Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis and application of novel P-chiral monophosphorus ligands

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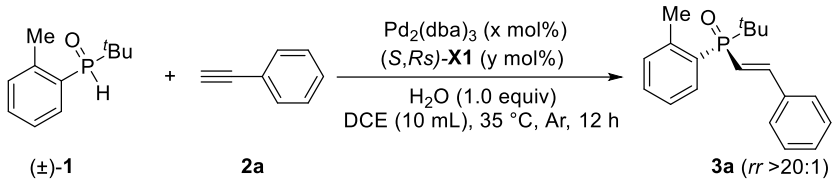
Contents

1. General Information

All reactions were carried out under an atmosphere of nitrogen in flame-dried sealed tube with magnetic stirring. The $[\alpha]_D$ was recorded using PolAAr 3005 High Accuracy Polarimeter. ^{1}H NMR spectra, ^{13}C NMR spectra, ^{19}F NMR spectra and ^{31}P NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. All signals are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR) as the internal standard. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). HRMS spectra were recorded on GCQTOF 7200 and Bruker McriOTOF11. SAESI-MS spectra were recorded on a Thermo TSQ Quantum Access triplequadrupole mass spectrometer (Thermo Fisher Scientific, Waltham, MA) equipped with a home-made SAESI ion source in positive mode. The instrumentation used for the crystal measurement was D8 VENTURE MetalJet. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Toluene and CH_2Cl_2 was freshly distilled from CaH_2; THF, mesitylene, xylene and dioxane were freshly distilled from sodium metal prior to use; EtOAc (AR grade), DCE (AR grade), CH_3OH (AR grade) and *n*-hexane (anhydrous) were purchased from Sinopharm. Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with CH_3OH/ ethyl acetate or petroleum ether/ethyl acetate. The substrates (±)**1** [1], and **X1**[3] were synthesized according to published procedures, the others are commercially available. The spectral data of the substrates were consisted with that reported in the literature. The enantionmeric excesses of the products were determined by chiral stationary phase Shimadzu HPLC using a Chiralpak AD-H, IC, OD-H, OZ-H.

2. Optimization of reaction conditions

2.1 Table S1. Investigate the effect of the amount of palladium source on the reaction

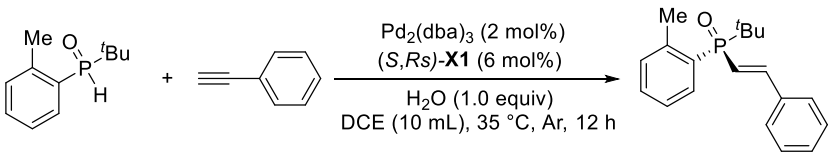


(±)-**1** **2a** **3a** (*rr* >20:1)

Entry	x	y	Yield [%][a]	ee [%][b]
1	5	15	84	98
2	4	12	81	96
3	3	9	79	97
4	2	6	72	97
5	1	3	60	97
6	2	5	74	90
7	2	4	69	85

Reaction conditions: (±)-**1** (2 mmol, 2.0 equiv.), **2a** (1 mmol, 1.0 equiv.), H_2O (1.0 equiv), DCE (10 mL), under argon atmosphere, 12 h. [a] Isolated yield, the ratio of regioselectivities (3:3' > 20:1 in all conditions) were determined by ^1H NMR analysis of the crude product [b] Enantiomeric excesses were determined by HPLC on chiral stationary phases.

2.2 Table S2. Investigate the effect of amount of substrates on the reaction

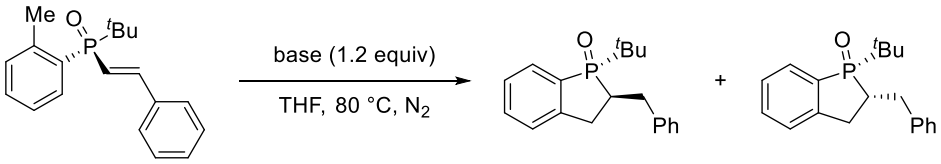


(±)-**1** **2a** **3a** (*rr* >20:1)

Entry	**1** (mmol)	**2a** (mmol)	Yield [%][a]	ee [%][b]
1	1.8	1	76	98
2	1.9	1	82	98
3	2.0	1	72	97
4	2.1	1	68	97
5	2.2	1	61	97
6	15.2	8	80	98

Reaction conditions: $Pd_2(dba)_3$ (2 mol%), (*S,Rs*)-**X1** (6 mol%), H_2O (1.0 equiv), DCE (10 mL), under argon atmosphere, 12 h. [a] Isolated yield, the ratio of regioselectivities (3:3' > 20:1 in all conditions) were determined by ^1H NMR analysis of the crude product. [b] Enantiomeric excesses were determined by HPLC on chiral stationary phases.

2.3 Table S3. Investigate the effect of bases on the reaction



3a
6 mmol

4a **4a'**

Entry	Base	Yield (4a+4a') [%][a]	dr[b]
1	^{t}BuOLi	56	1:1
2	^{t}BuONa	61	2:1
3	^{t}BuOK	65	2:1
4	CH_3ONa	ND[c]	/
5	NaOH	ND[c]	/
6	KOH	ND[c]	/

Reaction conditions: **3a** (6 mmol, 1.0 equiv.), THF (30 mL), under Nitrogen atmosphere, 24 h. [a] Isolated yield. [b] dr were determined by ^1H NMR analysis of the crude product. [c] ND = Not detected.

3. General procedure

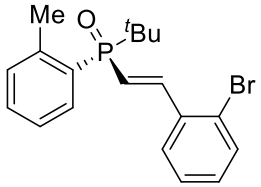
General procedure A： A sealed tube with a magnetic stir bar was charged with $Pd_2(dba)_3$ (0.16 mmol), (*S*, R_S)-**X1** (0.48 mmol), racemic SPO (15.2 mmol), alkyne (8.0 mmol) and water (8.0 mmol). Anhydrous DCE (80.0 ml) was then added as solvent. The reaction tube was sealed, frozen by liquid nitrogen and evacuated under vacuum and backfilled with argon three times through a three-way stopcock. The reaction tube was sealed and allowed to stir at 35°C for 24-36 h. On completion (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **3**.[1] Product **3** could be further elevated to enantiomerically pure level *via* recrystallization from Hexane/DCM.

General procedure B: A sealed tube equipped with a stir bar under argon atmosphere was charged with 3 (>99% ee, 4.0 mmol) and ^{t}BuOK (1.2 equiv). THF (40.0 mL) was added as solvent and then the vial was capped. The reaction mixture was stirred at 80 °C for 20-36 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with CH_3OH/ethyl acetate as eluent to afford the adduct **4** and **4'** as a pair of diastereomers.[1]

General procedure C： To a solution of 4 (2.0 mmol, 1 equiv), triethylamine (20.0 mmol, 10 equiv) in toluene (20 mL) at rt was added trichlorosilane (10.0 mmol, 5 equiv). The mixture was heated to 80 °C and stirred under nitrogen for 12 h. To the mixture at 0 °C was added BH_3·THF complex (1.0 M, 26.0 mmol), and the resulting mixture was stirred at rt for about 2 h. Water (30.0 mL) was then added and the aqueous layer was extracted three times with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and removed in vacuo and the residue was purified by flash column chromatography on silica gel using hexanes/ethyl acetate as eluent to provide the title phosphine borane adducts **5**.[2]

Date of product **3a**、**4a**、**4a'** was matched of the reported literature.[1]

3.1 (*R*,*E*)-(2-bromostyryl)(tert-butyl)(o-tolyl)phosphine oxide (3b)



Prepared according to general procedure A from **2b** (8.0 mmol), racemic SPO **1** (15.2 mmol), after a flash column chromatography (hexanes: EA = 1:1) afforded the product **3b**. After recrystallization from Hexane/DCM, product **3b** could be obtained as a colorless solid (1.68 g, 56% yield) with 99% *ee*. M.p.: 170.1-171.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03-7.95 (m, 1H), 7.67-7.60 (m, 2H), 7.59-7.54 (m, 1H), 7.45-7.32 (m, 2H), 7.32-7.18 (m, 3H), 7.01 (dd, J = 23.7, 17.1 Hz, 1H), 2.83 (s, 3H), 1.22 (d, J = 15.0 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.2 (d, $J_{C\text{-}P}$ = 3.7 Hz), 144.0 (d, $J_{C\text{-}P}$ = 7.2 Hz), 136.1 (d, $J_{C\text{-}P}$ = 16.0 Hz), 133.4, 132.9 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.5 (d, $J_{C\text{-}P}$ = 10.8 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.5, 128.9, 130.0, 127.5, 124.7 (d, $J_{C\text{-}P}$ = 11.4 Hz), 124.5, 121.2 (d, $J_{C\text{-}P}$ = 90.9 Hz), 34.4 (d, $J_{C\text{-}P}$ = 72.6 Hz), 24.6, 22.2 (d, $J_{C\text{-}P}$ = 2.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 41.8. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{19}H_{22}BrOP$: 376.0592, found 376.0589. HPLC (AD-H, 2-propanol /n-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) tR = 15.4 min (major), 12.6 min (minor). $[\alpha]_D^{20}$ = 54.8 (*c* = 0.5, $CHCl_3$).

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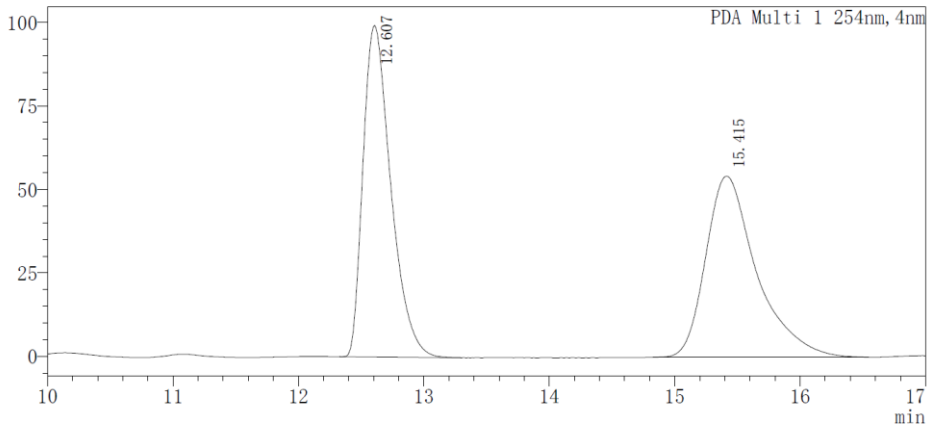

<Peak Table>
PDA Ch1 254nm

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1	12.607	99296	64.658	1529785	50.025
2	15.415	54274	35.342	1528248	49.975
Total		153570	100.000	3058033	100.000

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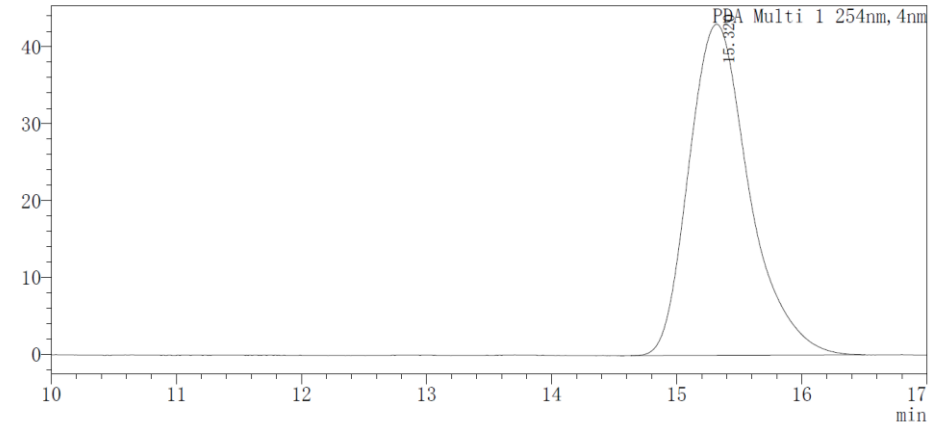

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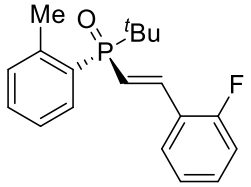
PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	15.320	43039	100.000	1443016	100.000
总计		43039	100.000	1443016	100.000

Total

3.2 (*R*,*E*)-tert-butyl(2-fluorostyryl)(o-tolyl)phosphine oxide (3c)



Prepared according to general procedure A from **2c** (8.0 mmol), racemic SPO **1** (15.2 mmol), after a flash column chromatography (hexanes: EA = 1:1) afforded the product

3c. After recrystallization from Hexane/DCM, product **3c** could be obtained as a colorless solid (1.29 g, 51% yield) with 99% *ee*. M.p.: 191.1-191.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 17.6 Hz, 1H), 7.60-7.51 (m, 2H), 7.42-7.31 (m, 2H), 7.29-7.20 (m, 3H), 7.19-7.15 (m, 1H), 7.12 (dd, *J* = 10.7, 8.7 Hz, 1H), 2.82 (s, 3H), 1.21 (d, *J* = 15.0 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.2 (d, J_{C-F} = 253.5 Hz), 143.8 (d, J_{C-P} = 7.2 Hz), 141.7 (d, J_{C-P} = 3.0 Hz), 133.0 (d, J_{C-P} = 10.4 Hz), 132.4 (d, J_{C-P} = 10.9 Hz), 131.1 (d, J_{C-P} = 2.5 Hz), 130.9 (d, J_{C-P} = 8.8 Hz), 130.0 (d, J_{C-F} = 3.2 Hz), 128.8 (d, J_{C-P} = 91.5 Hz), 124.7 (d, J_{C-P} = 11.5 Hz), 124.3 (d, J_{C-F} = 3.5 Hz), 121.4 (d, J_{C-F} = 8.5 Hz), 120.5 (d, J_{C-F} = 8.2 Hz), 116.2 (d, J_{C-F} = 22.0 Hz), 34.3 (d, J_{C-P} = 72.2 Hz), 24.5, 22.2 (d, J_{C-P} = 2.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 42.0; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.4. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{19}H_{22}FOP$: 316.1392, found 316.1386. HPLC (AD-H, 2-propanol /n-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) tR = 18.3 min (major), 15.2 min (minor). $[\alpha]_D^{20}$ = 138.2 (*c* = 0.5, $CHCl_3$).

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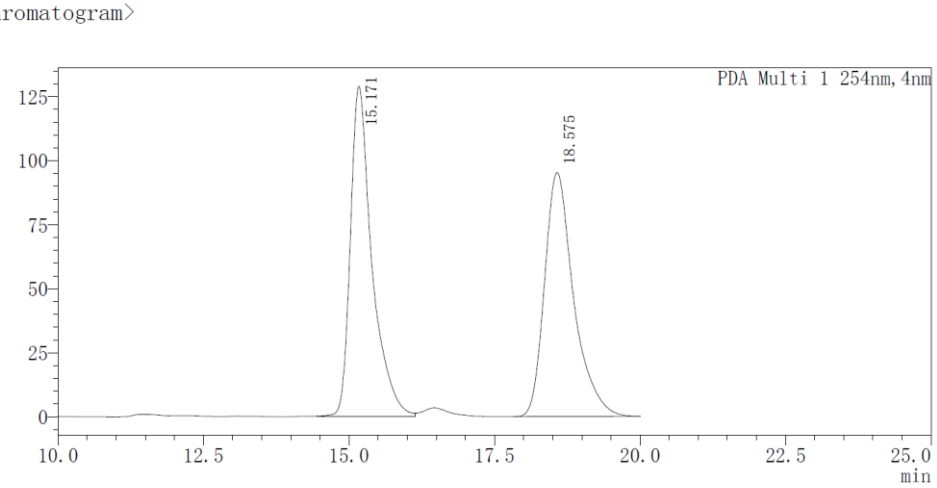

<Peak Table>

PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	15.171	128971	57.504	3328168	50.121
2	18.575	95309	42.496	3312109	49.879
Total		224281	100.000	6640277	100.000

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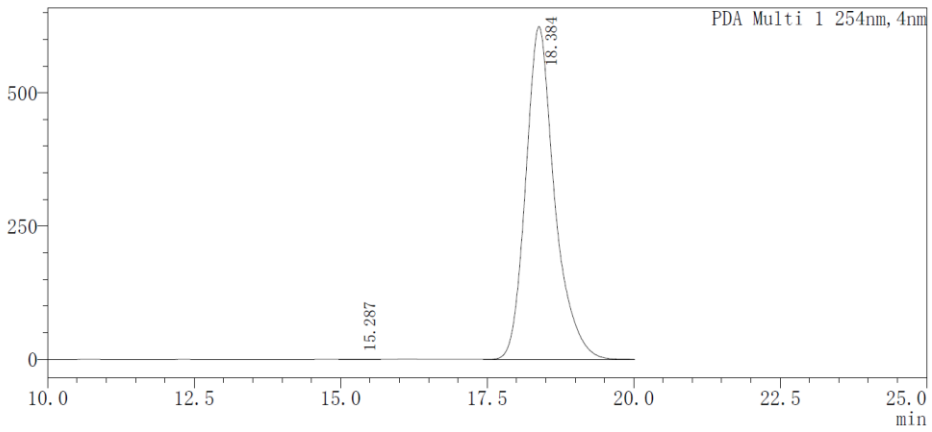
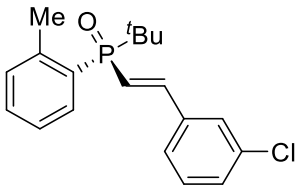


<Peak Table>
PDA Ch1 254nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	15.287	350	0.056	10002	0.047
2	18.384	624120	99.944	21470515	99.953
Total		624470	100.000	21480517	100.000

3.3 (*R*,*E*)-tert-butyl(3-chlorostyryl)(o-tolyl)phosphine oxide (3d)



Prepared according to general procedure A from **2d** (8.0 mmol), racemic SPO **1** (15.2 mmol), after a flash column chromatography (hexanes: EA = 1:1) afforded the product **3d**. After recrystallization from Hexane/DCM, product **3d** could be obtained as a colorless solid (1.51 g, 57% yield) with 99% *ee*. M.p.: 160.0-160.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.49 (m, 3H), 7.39 (dd, *J* = 11.6, 5.0 Hz, 2H), 7.35-7.30 (m, 2H), 7.29 -7.20 (m, 2H), 7.05 (dd, *J* = 23.6, 17.2 Hz, 1H), 2.80 (s, 3H), 1.19 (d, *J* = 15.1 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 143.8 (d, $J_{C\text{-}P}$ = 7.1 Hz), 137.4 (d, $J_{C\text{-}P}$ = 16.1 Hz), 134.8, 133.0 (d, $J_{C\text{-}P}$ = 10.8 Hz), 132.5 (d, $J_{C\text{-}P}$ = 10.8 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.1, 129.6, 129.0, 128.1, 127.0, 126.3, 124.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 34.5 (d, $J_{C\text{-}P}$ = 72.7 Hz), 24.5, 22.2 (d, $J_{C\text{-}P}$ = 2.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 42.3-41.9 (m). **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{19}H_{22}ClOP$: 332.1097, found 332.1092. HPLC (IC, 2-propanol /n-hexane = 20/80, flow rate = 1.0 mL/min, l = 254 nm) tR = 7.9 min (major), 10.3 min (minor). $[\alpha]_D^{20}$ = 169.5 (*c* = 0.2, $CHCl_3$).

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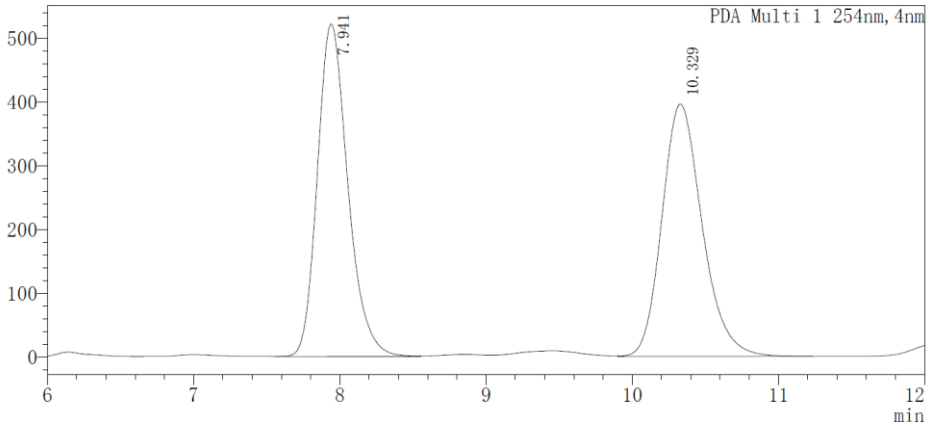

<Peak Table>
PDA Ch1 254nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	7.941	521342	56.855	7566935	49.969
2	10.329	395618	43.145	7576405	50.031
Total		916960	100.000	15143340	100.000

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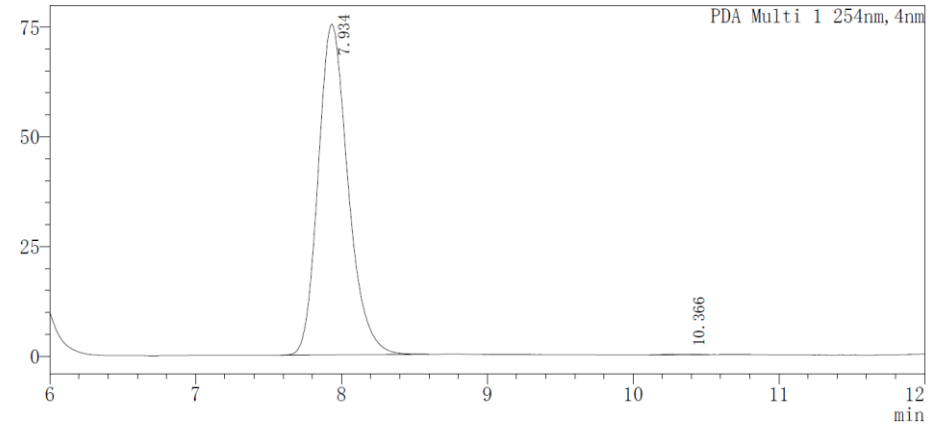
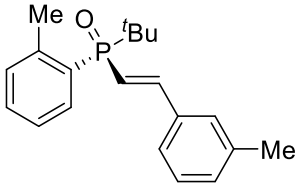


<Peak Table>
PDA Ch1 254nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	7.934	75372	99.828	1074850	99.836
2	10.366	130	0.172	1764	0.164
Total		75501	100.000	1076614	100.000

3.4 (*R*,*E*)-tert-butyl(3-methylstyryl)(o-tolyl)phosphine oxide (3e)



Prepared according to general procedure A from **2e** (8.0 mmol), racemic SPO **1** (15.2 mmol), after a flash column chromatography (hexanes: EA = 1:1) afforded the product

3e. After recrystallization from Hexane/DCM, product **3e** could be obtained as a colorless solid (1.50 g, 60% yield) with 99% *ee*. M.p.: 180.0-180.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (t, *J* = 17.2 Hz, 1H), 7.57 (dd, *J* = 11.5, 7.9 Hz, 1H), 7.43-7.34 (m, 3H), 7.30-7.25 (m, 4H), 7.01 (dd, *J* = 24.4, 17.2 Hz, 1H), 2.82 (s, 3H), 2.39 (s, 3H), 1.20 (d, *J* = 15.0 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.6 (d, $J_{C\text{-}P}$ = 2.5 Hz), 143.7 (d, $J_{C\text{-}P}$ = 7.0 Hz), 138.4, 135.5 (d, $J_{C\text{-}P}$ = 15.9 Hz), 133.0 (d, $J_{C\text{-}P}$ = 10.6 Hz), 132.3 (d, $J_{C\text{-}P}$ = 10.7 Hz), 131.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.5, 128.9 (d, $J_{C\text{-}P}$ = 91.1 Hz), 128.6, 128.0, 124.9, 124.6 (d, $J_{C\text{-}P}$ = 11.4 Hz), 116.5 (d, $J_{C\text{-}P}$ = 93.6 Hz), 34.3 (d, $J_{C\text{-}P}$ = 72.7 Hz), 24.5, 22.2 (d, $J_{C\text{-}P}$ = 2.2 Hz), 21.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 42.5-42.1 (m). **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{20}H_{25}OP$: 312.1643, found 312.1638. HPLC (IC, 2-propanol /n-hexane = 25/75, flow rate = 1.0 mL/min, l = 254 nm) tR = 7.4 min (major), 9.7 min (minor). $[\alpha]_D^{20}$ = 154.5 (*c* = 0.5, $CHCl_3$).

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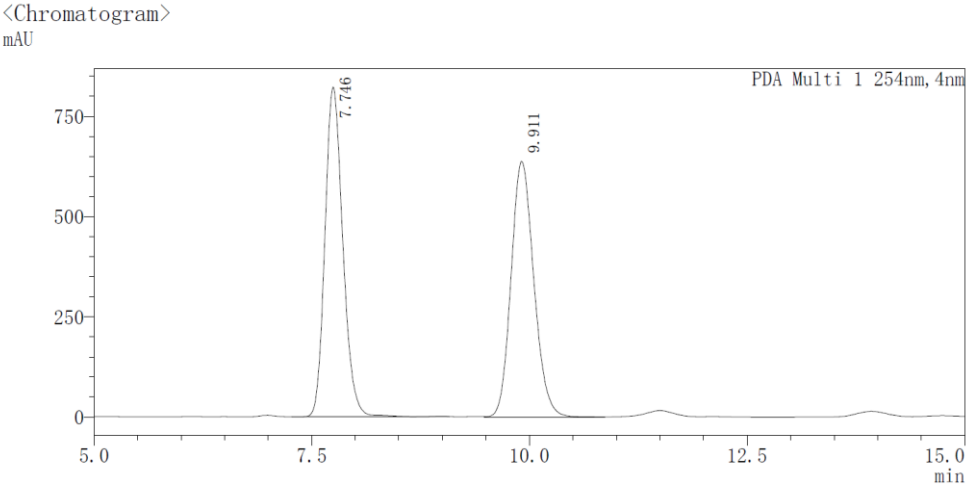

<Peak Table>

PDA Ch1 254nm

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1	7.746	821920	56.295	11740361	50.237
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Total		1460035	100.000	23369975	100.000

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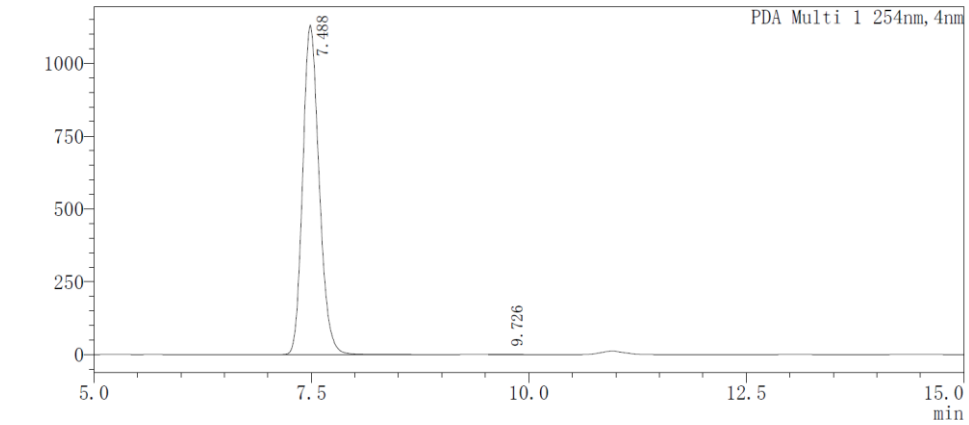

<Peak Table>
PDA Ch1 254nm

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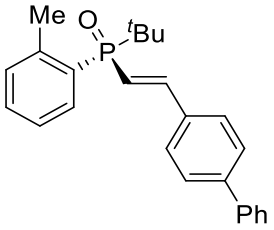
1	7.488	1130402	99.935	14862908	99.919
2	9.726	738	0.065	12073	0.081
Total		1131140	100.000	14874982	100.000

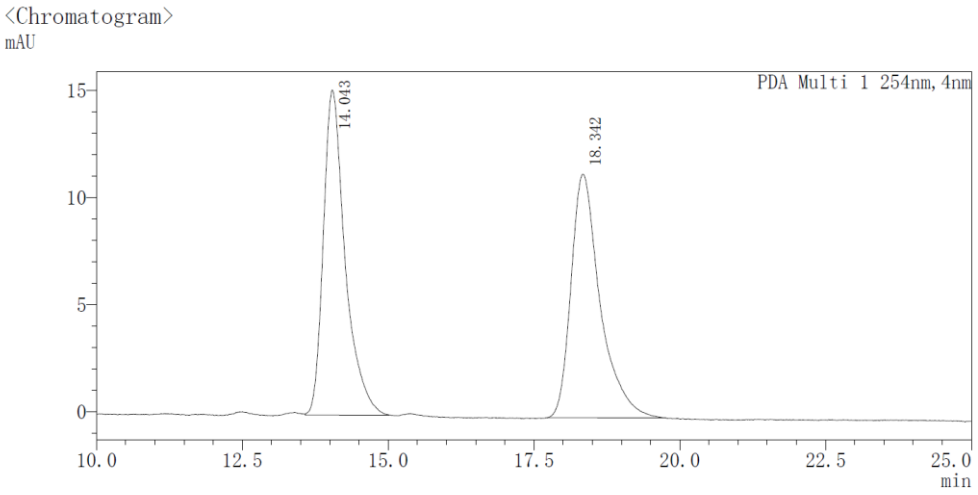
3.5 (*R*,*E*)-(2-([1,1'-biphenyl]-4-yl)vinyl)(tert-butyl)(o-tolyl)phosphine oxide (3f)



Prepared according to general procedure A from **2f** (8.0 mmol), racemic SPO **1** (15.2 mmol), after a flash column chromatography (hexanes: EA = 1:1) afforded the product **3f**. After recrystallization from Hexane/DCM, product **3f** could be obtained as a yellow solid (1.41 g, 47% yield) with 99% *ee*. M.p.: 145.0-145.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (t, *J* = 17.2 Hz, 1H), 7.70-7.54 (m, 7H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 6.3 Hz, 2H), 7.33-7.21 (m, 2H), 7.09 (dd, *J* = 24.2, 17.2 Hz, 1H), 2.84 (s, 3H), 1.23 (d, *J* = 15.0 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 143.7 (d, $J_{C\text{-}P}$ = 7.1 Hz), 142.4, 140.2, 134.5 (d, $J_{C\text{-}P}$ = 16.1 Hz), 133.0 (d, $J_{C\text{-}P}$ = 10.7 Hz), 132.4 (d, $J_{C\text{-}P}$ = 10.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.5 Hz), 128.8 (d, $J_{C\text{-}P}$ = 91.4 Hz), 128.8, 128.0, 127.7, 127.4, 127.0, 124.7 (d, $J_{C\text{-}P}$ = 11.5 Hz), 116.7 (d, $J_{C\text{-}P}$ = 93.4 Hz), 34.4 (d, $J_{C\text{-}P}$ = 72.7 Hz), 24.5, 22.2 (d, $J_{C\text{-}P}$ = 2.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 42.9-42.1 (m). **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{25}H_{27}OP$: 374.1800, found 374.1794. HPLC (AD-H, 2-propanol /n-hexane = 15/85, flow rate = 1.0 mL/min, l = 254 nm) tR = 14.0 min

(major), 18.3 min (minor). $[\alpha]_D^{20}$ = 187.8 (*c* = 0.5, $CHCl_3$).

<Chromatogram>

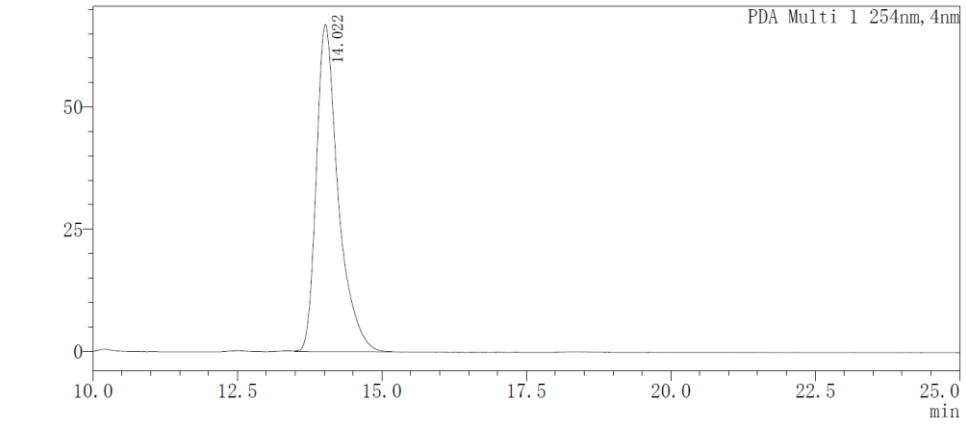


<Peak Table>

PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	14.043	15160	57.143	394566	49.990
2	18.342	11370	42.857	394729	50.010
Total		26530	100.000	789295	100.000

<Chromatogram>



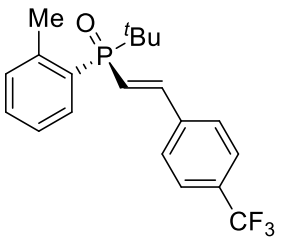
<Peak Table>

PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	14.022	66996	100.000	1768878	100.000
总计		66996	100.000	1768878	100.000

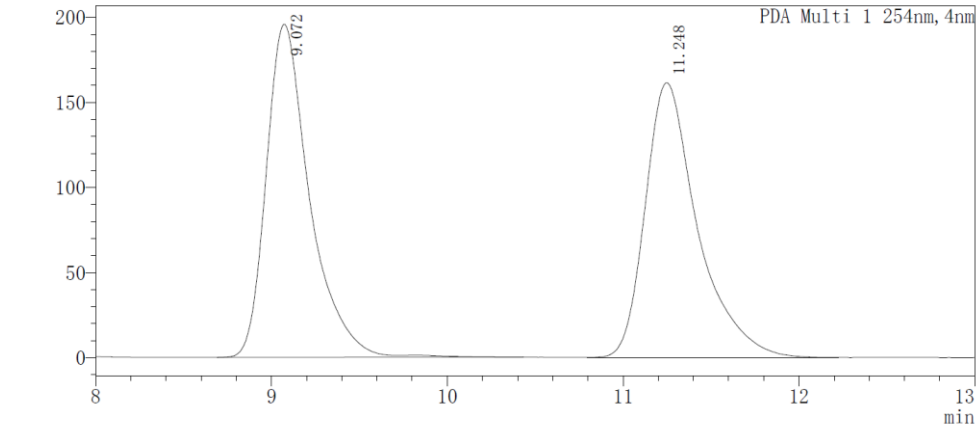
Total

3.6 (*R*,*E*)-tert-butyl(o-tolyl)(4-(trifluoromethyl)styryl)phosphine oxide (3g)



Prepared according to general procedure A from **2g** (8.0 mmol), racemic SPO **1** (15.2 mmol), after a flash column chromatography (hexanes: EA = 1:1) afforded the product **3g**. After recrystallization from Hexane/DCM, product **3g** could be obtained as a colorless solid (1.26 g, 43% yield) with 99% *ee*. M.p.: 156.0-156.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 17.0 Hz, 1H), 7.67 (s, 4H), 7.55 (dd, J = 11.5, 7.9 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.29-7.23 (m, 2H), 7.16 (dd, J = 23.5, 17.2 Hz, 1H), 2.82 (s, 3H), 1.21 (d, J = 15.1 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.9 (d, $J_{C\text{-}P}$ = 2.8 Hz), 143.9 (d, $J_{C\text{-}P}$ = 7.3 Hz), 138.9 (d, $J_{C\text{-}F}$ = 15.9 Hz), 132.7 (d, $J_{C\text{-}P}$ = 10.8 Hz), 132.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.3 (d, $J_{C\text{-}F}$ = 32.3 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 128.4 (d, $J_{C\text{-}P}$ = 91.8 Hz), 127.8, 126.2 (q, $J_{C\text{-}F}$ = 272.7 Hz), 125.8 (q, $J_{C\text{-}P}$= 3.8 Hz), 124.8 (d, $J_{C\text{-}F}$ = 11.3 Hz), 120.3 (d, $J_{C\text{-}P}$ = 90.7 Hz), 34.4 (d, $J_{C\text{-}P}$ = 72.6 Hz), 24.5, 22.2 (d, $J_{C\text{-}P}$ = 2.5 Hz); **^{31}P NMR** (162 MHz, C_6D_6) δ 41.8; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.8. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{20}H_{22}F_3OP$: 366.1360, found 366.1355. HPLC (AD-H, 2-propanol /n-hexane = 15/85, flow rate = 1.0 mL/min, l = 254 nm) tR = 9.0 min (major), 11.2 min (minor). $[\alpha]_D^{20}$ = 138.3 (c = 0.5, $CHCl_3$).

<Chromatogram>

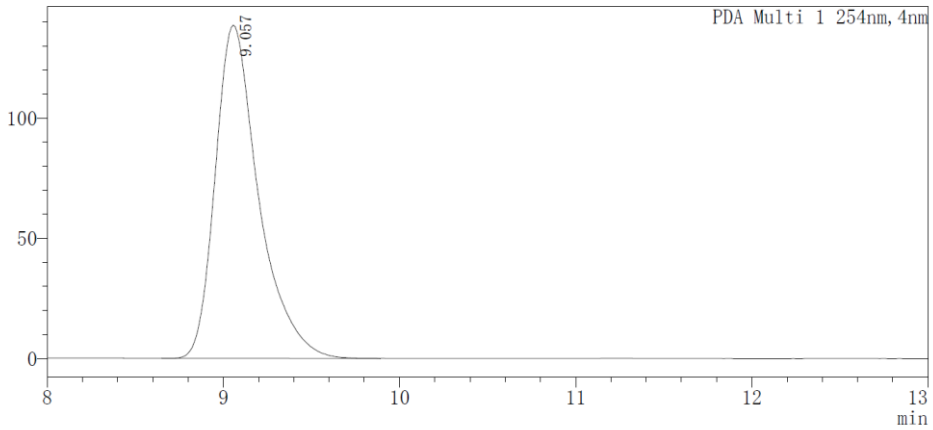


<Peak Table>

PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	9.072	195609	54.806	3365819	50.227
2	11.248	161305	45.194	3335350	49.773
Total		356913	100.000	6701169	100.000

<Chromatogram>
mAU

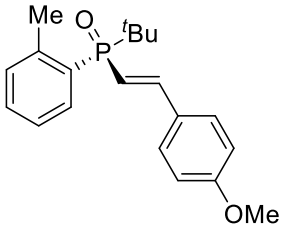


<Peak Table>
PDA Ch1 254nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	9.057	138617	100.000	2380090	100.000
总计		138617	100.000	2380090	100.000

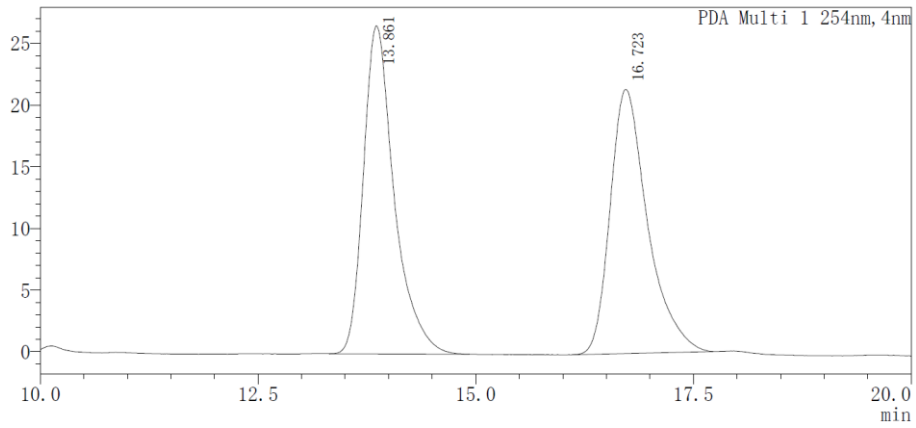
Total

3.7 (*R*,*E*)-tert-butyl(4-methoxystyryl)(o-tolyl)phosphine oxide (3h)



Prepared according to general procedure A from **2h** (8.0 mmol), racemic SPO **1** (15.2 mmol), after a flash column chromatography (hexanes: EA = 1:1) afforded the product **3h**. After recrystallization from Hexane/DCM, product **3h** could be obtained as a colorless solid (1.50 g, 57% yield) with 99% *ee*. M.p.: 127.0-127.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72-7.47 (m, 4H), 7.38 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.31-7.19 (m, 2H), 6.99-6.75 (m, 3H), 3.85 (s, 3H), 2.81 (s, 3H), 1.20 (d, *J* = 14.9 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9, 148.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 143.7 (d, $J_{C\text{-}P}$ = 7.2 Hz), 133.1 (d, $J_{C\text{-}P}$ = 10.4 Hz), 132.4 (d, $J_{C\text{-}P}$ = 10.3 Hz), 131.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 129.7, 129.17, 128.6 (d, $J_{C\text{-}P}$ = 16.1 Hz), 124.7 (d, $J_{C\text{-}P}$ = 11.4 Hz), 114.2, 113.8 (d, $J_{C\text{-}P}$ = 95.3 Hz), 55.4, 34.4 (d, $J_{C\text{-}P}$ = 72.7 Hz), 24.6, 22.3 (d, $J_{C\text{-}P}$ = 2.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 42.9-42.4 (m). **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{20}H_{25}O_2P$: 328.1592, found 328.1584. HPLC (AD-H, 2-propanol /n-hexane = 15/85, flow rate = 1.0 mL/min, l = 254 nm) tR = 13.9 min (major), 16.8 min (minor). $[\alpha]_D^{20}$ = 192.9 (*c* = 0.5, $CHCl_3$).

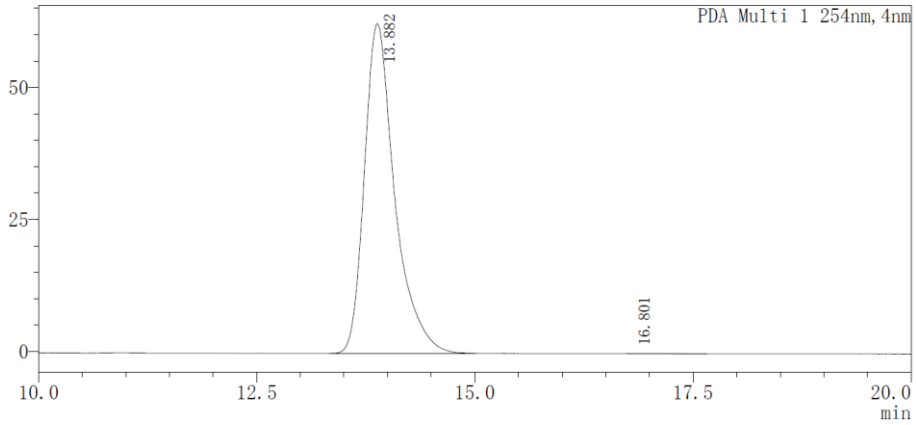
<Chromatogram>
mAU



<Peak Table>
PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	13.861	26602	55.397	655434	50.545
2	16.723	21419	44.603	641295	49.455
Total		48020	100.000	1296729	100.000

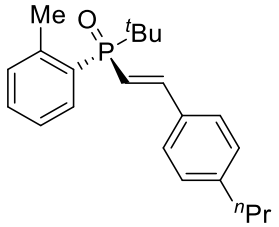
<Chromatogram>
mAU



<Peak Table>
PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	13.882	62397	99.973	1510993	99.990
2	16.801	17	0.027	154	0.010
Total		62414	100.000	1511147	100.000

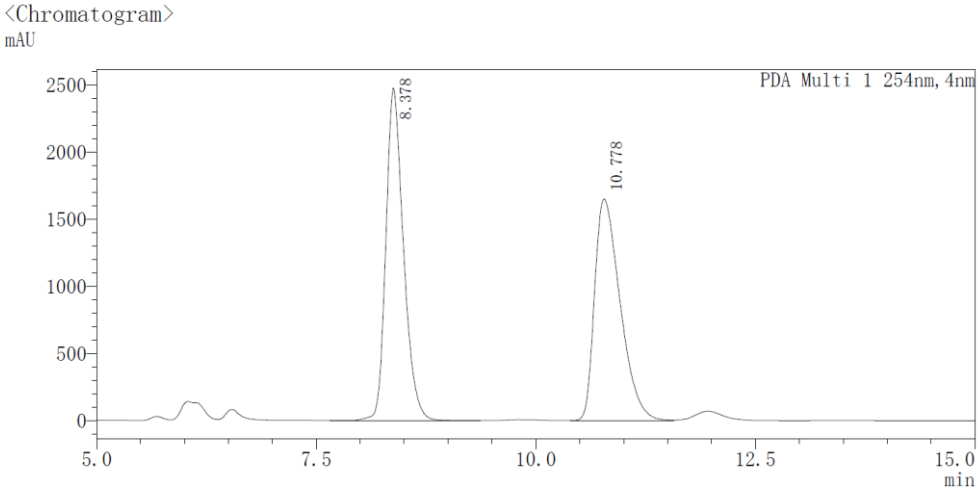
3.8 (*R*,*E*)-tert-butyl(4-propylstyryl)(o-tolyl)phosphine oxide (3i)



Prepared according to general procedure A from **2i** (8.0 mmol), racemic SPO **1** (15.2

mmol), after a flash column chromatography (hexanes: EA = 1:1) afforded the product **3i**. After recrystallization from Hexane/DCM, product **3i** could be obtained as a colorless solid (1.22 g, 45% yield) with 99% *ee*. M.p.: 135.0-135.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.62 (m, 1H), 7.59-7.49 (m, 3H), 7.37-7.35 (m, 1H), 7.28-7.21 (m, 4H), 7.03-6.92 (m, 1H), 2.81 (s, 3H), 2.62 (t, *J* = 7.2 Hz, 2H), 1.66 (dd, *J* = 14.4, 7.1 Hz, 2H), 1.20 (d, *J* = 14.9 Hz, 9H), 0.96 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.5 (d, J_{C-P} = 2.3 Hz), 144.8, 143.8 (d, J_{C-P} = 7.0 Hz), 133.3, 133.1 (d, J_{C-P} = 10.7 Hz), 132.4 (d, J_{C-P} = 10.6 Hz), 131.1 (d, J_{C-P} = 2.5 Hz), 129.1 (d, J_{C-P} = 91.3 Hz), 129.0, 127.6, 124.7 (d, J_{C-P} = 11.4 Hz), 115.5 (d, J_{C-P} = 94.3 Hz), 37.9, 34.4 (d, J_{C-P} = 72.7 Hz), 24.6, 24.4, 22.3, 13.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 42.5 (s). **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{22}H_{29}OP$: 340.1956, found 340.1950. HPLC (AD-H, 2-propanol /n-hexane = 20/80, flow rate = 1.0 mL/min, l = 254 nm) tR = 8.3 min (major), 10.7 min (minor). $[\alpha]_D^{20}$ = 165.6 (*c* = 0.5, $CHCl_3$).

<Chromatogram>

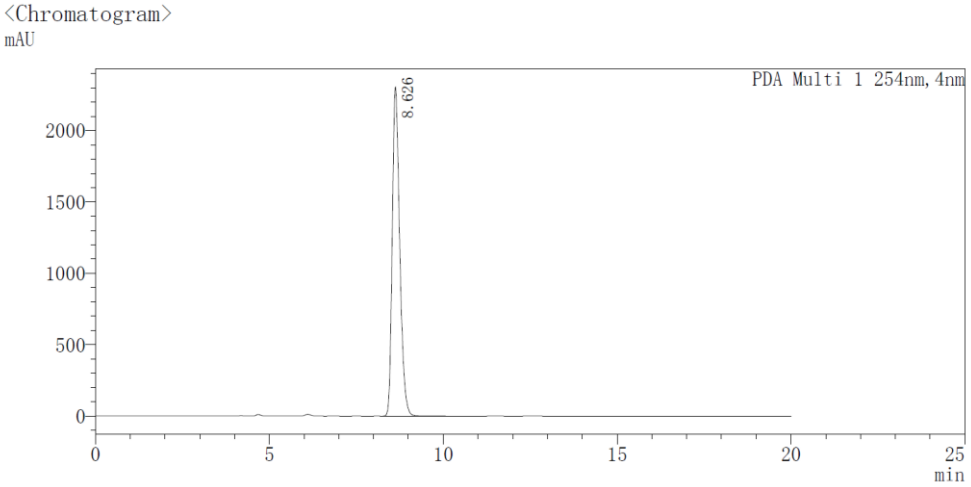


<Peak Table>

PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	8.378	2474725	59.989	34499116	50.754
2	10.778	1650567	40.011	33474176	49.246
Total		4125292	100.000	67973292	100.000

<Chromatogram>

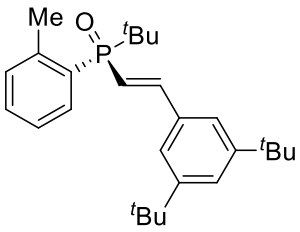


<Peak Table>
PDA Ch1 254nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	8.626	2304455	100.000	34357769	100.000
总计		2304455	100.000	34357769	100.000

Total

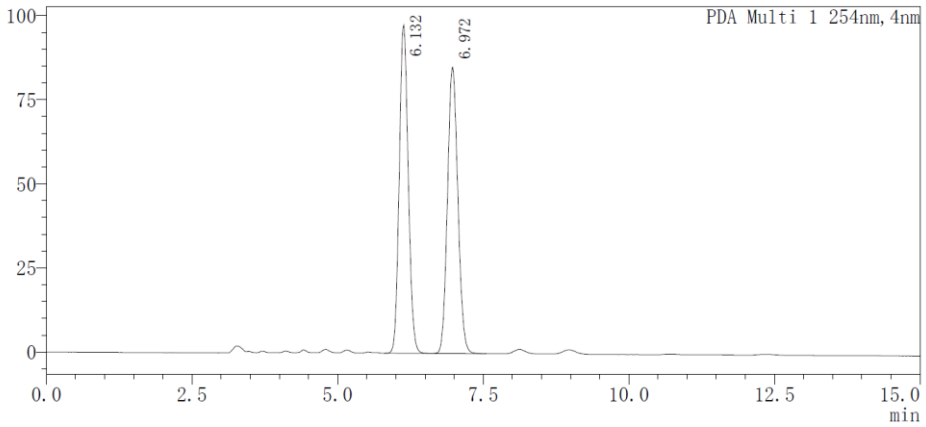
3.9 (*R*,*E*)-tert-butyl(3,5-di-tert-butylstyryl)(o-tolyl)phosphine oxide (3j)



Prepared according to general procedure A from **2j** (8.0 mmol), racemic SPO **1** (15.2 mmol), after a flash column chromatography (hexanes: EA = 1:1) afforded the product **3j**. After recrystallization from Hexane/DCM, product **3j** could be obtained as a colorless solid (2.10 g, 64% yield) with 99% *ee*. M.p.: 138.0-138.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (t, *J* = 17.3 Hz, 1H), 7.58 (ddd, *J* = 11.8, 7.8, 1.4 Hz, 1H), 7.47 (t, *J* = 1.8 Hz, 1H), 7.44-7.37 (m, 3H), 7.28 (q, *J* = 6.0 Hz, 2H), 7.10-6.80 (m, 1H), 2.95-2.71 (m, 3H), 1.37 (s, 18H), 1.22 (d, *J* = 14.9 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.3, 149.7 (d, $J_{C\text{-}P}$ = 2.8 Hz), 143.8 (d, $J_{C\text{-}P}$ = 7.1 Hz), 134.9 (d, $J_{C\text{-}P}$ = 15.5 Hz), 133.1 (d, $J_{C\text{-}P}$ = 10.9 Hz), 132.4 (d, $J_{C\text{-}P}$ = 10.4 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 129.1 (d, $J_{C\text{-}P}$ = 91.3 Hz), 124.8, 124.2, 122.0, 115.6 (d, $J_{C\text{-}P}$ = 93.8 Hz), 34.9, 34.4 (d, $J_{C\text{-}P}$ = 72.7 Hz), 31.4, 24.6, 22.3 (d, $J_{C\text{-}P}$ = 2.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 42.72. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{27}H_{39}OP$: 410.2739, found 410.2732. HPLC (IC, 2-propanol /n-hexane = 20/80, flow rate = 1.0 mL/min, l = 254 nm) tR = 6.1 min (major), 6.9 min

(minor). $[\alpha]_D^{20} = 118.1$ ($c = 0.5$, $CHCl_3$).

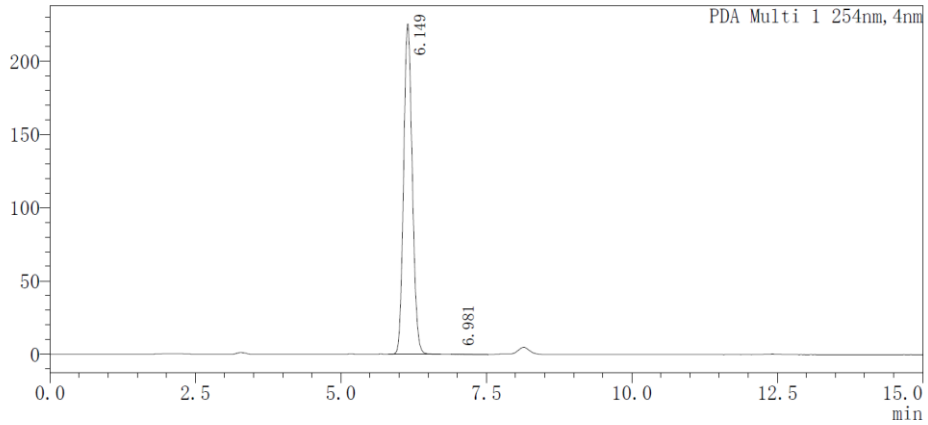
<Chromatogram>
mAU



<Peak Table>
PDA Ch1 254nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	6.132	97582	53.423	1050904	49.842
2	6.972	85078	46.577	1057570	50.158
Total		182660	100.000	2108474	100.000

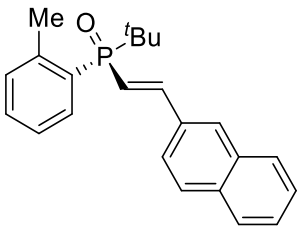
<Chromatogram>
mAU



<Peak Table>
PDA Ch1 254nm

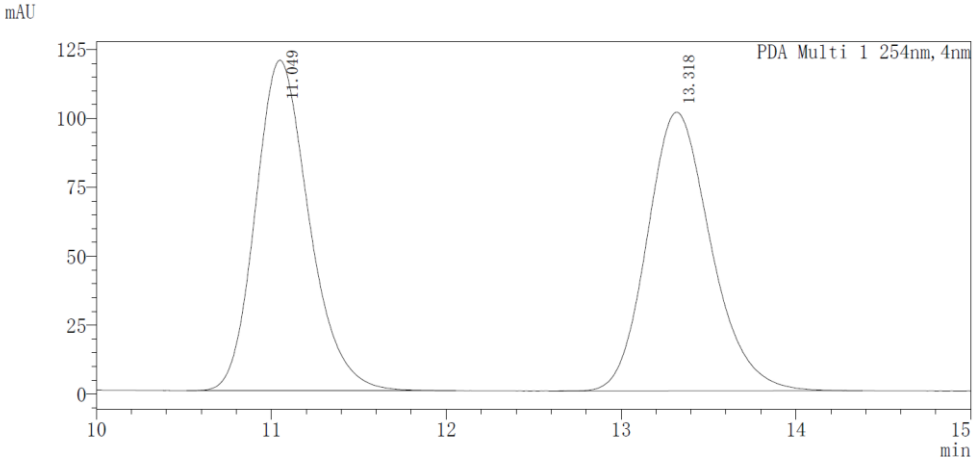
No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	6.149	225383	99.995	2343158	99.999
2	6.981	11	0.005	21	0.001
Total		225394	100.000	2343179	100.000

3.10 (*R*,*E*)-tert-butyl(2-(naphthalen-2-yl)vinyl)(o-tolyl)phosphine oxide (3k)



Prepared according to general procedure A from **2k** (8.0 mmol), racemic SPO **1** (15.2 mmol), after a flash column chromatography (hexanes: EA = 1:1) afforded the product **3k**. After recrystallization from Hexane/DCM, product **3k** could be obtained as a yellow solid (1.53 g, 55% yield) with 99% *ee*. M.p.: 164.0-164.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.92-7.80 (m, 4H), 7.76 (d, J = 8.5 Hz, 1H), 7.62 (dd, J = 11.5, 7.9 Hz, 1H), 7.52 (dd, J = 5.6, 2.7 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.34-7.23 (m, 2H), 7.15 (dd, J = 24.1, 17.2 Hz, 1H), 2.85 (s, 3H), 1.24 (d, J = 15.0 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 143.9 (d, $J_{C\text{-}P}$ = 7.1 Hz), 134.0, 133.4, 133.2, 133.1, 133.0, 132.5 (d, $J_{C\text{-}P}$ = 10.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 129.4, 129.0, 128.6 (d, $J_{C\text{-}P}$ = 4.4 Hz), 127.7, 126.8 (d, $J_{C\text{-}P}$ = 32.7 Hz), 126.3, 124.8 (d, $J_{C\text{-}P}$ = 11.5 Hz), 123.6, 117.1 (d, $J_{C\text{-}P}$ = 93.3 Hz), 34.5 (d, $J_{C\text{-}P}$ = 72.8 Hz), 24.6, 22.3 (d, $J_{C\text{-}P}$ = 2.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 42.5-42.1 (m). **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{23}H_{25}OP$: 348.1643, found 348.1641. HPLC (IC, 2-propanol /n-hexane = 20/80, flow rate = 1.0 mL/min, l = 254 nm) tR = 11.0 min (major), 13.3 min (minor). $[\alpha]_D^{20}$ = 166.9 (c = 0.5, $CHCl_3$).

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	11.049	120025	54.263	2561754	49.969
2	13.318	101168	45.737	2564912	50.031
Total		221193	100.000	5126667	100.000

<Chromatogram>
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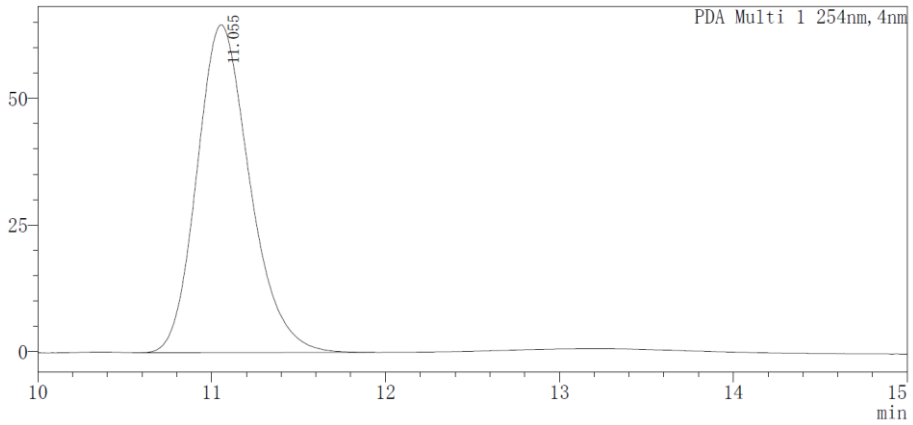
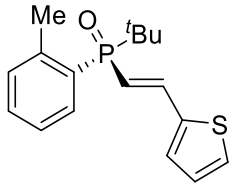


<Peak Table>
PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	11.055	64713	100.000	1369659	100.000
总计		64713	100.000	1369659	100.000

Total

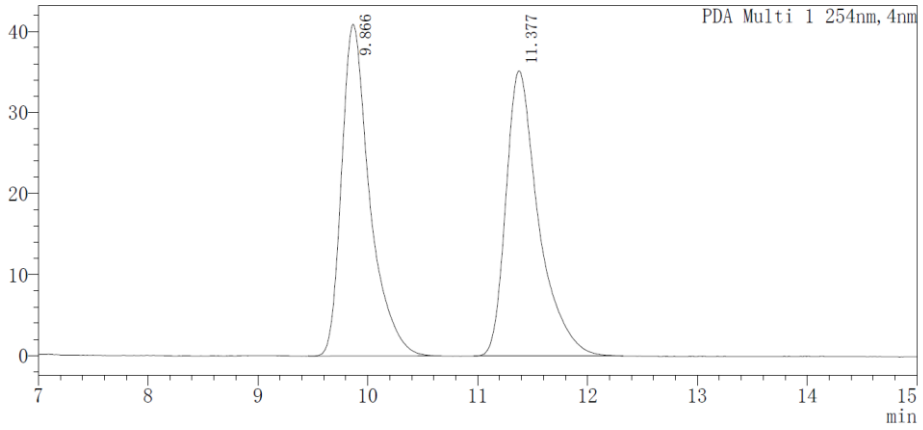
3.11 (*R*,*E*)-tert-butyl(2-(thiophen-2-yl)vinyl)(o-tolyl)phosphine oxide (3l)



Prepared according to general procedure A from **2l** (8.0 mmol), racemic SPO **1** (15.2 mmol), after a flash column chromatography (hexanes: EA = 1:1) afforded the product **3l**. After recrystallization from Hexane/DCM, product **3l** could be obtained as a yellow solid (1.29 g, 53% yield) with 99% *ee*. M.p.: 167.0-167.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (t, *J* = 16.7 Hz, 1H), 7.49 (dd, *J* = 23.2, 12.2 Hz, 1H), 7.41-7.29 (m, 2H), 7.22 (dd, *J* = 30.8, 11.9 Hz, 3H), 7.02 (d, *J* = 3.6 Hz, 1H), 6.87-6.59 (m, 1H), 2.78 (s, 3H), 1.17 (dd, *J* = 15.0, 3.1 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5 (d, $J_{C\text{-}P}$ = 7.1 Hz), 141.2 (d, $J_{C\text{-}P}$ = 18.2 Hz), 140.8, 132.9 (d, $J_{C\text{-}P}$ = 10.7 Hz), 132.3 (d, $J_{C\text{-}P}$ = 10.7 Hz), 131.0 (d, $J_{C\text{-}P}$ = 2.5 Hz), 129.5, 129.1, 128.2, 127.6 (d, $J_{C\text{-}P}$ = 67.4 Hz), 124.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 115.4 (d, $J_{C\text{-}P}$ = 94.3 Hz), 34.3 (d, $J_{C\text{-}P}$ = 72.9 Hz), 24.4, 22.1 (d, $J_{C\text{-}P}$ = 2.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 42.7-42.0 (m). **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{17}H_{21}OPS$: 304.1051, found 304.1047. HPLC (AD-H, 2-propanol /n-hexane = 15/85, flow rate = 1.0 mL/min, l = 254 nm) tR = 9.8 min (major), 11.3 min (minor).

$[\alpha]_D^{20} = 208.1$ ($c = 0.5$, $CHCl_3$).

