Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.
This journal is © the Partner Organisations 2016

Supporting Information

Visible Light Mediated Aerobic Radical C-H Phosphorization toward Arylphosphonates

Pan Peng, Long Peng, Guangyu Wang, Fangyu Wang, Yi Luo and Aiwen Lei*

aiwenlei@whu.edu.cn

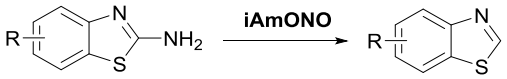
Table of Contents

General information

All reactions were run under air atmosphere with a dry air balloon fitted on a Schlenk tube. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel. EPR spectra were recorded on a Bruker A-200 spectrometer. HPLC yields were recorded with a DIONEX P680 HPLC Pump. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. High resolution mass spectra (HRMS) were measured with a Thermo Fisher Scientific LTQ FT Ultra. The known compounds were characterized by ^{1}H NMR, ^{13}C NMR. ^{1}H and ^{13}C NMR data were recorded with ADVANCE III 400 MHz spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), and $CDCl_3$ (77.16 ppm for ^{13}C), respectively.

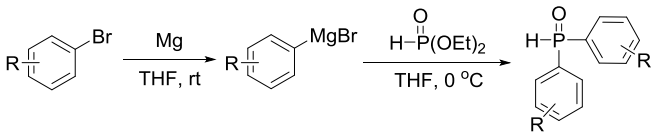
Experimental section

1) General Procedure for Preparation of Benzothiazoles[1]



A 50 mL Schlenk tube was charged with 2-aminobenzothiazole derivative (6.5 mmol) and 10 mL of THF, and then isoamyl nitrite (14.3 mmol) was added slowly into the solution. The resultant mixture was refluxed for 30 minutes, and poured into ice-water, and the resultant aqueous mixture was extracted with ethyl acetate (3×30 mL). The organic extracts were combined and washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuum and purified by column chromatography, giving the desired benzothiazoles in similar yields with the reported procedure.

2) General Procedure for Preparation of Phosphine Oxides[2]



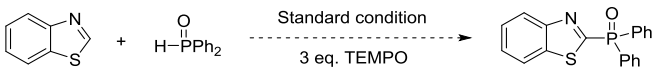
Phenylmagnesium bromide was prepared from aryl bromides (32.6 mmol) and magnesium (0.95 g, 39.6 mmol). Diethylphosphite (1.29 mL, 10.0 mmol) was added dropwisely to a solution of

phenylmagnesium bromide at 0 °C. The mixture was aged for 15 minutes at 0 °C, then stirred at ambient temperature for two hours. After that cooled again to 0 °C, and 75 mL NH_4Cl aqueous was added slowly. The mixture was extracted with diethyl ether. Washed the organic phase with $NaHCO_3$ aqueous and brine, then dried over with Na_2SO_4. After the solvent was completely removed under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 1/1 as eluent to give the product.

3) Mechanism Study

3.1 Radical Trapping Experiment

Diphenylphosphine oxide **2a** (121.3 mg, 0.6 mmol), TEMPO (93.8mg, 0.6mmol) and Na_2Eosin Y (4.2 mg, 0.006 mmol) was added to Schlenk tube equipped with a stir bar, a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. Then, benzothiazole **1a** (23.6 mg, 0.2 mmol), $CHCl_3$ (1.0 mL) was injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir at room temperature under 23w white light for 16 h. The result was detected by HPLC.



3.2 “Light/dark” experiments over the time.

We determined the reaction yield at different time with or without visible light at the standard condition. The yield was determined by ^{31}P NMR analysis using $OPPh_3$ as internal standard.

Table 1 “Light/dark” experiments over the time.

Time / h	0	4	6	10	12	16
Yield / %	0	12	12	34	34	55

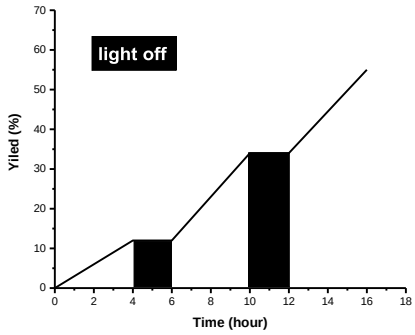


Fig. 1 “Light/dark” experiments over the time.

3.3 General Procedure for the Electron Paramagnetic Resonance (EPR) Experiment

Typical procedure: Diphenylphosphine oxide **2a** (121.3 mg, 0.6 mmol) and Na_2Eosin Y (4.2 mg, 0.006 mmol) was added to Schlenk tube equipped with a stir bar, a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. $CHCl_3$ (1.0 mL) was injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir at room temperature under 23 w white light for 1 h, followed by the addition of 10 ul DMPO and stir at room temperature under 23 w white light for 5 min. Then, this reaction was taken out by capillary and was analyzed by EPR at room temperature. This result was shown in Figure 2.

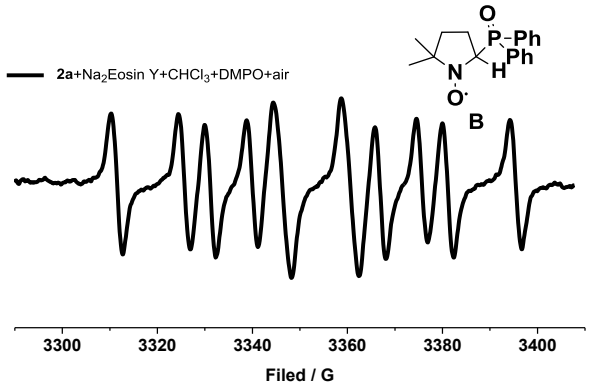
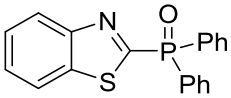


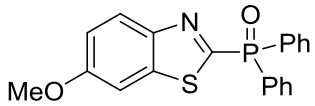
Fig. 2 The electron paramagnetic resonance (EPR) spectra (X band, 9.4 GHz, room temperature)

4) Procedure and analytical data of compounds 3aa-3ah

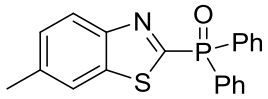


Benzo[d]thiazol-2-yldiphenylphosphine oxide (3aa):[3] Typical procedure: Diphenylphosphine oxide **2a** (121.3 mg, 0.6 mmol) and Na_2Eosin Y (4.2 mg, 0.006 mmol) was added to Schlenk tube equipped with a stir bar, a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. Then, benzothiazole **1a** (23.6 mg, 0.2 mmol), $CHCl_3$ (1.0 mL) was injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir at room temperature under 23w white light for 16 h. Thereafter, the reaction organic layers were concentrated under reduced pressure. The residue was separated on a silica gel column with petroleum ether (60-90 ºC), ethyl acetate (2:1) as eluent to afford the desired product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.2 Hz, 1H), 8.00-7.95

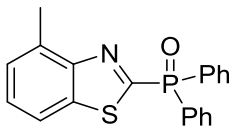
(m, 5H), 7.57-7.49 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8 (d, J_{C-P} = 127.5 Hz), 155.4 (d, J_{C-P} = 21.5 Hz), 136.8, 132.7 (d, J_{C-P} = 2.8 Hz), 132.0 (d, J_{C-P} = 10.2 Hz), 131.0 (d, J_{C-P} = 108.9 Hz), 128.7 (d, J_{C-P} = 12.8 Hz), 126.8, 126.7, 124.8, 122.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.11.



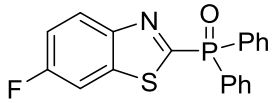
(6-Methoxybenzo[d]thiazol-2-yl)diphenylphosphine oxide (3ba):[3] The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 1H), 7.98-7.93 (m, 4H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.52-7.48 (m, 4H), 7.42 (s, 1H), 7.16-7.14 (m, 1H), 3.90 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (d, J_{C-P} = 130.5 Hz), 159.0, 150.3 (d, J_{C-P} = 22.0 Hz), 138.8, 132.7 (d, J_{C-P} = 2.8 Hz), 132.0 (d, J_{C-P} = 10.2 Hz), 131.3 (d, J_{C-P} = 108.9 Hz), 128.8 (d, J_{C-P} = 12.8 Hz), 125.4, 117.3, 103.5, 56.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.00.



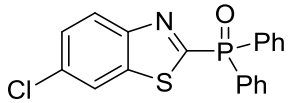
(6-Methylbenzo[d]thiazol-2-yl)diphenylphosphine oxide (3ca):[3] The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.98 – 7.93 (m, 4H), 7.79 (s, 1H), 7.58 – 7.54 (m, 2H), 7.51 – 7.46 (m, 4H), 7.35 (dd, *J* = 8.5, 1.3 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (d, J_{C-P} = 128.4 Hz), 153.7 (d, J_{C-P} = 21.7 Hz), 137.2, 137.2, 132.7 (d, J_{C-P} = 2.9 Hz), 132.0 (d, J_{C-P} = 10.2 Hz), 131.2 (d, J_{C-P} = 108.9 Hz), 128.7 (d, J_{C-P} = 12.8 Hz), 128.6, 124.3, 121.7, 21.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.18.



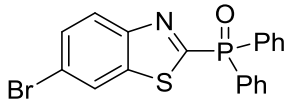
(4-Methylbenzo[d]thiazol-2-yl)diphenylphosphine oxide (3da):[4] The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (m, 4H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.57-7.53 (m, 2H), 7.53 – 7.49 (m, 4H), 7.38-7.31 (m, 2H), 2.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9 (d, J_{C-P} = 129.0 Hz), 155.0 (d, J_{C-P} = 21.1 Hz), 136.7, 134.9, 132.6 (d, J_{C-P} = 2.8 Hz), 131.9 (d, J_{C-P} = 10.2 Hz), 130.8, 128.6 (d, J_{C-P} = 12.8 Hz), 127.0, 126.7, 119.5, 18.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.38.



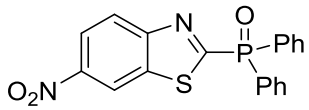
(6-Fluorobenzo[d]thiazol-2-yl)diphenylphosphine oxide (3ea):[3] The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 9.1, 4.8 Hz, 1H), 8.16 – 8.12 (m, 4H), 7.68 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.53 – 7.49 (m, 4H), 7.32 – 7.27 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8 (d, $J_{C\text{-}P,\ C\text{-}F}$ = 126.2, 3.6 Hz), 161.3 (d, $J_{C\text{-}F}$ = 248.9 Hz), 152.2 (d, *J* = 21.8 Hz), 138.1 (d, $J_{C\text{-}F}$ = 11.3 Hz), 132.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.0 (d, $J_{C\text{-}P}$ = 10.3 Hz), 130.8 (d, $J_{C\text{-}P}$ = 109.2 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.9 Hz), 126.0 (d, $J_{C\text{-}F}$ = 9.7 Hz), 116.0 (d, $J_{C\text{-}F}$ = 25.2 Hz), 108.1 (d, $J_{C\text{-}F}$ = 26.5 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ 19.93.



(6-Chlorobenzo[d]thiazol-2-yl)diphenylphosphine oxide (3fa):[5] The synthesis procedure is the same as for **3aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.98 – 7.93 (m, 5H), 7.60-7.57 (m, 2H), 7.53 – 7.48 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9 (d, $J_{C\text{-}P}$ = 125.1 Hz), 154.0 (d, $J_{C\text{-}P}$ = 21.6 Hz), 138.1, 133.0, 132.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.0 (d, $J_{C\text{-}P}$ = 10.3 Hz), 130.8 (d, $J_{C\text{-}P}$ = 109.2 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.9 Hz), 127.8, 125.6, 121.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.89.

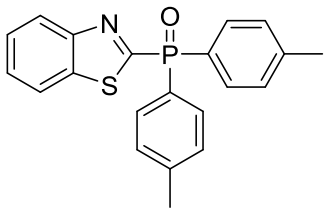


(6-Bromo-1H-inden-2-yl)diphenylphosphine oxide (3ga):[3] The synthesis procedure is the same as for **3aa.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 1.8 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.98-7.93 (m, 4H), 7.63 (dd, J=8.8, 1.9 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.65 – 7.56 (m, 3H), 7.53 – 7.48 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 (d, $J_{C\text{-}P}$ = 124.9 Hz), 154.3 (d, $J_{C\text{-}P}$ = 21.5 Hz), 138.5, 132.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.0 (d, $J_{C\text{-}P}$ = 10.3 Hz), 130.7 (d, $J_{C\text{-}P}$ = 109.2 Hz), 130.4, 128.82 (d, $J_{C\text{-}P}$ = 12.9 Hz), 125.9, 124.7, 120.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.98.

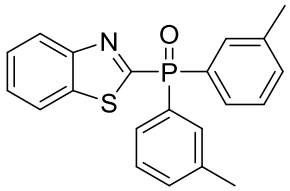


(6-Nitrobenzo[d]thiazol-2-yl)diphenylphosphine oxide (3ha):[4] The synthesis procedure is the same as for **3aa.** ^{1}H NMR (400 MHz, DMSO) δ 9.34 (d, *J* = 1.0 Hz, 1H), 8.42 – 8.37 (m, 2H), 7.88 (dd, *J* = 12.6, 7.4 Hz, 4H), 7.70 (t, *J* = 7.1 Hz, 2H), 7.72 – 7.59 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 174.5 (d, $J_{C\text{-}P}$ = 118.2 Hz), 157.9 (d, $J_{C\text{-}P}$ = 20.8 Hz), 145.5, 136.7, 133.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.5 (d, $J_{C\text{-}P}$ =

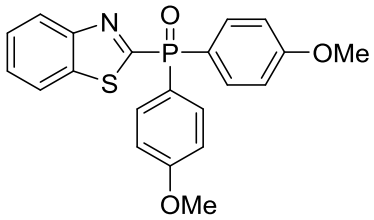
10.3 Hz), 130.1 (d, J_{C-P} = 108.1 Hz), 129.2 (d, J_{C-P} = 12.6 Hz), 125.1, 122.3, 120.4.^{31}P NMR (162 MHz, DMSO) δ 18.49.



Benzo[d]thiazol-2-yldi-p-tolylphosphine oxide (3ab):[3] The synthesis procedure is the same as for **3aa.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.83 (dd, *J* = 12.5, 8.1 Hz, 4H), 7.55-7.45 (m, 2H), 7.31-7.27 (m, 4H), 2.39 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5 (d, J_{C-P} = 126.2 Hz), 155.4 (d, J_{C-P} = 21.4 Hz), 143.3 (d, J_{C-P} = 2.9 Hz), 136.9, 132.1 (d, J_{C-P} = 10.6 Hz), 129.5 (d, J_{C-P} = 13.2 Hz), 127.8 (d, J_{C-P} = 111.6 Hz), 126.6 (d, J_{C-P} = 7.6 Hz), 124.8, 122.2, 21.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.93.

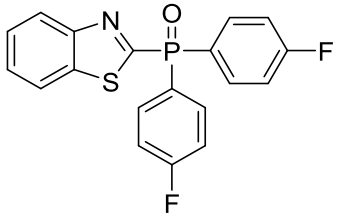


Benzo[d]thiazol-2-yldi-m-tolylphosphine oxide (3ac):[4] The synthesis procedure is the same as for **3aa.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.9 Hz, 1H), 8.01 – 7.99 (m, 1H), 7.79 (d, *J*=13.0 Hz, 1H), 7.76 – 7.71(m, 4H), 7.56-7.46 (m, 2H), 7.40-7.36 (m, 4H), 2.37 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2 (d, J_{C-P} = 126.0 Hz), 155.5 (d, J_{C-P} = 21.4 Hz), 138.7 (d, J_{C-P} = 12.7 Hz), 136.9, 133.6 (d, J_{C-P} = 2.9 Hz), 132.3 (d, J_{C-P} = 10.0 Hz), 130.8 (d, J_{C-P} = 108.4 Hz), 129.2 (d, J_{C-P} = 10.5 Hz), 128.6 (d, J_{C-P} = 13.6 Hz), 126.7, 126.6, 124.8, 122.2, 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.69.

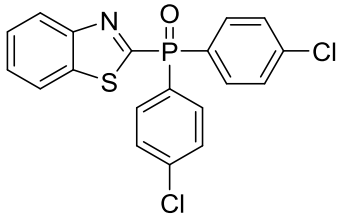


Benzo[d]thiazol-2-ylbis(4-methoxyphenyl)phosphine oxide (3ad):[4] The synthesis procedure is the same as for **3aa.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 1H), 8.01 – 7.99 (m, 1H), 7.89 – 7.82 (m, 4H), 7.55-7.46 (m, 2H), 7.00 – 6.98 (m, 4H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9 (d,

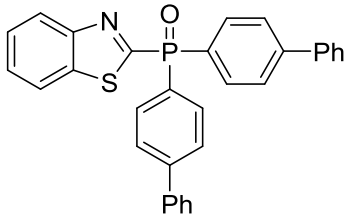
$J_{C\text{-}P}$ = 127.0 Hz), 163.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 155.4 (d, $J_{C\text{-}P}$ = 21.3 Hz), 136.9, 134.0 (d, $J_{C\text{-}P}$ = 11.7 Hz), 126.6 (d, $J_{C\text{-}P}$ = 10.0 Hz), 124.8, 122.3 (d, $J_{C\text{-}P}$ = 116.3 Hz), 122.2, 114.3 (d, $J_{C\text{-}P}$ = 13.9 Hz), 55.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.74.



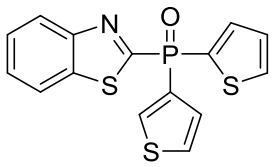
Benzo[d]thiazol-2-ylbis(4-fluorophenyl)phosphine oxide (3ae):[3] The synthesis procedure is the same as for **3aa.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.8 Hz, 1H), 8.05 – 8.02 (m, 1H), 8.01 – 7.94 (m, 4H), 7.60 – 7.50 (m, 2H), 7.20 (td, J = 8.7, 2.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (dd, $J_{C\text{-}P,\ C\text{-}F}$ = 255.2, 3.1 Hz), 165.1 (dd, $J_{C\text{-}P}$ = 119.9 Hz), 155.4 (d, $J_{C\text{-}P}$ = 21.9 Hz), 136.9, 134.6 (dd, $J_{C\text{-}P,\ C\text{-}F}$ = 11.8, 9.0 Hz), 127.0, 126.9 (dd, $J_{C\text{-}P,\ C\text{-}F}$ = 113.0, 3.3 Hz), 124.9, 122.3, 116.4 (dd, $J_{C\text{-}P,\ C\text{-}F}$ = 21.6, 14.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.53.



Benzo[d]thiazol-2-ylbis(4-chlorophenyl)phosphine oxide (3af): The synthesis procedure is the same as for **3aa.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.94 – 7.88 (m, 8.5 Hz, 4H), 7.58 – 7.47 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (d, $J_{C\text{-}P}$ = 130.7 Hz), 155.3 (d, $J_{C\text{-}P}$ = 22.0 Hz), 139.6 (d, $J_{C\text{-}P}$ = 3.5 Hz), 136.7, 133.3 (d, $J_{C\text{-}P}$ = 11.1 Hz), 129.2 (d, $J_{C\text{-}P}$ = 13.5 Hz), 129.2 (d, $J_{C\text{-}P}$ = 111.1 Hz), 127.0, 124.8, 122.2.^{31}P NMR (162 MHz, $CDCl_3$) δ 18.40. HRMS (ESI+) calculated for $C_{19}H_{13}Cl_2NOPS$ (M+H): 403.9827; found: 403.9825.



