Supporting Information

Multinuclear Cu-Catalysts Based on SPINOL-PHOS in Asymmetric Conjugate Addition of Organozinc Reagents

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Contents:

1. General Instruments and Chemicals

General: All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Analytical thin-layer chromatography was performed on a glass plates coated with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). Thin layer chromatography plates were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in an acidic staining solution of *p*-anisaldehyde followed by heating. Organic solutions were concentrated by rotary evaporation at c.a. 30 mmHg. Flash column chromatography was performed on Kanto Silica gel 60 (spherical, neutral, 140–325 mesh) as described by Still *et al*.[1]

Instrumentation: IR spectra were recorded with a Horiba FT730 spectrophotometer. NMR spectra were measured with JEOL AL-400 spectrometer for ^{1}H and ^{13}C NMR, Lambda-500 for ^{19}F NMR and ^{31}P NMR, using tetramethylsilane as an internal reference, phosphoric acid and trifluoroacetic acid as external references and $CDCl_3$ as a solvent. Chemical shift values for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual proton of $CDCl_3$ (δ 7.26). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz: chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of $CDCl_3$ (δ 77.0). Fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded at 470 MHz: chemical shifts for fluorine are reported in parts per million (ppm, δ scale) referenced to the fluorine resonance of trifluoroacetic acid (δ –76.5). Phosphorous nuclear magnetic resonance spectra (^{31}P NMR) were recorded at 202 MHz: chemical shifts for phosphorous are reported in parts per million (ppm, δ scale) referenced to the phosphorous resonance of phosphoric acid (δ 0). Data are presented as following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers, assignment (*italic*). Mass spectra were measured with a JEOL JMS-SX102A. ESI-MS spectra were measured with LCQ-DECA.

Chemicals: All reagents were purchased as commercially available source unless otherwise noted. (*R*)-BINOL (>99.0% *ee*) was purchased from Fuji Molecular Planning Co., Ltd. Enones were purchased as commercially available source or prepared according to the previously reported protocols.

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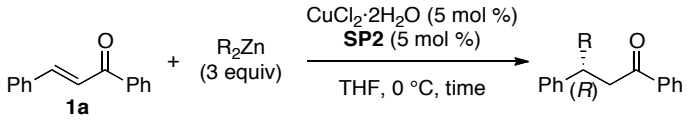
[1] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.

2. Other Dialkylzinc Reagents

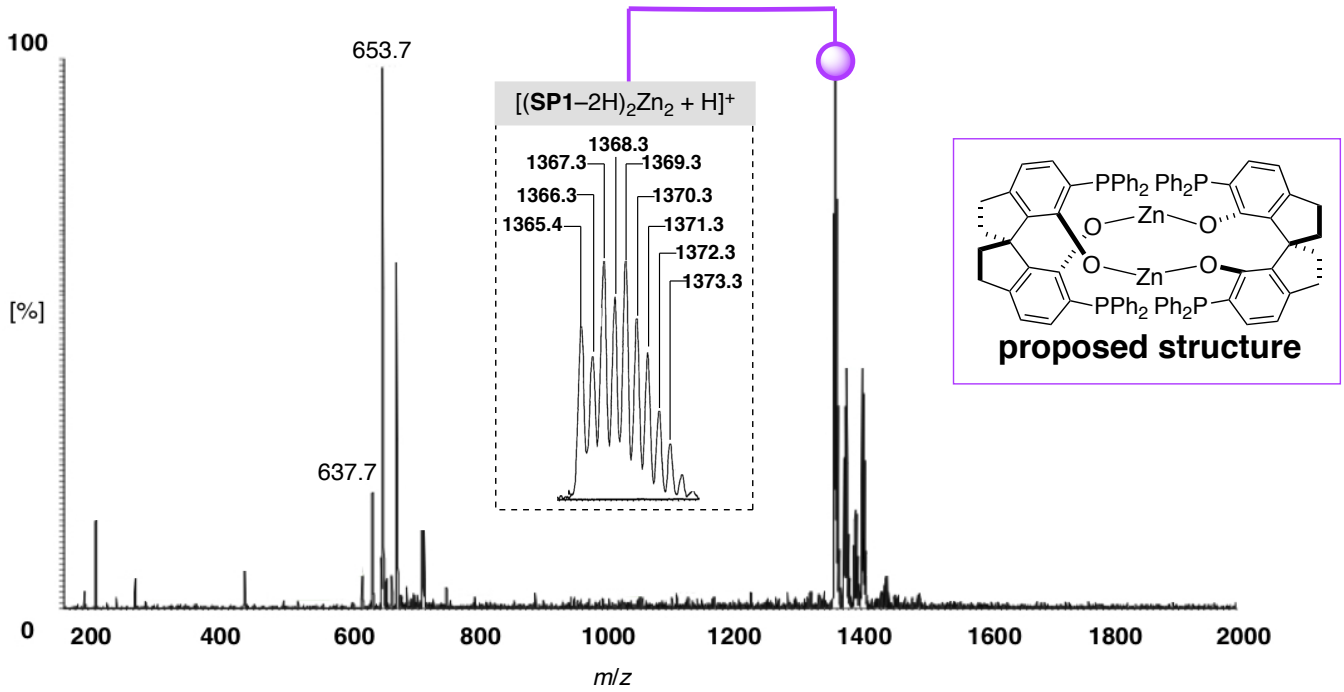
Table S1. Screening of Organozinc Reagents with **SP2**



entry	R	time (h)	yield, ee (%)[a]
1	Et	2	93, 95
2	Me	17	20, 93
3	*n*-Bu	17	19, 86

[a] Isolated yields. Ee was determined by chiral HPLC analysis.

