Chiral Brønsted Acid-Catalyzed Enantioselective Friedel-Crafts Reaction of 2-Methoxyfuran with Aliphatic Ketimines Generated in Situ

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Electronic Supplementary Information

Contents:

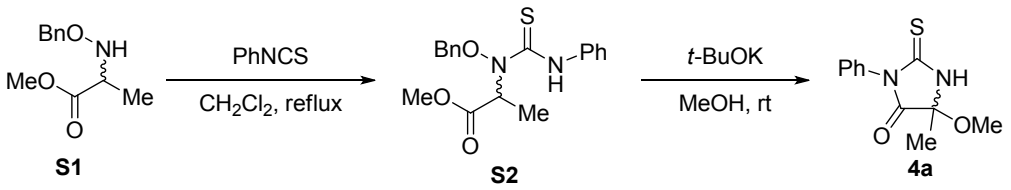
1. General Information:

^{1}H NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, CD_3OD: 3.31 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, br = broad, m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECA600 (150.9 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm, CD_3OD: 49.0 ppm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on silica gel 60 N (Merck: 0.040-0.063 mm, 230-400 mesh ASTM). High-performance liquid chromatography (HPLC) was performed on a Jasco equipped with a variable wavelength detector using Daicel chiral column (0.46 × 25 cm). Optical rotations were measured on a Jasco P-1020 digital polarimeter with a sodium lamp and reported as follows; $[\alpha]^{T\,^{\circ}C}_{D}$ (c = g/100 mL, solvent). Infrared (IR) spectra were recorded on a Jasco FT/IR-4100 spectrometer. Mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T spectrometer at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University. Unless otherwise noted, all reactions were carried out under argon atmosphere in dried glassware. All substrates were purified by column chromatography to use. Toluene, dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents were dried over activated MS 4A and used under argon atmosphere. Reagents were purchased from commercial suppliers and used without further purification. The other simple chemicals were used as such.

2. Experimental Procedure

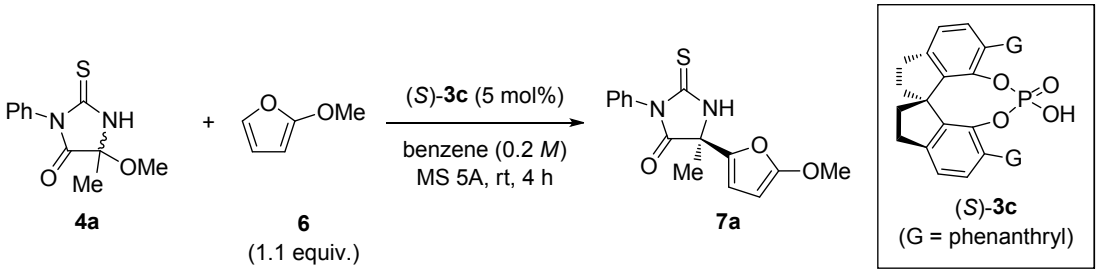
2-1. Preparation of Hemiaminal Methyl Ester 4

Synthesis of **4a** is representative. Hydantoin derivatives **5** were synthesized according to the similar procedure using isocyanates instead of isothiocyanates.



Representative Procedure: To a solution of **S1** (0.42 g, 2.0 mmol) in CH_2Cl_2 (1.0 mL) was added phenylisothiocyanate (1.2 mL, 10 mmol) at room temperature.[1] The reaction mixture was stirred at 40 °C for 2 days. Then the reaction mixture was directly purified by column chromatography (Hexane/EtOAc = 10/1-4/1 as eluent) to give **S2** quantitatively as colorless oil. **S2** (0.69 g, 2.0 mmol) thus obtained was dissolved in MeOH (20 mL) and cooled to 0 °C. *t*-BuOK (0.45 g, 4.0 mmol) was added to the solution at 0 °C. The resulting mixture was stirred at room temperature for 2 days. The reaction mixture was then passed through a pad of silica gel using CH_2Cl_2 as eluent. After removing the solvent under reduced pressure, the crude material was purified by flash column chromatography on silica gel (Hexane/EtOAc = 4/1) to provide hemiaminal methyl ether **4a** in 69% yield (over 2 steps) as a white solid.

2-2. Main Reaction



Representative Procedure: To a suspension of **4a** (24 mg, 0.10 mmol), 2-methoxyfuran[2] (10 μL, 0.11 mmol) and MS 5A (100 mg) in benzene (0.50 mL) was added (*S*)-**3c** (5 mol%, 3.3 mg, 5.0 μmol) at room temperature. After stirring for 4 h at room temperature, the reaction mixture was directly subjected to purification by silica gel column chromatography (Hexane/EtOAc = 4/1-2/1 as eluent) to give **7a** (30 mg, >99%) as a white solid. The enantiomeric excess of **7a** was determined by chiral stationary phase HPLC analysis.

Configuration Assignment: The absolute configuration of **7a** was determined to be (*S*) by X-ray crystallographic analysis; See section 5 for details.

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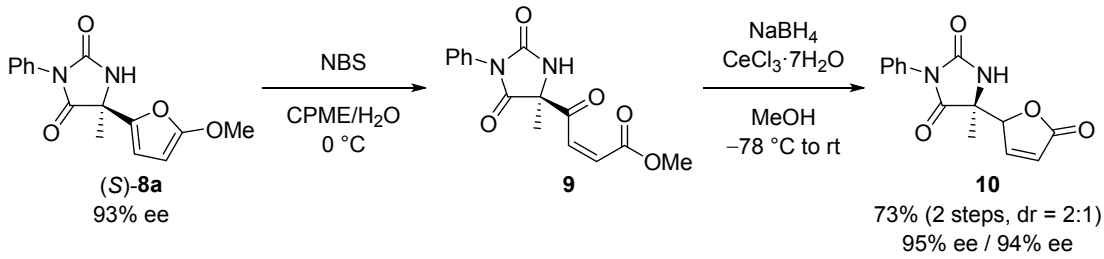
1 Amino acid ester **S1** was prepared according to a modified procedure of the known method, see (a) S. Hanessian and R.-Y. Yang, *Tetrahedron Lett.*, 1996, **37**, 5835; (b) T. Naito, K. Yamakawa, N. Yoshioka, M. Ueda and H. Miyabe, *Tetrahedron*, 2000, **56**, 2413.

2 2-Methoxyfuran was purified by distillation to use.

2-3. Derivatization of Product



(*S*)-**8a**
93% ee

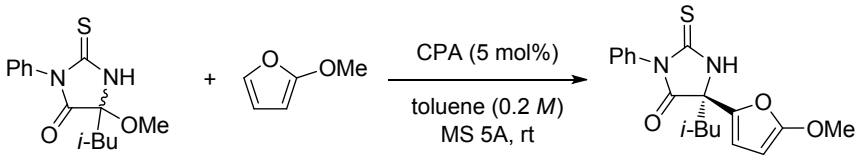
9

10
73% (2 steps, dr = 2:1)
95% ee / 94% ee

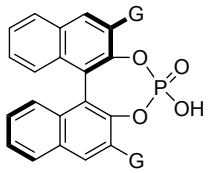
To a solution of (*S*)-**8a** (93% ee, 73 mg, 0.25 mmol) in a mixture of 2.5 mL of cyclopentyl methyl ether and 0.60 mL of H_2O was added NBS (48 mg, 0.27 mmol) at 0 °C. After stirring for 30 min at 0 °C, 1.0 mL of sat. $NaHCO_3$ aq. was added, and the mixture was stirred for 15 min at that temperature. Then, the resulting biphasic solution was extracted with $CHCl_3$ (×3), and the combined organic layer was washed with H_2O (×2), dried over Na_2SO_4, filtrated and evaporated to provide **9** as a white solid in 90% NMR yield. The crude mixture was used without other purification in the following step. To a solution of **9** in 5.0 mL of MeOH was added $CeCl_3 \cdot 7H_2O$ (0.14 g, 0.38 mmol). The resulting solution was cooled to -78 °C and $NaBH_4$ (9.6 mg, 0.25 mmol) was added portionwise. After stirring for 15 min at -78 °C, the resulting solution was allowed to warm to room temperature and stirred for additional 3 h. The reaction mixture was then diluted with sat. NH_4Cl aq. and extracted with EtOAc (×3). The combined organic phase was dried over Na_2SO_4 and filtrated. After concentration, the crude mixture was purification by silica gel column chromatography (Hexane/EtOAc = 1/2-1/4 as eluent) to afford **10** as a white solid in 73% yield (2 steps, dr = 68:32, 95% ee (major), 94% ee (minor)).

3. Exploratory Investigation of the Effect of Catalysts and Solvents

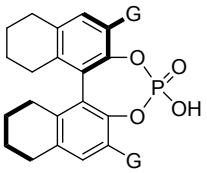
3-1. Preliminary Screening of Catalysts[a]



(±)-**4b** **6** (1.1 equiv.) **7b**



(*R*)-**1**



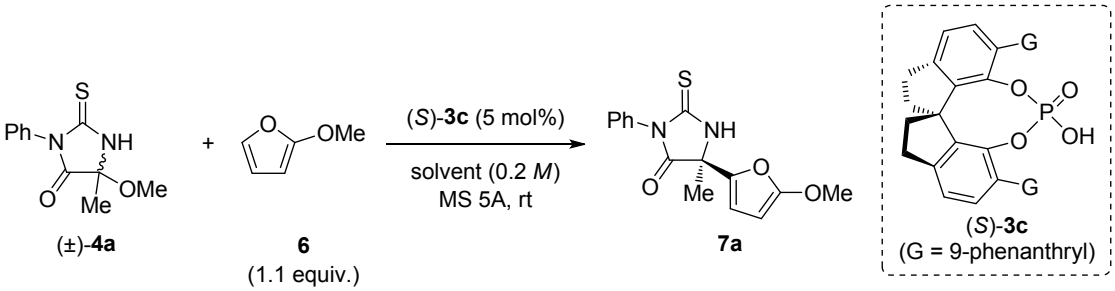
(*R*)-**2**

a: G = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$
b: G = 9-anthryl
c: G = 9-phenanthryl
d: G = 2-naphthyl
e: G = 4-PhC$_6$H$_4$
f: G = 3,5-Ph$_2$C$_6$H$_3$
g: G = 3,5-(CF$_3$)$_2$C$_6$H$_3$
h: G = C$_6$F$_5$
I: G = Ph$_3$Si

entry	CPA	time (h)	yield (%)[b]	ee (%)[c]
1	(*R*)-**1a**	4	99	76
2	(*R*)-**1b**	1	97	67
3	(*R*)-**1c**	1	95	79
4	(*R*)-**1d**	6	76	27
5	(*R*)-**1e**	3	87	19
6	(*R*)-**1f**	2	87	8
7	(*R*)-**1g**	1	98	-14
8	(*R*)-**1h**	1	88	25
9	(*R*)-**1i**	40	99	-63
10	(*R*)-**2a**	12	99	45
11	(*R*)-**2b**	2	95	74
12	(*R*)-**2c**	3	96	87

[a]Reaction conditions: **4b** (0.10 mmol), **6** (0.11 mmol), CPA (5.0 μmol), MS 5A (100 mg), toluene (0.50 mL). [b]Isolated yields. [c]The ee values of **7a** was determined by chiral stationary phase HPLC analysis.

3-2. Solvent Effect[a]

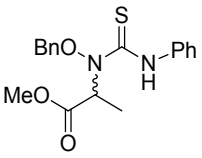


entry	solvent	time (h)	yield (%)[b]	ee (%)[c]
1	toluene	4	94	92
2	benzene	4	>99	93
3	CH_2Cl_2	2	96	90
4	THF	96	47	83
5	EtOAc	24	91	85
6	CH_3CN	96	64	77

[a]Reaction conditions: **4b** (0.10 mmol), **6** (0.11 mmol), CPA (5.0 μmol), MS 5A (100 mg), toluene (0.50 mL). [b]Isolated yields. [c]The ee values of **7a** was determined by chiral stationary phase HPLC analysis.

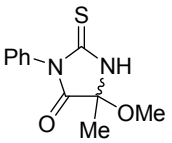
4. Analytical Data

4-1. Analytical Data of Substrates



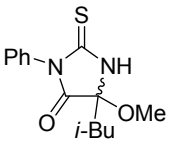
S2

Thiourea S2: colorless oil; R_f = 0.25 (Hexane/EtOAc = 6/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.69 (3H, d, *J* = 7.2 Hz), 3.77 (3H, s), 5.03 (2H, dd, *J* = 27.9, 11.1 Hz), 6.12 (1H, q, *J* = 7.2 Hz), 7.17-7.21 (1H, m), 7.30-7.36 (4H, m), 7.39-7.44 (5H, m), 8.63-8.72 (1H, brs).



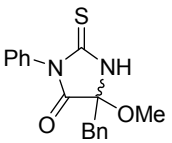
4a

5-methoxy-5-methyl-3-phenyl-2-thioxoimidazolidin-4-one (4a): 69% yield (2 steps); White solid; R_f = 0.40 (Hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.73 (3H, s), 3.36 (3H, s), 7.16-7.28 (1H, brs), 7.29-7.31 (2H, m), 7.45-7.49 (1H, m), 7.49-7.53 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 22.6, 51.9, 88.0, 128.2, 129.2, 129.5, 132.2, 170.9, 183.0; IR (ATR): 3154, 2965, 2932, 1771, 1507, 1450, 1400, 1277, 1204, 1165, 1132, 1048, 842 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{12}N_2NaO_2S$ ([M + Na]$^+$) 259.0512, Found 259.0512.



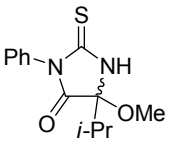
4b

5-isobutyl-5-methoxy-3-phenyl-2-thioxoimidazolidin-4-one (4b): 77% yield (2 steps); White solid; R_f = 0.35 (Hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.99 (3H, d, *J* = 6.6 Hz), 1.02 (3H, d, *J* = 6.6 Hz), 1.83-1.92 (1H, m), 1.94-2.01 (2H, m), 3.34 (3H, s), 7.26-7.30 (2H, m), 7.32-7.44 (1H, brs), 7.45-7.49 (1H, m), 7.49-7.53 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.5, 23.9, 44.2, 51.4, 90.5, 128.1, 129.2, 129.5, 132.3, 171.0, 183.3; IR (ATR): 3309, 2958, 2932, 2831, 1765, 1501, 1398, 1301, 1278, 1233, 1198, 1158, 1127, 1071, 1037, 995, 853 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{18}N_2NaO_2S$ ([M + Na]$^+$) 301.0981, Found 301.0982.



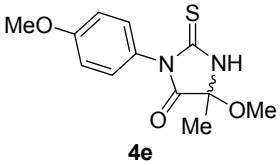
4c

5-benzyl-5-methoxy-3-phenyl-2-thioxoimidazolidin-4-one (4c): 57% yield (2 steps); White solid; R_f = 0.20 (Hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.25-3.34 (2H, m), 3.40 (3H, s), 6.85-6.89 (2H, m), 7.26-7.30 (2H, m), 7.33-7.36 (3H, m), 7.39-7.42 (3H, m), 7.58-7.68 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 42.3, 52.2, 91.6, 128.0$_0$, 128.0$_2$, 128.7, 129.1, 129.4, 130.5, 131.9$_8$, 132.0$_2$, 170.3, 183.1; IR (ATR): 3309, 3065, 3031, 2962, 2933, 2832, 1762, 1596, 1500, 1454, 1434, 1399, 1318, 1263, 1190, 1134, 1099, 1048, 1005, 856 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{16}N_2NaO_2S$ ([M + Na]$^+$) 335.0825, Found 335.0825.



4d

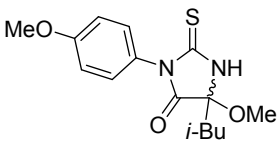
5-isopropyl-5-methoxy-3-phenyl-2-thioxoimidazolidin-4-one (4d): 75% yield (2 steps); White solid; R_f = 0.35 (Hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.02 (3H, d, *J* = 6.9 Hz), 1.10 (3H, d, *J* = 6.9 Hz), 2.37 (1H, sep, *J* = 6.9 Hz), 3.37 (3H, s), 7.25-7.28 (2H, m), 7.29-7.44 (1H, brs), 7.45-7.52 (3H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 15.5, 16.1, 34.6, 52.1, 93.5, 128.2, 129.2, 129.5, 132.3, 171.0, 183.9; IR (ATR): 3177, 2970, 2934, 2880, 1766, 1507, 1457, 1404, 1339, 1250, 1209, 1110, 1057, 1014, 985, 835 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{16}N_2NaO_2S$ ([M + Na]$^+$) 287.0825, Found 287.0825.



4e

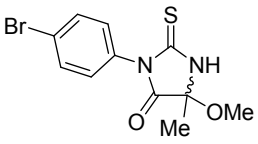
5-methoxy-3-(4-methoxyphenyl)-5-methyl-2-thioxoimidazolidin-4-one (4e): 63% yield (2 steps); White solid; R_f = 0.30 (Hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.71 (3H, s), 3.34 (3H, s), 3.85 (3H, s), 6.98-7.02 (2H, m), 7.18-7.22 (2H, m), 7.31-7.35 (1H, brs);

^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 22.6, 51.9, 55.5, 88.0, 114.5, 124.7, 129.3, 160.1, 171.1, 183.4; IR (ATR): 3300, 3000, 2962, 2936, 2837, 1763, 1607, 1514, 1484, 1446, 1402, 1279, 1252, 1201, 1163, 1128, 1051, 1018, 823 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{14}N_2NaO_3S$ ([M + Na]$^+$) 289.0617, Found 289.0617.



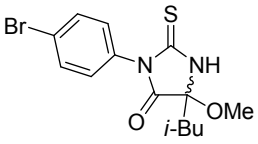
4f

5-isobutyl-5-methoxy-3-(4-methoxyphenyl)-2-thioxoimidazolidin-4-one (4f): 65% yield (2 steps); White solid; R_f = 0.45 (Hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.98 (3H, d, *J* = 6.6 Hz), 1.01 (3H, d, *J* = 6.6 Hz), 1.82-1.91 (1H, m), 1.92-2.00 (2H, m), 3.32 (3H, s), 3.84 (3H, s), 6.99-7.02 (2H, m), 7.16-7.20 (2H, m), 7.36-7.40 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.4, 23.9, 44.2, 51.4, 55.5, 90.5, 114.6, 124.8, 129.2, 160.1, 171.2, 183.7; IR (ATR): 3302, 2960, 2935, 2836, 1767, 1514, 1481, 1301, 1252, 1199, 1078, 1032, 825 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{20}N_2NaO_3S$ ([M + Na]$^+$) 331.1087, Found 331.1087.



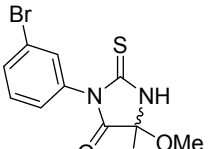
4g

3-(4-bromophenyl)-5-methoxy-5-methyl-2-thioxoimidazolidin-4-one (4g): 60% yield (2 steps); White solid; R_f = 0.40 (Hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.72 (3H, s), 3.34 (3H, s), 7.18-7.21 (2H, m), 7.35-7.40 (1H, brs), 7.62-7.65 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 22.6, 51.9, 88.0, 123.6, 129.7, 131.1, 132.4, 170.6, 182.4; IR (ATR): 3304, 2997, 2959, 2934, 2831, 1766, 1492, 1449, 1400, 1276, 1201, 1163, 1130, 1069, 1052, 1016, 849, 811 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{11}BrN_2NaO_2S$ ([M + Na]$^+$) 336.9617, Found 336.9617.



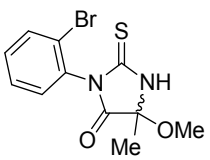
4h

3-(4-bromophenyl)-5-isobutyl-5-methoxy-2-thioxoimidazolidin-4-one (4h): 58% yield (2 steps); White solid; R_f = 0.40 (Hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.97 (3H, d, *J* = 6.0 Hz), 1.01 (3H, d, *J* = 6.6 Hz), 1.81-1.90 (1H, m), 1.92-2.00 (2H, m), 3.32 (3H, s), 7.16-7.19 (2H, m), 7.33-7.39 (1H, brs), 7.62-7.65 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.4, 23.8, 44.2, 51.5, 90.6, 123.6, 129.7, 131.2, 132.5, 170.7, 182.6; IR (ATR): 3312, 2959, 2872, 1768, 1492, 1400, 1305, 1277, 1236, 1199, 1156, 1128, 1070, 1014, 859, 811 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{17}BrN_2NaO_2S$ ([M + Na]$^+$) 379.0086, Found 379.0086.



4i

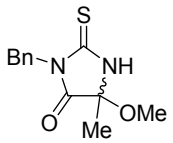
3-(3-bromophenyl)-5-methoxy-5-methyl-2-thioxoimidazolidin-4-one (4i): 59% yield (2 steps); White solid; R_f = 0.20 (Hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.72 (3H, s), 3.35 (3H, s), 7.25-7.28 (1H, m), 7.29-7.36 (1H, brs), 7.38 (1H, t, *J* = 7.8 Hz), 7.48 (1H, t, *J* = 1.8 Hz), 7.61, (1H, ddd, *J* = 7.8, 1.8, 1.2 Hz); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 22.6, 52.0, 88.1, 122.4, 127.0, 130.4, 131.4, 132.6, 133.3, 170.6, 182.2; IR (ATR): 3305, 2997, 2935, 2828, 1767, 1577, 1483, 1446, 1393, 1278, 1202, 1164, 1131, 1052, 845 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{11}BrN_2NaO_2S$ ([M + Na]$^+$) 336.9617, Found 336.9617.



4j

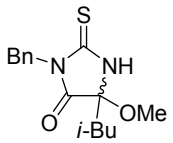
3-(2-bromophenyl)-5-methoxy-5-methyl-2-thioxoimidazolidin-4-one (4j): 67% yield (2 steps, dr = 55/45); White solid; R_f = 0.40 (Hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.73 (1.35H, s), 1.76 (1.65H, s), 3.38 (1.65H, s), 3.49 (1.35H, s), 6.95-7.10 (1H, brs), 7.22-7.29 (1H, m), 7.34-7.38 (1H, m), 7.43-7.48 (1H, m), 7.72-7.75 (1H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.0,

23.4, 52.0, 53.2, 88.7$_6$, 88.8$_3$, 123.1, 123.4, 128.4$_6$, 128.5$_4$, 131.0$_5$, 131.0$_7$, 131.4$_5$, 131.4$_9$, 131.8, 132.1, 133.6, 133.7, 170.0, 170.5, 181.7, 181.9; HRMS (ESI) Calcd for $C_{11}H_{11}BrN_2NaO_2S$ ([M + Na]$^+$) 336.9617, Found 336.9617.



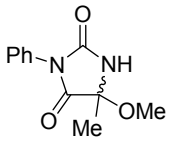
4k

3-benzyl-5-methoxy-5-methyl-2-thioxoimidazolidin-4-one (4k): 91% yield (2 steps); White solid; R_f = 0.25 (Hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.59 (3H, s), 3.10 (3H, s), 4.98-5.07 (2H, m), 7.08-7.16 (1H, br), 7.26-7.33 (3H, m), 7.43-7.46 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 22.5, 44.5, 51.8, 87.7, 128.0, 128.6, 128.7, 135.5, 171.4, 183.0; IR (ATR): 3300, 2994, 2935, 2831, 1749, 1482, 1449, 1400, 1340, 1312, 1252, 1195, 1169, 1132, 1052, 989, 892 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{14}N_2NaO_2S$ ([M + Na]$^+$) 273.0668, Found 273.0668.



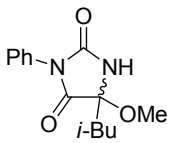
4l

3-benzyl-5-isobutyl-5-methoxy-2-thioxoimidazolidin-4-one (4l): 81% yield (2 steps); Colorless oil; R_f = 0.40 (Hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.82 (3H, d, *J* = 6.6 Hz), 0.91 (3H, d, *J* = 7.2 Hz), 1.65-1.75 (1H, m), 1.76-1.81 (1H, m), 1.83-1.88 (1H, m), 3.07 (3H, s), 5.02 (2H, s), 7.17-7.23 (1H, brs), 7.25-7.32 (3H, m), 7.45-7.49 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.4, 23.6, 23.8, 44.1, 44.5, 51.4, 90.1, 128.0, 128.5, 128.9, 135.4, 171.5, 183.2; IR (ATR): 3300, 2958, 2934, 2873, 2831, 1748, 1481, 1432, 1402, 1348, 1312, 1191, 1159, 1131, 1078, 942 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{20}N_2NaO_2S$ ([M + Na]$^+$) 315.1138, Found 315.1138.



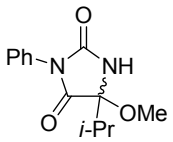
5a

5-methoxy-5-methyl-3-phenylimidazolidine-2,4-dione (5a): 83% yield (2 steps); White solid; R_f = 0.20 (Hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.68 (3H, s), 3.31 (3H, s), 6.65-6.71 (1H, brs), 7.38-7.44 (3H, m), 7.46-7.50 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.0, 51.1, 86.7, 126.0, 128.5, 129.1, 130.9, 155.0, 171.0; IR (ATR): 3309, 3170, 2998, 2933, 1786, 1719, 1505, 1455, 1420, 1379, 1300, 1207, 1178, 1136, 1052, 1038, 856 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{12}N_2NaO_3$ ([M + Na]$^+$) 243.0740, Found 243.0740.



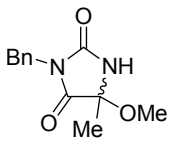
5b

5-isobutyl-5-methoxy-3-phenylimidazolidine-2,4-dione (5b): 15% yield (2 steps); White solid; R_f = 0.40 (Hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.97 (3H, d, *J* = 6.6 Hz), 1.00 (3H, d, *J* = 6.6 Hz), 1.82-1.90 (1H, m), 1.91-1.98 (2H, m), 3.32 (3H, s), 6.16-6.21 (1H, brs), 7.37-7.42 (3H, m), 7.46-7.50 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.4, 23.8, 23.9, 44.4, 50.8, 89.2, 125.9, 128.5, 129.2, 130.9, 155.0, 170.9; IR (ATR): 3306, 2960, 2873, 2833, 1792, 1724, 1600, 1503, 1457, 1405, 1306, 1195, 1131, 1073, 870 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{18}N_2NaO_3$ ([M + Na]$^+$) 285.1210, Found 285.1210.



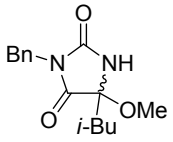
5c

5-isopropyl-5-methoxy-3-phenylimidazolidine-2,4-dione (5c): 85% yield (2 steps); White solid; R_f = 0.40 (Hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.00 (3H, d, *J* = 6.6 Hz), 1.06 (3H, d, *J* = 6.6 Hz), 2.35 (1H, sep, *J* = 6.6 Hz), 3.35 (3H, s), 6.07-6.17 (1H, brs), 7.36-7.42 (3H, m), 7.45-7.50 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 15.4, 16.4, 34.2, 51.4, 92.1, 126.0, 128.5, 129.2, 130.9, 155.5, 170.9; IR (ATR): 3255, 3103, 3071, 2971, 2937, 2878, 1788, 1724, 1597, 1495, 1461, 1418, 1364, 1333, 1282, 1208, 1138, 1111, 1072, 1026, 986, 890, 857 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{16}N_2NaO_3$ ([M + Na]$^+$) 271.1053, Found 271.1053.



5d

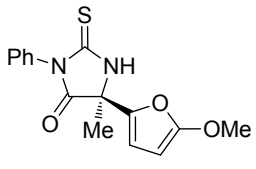
3-benzyl-5-methoxy-5-methylimidazolidine-2,4-dione (5d): 70% yield (2 steps); White solid; R_f = 0.25 (Hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.58 (3H, s), 3.11 (3H, s), 4.64-4.72 (2H, m), 5.87-5.93 (1H, brs), 7.26-7.34 (3H, m), 7.36-7.40 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.1, 42.2, 51.1, 87.0, 128.0, 128.4, 128.7, 135.8, 155.4, 171.7; IR (ATR): 3284, 3001, 2938, 2831, 1786, 1719, 1443, 1417, 1346, 1316, 1269, 1226, 1171, 1133, 1054, 895 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{14}N_2NaO_3$ ([M + Na]$^+$) 257.0897, Found 257.0897.



5e

3-benzyl-5-isobutyl-5-methoxyimidazolidine-2,4-dione (5e): 39% yield (2 steps); Colorless oil; R_f = 0.45 (Hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.82 (3H, d, J = 6.6 Hz), 0.91 (3H, d, J = 6.6 Hz), 1.66-1.73 (1H, m), 1.74-1.87 (2H, m), 3.09 (3H, s), 4.64-7.72 (2H, m), 5.89-5.93 (1H, brs), 7.25-7.33 (3H, m), 7.38-7.42 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.3, 23.6, 23.9, 42.2, 44.3, 50.7, 89.5, 128.1, 128.6, 128.7, 135.7, 155.8, 171.7; IR (ATR): 3307, 2958, 2873, 2830, 1785, 1718, 1442, 1415, 1348, 1316, 1168, 1125, 1072, 962 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{20}N_2NaO_3$ ([M + Na]$^+$) 299.1366, Found 299.1366.

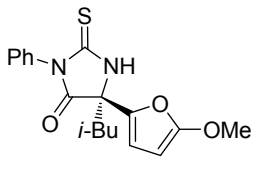
3-2. Spectral Data of Products



7a

5-(5-methoxyfuran-2-yl)-5-methyl-3-phenyl-2-thioxoimidazolidin-4-one (7a): >99% yield; White solid; R_f = 0.25 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak IA-3 (Hex:IPA = 95:5, 1.0 mL/min, 254 nm, 40 °C) 22.0 (minor), 28.5 (major) min, (93% ee); $[\alpha]^{24}_D$ = -66.9 (*c* 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.86 (3H, s), 3.84 (3H, s), 5.14 (1H, d, J = 3.3 Hz), 6.33 (1H, d, J = 3.3 Hz), 7.33-7.36 (2H, m), 7.43-7.47 (1H, m), 7.48-7.52 (2H, m), 7.58-7.72 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.3, 57.9, 62.4, 80.6, 110.4, 128.4, 129.1, 129.3, 132.8, 138.4, 162.2, 172.6, 182.6; IR (ATR): 3332, 2922, 2852, 1756, 1616, 1580, 1505, 1449, 1401, 1371, 1261, 1237, 1108, 1048 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{14}N_2NaO_3S$ ([M + Na]$^+$) 325.0617, Found 325.0617

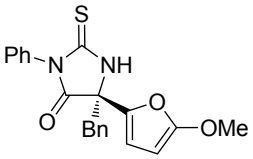
Configuration Assignment: The absolute configuration of **7a** was determined to be (*S*) by X-ray crystallographic analysis; see section 5 for details.



7b

5-isobutyl-5-(5-methoxyfuran-2-yl)-3-phenyl-2-thioxoimidazolidin-4-one (7b): 98% yield; White solid; R_f = 0.25 (Hexane/EtOAc = 4/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 80/20, 1.0 mL/min, 254 nm, 30 °C) 8.7 (major), 14.5 (minor) min, (86% ee); $[\alpha]^{25}_D$ = -41.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.98 (3H, d, J = 6.6 Hz), 1.00 (3H, d, J = 6.6 Hz), 1.81-1.91 (1H, m), 2.13-2.22 (2H, m), 3.84 (3H, s), 5.12 (1H, d, J = 3.0 Hz), 6.29 (1H, d, J = 3.0 Hz), 7.30-7.33 (2H, m), 7.43-7.47 (1H, m), 7.47-7.52 (2H, m), 7.83-7.89 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.4, 23.9, 24.5, 43.0, 57.9, 65.9, 80.6, 109.6, 128.3, 129.1, 129.3, 132.8, 138.5, 162.1, 172.2, 182.9; IR (ATR): 3318, 3147, 2960, 2873, 1762, 1615, 1577, 1502, 1397, 1370, 1262, 1217, 1161, 1122, 1054, 1023 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{20}N_2NaO_3S$ ([M + Na]$^+$) 367.1087, Found 367.1086.

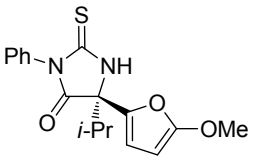
Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



7c

5-benzyl-5-(5-methoxyfuran-2-yl)-3-phenyl-2-thioxoimidazolidin-4-one (7c): 67% yield; White solid; R_f = 0.30 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 80/20, 1.0 mL/min, 254 nm, 30 °C) 11.3 (major), 17.2 (minor) min, (67% ee); $[\alpha]^{24}_D$ = +23.8 (*c* 1.03, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.40-3.57 (2H, m), 3.87 (3H, s), 5.19 (1H, d, *J* = 3.6 Hz), 6.41 (1H, d, *J* = 3.6 Hz), 6.77-6.80 (2H, m), 7.25-7.28 (2H, m), 7.33-7.38 (6H, m), 7.78-7.82 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 41.3, 57.9, 67.1, 80.7, 110.3, 128.0, 128.1, 128.6, 129.0, 129.2, 130.5, 132.4, 132.5, 137.5, 162.3, 171.3, 182.6; IR (ATR): 3314, 3132, 2970, 2938, 1759, 1614, 1577, 1501, 1454, 1437, 1398, 1369, 1260, 1194, 1028 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{18}N_2NaO_3S$ ([M + Na]$^+$) 401.0930, Found 401.0930.

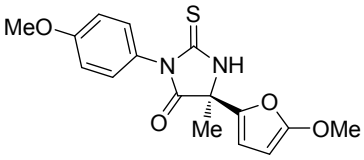
Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



7d

5-isopropyl-5-(5-methoxyfuran-2-yl)-3-phenyl-2-thioxoimidazolidin-4-one (7d): 50% yield; White solid; R_f = 0.20 (Hexane/EtOAc = 4/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 80/20, 1.0 mL/min, 254 nm, 30 °C) 11.2 (major), 14.3 (minor) min, (85% ee); $[\alpha]^{25}_D$ = +31.2 (*c* 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.04 (3H, d, *J* = 6.6 Hz), 1.06 (3H, d, *J* = 6.6 Hz), 2.70 (1H, sep, 6.6 Hz), 3.84 (3H, s), 5.15 (1H, d, *J* = 3.6 Hz), 6.33 (1H, d, *J* = 3.6 Hz), 7.27-7.30 (2H, m), 7.42-7.46 (1H, m), 7.47-7.51 (2H, m), 7.87-7.91 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 16.3, 17.0, 34.4, 57.9, 70.0, 80.6, 109.9, 128.3, 129.1, 129.3, 132.6, 137.5, 162.1, 171.8, 183.6; IR (ATR): 3309, 3156, 2969, 2938, 2873, 1758, 1613, 1577, 1505, 1400, 1368, 1263, 1220, 1052, 1021 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{18}N_2NaO_3S$ ([M + Na]$^+$) 353.0930, Found 353.0930.

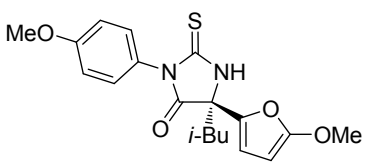
Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



7e

5-(5-methoxyfuran-2-yl)-3-(4-methoxyphenyl)-5-methyl-2-thioxoimidazolidin-4-one (7e): 87% yield; White solid; R_f = 0.20 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 70/30, 1.0 mL/min, 254 nm, 40 °C) 11.9 (minor), 16.2 (major) min, (90% ee); $[\alpha]^{23}_D$ = -71.2 (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.85 (3H, s), 3.84 (6H, m), 5.13 (1H, d, *J* = 3.0 Hz), 6.32 (1H, d, *J* = 3.0 Hz), 6.98-7.02 (2H, m), 7.23-7.26 (2H, m), 7.55-7.59 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.4, 55.4, 57.9, 62.3, 80.5, 110.3, 114.4, 125.3, 129.5, 138.4, 160.1, 162.2, 172.8, 183.0; IR (ATR): 3328, 2961, 2924, 2852, 1751, 1616, 1581, 1513, 1463, 1401, 1370, 1301, 1252, 1229, 1167, 1105, 1027, 965, 945, 827 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}N_2NaO_4S$ ([M + Na]$^+$) 355.0723, Found 355.0723.

Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.

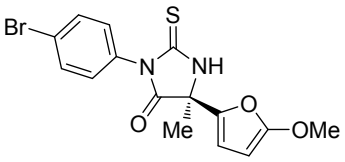


7f

5-isobutyl-5-(5-methoxyfuran-2-yl)-3-(4-methoxyphenyl)-2-thioxoimidazolidin-4-one (7f): 98% yield; White solid; R_f = 0.15 (Hexane/EtOAc = 4/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 80/20, 1.0 mL/min, 254 nm, 40 °C) 14.0 (major), 22.4 (minor) min, (90% ee); $[\alpha]^{24}_D$ = -45.1 (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.97 (3H, d, *J* = 6.6 Hz), 1.00 (3H, d, *J* = 1.2 Hz) 1.81-1.90 (1H, m), 2.12-2.21 (2H, m), 3.83$_6$ (3H, s), 3.84$_1$ (3H, s), 5.13 (1H, d, *J* = 3.3 Hz), 6.28 (1H, d, *J* = 3.3 Hz), 6.98-7.01 (2H, m), 7.20-7.23

(2H, m), 7.46-7.53 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.3, 23.8, 24.4, 43.0, 55.4, 57.8, 65.8, 80.5, 109.5, 114.4, 125.3, 129.4, 138.5, 160.0, 162.0, 172.5, 183.3; IR (ATR): 3309, 3147, 2960, 2937, 2872, 2839, 1756, 1614, 1576, 1513, 1486, 1436, 1401, 1369, 1301, 1250, 1214, 1160, 1106, 1054, 1028, 958, 823 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{22}N_2NaO_4S$ ($[M + Na]^+$) 397.1193, Found 397.1192.

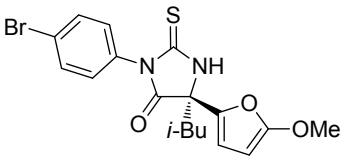
Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



7g

3-(4-bromophenyl)-5-(5-methoxyfuran-2-yl)-5-methyl-2-thioxoimidazolidin-4-one (7g): 97% yield; White solid; R_f = 0.40 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 70/30, 1.0 mL/min, 254 nm, 40 °C) 10.3 (minor), 13.8 (major) min, (90% ee); $[\alpha]^{25}_D$ = -69.0 (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.85 (3H, s), 3.84 (3H, s), 5.13 (1H, d, *J* = 3.6 Hz), 6.32 (1H, d, *J* = 3.6 Hz), 7.24-7.26 (2H, m), 7.60-7.64 (2H, m), 7.72-7.77 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.3, 57.9, 62.4, 80.6, 110.6, 123.4, 130.0, 131.7, 132.3, 138.1, 162.2, 172.3, 182.0; IR (ATR): 3307, 2979, 2933, 1760, 1616, 1577, 1492, 1449, 1400, 1371, 1263, 1236, 1102, 1069, 1050, 1015, 966 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{13}BrN_2NaO_3S$ ($[M + Na]^+$) 402.9723, Found 402.9722.

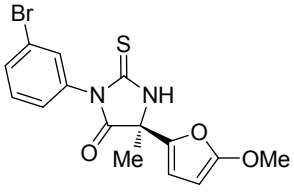
Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



7h

3-(4-bromophenyl)-5-isobutyl-5-(5-methoxyfuran-2-yl)-2-thioxoimidazolidin-4-one (7h): 99% yield; White solid; R_f = 0.25 (Hexane/EtOAc = 4/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 70/30, 1.0 mL/min, 254 nm, 40 °C) 8.0 (major), 11.7 (minor) min, (88% ee); $[\alpha]^{24}_D$ = -40.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.96 (3H, d, *J* = 6.6 Hz), 1.00 (3H, d, *J* = 6.6 Hz), 1.79-1.89 (1H, m), 2.13-2.21 (2H, m), 3.84 (3H, s), 5.12 (1H, d, *J* = 3.6 Hz), 6.28 (1H, d, *J* = 3.6 Hz), 7.19-7.23 (2H, m), 7.60-7.64 (2H, m), 7.80-7.84 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.3, 23.8, 24.5, 42.9, 57.9, 66.0, 80.5, 109.7, 123.4, 129.8, 131.7, 132.4, 138.2, 162.1, 172.0, 182.3; IR (ATR): 3314, 3149, 2961, 2938, 2873, 1759, 1614, 1575, 1491, 1436, 1399, 1369, 1304, 1261, 1213, 1164, 1123, 1069, 1015, 973, 959, 900, 838, 814 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{19}BrN_2NaO_3S$ ($[M + Na]^+$) 445.0192, Found 445.0191.

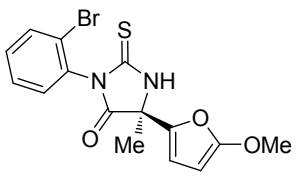
Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



7i

3-(3-bromophenyl)-5-(5-methoxyfuran-2-yl)-5-methyl-2-thioxoimidazolidin-4-one (7i): 99% yield; White solid; R_f = 0.20 (Hexane/EtOAc = 4/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 90/10, 1.0 mL/min, 254 nm, 40 °C) 17.0 (minor), 20.7 (major) min, (89% ee); $[\alpha]^{25}_D$ = -62.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.86 (3H, s), 3.84 (3H, s), 5.14 (1H, d, *J* = 3.3 Hz), 6.34 (1H, d, *J* = 3.3 Hz), 7.31 (1H, ddd, *J* = 7.8, 1.8, 0.9 Hz), 7.37 (1H, t, *J* = 7.8 Hz), 7.52 (1H, t, *J* = 1.8 Hz), 7.58 (1H, ddd, *J* = 7.8, 1.8, 0.9 Hz), 7.64-7.70 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.3, 57.9, 62.4, 80.6, 110.6, 122.3, 127.2, 130.2, 131.5, 132.4, 133.9, 138.1, 162.3, 172.3, 181.9; IR (ATR): 3307, 2979, 2938, 1761, 1616, 1577, 1486, 1448, 1393, 1373, 1262, 1236, 1163, 1108, 1049, 1022, 966, 944 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{13}BrN_2NaO_3S$ ($[M + Na]^+$) 402.9723, Found 402.9722.

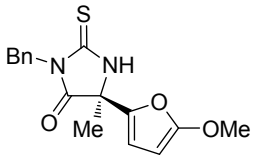
Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



7j

3-(2-bromophenyl)-5-(5-methoxyfuran-2-yl)-5-methyl-2-thioxoimidazolidin-4-one (7j): 86% yield (dr = 60/40); White solid; R_f = 0.40 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-3 (Hexane/IPA = 95/5, 1.0 mL/min, 254 nm, 40 °C) *major isomer*: 38.4 (minor), 44.1 (major), (67% ee), *minor isomer*: 41.5 (minor), 69.2 (major) min, (94% ee); ^{1}H NMR ($CDCl_3$, 600 MHz) *major isomer*: δ 1.91 (3H, s), 3.85 (3H, s), 5.14 (1H, d, *J* = 3.6 Hz), 6.34 (1H, d, *J* = 3.6 Hz), 7.35-7.39 (2H, m), 7.44-7.48 (1H, m), 7.61-7.65 (1H, brs), 7.71-7.74 (1H, m), *minor isomer*: δ 1.88 (3H, s), 3.84 (3H, s), 5.14 (1H, d, *J* = 3.3 Hz), 6.37 (1H, d, *J* = 3.3 Hz), 7.31-7.38 (2H, m), 7.71-7.73 (1H, m), 7.44-7.47 (1H, m), 7.82-7.86 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) *major isomer*: δ 21.7, 57.8$_9$, 62.9$_0$, 80.6, 110.6$_3$, 123.5$_5$, 128.5, 131.3$_5$, 131.3$_9$, 132.3$_1$, 133.5, 138.2, 162.2, 171.6$_7$, 181.5, *minor isomer*: δ 21.8, 57.8$_8$, 62.9$_3$, 80.8, 110.5$_6$, 123.6$_0$, 128.3, 131.1, 131.2$_9$, 132.3$_4$, 133.7, 137.9, 162.1, 171.7$_4$, 181.4; HRMS (ESI) Calcd for $C_{15}H_{13}BrN_2NaO_3S$ ([M + Na]$^+$) 402.9723, Found 402.9722.

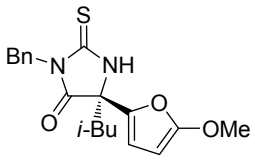
Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



7k

3-benzyl-5-(5-methoxyfuran-2-yl)-5-methyl-2-thioxoimidazolidin-4-one (7k): 98% yield; White solid; R_f = 0.25 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-3 (Hexane/IPA = 95/5, 1.0 mL/min, 254 nm, 40 °C) 24.5 (minor), 27.6 (major) min, (90% ee); $[\alpha]^{25}_D$ = -33.9 (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.72 (3H, s), 3.78 (3H, s), 5.04 (2H, s), 5.09 (1H, d, *J* = 3.6 Hz), 6.22 (1H, d, *J* = 3.6 Hz), 7.24-7.28 (1H, m), 7.29-7.33 (2H, m), 7.39-7.42 (2H, m), 7.43-7.49 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.1, 44.7, 57.8, 61.9, 80.6, 110.2, 127.7, 128.2, 128.5, 135.5, 138.3, 162.0, 173.2, 182.5; IR (ATR): 3310, 2982, 2939, 2839, 1751, 1616, 1579, 1485, 1452, 1428, 1401, 1370, 1342, 1262, 1215, 1124, 1050, 994, 931 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}N_2NaO_3S$ ([M + Na]$^+$) 339.0774, Found 339.0773.

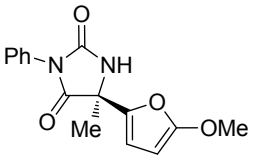
Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



7l

3-benzyl-5-isobutyl-5-(5-methoxyfuran-2-yl)-2-thioxoimidazolidin-4-one (7l): 99% yield; Colorless oil; R_f = 0.50 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-3 (Hexane/IPA = 90/10, 1.0 mL/min, 254 nm, 30 °C) 8.5 (minor), 13.1 (major) min, (90% ee); $[\alpha]^{24}_D$ = -9.4 (*c* 1.04, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.76 (3H, d, *J* = 6.6 Hz), 0.87 (3H, d, *J* = 6.6 Hz), 1.59-1.67 (1H, m), 2.01-2.08 (2H, m), 3.78 (3H, s), 4.97-5.07 (2H, m), 5.07 (1H, d, *J* = 3.0 Hz), 6.17 (1H, d, *J* = 3.0 Hz), 7.23-7.27 (1H, m), 7.27-7.31 (2H, m), 7.42-7.45 (2H, m), 7.58-7.67 (1H, brs); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.3, 23.8, 24.2, 42.9, 44.8, 57.8, 65.5, 80.6, 109.3, 127.8, 128.4, 128.5, 135.4, 138.4, 161.9, 172.7, 182.9; IR (ATR): 3305, 3174, 2959, 1751, 1615, 1577, 1495, 1434, 1401, 1369, 1350, 1310, 1262, 1200, 1132, 1053, 1025, 950 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{22}N_2NaO_3S$ ([M + Na]$^+$) 381.1243, Found 381.1243.

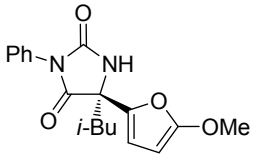
Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



8a

5-(5-methoxyfuran-2-yl)-5-methyl-3-phenylimidazolidine-2,4-dione (8a): 86% yield; White solid; R_f = 0.35 (Hexane/EtOAc = 1/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 80/20, 1.0 mL/min, 254 nm, 40 °C) 11.3 (minor), 14.2 (major) min, (93% ee); $[\alpha]^{24}_D$ = -87.7 (*c* 1.02, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz) δ 1.84 (3H, s), 3.84 (3H, s), 5.13 (1H, d, *J* = 3.3 Hz), 5.83-5.87 (1H, brs), 6.32 (1H, d, *J* = 3.3 Hz), 7.36-7.40 (1H, m), 7.41-7.44 (2H, m), 7.45-7.49 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 22.1, 57.8, 60.0, 80.5, 109.9, 126.2, 128.3, 129.1, 131.5, 139.8, 155.1, 162.0, 172.0; IR (ATR): 3314, 2986, 2942, 1780, 1722, 1617, 1579, 1501, 1456, 1411, 1374, 1290, 1263, 1207, 1125, 1050, 1022, 967, 939, 894 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{14}N_2NaO_4$ ($[M + Na]^+$) 309.0846, Found 309.0846.

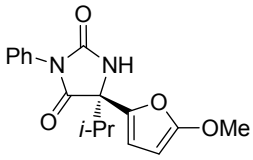
Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



8b

5-isobutyl-5-(5-methoxyfuran-2-yl)-3-phenylimidazolidine-2,4-dione (8b): 98% yield; Colorless oil; R_f = 0.40 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 90/10, 1.0 mL/min, 254 nm, 40 °C) 17.2 (major), 19.3 (minor) min, (92% ee); $[\alpha]^{25}_D$ = -41.2 (*c* 0.98, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz) δ 0.97 (3H, d, *J* = 6.6 Hz), 0.99 (3H, d, *J* = 6.6 Hz), 1.82-1.89 (1H, m), 2.10-2.18 (2H, m), 3.83 (3H, s), 5.12 (1H, d, *J* = 3.6 Hz), 6.02-6.05 (1H, brs), 6.28 (1H, d, *J* = 3.6 Hz), 7.35-7.42 (3H, m), 7.43-7.48 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.3, 24.0, 24.3, 42.9, 57.8, 63.4, 80.5, 109.0, 126.1, 128.2, 129.0, 131.5, 140.0, 155.8, 161.9, 171.7; IR (ATR): 3292, 2960, 2940, 2871, 2841, 1783, 1720, 1614, 1576, 1502, 1457, 1409, 1369, 1291, 1262, 1194, 1131, 1056, 1025, 960, 847 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{20}N_2NaO_4$ ($[M + Na]^+$) 351.1315, Found 351.1315.

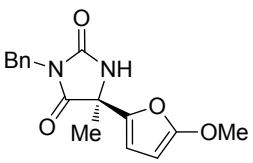
Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



8c

5-isopropyl-5-(5-methoxyfuran-2-yl)-3-phenylimidazolidine-2,4-dione (8c): 51% yield; White solid; R_f = 0.30 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 90/10, 1.0 mL/min, 254 nm, 40 °C) 18.6 (major), 20.8 (minor) min, (89% ee); $[\alpha]^{24}_D$ = +36.8 (*c* 1.03, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz) δ 0.97 (3H, d, *J* = 7.2 Hz), 1.04 (3H, d, *J* = 7.2 Hz), 2.69 (1H, sep, *J* = 7.2 Hz), 3.83 (3H, s), 5.14 (1H, d, *J* = 3.3 Hz), 6.27-6.31 (1H, brs), 6.32 (1H, d, *J* = 3.3 Hz), 7.34-7.40 (3H, m), 7.42-7.47 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 16.2, 16.9, 33.5, 57.8, 67.4, 80.5, 109.3, 126.2, 128.3, 129.0, 131.4, 139.0, 156.2, 161.9, 171.3; IR (ATR): 3283, 2968, 2936, 2876, 2853, 1781, 1714, 1613, 1576, 1502, 1457, 1407, 1369, 1331, 1261, 1198, 1129, 1092, 1054, 1021, 959, 913, 820 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{18}N_2NaO_4$ ($[M + Na]^+$) 337.1159, Found 337.1159.

Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.

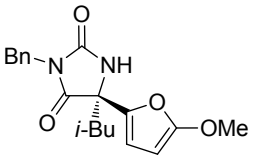


8d

3-benzyl-5-(5-methoxyfuran-2-yl)-5-methylimidazolidine-2,4-dione (8d): 95% yield; White solid; R_f = 0.20 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 80/20, 1.0 mL/min, 254 nm, 40 °C) 10.3 (minor), 15.3 (major) min, (93% ee); $[\alpha]^{25}_D$ = -53.7 (*c* 1.01, $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz) δ 1.71 (3H, s), 3.77 (3H, s), 4.69 (2H, s), 5.08 (1H, d, *J* = 3.6 Hz), 5.90-5.94 (1H, brs), 6.21 (1H, d, *J* = 3.6 Hz), 7.24-7.28 (1H, m), 7.29-7.33 (2H, m), 7.34-7.38 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.8, 42.4, 57.8, 60.2, 80.5, 109.6, 127.8, 128.1, 128.6, 135.9, 139.8,

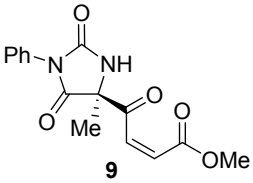
155.9, 161.8, 172.9; IR (ATR): 3310, 2927, 2855, 1779, 1715, 1617, 1579, 1439, 1416, 1363, 1262, 1050, 966, 936 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}N_2NaO_4$ ([M + Na]$^+$) 323.1002, Found 323.1002.