Di([1,1'-biphenyl]-4-yl)(benzo[d]thiazol-2-yl)phosphine oxide (3ag): The synthesis procedure is the same as for **3aa.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 8.11 – 8.06 (m, 4H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.71 (m, 4H), 7.59 – 7.35 (m, 12H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0 (d, J_{C-P} = 127.4 Hz), 155.4 (d, J_{C-P} = 21.6 Hz), 145.5 (d, J_{C-P} = 2.9 Hz), 139.8, 136.9, 132.5 (d, J_{C-P} = 10.6 Hz), 129.5 (d, J_{C-P} = 110.5 Hz), 129.0, 128.3, 127.5 (d, J_{C-P} = 13.2 Hz), 127.4, 126.8, 126.7, 124.8, 122.2.^{31}P NMR (162 MHz, $CDCl_3$) δ 20.14. HRMS (ESI+) calculated for $C_{31}H_{23}NOPS$ (M+H): 488.1232; found: 488.1226.



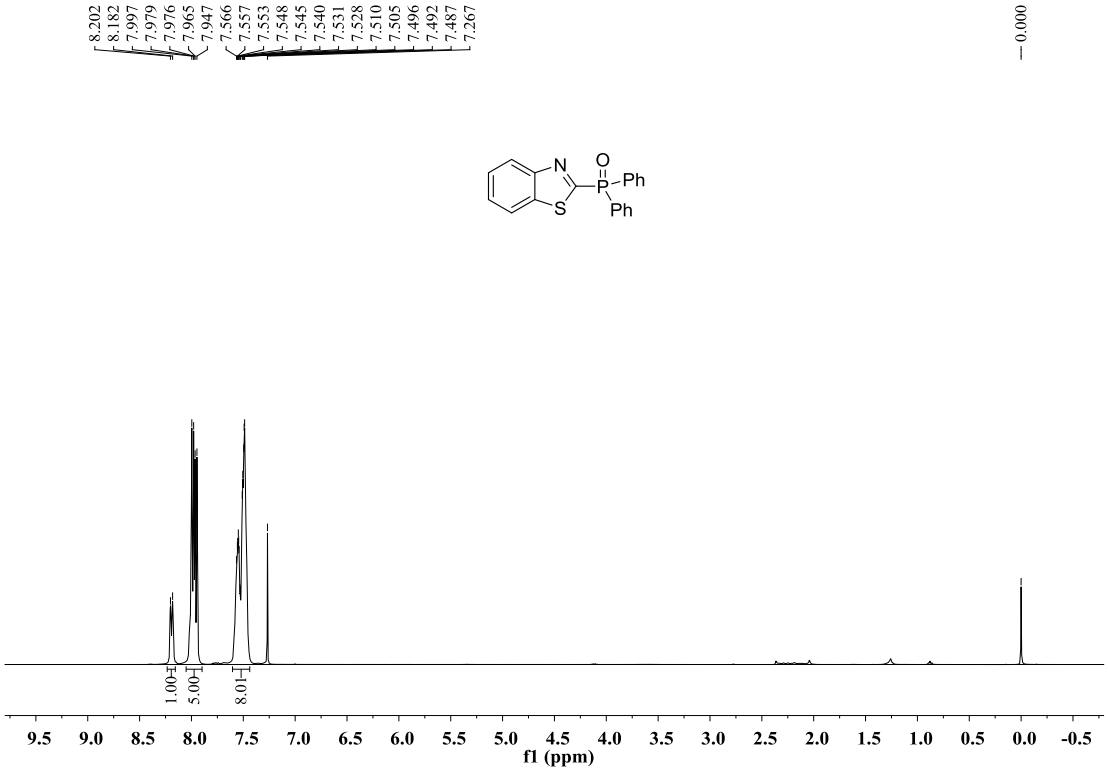
Benzo[d]thiazol-2-yldi(thiophen-2-yl)phosphine oxide (3ah): The synthesis procedure is the same as for **3aa.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.80 (m, 4H), 7.58 – 7.48 (m, 2H), 7.23 – 7.21 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3 (d, J_{C-P} = 147.1 Hz), 155.0 (d, J_{C-P} = 24.1 Hz), 137.8 (d, J_{C-P} = 11.2 Hz), 136.8, 135.4 (d, J_{C-P} = 5.8 Hz), 131.7 (d, J_{C-P} = 128.5 Hz), 128.5 (d, J_{C-P} = 15.5 Hz), 127.0, 126.9, 124.9, 122.2.^{31}P NMR (162 MHz, $CDCl_3$) δ 7.00. HRMS (ESI+) calculated for $C_{15}H_{11}NOPS_3$ (M+H): 347.9735; found: 347.9733.

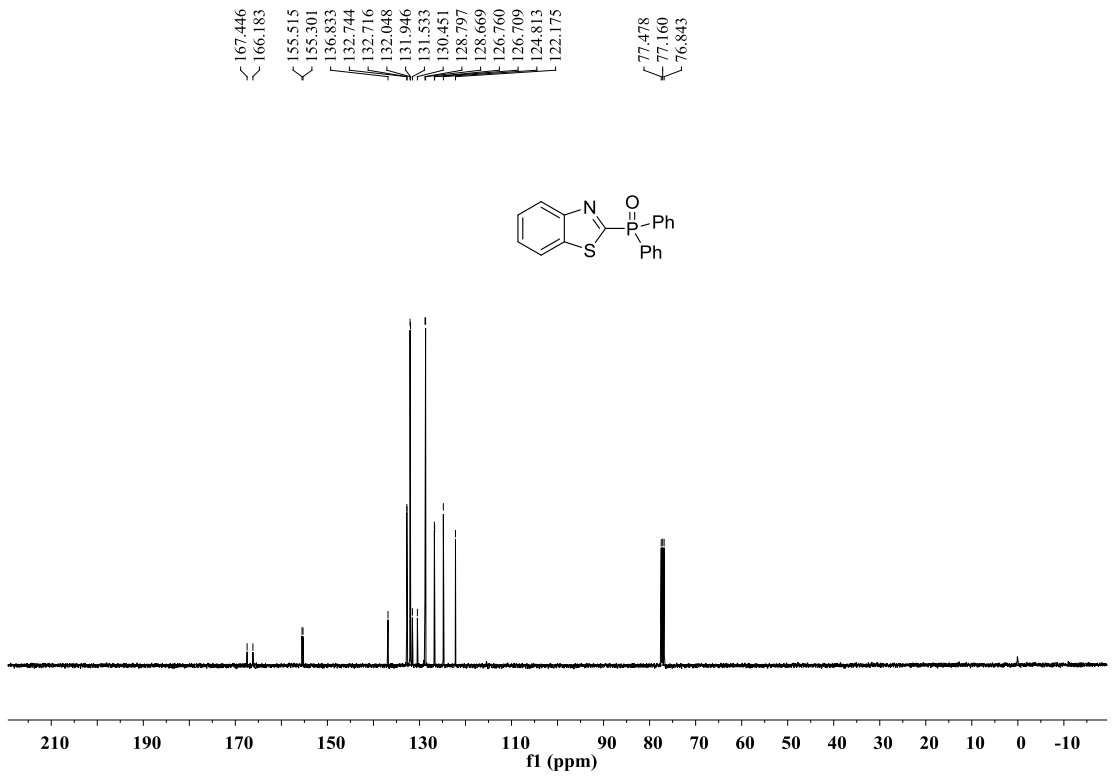
References

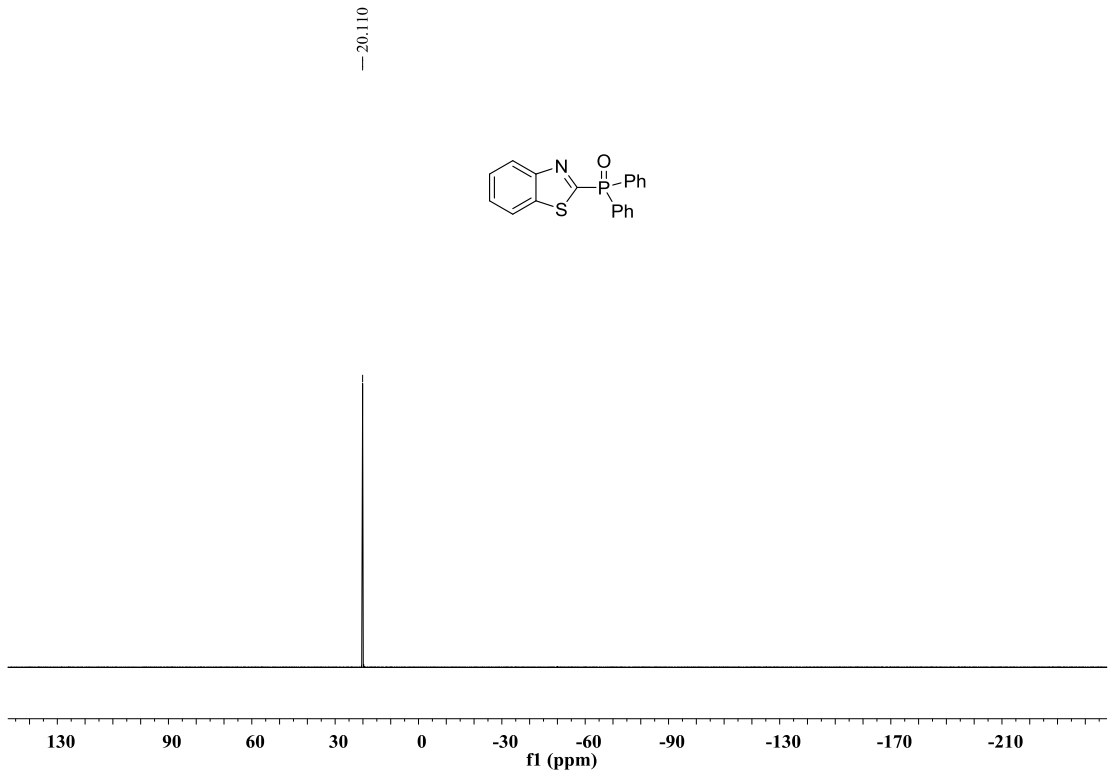
1. A. Tsuruoka, Y. Kaku, H. Kakinuma, I. Tsukada, M. Yanagisawa, K. Nara and T. Naito, *Chem. Pharm. Bull.*, 1998, **46**, 623-630.
2. C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei and C. H. Senanayake, *Org. Lett.*, 2005, **7**, 4277-4280.
3. H.-J. Zhang, W. Lin, Z. Wu, W. Ruan and T.-B. Wen, *Chem. commun.*, 2015, **51**, 3450-3453.
4. K. Luo, Y.-Z. Chen, W.-C. Yang, J. Zhu and L. Wu, *Org. Lett.*, 2016, **18**, 452-455.
5. X.-L. Chen, X. Li, L.-B. Qu, Y.-C. Tang, W.-P. Mai, D.-H. Wei, W.-Z. Bi, L.-K. Duan, K. Sun, J.-Y. Chen, D.-D. Ke and Y.-F. Zhao, *J. Org. Chem.*, 2014, **79**, 8407-8416.

NMR Spectra of Products

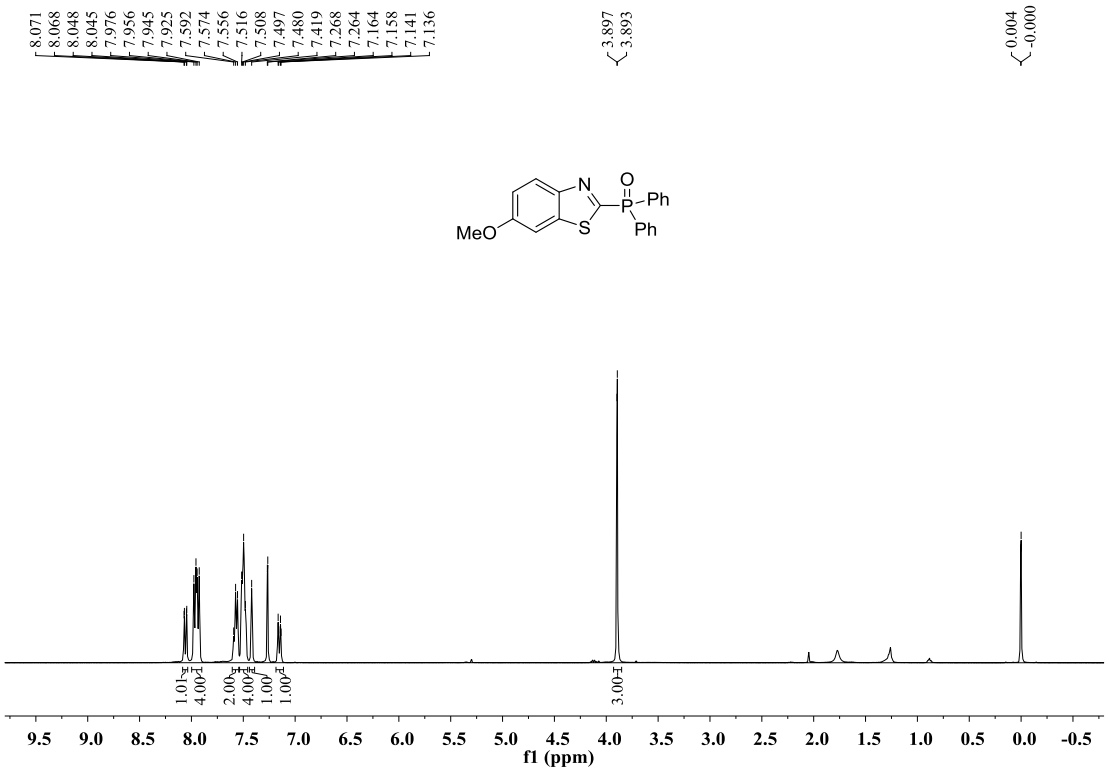
3aa

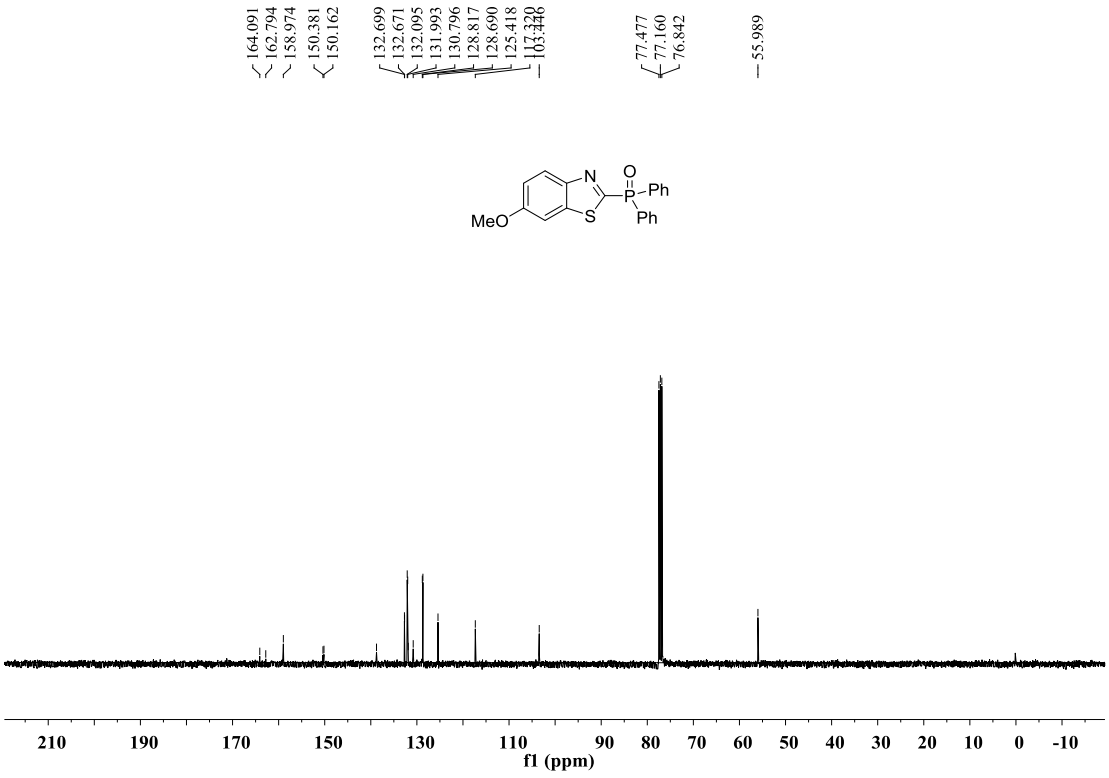


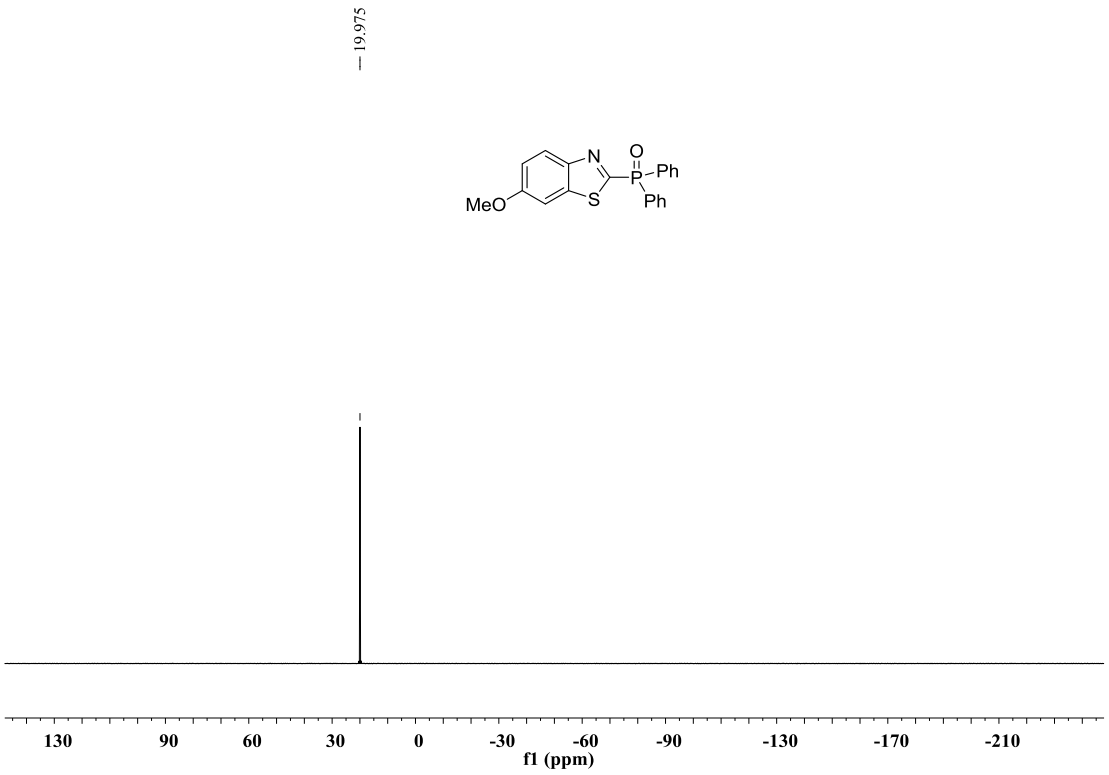

167.446
166.183
155.515
155.301
136.833
132.744
132.716
132.048
131.946
131.533
130.451
128.797
128.669
126.760
126.709
124.813
122.175
77.478
77.160
76.843
N
O
P
Ph
Ph
S
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


