Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Regioselective Synthesis of 2-Phosphinoylindoles via Rh(III)-Catalyzed C−H Activation

Huanan Wang,[a] Shuaiqi Li,[a] Baiquan Wang,[a,b,c] and Bin Li,[*,a]

nklibin@nankai.edu.cn

[a]*State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, P. R. China.*

[b]*Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300071, P. R. China*

[c]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China*

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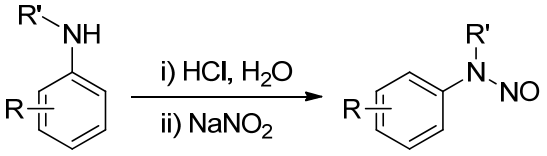
General Experimental Section

Analytic methods. All the reactions were carried out under argon atmosphere using standard Schlenk technique. ^{1}H NMR (400 MHz), ^{31}P NMR (162 MHz) and ^{13}C NMR (101 MHz) were recorded on Bruker AV400 NMR spectrometer with $CDCl_3$ as solvent, ^{19}F NMR (376 MHz) were recorded on Varian AV400 NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H, $^{13}C\{^{1}H\}$, ^{31}P, and ^{19}F NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200-300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). HRMS were done on Agilent 6520 Q-TOF LC/MS or Varian 7.0T FTMS.

General preparation for chemicals. $[Cp^*RhCl_2]_2$ was prepared from $RhCl_3 \cdot 3H_2O$ following a literature procedure.[1]

General procedure for preparation of *N*-nitrosoaniline substrates 1[2]



A mixture of aniline (0.05 mol), concentrated HCl (7.3 mL, 0.24 mol), and ice (20 g) was placed in a round-bottom flask equipped with a magnetic stir bar. The mixture was stirred vigorously while maintained at 0°C. To this mixture was added an aqueous solution (13 mL) of $NaNO_2$ (3.5 g, 0.05 mol) over the course of 10 min. The reaction was allowed to proceed for at least 1 h. The mixture was then extracted with CH_2Cl_2. The organic phase was washed with saturated brine solution, dried over $MgSO_4$, concentrated under reduced pressure, and purified by flash silica gel column chromatography (petroleum ether / ethyl acetate = 20:1) to give the corresponding *N*-nitroso aniline substrates **1**.

1-Alkynylphosphine oxides[3] were prepared according to the literature procedures. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification.

Single crystal X-ray structure of complex 3ca, 3ai.

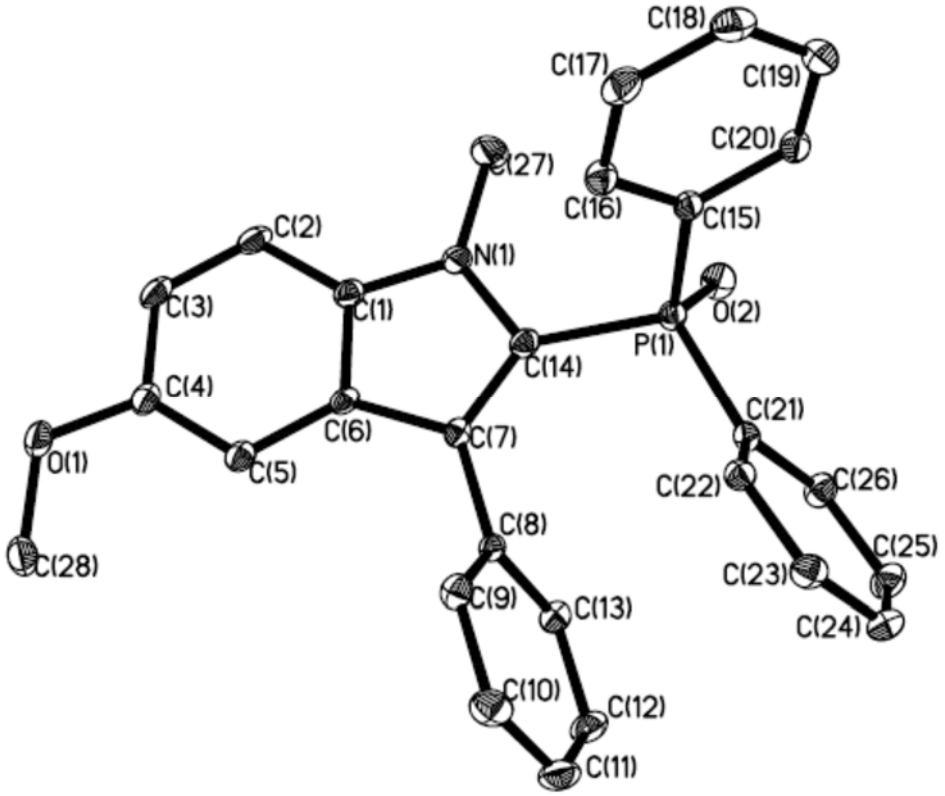


Figure S1. ORTEP diagram of complex **3ca**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

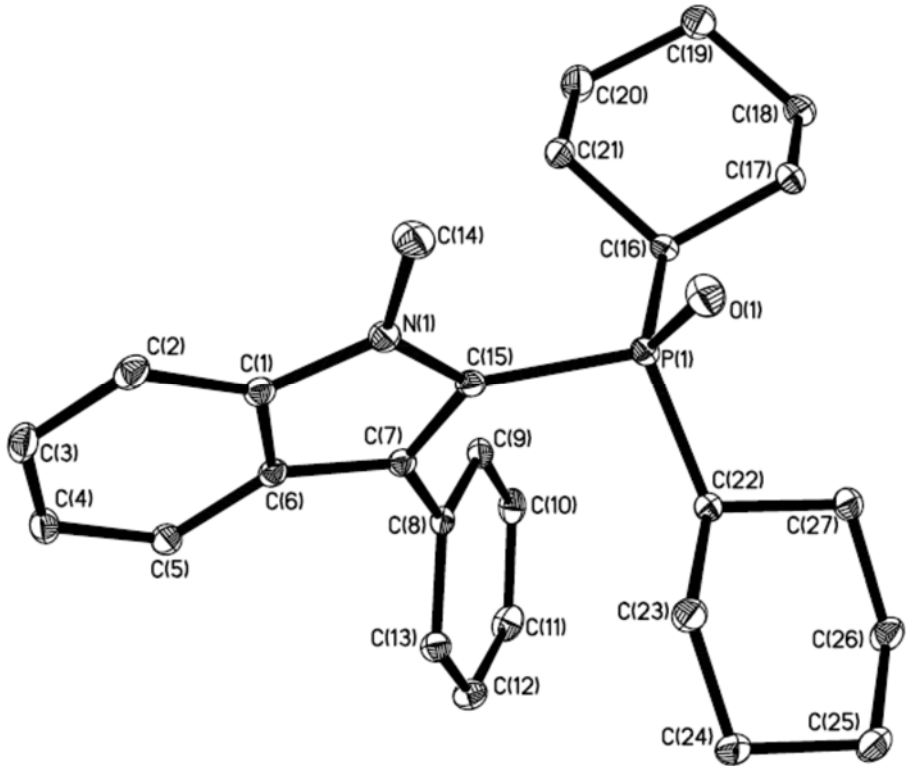
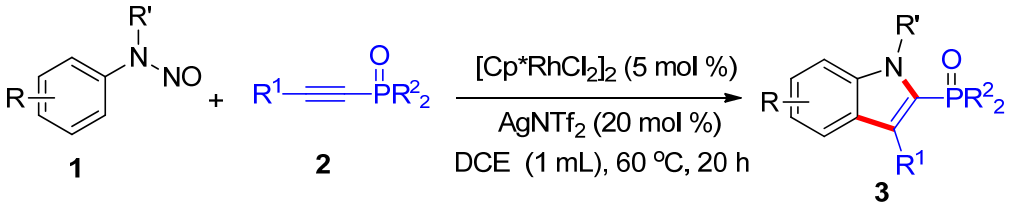


Figure S2. ORTEP diagram of complex **3ai**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

Table *S1*. Crystal Data and Summary of X-ray Data Collection for 3ca and 3ai.

	3ca	**3ai**
formula	$C_{28}H_{24}NO_2P$	$C_{27}H_{34}NOP{\cdot}0.5H_2O$
fw	437.45	428.53
crystal system	Monoclinic	Monoclinic
space group	C2/c	C2/c
a (Å)	24.609(6)	10.5217(13)
b (Å)	9.508(2)	14.8118(18)
c (Å)	21.415(5)	29.451(3)
α (deg)	90	90
β (deg)	115.972(4)	94.420(3)
γ (deg)	90	90
V (Å^3)	4504.5(18)	4576.2(9)
Z	8	8
D_{calcd} (g cm^{-3})	1.290	1.244
μ (mm^{-1})	0.148	0.142
F(000)	1840.0	1848
cryst size (mm)	0.20×0.18× 0.12	0.20×0.18× 0.12
max. 2θ (deg)	55.086	54.98
no. of reflns collected	22409	22998
no. of indep reflns/R_{int}	5094/ 0.0964	5190 / 0.0331
no. of params	291	277
goodness-of-fit on F^2	1.029	1.057
R1, wR2 ($I > 2\sigma(I)$)	0.0471, 0.1320	0.0375, 0.0934
R1, wR2 (all data)	0.0569, 0.1488	0.0427, 0.0968

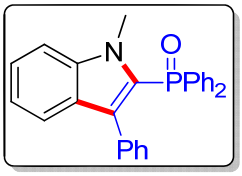
General Procedure 1: Rhodium(III)-Catalyzed C-H Annulation of *N*-nitrosoanilines 1 with 1-alkynylphosphine oxides 2.



A mixture of *N*-nitrosoanilines (**1**, 0.6 mmol, 3.0 equiv), 1-alkynylphosphine oxides (**2**, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %), and $AgNTf_2$ (15.5 mg, 0.04 mmol, 20 mol %) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 60 °C for 20 h under vigorous stirring. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether/EtOAc.

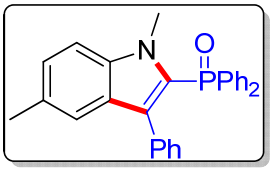
Characterization of Products 3

(1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3aa)[4]



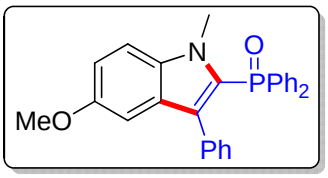
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 85% yield (69.3 mg) following the general procedure 1; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53-7.47 (m, 4H), 7.40-7.33 (m, 5H), 7.25-7.20 (m, 4H), 7.14-7.09 (m, 1H), 6.99-6.89 (m, 5H), 3.92 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 139.2 (d, *J* = 7.8 Hz), 133.3, 132.5 (d, *J* = 110.6 Hz), 131.9, 131.8, 130.6, 128.5, 128.3 (d, *J* = 12.5 Hz), 127.9 (d, *J* = 11.7 Hz), 127.4, 126.3, 125.1 (d, *J* = 120.6 Hz), 125.0, 121.3, 120.3, 109.6, 32.9; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 21.16.

(1,5-dimethyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ba)



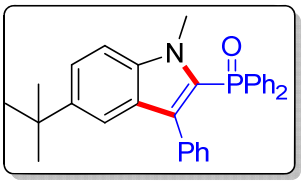
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 75% yield (63.2 mg) following the general procedure 1; mp: 147-149 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52-7.47 (m, 4H), 7.37-7.29 (m, 3H), 7.24-7.20 (m, 5H), 7.14 (s, 1H), 7.00-6.96 (m, 1H), 6.94-6.90 (m, 4H), 3.90 (s, 3H), 2.38 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 137.7 (d, *J* = 8.3 Hz), 133.5, 132.6 (d, *J* = 109.2 Hz), 131.8 (d, *J* = 10.3 Hz), 131.7 (d, *J* = 2.8 Hz), 130.7, 129.8, 128.2 (d, *J* = 12.6 Hz), 128.0 (d, *J* = 11.7 Hz), 127.9 (d, *J* = 14.8 Hz), 127.4, 126.9, 126.2, 125.0 (d, *J* = 120.0 Hz), 120.4, 109.4, 32.9, 21.2; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 21.12; **HRMS (ESI):** Calcd for $C_{28}H_{25}NOP$ $[M+H]^+$ 422.1668, Found: 422.1670.

(5-methoxy-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ca)



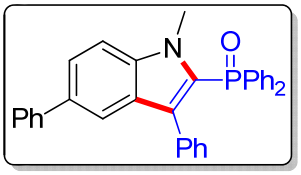
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 69% yield (60.4 mg) following the general procedure 1; mp: 200-202 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51-7.46 (m, 4H), 7.37-7.33 (m, 2H), 7.30 (d, *J* = 9.0 Hz, 1H), 7.24-7.19 (m, 4H), 7.05 (dd, *J* = 9.0, 2.3 Hz, 1H), 6.99-6.95 (m, 1H), 6.94-6.91 (m, 4H), 6.74 (d, *J* = 2.3 Hz, 1H), 3.89 (s, 3H), 3.73 (s,3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 154.7, 134.8 (d, *J* = 8.2 Hz), 133.5, 132.6 (d, *J* = 109.4 Hz), 131.8 (d, *J* = 10.2 Hz), 131.6 (d, *J* = 1.3 Hz), 130.6, 128.2 (d, *J* = 12.7 Hz), 128.0 (d, *J* = 11.7 Hz), 127.7 (d, *J* = 14.8 Hz), 127.5, 126.2, 125.4 (d, *J* = 119.8 Hz), 116.4, 110.5, 101.3, 55.7, 33.0; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 21.00; **HRMS (ESI):** Calcd for $C_{28}H_{25}NO_2P$ $[M+H]^+$ 438.1617, Found: 438.1621.

(5-(tert-butyl)-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3da)



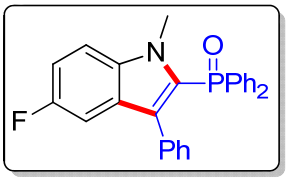
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 57% yield (52.8 mg) following the general procedure 1; mp: 160-162 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52-7.47 (m, 5H), 7.36-7.32 (m, 4H), 7.24-7.19 (m, 4H), 6.99-6.90 (m, 5H), 3.90 (s, 3H), 1.31 (s, 9H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 143.3, 137.6 (d, *J* = 8.3 Hz), 133.4, 132.7 (d, *J* = 109.4 Hz), 131.8 (d, *J* = 10.3 Hz), 131.6, 130.6, 128.4 (d, *J* = 14.6 Hz), 128.2 (d, *J* = 12.5 Hz), 127.5, 127.4, 126.2, 125.2 (d, *J* = 119.5 Hz), 123.6, 116.4, 109.2, 34.6, 32.9, 31.7; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 20.99; **HRMS (ESI):** Calcd for $C_{31}H_{31}NOP$ $[M+H]^+$ 464.2138, Found: 464.2134.

(1-methyl-3,5-diphenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ea)



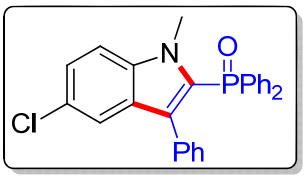
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 74% yield (71.5 mg) following the general procedure 1; mp: 219-221 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.56-7.52 (m, 5H), 7.51-7.46 (m, 3H), 7.40-7.35 (m, 4H), 7.30-7.28 (m, 1H), 7.26-7.21 (m, 4H), 6.99-6.90 (m,5H), 3.96 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 141.8, 138.8 (d, *J* = 8.3 Hz), 133.5 (d, *J* = 113.3 Hz), 133.2, 131.89, 131.86, 131.81, 131.79, 130.7, 128.8 (d, *J* = 14.6 Hz), 128.6, 128.4 (d, *J* = 11.7 Hz), 128.3 (d, *J* = 12.8 Hz), 127.5, 127.3, 126.5 (d, *J* = 13.1 Hz), 125.8 (d, *J* = 120.7 Hz), 125.0, 119.5, 110.0, 33.1; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 21.19; **HRMS (ESI):** Calcd for $C_{33}H_{27}NOP$ $[M+H]^+$ 484.1825, Found: 484.1830.

(5-fluoro-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3fa)



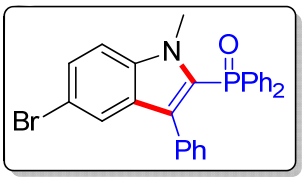
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 60% yield (51.0 mg) following the general procedure 1; mp: 180-182 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52-7.47 (m, 4H), 7.38-7.31 (m, 3H), 7.25-7.20 (m, 4H), 7.13 (td, *J* = 9.0, 2.3 Hz, 1H 1H), 7.00-6.95 (m, 2H), 6.93-6.88 (m, 4H), 3.91 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 158.2 (d, *J* = 236.9 Hz), 135.8 (d, *J* = 7.9 Hz), 132.3 (d, *J* = 109.4 Hz), 131.8, 131.7, 130.4, 128.3, 128.2, 128.1 (d, *J* = 10.9 Hz), 127.9 (d, *J* = 8.9 Hz), 127.5, 126.9 (d, *J* = 125.2 Hz), 126.5, 113.9 (d, *J* = 26.8 Hz), 110.5 (d, *J* = 9.4 Hz), 105.4 (d, *J* = 23.6 Hz), 33.1; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 21.10; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -123.45; **HRMS (ESI):** Calcd for $C_{27}H_{22}FNOP$ $[M+H]^+$ 426.1418, Found: 426.1426.

(5-chloro-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ga)



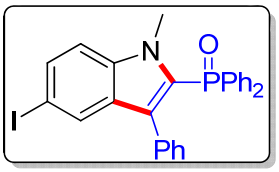
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 62% yield (54.8 mg) following the general procedure 1; mp: 194-196 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51-7.46 (m, 4H), 7.39-7.35 (m, 2H), 7.32 (br s, 3H), 7.25-7.21 (m, 4H), 7.01-6.97 (m, 1H), 6.94-6.88 (m, 4H), 3.91 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 137.5 (d, *J* = 7.8 Hz), 132.6, 132.2 (d, *J* = 109.4 Hz), 131.8 (d, *J* = 2.4 Hz), 131.7 (d, *J* = 10.3 Hz), 130.5, 128.8 (d, *J* = 12.0 Hz), 128.4, 128.3, 127.5, 127.1 (d, *J* = 112.4 Hz), 126.6, 126.1, 125.4, 120.4, 110.7, 33.1; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 21.01; **HRMS (ESI):** Calcd for $C_{27}H_{22}ClONP$ $[M+H]^+$ 442.1122, Found: 442.1122.

(5-bromo-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ha)



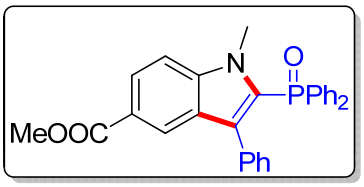
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 58% yield (56.4 mg) following the general procedure 1; mp: 195-197 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51-7.42 (m, 6H), 7.38-7.35 (m, 2H), 7.28 (s, 1H), 7.26-7.21 (m, 4H), 7.01-6.97 (m, 1H), 6.94-6.87 (m, 4H), 3.90 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 137.8 (d, *J* = 8.2 Hz), 132.6, 132.2 (d, *J* = 109.6 Hz), 131.9 (d, *J* = 2.5 Hz), 131.8, 131.7, 130.5, 129.5 (d, *J* = 12.0 Hz), 128.4 (d, *J* = 12.7 Hz), 127.58 (d, *J* = 14.0 Hz), 127.57, 126.6, 126.5 (d, *J* = 117.4 Hz), 123.5, 113.6, 111.2, 33.1; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 20.96; **HRMS (ESI):** Calcd for $C_{27}H_{22}BrNOP$ $[M+H]^+$ 486.0617, Found: 486.0612.

(5-iodo-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ia)



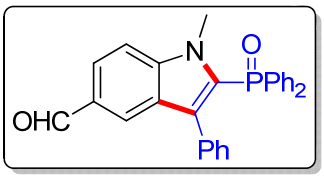
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 71% yield (75.7 mg) following the general procedure 1 but for 30 hours; mp: 190-192 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (br s, 1H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.50-7.45 (m, 4H), 7.38-7.34 (m, 2H), 7.25-7.20 (m, 4H), 7.18 (d, *J* = 8.7 Hz, 1H), 7.01-6.97 (m, 1H), 6.94-6.87 (m, 4H), 3.90 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 138.2 (d, *J* = 8.1 Hz), 133.2, 132.5, 132.1 (d, *J* = 109.6 Hz), 131.9 (d, *J* = 2.8 Hz), 131.7 (d, *J* = 10.4 Hz), 130.5, 130.3 (d, *J* = 11.8 Hz), 129.9, 128.3 (d, *J* = 12.7 Hz), 127.6, 127.3 (d, *J* = 14.5 Hz), 126.6, 126.1 (d, *J* = 117.2 Hz), 111.6, 83.7, 33.0; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 21.18; **HRMS (ESI):** Calcd for $C_{27}H_{22}INOP$ $[M+H]^+$ 534.0478, Found: 534.0479.

Methyl 2-(diphenylphosphoryl)-1-methyl-3-phenyl-1*H*-indole-5-carboxylate (3ja)



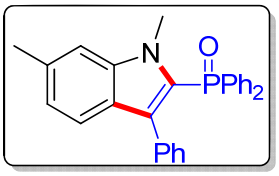
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 67% yield (62.4 mg) following the general procedure 1; mp: 66-68 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 1.1 Hz, 1H), 8.07-8.04 (m, 1H), 7.52-7.47 (m, 4H), 7.42-7.36 (m, 3H), 7.26-7.22 (m, 4H), 7.01-6.99 (m, 1H), 6.96-6.92 (m, 4H), 3.94 (s, 3H), 3.86 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 167.5, 141.3 (d, *J* = 7.8 Hz), 132.4, 132.0 (d, *J* = 109.0 Hz), 131.9 (d, *J* = 2.2 Hz), 131.7 (d, *J* = 10.3 Hz), 130.5, 129.7 (d, *J* = 13.8 Hz), 128.3 (d, *J* = 12.6 Hz), 127.55, 127.48, 127.0 (d, *J* = 118.0 Hz), 126.7, 126.0, 124.4, 122.5, 109.4, 51.8, 33.2; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 20.97; **HRMS (ESI):** Calcd for $C_{29}H_{25}NO_3P$ $[M+H]^+$ 466.1567, Found: 466.1574.

2-(diphenylphosphoryl)-1-methyl-3-phenyl-1*H*-indole-5-carbaldehyde (3ka)



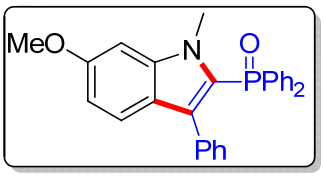
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 1/5) as a white solid in 62% yield (54.3 mg) following the general procedure 1; mp: 184-186 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.92 (s, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.86 (s, 1H), 7.53-7.48 (m, 5H), 7.39-7.36 (m, 2H), 7.26-7.24 (m, 4H), 7.04-7.01 (m, 1H), 6.97-6.91 (m, 4H), 3.96 (s,3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.8, 142.0 (d, *J* = 7.4 Hz), 132.2, 132.0, 131.8 (d, *J* = 110.9 Hz), 131.7 (d, *J* = 10.1 Hz), 131.3, 130.4, 130.2, 130.0, 128.4 (d, *J* = 12.6 Hz), 127.9 (d, *J* = 11.5 Hz), 127.7, 127.2, 126.9, 124.5, 110.4, 33.3; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 20.74; **HRMS (ESI):** Calcd for $C_{28}H_{23}NO_2P$ $[M+H]^+$ 436.1461, Found: 434.1465.

(1,6-dimethyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3la)



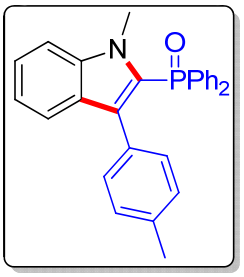
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 70% yield (59.0 mg) following the general procedure 1; mp: 197-199 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52-7.46 (m, 4H), 7.37-7.32 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.24-7.19 (m, 5H), 6.96-6.88 (m, 6H), 3.88 (s, 3H), 2.52 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 139.6 (d, *J* = 8.3 Hz), 135.3, 133.5, 132.7 (d, *J* = 109.4 Hz), 131.8 (d, *J* = 10.4 Hz), 131.6 (d, *J* = 2.9 Hz), 130.6, 128.5 (d, *J* = 14.6 Hz), 128.2 (d, *J* = 12.7 Hz), 127.3, 126.2, 125.9 (d, *J* = 11.9 Hz), 124.4 (d, *J* = 121.0 Hz), 122.4, 120.9, 109.3, 32.8 (d, *J* = 1.3 Hz), 22.0; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 20.99; **HRMS (ESI):** Calcd for $C_{28}H_{25}NOP$ $[M+H]^+$ 422.1668, Found: 422.1669.

(6-methoxy-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ma)



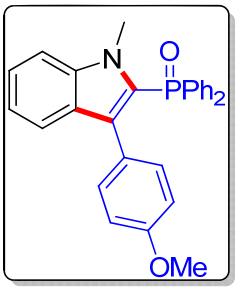
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 52% yield (45.5 mg) following the general procedure 1 but using DCE/TFE (0.5 mL/0.5 mL) as solvent; mp: 142-144 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47-7.42 (m, 4H), 7.36-7.32 (m, 2H), 7.29-7.25(m, 1H), 7.23-7.20 (m, 4H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.92-6.88 (m, 3H), 6.81-6.78 (m, 2H), 6.44 (d, *J* = 7.7 Hz, 1H), 3.92 (s, 3H), 3.52 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 155.6, 140.9 (d, *J* = 8.1 Hz), 134.6, 132.8 (d, *J* = 109.6 Hz), 131.8 (d, *J* = 10.5 Hz), 131.5 (d, *J* = 2.0 Hz), 131.1, 129.8 (d, *J* = 3.5 Hz), 128.2 (d, *J* = 12.5 Hz), 127.8 (d, *J* = 15.5 Hz), 126.3, 125.8 (d, *J* = 31.6 Hz), 124.1 (d, *J* = 121.3 Hz), 117.5 (d, *J* = 12.0 Hz), 102.7, 100.2, 55.1, 33.2; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 21.77; **HRMS (ESI):** Calcd for $C_{28}H_{25}NO_2P$ $[M+H]^+$ 438.1617, Found: 438.1616.

(1-methyl-3-(p-tolyl)-1*H*-indol-2-yl)diphenylphosphine oxide (3ab)



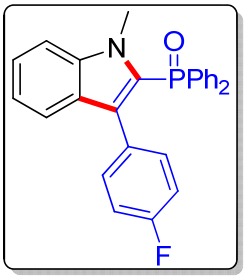
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 60% yield (50.6 mg) following the general procedure 1; mp: 164-166 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51-7.45 (m, 4H), 7.41-7.35 (m, 5H), 7.24-7.21 (m, 4H), 7.13-7.09 (m, 1H), 6.80 (d, *J* = 7.6 Hz, 2H), 6.69 (d, *J* = 7.5 Hz, 2H), 3.92 (s, 3H), 2.21 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 139.2 (d, *J* = 8.0 Hz), 135.7, 132.7 (d, *J* = 109.3 Hz), 131.8 (d, *J* = 10.3 Hz), 131.3, 130.4, 130.1, 128.4 (d, *J* = 14.8 Hz), 128.2 (d, *J* = 12.7 Hz), 128.0, 127.8 (d, *J* = 11.7 Hz), 125.3 (d, *J* = 120.3 Hz), 124.9, 121.2, 120.2, 109.5, 32.8, 21.0; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 21.16; **HRMS (ESI):** Calcd for $C_{28}H_{25}NOP$ $[M+H]^+$ 422.1668, Found: 422.1672.

(3-(4-methoxyphenyl)-1-methyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ac)



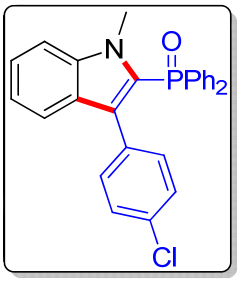
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 58% yield (50.8 mg) following the general procedure 1; mp: 200-202 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52-7.47 (m, 4H), 7.41-7.35 (m, 5H), 7.26-7.24 (m, 4H), 7.13-7.10 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.45 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H), 3.72 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 158.0, 139.2 (d, *J* = 8.1 Hz), 132.8 (d, *J* = 109.3 Hz), 131.8 (d, *J* = 10.2 Hz), 131.6, 131.52, 131.50, 128.2 (d, *J* = 12.6 Hz), 127.9 (d, *J* = 12.0 Hz), 125.5, 125.2 (d, *J* = 121.9 Hz), 124.9, 121.2, 120.2, 113.0, 109.5, 55.1, 32.9; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 20.91; **HRMS (ESI):** Calcd for $C_{28}H_{25}NO_2P$ $[M+H]^+$ 438.1617, Found: 438.1624.

(3-(4-fluorophenyl)-1-methyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ad)



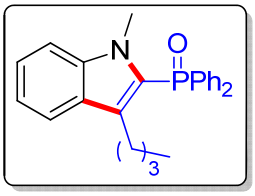
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 66% yield (56.2 mg) following the general procedure 1; mp: 151-153 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52-7.49 (m, 4H), 7.42-7.39 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.28-7.26 (m, 4H), 7.15-7.11 (m, 1H), 6.90 (t, *J* = 6.8 Hz, 2H), 6.62 (t, *J* = 8.5 Hz, 2H), 3.91 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 161.4 (d, *J* = 245.4 Hz), 139.1 (d, *J* = 8.2 Hz), 132.4 (d, *J* = 114.7 Hz), 132.1 (d, *J* = 8.1 Hz), 131.8, 131.73 (d, *J* = 2.8 Hz), 131.71, 129.2 (d, *J* = 3.1 Hz), 128.3 (d, *J* = 12.6 Hz), 127.8 (d, *J* = 11.5 Hz), 127.1 (d, *J* = 14.5 Hz), 125.5 (d, *J* = 120.1 Hz), 125.1, 120.7 (d, *J* = 48.1 Hz), 114.3 (d, *J* = 21.4 Hz), 109.6, 32.9; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 20.83; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -116.15; **HRMS (ESI):** Calcd for $C_{27}H_{22}FNOP$ $[M+H]^+$ 426.1418, Found: 426.1422.

(3-(4-chlorophenyl)-1-methyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ae)



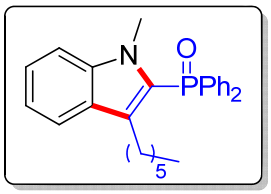
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 49% yield (43.3 mg) following the general procedure 1; mp: 177-179 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51-7.46 (m, 4H), 7.44-7.39 (m, 4H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.28-7.24 (m, 4H), 7.16-7.12 (m, 1H), 6.88-6.83 (m, 4H), 3.92 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 139.2 (d, *J* = 8.1 Hz), 132.43, 132.36 (d, *J* = 111.2 Hz), 131.87, 131.81, 131.77, 131.73, 128.5, 128.3, 127.5, 126.96 (d, *J* = 132.2 Hz), 126.88 (d, *J* = 14.4 Hz), 125.2, 120.9, 120.6, 109.7, 32.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.76; **HRMS (ESI):** Calcd for $C_{27}H_{22}ClNOP$ $[M+H]^+$ 442.1122, Found: 442.1120.