Configuration Assignment: The absolute configuration was assigned as (*S*) by analogy.



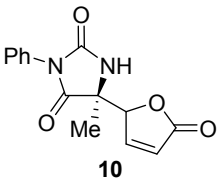
8e

3-benzyl-5-isobutyl-5-(5-methoxyfuran-2-yl)imidazolidine-2,4-dione (8e): 97% yield; Colorless oil; R_f = 0.40 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-3 (Hexane/EtOH = 90/10, 1.0 mL/min, 254 nm, 40 °C) 14.8 (minor), 21.0 (major) min, (92% ee); $[\alpha]^{24}_D$ = -32.7 (*c* 1.07, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.77 (3H, d, *J* = 6.6 Hz), 0.86 (3H, d, *J* = 6.6 Hz), 1.59-1.68 (1H, m), 1.96-2.05 (2H, m), 3.78 (3H, s), 4.64-4.71 (2H, m), 5.07 (1H, d, *J* = 3.3 Hz), 5.96-6.00 (1H, brs), 6.17 (1H, d, *J* = 3.3 Hz), 7.23-7.31 (3H, m), 7.35-7.38 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.3, 24.0, 24.1, 42.4, 42.9, 57.8, 63.7, 80.5, 108.8, 127.8, 128.3, 128.6, 135.7, 139.9, 156.5, 161.7, 172.5; IR (ATR): 3284, 3034, 2958, 2938, 2872, 1776, 1710, 1613, 1576, 1497, 1438, 1415, 1368, 1349, 1261, 1123, 1076, 1055, 1025, 970, 952 cm^{-1}; HRMS (APCI) Calcd for $C_{19}H_{23}N_2O_4$ ([M + H]$^+$) 343.1652, Found 343.1652.



9

(*Z*)-methyl 4-(4-methyl-2,5-dioxo-1-phenylimidazolidin-4-yl)-4-oxobut-2-enoate (9): White solid; R_f = 0.40 (Hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.80 (3H, s), 3.72 (3H, s), 6.23 (1H, d, *J* = 12.0 Hz), 6.45-6.49 (1H, br), 6.73 (1H, d, *J* = 12.0 Hz), 7.35-7.42 (3H, m), 7.44-7.49 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.9, 52.6, 70.2, 126.1, 127.3, 128.5, 129.1, 131.2, 138.4, 155.3, 166.2, 169.4, 196.8.



10

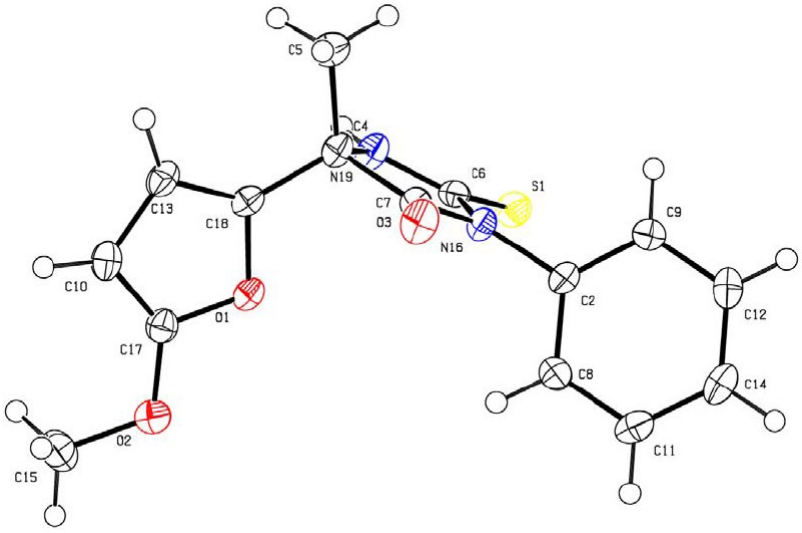
5-methyl-5-(5-oxo-2,5-dihydrofuran-2-yl)-3-phenylimidazolidine-2,4-dione (10): 73% yield (2 steps, dr = 68/32); White solid; R_f = 0.35 (Hexane/EtOAc = 1/4) (minor), R_f = 0.20 (Hexane/EtOAc = 1/4) (major) ; HPLC analysis Chiralpak IA-3 (Hexane/EtOH = 94/6, 0.5 mL/min, 220 nm, 15 °C) 20.7 (major), 31.1 (minor) min, (94% ee (minor isomer)) 34.1 (major), 61.2 (minor) min, (95% ee (major isomer)); ^{1}H NMR (CD_3OD, 600 MHz) δ 1.56 (2.04H, s), 1.65 (0.96H, s), 5.31 (0.32H, t, *J* = 1.8 Hz), 5.39 (0.68H, t, *J* = 1.8 Hz), 6.28 (0.32H, dd, *J* = 6.0, 1.8 Hz), 6.35 (0.68H, dd, *J* = 6.0, 1.8 Hz), 7.28-7.40 (3H, m), 7.42-7.47 (2H, m), 7.66 (0.32H, dd, *J* = 6.0, 1.8 Hz), 7.76 (0.68H, dd, *J* = 6.0, 1.8 Hz); ^{13}C NMR (CD_3OD, 150.9 MHz) δ 19.1, 20.5, 63.6, 64.5, 85.8, 86.8, 124.5, 125.1, 127.8$_3$, 127.8$_5$, 129.5, 129.6, 130.0$_6$, 130.0$_9$, 132.9, 133.0, 153.4, 153.7, 157.0, 157.3, 173.5, 173.9, 174.0, 174.9; HRMS (ESI) Calcd for $C_{14}H_{12}N_2NaO_4$ ([M + Na]$^+$) 295.0689, Found 295.0689.

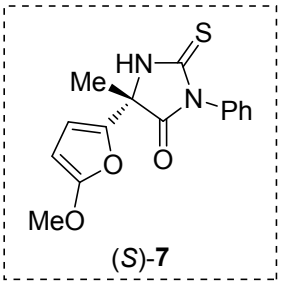
5. Determination of Absolute Configuration of 7a

Preparation of Enantio-pure 7a: Optical purity of **7a** (93% ee) was enhanced by recrystallization from $CHCl_3$/Hexane. The single crystal of enantio-pure **7a** for X-ray crystallographic analysis was grown from the mixture of $CHCl_3$/Hexane at 0 °C.

The absolute configuration **7a** was determined by X-ray crystallographic analysis. The absolute configuration was assigned to be (*S*) by refinement of Flack Parameter (absolute structure parameter). CCDC 1405286 contains the supplementary crystallographic data. The data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Figure S1. ORTEP Drawing of (*S*)-**7a**





(*S*)-**7**

6. DFT Studies

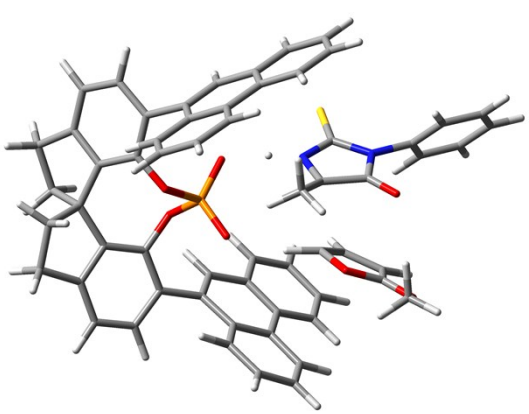
6.1 Full citation of reference 13

Gaussian 09, Revision C.01; M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, **2010**.

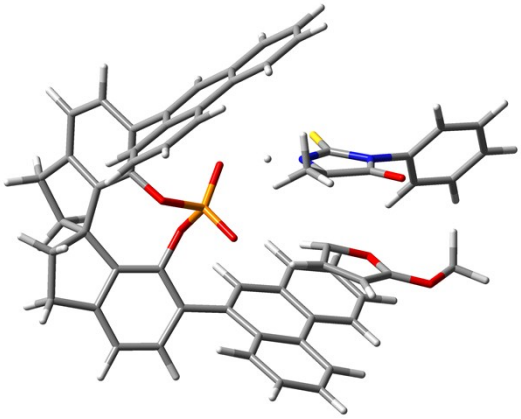
6.2 3D structures of TS*s-re*, TS*s-si*, TS*r-re*, and TS*r-si* from 4a

The geometries of **TS*s***s and **TS*r***s were fully optimized and characterized using frequency calculations at the B3LYP density functional theory with the 6-31G(d) basis set. Relative energies of the optimized structures in the gas phase are shown in kcal/mol. Relative Gibbs free energies (in kcal/mol) are shown in parentheses. Relative energies (in kcal/mol) obtained by single-point energy calculations at the B3LYP/6-311+G(d,p) level with the SCRF method based on PCM (ϵ = 2.2706 for benzene) are shown in brackets.

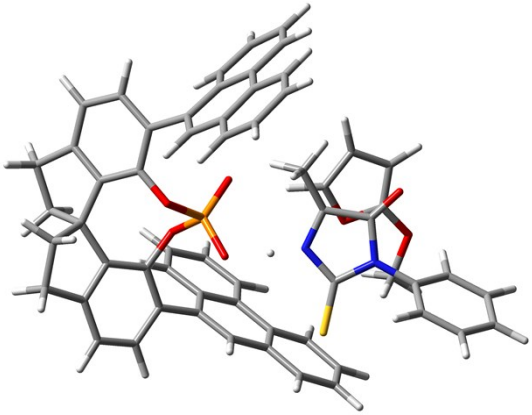
Figure S2. 3D structures and relative energies of the transition states **TS*s***s and **TS*r***s from **4a**



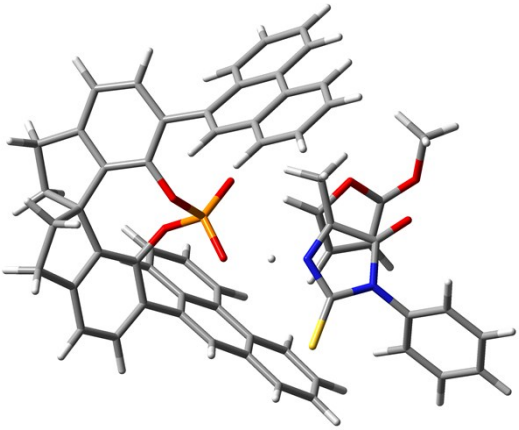
TS*s-re*
0.0 (0.0) [0.0]



TS*s-si*
2.3 (2.2) [3.8]



TS*r-re*
3.8 (3.8) [4.0]

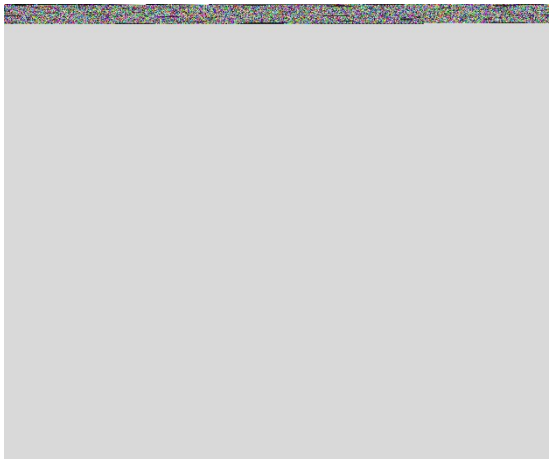


TS*r-si*
1.1 (1.4) [1.8]

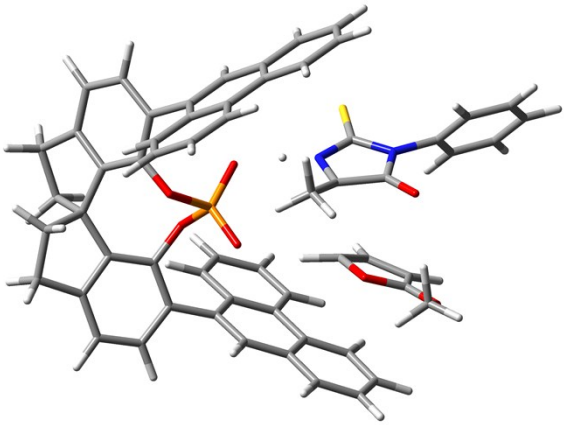
6.3 Screening of the orientation of the phenanthryl substituent in TS*s-re*s and TS*r-si*s

The geometries of **TS*s-re*s** were fully optimized and characterized using frequency calculations at the B3LYP density functional theory with the 6-31G(d) basis set. Relative energies of the optimized structures in the gas phase are shown in kcal/mol. The absolute configurations of the axial chirality at the phenanthryl-phenyl axis are shown in parentheses, for example (*S*,*R*) and (*S*,*S*) etc. The fomer letter indicates the absolute configration of the top-side phenanthryl-phenyl axis in the following figure. The most enagetically stable transition state, thus **TS*s-re*** (*S*,*R*), is identical to **TS*s-re*** as shown in Figure S3.

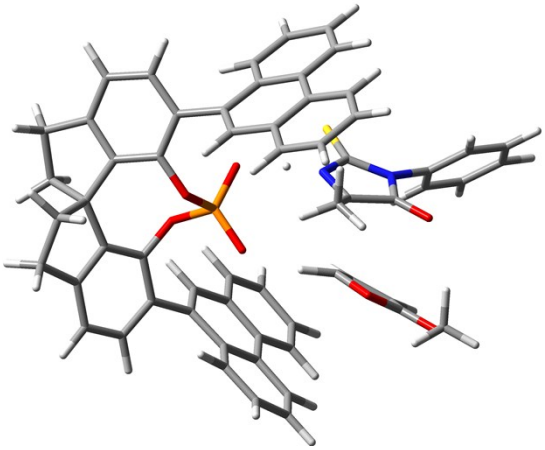
Figure S3. 3D structures and relative energies of transition states **TS*s-re*s**



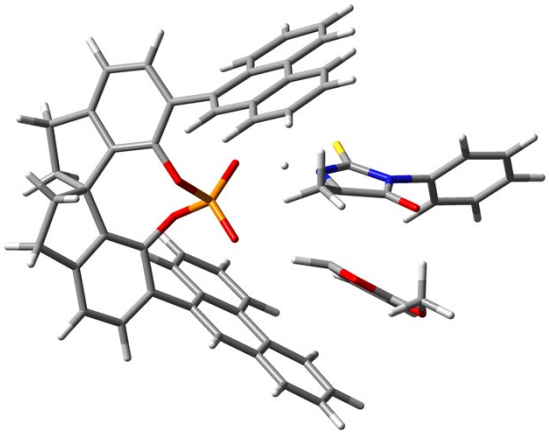
0.0
TS*s-re* (*S*,*R*) = **TS*s-re***: B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = -3689.21965995 a.u.
Number of imaginary frequency = 1



0.5
TS*s-re* (*S*,*S*): B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = -3689.21889602 a.u.
Number of imaginary frequency = 1



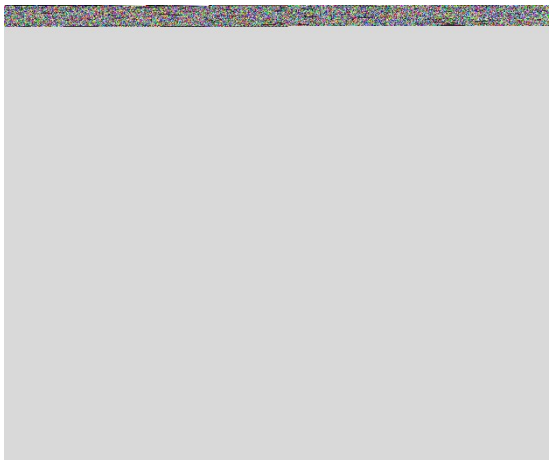
0.1
TS*s-re* (*R*,*R*): B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = -3689.21952492 a.u.
Number of imaginary frequency = 1



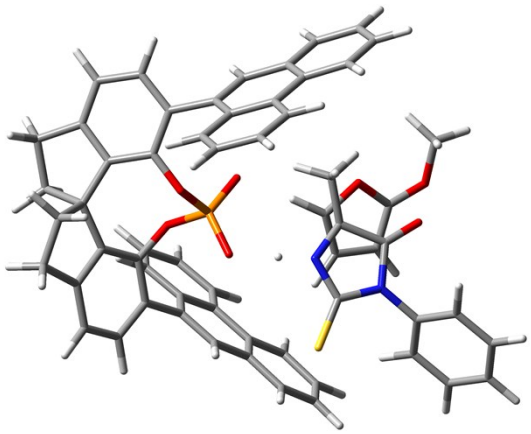
0.6
TS*s-re* (*R*,*S*): B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = -3689.21872709 a.u.
Number of imaginary frequency = 1

The geometries of **TS*r-si*s** were fully optimized and characterized using frequency calculations at the B3LYP density functional theory with the 6-31G(d) basis set. Relative energies of the optimized structures in the gas phase are shown in kcal/mol. The absolute configurations of the axial chirality at the phenanthryl-phenyl axis are shown in parentheses, for example (*S*,*R*) and (*S*,*S*) etc. The fomer letter indicates the absolute configration of the bottom-side phenanthryl-phenyl axis in the following figure. The most enagetically stable transition state, thus **TS*r-si*** (*S*,*R*), is identical to **TS*r-si*** as shown in Figure S4.

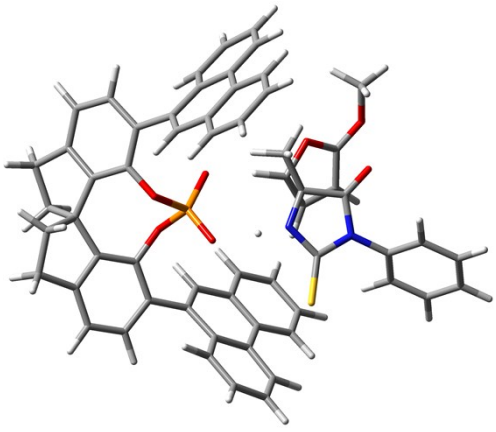
Figure S4. 3D structures and relative energies of transition states **TS*s-si*s**



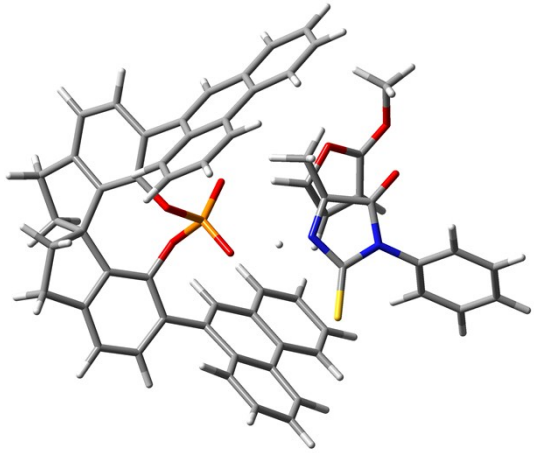
0.0
TS*r-si* (*S*,*R*) = **TS*r-si***: B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = -3689.21790557 a.u.
Number of imaginary frequency = 1



0.2
TS*r-si* (*S*,*S*): B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = -3689.21760446 a.u.
Number of imaginary frequency = 1



1.0
TS*r-si* (*R*,*R*): B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = -3689.21623815 a.u.
Number of imaginary frequency = 1

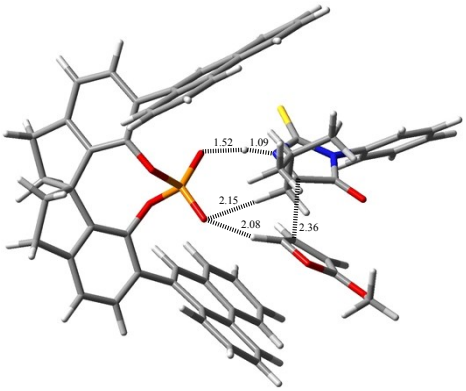


1.5
TS*r-si* (*R*,*S*): B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = -3689.21551016 a.u.
Number of imaginary frequency = 1

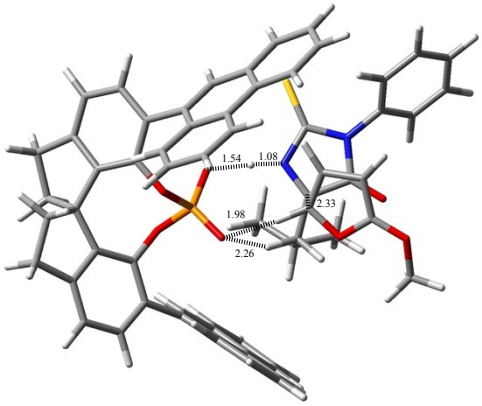
6.4 3D structures of TS*s-re* and TS*s-si* from 4b and 4d

The geometries of **TS*s-re*s** and **TS*r-si*s** in which Me was substituted by *i*-Bu or *i*-Pr were fully optimized and characterized using frequency calculations at the B3LYP density functional theory with the 6-31G(d) basis set. Relative energies of the optimized structures in the gas phase are shown in kcal/mol. Relative Gibbs free energies (in kcal/mol) are shown in parentheses. Relative energies (in kcal/mol) obtained by single-point energy calculations at the M06-2X/6-311+G(d,p) level with the SCRF method based on PCM (ϵ = 2.2706 for benzene) are shown in double parentheses.

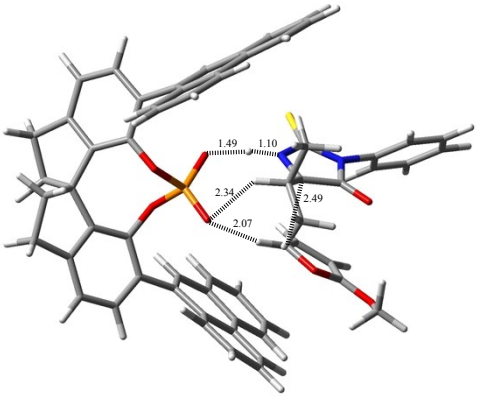
Figure S5. 3D structures and relative energies of the transition states **TS*s-re*s** and **TS*r-si*s** from **4b** and **4d**



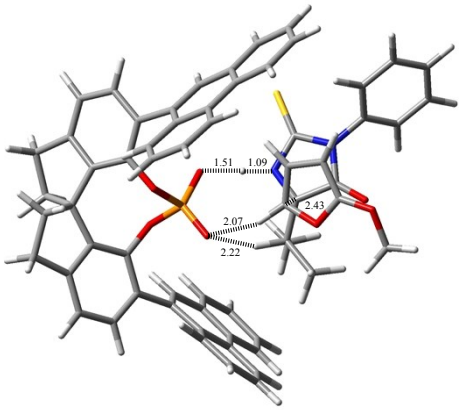
TS*s-re-iBu*
0.0 (0.0) ((0.0))



TS*r-si-iBu*
1.5 (2.7) ((3.6))



TS*s-re-iPr*
0.0 (0.0) ((0.0))



TS*r-si-iPr*
-0.2 (0.7) ((2.9))

6.4 Cartesian coordinates of DFT calculations

TS*s-rs* B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = -3689.21965995 a.u.
Sum of electronic and thermal Free Energies = -3688.407994 a.u.
Thermal correction to Gibbs Free Energies = 0.811666 a.u.
Number of imaginary frequency = 1
PCM (benzene)/B3LYP/6-311+G(d,p); SCF Done: E(B3LYP) = -3690.02576108 a.u
PCM (benzene)/M06-2X/6-311+G(d,p) ; SCF Done : E(RM062X) = -3688.82661123 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.241077	-0.873389	1.312740
2	6	0	2.005146	1.299990	0.565584
3	1	0	0.561868	1.040374	-1.005916
4	6	0	3.178324	-1.517454	0.494019
5	6	0	4.379441	-1.624590	1.197127
6	6	0	4.117912	-1.070198	2.449042
7	8	0	2.846381	-0.669590	2.556531
8	1	0	1.151578	-0.930704	1.317617
9	1	0	2.979646	-1.852589	-0.515421
10	1	0	5.330563	-2.014054	0.868212
11	8	0	4.932743	-0.935594	3.468479
12	6	0	4.503025	-0.098847	4.565743
13	1	0	3.609688	-0.516907	5.036219
14	1	0	5.338735	-0.099229	5.264045
15	1	0	4.304567	0.909941	4.196659
16	6	0	3.487368	1.485002	0.523760
17	6	0	2.651902	1.288323	-1.607948
18	7	0	1.590767	1.255623	-0.710411
19	8	0	4.258512	1.623066	1.456141
20	6	0	1.145500	1.757666	1.694603
21	1	0	0.893255	2.812537	1.524218
22	1	0	0.218468	1.178780	1.740399
23	1	0	1.692184	1.673758	2.634806
24	16	0	2.519217	1.202293	-3.244538
25	7	0	3.811155	1.430251	-0.839344
26	6	0	-4.755937	0.298600	-1.133135
27	6	0	-3.757471	1.098870	-0.577937
28	6	0	-3.607558	2.440181	-0.983116
29	6	0	-4.434623	2.924782	-2.006710
30	6	0	-5.373292	2.105810	-2.636481
31	6	0	-5.525971	0.795545	-2.196594
32	1	0	-4.313211	3.956506	-2.324993
33	1	0	-5.968407	2.489787	-3.461414
34	6	0	-6.434053	-0.285506	-2.743184
35	1	0	-7.475226	-0.132942	-2.424778
36	1	0	-6.441757	-0.312401	-3.838980
37	6	0	-5.237922	-1.098115	-0.752092
38	6	0	-5.837999	-1.566689	-2.119819
39	1	0	-5.022996	-1.939226	-2.750610
40	1	0	-6.567156	-2.375090	-2.002843
41	6	0	-6.372981	-1.037144	0.326070
42	1	0	-6.045817	-0.383111	1.142474
43	1	0	-7.308538	-0.631838	-0.072756
44	6	0	-6.501964	-2.486876	0.842765
45	1	0	-7.213303	-3.065580	0.236158
46	1	0	-6.858564	-2.537491	1.878127
47	6	0	-5.091559	-3.012760	0.687386
48	6	0	-4.337975	-2.163493	-0.135361
49	6	0	-4.516295	-4.144812	1.255987
50	1	0	-5.101661	-4.812259	1.883778
51	6	0	-2.975350	-2.403567	-0.310249
52	6	0	-3.169801	-4.413152	1.013066
53	6	0	-2.368058	-3.546706	0.250286
54	1	0	-2.714906	-5.304588	1.435360
55	8	0	-2.887768	0.565636	0.360535
56	8	0	-2.219992	-1.494575	-1.031681
57	15	0	-1.541352	-0.231066	-0.202134
58	8	0	-0.795914	-0.691180	1.015897
59	8	0	-0.851271	0.593031	-1.267851
60	6	0	-0.936644	-3.885645	0.002362
61	6	0	-0.491925	-4.013938	-1.284203
62	6	0	-0.020024	-4.158462	1.096606
63	6	0	0.830540	-4.454873	-1.604639
64	1	0	-1.166489	-3.793844	-2.106154
65	6	0	1.293302	-4.653740	0.821096
66	6	0	1.730489	-4.813428	-0.559596
67	6	0	-2.574225	3.340596	-0.386939
68	6	0	-1.503760	3.718719	-1.145294
69	6	0	-2.716383	3.862961	0.958710
70	6	0	-0.487963	4.600618	-0.654912
71	1	0	-1.388863	3.305734	-2.142619
72	6	0	-1.733340	4.758811	1.483914
73	6	0	-0.586909	5.131766	0.664353
74	6	0	-1.916333	5.258620	2.795180
75	1	0	-1.188956	5.944341	3.216521
76	6	0	0.622274	4.938914	-1.466046
77	1	0	0.681111	4.517580	-2.466708
78	6	0	0.445196	5.992778	1.110147
79	6	0	1.520321	6.311866	0.299383
80	1	0	2.294816	6.977922	0.670796
81	6	0	1.613896	5.780438	-1.001245
82	1	0	2.459436	6.033415	-1.635422
83	1	0	0.403458	6.418516	2.107034
84	6	0	-0.385985	-3.913245	2.443140
85	1	0	-1.354146	-3.471770	2.645910
86	6	0	2.142384	-4.947686	1.915370
87	1	0	3.135685	-5.343727	1.733441
88	6	0	0.472750	-4.196549	3.487247
89	1	0	0.166123	-3.996664	4.510553
90	6	0	1.743640	-4.736208	3.221511
91	1	0	2.418735	-4.976055	4.039159
92	6	0	3.013438	-5.288034	-0.924061
93	6	0	3.394054	-5.394899	-2.250186
94	1	0	4.385429	-5.765620	-2.497564
95	6	0	2.503498	-5.029776	-3.278013
96	1	0	2.806790	-5.112684	-4.318131
97	6	0	1.242641	-4.570245	-2.954344
98	1	0	0.541912	-4.287722	-3.736132
99	1	0	3.722093	-5.581019	-0.156595
100	6	0	-3.827399	3.518104	1.765020
101	1	0	-4.574903	2.844783	1.360374
102	6	0	-3.975015	4.022142	3.042009
103	1	0	-4.836829	3.741123	3.641321
104	6	0	-3.009179	4.901219	3.562051
105	1	0	-3.120985	5.304139	4.565245
106	6	0	5.154255	1.521406	-1.330440
107	6	0	5.921312	2.640317	-1.000415
108	6	0	5.692024	0.488781	-2.101640
109	6	0	7.239319	2.723854	-1.448380
110	1	0	5.489313	3.432012	-0.397950
111	6	0	7.006642	0.587608	-2.554953
112	1	0	5.083680	-0.373100	-2.351513
113	6	0	7.782471	1.701637	-2.228130
114	1	0	7.838384	3.592492	-1.190824
115	1	0	7.424096	-0.209847	-3.162885
116	1	0	8.807454	1.772755	-2.581016

TS*s-si* B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = -3689.21605688 a.u.
Sum of electronic and thermal Free Energies = -3688.404477 a.u.
Thermal correction to Gibbs Free Energies = 0.811580 a.u.
Number of imaginary frequency = 1
PCM (benzene)/B3LYP/6-311+G(d,p); SCF Done: E(B3LYP) = -3690.01974565 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.292196	1.214439	-1.141312
2	6	0	2.239558	-0.078800	1.322438
3	6	0	1.787017	-0.012222	2.650887
4	6	0	2.890776	0.158469	3.479261
5	6	0	4.001045	0.108755	2.630859
6	8	0	3.647623	-0.096668	1.360794
7	1	0	1.803842	-0.629725	0.505006
8	1	0	0.739535	-0.073092	2.909226
9	1	0	2.927673	0.304450	4.548071
10	8	0	5.265851	0.222168	2.949102
11	6	0	6.225334	0.377879	1.876491
12	1	0	6.016031	1.306318	1.340159
13	1	0	7.194025	0.421716	2.372041
14	1	0	6.176635	-0.474380	1.194905
15	6	0	3.066871	2.320361	0.320293
16	6	0	1.626742	1.915406	0.373867
17	6	0	2.371958	1.571333	-1.743518
18	7	0	1.281655	1.586725	-0.886525
19	8	0	3.757105	2.777820	1.212584
20	6	0	0.639001	2.482379	1.339174
21	1	0	0.251821	3.421320	0.923044
22	1	0	-0.197683	1.794893	1.479372
23	1	0	1.127862	2.691553	2.292074
24	16	0	2.340940	1.148966	-3.331638
25	7	0	3.464916	2.016973	-0.989503
26	6	0	-4.571857	-1.077569	-1.395535
27	6	0	-4.000464	0.010362	-0.736980
28	6	0	-4.331704	1.328747	-1.107149
29	6	0	-5.185174	1.519045	-2.203072
30	6	0	-5.683772	0.439521	-2.934888
31	6	0	-5.371415	-0.852912	-2.527465
32	1	0	-5.434149	2.535442	-2.495468
33	1	0	-6.301802	0.612633	-3.812535
34	6	0	-5.751731	-2.167422	-3.175415
35	1	0	-6.799751	-2.427859	-2.969089
36	1	0	-5.643109	-2.144221	-4.265924
37	6	0	-4.532171	-2.568791	-1.075458
38	6	0	-4.782404	-3.163984	-2.501615
39	1	0	-3.831376	-3.179944	-3.045833
40	1	0	-5.166303	-4.188909	-2.467370
41	6	0	-5.708136	-2.975892	-0.123833
42	1	0	-5.725145	-2.285518	0.727353
43	1	0	-6.683951	-2.921907	-0.617124
44	6	0	-5.344246	-4.394360	0.365406
45	1	0	-5.729024	-5.164485	-0.318402
46	1	0	-5.755973	-4.620166	1.355981
47	6	0	-3.831587	-4.360086	0.359002
48	6	0	-3.366489	-3.256258	-0.370119
49	6	0	-2.938779	-5.232749	0.972741
50	1	0	-3.295359	-6.100996	1.521544
51	6	0	-2.000743	-2.971173	-0.396165
52	6	0	-1.571827	-4.976749	0.879136
53	6	0	-1.072804	-3.836390	0.224726
54	1	0	-0.866358	-5.664311	1.336246
55	8	0	-3.072788	-0.201061	0.270685
56	8	0	-1.569005	-1.828789	-1.040824
57	15	0	-1.488753	-0.406943	-0.181919
58	8	0	-0.698044	-0.559150	1.080788
59	8	0	-1.100822	0.621338	-1.223561
60	6	0	0.399845	-3.609869	0.151827
61	6	0	0.995742	-3.416124	-1.065033
62	6	0	1.235624	-3.665568	1.341430
63	6	0	2.414035	-3.318155	-1.226371
64	1	0	0.379127	-3.350876	-1.955841
65	6	0	2.661058	-3.638985	1.216582
66	6	0	3.268845	-3.468613	-0.096369
67	6	0	-3.762054	2.511874	-0.394176
68	6	0	-2.851032	3.300448	-1.035502
69	6	0	-4.187381	2.858689	0.948580
70	6	0	-2.267934	4.454826	-0.421267
71	1	0	-2.515536	3.021202	-2.029470
72	6	0	-3.635983	4.007335	1.597029
73	6	0	-2.645672	4.820547	0.903341
74	6	0	-4.084197	4.317539	2.902803
75	1	0	-3.686116	5.186109	3.416371
76	6	0	-1.304133	5.227123	-1.113820
77	1	0	-1.030924	4.930199	-2.123720
78	6	0	-2.029528	5.958481	1.476863
79	6	0	-1.089169	6.698834	0.782251
80	1	0	-0.634684	7.567575	1.251274
81	6	0	-0.720067	6.332634	-0.526329
82	1	0	0.016794	6.918206	-1.069779
83	1	0	-2.289655	6.266387	2.483944

84	6	0	0.671070	−3.711290	2.640748
85	1	0	−0.406152	−3.657732	2.741194
86	6	0	3.440353	−3.747890	2.394049
87	1	0	4.522857	−3.759634	2.322800
88	6	0	1.460798	−3.797371	3.770848
89	1	0	0.998666	−3.830336	4.753893
90	6	0	2.860198	−3.837210	3.645087
91	1	0	3.487606	−3.923123	4.528479
92	6	0	4.666815	−3.416726	−0.310622
93	6	0	5.196879	−3.213259	−1.573044
94	1	0	6.275501	−3.188831	−1.706670
95	6	0	4.346431	−3.049558	−2.684369
96	1	0	4.764865	−2.889071	−3.674175
97	6	0	2.977866	−3.105178	−2.508090
98	1	0	2.308585	−2.985646	−3.356090
99	1	0	5.349137	−3.546558	0.522969
100	6	0	−5.158097	2.087875	1.631590
101	1	0	−5.579772	1.222677	1.132185
102	6	0	−5.573577	2.417669	2.906399
103	1	0	−6.320032	1.809100	3.409799
104	6	0	−5.029745	3.543632	3.548642
105	1	0	−5.353727	3.810249	4.551260
106	6	0	4.817252	2.128159	−1.446126
107	6	0	5.495782	0.990876	−1.892934
108	6	0	5.453460	3.369988	−1.399070
109	6	0	6.821270	1.109275	−2.309730
110	1	0	4.990514	0.031080	−1.914494
111	6	0	6.783698	3.474073	−1.807037
112	1	0	4.911788	4.240133	−1.044125
113	6	0	7.467125	2.347222	−2.266511
114	1	0	7.349281	0.229931	−2.667544
115	1	0	7.281377	4.438816	−1.770716
116	1	0	8.500313	2.433203	−2.591320

TS*r-re* B3LYP/6−31G(d)
SCF Done : E(RB3LYP) = −3689.21361007 a.u.
Sum of electronic and thermal Free Energies = −3688.401940 a.u.
Thermal correction to Gibbs Free Energies = 0.811670 a.u.
Number of imaginary frequency = 1
PCM (benzene)/B3LYP/6−311+G(d,p); SCF Done: E(B3LYP) = −3690.01934046 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	−0.805198	0.456574	−1.301721
2	6	0	−1.743075	1.048325	1.882709
3	6	0	−2.067575	2.032144	2.808124
4	6	0	−3.397248	1.834873	3.216038
5	6	0	−3.814870	0.694432	2.545196
6	8	0	−2.847571	0.197493	1.759186
7	1	0	−0.782102	0.625566	1.590630
8	1	0	−1.394060	2.812656	3.135752
9	1	0	−3.995295	2.424559	3.893569
10	8	0	−4.996330	0.107821	2.562792
11	6	0	−5.137399	−1.151931	1.858335
12	1	0	−4.999386	−1.008728	0.785108
13	1	0	−6.153840	−1.478142	2.072253
14	1	0	−4.413724	−1.880288	2.228978
15	6	0	−3.088136	2.658928	−0.223383
16	6	0	−1.677173	2.138726	−0.268799
17	6	0	−2.954048	0.827642	−1.605786
18	7	0	−1.675221	1.109692	−1.120685
19	8	0	−3.524722	3.612510	0.382820
20	6	0	−0.486843	2.972696	0.037050
21	1	0	−0.156182	3.459726	−0.890374
22	1	0	0.341032	2.362374	0.410660
23	1	0	−0.751027	3.745995	0.759383
24	16	0	−3.323316	−0.385766	−2.646216
25	7	0	−3.806043	1.789332	−1.062149
26	6	0	3.416147	−2.804535	−1.424270
27	6	0	2.164338	−2.816654	−0.810176
28	6	0	1.181186	−3.743895	−1.208604
29	6	0	1.447295	−4.550093	−2.326433
30	6	0	2.644053	−4.446183	−3.037569
31	6	0	3.628637	−3.579911	−2.574174
32	1	0	0.688358	−5.260308	−2.642457
33	1	0	2.803979	−5.047239	−3.929359
34	6	0	4.998061	−3.296956	−3.156675
35	1	0	5.690843	−4.130221	−2.971497
36	1	0	4.968810	−3.149666	−4.242587
37	6	0	4.719069	−2.130367	−1.008234
38	6	0	5.433138	−2.023539	−2.395457
39	1	0	5.057888	−1.134738	−2.915091
40	1	0	6.519453	−1.923407	−2.300532
41	6	0	5.544461	−3.066120	−0.058595
42	1	0	4.878469	−3.443904	0.725755
43	1	0	5.963870	−3.929994	−0.584105
44	6	0	6.614001	−2.148878	0.571944
45	1	0	7.520004	−2.105598	−0.049618
46	1	0	6.930391	−2.487116	1.565502
47	6	0	5.911292	−0.809448	0.606199
48	6	0	4.780720	−0.826797	−0.222492
49	6	0	6.240142	0.329217	1.335210
50	1	0	7.117371	0.346637	1.977304
51	6	0	3.935428	0.281482	−0.263307
52	6	0	5.427971	1.457211	1.226988
53	6	0	4.264885	1.458838	0.438351
54	1	0	5.688452	2.362735	1.767942
55	8	0	1.877256	−1.905074	0.194053
56	8	0	2.767941	0.203772	−1.003191
57	15	0	1.404828	−0.379451	−0.253210
58	8	0	1.115374	0.363593	1.016907
59	8	0	0.375304	−0.439375	−1.363767
60	6	0	3.482300	2.721920	0.295692
61	6	0	3.390844	3.307632	−0.935841
62	6	0	2.897889	3.392143	1.443380
63	6	0	2.792494	4.591768	−1.138129
64	1	0	3.813779	2.801274	−1.799061
65	6	0	2.317142	4.690658	1.291917
66	6	0	2.278533	5.316471	−0.023724
67	6	0	−0.108958	−3.919651	−0.476885
68	6	0	−1.289254	−3.700582	−1.128890
69	6	0	−0.131562	−4.426680	0.885774
70	6	0	−2.561878	−3.964876	−0.526701
71	1	0	−1.272806	−3.300965	−2.138616
72	6	0	−1.381478	−4.682923	1.530873
73	6	0	−2.626102	−4.459318	0.807560
74	6	0	−1.364319	−5.172724	2.858285
75	1	0	−2.299326	−5.368776	3.371997
76	6	0	−3.758798	−3.760209	−1.254336
77	1	0	−3.687972	−3.393368	−2.274339
78	6	0	−3.904010	−4.728590	1.354399
79	6	0	−5.062431	−4.521682	0.623799
80	1	0	−6.027496	−4.754534	1.067180
81	6	0	−4.992689	−4.030801	−0.694076
82	1	0	−5.901415	−3.876971	−1.269847
83	1	0	−3.990784	−5.123390	2.361150
84	6	0	2.851848	2.764250	2.711844
85	1	0	3.237879	1.756308	2.805175
86	6	0	1.763083	5.313003	2.436598
87	1	0	1.324990	6.301695	2.352290
88	6	0	2.293376	3.395288	3.806337
89	1	0	2.265462	2.890010	4.768005
90	6	0	1.754389	4.687360	3.669698
91	1	0	1.323916	5.194119	4.529755
92	6	0	1.738003	6.602590	−0.262082
93	6	0	1.696308	7.143315	−1.534771
94	1	0	1.275485	8.133941	−1.684987
95	6	0	2.196517	6.418392	−2.633261
96	1	0	2.160430	6.846505	−3.631357
97	6	0	2.736800	5.163982	−2.431903
98	1	0	3.133601	4.594066	−3.268680
99	1	0	1.346743	7.188718	0.562582
100	6	0	1.064455	−4.702073	1.590917
101	1	0	2.013580	−4.531757	1.096998
102	6	0	1.047111	−5.184593	2.884386
103	1	0	1.981548	−5.383784	3.401997
104	6	0	−0.180430	−5.416542	3.527489
105	1	0	−0.201814	−5.792571	4.546966
106	6	0	−5.195653	1.967059	−1.371347
107	6	0	−6.135469	1.938869	−0.339552
108	6	0	−5.588695	2.209890	−2.689512
109	6	0	−7.482470	2.149756	−0.635129
110	1	0	−5.818685	1.759002	0.681556
111	6	0	−6.938265	2.408270	−2.975535
112	1	0	−4.845495	2.239732	−3.478485
113	6	0	−7.886480	2.380052	−1.950723
114	1	0	−8.214805	2.132226	0.166853
115	1	0	−7.246353	2.591785	−4.000705
116	1	0	−8.936745	2.540442	−2.177302

TS*r-si* B3LYP/6−31G(d)
SCF Done : E(RB3LYP) = −3689.21790557 a.u.
Sum of electronic and thermal Free Energies = −3688.405731 a.u.
Thermal correction to Gibbs Free Energies = 0.812175 a.u.
Number of imaginary frequency = 1
PCM (benzene)/B3LYP/6−311+G(d,p); SCF Done: E(B3LYP) = −3690.02291959 a.u.
PCM (benzene)/M06−2X/6−311+G(d,p) ; SCF Done : E(RM062X) = −3688.83569225 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.935844	0.559897	1.681284
2	6	0	−1.860284	1.793727	−0.352081
3	1	0	−0.731930	0.368522	−1.493709
4	6	0	−2.965114	−0.375584	1.549941
5	6	0	−4.063526	0.075107	2.291563
6	6	0	−3.643530	1.264427	2.879484
7	8	0	−2.369142	1.543669	2.570892
8	1	0	−0.855093	0.463612	1.575638
9	1	0	−2.905229	−1.277643	0.954447
10	1	0	−5.046204	−0.361238	2.382582
11	8	0	−4.312200	2.070934	3.672194
12	6	0	−3.748396	3.375942	3.929587
13	1	0	−2.793197	3.282708	4.452348
14	1	0	−4.480611	3.879916	4.558991
15	1	0	−3.615450	3.907394	2.984466
16	6	0	−3.330604	2.053714	−0.294818
17	6	0	−2.861892	0.521282	−1.938736
18	7	0	−1.662298	0.922578	−1.350332
19	8	0	−3.936584	2.806809	0.445549
20	6	0	−0.831547	2.752663	0.133301
21	1	0	−0.618394	3.462751	−0.677533
22	1	0	0.097580	2.237452	0.396057
23	1	0	−1.211614	3.308999	0.990795
24	16	0	−2.997086	−0.517657	−3.203117
25	7	0	−3.875750	1.216029	−1.277475
26	6	0	3.584703	−2.832752	−1.157619
27	6	0	2.313068	−2.831467	−0.585822
28	6	0	1.364102	−3.809781	−0.944210
29	6	0	1.691185	−4.706200	−1.972701
30	6	0	2.914889	−4.636641	−2.641012
31	6	0	3.857669	−3.702457	−2.224959
32	1	0	0.958641	−5.456321	−2.257270
33	1	0	3.124791	−5.309834	−3.468574
34	6	0	5.233913	−3.425605	−2.793119
35	1	0	5.950970	−4.206652	−2.502736
36	1	0	5.235104	−3.390732	−3.888748
37	6	0	4.848517	−2.066199	−0.778494
38	6	0	5.594346	−2.065501	−2.153907
39	1	0	5.195396	−1.250305	−2.768012
40	1	0	6.672427	−1.907368	−2.045650
41	6	0	5.689340	−2.864276	0.276988
42	1	0	5.022672	−3.183113	1.086519
43	1	0	6.151947	−3.761282	−0.147053
44	6	0	6.711866	−1.844093	0.821774
45	1	0	7.627544	−1.831896	0.213076
46	1	0	7.021625	−2.062773	1.850353
47	6	0	5.958145	−0.537493	0.705169
48	6	0	4.840174	−0.687488	−0.127386
49	6	0	6.232568	0.683675	1.313091
50	1	0	7.102950	0.804611	1.953387
51	6	0	3.948636	0.373672	−0.283137
52	6	0	5.372572	1.758031	1.089196
53	6	0	4.213871	1.627608	0.304790

54	1	0	5.588886	2.723162	1.538505
55	8	0	1.966690	−1.853384	0.331251
56	8	0	2.797620	0.176666	−1.024187
57	15	0	1.443969	−0.389045	−0.248007
58	8	0	1.103449	0.432386	0.960186
59	8	0	0.441095	−0.579390	−1.366645
60	6	0	3.353964	2.821340	0.054383
61	6	0	3.172290	3.254255	−1.229636
62	6	0	2.774907	3.584285	1.146358
63	6	0	2.476233	4.463464	−1.546650
64	1	0	3.591224	2.679092	−2.050331
65	6	0	2.107769	4.820862	0.877557
66	6	0	1.961775	5.279626	−0.497854
67	6	0	0.033771	−3.912560	−0.274229
68	6	0	−1.102886	−3.742374	−1.012862
69	6	0	−0.076567	−4.262226	1.132267
70	6	0	−2.413376	−3.891548	−0.453701
71	1	0	−1.020674	−3.457771	−2.057685
72	6	0	−1.365675	−4.395834	1.735725
73	6	0	−2.563733	−4.208302	0.928023
74	6	0	−1.433004	−4.730085	3.109138
75	1	0	−2.398809	−4.832986	3.591899
76	6	0	−3.564315	−3.731122	−1.263463
77	1	0	−3.428943	−3.497007	−2.315628
78	6	0	−3.877853	−4.336458	1.440008
79	6	0	−4.988782	−4.174457	0.630937
80	1	0	−5.983709	−4.290812	1.052923
81	6	0	−4.833946	−3.873370	−0.736297
82	1	0	−5.706515	−3.764662	−1.375380
83	1	0	−4.030689	−4.576456	2.486650
84	6	0	2.825958	3.111742	2.480551
85	1	0	3.271753	2.142919	2.671002
86	6	0	1.584063	5.550135	1.972305
87	1	0	1.089173	6.499719	1.798427
88	6	0	2.293492	3.842638	3.524307
89	1	0	2.342906	3.455191	4.538412
90	6	0	1.680061	5.081627	3.269043
91	1	0	1.269924	5.667947	4.087504
92	6	0	1.318487	6.488961	−0.854792
93	6	0	1.181958	6.871100	−2.177479
94	1	0	0.683772	7.806405	−2.418767
95	6	0	1.685435	6.056401	−3.209553
96	1	0	1.574717	6.359418	−4.247194
97	6	0	2.322950	4.873510	−2.893030
98	1	0	2.721610	4.235219	−3.677907
99	1	0	0.920622	7.140445	−0.083998
100	6	0	1.072235	−4.498884	1.924494
101	1	0	2.049623	−4.419533	1.463290
102	6	0	0.972423	−4.829502	3.261218
103	1	0	1.871515	−5.003435	3.846103
104	6	0	−0.293394	−4.940132	3.861422
105	1	0	−0.379084	−5.197118	4.913919
106	6	0	−5.282162	1.121476	−1.538566
107	6	0	−5.982134	2.270988	−1.908468
108	6	0	−5.938485	−0.101935	−1.389864
109	6	0	−7.356147	2.192657	−2.133902
110	1	0	−5.455756	3.213534	−2.014614
111	6	0	−7.310394	−0.170997	−1.628449
112	1	0	−5.380990	−0.985722	−1.098334
113	6	0	−8.020832	0.972929	−1.998198
114	1	0	−7.904116	3.085636	−2.420207
115	1	0	−7.824753	−1.121754	−1.520981
116	1	0	−9.090310	0.913659	−2.179733