<Chromatogram>
mAU



<Peak Table>
PDA Ch1 254nm

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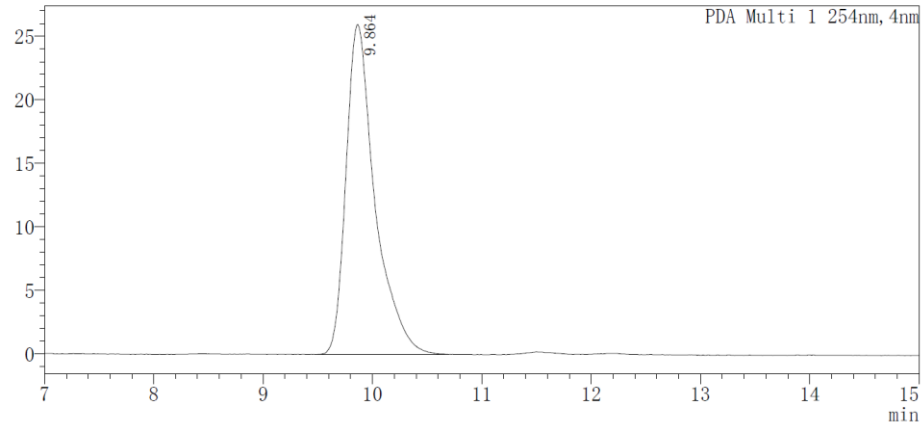
2	11.377	35191	46.223	728393	49.971
Total		76133	100.000	1457622	100.000

<Chromatogram>
mAU

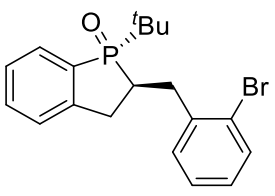


<Peak Table>
PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	9.864	25972	100.000	478462	100.000
总计		25972	100.000	478462	100.000

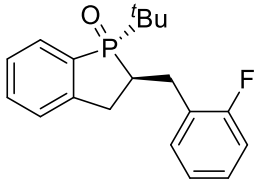
Total

3.12 (1*R*,2*R*)-2-(2-bromobenzyl)-1-(tert-butyl)-2,3-dihydrophosphindole 1-oxide (4b)



Prepared according to general procedure B from **3b** (4.5 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.6) afforded the product **4b** (major isomer) as a colorless liquid (1.20 g, 71% yield). The minor isomer **4b'** (EA: CH_3OH = 40:1, Rf = 0.55) was failed to be isolated as a pure form (80 mg, 4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) (major isomer) δ 7.82-7.73 (m, 1H), 7.62-7.54 (m, 1H), 7.53-7.43 (m, 1H), 7.38-7.33 (m, 1H), 7.29-7.24 (m, 3H), 7.18-7.04 (m, 1H), 3.49-3.43 (m, 1H), 3.01-2.97 (m, 3H), 2.88-2.73 (m, 1H), 1.24-1.20 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.0 (d, $J_{C\text{-}P}$ = 27.3 Hz), 139.3 (d, $J_{C\text{-}P}$ = 11.8 Hz), 133.0, 132.4 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.0, 129.7 (d, $J_{C\text{-}P}$ = 8.3 Hz), 128.7 (d, $J_{C\text{-}P}$ = 42.4 Hz), 128.2, 127.4, 127.3 (d, $J_{C\text{-}P}$ = 9.4 Hz), 126.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 124.6, 35.5 (d, $J_{C\text{-}P}$ = 2.0 Hz), 35.0 (d, $J_{C\text{-}P}$ = 5.1 Hz), 33.4 (d, $J_{C\text{-}P}$ = 67.2 Hz), 30.8 (d, $J_{C\text{-}P}$ = 61.4 Hz), 24.0; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 72.8. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{19}H_{22}BrOP$: 376.0592, found 376.0586. $[\alpha]_D^{20}$ = 5.9 (*c* = 0.25, $CHCl_3$).

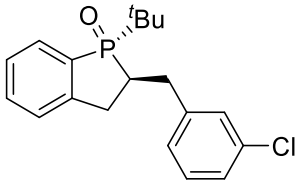
(1*R*,2*S*)-1-(tert-butyl)-2-(2-fluorobenzyl)-2,3-dihydrophosphindole 1-oxide (4c)



Prepared according to general procedure B from **3c** (4.1 mmol), after a flash column chromatography (EA: CH_3OH = 50:1, Rf = 0.5) afforded the product **4c** (major isomer) as a colorless solid (890 mg, 69% yield). M.p.: 149.0-149.9 ℃. The minor isomer **4c'** (EA: CH_3OH = 40:1, Rf = 0.45) was failed to be isolated as a pure form (148 mg, 11% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) (major isomer) δ 7.77 (t, *J* = 7.4 Hz, 1H), 7.50-7.46 (m, 1H), 7.38-7.34 (m, 1H), 7.29-7.23 (m, 3H), 7.16-6.99 (m, 2H), 3.45-3.29 (m, 1H), 3.08-2.96 (m, 2H), 2.84-2.59 (m, 2H), 1.22 (d, *J* = 14.8 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4 (d, $J_{C\text{-}F}$ = 245.4 Hz), 146.0 (d, $J_{C\text{-}P}$ = 26.9 Hz), 132.5 (d, $J_{C\text{-}F}$ = 2.2 Hz), 131.6 (d, $J_{C\text{-}P}$ = 5.0 Hz), 130.4 (d, $J_{C\text{-}P}$ = 90.8 Hz), 129.8 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.2 (d, $J_{C\text{-}F}$ = 8.4 Hz), 127.3 (d, $J_{C\text{-}P}$ = 9.3 Hz), 127.1 (d, $J_{C\text{-}P}$ = 12.4 Hz), 126.5 (d, $J_{C\text{-}P}$ = 10.3 Hz), 124.0 (d, $J_{C\text{-}F}$ = 3.6 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.9 Hz), 35.4 (d, $J_{C\text{-}P}$ = 5.1 Hz), 33.4 (d, $J_{C\text{-}P}$ = 67.5 Hz), 31.6 (d, $J_{C\text{-}P}$ = 60.0 Hz), 29.3, 24.0; **^{31}P NMR** (162 MHz,

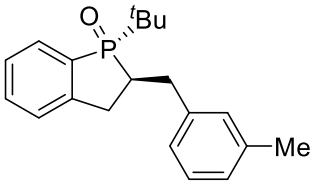
Acetone) δ 71.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 117.6. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{19}H_{22}FOP$: 316.1392, found 316.1390. $[\alpha]_D^{20}$ = 44.4 (*c* = 0.5, $CHCl_3$).

3.13 (1*R*,2*S*)-1-(tert-butyl)-2-(3-chlorobenzyl)-2,3-dihydrophosphindole 1-oxide (4d)



Prepared according to general procedure B from **3d** (4.6 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.5) afforded the product **4d** (major isomer) as a colorless solid (842 mg, 55% yield). M.p.: 110.0-110.9 ℃. The minor isomer **4d'** (EA: CH_3OH = 40:1, Rf = 0.45) was failed to be isolated as a pure form (270 mg, 18% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) (major isomer) δ 7.79-7.75 (m, 1H), 7.51-7.48 (m, 1H), 7.40-7.35 (m, 1H), 7.29-7.24 (m, 4H), 7.15 (d, *J* = 7.1 Hz, 1H), 3.40-3.29 (m, 1H), 3.10-3.03 (m, 1H), 2.96-2.86 (m, 1H), 2.75-2.54 (m, 2H), 1.22 (d, *J* = 14.8 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8 (d, $J_{C\text{-}P}$ = 27.0 Hz), 142.3 (d, $J_{C\text{-}P}$ = 11.8 Hz), 134.4, 132.7 (d, $J_{C\text{-}P}$ = 2.4 Hz), 130.2 (d, $J_{C\text{-}P}$ = 90.8 Hz), 130.0, 129.7, 129.0, 127.5 (d, $J_{C\text{-}P}$ = 9.4 Hz), 127.4, 126.7 (d, $J_{C\text{-}P}$ = 10.9 Hz), 126.6, 35.4 (d, $J_{C\text{-}P}$ = 5.2 Hz), 34.8 (d, $J_{C\text{-}P}$ = 2.6 Hz), 33.5 (d, $J_{C\text{-}P}$ = 67.6 Hz), 33.0 (d, $J_{C\text{-}P}$ = 61.3 Hz), 24.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 72.5. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{19}H_{22}ClOP$: 332.1097, found 332.1092. $[\alpha]_D^{20}$ = 58.5 (*c* = 0.5, $CHCl_3$).

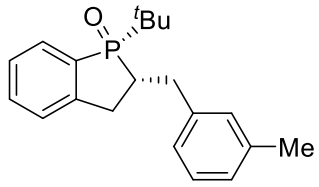
3.14 (1*R*,2*S*)-1-(tert-butyl)-2-(3-methylbenzyl)-2,3-dihydrophosphindole 1-oxide (4e)



Prepared according to general procedure B from **3e** (4.8 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.6) afforded the product **4e** (major isomer) as colorless solids (580 mg, 38% yield). M.p.: 151.0-151.9 ℃. **^{1}H NMR** (400 MHz,

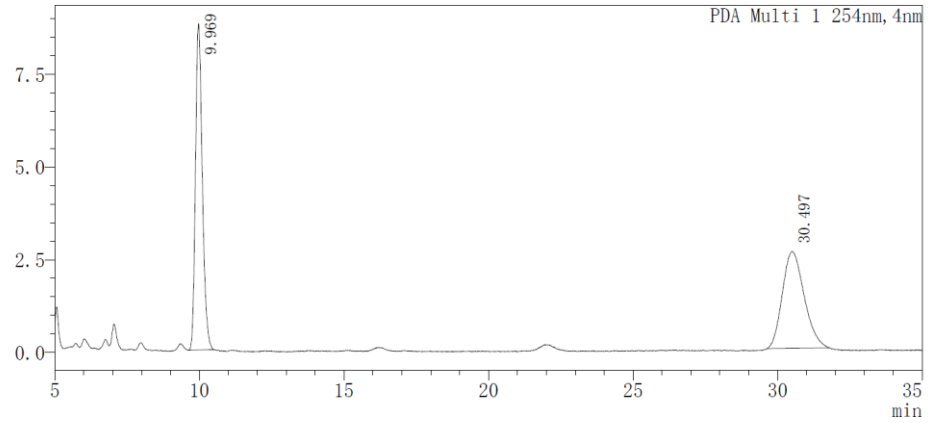
$CDCl_3$) δ 7.80-7.77 (m, 1H), 7.51-7.47 (m, 1H), 7.40-7.35 (m, 1H), 7.28-7.22 (m, 2H), 7.09-7.06 (m, 3H), 3.38-3.33 (m, 1H), 3.13-2.90 (m, 2H), 2.74-2.68 (m, 1H), 2.65-2.56 (m, 1H), 2.38 (s, 3H), 1.24 (d, J = 14.6 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.1 (d, $J_{C\text{-}P}$ = 27.5 Hz), 140.1 (d, $J_{C\text{-}P}$ = 12.4 Hz), 138.1, 132.5 (d, $J_{C\text{-}P}$ = 2.4 Hz), 130.8, 129.9 (d, $J_{C\text{-}P}$ = 8.3 Hz), 129.7, 128.4, 127.3 (d, $J_{C\text{-}P}$ = 9.4 Hz), 127.1, 126.6 (d, $J_{C\text{-}P}$ = 10.2 Hz), 126.0, 35.3 (d, $J_{C\text{-}P}$ = 5.3 Hz), 34.8 (d, $J_{C\text{-}P}$ = 2.3 Hz), 33.5 (d, $J_{C\text{-}P}$ = 66.9 Hz), 33.1 (d, $J_{C\text{-}P}$ = 61.6 Hz), 24.1, 21.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 72.4. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{20}H_{25}OP$: 312.1643, found 312.1638. $[\alpha]_D^{20}$ = 60.6 (c = 0.5, $CHCl_3$).

3.15 (1*R*,2*R*)-1-(tert-butyl)-2-(3-methylbenzyl)-2,3-dihydrophosphindole 1-oxide (4e')



Prepared according to general procedure B from **3e** (4.8 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.5) afforded the product **4e'** (minor isomer) as colorless solids (289 mg, 20% yield). M.p.: 155.0-155.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99-7.95 (m, 1H), 7.48-7.39 (m, 2H), 7.30-7.21 (m, 2H), 7.11-7.10 (m, 3H), 3.36-3.29 (m, 1H), 3.07-2.87 (m, 2H), 2.53-2.25 (m, 5H), 1.21 (d, J = 14.7 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2 (d, $J_{C\text{-}P}$ = 13.1 Hz), 143.6 (d, $J_{C\text{-}P}$ = 7.7 Hz), 138.5, 132.5 (d, $J_{C\text{-}P}$ = 5.9 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.3 Hz), 129.1 (d, $J_{C\text{-}P}$ = 9.5 Hz), 128.7, 127.7, 127.6, 127.2, 126.7 (d, $J_{C\text{-}P}$ = 10.1 Hz), 123.4, 39.8 (d, $J_{C\text{-}P}$ = 4.3 Hz), 38.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 33.3 (d, $J_{C\text{-}P}$ = 70.4 Hz), 32.3 (d, $J_{C\text{-}P}$ = 56.8 Hz), 24.0, 21.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 40.7. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{20}H_{25}OP$: 312.1643, found 312.1638. HPLC (AD-H, 2-propanol /n-hexane = 20/80, flow rate = 1.0 mL/min, l = 254 nm) tR = 9.9 min (major), 30.5 min (minor). $[\alpha]_D^{20}$ = 70.5 (c = 0.5, $CHCl_3$).

<Chromatogram>
mAU



<Peak Table>
PDA Ch1 254nm

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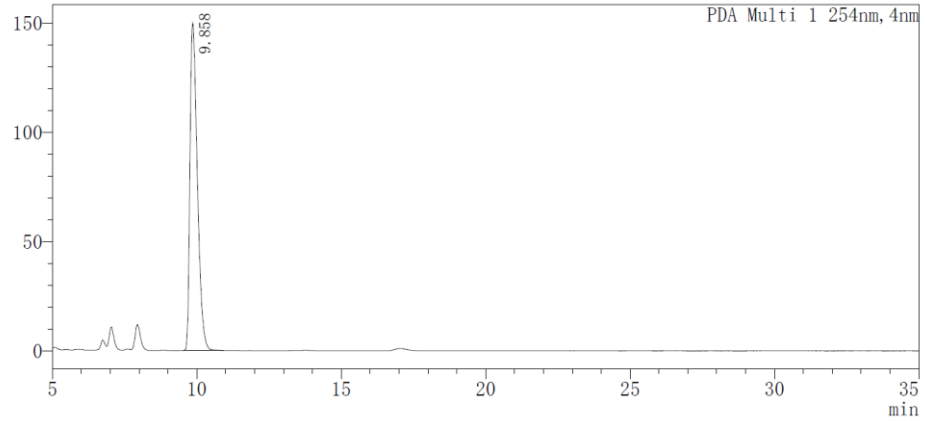

<Peak Table>
PDA Ch1 254nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
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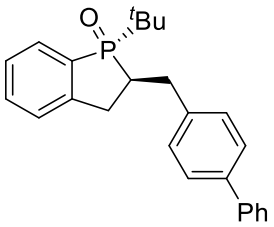
总计		149859	100.000	2675075	100.000

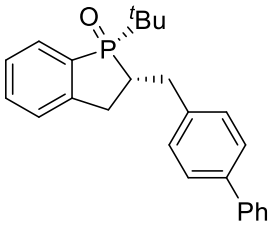
Total

3.16 (1*R*,2*S*)-2-([1,1'-biphenyl]-4-ylmethyl)-1-(tert-butyl)-2,3-dihydrophosphindole 1-oxide (4f)



Prepared according to general procedure B from **3f** (3.8 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.5) afforded the product **4f** (major isomer) as colorless solids (740 mg, 52% yield). M.p.: 117.0-117.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (t, J = 7.4 Hz, 1H), 7.65-7.58 (m, 4H), 7.55-7.43 (m, 3H), 7.41-7.39 (m, 4H), 7.32-7.26 (m, 1H), 3.50-3.31 (m, 1H), 3.20-2.95 (m, 2H), 2.81-2.68 (m, 2H), 1.25 (d, J = 14.8 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.1 (d, $J_{C\text{-}P}$ = 27.0 Hz), 140.9, 139.4, 139.3, 132.7, 130.2 (d, $J_{C\text{-}P}$ = 91.8 Hz), 130.0 (d, $J_{C\text{-}P}$ = 8.1 Hz), 129.5, 128.8, 127.4 (d, $J_{C\text{-}P}$ = 9.2 Hz), 127.3, 127.2, 127.0, 126.7 (d, $J_{C\text{-}P}$ = 10.3 Hz), 35.5 (d, $J_{C\text{-}P}$ = 5.4 Hz), 34.7, 33.6 (d, $J_{C\text{-}P}$ = 66.6 Hz), 33.2 (d, $J_{C\text{-}P}$ = 61.5 Hz), 24.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 72.9. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{25}H_{27}OP$: 374.1800, found 374.1797. $[\alpha]_D^{20}$ = 74.0 (c = 0.5, $CHCl_3$).

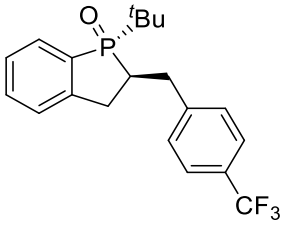
3.17 (1*R*,2*R*)-2-([1,1'-biphenyl]-4-ylmethyl)-1-(tert-butyl)-2,3-dihydrophosphindole 1-oxide (4f')



Prepared according to general procedure B from **3f** (3.8 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.4) afforded the product **4f'** (minor isomer) as colorless solids (246 mg, 18% yield). M.p.: 224.0-224.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02-7.95 (m, 1H), 7.65-7.59 (m, 4H), 7.51-7.44 (m, 4H), 7.39 (dd, J = 8.3, 2.5 Hz, 3H), 7.26 (dd, J = 7.6, 4.4 Hz, 1H), 3.46-3.38 (m, 1H), 3.09-2.95 (m, 2H), 2.55-2.30 (m, 2H), 1.23 (d, J = 14.8 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2 (d, $J_{C\text{-}P}$ = 13.1 Hz), 143.5 (d, $J_{C\text{-}P}$ = 8.0 Hz), 140.6, 139.9, 132.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.4 Hz), 129.1 (d, $J_{C\text{-}P}$ = 9.9 Hz), 128.8, 127.5, 127.3,

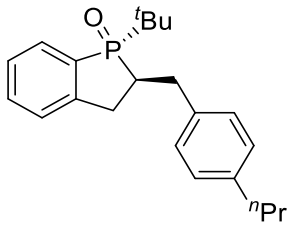
126.9 (d, $J_{C\text{-}P}$ = 10.6 Hz), 126.9, 126.8 (d, $J_{C\text{-}P}$ = 9.9 Hz), 126.7, 39.9 (d, $J_{C\text{-}P}$ = 4.0 Hz), 37.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 33.4 (d, $J_{C\text{-}P}$ = 70.4 Hz), 32.2 (d, $J_{C\text{-}P}$ = 57.0 Hz), 24.0; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 41.0-40.7 (m). **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{25}H_{27}OP$: 374.1800, found 374.1795. $[\alpha]_D^{20}$ = 80.8 (*c* = 0.1, $CHCl_3$).

3.18 (1*R*,2*S*)-1-(tert-butyl)-2-(4-(trifluoromethyl)benzyl)-2,3-dihydrophosphindole 1-oxide (4g)



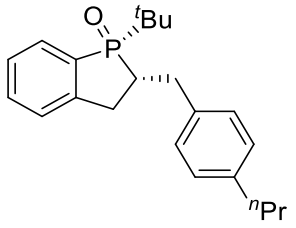
Prepared according to general procedure B from **3g** (3.4 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.5) afforded the product **4g** (major isomer) as a colorless solid (138 mg, 11% yield). M.p.: 180.0-180.9 °C. The minor isomer **4g'** (EA: CH_3OH = 40:1, Rf = 0.45) was failed to be isolated as a pure form (34 mg, 3% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 7.4 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.52-7.48 (m, 1H), 7.39 (dd, *J* = 8.0, 2.3 Hz, 3H), 7.27-7.24 (m, 1H), 3.48-3.34 (m, 1H), 3.11-3.03 (m, 1H), 2.97-2.89 (m, 1H), 2.77-2.64 (m, 2H), 1.21 (d, *J* = 14.8 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6 (d, $J_{C\text{-}P}$ = 26.9 Hz), 144.3 (d, $J_{C\text{-}P}$ = 11.7 Hz), 132.7 (d, $J_{C\text{-}F}$ = 2.7 Hz), 130.0 (d, $J_{C\text{-}P}$ = 91.1 Hz), 129.9 (d, $J_{C\text{-}F}$ = 8.1 Hz), 129.4 (d, $J_{C\text{-}P}$ = 50.5 Hz), 129.3, 128.7 (d, $J_{C\text{-}F}$ = 32.4 Hz), 128.6 (d, $J_{C\text{-}P}$ = 60.6 Hz), 127.5 (d, $J_{C\text{-}F}$ = 9.3 Hz), 126.6 (d, $J_{C\text{-}P}$ = 10.2 Hz), 125.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.2 (q, $J_{C\text{-}F}$ = 272.7 Hz), 35.4 (d, $J_{C\text{-}P}$ = 5.7 Hz), 35.0 (d, $J_{C\text{-}P}$ = 2.2 Hz), 33.5 (d, $J_{C\text{-}P}$ = 67.4 Hz), 32.9 (d, $J_{C\text{-}P}$ = 61.1 Hz), 24.0; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 72.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.4. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{20}H_{22}F_3OP$: 366.1360, found 366.1356. $[\alpha]_D^{20}$ = 80.8 (*c* = 0.5, $CHCl_3$).

3.19 (1*R*,2*S*)-1-(tert-butyl)-2-(4-propylbenzyl)-2,3-dihydrophosphindole 1-oxide (4i)



Prepared according to general procedure B from **3i** (3.6 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.6) afforded the product **4i** (minor isomer) as colorless solids (186 mg, 15% yield). M.p.: 169.0-169.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (t, J = 7.4 Hz, 1H), 7.51-7.46 (m, 1H), 7.39-7.35 (m, 1H), 7.32-7.23 (m, 1H), 7.21-7.11 (m, 4H), 3.38-3.32 (m, 1H), 3.14-2.88 (m, 2H), 2.83-2.44 (m, 4H), 1.70-1.61 (m, 2H), 1.23 (d, J = 14.7 Hz, 9H), 0.96 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.1 (d, $J_{C\text{-}P}$ = 27.3 Hz), 140.7, 137.3 (d, $J_{C\text{-}P}$ = 12.4 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.7, 129.8 (d, $J_{C\text{-}P}$ = 8.2 Hz), 128.7 (d, $J_{C\text{-}P}$ = 19.5 Hz), 128.1, 127.2 (d, $J_{C\text{-}P}$ = 9.3 Hz), 126.5 (d, $J_{C\text{-}P}$ = 10.3 Hz), 37.6, 35.3 (d, $J_{C\text{-}P}$ = 5.6 Hz), 34.5 (d, $J_{C\text{-}P}$ = 2.5 Hz), 33.4 (d, $J_{C\text{-}P}$ = 66.9 Hz), 33.2 (d, $J_{C\text{-}P}$ = 61.2 Hz), 24.5, 24.0, 13.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 72.6. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{22}H_{29}OP$: 340.1956, found 340.1955. $[\alpha]_D^{20}$ = 67.8 (c = 0.5, $CHCl_3$).

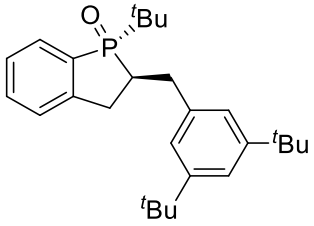
3.20 (1*R*,2*S*)-1-(tert-butyl)-2-(4-propylbenzyl)-2,3-dihydrophosphindole 1-oxide (4i')



Prepared according to general procedure B from **3i** (3.6 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.5) afforded the product **4i'** (major isomer) as colorless solids (560 mg, 46% yield). M.p.: 165.0-165.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05-7.87 (m, 1H), 7.56-7.37 (m, 2H), 7.24-7.18 (m, 5H), 3.43-3.23 (m, 1H), 3.06-2.85 (m, 2H), 2.62-2.58 (m, 2H), 2.49-2.21 (m, 2H), 1.69-1.64 (m, 2H), 1.20 (d, J = 14.8 Hz, 9H), 0.97 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7 (d, $J_{C\text{-}P}$ = 8.0 Hz), 142.4 (d, $J_{C\text{-}P}$ = 13.1 Hz), 141.3, 132.5 (d, $J_{C\text{-}P}$ = 6.1 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.6

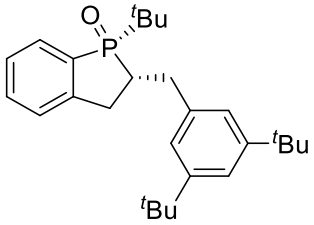
Hz), 129.1 (d, J_{C-P} = 9.6 Hz), 128.8, 127.4, 126.7 (d, J_{C-P} = 10.4 Hz), 126.2, 39.9 (d, J_{C-P} = 4.3 Hz), 37.6 (d, J_{C-P} = 2.9 Hz), 37.5, 33.3 (d, J_{C-P} = 70.4 Hz), 32.2 (d, J_{C-P} = 57.1 Hz), 24.5, 23.9, 13.8; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 41.3-40.8 (m). **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{22}H_{29}OP$: 340.1956, found 340.1950. $[\alpha]_D^{20}$ = 61.9 (*c* = 0.5, $CHCl_3$).

3.21 (1*R*,2*S*)-1-(tert-butyl)-2-(3,5-di-tert-butylbenzyl)-2,3-dihydrophosphindole 1-oxide (4j)



Prepared according to general procedure B from **3j** (5.1 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.5) afforded the product **4j** (minor isomer) as colorless solids (400 mg, 19% yield). M.p.: 145.0-145.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.78 (m, 1H), 7.51-7.48 (m, 1H), 7.42-7.25 (m, 3H), 7.16-7.05 (m, 2H), 3.48-3.31 (m, 1H), 3.11-3.00 (m, 2H), 2.74-2.61 (m, 2H), 1.36 (s, 18H), 1.24 (d, *J* = 14.7 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.8, 146.1 (d, J_{C-P} = 27.4 Hz), 139.2 (d, J_{C-P} = 11.8 Hz), 132.4 (d, J_{C-P} = 2.2 Hz), 130.8, 129.9 (d, J_{C-P} = 7.9 Hz), 127.2 (d, J_{C-P} = 9.3 Hz), 126.5 (d, J_{C-P} = 10.2 Hz), 123.1, 120.2, 35.5 (d, J_{C-P} = 5.8 Hz), 35.2 (d, J_{C-P} = 2.6 Hz), 34.7, 33.4 (d, J_{C-P} = 66.8 Hz), 33.3 (d, J_{C-P} = 61.1 Hz), 31.4, 24.1; **^{31}P NMR** (162 MHz, CD_2Cl_2) δ 72.5. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{27}H_{39}OP$: 410.2739, found 410.2726. $[\alpha]_D^{20}$ = 76.1 (*c* = 0.5, $CHCl_3$).

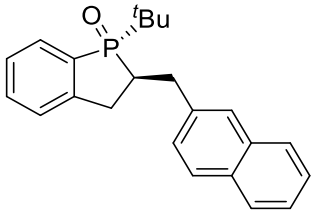
3.22 (1*R*,2*R*)-1-(tert-butyl)-2-(3,5-di-tert-butylbenzyl)-2,3-dihydrophosphindole 1-oxide (4j')



Prepared according to general procedure B from **3j** (5.1 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.4) afforded the product **4j'** (major isomer)

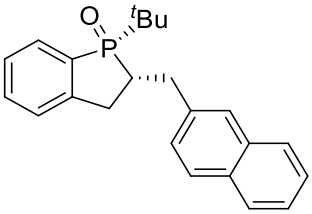
as colorless solids (800 mg, 38% yield). M.p.: 142.0-142.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03-7.95 (m, 1H), 7.51-7.35 (m, 3H), 7.27-7.24 (m, 1H), 7.15 (d, J = 1.8 Hz, 2H), 3.43-3.33 (m, 1H), 3.16-2.94 (m, 2H), 2.55-2.41 (m, 1H), 2.35-2.27 (m, 1H), 1.37 (s, 18H), 1.21 (d, J = 14.7 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.2, 144.4 (d, $J_{C\text{-}P}$ = 13.0 Hz), 143.9 (d, $J_{C\text{-}P}$ = 8.1 Hz), 132.6 (d, $J_{C\text{-}P}$ = 6.4 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.3 Hz), 129.1 (d, $J_{C\text{-}P}$ = 9.5 Hz), 127.6, 126.7 (d, $J_{C\text{-}P}$ = 10.3 Hz), 121.0, 120.5, 39.3 (d, $J_{C\text{-}P}$ = 4.1 Hz), 38.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 34.9, 33.3 (d, $J_{C\text{-}P}$ = 70.1 Hz), 33.0 (d, $J_{C\text{-}P}$ = 56.2 Hz), 31.5, 24.0; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 41.2-40.9 (m). **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{27}H_{39}OP$: 410.2739, found 410.2734. $[\alpha]_D^{20}$ = 76.1 (c = 0.5, $CHCl_3$).

3.23 (1*R*,2*S*)-1-(tert-butyl)-2-(naphthalen-2-ylmethyl)-2,3-dihydrophosphindole 1-oxide (4k)



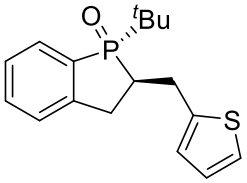
Prepared according to general procedure B from **3k** (4.4 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.6) afforded the product **4k** (major isomer) as colorless solids (1.03 g, 67% yield). M.p.: 142.0-142.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.79 (m, 4H), 7.69 (s, 1H), 7.55-7.46 (m, 3H), 7.45-7.34 (m, 2H), 7.28-7.21 (m, 1H), 3.58-3.54 (m, 1H), 3.05-3.01 (m, 2H), 2.85-2.81 (m, 2H), 1.26 (d, J = 14.6 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.1 (d, $J_{C\text{-}P}$ = 27.4 Hz), 137.7 (d, $J_{C\text{-}P}$ = 12.3 Hz), 133.6, 132.6 (d, $J_{C\text{-}P}$ = 2.3 Hz), 132.2, 130.8, 130.0 (d, $J_{C\text{-}P}$ = 8.0 Hz), 128.4, 127.7, 127.5, 127.5, 127.4, 127.4 (d, $J_{C\text{-}P}$ = 11.0 Hz), 126.7 (d, $J_{C\text{-}P}$ = 10.3 Hz), 126.2, 125.5, 35.4 (d, $J_{C\text{-}P}$ = 5.6 Hz), 35.2 (d, $J_{C\text{-}P}$ = 2.3 Hz), 33.6 (d, $J_{C\text{-}P}$ = 67.0 Hz), 33.1 (d, $J_{C\text{-}P}$ = 61.5 Hz), 24.2; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 72.4. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{23}H_{25}OP$: 348.1643, found 348.1639. $[\alpha]_D^{20}$ = 76.1 (c = 0.5, $CHCl_3$).

3.24 (1*R*,2*R*)-1-(tert-butyl)-2-(naphthalen-2-ylmethyl)-2,3-dihydrophosphindole 1-oxide (4k')



Prepared according to general procedure B from **3k** (4.4 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.5) afforded the product **4k'** (minor isomer) as colorless solids (260 mg, 17% yield). M.p.: 281.0-281.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (t, *J* = 8.7 Hz, 1H), 7.91-7.82 (m, 3H), 7.76-7.70 (m, 1H), 7.55-7.39 (m, 5H), 7.27 (dd, *J* = 8.6, 3.9 Hz, 1H), 3.57-3.51 (m, 1H), 3.09 (d, *J* = 9.0 Hz, 2H), 2.61-2.35 (m, 2H), 1.24 (d, *J* = 14.4 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6 (d, $J_{C\text{-}P}$ = 7.9 Hz), 142.6 (d, $J_{C\text{-}P}$ = 12.9 Hz), 133.6, 132.6 (d, $J_{C\text{-}P}$ = 5.8 Hz), 132.5, 131.8, 129.2 (d, $J_{C\text{-}P}$ = 9.4 Hz), 128.7, 127.7, 127.6, 126.9 (d, $J_{C\text{-}P}$ = 9.9 Hz), 126.4, 125.8, 125.7, 124.9 (d, $J_{C\text{-}P}$ = 48.8 Hz), 124.9, 40.0 (d, $J_{C\text{-}P}$ = 3.6 Hz), 38.3, 32.2 (d, $J_{C\text{-}P}$ = 57.1 Hz), 25.0 (d, $J_{C\text{-}P}$ = 85.7 Hz), 24.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 40.8. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{23}H_{25}OP$: 348.1643, found 348.1641. $[\alpha]_D^{20}$ = 92.0 (*c* = 0.5, $CHCl_3$).

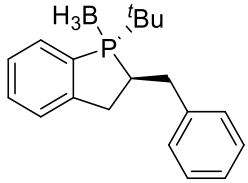
3.25 (1*R*,2*R*)-1-(tert-butyl)-2-(thiophen-2-ylmethyl)-2,3-dihydrophosphindole 1-oxide (4l)



Prepared according to general procedure B from **3l** (4.2 mmol), after a flash column chromatography (EA: CH_3OH = 40:1, Rf = 0.5) afforded the product **4l** (major isomer) as a colorless solid (632 mg, 49% yield). M.p.: 161.0-161.9 ℃. The minor isomer **4l'** (EA: CH_3OH = 40:1, Rf = 0.45) was failed to be isolated as a pure form (79 mg, 6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 7.5 Hz, 1H), 7.52-7.47 (m, 1H), 7.41-7.35 (m, 1H), 7.33-7.25 (m, 1H), 7.21-7.18 (m, 1H), 6.98-6.95 (m, 1H), 6.90 (d, *J* = 3.3 Hz, 1H), 3.64-3.46 (m, 1H), 3.29-3.01 (m, 2H), 2.97-2.89 (m, 1H), 2.80-2.58 (m, 1H), 1.22 (d, *J* = 14.8 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8 (d, $J_{C\text{-}P}$ = 27.4 Hz), 142.9 (d, $J_{C\text{-}P}$ = 13.8 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.0 (d, $J_{C\text{-}P}$ = 91.2 Hz), 129.9 (d,

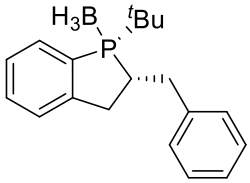
$J_{C\text{-}P}$ = 8.1 Hz), 127.4 (d, $J_{C\text{-}P}$ = 9.2 Hz), 126.9, 126.62 (d, $J_{C\text{-}P}$ = 10.3 Hz), 125.7, 123.8, 35.6 (d, $J_{C\text{-}P}$ = 5.2 Hz), 33.7 (d, $J_{C\text{-}P}$ = 61.0 Hz), 33.4 (d, $J_{C\text{-}P}$ = 67.4 Hz), 29.6 (d, $J_{C\text{-}P}$ = 1.9 Hz), 24.0; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 72.3. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{17}H_{21}OPS$: 304.1051, found 304.1049. $[\alpha]_D^{20}$ = 74.5 (*c* = 0.5, $CHCl_3$).

3.26 (1*S*,2*S*)-2-benzyl-1-(tert-butyl)-2,3-dihydrophosphindole 1-borane (5a)



Prepared according to general procedure C from **4a** (2.5 mmol), after a flash column chromatography (hexane : EA = 50:1) afforded the product **5a** as a colorless solid (577 mg, 78% yield). M.p.: 116.0-116.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 1H), 7.47-7.43 (m, 1H), 7.40-7.36 (m, 3H), 7.28-7.26 (m, 4H), 3.42-3.11 (m, 2H), 3.09-2.95 (m, 1H), 2.89-2.81 (m, 1H), 2.74-2.66 (m, 1H), 1.24 (d, *J* = 13.7 Hz, 9H), 1.24-0.47 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.2 (d, $J_{C\text{-}P}$ = 12.8 Hz), 140.2 (d, $J_{C\text{-}P}$ = 13.9 Hz), 131.4, 130.6 (d, $J_{C\text{-}P}$ = 10.2 Hz), 130.0 (d, $J_{C\text{-}P}$ = 53.0 Hz), 128.8, 128.6, 127.4 (d, $J_{C\text{-}P}$ = 8.8 Hz), 126.4, 125.6 (d, $J_{C\text{-}P}$ = 7.3 Hz), 38.4, 37.3 (d, $J_{C\text{-}P}$ = 5.4 Hz), 32.5 (d, $J_{C\text{-}P}$ = 31.5 Hz), 30.5 (d, $J_{C\text{-}P}$ = 27.7 Hz), 25.4 (d, $J_{C\text{-}P}$ = 2.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 64.3. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $C_{19}H_{23}P$: 282.1537, found 282.1529. $[\alpha]_D^{20}$ = 59.7 (*c* = 0.5, $CHCl_3$).

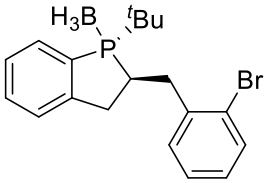
3.27 (1*S*,2*R*)-2-benzyl-1-(tert-butyl)-2,3-dihydrophosphindole 1-borane (5a')



Prepared according to general procedure C from **4a'** (1.2 mmol), after a flash column chromatography (hexane : EA = 50:1) afforded the product **5a'** as a colorless solid (277 mg, 75% yield). M.p.: 183.0-183.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.77 (m, 1H), 7.49-7.25 (m, 7H), 7.25-7.11 (m, 1H), 3.32-3.15 (m, 1H), 3.14-2.87 (m, 2H), 2.46-2.11 (m, 2H), 1.21 (d, *J* = 13.8 Hz, 9H), 1.24-0.47 (br., 3H); **^{13}C NMR** (101 MHz,

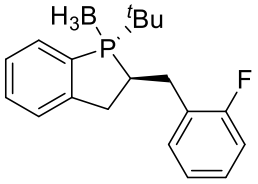
$CDCl_3$) δ 145.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 144.3, 133.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 130.6 (d, $J_{C\text{-}P}$ = 2.4 Hz), 129.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 128.8, 127.0, 126.8 (d, $J_{C\text{-}P}$ = 10.8 Hz), 126.5, 123.5 (d, $J_{C\text{-}P}$ = 47.3 Hz), 39.8 (d, $J_{C\text{-}P}$ = 3.4 Hz), 39.2 (d, $J_{C\text{-}P}$ = 3.8 Hz), 30.1 (d, $J_{C\text{-}P}$ = 30.7 Hz), 26.4 (d, $J_{C\text{-}P}$ = 32.1 Hz), 25.1 (d, $J_{C\text{-}P}$ = 2.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.2. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $C_{19}H_{23}P$: 282.1537, found 282.1532. $[\alpha]_D^{20}$ = 29.8 (*c* = 0.5, $CHCl_3$).

3.28 (1*S*,2*R*)-2-(2-bromobenzyl)-1-(tert-butyl)-2,3-dihydrophosphindole 1-borane (5b)



Prepared according to general procedure C from **4b** (3.2 mmol), after a flash column chromatography (hexane : EA = 50:1) afforded the product **5b** as a colorless solid (880 mg, 74% yield). M.p.: 128.0-128.9 ℃. **^{1}H NMR** δ 7.70-7.54 (m, 2H), 7.46-7.42 (m, 1H), 7.37-7.31 (m, 1H), 7.29-2.25 (m, 3H), 7.18-7.14 (m, 1H), 3.44-3.39 (m, 1H), 3.25-2.95 (m, 3H), 2.92-2.68 (m, 1H), 1.24 (d, *J* = 13.8 Hz, 9H), 1.24-0.42 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.1 (d, $J_{C\text{-}P}$ = 12.7 Hz), 139.4 (d, $J_{C\text{-}P}$ = 13.8 Hz), 133.2, 131.9, 131.4, 130.6 (d, $J_{C\text{-}P}$ = 10.2 Hz), 129.5 (d, $J_{C\text{-}P}$ = 121.6 Hz), 128.4, 127.6, 127.5, 125.6 (d, $J_{C\text{-}P}$ = 7.3 Hz), 124.6, 38.0, 37.8 (d, $J_{C\text{-}P}$ = 6.1 Hz), 30.6 (d, $J_{C\text{-}P}$ = 27.6 Hz), 30.6 (d, $J_{C\text{-}P}$ = 30.5 Hz), 25.6 (d, $J_{C\text{-}P}$ = 2.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 65.2. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{19}H_{25}BBrP$: 374.0970, found 374.0947. $[\alpha]_D^{20}$ = 1.3 (*c* = 0.5, $CHCl_3$).

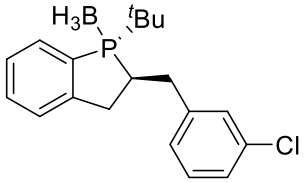
3.29 (1*S*,2*S*)-1-(tert-butyl)-2-(2-fluorobenzyl)-2,3-dihydrophosphindole 1-borane (5c)



Prepared according to general procedure C from **4c** (2.8 mmol), after a flash column

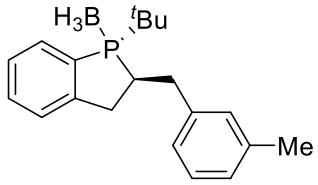
chromatography (hexane : EA = 50:1) afforded the product **5c** as a colorless solid (601 mg, 68% yield). M.p.: 123.0-123.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69-7.60 (m, 1H), 7.46-7.42 (m, 1H), 7.38-7.33 (m, 1H), 7.29-7.24 (m, 3H), 7.19-7.03 (m, 2H), 3.36-3.31 (m, 1H), 3.25-3.17 (m, 1H), 3.11-2.86 (m, 2H), 2.79-2.72 (m, 1H), 1.23 (d, J = 13.7 Hz, 9H), 1.24-0.42 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4 (d, $J_{C\text{-}F}$ = 245.2 Hz), 147.1 (d, $J_{C\text{-}P}$ = 13.0 Hz), 131.5 (d, $J_{C\text{-}F}$ = 5.1 Hz), 131.4 (d, $J_{C\text{-}F}$ = 2.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 10.1 Hz), 130.2 (d, $J_{C\text{-}P}$ = 53.1 Hz), 128.4 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.5 (d, $J_{C\text{-}P}$ = 8.8 Hz), 127.2 (d, $J_{C\text{-}F}$ = 15.0 Hz), 125.6 (d, $J_{C\text{-}P}$ = 7.4 Hz), 124.1 (d, $J_{C\text{-}P}$ = 3.6 Hz), 115.5 (d, $J_{C\text{-}F}$ = 21.9 Hz), 38.4, 31.6 (d, $J_{C\text{-}P}$ = 6.3 Hz), 31.2 (d, $J_{C\text{-}P}$ = 31.1 Hz), 30.5 (d, $J_{C\text{-}P}$ = 27.8 Hz), 25.4 (d, $J_{C\text{-}P}$ = 2.3 Hz); **^{31}P NMR** (162 MHz, C_6D_6) δ 62.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.5. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $C_{19}H_{22}FP$: 300.1443, found 300.1440. $[\alpha]_D^{20}$ = 34.2 (c = 0.5, $CHCl_3$).

3.30 (1*S*,2*S*)-1-(tert-butyl)-2-(3-chlorobenzyl)-2,3-dihydrophosphindole 1-borane (5d)



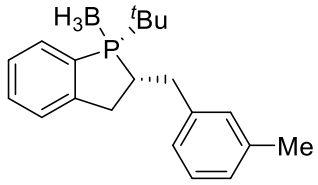
Prepared according to general procedure C from **4d** (3.3 mmol), after a flash column chromatography (hexane : EA = 50:1) afforded the product **5d** as a colorless solid (703 mg, 64% yield). M.p.: 115.0-115.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.59 (m, 1H), 7.45 (tt, J = 7.5, 1.4 Hz, 1H), 7.39-7.34 (m, 1H), 7.29-7.24 (m, 4H), 7.15-7.13 (m, 1H), 3.29-3.21 (m, 2H), 2.98-2.91 (m, 1H), 2.87-2.74 (m, 1H), 2.70-2.63 (m, 1H), 1.22 (d, J = 13.7 Hz, 9H), 1.24-0.41 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0 (d, $J_{C\text{-}P}$ = 12.5 Hz), 142.4 (d, $J_{C\text{-}P}$ = 14.5 Hz), 134.5, 131.5 (d, $J_{C\text{-}P}$ = 2.3 Hz), 130.7 (d, $J_{C\text{-}P}$ = 10.6 Hz), 130.0 (d, $J_{C\text{-}P}$ = 53.0 Hz), 129.9, 128.9, 127.6, 127.3, 126.8, 125.7 (d, $J_{C\text{-}P}$ = 7.3 Hz), 38.4, 37.1 (d, $J_{C\text{-}P}$ = 5.7 Hz), 32.3 (d, $J_{C\text{-}P}$ = 31.8 Hz), 30.7 (d, $J_{C\text{-}P}$ = 27.7 Hz), 25.5 (d, $J_{C\text{-}P}$ = 2.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 64.9. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $[C_{19}H_{22}ClP]^+$: 316.1148, found 316.1140. $[\alpha]_D^{20}$ = 67.8 (c = 0.5, $CHCl_3$).

3.31 (1*S*,2*S*)-1-(tert-butyl)-2-(3-methylbenzyl)-2,3-dihydrophosphindole 1-borane (5e)



Prepared according to general procedure C from **4e** (1.8 mmol), after a flash column chromatography (hexane : EA = 50:1) afforded the product **5e** as a colorless solid (368 mg, 66% yield). M.p.: 123.0-123.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.63 (m, 1H), 7.47-7.43 (m, 1H), 7.41-7.32 (m, 1H), 7.29-7.22 (m, 2H), 7.08 (q, *J* = 8.2 Hz, 3H), 3.37-3.17 (m, 2H), 3.02-2.96 (m, 1H), 2.88-2.79 (m, 1H), 2.75-2.55 (m, 1H), 2.40 (s, 3H), 1.23 (d, *J* = 13.7 Hz, 9H), 1.24-0.41 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.3 (d, $J_{C\text{-}P}$ = 12.6 Hz), 140.2 (d, $J_{C\text{-}P}$ = 14.1 Hz), 138.2, 131.4 (d, $J_{C\text{-}P}$ = 2.2 Hz), 130.6 (d, $J_{C\text{-}P}$ = 10.2 Hz), 130.0 (d, $J_{C\text{-}P}$ = 53.1 Hz), 129.6, 128.4, 127.4 (d, $J_{C\text{-}P}$ = 8.8 Hz), 127.2, 125.9, 125.6 (d, $J_{C\text{-}P}$ = 7.3 Hz), 38.4, 37.2 (d, $J_{C\text{-}P}$ = 5.2 Hz), 32.4 (d, $J_{C\text{-}P}$ = 31.8 Hz), 30.6 (d, $J_{C\text{-}P}$ = 28.0 Hz), 25.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 21.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 64.2. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $C_{20}H_{25}P$: 296.1694, found 296.1685. $[\alpha]_D^{20}$ = 46.1 (*c* = 0.5, $CHCl_3$).

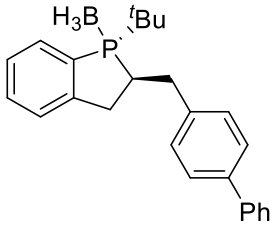
3.32 (1*S*,2*R*)-1-(tert-butyl)-2-(3-methylbenzyl)-2,3-dihydrophosphindole 1-borane (5e')



Prepared according to general procedure C from **4e'** (0.9 mmol), after a flash column chromatography (hexane : EA = 50:1) afforded the product **5e'** as a colorless solid (190 mg, 68% yield). M.p.: 174.0-174.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.77 (m, 1H), 7.46-7.34 (m, 2H), 7.33-7.26 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.13-7.11 (m, 3H), 3.22-3.17 (m, 1H), 3.14-2.90 (m, 2H), 2.41 (s, 3H), 2.37-2.18 (m, 2H), 1.21 (d, *J* = 13.8 Hz, 9H), 1.22-0.47 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2 (d, $J_{C\text{-}P}$ = 10.2 Hz),

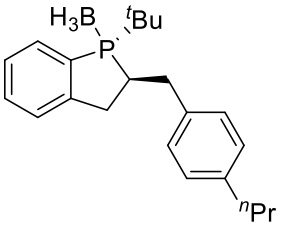
144.4, 138.5, 133.9 (d, $J_{C\text{-}P}$ = 13.1 Hz), 130.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 129.5 (d, $J_{C\text{-}P}$ = 5.9 Hz), 128.7, 127.7, 127.3, 126.7 (d, $J_{C\text{-}P}$ = 11.0 Hz), 123.5 (d, $J_{C\text{-}P}$ = 47.3 Hz), 123.4, 39.7, 39.1 (d, $J_{C\text{-}P}$ = 3.7 Hz), 30.1 (d, $J_{C\text{-}P}$ = 31.1 Hz), 26.5 (d, $J_{C\text{-}P}$ = 32.0 Hz), 25.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 21.4; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.2. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $C_{20}H_{25}P$: 296.1694, found 296.1691. $[\alpha]_D^{20}$ = 35.7 (*c* = 0.5, $CHCl_3$).

3.33 (1*S*,2*S*)-2-([1,1'-biphenyl]-4-ylmethyl)-1-(tert-butyl)-2,3-dihydrophosphindole 1-borane (5f)



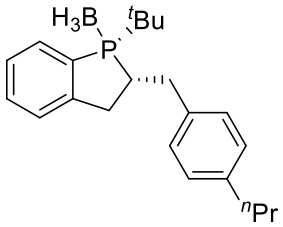
Prepared according to general procedure C from **4f** (2.6 mmol), after a flash column chromatography (hexane : EA = 50:1) afforded the product **5f** as a colorless solid (598 mg, 61% yield). M.p.: 110.0-110.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75-7.60 (m, 5H), 7.56-7.44 (m, 3H), 7.44-7.34 (m, 4H), 7.32-7.27 (m, 1H), 3.53-3.22 (m, 2H), 3.06 (ddd, *J* = 17.1, 7.1, 4.5 Hz, 1H), 3.01-2.86 (m, 1H), 2.81-2.74 (m, 1H), 1.27 (d, *J* = 13.7 Hz, 9H), 1.22-0.47 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.3 (d, $J_{C\text{-}P}$ = 12.4 Hz), 140.9, 139.5 (d, $J_{C\text{-}P}$ = 2.2 Hz), 139.3, 131.5 (d, $J_{C\text{-}P}$ = 2.2 Hz), 130.8 (d, $J_{C\text{-}P}$ = 10.2 Hz), 130.2 (d, $J_{C\text{-}P}$ = 53.0 Hz), 129.4, 128.9, 127.6 (d, $J_{C\text{-}P}$ = 8.8 Hz), 127.4, 127.3, 127.1, 125.8 (d, $J_{C\text{-}P}$ = 7.3 Hz), 38.6, 37.1 (d, $J_{C\text{-}P}$ = 5.3 Hz), 32.6 (d, $J_{C\text{-}P}$ = 31.6 Hz), 30.7 (d, $J_{C\text{-}P}$ = 28.1 Hz), 25.6 (d, $J_{C\text{-}P}$ = 2.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 64.5. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $C_{25}H_{27}P$: 358.1850, found 358.1848. $[\alpha]_D^{20}$ = 86.0 (*c* = 0.5, $CHCl_3$).

3.34 (1*S*,2*S*)-1-(tert-butyl)-2-(4-propylbenzyl)-2,3-dihydrophosphindole 1- borane (5i)



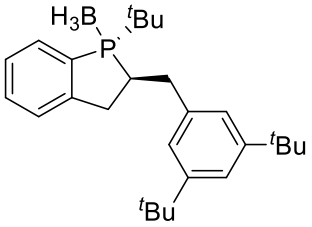
Prepared according to general procedure C from **4i** (0.5 mmol), after a flash column chromatography (hexane : EA = 50:1) afforded the product **5i** as a colorless solid (115 mg, 68% yield). M.p.: 122.0-122.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.63 (m, 1H), 7.46-7.43 (m, 1H), 7.39-7.34 (m, 1H), 7.28-7.26 (m, 1H), 7.19 (s, 4H), 3.32-3.22 (m, 2H), 3.05-2.97 (m, 1H), 2.86-2.81 (m, 1H), 2.71-2.61 (m, 3H), 1.70 (q, J = 7.5 Hz, 2H), 1.24 (d, J = 13.6 Hz, 9H), 1.00 (t, J = 7.3 Hz, 3H), 1.01-0.37 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.4 (d, $J_{C\text{-}P}$ = 12.6 Hz), 140.9, 137.5 (d, $J_{C\text{-}P}$ = 14.4 Hz), 131.4, 130.7 (d, $J_{C\text{-}P}$ = 10.2 Hz), 130.5, 129.9, 128.8 (d, $J_{C\text{-}P}$ = 5.1 Hz), 127.5 (d, $J_{C\text{-}P}$ = 8.8 Hz), 125.7 (d, $J_{C\text{-}P}$ = 7.3 Hz), 38.1 (d, $J_{C\text{-}P}$ = 82.4 Hz), 37.0 (d, $J_{C\text{-}P}$ = 5.3 Hz), 32.6 (d, $J_{C\text{-}P}$ = 31.5 Hz), 30.6 (d, $J_{C\text{-}P}$ = 27.8 Hz), 25.5 (d, $J_{C\text{-}P}$ = 2.2 Hz), 24.6, 13.9, 1.1; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 64.1. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $C_{22}H_{29}P$: 324.2007, found 324.2002. $[\alpha]_D^{20}$ = 54.3 (c = 0.5, $CHCl_3$).

3.35 (1*S*,2*R*)-1-(tert-butyl)-2-(4-propylbenzyl)-2,3-dihydrophosphindole 1- borane (5i')



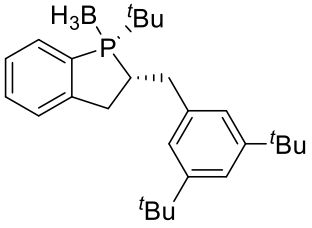
Prepared according to general procedure C from **4i'** (1.6 mmol), after a flash column chromatography (hexane : EA = 50:1) afforded the product **5i'** as a colorless liquid (368 mg, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.72 (m, 1H), 7.44-7.35 (m, 2H), 7.27-7.21 (m, 5H), 3.25-3.17 (m, 1H), 3.15-2.95 (m, 2H), 2.64 (t, J = 7.7 Hz, 2H), 2.46-2.11 (m, 2H), 1.70 (q, J = 7.5 Hz, 2H), 1.22 (d, J = 13.7 Hz, 9H), 1.01 (t, J = 7.3 Hz, 3H), 1.07-0.41 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 142.4 (d, $J_{C\text{-}P}$ = 10.3 Hz), 141.4, 133.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 130.6 (d, $J_{C\text{-}P}$ = 2.4 Hz), 129.4 (d, $J_{C\text{-}P}$ = 5.9 Hz), 128.8, 126.6 (d, $J_{C\text{-}P}$ = 11.0 Hz), 126.3, 123.5 (d, $J_{C\text{-}P}$ = 47.3 Hz), 39.3 (dd, $J_{C\text{-}P}$ = 104.0, 3.7 Hz), 37.5, 30.0 (d, $J_{C\text{-}P}$ = 31.1 Hz), 26.5 (d, $J_{C\text{-}P}$ = 31.9 Hz), 25.0 (d, $J_{C\text{-}P}$ = 2.5 Hz), 24.5, 13.8, 0.9; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.1. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $C_{22}H_{29}P$: 324.2007, found 324.2004. $[\alpha]_D^{20}$ = 13.0 (c = 0.5, $CHCl_3$).

3.36 (1*S*,2*S*)-1-(tert-butyl)-2-(3,5-di-tert-butylbenzyl)-2,3-dihydrophosphindole 1-borane (5j)



Prepared according to general procedure C from **4j** (1.0 mmol), after a flash column chromatography (hexane : EA = 50:1) afforded the product **5j** as a colorless liquid (322 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (t, *J* = 6.9 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.41-7.33 (m, 2H), 7.31-7.25 (m, 1H), 7.10 (s, 2H), 3.35-3.27 (m, 2H), 3.15-2.98 (m, 1H), 2.87-2.81 (m, 1H), 2.77-2.69 (m, 1H), 1.47-1.31 (m, 18H), 1.22 (d, *J* = 13.7 Hz, 9H), 1.17-0.43 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.9, 147.4 (d, $J_{C\text{-}P}$ = 13.0 Hz), 139.2 (d, $J_{C\text{-}P}$ = 13.2 Hz), 131.3, 130.7 (d, $J_{C\text{-}P}$ = 10.2 Hz), 130.1, 127.4 (d, $J_{C\text{-}P}$ = 8.8 Hz), 125.6 (d, $J_{C\text{-}P}$ = 7.3 Hz), 123.1, 120.3, 38.8, 37.7 (d, $J_{C\text{-}P}$ = 5.1 Hz), 34.8, 32.8 (d, $J_{C\text{-}P}$ = 31.1 Hz), 31.5, 30.5 (d, $J_{C\text{-}P}$ = 27.7 Hz), 25.5 (d, $J_{C\text{-}P}$ = 2.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 64.5. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $C_{27}H_{39}P$: 394.2789, found 394.2784. $[\alpha]_D^{20}$ = 16.0 (*c* = 0.5, $CHCl_3$).

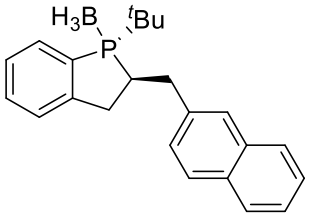
3.37 (1*S*,2*R*)-1-(tert-butyl)-2-(3,5-di-tert-butylbenzyl)-2,3-dihydrophosphindole 1-borane (5j')



Prepared according to general procedure C from **4j'** (2.0 mmol), after a flash column chromatography (hexane : EA = 50:1) afforded the product **5j'** as a colorless solid (645 mg, 79% yield). M.p.: 103.0-103.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.76 (m, 1H), 7.49-7.34 (m, 3H), 7.26-7.20 (m, 1H), 7.17-7.12 (m, 2H), 3.27-3.21 (m, 1H), 3.18-2.96 (m, 2H), 2.43-2.33 (m, 1H), 2.29-2.22 (m, 1H), 1.39 (d, *J* = 1.4 Hz, 18H), 1.23 (dd, *J* = 13.7, 1.3 Hz, 9H), 1.19-0.41 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.3, 144.6,

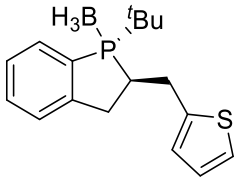
144.4 (d, $J_{C\text{-}P}$ = 10.2 Hz), 134.0 (d, $J_{C\text{-}P}$ = 13.0 Hz), 130.6 (d, $J_{C\text{-}P}$ = 2.3 Hz), 129.5 (d, $J_{C\text{-}P}$ = 6.3 Hz), 126.7 (d, $J_{C\text{-}P}$ = 11.2 Hz), 123.6 (d, $J_{C\text{-}P}$ = 47.7 Hz), 121.1, 120.5, 39.8 (d, $J_{C\text{-}P}$ = 3.7 Hz), 34.9, 31.5, 30.1 (d, $J_{C\text{-}P}$ = 31.0 Hz), 27.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 26.8 (d, $J_{C\text{-}P}$ = 31.4 Hz), 25.2 (d, $J_{C\text{-}P}$ = 2.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.2. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $C_{27}H_{39}P$: 394.2789, found 394.2789. $[\alpha]_D^{20}$ = 33.3 (*c* = 0.5, $CHCl_3$).

3.38 (1*S*,2*S*)-1-(tert-butyl)-2-(naphthalen-2-ylmethyl)-2,3-dihydrophosphindole 1-borane (5k)



Prepared according to general procedure C from **4k** (3.0 mmol), after a flash column chromatography (hexane : EA = 50:1) afforded the product **5k** as a colorless solid (737 mg, 71% yield). M.p.: 118.0-118.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.84 (m, 3H), 7.77-7.63 (m, 2H), 7.59-7.34 (m, 5H), 7.26-7.24 (m, 1H), 3.51-3.44 (m, 1H), 3.35-3.17 (m, 1H), 3.08-3.03 (m, 1H), 3.00-2.82 (m, 2H), 1.26 (dd, *J* = 13.8, 2.9 Hz, 9H), 1.12-0.47 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.3 (d, $J_{C\text{-}P}$= 12.3 Hz), 137.7 (d, $J_{C\text{-}P}$ = 14.1 Hz), 133.6, 132.3, 131.5, 130.8, 130.7, 130.1 (d, $J_{C\text{-}P}$ = 53.1 Hz), 128.4, 127.7, 127.6, 127.5, 127.3 (d, $J_{C\text{-}P}$ = 22.6 Hz), 126.3, 125.7 (d, $J_{C\text{-}P}$ = 7.6 Hz), 125.6. 38.5, 37.6 (d, $J_{C\text{-}P}$ = 5.5 Hz), 32.4 (d, $J_{C\text{-}P}$ = 31.6 Hz), 30.7 (d, $J_{C\text{-}P}$ = 27.7 Hz), 25.5; **^{31}P NMR** (162 MHz, C_6D_6) δ 64.3. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $C_{23}H_{25}P$: 332.1694, found 332.1689. $[\alpha]_D^{20}$ = 70.9 (*c* = 0.5, $CHCl_3$).

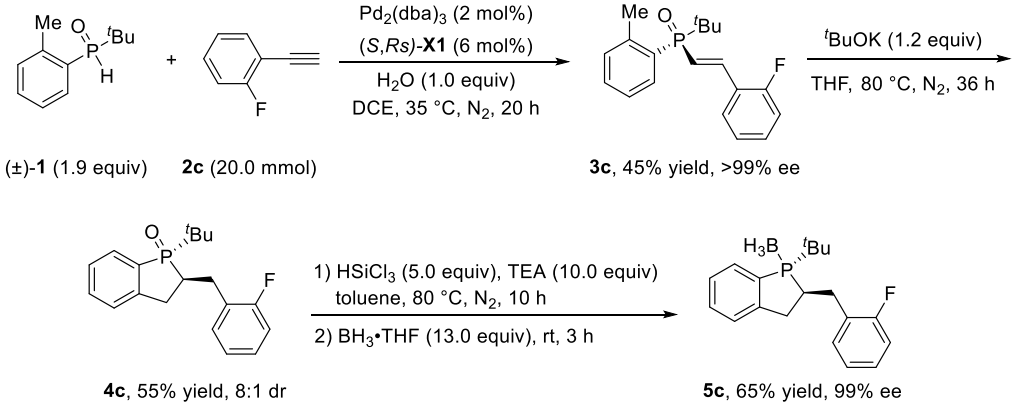
3.39 (1*S*,2*R*)-1-(tert-butyl)-2-(thiophen-2-ylmethyl)-2,3-dihydrophosphindole 1-borane (5l)



Prepared according to general procedure C from **4l** (2.1 mmol), after a flash column

chromatography (hexane : EA = 50:1) afforded the product **5l** as a colorless solid (470 mg, 75% yield). M.p.: 208.0-208.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69-7.62 (m, 1H), 7.48-7.43 (m, 1H), 7.38-7.34 (m, 1H), 7.32-7.28 (m, 1H), 7.22 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.07-6.98 (m, 1H), 6.91-6.89 (m, 1H), 3.60-3.33 (m, 2H), 3.19-2.93 (m, 2H), 2.84-2.81 (m, 1H), 1.22 (d, *J* = 13.7 Hz, 9H), 1.12-0.37 (br., 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.1 (d, *J* = 12.5 Hz), 143.1 (d, $J_{C\text{-}P}$ = 16.0 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.2 Hz), 130.7 (d, $J_{C\text{-}P}$ = 10.3 Hz), 129.8 (d, $J_{C\text{-}P}$ = 53.1 Hz), 127.5 (d, $J_{C\text{-}P}$ = 8.9 Hz), 126.9, 125.7 (d, $J_{C\text{-}P}$ = 7.4 Hz), 125.6, 123.9, 38.8, 33.1 (d, $J_{C\text{-}P}$ = 31.3 Hz), 31.9 (d, $J_{C\text{-}P}$ = 6.6 Hz), 30.6 (d, $J_{C\text{-}P}$ = 27.8 Hz), 25.3 (d, $J_{C\text{-}P}$ = 2.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 64.7. **HRMS** (EI): m/z: $[M\text{-}BH_3]^+$ Calcd for $C_{17}H_{21}PS$: 288.1102, found 288.1094. $[\alpha]_D^{20}$ = 74.4 (*c* = 0.5, $CHCl_3$).

4. Gram-scale synthesis of 5c



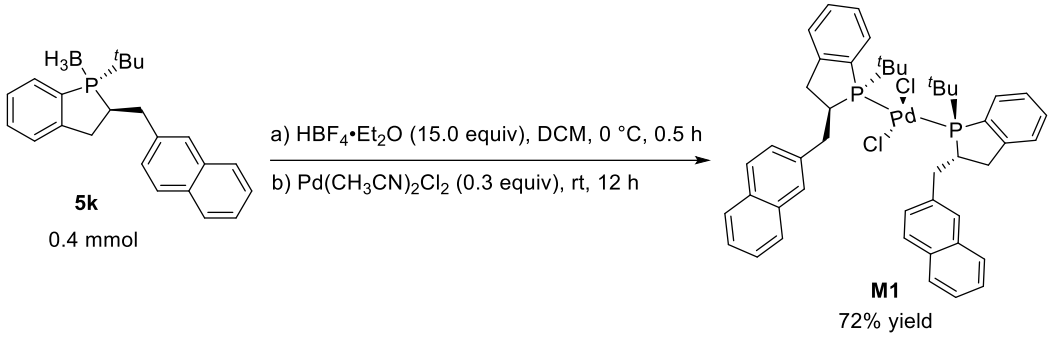
A sealed tube with a magnetic stir bar was charged with $Pd_2(dba)_3$ (0.4 mmol), (*S*, *R*S)-**X1** (1.2 mmol), racemic SPO (38.0 mmol), alkyne **2c** (20.0 mmol) and water (20.0 mmol). Anhydrous DCE (200.0 ml) was then added as solvent. The reaction tube was sealed, frozen by liquid nitrogen and evacuated under vacuum and backfilled with argon three times through a three-way stopcock. The reaction tube was sealed and allowed to stir at 35°C for 24-36 h. On completion, the reaction mixture was cooled to room temperature, solvent was removed in vacuo and the crude reaction mixture was purified on silica gel using hexanes/ethyl acetate as eluent to afford the desired product **3c** (50% yield, 96% ee). Enantiomerically pure level of **3c** could be easily achieved via the operable recrystallization process in good yield (2.84 g, 45% yield, >99% ee).

