Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis of 2,3-Dihydro-1*H*-phosphindole-1-oxides Via the *t*-BuLi-Mediated Rearrangement of Vinylbromide and Phosphine Oxide

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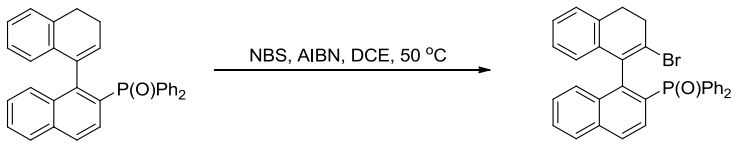
General Information

Nuclear magnetic resonances were recorded on Bruker-400 MHz instruments. Reference values for residual solvents were taken as δ = 7.26 ppm ($CDCl_3$) for ^1H NMR; δ = 77.00 ppm ($CDCl_3$) for ^{13}C NMR. All reactions were performed under an inert atmosphere of dry nitrogen in flame-dried glassware, unless otherwise stated. 1,4-Dioxane and tetrahydrofuran were distilled over sodium in the presence of benzophenone under an atmosphere of nitrogen. Toluene, dichloroethane were distilled over calcium hydride under an atmosphere of nitrogen.

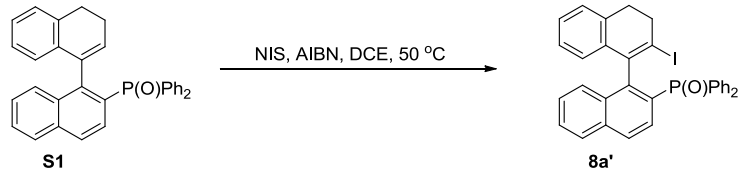
Typical procedure for the synthesis of vinyl bromides **8a** (**Typical procedure A**)



S1 **8a**

A mixture of vinylarene **S1** (0.228 g, 0.50 mmol, 1.0 equiv), NBS (97.9 mg, 0.55 mmol, 1.1 equiv), AIBN (8.2 mg, 0.05 mmol, 0.1 equiv) in 1,2-dichloroethane (10 ml) under N_2 was stirred at 50 °C for 5 hours. After being cooled to room temperature, H_2O (10 ml) was added and the mixture was extracted with DCM three times. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to give the desired product 8a (0.236 g, 88%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.87-7.81 (m, 2H), 7.74-7.65 (m, 2H), 7.61-7.56 (m, 1H), 7.54-7.52 (m, 1H), 7.51-7.48 (m, 2H), 7.47-7.44 (m, 2H), 7.43-7.38 (m, 2H), 7.37-7.35 (m, 1H), 7.30-7.22 (m, 2H), 7.10-6.99 (m, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 3.25-3.11 (m, 1H), 3.04-2.93 (m, 1H), 2.92-2.83 (m, 1H), 2.82-2.75 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8 (d, *J* = 7.1 Hz), 136.0, 134.5 (d, *J* = 2.2 Hz), 134.4 (d, *J* = 103.5 Hz), 133.7, 132.7, 132.2 (d, *J* = 9.7 Hz), 132.0, 131.9, 131.8 (d, *J* = 9.5 Hz), 131.4 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 2.7 Hz), 128.9, 128.8, 128.4, 128.19, 128.17, 128.16,128.0 (d, *J* = 2.8 Hz),127.9, 127.5, 127.44, 127.37, 126.6 (d, *J* = 102.8 Hz),127.0, 126.9, 126.5, 125.7, 34.8, 29.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.1 (s). HRMS (ESI) calcd for $C_{32}H_{25}BrOP$ $[M+H]^+$ 535.0826, found 535.0823.

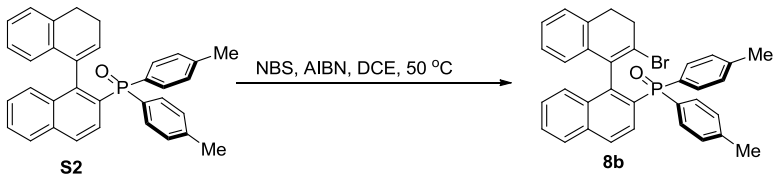
The iodide **8a'** was prepared following the **Typical Procedure A** expect NIS (0.124 g, 0.55 mmol, 1.1 equiv) was used instead of NBS stirred at 50 °C for 12 h. **8a'** (0.180 g, 62%).



S1 8a'

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53-7.47 (m, 4H), 7.46-7.42 (m, 2H), 7.42-7.37 (m, 2H), 7.37-7.33 (m, 1H), 7.28-7.20 (m, 1H), 7.08-7.00 (m, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.19 (d, *J* = 7.6 Hz, 1H), 3.28-3.15 (m, 1H), 3.14-2.93 (m, 2H), 2.85-2.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2 (d, *J* = 6.9 Hz), 140.4 (d, *J* = 4.6 Hz), 135.6, 134.6 (d, *J* = 2.2 Hz), 134.4, 133.4 (d, *J* = 103.1 Hz), 133.2 (d, *J* = 103.3 Hz), 132.4 (d, *J* = 9.7 Hz), 132.0, 131.8, 131.7 (d, *J* = 9.5 Hz), 131.5 (d, *J* = 2.8 Hz), 131.2 (d, *J* = 2.7 Hz), 128.8 (d, *J* = 12.8 Hz), 128.22, 128.20, 128.1, 128.0, 127.9, 127.8, 127.4, 127.3, 127.1, 127.0, 126.9, 126.6, 126.0, 125.9, 105.3, 39.4, 29.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ +30.8 (s). HRMS (ESI) calcd for $C_{32}H_{25}IOP$ $[M+H]^+$ 583.0688, found 583.0690.

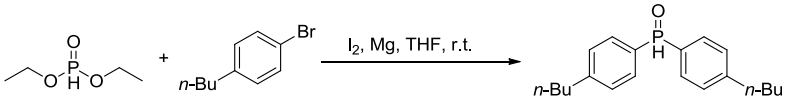
Compound **8b** was prepared following the **Typical Procedure A**.



S2 8b

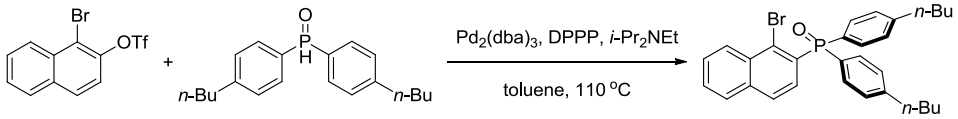
The reaction of vinylarene **S2** (0.242 g, 0.50 mmol) afforded **8b** (0.183 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.66-7.56 (m, 3H), 7.55-7.50 (m, 1H), 7.49-7.45 (m, 1H), 7.44-7.36 (m, 2H), 7.24-7.16 (m, 2H), 7.10-7.00 (m, 4H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.19 (d, *J* = 7.6 Hz, 1H), 3.25-3.11 (m, 1H), 3.08-2.95 (m, 1H), 2.92-2.77 (m, 2H), 2.38 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5 (d, *J* = 7.1 Hz), 141.7 (d, *J* = 2.7 Hz), 141.4 (d, *J* = 2.8 Hz), 135.9, 134.50, 134.48, 134.4, 133.6, 132.2 (d, *J* = 10.0 Hz), 131.9, 131.8, 131.7 (d, *J* = 9.9 Hz), 130.2 (d, *J* = 104.7 Hz), 130.0 (d, *J* = 105.5 Hz), 128.95, 128.92, 128.84, 128.80, 128.7 (d, *J* = 3.3 Hz), 128.6, 128.1, 128.0, 127.9, 127.4, 127.3, 127.2, 127.0, 126.6, 126.4, 126.0, 125.6, 34.8, 28.9, 21.5, 21.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.4 (s). HRMS (ESI) calcd for $C_{34}H_{29}BrOP$ $[M+H]^+$ 563.1140, found 563.1133.

Compound **S3** was prepared following the reported literature. [1, 2]

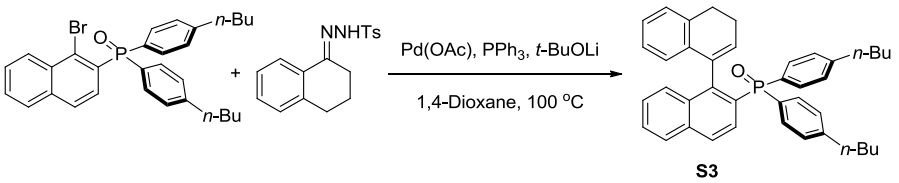


The mixture of magnesium turnings (0.80 g, 33.3 mmol, 3.3 equiv), a piece of iodine and small amount of 1-bromo-4-butylbenzene in THF (20 ml) was vigorously stirred under N_2. The flask was heated until the reaction was initiated (the solution become colorless). A solution of 1-bromo-4-butylbenzene (5.80 ml, 30.0 mmol, 3.0 equiv) in THF (30 ml) was added dropwise and stirred for 1 h. The flask was cooled to 0 °C by an ice-bath and diethyl phosphite (1.30 ml, 10.0 mmol, 1.0 equiv) in THF (10 ml) was added over 30 min. After stirring for additional 2 h at room temperature,

the reaction was quenched by the addition of 2 M HCl (20 ml) at 0 °C, and stirred for 15 min. The mixture was filtrated through a celite pad, and the filtrate was extracted with EtOAc three times. The combined organic layer was washed with brine and dried over Na_2SO_4. After evaporation, the residue was purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to afford desired product (1.660 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 478.8 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.29 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.12 (d, *J* = 6.0 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.651.50 (m, 4H), 1.40-1.26 (m, 4H), 0.97-0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9 (d, *J* = 2.7 Hz), 146.6, 131.2 (d, *J* = 10.7 Hz), 130.7 (d, *J* = 11.8 Hz), 128.9 (d, *J* = 13.2 Hz), 128.2 (d, *J* = 13.5 Hz), 127.8, 35.6 (d, *J* = 4.6 Hz), 33.2 (d, *J* = 3.1 Hz), 22.3 (d, *J* = 4.0 Hz), 13.8 (d, *J* = 0.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ +21.8 (s). HRMS (ESI) calcd for $C_{20}H_{28}OP$ $[M+H]^+$ 315.1878, found 315.1872.



A mixture of 1-bromonaphthalen-2-yl trifluoromethanesulfonate (1.970 g, 5.50 mmol, 1.05 equiv), bis(4-butylphenyl)phosphine oxide (1.660 g, 5.30 mmol, 1.0 equiv), $Pd_2(dba)_3$ (0.119 g, 0.13 mmol, 2.5 mol%), 1,3-bis(diphenylphosphino)propane (0.107 g, 0.26 mmol, 5 mol%), and *N,N*-diisopropylethylamine (1.40 mL, 7.95 mmol, 1.5 equiv) in toluene (30 mL) under N_2 was stirred at 110 °C overnight. After being cooled to room temperature, the mixture was filtered and concentrated and the residue was purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to give the desired product (1.560 g, 60%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44-8.36 (m, 1H), 7.86-7.76 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.61-7.56 (m, 2H), 7.45 (dd, *J* = 11.0, 8.6 Hz, 1H), 7.31-7.28 (m, 2H), 7.28-7.23 (m, 2H), 2.65 (t, *J* = 7.6 Hz, 4H), 1.65-1.55 (m, 4H), 1.40-1.29 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0 (d, *J* = 2.7 Hz), 135.6 (d, *J* = 2.1 Hz), 132.6 (d, *J* = 8.8 Hz), 132.0 (d, *J* = 10.2 Hz), 131.2 (d, *J* = 103.6 Hz), 123.0 (d, *J* = 10.7 Hz), 129.6 (d, *J* = 4.0 Hz), 129.5, 128.57, 128.54, 128.4, 128.1, 128.0, 127.8, 127.3 (d, *J* = 11.3 Hz), 35.5, 33.1, 22.2, 13.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ +31.9 (s). HRMS (ESI) calcd for $C_{30}H_{32}BrOPNa$ $[M+Na]^+$ 541.1272, found 541.1258.

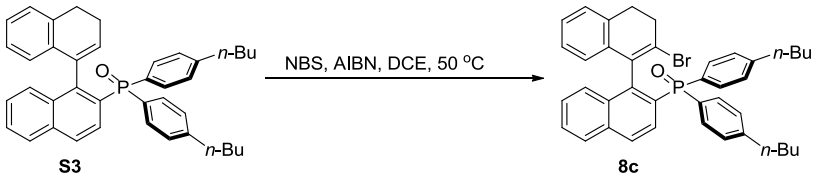


S3

The bromide (0.519 g, 1.0 mmol, 1.0 equiv), hydrazone (0.629 g, 2.0 mmol, 2.0 equiv), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 5 mol%), PPh_3 (39.3 mg, 0.15 mmol, 15 mol%), *t*-BuOLi (0.240 g, 3.0 mmol, 3.0 equiv) and 1,4-dioxane (30 mL) were added to a round-bottom flask under nitrogen atmosphere. And the reaction was stirred at 100 °C for 3 h. After being cooled to room temperature, the mixture was filtered through celite and the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to afford **S3** (0.359 g, 63%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.65 (dd, *J* = 11.2, 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.51-7.45 (m, 2H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 6.0 Hz, 2H), 6.98-6.87 (m, 4H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.22 (d, *J* = 7.8

Hz, 1H), 6.11 (t, *J* = 4.4 Hz, 1H), 2.77-2.76 (m, 1H), 2.65-2.54 (m, 3H), 2.44 (t, *J* = 7.6 Hz, 2H), 2.40-2.29 (m, 1H), 2.24-2.12 (m, 1H), 1.61-1.54 (m, 2H), 1.49-1.42 (m, 2H), 1.37-1.32 (m, 2H), 1.31-1.25 (m, 2H), 0.924 (t, *J* = 7.2, 3H), 0.919 (t, *J* = 7.2, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3 (d, *J* = 2.6 Hz), 146.0 (d, *J* = 2.6 Hz), 144.6 (d, *J* = 8.6 Hz), 135.2, 135.0, 134.6 (d, *J* = 2.0 Hz), 134.4 (d, *J* = 5.1 Hz), 133.2, 133.1 (d, *J* = 11.1 Hz), 132.0 (d, *J* = 9.4 Hz), 131.0 (d, *J* = 105.3 Hz), 131.1 (d, *J* = 10.0 Hz), 130.1 (d, *J* = 104.2 Hz), 130.4, 129.3, 129.1 (d, *J* = 12.8 Hz), 128.2 (d, *J* = 12.1 Hz), 127.8 (d, *J* = 4.1 Hz), 127.7 (d, *J* = 3.8 Hz), 127.6, 127.2, 127.1, 127.0, 126.5 (d, *J* = 6.8 Hz), 126.0, 125.6, 35.6, 35.5, 33.2, 27.2, 23.2, 22.3, 13.94, 13.91. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.8 (s). HRMS (ESI) calcd for $C_{40}H_{42}OP$ $[M+H]^+$ 569.2973, found 569.2964.

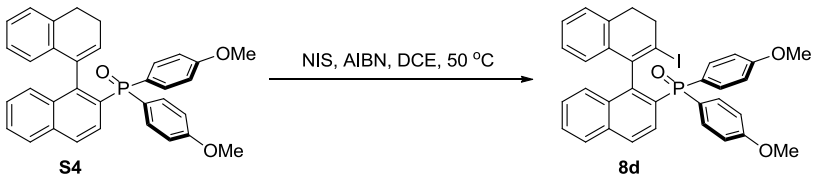
Compound **8c** was prepared following the **Typical Procedure A**.



S3 **8c**

The reaction of vinylarene **S3** (0.284 g, 0.50 mmol) afforded **8c** (0.227 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.84 (t, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.59-7.54 (m, 2H), 7.53-7.47 (m, 1H), 7.46-7.39 (m, 3H), 7.19 (d, *J* = 6.4 Hz, 2H), 7.08-7.00 (m, 4H), 6.75 (t, *J* = 7.0 Hz, 1H), 6.20 (d, *J* = 7.6 Hz, 1H), 3.21-3.10 (m, 1H), 3.03-2.93 (m, 1H), 2.92-2.75 (m, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 1.64-1.51 (m, 4H), 1.41-4.26 (m, 4H), 0.932 (t, *J* = 7.2 Hz, 3H), 0.929 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5 (d, *J* = 2.7 Hz), 146.3 (d, *J* = 2.7 Hz), 143.4 (d, *J* = 7.2 Hz), 135.9, 134.5 (d, *J* = 2.2 Hz), 134.4 (d, *J* = 4.7 Hz), 133.6, 132.2 (d, *J* = 10.0 Hz), 131.8 (d, *J* = 11.3 Hz), 131.7 (d, *J* = 9.8 Hz), 130.4 (d, *J* = 105.7 Hz), 130.2 (d, *J* = 105.4 Hz), 129.1, 129.0 (d, *J* = 12.5 Hz), 128.2, 128.1, 128.05, 128.01, 127.9, 127.3 (d, *J* = 12.3 Hz), 127.2, 127.0, 126.9, 126.7, 126.4, 126.0, 125.7, 35.6, 35.5, 34.8, 33.21, 33.18, 29.0, 22.29, 22.27, 13.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.4 (s). HRMS (ESI) calcd for $C_{40}H_{41}BrOP$ $[M+H]^+$ 647.2078, found 647.2080.

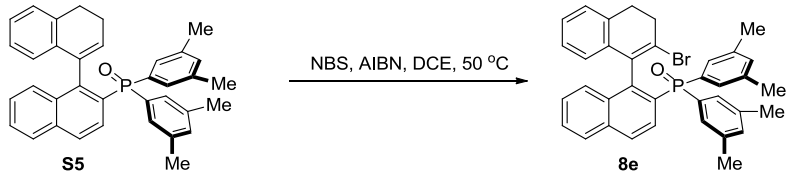
Compound **8d** was prepared following the **Typical Procedure A**.



S4 **8d**

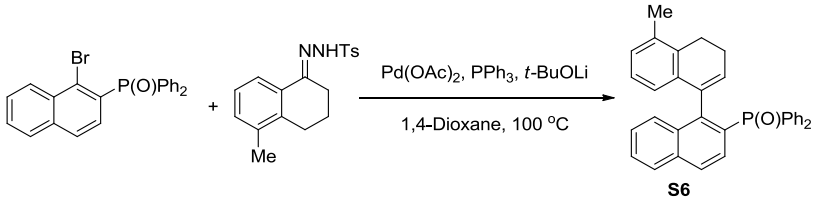
The reaction of vinylarene **S4** (0.258 g, 0.50 mmol) and NIS (0.124 g, 0.55 mmol, 1.1 equiv) afforded **8d** (0.161 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.87-7.80 (m, 2H), 7.68-7.60 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.51-7.43 (m, 2H), 7.43-7.35 (m, 2H), 7.09-6.98 (m, 2H), 6.90 (dd, *J* = 8.8, 2.0 Hz, 2H), 6.79-6.66 (m, 3H), 6.18 (d, *J* = 7.6 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.27-3.15 (m, 1H), 3.14-2.96 (m, 2H), 2.85-2.75 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 161.8, 146.76 (d, *J* = 7.2 Hz), 140.5 (d, *J* = 4.3 Hz), 135.6, 134.6, 134.5, 134.4, 134.2 (d, *J* = 11.0 Hz), 133.5 (d, *J* = 10.7 Hz), 131.9, 131.8, 129.0, 128.9, 128.3 (d, *J* = 102.1 Hz), 128.1 (d, *J* = 4.6 Hz), 127.4, 127.2, 127.1, 126.9, 126.62, 126.60, 125.5, 125.3, 124.4, 124.2, 113.7 (d, *J* = 13.1 Hz), 113.5 (d, *J* = 13.0 Hz), 105.3, 55.3, 55.2, 39.4, 29.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ +27.6 (s). HRMS (ESI) calcd for $C_{34}H_{29}IO_3P$ $[M+H]^+$ 643.0899, found 643.0895.

Compound **8e** was prepared following the **Typical Procedure A.**



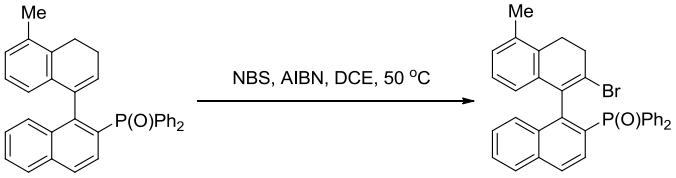
The reaction of vinylarene **S5** (0.256 g, 0.50 mmol) afforded **8e** (0.225 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.61-7.52 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 12.4 Hz, 2H), 7.16 (d, *J* = 12.0 Hz, 2H), 7.13-7.06 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.97 (s, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.22 (d, *J* = 8.0 Hz, 1H), 3.20-3.08 (m, 1H), 3.04-2.93 (m, 1H), 2.91-2.83 (m, 1H), 2.80-2.70 (m, 1H), 2.27 (s, 6H), 2.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1 (d, *J* = 7.2 Hz), 137.6 (d, *J* = 12.7 Hz), 137.4 (d, *J* = 12.6 Hz), 135.8, 134.5 (d, *J* = 2.1 Hz), 134.2 (d, *J* = 4.6 Hz), 133.1 (d, *J* = 102.6 Hz), 133.5, 132.8 (d, *J* = 102.3 Hz), 133.2 (d, *J* = 2.8 Hz), 133.0 (d, *J* = 2.8 Hz), 131.8, 131.7, 129.8 (d, *J* = 9.7 Hz), 129.4 (d, *J* = 9.4 Hz), 129.3, 129.0, 128.9, 128.3, 128.1, 128.0, 127.43, 127.38, 127.3, 127.2, 126.9, 126.8, 126.4, 125.9, 125.7, 34.8, 28.8, 21.2, 21.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.5 (s). HRMS (ESI) calcd for $C_{34}H_{33}BrOP$ $[M+H]^+$ 591.1453, found 591.1441.

Compound **S6** was prepared following the reported literature. [2]



The bromide (0.407 g, 1.0 mmol, 1.0 equiv), the hydrazone (0.657 g, 2.0 mmol, 2.0 equiv), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 5 mol%), PPh_3 (39.3 mg, 0.15 mmol, 15 mol%), *t*-BuOLi (0.240 g, 3.0 mmol, 3.0 equiv) and 1,4-dioxane (30 mL) were added to a round-bottom flask under nitrogen atmosphere. And the reaction was stirred at 100 °C for 3 h. After being cooled to room temperature, the mixture was filtered through celite and the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to afford **S6** (0.258 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.83-7.78 (m, 2H), 7.75 (dd, *J* = 12.0, 7.6 Hz, 2H), 7.59-7.50 (m, 3H), 7.49-7.42 (m, 2H), 7.41-7.34 (m, 3H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.10 (td, *J* = 7.6, 2.8 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.15 (d, *J* = 7.6 Hz, 1H), 6.04 (t, *J* = 4.4 Hz, 1H), 2.70-2.60 (m, 1H), 2.50-2.39 (m, 1H), 2.38-2.29 (m, 1H), 2.28-2.19 (m, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4 (d, *J* = 8.5 Hz), 134.9, 134.65, 134.62, 134.60, 134.55, 134.53, 134.4, 133.5, 133.4, 133.29, 133.27, 132.618 (d, *J* = 104.3 Hz), 132.624, 132.1, 132.0, 131.9, 131.1, 131.0, 130.7 (d, *J* = 2.8 Hz), 129.2 (d, *J* = 104.1 Hz), 128.9 (d, *J* = 13.1 Hz), 128.7, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.4, 127.2, 127.1, 126.6, 124.9, 124.2, 22.9, 22.8, 19.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.6 (s). HRMS (ESI) calcd for $C_{33}H_{28}OP$ $[M+H]^+$ 471.1878, found 471.1869.

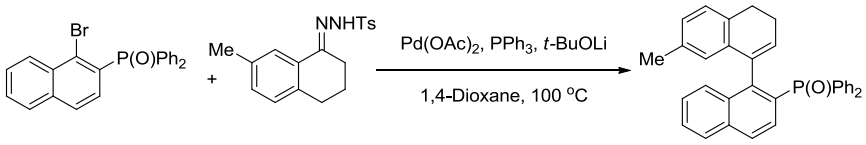
Compound **8f** was prepared following the **Typical Procedure A**.



S6 **8f**

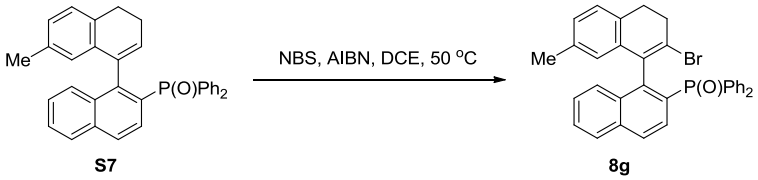
The reaction of vinylarene **S6** (0.235 g, 0.50 mmol) afforded **8f** (0.195 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.73-7.69 (m, 1H), 7.69-7.65 (m, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.55-7.52 (m, 1H), 7.52-7.50 (m, 1H), 7.50-7.47 (m, 2H), 7.47-7.45 (m, 1H), 7.41-7.39 (m, 1H), 7.39-7.37 (m, 1H), 7.37-7.34 (m, 1H), 7.27-7.24 (m, 1H), 7.24-7.21 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.66 (t, *J* = 8.0 Hz, 1H), 6.08 (d, *J* = 8.0 Hz, 1H), 3.03-2.87 (m, 3H), 2.86-2.77 (m, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 144.1, 135.8, 134.6 (d, *J* = 2.3 Hz), 134.53, 134.50, 133.48 (d, *J* = 103.3 Hz), 133.31 (d, *J* = 103.1 Hz), 132.26 (d, *J* = 9.7 Hz), 132.0, 131.9, 131.8, 131.7 (d, *J* = 9.5 Hz), 131.4 (d, *J* = 2.7 Hz), 131.1 (d, *J* = 2.7 Hz), 131.1, 129.1, 128.9 (d, *J* = 12.6 Hz), 128.4, 128.2, 128.1, 128.0, 127.8 (d, *J* = 11.9 Hz), 127.43, 127.40, 127.3, 126.70, 126.69, 126.6, 125.5, 124.0, 34.4, 25.0, 19.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.1 (s). HRMS (ESI) calcd for $C_{33}H_{27}BrOP$ $[M+H]^+$ 549.0983, found 549.0972.

Compound **S7** was prepared following the reported literature.[2]



The bromide (0.407 g, 1.0 mmol, 1.0 equiv), the hydrazone (0.657 g, 2.0 mmol, 2.0 equiv), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 5 mol%), PPh_3 (39.3 mg, 0.15 mmol, 15 mol%), *t*-BuOLi (0.240 g, 3.0 mmol, 3.0 equiv) and 1,4-dioxane (30 mL) were added to a round-bottom flask under nitrogen atmosphere. And the reaction was stirred at 100 °C for 3 h. After being cooled to room temperature, the mixture was filtered through celite and the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to afford **S7** (0.240 g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.83 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.75 (dd, *J* = 11.6, 7.2 Hz, 2H), 7.59-7.54 (m, 2H), 7.54-7.49 (m, 2H), 7.48-7.42 (m, 1H), 7.41-7.33 (m, 3H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.15 (dt, *J* = 7.6, 2.4 Hz, 2H), 6.80 (dd, *J* = 26.0, 7.6 Hz, 2H), 6.03 (t, *J* = 4.4 Hz, 1H), 5.98 (s, 1H), 2.78-2.56 (m, 2H), 2.41-2.28 (m, 1H), 2.23-2.12 (m, 1H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1 (d, *J* = 8.5 Hz), 135.0, 134.7, 134.6, 134.5 (d, *J* = 5.1 Hz), 133.8 (d, *J* = 103.3 Hz), 133.3, 133.2, 133.1, 132.1, 132.0 (d, *J* = 9.1 Hz), 132.03, 131.3, 131.2, 131.1, 130.9 (d, *J* = 2.8 Hz), 129.2 (d, *J* = 103.6 Hz), 129.0, 128.8, 128.1, 128.0, 127.9 (d, *J* = 5.7 Hz), 127.6, 127.5, 127.1 (d, *J* = 12.5 Hz), 127.0 (d, *J* = 11.3 Hz), 126.6, 26.8, 23.4, 21.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.6 (s). HRMS (ESI) calcd for $C_{33}H_{28}OP$ $[M+H]^+$ 471.1878, found 471.1875.

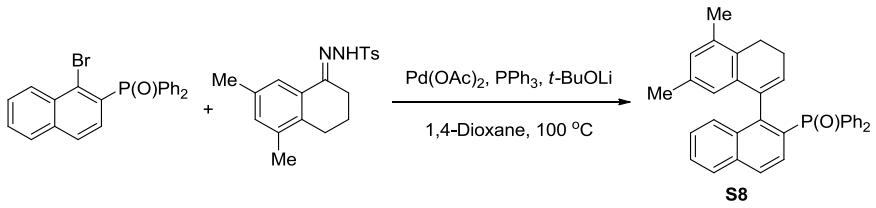
Compound **8g** was prepared following the **Typical Procedure A**.



S7 **8g**

The reaction of vinylarene **S7** (0.235 g, 0.50 mmol) afforded **8g** (0.198 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.67 (dd, *J* = 12.0, 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.54-7.50 (m, 1H), 7.50-7.47 (m, 3H), 7.46-7.44 (m, 1H), 7.43-7.34 (m, 3H), 7.30-7.23 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 5.93 (s, 1H), 3.22-3.10 (m, 1H), 3.04-2.93 (m, 1H), 2.92-2.78 (m, 2H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0 (d, *J* = 7.0 Hz), 135.6, 135.3, 134.5 (d, *J* = 2.2 Hz), 134.34, 134.30, 134.25, 133.0 (d, *J* = 102.9 Hz), 133.2, 132.2 (d, *J* = 9.7 Hz), 131.9 (d, *J* = 11.5 Hz), 131.7 (d, *J* = 9.4 Hz), 131.4 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 2.7 Hz), 130.8, 128.7 (d, *J* = 12.6 Hz), 127.8 (d, *J* = 101.1 Hz), 128.2, 128.14, 128.08, 128.0, 127.8 (d, *J* = 12.0 Hz), 127.5, 127.4, 127.3, 127.0, 126.5, 126.4, 35.0, 28.6, 20.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.2 (s). HRMS (ESI) calcd for $C_{33}H_{27}BrOP$ $[M+H]^+$ 549.0983, found 549.0983.

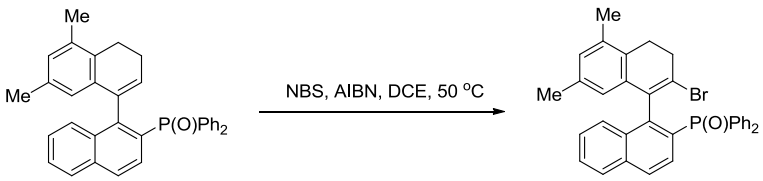
Compound **S8** was prepared following the reported literature [2].



S8

The phosphine oxide (0.814 g, 2.0 mmol, 1.0 equiv), hydrazone (1.370 g, 4.0 mmol, 2.0 equiv), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol, 5 mol%), PPh_3 (78.6 mg, 0.15 mmol, 15 mol%), *t*-BuOLi (0.480 g, 6.0 mmol, 3.0 equiv) and 1,4-dioxane (60 mL) were added to a round-bottom flask under nitrogen atmosphere. The reaction was stirred at 100 °C for 4 h. After being cooled to room temperature, the mixture was filtered through celite and the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to afford **S8** (0.592 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.79 (m, 3H), 7.79-7.75 (m, 1H), 7.75-7.71 (m, 1H), 7.59-7.54 (m, 2H), 7.54-7.48 (m, 2H), 7.45-7.41 (m, 1H), 7.41-7.34 (m, 3H), 7.24-7.19 (m, 1H), 7.14-7.08 (m, 2H), 6.68 (s, 1H), 6.05 (t, *J* = 4.4 Hz, 1H), 5.90 (s, 1H), 2.68-2.58 (m, 1H), 2.50-2.40 (m, 1H), 2.39-2.29 (m, 1H), 2.26-2.19 (m, 1H), 2.14 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5 (d, *J* = 8.6 Hz), 134.8, 134.64, 134.59, 134.4, 134.1, 133.8, 133.40, 133.36, 133.3, 133.1, 132.6, 132.1, 132.0 (d, *J* = 9.2 Hz), 131.2, 131.10, 131.06, 130.7 (d, *J* = 2.8 Hz), 130.2, 129.5, 129.0 (d, *J* = 103.7 Hz), 128.9 (d, *J* = 12.6 Hz), 128.0 (d, *J* = 11.8 Hz), 127.84, 127.75, 127.3 (d, *J* = 12.2 Hz), 127.0 (d, *J* = 12.5 Hz), 126.6, 124.8, 23.1, 22.6, 20.9, 19.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.6 (s). HRMS (ESI) calcd for $C_{34}H_{30}OP$ $[M+H]^+$ 485.2034, found 485.2037.

Compound **8h** was prepared following the **Typical Procedure A**.

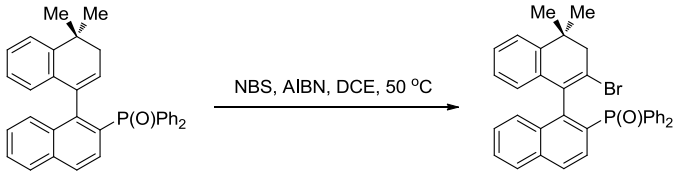


S8 **8h**

The reaction of vinylarene **S8** (0.242 g, 0.50 mmol) afforded **8h** (0.141 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 15.8, 7.8 Hz, 3H), 7.67 (dd, *J* = 11.6, 7.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.55-7.49 (m, 2H), 7.49-7.43 (m, 3H), 7.42-7.34 (m, 3H), 7.29-7.22 (m, 2H), 6.72 (s, 1H), 5.84 (s, 1H),

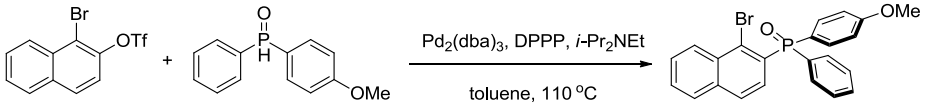
3.05-2.78 (m, 4H), 2.24 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ144.4 (d, *J* = 7.1 Hz), 135.6, 134.7, 134.6 (d, *J* = 2.2 Hz), 134.5, 134.43, 134.35, 133.7 (d, *J* = 103.6 Hz), 133.0 (d, *J* = 103.0 Hz), 132.2 (d, *J* = 9.7 Hz), 132.1, 131.9, 131.8 (d, *J* = 9.5 Hz), 131.4 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 2.7 Hz), 129.9, 129.0, 128.8 (d, *J* = 12.7 Hz), 128.2, 128.1, 128.0, 127.8 (d, *J* = 12.0 Hz), 127.38, 127.36, 127.2, 127.1, 126.73, 126.72, 126.6, 124.8, 34.6, 24.8, 20.8, 19.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.3 (s). HRMS (ESI) calcd for $C_{34}H_{29}BrOP$ $[M+H]^+$ 563.1140, found 563.1141.

Compound **8i** was prepared following the **Typical Procedure A**.

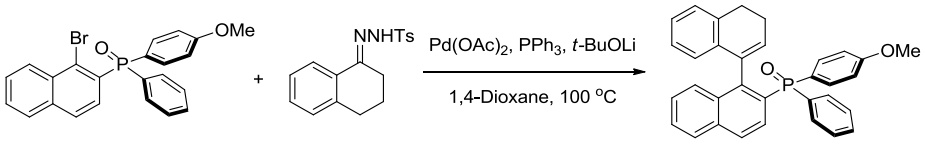


The reaction of vinylarene **S9** (0.242 g, 0.50 mmol) afforded **8i** (0.132 g, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.59-7.54 (m, 3H), 7.53-7.50 (m, 1H), 7.50-7.39 (m, 4H), 7.38-7.34 (m, 2H), 7.34-7.27 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.27 (d, *J* = 7.6 Hz, 1H), 2.77 (d, *J* = 17.0 Hz, 1H), 2.63 (d, *J* = 17.0 Hz, 1H), 1.51 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5 (d, *J* = 7.2 Hz), 141.7, 134.7 (d, *J* = 2.2 Hz), 134.3, 133.5 (d, *J* = 103.1 Hz), 134.0, 133.9, 133.3 (d, *J* = 103.4 Hz), 132.3, 132.2, 132.1, 132.01, 131.97, 131.93, 131.89, 131.87, 131.4 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 2.7 Hz), 129.7, 129.3, 129.0, 128.9, 128.7, 128.6, 128.3, 128.25, 128.18, 128.14, 128.06 (d, *J* = 2.3 Hz), 127.9 (d, *J* = 2.5 Hz), 127.6, 127.43, 127.40, 126.6, 126.4, 126.3, 126.0, 125.8, 123.8, 49.6, 36.3, 29.9, 28.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.6 (s). HRMS (ESI) calcd for $C_{34}H_{29}BrOP$ $[M+H]^+$ 563.1140, found 563.1142.

Compound **S10** was prepared following the reported literature.[2]



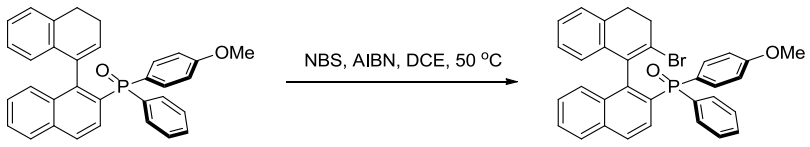
A mixture of 1-bromonaphthalen-2-yl trifluoromethanesulfonate (2.130 g, 6.0 mmol, 1.2 equiv), (4-methoxyphenyl)(phenyl)phosphine oxide (1.160 g, 5. 0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (0.114 g, 0.13 mmol, 2.5 mol%), 1,3-bis(diphenylphosphino)propane (0.103 g, 0.25 mmol, 5 mol%), and *N,N*-diisopropylethylamine (1.20 mL, 7.50 mmol, 1.5 equiv) in toluene (30 mL) under N_2 was stirred at 110 °C overnight. After being cooled to room temperature, the mixture was filtered and concentrated and the residue was purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to give the desired product (1.240 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47-8.34 (m, 1H), 7.85-7.80 (m, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H) 7.62-7.57 (m, 2H), 7.56-7.51 (m, 1H), 7.48-7.38 (m, 3H), 6.97 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, *J* = 2.9 Hz), 135.6 (d, *J* = 2.1 Hz), 134.0, 133.9, 133.1, 132.64 (d, *J* = 8.7 Hz), 131.9 (d, *J* = 9.9 Hz), 131.7 (d, *J* = 2.8 Hz), 131.1 (d, *J* = 104.1 Hz), 129.9 (d, *J* = 10.7 Hz), 129.7 (d, *J* = 4.0 Hz), 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.4 (d, *J* = 11.3 Hz), 123.5, 122.4, 114.1 (d, *J* = 13.4 Hz), 55.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ +31.4 (s). HRMS (ESI) calcd for $C_{23}H_{29}BrO_2P$ $[M+H]^+$ 437.0306, found 437.0302.



S10

The bromide (0.707 g, 1.60 mmol, 1.0 equiv), hydrazone (1. 0 g, 3.20 mmol, 2.0 equiv), $Pd(OAc)_2$ (18.0 mg, 0.08 mmol, 5 mol%), PPh_3 (62.9 mg, 0.24 mmol, 15 mol%), *t*-BuOLi (0.384 g, 4.8 mmol, 3.0 equiv) and 1,4-dioxane (40 mL) were added to a round-bottom flask under nitrogen atmosphere. And the reaction was stirred at 100 °C for 4 h. After being cooled to room temperature, the mixture was filtered through celite and the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to afford **S10** (0.542 g, 77%, d.r. = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 2.4 Hz, 0.5H), 7.81-7.78 (m, 1.5H), 7.77-7.73 (m, 1H), 7.73-7.70 (m, 0.5H), 7.70-7.66 (m, 1H), 7.65-7.63 (m, 0.5H), 7.58-7.54 (m, 1H), 7.54-7.51 (m, 1.5H), 7.51-7.49 (m, 0.5H), 7.49-7.46 (m, 1H), 7.46-7.42 (m, 1H), 7.41m7.32 (m, 2H), 7.21 (t, *J* = 7.0 Hz, 0.5H), 7.11 (td, *J* = 7.6, 2.8 Hz, 1H), 7.00-6.92 (m, 2H), 6.91-6.86 (m, 1H), 6.81-6.72 (m, 1H), 6.62 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.22 (t, *J* = 7.2 Hz, 1H), 6.11 (t, *J* = 4.6 Hz, 0.5H), 6.06 (t, *J* = 4.4 Hz, 0.5H), 3.80 (s, 1.5H), 3.69 (s, 1.5H), 2.77-2.55 (m, 2H), 2.42-2.31 (m, 1H), 2.28-2.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, *J* = 2.9 Hz), 161.6 (d, *J* = 2.9 Hz), 144.8 (d, *J* = 8.5 Hz), 144.6 (d, *J* = 8.6 Hz), 135.2 (d, *J* = 10. Hz), 135.0 (d, *J* = 12.6 Hz), 134.8, 134.6 (d, *J* = 2.2 Hz), 134.6 (d, *J* = 2.2 Hz), 134.5 (d, *J* = 5.2 Hz), 134.3 (d, *J* = 5.1Hz), 133.7 (d, *J* = 10.4 Hz), 133.1 (d, *J* = 104.6 Hz), 133.1 (d, *J* = 2.3 Hz), 133.0, 132.9, 132.0 (d, *J* = 9.9 Hz), 131.9, 131.8, 131.1, 130.9, 130.7 (d, *J* = 2.7 Hz), 129.8 (d, *J* = 103.7 Hz), 129.7 (d, *J* = 103.8 Hz), 129.0 (d, *J* = 5.1 Hz), 128.9 (d, *J* = 5.3 Hz), 128.4 (d, *J* = 12.0 Hz), 128.1 (d, *J* = 11.8 Hz), 127.8, 127.8, 127.7, 127.6, 127.2, 127.14, 127.08, 126.6 (d, *J* = 2.7 Hz), 126.5, 126.4, 125.9 (d, *J* = 2.8 Hz), 125.6 (d, *J* = 2.2 Hz), 125.3, 124.3, 123.7 (d, *J* = 99.2 Hz), 113.7 (d, *J* = 12.8 Hz), 113.3 (d, *J* = 13.1 Hz), 55.2, 55.1, 27.1, 27.1, 23.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ +28.7 (s), 28.5 (s). HRMS (ESI) calcd for $C_{33}H_{28}O_2P$ $[M+H]^+$ 487.1827, found 487.1831.

Compound **8j** was prepared following the **Typical Procedure A**.

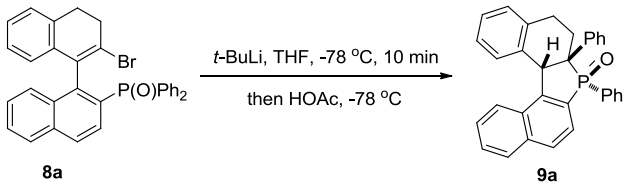


S10 **8j**

The reaction of vinylarene **S10** (0.243 g, 0.50 mmol) afforded **8j** (0.187 g, 66%, dr 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.87-7.79 (m, 2H), 7.74-7.65 (m, 1H), 7.64-7.55 (m, 2H), 7.53-7.49 (m, 1H), 7.49-7.47 (m, 1H), 7.47-7.46 (m, 1H), 7.46-7.43 (m, 1H), 742-7.38 (m, 1H), 7.38 -7.33 (m, 1H), 7.26-7.21 (m, 1H), 7.09-6.99 (m, 2H), 6.88 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.83-6.66 (m, 2H), 6.18 (d, *J* = 7.6 Hz, 1H), 3.82 (s, 1.5H), 3.77 (s, 1.5H), 3.26-3.10 (m, 1H), 3.05-2.93 (m, 1H), 2.92-2.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 2.8 Hz), 161.9 (d, *J* = 2.9 Hz), 143.6 (d, *J* = 3.9 Hz), 143.5 (d, *J* = 3.8 Hz), 136.0 (d, *J* = 1.4 Hz), 134.6 (d, *J* = 2.2 Hz), 134.5, 134.4, 134.3, 134.2, 134.1, 133.7, 133.6, 133.3, 133.1, 132.2 (d, *J* = 9.7 Hz), 131.9 (d, *J* = 2.1 Hz), 131.84 (d, *J* = 2.0 Hz), 131.80, 131.7, 131.3 (d, *J* = 2.6 Hz), 131.1 (d, *J* = 2.7 Hz), 128.9 (d, *J* = 4.0 Hz), 128.8 (d, *J* = 4.1 Hz), 128.1, 128.1, 128.0, 127.9, 127.8, 127.4, 127.4, 127.3, 127.1, 126.8, 126.7, 126.5, 126.1, 125.7, 125.1, 124.9, 124.0, 123.8, 113.7,

113.6, 113.5, 55.3, 55.2, 34.8, 29.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ +27.9 (s), +27.8 (s). HRMS (ESI) calcd for $C_{33}H_{27}BrO_2P$ $[M+H]^+$ 565.0932, found 565.0935.