TS*s-re-iPr* B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = −3767.83787553 a.u.
Sum of electronic and thermal Free Energies = −3766.973659 a.u.
Thermal correction to Gibbs Free Energies = 0.864217 a.u.
Number of imaginary frequency = 1
PCM (benzene)/M06-2X/6-311+G(d,p) ; SCF Done : E(RM062X) = −3767.44147048 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.480527	−0.601246	0.903324
2	6	0	1.631867	1.734165	0.737908
3	1	0	0.166769	1.324169	−0.784953
4	6	0	3.251567	−0.762615	−0.244142
5	6	0	4.602663	−0.793120	0.134675
6	6	0	4.591210	−0.680288	1.517799
7	8	0	3.340314	−0.600537	1.995714
8	1	0	1.433864	−0.818034	1.105881
9	1	0	2.852307	−0.843109	−1.246380
10	1	0	5.481095	−0.874052	−0.486257
11	8	0	5.608105	−0.666094	2.354538
12	6	0	5.331286	−0.350640	3.734247
13	1	0	4.657592	−1.094803	4.166895
14	1	0	6.300663	−0.376824	4.230611
15	1	0	4.888319	0.646137	3.803804
16	6	0	3.058779	2.175660	0.628719
17	6	0	2.068891	2.174848	−1.444741
18	7	0	1.120016	1.791754	−0.494809
19	8	0	3.897921	2.294091	1.501611
20	6	0	0.758976	1.864659	1.958410
21	1	0	−0.184929	1.365479	1.724575
22	16	0	1.785933	2.298468	−3.059113
23	7	0	3.243158	2.429918	−0.743917
24	6	0	−4.594994	−1.065399	−1.253916
25	6	0	−3.921520	0.000336	−0.655812
26	6	0	−4.176091	1.323121	−1.068389
27	6	0	−5.052094	1.528958	−2.145570
28	6	0	−5.654071	0.464012	−2.815676
29	6	0	−5.422087	−0.829635	−2.362885
30	1	0	−5.240578	2.549158	−2.467798
31	1	0	−6.291905	0.648540	−3.676617
32	6	0	−5.933353	−2.135738	−2.932093
33	1	0	−6.988595	−2.299690	−2.670647
34	1	0	−5.872471	−2.169525	−4.026080
35	6	0	−4.650971	−2.538701	−0.869629
36	6	0	−5.017265	−3.176134	−2.252057
37	1	0	−4.097865	−3.295794	−2.836287
38	1	0	−5.479147	−4.163487	−2.148424
39	6	0	−5.796818	−2.817647	0.160476
40	1	0	−5.718343	−2.090564	0.976854
41	1	0	−6.792307	−2.715954	−0.283626
42	6	0	−5.504456	−4.235432	0.697764
43	1	0	−5.984876	−5.005286	0.076878
44	1	0	−5.868924	−4.384796	1.720817
45	6	0	−3.996371	−4.315199	0.600285
46	6	0	−3.498829	−3.279639	−0.203554
47	6	0	−3.132411	−5.227508	1.196707
48	1	0	−3.514084	−6.037254	1.813817
49	6	0	−2.121165	−3.102895	−0.334302
50	6	0	−1.761455	−5.093249	0.985900
51	6	0	−1.225337	−4.031212	0.236356
52	1	0	−1.078228	−5.817924	1.419166
53	8	0	−2.984060	−0.250141	0.336399
54	8	0	−1.646016	−1.994395	−1.019242
55	15	0	−1.429761	−0.601152	−0.140937
56	8	0	−0.639738	−0.850878	1.108037
57	8	0	−0.962862	0.424441	−1.156163
58	6	0	0.246431	−3.986533	−0.001774
59	6	0	0.718048	−4.011607	−1.285076
60	6	0	1.193766	−4.036872	1.098673
61	6	0	2.107273	−4.159773	−1.594224
62	1	0	0.016020	−3.956070	−2.111962
63	6	0	2.584792	−4.239629	0.835049
64	6	0	3.054107	−4.321458	−0.541705
65	6	0	−3.550214	2.519166	−0.427283
66	6	0	−2.648845	3.258879	−1.137785
67	6	0	−3.963339	2.968640	0.889072
68	6	0	−2.096547	4.483015	−0.640394
69	1	0	−2.322315	2.904217	−2.110801
70	6	0	−3.444308	4.191186	1.419511
71	6	0	−2.501481	4.976311	0.633620
72	6	0	−3.875644	4.598806	2.704366
73	1	0	−3.496355	5.520614	3.132424
74	6	0	−1.156918	5.211937	−1.409105
75	1	0	−0.853902	4.811401	−2.373525
76	6	0	−1.953855	6.205724	1.071896
77	6	0	−1.042155	6.905646	0.301459
78	1	0	−0.641435	7.848043	0.665759
79	6	0	−0.633138	6.404448	−0.949122
80	1	0	0.085352	6.955626	−1.549932
81	1	0	−2.248289	6.620686	2.030006
82	6	0	0.771673	−3.854103	2.438773
83	1	0	−0.271190	−3.628999	2.627716
84	6	0	3.469397	−4.324372	1.937353
85	1	0	4.526097	−4.499550	1.766205
86	6	0	1.664533	−3.923033	3.490556
87	1	0	1.315223	−3.775816	4.509034
88	6	0	3.023701	−4.180458	3.238299
89	1	0	3.728062	−4.258514	4.062987
90	6	0	4.408618	−4.528465	−0.894490
91	6	0	4.813435	−4.561344	−2.217230
92	1	0	5.861101	−4.725057	−2.455821
93	6	0	3.875484	−4.387490	−3.253017
94	1	0	4.197281	−4.412541	−4.290669
95	6	0	2.544724	−4.193106	−2.940712
96	1	0	1.806514	−4.066479	−3.728996
97	1	0	5.155831	−4.666915	−0.120353
98	6	0	−4.891492	2.228532	1.659861
99	1	0	−5.291632	1.308037	1.250038
100	6	0	−5.291304	2.654376	2.911104
101	1	0	−6.002300	2.065596	3.484398
102	6	0	−4.776256	3.850919	3.439156
103	1	0	−5.086471	4.191997	4.423397
104	6	0	4.489018	2.875192	−1.294711
105	6	0	5.063681	4.047294	−0.799171
106	6	0	5.127591	2.132632	−2.290242
107	6	0	6.288705	4.478383	−1.306999
108	1	0	4.557317	4.610357	−0.022772
109	6	0	6.346317	2.578596	−2.799925
110	1	0	4.669232	1.225493	−2.666416
111	6	0	6.929576	3.748361	−2.309140
112	1	0	6.737819	5.388915	−0.921120
113	1	0	6.840221	2.007613	−3.580822
114	1	0	7.880786	4.090069	−2.707391
115	6	0	0.499641	3.389598	2.124399
116	1	0	0.119514	3.847056	1.208238
117	1	0	−0.253305	3.527615	2.906731
118	1	0	1.413886	3.910418	2.431655
119	6	0	1.299212	1.277254	3.268197
120	1	0	1.313440	0.186656	3.244481
121	1	0	2.302835	1.645251	3.496007
122	1	0	0.628049	1.579416	4.078814

TS*r-si-iPr* B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = −3767.83817138 a.u.
Sum of electronic and thermal Free Energies = −3766.972545 a.u.
Thermal correction to Gibbs Free Energies = 0.865626 a.u.
Number of imaginary frequency = 1
PCM (benzene)/M06-2X/6-311+G(d,p) ; SCF Done : E(RM062X) = −3767.43685482 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.713672	0.939165	1.678157
2	6	0	−1.388689	2.230424	−0.358036
3	1	0	−0.608220	0.599218	−1.515467
4	6	0	−2.768591	0.088909	1.348968
5	6	0	−3.911315	0.516283	2.038321
6	6	0	−3.491971	1.603306	2.795917
7	8	0	−2.181177	1.840088	2.634283
8	1	0	−0.638041	0.775498	1.644473
9	1	0	−2.697418	−0.738521	0.655802
10	1	0	−4.914425	0.121122	1.992463
11	8	0	−4.192849	2.362284	3.610471
12	6	0	−3.593913	3.600659	4.050591
13	1	0	−2.709019	3.401095	4.660511
14	1	0	−4.363651	4.090138	4.645897
15	1	0	−3.327246	4.206736	3.181496
16	6	0	−2.785305	2.774724	−0.266472
17	6	0	−2.665415	1.188775	−1.924699

18	7	0	−1.404546	1.327995	−1.351253
19	8	0	−3.241595	3.607818	0.494211
20	6	0	−0.118778	2.959933	0.004306
21	1	0	0.643308	2.196158	0.202763
22	16	0	−3.031846	0.196391	−3.181733
23	7	0	−3.499372	2.083029	−1.257617
24	6	0	2.541973	−3.713411	−1.160559
25	6	0	1.321866	−3.304543	−0.621900
26	6	0	0.124755	−3.941764	−1.008583
27	6	0	0.182235	−4.881145	−2.051151
28	6	0	1.378921	−5.186378	−2.700285
29	6	0	2.557549	−4.608844	−2.240576
30	1	0	−0.739057	−5.368935	−2.356610
31	1	0	1.385812	−5.880060	−3.537409
32	6	0	3.969530	−4.791327	−2.757200
33	1	0	4.371588	−5.776157	−2.479844
34	1	0	4.026894	−4.726416	−3.850039
35	6	0	3.969561	−3.427351	−0.709014
36	6	0	4.738396	−3.650083	−2.052609
37	1	0	4.672183	−2.733900	−2.650061
38	1	0	5.799041	−3.872620	−1.895935
39	6	0	4.432453	−4.488746	0.348160
40	1	0	3.652368	−4.584170	1.112382
41	1	0	4.588950	−5.478271	−0.093205
42	6	0	5.705209	−3.888893	0.982800
43	1	0	6.605743	−4.175973	0.420954
44	1	0	5.860571	−4.221552	2.015758
45	6	0	5.448125	−2.401629	0.880070
46	6	0	4.395418	−2.143992	−0.008884
47	6	0	6.092294	−1.358876	1.538249
48	1	0	6.912399	−1.554037	2.224903
49	6	0	3.934814	−0.838538	−0.178699
50	6	0	5.677005	−0.050813	1.295743
51	6	0	4.594953	0.239044	0.446048
52	1	0	6.194255	0.775150	1.775467
53	8	0	1.284499	−2.267578	0.295406
54	8	0	2.824071	−0.620932	−0.975334
55	15	0	1.320002	−0.704859	−0.276818
56	8	0	1.213478	0.178815	0.929528
57	8	0	0.367009	−0.551340	−1.443629
58	6	0	4.265252	1.664730	0.154813
59	6	0	4.355688	2.116351	−1.132399
60	6	0	3.972693	2.610241	1.217032
61	6	0	4.238469	3.500536	−1.474611
62	1	0	4.562061	1.410526	−1.931934
63	6	0	3.897187	4.008634	0.926630
64	6	0	4.045350	4.469728	−0.447747
65	6	0	−1.189800	−3.691055	−0.346492
66	6	0	−2.250898	−3.273895	−1.101828
67	6	0	−1.399505	−4.003944	1.058967
68	6	0	−3.575154	−3.145137	−0.569846
69	1	0	−2.092560	−3.022659	−2.146615
70	6	0	−2.700498	−3.860534	1.636240
71	6	0	−3.817587	−3.430793	0.805145
72	6	0	−2.865131	−4.167998	3.007956
73	1	0	−3.840080	−4.059453	3.470356
74	6	0	−4.650856	−2.749942	−1.402708
75	1	0	−4.447843	−2.544408	−2.450090
76	6	0	−5.141821	−3.293190	1.288040
77	6	0	−6.177972	−2.904468	0.457000
78	1	0	−7.185613	−2.820601	0.855797
79	6	0	−5.934122	−2.633640	−0.903718
80	1	0	−6.751731	−2.345169	−1.559280
81	1	0	−5.364768	−3.507956	2.327458
82	6	0	3.734778	2.172761	2.542813
83	1	0	3.726029	1.107990	2.743289
84	6	0	3.655326	4.901839	1.998502
85	1	0	3.613714	5.969290	1.810036
86	6	0	3.485811	3.070161	3.562700
87	1	0	3.302191	2.708699	4.570941
88	6	0	3.462532	4.449379	3.290611
89	1	0	3.280135	5.161792	4.091081
90	6	0	3.986665	5.832781	−0.825380
91	6	0	4.102150	6.220551	−2.148572
92	1	0	4.052816	7.275121	−2.406609
93	6	0	4.284612	5.257530	−3.159285
94	1	0	4.373328	5.566462	−4.197299
95	6	0	4.353386	3.920733	−2.821497
96	1	0	4.499577	3.165129	−3.589662
97	1	0	3.848788	6.599986	−0.070850
98	6	0	−0.345638	−4.481160	1.874752
99	1	0	0.634824	−4.617626	1.435550
100	6	0	−0.540931	−4.778917	3.208475
101	1	0	0.288350	−5.140125	3.810486
102	6	0	−1.812432	−4.613647	3.783378
103	1	0	−1.972148	−4.842331	4.833751
104	6	0	−4.894425	2.297258	−1.509633
105	6	0	−5.326105	3.572940	−1.877123
106	6	0	−5.803717	1.248851	−1.358261
107	6	0	−6.684302	3.799966	−2.096711
108	1	0	−4.605300	4.376291	−1.986513
109	6	0	−7.158248	1.484373	−1.590591
110	1	0	−5.455567	0.262440	−1.072349
111	6	0	−7.601087	2.756763	−1.957198
112	1	0	−7.022967	4.791945	−2.381277
113	1	0	−7.868235	0.669666	−1.480143
114	1	0	−8.658157	2.934901	−2.133762
115	6	0	0.310783	3.752743	−1.262826
116	1	0	1.242228	4.282390	−1.045684
117	1	0	0.483871	3.090097	−2.114897
118	1	0	−0.445451	4.496542	−1.543033
119	6	0	−0.210319	3.903966	1.210090
120	1	0	−0.946272	4.697366	1.048171
121	1	0	−0.473636	3.379283	2.129305
122	1	0	0.770554	4.363829	1.359815

TS*s-re-iBu* B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = −3807.15856337 a.u.
Sum of electronic and thermal Free Energies = −3806.266326 a.u.
Thermal correction to Gibbs Free Energies = 0.892237 a.u.
Number of imaginary frequency = 1
PCM (benzene)/M06-2X/6-311+G(d,p) ; SCF Done : E(RM062X) = −3806.75256836 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.503610	−0.619846	0.912755
2	6	0	1.752593	1.601892	0.628750
3	1	0	0.242631	1.211539	−0.849754
4	6	0	3.423696	−0.870955	−0.109061
5	6	0	4.709321	−0.838196	0.439481
6	6	0	4.517405	−0.605314	1.798356
7	8	0	3.216894	−0.518979	2.106357
8	1	0	1.452355	−0.884628	1.013850
9	1	0	3.158344	−1.047990	−1.142743
10	1	0	5.662841	−0.944334	−0.053975
11	8	0	5.418266	−0.492823	2.747173
12	6	0	4.970071	−0.038156	4.042351
13	1	0	4.253011	−0.746057	4.465351
14	1	0	5.870833	0.007094	4.652987
15	1	0	4.517283	0.951517	3.945370
16	6	0	3.162344	2.071640	0.478716
17	6	0	2.114141	2.055298	−1.565450
18	7	0	1.196105	1.669375	−0.590053
19	8	0	4.013913	2.196728	1.339770
20	6	0	0.985012	1.649526	1.907373
21	1	0	0.248456	0.837888	1.909252
22	1	0	1.690982	1.487234	2.727812
23	16	0	1.790476	2.188486	−3.171853
24	7	0	3.312387	2.310912	−0.897199
25	6	0	−4.538917	−1.260220	−1.314613
26	6	0	−3.894135	−0.167392	−0.732471
27	6	0	−4.166951	1.139574	−1.182196
28	6	0	−5.028727	1.302008	−2.278226
29	6	0	−5.600539	0.210169	−2.930733
30	6	0	−5.353130	−1.067003	−2.441254
31	1	0	−5.230348	2.310205	−2.628995
32	1	0	−6.227459	0.361282	−3.806092
33	6	0	−5.834447	−2.395040	−2.984753
34	1	0	−6.890067	−2.570797	−2.732484
35	1	0	−5.758829	−2.454436	−4.076733
36	6	0	−4.574366	−2.725232	−0.896124
37	6	0	−4.909999	−3.401984	−2.267743
38	1	0	−3.980411	−3.518949	−2.836185
39	1	0	−5.355601	−4.394804	−2.146471
40	6	0	−5.727818	−3.003097	0.125708
41	1	0	−5.673363	−2.257135	0.926857
42	1	0	−6.719324	−2.929962	−0.332717
43	6	0	−5.416189	−4.403611	0.697336
44	1	0	−5.876130	−5.195470	0.088799
45	1	0	−5.789224	−4.536931	1.719530
46	6	0	−3.905893	−4.458589	0.618136
47	6	0	−3.417900	−3.430241	−0.200396
48	6	0	−3.032019	−5.343354	1.241060
49	1	0	−3.405388	−6.148676	1.868940
50	6	0	−2.042840	−3.229434	−0.319567
51	6	0	−1.661394	−5.186780	1.043452
52	6	0	−1.136318	−4.128453	0.280789
53	1	0	−0.970128	−5.890194	1.498445
54	8	0	−2.968809	−0.376537	0.281055
55	8	0	−1.582856	−2.125637	−1.021064
56	15	0	−1.401766	−0.711572	−0.165363
57	8	0	−0.629371	−0.945230	1.100305
58	8	0	−0.930388	0.302882	−1.185306
59	6	0	0.337053	−4.056352	0.062440
60	6	0	0.827625	−4.077565	−1.213966
61	6	0	1.270138	−4.080231	1.176390
62	6	0	2.223752	−4.199556	−1.502471
63	1	0	0.136759	−4.038848	−2.051006
64	6	0	2.668315	−4.258534	0.933650
65	6	0	3.158317	−4.340749	−0.435869
66	6	0	−3.586489	2.368281	−0.558554
67	6	0	−2.665843	3.099162	−1.253244
68	6	0	−4.077984	2.862141	0.714177
69	6	0	−2.169817	4.357778	−0.782311
70	1	0	−2.282389	2.712911	−2.192796
71	6	0	−3.617685	4.119582	1.216154
72	6	0	−2.651214	4.893189	0.447467
73	6	0	−4.130080	4.572017	2.455650
74	1	0	−3.799715	5.522808	2.860412
75	6	0	−1.214861	5.080974	−1.537181
76	1	0	−0.854187	4.648261	−2.467262
77	6	0	−2.157794	6.154911	0.858166
78	6	0	−1.230294	6.848715	0.100746
79	1	0	−0.874924	7.817976	0.440922
80	6	0	−0.748337	6.307455	−1.106497
81	1	0	−0.018373	6.854640	−1.697023
82	1	0	−2.511167	6.602067	1.781333
83	6	0	0.826793	−3.893100	2.508934
84	1	0	−0.222284	−3.685010	2.681810
85	6	0	3.539705	−4.314134	2.048216
86	1	0	4.602117	−4.468030	1.892820
87	6	0	1.706439	−3.934943	3.573088
88	1	0	1.340417	−3.784159	4.585153
89	6	0	3.073825	−4.166743	3.341697
90	1	0	3.768845	−4.220931	4.176077
91	6	0	4.521294	−4.525572	−0.768553
92	6	0	4.946033	−4.553058	−2.085186
93	1	0	5.999655	−4.699369	−2.308318
94	6	0	4.020400	−4.396388	−3.134829
95	1	0	4.357779	−4.416534	−4.167605
96	6	0	2.681674	−4.226527	−2.842416
97	1	0	1.952921	−4.114751	−3.641617
98	1	0	5.258994	−4.651538	0.016794
99	6	0	−5.026897	2.130594	1.468039
100	1	0	−5.380518	1.182171	1.079412
101	6	0	−5.504237	2.599405	2.676031
102	1	0	−6.229467	2.016506	3.237397
103	6	0	−5.050265	3.832700	3.174800
104	1	0	−5.422945	4.208874	4.123940
105	6	0	4.539634	2.760372	−1.485198
106	6	0	5.119786	3.940854	−1.016963
107	6	0	5.157235	2.009927	−2.487928
108	6	0	6.329246	4.372865	−1.560238
109	1	0	4.629948	4.509381	−0.233860
110	6	0	6.360312	2.456594	−3.032901
111	1	0	4.694593	1.096016	−2.842526
112	6	0	6.948887	3.635099	−2.570054

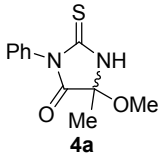
113	1	0	6.782764	5.290042	−1.195822
114	1	0	6.837830	1.879496	−3.819480
115	1	0	7.887787	3.977516	−2.995970
116	6	0	0.240681	3.001164	2.121067
117	1	0	−0.475309	3.114892	1.298707
118	6	0	−0.550356	2.911200	3.433039
119	1	0	−1.148579	3.816451	3.581759
120	1	0	−1.234073	2.055890	3.427022
121	1	0	0.123226	2.805132	4.293871
122	6	0	1.177995	4.215963	2.117779
123	1	0	1.965796	4.114230	2.875034
124	1	0	1.661529	4.362406	1.144516
125	1	0	0.613176	5.129469	2.330737

TS*r-si-iBu* B3LYP/6-31G(d)
SCF Done : E(RB3LYP) = −3807.15609712 a.u.
Sum of electronic and thermal Free Energies = −3806.262013 a.u.
Thermal correction to Gibbs Free Energies = 0.894084 a.u.
Number of imaginary frequency = 1
PCM (benzene)/M06-2X/6-311+G(d,p) ; SCF Done : E(RM062X) = −3806.74688562 a.u.

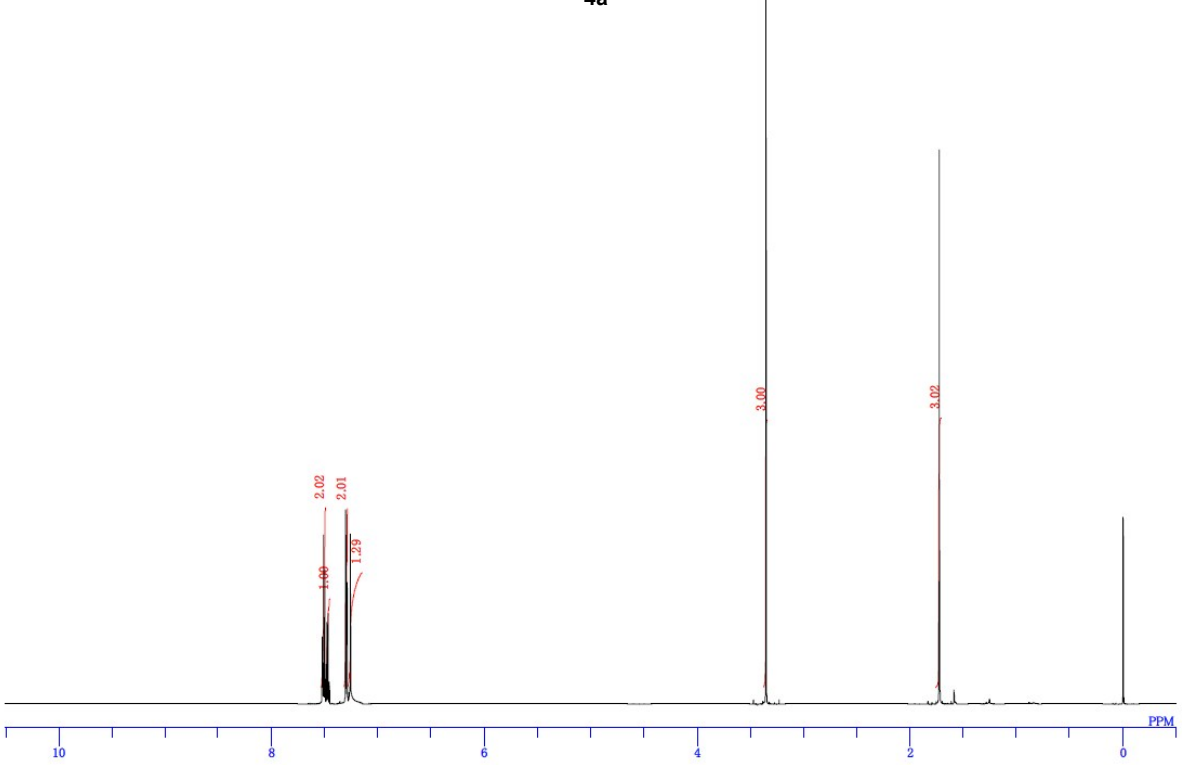
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.796648	0.818599	1.611736
2	6	0	−1.744294	1.807574	−0.500138
3	1	0	−0.834069	0.209554	−1.580047
4	6	0	−2.923942	−0.012044	1.654194
5	6	0	−3.907160	0.619286	2.420132
6	6	0	−3.325030	1.810428	2.850123
7	8	0	−2.059738	1.921296	2.428422
8	1	0	−0.740132	0.579562	1.471879
9	1	0	−3.003184	−0.967853	1.151751
10	1	0	−4.917685	0.301306	2.625564
11	8	0	−3.847020	2.755098	3.596920
12	6	0	−3.136538	4.011185	3.680793
13	1	0	−2.157379	3.865211	4.143523
14	1	0	−3.763367	4.647787	4.303656
15	1	0	−3.026182	4.432128	2.678938
16	6	0	−3.175543	2.226905	−0.387307
17	6	0	−2.976088	0.507009	−1.898562
18	7	0	−1.710948	0.820827	−1.412869
19	8	0	−3.656502	3.100420	0.312038
20	6	0	−0.589818	2.716258	−0.225876
21	1	0	0.283894	2.118032	0.052089
22	1	0	−0.857762	3.343396	0.628776
23	16	0	−3.304469	−0.606177	−3.061933
24	7	0	−3.866952	1.366573	−1.251555
25	6	0	3.015534	−3.393835	−1.321192
26	6	0	1.799455	−3.205074	−0.668133
27	6	0	0.693656	−4.027777	−0.963052
28	6	0	0.811947	−4.933306	−2.029724
29	6	0	1.977966	−5.019527	−2.792977
30	6	0	3.080294	−4.253403	−2.427480
31	1	0	−0.038555	−5.566179	−2.267234
32	1	0	2.022117	−5.689088	−3.648467
33	6	0	4.445979	−4.170003	−3.078777
34	1	0	5.037973	−5.076275	−2.887477
35	1	0	4.382292	−4.062698	−4.167947
36	6	0	4.410880	−2.883558	−0.982362
37	6	0	5.075055	−2.930937	−2.396732
38	1	0	4.798390	−2.023692	−2.945389
39	1	0	6.168200	−2.973124	−2.345499
40	6	0	5.130975	−3.900442	−0.027822
41	1	0	4.443667	−4.163981	0.784451
42	1	0	5.411188	−4.826497	−0.539671
43	6	0	6.332626	−3.125205	0.547478
44	1	0	7.214726	−3.215023	−0.103007
45	1	0	6.634780	−3.483109	1.538600
46	6	0	5.815035	−1.704771	0.570761
47	6	0	4.676579	−1.579106	−0.238150
48	6	0	6.310876	−0.616350	1.281089
49	1	0	7.194063	−0.714707	1.907505
50	6	0	3.994600	−0.360598	−0.286986
51	6	0	5.655875	0.608544	1.176899
52	6	0	4.492986	0.762513	0.403105
53	1	0	6.041020	1.474053	1.708961
54	8	0	1.666397	−2.188071	0.262462
55	8	0	2.830891	−0.272732	−1.029643
56	15	0	1.378588	−0.655654	−0.315739
57	8	0	1.115937	0.196646	0.890774
58	8	0	0.406580	−0.697062	−1.473186
59	6	0	3.899761	2.128935	0.285152
60	6	0	3.975798	2.786006	−0.910426
61	6	0	3.369493	2.821758	1.444685
62	6	0	3.599802	4.159437	−1.059409
63	1	0	4.372515	2.268340	−1.779726
64	6	0	3.008273	4.201567	1.348013
65	6	0	3.137116	4.892965	0.071695
66	6	0	−0.578925	−3.968833	−0.185834
67	6	0	−1.753312	−3.723036	−0.841235
68	6	0	−0.609158	−4.255166	1.240826
69	6	0	−3.023420	−3.728633	−0.177991
70	1	0	−1.731975	−3.494458	−1.902891
71	6	0	−1.852519	−4.235451	1.946841
72	6	0	−3.089557	−3.965798	1.225729
73	6	0	−1.842636	−4.509673	3.335186
74	1	0	−2.772396	−4.495726	3.893430
75	6	0	−4.218153	−3.507599	−0.906145
76	1	0	−4.148976	−3.340819	−1.977122
77	6	0	−4.364232	−3.947218	1.842723
78	6	0	−5.518393	−3.724471	1.112726
79	1	0	−6.482259	−3.727944	1.615139
80	6	0	−5.448797	−3.508762	−0.277264
81	1	0	−6.357363	−3.354462	−0.853707
82	1	0	−4.452678	−4.121620	2.909532
83	6	0	3.185692	2.148966	2.676883
84	1	0	3.407984	1.090018	2.728281
85	6	0	2.523708	4.848709	2.510094
86	1	0	2.254578	5.898848	2.469174
87	6	0	2.703584	2.808587	3.789889
88	1	0	2.567634	2.269299	4.723458
89	6	0	2.380712	4.174661	3.708213
90	1	0	2.010649	4.702049	4.583997
91	6	0	2.815514	6.259388	−0.111406
92	6	0	2.935736	6.870797	−1.346779
93	1	0	2.681577	7.921984	−1.454357
94	6	0	3.389738	6.139846	−2.461241
95	1	0	3.485297	6.624108	−3.429339
96	6	0	3.717033	4.806502	−2.313179
97	1	0	4.075020	4.229942	−3.162871
98	1	0	2.467921	6.851981	0.728145
99	6	0	0.568265	−4.584951	1.953830
100	1	0	1.508664	−4.628918	1.418157
101	6	0	0.543386	−4.855706	3.307343
102	1	0	1.464383	−5.103805	3.827791
103	6	0	−0.673825	−4.809578	4.007552
104	1	0	−0.700278	−5.017633	5.073926
105	6	0	−5.288309	1.411338	−1.432628
106	6	0	−5.875726	2.590844	−1.893080
107	6	0	−6.068269	0.297193	−1.117361
108	6	0	−7.260977	2.653608	−2.040986
109	1	0	−5.253504	3.447783	−2.128661
110	6	0	−7.451353	0.367258	−1.279115
111	1	0	−5.597897	−0.612256	−0.758974
112	6	0	−8.049658	1.542611	−1.737982
113	1	0	−7.721071	3.570649	−2.397409
114	1	0	−8.061968	−0.499271	−1.041671
115	1	0	−9.128180	1.592424	−1.858767
116	6	0	−0.219146	3.640040	−1.433599
117	1	0	0.581147	4.269612	−1.025847
118	6	0	−1.365190	4.567559	−1.862459
119	1	0	−2.168924	4.014891	−2.367053
120	1	0	−1.806055	5.096794	−1.010092
121	1	0	−0.997696	5.316147	−2.573410
122	6	0	0.361849	2.876201	−2.631585
123	1	0	1.141210	2.170962	−2.326451
124	1	0	−0.406808	2.310776	−3.170598
125	1	0	0.806090	3.584978	−3.339684

7. ^{1}H and ^{13}C NMR spectra, HPLC Charts

Me_Ph_SM



4a



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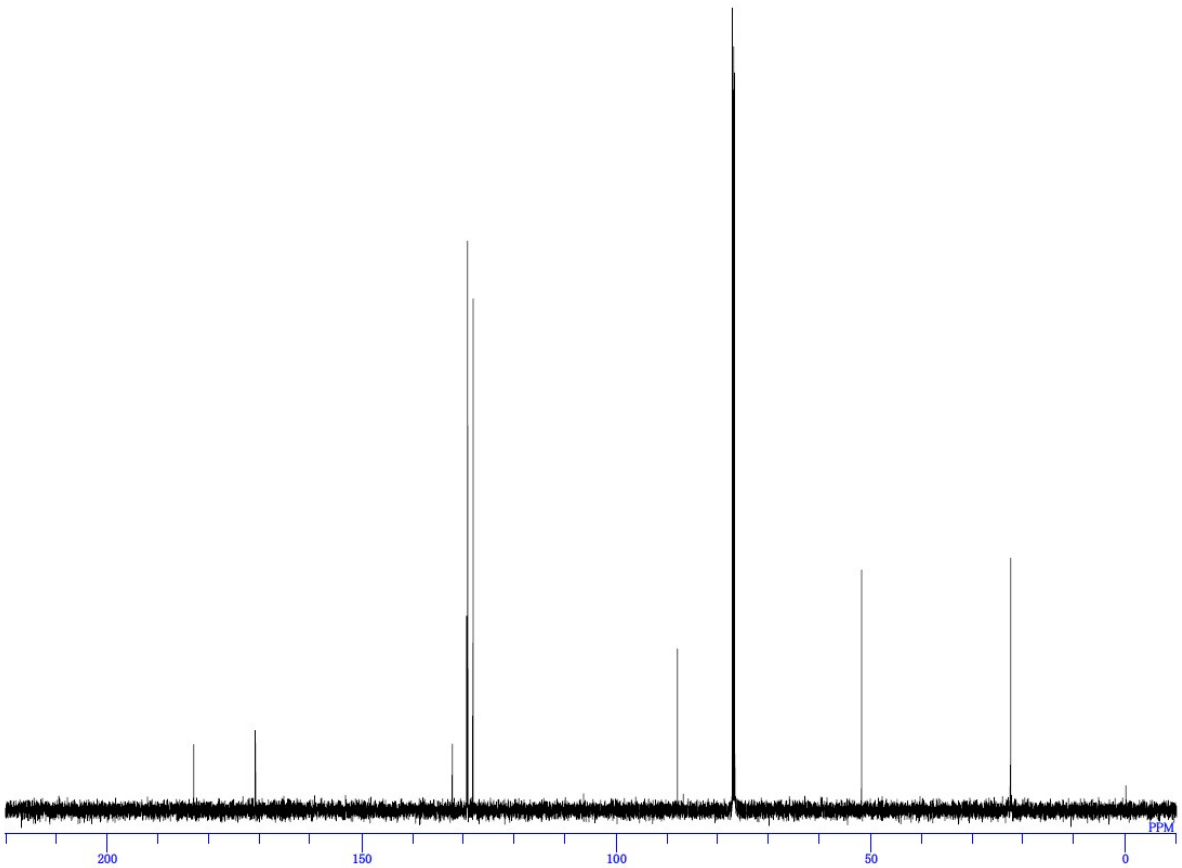

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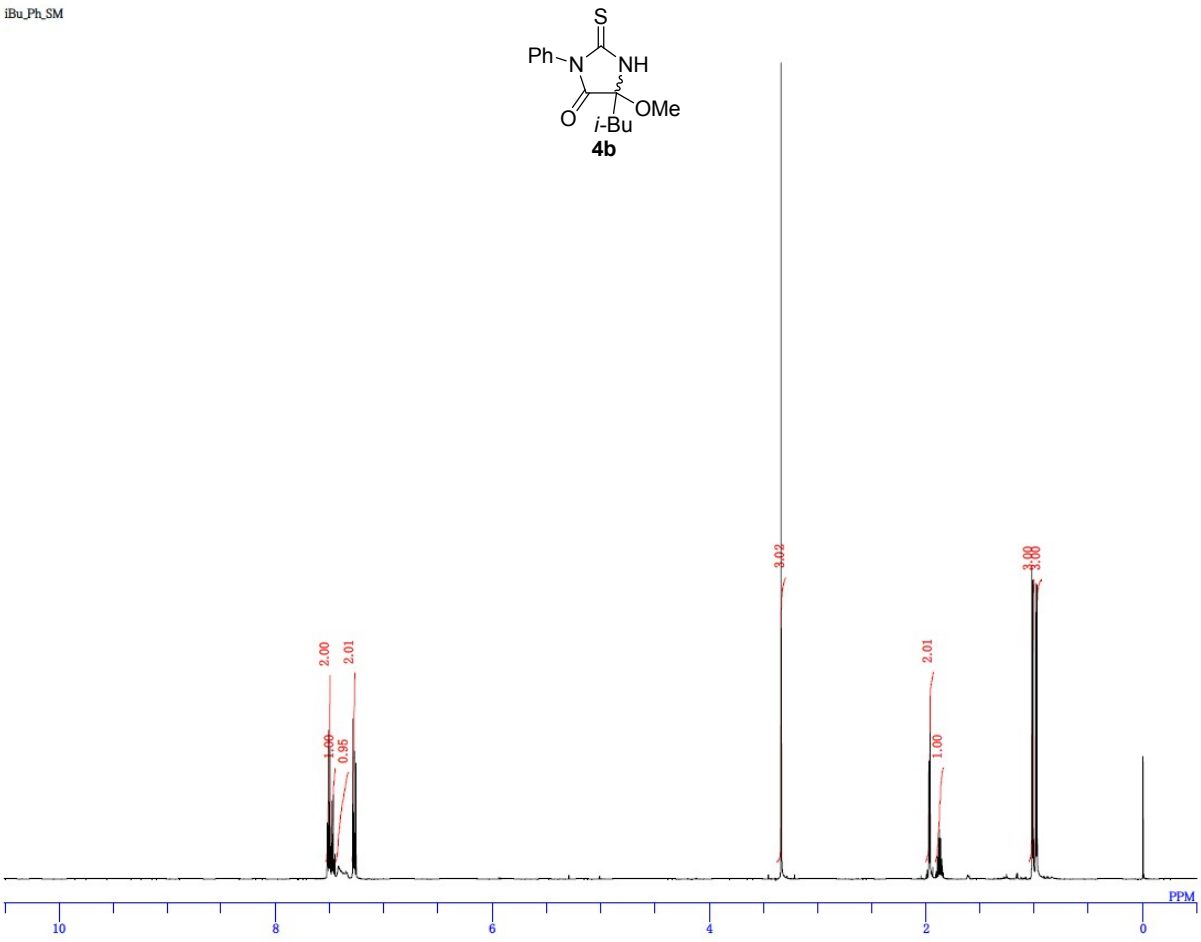

4b

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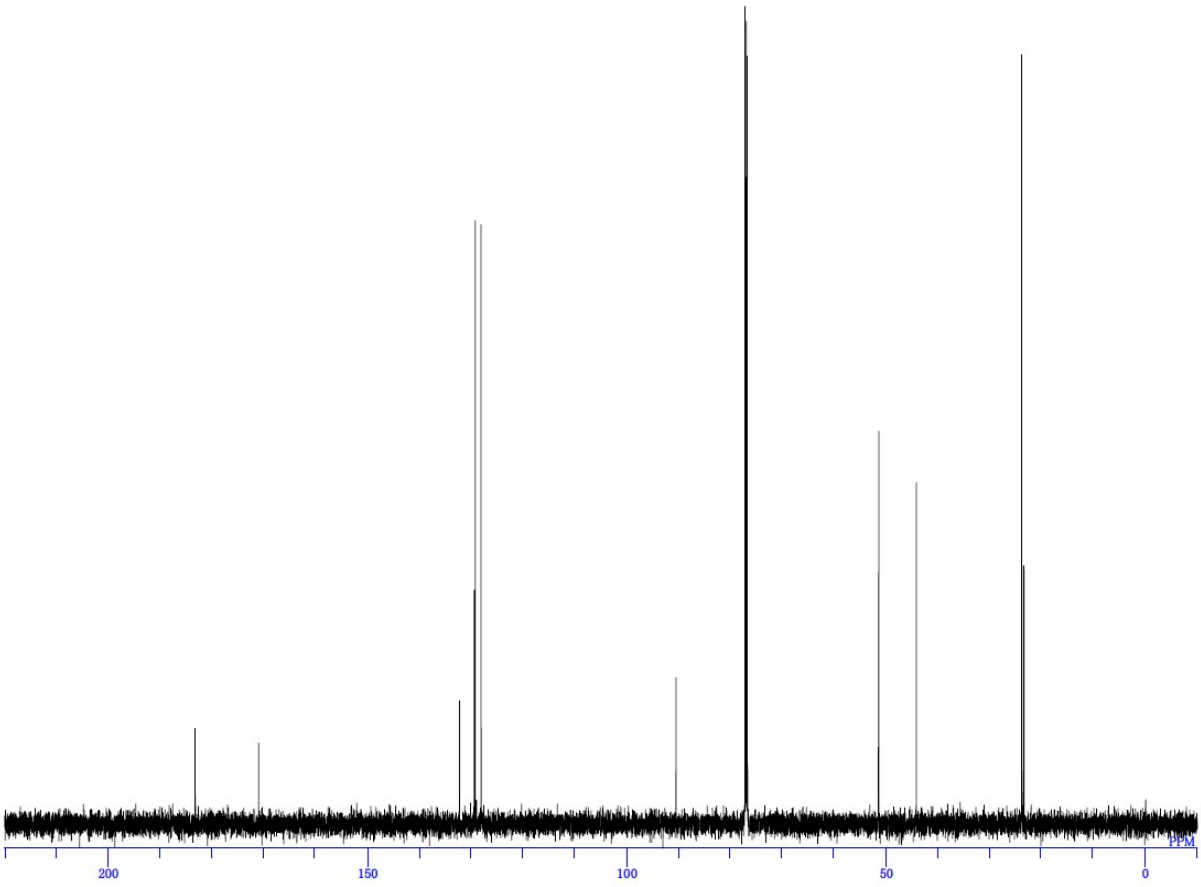

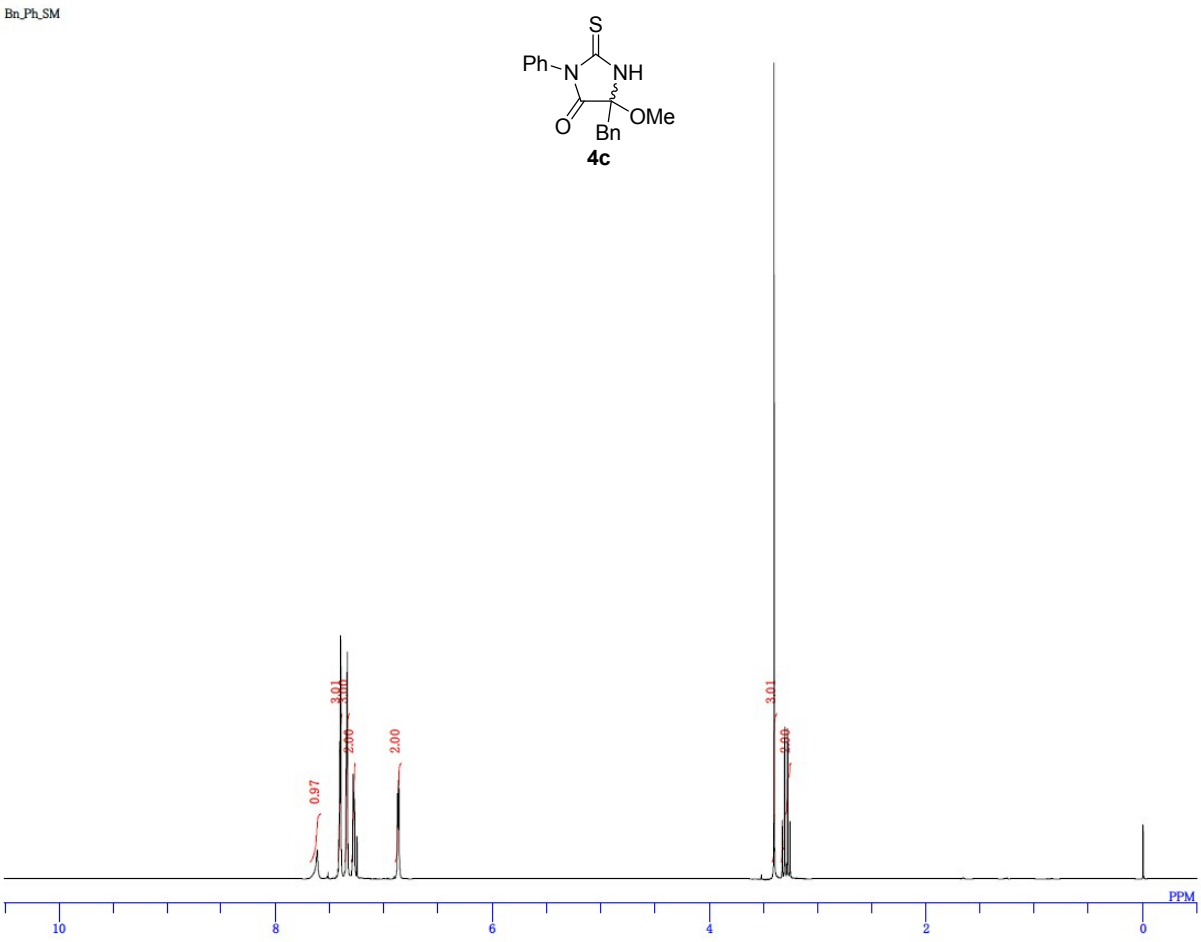
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Ph
N
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O
OMe
Bn
4c
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2.00
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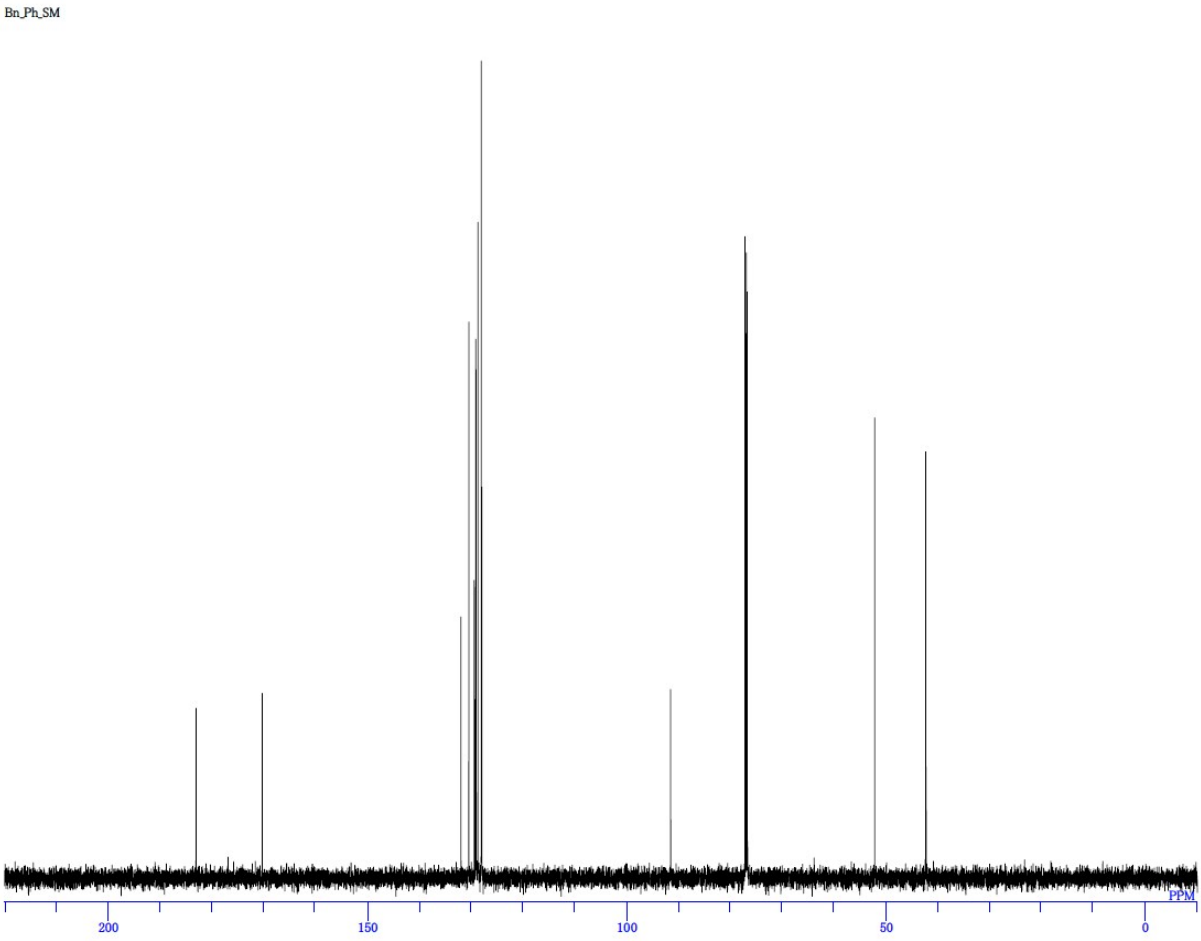
3.01
3.00
PPM
10
8
6
4
2
0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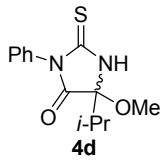
PPM
200
150
100
50
0

iPr_Ph_SM



4d

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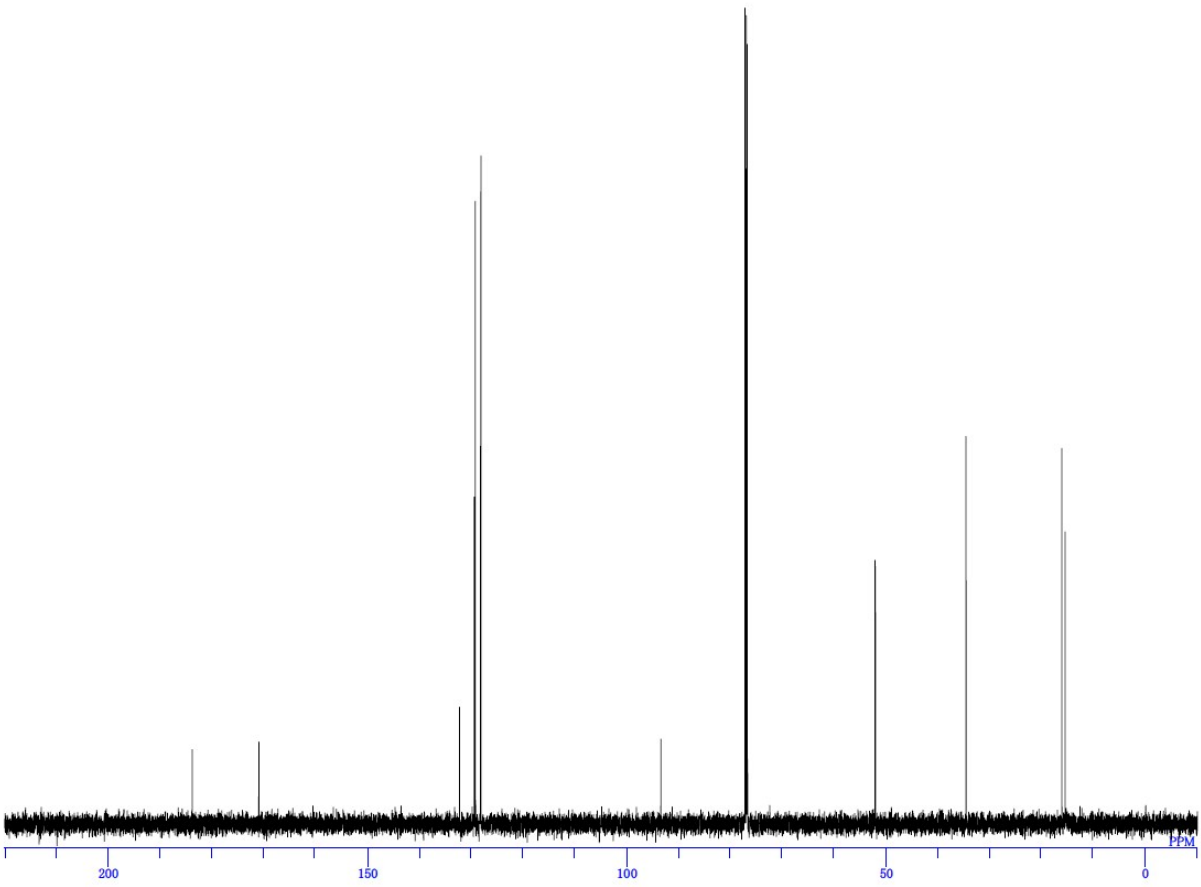
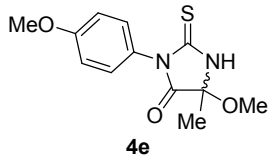
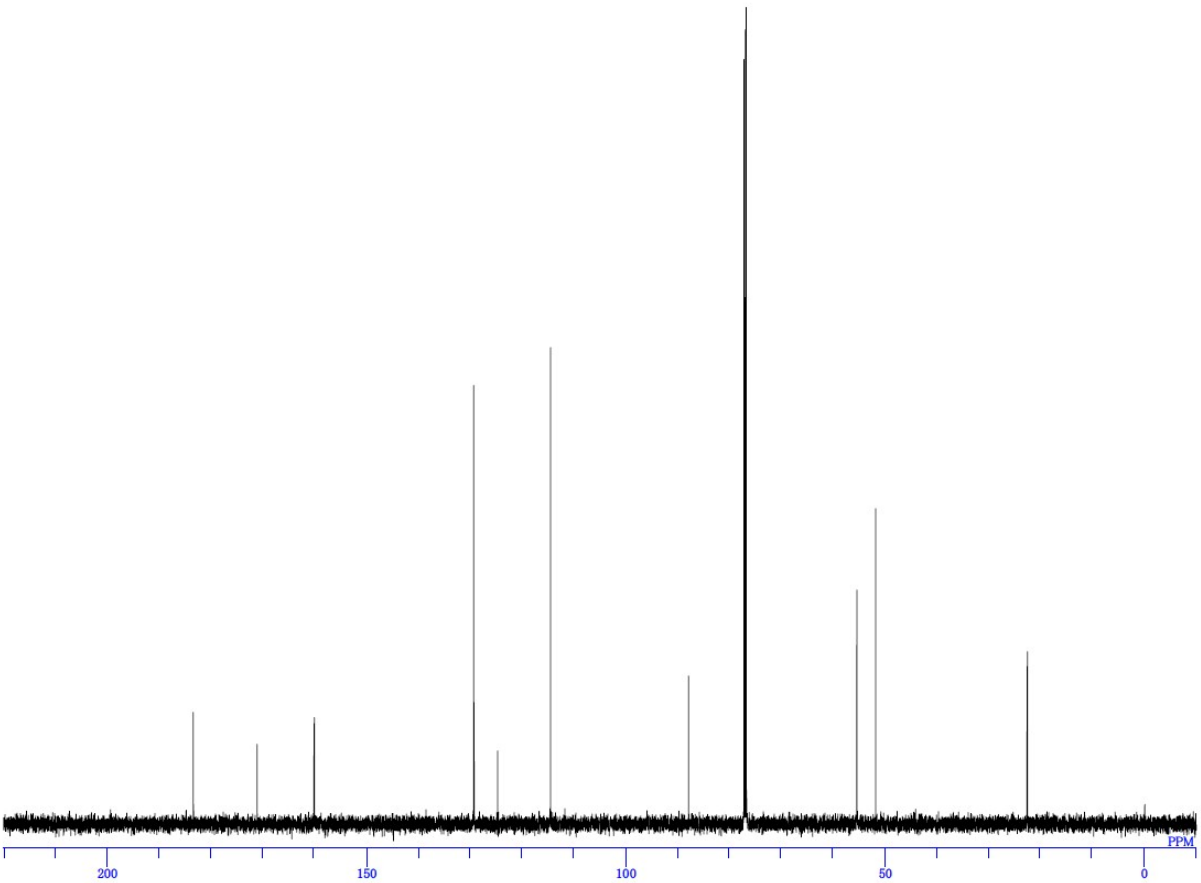