A sealed tube equipped with a stir bar under argon atmosphere was charged with **3c** (>99% ee, 9.0 mmol) and ^{t}BuOK (1.2 equiv). THF (60.0 mL) was added as solvent and then the vial was capped. The reaction mixture was stirred at 80 °C for 20-36 h. On completion, solvent was removed in vacuo and the crude reaction mixture was purified on silica gel using CH_3OH/ethyl acetate as eluent to afford the major isomer **4c** (1.56 g, 55% yield) and minor isomer **4c'** as a colorless solid (195 mg, 7% yield).

To a solution of **4c** (5.0 mmol, 1 equiv), triethylamine (50.0 mmol, 10 equiv) in toluene (50 mL) at rt was added trichlorosilane (25.0 mmol, 5 equiv). The mixture was heated to 80 °C and stirred under nitrogen for 12 h. To the mixture at 0 °C was added BH_3·THF complex (1.0 M, 65.0 mmol), and the resulting mixture was stirred at rt for about 2 h.

Water (60.0 mL) was then added and the aqueous layer was extracted three times with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and removed in vacuo and the residue was purified by flash column chromatography on silica gel using hexanes/ethyl acetate as eluent to provide the title phosphine borane adducts **5c** (1.02 g, 65% yield).

General experimental procedure for synthesis of M1:



A sealed tube equipped with a stir bar under argon atmosphere was charged with **5k** (>99% ee, 0.4 mmol) and DCM (2.0 mL) was added as solvent and then the vial was capped. The tube was cooled to 0 °C, then HBF_4•Et_2O[3] (15.0 equiv) was added with a syringe. The reaction mixture was stirred at 0 °C for 0.5 h. On completion, Water (10.0 mL) was then added and the aqueous layer was extracted two times with DCM (2*2 mL). The combined organic extracts were switched to another tube and $Pd(CH_3CN)_2Cl_2$ (0.3 equiv) was added. The reaction mixture was stirred at rt for 12 h. On completion, Water (10.0 mL) was then added and the aqueous layer was extracted three times with DCM. The combined organic extracts were dried over Na_2SO_4 and removed in vacuo and the residue was purified by flash column chromatography on silica gel using hexanes/ethyl acetate as eluent to provide the title Pd (II) complex **M1** (73 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59-8.34 (m, 1H), 7.83 (ddd, *J* = 14.5, 8.8, 5.4 Hz, 3H), 7.69 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.50-7.39 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.26 (s, 1H), 4.79-4.33 (m, 1H), 3.23 (d, *J* = 12.3 Hz, 1H), 3.04 (t, *J* = 4.9 Hz, 2H), 2.87 (t, *J* = 12.9 Hz, 1H), 1.39 (t, *J* = 7.4 Hz, 9H); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 57.4.

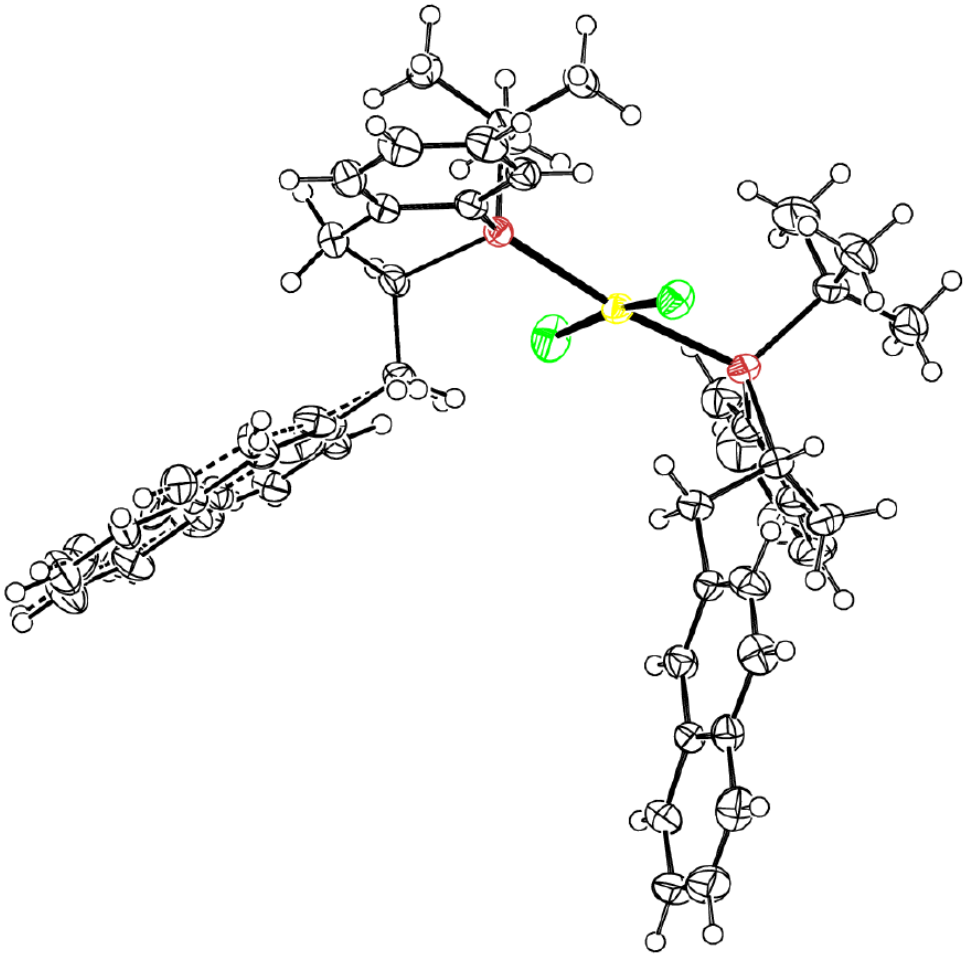


Figure S1. ORTEP drawing of **M1** (thermal ellipsoids set at 50% probability).

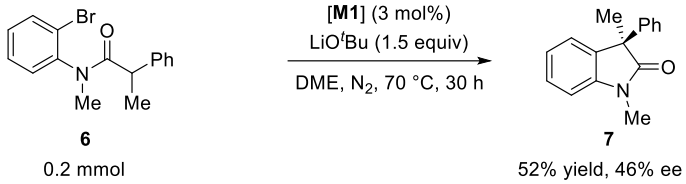
Recrystallization from pentane/CH_2Cl_2 afforded single crystals suitable for X-ray diffraction analysis, which allowed determination of the absolute configurations of the stereocenters.[4]

Table S4. Crystal data and structure refinement for ga_210702f_a.

Identification code	ga_210702f_a	
Empirical formula	C46 H50 Cl2 P2 Pd	
Formula weight	842.10	
Temperature	173(2) K	
Wavelength	1.34138 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 24.3145(6) Å	α= 90 °.
	b = 8.8177(2) Å	β= 106.7980(10) °.
	c = 19.6690(5) Å	γ = 90 °.
Volume	4037.05(17) $Å^3$	
Z	4	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	3.970 mm^{-1}	
F(000)	1744	
Crystal size	0.180 x 0.090 x 0.090 mm^3	
Theta range for data collection	3.344 to 61.499 °.	
Index ranges	-31<=h<=31, -11<=k<=11, -25<=l<=24	
Reflections collected	28300	
Independent reflections	9324 [R(int) = 0.0485]	
Completeness to theta = 53.594 °	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.752 and 0.536	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9324 / 141 / 557	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0625	
R indices (all data)	R1 = 0.0351, wR2 = 0.0649	
Absolute structure parameter	0.012(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.369 and -1.029 e.$Å^{-3}$	

General experimental procedure for synthesis of 7, 9, 12:

Synthesis and date of substrate **6**,[5] **8**,[6] and **10**[7] were matched of the reported literature.

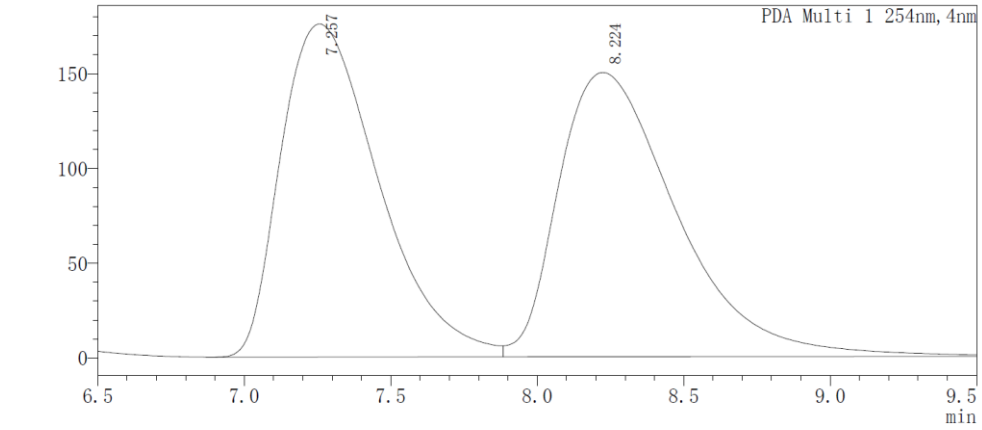


6
0.2 mmol

7
52% yield, 46% ee

To a sealed tube was added **M1** (3 mol%), LiO^{t}Bu (1.5 equiv), **6** (0.2 equiv). The flask was evacuated and refilled with argon and DME (3.0 mL) was added to the tube. The reaction mixture was kept stirring at 70 ºC for 30 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography (hexanes: EA = 10:1) afforded the desired product **7** as a yellow oil (25 mg, 52% yield, 46% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.26 (m, 6H), 7.23-7.21 (m, 1H), 7.12 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 7.8 Hz, 1H), 3.27 (s, 3H), 1.82 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.5, 143.3, 140.8, 134.9, 128.5, 128.1, 127.2, 126.7, 124.2, 122.8, 108.3, 52.2, 26.5, 23.9; **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{16}H_{15}NO$: 237.1154, found 237.1149. HPLC (OD-H, 2-propanol /n-hexane = 1/99, flow rate = 1.0 mL/min, l = 254 nm) tR = 7.2 min (major), 8.2 min (minor). $[\alpha]_D^{20}$ = 96.1 (c = 0.5, $CHCl_3$).

<Chromatogram>

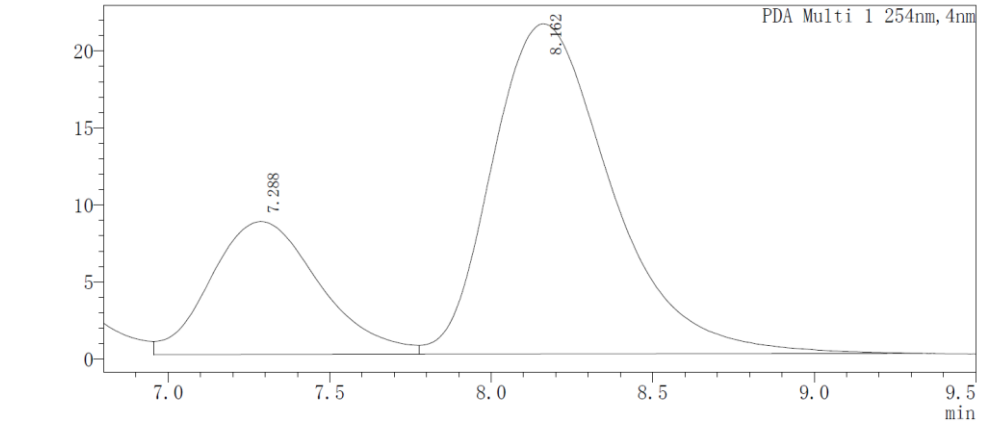


<Peak Table>

PDA Ch1 254nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	7.257	175796	53.947	4098425	49.199
2	8.224	150070	46.053	4231832	50.801
Total		325865	100.000	8330257	100.000

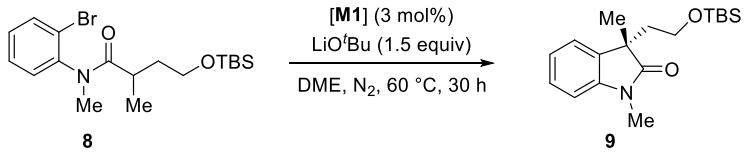
<Chromatogram>



<Peak Table>

PDA Ch1 254nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	7.288	8627	28.696	202519	26.920
2	8.162	21438	71.304	549789	73.080
Total		30065	100.000	752308	100.000

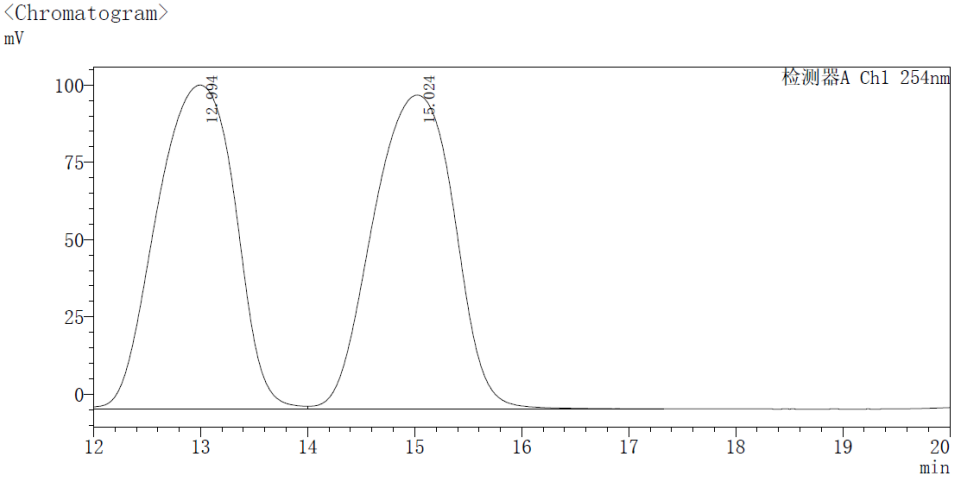


8
0.2 mmol

9
60% yield, 73% ee

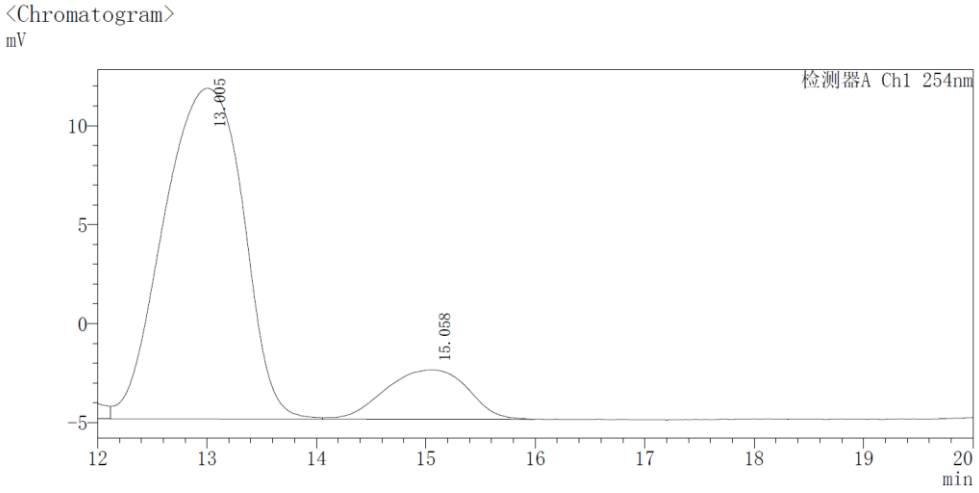
To a sealed tube was added **M1** (3 mol%), LiO^{t}Bu (1.5 equiv), **8** (0.2 equiv). The flask was evacuated and refilled with argon and DME (3.0 mL) was added to the tube. The

reaction mixture was kept stirring at 60 ºC for 30 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography (hexanes: EA = 10:1) afforded the desired product **9** as a yellow oil (38 mg, 60% yield, 73% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.24 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.11-7.01 (m, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.38 (t, *J* = 6.5 Hz, 2H), 3.21 (s, 3H), 2.37-2.18 (m, 1H), 2.02-1.96 (m, 1H), 1.38 (s, 3H), 0.79 (s, 9H), 0.11 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.5, 143.3, 133.7, 127.6, 122.7, 122.2, 107.9, 59.6, 46.6, 40.4, 26.2, 25.8, 24.8, 18.2. **HRMS** (ESI): m/z: $[M]^+$ Calcd for $C_{18}H_{29}NO_2Si$: 319.1968, found 320.2102. HPLC (OZ-H, 2-propanol /n-hexane = 1/99, flow rate = 0.6 mL/min, l = 254 nm) tR = 13.0 min (major), 15.0 min (minor). $[\alpha]_D^{20}$ = -126.1 (*c* = 0.5, $CHCl_3$).



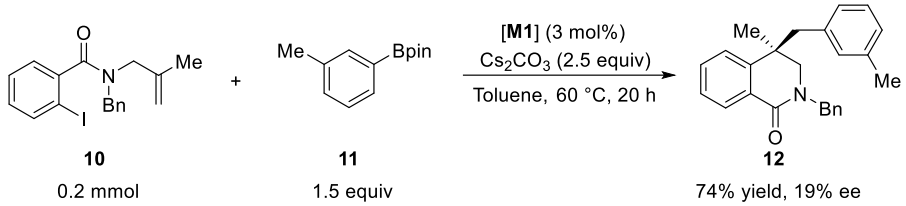
检测器A Ch2 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	12.995	104745	50.783	5352005	49.978
2	15.027	101513	49.217	5356795	50.022
总计		206259	100.000	10708800	100.000



检测器A Ch2 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	13.010	16713	86.981	846123	86.579
2	15.066	2501	13.019	131162	13.421
总计		19215	100.000	977285	100.000

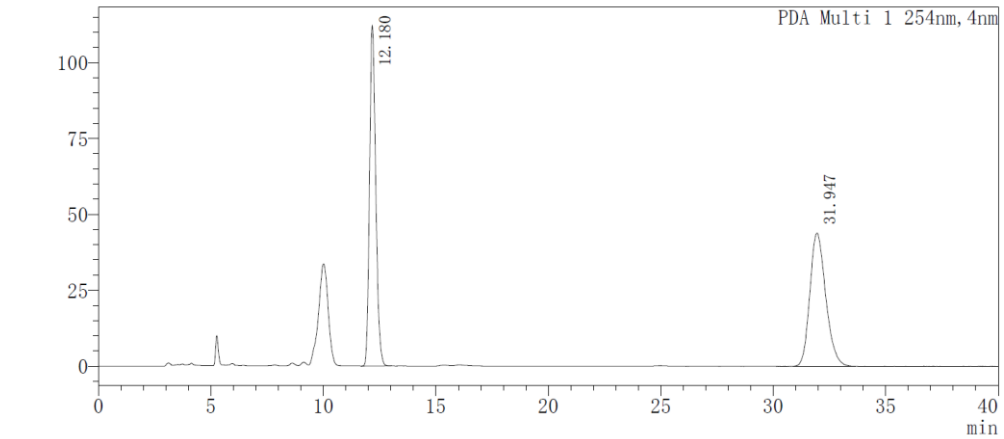


10 0.2 mmol | **11** 1.5 equiv | **12** 74% yield, 19% ee

To a sealed tube was added **M1** (3 mol%), Cs_2CO_3 (2.5 equiv), **11** (1.5 equiv), *N*-allyl carboxamide **10** (0.2 mmol). The flask was evacuated and refilled with argon and toluene (2.0 mL) was added to the tube. The reaction mixture was kept stirring at 60 °C for 20 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography (hexanes: EA = 10:1) afforded the desired product **12** as a yellow oil (52 mg, 74% yield, 19% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 5.6, 3.3 Hz, 1H), 7.46-7.26 (m, 7H), 7.13-7.01 (m, 2H), 6.98-6.90 (m, 1H), 6.57-6.55 (m, 2H), 5.02 (d, *J* = 14.4 Hz, 1H), 4.72 (d, *J* = 14.4 Hz, 1H), 3.41 (d, *J* = 12.6 Hz, 1H), 3.14 (d, *J* = 12.6 Hz, 1H), 2.85 (d, *J* = 13.2 Hz, 1H), 2.62 (d, *J* = 13.2 Hz, 1H), 2.26 (s, 3H), 1.24 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4, 145.0, 137.2, 136.9, 136.7, 131.5, 131.4, 128.7, 128.6, 128.6, 128.1, 127.6, 127.5,127.5, 127.1, 126.9, 124.9, 55.6, 50.9, 45.8, 37.9, 22.0, 21.3. **HRMS** (EI): m/z: $[M]^+$ Calcd for $C_{25}H_{25}NO$: 355.1936, found 355.1935. HPLC

(AD-H, 2-propanol /n-hexane = 10/90, flow rate = 1.0 mL/min, l = 254 nm) tR = 12.1 min (major), 32.1 min (minor). $[\alpha]_D^{20}$ = -86.1 (*c* = 0.5, $CHCl_3$).

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

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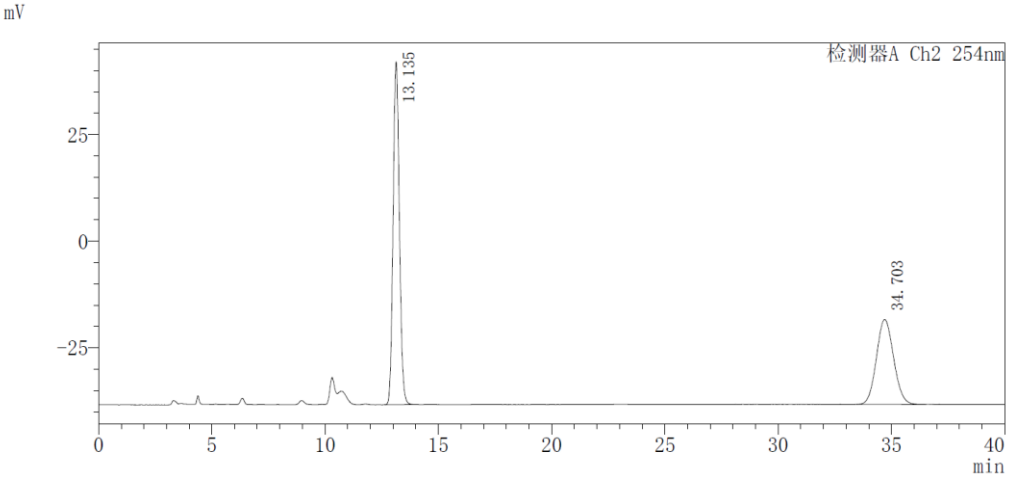
Total		155959	100.000	4309112	100.000



检测器A Ch2 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	13.135	1554009	80374	59.631		V	
2	34.703	1052032	19934	40.369		S	
总计		2606041	100307				

Reference:

[1] Q. Dai, L. Liu, Y. Qian, W. Li, J. Zhang, *Angew. Chem. Int. Ed.* **2020**, *59*, 2.

[2] W. Tang, B. Qu, A. G. Capacci, S. Rodriguez, X. Wei, N. Haddad, B. Narayanan, S. Ma, N. Grinberg, N. K. Yee, D. Krishnamurthy, C. H. Senanayake, *Org. Lett.* **2010**, *12*, 176.

[3] R. Huber, A. Passera, E. Gubler, A. Mezzetti, *Adv. Synth. Catal.* **2018**, *360*, 2900.

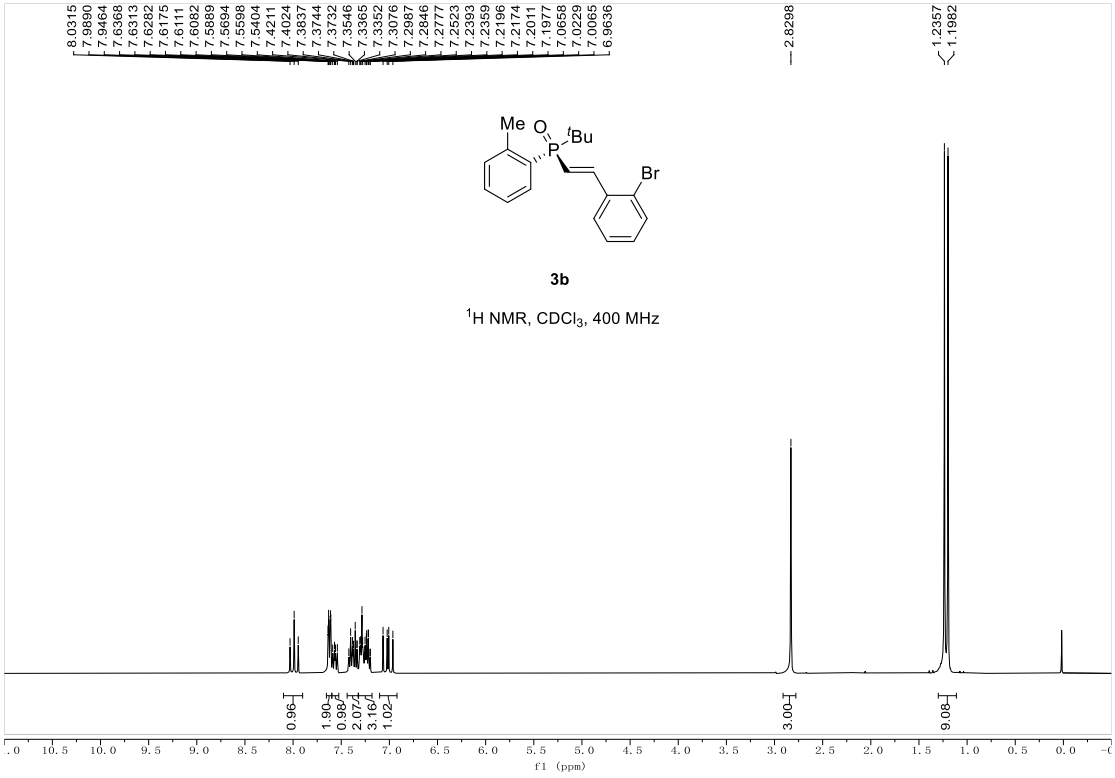
[4] CCDC 2123418 (**M1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

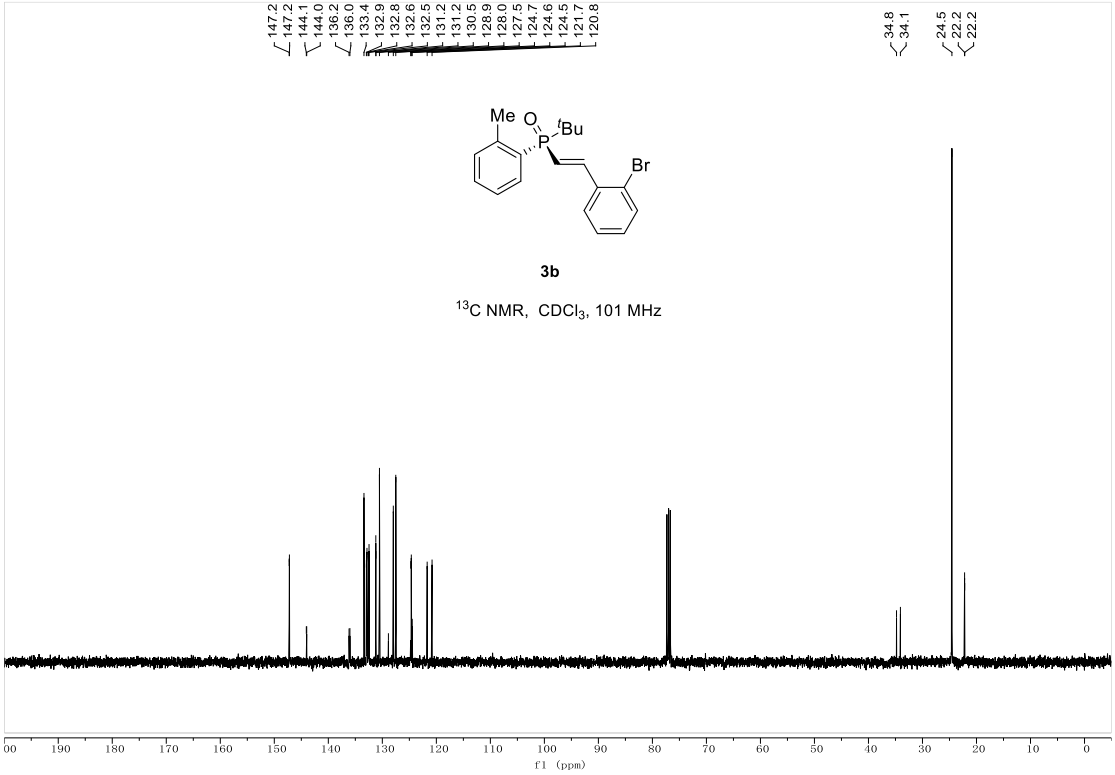
[5] (a) S. Lee, J. F. Hartwig, *J. Org. Chem.* **2001**, *66*, 3402; (b) E. P. Kündig, T. M. Seidel, Y. Jia, G. Bernardinelli, *Angew. Chem.* **2007**, *119*, 8636.

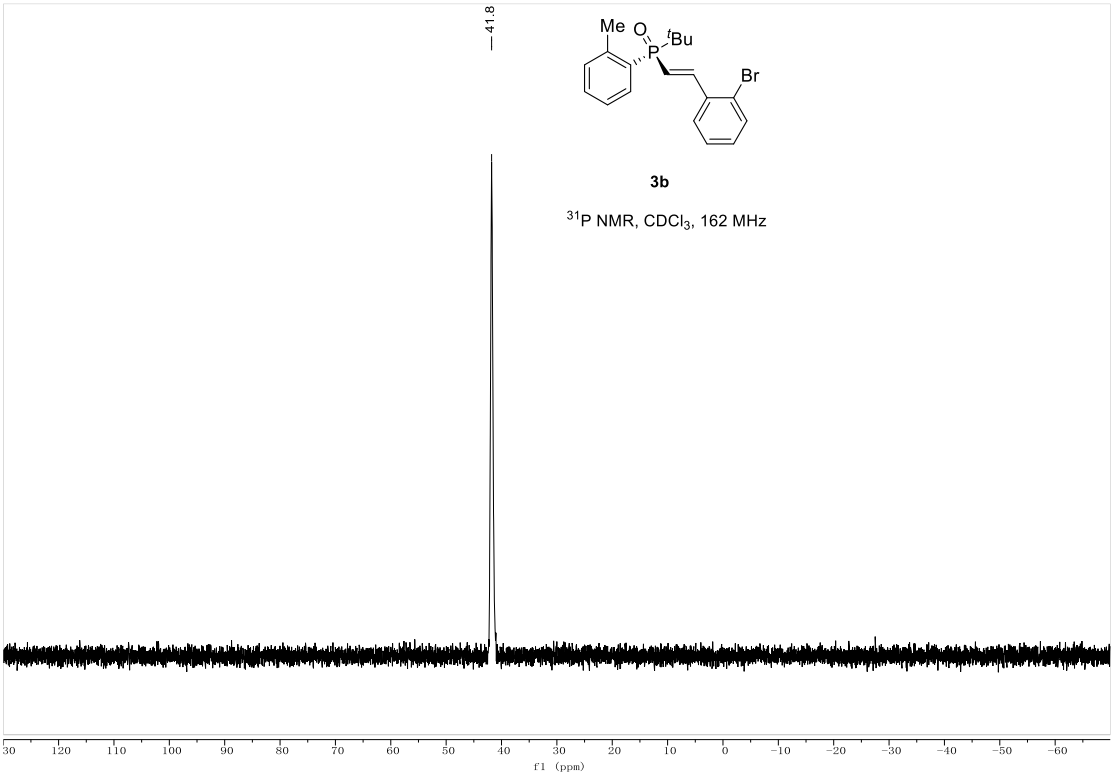
[6] T. Y. Zhang, H. Zhang, *Tetrahedron Letters* **2002**, *43*, 1363.

[7] Q. Chen, S. Li, X. Xie, H. Guo, J. Yang, J. Zhang, *Org. Lett.* **2021**, *23*, 4099.

6. NMR spectra of products:



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P
Br
3b
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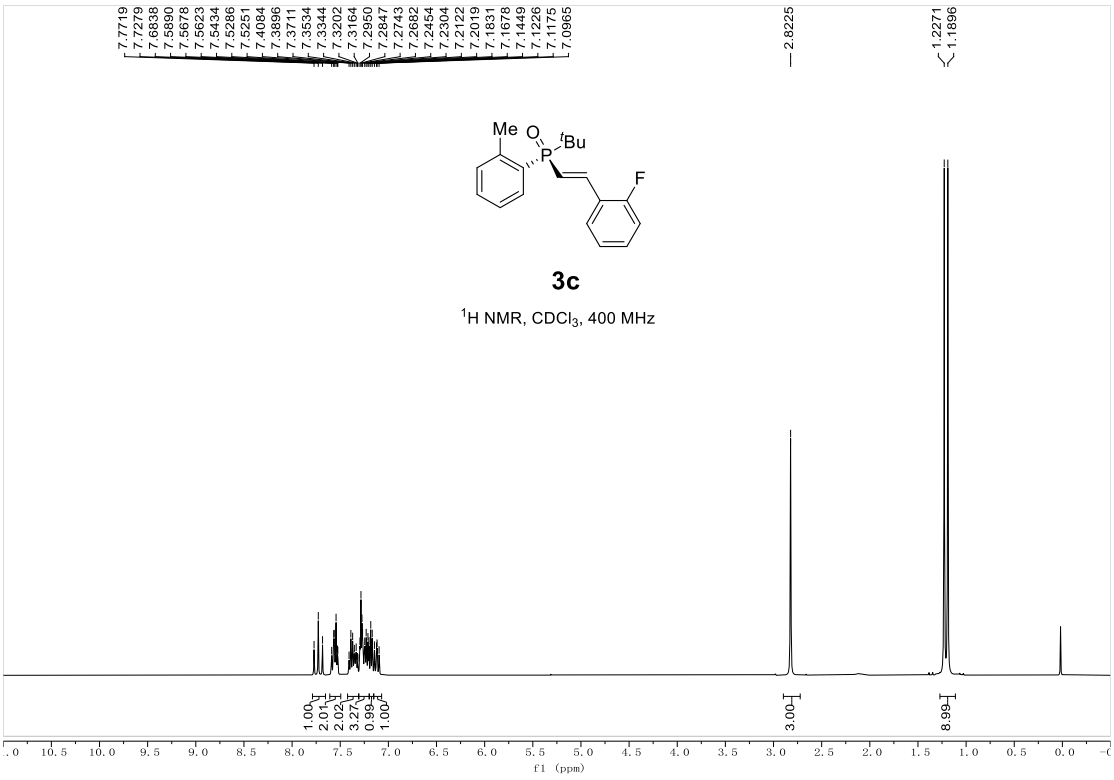
f1 (ppm)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7.3896
7.3711
7.3534
7.3344
7.3202
7.3164
7.2950
7.2847
7.2743
7.2682
7.2454
7.2304
7.2122
7.2019
7.1831
7.1678
7.1449
7.1226
7.1175
7.0965
2.8225
1.2271
1.1896
Me
O
tBu
P
F
3c
1H NMR, CDCl3, 400 MHz
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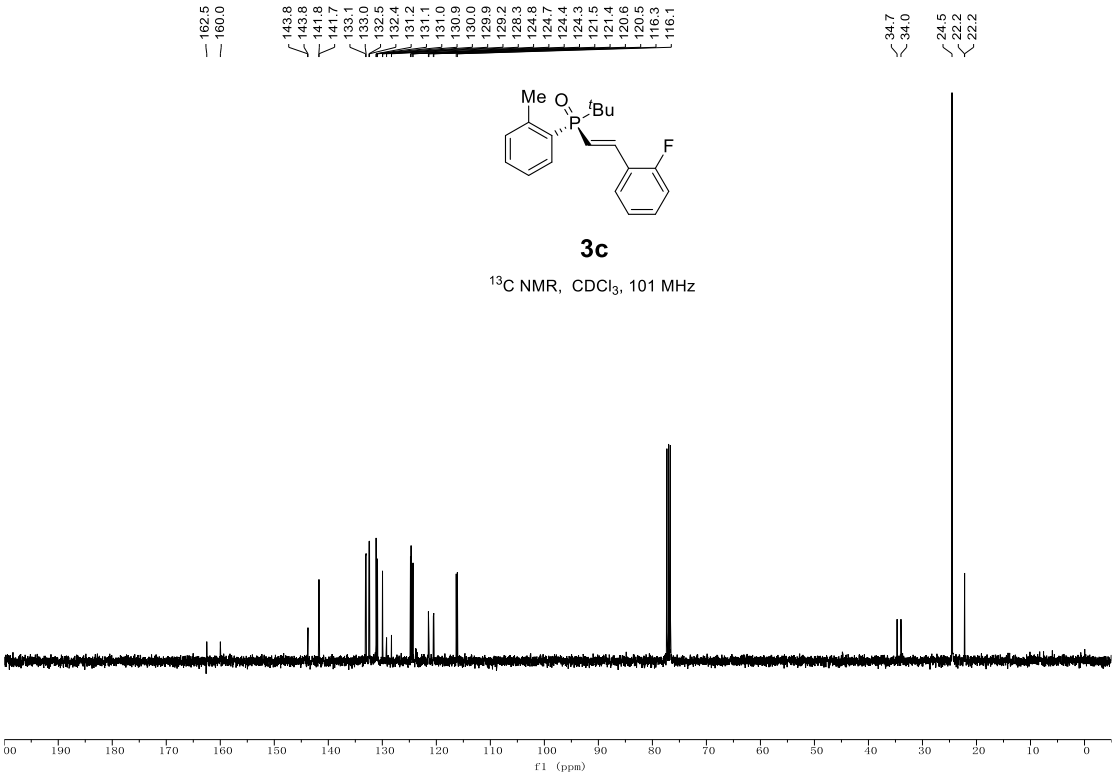
2.01
2.02
3.27
0.99
1.00
3.00
8.99
f1 (ppm)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131.2
131.1
131.0
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130.0
129.9
129.2
128.3
124.8
124.7
124.4
124.3
121.5
121.4
120.6
120.5
116.3
116.1
34.7
34.0
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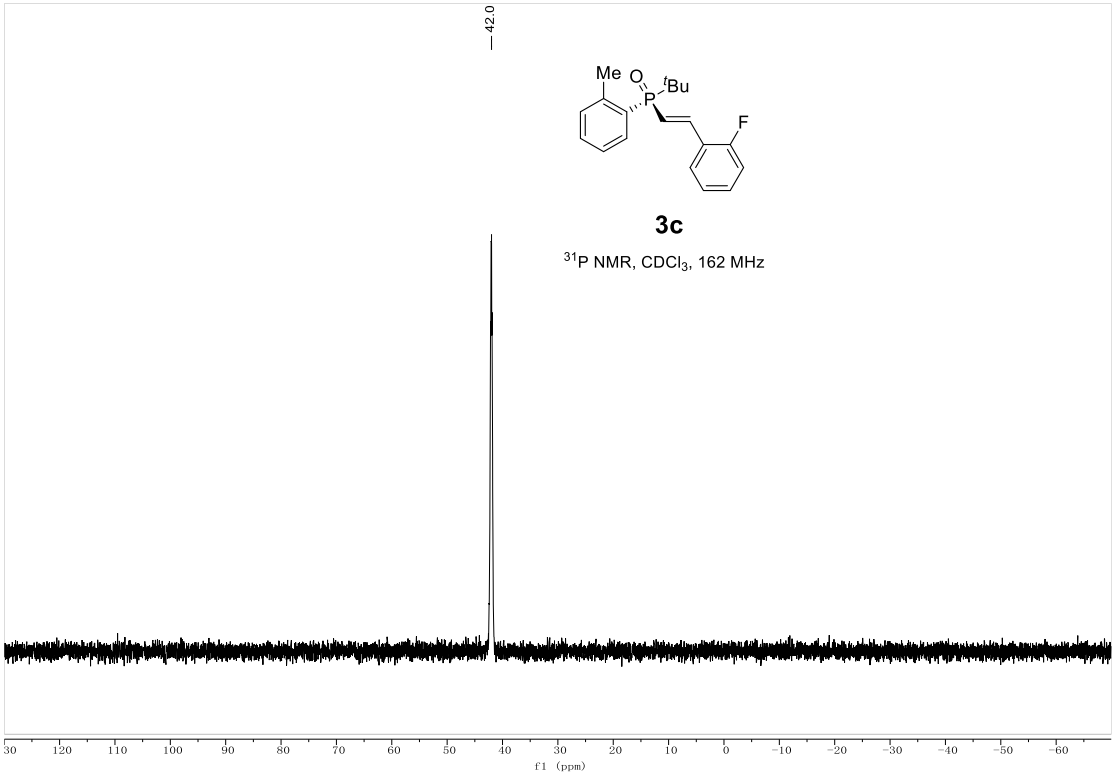
22.2
22.2
Me
O
tBu
P
F
3c
13C NMR, CDCl3, 101 MHz
f1 (ppm)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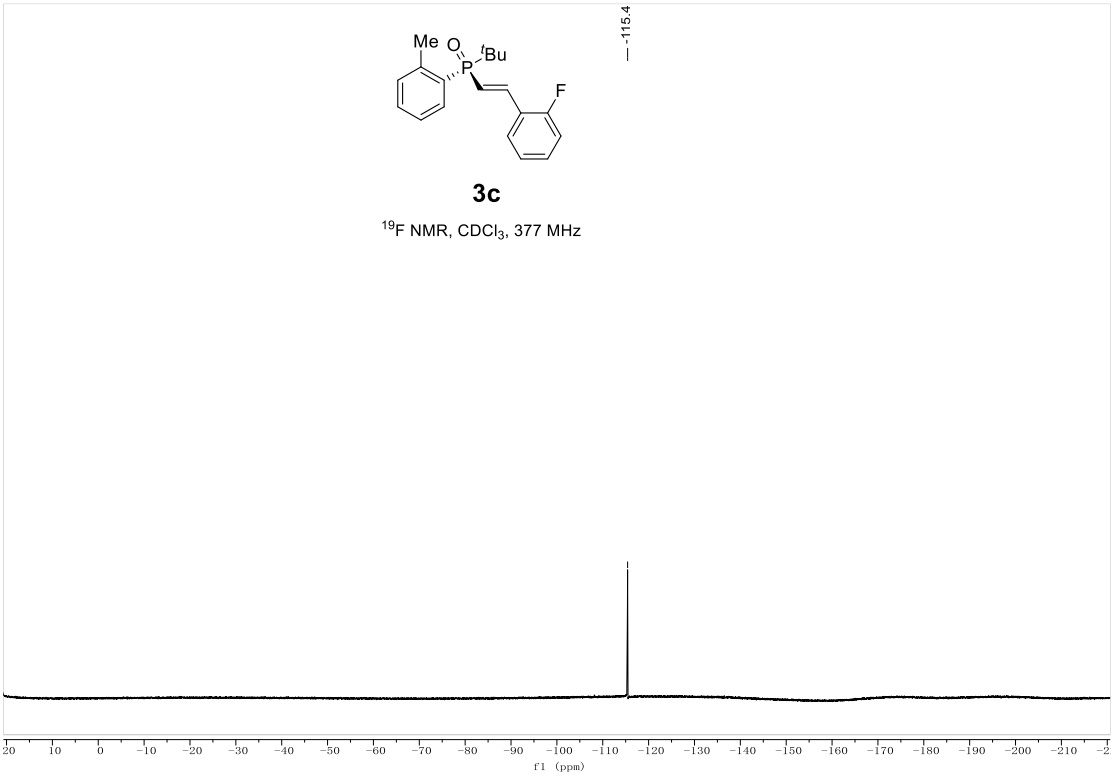
3c
31P NMR, CDCl3, 162 MHz
f1 (ppm)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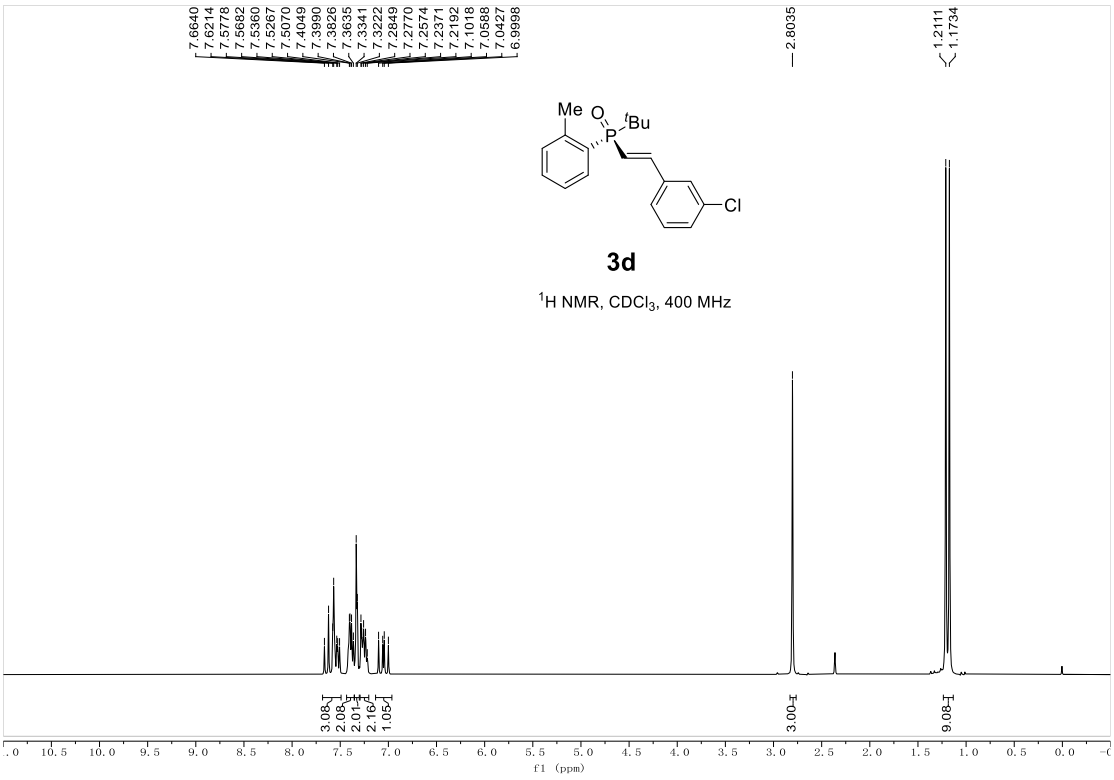
P
F
3c
19F NMR, CDCl3, 377 MHz
f1 (ppm)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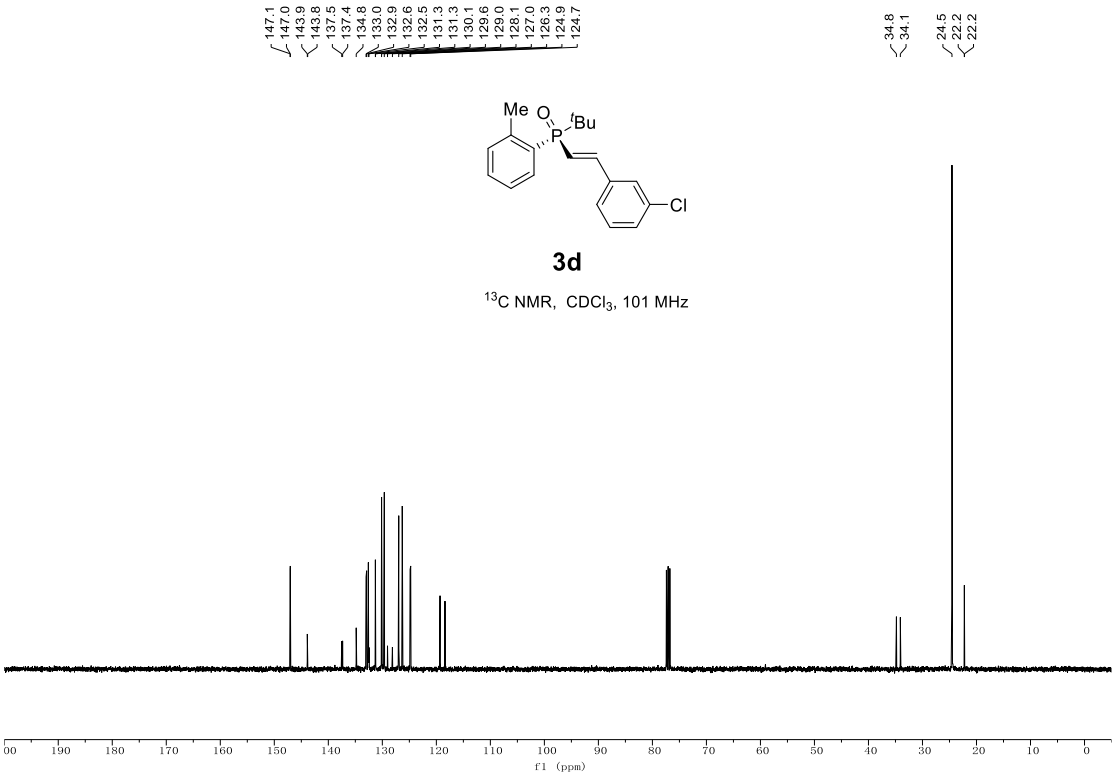
7.5360
7.5267
7.5070
7.4049
7.3990
7.3826
7.3635
7.3341
7.3222
7.2849
7.2770
7.2574
7.2371
7.2192
7.1018
7.0588
7.0427
6.9998
2.8035
1.2111
1.1734
Me
O
tBu
P
Cl
3d
1H NMR, CDCl3, 400 MHz
3.08
2.08
2.01
2.16
1.05
3.00
9.08
f1 (ppm)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137.4
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133.0
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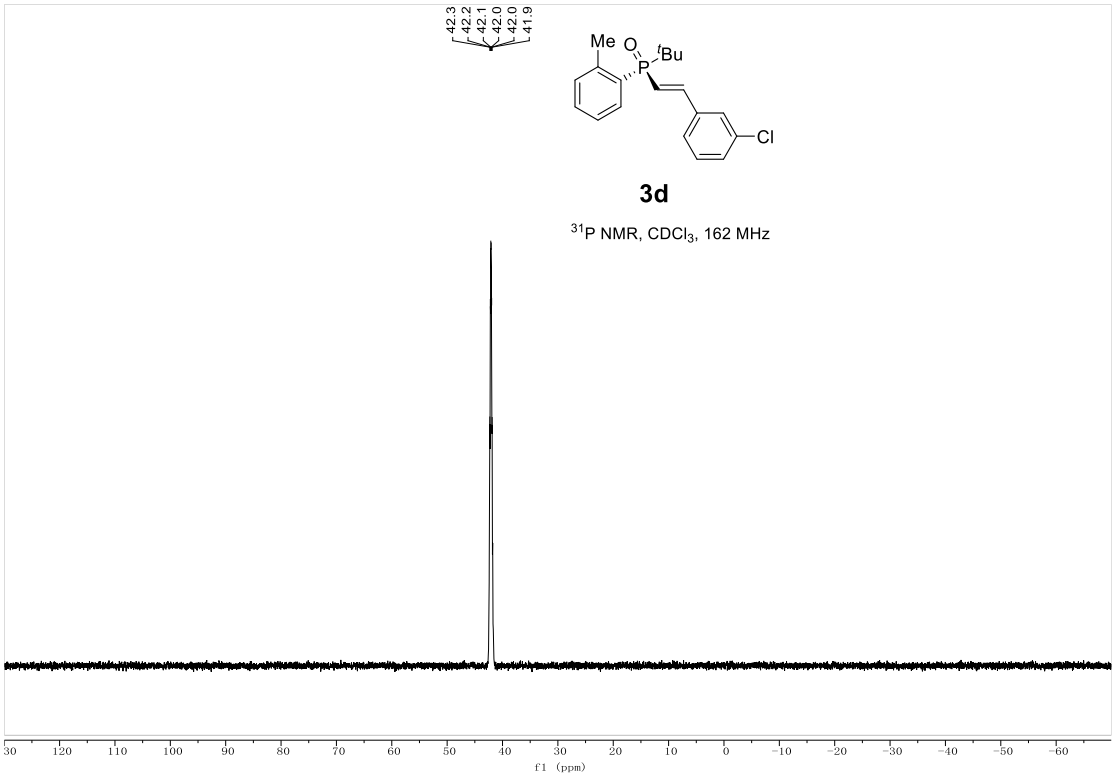
132.5
131.3
131.3
130.1
129.6
129.0
128.1
127.0
126.3
124.9
124.7
34.8
34.1
24.5
22.2
22.2
Me
O
P
tBu
Cl
3d
13C NMR, CDCl3, 101 MHz
f1 (ppm)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42.2
42.1
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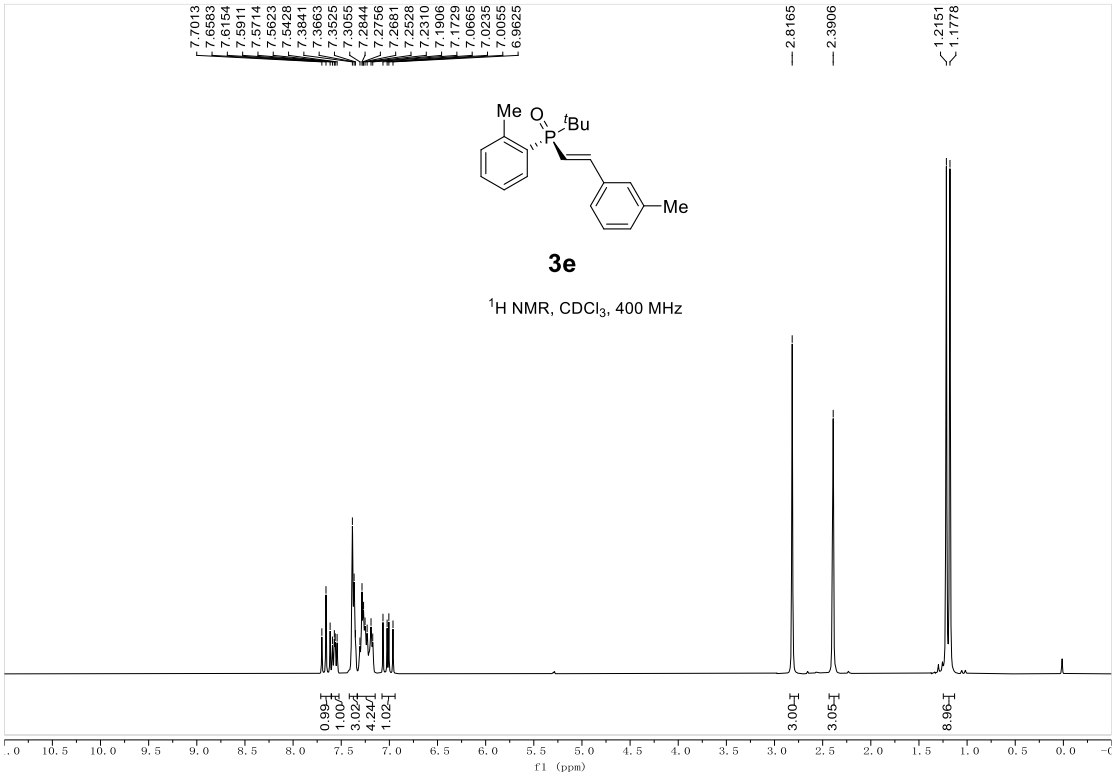
42.0
41.9
Me
O
P
tBu
Cl
3d
31P NMR, CDCl3, 162 MHz
f1 (ppm)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7.5714
7.5623
7.5428
7.3841
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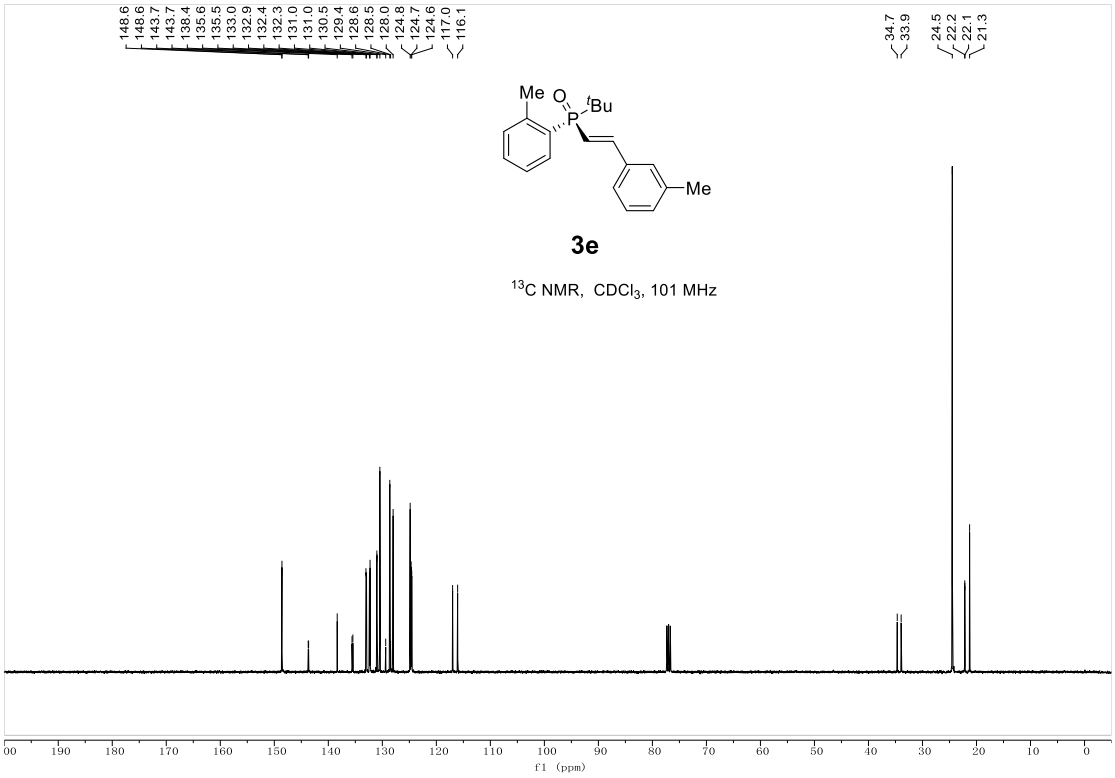
7.3055
7.2844
7.2756
7.2681
7.2528
7.2310
7.1906
7.1729
7.0665
7.0235
7.0055
6.9625
2.8165
2.3906
1.2151
1.1778
Me
O
P
tBu
Me
3e
1H NMR, CDCl3, 400 MHz
0.99
1.00
3.02
4.24
1.02
3.00
3.05
8.96
f1 (ppm)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143.7
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135.6
135.5
133.0
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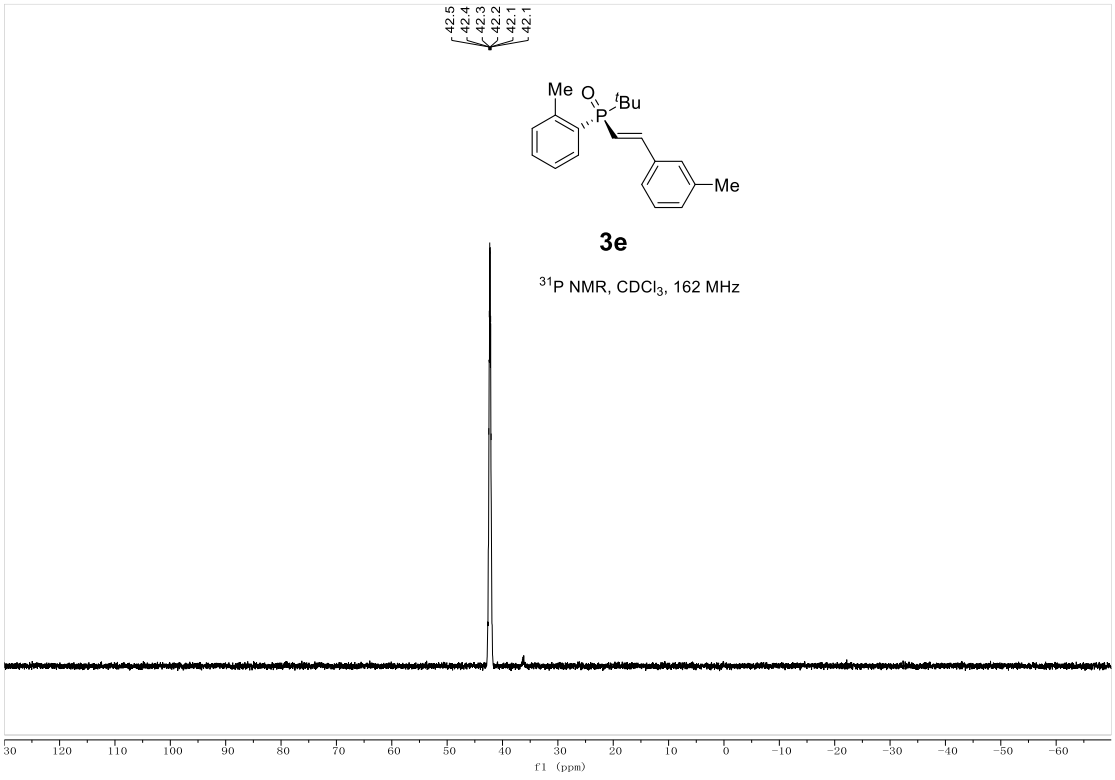
132.4
132.3
131.0
131.0
130.5
129.4
128.6
128.5
128.0
124.8
124.7
124.6
117.0
116.1
34.7
33.9
24.5
22.2
22.1
21.3
Me
O
P
tBu
Me
3e
13C NMR, CDCl3, 101 MHz
f1 (ppm)


