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Supporting Information

Iron-Catalysed Enantioselective Carbometalation of Azabicycloalkenes

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1. General Experimental

All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of argon. The air- and moisture-sensitive liquids and solutions were transferred *via* syringes or a PTFE cannula. Analytical TLC was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). The TLC plates were visualized by exposure to UV light (254 nm) and by immersion in an acidic staining solution of *p*-anisaldehyde, followed by heating on a hot plate. The organic solutions were concentrated using rotary evaporation at *ca.* 40 hPa. Column chromatography was performed on prepacked silicagel cartridges (SNAP Ultra; Biotage, Uppsala, Sweden). Flash column chromatography was performed on Merck Silica Flash® 60 (spherical, neutral, 140–325 mesh), as described by Still *et* al.[1]

Instrumentation

NMR spectroscopy

^{1}H and ^{13}C NMR spectra were obtained using JEOL ECS-400 (391.8 MHz) NMR spectrometers. The proton chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane (TMS) and are referenced to TMS (δ 0.0) and $CHCl_3$ (δ 7.26). The chemical shifts of the carbon atoms are reported in parts per million (ppm, δ scale) downfield from TMS and referenced to the carbon resonance of $CDCl_3$ (δ 77.16). The data are presented as chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiple resonances, and br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers.

GC, GPC and HPLC analysis

GC analyses were performed using a Shimadzu GC-2010 plus analyzer equipped with an FID detector and a ZB-1MS capillary column (10 m × 0.1 mm i.d., film thickness = 0.1 μm). Gel-permeation chromatography was performed using JAIGEL-1H and JAIGEL-2H (40 mm i.d.) columns with an LC-9104 system (Japan Analytical Industry Co., Ltd.). HPLC analysis was performed on a JASCO LC-2000 series HPLC with CHIRALCEL IC-3 column.

IR analysis

IR spectra were recorded using a Perkin Elmer Spectrum One FT-IR spectrometer;

(1) Still, W. C.; Kahn, M.; Mitra, A *J. Org. Chem.* **1978,** *43,* 2923.

characteristic IR absorptions are reported in cm^{-1}.

HRMS and melting point

High-resolution mass spectra (HRMS) were recorded using fast atom bombardment (FAB) ionization with a JEOL JMS-700 mass spectrometer or electron spray ionization (ESI) with a Bruker Daltonics GmbH SolariX FT-ICR-MS spectrometer. Melting points were recorded using a Yanaco MP-500D instrument.

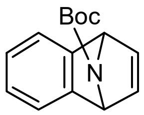
Materials

Anhydrous THF was purchased from Wako Pure Chemical Industries, Ltd. and distilled from benzophenone ketyl under argon (at atmospheric pressure) immediately before use. The water content of the solvent was determined using a Karl Fischer moisture titrator (MKC-610, Kyoto Electronics Manufacturing Co., Ltd.), and found to be <15 ppm.
Celite and Florisil (100–200 mesh) were purchased from NacalaiTesque, Inc. (*S,S)*-Chiraphos was purchased from Wako Pure Chemical Industries, Ltd. and Stream Chemicals Inc. and $FeCl_3$ (>99.99%) from Sigma-Aldrich Co. $ZnCl_2$ (99.9%) was purchased from Wako Pure Chemical Industries, Ltd. The commercially available aryl Grignard reagents were purchased from Kanto Chemical Co. Inc. or Sigma-Aldrich Co., and used without purification. We prepared other aryl Grignard reagents according to standard procedure.[2a,b] 2-Chloro-5-pyridylmagnesium bromide was prepared by direct insertion of magnesium into the C–Br bond in the presence of LiCl.[2c] Other chemicals were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., Ltd., Sigma-Aldrich Co., and other commercial suppliers, and were used after appropriate purification, unless otherwise stated.

(2) (a) *Handbook of Grignard Reagents;* Silverman, G. S., Rakita, P. E., Eds.; Marcel Dekker, Inc.: New York, 1996. (b) amEnde, D. J.; Clifford, P. J.; DeAntonis, D. M.; SantaMaria, C.; Brenek, S. J. *Organic Process Research & Development* **1999,** *3,* 319. (c) Leermann, T.; Leroux, F. R.; Colobert, F. *Org. Lett.* **2011,** *13,* 4479.

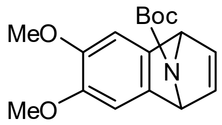
2. Preparation of Materials

***tert*-Butyl (1*R*,4*S*)-1,4-dihydro-1,4-epiminonaphthalene-11-carboxylate (1a)**



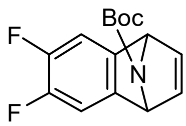
The title compound was prepared followed by the literature procedure.[3] The spectral data matched to that previously reported in the literature; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.37 (s, 9H, -C(CH_3)$_3$), 5.48 (br, 2H, -CHC*H*(N)C-), 6.94–7.00 (m, 4H, -C*H*CH(N)C-, -CC*H*CH-), 7.25–7.26 (m, 2H, -CCHC*H*-).

***tert*-Butyl (1*R*,4*S*)-6,7-dimethoxy-1,4-dihydro-1,4-epiminonaphthalene-11-carboxylate (1m)**



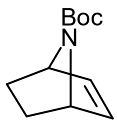
The title product was prepared followed by the literature.[3] The spectral data matched to that previously reported in the literature; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.38 (s, 9H, -C(CH_3)$_3$), 3.84 (s, 6H, -OCH_3), 5.44 (br, 2H), 6.97–7.02 (br, 4H).

***tert*-Butyl (1*R*,4*S*)-6,7-difluoro-1,4-dihydro-1,4-epiminonaphthalene-11-carboxylate (1l)**



The title product was prepared followed by the literature.[3] The spectral data matched to that previously reported in the literature; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.37 (s, 9H, -C(CH_3)$_3$), 5.44 (br, 2H, -CHC*H*(N)C-), 6.97 (br, 2H, -C*H*CH(N)C-), 7.09 (t, J = 7.4 Hz, 2H, -CC*H*CF-).

***tert*-Butyl (1*R*,4*S*)-7-azabicyclo[2.2.1]hept-2-ene-7-carboxylate (1n)**



The title product was prepared followed by the literature.[4] The spectral data matched to that previously reported in the literature; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.07 (d, J = 8.2 Hz, 2H, -C(N)CH_2CH$_2$-), 1.38 (s, 9H, -C(CH_3)$_3$), 1.82(d, J = 8.6 Hz, 2H, -C(N)CH_2CH$_2$-), 4.63 (br, 2H), 6.19 (br, 2H).

(3) Lautens, M.; Dockendorff, C. *Org. Lett.* **2003,** *5,* 3695-3698.
(4) Carroll, F. I.; Liang, F.; Navarro, H. A.; Brieaddy, L. E.; Abraham, P.; Damaj, M. I.; Martin, B. R. *J. Med. Chem.* **2001,** *44,* 2229.

3. Iron-Catalysed Asymmetric Carbometalation of Azabicyclic Alkenes with Arylzinc Reagents

General Procedure: Asymmetric Carbometalation Reaction

$ZnCl_2$ (1.7 equiv, 115.8 mg, 0.85 mmol) was dried by fusing *in vacuo* and cooled quickly followed by addition of 0.85 mL of THF to prepare a 1.0 M THF solution of $ZnCl_2$. After stirring for 20 minutes, ArMgBr (3.2 equiv) was added at 0 °C and stirred for 1.0 h to 2.0 h. Then, the solvent was removed and the resulting $Ar_2Zn \cdot 2MgBrCl$ was dried for 10 minutes under vacuum. To the arylzinc powder, a mixture of (*S,S*)-Chiraphos (8.5 mg, 0.02 mmol), THF (0.70 mL), toluene (3.2 mL), and $FeCl_3$ (100 µL, 0.1 M solution in THF, 0.01 mmol) was added followed by the addition of azabicyclic alkene (**1a**, 122 mg, 0.50 mmol) and the reaction mixture was stirred at −20 ºC or 0 ºC for 12–20 h. Degassed AcOH/MeOH (1:4) was added at 0 °C for quenching. The mixture was stirred for 10 minutes and then saturated aqueous NH_4Cl (1.0 mL) and MTBE were added. The separated aqueous layer was extracted with additional portions of MTBE (5 mL× 3). The combined organic extracts were passed through a pad of Florisil® and the filtrate was concentrated *in vacuo*. The residue was purified by silicagel column chromatography. The corresponding racemic sample was synthesized by using 1,2-bis(diphenylphosphino)benzene instead of (*S,S*)-Chiraphos.

4. Screening of Reaction Conditions for Iron-Catalysed Asymmetric Carbometalation Reactions

(a) Screening of chiral ligands and solvents

Based on our recent study on iron-catalysed enantioselective cross-coupling reactions,[5] we began our study by exploring effective chiral ligands and conditions for the carbometalation of azabicyclic alkene **1a** with diphenylzinc reagent **2a** in the presence of catalytic amounts of $FeCl_3$ and a ligand (Table S1 and Figure S1). Arene 1,2-bisphosphine ligands, bearing P-stereogenic centres, (*R,R*)-(+)-1,2-Bis(*tert*-butylmethylphosphino)benzene, (*R,R*)-BenzP* which is effective for the enantioselective cross-coupling reaction[5] did not show the reactivity for this carbometalation reaction (entry 1). However, (*R,R*)-2,3-Bis(*tert*-butylmethylphosphino)quinoxaline, (*R,R*)-QuinoxP* provided the product **3a** with moderate yield (50%) and low selectivity (12.3% ee, entry 2). The use of a P-chiral ligand, (1*S*,1*S'*,2*R*,2*R'*)-1,1'-di-*tert*-butyl-(2,2')-diphospholane, (*S,S',R,R'*)-Tangphos, with a rigid and chiral aliphatic backbone, provided the product with moderate selectivity (33.2% ee, entry 3). Axially chiral ligand (*R*)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, (*R*)-BINAP gave the racemic product with negligible yield (entry 4). The chiral alkylphosphine ligand (*R*)-(+)-1,2-bis(diphenylphosphino)propane, (*R*)-PROPHOS provided the product with high yield (94%) and moderate selectivity (42% ee, entry 5). Whereas, (2*S*,3*S*)-(−)-Bis(diphenylphosphino)butane**,** (*S,S*)-Chiraphos provided the product with the highest yield (>99%) and selectivity (77.2% ee, entry 6), suggesting that 1,2-bisphosphine containing chiral alkyl backbone is essential for achieving high enantioselectivity and high chemical yield. When we used (*S,S*)-xylyl-Chiraphos, we found selectivity of the product decreased (entry 7). Other bisphosphine ligands having flexible alkane backbone such as (−)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, (−)-DIOP;(2*S*,4*S*)-2,4-Bis(diphenylphosphino)pentane, (*S,S*)-BDPP and (+)-1,2-Bis((2*S*,5*S*)-2,5-diphenylphospholano)ethane, (*S,S*)-Ph-BPE showed moderate reactivity and selectivity (entries 8–10). Nitrogen-containing chiral ligands such as (*S*)-2-[2-(diphenylphosphino)phenyl]-4-isopropyl-4,5-dihydrooxazole, (*S*)-*i*-Pr-Phox and 2,6-Bis[(4*R*)-(+)-isopropyl-2-oxazolin-2-yl]pyridine, (*S,S*)-PyBOX showed moderate or no chiral induction (entries 11 and 12). In the absence of ligand, only 8% product was obtained (entry 13). Then we performed solvent screening and found mixed solvent toluene/THF = 4/1 is the best for achieving high chemical yield and high

(5) (a) Jin, M.; Adak, L.; Nakamura, M. *J. Am. Chem. Soc.* **2015,** *137,* 7128. (b) Sharma, A. K.; Sameera, W. M. C.; Jin, M.; Adak, L.; Okuzono, C.; Iwamoto, T.; Kato, M.; Nakamura, M.; Morokuma, K. *J. Am. Chem. Soc.* **2017,** *139,* 16117.

enantioselectivity (entries 14–18 vs 6). Dichloromethane, which is not a good solvent for iron-catalyzed cross-coupling reactions[5] but here it provided 80% yield and good selectivity (72% ee, entry 19). The reactivity decreased when 1,4-dioxane solvent was used (entry 20). This is because dioxane coordinates with the magnesium salts and consequently slows down the transmetalation step from *in-situ* generated diphenylzinc to iron centre (see the reaction mechanism). Another ethereal solvent, Methyl *tert*-butyl ether (MTBE) provided good yield (98%) and selectivity (74.6% ee, entry 21). The reaction did not proceed in *N*-methylpyrrolidinone (NMP) solvent, and 92% starting material was recovered, suggesting that this strongly coordinating solvent displace the chiral ligands from iron centers, facilitating the formation of ferrate species[6] (entry 22). The enantioselectivity of products increased by lowering the temperature, and the best selectivity (82% ee) was obtained at –20 ºC (entries 23 and 24).

Chiral ligands

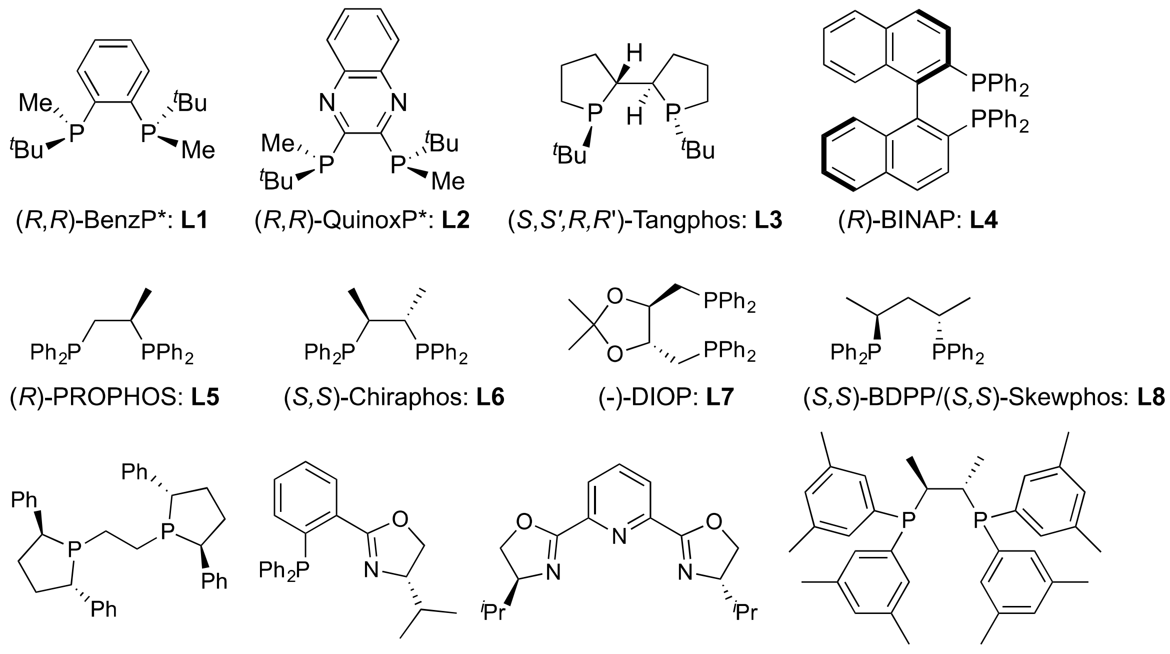
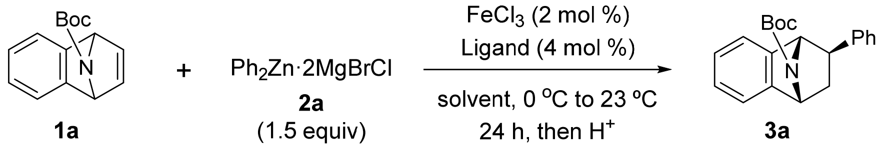


Figure S1. Chiral ligands used for screening (see Table S1).

(6) Fürstner, A.; Leitner, A.; Méndez, M.; Krause, H. *J. Am. Chem. Soc.* **2002,** *124,* 13856.

Table S1. Screening of Reaction Conditions for Iron-Catalysed Asymmetric Carbometalation Reactions[a]



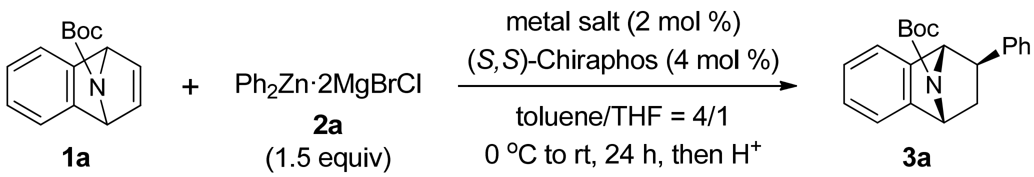
Entry	Ligand	Solvent	Yield (%)[b]	ee (%)[c]	RSM (%)[b]
1	(*R,R*)-BenzP*: **L1**	toluene/THF = 4/1	2	6	86
2	(*R,R*)-QuinoxP*: **L2**	toluene/THF = 4/1	50	12.3	41
3	(S,S'*R,R'*)-Tangphos: **L3**	toluene/THF = 4/1	25	33.2	65
4	(*R*)-BINAP: **L4**	toluene/THF = 4/1	5	<1	88
5	(*R*)-PROPHOS: **L5**	toluene/THF = 4/1	94	42	N.D.
6	**(*S,S*)-Chiraphos: L6**	**toluene/THF = 4/1**	**>99**	**77.2**	**0**
7	(*S,S*)-xylyl-chiraphos: **L12**	toluene/THF = 4/1	98	35.5	0
8	(-)-DIOP: **L7**	toluene/THF = 4/1	62	7	5
9	(*S,S*)-BDPP: **L8**	toluene/THF = 4/1	54	49.3	30
10	(*S,S*)-Ph-BPE: **L9**	toluene/THF = 4/1	54	<1	35
11	(*S*)-*i*-Pr-Phox: **L10**	toluene/THF = 4/1	27	17.3	65
12	(*S,S*)-PyBOX: **L11**	toluene/THF = 4/1	50	<1	40
13	none	toluene/THF = 4/1	8	-	86
14	(*S,S*)-Chiraphos: **L6**	toluene	99	77.0	0
15[d]	(*S,S*)-Chiraphos: **L6**	THF	93	74.8	0
16	(*S,S*)-Chiraphos: **L6**	toluene/THF = 1/1	97	77.19	0
17	(*S,S*)-Chiraphos: **L6**	toluene/THF = 2/1	99	76.5	0
18[d]	(*S,S*)-Chiraphos: **L6**	toluene/THF = 1/2	96	74.6	0
19	(*S,S*)-Chiraphos: **L6**	CH_2Cl_2	80	72	0
20	(*S,S*)-Chiraphos: **L6**	1,4-Dioxane	36	71.4	60
21	(*S,S*)-Chiraphos: **L6**	MTBE	98	74.6	0
22	(*S,S*)-Chiraphos: **L6**	NMP	0	-	92
23[e]	**(*S,S*)-Chiraphos: L6**	**toluene/THF = 4/1**	**99**	**78**	**0**
24[f]	**(*S,S*)-Chiraphos: L6**	**toluene/THF = 4/1**	**94**	**81.5**	**0**

[a]All reactions were performed on 0.5 mmol scale and reactions were quenched by using degassed MeOH/AcOH = 80/20 (1.0 mL). [b]Yields were determined by ^{1}H NMR analysis, using 1,1,2,2-tetrachloroethane as an internal standard. [c] The ee values were determined by chiral HPLC analysis on a CHIRALCEL IC-3 column (4.6 mm i.d., 150 mm length) under the following conditions: Hexane:IPA = 99:1, 1.0 mL/min, 4.4 °C. [d]Ring-opening product was obtained (1%). [e]This reaction was performed at 0 °C for 13 h. [f]Reaction was done at –20 °C for 17 h.

(b) Effect of Catalyst Amount and Metal Salts on Asymmetric Carbometalation Reaction

Table S2 shows the effects of the catalyst loading and other metal salts on the asymmetric carbometalation reaction of **1a** with **2a**. A 1:1 ratio of iron/ligand also achieved comparable chiral induction to give the corresponding product in 74.3% ee, while higher yields and ee were observed by using excess amounts of ligand to iron (entries 1−3). In the absence of iron salt, the reaction did not proceed and the starting material was recovered in a quantitative amount (entry 4). The results achieved with $Fe(acac)_3$, $Fe(acac)_2$, and $FeBr_3$ were comparable to those with $FeCl_3$ (entries 5, 6, and 7). Other transition-metal chlorides did not afford the desired products under the present conditions (entries 8− 11).

Table S2. Effect of Catalyst Amount and Metal Salts on Iron-Catalysed Asymmetric Carbometalation Reactions[a]



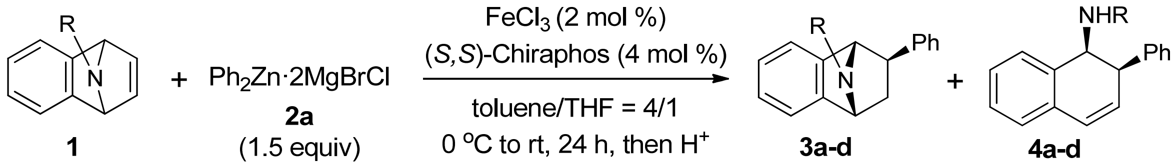
entry	metal salt (mol %)	(*S,S*)-Chiraphos (mol %)	yield (%)[b]	ee (%)[c]	RSM (%)[b]
1	$FeCl_3$ (2)	4	>99	77.2	N.D.
2	$FeCl_3$ (2)	2	86	74.3	7
3	$FeCl_3$ (1)	2	87	77.2	6
4	-	4	N.D.	-	>99
5	$Fe(acac)_3$ (2)	4	93[d]	72	N.D.
6	$Fe(acac)_2$ (2)	4	96[d]	74	N.D.
7	$FeBr_3$ (2)	4	95[d]	73	N.D.
8	$CoCl_2$ (2)	4	N.D.	-	86
9	$NiCl_2$ (2)	4	<1	-	85
10	$CuCl_2$ (2)	4	N.D.	-	>99
11	$Pd(CH_3CN)_2Cl_2$ (2)	4	N.D.	-	97

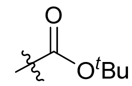
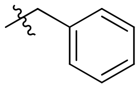
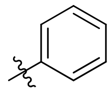
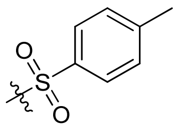
[a]All reactions were performed on 0.5 mmol scale and reactions were quenched by using degassed MeOH/AcOH = 80/20 (1.0 mL). [b]Yields were determined by ^{1}H NMR analysis, using 1,1,2,2-tetrachloroethane as an internal standard. [c]The ee values were determined by chiral HPLC analysis on a CHIRALCEL IC-3 column (4.6 mm i.d., 150 mm length) under the following conditions: Hexane:IPA = 99:1, 1.0 mL/min, 5 °C. [d]Isolated yield.

(c) Effect of Substituents on Nitrogen of Azabicyclic Alkenes

Several azabicyclic alkenes containing different nitrogen-protecting groups were studied for the iron-catalyzed enantioselective carbometalation reactions; the results are shown in Table S3. When *tert*-butoxycarbonyl (Boc) group was introduced as substituent, the target compound **3a** was obtained in 94% yields with an enantiomeric excess of 78% (entry 1). Once a benzyl group was introduced on nitrogen, the substrate was completely consumed but expected carbometalated compound **3b** was obtained with a low yield of 18% and also with a low enantiomeric excess of 7%. At this time, the ring-opened product **4b** was obtained as a by-product with a yield of 42% and an enantiomeric excess of 3% (entry 2). Subsequently, when a phenyl group was introduced as a substituent, the desired product **3c** was found in an amount of 29%, and the ring-opened product **4c** was given in a yield of 51% (entry 3). However, the enantiomeric excess was greatly improved, 82% of the preferred **3c**, 79% of the ring-opened product **4c**. Subsequently, when a tosyl group was introduced as a substituent, the reactivity was slightly low. 10% of the substrate was recovered and the desired product **3d** was obtained in a yield of 76% with low enantioselectivity (40%) (entry 4). The best yield and enantioselectivity of desired product were obtained when the Boc group was introduced as a substituent; the Boc group was determined as an optimal substituent on nitrogen.

Table S3. Effect of Substituents on Nitrogen of Azabicyclic Alkenes

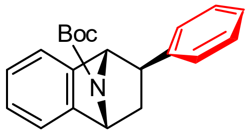


Entry	R	Yield (ee) of **3**^{a,b}	Yield (ee) of **4**^{a,b}	RSM (%)
1		94 (78) (**3a**)	N.D. (-) (**4a**)	N.D.
2		18 (7) (**3b**)	42 (3) (**4b**)	N.D.
3		29 (82) (**3c**)	51 (79) (**4c**)	N.D.
4		76^{c} (40) (**3d**)	7^{c} (57) (**4d**)	10

^{a}Isolated yield. ^{b}Enantiomeric excess were determined by chiral HPLC (CHIRALCEL IC-3, Hexane/IPA = 99/1, 5 °C). ^{c}The ratio of products were determined by ^{1}H NMR spectra.

5. Product Characterization Data

***tert*-Butyl (*1S,2R,4R*)-2-phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3a)** (Table 1)

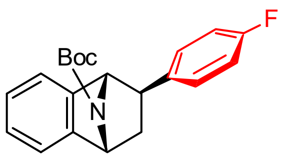


The reaction was carried out according to the general procedure using **1a** (121.7 mg, 0.50 mmol), phenylmagnesium bromide (1.73 mL, 0.925 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.85 mL of 1.0 M solution in THF, 1.7 equiv). The reaction was performed at −20 °C for 16 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 95/5) to give the title product in 94% yield (151.5 mg, 82% ee) as a white solid.

The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 99/1, 1.0 mL/min, 4.4 °C. Retention times (t_r) = 13.62 min (major) and 15.65 min (minor).

M.p. 98.8–100.3 °C; IR (neat) ν 666, 703, 748, 761, 851, 908, 948, 980, 1077, 1088, 1157, 1173, 1265, 1363, 1459, 1695, 2971, 3027 cm^{-1}; ^1H NMR (391.8 MHz, $CDCl_3$) δ 1.32 (s, 9H), 1.93 (dd, *J* = 11.9, 8.9 Hz, 1H), 2.19 (dt, *J* = 11.7, 4.5 Hz, 1H), 2.84 (dd, *J* = 8.5, 4.5 Hz, 1H), 5.08 (br, 1H), 5.24 (br, 1H), 7.15–7.39 (m, 9H); ^{13}C NMR (98.5 MHz,$CDCl_3$) δ 28.3 (3C), 37.4 (br), 46.6 (br), 61.2 (br), 67.3 (br), 80.2, 120.1, 126.5, 126.6 (2C), 126.7, 127.6 (2C), 128.6 (3C), 144.4, 146.0, 155.5; HRMS (FAB): *m/z* $[M+H]^+$calcd for $C_{21}H_{24}NO_2$ 322.1807, found 322.1804; Anal. Calcd for $C_{21}H_{23}NO_2$ C, 78.47; H, 7.21; N, 4.36. Found C, 78.22; H, 7.31; N, 4.20.$[\alpha]^{25}_D$ +63.7 (*c*1.0, CH_2Cl_2). All analytical data are in good accordance with those reported in the literature.[7]

***tert*-Butyl (1*S*,2*R*,4*R*)-2-(4-fluorophenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3b)** (Table 1)

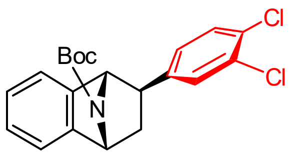


The reaction was carried out according to the general procedure using **1a** (122.0 mg, 0.50 mmol), 4-fluorophenylmagnesium bromide (1.60 mL, 1.00 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.85 mL of 1.0 M solution in THF, 1.7 equiv). Reaction was run at −20 °C for 12 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 95/5) to give the title product in 95% yield (161.9 mg, 83% ee) as a white solid. The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 99/1, 1.0 mL/min, 4.3 °C. Retention times (t_r) = 6.25 min (major) and 6.80 min (minor);

(7) Ito, S.; Itoh, T.; Nakamura, M. *Angew.Chem. Int. Ed.* **2011,** *50,* 454–457.

M.p. 78.3–80.9 °C; IR (neat): 568, 639, 754, 824, 900, 1087, 1138, 1164, 1230, 1281, 1363, 1419, 1509, 1606, 1692, 2977 cm^{-1}; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.32 (s, 9H), 1.93 (dd, J = 11.9, 8.7 Hz, 1H), 2,13 (dt, J = 12.1, 4.5 Hz, 1H), 2.82 (dd, J = 8.6, 4.5 Hz, 1H), 5.02 (br, 1H), 5.23 (br, 1H), 7.00 (t, J = 8.7 Hz, 2H), 7.14–7.17 (m, 2H), 7.29–7.35 (m, 4H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 28.3 (3C), 37.8 (br), 45.8 (br), 61.3 (br), 67.5 (br), 80.3, 115.3 (d, $J_{C\text{-}F}$ = 20.7 Hz, 2C), 120.1, 126.6 (2C), 126.7 (2C), 129.0 (d, $J_{C\text{-}F}$ = 7.5 Hz, 2C), 140.2 (d, $J_{C\text{-}F}$ = 2.8 Hz, 1C), 146.0, 155.7, 161.7 (d, $J_{C\text{-}F}$ = 244.3 Hz, 1C); HRMS (FAB): *m/z* [M+H]$^+$ calcd for $C_{21}H_{23}FNO_2$ 340.1713, found 340.1714; Anal. Calcd for $C_{21}H_{22}FNO_2$ C, 74.31; H, 6.53; N, 4.13; F, 5.60. Found C, 74.30; H, 6.64; N, 4.07; F, 5.61. $[\alpha]^{25}_{D}$ +55.8 (c1.0, CH_2Cl_2).

***tert*-Butyl (1*S*,2*R*,4*R*)-2-(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3c)** (Table 1)

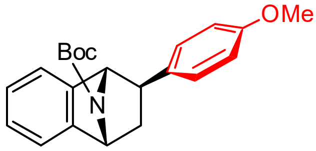


The reaction was carried out according to the general procedure using **1a** (121.9 mg, 0.50 mmol), 3,4-dichlorophenylmagnesium bromide (3.2 mL, 0.50 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.75 mL of 1.0 M solution in THF, 1.7equiv). Reaction was run at 0 °C for 16 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 95/5) to give the title product in 85% yield (166.2 mg, 77% ee) as a white solid.

The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 99/1, 1.0 mL/min, 5.3 °C. Retention times (t_r) = 10.86 min (major) and 11.93 min (minor);

M.p. 88.8–90.1 °C; IR (neat): 572, 705, 757, 792, 814, 949, 892, 905, 1027, 1075, 1089, 1140, 1153, 1169, 1288, 1259, 1273, 1290, 1328, 1366, 1392, 1461, 1476, 1560, 1679, 2974 cm^{-1}; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.34 (s, 9H), 1.93 (dd, J = 11.9, 8.7 Hz, 1H), 2.13 (dt, J = 11.8, 4.5 Hz, 1H), 2.78 (dd, J = 8.6, 4.5 Hz, 1H), 5.02 (br, 1H), 5.24 (br, 1H), 7.15–7.18 (m, 2H), 7.21 (d, J = 9.0 Hz, 1H), 7.29 (t, J = 3.4 Hz, 2H), 7.36 (d, J = 8.5 Hz, 1H), 7.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 28.3 (3C), 37.9 (br), 45.5 (br), 61.1 (br), 67.1, 80.6, 120.2, 126.7 (2C), 126.9, 127.1, 129.5, 130.5 (2C), 132.5, 144.8 (2C), 145.9, 155.3; HRMS (FAB): *m/z* [M+H]$^+$ calcd for $C_{21}H_{22}Cl_2NO_2$ 390.1028, found 390.1029; Anal. Calcd for $C_{21}H_{21}Cl_2NO_2$ C, 64.62; H, 5.42; N, 3.59. Found C, 64.78; H, 5.53; N, 3.61. $[\alpha]^{25}_{D}$ +58.6 (c1.0, CH_2Cl_2).

***tert*-Butyl (1*S*,2*R*,4*R*)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3d)** (Table 1)

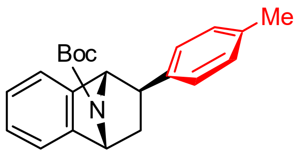


The reaction was carried out according to the general procedure using **1a** (121.7 mg, 0.50 mmol), 4-methoxyphenylmagnesium bromide (1.52 mL, 1.05 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.85 mL of 1.0 M solution in THF, 1.7 equiv). Reaction was run at −20 °C for 12 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 95/5) to give the title product in 99% yield (173.9 mg, 80% ee) as a white solid.

The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 90/10, 1.0 mL/min, 4.5 °C. Retention times (t_r) = 6.08 min (major) and 6.78 min (minor);

M.p. 78.0–80.2 °C; IR (neat): 656, 762, 790, 819, 903, 1031, 1081, 1141, 1156, 1168, 1245, 1284, 1339, 1459, 1512, 1608, 1693, 2977, 3024 cm^{-1}; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.32 (s, 9H), 1.91 (dd, J = 11.9, 8.7 Hz, 1H), 2.14 (dt, J = 12.1, 4.5 Hz, 1H), 2.79, (dd, J = 8.6, 4.5 Hz, 1H), 3.80 (s, 3H), 5.01 (br, 1H), 5.24 (br, 1H), 6.86 (d, J = 8.9 Hz, 2H), 7.13–7.16 (m, 2H), 7.27–7.30 (m, 4H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 28.3 (3C), 37.4 (br), 45.8 (br), 55.4, 61.0 (br), 67.6 (br), 80.1, 113.9 (2C), 120.0, 126.4 (2C), 126.5 (2C), 128.5 (2C), 136.5, 146.0, 155.6, 158.3; HRMS (FAB): m/z $[M+H]^+$ calcd for $C_{22}H_{26}NO_3$ 352.1913, found 352.1912; Anal. Calcd for $C_{22}H_{25}NO_3$ C, 75.19; H, 7.17; N, 3.99. Found C, 75.08; H, 7.26; N, 3.98. $[\alpha]^{25}_{D}$ +71.6 (c1.0, CH_2Cl_2).

***tert*-Butyl (1*S*,2*R*,4*R*)-2-(4-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3e)** (Table 1)

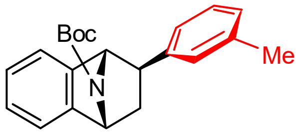


The reaction was carried out according to the general procedure using **1a** (122.0 mg, 0.50 mmol), 4-methylphenylmagnesium bromide (1.53 mL, 1.04 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.85 mL of 1.0 M solution in THF, 1.7 equiv). Reaction was run at −20 °C for 24 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 95/5) to give the title product in 91% yield (160.6 mg, 81% ee) as a white solid.

The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 99/1, 1.0 mL/min, 5.3 °C. Retention times (t_r) = 8.10 min (major) and 9.10 min (minor);

M.p. 91.4–93.1 °C; IR (neat): 655, 718, 732, 778, 807, 825, 842, 854, 871, 909, 939, 1007, 1020, 1088, 1134, 1156, 1174, 1254, 1282, 1365, 1385, 1459, 1514, 1691, 2974 cm^{-1}; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.32 (s, 9H), 1.92 (dd, J = 11.9, 8.7 Hz, 1H), 2.17 (dt, J = 11.9, 4.5 Hz, 1H), 2.34 (s, 3H), 2.80 (dd, J = 8.7, 4.5 Hz, 1H), 5.04 (br, 1H), 5.24 (br, 1H), 7.12–7.17 (m, 4H), 7.26 (d, J = 8.2 Hz, 4H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 20.9, 28.2 (3C), 37.3 (br), 46.0 (br), 61.0 (br), 67.4, 79.9, 119.9, 126.3, 126.4 (2C), 127.3 (2C), 128.9 (3C), 135.9, 141.2, 145.9, 155.4; HRMS (FAB): *m/z* $[M+H]^+$ calcd for $C_{22}H_{26}NO_2$ 336.1964, found 336.1962; Anal. Calcd for $C_{22}H_{25}NO_2$ C, 78.77; H, 7.51; N, 4.18. Found C, 78.74; H, 7.63; N, 4.07. $[\alpha]^{25}_D$ +73.0 (*c*1.0, CH_2Cl_2).

***tert*-Butyl (1*S*,2*R*,4*R*)-2-(3-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3f)** (Table 1)

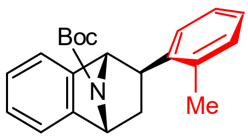


The reaction was carried out according to the general procedure using **1a** (121.8 mg, 0.50 mmol), 3-methylphenylmagnesium bromide (2.05 mL, 0.78 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.85 mL of 1.0 M solution in THF, 1.7 equiv). Reaction was run at −20 °C for 18 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 95/5) to give the title product in 88% yield (147.6 mg, 85% ee) as a white solid.

The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 98/2, 1.0 mL/min, 5.3 °C. Retention times (t_r) = 6.62 min (major) and 7.39 min (minor);

M.p. 81.6–82.1 °C; IR (neat): 660, 781, 797, 821, 851, 872, 907, 1022, 1092, 1140, 1154, 1173, 1250, 1290, 1368, 1393, 1459, 1597, 1692, 2982 cm^{-1}; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.32 (s, 9H), 1.91 (dd, J = 11.9, 8.7 Hz, 1H), 2.18 (dt, J = 11.8, 4.5 Hz, 1H), 2.35 (s, 3H), 2.80 (dd, J = 8.7, 4.5 Hz, 1H), 5.07 (br, 1H), 5.25 (br, 1H), 7.04 (d, J = 7.3 Hz, 1H), 7.13–7.23 (m, 5H), 7.25–7.29 (m, 2H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 21.6, 28.3 (3C), 37.4 (br), 46.5 (br), 60.9 (br), 67.3, 80.1, 119.8, 124.6, 126.5 (2C), 126.6, 127.3 (2C), 128.3, 128.5, 138.1, 144.4, 146.0, 155.4; HRMS (FAB): *m/z* $[M+Na]^+$ calcd for $C_{22}H_{25}NO_2Na$ 358.1783, found 358.1782; Anal. Calcd for $C_{22}H_{25}NO_2$ C, 78.77; H, 7.51; N, 4.18. Found C, 78.57; H, 7.59; N, 4.16. $[\alpha]^{25}_D$ +64.1 (*c*1.0, CH_2Cl_2).

***tert*-Butyl (1*S*,2*R*,4*R*)-2-(2-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3g)** (Table 1)

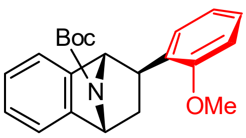


The reaction was carried out according to the general procedure using **1a** (127.7 mg, 0.52 mmol), 2-methylphenylmagnesium bromide (1.48 mL, 1.08 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.85 mL of 1.0 M solution in THF, 1.7 equiv). Rection was run at 0 °C for 24 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 95/5) to give the title product in 93% yield (163.8 mg, 99% ee) as a white solid.

The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 99/1, 1.0 mL/min, 4.4 °C. Retention times (t_r) = 8.93 min (major) and 10.27 min (minor);

M.p. 63.7–65.3 °C; IR (neat): 752, 762, 854, 908, 1086, 1138, 1157, 1175, 1265, 1364, 1376, 1459, 1693, 2954, 2972 cm^{-1}; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.34 (s, 9H), 1.94–2.06 (m, 2H), 2.21 (s, 3H), 2.97 (dd, J = 8.5, 4.9 Hz, 1H), 5.22 (br, 2H), 7.13–7.18 (m, 4H), 7.19–7.25 (m, 1H), 7.30 (br, 2H), 7.55 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 20.0, 28.3 (3C), 36.6 (br), 42.0 (br), 61.4 (br), 66.2 (br), 80.2, 120.2, 125.6, 126.2 (2C), 126.5 (2C), 126.6 (2C), 130.1, 135.9, 142.6, 146.3, 155.5; HRMS (FAB): *m/z* $[M+H]^+$ calcd for $C_{22}H_{26}NO_2$ 336.1964, found 336.1966; Anal. Calcd for $C_{22}H_{25}NO_2$ C, 78.77; H, 7.51; N, 4.18. Found C, 78.71; H, 7.43; N, 4.12. $[\alpha]^{25}_D$ +123.4 (*c*1.0, CH_2Cl_2).

***tert*-Butyl (1*S*,2*R*,4*R*)-2-(2-methoxyphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3h)** (Table 1)

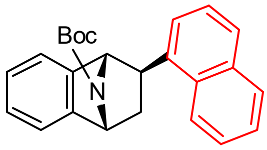


The reaction was carried out according to the general procedure using **1a** (128.0 mg, 0.53 mmol), 2-methoxyphenylmagnesium bromide (1.68 mL, 0.95 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.85 mL of 1.0 M solution in THF, 1.7 equiv). Reaction was run at 0 °C for 24 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 95/5) to give the title product in 90% yield (165.0 mg, 93% ee) as a white solid.

The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 90/10, 1.0 mL/min, 1 °C. Retention times (t_r) = 10.02 min (major) and 11.23 min (minor);

M.p. 149.6–151.7 °C; IR (neat): 662, 753, 764, 902, 911, 1029, 1120, 1137, 1156, 1176, 1238, 1347, 1357, 1458, 1493, 1601, 1686, 2939, 2989 cm^{-1}; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.32 (s, 9H), 1.91 (t, J = 10.1 Hz, 1H), 2.05 (br, 1H), 3.20 (dd, J = 8.1, 4.9 Hz, 1H), 3.78 (s, 3H), 5.18 (br, 2H), 6.84 (d, J = 8.1 Hz, 1H), 6.97 (t, J = 7.2 Hz, 1H), 7.13–7.30 (m, 5H), 7.51 (d, J = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 28.3 (3C), 35.6 (br), 39.3 (br), 55.4, 61.0 (br), 66.1 (br), 80.0, 110.0, 120.0, 120.8, 126.4, 126.5 (2C), 126.6, 127.3 (2C), 132.6, 146.2, 155.2, 157.2; HRMS (FAB): *m/z* $[M+H]^+$ calcd for $C_{22}H_{26}NO_3$ 352.1913, found 352.1913; Anal. Calcd for $C_{22}H_{25}NO_3$ C, 75.19; H, 7.17; N, 3.99. Found C, 75.09; H, 7.25; N, 3.95. $[\alpha]^{25}_D$ +92.6 (*c*1.0, CH_2Cl_2).

***tert*-Butyl (1*S*,2*R*,4*R*)-2-(naphthalen-1-yl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3i)** (Table 1)

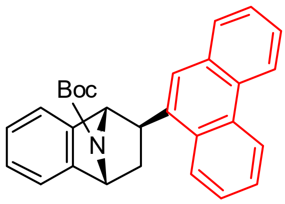


The reaction was carried out according to the general procedure using **1a** (126.3 mg, 0.52 mmol), 1-naphtyhlmagnesium bromide (4.95 mL, 0.323 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.85 mL of 1.0 M solution in THF, 1.7 equiv). Reaction was run at 0 °C for 24 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 95/5) to give the title product in 90% yield (168.1 mg, 97% ee) as a white solid.