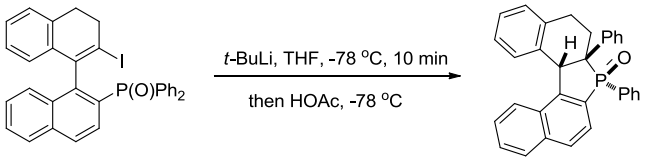
Typical procedure for the intramolecular addition/rearrangement of vinyllithium with phosphine oxides **8** (**Typical procedure B**)



8a **9a**

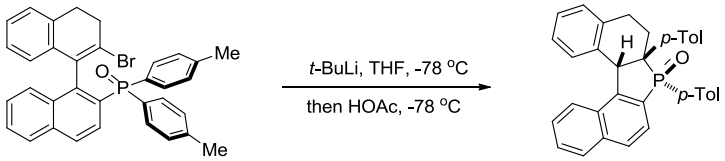
The phosphine oxides **8a** (53.5 mg, 0.10 mmol, 1.0 equiv) was dissolved in THF (3 ml) and cooled to -78 °C under N_2. A solution of *t*-BuLi (1.3 M in hexane, 0.30 ml, 4.0 equiv) was added to the above flask dropwise, and stirred for 10 min. The reaction was quenched by the addition of HOAc (1 ml) at -78 °C. The mixture was allowed to warm to r.t., and concentrated by evaporation under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to give the desired product **9a** (39.6 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.0, 3.0 Hz, 2H), 8.01 (dd, *J* = 8.2, 3.0 Hz, 1H), 7.80-7.64 (m, 3H), 7.52-7.41 (m, 2H), 7.32-7.27 (m, 2H), 7.27-7.24 (m, 3H), 7.23-7.16 (m, 1H), 7.15-7.08 (m, 2H), 7.07-7.05 (m, 1H), 7.04-7.00 (m, 1H), 6.99-6.93 (m, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 5.46 (d, *J* = 21.2 Hz, 1H), 2.89 (ddd, *J* = 13.6, 4.8, 2.4 Hz, 1H), 2.70-2.50 (m, 2H), 1.90-1.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1 (d, *J* = 26.0 Hz), 140.8, 139.6 (d, *J* = 5.2 Hz), 136.6, 135.8 (d, *J* = 2.0 Hz), 132.2 (d, *J* = 10.2 Hz), 131.2 (d, *J* = 94.2 Hz), 130.7 (d, *J* = 12.5 Hz), 130.1 (d, *J* = 10.3 Hz), 129.2 (d, *J* = 99.6 Hz), 129.5 (d, *J* = 4.0 Hz), 129.2, 128.3, 128.24, 128.22, 128.0, 127.9, 127.7, 127.4, 127.0 (d, *J* = 2.5 Hz), 126.7, 126.5, 125.7, 125.6, 125.3, 54.2 (d, *J* = 93.5 Hz), 48.6 (d, *J* = 12.3 Hz), 33.0 (d, *J* = 3.0 Hz), 29.1 (d, *J* = 9.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ +59.3 (s). HRMS (ESI) calcd for $C_{32}H_{26}OP$ $[M+H]^+$ 457.1721, found 457.1722.

The reaction of iodide **8a'** (58.2 mg, 0.10 mmol, 1.0 equiv) under identical reaction conditions gave compound **9a** (30.5 mg, 76%).



8a' **9a**

The compound **9b** was prepared following the **Typical Procedure B**.

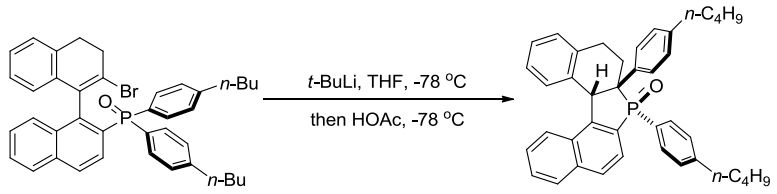


8b **9b**

The reaction of phosphine oxides **8b** (56.3 mg, 0.10 mmol) afforded **9b** (39.2 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8, 4.4 Hz, 2H), 7.99 (dd, *J* = 8.4, 3.2 Hz, 1H), 7.76-7.69 (m, 2H), 7.68-7.63 (m, 1H), 7.37-7.30 (m, 2H), 7.20-7.12 (m, 2H), 7.11-7.07 (m, 2H), 7.07-7.02 (m, 2H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.94-6.89 (m, 2H), 6.63 (d, *J* = 7.6 Hz, 1H), 5.43 (d, *J* = 20.8 Hz, 1H), 2.87 (dd, *J* = 13.6,

1.6 Hz, 1H), 2.67-2.60 (m, 2H), 2.25 (s, 3H), 2.23 (s, 3H), 1.86-1.72 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0 (d, *J* = 25.8 Hz), 141.9 (d, *J* = 2.9 Hz), 140.9, 136.8, 136.6, 136.5, 136.4, 135.7 (d, *J* = 2.0 Hz), 132.1 (d, *J* = 10.6 Hz), 130.7 (d, *J* = 12.5 Hz), 129.6 (d, *J* = 99.7 Hz),129.9 (d, *J* = 10.1 Hz), 129.4 (d, *J* = 3.9 Hz), 129.2, 129.0 (d, *J* = 2.1 Hz), 128.8, 128.6, 127.9 (d, *J* = 96.8 Hz), 128.2, 127.5, 127.4, 126.7, 126.4, 125.7, 125.6, 125.3, 53.9 (d, *J* = 63.9 Hz), 48.7 (d, *J* = 12.3 Hz), 32.9 (d, *J* = 3.3 Hz), 29.0 (d, *J* = 9.1 Hz), 21.4, 20.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ +59.2 (s). HRMS (ESI) calcd for $C_{34}H_{30}OP$ $[M+H]^+$ 485.2034, found 485.2037.

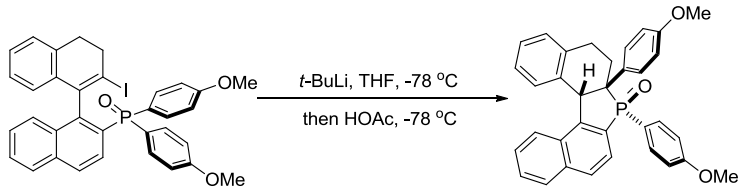
The compound **9c** was prepared following the **Typical Procedure B**.



8c **9c**

The reaction of phosphine oxides **8c** (64.8 mg, 0.10 mmol) afforded **9c** (48.9 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.0, 2.8 Hz, 2H), 8.00 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.76-7.69 (m, 2H), 7.69-7.64 (m, 1H), 7.38-7.31 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.09-7.04 (m, 3H), 7. 03-7.00 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.91 (dd, *J* = 8.0, 2.0 Hz, 2H), 6.61 (d, *J* = 7.6 Hz, 1H), 5.42 (d, *J* = 21.2 Hz, 1H), 2.87 (dd, *J* = 13.6, 2.4 Hz, 1H), 2.67-2.60 (m, 2H), 2.53-2.44 (m, 4H), 1.88-1.76 (m, 1H), 1.57-1.50 (m, 2H), 1.49-1.41 (m, 2H), 1.35-1.25 (m, 2H), 1.25-1.17 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8 (d, *J* = 2.8 Hz), 146.2, 146.0, 141.3 (d, *J* = 2.6 Hz), 140.8, 136.83, 136.78, 136.76, 135.7 (d, *J* = 1.9 Hz), 132.1 (d, *J* = 10.5 Hz), 130.8, 130.6, 129.5 (d, *J* = 99.9 Hz), 129.9 (d, *J* = 10.2 Hz), 129.3 (d, *J* = 3.9 Hz), 129.2, 128.5, 128.2 (d, *J* = 2.1 Hz), 128.1 (d, *J* = 2.5 Hz), 128.0, 127.6, 126.8 (d, *J* = 99.3 Hz), 126.6, 125.7 (d, *J* = 8.3 Hz), 125.6, 125.3, 53.9 (d, *J* = 74.1 Hz), 48.7 (d, *J* = 12.3 Hz), 35.4, 34.9, 33.1, 33.0, 32.8 (d, *J* = 3.2 Hz), 29.1 (d, *J* = 9.0 Hz), 22.4, 22.0, 13.9, 13.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ +59.3 (s). HRMS (ESI) calcd for $C_{40}H_{42}OP$ $[M+H]^+$ 569.2973, found 569.2961.

The compound **9d** was prepared following the **Typical Procedure B**.

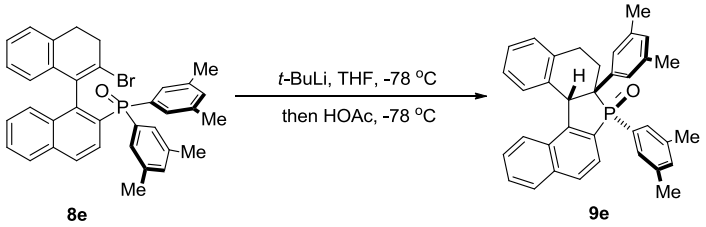


8d **9d**

The reaction of phosphine oxides **8d** (64.2 mg, 0.10 mmol) afforded **9d** (25.8 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.99 (dd, *J* = 8.0, 3.2 Hz, 1H), 7.76-7.64 (m, 3H), 7.34 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.21-7.13 (m, 2H), 7.10-7.03 (m, 2H), 7.00-6.92 (m, 1H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.63-6.58 (m, 3H), 5.38 (d, *J* = 21.6 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 2.82 (dd, *J* = 13.6, 2.0 Hz, 1H), 2.67-2.60 (m, 2H), 1.85-1.68 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 2.8 Hz), 158.3 (d, *J* = 2.4 Hz), 146.0, 145.8, 140.9, 136.8, 135.7 (d, *J* = 2.0 Hz), 133.9 (d, *J* = 11.6 Hz), 131.5 (d, *J* = 5.4 Hz), 130.8, 130.7, 130.6 (d, *J* = 3.9 Hz), 130.2, 130.0, 129.9, 129.2, 128.2, 127.6, 127.6, 127.3, 126.8, 126.5, 125.8, 125.7, 125.6, 125.3, 122.7, 121.8, 113.7 (d, *J* = 2.1 Hz), 113.5 (d, *J* = 12.9 Hz), 55.14, 55.07, 53.5 (d, *J* =

64.9 Hz), 48.8 (d, *J* = 12.5 Hz), 32.9, 29.0 (d, *J* = 9.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ +58.8 (s). HRMS (ESI) calcd for $C_{34}H_{30}O_3P$ $[M+H]^+$ 517.1932, found 517.1927.

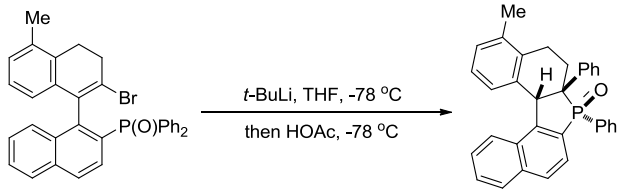
The compound **9e** was prepared following the **Typical Procedure B**.



8e **9e**

The reaction of phosphine oxides **8e** (59.2 mg, 0.10 mmol) afforded **9e** (34.4 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (t, *J* = 8.4 Hz, 2H), 8.00 (dd, *J* = 8.2, 3.0 Hz, 1H), 7.77-7.63 (m, 3H), 7.11-7.04 (m, 2H), 7.03 (s, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.89 (s, 2H), 6.86 (s, 1H), 6.81 (s, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 5.44 (d, *J* = 21.2 Hz, 1H), 2.84 (dd, *J* = 13.4, 2.6 Hz, 1H), 2.66-2.56 (m, 2H), 2.17 (s, 6H), 2.04 (s, 6H), 1.74-1.70 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2 (d, *J* = 25.7 Hz), 140.9, 139.6 (d, *J* = 5.1 Hz), 137.7 (d, *J* = 12.6 Hz), 137.2 (d, *J* = 2.3 Hz), 137.17, 135.7 (d, *J* = 2.0 Hz), 133.3 (d, *J* = 3.1 Hz), 130.9 (d, *J* = 93.7 Hz), 130.7 (d, *J* = 12.4 Hz), 130.2, 129.9 (d, *J* = 10.1 Hz), 129.7 (d, *J* = 10.4 Hz), 128.6 (d, *J* = 107.5 Hz), 128.8 (d, *J* = 2.5 Hz), 127.6, 127.58, 127.55, 127.4, 126.8, 126.3, 125.7 (d, *J* = 8.5 Hz), 125.5, 125.1, 54.2 (d, *J* = 63.1 Hz), 48.7 (d, *J* = 12.1 Hz), 33.1, 29.1 (d, *J* = 9.1 Hz), 21.7, 20.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ +59.4 (s). HRMS (ESI) calcd for $C_{36}H_{34}OP$ $[M+H]^+$ 513.2347, found 513.2352.

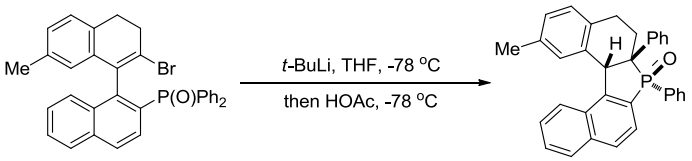
The compound **9f** was prepared following the **Typical Procedure B**.



8f **9f**

The reaction of phosphine oxides **8f** (54.9 mg, 0.10 mmol) afforded **9f** (33.5 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.03 (m, 2H), 7.99 (dd, *J* = 8.2, 3.0 Hz, 1H), 7.76-7.71 (m, 1H), 7.71-7.67 (m, 1H), 7.67-7.61 (m, 1H), 7.47-7.44 (m, 1H), 7.44-7.41 (m, 1H), 7.37-7.34 (m, 1H), 7.34-7.30 (m, 2H), 7.30-7.27 (m, 1H), 7.26-7.23 (m, 1H), 7.22-7.18 (m, 1H), 7.15 (td, *J* = 7.6, 2.4 Hz, 2H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 7.2 Hz, 1H), 5.47 (d, *J* = 20.4 Hz, 1H), 2.84-2.73 (m, 2H), 2.43-2.32 (m, 1H), 2.16 (s, 3H), 1.87-1.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5 (d, *J* = 25.2 Hz), 139.5 (d, *J* = 5.1 Hz), 139.0, 136.4, 135.8, 134.0, 132.2 (d, *J* = 10.3 Hz), 131.7, 131.62, 131.59, 130.9, 130.7, 130.0 (d, *J* = 10.0 Hz), 129.4 (d, *J* = 3.8 Hz), 129.2, 129.1 (d, *J* = 99.4 Hz), 128.2, 127.9 (d, *J* = 11.9 Hz), 127.5, 126.9 (d, *J* = 2.5 Hz), 125.7, 125.5 (d, *J* = 8.3 Hz), 125.4, 125.0, 54.1 (d, *J* = 63.9 Hz), 48.9 (d, *J* = 12.1 Hz), 32.5 (d, *J* = 2.7 Hz), 24.4 (d, *J* = 8.8 Hz), 19.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ +58.2 (s). HRMS (ESI) calcd for $C_{33}H_{28}OP$ $[M+H]^+$ 471.1878, found 471.1878.

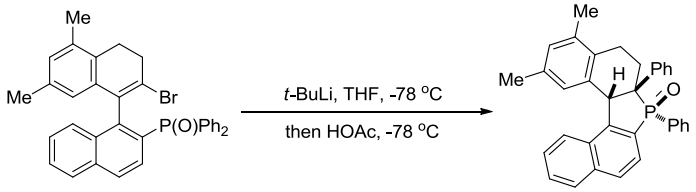
The compound **9g** was prepared following the **Typical Procedure B**.



8g **9g**

The reaction of phosphine oxides **8g** (54.9 mg, 0.10 mmol) afforded **9g** (34.0 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.07 (s, 1H), 8.04-7.99 (m, 1H), 7.77-7.69 (m, 2H), 7.69-7.65 (m, 1H), 7.44 (s, 1H), 7.42 (s, 1H), 7.33-7.27 (m, 3H), 7.25-7.21 (m, 2H), 7.21-7.15 (m, 1H), 7.15-7.08 (m, 2H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.42 (s, 1H), 5.43 (d, *J* = 21.2 Hz, 1H), 2.89-2.80 (m, 1H), 2.61-2.53 (m, 2H), 2.08 (s, 3H), 1.88-1.75 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3 (d, *J* = 25.8 Hz), 139.7 (d, *J* = 5.1 Hz), 137.7, 136.4, 135.8, 135.1, 132.3 (d, *J* = 10.2 Hz), 131.7, 131.58, 131.55, 130.8, 130.73, 130.70, 130.1 (d, *J* = 10.3 Hz), 129.6 (d, *J* = 2.9 Hz), 129.2, 129.1 (d, *J* = 99.6 Hz), 128.3, 128.21, 128.18, 128.1, 127.8 (d, *J* = 12.0 Hz), 127.6, 127.0, 126.9 (d, *J* = 2.5 Hz), 126.60, 125.57 (d, *J* = 8.3 Hz), 125.3, 54.4 (d, *J* = 63.6 Hz), 48.5 (d, *J* = 11.8 Hz), 33.2 (d, *J* = 2.8 Hz), 28.6 (d, *J* = 9.0 Hz), 21.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ +59.0 (s). HRMS (ESI) calcd for $C_{33}H_{28}OP$ $[M+H]^+$ 471.1878, found 471.1884.

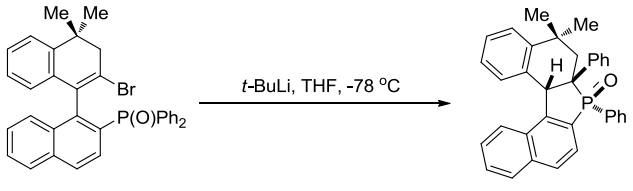
The compound **9h** was prepared following the **Typical Procedure B**.



8h **9h**

The reaction of phosphine oxides **8h** (56.3 mg, 0.10 mmol) afforded **9h** (45.0 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (t, *J* = 8.0 Hz, 2H), 7.99 (dd, *J* = 8.2, 3.0 Hz, 1H), 7.75-7.67 (m, 2H), 7.66-7.60 (m, 1H), 7.44-7.39 (m, 2H), 7.38-7.30 (m, 3H), 7.28-7.22 (m, 2H), 7.28-7.22 (m, 3H), 6.77 (s, 1H), 6.40 (s, 1H), 5.45 (d, *J* = 20.0 Hz, 1H), 2.81-2.65 (m, 2H), 2.39-2.26 (m, 1H), 2.11 (s, 3H), 2.07 (s, 3H), 1.92-1.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1 (d, *J* = 25.2 Hz), 139.6 (d, *J* = 4.9 Hz), 136.3, 135.8 (d, *J* = 2.0 Hz), 135.7, 134.3, 133.9, 132.4 (d, *J* = 10.3 Hz), 131.6 (d, *J* = 2.8 Hz), 131.20 (d, *J* = 94.0 Hz), 130.9 (d, *J* = 12.5 Hz), 129.9 (d, *J* = 10.3 Hz), 129.4 (d, *J* = 3.9 Hz), 129.2, 129.1 (d, *J* = 99.4 Hz), 128.9, 128.20, 128.18, 128.16, 127.9, 127.8, 127.4 (d, *J* = 0.5 Hz), 126.8 (d, *J* = 2.5 Hz), 126.5, 125.5, 125.44, 125.42, 54.2 (d, *J* = 64.1 Hz), 49.0 (d, *J* = 11.9 Hz), 32.6 (d, *J* = 2.5 Hz), 24.1 (d, *J* = 8.6 Hz), 21.1, 19.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ +57.8 (s). HRMS (ESI) calcd for $C_{34}H_{30}OP$ $[M+H]^+$ 485.2034, found 485.2026.

The compound **9i** was prepared following the **Typical Procedure B**.

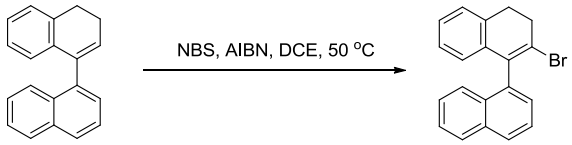


8i **9i**

The reaction of phosphine oxides **8i** (56.3 mg, 0.10 mmol) afforded **9i** (41.5 mg, 83%). ^{1}H NMR

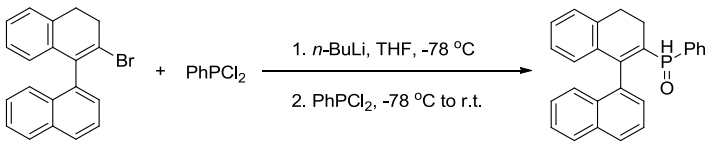
(400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 6.8 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.00 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.80-7.72 (m, 2H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.257.23- (m, 3H), 7.22-7.19 (m, 2H), 7.18-7.10 (m, 3H), 7.10-7.02 (m, 2H), 6.95 (t, *J* = 7.0 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 5.86 (d, *J* = 23.6 Hz, 1H), 2.68 (d, *J* = 13.6 Hz, 1H), 2.02 (dd, *J* = 20.4, 14.0 Hz, 1H), 1.66 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5 (d, *J* = 26.7 Hz), 146.2, 141.3 (d, *J* = 5.8 Hz), 135.7, 135.4, 132.1 (d, *J* = 10.2 Hz), 131.3 (d, *J* = 93.7 Hz), 131.4, 130.9, 130.8, 130.0 (d, *J* = 10.0 Hz), 129.2, 129.1, 129.0 (d, *J* = 3.8 Hz), 128.2, 128.1 (d, *J* = 2.2 Hz), 127.8, 127.7, 127.5, 126.6, 126.5 (d, *J* = 2.7 Hz), 125.6 (d, *J* = 8.3 Hz), 125.4, 125.1 (d, *J* = 0.4 Hz), 123.5, 53.8 (d, *J* = 60.5 Hz), 46.5 (d, *J* = 11.2 Hz), 45.3, 37.0 (d, *J* = 9.2 Hz), 29.9, 26.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ +61.2 (s). HRMS (ESI) calcd for $C_{34}H_{30}OP$ $[M+H]^+$ 485.2034, found 485.2029.

The compound **S12** was prepared following the **Typical Procedure A**.



S11 **S12**

The reaction of vinylarene **S11** (0.513 g, 2.0 mmol), NBS (0.392 g, 2.2 mmol, 1.1 equiv) and AIBN (32.8 mg, 0.2 mmol, 0.1 equiv) afforded **S12** (0.604 g, 90%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 6.8 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 7.6 Hz, 1H), 3.24-3.14 (m, 2H), 3.14-3.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.8, 135.6, 133.7, 133.7, 131.3, 128.4, 128.0, 127.4, 127.3, 127.2, 126.7, 126.3, 125.9, 125.9, 125.6, 125.5, 125.3, 35.1, 29.6. HRMS (EI) calcd for $C_{20}H_{15}Br$ $[M]^+$ 334.0357, found 334.0352.

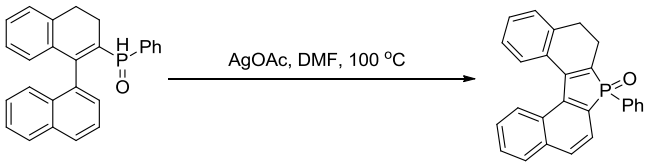


S12 **S13**

The compound **S12** (0.604 g, 1.8 mmol, 1.0 equiv) was dissolved in THF (10 ml) and cooled to -78 °C under N_2. A solution of *n*-BuLi (2.4 M in hexane, 0.90 ml, 1.2 equiv) was added dropwise to the above solution and maintained at that temperature for 1 h. Subsequently the dichlorophenylphosphine (0.30 ml, 2.2 mmol, 1.2 equiv) in THF (2 ml) was added at -78 °C, and stirred for 30 min. The solution was warmed to room temperature and stirred overnight. The reaction was quenched by the addition of H_2O (5 ml) and extracted with EtOAc three times. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silics gel (PE/EtOAc 1:1) to give the desired product **S13** (0.272 g, 54%), as a pair of diastereoisomers (dr ≈ 1:1) . ^1H NMR (400 MHz, $CDCl_3$) δ 7.98-7.86 (m, 2H), 7.78 (d, *J* = 8.4 Hz, 0.5H), 7.71-7.63 (m, 1H), 7.62-7.54 (m, 1.5H), 7.52-7.44 (m, 2.5H), 7.44-7.37 (m, 3H), 7.36-7.29 (m, 1H), 7.28-7.23 (m, 1H), 7.22-7.16 (m, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.58 (t, *J* = 7.4 Hz, 1H), 6.45 (s, 0.5H), 3.22-2.99 (m, 2H), 2.99-2.76 (m, 1H), 2.67-2.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4 (d, *J* = 10.3 Hz), 147.5 (d, *J* = 10.5 Hz), 136.5 (d, *J* = 2.1 Hz), 136.2 (d, *J* = 2.1 Hz), 134.5 (d, *J* = 12.7 Hz), 134.3, 134.2, 134.1, 133.8 (d, *J* = 10.0 Hz), 133.5, 133.4, 132.1, 132.0 (d,

J = 2.6 Hz), 131.9 (d, *J* = 2.8 Hz), 131.6, 130.2, 130.08, 130.06, 129.96, 129.7, 129.4, 129.3, 128.93, 128.90, 128.6, 128.5, 128.4, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 127.2, 127.1, 126.8, 126.54, 126.50, 126.2, 125.8, 125.7, 124.7, 27.7, 22.19. ^{31}P NMR (162 MHz, $CDCl_3$) δ +17.1 (s), +16.5 (s). HRMS (ESI) calcd for $C_{26}H_{22}OP$ $[M+H]^+$ 381.1408, found 381.1404.

Compound **11** was prepared from **S13** following the reported literature.[3]

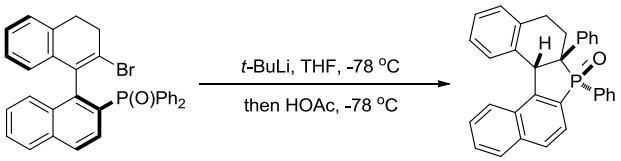


S13 **11**

Under N_2 a mixture of compound **S13** (76.1 mg, 0.20 mmol, 1.0 equiv) and AgOAc (66.8 mg, 0.40 mmol, 2.0 equiv) in 2 ml DMF under N_2 was stirred at 100 °C for 4 h. The mixture was cooled to room temperature and diluted with EtOAc. The organic layer was washed with brine for three times, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to give the desired product **11** (45.1 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, *J* = 8.8 Hz, 2H), 8.05 (dd, *J* = 14.2, 7.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.72 (dd, *J* = 12.4, 7.4 Hz, 2H), 7.68-7.59 (m, 2H), 7.53-7.49 (m, 1H), 7.48-7.42 (m, 1H), 7.41-7.36 (t, *J* = 7.1 Hz, 2H), 7.31 (s, 3H), 3.04-2.68 (m, 3H), 2.28-2.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3 (d, *J* = 5.3 Hz), 139.8 (d, *J* = 2.2 Hz), 134.5, 133.6 (d, *J* = 7.1 Hz), 133.4 (d, *J* = 2.6 Hz), 133.1 (d, *J* = 12.3 Hz), 132.9 (d, *J* = 8.4 Hz), 131.5, 131.5, 131.4, 130.5 (d, *J* = 1.7 Hz), 130.4, 129.6 (d, *J* = 6.2 Hz), 129.0 (d, *J* = 99.3 Hz), 128.8, 128.42, 128.37 (s), 128.30, 127.7, 127.4, 127.2, 126.4 (d, *J* = 101.5 Hz), 126.0 (d, *J* = 12.9 Hz), 125.7 (d, *J* = 14.2 Hz), 28.4 (d, *J* = 5.6 Hz), 23.5 (d, *J* = 8.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ +9.7 (s). HRMS (ESI) calcd for $C_{26}H_{20}OP$ $[M+H]^+$ 379.1252, found 379.1247.

Control experiments

a) "Chirality Transfer" Reaction

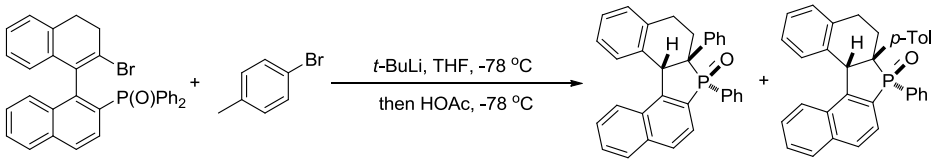


R-8a, 87%ee **9a**, 72%, 55%ee

The "Chirality Transfer" reaction was conducted following the **Typical Procedure B.**

The reaction of phosphine oxides **R-8a** [(53.5 mg, 0.10 mmol, 1.0 equiv), $[\alpha]_D^{20}$ -35.05 (c 0.95, CH_2Cl_2). HPLC conditions: Chiralpak IA, isopropanol/hexane = 18:82, flow: 0.8 mL/min, λ = 254 nm] with *t*-BuLi (1.3 M in hexane, 0.30 ml, 4.0 equiv) afforded **9a** (33.6 mg, 72%, 55% ee). $[\alpha]_D^{20}$ + 42.82 (c 1.00, CH_2Cl_2). HPLC conditions: Chiralpak IA, isopropanol/hexane = 18:82, flow: 0.8 mL/min, λ = 294 nm.

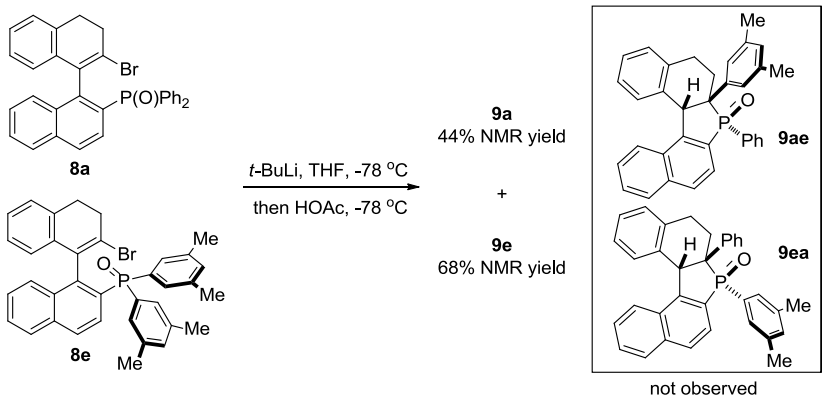
b) Crossover Studies



8a **9a**, 86% NMR yield **9ab**, not observed

The above reaction was conducted following the **Typical Procedure B.**

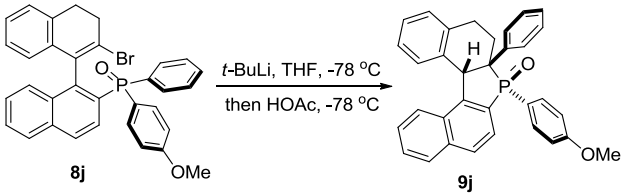
The phosphine oxides **8a** (53.5 mg, 0.10 mmol, 1.0 equiv) and 4-bromotoluene (12.3 μl, 0.1 mmol, 1.0 equiv) was dissolved in THF (3 ml) and cooled to -78 °C under N_2. A solution of *t*-BuLi (1.3 M in hexane, 0.60 ml, 8.0 equiv) was added dropwise at -78 °C and stirred for 10 min at the same temperature. The reaction was quenched by the addition of 1 ml HOAc. The mixture was allowed to warm to room temperature and extracted with EtOAc. The combined organic layer was washed with brine, and dried over Na_2SO_4. After evaporation, the residue was analysed by crude ^{1}H NMR using CH_2Br_2 as internal standard.



The above reaction was conducted following the **Typical Procedure B**.

The phosphine oxides **8a** (26.8 mg, 0.050 mmol, 1.0 equiv) and **8e** (29.6 mg, 0.050 mmol, 1.0 equiv) was dissolved in THF (3 ml) and cooled to -78 °C under N_2. A solution of *t*-BuLi (1.3 M in hexane, 0.30 ml, 0.39 mmol) was added and stirred for 10 min at the same temperature. The reaction was quenched by the addition of HOAc (1 ml). The mixture was allowed to warm to room temperature and extracted with EtOAc. The combined organic layer was washed with brine, and dried over Na_2SO_4. After evaporation, the residue was analysed by crude ^{1}H NMR using CH_2Br_2 as internal standard.

c) Studies on Unsymmetric Phosphine Oxide

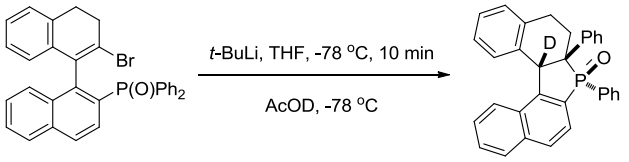


The compound **9j** was prepared following the **Typical Procedure B.**

The reaction of phosphine oxides **8j** (56.5 mg, 0.10 mmol) afforded **9j** (32.6 mg, 65%), and the structure was confirmed by single crystal X-ray analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.00 (dd, *J* = 8.2, 3.0 Hz, 1H), 7.76-7.64 (m, 3H), 7.46-7.39 (m, 2H), 7.29-7.23 (m, 3H), 7.22-7.14 (m, 3H), 7.10-7.03 (m, 2H), 7.00-6.94 (m, 1H), 6.67-6.56 (m, 3H), 5.43 (d, *J* = 20.8 Hz, 1H),

3.71 (s, 3H), 2.87 (dd, *J* = 13.6, 2.4 Hz, 1H), 2.69-2.54 (m, 2H), 1.87-1.72 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 2.8 Hz), 146.0 (d, *J* = 25.8 Hz), 136.7, 135.7 (d, *J* = 2.0 Hz), 134.0 (d, *J* = 11.6 Hz), 130.7 (d, *J* = 12.5 Hz), 130.0 (d, *J* = 10.2 Hz), 129.7 (d, *J* = 99.3 Hz), 129.5 (d, *J* = 4.0 Hz), 128.20, 128.18, 127.6, 127.4, 126.9, 126.8, 126.5, 125.7, 125.64, 125.55, 125.3, 122.1 (d, *J* = 100.3 Hz), 113.6 (d, *J* = 13.0 Hz), 55.1, 54.2 (d, *J* = 64.3 Hz), 48.6 (d, *J* = 12.2 Hz), 32.9 (d, *J* = 3.1 Hz), 29.1 (d, *J* = 9.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ +58.9 (s). HRMS (ESI) calcd for $C_{33}H_{28}O_2P$ $[M+H]^+$ 487.1827, found 487.1833.

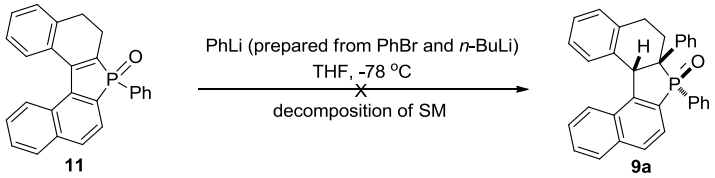
d) The reaction quenched with AcOD



8a **9a**-*d*, 70 %D

The reaction of phosphine oxides **8a** (53.8 mg, 0.10 mmol) afforded **9a**-*d* (33.1 mg, 72%, 70%D) following the **Typical Procedure B**, which was quenched with AcOD instead of AcOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 8.01 (dd, *J* = 8.0, 3.2 Hz, 1H), 7.78-7.73 (m, 1H), 7.73-7.65 (m, 2H), 7.47-7.42 (m, 2H), 7.31-7.27 (m, 3H), 7.26-7.23 (m, 2H), 7.22-7.17 (m, 1H), 7.14-7.08 (m, 2H), 7.07-7.04 (m, 1H), 7.03-7.00 (m, 1H), 6.96 (td, *J* = 7.4, 1.2 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.45 (d, *J* = 21.6 Hz, 0.3H), 2.88 (dd, *J* = 13.6, 2.0 Hz, 1H), 2.67-2.59 (m, 2H), 1.86-1.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (selected peaks) 146.1 (d, *J* = 25.7 Hz), 146.0 (d, *J* = 25.8 Hz), 140.77, 140.75, 139.59 (d, *J* = 5.1 Hz), 139.56 (d, *J* = 5.3 Hz), 136.53, 136.48, 135.7 (d, *J* = 2.0 Hz), 132.1 (d, *J* = 10.3 Hz), 131.13 (d, *J* = 104.8 Hz), 131.5 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 1.7 Hz), 130.1 (d, *J* = 10.3 Hz), 129.17 (d, *J* = 100.0 Hz), 129.6 (d, *J* = 3.9 Hz), 129.20, 128.3, 128.21, 128.19, 128.0, 127.8, 127.7, 127.4, 127.3, 126.9 (d, *J* = 2.4 Hz), 126.7, 126.5, 125.64, 125.62, 125.5, 125.2, 54.2 (d, *J* = 63.7 Hz), 54.1 (d, *J* = 63.7 Hz), 48.5 (d, *J* = 12.4 Hz), 33.0 (d, *J* = 2.9 Hz), 29.0 (d, *J* = 9.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ +59.2 (s). HRMS (ESI) calcd for $C_{32}H_{25}DOP$ $[M+H]^+$ 458.1784, found 458.1790.

e) The reaction of **11** with PhLi



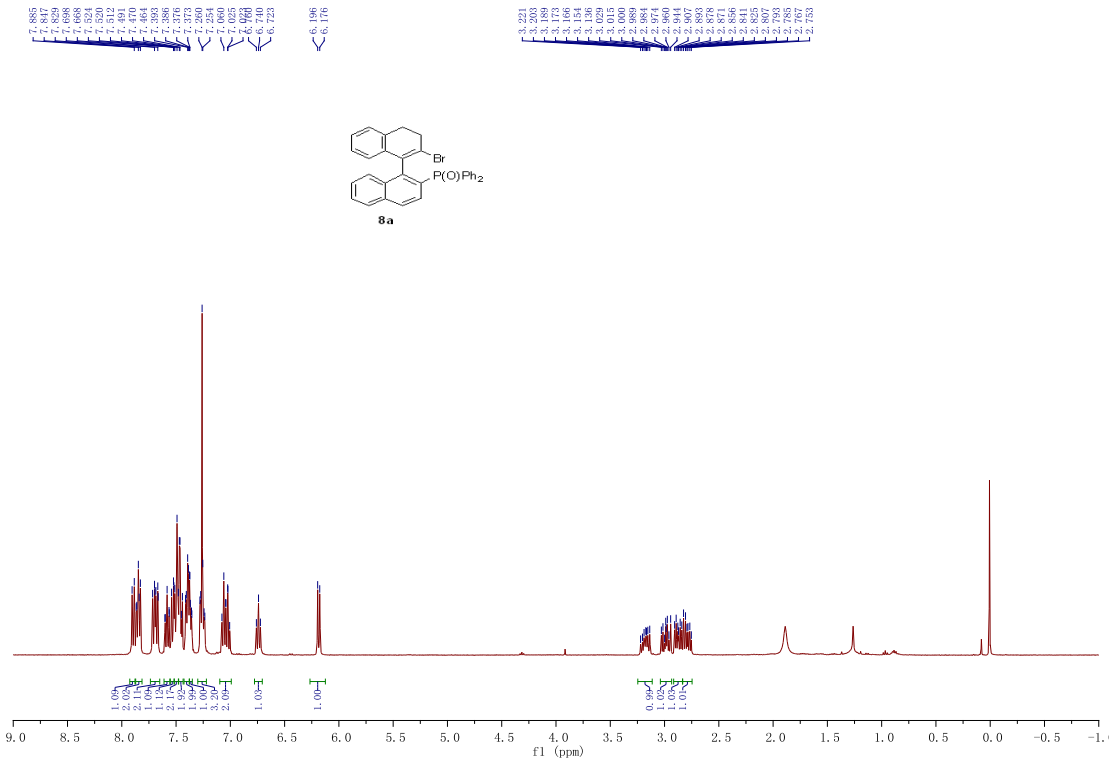
11 **9a**

The bromobenzene (42 µl, 0.4 mmol, 2.0 equiv) was dissolved in 2 ml THF and cooled to -78 °C under N_2. And then the solution was added *n*-BuLi (2.4 M in hexane, 0.17 ml, 2.0 equiv) and maintained at that temperature for 1 h. The phosphine oxides 8a (53.5 mg, 0.1 mmol, 1.0 equiv) in THF (2 ml) was added to the above mixture dropwise at -78 °C. The mixture was quenched by the addition of HOAc (1 ml), and analysed by TLC and ^{1}H NMR.