20.110
N
O
P
Ph
Ph
S
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

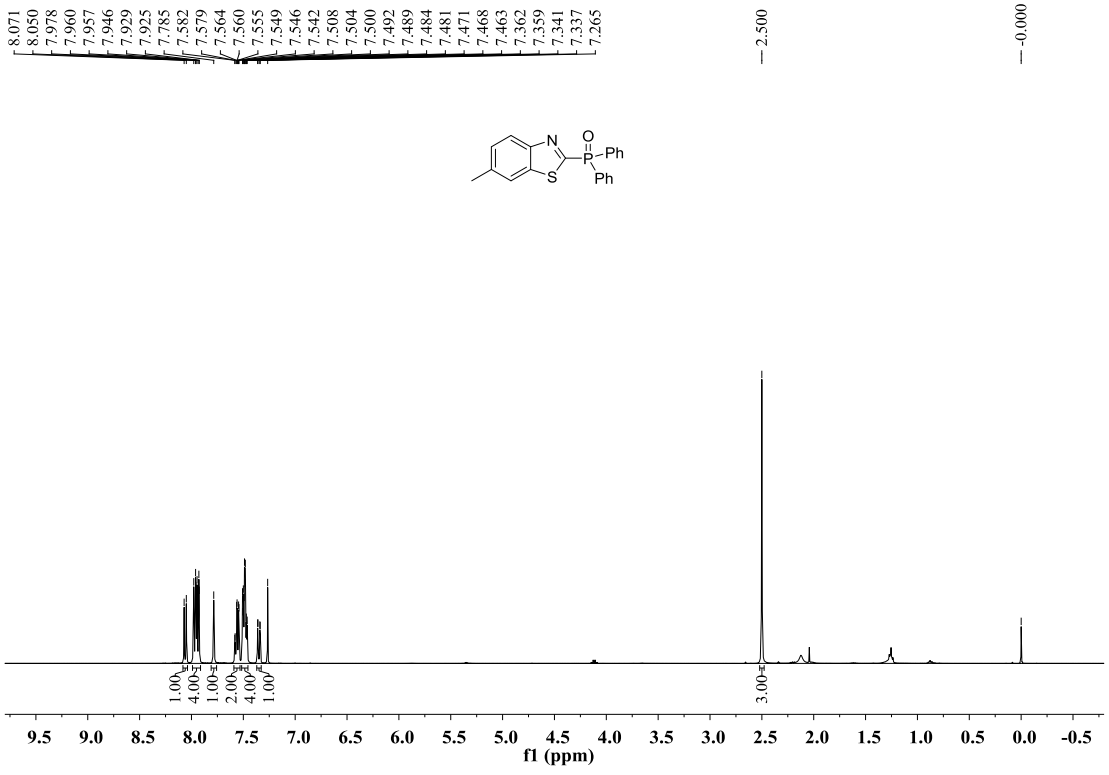
3ba

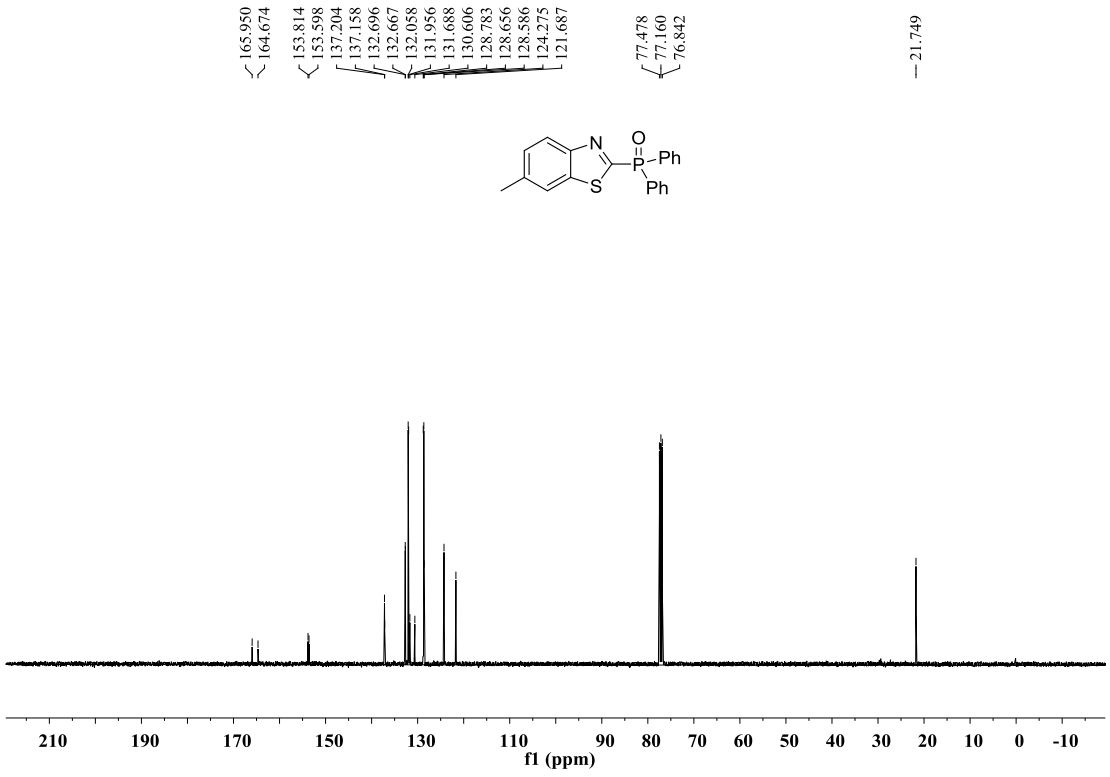

8.071
8.068
8.048
8.045
7.976
7.956
7.945
7.925
7.592
7.574
7.556
7.516
7.508
7.497
7.480
7.419
7.268
7.264
7.164
7.158
7.141
7.136
3.897
3.893
0.004
-0.000
N
O
P
Ph
Ph
S
MeO
1.01
4.00
2.00
4.00
1.00
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

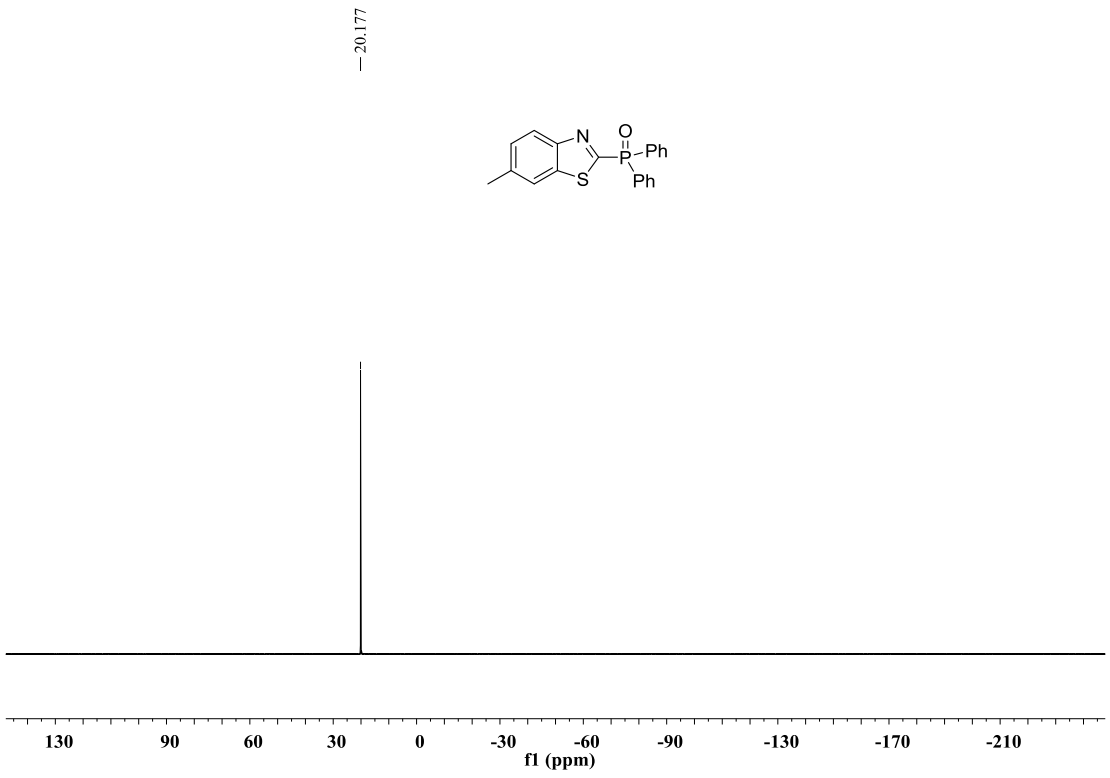

164.091
162.794
158.974
150.381
150.162
132.699
132.671
132.095
131.993
130.796
128.817
128.690
125.418
77.477
77.160
76.842
55.989
N
O
P
Ph
Ph
S
MeO
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


19.975
MeO
N
S
O
P
Ph
Ph
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

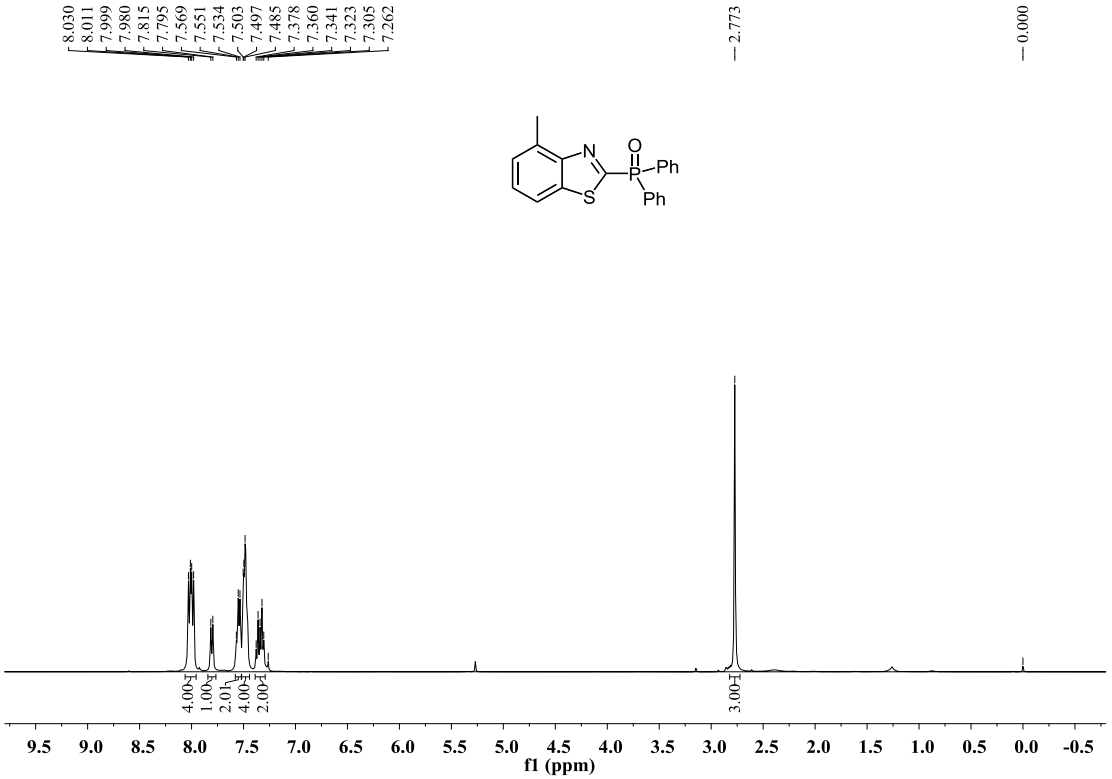
3ca

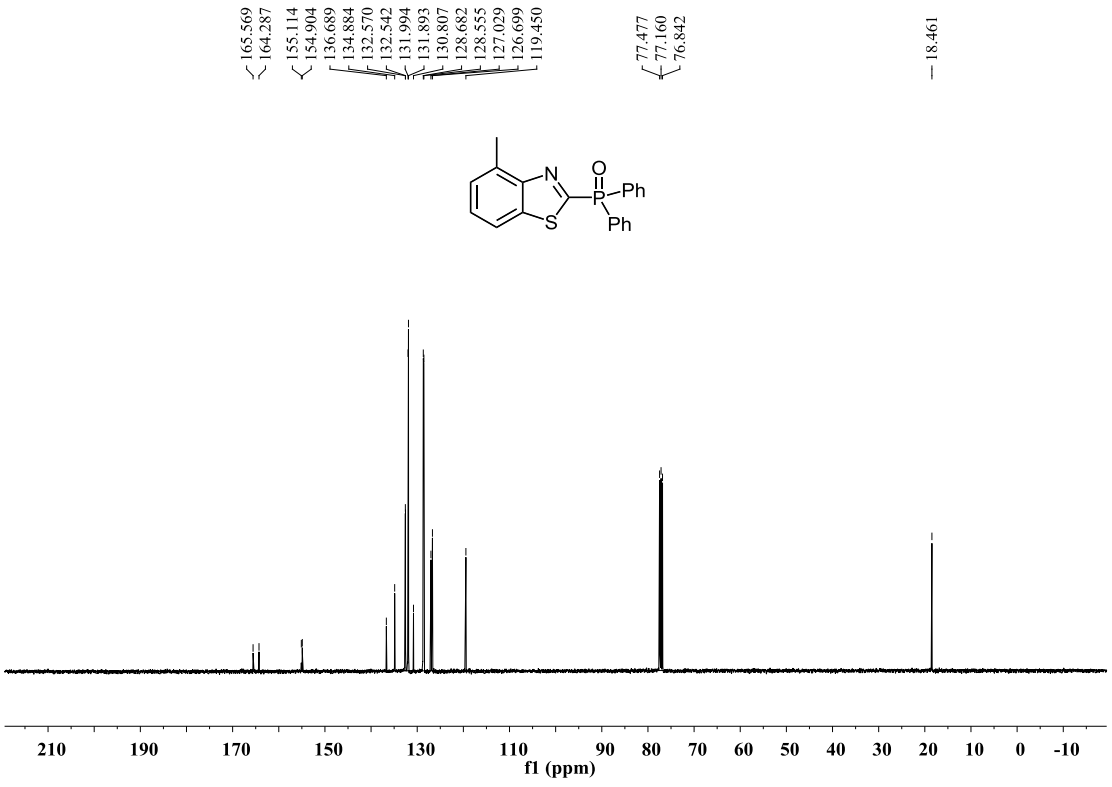

8.071
8.050
7.978
7.960
7.957
7.946
7.929
7.925
7.785
7.582
7.579
7.564
7.560
7.555
7.549
7.546
7.542
7.508
7.504
7.500
7.492
7.489
7.484
7.481
7.471
7.468
7.463
7.362
7.359
7.341
7.337
7.265
2.500
0.000
N
S
O
P
Ph
Ph
1.00
4.00
1.00
2.00
4.00
1.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

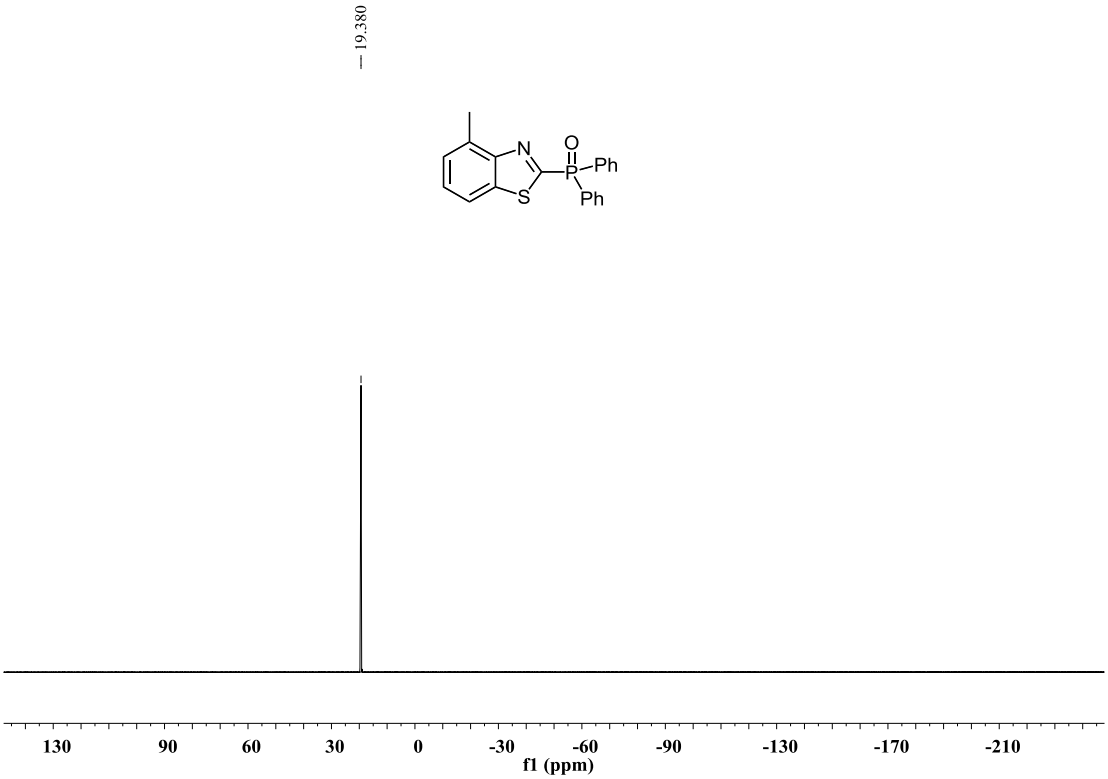

165.950
164.674
153.814
153.598
137.204
137.158
132.696
132.667
132.058
131.956
131.688
130.606
128.783
128.656
128.586
124.275
121.687
77.478
77.160
76.842
21.749
N
O
P
Ph
Ph
S
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


