Synthesis

Reviews and Full Papers in Chemical Synthesis

Supporting Information

for DOI: 10.1055/s-0034-1378719

Thieme

Iron Catalyzed Diastereoselective Intramolecular Olefin Aminobromination with Bromide Ion

Jun-Shan Tian,[‡] Cheng-Liang Zhu,[‡] Yun-Rong Chen, and Hao Xu
Department of Chemistry, Georgia State University, Atlanta GA 30303, United States

Supporting Material

A. General Information

General Procedures. All reactions were performed in flame-dried round-bottom flasks and vials. Stainless steel syringes and cannula were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed using silica gel 60 (230-400 mesh) from Sigma–Aldrich.

Materials. Tetraethylammonium bromide (TEAB) and tetra-*n*-octylammonium bromide (TOAB) were purchased from Sigma–Aldrich. They were further purified through recrystallization in the diethyl ether/acetone mixture and stored in a glove box under N_2 atmosphere. Other reagents were purchased from Sigma–Aldrich, Fluka, EM Science, and Lancaster and used directly as received. All solvents were used after being freshly distilled.

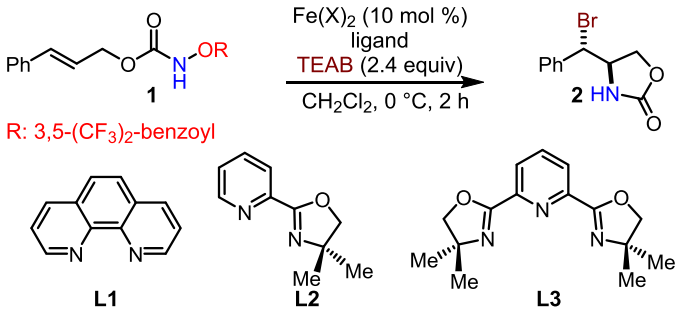
Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker UltraShield-400 (400 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to the NMR solvent residual peak ($CHCl_3$: δ 7.26). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$: δ 77.0). Data are represented as follows: chemical shift, multiplicity (br = broad signal, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets), coupling constants in Hertz (Hz), and integration. The mass spectroscopic data were obtained at the Georgia State University mass spectrometry facility using a Micromass Platform II single quadruple instrument. Infrared (IR) spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer. Data are represented as follows: frequency of absorption (cm^{-1}) and absorption strength (s = strong, m = medium, w = weak).

Abbreviations. CH_2Cl_2–dichloromethane, MS–molecular sieves, TLC–thin layer chromatography, TEAB−tetraethylammonium bromide, TOAB−tetra-*n*-octylammonium bromide.

B. Catalyst Discovery and Procedures for the Iron-Catalyzed Diastereoselective Olefin Aminobromination Reaction

a. Catalyst Discovery for the Iron-Catalyzed Diastereoselective Olefin Aminobromination

L1 was purchased from Sigma–Aldrich and used directly without further purification. **L2** and **L3** were synthesized according to literature procedures.[1,2]



entry[a]	$Fe(X)_2$	ligand (mol %)	conversion[b]	yield[c]	*dr*[b] (*anti*:*syn*)
1	$FeBr_2$	none	>95%	84%	0.86:1
2	$FeBr_2$	**L1** (20)	>95%	58%	18:1
3	$Fe(OTf)_2$	**L1** (20)	>95%	78%	18:1
4	$Fe(NTf_2)_2$	**L1** (20)	>95%	81%	>20:1
5	$Fe(NTf_2)_2$	**L2** (20)	>95%	78%	12:1
6	$Fe(NTf_2)_2$	**L3** (20)	>95%	75%	13:1

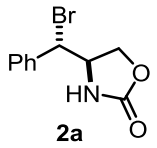
[a]Unless stated otherwise, the reactions were carried out under N_2 in the presence of 4 Å molecular sieves. [b]Conversion and *dr* were determined by ^1H NMR analysis. [c]Isolated yield. TEAB: tetraethylammonium bromide.

Table S1. Catalyst discovery for the iron-catalyzed diastereoselective olefin aminobromination

Procedure for the Catalyst Discovery

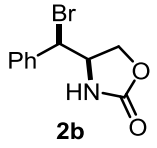
To a flame-dried sealable 2-dram vial (vial **A**) equipped with a magnetic stir bar were added an iron catalyst (0.02 mmol) and a ligand (0.04 mmol). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.0 mL) was added and the mixture was stirred at room temperature for 20 min. During this time, substrate **1** (0.2 mmol, 86 mg) and anhydrous TEAB (51 mg, 0.24 mmol) were dissolved in CH_2Cl_2 (4.0 mL) in a second flame-dried 3-dram vial (vial **B**) with a magnetic stir bar under N_2 atmosphere. Both vials were degassed by brief

evacuation and back filling with N_2 twice. The vial **B** was cooled down to 0 °C, and the solution in vial **A** was added to vial **B** drop wise via a syringe. The resulting solution was stirred at the same temperature until **1** was fully consumed monitored by TLC. The reaction was quenched with 1 mL saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 (1.5 mL × 3). The combined organic phase was concentrated and the residue was purified through a gradient silica gel flash column chromatography (hexanes/acetone: from 15:1 to 4:1) to afford the aminobromination product **2** as a white solid. The *dr* was determined by ^{1}H NMR analysis.



2a

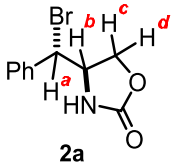
4-(Bromo(phenyl)methyl)oxazolidin-2-one (2a). By following the general procedure under the condition described in entry 4, **2a** was obtained as a white solid (41 mg, 81% yield, *dr* >20:1, m.p. 113–115 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.32 (m, 5H), 5.22 (s, 1H), 4.76 (d, J = 9.4 Hz, 1H), 4.69–4.58 (m, 1H), 4.52–4.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 137.0, 129.7, 129.4, 128.0, 69.5, 58.0, 54.5; IR ν_{max} (neat)/cm^{-1}: 3232 (m), 3133 (w), 2957 (w), 2853 (w), 1730 (s), 1236 (s), 1094 (s), 1022 (s), 650 (s); HRMS (ESI, m/z): calcd for $C_{10}H_{10}NO_2NaBr^+$ (M + Na^+), 277.9793, found 277.9801.



2b

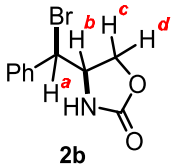
4-(Bromo(phenyl)methyl)oxazolidin-2-one (2b). By following the general procedure under the condition described in entry 1, **2a** and **2b** were obtained as a mixture (38 mg, 84% yield, *dr*: 1.18:1, m.p. 111–118 °C). **2b** is characterized as following: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.31 (m, 5H), 5.68 (s, 1H), 4.87 (d, J = 9.6 Hz, 1H), 4.50–4.43 (m, 1H), 4.23 (t, J = 9.4 Hz, 1H), 3.92 (dd, J = 9.5, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 136.4, 129.7, 129.4, 127.9, 67.3, 58.7, 56.7; HRMS (ESI, m/z): calcd for $C_{10}H_{10}NO_2NaBr^+$ (M + Na^+), 277.9793, found 277.9799.

Relative Stereochemistry Determination. The relative stereochemistry of **2** was determined by comparison of the NMR spectra of **2a** and **2b** with literature precedents, in which **2a** and **2b** were both characterized.[3]



2a

compound	**2a**	**2-*anti*** (literature data)
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.32 (m, 5H), 5.22 (s, 1H), 4.76 (d, *J* = 9.4 Hz, 1H, H^a), 4.69–4.58 (m, 1H, H^c), 4.52–4.36 (m, 2H, H^b and H^d);	^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.34 (m, 5H), 4.96 (brs, 1H), 4.76 (m, 1H), 4.66 (ddd, 1H, J = 11.0, 7.3, 2.7 Hz), 4.51–4.41 (m, 2H).
^{13}C NMR	^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 137.0, 129.7, 129.4, 128.0, 69.5, 58.0, 54.5.	^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 137.0, 129.7, 129.4, 128.0, 69.5, 58.0, 54.4.

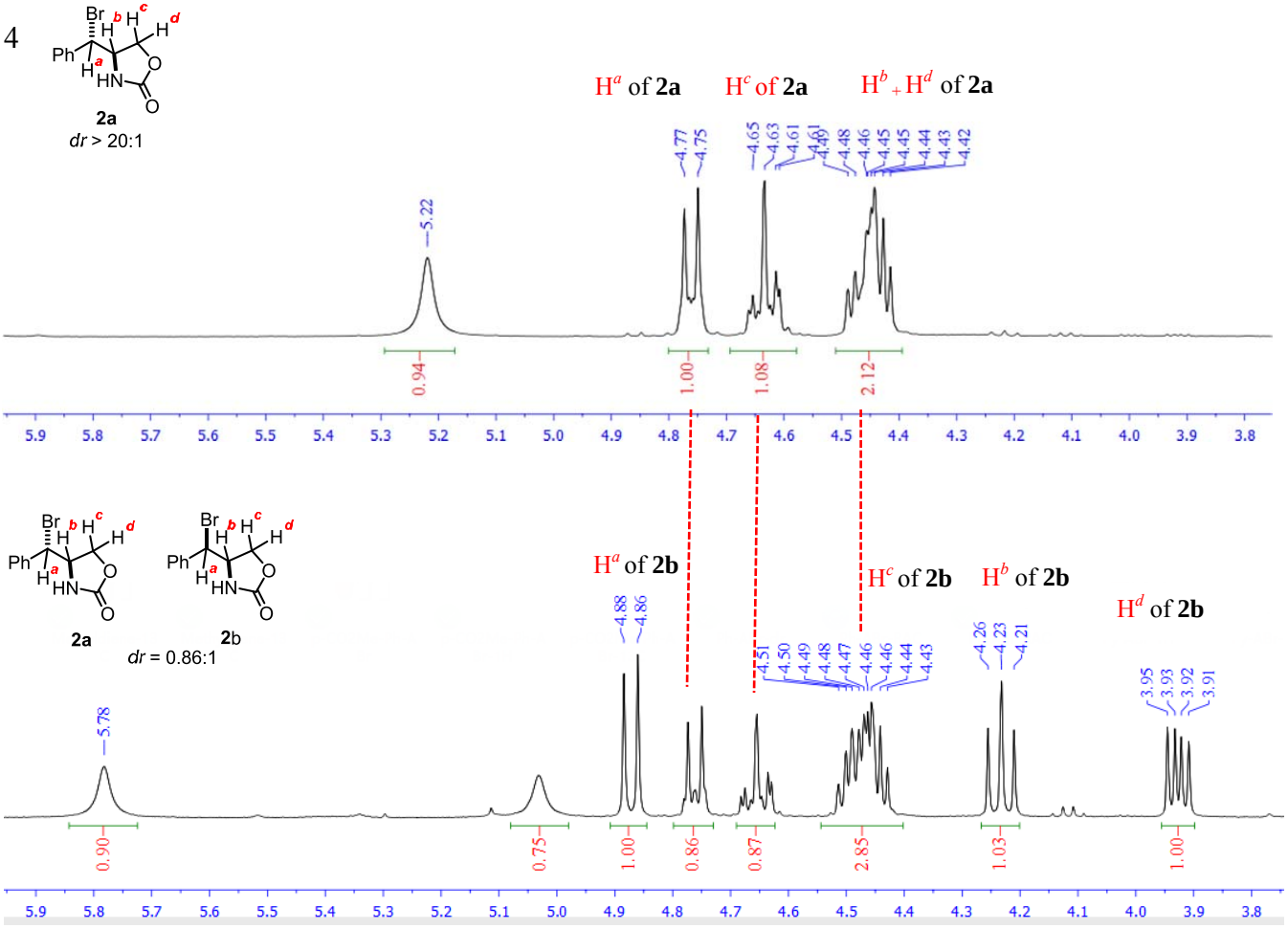


2b

compound	**2b**	**2-*syn*** (literature data)
^{1}H NMR	^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.31 (m, 5H), 5.68 (s, 1H), 4.87 (d, *J* = 9.6 Hz, 1H, H^a), 4.50–4.43 (m, 1H, H^b), 4.23 (t, *J* = 9.4 Hz, 1H, H^c), 3.92 (dd, *J* = 9.5, 5.2 Hz, 1H, H^d).	^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.30 (m, 5H), 6.01 (brs, 1H), 4.88 (d, 1H, *J* = 9.8 Hz), 4.49 (m, 1H), 4.24 (t, 1H, *J* = 9.2 Hz), 3.94 (dd, 1H, *J* = 9.8, 5.5 Hz).
^{13}C NMR	^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 136.4, 129.7, 129.4, 127.9, 67.3, 58.7, 56.7.	^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 136.4, 129.7, 129.3, 127.9, 67.3, 58.7, 56.7.

Summary: the diagnostic ^{1}H NMR signal to differentiate **2a** (*anti*-addition product) and **2b** (*syn*-addition product) are the δ H^d in both compounds: δ H^d in **2a** is 4.52–4.36 ppm and δ H^d in **2b** is 3.92 ppm. The chemical shift difference between two diastereomeric compounds is consistent with a broad range of products.

4

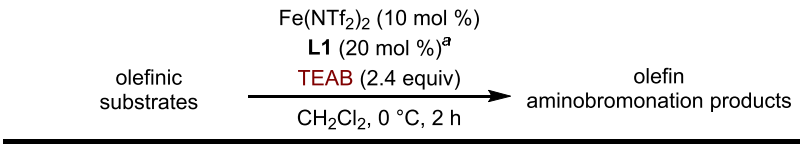


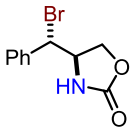
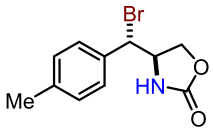
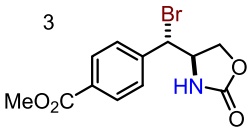
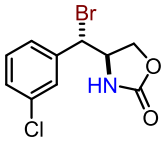
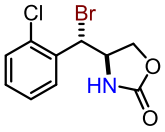
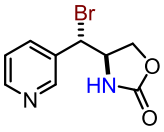
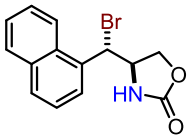
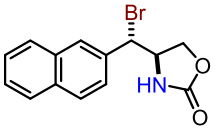
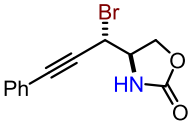
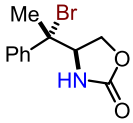
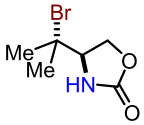
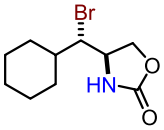
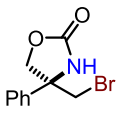
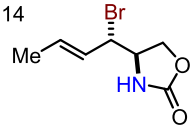
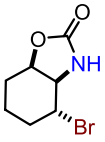
b. Synthesis of Substrates

The substrates were synthesized by following known procedures.[4]

c. General Procedure for the Iron-Catalyzed Diastereoselective Olefin Aminobromination and Product Characterization

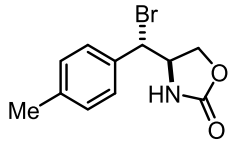
Table S1. Substrate scope for the iron-catalyzed diastereoselective olefin aminobromination reaction



1 	2 	3 	
81% yield, *dr* >20:1 from *E* olefin 74% yield, *dr*: 5.8:1 from *Z* olefin[b]	86% yield, *dr* >20:1[b, c]	90% yield, *dr* >20:1[c]	
4 	5 	6 	
86% yield, >20:1	87% yield, *dr*> 20:1[b]	65% yield, *dr* >20:1[c]	
7 	8 	9 	
66% yield, *dr* >20:1	73%, *dr* >20:1	85% yield, *dr*: 5.1:1 from *E* olefin[b] 82% yield, *dr*: 7.1:1 from *Z* olefin[b]	
10 	11 	12 	
45% yield, *dr* >20:1[b]	64% yield[c,d]	58% yield, *dr* 4:1[e]	
13 	14 	15 	
63% yield[e]	73% yield, *dr*: 1.2:1[b]	61% yield, *dr* >20:1	

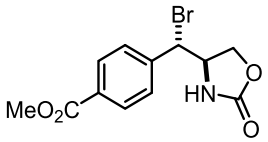
[a]Unless stated otherwise, the reactions were carried out under N_2 in the presence of 4 Å molecular sieves. [b]**L2** (20 mol %) was used as the ligand. [c]Reaction condition: -15 °C, 6 h. [d]TOAB was used as the bromide source. [e]Reaction condition: $Fe(NTf_2)_2 \cdot (\mathbf{L2})_2$ (15 mol %). TOAB: tetra-*n*-octylammonium bromide.

General procedure. To a flame-dried sealable 2-dram vial (vial **A**) equipped with a magnetic stir bar were added $Fe(NTf_2)_2$ (12.3 mg, 0.02 mmol, 10 mol %) and 1,10-phenanthroline (7.2 mg, 0.04 mmol, 20 mol %). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.0 mL) was added and the mixture was stirred at room temperature for 20 min. During this time, the substrate (0.2 mmol) and anhydrous TEAB (51 mg, 0.24 mmol) were dissolved in CH_2Cl_2 (4.0 mL) in a second flame-dried 3-dram vial (vial **B**) with a magnetic stir bar and freshly activated 4 Å molecular sieves under N_2 atmosphere. Both vials were degassed by brief evacuation and back filling with N_2 twice. The vial **B** was cooled down to 0 °C, and the solution in vial **A** was added to vial **B** drop wise via a syringe. The resulting solution was stirred at the same temperature until all the starting material was fully consumed monitored by TLC. The reaction was quenched by 1 mL saturated $NaHCO_3$ solution. After being extracted with CH_2Cl_2 (1.5 mL × 3), the combined organic phase was concentrated and the residue was purified through a gradient silica gel flash column chromatography (hexanes/acetone: from 15:1 to 4:1) to afford the aminobromination product. The *dr* was determined by ^{1}H NMR analysis of the crude reaction mixture.



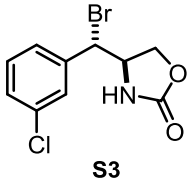
S1

4-(Bromo(*p*-tolyl)methyl)oxazolidin-2-one (**S1**) : by following the general procedure and carrying out reaction at -15 °C with ligand **L2**, **S1** was obtained as a white solid (46 mg, 86% yield, *dr* >20:1, m.p. 121–123 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.17 (m, 4H), 5.09 (s, 1H), 4.77 (d, J = 9.1 Hz, 1H), 4.72–4.61 (m, 1H), 4.55–4.39 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 139.8, 134.0, 130.0, 127.9, 69.5, 57.9, 54.7, 21.2; IR ν_{max} (neat)/cm^{-1}: 3239 (m), 3099 (w), 2921 (w), 1748 (s), 1239 (m), 1028 (m), 650 (s); HRMS (ESI, m/z): calcd for $C_{11}H_{13}NO_2Br^+$ ($M + H^+$), 270.0130, found 270.0127.