The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 99/1, 1.0 mL/min, 4.3 °C. Retention times (t_r) = 11.50 min (major) and 15.75 min (minor);

M.p. 120.4–121.1 °C; IR (neat): 600, 756, 775, 795, 904, 1089, 1140, 1156, 1168, 1251, 1334, 1364, 1459, 1597, 1689, 2952, 2976 cm^{-1}; ^1H NMR ($CDCl_3$, 391.8 MHz) δ 1.34 (s, 9H), 2.15 (br, 2H), 3.55 (t, J = 5.8 Hz, 1H), 5.29 (br, 2H), 7.19–7.21 (m, 2H), 7.32–7.45 (m, 4H), 7.49 (t, J = 7.8 Hz, 1H), 7.73 (d, J = 8.0 Hz 2H), 7.79–7.86 (m, 2H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 28.4 (3C), 37.4 (br), 41.6 (br), 61.5 (br), 65.9 (br), 80.2, 120.2 (br), 122.6, 123.3 (2C), 125.5, 126.0, 126.7 (2C), 126.8, 126.9, 129.0 (2C), 131.9, 133.9, 140.0, 146.4, 155.5; HRMS (FAB): m/z $[M+H]^+$ calcd for $C_{25}H_{26}NO_2$ 372.1964, found 372.1965. Anal. Calcd for $C_{25}H_{25}NO_2$ C, 80.83; H, 6.78; N, 3.77. Found C, 80.85; H, 6.97; N, 3.68. $[\alpha]^{25}_D$ +139.9 (c1.0, CH_2Cl_2).

***tert*-Butyl (1*S*,2*R*,4*R*)-9-(phenanthrene-1-yl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3j)** (Table 1)



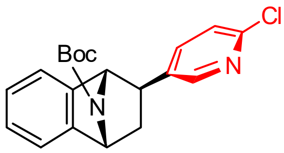
The reaction was carried out according to the general procedure using **1a** (122.0 mg, 0.50 mmol), 9-phenanthryhlmagnesium bromide (3.01 mL, 0.53 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.85 mL of 1.0 M solution in THF, 1.7 equiv). Reaction was run at −20 °C for 21 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 95/5) to give the title product in 75% yield (158.1 mg, 96% ee) as a white solid.

The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 95/5, 1.0 mL/min, 5 °C. Retention times (t_r) = 6.16 min (major) and 6.95 min (minor);

M.p. 100.4–102.1 °C; IR (neat): 660, 781, 797, 821, 851, 872, 907, 1022, 1092, 1140, 1155, 1173, 1250, 1290, 1368, 1393, 1459, 1597, 1692, 2982 cm^{-1}; ^1H NMR ($CDCl_3$, 391.8 MHz) δ 1.37 (s, 9H), 2.19 (br, 2H), 3.55 (t, J = 6.7 Hz, 1H), 5.32 (br, 1H), 5.50 (br, 1H), 7.22–7.25 (m, 2H), 7.37–7.41 (m, 2H), 7.57–7.65 (m, 4H), 7.87–7.96 (m, 3H), 8.66

(d, J = 7.6 Hz, 1H), 8.75 (d, J = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 28.5 (3C), 36.6 (br), 42.4 (br), 60.9 (br), 65.9 (br), 80.3, 120.3 (br), 122.4, 123.4, 123.5 (2C), 124.0, 126.3, 126.4, 126.7 (2C), 126.8 (2C), 128.9, 129.6, 130.8, 131.3, 132.0, 138.0 (2C), 146.5, 155.1; HRMS (FAB): m/z [M]$^+$ calcd for $C_{29}H_{27}NO_2$ 421.2042, found 421.2040. $[\alpha]^{25}_D$ +187.7 (c1.0, CH_2Cl_2).

***tert*-Butyl (1*S*,2*R*,4*R*)-2-(6-chloropyridin-3-yl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3k)** (Table 1)



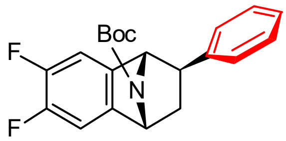
In a Schlenk tube under inert atmosphere, 5-bromo-2-chloropyridine (308 mg, 1.6 mmol) was dissolved in THF (2.0 mL). After cooling to 0 ºC, i-PrMgCl·LiCl (1.24 mL, 1.6 mmol, 1.292 M in THF) was added dropwise to the reaction mixture and it was stirred for 4 h at 0 °C. A THF solution of $ZnCl_2$ (0.84 mL, 1.0 M) was added to the reaction mixture and stirred for 1.5 h. Then, the solvent was removed and the resulting $Ar_2Zn{\cdot}2MgCl_2$ was dried for 45 minutes under vacuum. To the arylzinc, a mixture of (S,S)-Chiraphos (17.1 mg, 0.04 mmol), THF (0.80 mL), toluene (3.0 mL), and $FeCl_3$ (200 μL, 0.1 M solution in THF, 0.02 mmol) was added followed by the addition of **1a** (97 mg, 0.40 mmol) and the reaction mixture was stirred at 30 °C for 36 h. Degassed AcOH/MeOH (20/80) was added at 0 °C for quenching. The mixture was stirred for 10 minutes and then saturated aqueous NH_4Cl (1.0 mL) and MTBE were added. The separated aqueous layer was extracted with additional portions of MTBE (5 mL × 3). The combined organic extracts were passed through a pad of Florisil® and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/AcOEt = 80/20) to give the title product in 84% yield (119.9 mg, 45% ee) as a white solid.

The ee was determined by HPLC on a CHIRALCEL IG column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/EtOH/diethylamine = 50/50/0.1 (v/v/v), 1.0 mL/min, 25 °C. Retention times (t_r) = 3.87 min (minor) and 5.88 min (major);

M.p. 102.8–105.3 °C; IR (neat): 553, 633, 684, 736, 761, 830, 899, 1084, 1099, 1128, 1141, 1155, 1168, 1269, 1286, 1364, 1388, 1458, 1698, 2980 cm^{-1}; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.32 (s, 9H), 1.97 (dd, J = 11.9, 8.7 Hz, 1H), 2.12 (dt, J = 11.9, 4.5 Hz, 1H), 2.84 (dd, J = 8.6, 4.5 Hz, 1H), 5.00 (br, 1H), 5.25 (br, 1H), 7.17–7.20 (m, 2H), 7.27–7.33 (m, 3H), 7.76 (dd, J = 8.5, 1.8 Hz, 1H), 8.32 (d, J = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 28.3 (3C), 37.8 (br), 43.0 (br), 61.6 (br), 67.2, 80.7, 120.2, 124.3, 126.8 (2C), 127.0, 137.6, 139.0, 145.1, 145.8, 149.1, 149.8, 155.7; HRMS (ESI-FT-ICR): m/z [M+H]$^+$ calcd for $C_{20}H_{21}ClN_2O_2$ 357.13643, found 357.13895. Anal. Calcd for

$C_{20}H_{21}ClN_2O_2\cdot(H_2O)_{0.25}$ C, 66.48; H, 6.00; N, 7.75. Found C, 66.64; H, 5.94; N, 7.73. $[\alpha]^{25}{}_D$ +37.9 (*c*1.0, CH_2Cl_2).

***tert*-Butyl (1*S*,2*R*,4*R*)-6,7-difluoro-2-phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3l)** (Table 1)

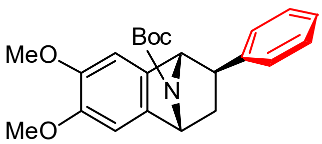


The reaction was carried out according to the general procedure using *tert*-butyl 6,7-difluoro-1,4-dihydro-1,4-epiminonaphthalene-11-carboxylate (**1b**; 134 mg, 0.48 mmol), phenylmagnesium bromide (1.73 mL, 0.92 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.85 mL of 1.0 M solution in THF, 1.7 equiv). Reaction was run at −20 °C for 24 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 95/5) to give the title product in 85% yield (132.9 mg, 78% ee) as a white solid.

The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 98/2, 1.0 mL/min, 5 °C. Retention times (t_r) = 9.25 min (major) and 14.28 min (minor);

M.p. 103.4–105.1 °C; IR (neat): 702, 733, 772, 805, 858, 891, 911, 1052, 1082, 1132, 1149, 1162, 1264, 1285, 1296, 1368, 1477, 1612, 1694, 2975 cm^{-1}; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.34 (s, 9H), 1.90 (dd, *J* = 12.1, 8.9 Hz, 1H), 2.19 (dt, *J* = 12.1, 4.5 Hz, 1H), 2.78 (dd, *J* = 8.9, 4.5 Hz, 1H), 5.04 (br, 1H), 5.21 (br, 1H), 7.13 (t, *J* = 8.3 Hz, 2H), 7.23–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 28.3 (3C), 37.6 (br), 46.2 (br), 61.3 (br), 67.1, 80.8, 110.1,126.8 (2C), 127.5 (2C), 128.7 (3C), 142.1, 143.8, 149.2 (ddd, *J* = 248.5, 15.5, 10.7 Hz, 2C), 155.6; HRMS (FAB): *m/z* $[M+Na]^+$ calcd for $C_{21}H_{21}F_2NO_2Na$ 380.1438, found 380.1439; Anal. Calcd for $C_{21}H_{21}F_2NO_2$ C, 70.57; H, 5.92; N, 3.92. Found C, 70.29; H, 6.06; N, 3.74. $[\alpha]^{25}{}_D$ +56.6 (*c*1.0, CH_2Cl_2).

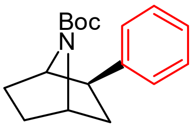
***tert*-Butyl (1*S*,2*R*,4*R*)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3m)** (Table 1)



The reaction was carried out according to the general procedure using *tert*-butyl 6,7-dimethoxy-1,4-dihydro-1,4-epimino-naphthalene-11-carboxylate (**1c**; 141.2 mg, 0.465 mmol), phenylmagnesium bromide (1.74 mL, 0.92 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.85 mL of 1.0 M solution in THF, 1.7 equiv). Reaction was run at −20 °C for 24 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 90/10) to give the title product in 91% yield (161.5 mg, 75% ee) as a white solid.

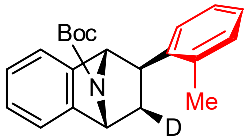
The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 30/70, 1.0 mL/min, 5 °C. Retention times (t_r) = 24.08 min (major) and 30.49 min (minor);
M.p. 111.6–112.9 °C; IR (neat): 675, 702, 755, 801, 827, 882, 899, 915, 1071, 1174, 1216, 1247, 1260, 1283, 1303, 1375, 1453, 1469, 1490, 1606, 1684, 2945 cm^{-1}; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.34 (s, 9H), 1.89 (dd, *J* = 11.7, 8.9 Hz, 1H), 2.15 (dt, *J* = 11.7, 4.5 Hz, 1H), 2.77 (dd, *J* = 8.8, 4.5 Hz, 1H), 3.89 (s, 6H), 5.01 (br, 1H), 5.21 (br, 1H), 6.92 (s, 2H), 7.21–7.25 (m, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 28.4 (3C), 37.8 (br), 47.1 (br), 56.3 (2C), 61.5 (br), 67.5 (br), 80.2, 105.0 (br), 126.5 (2C), 127.5 (2C), 128.6 (3C), 138.2, 144.5, 147.7, 147.8, 155.6; HRMS (FAB): *m/z* [M+H]$^+$ calcd for $C_{23}H_{28}NO_4$ 382.2018, found 382.2019; Anal. Calcd for $C_{23}H_{27}NO_4$ C, 72.42; H, 7.13; N, 3.67. Found C, 72.36; H, 7.22; N, 3.67. $[\alpha]^{25}_D$ +67.4 (*c*1.0, CH_2Cl_2).

***tert*-Butyl (1*R*,2*R*,4*S*)-2-phenyl-7-azabicyclo[2.2.1]heptane-7-carboxylate (3n)** (Table 1)



The reaction was carried out according to the general procedure using *tert*-butyl 7-azabicyclo[2.2.1]hept-2-ene-7-carboxylate (**1n**; 92 μL, 0.50 mmol), phenylmagnesium bromide (1.73 mL, 0.92 M in THF solution, 3.2 equiv) and $ZnCl_2$ (0.85 mL of 1.0 M solution in THF, 1.7 equiv). Reaction was run at 30 °C for 16 h. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 95/5) to give the title product in 67% yield (92.1 mg, 75% ee) as a white solid.
The ee was determined by HPLC on a CHIRALCEL AD-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 90/10, 1.0 mL/min, 5 °C. Retention times (t_r) = 3.49 min (minor) and 3.86 min (major);
M.p. 61.6–63.3°C; IR (neat): 530, 707, 761, 856, 891, 902, 1087, 1128, 1150, 1182, 1251, 1319, 1364, 1383, 1455, 1686, 2878, 2929, 2973, 3012 cm^{-1}; ^{1}H NMR ($CDCl_3$, 391.8 MHz) δ 1.41 (s, 9H), 1.48–1.59 (m, 2H), 1.82–1.98 (m, 4H), 2.86 (dd, *J* = 8.5, 5.8 Hz, 1H), 4.23 (br, 1H), 4.36 (br, 1H), 7.15–7.20 (m, 1H), 7.25–7.28 (m, 4H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 28.4 (3C), 28.9 (br), 30.4 (br), 40.3 (br), 48.4 (br), 55.7 (br), 62.2 (br), 79.5, 126.2 (2C), 127.2, 128.5 (2C), 145.9, 155.2; Anal. Calcd for $C_{17}H_{23}NO_2$ C, 74.69; H, 8.48; N, 5.12. Found C, 74.42; H, 8.51; N, 5.12. $[\alpha]^{25}_D$ +18.0 (*c*1.0, CH_2Cl_2).

***tert*-Butyl (1*S*,2*R*,3*R*,4*R*)-2-(2-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate-3-*d* (5a)** (Table 2)

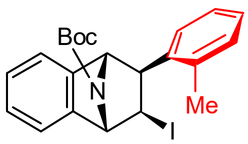


$ZnCl_2$ (545.2 mg, 4.0 mmol) was dried by fusing *in vacuo* and cooled quickly followed by addition of 4.0 mL of THF to prepare a 1.0 M THF solution of $ZnCl_2$. After stirring for 20 min, the THF solution of $ZnCl_2$ (0.85 mL, 1.0 M) was transferred to the other Schlenk flask, and 2-methylphenylmagnesium bromide (1.48 mL, 1.08 M solution in THF, 3.2 equiv) was added at 0 °C and stirred for 2.0 h. Then, the solvent was removed and the resulting arylzinc reagent was dried for 10 min under vacuum. To the arylzinc powder, a mixture of (*S,S*)-Chiraphos (8.5 mg, 0.020 mmol), THF (0.70 mL), toluene (3.2 mL), and $FeCl_3$ (1.62 mg, 0.01mmol) in THF (0.1 M, 100 μL) was added, followed by the addition of **1a** (127.7 mg, 0.52 mmol) and the reaction mixture was stirred for 24 h at 0 °C. Degassed CD_3COOD/CD_3OD (20/80) was added at −78 °C for quenching. The mixture was stirred overnight at rt and then saturated aqueous NH_4Cl (1.0 mL) and MTBE were added. The separated aqueous layer was extracted with additional portions of MTBE (5 mL × 3). The combined organic extracts were passed through a pad of Florisil® and the filtrate was concentrated *in vacuo*. The product was purified by flash chromatography on silica gel (hexane/AcOEt = 95/5) to give the title compound in 96% yield (172.8 mg, 99% ee) as white solid.

The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: hexane/IPA = 99/1, 1.0 mL/min, 4.3 °C. Retention times (t_r) = 7.73 min (major) and 8.50 min (minor);

M.p. 149.7–152.9 °C; IR (neat): 564, 588, 659, 744, 760, 847, 905, 1086, 1157, 1276, 1364, 1376, 1458, 1692, 2964 cm^{-1}; ^1H NMR ($CDCl_3$, 391.8 MHz) δ 1.34 (s, 9H), 1.95 (d, J = 8.5 Hz, 1H), 2.21 (s, 3H), 2.97 (d, J = 8.9 Hz, 1H), 5.22 (br, 2H), 7.14 (d, J = 4.9 Hz, 2H), 7.16–7.18 (m, 2H), 7.20–7.24 (m, 1H), 7.30 (br, 2H), 7.55 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 20.1, 28.4 (3C), 36.3 (br), 42.1 (br), 61.6 (br), 66.0 (br), 80.2, 119.9 (br), 125.6, 126.3 (2C), 126.6 (2C), 126.7, 130.2 (2C), 135.9, 142.6, 146.3, 155.4; Anal. Calcd for $C_{22}H_{24}NO_2$ C, 78.54; H, 7.51; N, 4.16. Found C, 78.40; H, 7.56; N, 4.05. $[\alpha]^{25}_D$ +125.2 (c1.0, CH_2Cl_2).

***tert*-Butyl (1*S*,2*R*,3*R*,4*S*)-2-iodo-3-(2-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (5b)** (Table 2)



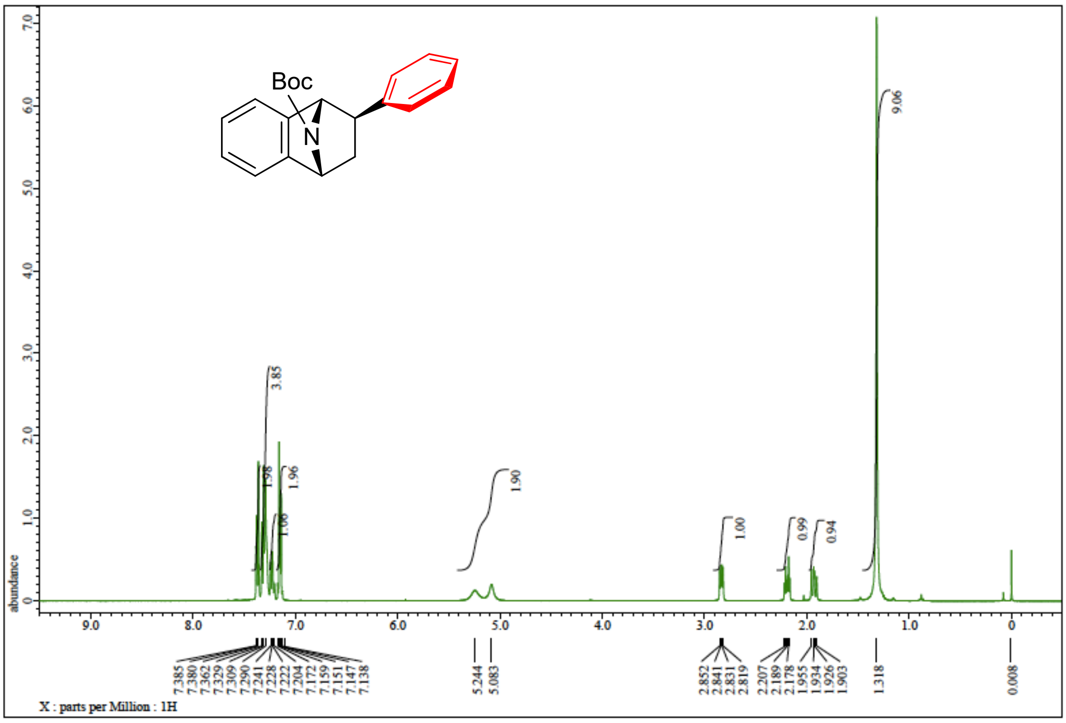
$ZnCl_2$ (545.2 mg, 4.0 mmol) was dried by fusing *in vacuo* and cooled quickly followed by addition of 4.0 mL of THF to prepare a 1.0 M THF solution of $ZnCl_2$. After stirring for 20 min, the THF solution of $ZnCl_2$ (0.85 mL, 1.0 M) was transferred to the other Schlenk flask, and 2-methylphenylmagnesium bromide (1.48 mL, 1.08 M solution in THF, 3.2 equiv) was added at 0 °C and stirred for 2.0 h. Then, the solvent was removed and the resulting arylzinc reagent was dried for 10 min under vacuum. To the arylzinc powder, a mixture of (*S,S*)-Chiraphos (8.5 mg, 0.020 mmol), THF (0.70 mL), toluene (3.2 mL), and $FeCl_3$ (1.62 mg, 0.01 mmol) in THF (0.1 M, 100 μL) was added, followed by the addition of **1a** (127.7 mg, 0.52 mmol) and the reaction mixture was stirred for 24 h at 0 °C. THF solution of I_2 (2.00 mL, 1.0 M, 2.00 mmol) was added at −78 °C. The mixture was stirred overnight at rt and then saturated aqueous NH_4Cl (1.0 mL) and MTBE were added. The separated aqueous layer was extracted with additional portions of MTBE (5 mL × 3). The combined organic extracts were passed through a pad of Florisil® and the filtrate was concentrated *in vacuo*. The product was purified by flash chromatography on silica gel (hexane/AcOEt = 95/5) to give the title compound in 84% yield (202.1 mg, 99% ee) as white solid.

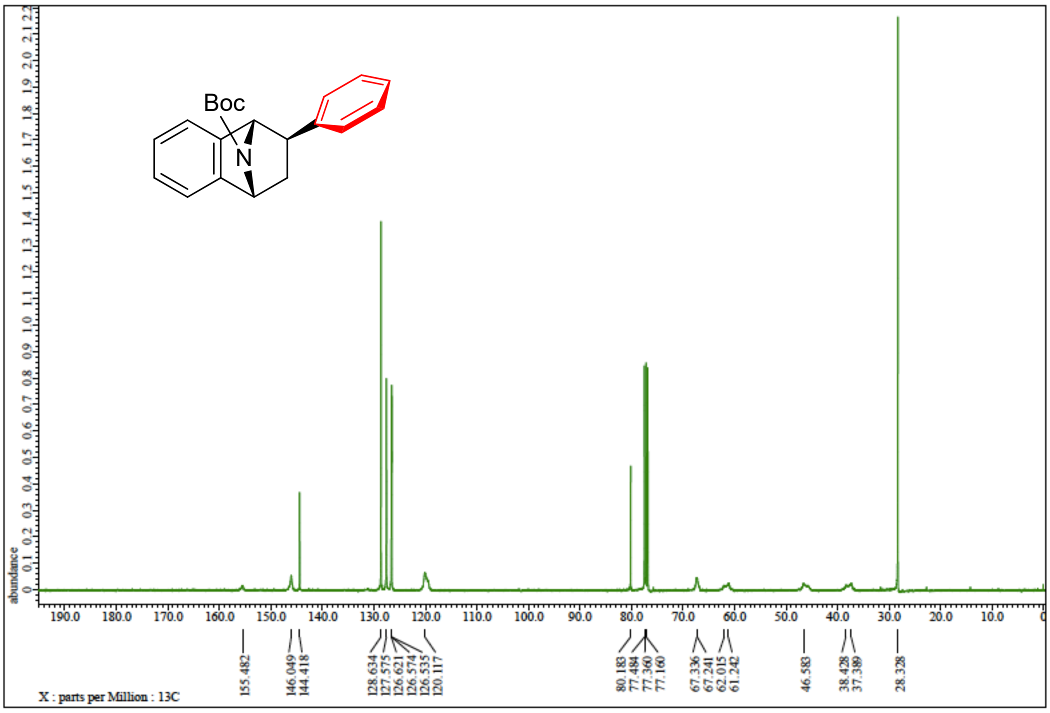
The ee was determined by HPLC on a CHIRALCEL IC-3 column (4.6 mm i.d.; 150 mm length) with following conditions: Hexane/IPA = 99/1, 1.0 mL/min, 5 °C. Retention times (t_r) = 7.77 min (minor) and 8.43 min (major);

M.p. 65.3–66.9 °C; IR (neat): 592, 656, 739, 751, 829, 902, 915, 1087, 1150, 1255, 1275, 1335, 1366, 1458, 1702, 2953, 2973 cm^{-1}; ^1H NMR ($CDCl_3$, 391.8 MHz) δ 1.39 (s, 9H), 2.07 (s, 3H), 2.97 (d, J = 7.6 Hz, 1H), 4.46 (d, J = 7.6 Hz, 1H), 5.39–5.45 (br, 2H), 7.15 (d, J = 7.2 Hz, 1H), 7.20–7.23 (m, 3H), 7.28–7.32 (m, 2H), 7.39 (br, 1H), 7.58 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 98.5 MHz) δ 20.6, 28.4 (3C), 34.1, 46.8, 65.4, 72.2, 80.9, 120.7, 126.3, 127.0, 127.2 (2C), 127.3, 127.7 (2C), 130.0, 136.7, 143.4, 147.0, 155.1; HRMS (FAB): *m/z* $[M+Na]^+$ calcd for $C_{22}H_{24}NO_2NaI$ 484.0750, found 484.0752; Anal. Calcd for $C_{22}H_{24}INO_2$ C, 57.28; H, 5.24; N, 3.04; I, 27.51. Found C, 57.13; H, 5.27; N, 3.09; I, 27.33. $[\alpha]^{25}_D$ +105.0 (c1.0, CH_2Cl_2).

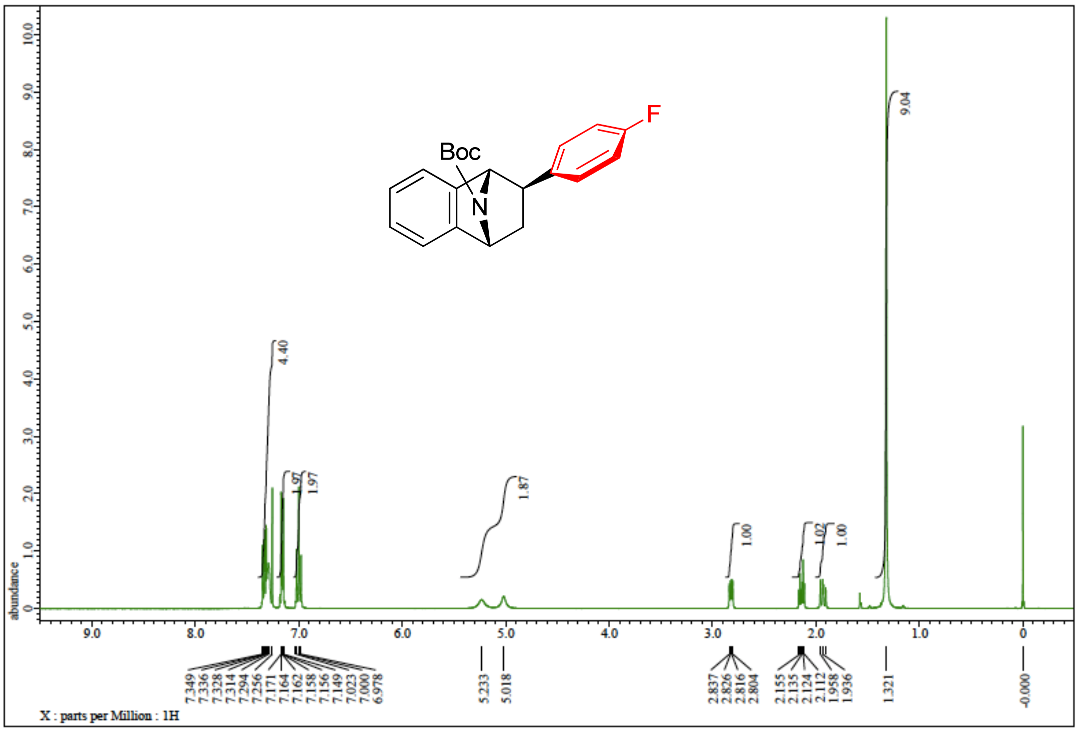
6. ^{1}H and ^{13}C NMR Spectra

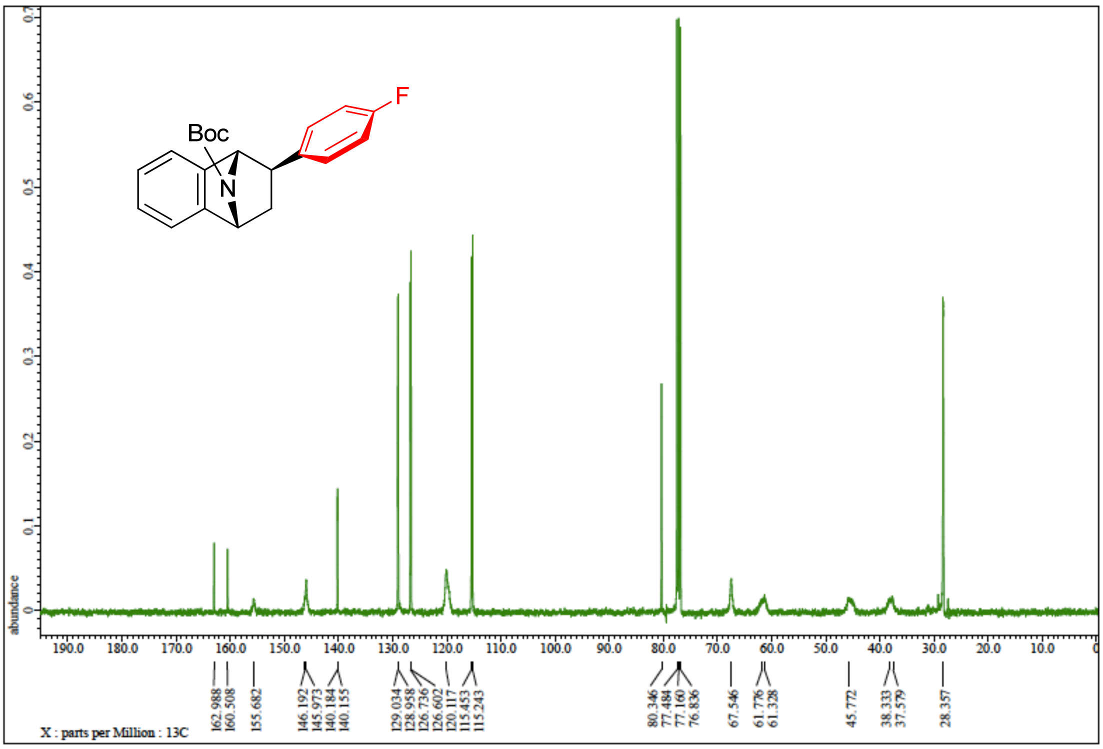
***tert*-Butyl(*1S,2R,4R*)-2-phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3a)**



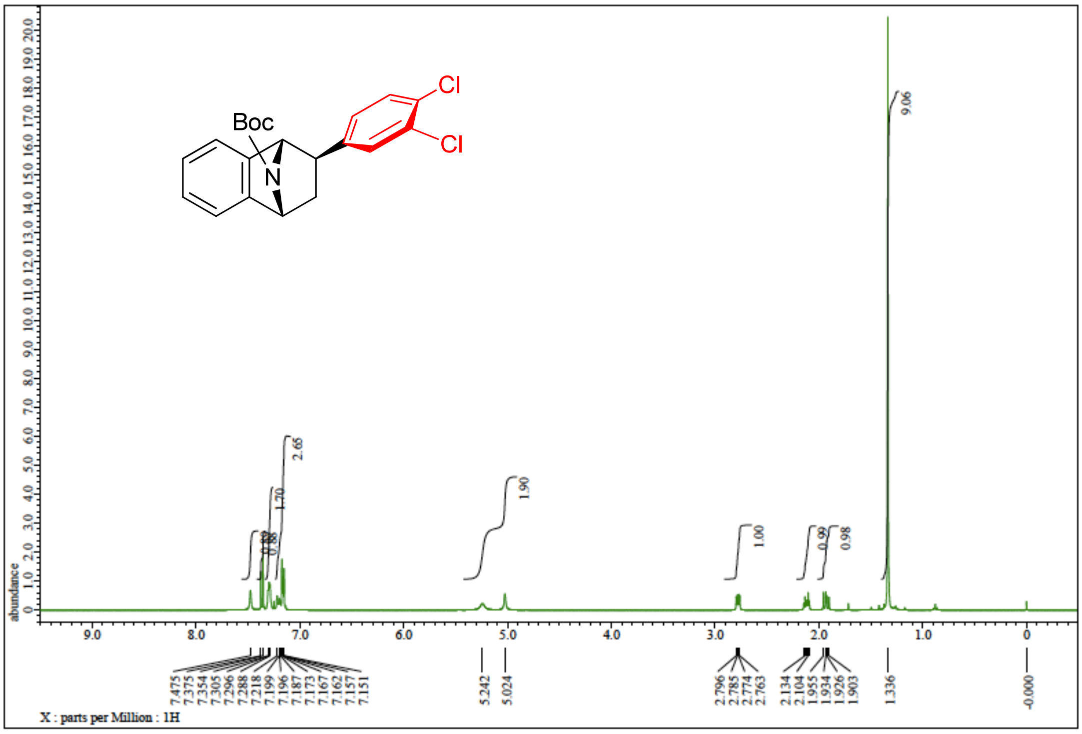


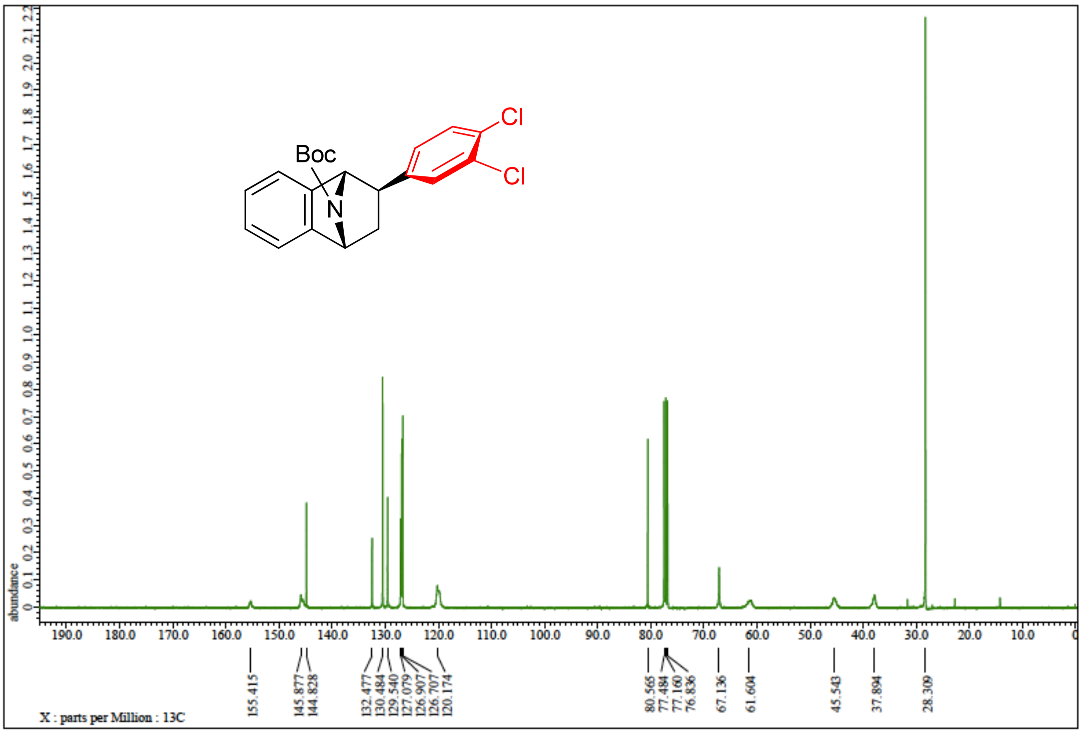
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(4-fluorophenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3b)**



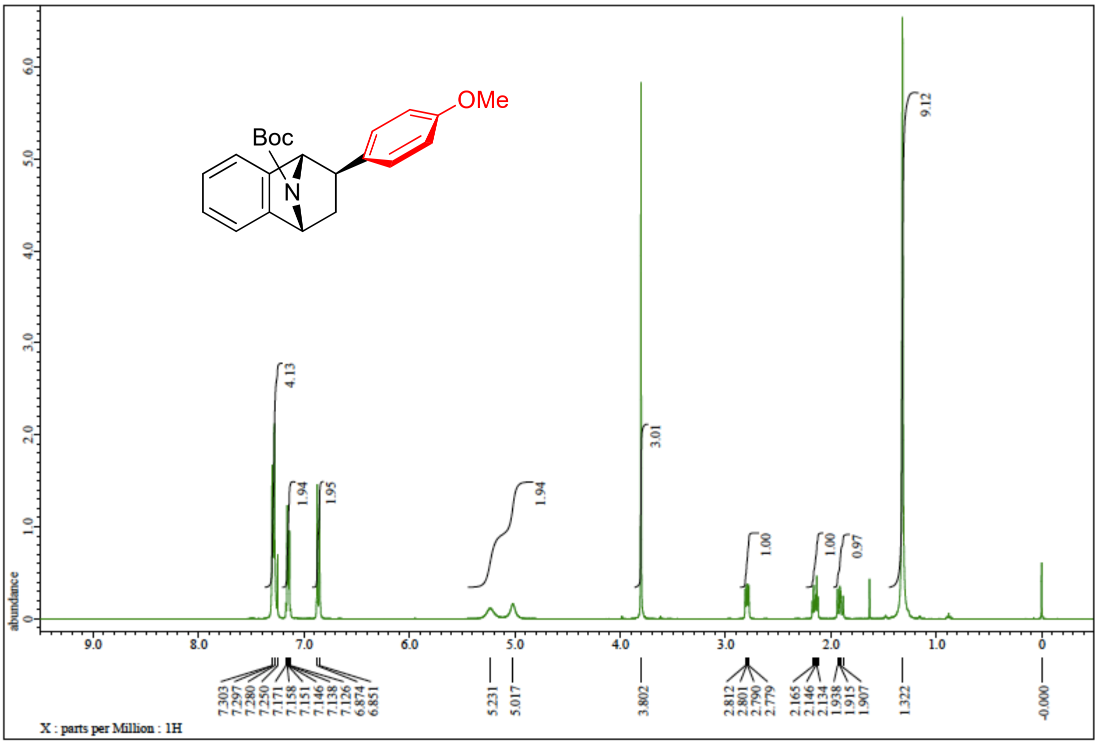


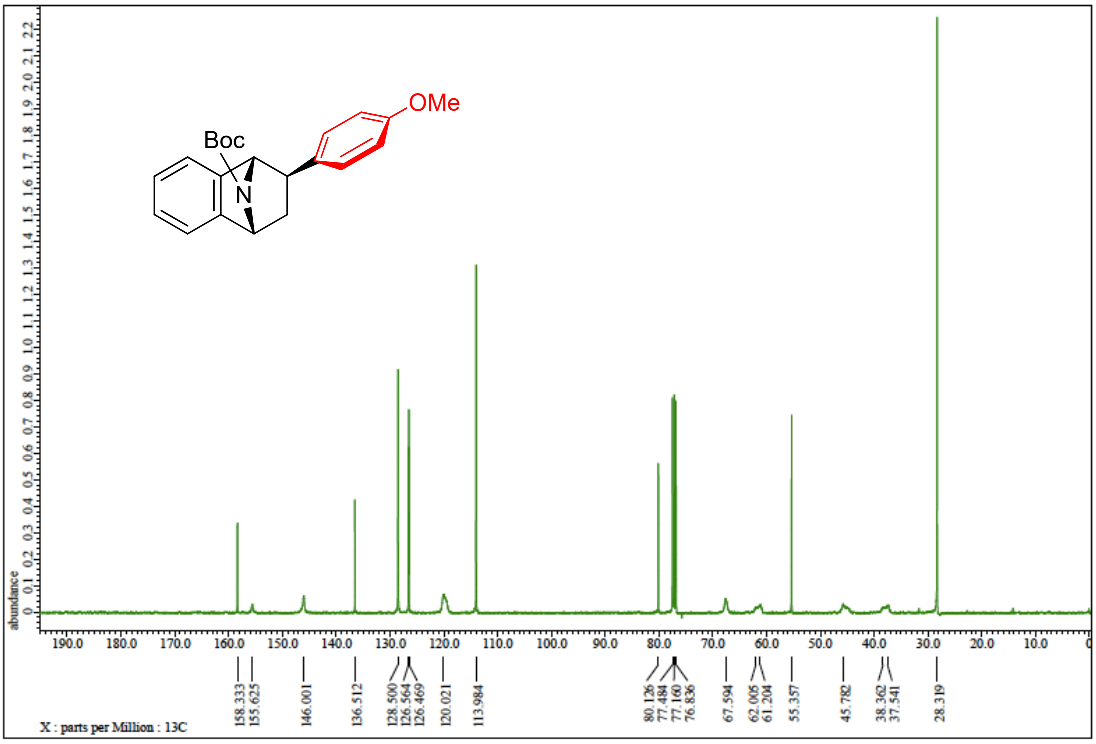
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3c)**



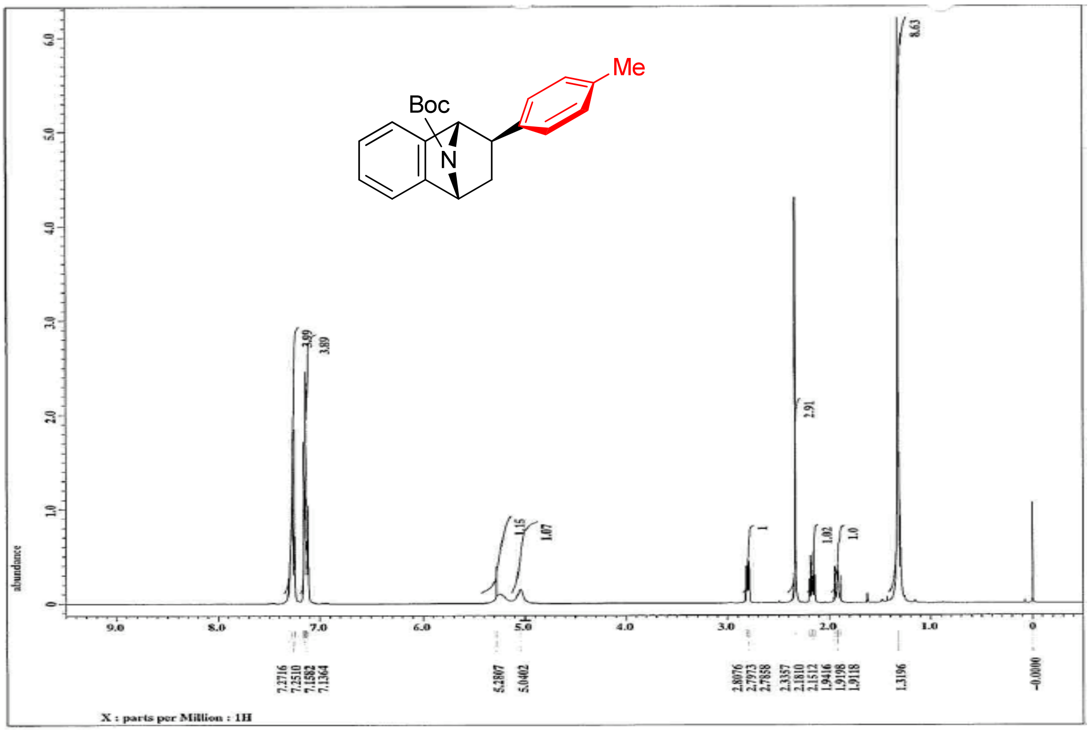


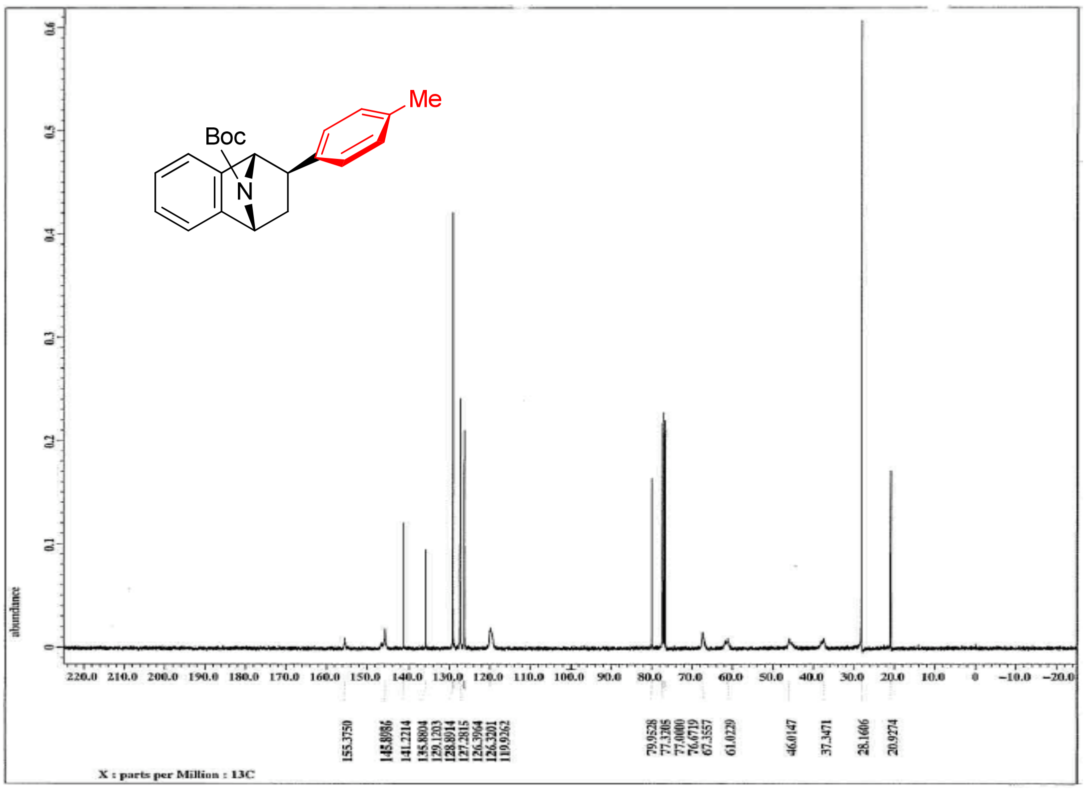
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3d)**



