Supplementary Information

Harnessing Phosphorus-Centered Radicals for the Synthesis of Cyclopenta[*b*]indole and Pyrrolo[1,2-*a*]indole Frameworks.

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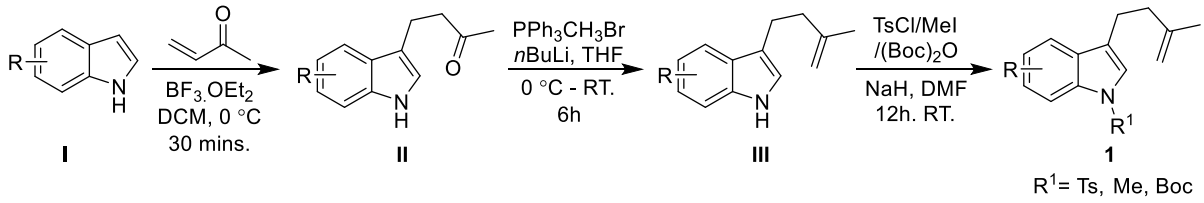
Contents

1. General Information:

Unless otherwise noted, all reactions were carried out in flame-dried or oven-dried glassware under a nitrogen atmosphere with magnetic stirring. Commercially available solvents and reagents were used as received without further purification. All solvents were reagent grade or HPLC grade. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone, and dichloromethane (CH_2Cl_2) was distilled from calcium hydride under a nitrogen atmosphere. Reactions were monitored by thin-layer chromatography (TLC) silica gel glass plates (60 F_{254}). TLC plates were visualized under UV light at 254 nm and *p*-Anisaldehyde stain. Column chromatography was carried out using silica gel (60-120 mesh & 100-200 mesh) packed in glass columns. The ^{1}H NMR and spectra were recorded at 400 and 500 MHz, ^{13}C NMR and spectra were recorded at 101 and 126 MHz and ^{31}P NMR and spectra were recorded at 162 and 202 MHz. ^{1}H and ^{13}C NMR Chemical shifts were calibrated to *tetra*-methylsilane as an external reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d= doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, brs = broad singlet, app = apparent), coupling constants (*J*) in Hertz (Hz), integration. Infrared spectra were recorded on a Bruker Alpha spectrophotometer. HRMS were obtained on an Agilent Q-TOF mass spectrometer with ESI resource (analyzer type: TOF).

2. Experimental Procedure:

2.1 General Procedure A: Synthesis of 3-alkyl indole substrate.



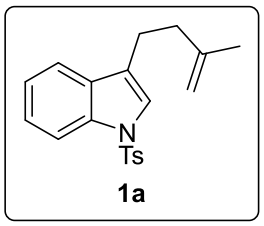
Scheme SI-1: Synthesis of indole derivatives **1**.

In an oven-dried round-bottom flask, indole **I** (1.0 mmol) was dissolved in dry DCM, followed by the addition of methyl vinyl ketone (1.3 mmol). The reaction mixture was cooled to 0 °C, and $BF_3 \cdot OEt_2$ (0.1 mmol) was added dropwise under stirring. The reaction was maintained at 0 °C for 30 minutes, after which completion was monitored *via* TLC. The reaction was then quenched with water (5 mL), and the organic layer was extracted using DCM, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product **II** was directly subjected to the next reaction without further purification.

In a separate oven-dried round-bottom flask, (methoxymethyl)triphenylphosphonium bromide (1.5 mmol) was dissolved in dry tetrahydrofuran (THF) and cooled to 0 °C. To this solution, n-BuLi (1.5 mmol, 2.5 M in hexane) was added dropwise, and the reaction mixture was stirred at 0 °C for 1 hour to generate the Wittig ylide. Subsequently, the crude product obtained from the previous step, dissolved in dry THF, was added dropwise to the in situ-generated Wittig reagent. The reaction mixture was stirred at 0 °C for 2 hours, then allowed to warm to room temperature and stirred for an additional 4 hours. Upon consumption of the starting material, as confirmed by TLC, the reaction was quenched with saturated aqueous ammonium chloride (NH_4Cl). The organic phase was extracted using ethyl acetate (EtOAc), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel using a gradient of 0–10% ethyl acetate in hexane as the eluent, affording compound **III**.

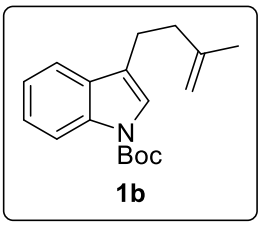
In the final transformation, compound **III** was dissolved in dimethylformamide (DMF), and sodium hydride (NaH, 2.0 mmol) was added portion-wise at 0 °C under stirring. After 10 minutes, a suitable electrophile, such as tosyl chloride (TsCl), methyl iodide (MeI), or di-*tert*-butyl dicarbonate ($(Boc)_2O$), was introduced slowly. The reaction mixture was stirred at room temperature for 12 hours. Upon completion, confirmed by TLC, the reaction was quenched with cold water. The organic layer was extracted with diethyl ether, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was subjected to purification via flash chromatography on silica gel using a 0–5% ethyl acetate in hexane gradient, yielding the final product, compound **1**.

3-(3-Methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 1H), 7.77 – 7.67 (m, 2H), 7.53 – 7.43 (m, 1H), 7.37 – 7.13 (m, 5H), 4.78 – 4.72 (m, 1H), 4.71 – 4.66 (m, 1H), 2.86 – 2.73 (m, 2H), 2.45 – 2.34 (m, 2H), 2.31 (s, 3H), 1.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.0, 144.8, 135.5, 135.4, 131.2, 129.9, 126.9, 124.7, 123.1, 122.8, 119.5, 113.9, 110.8, 37.0, 23.3, 22.6, 21.7; **IR** (neat): υ_{max} 3010, 2958, 1640, 1598, 1447, 1360, 1172, 1126, 748, 669 and 557 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{20}H_{22}NO_2S$ $[M+H]^+$ 340.1366; found: 340.1362.



1a

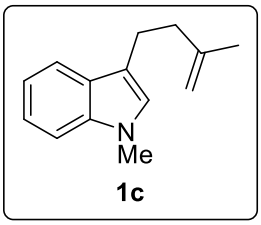
***tert*-Butyl 3-(3-methylbut-3-en-1-yl)-1*H*-indole-1-carboxylate (1b): ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, J = 5.6 Hz, 1H), 7.64 – 7.51 (m, 1H), 7.40 (s, 1H), 7.37 – 7.30 (m, 1H), 7.29 – 7.22 (m, 1H), 4.84 – 4.77 (m, 2H), 2.89 – 2.82 (m, 2H), 2.49 – 2.42 (m, 2H), 1.84 (s, 3H),



1b

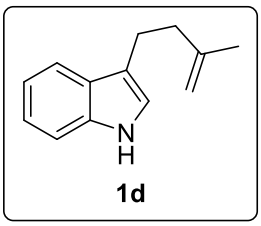
1.69 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.0, 145.4, 135.6, 130.8, 124.3, 122.4, 121.0, 119.0, 115.4, 110.5, 83.4, 37.4, 28.4, 23.4, 22.7; **IR** (neat): υ_{max} 3010, 2968, 1648, 1588, 1447, 1380, 1179, 1106, 757, 661 and 557 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{18}H_{24}NO_2$ $[M+H]^+$ 286.1802; found: 286.1799.

1-Methyl-3-(3-methylbut-3-en-1-yl)-1*H*-indole (1c): The compound was synthesized following General Procedure A, and its spectral data were consistent with those reported in the literature.[1]



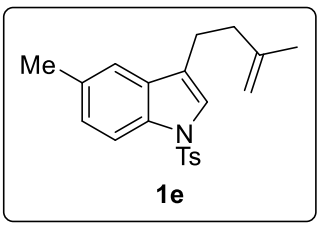
1c

3-(3-Methylbut-3-en-1-yl)-1*H*-indole (1d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (br, s, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.18 – 7.11 (m, 1H), 7.03 – 6.97 (m, 1H), 4.85 – 4.76 (m, 2H), 3.03 – 2.84 (m, 2H), 2.55 – 2.41 (m, 2H), 1.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.1, 136.4, 127.6, 122.0, 121.1, 119.2, 119.0, 116.7, 111.2, 110.1, 38.3, 23.7, 22.7; **IR** (neat): υ_{max} 3008, 2962, 1638, 1568, 1467, 1389, 1169, 1156, 775, 680 and 590 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{13}H_{16}N$ $[M+H]^+$ 186.1278; found: 186.1273.



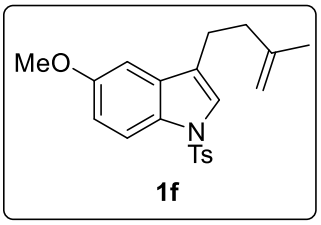
1d

5-Methyl-3-(3-methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.4 Hz, 1H), 4.76 (s, 1H), 4.70 (s, 1H), 2.82 – 2.73 (m, 2H), 2.42 (s, 3H), 2.41 – 2.35 (m, 2H), 2.32 (s, 3H), 1.78 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.0, 144.6, 135.5, 133.7, 132.7, 131.5, 129.8, 126.8, 126.1, 123.0, 119.4, 113.6, 110.7, 36.9, 23.2, 22.6, 21.6, 21.5; **IR** (neat): υ_{max} 3010, 2968, 1648, 1588, 1447, 1380, 1179, 1106, 757, 661 and 557 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{21}H_{24}NO_2S$ $[M+H]^+$ 354.1523; found: 354.1519.



1e

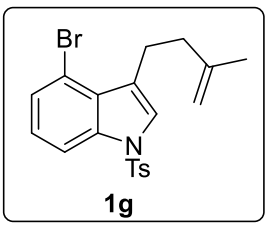
5-Methoxy-3-(3-methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 1H), 7.77 – 7.64 (m, 2H), 7.31 – 7.24 (m, 1H), 7.23 – 7.12 (m, 2H), 6.97 – 6.85 (m, 2H), 4.78 – 4.73 (m, 1H), 4.71 – 4.67 (m, 1H), 3.82 (s, 3H), 2.81 – 2.71 (m, 2H), 2.46 – 2.35 (m, 2H), 2.32 (s, 3H), 1.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.4, 144.9, 144.7,



1f

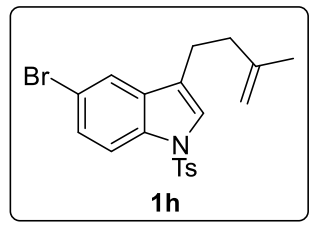
136.6, 135.4, 132.3, 129.8, 126.8, 123.7, 123.2, 114.8, 113.4, 110.8, 102.2, 55.8, 36.7, 23.3, 22.6, 21.7; **IR** (neat): υ_{max} 3050, 2978, 1658, 1568, 1467, 1366, 1159, 1136, 768, 664 and 557 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{21}H_{24}NO_3S$ $[M+H]^+$ 370.1472; found: 370.1468.

4-Bromo-3-(3-methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.22 (d, J = 8.3 Hz, 2H), 7.10 (t, J = 8.1 Hz, 1H), 4.80 – 4.76 (m, 1H), 4.75 – 4.70 (m, 1H), 3.11 – 3.02 (m, 2H), 2.44 – 2.37 (m, 2H), 2.35 (s, 3H), 1.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2, 145.0, 136.7, 135.1, 130.0, 129.2, 127.9, 126.9, 125.4, 124.6, 123.6, 114.7, 113.0, 110.7, 38.3, 24.9, 22.8, 21.7; **IR** (neat): υ_{max} 3056, 2978, 1624, 1588, 1447, 1367, 1191, 1126, 737, 687 and 557 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{20}H_{21}BrNO_2S$ $[M+H]^+$ 418.0471; found: 418.0469.



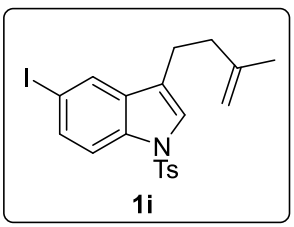
1g

5-Bromo-3-(3-methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1h): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 1.7 Hz, 1H), 7.39 (dd, J = 8.8, 1.8 Hz, 1H), 7.32 (s, 1H), 7.21 (d, J = 8.1 Hz, 2H), 4.76 (s, 1H), 4.67 (s, 1H), 2.74 (dd, J = 11.9, 3.7 Hz, 2H), 2.39 – 2.34 (m, 2H), 2.34 (s, 3H), 1.76 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.1, 144.6, 135.2, 134.1, 133.0, 130.0, 127.6, 126.8, 124.1, 122.4, 122.3, 116.7, 115.4, 111.0, 36.8, 23.1, 22.6, 21.7; **IR** (neat): υ_{max} 3056, 2978, 1622, 1558, 1447, 1376, 1177, 1126, 737, 647 and 577 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{20}H_{21}BrNO_2S$ $[M+H]^+$ 418.0471; found: 418.0467.



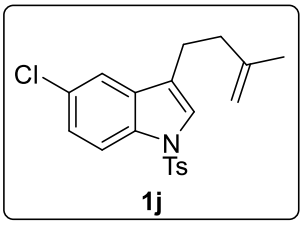
1h

5-Iodo-3-(3-methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 1.6 Hz, 1H), 7.74 (d, J = 8.6 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.56 (dd, J = 8.7, 1.7 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.24 – 7.18 (m, 2H), 4.79 – 4.73 (m, 1H), 4.70 – 4.65 (m, J = 1.0 Hz, 1H), 2.79 – 2.70 (m, 2H), 2.41 – 2.34 (m, 2H), 2.34 (s, 3H), 1.76 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.1, 144.7, 135.2, 134.7, 133.6, 133.2, 130.0, 128.5, 126.9, 123.7, 122.2, 115.8, 111.0, 87.4, 36.8, 23.0, 22.6, 21.7; **IR** (neat): υ_{max} 3056, 2948, 1688, 1548, 1467, 1345, 1191, 1126, 790, 645 and 557 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{20}H_{21}INO_2S$ $[M+H]^+$ 466.0334; found: 466.0331.



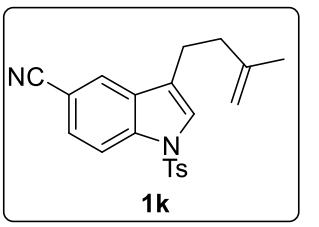
1i

5-Chloro-3-(3-methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1j): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 1.9 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.28 – 7.16 (m, 3H), 4.79 – 4.72 (m, 1H), 4.71 – 4.65 (m, 1H), 2.81 – 2.69 (m, 2H), 2.42 – 2.34 (m, 2H), 2.34 (s, 3H), 1.76 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.1, 144.6, 135.2, 133.8, 132.5, 130.0, 129.1, 126.8, 124.9, 124.3, 122.6, 119.3, 115.0, 111.0, 36.8, 23.1, 22.6, 21.7; **IR** (neat): υ_{max} 3056, 2978, 1622, 1558, 1447, 1376, 1177, 1126, 737, 647 and 577 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{20}H_{21}ClNO_2S$ $[M+H]^+$ 374.0977; found: 374.0973.



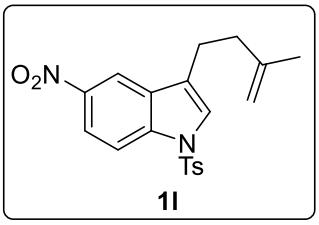
1j

3-(3-Methylbut-3-en-1-yl)-1-tosyl-1*H*-indole-5-carbonitrile (1k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.6, 0.6 Hz, 1H), 7.82 (dd, J = 1.5, 0.6 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.55 (dd, J = 8.6, 1.5 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.28 – 7.22 (m, 2H), 4.79 – 4.73 (m, 1H), 4.70 – 4.65 (m, 1H), 2.85 – 2.76 (m, 2H), 2.41 – 2.36 (m, 2H), 2.36 (s, 3H), 1.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 144.3, 137.0, 135.0, 131.2, 130.2, 127.7, 126.9, 124.9, 124.6, 122.6, 119.5, 114.6, 111.2, 106.7, 36.9, 23.0, 22.5, 21.7; **IR** (neat): υ_{max} 3065, 2978, 2243, 1622, 1588, 1447, 1336, 1177, 1116, 735, 647 and 577 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{21}H_{21}N_2O_2S$ $[M+H]^+$ 365.1319; found: 365.1314.



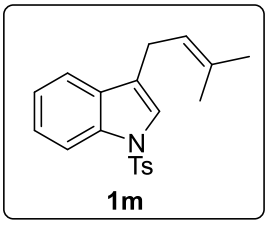
1k

3-(3-methylbut-3-en-1-yl)-5-nitro-1-tosyl-1*H*-indole (1l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 2.1 Hz, 1H), 8.19 (dd, J = 9.1, 2.1 Hz, 1H), 8.06 (d, J = 9.1 Hz, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.48 (s, 1H), 7.31 – 7.20 (m, 2H), 4.77 (s, 1H), 4.68 (s, 1H), 2.89 – 2.79 (m, 2H), 2.49 – 2.38 (m, 2H), 2.36 (s, 3H), 1.78 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8, 144.3, 144.1, 138.2, 134.9, 131.1, 130.2, 126.9, 125.7, 123.6, 119.9, 116.0, 113.9, 111.2, 36.8, 22.9, 22.5, 21.7; **IR** (neat): υ_{max} 3056, 2978, 1622, 1558, 1447, 1376, 1234, 1177, 1126, 737, 647 and 577 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{20}H_{21}N_2O_4S$ $[M+H]^+$ 385.1217; found: 385.1215.



1l

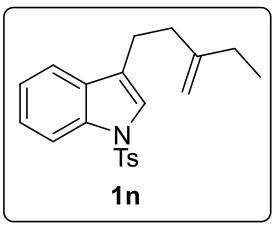
3-(3-methylbut-2-en-1-yl)-1-tosyl-1*H*-indole (1m): Compound **1m** was synthesized by reported procedure.[2] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 7.9 Hz, 1H), 7.37 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 5.43 – 5.28 (m, 1H), 3.34 (d, J = 6.7 Hz, 2H), 2.33 (s, 3H), 1.77 (d, J = 0.8 Hz, 3H), 1.72 (s, 3H); **^{13}C NMR** (101 MHz,



1m

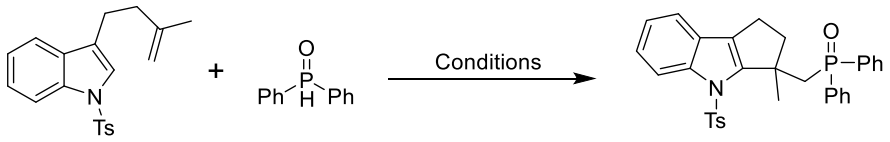
$CDCl_3$) δ 144.8, 135.6, 135.6, 133.8, 131.2, 129.9, 126.9, 124.7, 123.1, 122.9, 120.9, 119.7, 113.9, 25.9, 24.0, 21.7, 18.0; **IR** (neat): υ_{max} 3056, 2978, 1624, 1588, 1447, 1367, 1191, 1126, 737, 687 and 557 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{20}H_{22}NO_2S$ $[M+H]^+$ 340.1366; found: 340.1362.

3-(3-Methylenepentyl)-1-tosyl-1*H*-indole (1n): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (dt, J = 8.3, 0.7 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.49 – 7.45 (m, 1H), 7.32 (t, J = 1.0 Hz, 1H), 7.29 (m, 1H), 7.24 – 7.19 (m, 1H), 7.16 (m, 2H), 4.80 – 4.75 (m, 1H), 4.74 – 4.71 (m, 1H), 2.82 – 2.74 (m, 2H), 2.43 – 2.37 (m, 2H), 2.30 (s, 3H), 2.06 (q, J = 7.4 Hz, 2H), 1.04 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5, 144.7, 135.5, 135.4, 131.2, 129.8, 126.8, 124.7, 123.2, 123.1, 122.8, 119.5, 113.9, 108.5, 35.4, 28.9, 23.5, 21.6, 12.5; **IR** (neat): υ_{max} 3010, 2968, 1648, 1588, 1447, 1380, 1179, 1106, 757, 661 and 557 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{21}H_{24}NO_2S$ $[M+H]^+$ 354.2527; found: 354.2524.



1n

2.2 Synthesis of Cyclopenta[*b*]indole derivatives.



1a **2a** **3aa**

Table SI-1: Reaction Optimization:[a]

S.No	Oxidant	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1.	AgOAc	THF	60	18	35
2.	AgOAc	CH_3CN	80	18	51
3.	AgOAc	Dioxane	110	18	42
4.	AgOAc	Toluene	110	18	54
5.	AgOAc	DMF	120	18	35
6.	**AgOAc**	**DCE**	**82**	**18**	**86**
7.	CuOAc	DCE	82	18	29
8.	$Pd(OAc)_2$	DCE	82	18	25
9.	$Co(OAc)_2$	DCE	82	18	31
10.	$Mn(OAc)_2$	DCE	82	18	39
11.	$Mn(OAc)_3$. $2H_2O$	DCE	82	18	20
12.	Ag_2O	DCE	82	18	41
13.	Ag_2CO_3	DCE	82	18	31

14.	AgOTf	DCE	82	18	45
15.	$AgNO_3$	DCE	82	18	35
16.	AgOAc	DCE	RT	24	-
17.	-	DCE	82	24	-
18.	AgOAc (0.1 eq.), $Zn(NO_3)_2 \cdot 6H_2O$ (2.0)	DCE	82	24	Trace
19.	AgOAc (0.1 eq.), $Mg(NO_3)_2 \cdot 6H_2O$ (2.0)	DCE	82	24	Trace
20.	AgOAc (0.5 eq.), $Zn(NO_3)_2.6H_2O$ (2.0 eq.)	DCE	82	18	Trace
21.	AgOAc (0.2 eq.), $Zn(NO_3)_2.6H_2O$ (3.5 eq.)	DCE	82	18	Trace
22.	$Cu(OTf)_2$ (0.1 eq.), TBHP (3.0 eq.)	DCE	82	24	-

[a]Reactions conditions are as follows: **1a** (0.3 mmol), **2a** (0.36 mmol) and AgOAc (0.66 mmol) were dissolved in DCE (3.0 ml) and stirred at 82 °C for 18h. [b]Isolated yield.

With the library of indole derivatives **1** in hand, we turned our attention to their application in the proposed cascade radical cyclization to synthesize phosphorus-containing cyclopenta[*b*]indole derivatives. When the indole derivative **1a** was subjected to diphenylphosphine oxide and AgOAc at 60 °C in THF, tandem intramolecular radical cyclization proceeded smoothly, furnishing **3aa** in a moderate yield of 35% (Table SI-1, entry 1). The structure of **3aa** was confirmed through comprehensive ^{1}H and ^{13}C NMR spectroscopy, which revealed phosphorus directly attached to the CH_2 group, with clear carbon-phosphorus splitting at 39.9 ppm in the ^{13}C NMR spectrum.

Given the moderate yield obtained in the initial cyclization, we next sought to improve the reaction by optimizing the solvent. Switching to acetonitrile resulted in a notable increase in yield, providing **3aa** at 51% (Table SI-1, entry 2). We also tested other solvents, including DMF, toluene, and dioxane, observing lower yields (Table SI-1, entries 3–5). However, the most significant improvement came when using 1,2-dichloroethane as the solvent, which provided **3aa** in an outstanding 86% yield (Table SI-1, entry 6). These findings indicate that the polarity and solubility of the solvent play a critical role in optimizing the radical cyclization process. To further optimize the reaction, we examined a variety of oxidants under the optimal solvent conditions of 1,2-dichloroethane. The oxidants tested included copper acetate, palladium acetate, cobalt acetate, manganese acetate, silver oxide, silver carbonate, silver

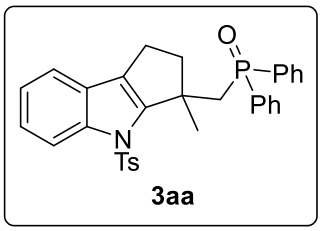
triflate and silver nitrate (Table SI-1, entries 7–15). However, none surpassed the performance of AgOAc. Notably, attempts to perform the reaction at room temperature or in the absence of an oxidant were unsuccessful, underscoring the essential role of AgOAc and temperature in initiating the radical cyclization. Further exploration involved a catalytic approach, combining metal nitrates with a catalytic amount of silver acetate to enhance the oxidation process. This approach aimed to leverage the oxidative properties of metal nitrates, but it yielded only trace amounts of the product, likely due to insufficient oxidation power or suboptimal catalytic activity under these conditions (Table SI-1, entries 18–22). Ultimately, the optimized conditions for the radical cyclization were identified as indole derivative **1a** (1.0 equiv.), diphenylphosphine oxide **2a** (1.2 equiv.), AgOAc (2.2 equiv.), and 1,2-dichloroethane as the solvent at 82 °C. These conditions consistently delivered **3aa** in high yields, demonstrating the robustness and efficiency of the process.

2.2.1 General Procedure B:

An oven-dried sealed tube was charged with indole derivative **1** (0.3 mmol) and silver acetate (0.66 mmol) in dichloroethane (3.0 ml) under a nitrogen atmosphere. Diphenyl phosphine oxide **2** (0.36 mmol) was then added, and the reaction mixture was stirred at 82 °C for 18 hours. Upon completion of the starting material, as confirmed by TLC, the mixture was cooled, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel, using a gradient of 0–50% ethyl acetate in hexane as the eluent, yielding the desired cyclopenta[*b*]indole derivatives **3**.

((3-Methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)diphenylphosphine oxide (3aa).

Following the general procedure **B**, **3aa** was obtained in 86% yield (139.0 mg) as yellow syrup. R_f = 0.3 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.79 (m, 3H), 7.63 – 7.50 (m, 4H), 7.50 – 7.42 (m, 3H), 7.24 – 7.11 (m, 5H), 7.11 – 6.98 (m, 3H), 3.42 – 3.26 (m, 1H), 3.20 (dd, *J* = 15.2, 8.4 Hz, 1H), 3.05 – 2.90 (m, 2H), 2.72 – 2.60 (m, 1H), 2.45 – 2.32 (m, 1H), 2.31 (s, 3H), 1.52 (d, *J* = 1.6 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 146.7 (d, *J* = 7.0 Hz), 144.6, 141.0, 137.0, 135.3 (d, *J* = 97.7 Hz), 132.3 (d, *J* = 98.0 Hz), 131.5 (d, *J* = 1.4 Hz), 130.7, 130.6, 130.4 (d, *J* = 1.4 Hz), 130.2, 130.0, 129.8, 129.5, 128.7, 128.6, 128.0, 127.8, 126.2, 124.1, 123.3, 119.6, 115.0, 45.2 (d, *J* = 3.7 Hz), 44.2, 39.9 (d, *J* = 70.0 Hz), 30.1 (d, *J* = 10.2 Hz), 22.4, 21.6; **^{31}P NMR** (162 MHz,

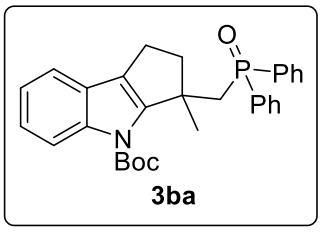


3aa

$CDCl_3$) δ 27.56; **IR** (neat): υ_{max} 2958, 2861, 1596, 1612, 1463, 1360, 1172, 1126, 1099, 748, and 557 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{32}H_{31}O_3NPS$ $[M + H]^+$: 540.17568, found: 540.17522.

***tert*-Butyl 3-((diphenylphosphoryl)methyl)-3-methyl-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (3ba):**

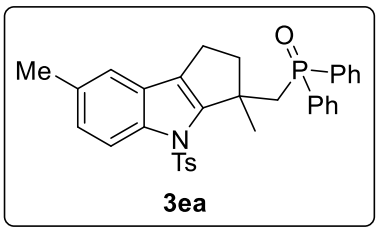
Following the general procedure **B**, **3ba** was obtained in 75% yield (109.0 mg) as colourless oil. R_f = 0.2 (40% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 2H), 7.62 – 7.55 (m, 1H), 7.52 – 7.40 (m, 3H), 7.36 – 7.28 (m, 2H), 7.26 – 7.24 (m, 1H), 7.15 – 7.07 (m, 2H), 6.98 – 6.92 (m, 1H), 6.88 – 6.79 (m, 2H), 3.48 (dd, J = 15.0, 6.7 Hz, 1H), 3.38 – 3.29 (m, 1H), 3.10 (ddd, J = 15.2, 8.9, 6.5 Hz, 1H), 2.81 (t, J = 15.0 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.47 –2.37 (m, 1H), 1.68 (s, 9H), 1.55 (d, J = 2.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.9, 146.7 (d, J = 4.5 Hz), 139.7, 135.7 (d, J = 97.6 Hz), 132.3 (d, J = 97.1 Hz), 131.4 (d, J = 1.6 Hz), 130.65, 130.57, 130.3, 130.2, 130.0 (d, J = 1.3 Hz), 128.6, 128.5, 127.4, 127.3, 127.2, 126.2, 123.3, 122.5, 119.2, 116.0, 83.5, 44.5, 44.4 (d, J = 4.3 Hz), 39.9 (d, J = 71.0 Hz), 30.5 (d, J = 13.2 Hz), 28.5, 22.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.29; **IR** (neat): υ_{max} 3055, 2977, 2901, 1723, 1448, 1366, 1163, 1108, 745, 709, and 696 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{30}H_{33}O_3NP$ $[M + H]^+$: 486.21926, found: 486.21899.



3ba

((3,7-Dimethyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)diphenyl-phosphine oxide (3ea).

Following the general procedure **B**, **3ea** was obtained in 85% yield (141.0 mg) as colorless oil. R_f = 0.2 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.83 (m, 2H), 7.72 (d, J = 8.5 Hz, 1H), 7.60 – 7.49 (m, 4H), 7.49 – 7.43 (m, 3H), 7.13 (d, J = 8.1 Hz, 2H), 7.10 – 7.05 (m, 3H), 7.03 – 6.96 (m, 2H), 3.39 – 3.23 (m, 1H), 3.20 – 2.95 (m, 2H), 2.95 – 2.80 (m, 1H), 2.61 (ddd, J = 15.2, 9.1, 2.6 Hz, 1H), 2.46 – 2.32 (m, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 1.49 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0 (d, J = 7.3 Hz), 144.5, 139.3, 137.0, 135.3 (d, J = 97.9 Hz), 133.0, 132.7 (d, J = 97.8 Hz), 131.4 (d, J = 1.7 Hz), 130.7, 130.7, 130.5 (d, J = 97.9 Hz), 130.2, 130.1, 129.8, 129.2, 128.7, 128.6, 128.0, 127.9, 126.4, 126.2, 125.4, 119.6, 114.7, 45.2 (d, J = 3.4 Hz), 44.1, 39.8 (d, J = 69.9 Hz), 29.8 (d, J = 9.4 Hz), 22.3, 21.6, 21.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ

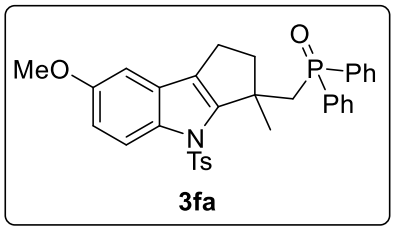


3ea

27.70; **IR** (neat): υ_{max} 3057, 2985, 2827, 1606, 1456, 1356, 1174, 1117, 810, 750, and 668 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{33}H_{33}O_3NPS$ $[M + H]^+$: 554.19133, found: 554.19122.

((7-Methoxy-3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl) diphenylphosphine oxide (3fa).

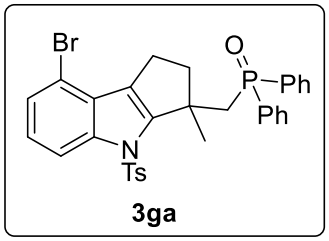
Following the general procedure **B**, **3fa** was obtained in 81% yield (138.0 mg) as colorless oil; R_f = 0.1 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.78 (m, 2H), 7.72 (d, J = 9.1 Hz, 1H), 7.62 – 7.39 (m, 7H), 7.17 – 7.11 (m, 2H), 7.10 – 7.04 (m, 3H), 6.78 (dd, J = 9.1, 2.6 Hz, 1H), 6.65 (d, J = 2.5 Hz, 1H), 3.81 (s, 3H), 3.42 – 3.24 (m, 1H), 3.17 (dd, J = 15.2, 8.4 Hz, 1H), 3.03 – 2.86 (m, 2H), 2.68 – 2.55 (m, 1H), 2.44 – 2.33 (m, 1H), 2.31 (s, 3H), 1.49 (d, J = 1.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.5, 147.5 (d, J = 6.8 Hz), 144.5, 137.0, 135.6, 135.3 (d, J = 97.6 Hz), 132.4 (d, J = 98.1 Hz), 131.4 (d, J = 1.7 Hz), 130.7, 130.6, 130.5 (d, J = 1.7 Hz), 130.2, 130.1, 129.8, 129.5, 128.7, 128.6, 128.0, 127.9, 127.1, 126.1, 115.9, 112.8, 102.1, 55.8, 45.2 (d, J = 3.6 Hz), 44.1, 40.0 (d, J = 70.0 Hz), 30.0 (d, J = 10.2 Hz), 22.4, 21.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.60; **IR** (neat): υ_{max} 3045, 2965, 2857, 1602, 1456, 1356, 1124, 1119, 840, 759, and 668 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{33}H_{33}O_4NPS$ $[M + H]^+$: 570.18624, found: 570.18560.



3fa

((8-Bromo-3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl) diphenylphosphine oxide (3ga).

Following the general procedure **B**, **3ga** was obtained in 80% yield (148.0 mg) as brown oil. R_f = 0.3 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.81 (m, 2H), 7.78 (d, J = 8.4 Hz, 1H), 7.62 – 7.49 (m, 4H), 7.49 – 7.41 (m, 3H), 7.25 (d, J = 8.9 Hz, 1H), 7.17 (d, J = 8.2 Hz, 2H), 7.09 – 6.91 (m, 4H), 3.40 – 3.17 (m, 3H), 3.01 – 2.78 (m, 2H), 2.39 – 2.25 (m, 1H), 2.33 (s, 3H), 1.53 (d, J = 1.7 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.3 (d, J = 5.5 Hz), 145.0, 141.2, 136.7, 135.2 (d, J = 98.2 Hz), 131.6 (d, J = 97.7 Hz), 131.5 (d, J = 1.7 Hz), 130.6, 130.5, 130.2 (d, J = 1.7 Hz), 130.1, 130.0, 129.9, 129.5, 128.7, 128.6, 127.9, 127.8, 126.5, 126.2, 124.9, 114.3, 113.9, 44.9 (d, J = 3.8 Hz), 43.9, 39.9 (d, J = 70.1 Hz), 30.4 (d, J = 11.1 Hz), 24.4, 21.7; **^{31}P NMR** (162 MHz,

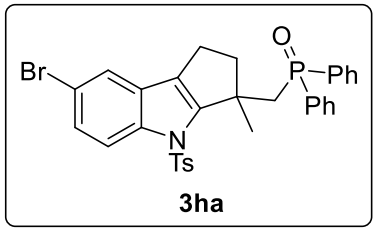


3ga

$CDCl_3$) δ 27.79; **IR** (neat): υ_{max} 3057, 2985, 2886, 1606, 1456, 1174, 1117, 750 and 668 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{32}H_{30}O_3NBrPS$ $[M + H]^+$: 617.07891, found: 617.07869.

((7-Bromo-3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl) diphenylphosphine oxide (3ha):

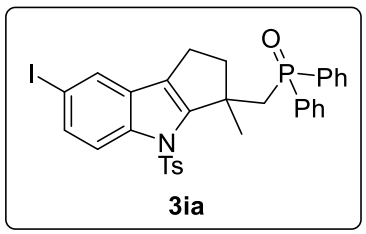
Following the general procedure **B**, **3ha** was obtained in 85% yield (159.0 mg) as brown oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.78 (m, 2H), 7.69 (d, J = 8.9 Hz, 1H), 7.61 – 7.40 (m, 7H), 7.32 (d, J = 1.9 Hz, 1H), 7.25 (dd, J = 7.1 Hz, 2.0 Hz, 1H), 7.15 (d, J = 8.2 Hz, 2H), 7.10 – 6.98 (m, 3H), 3.40 – 3.18 (m, 2H), 3.05 – 2.77 (m, 2H), 2.69 – 2.55 (m, 1H), 2.41 – 2.32 (m, 1H), 2.32 (s, 3H), 1.52 (d, J = 1.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8 (d, J = 5.8 Hz), 144.9, 139.6, 136.7, 135.1 (d, J = 98.3 Hz), 131.7 (d, J = 98.1 Hz), 131.5 (d, J = 1.5 Hz), 130.6, 130.5, 130.4 (d, J = 1.5 Hz), 130.2, 130.1, 129.9, 128.7, 128.7, 128.6, 128.0, 127.9, 127.8, 126.7, 126.1, 122.3, 116.7, 116.4, 45.1 (d, J = 4.0 Hz), 44.0, 40.0 (d, J = 70.2 Hz), 30.2 (d, J = 11.1 Hz), 22.2, 21.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.82; **IR** (neat): υ_{max} 3057, 2985, 2886, 1606, 1456, 1174, 1117, 1033, 810, 750 and 668 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{32}H_{30}O_3NBrPS$ $[M + H]^+$: 617.07891, found: 617.07854.



3ha

((7-Iodo-3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl) diphenylphosphine oxide (3ia).

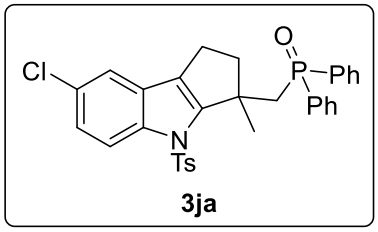
Following the general procedure **B**, **3ia** was obtained in 82% yield (164 mg) as yellow oil. R_f = 0.3 (40% EtOAc in hexane), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.80 (m, 2H), 7.58 (d, J = 8.8 Hz, 1H), 7.56 – 7.40 (m, 9H), 7.16 (d, J = 8.2 Hz, 2H), 7.10 – 6.98 (m, 3H), 3.38 – 3.19 (m, 2H), 3.04 – 2.80 (m, 2H), 2.66 – 2.53 (m, 1H), 2.41 – 2.33 (m, 1H), 2.32 (s, 3H), 1.51 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.4 (d, J = 5.3 Hz), 144.9, 140.3, 136.7, 135.1 (d, J = 98.1 Hz), 132.4, 131.7 (d, J = 97.9 Hz), 131.5, 130.6, 130.5, 130.4, 130.2, 130.1, 129.9, 128.7, 128.6, 128.5, 128.4, 128.0, 127.9, 126.1, 116.8, 87.4, 45.1 (d, J = 3.5 Hz), 44.0, 40.0 (d, J = 70.5 Hz), 30.2 (d, J = 11.0 Hz), 22.3, 21.7; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.67; **IR** (neat): υ_{max} 3057, 2985, 2886, 1606, 1456, 1254, 1147, 1147, 759 and 668 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{32}H_{30}O_3NIPS$ $[M + H]^+$: 666.07232, found: 666.07188.