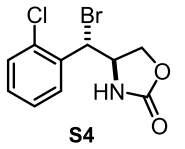
S2

Methyl 4-(bromo(2-oxooxazolidin-4-yl)methyl)benzoate (**S2**): by following the general procedure and carrying out reaction at -15 °C, **S2** were obtained as a white solid (56mg, 90% yield, *dr* >20:1, m.p. 101–103 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 7.9 Hz, 2H), 7.48 (d, J = 7.9 Hz, 2H), 5.25 (s, 1H), 4.79 (d, J = 9.2 Hz, 1H), 4.71–4.63 (m, 1H), 4.51–4.41 (m, 2H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 158.0, 141.7, 131.3, 130.6, 128.2, 69.4, 57.8, 53.4, 52.4; IR ν_{max} (neat)/cm^{-1}: 3323 (m), 2946 (w), 2834 (w), 1656 (m), 1449 (m), 1019 (s). HRMS (ESI, m/z): calcd for $C_{12}H_{13}NO_4Br^+$ (M + H$^+$), 314.0028, found 314.0027.



S3

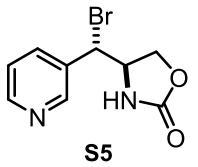
4-(Bromo(3-chlorophenyl)methyl)oxazolidin-2-one (**S3**) : by following the general procedure, **S3** was obtained as a white solid (50 mg, 86% yield, *dr* >20:1, m.p. 107–109 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.27 (m, 4H), 5.64 (s, 1H), 4.71 (d, J = 8.8 Hz, 1H), 4.67–4.57 (m, 1H), 4.46–4.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 139.0, 135.2, 130.6, 129.82, 128.3, 126.3, 69.4, 57.9, 53.5. IR ν_{max} (neat)/cm^{-1}: 3240 (w), 2985 (w), 2863 (w), 1737 (s), 1235(s), 1044 (s), 732 (s). HRMS (ESI, m/z): calcd for $C_{10}H_{10}NO_2ClBr^+$ (M + H$^+$), 289.9583, found 289.9584.



S4

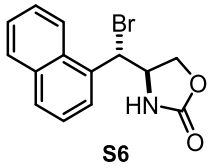
4-(Bromo(2-chlorophenyl)methyl)oxazolidin-2-one (**S4**) : by following the general procedure and carrying out reaction with ligand **L2**, **S4** was obtained as a white solid (51 mg, 87% yield,

dr >20:1, m.p. 123–125 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.43 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.39–7.29 (m, 2H), 5.40 (s, 1H), 5.39 (d, *J* = 8.8 Hz, 1H), 4.66–4.54 (m, 2H), 4.45 (dd, *J* = 8.8, 4.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 134.5, 133.9, 130.6, 130.4, 129.1, 128.0, 69.1, 57.0, 49.5. IR ν_{max} (neat)/cm^{-1}: 3260 (m), 3102 (w), 2923(w), 1752 (s), 1475 (m), 1233 (m), 1030 (m), 734(m), 509 (s). HRMS (ESI, m/z): calcd for $C_{10}H_{10}NO_2ClBr^+$ ($M + H^+$), 289.9583, found 289.9580.



S5

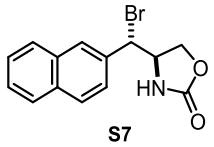
4-(Bromo(pyridin-3-yl)methyl)oxazolidin-2-one (**S5**) : by following the general procedure, **S5** was obtained as a white solid (33 mg, 65% yield, *dr* >20:1, m.p. >200 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.56 (d, *J* = 4.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 7.9, 4.8 Hz, 1H), 5.60 (s, 1H), 4.78 (d, *J* = 9.0 Hz, 1H), 4.66 (t, *J* = 8.2 Hz, 1H), 4.50–4.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 150.1, 148.8, 136.1, 133.5, 124.1, 69.2, 58.0, 51.4; IR ν_{max} (neat)/cm^{-1}: 3300 (m), 2985 (w), 1737 (s), 1372 (m), 1234 (s), 1044 (s), 504 (s); HRMS (ESI, m/z): calcd for $C_9H_{10}N_2O_2Br^+$ ($M + H^+$), 256.9926, found 256.9935.



S6

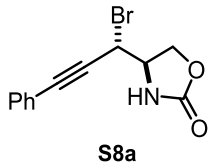
4-(Bromo(naphthalen-1-yl)methyl)oxazolidin-2-one (S6) : by following the general procedure, **S6** was obtained as a white solid (40 mg, 66% yield, *dr* >20:1, m.p. 119–121 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.92 (t, *J* = 7.7 Hz, 2H), 7.66–7.62 (m, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 5.63 (s, 1H), 5.09 (s, 1H), 4.90–4.80 (m, 1H), 4.76 (t, *J* = 9.2 Hz, 1H), 4.61 (dd, *J* = 9.3, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 134.1, 130.7, 130.5, 129.3, 127.3, 126.6, 125.4, 122.5, 77.2, 69.9, 56.7; IR ν_{max} (neat)/cm^{-1}: 3242 (m), 2913 (w), 1766(s), 1702

(s), 1480 (m), 1410 (m), 1212(s), 1028(s), 763 (s); HRMS (ESI, *m/z*): calcd for $C_{14}H_{13}O_2NBr^+$ ($M + H^+$), 306.0105, found 306.0110.



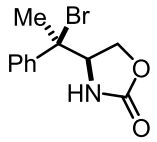
S7

4-(Bromo(naphthalen-2-yl)methyl)oxazolidin-2-one (**S7**): by following the general procedure, **S7** was obtained as a white solid (45 mg, 73% yield, *dr* >20:1, m.p. 116–118 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.6 Hz, 1H), 7.88–7.79 (m, 3H), 7.59–7.52 (m, 2H), 7.50 (d, *J* = 8.5 Hz, 1H), 5.02 (s, 1H), 4.92 (d, *J* = 9.6 Hz, 1H), 4.66 (t, *J* = 8.4 Hz, 1H), 4.60–4.51 (m, 1H), 4.48 (dd, *J* = 8.7, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 134.1, 133.6, 132.9, 129.7, 128.1, 127.8, 127.8, 127.4, 127.2, 124.5, 69.6, 57.8, 55.1; IR ν_{max} (neat)/cm^{-1}: 3250 (m), 3134(w), 2920 (w), 1756 (s), 1712(s), 1434 (m), 1409 (m), 1248(s), 1019(s), 766 (s); HRMS (ESI, *m/z*): calcd for $C_{14}H_{13}O_2NBr^+$ ($M + H^+$), 306.0105, found 306.0110.



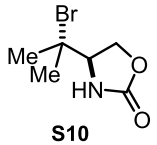
S8a

4-(1-Bromo-3-phenylprop-2-yn-1-yl)oxazolidin-2-one (**S8a**): by following the general procedure and carrying out reaction at -15 °C, **S8a** and its *syn*-diastereomer (**S8b**): were obtained as a white solid (47 mg, 85% yield, *dr*: 7.1:1). **S8a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.44 (m, 2H), 7.37–7.32 (m, 3H), 6.71 (s, 1H), 4.73 (d, *J*=5.7 Hz, 1H), 4.59–4.51 (m, 2H), 4.29–4.19 (m, 1H); ^{13}C NMR (100 MHz, CDCl3): δ 159.1, 132.0, 129.4, 128.4, 121.0, 89.3, 82.5, 67.6, 57.4, 39.0. **S8b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.44 (m, 2H), 7.37–7.32 (m, 3H), 6.61 (s, 1H), 4.70 (d, *J* = 6.2 Hz, 1H), 4.59–4.51 (m, 2H), 4.40 (dd, *J* = 9.5, 4.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 132.1, 129.6, 128.5, 120.8, 88.9, 81.8, 67.1, 57.6, 39.2; IR ν_{max} (neat)/cm^{-1}: 3269 (m), 2987 (w), 2224 (m), 1754 (s), 1228 (w), 1037 (m), 933 (m), 758 (m). HRMS (ESI, m/z): calcd for $C_{12}H_{11}NO_2Br^+$ ($M+H^+$), 279.9973, found 279.9976.



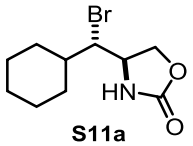
S9

4-(1-Bromo-1-phenylethyl)oxazolidin-2-one (**S9**) : by following the general procedure, **S9** was obtained as a white solid (24 mg, 45% yield, *dr* >20:1, m.p. 121–123 °C). Its relative chemistry was determined by comparison of the ^{1}H NMR data with the literature data.{Zhu, 2015 #11;Lu, 2014 #89} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.3 Hz, 2H), 7.43–7.32 (m, 3H), 5.57 (s, 1H), 4.56–4.50 (m, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 140.9, 128.9, 127.1, 67.6, 67.4, 62.3, 24.9; IR ν_{max} (neat)/cm^{-1}: 3270 (m), 3101 (w), 2995 (w), 1751 (s), 1407 (w), 1239 (m), 1052 (m); HRMS (ESI, m/z): calcd for $C_{11}H_{13}NO_2Br^+$ (M + H$^+$), 270.0130, found 270.0138.



S10

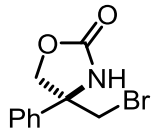
4-(2-Bromopropan-2-yl)oxazolidin-2-one (**S10**) : by following the general procedure and carrying out reaction at -15 °C with TOAB as bromide source, **S10** was obtained as a white solid (27 mg, 64% yield, m.p. 65–68 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (s, 1H), 4.48 (t, J = 9.2 Hz, 1H), 4.37 (dd, J = 9.5, 4.7 Hz, 1H), 4.01 (dd, J = 8.3, 4.7 Hz, 1H), 1.73 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 67.6, 65.4, 62.4, 29.7, 27.9; IR ν_{max} (neat)/cm^{-1}: 2920 (s), 2870(s), 1767 (s), 1483 (w), 1342 (m), 1215(s), 1040(s), 859 (s); HRMS (ESI, *m/z*): calcd for $C_6H_{11}NO_2Br^+$ (M + H$^+$), 207.9922, found 207.9926.



S11a

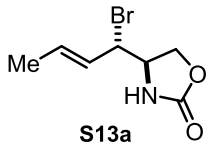
(±)-4-(Bromo(cyclohexyl)methyl)oxazolidin-2-one (S11a) : by following the general procedure and carrying out the reaction with 15 mol % of $Fe(NTf_2)_2$ and 30 mol % of **L2**, **S11a** and its

diastereomer **S11b** were obtained as white solid (30 mg, 58% yield, *dr* =4:1). **S11a** (m.p. 72–76 °C): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (s, 1H), 4.54 (t, *J* = 8.7 Hz, 1H), 4.30 (dd, *J* = 9.1, 5.7 Hz, 1H), 4.20 (td, *J* = 8.6, 5.6 Hz, 1H), 3.87 (dd, *J* = 8.9, 3.0 Hz, 1H), 1.87–1.74 (m, 2H), 1.73–1.51 (m, 4H), 1.47–1.07 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 70.1, 65.0, 54.6, 39.7, 31.9, 27.2, 25.9, 25.9, 25.4; **S11b** (m.p. 71–74 °C): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.58 (s, 1H), 4.49 (t, *J* = 8.2 Hz, 1H), 4.28–4.17 (m, 2H), 3.90 (dd, *J* = 7.7, 3.9 Hz, 1H), 1.84–1.74 (m, 2H), 1.74–1.61 (m, 3H), 1.53–1.13 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 68.0, 65.8, 55.4, 40.6, 31.8, 28.7, 25.9, 25.9, 25.7; IR ν_{max} (neat)/cm^{-1}: 2925 (s), 2851(s), 1759 (s), 1482 (w), 1375 (m), 1227(s), 1149(s), 1035 (s), 820 (s); HRMS (ESI, *m/z*): calcd for $C_{10}H_{17}O_2NCl^+$ (M + H^+), 218.0942, found 218.0937.



S12

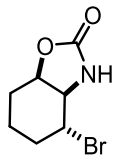
4-(Bromomethyl)-4-phenyloxazolidin-2-one (**S12**): by following the general procedure and carrying out the reaction with 15 mol % of $Fe(NTf_2)_2$ and 30 mol % of **L2**, **S12** was obtained as a white solid (32 mg, 63% yield, m.p. 94–96 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.28 (m, 5H), 6.90 (s, 1H), 4.68 (d, *J* = 8.8 Hz, 1H), 4.49 (d, *J* = 8.8 Hz, 1H), 3.80 (q, *J* = 11.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 139.9, 129.3, 128.7, 124.8, 74.7, 63.5, 40.6; IR ν_{max} (neat)/cm^{-1} 3252 (m), 2932 (w), 2853 (w), 1733 (s), 1376 (w), 1089 (s), 1061 (w); HRMS (ESI, m/z): calcd for $C_{10}H_{11}NO_2Br^+$ (M + H^+), 255.9973, found 255.9965.



S13a

4-(*E*-1-Bromobut-2-en-1-yl)oxazolidin-2-one (**S13a**) : by following the general procedure and carrying out the reaction with ligand **L2**, **S13a** and its *syn*-diastereomer (**S13b**) were obtained as white solids (33 mg, 73% yield, *dr*: 1.2:1). **S13a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.23 (s, 1H), 5.93–5.83 (m, 1H), 5.59–5.50 (m, 1H),4.50 (t, *J* = 8.8 Hz, 1H), 4.34 (dd, *J* = 9.8, 7.9 Hz, 1H),

4.27 (dd, J = 9.3, 5.0 Hz, 1H), 4.13–4.05 (m, 1H), 1.78–1.76 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 133.8, 127.1, 68.7, 57.5, 56.6 17.9; **S13b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (s, 1H), 5.93–5.83 (m, 1H), 5.59–5.50 (m, 1H),4.45–4.41 (m, 2H), 4.18 (dd, J = 9.4, 4.7 Hz, 1H), 4.11–4.06 (m, 1H), 1.76–1.74 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 133.7, 126.3, 67.3, 57.2, 55.6, 17.8; IR ν_{max} (neat)/cm^{-1}: 3276 (m), 2919 (w), 1751 (s), 1407 (w), 1233 (s), 1023 (m), 532 (m); HRMS (ESI, m/z): calcd for $C_7H_{11}NO_2Br^+$ (M + H$^+$), 219.9973, found 219.9976.

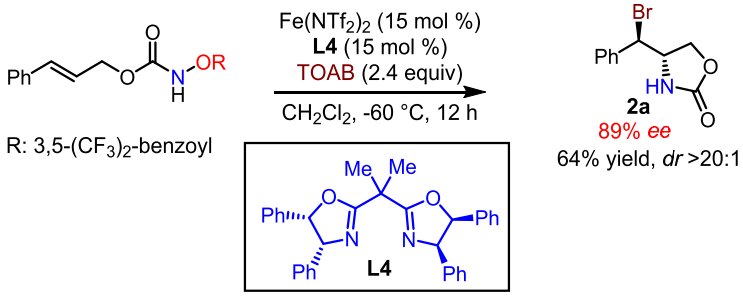


S14

4-Bromohexahydrobenzo[*d*]oxazol-2(3H)-one (**S14**): by following the general procedure, **S14** was obtained as a white solid (27 mg, 61% yield, *dr* >20:1, m.p. 115–117 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71 (s, 1H), 4.67–4.65 (m, 1H), 3.90–3.84 (m, 1H), 3.78 (dd, J = 8.8, 5.9 Hz, 1H), 2.27–2.23 (m, 2H), 1.78–1.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 77.0, 60.9, 53.8, 32.7, 25.9, 20.7; IR ν_{max} (neat)/cm^{-1}: 3272 (m), 2948 (w), 2885 (w), 1751 (s), 1201 (w); HRMS (ESI, *m/z*): calcd for $C_7H_{11}NO_2Br^+$ (M + H$^+$), 219.9973, found 219.9972. The NMR data of **S14** was in consistent with reported data.[3]

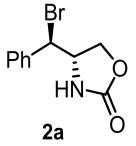
C. Procedures for the Iron-Catalyzed Asymmetric Olefin Aminobromination Reaction and Product Characterization

Chiral ligands **L4** were synthesized by following literature procedures.[5]



General Procedure. To a flame-dried sealable 2-dram vial (vial **A**) equipped with a magnetic stir bar were added $Fe(NTf_2)_2$ (9.2 mg, 0.015 mmol, 15 mol %) and ligand **L4** (7.3 mg, 0.015 mmol, 15 mol %). After the vial was evacuated and backfilled with N_2 for three times, anhydrous CH_2Cl_2 (1.0 mL) was added and the mixture was stirred at room temperature for 20 min. Meanwhile, a second flame-dried and N_2-protected 2-dram vial (vial **B**) with a magnetic stir bar was charged with the substrate (0.1 mmol), anhydrous TOAB (137 mg, 0.24 mmol), freshly activated 4 Å molecular sieves and anhydrous CH_2Cl_2 (3.0 mL). Both vials were degassed by brief evacuation and back filling with N_2 twice. Vial **B** was cooled down to -60 °C, and the catalyst solution in vial **A** was added to vial **B** drop wise via a syringe. The resulting solution was stirred at this temperature for 12 h and then gradually warmed to room temperature. The reaction was quenched with 1 mL saturated $NaHCO_3$ solution. The reaction mixture was extracted with CH_2Cl_2 (1.5 mL × 3), and the combined organic phase was concentrated *in vacuo*. The residue was purified through a gradient silica gel flash column chromatography (hexanes/acetone: from 15:1 to 4:1) to afford the aminobromination product. The *dr* was determined by ^1H NMR analysis and the *ee* was measured by chiral HPLC analysis. The absolute stereochemistry was determined according to the X-ray crystallographic analysis of the corresponding olefin aminochlorination product.[4]

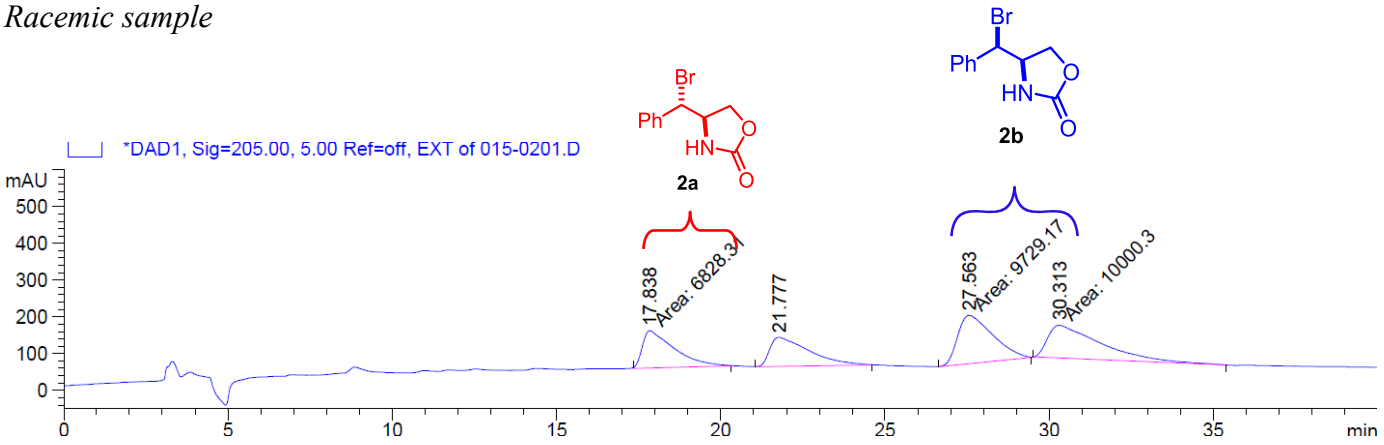
The racemic products with low *dr* (for HPLC assay purposes) were obtained by following the general procedure of the iron-catalyzed olefin aminobromination under the ligand-free condition (Table S1, entry 1).