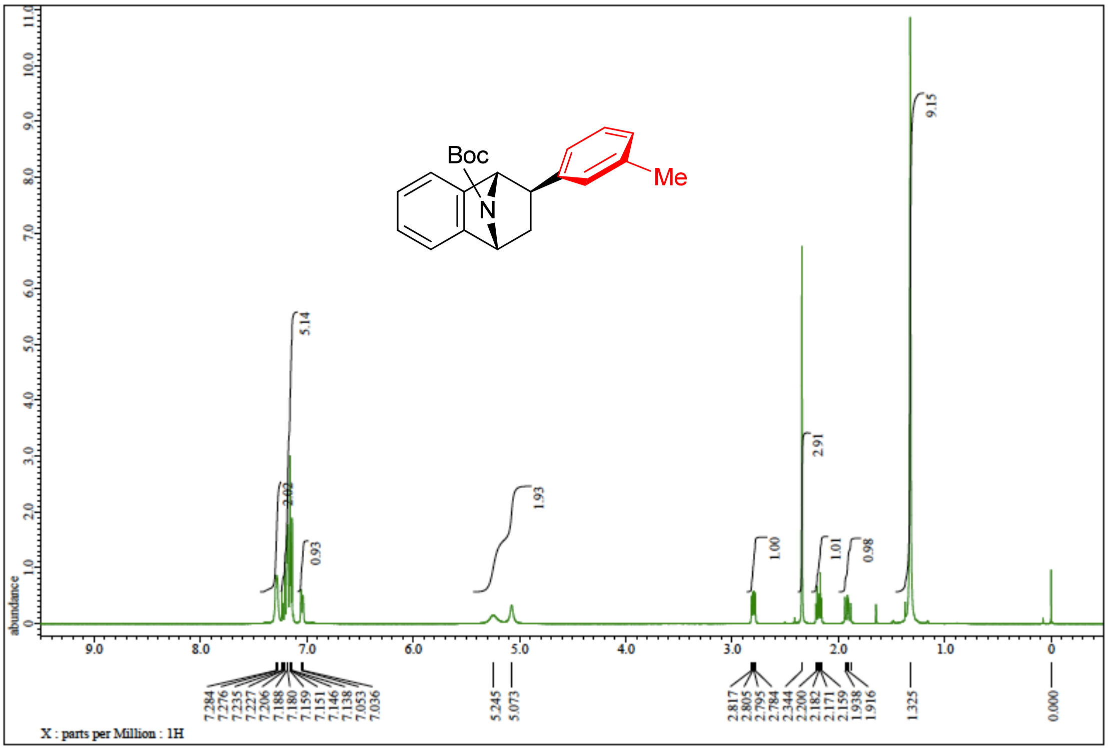


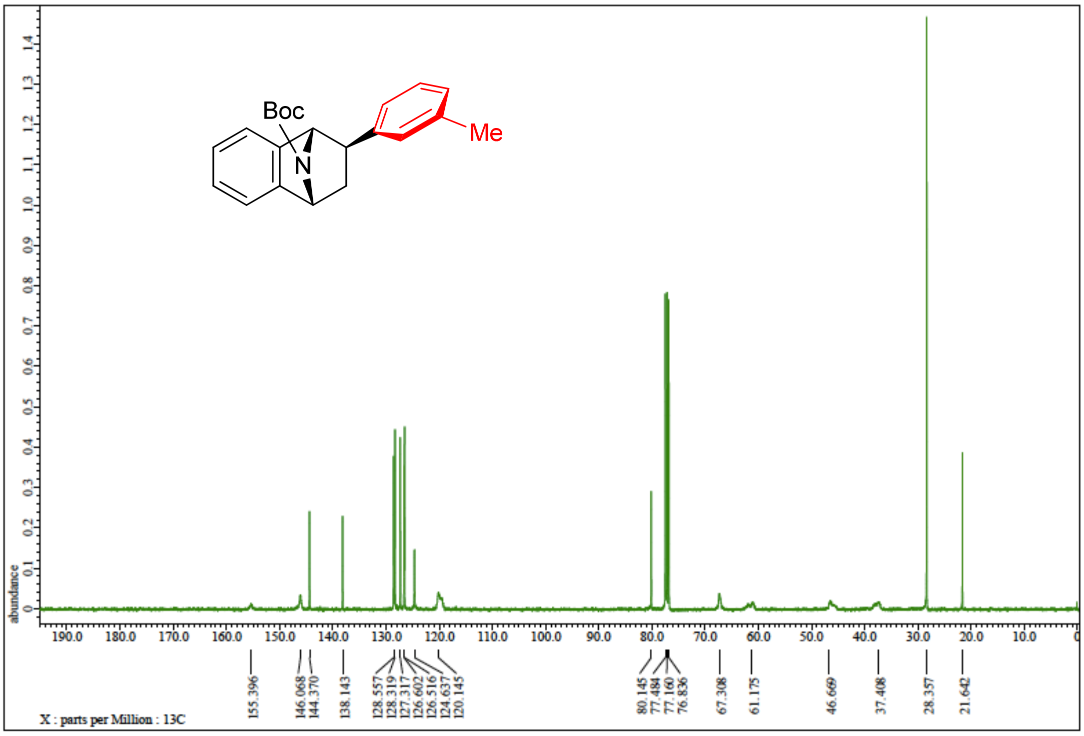
tert-Butyl (1_S_,2_R_,4_R_)-2-(4-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3e)



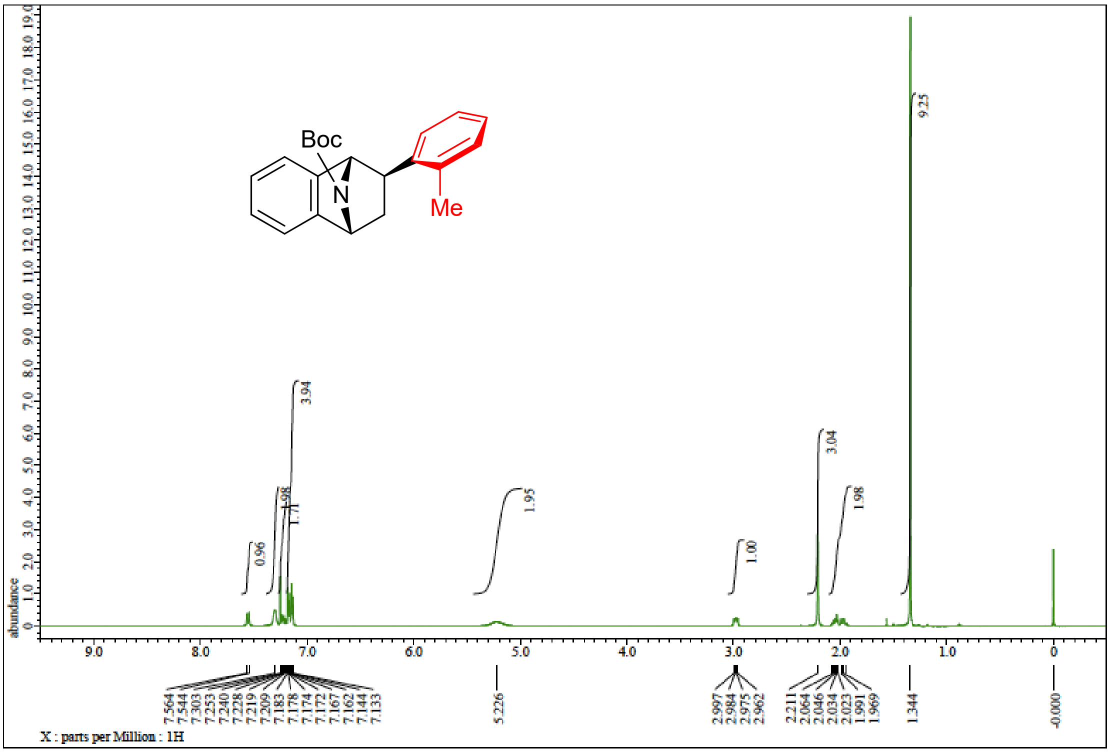


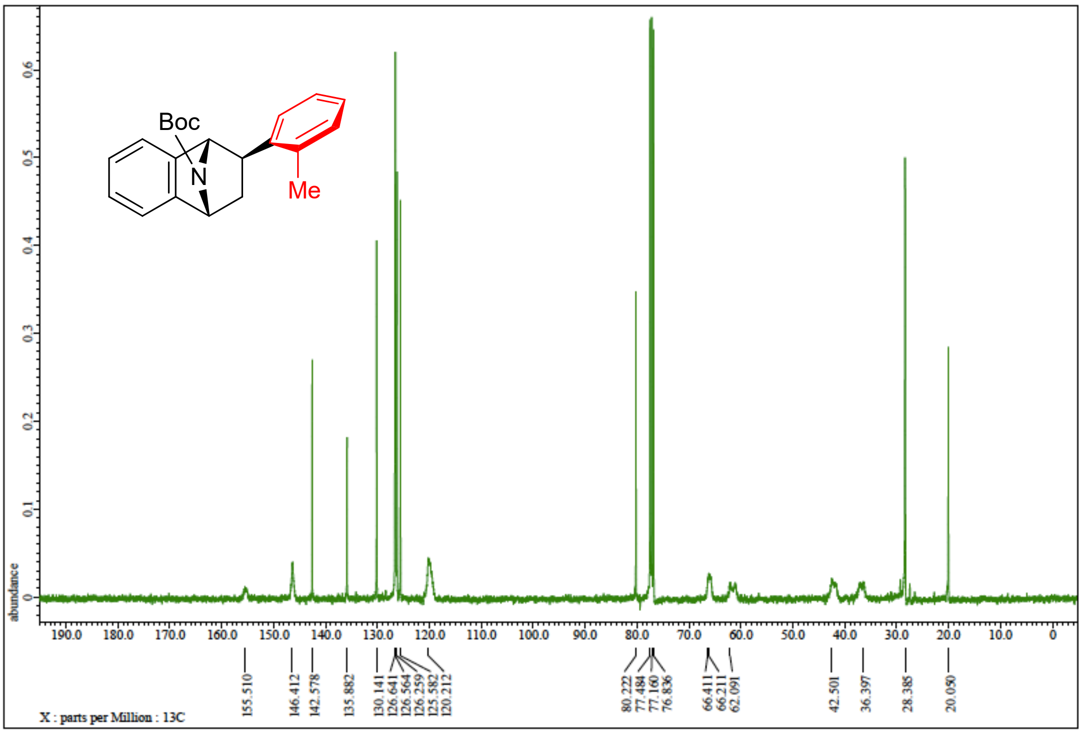
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(3-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3f)**



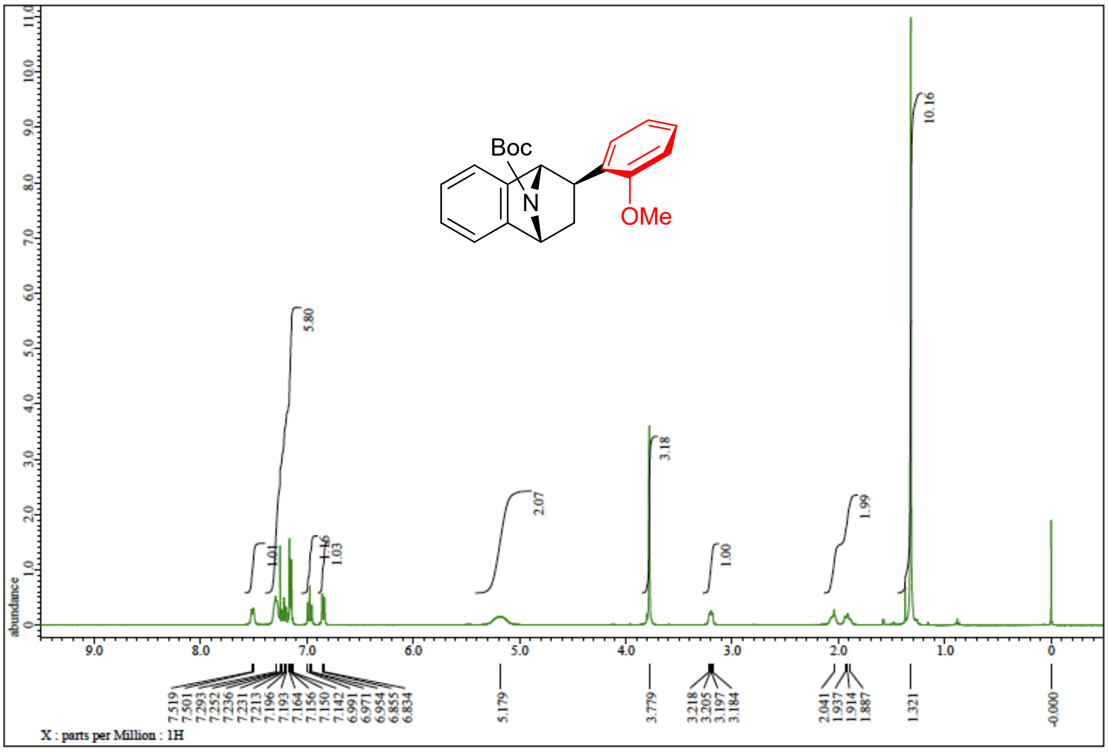


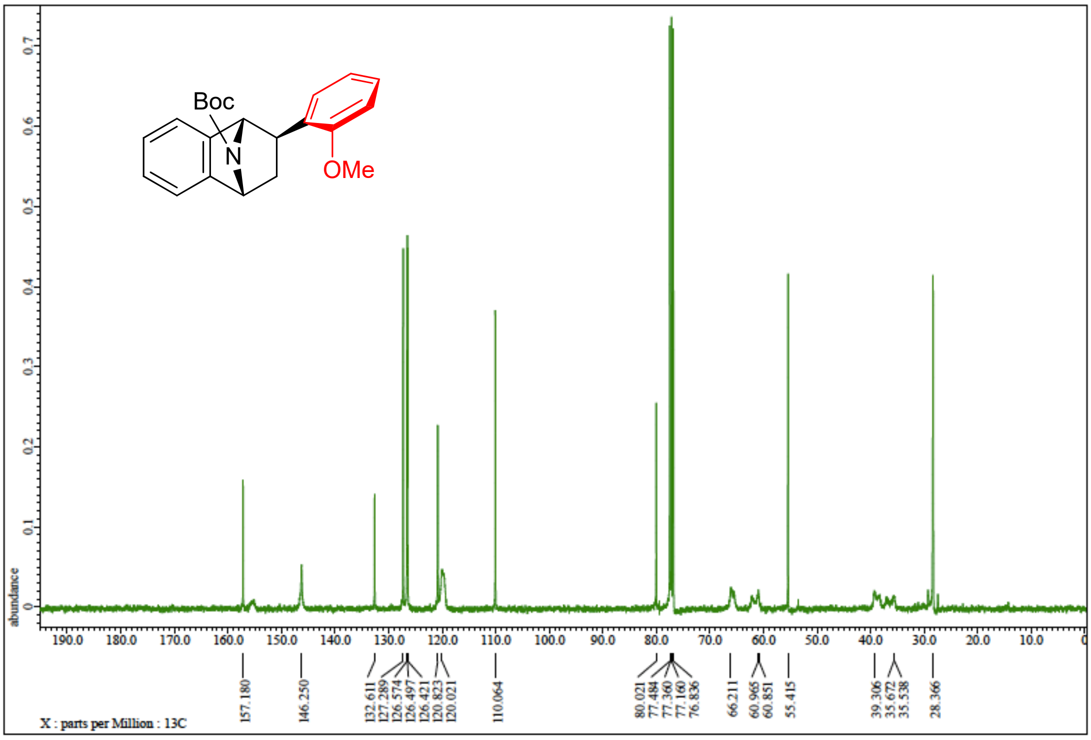
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(2-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3g)**



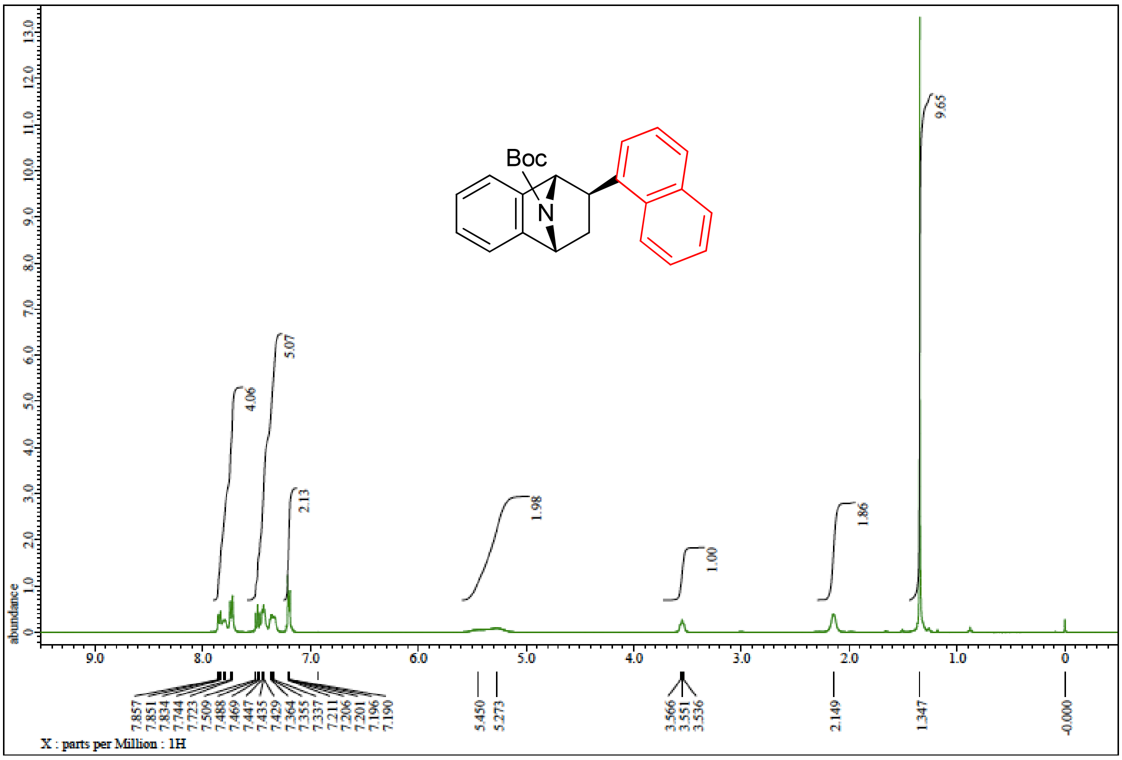


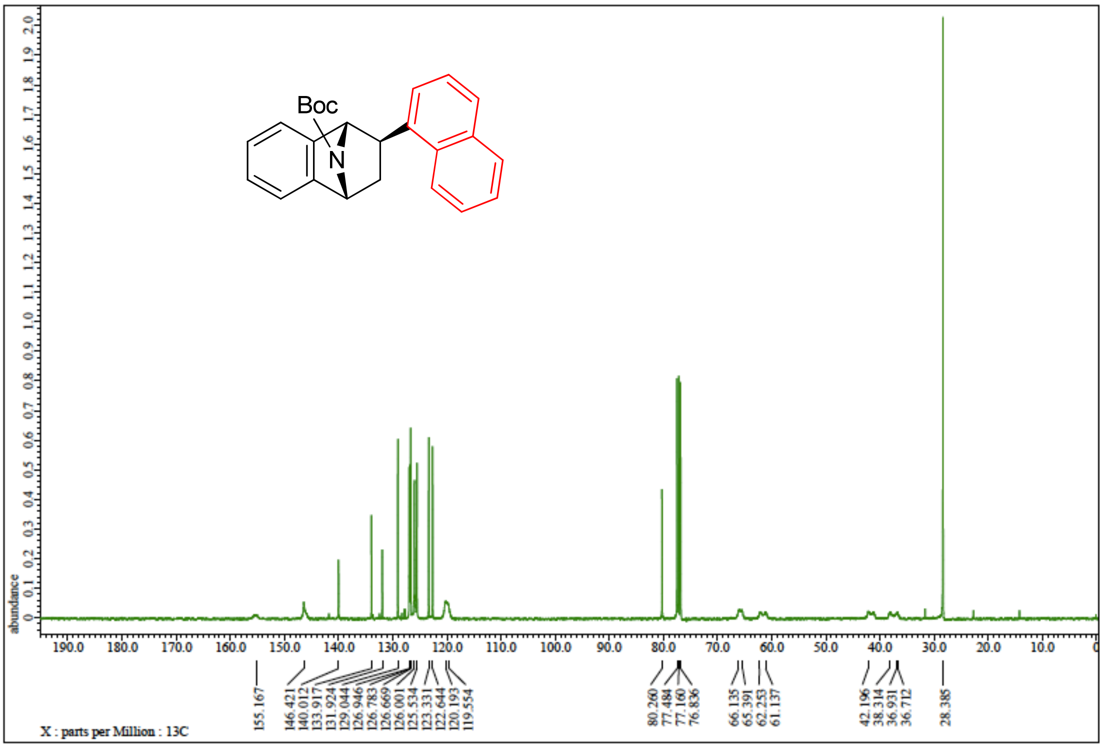
tert-Butyl (1S,2R,4R)-2-(2-methoxyphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3h)



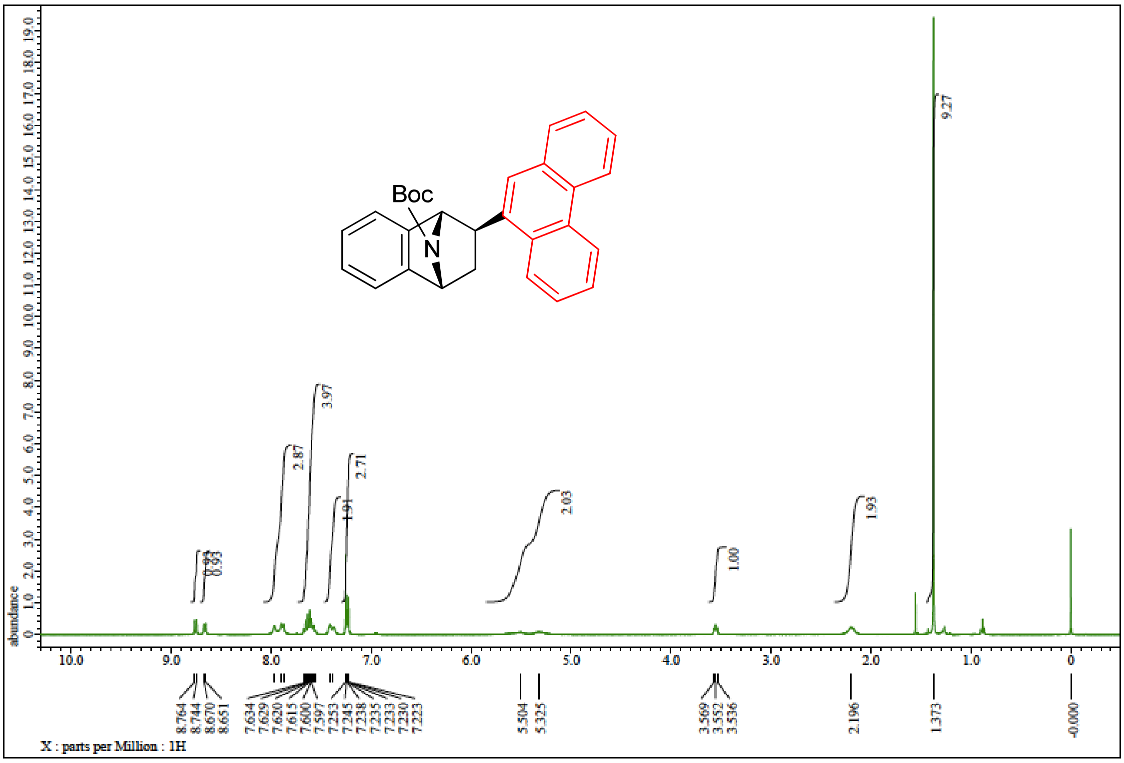


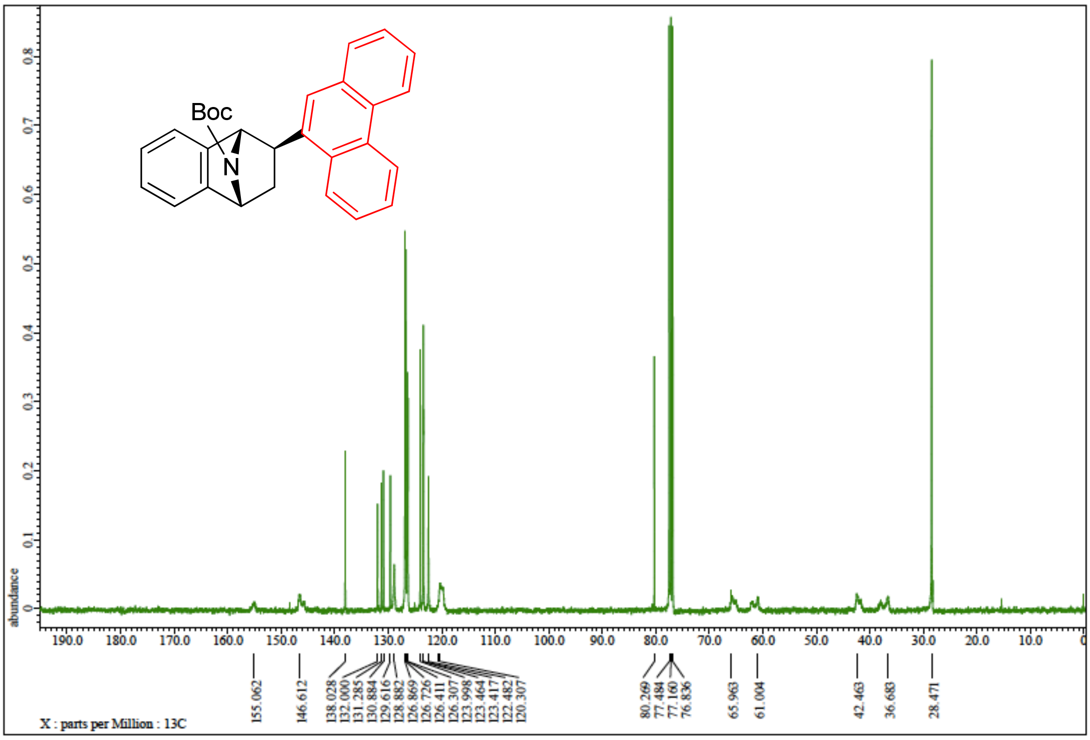
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(naphthalen-1-yl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3i)**



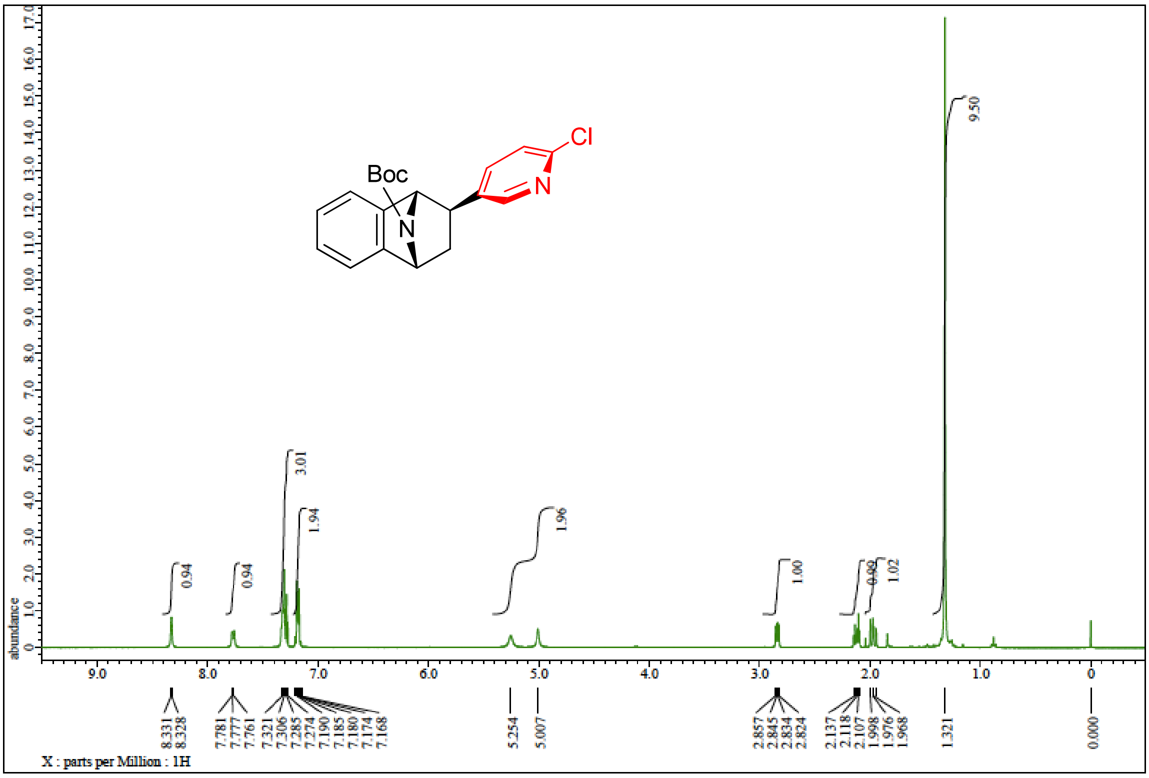


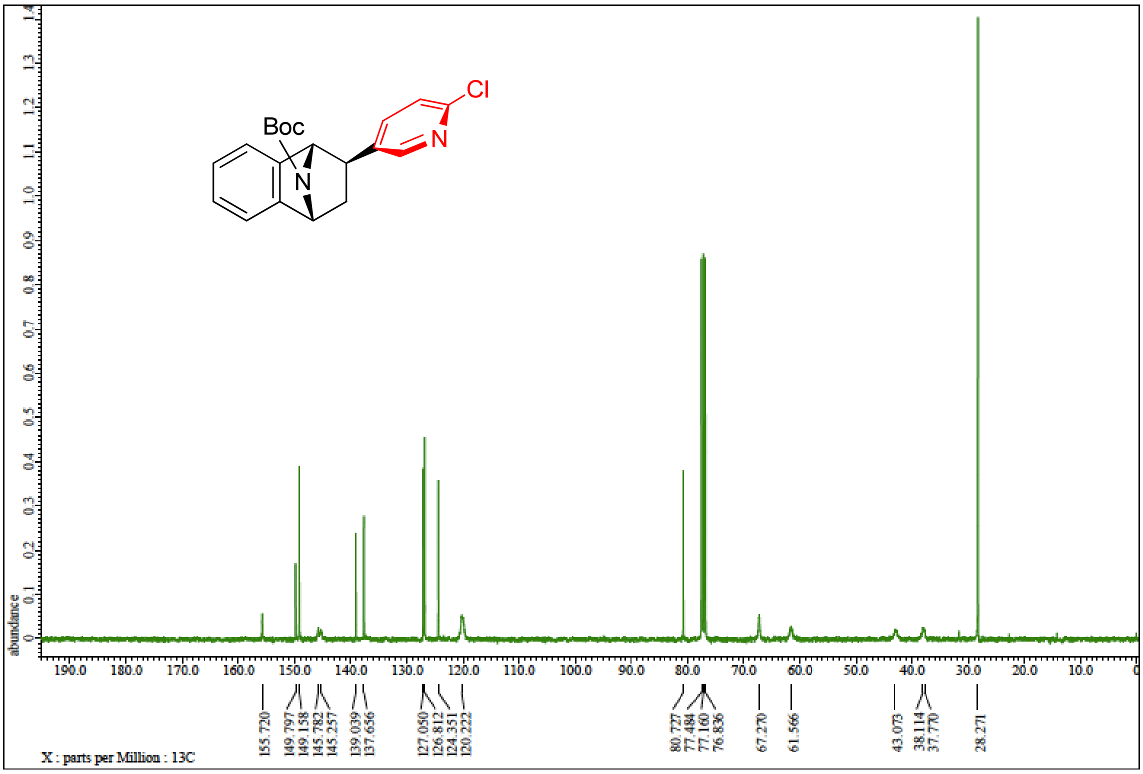
***tert*-Butyl (1*S*,2*R*,4*R*)-9-(phenanthrene-1-yl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3j)**



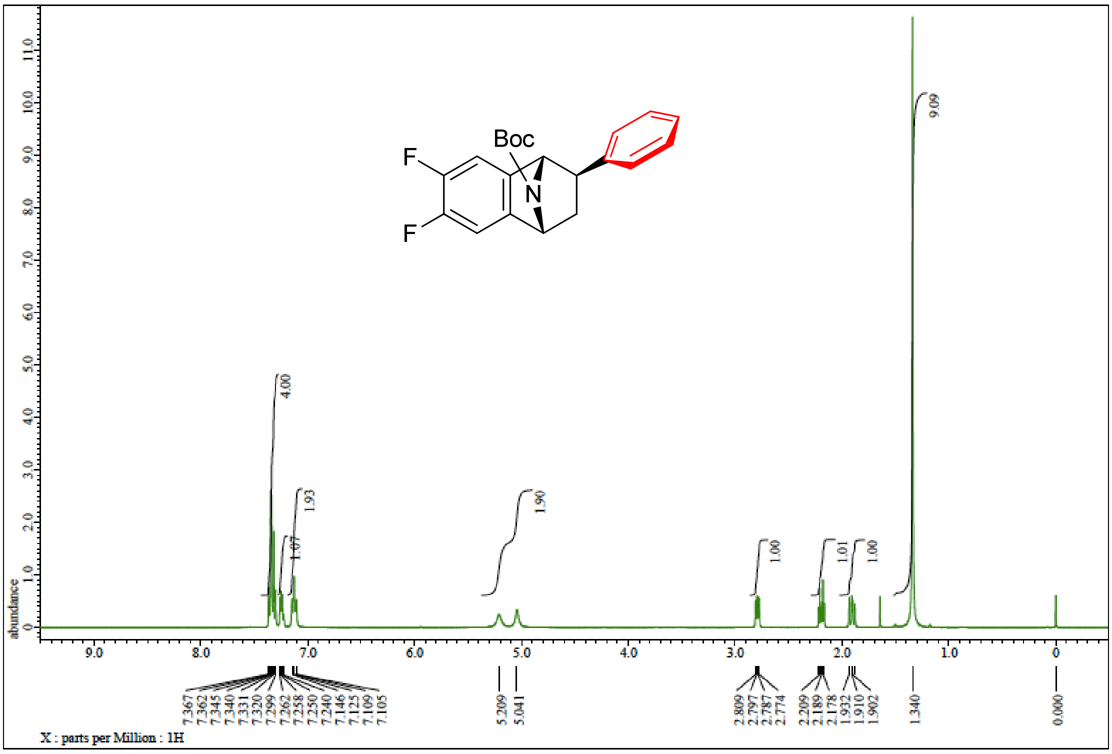


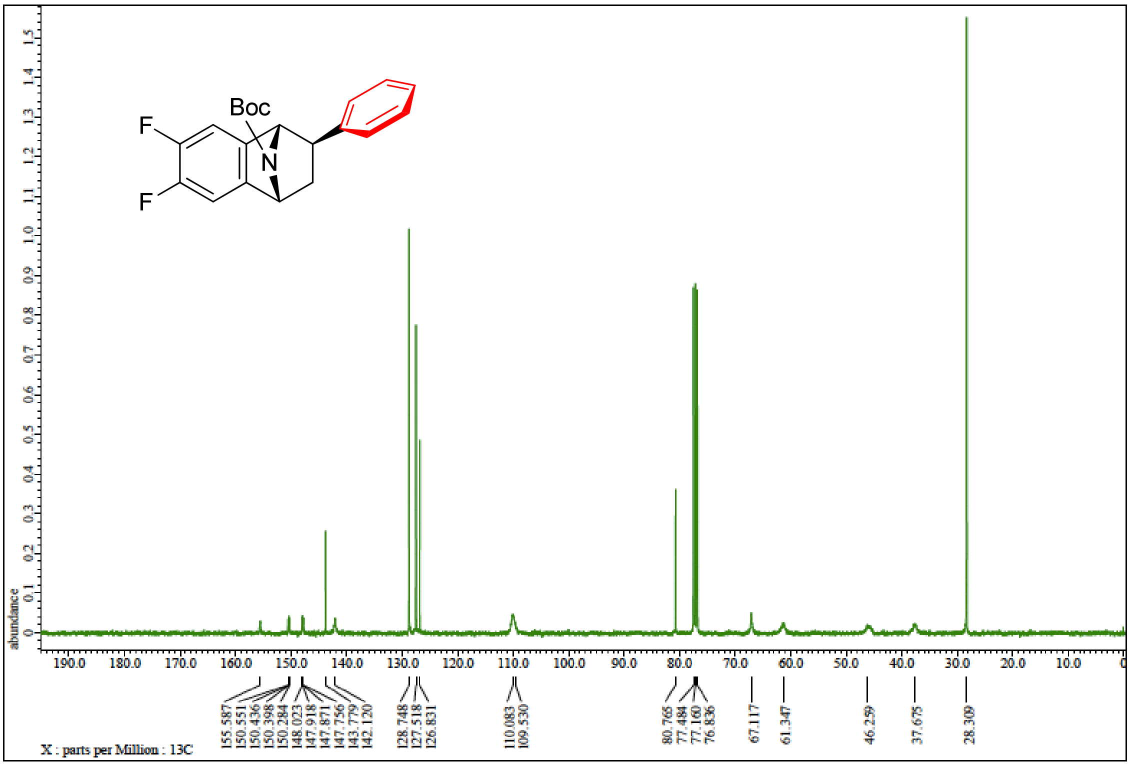
tert-Butyl (1_S_,2_R_,4_R_)-2-(6-chloropyridin-3-yl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3k)



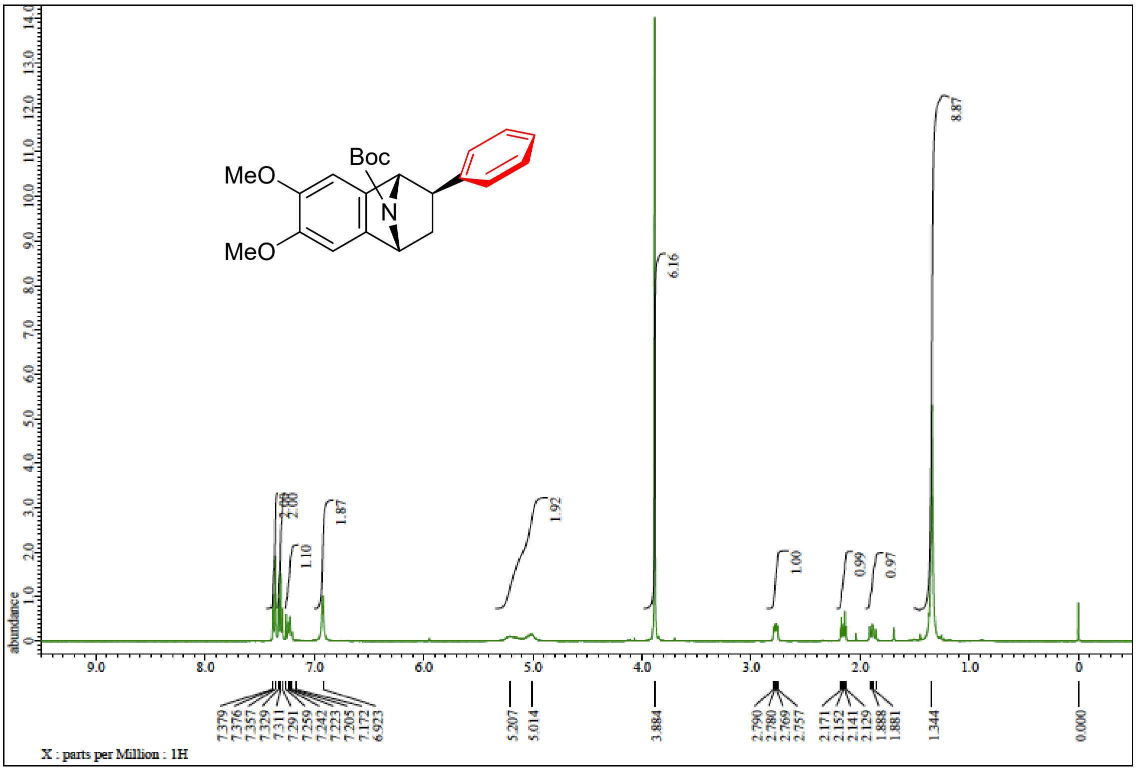


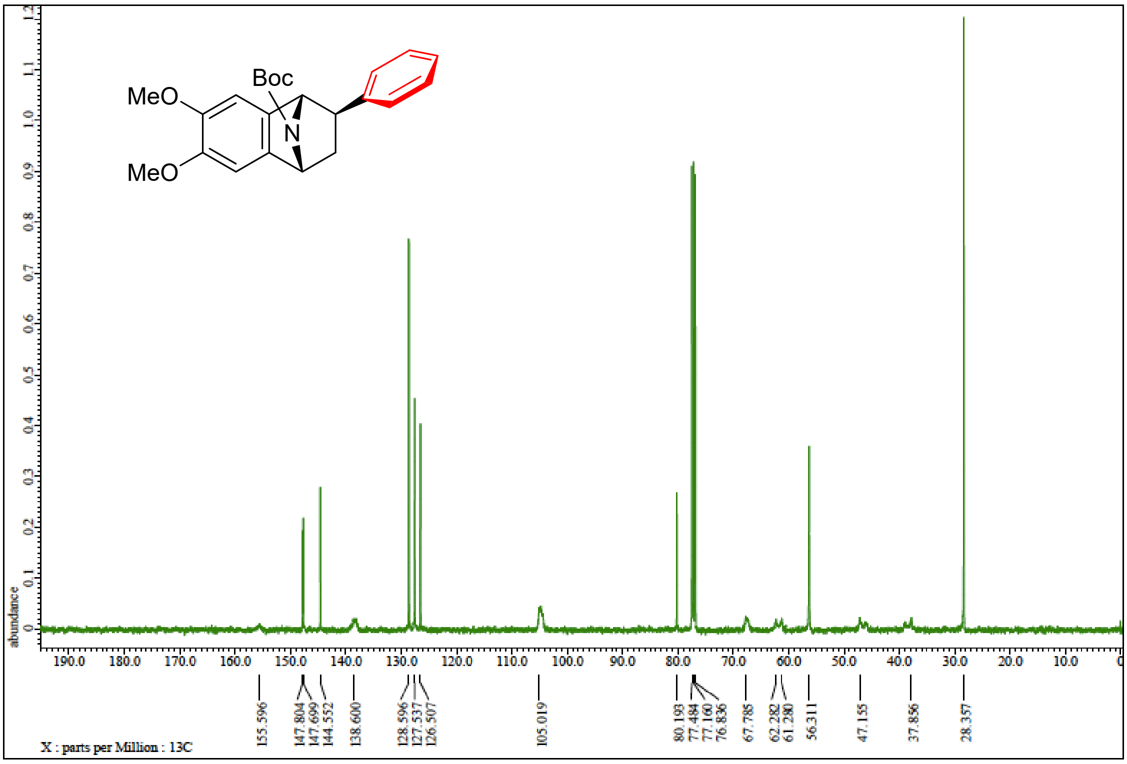
***tert*-Butyl (1*S*,2*R*,4*R*)-6,7-difluoro-2-phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3l)**