3. ESI-MS of Dinuclear Zn-Complexes



3. Synthetic Procedures and Physical Property of New Compounds

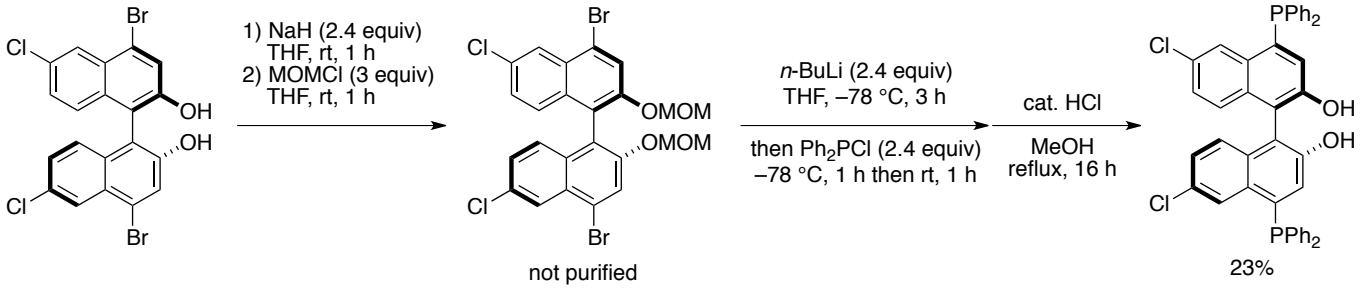
3-1. Representative Procedures

A mixture of $CuCl_2 \cdot 2H_2O$ (0.005 mmol) and **SP1** (0.005 mmol) in THF (1 mL) was stirred at room temperature for 30 minutes and then cooled to 0 °C. A solution of Et_2Zn in hexane (0.3 mmol, 0.3 mL, 1 M) was added to the mixture. To the clear yellow solution was added enone (0.1 mmol) at once. The reaction was carried out at 0 °C and monitored by TLC analysis. After the completion of the reaction, a minimal amount of Sat. NH_4Cl aq. was added. After stirring at 0 °C for 30 minutes, the mixture was passed through a pad of silica gel with ether (50 mL). Concentration and purification by silica gel columun chromatography gave the desired product.

A mixture of $CuCl_2 \cdot 2H_2O$ (0.025 mmol) and **SP2** (0.025 mmol) in THF (5 mL) was stirred at room temperature for 30 minutes and then cooled to 0 °C. A solution of Et_2Zn in hexane (1.5 mmol, 1.5 mL, 1 M) was added to the mixture. To the clear yellow solution was added enone (0.5 mmol) at once. The reaction was carried out at 0 °C and monitored by TLC analysis. After the completion of the reaction, a minimal amount of Sat. NH_4Cl aq. was added. After stirring at 0 °C for 30 minutes, the mixture was passed through a pad of silica gel with ether (50 mL). Concentration and purification by silica gel columun chromatography gave the desired product.

3-2. Ligands

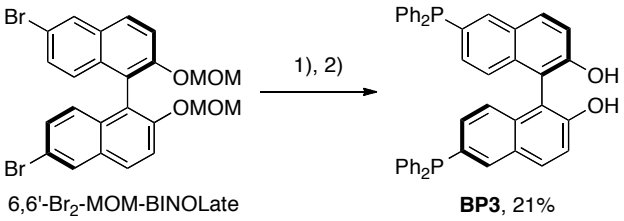
Synthesis of BP2



To a solution of Br_2Cl_2BINOL[2] (ca. 5 mmol including inseparable impurities) in THF (50 mL) was added NaH (ca. 12 mmol, 55% oil dispersion) at rt. After 1 h stirring, MOMCl (15 mmol) was added dropwise at rt. The reaction mixture was stirred at rt for 1 h. The excess NaH was killed with a minimal amount of Sat. NH_4Cl aq. The mixture was filtrated through a pad of silica gel with EtOAc (200 mL). Concentration gave a solid containing Br_2Cl_2-MOM-BINOLate, which was used without purification. To a solution of Br_2Cl_2-MOM-BINOLate (ca. 5 mmol including some impurities) in THF 50 mL was added *n*-BuLi (12 mmol, 1.65 M in hexane) dropwise at –78 °C. After stirring at the temperature for 3 h, Ph_2PCl (12 mmol) was added dropwise at –78 °C. The mixture was stirred at –78 °C for 1 h and then room temperature for 1 h. The reaction was terminated with a minimal amount of Sat. $NaHCO_3$ aq. The mixture was passed through a pad of silica gel with ether to give a crude mixture, which was concentrated under vacuo to give a residue. The deprotection was carried out in refluxing MeOH 50 mL with a few drops of conc. HCl aq. for 16 h. The resulting solution was treated with a minimal amount of Sat. $NaHCO_3$ aq. and concentrated. The residue was purified by silica gel column chromatography (10% EtOAc/hexane) to give **BP2** in 832 mg, 23% yield as a white powder; mp 145 °C (decompose); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 (s, 2H), 6.94 (d, J = 4.4 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 7.37–7.40 (m, 20H), 8.43–8.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.0, 124.6, 125.8, 126.4, 128.5, 128.9, 129.0, 129.4, 130.6, 131.7, 131.8, 132.0, 132.2, 134.1, 134.2, 134.3, 134.4, 134.9, 135.0 (2C), 139.1, 139.2, 152.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ –13.5 (s); IR (cm^{-1}, CH_2Cl_2) 3525, 1571, 1494, 1434, 1371, 1319, 1182, 1139, 1093; $[\alpha]^{27.1}_D$ = 84.2 (c = 1.02, $CHCl_3$); HRMS (FAB, positive) *m/z* calcd. for $C_{44}H_{30}Cl_2O_2P_2$ $[M]^+$, 722.1098; found 722.1108.

[2] Valente, C.; Choi, E.; Belowich, M. E.; Doonan, C. J.; Li, Q.; Gasa, T. B.; Botros, Y. Y.; Yaghi, O. M.; Stoddart, J. F. *Chem. Commun.* **2010**, *46*, 4911.

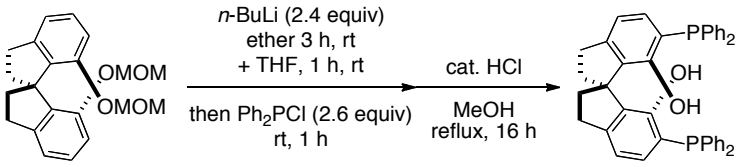
Synthesis of BP3



1) *n*-BuLi (2.4 equiv), THF, –78 °C, 3 h
then Ph_2PCl (2.4 equiv), –78 °C, 1 h then rt, 1 h
2) cat. HCl, MeOH, reflux, 16 h

To a solution of 6,6'-Br_2-MOM-BINOLate[3] (7 mmol) in THF 50 mL was added *n*-BuLi (16.8 mmol, 1.65 M in hexane) dropwise at –78 °C. After stirring at the temperature for 3 h, Ph_2PCl (16.8 mmol) was added dropwise at –78 °C. The mixture was stirred at –78 °C for 1 h and then room temperature for 1 h. The reaction was terminated with a minimal amount of Sat. $NaHCO_3$ aq. The mixture was passed through a pad of silica gel with ether to give a crude mixture, which was concentrated under vacuo to give a residue. The deprotection was carried out in refluxing MeOH 50 mL with a few drops of conc. HCl aq. for 16 h. The resulting solution was treated with a minimal amount of Sat. $NaHCO_3$ aq. and concentrated. The residue was purified by silica gel column chromatography (20% EtOAc/hexane) to give **BP3** in 990 mg, 21% yield as a white powder; mp. 125 °C (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (broad d, 2H), 7.08–7.35 (m, 26H), 7.79–7.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, some of the peaks overlapped) δ 117.7, 118.1, 124.1 (2C), 127.5, 128.4, 128.5 (3C), 128.7, 131.5, 131.6, 133.6 (2C), 133.8 (2C), 153.5; ^{31}P NMR (202 MHz, $CDCl_3$) δ –4.8 (s); IR (cm^{-1}, CH_2Cl_2) 3523, 3054, 1734, 1514, 1269, 897; $[\alpha]^{34}_D$ = –127.6 (c = 1.02, $CHCl_3$); HRMS (FAB, positive) *m/z* calcd. for $C_{44}H_{32}O_2P_2$ $[M]^+$, 654.1878; found 654.1870.