2a

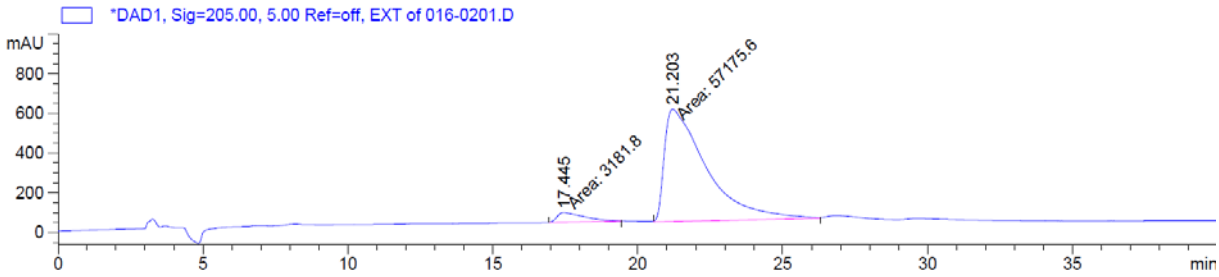
(*S*)-4-((*R*)-Bromo(phenyl)methyl)oxazolidin-2-one (**2a**): by following the general procedure, the product **2a** obtained as a white solid (17 mg, 64% yield, *dr* >20:1). $[\alpha]_D^{20}$ = + 77 ° (*c*=0.65, CH_2Cl_2). The *ee* was determined by Chiral HPLC analysis (Chiral AD-H column, 10% isopropyl alcohol in hexanes, flow rate = 1.0 mL/min, UV detection at 205 nm). The *anti*-diastereomer (**2a**): t_r (minor) = 17.45 min, t_r (major) = 21.20 min, 89% *ee*.

Racemic sample

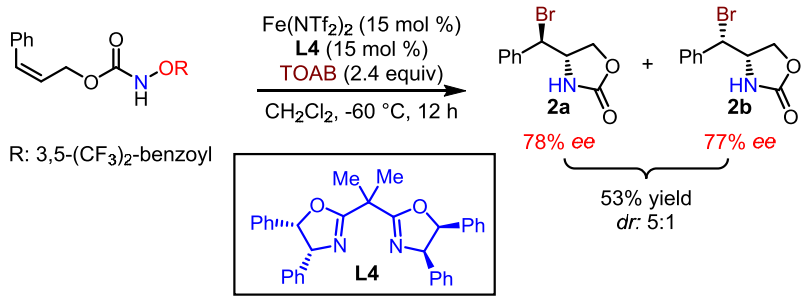


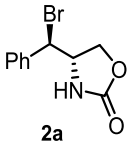
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.838	FM	1.1229	6828.31250	101.34515	20.5984
2	21.777	BB	0.9985	6591.87793	78.91470	19.8852
3	27.563	MM	1.2330	9729.17188	131.51183	29.3492
4	30.313	MM	1.8762	1.00003e4	88.83601	30.1671
Totals :				3.31497e4	400.60769	

Enantio-enriched sample (*anti*-diastereomer, **2a**, 89% *ee*)



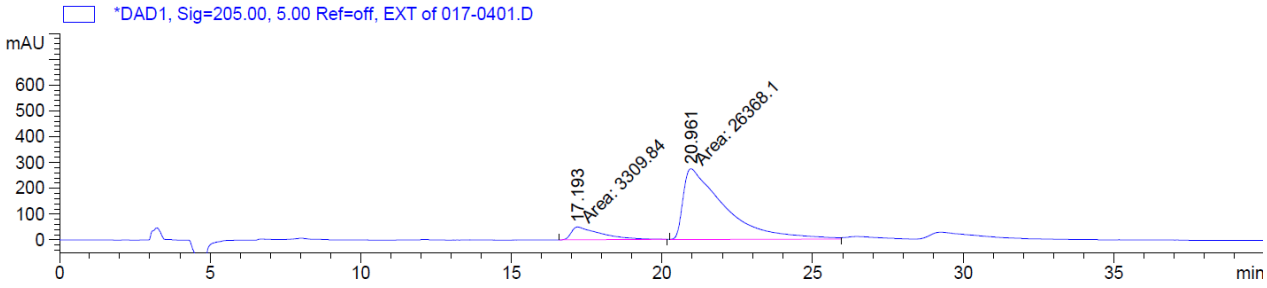
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.445	FM	1.0791	3181.79761	49.14471	5.2716
2	21.203	MM	1.6809	5.71756e4	566.90674	94.7284
Totals :				6.03574e4	616.05145	





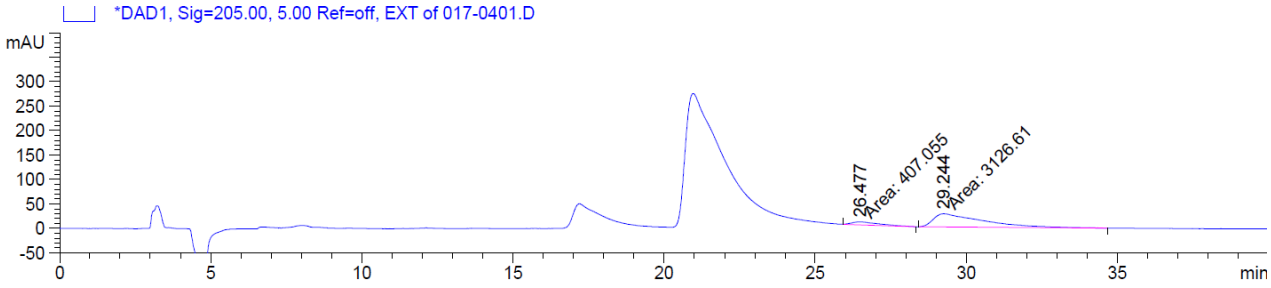
(*S*)-4-((*R*)-Bromo(phenyl)methyl)oxazolidin-2-one (**2a**): by following the general procedure, the product **2a** obtained as a white solid (14 mg, 53% yield, *dr*: 5:1). The *ee* was determined by Chiral HPLC analysis (Chiral AD-H column, 10% isopropyl alcohol in hexanes, flow rate = 1.0 mL/min, UV detection at 205 nm). The *anti*-diastereomer (**2a**): t_r (minor) = 17.20 min, t_r (major) = 20.96 min, 77% *ee*; the *syn*-diastereomer (**2b**): t_r (minor) = 26.48 min, t_r (major) = 29.24 min, 77% *ee*.

Enantio-enriched sample (*anti*-diastereomer, **2a**, 77% *ee*)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.193	MM	1.1128	3309.83887	49.57072	11.1525
2	20.961	MF	1.6036	2.63681e4	274.04437	88.8475
Totals :				2.96779e4	323.61509	

Enantio-enriched sample (*syn*-diastereomer, **2b**, 77% *ee*)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.477	MM	1.0814	407.05539	6.27349	11.5194
2	29.244	MM	1.9192	3126.61060	27.15145	88.4806
Totals :				3533.66599	33.42494	

D. References

(1) Lu, D.-F.; Liu, G.-S.; Zhu, C.-L.; Yuan, B.; Xu, H. *Org. Lett.* **2014**, *16*, 2912.

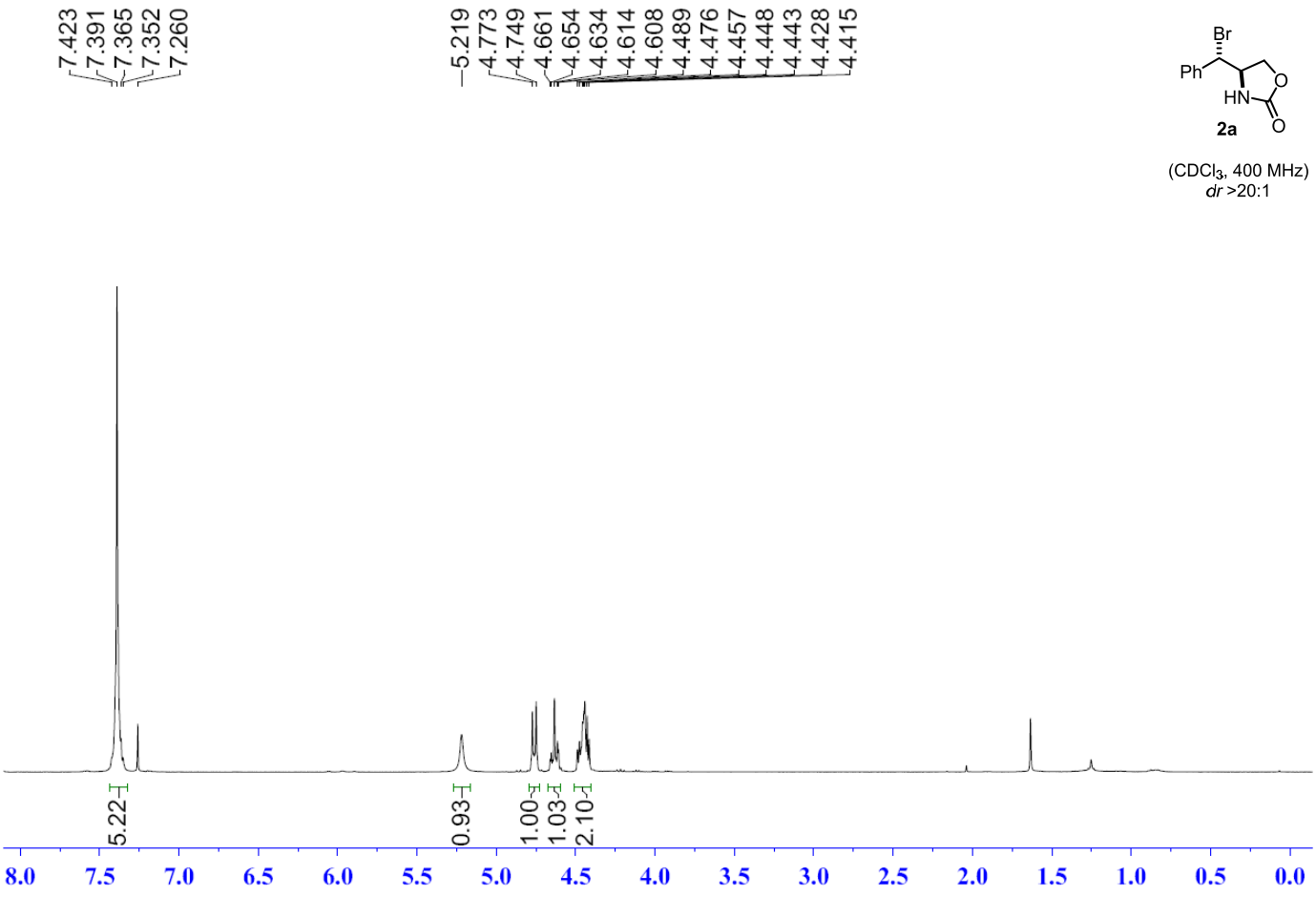
(2) Lu, D.-F.; Zhu, C.-L.; Jia, Z.-X.; Xu, H. *J. Am. Chem. Soc.* **2014**, *136*, 13186.

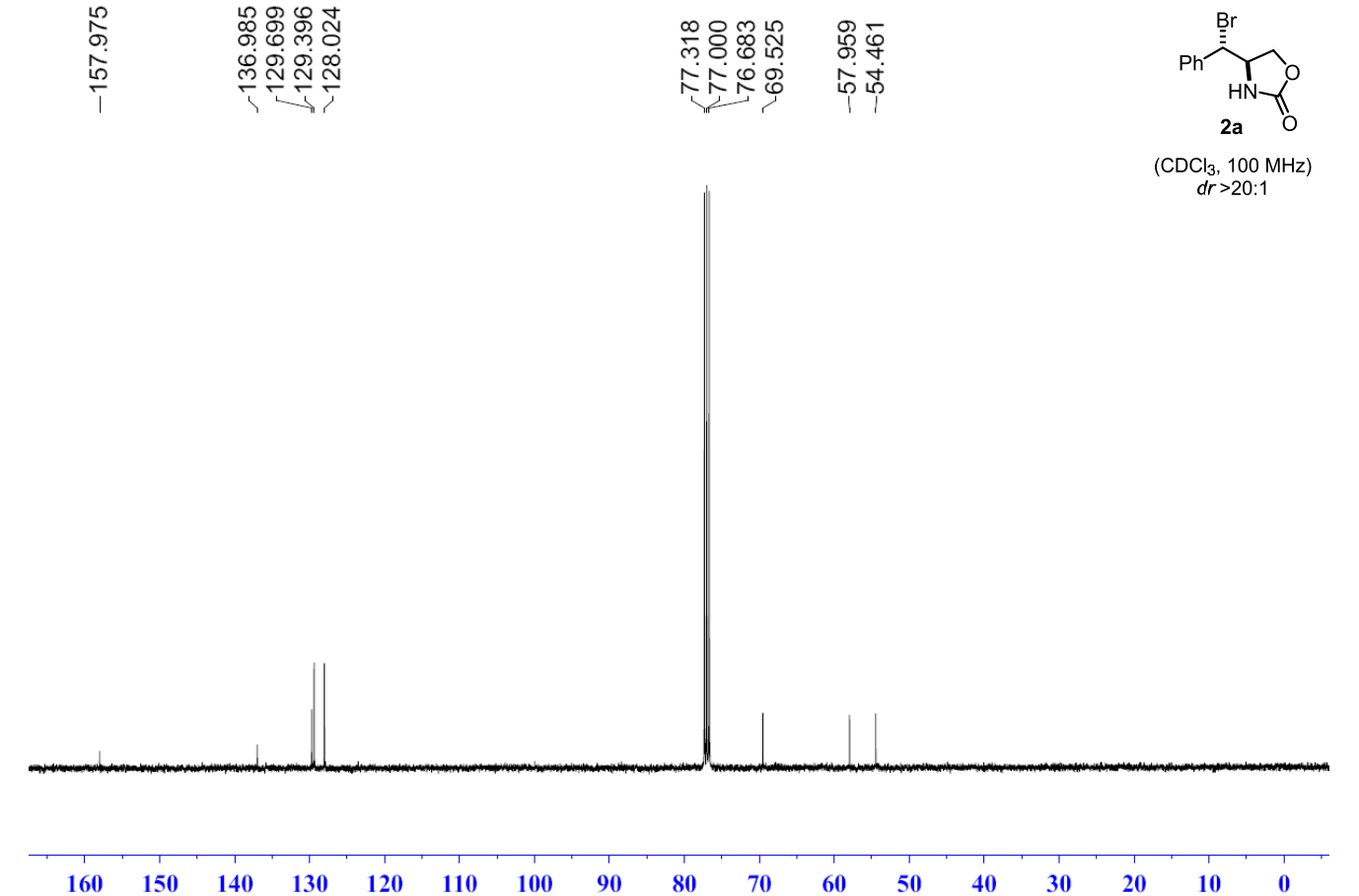
(3) Kamon, T.; Shigeoka, D.; Tanaka, T.; Yoshimitsu, T. *Org. Biomol. Chem.* **2012**, *10*, 2363.

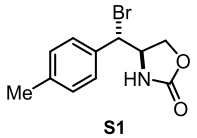
(4) Zhu, C.-L.; Tian, J.-S.; Gu, Z.-Y.; Xing, G.-W.; Xu, H. *Chem. Sci.* **2015**, *6*, 3044.

(5) Cornejo, A.; Fraile, J. M.; García, J. I.; Gil, M. J.; Martínez-Merino, V.; Mayoral, J. A.; Pires, E.; Villalba, I. *Synlett* **2005**, 2321.