20.177
N
O
P
Ph
Ph
S
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

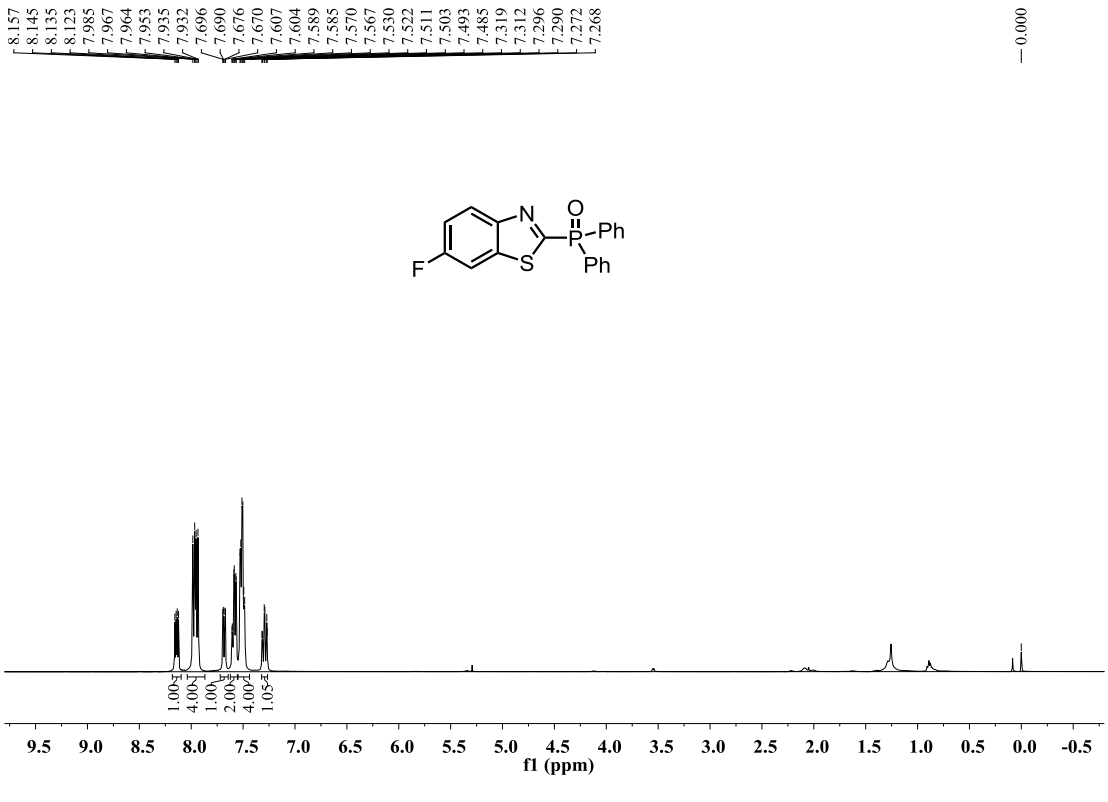
3da

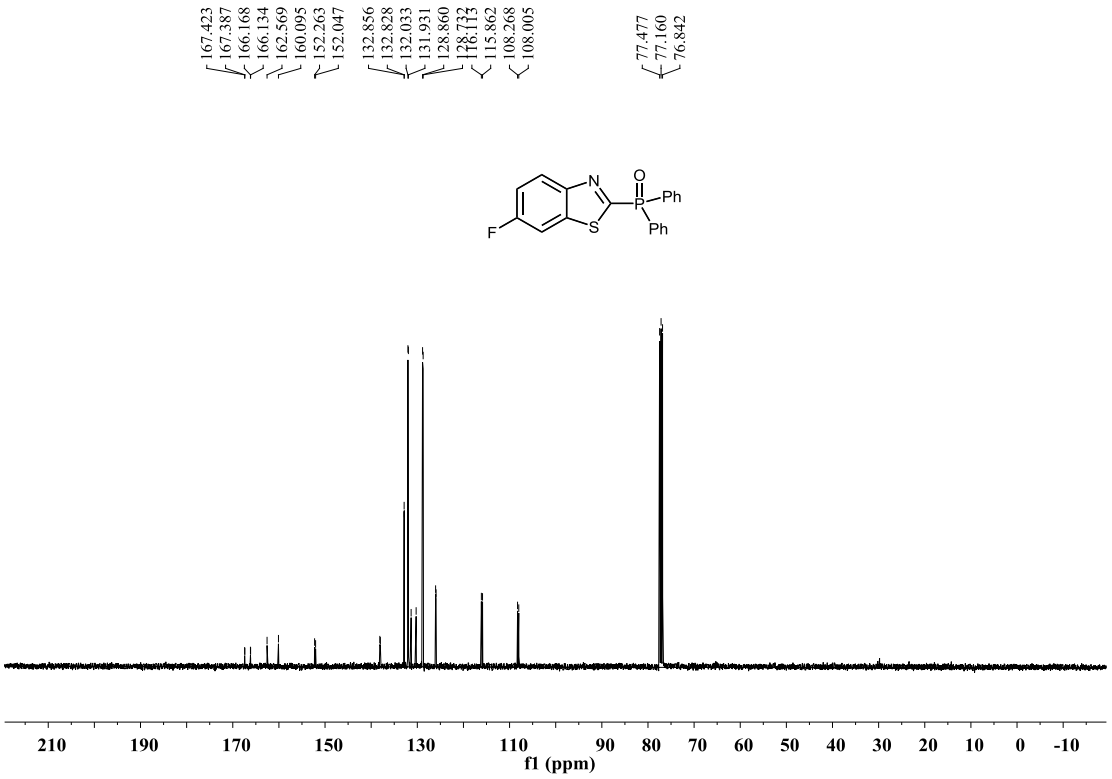

8.030
8.011
7.999
7.980
7.815
7.795
7.569
7.551
7.534
7.503
7.497
7.485
7.378
7.360
7.341
7.323
7.305
7.262
2.773
0.000
N
O
P
Ph
Ph
S
4.00
1.00
2.01
4.00
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

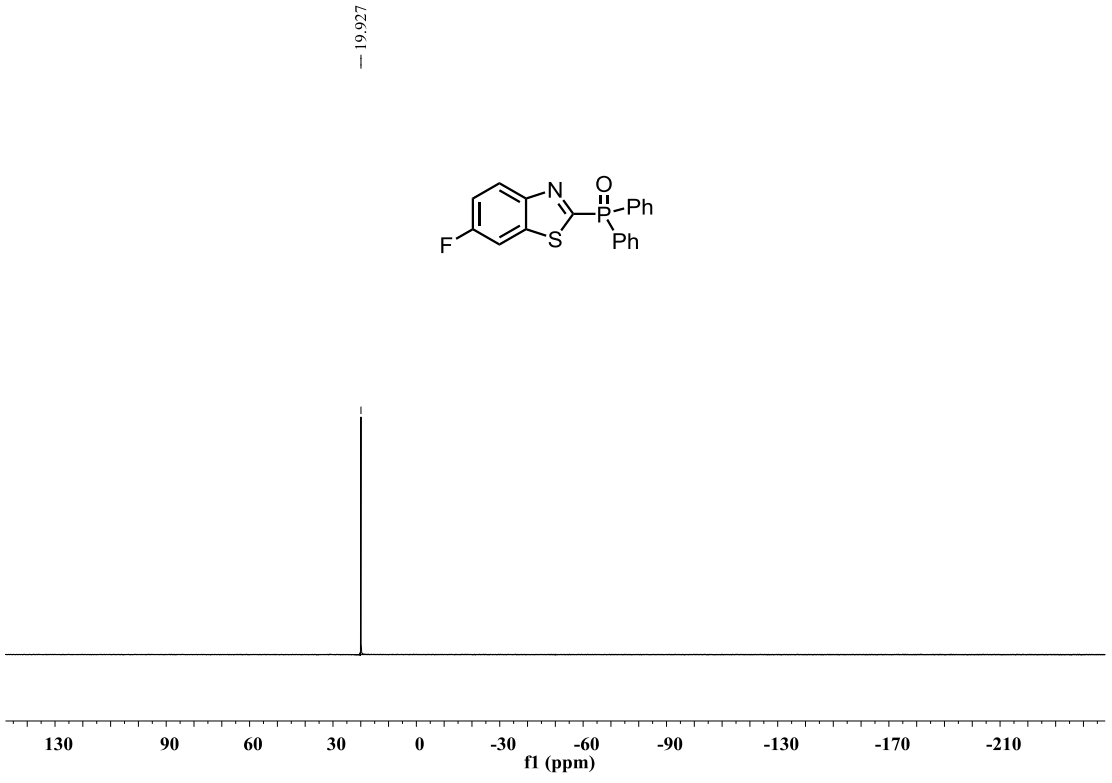

165.569
164.287
155.114
154.904
136.689
134.884
132.570
132.542
131.994
131.893
130.807
128.682
128.555
127.029
126.699
119.450
77.477
77.160
76.842
18.461
N
O
P
Ph
Ph
S
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


19.380
N
O
P
Ph
Ph
S
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

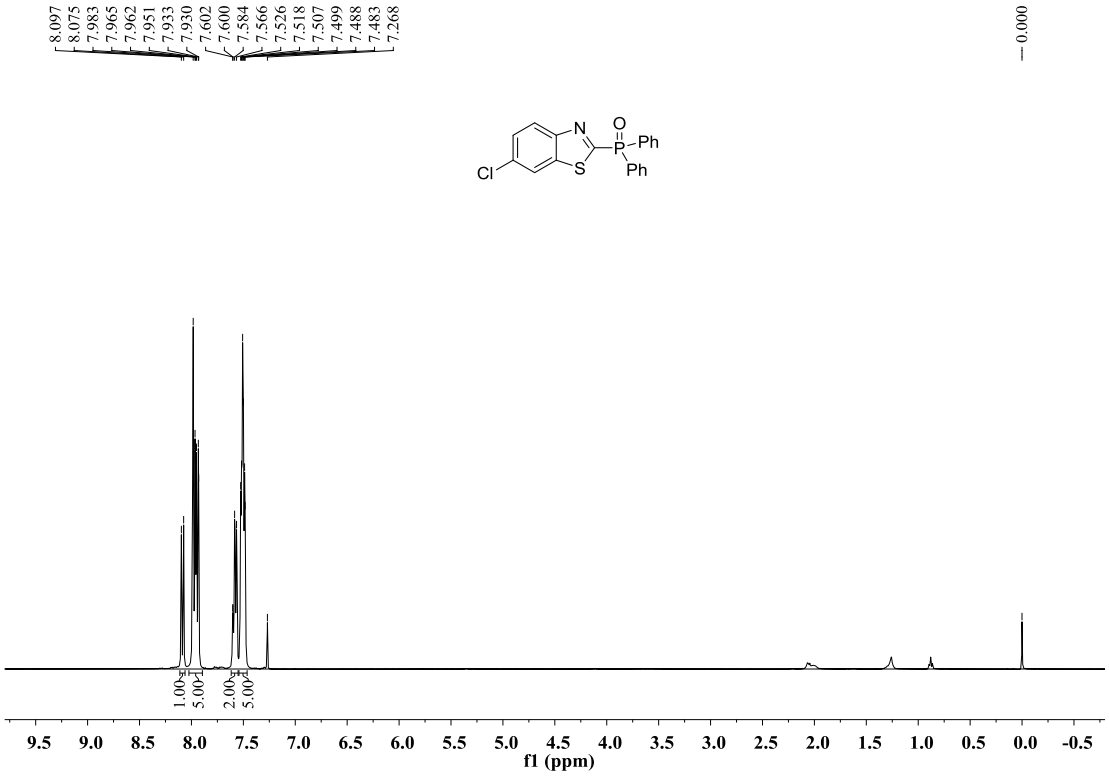
3ea

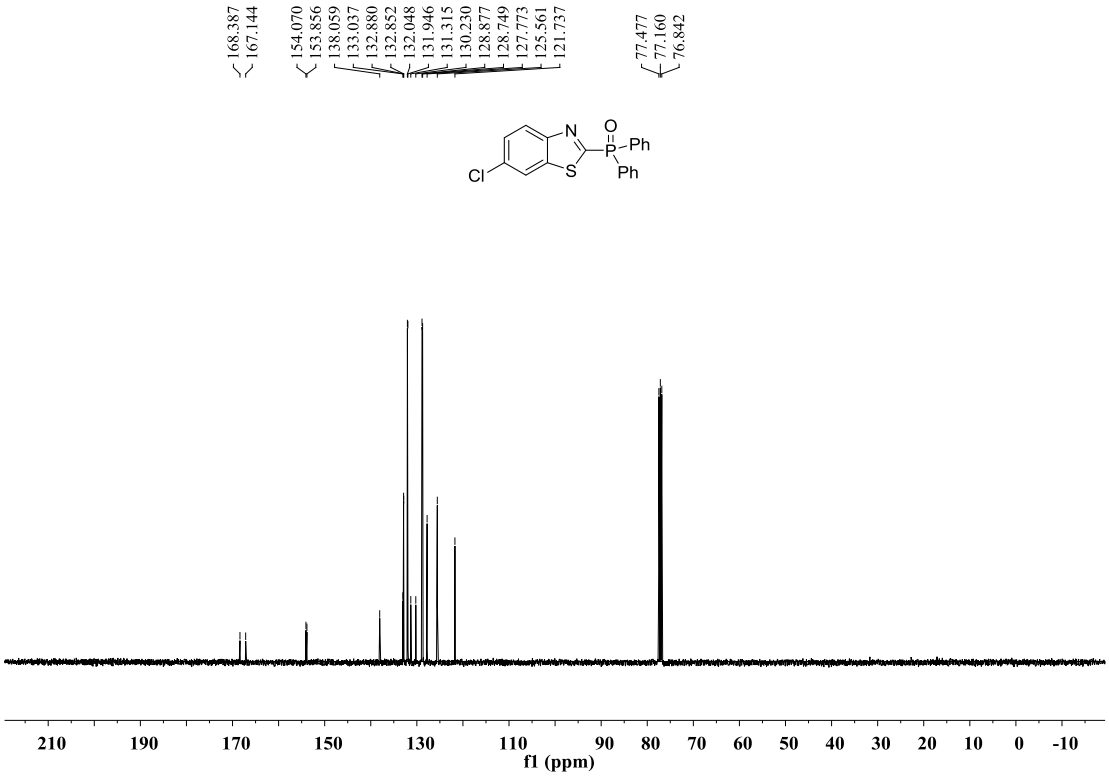

8.157
8.145
8.135
8.123
7.985
7.967
7.964
7.953
7.935
7.932
7.696
7.690
7.676
7.670
7.607
7.604
7.589
7.585
7.570
7.567
7.530
7.522
7.511
7.503
7.493
7.485
7.319
7.312
7.296
7.290
7.272
7.268
0.000
N
O
P
Ph
Ph
F
S
1.00
4.00
1.00
2.00
4.00
1.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

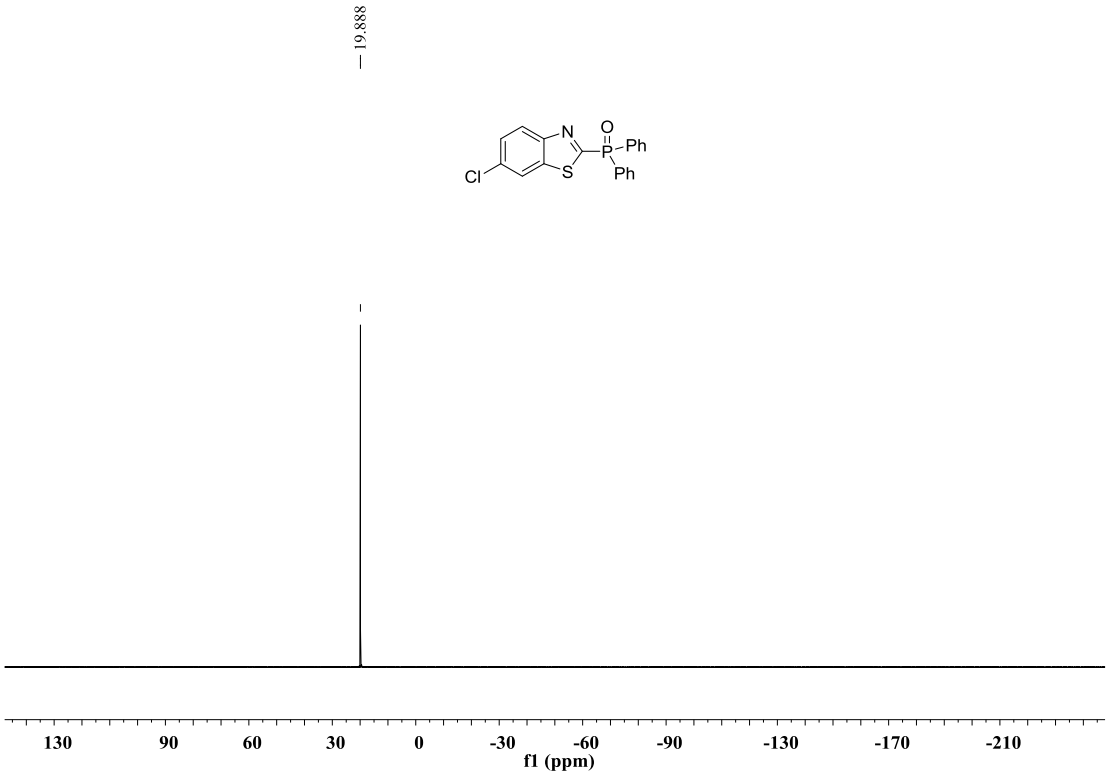

167.423
167.387
166.168
166.134
162.569
160.095
152.263
152.047
132.856
132.828
132.033
131.931
128.860
128.732
128.113
115.862
108.268
108.005
77.477
77.160
76.842
N
O
P
Ph
Ph
S
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