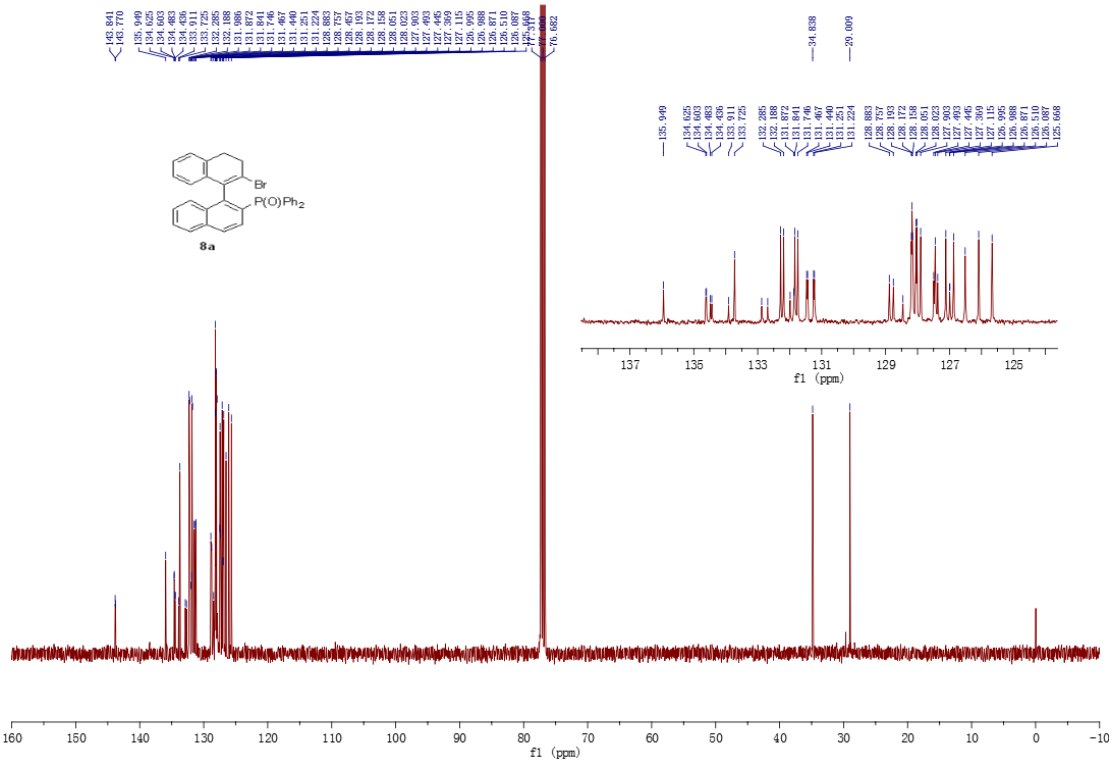
References

[1] C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, *Org. Lett.* **2005**, *7* (19), 4277.
[2] J. Feng, B. Li, Y. He, Z, Gu, *Angew. Chem. Int. Ed.* **2016**, *55*, 2186

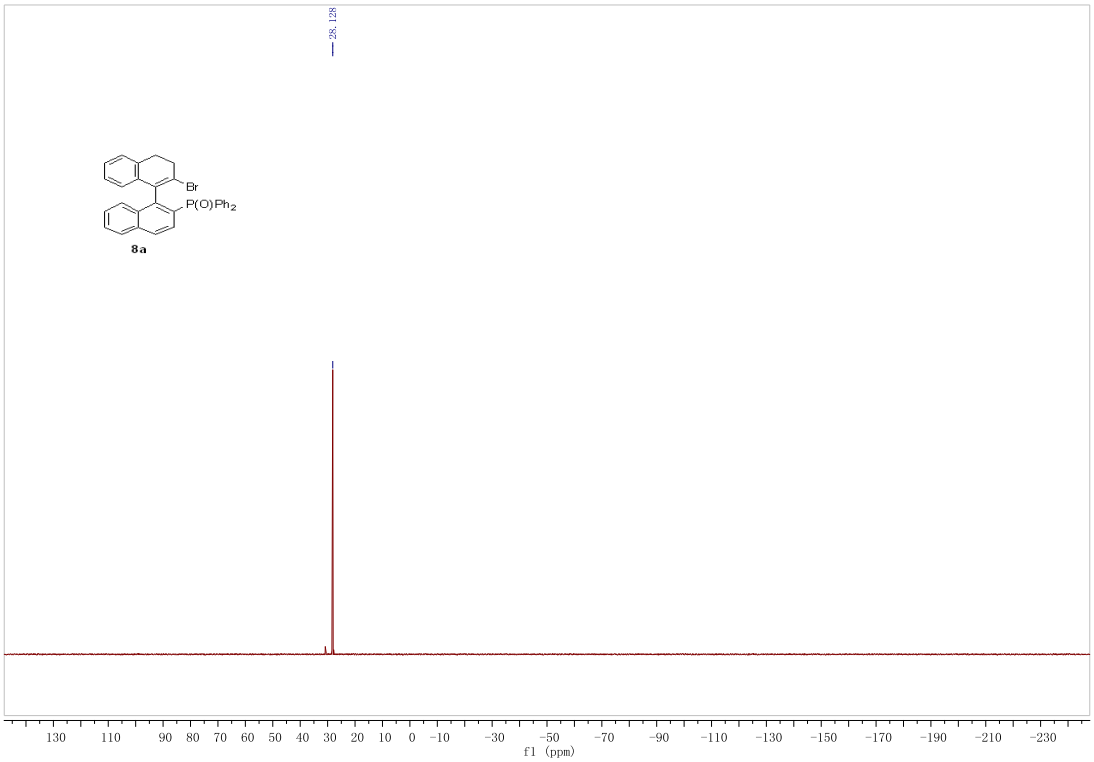
[3] Y. Unoh, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2013**, *52*, 12975



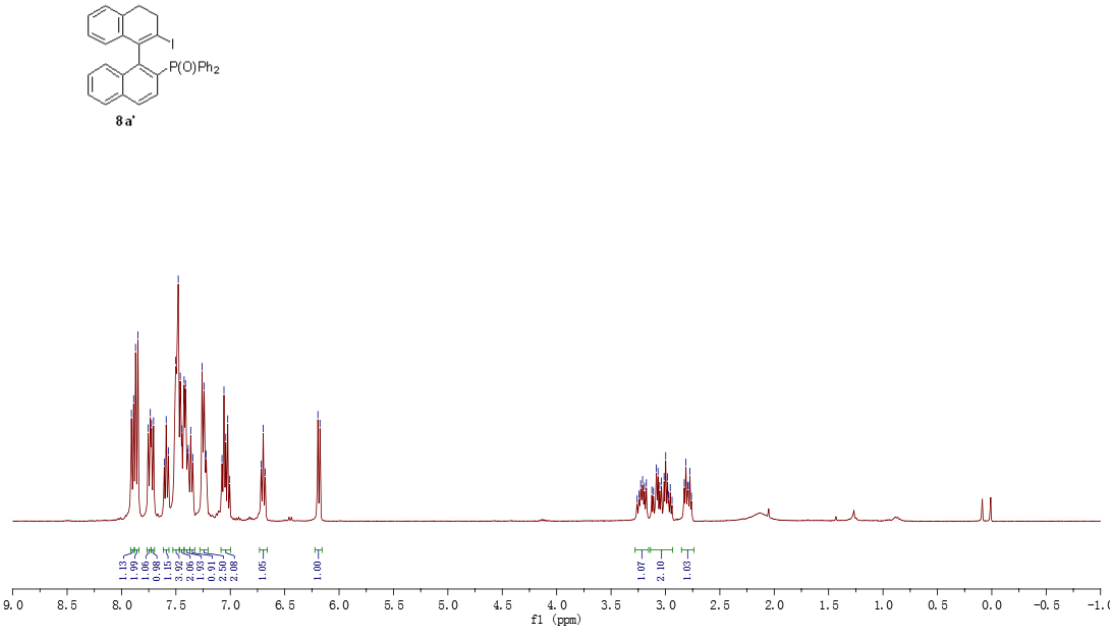
^{1}H NMR



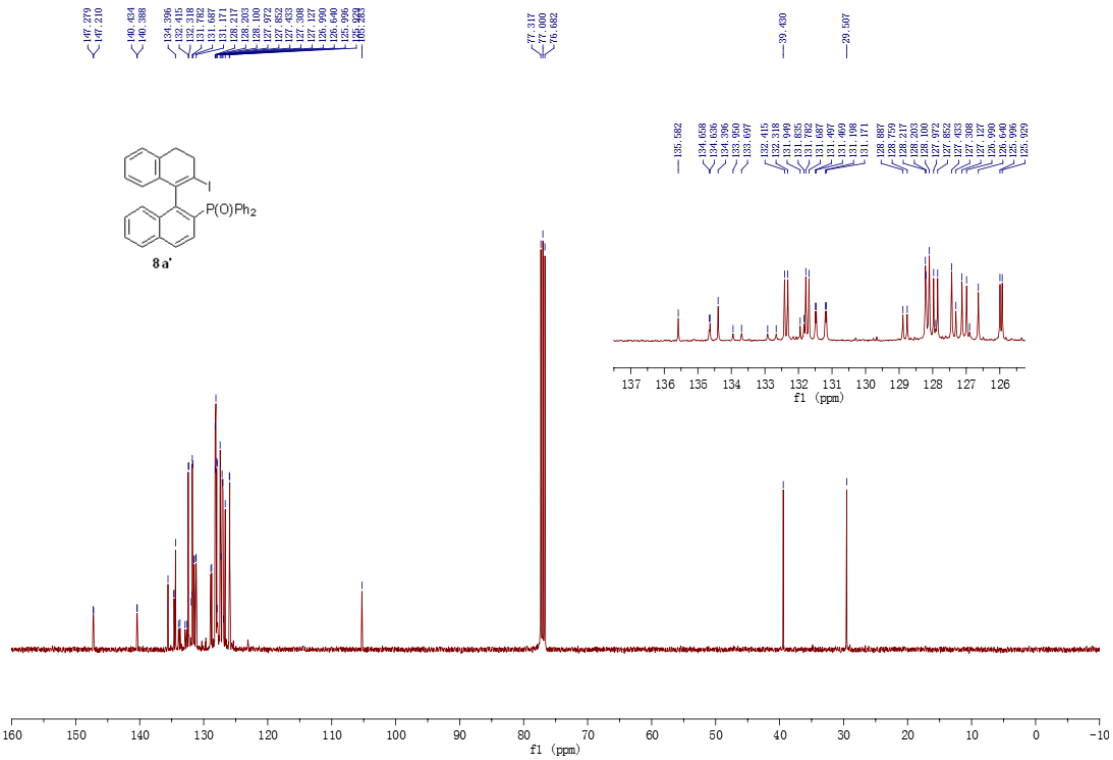
^{13}C NMR



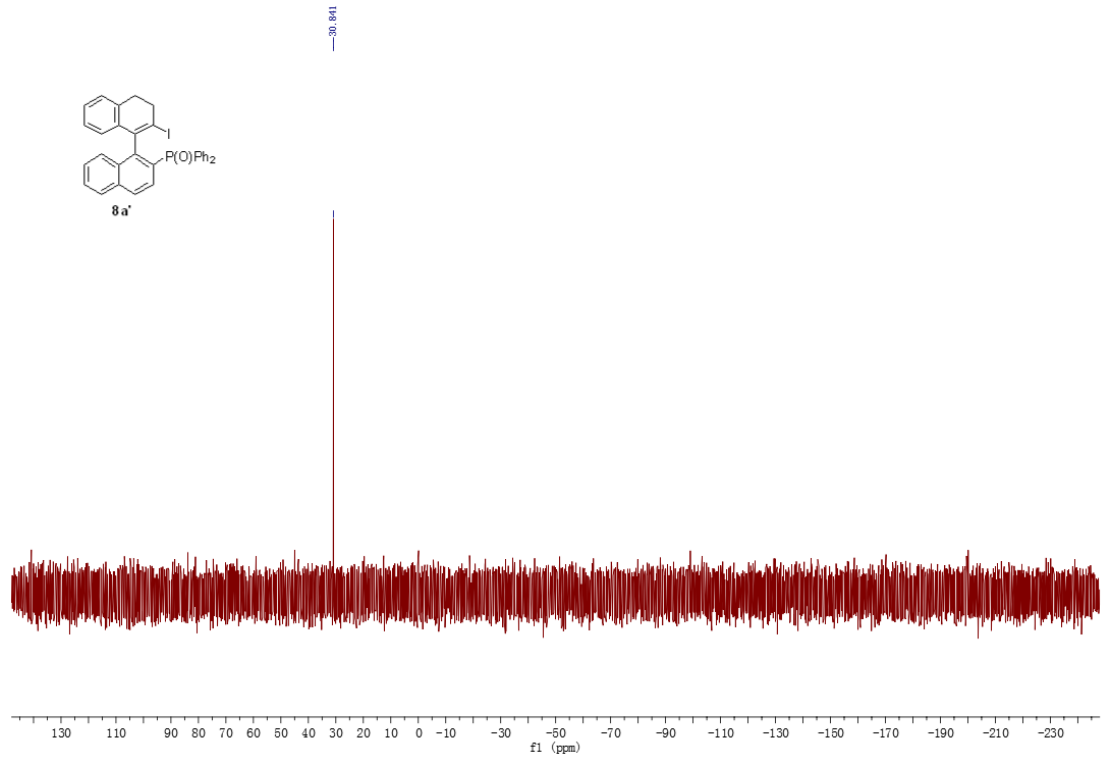
^{31}P NMR



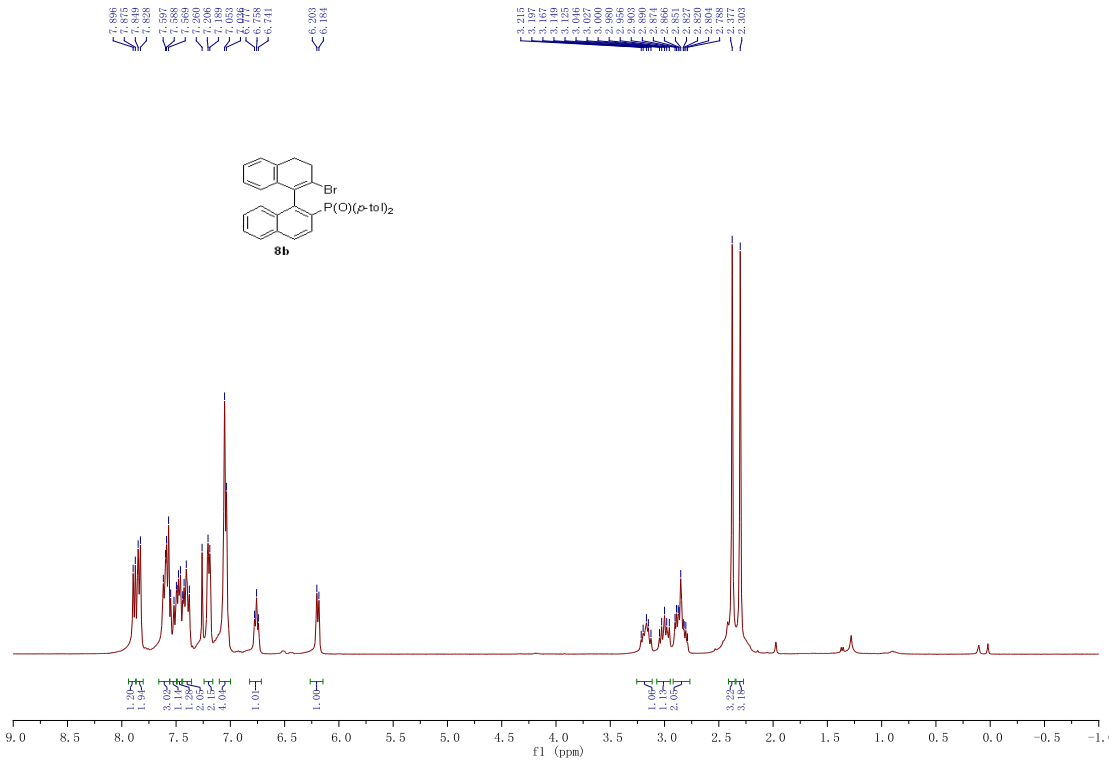
^{1}H NMR



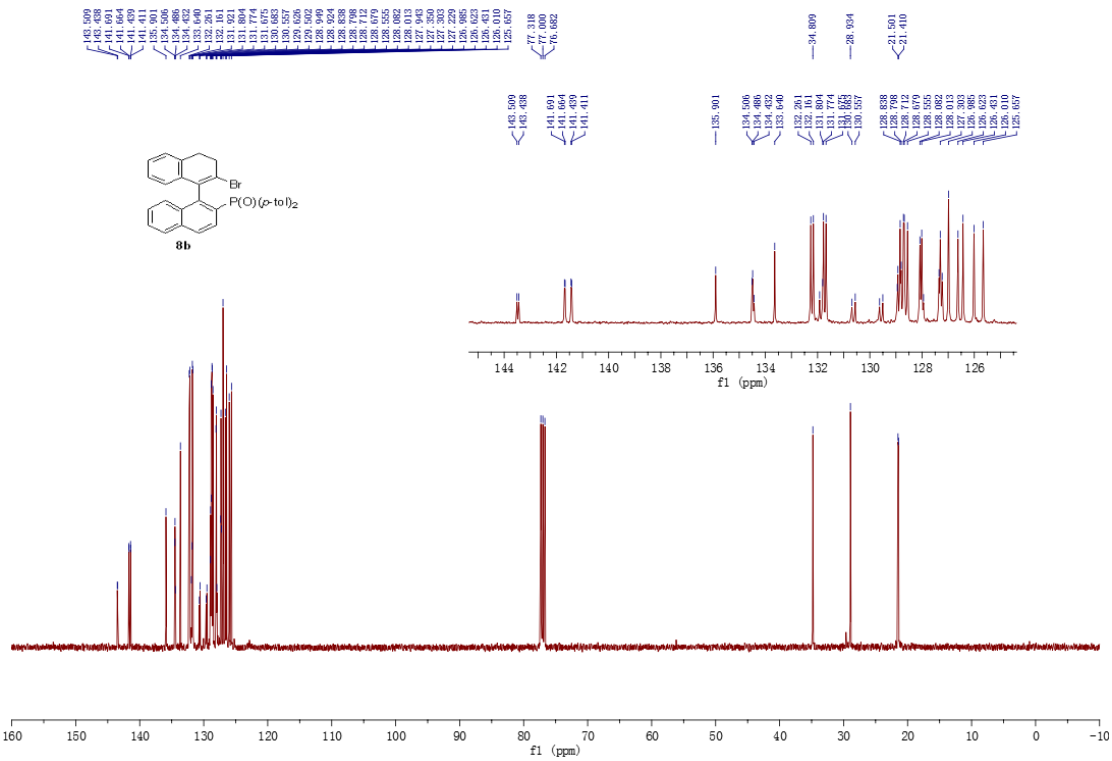
^{13}C NMR



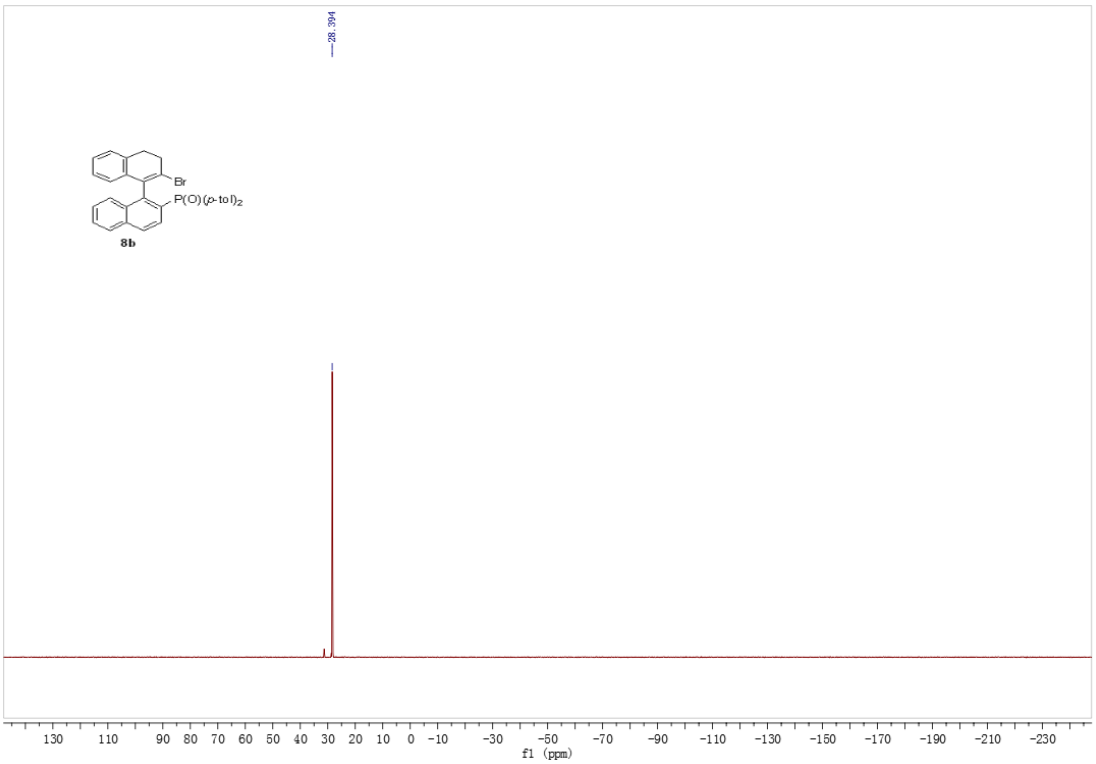
^{31}P NMR



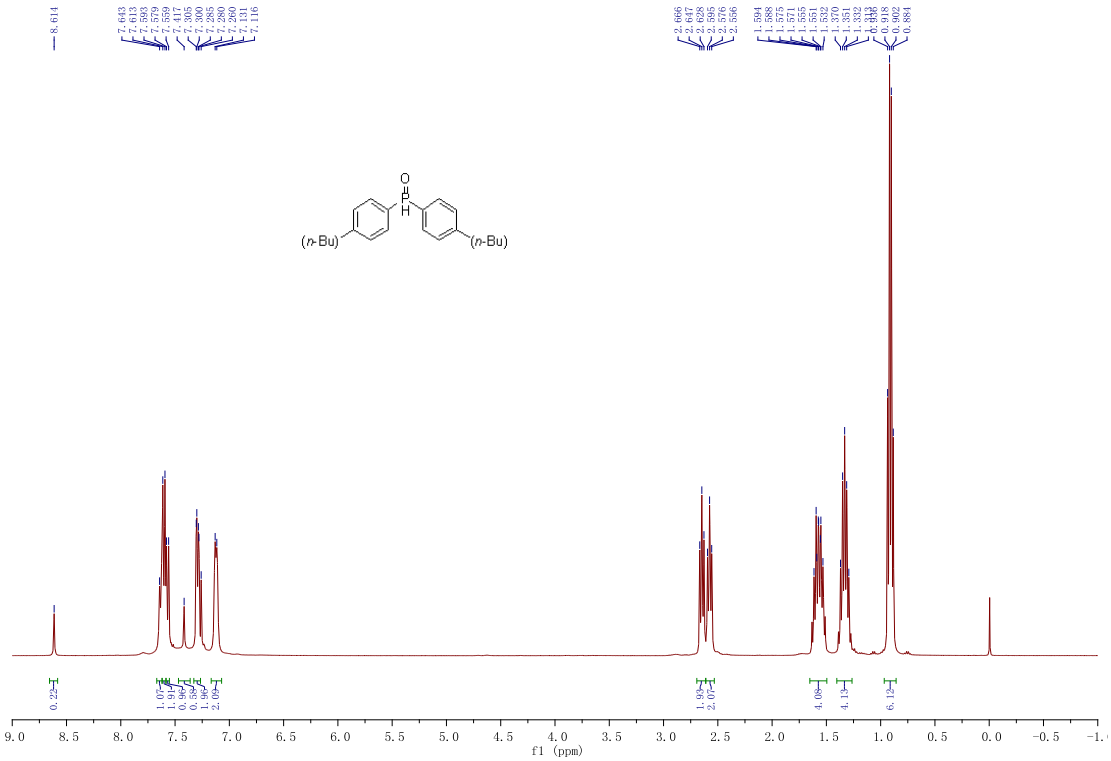
^{1}H NMR



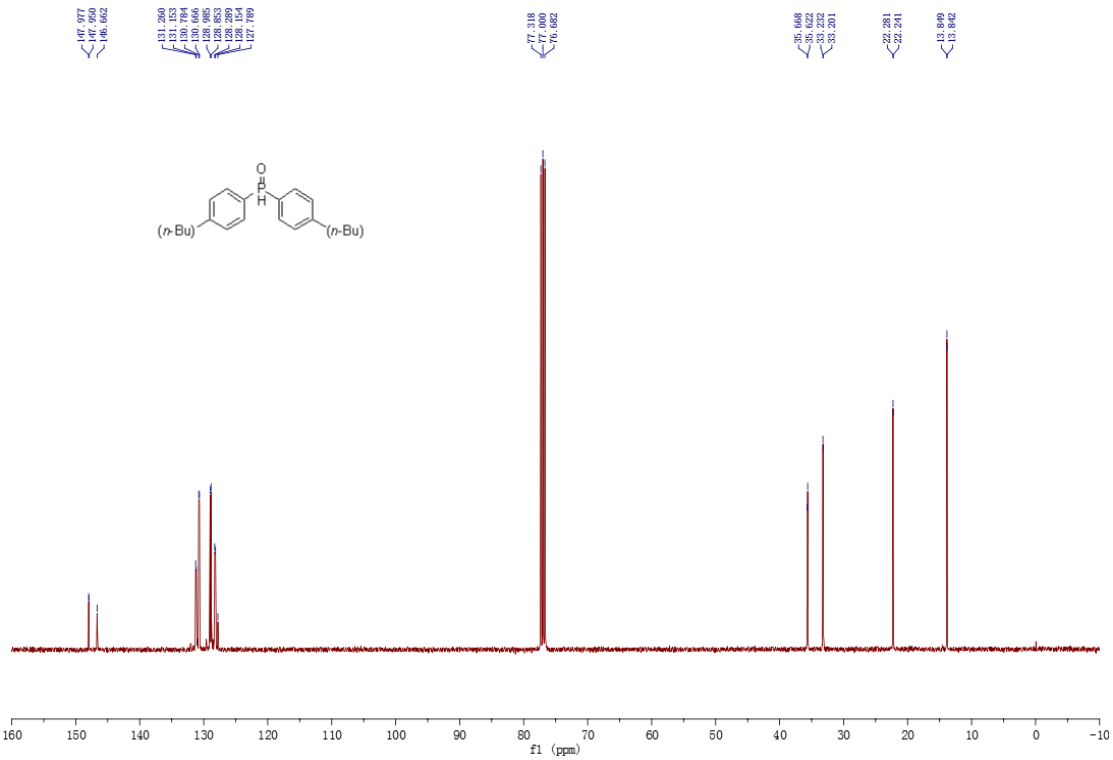
^{13}C NMR



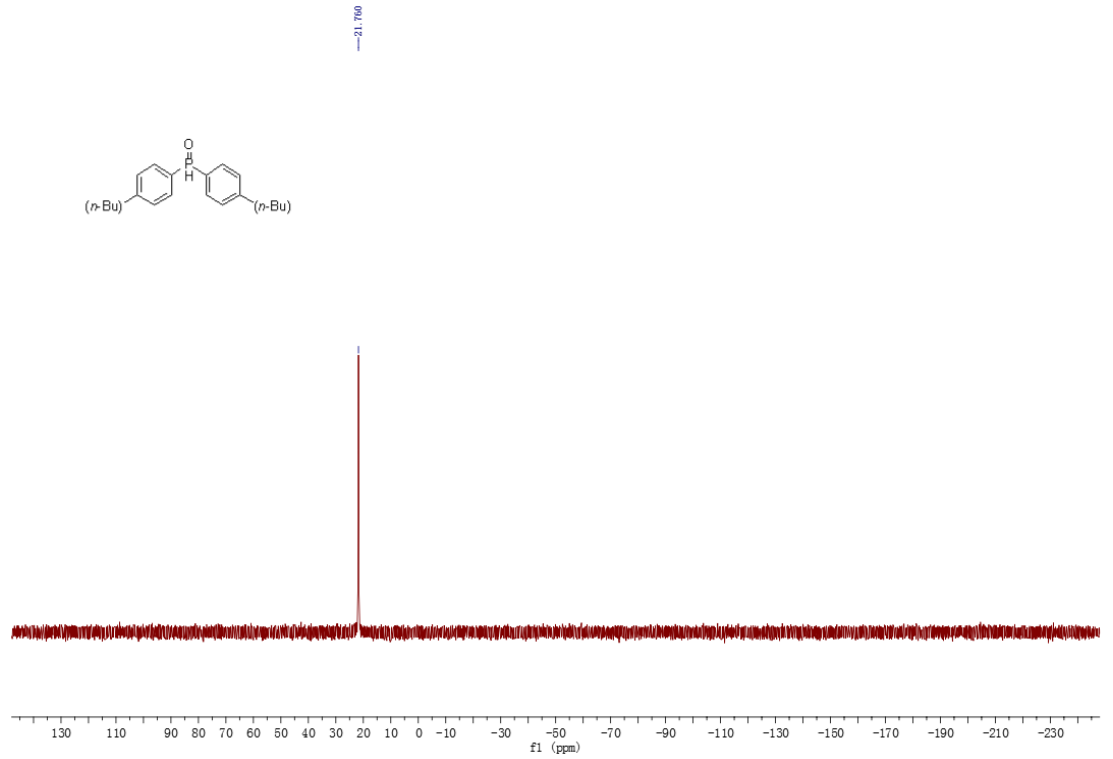
^{31}P NMR



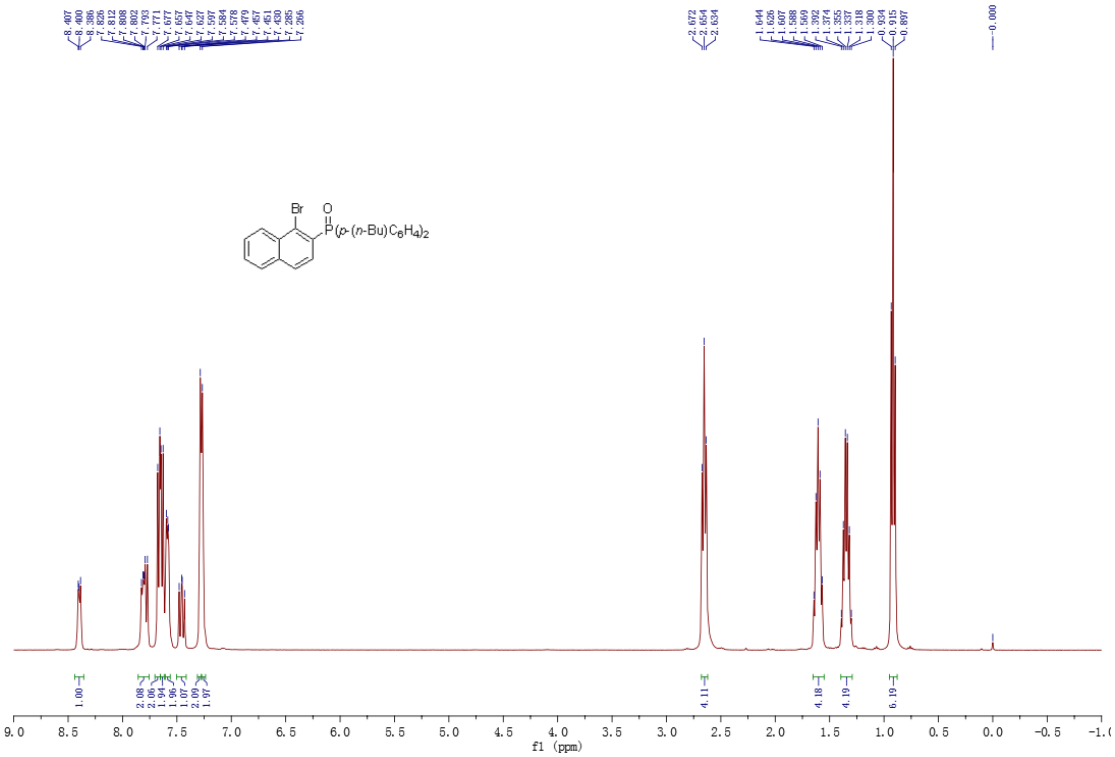
^{1}H NMR



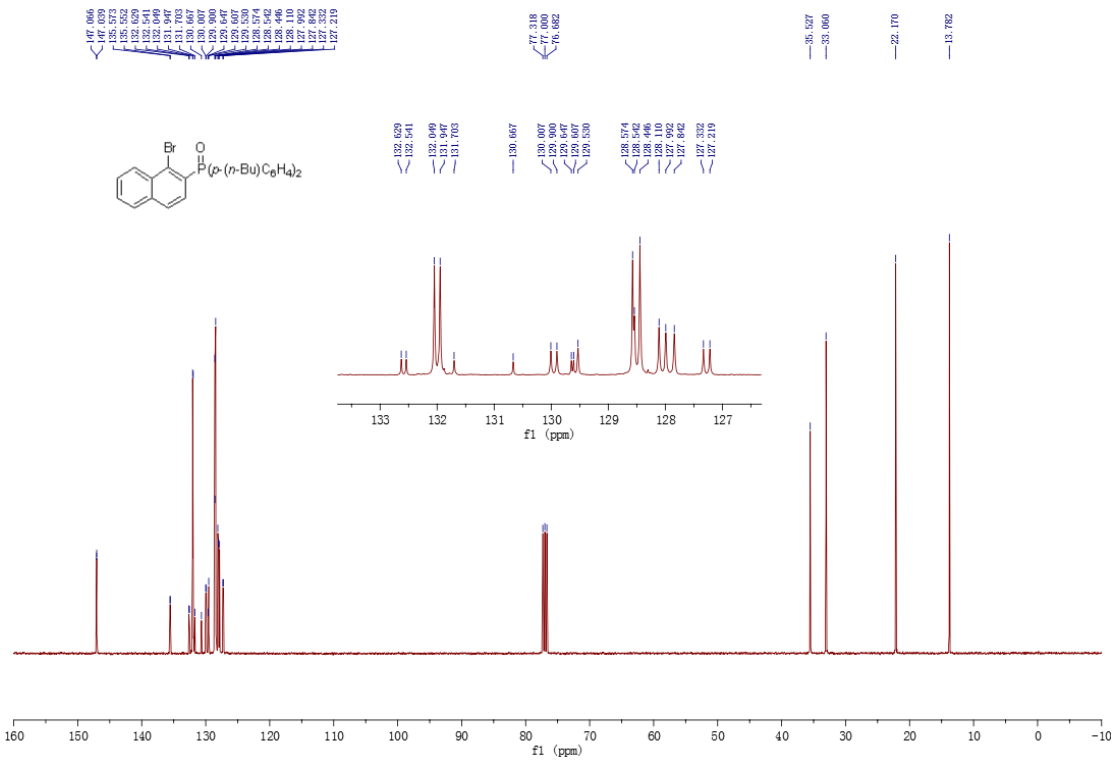
^{13}C NMR



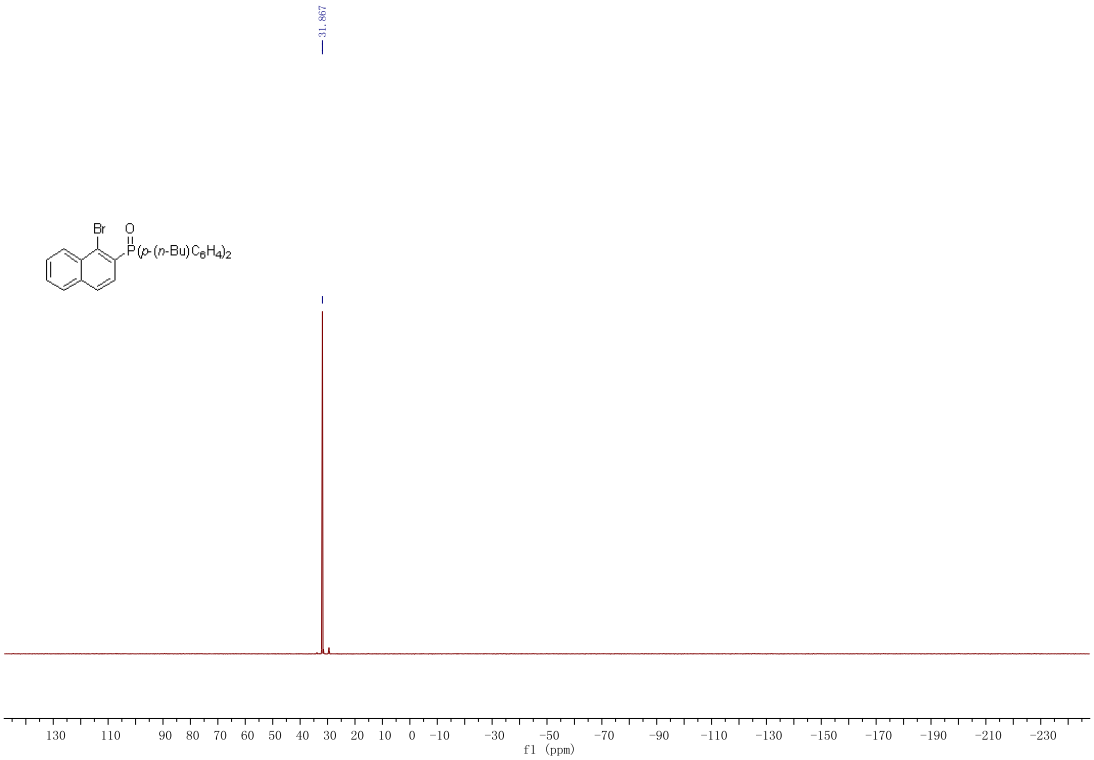
^{31}P NMR



^{1}H NMR



^{13}C NMR



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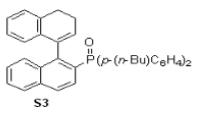

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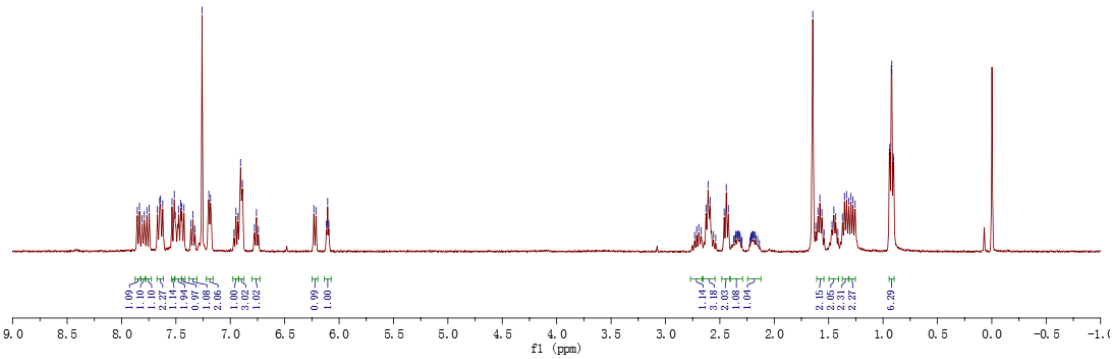

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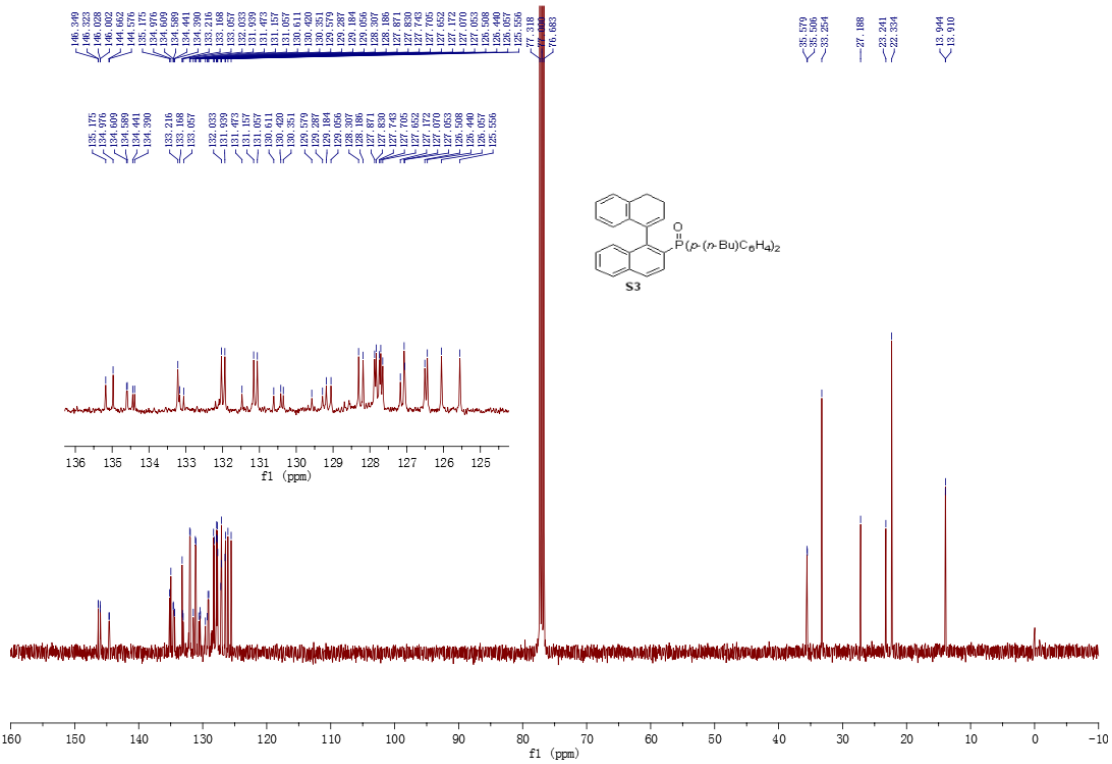

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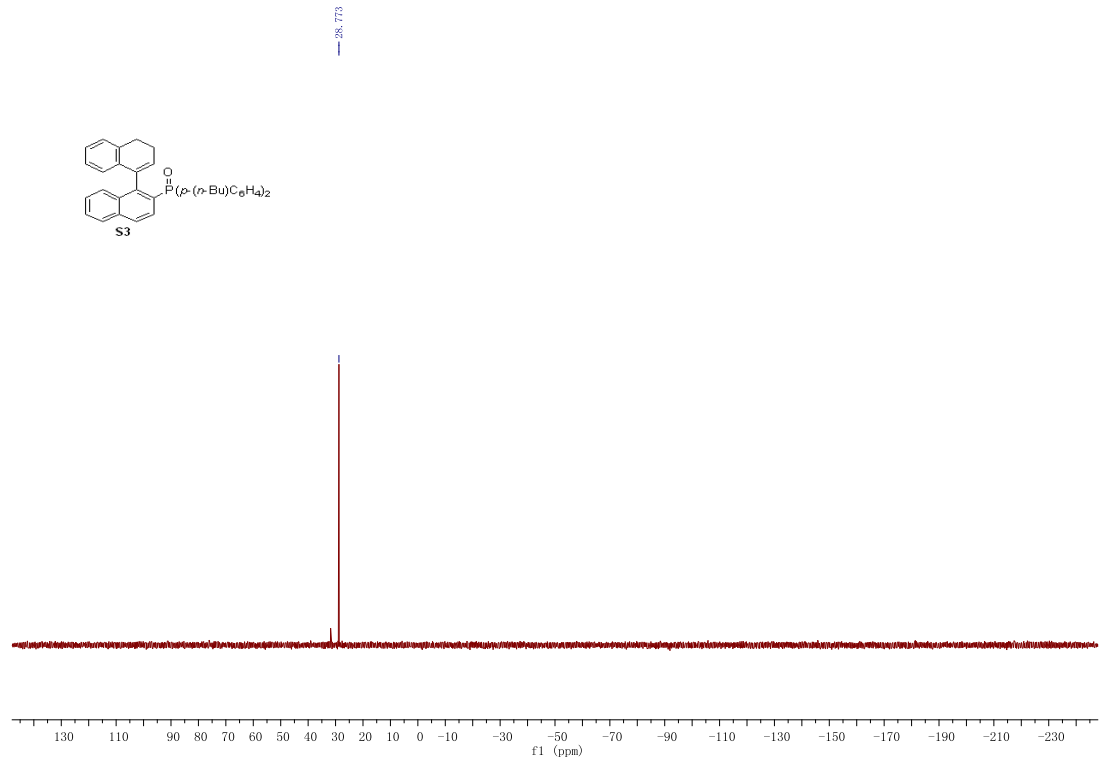

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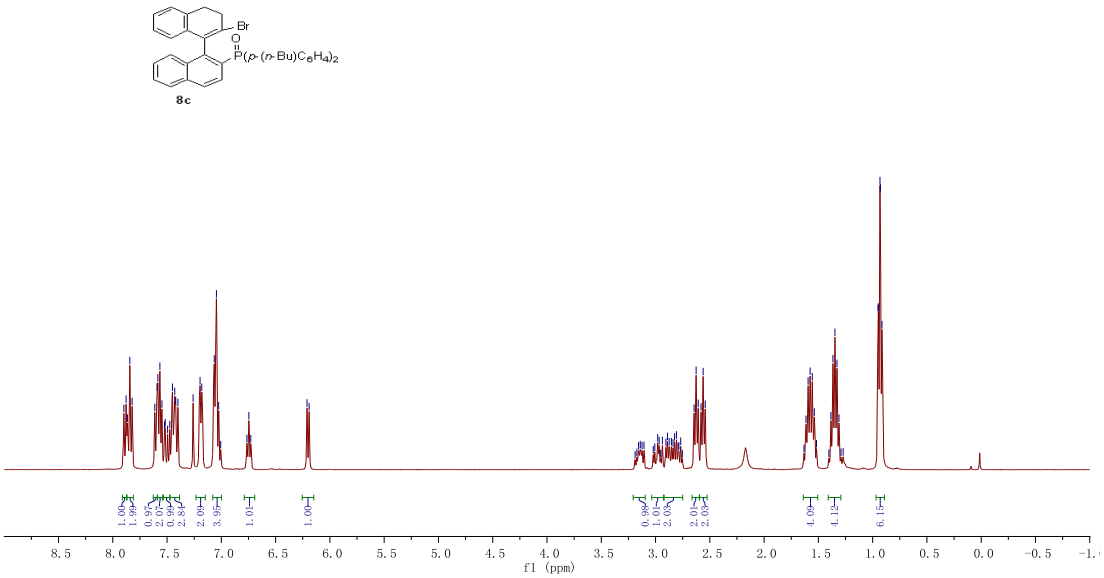

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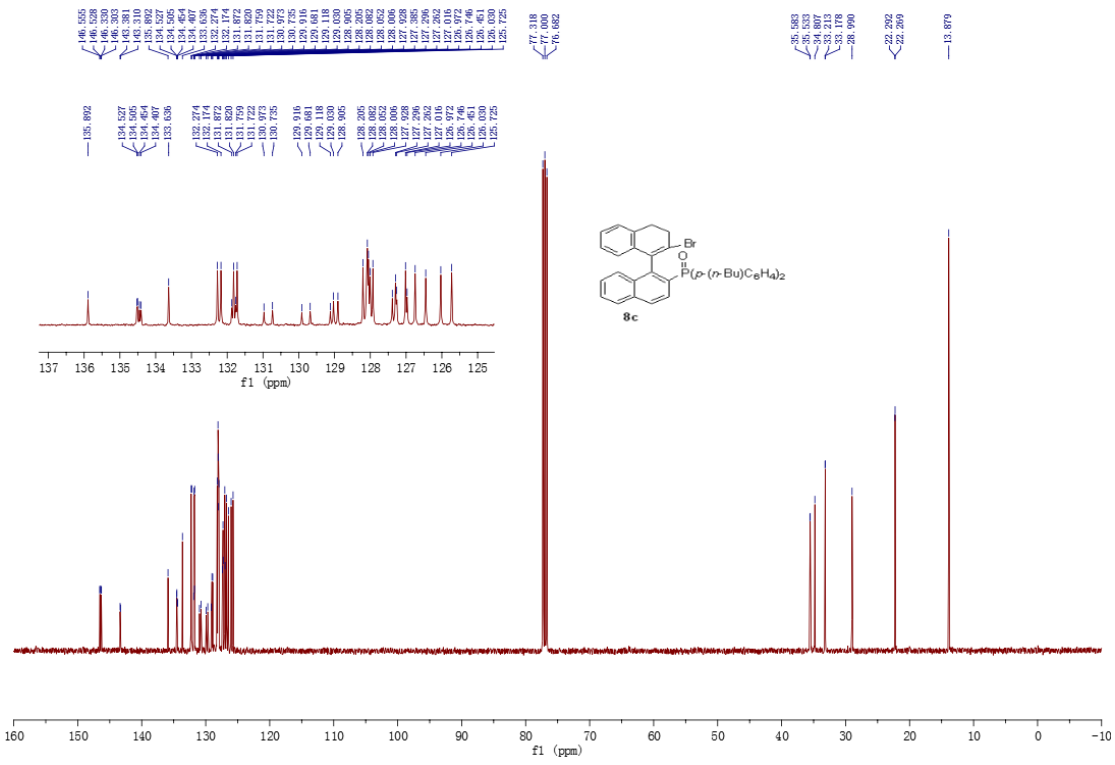