3ia

((7-Chloro-3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl) diphenylphosphine oxide (3ja).

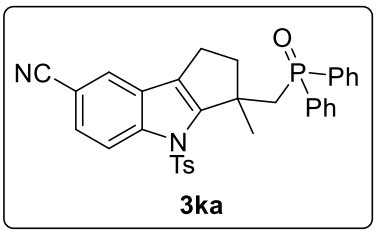
Following the general procedure **B**, **3ja** was obtained in 85% (146.0 mg) as yellow oil. R_f = 0.2 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.78 (m, 2H), 7.74 (d, J = 8.9 Hz, 1H), 7.58 – 7.41 (m, 7H), 7.20 – 7.08 (m, 4H), 7.09 – 7.00 (m, 3H), 3.40 – 3.19 (m, 2H), 3.03 – 2.93 (m, 1H), 2.88 (t, J = 14.7 Hz, 1H), 2.60 (ddd, J = 15.1, 9.1, 2.1 Hz, 1H), 2.42 – 2.33 (m, 1H), 2.32 (s, 3H), 1.52 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0 (d, J = 5.4 Hz), 144.9, 139.3, 136.7, 135.2 (d, J = 98.4 Hz), 131.8 (d, J = 97.8 Hz), 131.5, 130.6, 130.5, 130.4, 130.2, 130.1, 129.9, 129.1, 128.8, 128.7, 128.6, 128.0, 127.9, 127.3, 126.1, 124.0, 119.2, 116.0, 45.1 (d, J = 3.5 Hz), 44.0, 40.0 (d, J = 70.4 Hz), 30.2 (d, J = 10.9 Hz), 22.3, 21.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.57; **IR** (neat): υ_{max} 3057, 2985, 2886, 1606, 1456, 1174, 1117, 1033, 810, 750 and 668 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{32}H_{30}O_3NClPS$ $[M + H]^+$: 574.13671, found: 574.13651.



3ja

3-((Diphenylphosphoryl)methyl)-3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole -7-carbonitrile (3ka):

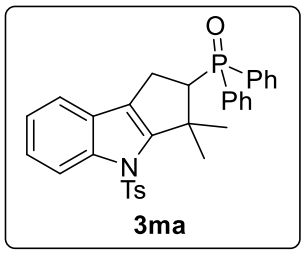
Following the general procedure **B**, **3ka** was obtained in 79% yield (134.0 mg) as yellow oil. R_f = 0.1 (40% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.8, 0.4 Hz, 1H), 7.85 – 7.77 (m, 2H), 7.58 – 7.49 (m, 5H), 7.50 – 7.43 (m, 3H), 7.41 (dd, J = 8.7, 1.7 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.08 – 6.93 (m, 3H), 3.43 – 3.29 (m, 2H), 3.13 – 3.03 (m, 1H), 2.82 (t, J = 15.1 Hz, 1H), 2.69 – 2.57 (m, 1H), 2.48 – 2.35 (m, 1H), 2.34 (s, 3H) 1.55 (d, J = 1.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.8 (d, J = 4.6 Hz), 145.4, 142.6, 136.4, 135.1 (d, J = 98.5 Hz), 131.62, 131.59 (d, J = 98.5 Hz), 130.5, 130.4, 130.4, 130.2, 130.1, 129.0, 128.8, 128.7, 128.0, 127.9, 127.0, 126.2, 126.1, 124.3, 119.5, 115.6, 106.7, 45.3 (d, J = 4.1 Hz), 44.1, 40.1 (d, J = 70.6 Hz), 30.5 (d, J = 11.6 Hz), 22.3, 21.7; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.24; **IR** (neat): υ_{max} 3059, 2882, 1594, 1438, 1357, 1226, 1176, 749, 665 and 761 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{33}H_{30}O_3N_2PS$ $[M + H]^+$: 565.17093, found: 565.17078.



3ka

(3,3-Dimethyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-2-yl)diphenylphosphine oxide (3ma):

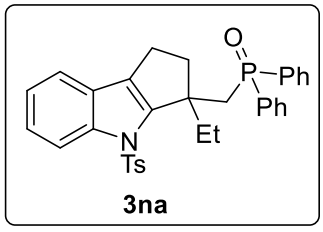
Following the general procedure **B**, **3ma** was obtained in 85% yield (137.0 mg) as white syrup. R_f = 0.2 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 1H), 8.01 – 7.89 (m, 4H), 7.60 – 7.44 (m, 8H), 7.26 – 7.10 (m, 5H), 3.56 (td, J = 9.4, 4.9 Hz, 1H), 3.23 (td, J = 14.5, 10.0 Hz, 1H), 2.69 (ddd, J = 15.1, 8.7, 1.6 Hz, 1H), 2.31 (s, 3H), 1.72 (s, 3H), 1.48 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.6 (d, J = 12.1 Hz), 144.6, 141.2, 136.5, 134.1 (d, J = 84.5 Hz), 133.2 (d, J = 83.2 Hz), 131.9 (d, J = 1.7 Hz), 131.7 (d, J = 1.3 Hz), 131.5, 131.4, 130.9, 130.8, 129.8, 128.9, 128.8, 128.7, 126.4, 126.1, 125.0 (d, J = 12.2 Hz), 124.3, 123.7, 119.3, 115.4, 53.5 (d, J = 71.2 Hz), 47.8, 29.6, 24.5 (d, J = 4.7 Hz), 24.3, 21.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.64; **IR** (neat): 3059, 2882, 1594, 1438, 1357, 1311, 1266, 1156, 739, 669 and 761 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{32}H_{31}O_3NPS$ $[M + H]^+$: 540.17568, found: 540.17470.



3ma

((3-Ethyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)diphenylphosphine oxide (3na):

Following the general procedure **B**, **3na** was obtained in 81% yield (134.0 mg) as white syrup. R_f = 0.3 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.83 (m, 3H), 7.57 – 7.50 (m, 4H), 7.49 – 7.45 (m, 3H), 7.23 – 7.10 (m, 5H), 7.06 – 6.95 (m, 3H), 3.38 – 3.19 (m, 2H), 3.03 (t, J = 14.9 Hz, 1H), 2.97 – 2.88 (m, 1H), 2.66 – 2.56 (m, 1H), 2.55 – 2.46 (m, 1H), 2.32 (s, 3H), 2.02 – 1.78 (m, 2H), 0.47 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.9 (d, J = 6.3 Hz), 144.6, 141.4, 137.3, 135.6 (d, J = 97.7 Hz), 132.4 (d, J = 97.6 Hz), 131.4 (d, J = 1.4 Hz), 130.6, 130.6, 130.5, 130.3 (d, J = 1.6 Hz), 130.2, 130.1, 129.8, 128.7, 128.6, 127.85, 127.77, 126.2, 126.1, 124.0, 123.3, 119.5, 115.1, 49.6 (d, J = 4.1 Hz), 39.4, 39.5 (d, J = 70.5 Hz), 33.7 (d, J = 10.7 Hz), 22.8, 21.7, 9.1;**^{31}P NMR** (203 MHz, $CDCl_3$) δ 28.03; **IR** (neat): υ_{max} 3057, 2985, 2827, 1606, 1456, 1356, 1174, 1117, 810, 750, and 668 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{33}H_{33}O_3NPS$ $[M + H]^+$: 554.19133, found: 554.19115.

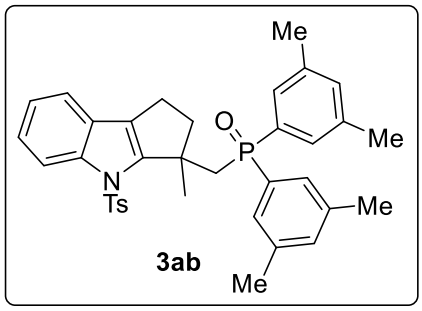


3na

***bis*(3,5-Dimethylphenyl)((3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)phosphine oxide (3ab):**

Following the general procedure **B**, **3ab** was obtainedin 86% yield (154.0 mg) as white syrup; R_f = 0.1 (60% EtOAc in hexane); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87 (d, J = 7.7 Hz, 1H), 7.48 (dd, J = 12.7, 10.2 Hz, 4H), 7.25 – 7.06 (m, 8H), 6.62 (s, 1H), 3.41 – 3.26 (m, 1H), 3.20 (dd, J

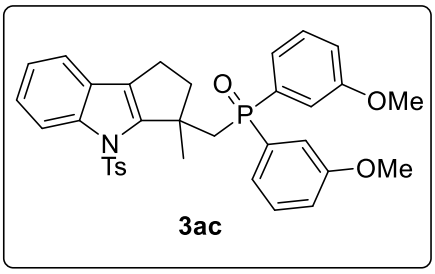
= 15.2, 7.9 Hz, 1H), 3.11 – 2.94 (m, 1H), 2.92 – 2.78 (m, 1H), 2.64 (ddd, *J* = 15.2, 9.1, 2.1 Hz, 1H), 2.34 (s, 6H), 2.31 (s, 3H), 2.31 – 2.25 (m, 1H), 2.08 (s, 6H), 1.50 (d, *J* = 1.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.5 (d, *J* = 6.0 Hz), 144.5, 141.2, 138.3, 138.1, 137.7, 137.6, 137.2, 135.3 (d, *J* = 97.3 Hz), 133.1 (d, *J* = 1.8 Hz), 132.3 (d, *J* = 1.8 Hz), 132.0 (d, *J* = 96.7 Hz), 129.8, 128.2, 128.1, 127.8, 127.8, 126.3, 126.1, 124.0, 123.3, 119.5, 114.8, 45.1 (d, *J* = 3.7 Hz), 44.2, 39.9 (d, *J* = 69.8 Hz), 30.5 (d, *J* = 10.7 Hz), 22.4, 21.6, 21.5, 21.3; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 27.80; **IR** (neat): υ_{max} 2958, 1598, 1447, 1360, 1226, 1172, 854, 748, 669 and 575 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{36}H_{39}O_3NPS$ $[M + H]^+$: 596.23828, found: 596.23748.



3ab

***bis*(3-Methoxyphenyl)((3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)phosphine oxide (3ac):**

Following the general procedure **B**, **3ac** was obtained in 80% (144.0 mg) as colorless oil; R_f = 0.1 (60% EtOAc in hexane); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.92 – 7.81 (m, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.31 (m, 3H), 7.26 – 6.95 (m, 9H), 6.58 (dd, *J* = 7.7, 1.9 Hz, 1H), 3.83 (s, 3H), 3.65 (s, 3H), 3.39 – 3.25 (m, 1H), 3.18 (dd, *J* = 15.2, 8.5 Hz, 1H), 3.08 – 2.86 (m, 2H), 2.65 (ddd, *J* = 15.1, 9.0, 2.4 Hz, 1H), 2.45 – 2.32 (m, 1H), 2.31 (s, 3H), 1.52 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7 (d, *J* = 14.0 Hz), 159.0 (d, *J* = 14.0 Hz), 146.8 (d, *J* = 6.8 Hz), 144.6, 141.1, 137.0, 136.6 (d, *J* = 97.3 Hz), 133.7 (d, *J* = 97.3 Hz), 129.9, 129.8, 129.5, 129.3 (d, *J* = 13.8 Hz), 126.22, 126.18, 124.1, 123.3, 122.8 (d, *J* = 8.8 Hz), 122.5 (d, *J* = 9.6 Hz), 119.5, 118.0, 116.7, 115.2 (d, *J* = 9.8 Hz), 115.0, 114.9, 55.6, 55.2, 45.2 (d, *J* = 3.9 Hz), 44.2, 39.9 (d, *J* = 70.3 Hz), 30.1 (d, *J* = 10.4 Hz), 22.4, 21.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.03; **IR** (neat): υ_{max} 2980, 2829, 1725, 1588, 1478, 1361, 1242, 1175, 1115, and 750 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{34}H_{35}O_5NPS$ $[M + H]^+$: 600.19681, found: 600.19610.

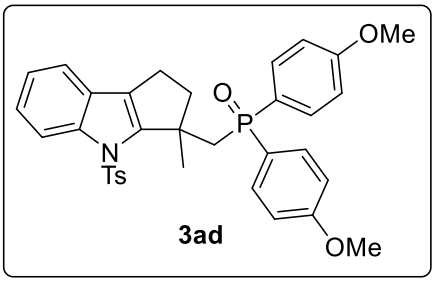


3ac

bis(4-Methoxyphenyl)((3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)phosphine oxide (3ad):

Following the general procedure **B**, **3ad** was obtained in 81% yield (145.0 mg) as white syrup; R_f = 0.1 (60% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 1H), 7.79 –

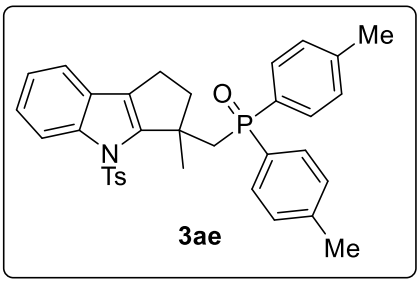
7.68 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.42 (dd, *J* = 11.1, 8.8 Hz, 2H), 7.24 – 7.17 (m, 1H), 7.18 – 7.11 (m, 4H), 6.95 (dd, *J* = 8.9, 2.2 Hz, 2H), 6.52 (dd, *J* = 8.8, 2.2 Hz, 2H), 3.82 (s, 3H), 3.60 (s, 3H), 3.39 – 3.28 (m, 1H), 3.19 (dd, *J* = 15.3, 7.6 Hz, 1H), 3.05 – 2.88 (m, 1H), 2.87 – 2.75 (m, 1H), 2.63 (ddd, *J* = 15.2, 9.2, 2.5 Hz, 1H), 2.40 – 2.32 (m, 1H), 2.31 (s, 3H), 1.51 (d, *J* = 1.8 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.1, 161.4, 146.6 (d, *J* = 5.7 Hz), 144.6, 141.2, 137.1, 132.4, 132.3, 131.9, 131.8, 129.8, 129.5, 127.0 (d, *J* = 104.3 Hz), 126.3, 126.2, 124.0, 123.4 (d, *J* = 104.6 Hz), 123.2, 119.6, 114.9, 114.2, 114.1, 113.5, 113.4, 55.4, 55.0, 45.1 (d, *J* = 3.7 Hz), 44.1, 40.2 (d, *J* = 71.0 Hz), 30.5 (d, *J* = 11.0 Hz), 22.4, 21.7; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 28.06; **IR** (neat): υ_{max} 2888, 2831, 1725, 1588, 1417, 1364, 1278, 1169, 1040, 983, 790 and 575 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{34}H_{35}O_5NPS$ $[M + H]^+$: 600.19681, found: 600.19650.



3ad

((3-Methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)di-*p*-tolylphosphine oxide (3ae):

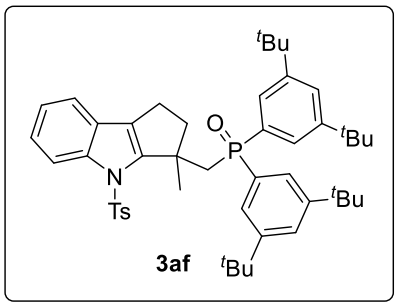
Following the general procedure **B**, **3ae** was obtained in 82% yield (139.0 mg) as colourless oil; R_f = 0.2 (60% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 1H), 7.72 (dd, *J* = 10.8, 8.1 Hz, 2H), 7.57 – 7.49 (m, *J* = 8.4 Hz, 2H), 7.45 – 7.36 (m, 2H), 7.26 – 7.21 (m, 2H), 7.21 – 7.18 (m, 1H), 7.17 – 7.11 (m, 4H), 6.83 (dd, *J* = 8.0, 2.0 Hz, 2H), 3.42 – 3.26 (m, 1H), 3.20 (dd, *J* = 15.2, 7.8 Hz, 1H), 3.04 – 2.91 (m, 1H), 2.84 (t, *J* = 14.7 Hz, 1H), 2.62 (ddd, *J* = 15.2, 9.2, 2.4 Hz, 1H), 2.41 – 2.33 (m, 4H), 2.31 (s, 3H), 2.06 (s, 3H), 1.51 (d, *J* = 1.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.5 (d, *J* = 5.6 Hz), 144.6, 141.7 (d, *J* = 0.8 Hz), 141.1, 141.0 (d, *J* = 0.8 Hz), 137.1, 135.2 (d, *J* = 101.4 Hz), 132.3 (d, *J* = 100.6 Hz), 130.6, 130.5, 130.1, 130.0, 129.8, 129.5, 129.4, 129.3, 129.2, 128.8, 128.6, 126.2, 124.1, 123.2, 119.6, 114.9, 45.1 (d, *J* = 3.5 Hz), 44.1, 39.9 (d, *J* = 70.0 Hz), 30.4 (d, *J* = 11.0 Hz), 29.8, 22.4, 21.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.13; **IR** (neat): υ_{max} 2980, 2829, 1725, 1588, 1478, 1361, 1242, 1175, 1115, and 750 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{34}H_{35}O_3NPS$ $[M + H]^+$: 568.20698, found: 568.20691.



3ae

bis(3,5-di-*tert*-Butylphenyl)((3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)phosphine oxide (3af):

Following the general procedure **B**, **3af** was obtained in 75% yield (171.0 mg) as white oil; R_f = 0.5 (50% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 1H), 7.83 (dd, *J* = 12.0, 1.3 Hz, 2H), 7.58 – 7.46 (m, 5H), 7.43 – 7.39 (m, 1H), 7.35 – 7.30 (m, 1H), 7.23 – 7.16 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 3.51 (dd, *J* = 15.2, 8.6 Hz, 1H), 3.43 – 3.31 (m, 1H), 2.88 – 2.75 (m, 1H), 2.73 – 2.60 (m, 2H), 2.43 – 2.34 (m, 1H), 2.29 (s, 3H), 1.38 (s, 3H), 1.37 (s, 18H), 1.24 (s, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0, 150.94, 150.86, 150.7, 149.5 (d, *J* = 12.9 Hz), 144.5, 141.2, 137.0, 134.3 (d, *J* = 95.3 Hz), 133.3 (d, *J* = 95.9 Hz), 129.8, 128.3, 126.5, 126.2, 125.7, 125.55, 125.50, 125.46, 124.5, 124.4, 124.2, 123.5, 119.7, 115.1, 45.9 (d, *J* = 2.7 Hz), 44.2, 39.3 (d, *J* = 67.3 Hz), 35.3, 35.1, 31.6, 31.4, 27.9 (d, *J* = 4.0 Hz), 22.2, 21.6; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.60; **IR** (neat): υ_{max} 3057, 2985, 2827, 1606, 1456, 1356, 1174, 1117, 810, 750, and 668 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{48}H_{63}O_3NPS$ $[M + H]^+$: 764.42663, found: 764.42615.



2.3. Synthesis of N-fused indole and pyrrole derivatives:

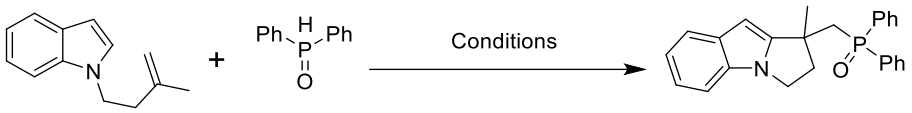


Table SI-2: Reaction Optimization:[a]

Sl. no.	Catalytic system (eq.)	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1.	AgOAc (2.2)	DCE	82	18h	90
2.	**AgOAc (0.2), $Zn(NO_3)_2.6H_2O$ (2.0 eq.)**	**DCE**	**82**	**18h**	**88**
3.	AgOAc (0.2), $Mg(NO_3)_2.6H_2O$ (2.0 eq.)	DCE	82	18	69
4.	AgOAc (0.2), TBHP (2.0 eq.)	DCE	82	18	Trace
5.	AgOAc (0.2), $Zn(NO_3)_2.6H_2O$ (2.0 eq.)	CH_3CN	82	18	57
6.	AgOAc (0.2), $Zn(NO_3)_2.6H_2O$ (2.0 eq.)	Dioxane	110	18	30
7.	AgOAc (0.2), $Zn(NO_3)_2.6H_2O$ (2.0 eq.)	DMF	130	18	37

8.	AgOAc (0.1), $Zn(NO_3)_2.6H_2O$ (2.0 eq.)	DCE	82	18	62
9.	AgOAc (0.2), $Zn(NO_3)_2.6H_2O$ (1.5 eq.)	DCE	82	18	67
10.	AgOAc (0.2), $Zn(NO_3)_2.6H_2O$ (2.0 eq.)	DCE	RT	24	-
11.	$Zn(NO_3)_2.6H_2O$ (2.0 eq.)	DCE	82	24	-
12.	AgOAc (0.5), $Zn(NO_3)_2.6H_2O$ (2.0 eq.)	DCE	82	18	75

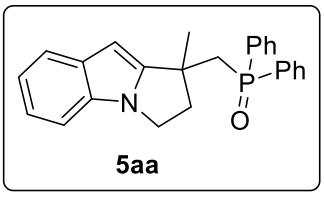
[a]Reactions conditions are as follows: **4a** (0.4 mmol), **2a** (0.48 mmol), AgOAc (0.08 mmol) and $Zn(NO_3)_2.6H_2O$ (0.8 mmol) were dissolved in DCE (3.0 ml) and stirred at 82 °C for 18h. [b]Isolated yield.

2.3.1 General procedure C:

An oven-dried sealed tube was charged with indole derivative **4** (0.4 mmol) [prepared from known procedure[3]], silver acetate (0.08 mmol) and $Zn(NO_3)_2.6H_2O$ (0.8 mmol) in dichloroethane (3.0 ml.) under a nitrogen atmosphere. Diphenyl phosphine oxide **2** (0.48 mmol) was then added, and the reaction mixture was stirred at 82 °C for 18 hours. Upon completion of the starting material, as confirmed by TLC, the mixture was cooled, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel, using a gradient of 0–50% ethyl acetate in hexane as the eluent, yielding the desired Pyrrolo[1,2-*a*]indole derivatives **5**.

((1-Methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphineoxide (5aa).

Following the general procedure **C** on a 0.4 mmol scale, compound **5aa** was obtained with 88% yield (137.0 mg) as yellow liquid. R_f = 0.2 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.74 (m, 2H), 7.69 – 7.59 (m, 2H), 7.53 – 7.42 (m, 4H), 7.38 – 7.27 (m, 3H), 7.19 – 6.98 (m, 3H), 6.02 (s, 1H), 4.18 – 4.06 (m, 1H), 4.06 – 3.96 (m, 1H), 3.08 – 2.97 (m, 1H), 2.88 (dd, J = 15.2, 10.6 Hz, 1H), 2.75 (dd, J = 15.2, 10.0 Hz, 1H), 2.53 – 2.43 (m, 1H), 1.49 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.1 (d, J = 12.7 Hz), 134.9 (d, J = 64.6 Hz), 133.6 (d, J = 64.9 Hz), 132.8, 132.2, 131.7 (d, J = 2.1 Hz), 131.5 (d, J = 2.1 Hz), 130.7, 130.6, 130.5, 130.4, 128.9, 128.7, 128.5, 128.4, 120.7, 120.7, 119.3, 109.6, 90.8, 42.8, 41.9 (d, J = 2.2 Hz), 40.8 (d, J = 3.6 Hz), 40.7 (d, J = 68.6 Hz), 28.0 (d, J = 4.6 Hz); **^{31}P NMR** (162

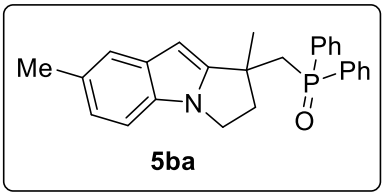


5aa

MHz, $CDCl_3$) δ 27.34; **IR** (neat): υ_{max} 3020, 2861, 1449, 1213, 1099, 745, and 661 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{25}H_{25}ONP$ $[M + H]^+$: 386.16683, found: 386.16632.

((1,7-Dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5ba):

Following the general procedure **C** on a 0.4 mmol scale, compound **5ba** was obtained with 86% yield (137.0 mg) as colourless oil. R_f= 0.1 (40 % EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.75 (m, 2H), 7.72 – 7.60 (m, 2H), 7.57 – 7.42 (m, 3H), 7.42 – 7.29 (m, 3H),

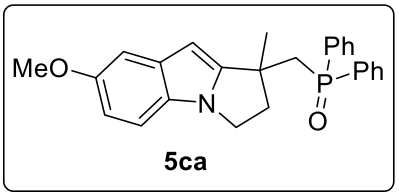


5ba

7.25 – 7.22 (m, 1H), 7.04 (d, J = 8.2 Hz, 1H), 6.92 (dd, J = 8.2, 1.2 Hz, 1H), 5.94 (d, J = 0.6 Hz, 1H), 4.10 – 3.90 (m, 2H), 3.04 – 2.94 (m, 1H), 2.88 (dd, J = 15.3, 10.4 Hz, 1H), 2.74 (dd, J = 15.2, 10.1 Hz, 1H), 2.52 – 2.42 (m, 1H), 2.41 (s, 3H), 1.47 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3 (d, J = 13.0 Hz), 134.7 (d, J = 68.6 Hz), 133.7 (d, J = 68.8 Hz), 133.0, 131.7 (d, J = 1.7 Hz), 131.5 (d, J = 1.7 Hz), 130.7, 130.6, 130.5, 130.4, 128.8, 128.7, 128.6, 128.5, 122.2, 120.4, 109.2, 90.2, 42.8, 41.9 (d, J = 1.6 Hz), 40.8 (d, J = 3.5 Hz), 40.6 (d, J = 68.4 Hz), 27.8 (d, J = 4.0 Hz), 21.6; **^{31}P NMR** (162 MHz, CDCl3) δ 27.64; **IR** (neat): υ_{max} 3039, 2861, 14786, 1364, 1251, 1039, 756, and 658 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{26}H_{27}ONP$ $[M + H]^+$: 400.18248, found: 400.18212.

((7-Methoxy-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenyl phosphine oxide (5ca).

Following the general procedure **C** on a 0.4 mmol scale, compound **5ca** was obtained in 84% yield (139.0 mg) as colourless oil. R_f =0.2 (50% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 2H), 7.67 – 7.59 (m, 2H), 7.54 – 7.40 (m, 3H), 7.38 – 7.32 (m, 1H),

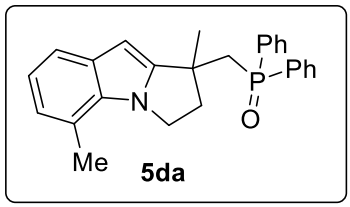


5ca

7.32 – 7.26 (m, 2H), 7.03 (d, J = 8.7, 1H), 6.93 (d, J = 2.3 Hz, 1H), 6.76 (dd, J = 8.7, 2.4 Hz, 1H), 5.94 (s, 1H), 4.12 – 4.02 (m, 1H), 4.02 – 3.93 (m, 1H), 3.82 (s, 3H), 3.07 – 2.93 (m, 1H), 2.86 (dd, J = 15.2, 10.8 Hz, 1H), 2.74 (dd, J = 15.2, 9.9 Hz, 1H), 2.50 – 2.38 (m, 1H), 1.48 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.0, 152.7 (d, J = 12.2 Hz), 135.1, 134.1, 133.1, 131.7 (d, J = 2.0 Hz), 131.4 (d, J = 1.9 Hz), 130.6, 130.5, 130.5, 130.4, 128.8, 128.7, 128.5, 128.4, 127.6, 110.7, 110.2, 103.1, 90.6, 56.2, 43.0, 41.8 (d, J = 2.0 Hz), 40.9 (d, J = 3.7 Hz), 40.8 (d, J = 68.5 Hz), 28.0 (d, J = 4.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.58; **IR** (neat): υ_{max} 3029, 2771, 1463, 1364, 1251, 1099, 973, 765 and 661 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{26}H_{27}O_2NP$ $[M + H]^+$: 416.17739, found: 416.17700.

((1,5-Dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5da):

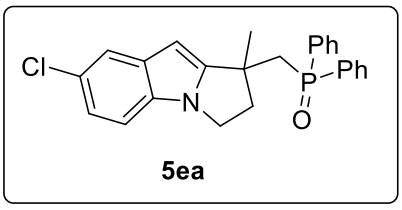
Following the general procedure **C** on a 0.4 mmol scale, compound **5da** was obtained in 85% yield (135.0 mg) as yellow syrup. R_f=0.2 (40 % EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.74 (m, 2H), 7.69 – 7.56 (m, 2H), 7.55 – 7.41 (m, 3H), 7.36 – 7.23 (m, 4H), 6.91 – 6.85 (m, 1H), 6.80 (d, J = 7.1 Hz, 1H), 6.00 (s, 1H), 4.48 – 4.37 (m, 1H), 4.36 – 4.25 (m, 1H), 3.10 – 2.94 (m, 1H), 2.86 (dd, J = 15.2, 11.0 Hz, 1H), 2.74 (dd, J = 15.2, 9.9 Hz, 1H), 2.57 (s, 3H), 2.50 – 2.39 (m, 1H), 1.48 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.4 (d, J = 12.0 Hz), 134.7 (d, J = 98.5 Hz), 133.6 (d, J = 98.2 Hz), 132.9, 131.8, 131.7, 131.4, 130.6, 130.6, 130.5, 130.4, 128.8, 128.7, 128.4, 128.3, 122.2, 120.7, 119.5, 118.6, 91.1, 45.8, 41.9, 41.0 (d, J = 68.6 Hz), 40.0 (d, J = 2.9 Hz), 28.2 (d, J = 4.5 Hz), 18.0; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.66; **IR** (neat): υ_{max} 3039, 2861, 14786, 1364, 1251, 1039, 756, and 658 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{26}H_{27}ONP$ $[M + H]^+$: 400.18248, found: 400.18208.



5da

((7-Chloro-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenyl phosphine oxide (5ea):

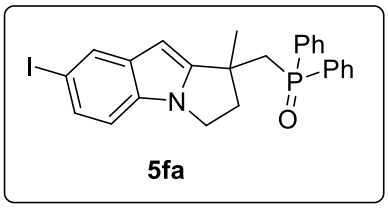
Following the general procedure **C** on a 0.4 mmol scale, compound **5ea** was obtained in 88% yield (147.0 mg) as yellow oil. R_f=0.2 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H), 7.65 – 7.54 (m, 2H), 7.53 – 7.41 (m, 3H), 7.35 (t, J = 1.2 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.28 – 7.21 (m, 2H), 7.02 (d, J = 1.2 Hz, 2H), 5.92 (s, 1H), 4.20 – 4.07 (m, 1H), 4.04 – 3.95 (m, 1H), 3.13 – 3.01 (m, 1H), 2.85 (dd, J = 15.2, 11.2 Hz, 1H), 2.73 (dd, J = 15.2, 9.6 Hz, 1H), 2.53 – 2.41 (m, 1H), 1.50 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.9 (d, J = 10.9 Hz), 134.5 (d, J = 98.5 Hz), 133.7, 133.1 (d, J = 98.5 Hz), 131.8 (d, J = 2.0 Hz), 131.5 (d, J = 2.1 Hz), 130.6, 130.5, 130.4, 130.4, 128.8, 128.7, 128.4, 128.3, 124.9, 120.8, 120.0, 110.5, 91.0, 43.1, 41.8 (d, J = 2.3 Hz), 40.9 (d, J = 68.9 Hz), 40.8 (d, J = 3.8 Hz), 28.4 (d, J = 6.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.55; **IR** (neat): υ_{max} 3020, 2861, 1463, 1213, 1151, 973, 745 and 669 cm^{-1}; **HRMS** (ESI-TOF calculated for $C_{25}H_{24}ONClP$ $[M + H]^+$: 420.12786, found: 420.12748.



5ea

((7-Iodo-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5fa):

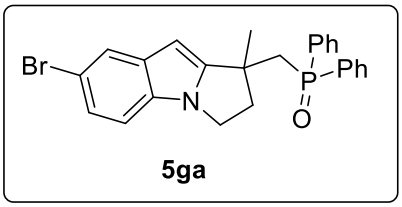
Following the general procedure **C** on a 0.4 mmol scale, compound **5fa** was obtained in 86% yield (176.0 mg) as yellow oil. R_f = 0.3 (40 % EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 2H), 7.72 (d, J = 1.5 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.53 – 7.40 (m, 3H), 7.35 – 7.28 (m, 2H), 7.26 – 7.21 (m, 2H), 6.90 (d, J = 8.5 Hz, 1H), 5.89 (d, J = 0.4 Hz, 1H), 4.20 – 4.07 (m, 1H), 4.04 – 3.92 (m, 1H), 3.15 – 2.95 (m, 1H), 2.84 (dd, J = 15.2, 11.2 Hz, 1H), 2.72 (dd, J = 15.2, 9.7 Hz, 1H), 2.53 – 2.40 (m, 1H), 1.49 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.4 (d, J = 10.5 Hz), 135.2, 134.5 (d, J = 98.6 Hz), 133.1 (d, J = 98.2 Hz), 131.8 (d, J = 1.8 Hz), 131.5 (d, J = 1.7 Hz), 131.2, 130.6, 130.5, 130.4, 130.4, 129.4, 128.9, 128.9, 128.7, 128.4, 128.3, 111.6, 90.6, 82.7, 43.0, 41.8 (d, J = 1.4 Hz), 40.9 (d, J = 69.0 Hz), 40.7 (d, J = 3.7 Hz), 28.4 (d, J = 5.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.25; **IR** (neat): υ_{max} 3029, 2771, 1463, 1364, 1251, 1099, 973, 765 and 661 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{25}H_{24}ONIP$ $[M + H]^+$: 512.06347, found: 512.06296.



5fa

((7-Bromo-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5ga):

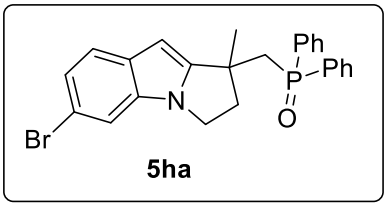
Following the general procedure **C** on a 0.4 mmol scale, compound **5ga** was obtained in 83% yield (154.0 mg) as brown oil. R_f = 0.3 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H), 7.63 – 7.53 (m, 2H), 7.51 (d, J = 1.7 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.35 – 7.28 (m, 1H), 7.26 – 7.22 (m, 2H), 7.15 (dd, J = 8.6, 1.9 Hz, 1H), 6.98 (d, J = 8.6 Hz, 1H), 5.91 (d, J = 0.7 Hz, 1H), 4.20 – 4.07 (m, 1H), 4.05 – 3.94 (m, 1H), 3.14 – 3.01 (m, 1H), 2.84 (dd, J = 15.2, 11.2 Hz, 1H), 2.73 (dd, J = 15.2, 9.6 Hz, 1H), 2.56 – 2.42 (m, 1H), 1.50 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.7 (d, J = 10.7 Hz), 134.4 (d, J = 98.4 Hz), 134.2, 133.1 (d, J = 98.5 Hz), 131.7 (d, J = 1.7 Hz), 131.4 (d, J = 1.7 Hz), 130.7, 130.5, 130.4, 130.3, 130.3, 128.7, 128.6, 128.3, 128.2, 123.3, 123.0, 112.4, 110.9, 90.8, 43.0, 41.8 (d, J = 1.8 Hz), 40.8 (d, J = 68.8 Hz), 40.7 (d, J = 3.6 Hz), 28.34 (d, J = 6.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.27; **IR** (neat): υ_{max} 3020, 2861, 1463, 1213, 1151, 973, 745 and 669 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{25}H_{24}ONBrP$ $[M + H]^+$: 464.07734, found: 464.07704.



5ga

((6-Bromo-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5ha):

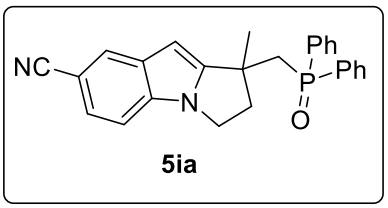
Following the general procedure **C** on a 0.4 mmol scale, compound **5ha** was obtained in 80% yield (148.5 mg) as brown oil; R_f = 0.3 (40% EtOAc in hexane); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87 – 7.70 (m, 2H), 7.68 – 7.54 (m, 2H), 7.53 – 7.40 (m, 3H), 7.36 – 7.20 (m, 5H), 7.09 (dd, J = 8.4, 1.7 Hz, 1H), 5.96 (d, J = 0.7 Hz, 1H), 4.21 – 4.03 (m, 1H), 4.04 – 3.89 (m, 1H), 3.14 – 2.95 (m, 1H), 2.93 – 2.60 (m, 2H), 2.55 – 2.38 (m, 1H), 1.50 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3 (d, J = 10.9 Hz), 134.5 (d, J = 98.4 Hz), 133.3 (d, J = 98.2 Hz), 132.9, 131.8, 131.6, 131.5, 130.6, 130.5, 130.4, 128.8, 128.7, 128.5, 128.4, 122.4, 121.9, 113.9, 112.6, 91.5, 42.9, 41.9 (d, J = 1.8 Hz), 40.9 (d, J = 68.9 Hz), 40.7 (d, J = 3.4 Hz), 28.3 (d, J = 5.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.40; **IR** (neat): υ_{max} 3020, 2869, 1463, 1213, 1155, 947, 745 and 669 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{25}H_{24}ONBrP$ $[M + H]^+$: 464.07734, found: 464.07675.



5ha

1-((Diphenylphosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-7-carbonitrile (5ia):

Following the general procedure **C** on a 0.4 mmol scale, compound **5ia** was obtained in 78% yield (128.0 mg) as colourless syrup. R_f = 0.1 (40 % EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.70 (m, 2H), 7.68 (d, J = 0.9 Hz, 1H), 7.61 – 7.39 (m, 5H), 7.34 – 7.10 (m, 5H), 6.01 (d, J = 0.6 Hz, 1H), 4.35 – 4.20 (m, 1H), 4.10 – 3.93 (m, 1H), 3.18 – 3.09 (m, 1H), 2.85 (dd, J = 15.2, 11.7 Hz, 1H), 2.74 (dd, J = 15.2, 9.3 Hz, 1H), 2.58 – 2.43 (m, 1H), 1.53 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.3 (d, J = 9.3 Hz), 134.2 (d, J = 99.4 Hz), 133.6, 132.6 (d, J = 98.7 Hz), 132.3, 131.7 (d, J = 2.5 Hz), 131.3 (d, J = 2.4 Hz), 130.4, 130.3, 130.2, 128.8, 128.7, 128.2, 128.1, 126.0, 123.6, 121.2, 110.3, 101.9, 92.6, 43.1, 41.8 (d, J = 2.8 Hz), 40.9 (d, J = 69.8 Hz), 40.5 (d, J = 4.1 Hz), 28.8 (d, J = 7.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.35; **IR** (neat): υ_{max} 2981, 2885, 2217, 1612, 1473, 1389, 1184, 1115, 804, and 750 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{26}H_{24}O_2NP$ $[M + H]^+$: 411.16208, found: 411.16160.