19.927
N
O
P
Ph
Ph
S
F
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

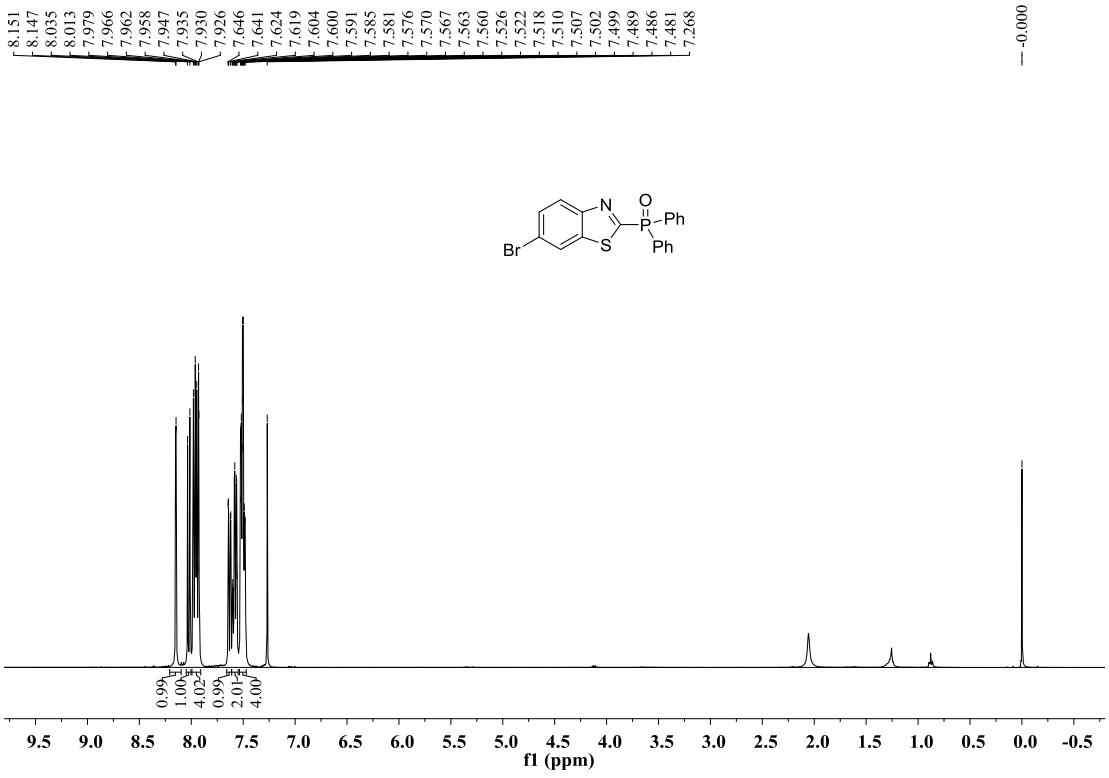
3fa

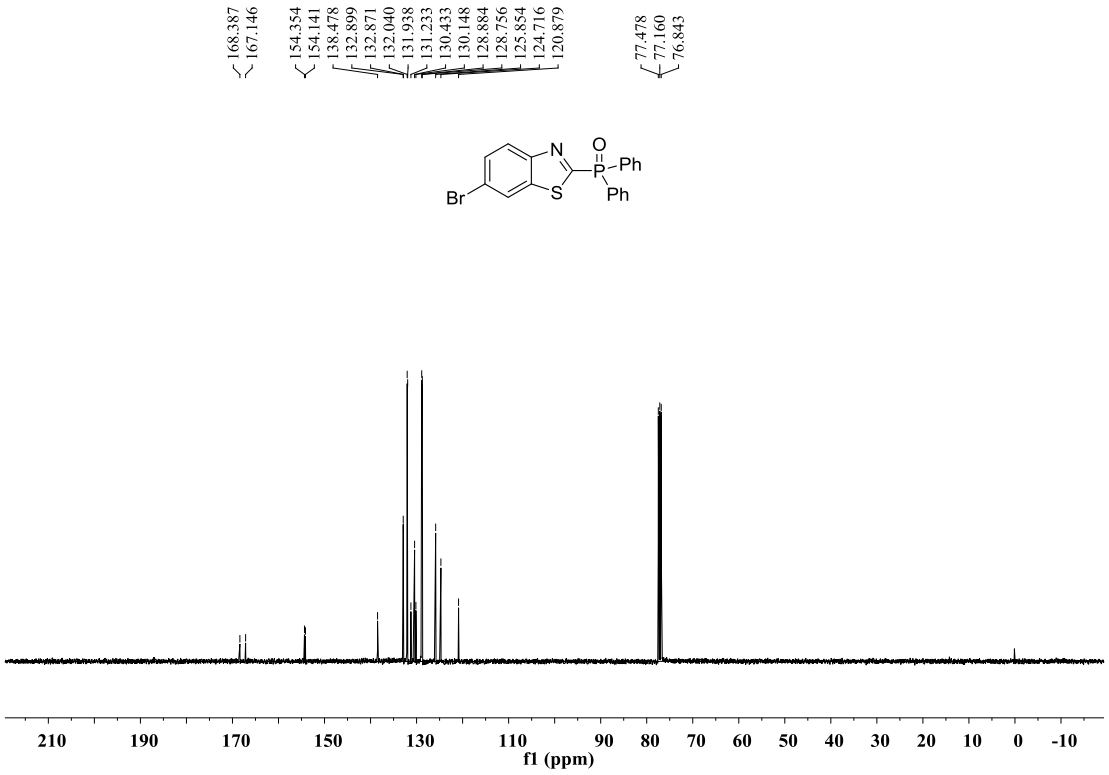

8.097
8.075
7.983
7.965
7.962
7.951
7.933
7.930
7.602
7.600
7.584
7.566
7.526
7.518
7.507
7.499
7.488
7.483
7.268
0.000
N
O
P
Ph
Ph
S
Cl
1.00
5.00
2.00
5.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

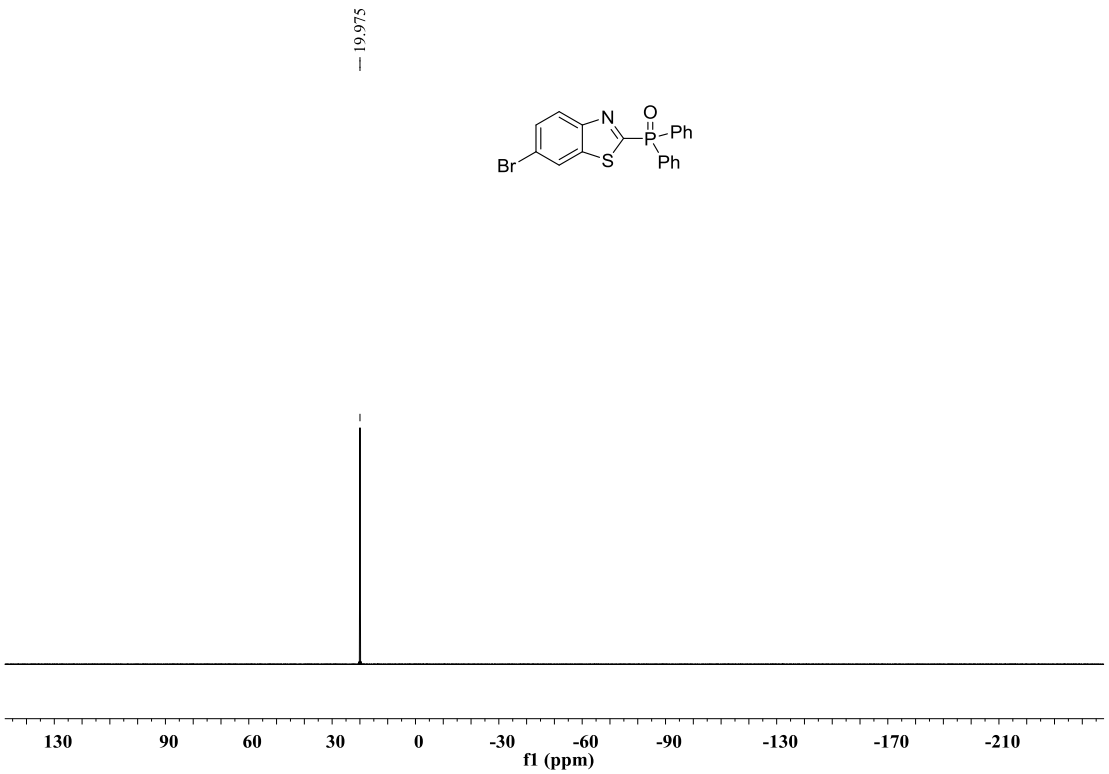

168.387
167.144
154.070
153.856
138.059
133.037
132.880
132.852
132.048
131.946
131.315
130.230
128.877
128.749
127.773
125.561
121.737
77.477
77.160
76.842
N
O
P
Ph
Ph
S
Cl
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


19.888
N
O
P
Ph
Ph
S
Cl
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

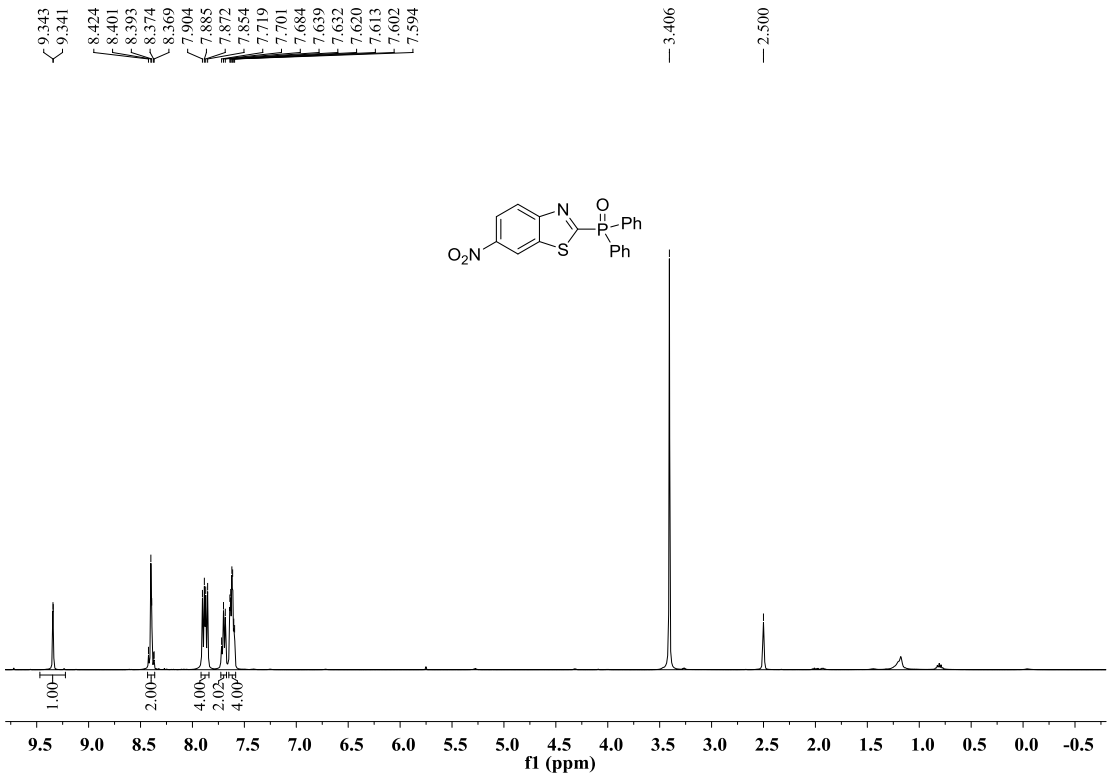
3ga

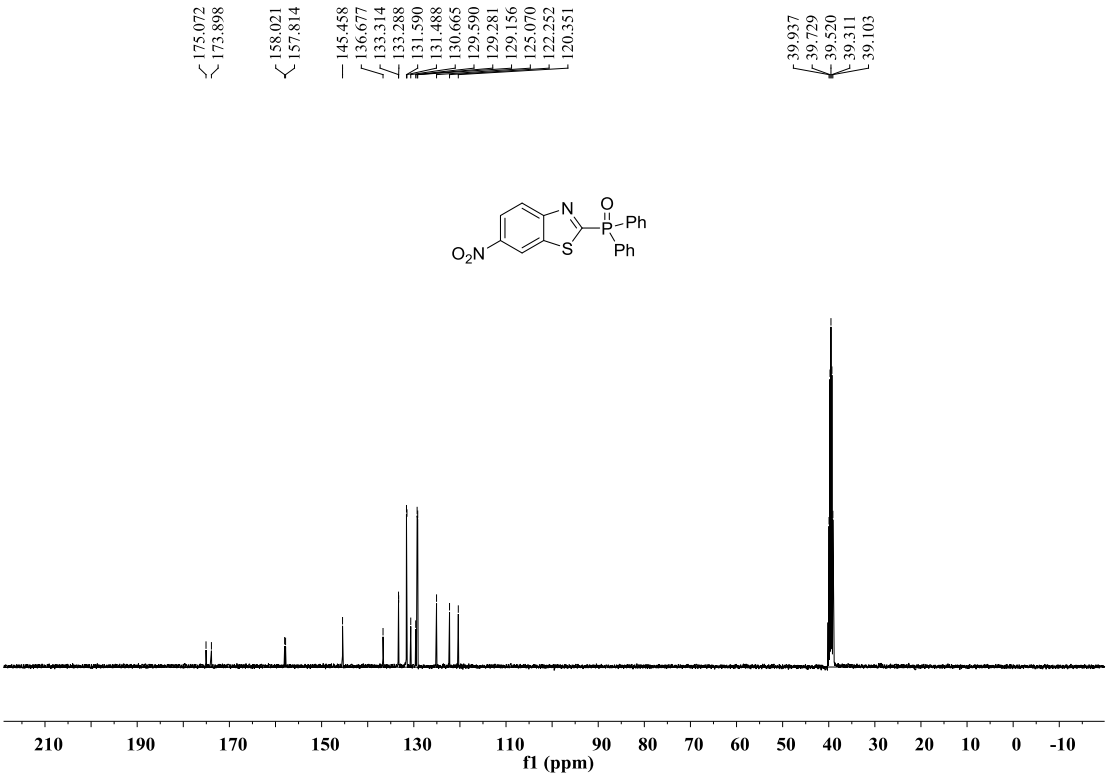

8.151
8.147
8.035
8.013
7.979
7.966
7.962
7.958
7.947
7.935
7.930
7.926
7.646
7.641
7.624
7.619
7.604
7.600
7.591
7.585
7.581
7.576
7.570
7.567
7.563
7.560
7.526
7.522
7.518
7.510
7.507
7.502
7.499
7.489
7.486
7.481
7.268
-0.000
N
O
P
Ph
Ph
Br
S
0.99
1.00
4.02
0.99
2.01
4.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

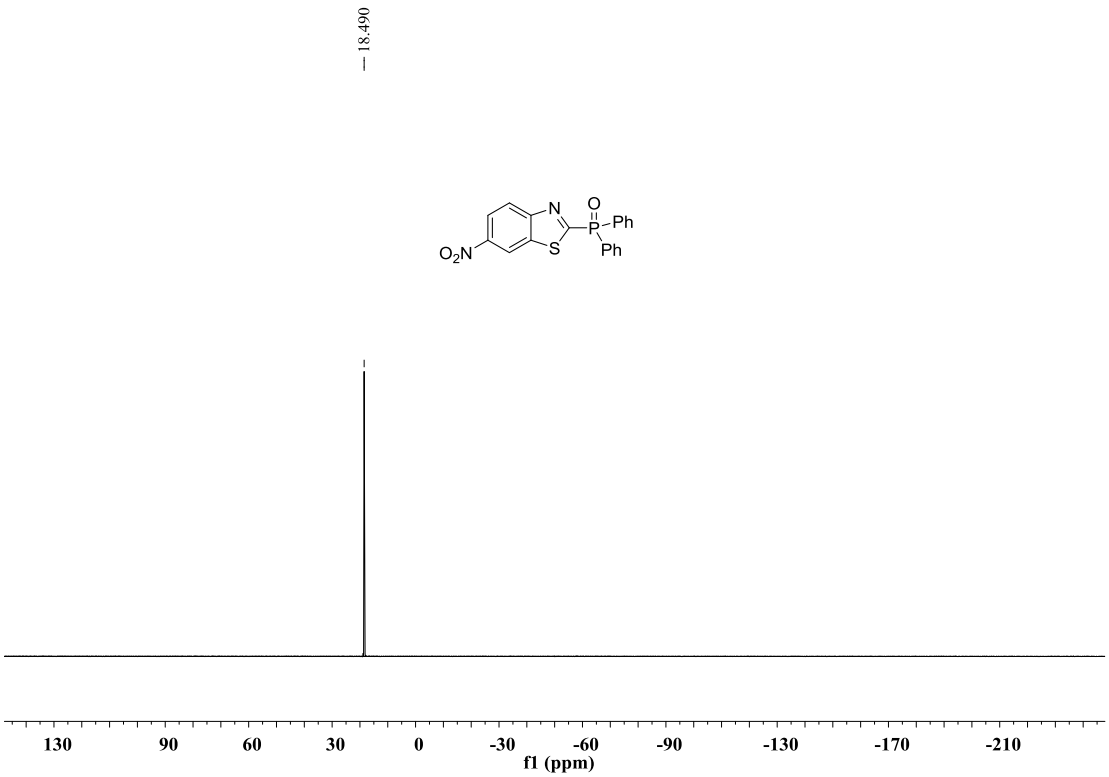

168.387
167.146
154.354
154.141
138.478
132.899
132.871
132.040
131.938
131.233
130.433
130.148
128.884
128.756
125.854
124.716
120.879
77.478
77.160
76.843
N
O
P
Ph
Ph
S
Br
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


