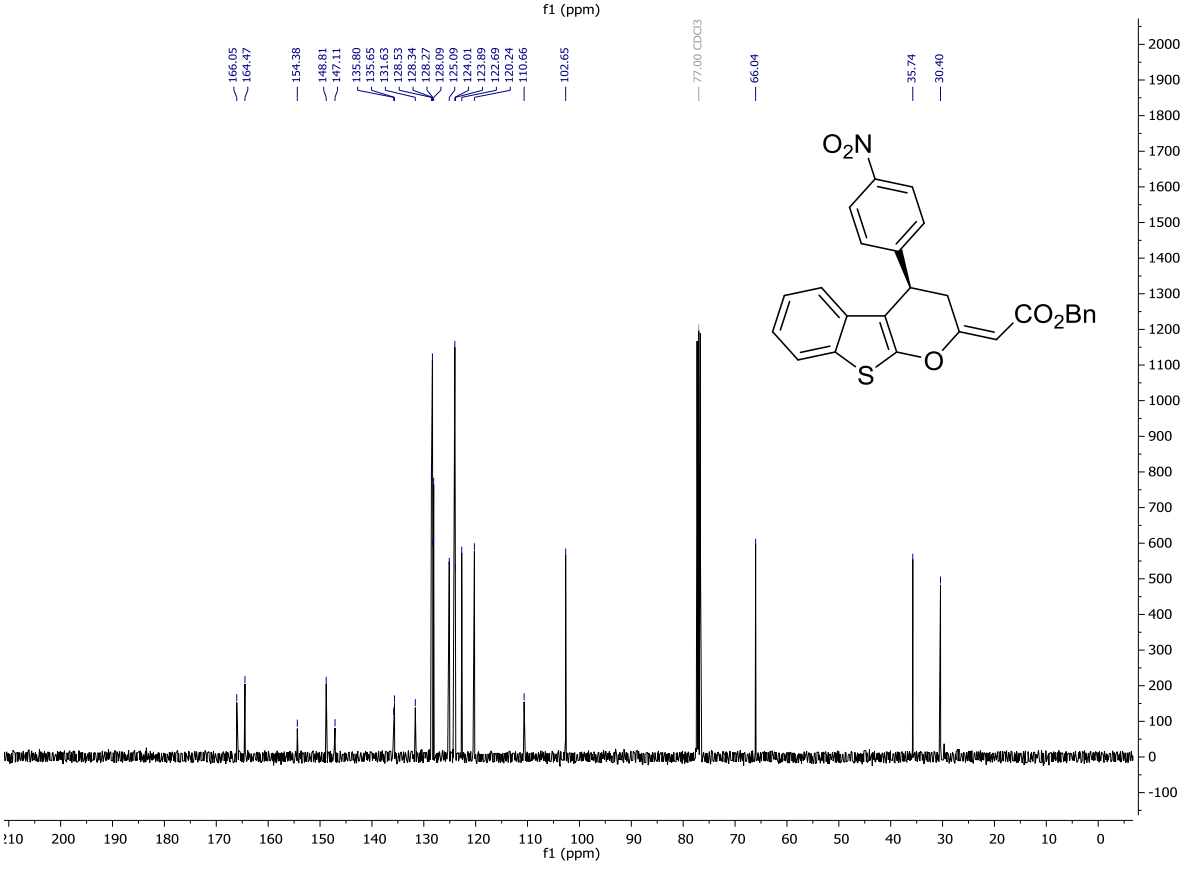
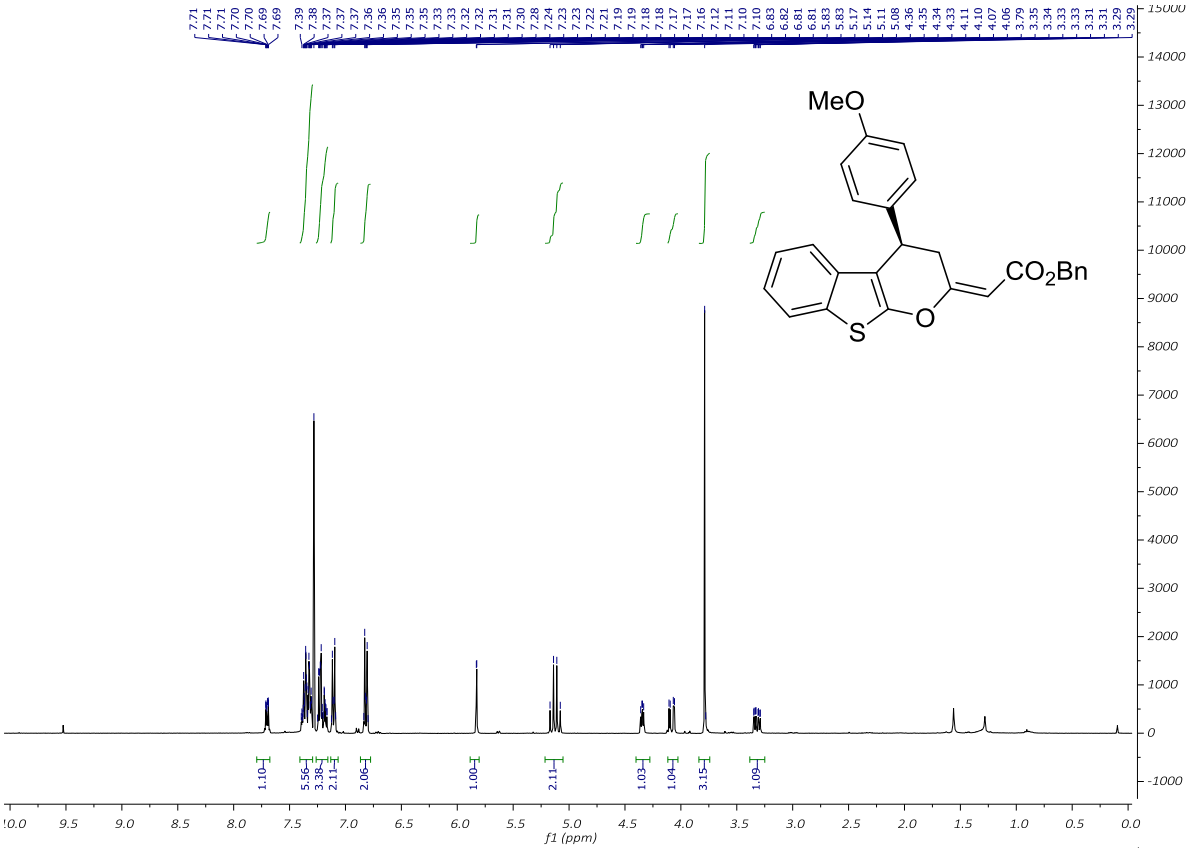
0
-1000
-2000
-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

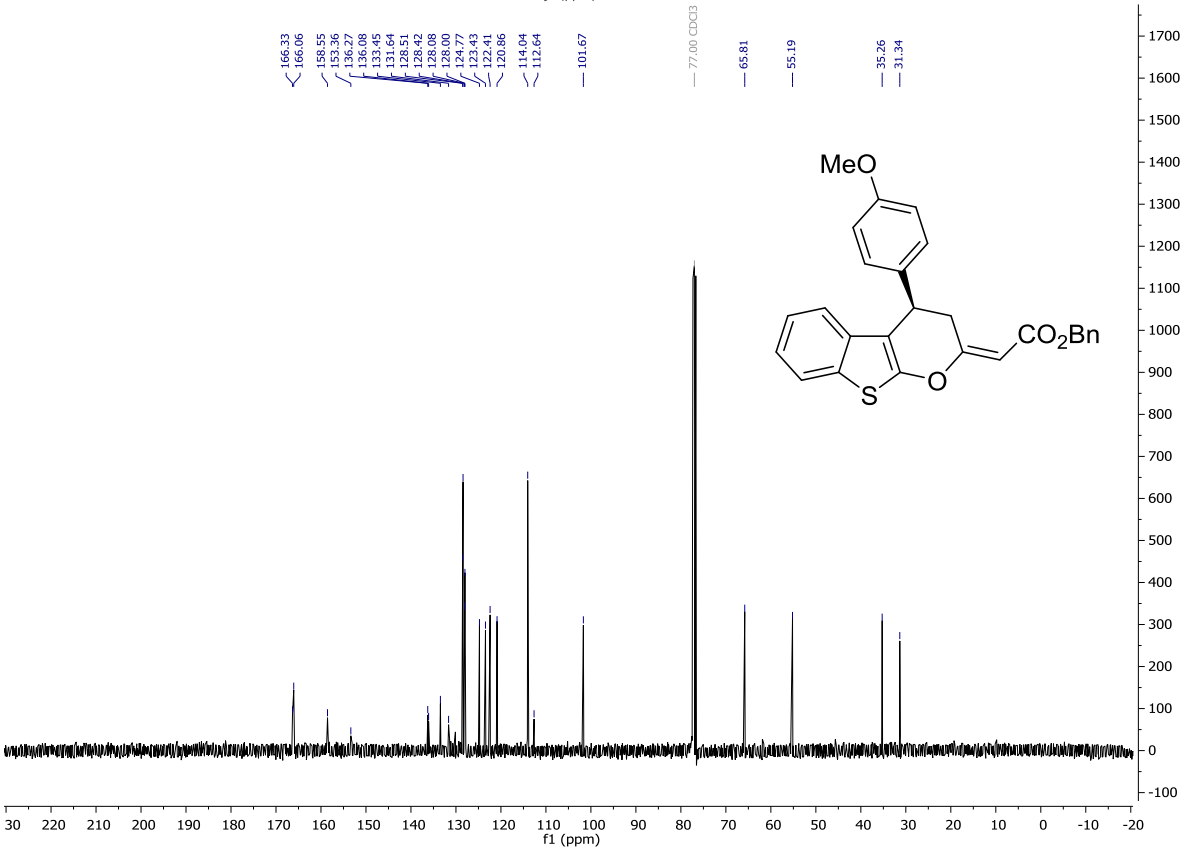
Benzyl (*R*,*E*)-2-(4-(4-nitrophenyl)-3,4-dihydro-2H-benzo[4,5]thieno[2,3-b]pyran-2-ylidene)acetate (3k)



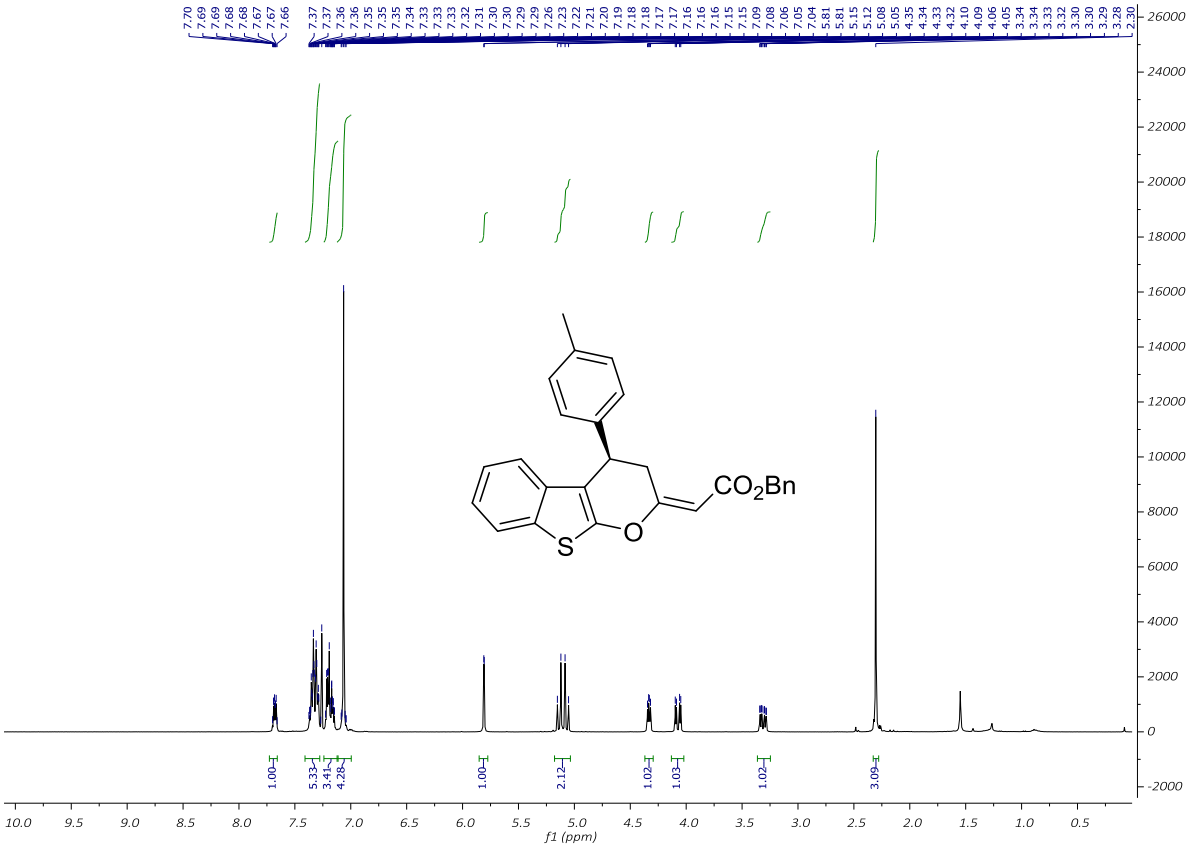


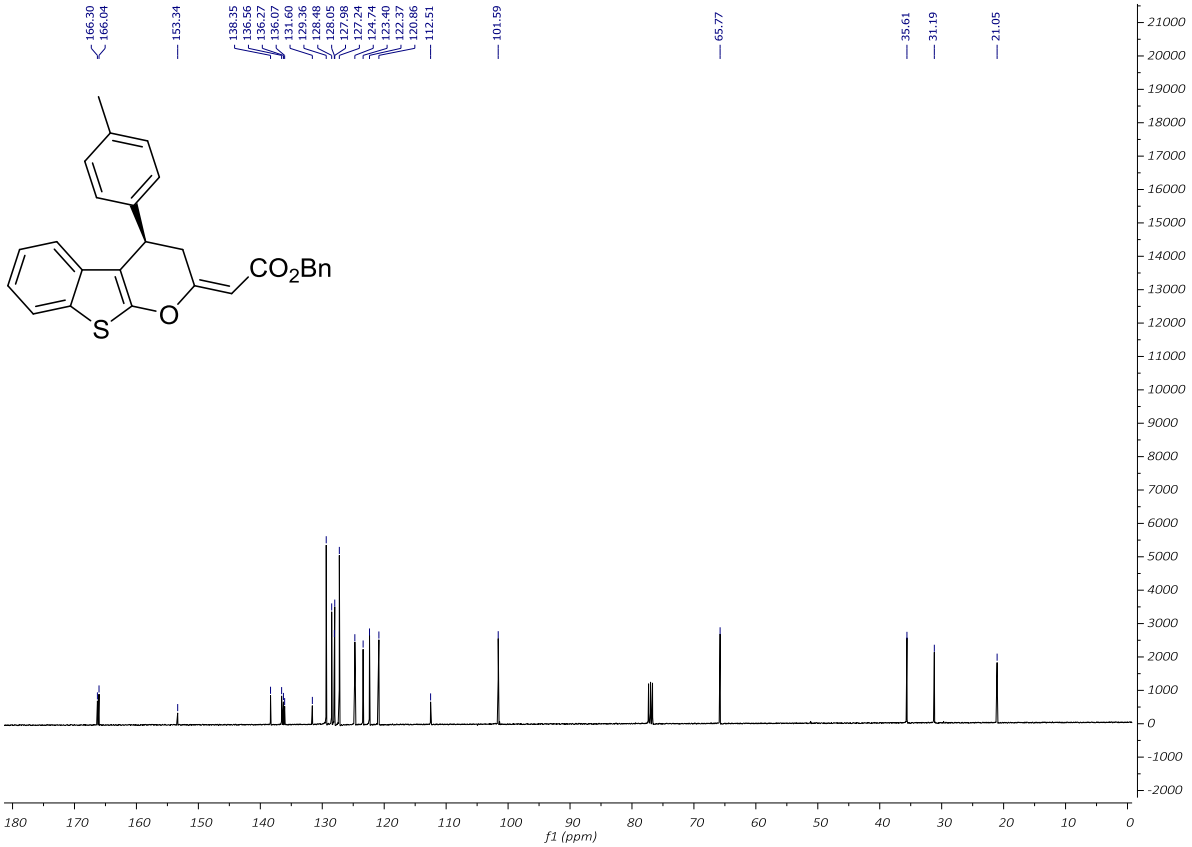
Benzyl (*R*,*E*)-2-(4-(4-methoxyphenyl)-3,4-dihydro-2H-benzo[4,5]thieno[2,3-b]pyran-2-ylidene)acetate (3l)



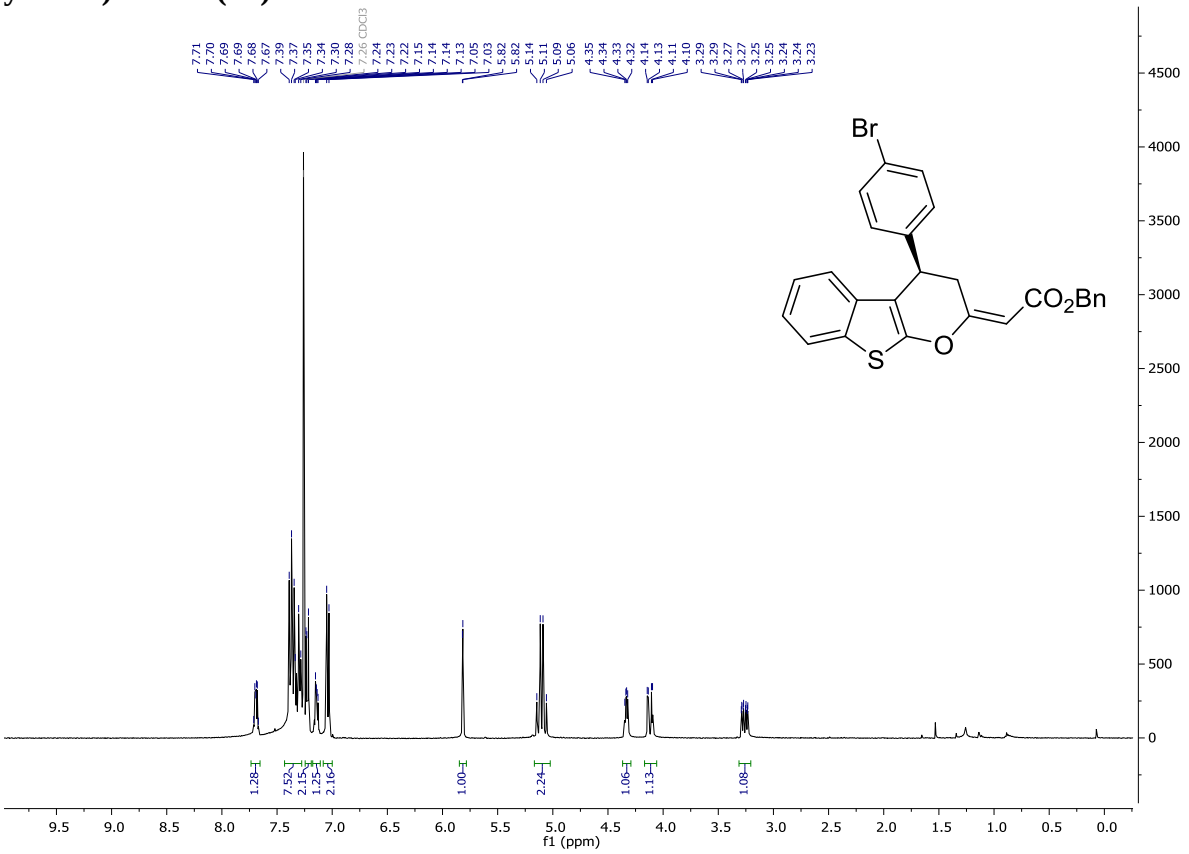


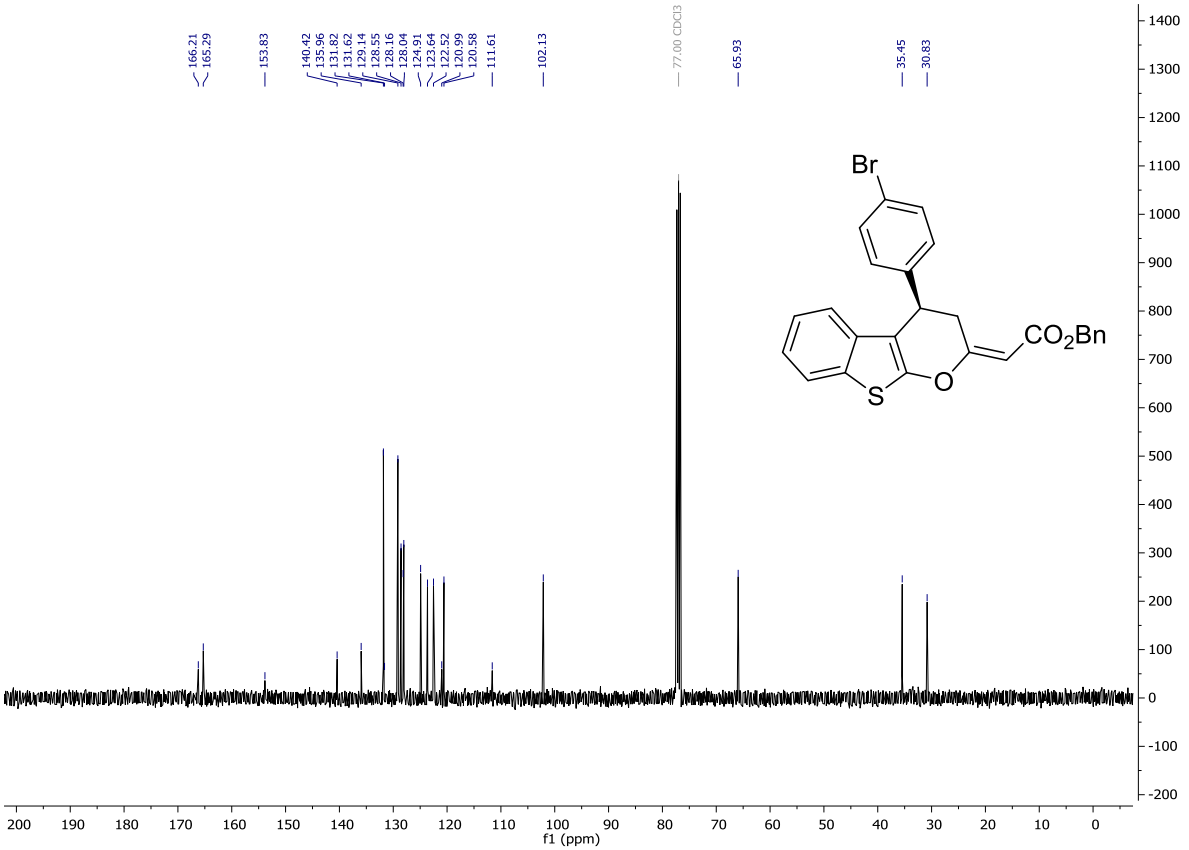
Benzyl (*R*,*E*)-2-(4-(*p*-tolyl)-3,4-dihydro-2H-benzo[4,5]thieno[2,3-b]pyran-2-ylidene)acetate (3m)



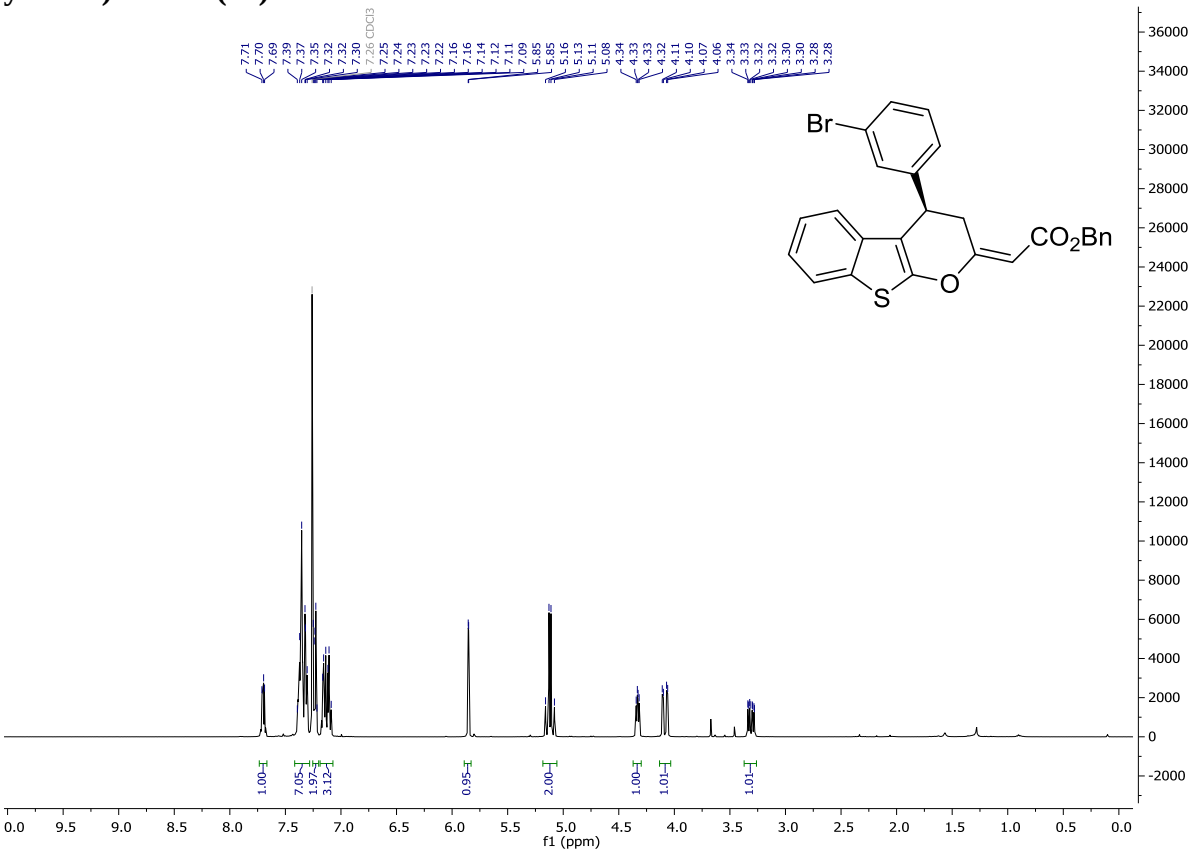


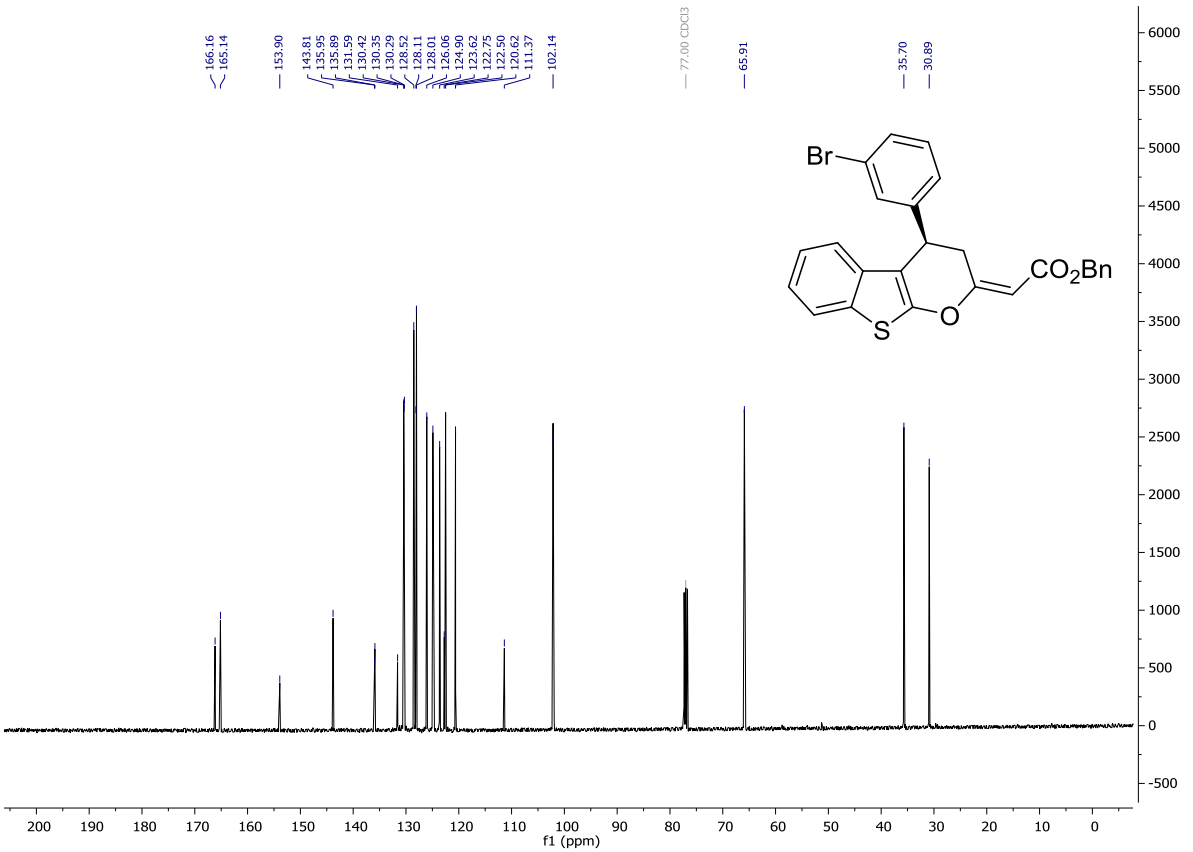
Benzyl (*R*,*E*)-2-(4-(4-bromophenyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3n)