(3-butyl-1-methyl-1*H*-indol-2-yl)diphenylphosphine oxide (3af)



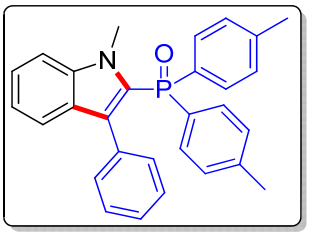
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 87% yield (67.4 mg) following the general procedure 1 but at 80 °C; mp: 99-101 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73-7.68 (m, 4H), 7.62-7.56 (m, 3H), 7.50-7.46 (m, 4H), 7.36-7.31 (m, 2H), 7.15-7.11 (m, 1H), 3.82 (s, 3H), 2.11-2.04 (m, 2H), 1.28-1.18 (m, 2H), 0.97-0.88 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 139.7 (d, *J* = 8.3 Hz), 133.1 (d, *J* = 108.6 Hz), 132.2 (d, *J* = 2.0 Hz), 131.9 (d, *J* = 10.5 Hz), 128.6 (d, *J* = 12.4 Hz), 127.6 (d, *J* = 15.5 Hz), 127.3 (d, *J* = 12.6 Hz), 124.5, 124.0 (d, *J* = 118.2 Hz), 120.2, 119.4, 109.6, 34.3, 32.6, 24.6, 22.9, 13.7; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 22.07; **HRMS (ESI):** Calcd for $C_{25}H_{27}NOP$ $[M+H]^+$ 388.1825, Found: 388.1828.

(3-hexyl-1-methyl-*1H*-indol-2-yl)diphenylphosphine oxide (3ag)



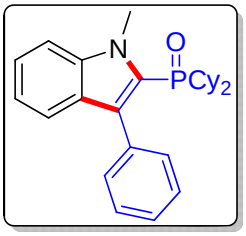
The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as an colorless oil in 67% yield (55.7 mg) following the general procedure 1 but at 80 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73-7.68 (m, 4H), 7.62-7.56 (m, 3H), 7.52-7.47 (m, 4H), 7.32 (s, 2H), 7.13 (br s, 1H), 3.82 (s, 3H), 2.10-2.06 (m, 2H), 1.26-1.16 (m, 4H), 1.09-1.05 (m, 2H), 0.92-0.88 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 139.8 (d, *J* = 8.2 Hz), 133.2 (d, *J* = 108.3 Hz), 132.2, 131.9 (d, *J* = 10.2 Hz), 128.7 (d, *J* = 12.4 Hz), 127.6 (d, *J* = 15.3 Hz), 127.3 (d, *J* = 12.6 Hz), 124.5, 124.0 (d, *J* = 122.1 Hz), 120.3, 119.4, 109.7, 32.6, 32.2, 31.5, 29.6, 24.9, 22.5, 14.0; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 22.09; **HRMS (ESI):** Calcd for $C_{27}H_{31}NOP$ $[M+H]^+$ 416.2138, Found: 416.2143.

(1-methyl-3-phenyl-*1H*-indol-2-yl)di-*p*-tolylphosphine oxide (3ah)



The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 62% yield (54.0 mg) following the general procedure 1; mp: 85-87 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41-7.35 (m, 7H), 7.12-7.09 (m, 1H), 7.01 (d, *J* = 7.4 Hz, 5H), 6.90 (d, *J* = 4.3 Hz, 4H), 3.94 (s, 3H), 2.30 (s, 6H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 142.1 (d, *J* = 2.5 Hz), 139.1 (d, *J* = 8.0 Hz), 133.5, 131.8 (d, *J* = 10.7 Hz), 130.7, 129.2 (d, *J* = 112.1 Hz), 129.0 (d, *J* = 13.0 Hz), 128.02 (d, *J* = 25.1 Hz), 128.01, 127.2, 125.8 (d, *J* = 118.7 Hz), 125.5, 124.8, 121.1, 120.2, 109.5, 32.8, 21.4; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 21.54; **HRMS (ESI):** Calcd for $C_{29}H_{27}NOP$ $[M+H]^+$ 436.1825, Found: 436.1830.

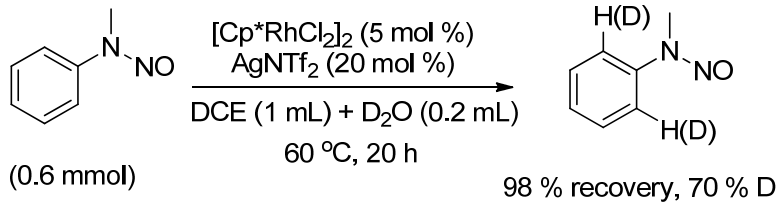
dicyclohexyl(1-methyl-3-phenyl-1*H*-indol-2-yl)phosphine oxide (3ai)



The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 76% yield (63.8 mg) following the general procedure 1; mp: 100-102 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.44-7.43 (m, 4H), 7.36-7.29 (m, 3H), 7.26-7.24 (m, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.26 (s, 3H), 1.93-1.90 (m, 2H), 1.78-1.73 (m, 2H), 1.69-1.66 (m, 2H), 1.61-4.48 (m, 8H), 1.45-1.38 (m,2H), 1.18-0.94 (m, 6H). **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 139.3 (d, *J* = 6.5 Hz), 135.2, 130.7, 128.4 (d, *J* = 11.2 Hz), 128.2, 127.6, 124.4 (d, *J* = 91.2 Hz), 123.9, 123.5 (d, *J* = 13.9 Hz), 120.4, 120.1, 109.6, 38.6 (d, *J* = 69.0 Hz), 32.9, 26.4 (d, *J* = 13.0 Hz), 26.2, 26.0, 25.6, 25.5 (d, *J* = 2.2 Hz). **^{31}P NMR (162 MHz, CDCl$_3$)** δ 49.19. **HRMS (ESI):** Calcd for $C_{27}H_{35}NOP$ $[M+H]^+$ 420.2451, Found: 420.2458.

Mechanism Studies

H/D exchange

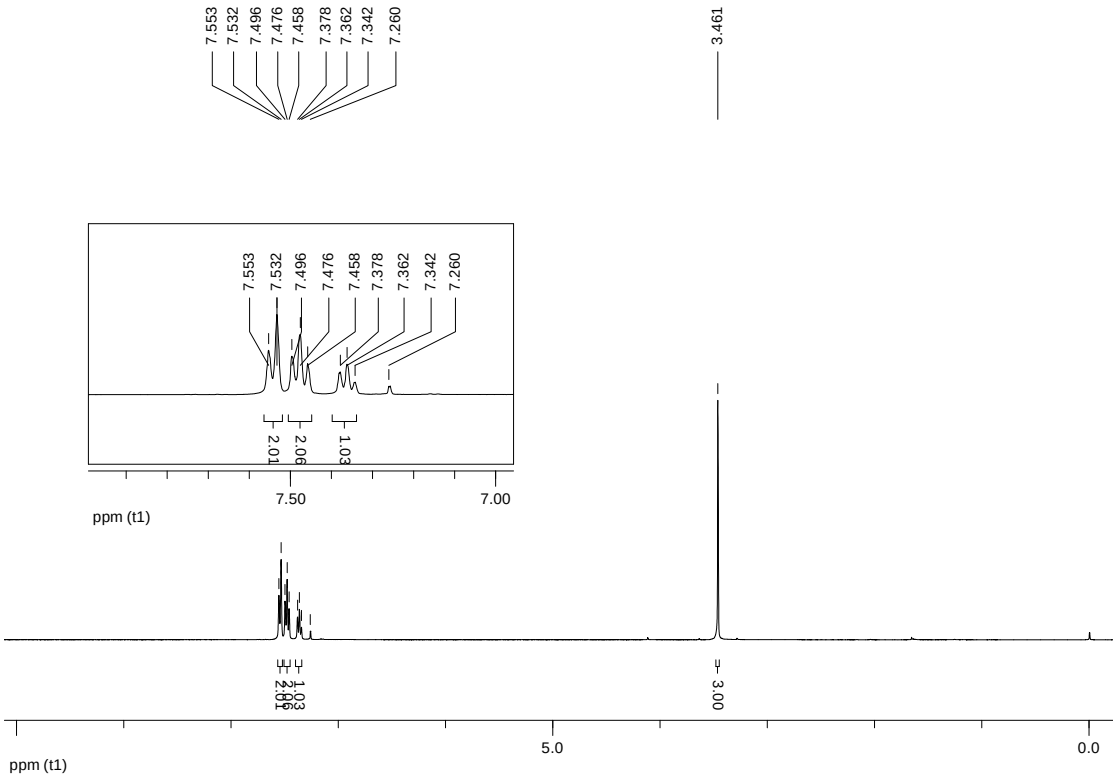


(0.6 mmol)

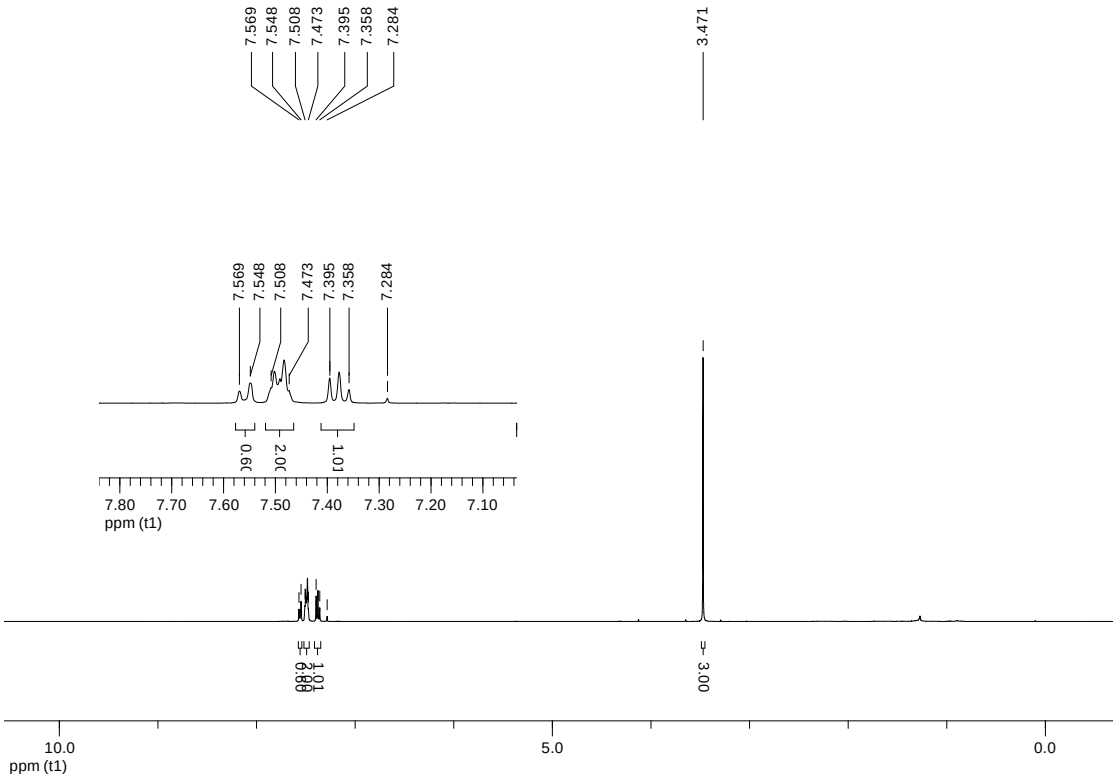
98 % recovery, 70 % D

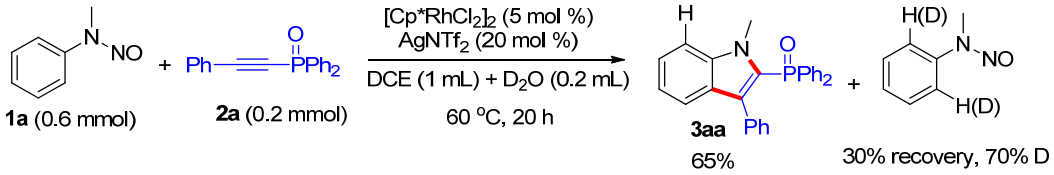
According to the **General Procedure 1**, but with addition of D_2O (0.2 mL) and without 1-alkynylphosphine oxide. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether/EtOAc. According to the NMR spectrum, ***70% deuterium incorporation at both ortho positions of the directing group***.

1a:



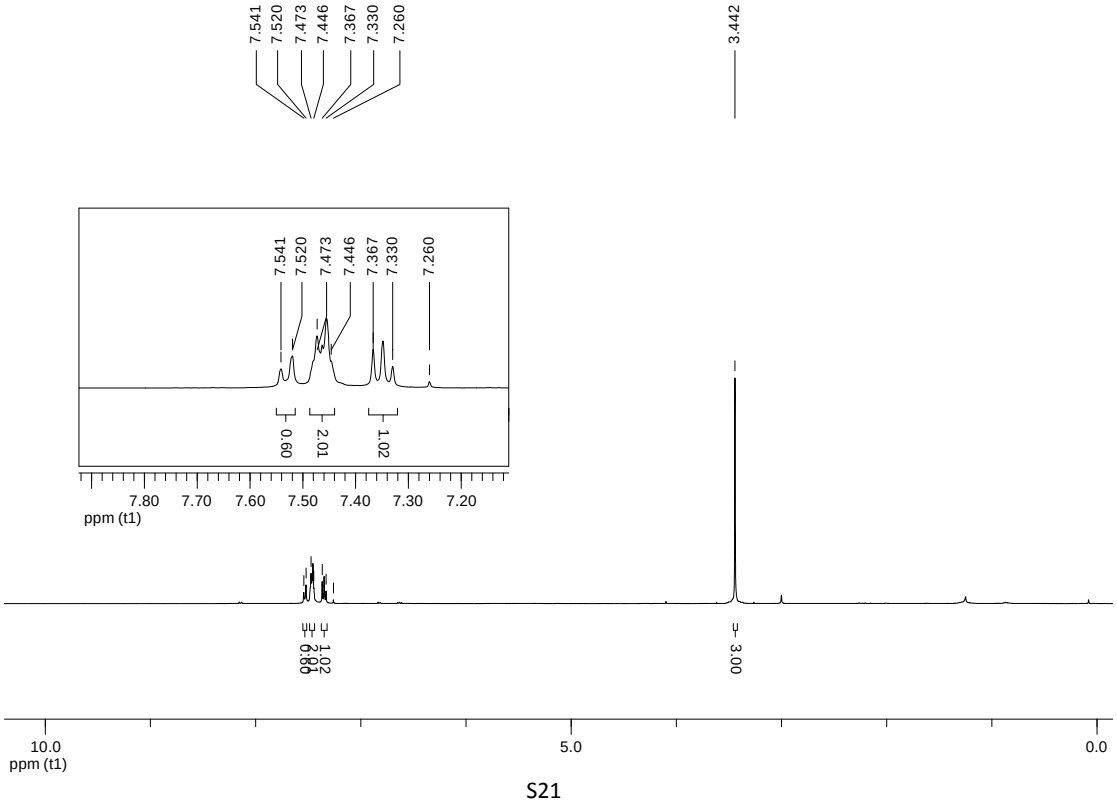
Recovered 1a after the reaction:



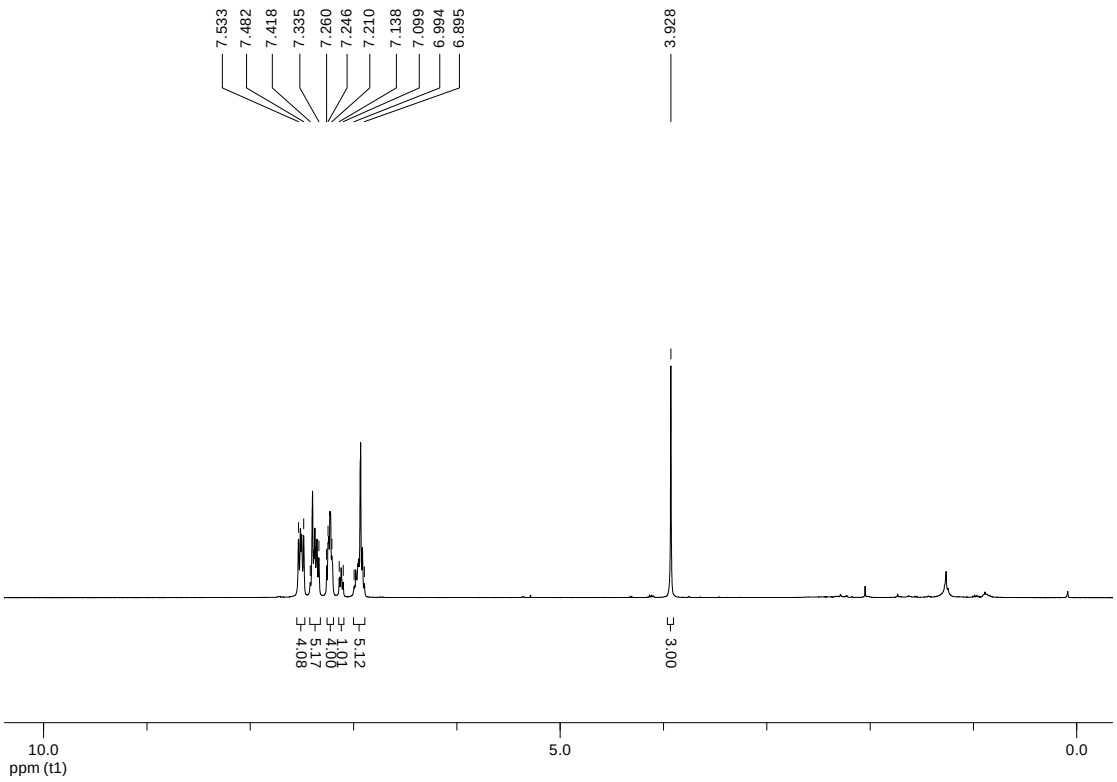


A mixture of N-nitrosoaniline (**1a**, 0.6 mmol, 3.0 equiv), 1-alkynylphosphine oxides (**2a**, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %), and $AgNTf_2$ (15.5 mg, 0.04 mmol, 20 mol %) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.0 mL) ,D_2O (0.2 mL) were added and the resulting mixture was then put in a pre-heated oil bath at 60 °C for 20 h under vigorous stirring. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether/EtOAc. Product **3aa** was isolated in 65% yield and 30% of **1a** was recovered. According to the NMR spectrum, ***no deuterium incorporation was detected in product 3aa while 70% deuterium incorporation at the ortho position of the directing group in the unreacted 1a***.

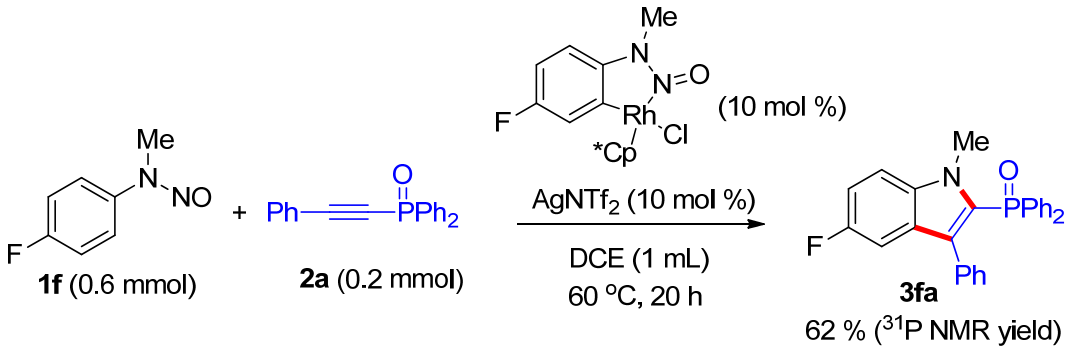
Recovered 1a after the reaction:



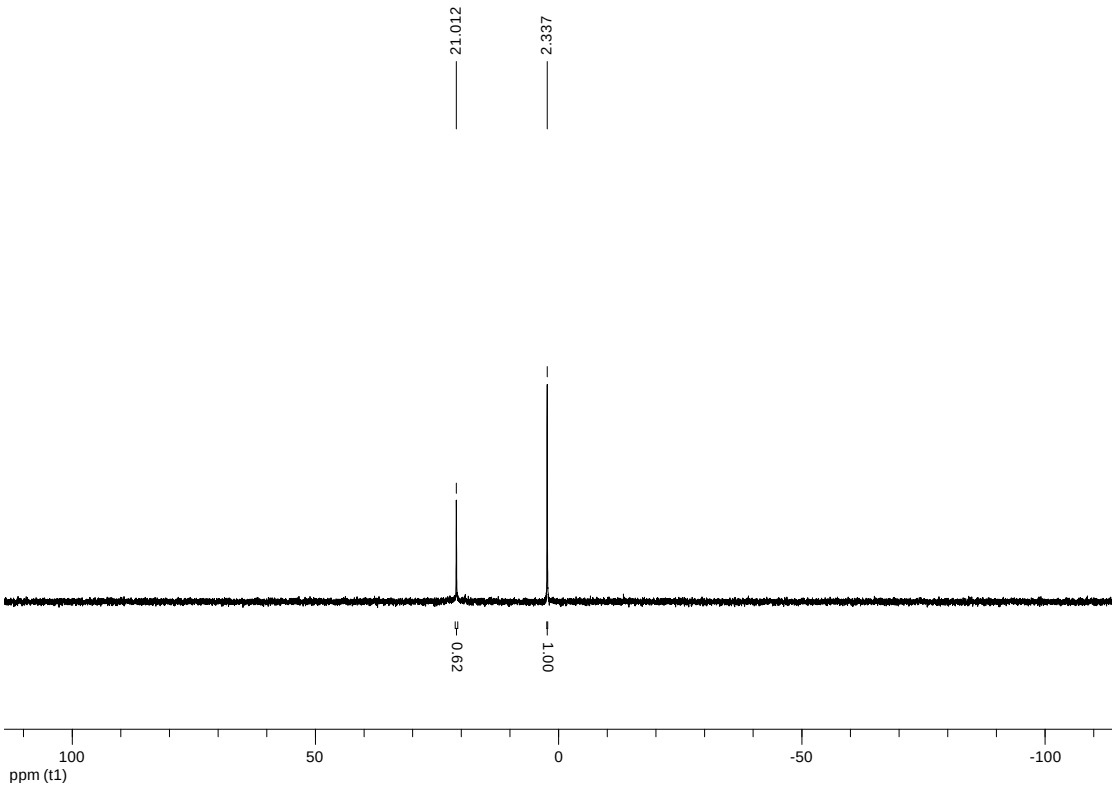
3aa:


7.533
7.482
7.418
7.335
7.260
7.246
7.210
7.138
7.099
6.994
6.895
3.928
4.08
5.17
4.00
1.01
5.12
3.00
10.0
ppm (t1)
5.0
0.0

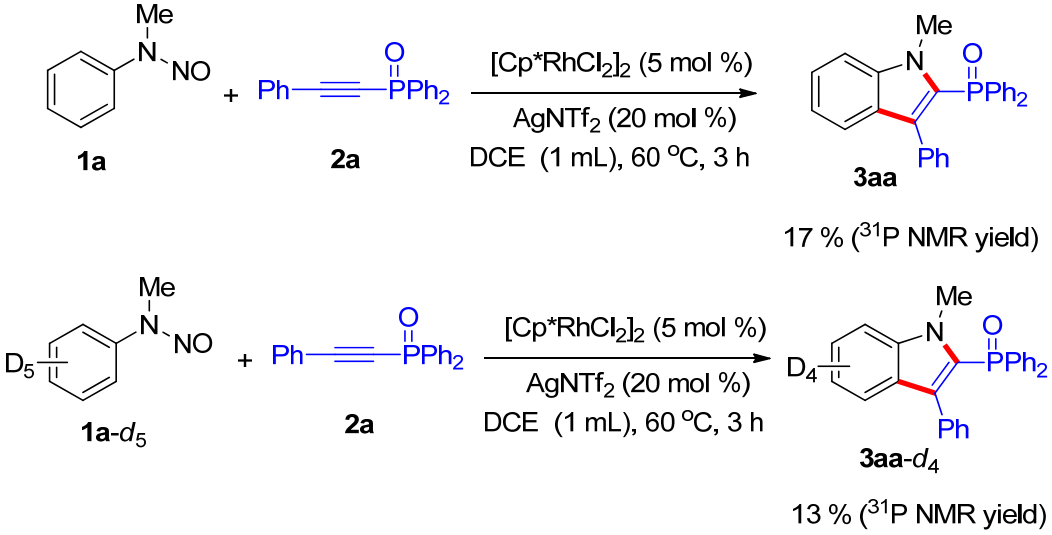
Intermediate catalysis



A mixture of *N*-nitrosoaniline (**1f**, 0.6 mmol, 3.0 equiv), 1-alkynylphosphine oxides (**2a**, 0.2 mmol, 1.0 equiv), rhodacycle **A** (5.8 mg, 0.02 mmol, 10 mol %), and $AgNTf_2$ (7.8 mg, 0.02 mmol, 10 mol %) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 60 °C for 20 h under vigorous stirring. The solvent was evaporated and the resulting mixture was submitted to NMR using trimethylphosphate (28 mg, 0.2 mmol) as the internal standard.

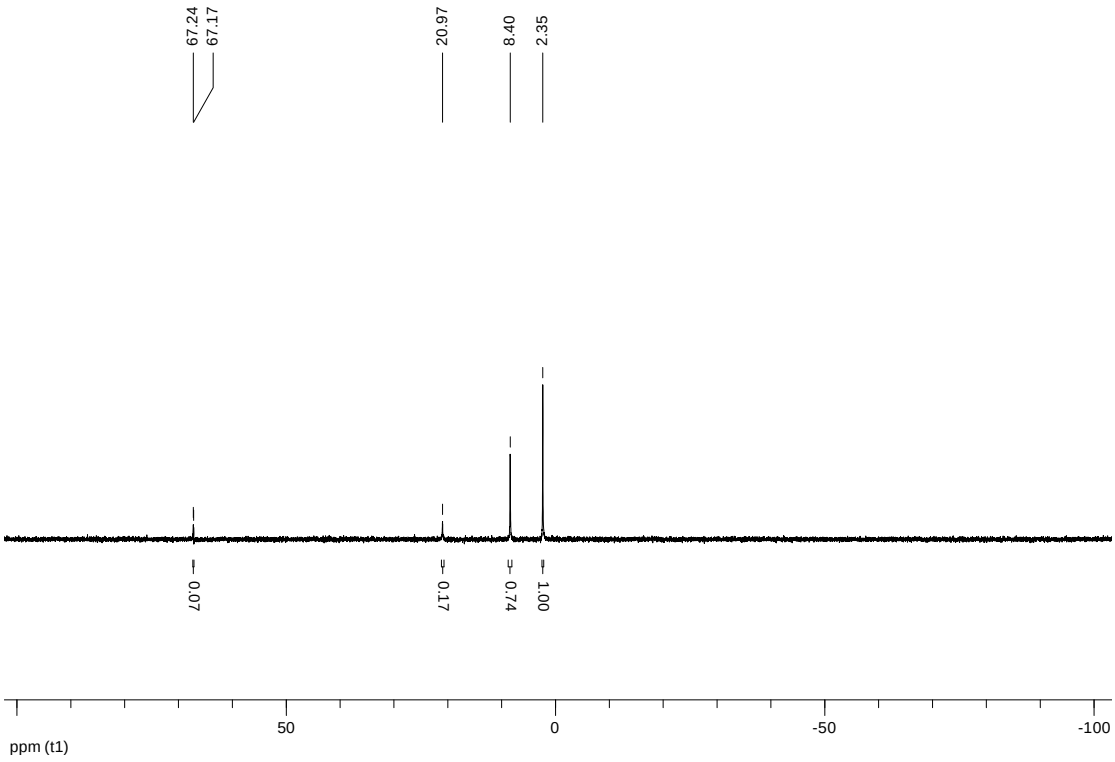


KIE experiments

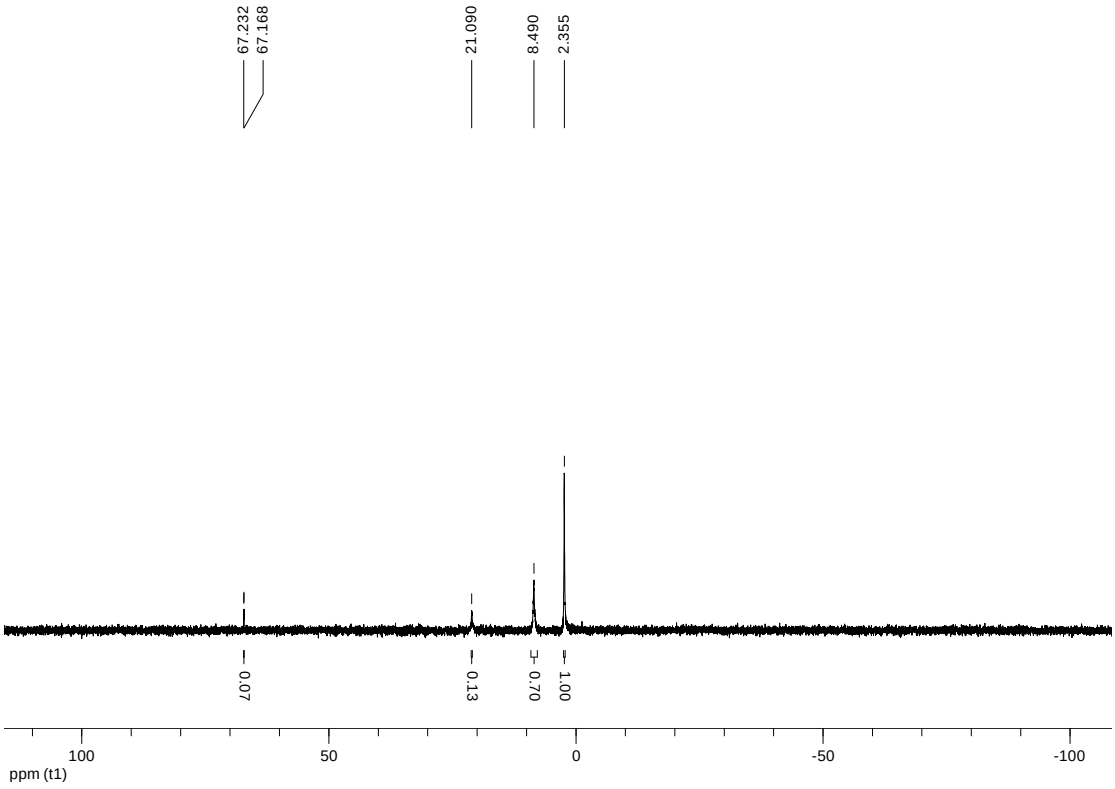


KIE value was determined by comparing the initial rates measured separately using **1a** or **1a-*d*$_5$** as substrate. Following general procedure 1, but with reaction temperature 60 °C, **1a** (81.6 mg, 0.6 mmol, 3.0 equiv.) or **1a-*d*$_5$** (84.7 mg, 0.6 mmol, 3.0 equiv.), **2a** (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %), and $AgNTf_2$ (15.5 mg, 0.04 mmol, 20 mol %) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.0 mL) was added and the resulting mixture was then put in a pre-heated oil bath at 60 °C for 3 h under vigorous stirring. The reaction was cooled to 0 °C and purification was performed by flash column chromatography on silica gel with DCM. The solvent was then removed under reduced pressure and ^{31}P NMR was taken using trimethylphosphate (28 mg, 0.2 mmol) as the internal standard. According to the NMR yield [**3aa** (17%), **3aa-*d*$_5$** (13%)], the KIE was found to be 1.3 (crude NMR was shown below).