19.975
N
O
P
Ph
Ph
S
Br
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

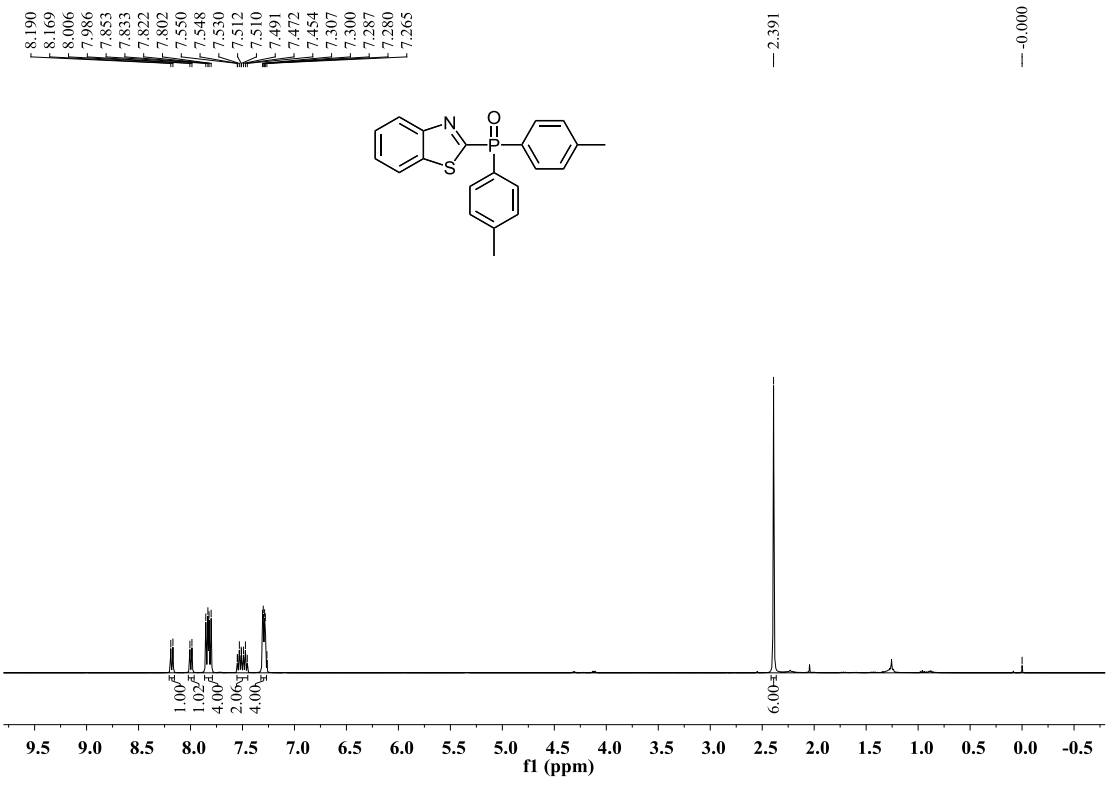
3ha

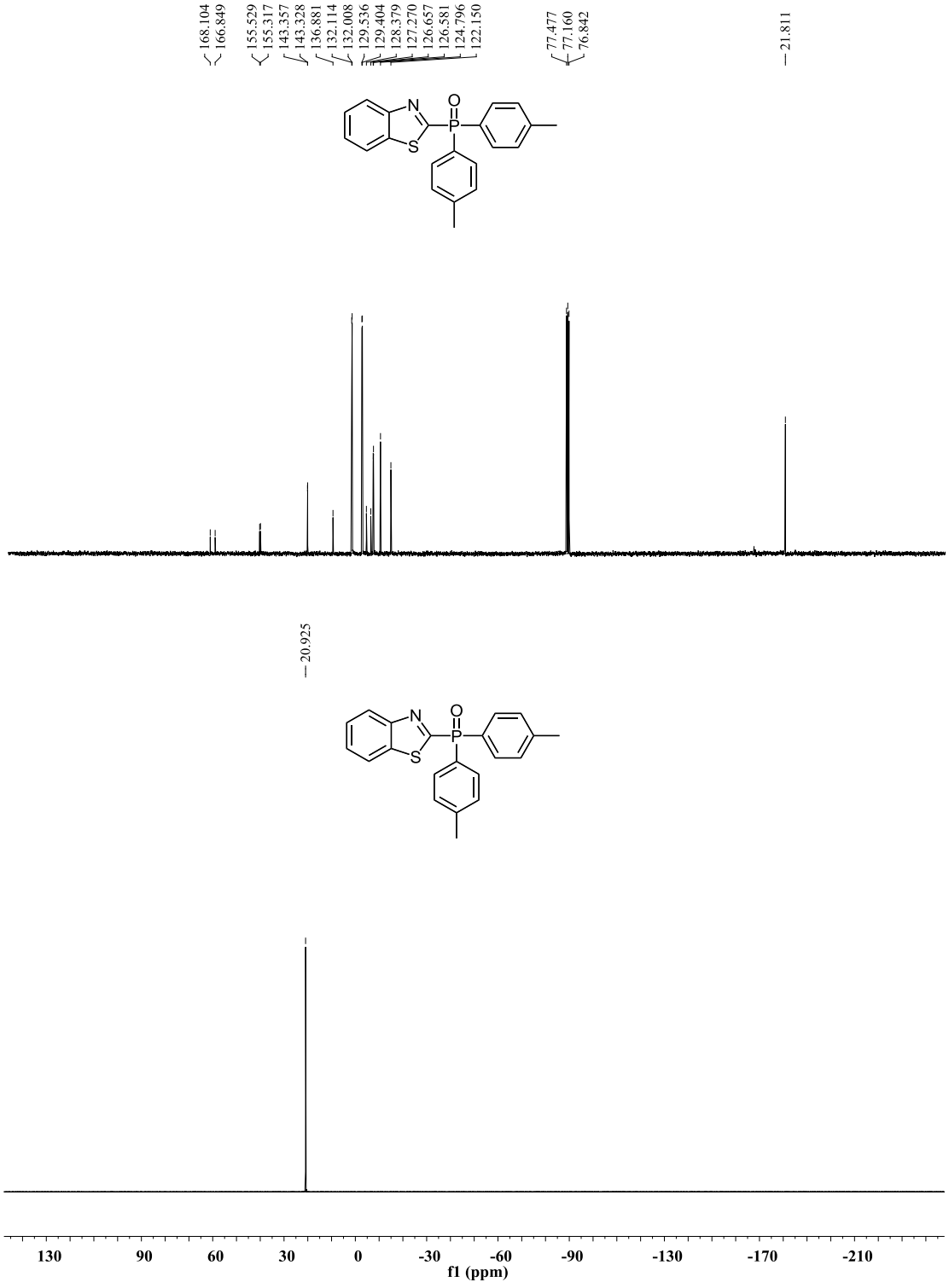

9.343
9.341
8.424
8.401
8.393
8.374
8.369
7.904
7.885
7.872
7.854
7.719
7.701
7.684
7.639
7.632
7.620
7.613
7.602
7.594
3.406
2.500
O2N
N
S
O
P
Ph
Ph
1.00
2.00
4.00
2.02
4.00
f1 (ppm)


175.072
173.898
158.021
157.814
145.458
136.677
133.314
133.288
131.590
131.488
130.665
129.590
129.281
129.156
125.070
122.252
120.351
39.937
39.729
39.520
39.311
39.103
O2N
N
S
O
P
Ph
Ph
f1 (ppm)

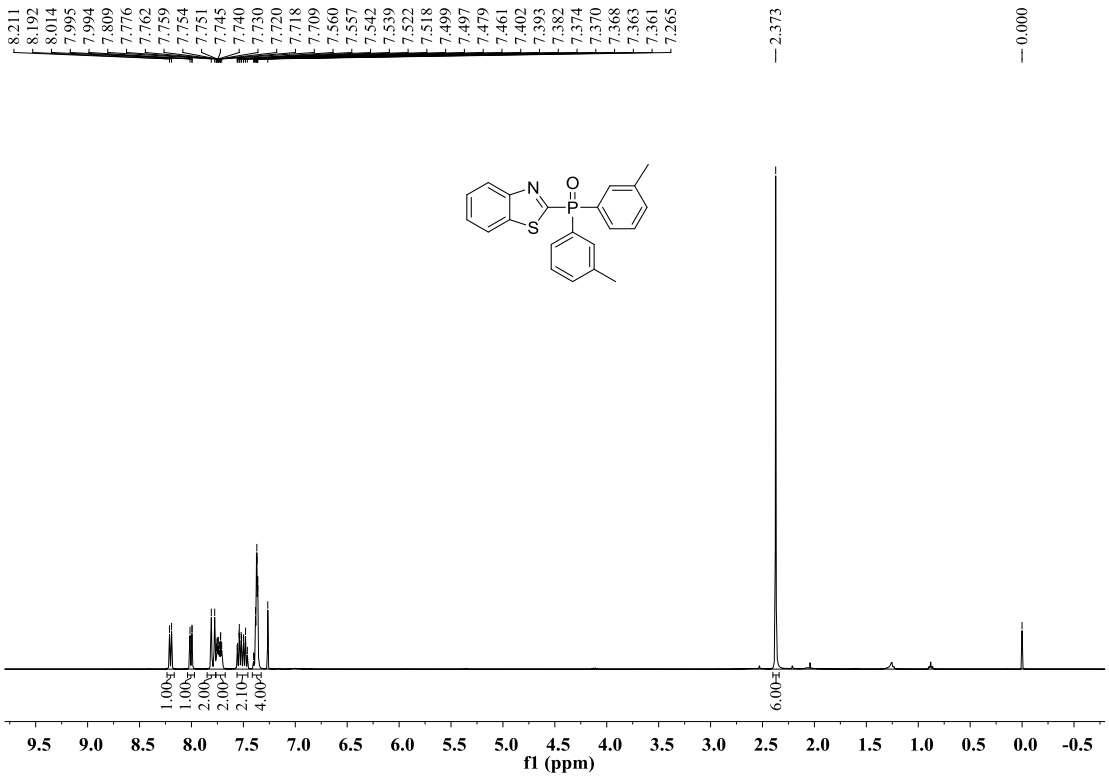

18.490
N
O
P
Ph
Ph
S
O_2N
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

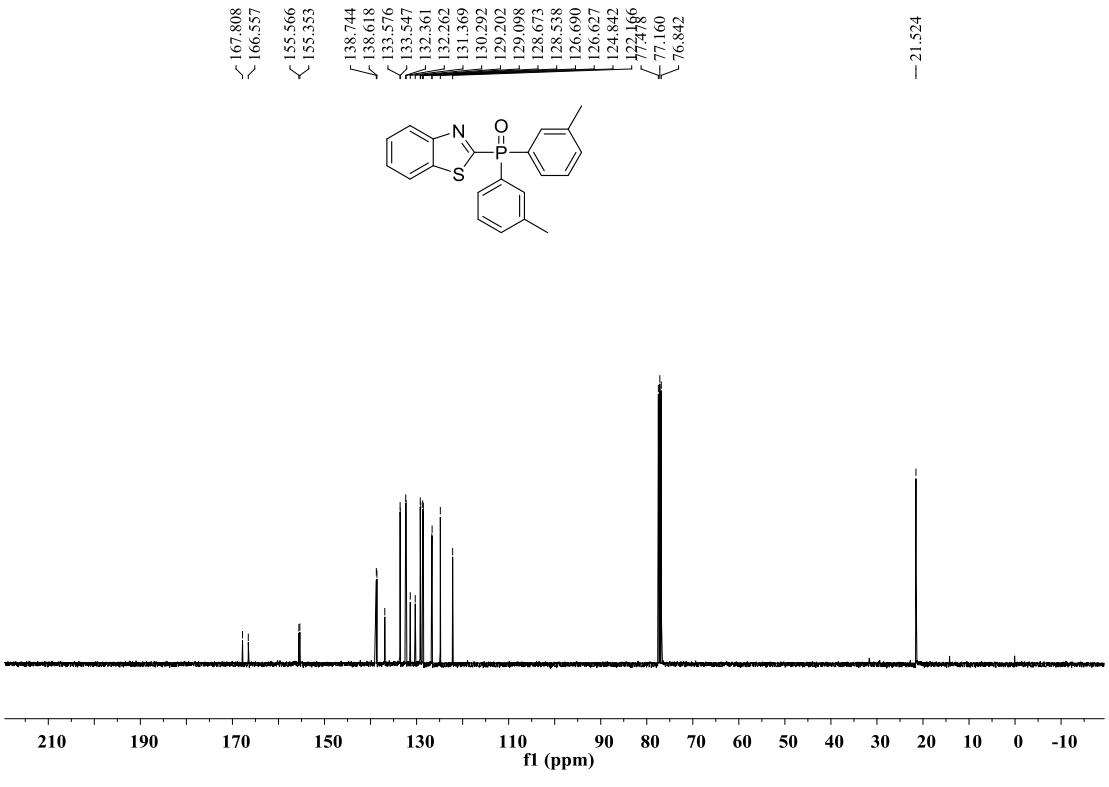
3ab

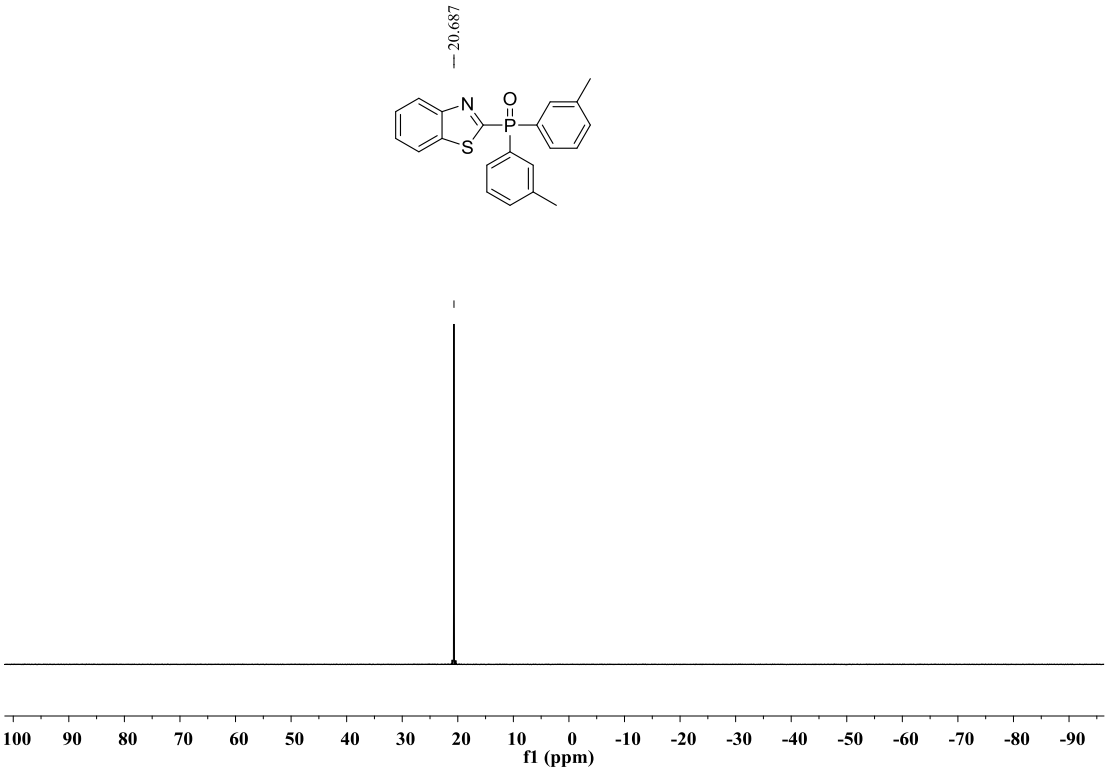

8.190
8.169
8.006
7.986
7.853
7.833
7.822
7.802
7.550
7.548
7.530
7.512
7.510
7.491
7.472
7.454
7.307
7.300
7.287
7.280
7.265
2.391
-0.000
N
O
P
S
1.00
1.02
4.00
2.06
4.00
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


168.104
166.849
155.529
155.317
143.357
143.328
136.881
132.114
132.008
129.536
129.404
128.379
127.270
126.657
126.581
124.796
122.150
77.477
77.160
76.842
21.811
20.925
N
S
O
P
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

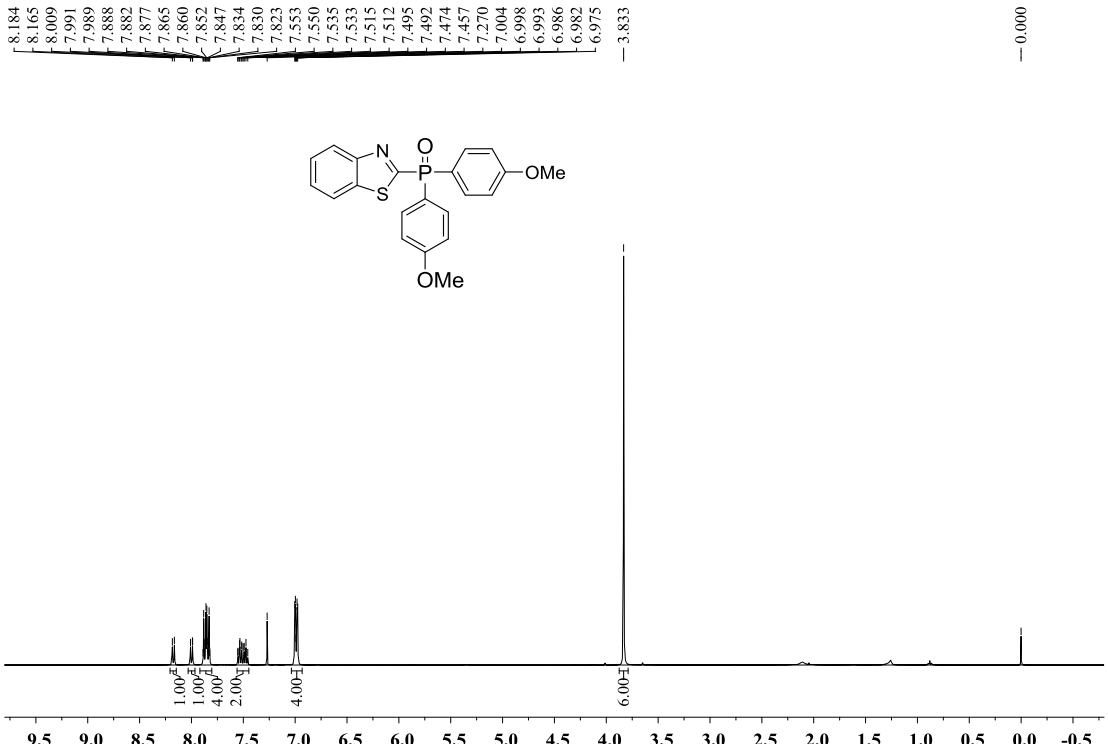
3ac

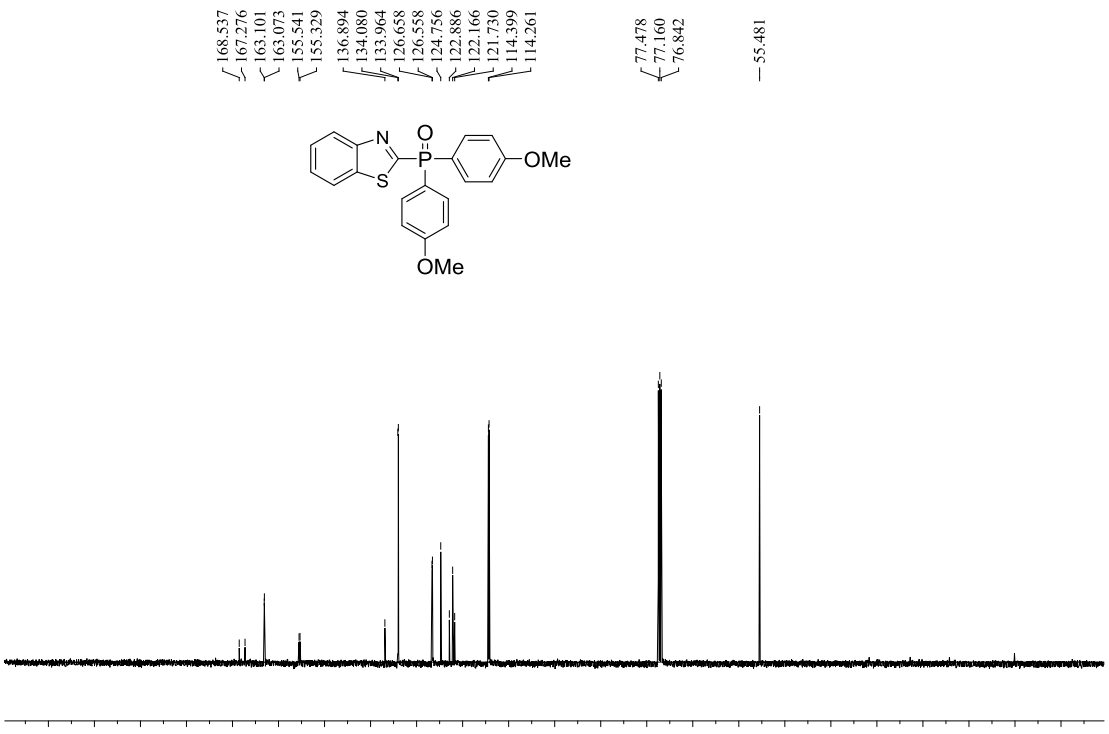

8.211
8.192
8.014
7.995
7.994
7.809
7.776
7.762
7.759
7.754
7.751
7.745
7.740
7.730
7.720
7.718
7.709
7.560
7.557
7.542
7.539
7.522
7.518
7.499
7.497
7.479
7.461
7.402
7.393
7.382
7.374
7.370
7.368
7.363
7.361
7.265
2.373
0.000
N
O
P
S
1.00
1.00
2.00
2.00
2.10
4.00
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