F. NMR Spectra



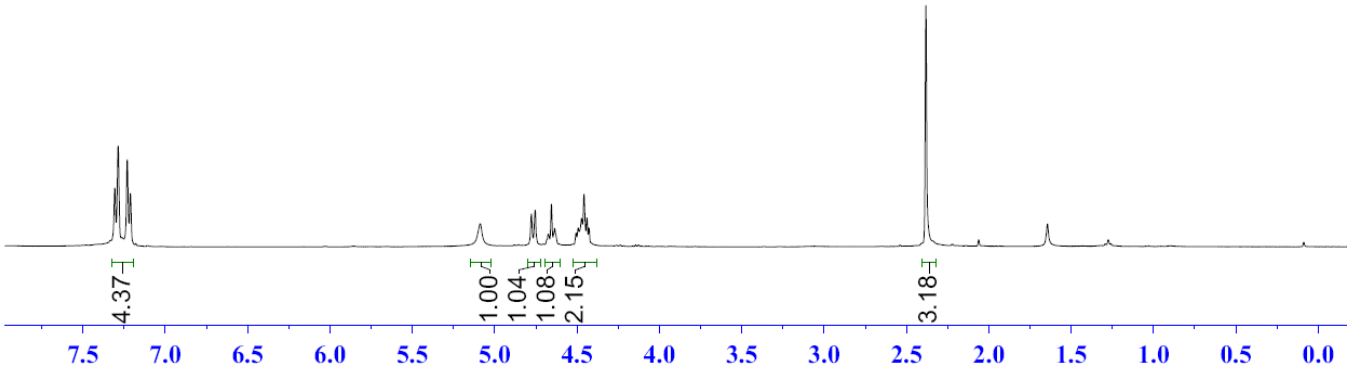


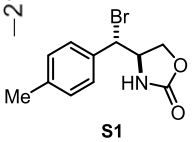


S1

($CDCl_3$, 400 MHz)

dr >20:1

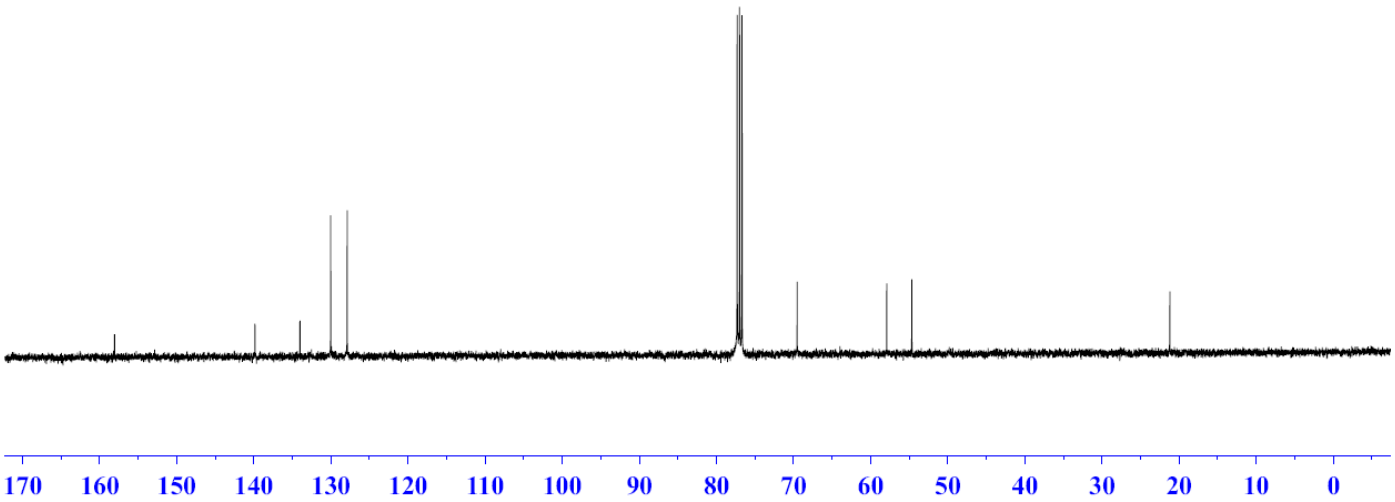


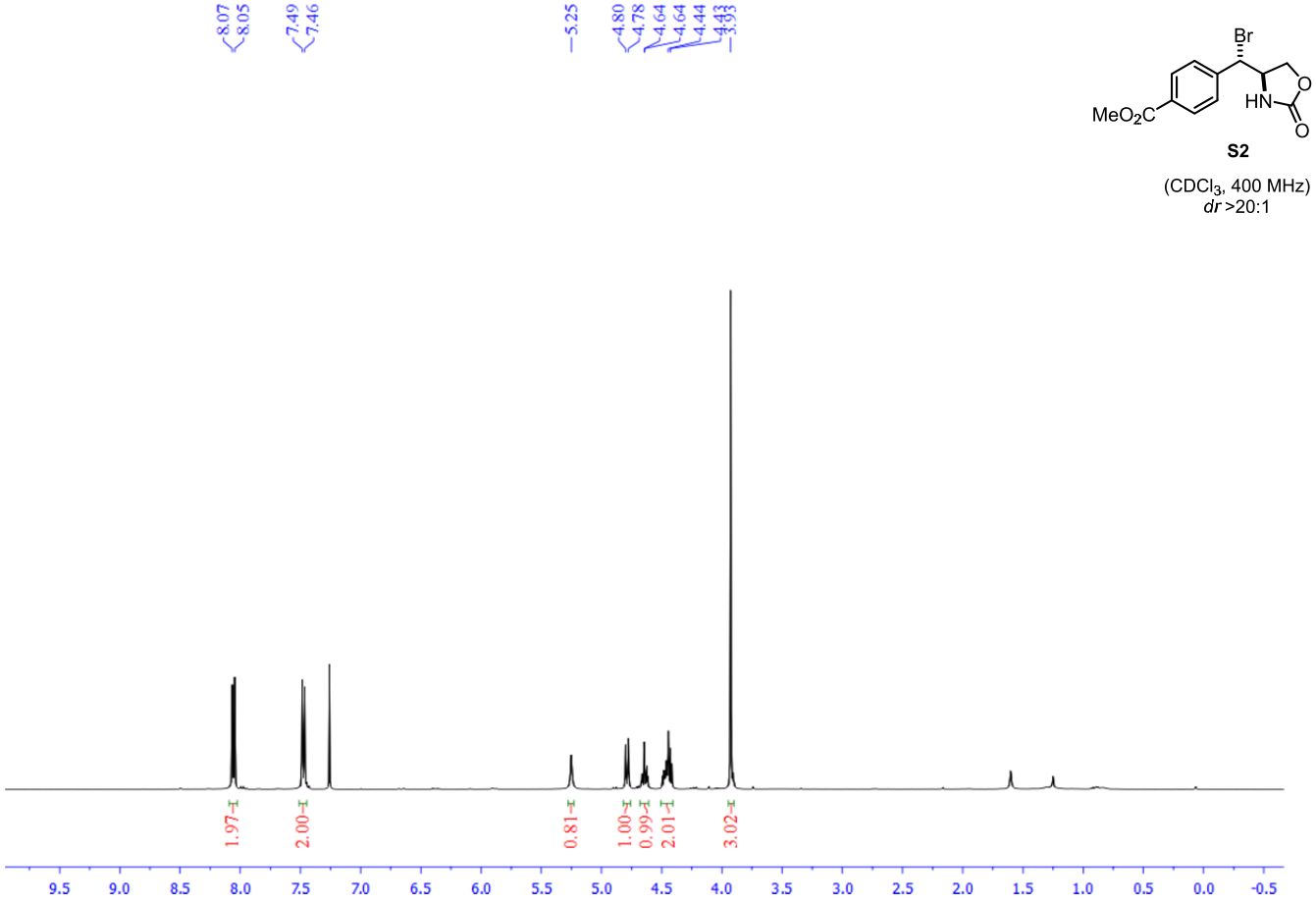


S1

($CDCl_3$, 100 MHz)