42.5
42.4
42.3
42.2
42.1
42.1
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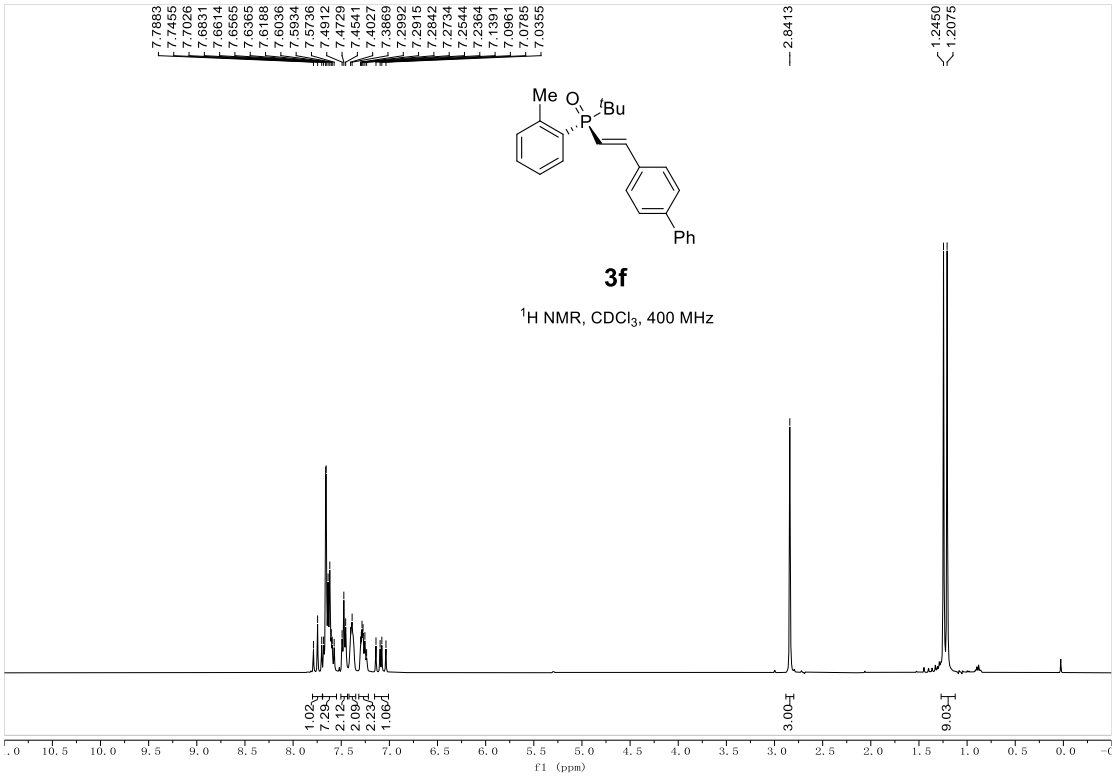
O
P
tBu
Me
3e
31P NMR, CDCl3, 162 MHz
f1 (ppm)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7.5736
7.4912
7.4729
7.4541
7.4027
7.3869
7.2992
7.2915
7.2842
7.2734
7.2544
7.2364
7.1391
7.0961
7.0785
7.0355
2.8413
1.2450
1.2075
Me
O
P
tBu
Ph
3f
1H NMR, CDCl3, 400 MHz
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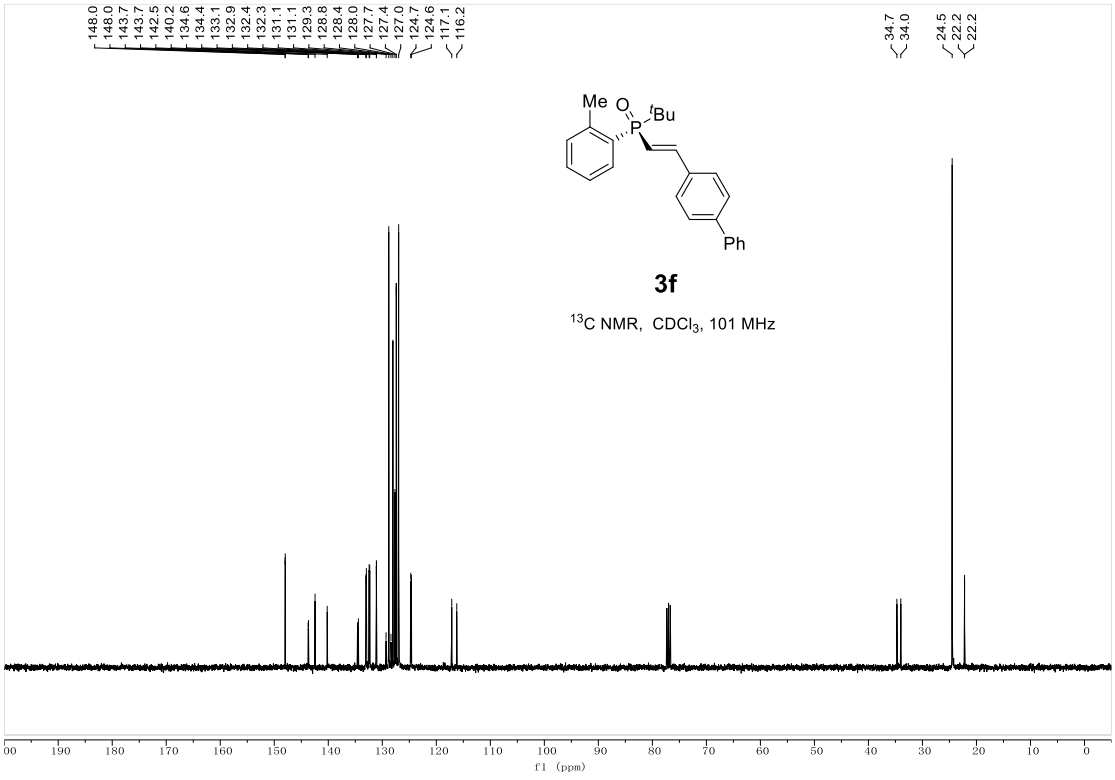
7.29
2.12
2.09
2.23
1.06
3.00
9.03
f1 (ppm)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140.2
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132.4
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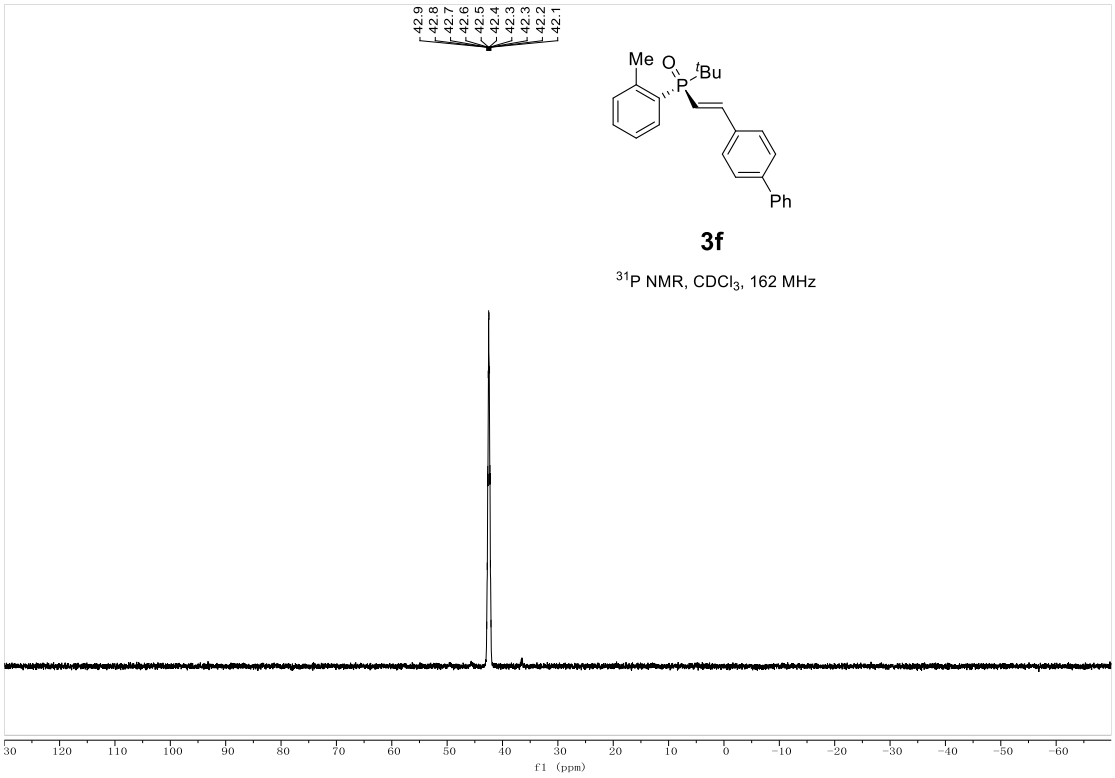
131.1
131.1
129.3
128.8
128.4
128.0
127.7
127.4
127.0
124.7
124.6
117.1
116.2
34.7
34.0
24.5
22.2
22.2
Me
O
P
tBu
Ph
3f
13C NMR, CDCl3, 101 MHz
f1 (ppm)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42.8
42.7
42.6
42.5
42.4
42.3
42.3
42.2
42.1
Me
O
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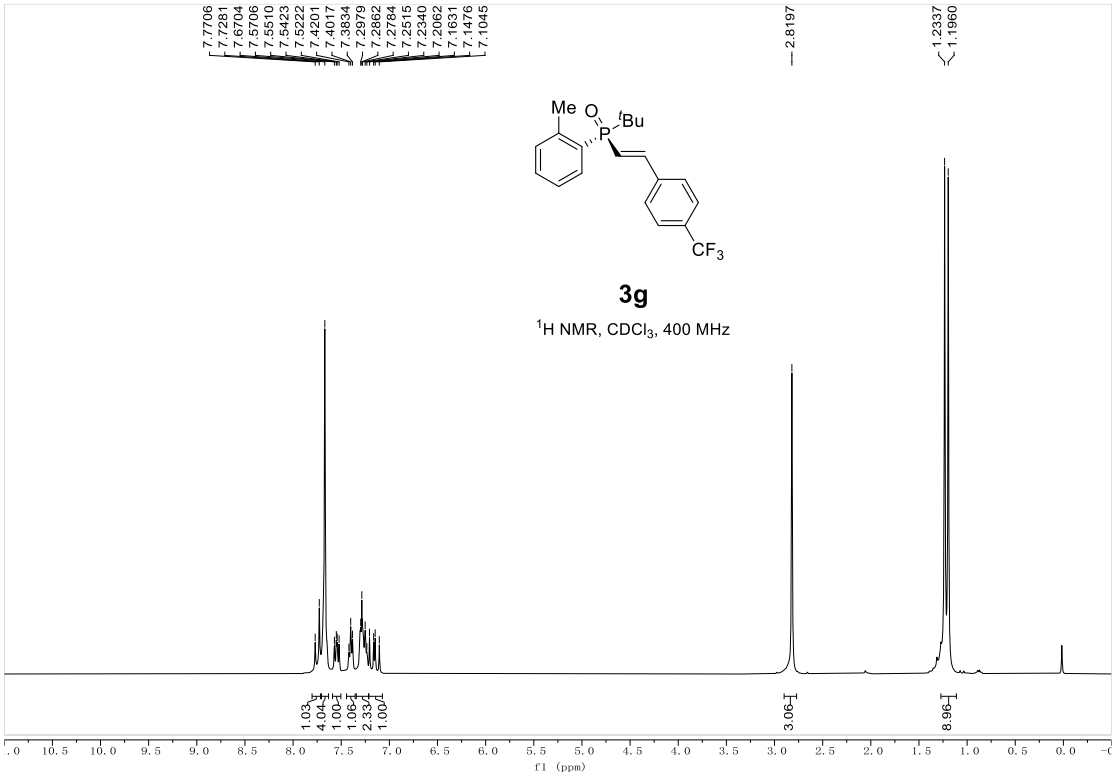
P
Ph
3f
31P NMR, CDCl3, 162 MHz
f1 (ppm)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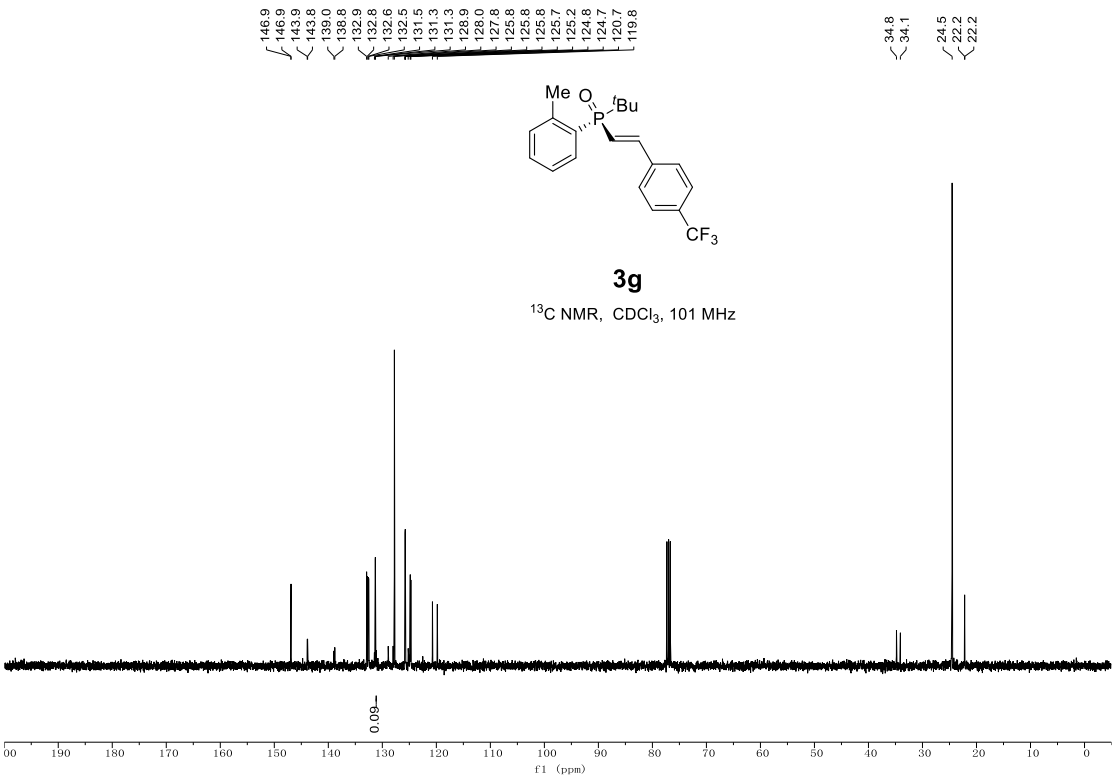
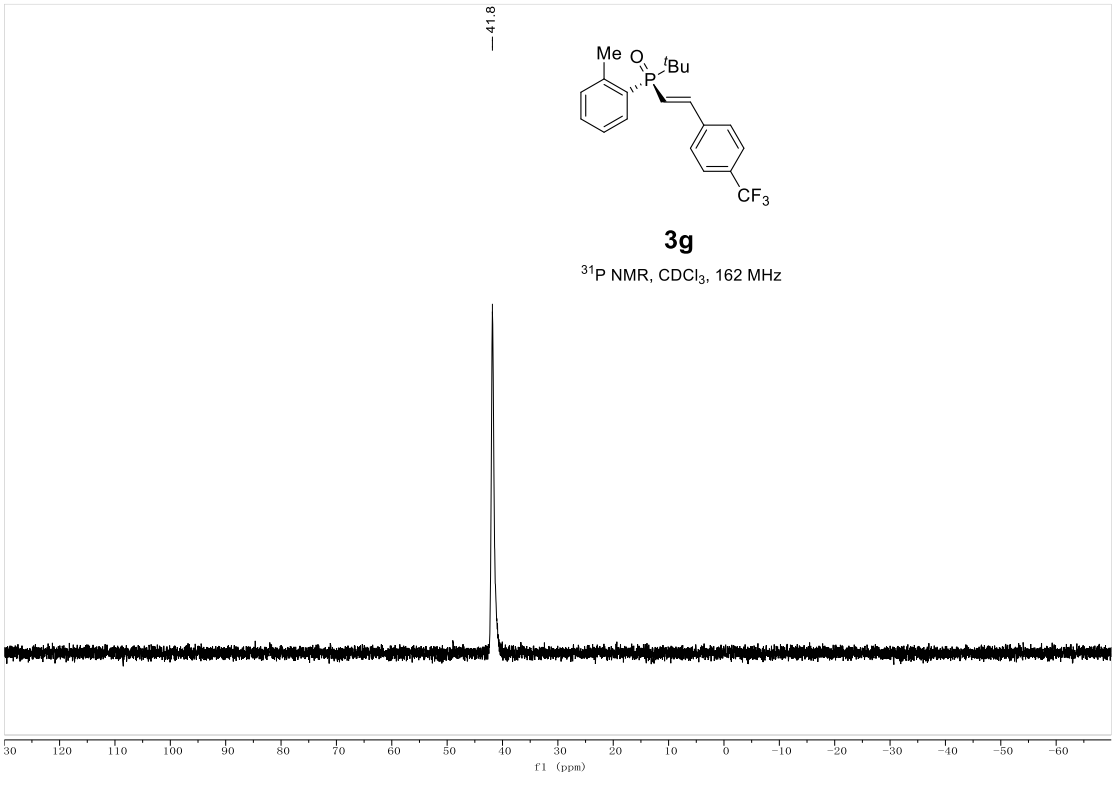
7.2862
7.2784
7.2515
7.2340
7.2062
7.1631
7.1476
7.1045
2.8197
1.2337
1.1960
Me
O
tBu
P
CF3
3g
1H NMR, CDCl3, 400 MHz
1.03
4.04
1.00
1.06
2.33
1.00
3.06
8.96
f1 (ppm)



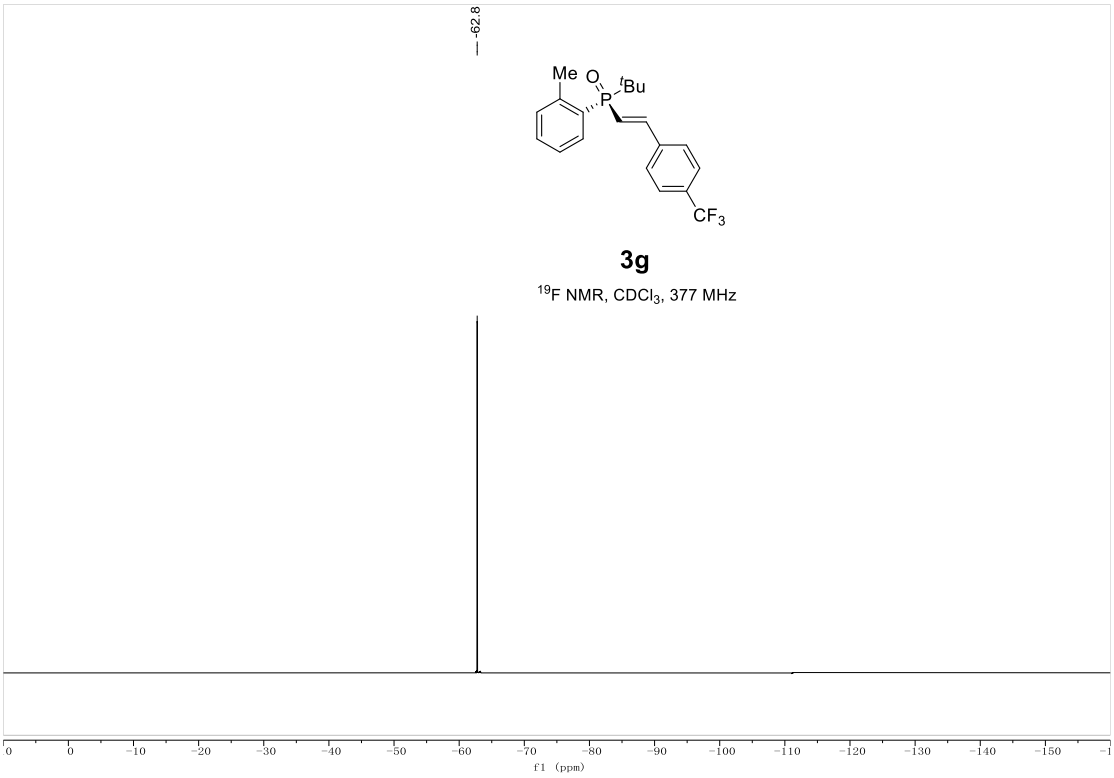
3g

^{13}C NMR, $CDCl_3$, 101 MHz



3g

^{31}P NMR, $CDCl_3$, 162 MHz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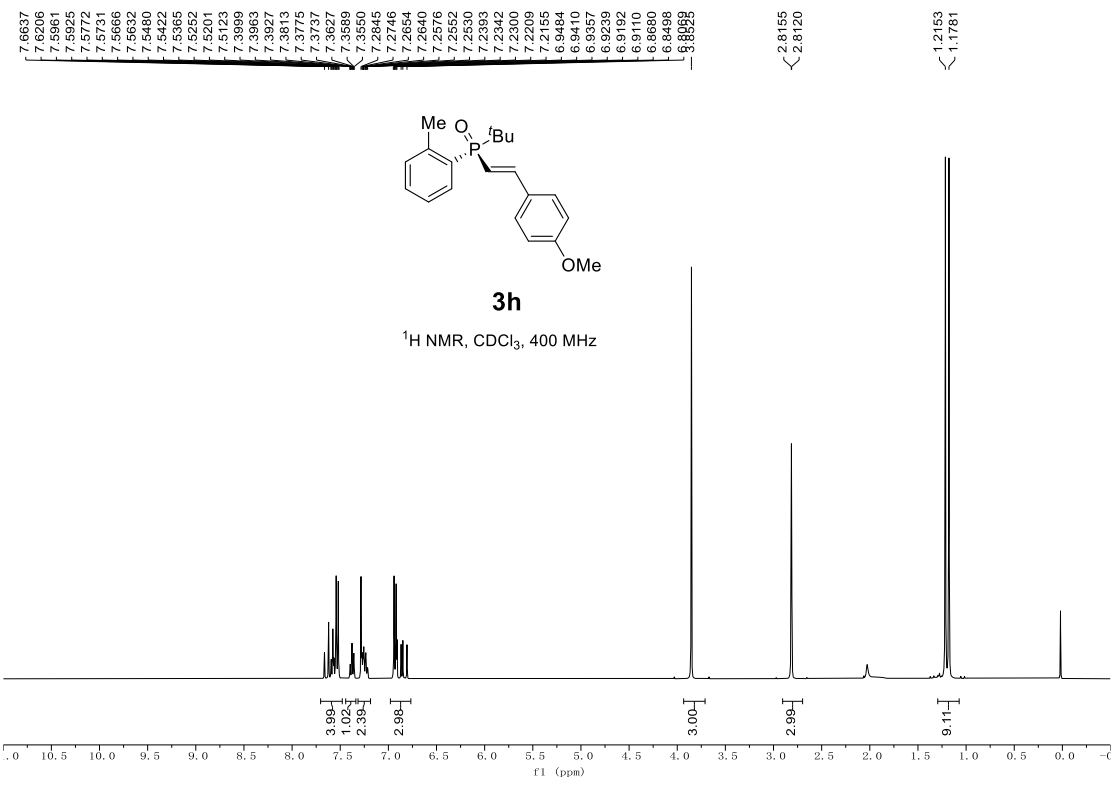
O
P
tBu
CF3
3g
19F NMR, CDCl3, 377 MHz
f1 (ppm)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O
P
tBu
OMe
3h
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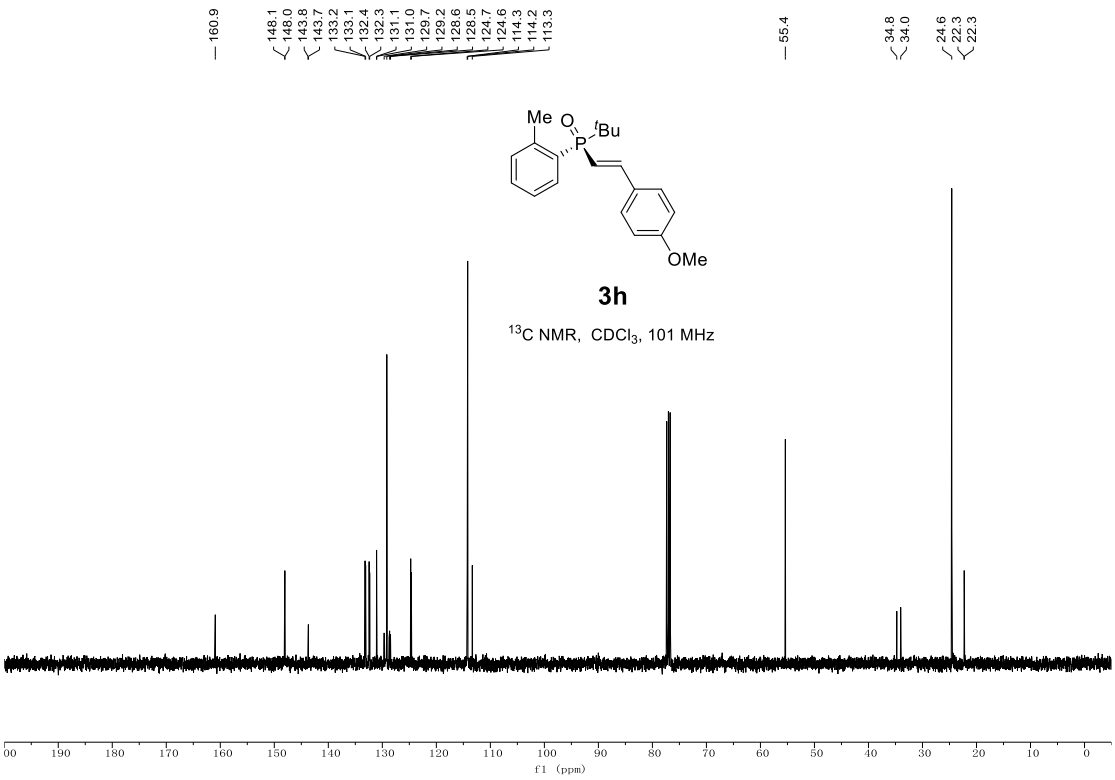
3.00
2.99
9.11
f1 (ppm)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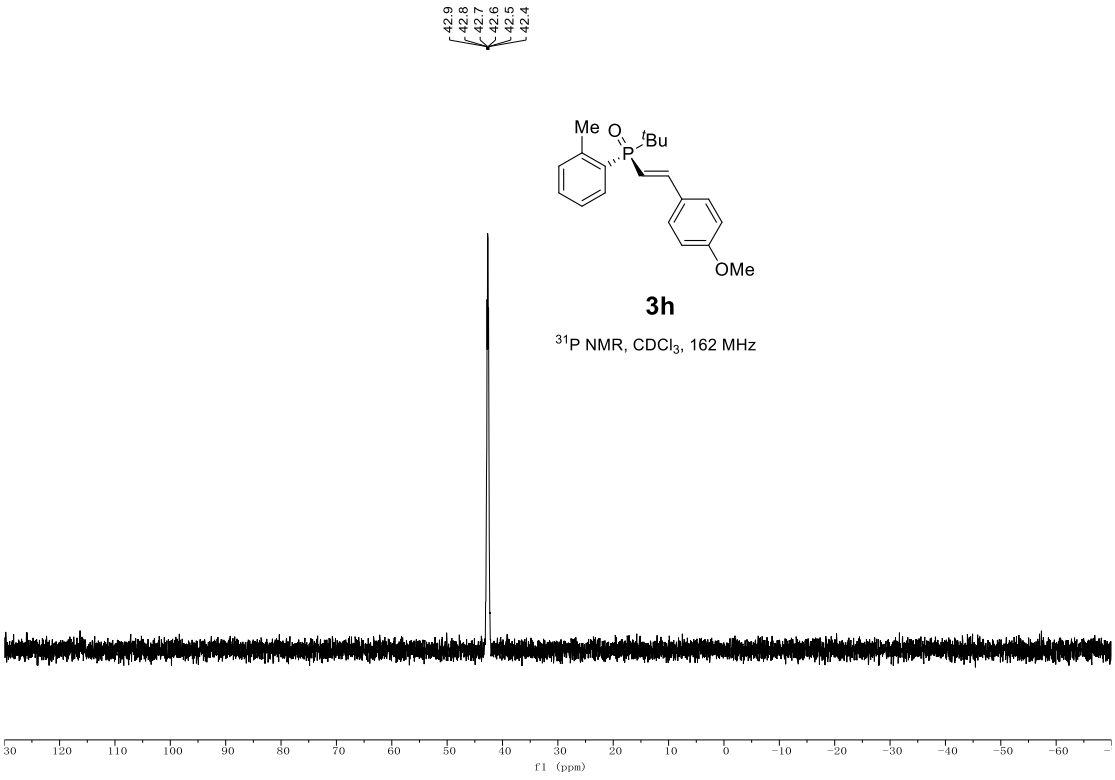
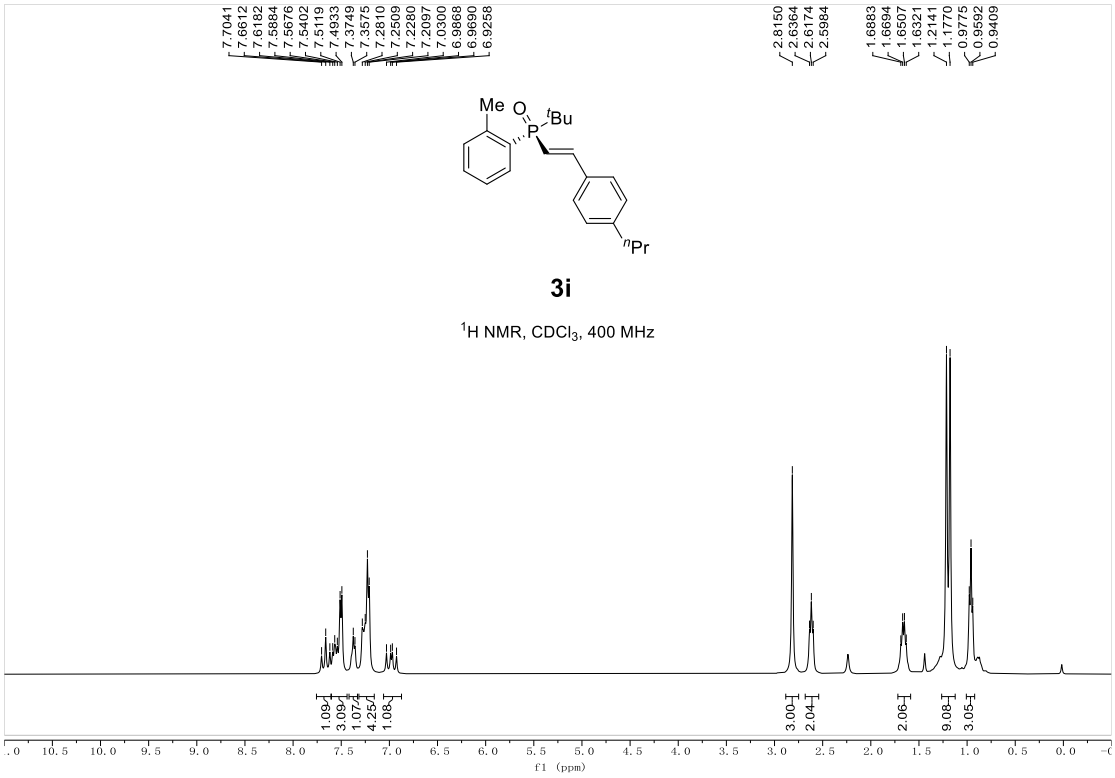
143.8
143.7
133.2
133.1
132.4
132.3
131.1
131.0
129.7
129.2
128.6
128.5
124.7
124.6
114.3
114.2
113.3
55.4
34.8
34.0
24.6
22.3
22.3
Me
O
P
tBu
OMe
3h
13C NMR, CDCl3, 101 MHz
f1 (ppm)


42.9
42.8
42.7
42.6
42.5
42.4
Me
O
P
tBu
OMe
3h
31P NMR, CDCl3, 162 MHz
f1 (ppm)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7.2509
7.2280
7.2097
7.0300
6.9868
6.9690
6.9258
2.8150
2.6364
2.6174
2.5984
1.6883
1.6694
1.6507
1.6321
1.2141
1.1770
0.9775
0.9592
0.9409
Me
O
P
tBu
nPr
3i
1H NMR, CDCl3, 400 MHz
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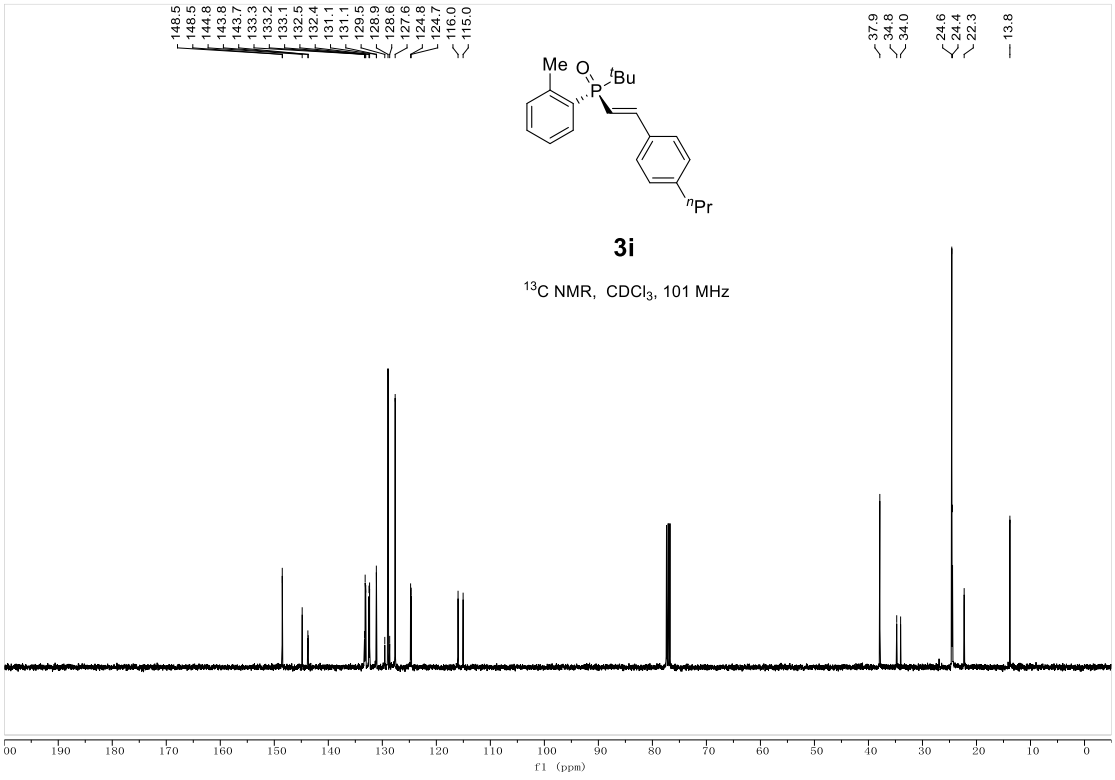
1.07
4.25
1.08
3.00
2.04
2.06
9.08
3.05
f1 (ppm)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124.8
124.7
116.0
115.0
37.9
34.8
34.0
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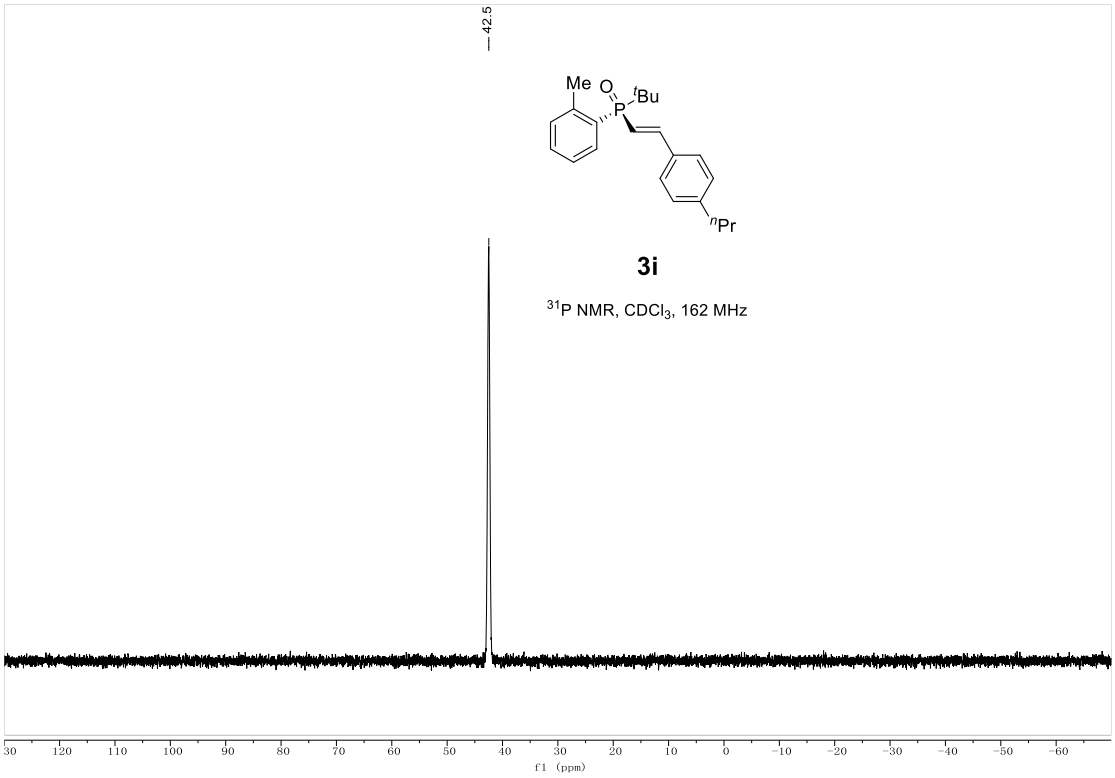
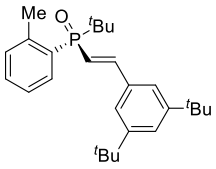
22.3
13.8
Me
O
P
tBu
nPr
3i
13C NMR, CDCl3, 101 MHz
f1 (ppm)



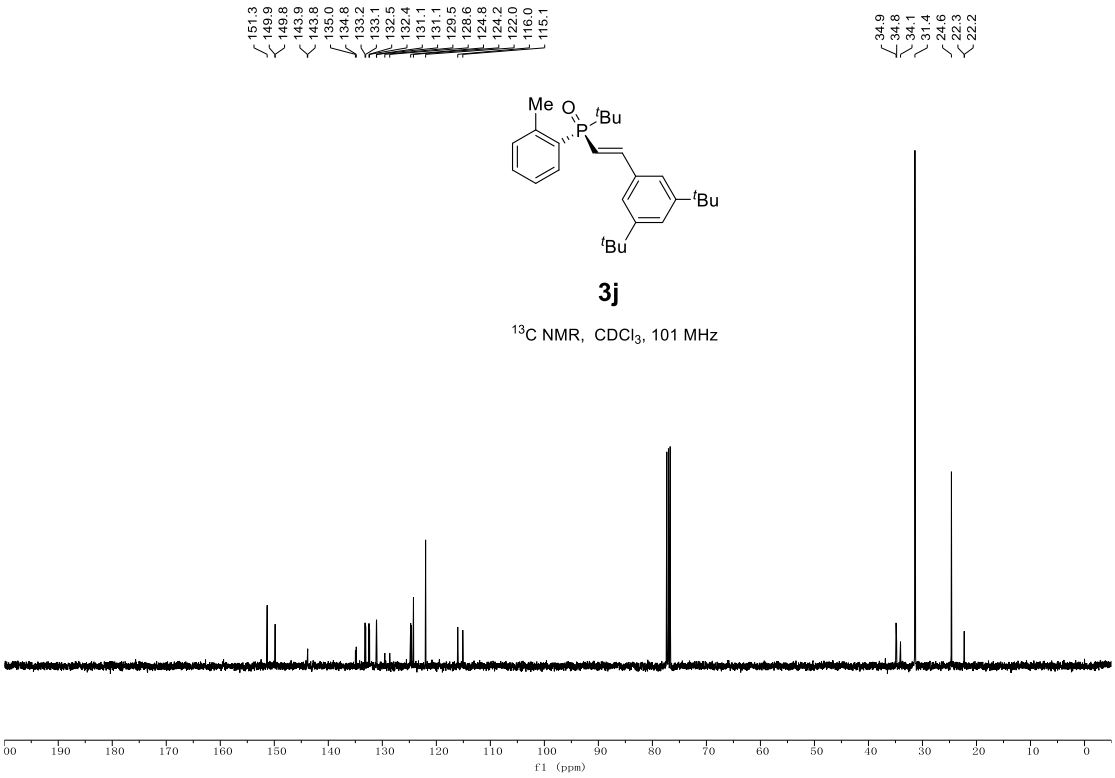
3i

^{31}P NMR, $CDCl_3$, 162 MHz



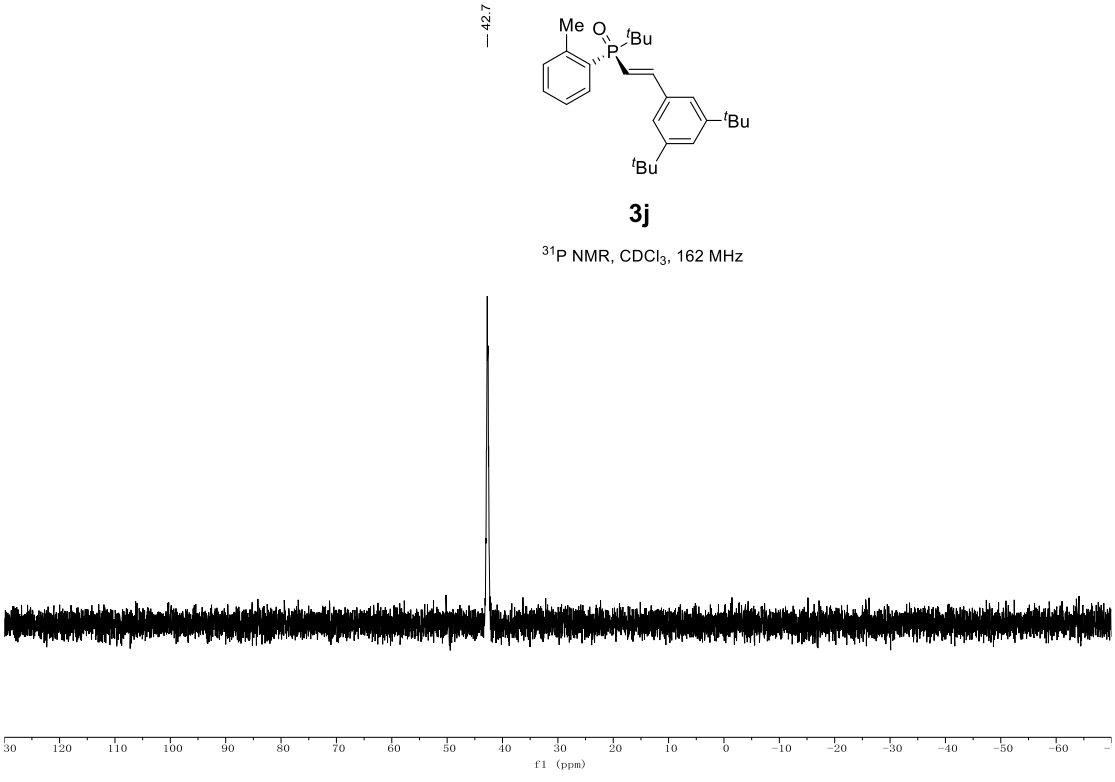
3j

^{1}H NMR, $CDCl_3$, 400 MHz



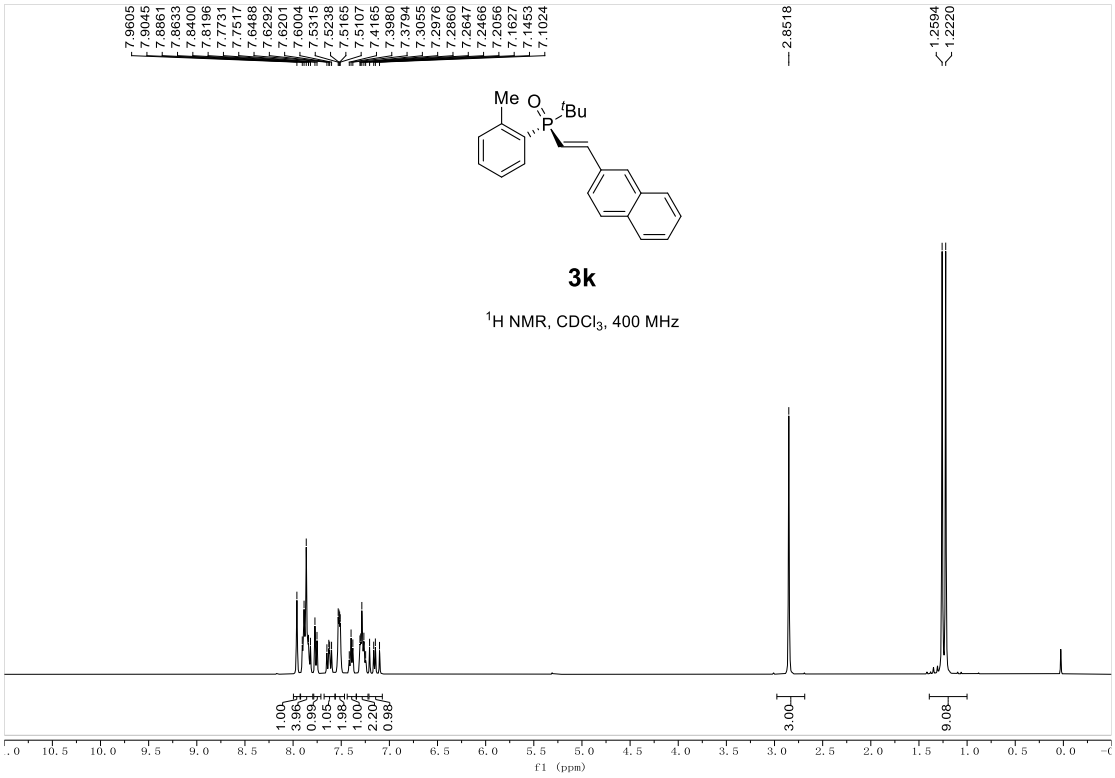
3j

^{13}C NMR, $CDCl_3$, 101 MHz



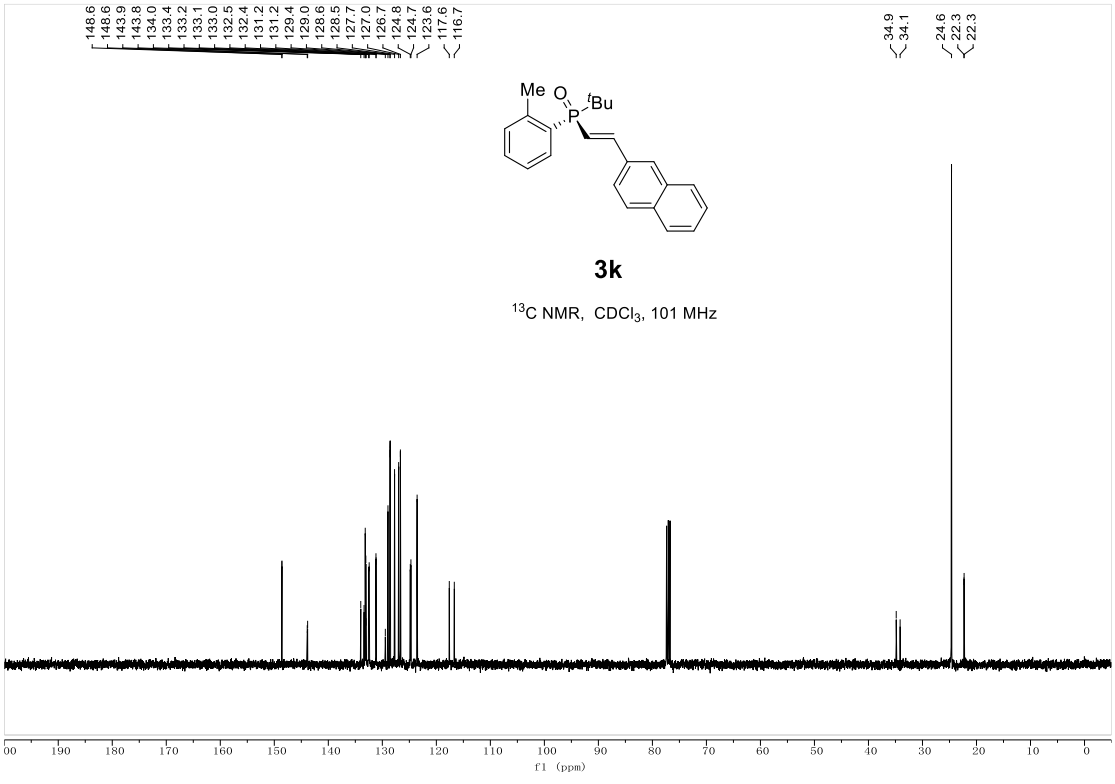
3j

^{31}P NMR, $CDCl_3$, 162 MHz



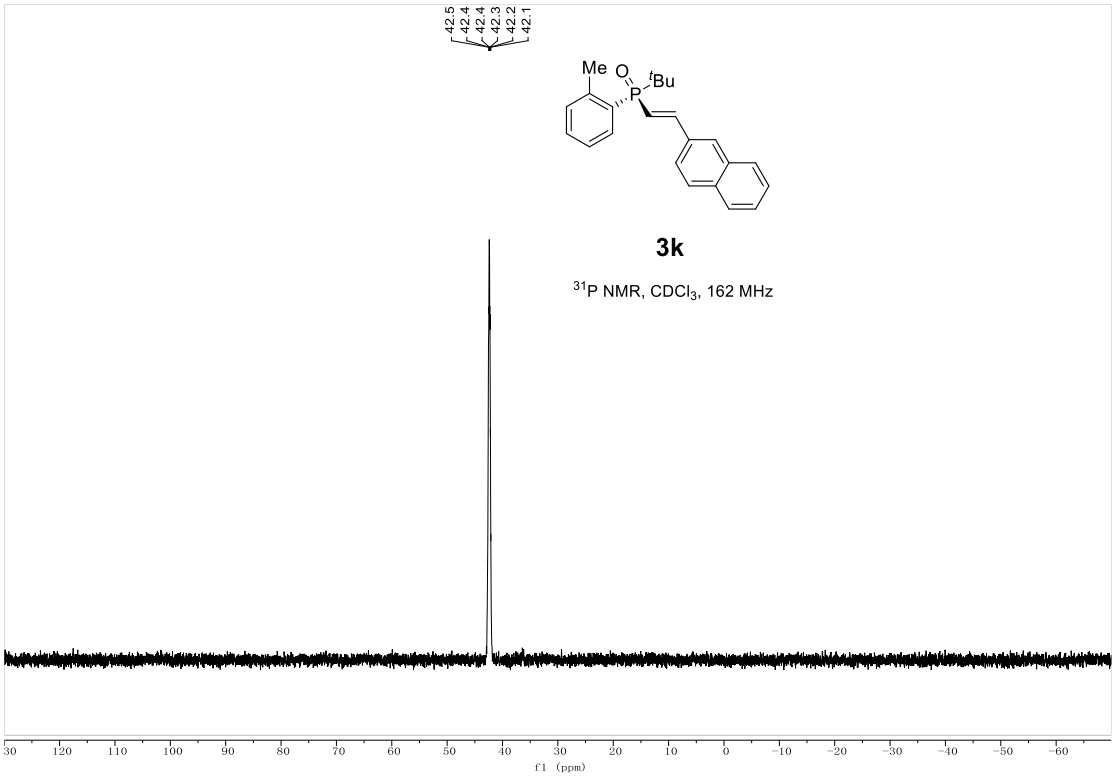
3k

^{1}H NMR, $CDCl_3$, 400 MHz



3k

^{13}C NMR, $CDCl_3$, 101 MHz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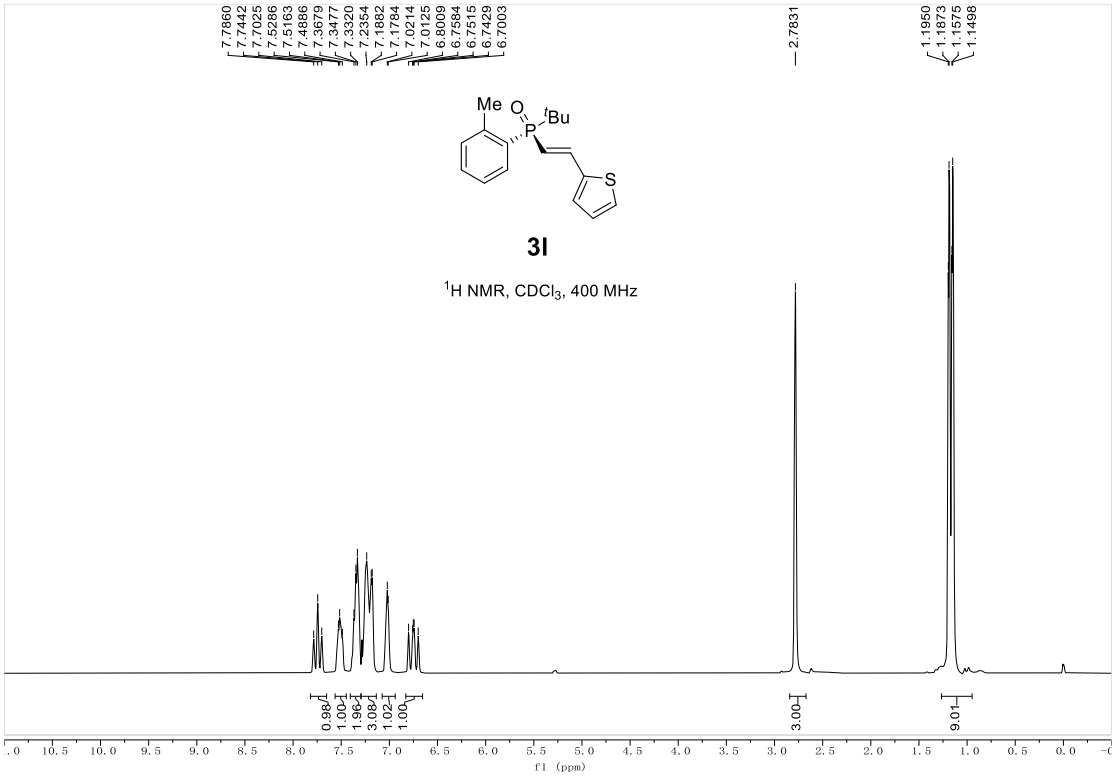
42.4
42.4
42.3
42.2
42.1
Me
O
P
tBu
3k
31P NMR, CDCl3, 162 MHz
f1 (ppm)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7.3320
7.2354
7.1882
7.1784
7.0214
7.0125
6.8009
6.7584
6.7515
6.7429
6.7003
2.7831
1.1950
1.1873
1.1575
1.1498
Me
O
P
tBu
S
3l
1H NMR, CDCl3, 400 MHz
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1.96
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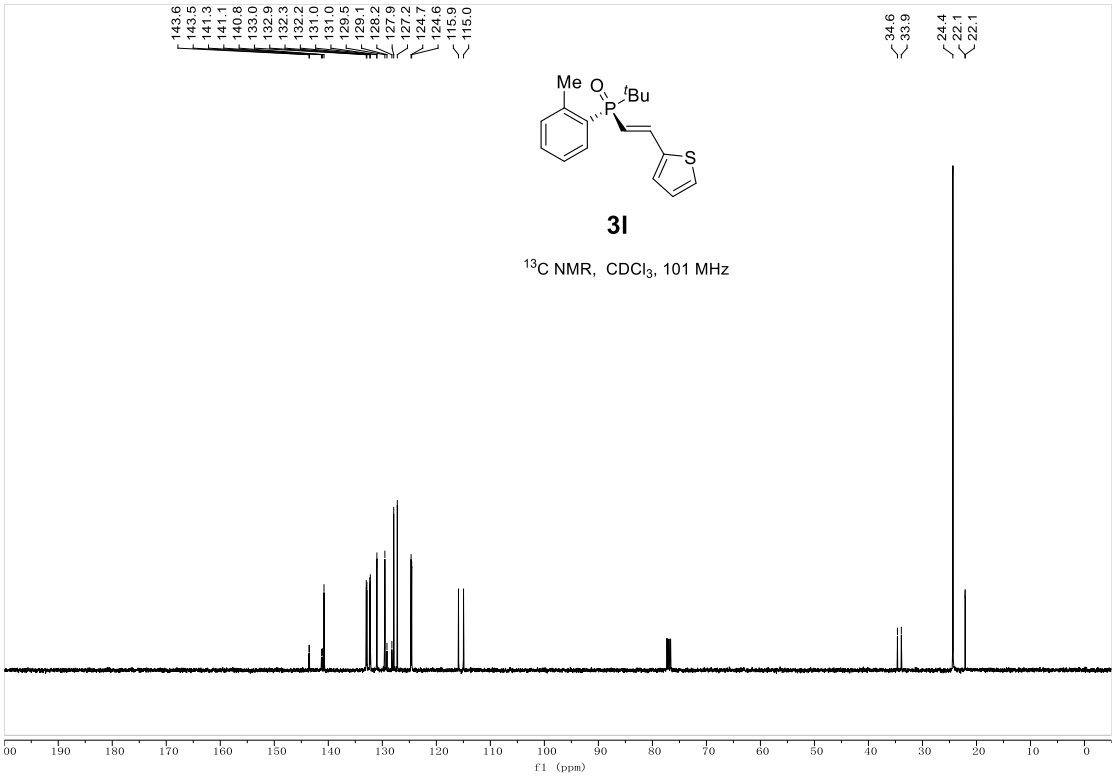
1.02
1.00
3.00
9.01
f1 (ppm)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129.1
128.2
127.9
127.2
124.7
124.6
115.9
115.0
34.6
33.9
24.4
22.1
22.1
Me
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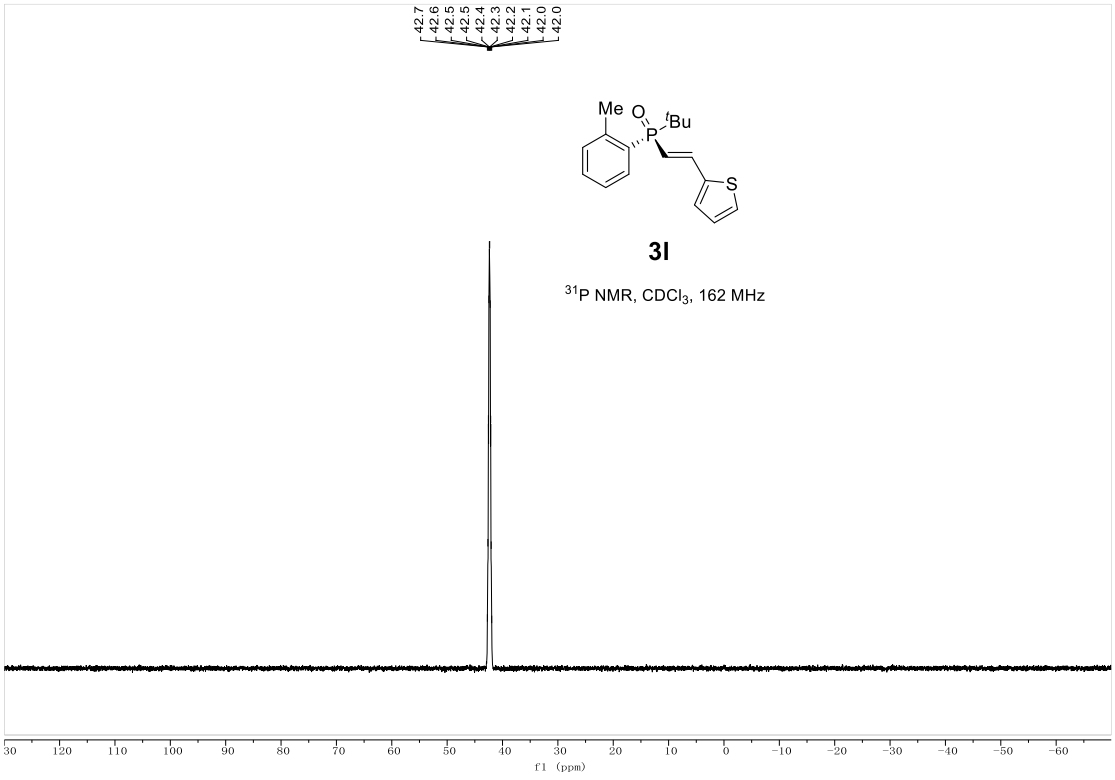
P
tBu
S
3l
13C NMR, CDCl3, 101 MHz
f1 (ppm)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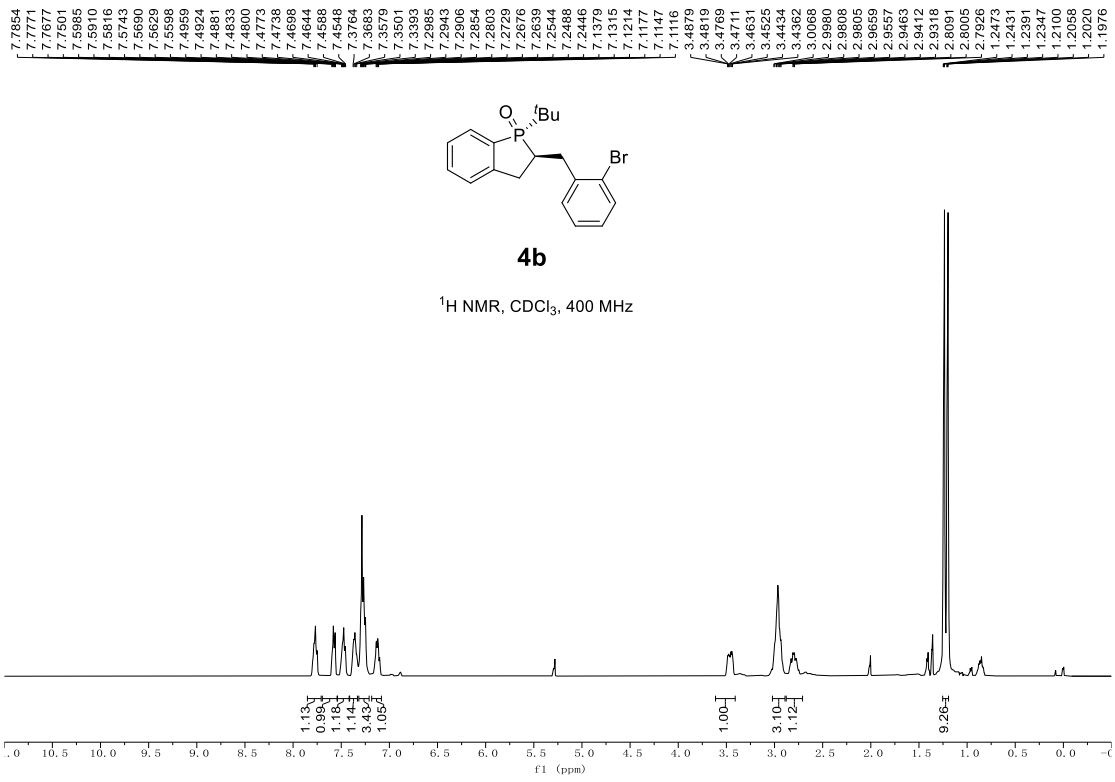
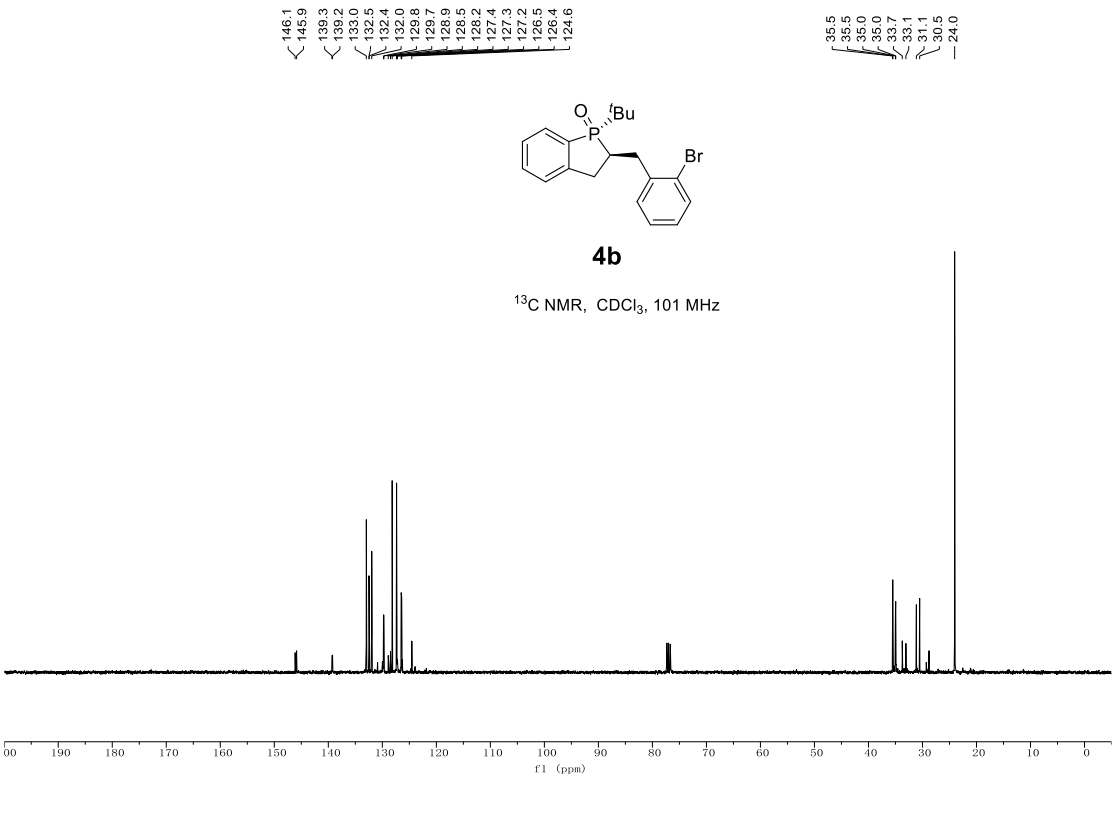
42.6
42.5
42.5
42.4
42.3
42.2
42.1
42.0
42.0
Me
O
P
tBu
S
3l
31P NMR, CDCl3, 162 MHz
f1 (ppm)