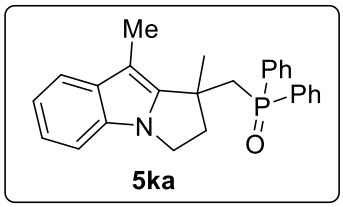


5ia

((1,9-Dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5ka):

Following the general procedure **C** on a 0.4 mmol scale, compound **5ka** was obtained in 86% yield (137.0 mg) as colorless oil. R_f = 0.2 (40% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 2H), 7.58 – 7.42 (m, 5H), 7.36 – 7.30 (m, 1H), 7.26 – 7.22 (m, 1H), 7.21 –

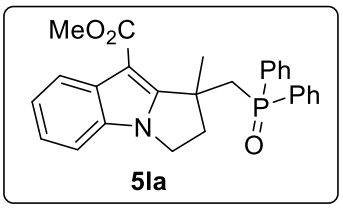
7.14 (m, 2H), 7.12 – 7.05 (m, 2H), 7.03 – 6.96 (m, 1H), 4.18 – 4.10 (m, 1H), 4.02 – 3.92 (m, 1H), 3.16 – 3.04 (m, 1H), 2.91 (dd, J = 15.2, 11.4 Hz, 1H), 2.78 (dd, J = 15.2, 9.4 Hz, 1H), 2.53 – 2.40 (m, 1H), 2.18 (s, 3H), 1.57 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.8 (d, J = 10.4 Hz), 134.8 (d, J = 97.9 Hz), 133.2 (d, J = 98.1 Hz), 133.2, 131.7 (d, J = 2.6 Hz), 131.7, 131.3 (d, J = 1.8 Hz), 130.6, 130.5, 130.3, 130.2, 128.8, 128.7, 128.2, 128.1, 120.6, 118.5, 109.4, 100.1, 42.4, 42.2 (d, J = 1.1 Hz), 40.8 (d, J = 3.6 Hz), 40.0 (d, J = 68.6 Hz), 27.9 (d, J = 6.4 Hz), 8.3; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.52; **IR** (neat): υ_{max} 3029, 2771, 1463, 1364, 1251, 1099, 973, 765 and 661 cm^{-1} ; **HRMS** (ESI-TOF): calculated for $C_{26}H_{27}ONP$ $[M + H]^+$: 400.18248, found: 400.18202.



5ka

Methyl 1-((diphenylphosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5la):

Following the general procedure **C** on a 0.4 mmol scale, compound **5la** was obtained in 89% yield (157.7 mg) as white crystalline solid. R_f = 0.1 (50% EtOAc in hexane); **M.P.** 240 – 245 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.93 – 7.72 (m, 3H), 7.57 – 7.41 (m, 3H), 7.37 – 7.27 (m, 2H), 7.20 – 7.08 (m, 3H), 7.07 – 6.99 (m, 1H), 6.96 – 6.86 (m, 2H), 4.55 – 4.38 (m, 1H), 4.18 – 4.02 (m, 1H), 3.87 (s, 3H), 3.52 – 3.37 (m, 2H), 3.09 (dd, J = 15.0, 13.2 Hz, 1H), 2.65 – 2.50 (m, 1H), 1.65 (d, J = 1.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 156.1 (d, J = 6.6 Hz), 134.9 (d, J = 98.3 Hz), 132.0 (d, J = 98.2 Hz), 131.7 (d, J = 1.9 Hz), 131.6, 130.9 (d, J = 1.9 Hz), 130.8, 130.6, 130.5, 130.0, 129.9, 128.8, 128.7, 127.6, 127.5, 122.0, 122.0, 121.7, 110.2, 99.4, 50.7, 44.0, 42.6 (d, J = 4.3 Hz), 41.2, 38.4 (d, J = 70.1 Hz), 28.6 (d, J = 11.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.52; **IR** (neat): υ_{max} 3039, 2861, 1656, 1533, 1486, 1364, 1251, 1039, 756, and 658 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{27}H_{27}O_3NP$ $[M + H]^+$: 444.17231, found: 444.17198.

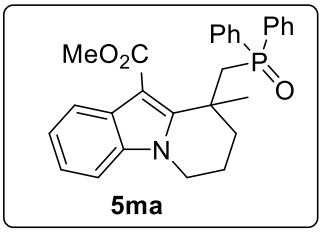


5la

Methyl 9-((diphenylphosphoryl)methyl)-9-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-10-carboxylate (5ma):

Following the general procedure **C** on a 0.4 mmol scale, compound **5ma** was obtained in 89% yield (162.6 mg) as yellow oil. R_f = 0.2 (40% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.84 (d, J = 7.8 Hz, 1H), 7.55 – 7.43 (m, 3H), 7.35 – 7.27 (m, 2H), 7.25 – 7.13 (m, 3H), 7.10 – 7.01 (m, 1H), 6.99 – 6.87 (m, 2H), 4.20 – 4.08 (m, 1H), 4.09 – 3.95 (m, 2H), 3.82 (s, 3H), 3.18 – 3.02 (m, 2H), 2.23 – 2.10 (m, 1H), 2.02 – 1.87 (m, 2H), 1.62 (d, J =

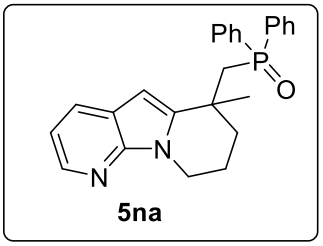
1.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 149.4 (d, J = 7.5 Hz), 135.2, 134.9 (d, J = 98.2 Hz), 133.1 (d, J = 98.7 Hz), 131.6 (d, J = 1.9 Hz), 130.8, 130.7, 130.3, 130.2, 128.7, 128.6, 127.6, 127.5, 126.9, 122.2, 122.0, 109.4, 103.7, 50.8, 43.4, 38.4 (d, J = 68.9 Hz), 36.8 (d, J = 4.3 Hz), 35.9, 28.1 (d, J = 10.8 Hz), 19.9; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.40; ; **IR** (neat): 3030, 2856, 1665, 1563, 1436, 1364, 1251, 1039, 756, 709 and 658 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{28}H_{29}O_3NP$ $[M + H]^+$: 458.18796, found: 458.18755.



5ma

((6-Methyl-6,7,8,9-tetrahydropyrido[3,2-*b*]indolizin-6-yl)methyl)diphenylphosphine oxide (5na):

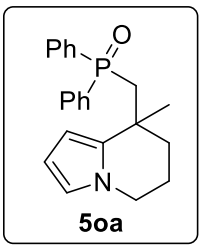
Following the general procedure **C** on a 0.4 mmol scale, compound **5na** was obtained in 82% yield (131.0 mg) as white oil; R_f = 0.2 (50% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 4.8, 1.5 Hz, 1H), 7.78 – 7.59 (m, 5H), 7.46 – 7.28 (m, 6H), 6.95 (dd, J = 7.8, 4.8 Hz, 1H), 6.22 (s, 1H), 4.23 – 4.12 (m, 1H), 4.10 – 3.99 (m, 1H), 2.95 – 2.72 (m, 2H), 2.37 – 2.25 (m, 1H), 2.15 – 1.95 (m, 2H), 1.95 – 1.82 (m, 1H), 1.63 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.3, 145.3 (d, J = 11.2 Hz), 141.8, 134.8 (d, J = 40.6 Hz), 133.8 (d, J = 41.1 Hz), 131.5 (d, J = 1.9 Hz), 131.3 (d, J = 2.0 Hz), 130.6, 130.5, 130.4, 130.4, 128.6, 128.5, 128.5, 128.4, 127.8, 120.7, 116.0, 96.0, 42.1 (d, J = 68.6 Hz), 41.0, 35.7 (d, J = 3.2 Hz), 34.3 (d, J = 4.6 Hz), 30.3 (d, J = 3.4 Hz), 19.5; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 27.47; **IR** (neat): 3011, 2865, 1665, 1563, 1463, 1361, 1225, 1039, 756, 709 and 658 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{25}H_{26}ON_2P$ $[M + H]^+$: 401.17773, found: 401.17731.



5na

((8-Methyl-5,6,7,8-tetrahydroindolizin-8-yl)methyl)diphenylphosphine oxide (5oa):

Following the general procedure **C** on a 0.4 mmol scale, compound **5oa** was obtained in 88% yield (123.0 mg) as a yellow oil. R_f = 0.3 (40% EtOAc in hexane); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 2H), 7.73 – 7.61 (m, 2H), 7.56 – 7.34 (m, 6H), 6.38 (dd, J = 2.6, 1.8 Hz, 1H), 6.04 (dd, J = 3.5, 2.8 Hz, 1H), 5.90 (dd, J = 3.6, 1.7 Hz, 1H), 3.80 (t, J = 6.0 Hz, 2H), 2.78 (dd, J = 10.2, 3.6 Hz, 2H), 2.36 – 2.19 (m, 1H), 1.97 – 1.76 (m, 3H), 1.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4 (d, J = 14.4 Hz), 135.5, 134.5, 131.5 (d, J = 2.1 Hz), 131.3 (d, J = 2.1 Hz), 130.65, 130.59, 130.56, 130.5, 128.7, 128.6, 128.5, 118.5, 107.6, 103.1, 45.3, 42.5 (d, J = 66.4 Hz), 35.5 (d, J = 2.9 Hz), 33.9 (d, J = 2.5 Hz), 30.4 (d, J = 2.6 Hz), 20.2; **^{31}P NMR** (202

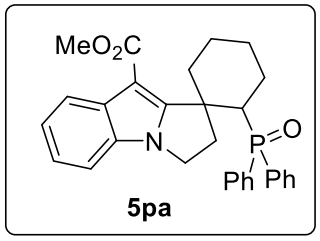


5oa

MHz, $CDCl_3$) δ 27.12; **IR** (neat): υ_{max} 3055, 2929, 2882, 1697, 1485, 1438, 1328, 1271, 1184, 1113, 741, and 704 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{22}H_{25}ONP$ $[M + H]^+$: 350.16683, found: 350.16649.

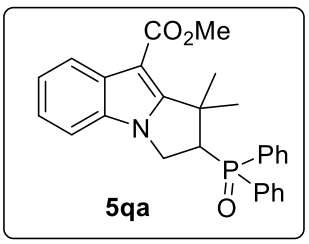
Methyl 2-(diphenylphosphoryl)-2',3'-dihydrospiro[cyclohexane-1,1'-pyrrolo[1,2-*a*]indole]-9'-carboxylate (5pa):

Following the general procedure **C** on a 0.4 mmol scale, compound **5pa** was obtained in 87% yield (168.0 mg) as colorless oil. R_f = 0.2 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.95 – 7.80 (m, 2H), 7.65 – 7.55 (m, 1H), 7.5 – 7.4 (m, 3H), 7.37 – 7.21 (m, 2H), 7.16 – 6.97 (m, 3H), 6.69 – 6.51 (m, 3H), 4.50 – 4.40 (m, 1H), 4.18 – 3.96 (m, 2H), 3.95 (s, 3H), 3.73 – 3.62 (m, 1H), 2.73 – 2.61 (m, 1H), 2.53 – 2.38 (m, 1H), 1.90 – 1.68 (m, 4H), 1.65 – 1.41 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 166.3, 156.4, 133.7 (d, *J* = 95.6 Hz), 131.4, 131.4 (d, *J* = 1.7 Hz),131.3 (d, *J* = 95.3 Hz), 130.8, 130.6, 130.5, 130.1 (d, *J* = 2.2 Hz), 129.4, 129.3, 128.9, 128.8, 126.8, 126.7, 121.8, 121.8, 121.5, 110.1, 100.0, 50.9, 46.8 (d, *J* = 3.9 Hz), 43.8, 40.3 (d, *J* = 70.6 Hz), 37.7 (d, *J* = 10.0 Hz), 34.6, 25.8 (d, *J* = 13.2 Hz), 23.7, 22.5; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 33.44; **IR** (neat): υ_{max} 2949, 1681, 1528, 1436, 1205, 1114, and 747 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{30}H_{31}O_3NP$ $[M + H]^+$: 484.20361, found: 484.20336.



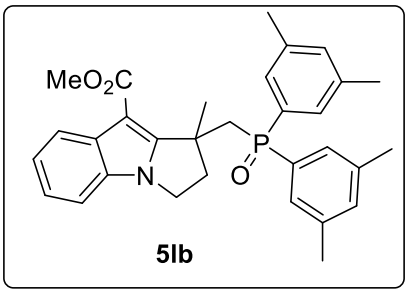
Methyl 2-(diphenylphosphoryl)-1,1-dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5qa):

Following the general procedure **C** on a 0.4 mmol scale, compound **5qa** was obtained in 89% yield (157.5 mg) as colorless oil. R_f = 0.3 (50% EtOAc in hexane); **^{1}H NMR** (300 MHz, $CDCl_3$) *δ* 8.17 – 8.07 (m, 1H), 8.07 – 7.91 (m, 4H), 7.68 – 7.42 (m, 6H), 7.24 – 7.03 (m, 3H), 4.47 (q, *J* = 10.8 Hz, 1H), 4.17 – 3.98 (m, 1H), 3.87 (s, 3H), 3.75 – 3.58 (m, 1H), 1.69 (s, 3H), 1.51 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) *δ* 165.3, 158.4 (d, *J* = 8.6 Hz), 133.5 (d, *J* = 97.7 Hz), 132.4 (d, *J* = 1.5 Hz), 132.2 (d, *J* = 1.5 Hz), 131.9 (d, *J* = 97.9 Hz), 131.7, 131.5, 131.4, 131.1, 130.7, 130.6, 129.3, 129.2, 129.0, 128.9, 122.2, 122.2, 122.0, 109.9, 98.4, 51.6 (d, *J* = 73.2 Hz), 50.8, 45.3, 44.2 (d, *J* = 1.6 Hz), 27.5, 23.0 (d, *J* = 4.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) *δ* 24.24; **IR** (neat): υ_{max} 3059, 2959, 2887, 1647, 1543, 1485, 1438, 1328, 1271, 1184, 1113, 741, and 704 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{27}H_{27}O_3NP$ $[M + H]^+$: 443.16503, found: 443.16484.



Methyl 1-((bis(3,5-dimethylphenyl)phosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5lb):

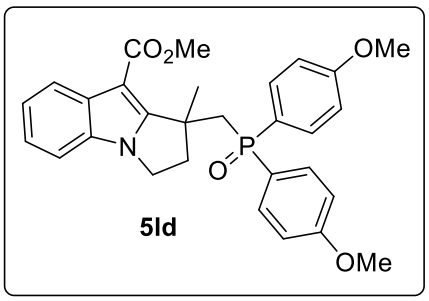
Following the general procedure **C** on a 0.4 mmol scale, compound **5lb** was obtained in 86% yield (171.0 mg) as colorless oil. R_f = 0.2 (60% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.70 (m, 1H), 7.40 (d, J = 11.3 Hz, 2H), 7.20 – 7.05 (m, 4H), 6.88 (d, J = 12.0 Hz, 2H), 6.54 (s, 1H), 4.62 – 4.48 (m, 1H), 4.18 – 4.00 (m, 1H), 3.88 (s, 3H), 3.59 – 3.43 (m, 2H), 2.83 (t, J = 14.7 Hz, 1H), 2.60 – 2.46 (m, 1H), 2.33 (s, 6H), 1.91 (s, 6H), 1.69 (d, J = 2.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 155.8 (d, J = 4.5 Hz), 138.4, 138.3, 137.4, 137.3, 134.9 (d, J = 97.9 Hz), 133.3 (d, J = 2.0 Hz), 132.4 (d, J = 2.3 Hz), 131.7, 131.1 (d, J = 97.3 Hz), 130.8, 128.0, 127.9, 127.6, 127.5, 121.9, 121.7, 121.6, 110.1, 99.4, 50.6, 44.1, 42.4 (d, J = 4.5 Hz), 41.1, 38.6 (d, J = 69.9 Hz), 29.4 (d, J = 12.9 Hz), 21.4, 21.0; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.45; **IR** (neat): υ_{max} 2984, 2888, 1823, 1687, 1529, 1434, 1201, 1123, 751, and 706 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{31}H_{35}O_3NP$ $[M + H]^+$: 500.23491, found: 500.23458.



5lb

Methyl 1-((bis(4-methoxyphenyl)phosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5ld):

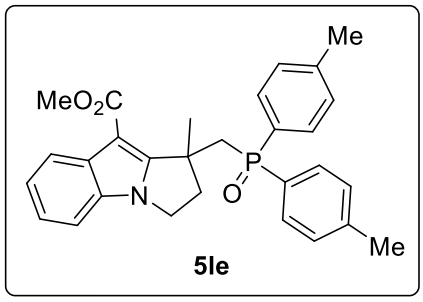
Following the general procedure **C** on a 0.4 mmol scale, compound **5ld** was obtained in 78% yield (156.0 mg) as colorless oil. R_f = 0.1 (60% EtOAc in hexane); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.84 – 7.64 (m, 3H), 7.23 – 7.06 (m, 5H), 7.01 – 6.91 (m, 2H), 6.38 – 6.24 (m, 2H), 4.60 – 4.38 (m, 1H), 4.09 (td, J = 9.7, 3.9 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.54 (s, 3H), 3.53 – 3.38 (m, 2H), 2.89 (t, J = 14.5 Hz, 1H), 2.65 – 2.45 (m, 1H), 1.66 (d, J = 2.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8,162.3 (d, J = 2.0 Hz), 161.6 (d, J = 2.0 Hz), 156.2 (d, J = 5.0 Hz), 132.3, 132.2, 131.8, 131.7, 131.0, 126.4 (d, J = 104.7 Hz), 122.8 (d, J = 105.4 Hz), 121.9, 121.7, 121.6, 114.3, 114.2, 113.1, 112.9, 110.2, 99.3, 55.4, 55.0, 50.7, 44.0, 42.5 (d, J = 4.4 Hz), 41.0, 38.8 (d, J = 71.2 Hz), 29.2 (d, J = 12.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.61; **IR** (neat): υ_{max} 2980, 2829, 1725, 1588, 1478, 1361, 1242, 1175, 1115, and 750 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{29}H_{31}O_5NP$ $[M + H]^+$: 504.19344, found: 504.19331.



5ld

Methyl 1-((di-*p*-tolylphosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5le):

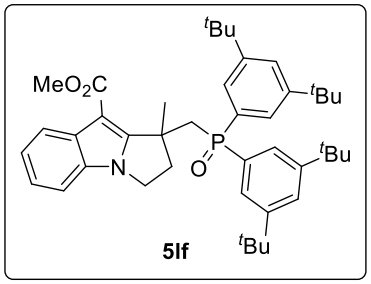
Following the general procedure **C** on a 0.4 mmol scale, compound **5le** was obtained in 83% yield (156.0 mg) as colourless oil. R_f = 0.1 (50 % EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 1H), 7.69 (dd, J = 11.0, 8.1 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.20 – 7.08 (m, 5H), 6.65 (dd, J = 8.0, 2.3 Hz, 2H), 4.56 – 4.38 (m, 1H), 4.08 (td, J = 9.6, 3.9 Hz, 1H), 3.88 (s, 3H), 3.54 – 3.35 (m, 2H), 3.06 – 2.85 (m, 1H), 2.64 – 2.48 (m, 1H), 2.37 (s, 3H), 2.05 (s, 3H), 1.65 (d, J = 2.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.7, 156.2 (d, J = 5.8 Hz), 142.1, 141.5, 131.7 (d, J = 101.0 Hz), 131.6, 131.0, 130.5, 130.5, 130.0, 129.9, 129.5, 129.4, 128.4 (d, J = 100.7 Hz), 128.4, 128.3, 122.0, 121.72, 121.67, 110.1, 99.3, 50.7, 44.0, 42.5 (d, J = 4.3 Hz), 41.1, 38.5 (d, J = 70.4 Hz), 29.0 (d, J = 12.1 Hz), 21.7, 21.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.82; **IR** (neat): υ_{max} 3055, 2980, 2825, 1725, 1548, 1478, 1366, 1222, 1154, 1115, and 750 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{29}H_{31}O_3NP$ $[M + H]^+$: 472.20361, found: 472.20281.



5le

Methyl 1-((bis(3,5-di-*tert*-butylphenyl)phosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5lf):

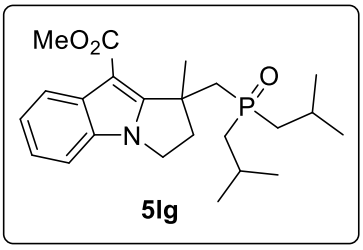
Following the general procedure **C** on a 0.4 mmol scale, compound **5lf** was obtained in 85% yield (227.0 mg) as colourless oil. R_f = 0.5 (50 % EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 1H), 7.79 (dd, J = 12.0, 1.8 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.41 (dd, J = 12.2, 1.8 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.17 – 7.08 (m, 3H), 4.39 – 4.29 (m, 1H), 4.12 – 4.03 (m, 1H), 3.89 (s, 3H), 3.59 – 3.49 (m, 1H), 3.40 (dd, J = 15.3, 11.7 Hz, 1H), 3.19 (dd, J = 15.3, 9.3 Hz, 1H), 2.67 – 2.55 (m, 1H), 1.54 (s, 3H), 1.36 (s, 18H), 1.16 (s, 18H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.7, 157.9 (d, J = 9.3 Hz), 151.1, 151.0, 150.5, 150.4, 133.7 (d, J = 97.9 Hz), 132.2 (d, J = 97.5 Hz), 131.7, 130.6, 125.9, 125.7, 125.2, 125.1, 124.4, 124.3, 122.0, 121.6, 110.2, 98.8, 50.7, 43.9, 42.9 (d, J = 3.5 Hz), 41.3, 38.6 (d, J = 68.5 Hz), 35.3, 34.9, 31.5, 31.3, 27.4 (d, J = 8.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.83; **IR** (neat): υ_{max} 3055, 2984, 2888, 1823, 1687, 1529, 1434, 1201, 1123, 751, and 706 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{43}H_{59}O_3NP$ $[M + H]^+$: 668.42326, found: 668.42291.



5lf

Methyl 1-((diisobutylphosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5lg):

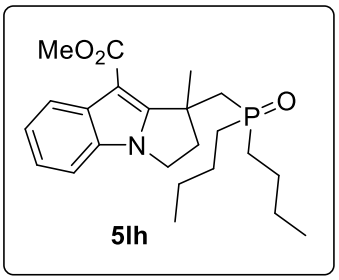
Following the general procedure **C**, compound **5lg** was obtained in 84% yield (135.5 mg) as a colorless oil. R_f = 0.3 (40% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 1H), 7.34 – 7.25 (m, 1H), 7.25 – 7.19 (m, 2H), 4.45 – 4.35 (m, 1H), 4.2 – 4.05 (m, 1H), 3.92 (s, 3H), 3.38 – 3.25 (m, 1H), 2.64 – 2.57 (m, 1H), 2.57 – 2.54 (m, 2H), 2.24 – 2.05 (m, 1H), 1.82 – 1.73 (m, 1H), 1.72 (d, J = 0.9 Hz, 3H), 1.71 – 1.62 (m, 2H), 1.32 – 1.15 (m, 1H), 1.10 (d, J = 4.1 Hz, 3H), 1.09 (d, J = 4.0 Hz, 3H), 1.08 – 0.98 (m, 1H), 0.79 (d, J = 6.6 Hz, 3H), 0.68 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.0, 157.6 (d, J = 7.5 Hz), 132.0, 130.8, 122.4, 122.1, 122.0, 110.4, 99.0, 50.9, 44.0, 42.7 (d, J = 4.4 Hz), 41.1, 40.5 (d, J = 63.9 Hz), 38.6, 38.1, 27.9 (d, J = 9.2 Hz), 25.1 (d, J = 8.8 Hz), 24.9 (d, J = 8.3 Hz), 24.9 (d, J = 6.7 Hz), 24.3 (d, J = 7.5 Hz), 23.9 (d, J = 3.6 Hz), 23.5 (d, J = 3.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 46.34; **IR** (neat): υ_{max} 2962, 2884, 2822, 1692, 1533, 1425, 1281, 1199, 1122, 841, and 749 cm^{-1}; **HRMS** (ESI-TOF calculated for $C_{23}H_{35}O_3NP$ $[M + H]^+$: 404.23491, found: 404.23450.



5lg

Methyl 1-((dibutylphosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5lh):

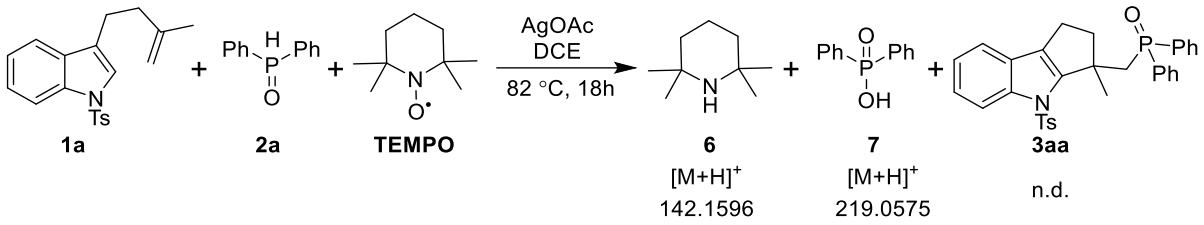
Following the general procedure **C**, compound **5lh** was obtained in 81% yield (130.0 mg) as a colorless oil. R_f = 0.3 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 1H), 7.31 – 7.25 (m, 1H), 7.25 – 7.19 (m, 2H), 4.49 – 4.38 (m, 1H), 4.22 – 4.08 (m, 1H), 3.93 (s, 3H), 3.43 – 3.28 (m, 1H), 2.71 (dd, J = 15.1, 6.6 Hz, 1H), 2.63 – 2.52 (m, 1H), 2.44 (dd, J = 15.1, 12.4 Hz, 1H), 1.72 (d, J = 1.4 Hz, 3H), 1.62 – 1.48 (m, 3H), 1.50 – 1.34 (m, 3H), 1.33 – 1.16 (m, 2H), 1.18 – 1.09 (m, 1H), 1.07 – 0.98 (m, 3H), 0.94 (t, J = 7.3 Hz, 3H), 0.66 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 157.3, 132.0, 130.9, 122.5, 122.2, 122.1, 110.5, 99.1, 50.9, 44.1, 42.5, 41.1, 29.8, 28.4, 28.3, 24.4, 24.3, 24.2, 24.1, 23.8, 13.8, 13.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 48.30; **IR** (neat): υ_{max} 2962, 2822, 1672, 1533, 1454, 1218, 1165, 1122, 841, and 749 cm^{-1}; **HRMS** (ESI-TOF): calculated for $C_{23}H_{35}O_3NP$ $[M + H]^+$: 404.23491, found: 404.23446.



5lh

2.4. Control experiments:

2.4.1 Control experiment I



Scheme SI-2: Control experiment using TEMPO

An oven-dried sealed tube equipped with a magnetic stir bar was charged with compound **1a** (34.0 mg, 0.1 mmol, 1.0 equiv.), silver acetate (37.0 mg, 0.22 mmol, 2.2 equiv.), diphenyl phosphine oxide (24.0 mg, 0.12 mmol, 1.2 equiv.) and TEMPO (47.0 mg, 0.3 mmol, 3.0 equiv.). The reagents were dissolved in 2 mL of DCE, and the reaction mixture was stirred at 82 °C for 18 hours. No product (**3aa**) was detected, and compound **1a** was recovered in 89%. The crude mixture was analyzed by High Resolution Mass Spectrometry (HRMS).

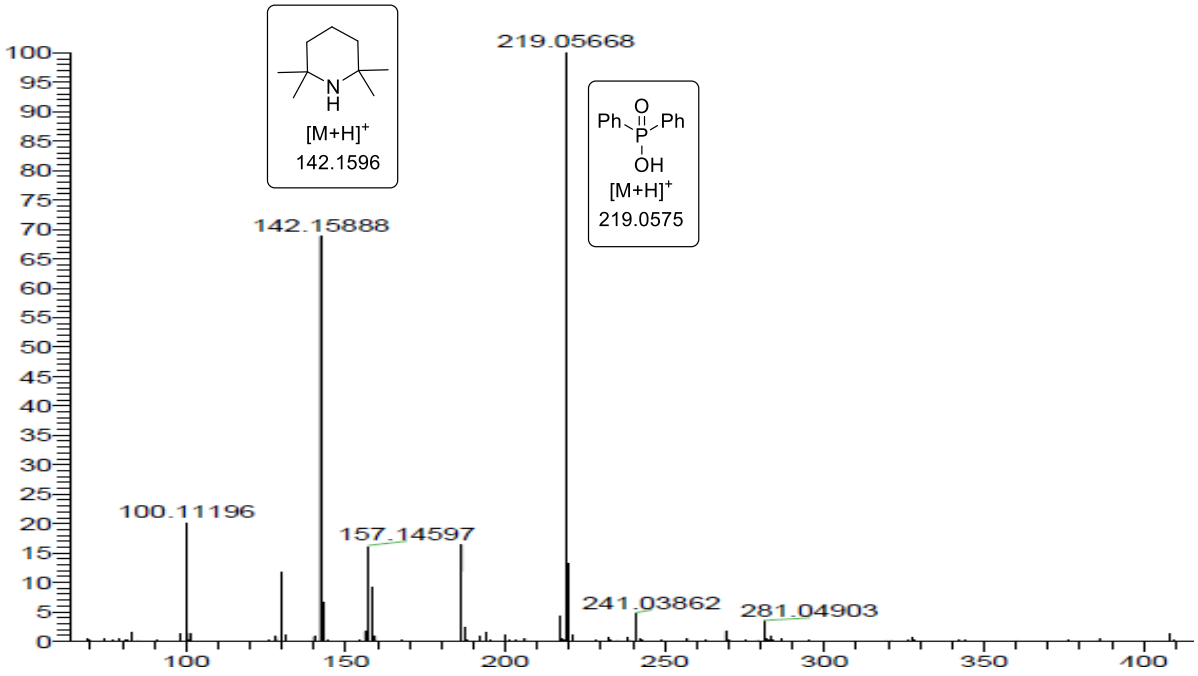
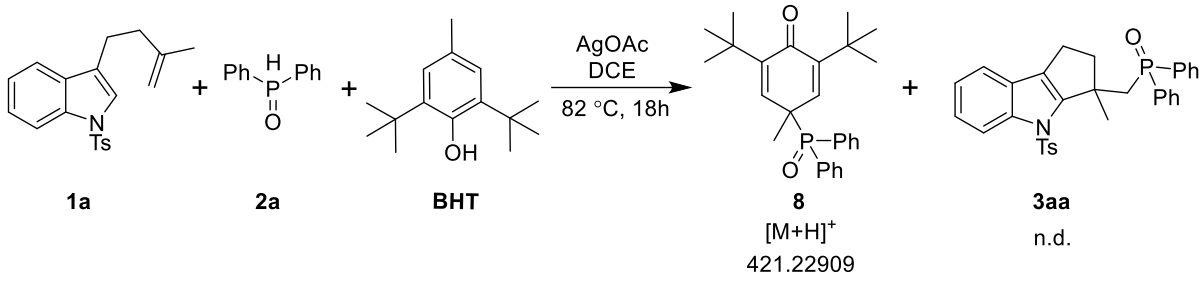


Fig SI-1: Mass spectrum analysis for control experiment I.

2.4.2 Control experiment II



Scheme SI-3: Control experiment using BHT.

An oven-dried sealed tube equipped with a magnetic stir bar was charged with compound **1** (34.0 mg, 0.1 mmol, 1.0 equiv.), silver acetate (37.0 mg, 0.22 mmol, 2.2 equiv.), diphenyl phosphine oxide (24.0 mg, 0.12 mmol, 1.2 equiv.) and BHT (66.0 mg, 0.3 mmol, 3.0 equiv.). The reagents were dissolved in 2 mL of DCE, and the reaction mixture was stirred at 82 °C for 18 hours. No product (**3aa**) was detected, and compound **1a** was recovered in 85%. The crude mixture was analyzed by High Resolution Mass Spectrometry.

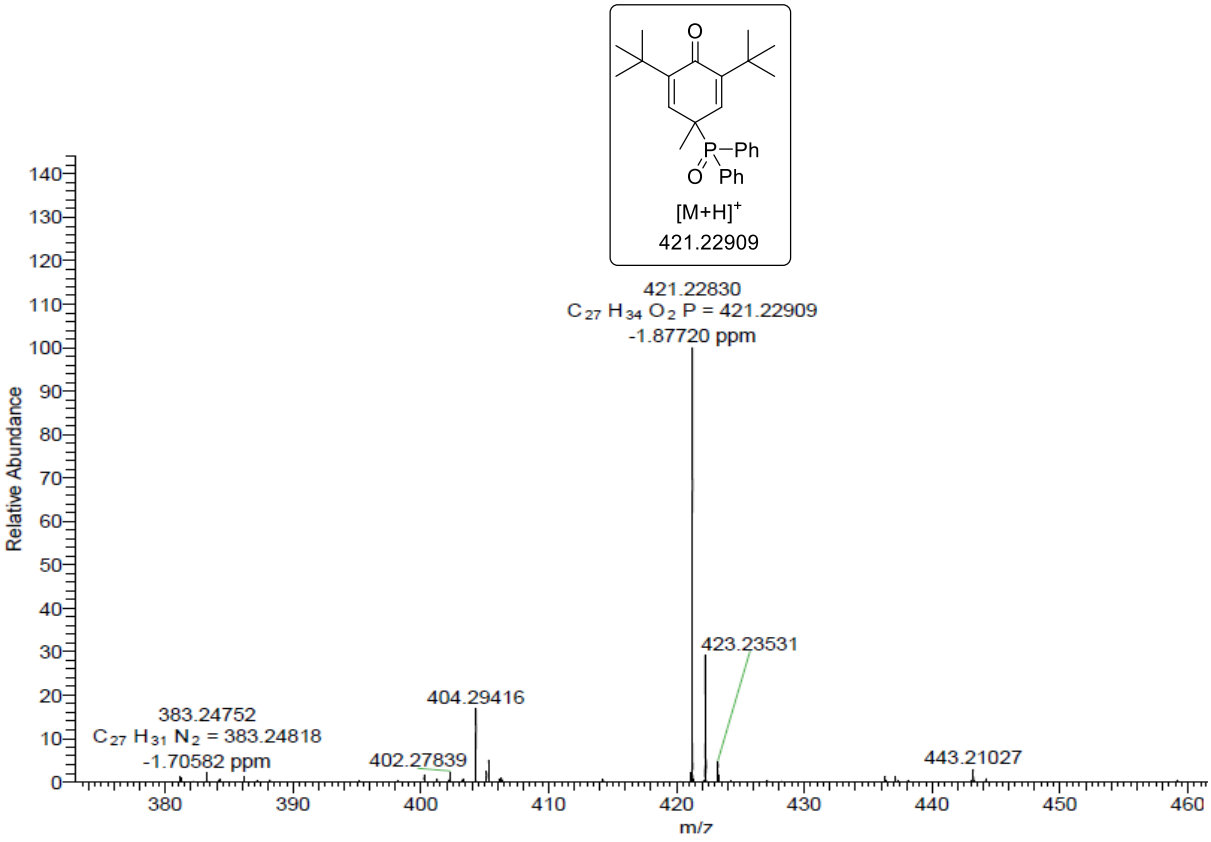
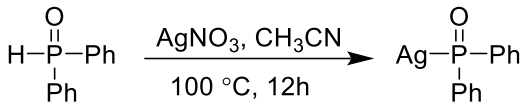


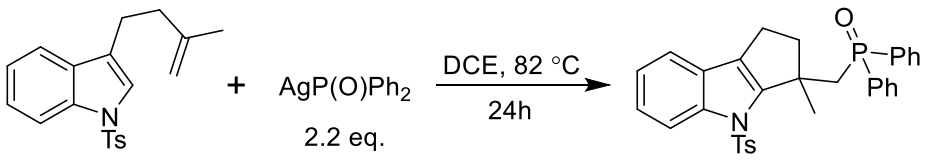
Fig SI-2: Mass spectrum analysis for control experiment II**.**

2.4.3 Synthesis of $AgP(O)Ph_2$:



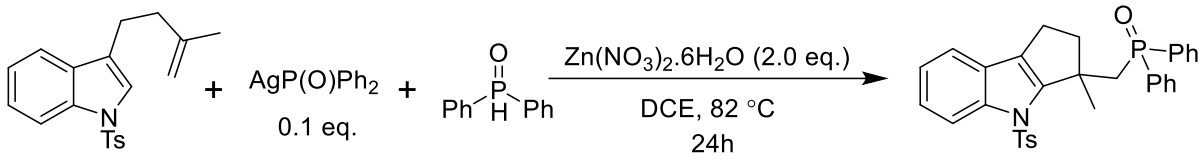
In a Schlenk tube, diphenylphosphine oxide (202 mg, 1.0 mmol) and silver nitrate ($AgNO_3$, 203 mg, 1.2 mmol) were combined. The tube was subjected to three vacuum/N_2 cycles to ensure an inert atmosphere. Acetonitrile (CH_3CN, 4 mL) was then added to the mixture and stirred at 100 °C for overnight. After completion, the mixture was filtered, and the solid residue (filter cake) was washed with acetonitrile. The resulting product was dried under vacuum, yielding $AgP(O)Ph_2$ as a white solid.

2.4.4 Reaction using $AgP(O)Ph_2$:



1a **3aa** (not detected)

In an oven-dried sealed tube, compound **1a** (0.1 mmol, 34.0 mg, 1.0 equiv.) and $AgP(O)Ph_2$ (0.22 mmol, 68.0 mg, 2.2 equiv.) were combined and dissolved in dichloroethane (2.0 ml). The reaction vessel was purged with nitrogen (N_2) three times to ensure an inert atmosphere. The mixture was then stirred at 82 °C for 24 hours. Analysis by thin-layer chromatography (TLC) revealed that the desired product **3aa** was not detected.