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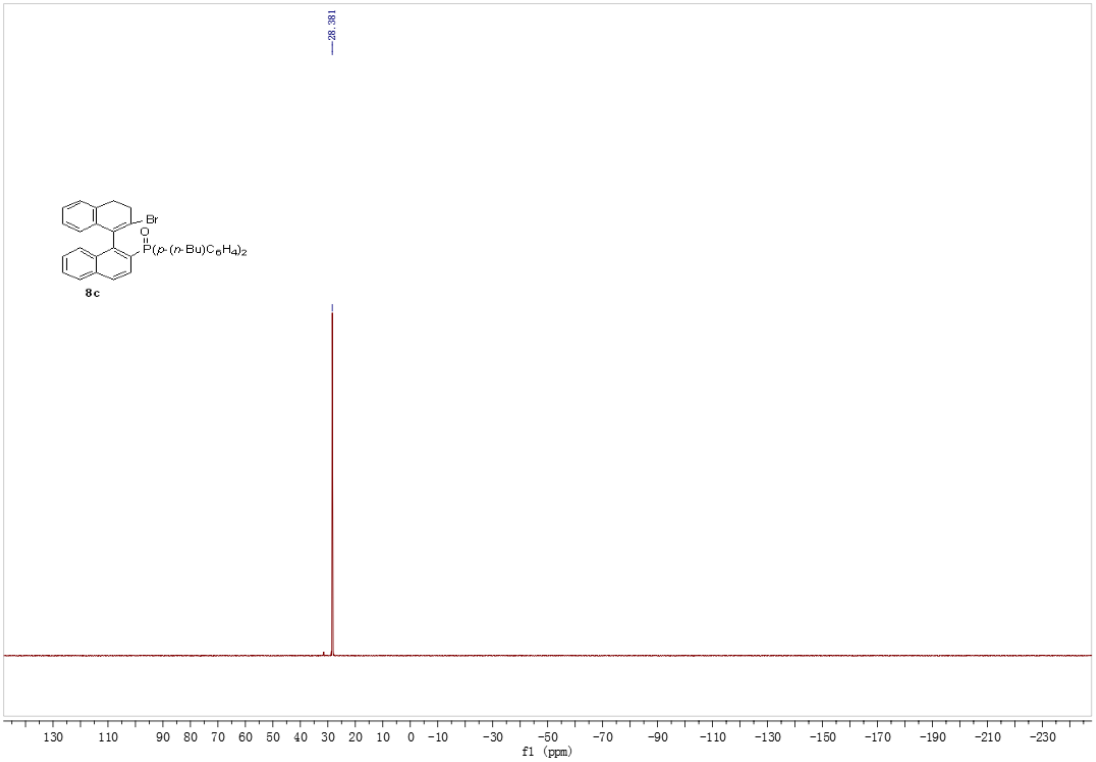

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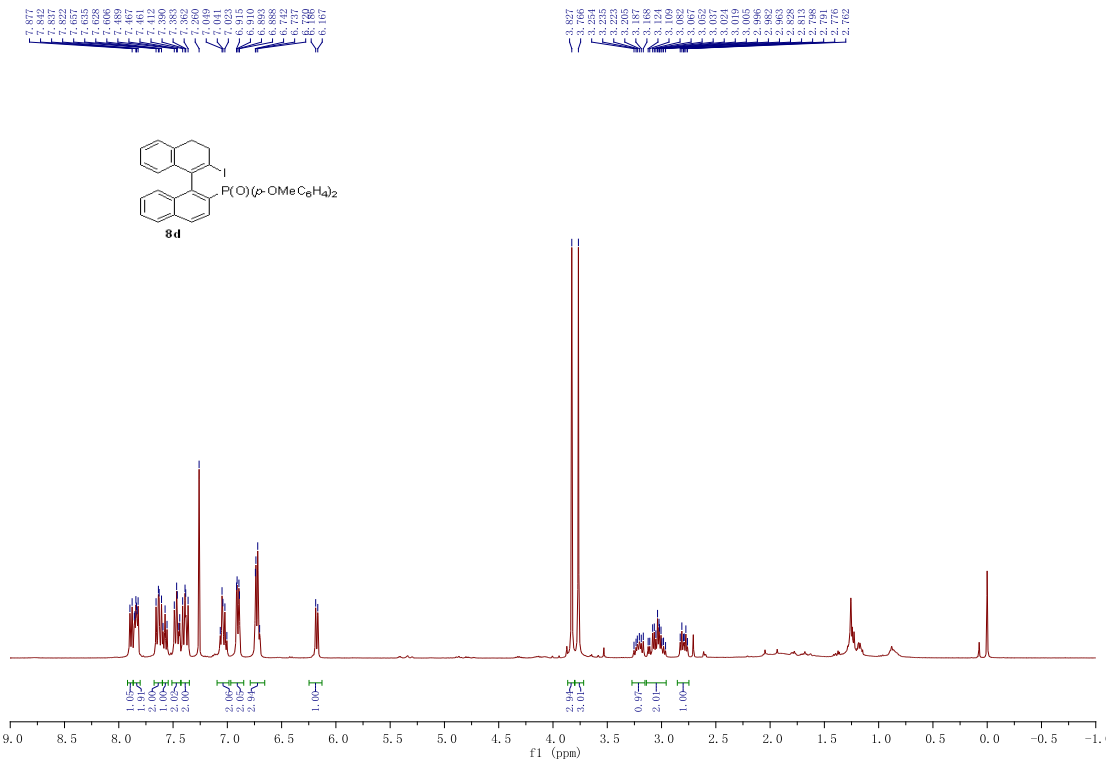

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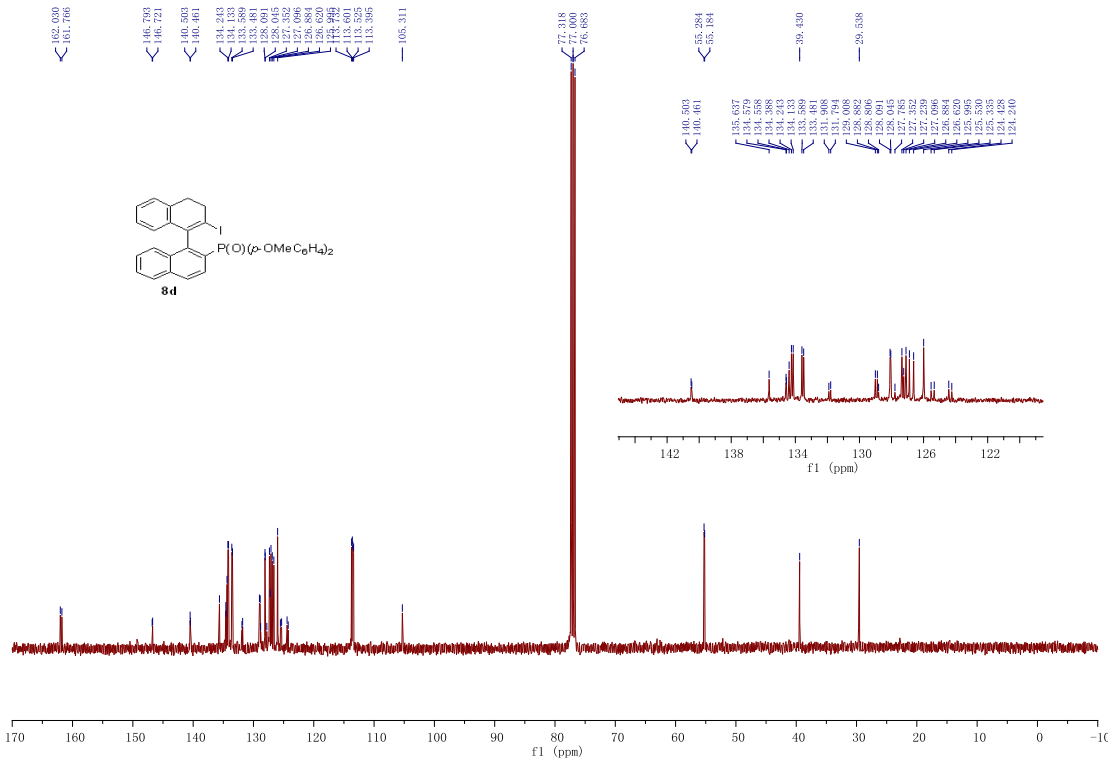

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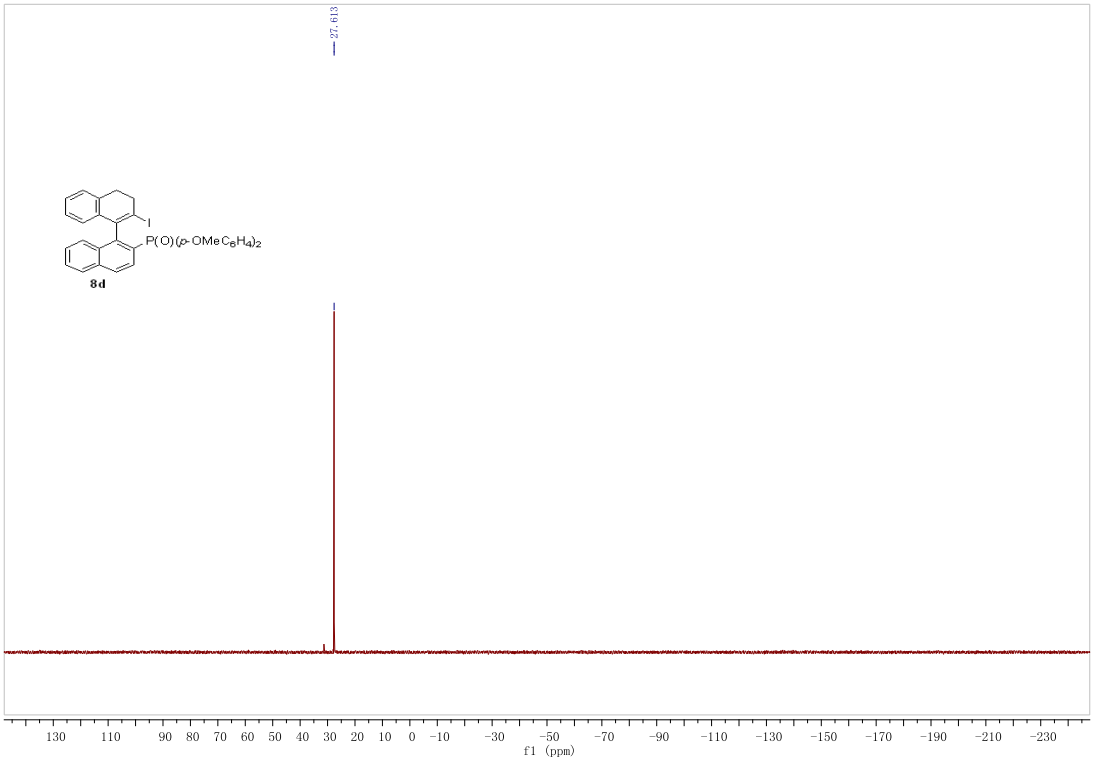

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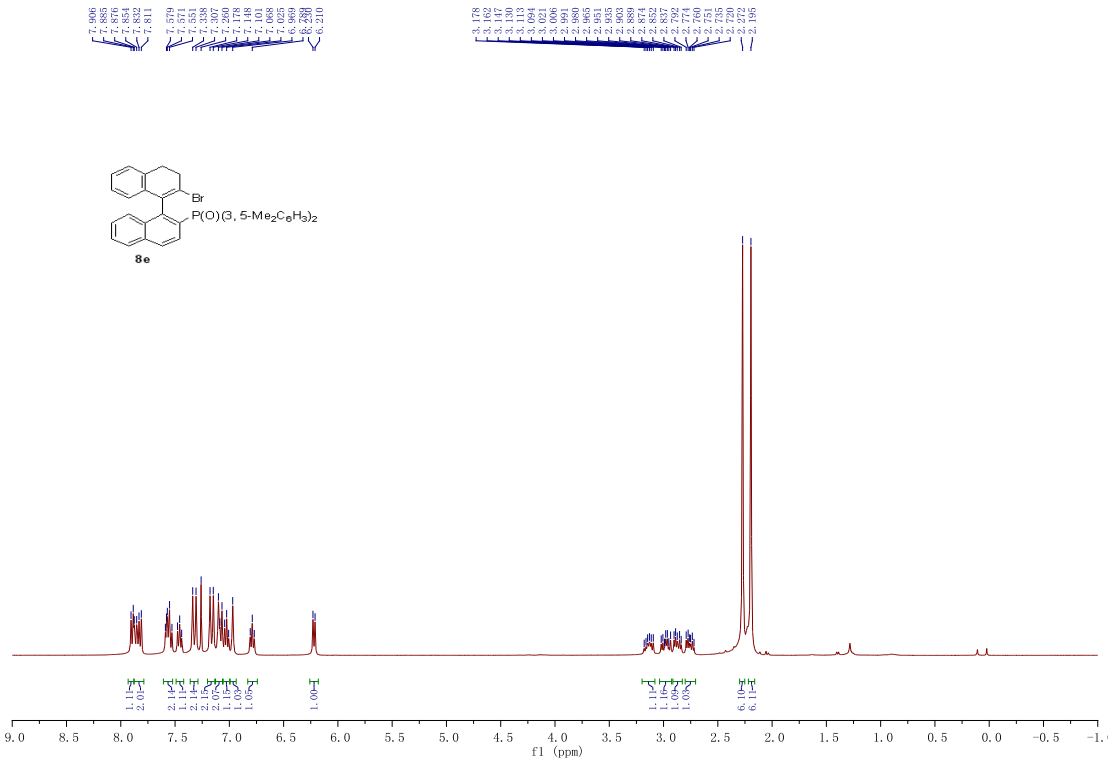

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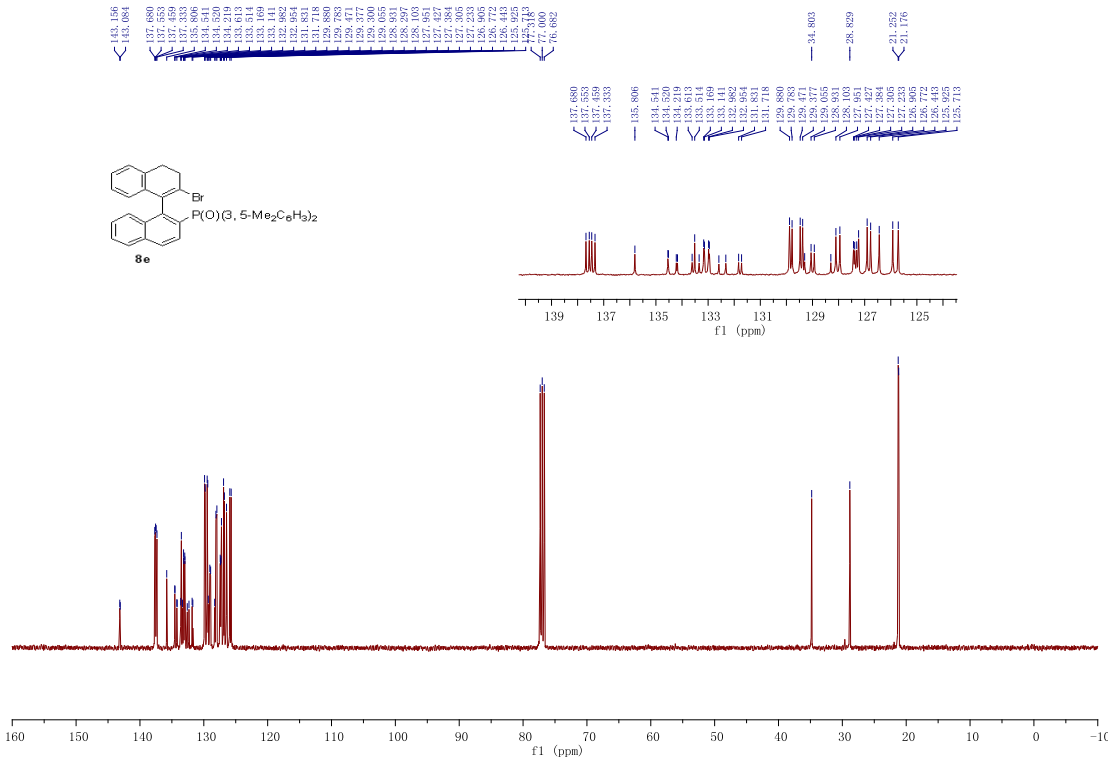

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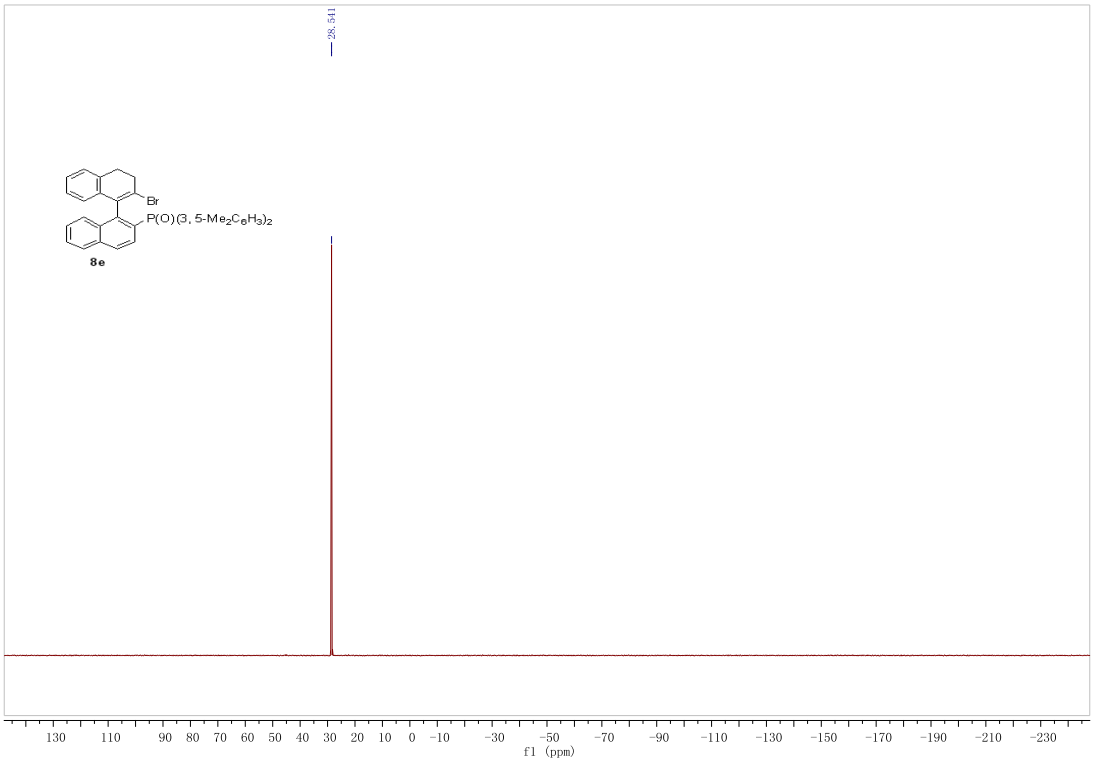

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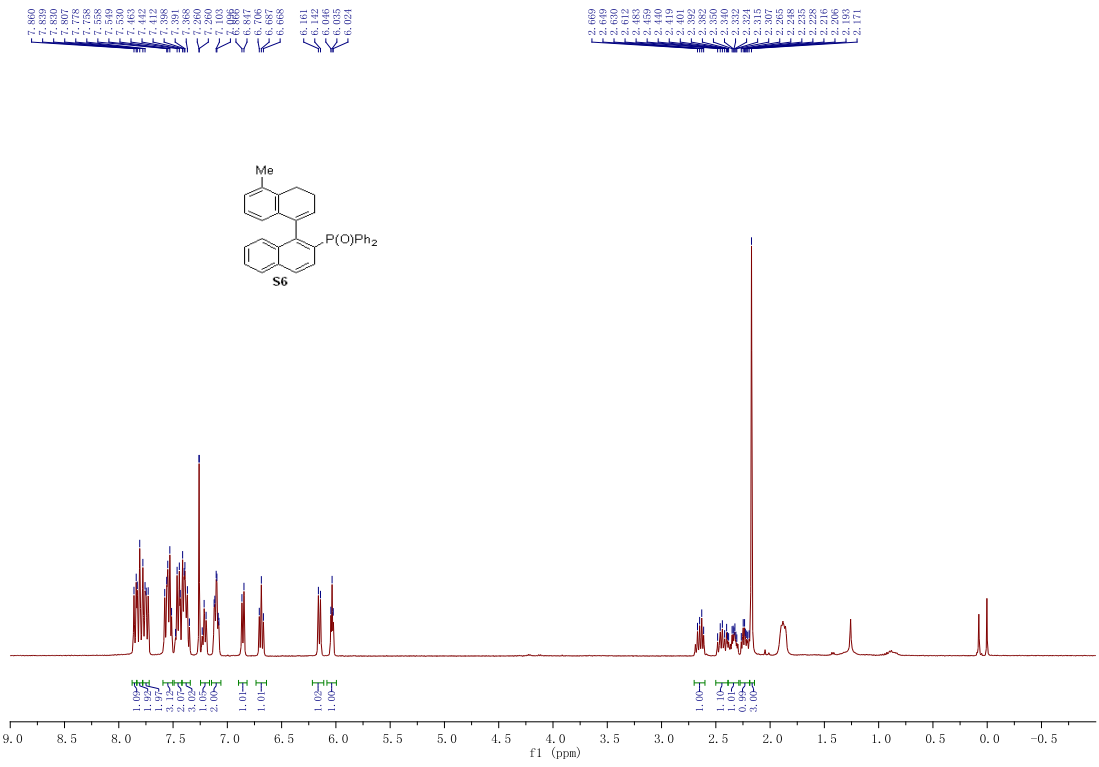

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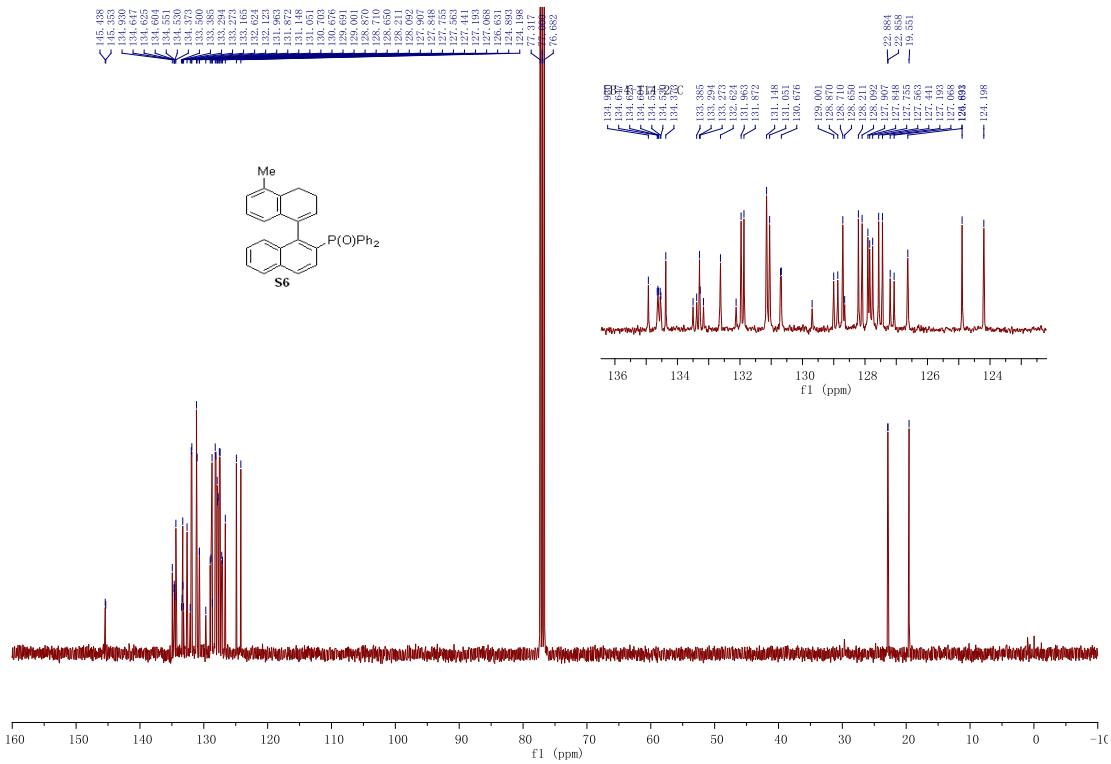

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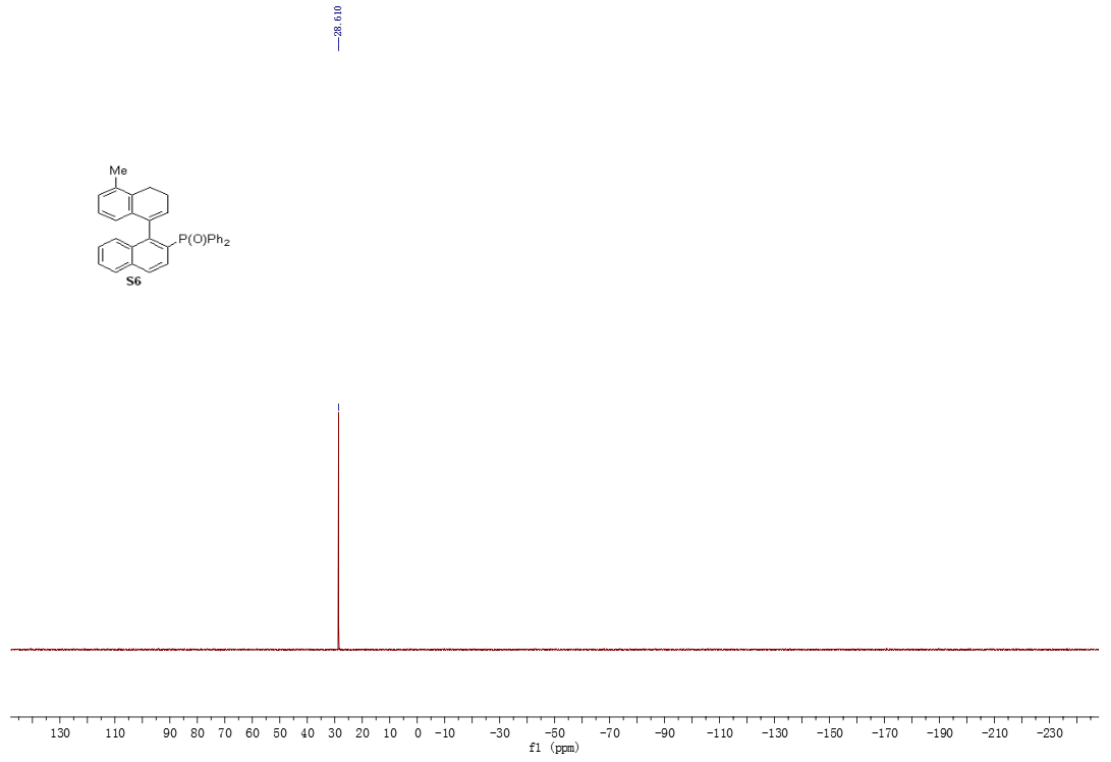

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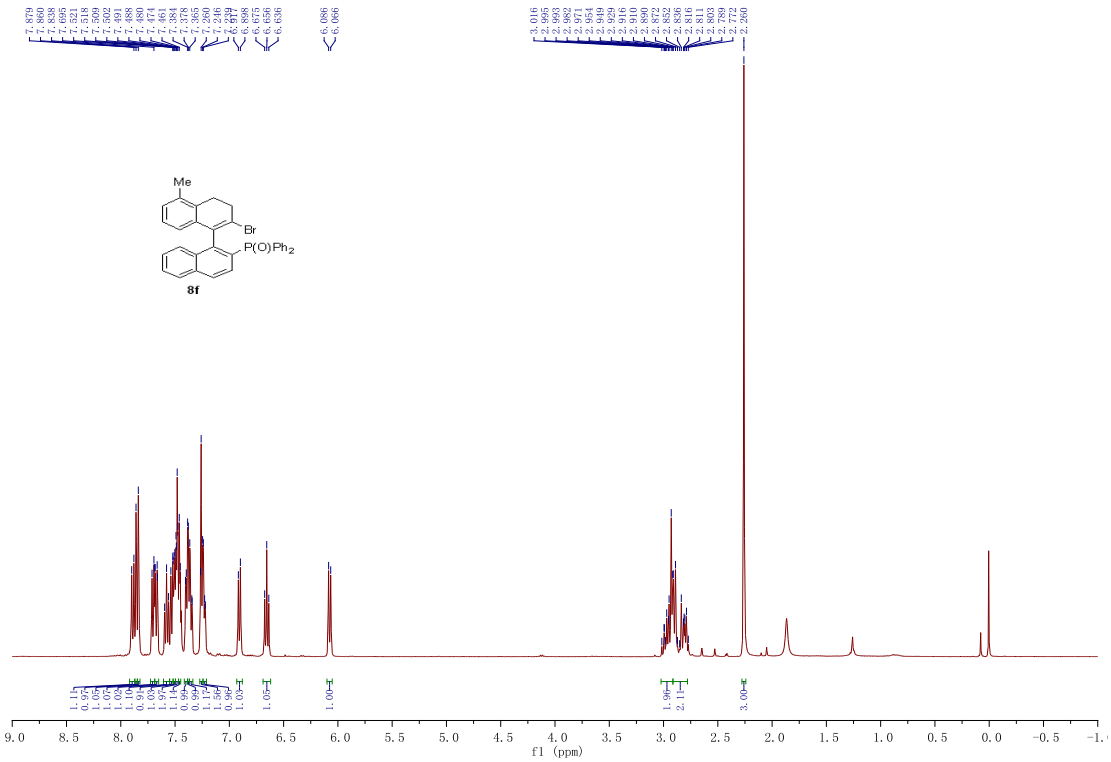

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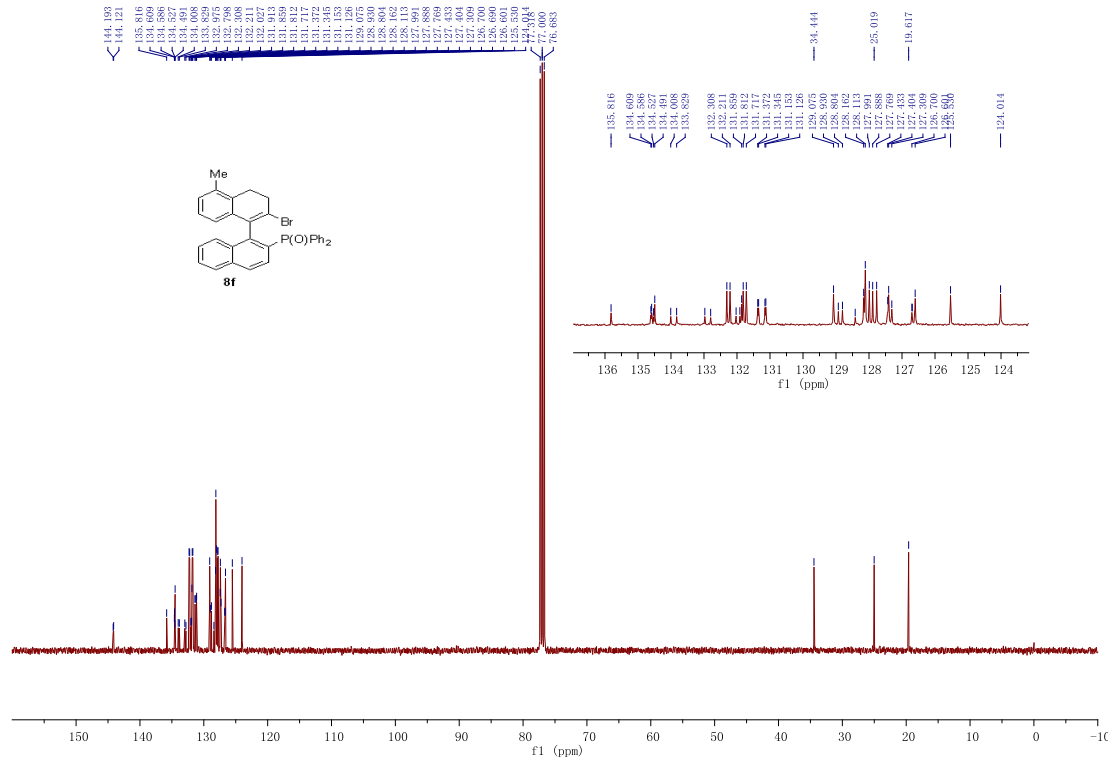

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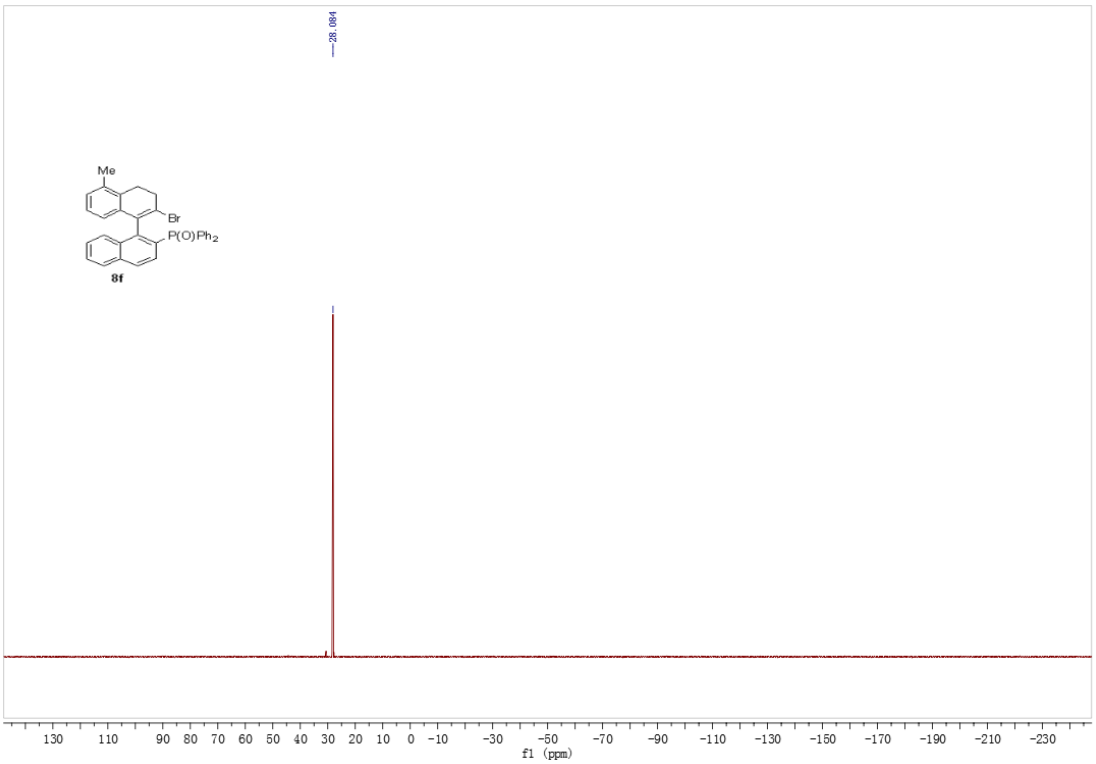

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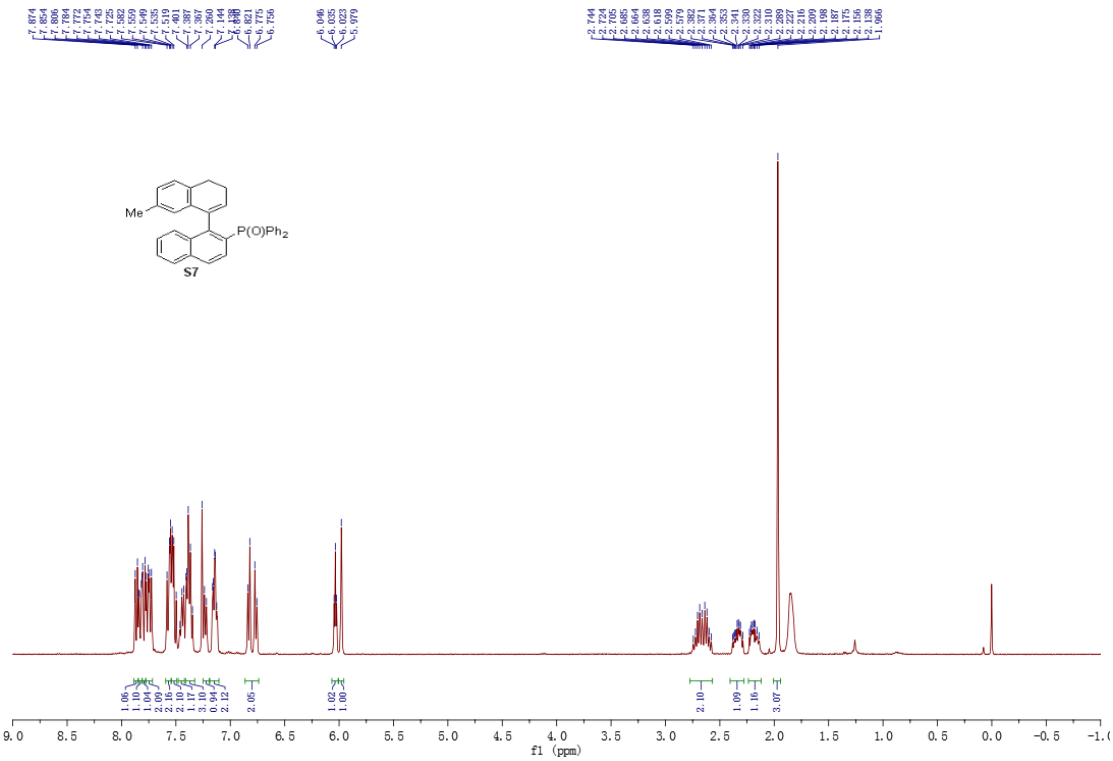

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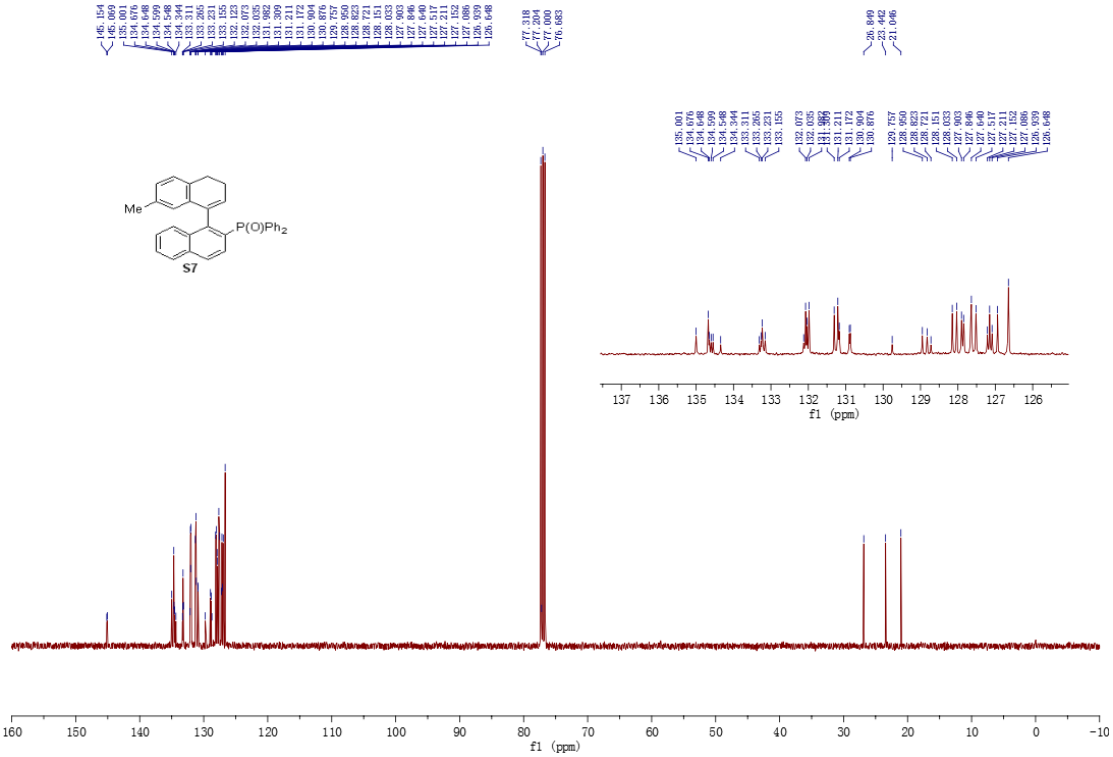

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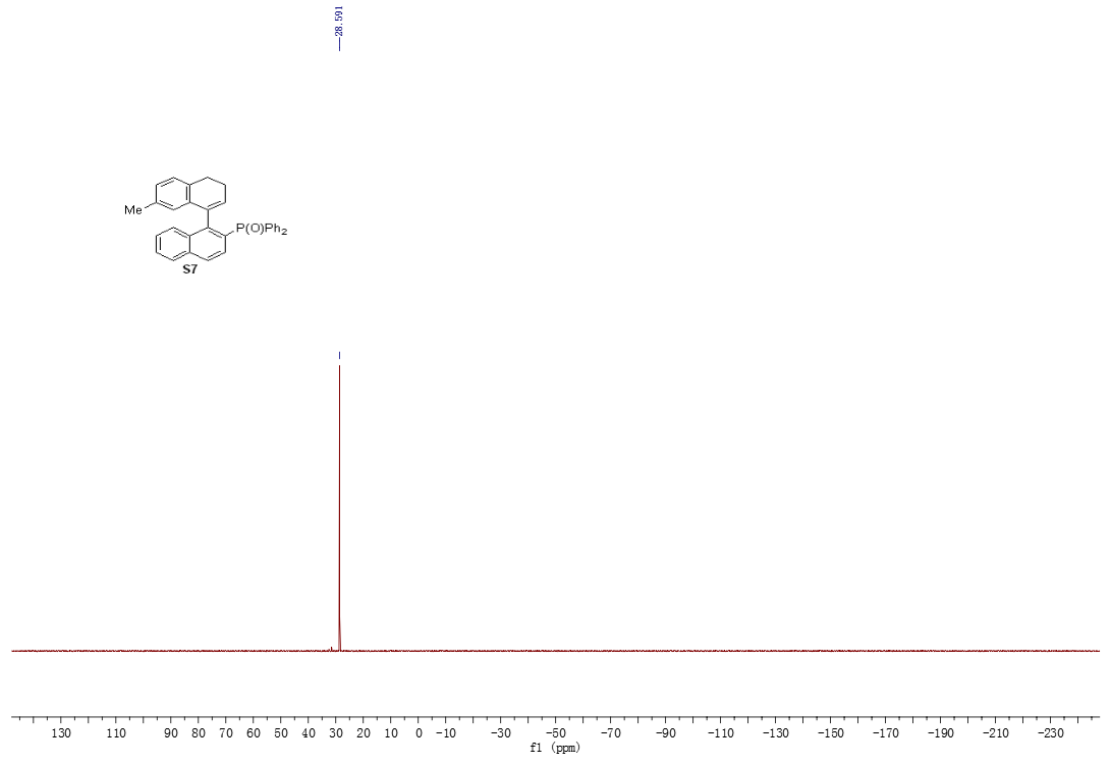