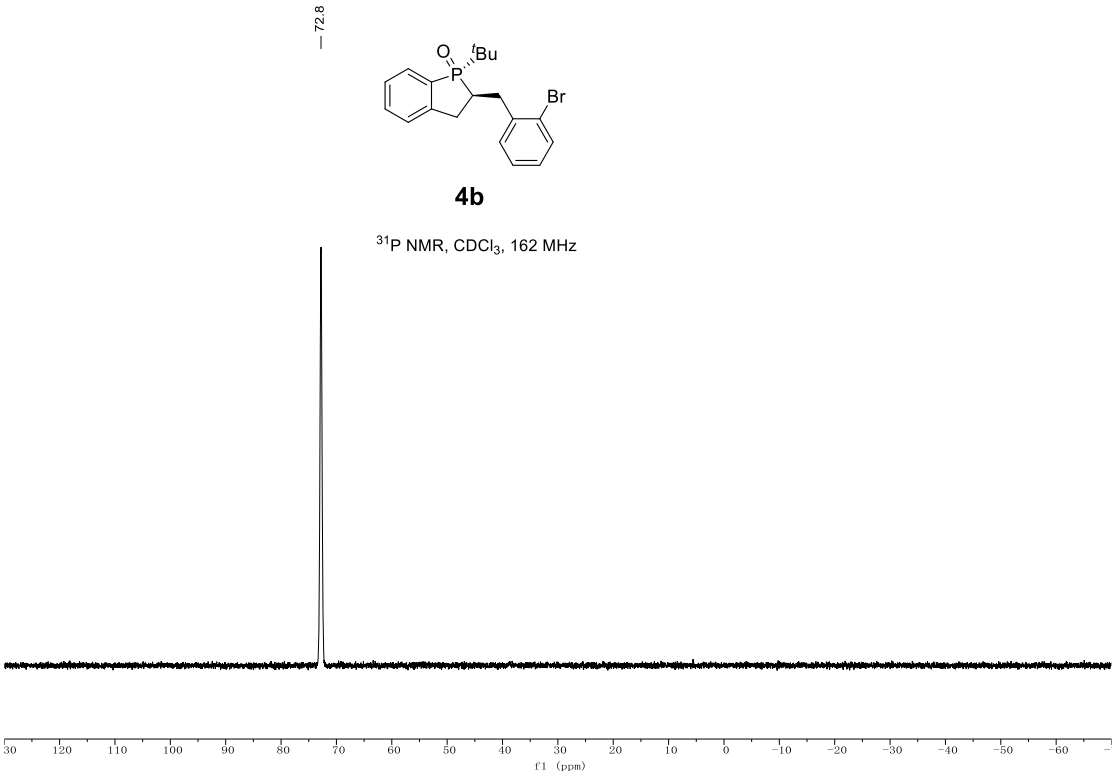
4b

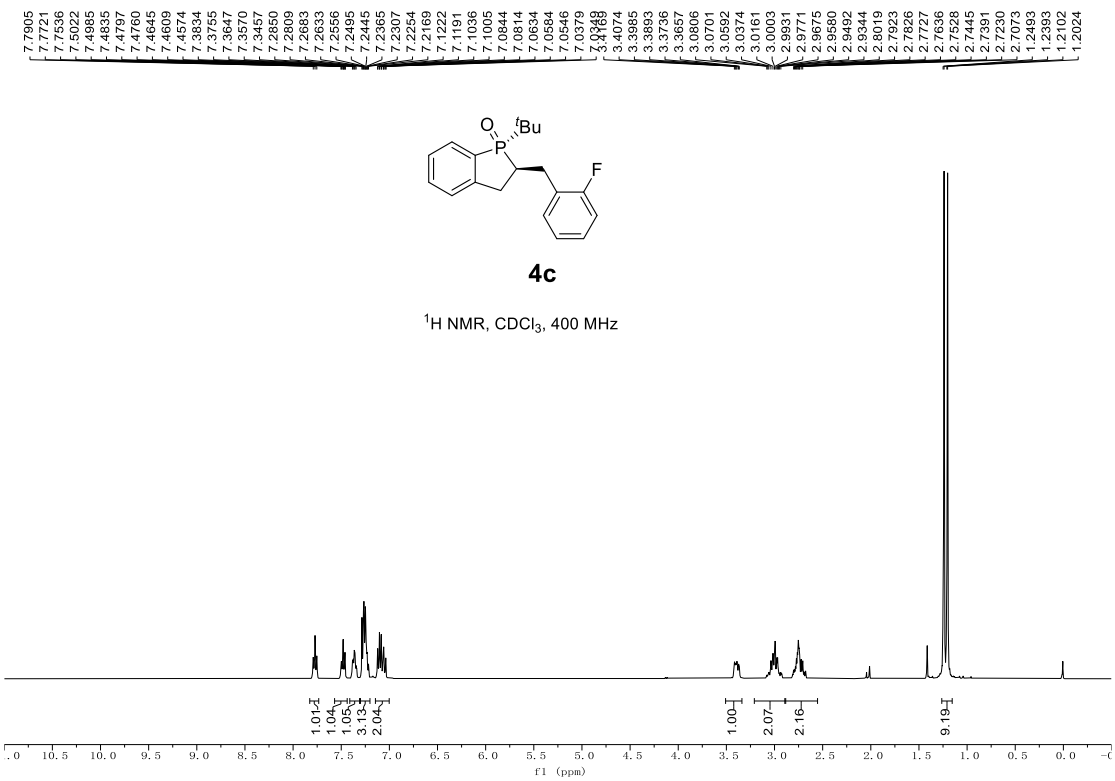
^{1}H NMR, $CDCl_3$, 400 MHz

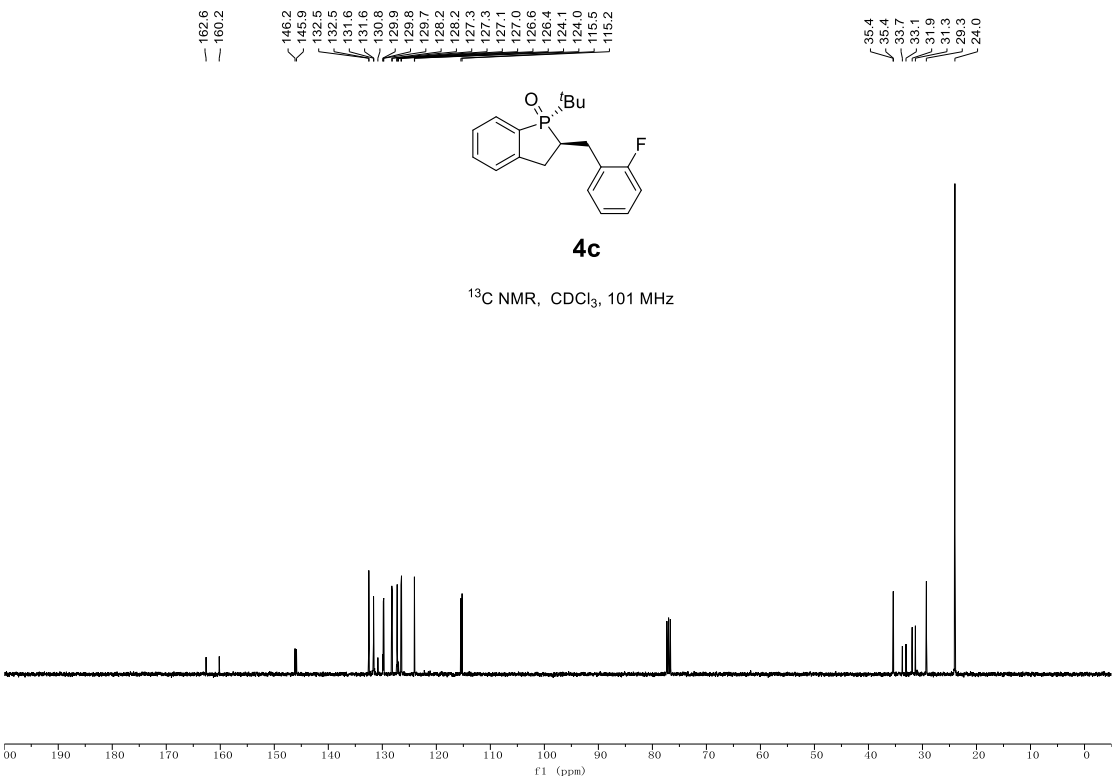


4b

^{13}C NMR, $CDCl_3$, 101 MHz

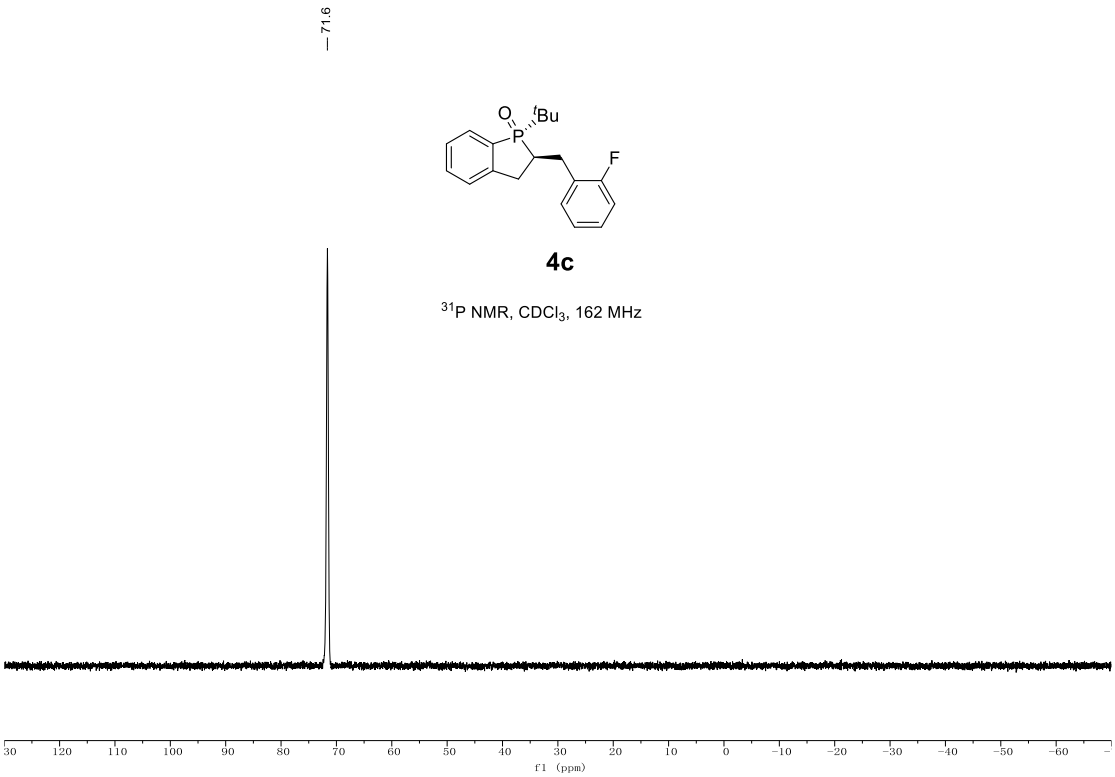

72.8
O
tBu
P
Br
4b
31P NMR, CDCl3, 162 MHz
f1 (ppm)


O
tBu
P
F
4c
1H NMR, CDCl3, 400 MHz
1.01
1.04
1.05
3.13
2.04
1.00
2.07
2.16
9.19
f1 (ppm)



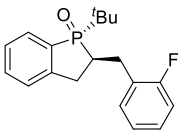
4c

^{13}C NMR, $CDCl_3$, 101 MHz



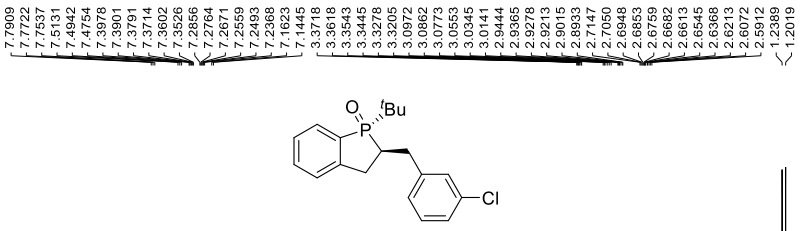
4c

^{31}P NMR, $CDCl_3$, 162 MHz



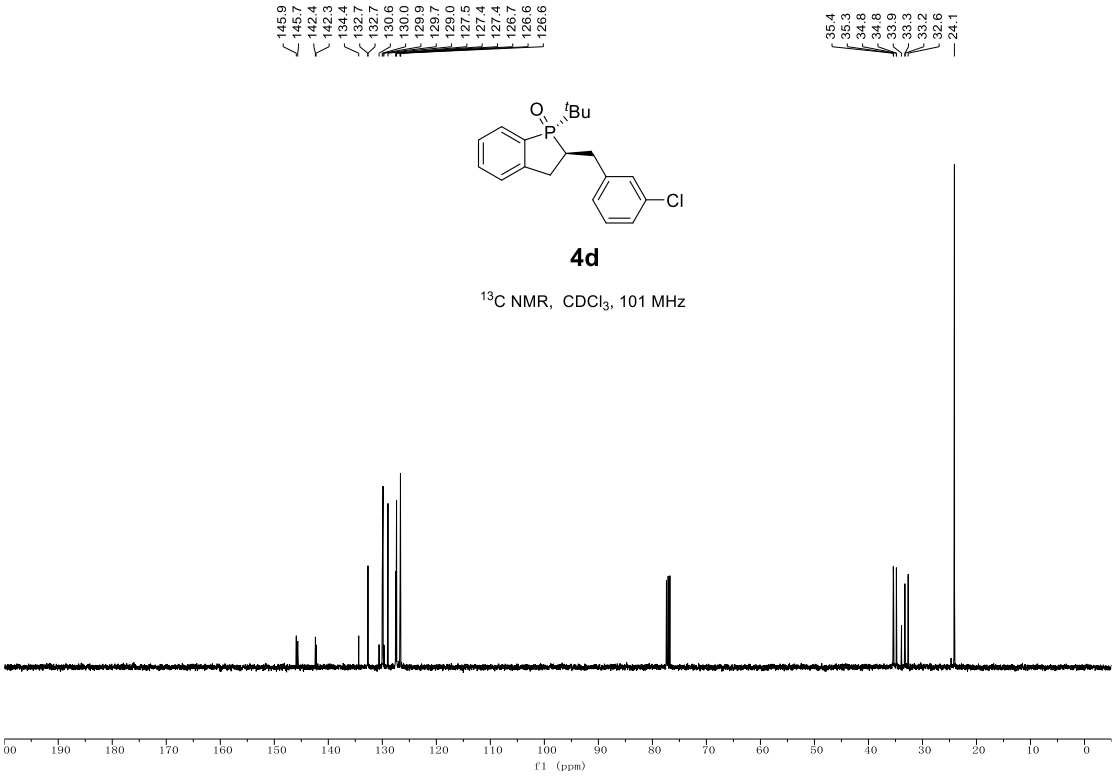
4c

^{19}F NMR, $CDCl_3$, 377 MHz



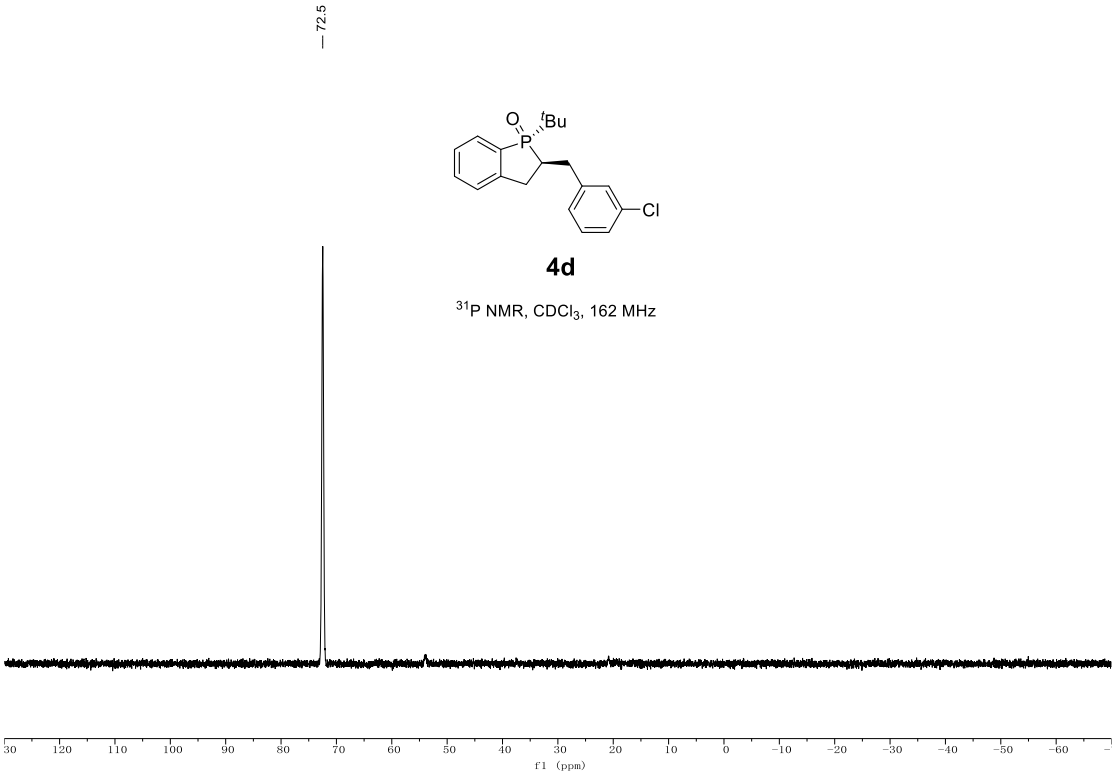
4d

^{1}H NMR, $CDCl_3$, 400 MHz



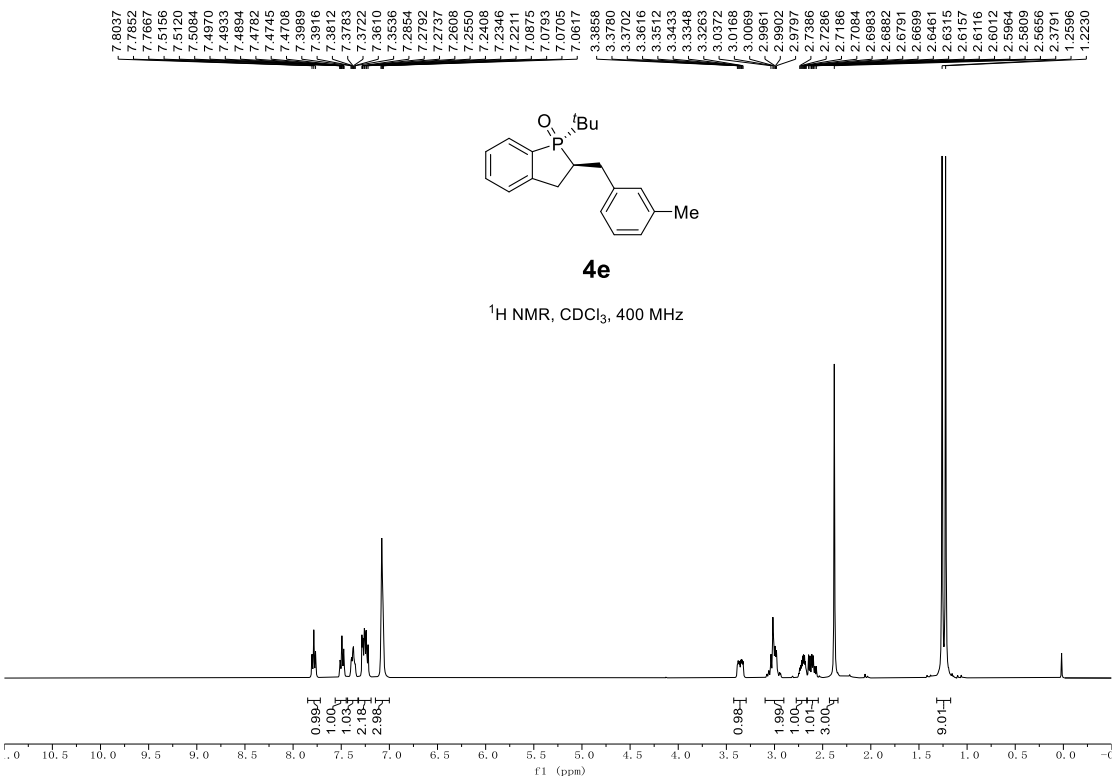
4d

^{13}C NMR, $CDCl_3$, 101 MHz



4d

^{31}P NMR, $CDCl_3$, 162 MHz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7.5120
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7.4970
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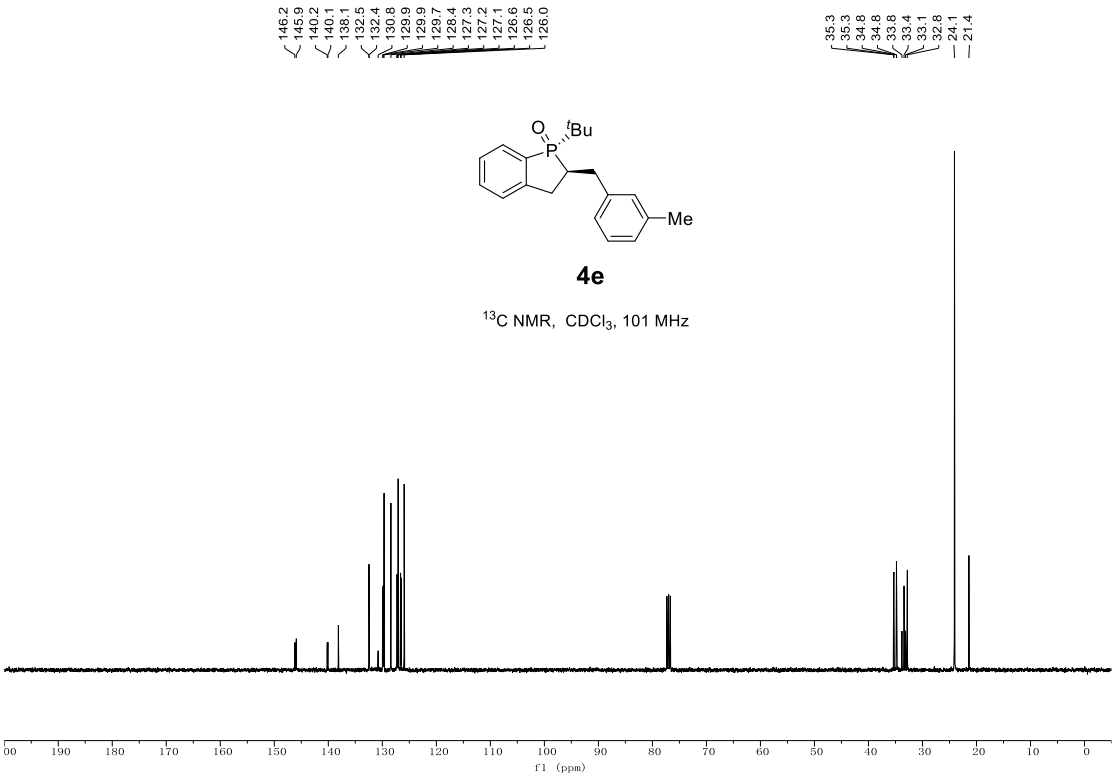
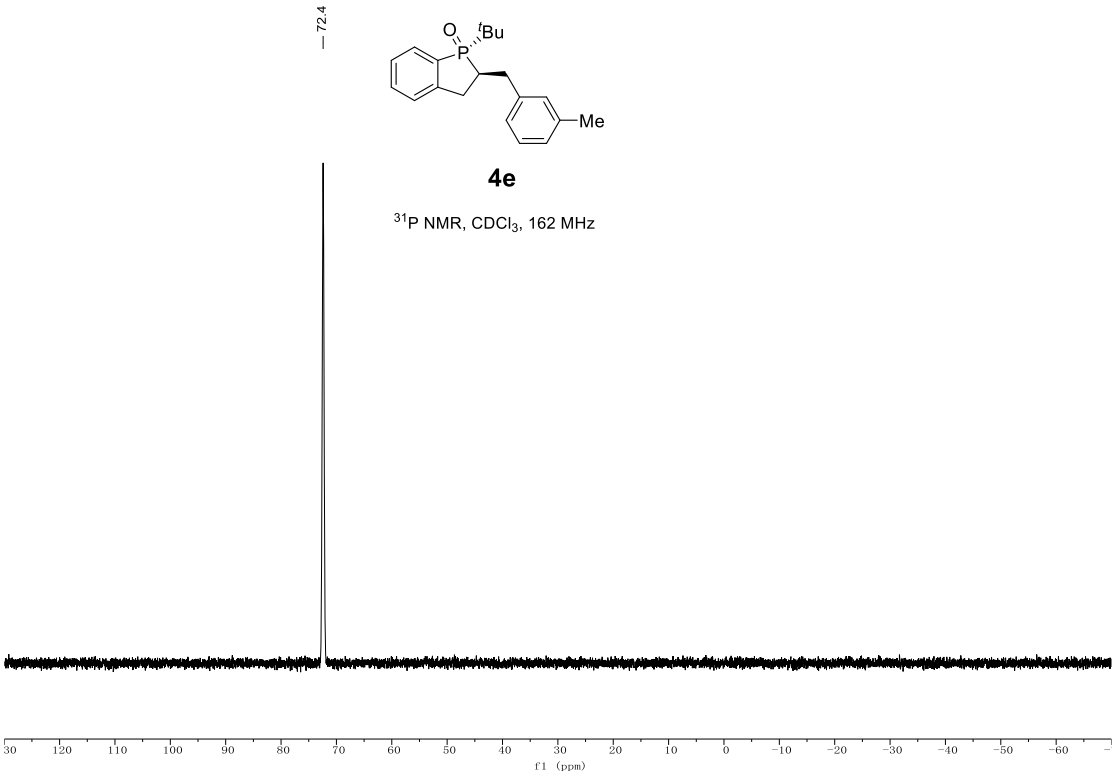
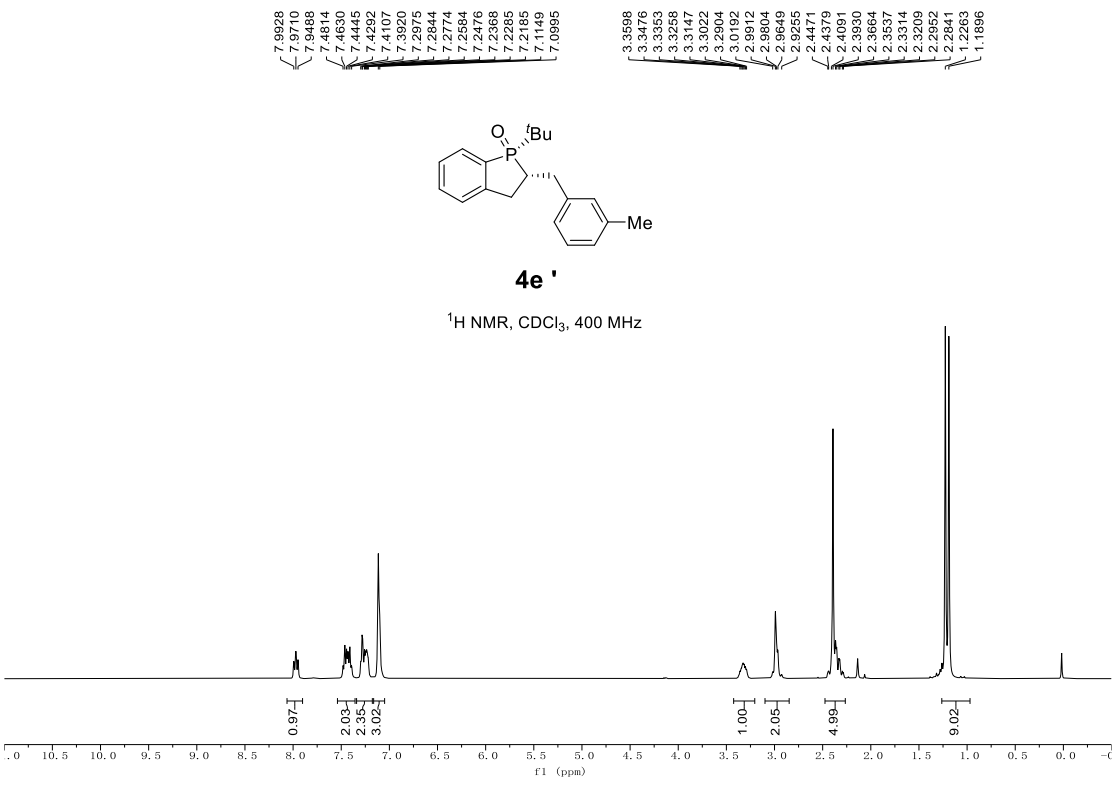
7.4894
7.4782
7.4745
7.4708
7.3989
7.3916
7.3812
7.3783
7.3722
7.3610
7.3536
7.2854
7.2792
7.2737
7.2608
7.2550
7.2408
7.2346
7.2211
7.0875
7.0793
7.0705
7.0617
3.3858
3.3780
3.3702
3.3616
3.3512
3.3433
3.3348
3.3263
3.3072
3.0168
3.0069
2.9961
2.9902
2.9797
2.7386
2.7286
2.7186
2.7084
2.6983
2.6882
2.6791
2.6699
2.6461
2.6315
2.6157
2.6116
2.6012
2.5964
2.5809
2.5656
2.3791
1.2596
1.2230
O
P
tBu
Me
4e
1H NMR, CDCl3, 400 MHz
0.99
1.00
1.03
2.18
2.98
0.98
1.99
1.00
1.01
3.00
9.01
f1 (ppm)


146.2
145.9
140.2
140.1
138.1
132.5
132.4
130.8
129.9
129.9
129.7
128.4
127.3
127.2
127.1
126.6
126.5
126.0
35.3
35.3
34.8
34.8
33.8
33.4
33.1
32.8
24.1
21.4
O
P
tBu
Me
4e
13C NMR, CDCl3, 101 MHz
f1 (ppm)



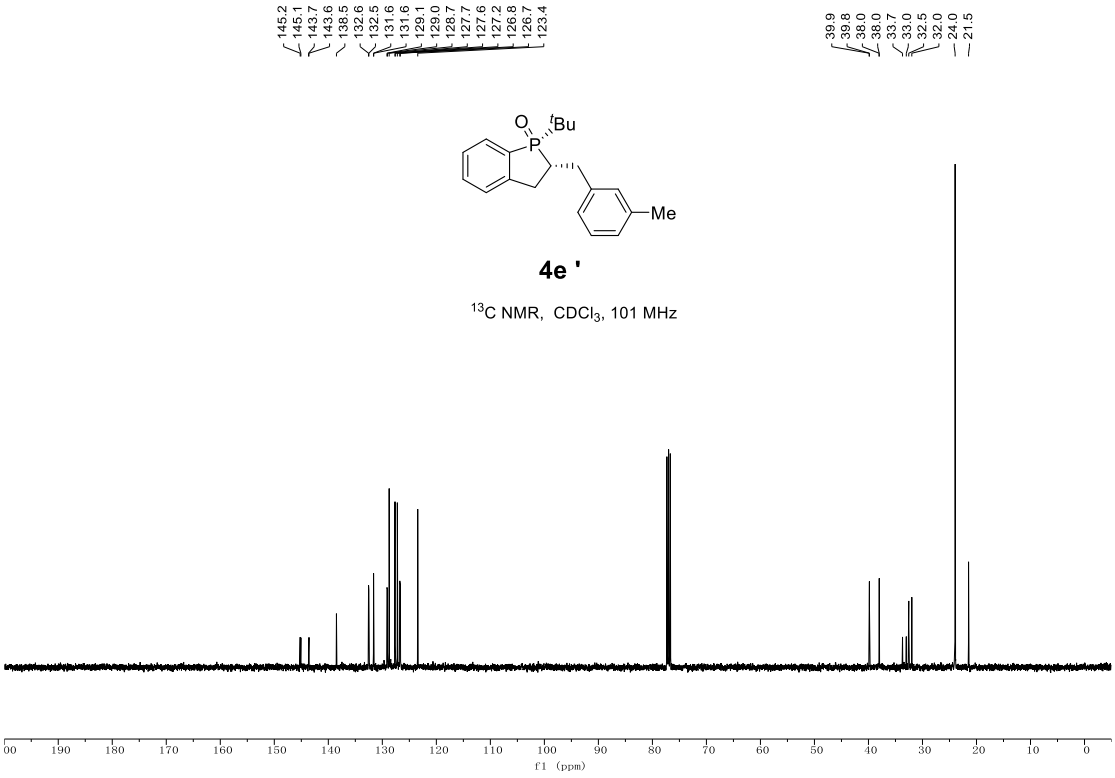
4e

^{31}P NMR, $CDCl_3$, 162 MHz



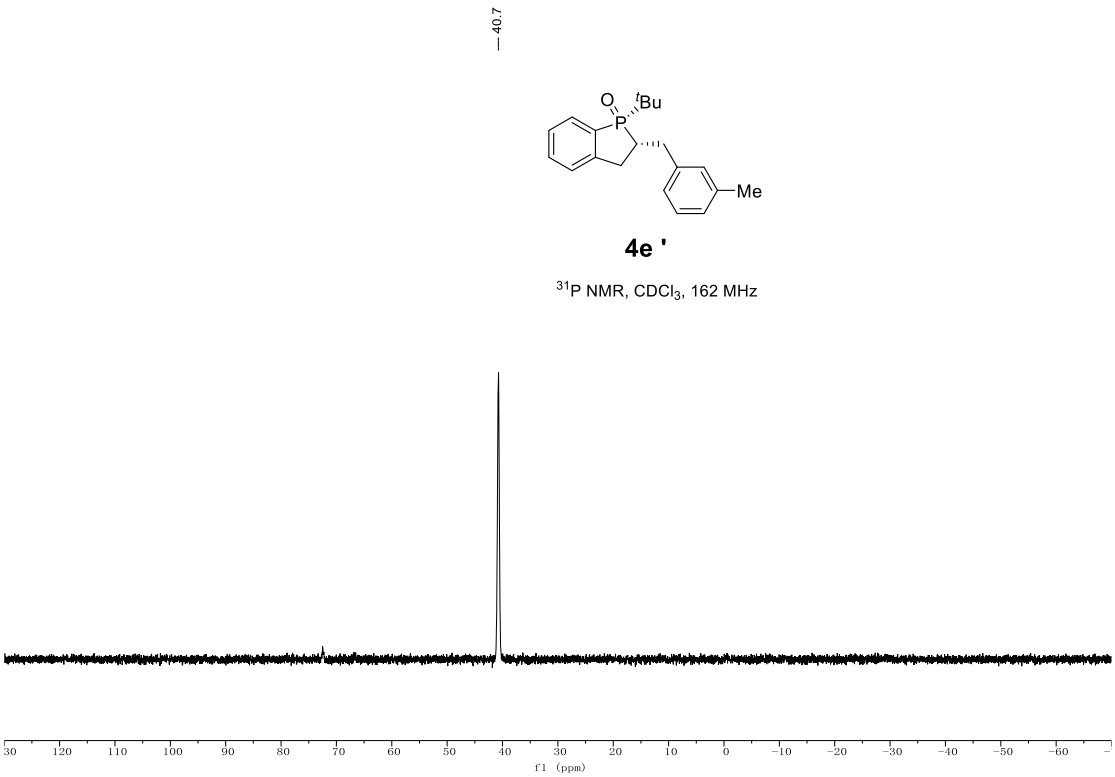
4e '

^{1}H NMR, $CDCl_3$, 400 MHz



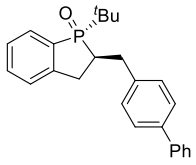
4e '

^{13}C NMR, $CDCl_3$, 101 MHz



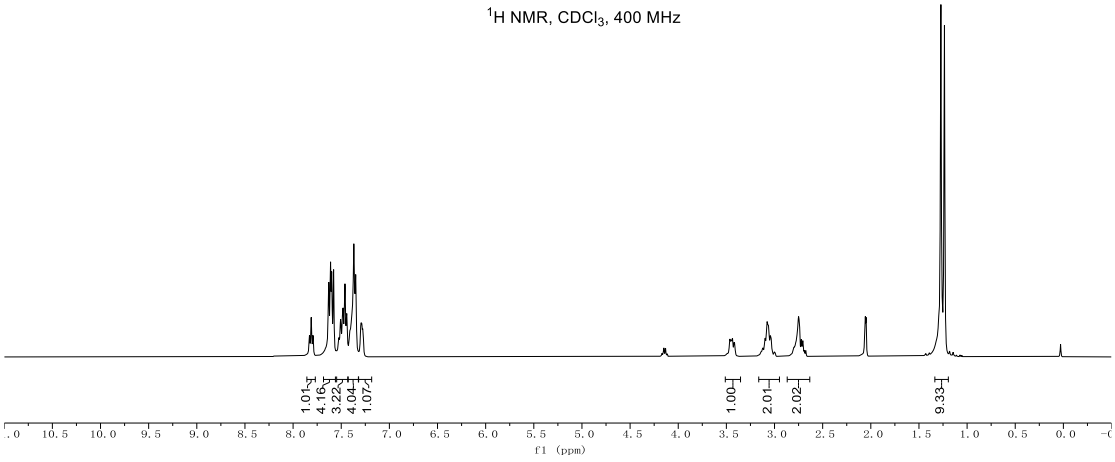
4e '

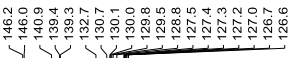
^{31}P NMR, $CDCl_3$, 162 MHz

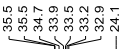


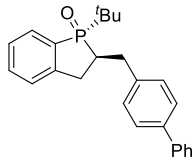
4f

^{1}H NMR, $CDCl_3$, 400 MHz



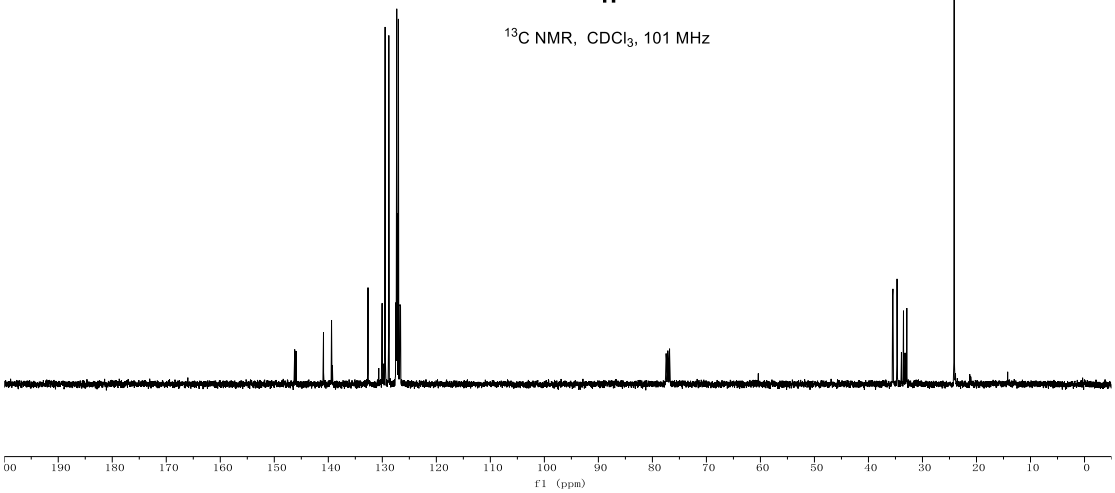


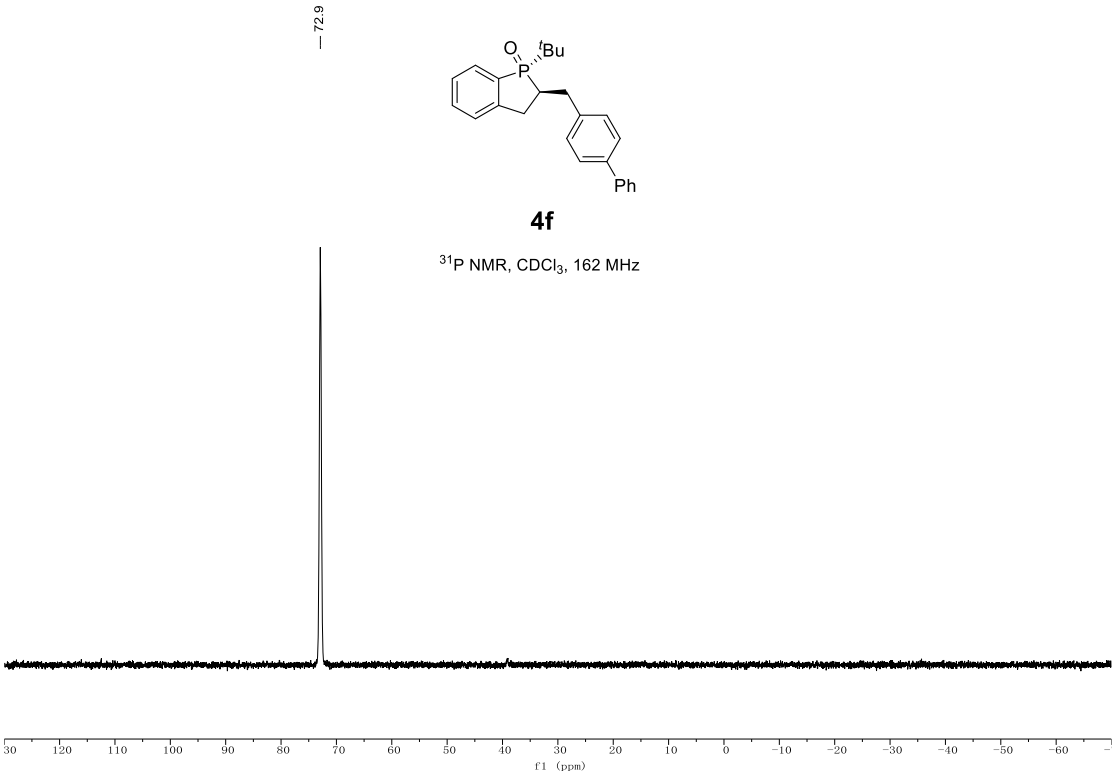




4f

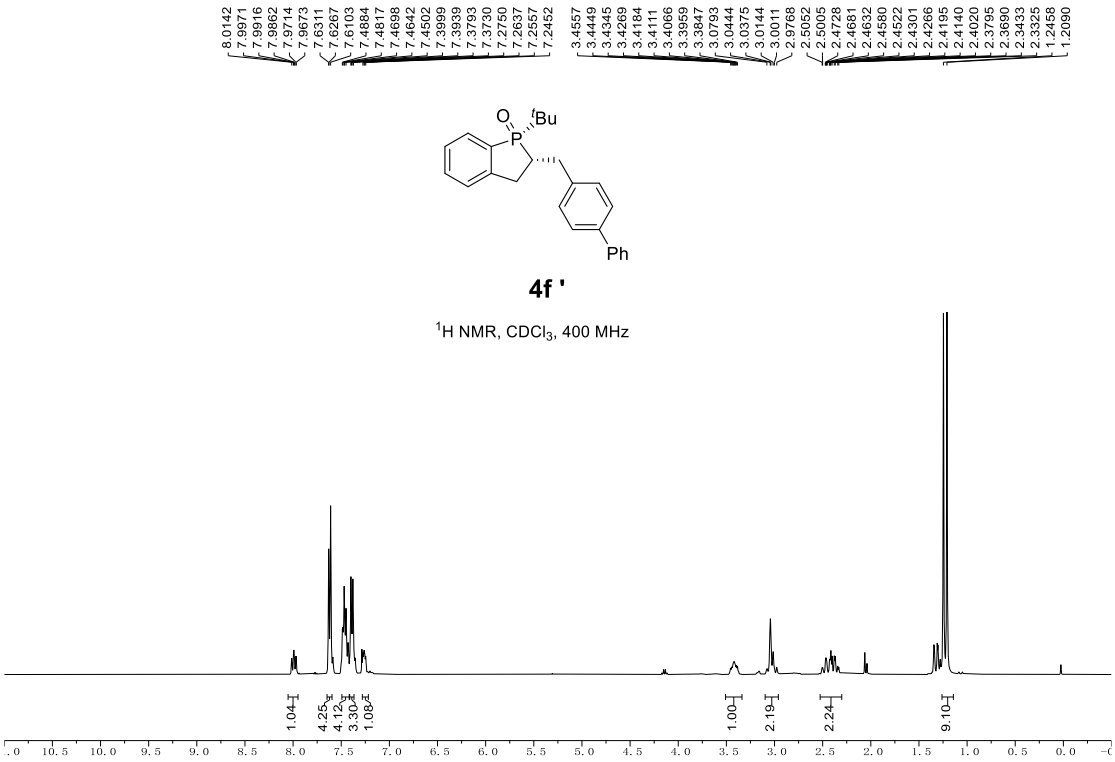
^{13}C NMR, $CDCl_3$, 101 MHz





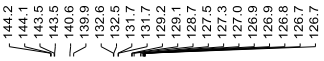
4f

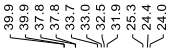
^{31}P NMR, $CDCl_3$, 162 MHz

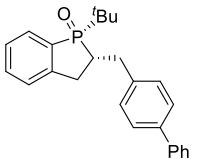


4f '

^{1}H NMR, $CDCl_3$, 400 MHz

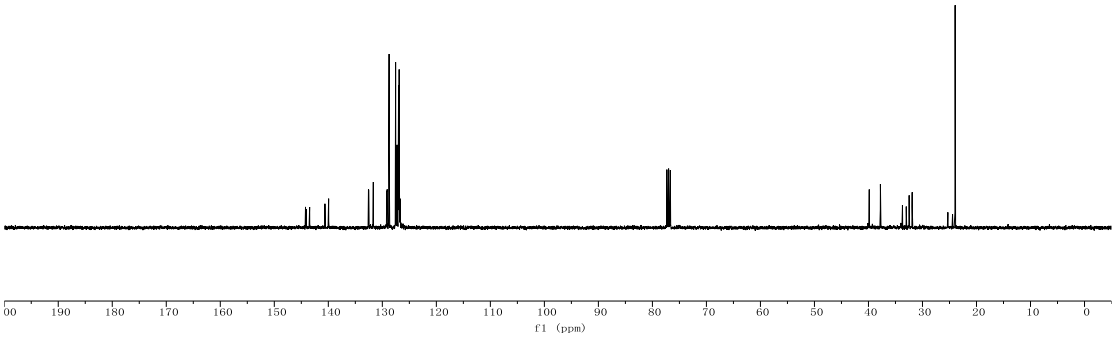


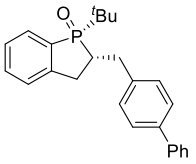




4f '

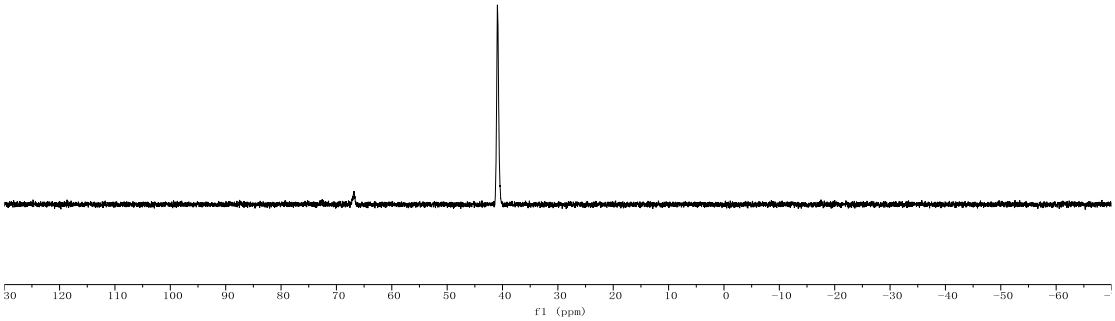
^{13}C NMR, $CDCl_3$, 101 MHz

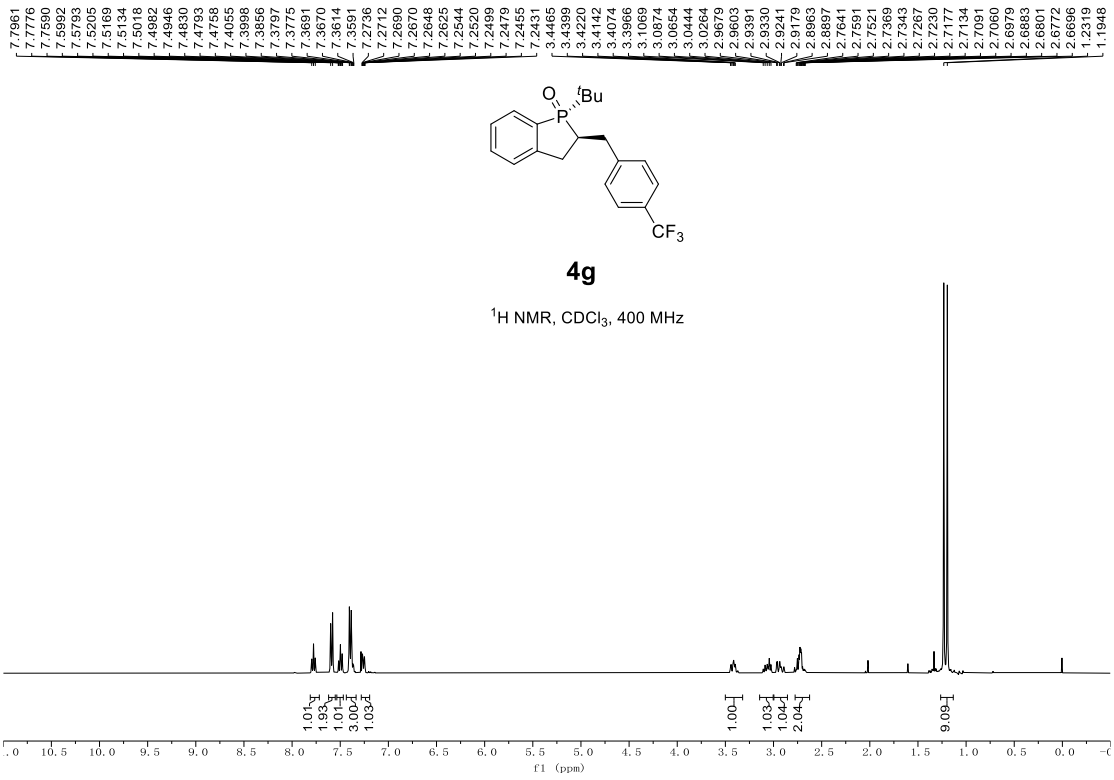




4f '

^{31}P NMR, $CDCl_3$, 162 MHz

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7.4830
7.4793
7.4758
7.4055
7.3998
7.3856
7.3797
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7.3670
7.3614
7.3591
7.2736
7.2712
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7.2670
7.2648
7.2625
7.2544
7.2520
7.2499
7.2479
7.2455
7.2431
3.4465
3.4399
3.4220
3.4142
3.4074
3.3966
3.1069
3.0874
3.0654
3.0444
3.0264
2.9679
2.9603
2.9391
2.9330
2.9241
2.9179
2.8963
2.8897
2.7641
2.7591
2.7521
2.7369
2.7343
2.7267
2.7230
2.7177
2.7134
2.7091
2.7060
2.6979
2.6883
2.6801
2.6772
2.6696
1.2319
1.1948
O
P
tBu
CF3
4g
1H NMR, CDCl3, 400 MHz
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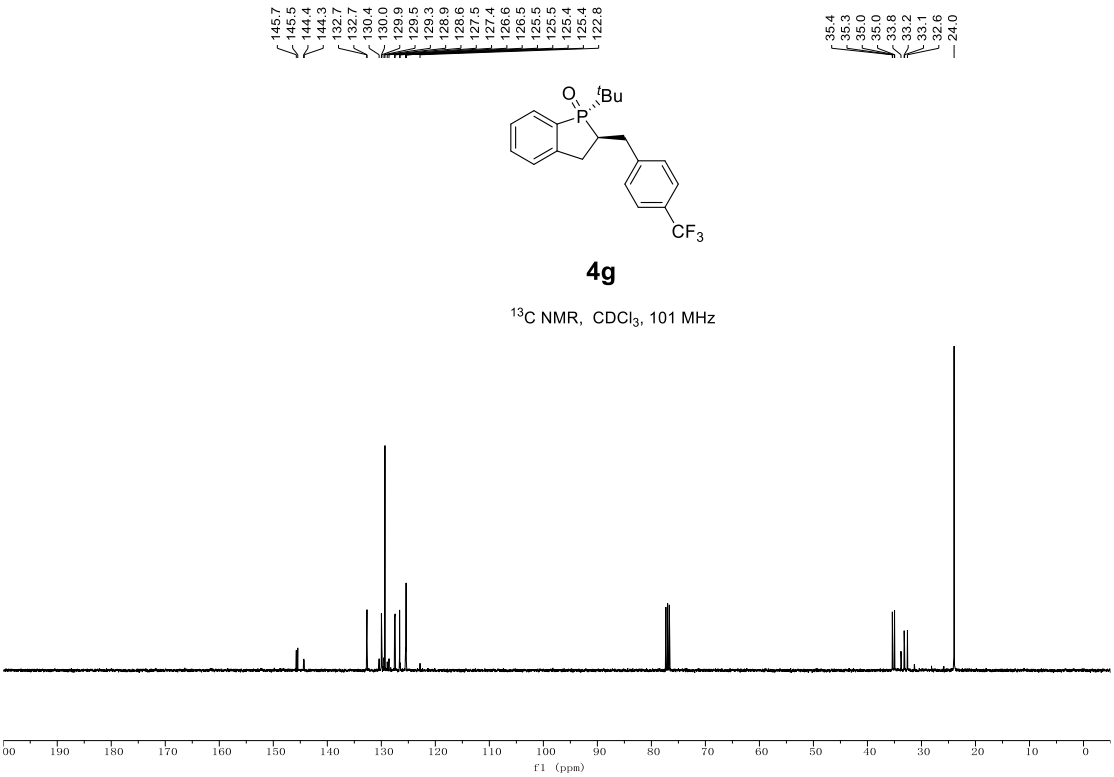
1.01
3.00
1.03
1.00
1.03
1.04
2.04
9.09
f1 (ppm)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132.7
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128.9
128.6
127.5
127.4
126.6
126.5
125.5
125.5
125.4
125.4
122.8
35.4
35.3
35.0
35.0
33.8
33.2
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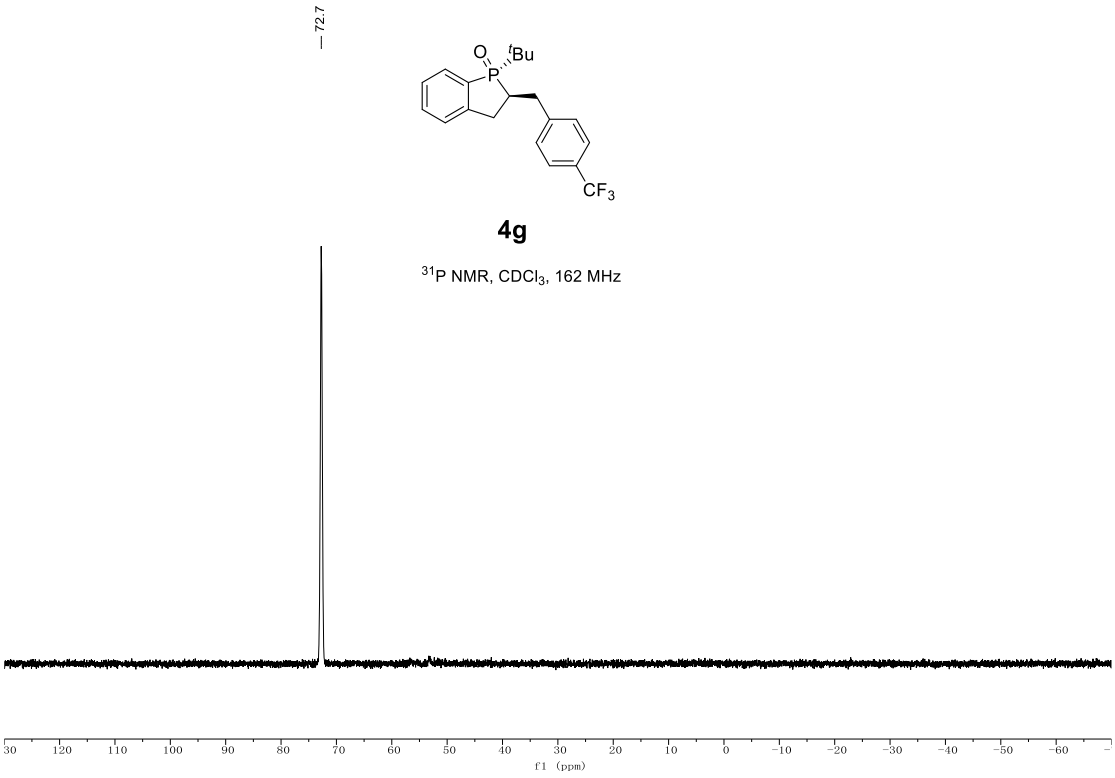
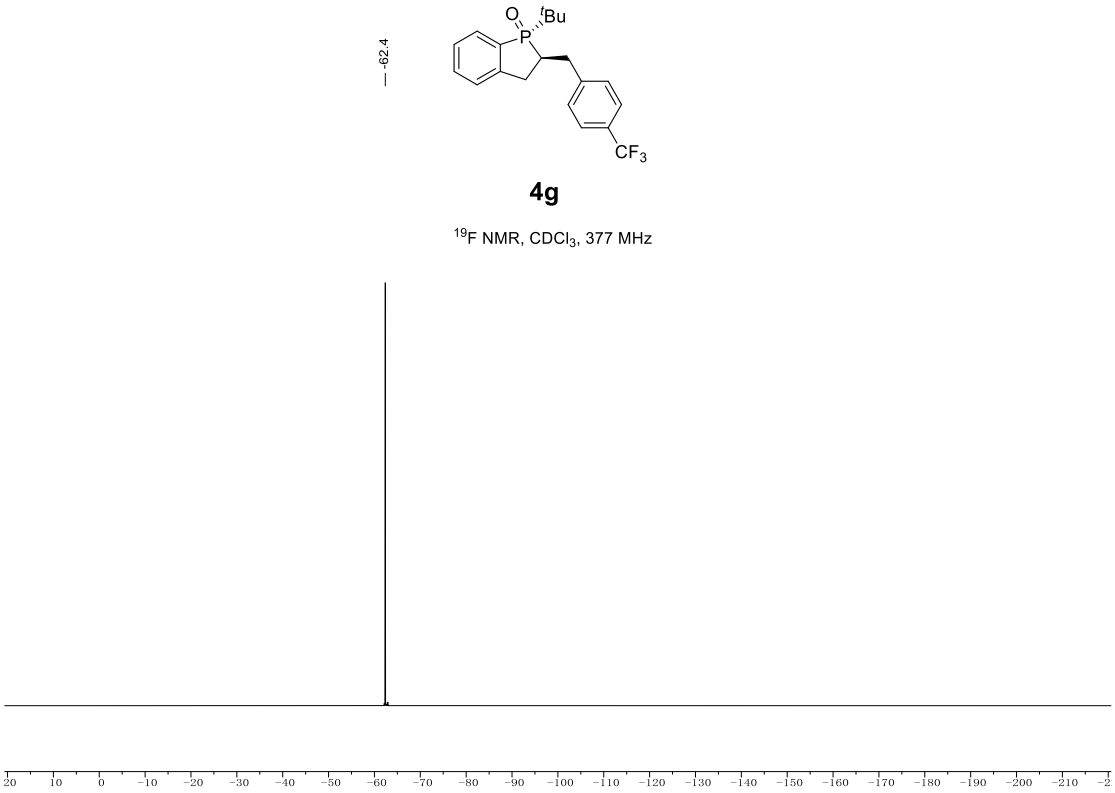
32.6
24.0
O
P
tBu
CF3
4g
13C NMR, CDCl3, 101 MHz
f1 (ppm)