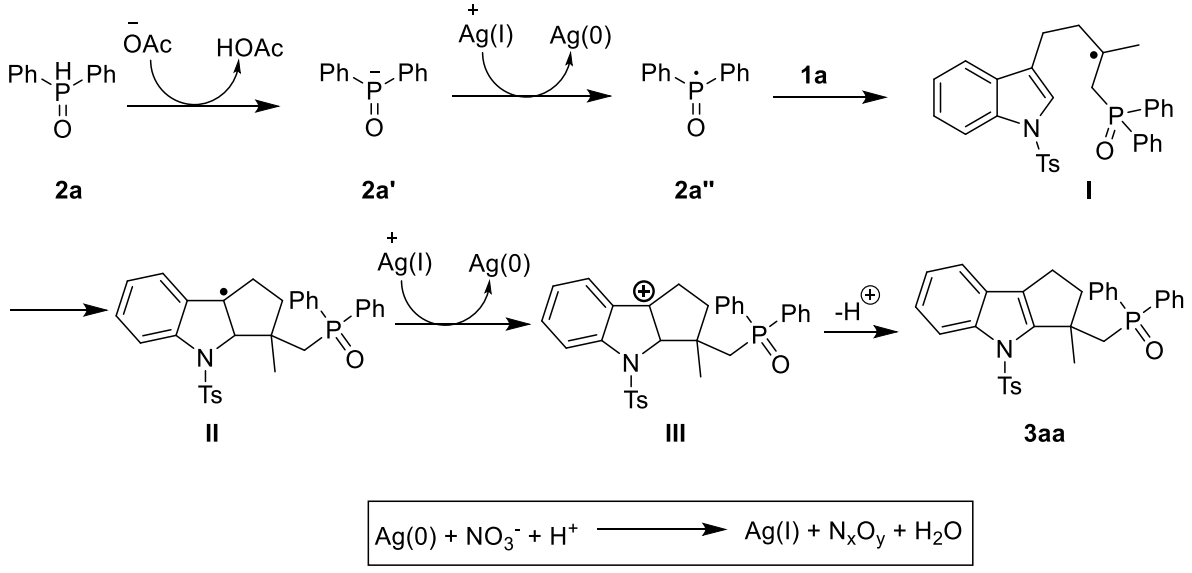


1a **2a** (1.2 eq.) **3aa** (not detected)

An oven-dried sealed tube was charged with indole derivative **1a** (0.1 mmol, 34.0 mg, 1.0 eq.), $AgP(O)Ph_2$ (0.01 mmol, 6.8 mg, 0.1 equiv.) and $Zn(NO_3)_2.6H_2O$ (0.2 mmol, 60.0 mg, 2.0 eq.) in dichloroethane (2.0 ml) under a nitrogen atmosphere. Diphenyl phosphine oxide **2a** (0.12 mmol, 24.0 mg, 1.2 eq.) was then added, and the reaction mixture was stirred at 82 °C for 24 hours. Analysis by thin-layer chromatography (TLC) revealed that the desired product **3aa** was not detected.

3.0 Plausible mechanism:

To gain a deeper understanding of the reaction mechanism, a series of control experiments were performed to confirm the involvement of radical intermediates. Radical scavengers, TEMPO and BHT, were added to the reaction, and as expected, no cyclized product was formed, indicating the involvement of radical intermediates. Mass spectrometric analysis revealed adducts between the scavengers and reactive intermediates, further supporting this conclusion. No product formation was observed when $Ph_2P(O)Ag$ was used in either stoichiometric or catalytic amounts, suggesting that $Ph_2P(O)Ag$ is not directly involved in the reaction. Based on these findings and literature[4] precedents the proposed mechanism begins with the generation of a phosphorus-centered radical from the phosphine oxide precursor in the presence of silver acetate. This radical reacts with the C3-substituted indole derivative, forming a stable tertiary radical (intermediate **I**). The tertiary radical then undergoes intramolecular attack at the C2 position of the indole, forming intermediate **II**, which is readily oxidized by a second equivalent of silver acetate to generate a benzylic cation (intermediate **III**). The final product is obtained through aromatization, restoring the indole's aromaticity. Silver acetate serves a dual role as both a radical initiator and oxidizing agent, enabling the formation of key intermediates that steer the reaction toward the efficient synthesis of the target compound. In the presence of NO_3^- and H^+, the Ag(0) formed during the reaction is oxidized back to Ag(I), enabling the catalytic cycle to continue efficiently.[5]



Scheme SI-4: Plausible mechanism.

4.0 X-ray Crystallographic Data for Compound 5la:

Compound **5la** was dissolved in the ethanol solvent and crystallized in a 5 mL glass vial at room temperature. Appropriate single crystal was selected under microscope and mounted with Paratone Oil on a Cryoloop. X-ray data for the compound was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[6] The structure was solved using intrinsic phasing method[4] and further refined with the SHELXL[7] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

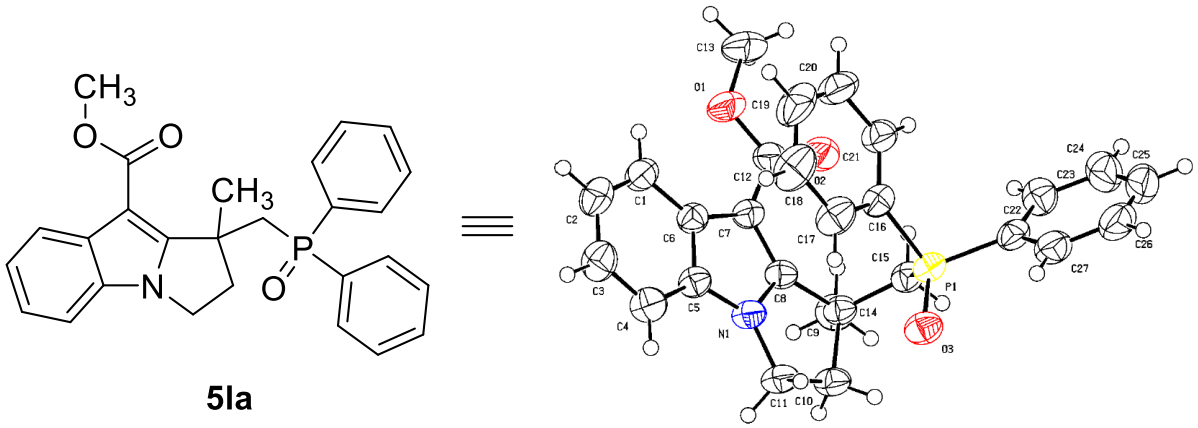


Figure SI-3: ORTEP diagram of **5la** with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal structure determination of 5la

Crystal Data for $C_{27}H_{26}NO_3P$ (M =443.46 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 10.0643(19) Å, b = 8.1662(15) Å, c = 28.399(5) Å, β = 99.579(5)°, V = 2301.5(7) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 0.148 mm^{-1}, *Dcalc* = 1.280 g/cm^3, 41168 reflections measured (4.62° ≤ 2Θ ≤ 56.68°), 5732 unique (R_{int} = 0.0480, R_{sigma} = 0.0361) which were used in all calculations. The final R_1 was 0.0439 (I > 2σ(I)) and wR_2 was 0.1133 (all data). **CCDC 2422565** deposition number contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

5.0 References

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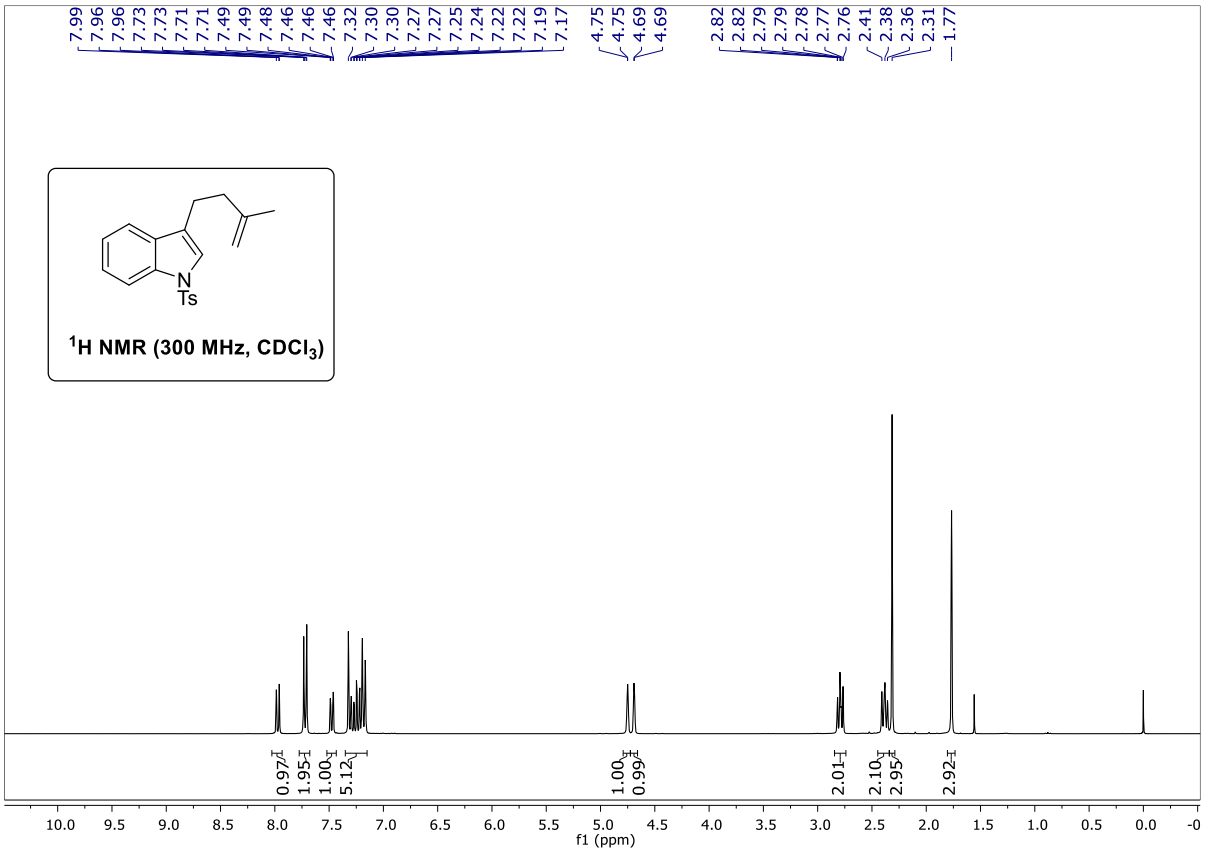
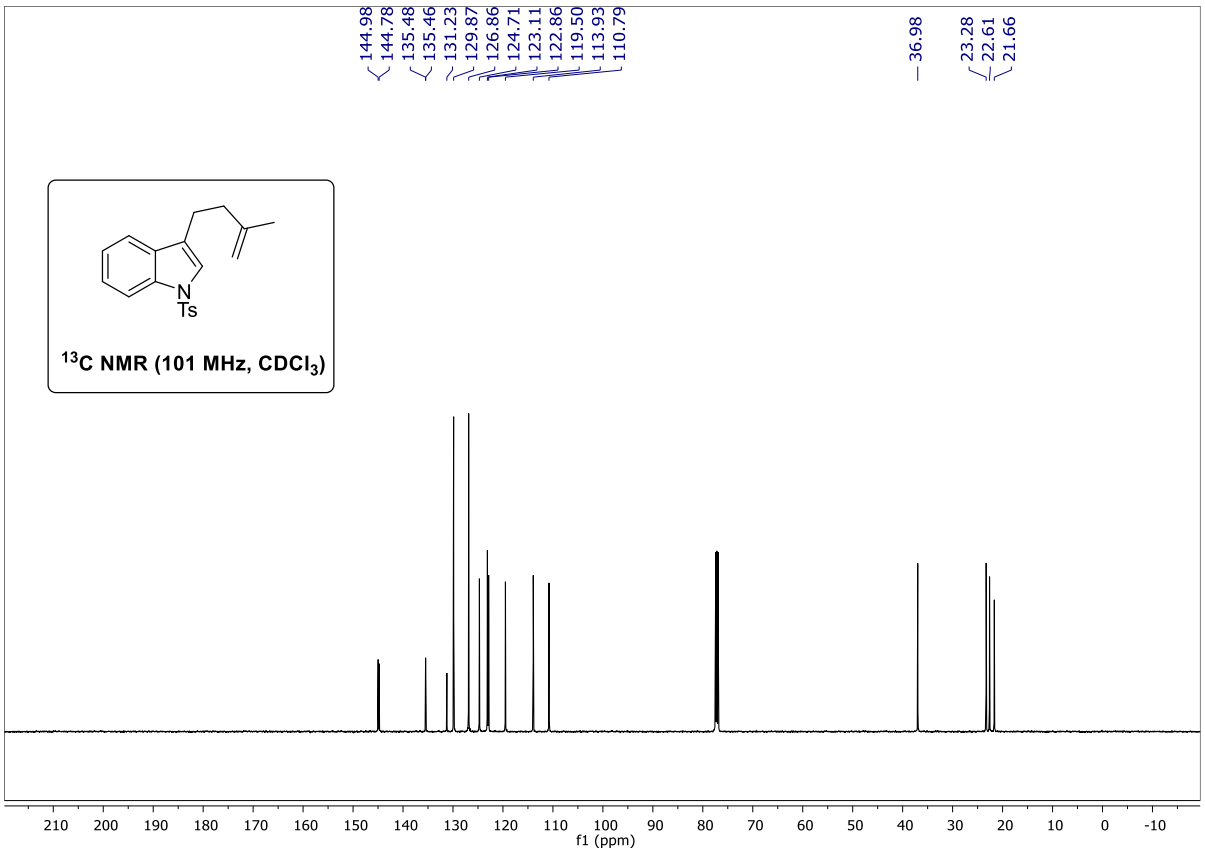
6. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.

7. Sheldrick G. M. (2015). Acta Crystallogr C71: 3-8.

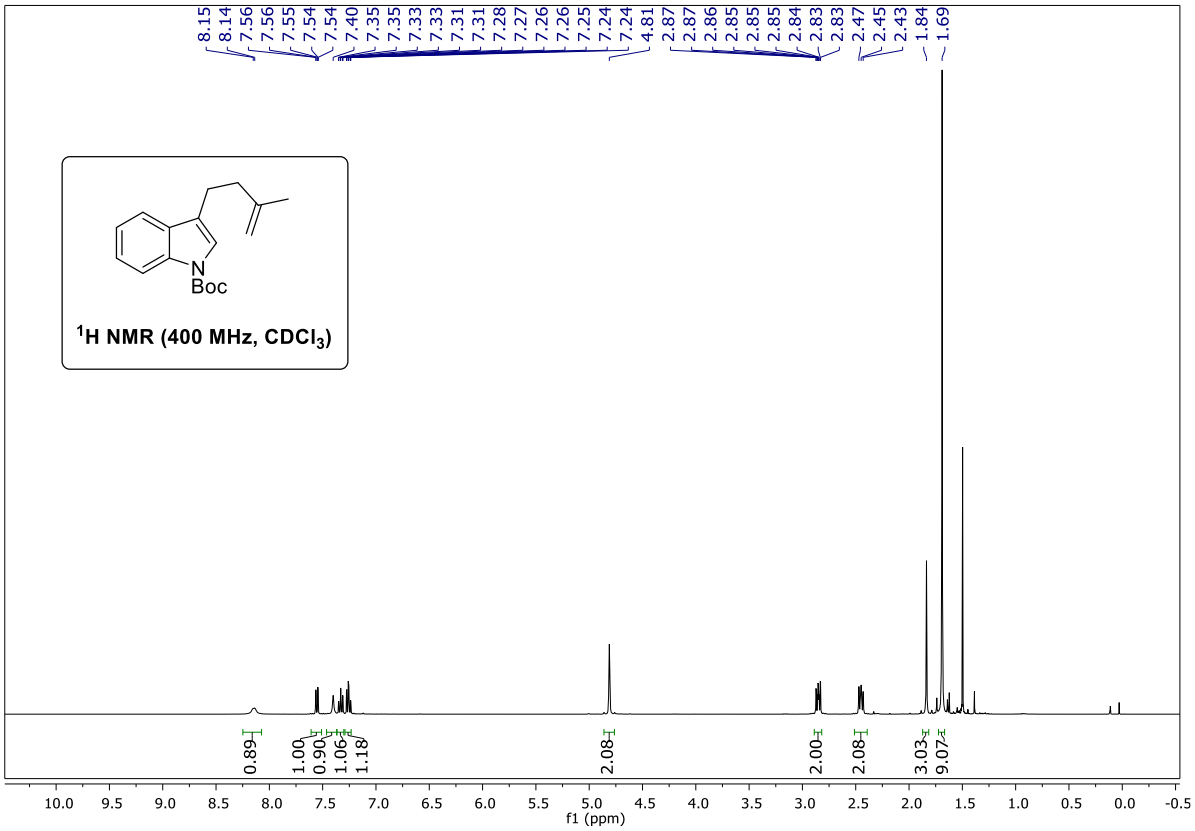
6.0 ^{1}H NMR, ^{13}C NMR & ^{31}P NMR Spectra for New Compounds:

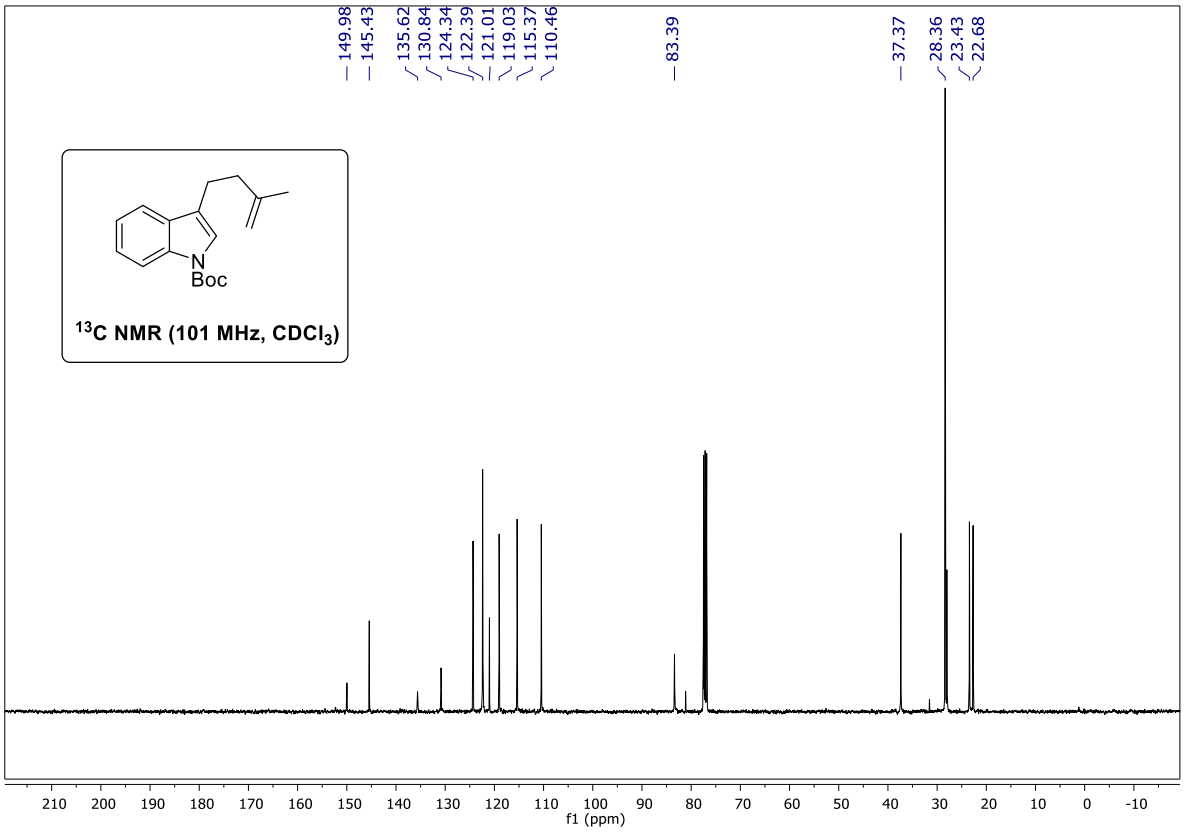
3-(3-Methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1a):



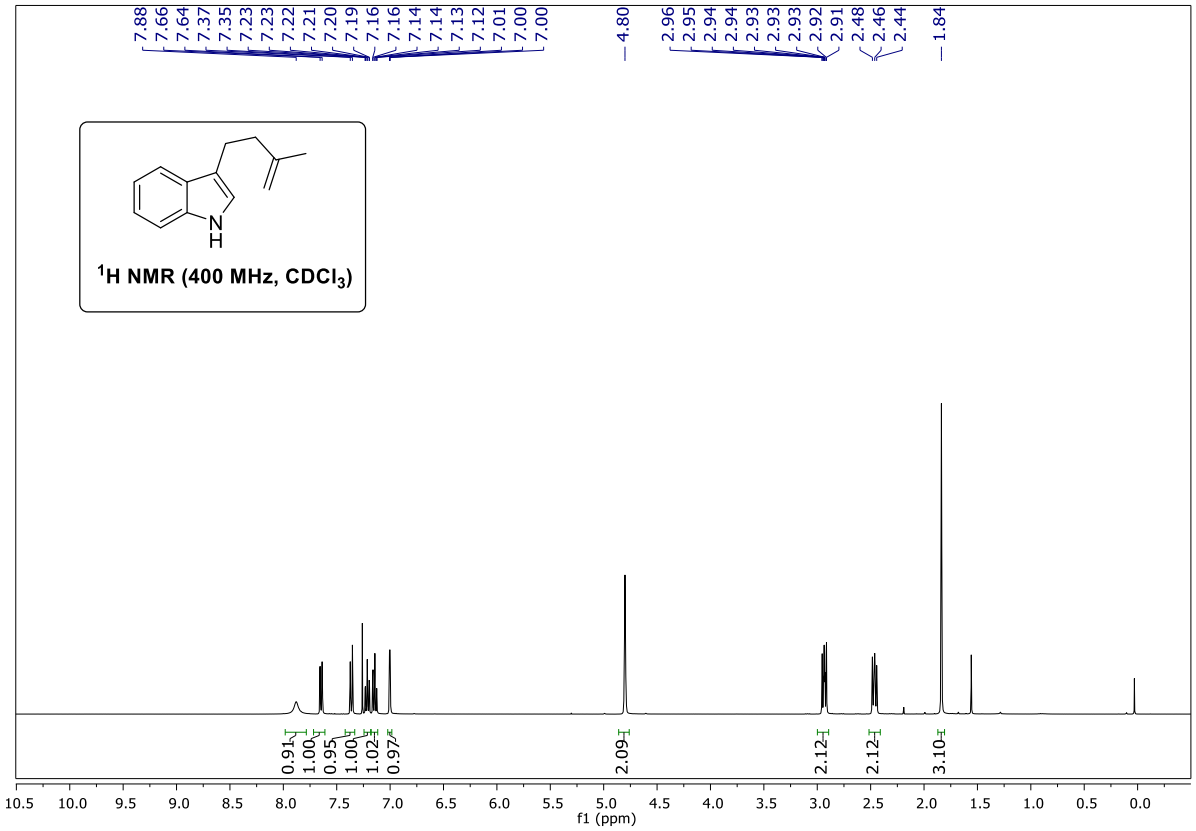


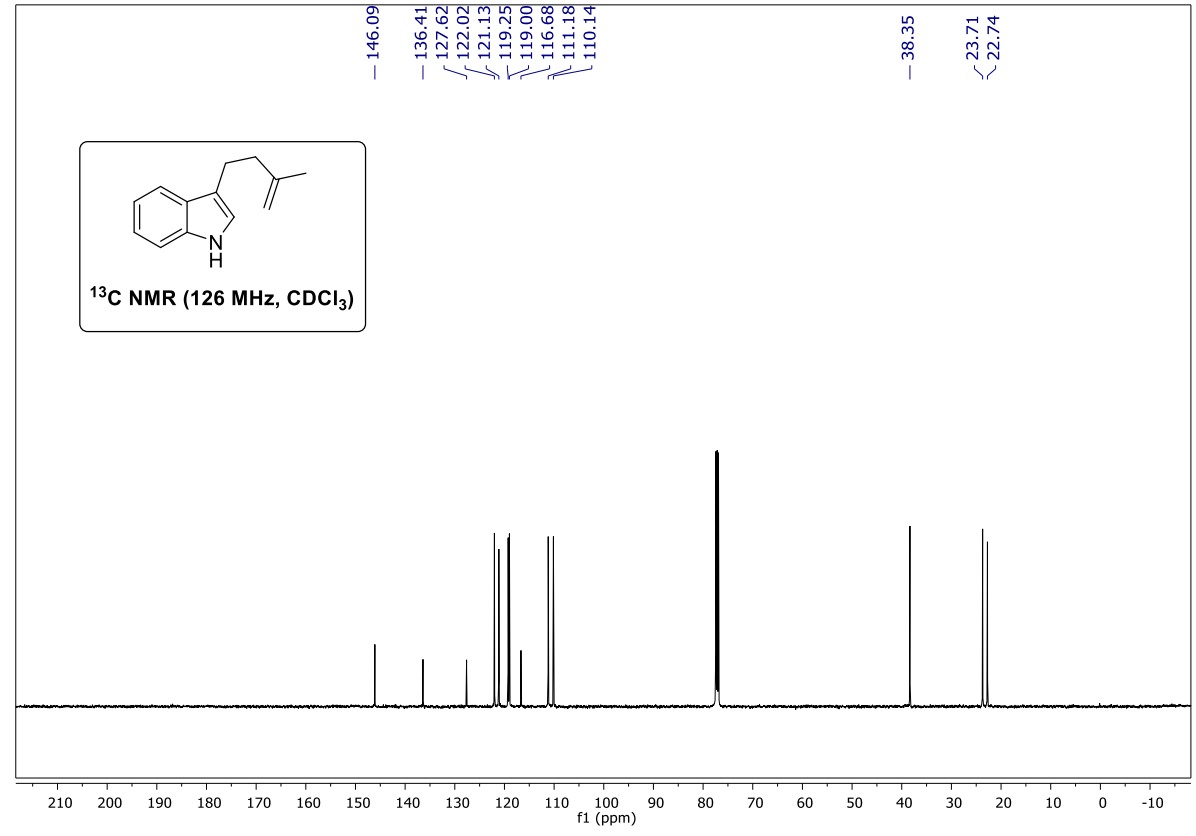
***tert*-Butyl 3-(3-methylbut-3-en-1-yl)-1*H*-indole-1-carboxylate (1b):**



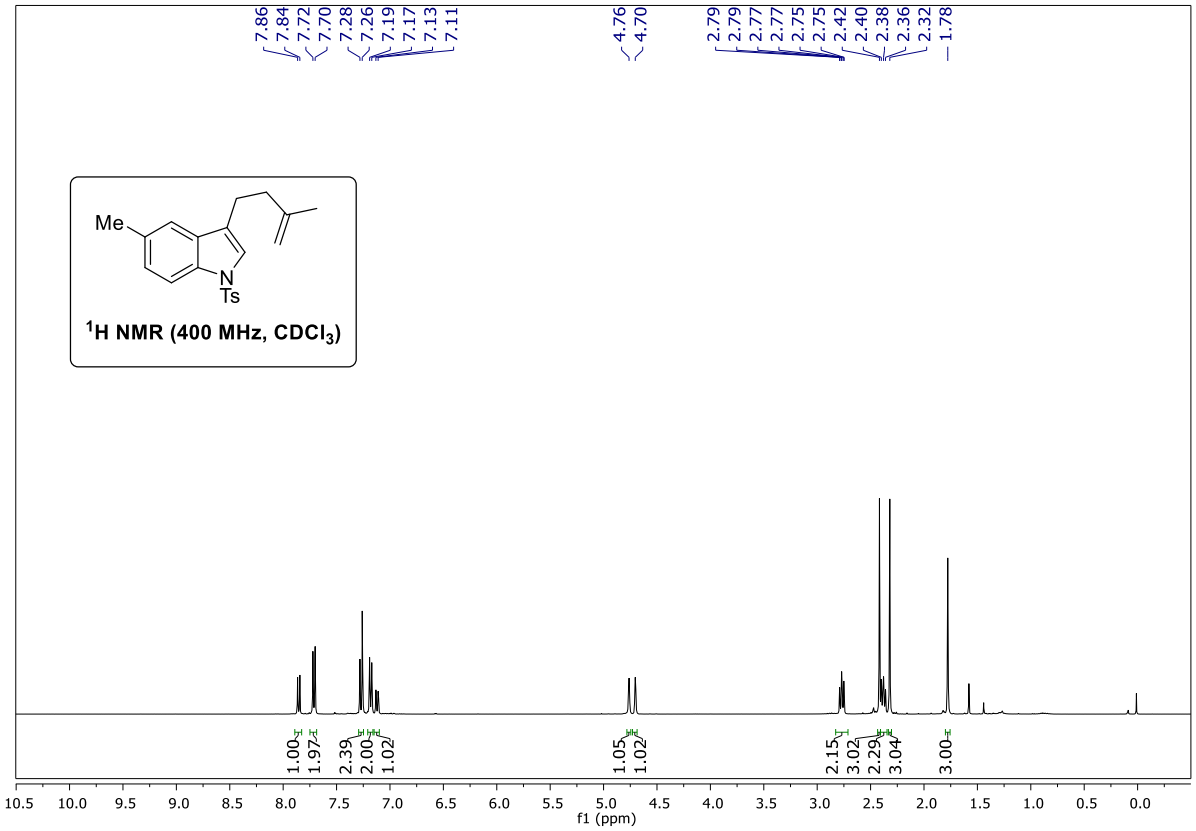


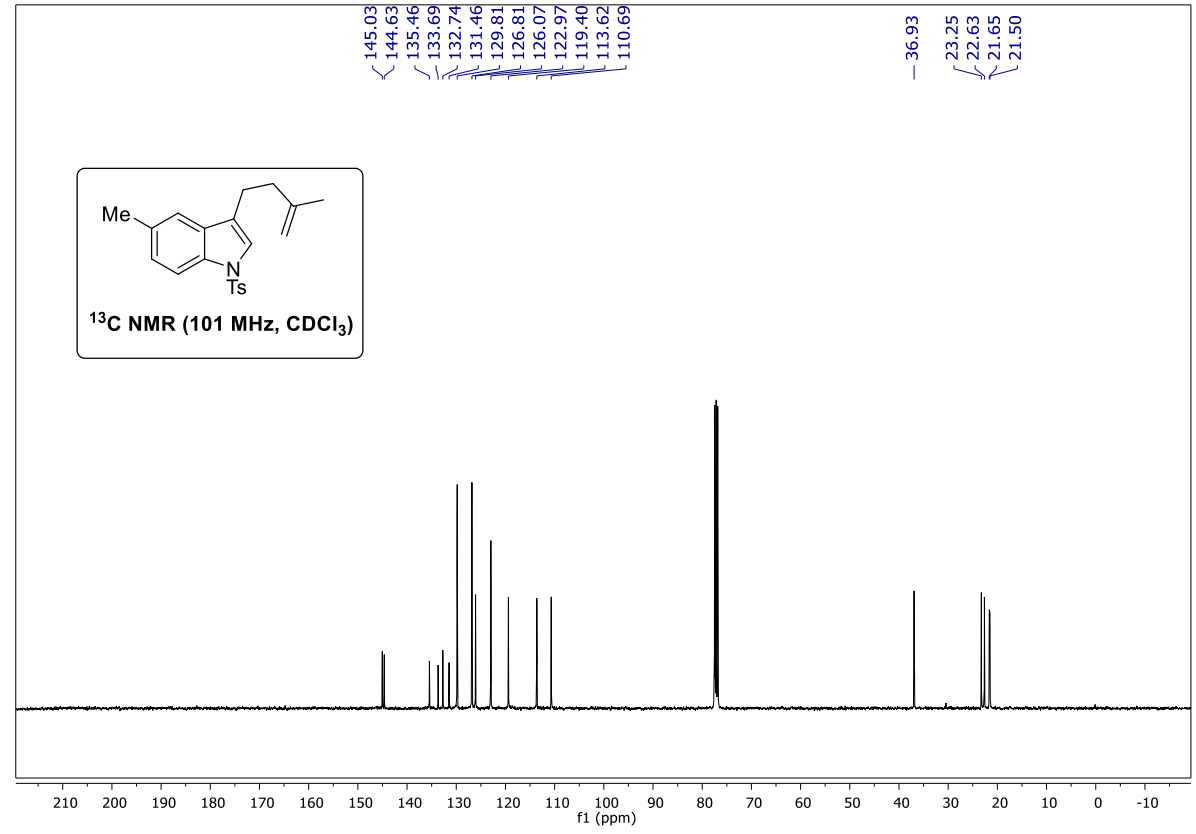
3-(3-Methylbut-3-en-1-yl)-1*H*-indole (1d):



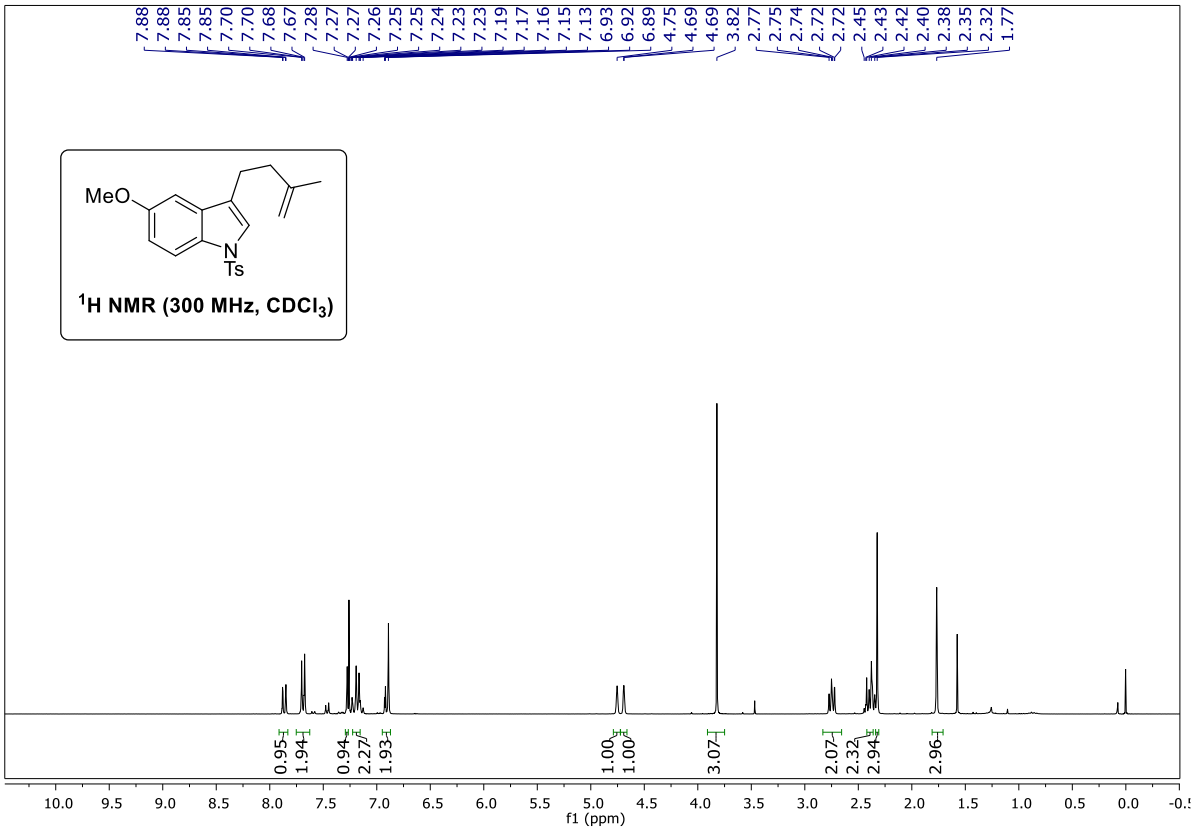


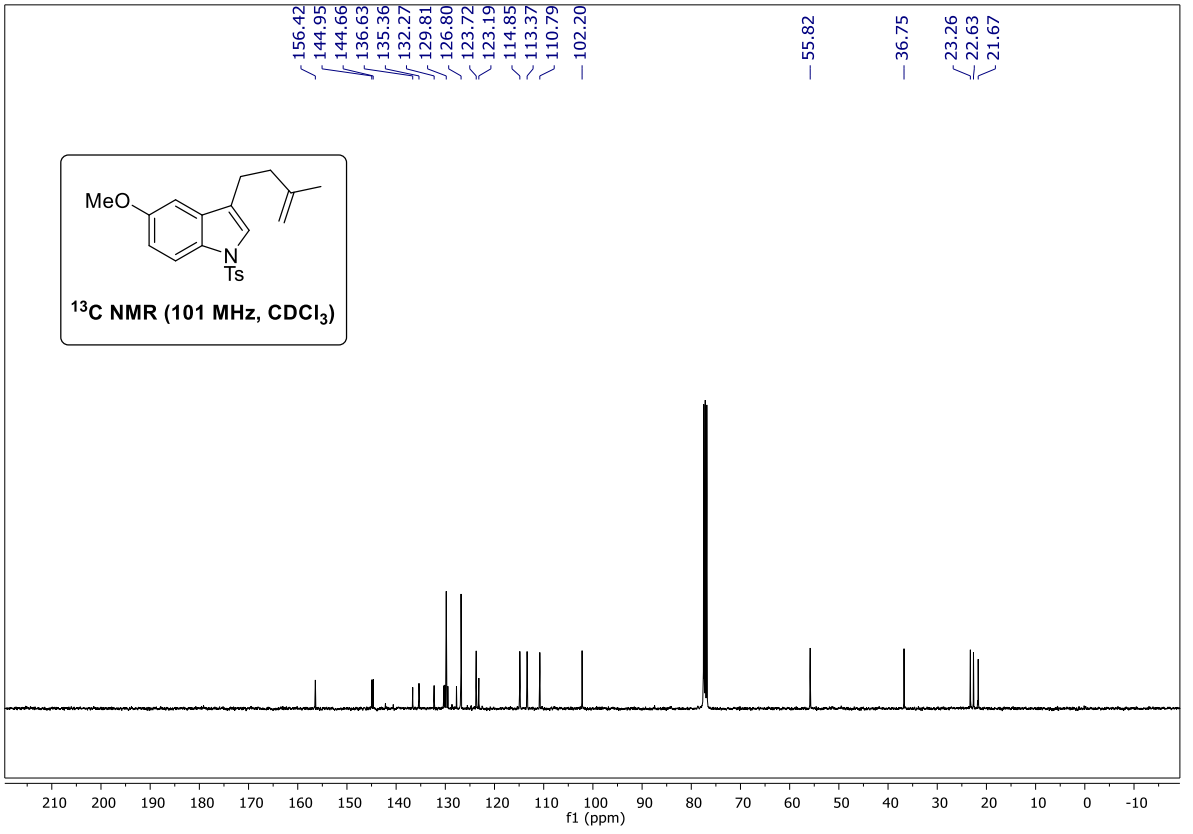
5-Methyl-3-(3-methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1e):