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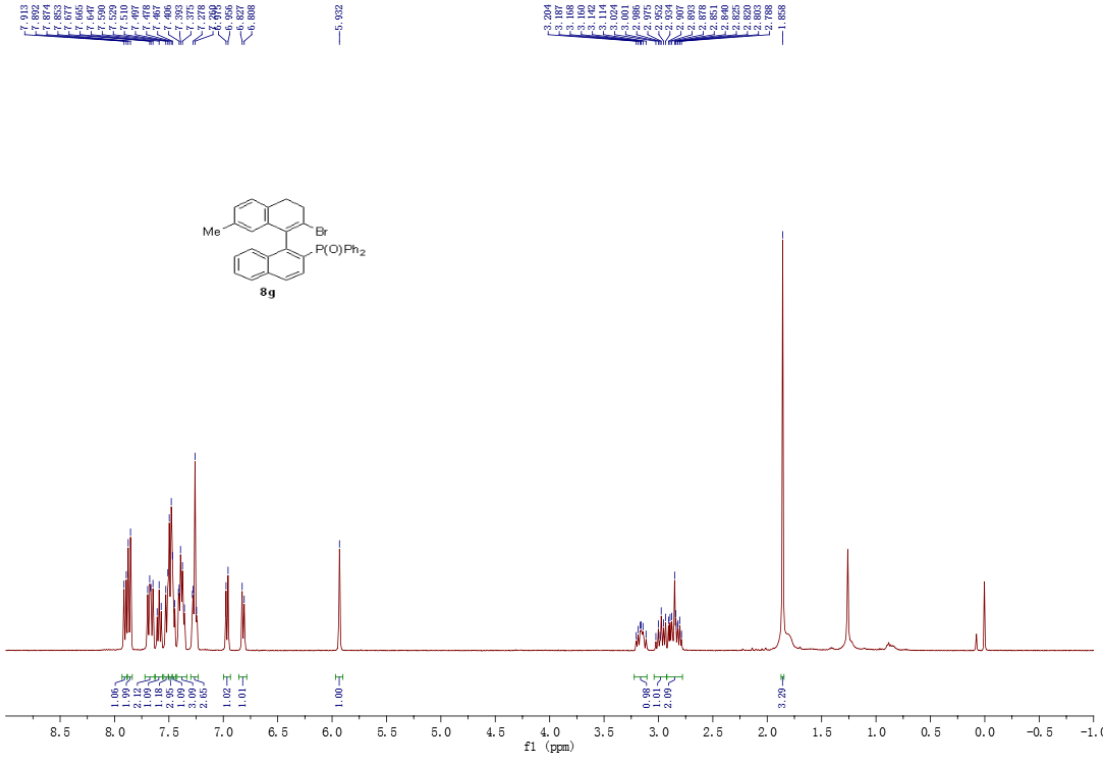

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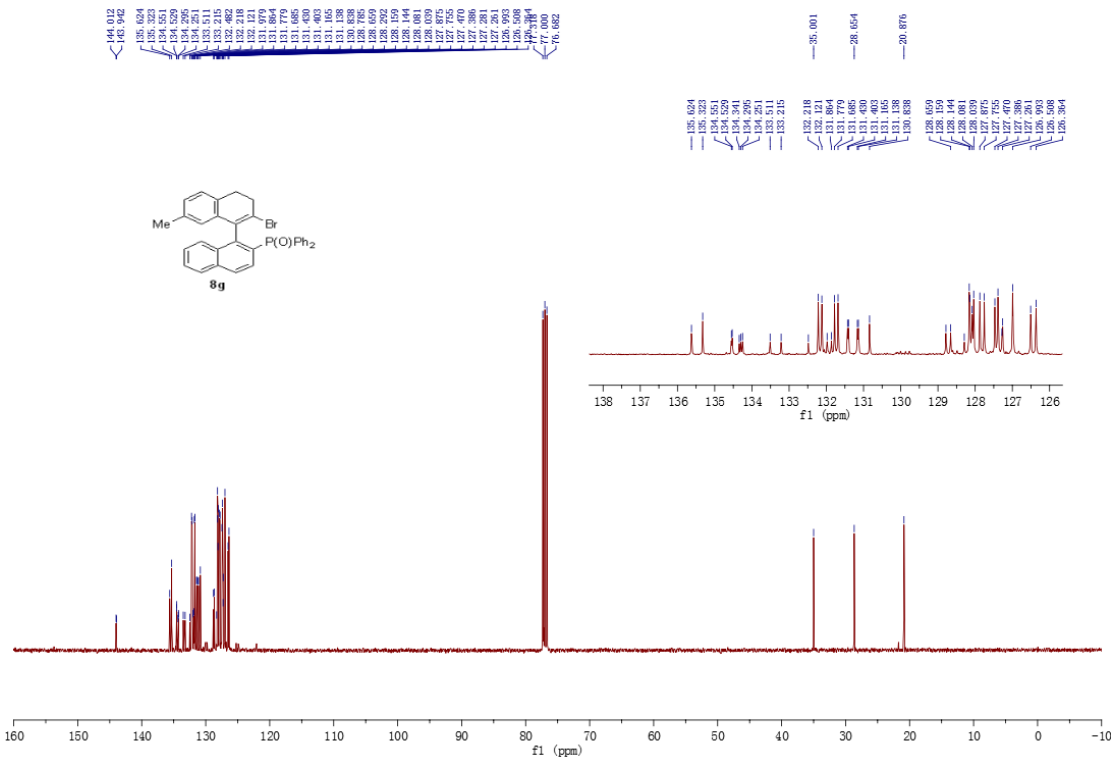

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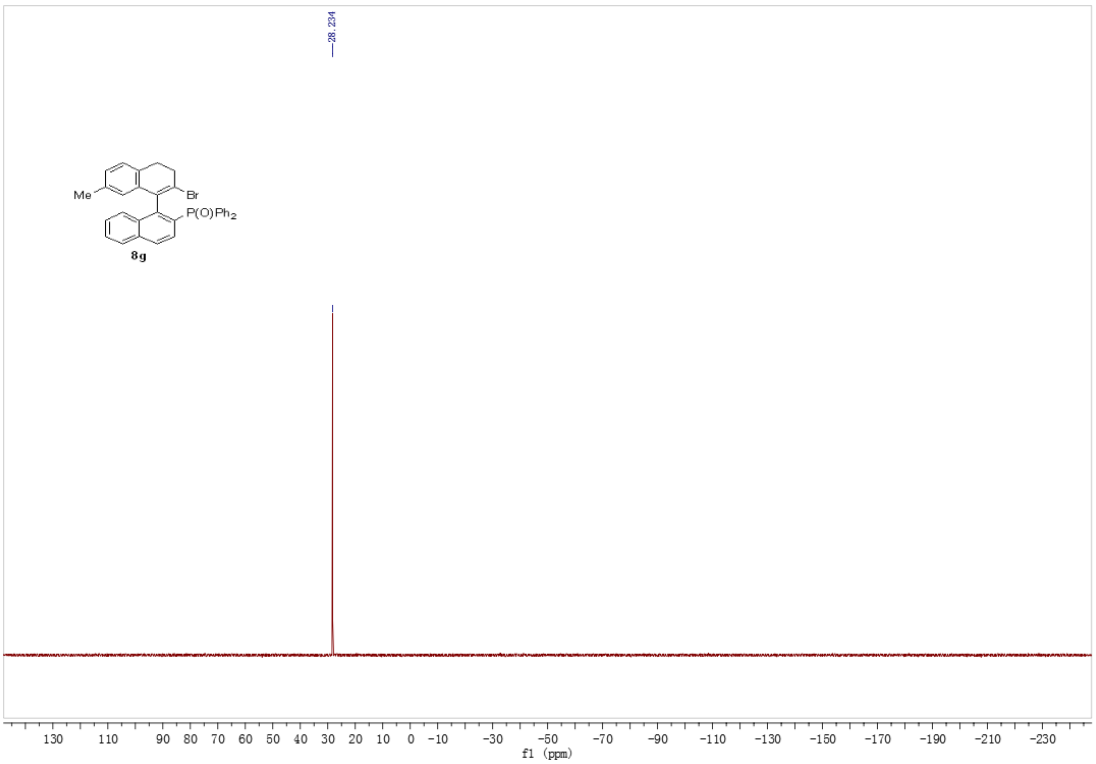

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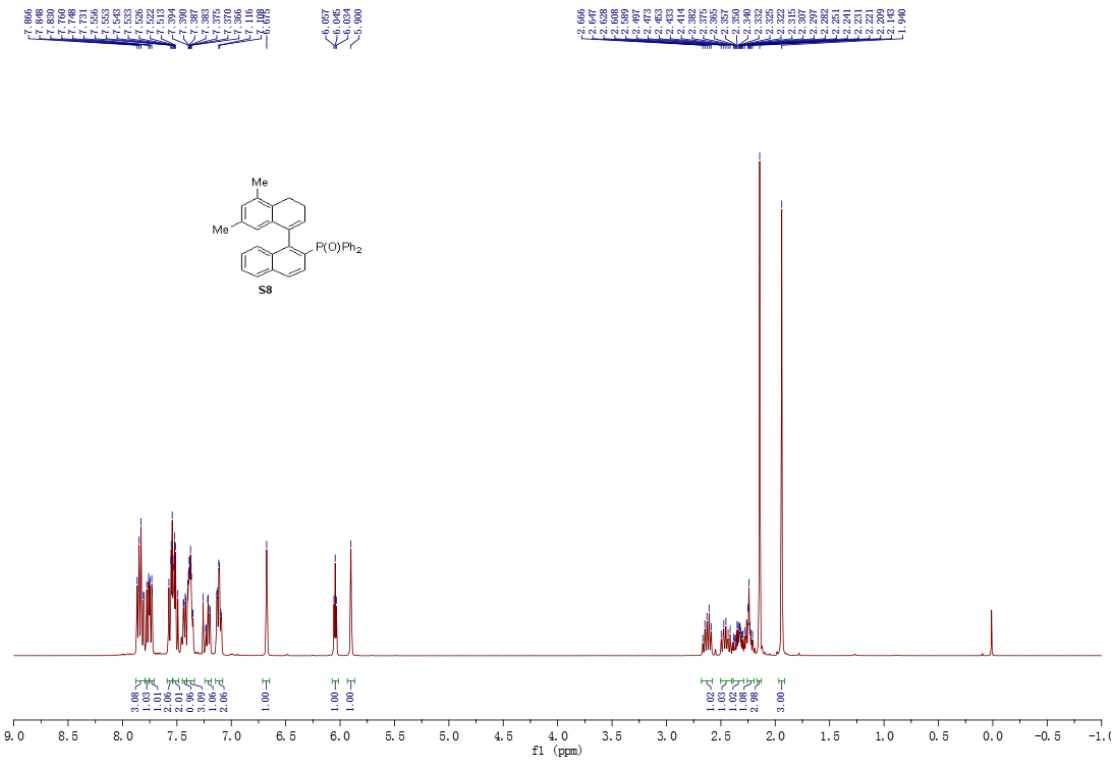

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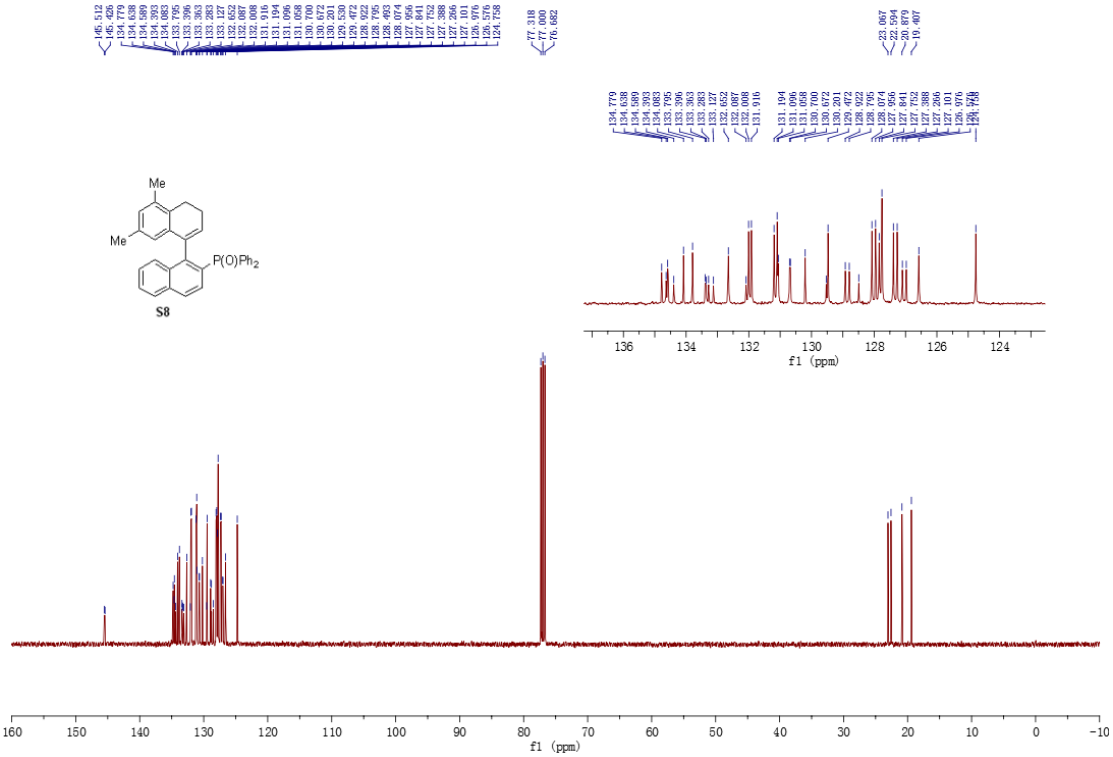

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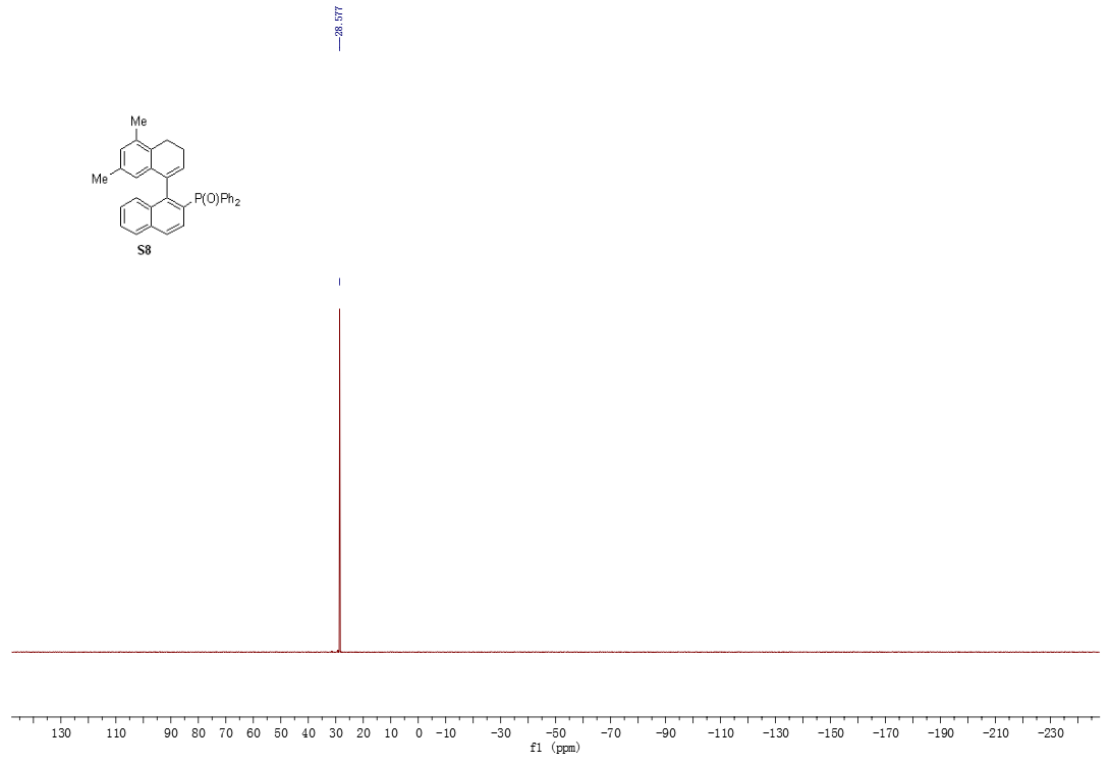

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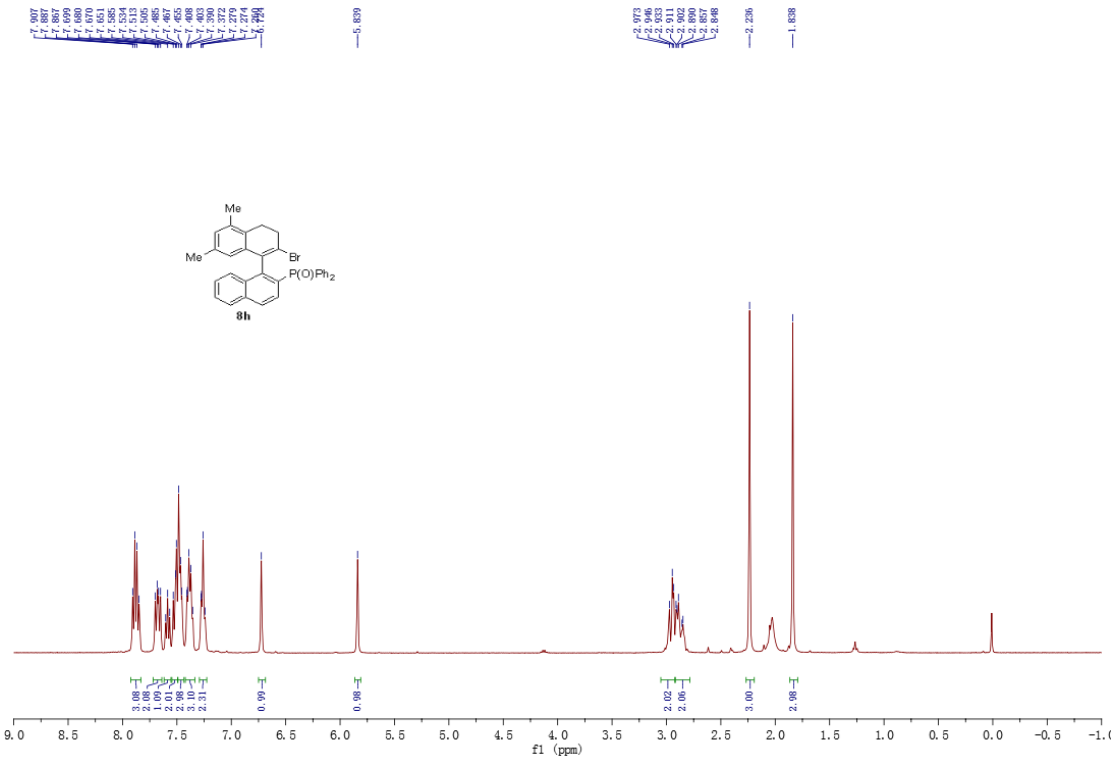

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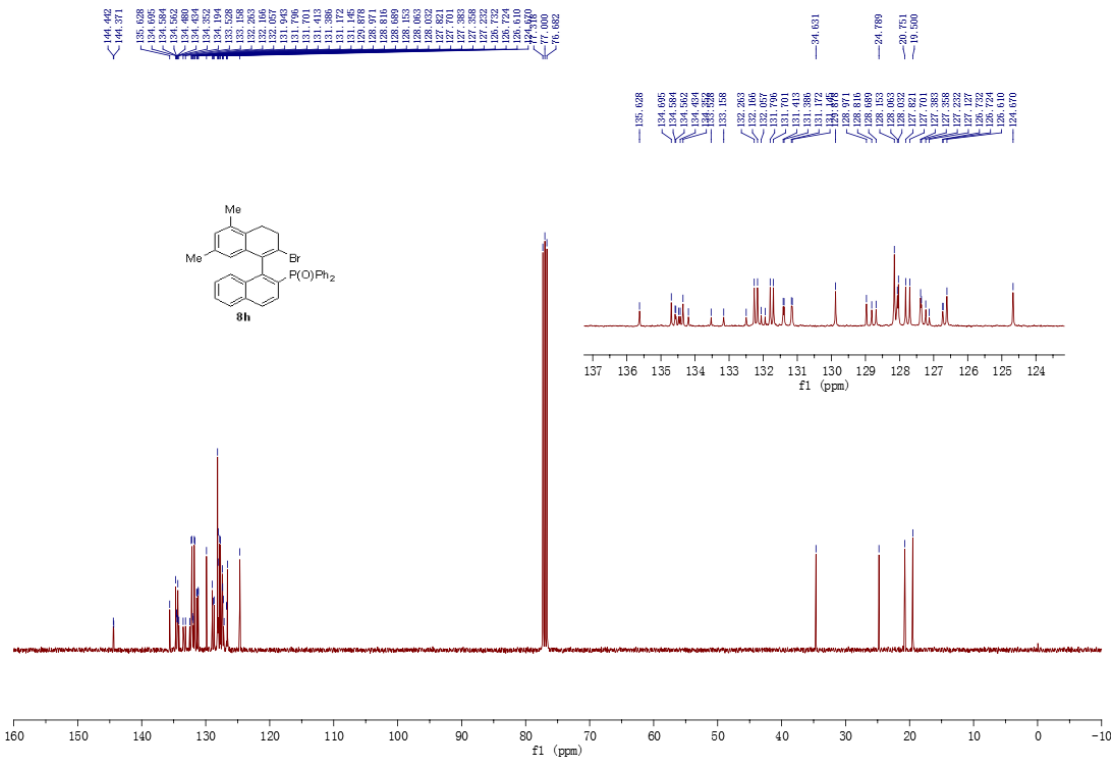

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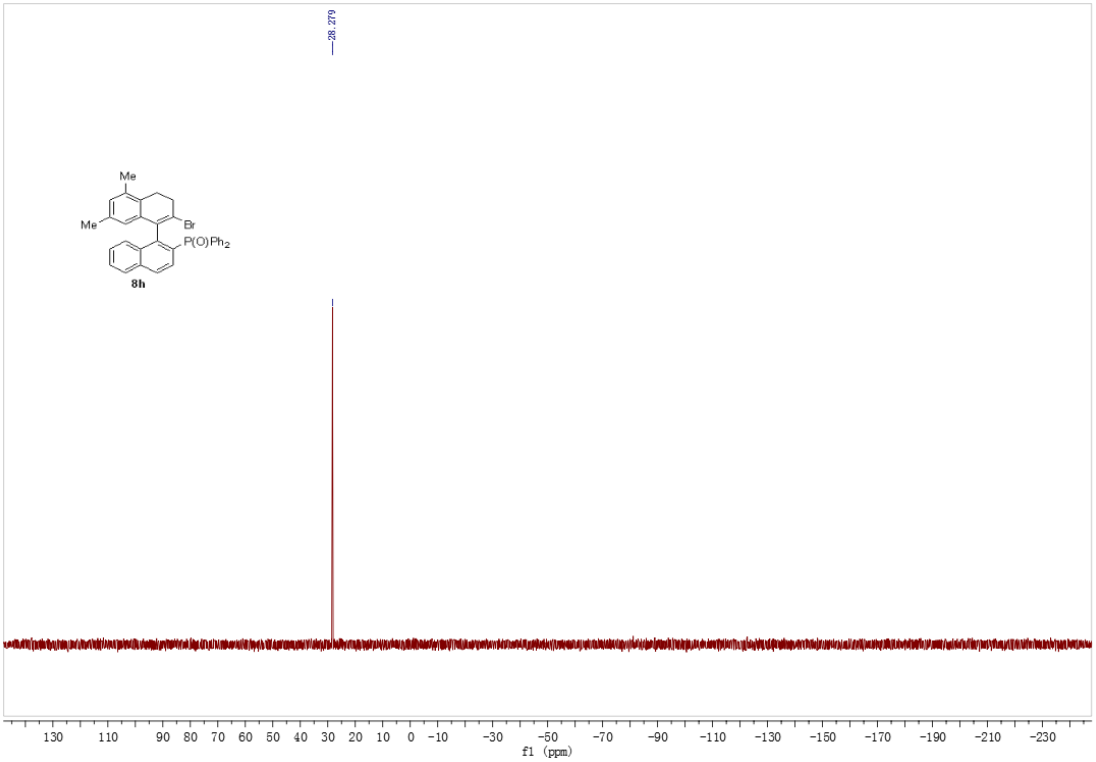

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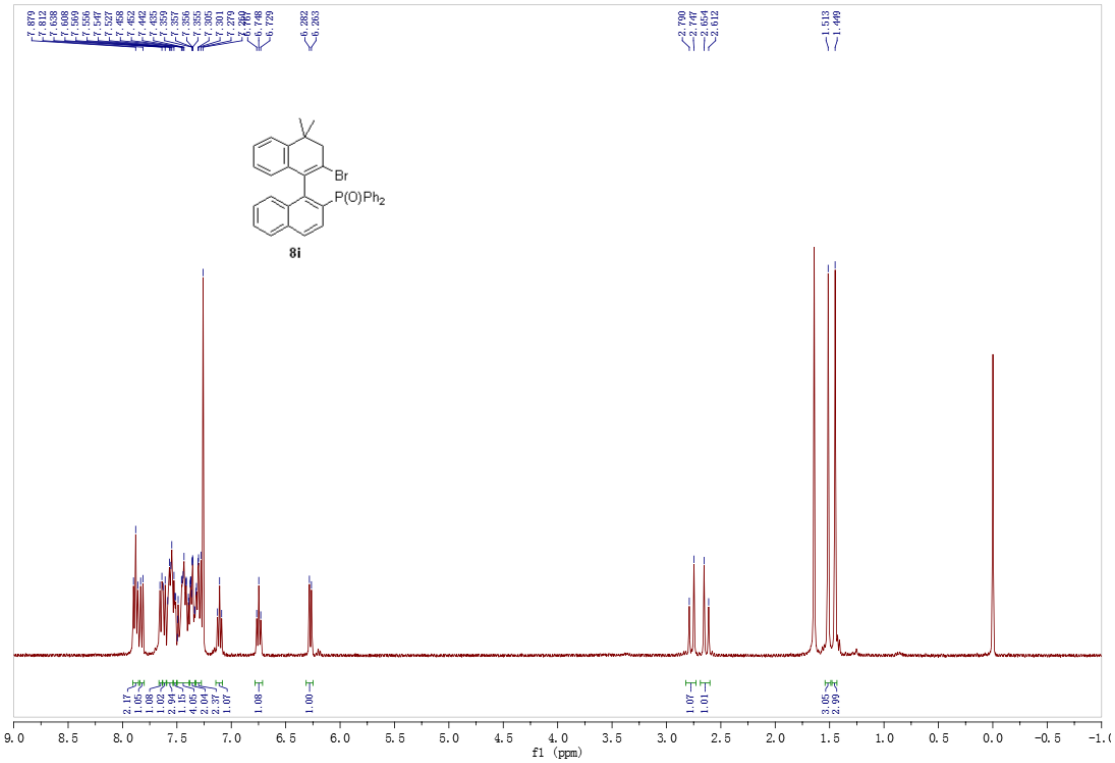

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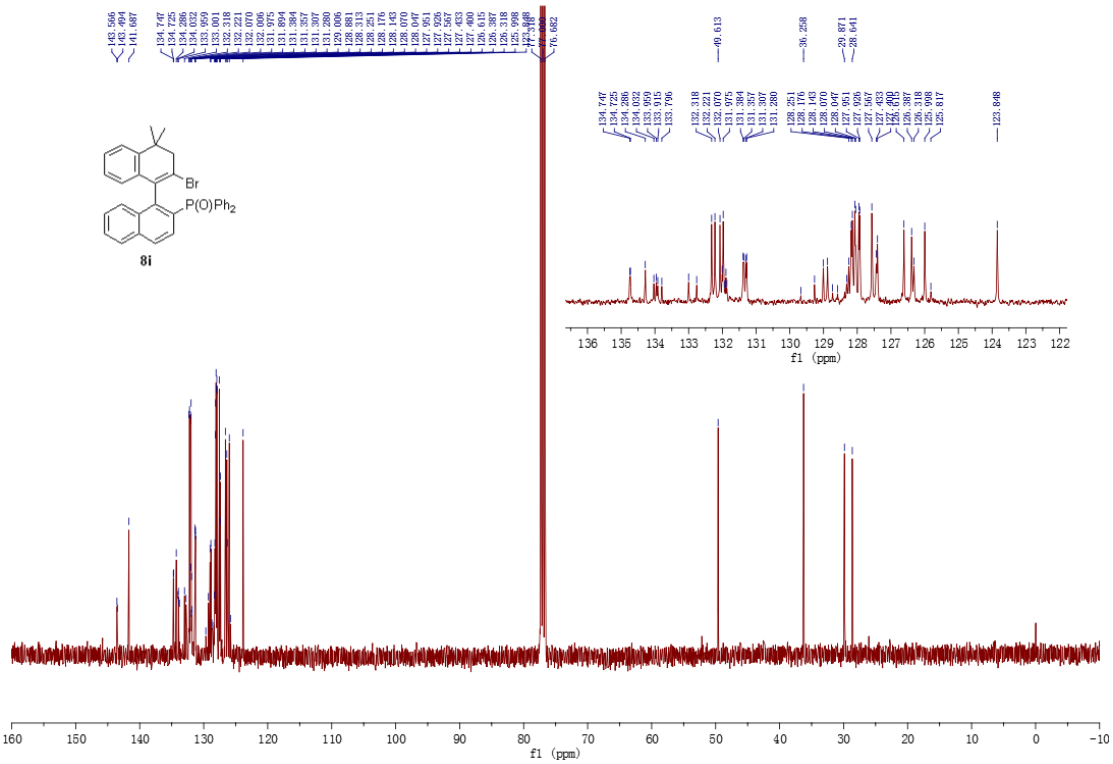

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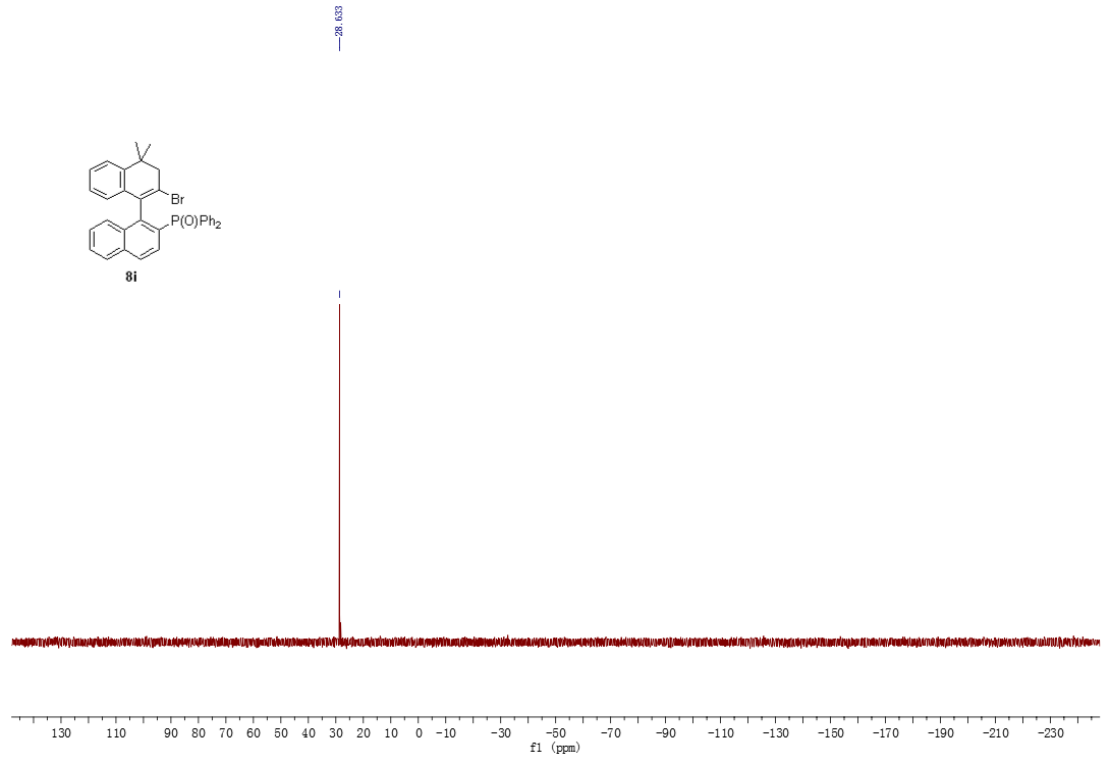

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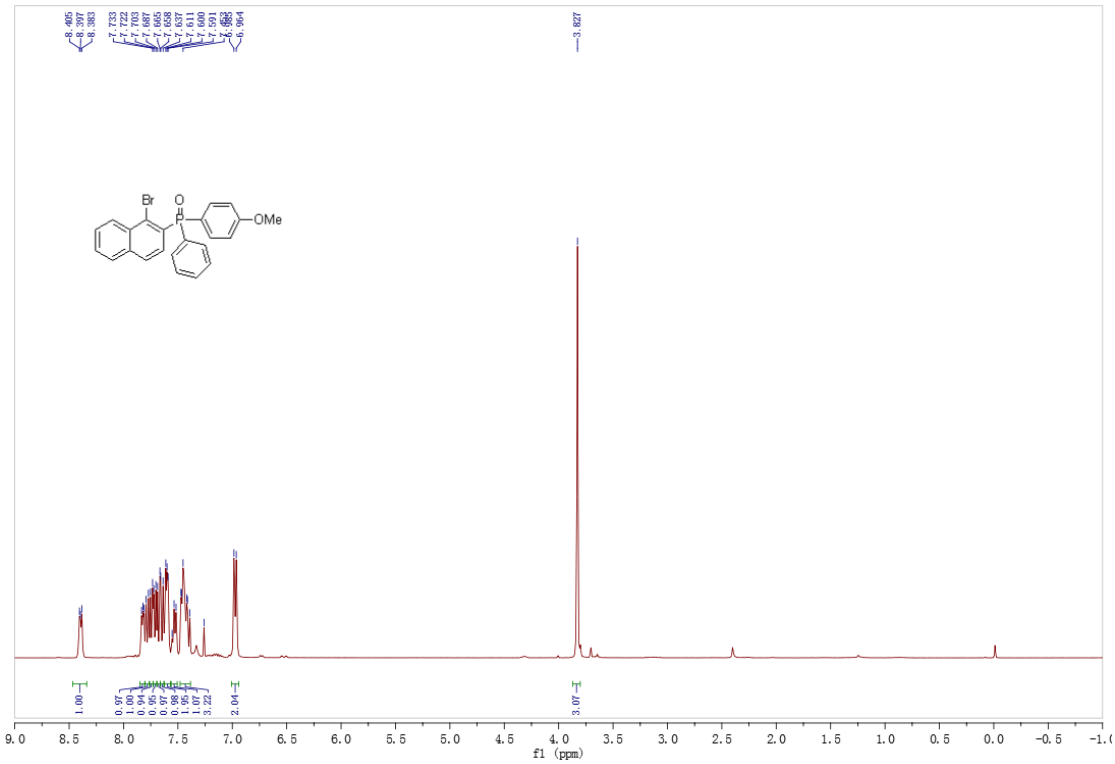

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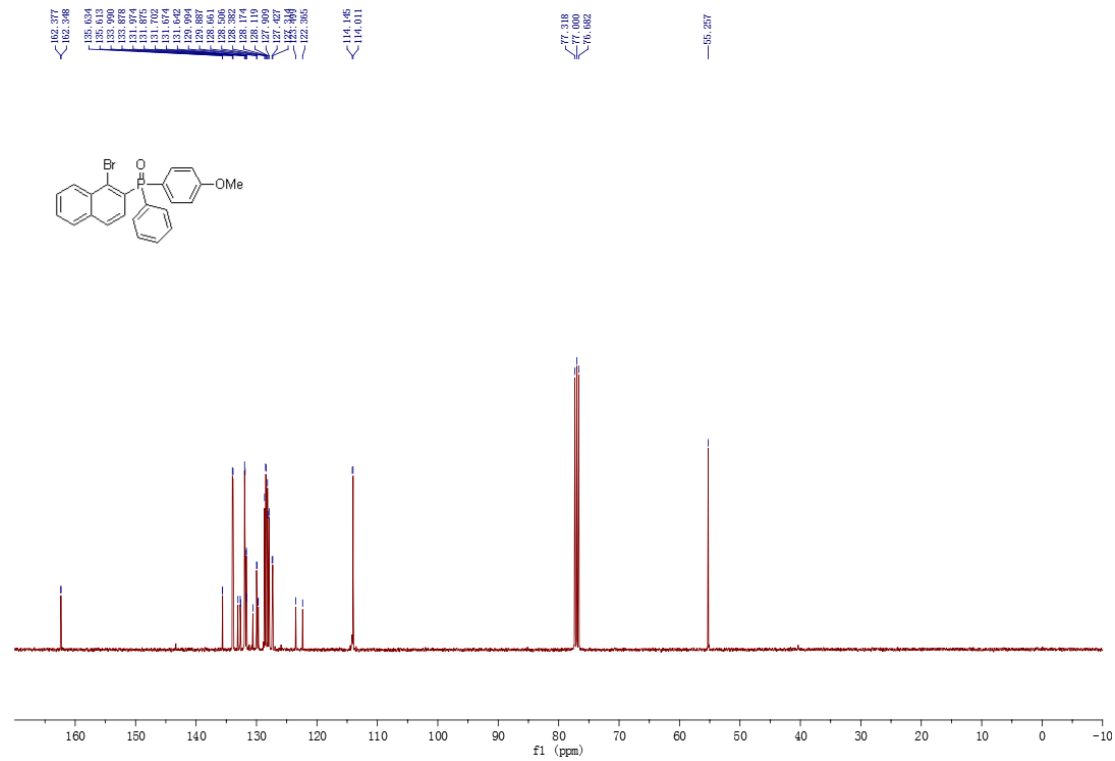

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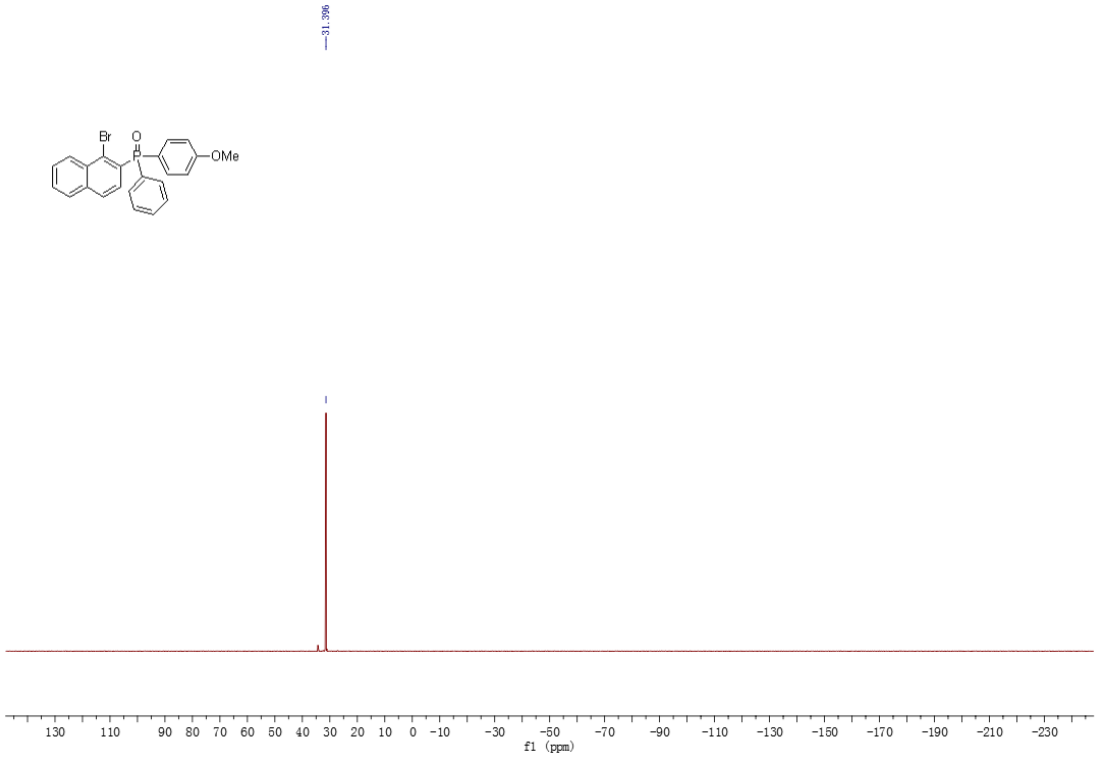

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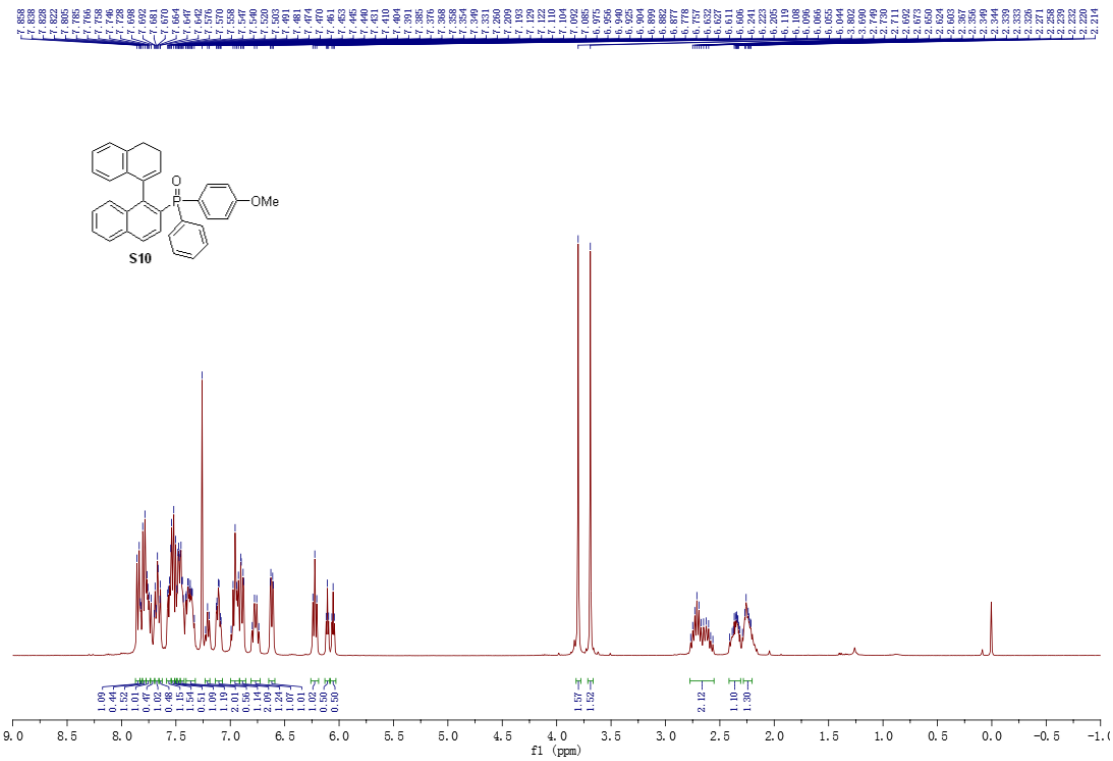