Me_4-MeO_SM

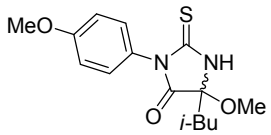


4e

Me_4-MeO_SM

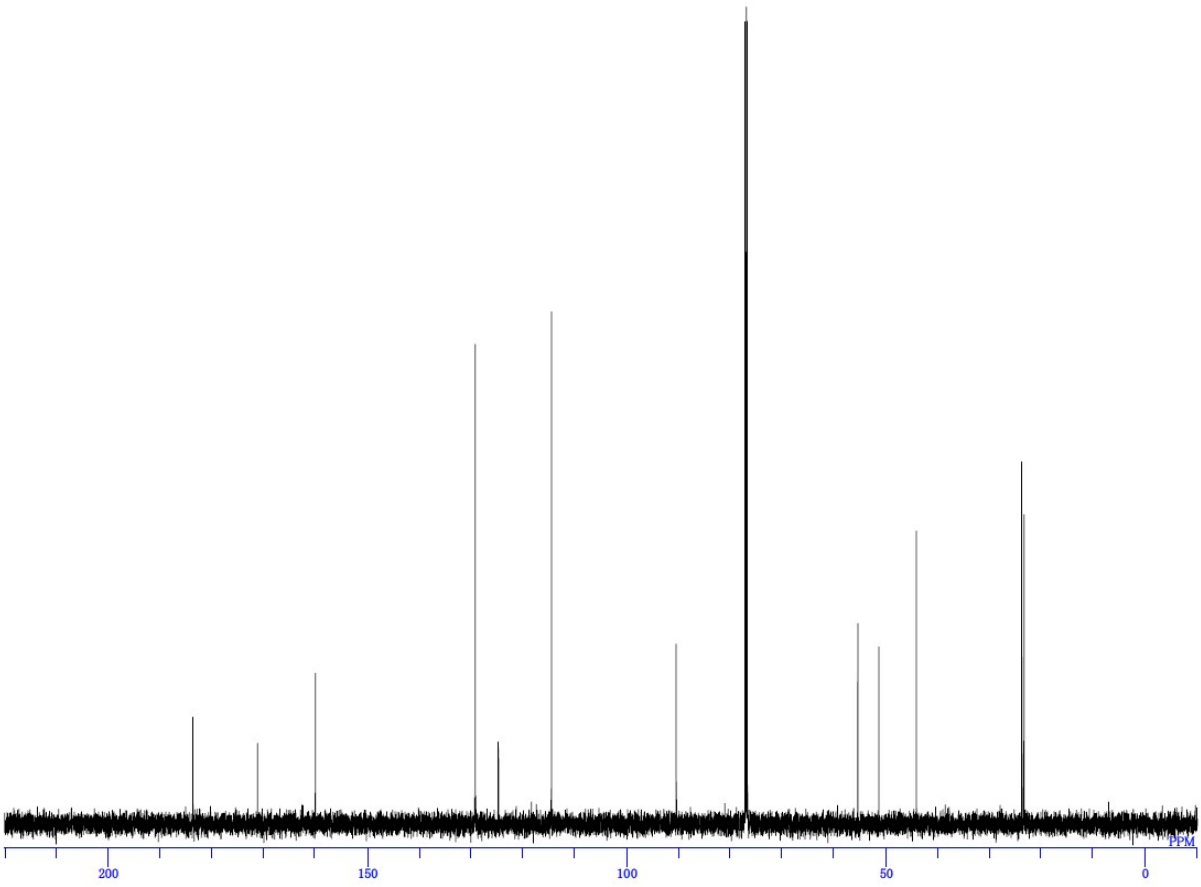


iBu_4-MeO_SM

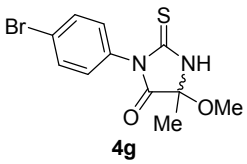


4f

iBu_4-MeO_SM

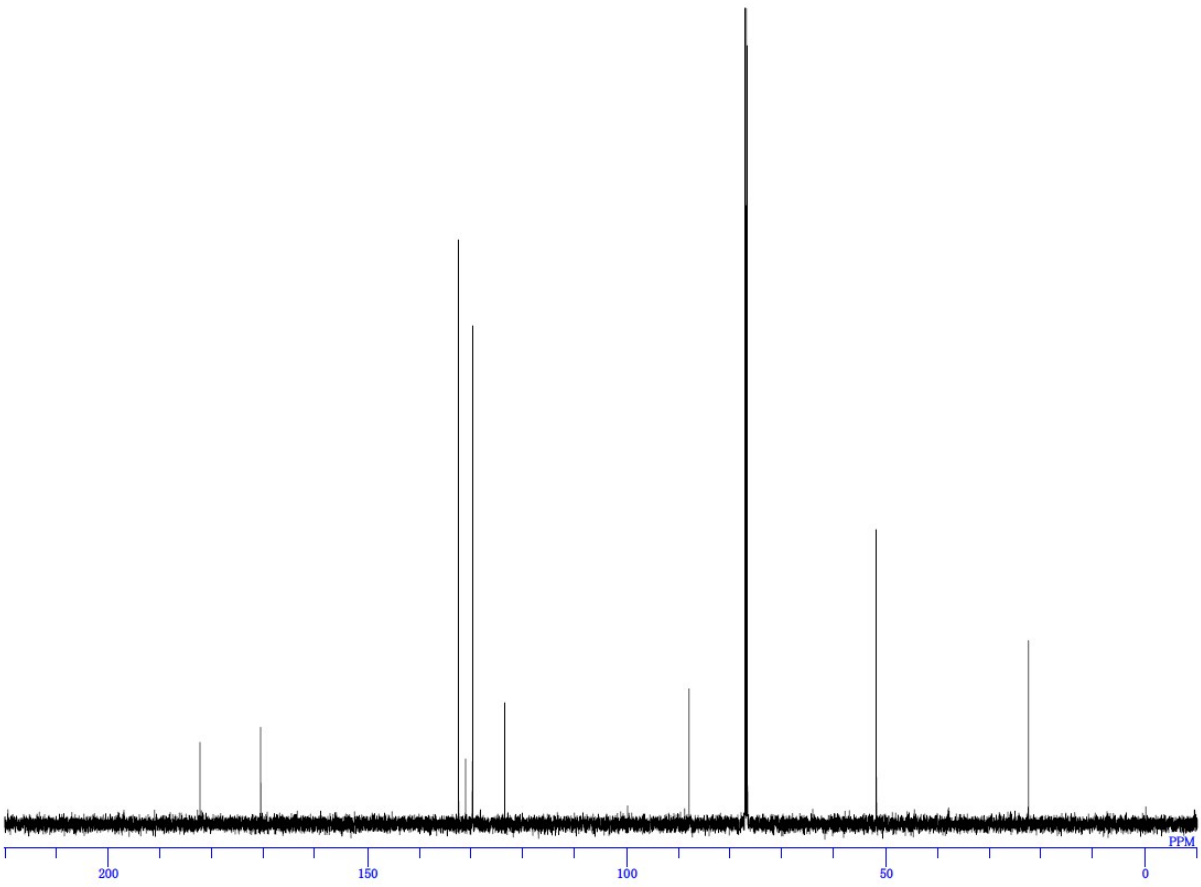


Me_4-Br_SM

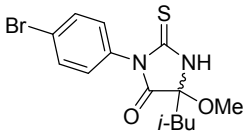


4g

Me_4-Br_SM

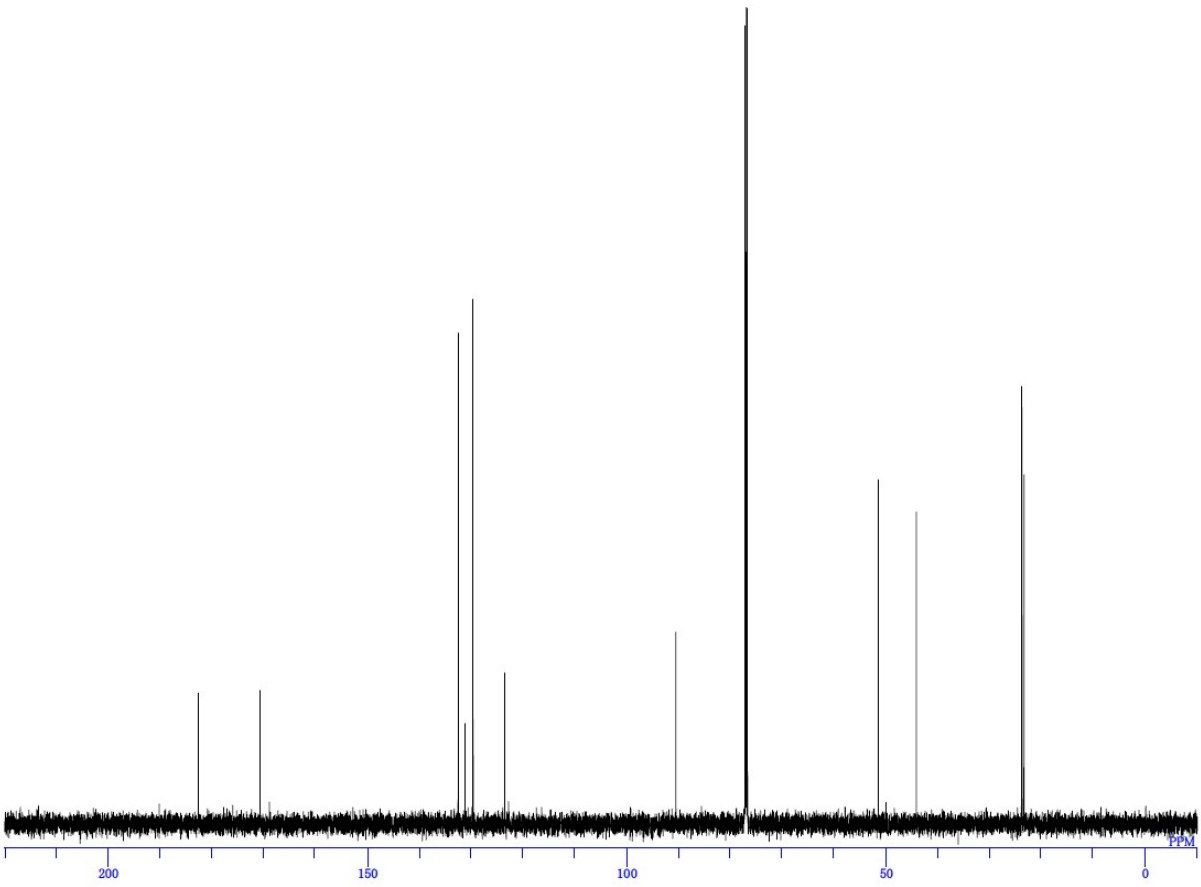


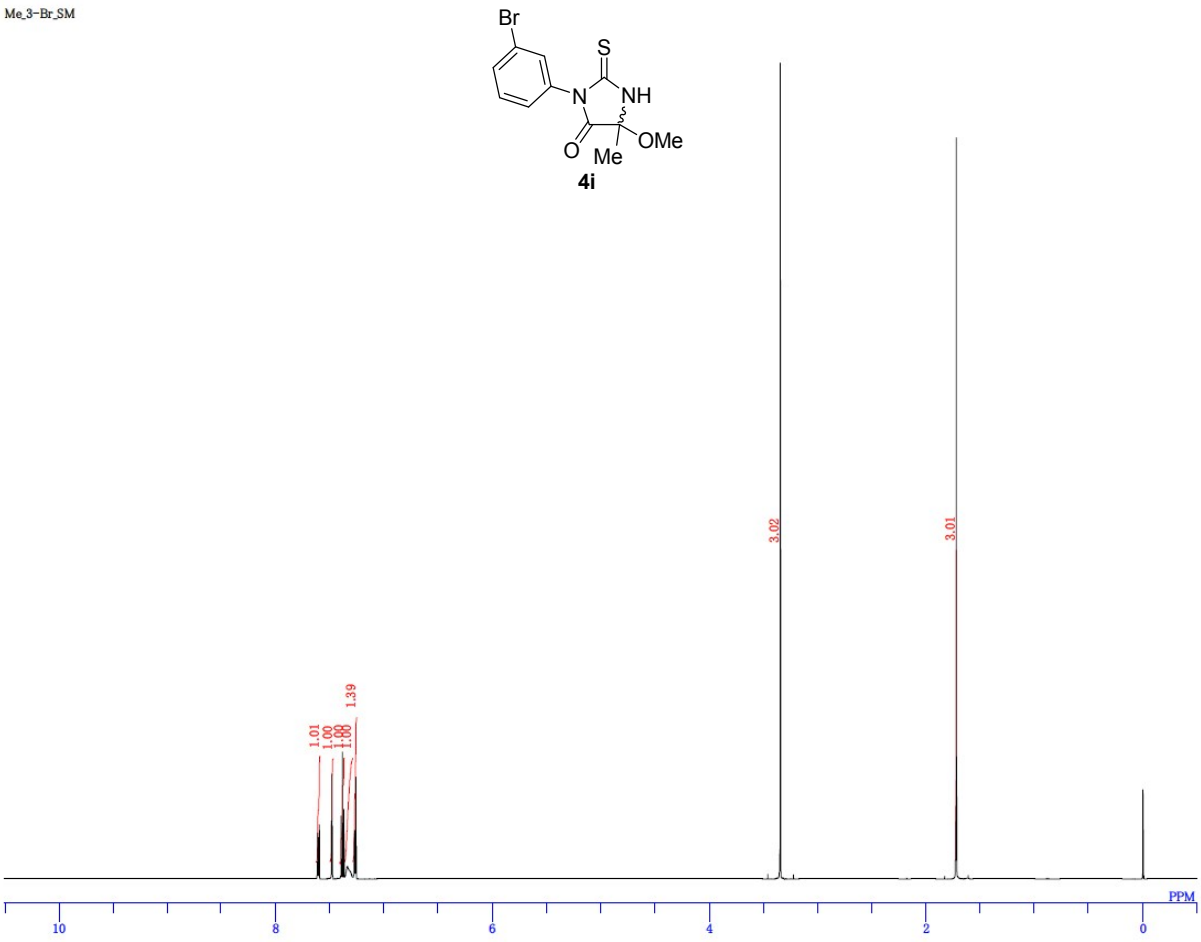
iBu_4-Br

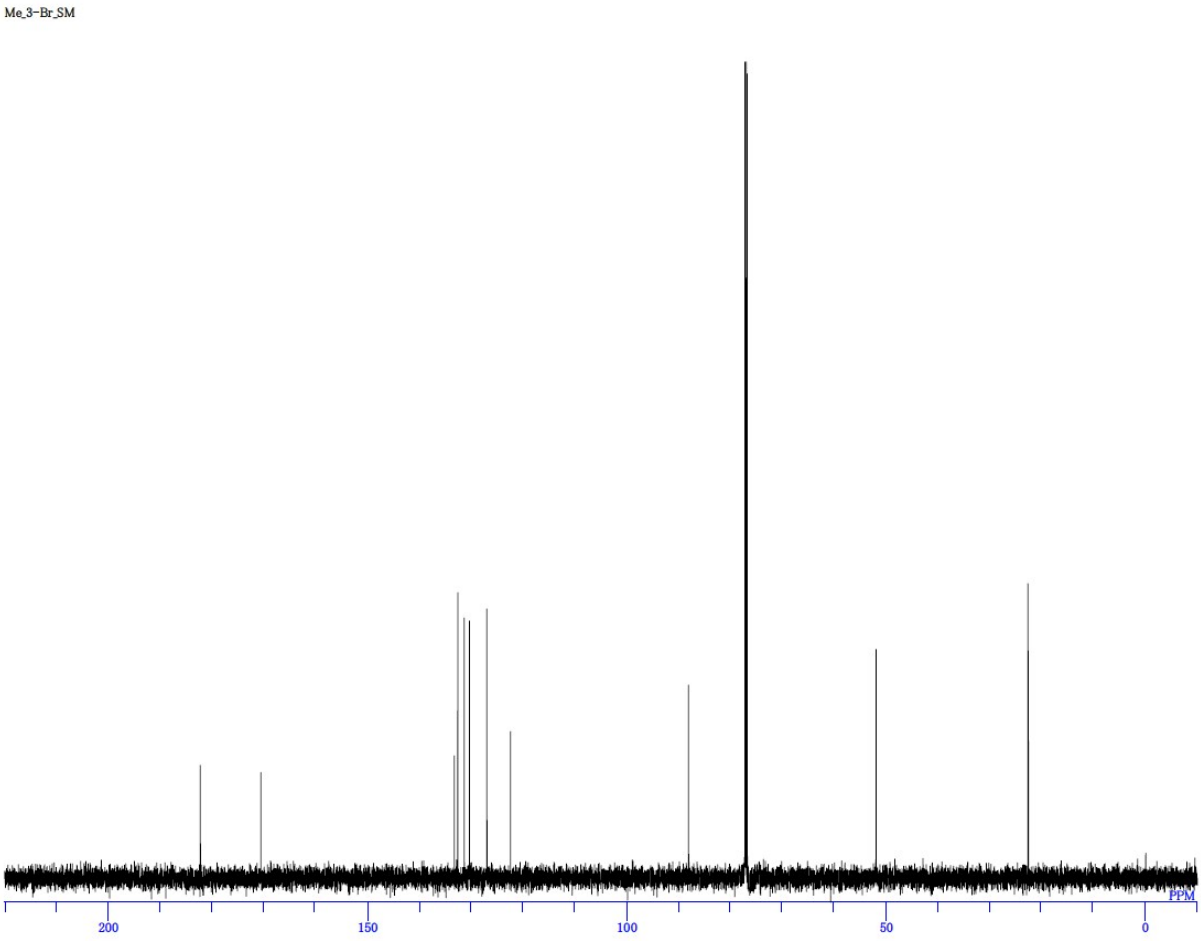


4h

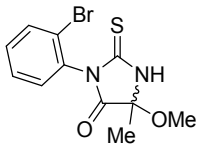
iBu_4-Br_SM




Me_3-Br_SM
Br
S
N
NH
O
Me
OMe
4i
3.02
3.01
1.39
1.01
1.00
1.00
1.00
PPM
10
8
6
4
2
0


Me_3-Br_SM
PPM
200
150
100
50
0

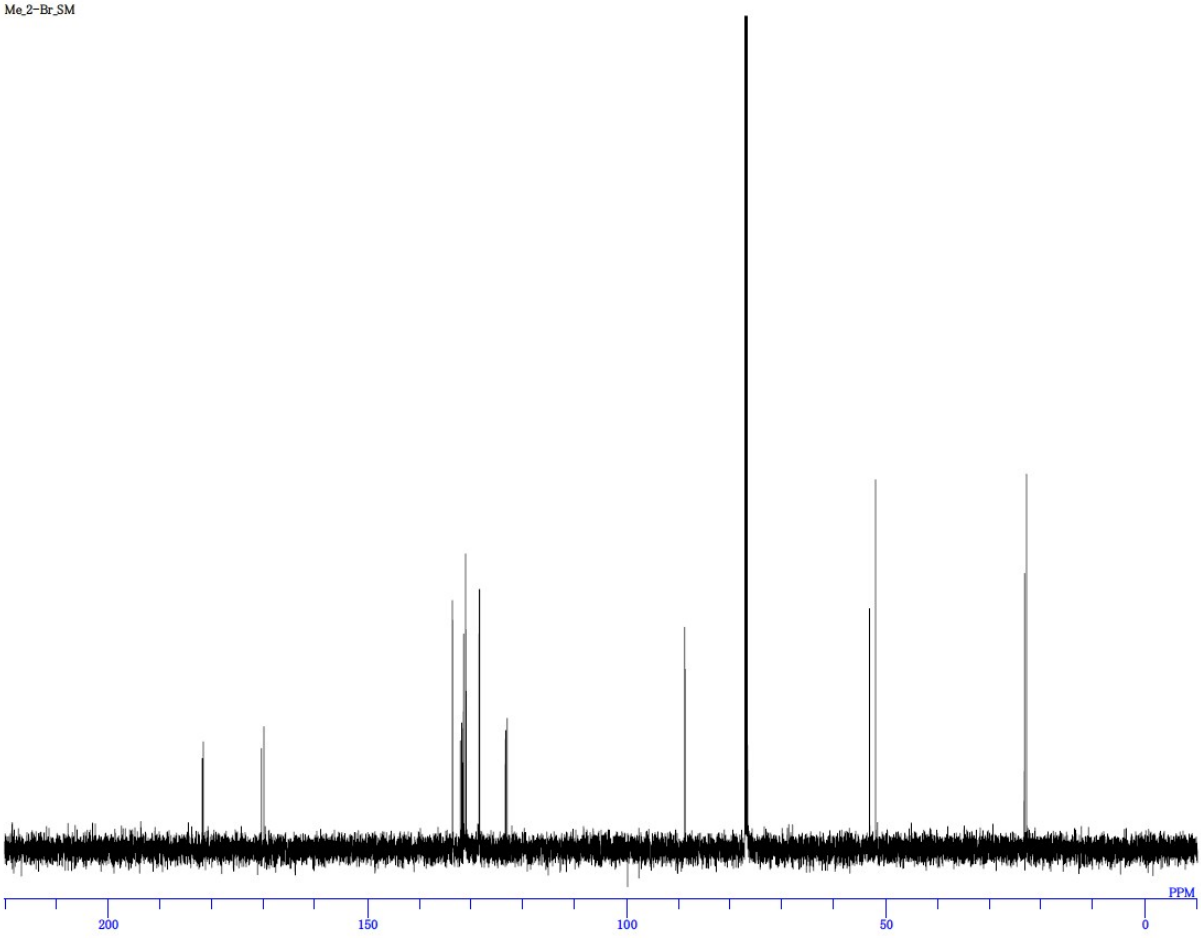
Me_2-Br_SM

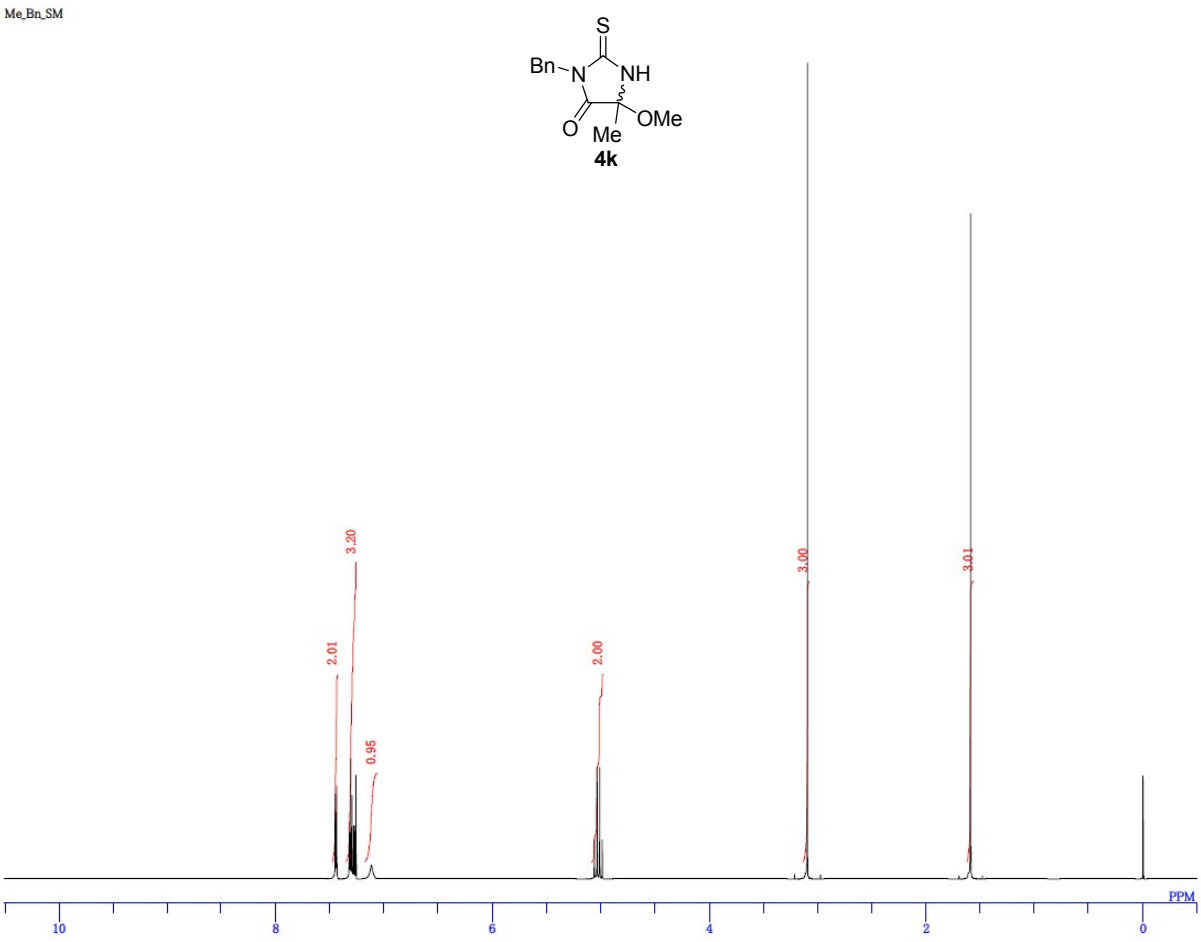


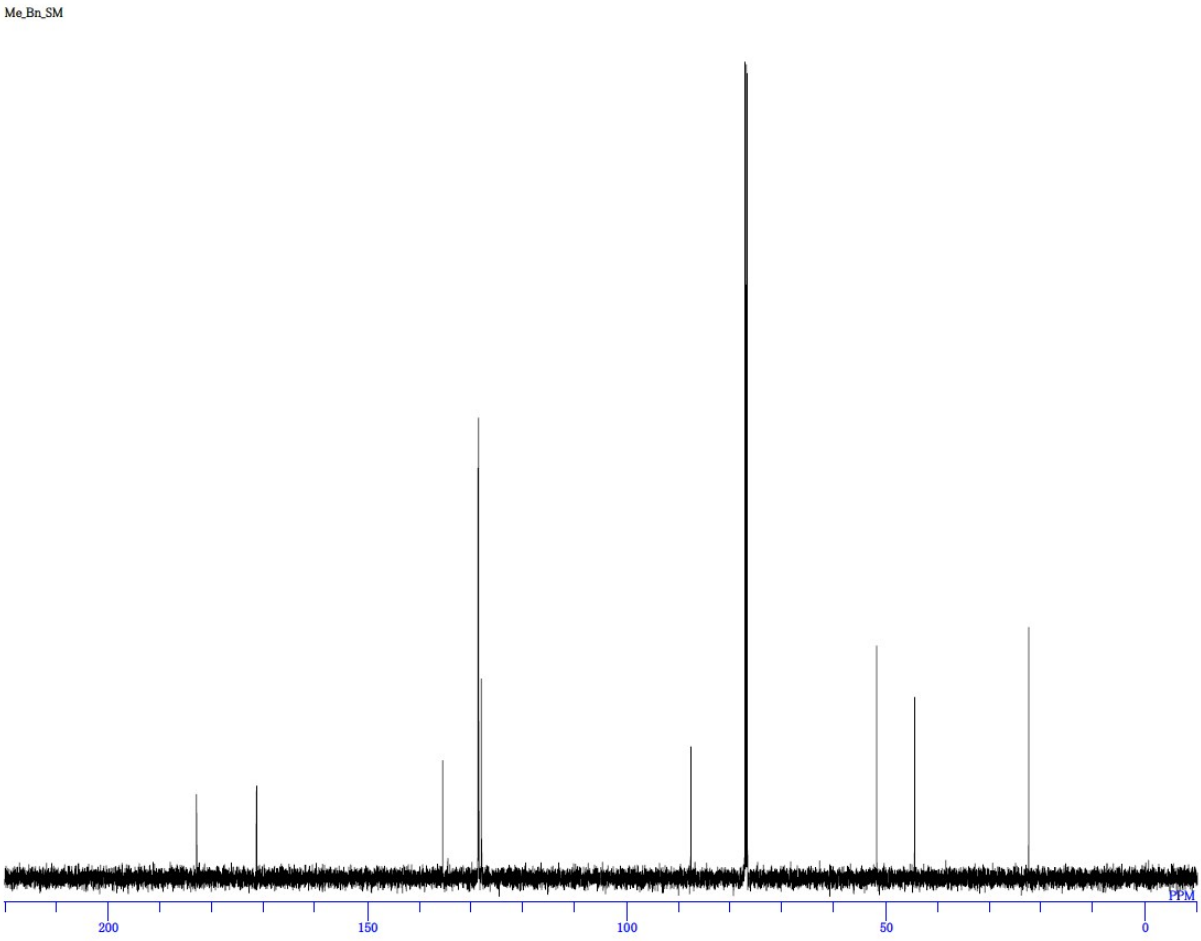
4j

(dr = 55:45)

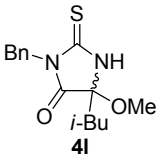
Me_2-Br_SM




Me_Bn_SM
S
Bn
N
NH
O
Me
OMe
4k
3.20
2.01
0.95
2.00
3.00
3.01
PPM
10
8
6
4
2
0

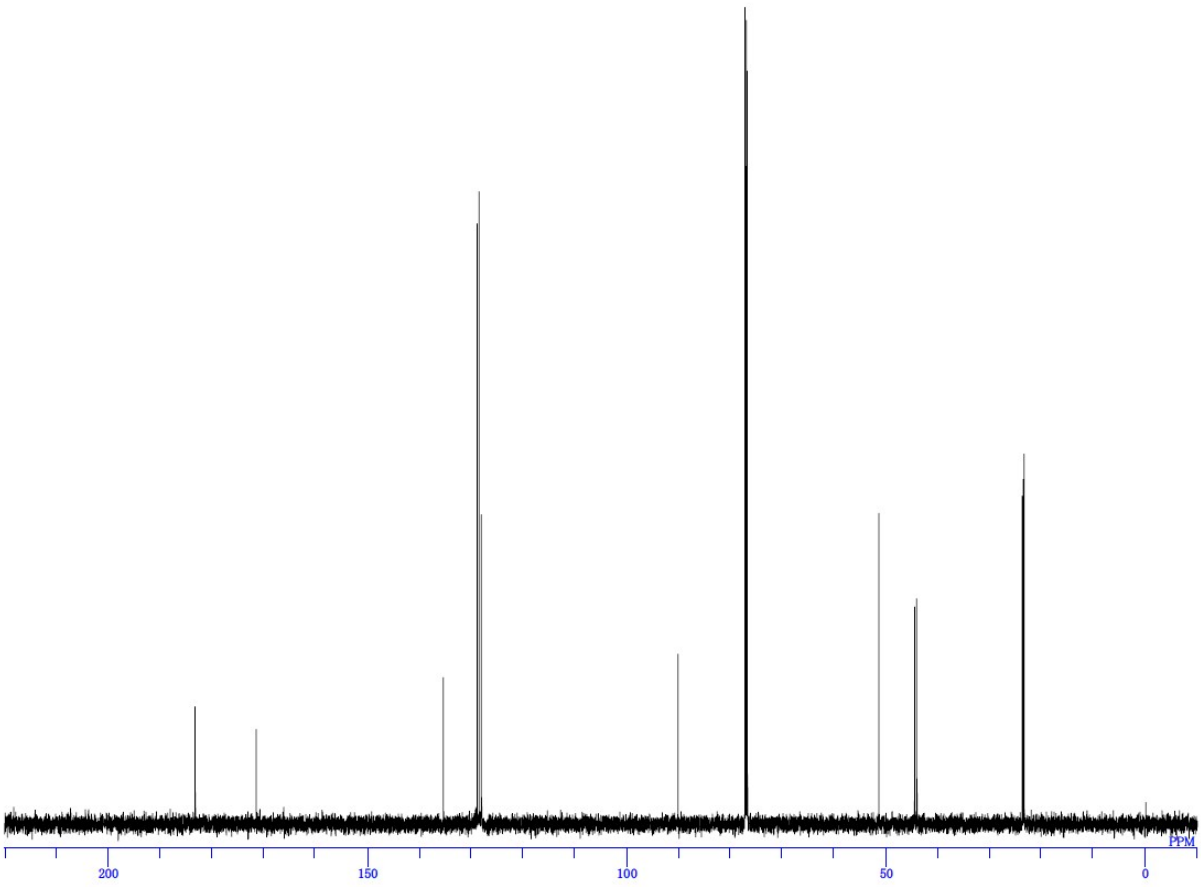

Me_Bn_SM
PPM
200
150
100
50
0

iBu_Bn_SM

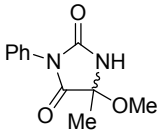


4l

iBu_Bn_SM

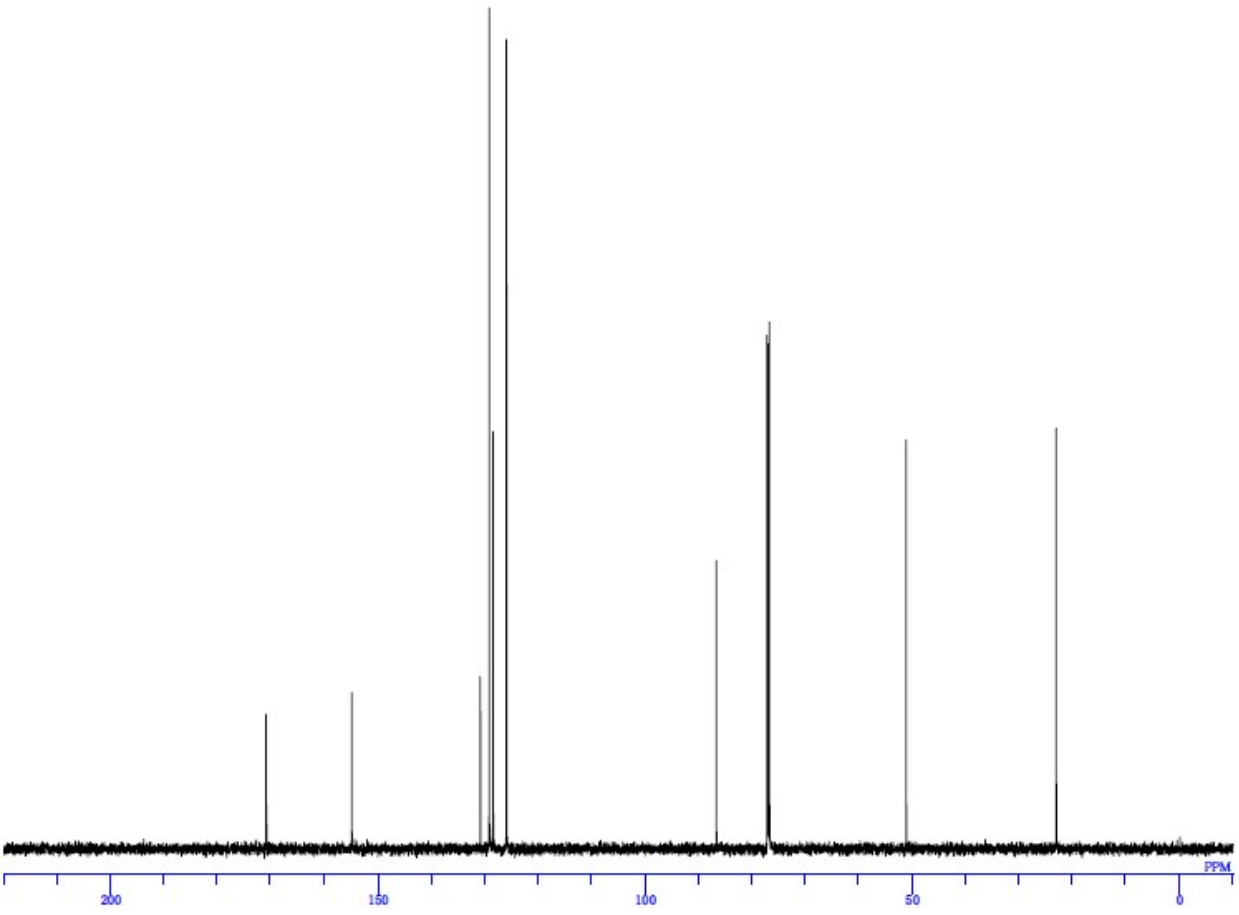


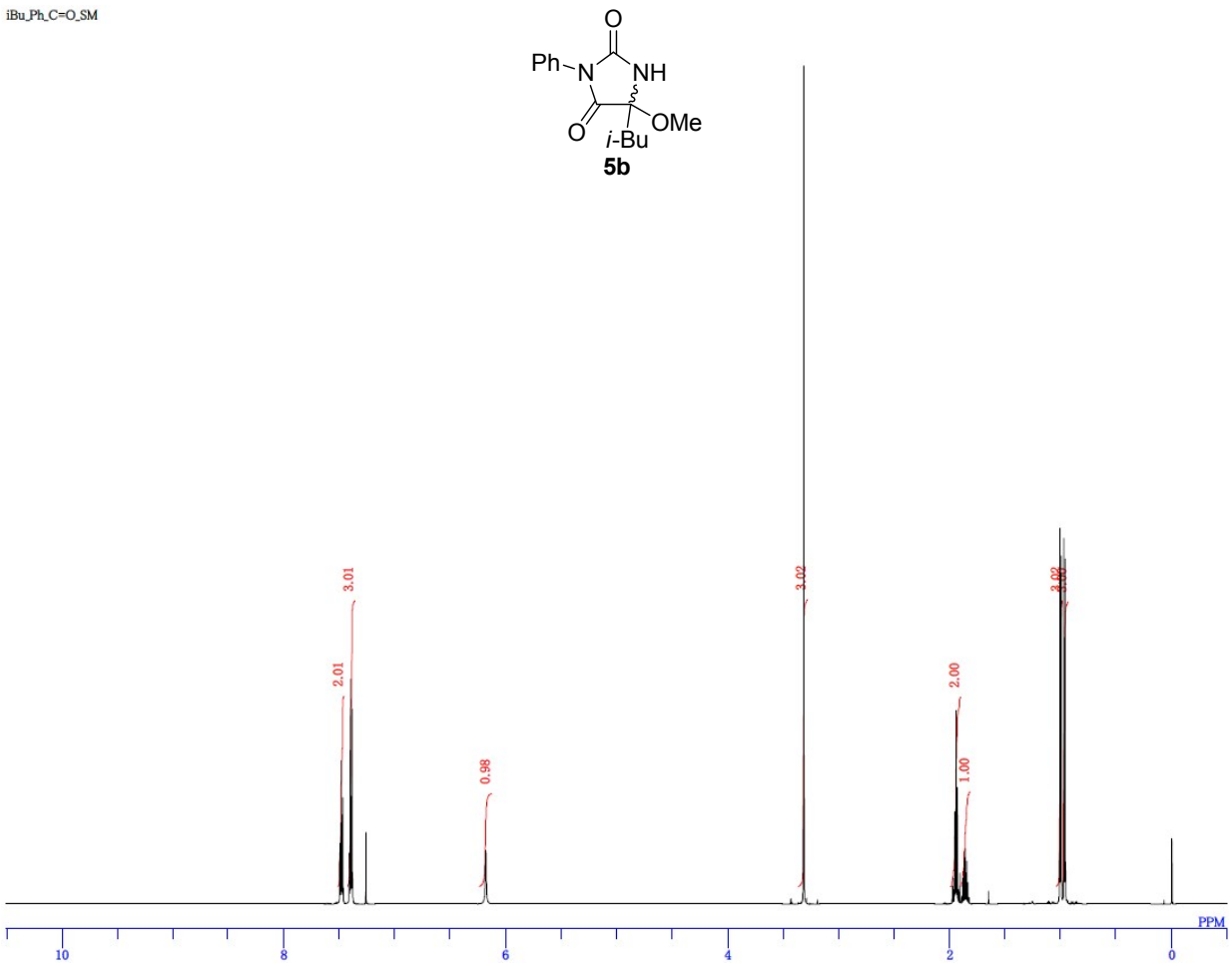
Me_Ph_C=O_SM



5a

Me_Ph_C=O_SM




iBu_Ph_C=O_SM
Ph
N
NH
O
O
OMe
i-Bu
5b
3.01
2.01
0.98
3.02
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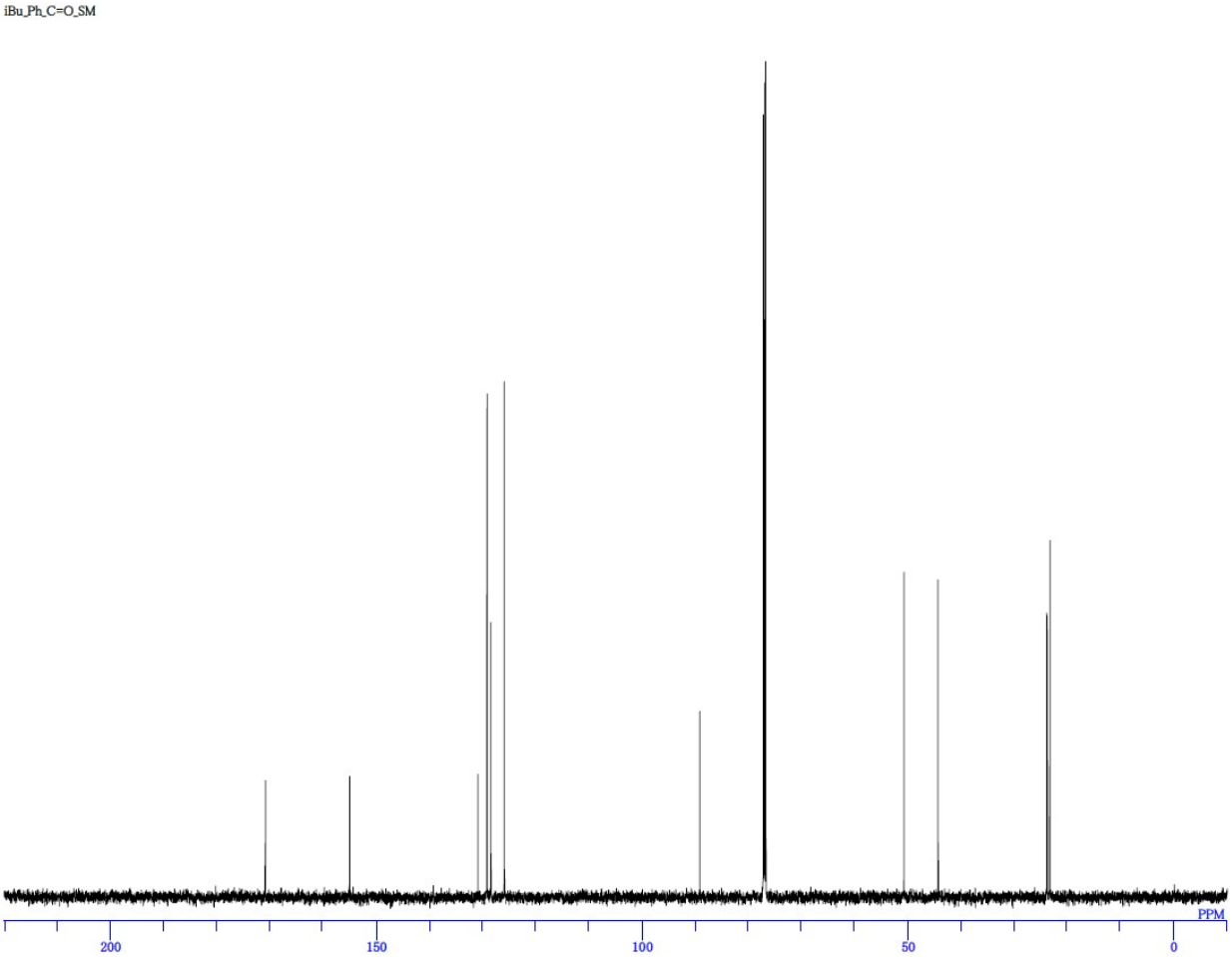
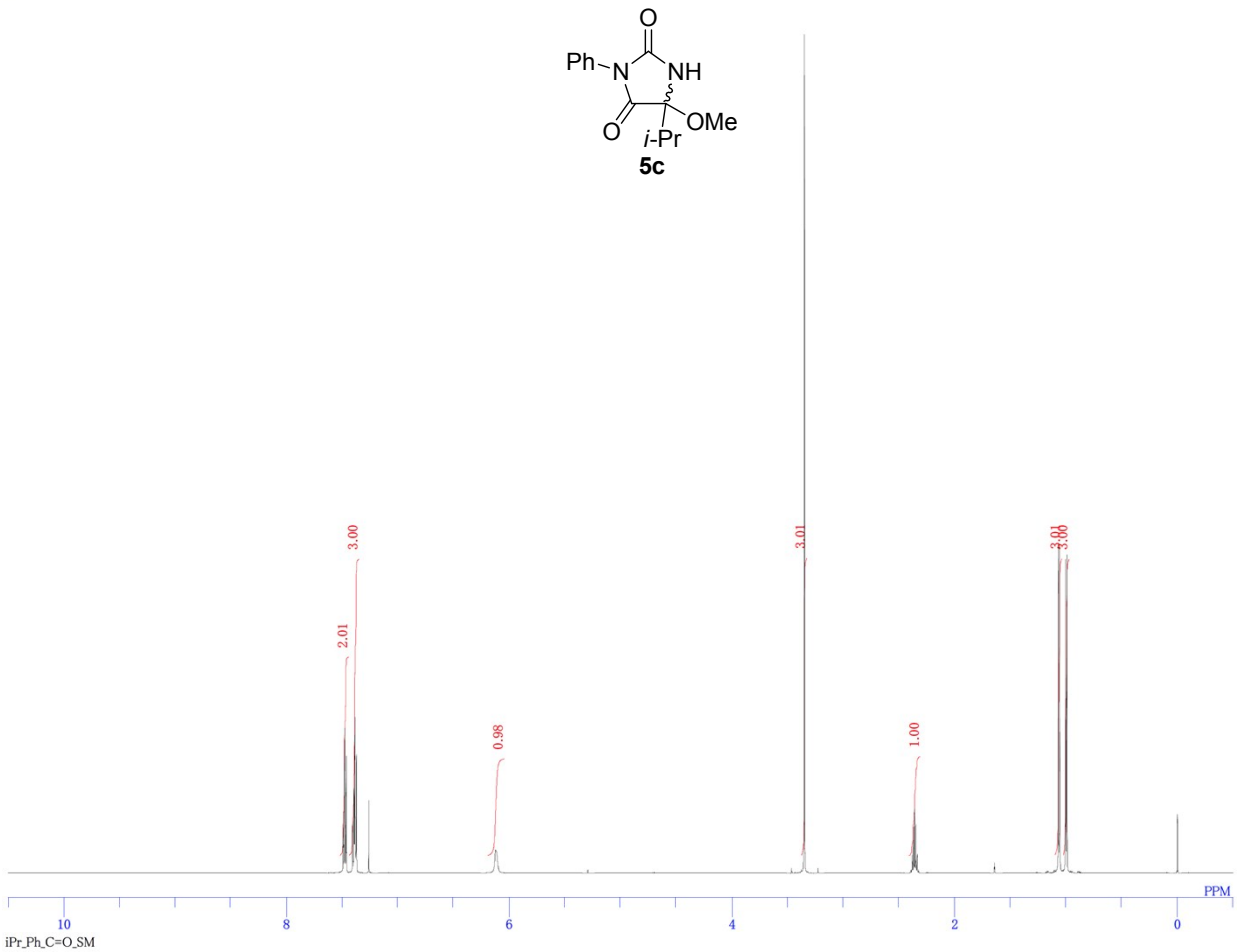
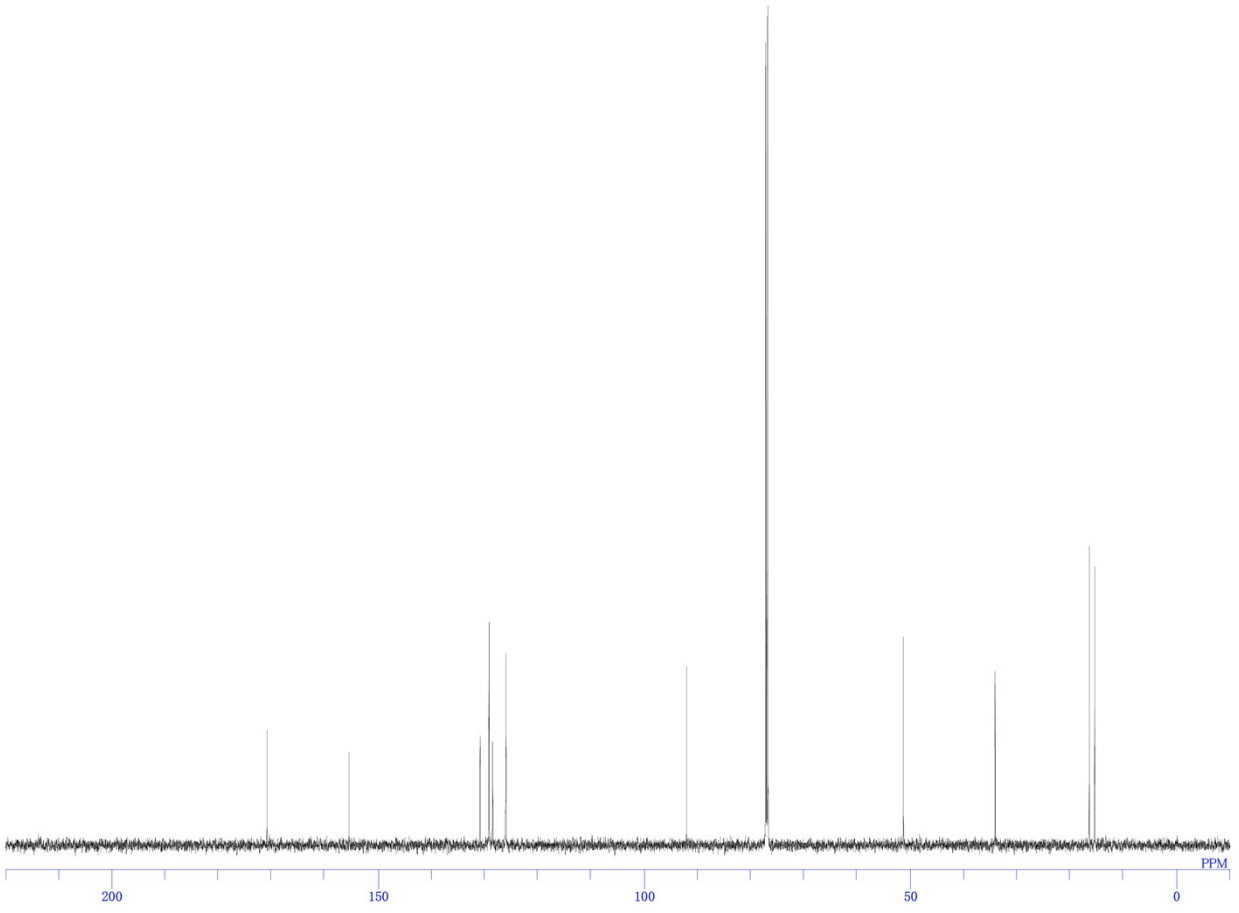
3.02
3.02
PPM
10
8
6
4
2
0