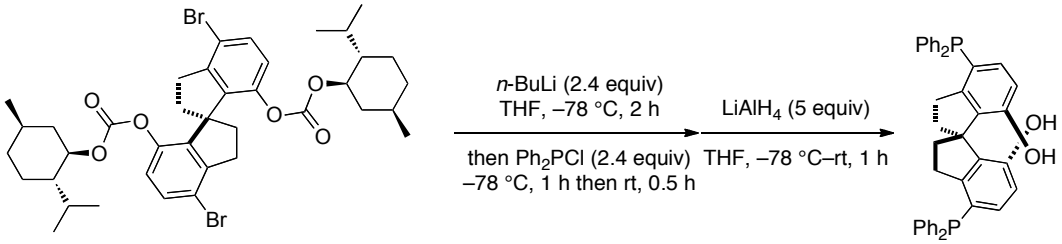
Synthesis of SP1



SP1, 25%

To a suspension mixture of MOM-protected (*S*)-SPINOL[4] (275mg, 0.81 mmol) in ether (15 mL) was added *n*-BuLi (1.60 M, 2.0 mmol, 2.4 equiv) at room temperature. After 3 h stirring, at ambient conditions, THF (10 mL) was added. The orange solution with some precipitates was stirred further for 1 h. Then Ph_2PCl (2.0 mmol, 2.4 equiv) was added at 0 °C. After stirring at room temperature for 30 min, Sat. NH_4Cl aq. (1 mL) was added. Concentration under vacuum gave a residue, which was filtered through a pad of silica gel with AcOEt. Concentration gave a white solid, which was treated with a few drops of conc. HCl aq. in refluxing MeOH for 3 h. Concentration gave the residue, which was passed through a pad of silica gel with CH_2Cl_2. Concentration and purification by silica gel column chromatography gave **SP1** in 124 mg, 0.2 mmol, 25% yield; white powder; mp. 83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22–2.36 (m, 4H), 2.93–3.07 (m, 4H), 5.70 (broad s, 2H), 6.73–6.79 (m, 4H), 7.24–7.35 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.1, 37.6, 58.2, 117.7 (2C), 119.7, 119.8, 128.3, 128.4, 128.5 (2C), 128.6, 128.8, 132.3, 133.0, 133.2, 133.5, 133.7, 134.3, 135.8, 135.9 (3C), 147.9, 155.3, 155.5; ^{31}P NMR (202 MHz, $CDCl_3$) δ –24.7 (s); IR (cm^{-1}, CH_2Cl_2) 3515, 2950, 1434, 1419, 1261, 809; $[\alpha]^{28.2}_D$ = –5.0 (c = 1.09, $CHCl_3$); HRMS (FAB, positive) *m/z* calcd. for $C_{41}H_{35}O_2P_2$ $[M + H]^+$, 621.2107; found 621.2118.

Synthesis of SP2



SP2, 58%

To a solution of (*S*)-Br_2-SPINOLate[5] (8.7 mmol) in THF (200 mL) was added *n*-BuLi (21 mmol, 1.59 M in hexane) dropwise at –78 °C. After stirring at the temperature for 2 h, Ph_2PCl (21 mmol) was added at –78 °C. The mixture was stirred at –78 °C

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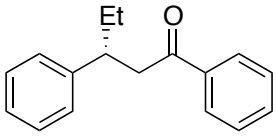
[3] Yang, L.; Yang, F.; Lan, J.; Gao, G.; You, J.; Su, X. *Org. Biomol. Chem.* **2011**, *9*, 2618.
[4] Yang, Y.; Zhu, S.-F.; Duan, H.-F.; Zhou, C.-Y.; Wang, L.-X.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2007**, *129*, 2248.
[5] Birman, V. B.; Rheingold, A. L.; Lam, K.-C.; *Tetrahedron: Asymm.* **1999**, *10*, 125.

for 1 h and then room temperature for 0.5 h. The mixture was treated with a minimal amount of H_2O and concentrated. The residue was passed through a pad of silica gel with 5% EtOAc/hexane. The volatiles were removed under vacuo to give a crude product, which was treated with $LiAlH_4$ (44 mmol) in THF at –78 °C. After stirring at room temperature for 1 h, the mixture was treated with H_2O carefully at 0 °C. The resulting mixture was passed through a pad of silica gel. The volatiles were removed under vacuo to give a residue. A plenty of hexane was added and placed at –78 °C to form white powder. The filtration gave a white powder. The mother liquor was concentrated and placed at –78 °C to form second white powder. The combined yield of **SP2** was 58%; white powder; mp. 111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14–2.25 (m, 4H), 2.73–2.82 (m, 2H), 3.09–3.14 (m, 2H), 4.83 (broad s, 2H), 6.61–6.72 (m, 4H), 7.26–6.36 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.1, 31.2, 57.6, 115.1 (2C), 124.7, 124.8, 128.5 (2C), 128.6 (2C), 128.7, 130.7 (2C), 133.6 (2C), 133.8 (2C), 134.3, 136.4, 136.5, 136.6, 136.7, 150.3, 150.6, 153.7; ^{31}P NMR (202 MHz, $CDCl_3$) δ –14.4 (s); IR (cm^{-1}, CH_2Cl_2) 3532, 1581, 1471, 1205, 823; $[\alpha]^{28.3}_{D}$ = 47.6 (c = 1.06, $CHCl_3$); HRMS (FAB, positive) *m/z* calcd. for $C_{41}H_{34}O_2P_2$, 620.2034; found 620.2034.

3-3. Products[6]



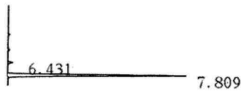
(*R*)-1,3-diphenylpentan-1-one (2a); $[\alpha]^{24.3}_{D}$ = –3.18 (c = 1.38, $CHCl_3$); HPLC (CHIRALPAK AD-H, Daicel, 4.6 x 250 mm, hexane/IPA = 95/5, 1.0 mL/min, 254 nm), t_r (major) = 6.0 min, t_r (minor) = 7.2 min.