3aa:

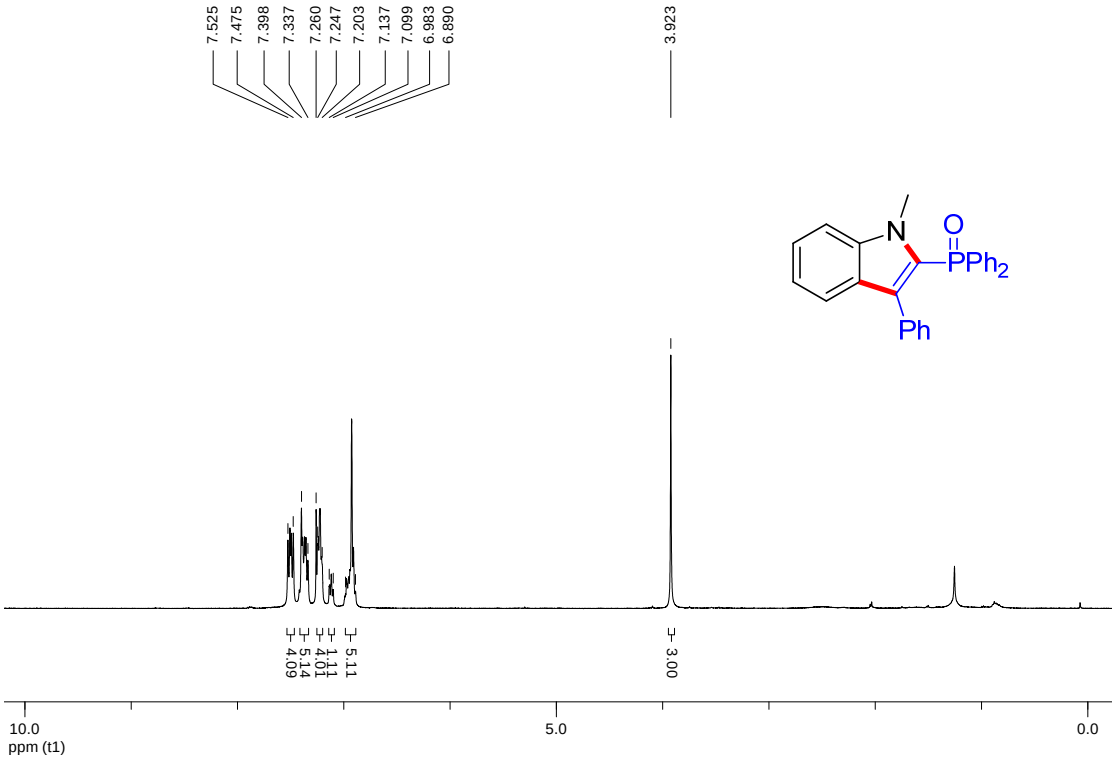

67.24
67.17
20.97
8.40
2.35
0.07
0.17
0.74
1.00
50
0
-50
-100
ppm (t1)

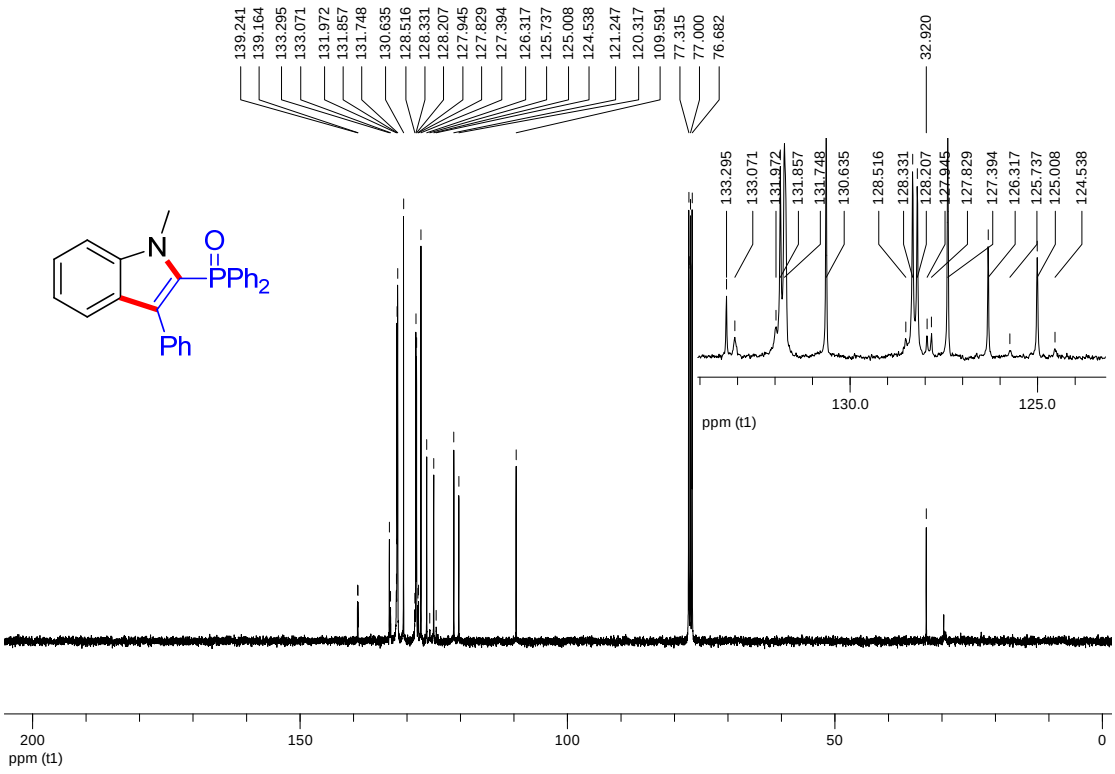
3aa-d_5:

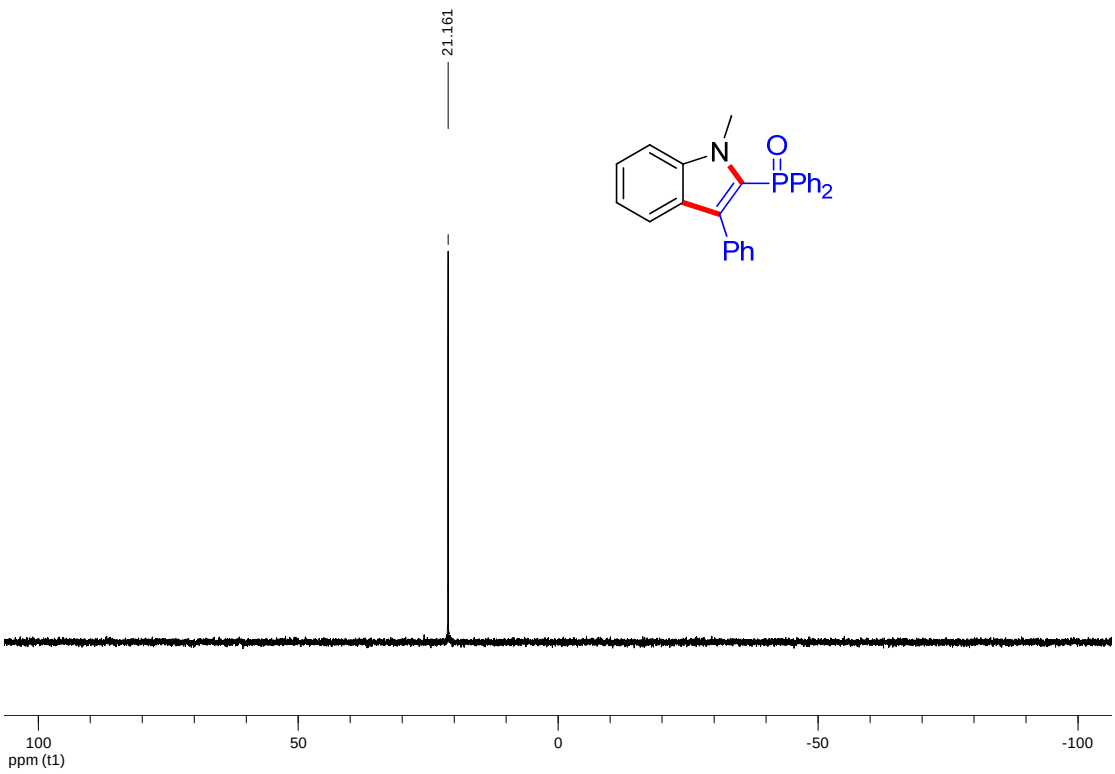

67.232
67.168
21.090
8.490
2.355
0.07
0.13
0.70
1.00
100
50
0
-50
-100
ppm (t1)

Spectral Copies of ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR of Compounds Obtained in This Study

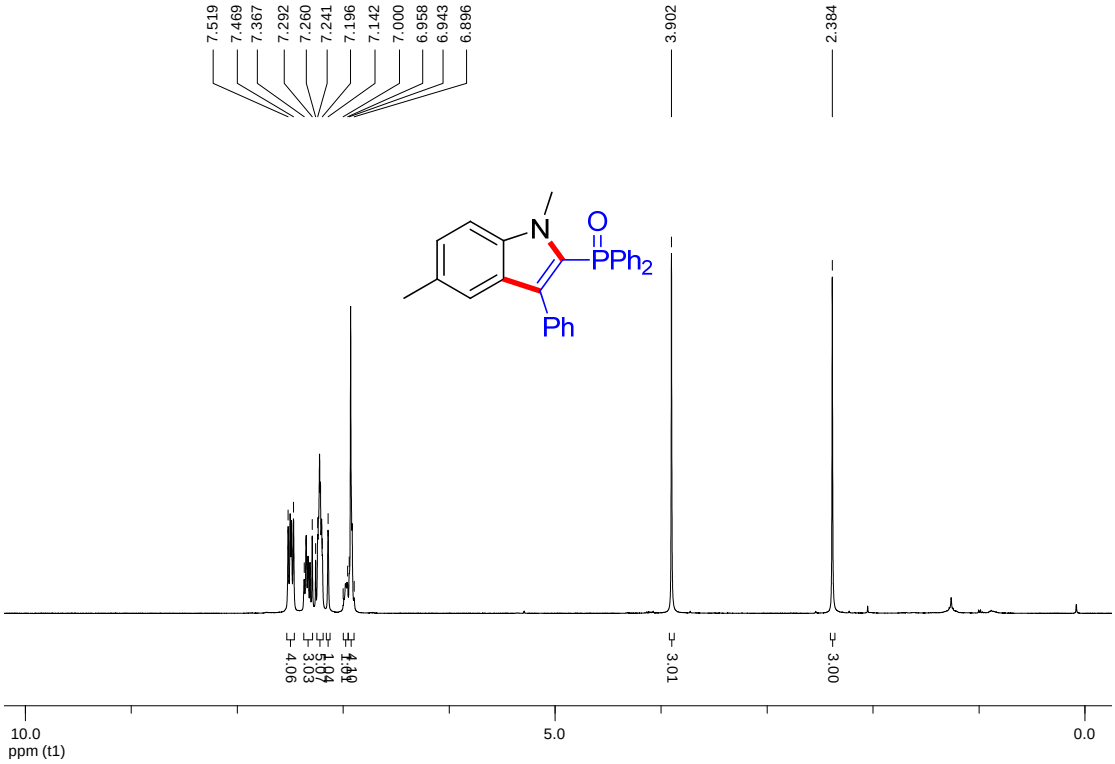
(1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3aa)

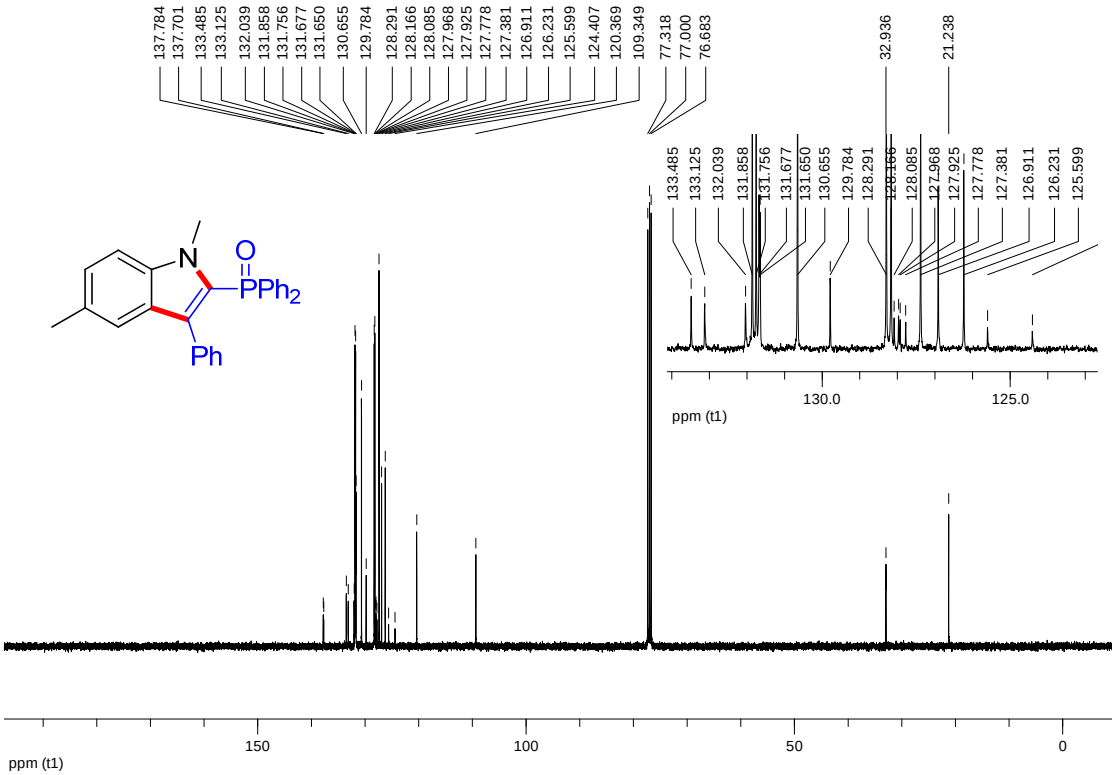


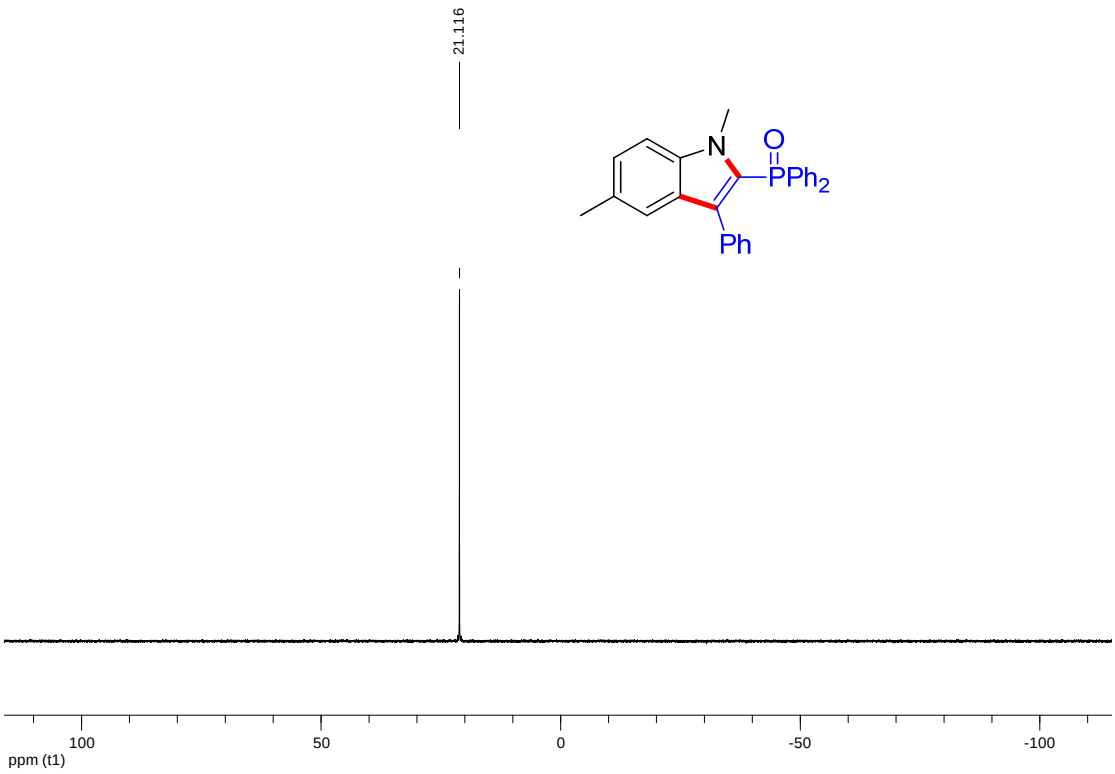



21.161
N
O
PPh2
Ph
100
ppm (t1)
50
0
-50
-100

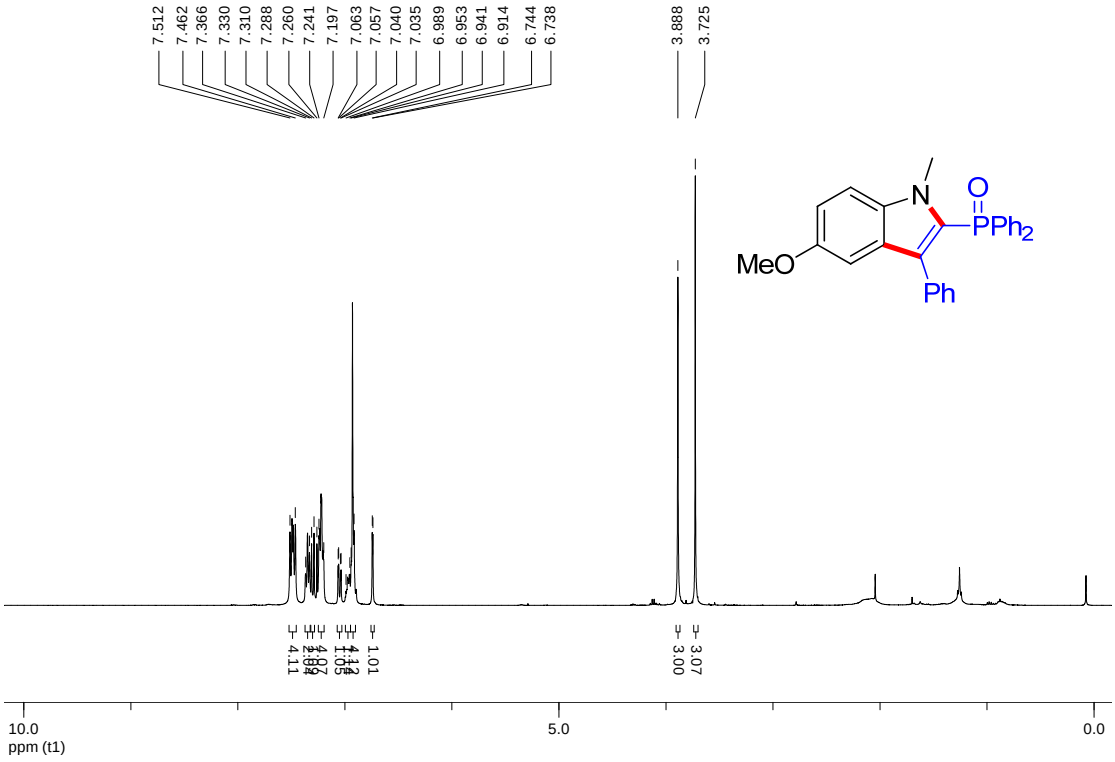
(1,5-dimethyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ba)

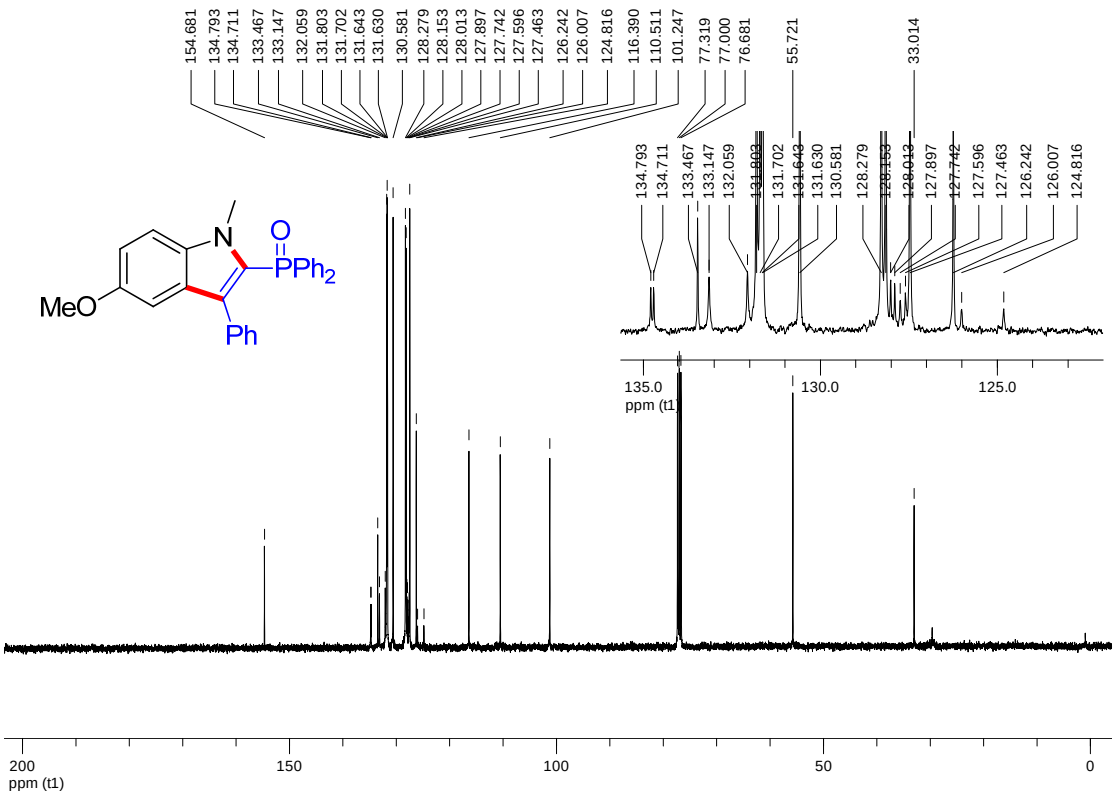


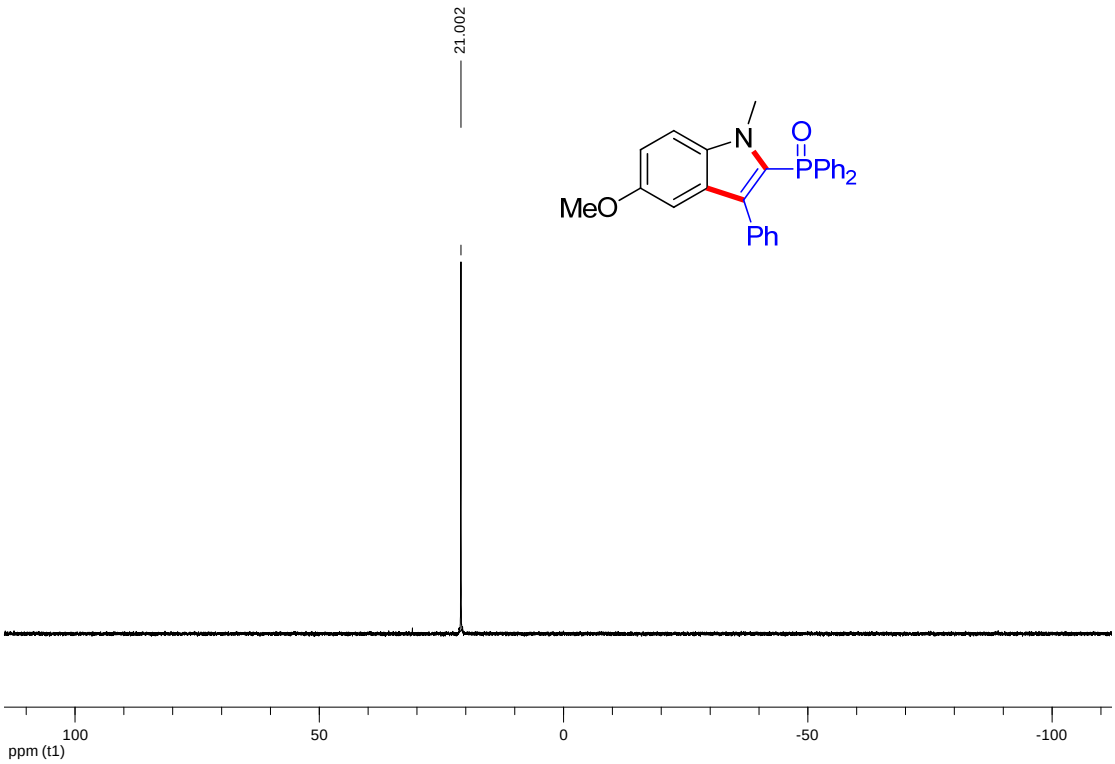



21.116
N
O
PPh2
Ph
100
50
0
-50
-100
ppm (t1)

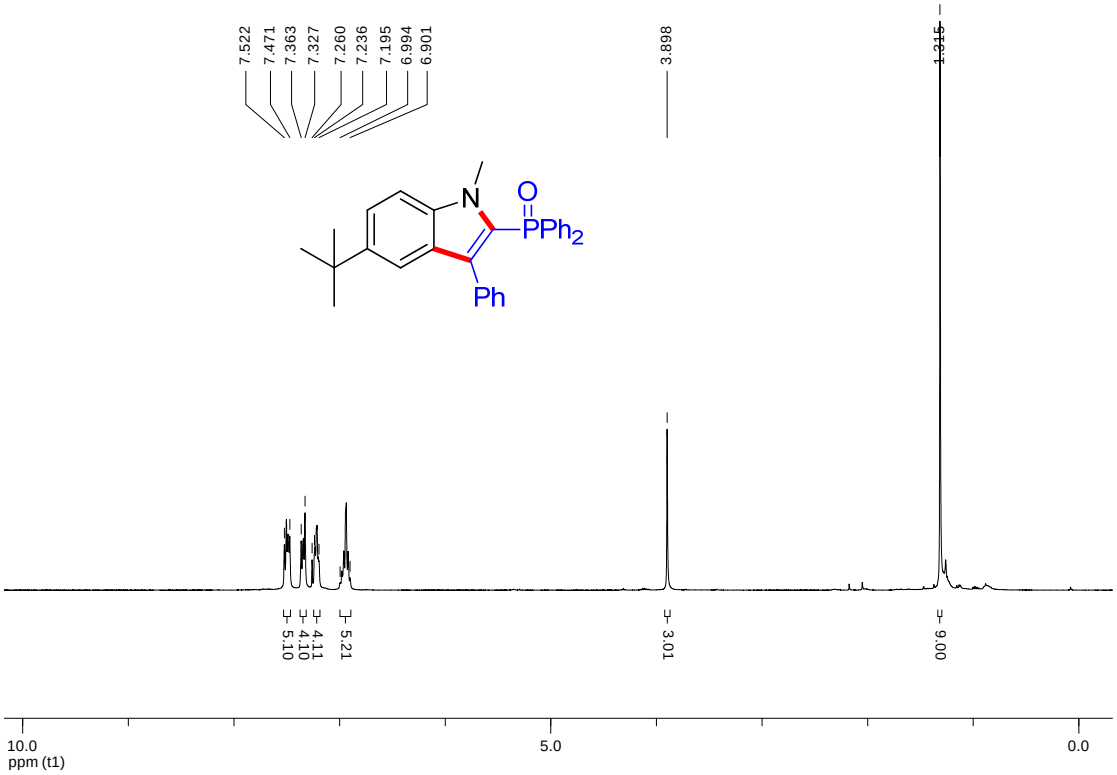
(5-methoxy-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ca)