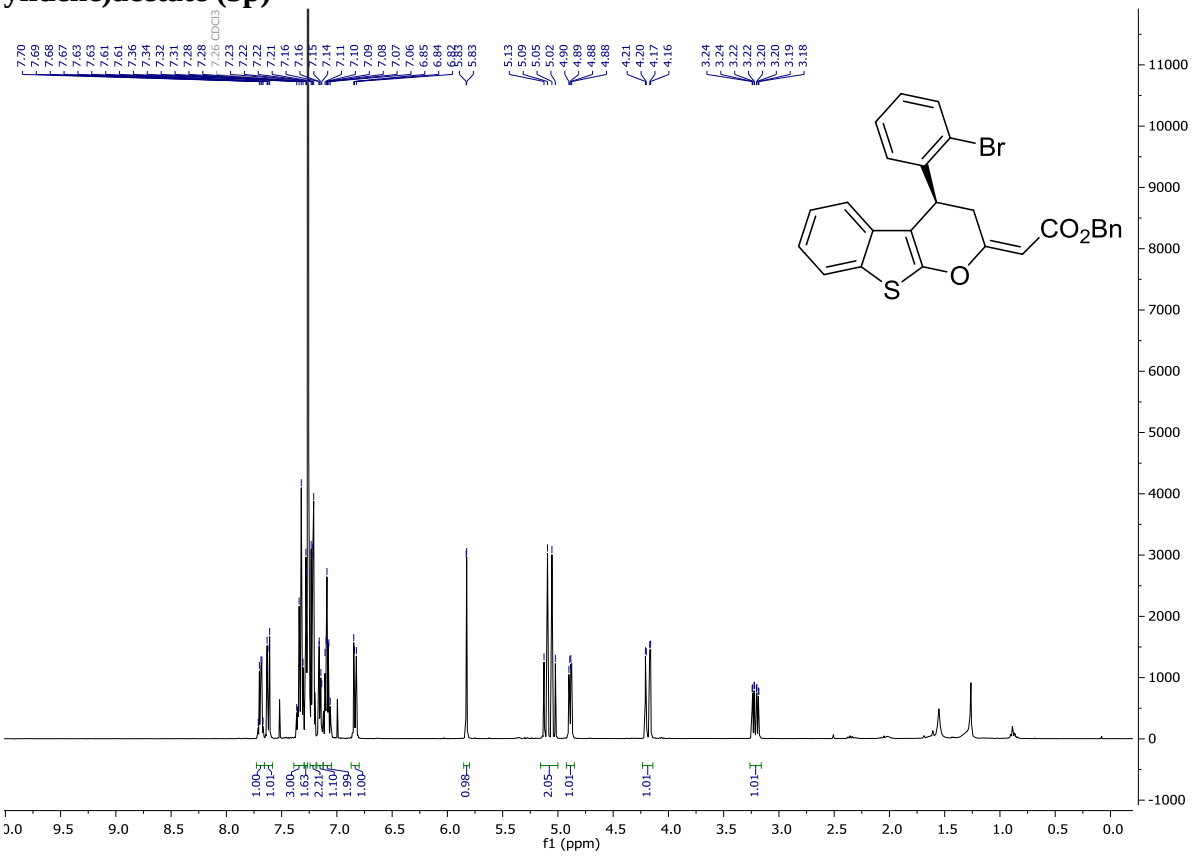


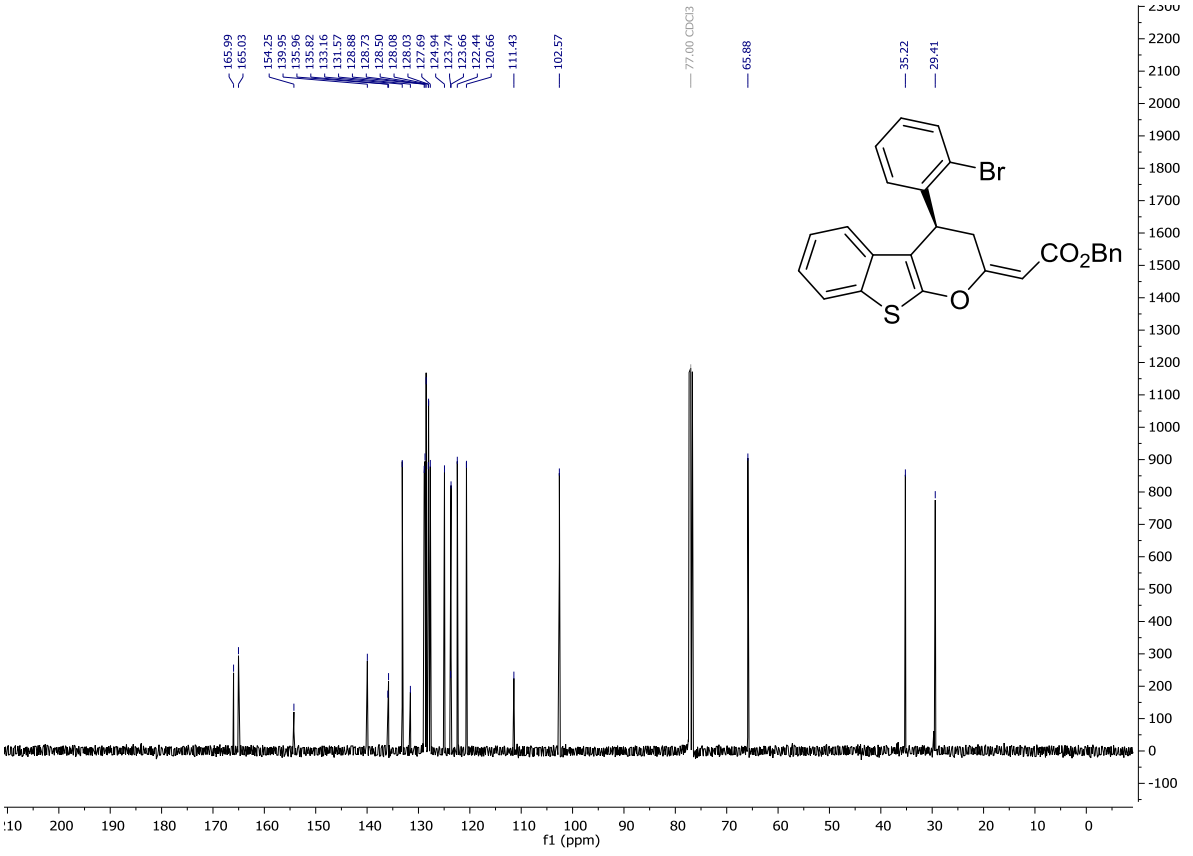
Benzyl (*R*,*E*)-2-(4-(3-bromophenyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3o)



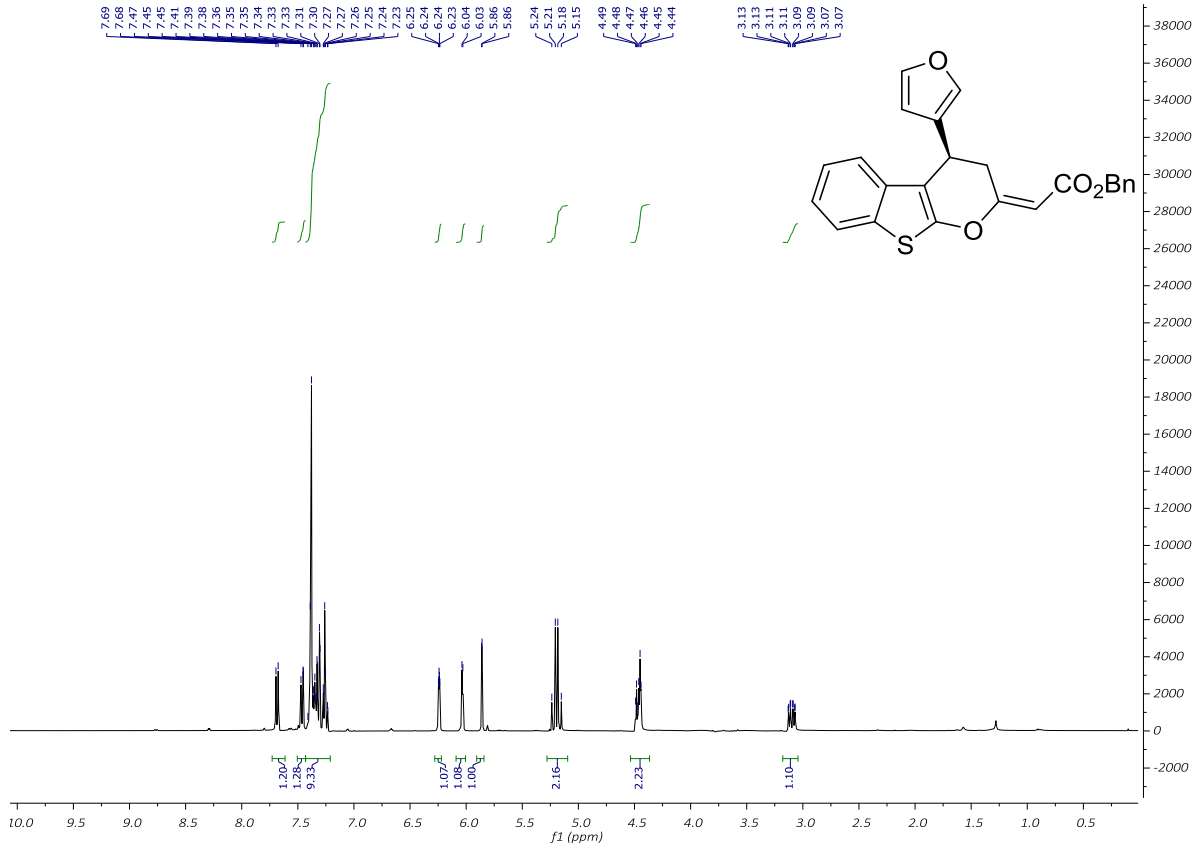


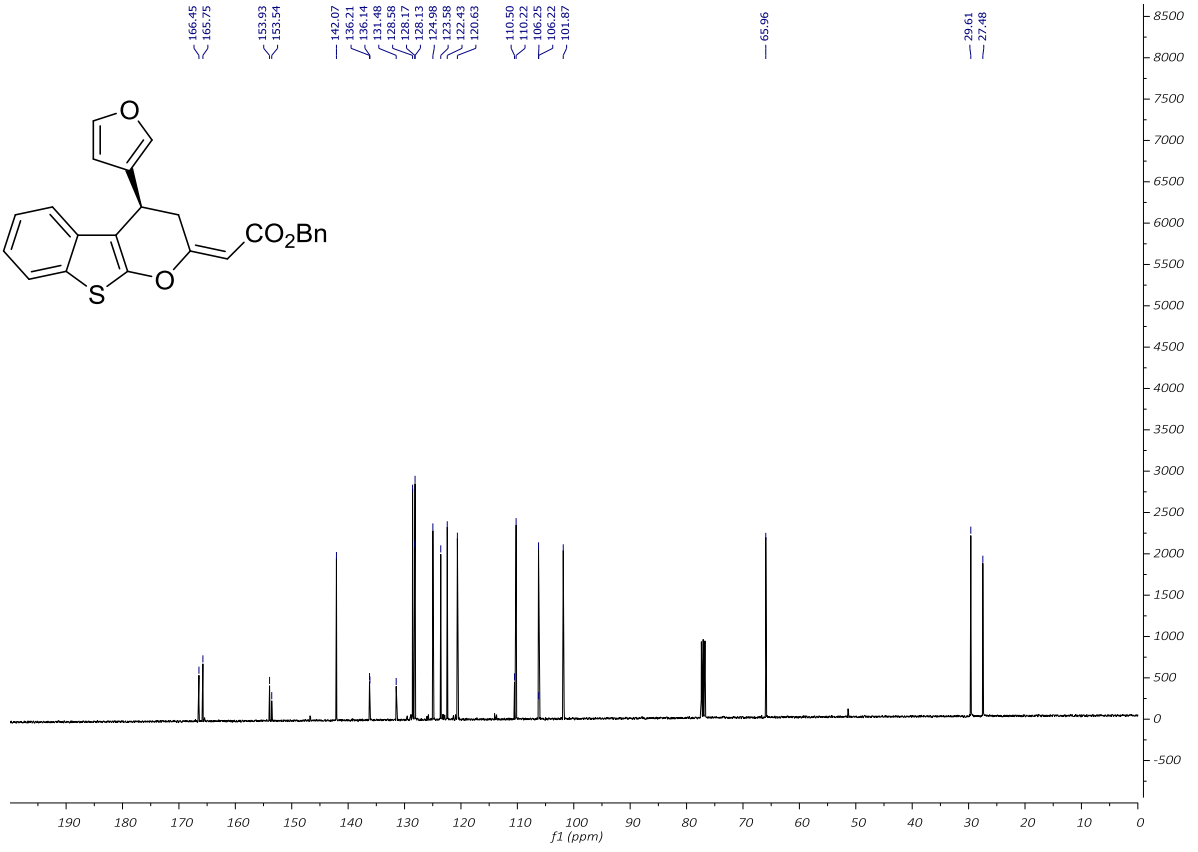
Benzyl (*R*,*E*)-2-(4-(2-bromophenyl)-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3p)



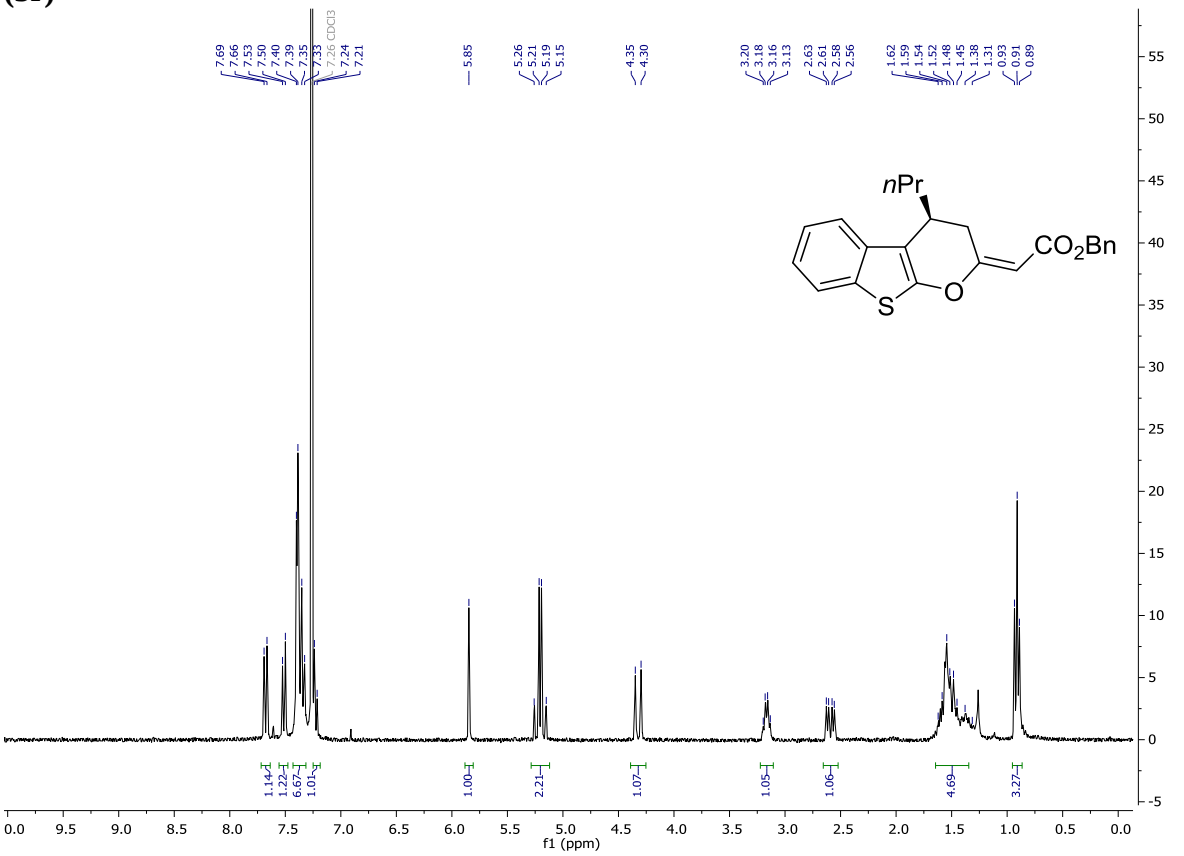


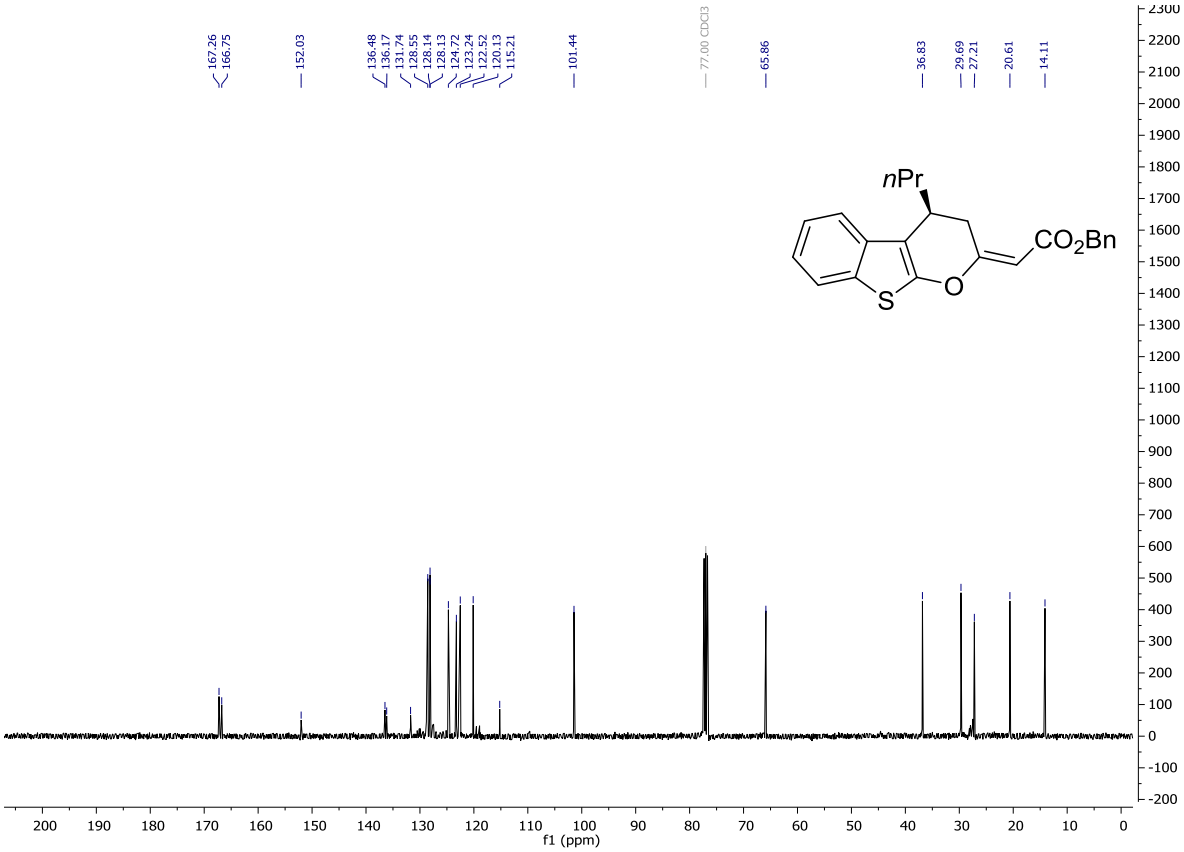
Benzyl (*R*,*E*)-2-(4-(furan-3-yl)-3,4-dihydro-2H-benzo[4,5]thieno[2,3-b]pyran-2-ylidene)acetate (3q)



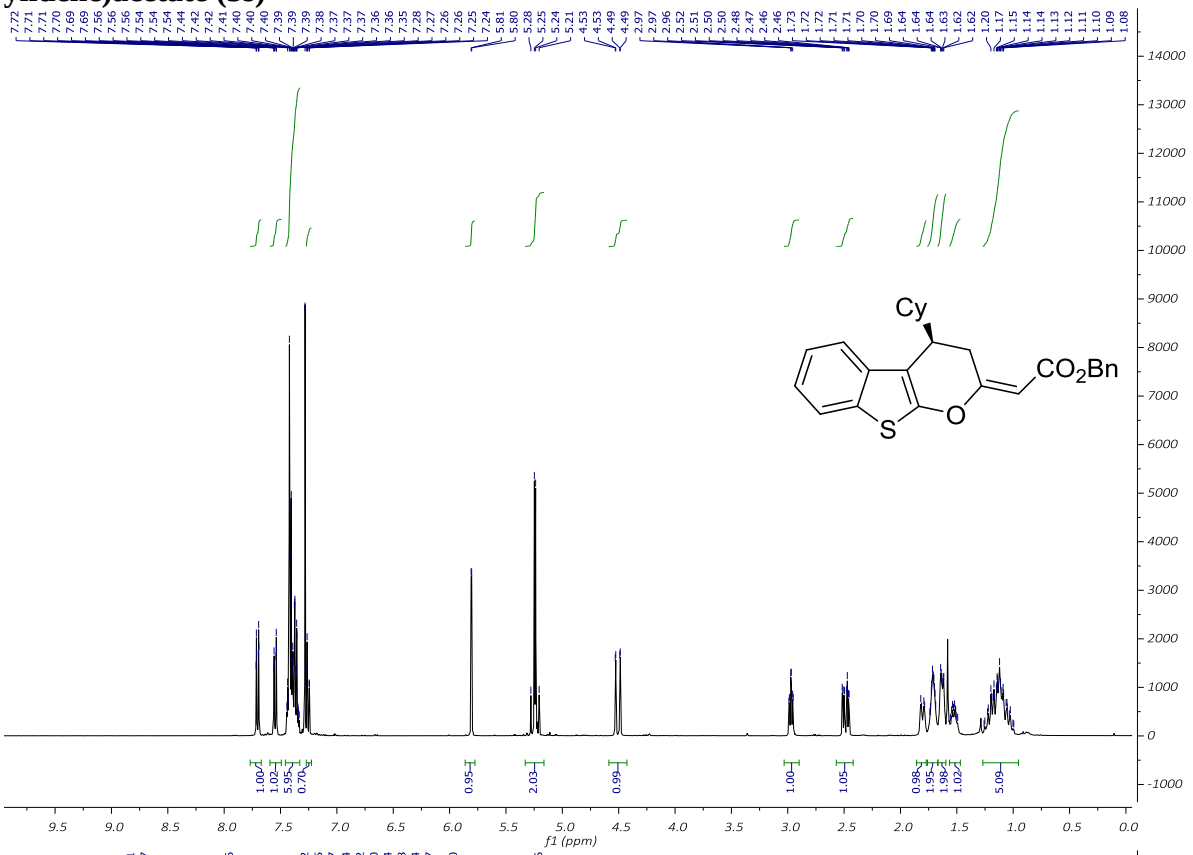


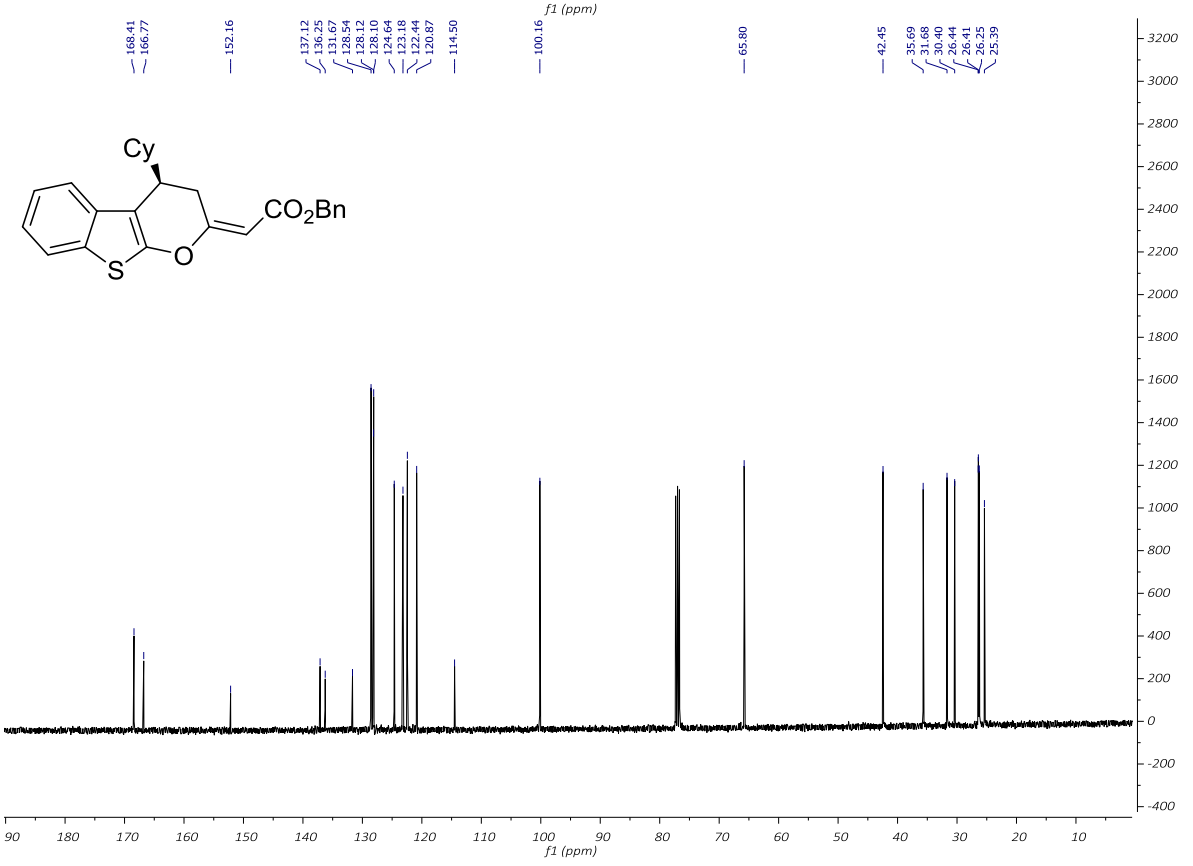
Benzyl (*S*,*E*)-2-(4-propyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3r)