Chiral HPLC: (*S*)-2a (90% ee) with SP1

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	2	6.089	187693	19268			95.2249
	4	7.327	9412	826			4.7751
		TOTAL	197105	20094			100

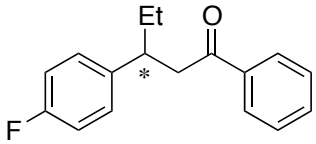
Chiral HPLC: (*R*)-2a (95% ee) with SP2



** CALCULATION REPORT **

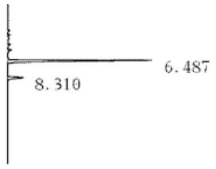
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	3	6.431	10270	1035			2.3123
	5	7.809	433887	36611			97.6877
		TOTAL	444157	37646			100

(–)-3-(4-fluorophenyl)-1-phenylpentan-1-one (2b)



$[\alpha]^{26.3}_{D}$ = –1.95 (c = 1.31, $CHCl_3$); HPLC (CHIRALPAK AD-H, Daicel, 4.6 x 250 mm, hexane/IPA = 95/5, 1.0 mL/min, 254 nm), t_r = 6.3 min, t_r = 8.0 min.

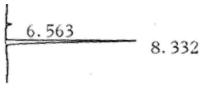
Chiral HPLC: (+)-2b (75% ee) with SP1



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	6	6.487	124221	14147			87.4274
	10	8.31	17864	1595			12.5726
		TOTAL	142085	15742			100

Chiral HPLC: (–)-2b (94% ee) with SP2

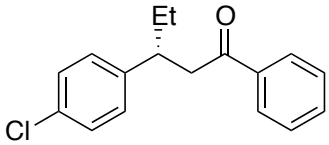


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	6.563	10782	1005			3.189
	3	8.332	327320	24713			96.811
		TOTAL	338102	25717			100

[6] We already reported the physical properties of products: Endo, K. Ogawa, M.; Shibata, T. *Angew. Chem. Int. Ed.* **2010**, *49*, 2410.

(*R*)-3-(4-chlorophenyl)-1-phenylpentan-1-one (2c)



$[\alpha]^{26.4}_{D}$ = +2.1 (c = 1.78, $CHCl_3$); HPLC (CHIRALPAK AD-H, Daicel, 4.6 x 250 mm, hexane/IPA = 95/5, 0.5 mL/min, 254 nm), t_r = 6.3 min, t_r = 8.6 min.

Chiral HPLC: (*S*)-2c (85% ee) with SP1

** CALCULATION REPORT **

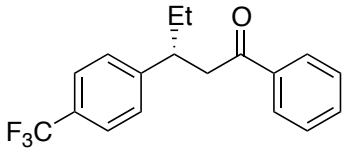
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	16	6.488	33288	3712			92.4712
	19	9.005	2710	227			7.5288
		TOTAL	35998	3939			100

Chiral HPLC: (*R*)-2c (95% ee) with SP2

** CALCULATION REPORT **

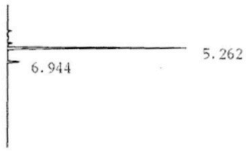
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	3	6.131	10270	1035			2.3123
	5	7.809	433887	36611			97.6877
		TOTAL	444157	37646			100

(*R*)-1-phenyl-3-(4-(trifluoromethyl)phenyl)pentan-1-one (2d)



$[\alpha]^{18.0}_{D}$ = +7.76 (c = 1.39, $CHCl_3$); HPLC (CHIRALPAK AD-H, Daicel, 4.6 x 250 mm, hexane/IPA = 95/5, 0.5 mL/min, 254 nm), t_r = 5.2 min, t_r = 6.7 min.

Chiral HPLC: (*S*)-2d (84% ee) with SP1



** CALCULATION REPORT **

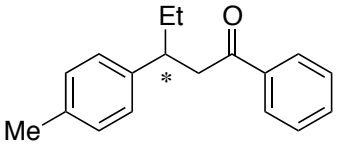
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	3	5.262	75302	9916			92.1785
	5	6.944	6390	656			7.8215
		TOTAL	81691	10571			100

Chiral HPLC: (*R*)-2d (92% ee) with SP2

** CALCULATION REPORT **

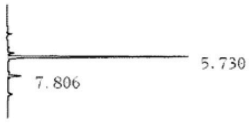
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	10	5.265	43416	4983			4.1245
	13	6.937	1009214	88342			95.8755
		TOTAL	1052630	93325			100

(–)-1-phenyl-3-(*p*-tolyl)pentan-1-one (2e)



$[\alpha]^{24.6}_{D}$ = –6.31 (c = 1.33, $CHCl_3$); HPLC (CHIRALPAK AD-H, Daicel, 4.6 x 250 mm, hexane/IPA = 95/5, 1.0 mL/min, 254 nm), t_r = 5.6 min, t_r = 7.5 min.

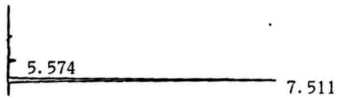
Chiral HPLC: (+)-2e (83% ee) with SP1



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	14	5.73	70975	8750			91.6646
	19	7.806	6454	612			8.3354
		TOTAL	77429	9362			100

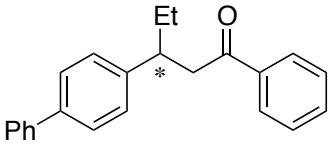
Chiral HPLC: (–)-2e (96% ee) with SP2



** CALCULATION REPORT **

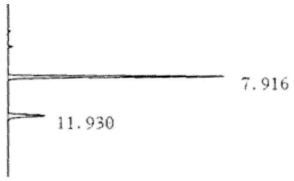
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	2	5.574	5980	644			2.0404
	5	7.511	287095	24379			97.9596
		TOTAL	293075	25022			100

(+)-3-([1,1'-biphenyl]-4-yl)-1-phenylpentan-1-one (2f)



$[\alpha]^{25.3}_{D}$ = –3.96 (c = 1.23, $CHCl_3$); HPLC (CHIRALPAK AD-H, Daicel, 4.6 x 250 mm, hexane/IPA = 95/5, 1.0 mL/min, 254 nm), t_r = 7.6 min, t_r = 10.9 min.

Chiral HPLC: (–)-2f (59% ee) with SP1



** CALCULATION REPORT **

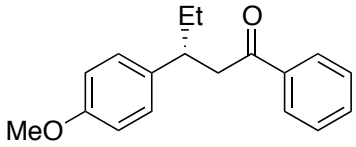
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	10	7.916	222052	20161			79.3531
	16	11.93	57776	3455			20.6469
		TOTAL	279827	23616			100

Chiral HPLC: (+)-2f (94% ee) with SP2

** CALCULATION REPORT **

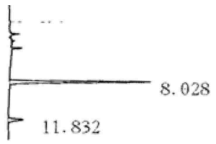
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	4	7.844	70455	5613			3.1929
	7	11.671	2136150	114291			96.8071
		TOTAL	2206604	119904			100

(*R*)-3-(4-methoxyphenyl)-1-phenylpentan-1-one (2g)



$[\alpha]^{25.1}_{D}$ = –5.78 (c = 2.1, $CHCl_3$); HPLC (CHIRALPAK AD-H, Daicel, 4.6 x 250 mm, hexane/IPA = 95/5, 1.0 mL/min, 254 nm), t_r (major) = 7.8 min, t_r (minor) = 11.4 min.