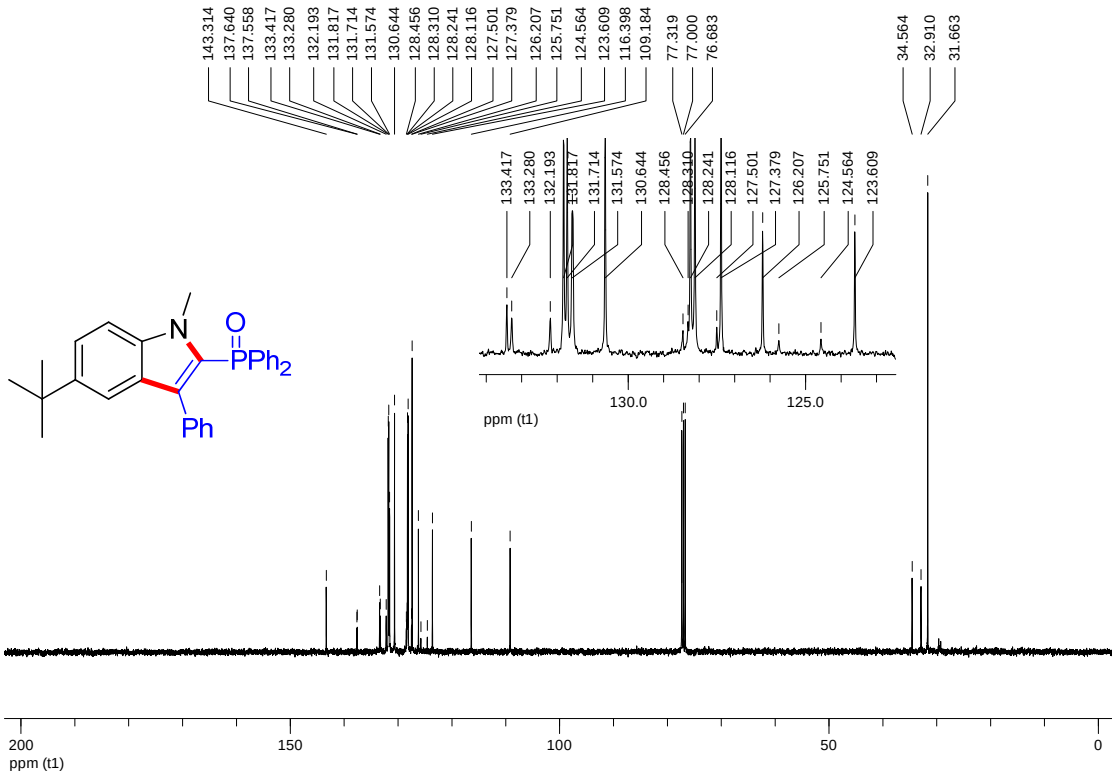


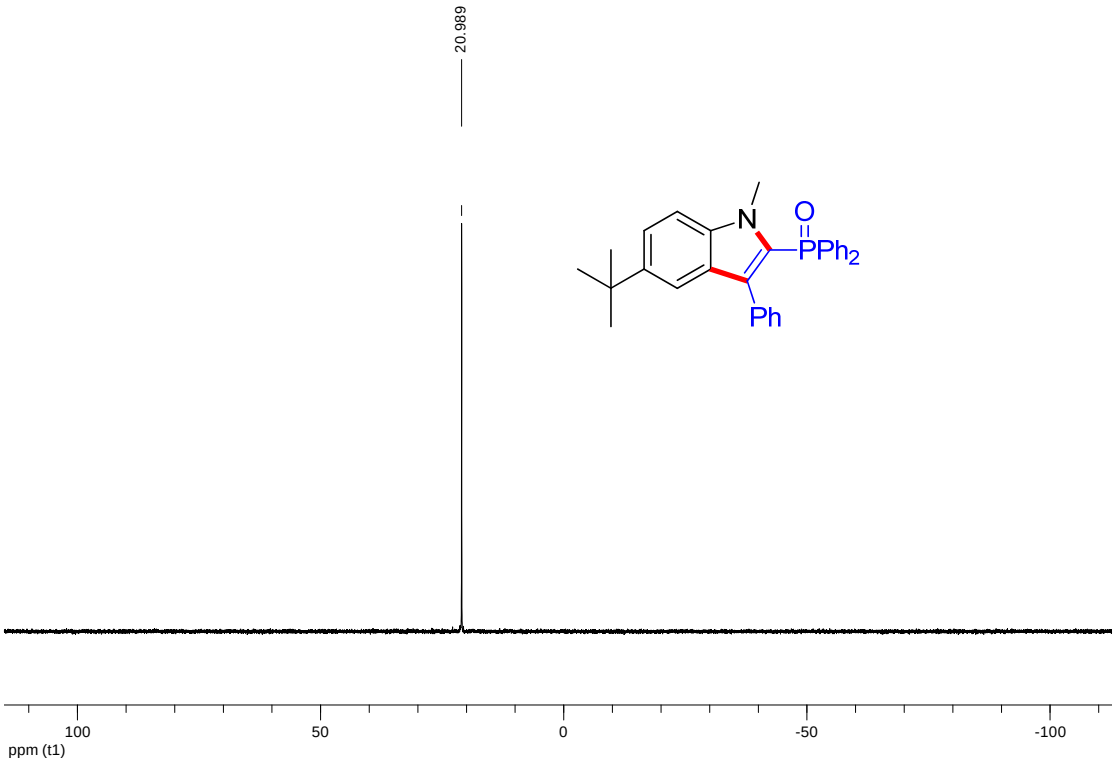



21.002
N
O
PPh2
MeO
Ph
100
50
0
-50
-100
ppm (t1)

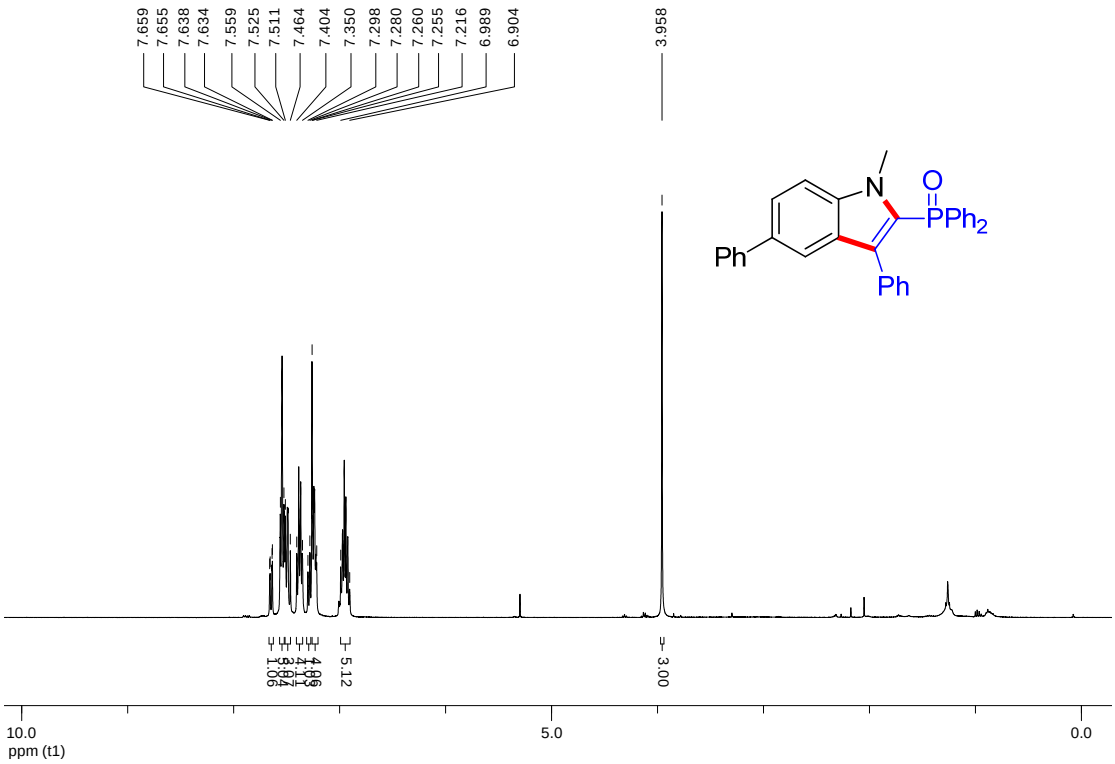
(5-(tert-butyl)-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3da)

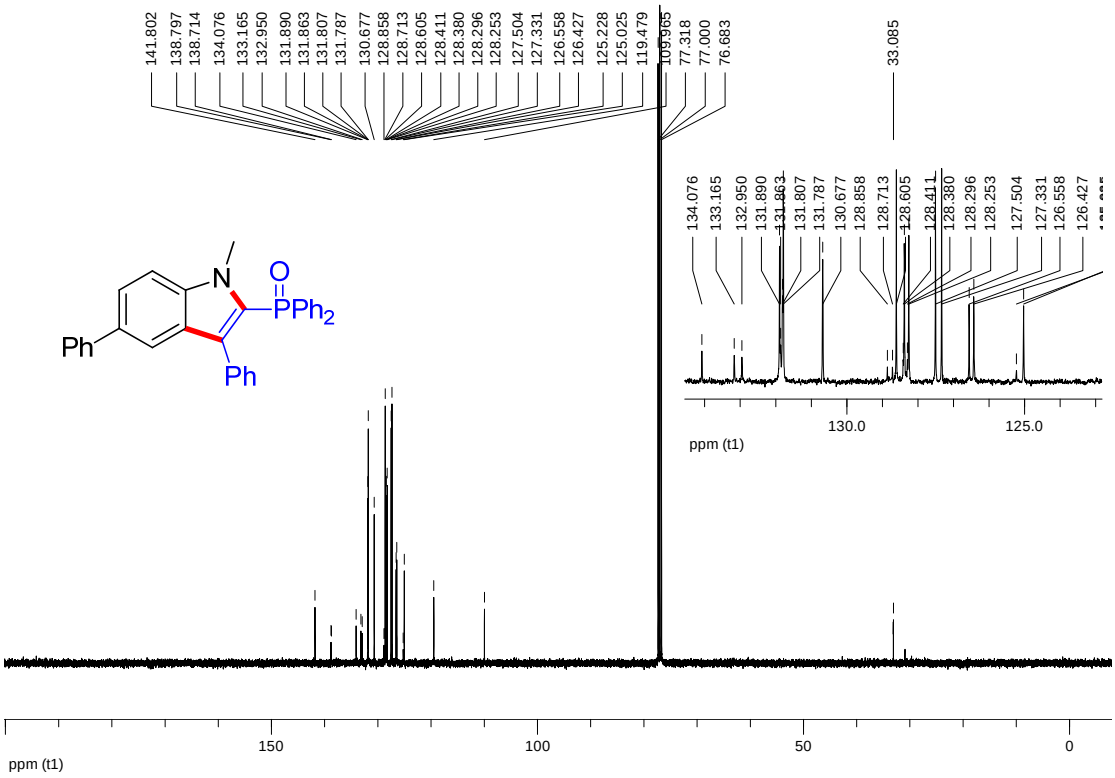


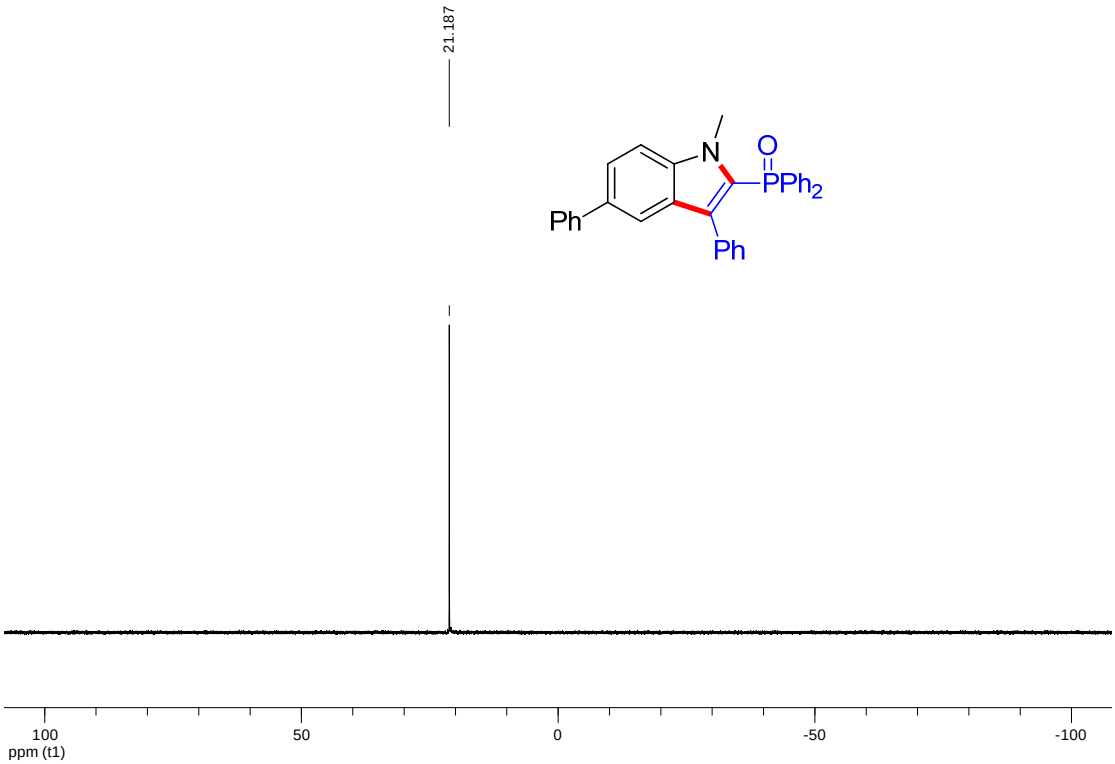



20.989
N
O
PPh2
Ph
100
50
0
-50
-100
ppm (t1)

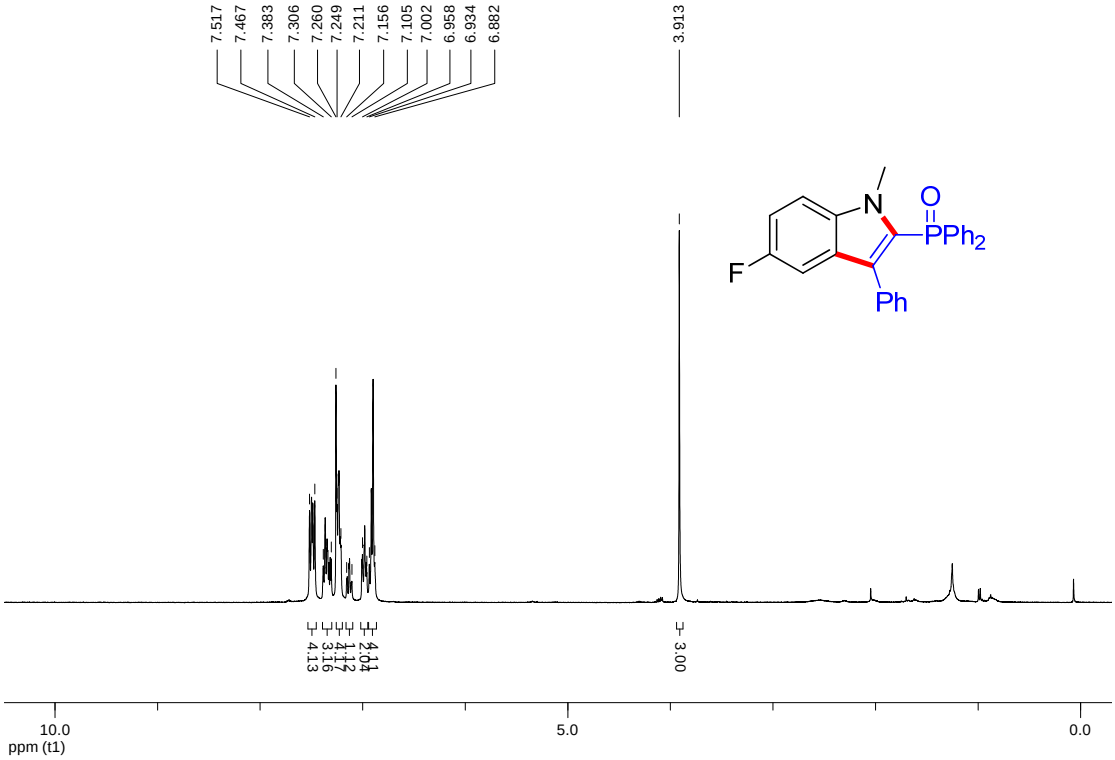
(1-methyl-3,5-diphenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ea)

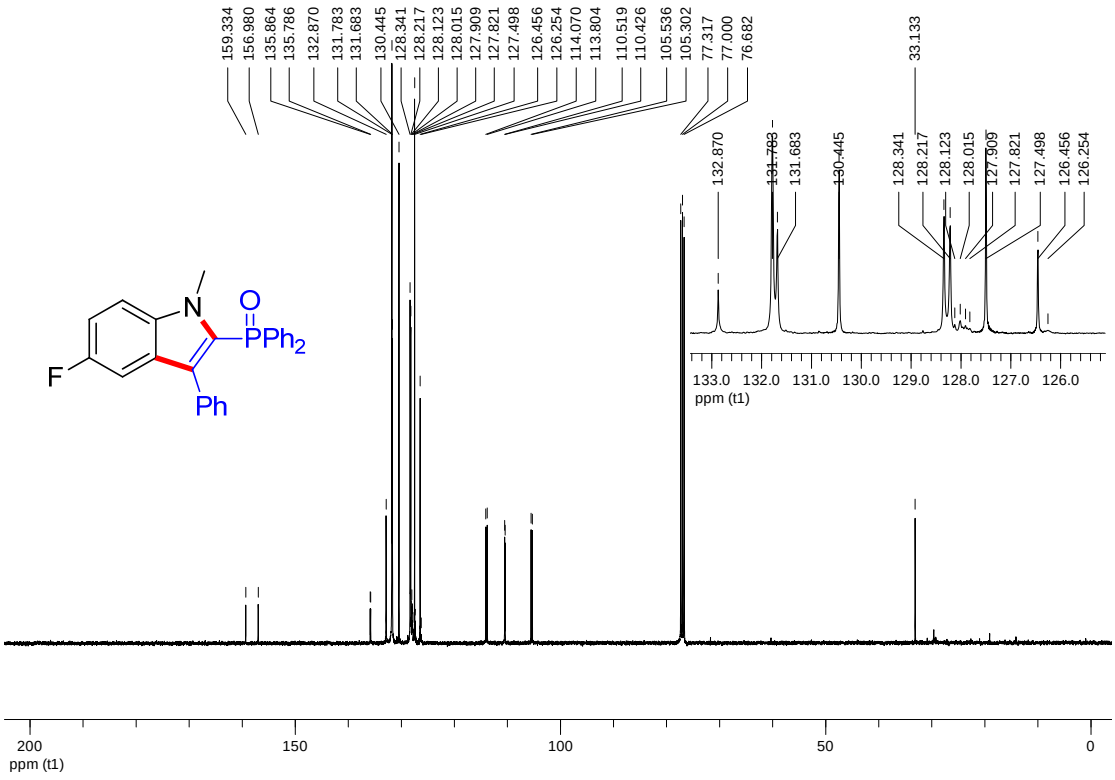


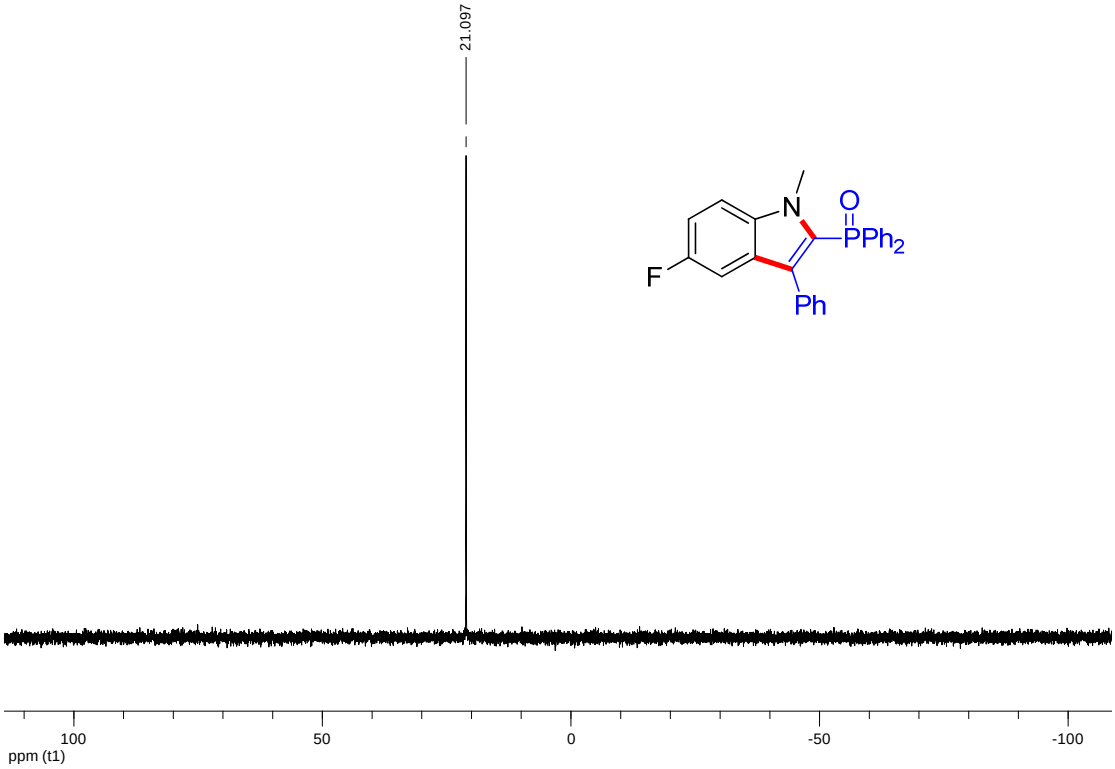


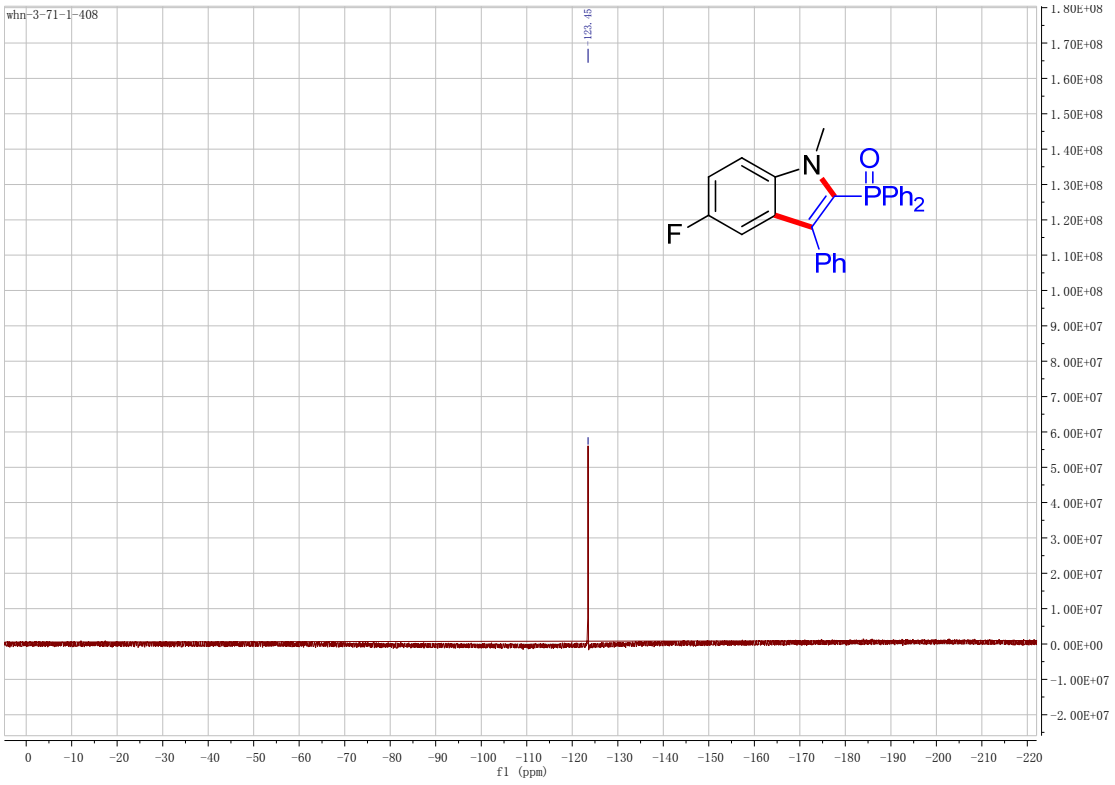

21.187
N
O
PPh2
Ph
Ph
100
ppm (t1)
50
0
-50
-100

(5-fluoro-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3fa)

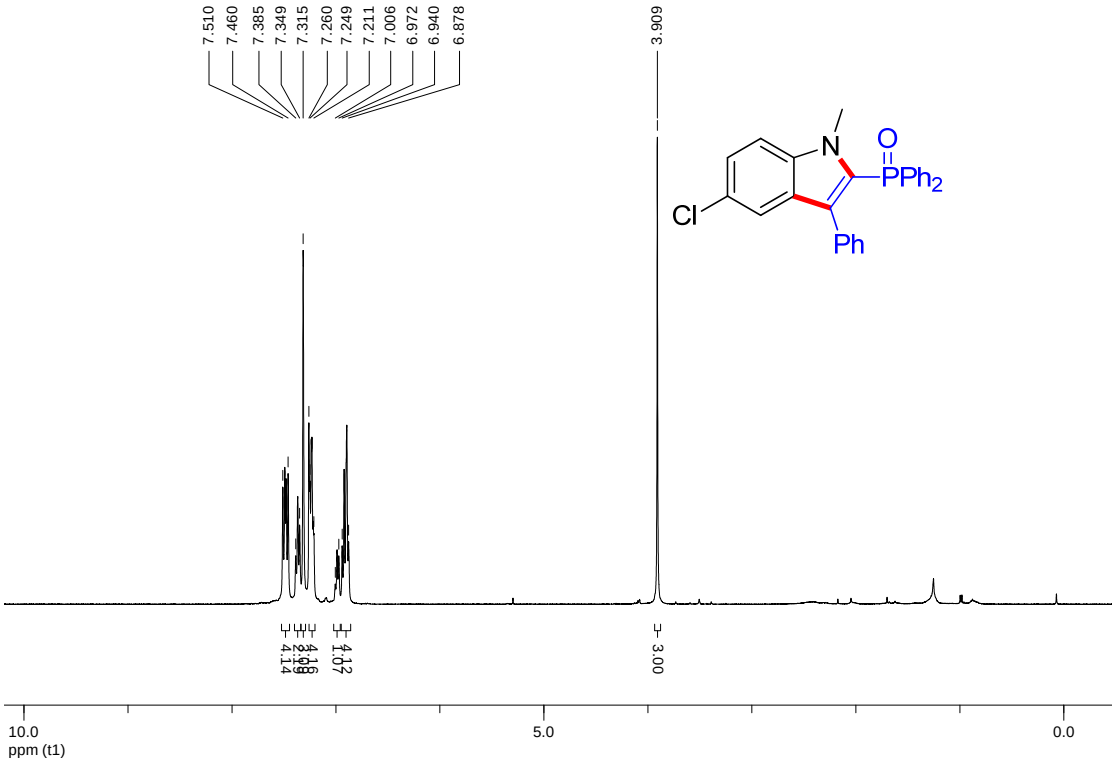


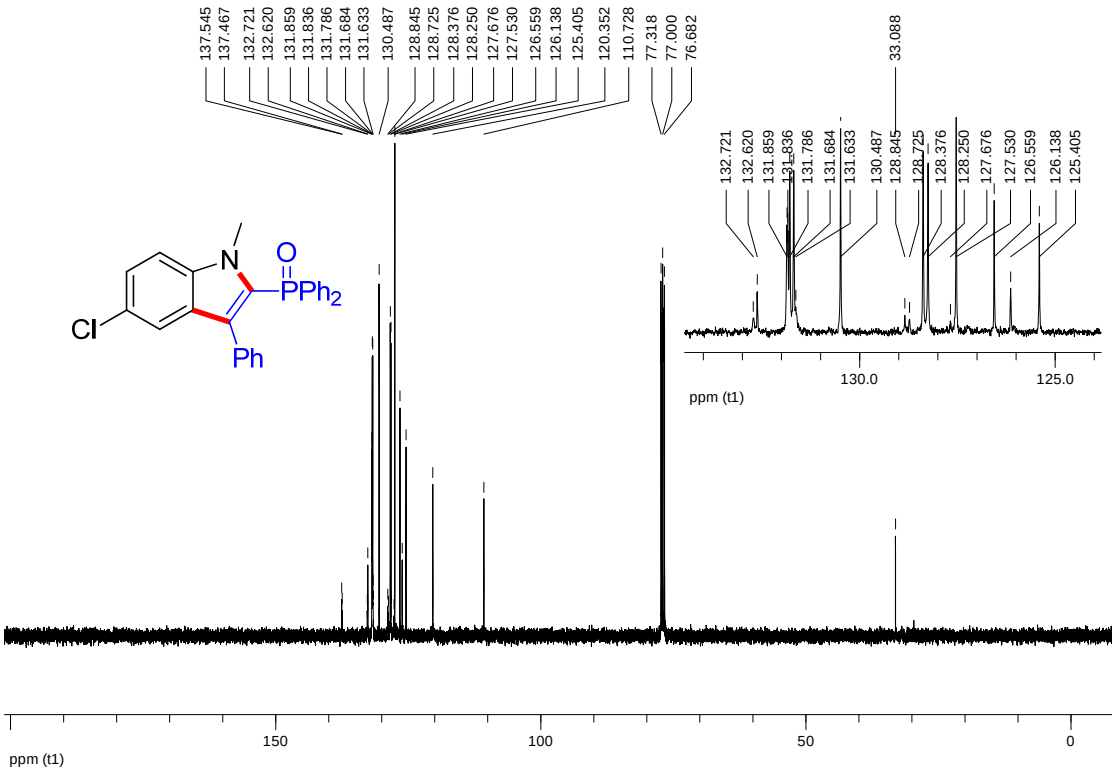


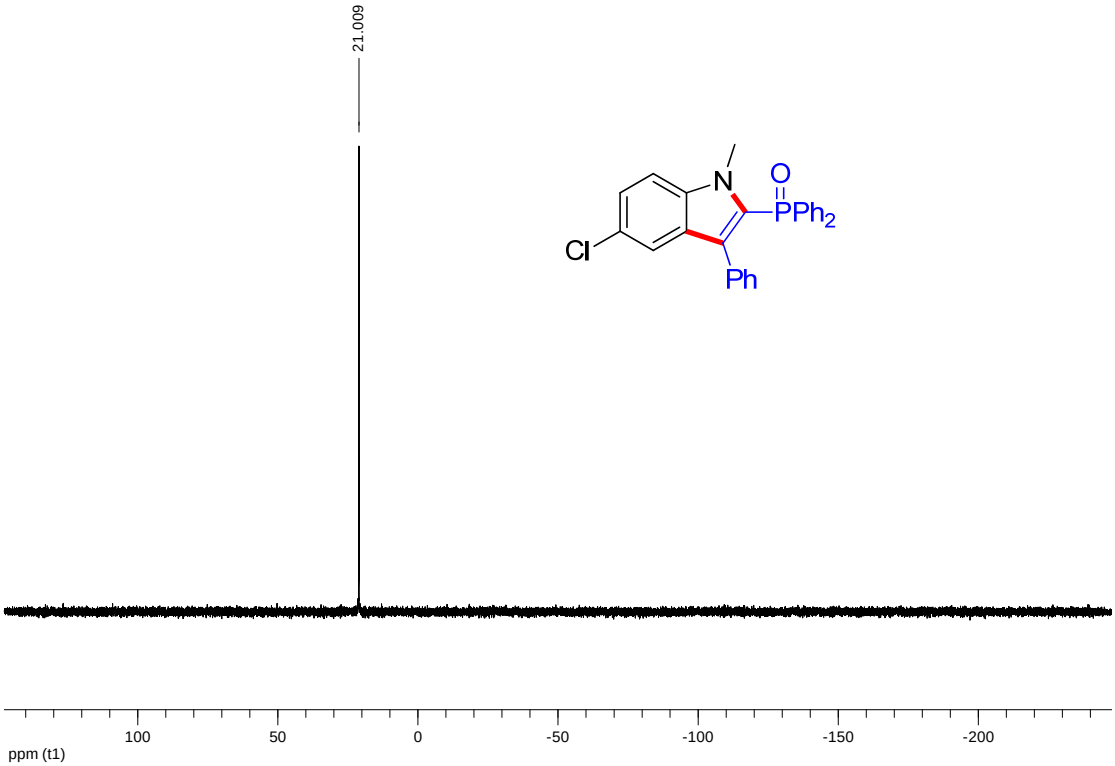

21.097
N
O
PPh2
F
Ph
100
50
0
-50
-100
ppm (t1)


whn-3-71-1-408
123.45
N
O
PPh2
F
Ph
f1 (ppm)

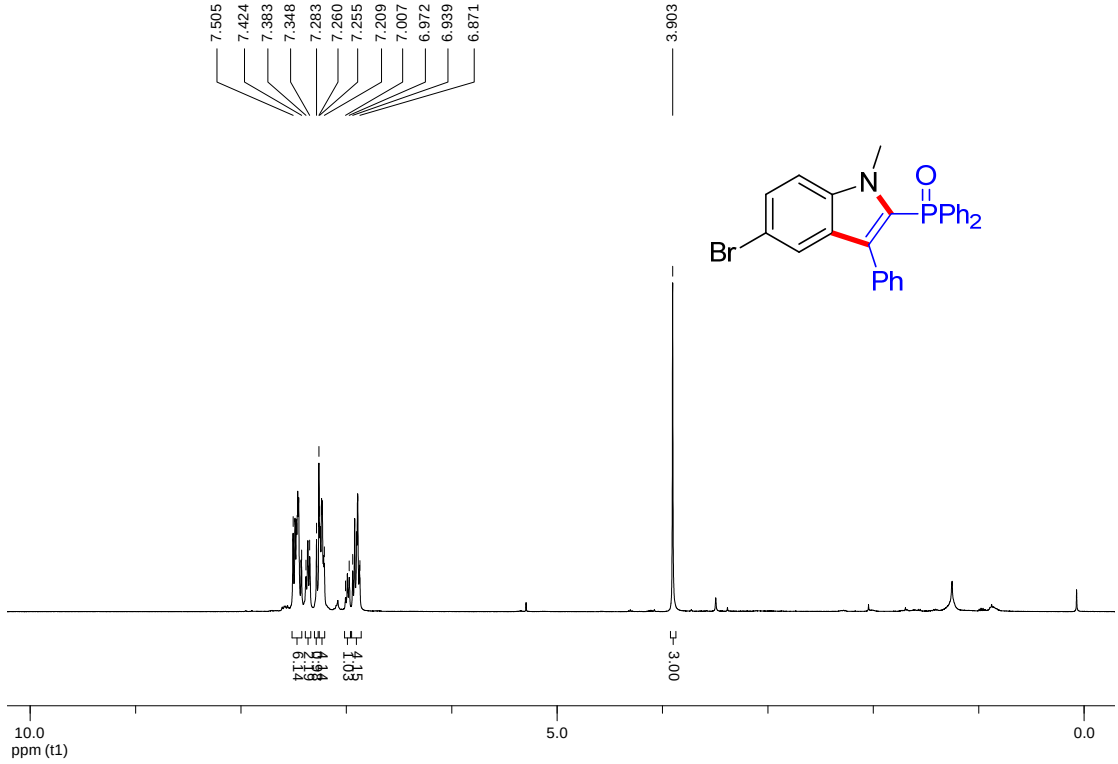
(5-chloro-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ga)