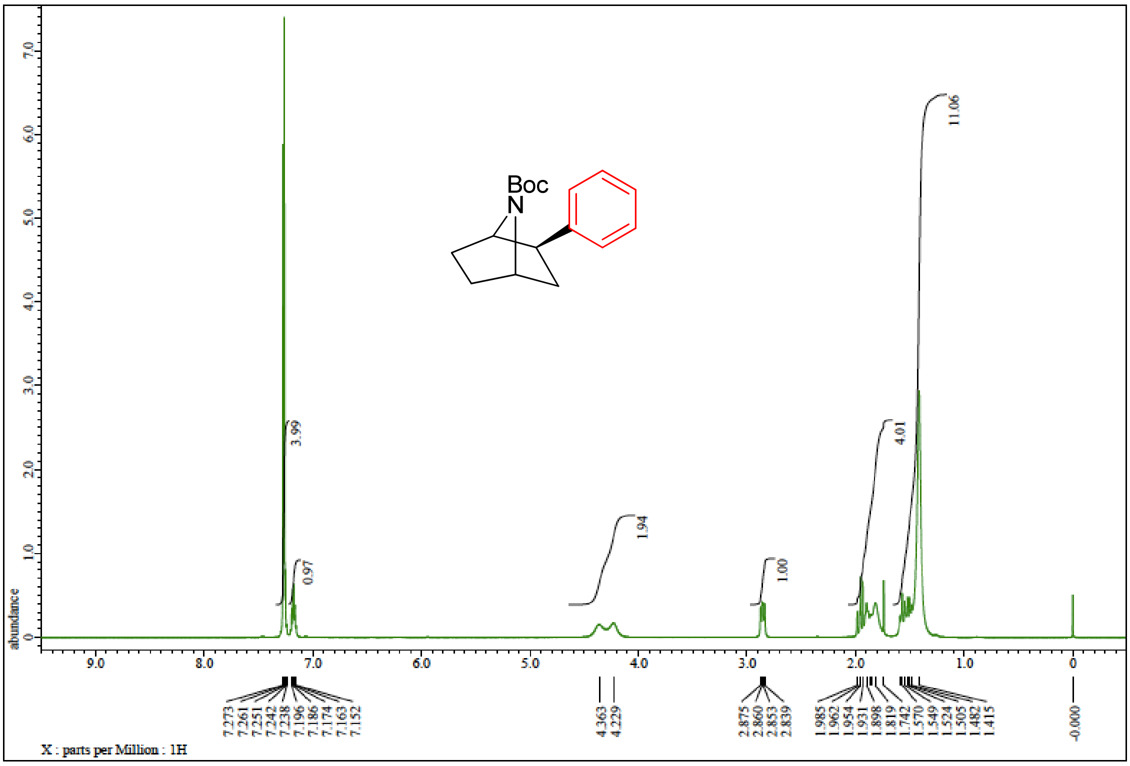


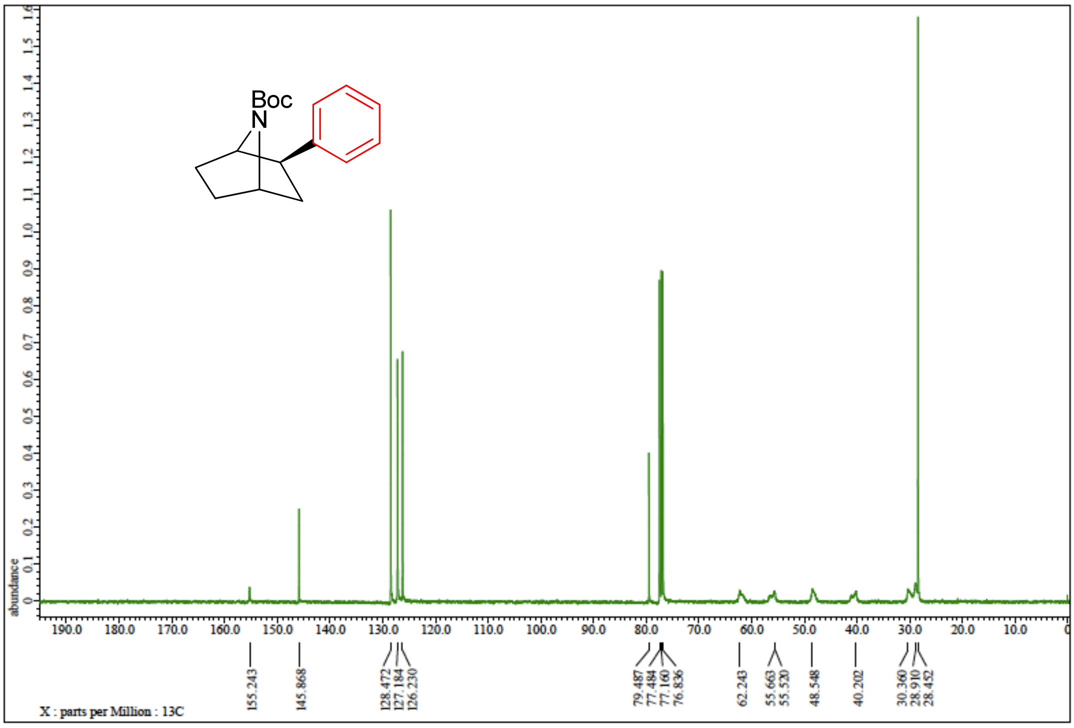
***tert*-Butyl (1*S*,2*R*,4*R*)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3m)**



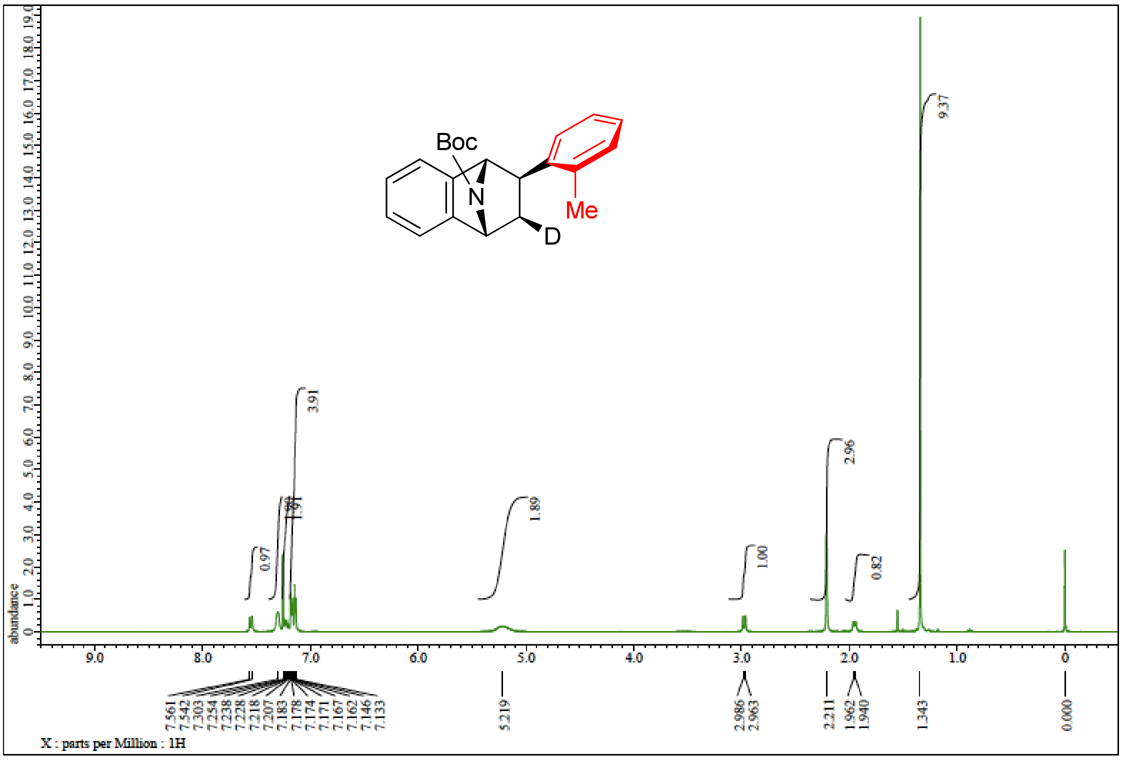


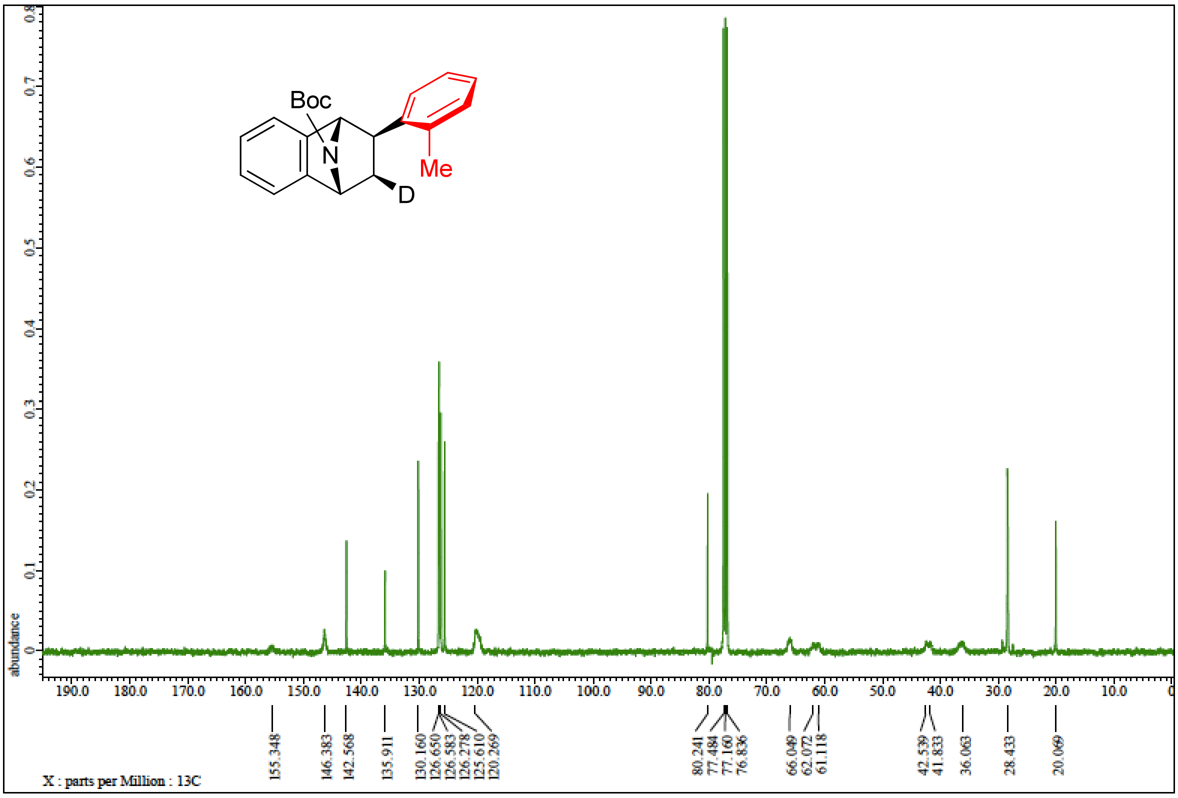
***tert*-Butyl (1*R*,2*R*,4*S*)-2-phenyl-7-azabicyclo[2.2.1]heptane-7-carboxylate (3n)**



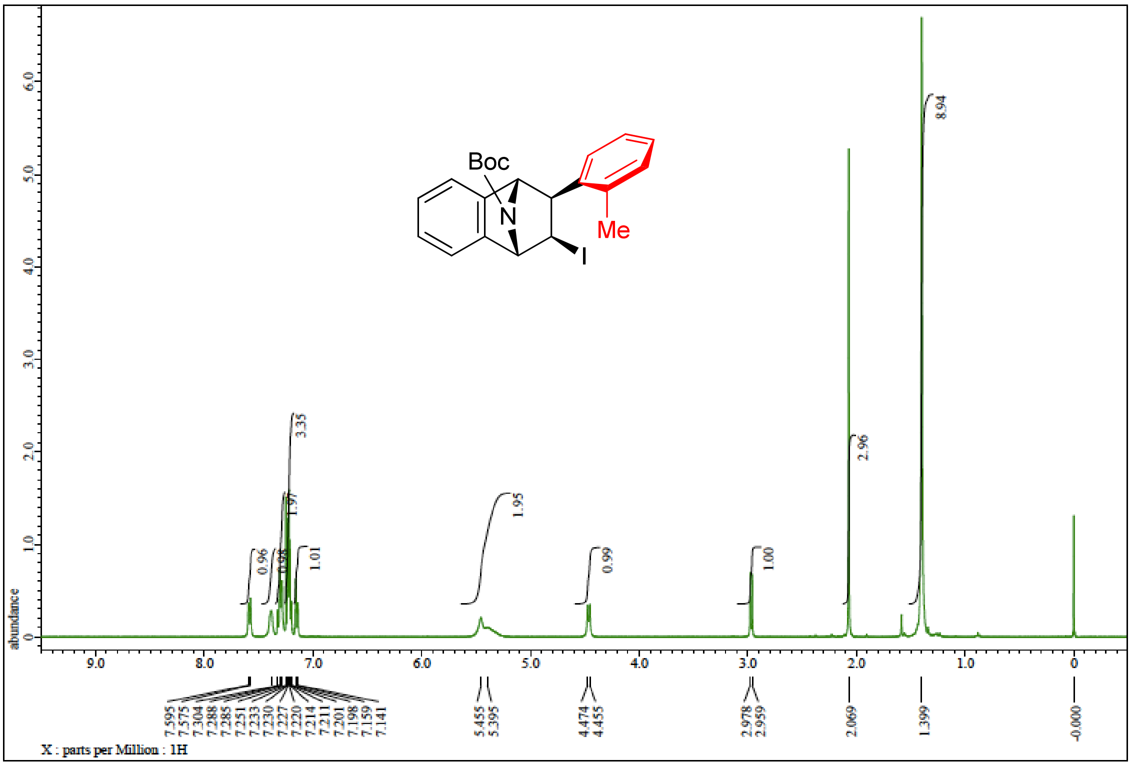


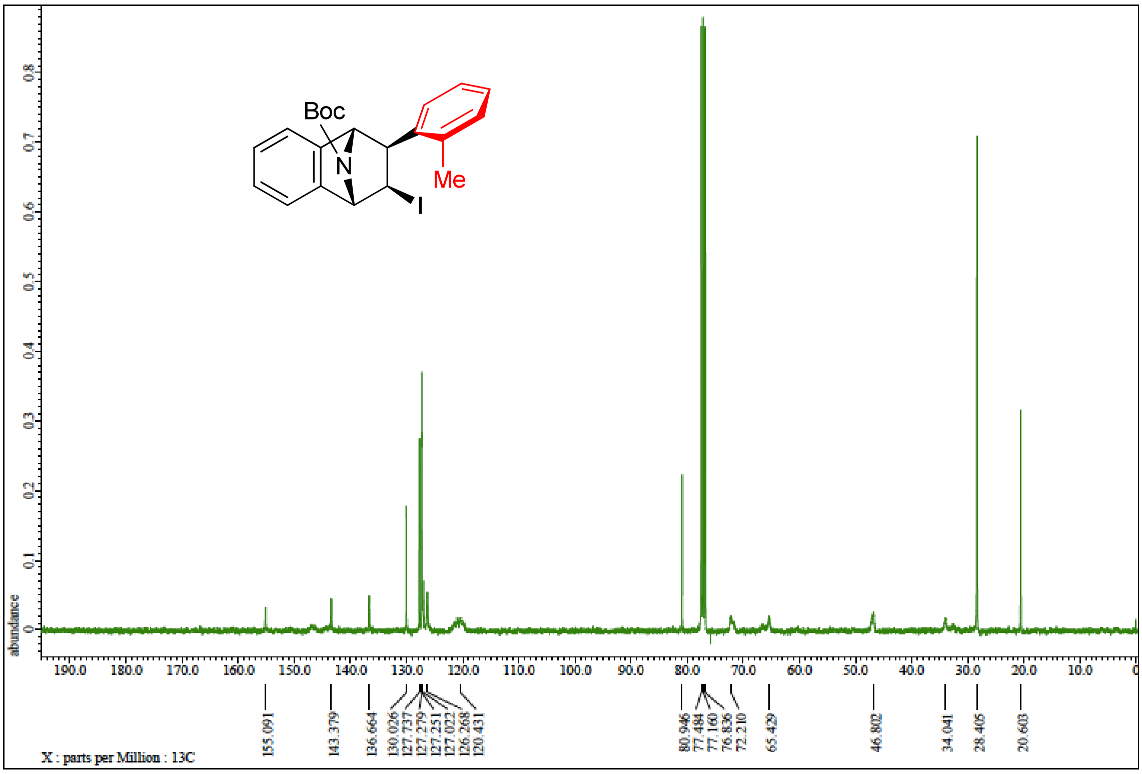
***tert*-Butyl (1*S*,2*R*,3*R*,4*R*)-2-(2-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate-3-*d* (5a)**





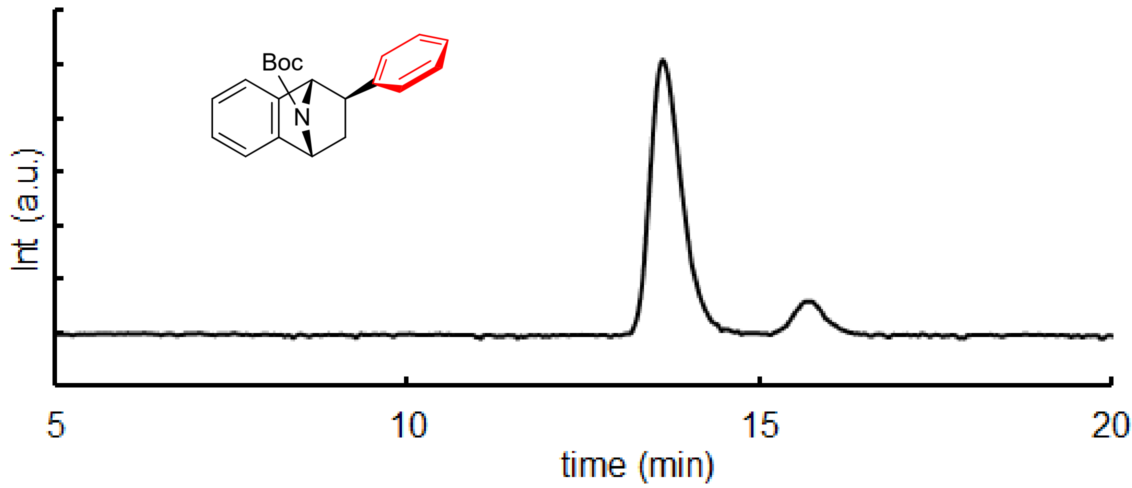
***tert*-Butyl (1*S*,2*R*,3*R*,4*S*)-2-iodo-3-(2-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (5b)**



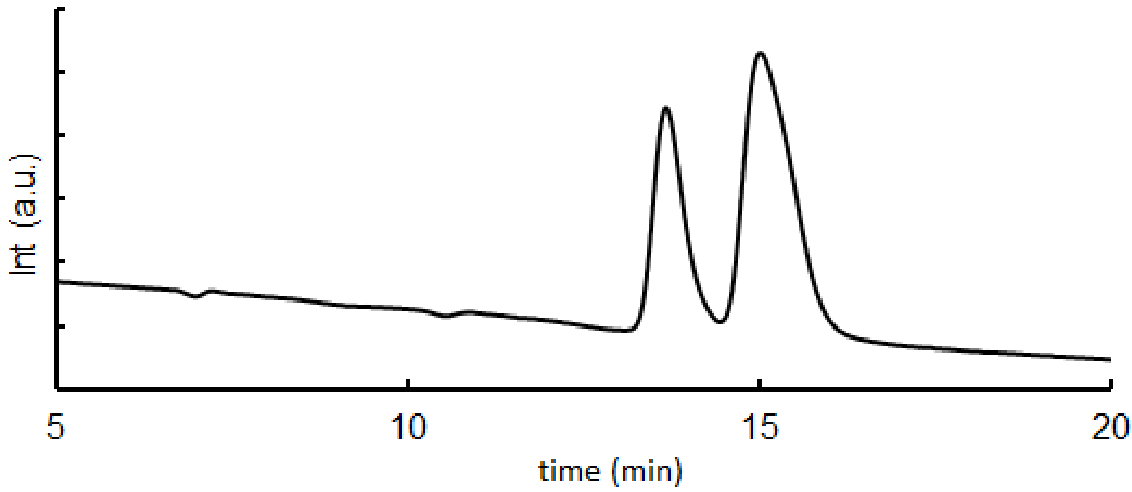


7. Chiral HPLC Chromatograms

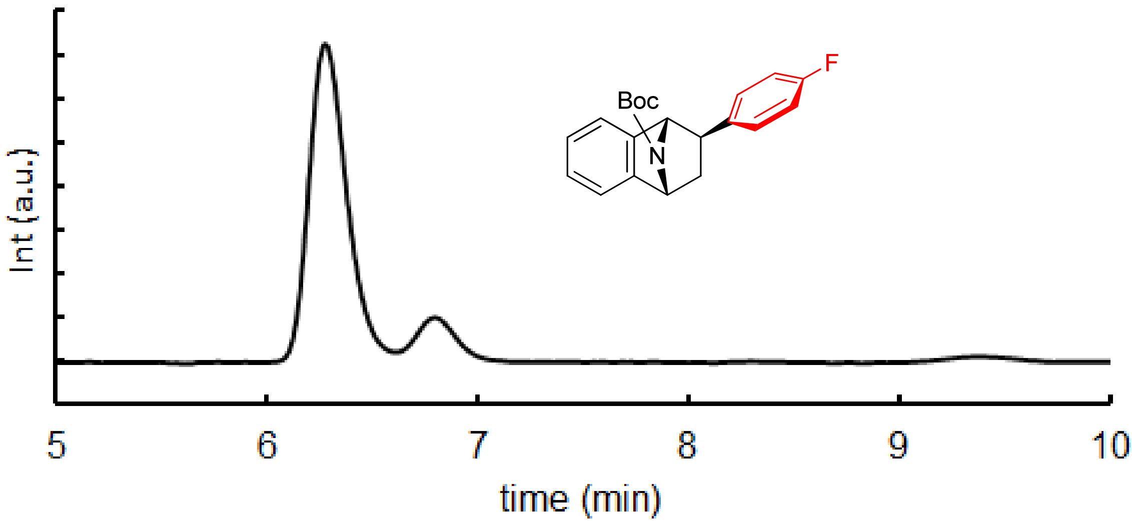
***tert*-Butyl(*1S,2R,4R*)-2-phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3a)**



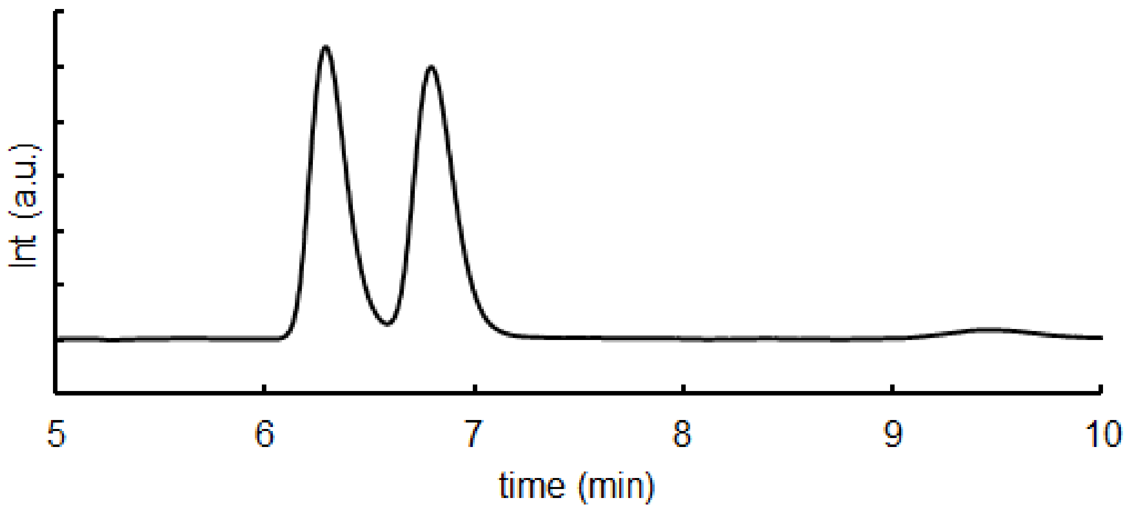
***Racemic tert*-Butyl(*1S,4R*)-2-phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate**



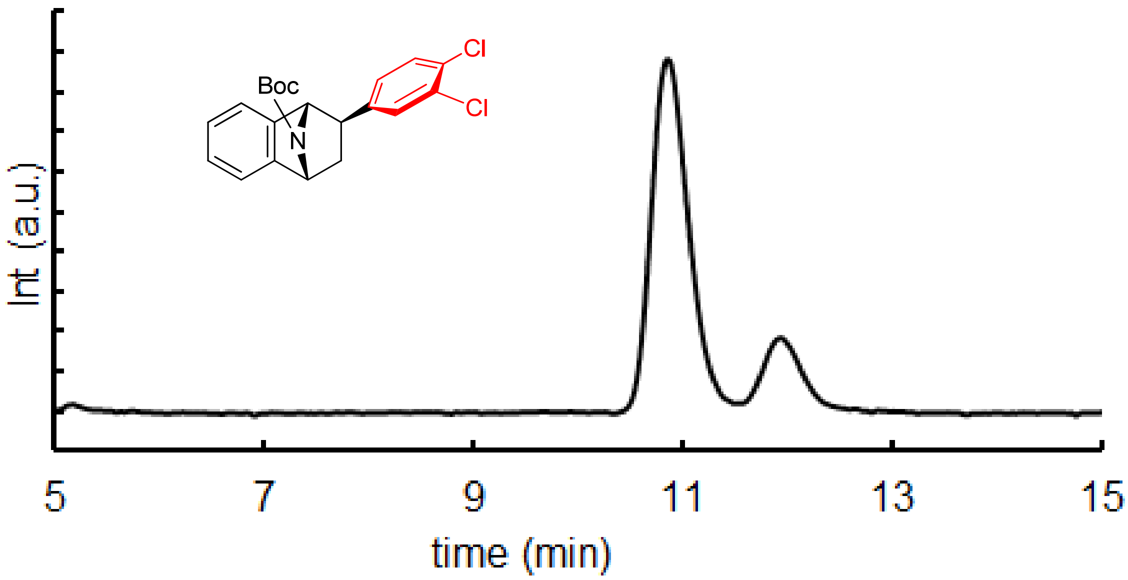
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(4-fluorophenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3b)**



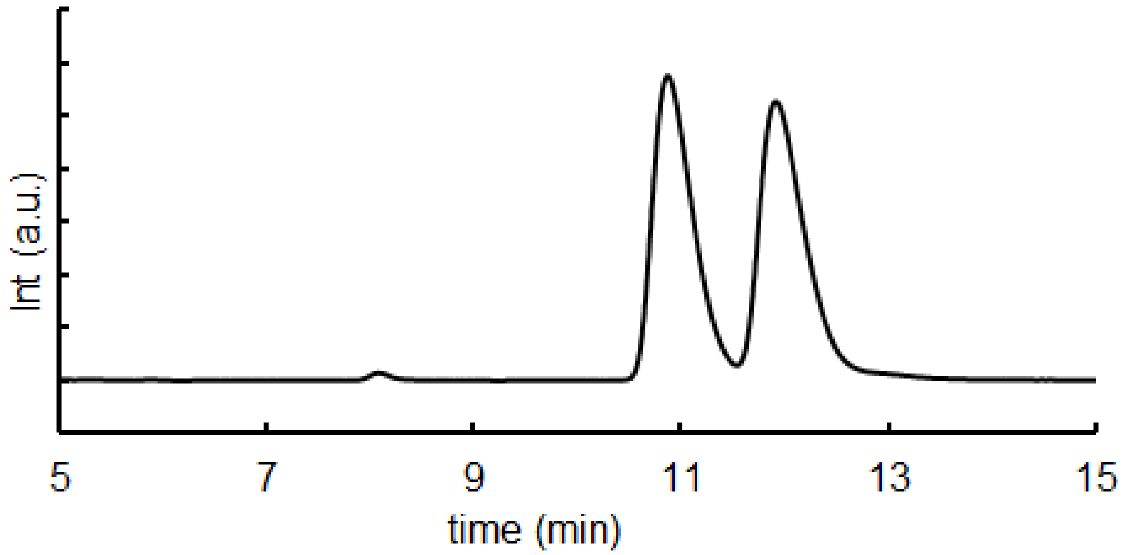
***Racemic* *tert*-Butyl (1*S*,4*R*)-2-(4-fluorophenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate**



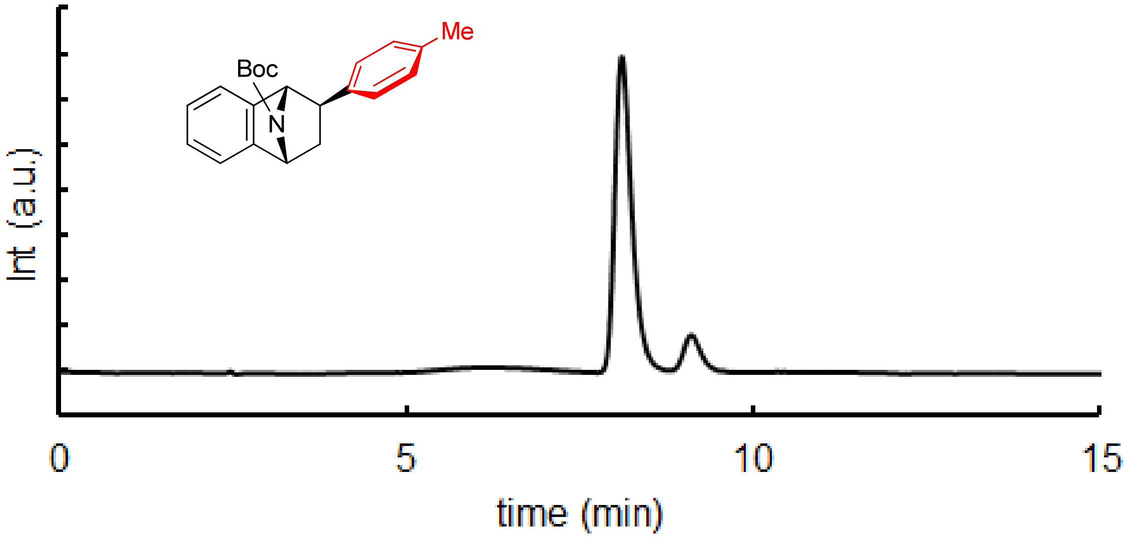
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3c)**



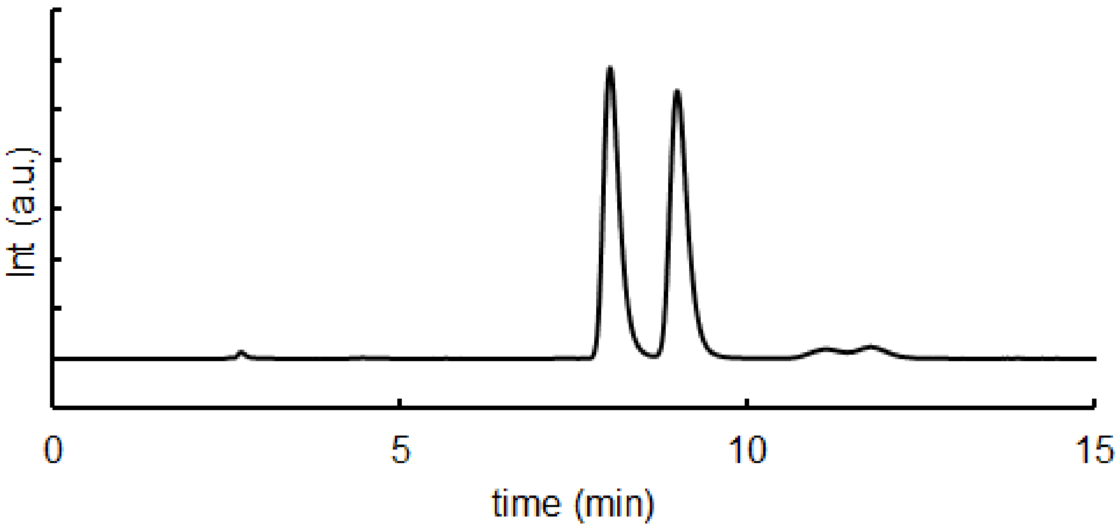
***Racemic tert*-Butyl (1*S*,4*R*)-2-(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate**



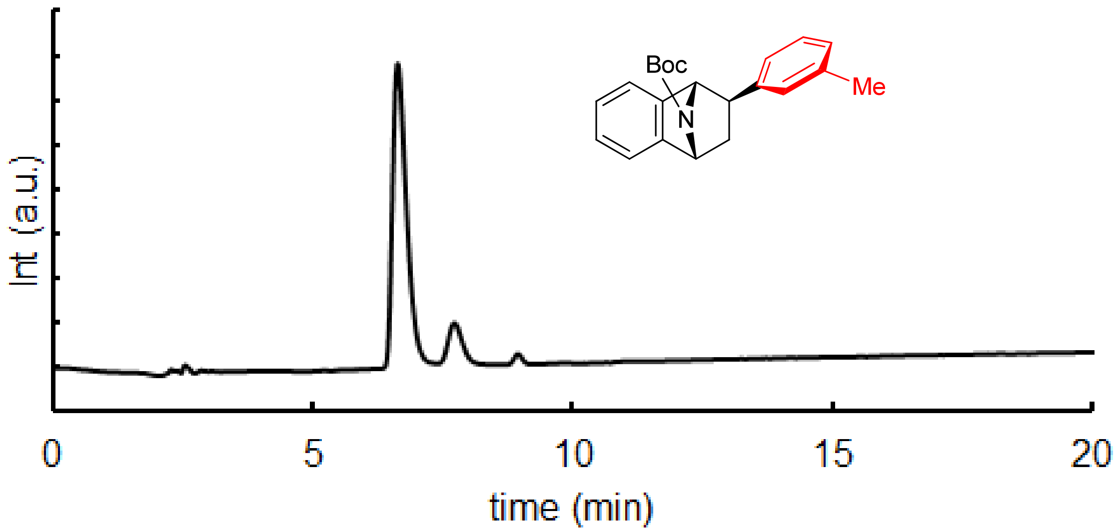
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(4-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3e)**



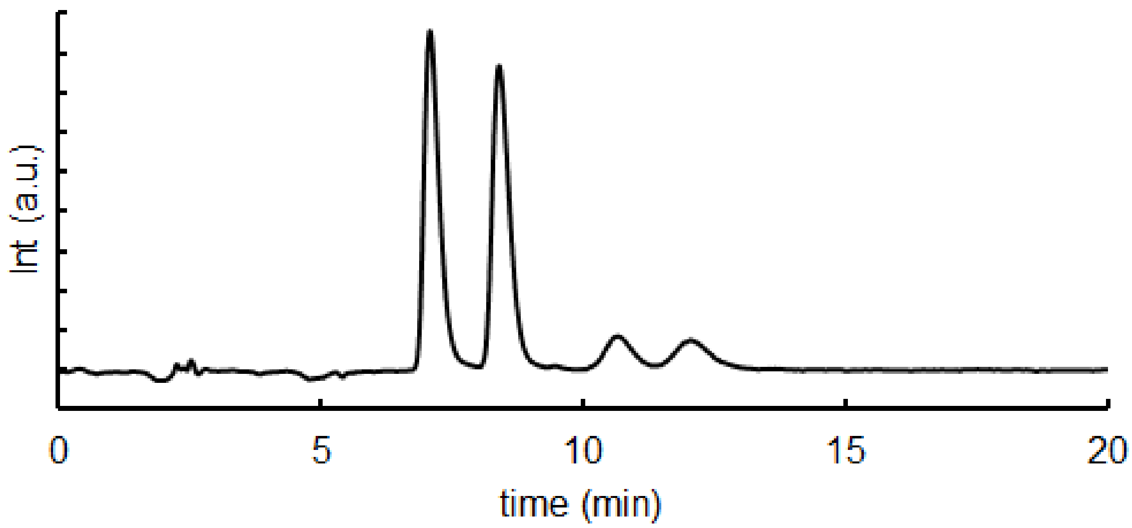
***Racemin tert*-Butyl (1*S*,4*R*)-2-(4-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate**



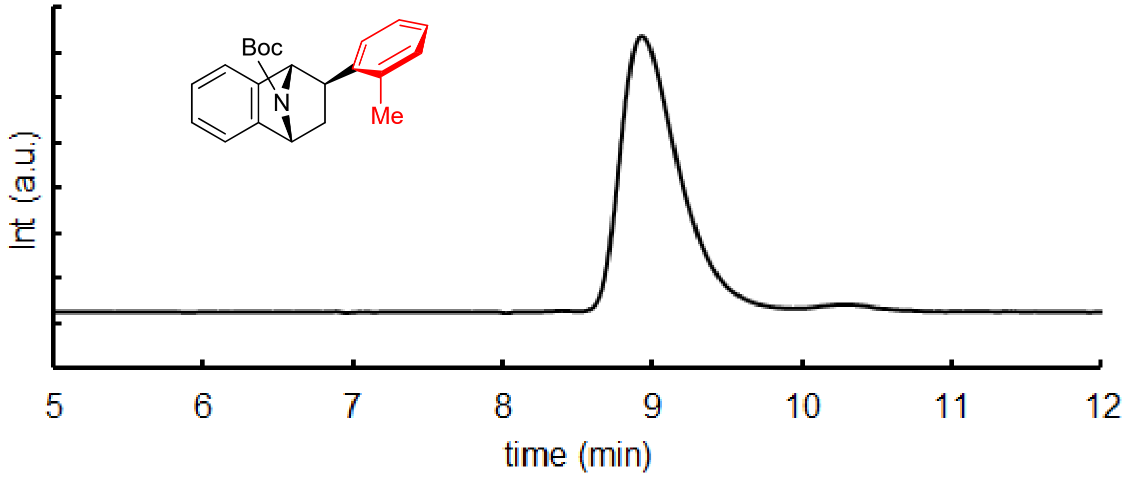
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(3-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3f)**



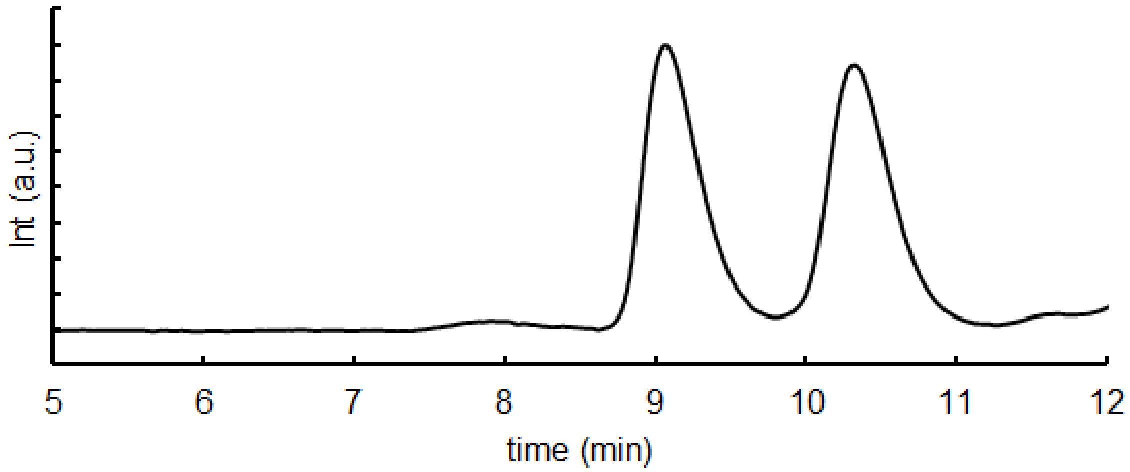
***Racemin tert*-Butyl (1*S*,4*R*)-2-(3-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate**



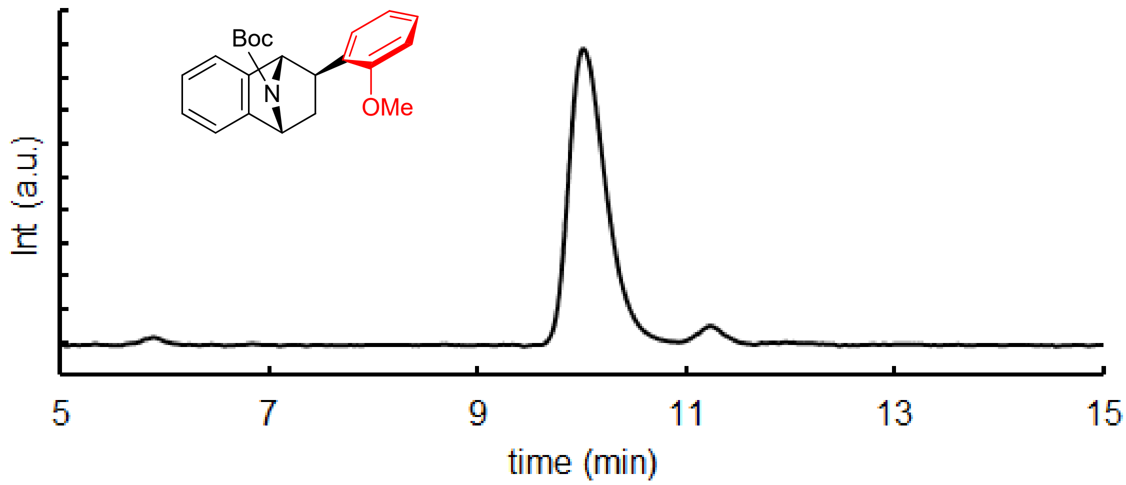
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(2-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3g)**