iBu_Ph_C=O_SM
PPM
200
150
100
50
0

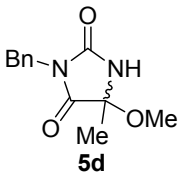
iPr_Ph_C=O_SM



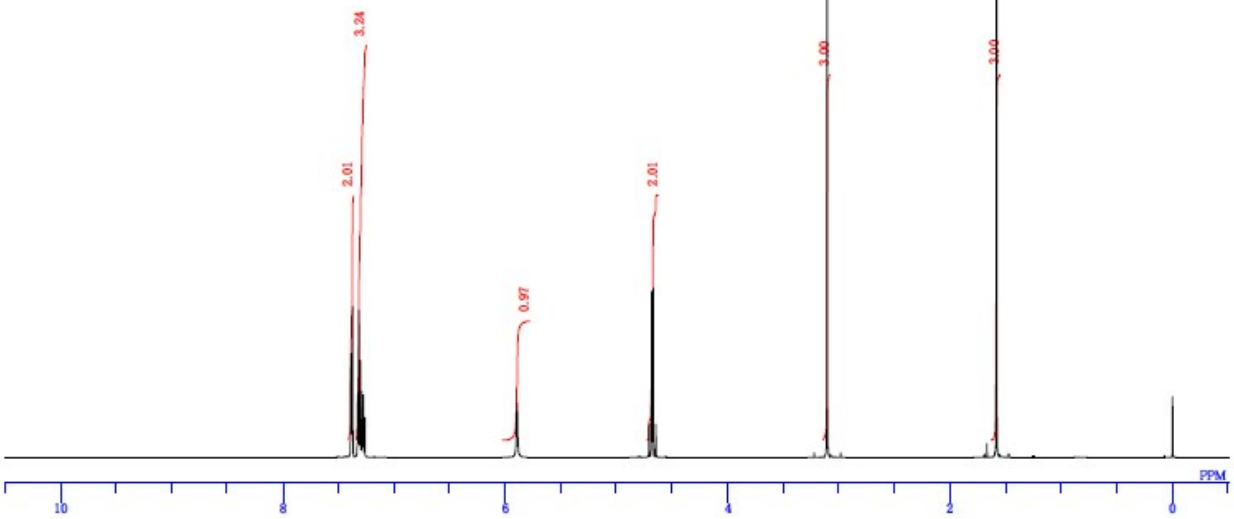
iPr_Ph_C=O_SM



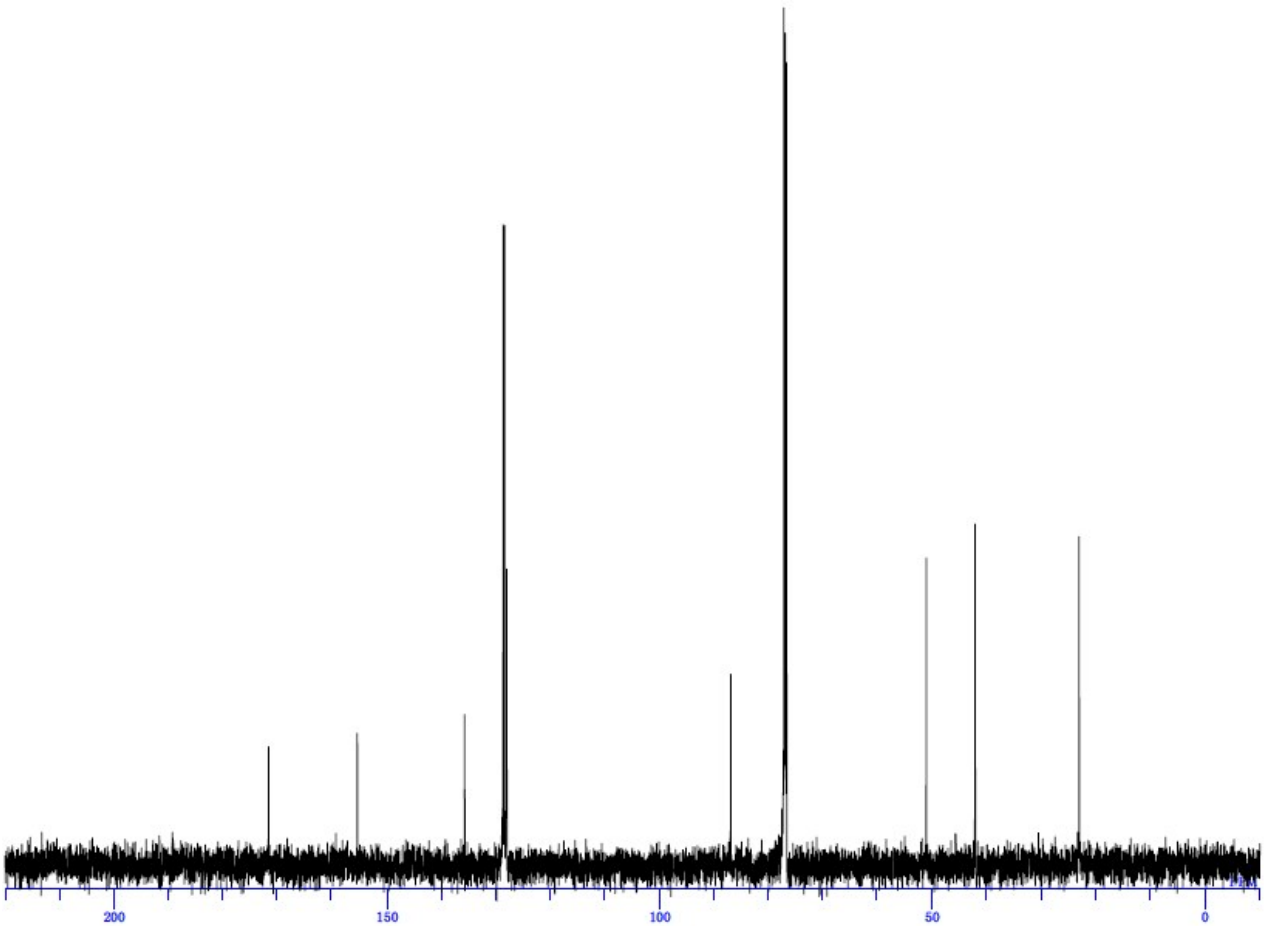
Me_Bn_C=O_SM



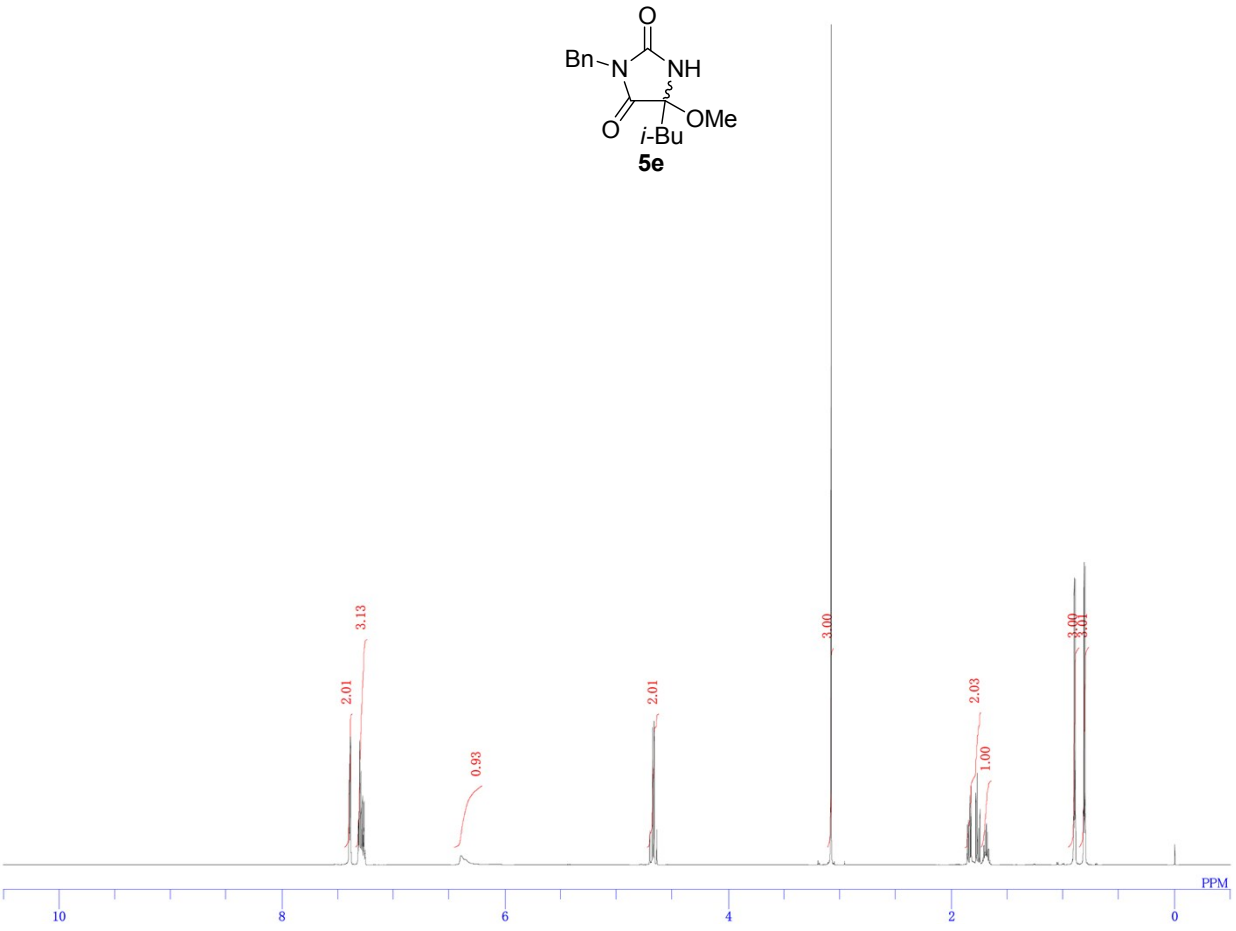
5d



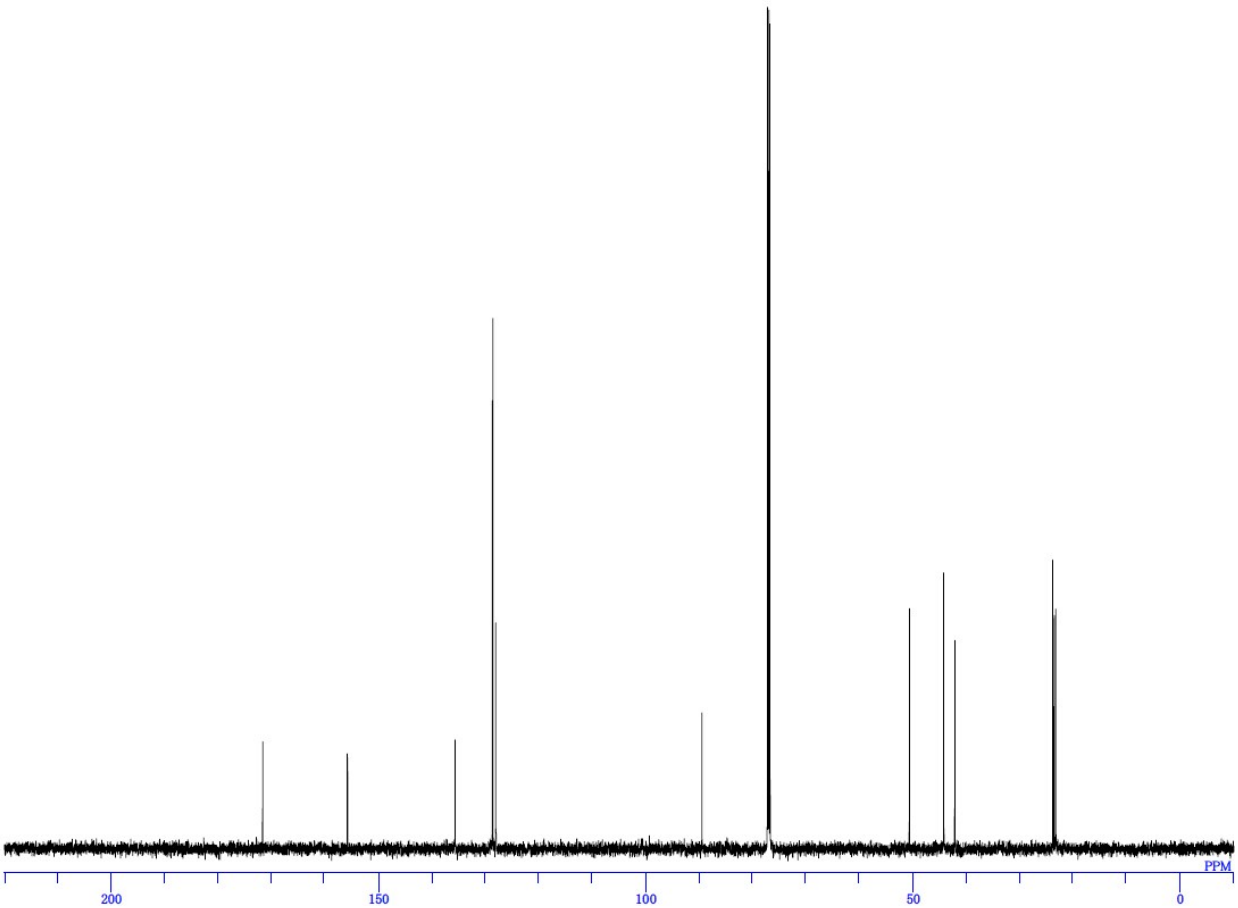
Me_Bn_C=O_SM



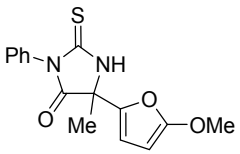
iBu_Bn_C=O_SM



iBu_Bn_C=O_SM

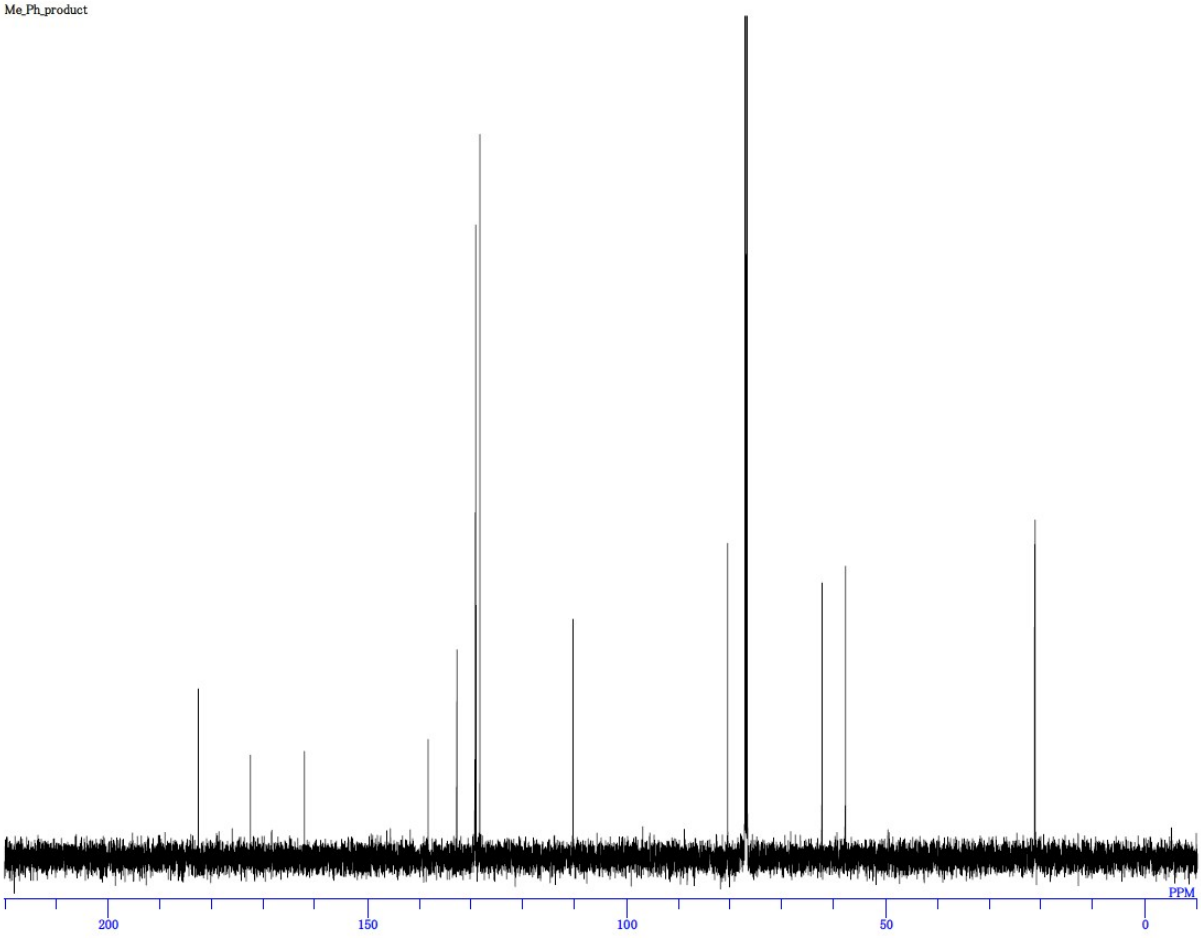


Me_Ph

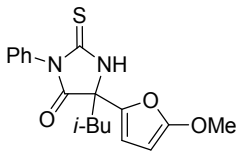


7a

Me_Ph_product

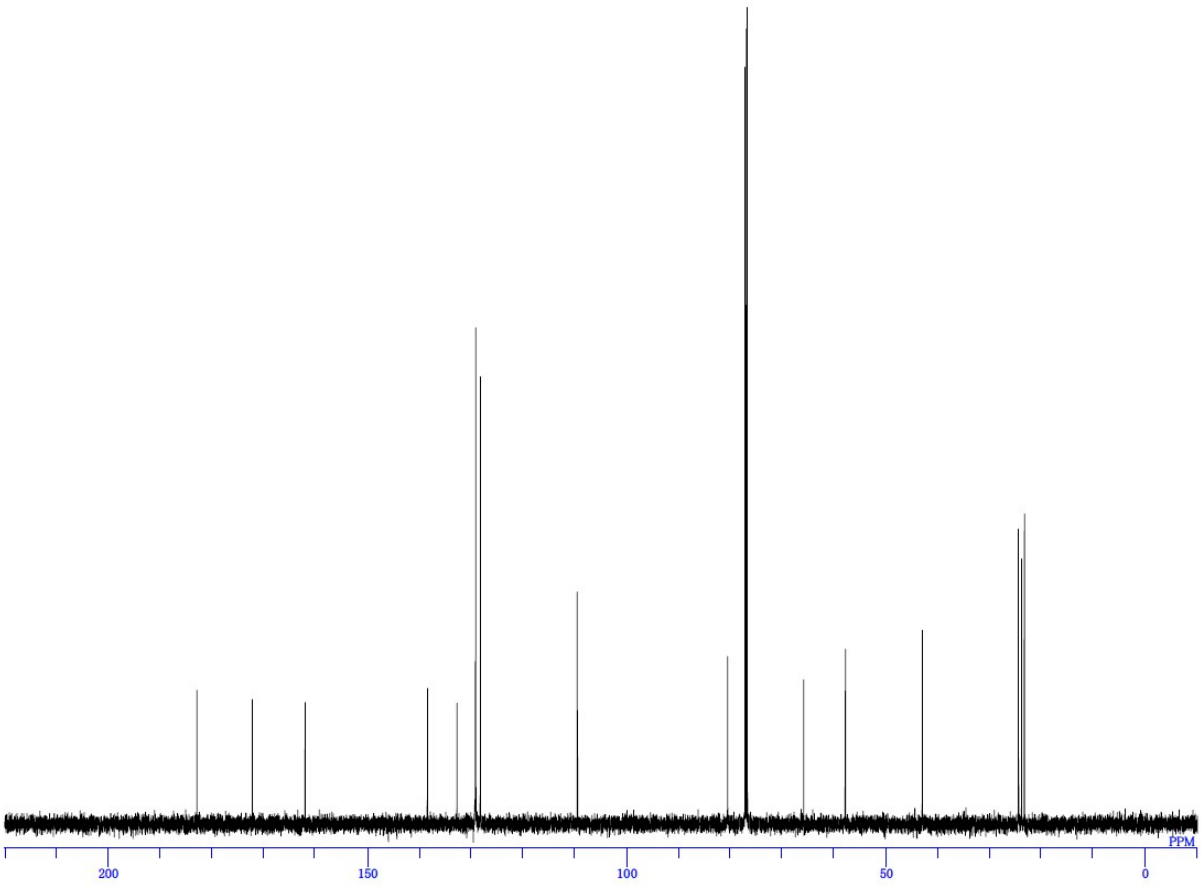


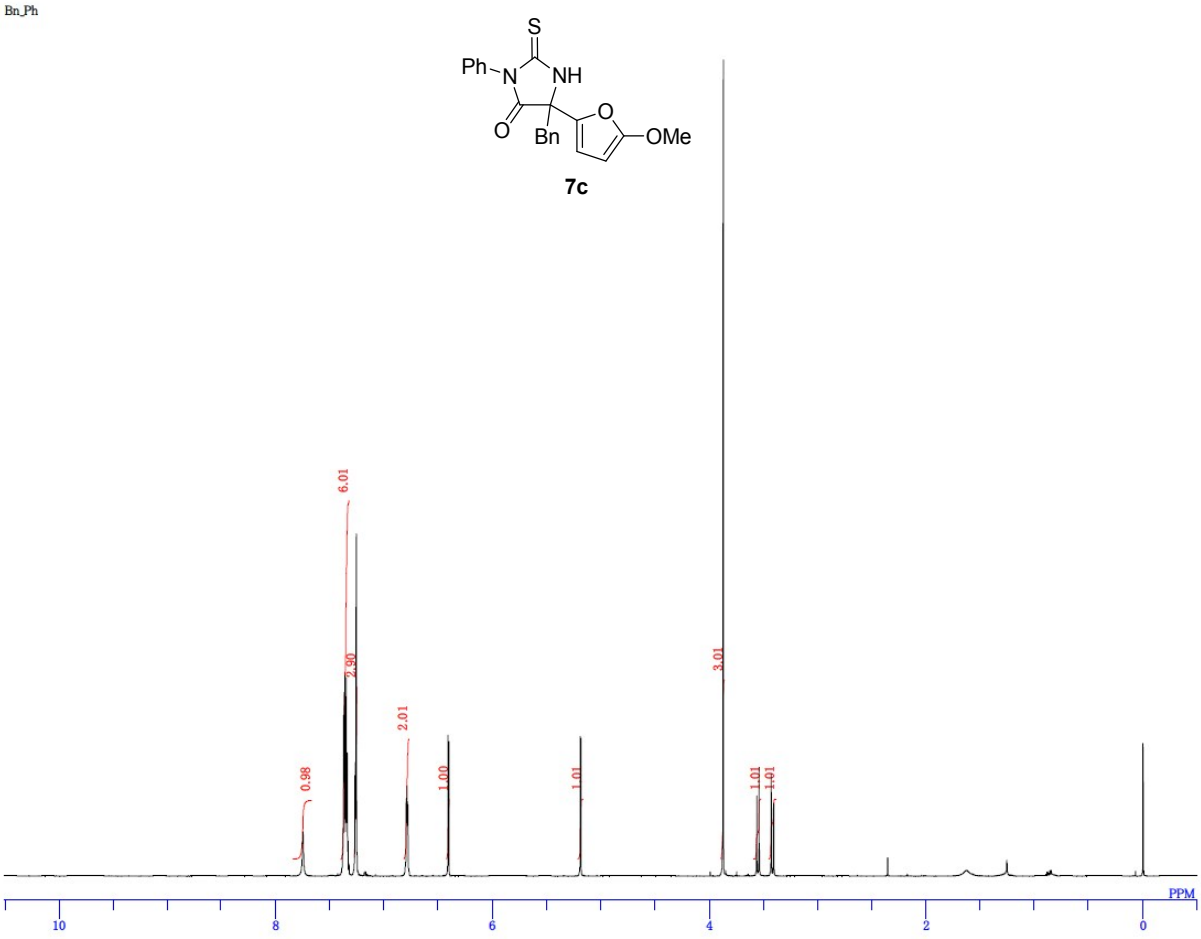
iBu_Ph

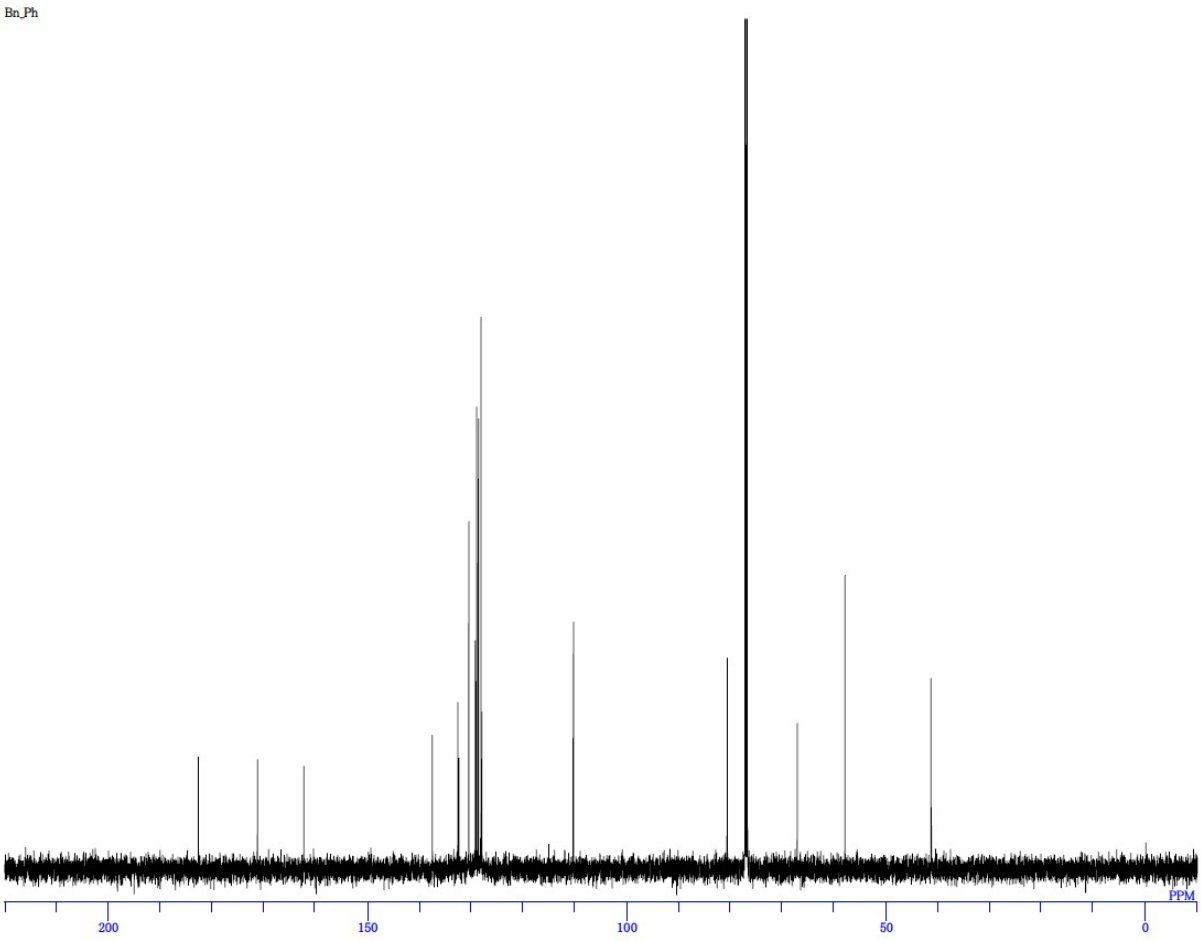


7b

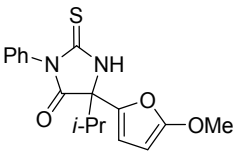
iBu_Ph




Bn_Ph
S
Ph
N
NH
O
Bn
O
OMe
7c
6.01
2.90
2.01
1.00
0.98
1.01
3.01
1.01
1.01
PPM
10
8
6
4
2
0

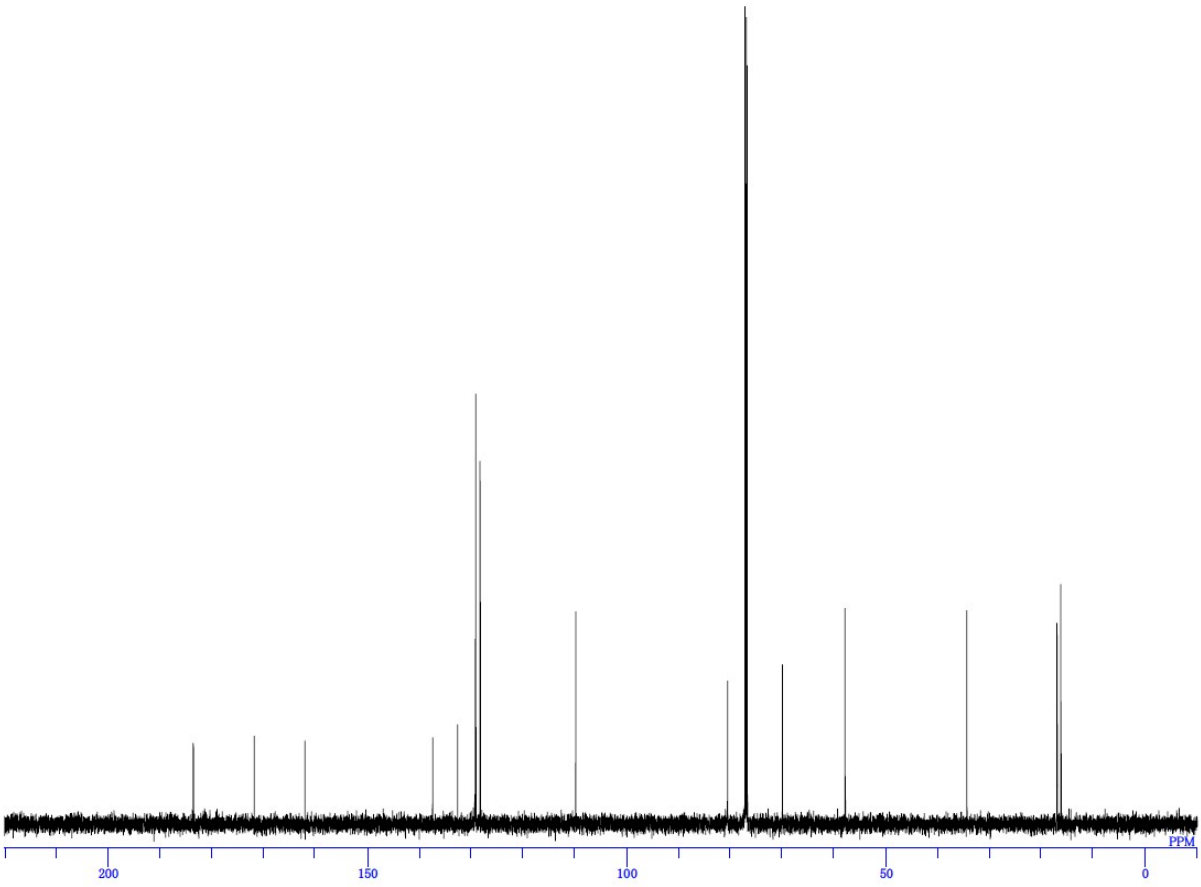

Bn_Ph
PPM
200
150
100
50
0

iPr_Ph

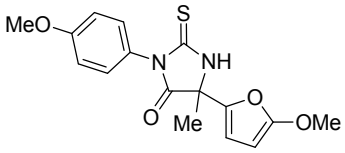


7d

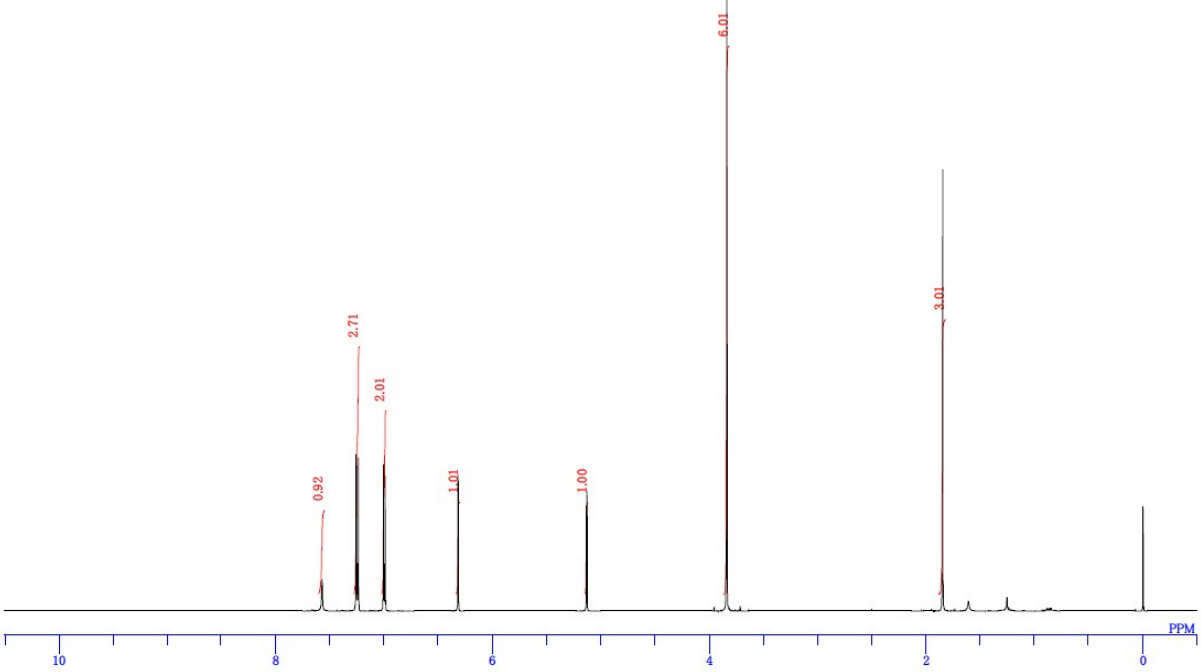
iPr_Ph



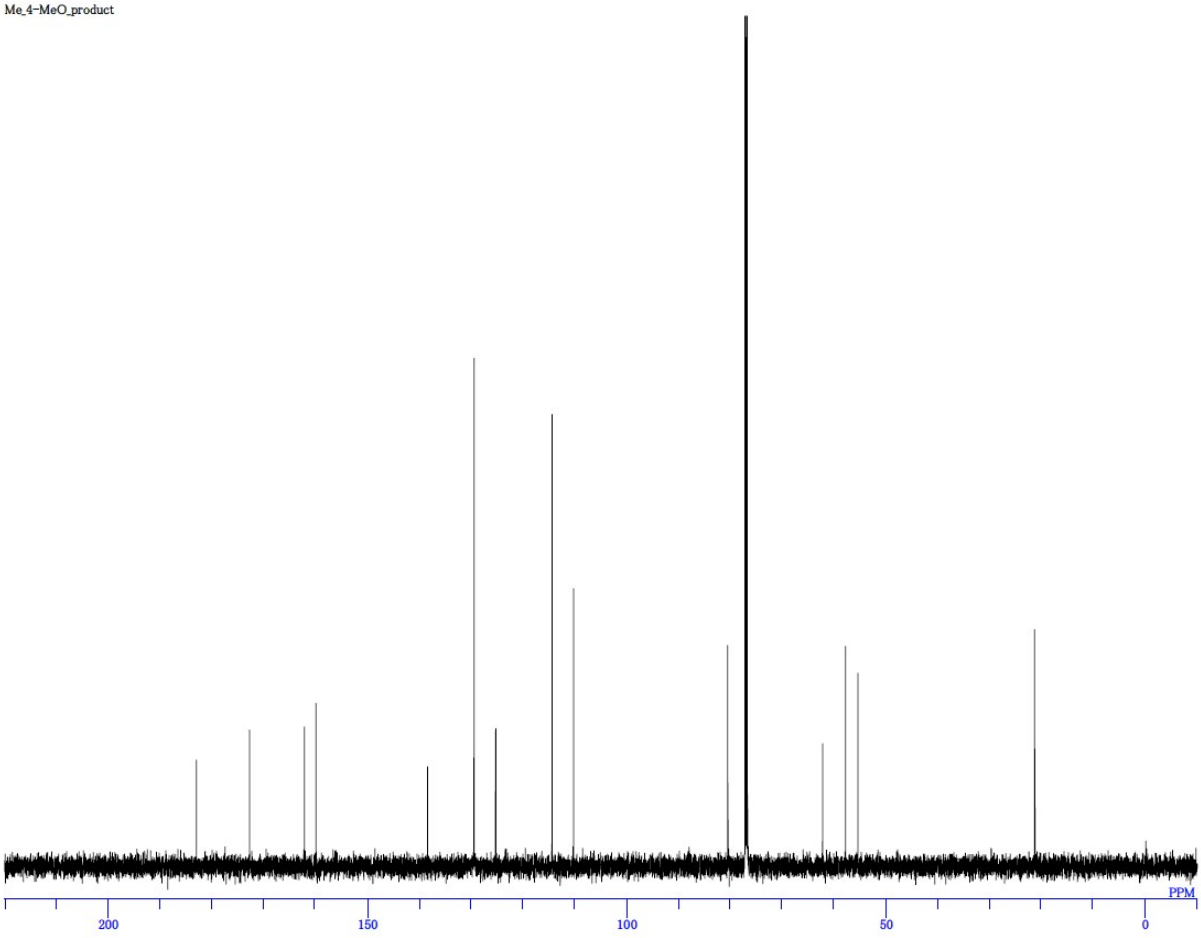
Me_4-MeO



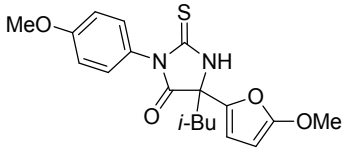
7e



Me_4-MeO_product

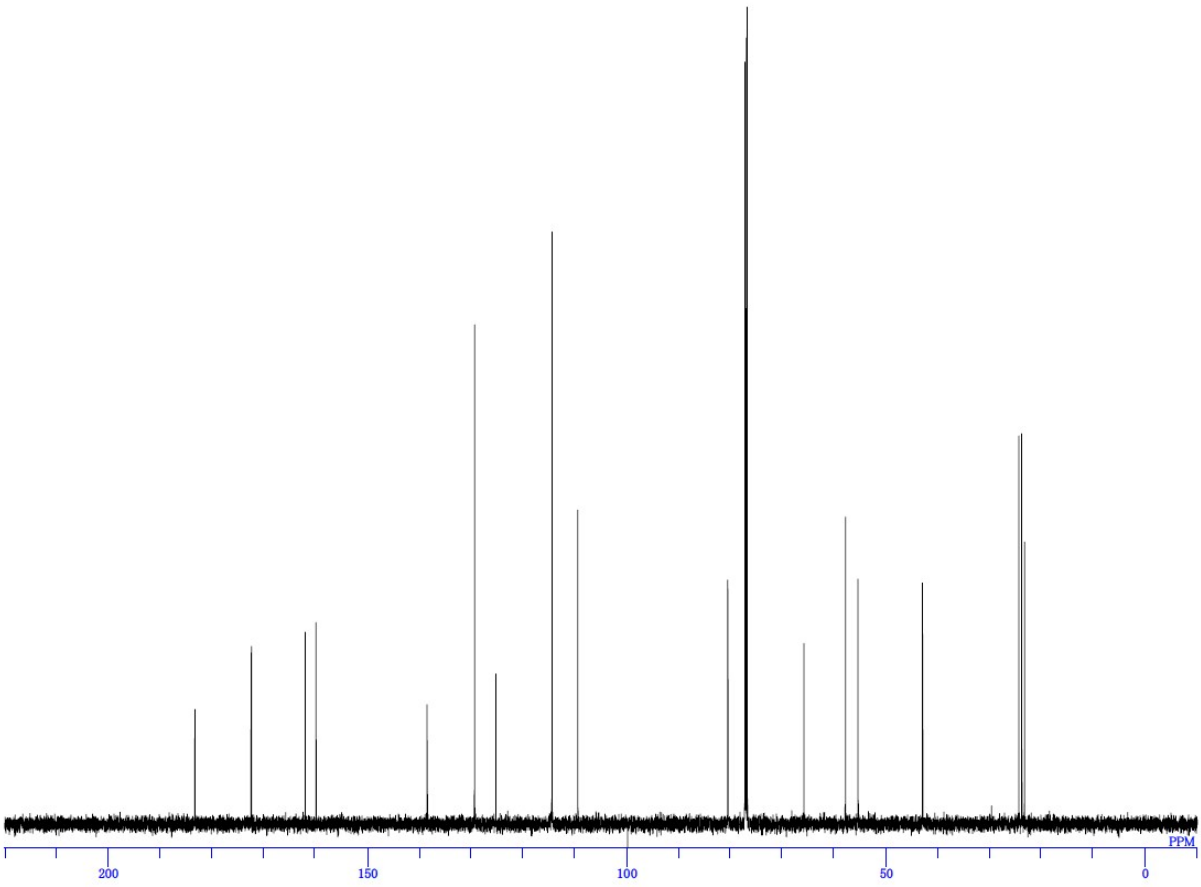


iBu_4-MeO

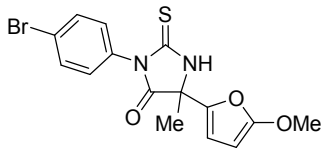


7f

iBu_4-MeO

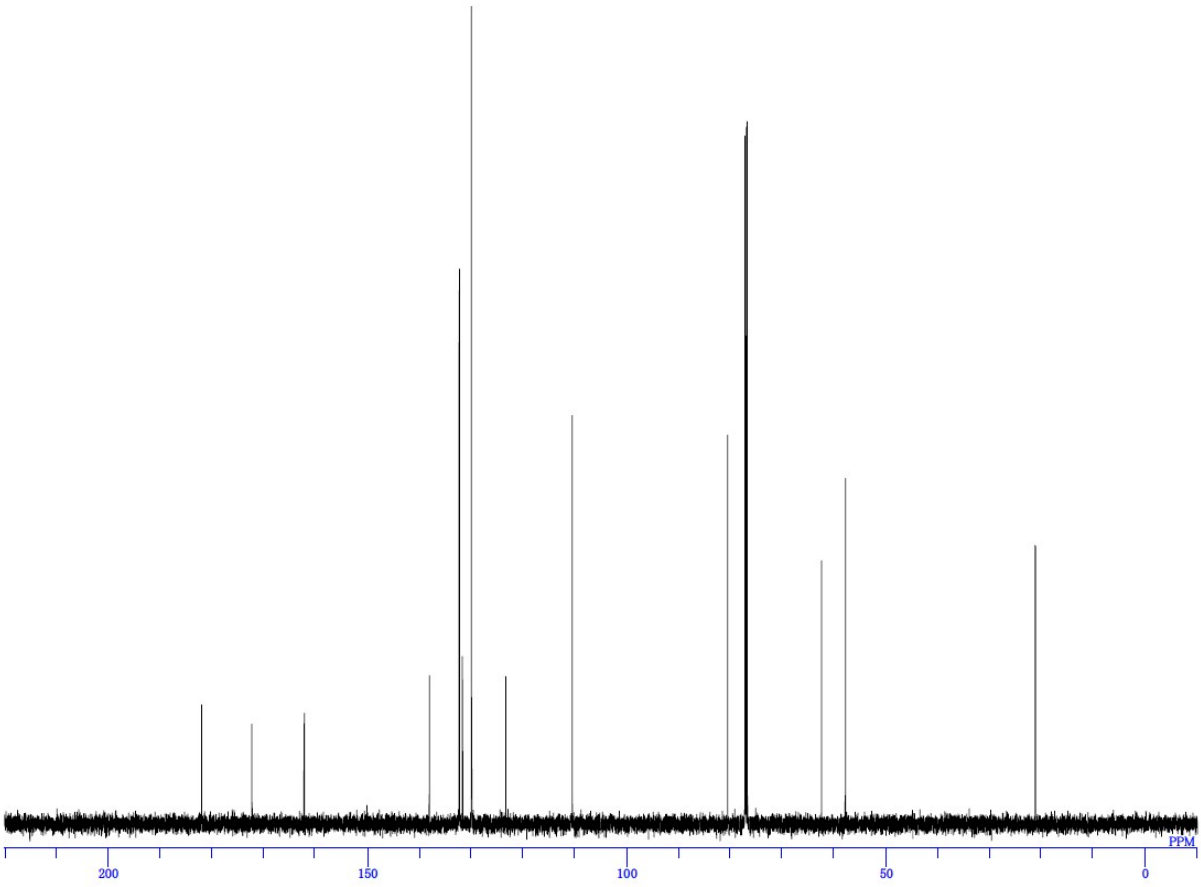


Me_4-Br_SM

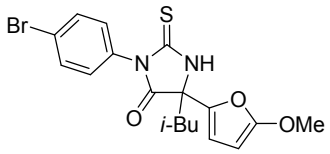


7g

Me_4-Br_SM

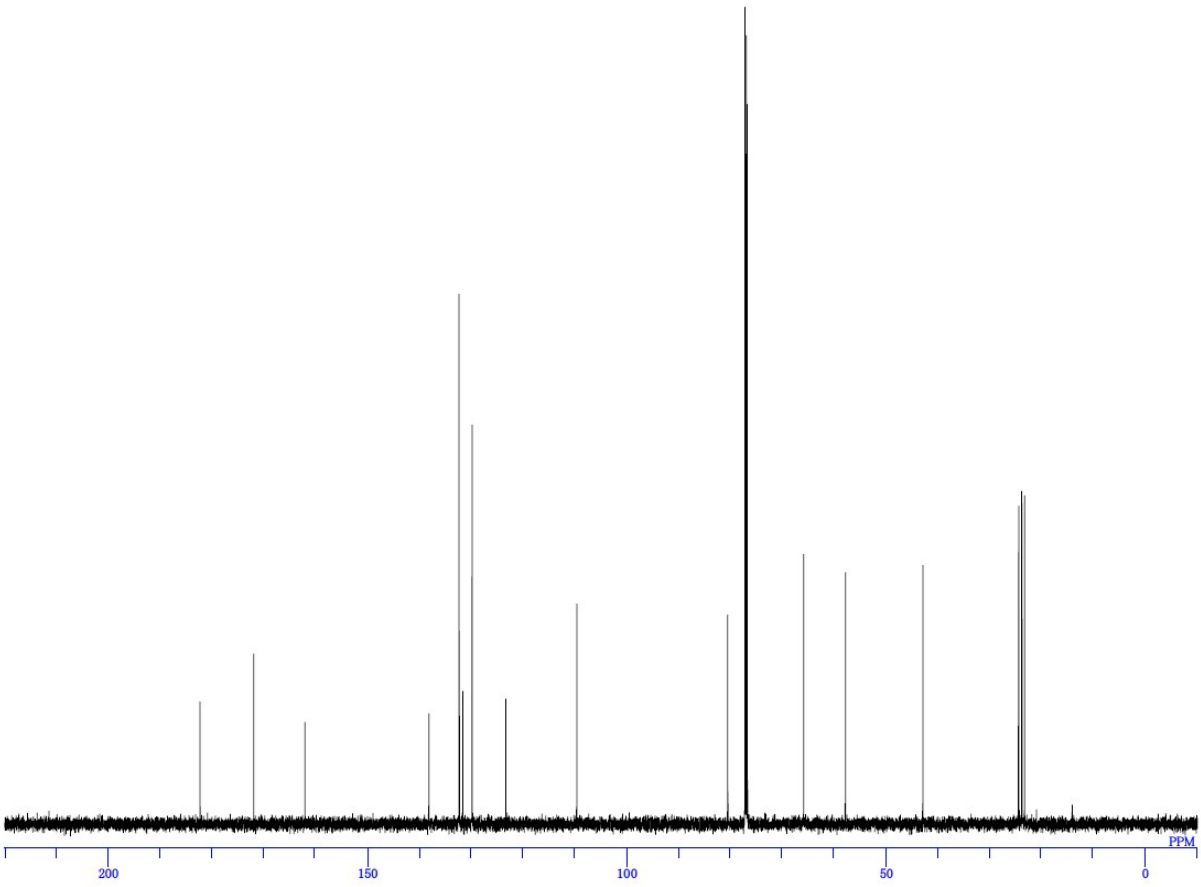


iBu_4-Br

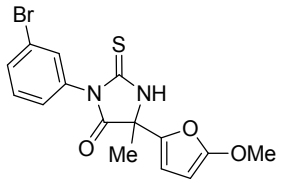


7h

iBu_4-Br

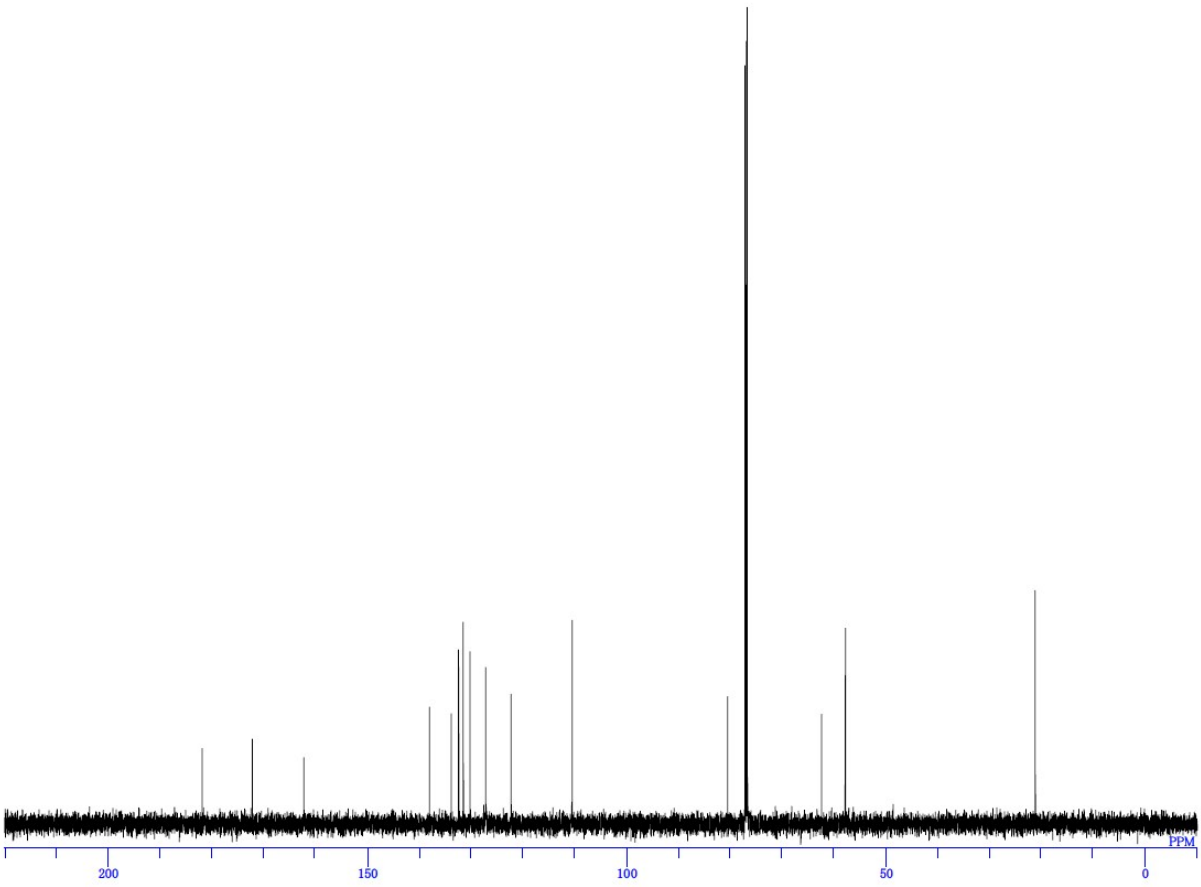


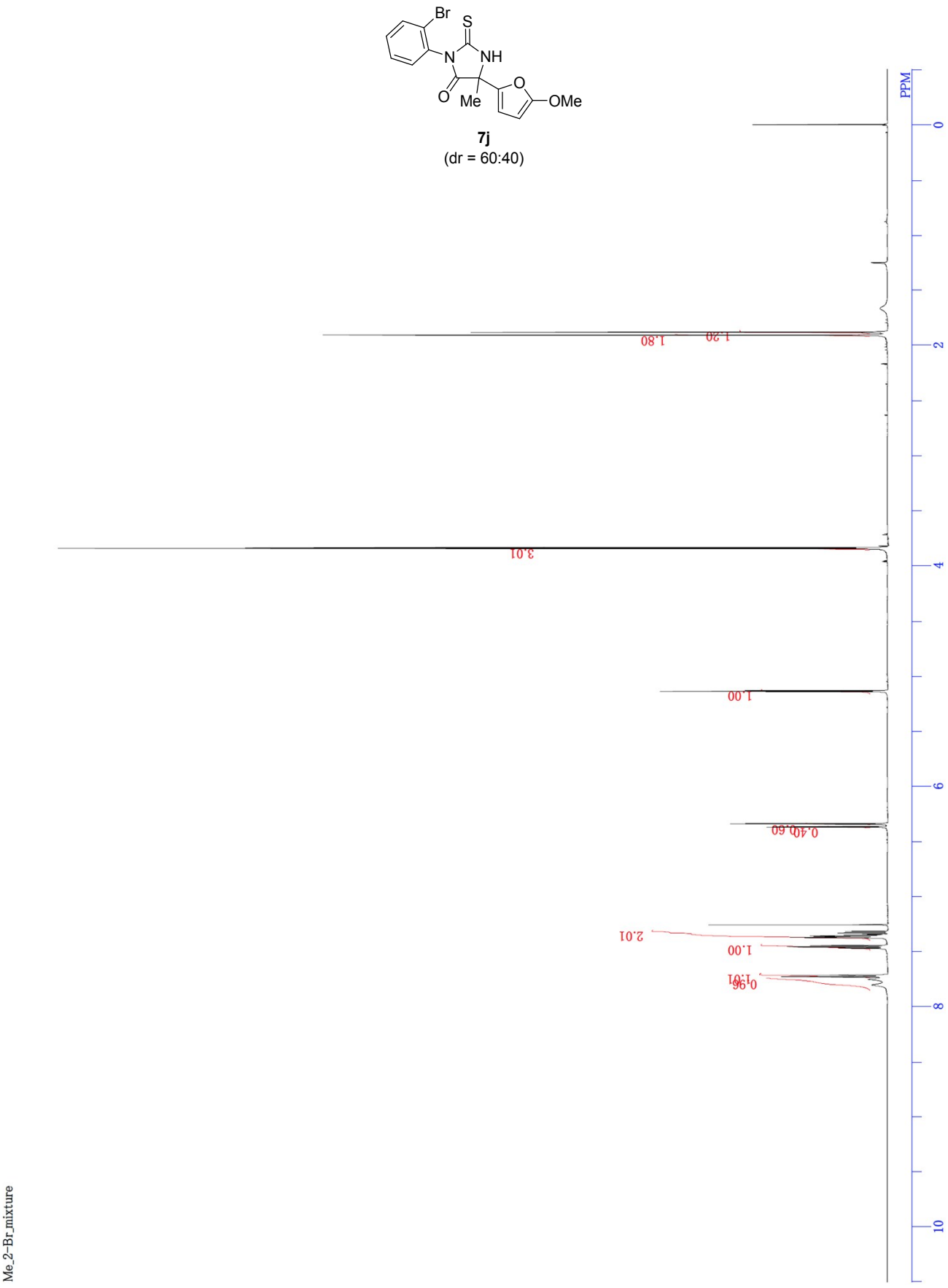
Me_3-Br



7i

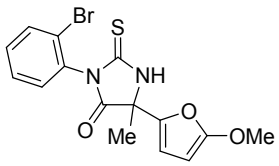
Me_3-Br




Br
S
N
NH
O
Me
O
OMe
PPM
0
2
4
6
8
10
1.80
1.20
3.01
1.00
0.40
0.60
2.01
1.00
0.96
1.01
Me_2-Br_mixture