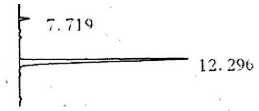
Chiral HPLC: (*S*)-2g (73% ee) with SP1



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	15	8.028	34860	3201			86.6299
	18	11.832	5380	344			13.3701
		TOTAL	40240	3545			100

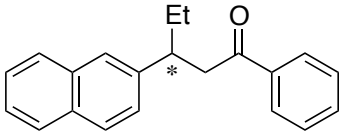
Chiral HPLC: (*R*)-2g (93% ee) with SP2



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	4	7.719	2911	256			3.5781
	12	12.296	78454	4084			96.4219
		TOTAL	81365	4340			100

(+)-3-(naphthalen-2-yl)-1-phenylpentan-1-one (2h)



$[\alpha]^{26.2}_{D}$ = +5.4 (c = 2.1, $CHCl_3$); HPLC (CHIRALPAK AD-H, Daicel, 4.6 x 250 mm, hexane/IPA = 95/5, 1.0 mL/min, 254 nm), t_r = 7.6 min, t_r = 9.5 min.

Chiral HPLC: (–)-2h (76% ee) with SP1

** CALCULATION REPORT **

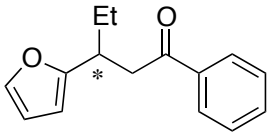
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	15	7.691	1353428	127077			87.9606	
	18	9.559	185248	14275			12.0394	
		TOTAL	1538675	141352			100	

Chiral HPLC: (+)-2h (94% ee) with SP2

** CALCULATION REPORT **

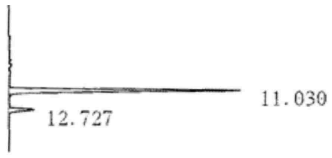
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	4	7.883	22166	1733	V		3.2034
	6	9.867	669777	43677			96.7966
		TOTAL	691943	45410			100

(+)-3-(furan-2-yl)-1-phenylpentan-1-one (2i)



$[\alpha]^{25.6}_{D}$ (90% *ee*) = +0.28 (c = 1.47, $CHCl_3$); HPLC (CHIRALPAK AD-H, Daicel, 4.6 x 250 mm, hexane/IPA = 95/5, 0.5 mL/min, 254 nm), t_r = 11 min, t_r = 12.7 min.

Chiral HPLC: (–)-2i (79% ee) with SP1



** CALCULATION REPORT **

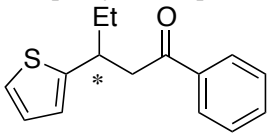
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	2	11.03	1078210	74942	V		89.3233
	3	12.727	128877	8159			10.6767
		TOTAL	1207087	83100			100

Chiral HPLC: (+)-2i (90% ee) with SP2

** CALCULATION REPORT **

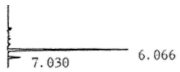
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	2	11.018	13712	850			4.8903
	4	12.737	266679	14657			95.1096
		TOTAL	280391	15507			100

(–)-1-phenyl-3-(thiophen-2-yl)pentan-1-one (2j)



$[\alpha]^{24.2}_{D}$ = –7.47 (c = 1.06, $CHCl_3$); HPLC (CHIRALPAK AD-H, Daicel, 4.6 x 250 mm, hexane/IPA = 95/5, 1 mL/min, 254 nm), t_r = 6 min, t_r = 7 min.

Chiral HPLC: (+)-2j (78% ee) with SP1



** CALCULATION REPORT **

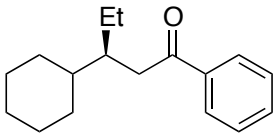
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	11	6.066	57196	7132			88.7778
	13	7.03	7230	725			11.2222
		TOTAL	64426	7856			100

Chiral HPLC: (–)-2j (90% ee) with SP2

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	2	6.311	17189	1732			5.3496
	3	7.386	304113	26639			94.6503
		TOTAL	321302	28371			100

(*R*)-3-cyclohexyl-1-phenylpentan-1-one (2k)



$[\alpha]^{24.2}_{D}$ = +3.53 (c = 1.79, $CHCl_3$); HPLC (CHIRALPAK AD-H, Daicel, 4.6 x 250 mm, hexane/IPA = 98/2, 0.7 mL/min, 254 nm), t_r (major) = 7.8 min, t_r (minor) = 8.6 min.

Chiral HPLC: (S)-2k (91% ee) with SP1

** CALCULATION REPORT **

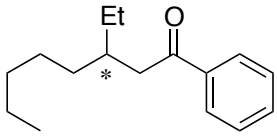
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	8.635	805627	67335			95.5547
	2	9.345	37478	3080			4.4453
		TOTAL	843105	70414			100

Chiral HPLC: (*R*)-2k (99% ee) with SP2

** CALCULATION REPORT **

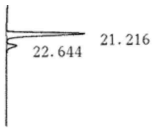
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	8.641	633321	44766			99.6139
	3	9.69	2455	182			0.3861
		TOTAL	635775	44948			100

(–)-3-ethyl-1-phenyloctan-1-one (2l)



$[\alpha]^{23.4}_{D}$ = –2.43 (c = 1.76, $CHCl_3$); HPLC (CHIRALPAK AD-H x 2, Daicel, 4.6 x 250 mm, hexane/IPA = 99.9/0.1, 1.0 mL/min, 254 nm), t_r = 23.4 min, t_r = 24.2 min.

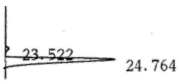
Chiral HPLC: (+)-2l (75% ee) with SP1



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	21.216	427663	16939			87.6375
	2	22.644	60328	2206			12.3625
		TOTAL	487991	19145			100

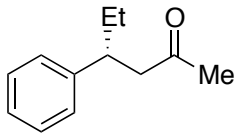
Chiral HPLC: (–)-2l (96% ee) with SP2



** CALCULATION REPORT **

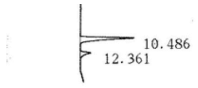
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	8	23.522	18792	777			2.2837
	9	24.764	804068	23180			97.7163
		TOTAL	822860	23956			100

(*R*)-4-phenylhexan-2-one (2m)



$[\alpha]^{26.7}_{D}$ = –33.3 (c = 0.95, $CHCl_3$); chiral HPLC (CHIRALPAK OJ-H, Daicel, 4.6 x 250 mm, hexane/IPA = 98/2, 1.0 mL/min, 254 nm), t_r = 10.4 min, t_r = 12.2 min.