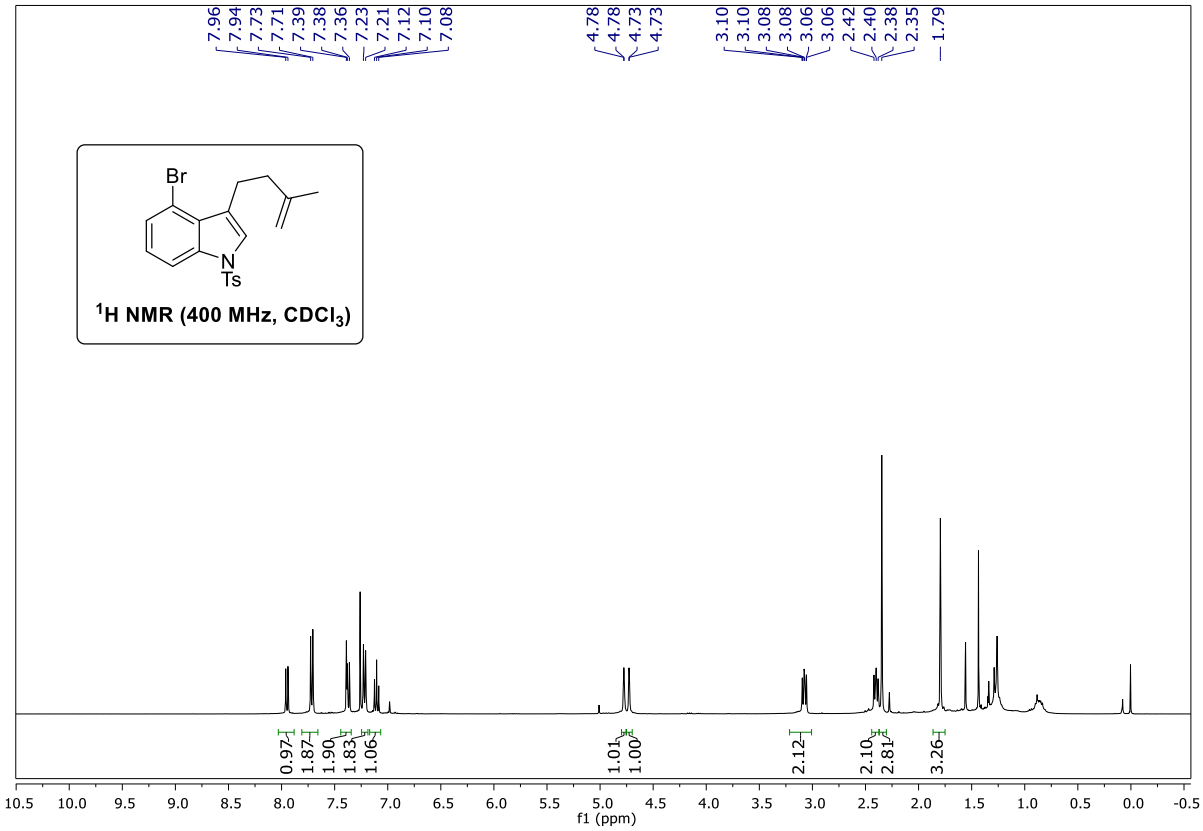


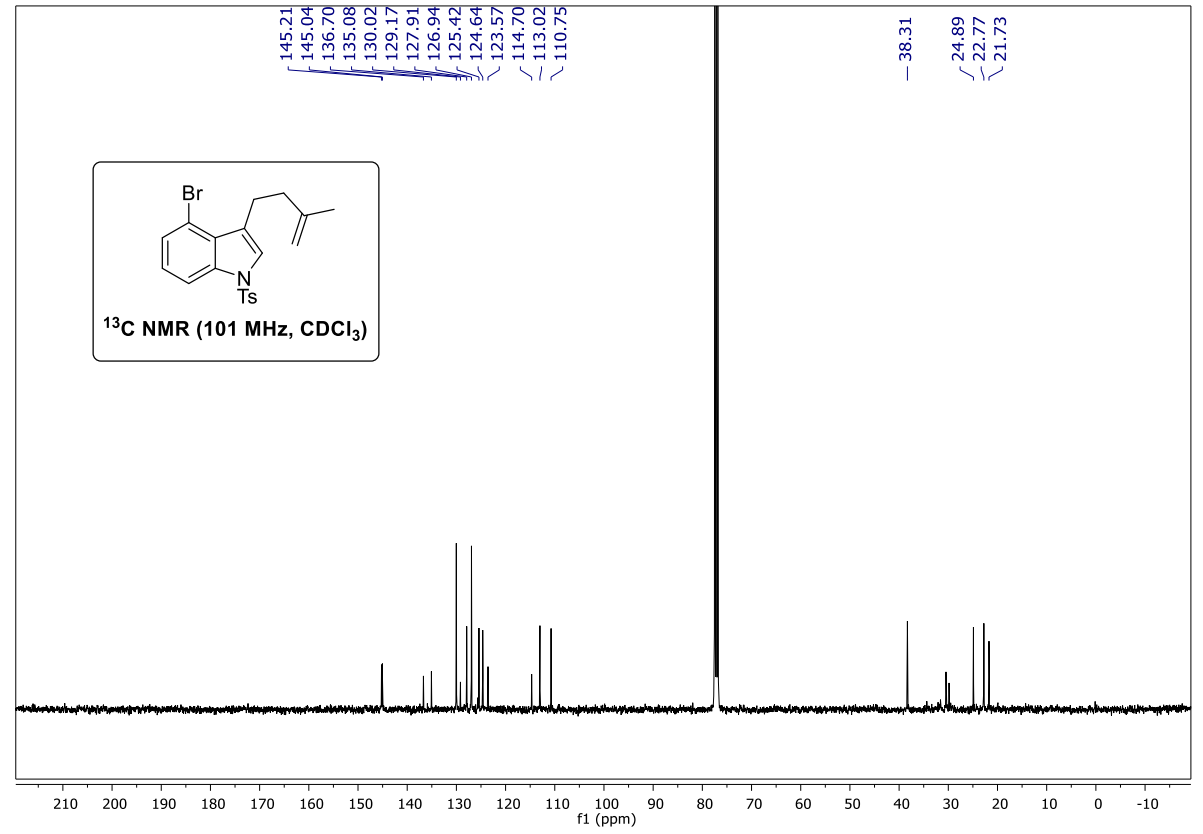
5-Methoxy-3-(3-methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1f):



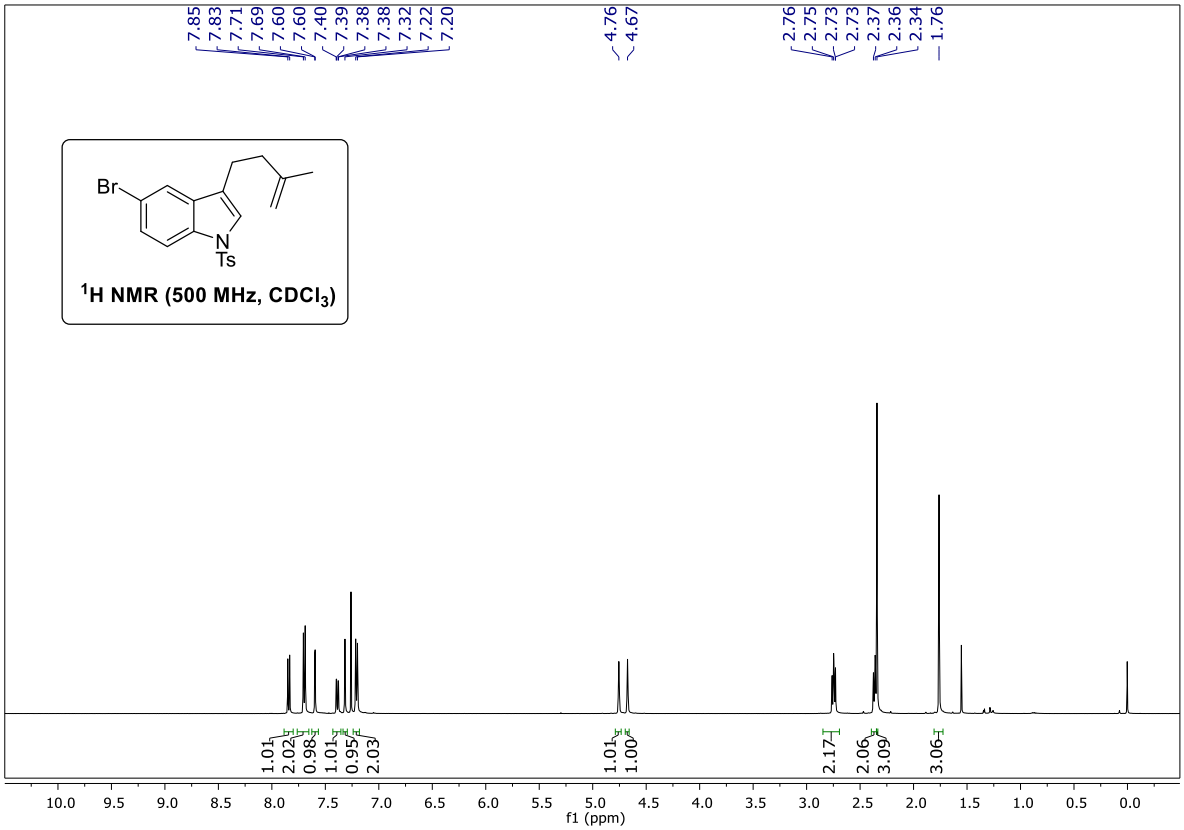


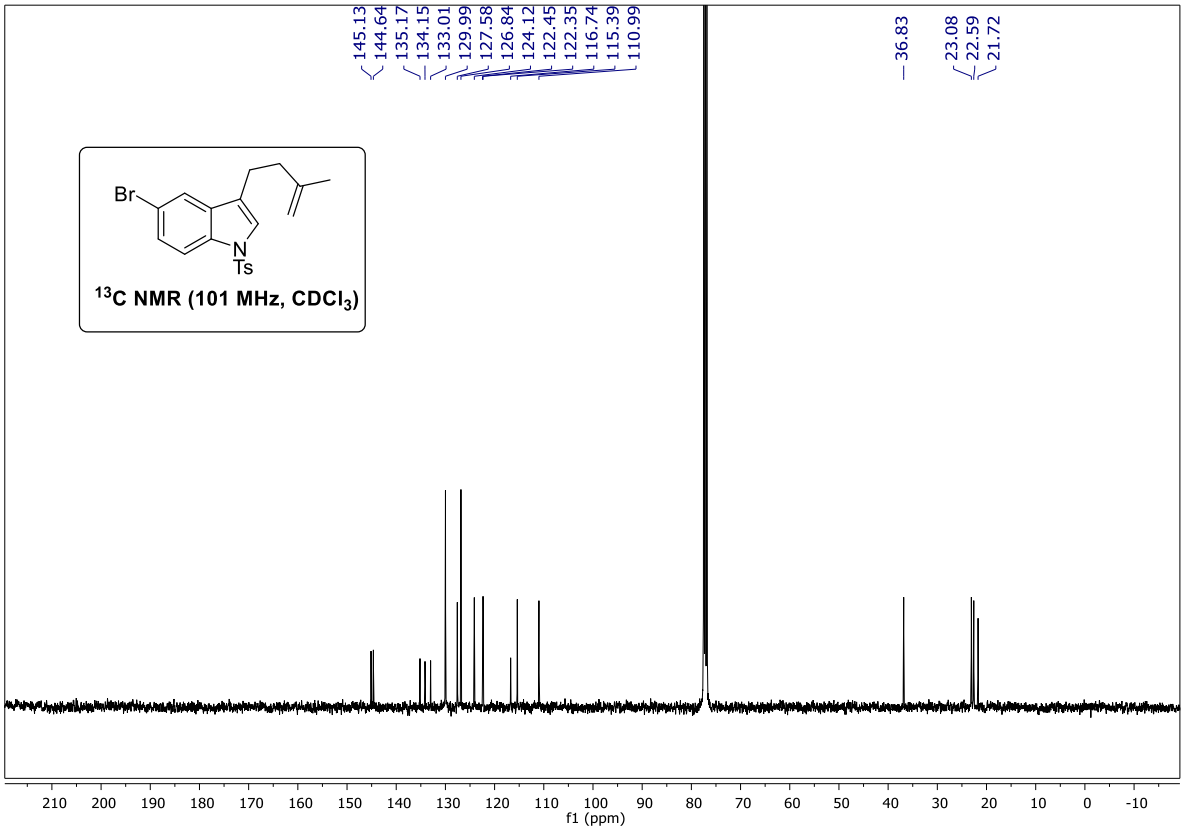
4-Bromo-3-(3-methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1g):



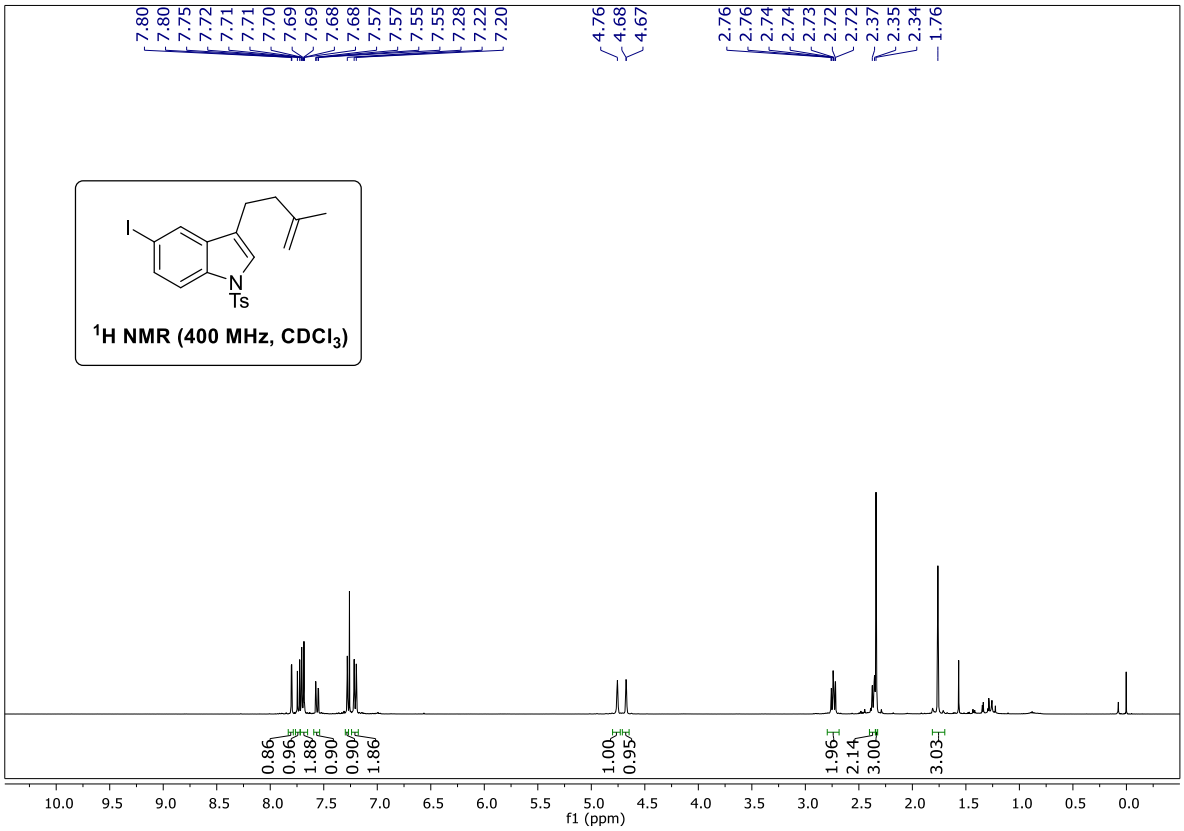


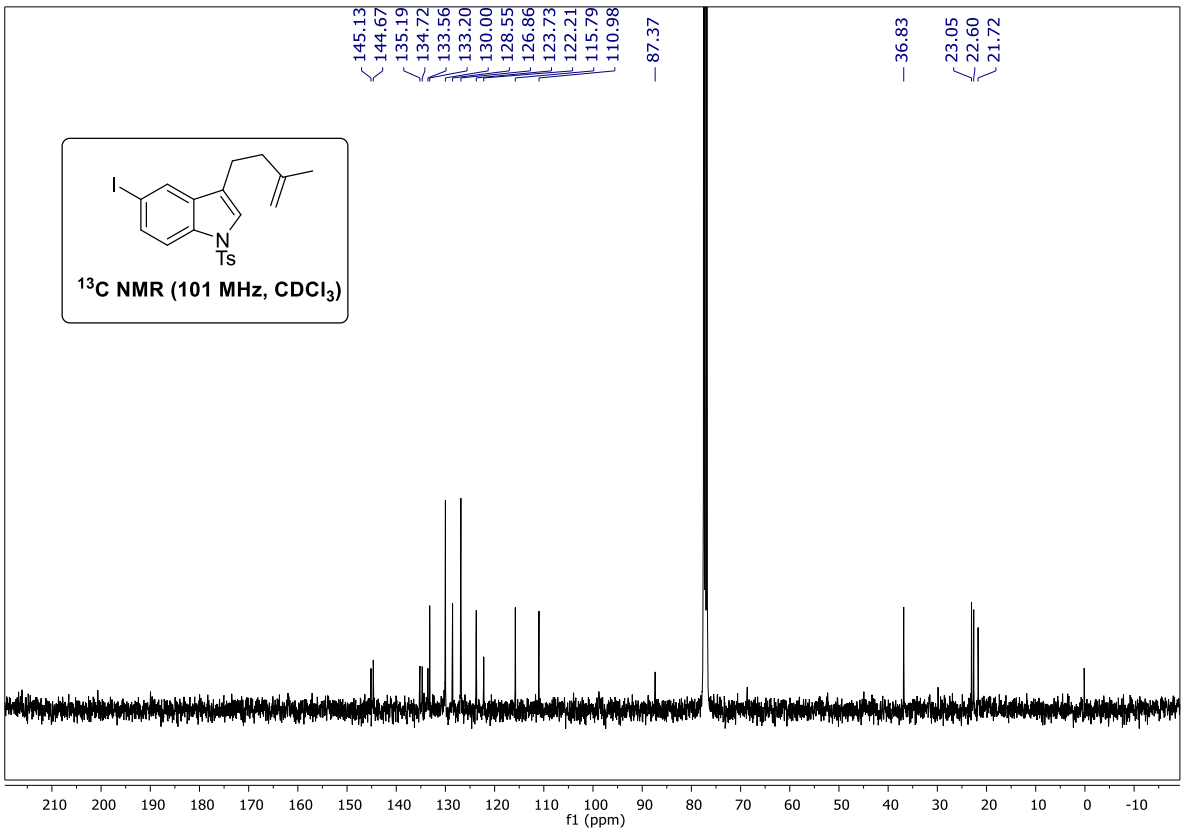
5-Bromo-3-(3-methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1h):



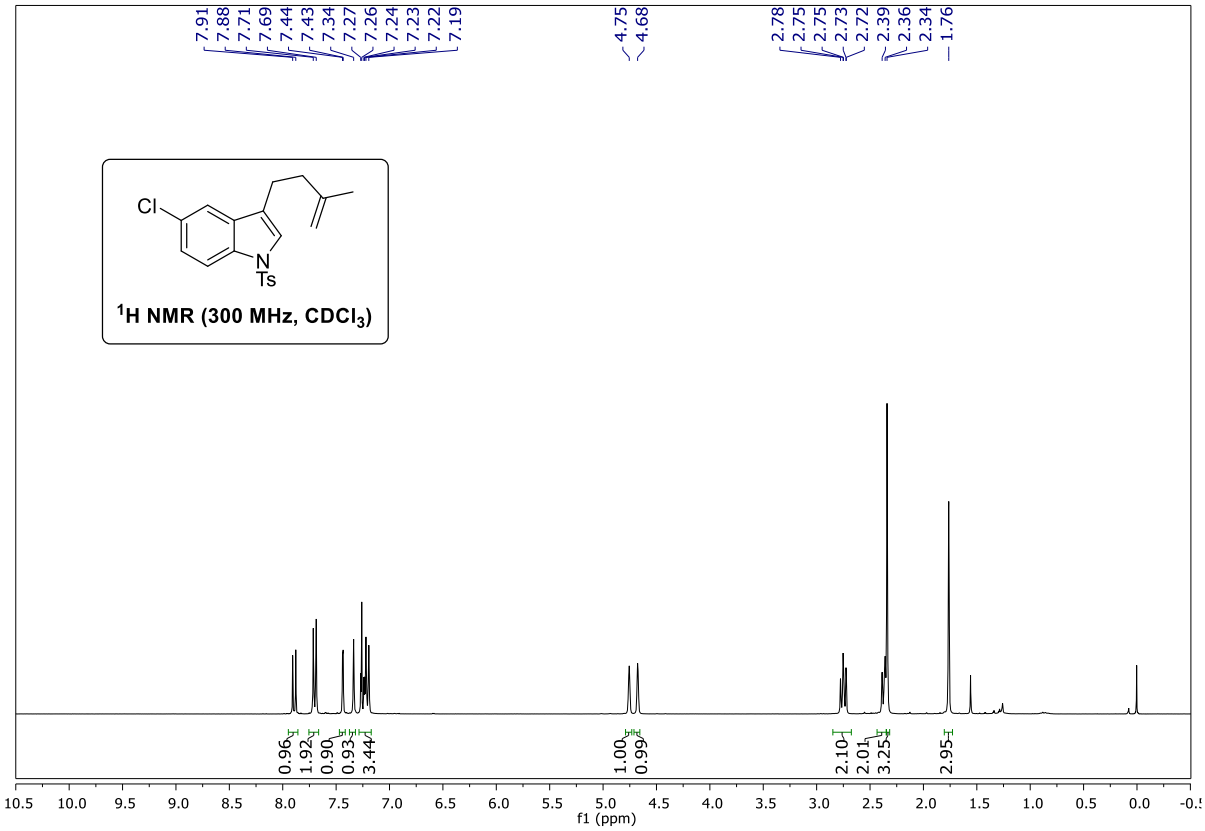


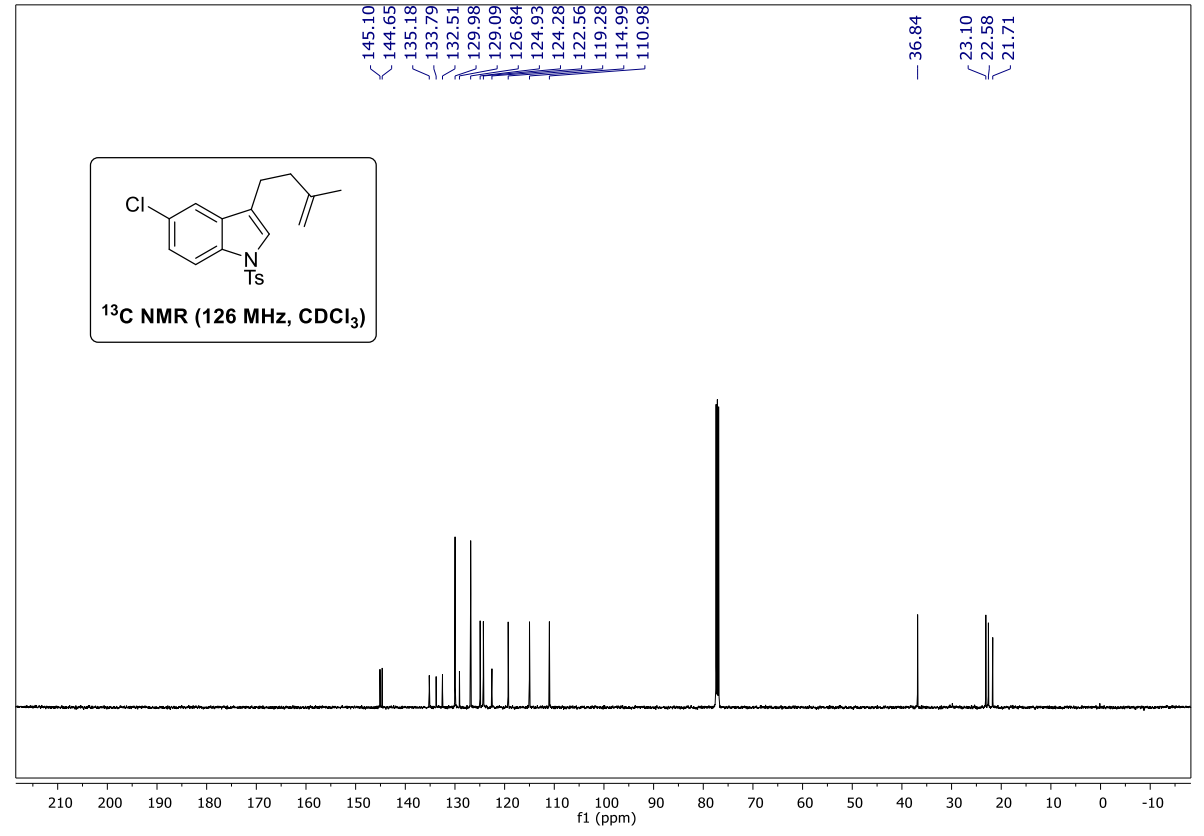
5-Iodo-3-(3-methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1i):



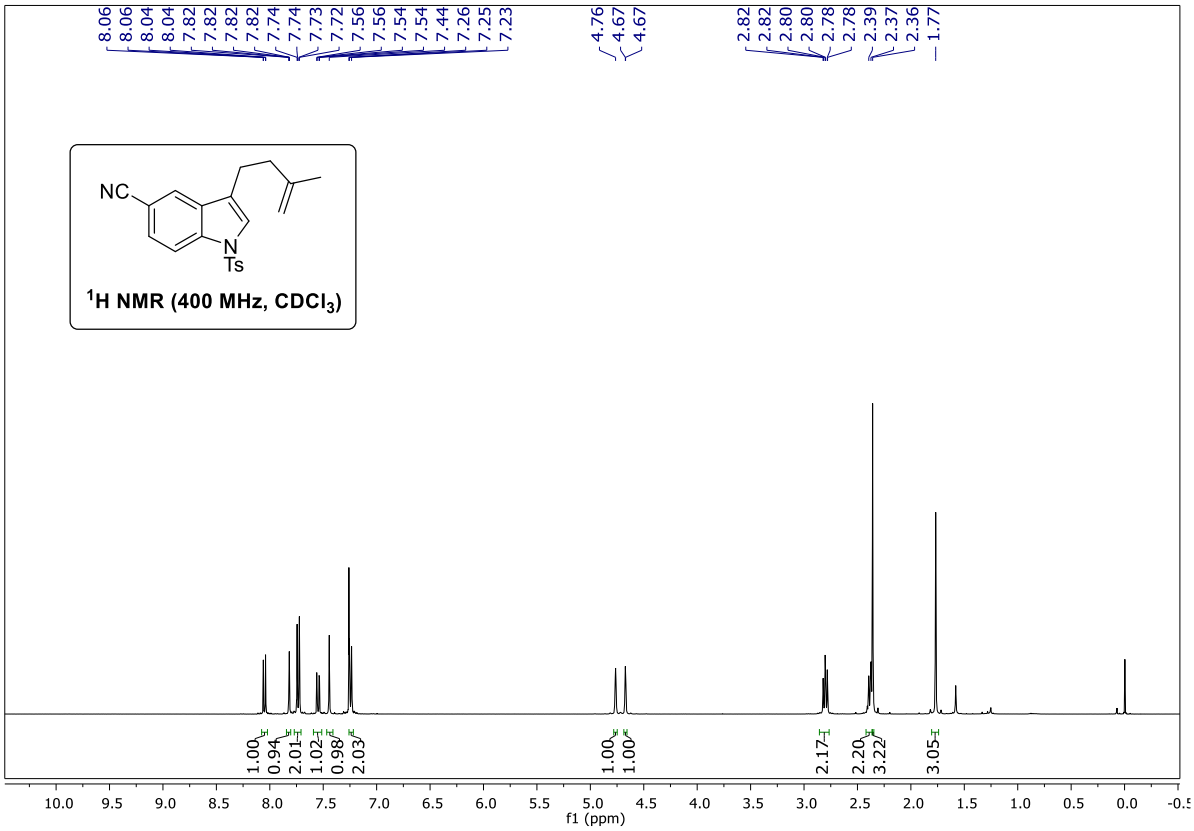


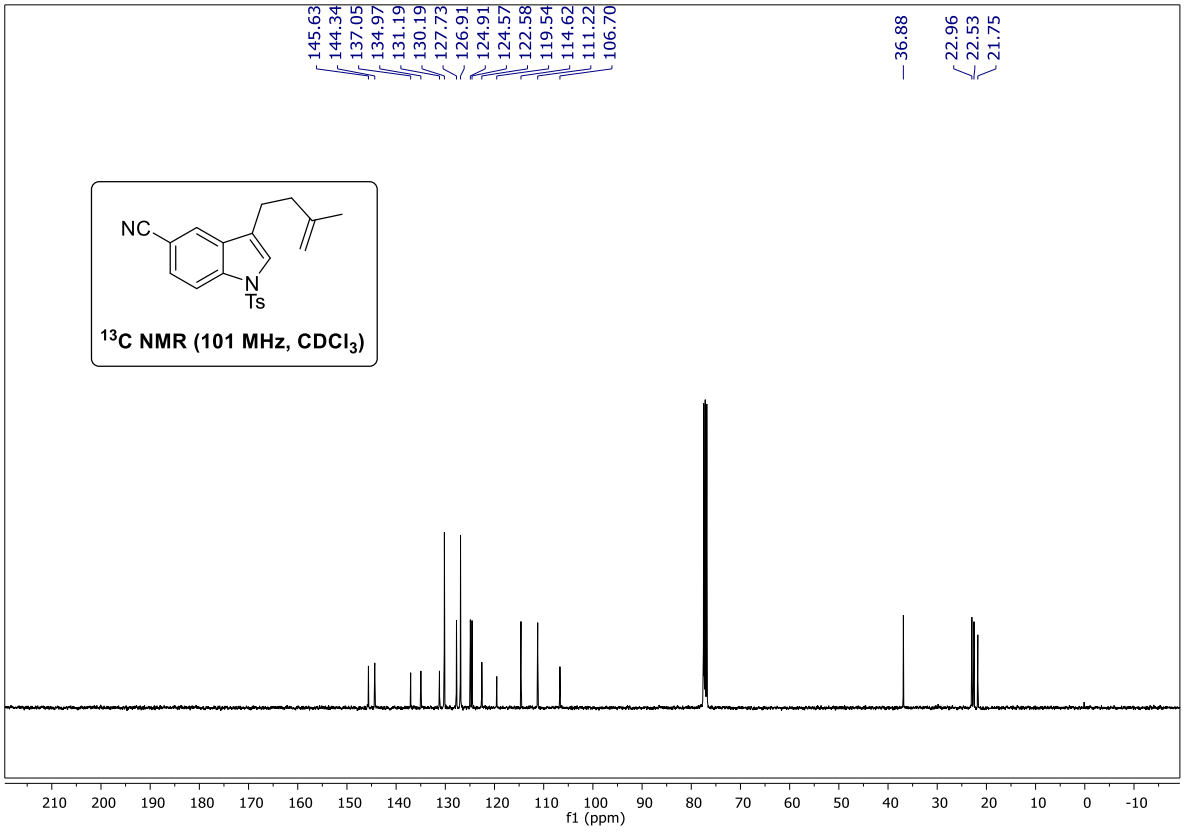
5-Chloro-3-(3-methylbut-3-en-1-yl)-1-tosyl-1*H*-indole (1j):



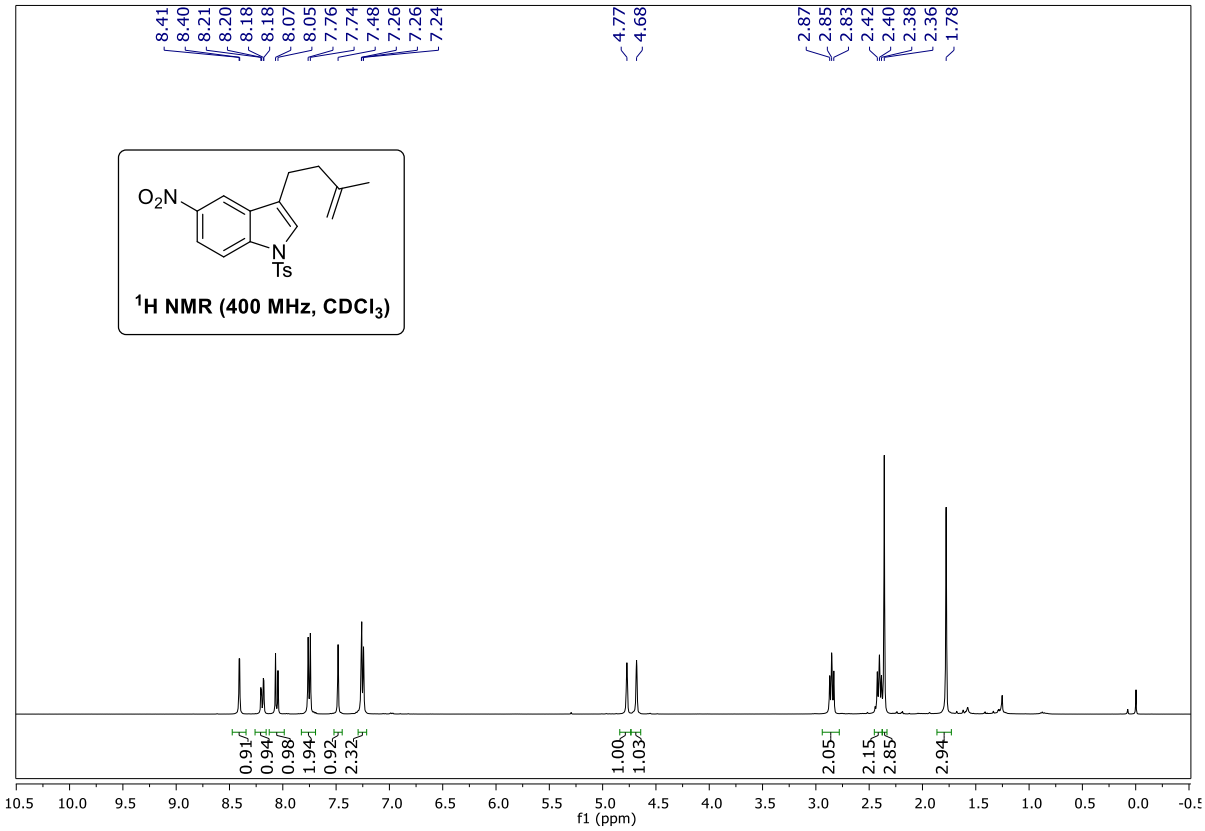


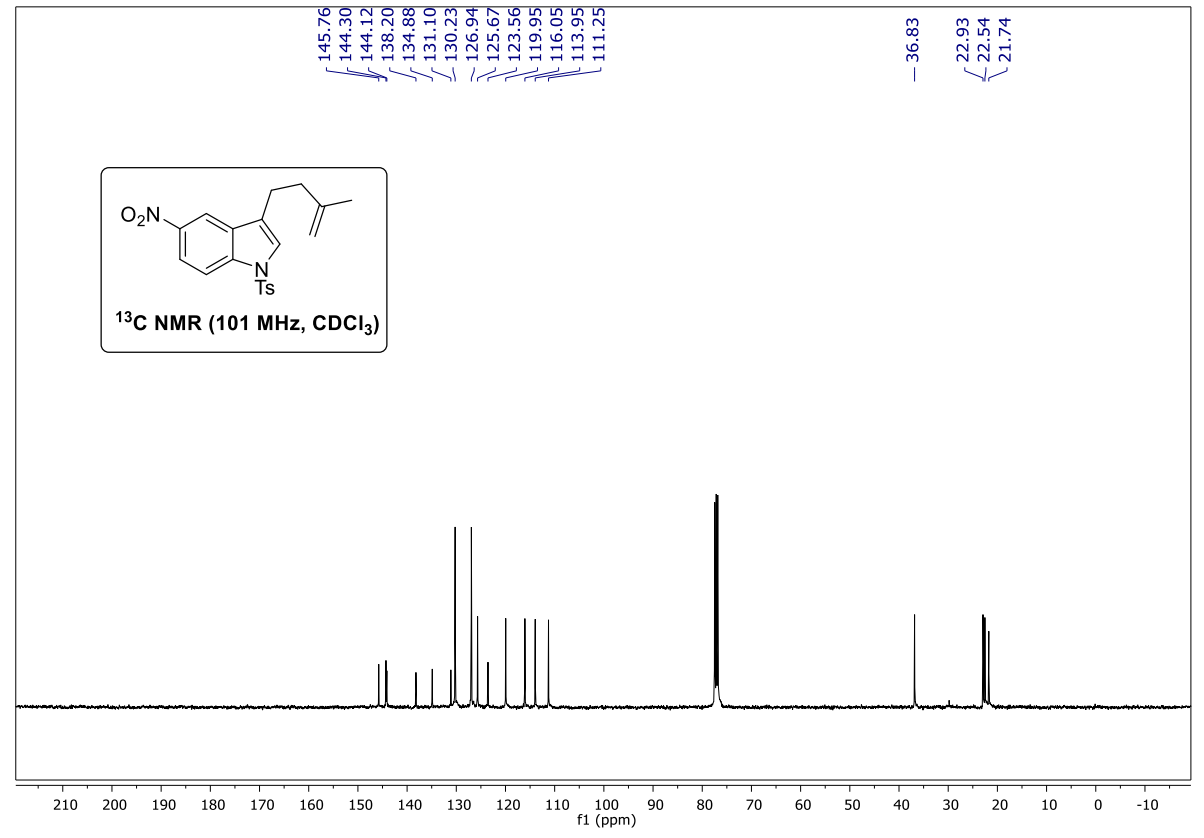
3-(3-Methylbut-3-en-1-yl)-1-tosyl-1*H*-indole-5-carbonitrile (1k):