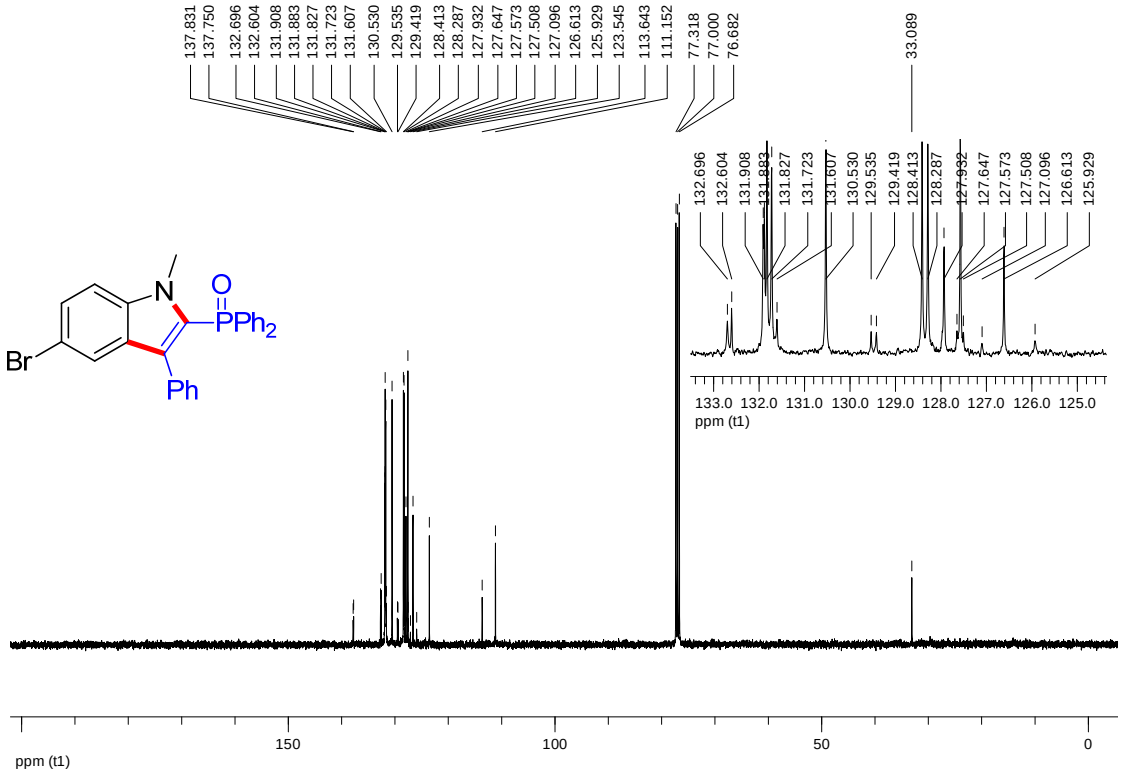


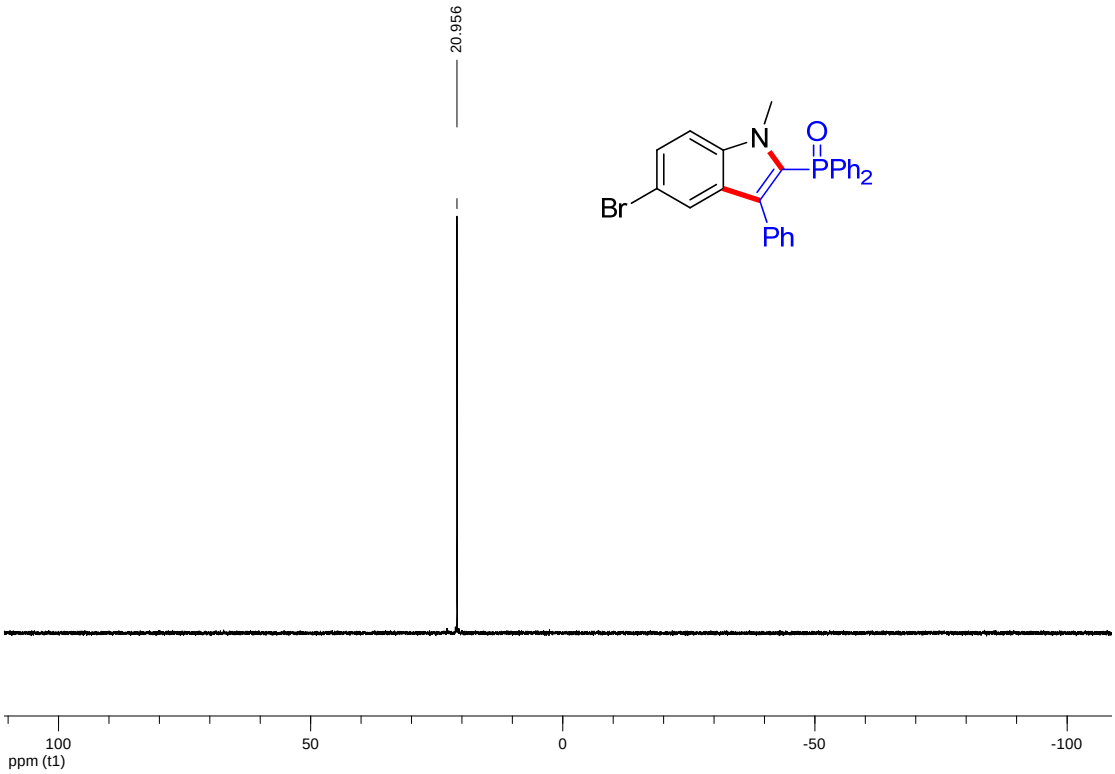



21.009
N
O
PPh2
Cl
Ph
100
50
0
-50
-100
-150
-200
ppm (t1)

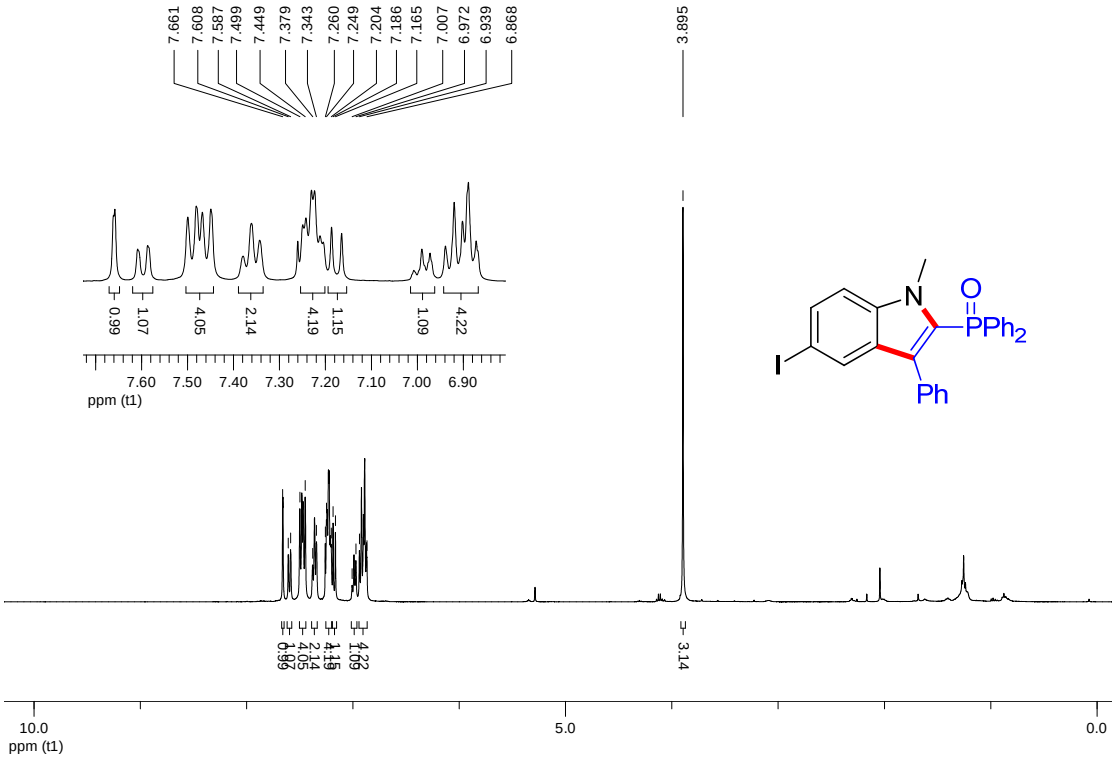
(5-bromo-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ha)

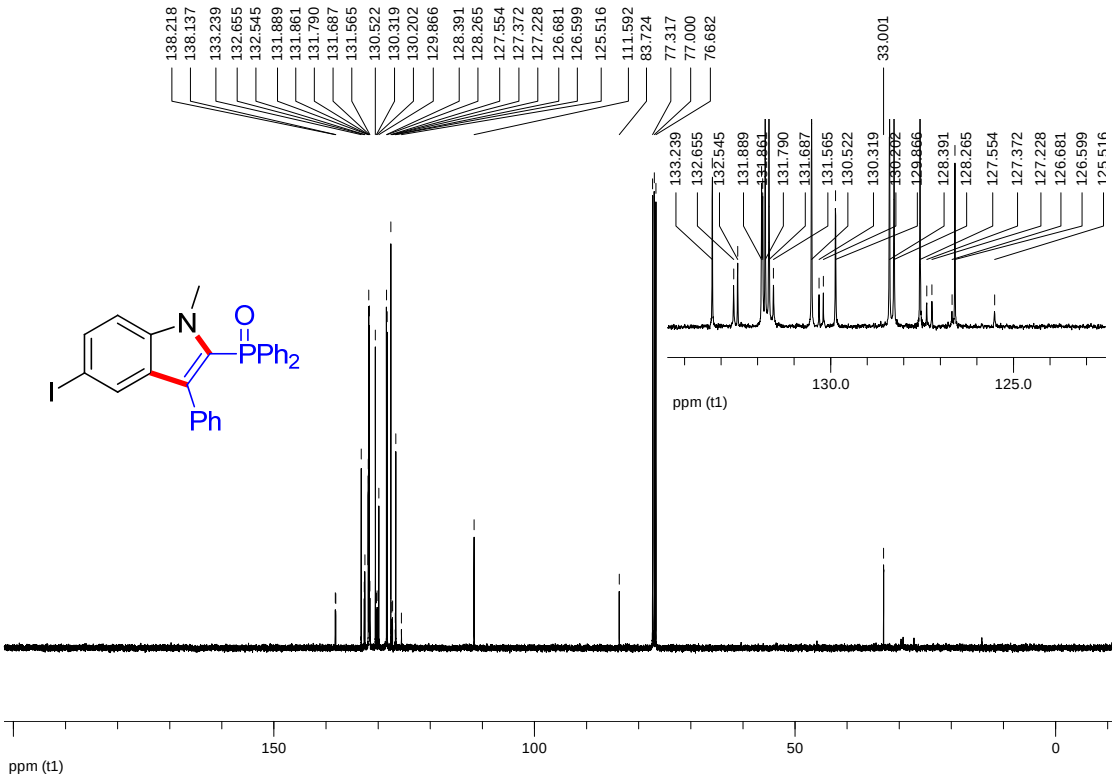


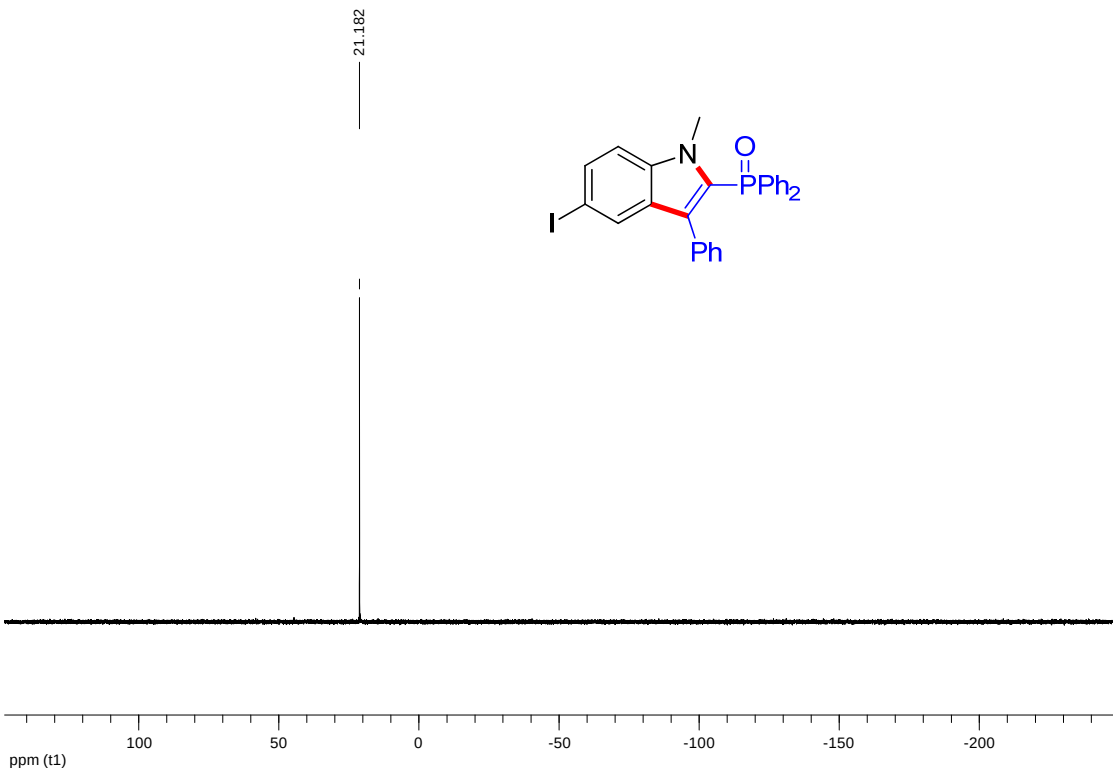



20.956
N
O
PPh2
Br
Ph
100
50
0
-50
-100
ppm (t1)

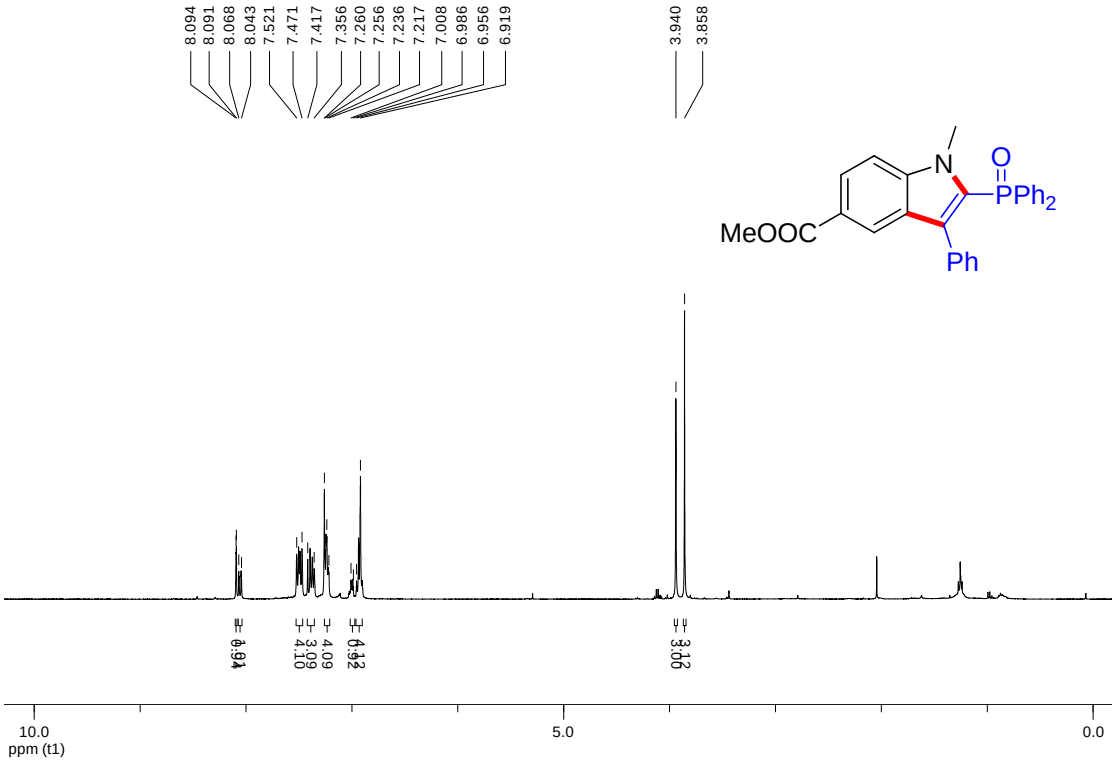
(5-iodo-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ia)

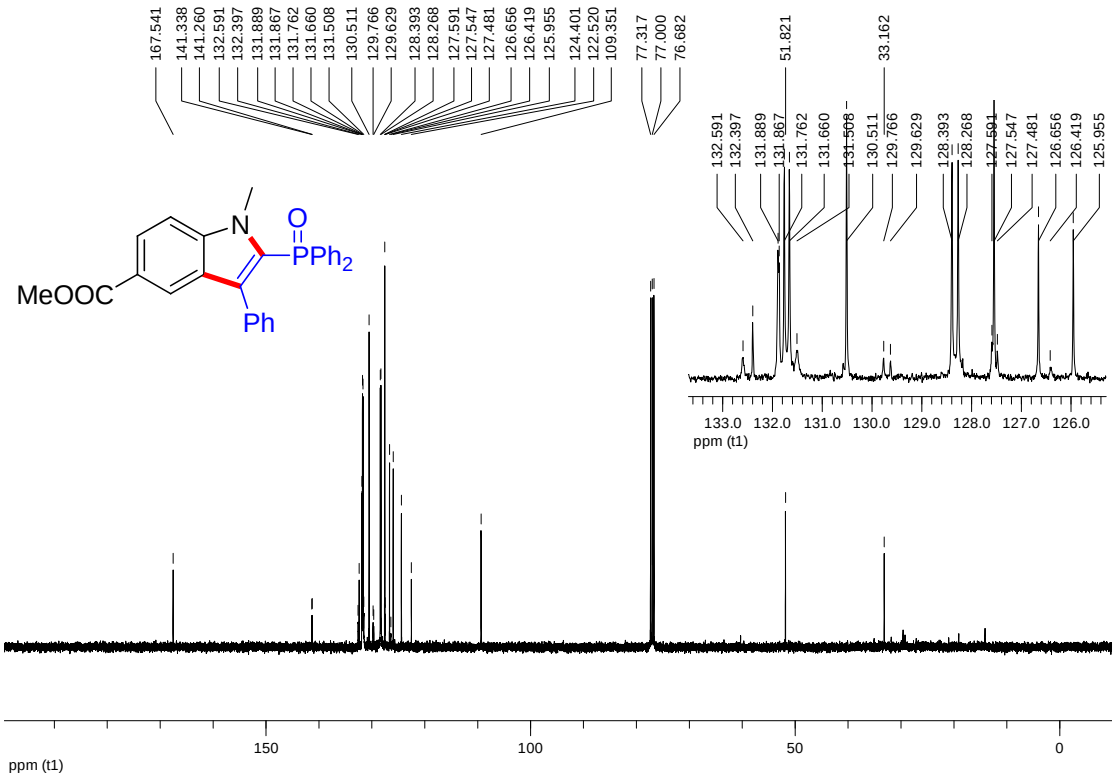


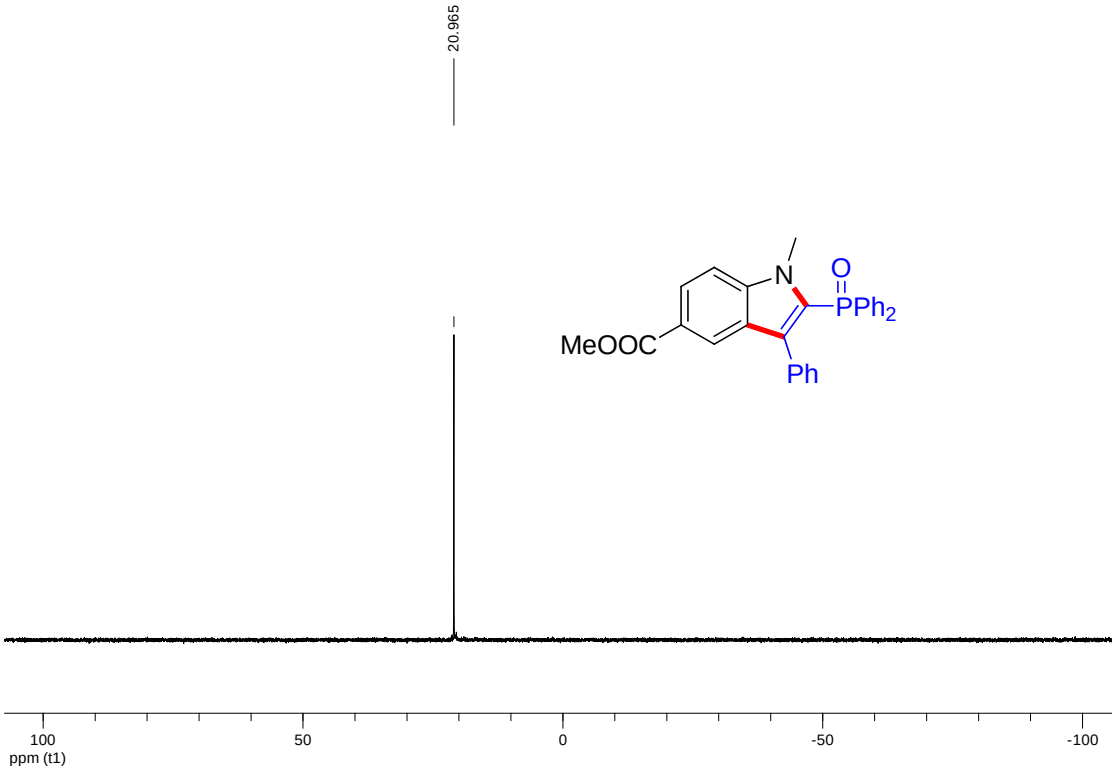



21.182
N
O
PPh2
I
Ph
100
50
0
-50
-100
-150
-200
ppm (t1)

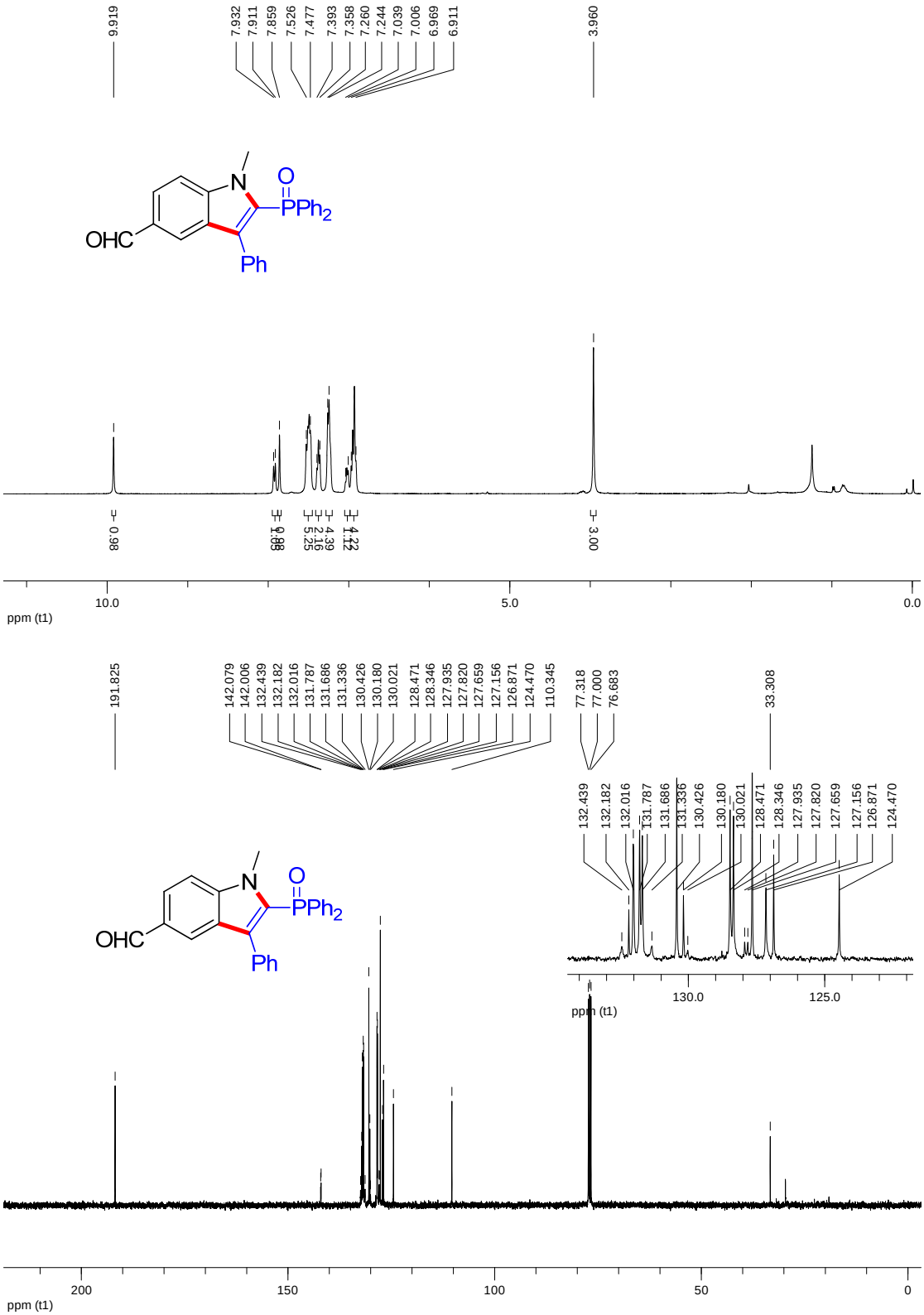
Methyl 2-(diphenylphosphoryl)-1-methyl-3-phenyl-1*H*-indole-5-carboxylate (3ja)

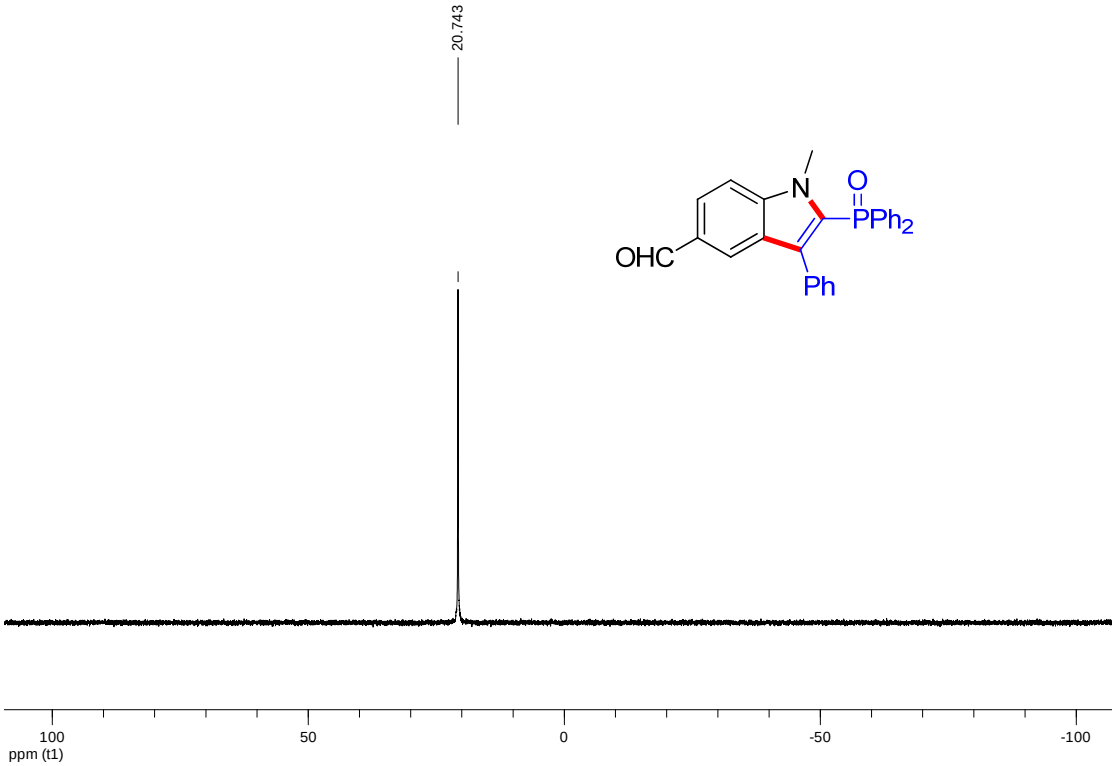




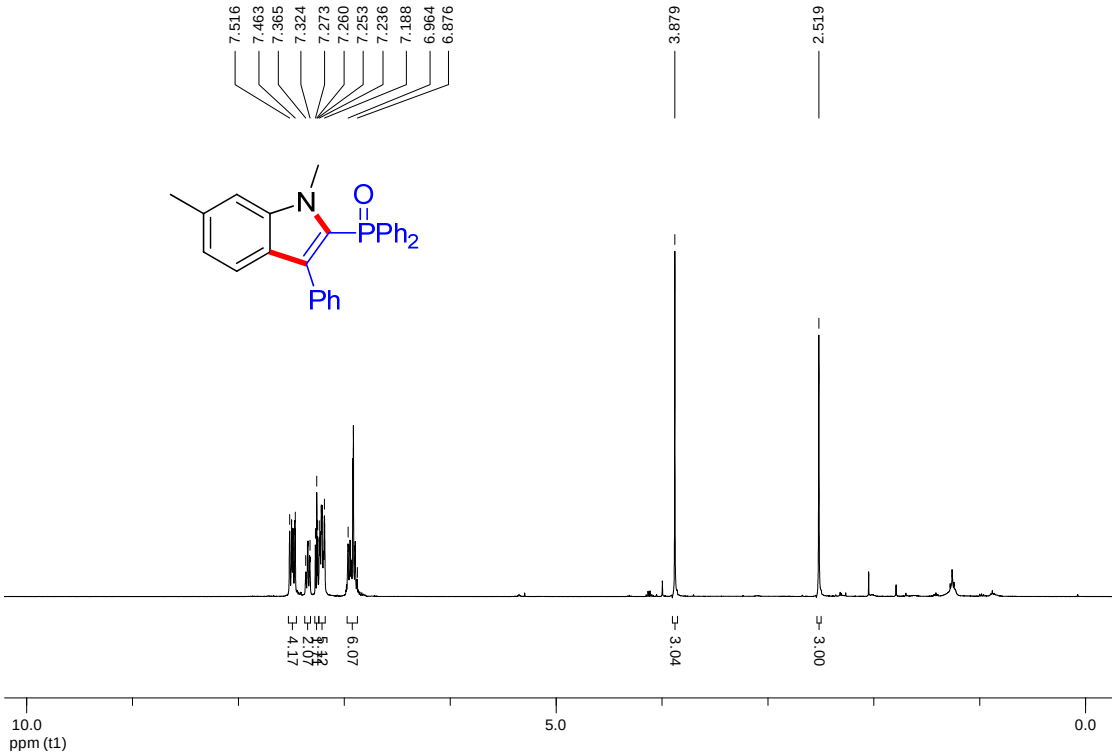

20.965
N
O
PPh2
MeOOC
Ph
100
ppm (t1)
50
0
-50
-100

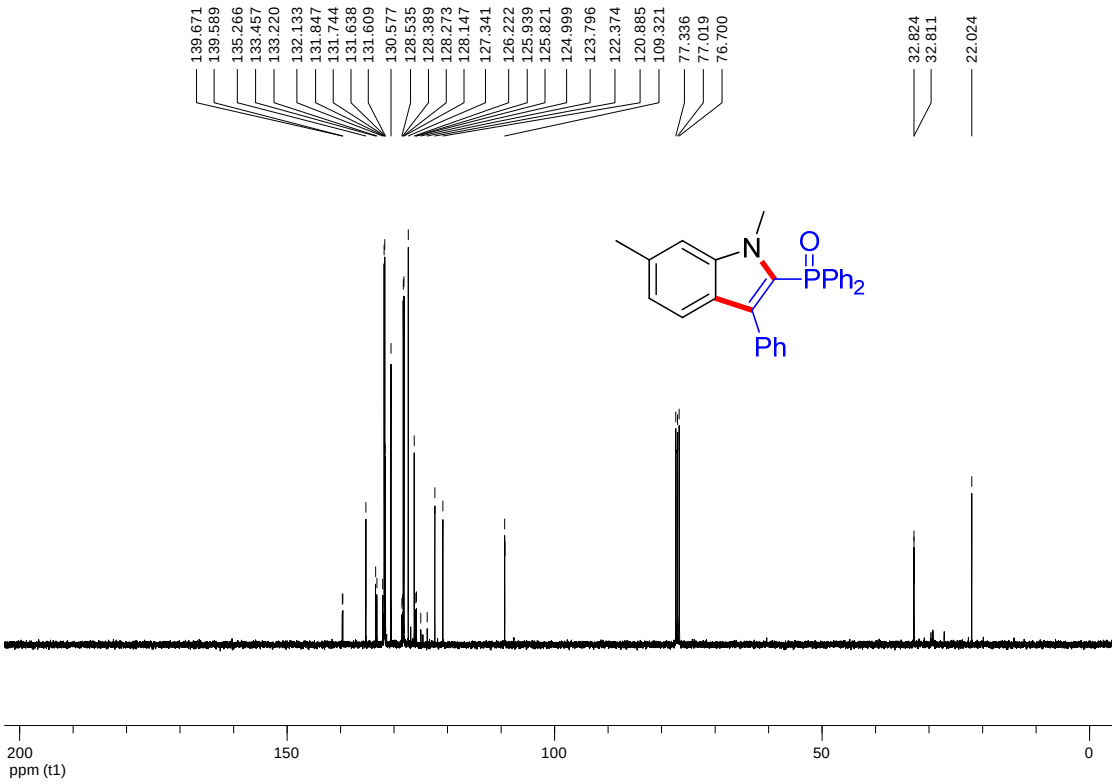
2-(diphenylphosphoryl)-1-methyl-3-phenyl-1*H*-indole-5-carbaldehyde (3ka)