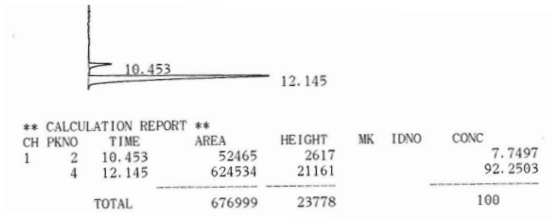
Chiral HPLC: (*S*)-2m (64% ee) with SP1



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	18	10.486	64761	3091			81.9192
	20	12.361	14294	603			18.0808
		TOTAL	79055	3694			100

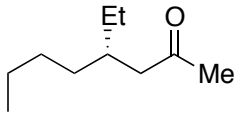
Chiral HPLC: (*R*)-2m (85% ee) with SP2



** CALCULATION REPORT **

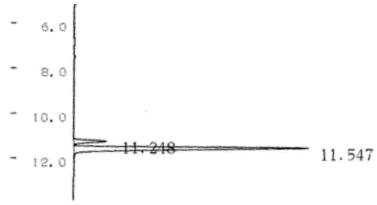
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	2	10.453	52465	2617			7.7497
	4	12.145	624534	21161			92.2503
		TOTAL	676999	23778			100

(*S*)-4-ethyloctan-2-one (2n)



$[\alpha]^{21.5}_{D}$ = –1.80 (c = 1.41, $CHCl_3$); chiral GC (RT-bDEXsm, 0.25 mm x 30 m, 90 °C, 30 mL/min), t_r = 11.2 min, t_r = 11.6 min.

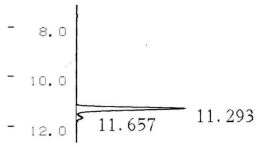
Chiral GC: (*R*)-2n (78% ee) with SP1



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	11.248	48022	6688			11.2079
	2	11.547	380446	47727	V		88.7921
		TOTAL	428468	54415			100

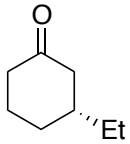
Chiral GC: (*S*)-2n (88% ee) with SP2



** CALCULATION REPORT **

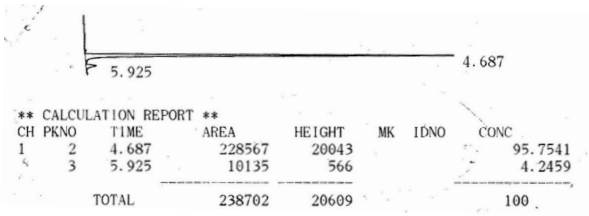
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	11.293	338771	40657			93.9777
	2	11.657	21709	2293	V		6.0223
		TOTAL	360480	42949			100

(*R*)-3-ethylcyclohexanone (2o)

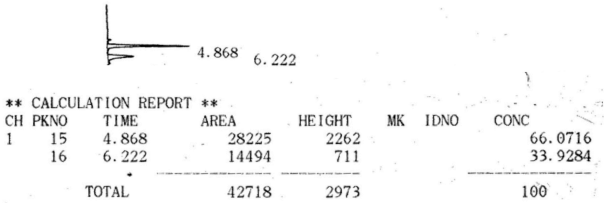


$[\alpha]^{22.5}_{D}$ = +2.8 (c = 0.51, $CHCl_3$); HPLC (CHIRALPAK AD-H, Daicel, 4.6 x 250 mm, hexane/IPA = 99.5/0.5, 1.0 mL/min, 254 nm), t_r = 4.7 min, t_r = 5.9 min.