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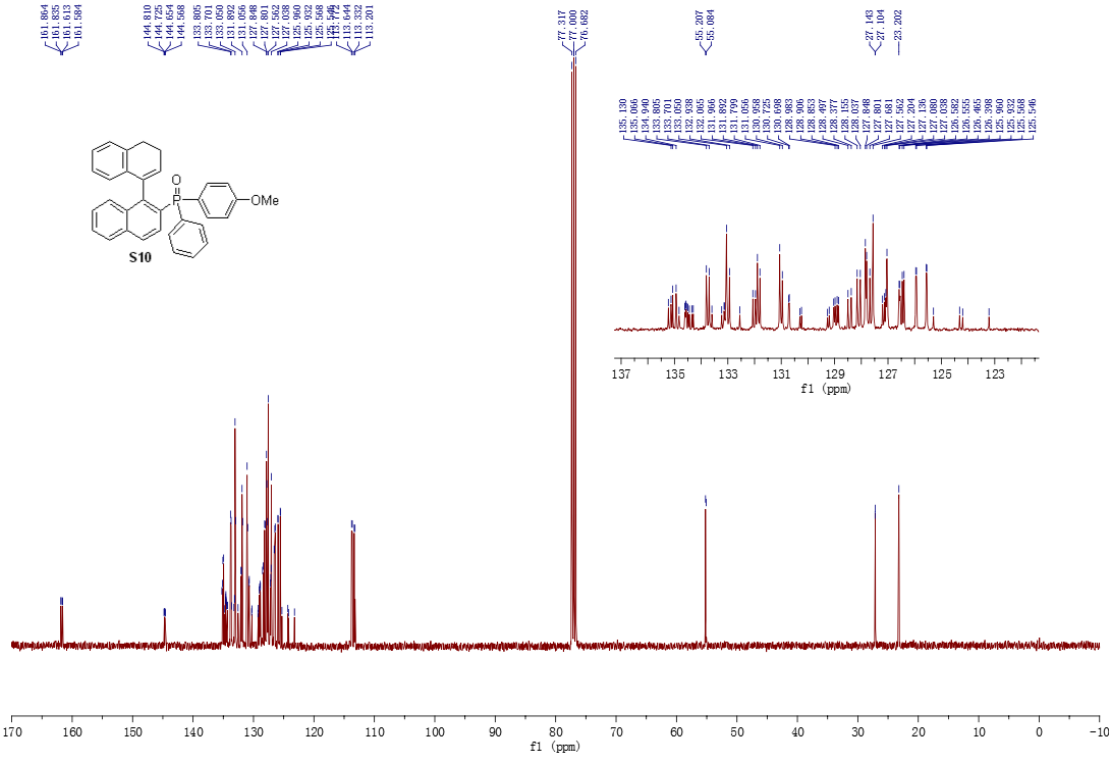

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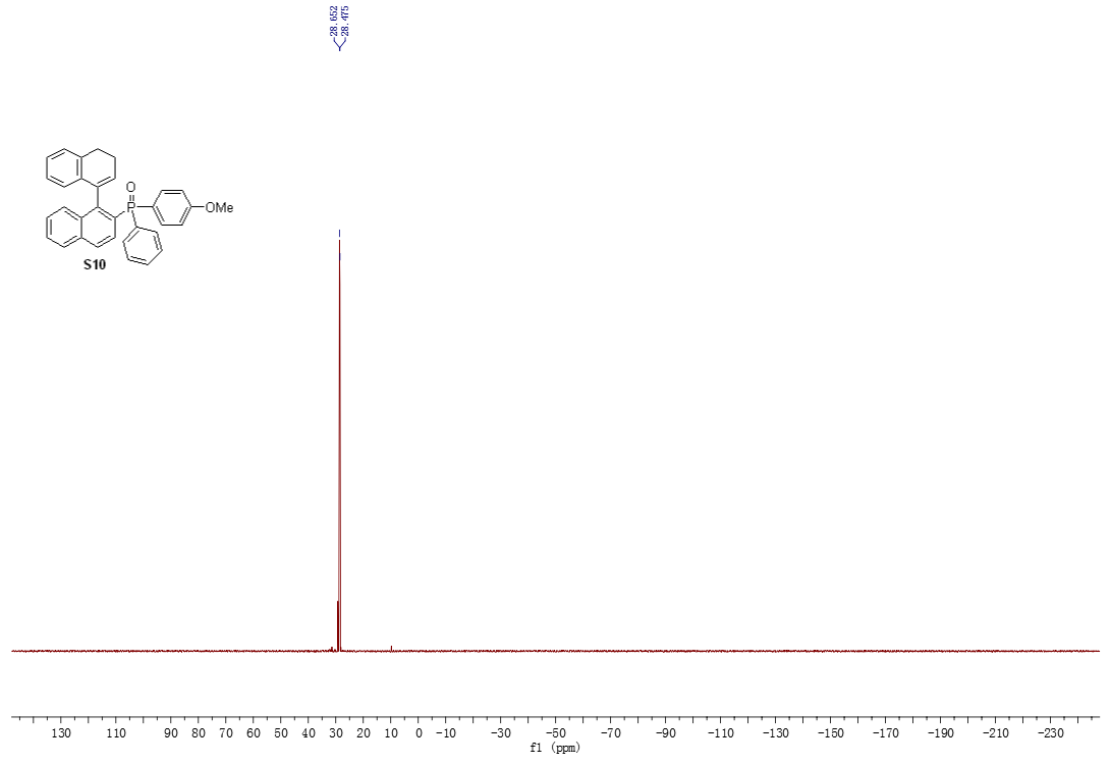

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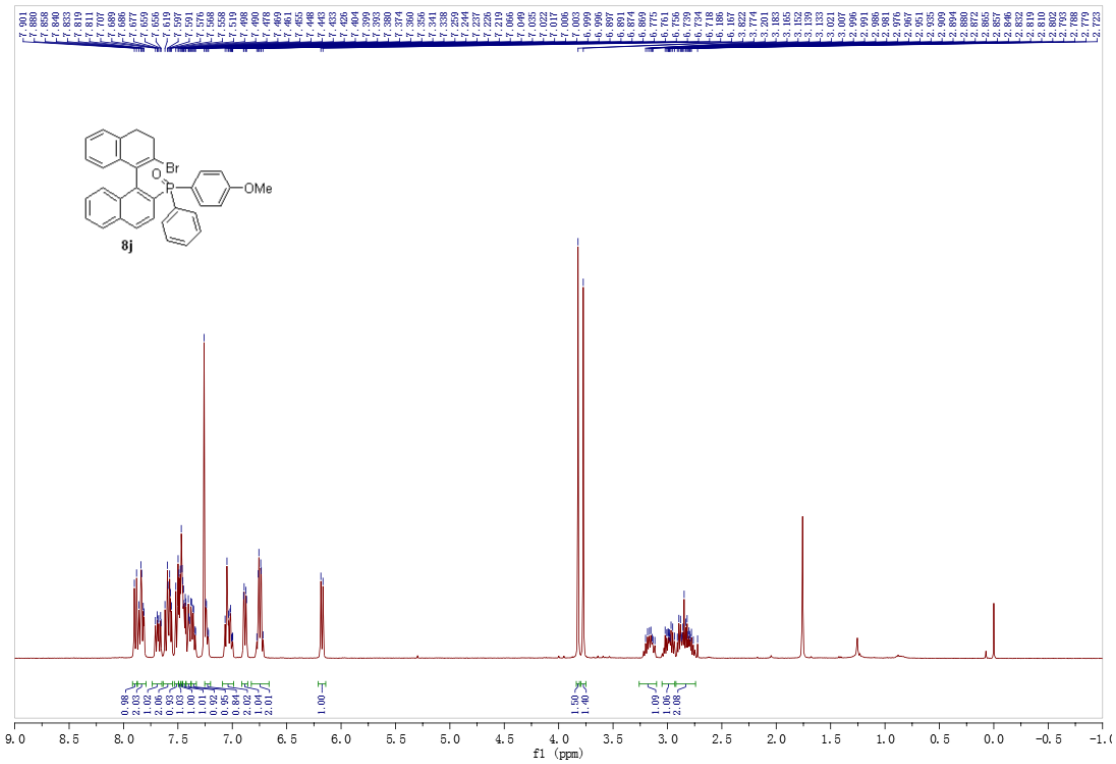

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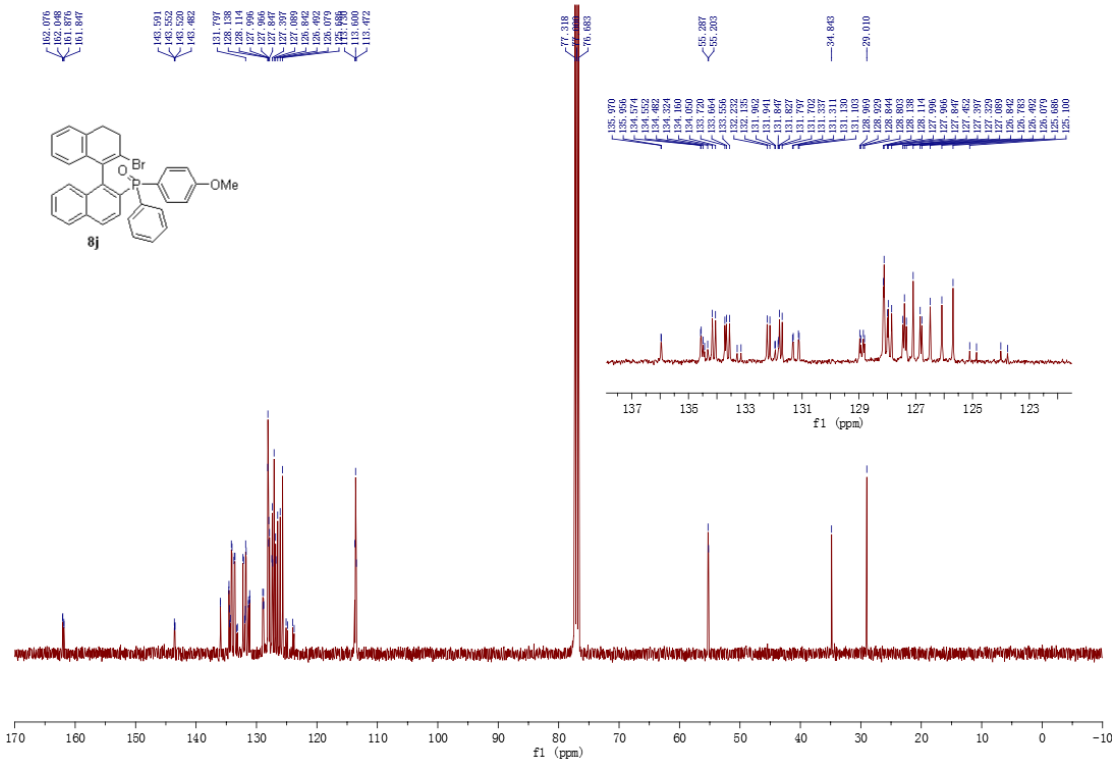

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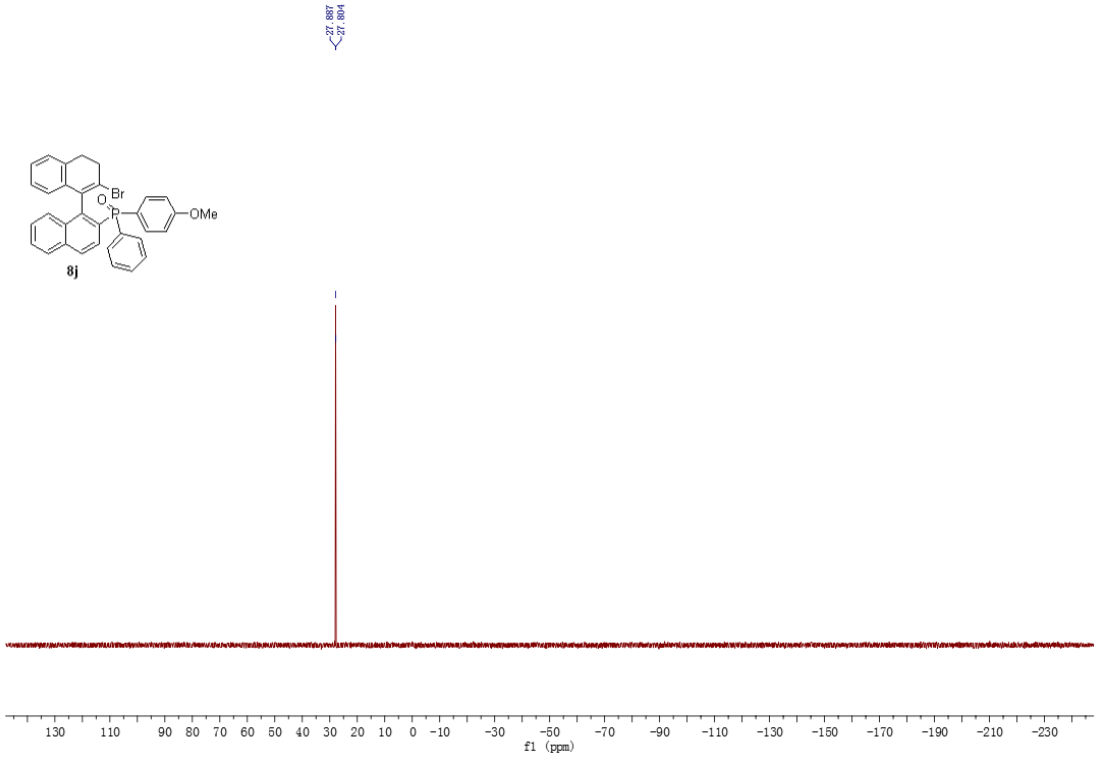

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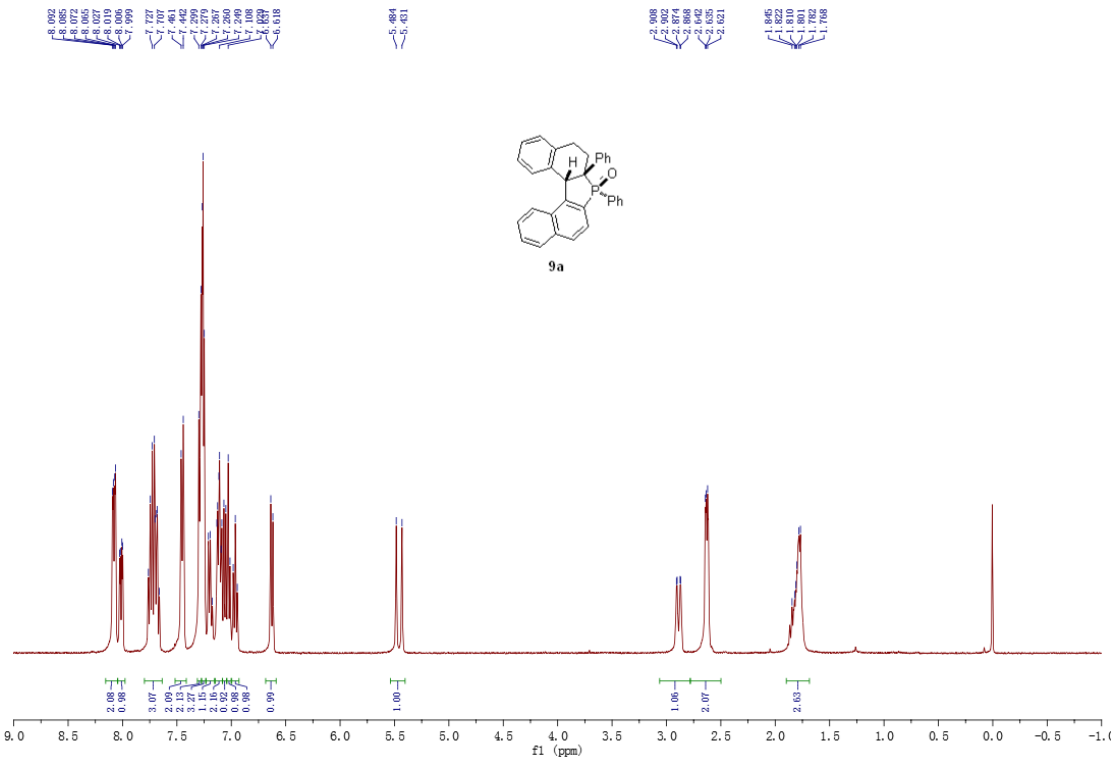

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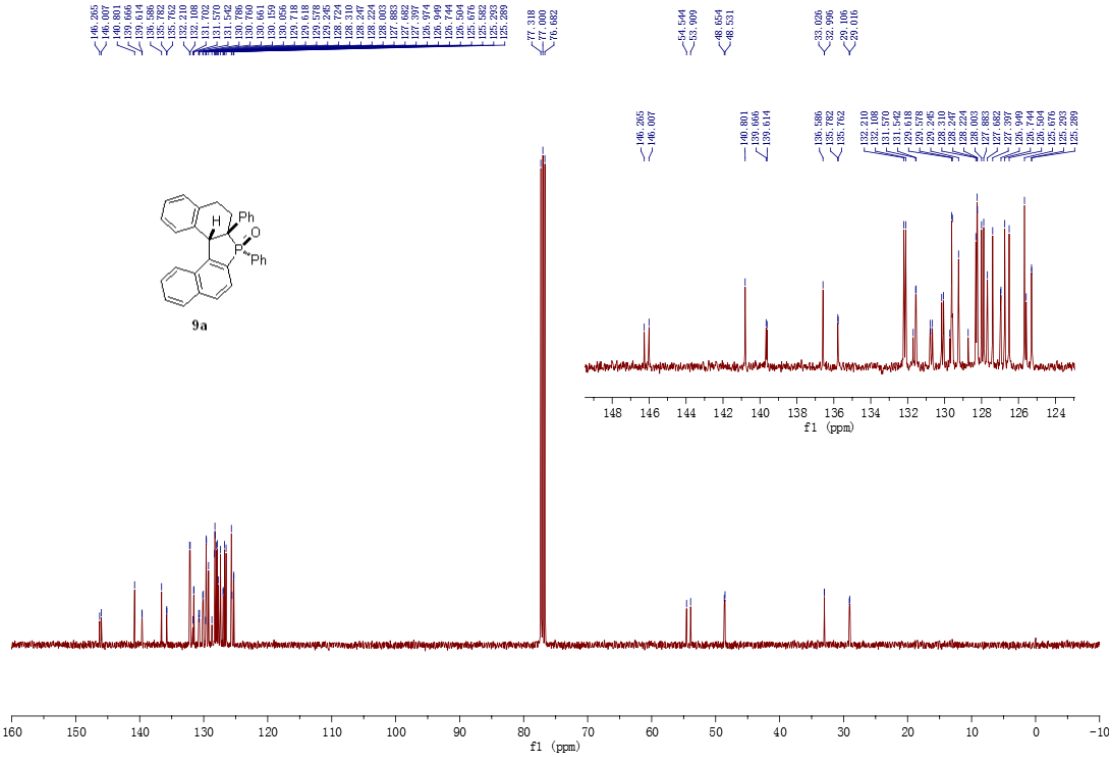

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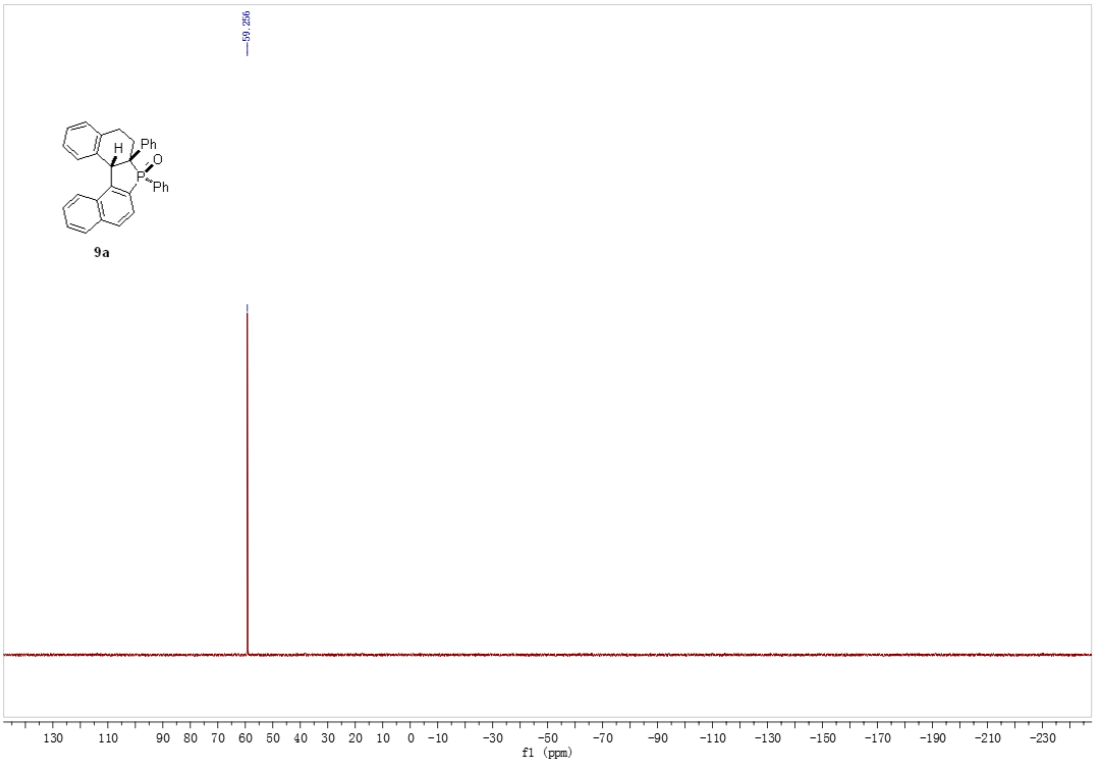

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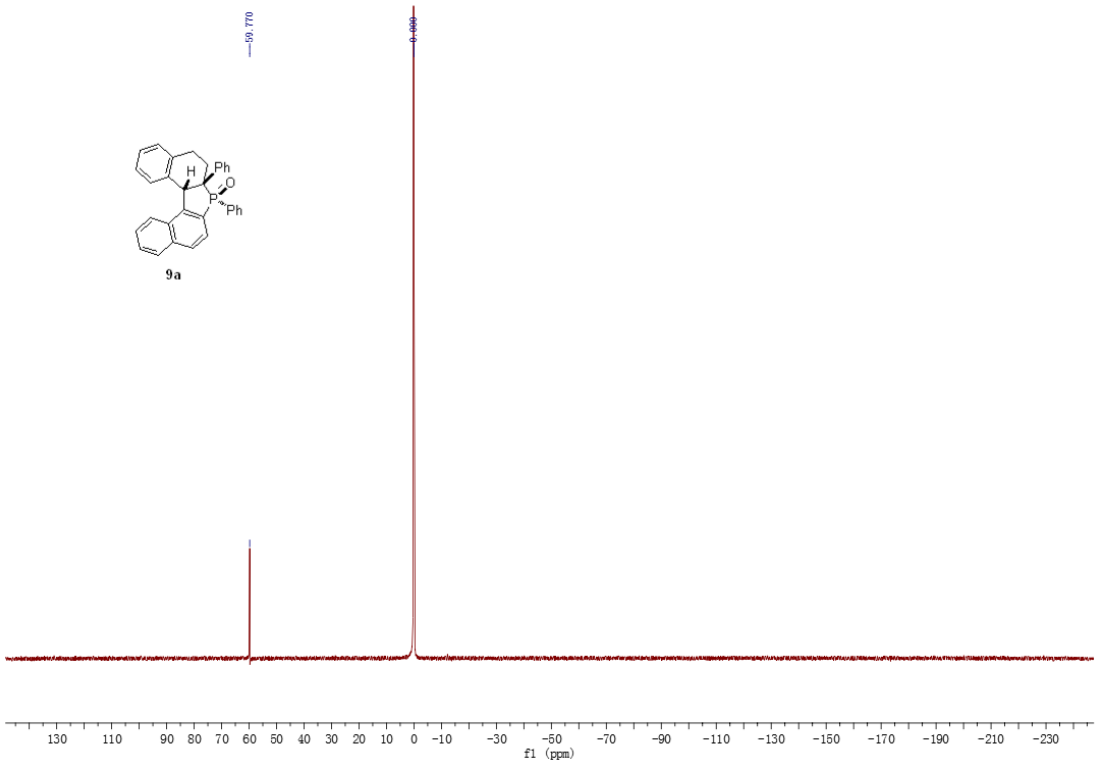
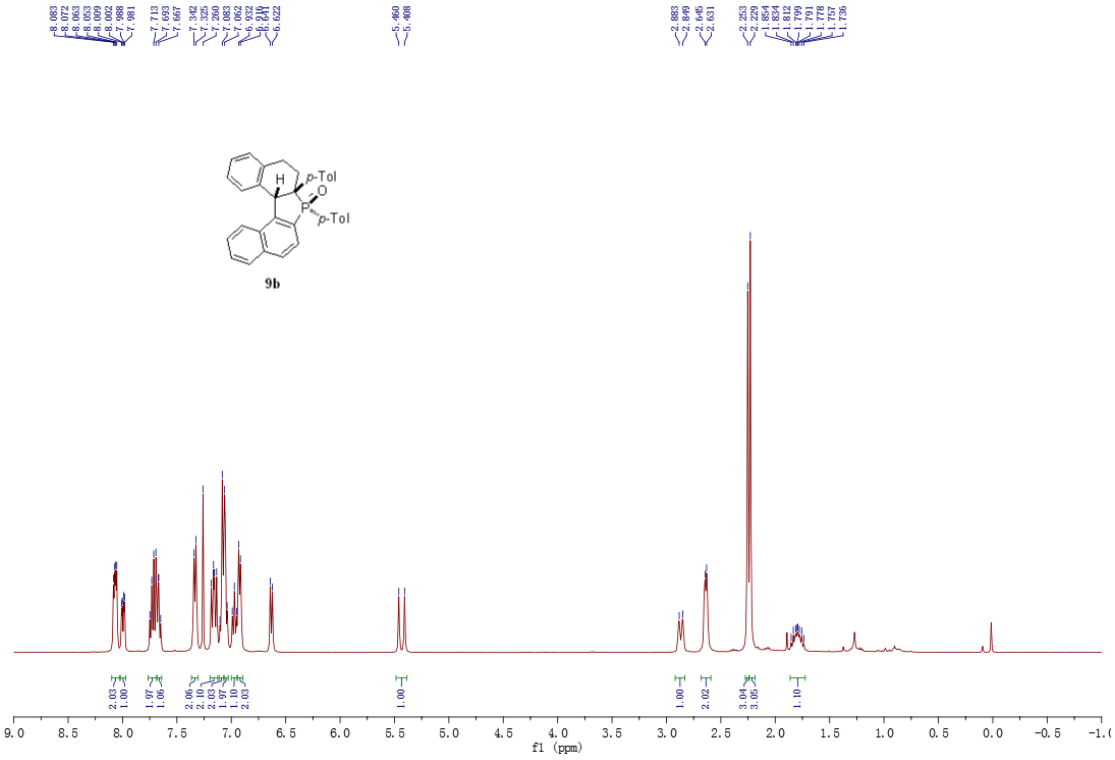


^{31}P NMR (analysed by the use of H_3PO_4 (85 %) as internal standard.)



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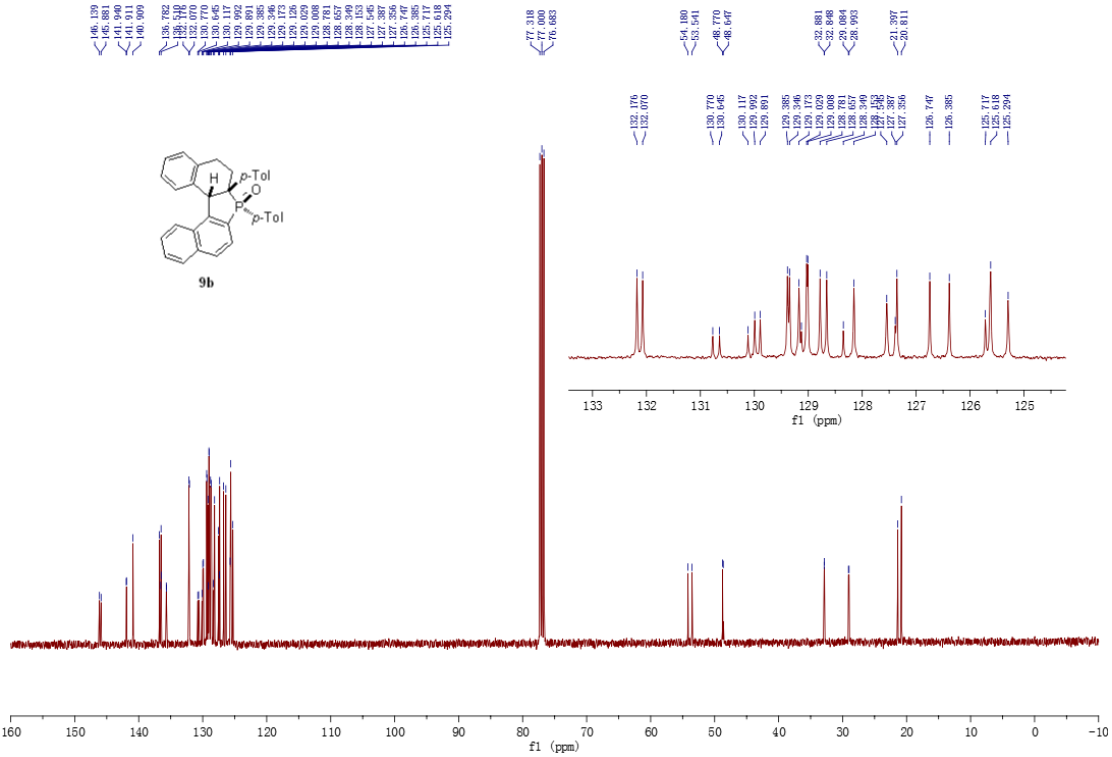

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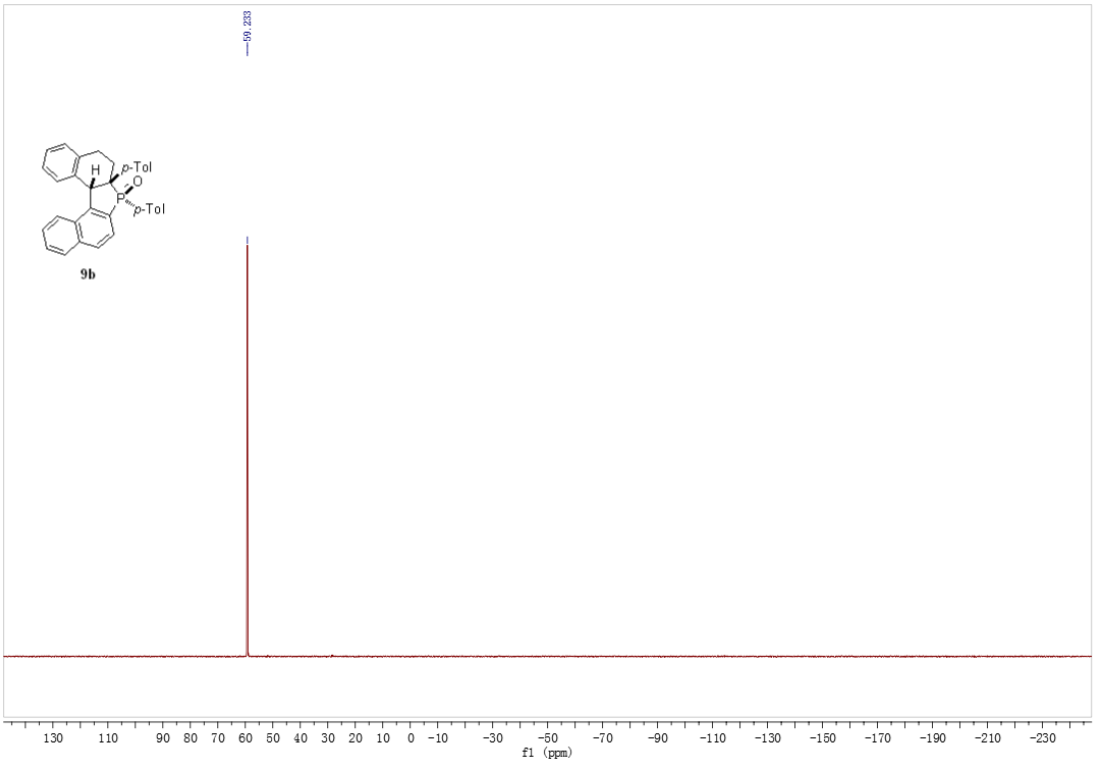

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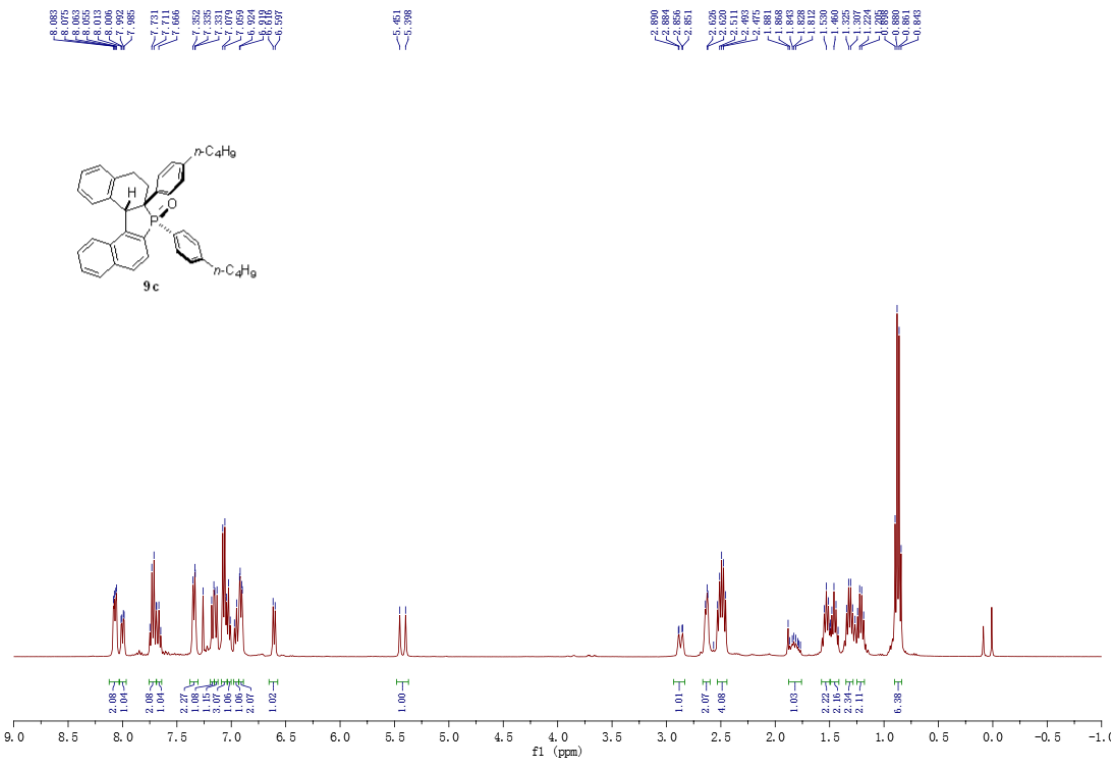

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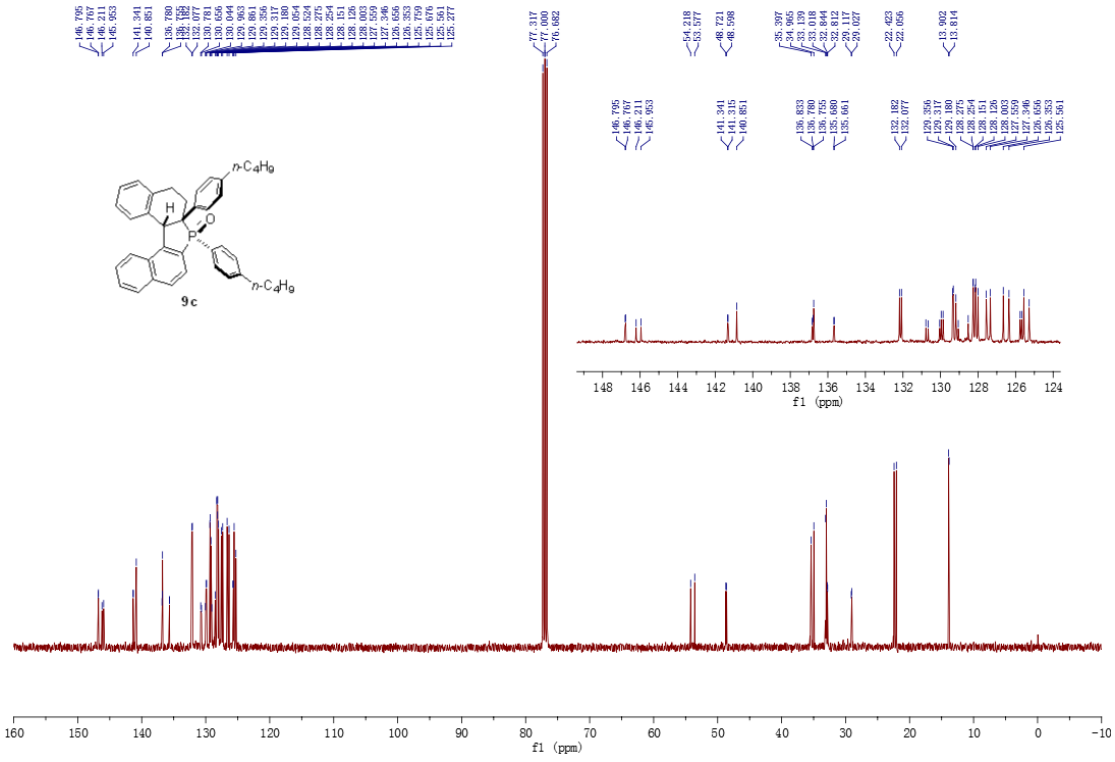

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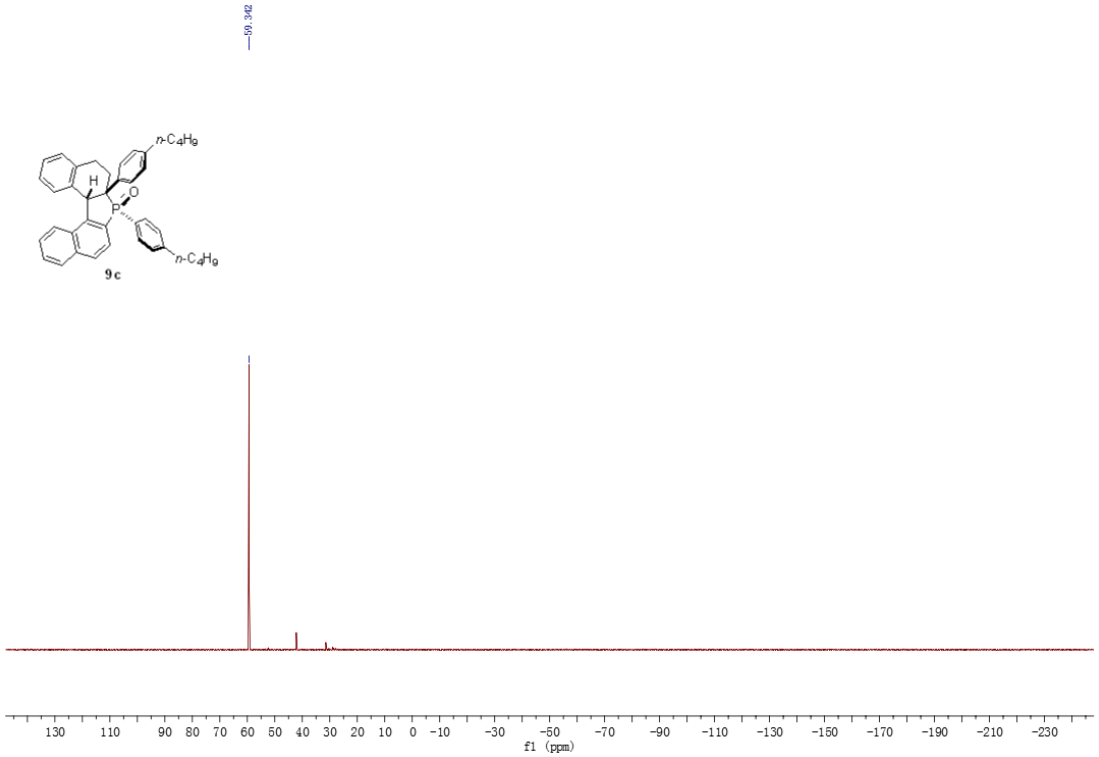

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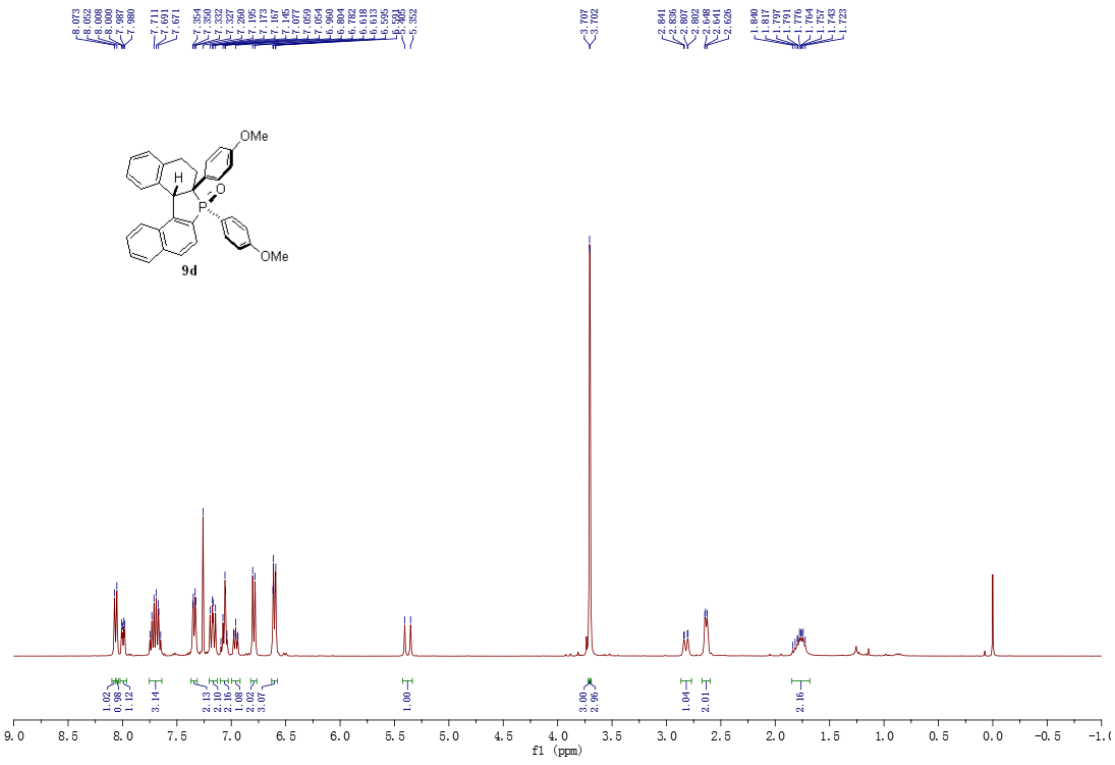