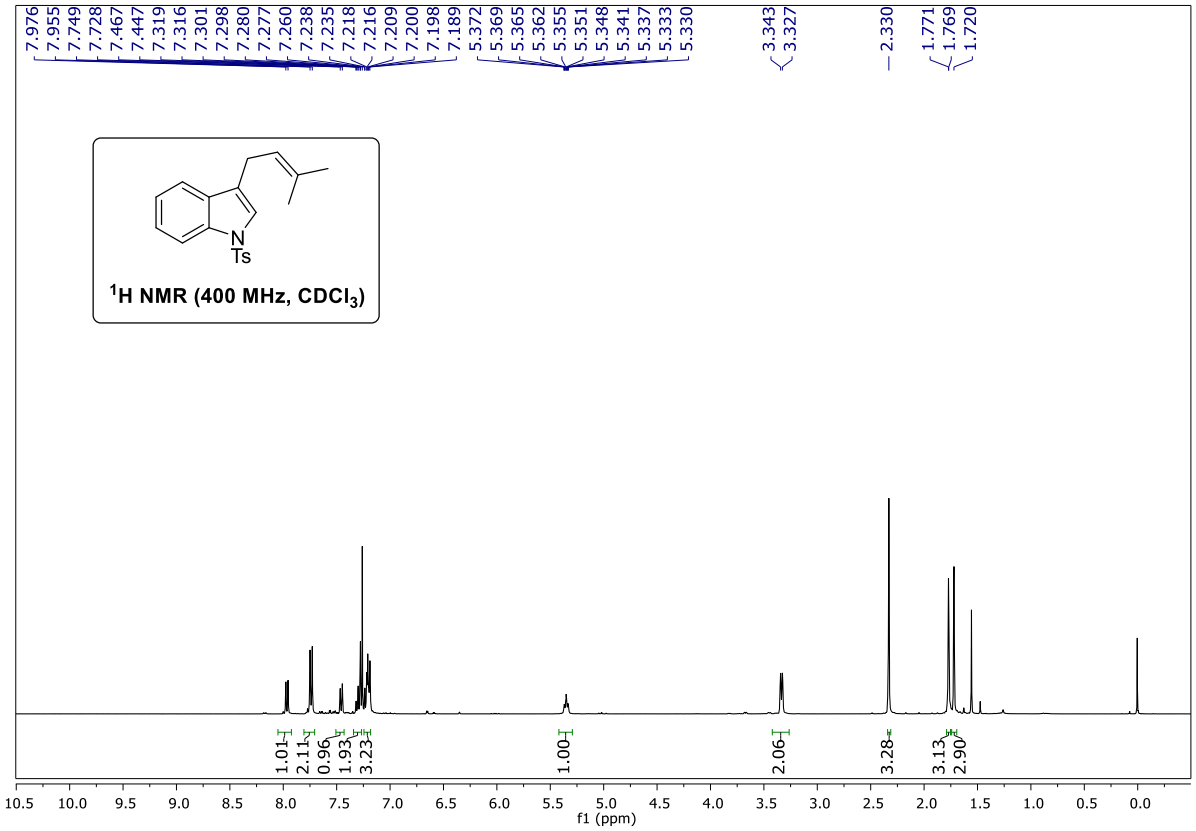


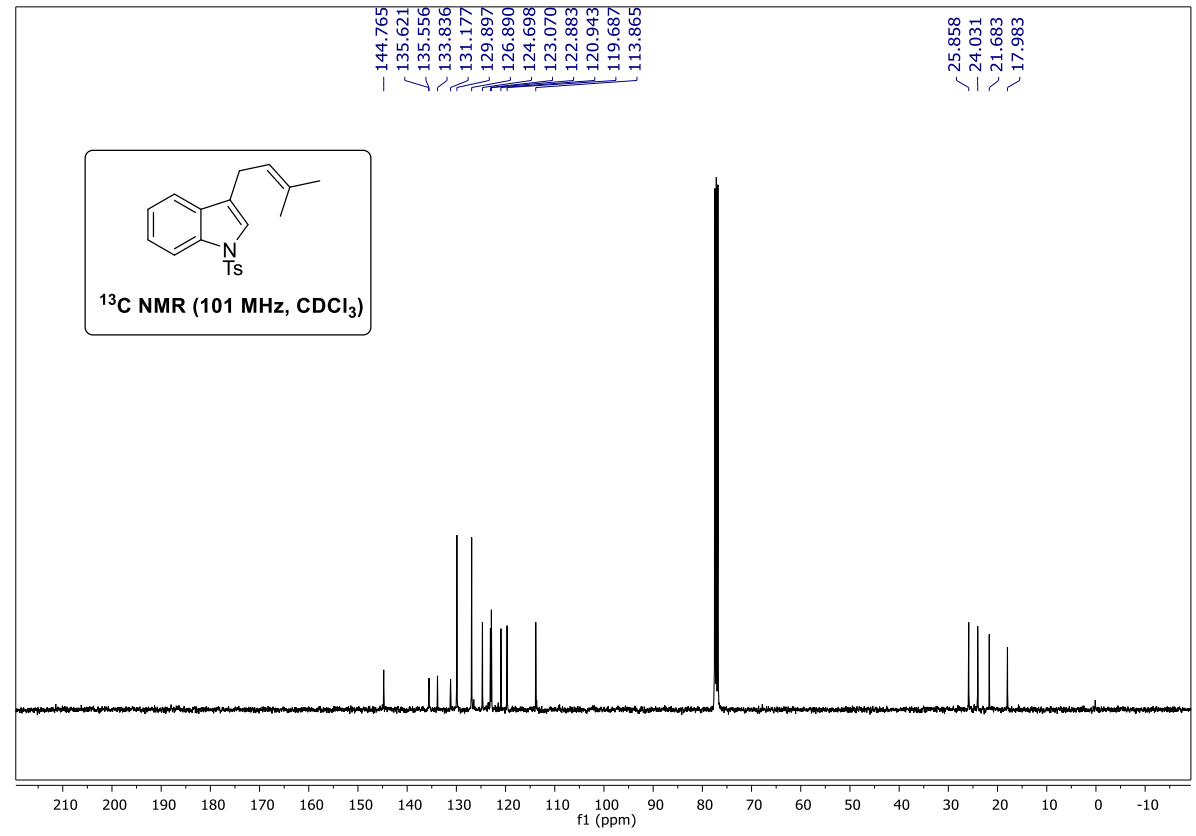
3-(3-methylbut-3-en-1-yl)-5-nitro-1-tosyl-1*H*-indole (1l):



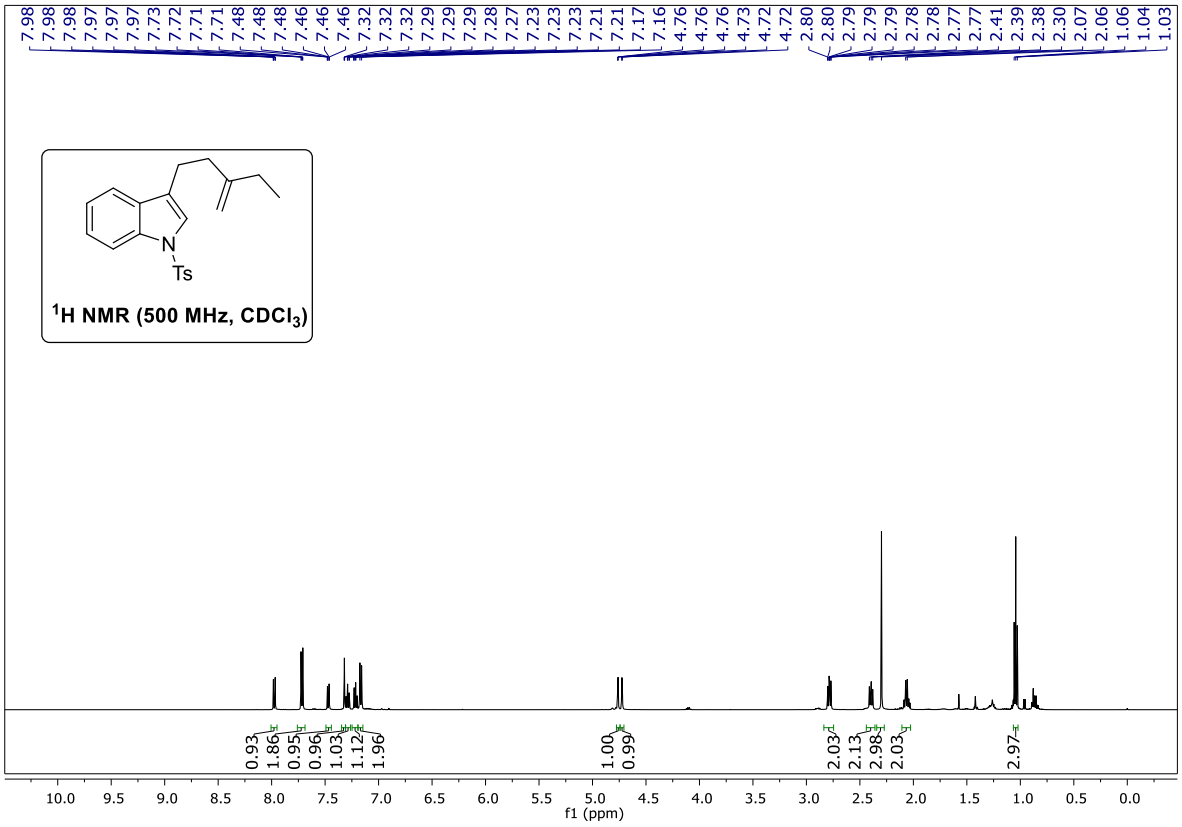


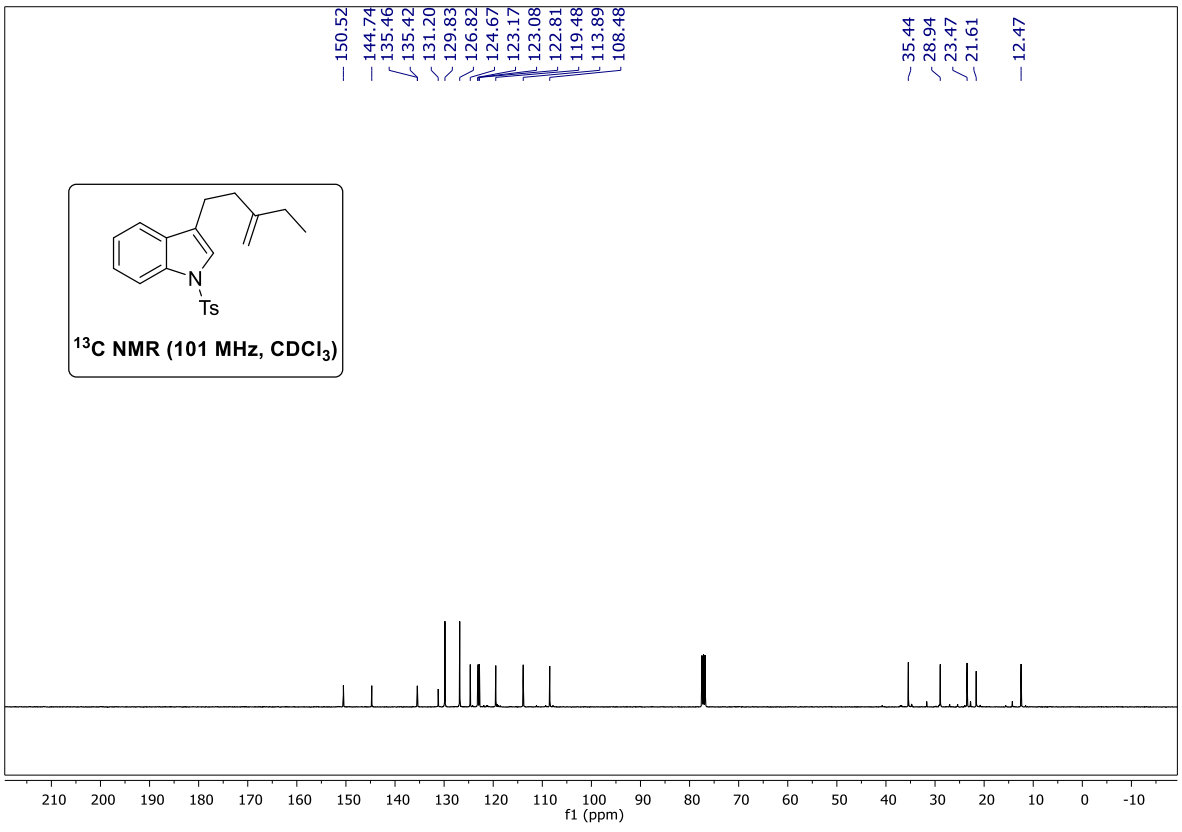
3-(3-methylbut-2-en-1-yl)-1-tosyl-1*H*-indole (1m):



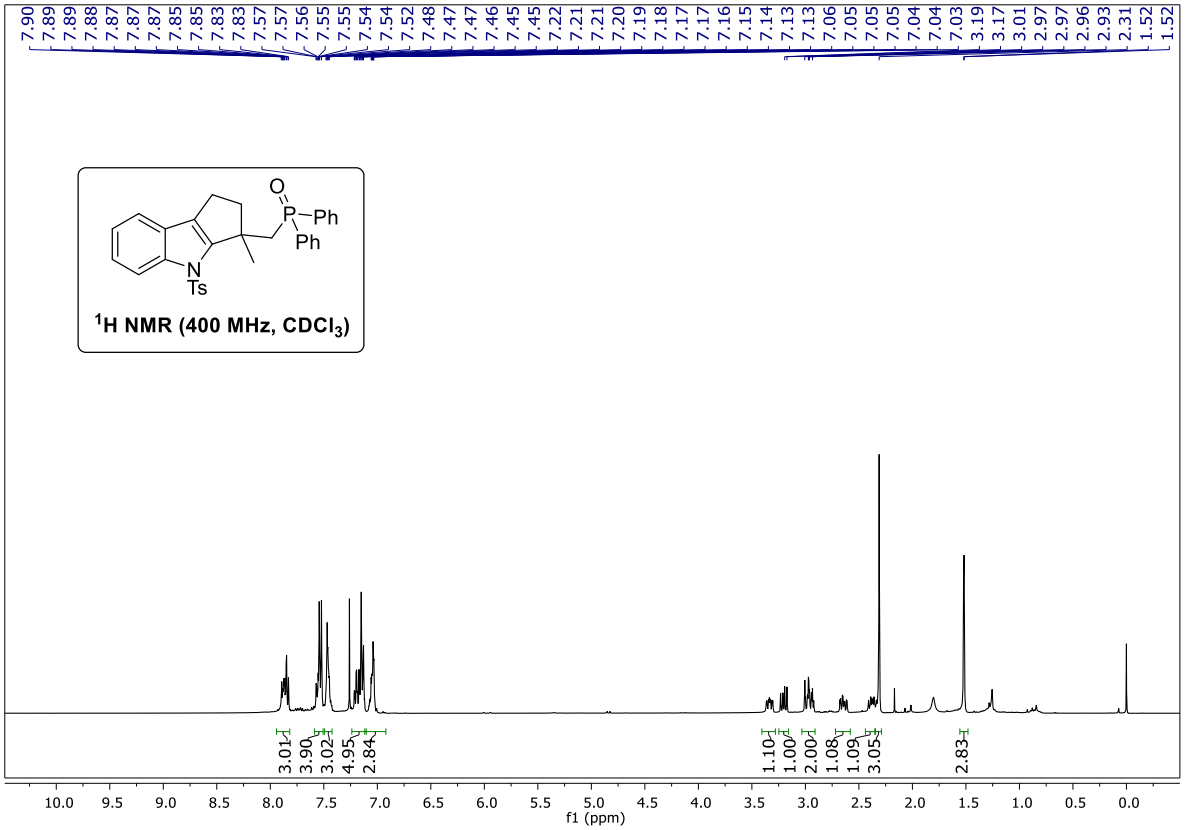


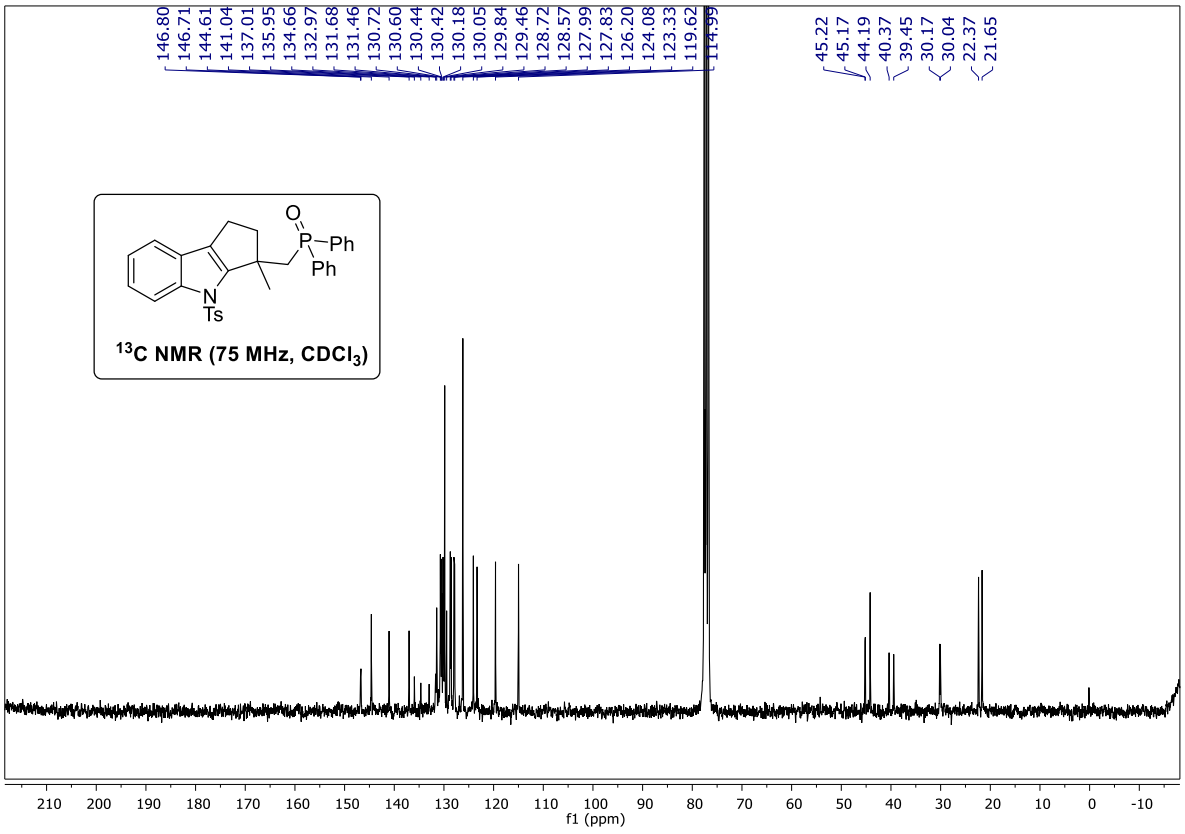
3-(3-methylenepentyl)-1-tosyl-1*H*-indole (1n):

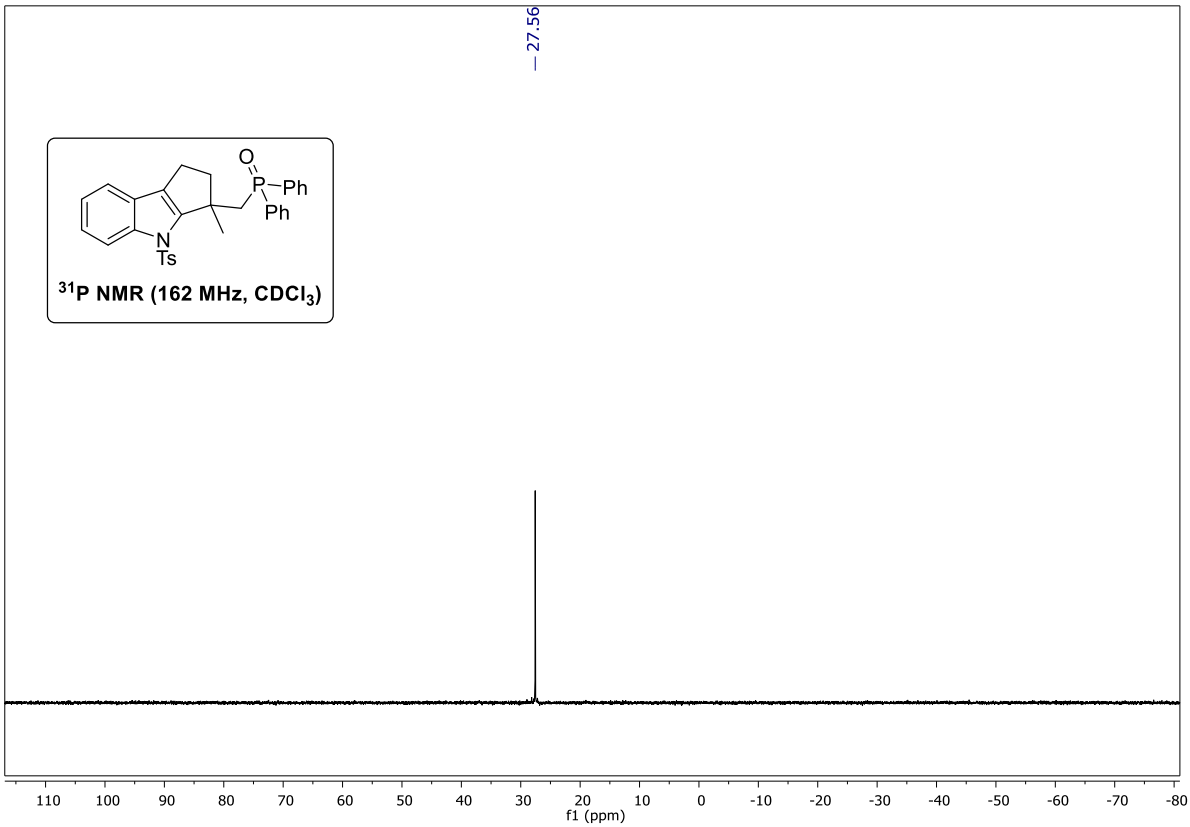




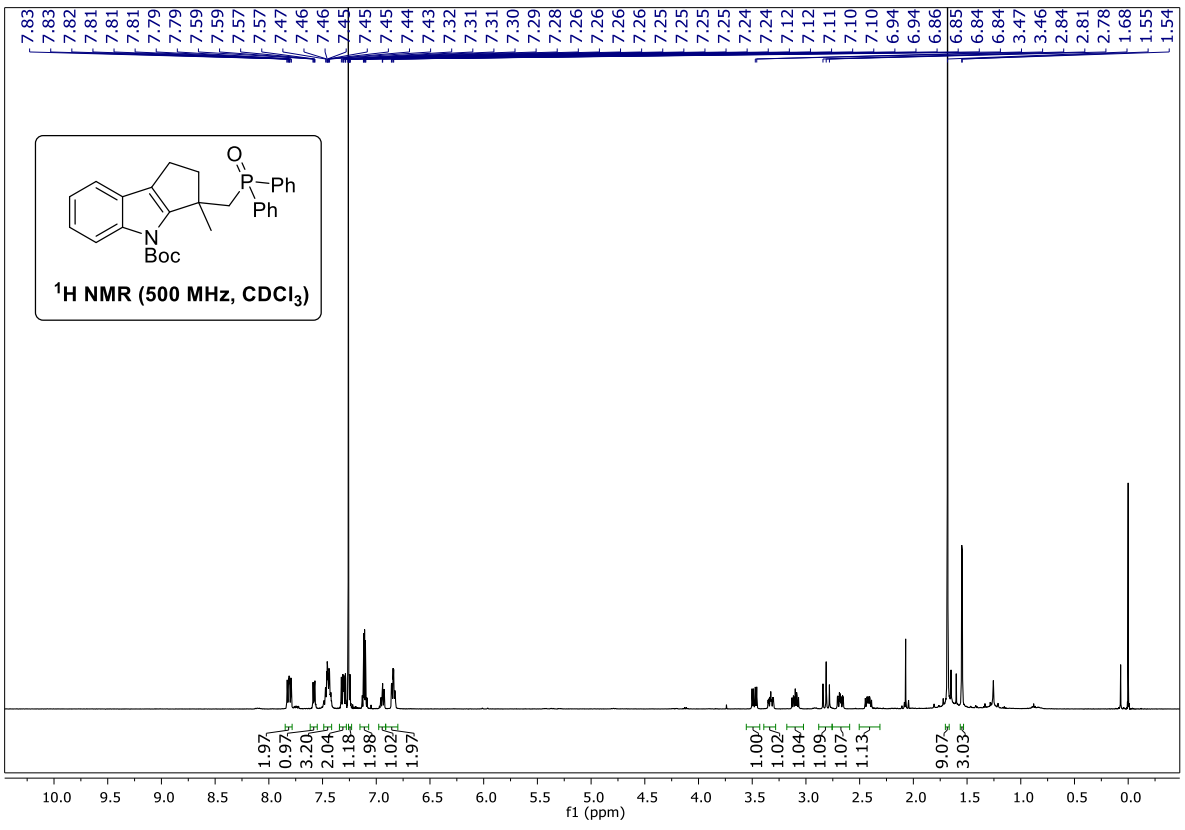
((3-Methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)diphenylphosphine oxide (3aa).

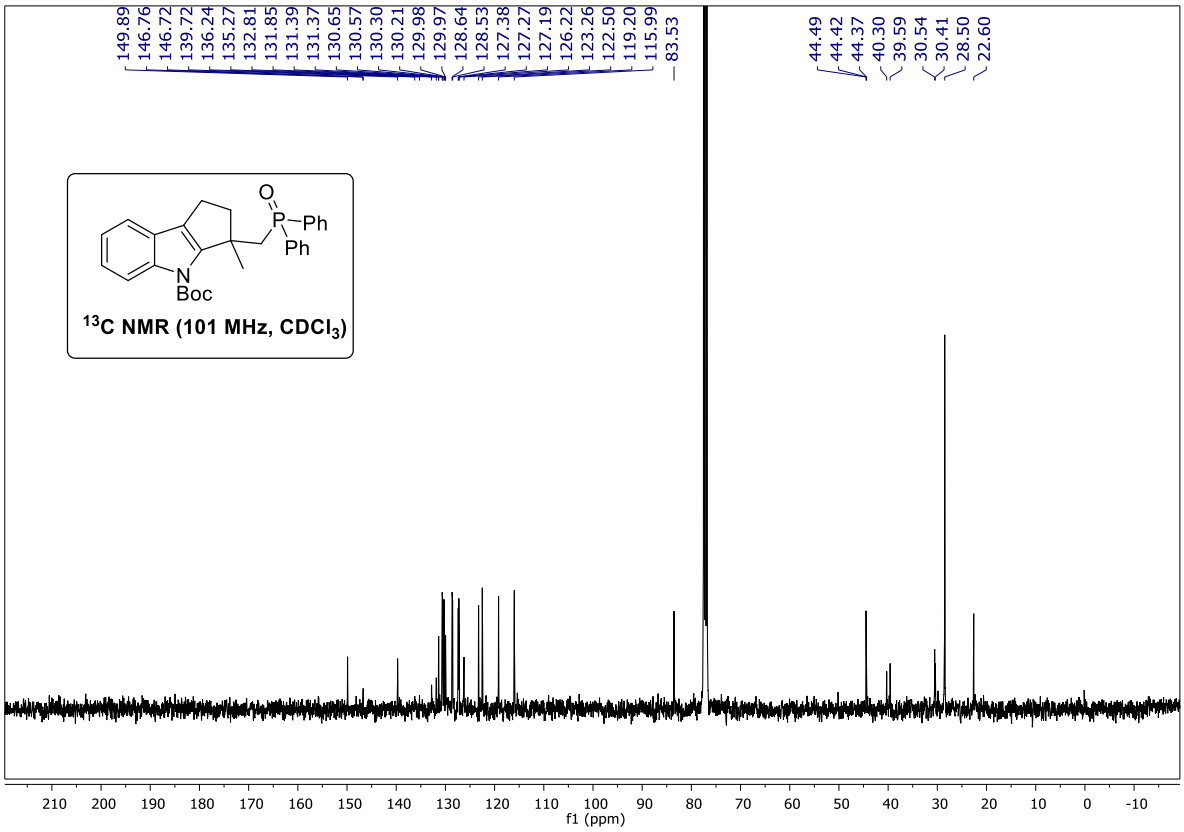


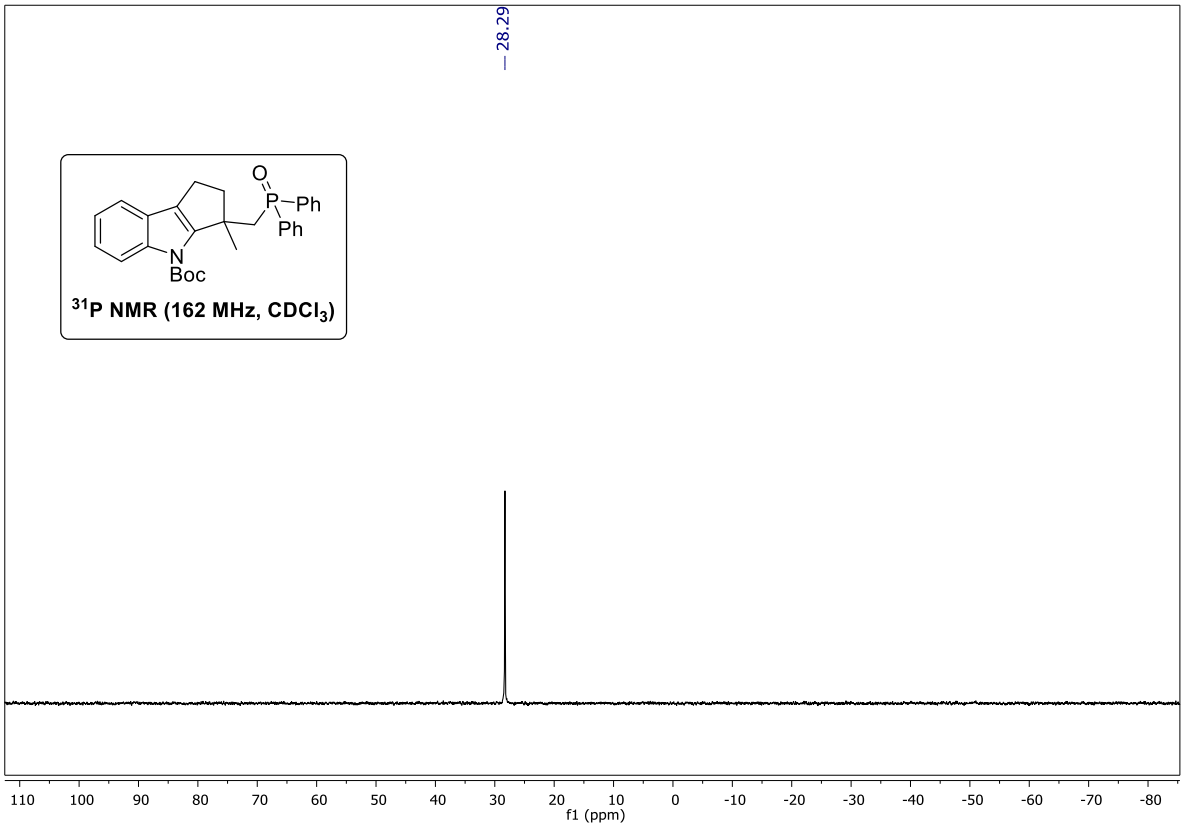




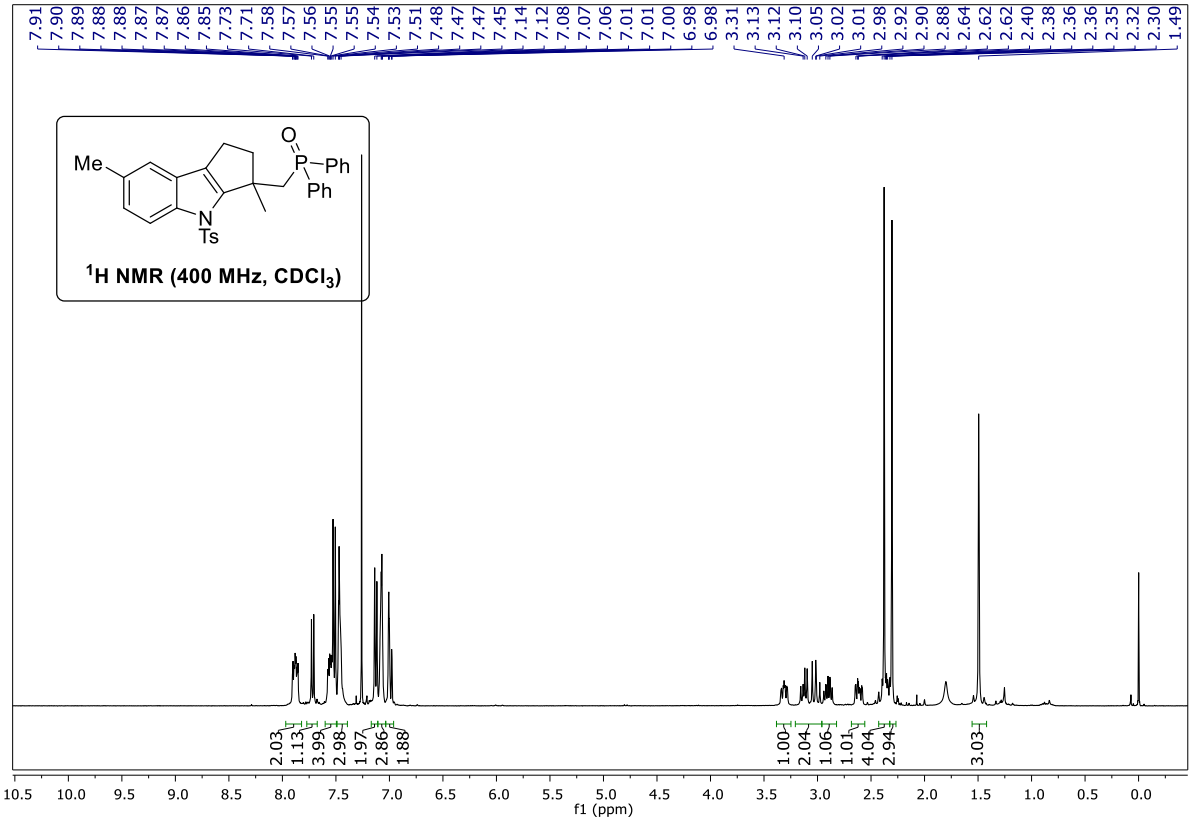
***tert*-Butyl 3-((diphenylphosphoryl)methyl)-3-methyl-2,3-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (3ba):**

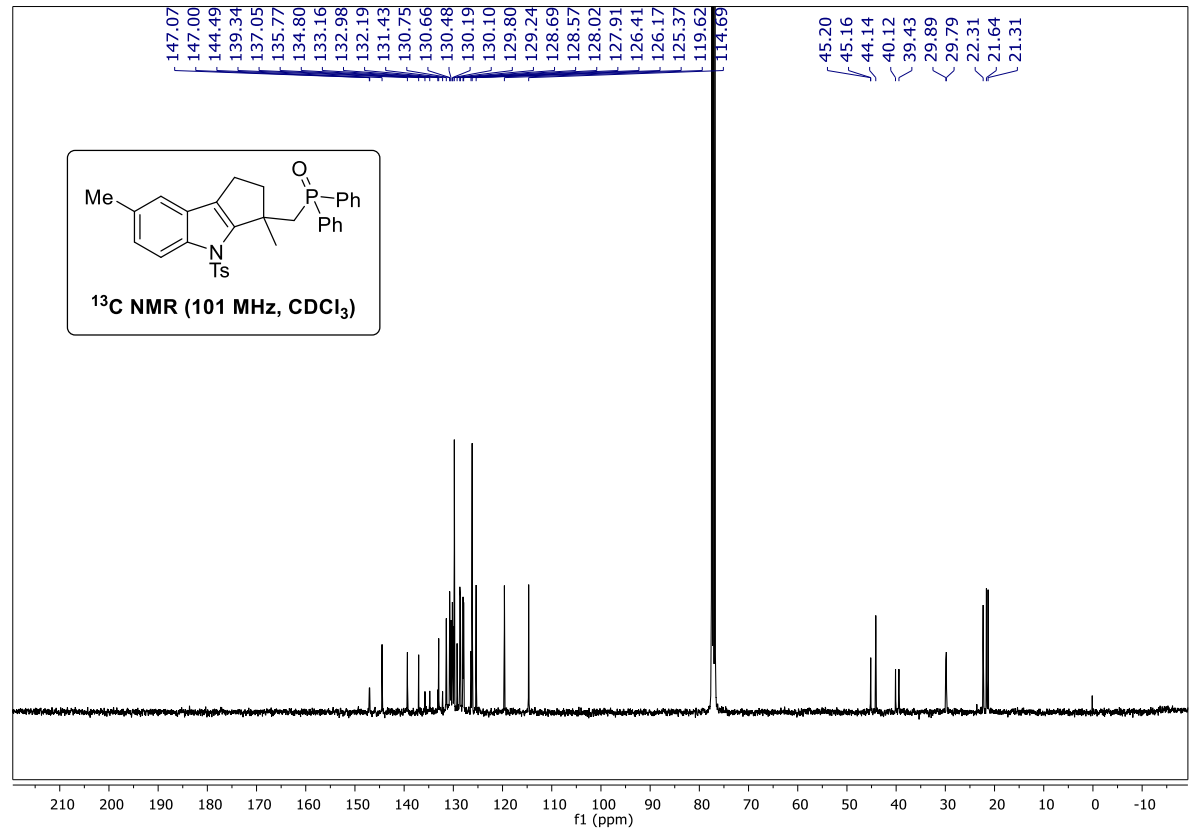


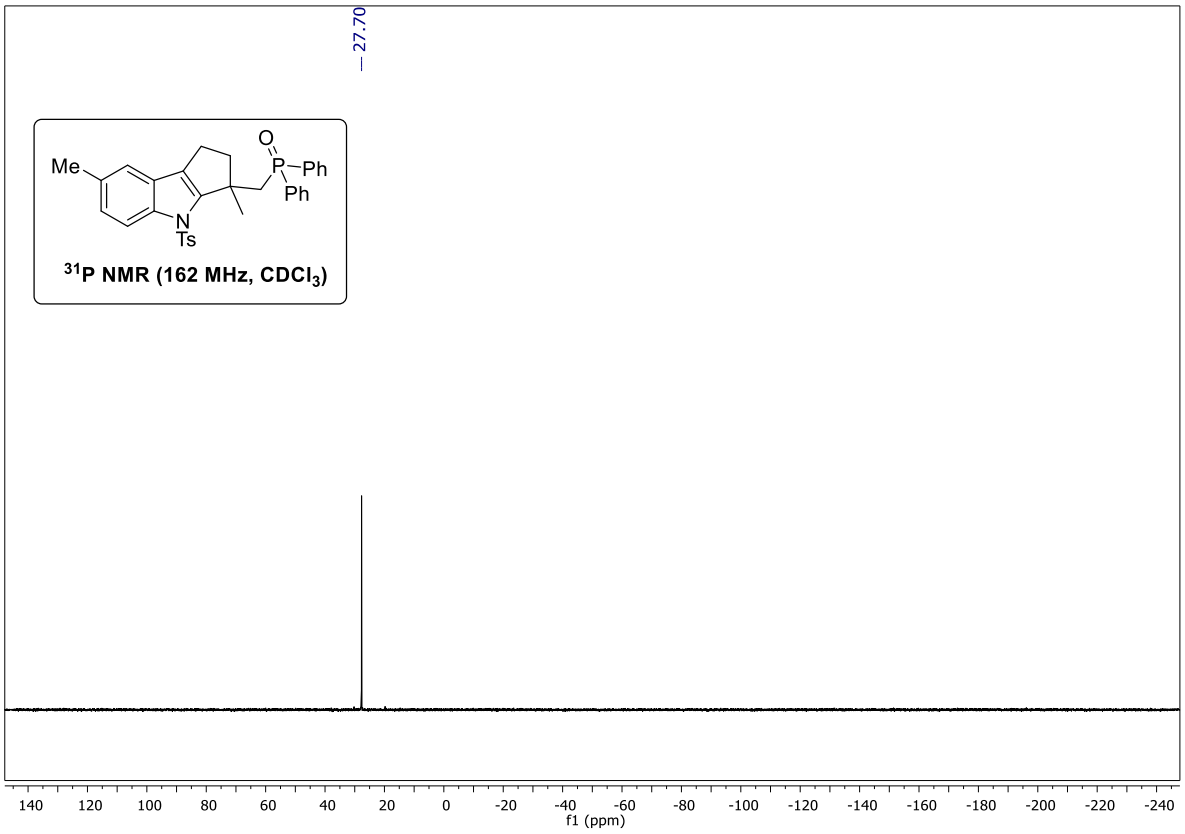

149.89
146.76
146.72
139.72
136.24
135.27
132.81
131.85
131.39
131.37
130.65
130.57
130.30
130.21
129.98
129.97
128.64
128.53
127.38
127.27
127.19
126.22
123.26
122.50
119.20
115.99
83.53
44.49
44.42
44.37
40.30
39.59
30.54
30.41
28.50
22.60
O
P
Ph
Ph
N
Boc
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