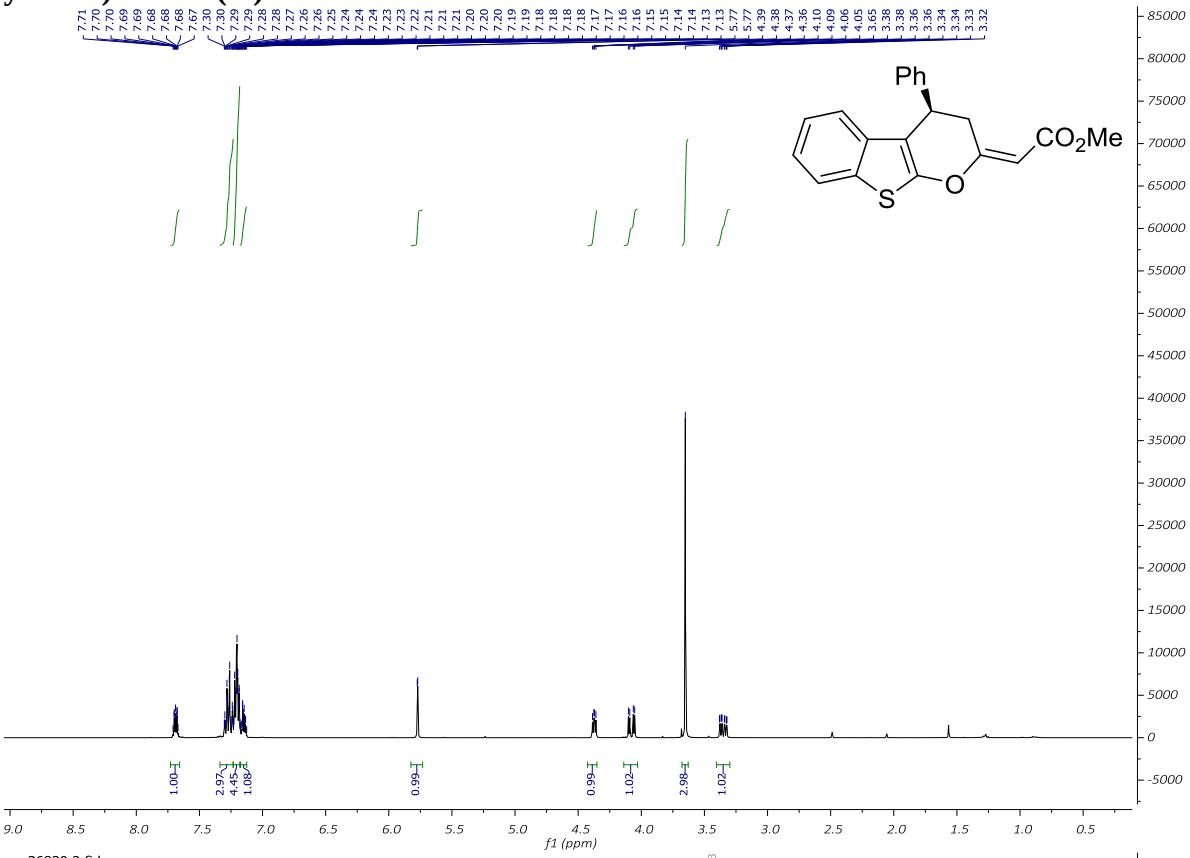


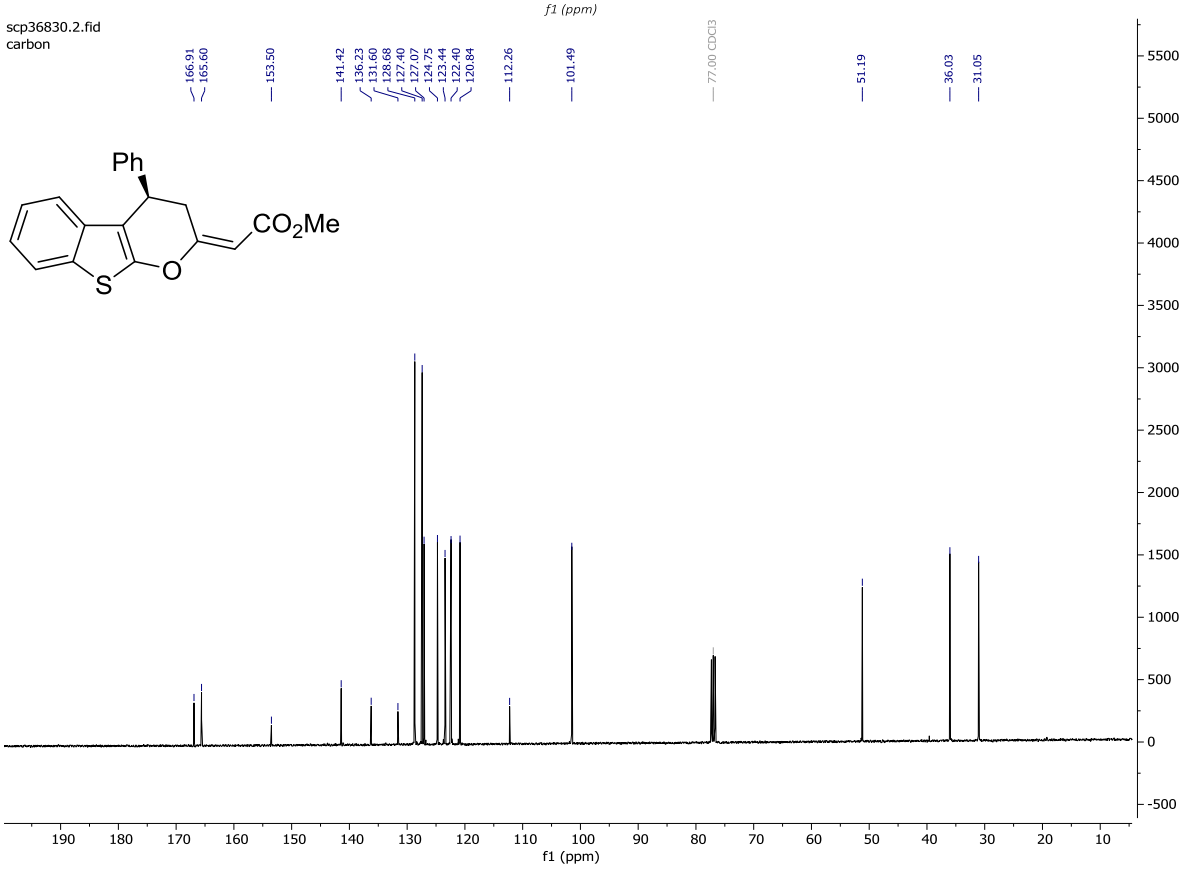
Benzyl (*R*,*E*)-2-(4-cyclohexyl-3,4-dihydro-2H-benzo[4,5]thieno[2,3-b]pyran-2-ylidene)acetate (3s)



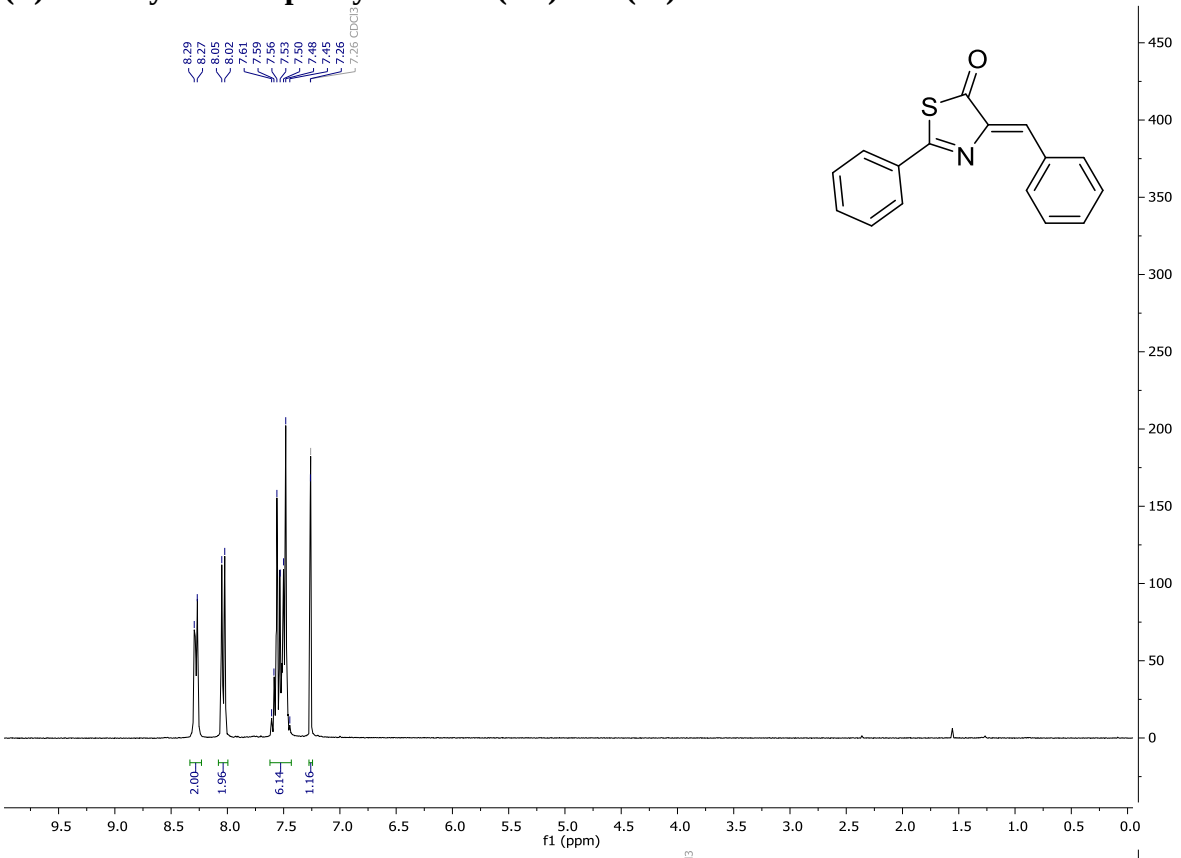


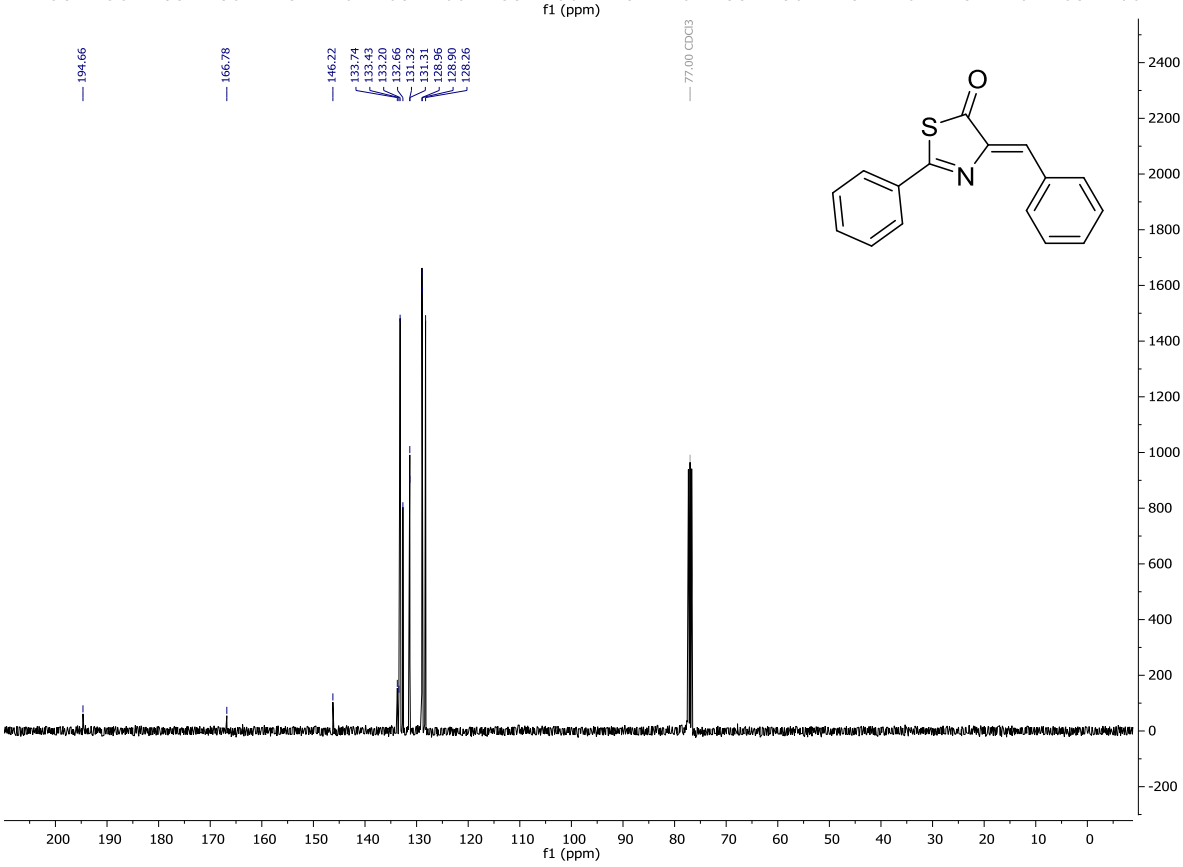
Methyl (*R*,*E*)-2-(4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (3t)



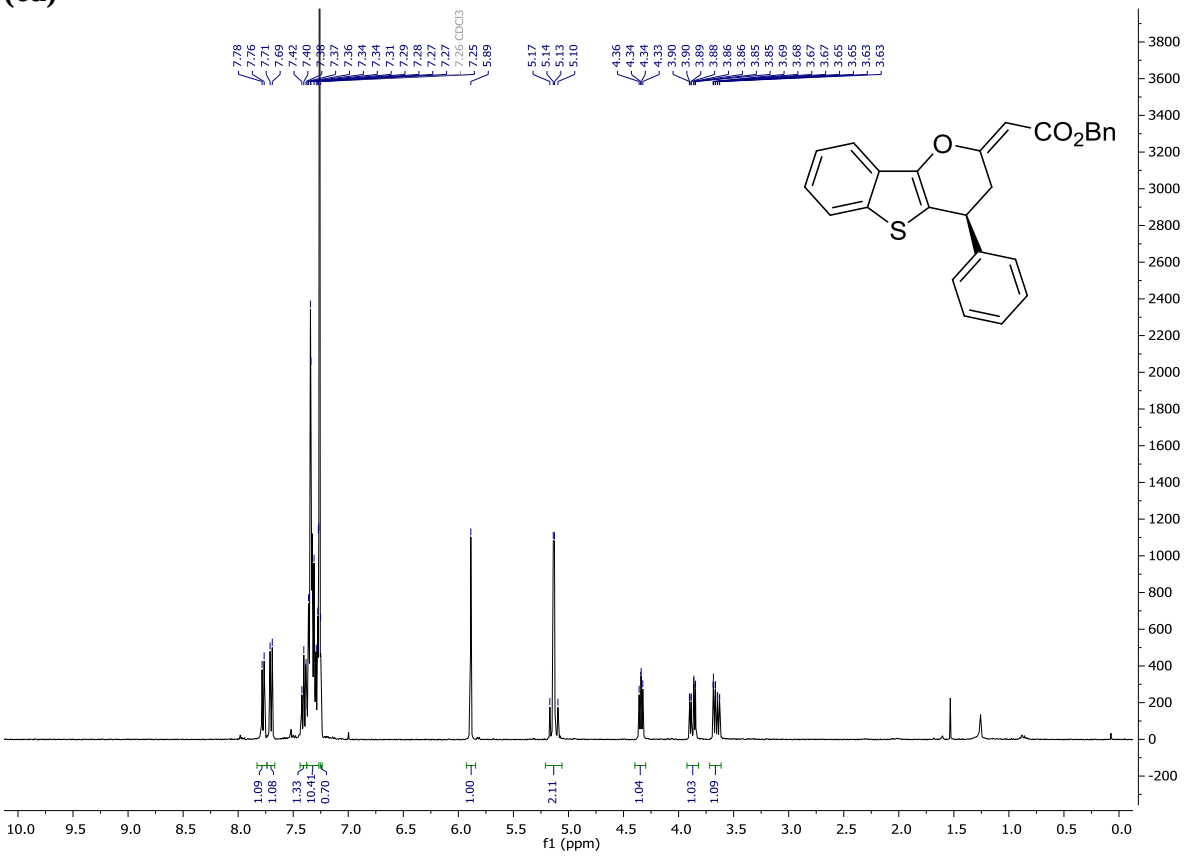


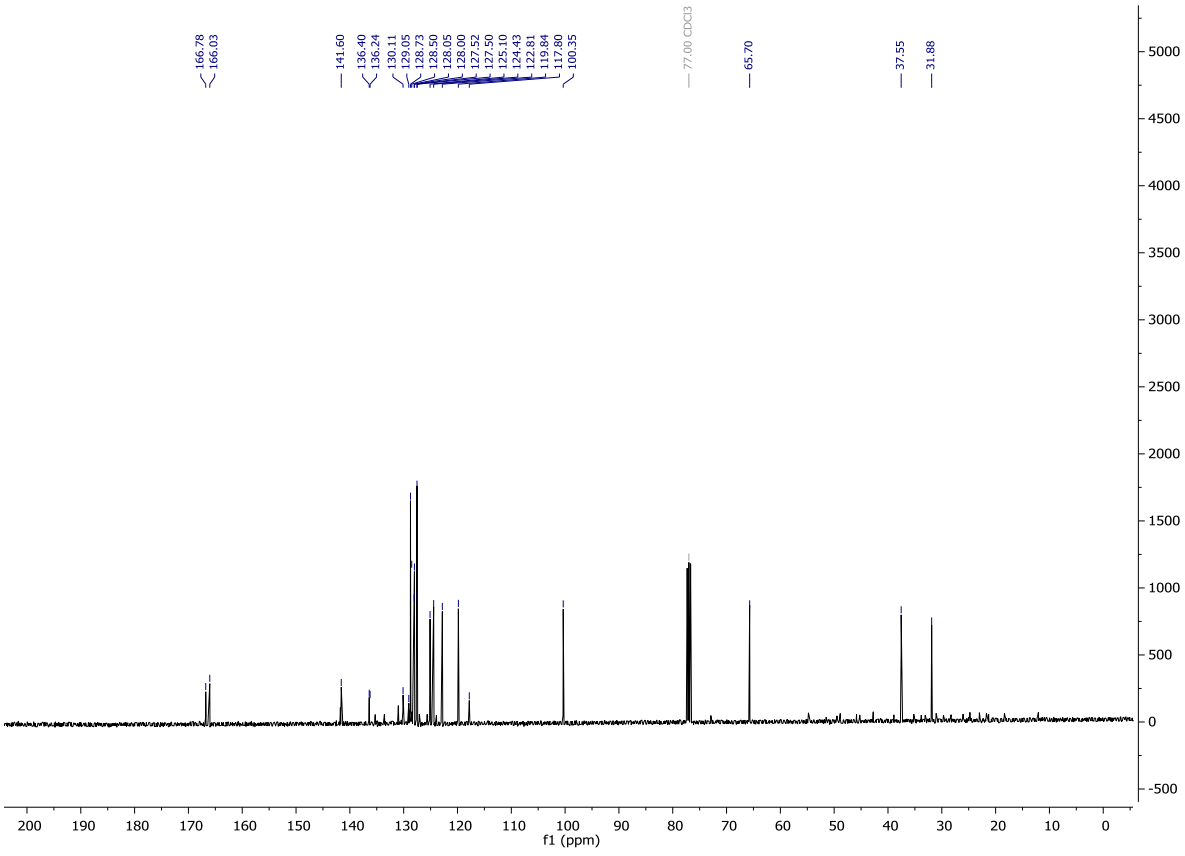
(*Z*)-4-Benzylidene-2-phenylthiazol-5(4*H*)-one (5c)



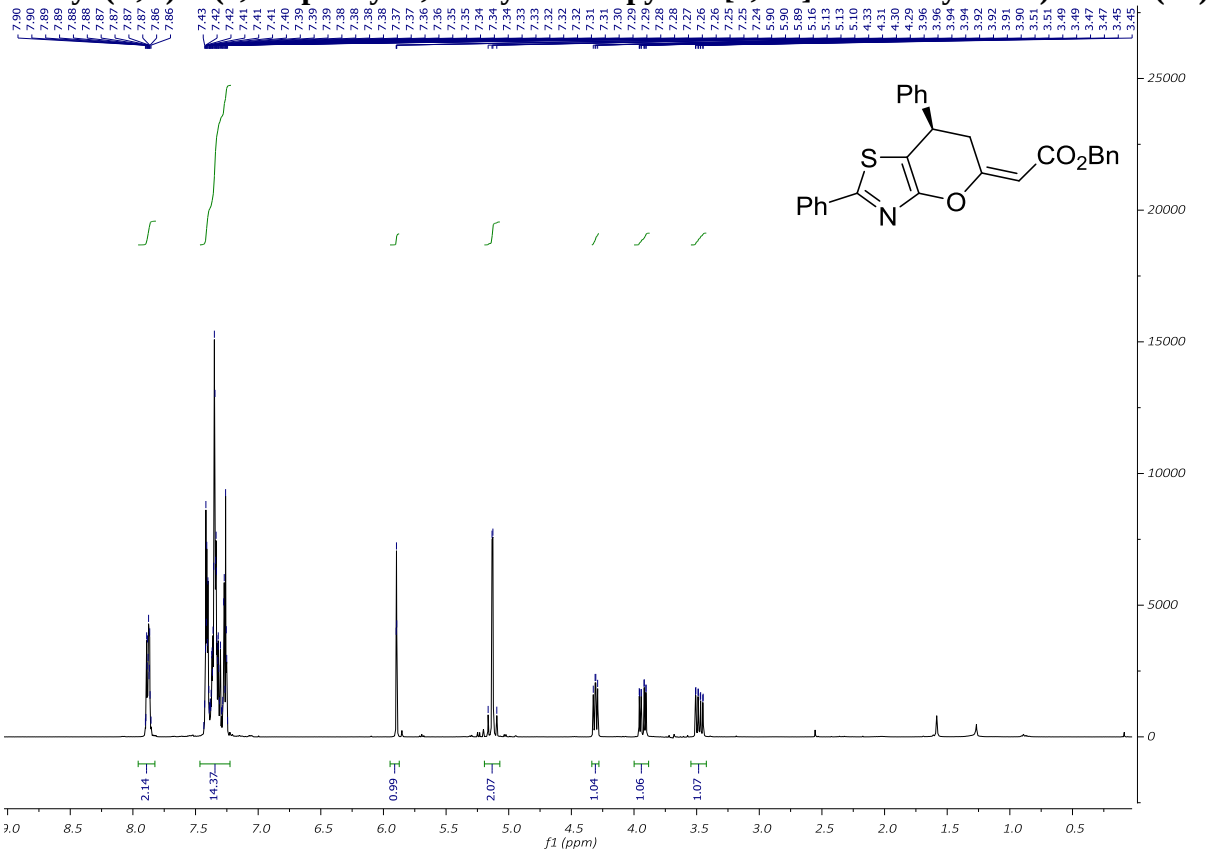


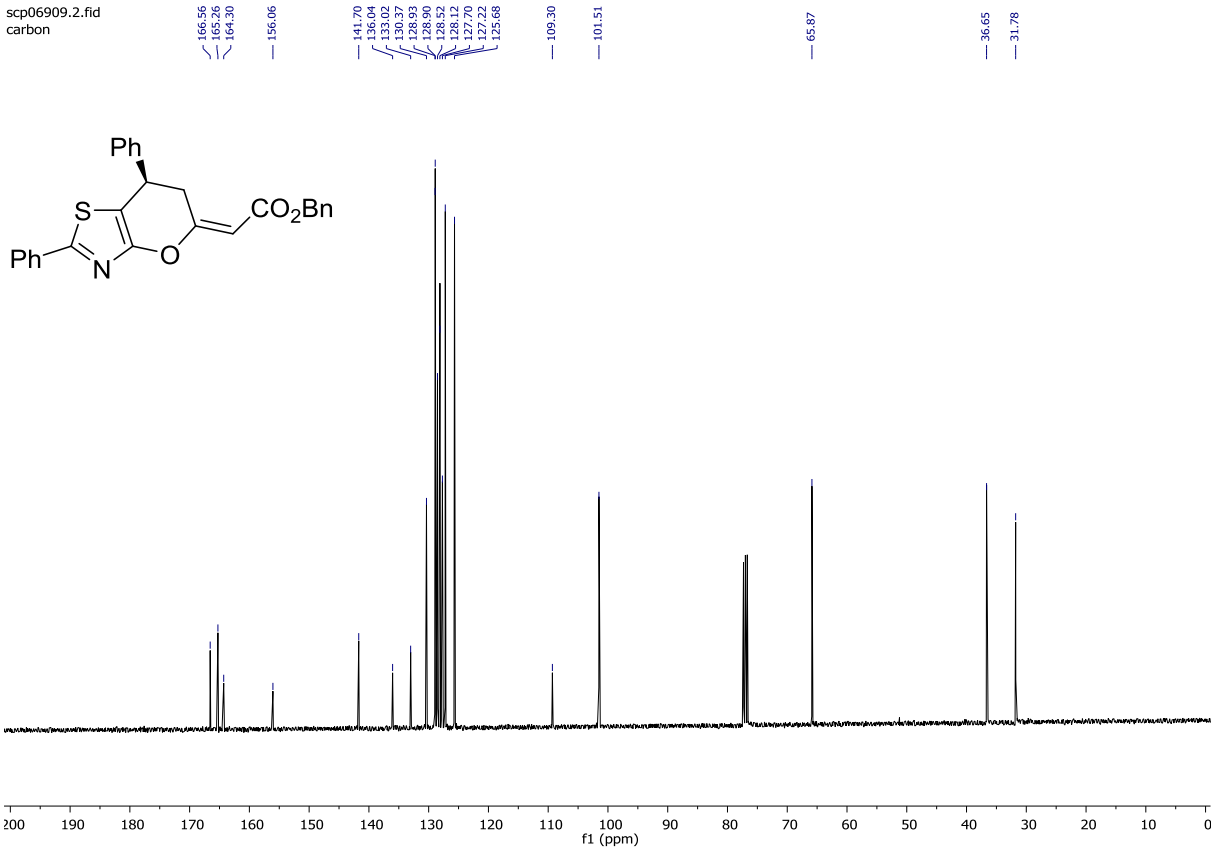
Benzyl (*S*,*E*)-2-(4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[3,2-*b*]pyran-2-ylidene)acetate (6a)



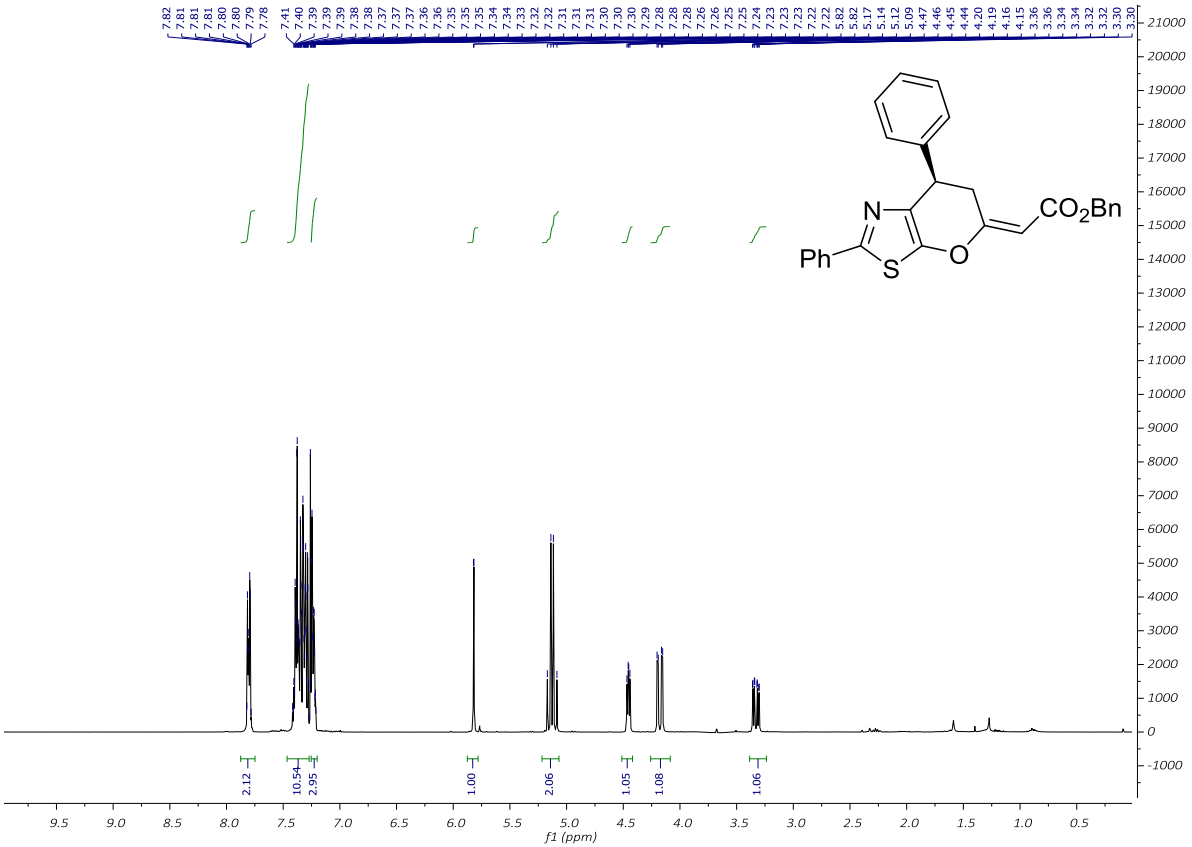


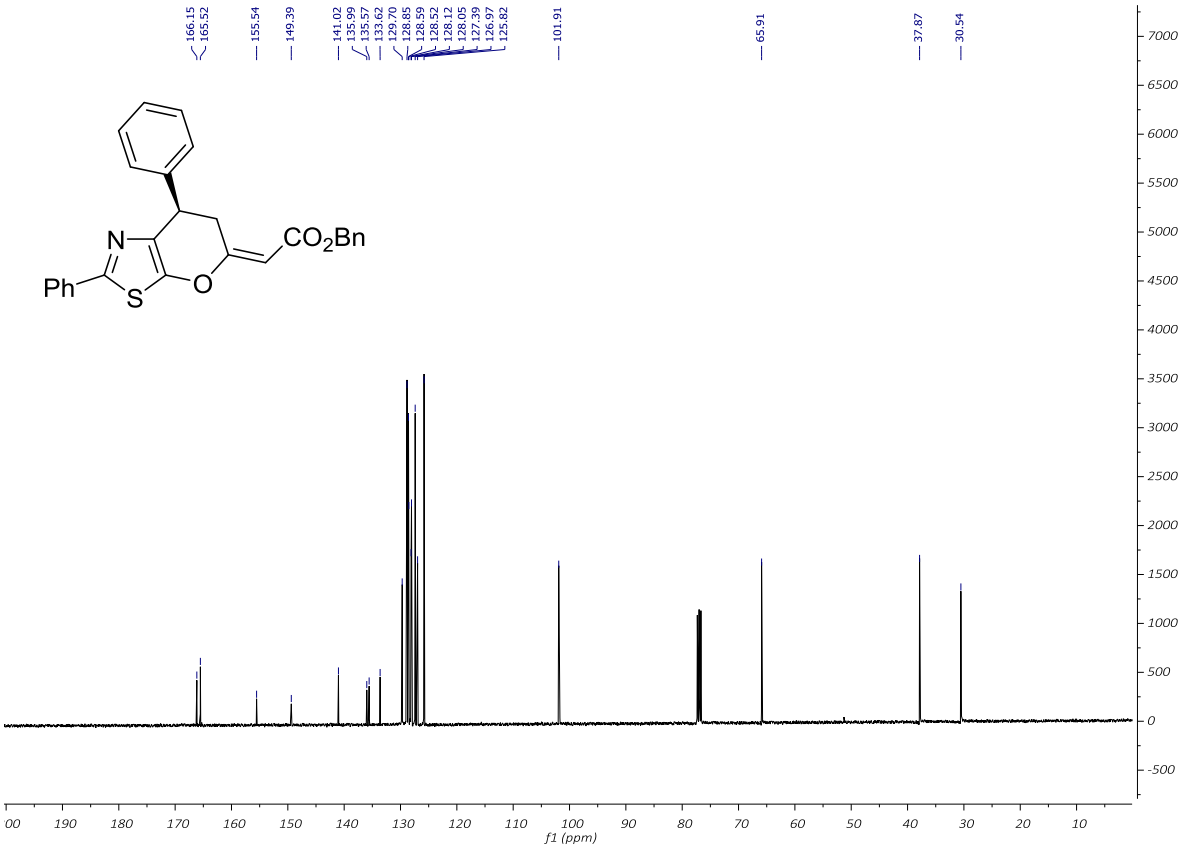
Benzyl (*R*,*E*)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazol-5-ylidene)acetate (6b)