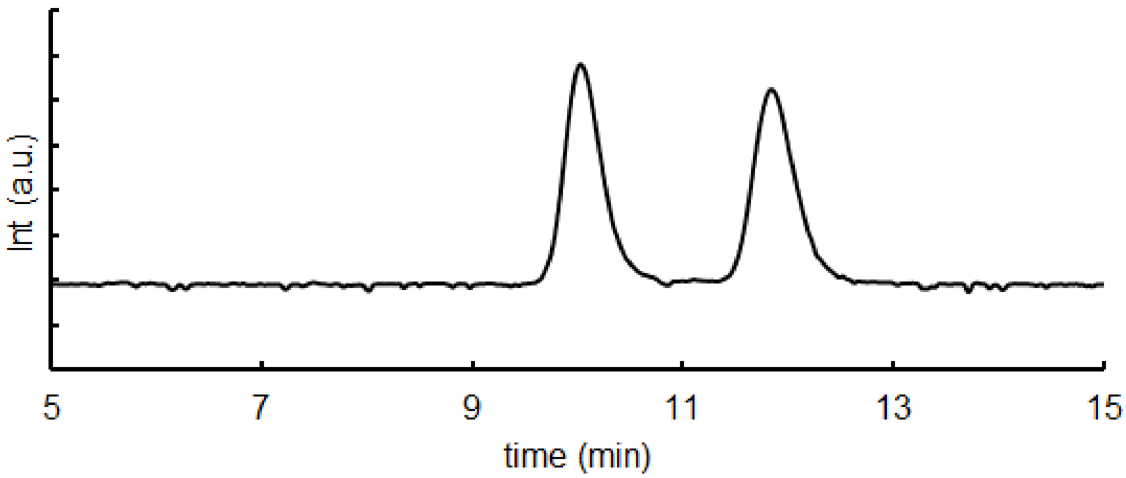
***Racemic tert*-Butyl (1*S*,4*R*)-2-(2-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate**



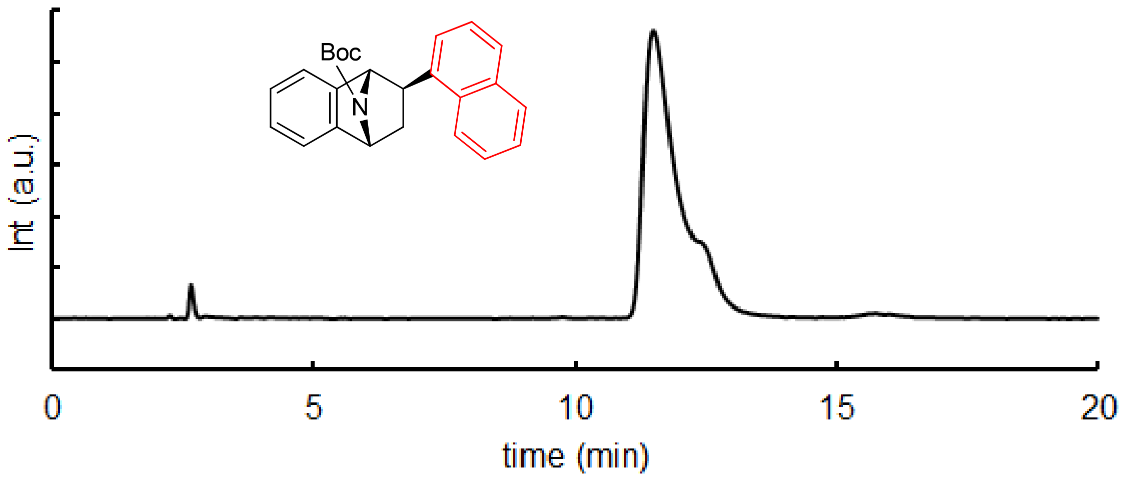
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(2-methoxyphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3h)**



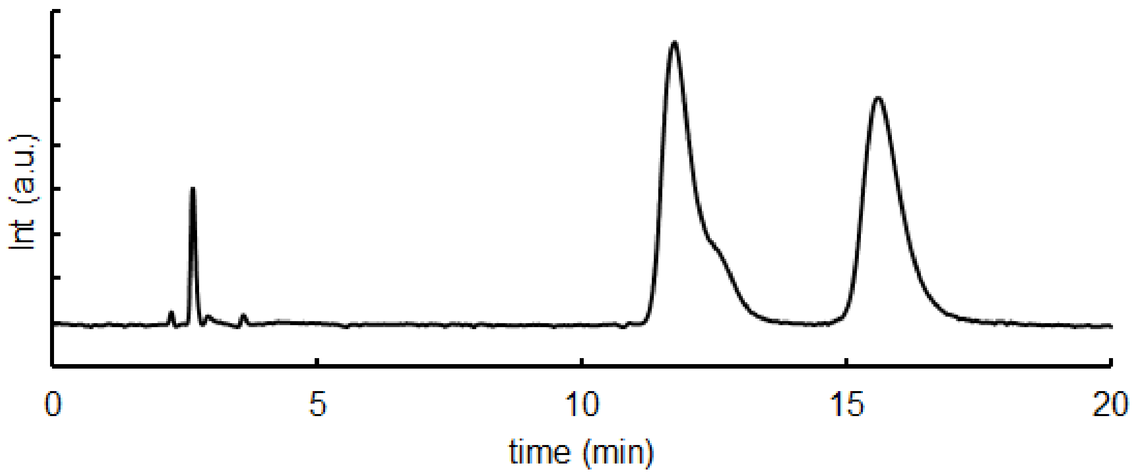
***Racemic tert*-Butyl (1*S*,4*R*)-2-(2-methoxyphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate**



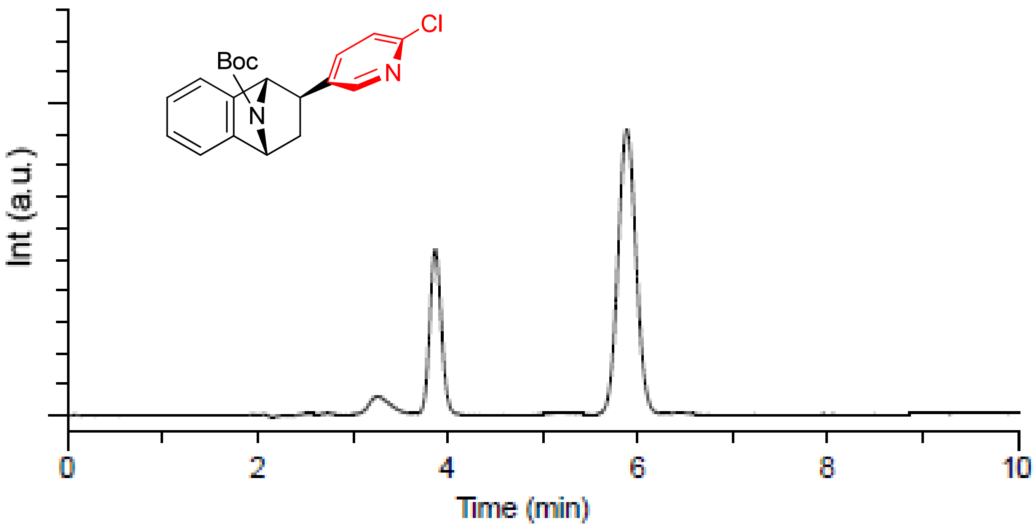
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(naphthalen-1-yl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3i)**



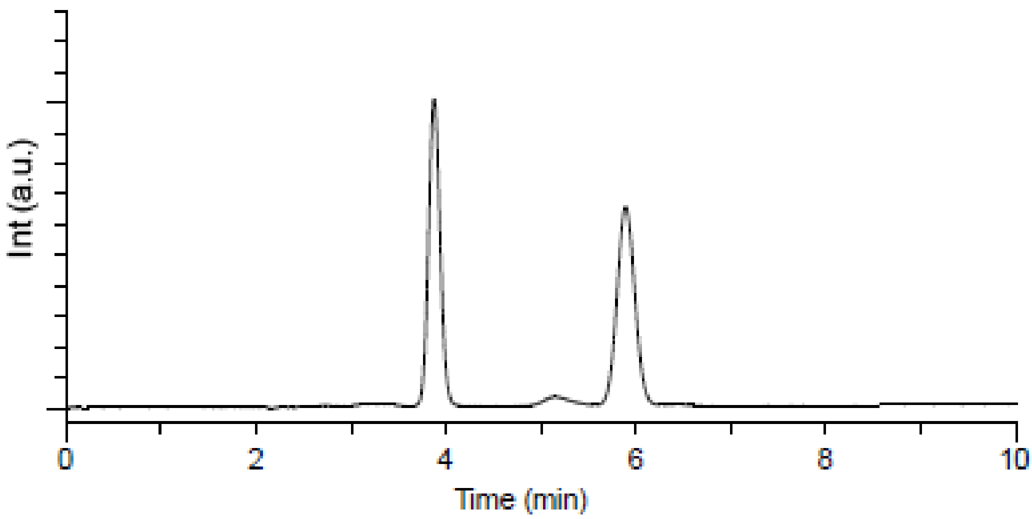
***Racemic* *tert*-Butyl (1*S*,4*R*)-2-(naphthalen-1-yl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate**



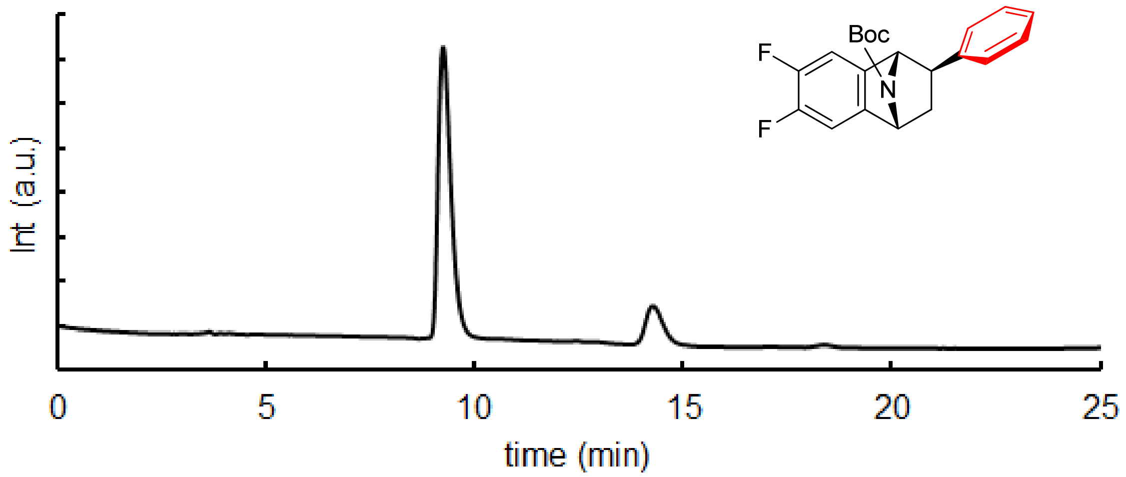
***tert*-Butyl (1*S*,2*R*,4*R*)-2-(6-chloropyridin-3-yl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3k)**



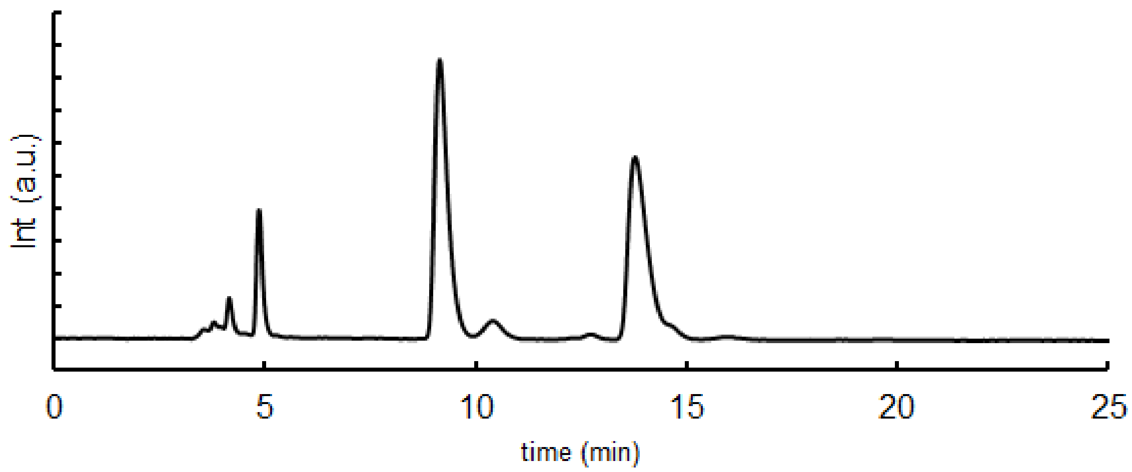
***Racemic tert*-Butyl (1*S*,4*R*)-2-(6-chloropyridin-3-yl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate**



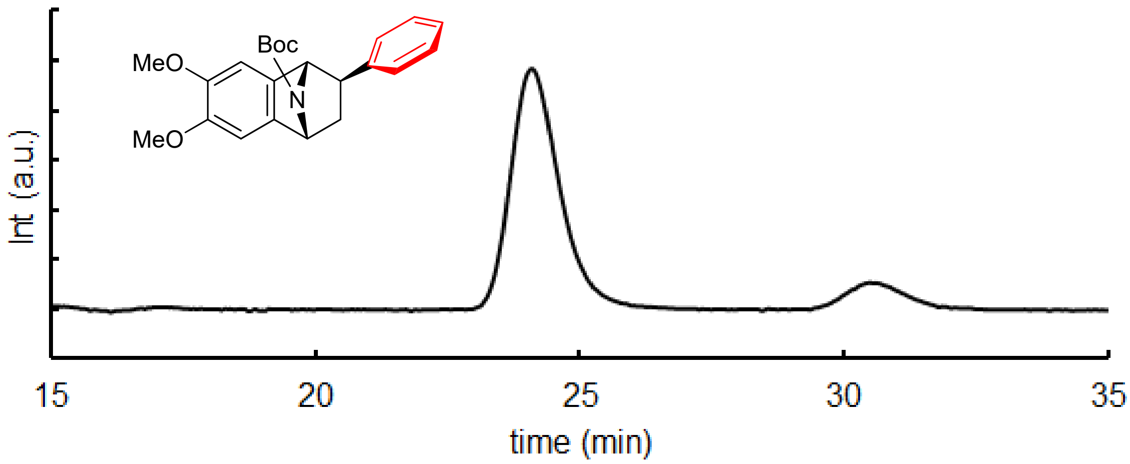
***tert*-Butyl (1*S*,2*R*,4*R*)-6,7-difluoro-2-phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3l)**



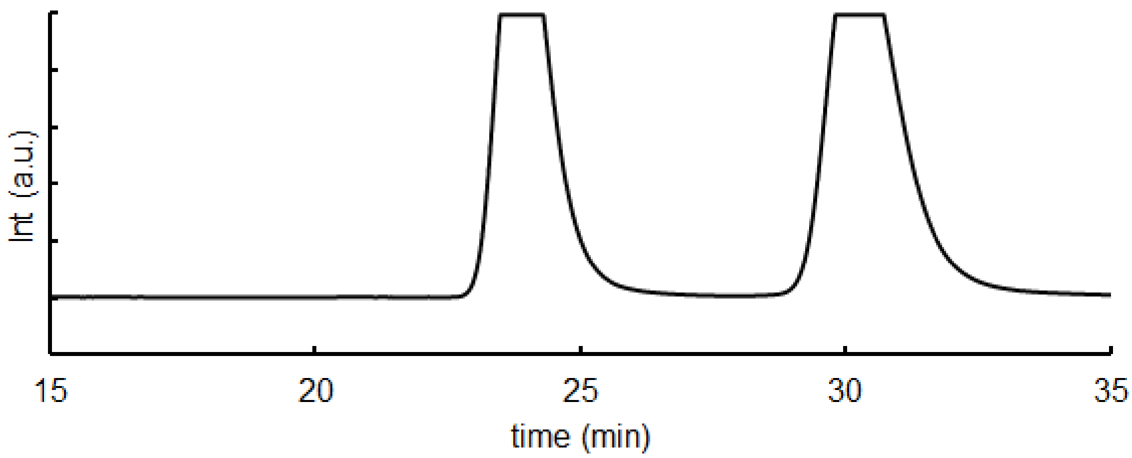
***Racemic tert*-Butyl (1*S*,4*R*)-6,7-difluoro-2-phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate**



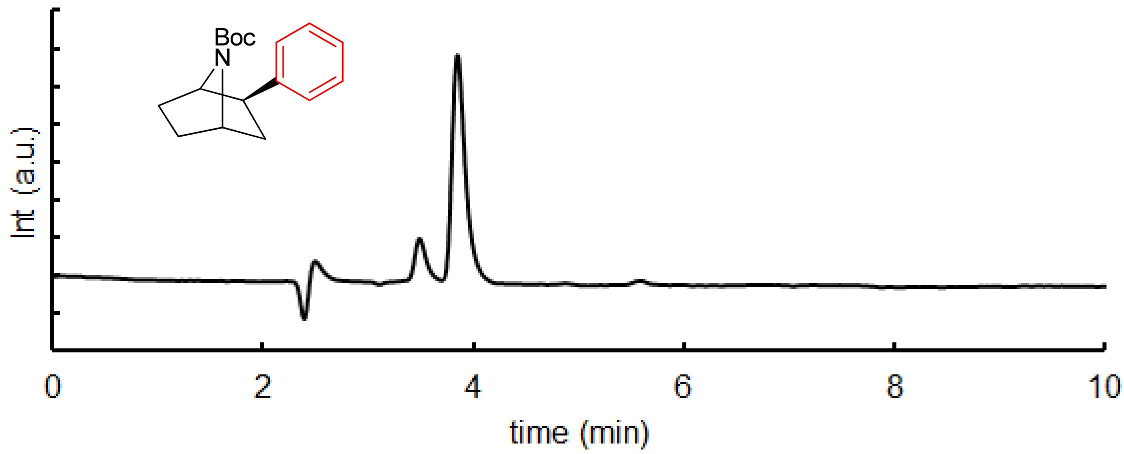
***tert*-Butyl (1*S*,2*R*,4*R*)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (3m)**



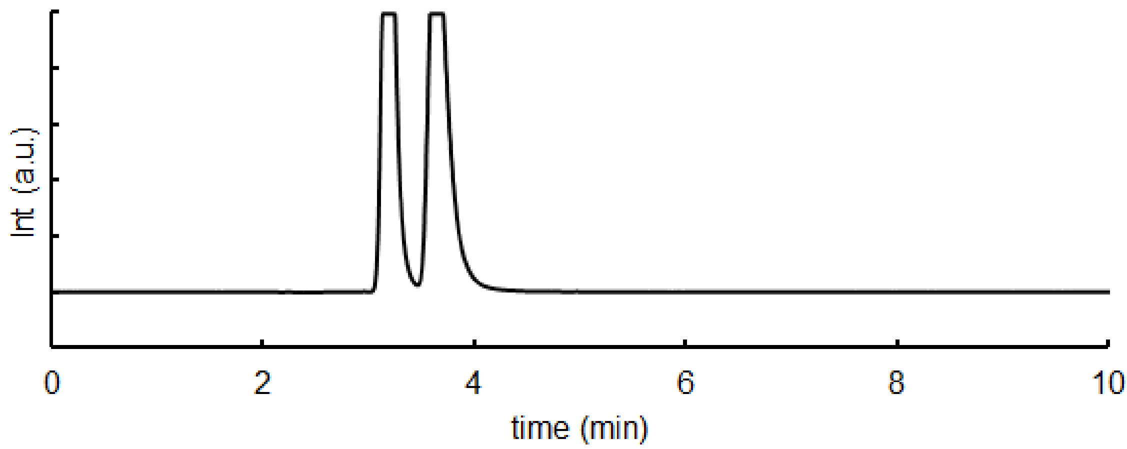
***Racemic tert*-Butyl (1*S*,4*R*)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate**



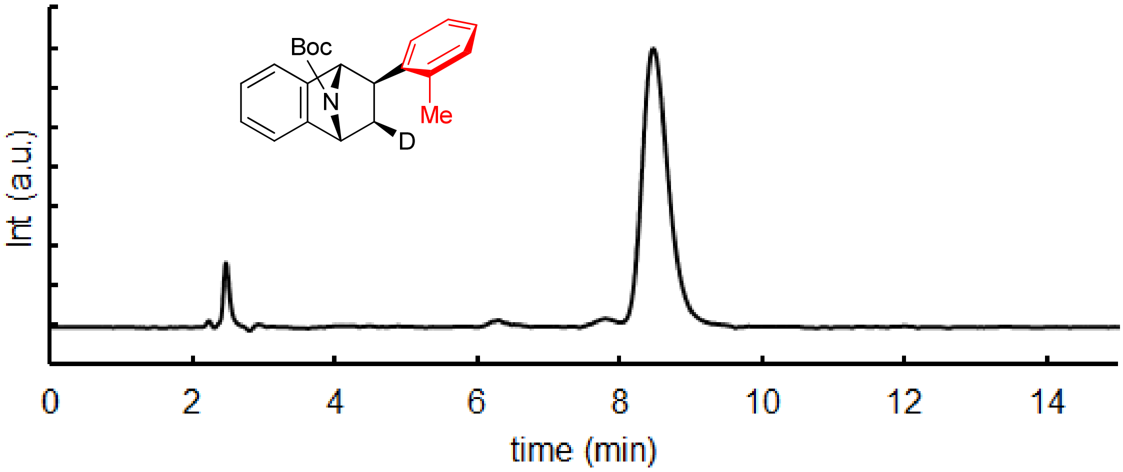
***tert*-Butyl (1*R*,2*R*,4*S*)-2-phenyl-7-azabicyclo[2.2.1]heptane-7-carboxylate (3n)**



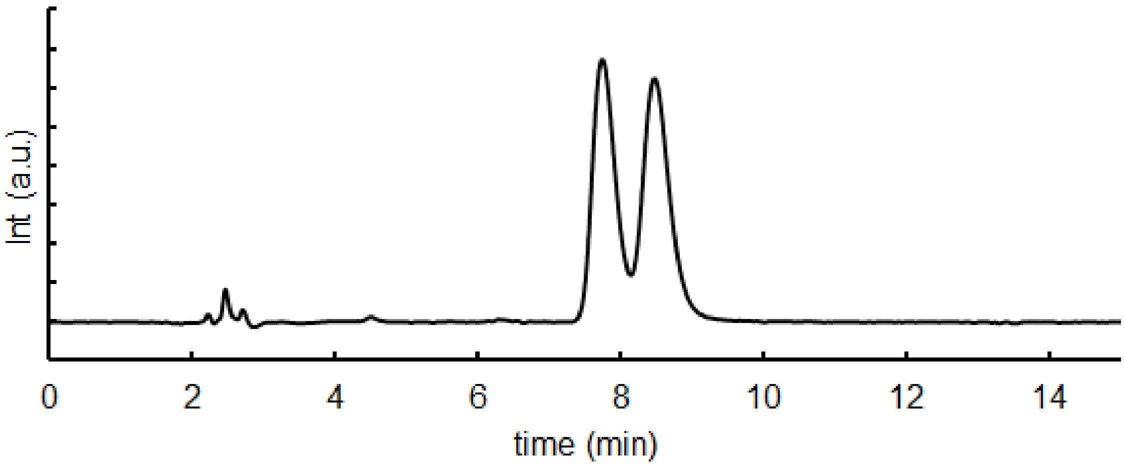
***Racemic tert*-Butyl (1*R*,4*S*)-2-phenyl-7-azabicyclo[2.2.1]heptane-7-carboxylate**



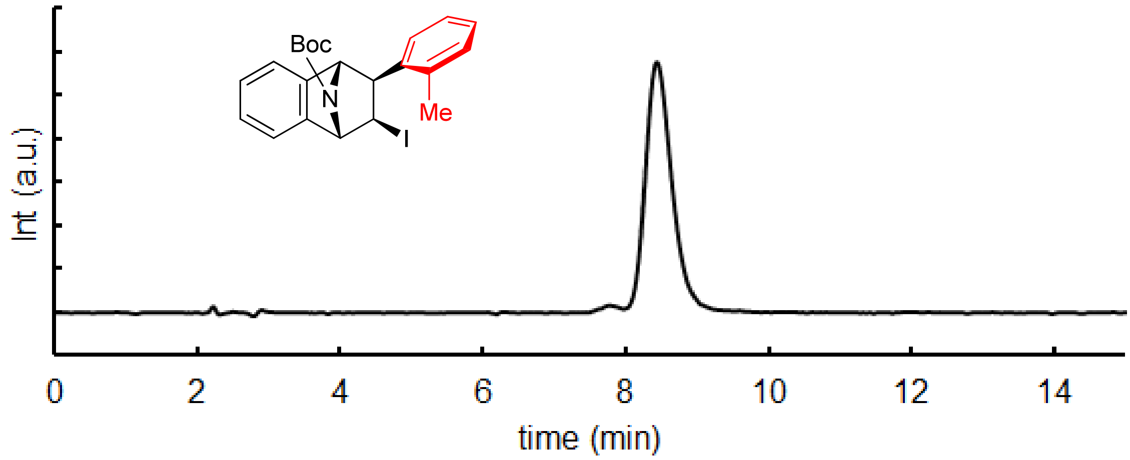
***tert*-Butyl (1*S*,2*R*,3*R*,4*R*)-2-(2-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate-3-*d* (5a)**



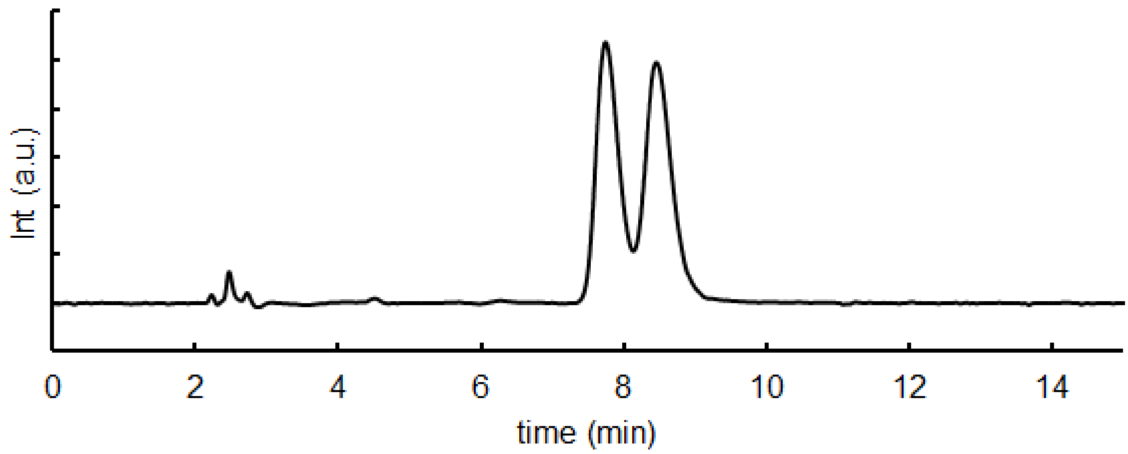
Racemic tert*-Butyl (1*S*,4*R*)-2-(2-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate-3-*d



***tert*-Butyl (1*S*,2*R*,3*R*,4*S*)-2-iodo-3-(2-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate (5b)**



***Racemic* *tert*-Butyl (1*S*,4*S*)-2-iodo-3-(2-methylphenyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-11-carboxylate**



8. Crystallographic Data

Single-crystal X-ray structure determination for 3c and 5b

Single crystals of **3c** and **5b** suitable for X-ray diffraction studies were analyzed by using a Rigaku AFC-10R diffractometer with Saturn 724 CCD detector using graphite-monochromated Mo-*Kα* radiation (λ = 0.71070 Å) and synchrotron radiation at beam line BL02B1 (λ = 0.70090 Å) of SPring-8 (Hyogo, Japan) with Rigaku Mercury II detector. The structures of **3c** and **5b** were solved by direct methods and refined by the full-matrix least squares method by using SHELX-97. The position of all non-hydrogen atoms was found from difference Fourier electron density maps and refined anisotropically. All calculations were performed using the Rigaku Crystal Structure ver 4.0 crystallographic software packages and illustrations were drawn by using ORTEP.

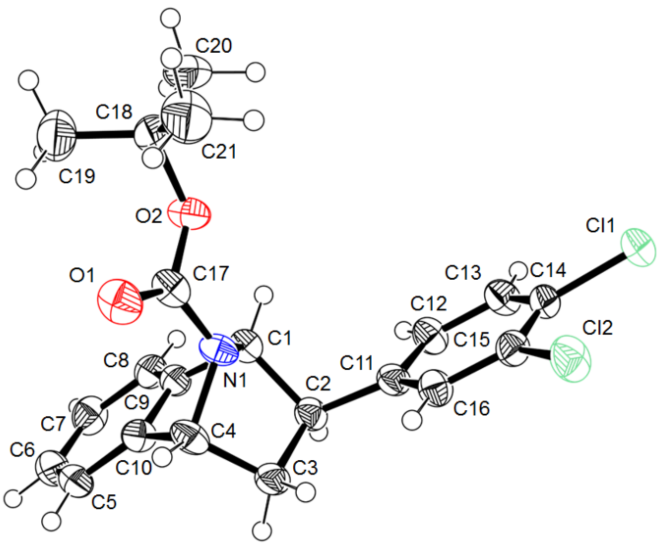


Figure S2. ORTEP drawing for **3c**. Thermal ellipsoids are drawn at 50% probability level.

Table S4. Crystallographic Data for 3c Obtained from EtOH–H_2O.

Molecular Formula	$C_{21}H_{21}Cl_2NO_2$
Formula Weight	390.31
Crystal Dimensions (mm)	0.40 × 0.30 × 0.10
Crystal Color, Habit	colorless, block
Crystal System	monoclinic
Lattice Type	primitive
Space Group	$P2_1$(#4)
a (Å)	9.168(3)
b (Å)	6.287(2)
c (Å)	17.508(5)
β (°)	104.478(4)
Cell Volume (Å^3)	977.1(5)
Z Value	2
F (000)	408.00
D_{calc} (g/cm^{-3})	1.327
Temperature (°C)	−99.8
Radiation	graphite monochromated Mo-$K\alpha$ (λ = 0.71075 Å)
μ(Mo-$K\alpha$) (cm^{-1})	3.465
$2\theta_{max}$ (°)	62.9
Total Number of Reflections	11150
Number of Unique Reflections	4030
Number of Variables	319
Reflection / Parameter Ratio	12.63
Final R_{all} and $_wR_2$	0.0478; 0.1128
Goodness of Fit	1.121
Max Shift / Error	0.000
Flack parameter	0.000
Method of phase determination	Direct Methods (SIR-2008)

Table S5. Atomic Coordinates and B_{eq} for 3c.

atom	x	y	z	B_{eq}
Cl1	-0.36571(9)	-0.1441(2)	0.08504(6)	3.23(2)
Cl2	-0.27279(10)	0.3068(2)	0.03088(6)	3.54(3)
O1	0.3420(4)	0.6723(5)	0.3147(2)	3.52(6)
O2	0.2621(3)	0.3639(5)	0.3601(2)	2.99(5)
N1	0.3169(4)	0.3658(6)	0.2427(2)	2.51(6)
C1	0.3468(5)	0.1349(6)	0.2435(3)	2.33(6)
C2	0.2939(4)	0.0927(7)	0.1523(3)	2.48(7)
C3	0.3474(4)	0.2982(8)	0.1182(2)	2.74(7)
C4	0.4188(5)	0.4302(7)	0.1933(3)	2.76(7)
C5	0.7131(5)	0.3540(9)	0.2388(3)	3.08(8)
C6	0.8191(5)	0.2025(9)	0.2751(3)	3.58(9)
C7	0.7735(5)	0.0174(8)	0.3045(3)	3.34(8)
C8	0.6216(5)	-0.0246(7)	0.2995(3)	2.80(7)
C9	0.5182(4)	0.1286(6)	0.2648(2)	2.31(6)
C10	0.5632(4)	0.3157(7)	0.2342(2)	2.56(7)
C11	0.1265(4)	0.0402(7)	0.1286(3)	2.53(7)
C12	0.0828(4)	-0.1620(8)	0.1478(3)	2.87(7)
C13	-0.0683(5)	-0.2179(8)	0.1337(3)	2.99(8)
C14	-0.1781(4)	-0.0733(7)	0.0987(2)	2.63(7)
C15	-0.1368(4)	0.1243(7)	0.0765(2)	2.60(7)
C16	0.0141(5)	0.1816(7)	0.0913(3)	2.63(7)
C17	0.3118(5)	0.4828(7)	0.3081(3)	2.62(7)
C18	0.2290(5)	0.4638(8)	0.4307(3)	3.32(8)
C19	0.3670(7)	0.5693(12)	0.4813(4)	4.62(11)
C20	0.1821(8)	0.2733(12)	0.4713(4)	5.09(13)
C21	0.1002(7)	0.6198(12)	0.4031(4)	5.14(13)

$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S6. Anisotropic Displacement Parameters for 3c.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl1	0.0261(4)	0.0516(7)	0.0455(5)	-0.0034(5)	0.0102(4)	-0.0016(5)
Cl2	0.0285(5)	0.0501(7)	0.0529(6)	0.0082(5)	0.0047(4)	0.0106(5)
O1	0.055(2)	0.024(2)	0.057(2)	-0.002(2)	0.019(2)	0.001(2)
O2	0.048(2)	0.030(2)	0.042(2)	-0.002(2)	0.0253(12)	-0.0009(13)
N1	0.035(2)	0.026(2)	0.038(2)	0.001(2)	0.0169(13)	0.007(2)
C1	0.030(2)	0.024(2)	0.035(2)	0.002(2)	0.009(2)	0.003(2)
C2	0.025(2)	0.035(2)	0.035(2)	0.002(2)	0.008(2)	0.002(2)
C3	0.026(2)	0.047(3)	0.032(2)	0.001(2)	0.008(2)	0.007(2)
C4	0.032(2)	0.030(2)	0.045(2)	0.000(2)	0.014(2)	0.012(2)
C5	0.032(2)	0.048(3)	0.038(2)	-0.007(2)	0.011(2)	0.003(2)
C6	0.027(2)	0.067(4)	0.042(3)	-0.005(2)	0.008(2)	-0.001(3)
C7	0.033(2)	0.048(3)	0.042(3)	0.009(2)	0.002(2)	0.001(2)
C8	0.035(2)	0.037(3)	0.032(2)	0.002(2)	0.005(2)	0.002(2)
C9	0.030(2)	0.028(2)	0.031(2)	-0.000(2)	0.009(2)	-0.002(2)
C10	0.031(2)	0.034(2)	0.032(2)	0.003(2)	0.009(2)	0.003(2)
C11	0.026(2)	0.038(3)	0.033(2)	0.002(2)	0.009(2)	0.004(2)
C12	0.028(2)	0.035(3)	0.046(2)	0.006(2)	0.009(2)	0.005(2)
C13	0.032(2)	0.038(3)	0.044(3)	0.001(2)	0.011(2)	0.005(2)
C14	0.024(2)	0.043(3)	0.032(2)	-0.002(2)	0.006(2)	-0.004(2)
C15	0.025(2)	0.040(3)	0.033(2)	0.005(2)	0.005(2)	-0.001(2)
C16	0.028(2)	0.035(3)	0.038(2)	0.003(2)	0.008(2)	-0.000(2)
C17	0.031(2)	0.027(2)	0.043(2)	0.003(2)	0.010(2)	0.008(2)
C18	0.040(3)	0.049(3)	0.040(3)	-0.005(2)	0.014(2)	-0.013(2)
C19	0.054(4)	0.063(4)	0.053(3)	-0.013(3)	0.002(3)	-0.005(3)
C20	0.078(4)	0.079(5)	0.047(3)	-0.023(4)	0.035(3)	-0.007(3)
C21	0.045(3)	0.073(5)	0.080(4)	0.012(3)	0.020(3)	-0.020(4)

The general temperature factor expression: $\exp(-2p^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S7. Bond Lengths (Å) for 3c.

Atom	atom	distance	atom	atom	distance
Cl1	C14	1.734(4)	Cl2	C15	1.735(4)
O1	C17	1.222(5)	O2	C17	1.342(6)
O2	C18	1.484(6)	N1	C1	1.477(6)
N1	C4	1.480(6)	N1	C17	1.372(6)
C1	C2	1.572(6)	C1	C9	1.522(6)
C2	C3	1.553(7)	C2	C11	1.523(6)
C3	C4	1.554(6)	C4	C10	1.519(6)
C5	C6	1.395(7)	C5	C10	1.378(6)
C6	C7	1.379(8)	C7	C8	1.399(7)
C8	C9	1.381(6)	C9	C10	1.397(6)
C11	C12	1.399(7)	C11	C16	1.393(6)
C12	C13	1.390(6)	C13	C14	1.381(6)
C14	C15	1.382(6)	C15	C16	1.389(6)
C18	C19	1.505(7)	C18	C20	1.509(9)
C18	C21	1.518(8)			

Table S8. Bond Angles (°) for 3c.

atom	atom	atom	angle	atom	atom	atom	angle
C17	O2	C18	120.3(4)	C1	N1	C4	97.6(3)
C1	N1	C17	124.3(4)	C4	N1	C17	120.0(4)
N1	C1	C2	98.4(3)	N1	C1	C9	101.9(3)
C2	C1	C9	106.4(4)	C1	C2	C3	101.7(3)
C1	C2	C11	110.3(4)	C3	C2	C11	118.0(3)
C2	C3	C4	103.1(3)	N1	C4	C3	98.9(3)
N1	C4	C10	101.4(3)	C3	C4	C10	106.2(4)
C6	C5	C10	118.6(5)	C5	C6	C7	120.3(4)
C6	C7	C8	121.7(4)	C7	C8	C9	117.3(4)
C1	C9	C8	132.7(4)	C1	C9	C10	105.7(3)
C8	C9	C10	121.3(4)	C4	C10	C5	133.1(4)
C4	C10	C9	105.9(4)	C5	C10	C9	120.7(4)
C2	C11	C12	117.5(4)	C2	C11	C16	124.5(4)
C12	C11	C16	118.0(4)	C11	C12	C13	121.3(4)
C12	C13	C14	119.8(4)	Cl1	C14	C13	118.7(4)
Cl1	C14	C15	121.6(3)	C13	C14	C15	119.7(4)
Cl2	C15	C14	120.5(3)	Cl2	C15	C16	118.8(4)
C14	C15	C16	120.7(4)	C11	C16	C15	120.5(4)
O1	C17	O2	125.9(4)	O1	C17	N1	123.1(4)
O2	C17	N1	110.9(4)	O2	C18	C19	111.1(5)
O2	C18	C20	101.4(4)	O2	C18	C21	108.3(4)
C19	C18	C20	111.7(5)	C19	C18	C21	112.0(5)
C20	C18	C21	111.9(5)				

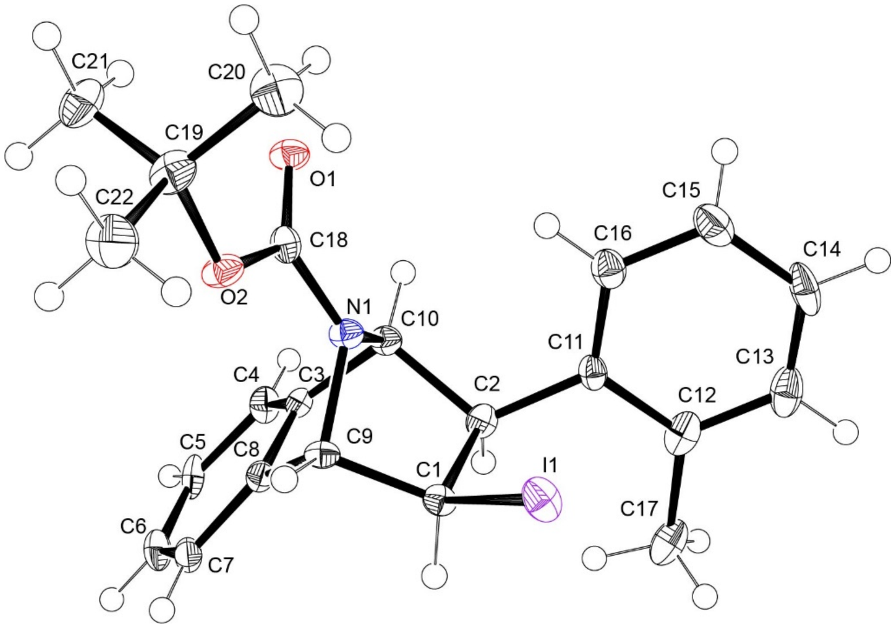


Figure S3. ORTEP drawing for **5b**. Thermal ellipsoids are drawn at 50% probability level.

Table S9. Crystallographic Data for 5b Obtained from EtOH–H_2O.