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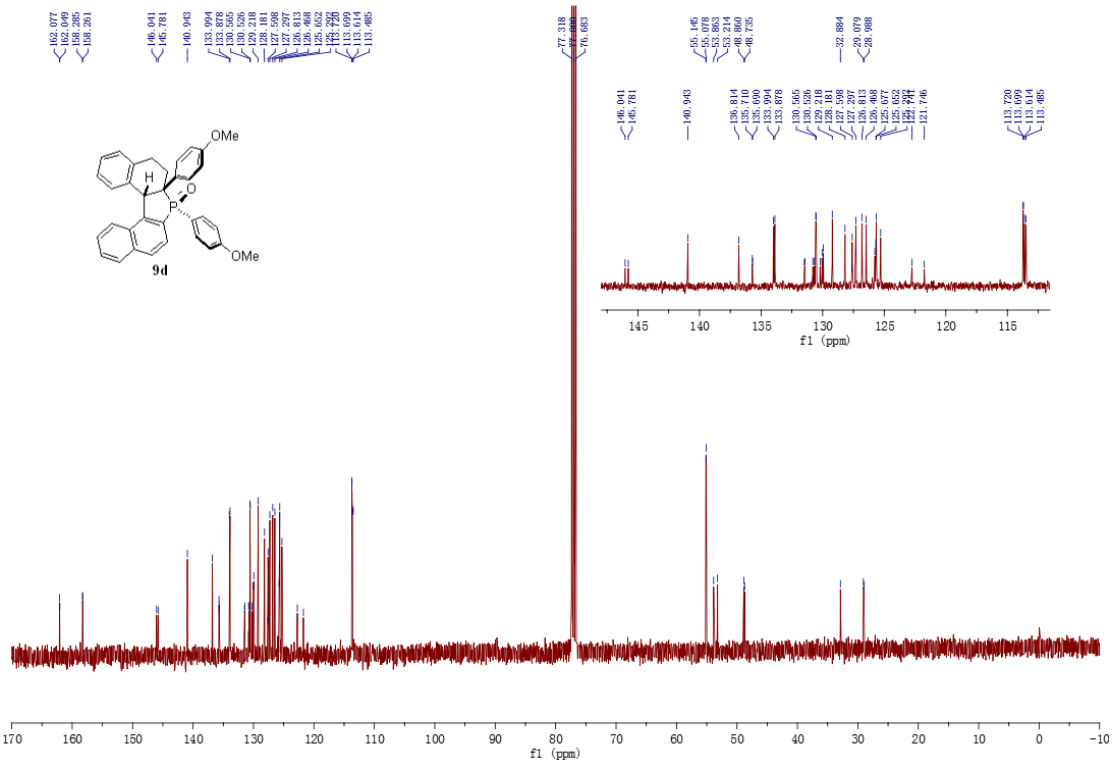
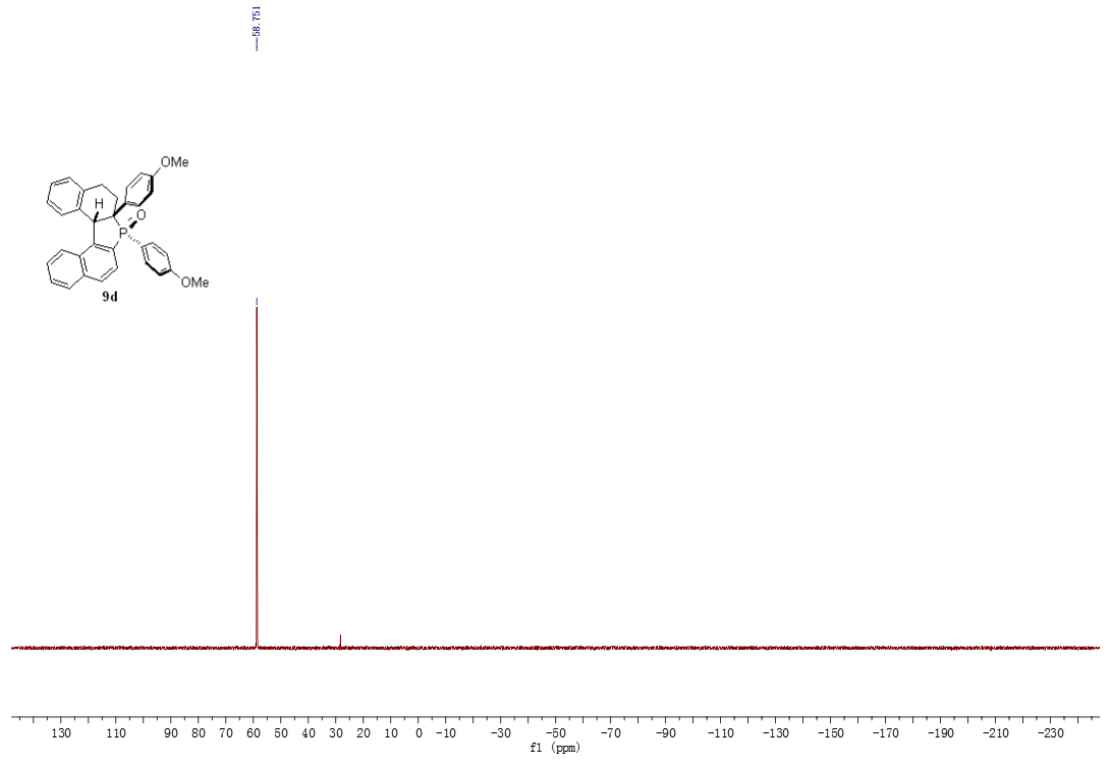
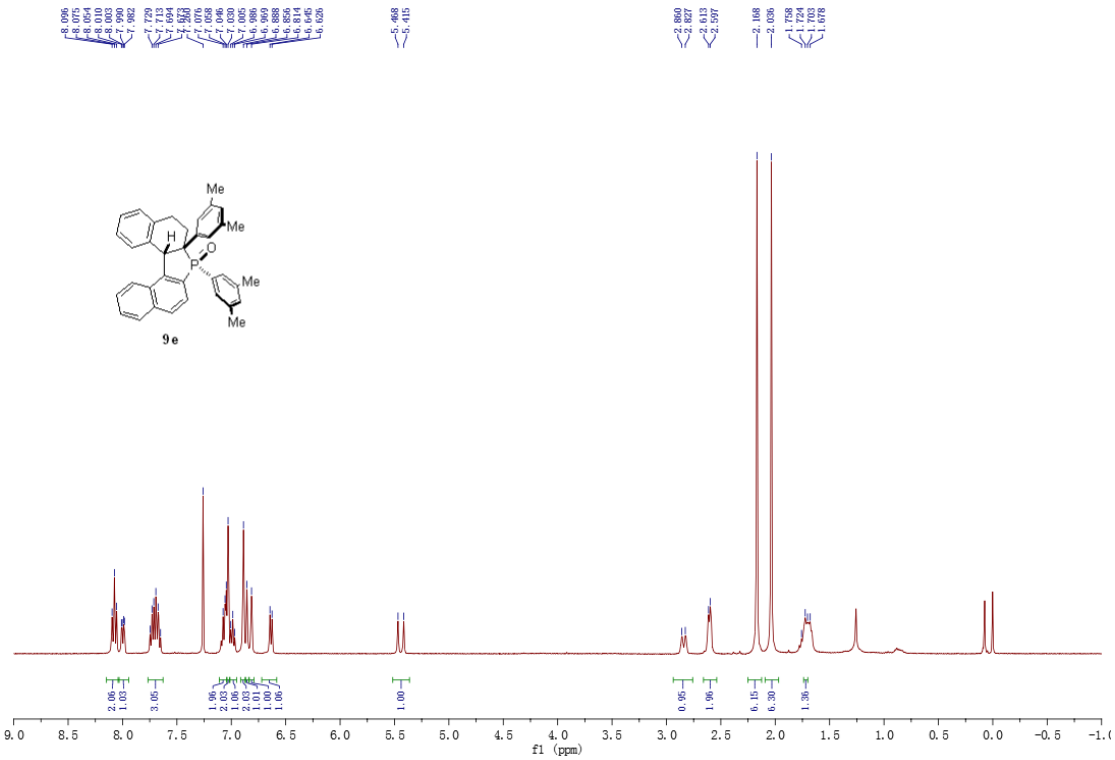


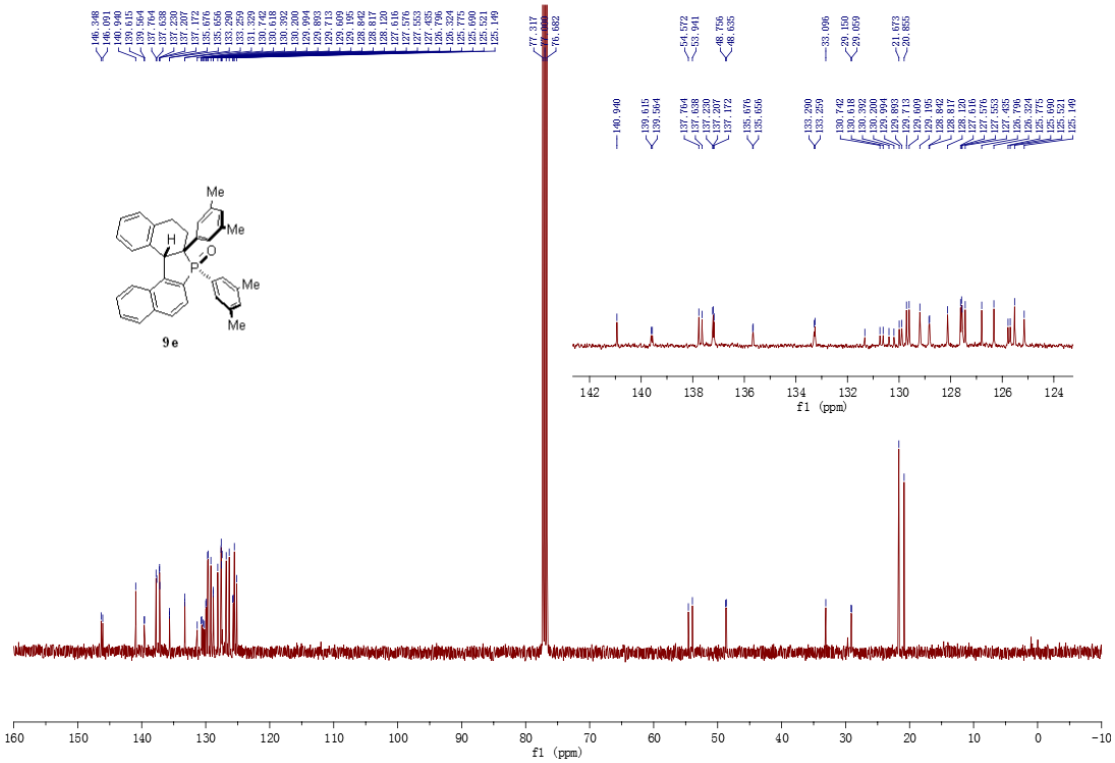
^{13}C NMR



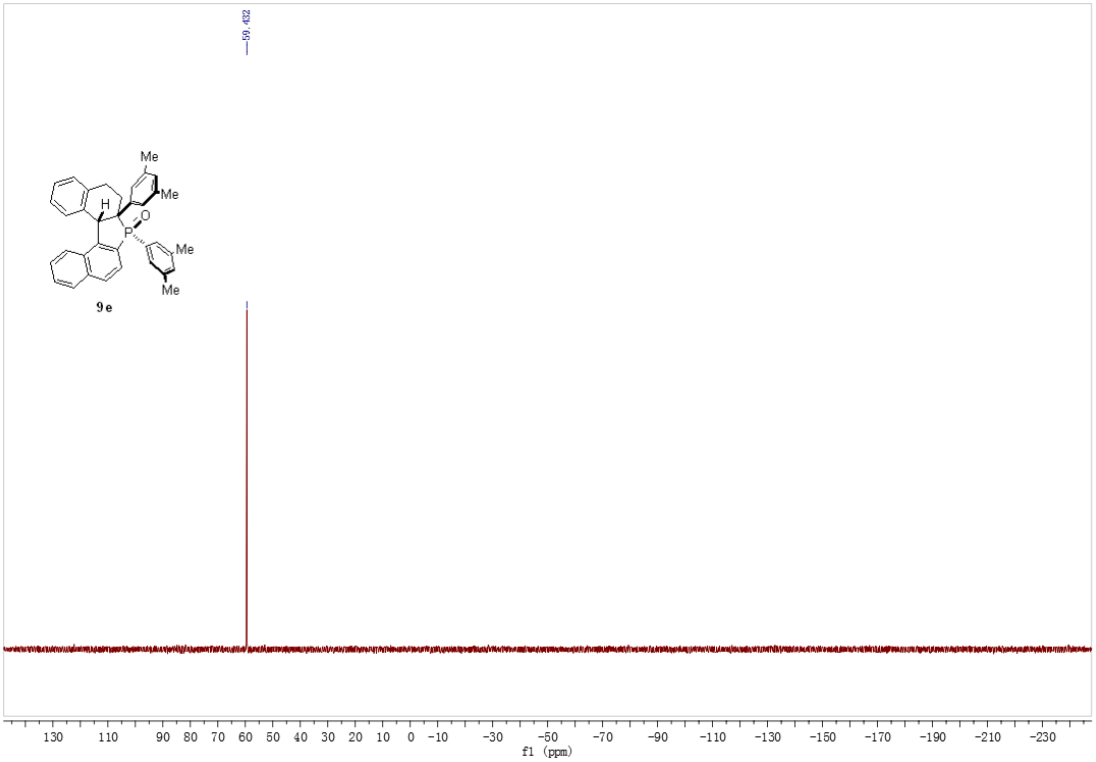
^{31}P NMR



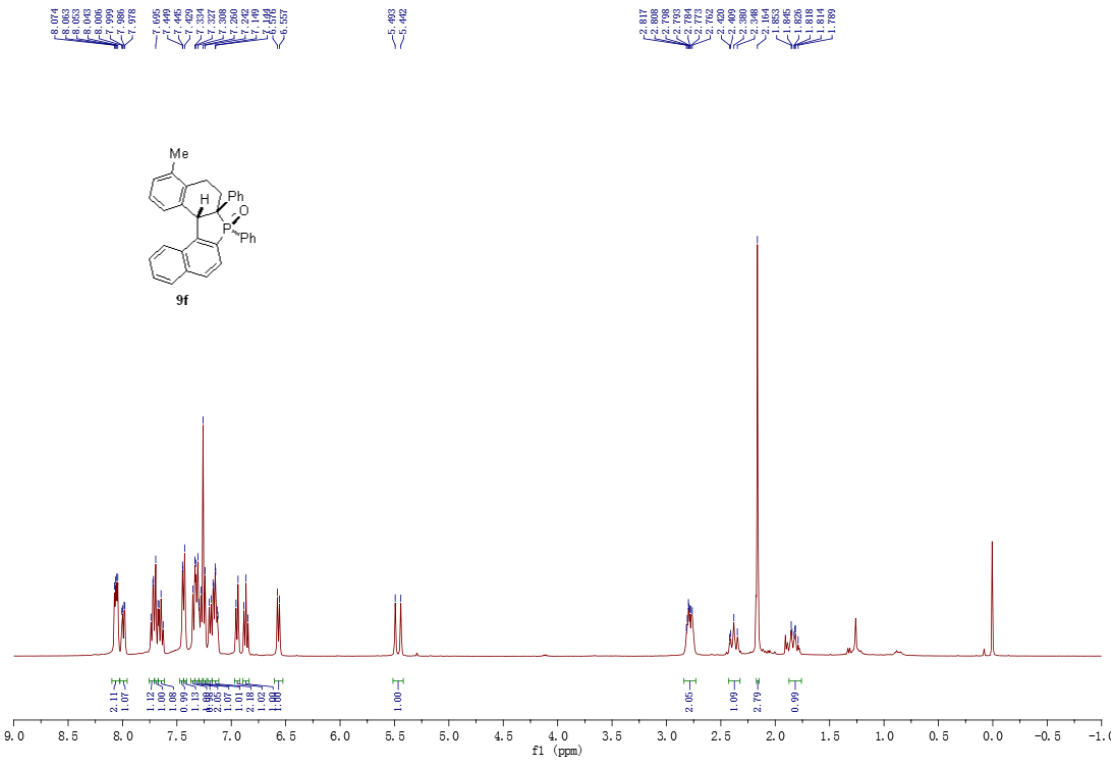
^{1}H NMR



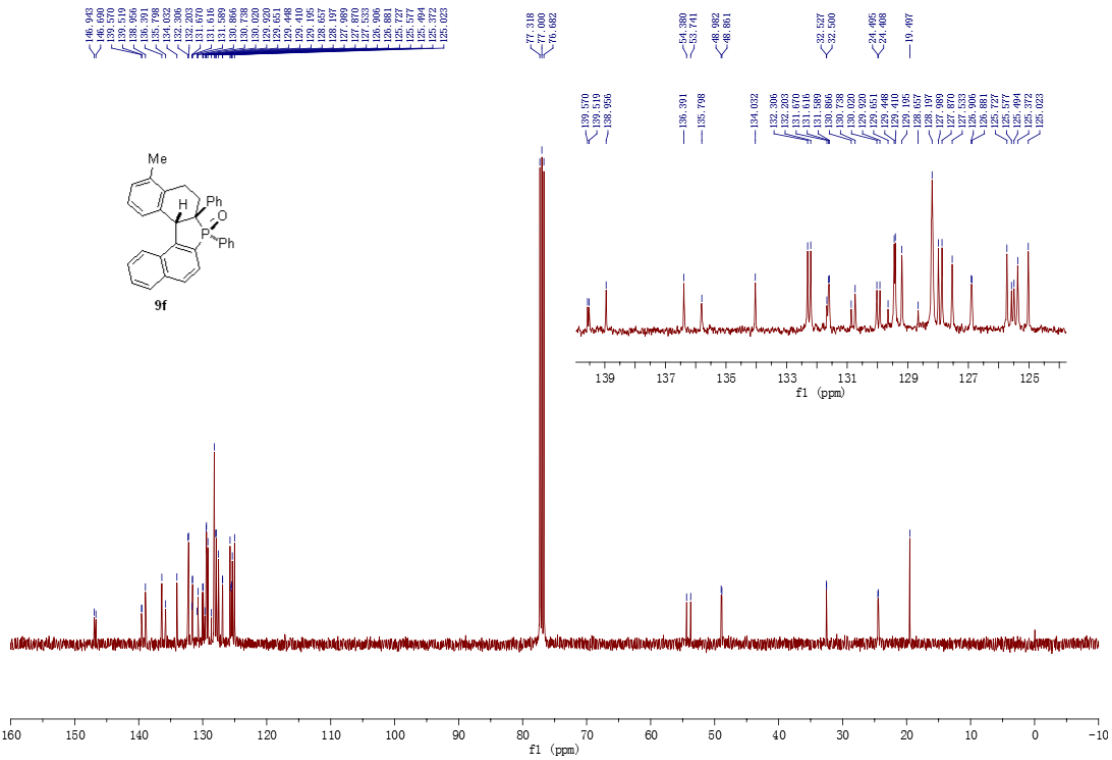
^{13}C NMR



^{31}P NMR



^{1}H NMR



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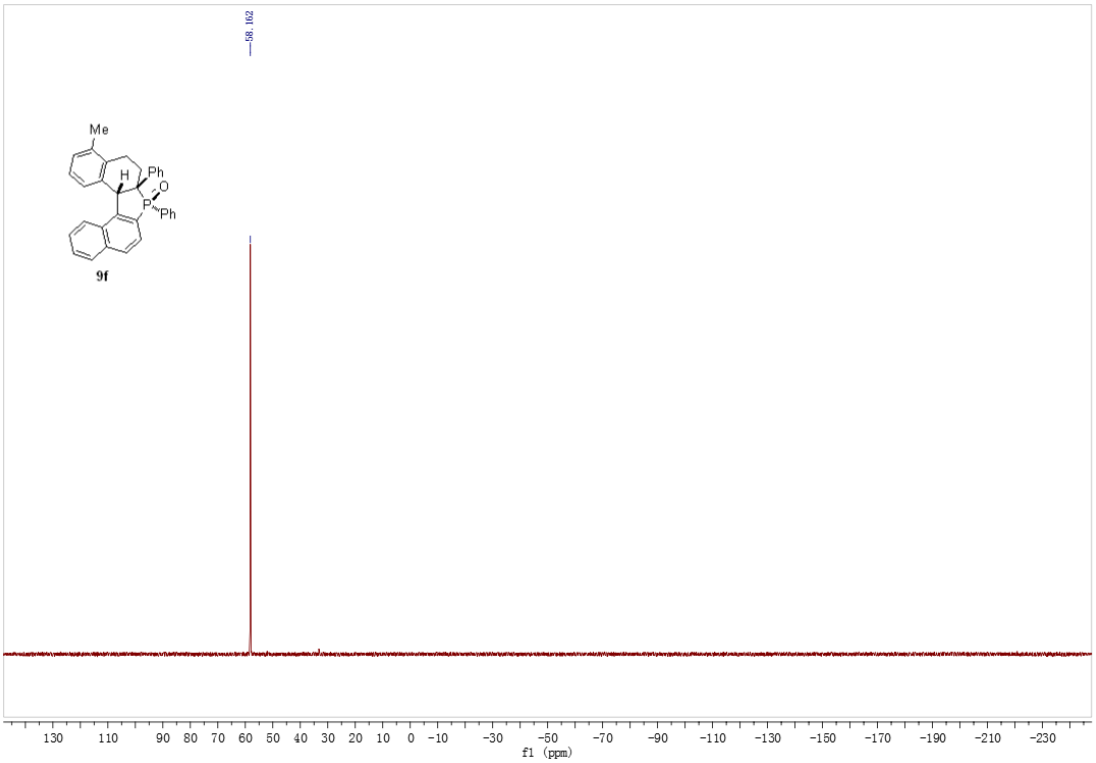
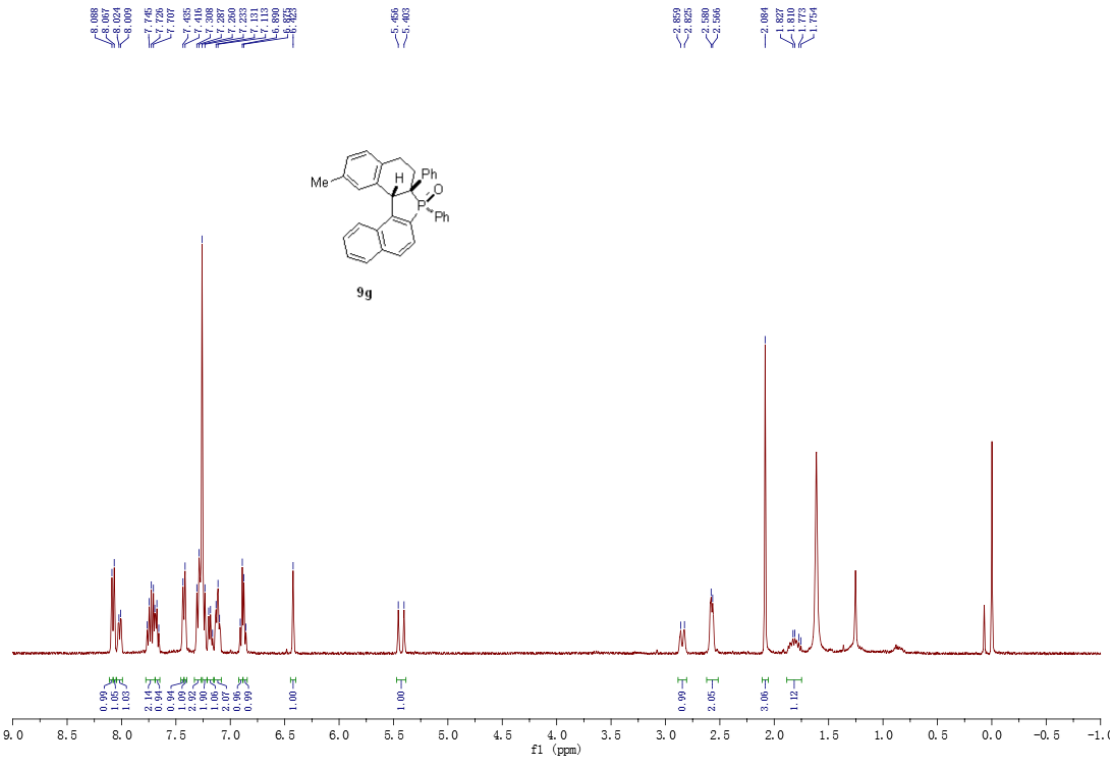
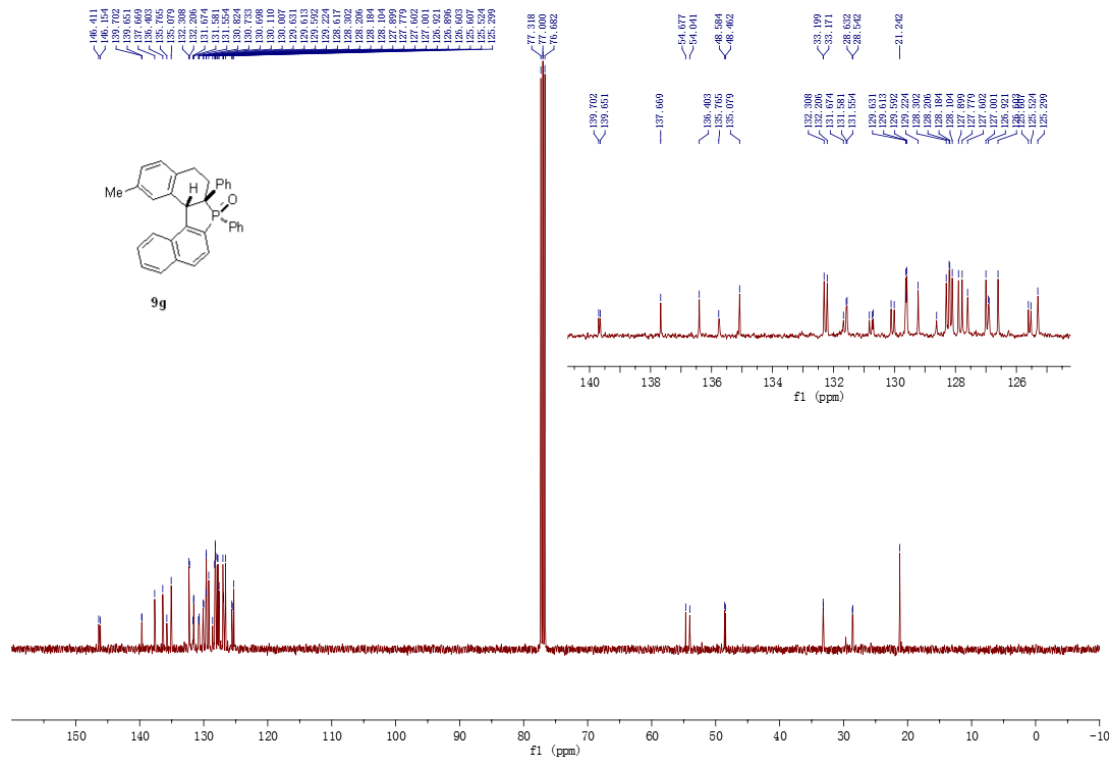


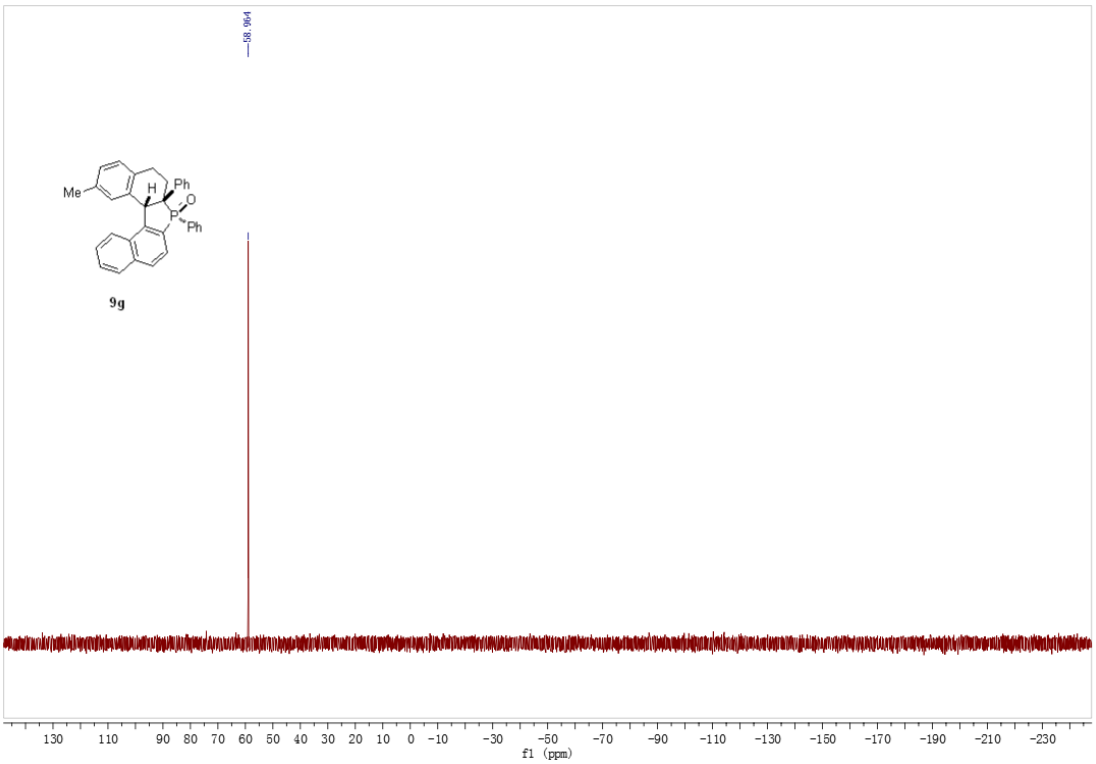
^{31}P NMR



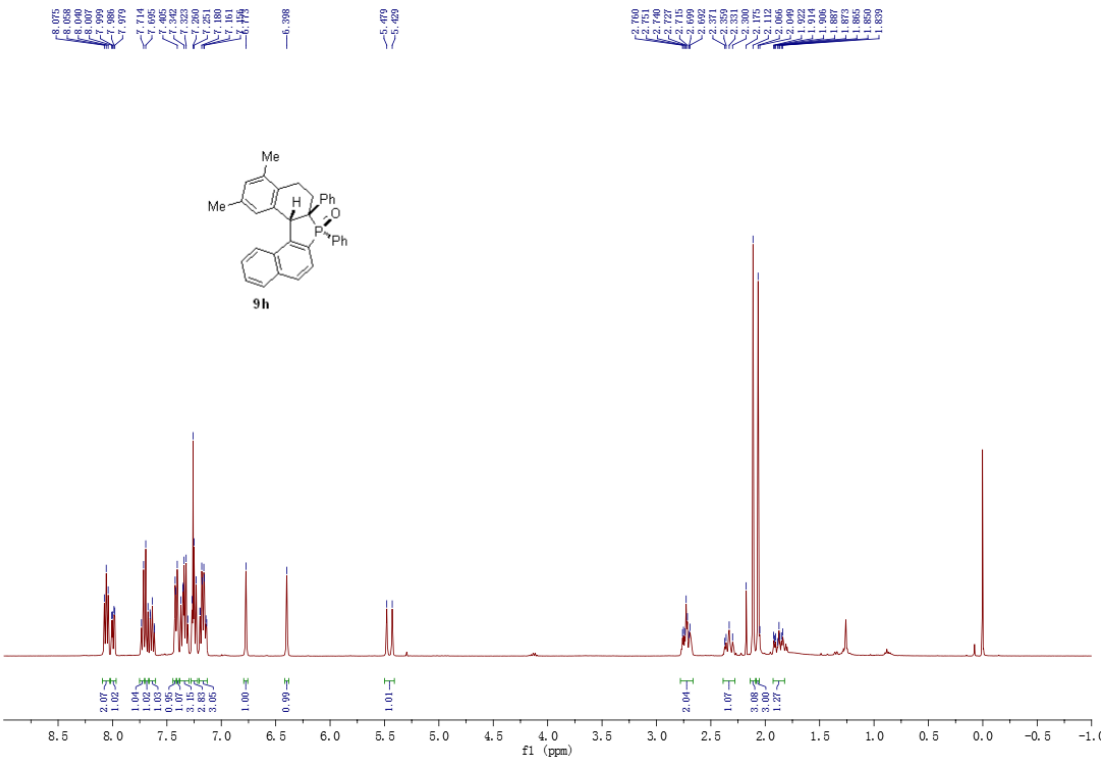
^{1}H NMR



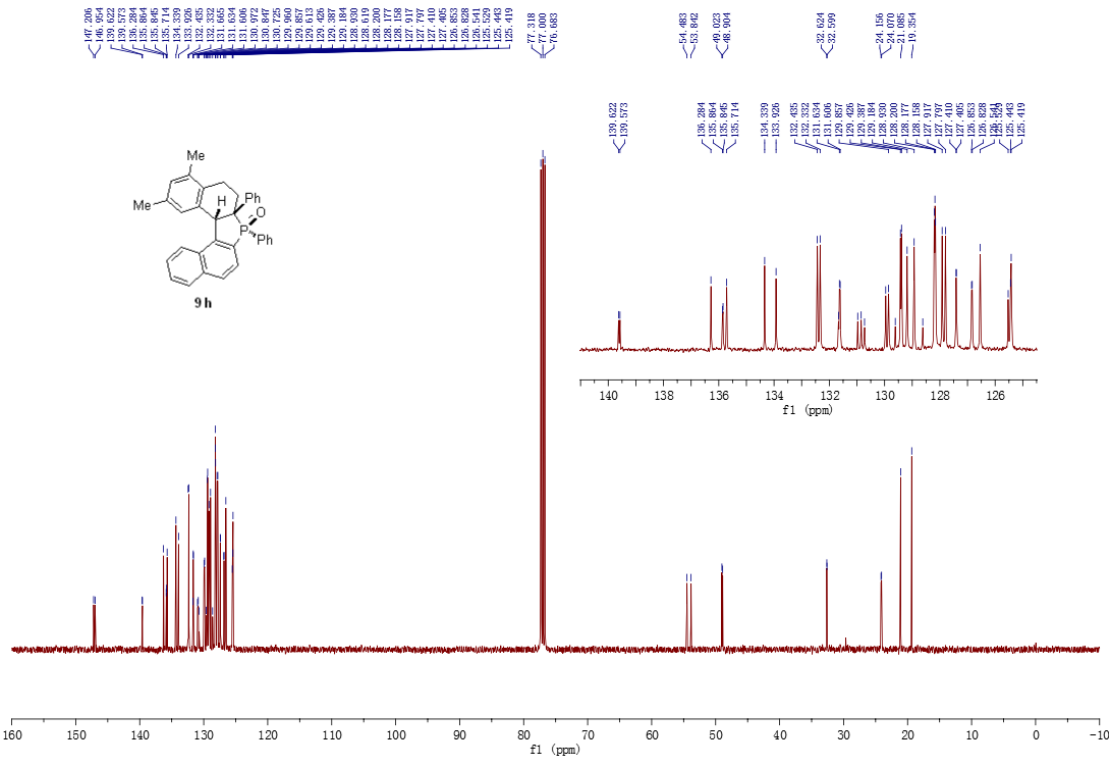
^{13}C NMR



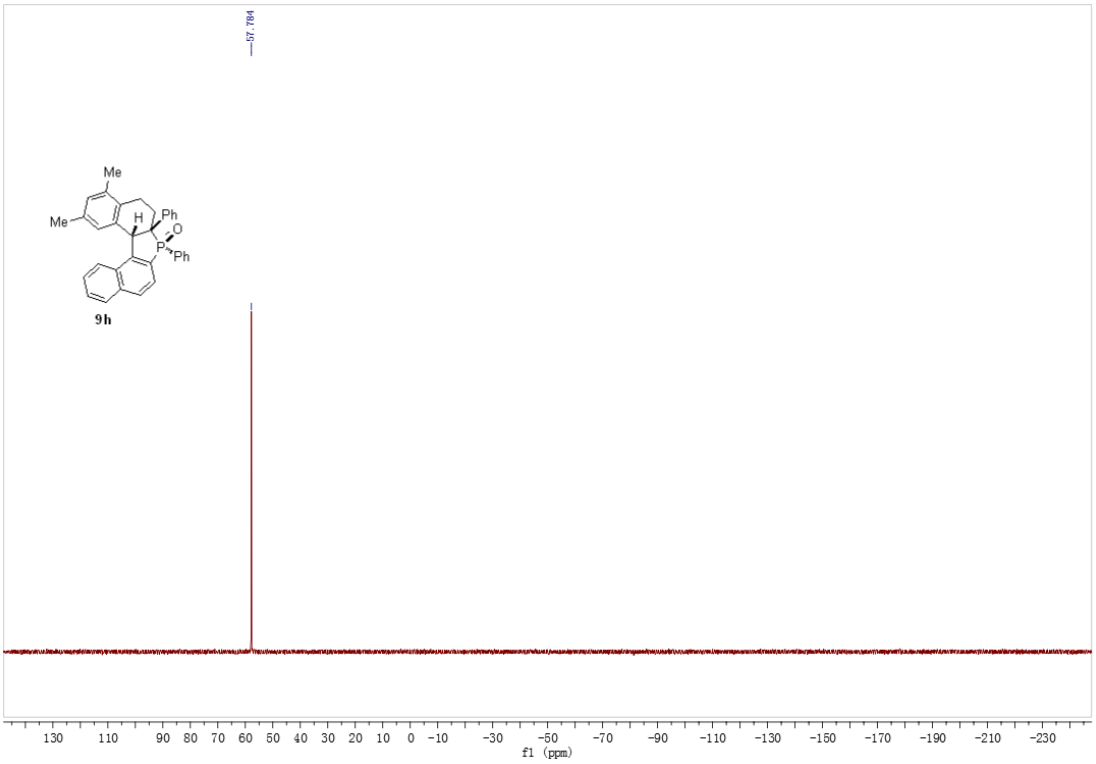
^{31}P NMR



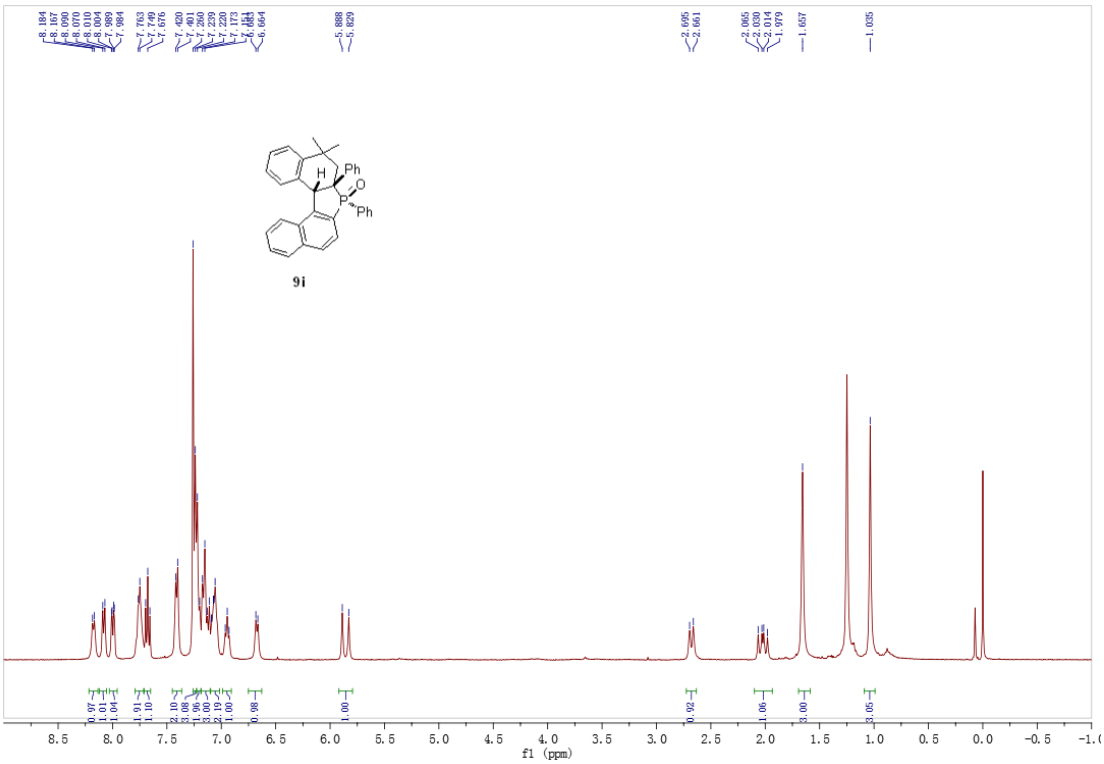
^{1}H NMR



^{13}C NMR



^{31}P NMR



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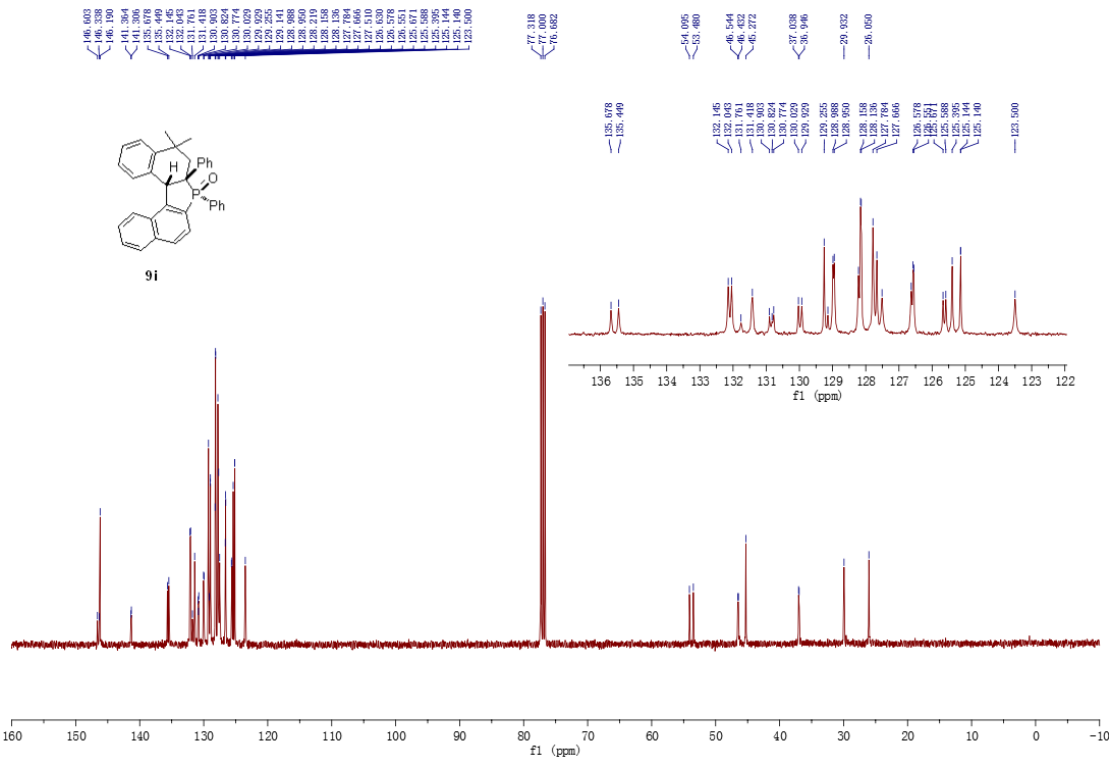
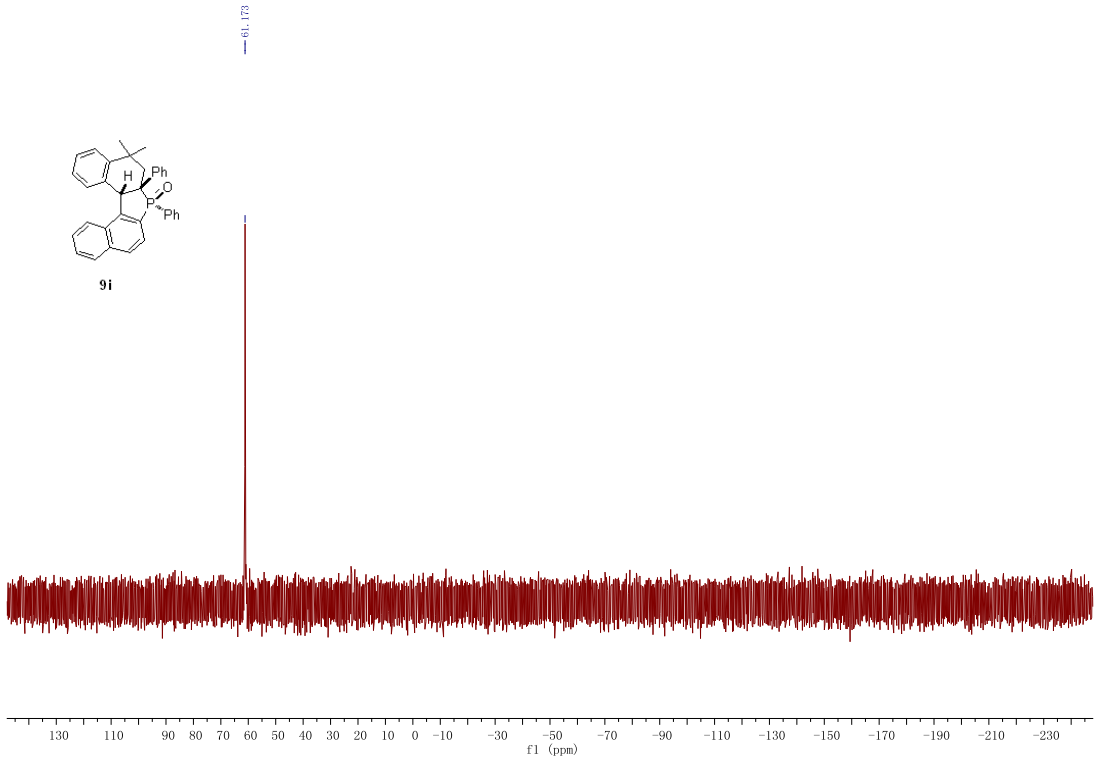
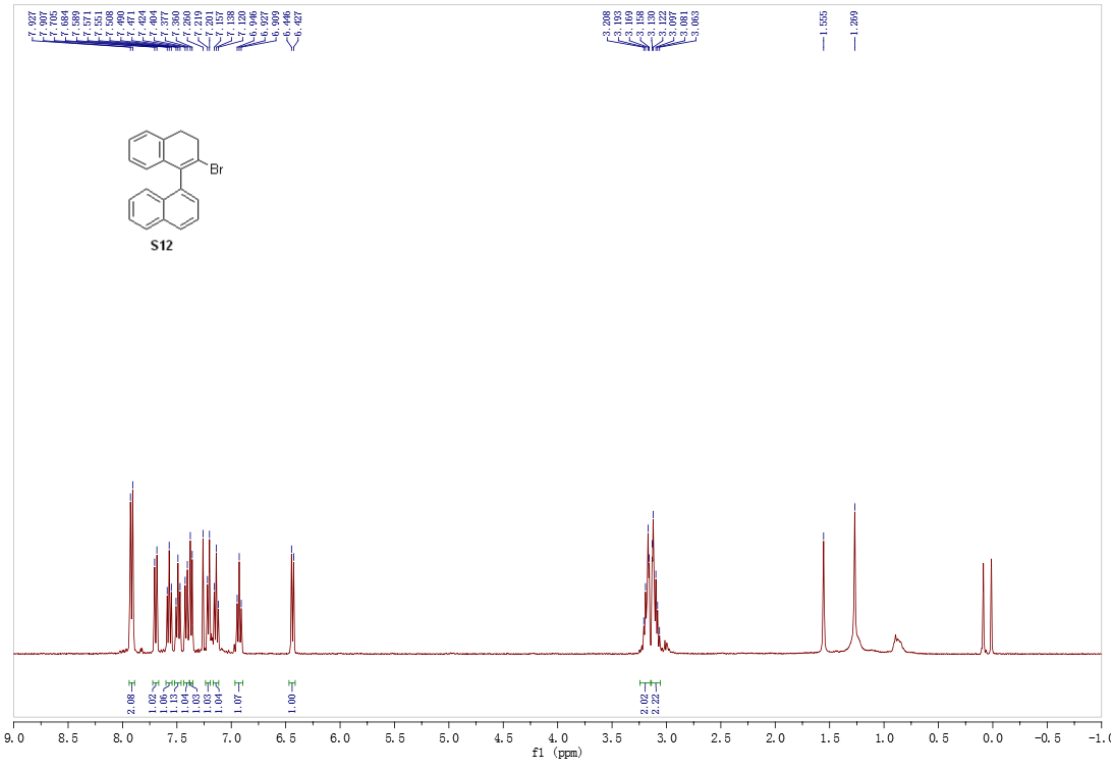