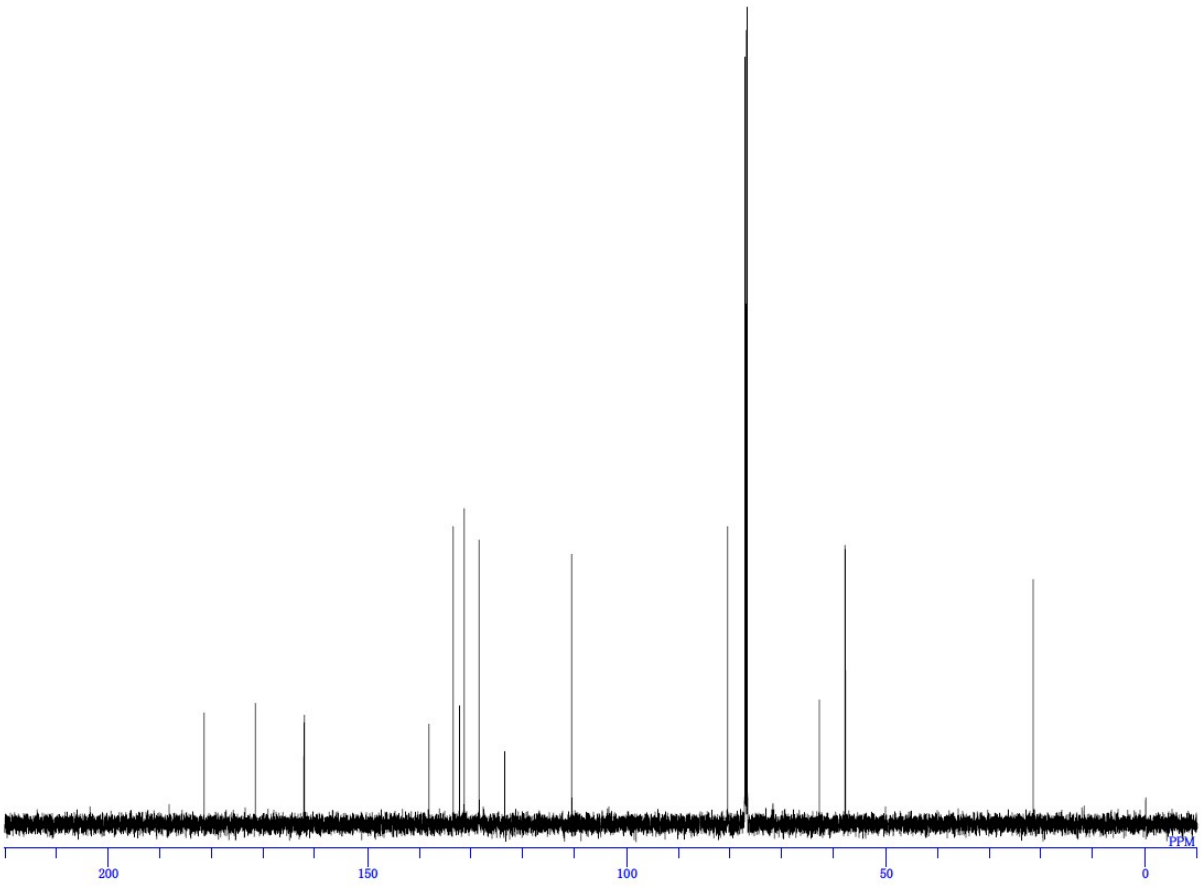
7j
(dr = 60:40)

Me_2-Br_major

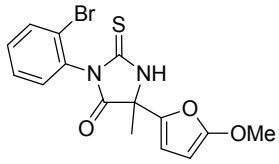


7j
(major isomer)

Me_2-Br_major

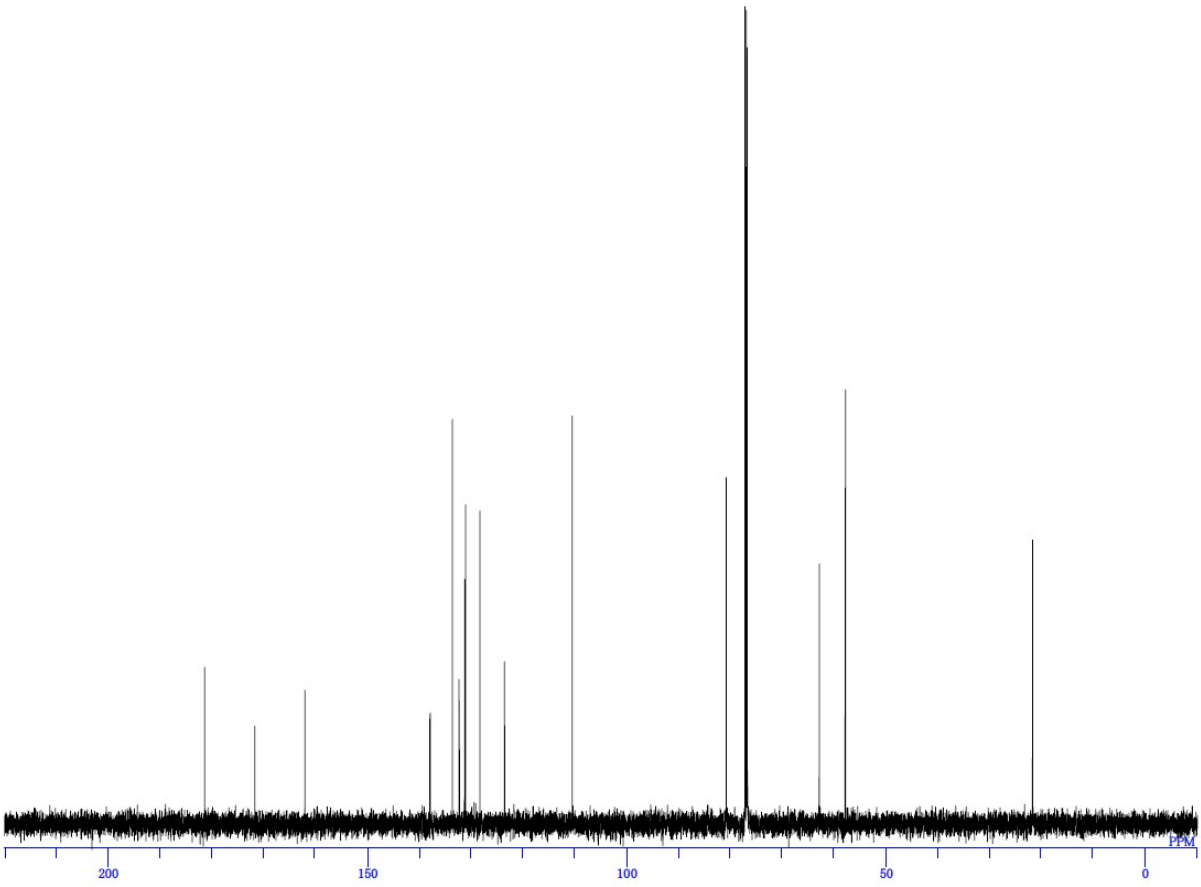


Me_2-Br_minor

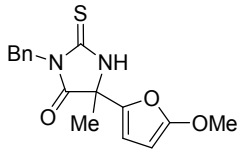


7j
(minor isomer)

Me_2-Br_minor

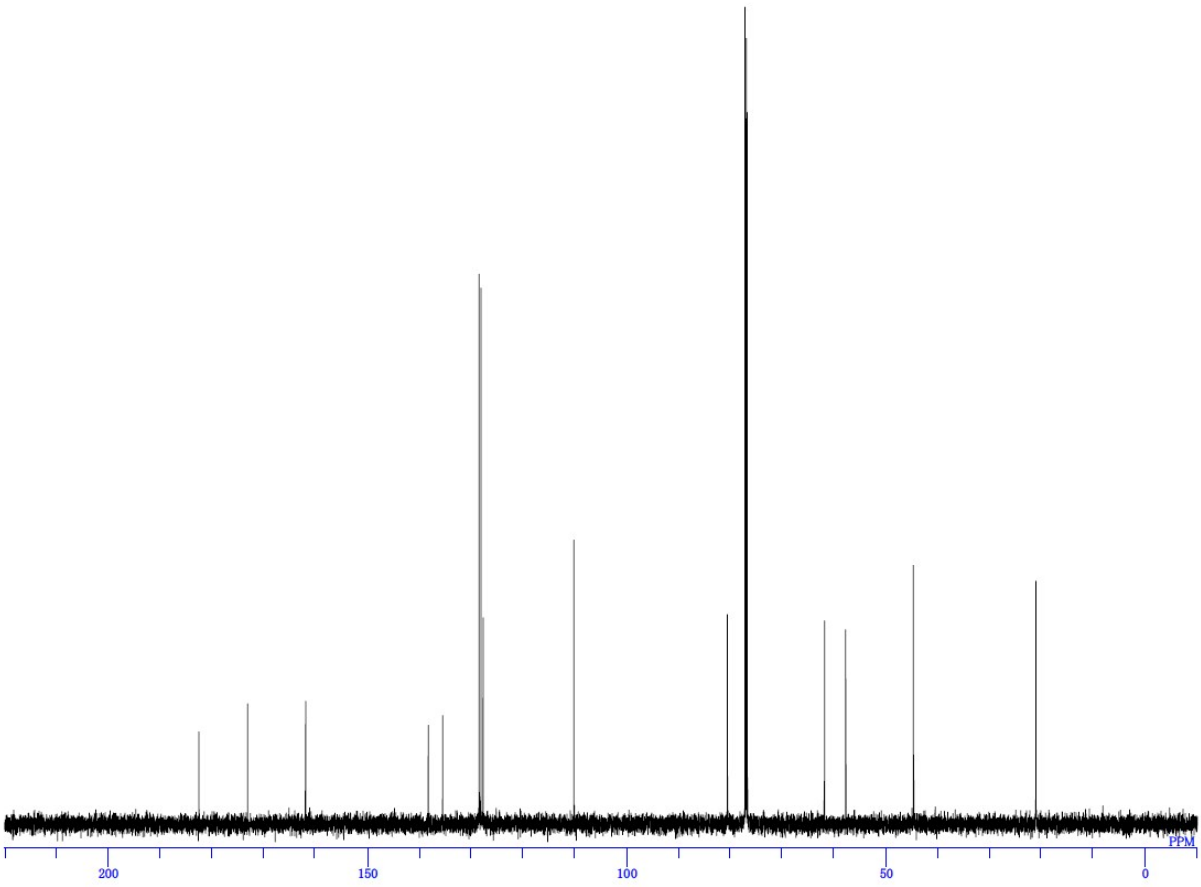


Me_Bn

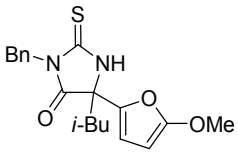


7k

Me_Bn_product

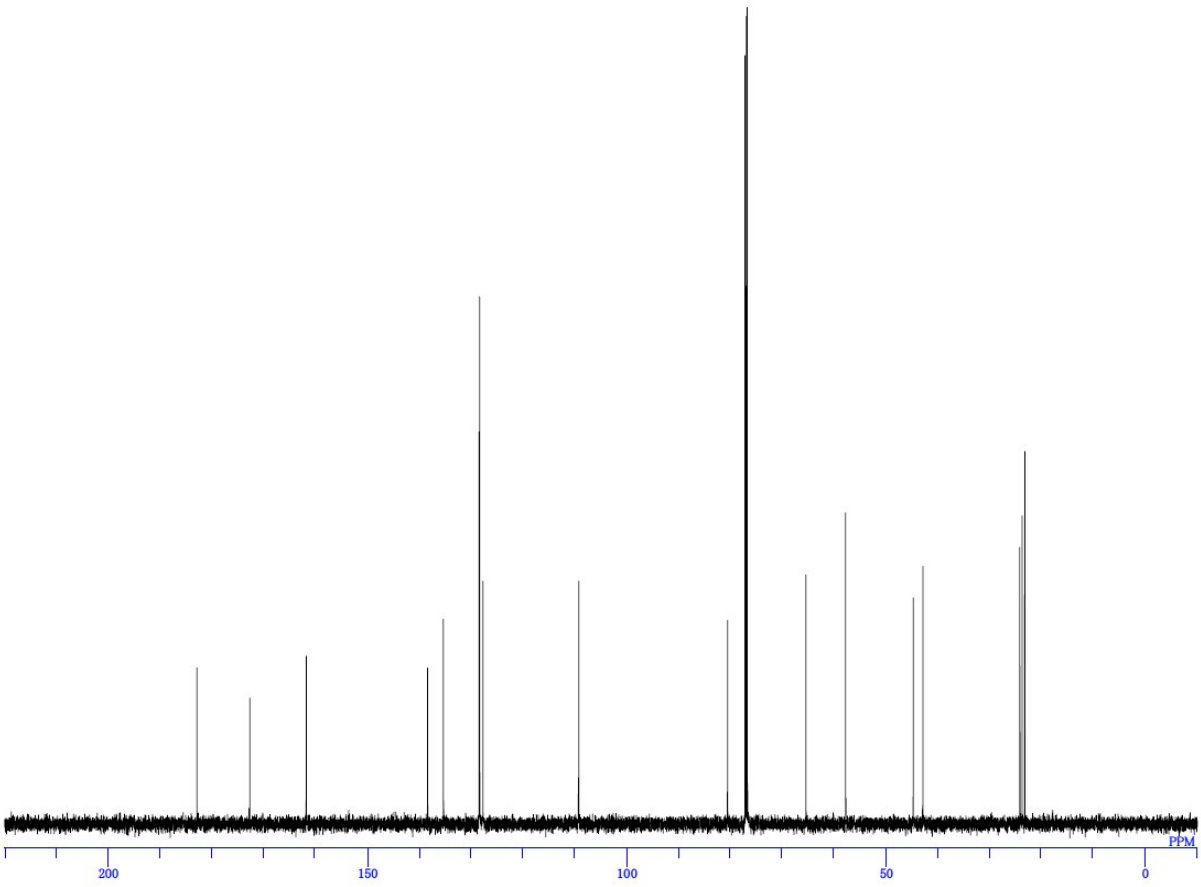


iBu_Bn

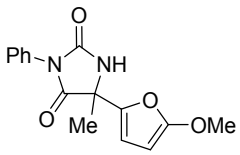


7l

iBu_Bn

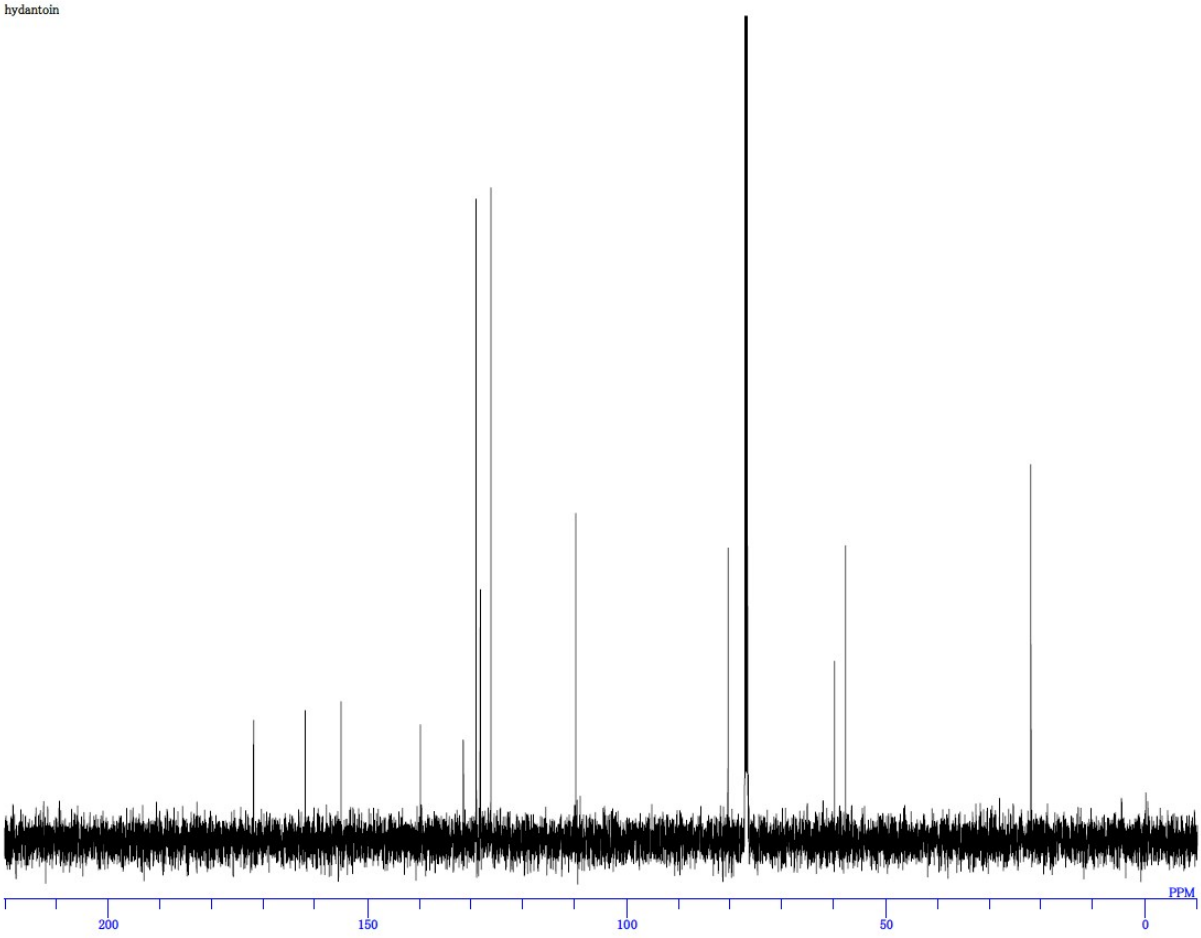


hydantoin

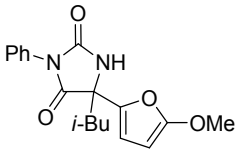


8a

hydantoin

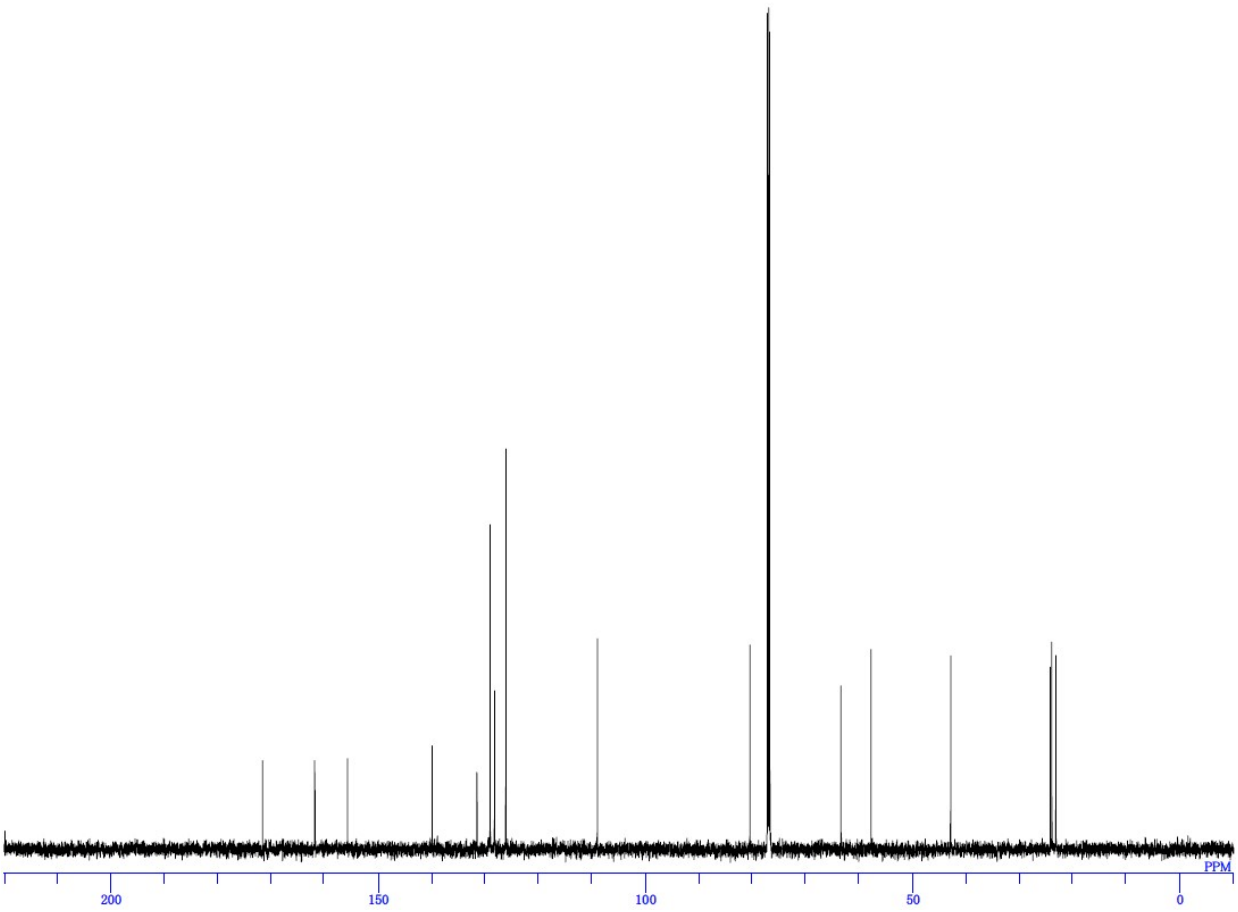


iBu_Ph_C=O_product

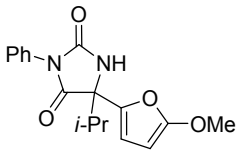


8b

iBu_Ph_C=O_product

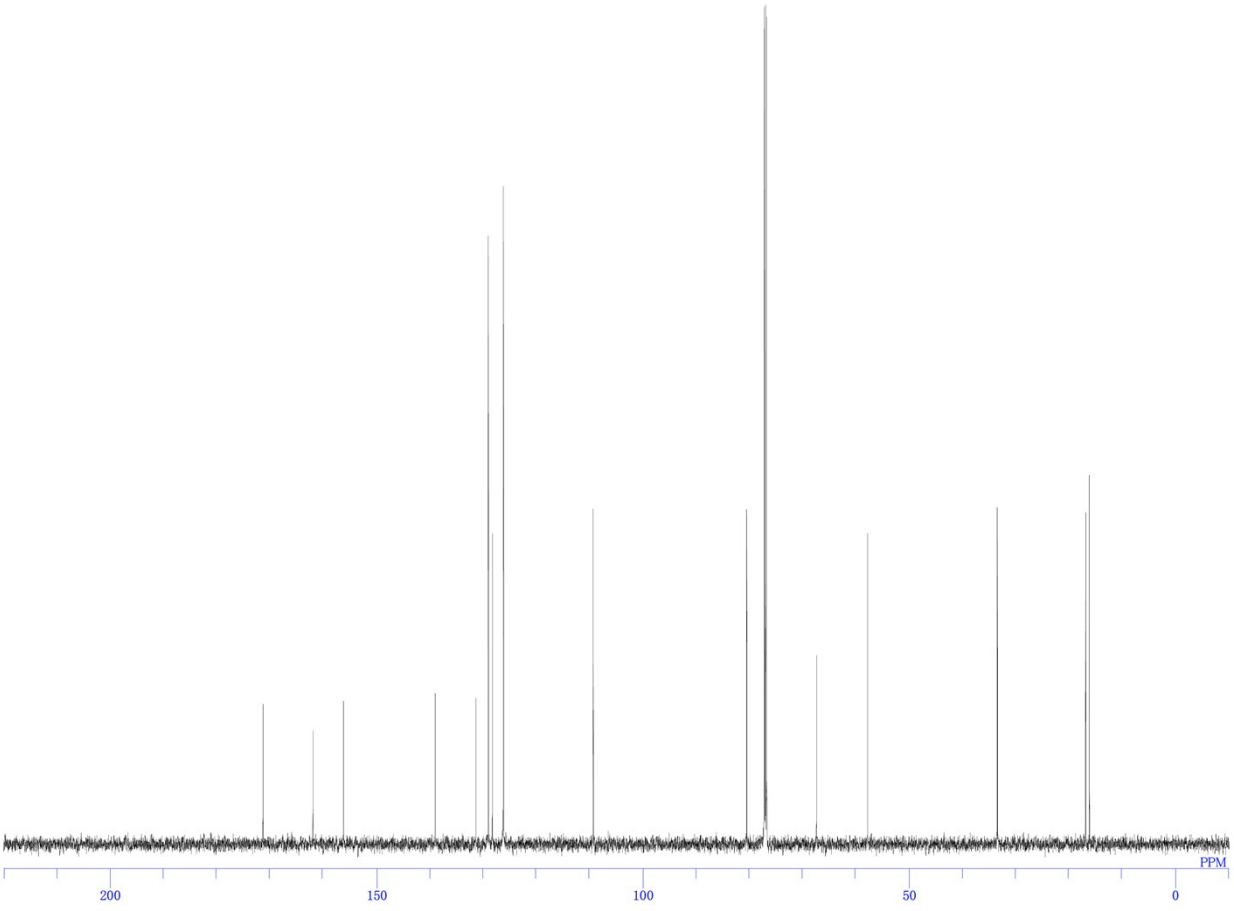


iPr_Ph_C=O_product

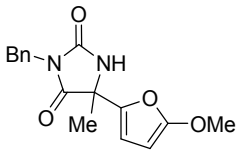


8c

iPr_Ph_C=O_product

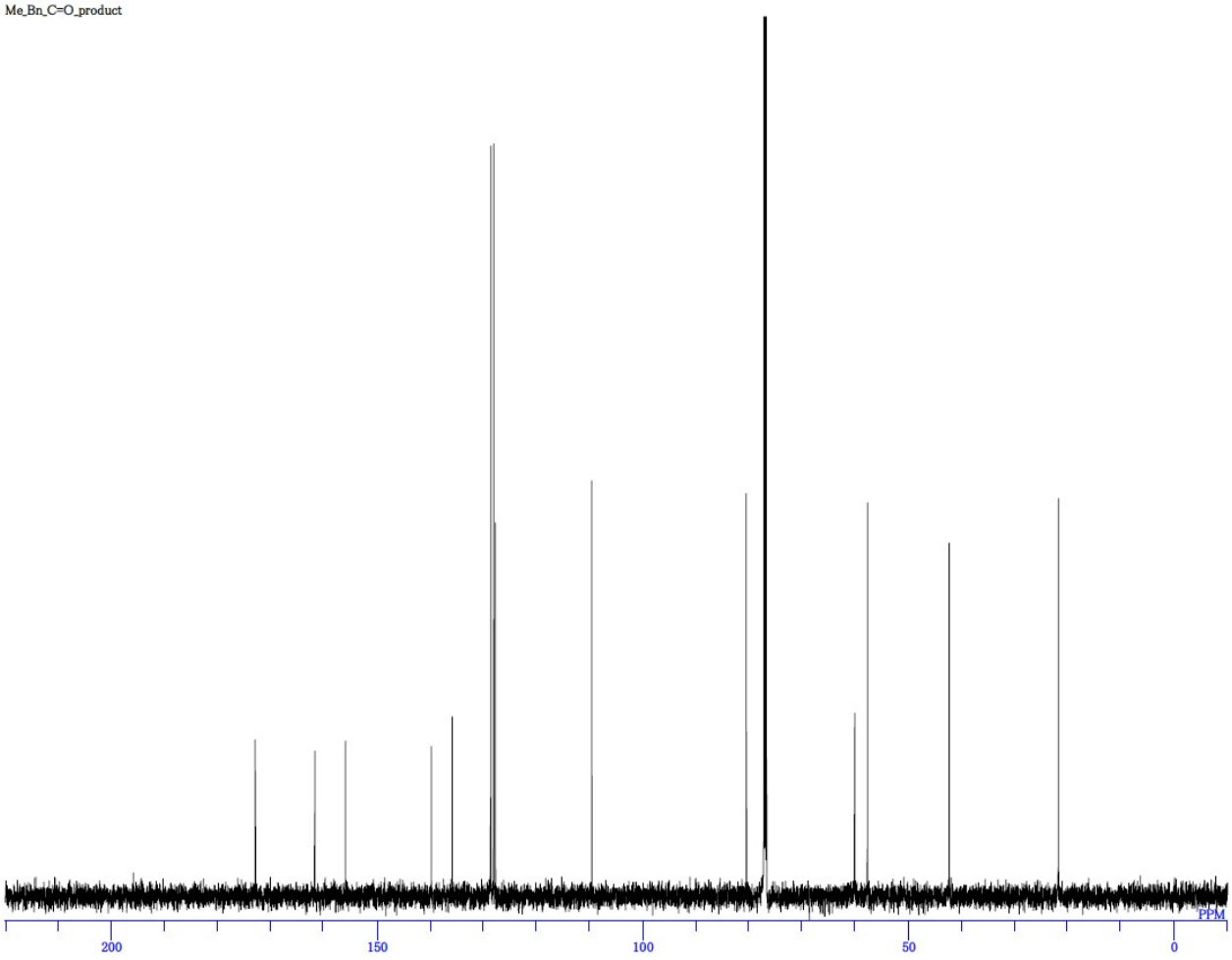


Me_Bn_C=O_product

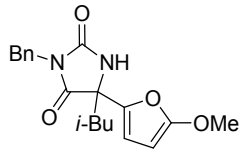


8d

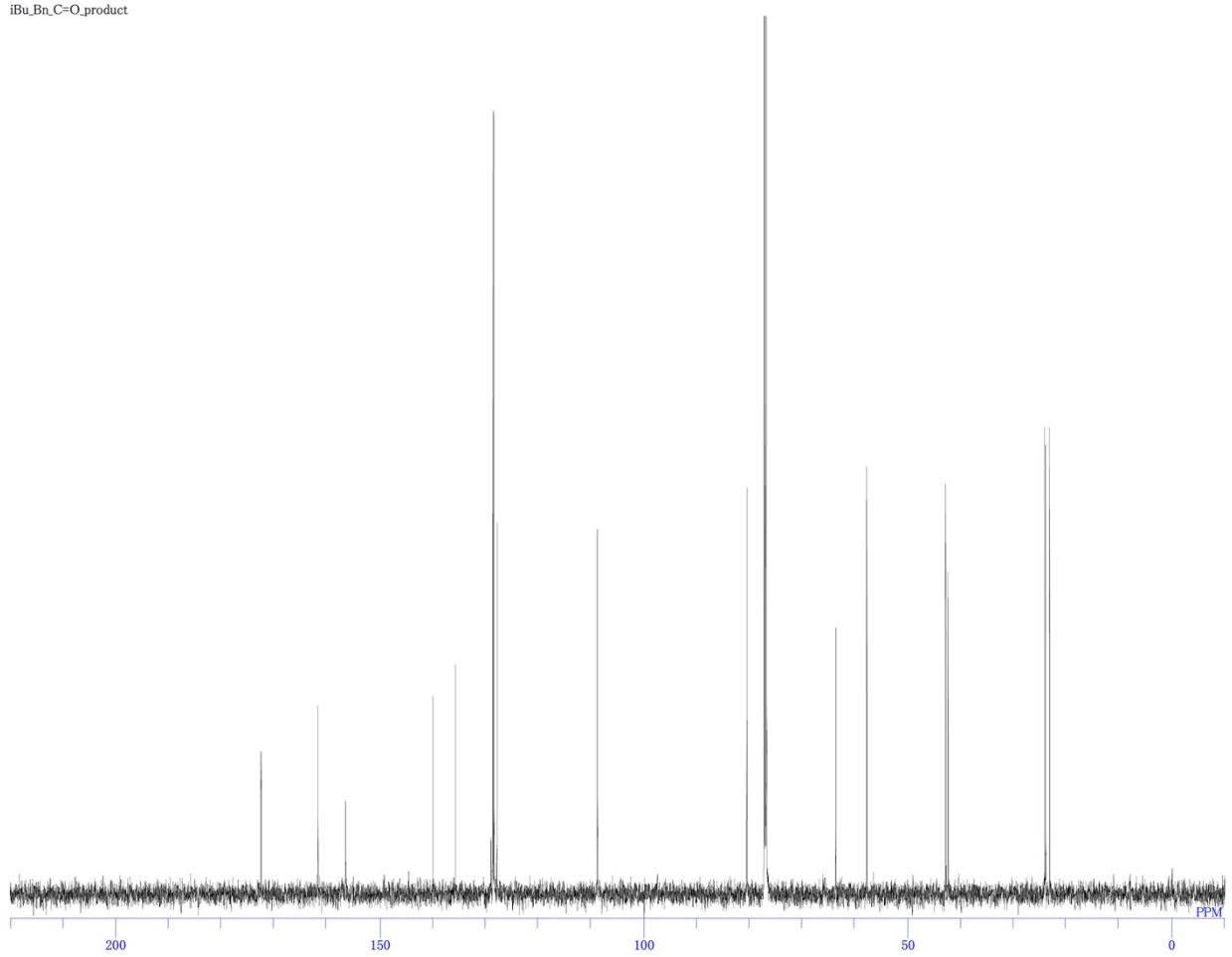
Me_Bn_C=O_product



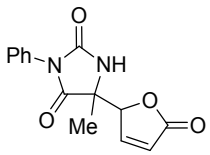
iBu_Bn_C=O_product



8e

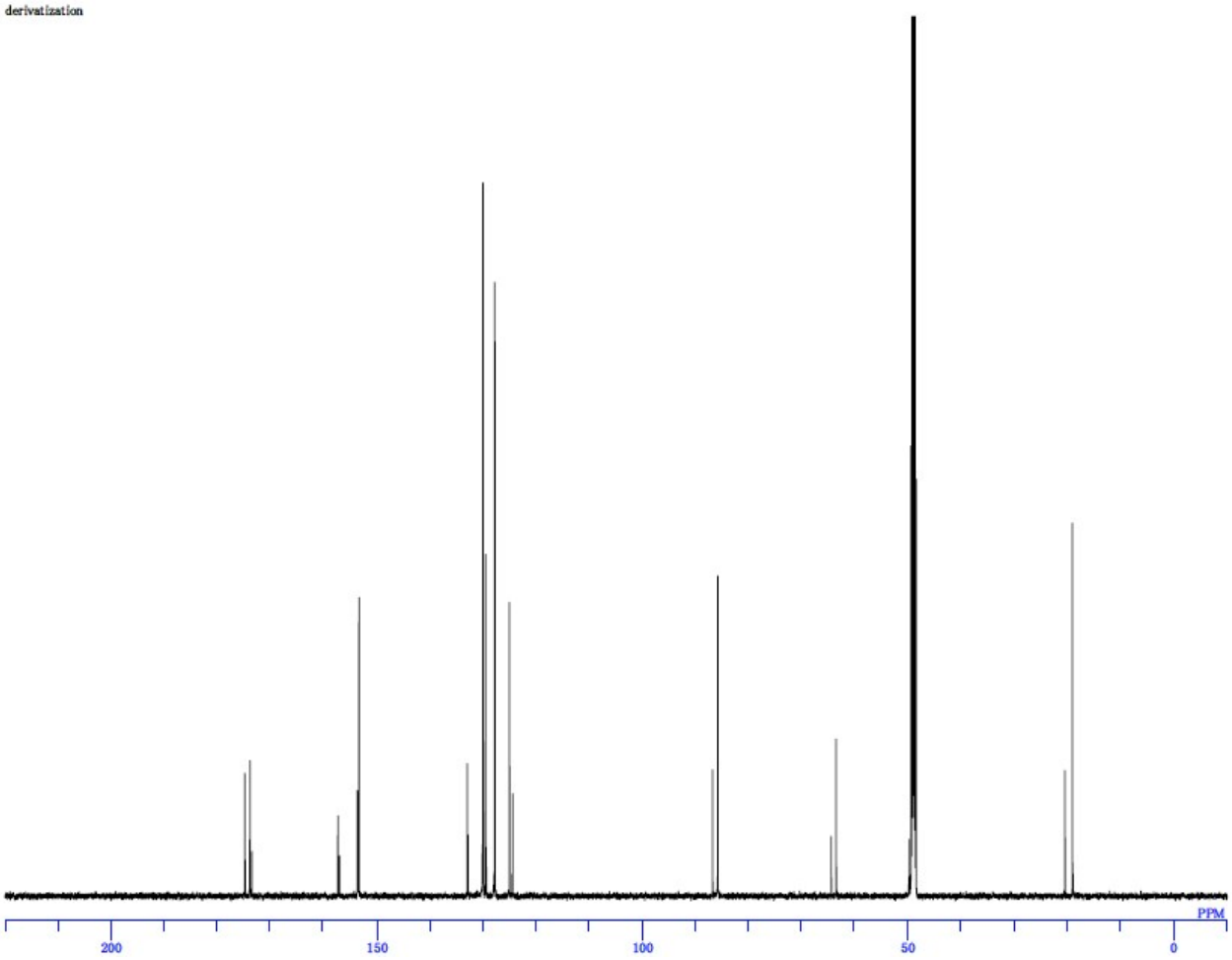


derivatization

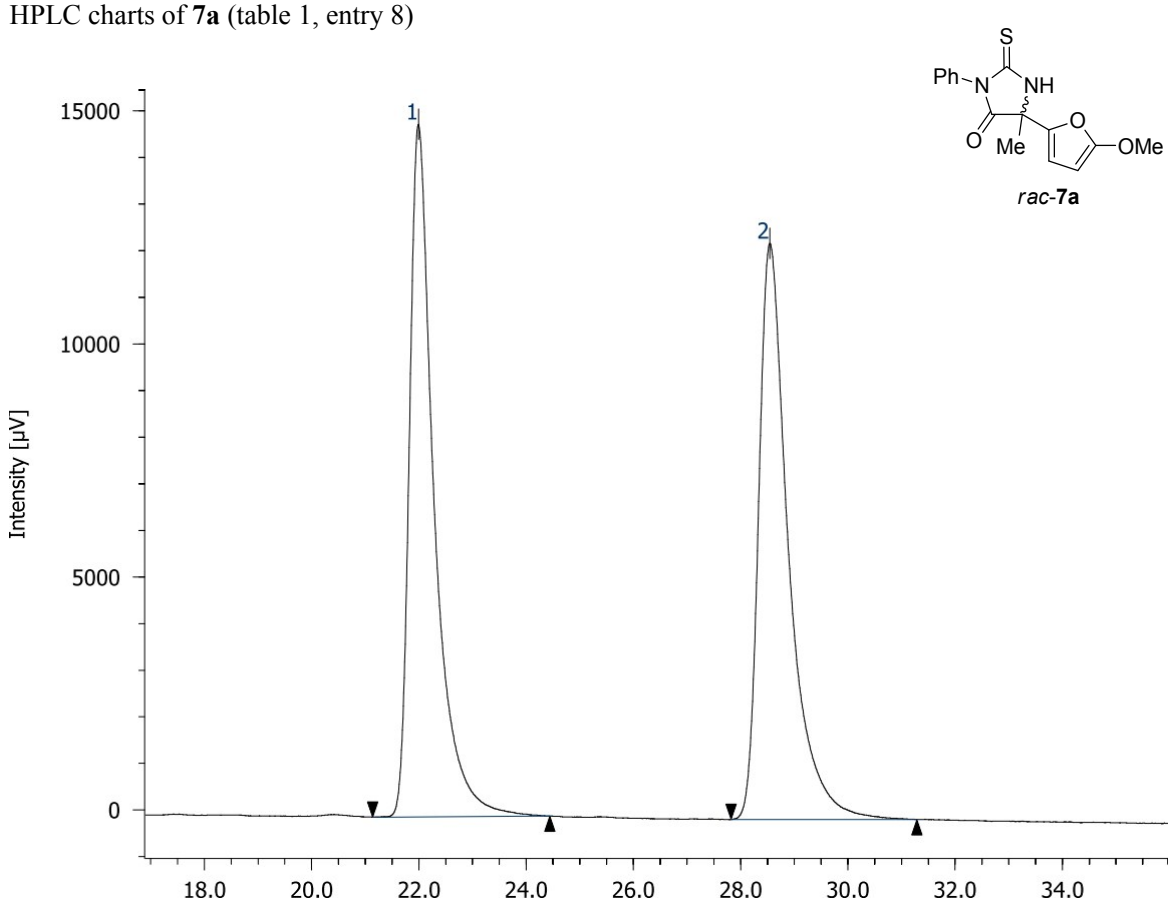


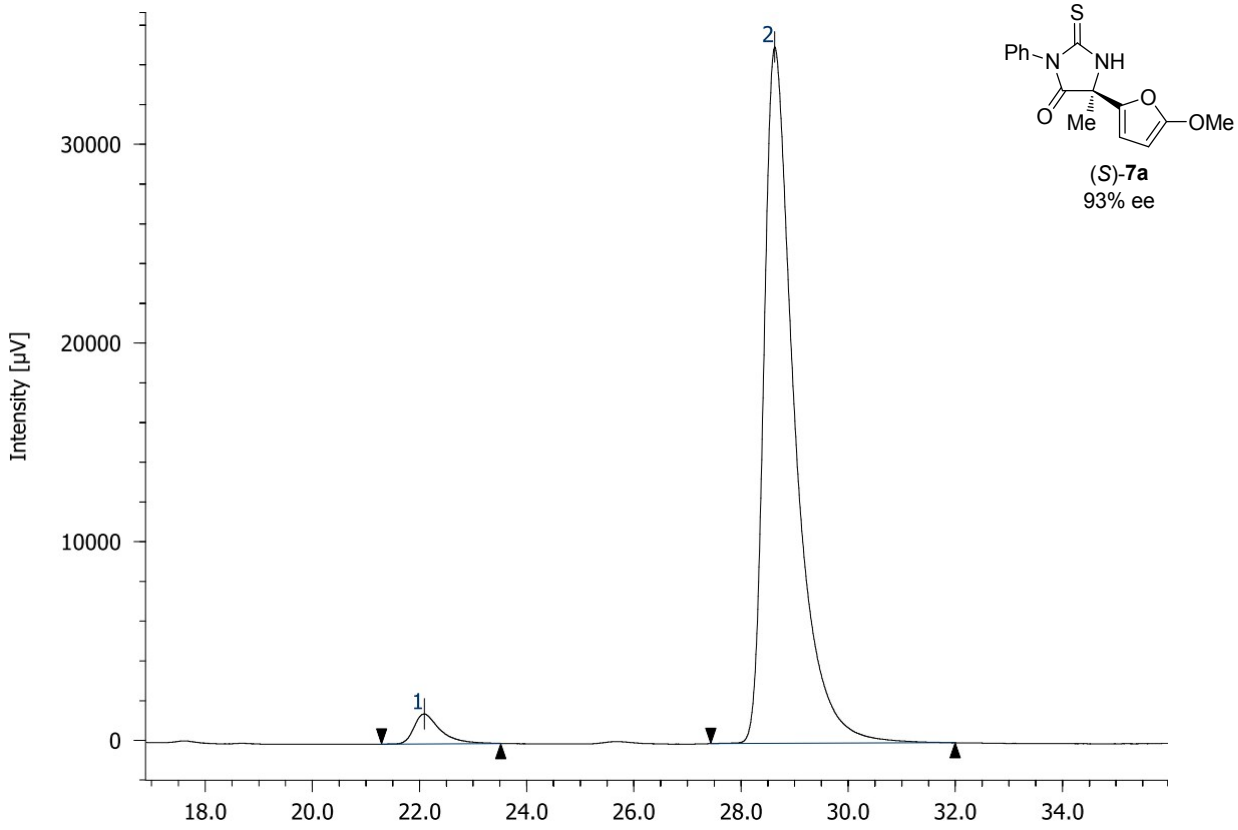
10
(dr = 68:32)

derivatization

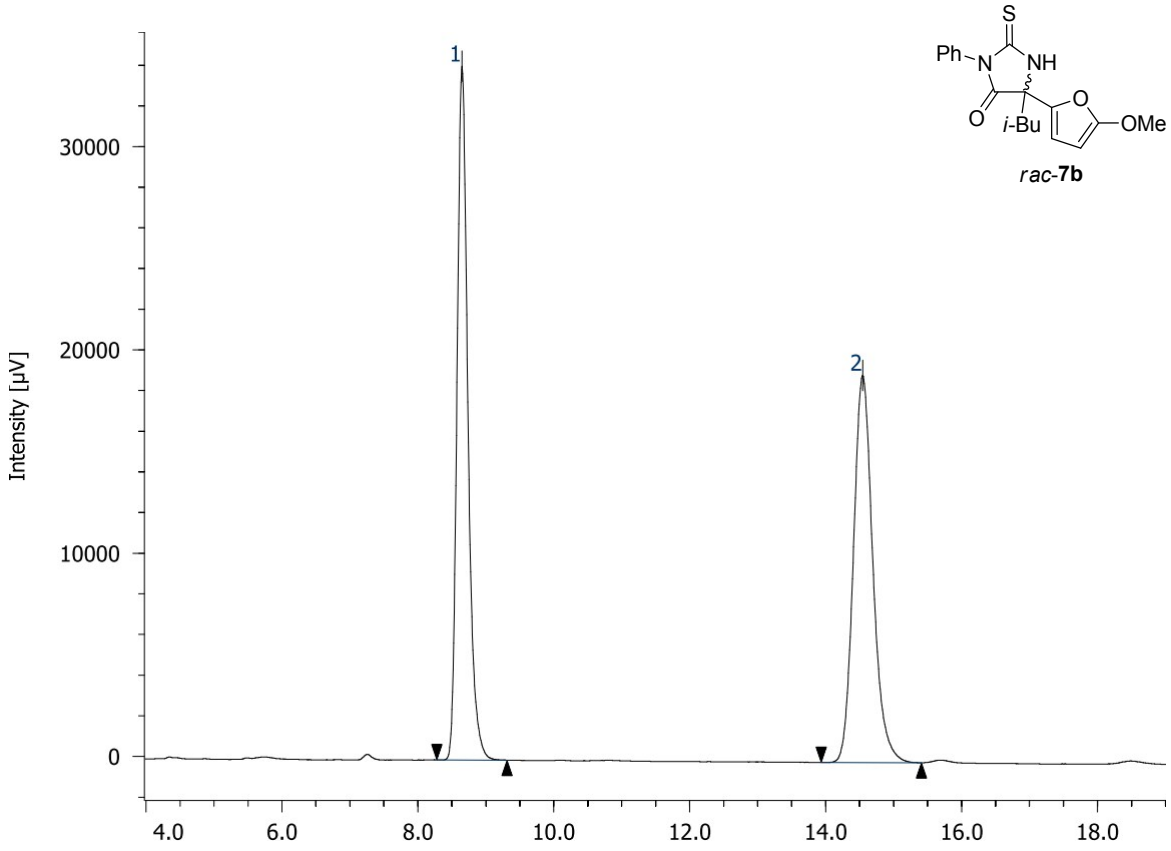


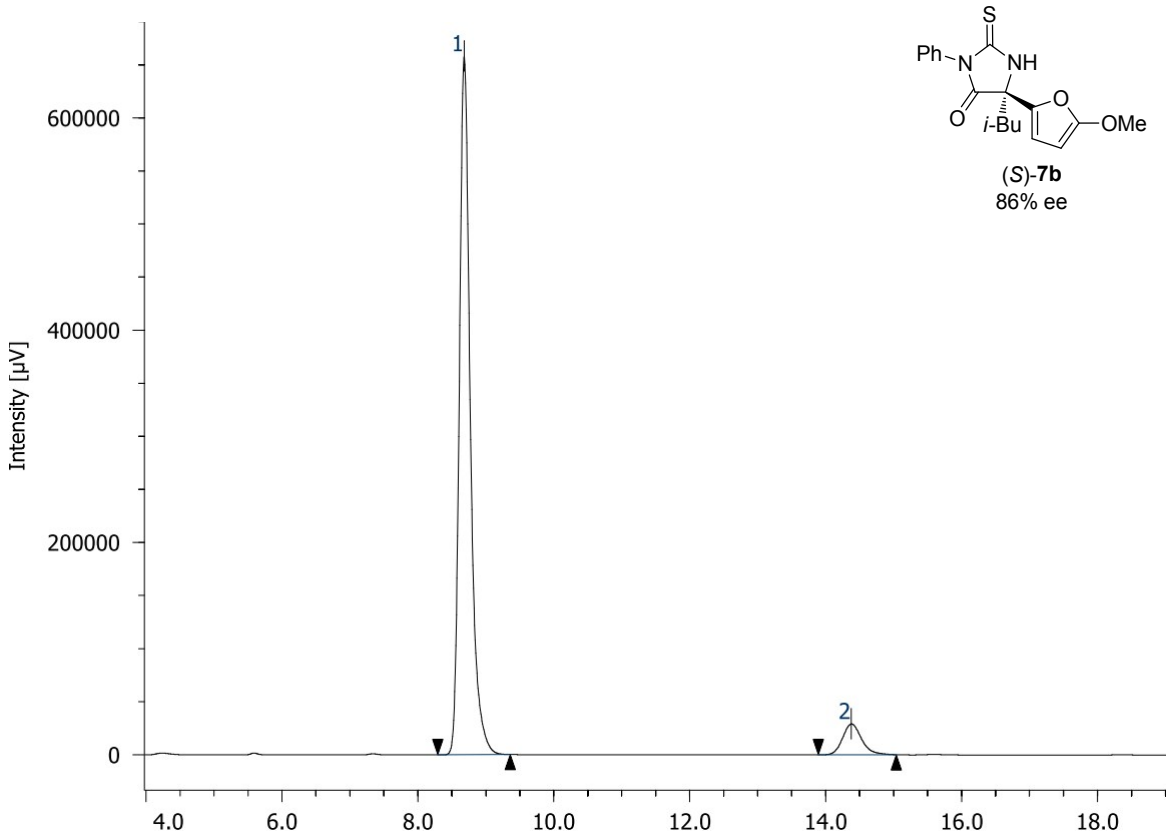
HPLC charts of **7a** (table 1, entry 8)