Chiral GC: (*S*)-2o (92% ee) with SP1

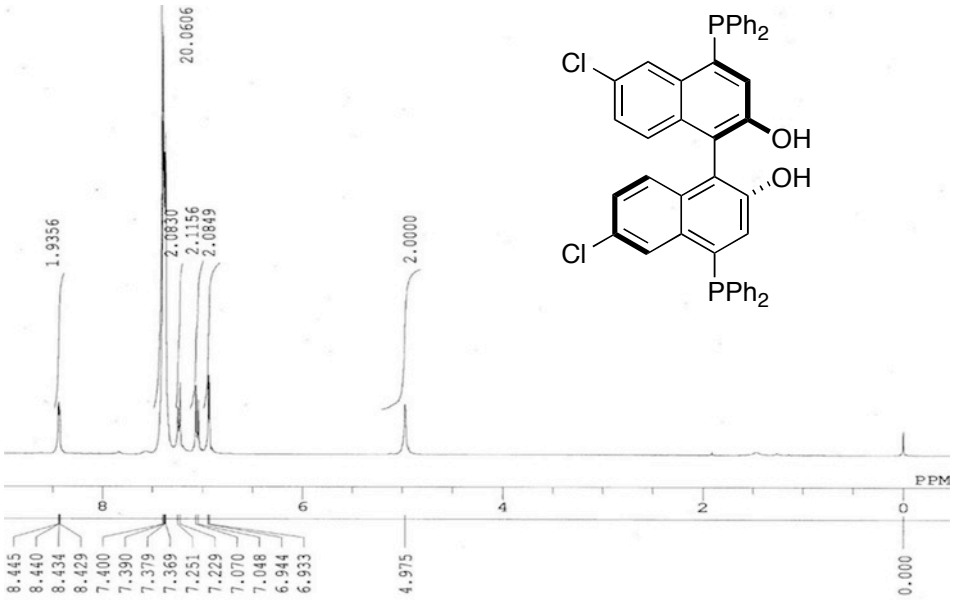


Chiral GC: (*R*)-2o (33% ee) with SP2

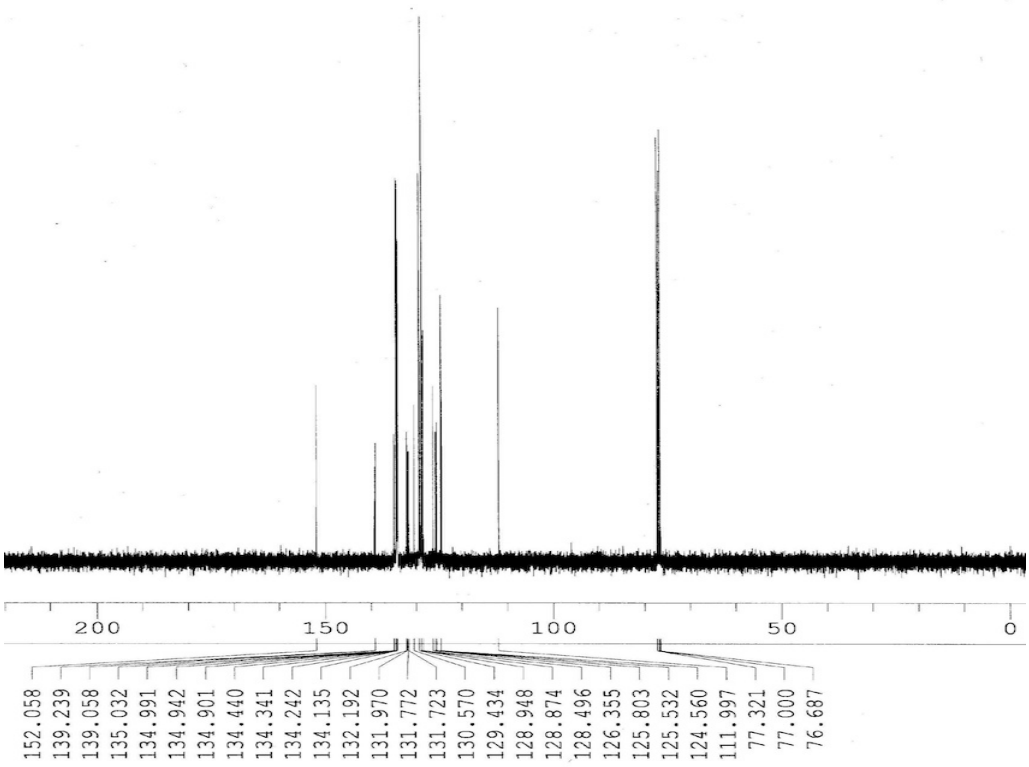


4. NMR Spectra of New Compounds

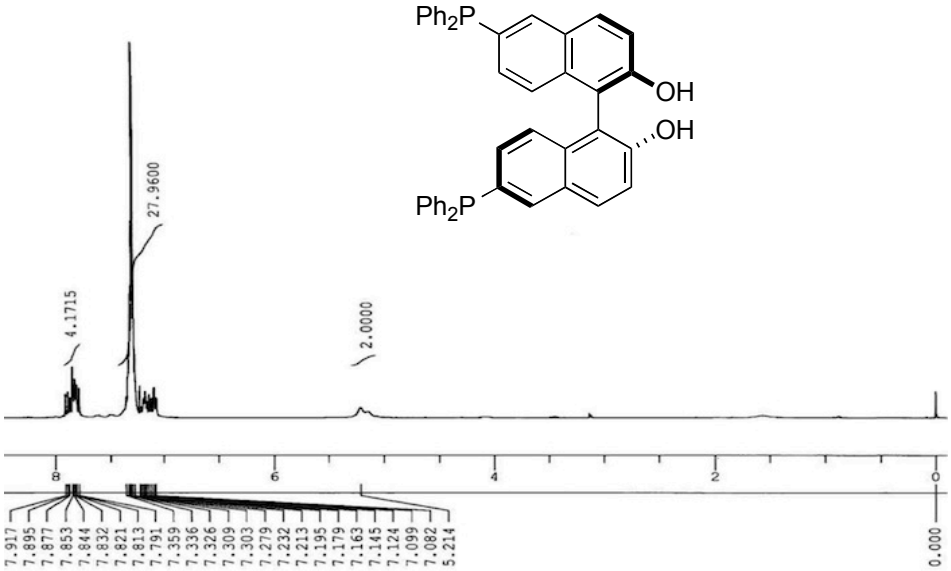
^{1}H NMR (400 MHz) BP2



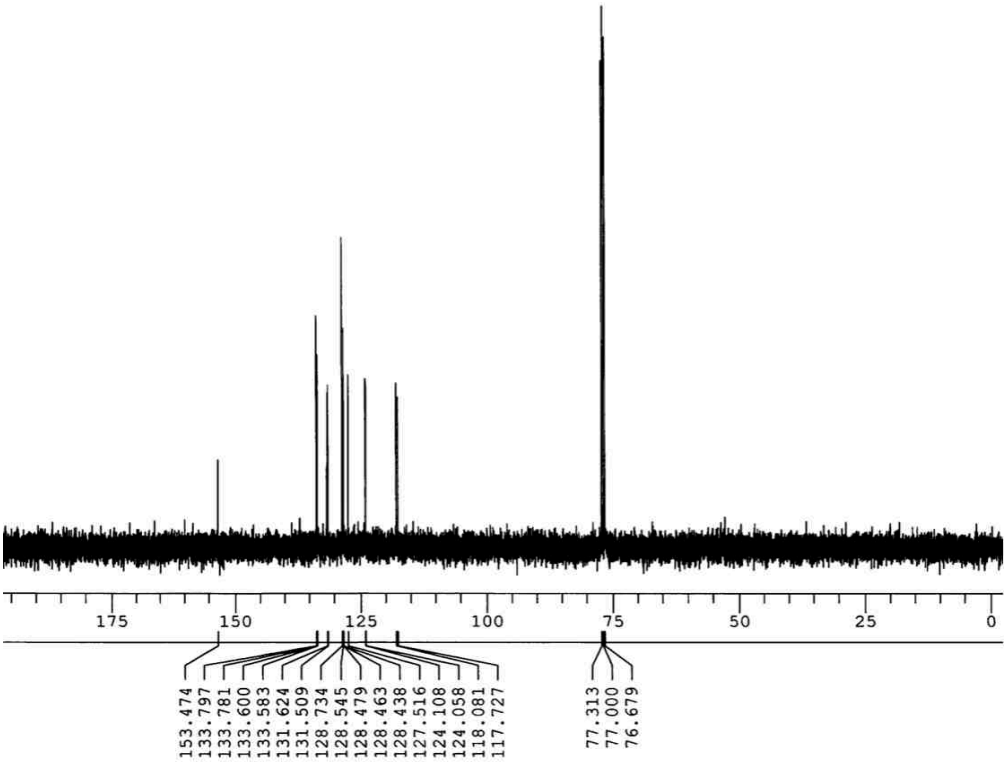