^{13}C NMR



^{31}P NMR



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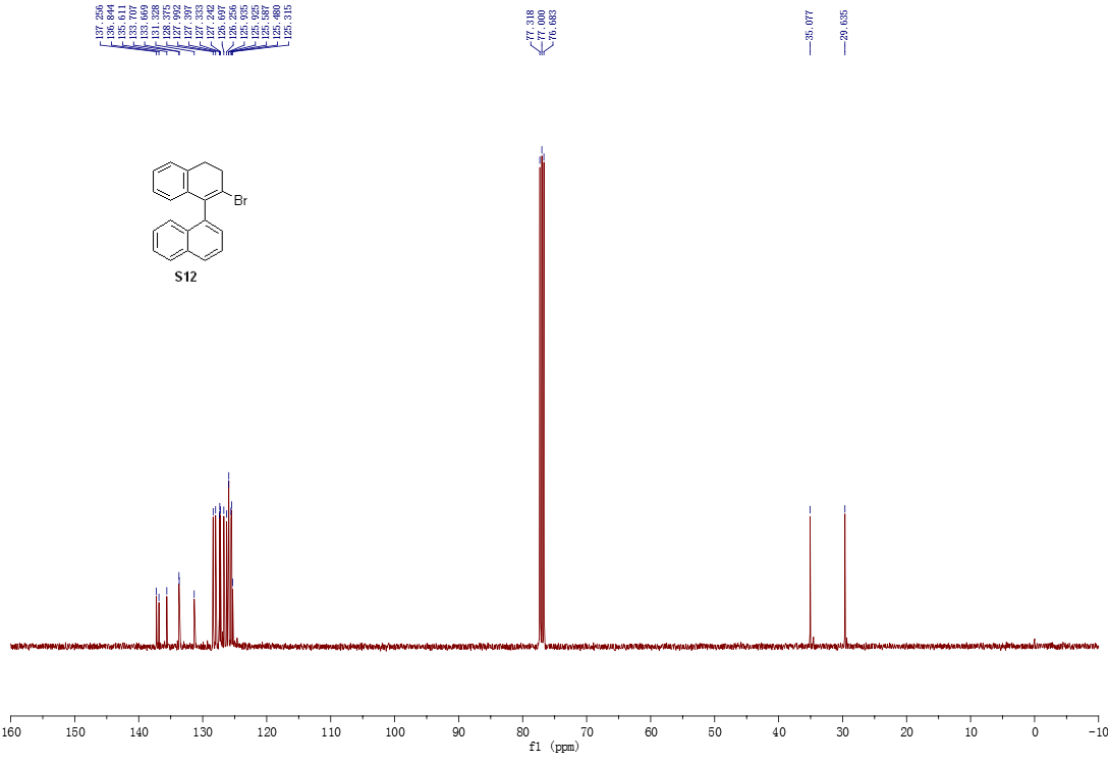

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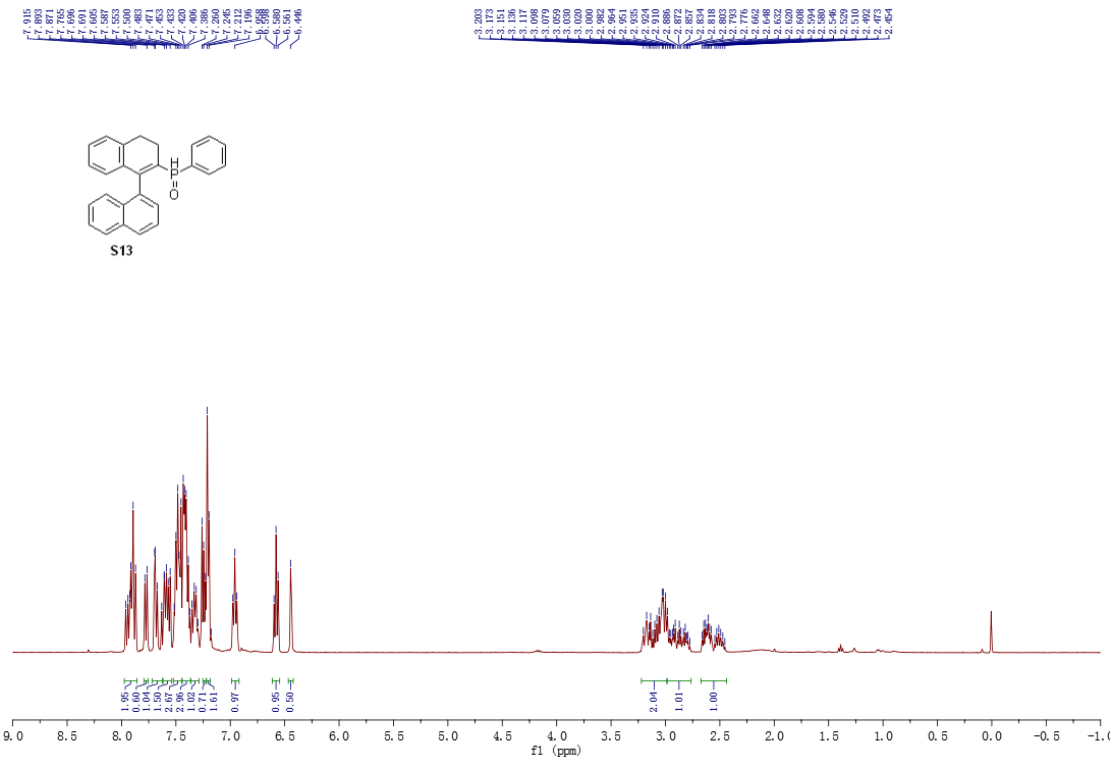

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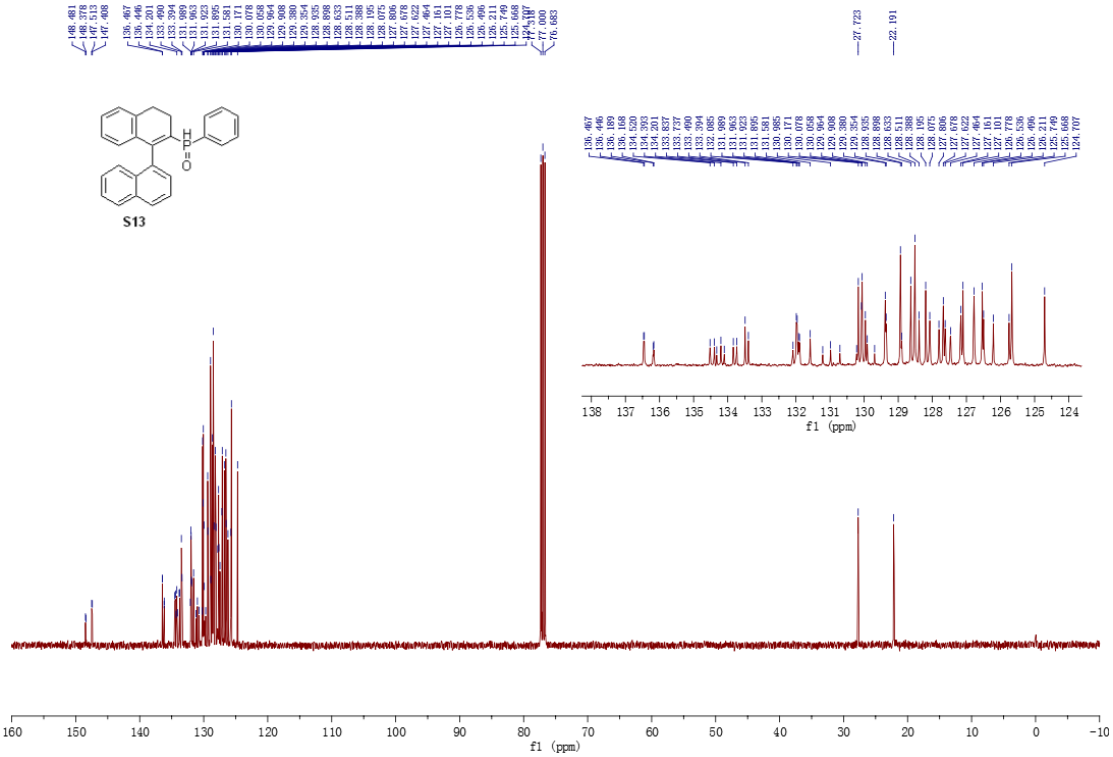

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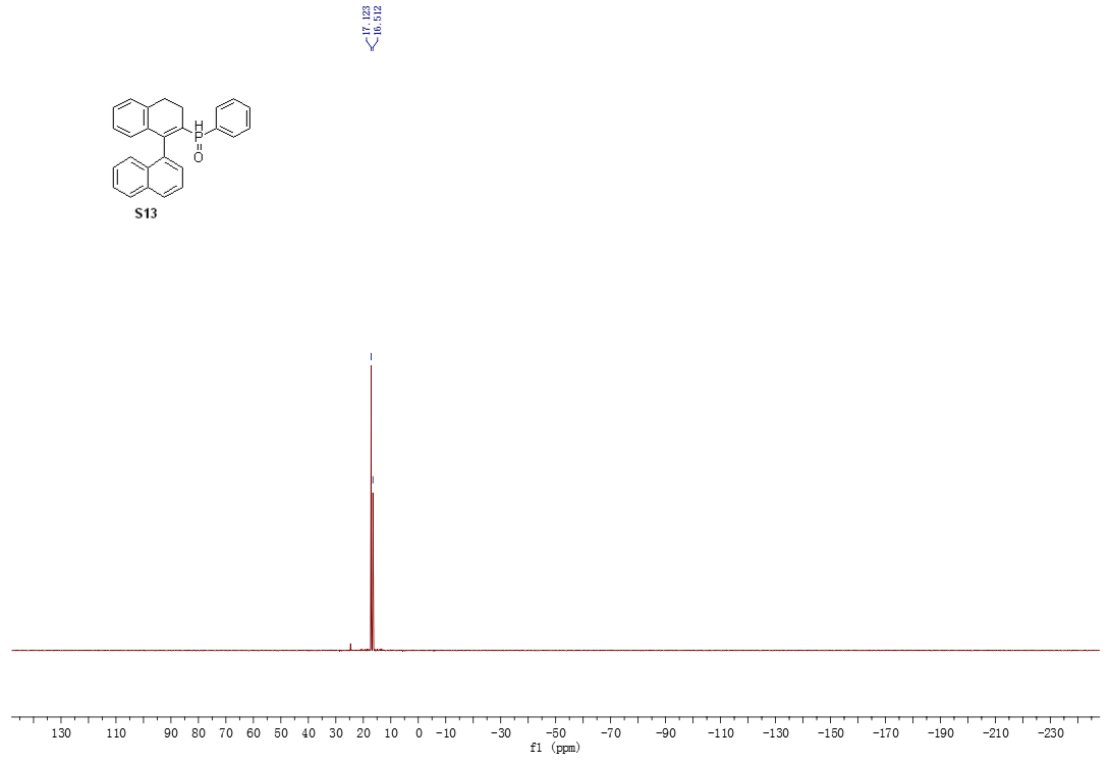

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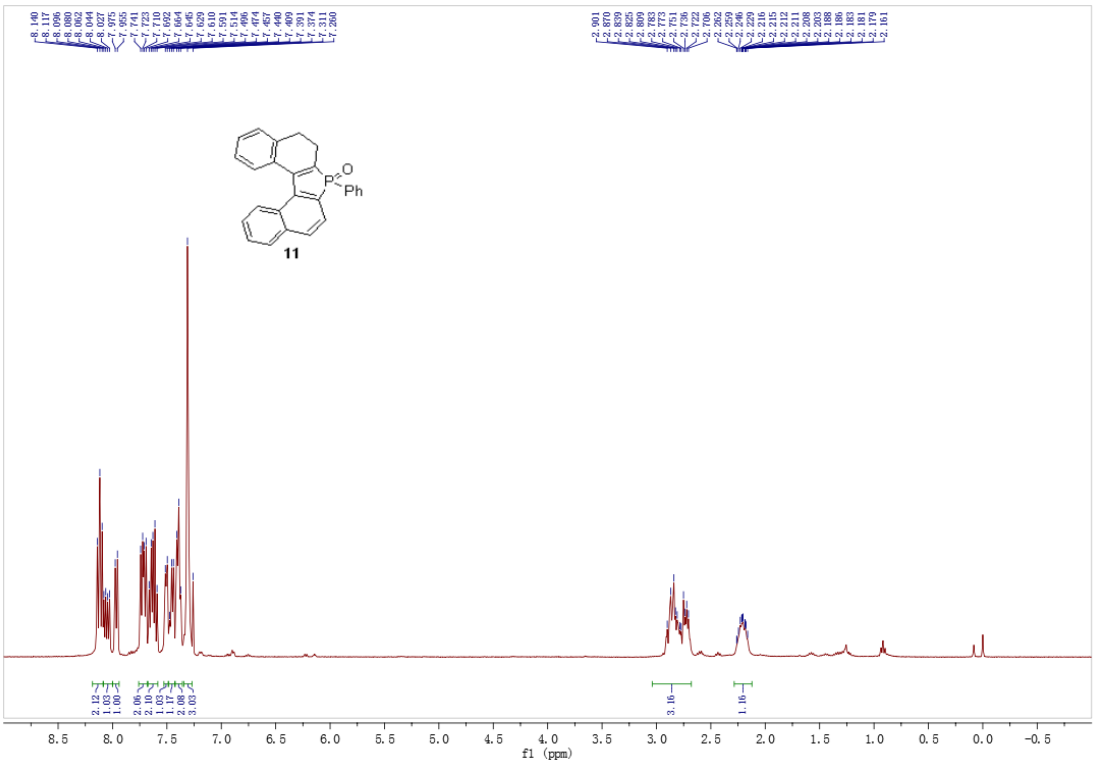

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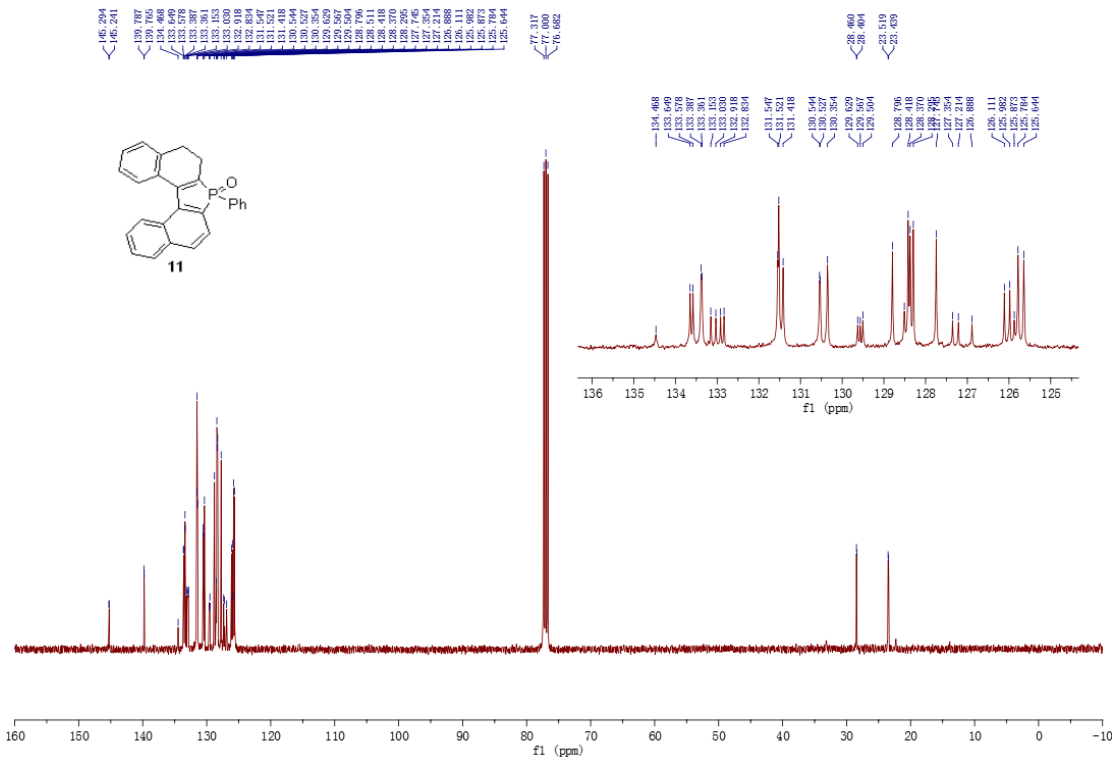

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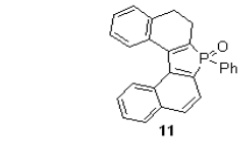
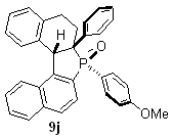


11

^{31}P NMR



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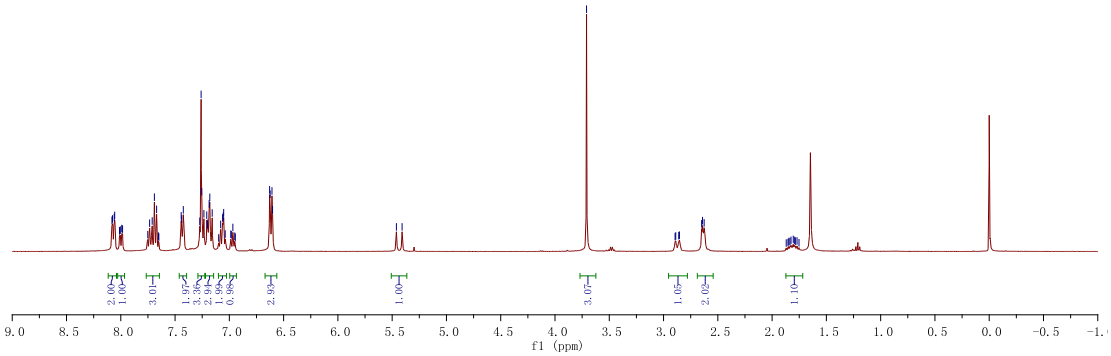

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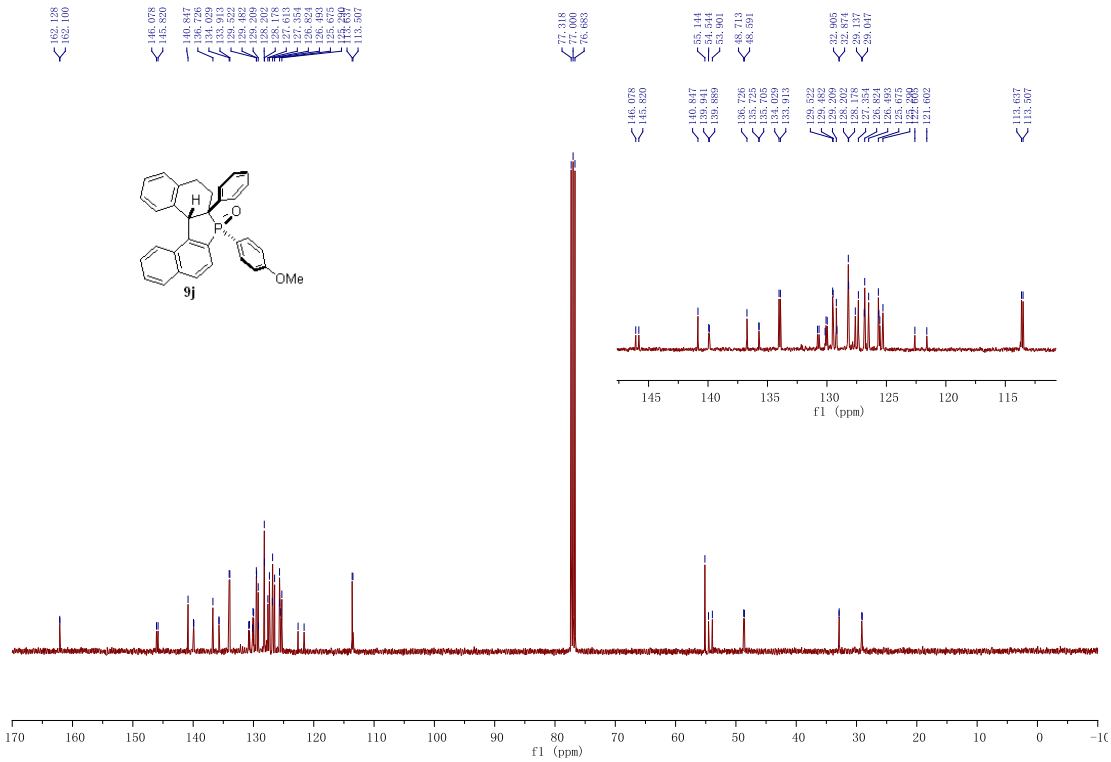

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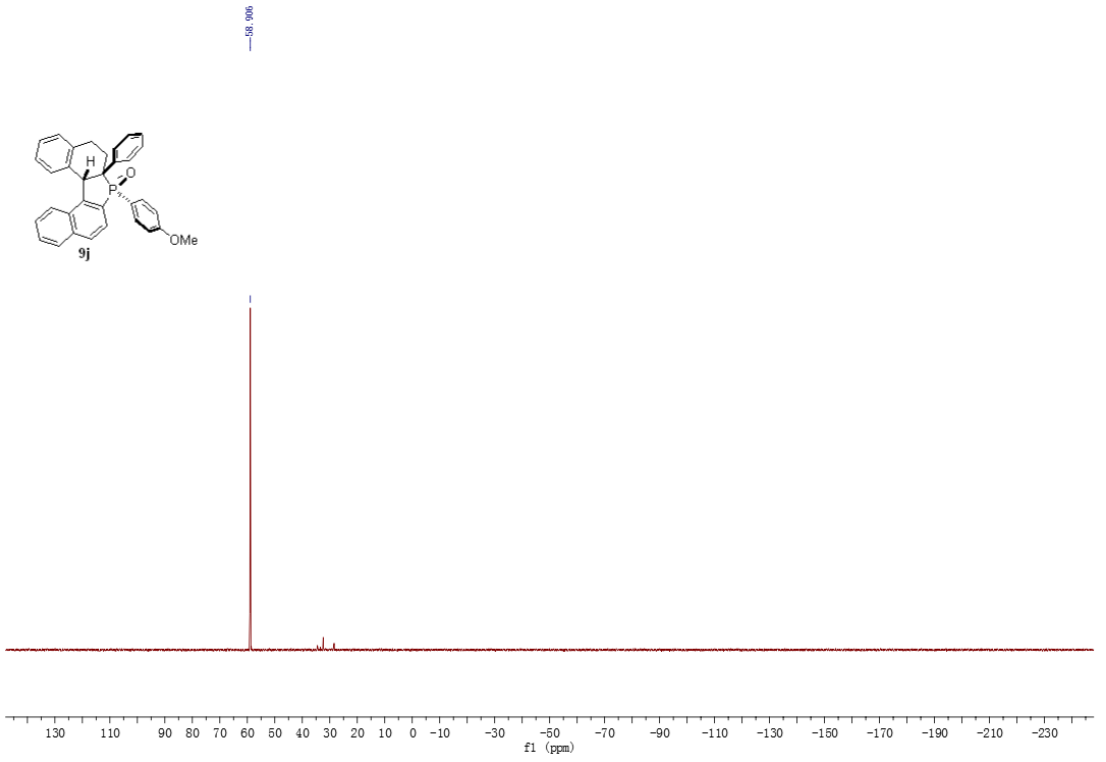

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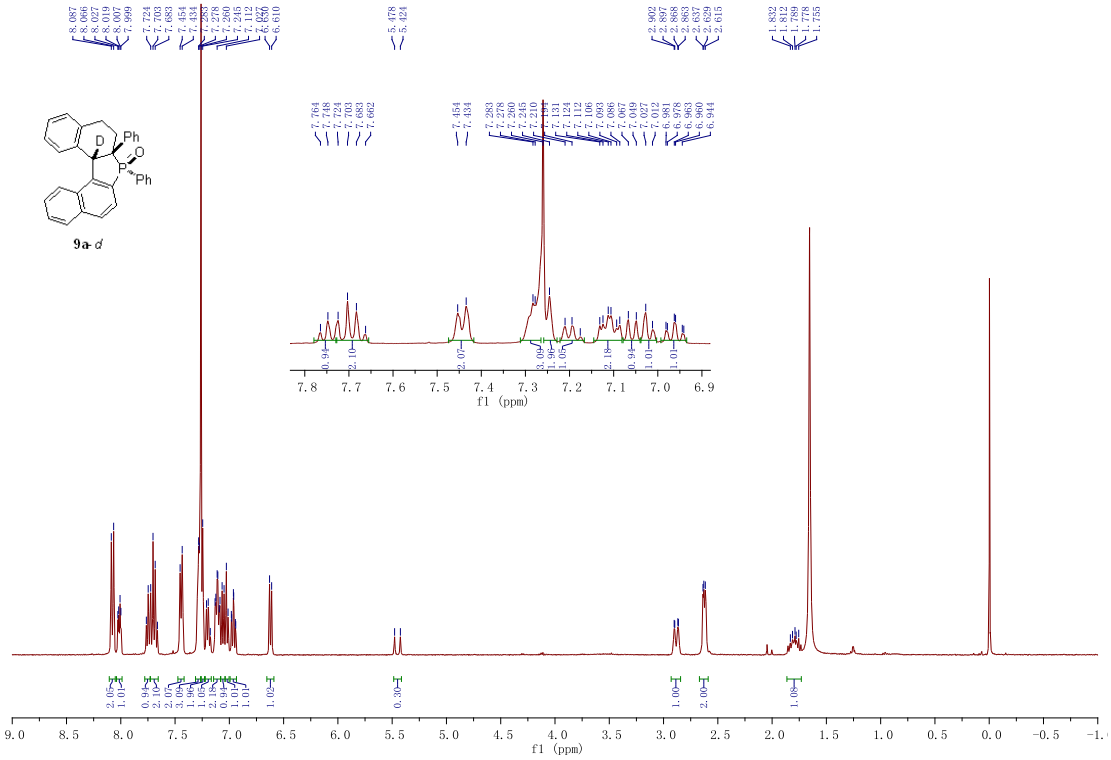

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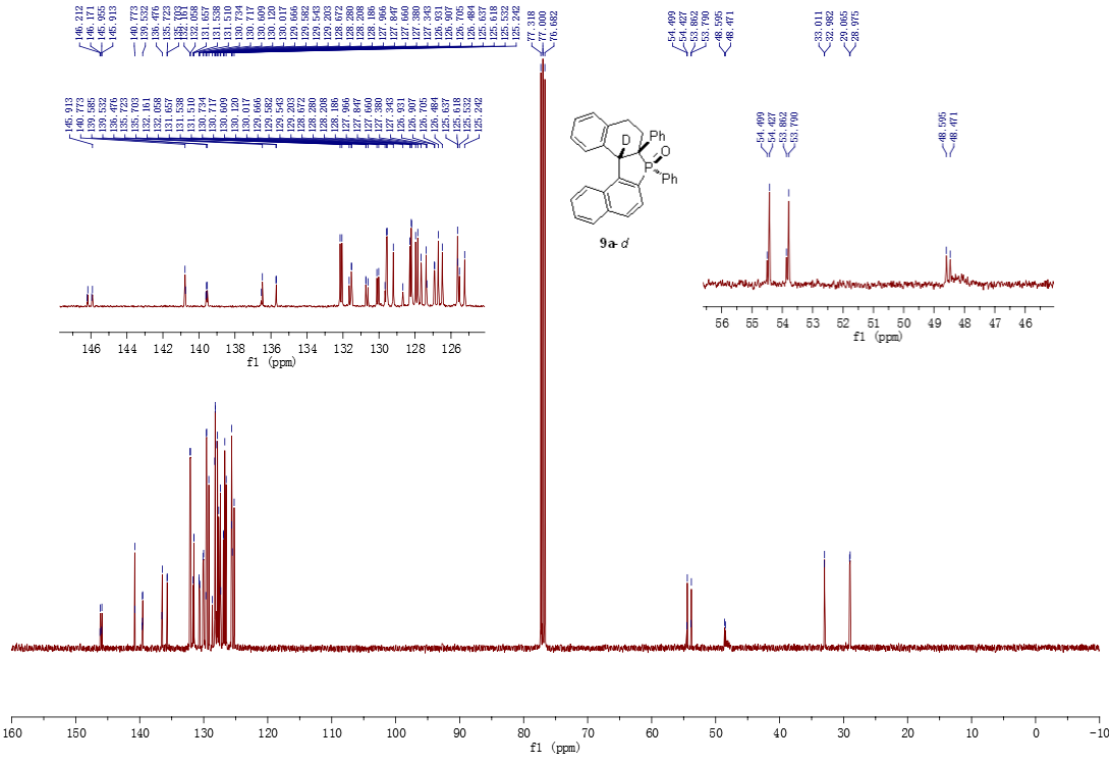

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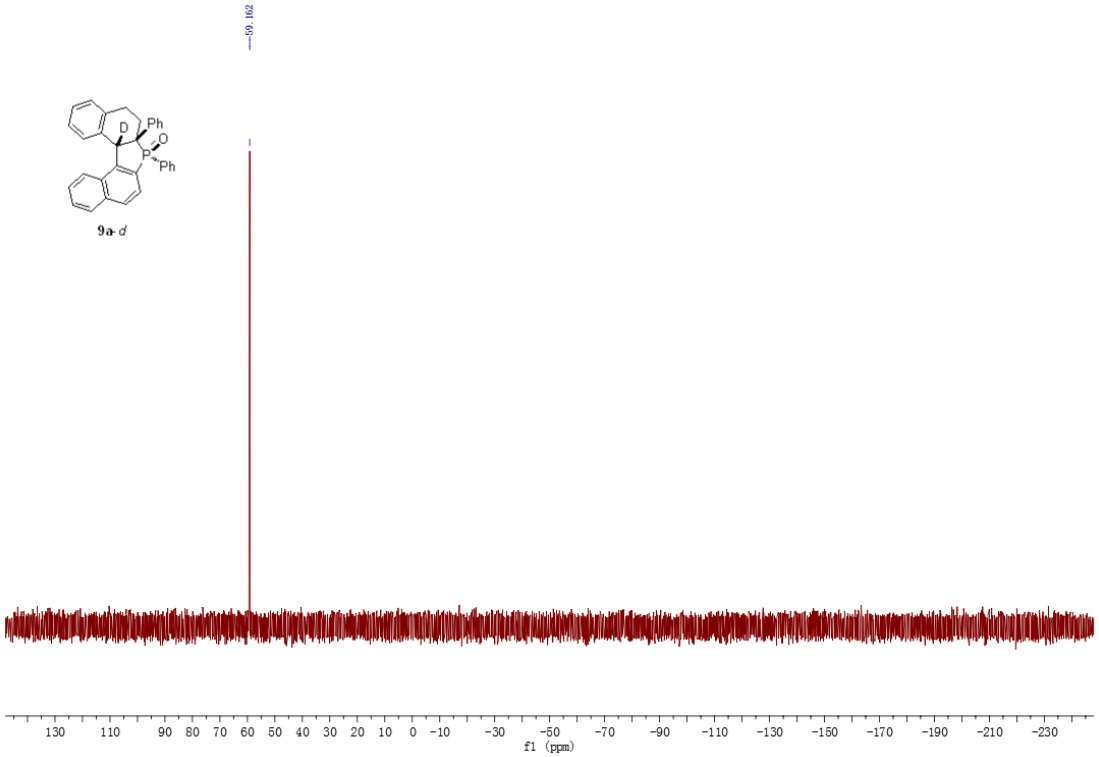
59.162
D
Ph
O
P
Ph
9a-d
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

^{31}P NMR

Data File F:\DATA\LIBIN\DATA\lb-8a-rac(IA,18%,0.8)-2.D
Sample Name: lb-8a-rac(IA,18%,0.8)-2

```
==========================================================================
Acq. Operator   : 系统
Sample Operator : 系统
Acq. Instrument : LC1260                          Location :   1
Injection Date  : 4/7/2017 10:11:27 AM
                                                  Inj Volume : Manually
Acq. Method     : F:\METHOD\JFeng.M
Last changed    : 4/7/2017 9:35:28 AM by 系统
                  (modified after loading)
Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
Last changed    : 4/7/2017 11:06:01 AM by 系统
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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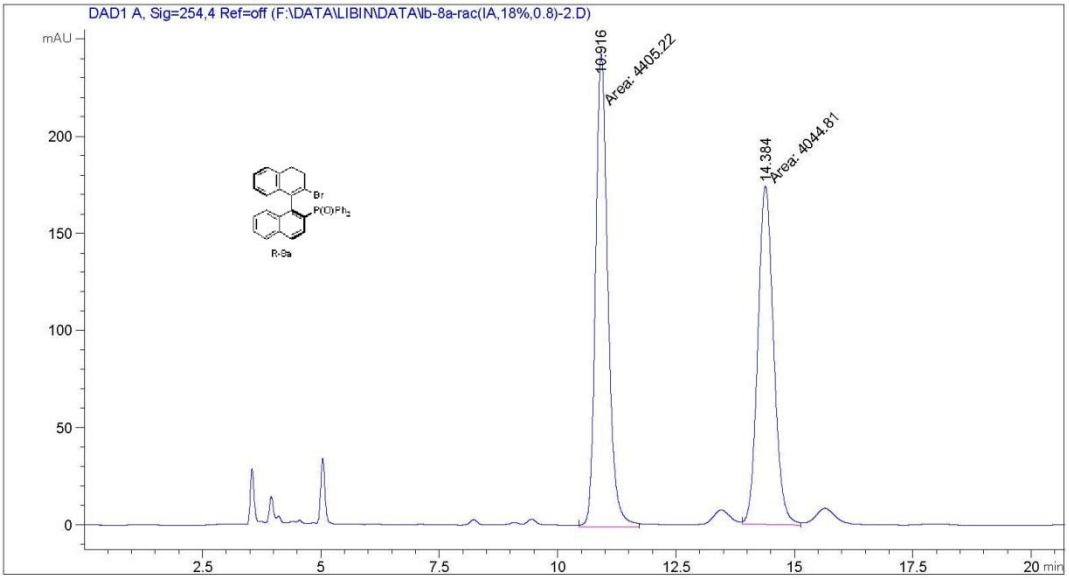


```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.916 MM    0.3012 4405.21631  243.73369  52.1326
   2  14.384 MM    0.3871 4044.80615  174.13228  47.8674

Totals :                 8450.02246  417.86597
```

Data File F:\DATA\LIBIN\DATA\lb-8a-ee(IA,18%,0.8)-2.D
Sample Name: lb-8a-ee(IA,18%,0.8)-2

```
==========================================================================
Acq. Operator   : 系统
                                                    Location :   1
Injection Date  : 4/7/2017 11:10:15 AM
Acq. Method     : JFeng.M
Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
Last changed    : 4/7/2017 11:06:01 AM by 系统
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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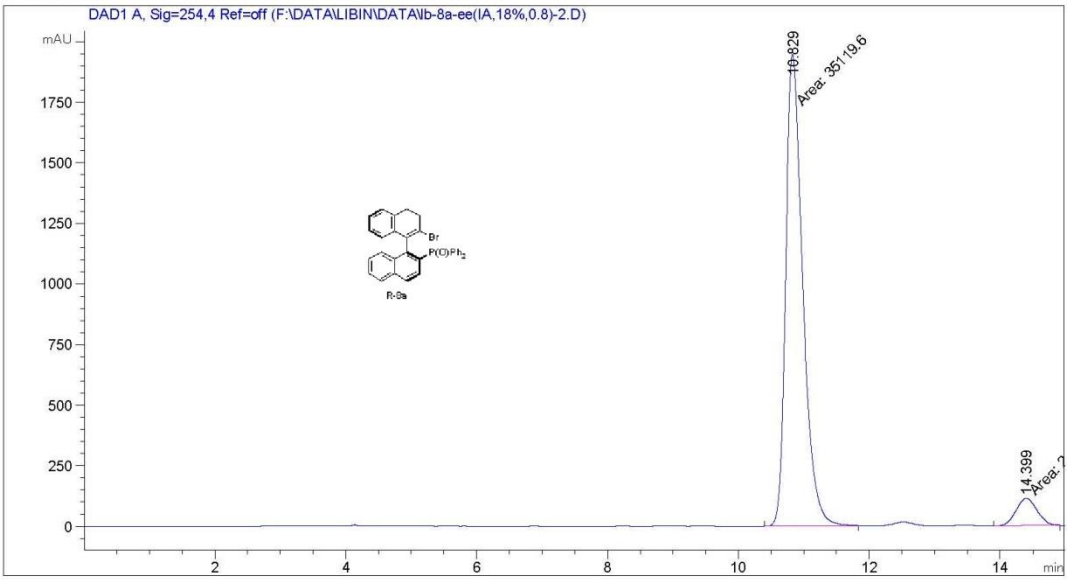


```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.829 MM    0.3004 3.51196e4  1948.36487  93.4107
   2  14.399 MM    0.3671 2477.38354  112.47592   6.5893

Totals :                  3.75970e4  2060.84079

==========================================================================
                          *** End of Report ***
```

LC1260 4/7/2017 11:27:06 AM 系统 Page 1 of 1

Data File F:\DATA\LIBIN\DATA\ZMK-1-151-IA-RAC.D
Sample Name: ZMK-1-151-IA-RAC

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==========================================================================
Acq. Operator   : 系统
Sample Operator : 系统
Acq. Instrument : LC1260                        Location :   1
Injection Date  : 4/1/2017 9:44:45 PM
                                                Inj Volume : Manually
Acq. Method     : F:\METHOD\HECF.M
Last changed    : 4/1/2017 8:30:28 PM by 系统
                  (modified after loading)
Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
Last changed    : 2/13/2014 11:27:44 PM by SYSTEM
Additional Info : Peak(s) manually integrated
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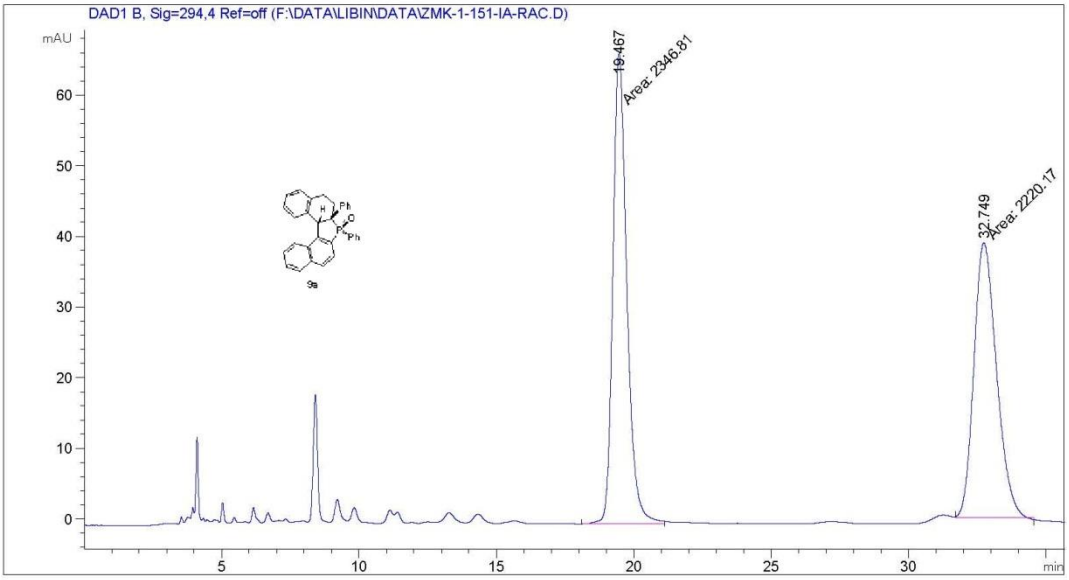


```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=294,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.467 MM    0.5873 2346.81177   66.59821  51.3865
   2  32.749 MM    0.9518 2220.17334   38.87541  48.6135

Totals :                  4566.98511  105.47363
```

Data File F:\DATA\LIBIN\DATA\ZMK-1-147-IA-7.D
Sample Name: ZMK-1-147-IA-7

```
======================================================================
Acq. Operator   : 系统
                                                    Location :   1
Injection Date  : 4/1/2017 8:36:52 PM
Acq. Method     : HECF.M
Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
Last changed    : 2/13/2014 11:27:44 PM by SYSTEM
Additional Info : Peak(s) manually integrated
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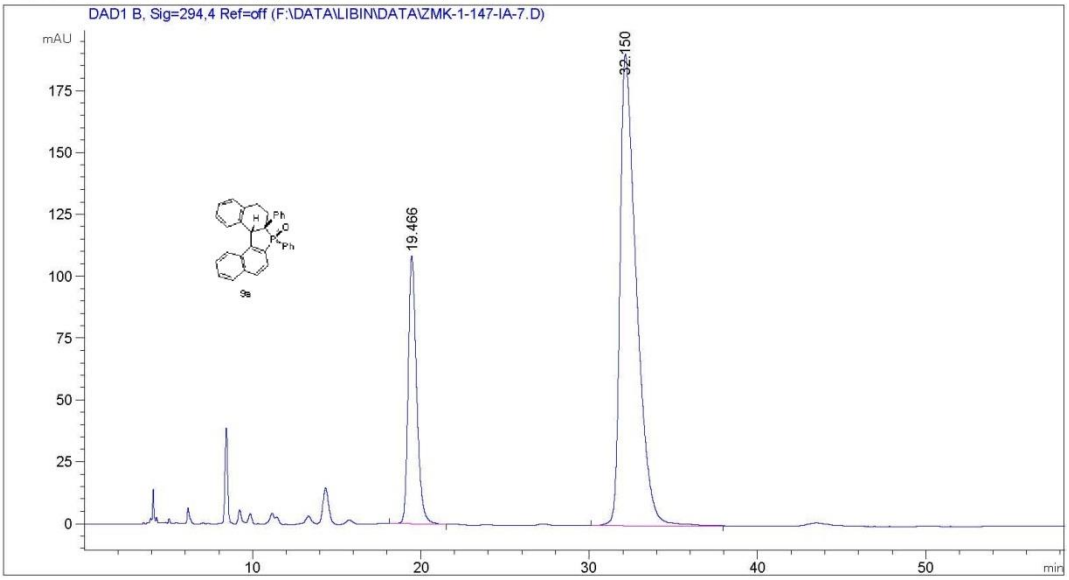


```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=294,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.466 BB    0.5299 3773.41406  108.44649  22.7233
   2  32.150 BB    0.9817 1.28325e4   190.53664  77.2767

Totals :                  1.66059e4   298.98312

======================================================================
                        *** End of Report ***
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