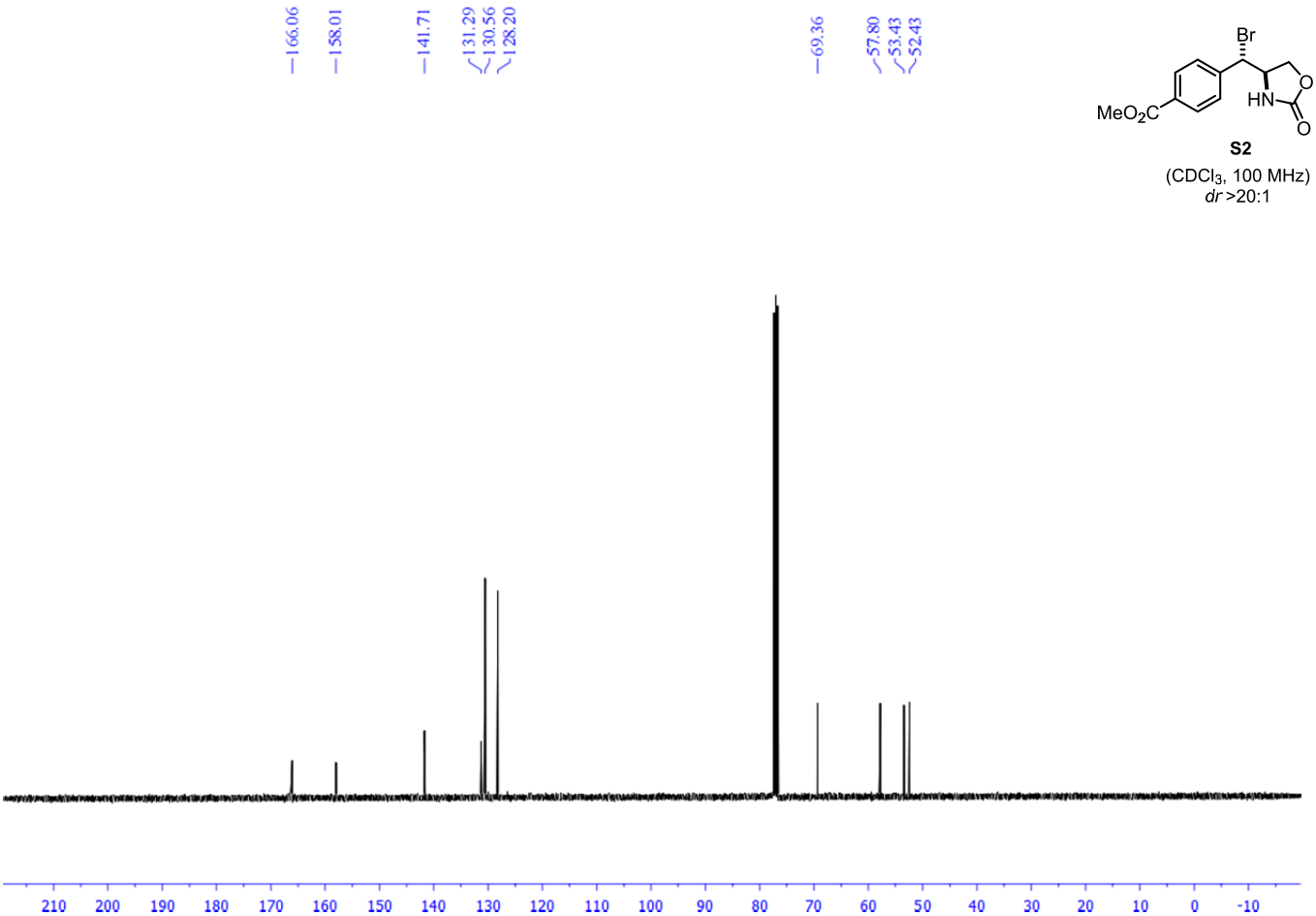
dr >20:1





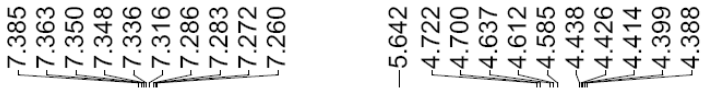
S2

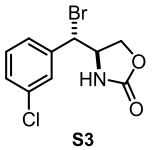
($CDCl_3$, 400 MHz)
dr >20:1



S2

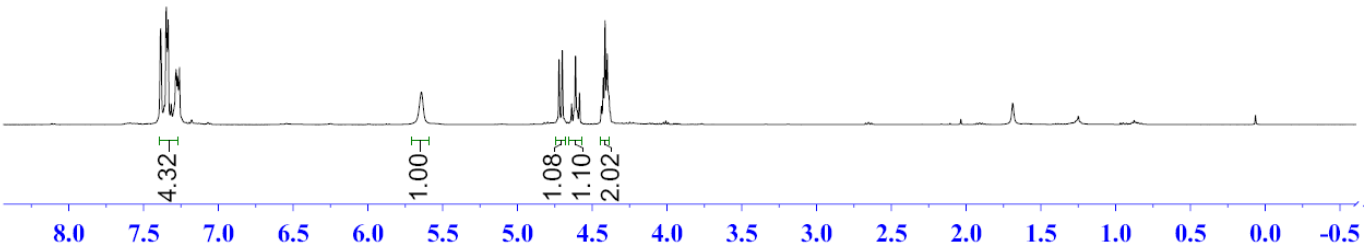
($CDCl_3$, 100 MHz)
dr >20:1

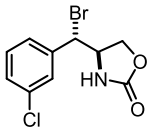




S3

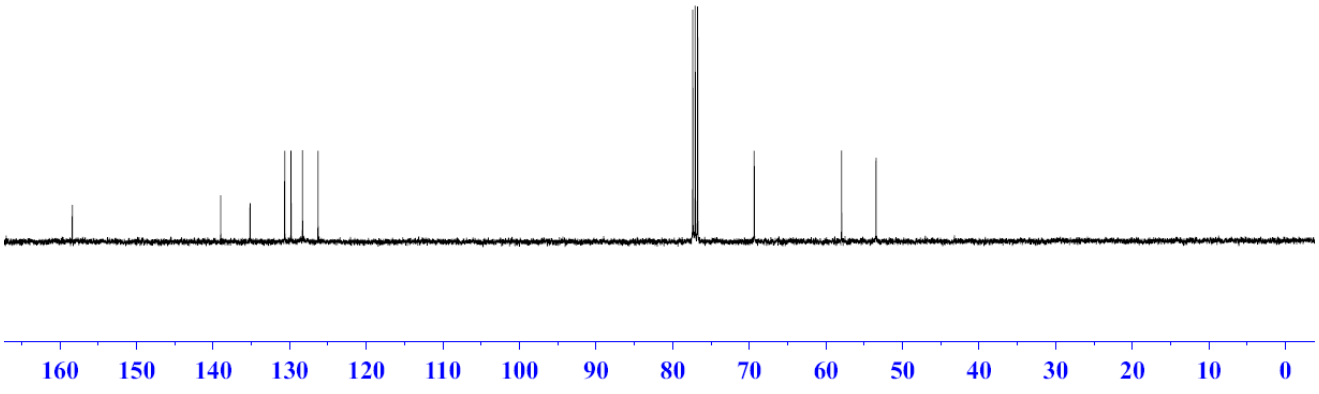
($CDCl_3$, 400 MHz)
dr >20:1

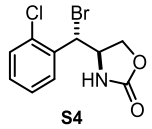




S3

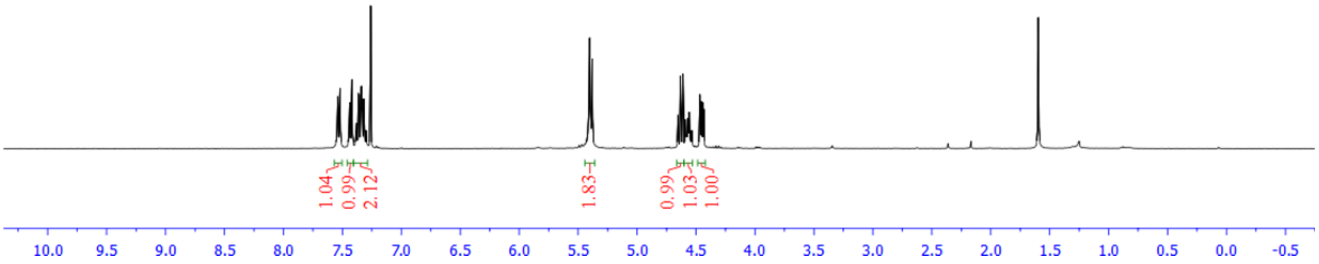
($CDCl_3$, 100 MHz)
dr >20:1

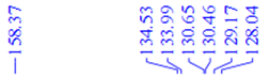


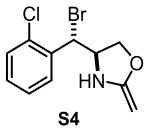


S4

($CDCl_3$, 400 MHz)
dr >20:1

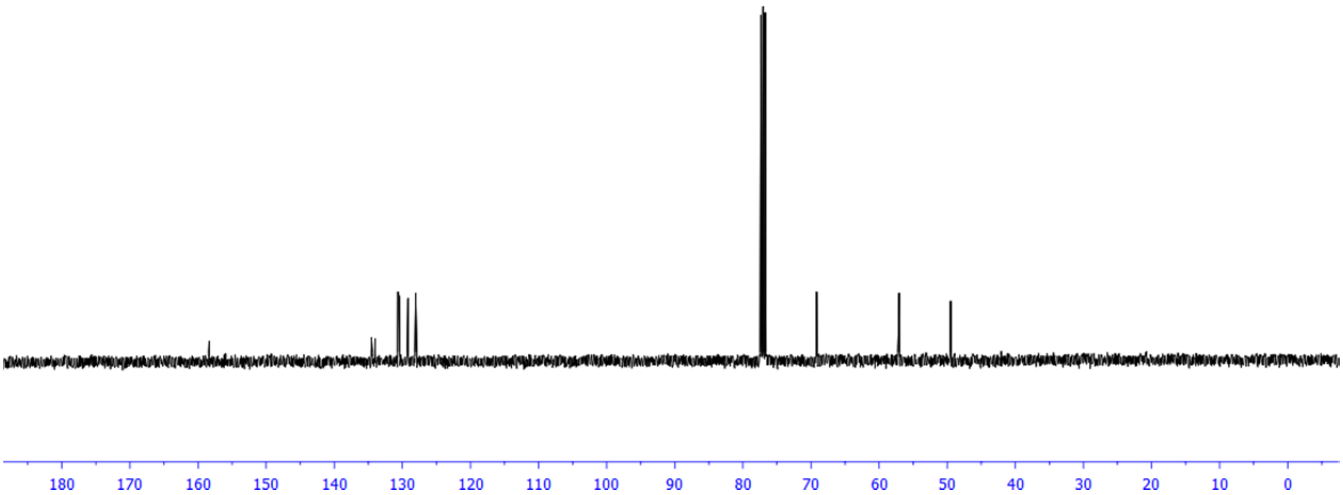


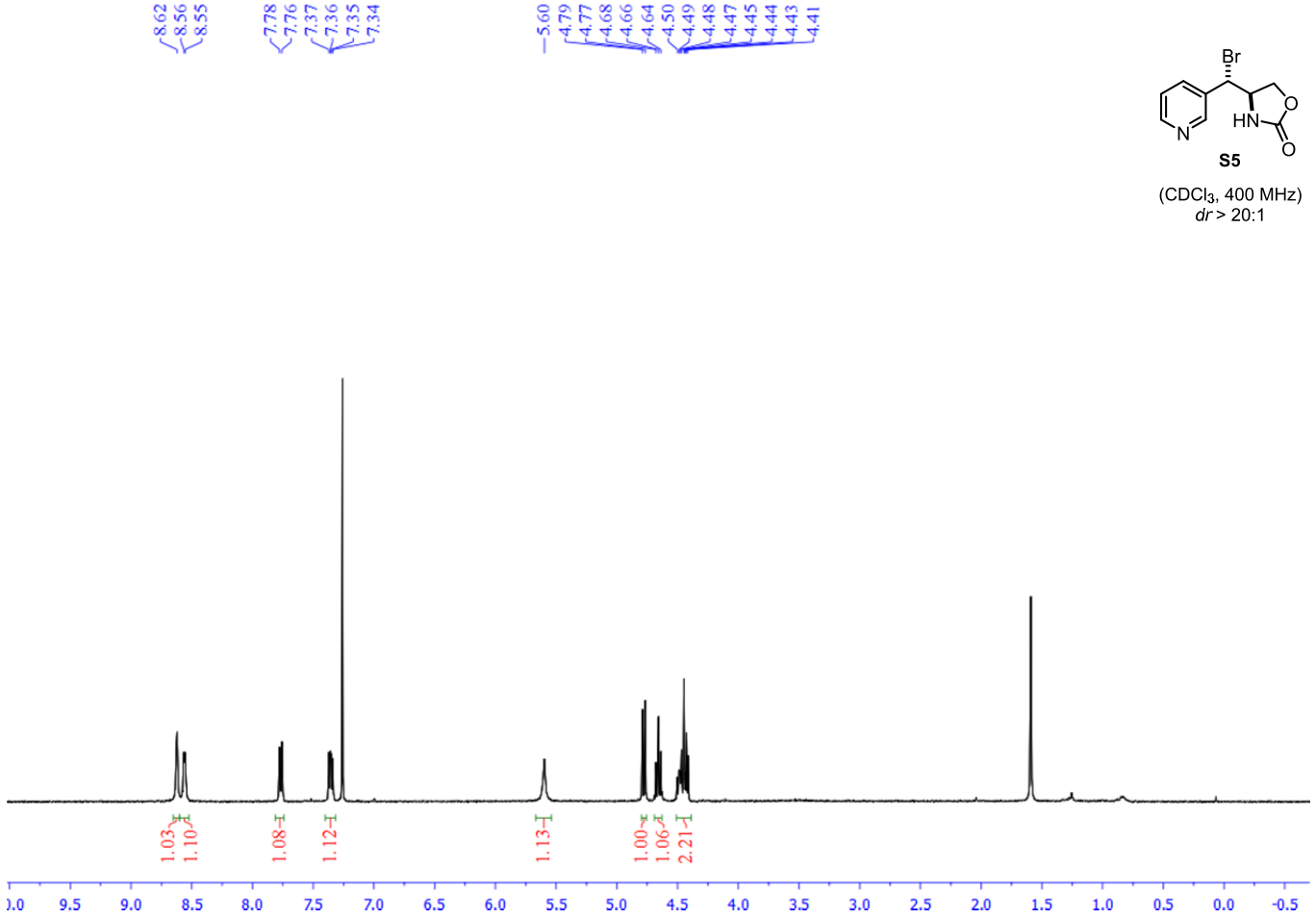




S4

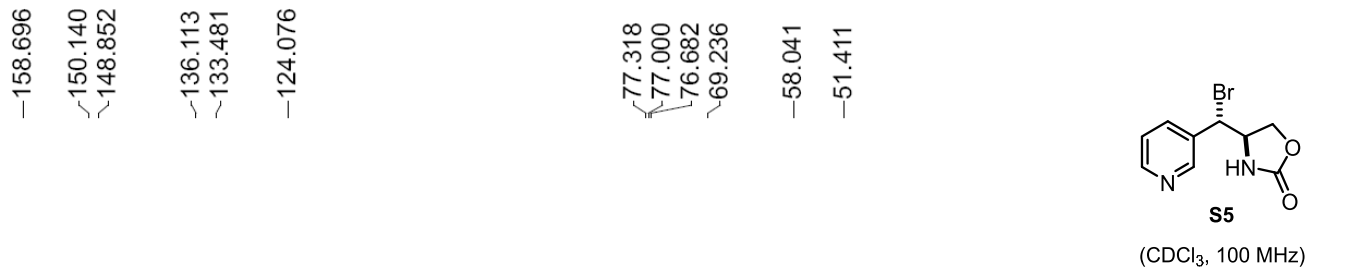
($CDCl_3$, 100 MHz)
dr >20:1





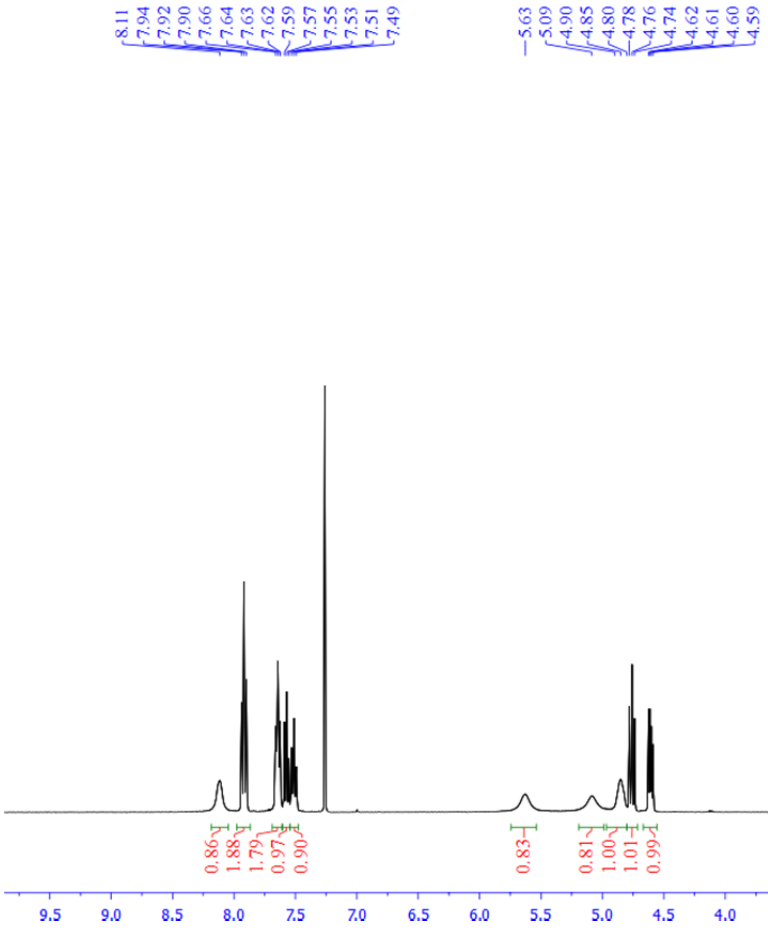
S5

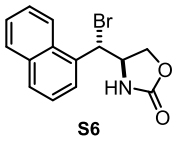
($CDCl_3$, 400 MHz)
dr > 20:1



S5

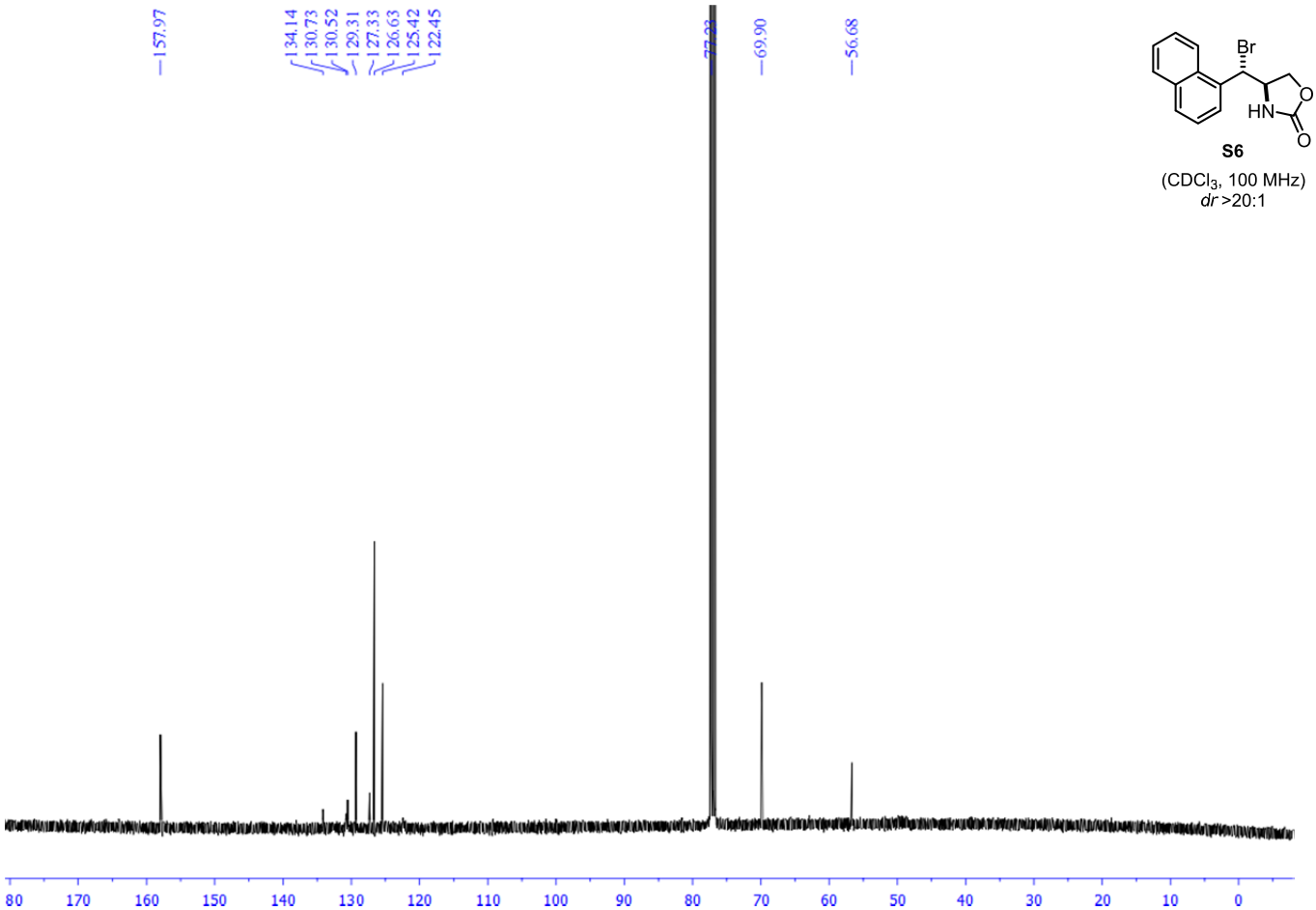
($CDCl_3$, 100 MHz)
dr >20:1





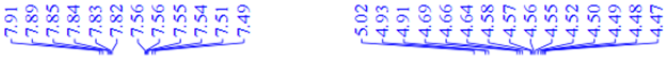
S6

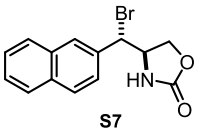
($CDCl_3$, 400 MHz)
dr >20:1



S6

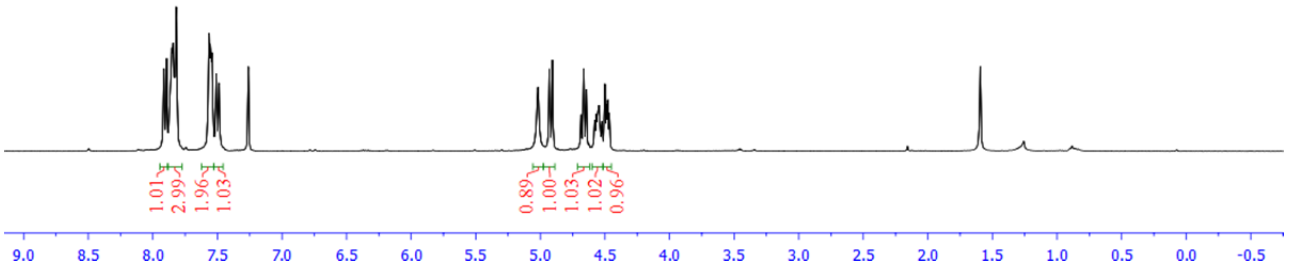
($CDCl_3$, 100 MHz)
dr >20:1

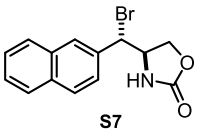




S7

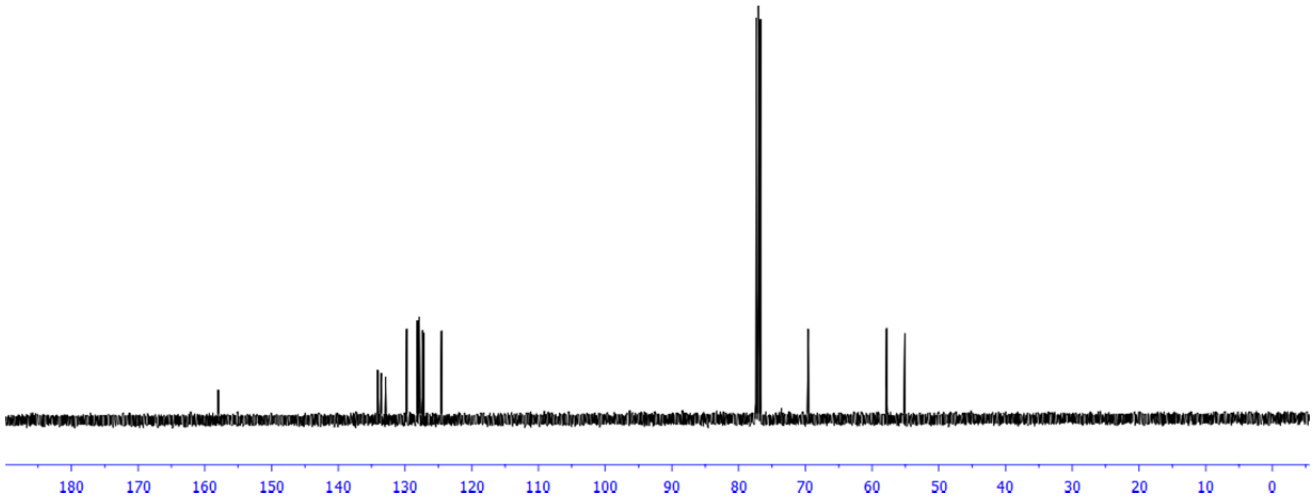
(CDCl$_3$, 400 MHz)
dr >20:1

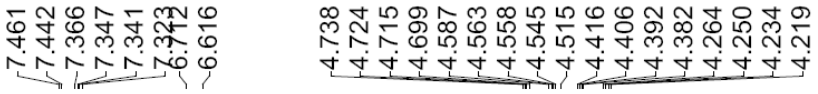


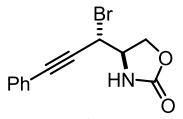


S7

(CDCl$_3$, 100 MHz)
dr >20:1



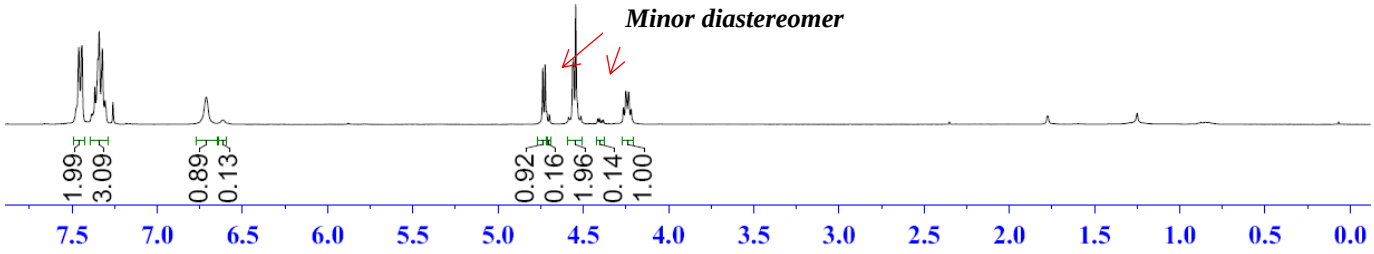


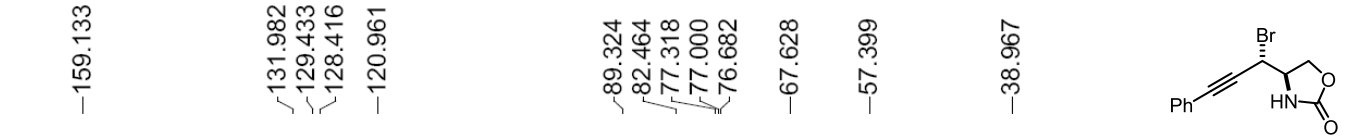


S8

($CDCl_3$, 400 MHz)