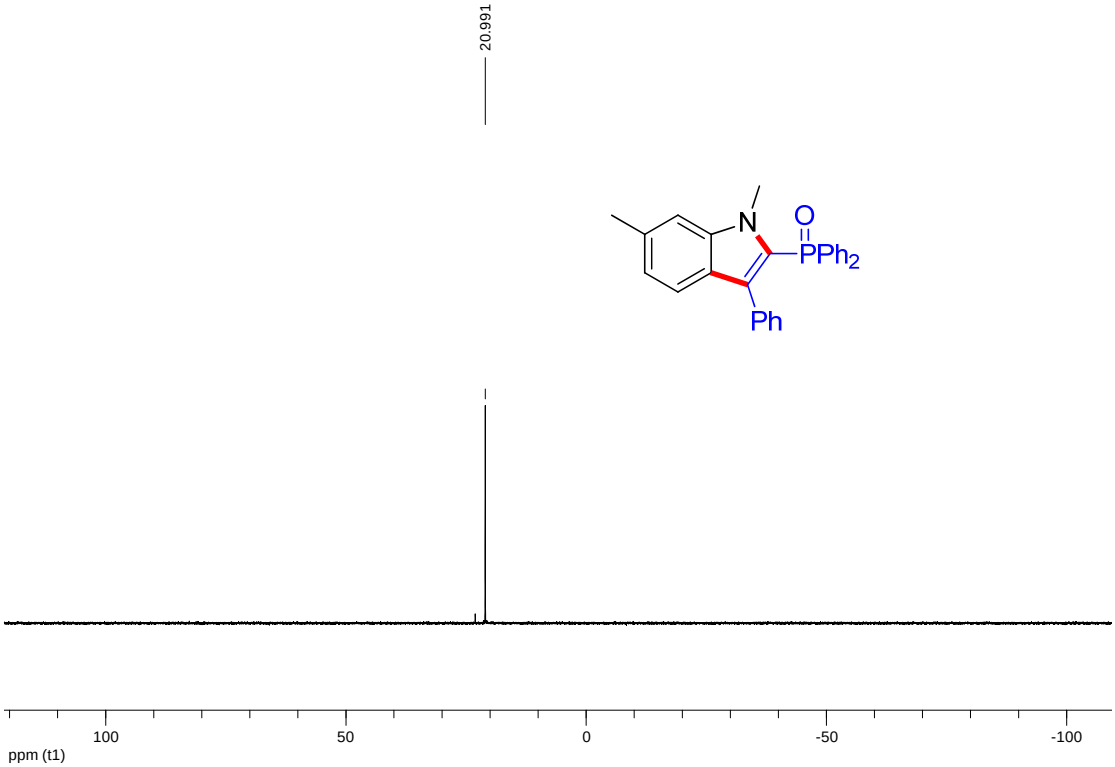


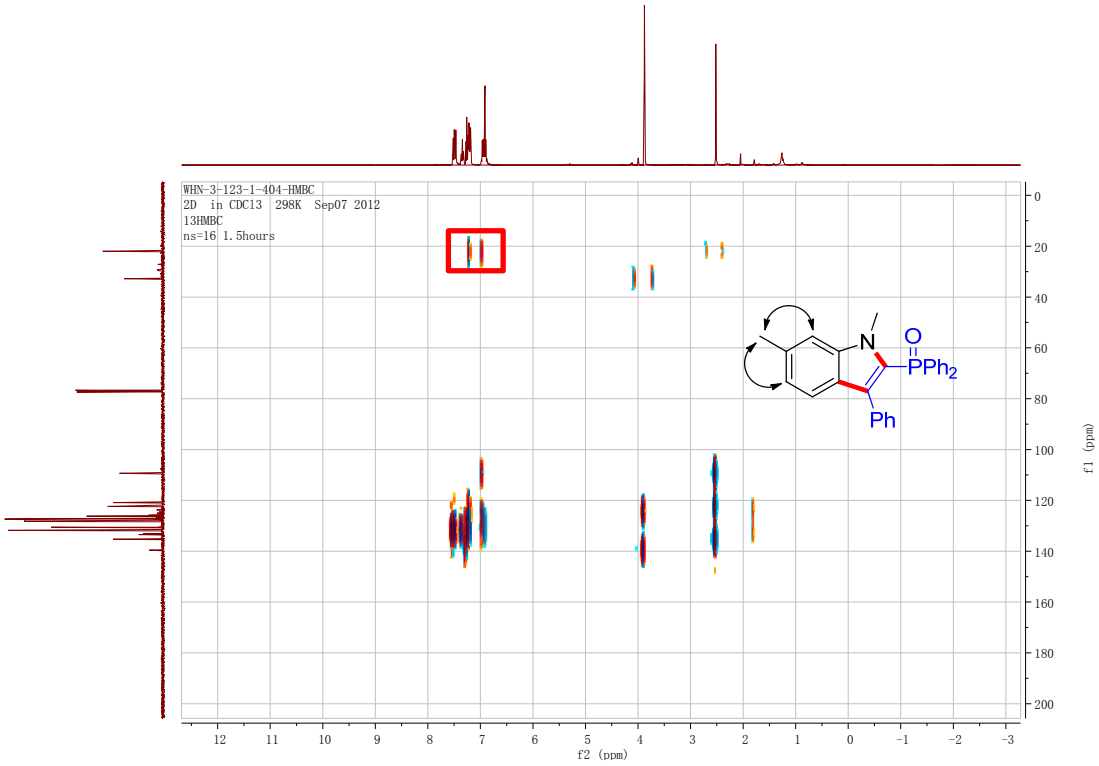

20.743
N
O
PPh2
OHC
Ph
100
50
0
-50
-100
ppm (t1)

(1,6-dimethyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3la)

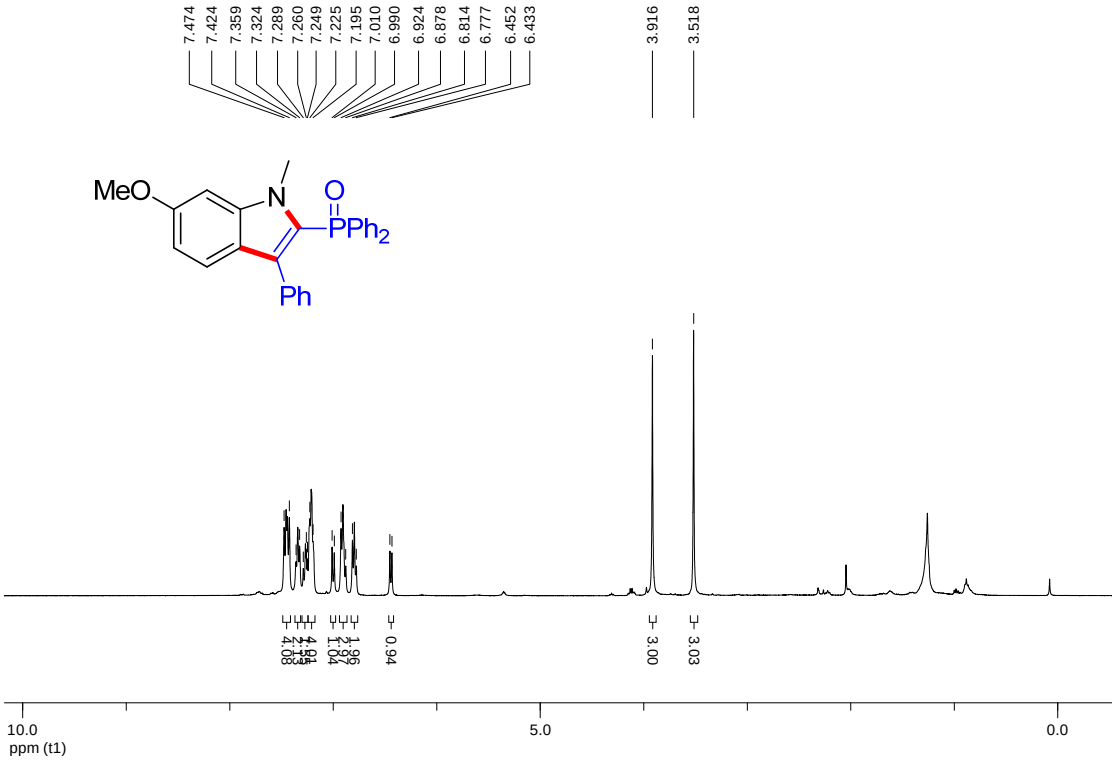


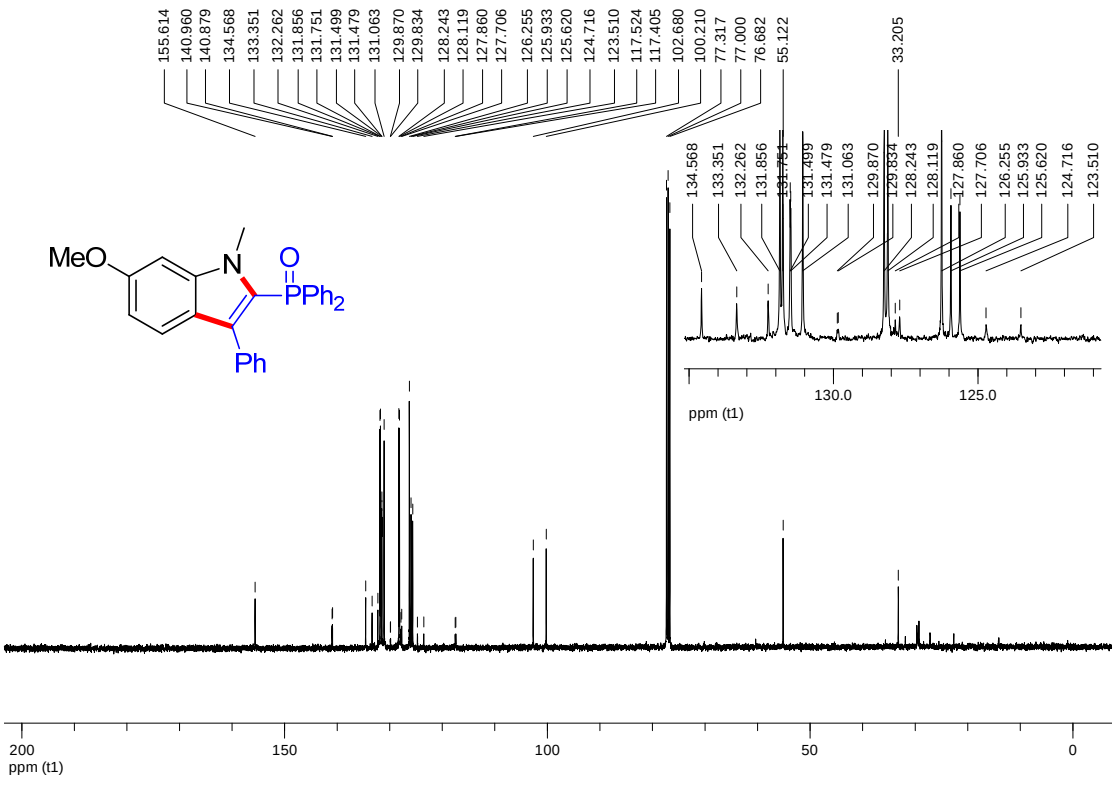


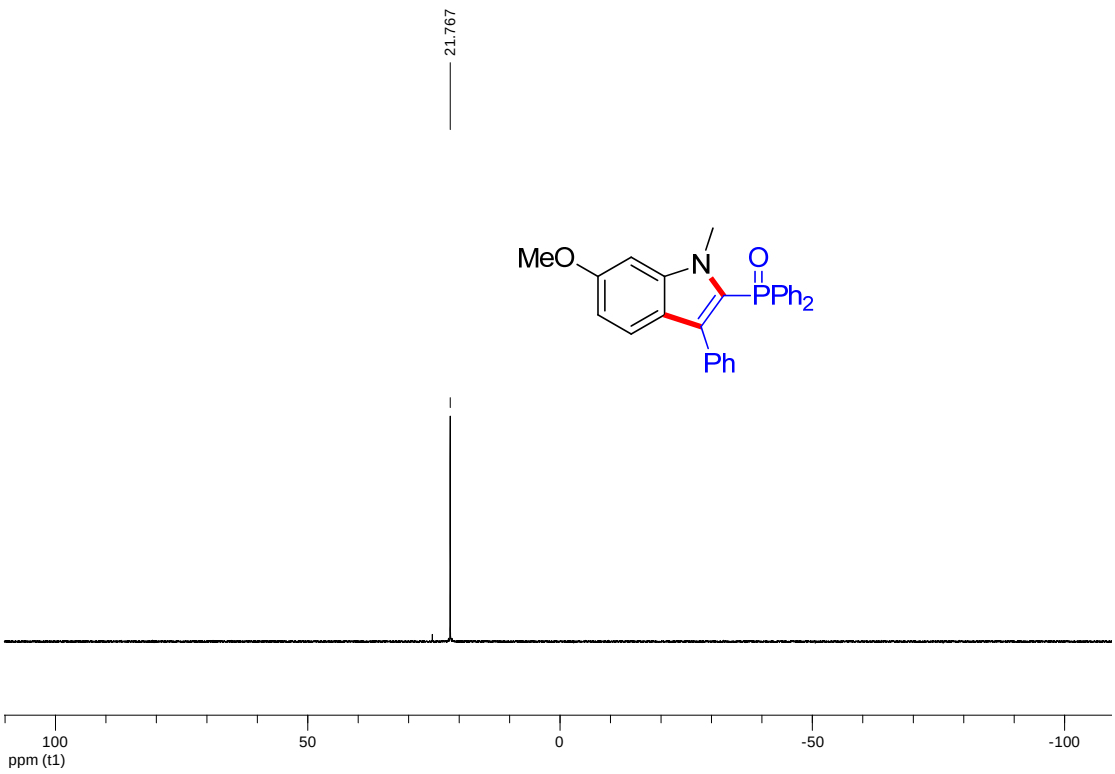

20.991
N
O
PPh2
Ph
100
50
0
-50
-100
ppm (t1)


WHN-3-123-1-404-HMBC
2D in CDCl3 298K Sep07 2012
13HMBC
ns=16 1.5hours
N
O
PPh2
Ph
f2 (ppm)
f1 (ppm)

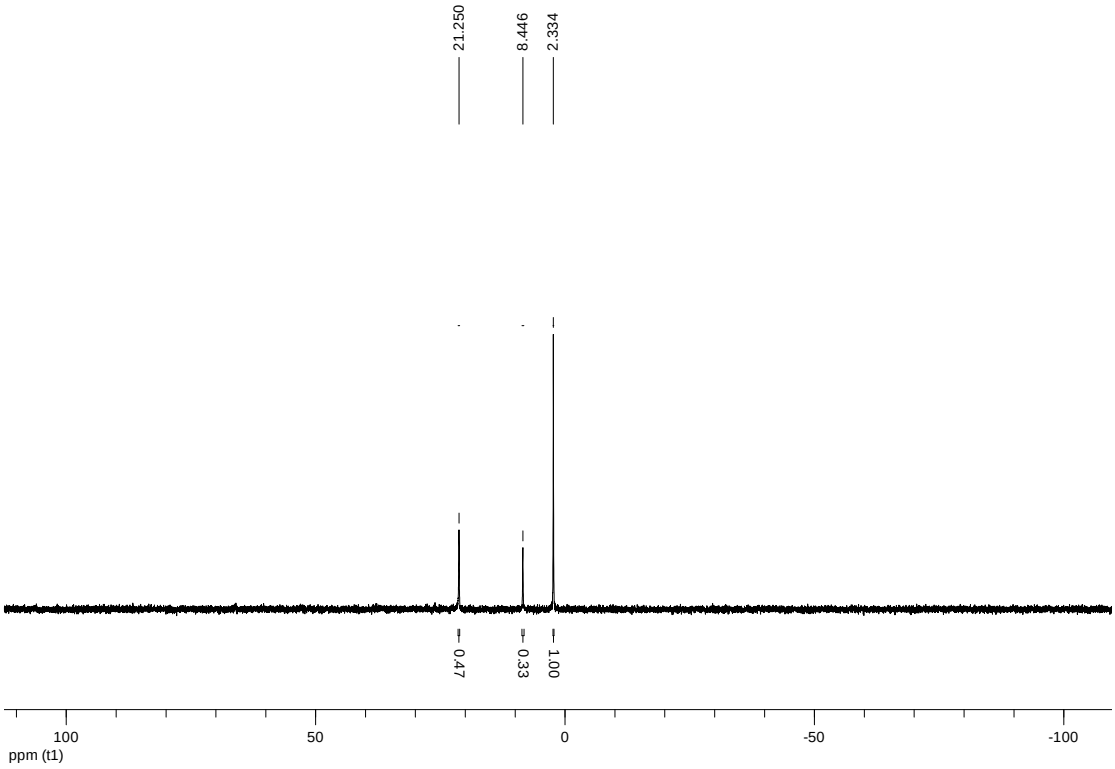
(6-methoxy-1-methyl-3-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ma)



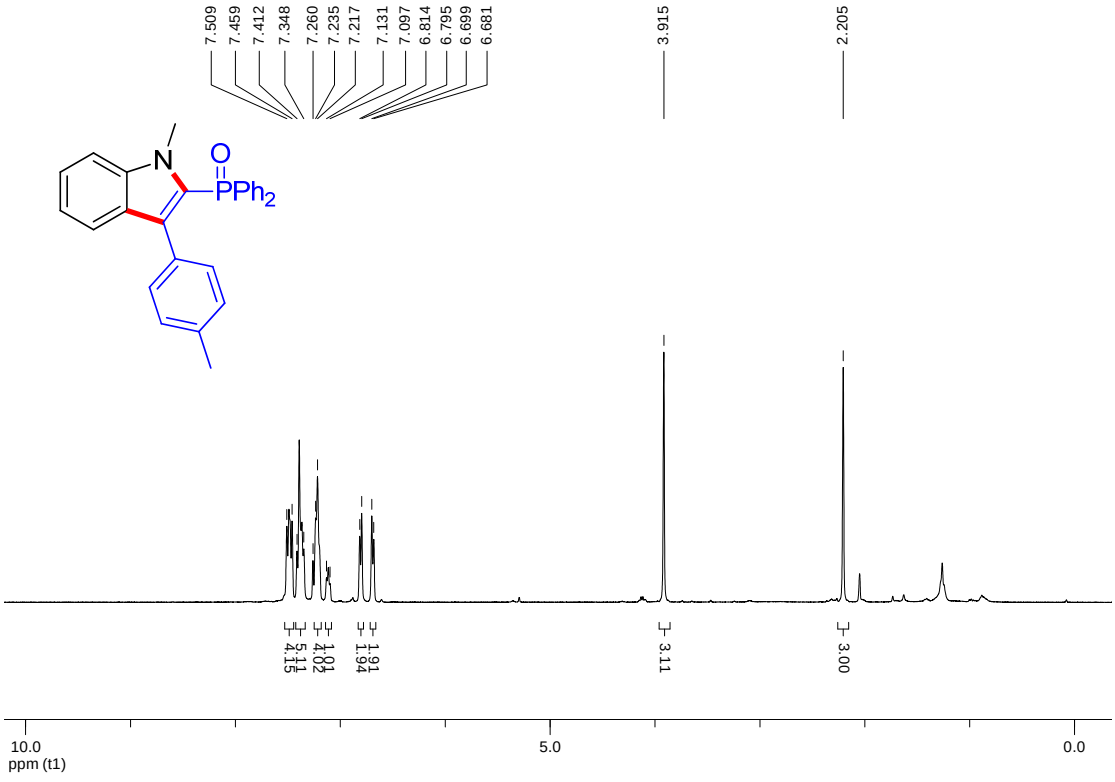


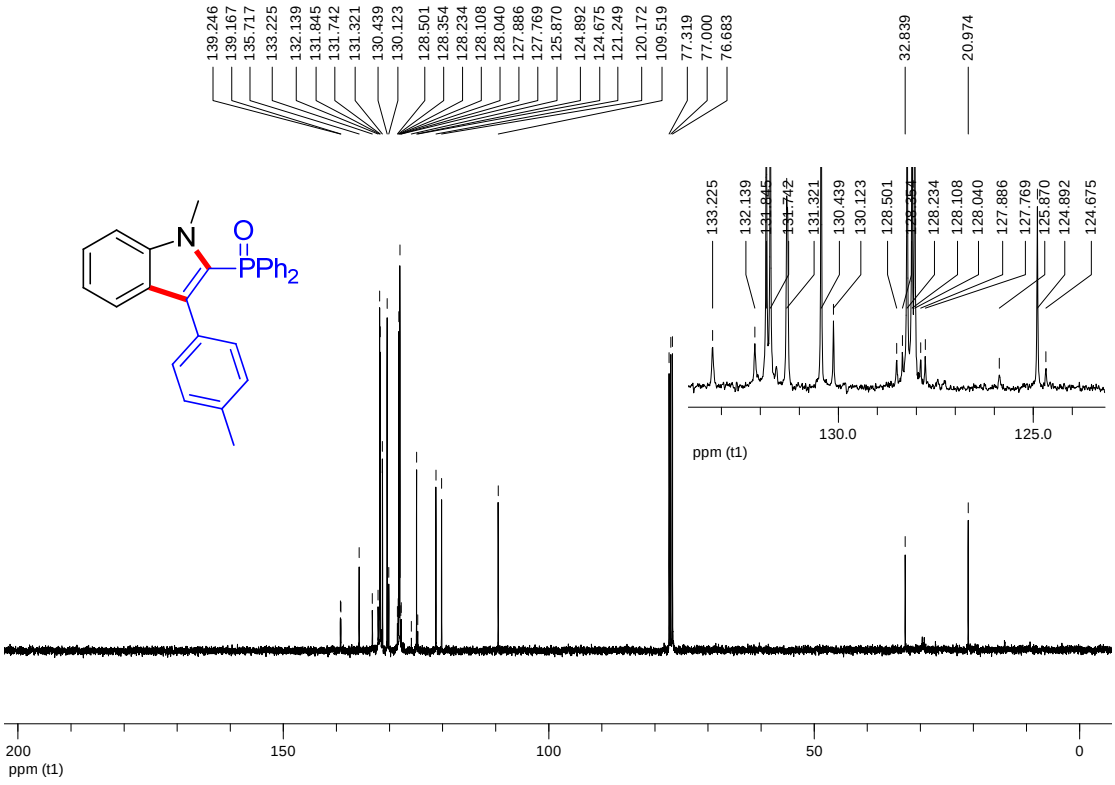

21.767
MeO
N
O
PPh2
Ph
100
50
0
-50
-100
ppm (t1)

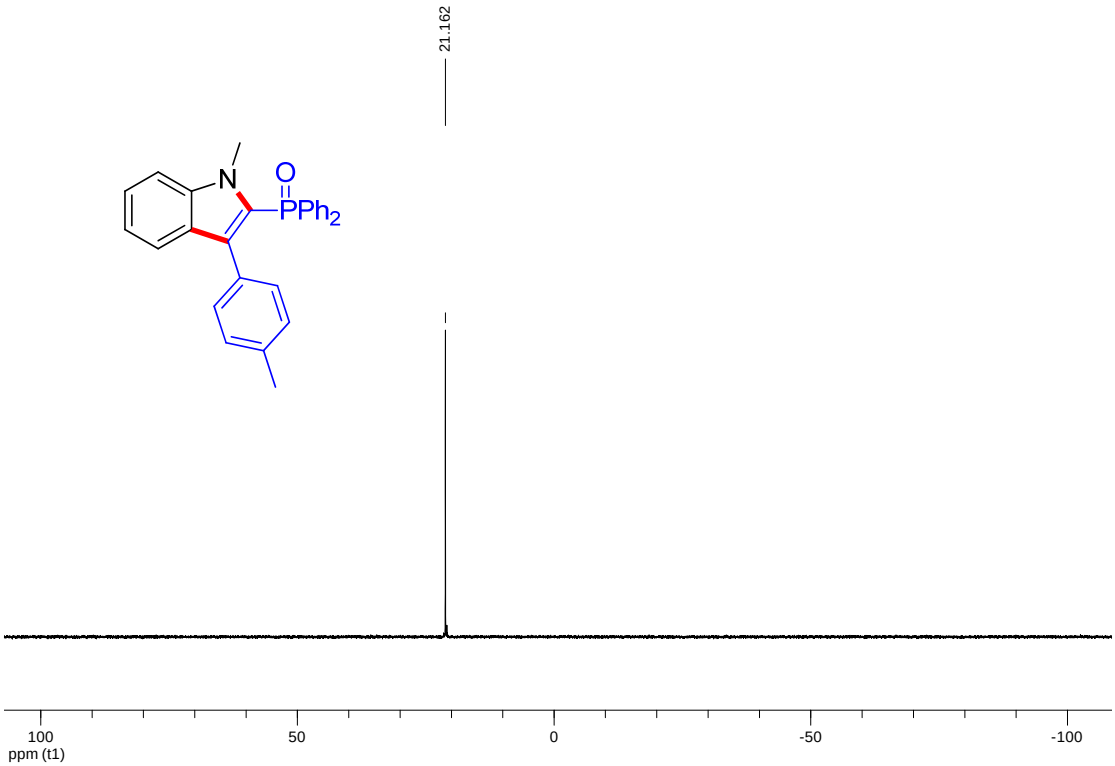
Yield of crude reaction mixture determined by ^{31}P NMR for 3ma



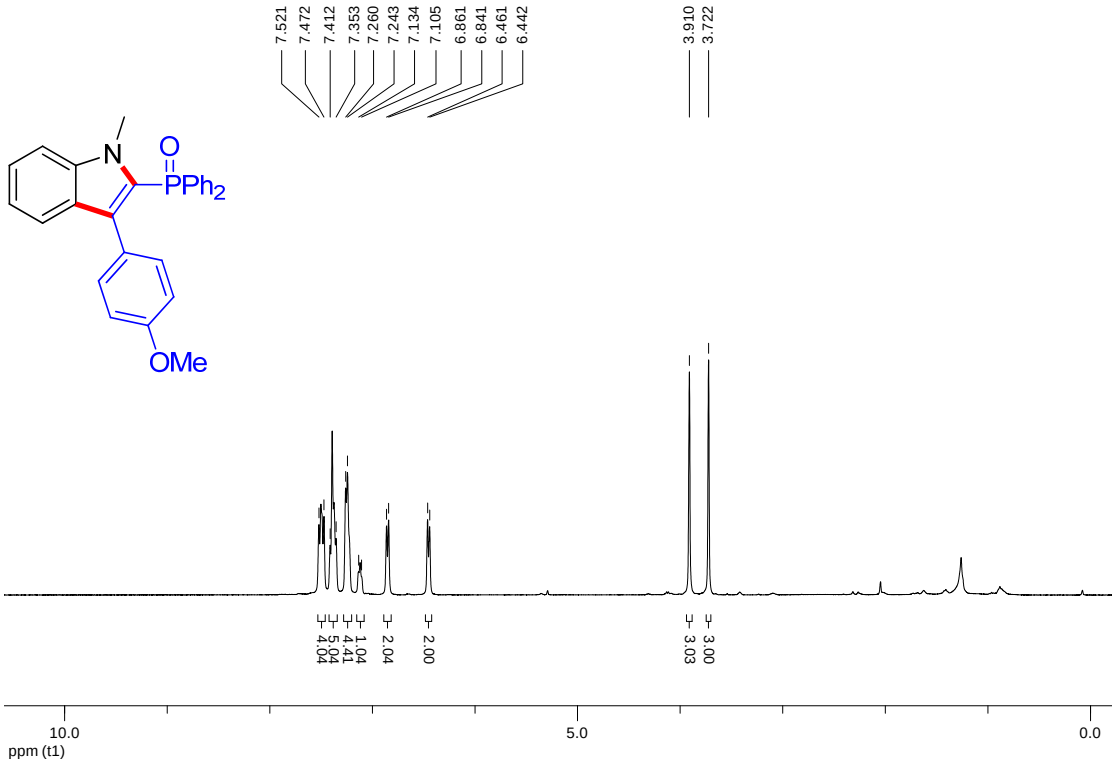
(1-methyl-3-(p-tolyl)-1*H*-indol-2-yl)diphenylphosphine oxide (3ab)