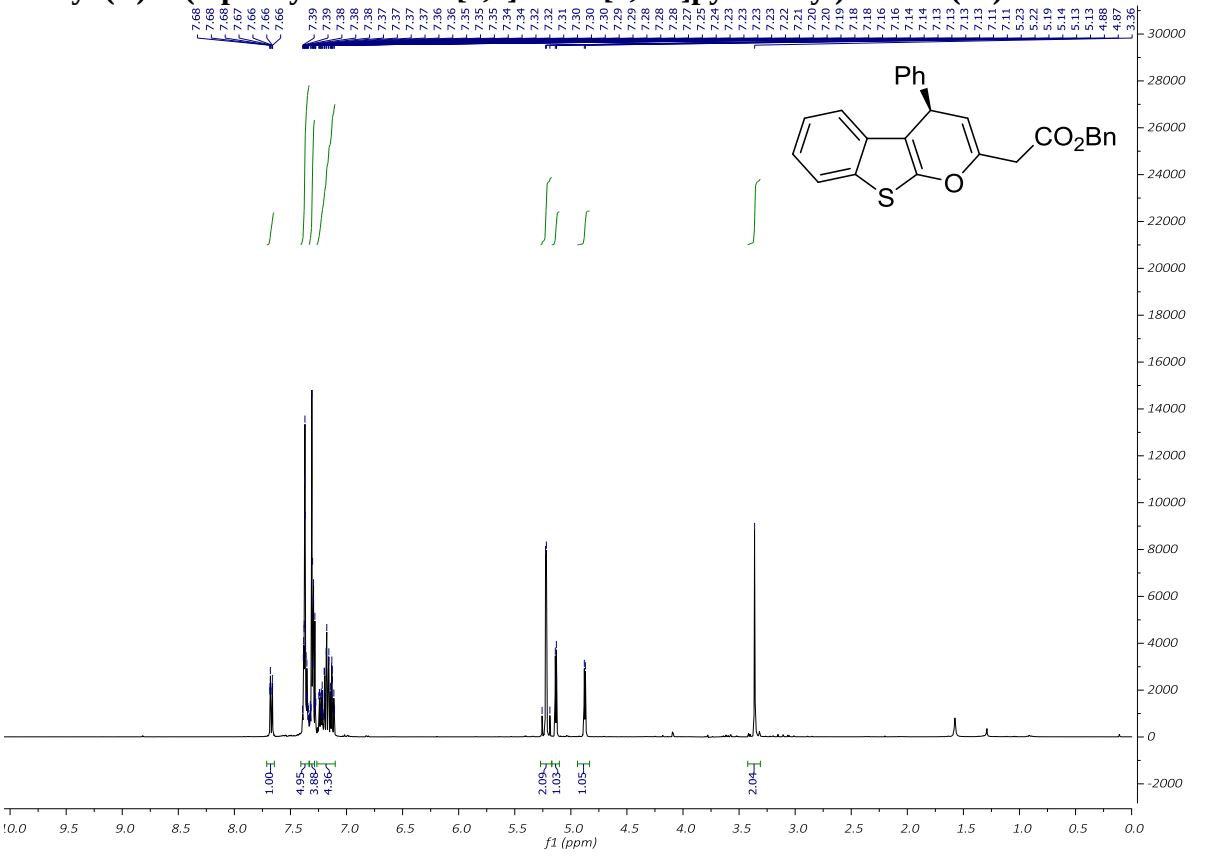


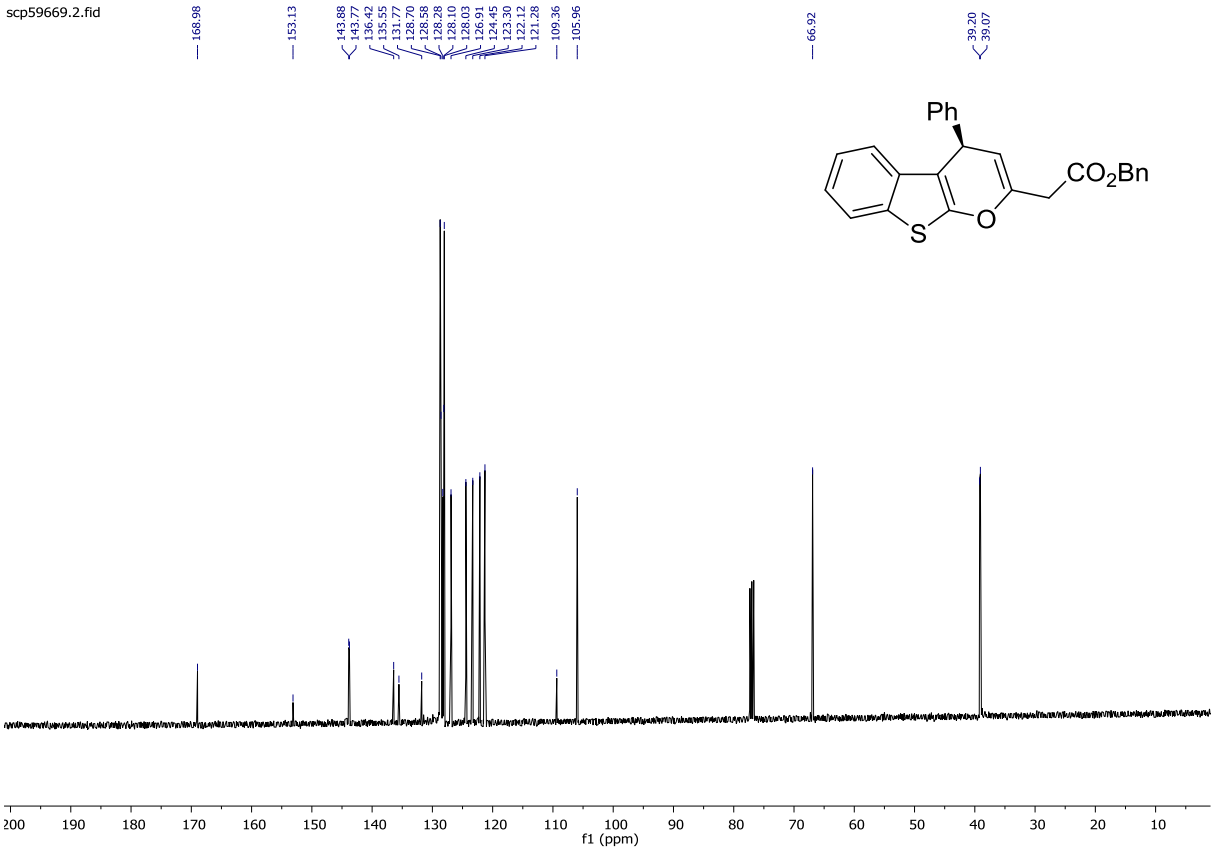
Benzyl (*R*,*E*)-2-(2,7-diphenyl-6,7-dihydro-5*H*-pyrano[3,2-*d*]thiazol-5-ylidene)acetate (6c)



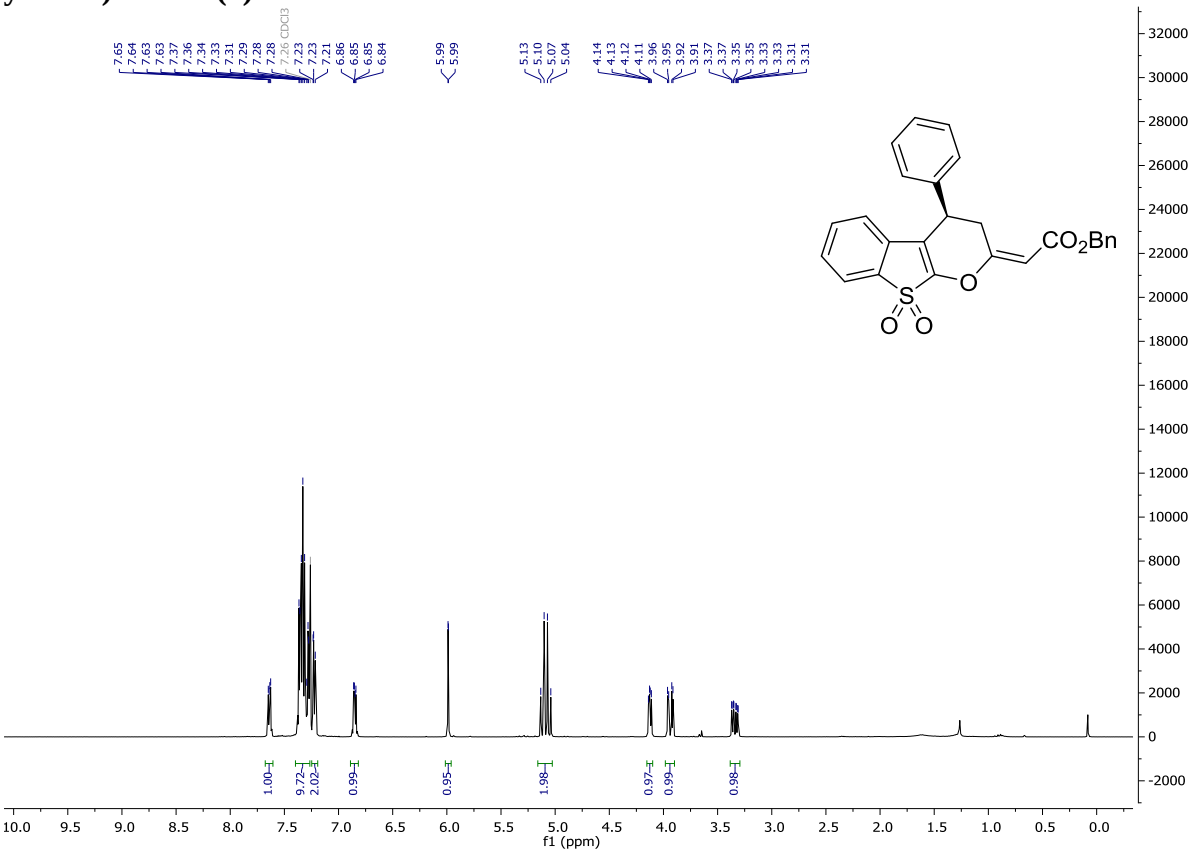


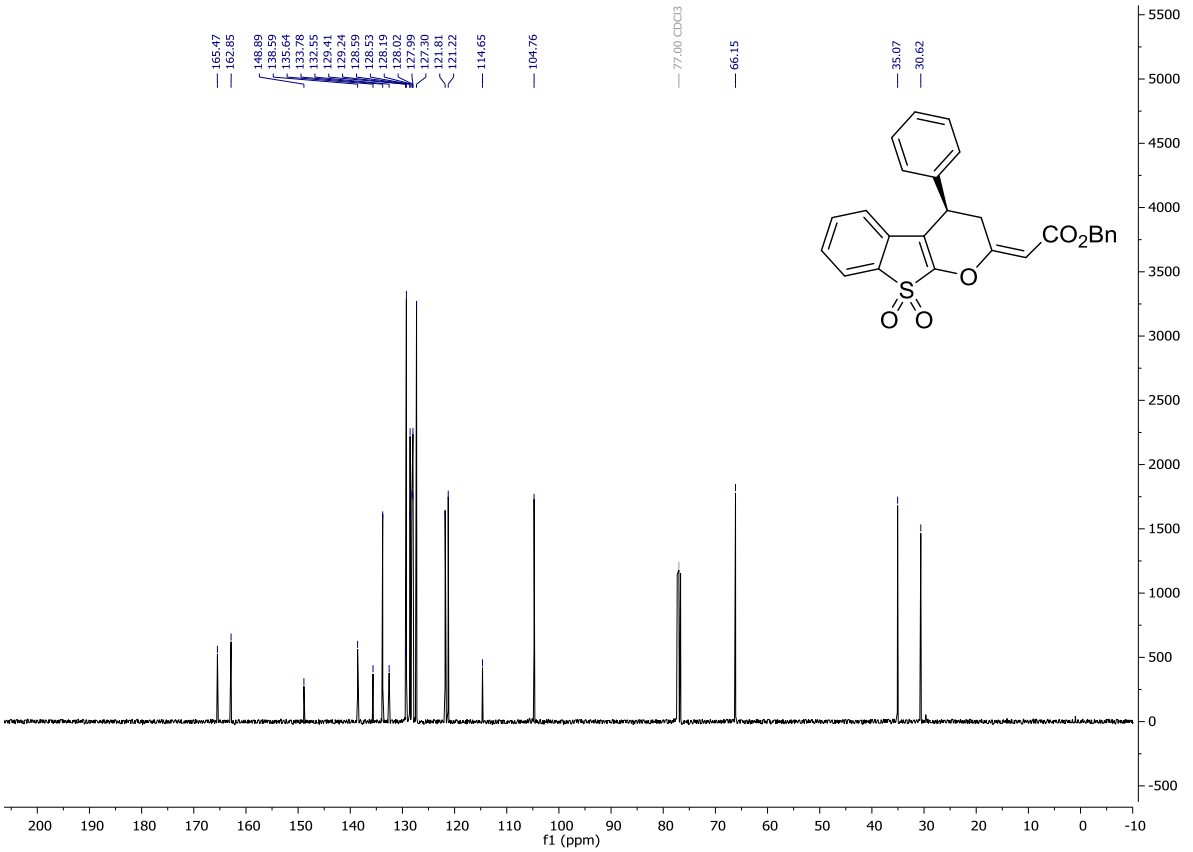
Benzyl (*R*)-2-(4-phenyl-4*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-yl)acetate (4a)



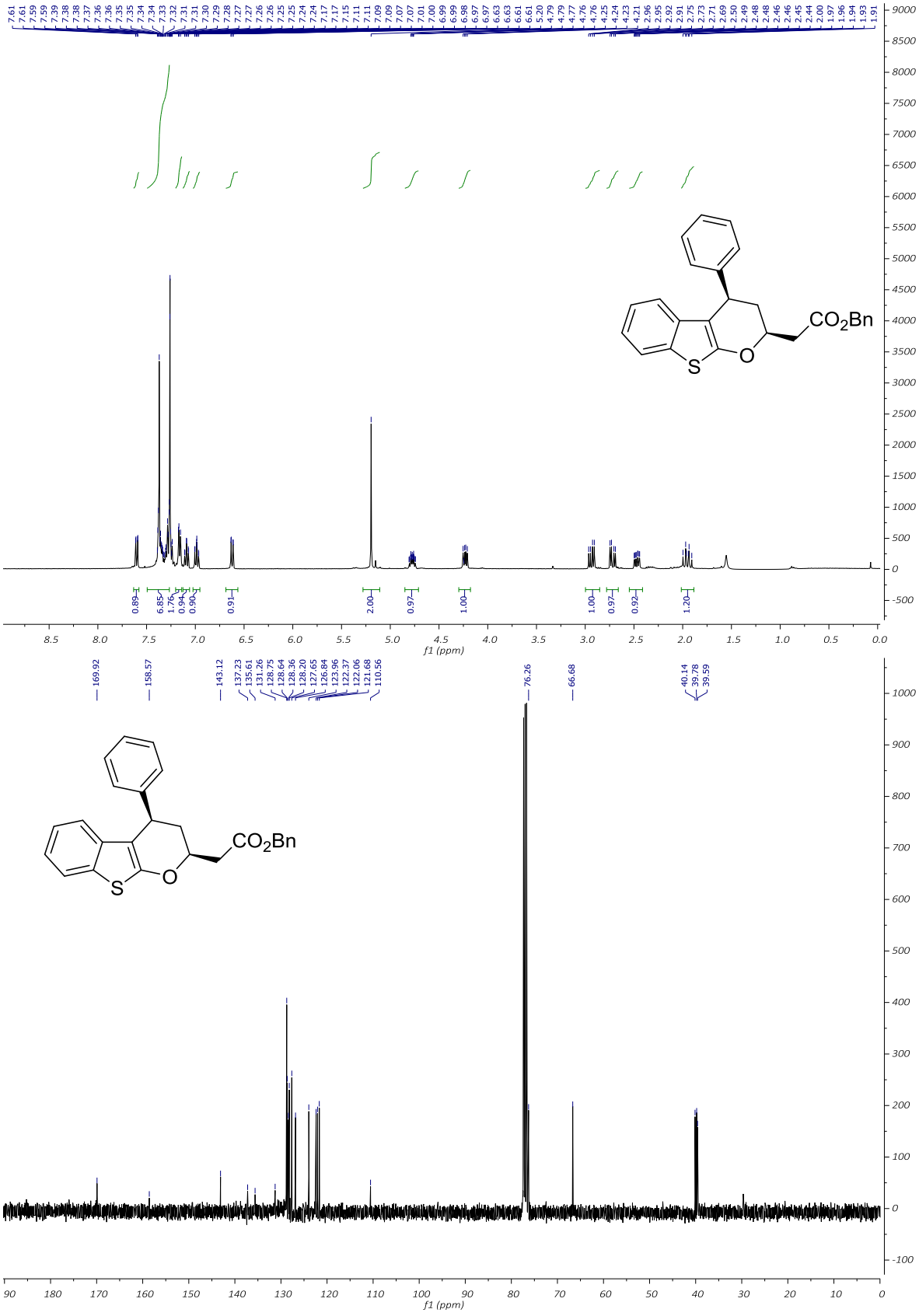


Benzyl (*R*,*E*)-2-(9,9-dioxido-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-b]pyran-2-ylidene)acetate (8)

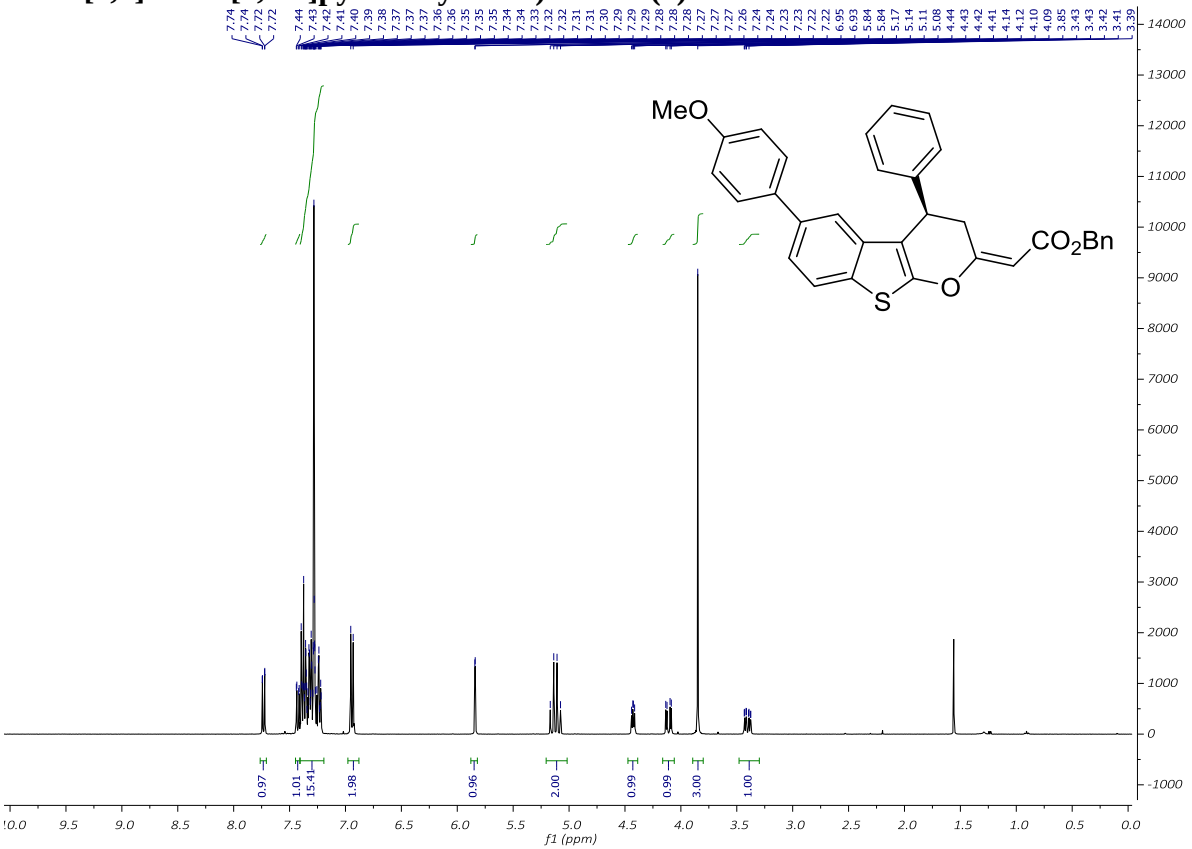


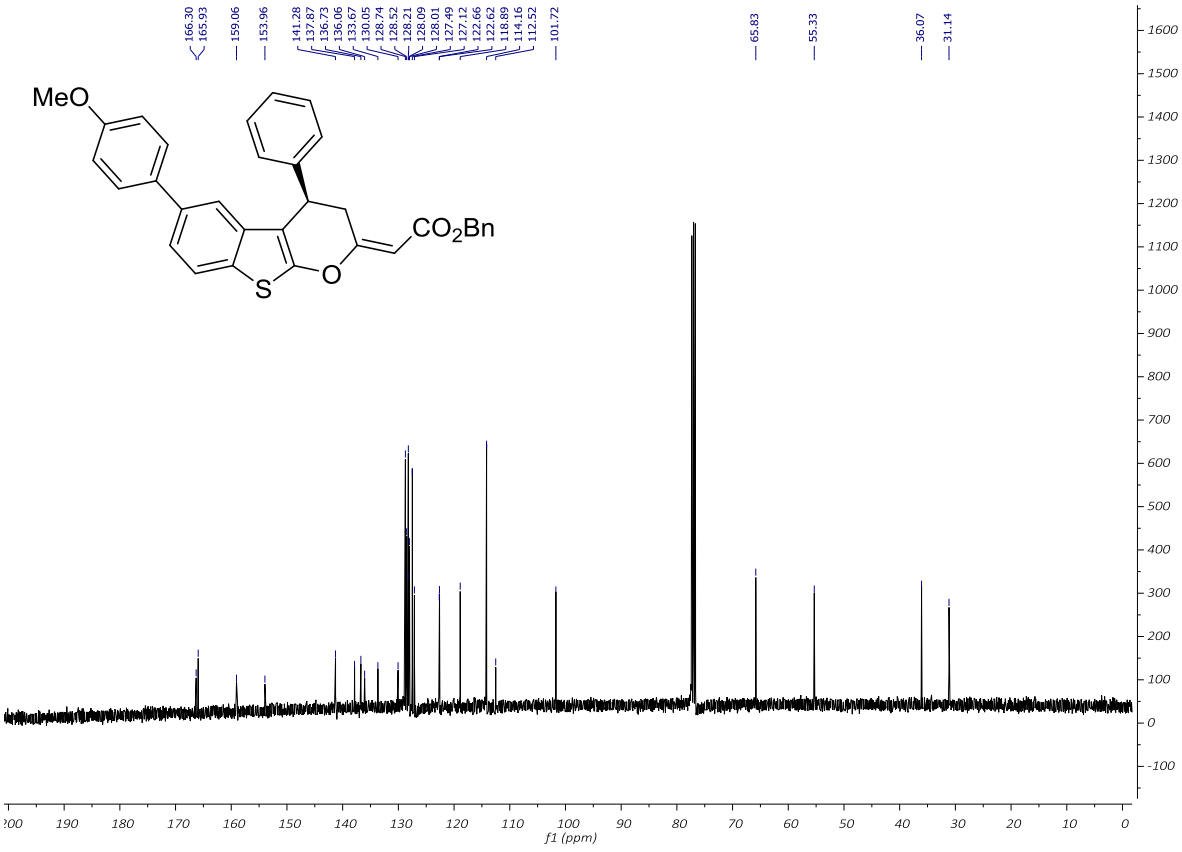


Benzyl 2-((2*S*,4*R*)-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-yl)acetateacetate (9)



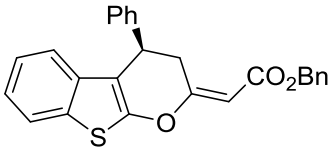
Benzyl (*R*,*E*)-2-(6-(4-methoxyphenyl)-4-phenyl-3,4-dihydro-2*H*-benzo[4,5]thieno[2,3-*b*]pyran-2-ylidene)acetate (9)



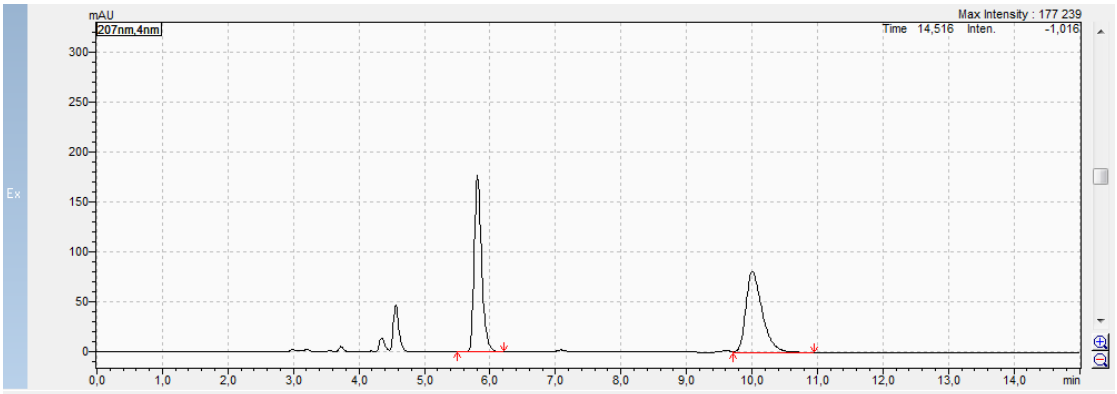


Chiral HPLC

Conditions: IB column



mobile phase: heptane / *i*-PrOH – 90:10
λ= 207 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3a**: t_R= 5.8 min (minor), t_R= 10.0 min (major).

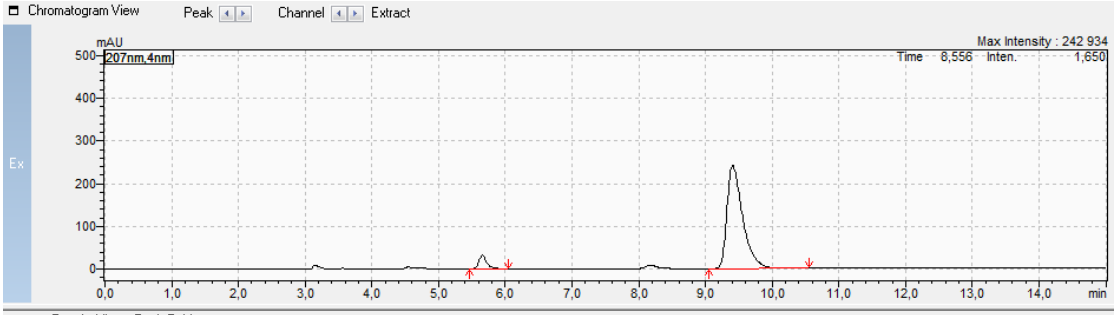


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,809	50,226	1412586	177793	0,000000		5,493	6,208	50,226
2	10,007	49,774	1399858	81332	0,000000	M	9,717	10,955	49,774
Total		100,000	2812444	259125					100,000

Method A:



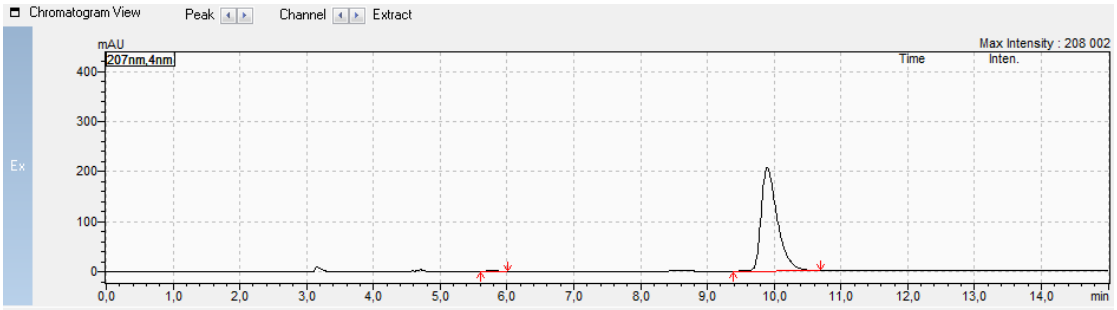
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,709	5,067	152998	19211	0,000000	M	5,525	6,016	5,067
2	9,618	94,933	2866364	171133	0,000000	M	9,205	10,603	94,933
Total		100,000	3019362	190344					100,000

ee = 90 %

Method B:



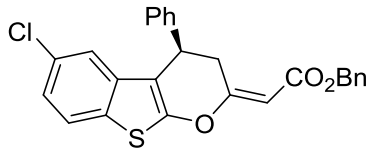
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

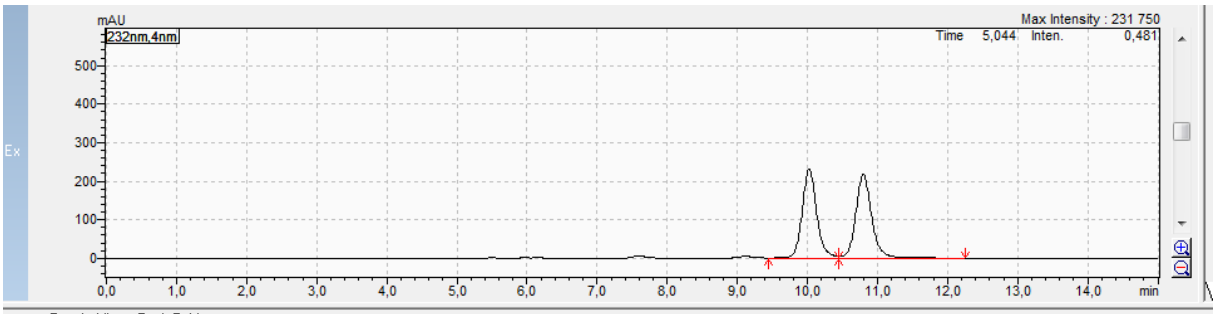
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,797	0,477	16803	1714	0,000000	M	5,611	6,016	0,477
2	9,895	99,523	3503413	206190	0,000000	M	9,387	10,699	99,523
Total		100,000	3520216	207905					100,000

ee = 99 %

Conditions: IA column



mobile phase: heptane / *i*-PrOH – 97:3
λ = 232 nm, V = 1.0 ml/min, t = 25 °C
for **3b**: t_R= 10.0 min (minor), t_R= 10.7 min (major).