^{13}C NMR (100 MHz) BP2



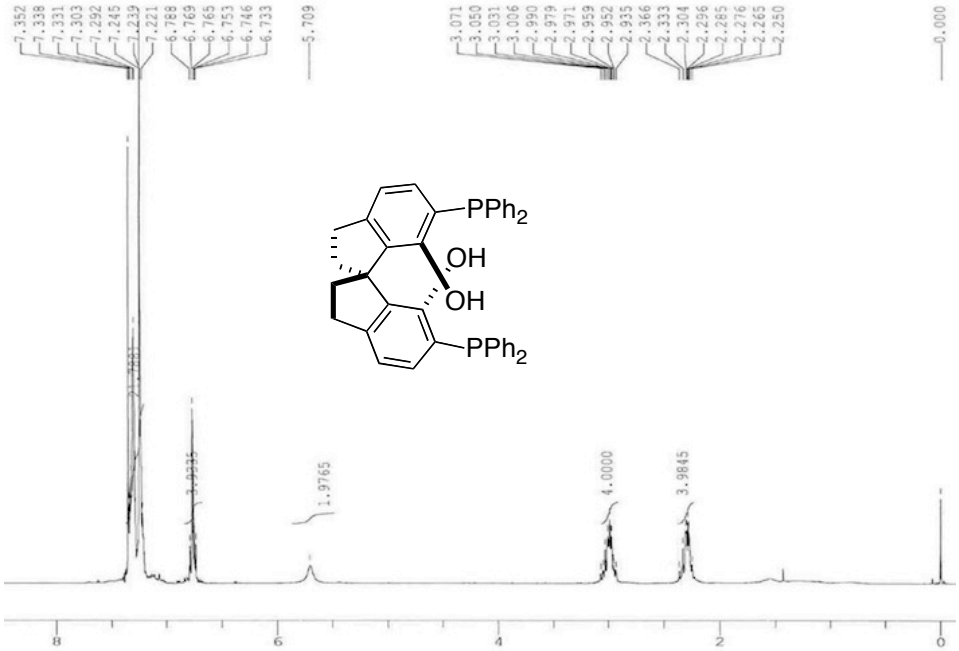
^{1}H NMR (400 MHz) BP3



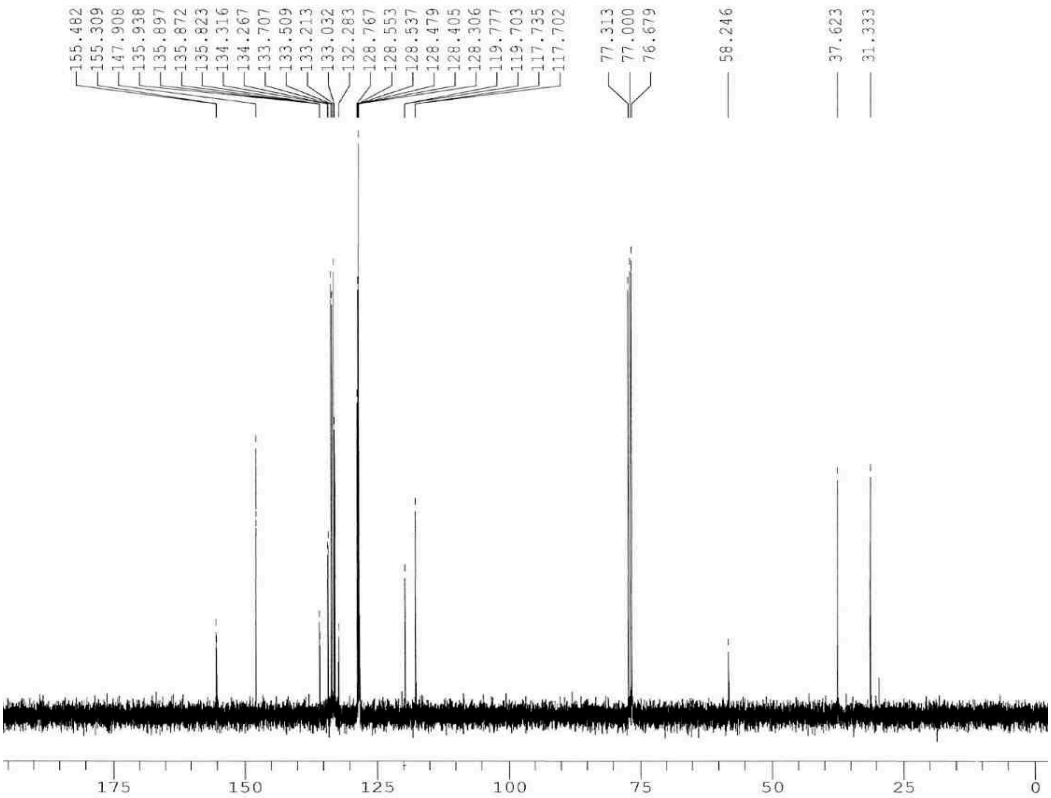
^{13}C NMR (100 MHz) BP3



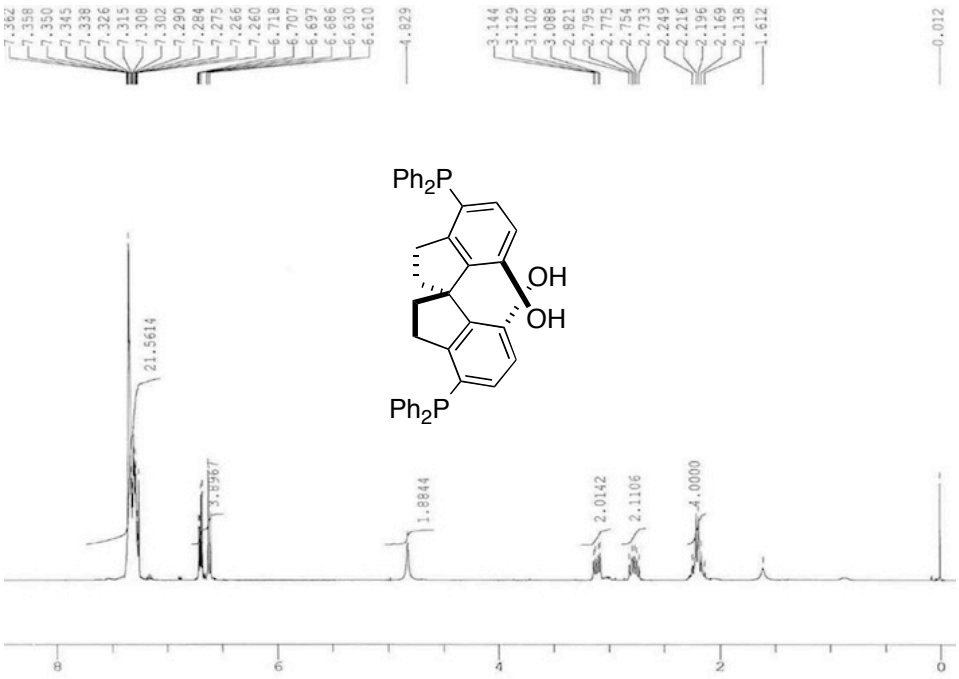
^{1}H NMR (400 MHz) SP1



^{13}C NMR (100 MHz) SP1



^{1}H NMR (400 MHz) SP2



^{13}C NMR (100 MHz) SP2