28.29
O
P
Ph
Ph
N
Boc
31P NMR (162 MHz, CDCl3)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

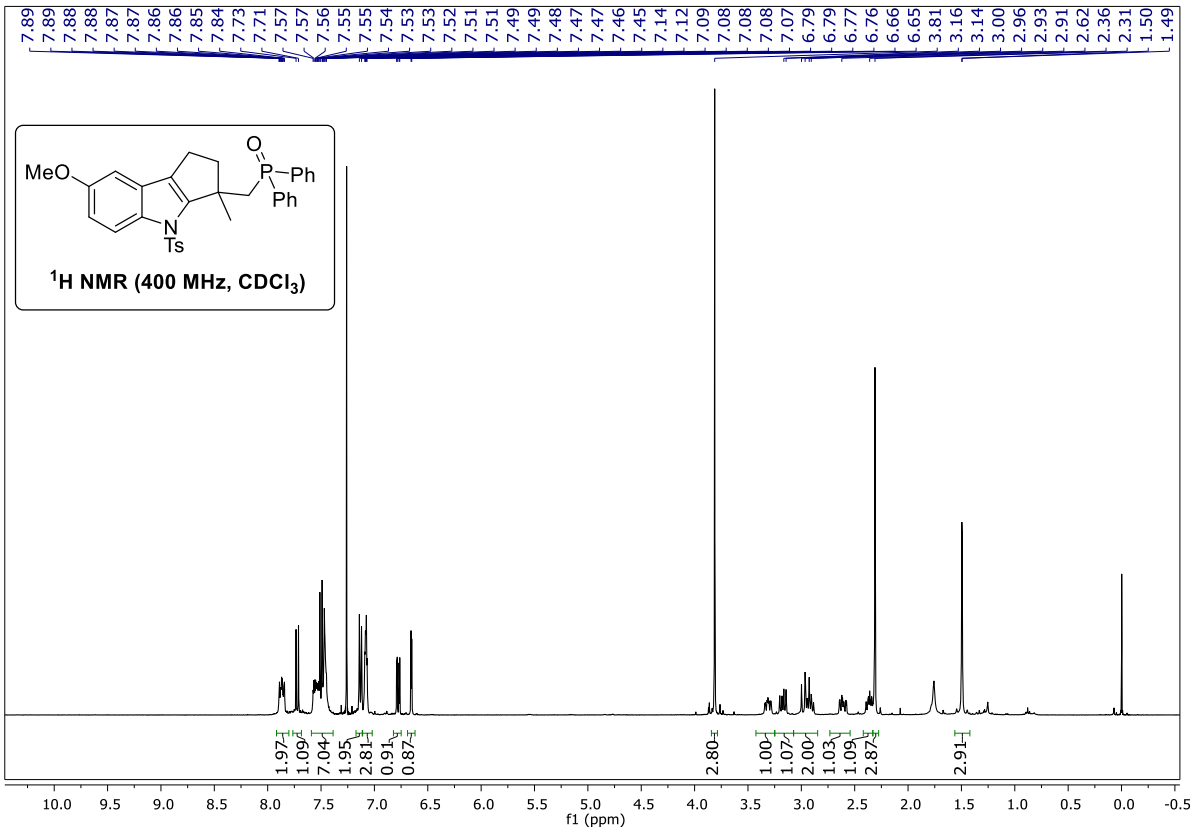
((3,7-Dimethyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)diphenyl-phosphine oxide (3ea):

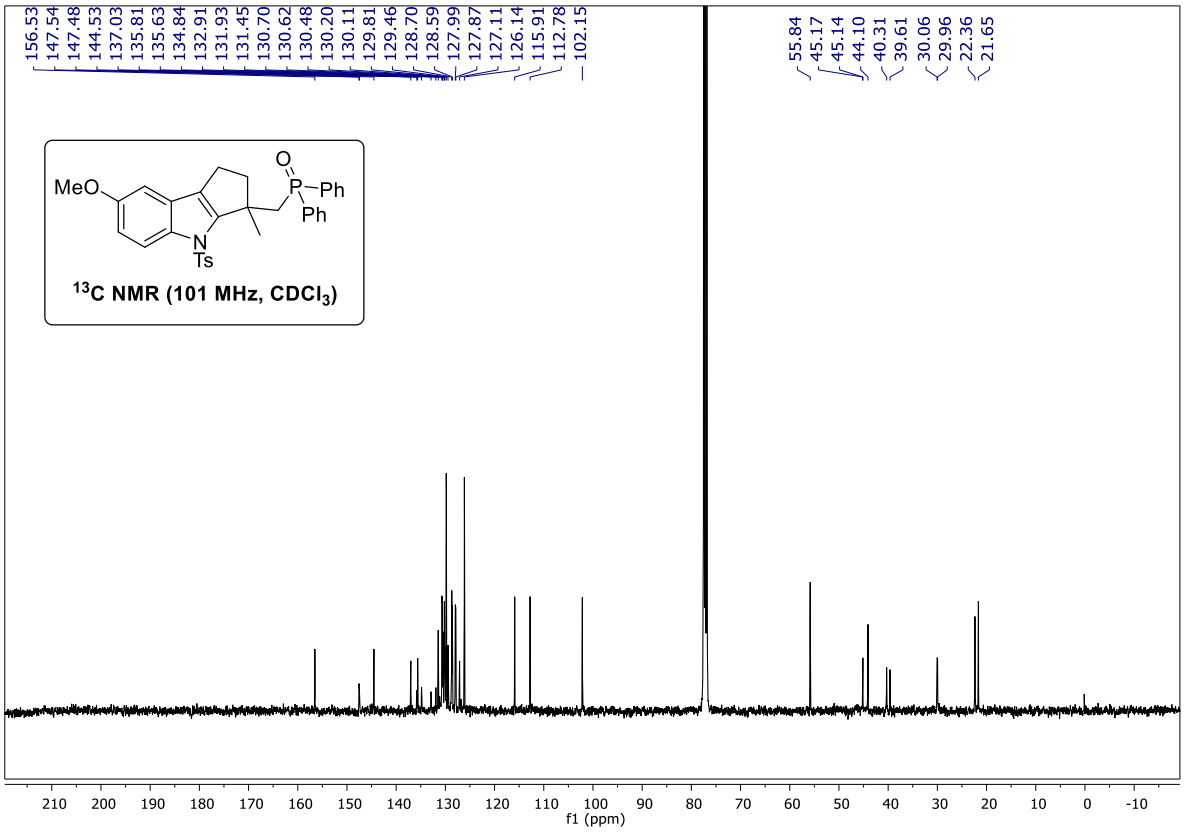


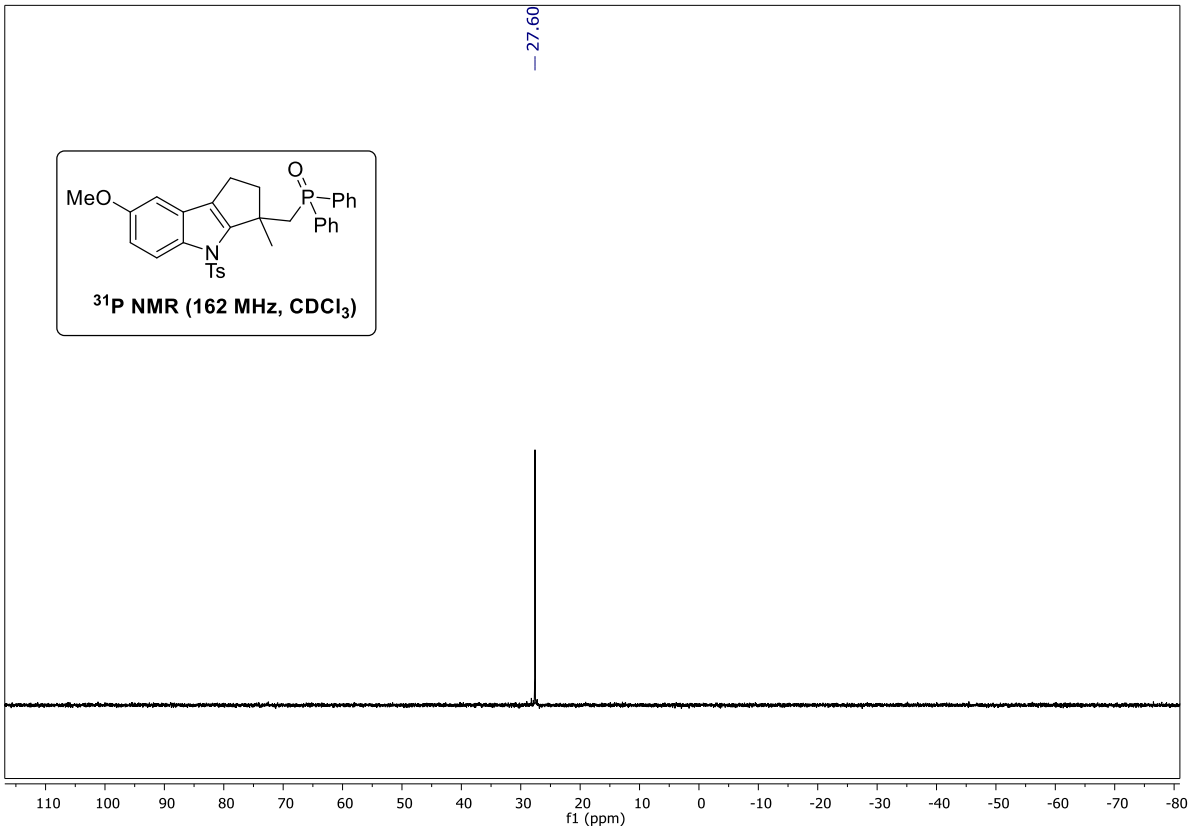




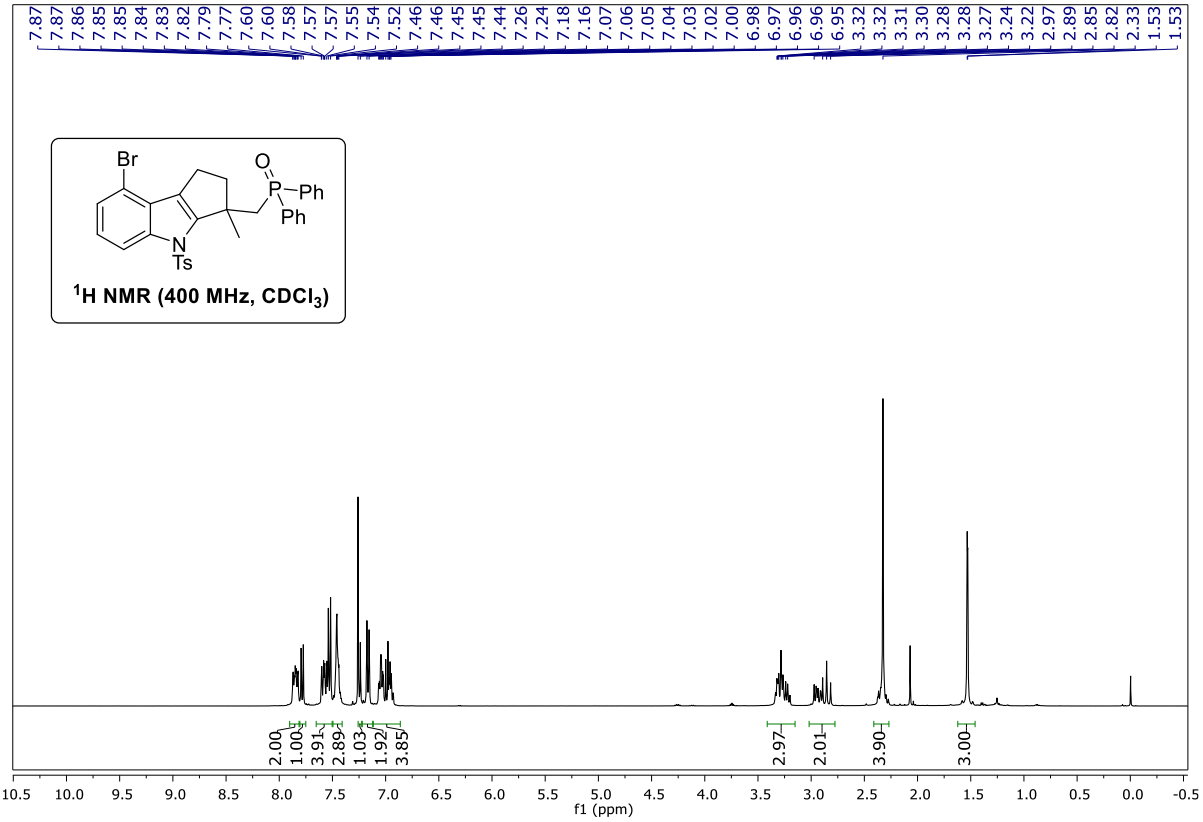
((7-Methoxy-3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl) diphenylphosphine oxide (3fa):

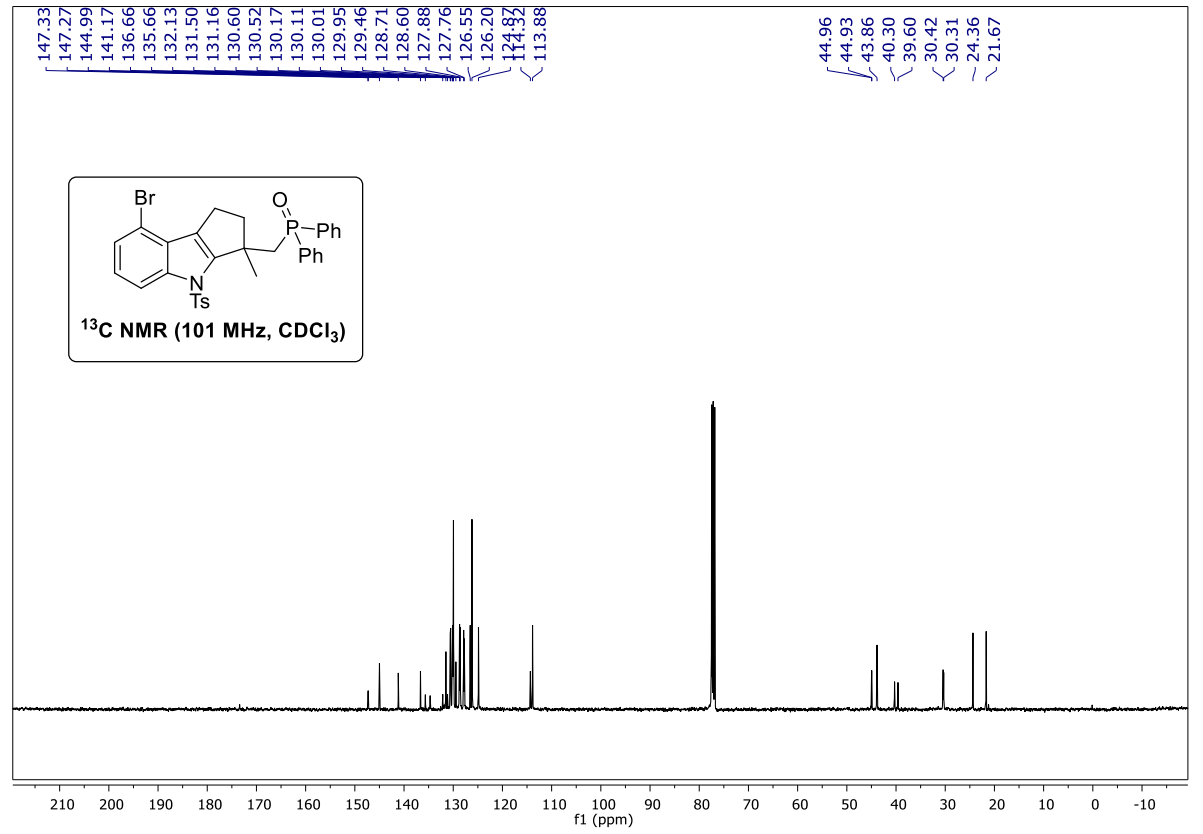


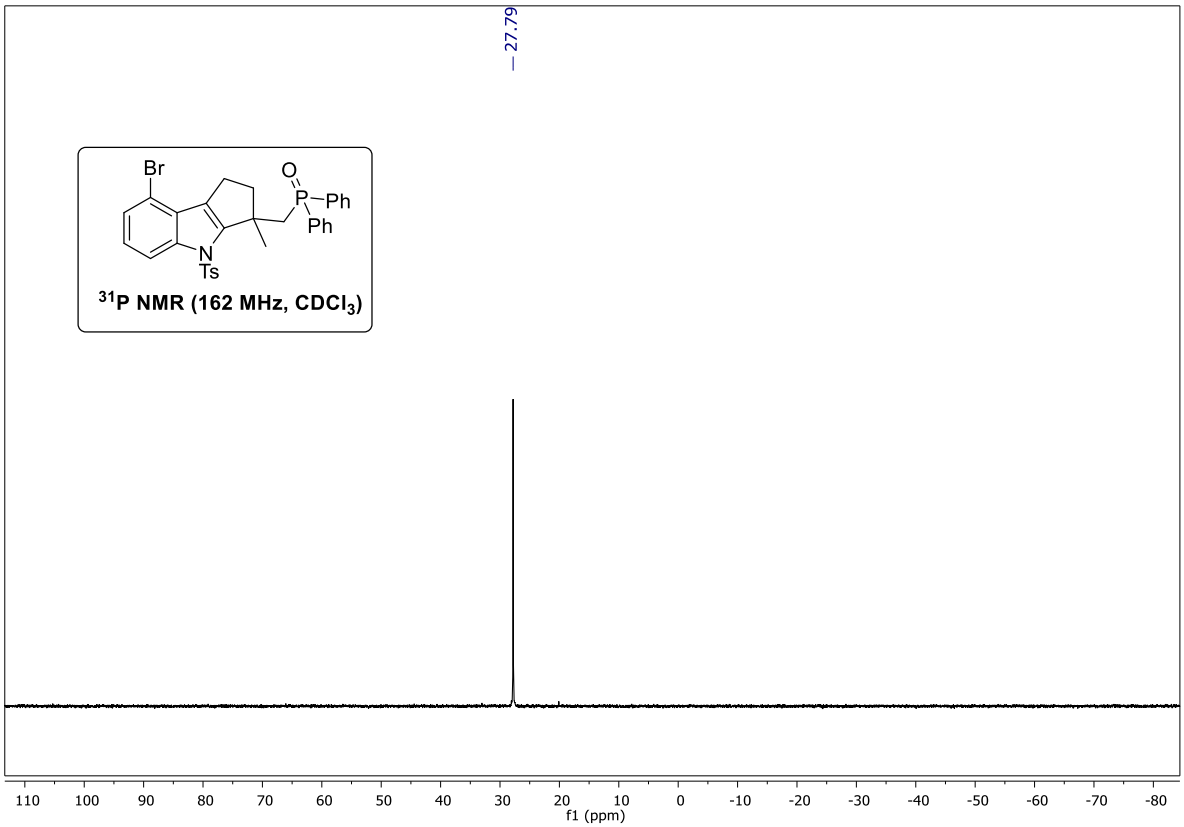

156.53
147.54
147.48
144.53
137.03
135.81
135.63
134.84
132.91
131.93
131.45
130.70
130.62
130.48
130.20
130.11
129.81
129.46
128.70
128.59
127.99
127.87
127.11
126.14
115.91
112.78
102.15
55.84
45.17
45.14
44.10
40.31
39.61
30.06
29.96
22.36
21.65
MeO
O
P
Ph
Ph
N
Ts
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


27.60
MeO
O
P
Ph
Ph
N
Ts
31P NMR (162 MHz, CDCl3)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

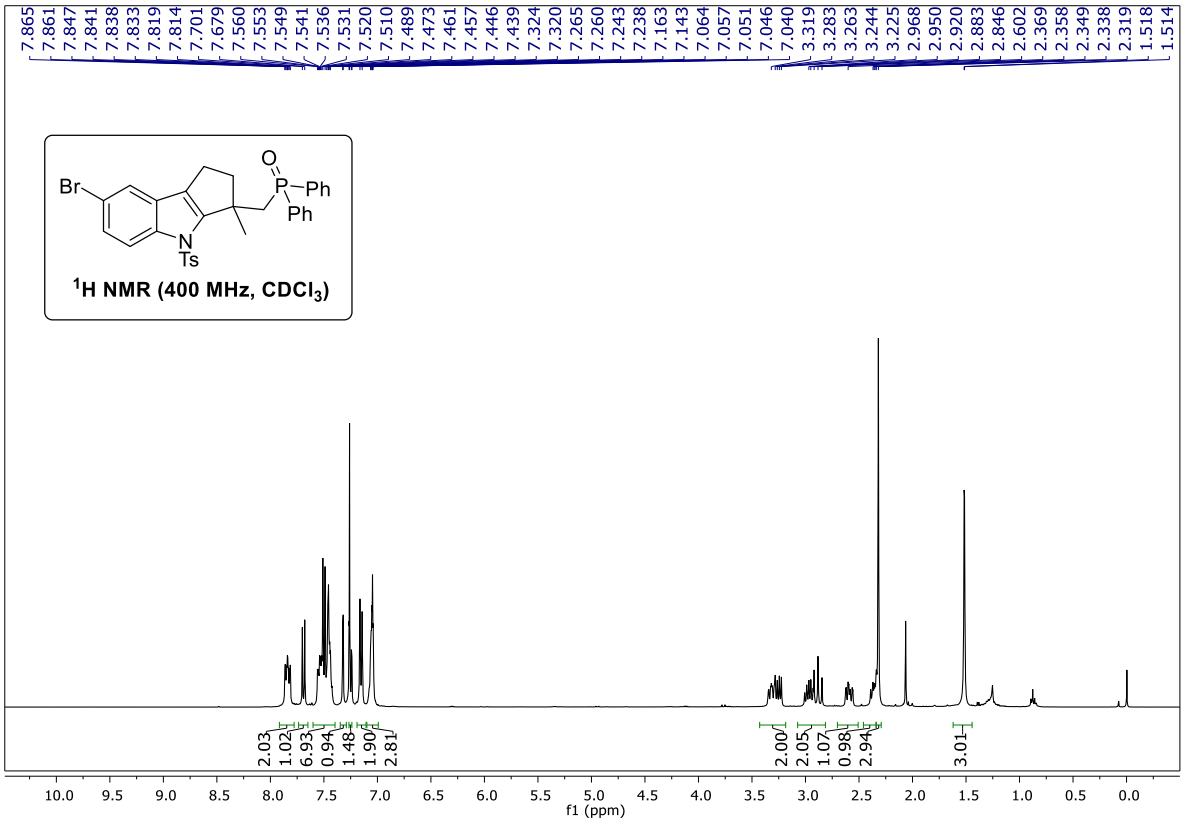
((8-Bromo-3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl) diphenylphosphine oxide (3ga):

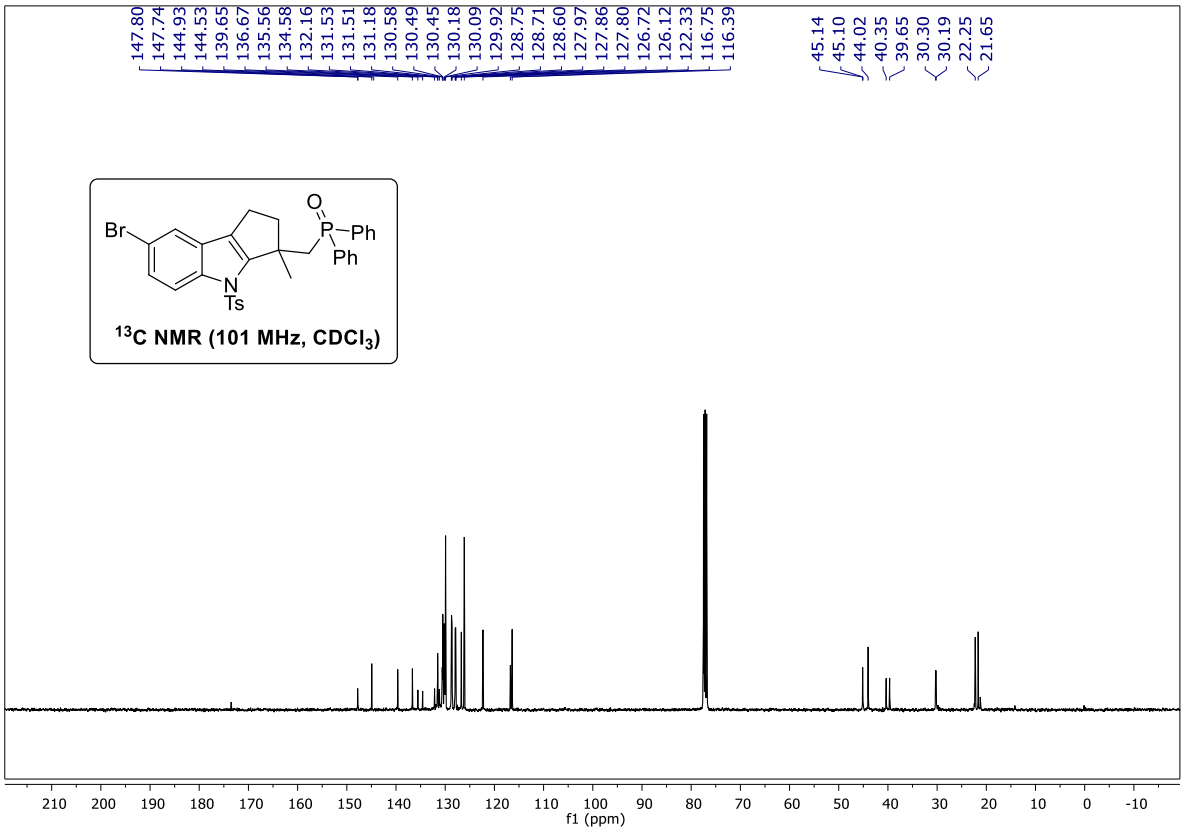


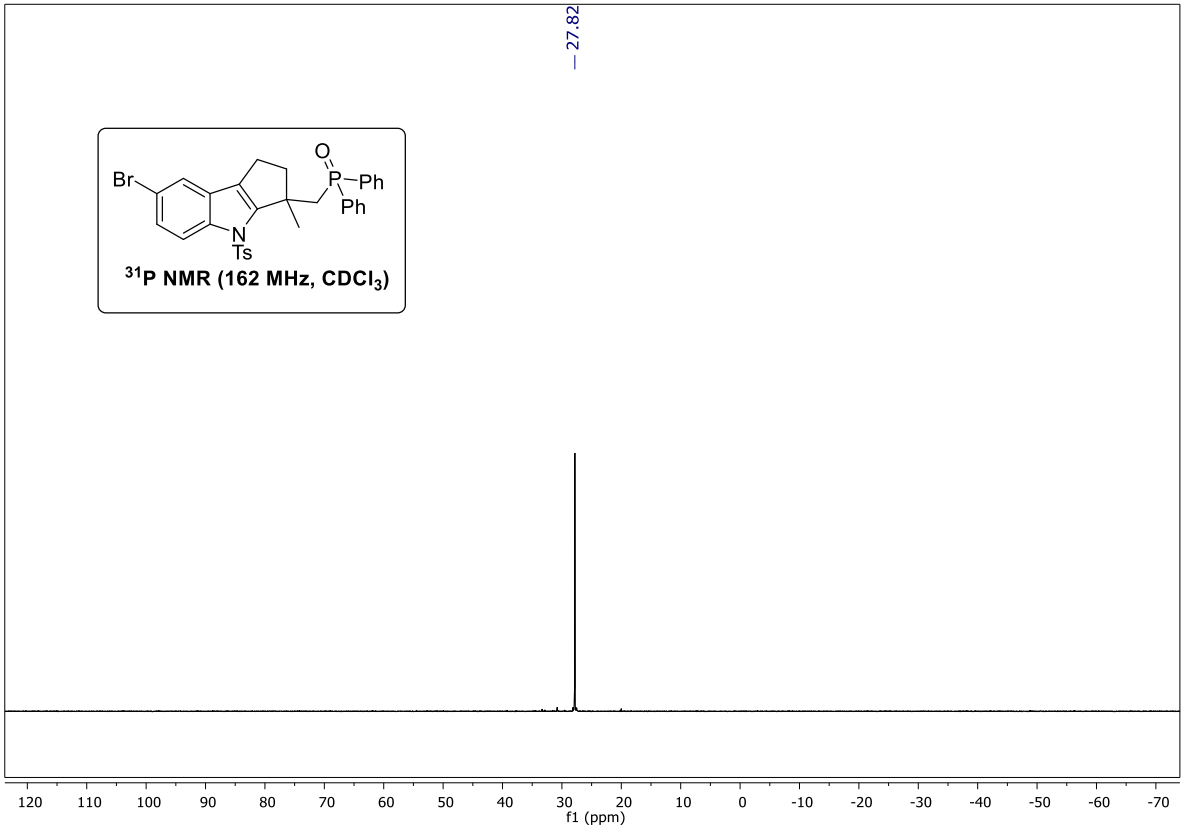




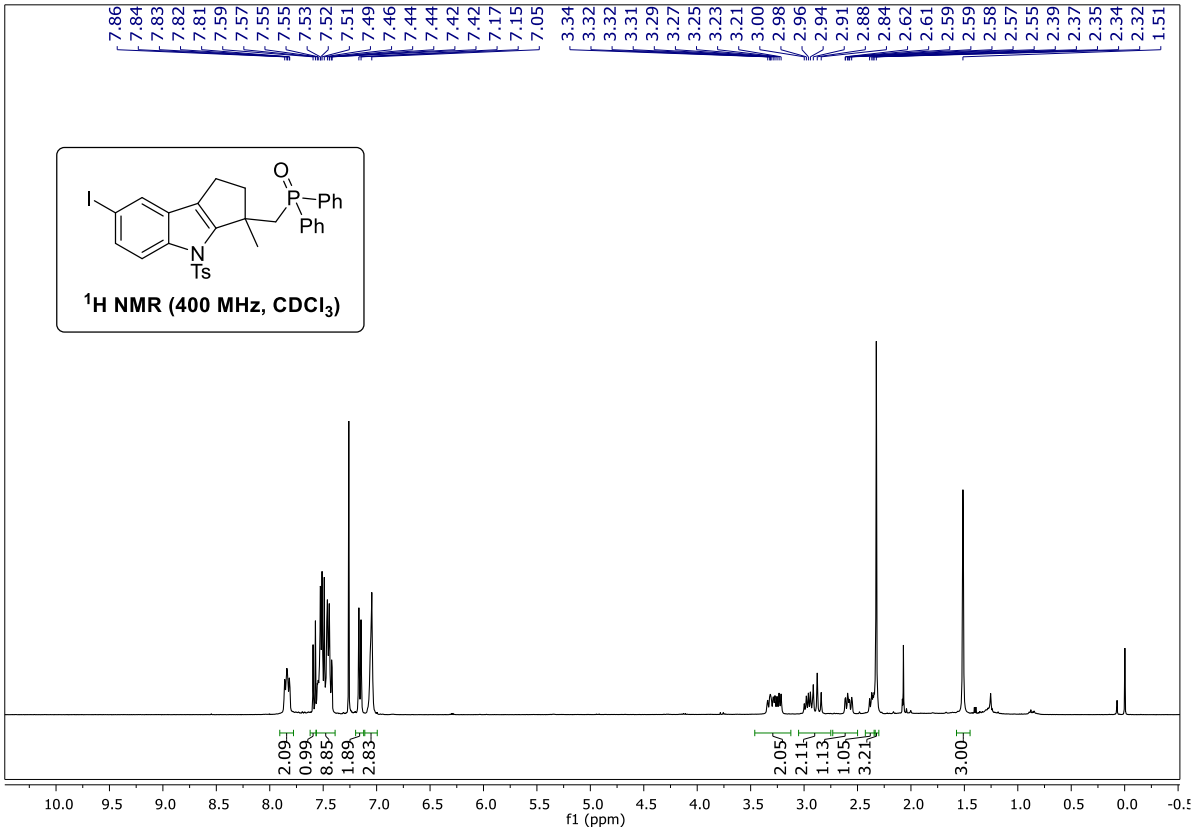
((7-Bromo-3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl) diphenylphosphine oxide (3ha):

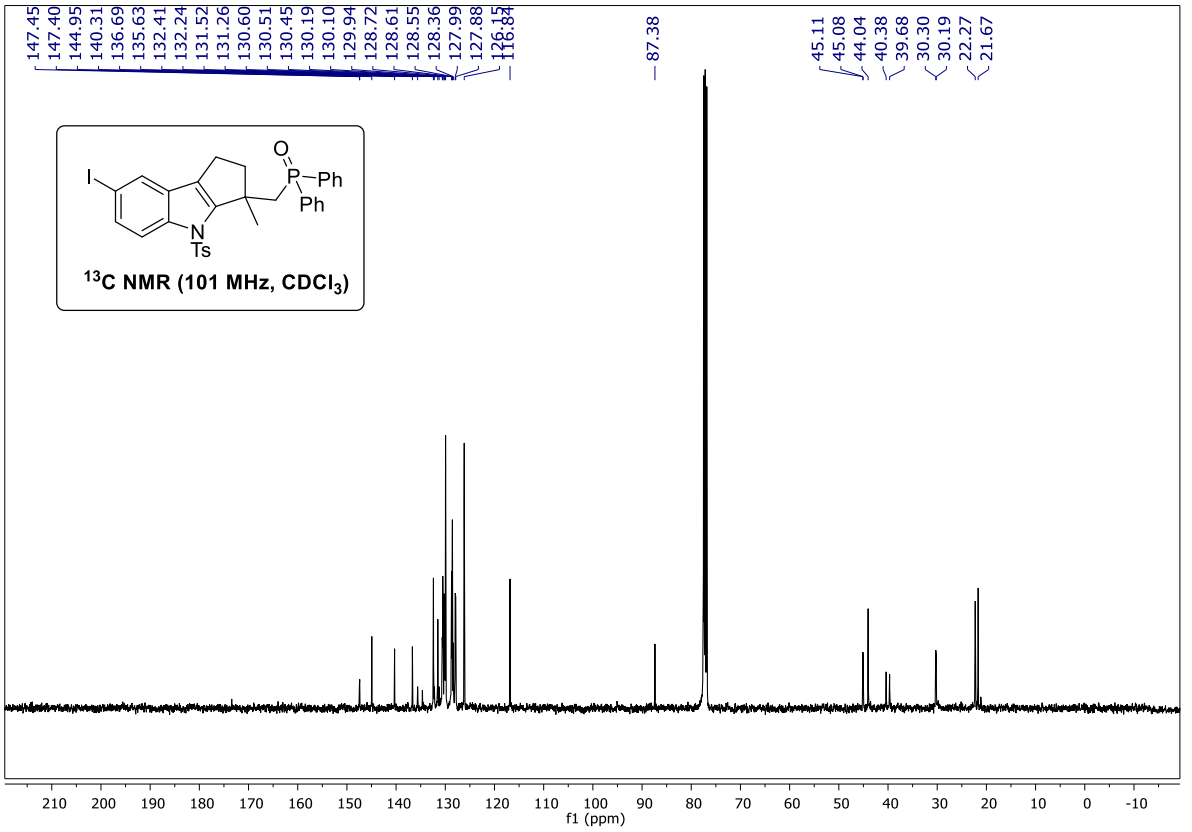


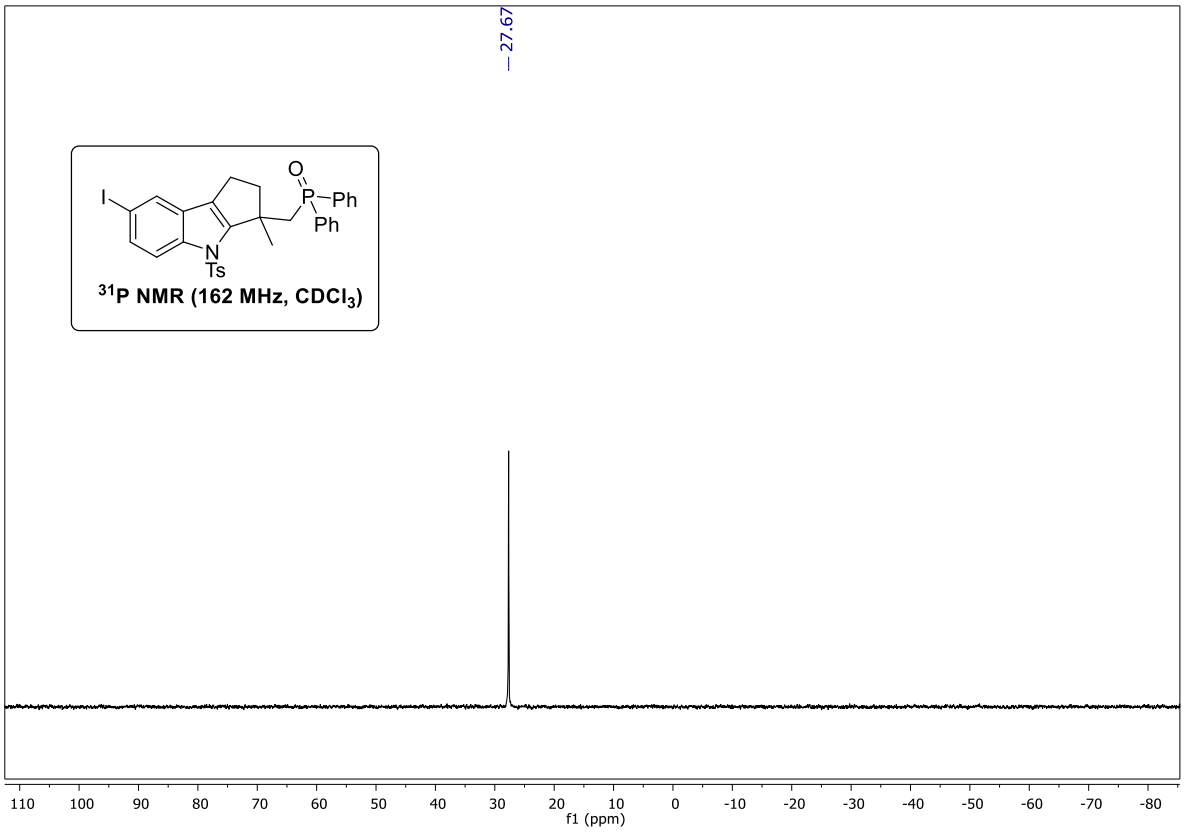

147.80
147.74
144.93
144.53
139.65
136.67
135.56
134.58
132.16
131.53
131.51
131.18
130.58
130.49
130.45
130.18
130.09
129.92
128.75
128.71
128.60
127.97
127.86
127.80
126.72
126.12
122.33
116.75
116.39
45.14
45.10
44.02
40.35
39.65
30.30
30.19
22.25
21.65
Br
O
P
Ph
Ph
N
Ts
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