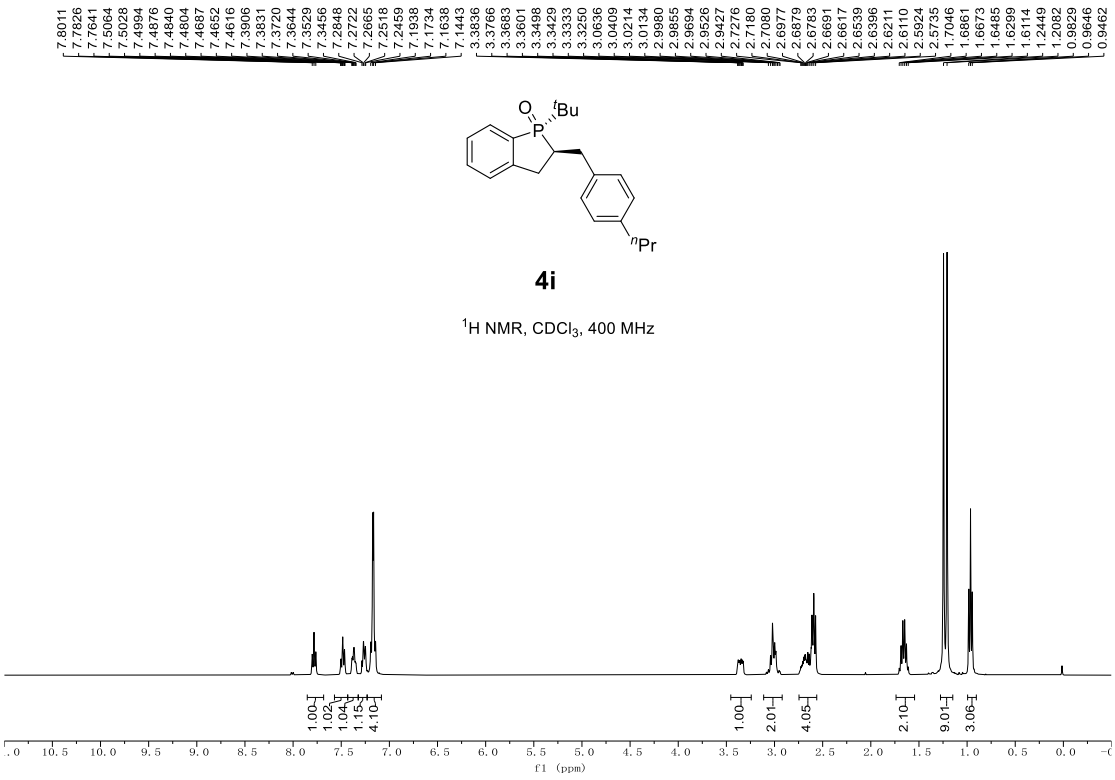
4g

^{31}P NMR, $CDCl_3$, 162 MHz



4g

^{19}F NMR, $CDCl_3$, 377 MHz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7.4876
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7.4652
7.4616
7.3906
7.3831
7.3720
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7.3529
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7.2848
7.2722
7.2665
7.2518
7.2459
7.1938
7.1734
7.1638
7.1443
3.3836
3.3766
3.3683
3.3601
3.3498
3.3429
3.3333
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3.0409
3.0214
3.0134
2.9980
2.9855
2.9694
2.9526
2.9427
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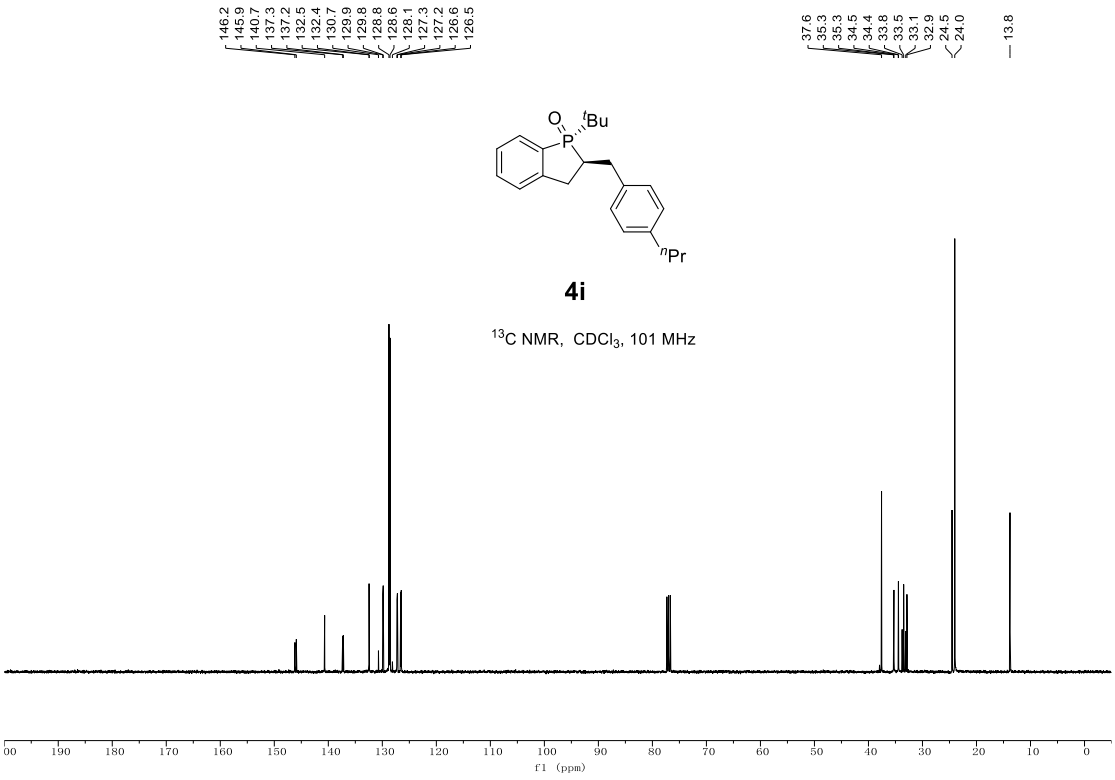
2.7180
2.7080
2.6977
2.6879
2.6783
2.6691
2.6617
2.6539
2.6396
2.6211
2.6110
2.5924
2.5735
1.7046
1.6861
1.6673
1.6485
1.6299
1.6114
1.2449
1.2082
0.9829
0.9646
0.9462
O
P
tBu
nPr
4i
1H NMR, CDCl3, 400 MHz
1.00
1.02
1.04
1.15
4.10
1.00
2.01
4.05
2.10
9.01
3.06
f1 (ppm)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145.9
140.7
137.3
137.2
132.5
132.4
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128.6
128.1
127.3
127.2
126.6
126.5
37.6
35.3
35.3
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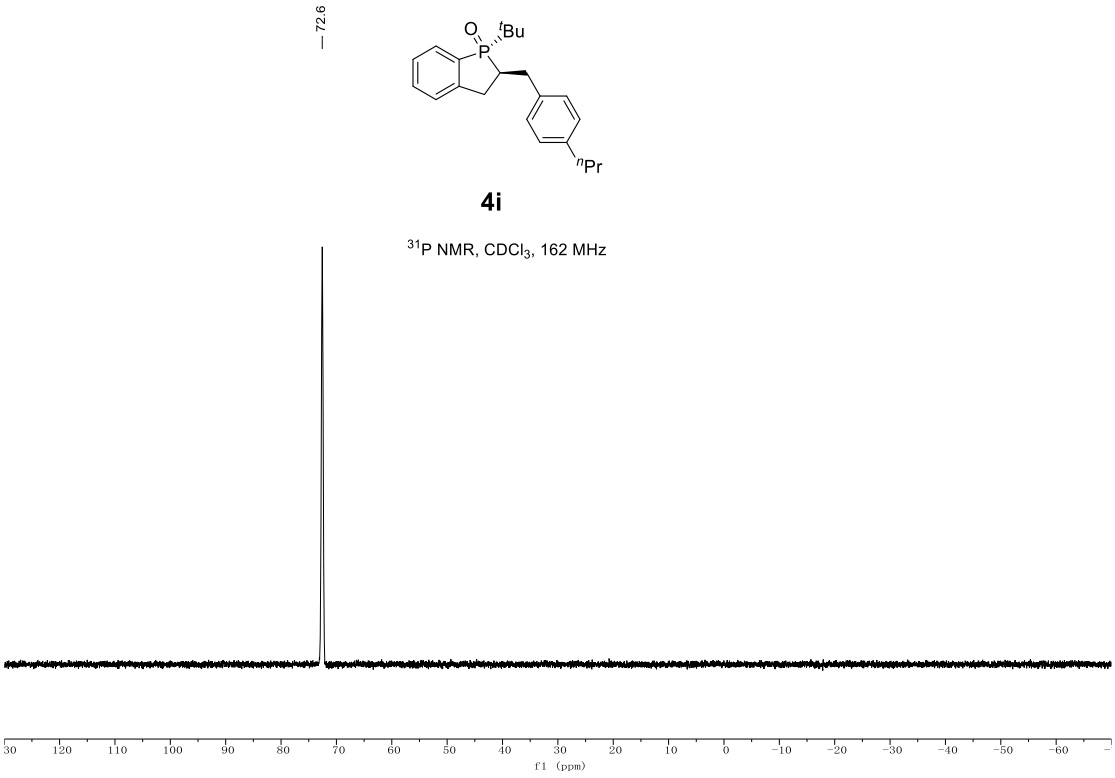
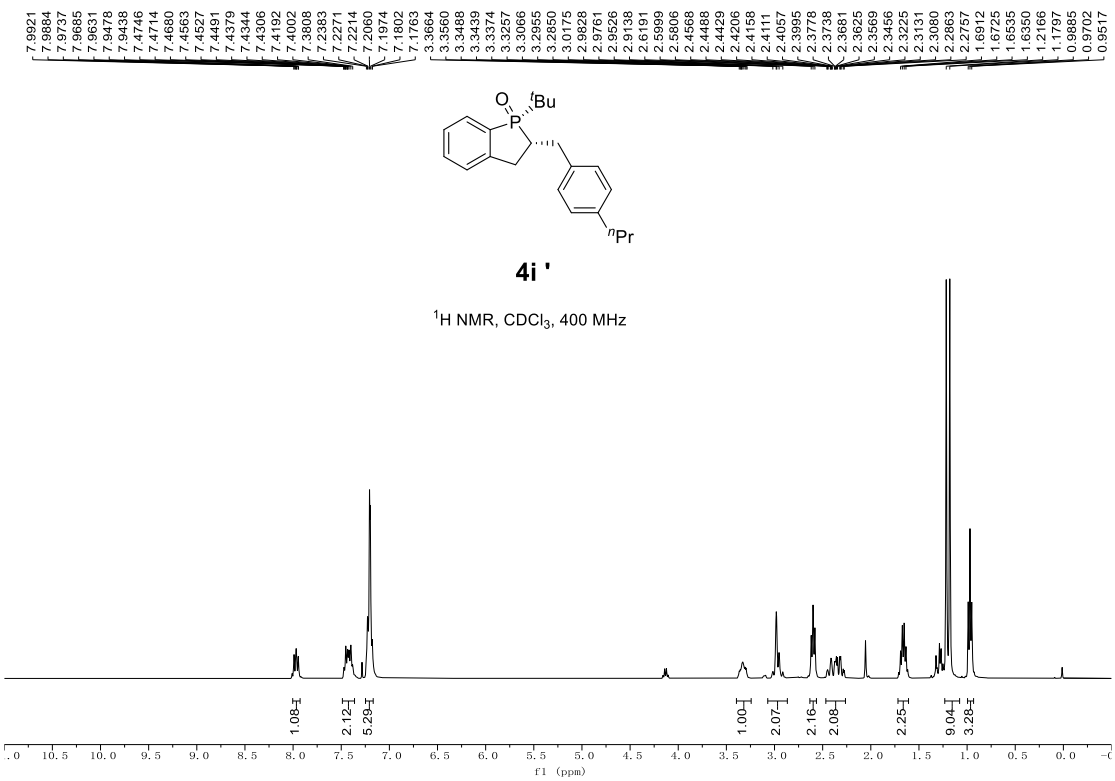
34.4
33.8
33.5
33.1
32.9
24.5
24.0
13.8
O
P
tBu
nPr
4i
13C NMR, CDCl3, 101 MHz
f1 (ppm)


72.6
O
tBu
P
nPr
4i
31P NMR, CDCl3, 162 MHz
f1 (ppm)


O
tBu
P
nPr
4i '
1H NMR, CDCl3, 400 MHz
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5.29
1.00
2.07
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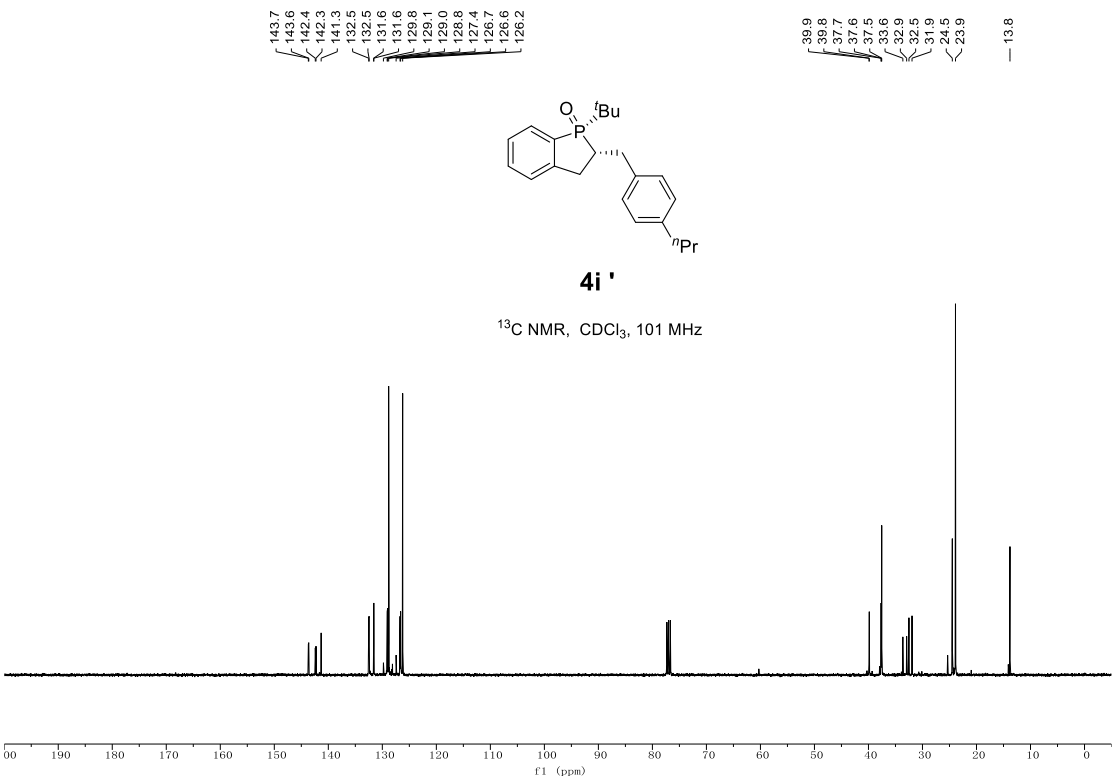
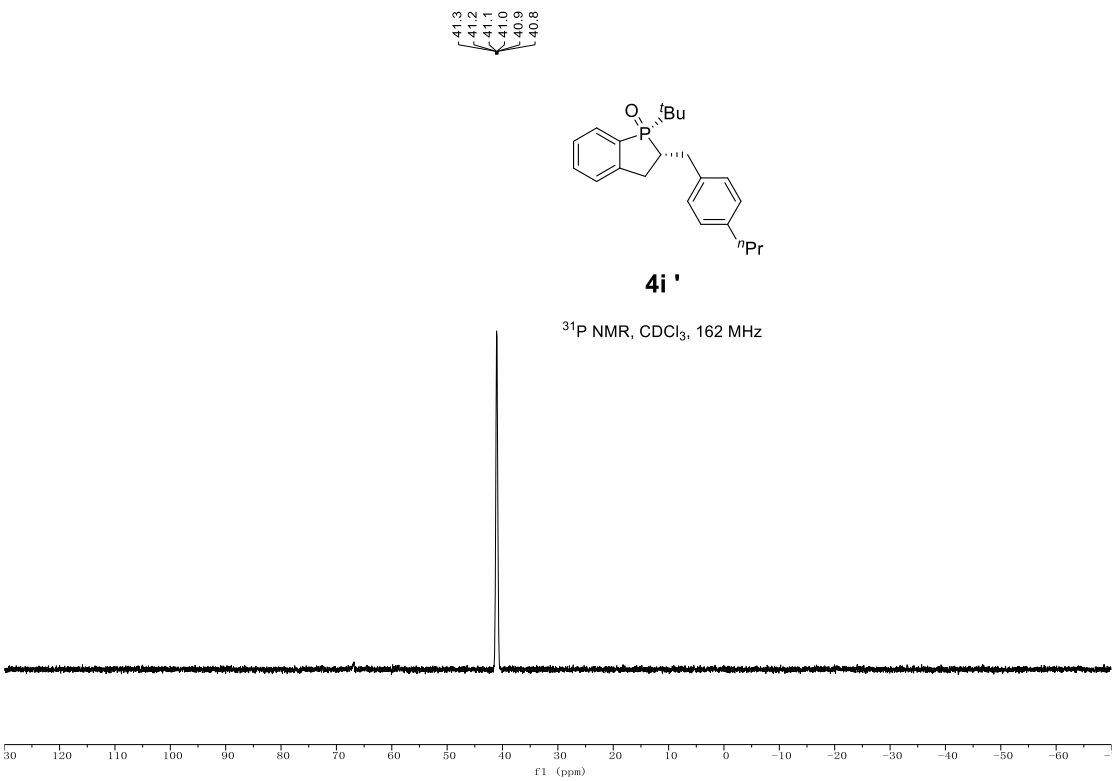
2.08
2.25
9.04
3.28
f1 (ppm)



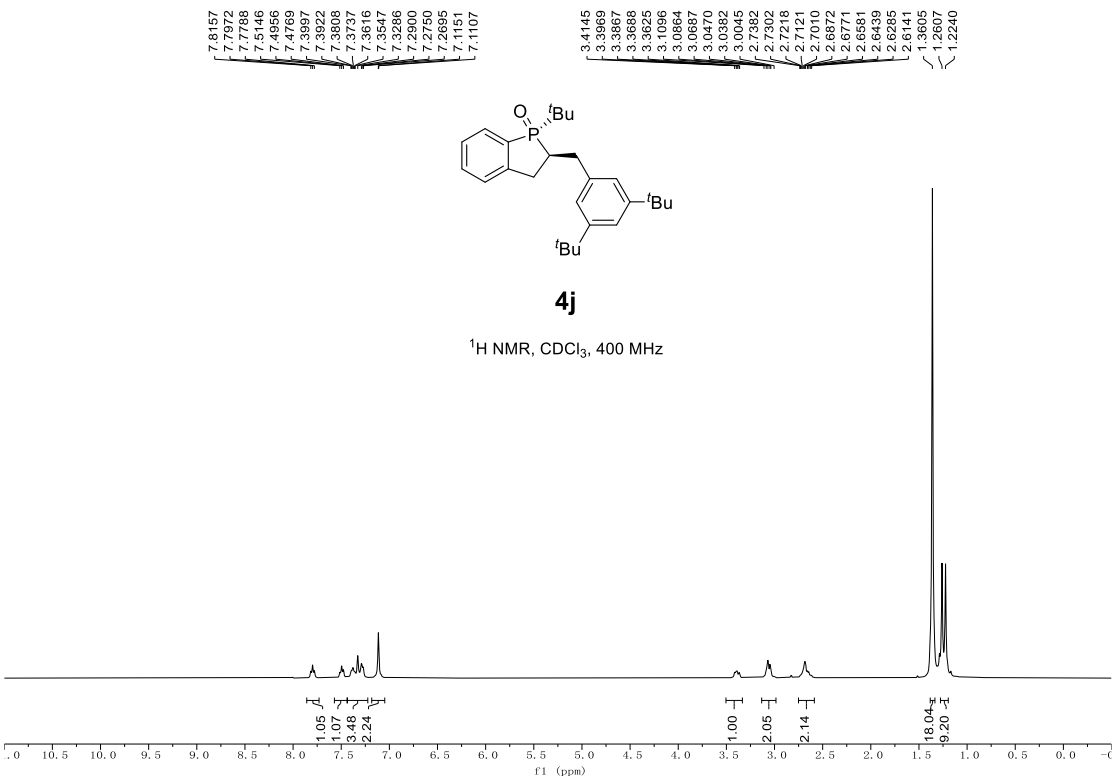
4i '

^{13}C NMR, $CDCl_3$, 101 MHz



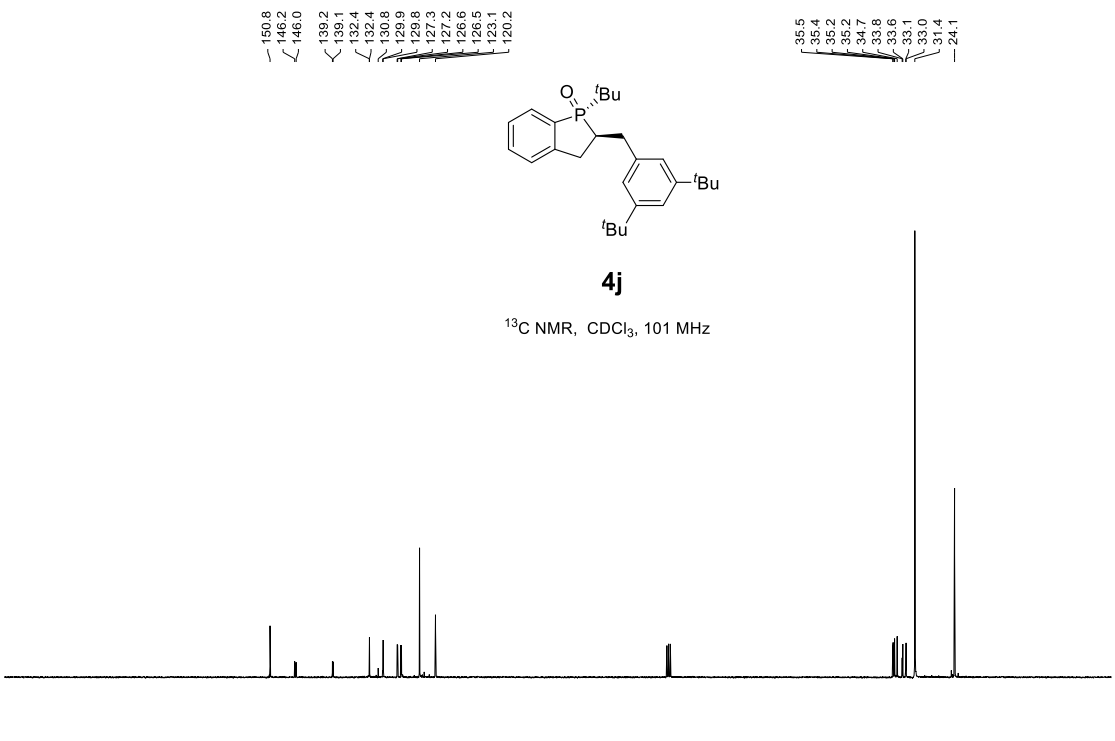
4i '

^{31}P NMR, $CDCl_3$, 162 MHz



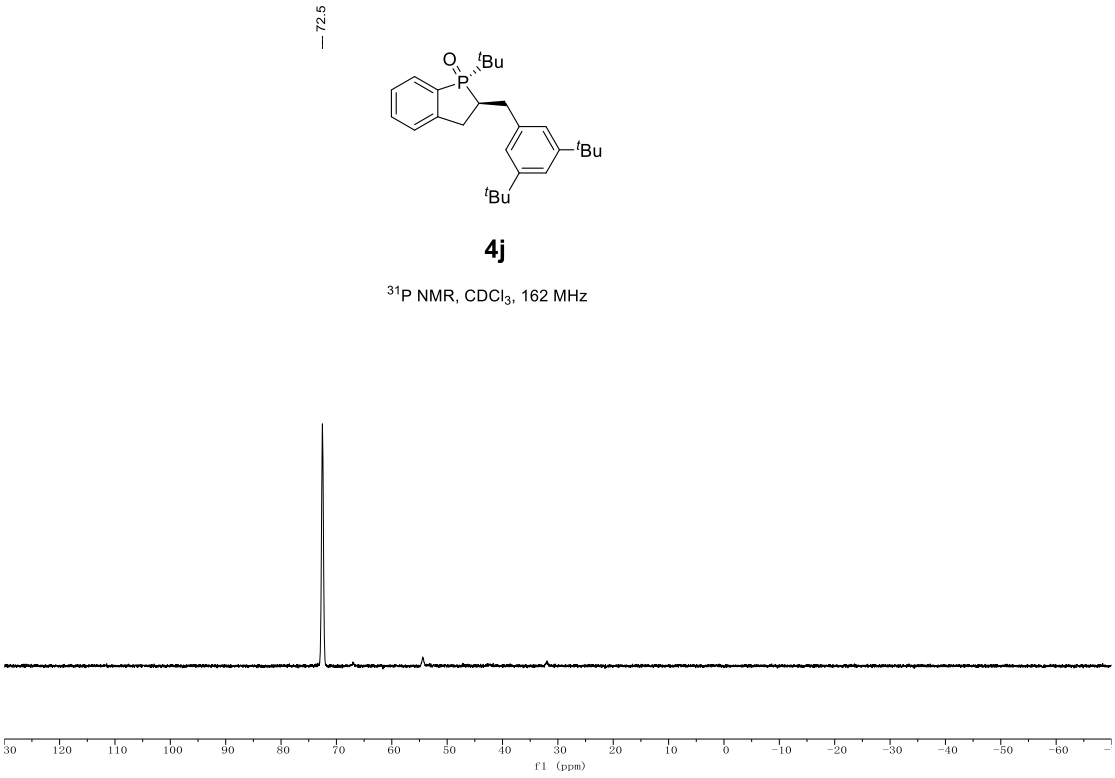
4j

^{1}H NMR, $CDCl_3$, 400 MHz



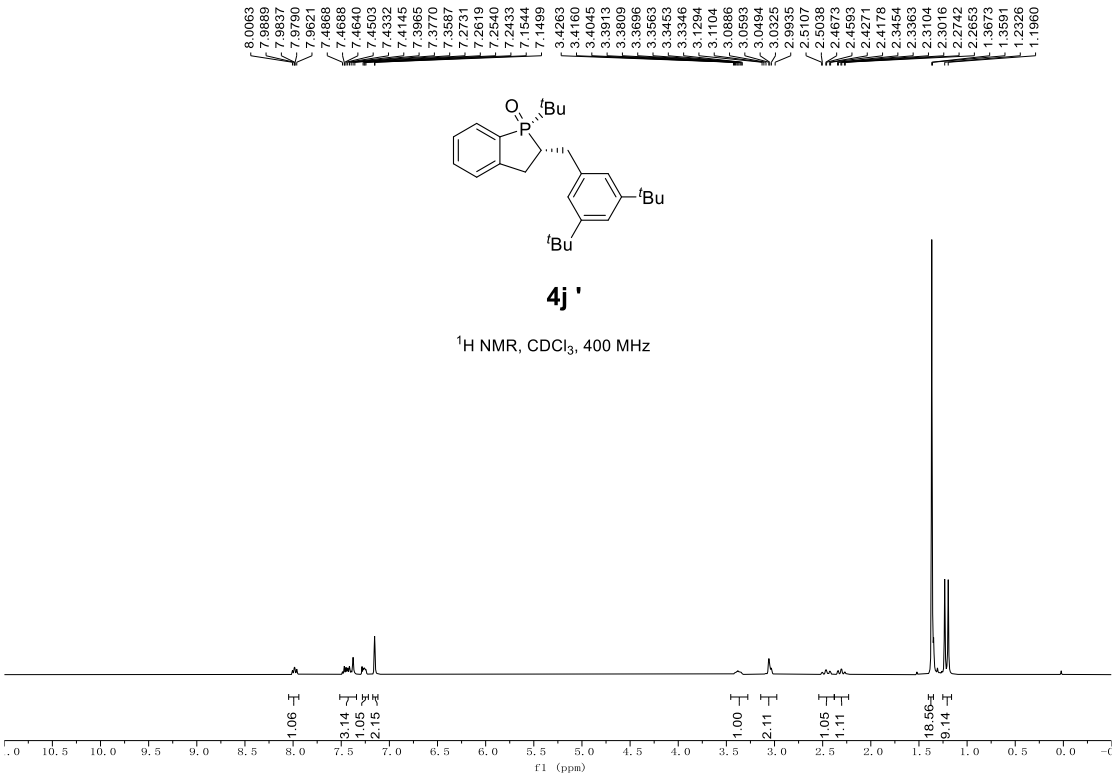
4j

^{13}C NMR, $CDCl_3$, 101 MHz



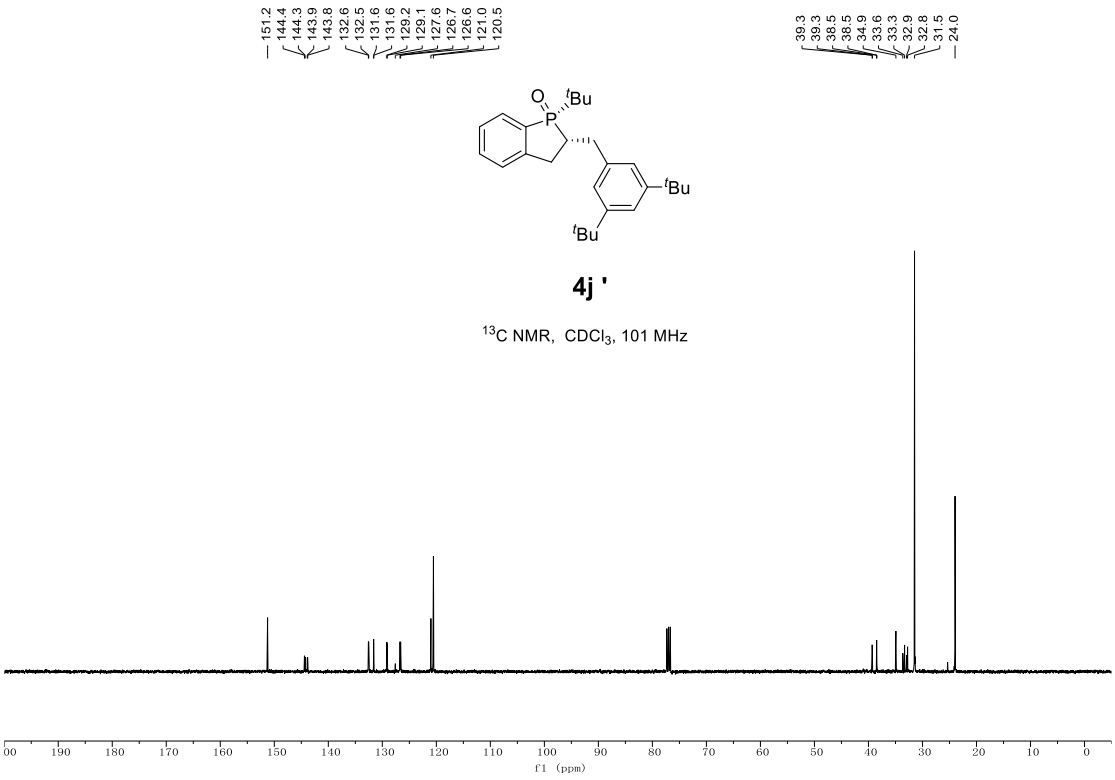
4j

^{31}P NMR, $CDCl_3$, 162 MHz



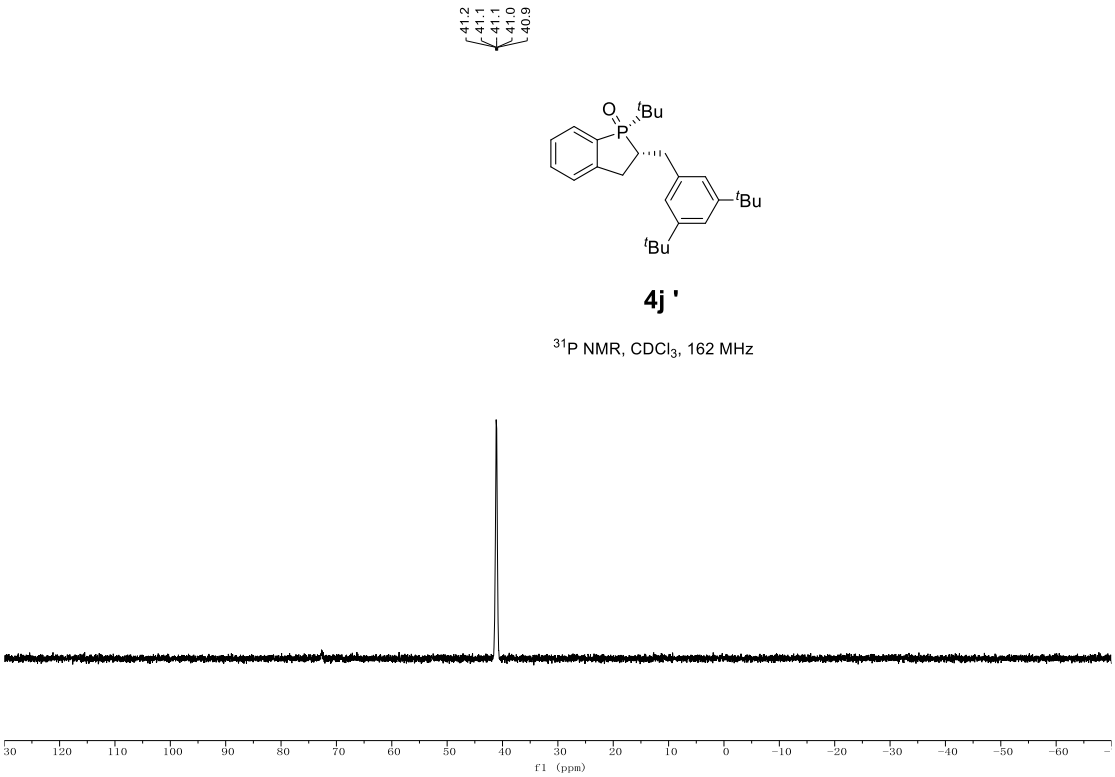
4j '

^{1}H NMR, $CDCl_3$, 400 MHz



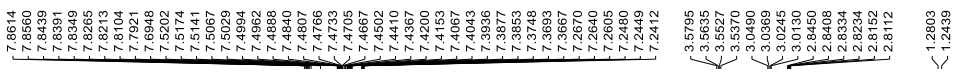
4j '

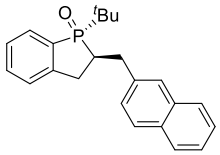
^{13}C NMR, $CDCl_3$, 101 MHz



4j '

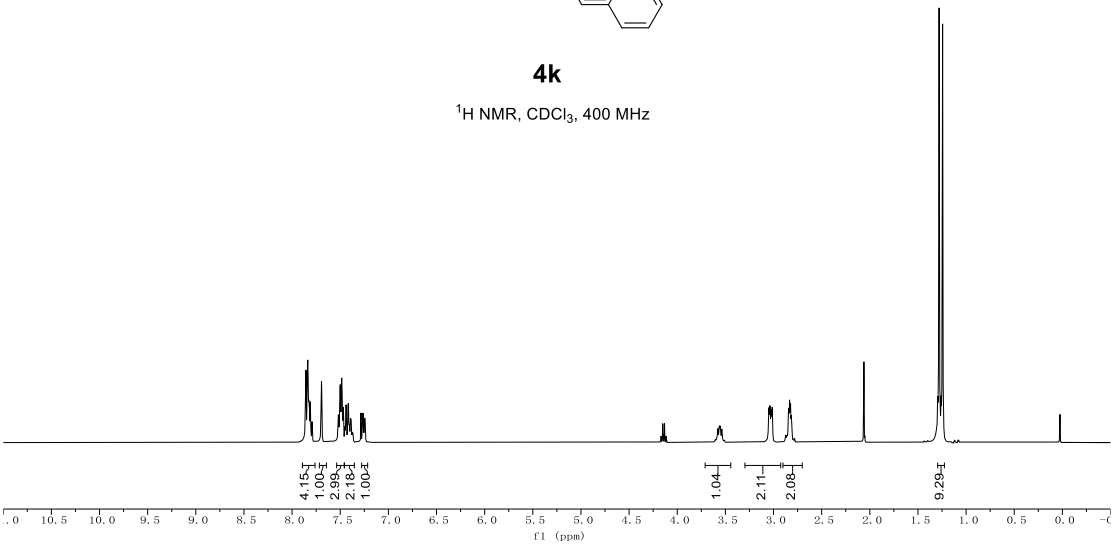
^{31}P NMR, $CDCl_3$, 162 MHz

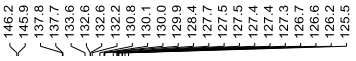


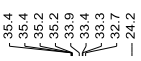


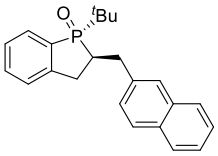
4k

^{1}H NMR, $CDCl_3$, 400 MHz



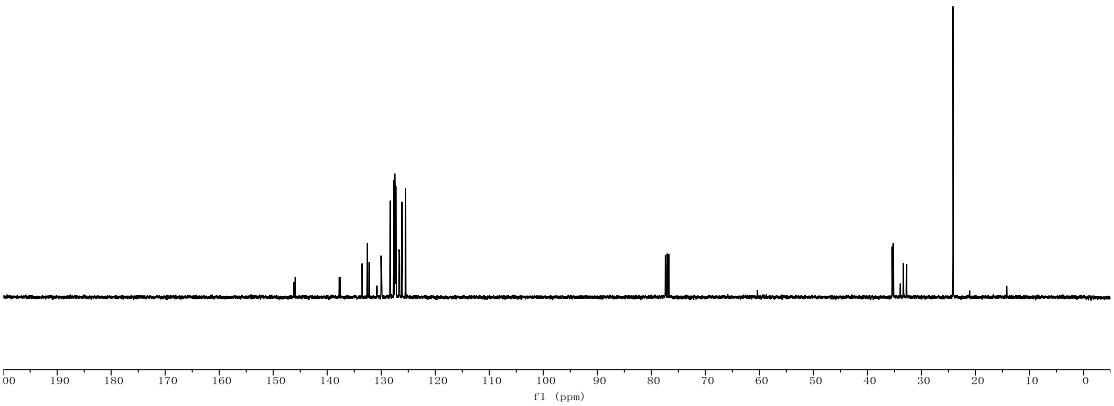


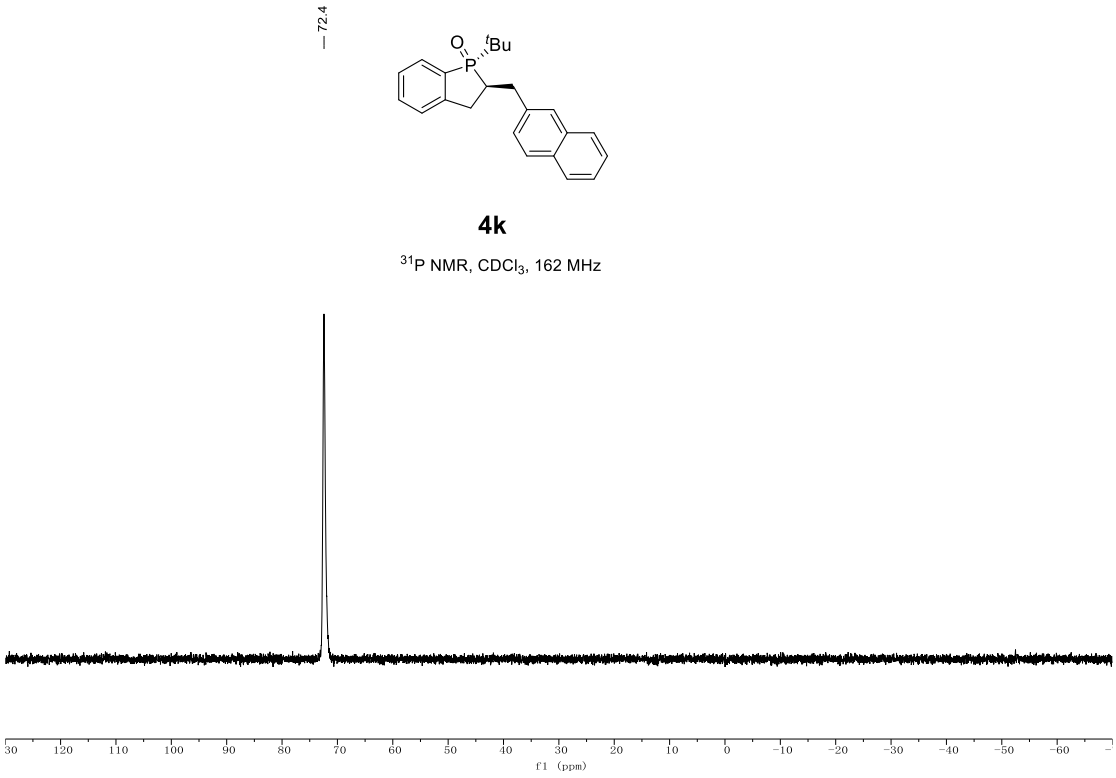




4k

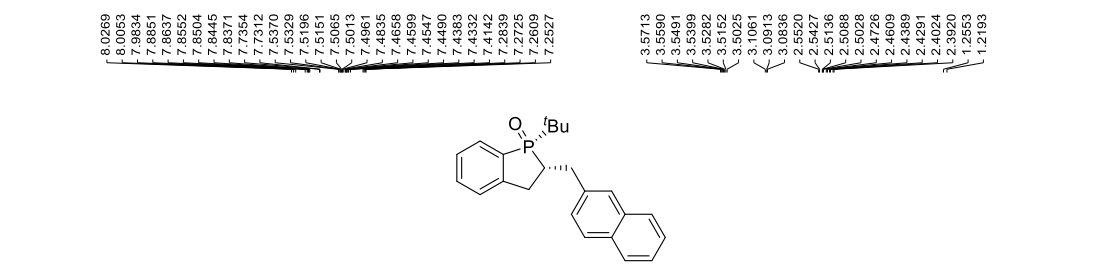
^{13}C NMR, $CDCl_3$, 101 MHz





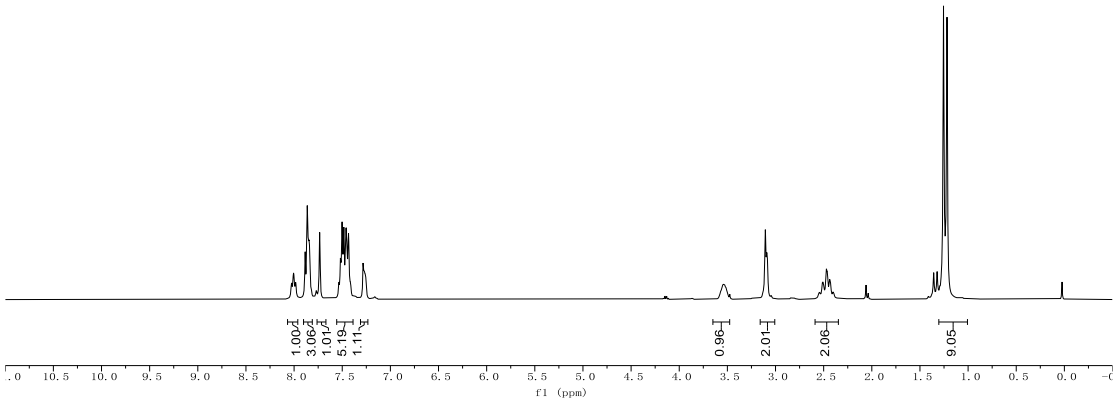
4k

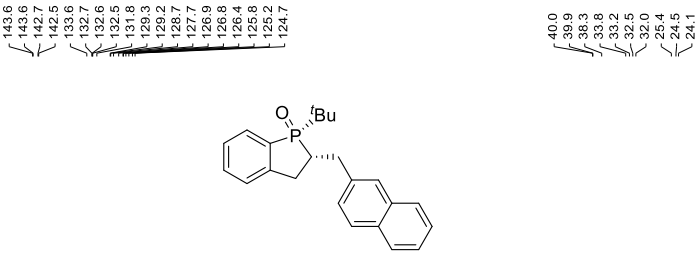
^{31}P NMR, $CDCl_3$, 162 MHz



4k '

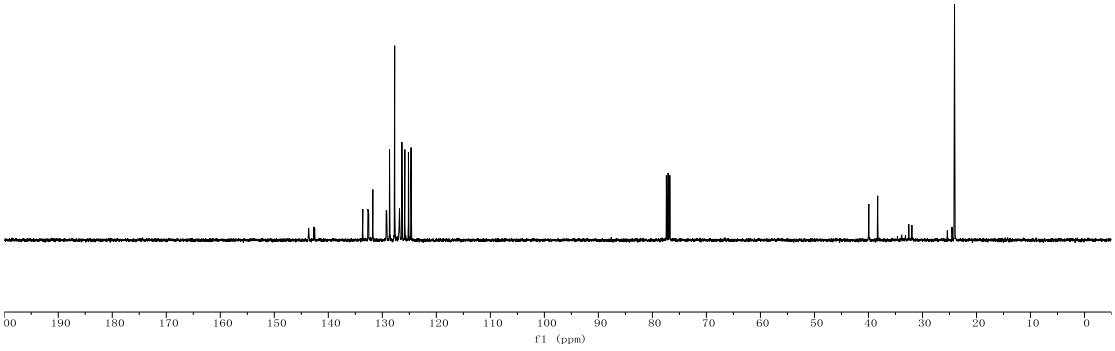
^{1}H NMR, $CDCl_3$, 400 MHz

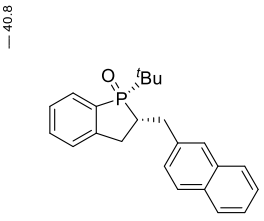




4k '

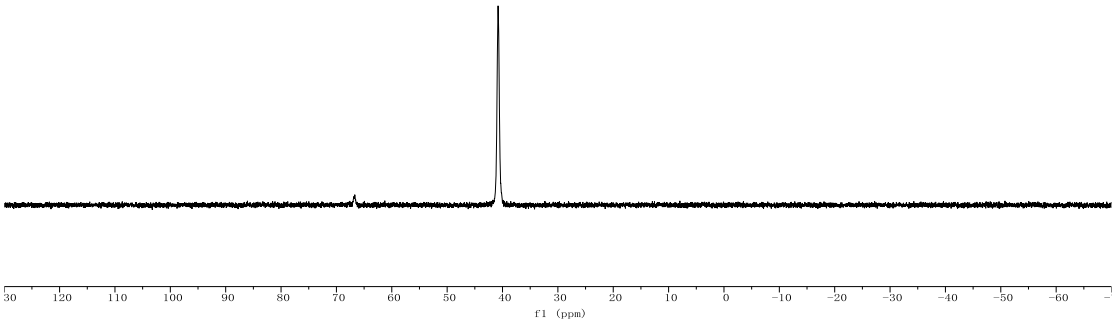
^{13}C NMR, $CDCl_3$, 101 MHz

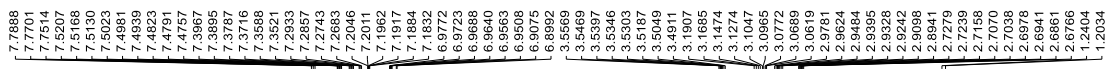


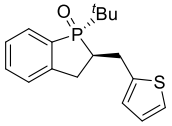


4k '

^{31}P NMR, $CDCl_3$, 162 MHz

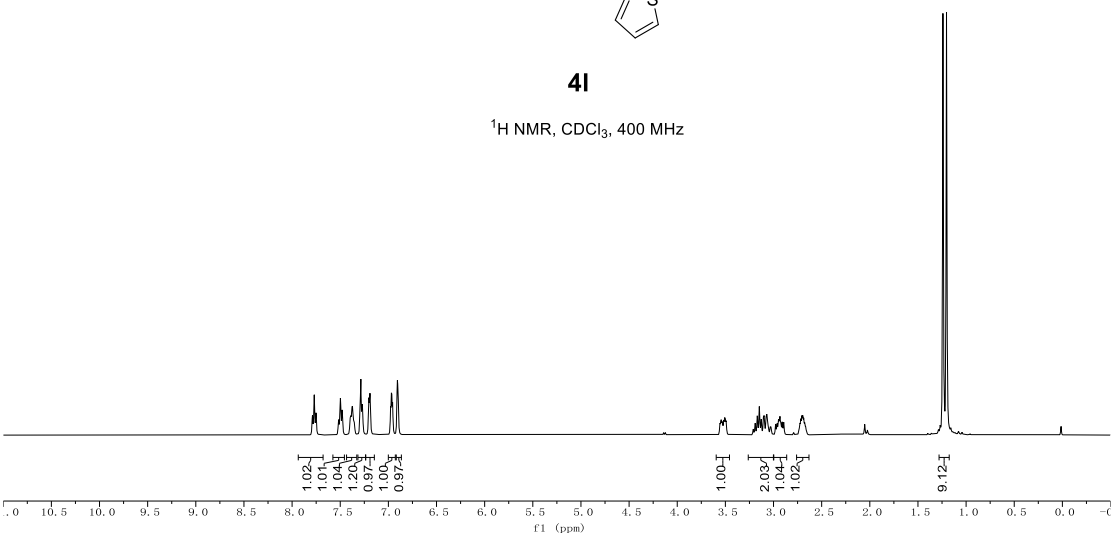


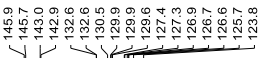


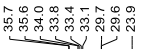


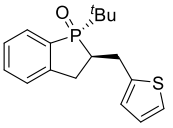
4l

^{1}H NMR, $CDCl_3$, 400 MHz



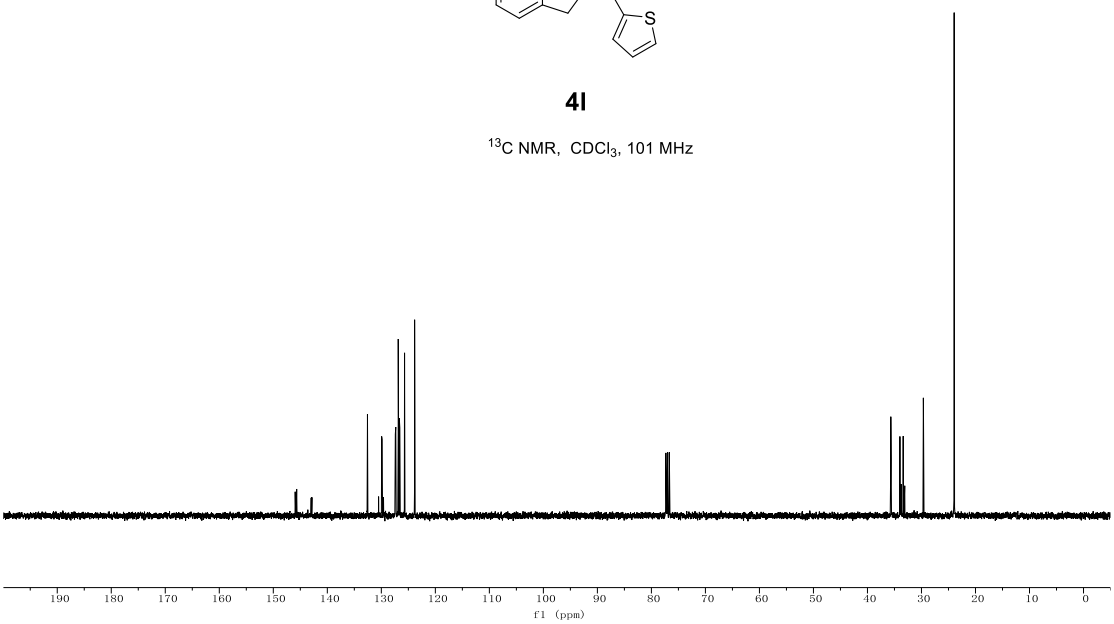


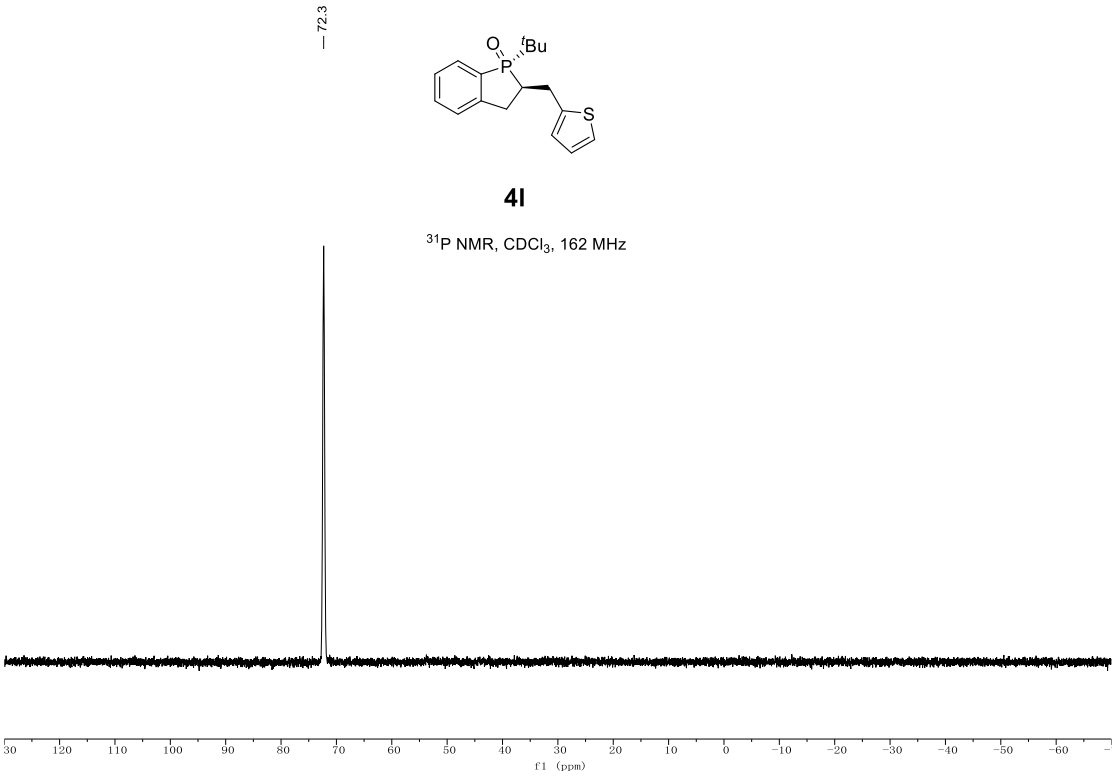




4l

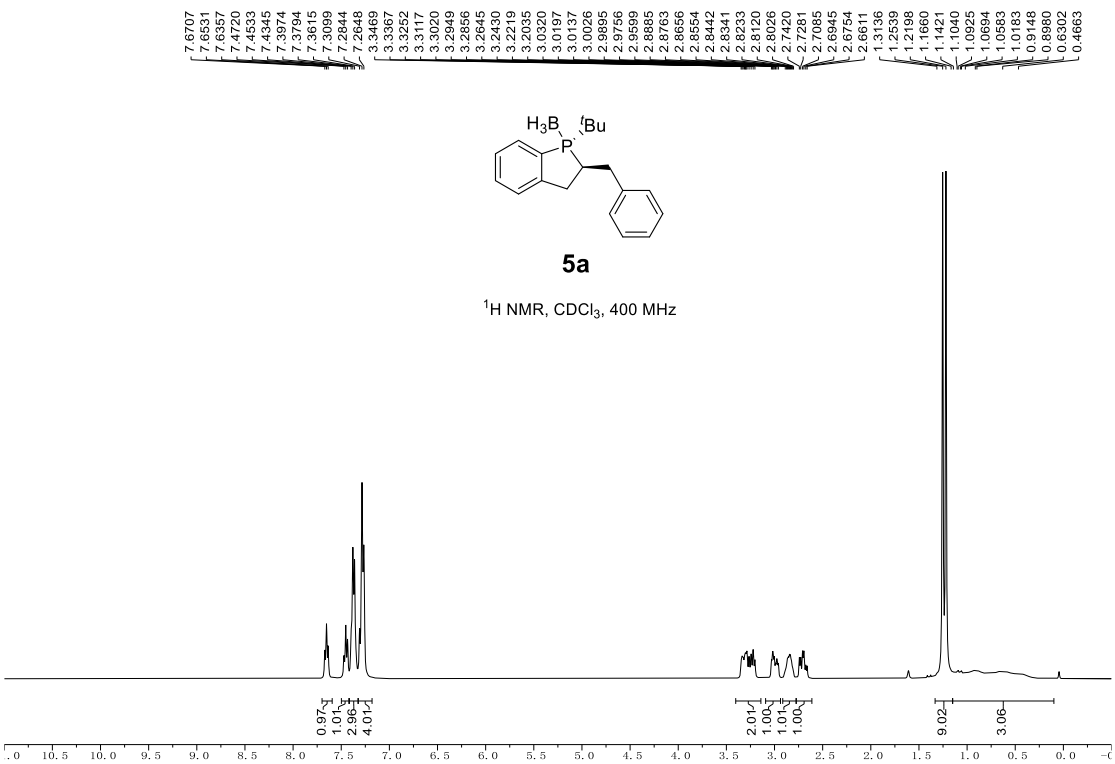
^{13}C NMR, $CDCl_3$, 101 MHz





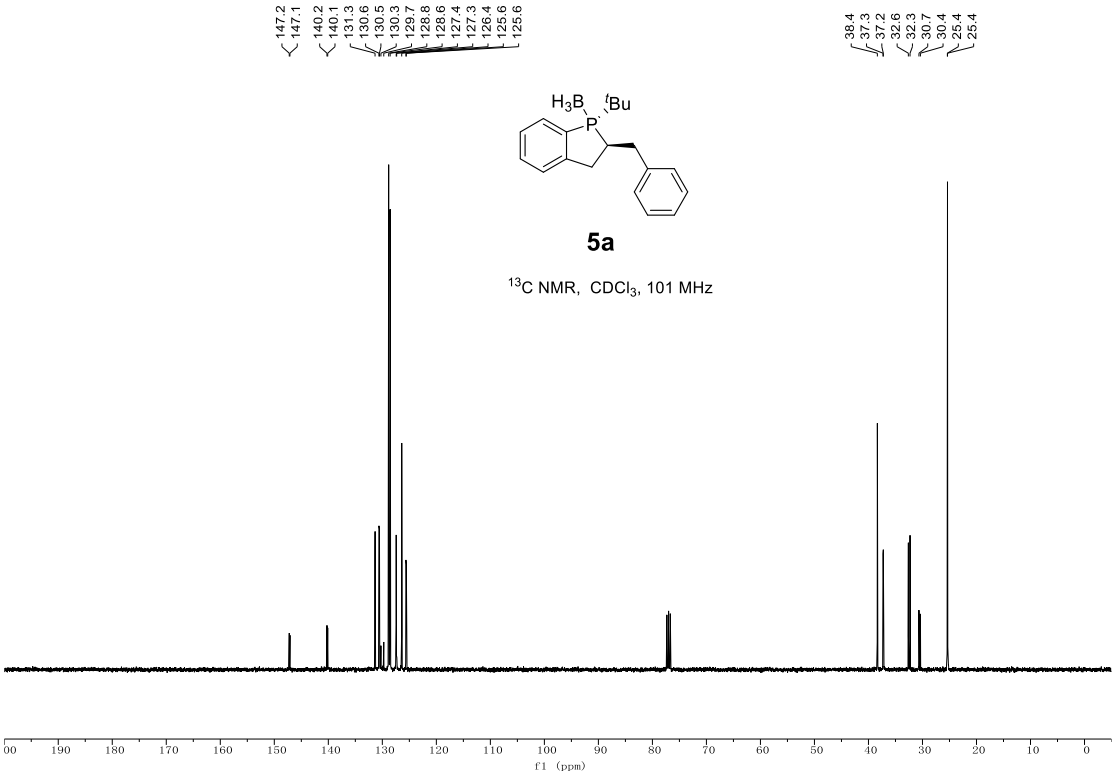
4l

^{31}P NMR, $CDCl_3$, 162 MHz



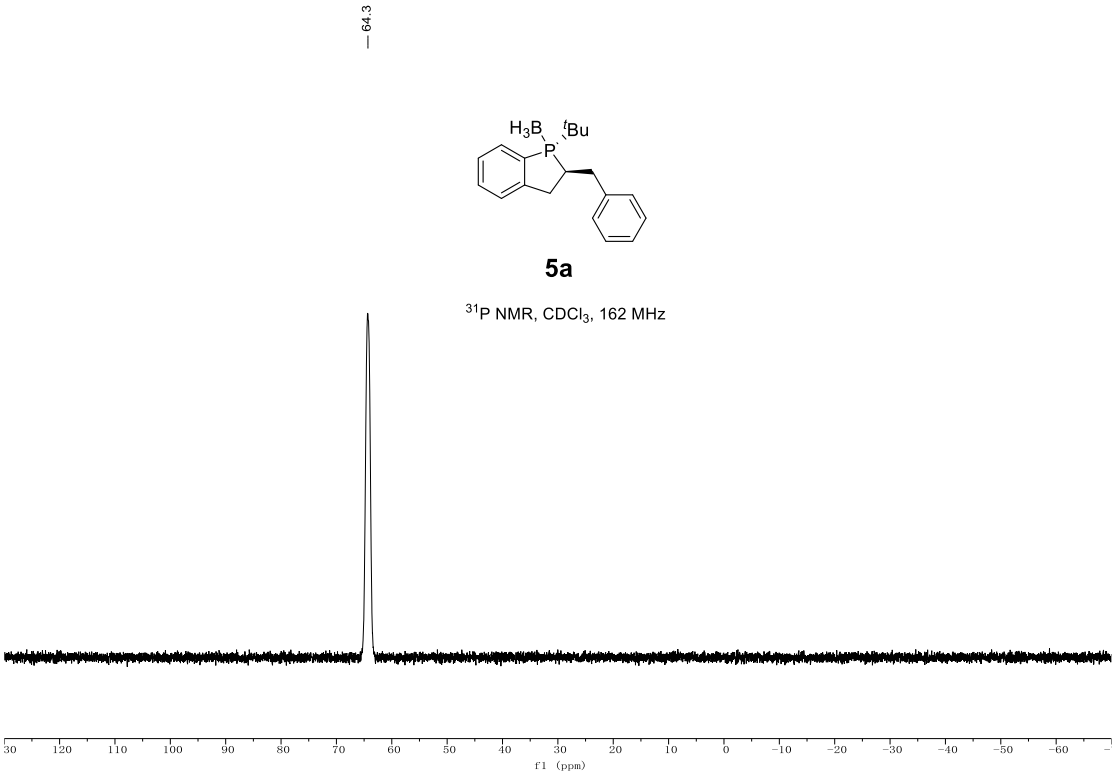
5a

^{1}H NMR, $CDCl_3$, 400 MHz



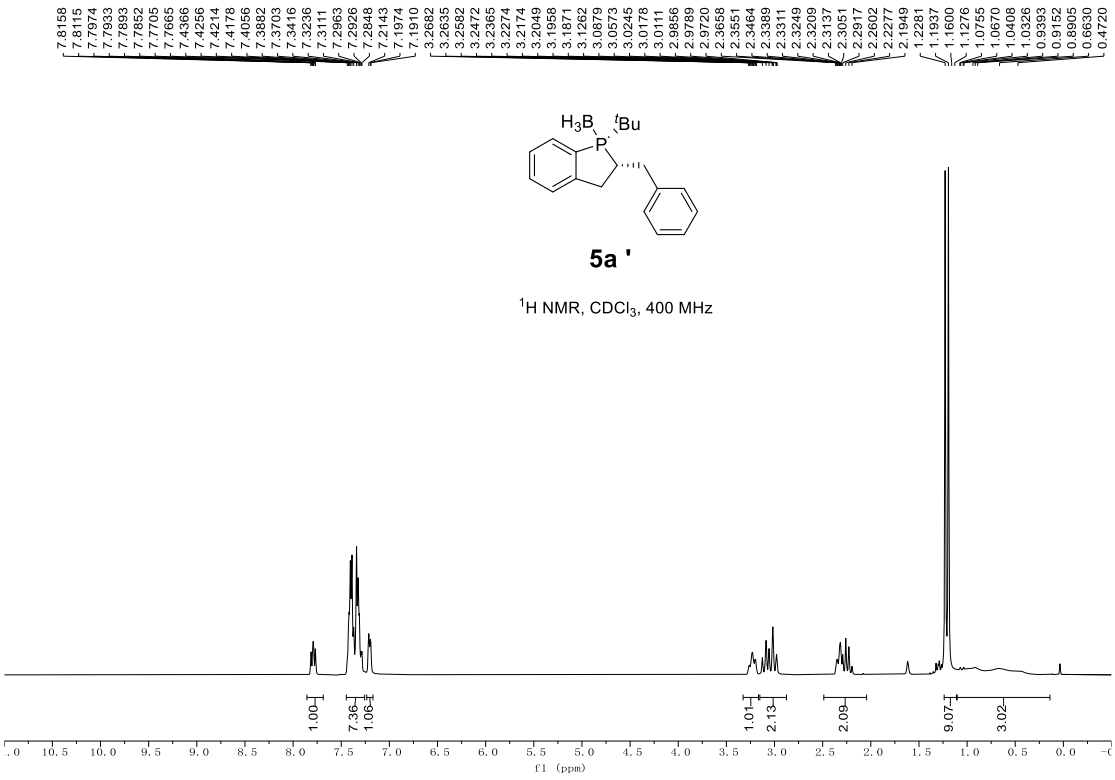
5a

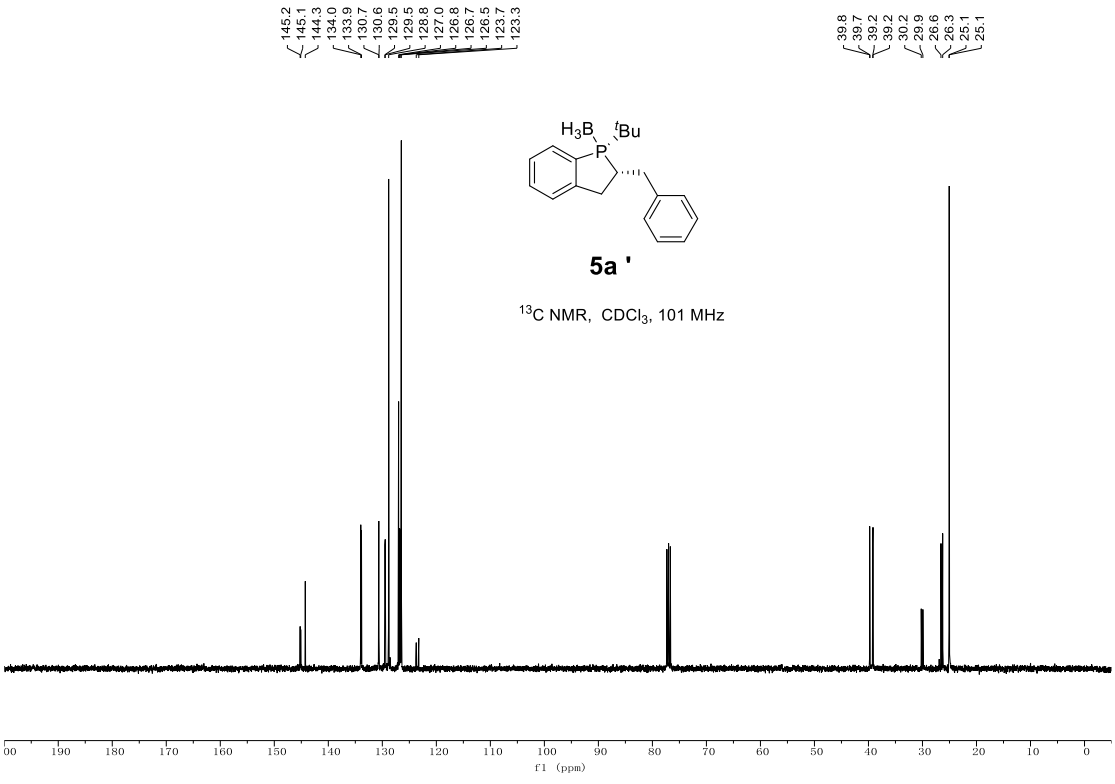
^{13}C NMR, $CDCl_3$, 101 MHz

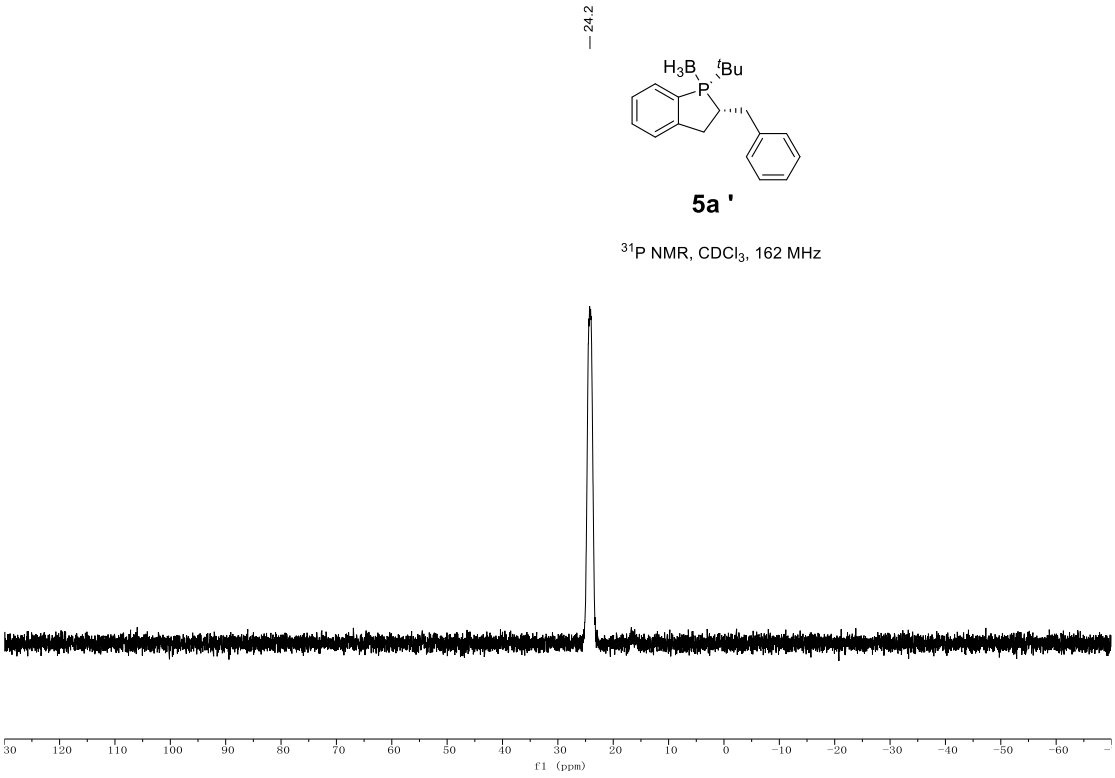


5a

^{31}P NMR, $CDCl_3$, 162 MHz

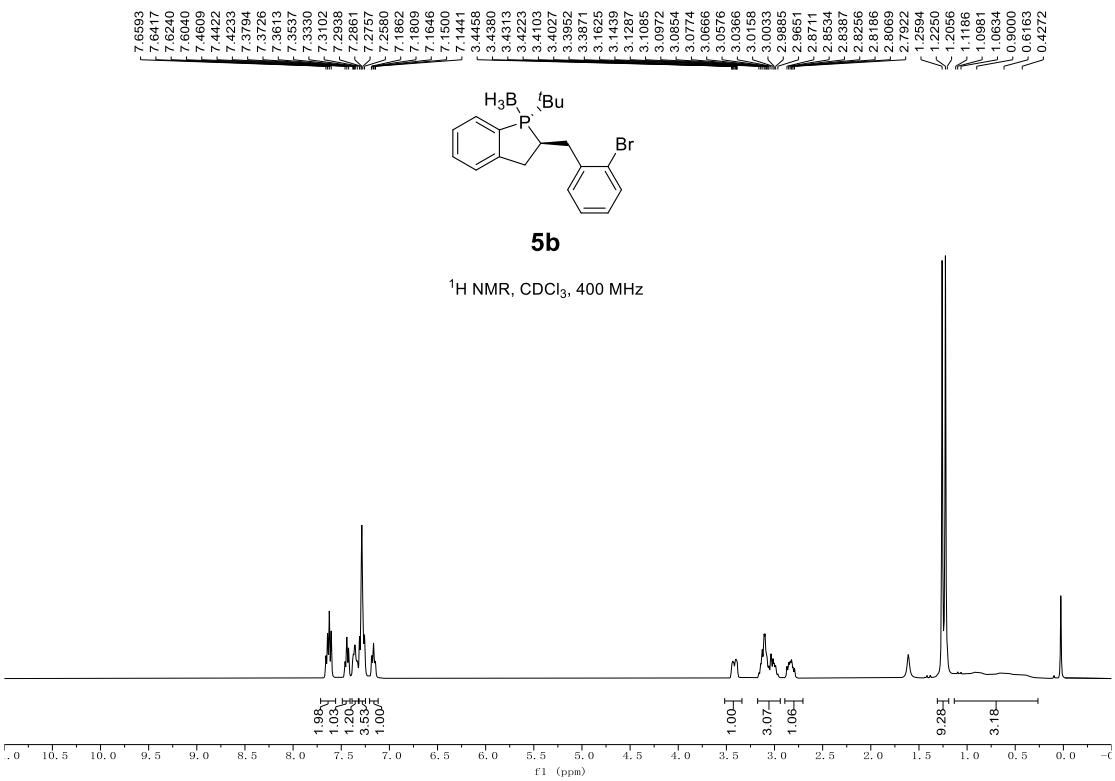

7.8158
7.8115
7.7974
7.7933
7.7893
7.7852
7.7705
7.7665
7.4366
7.4256
7.4214
7.4178
7.4056
7.3882
7.3703
7.3416
7.3236
7.3111
7.2963
7.2926
7.2848
7.2143
7.1974
7.1910
3.2682
3.2635
3.2582
3.2472
3.2365
3.2274
3.2174
3.2049
3.1958
3.1871
3.1262
3.0879
3.0573
3.0245
3.0178
3.0111
2.9856
2.9789
2.9720
2.3658
2.3551
2.3464
2.3389
2.3311
2.3249
2.3209
2.3137
2.3051
2.2917
2.2602
2.2277
2.1949
1.2281
1.1937
1.1600
1.1276
1.0755
1.0670
1.0408
1.0326
0.9393
0.9152
0.8905
0.6630
0.4720
H3B
tBu
P
5a '
1H NMR, CDCl3, 400 MHz
1.00
7.36
1.06
1.01
2.13
2.09
9.07
3.02
f1 (ppm)