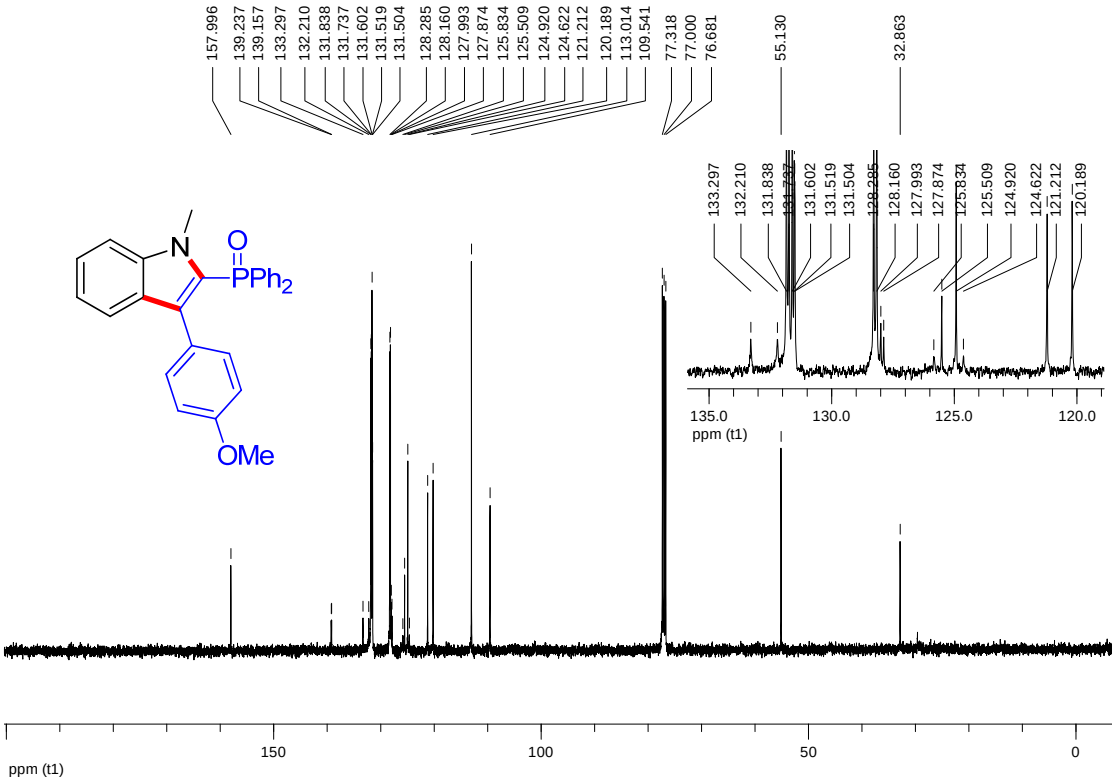


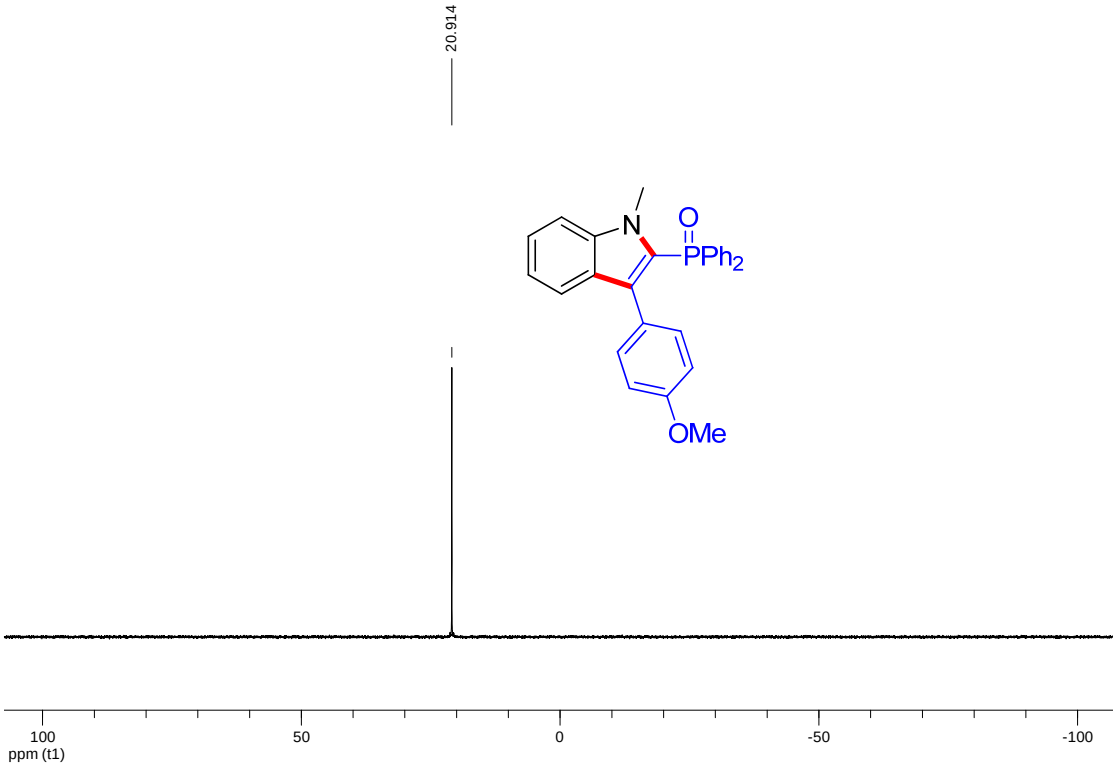



21.162
N
O
PPh2
100
ppm (t1)
50
0
-50
-100

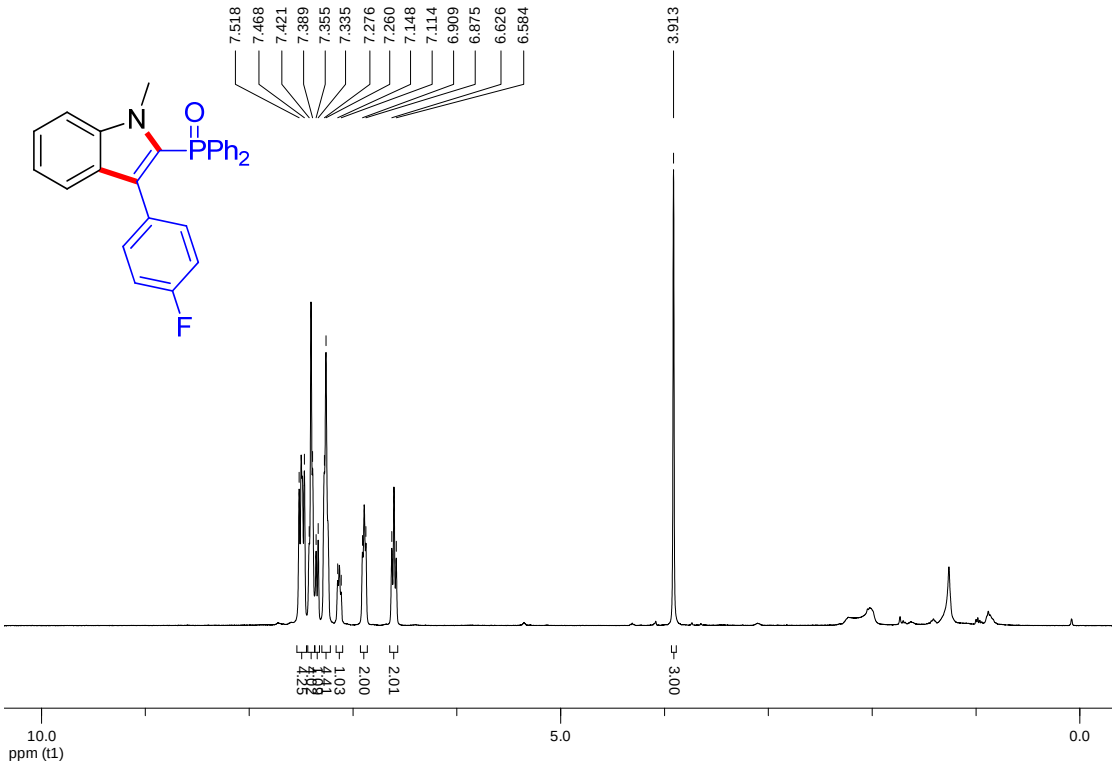
(3-(4-methoxyphenyl)-1-methyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ac)

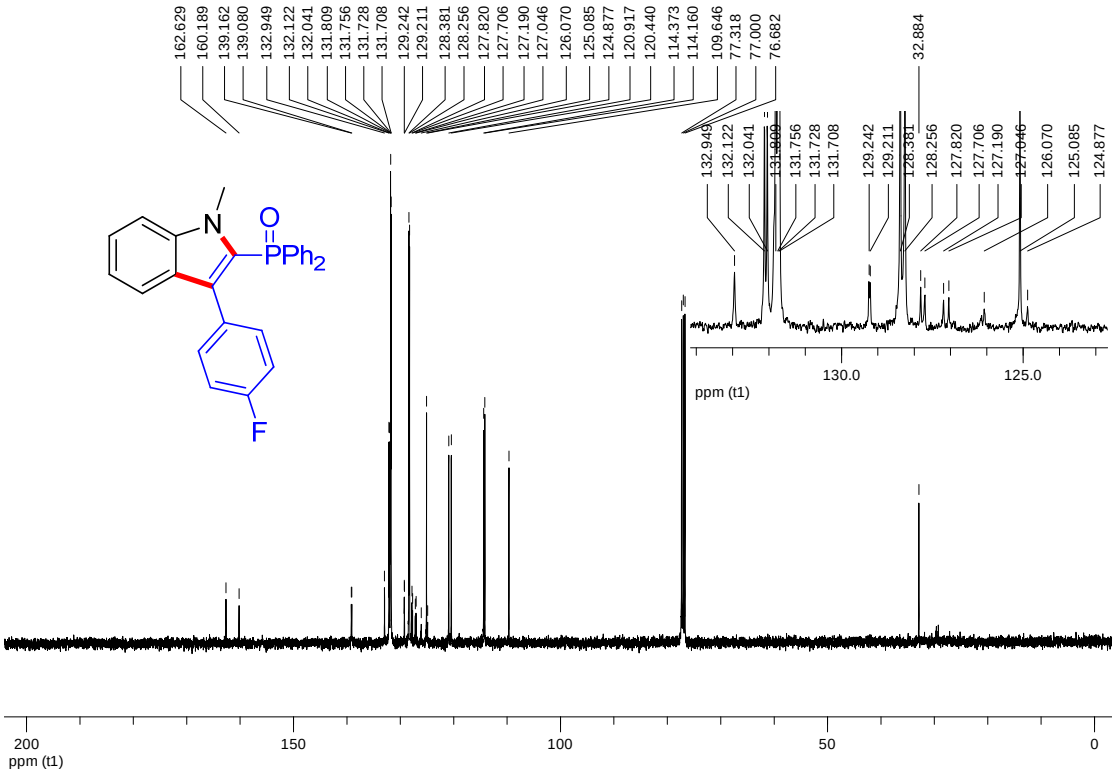


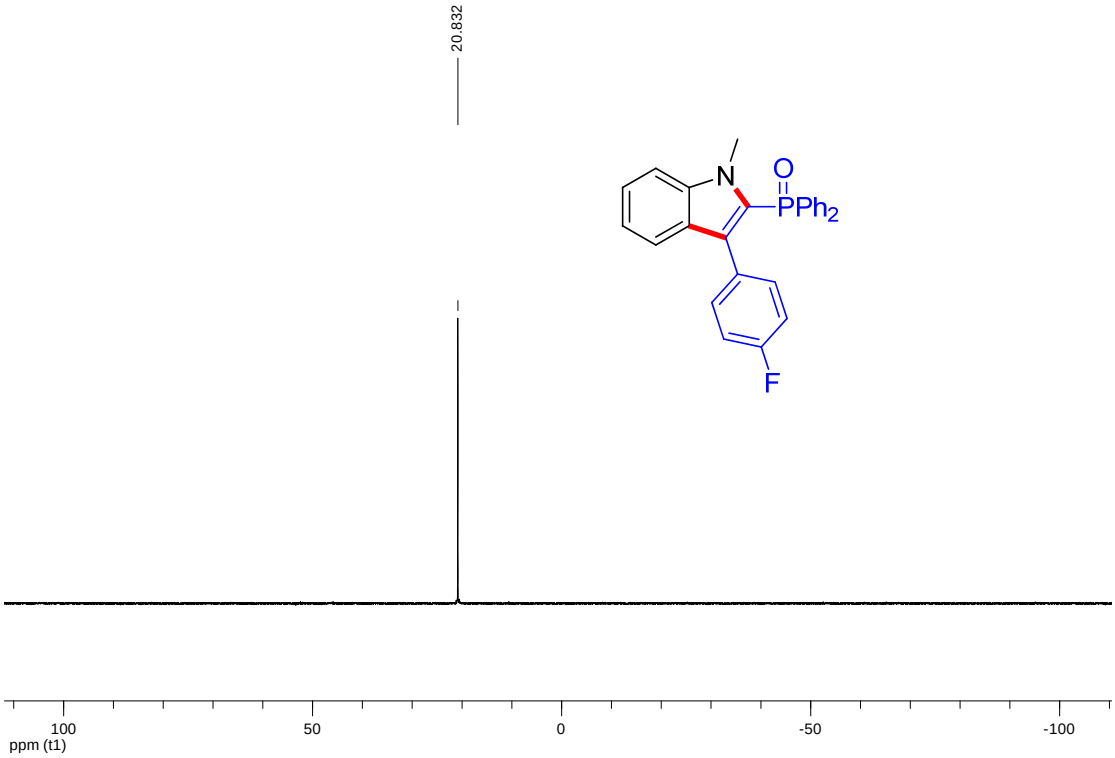


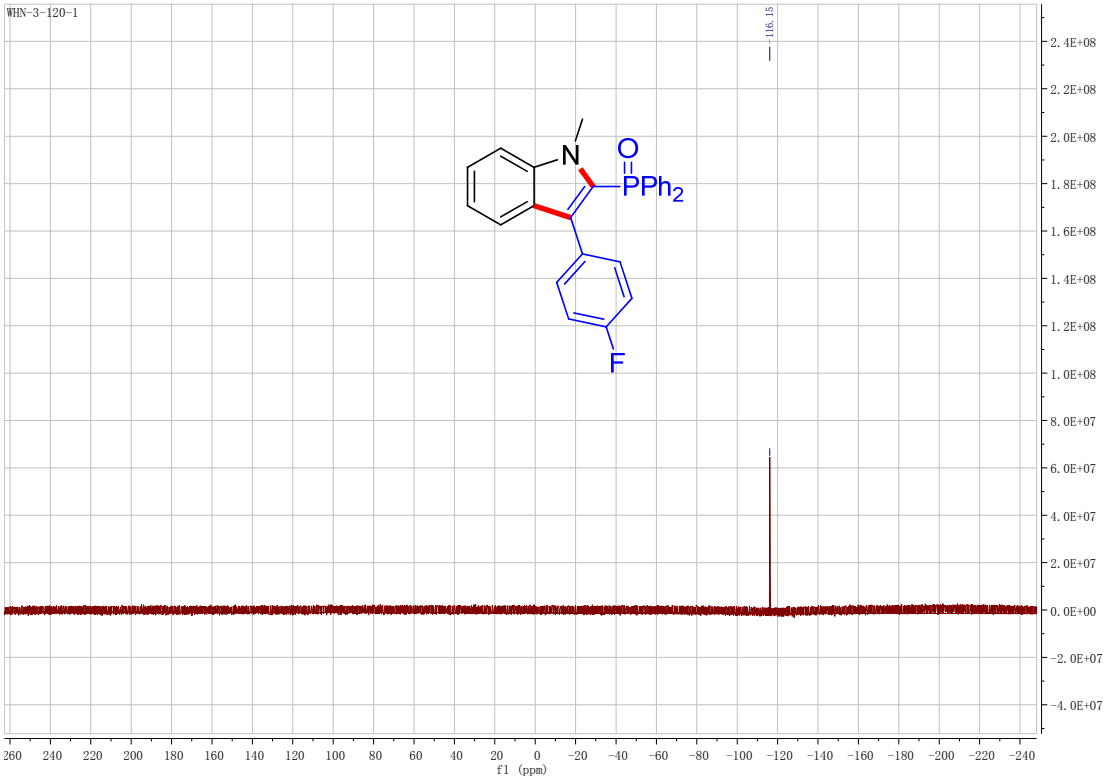

20.914
N
O
PPh2
OMe
100
ppm (t1)
50
0
-50
-100

(3-(4-fluorophenyl)-1-methyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ad)

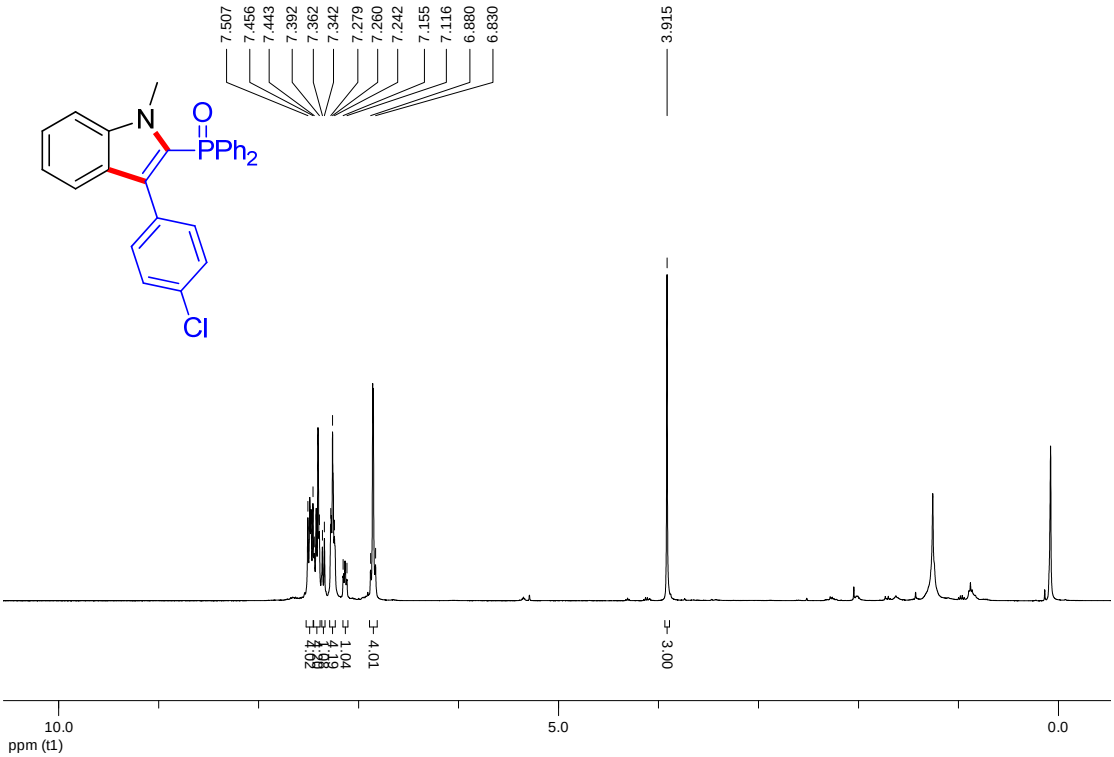


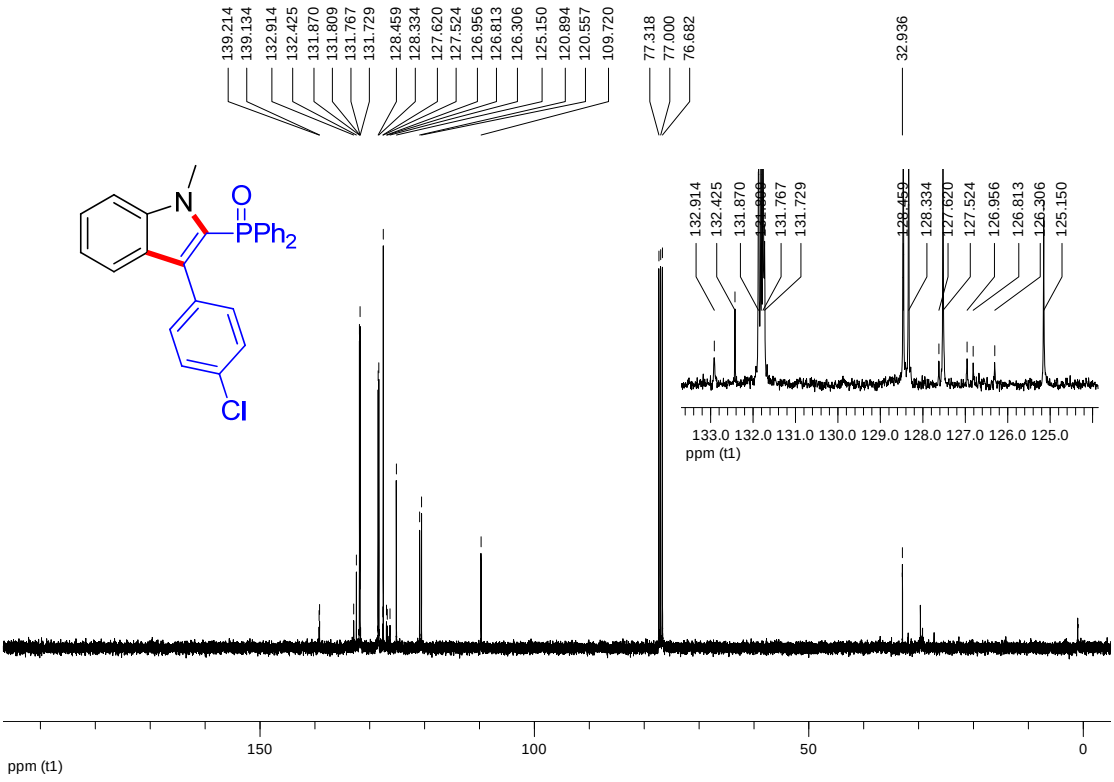


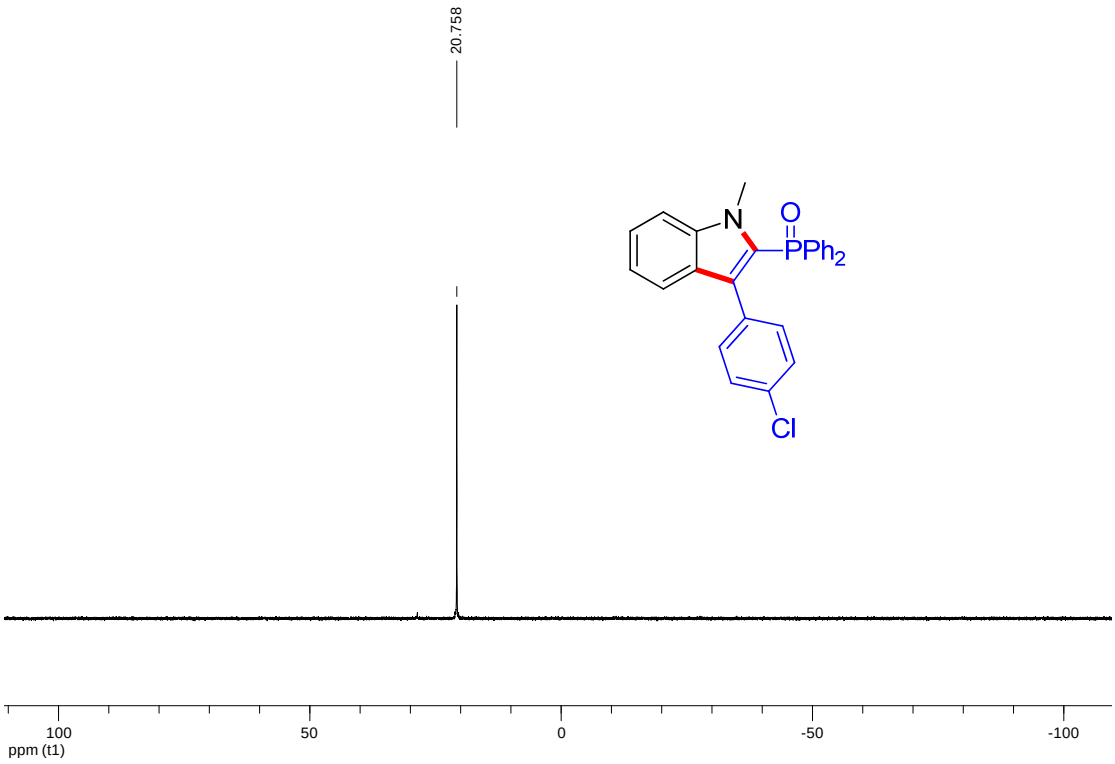

20.832
N
O
PPh2
F
100
50
0
-50
-100
ppm (t1)


WHN-3-120-1
116.15
N
O
PPh2
F
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
-4.0E+07
f1 (ppm)

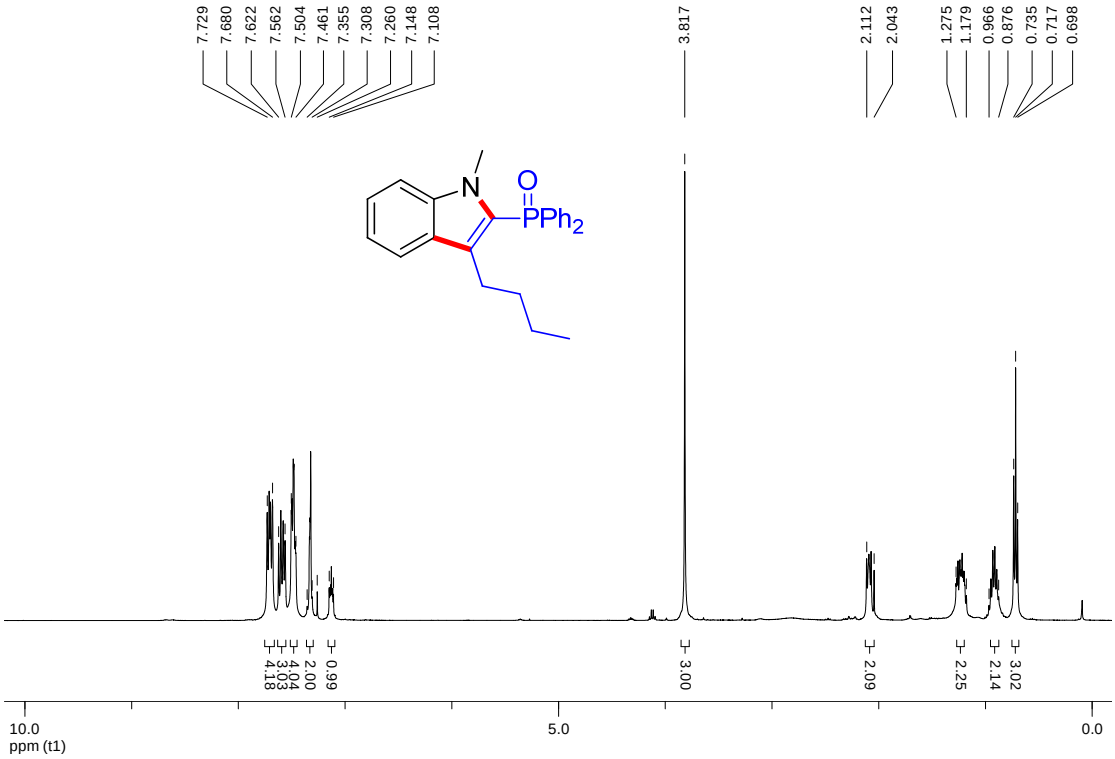
(3-(4-chlorophenyl)-1-methyl-1*H*-indol-2-yl)diphenylphosphine oxide(3ae)