Molecular Formula	$C_{22}H_{24}INO_2$
Formula Weight	461.34
Crystal Dimensions (mm)	0.10 × 0.10 × 0.50
Crystal Color, Habit	colorless, needle
Crystal System	monoclinic
Lattice Type	primitive
Space Group	$P2_1$(#4)
a (Å)	6.4237(9)
b (Å)	10.1859(14)
c (Å)	15.326(2)
β (°)	91.632(7)
Cell Volume (Å^3)	1002.4(2)
Z Value	2
F (000)	464.00
D_{calc} (g/cm^{-3})	1.528
Temperature (°C)	23.0
Radiation	synchrotron (λ = 0.70090 Å)
μ(cm^{-1})	0.000
$2\theta_{max}$ (º)	54.1
Total Number of Reflections	13303
Number of Unique Reflections	4570
Number of Variables	235
Reflection / Parameter Ratio	19.45
Final R_{all} and $_{w}R_2$	0.0368; 0.0777
Goodness of Fit	1.010
Max Shift / Error	0.001
Flack parameter	0.00(3)
Method of phase determination	Direct Methods (SIR2004)

Table S10. Atomic Coordinates and B_{eq} for 5b.

atom	x	y	z	B_{eq}
I1	0.44074(6)	0.73734(5)	0.73855(2)	1.666(10)
O1	-0.2338(7)	1.0088(5)	0.6616(3)	1.53(8)
O2	0.0245(7)	0.9740(5)	0.5674(3)	1.52(8)
N1	0.0972(9)	0.9862(6)	0.7082(4)	1.20(9)
C1	0.4046(11)	0.9373(6)	0.7774(4)	1.18(10)
C2	0.2368(11)	0.9603(7)	0.8482(4)	1.27(10)
C3	0.1719(11)	1.1754(7)	0.7839(5)	1.27(11)
C4	0.1432(13)	1.2944(8)	0.8227(5)	1.68(12)
C5	0.2791(12)	1.3956(7)	0.8020(5)	1.74(12)
C6	0.4405(12)	1.3748(8)	0.7479(5)	1.83(13)
C7	0.4708(10)	1.2542(9)	0.7082(4)	1.43(13)
C8	0.3311(11)	1.1561(7)	0.7254(4)	1.23(10)
C9	0.3191(10)	1.0139(6)	0.6988(4)	1.17(10)
C10	0.0735(10)	1.0433(7)	0.7950(5)	1.23(10)
C11	0.1572(10)	0.8387(6)	0.8913(4)	1.25(10)
C12	0.2717(13)	0.7855(8)	0.9617(5)	1.78(12)
C13	0.2052(14)	0.6695(8)	0.9982(5)	2.17(14)
C14	0.0293(13)	0.6081(8)	0.9675(5)	2.16(13)
C15	-0.0857(13)	0.6626(8)	0.8989(6)	2.09(13)
C16	-0.0200(12)	0.7767(7)	0.8617(5)	1.67(12)
C17	0.4696(13)	0.8483(9)	0.9951(5)	2.39(14)
C18	-0.0544(11)	0.9933(7)	0.6461(4)	1.28(10)
C19	-0.1139(12)	0.9351(8)	0.4933(5)	1.88(12)
C20	-0.2266(14)	0.8117(8)	0.5160(5)	2.35(14)
C21	-0.2614(13)	1.0441(9)	0.4699(5)	2.37(14)
C22	0.0363(14)	0.9115(10)	0.4229(5)	2.62(15)

$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S11. Anisotropic Displacement Parameters for 5b.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I1	0.0257(2)	0.01317(19)	0.0248(2)	-0.0000(3)	0.00746(14)	-0.0027(3)
O1	0.013(2)	0.025(3)	0.020(2)	0.0020(19)	0.0012(19)	-0.002(2)
O2	0.015(2)	0.030(3)	0.013(2)	0.002(2)	-0.0008(18)	-0.003(2)
N1	0.013(3)	0.019(3)	0.013(3)	0.000(2)	0.001(2)	-0.003(2)
C1	0.016(3)	0.012(3)	0.017(3)	-0.001(2)	0.002(2)	-0.003(2)
C2	0.018(3)	0.014(3)	0.016(3)	0.002(2)	-0.000(3)	-0.000(2)
C3	0.014(3)	0.017(3)	0.017(3)	0.001(3)	-0.003(3)	0.002(3)
C4	0.024(4)	0.019(3)	0.021(4)	0.003(3)	0.002(3)	0.003(3)
C5	0.036(4)	0.013(3)	0.016(3)	0.002(3)	-0.001(3)	0.005(3)
C6	0.031(4)	0.013(3)	0.025(4)	-0.001(3)	0.000(3)	0.006(3)
C7	0.020(3)	0.018(5)	0.016(3)	-0.000(3)	0.001(2)	0.004(3)
C8	0.018(3)	0.015(3)	0.014(3)	-0.000(3)	-0.001(2)	0.002(2)
C9	0.012(3)	0.017(3)	0.016(3)	-0.000(2)	0.001(2)	-0.004(2)
C10	0.014(3)	0.018(3)	0.015(3)	0.000(3)	0.001(2)	-0.001(3)
C11	0.019(3)	0.015(3)	0.014(3)	0.002(3)	0.005(3)	0.001(2)
C12	0.030(4)	0.023(3)	0.015(3)	0.009(3)	0.002(3)	-0.002(3)
C13	0.041(5)	0.025(4)	0.018(4)	0.010(4)	0.009(3)	0.005(3)
C14	0.040(4)	0.018(3)	0.025(4)	0.000(3)	0.019(3)	0.006(3)
C15	0.025(4)	0.021(4)	0.034(4)	-0.002(3)	0.009(3)	0.000(3)
C16	0.021(4)	0.021(4)	0.021(3)	0.001(3)	0.006(3)	0.000(3)
C17	0.035(4)	0.032(4)	0.023(4)	0.007(4)	-0.008(3)	0.004(3)
C18	0.020(3)	0.013(3)	0.016(3)	0.000(3)	0.002(3)	0.000(2)
C19	0.026(4)	0.031(4)	0.014(3)	0.001(3)	-0.003(3)	-0.006(3)
C20	0.036(4)	0.028(4)	0.025(4)	-0.003(3)	-0.001(3)	-0.007(3)
C21	0.035(4)	0.034(5)	0.020(4)	0.002(4)	-0.009(3)	0.001(3)
C22	0.035(5)	0.049(6)	0.016(4)	-0.004(4)	0.005(3)	-0.003(3)

The general temperature factor expression: $\exp(-2p^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S12. Bond Lengths (Å) for 5b.

Atom	atom	distance	atom	atom	distance
I1	C1	2.137(6)	O1	C18	1.193(8)
O2	C18	1.336(8)	O2	C19	1.477(9)
N1	C9	1.464(8)	N1	C10	1.464(9)
N1	C18	1.344(9)	C1	C2	1.568(10)
C1	C9	1.525(9)	C2	C10	1.559(9)
C2	C11	1.501(9)	C3	C4	1.366(11)
C3	C8	1.393(10)	C3	C10	1.498(10)
C4	C5	1.394(11)	C5	C6	1.362(11)
C6	C7	1.388(12)	C7	C8	1.374(11)
C8	C9	1.505(9)	C11	C12	1.397(10)
C11	C16	1.368(10)	C12	C13	1.381(11)
C12	C17	1.500(12)	C13	C14	1.364(12)
C14	C15	1.384(11)	C15	C16	1.367(11)
C19	C20	1.497(12)	C19	C21	1.497(12)
C19	C22	1.487(11)			

Table S13. Bond Angles (°) for 5b.

atom	atom	atom	angle	atom	atom	atom	angle
C18	O2	C19	119.9(5)	C9	N1	C10	98.0(5)
C9	N1	C18	127.5(6)	C10	N1	C18	122.0(6)
I1	C1	C2	114.7(4)	I1	C1	C9	107.9(4)
C2	C1	C9	103.3(5)	C1	C2	C10	100.6(5)
C1	C2	C11	115.5(6)	C10	C2	C11	116.4(6)
C4	C3	C8	121.1(7)	C4	C3	C10	133.3(7)
C8	C3	C10	105.4(6)	C3	C4	C5	117.6(7)
C4	C5	C6	121.1(7)	C5	C6	C7	121.6(7)
C6	C7	C8	117.3(6)	C3	C8	C7	121.1(6)
C3	C8	C9	106.1(6)	C7	C8	C9	132.5(6)
N1	C9	C1	98.8(5)	N1	C9	C8	101.6(5)
C1	C9	C8	105.3(5)	N1	C10	C2	100.0(5)
N1	C10	C3	101.5(5)	C2	C10	C3	105.4(5)
C2	C11	C12	118.8(6)	C2	C11	C16	121.7(6)
C12	C11	C16	119.5(6)	C11	C12	C13	118.9(7)
C11	C12	C17	121.4(7)	C13	C12	C17	119.7(7)
C12	C13	C14	121.0(8)	C13	C14	C15	119.8(7)
C14	C15	C16	119.6(7)	C11	C16	C15	121.2(7)
O1	C18	O2	126.3(6)	O1	C18	N1	123.4(6)
O2	C18	N1	110.2(6)	O2	C19	C20	109.3(6)
O2	C19	C21	110.4(6)	O2	C19	C22	102.3(6)
C20	C19	C21	111.8(7)	C20	C19	C22	111.2(7)
C21	C19	C22	111.4(7)				

9. X-ray Absorption Spectroscopy (XAS) of the Iron Intermediates

XAS Measurements.

X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were performed at BL14B2 beamline of SPring-8 under standard beamline conditions. The Fe K-edge (7.11 keV) XAS data were collected by transmission mode using N_2/Ar mixed gas-filled ionization chambers with optimized gas ratio and pressure or fluorescence mode using 19SSD detector. For solution phase XAS, air- and moisture-sensitive sample solutions were transferred into a specially designed quarts-made solution cell equipped with 20 μm Teflon membrane windows. All the process for sample preparation were performed under an argon-filled glovebox.

Typical Procedure for XAS Analysis of Stoichiometric Reactions of $FeBr_3$ and (*S*,*S*)-Chiraphos with Phenylzinc reagent.

In the argon-filled glovebox, a mixture of $FeBr_3$ (8.9 mg, 0.03 mmol) and THF (0.375 mL) was diluted by toluene (1.125 mL) to prepare a toluene:THF (4:1) solution of $FeBr_3$. To the $FeBr_3$ solution was added equimolar amounts of (*S*,*S*)-Chiraphos (1.0 M, 30 μL, 0.03 mmol) followed by $Ph_2Zn \cdot MgBrCl$ (1.0 M, 30 μL, 0.03 mmol for 1 equiv; 60 μL, 0.06 mmol for 2 equiv) at rt. The resulting reaction mixture was stirred for 10 min at rt, then filtered and a part of the solution was transferred into the XAS cell to measure Fe K-edge XANES and EXAFS spectra at the BL14B2 beamline of SPring-8 (Figure S5). After 30 min, the remaining part of the sample solution was quenched and analyzed by GC.

Stoichiometric Reaction with XAS Analysis.

The complexation step of $FeBr_3$ and (*S*,*S*)-Chiraphos was investigated by in situ XAS monitoring (Figure S4). A remarkable lower energy shift of the rising edge of XANES spectrum was observed by the addition of 1 equiv of (*S*,*S*)-Chiraphos to $FeBr_3$, indicating the increase of electron density of iron center corresponding complexation with (*S*,*S*)-Chiraphos to form 1:1 complex of [$FeBr_3$(Chiraphos)]. The addition of 2 equiv of (*S*,*S*)-Chiraphos shows negligible change in both XANES and EXAFS spectrum from those with 1 equiv, clarifying the retaining of [$FeBr_3$(Chiraphos)] complex which does not accept the further coordination of (*S*,*S*)-Chiraphos in this concentration.

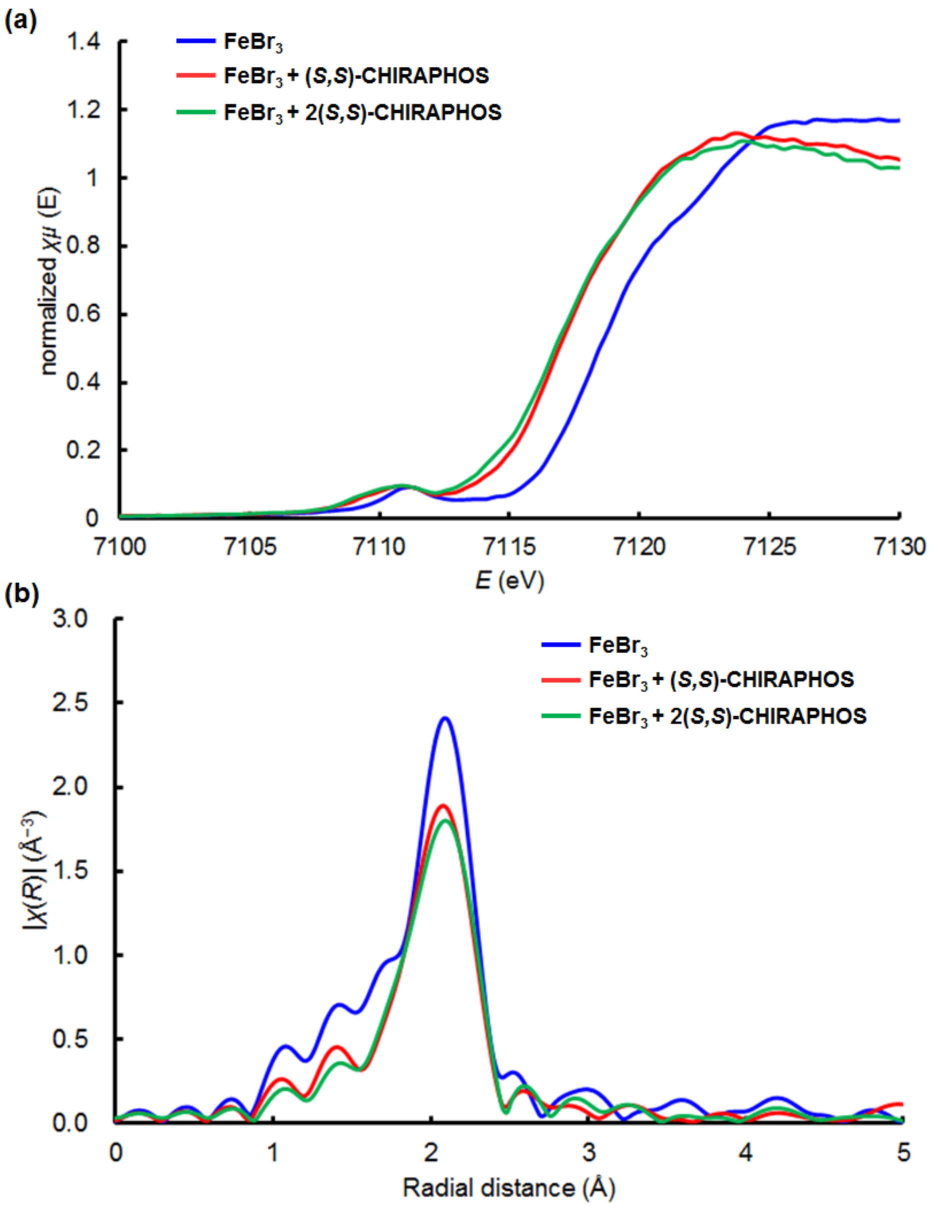


Figure S4. Fe K-edge (a) XANES and (b) EXAFS spectra for $FeBr_3$ solution (20 mM in THF/toluene) of $FeBr_3$ (blue line), with 1.0 equiv (red line), and 2.0 equiv (green line) of (*S*,*S*)-Chiraphos.

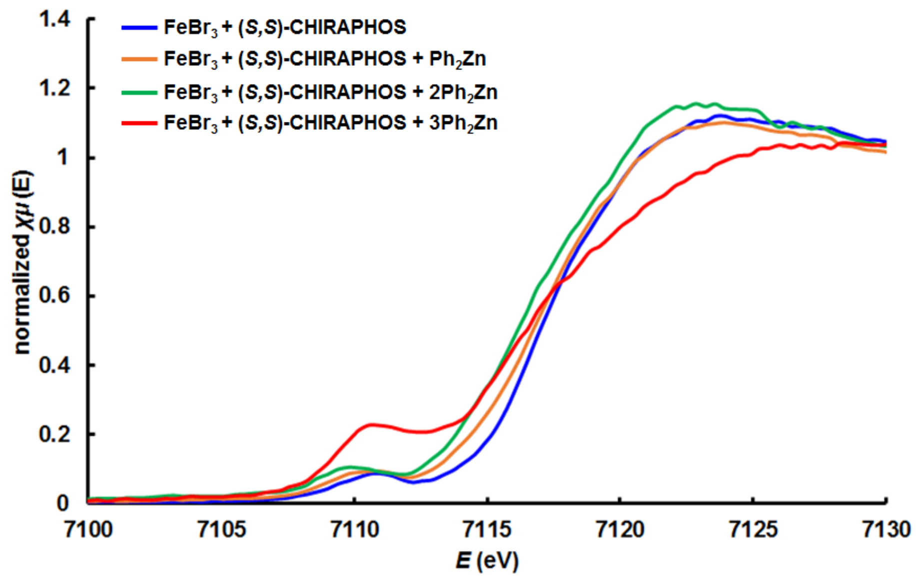


Figure S5. Fe K-edge XANES spectra for 1:1 mixture solution (20 mM in THF/toluene) of $FeBr_3$ and (*S*,*S*)-Chiraphos (blue line), with 1.0 equiv (orange line), 2.0 equiv (green line), and 3.0 equiv (red line) of $Ph_2Zn{\cdot}2MgBrCl$.

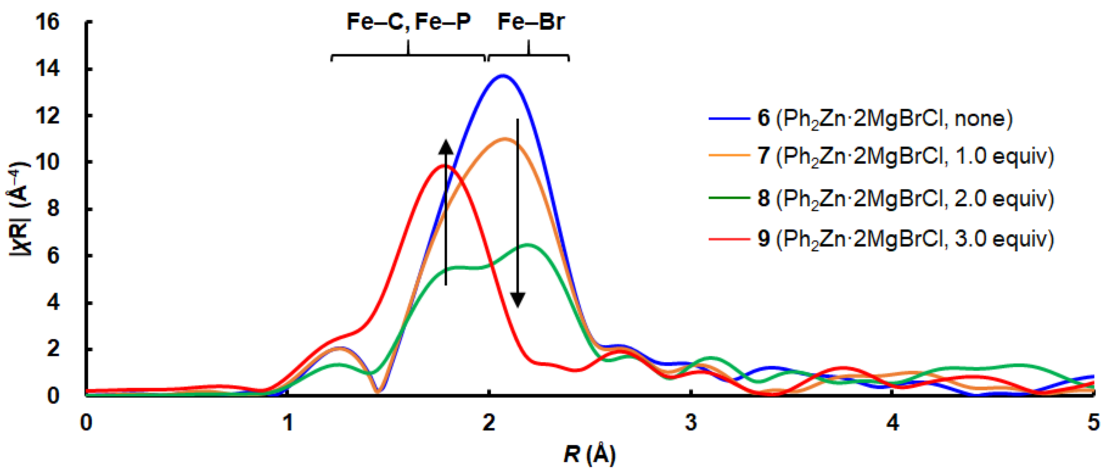


Figure S6. Fe K-edge EXAFS spectra for 1:1 mixture solution (20 mM in THF/toluene) of $FeBr_3$ and (*S*,*S*)-Chiraphos (blue line), with 1.0 equiv (orange line), 2.0 equiv (green line), and 3.0 equiv (red line) of $Ph_2Zn{\cdot}2MgBrCl$.

Next, the transmetalation–reductive elimination step forming diaryliron(II) intermediates was investigated by the stoichiometric reaction of $FeBr_3$, (*S*,*S*)-Chiraphos, and 1–3 equiv of $Ph_2Zn\cdot 2MgBrCl$ (Figure S5). By the addition of 1 and 2 equiv of $Ph_2Zn\cdot 2MgBrCl$, the rising edge gradually shifted to lower energy side, suggesting that the transmetalation between Fe–Br and Ph–Zn species takes place and following reductive elimination–comproportionation generates divalent aryliron(II) bromide species of [FeBr(Ph)(Chiraphos)]. The following 3 equiv addition of $Ph_2Zn\cdot 2MgBrCl$ does not cause a significant shift of the rising energy, indicating the formation of diaryliron(II) species retaining the oxidation state of iron center. However, the remarkable change was observed at the pre-edge showing the intense peak at 7110.5 eV, together with the appearance of shoulder at 7116.6 eV. Previously, we reported the XAS study on the diaryliron intermediates of the Grignard coupling reaction, in which [Fe(Mes)$_2$(SciOPP)] complex showed a 1s–4p$_z$ transition at 7112.3 eV together with the pre-edge peak at 7109.5 eV.[8] The shoulder peak at 7112.3 eV originates from the 3d–4p orbital mixing of slightly distorted square planar geometry of [Fe(Mes)$_2$(SciOPP)] complex. The observed shoulder peak at 7116.6 eV with 3 equiv of $Ph_2Zn\cdot 2MgBrCl$ is also considered to originate from the 1s–4p$_z$ transition of diaryliron(II) species of [Fe(Ph)$_2$(Chiraphos)]. A little higher energy transition than that of [Fe(Mes)$_2$(Chiraphos)] suggests the tetrahedral geometry of [Fe(Ph)$_2$(Chiraphos)]. Relating to this energy shift, we considered that the intense pre-edge peak originates from 1s–3d transition of the tetrahedral iron center.[9] EXAFS spectra also show the corresponding spectral change by the addition of $Ph_2Zn.2MgBrCl$ (Figure S6). The stepwise decreasing of the peak at 2.09 Å accompanied by the increasing of the peak at around 1.0–2.0 Å. These spectral changes can be attributed to the conversion of Fe–Br bonds to Fe–C bonds, resulting from the transmetalation-reductive elimination steps generating diaryliron species, [Fe(Ph)$_2$(Chiraphos)].

(8) Takaya, H.; Nakajima, S.; Nakagawa, N.; Isozaki, K.; Iwamoto, T.; Imayoshi, R.; Gower, N. J.; Adak, L.; Hatakeyama, T.; Honma, T.; Takagaki, M.; Sunada, Y.; Nagashima, H.; Hashizume, D.; Takahashi, O.; Nakamura, M. *Bull. Chem. Soc. Jpn.* **2015,** *88,* 410–418.
(9) Recently, we reported the similar X-ray absorption spectral feature of tetrahedral alkyliron intermediate showing an intense pre-edge peak at 7110 eV, see: Agata, R.; Takaya, H.; Matsuda, H.; Nakatani, N.; Takeuchi, K.; Iwamoto, T.; Hatakeyama, T.; Nakamura, M. *Bull. Chem. Soc. Jpn.* **2019,** *92,* 381–390.

FEFF Fitting Analysis of Diaryliron Intermediate based on the DFT-optimized geometries.

For structural analysis of the in situ prepared diaryliron intermediate of [Fe(Ph)$_2$(Chiraphos)] by the reaction of $FeBr_3$, (*S*,*S*)-Chiraphos, and 3 equiv of $Ph_2Zn{\cdot}2MgBrCl$, FEFF fitting analyses on EXAFS spectrum was carried out using the atomic coordinates obtained from DFT-optimized geometries.[10] Energetically favorable two possible structures with different spin states were provided by DFT calculation at the PCM$_{toluene}$/B3LYP-D2/SDD(Fe),6-31G*(C,H,O,P) level of theory (Table S14, **L1**). The FEFF fitting analysis based on the above DFT-calculated tetrahedral (Td) geometry with high spin state (S = 2) and square planar (SqP) geometry with intermediate spin state (S = 1) showed a good agreement with adequate R value and χ statics. These FEFF fitting results indicated that diaryliron intermediates [Fe(Ph)$_2$(Chiraphos)] with tetrahedral geometry is the predominant species.

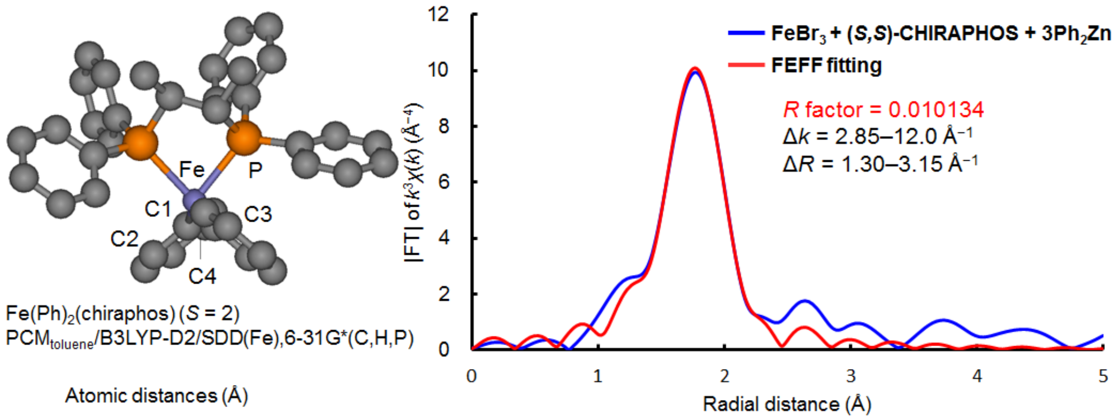
The corresponding XAFS data were processed using Athena by extracting the EXAFS oscillations $\chi(k)$ as a function of photoelectron wave number k. Fourier transformation of the k^3-weighted χ from k space to r space was carried out to obtain the radial distribution function. The EXAFS fitting calculation was performed by FEFF6[1] program embedded with Artemis, where the theoretical scattering paths were generated from DFT-optimized structure as depicted in Figures S7, S9, and Table S14. The parameters for FEFF fitting analysis are as follows: Ab-Sc: the X-ray absorbing atom and the scattering atom; CN: coordination number; *DW*: Debye-Waller factor (Å^2); ΔE: energy shift (eV); R: atomic distance (Å). The parameter for the many-body effect of S_0^2 is fixed to 1.0 for all fitting calculations.

For fitting calculation of tetrahedral [Fe(Ph$_2$)((*S*,*S*)-Chiraphos)] (S = 2)·based on DFT-optimized geometry, eight independent parameters (Fe–C1: S_0^2, e1, r1, σ1; Fe–P: S_0^2, e2, r2, σ1; Fe–C2/C3/C4: S_0^2, e2, r3, σ2) with three scattering paths (1st shell: Fe–C1, 2nd shell: Fe–P, 3rd shell: Fe–C2/C3/C4) give the fitting results with adequate accuracy as shown in Figures S7, where the many-body effect S_0^2 parameter was fixed with an appropriate values for Fe–C1 as S_0^2 = 1.1 and for

(10) The fitting calculation was performed by the FEFF6 program (revision 9.6.4) embedded with Artemis. For the FEFF6 program, see: (a) Rehr, J. J.; Kas, J. J.; Vila, F. D.; Prange, M. P.; Jorissen, K. *Phys. Chem. Chem. Phys.* **2010,** *12,* 5503–5513. (b) Rehr, J. J.; Albers, R. C. *Rev. Mod. Phys.* **2000,** *72,* 621–654. For Artemis software, see: (c) Newville, M.; *J. Synchrotron Radiat.* **2001,** *8,* 322–324. (d) Ravel, B.; Newville, M. *J. Synchrotron Radiat.* **2005,** *12,* 537–541.

Fe–CP/C2/C3/C4 as $S_0^2 = 1.0$, respectively.

For fitting calculation of square planar [Fe(Ph_2)((S,S)-Chiraphos]] (S = 1) based on DFT-optimized geometry, seven independent parameters (Fe–C1: S_0^2, e1, r1, σ1; Fe–P: S_0^2, e2, r2, σ1; Fe–C2/C3/C4: S_0^2, e2, r3, σ2) with three scattering paths (1st shell: Fe–C1, 2nd shell: Fe–P, 3rd shell: Fe–C2/C3/C4) give the fitting results with adequate accuracy as shown in Figures S8, where the many-body effect S_0^2 parameter was fixed with an appropriate value as $S_0^2 = 1.0$.



Atomic distances (Å)

Fe-C1: 2.06
Fe-P: 2.48
Fe-C2: 2.96

Ab–Sc	CN	Δ*E* (eV)	R (Å)	*DW* (Å^{-1})
Fe–C1	2.0	−3.984 ± 9.46	1.63 ± 0.05	0.00322 ± 0.0008
Fe–P	2.0	1.225 ± 3.86	2.05 ± 0.34	0.00322 ± 0.0008
Fe–C2	1.0	1.225 ± 3.86	2.41 ± 0.34	0.03697 ± 0.0272
Fe–C3	2.0	1.225 ± 3.86	2.41 ± 0.34	0.03697 ± 0.0272
Fe–C4	1.0	1.225 ± 3.86	2.41 ± 0.34	0.03697 ± 0.0272

Figure S7. FEFF fitting analysis on the EXAFS spectrum of the reaction mixture of $FeBr_3$, (*S*,*S*)-Chiraphos (1 equiv), and $Ph_2Zn \cdot MgBrCl$ (3 equiv) using the DFT-optimized tetrahedral geometry of $Fe(Ph_2)$[(*S*,*S*)-Chiraphos] (*S* = 2) (red line) at the $PCM_{toluene}$/B3LYP-D2/SDD(Fe),6-31G*(C,H,P) level of theory shown in Table S14, **L1**.

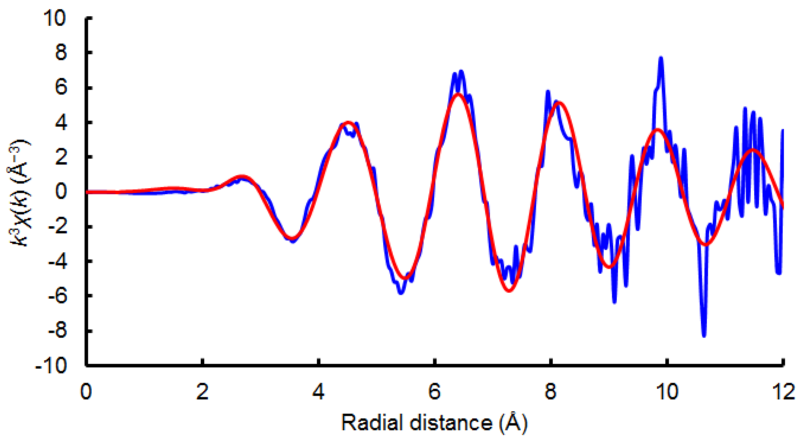
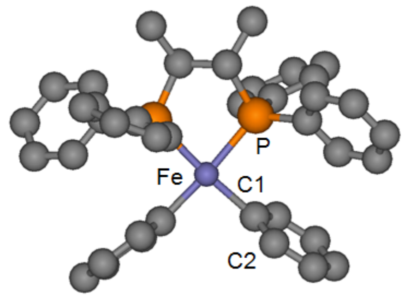


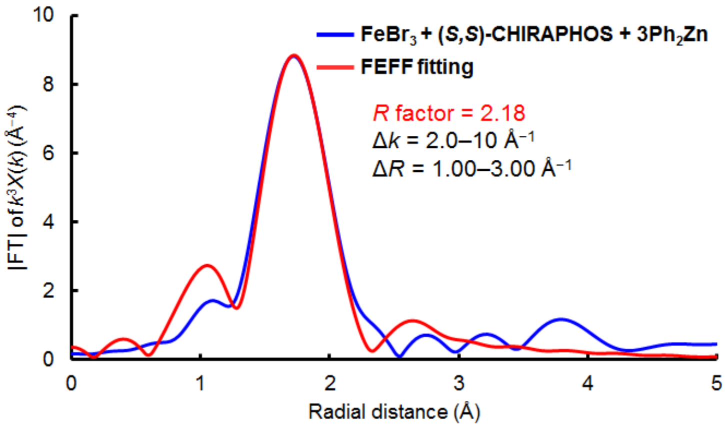
Figure S8. FEFF fitting in *k*-space.



Fe(Ph)$_2$(chiraphos) (S = 1)
PCM$_{toluene}$/B3LYP-D2/SDD(Fe),6-31G*(C,H,P)

Atomic distances (Å)

Fe-C1: 1.97
Fe-P: 2.31
Fe-C2: 2.96



Ab–Sc	CN	ΔE (eV)	R (Å)	DW (Å^{-1})
Fe–C1	2.0	−34.91	1.76 ± 0.03	0.00024 ± 0.001
Fe–P	2.0	−34.91	2.09 ± 0.03	0.00024 ± 0.001
Fe–C2	4.0	−42.26	2.71 ± 0.05	0.02307 ± 0.007

Figure S9. FEFF fitting analysis on the EXAFS spectrum of the reaction mixture of $FeBr_3$, (*S*,*S*)-Chiraphos (1 equiv), and $Ph_2Zn\cdot MgBrCl$ (3 equiv) using the DFT-optimized square planar geometry of Fe(Ph_2)[(*S*,*S*)-Chiraphos] (S = 1) (red line) at the PCM$_{toluene}$/B3LYP-D2/SDD(Fe),6-31G*(C,H,P) level of theory shown in Table S14, **L1**.

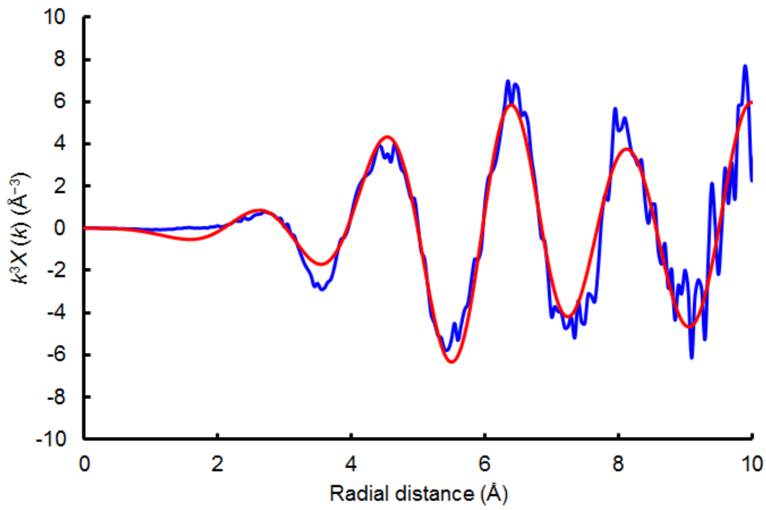


Figure S10. FEFF fitting in *k*-space.

Computational Methods

All DFT calculations were performed using Gaussian 16 program.[11] The B3LYP functional,[12] including Grimme's empirical dispersion correction (version D2),[13] was employed for the DFT calculations. All calculations for iron-complexes were performed using the unrestricted-B3LYP level of theory, and stability of wavefunction was ascertained for all singlet iron-complexes. The SDD basis sets, with the associated effective core potentials, were used for Fe and Zn.[14] The 6-31G* basis sets were used for H, C, O, P, and Br atoms.[15] Solvent effects were included in all calculations using the integral equation formalism–Polarizable Continuum Model (IEF-PCM) with toluene as a solvent (ε = 2.3741).[16] The nature of all stationary points was confirmed by performing vibrational frequency calculations, with no imaginary frequency for minima. The potential energies of all stationary points were further improved using the ECP10MDF basis set with associated ECPs were used for Fe and Zn,[17] and 6-311+G** basis set for all other atoms (H, C, O, P, and Br).[18]

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Table S14. Relative Energies (kcal/mol) of Diaryliron Intermediates for Different Geometries and Spin States

		L1[a]		L2[c]	
SpinState	Geometry	ΔE_{ZPE}	ΔG^a	$\Delta E_{ZPE}{}^a$	ΔG^a
		[Fe(Ph)2(*S,S*-Chiraphos)]			
S=0	**Td**	23.2	26.2	23.2	26.1
S=0	**SqP**	15.4	16.3	14.3	15.1
S=1	**Td**	17.3	18.5	17.2	18.4
S=1	**SqP**	2.4	3.1	1.7	2.4
S=2	**Td**	**0.0**	**0.0**	**0.0**	**0.0**
S=2	**SqP**	12.5	12.7	16.6	16.7
		[Fe(Ph)2(*S,S*-Chiraphos)(THF)]			
S=0	**TBPy**	-0.4	17.4	2.9	20.7
S=0	**SqPy**	-3.6	13.9	-0.6	16.8
S=1	**TBPy**	-8.7	6.8	-5.5	10.0
S=1	**SqPy**	-15.0	1.1	-11.9	4.3
S=2	**TBPy**	-13.9	**-0.7**	-10.7	2.6
S=2	**Td**[c]	-7.6	5.3	-5.0	7.9

[a]L1=$PCM_{Toluene}$/B3LYP-D2/SDD(Fe),6-31G*(C,H,O,P); [b]L2 = $PCM_{Toluene}$/B3LYP-D2/ECP10-MDF(Fe),6-311+G**(C,H,O,P)//$PCM_{Toluene}$/B3LYP-D2/SDD(Fe),6-31G*(C,H,O,P). [c]One phosphorus decoordinates from Fe.

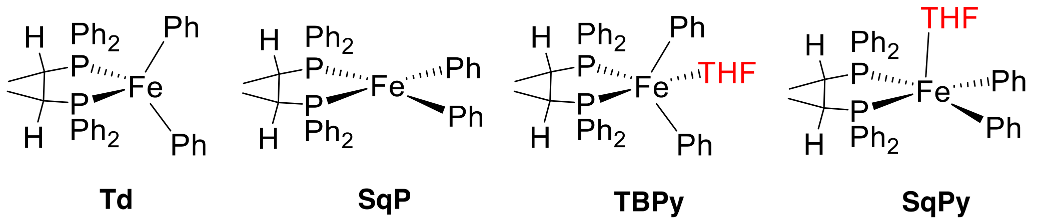


Chart S1. DFT analysis of probability of *S,S*-Chiraphos (PP) coordination to zinc reagent (all energies are at $PCM_{Toluene}$/B3LYP-D2/ECP10MDF(Fe,Zn),6-311+G**(C,H,O,P) //$PCM_{Toluene}$/B3LYP-D2/SDD(Fe),6-31G*(C,H,O,P) level of theory). From the computed reaction energies, it is clear that coordination of *S,S*-Chiraphos (PP) to Zn reagent is endergonic and less likely in current reaction.

$^3Fe(Ph)_2(PP) + Zn(Ph)_2(THF)_2$ ----> $^5Fe(Ph)_2(THF)_2 + Zn(Ph)_2(PP)$ $\Delta G(\Delta E_{ZPE}) = 6.4\ (8.3)$

$^3Fe(Ph)_2(PP) + ZnBr_2(THF)_2$ ----> $^5Fe(Ph)_2(THF)_2 + ZnBr_2(PP)$ $\Delta G(\Delta E_{ZPE}) = 2.1\ (3.1)$

$^3Fe(Ph)_2(PP) + ZnBr(Ph)(THF)_2$ ----> $^5Fe(Ph)_2(THF)_2 + ZnBr(Ph)(PP)$ $\Delta G(\Delta E_{ZPE}) = 2.8\ (4.6)$

Table S15. The Total Electronic Energies (E0 and E0-Low) of the Optimized Stationary Points with Zero-Point-Energy (zpe), Thermal Correction to Gibbs Free Energy (G-Corr-298, where G = E0 + G-Corr-298), Number of Imaginary Frequency Information (NImag), and $<S^2>$ value

Geometry, Spin	E0 [a]	E0-Low [b]	ZPE [b]	G-Corr-298 [b]	NImag	$<S^2>$ [a]
[Fe(Ph)$_2$(Chiraphos)]						
Td, S=0	-2354.324355	−2353.8519146	0.663352	0.590097	0	0.127616
SqP, S=0	-2354.336576	−2353.8624034	0.661447	0.584841	0	0.087724
Td, S=1	-2354.332881	−2353.8603817	0.662396	0.586369	0	2.002415
SqP, S=1	-2354.356786	−2353.8832791	0.661528	0.584741	0	2.001479
Td, S=2	-2354.359842	−2353.8874831	0.661936	0.583973	0	6.000325
SqP, S=2	-2354.332686	−2353.8667699	0.661219	0.583503	0	6.000226
[Fe(Ph)$_2$(Chiraphos)(THF)]						
TBPy, S=0	-2586.891559	−2586.3510451	0.783957	0.705984	0	0.006252
SqPy, S=0	-2586.896548	−2586.3554074	0.783311	0.704800	0	0.064982
TBPy, S=1	-2586.903612	−2586.3629453	0.782630	0.700905	0	2.001277
SqPy, S=1	-2586.913736	−2586.3729942	0.782616	0.702003	0	2.002073
TBPy, S=2	-2586.910108	−2586.3695008	0.780866	0.695658	0	6.00025
Td, S=2	-2586.900507	−2586.3587977	0.780328	0.694515	0	6.000179
THF	-232.5309368	-232.4575174	0.116638	0.088225	0	
ZnBr$_2$(THF)$_2$	-5840.696469	-5835.073377	0.240158	0.190899	0	
Fe(Ph)$_2$(THF)$_2$ (S=2)	-1052.453473	-1052.1967304	0.416748	0.35756	0	6.000107
Zn(Ph)$_2$(THF)$_2$	-1155.686112	-1155.4209238	0.418175	0.362706	0	
ZnBr(Ph)(THF)$_2$	-3498.193169	-3495.2493079	0.328944	0.276001	0	
Zn(Ph)$_2$(Chiraphos)	-2457.576115	-2457.1028702	0.662845	0.586841	0	
ZnBr$_2$(Chiraphos)	-7142.594835	-7136.7640714	0.484906	0.416448	0	
ZnBr(Ph) (Chiraphos)	-4800.088826	-4796.9363509	0.573428	0.500062	0	

[a] Total electronic energies and $<S^2>$ value at $PCM_{Toluene}$/B3LYP-D2/ECP10MDF(Fe,Zn),6-311+G**(C,H,O,P)//$PCM_{Toluene}$/B3LYP-D2/SDD(Fe,Zn)6-31G*(C,H,O,P,Br) level of theory. [b] Energies at $PCM_{Toluene}$/B3LYP-D2/SDD(Fe,Zn),6-31G*(C,H,O,P,Br).

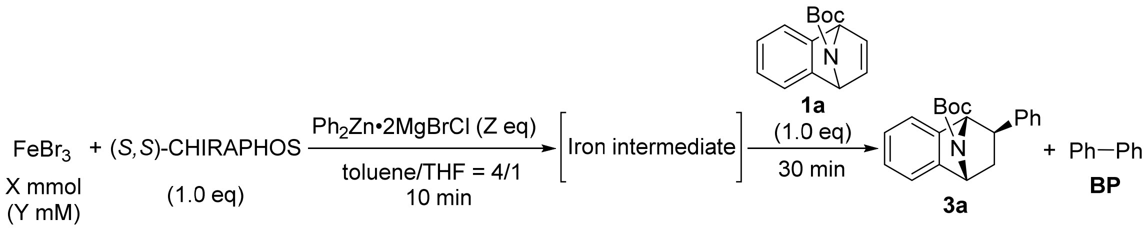
Stoichiometric Reaction via [Fe(Ph)$_2$(Chiraphos)] Intermediate.

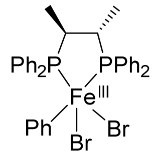
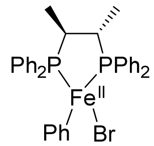
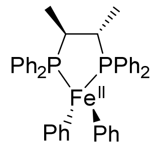
Further insight into the reaction mechanism was obtained by the stoichiometric reaction of azabicycloalkene substrate and iron intermediates (Table S16). A series of iron intermediates were prepared as similar to the above-mentioned XAS experiments by the addition of 1–3 equiv of $Ph_2Zn \cdot MgBrCl$ to the mixture of $FeBr_3$ and (*S*,*S*)-Chiraphos. Then, 1 equiv of azabicycloalkene **1a** was added and stirred at room temperature. After 30 min, the reaction was quenched according to the general procedure and subjected to GC analysis.

The product **3a** and biphenyl (**BP**) were not formed with 1 equiv of $Ph_2Zn \cdot MgBrCl$ (entry 1), suggesting only the transmetalation takes place in this step. In the case of 2 and 3 equiv of $Ph_2Zn \cdot MgBrCl$, the expected carbometalation product **3a** was obtained in 10 and 75% yield, respectively, together with the formation of **BP** (entries 2 and 3). The formation of **BP** indicates that the reductive elimination takes place when 2 equiv of $Ph_2Zn \cdot MgBrCl$ was added. Most importantly, the formation of the carbometalation product **3a** in 75% yield with 3 equiv of diarylzinc reagents clarifies that the catalytically active species is the diaryliron complex [Fe(Ph)$_2$(Chiraphos)] as characterized by XAS analysis. The lower product yield (10%) with 2 equiv of diarylzinc reagents suggests the formation of less reactive aryliron species which is considered to be [FeBr(Ph)(Chiraphos)]. The higher electrophilic reactivity of [Fe(Ar)$_2$(bisphosphine)] complex than [FeX(Ar)(bisphosphine)] complex was previously observed in iron-catalysed cross-coupling reaction,[8] which corresponds well with the current diaryliron intermediates showing higher electrophilic reactivity towards azabicycloalkene. From these results, the mechanism for the formation of diaryliron species is proposed as Figure S11.

Stepwise transmetalation of $FeBr_3$(Chiraphos) **6** with diarylzinc reagents generates trivalent diaryliron species **7** and **10** which facilitates the reductive elimination forming monovalent bromoiron species **11**. The comproportionation between **10** and **11** forms divalent aryliron species **8**. The additional arylzinc reagent generates the highly active diaryliron intermediate **9**, of which geometry is suggested to be tetrahedral with a high spin state by EXAFS analysis combined with DFT-calculation.

Table S16. Stoichiometric Carbometalation Reaction



Entry	X (mmol)	Y (mM)	Z (eq)	Iron intermediate	**3a** (%)[a]	**BP**[b]
1	0.03	20	1		N.D	N.D
2	0.03	20	2		10	detected
3	0.075	50	3		75	detected

[a]Caluclated by the GC area ratio of starting material and product **3a**. [b]**BP** was detected by GC.