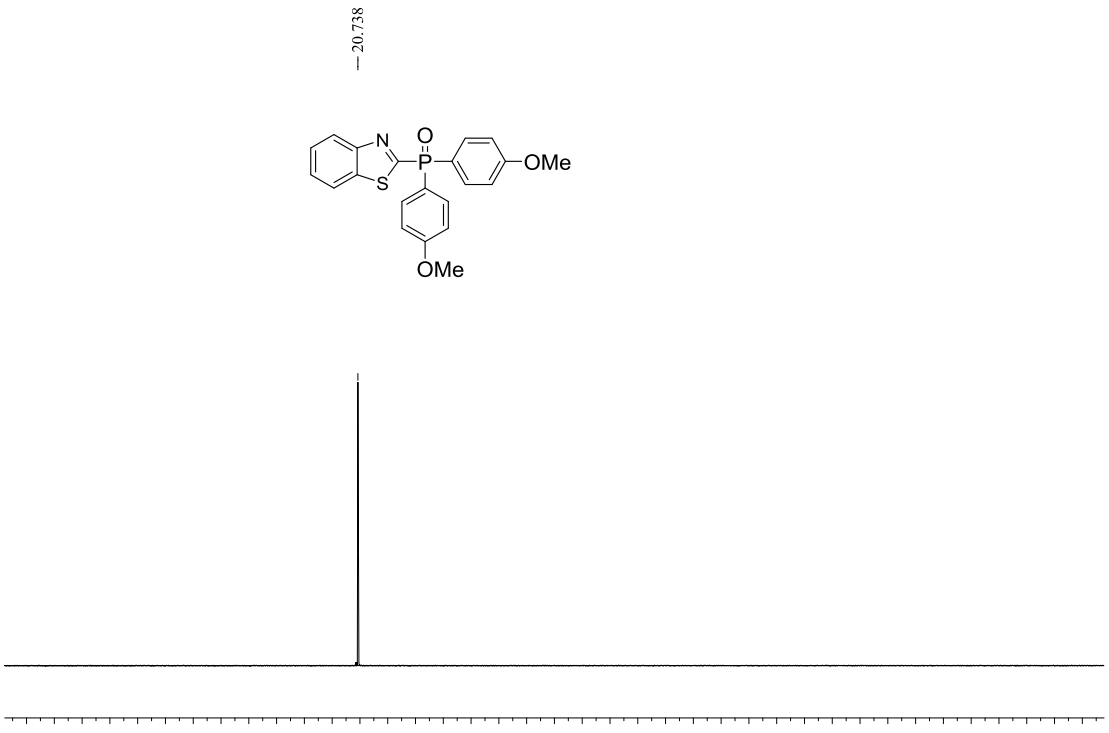

167.808
166.557
155.566
155.353
138.744
138.618
133.576
133.547
132.361
132.262
131.369
130.292
129.202
129.098
128.673
128.538
126.690
126.627
124.842
77.160
76.842
21.524
N
O
P
S
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


20.687
N
O
P
S
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

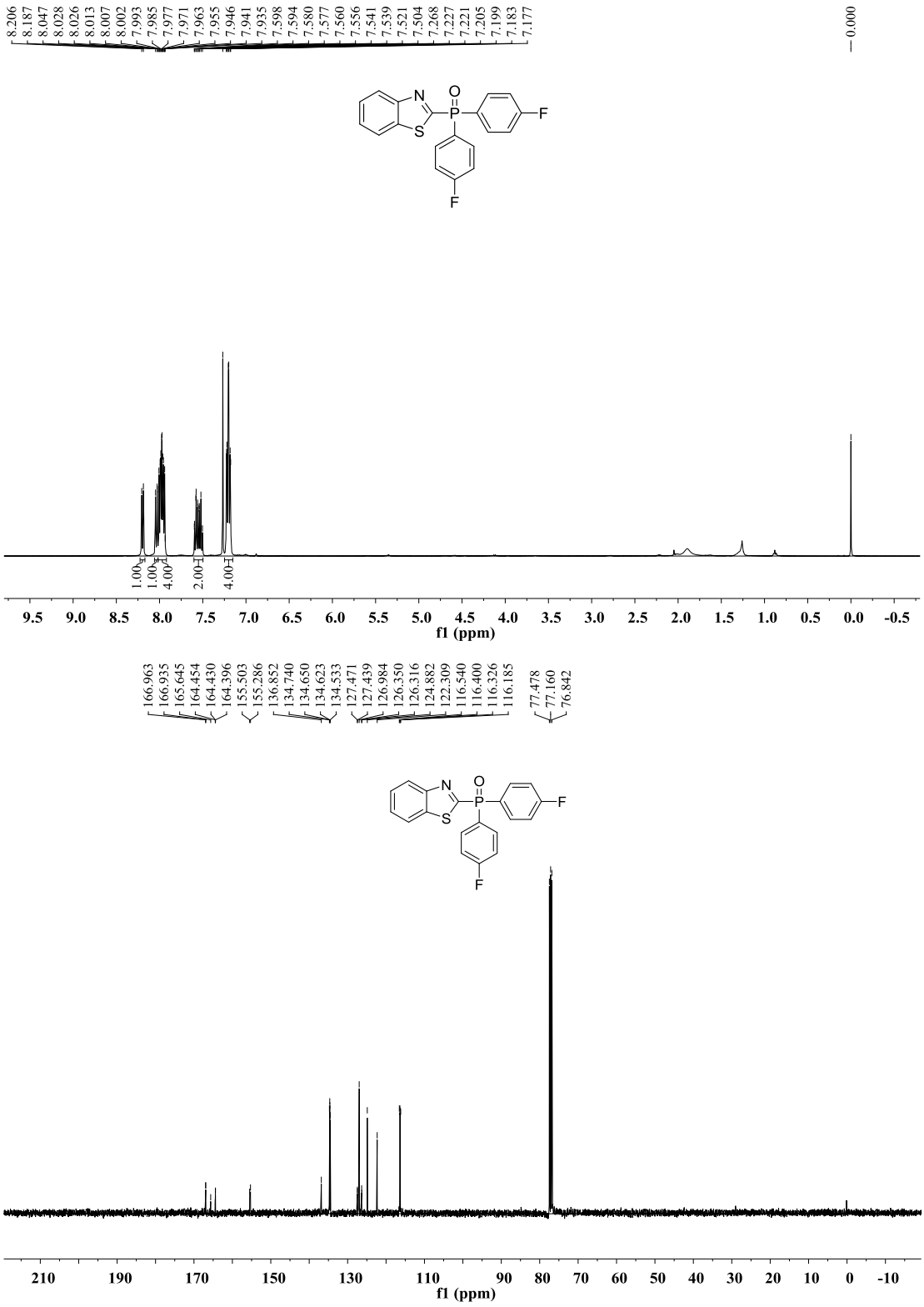
3ad

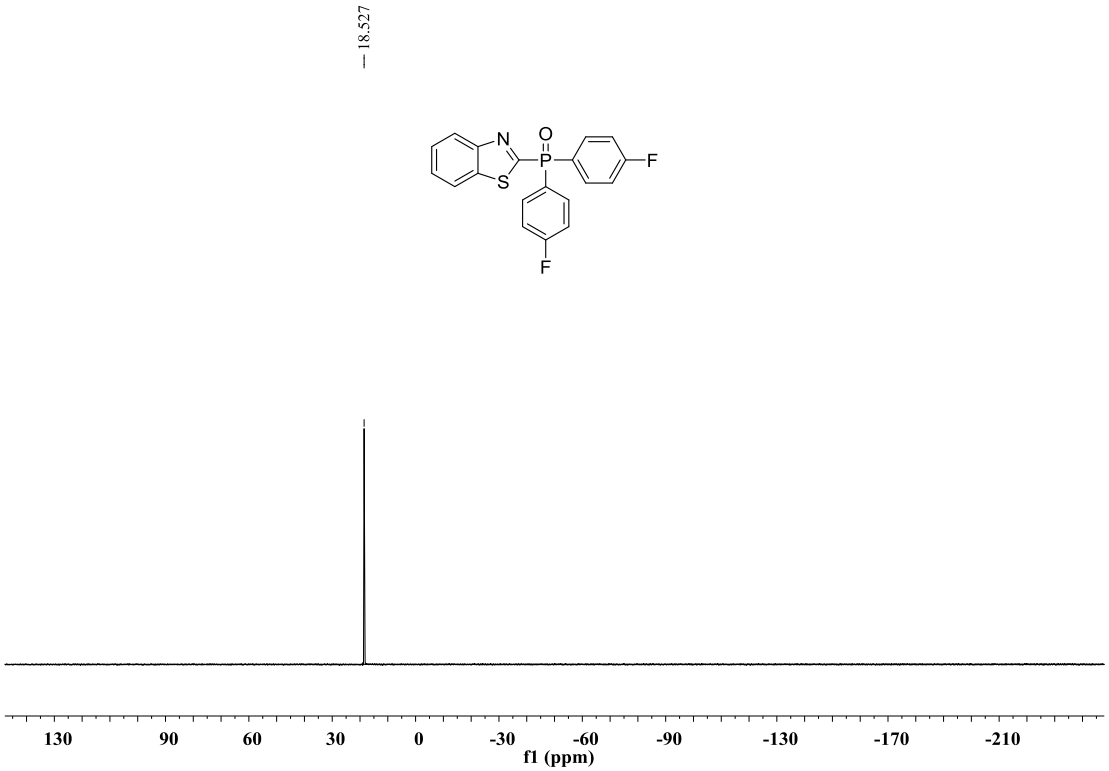

8.184
8.165
8.009
7.991
7.989
7.888
7.882
7.877
7.865
7.860
7.852
7.847
7.834
7.830
7.823
7.553
7.550
7.535
7.533
7.515
7.512
7.495
7.492
7.474
7.457
7.270
7.004
6.998
6.993
6.986
6.982
6.975
3.833
0.000
N
O
P
S
OMe
OMe
1.00
1.00
4.00
2.00
4.00
6.00


168.537
167.276
163.101
163.073
155.541
155.329
136.894
134.080
133.964
126.658
126.558
124.756
122.886
122.166
121.730
114.399
114.261
77.478
77.160
76.842
55.481
N
S
O
P
OMe
OMe

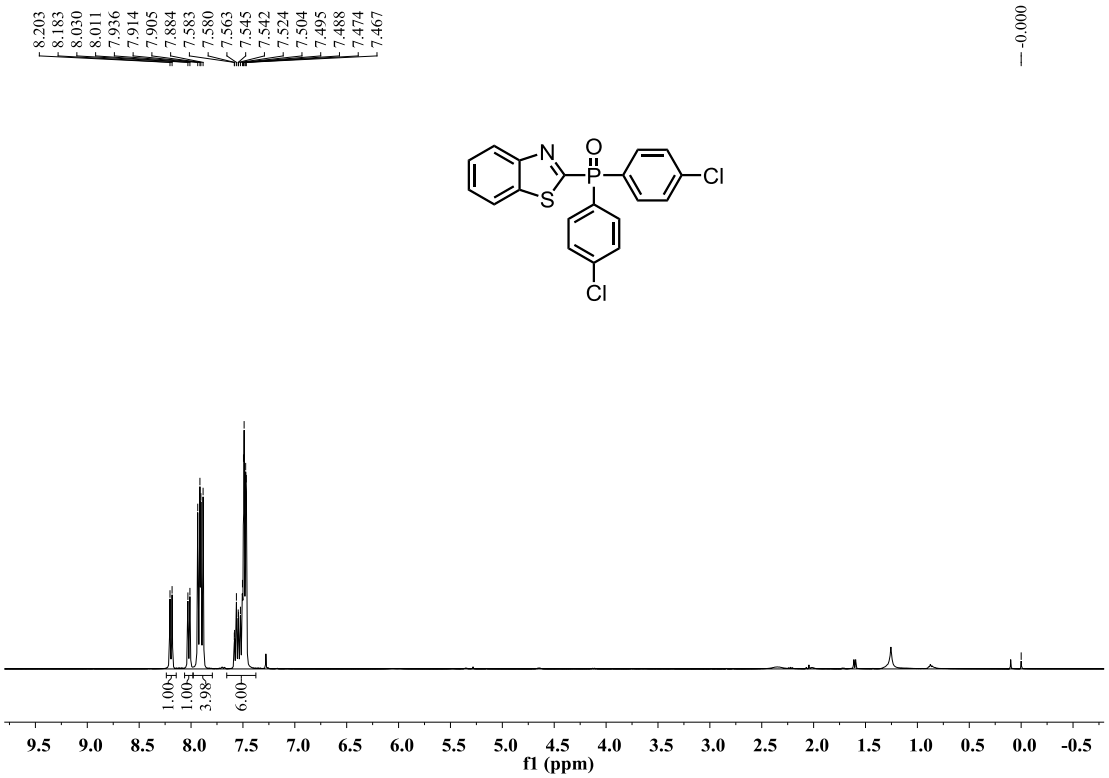

20.738
N
S
O
P
OMe
OMe

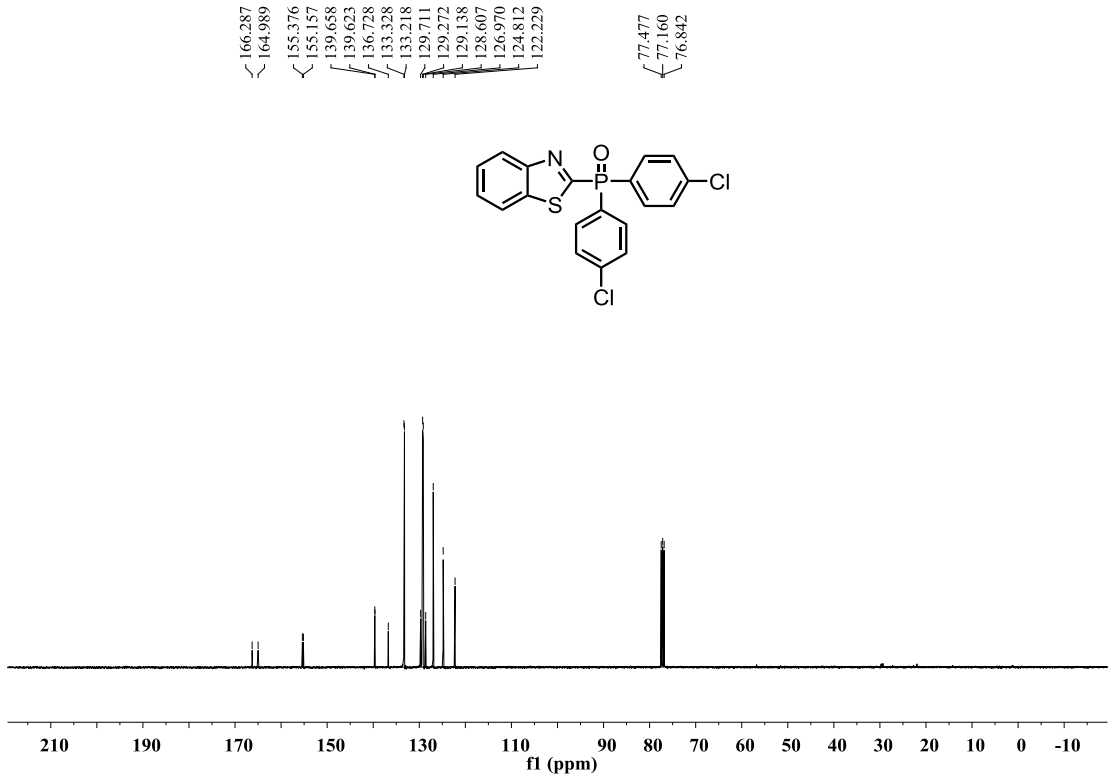
3ae

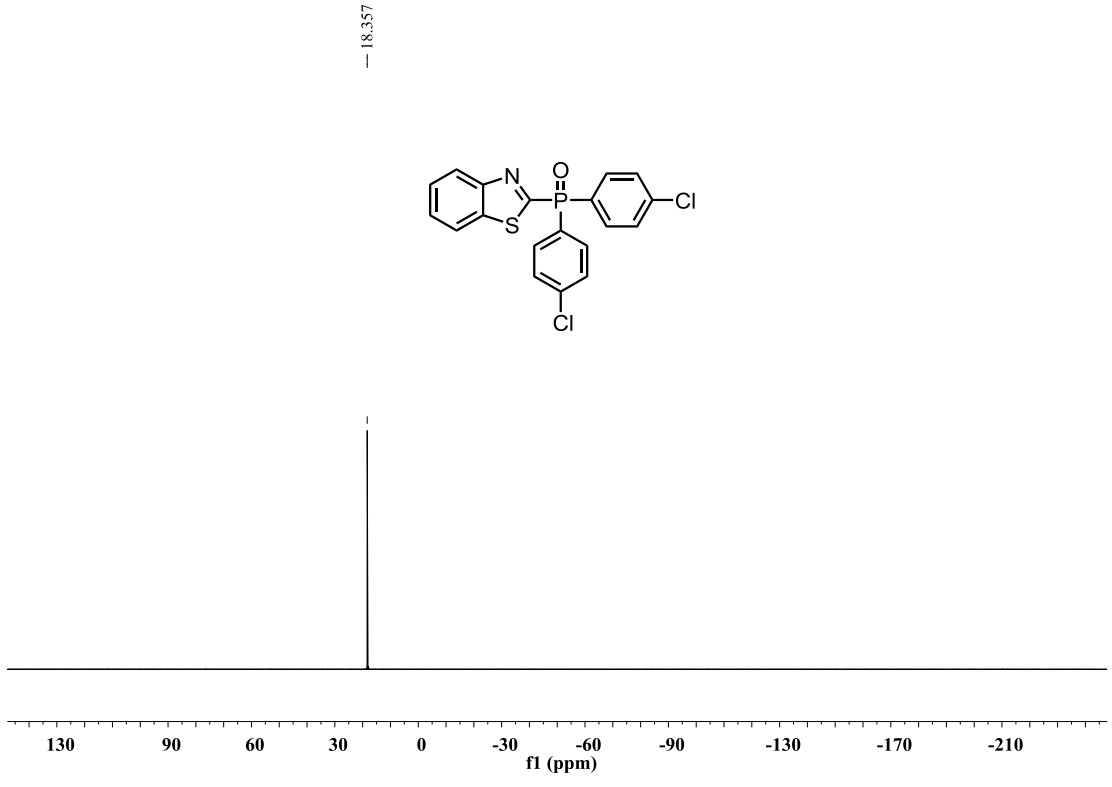

8.206
8.187
8.047
8.028
8.026
8.013
8.007
8.002
7.993
7.985
7.977
7.971
7.963
7.955
7.946
7.941
7.935
7.598
7.594
7.580
7.577
7.560
7.556
7.541
7.539
7.521
7.504
7.268
7.227
7.221
7.205
7.199
7.183
7.177
0.000
N
O
P
S
F
F
1.00
1.00
4.00
2.00
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
166.963
166.935
165.645
164.454
164.430
164.396
155.503
155.286
136.852
134.740
134.650
134.623
134.533
127.471
127.439
126.984
126.350
126.316
124.882
122.309
116.540
116.400
116.326
116.185
77.478
77.160
76.842
N
O
P
S
F
F
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