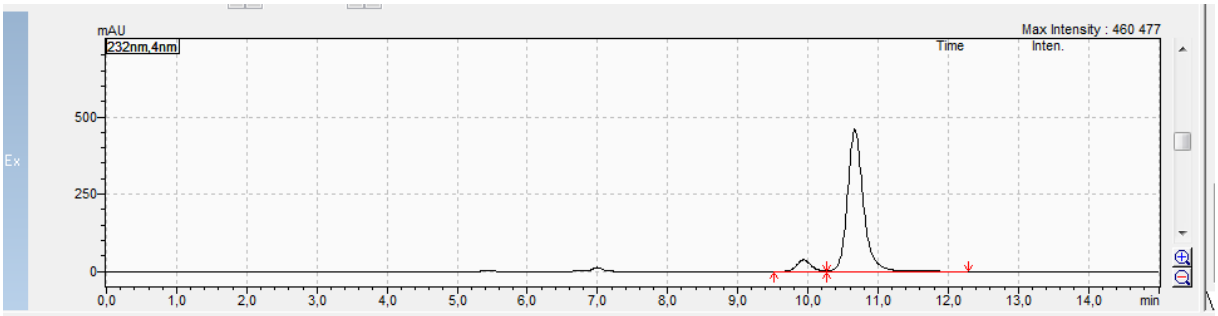


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,025	49,564	3342952	231084	0,000000		9,451	10,453	49,564
2	10,799	50,436	3401822	216512	0,000000	SV	10,453	12,256	50,436
Total		100,000	6744774	447596					100,000

Method A:



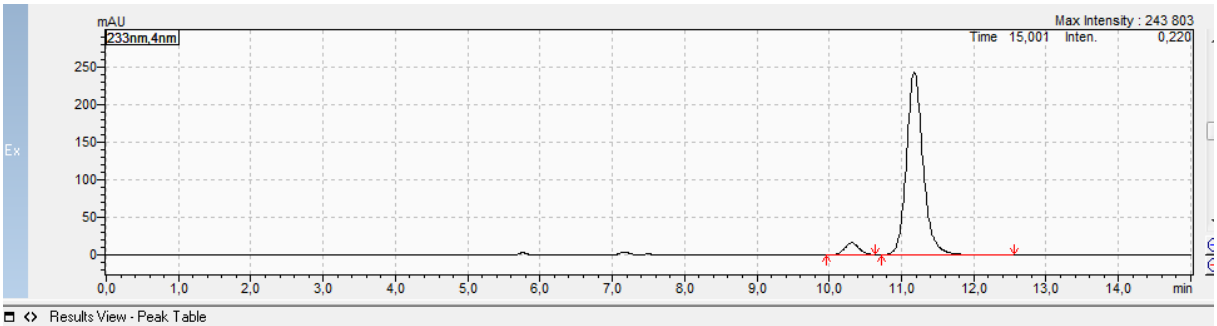
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	9,937	6,924	540734	37573	0,000000		9,525	10,272	6,924
2	10,669	93,076	7268872	460271	0,000000	V	10,272	12,288	93,076
Total		100,000	7809606	497844					100,000

ee = 86 %

Method B:



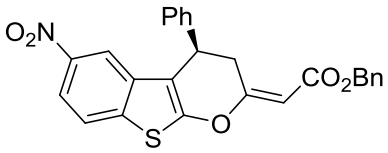
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

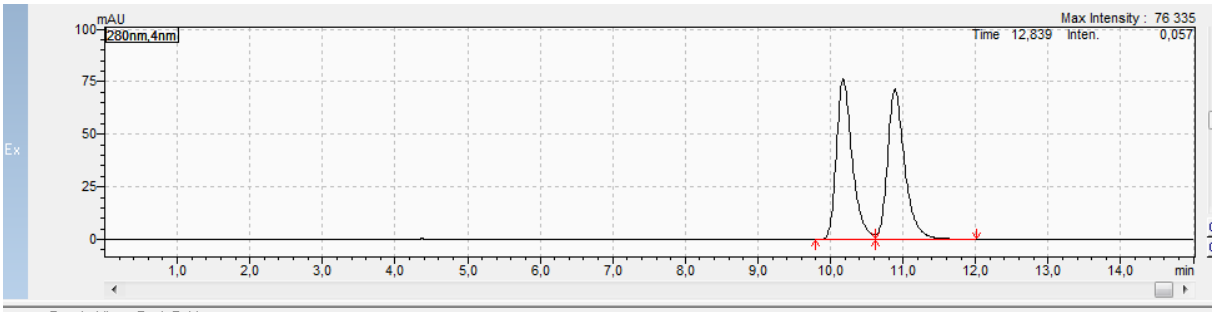
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,310	5,443	225919	16091	0,000000	M	9,963	10,635	5,443
2	11,177	94,557	3924839	243481	0,000000		10,720	12,555	94,557
Total		100,000	4150758	259572					100,000

ee = 89 %

Conditions: IB column



mobile phase: heptane / *i*-PrOH – 90:10
λ = 280 nm, V = 1.0 ml/min, t = 25 °C
for **3c**: t_R = 10.2 min (major), t_R = 10.9 min (minor).

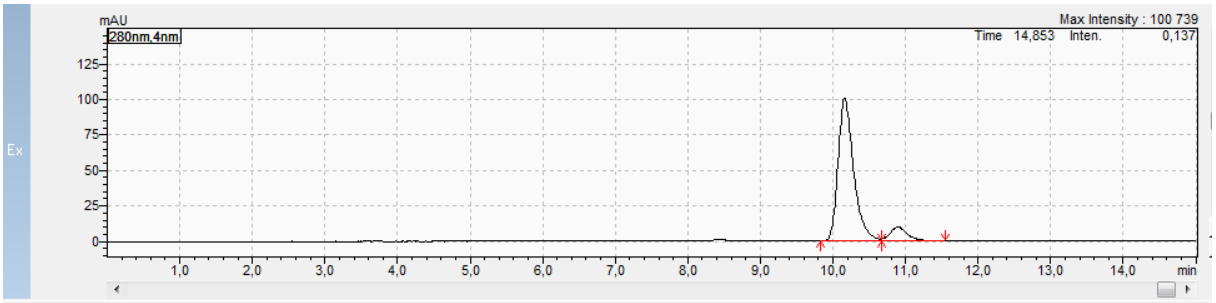


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,176	49,524	1156362	76312	0,000000		9,792	10,613	49,524
2	10,889	50,476	1178569	71496	0,000000	V	10,613	12,011	50,476
Total		100,000	2334931	147808					100,000

Method A:



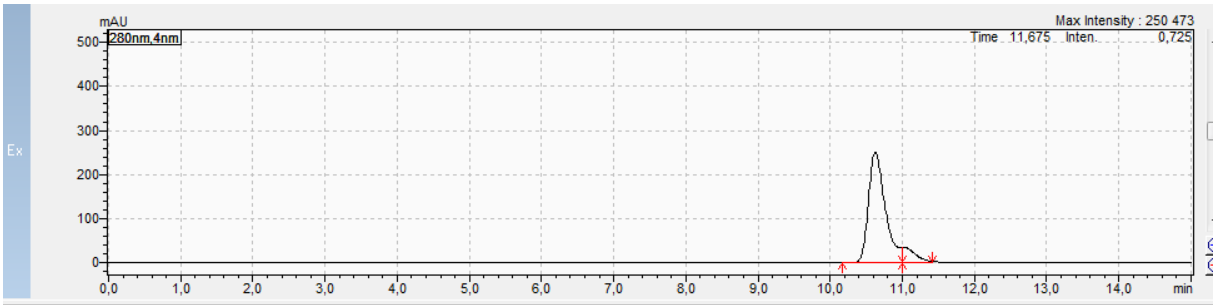
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,162	89,920	1513200	100605	0,000000		9,824	10,667	89,920
2	10,894	10,080	169637	10110	0,000000	V	10,667	11,541	10,080
Total		100,000	1682837	110715					100,000

ee = 80 %

Method B:



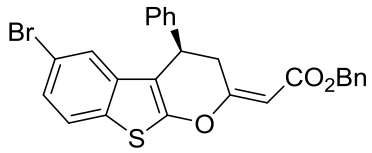
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

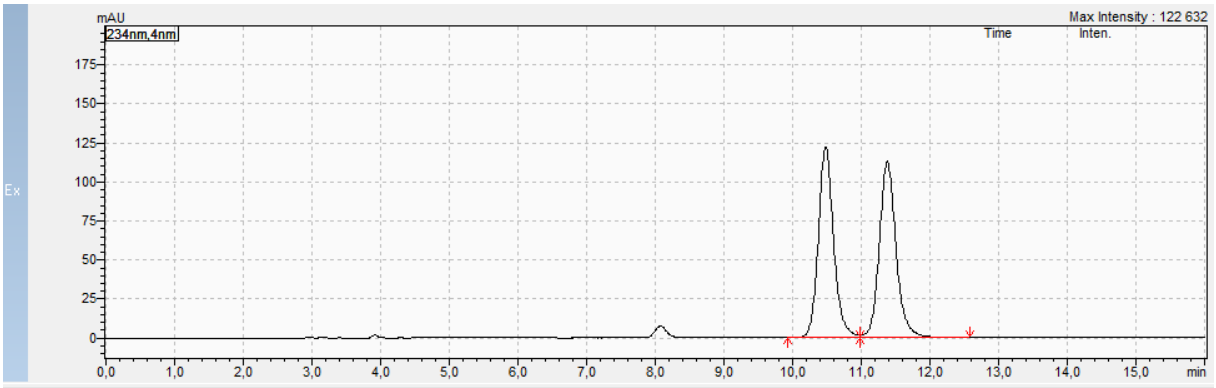
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,625	90,683	4061820	250295	0,000000	M	10,165	10,997	90,683
2	11,029	9,317	417327	34036	0,000000	M	10,997	11,413	9,317
Total		100,000	4479146	284331					100,000

ee = 80 %

Conditions: IA column



mobile phase: heptane / *i*-PrOH – 97:3
λ= 234 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3e**: t_R= 10.5 min (minor), t_R= 11.4 min (major).

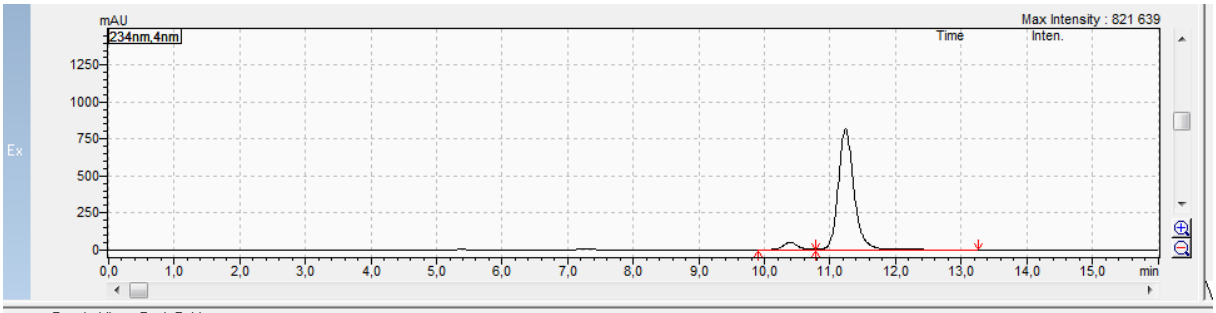


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,476	49,704	1900759	122396	0,000000		9,931	10,976	49,704
2	11,373	50,296	1923377	113144	0,000000	V	10,976	12,576	50,296
Total		100,000	3824135	235540					100,000

Method A:



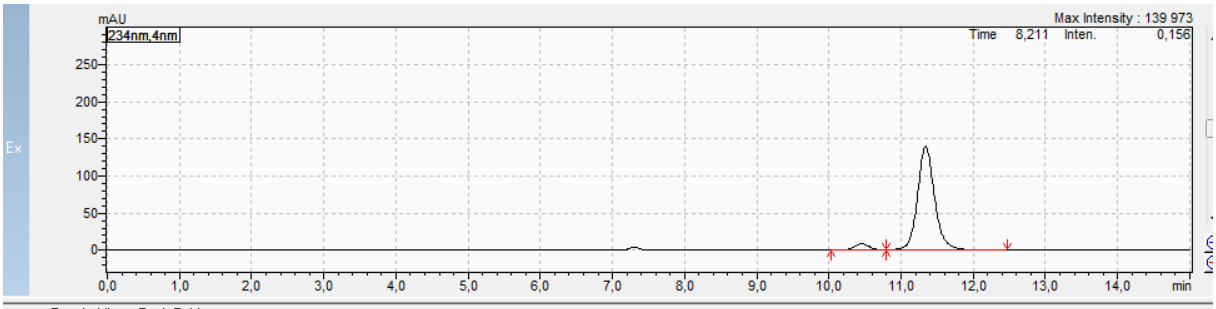
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,390	5,325	765053	50757	0,000000		9,909	10,773	5,325
2	11,235	94,675	13602938	821097	0,000000	V	10,773	13,259	94,675
Total		100,000	14367991	871854					100,000

ee = 89 %

Method B:



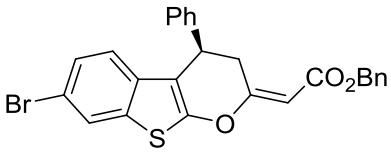
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

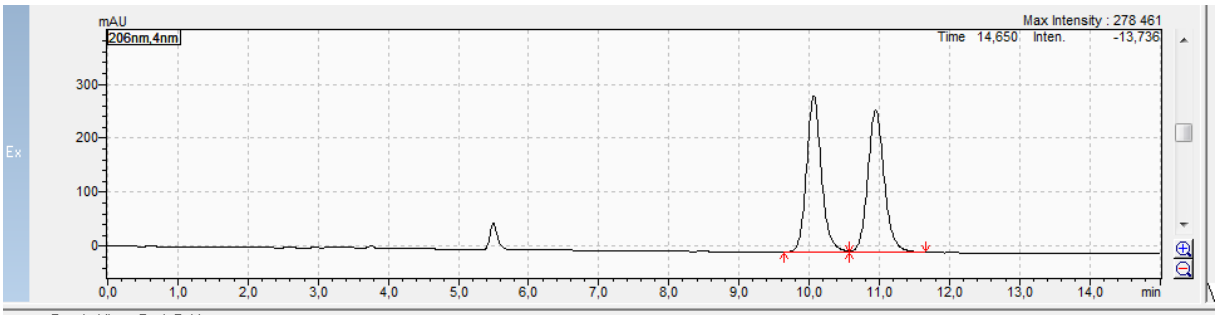
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,453	5,244	128347	8644	0,000000		10,037	10,784	5,244
2	11,341	94,756	2319287	139863	0,000000	V	10,784	12,480	94,756
Total		100,000	2447633	148508					100,000

ee = 90 %

Conditions: IA column



mobile phase: heptane / *i*-PrOH – 97:3
λ= 206 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3f**: t_R= 10.1 min (minor), t_R= 11.0 min (major).

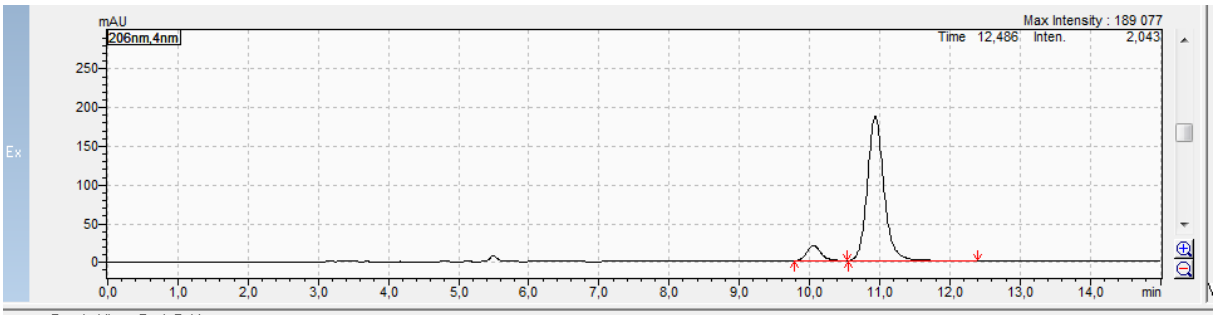


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,065	49,995	4307936	289464	0,000000		9,643	10,571	49,995
2	10,949	50,005	4308852	263565	0,000000	V	10,571	11,659	50,005
Total		100,000	8616787	553028					100,000

Method A:



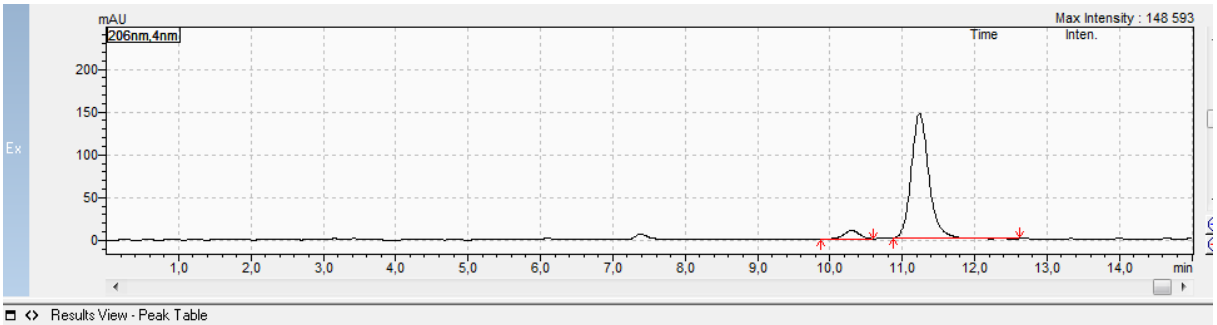
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,057	8,372	278214	19659	0,000000	M	9,781	10,539	8,372
2	10,938	91,628	3044992	186617	0,000000	M	10,549	12,395	91,628
Total		100,000	3323206	206276					100,000

ee = 83 %

Method B:



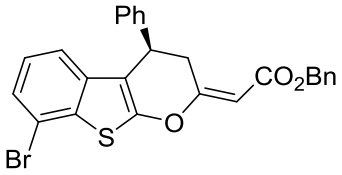
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

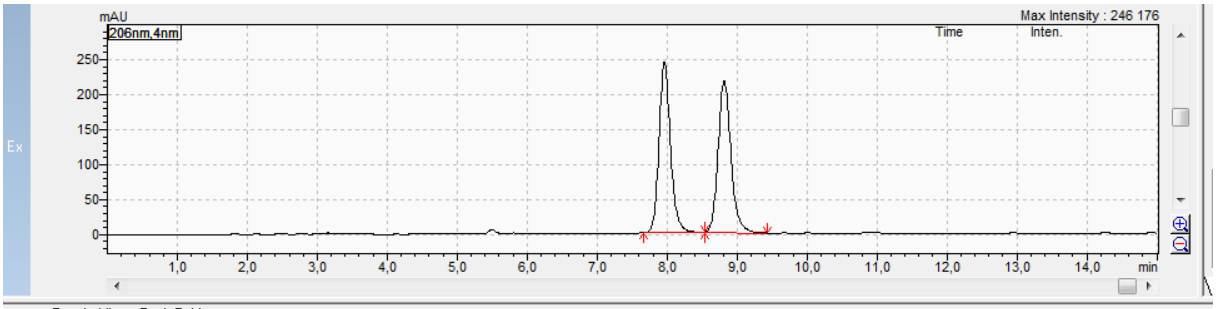
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,302	6,786	179545	10733	0,000000		9,877	10,603	6,786
2	11,239	93,214	2466112	146441	0,000000	M	10,869	12,619	93,214
Total		100,000	2645657	157174					100,000

ee = 87 %

Conditions: IA column



mobile phase: heptane / *i*-PrOH – 97:3
λ= 206 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3g**: t_R= 8.0 min (minor), t_R= 8.8 min (major).

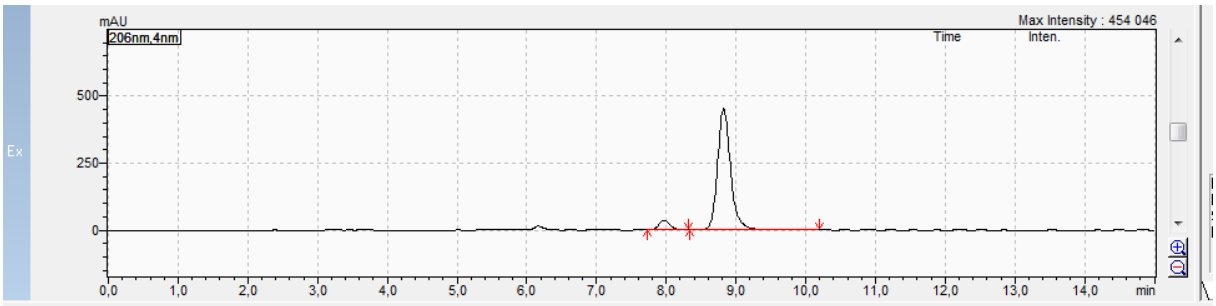


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	7,962	49,815	2755099	242991	0,000000	M	7,659	8,533	49,815
2	8,816	50,185	2775607	217228	0,000000	M	8,533	9,440	50,185
Total		100,000	5530706	460219					100,000

Method A:



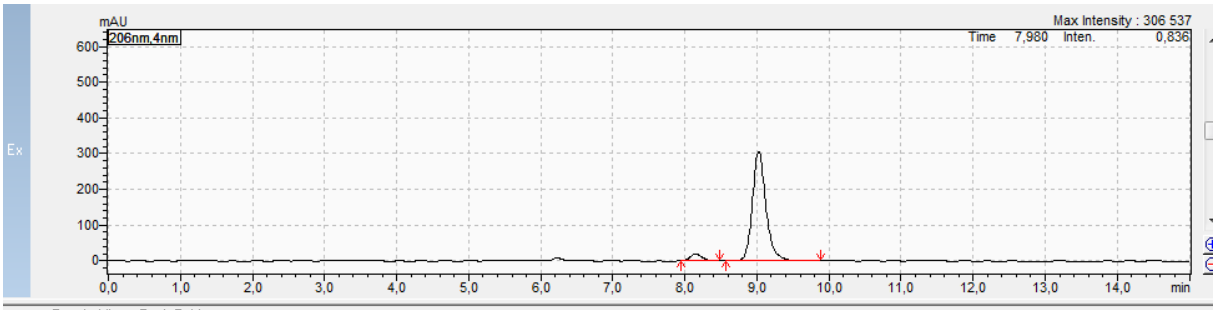
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	7,969	6,364	399627	36391	0,000000	M	7,733	8,320	6,364
2	8,822	93,636	5879459	452664	0,000000	M	8,341	10,197	93,636
Total		100,000	6279085	489055					100,000

ee = 87 %

Method B:



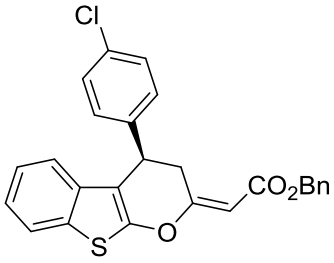
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

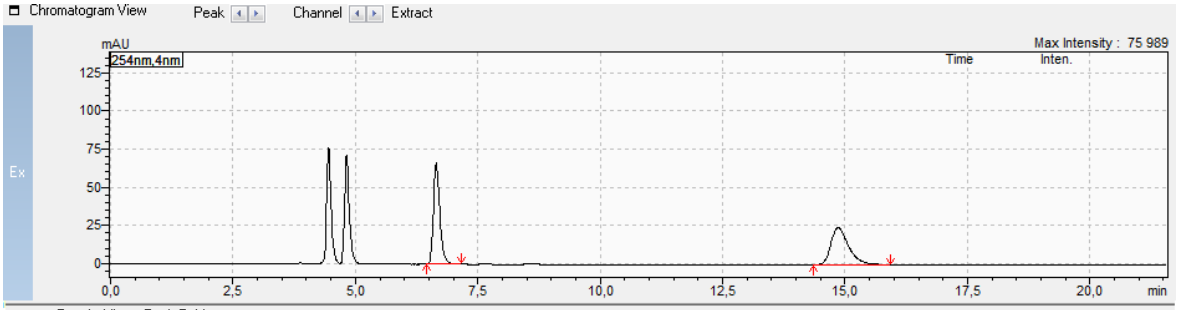
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	8,150	5,266	223647	19817	0,000000	M	7,947	8,480	5,266
2	9,025	94,734	4023104	306418	0,000000	M	8,565	9,888	94,734
Total		100,000	4246751	326235					100,000

ee = 90 %

Conditions: IB column

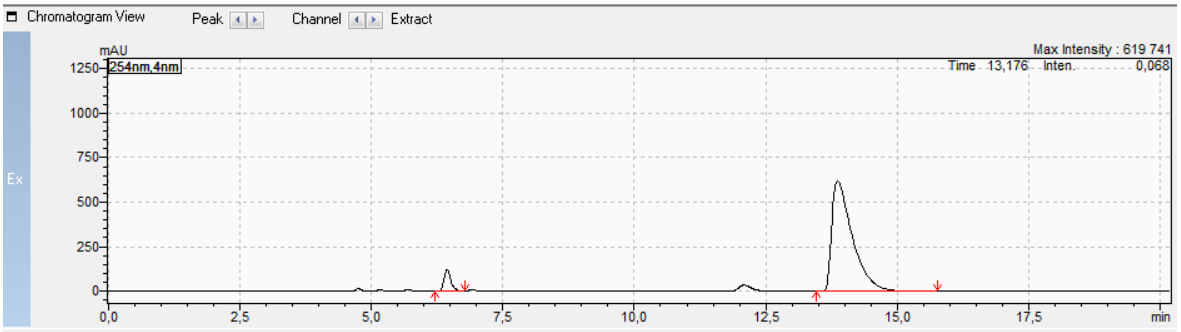


mobile phase: heptane / *i*-PrOH – 90:10
λ= 254 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3h**: t_R= 6.5 min (minor), t_R= 14.0 min (major).