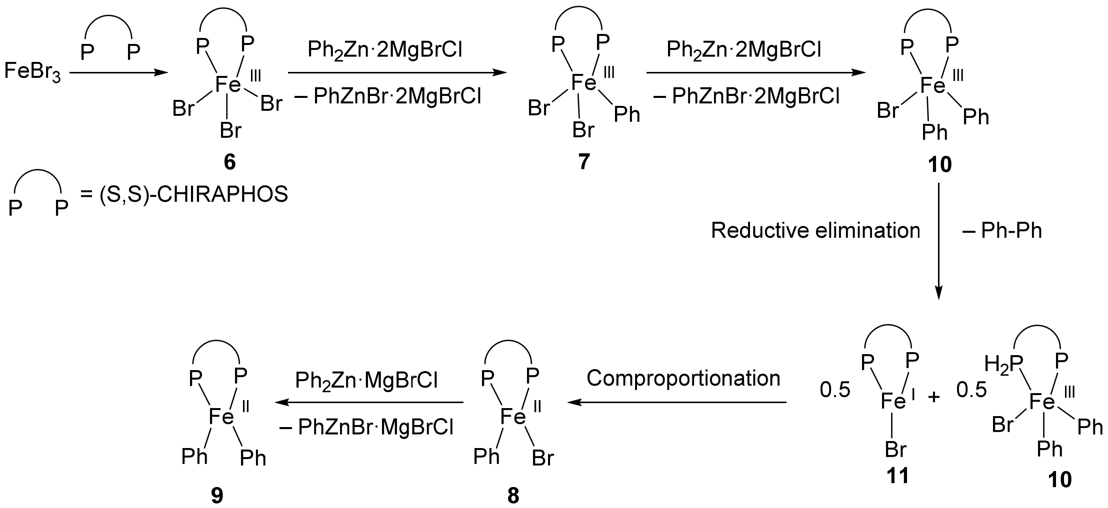


Figure S11. Proposed mechanism for formation of diaryl iron intermediates involving transmetalation-comproportionation steps.

Cartesian coordinates of the optimized geometries at $PCM_{Toluene}$/B3LYP-D2/SDD(Fe,Zn),6-31G*(C,H,O,P,Br) level of theory (For energies see Table S15).

^{1}[Fe(Ph)$_2$(Chiraphos)] (Td, S=0)

Fe	-0.0222640319	0.6164357363	-0.3122711153
P	-1.2684566275	-1.117537878	0.2063269056
P	1.2011188636	0.1170490568	1.5081136886
C	1.012853683	0.0777522081	-1.8984760599
C	0.8248425393	-0.9285901981	-2.8700363495
C	1.4610505495	-0.8945091183	-4.116125132
H	1.2869165204	-1.6914188648	-4.8374404145
C	2.3217797422	0.1599667988	-4.4399515308
C	2.5319050028	1.1833157034	-3.5102615045
H	3.1997949928	2.0094511745	-3.7480273522
C	1.8844921439	1.1333501449	-2.2699057895
C	-1.3484105321	-1.0579761669	2.0793659788
H	-1.8576735885	-0.1143406206	2.2890642368
C	0.0980979579	-0.9708545608	2.6246284329
H	0.5252417353	-1.9755636939	2.5240772887
C	-3.0176013922	-1.1197472337	-0.3278401341
C	-3.9382246173	-0.2594886316	0.294508792
H	-3.6238881054	0.3784155859	1.1136338604
C	-5.2547464383	-0.1888681088	-0.1626472905
H	-5.9548366205	0.4822987509	0.3273243521
C	-5.6657987397	-0.9618823981	-1.2525992996
H	-6.6910323346	-0.9020853281	-1.6083153233
C	-4.750970595	-1.8049153239	-1.8894255241
H	-5.0600293918	-2.4032244897	-2.7424571783
C	-3.4338751103	-1.8823919655	-1.4309509664
H	-2.7291628	-2.5436878044	-1.9261793434
C	-0.6701485835	-2.8292509451	-0.0956378038
C	-1.4911095364	-3.9608644415	0.0518162759
H	-2.5502007623	-3.8352382855	0.2523403735
C	-0.9527745623	-5.2437691926	-0.0610442325
H	-1.598189653	-6.1111874933	0.0505325669
C	0.4140654183	-5.4123119304	-0.3105044883
H	0.8315939537	-6.4125722497	-0.3924125216
C	1.2369367477	-4.2935690692	-0.458456238
H	2.2990413475	-4.4117443117	-0.6553811802
C	0.6952542619	-3.0096109129	-0.3590306489
H	1.3260199449	-2.1414497193	-0.501570481
C	2.7189959464	-0.9252711806	1.36434213
C	3.1002800521	-1.8431785717	2.3570173045
H	2.5012315856	-1.9612517429	3.2549275025
C	4.2511536536	-2.6198340433	2.206029019
H	4.5281994655	-3.3284330304	2.9821788171
C	5.0396743543	-2.4879446134	1.0597287428
H	5.9312267117	-3.0974322607	0.9380611677
C	4.6750526304	-1.5694030513	0.0716032339
H	5.280012385	-1.4615667461	-0.8247471258
C	3.5244596489	-0.7918404439	0.2232406703
H	3.2316103796	-0.1058887991	-0.563230142
C	1.8350059521	1.517179281	2.5284115772
C	1.4341821123	2.820858676	2.1999582416

H	0.7338180518	2.9732131112	1.3863593194
C	1.9181930756	3.91614948	2.9216090599
H	1.5961687242	4.9194267277	2.6555125769
C	2.8124283105	3.720528209	3.9757244366
H	3.1898097359	4.5713215423	4.5370025996
C	3.2328402474	2.4255876528	4.2993659911
H	3.9407736508	2.2676744728	5.1087948525
C	2.7537904799	1.3336253477	3.576028421
H	3.11167145	0.3369970922	3.8133661679
C	-1.3829052905	1.8401704293	0.4873188859
C	-2.1794532728	2.334159558	-0.5724608743
C	-1.754965143	2.2723216791	1.7776260563
C	-3.2762961283	3.1789424386	-0.3686432145
C	-2.8530163555	3.1092971514	2.0049365209
C	-3.6246142447	3.5629566087	0.929332029
H	-3.8653893329	3.5222432427	-1.2168230655
H	-3.1072404414	3.4084068301	3.0204930308
H	0.168146083	-1.7674828479	-2.6475253548
H	2.8226090726	0.1840939184	-5.4051804009
H	2.0838888649	1.9411540784	-1.5573966196
H	-1.9656886883	2.0245018368	-1.6005166999
H	-4.4817048121	4.2100304989	1.1009216029
H	-1.1718475541	1.9488251731	2.6389838175
C	0.123477473	-0.5589013488	4.1015652267
H	1.1387363886	-0.5804070505	4.5094015543
H	-0.2594825849	0.4608459267	4.2259852501
H	-0.496770987	-1.2373242155	4.6980272491
C	-2.1371875852	-2.207036632	2.7164968221
H	-1.6179394073	-3.1622063707	2.5797768547
H	-2.2713221327	-2.0370825972	3.7911081009
H	-3.1316489071	-2.2867276402	2.2624618148

^{1}[Fe(Ph)$_2$(Chiraphos)] (SqP, S=0)

C	0.703842853	-2.4732636432	-0.2809083194
H	0.5629886288	-2.4984141744	-1.3711393038
C	-0.7026981601	-2.4580125357	0.3664251325
H	-0.5606571318	-2.4377459074	1.4563732065
P	1.5417002774	-0.8249520769	0.0678243939
P	-1.5364341735	-0.8230905843	-0.0480446408
C	3.0321485291	-0.7986163817	-0.9868504136
C	3.9574002268	0.2451672569	-0.7967124933
C	3.2361873719	-1.7112210392	-2.0343762212
C	5.0719804292	0.3530899555	-1.6282971262
H	3.7991591748	0.9790754979	-0.0135334864
C	4.3519734239	-1.5940061187	-2.8679375674
H	2.5319780665	-2.5181522668	-2.2069194198
C	5.2736063807	-0.5643459268	-2.6643015104
H	5.7737771188	1.1674961489	-1.4719439896
H	4.4992559985	-2.309730369	-3.6723956618
H	6.1409311397	-0.4737069097	-3.3128766096
C	-3.028464187	-0.7539673386	1.0023901577
C	-3.9556614516	0.2773155398	0.7614058889
C	-3.2318294937	-1.6161785167	2.0918043448
C	-5.0719016559	0.4222640038	1.584925459

H	-3.7970631503	0.974050996	-0.0550852911
C	-4.349440418	-1.4620224677	2.9170502937
H	-2.5259454902	-2.4123730522	2.3035756596
C	-5.2730686192	-0.4453636196	2.6630710079
H	-5.7749533801	1.2269933256	1.3892281699
H	-4.4965674069	-2.1388367134	3.7545330673
H	-6.1415835075	-0.325857583	3.305349477
C	-2.15611573	-1.0843961316	-1.7506011802
C	-1.30027057	-0.7572297289	-2.8153187293
C	-3.4247446597	-1.6128178267	-2.0281538401
C	-1.7016090465	-0.9670142768	-4.1363260327
H	-0.3219247233	-0.3266052939	-2.6111537656
C	-3.8284381277	-1.8151605434	-3.3496397727
H	-4.0962005688	-1.8542550576	-1.2098410218
C	-2.9675806247	-1.4957210617	-4.4043915505
H	-1.0326478328	-0.7072028663	-4.9521964485
H	-4.8150364691	-2.221501341	-3.5558135514
H	-3.2852288164	-1.6517510233	-5.4317625923
C	2.1572259152	-1.0195275833	1.7810370504
C	1.2749434216	-0.7021203456	2.8274453394
C	3.4466013162	-1.4763705023	2.0867389068
C	1.6719691677	-0.8494242109	4.1578835216
H	0.2778562091	-0.3296808049	2.6005957137
C	3.8459237987	-1.6154057498	3.4179835781
H	4.1381002304	-1.7100380829	1.2830606518
C	2.960050258	-1.3049014965	4.4542880071
H	0.9821331336	-0.5977207781	4.9588059475
H	4.8492538658	-1.9653076494	3.6458272724
H	3.2745968467	-1.4110970942	5.488947869
Fe	0.0040645592	0.8867667786	-0.0104098194
C	1.4197797282	2.2554238328	0.0272368352
C	1.8852918685	2.8832920982	-1.1472520788
C	2.145149439	2.5329383787	1.2084573589
C	3.0227219881	3.6983226017	-1.1591737743
H	1.3522266559	2.7240350674	-2.0855968572
C	3.2788038454	3.3544859752	1.2129889344
H	1.841550012	2.0692471834	2.1476313899
C	3.7328063725	3.9333785049	0.0225068779
H	3.3553301876	4.1515175465	-2.0918937793
H	3.814178968	3.5349337443	2.1441358129
H	4.617368709	4.566402149	0.0189146459
C	-1.4115049977	2.2533448855	-0.0870331041
C	-1.9010962634	2.8991391818	1.0677275519
C	-2.1142309258	2.5106324842	-1.2863572916
C	-3.0376859818	3.7149536273	1.0433642256
H	-1.3878166501	2.7548829372	2.0193840997
C	-3.2478445087	3.3310456099	-1.3270579426
H	-1.7914773361	2.0320073795	-2.2117742662
C	-3.7245010444	3.9303576374	-0.1556973747
H	-3.3884219666	4.1834832388	1.96172986
H	-3.7649918013	3.495256866	-2.2714277155
H	-4.6086754786	4.5634684011	-0.1801337403
C	1.5311415926	-3.6869030808	0.1631421827
H	1.6058111171	-3.7114813167	1.2563402035

H	1.068365069	-4.6207809731	-0.175433071
H	2.5472172855	-3.64205404	-0.2425248623
C	-1.5325886733	-3.6881344488	-0.023455181
H	-1.6102227098	-3.7604698227	-1.1142503274
H	-1.070527111	-4.6069733037	0.3548543276
H	-2.547545337	-3.6239761743	0.382504303

^{3}[Fe(Ph)$_2$(Chiraphos)] (Td, S=1)

Fe	-0.0201471753	0.7091354607	-0.3822159198
P	-1.2487634044	-1.0412163663	0.1806407017
P	1.2919431288	0.1793981485	1.5605646984
C	0.9302636578	0.0612085662	-1.9990615036
C	0.6331232434	-0.955406477	-2.9305262501
C	1.2843820598	-1.0494169332	-4.1646736527
H	1.0236844639	-1.8473459237	-4.8579195743
C	2.2733478529	-0.1216086959	-4.5117539265
C	2.5955357269	0.9041216838	-3.6189736231
H	3.3631381947	1.6320273975	-3.8754345033
C	1.9283429407	0.9858225417	-2.3897584601
C	-1.2953770307	-0.9844320003	2.0603845258
H	-1.7749456572	-0.0279127172	2.284305234
C	0.1570147223	-0.9530192921	2.602346646
H	0.5688930986	-1.956125896	2.4389788278
C	-3.0086097456	-1.0898413829	-0.3165137081
C	-3.9479399072	-0.2749211111	0.3373004501
H	-3.6423151057	0.3492125153	1.1701724373
C	-5.2711444649	-0.2307881116	-0.1036938745
H	-5.9851807343	0.4061050892	0.4113887323
C	-5.6720854197	-0.9873195784	-1.2088000611
H	-6.7025674834	-0.9488147732	-1.5520627241
C	-4.7398847564	-1.7866856162	-1.8761909953
H	-5.0408451241	-2.3725877334	-2.7407200476
C	-3.4160124593	-1.8364389818	-1.4339062248
H	-2.6981305712	-2.4641215683	-1.9537641471
C	-0.6313948592	-2.7511455241	-0.1121621556
C	-1.4432056091	-3.8890068199	0.0359855805
H	-2.5046007477	-3.7717461376	0.2289203774
C	-0.8938722809	-5.1684987931	-0.0668943792
H	-1.5335892835	-6.0401952596	0.0445346348
C	0.4755547676	-5.3278015599	-0.3060128298
H	0.9017793507	-6.325002966	-0.3803121983
C	1.2901459729	-4.2027292466	-0.4536883451
H	2.3547343643	-4.3125022986	-0.6419791971
C	0.7370331285	-2.9231602769	-0.3653750673
H	1.3635123015	-2.0524542675	-0.5102143352
C	2.7945162075	-0.8702284606	1.3836049744
C	3.1662453494	-1.8336495907	2.3358528773
H	2.5695551354	-1.9755401133	3.2318962739
C	4.2985729147	-2.6269825686	2.1404009798
H	4.5708331585	-3.370381678	2.8850072946
C	5.0753248832	-2.4679292121	0.9889035711
H	5.9521983769	-3.090709228	0.8330134346
C	4.7169230239	-1.5083101938	0.0383529197
H	5.3100227404	-1.3833190744	-0.8635913531

C	3.5848306897	-0.7136320314	0.2346387749
H	3.2927127324	0.0021796615	-0.5259765668
C	1.8807745522	1.5215006058	2.6776758478
C	1.4025272467	2.8215236846	2.4516022022
H	0.696090632	2.9985666354	1.6468466881
C	1.8246699688	3.8835042022	3.2569092034
H	1.4421434505	4.8838239728	3.0722526951
C	2.7403100724	3.6591477392	4.2871422083
H	3.0729286946	4.4845620555	4.9110771697
C	3.2406000016	2.3705780284	4.5054818821
H	3.9654969139	2.1934716213	5.2957409725
C	2.8164628587	1.310162799	3.7044248611
H	3.2277345551	0.3184082127	3.8651464507
C	-1.4760541372	1.8882292374	0.3460957682
C	-2.3037778568	2.3497766445	-0.7040332574
C	-1.8108484939	2.3492612686	1.6361838309
C	-3.3878316891	3.2070902354	-0.4891257149
C	-2.8953969892	3.2026929756	1.8718276667
C	-3.6936962385	3.6325293501	0.807282938
H	-4.0030170362	3.5274064066	-1.3277878999
H	-3.1182130945	3.529477265	2.8861711254
H	-0.1212456939	-1.6998808347	-2.684554109
H	2.786481769	-0.1980155151	-5.4677282819
H	2.2119266112	1.7926952325	-1.7074180397
H	-2.1193215503	2.0037939277	-1.723743085
H	-4.5421247281	4.2891529236	0.9855971233
H	-1.2132703581	2.0392093133	2.4922140668
C	0.1940361741	-0.6343632075	4.1024372749
H	1.214967798	-0.6664901915	4.4951890616
H	-0.1992172437	0.3710822289	4.294835271
H	-0.4085646109	-1.3563583093	4.6642141836
C	-2.1143555865	-2.1162424316	2.693906383
H	-1.6109761712	-3.0808958262	2.5637372274
H	-2.2559249763	-1.9416982065	3.7665701819
H	-3.1052922116	-2.1793026488	2.2307677819

^{3}[Fe(Ph)$_2$(Chiraphos)] (SqP, S=1)

C	-0.1959963217	0.7454670095	-2.4539575057
H	-1.294586178	0.7895081745	-2.4519260257
C	0.206222812	-0.7493026013	-2.4490512493
H	1.3047095895	-0.7934642312	-2.4384469252
P	0.3277485017	1.5117441882	-0.8177115759
P	-0.3282516642	-1.5061783018	-0.8124491006
C	-0.4710015475	3.1533283758	-0.7683768846
C	-0.1017680671	4.0353835916	0.2645509114
C	-1.4961893239	3.5260505419	-1.6525440516
C	-0.7361219757	5.2711490893	0.3904814341
H	0.6664370773	3.7518505758	0.9762123155
C	-2.1318561289	4.7635131475	-1.5175158367
H	-1.8043753356	2.859896233	-2.4513822815
C	-1.7509419589	5.6395022188	-0.4983820318
H	-0.4436355415	5.9380160387	1.1966886771
H	-2.9211772897	5.040598469	-2.2112722564
H	-2.245904926	6.6013832409	-0.3938421345

C	0.4554631359	-3.1544346263	-0.7565517656
C	0.0640007645	-4.0347468199	0.2693314494
C	1.4905206453	-3.5339186649	-1.6261382636
C	0.6858074315	-5.2759958531	0.402620748
H	-0.7113234081	-3.7451141806	0.9708792744
C	2.1135864762	-4.7770549724	-1.4840479775
H	1.8161791655	-2.8686008691	-2.4188462934
C	1.7101294537	-5.6515304958	-0.4722247192
H	0.3764355681	-5.9413072468	1.2037541426
H	2.9107165968	-5.0597767532	-2.1665104976
H	2.1953816518	-6.6177322798	-0.3621423061
C	-2.1135190794	-1.828387962	-1.0556534441
C	-3.0137880424	-0.8079061858	-0.7075136432
C	-2.6076005635	-3.0263456081	-1.591052056
C	-4.3859504957	-0.9777774567	-0.9037371966
H	-2.6388255596	0.1150855765	-0.2696901418
C	-3.9805399416	-3.1983046267	-1.7798509161
H	-1.917581584	-3.8241845367	-1.8482178673
C	-4.8704600719	-2.1745063843	-1.4396530757
H	-5.0739713693	-0.1833408294	-0.6276249275
H	-4.355608469	-4.1314092109	-2.1917415145
H	-5.9385034814	-2.3120604159	-1.5851825177
C	2.1114940222	1.8453436785	-1.0563779036
C	3.0124460841	0.8163227884	-0.7355942642
C	2.6051131791	3.0592784235	-1.5541078536
C	4.3848723945	0.9941249776	-0.9213106155
H	2.6372030515	-0.1199696856	-0.3270601164
C	3.978711209	3.2392246713	-1.731697791
H	1.9147823861	3.8633919205	-1.7900694672
C	4.8693358711	2.2075600086	-1.4186200287
H	5.0732483403	0.1929238896	-0.6664171785
H	4.353629872	4.1850514252	-2.1136398902
H	5.9377314233	2.3515421108	-1.5550064753
Fe	0.0111506206	0.0030628412	0.9107591165
C	0.3535190842	1.3948471672	2.2717380222
C	-0.6968227543	2.0676256839	2.9303861654
C	1.6538715531	1.9056627651	2.4878939944
C	-0.4773178671	3.2038589783	3.7175885994
H	-1.7180289445	1.7015511679	2.820548969
C	1.8881029541	3.0346926954	3.2816666265
H	2.5062803432	1.4338690249	1.9989501495
C	0.8184613247	3.6997199591	3.8921911604
H	-1.3185822047	3.7019703913	4.197193182
H	2.9046377654	3.401621407	3.4162162287
H	0.99454964	4.581411333	4.5044117199
C	-0.3210878971	-1.3899745804	2.2724259424
C	0.7293422548	-2.0902185533	2.9014476125
C	-1.6266834777	-1.8734379124	2.5171442544
C	0.5035785325	-3.2245949156	3.6892721358
H	1.7558446475	-1.7477200482	2.7673920783
C	-1.8670532062	-3.0014826447	3.3104541617
H	-2.4799391009	-1.3792562395	2.0519814365
C	-0.7983266427	-3.6926425357	3.8928303375
H	1.3449296997	-3.7435643684	4.1460114666

H	-2.8880254044	-3.3466248267	3.4672967329
H	-0.9793655831	-4.5731499628	4.505298256
C	0.3493561709	1.4893392587	-3.6801688475
H	1.4383363424	1.3785271137	-3.7348390949
H	-0.0880909222	1.0935404658	-4.6036949109
H	0.122231805	2.5591795615	-3.6252728441
C	-0.32918521	-1.4981189552	-3.6764396613
H	-1.4179492613	-1.3898914193	-3.7394703061
H	0.1142834233	-1.1043941609	-4.597944843
H	-0.1000050634	-2.5672242573	-3.6166302259

^{5}[Fe(Ph)$_2$(Chiraphos)] (Td, S=2)

Fe	-0.0155022105	0.8453006695	-0.4361129766
P	-1.3634813282	-1.1470052462	0.1953348084
P	1.2748785232	0.112822937	1.5437770832
C	1.1263956057	0.6443707649	-2.1219452833
C	1.0343829973	-0.4847758863	-2.9670957796
C	1.9146630298	-0.6998201785	-4.0344743078
H	1.8112443151	-1.5866241849	-4.6577093665
C	2.9307528579	0.2237271489	-4.2976515985
C	3.0472942708	1.3630797236	-3.4937869396
H	3.8310601795	2.0916071008	-3.6944986559
C	2.1566180813	1.5629217703	-2.4324595927
C	-1.3515989991	-0.8938157345	2.070051415
H	-1.7214656567	0.1302146315	2.1979532363
C	0.1088346847	-0.9715070673	2.5915579617
H	0.454226642	-1.9963848392	2.411010368
C	-3.1394359595	-1.237064222	-0.2206711203
C	-3.9912978548	-0.2168920306	0.2408896011
H	-3.6052131954	0.5803719636	0.867535117
C	-5.3367693344	-0.2063131555	-0.127920879
H	-5.9797893875	0.5916274589	0.2330850383
C	-5.8478616855	-1.2015300886	-0.9665902762
H	-6.8958448324	-1.1885177483	-1.2541680628
C	-5.0030060019	-2.2082731779	-1.4413328639
H	-5.3901953544	-2.9819062214	-2.0992854785
C	-3.6553517782	-2.2264125487	-1.0728310764
H	-3.0058618351	-3.012079881	-1.44607667
C	-0.6899780767	-2.8405831806	0.0177828359
C	-1.3752062058	-3.9975913303	0.4299924728
H	-2.3978062268	-3.9199170496	0.7845029982
C	-0.7488990081	-5.243525042	0.3748410635
H	-1.2872764017	-6.1325787367	0.6926047391
C	0.5707327719	-5.3475234597	-0.0814946824
H	1.057828768	-6.3185980991	-0.1139267825
C	1.2565771443	-4.2051951349	-0.499037777
H	2.2817231224	-4.2726096261	-0.8516917404
C	0.6245915481	-2.9595569137	-0.4597609206
H	1.1582311014	-2.0788101847	-0.7985742588
C	2.7010211484	-1.004452998	1.2503029192
C	3.0670343523	-2.012236916	2.157114611
H	2.5179144684	-2.137364786	3.0858706923
C	4.1282689695	-2.8723533912	1.8695485336
H	4.3990541805	-3.6507336497	2.5779381981

C	4.8351316481	-2.7353759164	0.6707934404
H	5.6557947724	-3.41062335	0.4433935713
C	4.4820678729	-1.7299125862	-0.2335928667
H	5.021715715	-1.6202811153	-1.1702576195
C	3.4223446053	-0.8659361458	0.0536573951
H	3.1338335199	-0.1085015093	-0.6684368666
C	1.9440400175	1.4084105091	2.6565267478
C	1.4529918278	2.714364979	2.5022707782
H	0.7157597084	2.9229702085	1.7320074242
C	1.9180491857	3.7447212851	3.3248488942
H	1.5296800486	4.7516884424	3.1983987757
C	2.8875654047	3.4808316776	4.2950515853
H	3.2542062889	4.2823887339	4.9307748022
C	3.3987163393	2.1857490136	4.4382850972
H	4.1644032791	1.9811121715	5.1819290524
C	2.9313615949	1.1550556891	3.6225733326
H	3.3443115308	0.1556154089	3.7236469435
C	-1.519273711	2.1587147788	0.0947400227
C	-2.4089541429	2.518534723	-0.9445716118
C	-1.9208101153	2.5369184377	1.3953187351
C	-3.6163816139	3.184814902	-0.7094830625
C	-3.1272813527	3.2011731377	1.6528110997
C	-3.9851835467	3.5224588022	0.5967150319
H	-4.2751660648	3.4295825316	-1.5405975977
H	-3.3983254125	3.4637886458	2.6741449606
H	0.2608643556	-1.2300123265	-2.7812420101
H	3.6217389391	0.0606435279	-5.121909906
H	2.2803174587	2.4566107338	-1.8187982406
H	-2.1634859588	2.247012821	-1.9719460709
H	-4.9262309587	4.0332213712	0.7884766284
H	-1.2869670947	2.2977431056	2.2492915928
C	0.2032458435	-0.6760918182	4.0946576484
H	1.2373856722	-0.7442099915	4.446807161
H	-0.1522788495	0.3371994056	4.3166892542
H	-0.3985457588	-1.3901502648	4.6665019345
C	-2.2746453539	-1.8590379464	2.8256769466
H	-1.8604457721	-2.8740914191	2.8171814694
H	-2.3924100431	-1.545962152	3.8690300976
H	-3.2690501288	-1.8839545812	2.3680000765

^{5}[Fe(Ph)$_2$(Chiraphos)] (SqP, S=2)

C	0.6523829021	-2.4369543704	-0.3434057213
H	0.3668705825	-2.5130045031	-1.401095498
C	-0.6594262176	-2.4130306126	0.4931750192
H	-0.3750101448	-2.4308504266	1.553725362
P	1.5323595555	-0.7779059907	-0.1764608606
P	-1.5349005234	-0.7639028544	0.2313523987
C	2.99215079	-0.8491764729	-1.2624637403
C	3.9831645496	0.1397012062	-1.1034993964
C	3.0869361401	-1.7508043738	-2.3349992859
C	5.058452547	0.1987058267	-1.989765831
H	3.9085587863	0.8629359142	-0.2969814808
C	4.1641437171	-1.680774731	-3.2224591717
H	2.3237266848	-2.5089195756	-2.4815755736

C	5.1538591017	-0.7099039701	-3.0494808578
H	5.8163654285	0.9655715572	-1.8551319258
H	4.2291399919	-2.3874125906	-4.0456450052
H	5.9915716402	-0.6573849008	-3.739704118
C	-3.0086316059	-0.7772926008	1.3004654418
C	-4.0035368652	0.1927783791	1.0679511041
C	-3.1112198576	-1.6110349411	2.4259311255
C	-5.0899301128	0.2997739447	1.9359820062
H	-3.9233517737	0.8646095372	0.2187085857
C	-4.1999085419	-1.4933686435	3.2941063699
H	-2.3451208794	-2.3532946472	2.6285843506
C	-5.1931506313	-0.5417465889	3.0489685566
H	-5.8505215088	1.0518450527	1.7448376543
H	-4.271144418	-2.1478832246	4.1588179229
H	-6.0397043155	-0.4519320212	3.7244027403
C	-2.1628516661	-0.9797805152	-1.479290526
C	-1.2840172504	-0.7303175594	-2.5474713812
C	-3.4706175942	-1.3973183743	-1.7603246602
C	-1.7050419175	-0.8952807097	-3.8678881906
H	-0.2772403099	-0.3710775555	-2.3527076394
C	-3.8944406416	-1.5533696516	-3.0822426406
H	-4.161832969	-1.5871967249	-0.9457347213
C	-3.0140248301	-1.3042556454	-4.1385741732
H	-1.0153750218	-0.6899020483	-4.6820951238
H	-4.9139415547	-1.8702498958	-3.2854751835
H	-3.3466361446	-1.4240656621	-5.1660528915
C	2.1796464806	-0.9033067799	1.5355339227
C	1.3053668576	-0.6160928651	2.5980714817
C	3.497876975	-1.2800159593	1.8245471687
C	1.7415204477	-0.7034207589	3.920969154
H	0.2897385848	-0.2881504492	2.3947377089
C	3.9365058111	-1.3585491947	3.1485001838
H	4.1855514035	-1.4982556203	1.014095992
C	3.0609939207	-1.0715970314	4.199298049
H	1.0552550535	-0.4695775085	4.7303610752
H	4.9639520918	-1.6443594288	3.3576992506
H	3.4053653991	-1.1306707793	5.2281789692
Fe	-0.0004298845	1.3548402852	-0.0199035606
C	1.7374154857	2.3886598217	0.4247161585
C	2.2235046651	3.1231241359	-0.6830634706
C	2.5988323267	2.3240371515	1.5417527858
C	3.4869180658	3.7256156025	-0.696046715
H	1.6038177535	3.2150894993	-1.5767323577
C	3.8634743687	2.9255831788	1.5487286169
H	2.2969715587	1.7689686128	2.4263580908
C	4.3184502787	3.6202938179	0.4227768344
H	3.8244127422	4.2685566257	-1.5772117178
H	4.4984424908	2.8431593743	2.429404599
H	5.3053318437	4.0782429199	0.420366915
C	-1.7375105517	2.3615989354	-0.5291387249
C	-2.2448116032	3.1374268165	0.5401591293
C	-2.5785949937	2.2515104461	-1.6579701262
C	-3.5088489166	3.7377517687	0.5067250663
H	-1.6418728374	3.2651088315	1.4408738934

C	-3.8437057344	2.8497301678	-1.7113713835
H	-2.260110236	1.6627808624	-2.5145489792
C	-4.3198329805	3.5872164409	-0.6219493812
H	-3.8629187854	4.3139390262	1.3598136594
H	-4.4625005877	2.7316863649	-2.5994883452
H	-5.3070935876	4.0431313779	-0.6553805273
C	1.5392469134	-3.6309733915	0.039724871
H	1.7676544032	-3.6012672326	1.1109635394
H	1.0357702631	-4.5782073206	-0.1841620823
H	2.4866237706	-3.6107386287	-0.5083183457
C	-1.5471384049	-3.6255519699	0.1760983028
H	-1.7747694945	-3.6550278713	-0.895306184
H	-1.0445703767	-4.5593193275	0.4524065821
H	-2.4947971021	-3.5743939824	0.7215768611

THF

C	-0.0685637822	1.2404308805	0.1832342979
C	1.4152520267	1.2115949153	-0.2134597564
C	1.843454865	2.643428646	0.1311140286
C	-0.4683519141	2.6526475621	-0.2617934349
H	-0.6671608567	0.4600154943	-0.2977929134
H	-0.1708343213	1.1400067953	1.270902094
H	1.5147315007	1.032669159	-1.2912607119
H	1.9984959231	0.4552696128	0.321846132
H	2.1453927864	2.7151643945	1.1879709582
H	2.6700545645	3.0086622257	-0.4904797956
H	-1.2870623056	3.0772434478	0.3319009966
H	-0.7695401769	2.6556582297	-1.3212913214
O	0.6957926905	3.4729636368	-0.0944745736

^{1}[Fe(Ph)$_2$(Chiraphos)(THF)] (TBPy, S=0)

Fe	-0.1235026828	-0.4850303854	0.6019827153
P	-1.3139723546	0.7341711365	-0.7911774998
P	1.6457590899	0.2040546092	-0.6662631047
C	-1.4780163754	-0.3152610031	2.0480755784
C	-2.883694876	-0.4422881239	2.0713165029
C	-3.6590729636	-0.0570101413	3.1696280084
H	-4.7409957045	-0.179507794	3.1374932054
C	-3.0538605039	0.4944343499	4.3051515099
C	-1.6640281082	0.6359141799	4.328198297
H	-1.1721443278	1.0513445871	5.2072060999
C	-0.9039812387	0.2262131721	3.2248025677
C	-0.4822322688	0.6475042941	-2.4793300554
H	-0.6311453322	-0.4002008139	-2.7568112165
C	1.039307699	0.89399543	-2.3341736036
H	1.1797387433	1.9790740746	-2.2634708713
C	-3.0414437479	0.2650591261	-1.1913740828
C	-3.2880524103	-0.8971694632	-1.9417577629
H	-2.4649602504	-1.4977632512	-2.3119893402
C	-4.5979373222	-1.3129618765	-2.1877923123
H	-4.7695767468	-2.2176486218	-2.7649354294
C	-5.677368531	-0.5831076249	-1.6826456468
H	-6.6960878167	-0.9115319519	-1.8725574123
C	-5.44011436	0.5669477911	-0.9248076047

H	-6.2722586213	1.1364264172	-0.5188446007
C	-4.1311588459	0.9864891551	-0.6792415629
H	-3.9559781628	1.8708029797	-0.076159064
C	-1.4143617927	2.5315579584	-0.4150906044
C	-2.120174223	3.4585616514	-1.2023422793
H	-2.7058574357	3.1108179107	-2.0461259313
C	-2.0905319776	4.8192036887	-0.89342862
H	-2.6410406733	5.5248995906	-1.5102615503
C	-1.3566821862	5.2734417502	0.2084335718
H	-1.3309916248	6.3342446623	0.4442824852
C	-0.6704591897	4.3594580474	1.0104845566
H	-0.1071115619	4.6999480061	1.875022225
C	-0.7094271294	2.9973242599	0.7032184856
H	-0.2022449828	2.287112958	1.3445120999
C	2.4583636378	1.6935041222	0.0664513759
C	3.1412965247	2.6483698915	-0.7039773025
H	3.2188350578	2.5230051306	-1.7805553988
C	3.7144198279	3.7728601498	-0.1065988362
H	4.2366303168	4.5024290956	-0.7198643241
C	3.6112573555	3.9622103794	1.2747026209
H	4.0517368055	4.8404080303	1.7389406096
C	2.9324798078	3.0216693877	2.0535398371
H	2.8374766074	3.1654156627	3.1266615466
C	2.3626155283	1.8980194148	1.4511605256
H	1.81542396	1.1886832048	2.0635020151
C	3.0952772964	-0.8920627724	-0.9975320912
C	2.9613757739	-2.247795591	-0.6553030771
H	2.0207842037	-2.5971201619	-0.244241301
C	4.0299710309	-3.131637884	-0.8281542414
H	3.9112553348	-4.1784322413	-0.5602215597
C	5.2456413126	-2.6704853202	-1.3394558021
H	6.0775587718	-3.3570335087	-1.4732255534
C	5.3934811181	-1.3189532927	-1.6689704926
H	6.340424402	-0.9521684793	-2.0565212
C	4.3268085269	-0.4356788307	-1.4939256491
H	4.4610000846	0.6156919763	-1.7273082678
C	-0.6587372729	-2.0975666159	-0.4360101473
C	-1.7063292077	-2.9054876828	0.0671712394
C	-0.1328124858	-2.5295288938	-1.6753958942
C	-2.2137668886	-4.0132967718	-0.6187321726
C	-0.6312873061	-3.6304087294	-2.3847929936
C	-1.6893213922	-4.3782694628	-1.8629336899
H	-3.0321212937	-4.5863871642	-0.1848907658
H	-0.1903693796	-3.8994348049	-3.3437839941
H	-3.3904284941	-0.8556405286	1.2031978409
H	-3.6547223335	0.8002791787	5.1589260999
H	0.1818707424	0.3231241649	3.295415586
H	-2.1503057948	-2.6481336824	1.022660531
H	-2.088845652	-5.2310229152	-2.4074456155
H	0.6962337939	-1.9885311708	-2.1260082218
C	1.8199581643	0.3714588167	-3.5466389195
H	2.8824879812	0.6273109399	-3.4820192731
H	1.7464090236	-0.7204356919	-3.6156047098
H	1.4204116943	0.8015032783	-4.4723047113

C	-1.0993447072	1.530846188	-3.5685217042
H	-0.8972755688	2.5902150756	-3.3747591472
H	-0.6838986581	1.2780409684	-4.5514518196
H	-2.1846808002	1.3856661811	-3.6152099338
C	2.3485225873	-1.3602735739	2.4706636631
C	0.4929186757	-2.8421785261	2.4974476597
C	2.8344785061	-2.708939505	2.985506846
H	2.2360721029	-0.6370548073	3.291787561
H	2.9724872626	-0.9289190929	1.6867509768
C	1.5265950135	-3.3115252976	3.5256945549
H	0.3447390305	-3.5564747288	1.6842572091
H	-0.4759482895	-2.5730829614	2.9212866809
H	3.2207757569	-3.3011527983	2.1472782295
H	3.616594808	-2.6116613844	3.7449565837
H	1.5549790736	-4.4023500671	3.6095601249
H	1.3027075665	-2.8917259974	4.5135835386
O	1.0566052532	-1.6394540359	1.9024716011

^{1}[Fe(Ph)$_2$(Chiraphos)(THF)] (SqPy, S=0)

C	-0.8633761645	-1.1531005286	-2.2897888249
H	-0.7379075865	-2.1815882574	-1.9326011063
C	0.572555059	-0.6347280548	-2.5488990884
H	0.5144550181	0.4045013683	-2.904400562
P	-1.6453714092	-0.2388100944	-0.8248742377
P	1.4213062394	-0.5628381562	-0.8675203283
C	-2.8286429943	-1.4703601753	-0.1330243178
C	-3.6423927839	-1.0488481916	0.9360089045
C	-2.9444384125	-2.7943611678	-0.5861885435
C	-4.5382102876	-1.9339799504	1.5351504201
H	-3.5729375179	-0.0330508746	1.3065743781
C	-3.8414056285	-3.6797782583	0.0199243472
H	-2.3494138692	-3.1540255931	-1.4177200036
C	-4.6387241684	-3.2533996242	1.0837564944
H	-5.1486177204	-1.5879334208	2.3646104746
H	-3.9160804958	-4.7003041699	-0.3466647395
H	-5.3334870501	-3.9428766005	1.5562825723
C	3.1142141497	0.0474827885	-1.1785409824
C	4.0620764251	-0.0962811651	-0.1489842814
C	3.4628287567	0.7724822892	-2.3289720607
C	5.3287471826	0.4757000485	-0.275449659
H	3.803924182	-0.6385268262	0.7544535626
C	4.7302165734	1.3468740595	-2.4507754942
H	2.7432260488	0.9000837266	-3.1318234781
C	5.6657116868	1.2004066255	-1.4228618159
H	6.0462018676	0.3638208079	0.532773548
H	4.9849623435	1.9055563719	-3.3475297995
H	6.6511924593	1.6491538618	-1.5153398607
C	1.6467113331	-2.3471094757	-0.4987909014
C	0.6160867775	-3.0092363904	0.187362062
C	2.7679345736	-3.0799258537	-0.9132515221
C	0.695483104	-4.3794530551	0.4418531808
H	-0.2513633362	-2.4524129423	0.53046032
C	2.8553032238	-4.448431021	-0.6467053691
H	3.5753291691	-2.5760610613	-1.435604142

C	1.8184546048	-5.1010929181	0.0273249469
H	-0.1138217544	-4.8758032988	0.9705011636
H	3.7319433142	-5.0050693757	-0.9675791285
H	1.88829394	-6.1660495153	0.2324964528
C	-2.7816478446	0.9871872327	-1.5920329152
C	-2.3619509353	2.3198771715	-1.7141688643
C	-4.0496357162	0.6241820823	-2.0738879094
C	-3.1852837503	3.2684112936	-2.3269293232
H	-1.4080803457	2.6129113357	-1.2941172319
C	-4.872929449	1.5726632786	-2.6822723039
H	-4.3945952466	-0.3990686204	-1.9625503077
C	-4.4402448659	2.8963072627	-2.8146675132
H	-2.8513095106	4.29958507	-2.4100297502
H	-5.852827946	1.2797841098	-3.050142912
H	-5.0836868195	3.6346839377	-3.285832962
Fe	0.0584453471	0.424798792	0.6662762518
C	-1.2753574394	0.9548024394	2.0429421005
C	-1.5085621706	0.16576659	3.1899422804
C	-2.1948120905	2.0102579999	1.8368383294
C	-2.5973131058	0.3774924571	4.0443735689
H	-0.820965332	-0.6456626852	3.4215266654
C	-3.2796833277	2.2469702771	2.6883571861
H	-2.0855564123	2.6446688507	0.9597656161
C	-3.4966721909	1.4187082803	3.7957527184
H	-2.7431132032	-0.2711411849	4.9073309716
H	-3.9666643128	3.0661614026	2.478555947
H	-4.3449796916	1.588258112	4.4555185457
C	1.5190593539	0.260635268	2.0135042791
C	2.5294729332	1.2131604365	2.2610797279
C	1.6719445913	-0.9655616396	2.7029728161
C	3.6073206404	0.9737866064	3.1214203019
H	2.5085168743	2.1642649183	1.7423894577
C	2.7524608161	-1.2318924311	3.5510464119
H	0.9375731661	-1.7565879262	2.5558111405
C	3.7339361625	-0.2584811697	3.76747452
H	4.360168776	1.7470879338	3.2702260525
H	2.8279947695	-2.200959667	4.0424092498
H	4.5756914219	-0.4565225697	4.4274172105
C	-1.738061499	-1.1776263202	-3.547507392
H	-1.8514922493	-0.1700518143	-3.9633416827
H	-1.2981588885	-1.8261257319	-4.3136178704
H	-2.7391481531	-1.5562118799	-3.314572735
C	1.3004205422	-1.5014257852	-3.585656092
H	1.264626759	-2.5542247735	-3.2821700883
H	0.8318980629	-1.4095083115	-4.572276146
H	2.3527418037	-1.2157758204	-3.6795967678
C	1.1239224925	2.9674701294	-1.1630930885
C	0.499740695	3.5475385672	0.9920492537
C	2.371625495	3.6116904703	-0.5735925441
H	0.5109525451	3.7034073712	-1.7082927023
H	1.3106641002	2.1098725585	-1.8050872625
C	1.7908537507	4.3376538122	0.6622352779
H	0.5081912644	3.0373158401	1.9537425828
H	-0.393734076	4.1782883064	0.9238613292

H	3.0742868502	2.8258690157	-0.2799182913
H	2.8701944936	4.2898502685	-1.2730849048
H	2.4900268241	4.3383521491	1.5036074418
H	1.5491535389	5.3780593	0.4204010069
O	0.3977906496	2.5060044721	-0.0138502616

³[Fe(Ph)₂(Chiraphos)(THF)] (TBPy, S=1)