dr :7.1:1

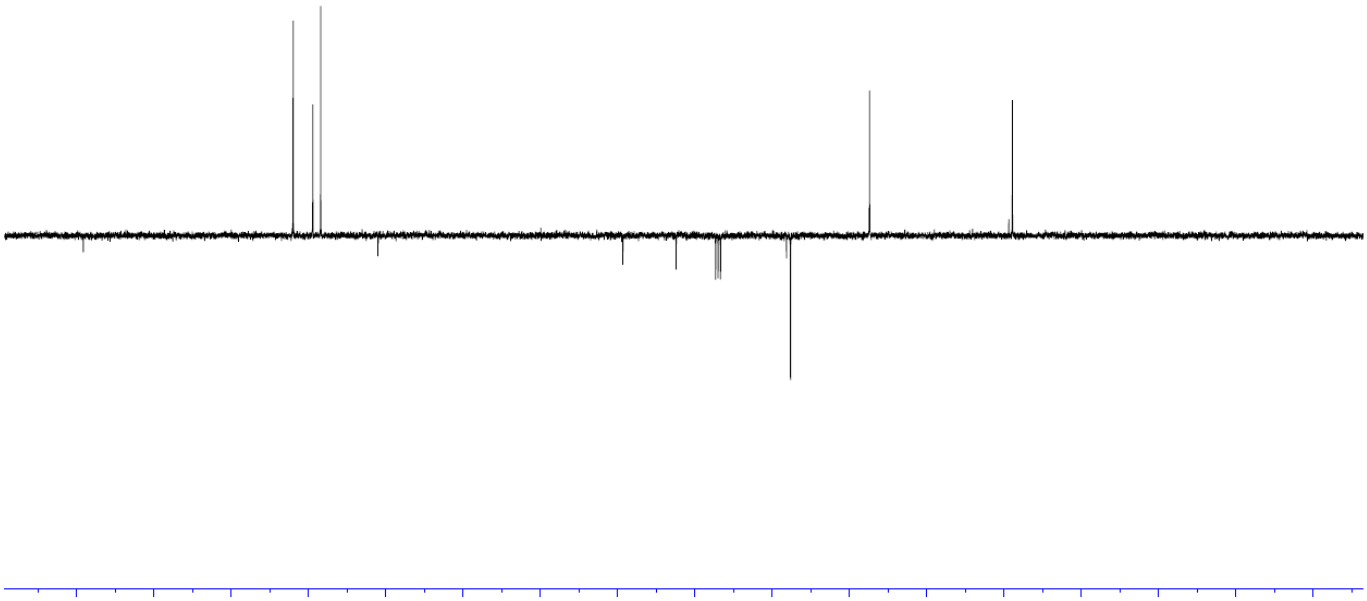


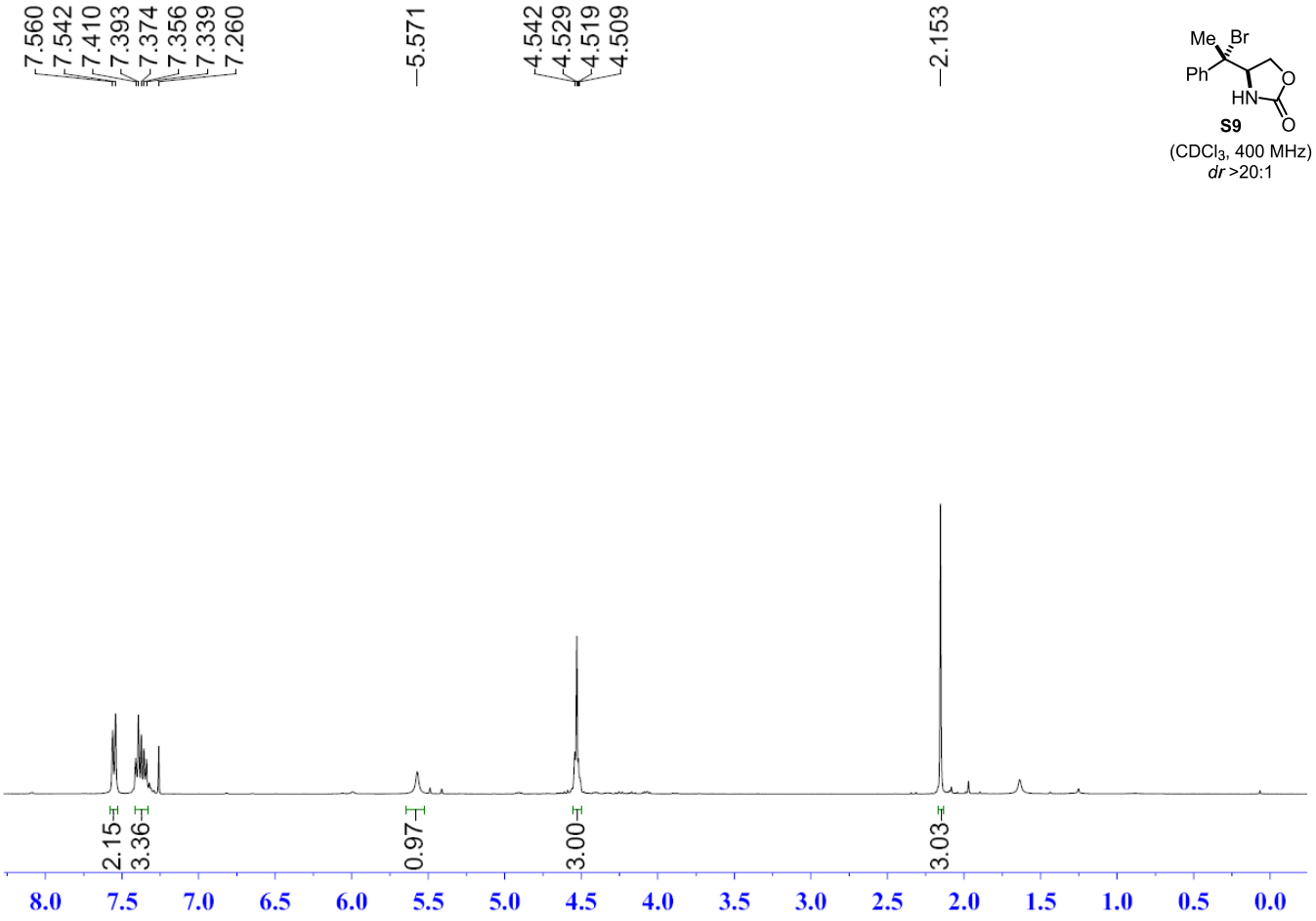


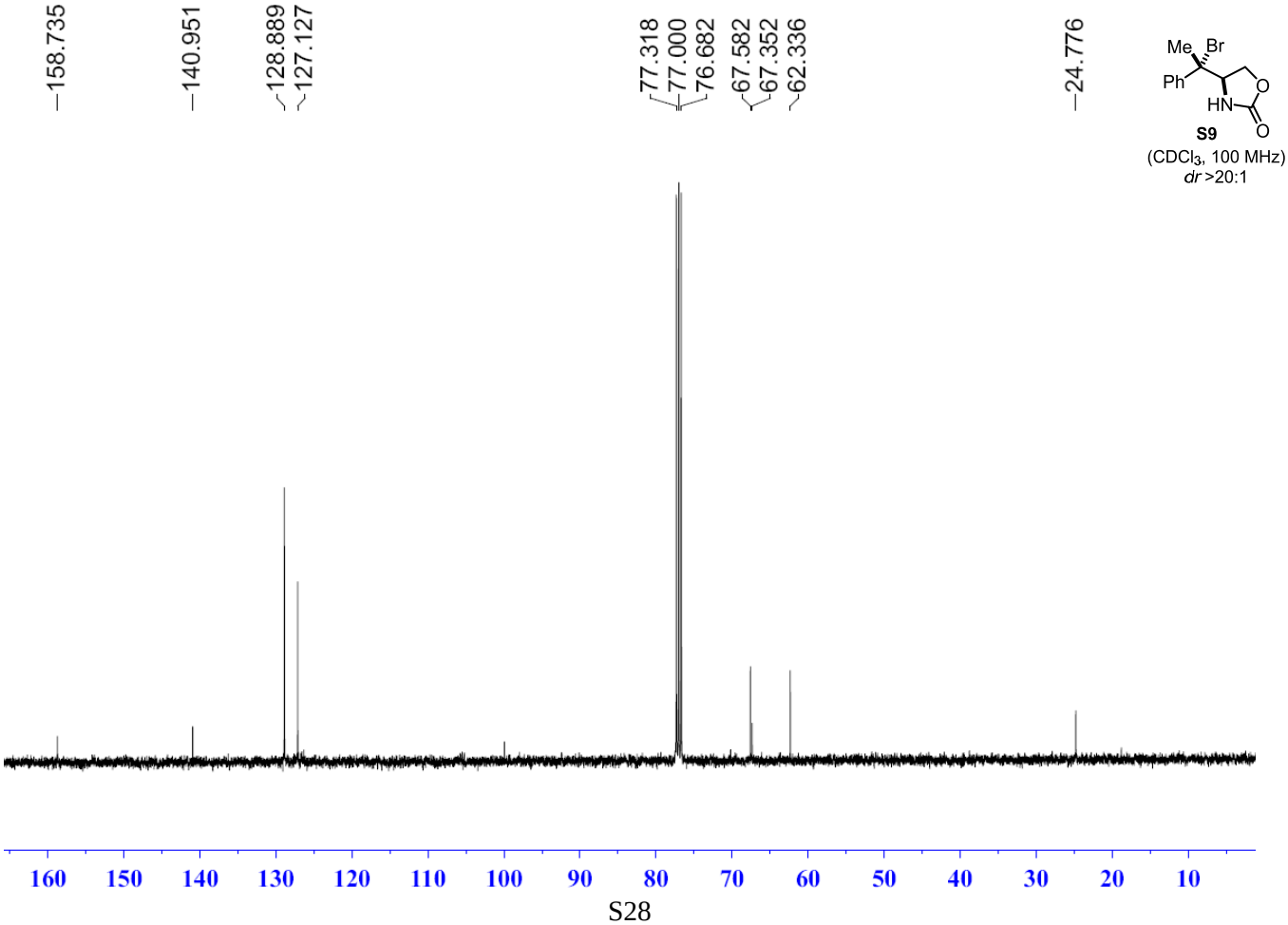
S8

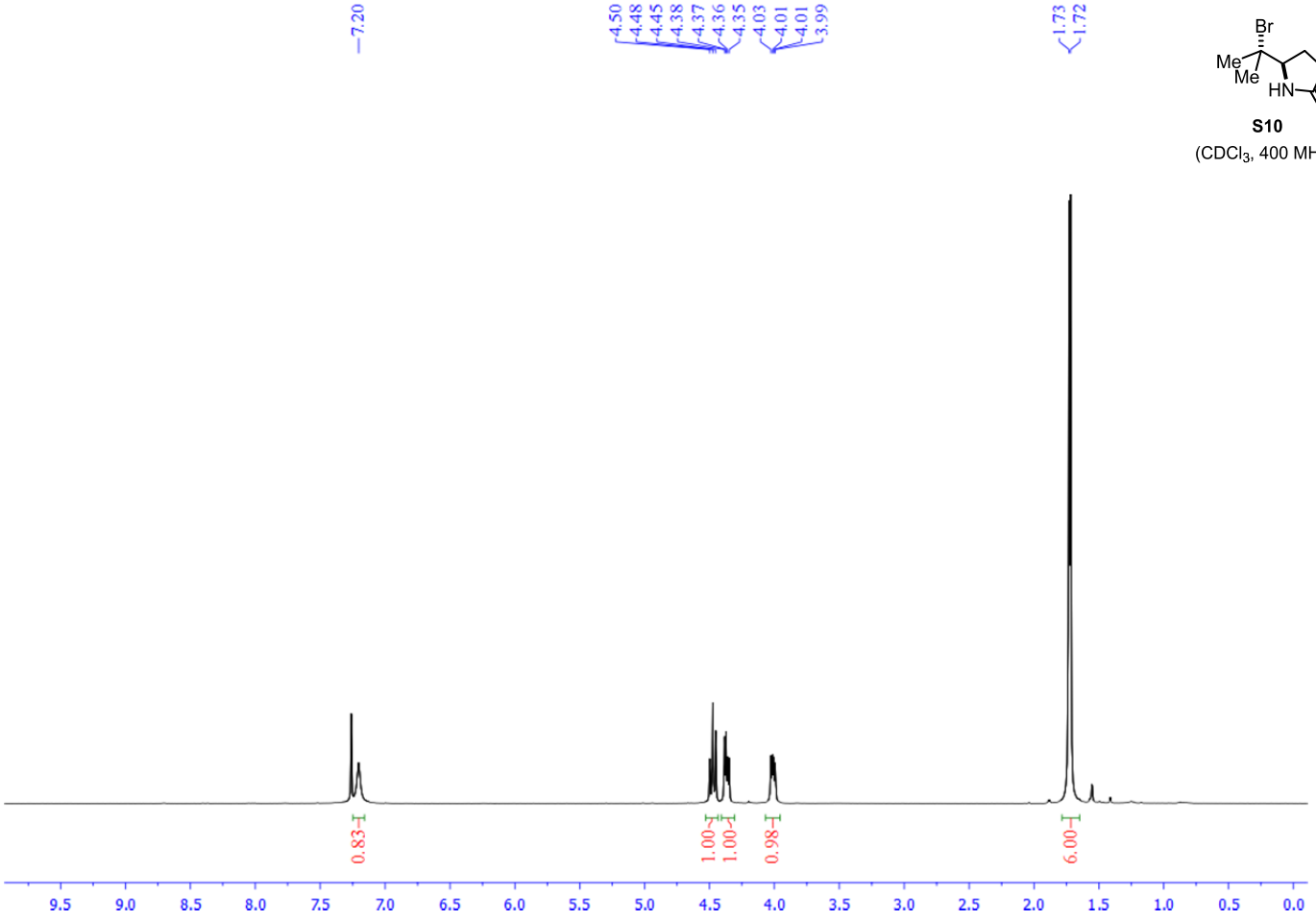
($CDCl_3$, 100 MHz)

dr :7.1:1



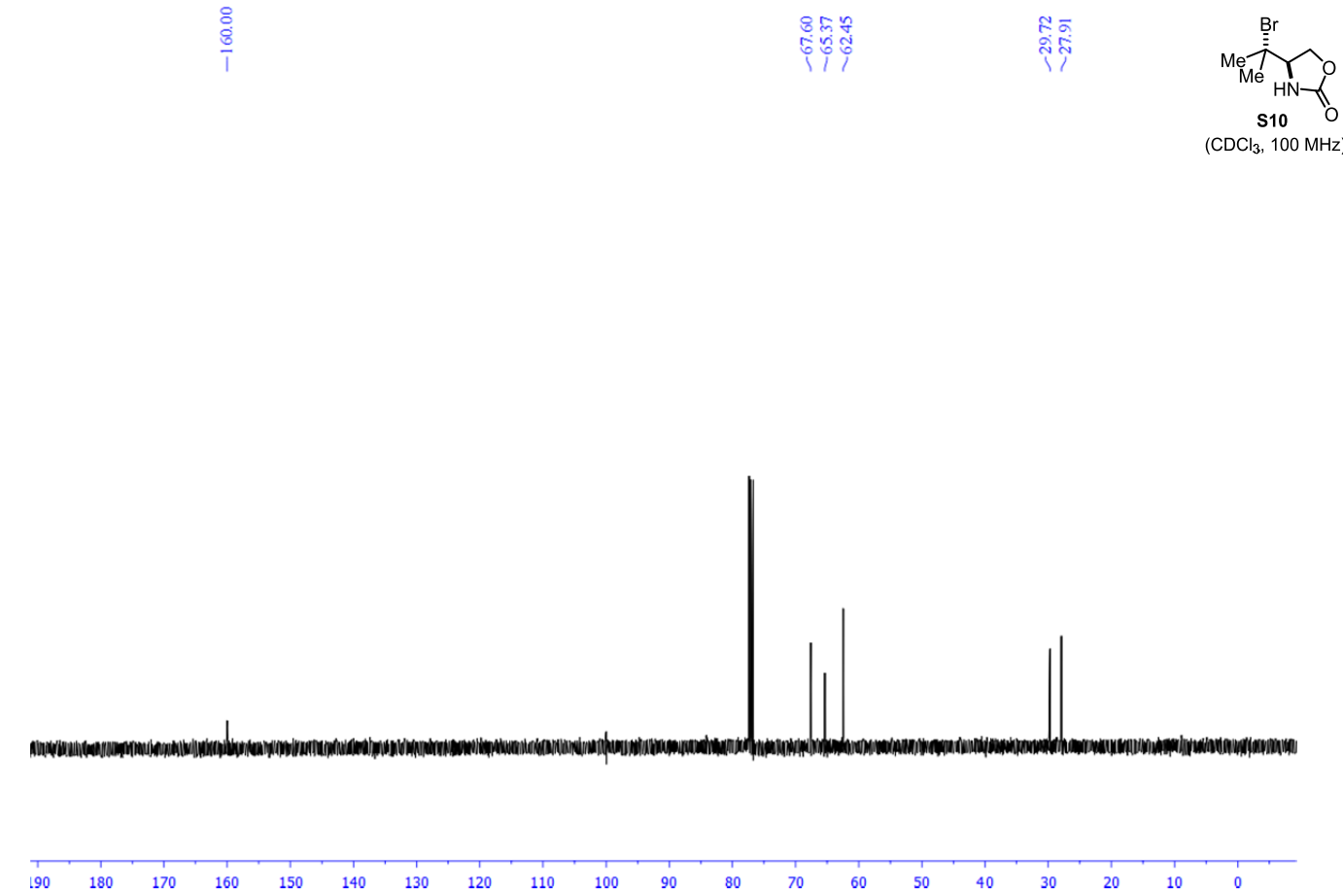

7.560
7.542
7.410
7.393
7.374
7.356
7.339
7.260
5.571
4.542
4.529
4.519
4.509
2.153
Me
Br
Ph
HN
O
O
S9
(CDCl3, 400 MHz)
dr >20:1
2.15
3.36
0.97
3.00
3.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


158.735
140.951
128.889
127.127
77.318
77.000
76.682
67.582
67.352
62.336
24.776
Me
Br
Ph
HN
O
O
S9
(CDCl3, 100 MHz)
dr >20:1
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