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,650	50,021	608292	66152	0,000000	V M	6,453	7,168	50,021
2	14,857	49,979	607783	24223	0,000000		14,347	15,936	49,979
Total		100,000	1216075	90375					100,000

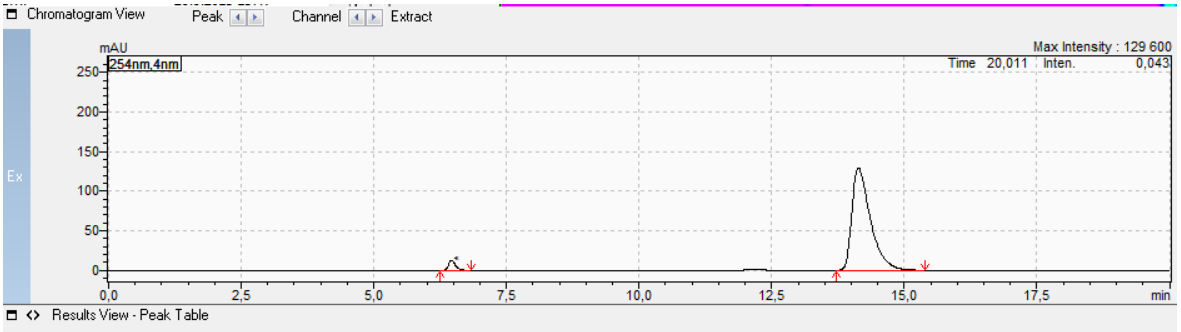
Method A:



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,438	6,108	1098928	123559	0,000000	M	6,197	6,773	6,108
2	13,869	93,892	16893898	619584	0,000000	M	13,451	15,765	93,892
Total		100,000	17992826	743143					100,000

ee = 88 %

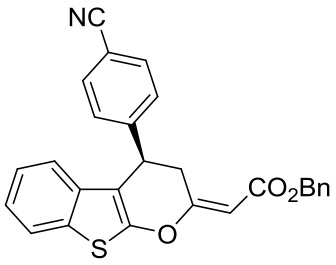
Method B:



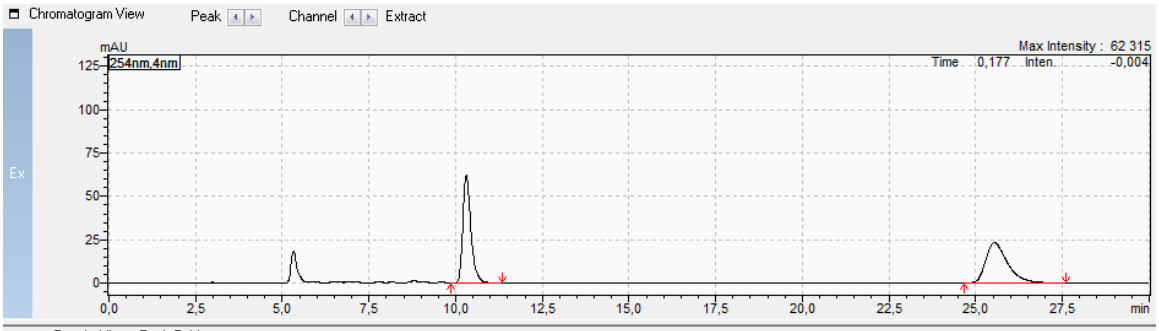
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,465	3,492	113605	12809	0,000000	M	6,240	6,837	3,492
2	14,136	96,508	3139295	129526	0,000000	M	13,707	15,392	96,508
Total		100,000	3252900	142335					100,000

ee = 93 %

Conditions: IB column



mobile phase: heptane / *i*-PrOH – 80:20
λ= 254 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3i**: t_R= 10.3 min (minor), t_R= 25.4 min (major).

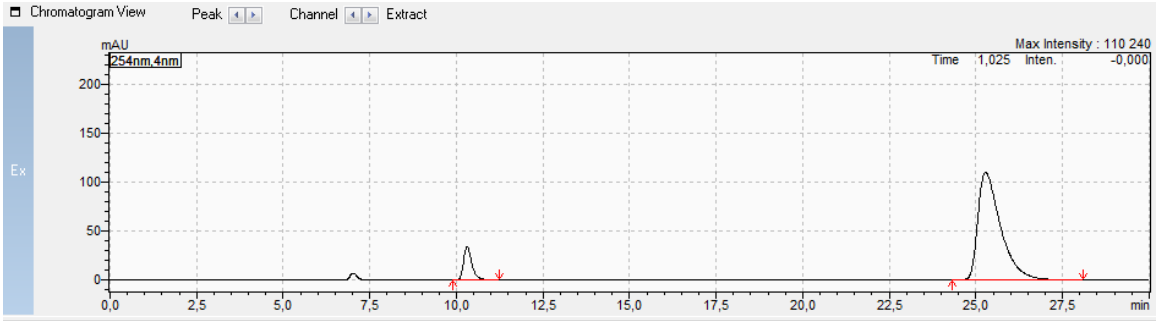


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,307	49,838	1009297	62074	0,000000	M	9,856	11,339	49,838
2	25,541	50,162	1015868	23242	0,000000	M	24,661	27,616	50,162
Total		100,000	2025166	85317					100,000

Method A:



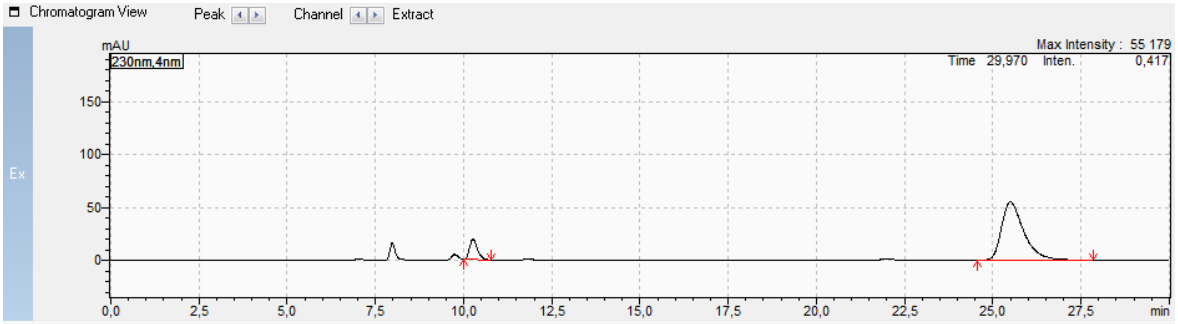
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,310	9,806	544359	34022	0,000000	M	9,888	11,243	9,806
2	25,280	90,194	5006807	110058	0,000000	M	24,320	28,096	90,194
Total		100,000	5551166	144080					100,000

ee = 80 %

Method B:



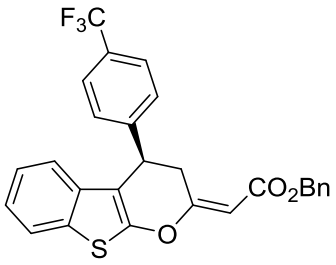
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

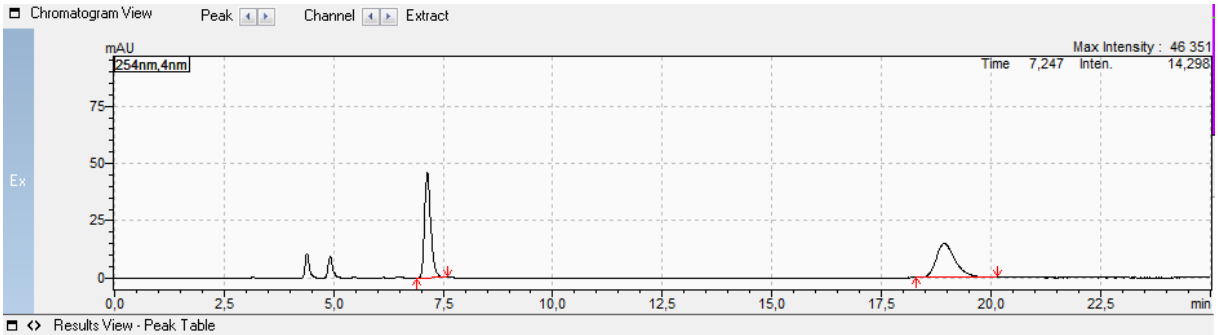
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,266	11,031	297012	19158	0,000000	M	10,005	10,784	11,031
2	25,498	88,969	2395590	54843	0,000000	M	24,565	27,851	88,969
Total		100,000	2692603	74001					100,000

ee = 78 %

Conditions: IB column



mobile phase: heptane / *i*-PrOH – 90:10
λ= 254 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3j**: t_R= 7.0 min (minor), t_R= 17.8 min (major).

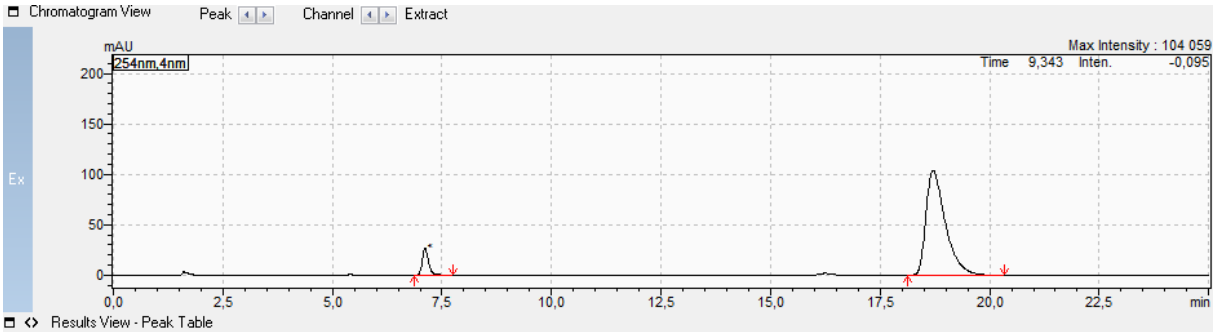


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	7,136	50,062	455034	46240	0,000000		6,901	7,605	50,062
2	18,935	49,938	453912	14922	0,000000		18,304	20,149	49,938
Total		100,000	908946	61162					100,000

Method A:



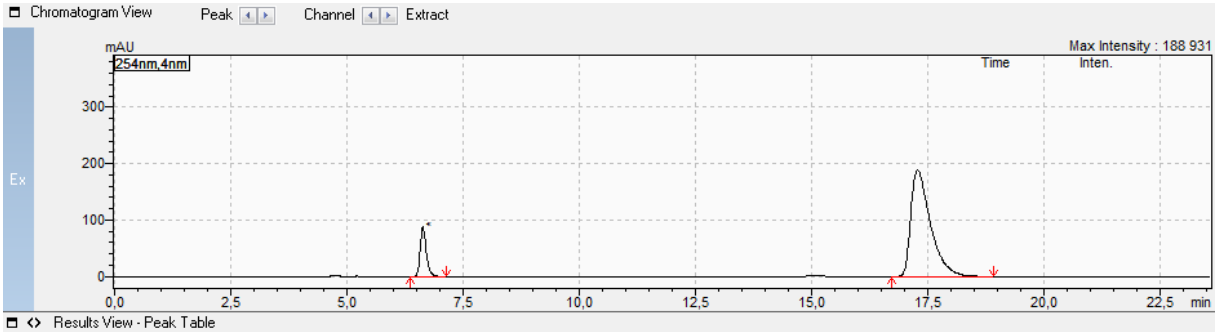
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	7,112	7,874	274959	27353	0,000000		6,859	7,744	7,874
2	18,708	92,126	3216848	104094	0,000000		18,123	20,331	92,126
Total		100,000	3491807	131447					100,000

ee = 84 %

Method B:



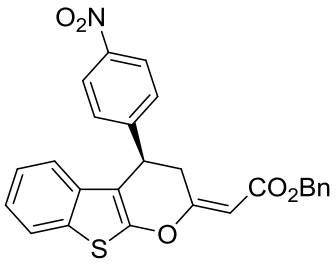
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

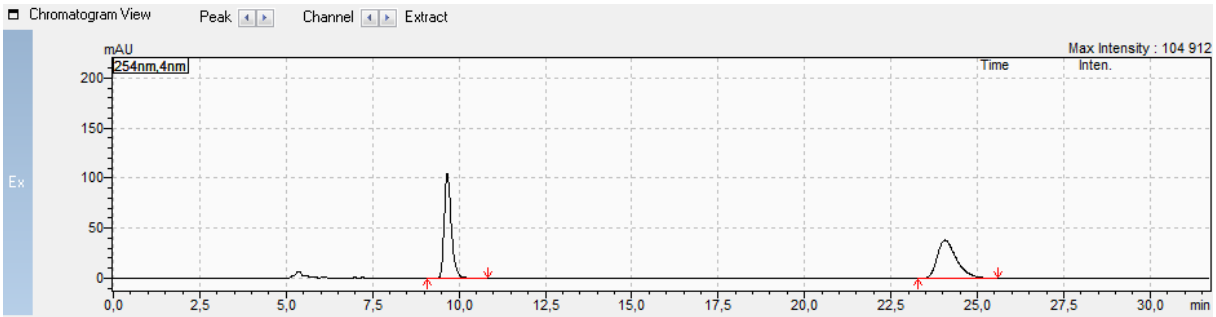
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,638	12,709	806556	87911	0,000000	M	6,357	7,136	12,709
2	17,290	87,291	5539695	188847	0,000000	M	16,725	18,933	87,291
Total		100,000	6346252	276758					100,000

ee = 75 %

Conditions: IB column

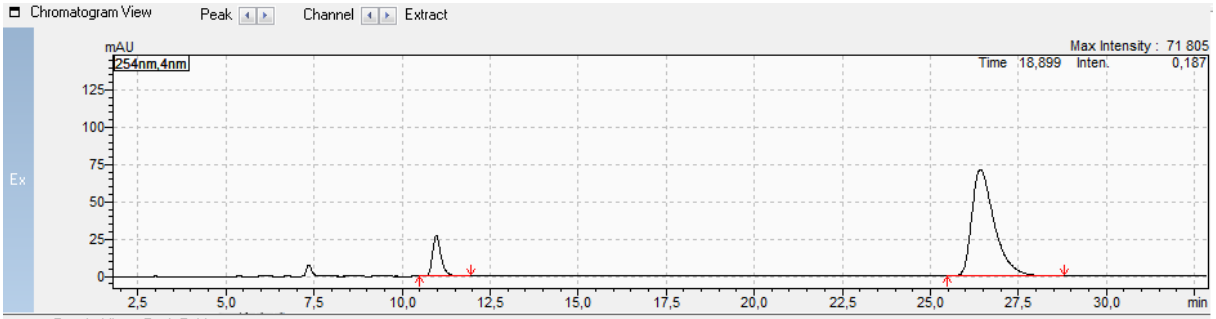


mobile phase: heptane / *i*-PrOH – 80:20
λ= 254 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3k**: t_R= 9.8 min (minor), t_R= 24.2 min (major).



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	9,665	50,298	1521532	105297	0,000000	M	9,099	10,837	50,298
2	24,063	49,702	1503489	38412	0,000000	M	23,285	25,611	49,702
Total		100,000	3025021	143709					100,000

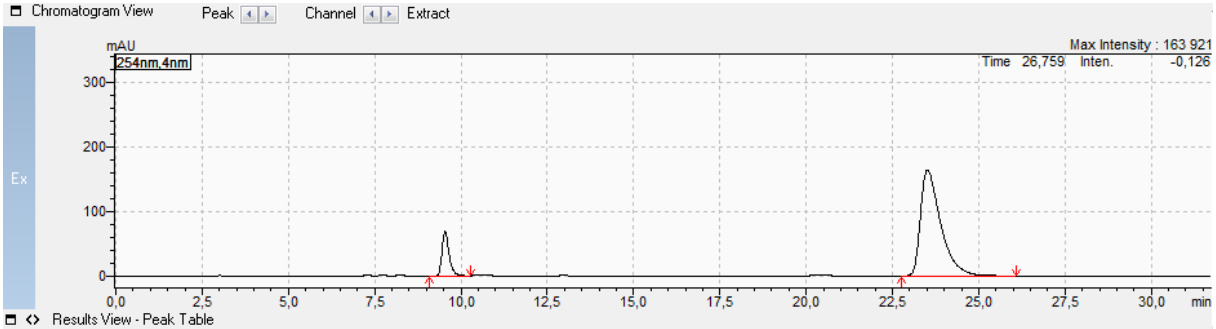
Method A:



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	10,971	12,551	455840	27436	0,000000	M	10,485	11,968	12,551
2	26,421	87,449	3176010	71558	0,000000	M	25,472	28,789	87,449
Total		100,000	3631850	98995					100,000

ee = 75 %

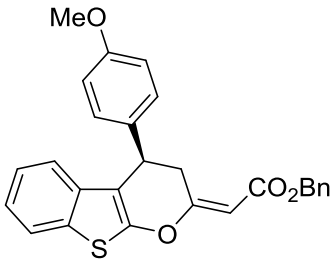
Method B:



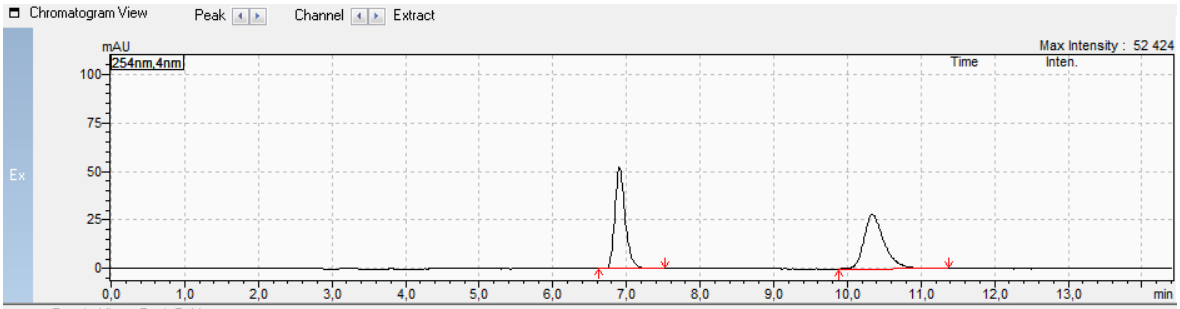
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	9,540	12,761	974976	68846	0,000000	M	9,077	10,272	12,761
2	23,517	87,239	6665498	164097	0,000000	M	22,763	26,101	87,239
Total		100,000	7640475	232943					100,000

ee = 73 %

Conditions: IB column

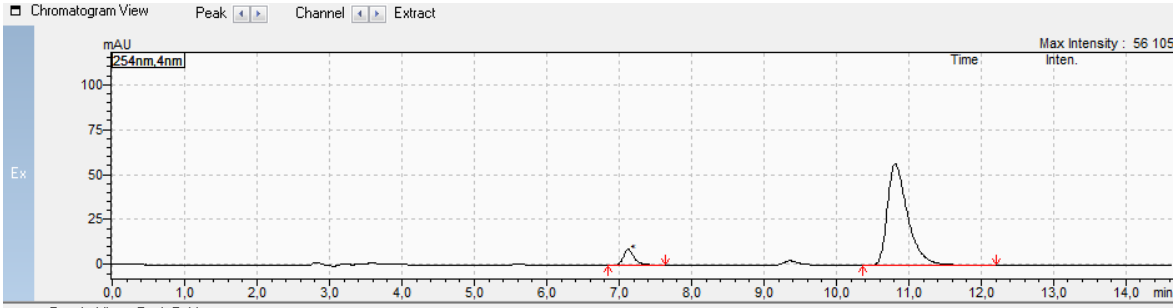


mobile phase: heptane / *i*-PrOH – 90:10
λ= 254 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3l**: t_R= 7.1 min (minor), t_R= 10.8 min (major).



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,903	49,009	510941	52489	0,000000	M	6,624	7,531	49,009
2	10,339	50,991	531600	27862	0,000000	M	9,888	11,381	50,991
Total		100,000	1042541	80351					100,000

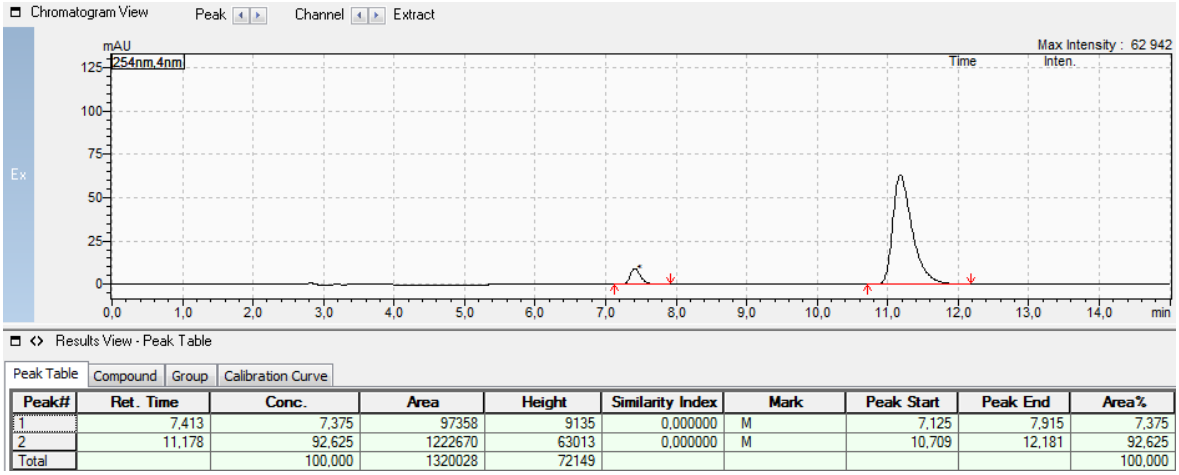
Method A:



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	7,124	7,543	88776	8734	0,000000	M	6,848	7,637	7,543
2	10,812	92,457	1088096	56390	0,000000	M	10,368	12,213	92,457
Total		100,000	1176872	65124					100,000

ee = 85 %

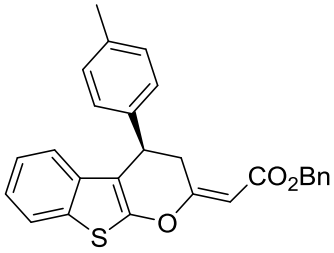
Method B:



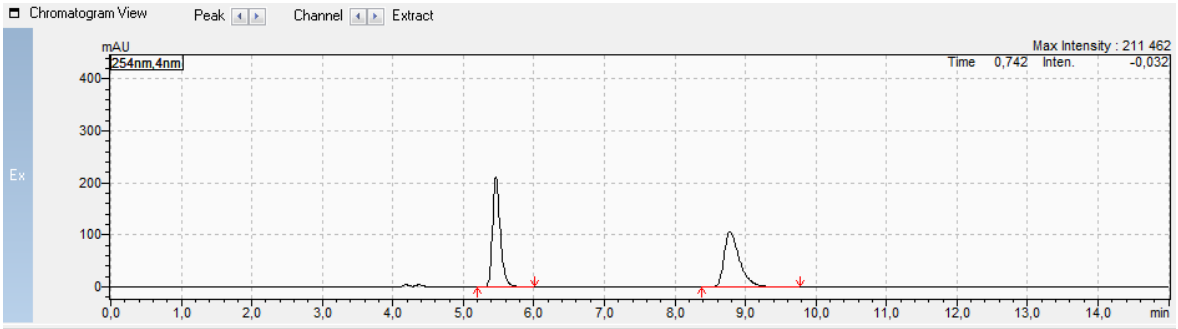
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	7,413	7,375	97358	9135	0,000000	M	7,125	7,915	7,375
2	11,178	92,625	1222670	63013	0,000000	M	10,709	12,181	92,625
Total		100,000	1320028	72149					100,000

ee = 85 %

Conditions: IB column



mobile phase: heptane / *i*-PrOH – 90:10
λ= 254 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3m**: t_R= 5.5 min (minor), t_R= 8.9 min (major).

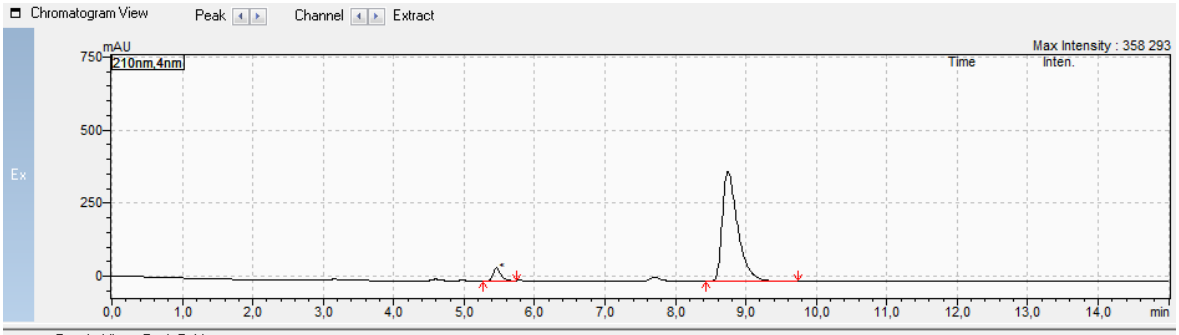


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,461	49,993	1616336	211514	0,000000	M	5,195	6,016	49,993
2	8,782	50,007	1616813	105928	0,000000	M	8,384	9,771	50,007
Total		100,000	3233149	317441					100,000

Method A:



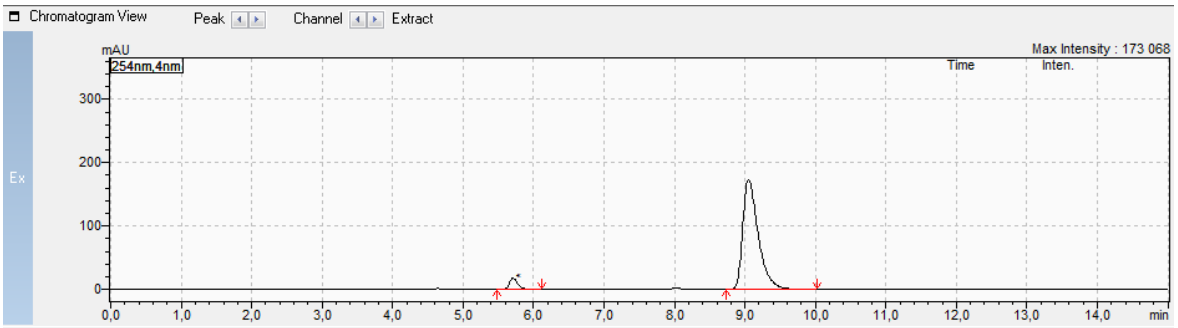
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,460	5,322	321594	43498	0,000000	M	5,269	5,739	5,322
2	8,745	94,678	5721633	375382	0,000000	M	8,427	9,739	94,678
Total		100,000	6043227	418879					100,000

ee = 89 %

Method B:



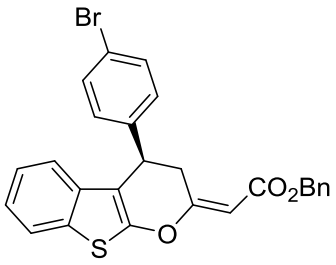
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

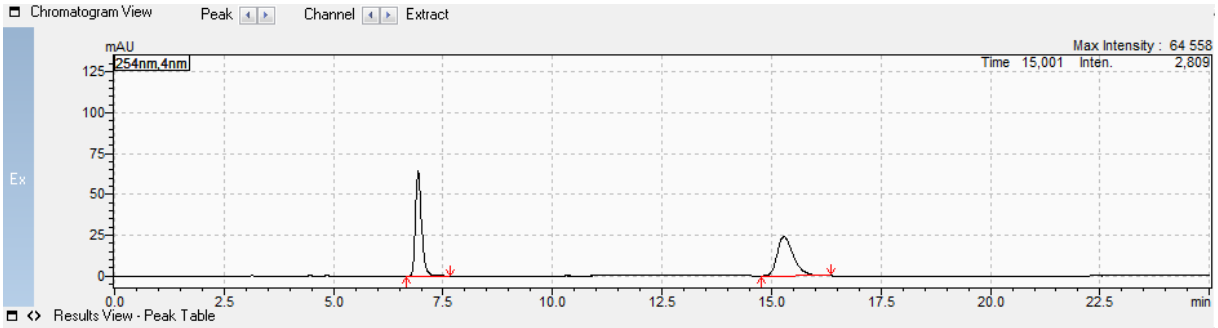
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,709	5,344	148413	18206	0,000000	M	5,472	6,112	5,344
2	9,052	94,656	2628924	172925	0,000000	M	8,725	10,027	94,656
Total		100,000	2777338	191131					100,000

ee = 89 %

Conditions: IB column



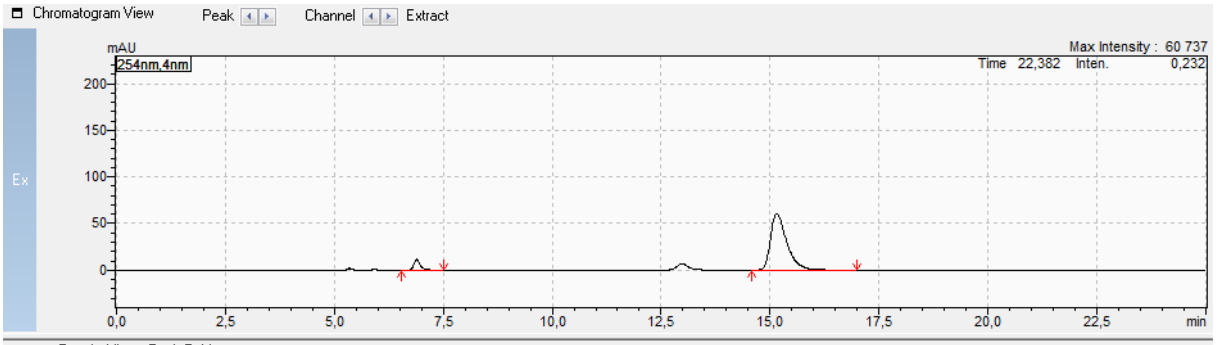
mobile phase: heptane / *i*-PrOH – 90:10
λ= 254 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3n**: t_R= 7.2 min (minor), t_R= 15.2 min (major).



Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,931	50,239	622148	64395	0,000000		6,667	7,669	50,239
2	15,282	49,761	616241	24075	0,000000		14,763	16,363	49,761
Total		100,000	1238389	88470					100,000

Method A:

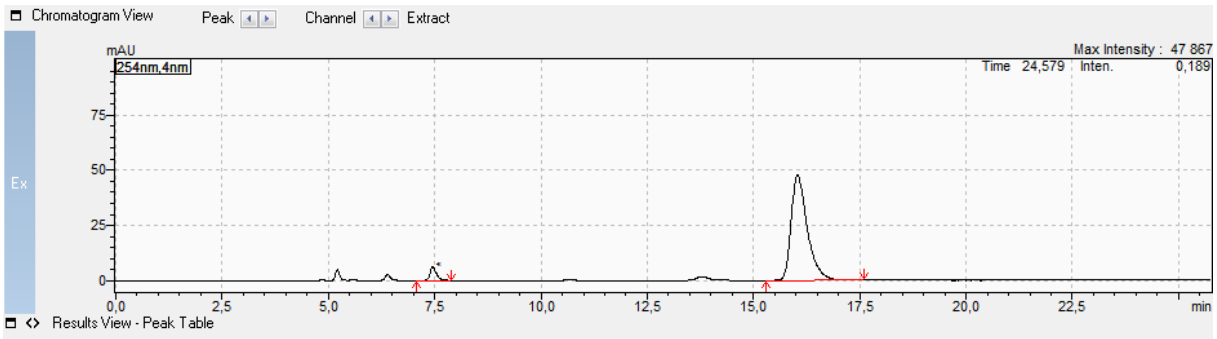


Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,885	6,957	116503	11541	0,000000	M	6,549	7,520	6,957
2	15,152	93,043	1558154	60542	0,000000	M	14,592	16,992	93,043
Total		100,000	1674657	72083					100,000

ee = 86 %

Method B:

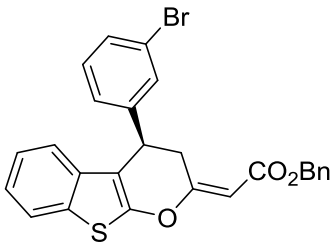


Peak Table | Compound | Group | Calibration Curve

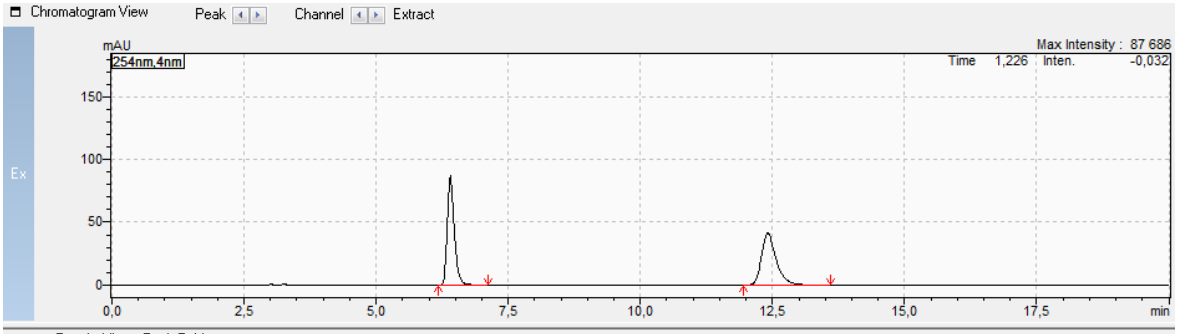
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	7,457	4,832	64065	6196	0,000000	M	7,061	7,904	4,832
2	16,036	95,168	1261775	47715	0,000000	M	15,285	17,611	95,168
Total		100,000	1325840	53912					100,000

ee = 90 %

Conditions: IB column

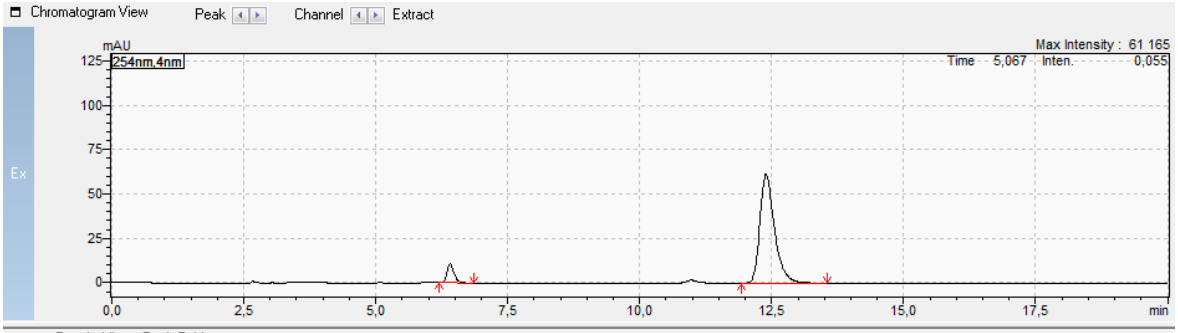


mobile phase: heptane / *i*-PrOH – 80:20
λ= 254 nm, *V*= 1.0 ml/min, *t* = 25 °C
for **3o**: t_R= 6.2 min (minor), t_R= 12.4 min (major).



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,404	50,026	798540	87782	0,000000		6,176	7,125	50,026
2	12,411	49,974	797701	41256	0,000000	S	11,957	13,589	49,974
Total		100,000	1596241	129038					100,000

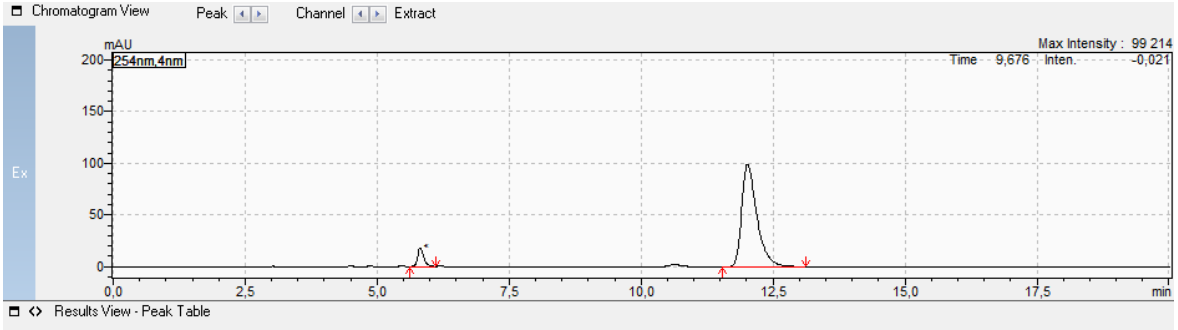
Method A:



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,408	7,624	97840	11003	0,000000	M	6,197	6,869	7,624
2	12,393	92,376	1185541	61414	0,000000	M	11,936	13,557	92,376
Total		100,000	1283381	72417					100,000

ee = 85 %

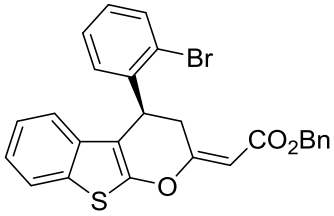
Method B:



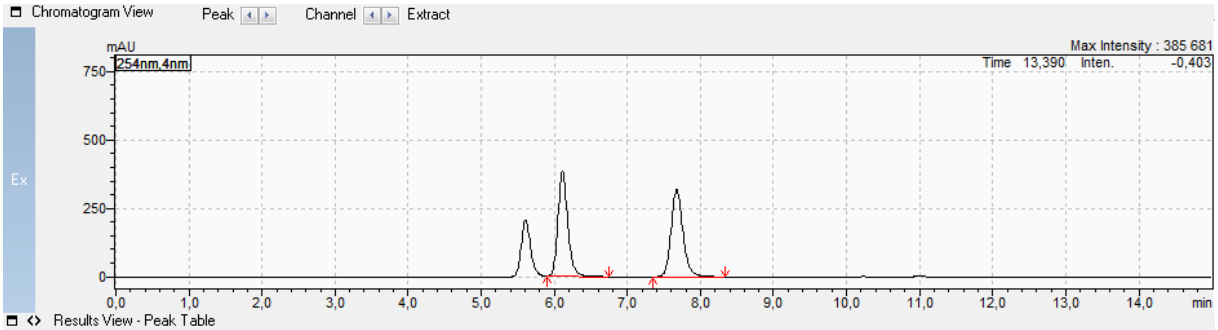
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,819	6,879	146503	18006	0,000000	M	5,611	6,112	6,879
2	12,017	93,121	1983271	99188	0,000000	M	11,541	13,109	93,121
Total		100,000	2129774	117194					100,000

ee = 86 %

Conditions: IA column

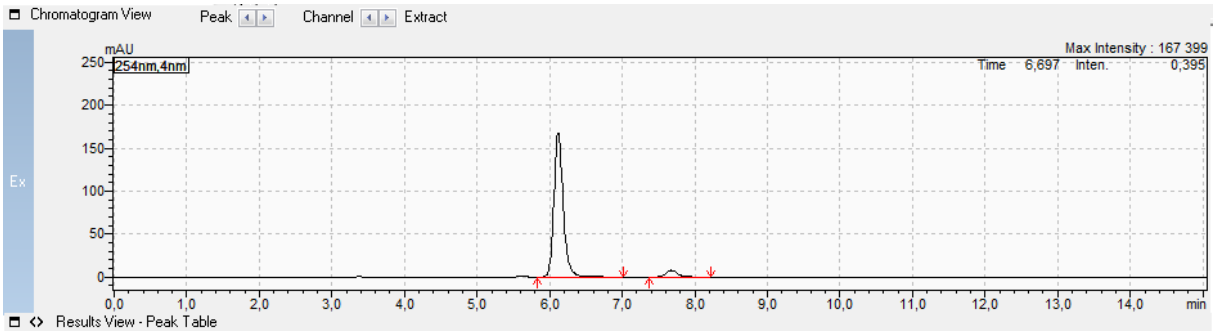


mobile phase: heptane / *i*-PrOH – 97:3
λ= 254 nm, *V*= 1.0 ml/min, *t* = 25 °C
for **3p**: t_R= 6.1 min (major), t_R= 7.7 min (minor).



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,112	49,784	3592276	383718	0,000000	M	5,899	6,752	49,784
2	7,674	50,216	3623453	317482	0,000000	M	7,349	8,341	50,216
Total		100,000	7215730	701199					100,000

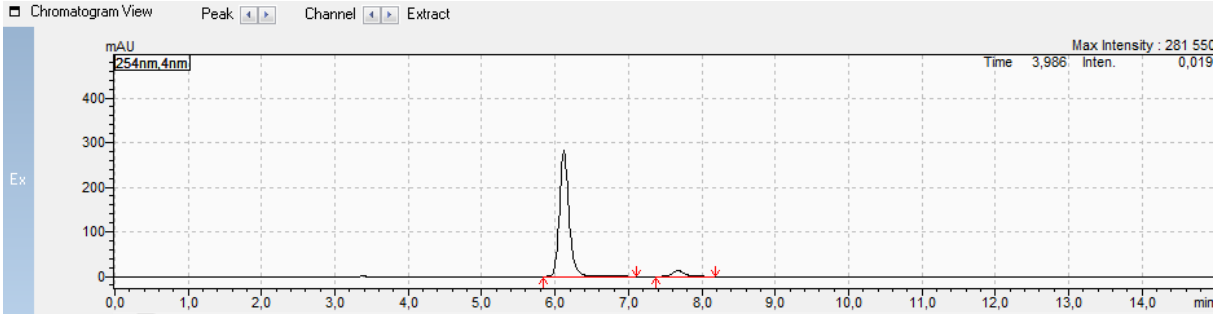
Method A:



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,118	94,621	1497859	167236	0,000000		5,835	7,008	94,621
2	7,678	5,379	85150	7697	0,000000		7,371	8,213	5,379
Total		100,000	1583008	174933					100,000

ee = 89 %

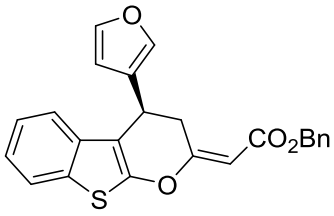
Method B:



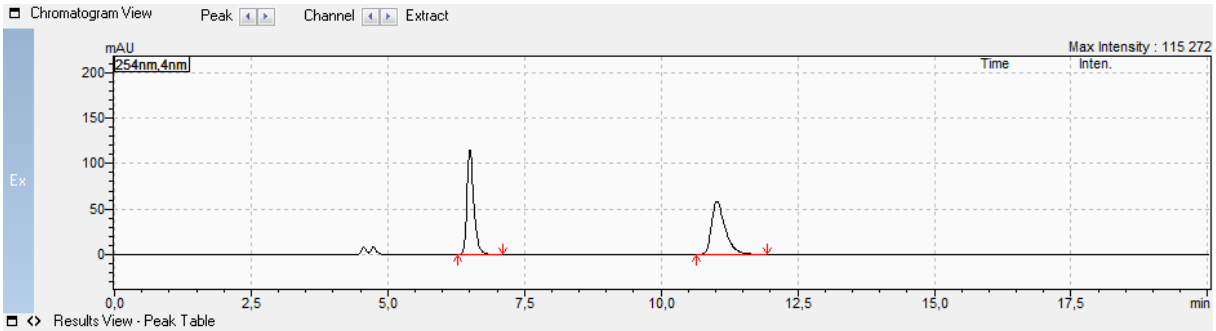
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,118	94,549	2560153	281485	0,000000		5,835	7,115	94,549
2	7,676	5,451	147604	13322	0,000000		7,371	8,192	5,451
Total		100,000	2707757	294807					100,000

ee = 88 %

Conditions: IB column



mobile phase: heptane / *i*-PrOH – 90:10
λ= 254 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3q**: t_R= 6.3 min (minor), t_R= 10.6 min (major).

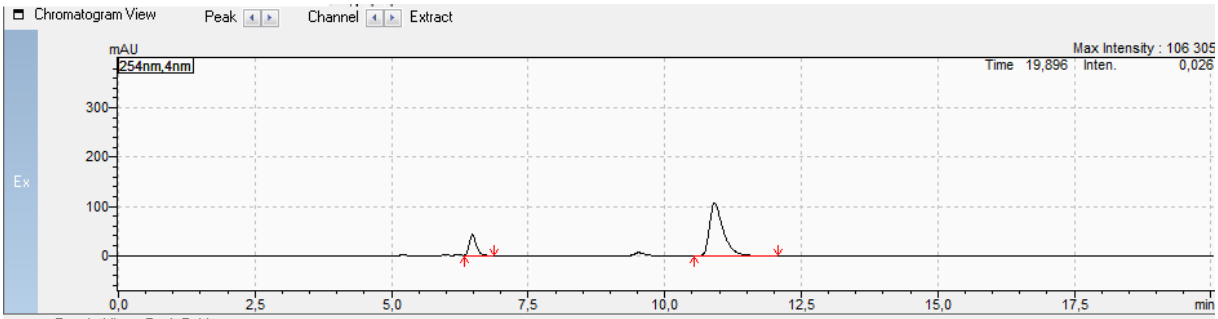


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,503	50,046	1011948	115173	0,000000		6,283	7,115	50,046
2	11,021	49,954	1010088	58095	0,000000		10,656	11,947	49,954
Total		100,000	2022036	173268					100,000

Method A:



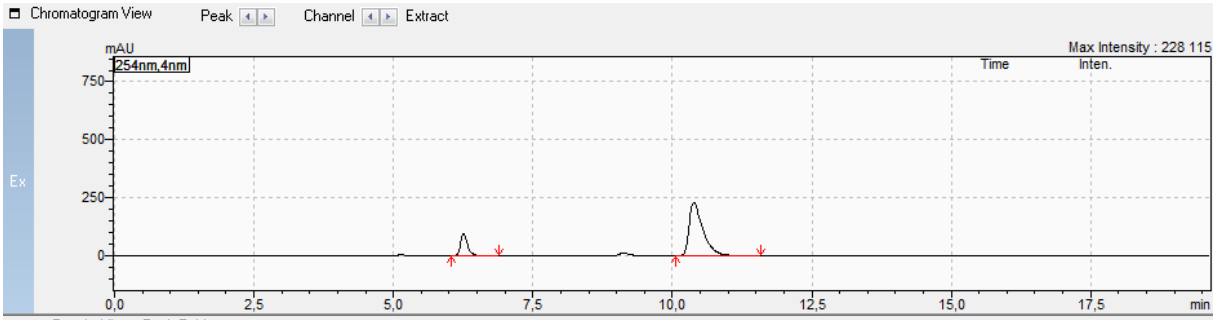
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,480	16,818	374301	43231	0,000000	M	6,325	6,880	16,818
2	10,914	83,182	1851288	106304	0,000000	M	10,549	12,064	83,182
Total		100,000	2225589	149535					100,000

ee = 66 %

Method B:



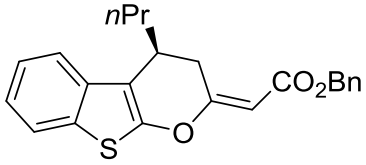
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

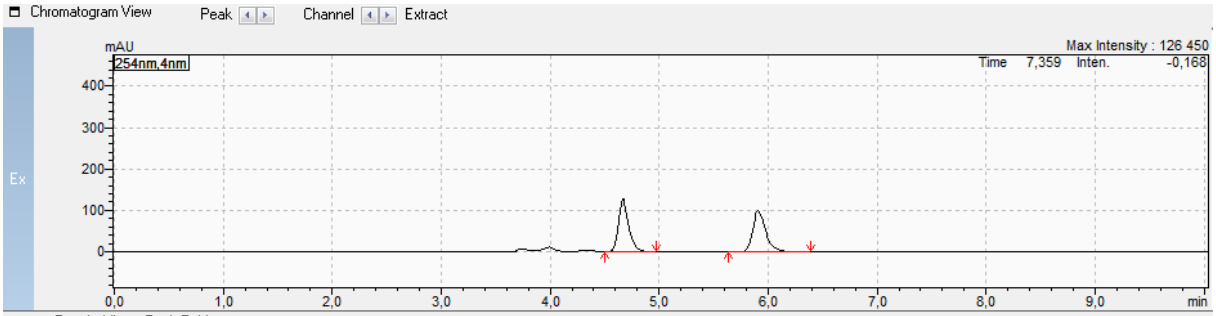
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,258	17,077	809693	94488	0,000000		6,027	6,880	17,077
2	10,385	82,923	3931786	228029	0,000000		10,059	11,595	82,923
Total		100,000	4741480	322517					100,000

ee = 66 %

Conditions: IB column



mobile phase: heptane / *i*-PrOH – 90:10
λ= 254 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3r**: t_R= 4.6 min (minor), t_R= 5.9 min (major).

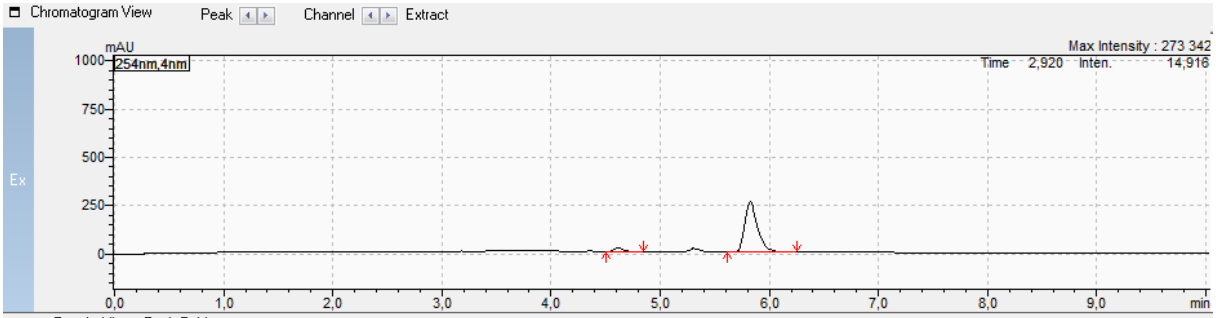


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	4,667	50,027	823617	126304	0,000000	M	4,501	4,971	50,027
2	5,910	49,973	822729	99964	0,000000	M	5,632	6,389	49,973
Total		100,000	1646346	226268					100,000

Method A:



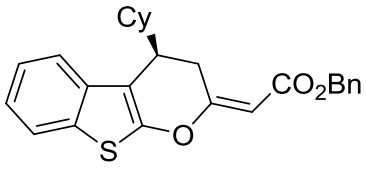
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

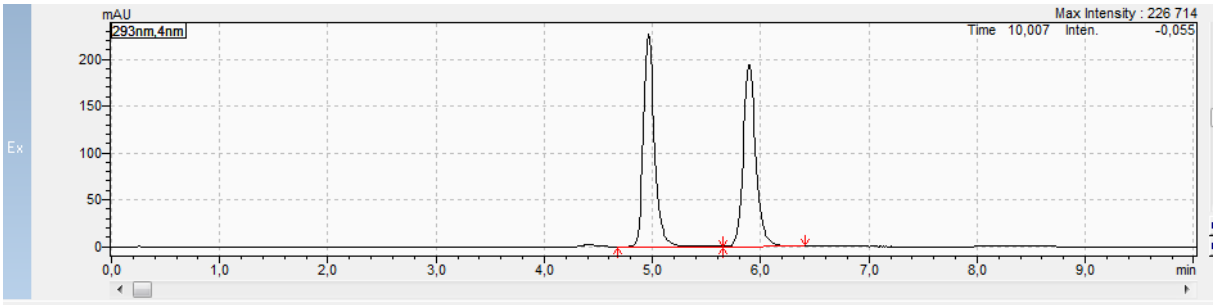
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	4,613	5,592	125550	19615	0,000000	M	4,501	4,843	5,592
2	5,825	94,408	2119650	262810	0,000000	M	5,611	6,251	94,408
Total		100,000	2245200	282425					100,000

ee = 89 %

Conditions: IA column



mobile phase: heptane / *i*-PrOH – 97:3
λ= 293 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3s**: t_R= 5.0 min (major), t_R= 6.0 min (minor).

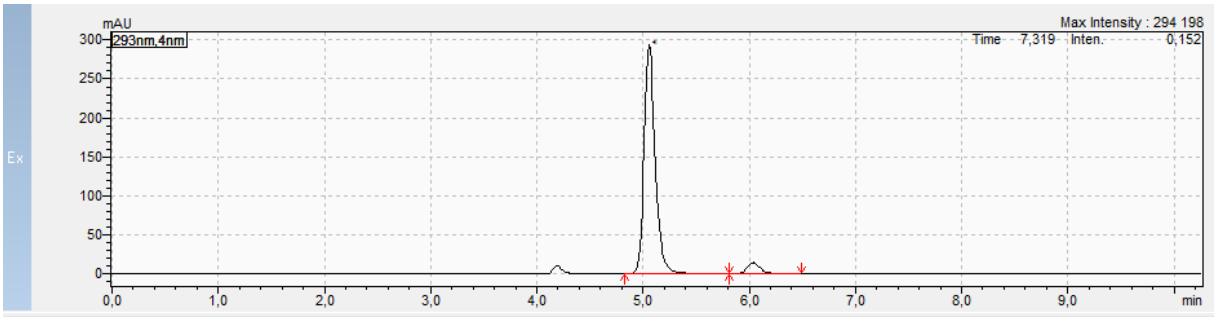


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	4,963	50,246	1606823	226736	0,000000	S	4,672	5,653	50,246
2	5,893	49,754	1591097	193411	0,000000	V	5,653	6,411	49,754
Total		100,000	3197919	420147					100,000

Method A:



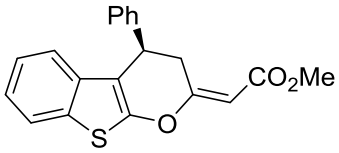
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

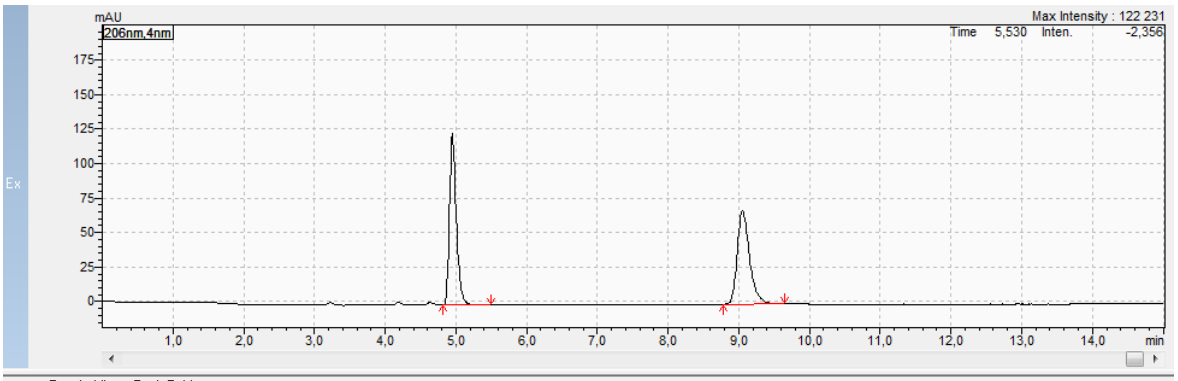
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,059	94,568	2133166	294073	0,000000		4,832	5,813	94,568
2	6,038	5,432	122519	14363	0,000000	V	5,813	6,496	5,432
Total		100,000	2255685	308437					100,000

ee = 89 %

Conditions: IB column



mobile phase: heptane / *i*-PrOH – 90:10
λ= 206 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **3t**: t_R= 5.0 min (minor), t_R= 9.1 min (major).

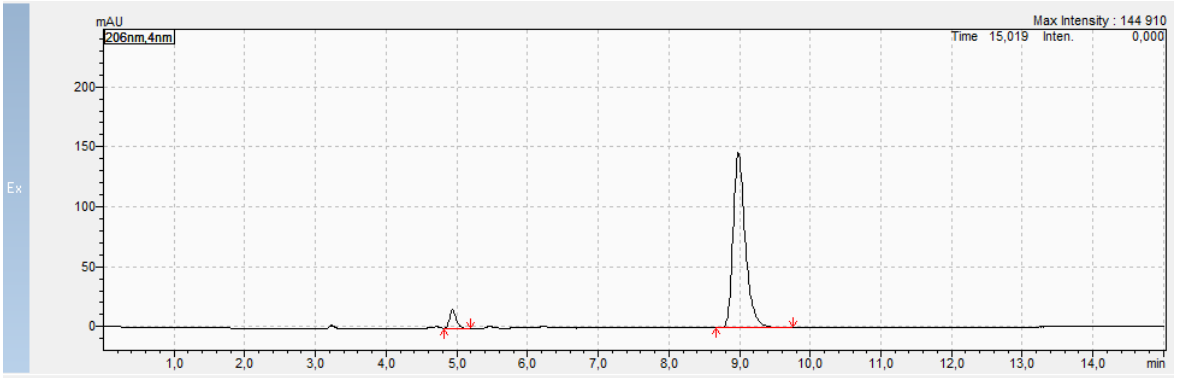


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	4,951	50,084	828835	124713	0,000000	S	4,811	5,504	50,084
2	9,054	49,916	826055	68233	0,000000		8,779	9,643	49,916
Total		100,000	1654890	192946					100,000

Method A:



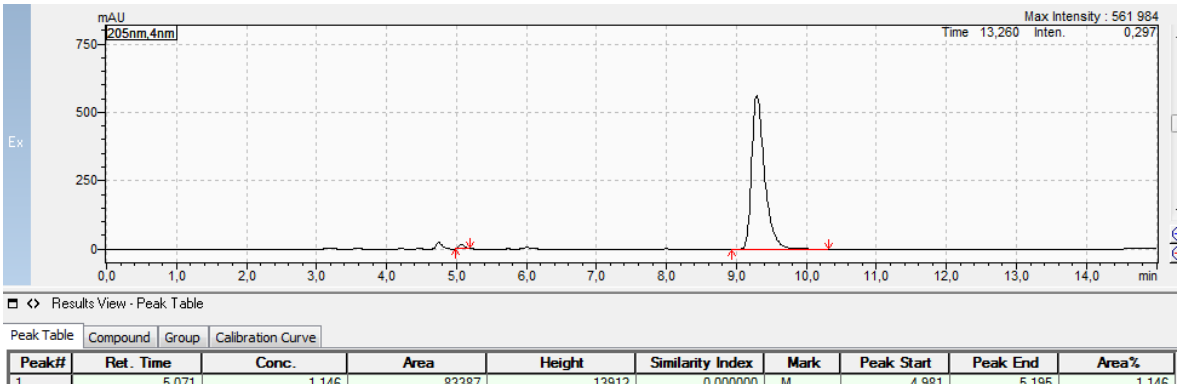
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	4,937	5,530	102547	15725	0,000000		4,821	5,195	5,530
2	8,983	94,470	1751914	145774	0,000000	S	8,661	9,760	94,470
Total		100,000	1854461	161499					100,000

ee = 89 %

Method B:



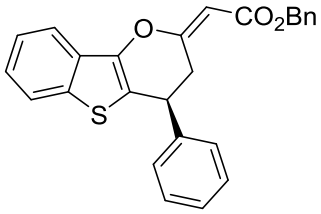
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

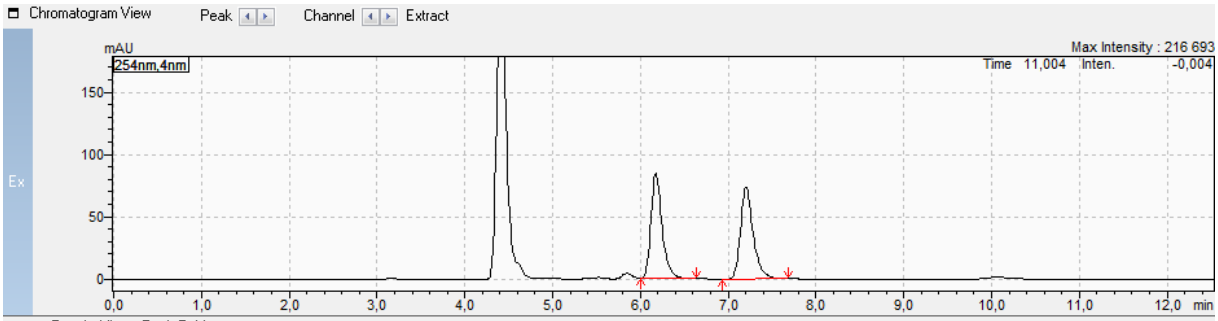
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,071	1,146	83387	13912	0,000000	M	4,981	5,195	1,146
2	9,291	98,854	7192132	561797	0,000000	M	8,928	10,315	98,854
Total		100,000	7275520	575709					100,000

ee = 98 %

Conditions: IB column

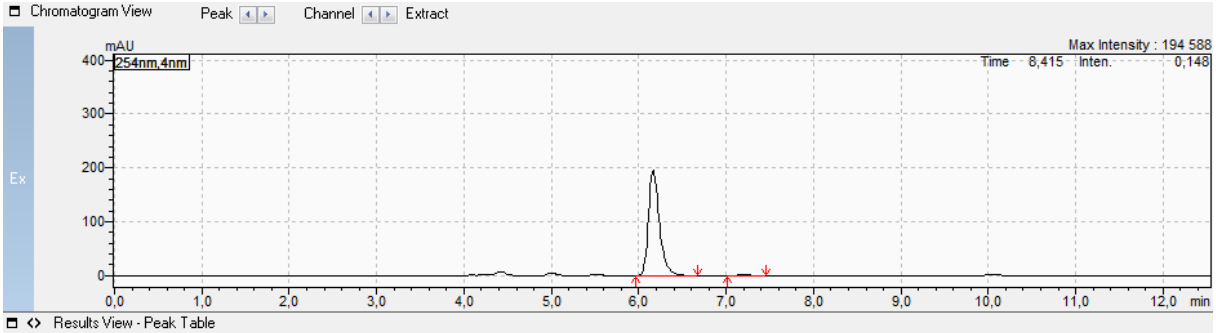


mobile phase: heptane / *i*-PrOH – 90:10
λ= 254 nm, V= 1.0 ml/min, t= 25 °C
for **6a**: t_R= 6.2 min (major), t_R= 7.2 min (minor).