145.2
145.1
144.3
134.0
133.9
130.7
130.6
129.5
129.5
128.8
127.0
126.8
126.7
126.5
123.7
123.3
39.8
39.7
39.2
39.2
30.2
29.9
26.6
26.3
25.1
25.1
H3B
tBu
P
5a '
13C NMR, CDCl3, 101 MHz
f1 (ppm)



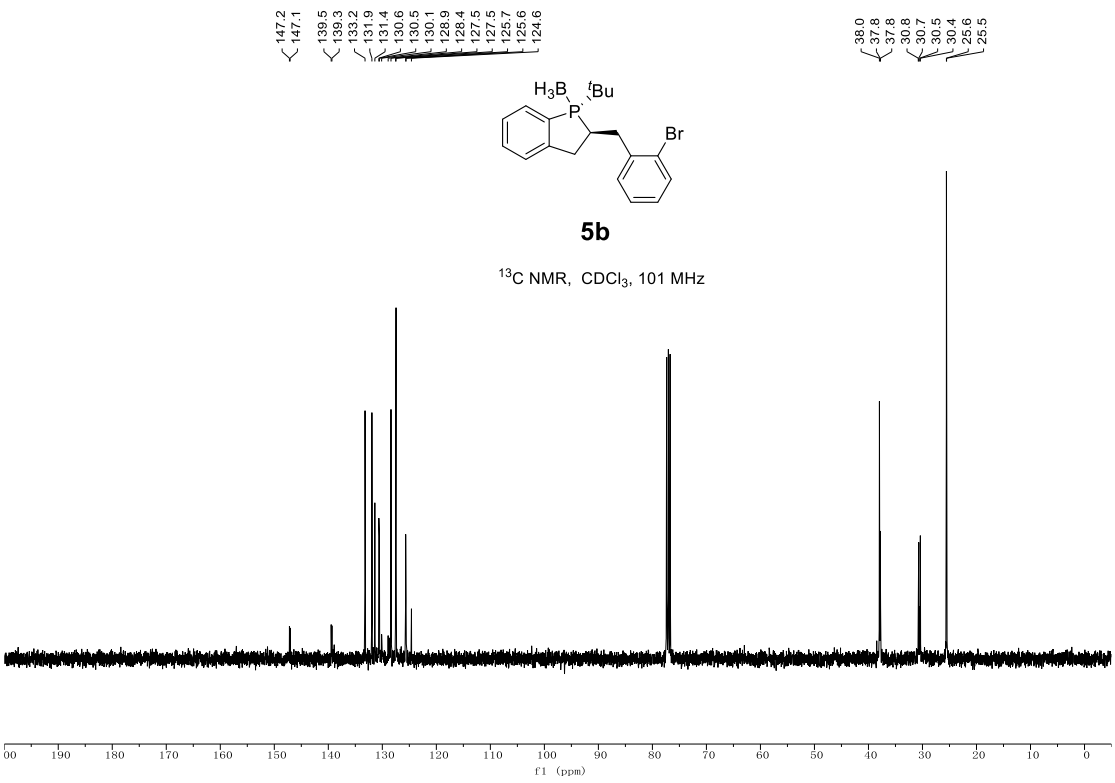
5a '

^{31}P NMR, $CDCl_3$, 162 MHz



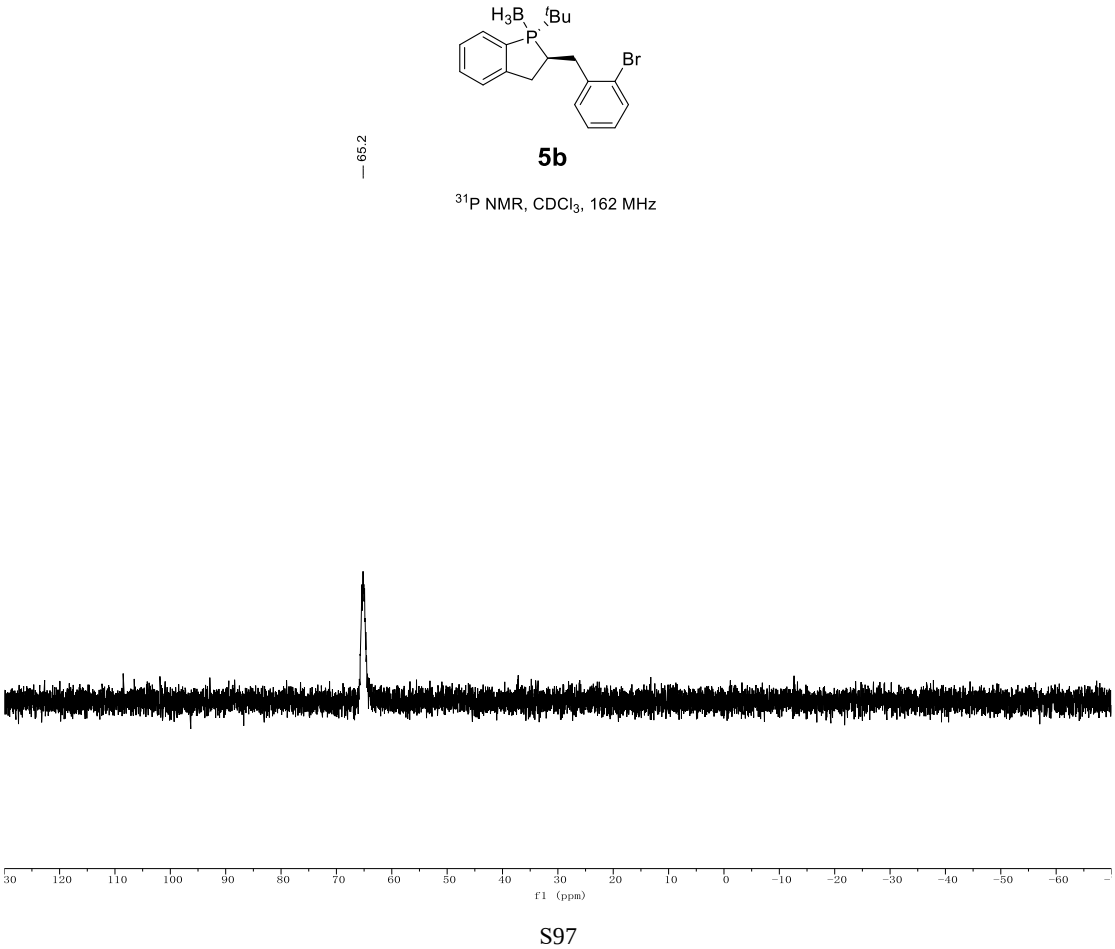
5b

^{1}H NMR, $CDCl_3$, 400 MHz



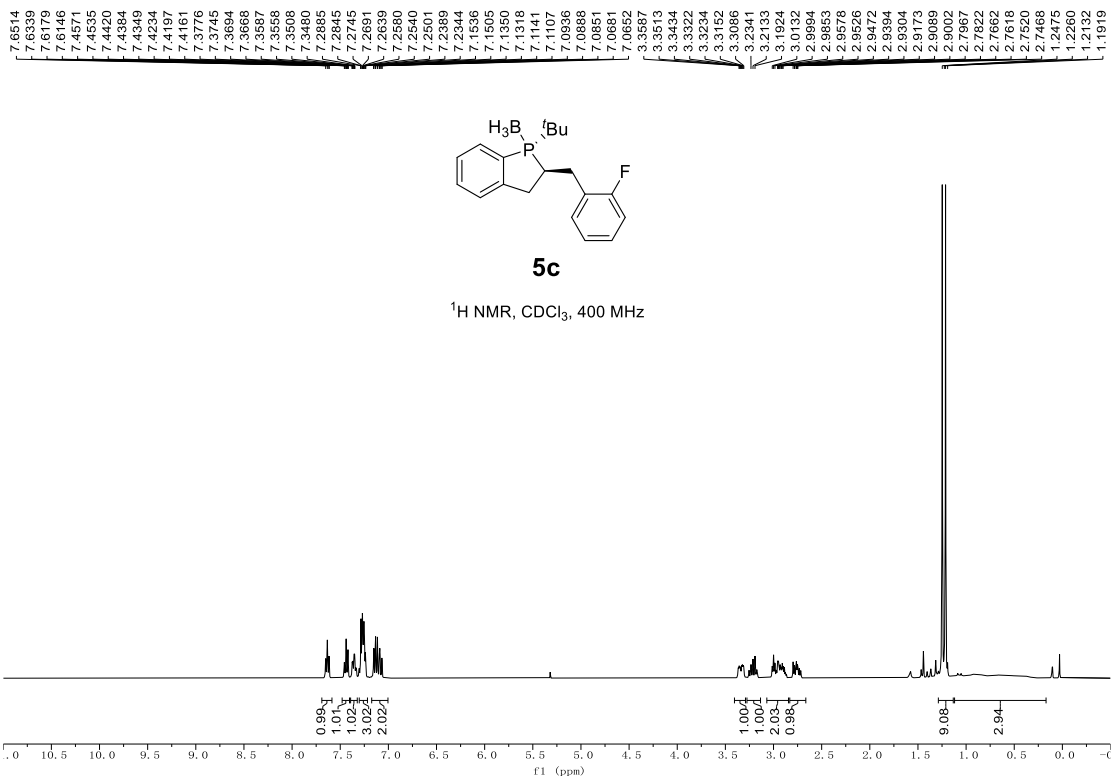
5b

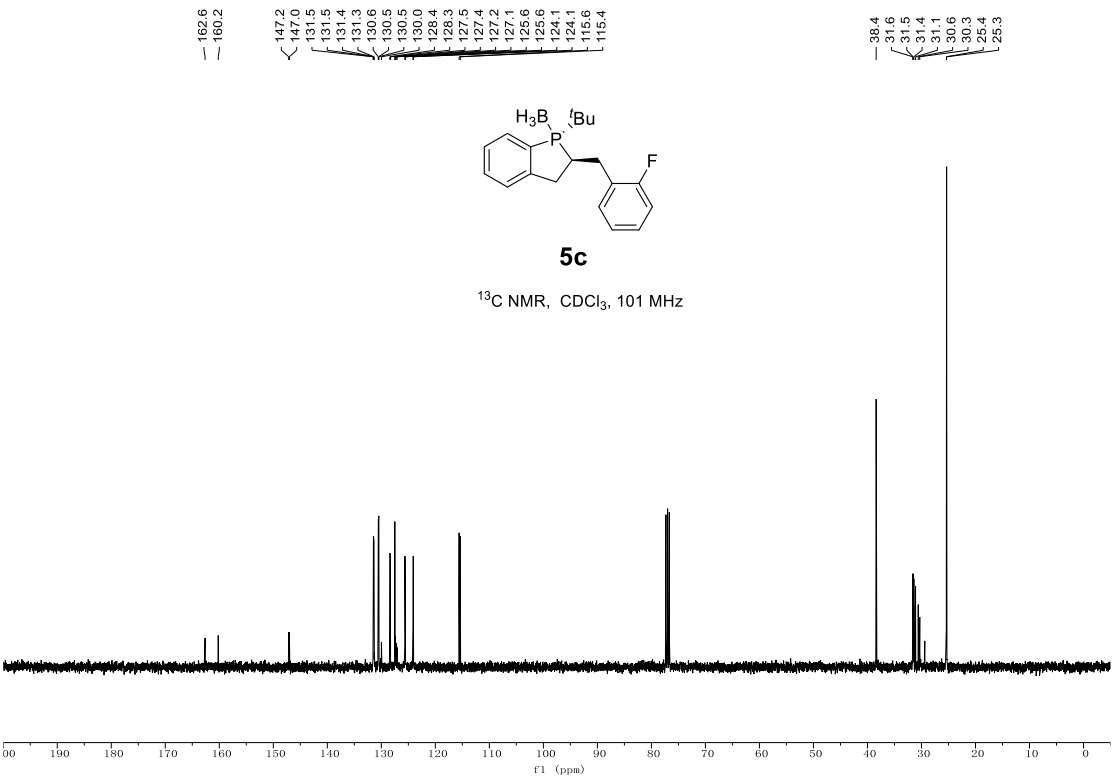
^{13}C NMR, $CDCl_3$, 101 MHz



5b

^{31}P NMR, $CDCl_3$, 162 MHz


7.6514
7.6339
7.6179
7.6146
7.4571
7.4535
7.4420
7.4384
7.4349
7.4234
7.4197
7.4161
7.3776
7.3745
7.3694
7.3668
7.3587
7.3558
7.3508
7.3480
7.2885
7.2845
7.2745
7.2691
7.2639
7.2580
7.2540
7.2501
7.2389
7.2344
7.1536
7.1505
7.1350
7.1318
7.1141
7.1107
7.0936
7.0888
7.0851
7.0681
7.0652
3.3587
3.3513
3.3434
3.3322
3.3234
3.3152
3.3086
3.2341
3.2133
3.1924
3.0132
2.9994
2.9853
2.9578
2.9526
2.9472
2.9394
2.9304
2.9173
2.9089
2.9002
2.7967
2.7822
2.7662
2.7618
2.7520
2.7468
1.2475
1.2260
1.2132
1.1919
H3B
tBu
P
F
5c
1H NMR, CDCl3, 400 MHz
0.99
1.01
1.02
3.02
2.02
1.00
1.00
2.03
0.98
9.08
2.94
f1 (ppm)


162.6
160.2
147.2
147.0
131.5
131.5
131.4
131.3
130.6
130.5
130.5
130.0
128.4
128.3
127.5
127.4
127.2
127.1
125.6
125.6
124.1
124.1
115.6
115.4
38.4
31.6
31.5
31.4
31.1
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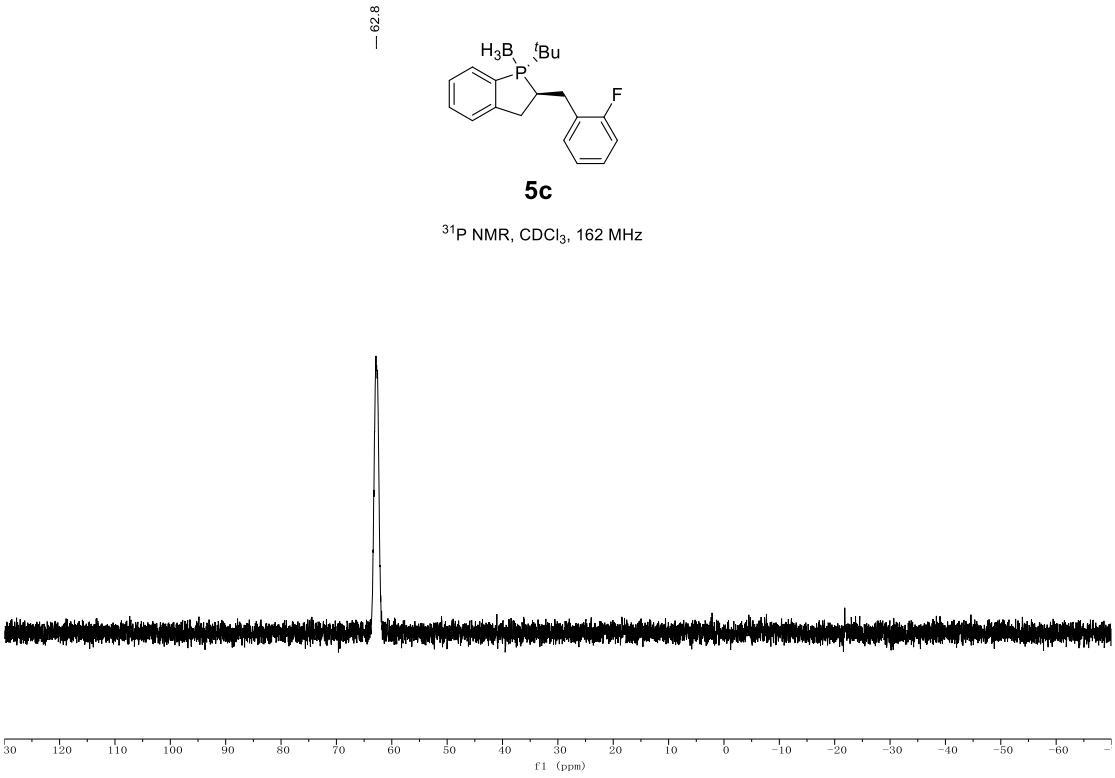
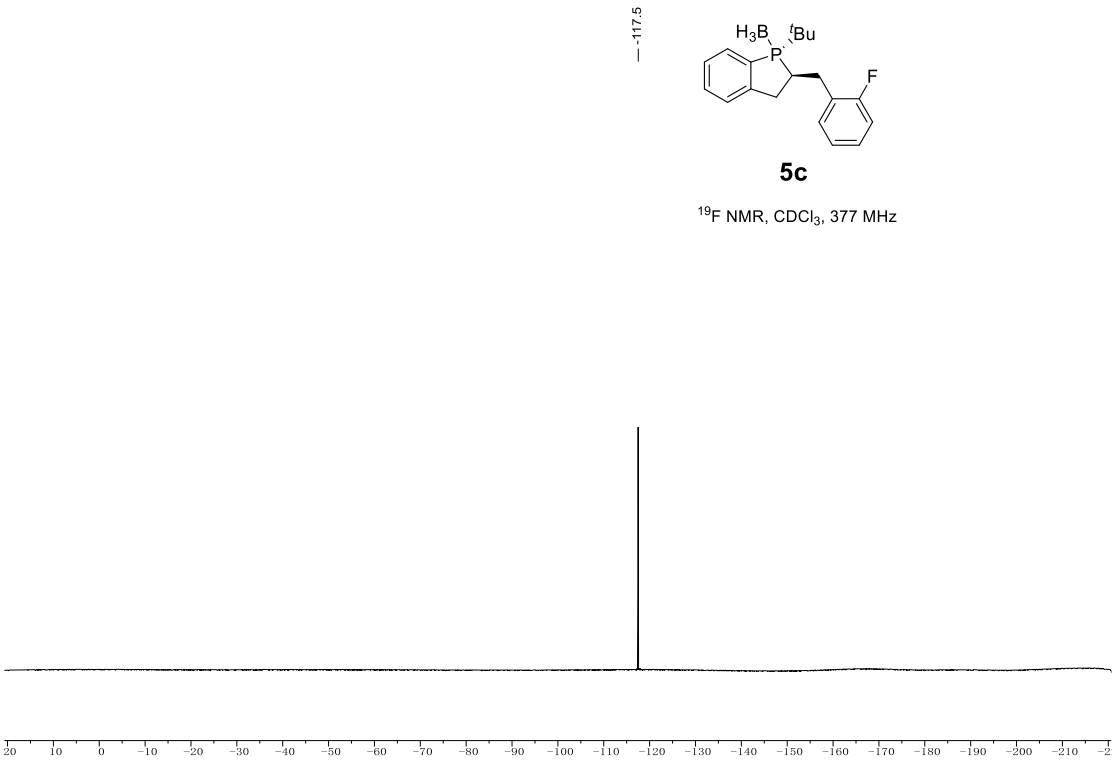
25.3
H3B
tBu
P
F
5c
13C NMR, CDCl3, 101 MHz
f1 (ppm)



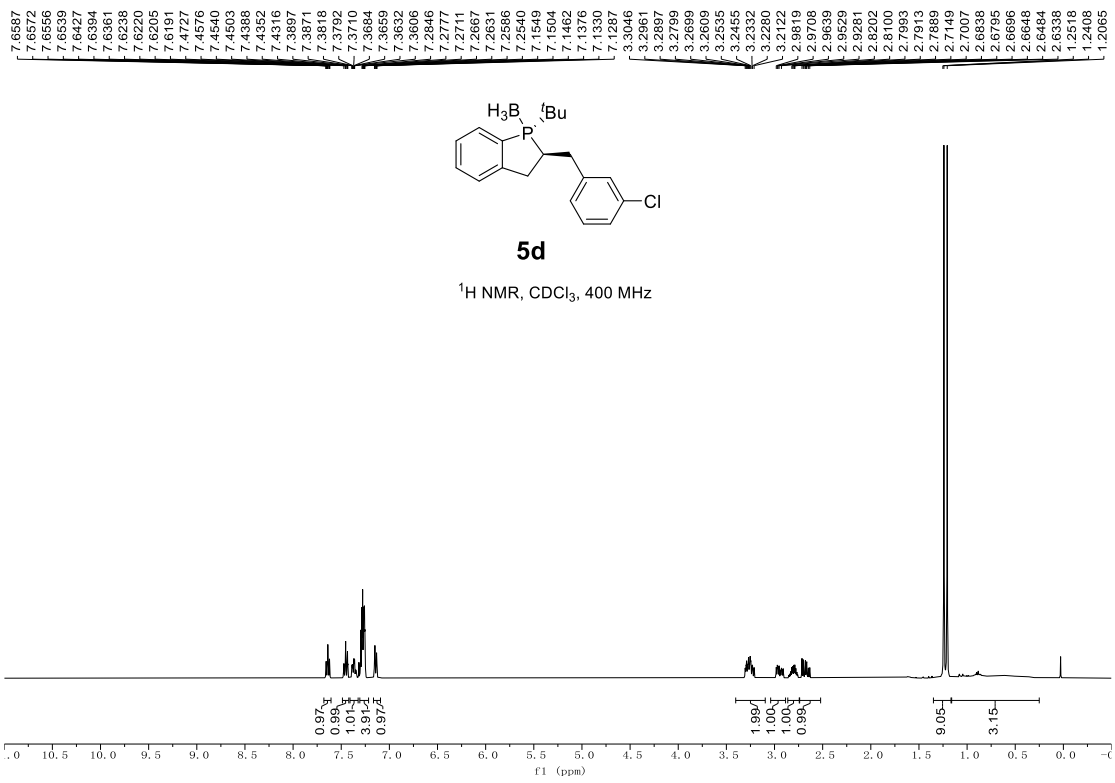
5c

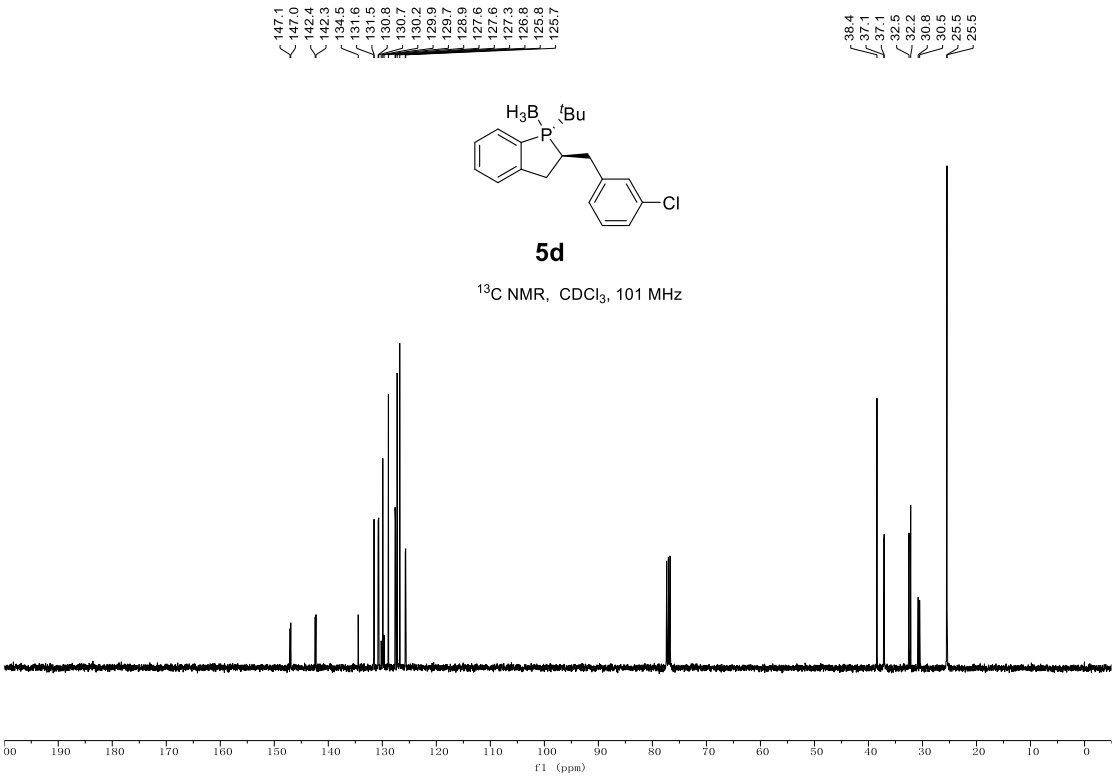
^{31}P NMR, $CDCl_3$, 162 MHz



5c

^{19}F NMR, $CDCl_3$, 377 MHz


7.6587
7.6572
7.6556
7.6539
7.6427
7.6394
7.6361
7.6238
7.6220
7.6205
7.6191
7.4727
7.4576
7.4540
7.4503
7.4388
7.4352
7.4316
7.3897
7.3871
7.3818
7.3792
7.3710
7.3684
7.3659
7.3632
7.3606
7.2846
7.2777
7.2711
7.2667
7.2631
7.2586
7.2540
7.1549
7.1504
7.1462
7.1376
7.1330
7.1287
3.3046
3.2961
3.2897
3.2799
3.2699
3.2609
3.2535
3.2455
3.2332
3.2280
3.2122
2.9819
2.9708
2.9639
2.9529
2.9281
2.8202
2.8100
2.7993
2.7913
2.7889
2.7149
2.7007
2.6838
2.6795
2.6696
2.6648
2.6484
2.6338
1.2518
1.2408
1.2065
H3B
tBu
P
Cl
5d
1H NMR, CDCl3, 400 MHz
0.97
0.99
1.01
3.91
0.97
1.99
1.00
1.00
0.99
9.05
3.15
f1 (ppm)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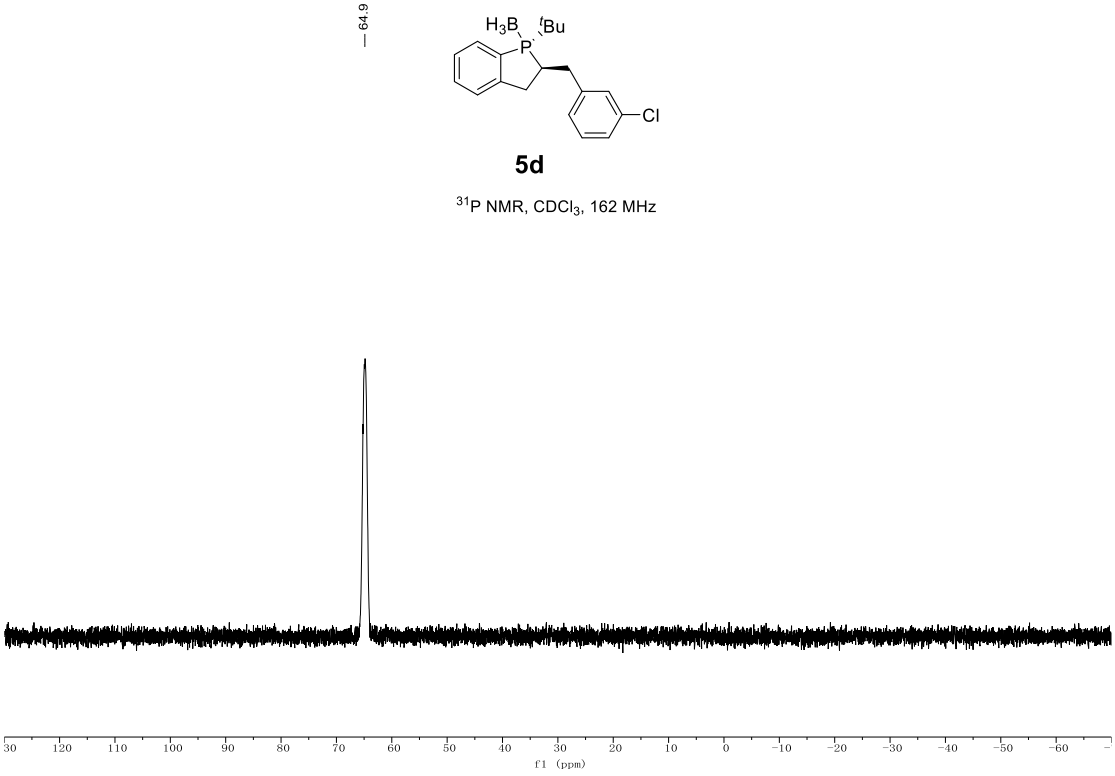
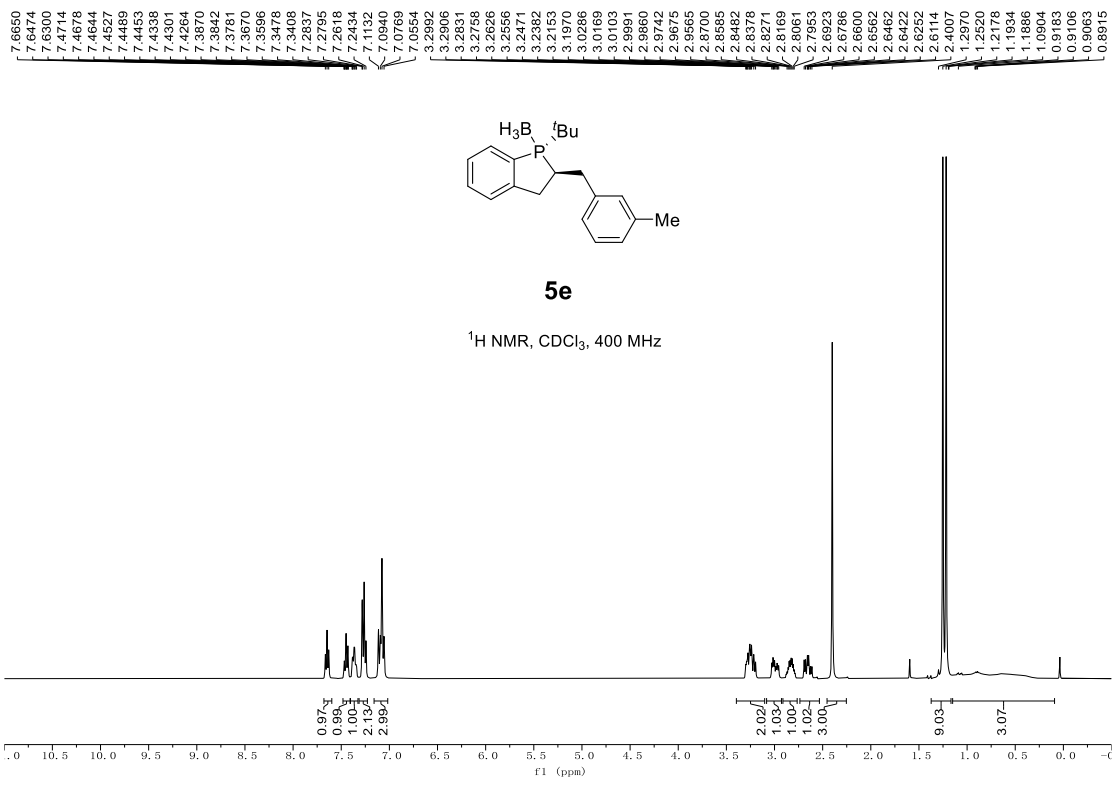
147.0
142.4
142.3
134.5
131.6
131.5
130.8
130.7
130.2
129.9
129.7
128.9
127.6
127.6
127.3
126.8
125.7
38.4
37.1
37.1
32.5
32.2
30.8
30.5
25.5
25.5
H3B
tBu
P
Cl
5d
13C NMR, CDCl3, 101 MHz
f1 (ppm)


64.9
H3B
tBu
P
Cl
5d
31P NMR, CDCl3, 162 MHz
f1 (ppm)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7.6300
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7.4527
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7.4453
7.4338
7.4301
7.4264
7.3870
7.3842
7.3781
7.3670
7.3596
7.3478
7.3408
7.2837
7.2795
7.2618
7.2434
7.1132
7.0940
7.0769
7.0554
3.2992
3.2906
3.2831
3.2758
3.2626
3.2556
3.2471
3.2382
3.2153
3.1970
3.0286
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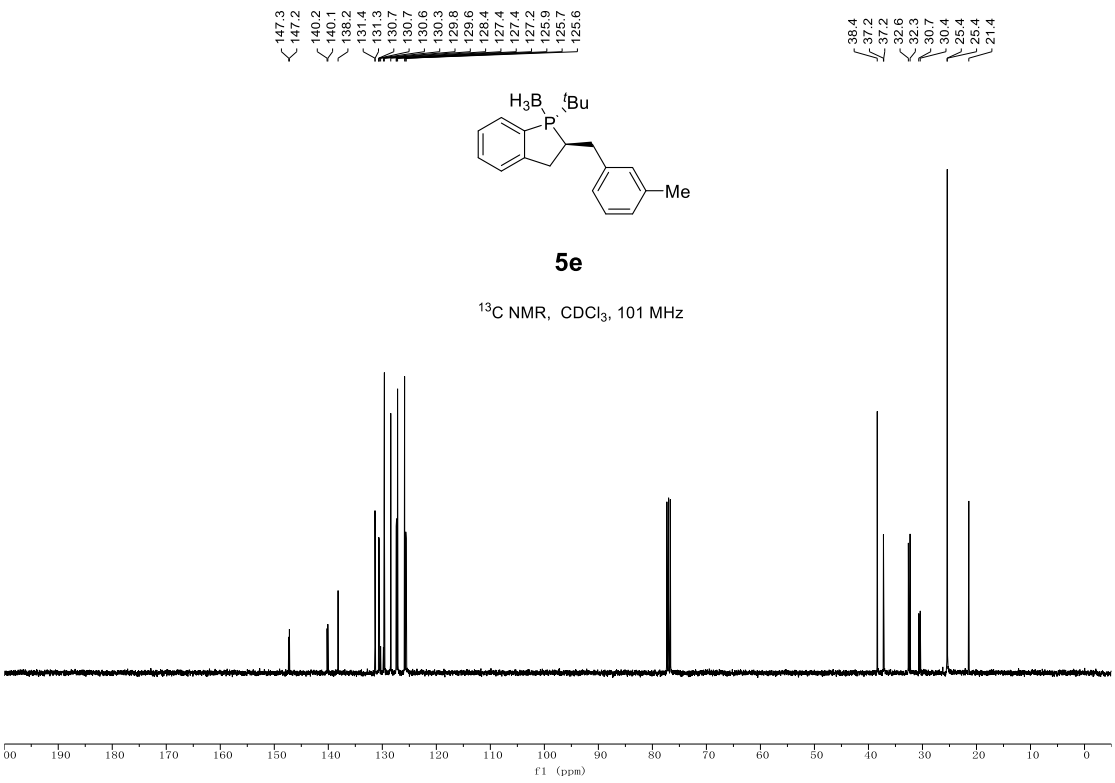
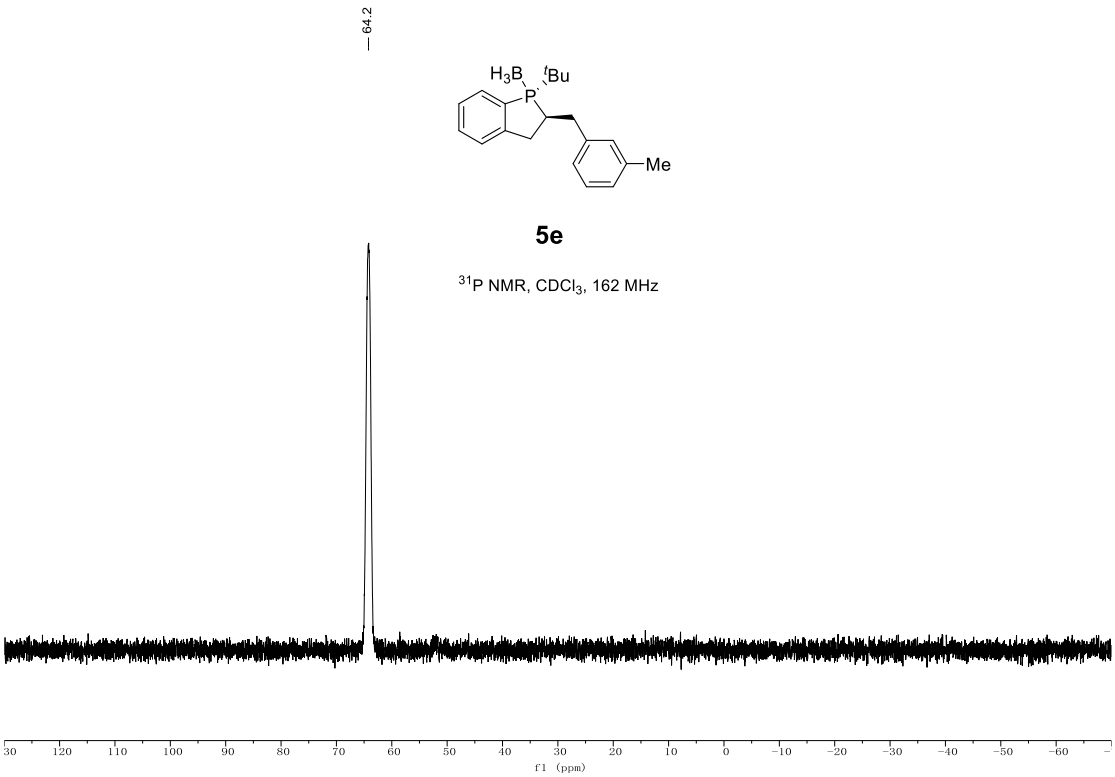
3.0103
2.9991
2.9860
2.9742
2.9675
2.9565
2.8700
2.8585
2.8482
2.8378
2.8271
2.8169
2.8061
2.7953
2.6923
2.6786
2.6600
2.6562
2.6462
2.6422
2.6252
2.6114
2.4007
1.2970
1.2520
1.2178
1.1934
1.1886
1.0904
0.9183
0.9106
0.9063
0.8915
H3B
tBu
P
Me
5e
1H NMR, CDCl3, 400 MHz
0.97
0.98
1.00
2.13
2.99
2.02
1.03
1.00
1.02
3.00
9.03
3.07
f1 (ppm)



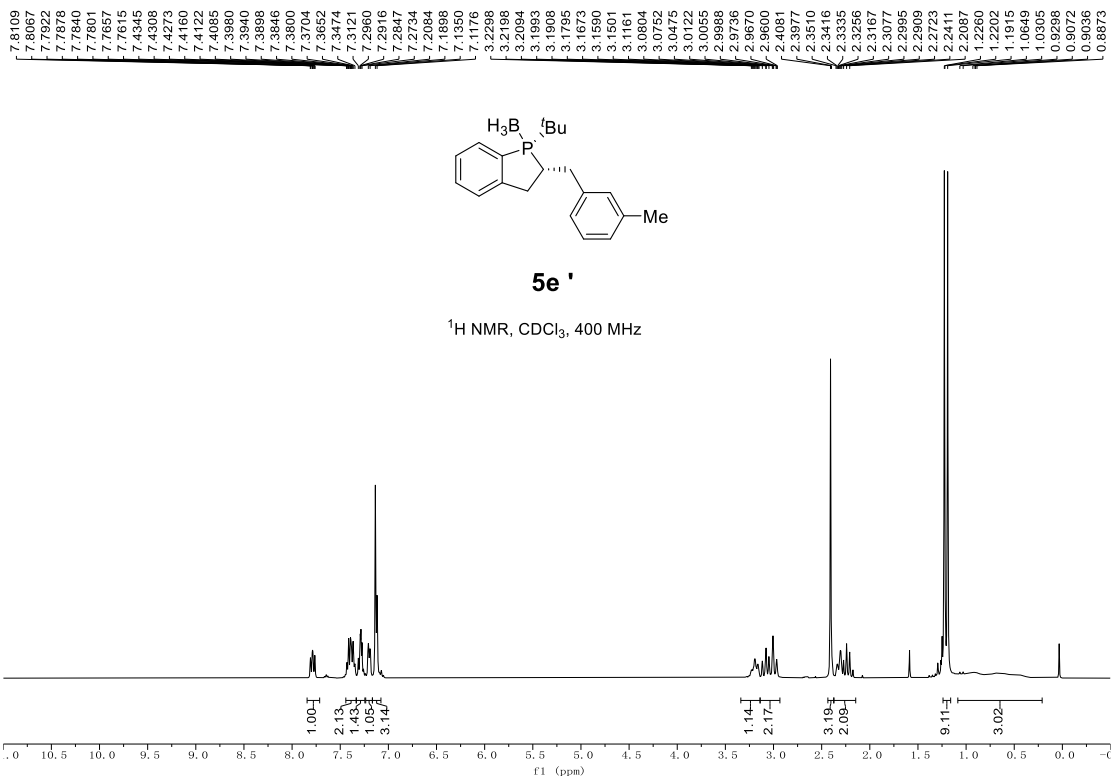
5e

^{13}C NMR, $CDCl_3$, 101 MHz



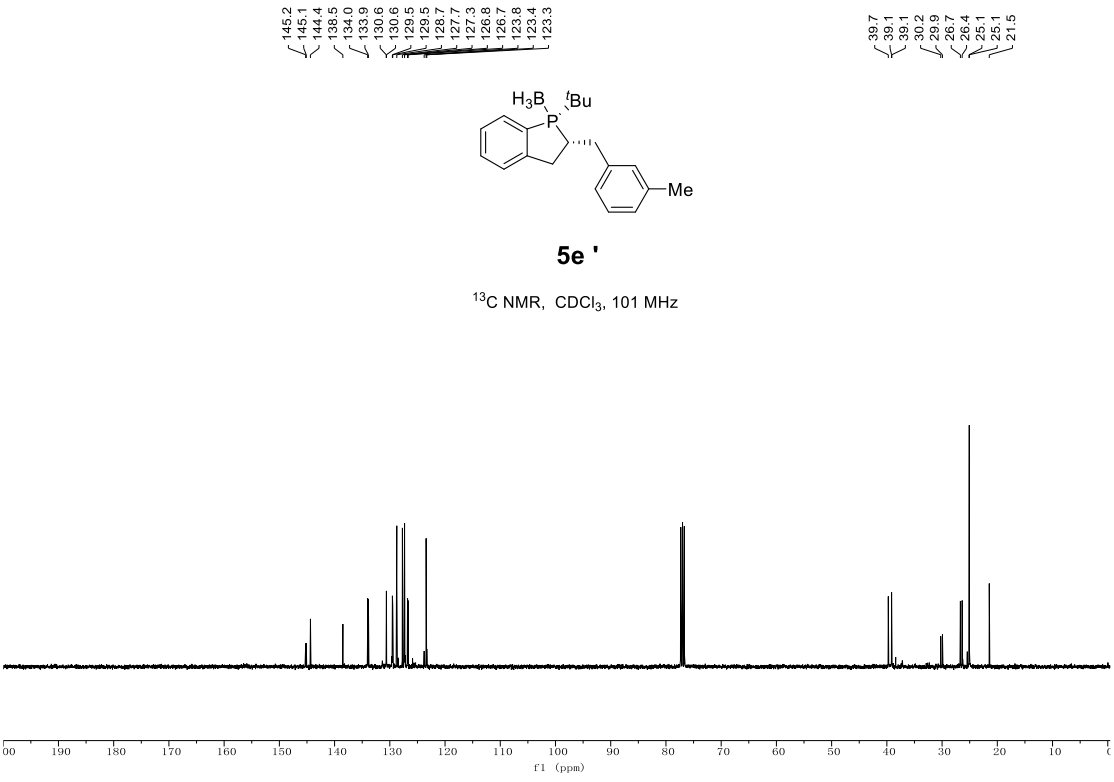
5e

^{31}P NMR, $CDCl_3$, 162 MHz



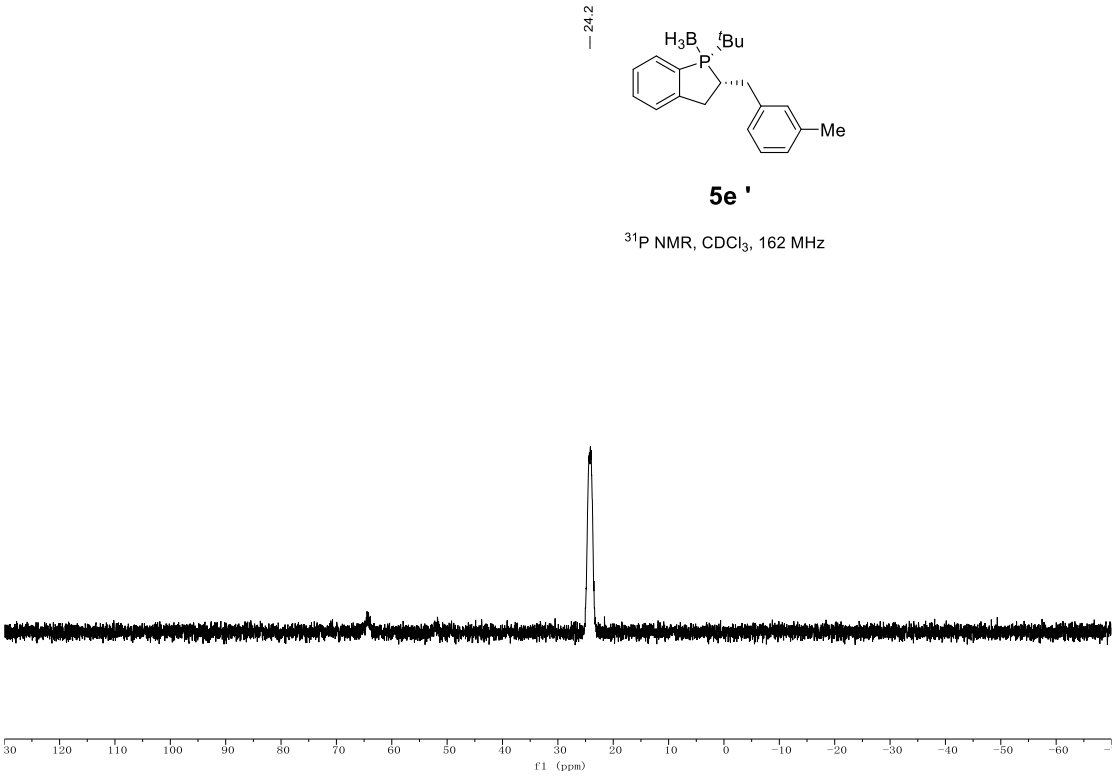
5e '

^{1}H NMR, $CDCl_3$, 400 MHz



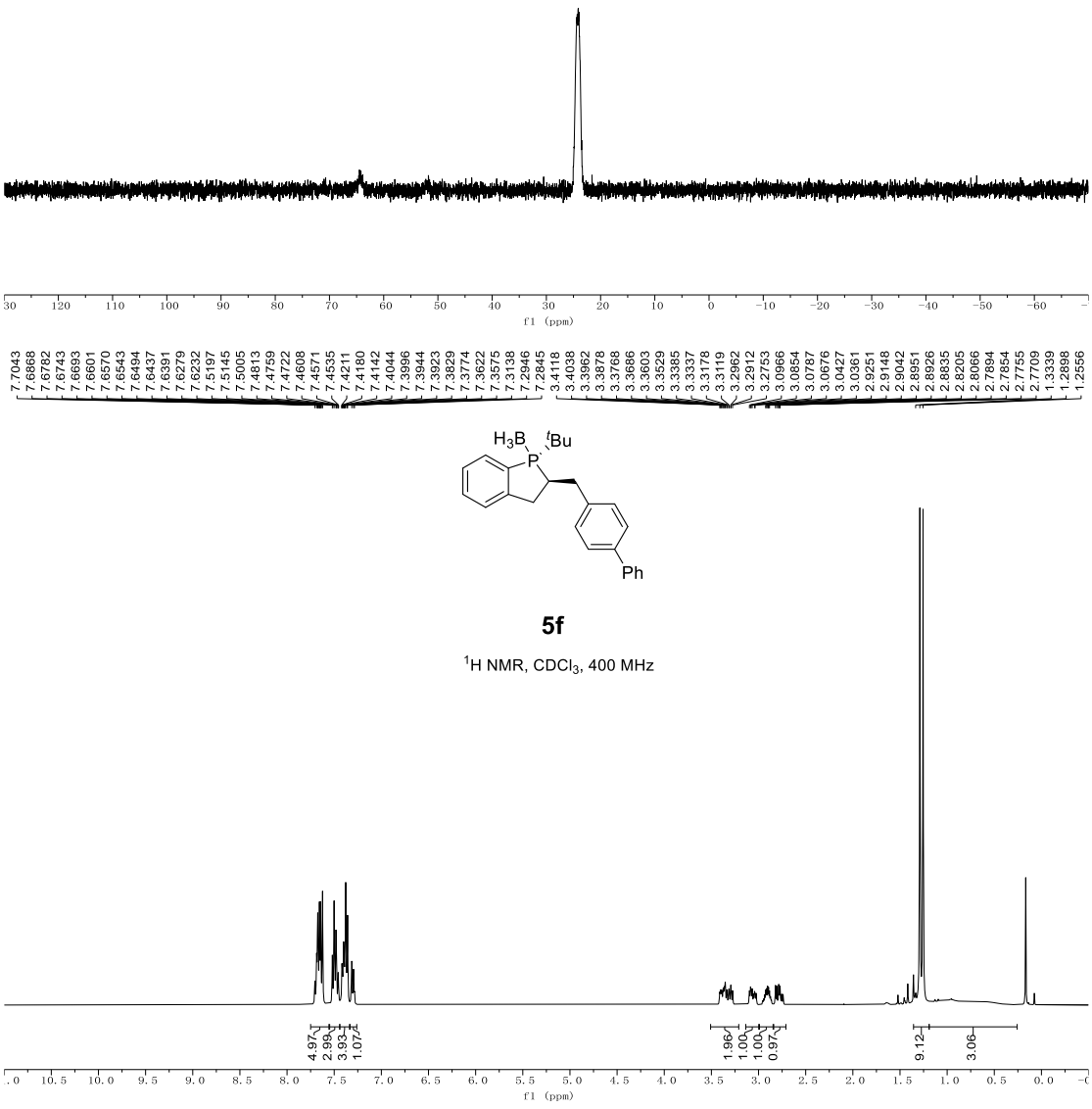
5e '

^{13}C NMR, $CDCl_3$, 101 MHz



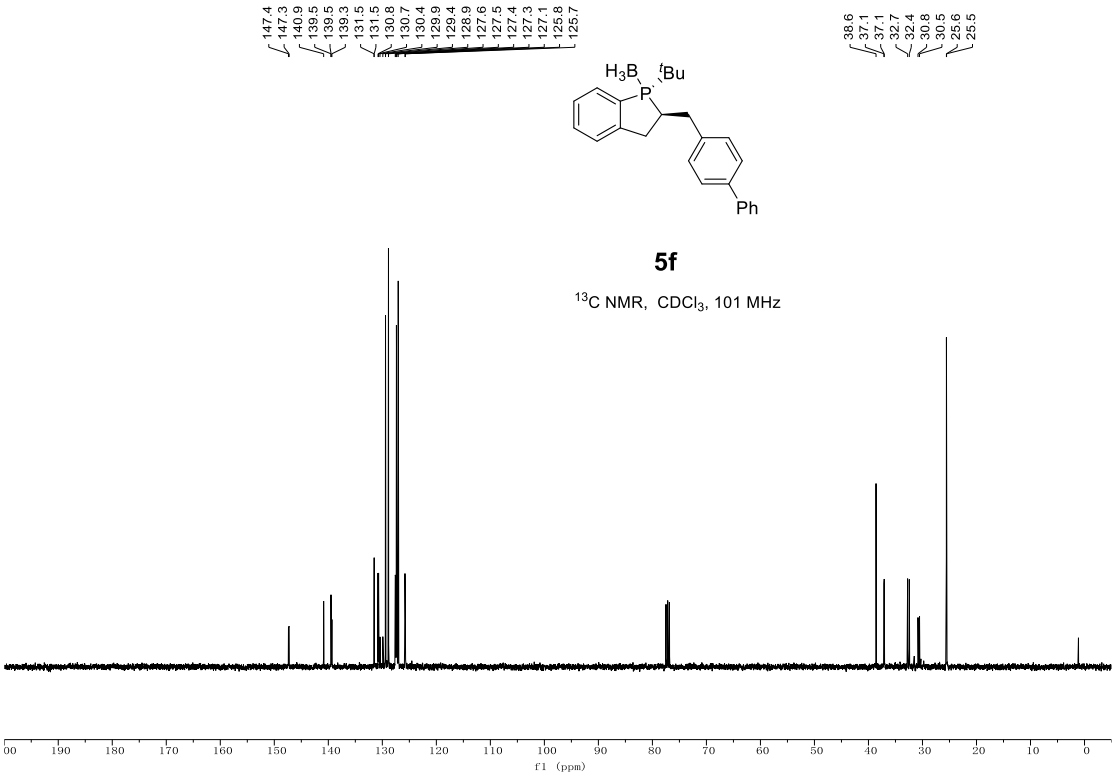
5e '