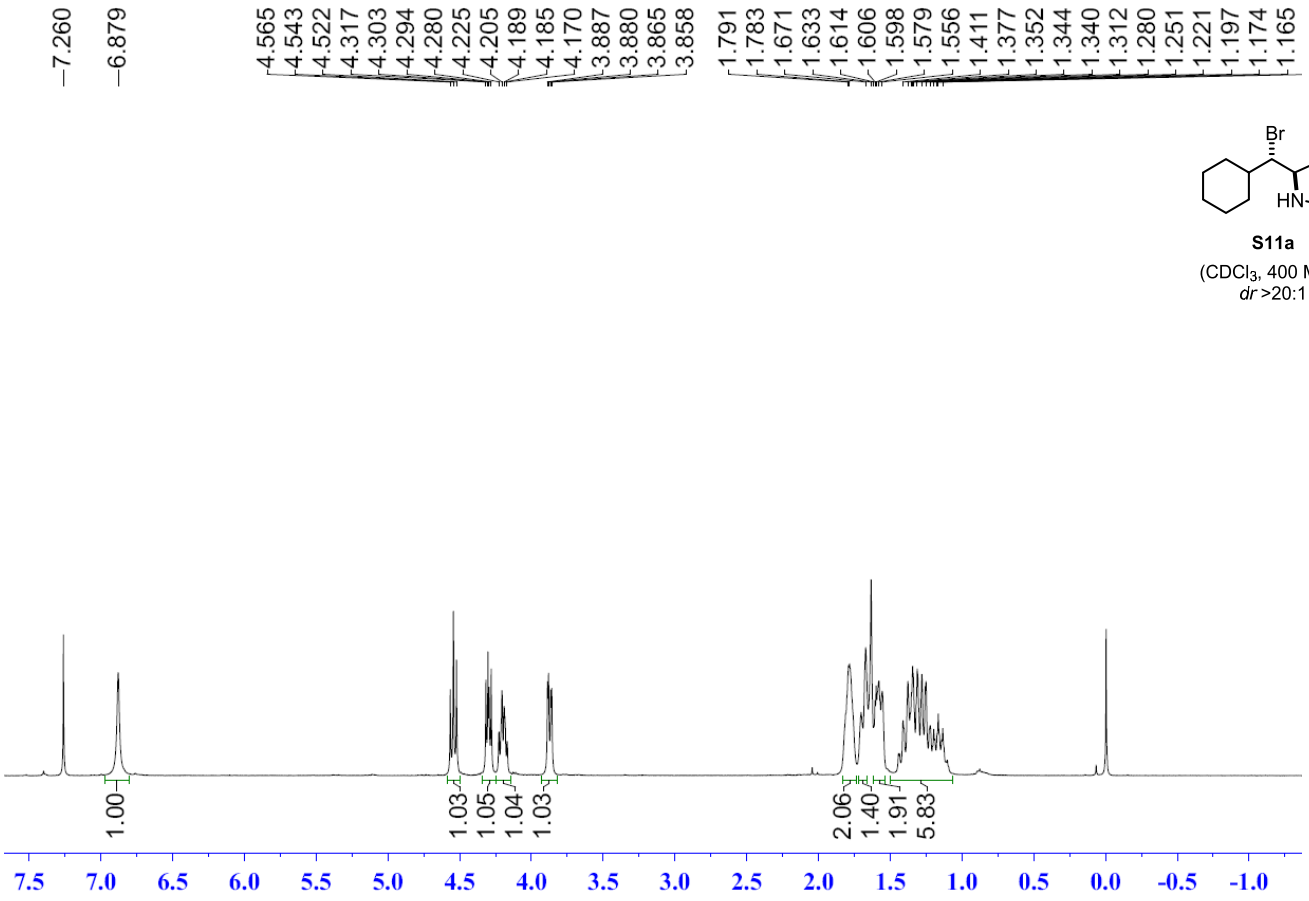
S10

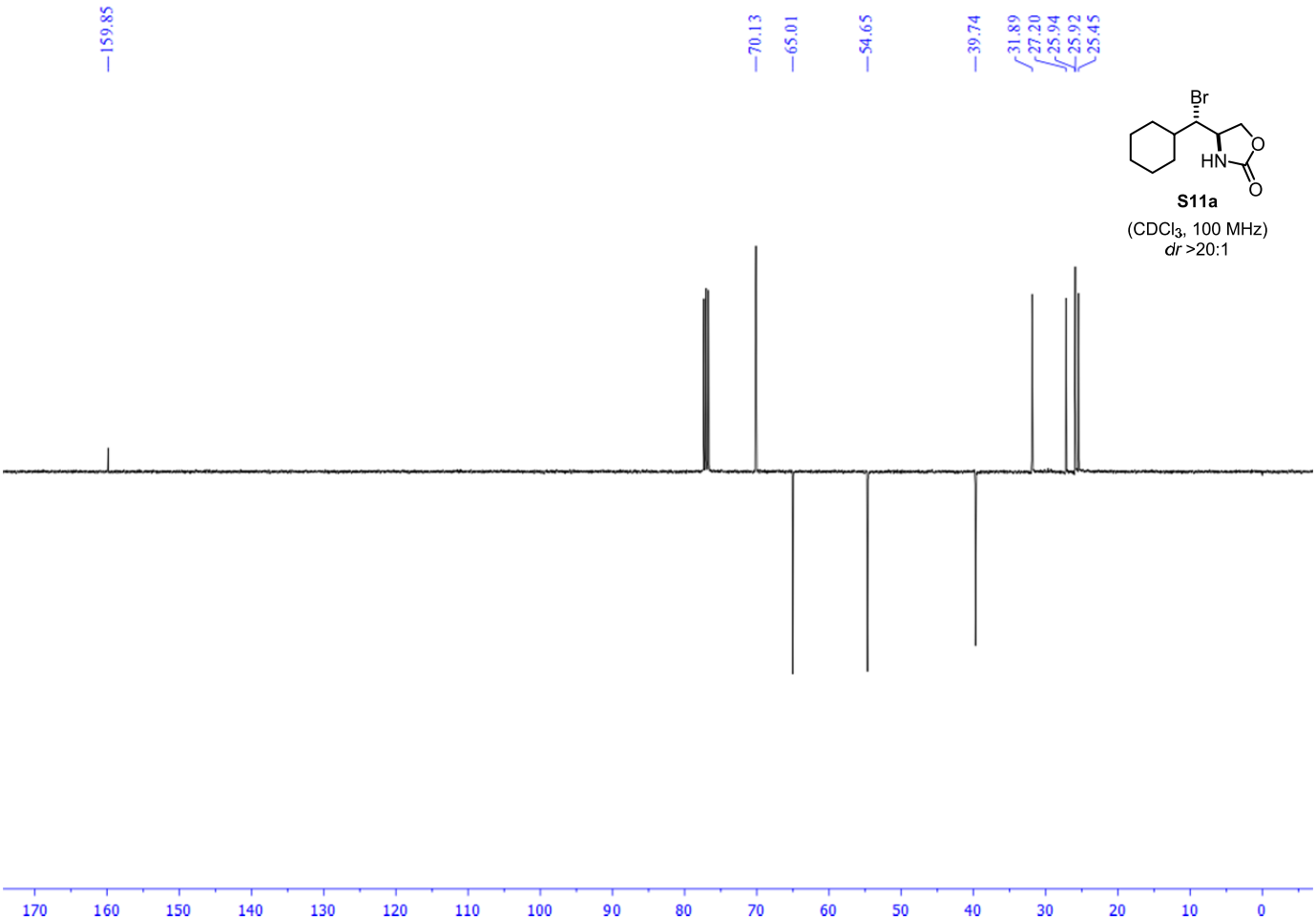
($CDCl_3$, 400 MHz)

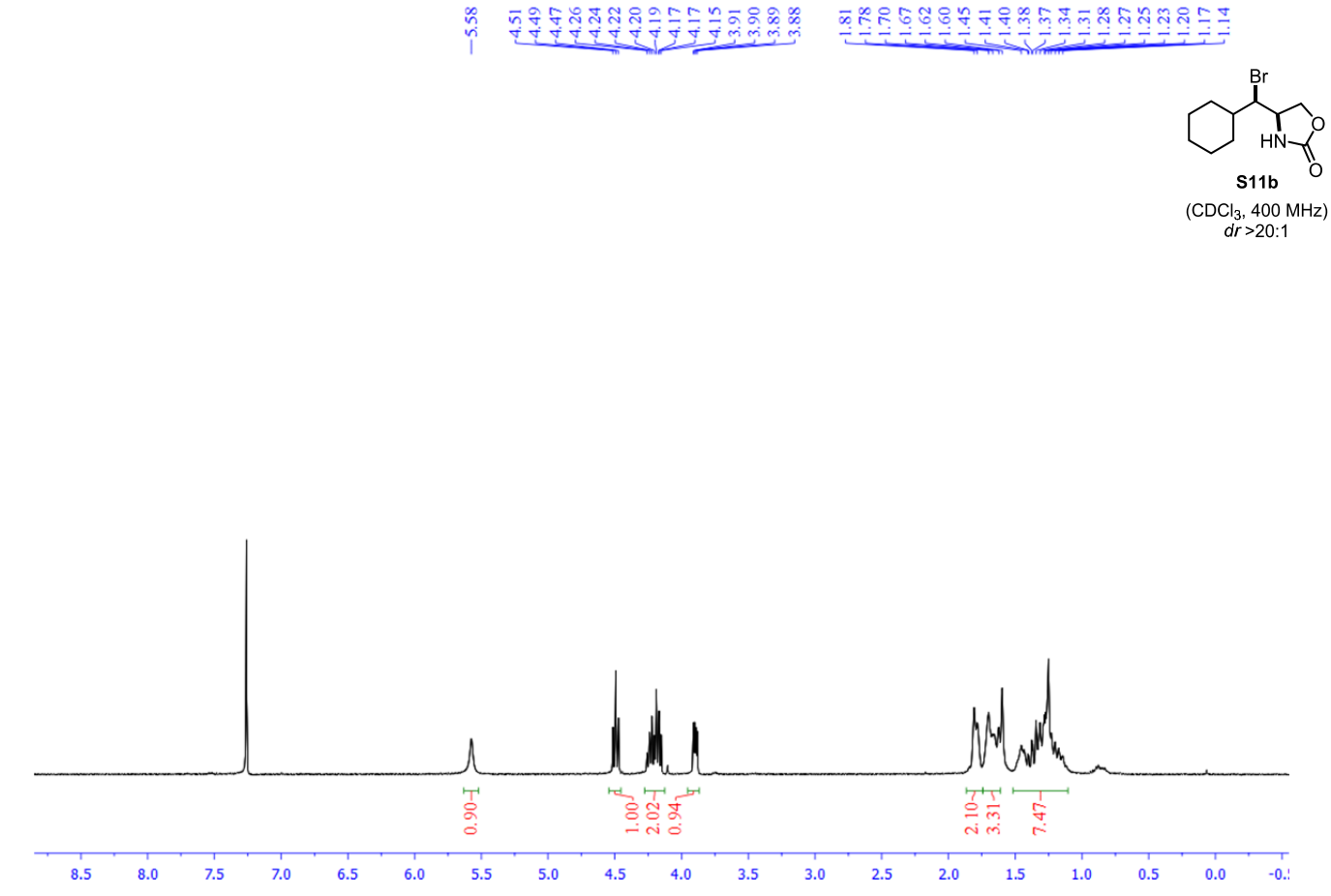


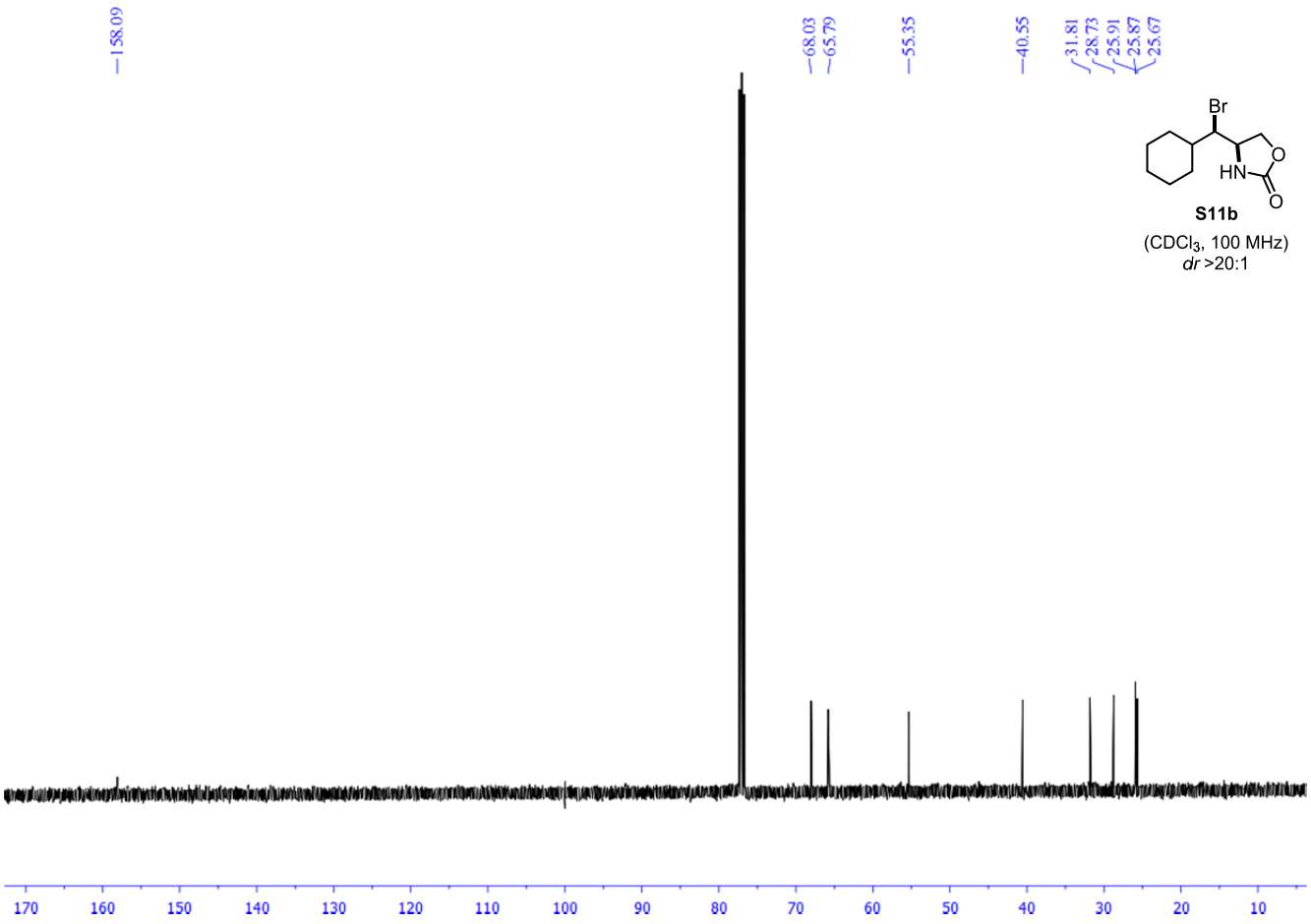
S10

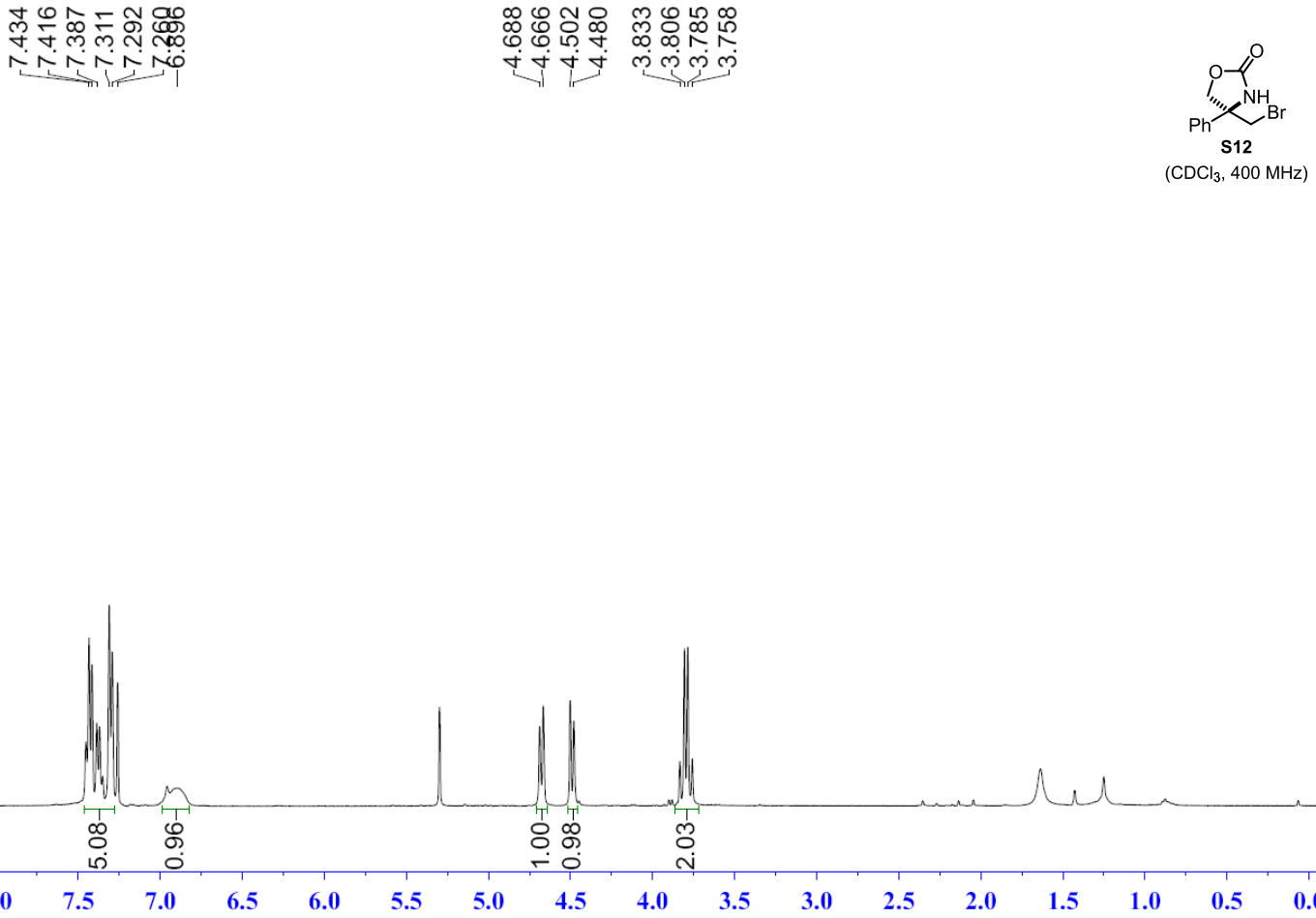
($CDCl_3$, 100 MHz)

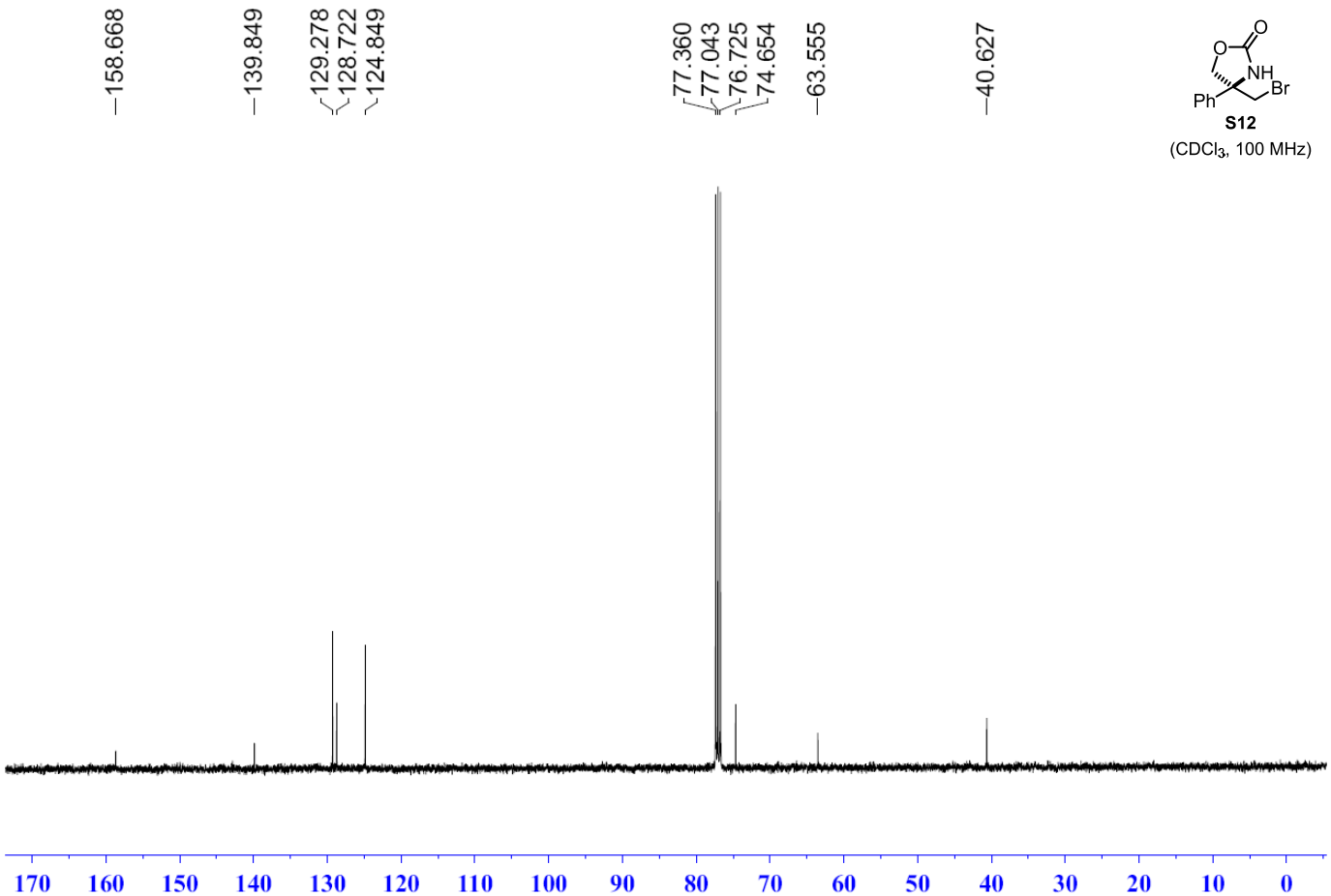

7.260
6.879
4.565
4.543
4.522
4.317
4.303
4.294
4.280
4.225
4.205
4.189
4.185
4.170
3.887
3.880
3.865
3.858
1.791
1.783
1.671
1.633
1.614
1.606
1.598
1.579
1.556
1.411
1.377
1.352
1.344
1.340
1.312
1.280
1.251
1.221
1.197
1.174
1.165
Br
HN
O
O
S11a
(CDCl3, 400 MHz)
dr >20:1
1.00
1.03
1.05
1.04
1.03
2.06
1.40
1.91
5.83
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