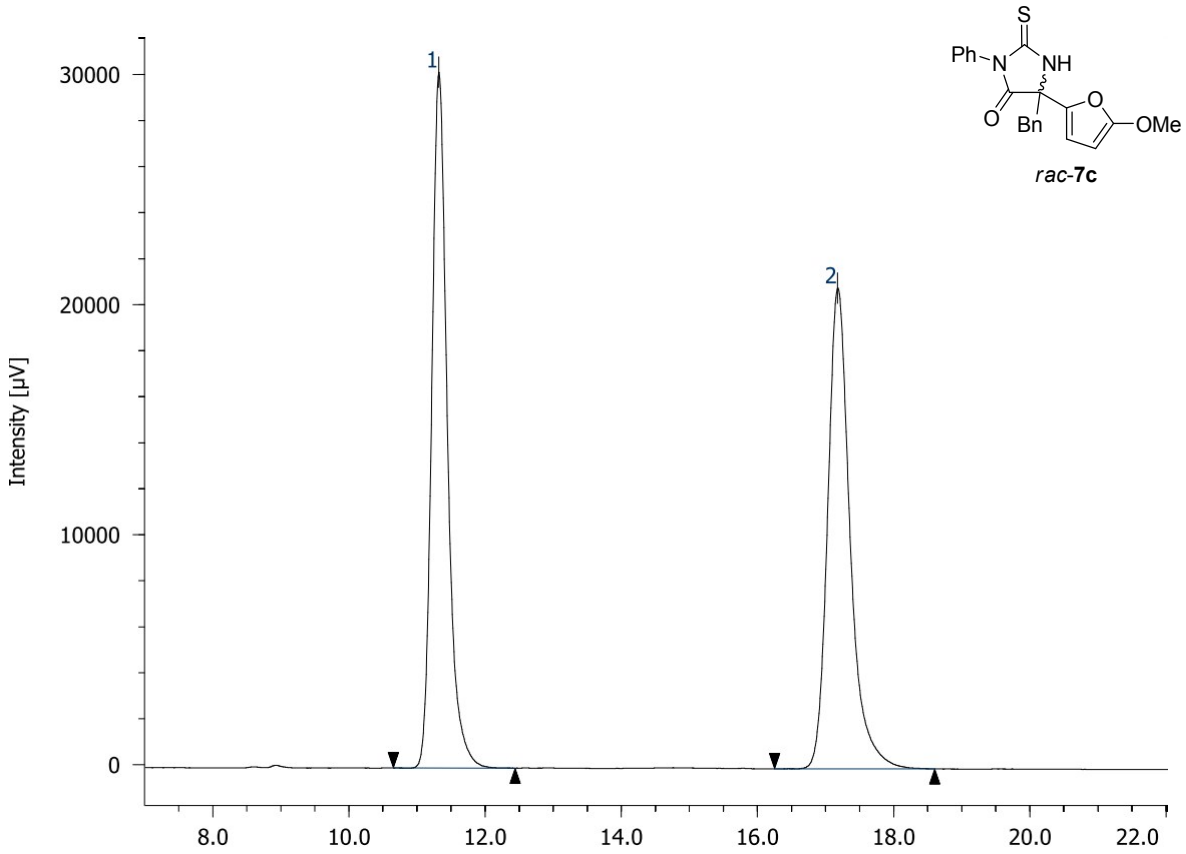


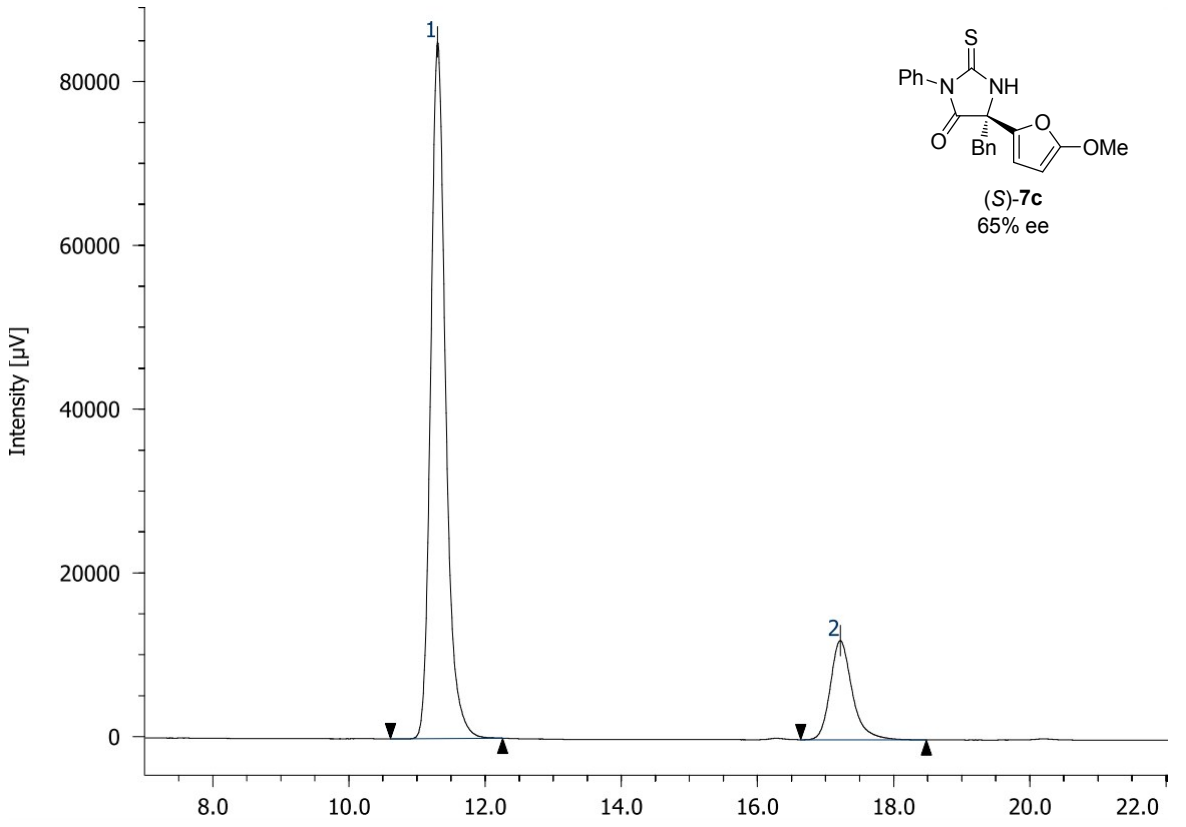
HPLC charts of **7b** (table 2, entry 1)



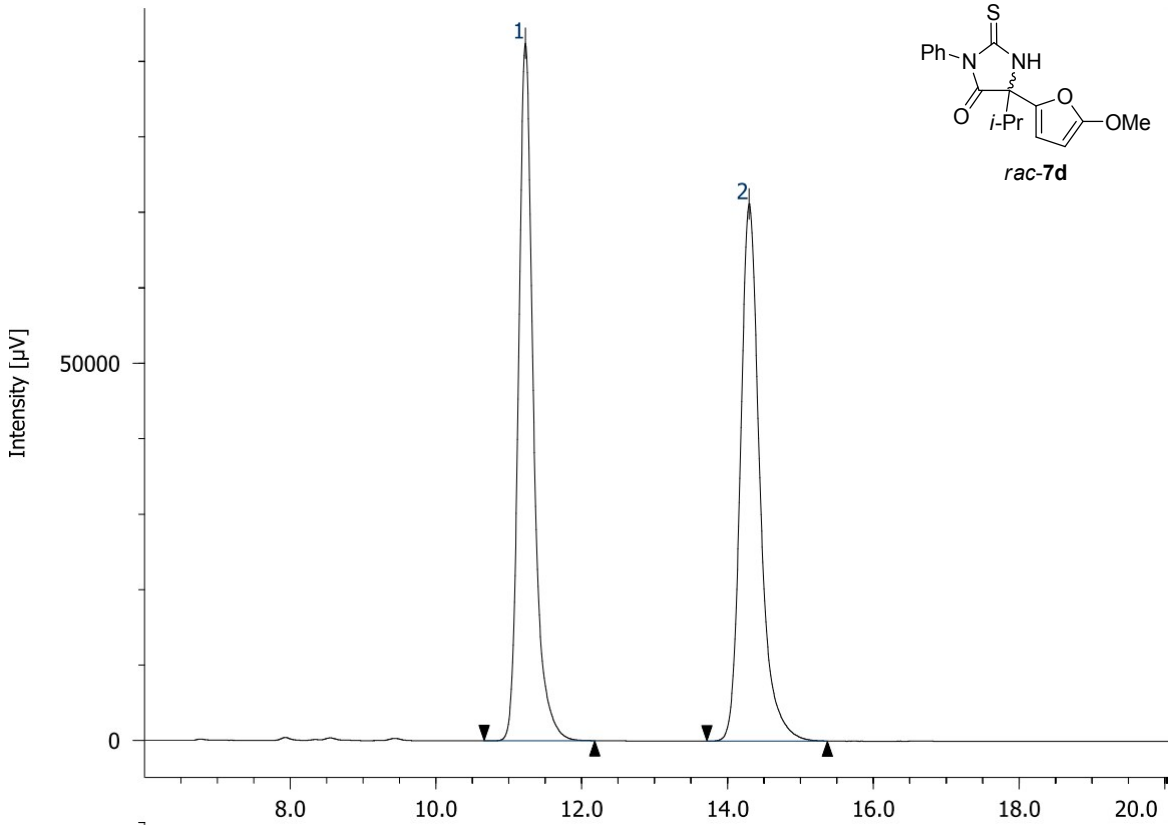


HPLC charts of **7c** (table 2, entry 2)

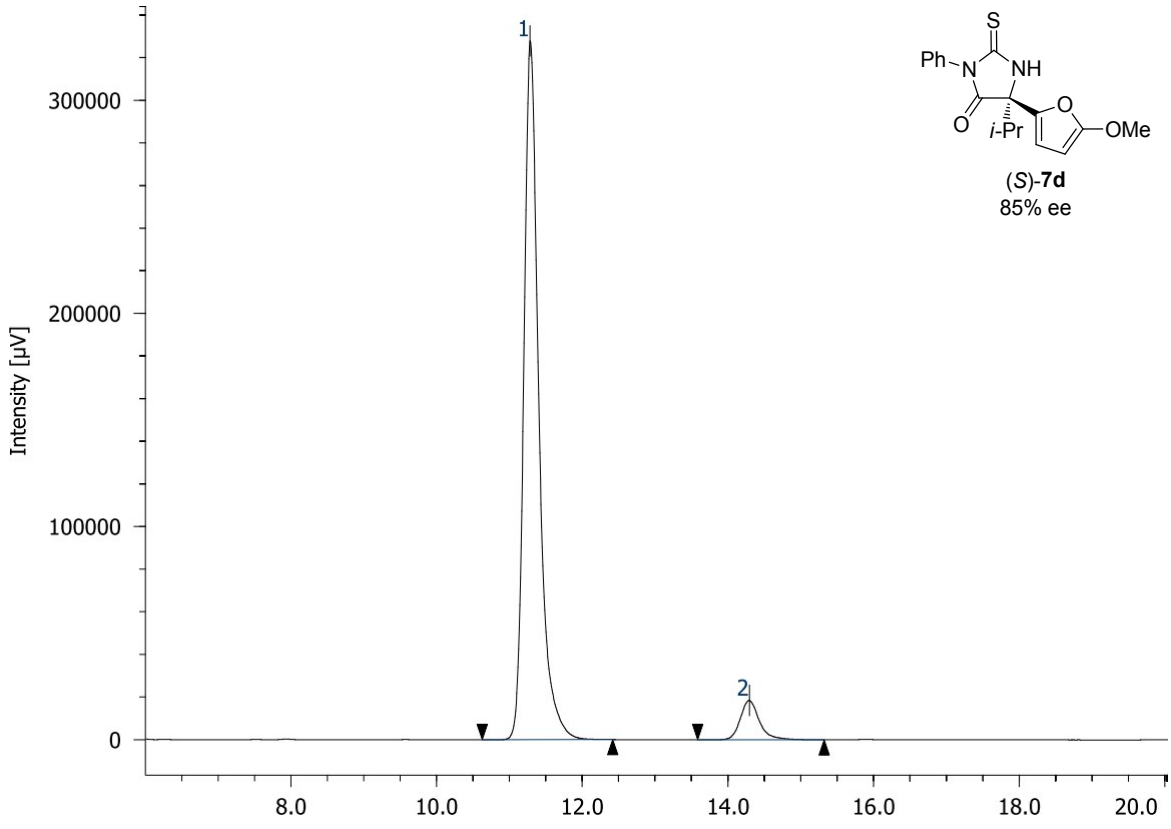




HPLC charts of **7d** (table 2, entry 3)

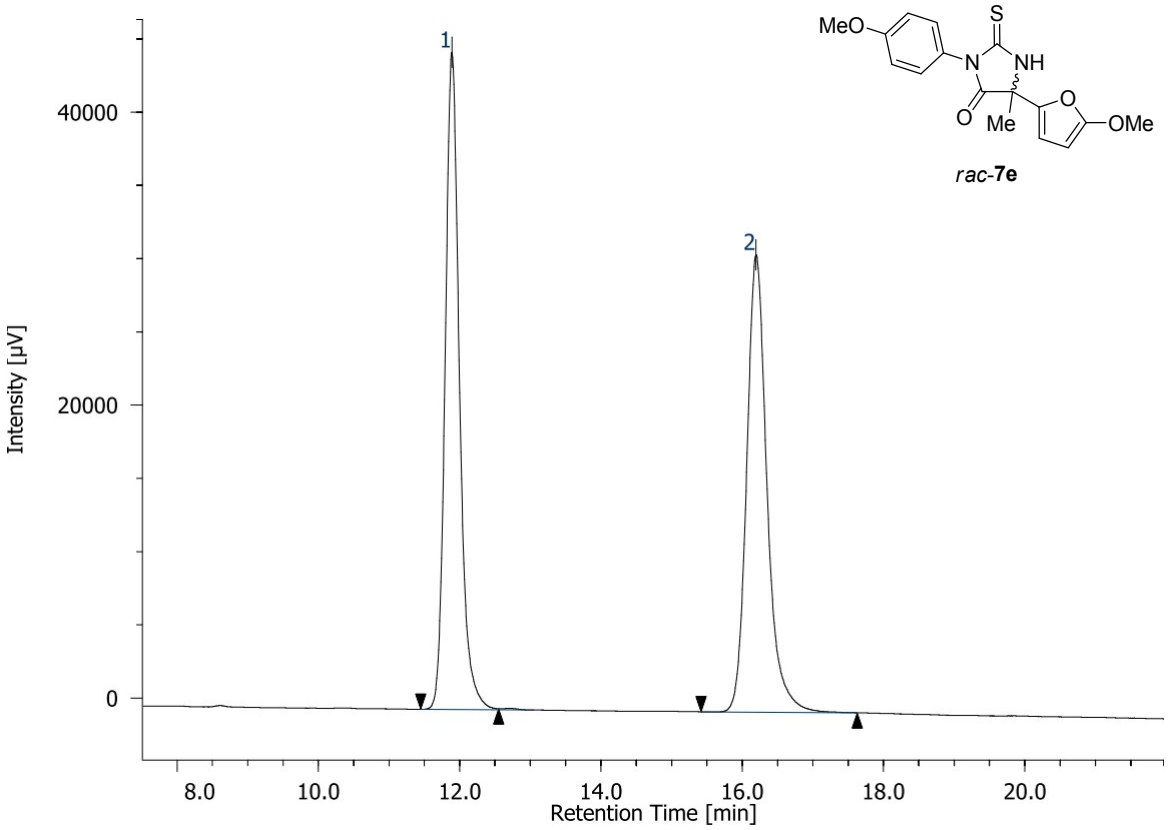


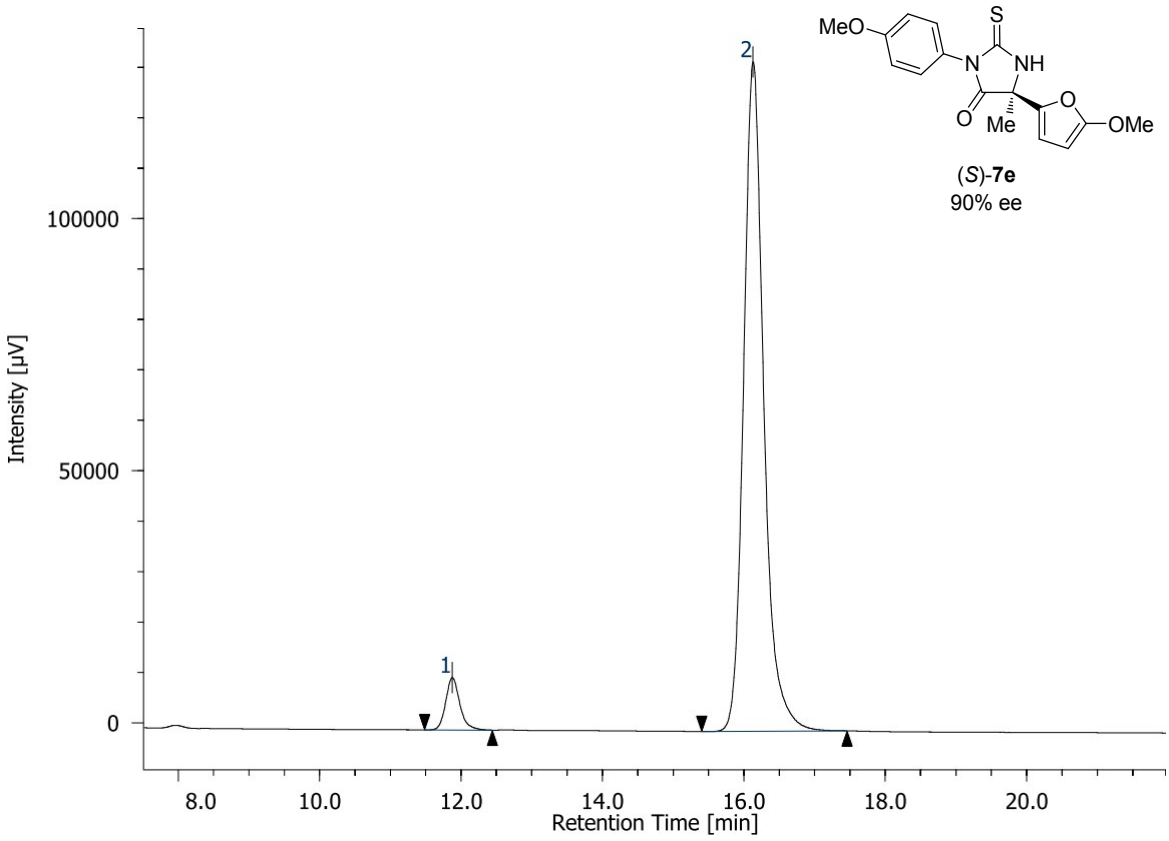
rac-**7d**



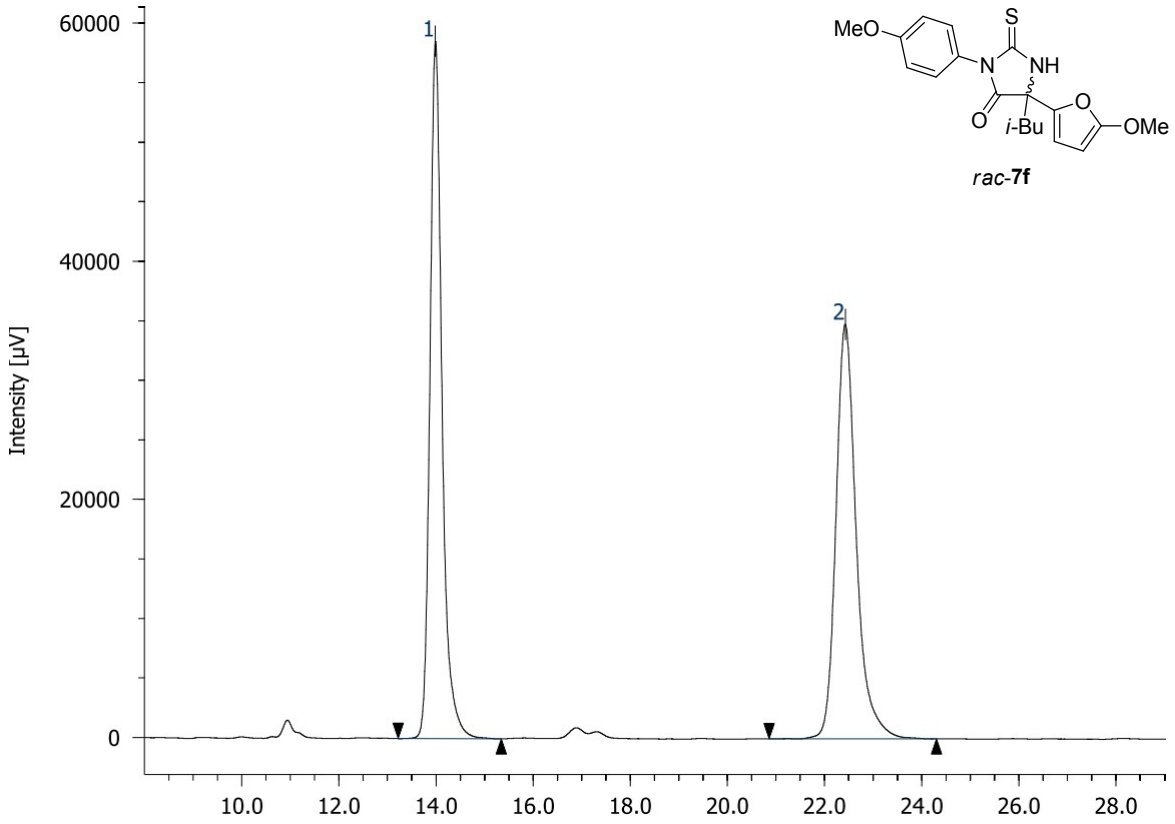
(*S*)-**7d**
85% ee

HPLC charts of **7e** (table 2, entry 5)

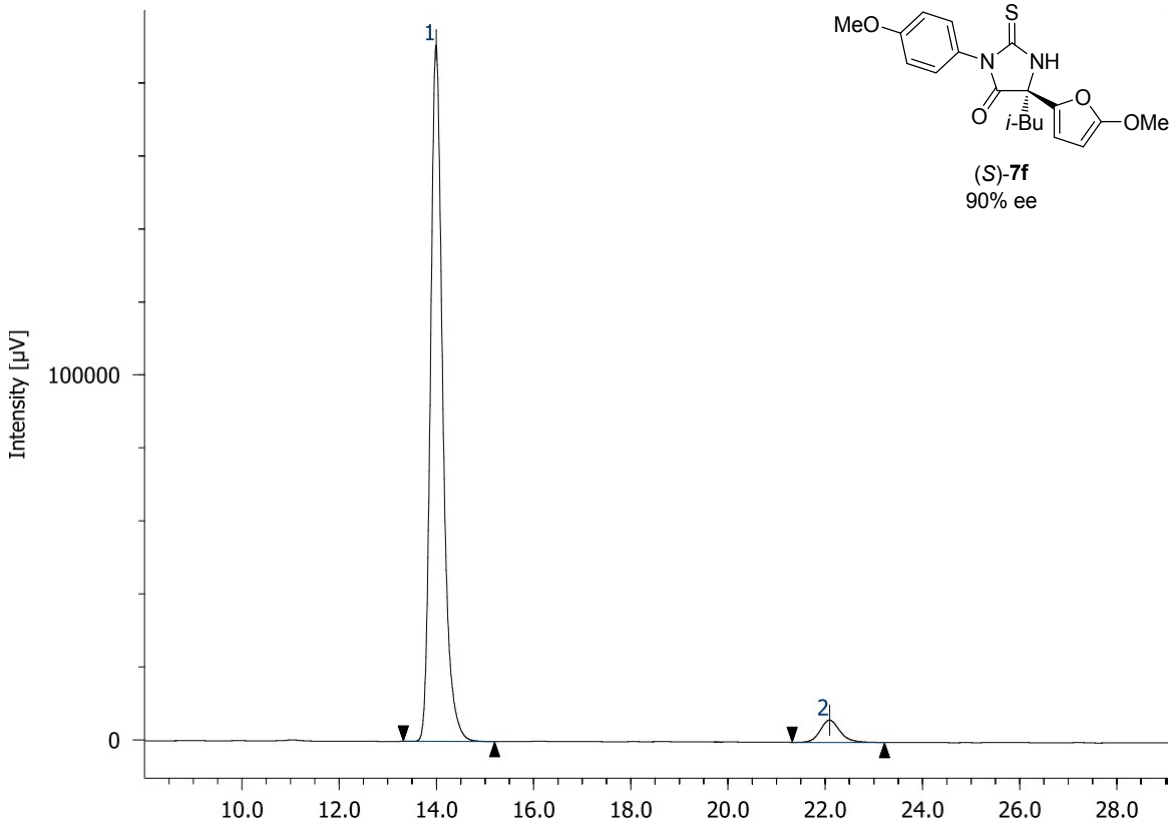




HPLC charts of **7f** (table 2, entry 6)

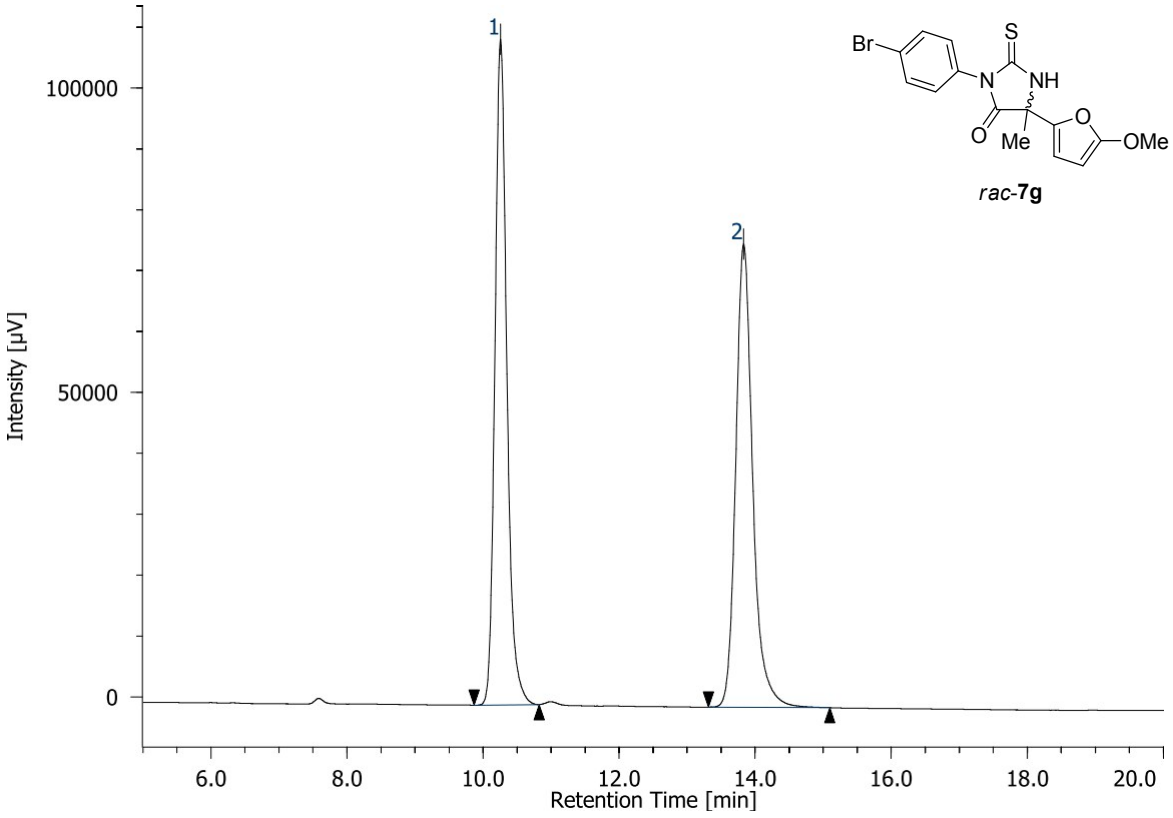


rac-**7f**

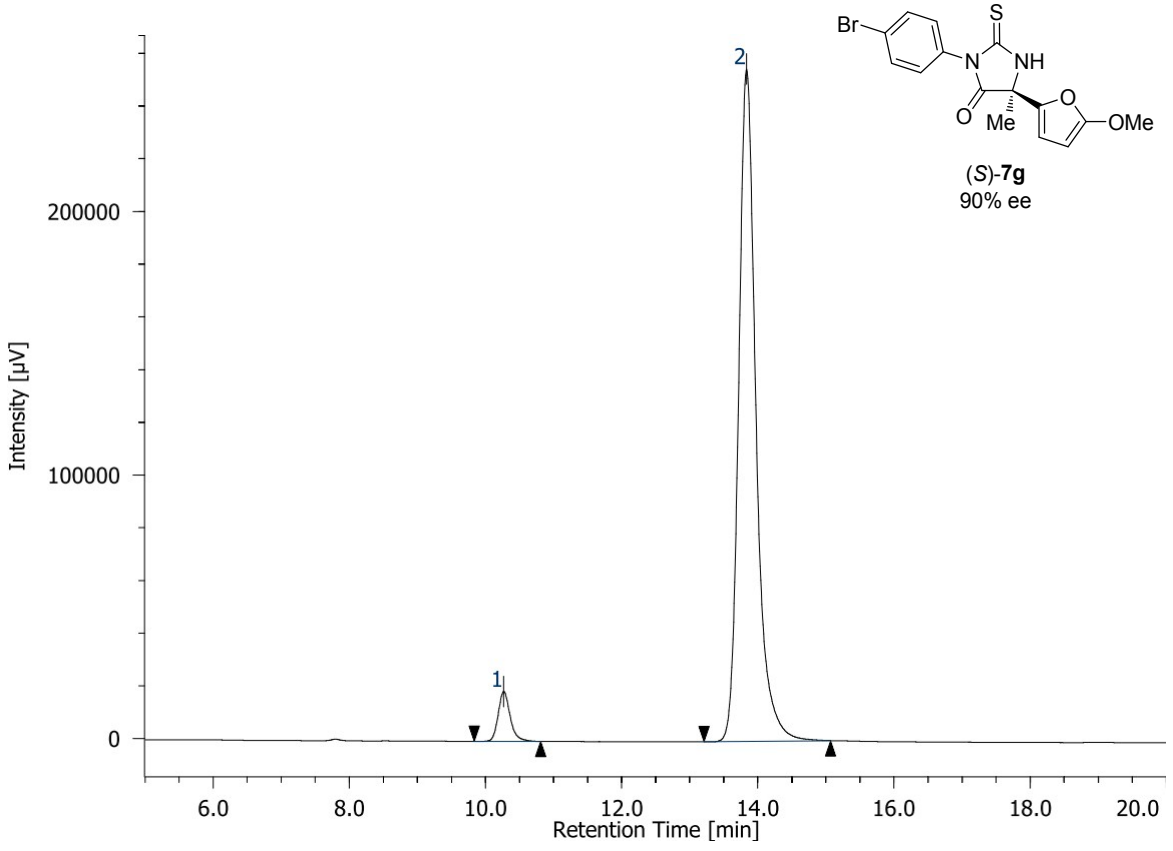


(*S*)-**7f**
90% ee

HPLC charts of **7g** (table 2, entry 7)

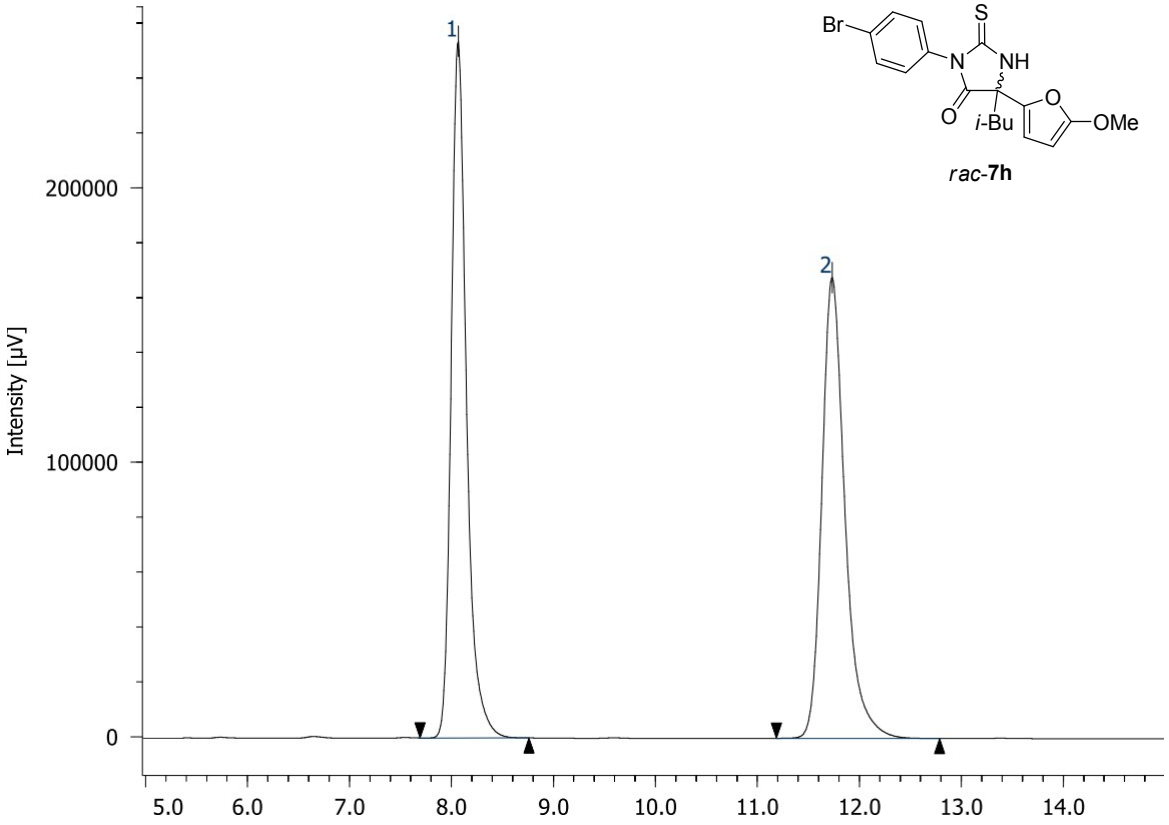


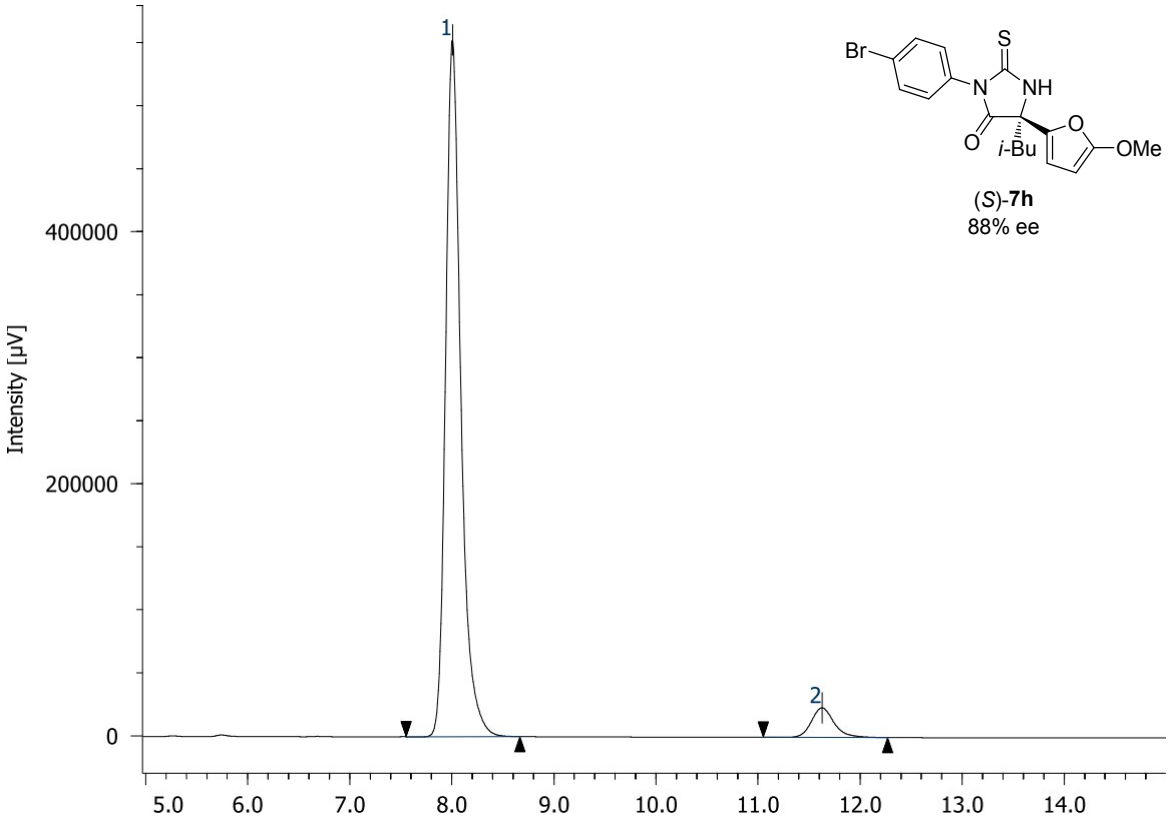
rac-**7g**



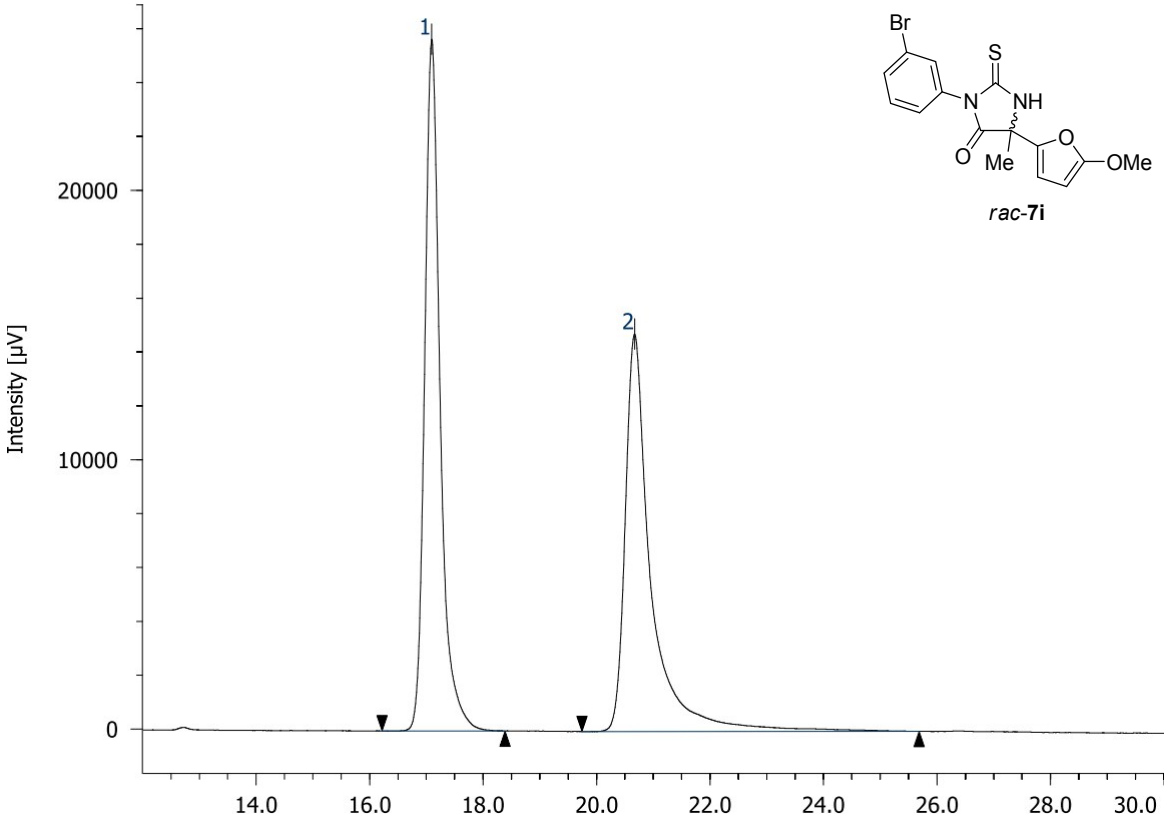
(*S*)-**7g**
90% ee

HPLC charts of **7h** (table 2, entry 8)

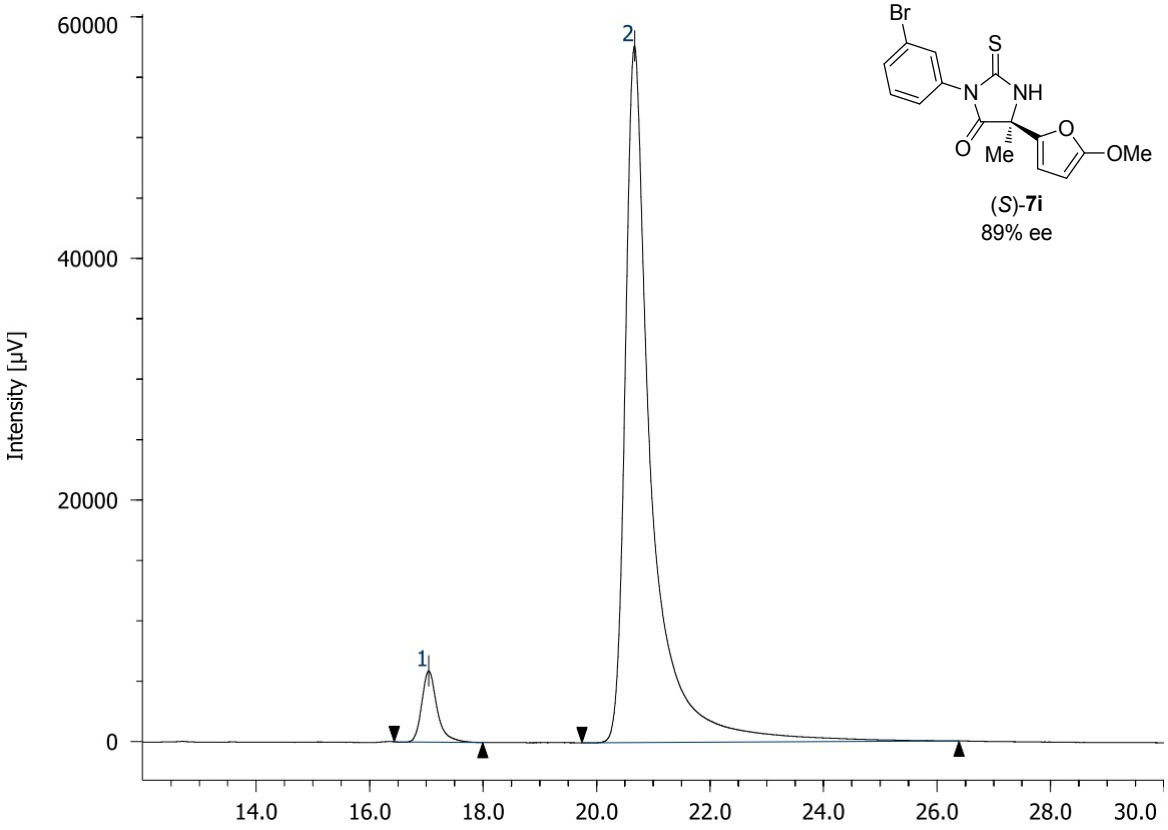




HPLC charts of **7i** (table 2, entry 9)

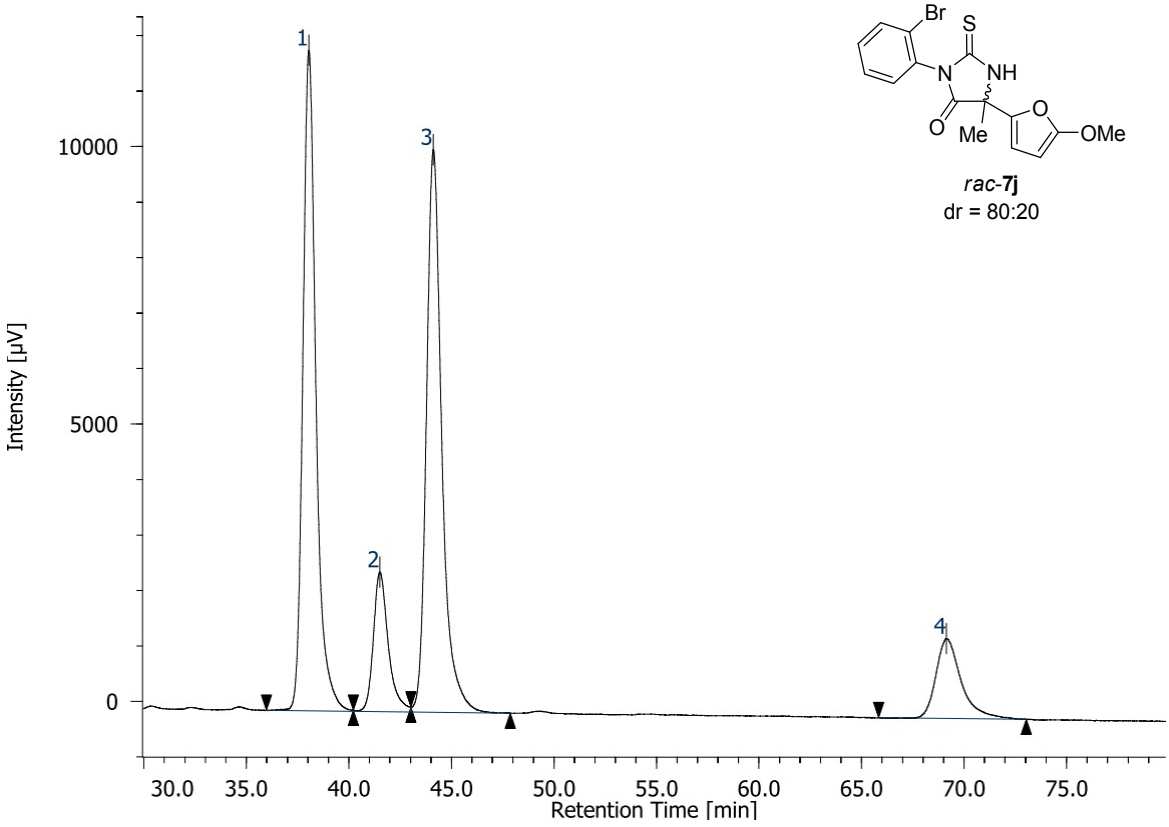


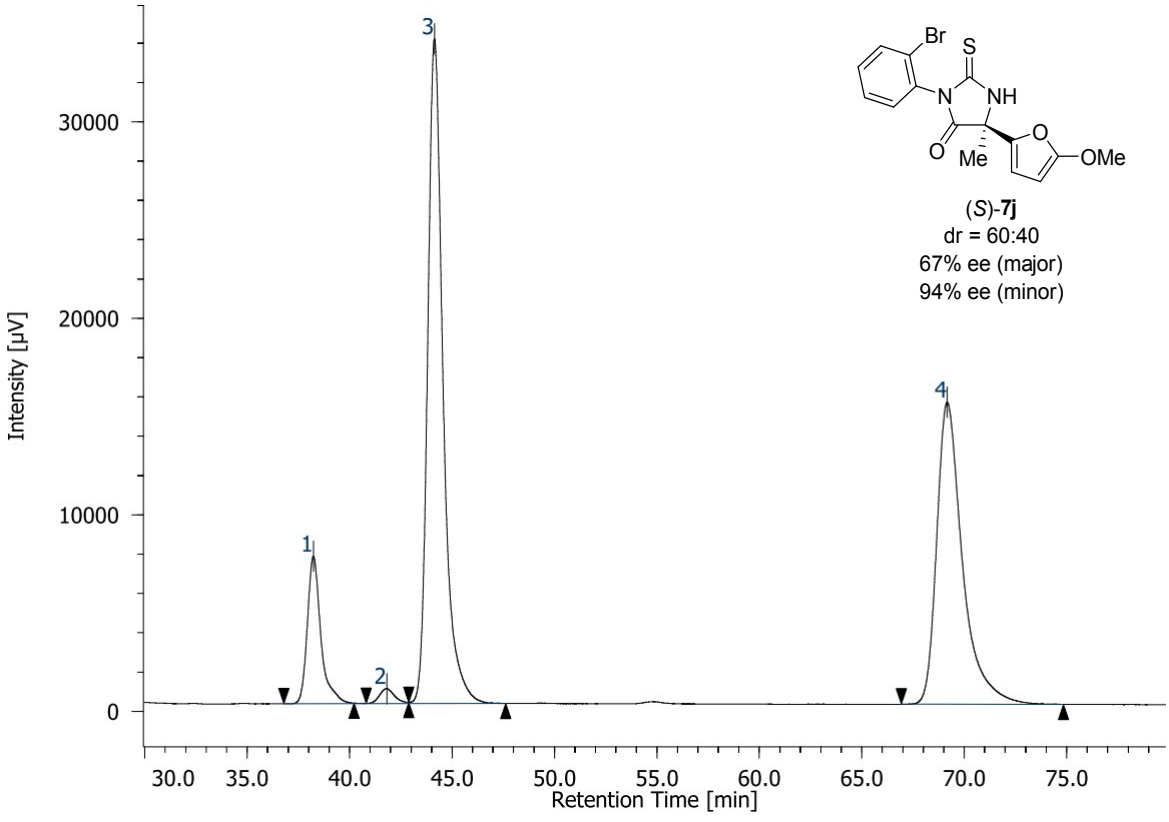
rac-**7i**



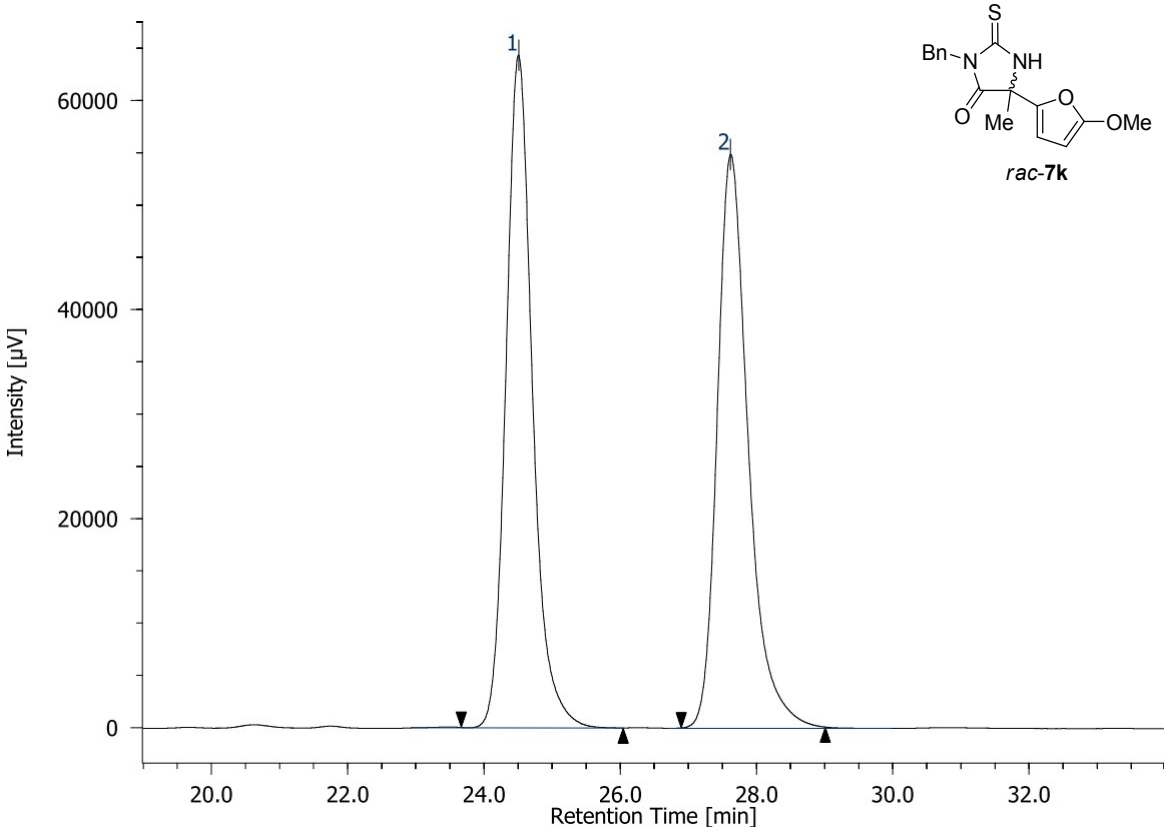
(*S*)-**7i**
89% ee

HPLC charts of **7j** (table 2, entry 10)