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,175	50,115	746450	85037	0,000000	M	6,005	6,635	50,115
2	7,203	49,885	743023	73491	0,000000	M	6,933	7,680	49,885
Total		100,000	1489474	158528					100,000

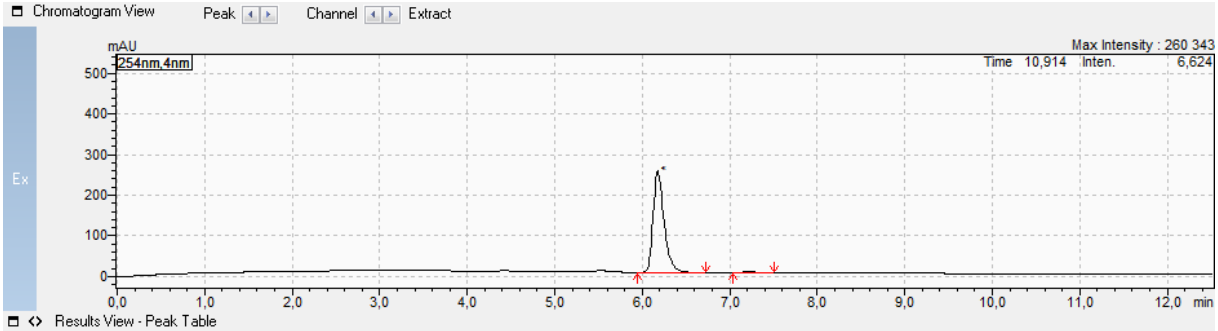
Method A:



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,164	99,069	1692415	194345	0,000000	M	5,963	6,677	99,069
2	7,195	0,931	15904	1654	0,000000	M	7,008	7,456	0,931
Total		100,000	1708319	195998					100,000

ee = 98 %

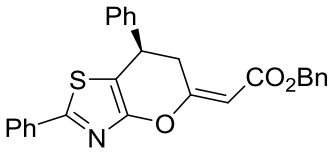
Method B:



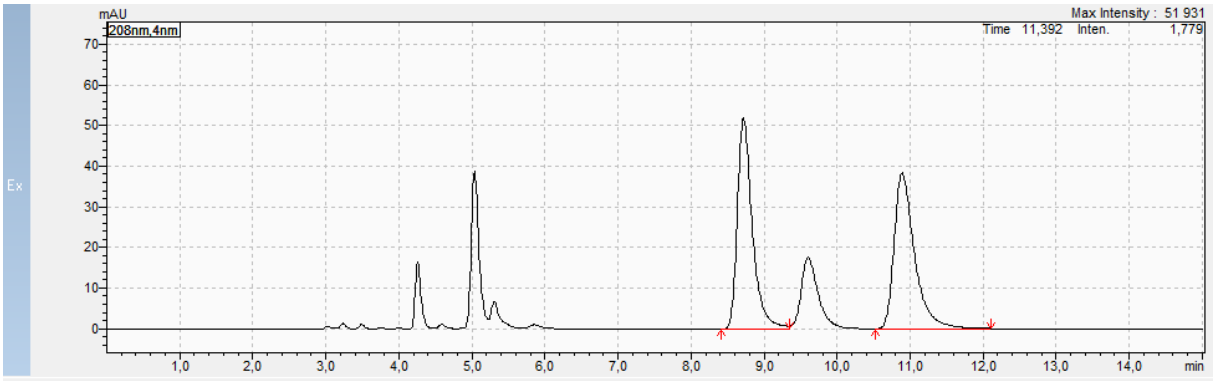
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	6,177	98,811	2176247	250242	0,000000	M	5,941	6,731	98,811
2	7,218	1,189	26197	2726	0,000000	M	7,040	7,509	1,189
Total		100,000	2202444	252968					100,000

ee = 98 %

Conditions: IB column



mobile phase: heptane / *i*-PrOH – 80:20
λ= 208 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **6b**: t_R= 8.7 min (major), t_R= 10.9 min (minor).

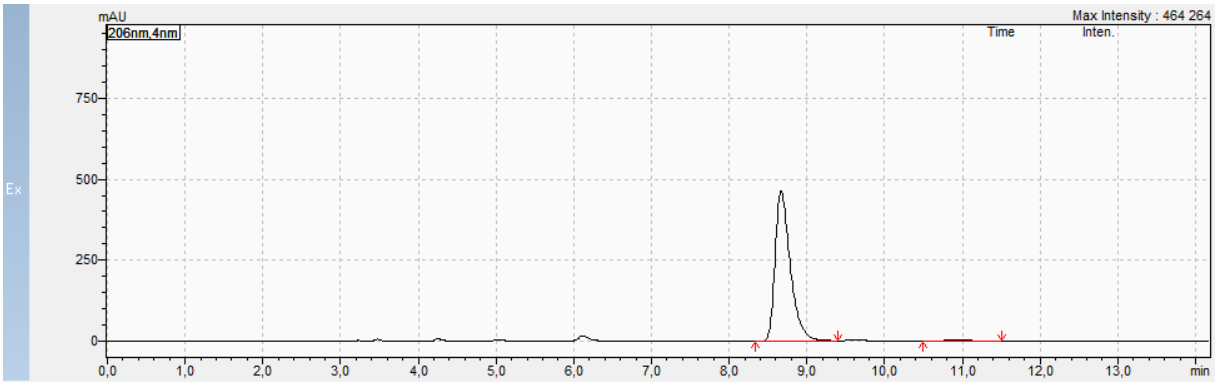


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	8,718	49,993	745090	52047	0,000000		8,405	9,344	49,993
2	10,891	50,007	745299	38330	0,000000	S	10,517	12,107	50,007
Total		100,000	1490388	90377					100,000

Method A:



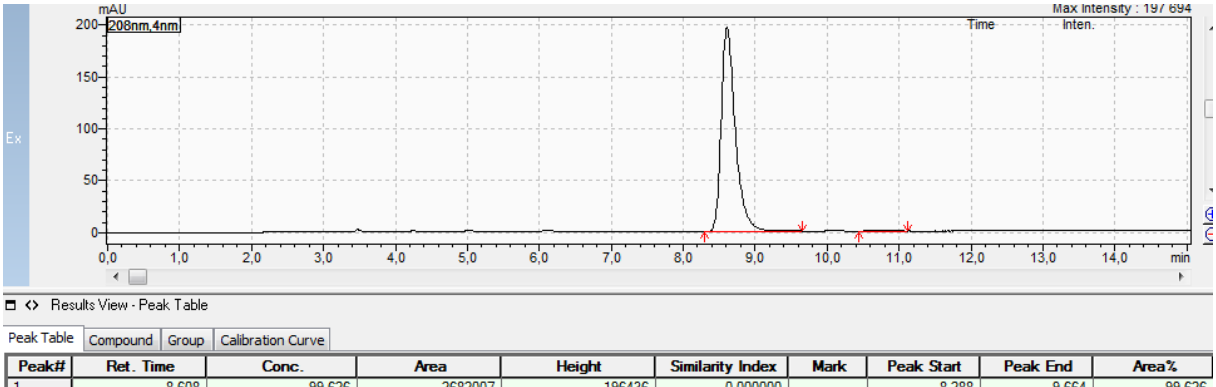
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	8,666	98,742	6286082	464362	0,000000	M	8,331	9,397	98,742
2	10,914	1,258	80109	4338	0,000000		10,496	11,499	1,258
Total		100,000	6366192	468700					100,000

ee = 98 %

Method B:



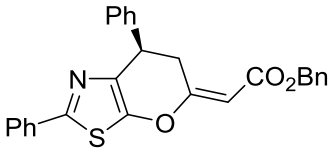
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

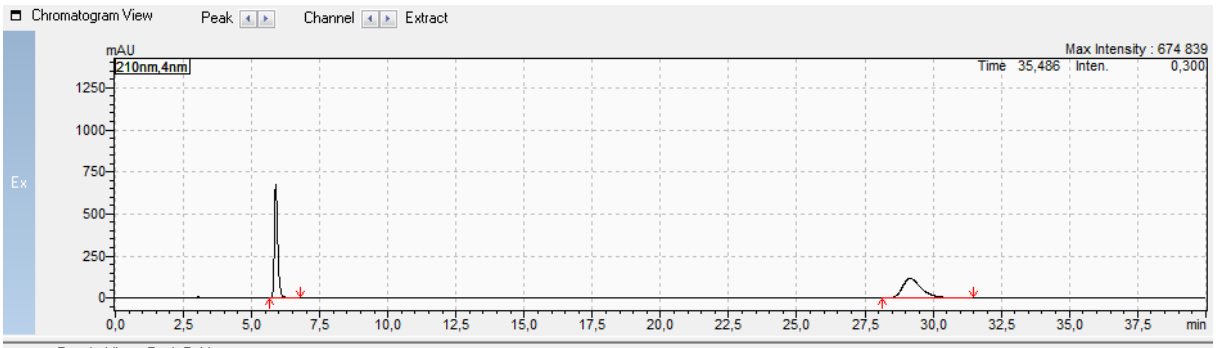
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	8,608	99,626	2682007	196436	0,000000		8,288	9,664	99,626
2	10,729	0,374	10061	597	0,000000		10,443	11,115	0,374
Total		100,000	2692068	197033					100,000

ee = 99 %

Conditions: IB column

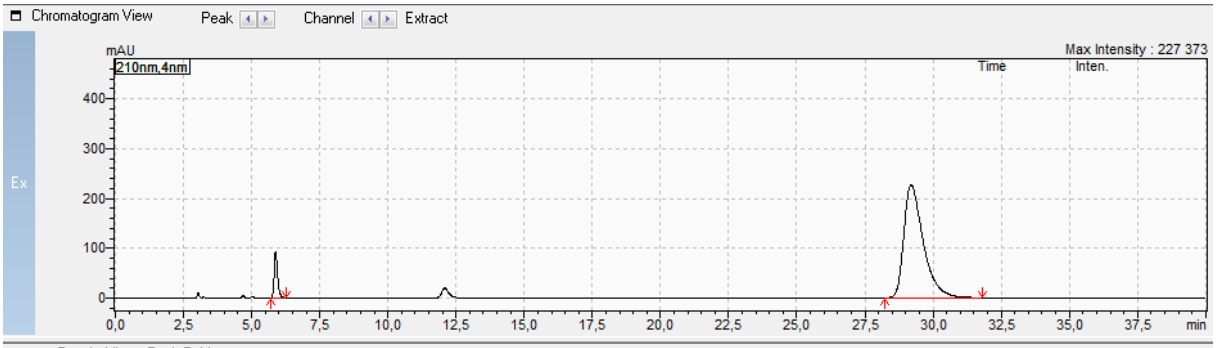


mobile phase: heptane / *i*-PrOH – 80:20
λ= 210 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **6c**: t_R= 5.9 min (minor), t_R= 29.2 min (major).



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,887	50,393	5715740	673818	0,000000	M	5,664	6,784	50,393
2	29,158	49,607	5626515	116521	0,000000		28,139	31,488	49,607
Total		100,000	11342256	790339					100,000

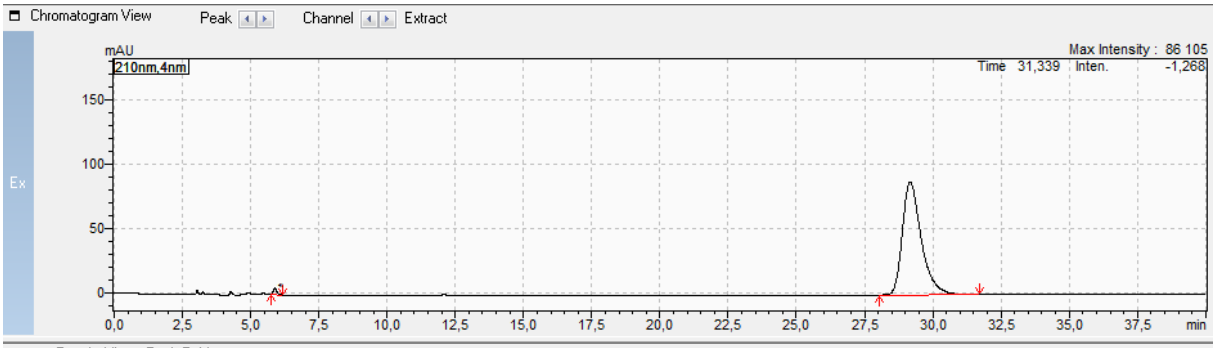
Method A:



Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,881	6,581	786825	92650	0,000000	M	5,696	6,283	6,581
2	29,197	93,419	11168539	226224	0,000000		28,213	31,829	93,419
Total		100,000	11955363	318873					100,000

ee = 87 %

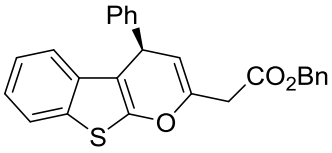
Method B:



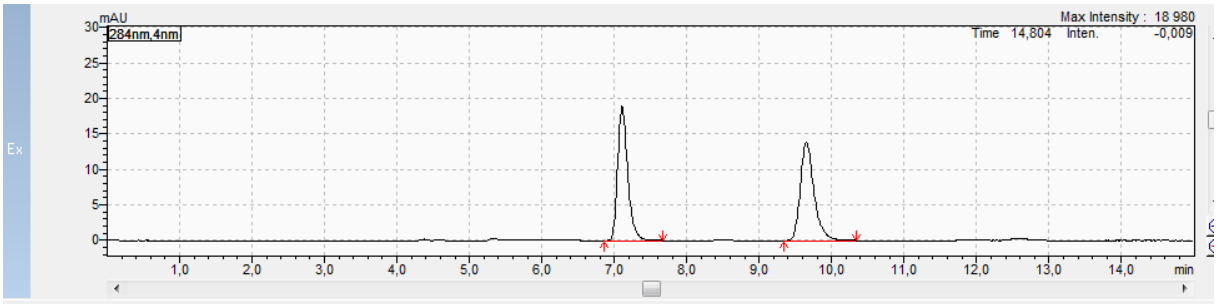
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	5,887	0,980	41764	4925	0,000000	M	5,728	6,176	0,980
2	29,172	99,020	4221420	87581	0,000000	M	28,032	31,733	99,020
Total		100,000	4263184	92506					100,000

ee = 98 %

Conditions: IB column



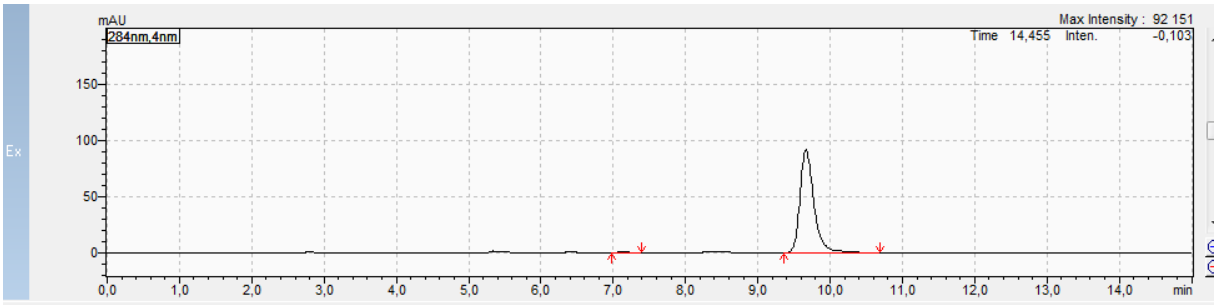
mobile phase: heptane / *i*-PrOH – 90:10
λ= 284 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **4a**: t_R= 7.1 min (minor), t_R= 9.7 min (major).



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	7,108	49,965	183220	18999	0,000000		6,859	7,669	49,965
2	9,652	50,035	183476	13930	0,000000		9,344	10,336	50,035
Total		100,000	366695	32928					100,000



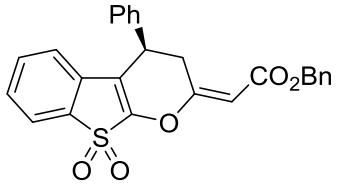
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

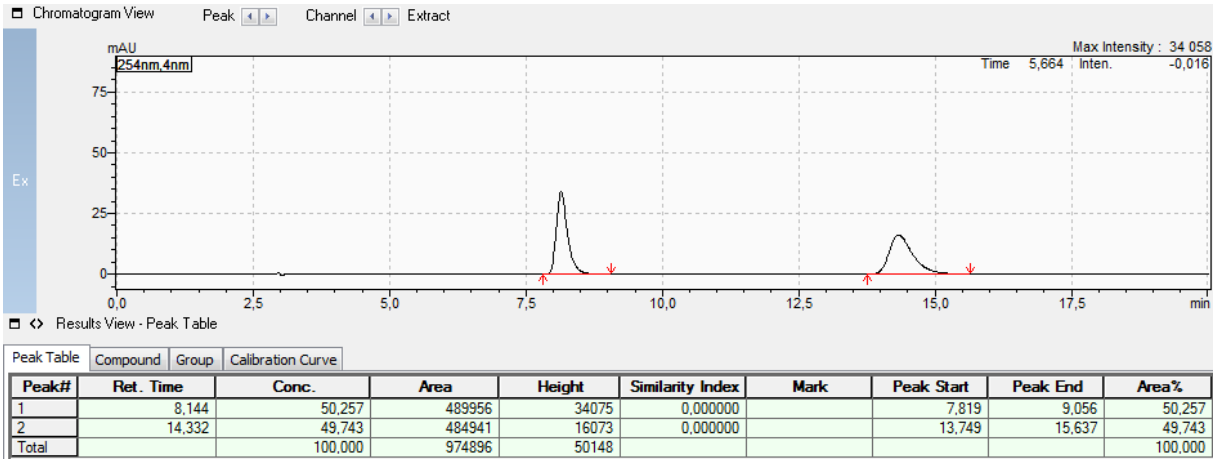
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	7,130	0,501	6164	679	0,000000		6,976	7,392	0,501
2	9,668	99,499	1223673	92218	0,000000		9,365	10,699	99,499
Total		100,000	1229837	92898					100,000

ee = 99 %

Conditions: IB column



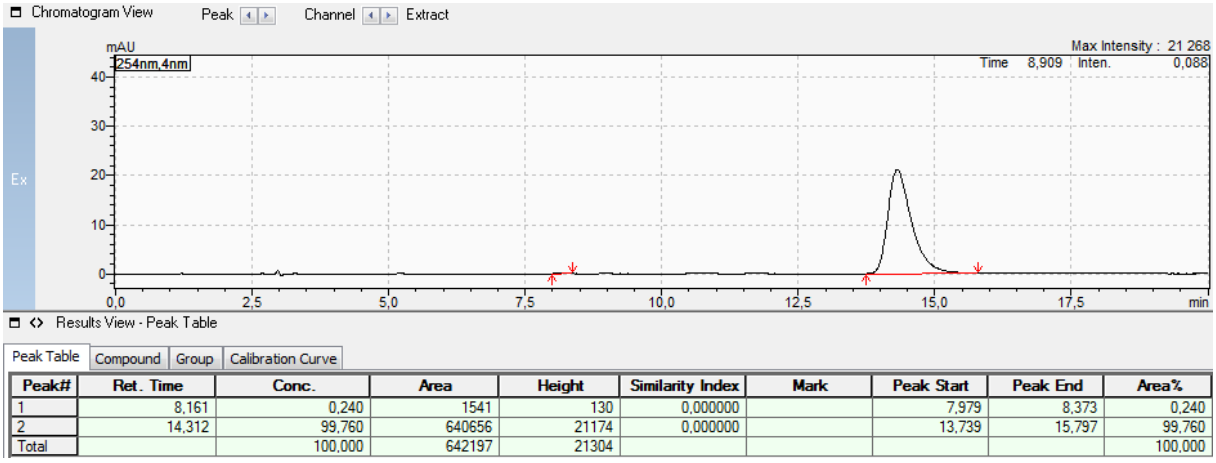
mobile phase: heptane / *i*-PrOH – 60:40
λ= 254 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **8**: t_R= 8.1 min (minor), t_R= 10.9 min (major).



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	8,144	50,257	489956	34075	0,000000		7,819	9,056	50,257
2	14,332	49,743	484941	16073	0,000000		13,749	15,637	49,743
Total		100,000	974896	50148					100,000



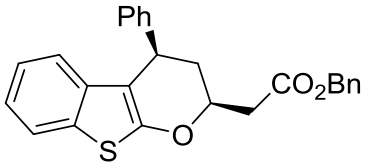
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

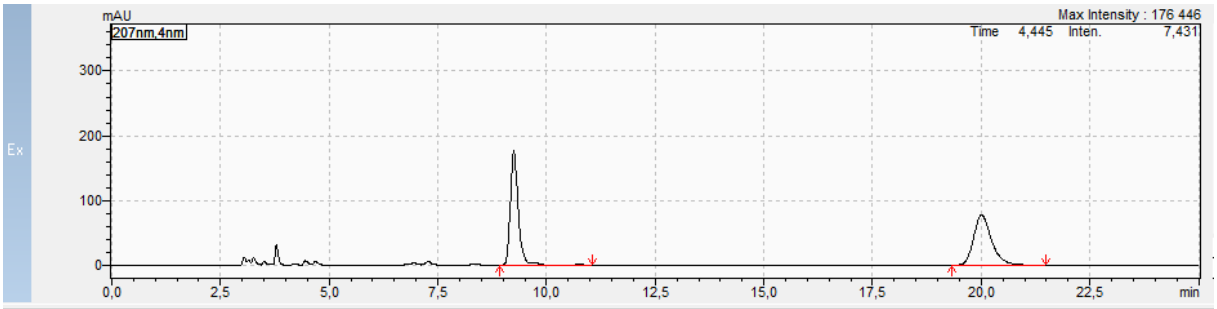
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	8,161	0,240	1541	130	0,000000		7,979	8,373	0,240
2	14,312	99,760	640656	21174	0,000000		13,739	15,797	99,760
Total		100,000	642197	21304					100,000

ee = 99 %

Conditions: IB column



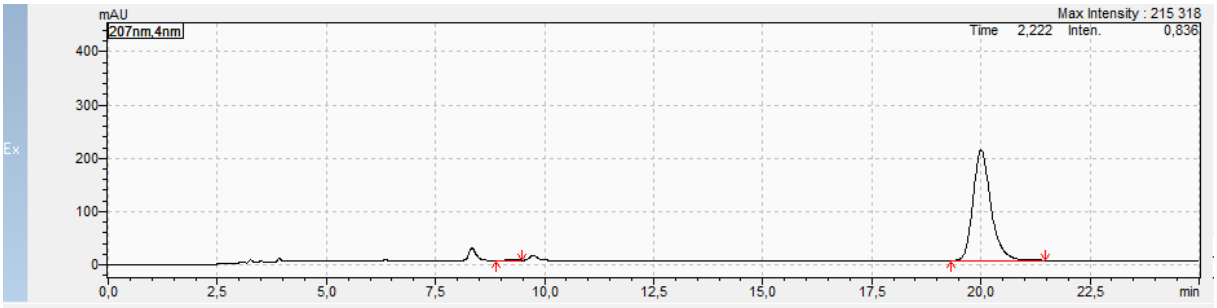
mobile phase: heptane / *i*-PrOH – 90:10
λ= 207 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **9**: t_R= 9.2 min (minor), t_R= 20.0 min (major).



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	9,248	50,716	2262539	175937	0,000000	S	8,907	11,061	50,716
2	20,010	49,284	2198668	77127	0,000000	SV	19,317	21,472	49,284
Total		100,000	4461208	253064					100,000



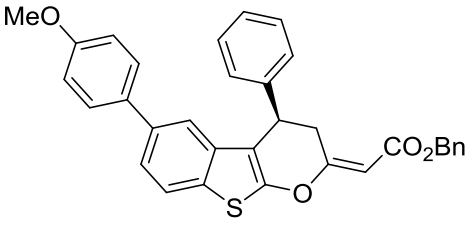
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

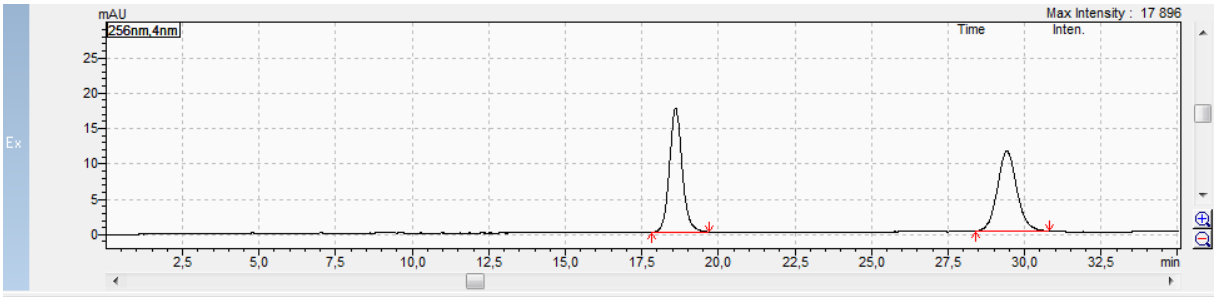
Peak#	Ret. Time	Conc.	Area	Height	Similarity Index	Mark	Peak Start	Peak End	Area%
1	9,246	0,455	26840	2087	0,000000		8,885	9,483	0,455
2	20,005	99,545	5875411	206800	0,000000	S	19,328	21,483	99,545
Total		100,000	5902251	208887					100,000

ee = 99 %

Conditions: IA column



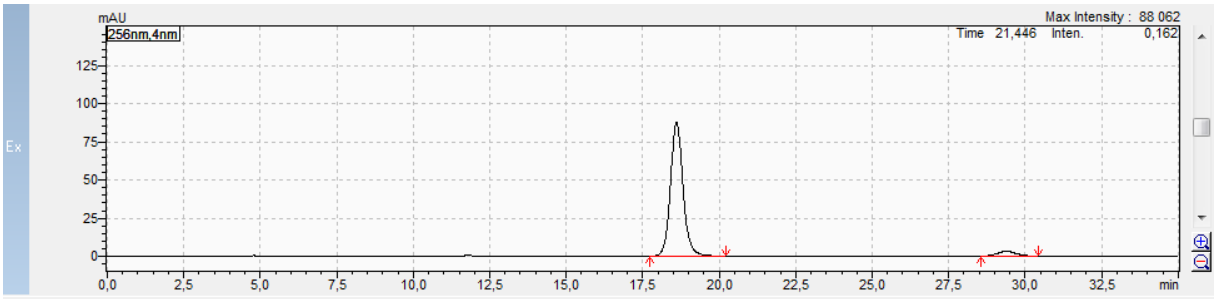
mobile phase: heptane / *i*-PrOH – 97:3
λ= 256 nm, *V*= 1.0 ml/min, *t*= 25 °C
for **10**: t_R= 18.6 min (major), t_R= 9.7 min (minor).



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	18,601	50,316	508648	17540	0,000000		17,813	19,691	50,316
2	29,416	49,684	502257	11352	0,000000		28,384	30,827	49,684
Total		100,000	1010905	28891					100,000



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	18,605	94,890	2528726	87873	0,000000		17,717	20,224	94,890
2	29,395	5,110	136181	3099	0,000000		28,555	30,421	5,110
Total		100,000	2664907	90973					100,000

ee = 90 %