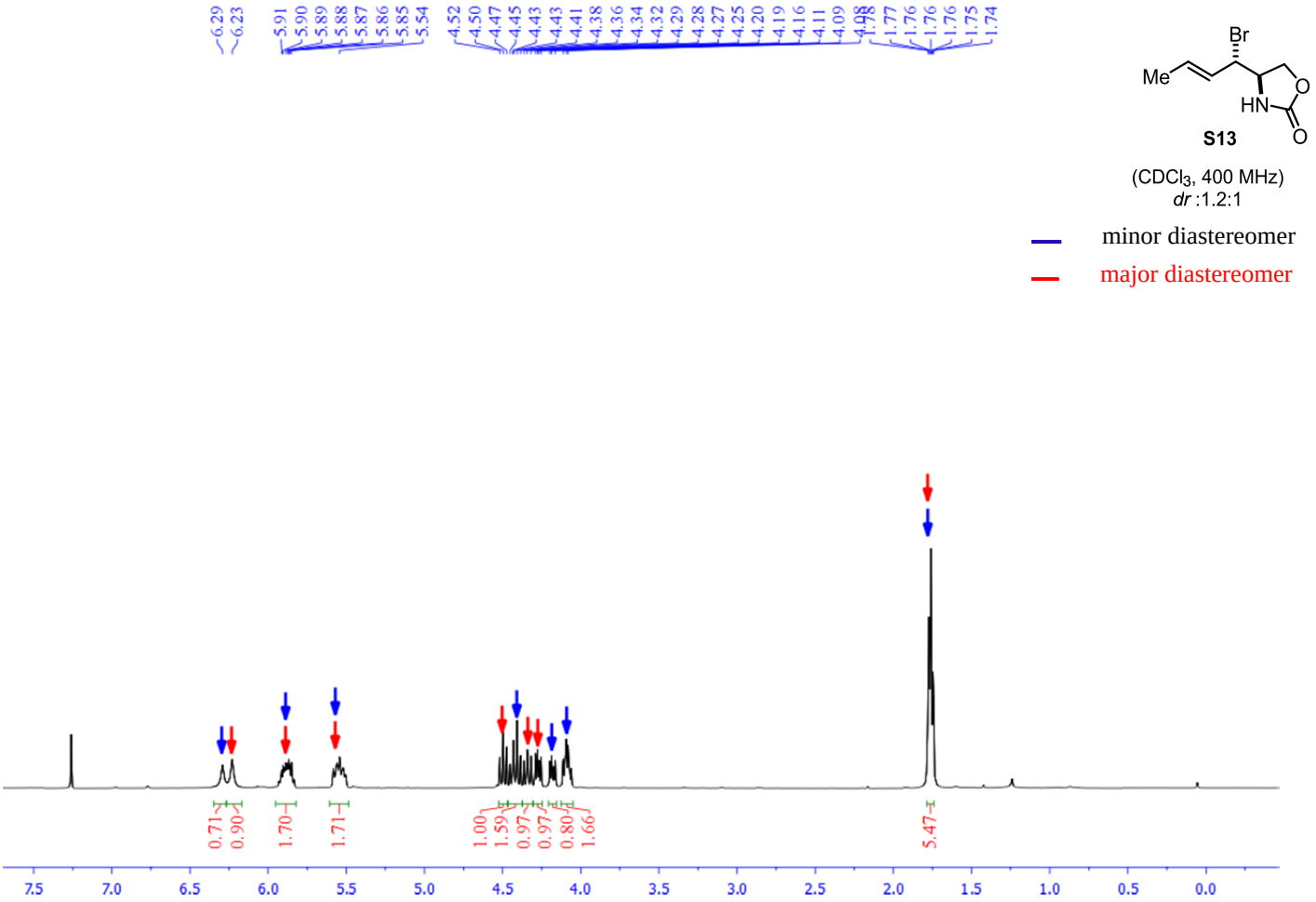

159.85
70.13
65.01
54.65
39.74
31.89
27.20
25.94
25.92
25.45
Br
HN
O
O
S11a
(CDCl3, 100 MHz)
dr >20:1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

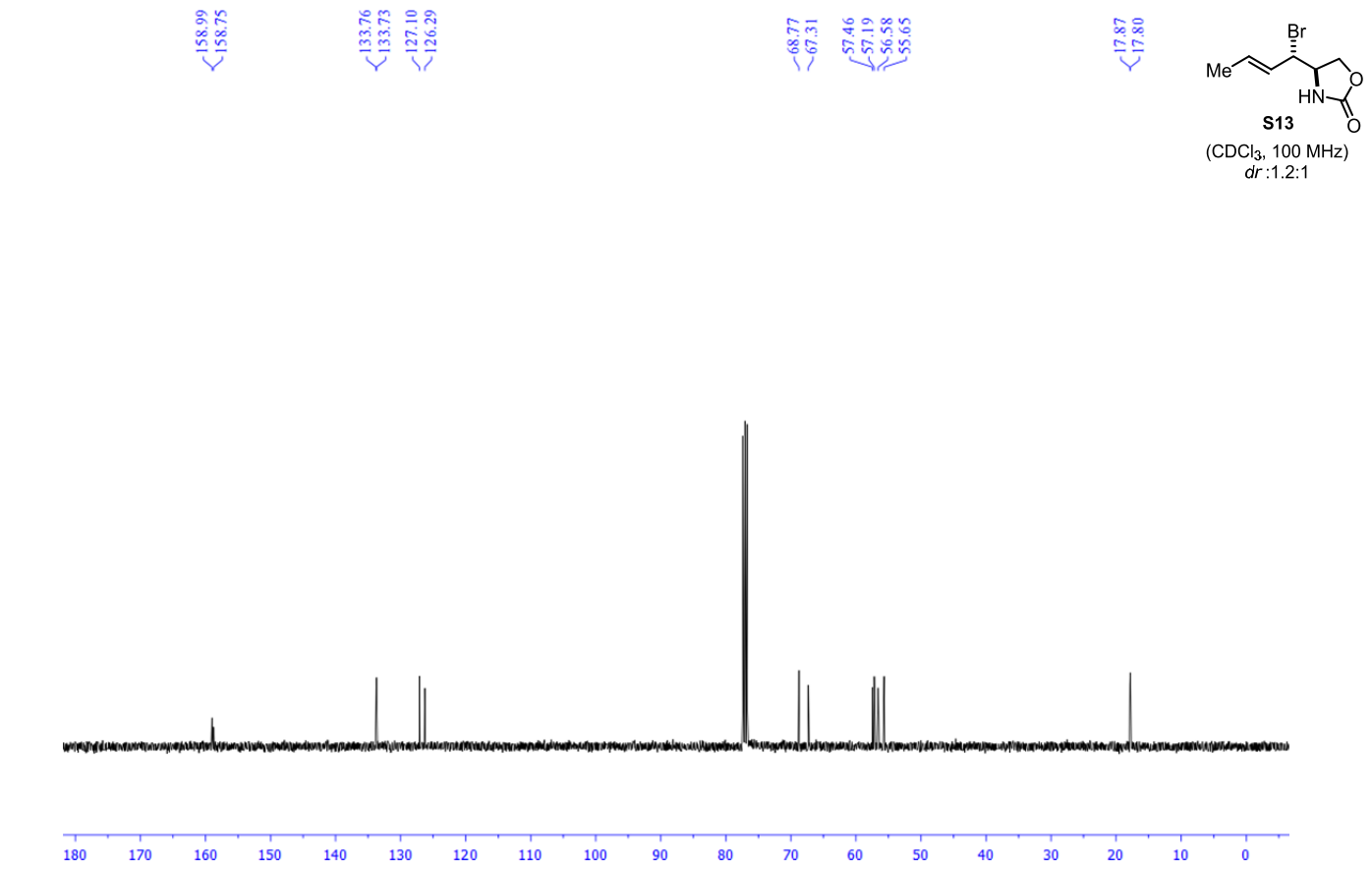

5.58
4.51
4.49
4.47
4.26
4.24
4.22
4.20
4.19
4.17
4.17
4.15
3.91
3.90
3.89
3.88
1.81
1.78
1.70
1.67
1.62
1.60
1.45
1.41
1.40
1.38
1.37
1.34
1.31
1.28
1.27
1.25
1.23
1.20
1.17
1.14
Br
HN
O
O
S11b
(CDCl3, 400 MHz)
dr >20:1
0.90
1.00
2.02
0.94
2.10
3.31
7.47
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

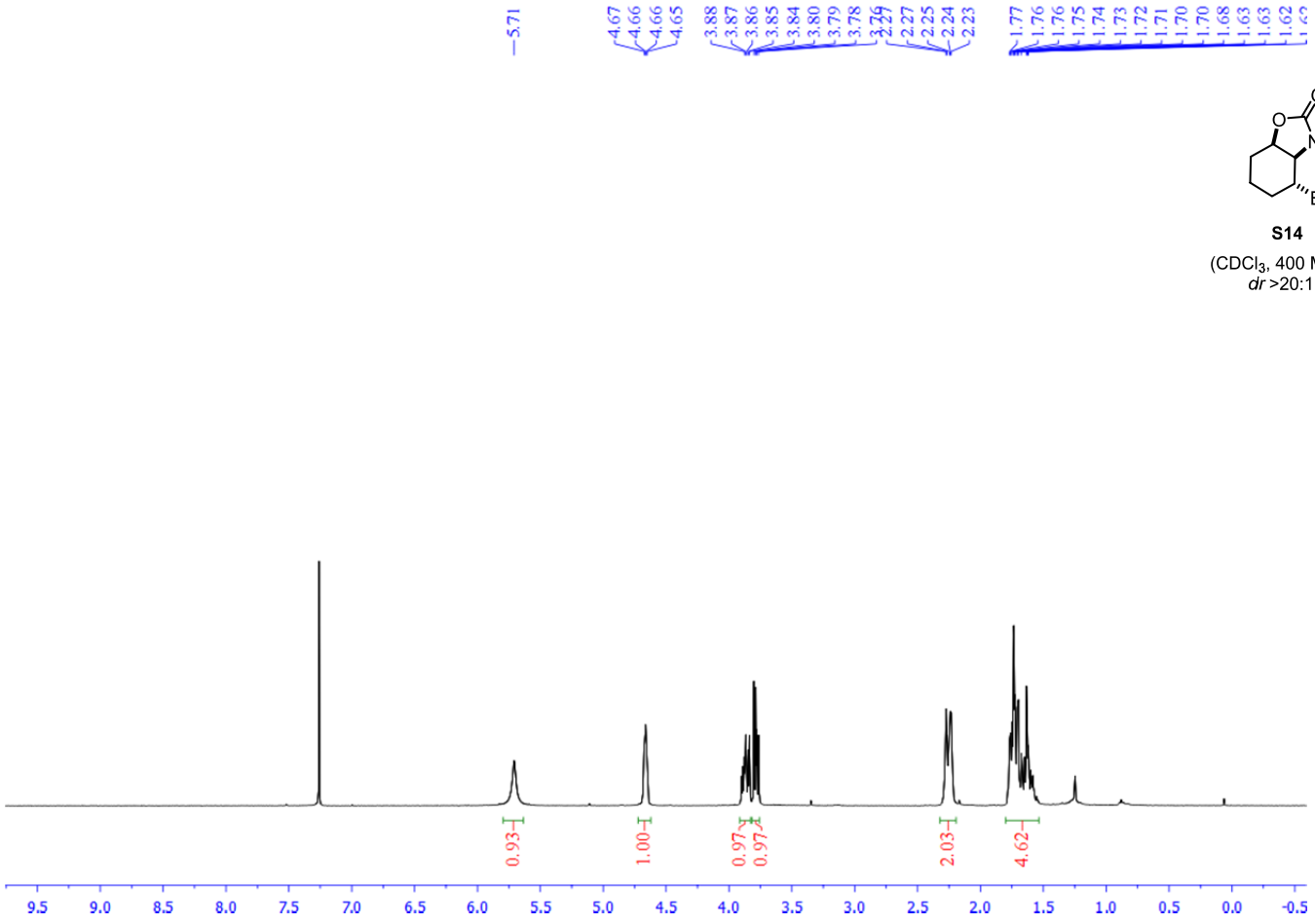

158.09
68.03
65.79
55.35
40.55
31.81
28.73
25.91
25.87
25.67
Br
HN
O
O
S11b
(CDCl3, 100 MHz)
dr >20:1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.434
7.416
7.387
7.311
7.292
7.260
6.896
4.688
4.666
4.502
4.480
3.833
3.806
3.785
3.758
O
O
NH
Br
Ph
S12
(CDCl3, 400 MHz)
5.08
0.96
1.00
0.98
2.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


158.668
139.849
129.278
128.722
124.849
77.360
77.043
76.725
74.654
63.555
40.627
O
O
NH
Br
Ph
S12
(CDCl3, 100 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

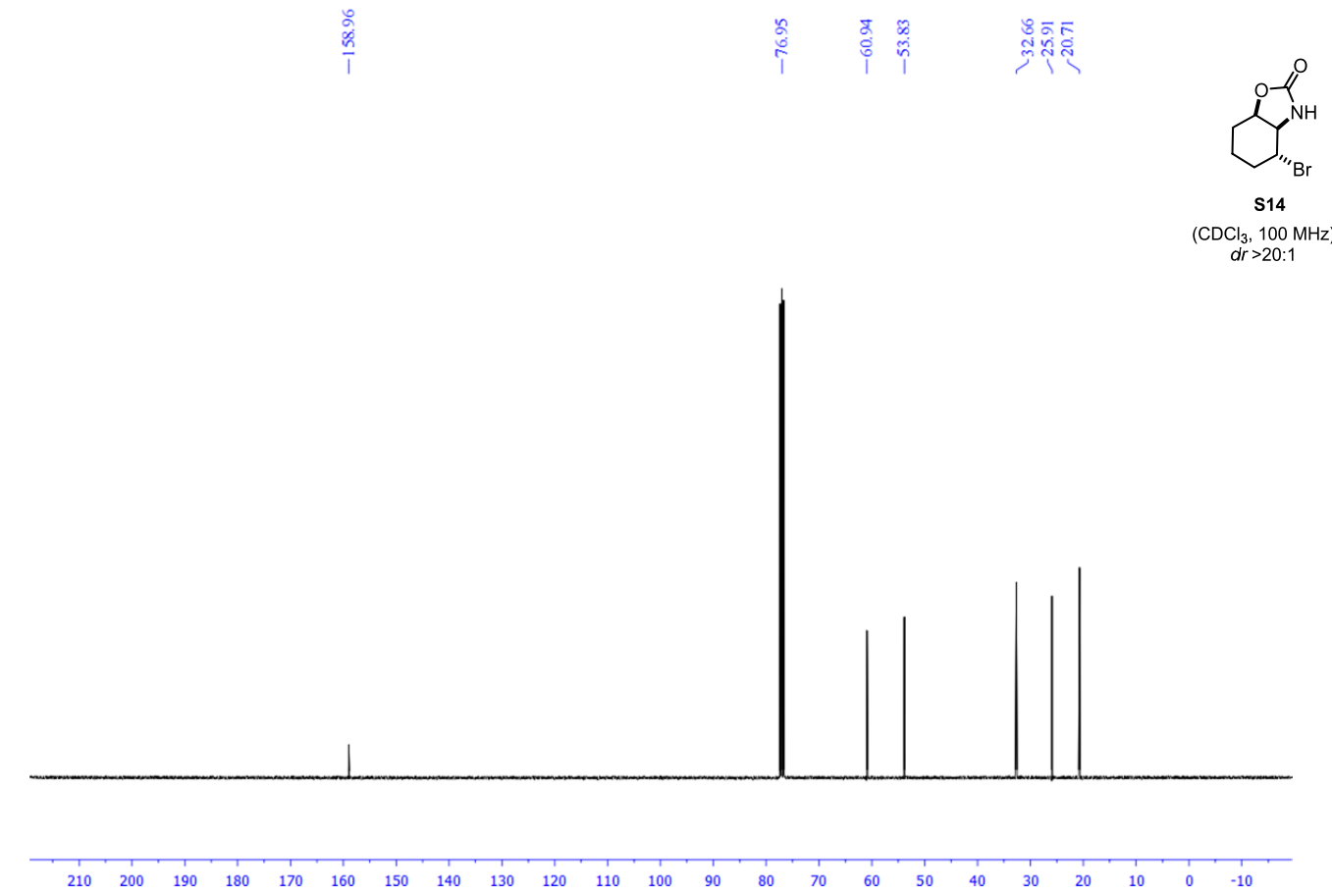

6.29
6.23
5.91
5.90
5.89
5.88
5.87
5.86
5.85
5.54
4.52
4.50
4.47
4.45
4.43
4.43
4.41
4.38
4.36
4.34
4.32
4.29
4.28
4.27
4.25
4.20
4.19
4.16
4.11
4.09
1.77
1.76
1.76
1.76
1.75
1.74
Br
Me
HN
O
O
S13
(CDCl3, 400 MHz)
dr :1.2:1
minor diastereomer
major diastereomer
0.71
0.90
1.70
1.71
1.00
1.59
0.97
0.97
0.80
1.66
5.47
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


158.99
158.75
133.76
133.73
127.10
126.29
68.77
67.31
57.46
57.19
56.58
55.65
17.87
17.80
Br
Me
HN
O
O
S13
(CDCl3, 100 MHz)
dr :1.2:1
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



S14

($CDCl_3$, 400 MHz)
dr >20:1



S14

($CDCl_3$, 100 MHz)
dr >20:1