Fe	-0.1681799164	-0.5934227251	0.6297665992
P	-1.3597081833	0.6389602467	-0.7396463188
P	1.6394020946	0.1270469345	-0.7903794538
C	-0.7871654463	0.5089604099	2.202388852
C	-2.0995113596	0.3024555212	2.688030408
C	-2.5430082014	0.815313346	3.914095323
H	-3.5645494207	0.6289488822	4.2429981825
C	-1.6803064663	1.5741094401	4.7103565758
C	-0.3797674105	1.8165510427	4.2565059778
H	0.3016190737	2.4189885505	4.8561612442
C	0.0458661092	1.2953148927	3.0287529537
C	-0.6577427195	0.3917629416	-2.4648007026
H	-0.7734274468	-0.6801141287	-2.6481379203
C	0.8530269227	0.729600311	-2.417981833
H	0.9195807821	1.8225650394	-2.3535107943
C	-3.144387603	0.2762205316	-0.9041223408
C	-3.5849470327	-0.7737805309	-1.7253165068
H	-2.869151633	-1.3508372476	-2.3009797601
C	-4.9382140164	-1.1109641362	-1.7742160558
H	-5.263502701	-1.9280296933	-2.4125600211
C	-5.8656433561	-0.4153455219	-0.9930984205
H	-6.9188322737	-0.6820055308	-1.0294354966
C	-5.432565395	0.6190419552	-0.1583512689
H	-6.1461262742	1.1595536045	0.4582819106
C	-4.0795955779	0.9629632294	-0.1137108039
H	-3.7457954509	1.7649183977	0.5373077422
C	-1.299474213	2.4741139723	-0.5878641103
C	-2.2088492048	3.3221959062	-1.2418241499
H	-3.0435636848	2.8949873004	-1.7882597244
C	-2.0519131146	4.7085997943	-1.1857514296
H	-2.7661387127	5.353417736	-1.6915705581
C	-0.9772619546	5.265338104	-0.4839673596
H	-0.8542385526	6.3447166684	-0.4442219243
C	-0.0687598231	4.4302269137	0.1707012065
H	0.7671144218	4.8515691525	0.722913117
C	-0.2362666165	3.0442980542	0.1251414823
H	0.451045747	2.3993837294	0.6559948716
C	2.7751669296	1.5223714333	-0.3751593782
C	3.2314336013	2.4666859472	-1.3077965616
H	2.9373492878	2.3940028524	-2.3499421013
C	4.0672335022	3.514226232	-0.9113585851
H	4.4067795905	4.2385788629	-1.6470926474
C	4.4640418801	3.6312937848	0.4232037903
H	5.1084669869	4.4501043763	0.7314591366
C	4.0269935416	2.6893677876	1.3591960705
H	4.3294953134	2.7713816568	2.3998550614
C	3.1901753391	1.6455543787	0.9606902352

H	2.8462062152	0.9243147677	1.6943744653
C	2.8562637855	-1.189489334	-1.2227021934
C	2.5768021753	-2.5024734772	-0.8110529842
H	1.65639144	-2.7078206918	-0.2751445384
C	3.4800509882	-3.535204008	-1.080465758
H	3.2500400438	-4.547970366	-0.7596053026
C	4.6738664696	-3.2652614274	-1.7533266195
H	5.3772091707	-4.0676165547	-1.9606893144
C	4.9697460473	-1.9556833646	-2.1486818289
H	5.9039843435	-1.7380247079	-2.6599102545
C	4.0692040041	-0.9244749796	-1.880179427
H	4.3161506044	0.09402705	-2.1648153231
C	-1.0266577277	-2.192025522	-0.3277874504
C	-2.1442141445	-2.7446989476	0.3395828734
C	-0.6527656808	-2.8561013974	-1.5143064573
C	-2.8417974022	-3.8592403509	-0.1351841509
C	-1.3395064707	-3.9719948448	-2.0126358619
C	-2.4451987983	-4.4788513061	-1.3250803607
H	-3.7038950862	-4.2353653376	0.413638996
H	-1.0109308229	-4.4414333261	-2.9390100024
H	-2.805187906	-0.2658705124	2.0833466562
H	-2.0181334513	1.9797232499	5.6614809406
H	1.0584854105	1.5299897309	2.7027235644
H	-2.4996421714	-2.2739351915	1.2560349759
H	-2.9878010819	-5.3403115382	-1.7082716182
H	0.2046555123	-2.4993973583	-2.0841557324
C	1.5882844081	0.2531857908	-3.6760557638
H	2.6410745587	0.5533642884	-3.664517188
H	1.5587989434	-0.8403712178	-3.7494970692
H	1.124591595	0.6739929709	-4.5755027916
C	-1.3809224851	1.1721079833	-3.5685700998
H	-1.2204213925	2.2498926772	-3.4512428191
H	-1.0166287841	0.8745288484	-4.5590120162
H	-2.4588760435	0.9792168736	-3.534176617
C	2.0671909279	-1.5250605597	2.5246548225
C	0.0095769456	-2.6696470381	2.8204068399
C	2.3200850475	-2.6595298333	3.5087538557
H	1.9335551559	-0.5669150636	3.0417478088
H	2.8103259326	-1.430148321	1.7298423579
C	0.9003049848	-2.908576619	4.0482637094
H	-0.2699069021	-3.5843578571	2.2932412173
H	-0.8855224304	-2.0872339726	3.0493064628
H	2.695286692	-3.5405137407	2.9746867682
H	3.0350347583	-2.3849227402	4.2905719435
H	0.7676022486	-3.9129374125	4.4617263303
H	0.667097953	-2.1763425491	4.8291657843
O	0.8237930576	-1.8915041679	1.8889516572

^{3}[Fe(Ph)$_2$(Chiraphos)(THF)] (SqPy, S=1)

C	-0.8751385223	-1.2135421508	-2.2668704722
H	-0.7125640063	-2.230715	-1.8919401768
C	0.5364931049	-0.6504419476	-2.5589580304
H	0.4375675808	0.3853460172	-2.9172902624
P	-1.6464157953	-0.2862297923	-0.8113687789

P	1.4124337754	-0.5353821471	-0.8918490044
C	-2.8395299736	-1.489037974	-0.097093603
C	-3.6912478018	-1.0226315656	0.9223944622
C	-2.9137388236	-2.8388579451	-0.4753288004
C	-4.5889057138	-1.889768433	1.5441319667
H	-3.647773575	0.0136426456	1.2378463001
C	-3.8128436366	-3.7058942699	0.1538296246
H	-2.282721161	-3.2321852969	-1.2641658354
C	-4.6513222104	-3.234543295	1.1657900868
H	-5.2300734645	-1.51061306	2.3350112771
H	-3.8568270373	-4.7474205406	-0.1539151976
H	-5.3480803416	-3.9094667584	1.6560496122
C	3.0807915197	0.1168895737	-1.2575303949
C	4.0726071811	-0.0136039456	-0.2687415518
C	3.3707540972	0.854575949	-2.416259186
C	5.3202553524	0.5886713678	-0.4377750101
H	3.861605488	-0.5709800961	0.6369935021
C	4.6192068737	1.4583731526	-2.5822691847
H	2.6196837315	0.9688054805	-3.1917397754
C	5.5962645233	1.3289597634	-1.5915595144
H	6.072890784	0.4848761859	0.3390929608
H	4.8269654382	2.0268472664	-3.4849500996
H	6.5669534406	1.800789146	-1.7184981342
C	1.7026119034	-2.3111854521	-0.5222804058
C	0.7156412167	-2.9974527811	0.2024455757
C	2.8233592347	-3.0169721219	-0.9827985818
C	0.8366999326	-4.366057775	0.4491526733
H	-0.1448829171	-2.4545702542	0.5828955201
C	2.9531933119	-4.3835245527	-0.7234048444
H	3.5967267519	-2.4942093716	-1.5371446593
C	1.9586879308	-5.0610279266	-0.0112116161
H	0.0616044335	-4.8825591118	1.0090198572
H	3.8291310302	-4.9191723016	-1.0800458926
H	2.0610272603	-6.1244941386	0.1882425165
C	-2.7594652649	0.9504104295	-1.593191246
C	-2.3005451353	2.2657465636	-1.7554836901
C	-4.0411655531	0.6120288567	-2.0555282462
C	-3.10066301	3.2219610538	-2.3865798808
H	-1.3340756671	2.5423248235	-1.3522828736
C	-4.8416083097	1.5686676789	-2.6815801898
H	-4.4141234532	-0.3977771424	-1.9156739944
C	-4.3710425056	2.8748242353	-2.8526527761
H	-2.7366314153	4.2399037212	-2.5008567171
H	-5.8328911967	1.2956228828	-3.0338548642
H	-4.9967155348	3.6194661835	-3.3376956849
Fe	0.0348730424	0.4374461917	0.6622588398
C	-1.3109936997	0.9596569756	2.033897896
C	-1.6060480771	0.1767277495	3.1685629009
C	-2.1847469434	2.045910924	1.793993458
C	-2.7153351967	0.4263348058	3.9854435546
H	-0.9544184182	-0.6568708333	3.42100369
C	-3.2913331517	2.3160323427	2.6067467336
H	-2.0182663188	2.6799854639	0.9255161397
C	-3.5718555389	1.4953182175	3.7053737271

H	-2.9121290175	-0.216353434	4.8425470794
H	-3.9430538003	3.1577061073	2.375198522
H	-4.4364230196	1.6923371281	4.3356944023
C	1.4655768902	0.1249591656	2.0354784623
C	2.5116258907	1.0451476734	2.2571091533
C	1.5346571683	-1.0641265747	2.7936285277
C	3.5432877768	0.8139674631	3.1743421797
H	2.5520896945	1.9565450769	1.6704885093
C	2.570553862	-1.3237796138	3.6981310791
H	0.7687217825	-1.8267508246	2.6643949758
C	3.583580589	-0.3802282792	3.899260887
H	4.326577062	1.5595492036	3.3064597003
H	2.5854042056	-2.2638077903	4.2479199443
H	4.3881629583	-0.5736102314	4.6053833795
C	-1.7755151288	-1.2877405807	-3.5043962945
H	-1.9216519641	-0.2933014092	-3.9408404838
H	-1.3362477037	-1.9437878748	-4.2644895528
H	-2.7617443226	-1.6848585233	-3.2397687679
C	1.2704291824	-1.498285786	-3.6062805816
H	1.2786514802	-2.5496196514	-3.2962184695
H	0.7751434147	-1.4290424842	-4.5817319879
H	2.3093814603	-1.1762788237	-3.727126031
C	1.162761635	3.0688218017	-1.1181910166
C	0.6065498012	3.5505432974	1.075160855
C	2.4525749315	3.6216567641	-0.5228200427
H	0.5719909564	3.862502776	-1.6042290377
H	1.2946089309	2.2403893585	-1.8120191677
C	1.9404970748	4.2816188074	0.780162456
H	0.5903561516	2.9929068999	2.0105654238
H	-0.2496512699	4.2347533014	1.0456392837
H	3.130990586	2.7909968415	-0.3061745432
H	2.9601335884	4.3264878965	-1.1885993297
H	2.6530512222	4.1660892309	1.6021113419
H	1.764075427	5.3519817459	0.6309412817
O	0.4451179352	2.5712366751	0.0191251631

^{5}[Fe(Ph)$_2$(Chiraphos)(THF)] (TBPy, S=2)

Fe	0.0752697808	-0.7771290786	0.8722866946
P	-1.8690744649	0.3046739403	-0.5261568239
P	1.3478386706	0.5734253495	-0.7641183896
C	-0.3605306332	0.0527850731	2.7239889966
C	-1.617983065	0.6285223058	3.017318267
C	-1.9133446239	1.2249439493	4.2489535037
H	-2.897850667	1.6562926277	4.4240698368
C	-0.9419193306	1.271328587	5.253593812
C	0.312765234	0.7030348545	5.0128302407
H	1.0764358005	0.7231896229	5.7895287072
C	0.5834554511	0.1048730697	3.775867711
C	-1.0598719681	0.1508956467	-2.2321519195
H	-0.7960974539	-0.9111977692	-2.3028222539
C	0.2439458652	0.9940087386	-2.254733168
H	-0.0438410139	2.0399866187	-2.0937067976
C	-3.5006400368	-0.4890494455	-0.7482115647
C	-3.5602975795	-1.7816042544	-1.3010625546

H	-2.655779477	-2.2732944809	-1.6431643357
C	-4.7790705622	-2.4551137288	-1.3874926635
H	-4.8039579097	-3.4546233675	-1.8132618511
C	-5.9520901959	-1.8592418872	-0.9143534633
H	-6.8994245008	-2.3880775258	-0.9799187947
C	-5.8981880599	-0.5829328466	-0.3476513289
H	-6.8033324736	-0.113498965	0.0293092352
C	-4.6811283084	0.0978991308	-0.2628596805
H	-4.6499284794	1.0897352042	0.1775622594
C	-2.2023340467	2.1087483842	-0.4338417496
C	-3.1351806324	2.7810852585	-1.2435019456
H	-3.780296503	2.2120163143	-1.9050765768
C	-3.2434355658	4.1717744096	-1.1906244974
H	-3.9694747092	4.6814745786	-1.8189466937
C	-2.4156162505	4.9086905297	-0.3350776489
H	-2.4967310386	5.9922317407	-0.3025081878
C	-1.4936003771	4.2496283461	0.4807972489
H	-0.8473280845	4.8108311335	1.1498503655
C	-1.3966559975	2.8561381393	0.4396809053
H	-0.6979573904	2.3449687746	1.0922822629
C	1.8495271648	2.2229876612	-0.1469846431
C	2.0232757614	3.3310936547	-0.9911817076
H	1.888295207	3.2236662925	-2.0638487851
C	2.3481344909	4.5803238781	-0.45977834
H	2.4760983546	5.432583254	-1.121751684
C	2.4984939545	4.7351339457	0.9222226773
H	2.7425478012	5.7099121092	1.3361068644
C	2.3242729635	3.6374885936	1.7698769453
H	2.4219823575	3.7548003002	2.8456915151
C	2.0018328637	2.3862117609	1.2389958925
H	1.8172039836	1.5489440498	1.9062264119
C	2.8861315009	-0.1473766723	-1.4629858837
C	3.0178866371	-1.5444339113	-1.4314221482
H	2.2469023505	-2.1443515895	-0.9613714677
C	4.1585081806	-2.1589290405	-1.9541673263
H	4.2493214363	-3.241461279	-1.9190441786
C	5.1868574364	-1.3829633018	-2.4950688329
H	6.0781837616	-1.8597362613	-2.8939914123
C	5.0734495461	0.0115317673	-2.5074626453
H	5.8766104694	0.6199934937	-2.9146785661
C	3.9292651344	0.6262485983	-1.9958488974
H	3.8521080223	1.7093761606	-1.9967106398
C	-0.5315511839	-2.6082237913	0.0696280807
C	-1.4657755848	-3.3391097382	0.841691127
C	-0.2470773699	-3.1563982526	-1.2003897335
C	-2.0765996523	-4.5123929231	0.3870639819
C	-0.8517120935	-4.3274568255	-1.6801982523
C	-1.7750147779	-5.0111921527	-0.8851828933
H	-2.7981166562	-5.0307819106	1.0163818258
H	-0.6056822587	-4.7006634639	-2.6734913869
H	-2.3990498011	0.6187081499	2.2572427937
H	-1.1612409468	1.7384108667	6.2115533441
H	1.5656635856	-0.3389532836	3.6255999799
H	-1.7431585304	-2.9648329251	1.8282212963

H	-2.2522415081	-5.9182719317	-1.2497732005
H	0.4519310922	-2.6504578981	-1.8668781
C	0.9855812602	0.8909853706	-3.5950991375
H	1.9087312355	1.4798410244	-3.5834812738
H	1.2622250204	-0.1481150595	-3.8101695873
H	0.355652571	1.2603393664	-4.4109435996
C	-1.9851259565	0.5146879933	-3.4011970399
H	-2.1556671339	1.5971347084	-3.4348468057
H	-1.5431848386	0.2085992388	-4.3563374455
H	-2.9528261708	0.0126731832	-3.301086188
C	3.4179241984	-1.1144049686	1.8113219666
C	2.1762025701	-3.0347946655	2.0810092841
C	4.4106781749	-2.2802353658	1.5776736805
H	3.5095660541	-0.7130190359	2.830584729
H	3.5212094428	-0.2981558545	1.0949722788
C	3.4990076553	-3.5312238526	1.4910889516
H	1.2837253412	-3.5349422687	1.7028567897
H	2.1875807278	-3.0637527366	3.1817017495
H	4.978546121	-2.1384132035	0.6546358193
H	5.1162054508	-2.3556299698	2.4114446299
H	3.3453381778	-3.8169316642	0.4449808494
H	3.903714704	-4.3924243433	2.0318662842
O	2.1063362989	-1.670832259	1.6428958959

^{5}[Fe(Ph)$_2$(Chiraphos)(THF)] (Td, S=2)

C	1.449175946	1.3877598933	-2.0687507229
H	1.2837408726	2.4290587991	-1.7598563404
C	0.0560081893	0.804154973	-2.4291402641
H	0.2068345459	-0.2176067901	-2.8062873365
P	2.1323108941	0.5499059457	-0.5209910295
P	-1.0376029015	0.6084892106	-0.8807624005
C	3.6907576155	1.4574342014	-0.1910203585
C	4.6179388582	0.8561733983	0.6822054046
C	3.9357902718	2.7673574476	-0.634296977
C	5.7700783211	1.5375999962	1.0728938219
H	4.4271748997	-0.142071375	1.06735854
C	5.0881362506	3.4514307865	-0.234745964
H	3.230805775	3.2608961836	-1.2961692273
C	6.011364996	2.8378955748	0.6146721971
H	6.4764352533	1.0558161145	1.7443028617
H	5.2632029992	4.4630306055	-0.5925061338
H	6.9077668444	3.3694386024	0.9232138109
C	-2.6923600826	0.2215180906	-1.5740832825
C	-3.8563082943	0.6075688618	-0.8892237168
C	-2.8158957704	-0.6165279751	-2.696886794
C	-5.1092972013	0.1711922517	-1.3249274584
H	-3.7854072466	1.2287076235	-0.0034859909
C	-4.0688234487	-1.0548766302	-3.1282208672
H	-1.9290205278	-0.9272980956	-3.242627165
C	-5.2214829666	-0.6610223752	-2.4414399383
H	-5.9947003476	0.47260729	-0.7727222739
H	-4.1433231882	-1.6993430046	-4.0002088603
H	-6.1981964672	-1.0021096411	-2.7742862481
C	-1.1539190787	2.3440530441	-0.2995474148

C	-0.3243557021	2.7383785784	0.7633102382
C	-2.0068766213	3.2893739199	-0.8877052942
C	-0.3399978448	4.0572794353	1.2212170504
H	0.329172297	2.0087523073	1.2347346234
C	-2.0305869903	4.6058938536	-0.4209767468
H	-2.6650632764	2.9888897726	-1.6966037493
C	-1.1949501315	4.9926999997	0.6309368092
H	0.3068423204	4.3493102428	2.0440726289
H	-2.7016071013	5.3281105505	-0.8785339891
H	-1.2139599293	6.0174484583	0.992300365
C	2.7269578843	-1.043705858	-1.2255124221
C	1.8494437712	-2.137449865	-1.1650941964
C	3.9768593636	-1.2137668177	-1.8418803143
C	2.1994243393	-3.3667333912	-1.7281486857
H	0.90459305	-2.0303925633	-0.6468274555
C	4.3339267415	-2.4461006852	-2.39358019
H	4.67165608	-0.3806020211	-1.8812142209
C	3.4438555114	-3.524288734	-2.3435893352
H	1.5080161468	-4.2040090908	-1.6694376093
H	5.3058583471	-2.5644296679	-2.8660830668
H	3.7236759986	-4.4823262685	-2.7741608432
Fe	-0.725859238	-0.7002453552	1.2817909878
C	1.0590168997	-1.019621432	2.2527332997
C	1.6931843227	-0.0115519377	3.0144565835
C	1.766939698	-2.235136936	2.1364049202
C	2.9484759912	-0.1891946984	3.6047965378
H	1.2039026637	0.9568678405	3.1348249095
C	3.0267697834	-2.4323555278	2.7166558516
H	1.3352841331	-3.0463174579	1.5510373502
C	3.6244343995	-1.4056832446	3.4534758114
H	3.4060585869	0.6198963729	4.171524136
H	3.5439057202	-3.3824471404	2.5900118104
H	4.6042294995	-1.5497321721	3.9042947577
C	-2.5890495373	-0.1432278516	1.9980538503
C	-3.7346799613	-0.958635846	1.8733735842
C	-2.8224470638	1.1553408825	2.5073560962
C	-5.0205932659	-0.5193976321	2.2081580054
H	-3.637325942	-1.963183132	1.469928144
C	-4.1011848941	1.6193751137	2.8368871881
H	-1.9876082778	1.8448051642	2.6205881121
C	-5.2110204804	0.7810138717	2.6828374919
H	-5.8744927446	-1.1833746326	2.0818553689
H	-4.2336280078	2.6340644727	3.2088503857
H	-6.2084297691	1.136393301	2.9329036306
C	2.4005515135	1.3557097588	-3.2747550219
H	2.4804926493	0.3350482056	-3.665707749
H	2.0507829035	2.0117639676	-4.0802009633
H	3.4040240304	1.6829469689	-2.985052171
C	-0.6085269604	1.6669411628	-3.5155110341
H	-0.6706576675	2.7072588286	-3.1756327989
H	-0.0160819781	1.6422565915	-4.4364337123
H	-1.618122175	1.3257406547	-3.7563789361
C	-1.4485194338	-3.1430540883	-0.8038415315
C	-1.6304673925	-3.6894134276	1.4509741331

C	-2.8872551006	-3.6160372075	-0.6424391972
H	-0.7814808996	-3.958975758	-1.1196658467
H	-1.3214540456	-2.2884875991	-1.4656092914
C	-2.8363435759	-4.3375138397	0.7256077188
H	-1.9032435383	-3.1331595755	2.3493131335
H	-0.8497575121	-4.4192450323	1.6938030799
H	-3.5479654292	-2.7441351609	-0.6080111675
H	-3.2108780156	-4.2720231552	-1.456291521
H	-3.7638592573	-4.2069421362	1.2907266841
H	-2.6673279014	-5.4108679771	0.591843509
O	-1.0773759947	-2.7225263668	0.5211224032

XYZ Cartesian coordinates for DFT analysis of probability of *S,S*-Chiraphos coordination to zinc reagent.

$ZnBr_2(THF)_2$

Zn	-0.5325837567	-0.7398232685	0.7585629446
O	-2.6206062204	-0.6037053983	1.027977689
C	-3.3062134259	0.3417541561	0.153594411
C	-3.3551974303	-1.8720741004	1.0464346277
C	-4.082564656	-0.5384367777	-0.8148092589
H	-3.968471142	0.957570396	0.7748911434
H	-2.5392795226	0.9634074695	-0.3093305797
C	-4.5538129859	-1.6740775025	0.1095107123
H	-2.6755316854	-2.6496452153	0.6871312564
H	-3.632052535	-2.082750886	2.0824381007
H	-3.399575543	-0.9183314486	-1.5824335776
H	-4.9091306483	-0.0057115475	-1.2949663262
H	-4.7996106119	-2.5931010974	-0.430556036
H	-5.4363890783	-1.3582400909	0.6774700816
O	-0.467287009	1.3180132099	1.2623690941
C	0.7875448126	1.985257107	0.967319222
C	-0.7506196914	1.6085795109	2.6600147548
C	1.6488732524	1.700529841	2.1979764622
H	1.1550080469	1.5657387822	0.0287537677
H	0.5805641035	3.0565241928	0.8455633275
C	0.6218147869	1.6829197365	3.3625194099
H	-1.2835451479	2.5661203181	2.6931198593
H	-1.3975148356	0.8079309769	3.0201342901
H	2.4330910504	2.4513222882	2.3333080382
H	2.115006032	0.7156802907	2.0986042526
H	0.6893027081	2.5851420082	3.9781312664
H	0.7770927305	0.8074663073	3.9968611271
Br	0.2596887208	-1.906455691	2.6242952537
Br	-0.2370403186	-0.7733435673	-1.564485314

$Fe(Ph)_2(THF)_2$

Fe	6.5766920017	7.4603153025	12.5843867579
O	4.9324606234	8.7412340181	13.3176630126
O	5.1548461737	6.705257496	11.0792255855
C	7.4078362946	4.7800565383	13.8814127911
C	7.2182124145	3.6499673749	14.685969799

C	6.1411403386	3.6006386967	15.5771215633
C	5.2674255793	4.6895799661	15.6578954882
C	5.4714781886	5.8084705617	14.8412173185
C	6.5404325167	5.894377627	13.9192154274
C	7.0878396792	9.381994845	10.3059135107
C	7.463401578	10.5894842773	9.7052671236
C	8.2865448051	11.4844123749	10.3963507618
C	8.7346495613	11.1533553174	11.6791511914
C	8.3511771253	9.9383403842	12.260471144
C	7.508651504	9.0132658284	11.6041017942
C	4.2537382514	9.5286486341	12.2986623523
H	4.5208916165	9.101040929	11.3318543637
H	3.1713136566	9.4428282605	12.4643027382
C	4.7489746632	10.9541437319	12.5099098711
H	4.0606318696	11.6981039348	12.0960411258
H	5.7347037286	11.07193527	12.0493318585
C	4.8534423342	11.0188475334	14.0427989536
H	5.5329327819	11.8014727629	14.3936985097
H	3.8652875138	11.1889489422	14.4866878993
C	5.3700646785	9.6201083331	14.3973816724
H	4.9746986481	9.2222818455	15.3364918053
H	6.464573299	9.592753885	14.4187783499
C	4.0087262809	6.0216930011	11.6463210775
H	3.8282122273	6.4713173729	12.6235442943
H	3.1504141676	6.1981416751	10.9847597055
C	4.3945631178	4.5295198708	11.7030723467
H	3.5658076538	3.9033668415	11.3577607199
H	4.6582839274	4.2421604486	12.723311685
C	5.6349272504	4.4195457272	10.7737920908
H	6.5300925826	4.2498698713	11.377897701
H	5.5453375572	3.614705614	10.03760082
C	5.7082085982	5.7956462541	10.1029751126
H	6.717631603	6.1464323733	9.8760442173
H	5.0880438195	5.8417525885	9.1966703503
H	8.7110394546	9.7164698336	13.2665517389
H	9.3773490606	11.8425357317	12.2244375152
H	8.5767585371	12.4282584655	9.9399805326
H	7.1108068388	10.8374523657	8.7053298984
H	6.422195166	8.7176225576	9.753078199
H	8.2541280016	4.7815432411	13.1925009626
H	7.9054981196	2.8083518835	14.6183153668
H	5.9865793192	2.7246323729	16.2033013464
H	4.4282595487	4.6623429104	16.3513380334
H	4.7632713927	6.6354002983	14.9101057869

$Zn(Ph)_2(THF)_2$

Zn	6.702332082	7.4702880863	12.6563484172
O	4.8648364352	8.7256475942	13.4062968291
O	5.1891912211	6.7169184233	11.0573740129
C	7.4146632592	4.8575679641	13.8973221372
C	7.2022444957	3.7260341521	14.6934689696
C	6.0999082	3.6737506097	15.551919688
C	5.2244374857	4.7624005649	15.610729656
C	5.4482211676	5.8845139606	14.8048923544

C	6.5411814736	5.9650837636	13.9163758386
C	6.9902773633	9.3033396252	10.3433312613
C	7.3535494292	10.4897630803	9.6967091732
C	8.1977601698	11.4039200348	10.3348095836
C	8.6806479831	11.1132232404	11.6138834394
C	8.3112871482	9.9192581893	12.2452053734
C	7.4484476942	8.9822528555	11.6379330334
C	4.217384468	9.4920499852	12.3598945774
H	4.4989525424	9.0435447834	11.4066383992
H	3.1296767321	9.4185798586	12.5011538163
C	4.7103159094	10.9245696559	12.5431692192
H	4.0199013692	11.6601945442	12.1176018878
H	5.6943382017	11.0389135603	12.078334698
C	4.8212034683	11.0165555134	14.073854522
H	5.4983411811	11.8074482871	14.4112721248
H	3.8337203583	11.1879456005	14.5193174688
C	5.3419591111	9.6230288176	14.4421098744
H	4.981369087	9.2534479042	15.407316577
H	6.4382092249	9.5995814011	14.4315049075
C	4.0885719977	5.9851911263	11.6357771829
H	3.9043264156	6.4204444575	12.6186951242
H	3.2077907698	6.1237692418	10.9931113065
C	4.5324435927	4.5067106905	11.6795759043
H	3.7324025836	3.8516233017	11.3198503447
H	4.7986935906	4.2145091851	12.6978990563
C	5.7805574477	4.4585673158	10.7569609115
H	6.6811674135	4.3342735109	11.3641504117
H	5.7366884054	3.6491392237	10.0213511829
C	5.785864325	5.838764294	10.0878187072
H	6.7792628798	6.2359295735	9.8634057653
H	5.1730249229	5.8477389972	9.1740202365
H	8.6979077949	9.7249709147	13.2454827155
H	9.3404773656	11.8158819993	12.1193041317
H	8.4776997776	12.3310050809	9.8397256205
H	6.972905401	10.7060286001	8.7001072607
H	6.3081655105	8.6230033306	9.8373567053
H	8.2787830053	4.8648179944	13.2330721528
H	7.8930160653	2.8865106536	14.6433341511
H	5.9274716505	2.7961199874	16.1708152066
H	4.3654455072	4.7334177776	16.2787619686
H	4.7431519666	6.7123866577	14.8506483833

ZnBr(Ph)(THF)$_2$

Zn	-0.1472115143	0.1022901879	-0.3703371135
O	0.6516536504	-1.3055066463	1.0743549265
O	-0.4810483266	1.4126205202	1.4007704508
C	-2.7750517032	-0.0073703746	-1.7719909443
C	-4.1013611841	-0.4187525179	-1.9457449698
C	-4.6300367829	-1.432870596	-1.1411597342
C	-3.8218336145	-2.034223483	-0.1717480193
C	-2.4977526228	-1.6118040152	-0.007870235
C	-1.9397564606	-0.5843665912	-0.7948675594
C	1.7197518895	-0.8121128059	1.9324631944
H	1.7453886398	0.271660005	1.818815753

H	1.4741924508	-1.0777967909	2.9690534406
C	2.9684056816	-1.5321692171	1.4411694115
H	3.7611390084	-1.5596823861	2.1953211788
H	3.3403667504	-1.0333896096	0.539503545
C	2.4087652281	-2.9237856348	1.1021553216
H	3.0351960195	-3.4831672559	0.4009381324
H	2.2919377818	-3.5182329549	2.0159814747
C	1.0387339951	-2.5910881369	0.5004592772
H	0.2581245021	-3.3175741514	0.7441546522
H	1.0916498225	-2.4693102528	-0.586648108
C	-1.6294985853	0.9747111021	2.1669474813
H	-1.647813862	-0.1144561385	2.1137679933
H	-1.4844571278	1.297337723	3.2061405071
C	-2.8560310127	1.6552787283	1.5203852018
H	-3.502382055	2.0941512236	2.2870104967
H	-3.4352086629	0.9348594987	0.9380782503
C	-2.2396424501	2.7383663477	0.5938387753
H	-2.3136250784	2.4162854543	-0.4494924796
H	-2.7240761157	3.7143710824	0.6957779177
C	-0.7688577447	2.7768648938	1.0198803052
H	-0.0611790088	3.0409543987	0.2317790236
H	-0.6142534335	3.4226957451	1.8956334182
H	-2.3903825502	0.7891766707	-2.4074005394
H	-4.7219724632	0.0517247073	-2.7056400398
H	-5.6610858958	-1.7534572724	-1.2707255141
H	-4.2237753336	-2.8266546169	0.4565907359
H	-1.8880450172	-2.0828247925	0.7622163977
Br	1.8117885459	1.1281930718	-1.1953181664

Zn(Ph)$_2$(Chiraphos)

Zn	-0.0906494318	1.0039304531	-0.5494945758
P	-1.3507578125	-1.1862635303	0.1327362067
P	1.2663079817	0.1777072068	1.4777085252
C	1.1171529661	0.6955150819	-2.1011709542
C	1.158983476	-0.5400190866	-2.7810173742
C	2.14851876	-0.8461571217	-3.7222359573
H	2.1504164853	-1.817202786	-4.2144767451
C	3.1397352577	0.0925543786	-4.0239592389
C	3.1154799242	1.3395736532	-3.3910675083
H	3.8754513772	2.0829645608	-3.625427143
C	2.1168614504	1.6290860498	-2.4529966697
C	-1.3356687224	-0.8954596679	2.0006436612
H	-1.7223555195	0.1228273502	2.1124302502
C	0.125888295	-0.9384635928	2.5210821966
H	0.4937466393	-1.9550046182	2.3396930466
C	-3.1315397758	-1.2480990332	-0.2726867955
C	-3.9871455562	-0.2573484653	0.2420825816
H	-3.6074875057	0.5005506657	0.9190158763
C	-5.3301583009	-0.22255607	-0.1356362111
H	-5.9744420749	0.5536621004	0.2678612322
C	-5.8364485745	-1.1653340608	-1.0347062747
H	-6.8825145732	-1.1345938675	-1.327862663
C	-4.9883250341	-2.1430158338	-1.5625356092
H	-5.3711872627	-2.8760770248	-2.2678117073

C	-3.6434592794	-2.1828566861	-1.1877875857
H	-2.9917124104	-2.9453756142	-1.6033491899
C	-0.7356328155	-2.910741227	0.0118926277
C	-1.4995596106	-4.0349846027	0.3728478346
H	-2.5390236637	-3.9089752382	0.6576269179
C	-0.9301094482	-5.3091150358	0.3575646194
H	-1.5306540412	-6.1717464064	0.6342914073
C	0.411676386	-5.4754682888	-0.0055262763
H	0.8534852684	-6.4685027954	-0.0095802968
C	1.1781721545	-4.365512081	-0.3664564737
H	2.2210184428	-4.481006383	-0.6477663209
C	0.6041753938	-3.091221815	-0.3678137495
H	1.203781567	-2.2381327766	-0.6642920246
C	2.7018361277	-0.9245837906	1.1588788975
C	3.0784855566	-1.9484791189	2.0446122107
H	2.5375411834	-2.0931284659	2.9753707301
C	4.1409712533	-2.7991681017	1.7356624258
H	4.4186773355	-3.5888782013	2.4287407933
C	4.8399288053	-2.6388342522	0.53472723
H	5.660494143	-3.3080222884	0.2895081482
C	4.4796312727	-1.6164273862	-0.3466979616
H	5.0110775131	-1.4857453001	-1.285165614
C	3.4195477738	-0.7601960723	-0.0369372951
H	3.1345846636	0.0130014717	-0.7409407734
C	1.9451269186	1.4609845428	2.600567006
C	1.4646654674	2.7726252817	2.4599154918
H	0.7214969446	2.9956130431	1.7001031396
C	1.9463271756	3.7941855462	3.2839910087
H	1.5650029881	4.8049519282	3.1672051836
C	2.9226759942	3.5166601187	4.2431919702
H	3.3015813425	4.3111540167	4.8805726568
C	3.4249024548	2.2166388274	4.3725298711
H	4.1963220899	2.0007965029	5.107043735
C	2.9418434207	1.1955605489	3.5541237167
H	3.3497029712	0.1930133014	3.6425698059
C	-1.5933910564	2.1695459133	0.0860332196
C	-2.554056172	2.5453317883	-0.8788634777
C	-1.9081055715	2.4993202872	1.421092356
C	-3.752661383	3.1831913121	-0.5402860253
C	-3.1038230292	3.1332289609	1.7809510081
C	-4.0370902131	3.47304052	0.7969977147
H	-4.4689581282	3.4420941848	-1.3175502306
H	-3.3064154937	3.3590835746	2.8263991756
H	0.4103822953	-1.297606852	-2.5547737836
H	3.9164877608	-0.1408359535	-4.7488611652
H	2.1364257916	2.6036410041	-1.964807942
H	-2.3747960721	2.312415555	-1.9279523984
H	-4.9699030088	3.961832527	1.0689159439
H	-1.2126638878	2.2451682141	2.2195254828
C	0.2162510262	-0.6449080584	4.0251423597
H	1.2524204407	-0.6911215201	4.3744602659
H	-0.1620753618	0.3591110849	4.2518559166
H	-0.3677637328	-1.3742484274	4.5959916633
C	-2.2414338443	-1.8645262001	2.772340951

H	-1.8148069926	-2.8745323063	2.7717037175
H	-2.3595435083	-1.5416041644	3.8126803634
H	-3.2373464872	-1.9078060077	2.3195741195

$ZnBr_2$(Chiraphos)

Zn	0.1943459663	0.5150759423	1.2737891862
P	1.4591822404	-0.8086654264	-0.3299852638
P	-1.4401245262	0.677958841	-0.5768969885
C	1.1137345431	0.2827495579	-1.8296497549
H	1.4053075594	1.285578366	-1.4883466324
C	-0.4103569743	0.2746016284	-2.1259229563
H	-0.683236196	-0.7580400883	-2.3718007929
C	3.2675267243	-0.9915684096	-0.2789648375
C	4.0562636682	0.1728636757	-0.2596528668
H	3.5826197258	1.1502543141	-0.2745427925
C	5.4459221417	0.0722291152	-0.189281939
H	6.0487797165	0.9759768874	-0.1751913344
C	6.0593129152	-1.1833231897	-0.1269340605
H	7.1418003805	-1.2577502409	-0.069633751
C	5.2772810066	-2.3409501144	-0.1295713589
H	5.7480569241	-3.3186182787	-0.0728026643
C	3.8852366003	-2.2489651436	-0.2051015218
H	3.2825889062	-3.1513979956	-0.20705109
C	0.7296002798	-2.4209149846	-0.759627949
C	1.1677411588	-3.1932195577	-1.8510514208
H	2.0490793759	-2.8921462449	-2.4078527271
C	0.4786778802	-4.3517742934	-2.2098601798
H	0.8228566918	-4.9457480127	-3.0521500001
C	-0.6565975239	-4.7443643694	-1.4901084199
H	-1.197280105	-5.6413193412	-1.7800076078
C	-1.0896094289	-3.9894987395	-0.3986581836
H	-1.9712576617	-4.2847421198	0.1617786752
C	-0.3935085017	-2.8364621349	-0.0270444016
H	-0.7240626292	-2.2619515801	0.8327910715
C	-2.7448681462	-0.6017896902	-0.5991876688
C	-3.2253056964	-1.1510927832	-1.7993379519
H	-2.8444116998	-0.7986607615	-2.7533321482
C	-4.1903469068	-2.1584486634	-1.7759872438
H	-4.5521587363	-2.5809634397	-2.7093227294
C	-4.6877558779	-2.6226193097	-0.5539654369
H	-5.4351994327	-3.4112204087	-0.5364754421
C	-4.2226901564	-2.0717254735	0.6429999704
H	-4.603517631	-2.4305854466	1.5950714254
C	-3.25542157	-1.0639485623	0.6232247095
H	-2.870666475	-0.6654308687	1.5569515642
C	-2.2904872199	2.2565720519	-0.9323541733
C	-1.5866809042	3.4559339389	-0.7330480145
H	-0.5784966018	3.4348921294	-0.329861234
C	-2.1923841848	4.6777947127	-1.0337668039
H	-1.6423260843	5.6013422948	-0.8757674901
C	-3.5014036904	4.713606263	-1.5225186241
H	-3.972018018	5.6664073676	-1.7495492773
C	-4.2080011636	3.5221006358	-1.7104223835
H	-5.2284968503	3.545111437	-2.0832263547

C	-3.6064672858	2.2962162603	-1.419197444
H	-4.159689197	1.3739645897	-1.5658168852
C	-0.7767738737	1.1776563139	-3.3129865803
H	-1.8588185034	1.1831460558	-3.4817616632
H	-0.4686797375	2.2124901684	-3.1255401389
H	-0.2872284556	0.8246038966	-4.2262577835
C	1.9326540527	-0.0928563204	-3.0721466256
H	1.556875153	-1.0225275333	-3.5152149314
H	1.8636128307	0.696321309	-3.8283166013
H	2.9891152195	-0.2265640719	-2.8187601971
Br	1.4901678091	2.547329602	1.2763858155
Br	-0.6030376239	-0.5422501162	3.2384749747

ZnBr(Ph)(Chiraphos)

Zn	0.1341686295	0.4443580657	1.3438804921
P	1.4093049197	-0.8143138084	-0.3519940872
P	-1.4511091817	0.7166963016	-0.6117745534
C	-0.7053405681	-0.4420454407	2.9058415693
C	-0.4606798629	-1.795666263	3.2154278063
C	-1.139045139	-2.4594314069	4.2446131432
H	-0.9244974231	-3.506316009	4.4514499157
C	-2.0931362721	-1.7775092035	5.0047500317
C	-2.3526984065	-0.4305823248	4.7319110805
H	-3.0890103115	0.1117342876	5.3220801587
C	-1.6656391451	0.2200227596	3.7004358073
C	1.0923093044	0.2881173804	-1.8508231451
H	1.3908462906	1.286066869	-1.5025681323
C	-0.4286501073	0.2965682179	-2.1613386943
H	-0.7128658071	-0.7332999618	-2.4069617112
C	3.2202475899	-0.9972486916	-0.2799570435
C	4.0145847767	0.1633375143	-0.3023941553
H	3.5453502617	1.1400361952	-0.3737551944
C	5.4025587592	0.0630041357	-0.2004492568
H	6.0077874282	0.9651499579	-0.2198846049
C	6.0110558692	-1.1889789221	-0.0654239289
H	7.0921255457	-1.2634678997	0.0148996987
C	5.2244968608	-2.3429432061	-0.0263218917
H	5.6903482733	-3.3183251514	0.0857316198
C	3.8345087348	-2.2503553221	-0.1321683588
H	3.2300486965	-3.1512717819	-0.1031951426
C	0.716027303	-2.4291905881	-0.8461899428
C	1.241209672	-3.2045471145	-1.8958901256
H	2.1633484114	-2.9016724877	-2.3810627714
C	0.5871150526	-4.3672950908	-2.3043472016
H	1.0003798514	-4.963091052	-3.1137558304
C	-0.6014006798	-4.7620128432	-1.6777480602
H	-1.1131879183	-5.6626880375	-2.0062363306
C	-1.124765764	-4.0025472444	-0.6297727757
H	-2.0488643243	-4.2958250113	-0.1409228655
C	-0.4628274257	-2.8463123217	-0.2091052393
H	-0.8695141982	-2.2678664449	0.6128762381
C	-2.7761817361	-0.547212036	-0.6409972077
C	-3.2661542745	-1.0957274854	-1.8374103234
H	-2.8888756379	-0.7433919983	-2.7930583143

C	-4.2321765801	-2.1024565616	-1.8095909534
H	-4.6007918257	-2.5231406858	-2.7412460945
C	-4.7206337185	-2.570045714	-0.5850852051
H	-5.4678591509	-3.3589073834	-0.5640091091
C	-4.2466613491	-2.0211514269	0.6094944067
H	-4.6187550695	-2.3813599541	1.5645858063
C	-3.2801626695	-1.0124934938	0.5838812241
H	-2.8942351663	-0.6128973234	1.5164804748
C	-2.290399031	2.2991543992	-0.9911632002
C	-1.5669431756	3.4918268284	-0.8203309549
H	-0.5533458184	3.4596894418	-0.4310479706
C	-2.1590406374	4.7186511187	-1.1279510963
H	-1.5924678309	5.6359486448	-0.9924023163
C	-3.4757282167	4.7681572885	-1.5947818088
H	-3.9359877635	5.7248296273	-1.8271605952
C	-4.202426411	3.5846773735	-1.7539599489
H	-5.2286637982	3.6178686306	-2.1103336301
C	-3.6136070446	2.353748378	-1.4564481175
H	-4.1824631806	1.4379796942	-1.5829631085
H	0.2706622503	-2.3557018757	2.6336138618
H	-2.6259895529	-2.2880840558	5.8037535081
H	-1.8930044725	1.2676157828	3.505690224
C	-0.7755432729	1.1982985087	-3.3550974742
H	-1.8565968069	1.2158667739	-3.5303408835
H	-0.4570135348	2.2305478889	-3.1705168887
H	-0.2845701335	0.8363273239	-4.2643929531
C	1.9188884156	-0.0977312176	-3.0846196836
H	1.5457653976	-1.0318711307	-3.5209344346
H	1.8539792054	0.6846215392	-3.8484803159
H	2.9740704034	-0.2291784949	-2.8248136596
Br	1.449774901	2.5046105292	1.2224047046