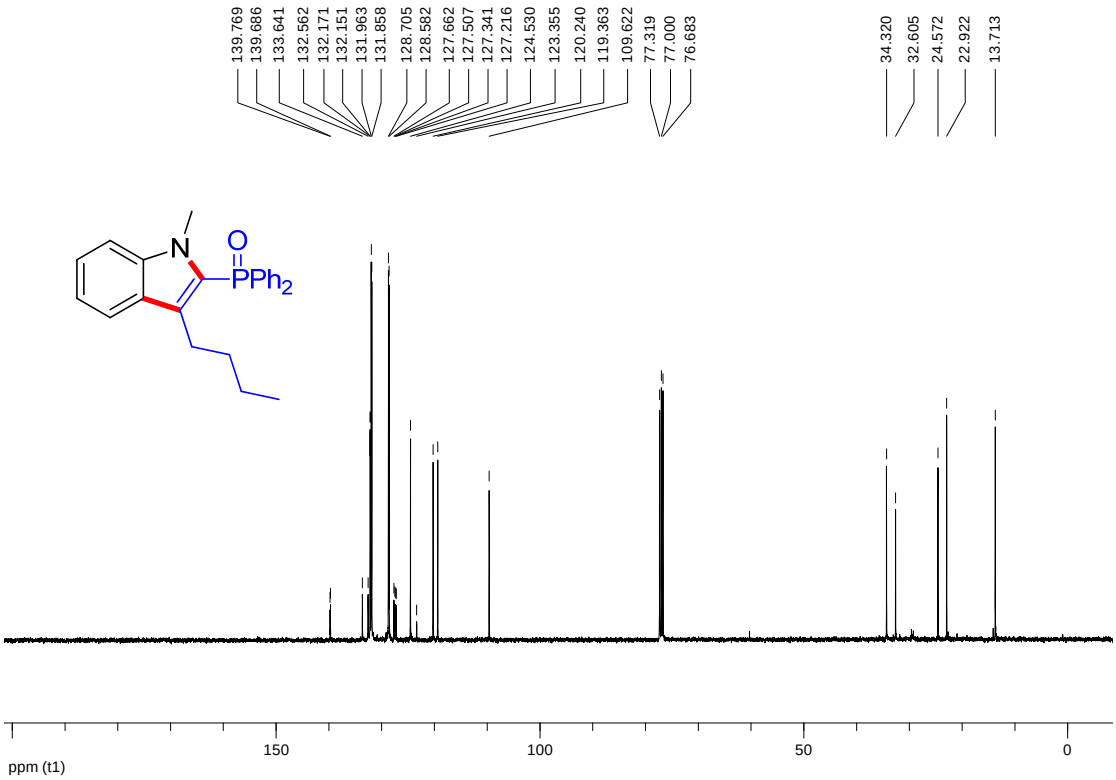


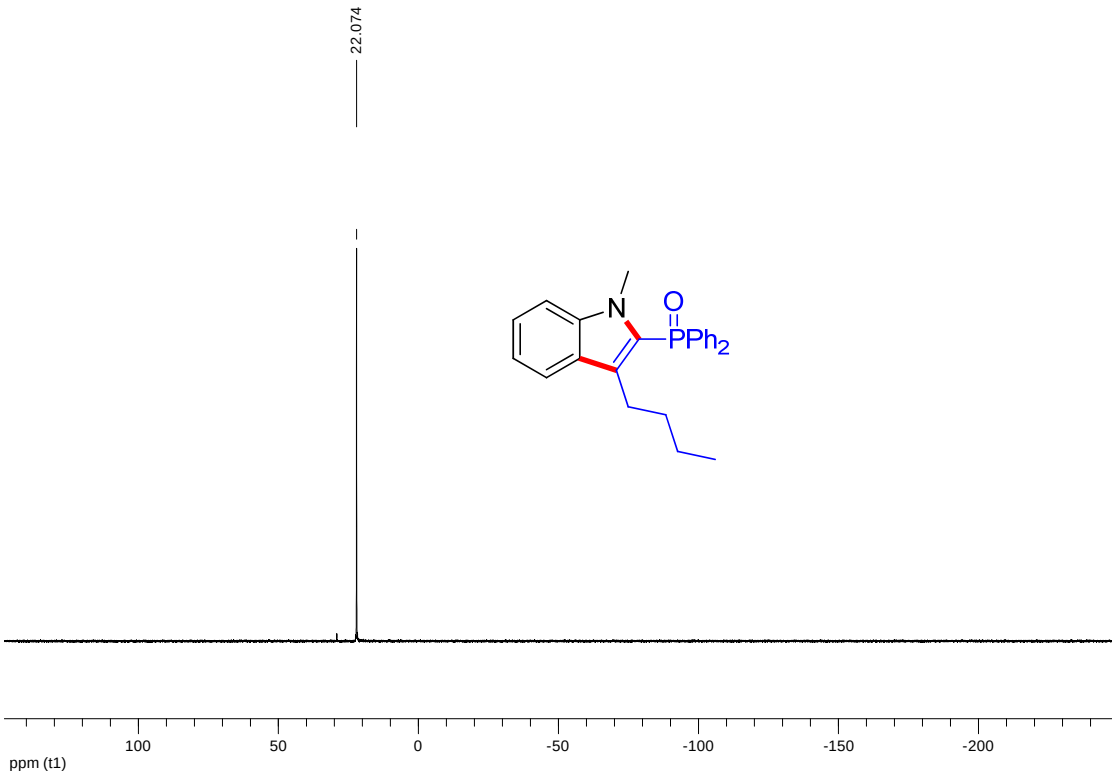


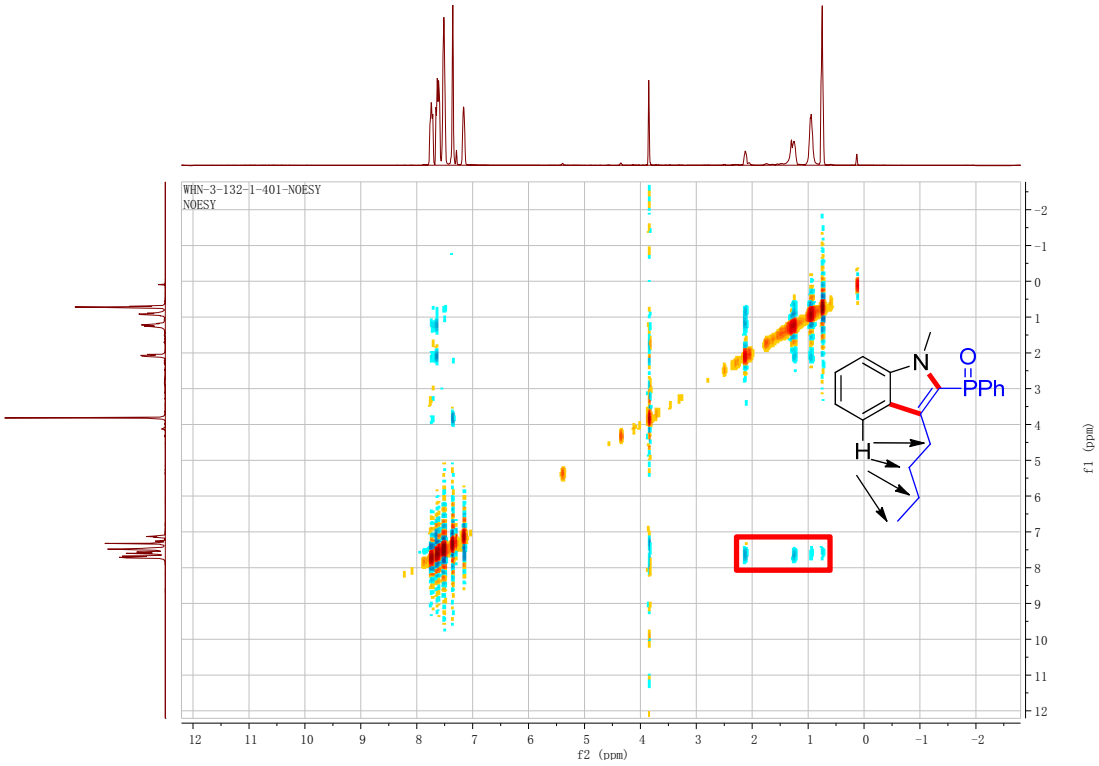

20.758
N
O
PPh2
Cl
100
50
0
-50
-100
ppm (t1)

(3-butyl-1-methyl-1*H*-indol-2-yl)diphenylphosphine oxide (3af)

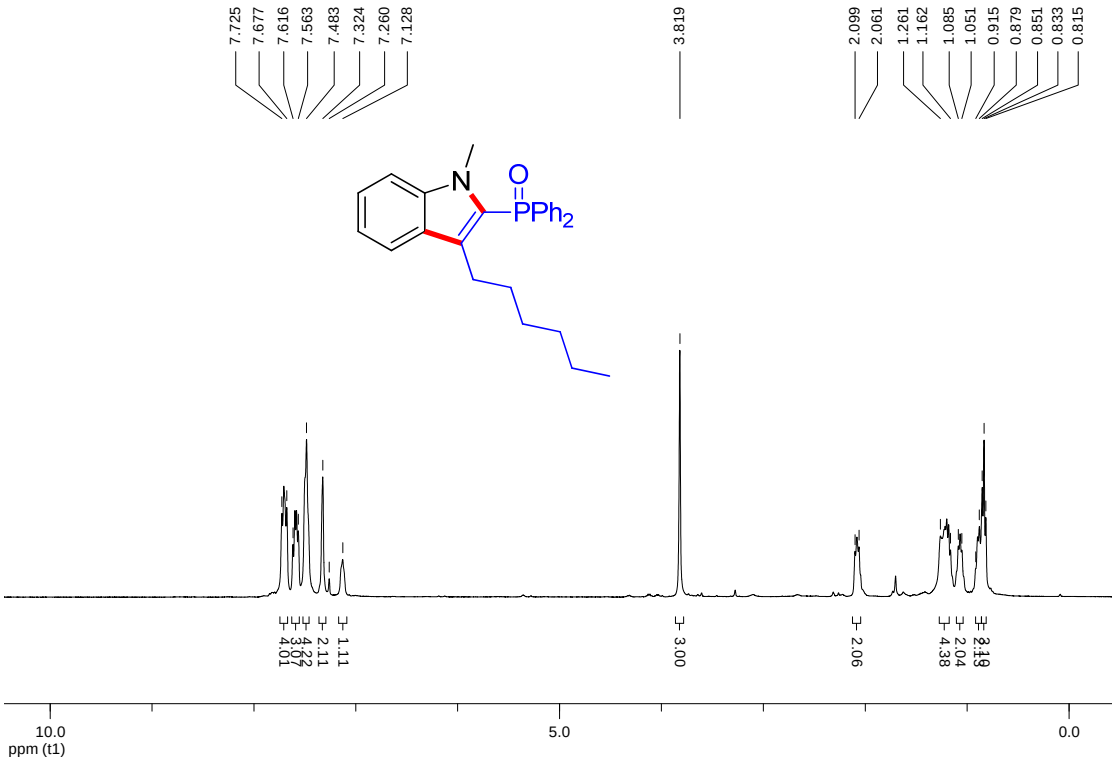


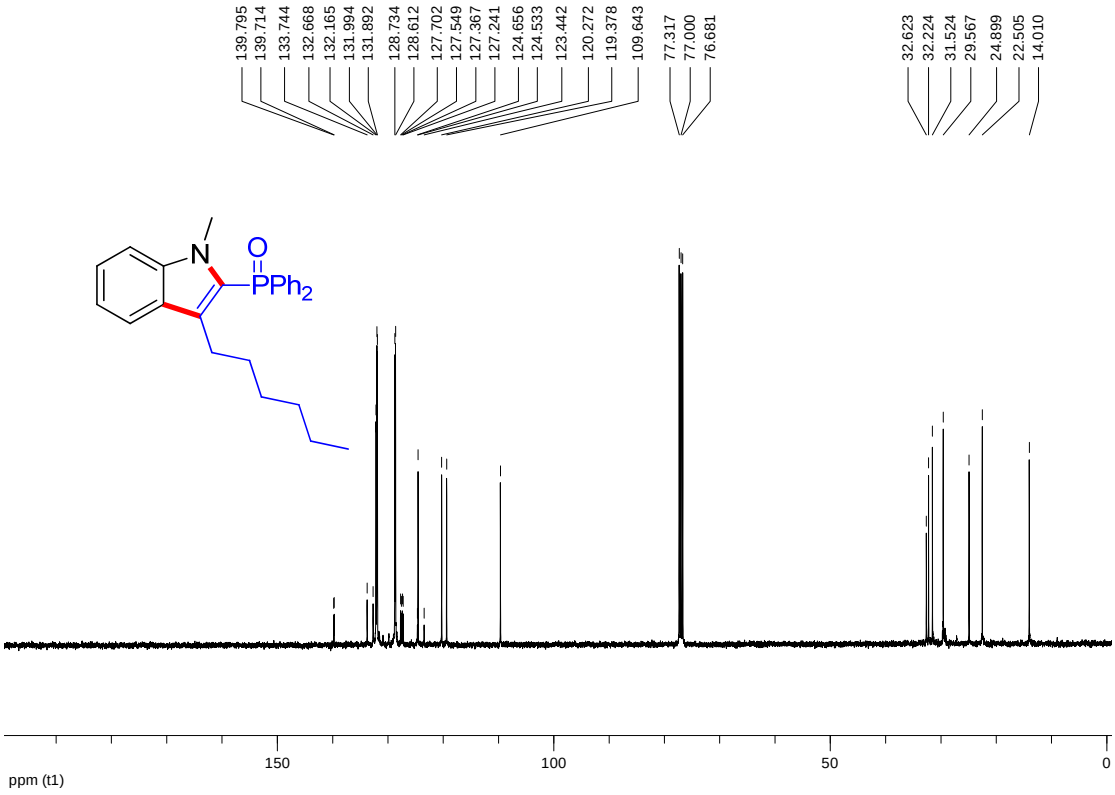


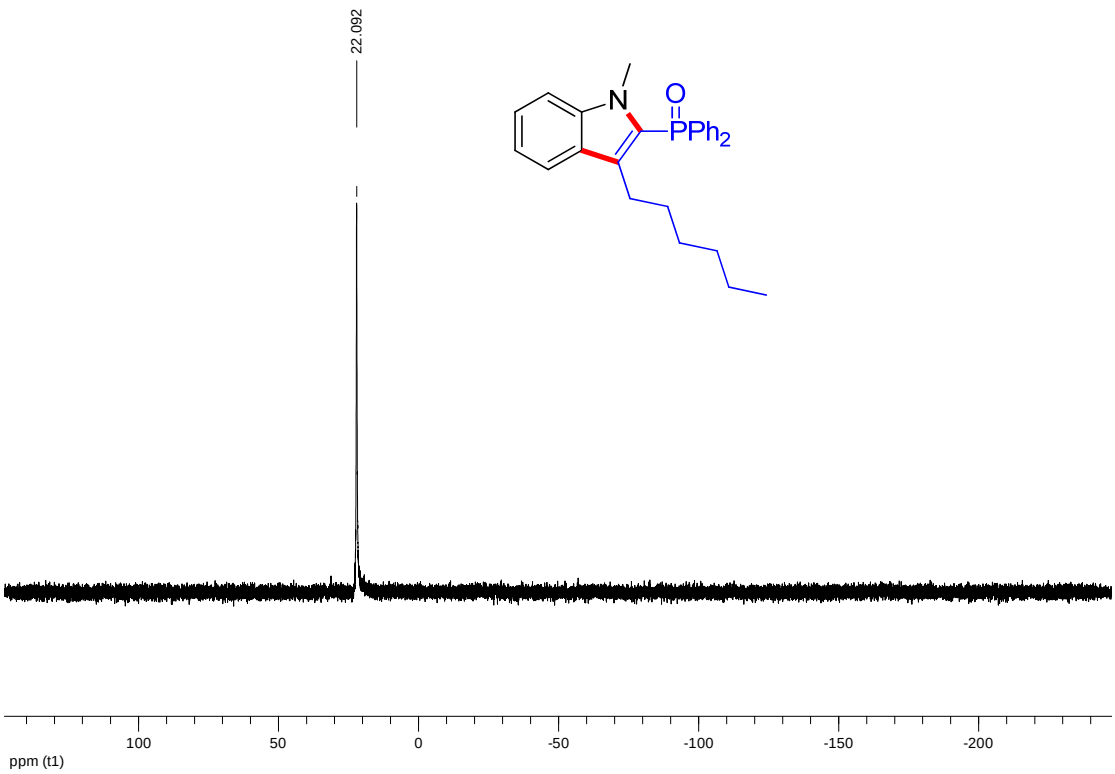

22.074
N
O
PPh2
100
50
0
-50
-100
-150
-200
ppm (t1)


WHN-3-132-1-401-NOESY
NOESY
N
O
PPh
H
f2 (ppm)
f1 (ppm)

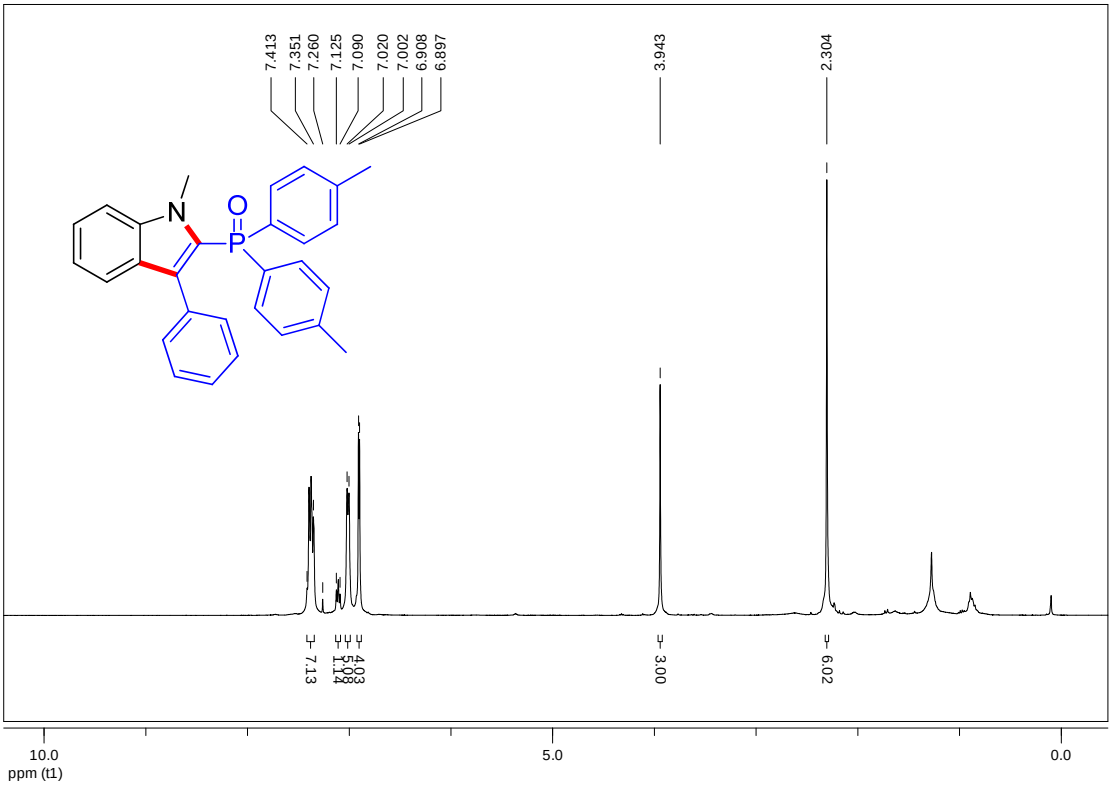
(3-hexyl-1-methyl-1*H*-indol-2-yl)diphenylphosphine oxide (3ag)

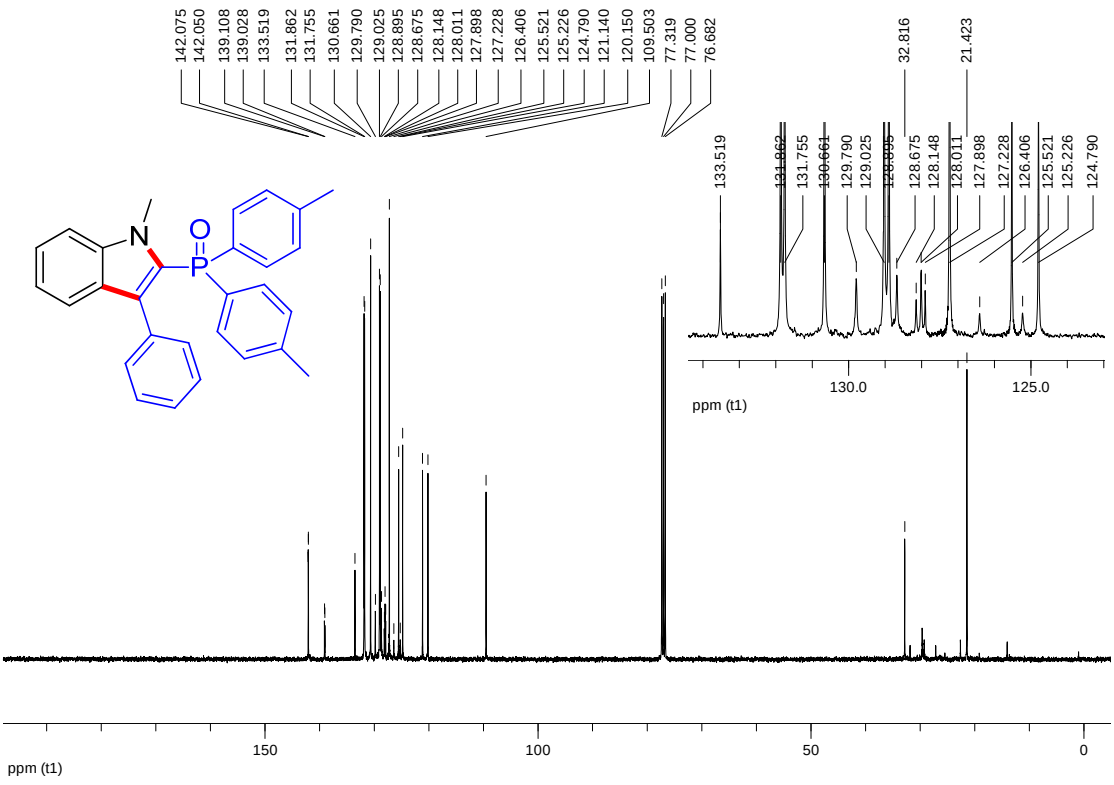


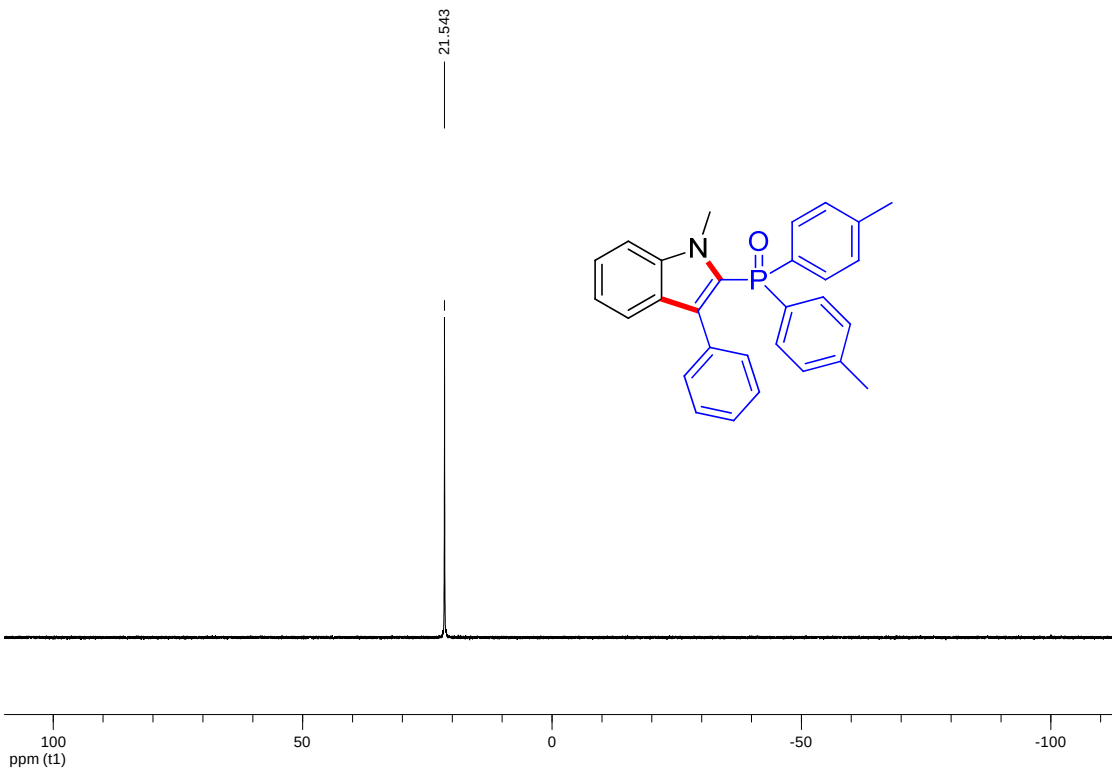



22.092
N
O
PPh2
100
50
0
-50
-100
-150
-200
ppm (t1)

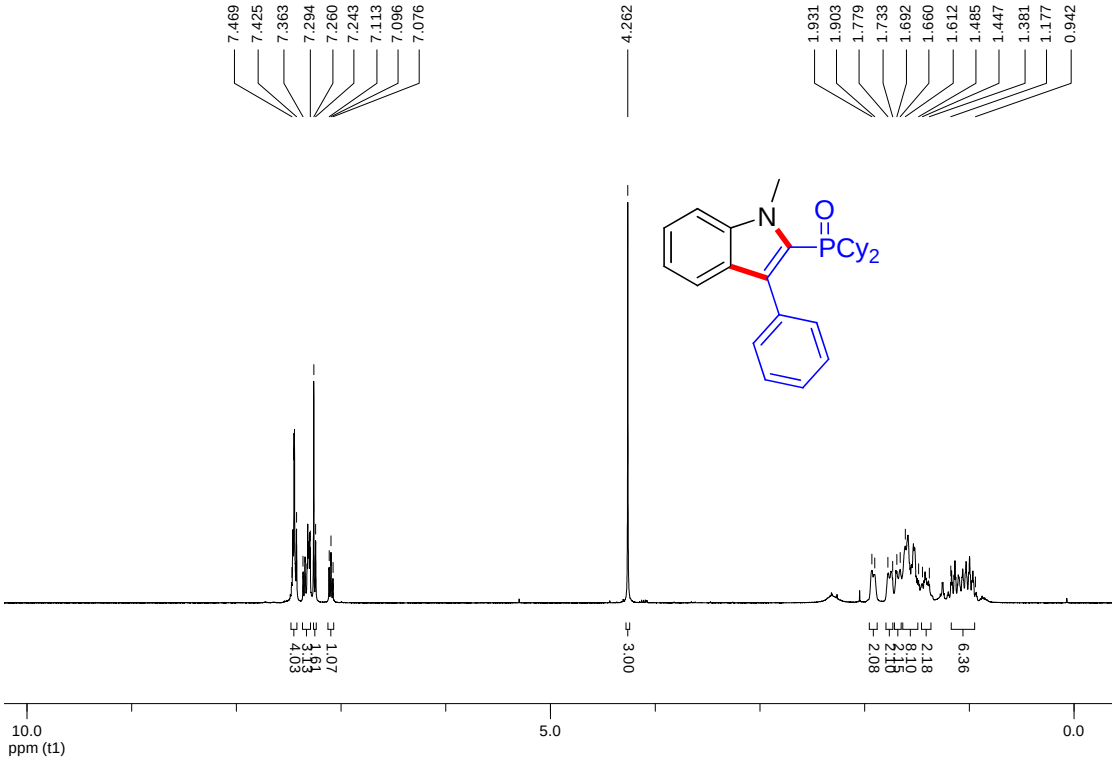
(1-methyl-3-phenyl-1*H*-indol-2-yl)di-p-tolylphosphine oxide (3ah)

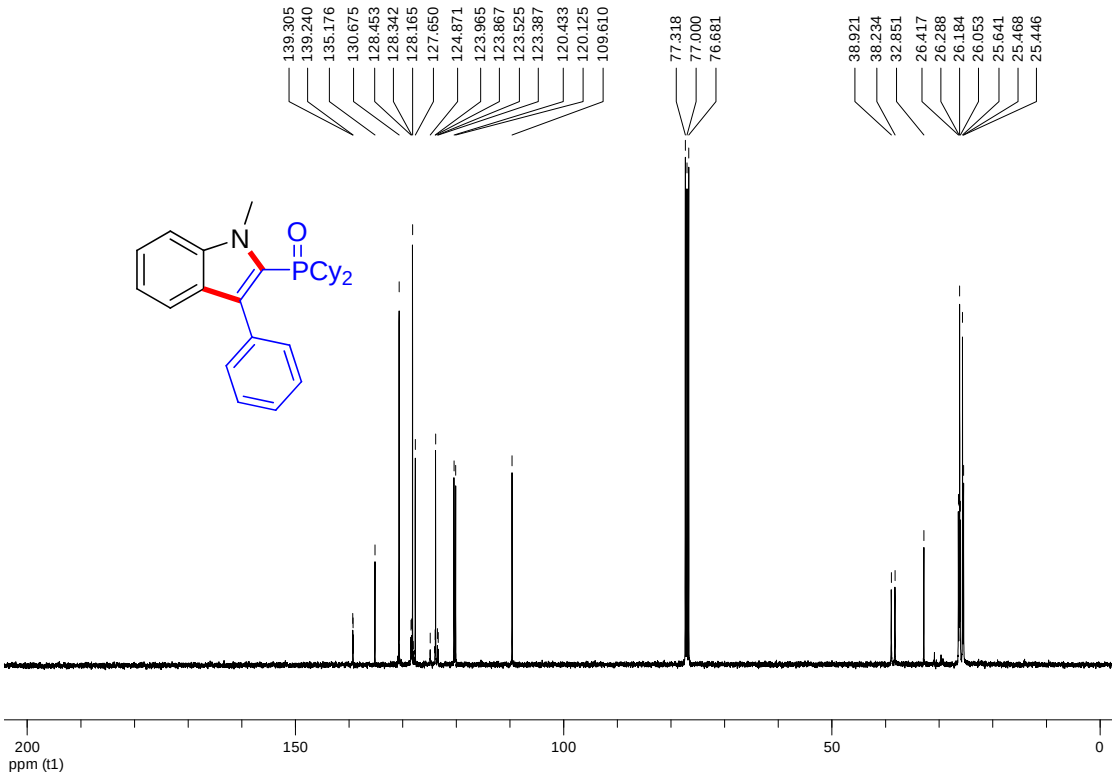


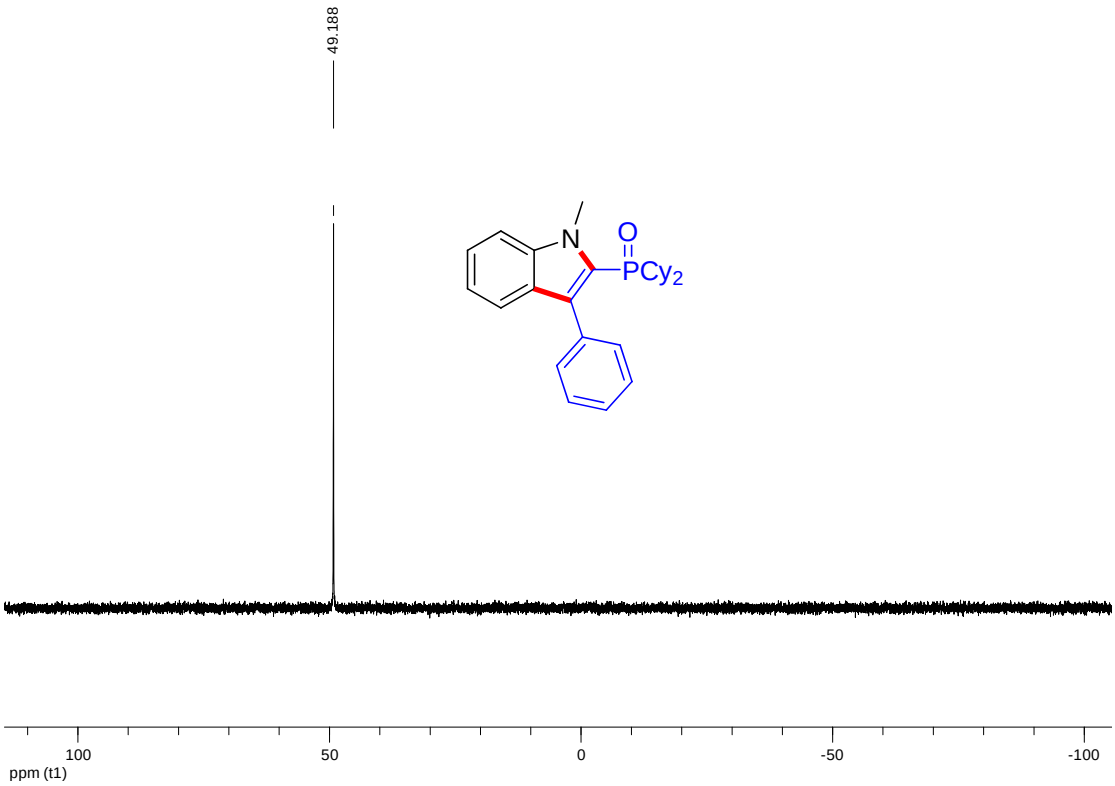



21.543
N
O
P
100
ppm (t1)
50
0
-50
-100

Dicyclohexyl(1-methyl-3-phenyl-1*H*-indol-2-yl)phosphine oxide (3ai)






49.188
N
O
PCy2
100
50
0
-50
-100
ppm (t1)

References

[1] White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228-234.

[2] Liu, B.; Song, C.; Sun, C.; Zhou, S.; Zhu, J. *J. Am. Chem. Soc.* **2013**, *135*, 16625−16631.

[3] Kondoh, A.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 4099-4104.

[4] Kondoh, A.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2010**, *12*, 1476-1479.