18.527
N
O
P
S
F
F
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

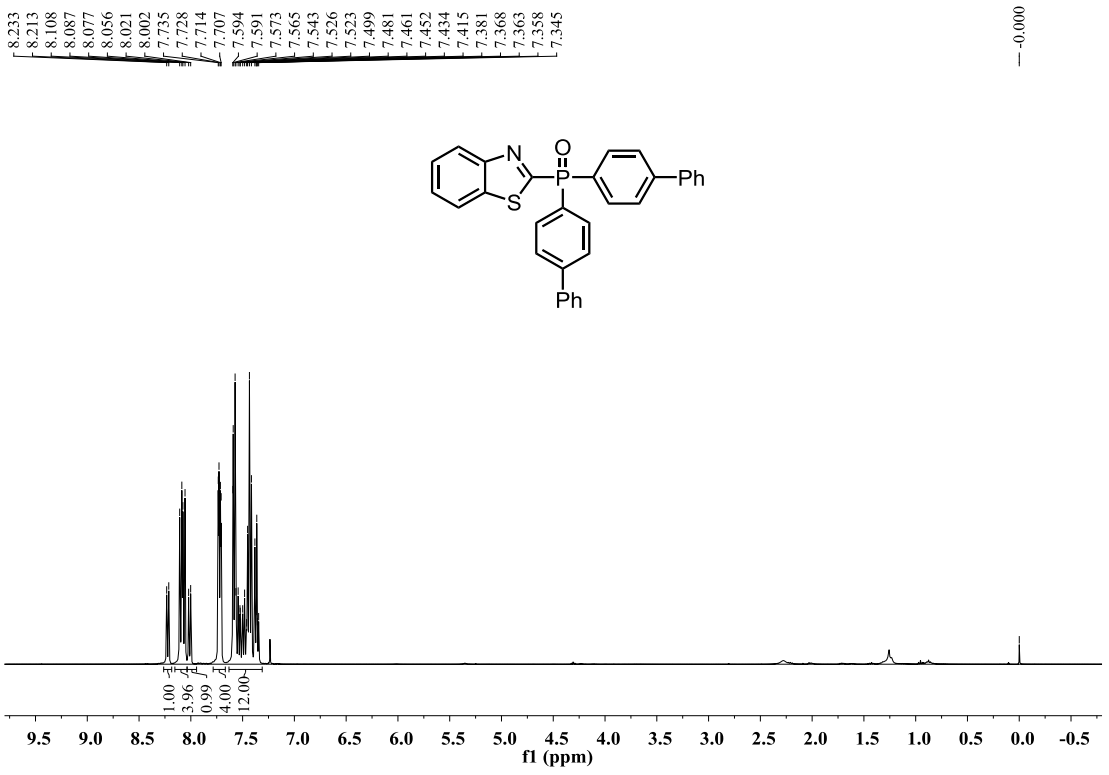
3af

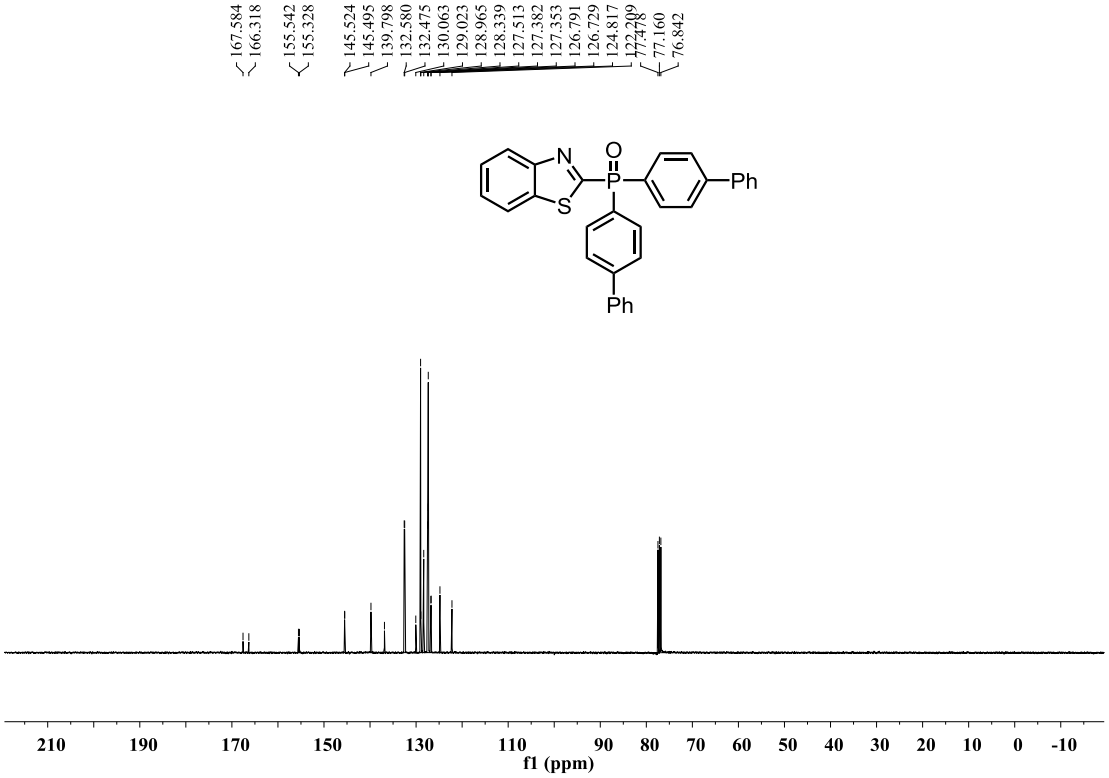

8.203
8.183
8.030
8.011
7.936
7.914
7.905
7.884
7.583
7.580
7.563
7.545
7.542
7.524
7.504
7.495
7.488
7.474
7.467
-0.000
N
O
P
S
Cl
Cl
1.00
1.00
3.98
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

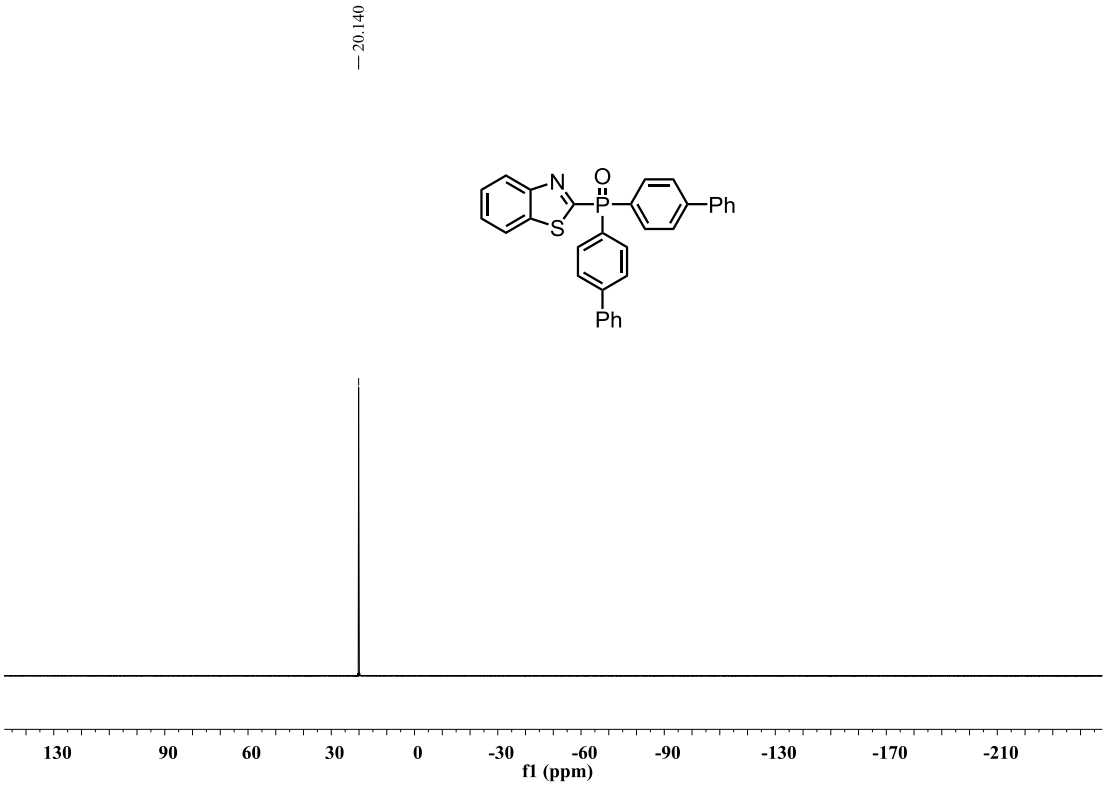

166.287
164.989
155.376
155.157
139.658
139.623
136.728
133.328
133.218
129.711
129.272
129.138
128.607
126.970
124.812
122.229
77.477
77.160
76.842
N
O
P
S
Cl
Cl
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


18.357
N
O
P
S
Cl
Cl
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

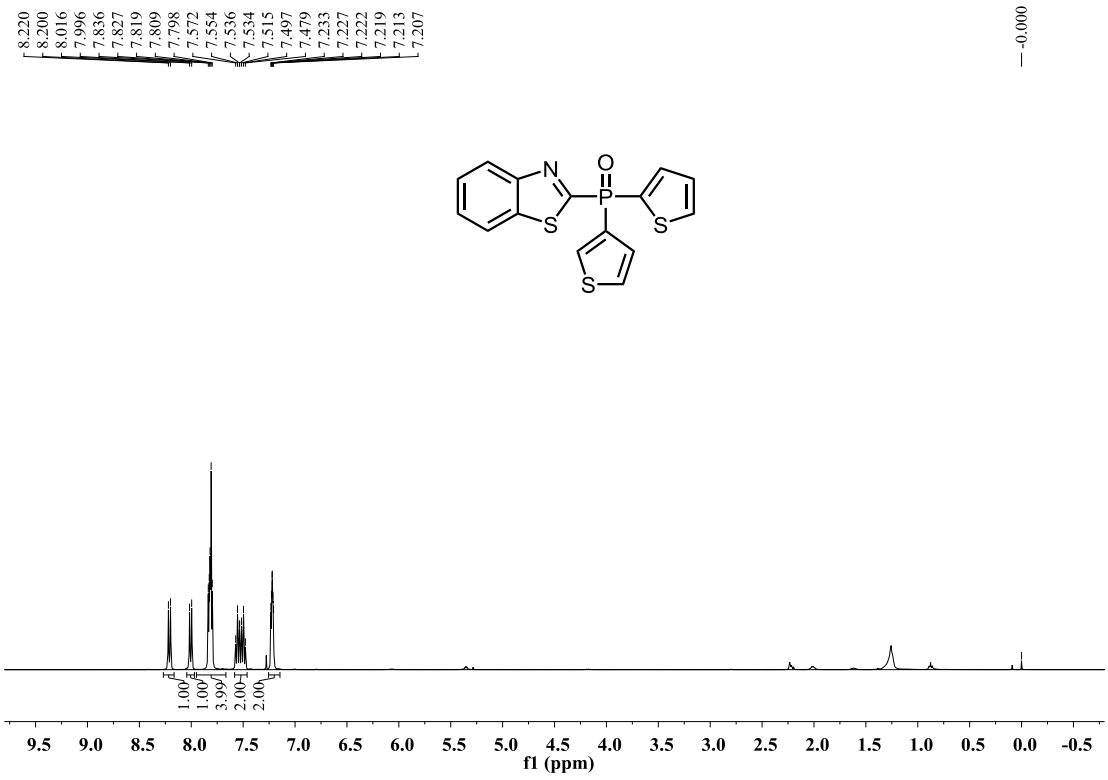
3ah

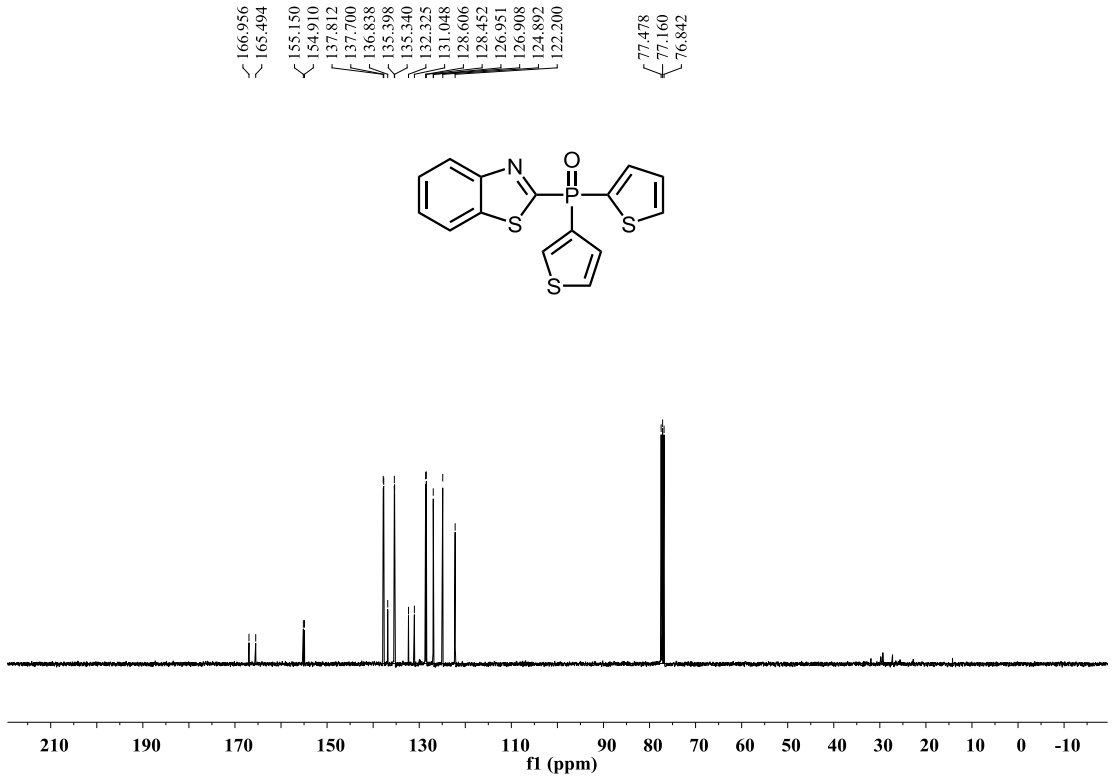

8.233
8.213
8.108
8.087
8.077
8.056
8.021
8.002
7.735
7.728
7.714
7.707
7.594
7.591
7.573
7.565
7.543
7.526
7.523
7.499
7.481
7.461
7.452
7.434
7.415
7.381
7.368
7.363
7.358
7.345
-0.000
N
O
P
S
Ph
Ph
1.00
3.96
0.99
4.00
12.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

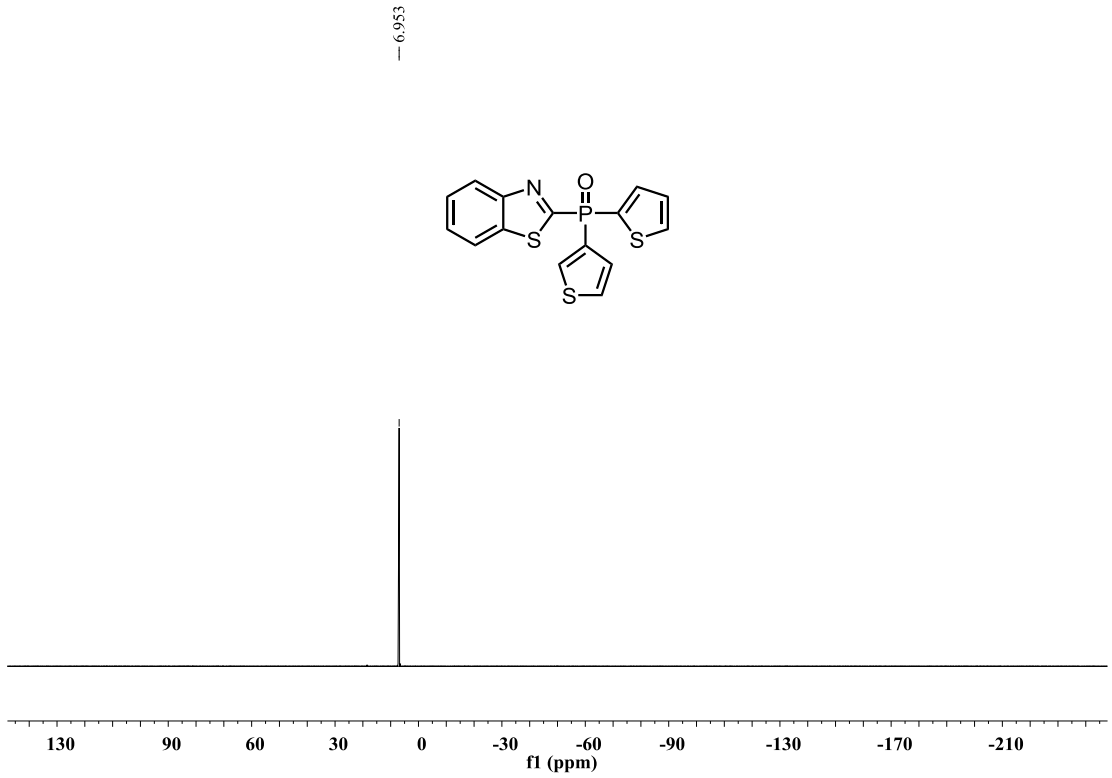

167.584
166.318
155.542
155.328
145.524
145.495
139.798
132.580
132.475
130.063
129.023
128.965
128.339
127.513
127.382
127.353
126.791
126.729
124.817
77.160
76.842
N
O
P
S
Ph
Ph
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


20.140
N
O
P
S
Ph
Ph
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

3ai


8.220
8.200
8.016
7.996
7.836
7.827
7.819
7.809
7.798
7.572
7.554
7.536
7.534
7.515
7.497
7.479
7.233
7.227
7.222
7.219
7.213
7.207
-0.000
N
O
P
S
S
S
1.00
1.00
3.99
2.00
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


166.956
165.494
155.150
154.910
137.812
137.700
136.838
135.398
135.340
132.325
131.048
128.606
128.452
126.951
126.908
124.892
122.200
77.478
77.160
76.842
N
O
P
S
S
S
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


6.953
N
O
P
S
S
S
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)