^{31}P NMR, $CDCl_3$, 162 MHz



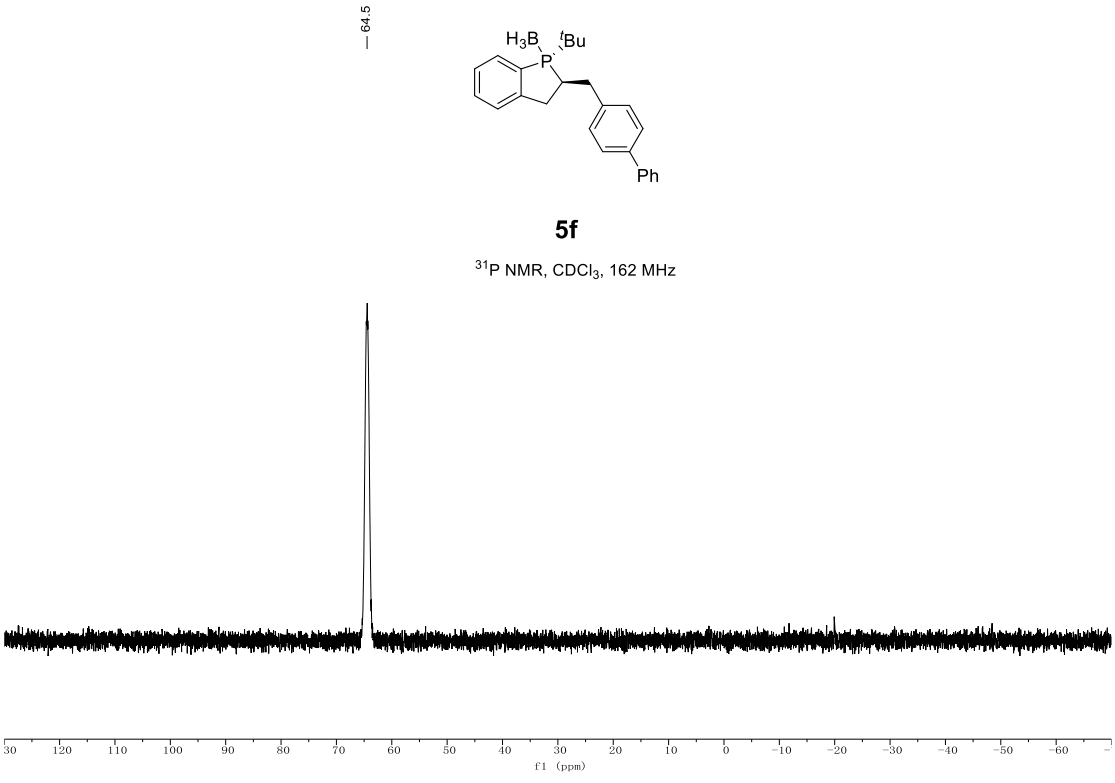
5f

^{1}H NMR, $CDCl_3$, 400 MHz



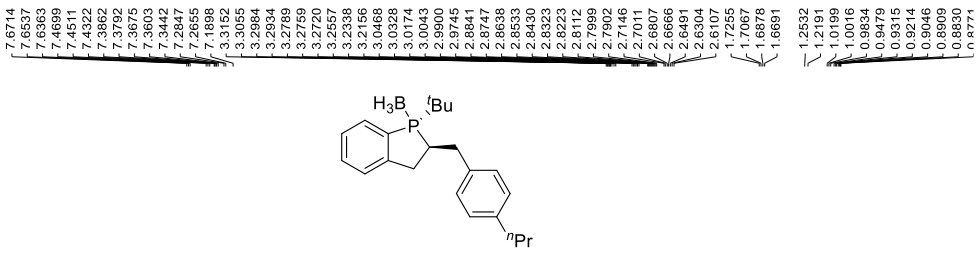
5f

^{13}C NMR, $CDCl_3$, 101 MHz



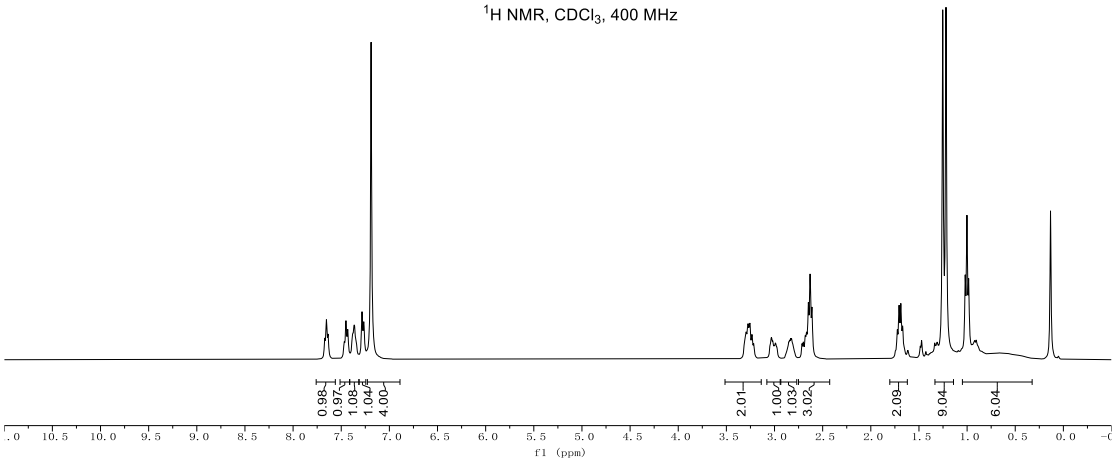
5f

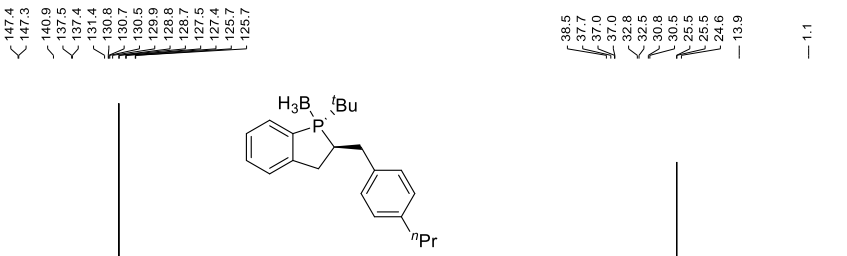
^{31}P NMR, $CDCl_3$, 162 MHz



5i

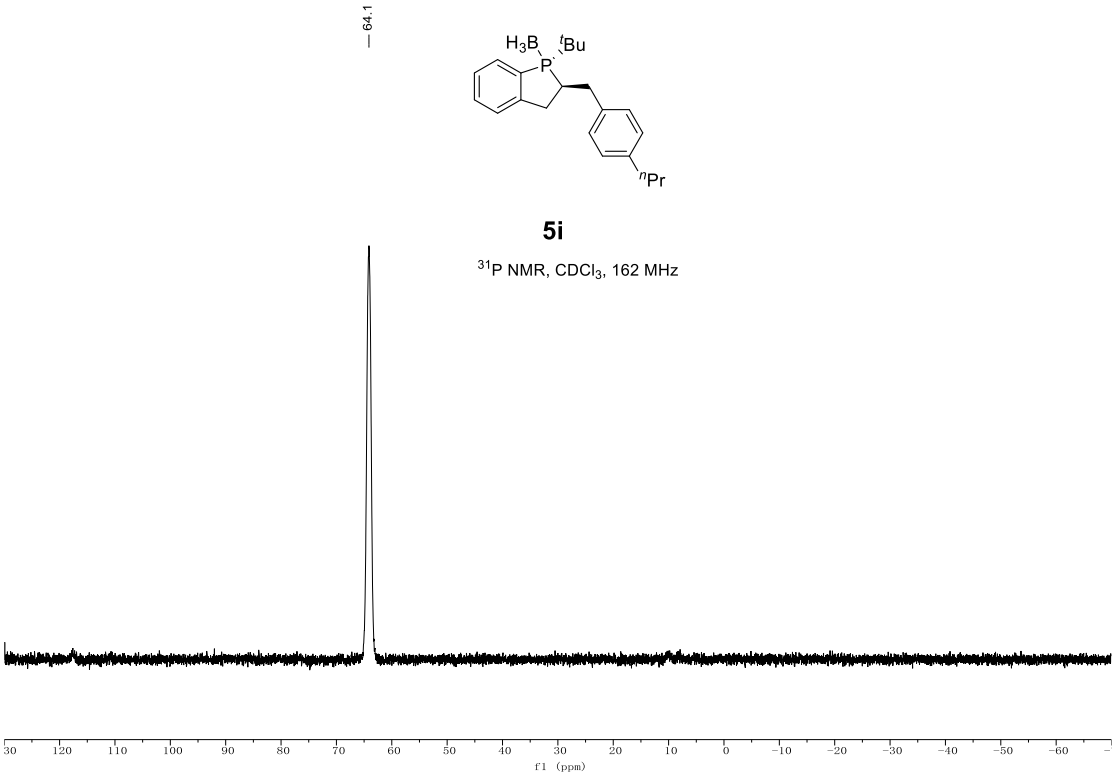
^{1}H NMR, $CDCl_3$, 400 MHz





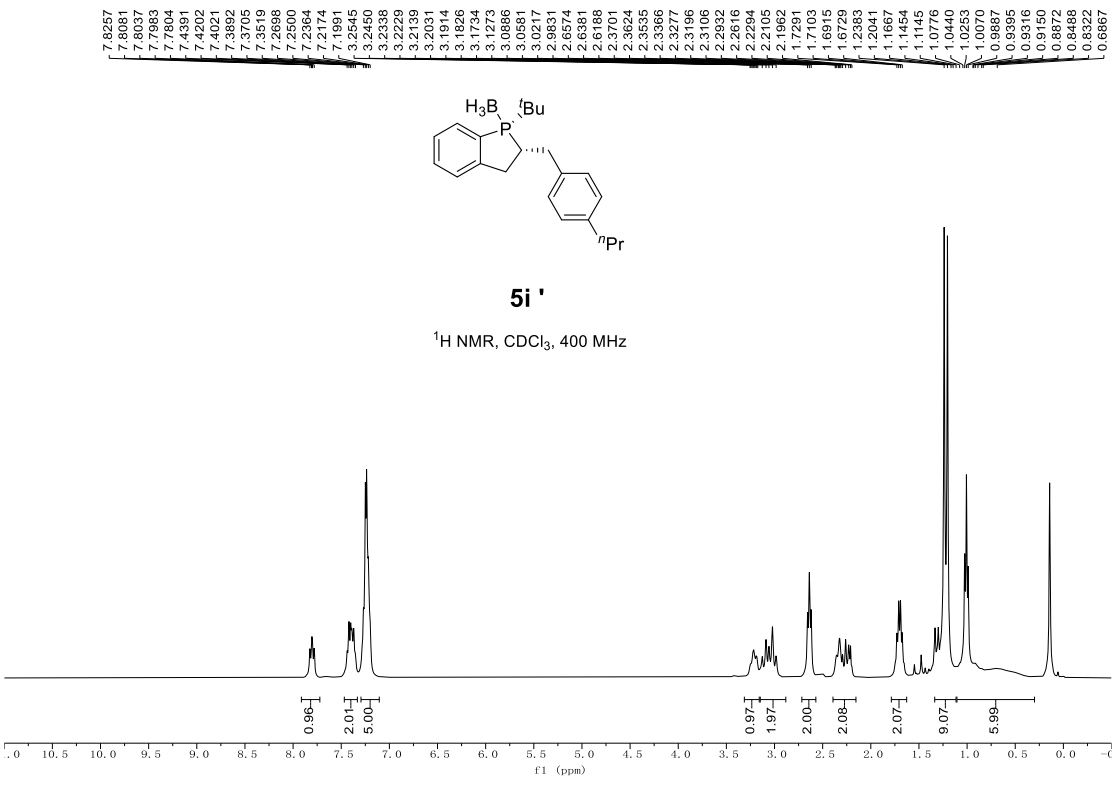
5i

^{13}C NMR, $CDCl_3$, 101 MHz



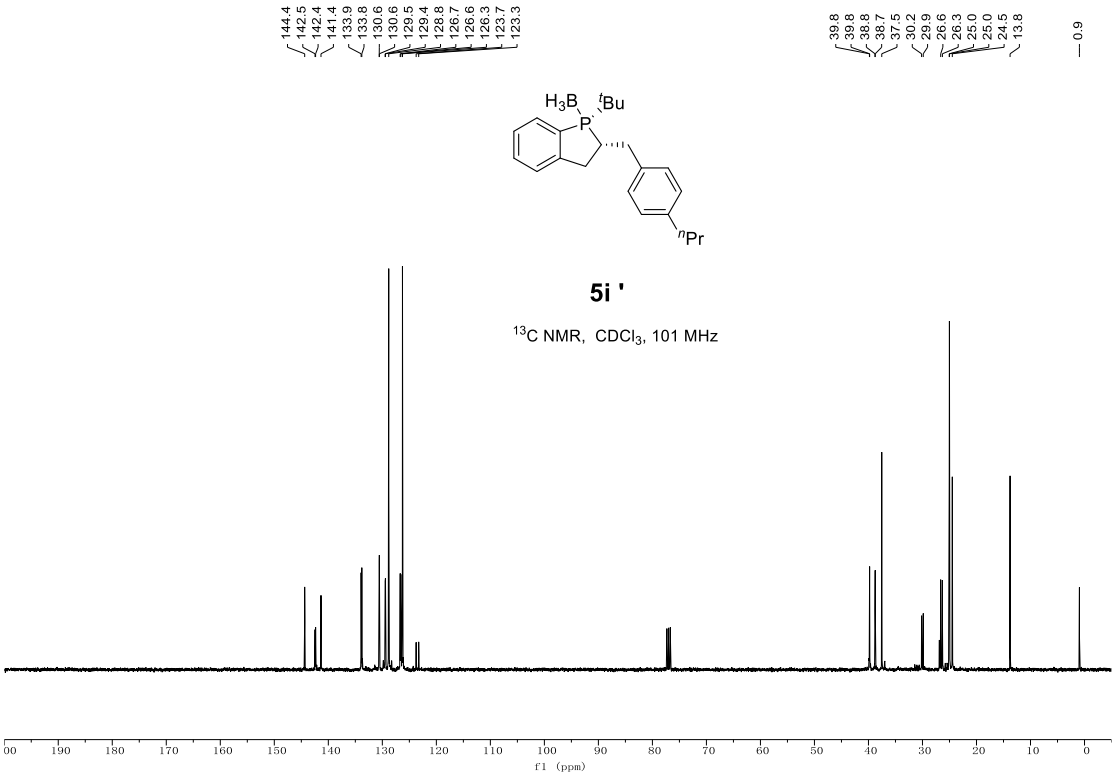
5i

^{31}P NMR, $CDCl_3$, 162 MHz



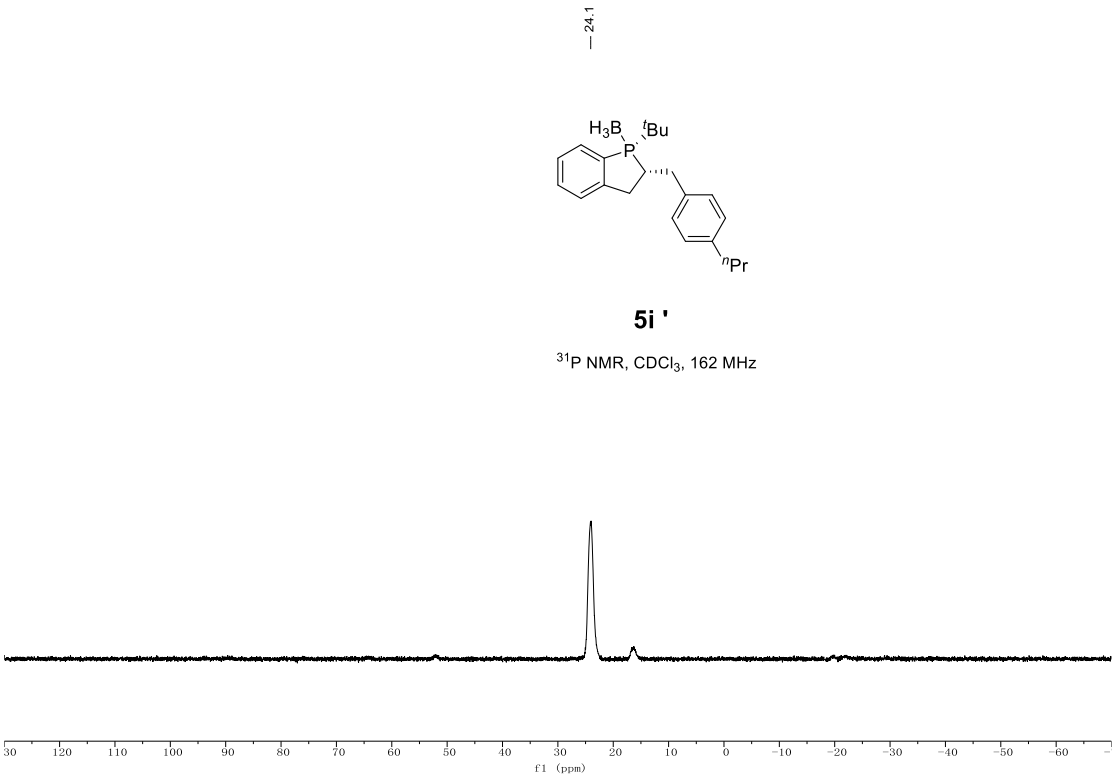
5i '

^{1}H NMR, $CDCl_3$, 400 MHz



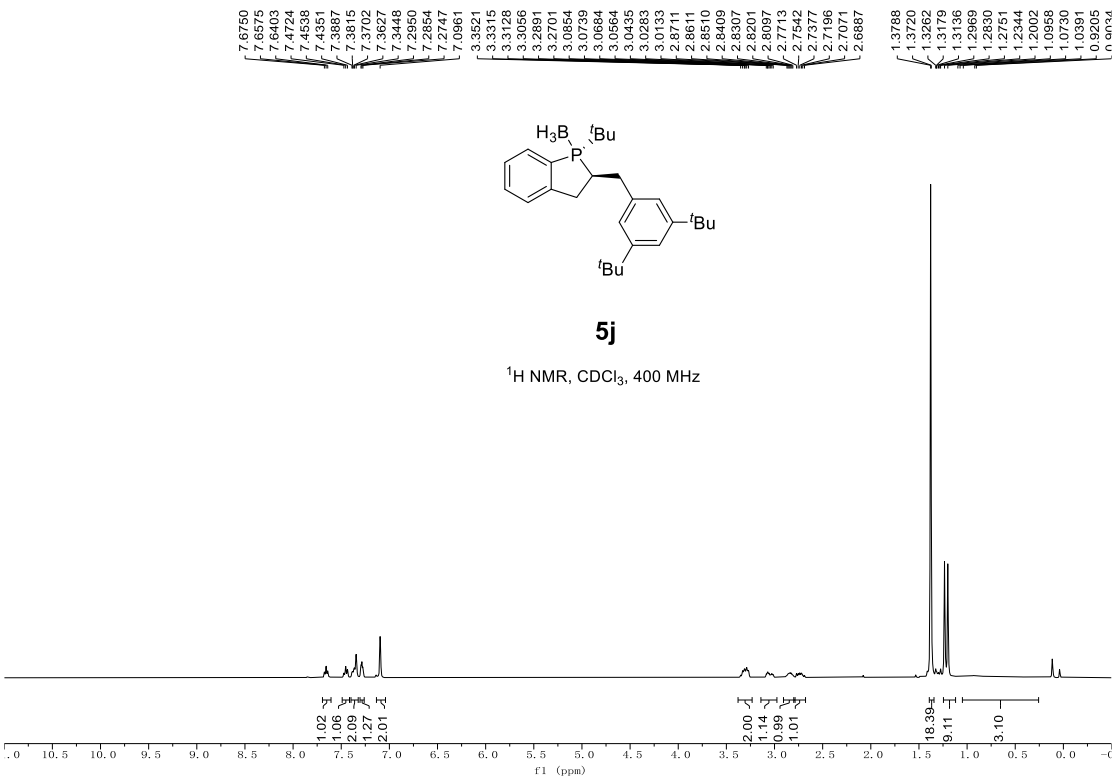
5i '

^{13}C NMR, $CDCl_3$, 101 MHz



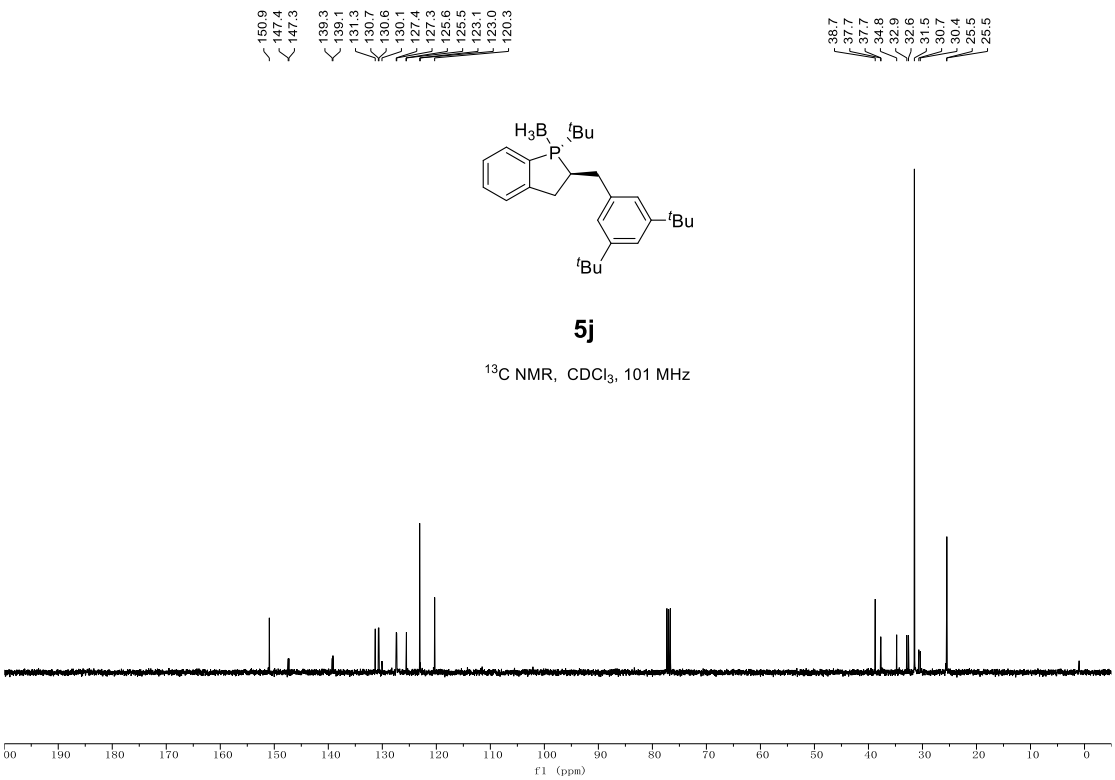
5i '

^{31}P NMR, $CDCl_3$, 162 MHz



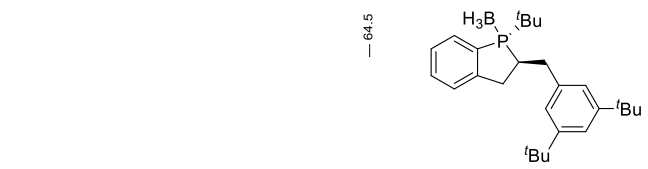
5j

^{1}H NMR, $CDCl_3$, 400 MHz



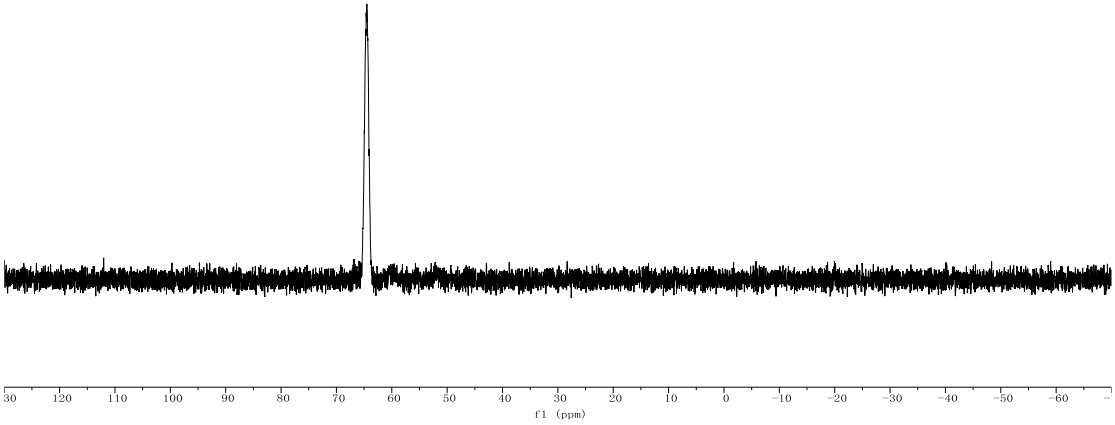
5j

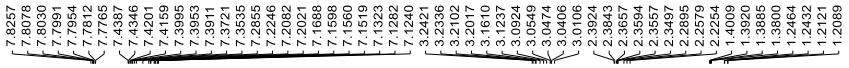
^{13}C NMR, $CDCl_3$, 101 MHz

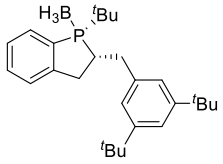


5j

^{31}P NMR, $CDCl_3$, 162 MHz

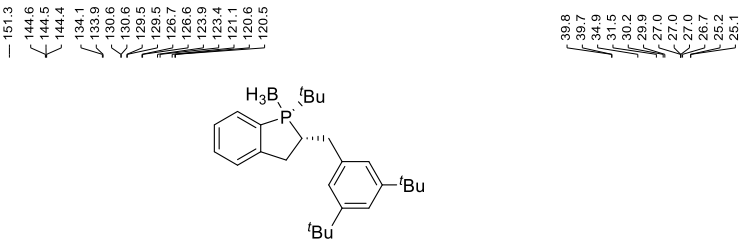






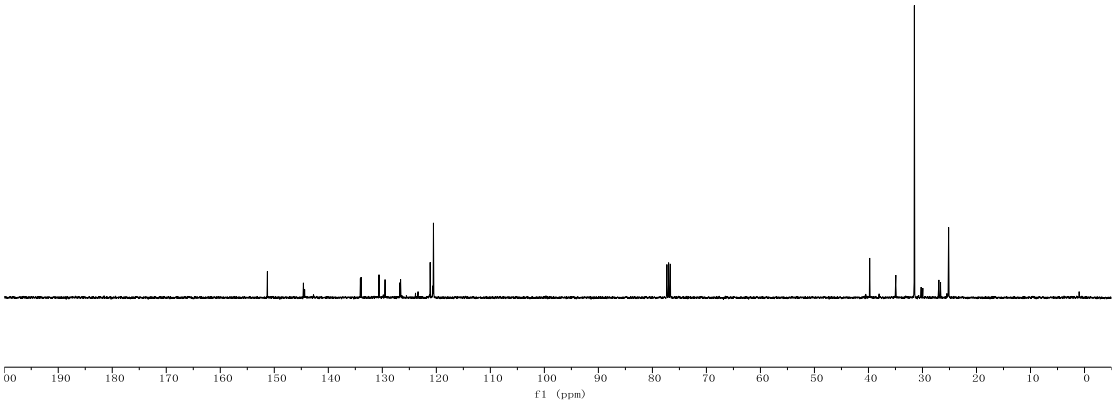
5j '

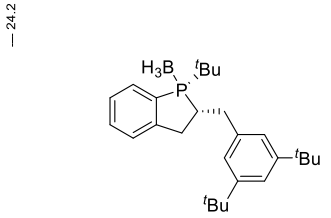
^{1}H NMR, $CDCl_3$, 400 MHz



5j '

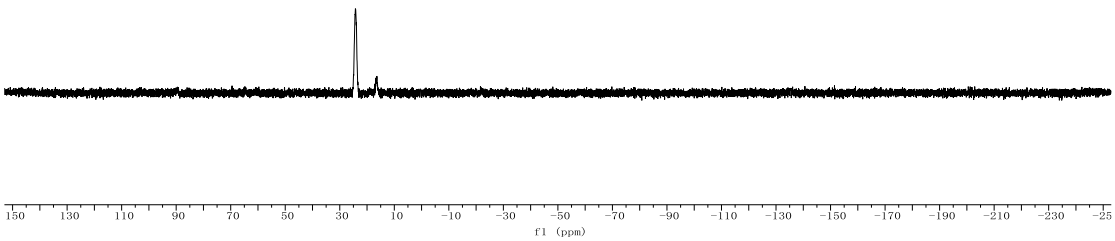
^{13}C NMR, $CDCl_3$, 101 MHz

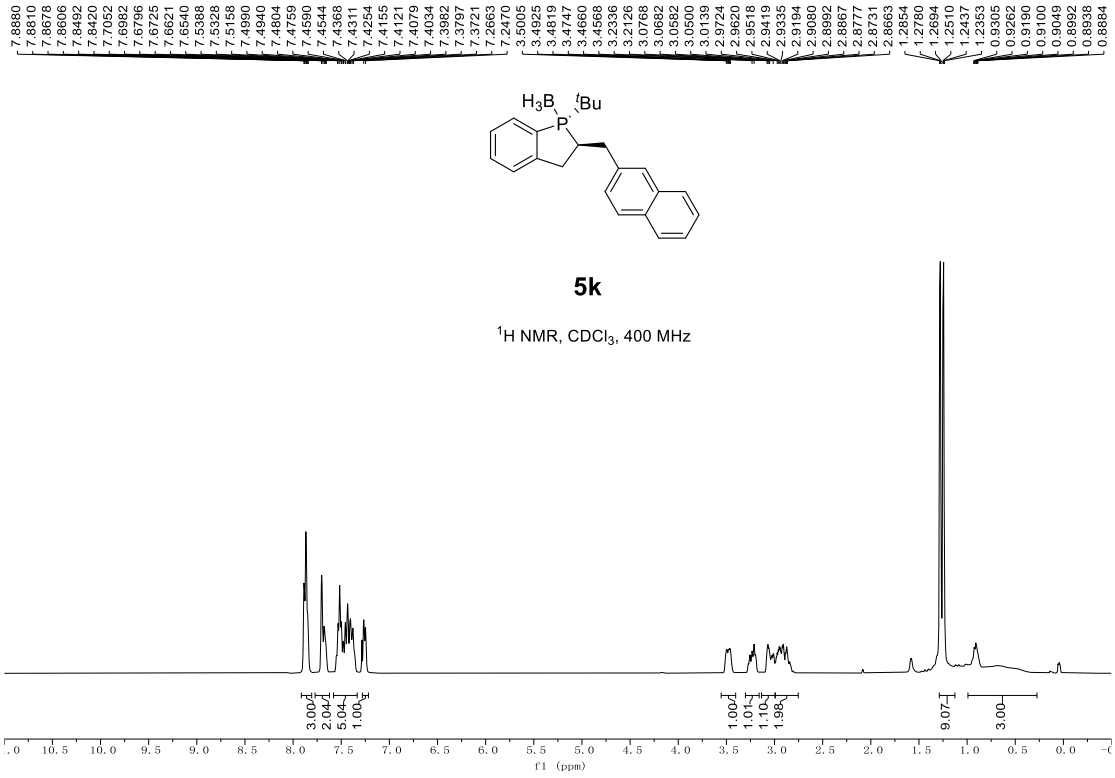




5j '

^{31}P NMR, $CDCl_3$, 162 MHz

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7.8492
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7.7052
7.6982
7.6796
7.6725
7.6621
7.6540
7.5388
7.5328
7.5158
7.4990
7.4940
7.4804
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7.4590
7.4544
7.4368
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7.4254
7.4155
7.4121
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7.4034
7.3982
7.3797
7.3721
7.2663
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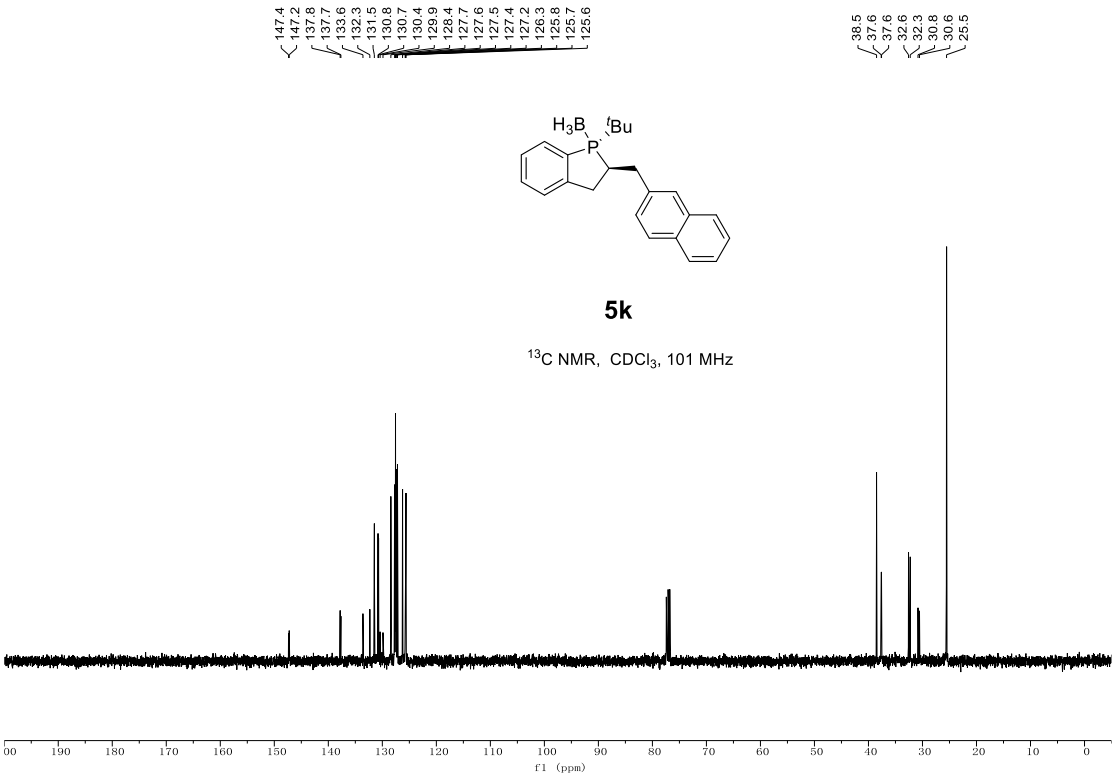
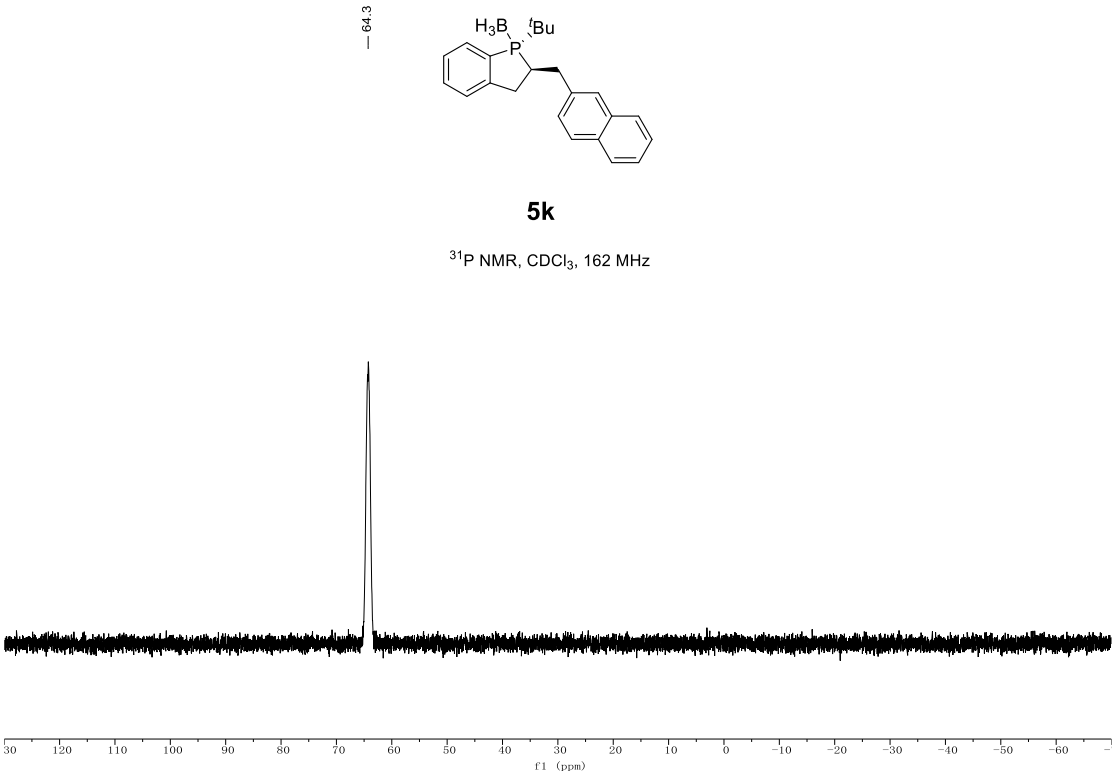
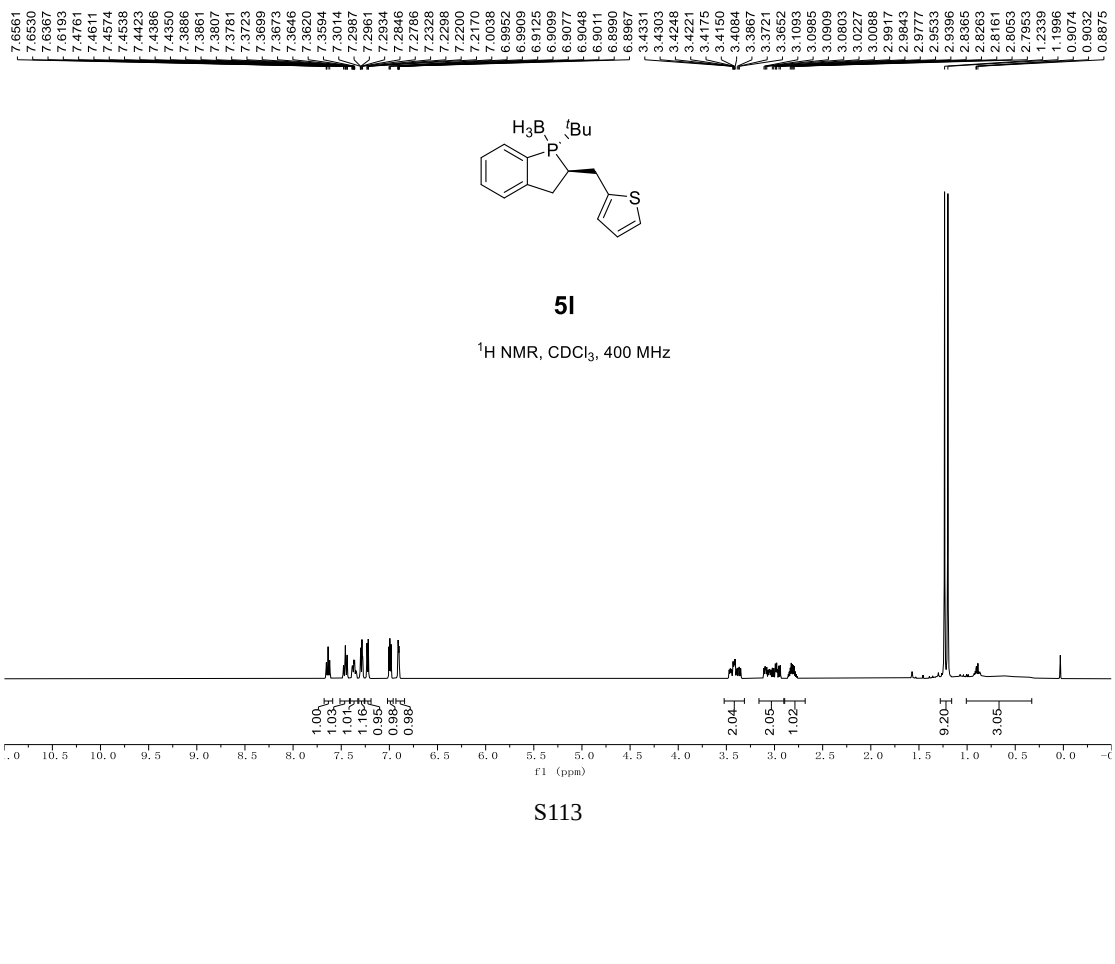
3.4925
3.4819
3.4747
3.4660
3.4568
3.2336
3.2126
3.0768
3.0682
3.0582
3.0500
3.0139
2.9724
2.9620
2.9518
2.9419
2.9335
2.9194
2.9080
2.8992
2.8867
2.8777
2.8731
2.8663
1.2854
1.2780
1.2694
1.2510
1.2437
1.2353
0.9305
0.9262
0.9190
0.9100
0.9049
0.8992
0.8938
0.8884
H3B
tBu
P
5k
1H NMR, CDCl3, 400 MHz
3.00
2.04
5.04
1.00
1.00
1.01
1.10
1.98
9.07
3.00
f1 (ppm)


147.4
147.2
137.8
137.7
133.6
132.3
131.5
130.8
130.7
130.4
129.9
128.4
127.7
127.6
127.5
127.4
127.2
126.3
125.8
125.7
125.6
38.5
37.6
37.6
32.6
32.3
30.8
30.6
25.5
H3B
tBu
P
5k
13C NMR, CDCl3, 101 MHz
f1 (ppm)



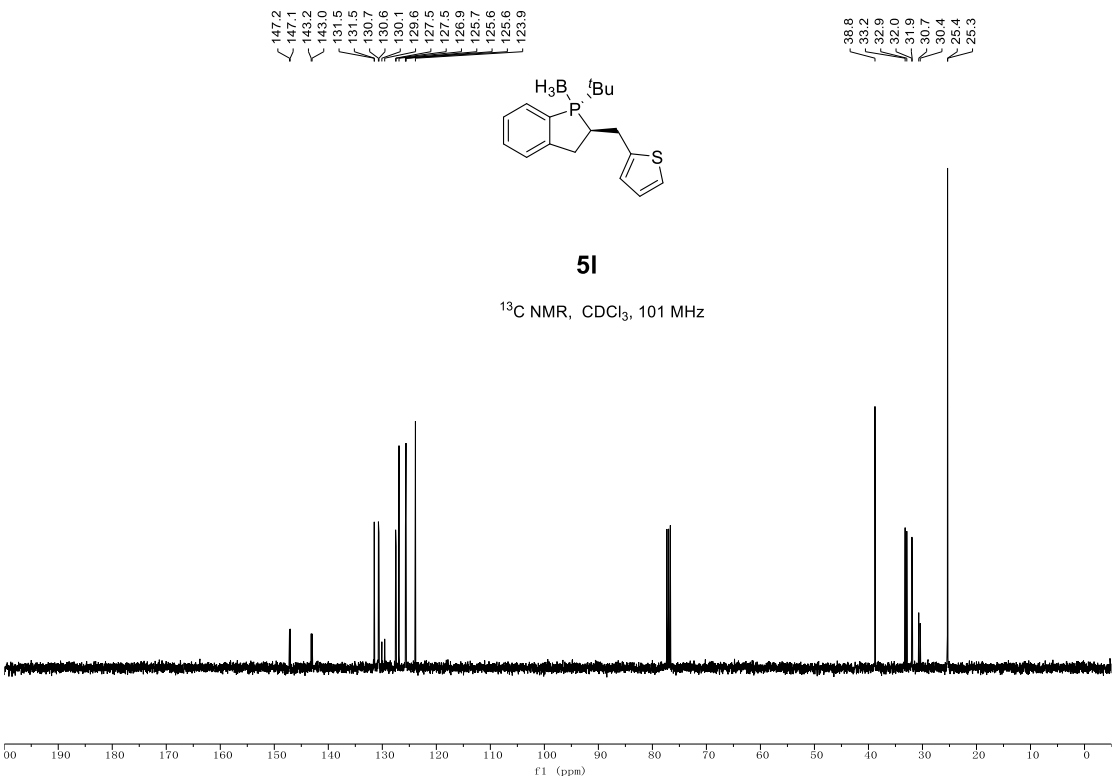
5k

^{31}P NMR, $CDCl_3$, 162 MHz



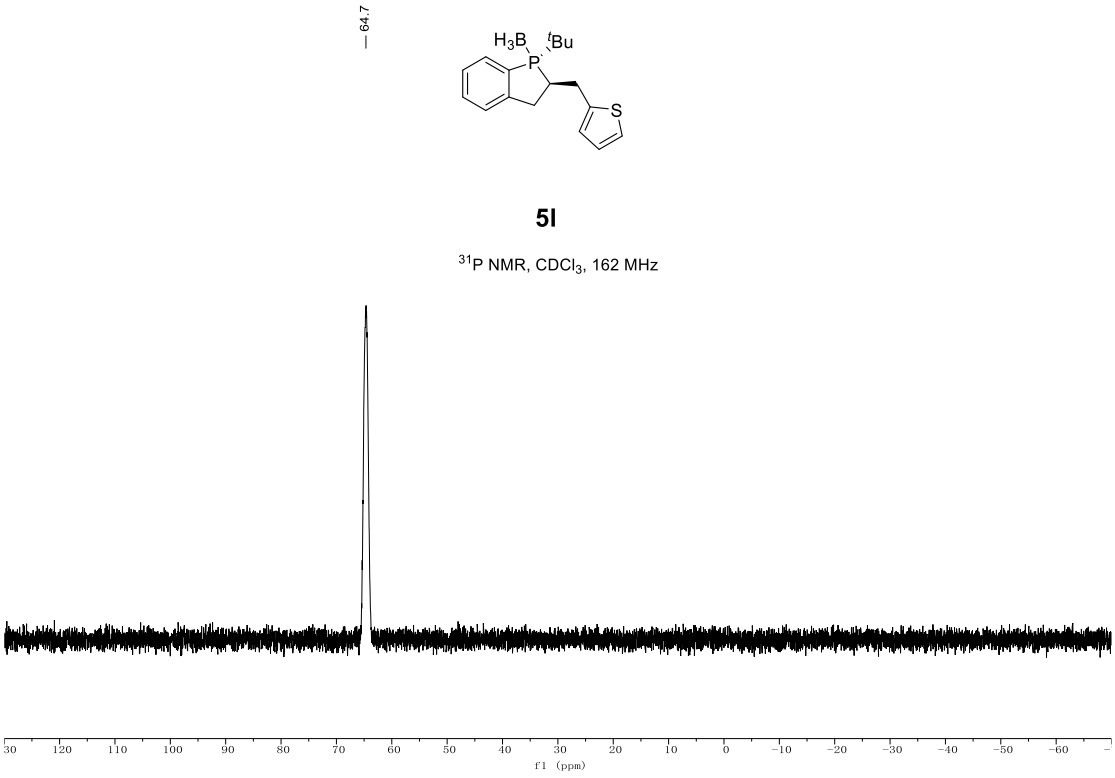
5l

^{1}H NMR, $CDCl_3$, 400 MHz



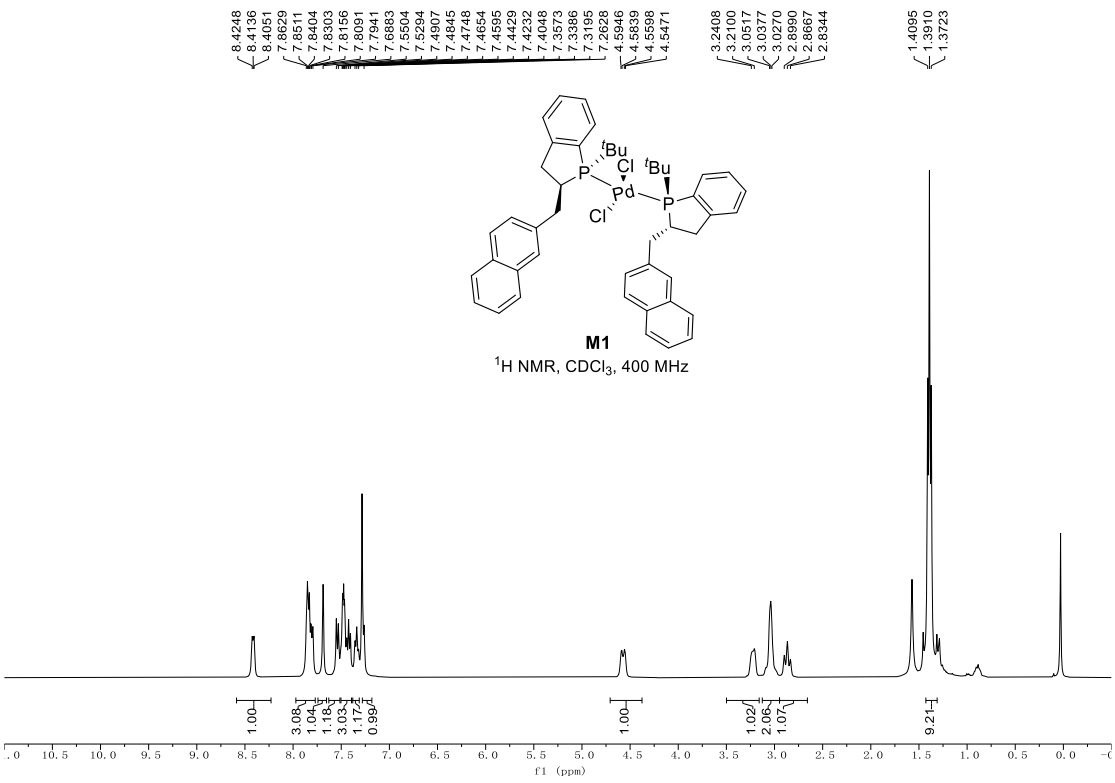
5l

^{13}C NMR, $CDCl_3$, 101 MHz



5l

^{31}P NMR, $CDCl_3$, 162 MHz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8.4051
7.8629
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7.8303
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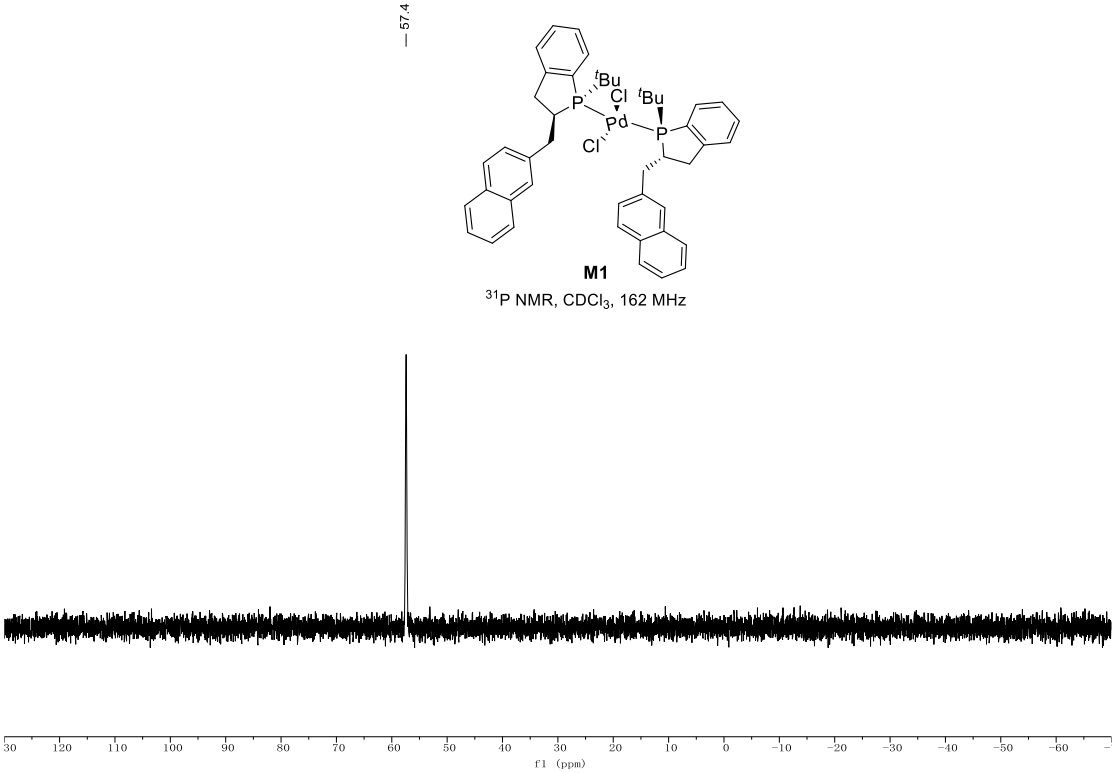
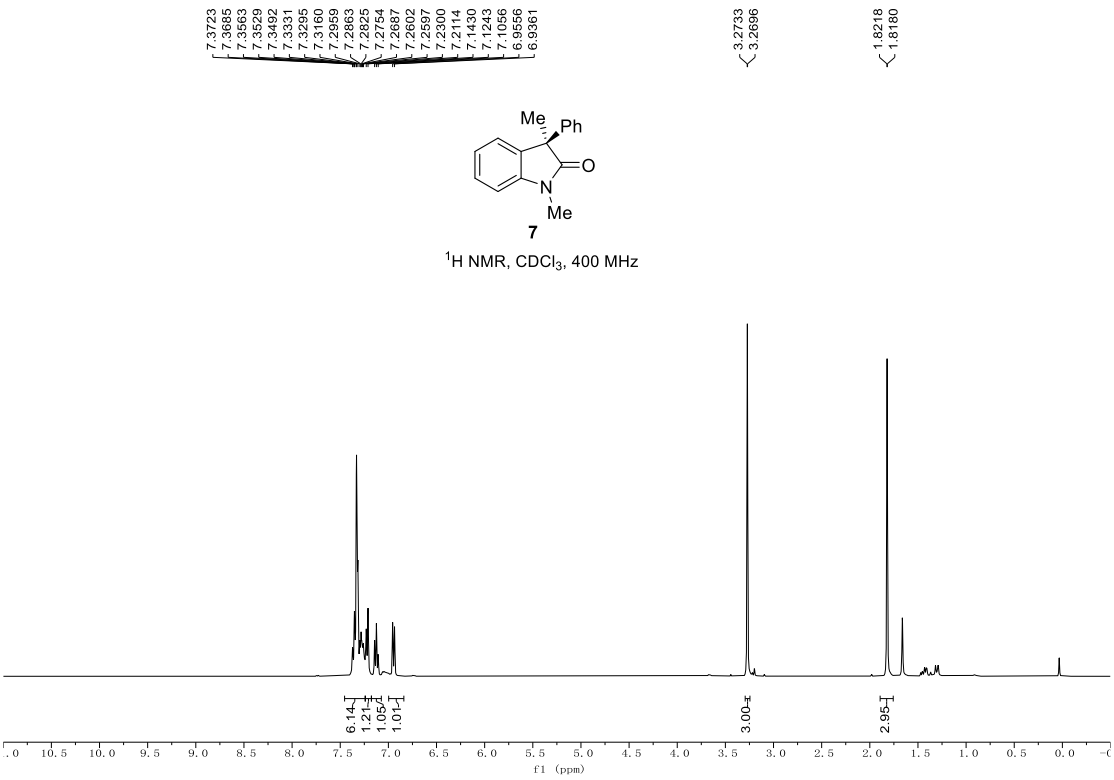
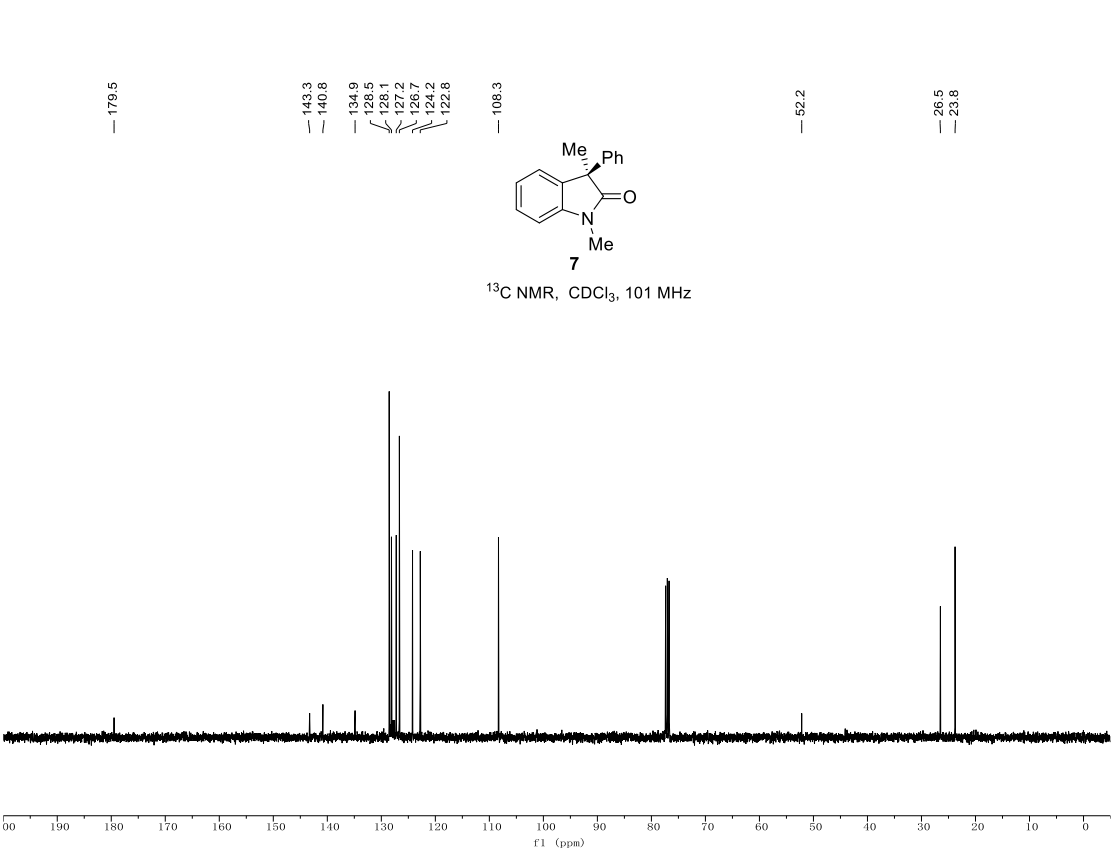
7.5504
7.5294
7.4907
7.4845
7.4748
7.4654
7.4595
7.4429
7.4232
7.4048
7.3573
7.3386
7.3195
7.2628
4.5946
4.5839
4.5598
4.5471
3.2408
3.2100
3.0517
3.0377
3.0270
2.8990
2.8667
2.8344
1.4095
1.3910
1.3723
tBu
Cl
tBu
P
Pd
P
Cl
M1
1H NMR, CDCl3, 400 MHz
1.00
3.08
1.04
1.18
3.03
1.17
0.99
1.00
1.02
2.06
1.07
9.21
f1 (ppm)


57.4
tBu
Cl
tBu
P
Pd
P
Cl
M1
31P NMR, CDCl3, 162 MHz
f1 (ppm)



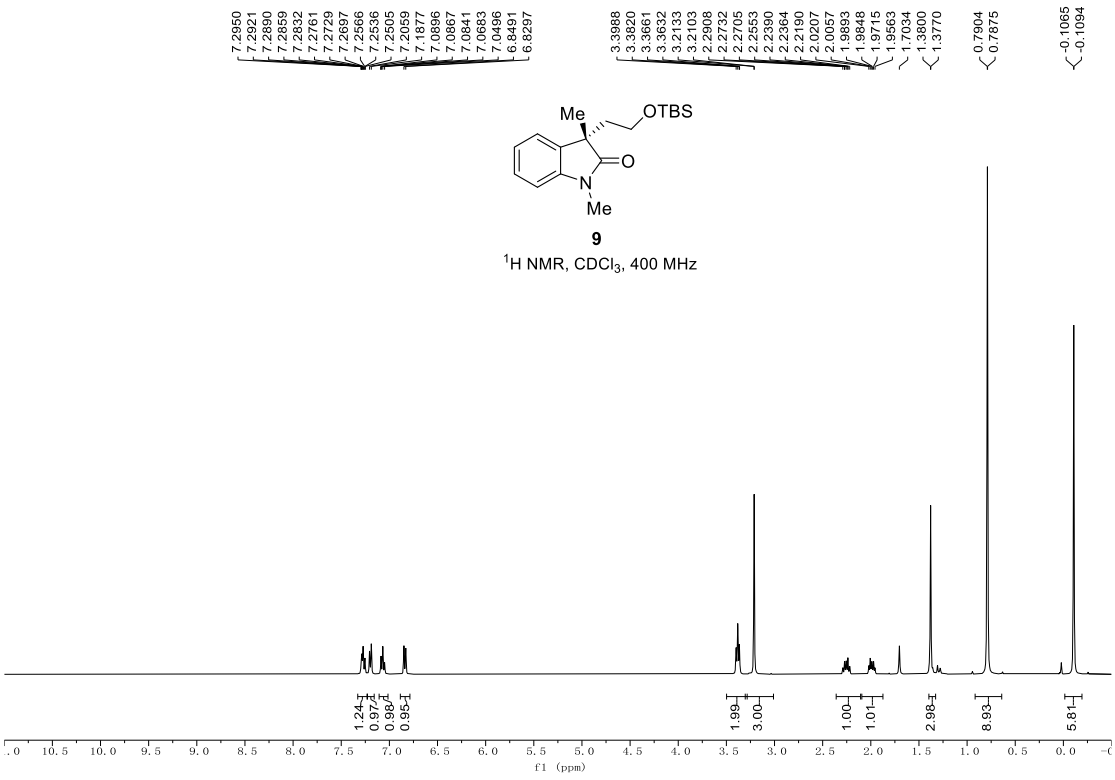
7

^{1}H NMR, $CDCl_3$, 400 MHz



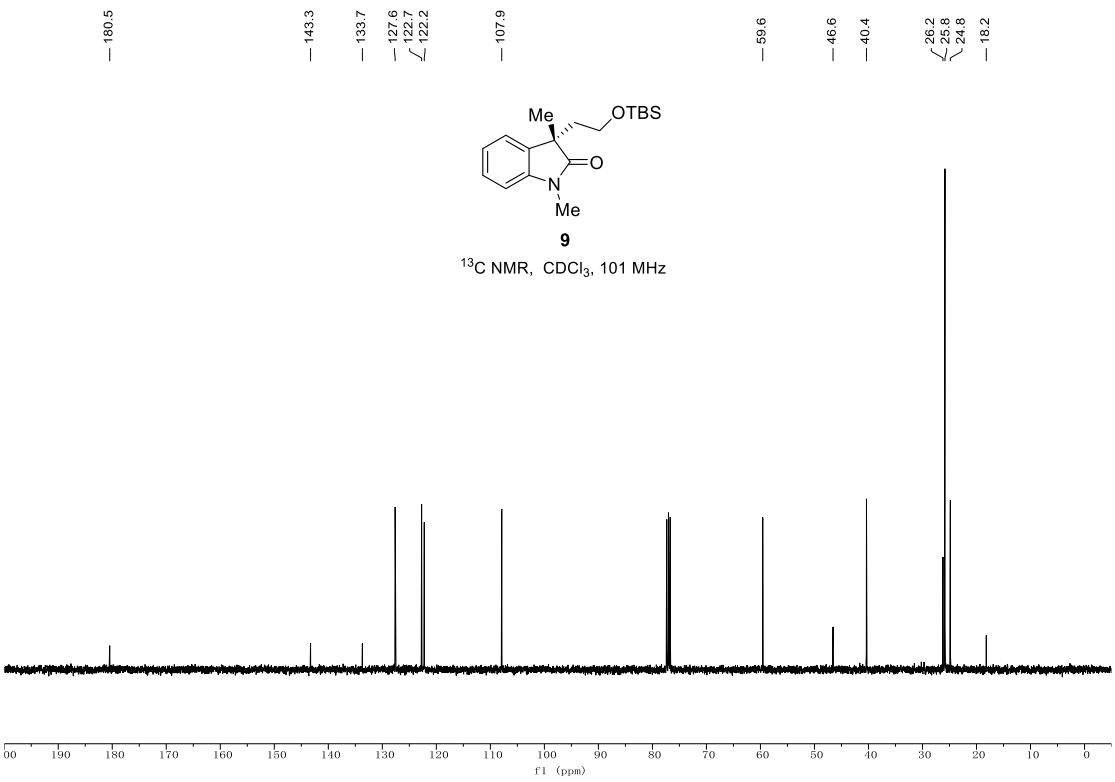
7

^{13}C NMR, $CDCl_3$, 101 MHz



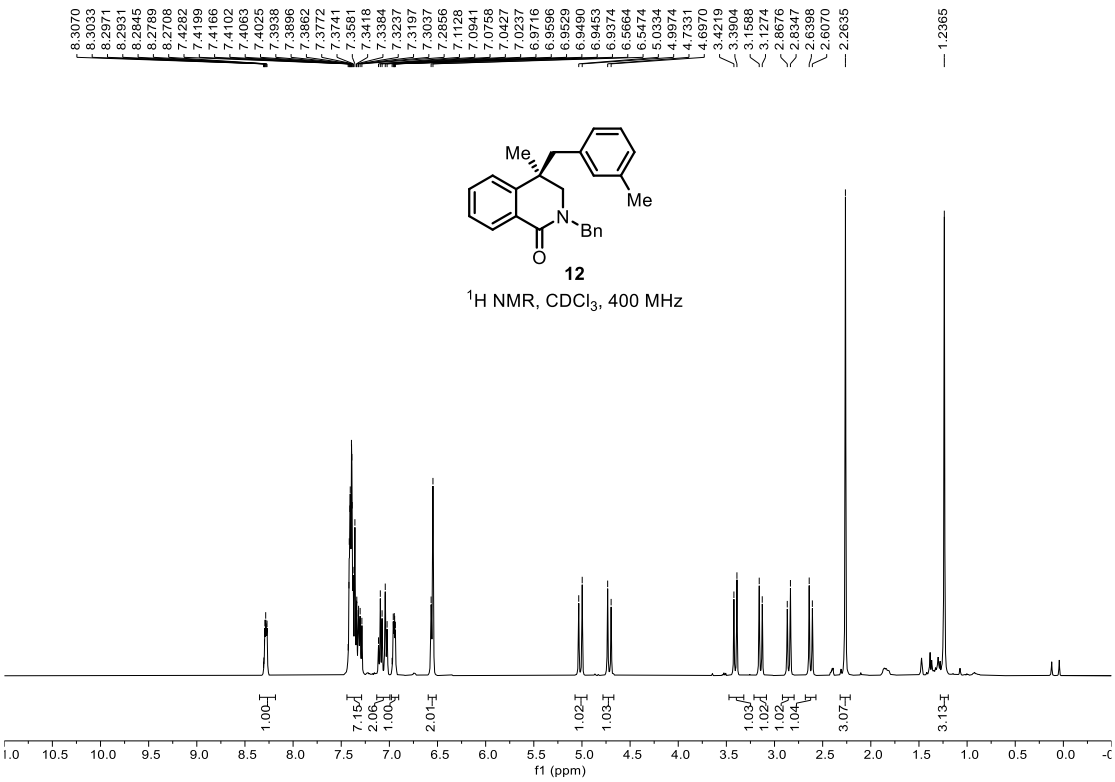
9

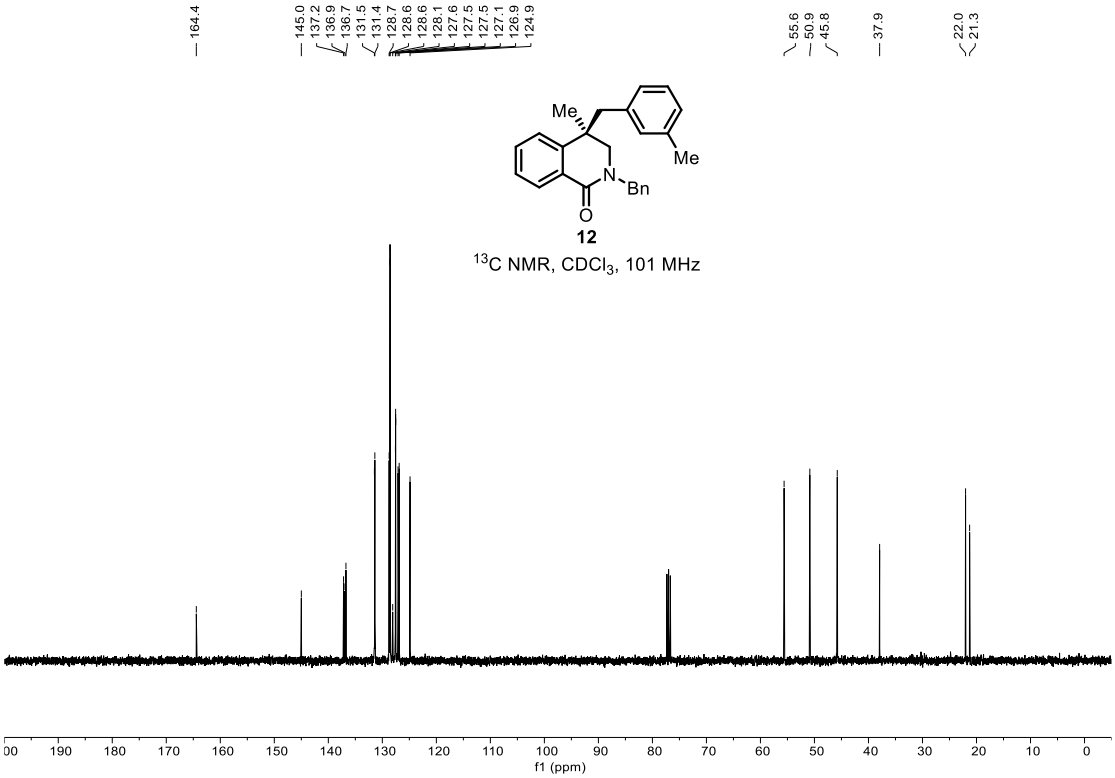
^{1}H NMR, $CDCl_3$, 400 MHz



9

^{13}C NMR, $CDCl_3$, 101 MHz


Me
Me
N
Bn
O
12
1H NMR, CDCl3, 400 MHz
f1 (ppm)


Me
Me
N
Bn
O
12
13C NMR, CDCl3, 101 MHz
f1 (ppm)