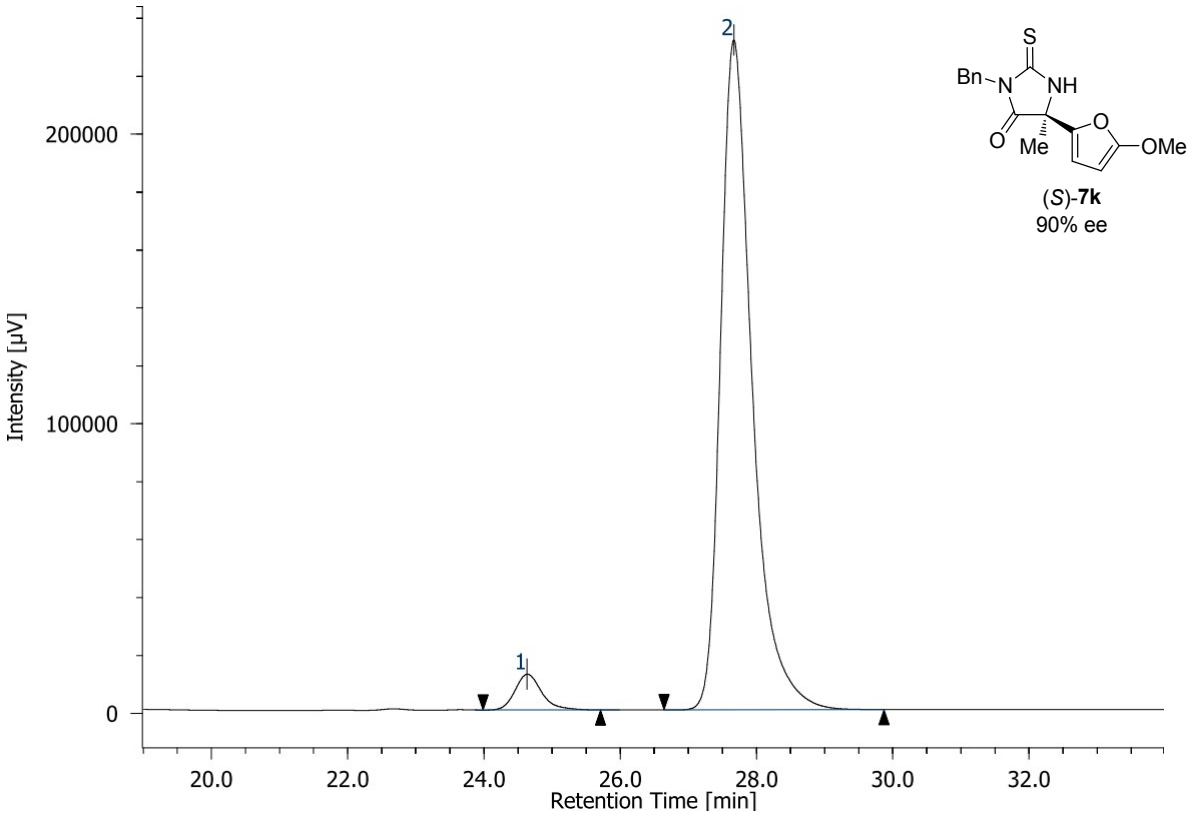




HPLC charts of **7k** (table 2, entry 11)

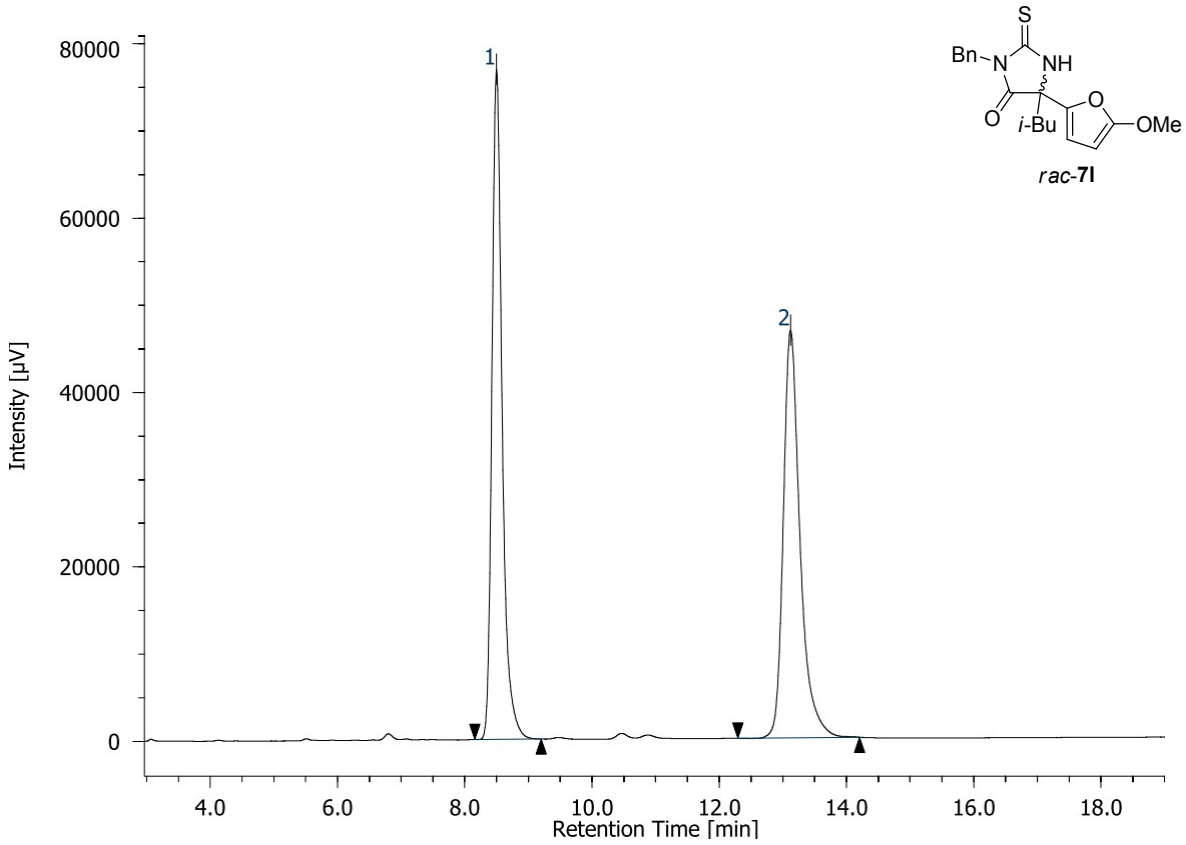


rac-**7k**

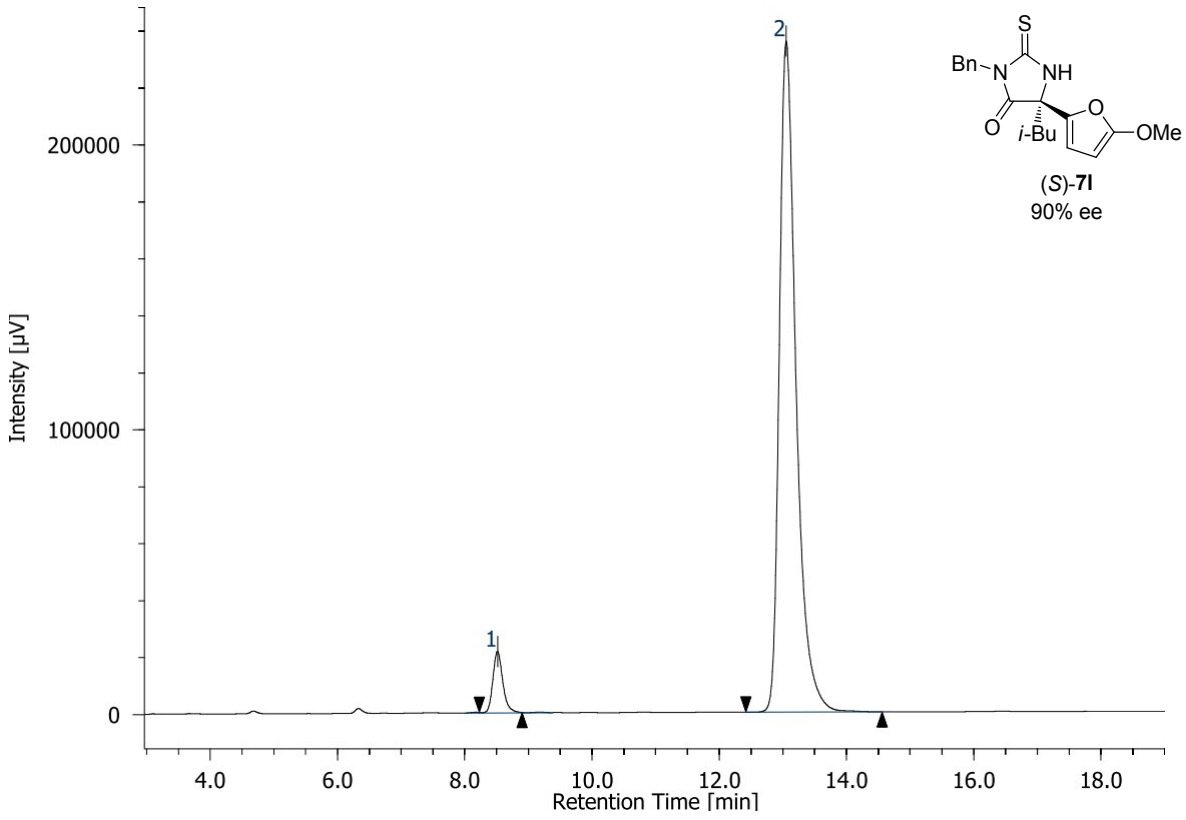


(*S*)-**7k**
90% ee

HPLC charts of **7l** (table 2, entry 12)

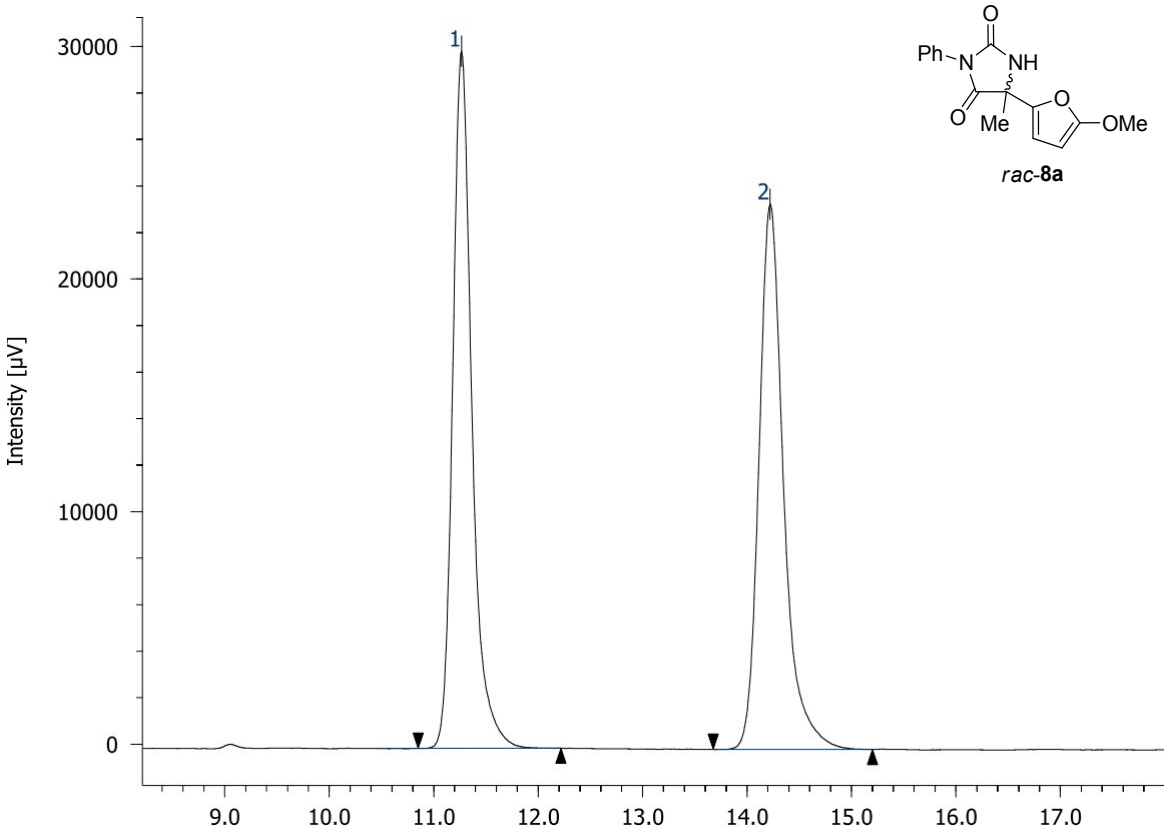


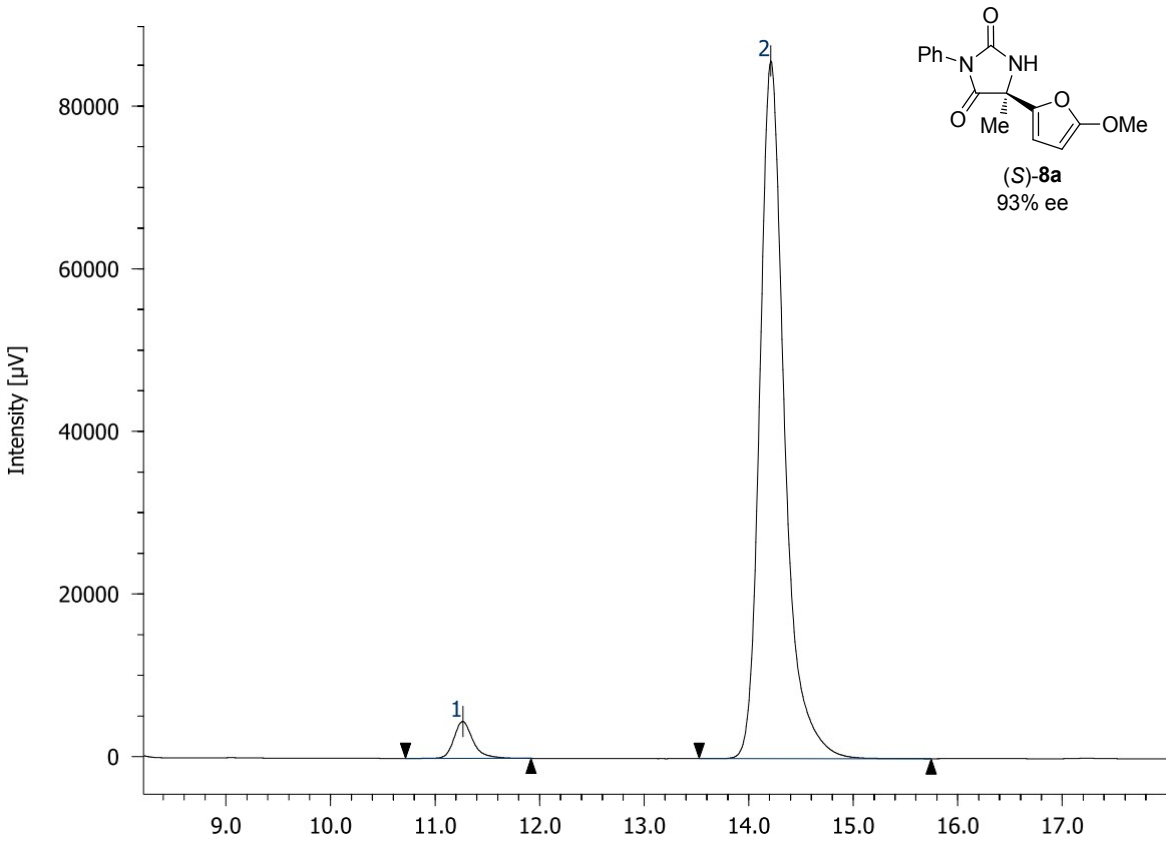
rac-**7l**



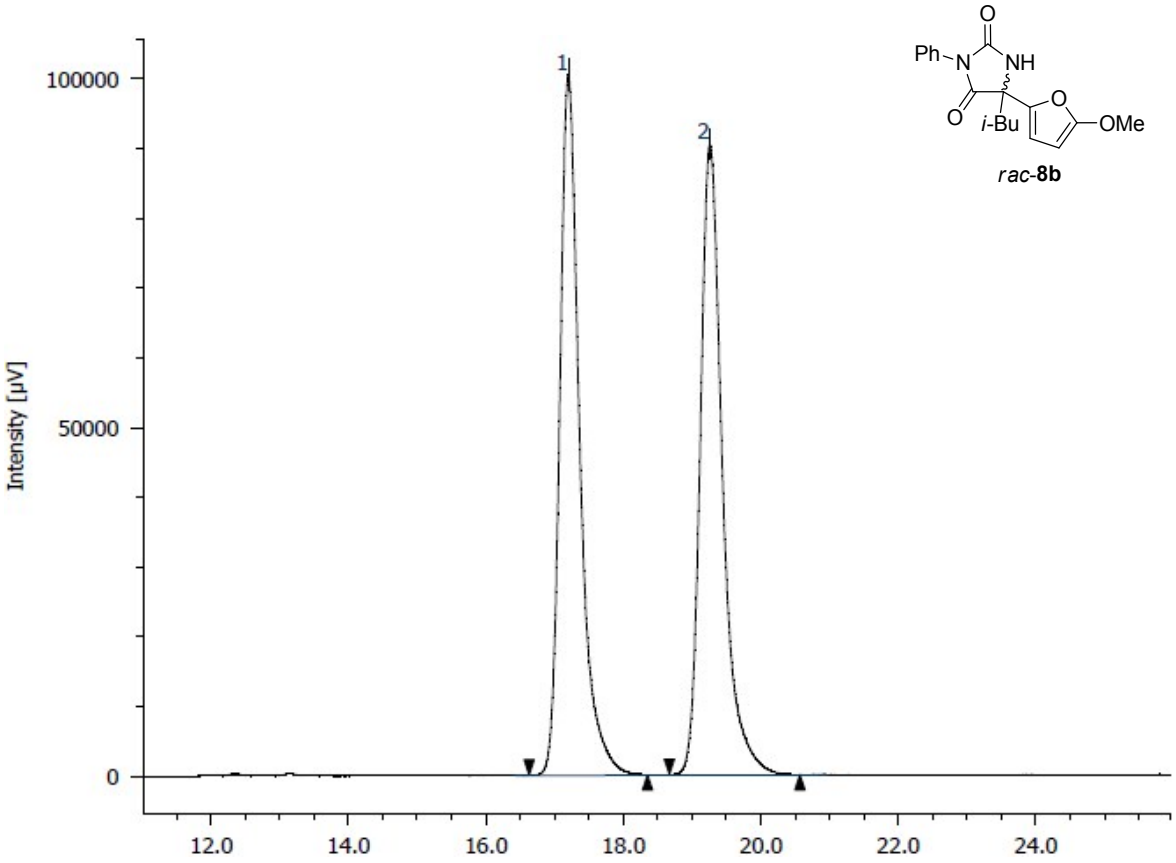
(*S*)-**7l**
90% ee

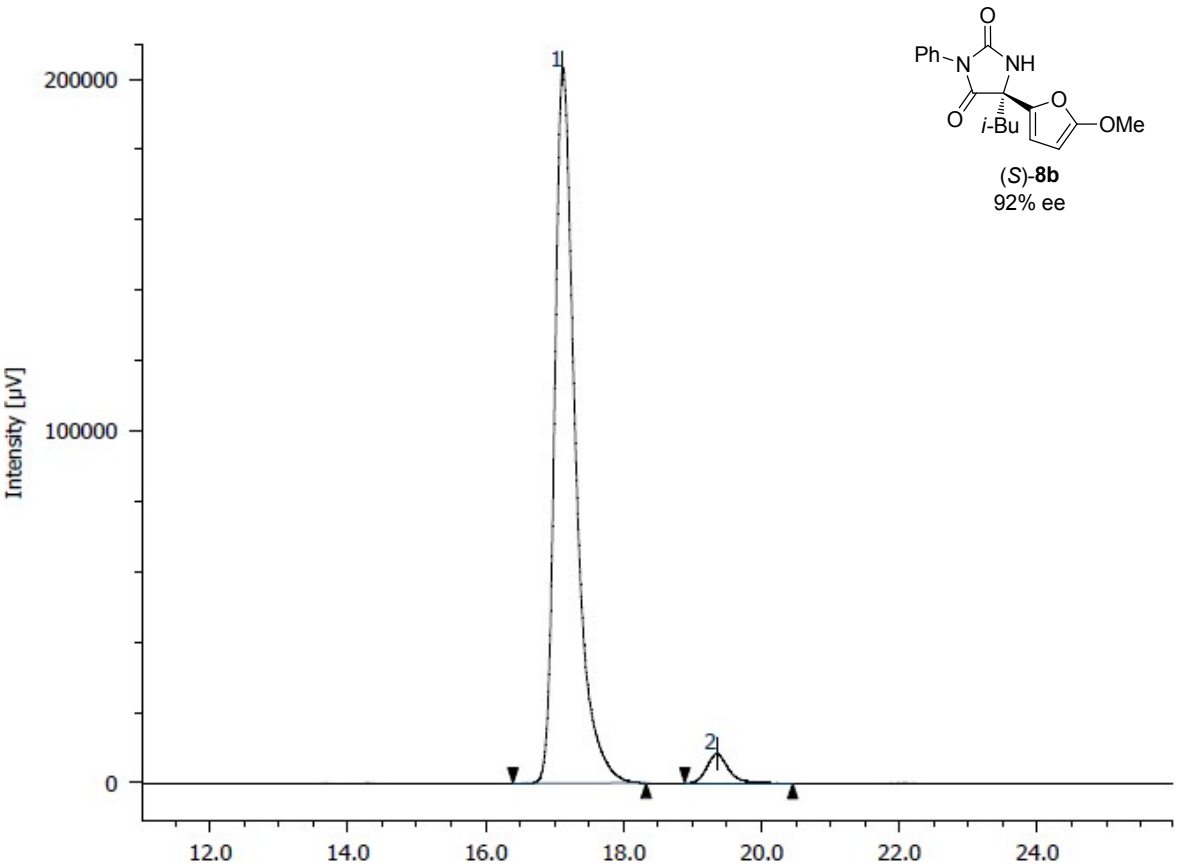
HPLC charts of **8a** (table 2, entry 13)



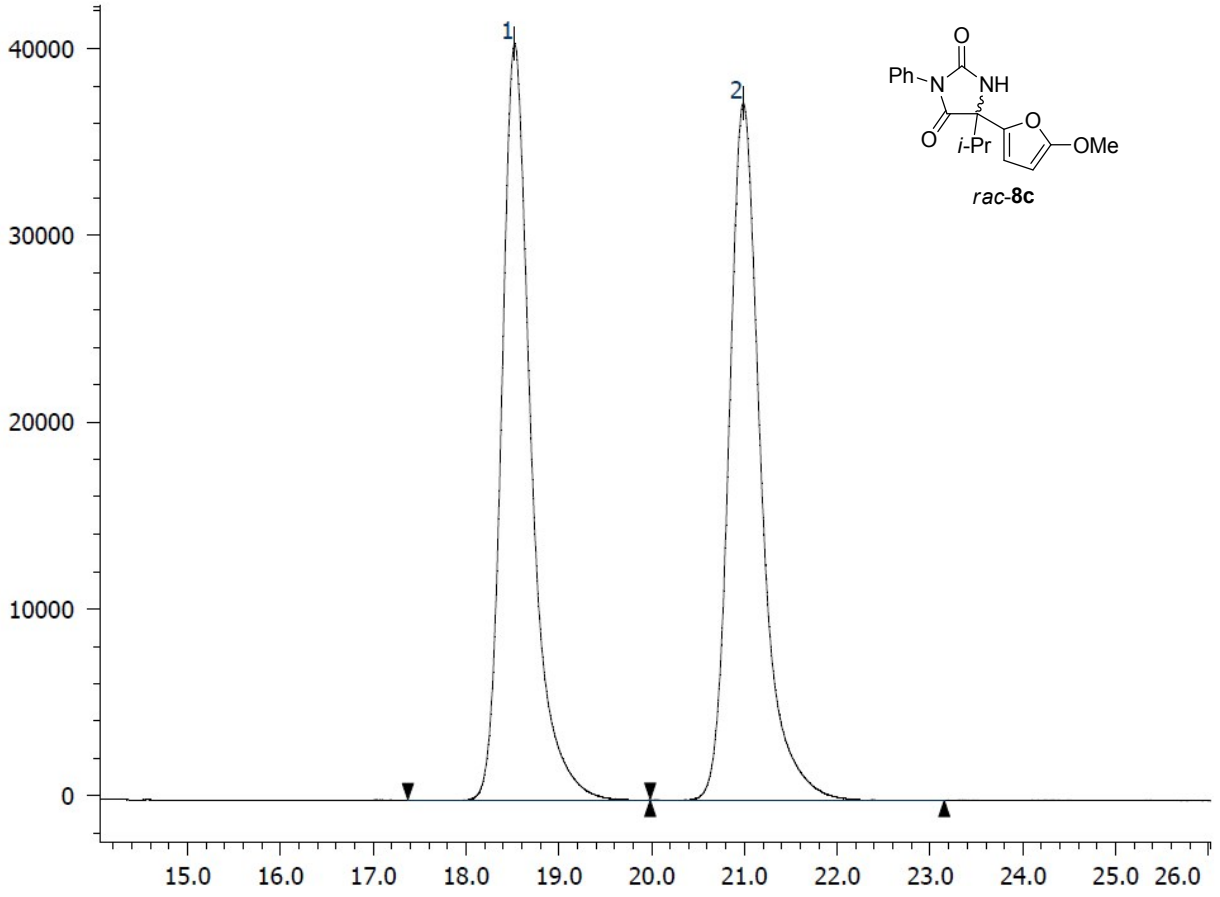


HPLC charts of **8b** (table 2, entry 14)

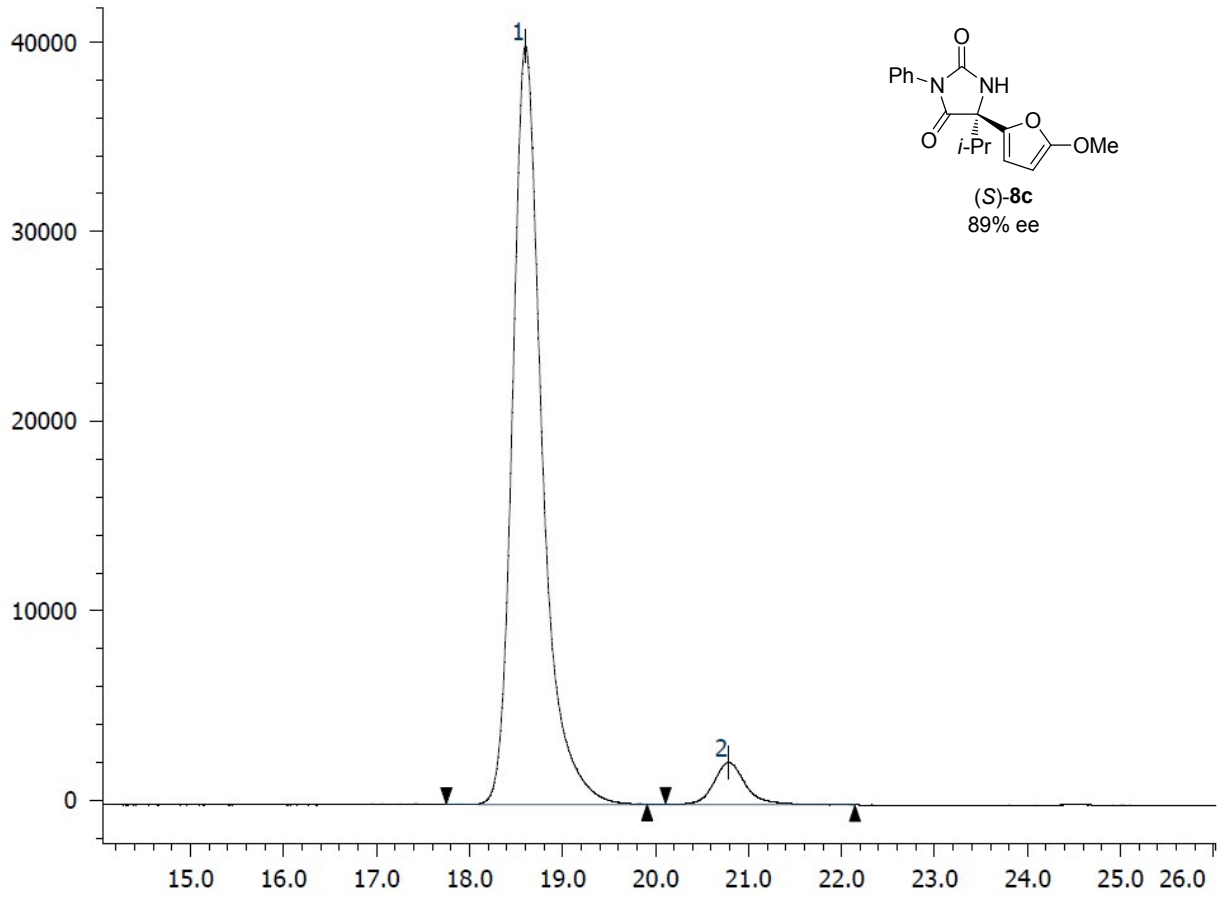




HPLC charts of **8c** (table 2, entry 15)

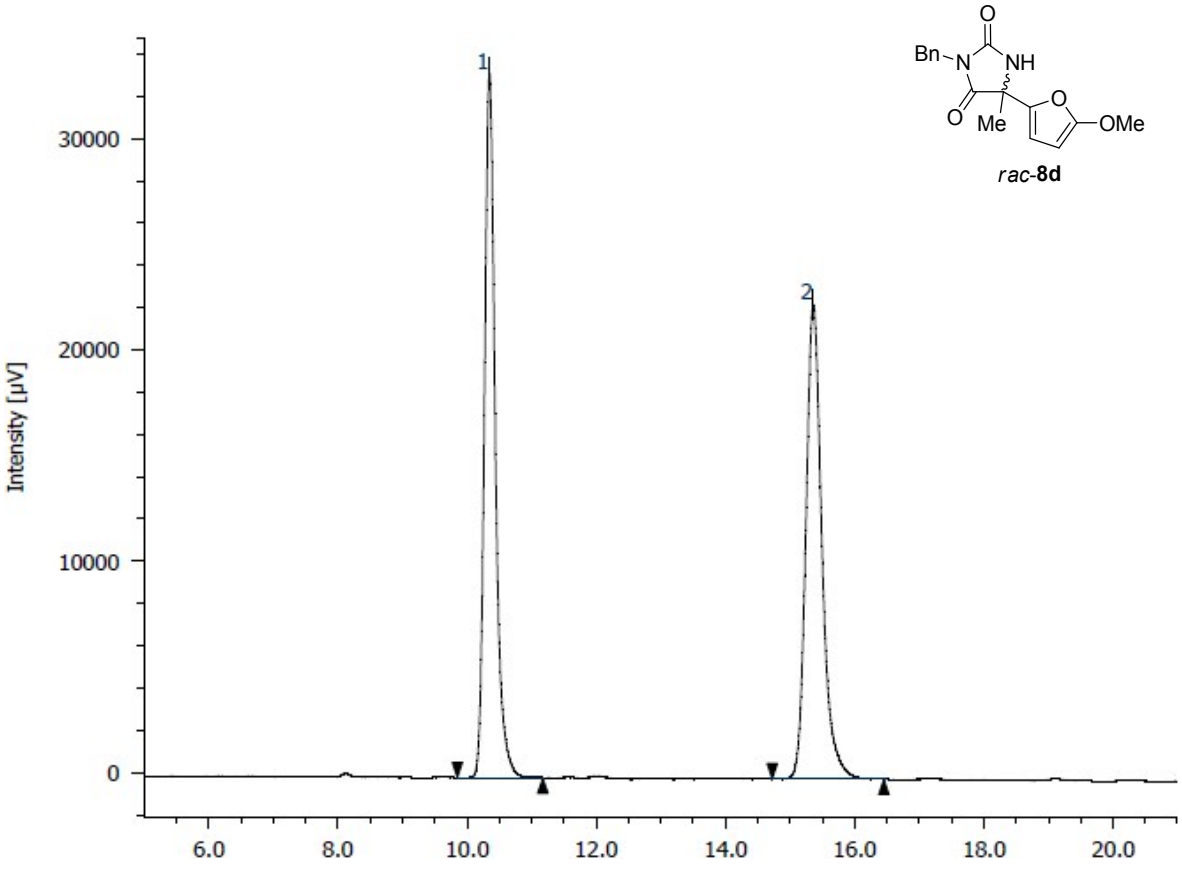


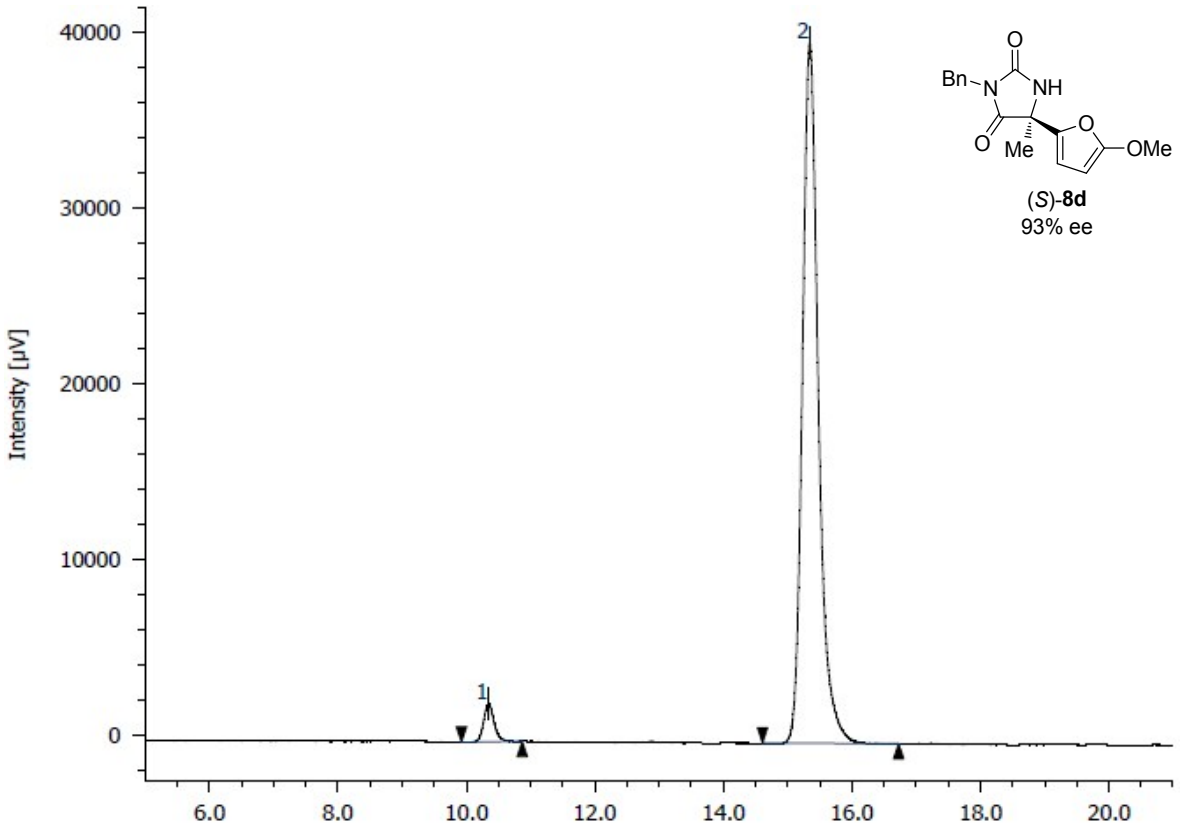
rac-**8c**



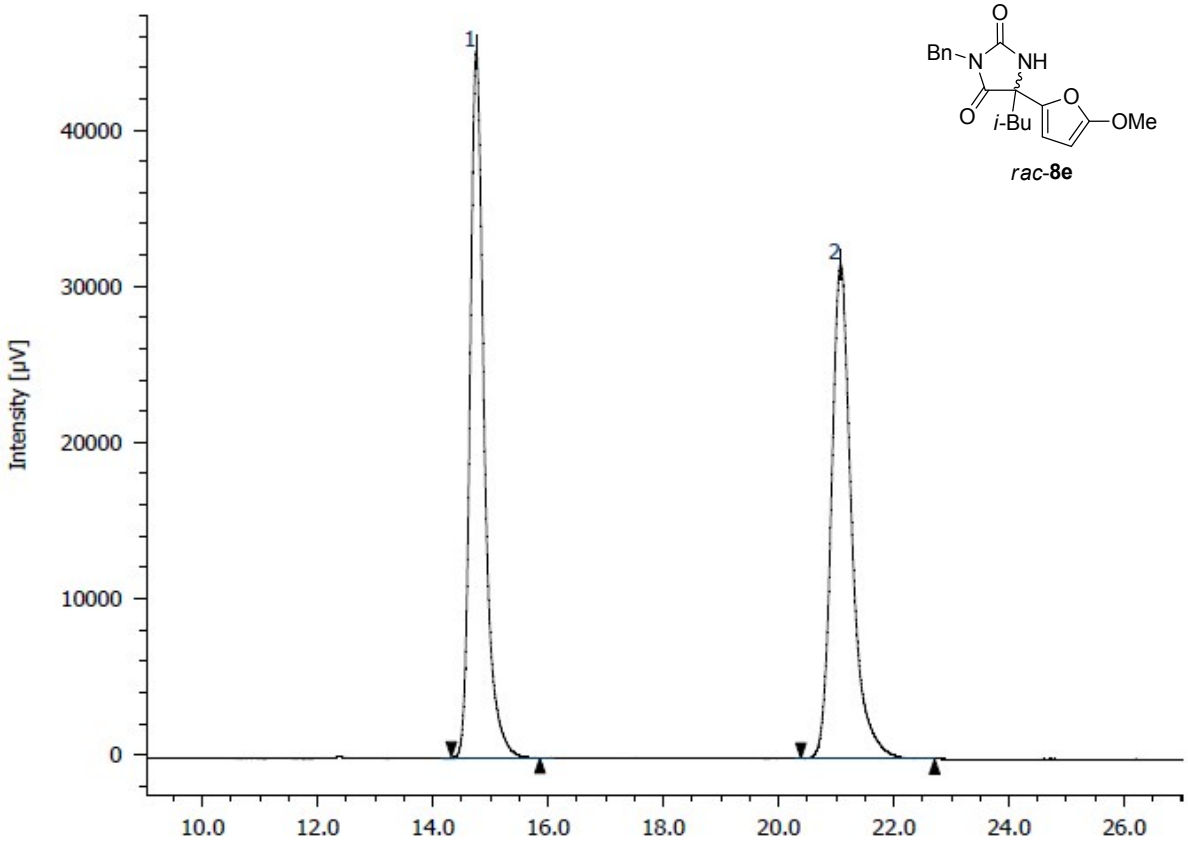
(*S*)-**8c**
89% ee

HPLC charts of **8d** (table 2, entry 16)

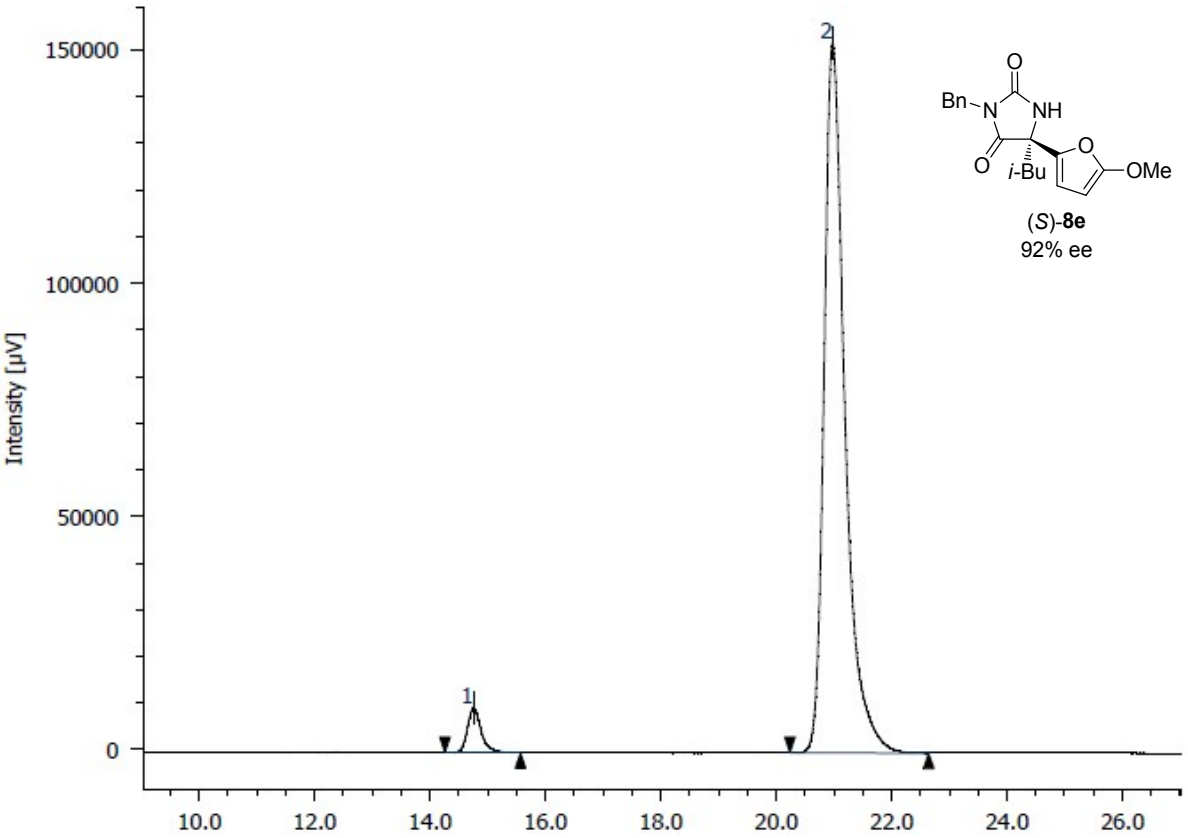




HPLC charts of **8e** (table 2, entry 17)

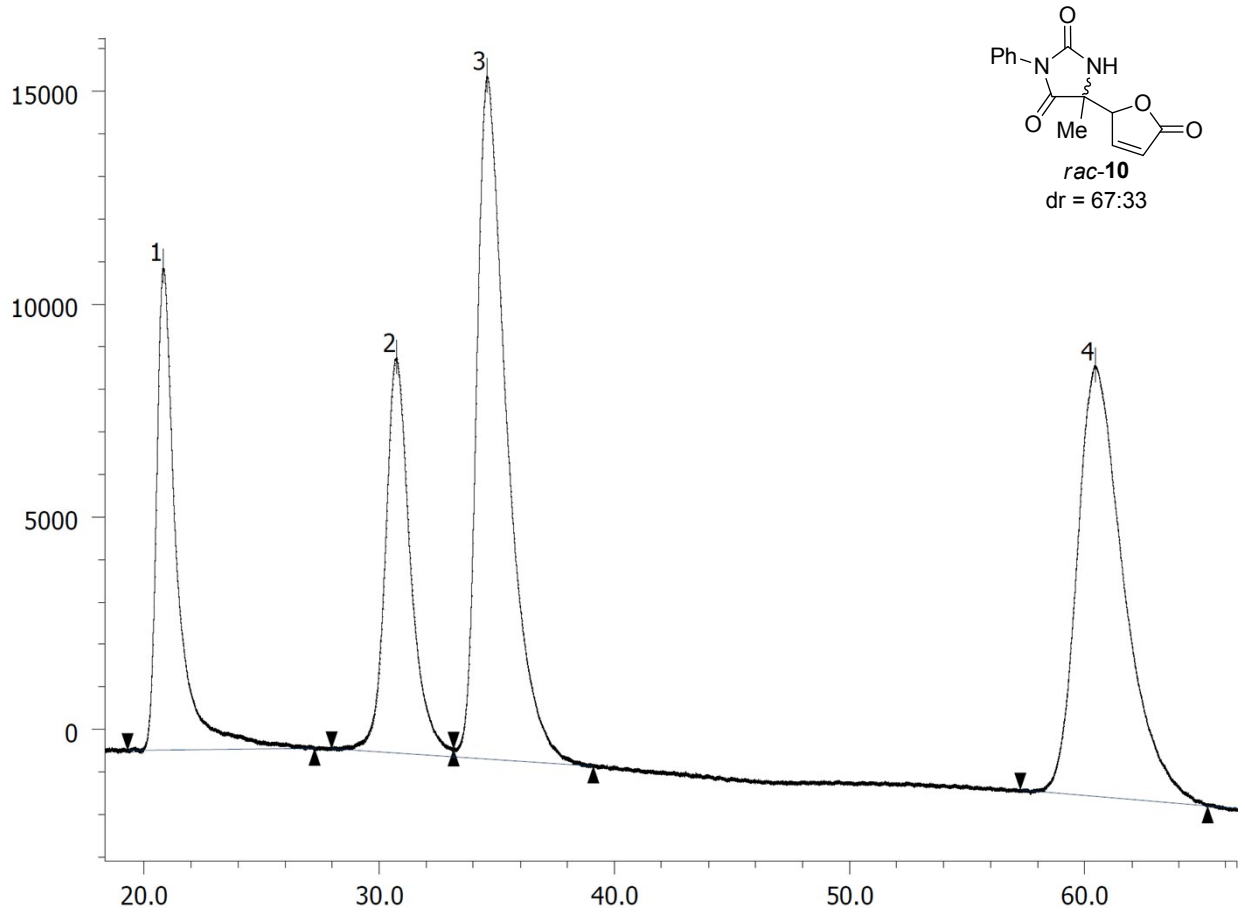


rac-**8e**

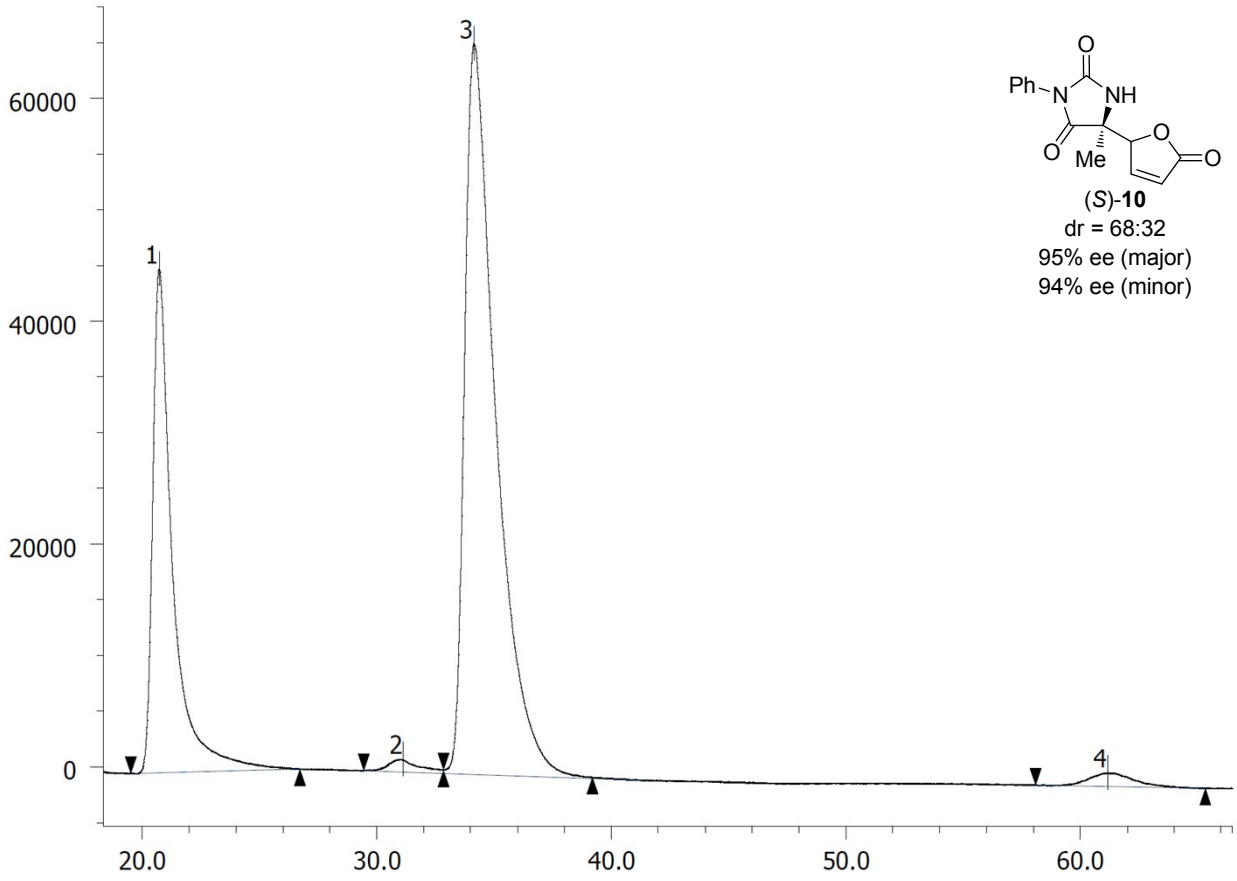


(*S*)-**8e**
92% ee

HPLC charts of **10** (Scheme 2)



rac-**10**
dr = 67:33



(*S*)-**10**
dr = 68:32
95% ee (major)
94% ee (minor)