27.82
Br
O
P
Ph
Ph
N
Ts
31P NMR (162 MHz, CDCl3)
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

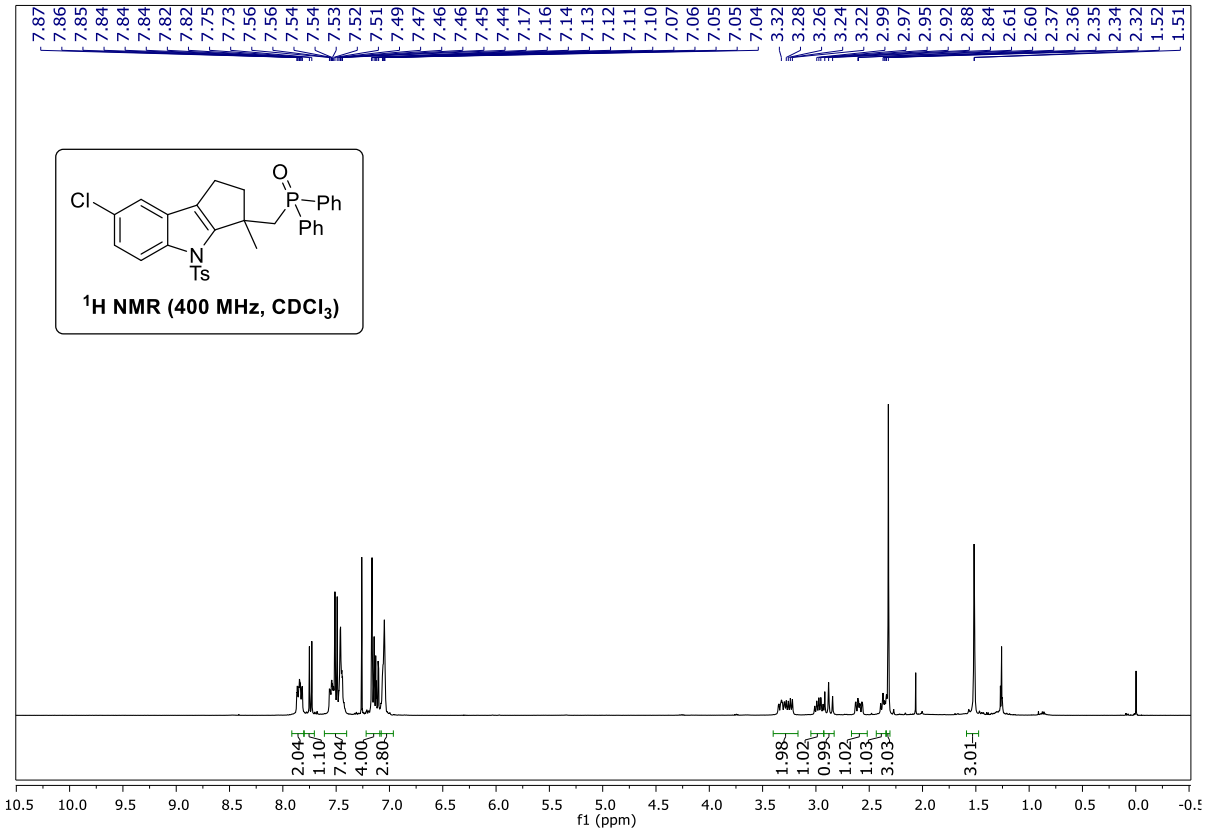
((7-Iodo-3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl) diphenylphosphine oxide (3ia):

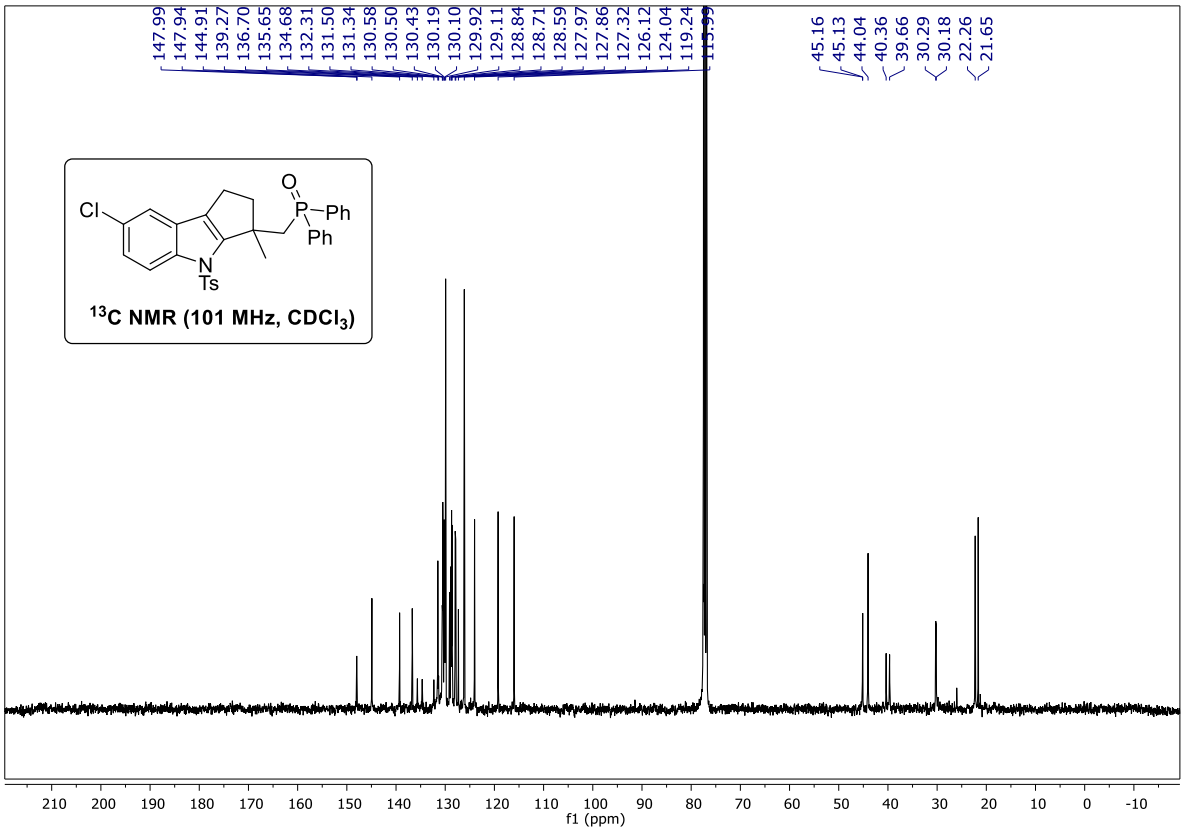


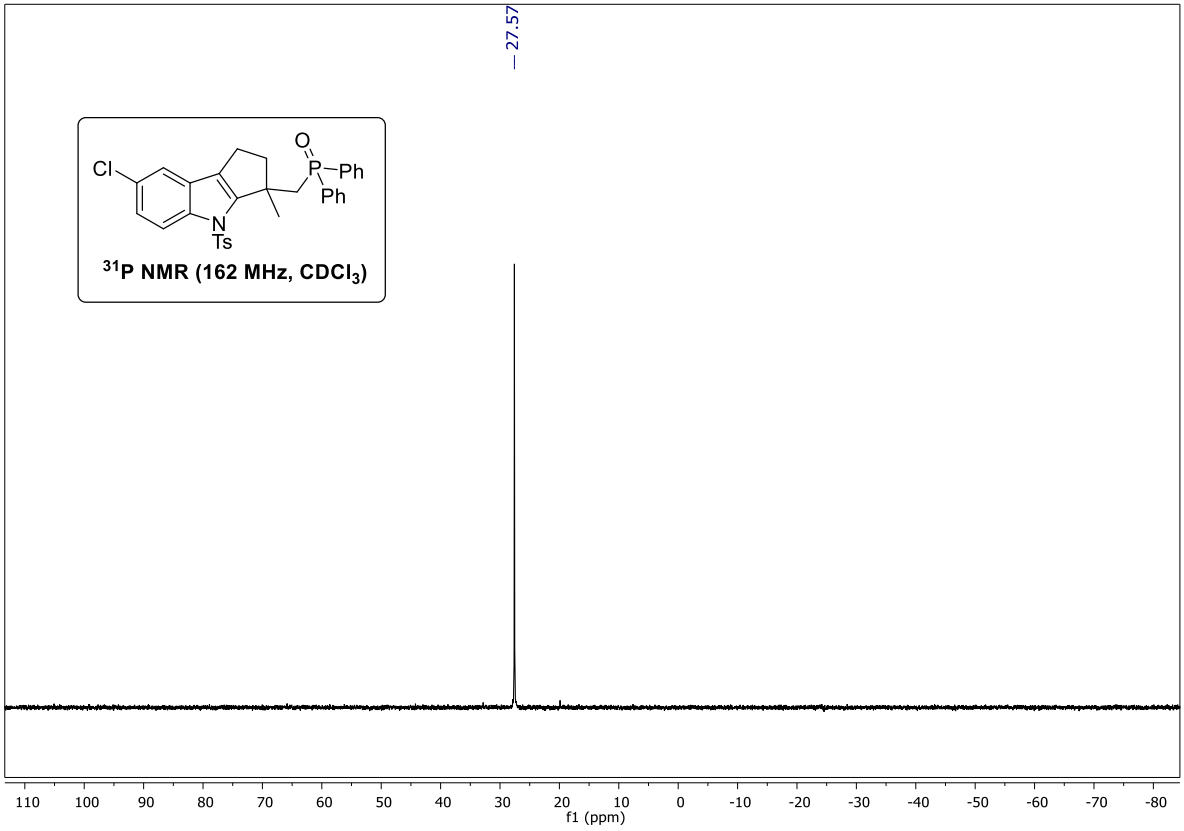




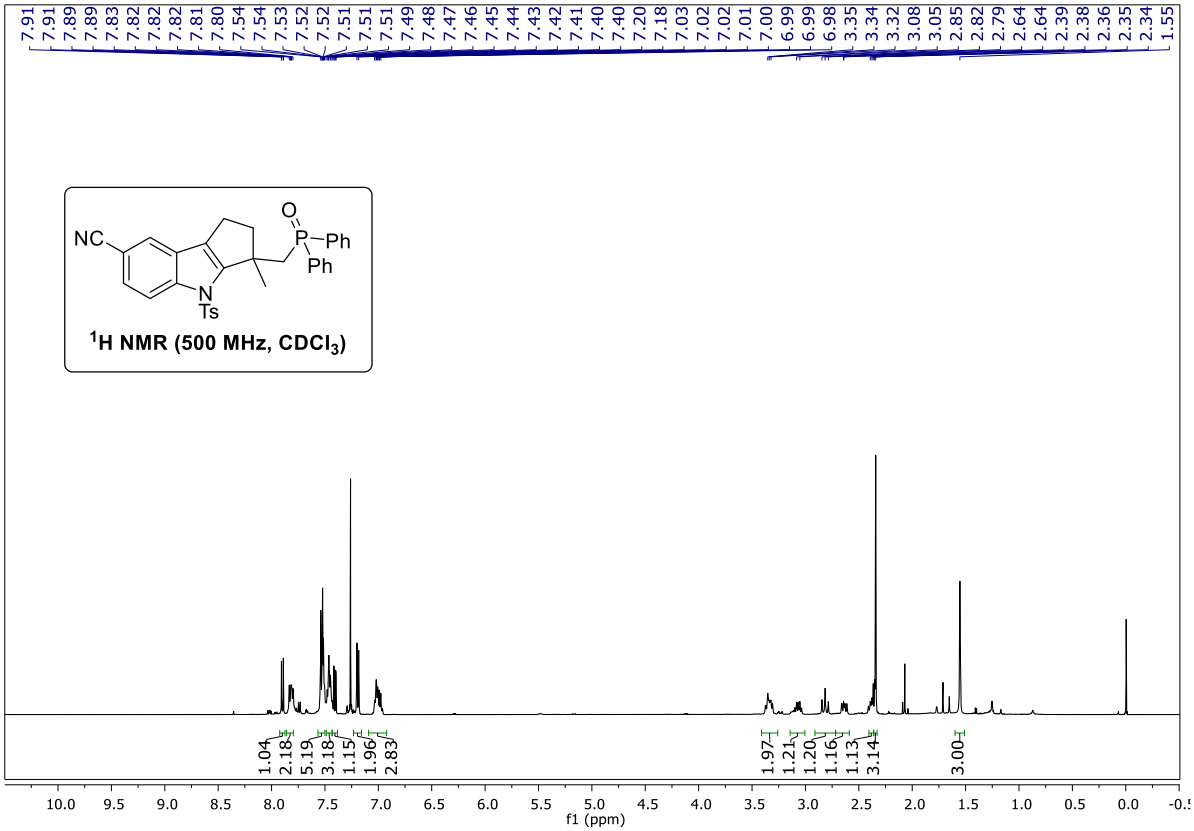
((7-Chloro-3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl) diphenylphosphine oxide (3ja):

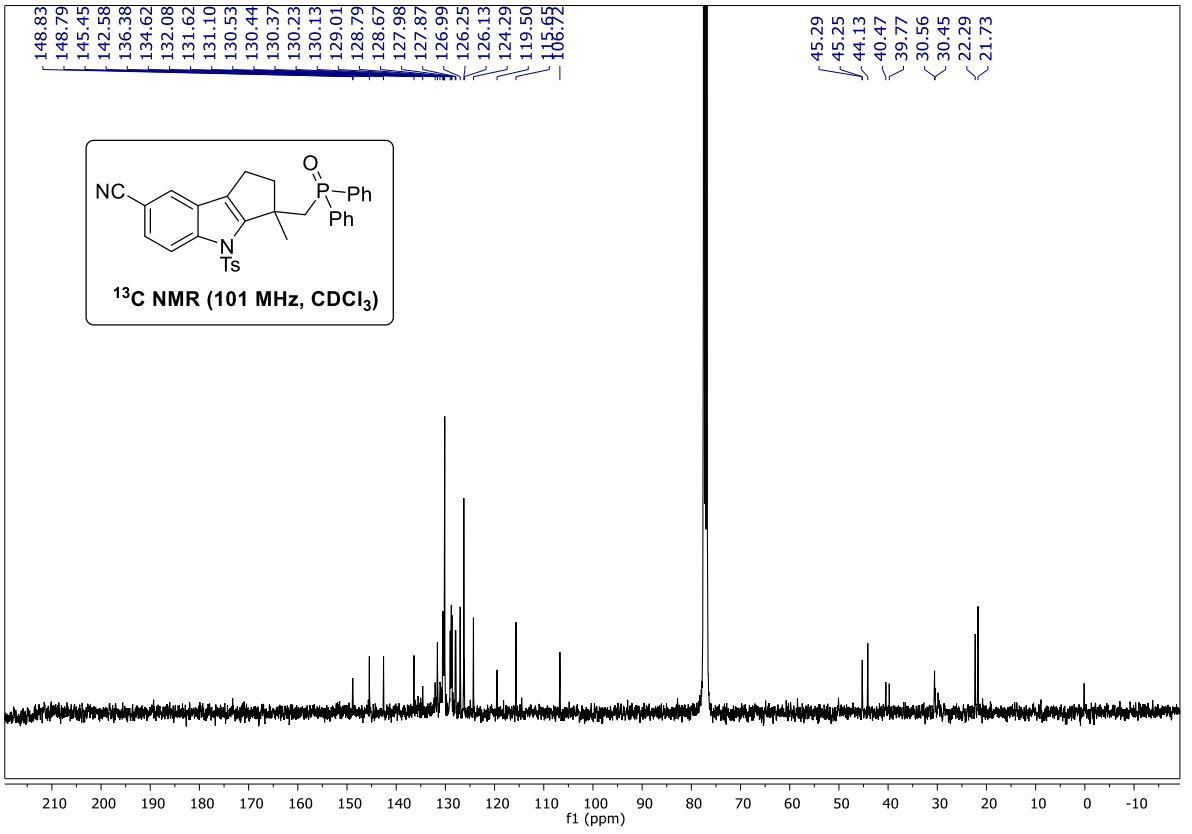


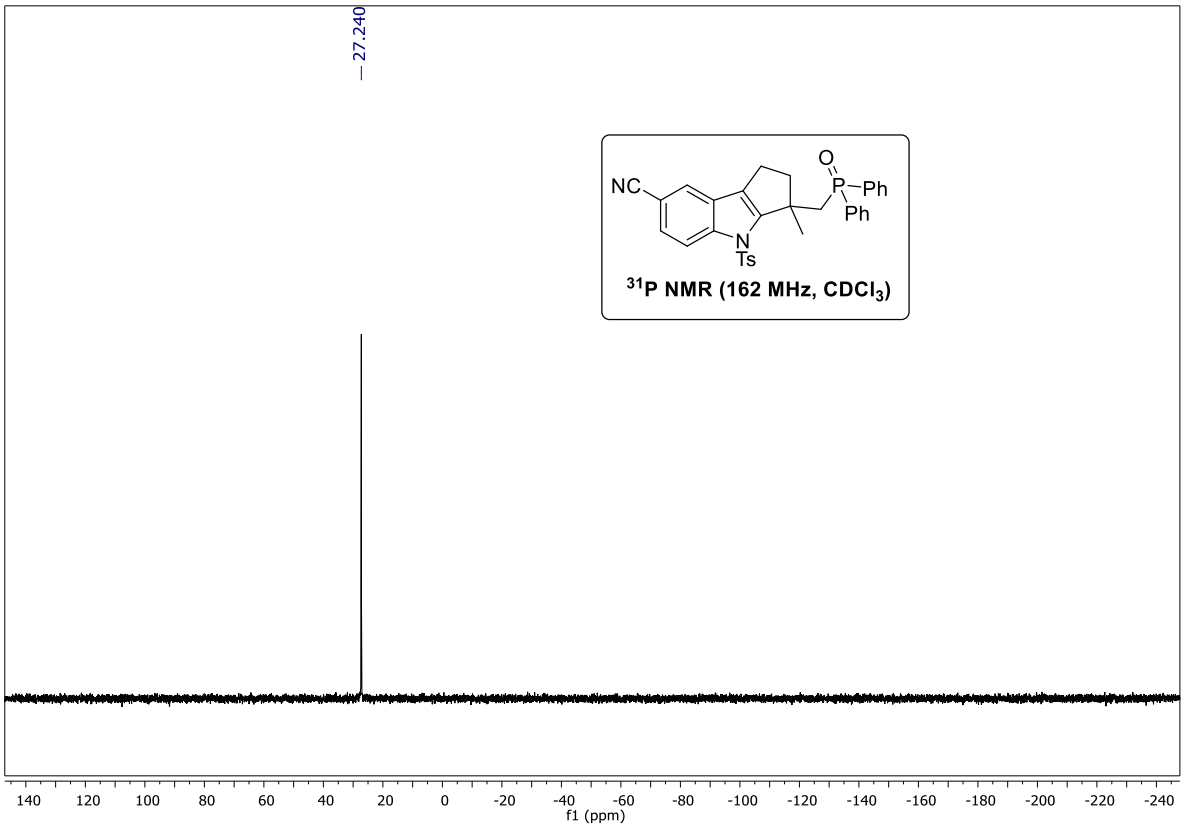

147.99
147.94
144.91
139.27
136.70
135.65
134.68
132.31
131.50
131.34
130.58
130.50
130.43
130.19
130.10
129.92
129.11
128.84
128.71
128.59
127.97
127.86
127.32
126.12
124.04
119.24
115.99
45.16
45.13
44.04
40.36
39.66
30.29
30.18
22.26
21.65
Cl
O
P
Ph
Ph
N
Ts
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


27.57
Cl
O
P
Ph
Ph
N
Ts
31P NMR (162 MHz, CDCl3)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

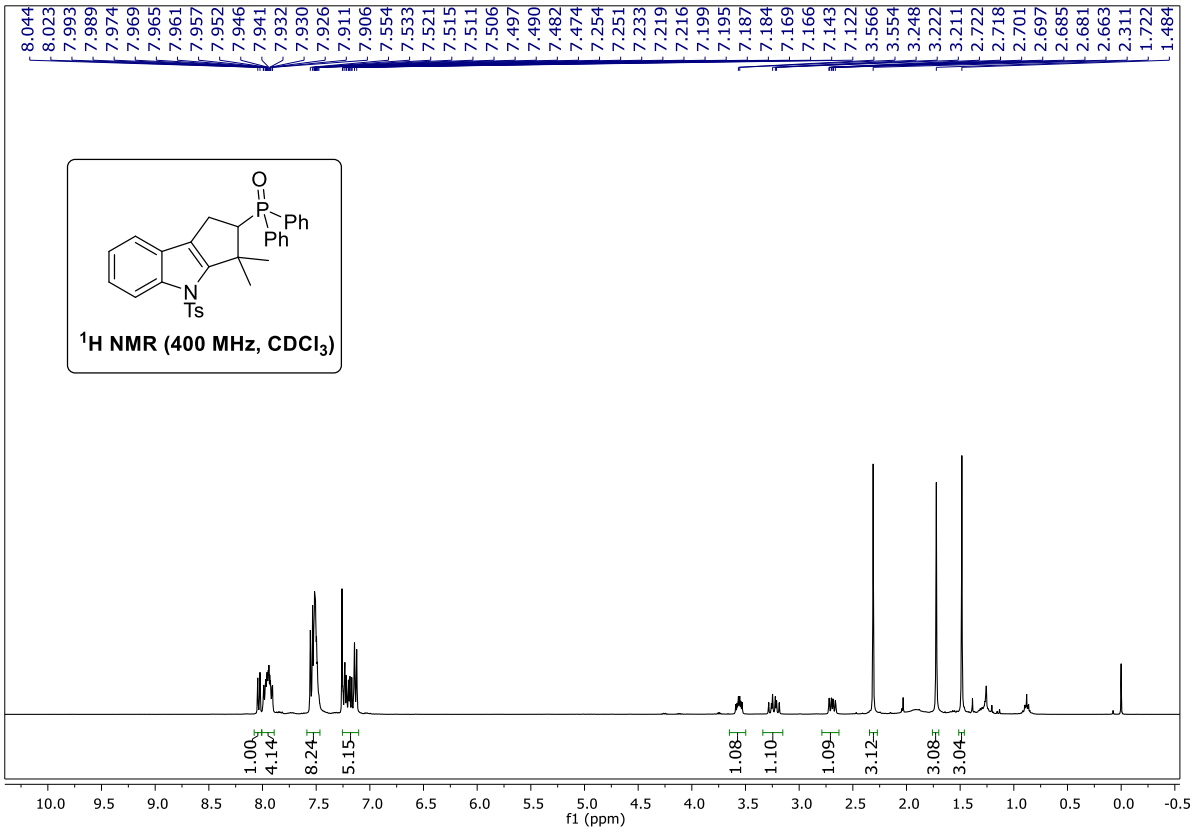
3-((Diphenylphosphoryl)methyl)-3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole -7-carbonitrile (3ka):

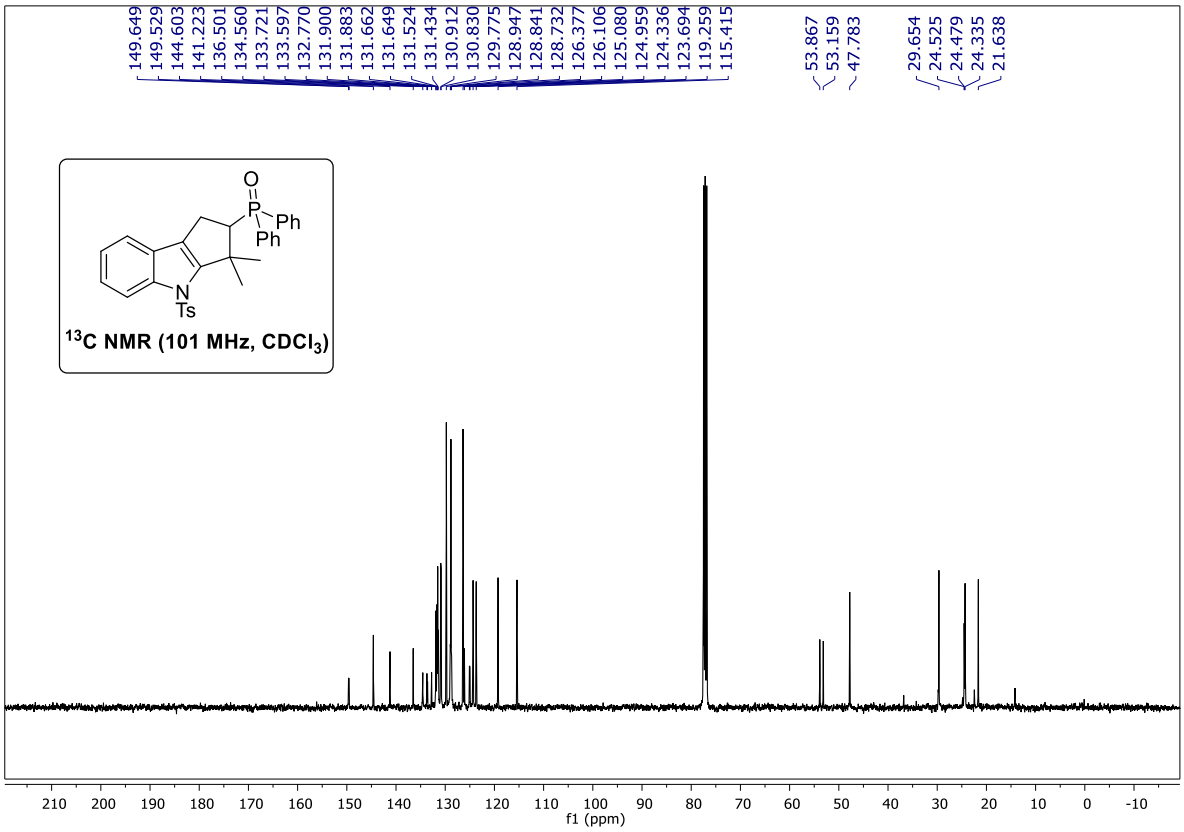


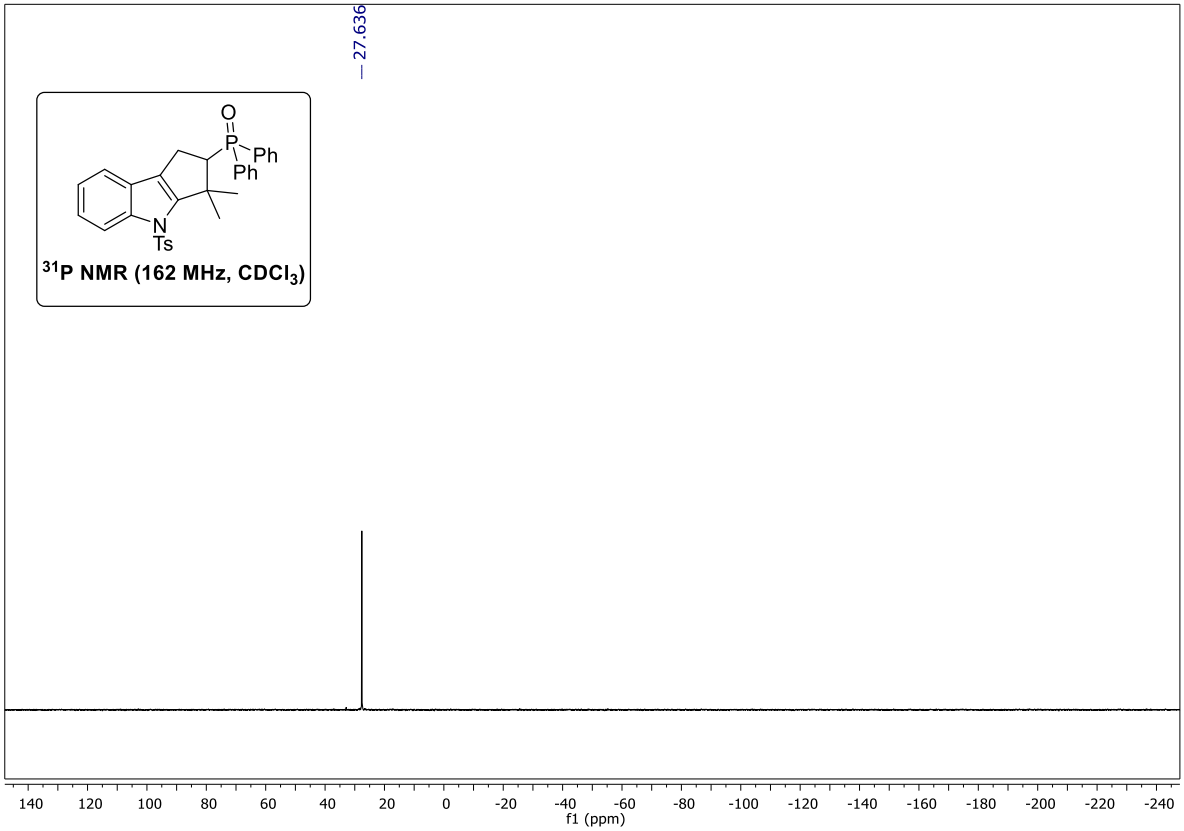




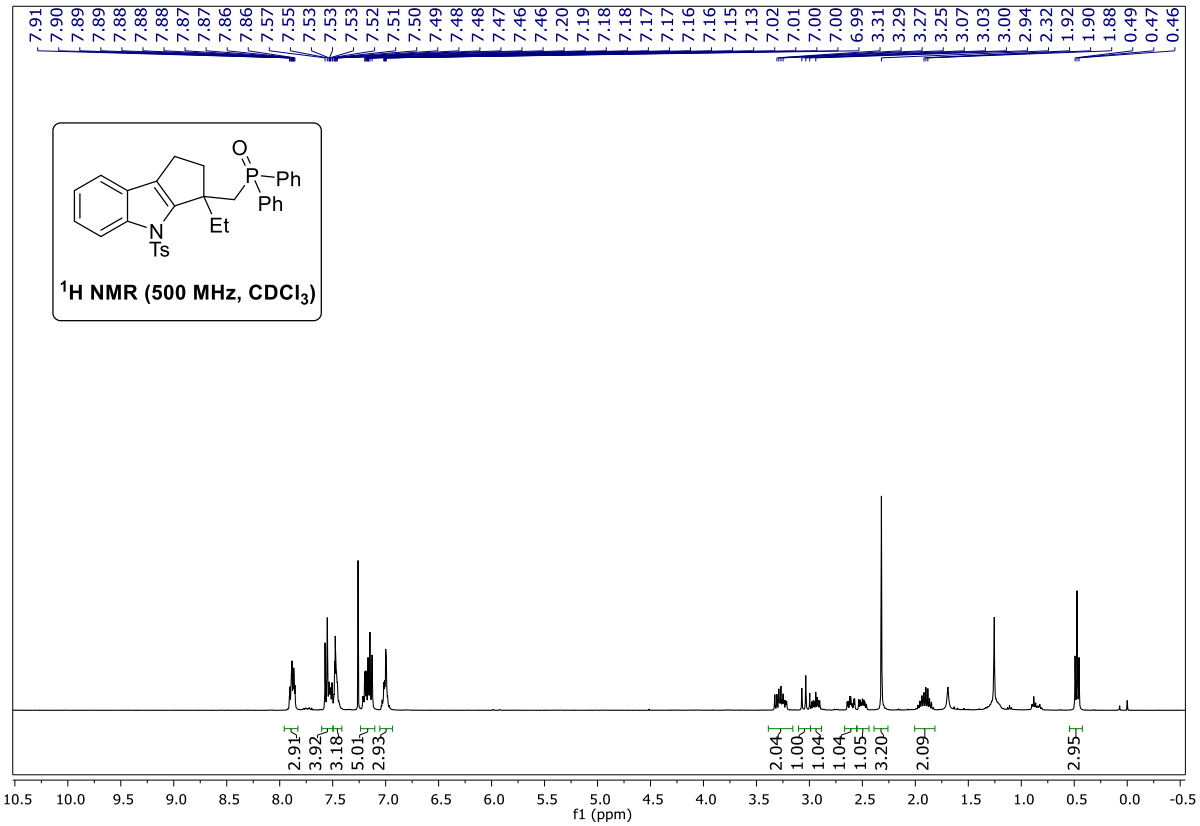
(3,3-Dimethyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-2-yl)diphenylphosphine oxide (3ma):

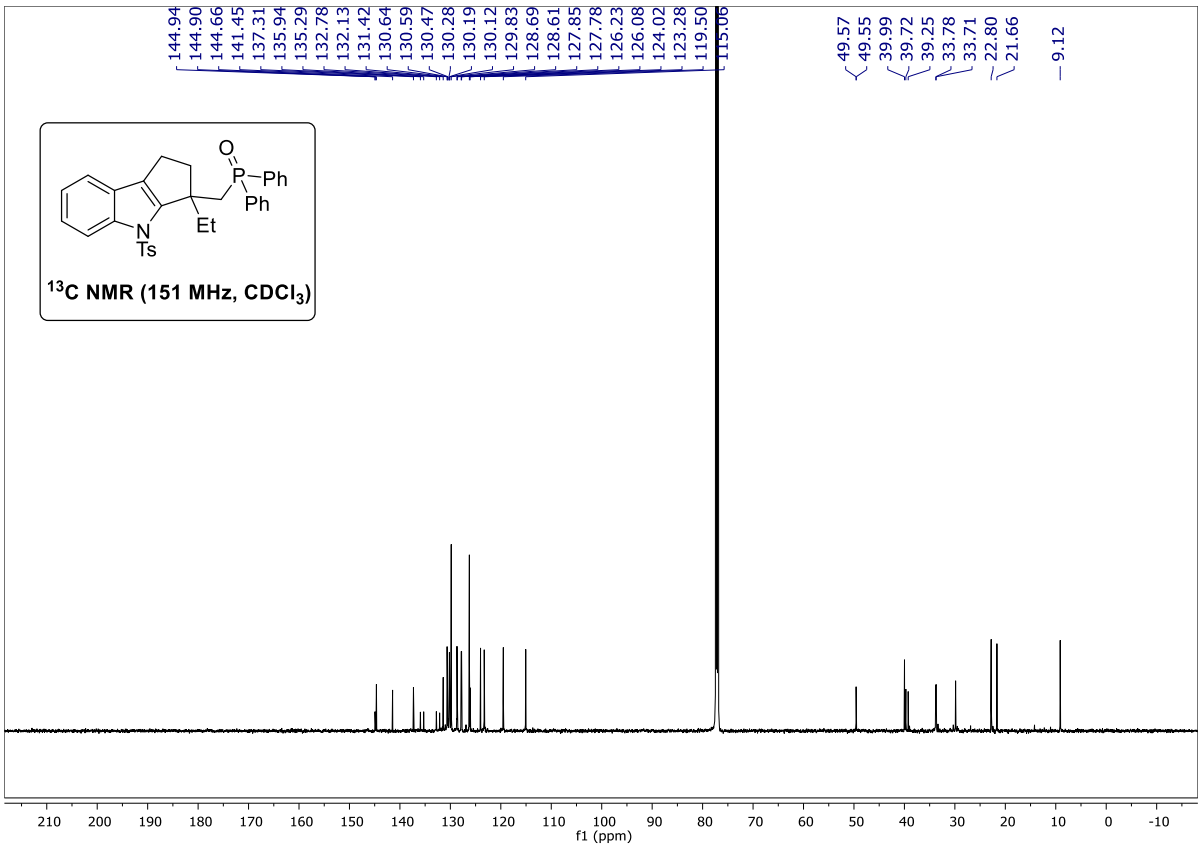


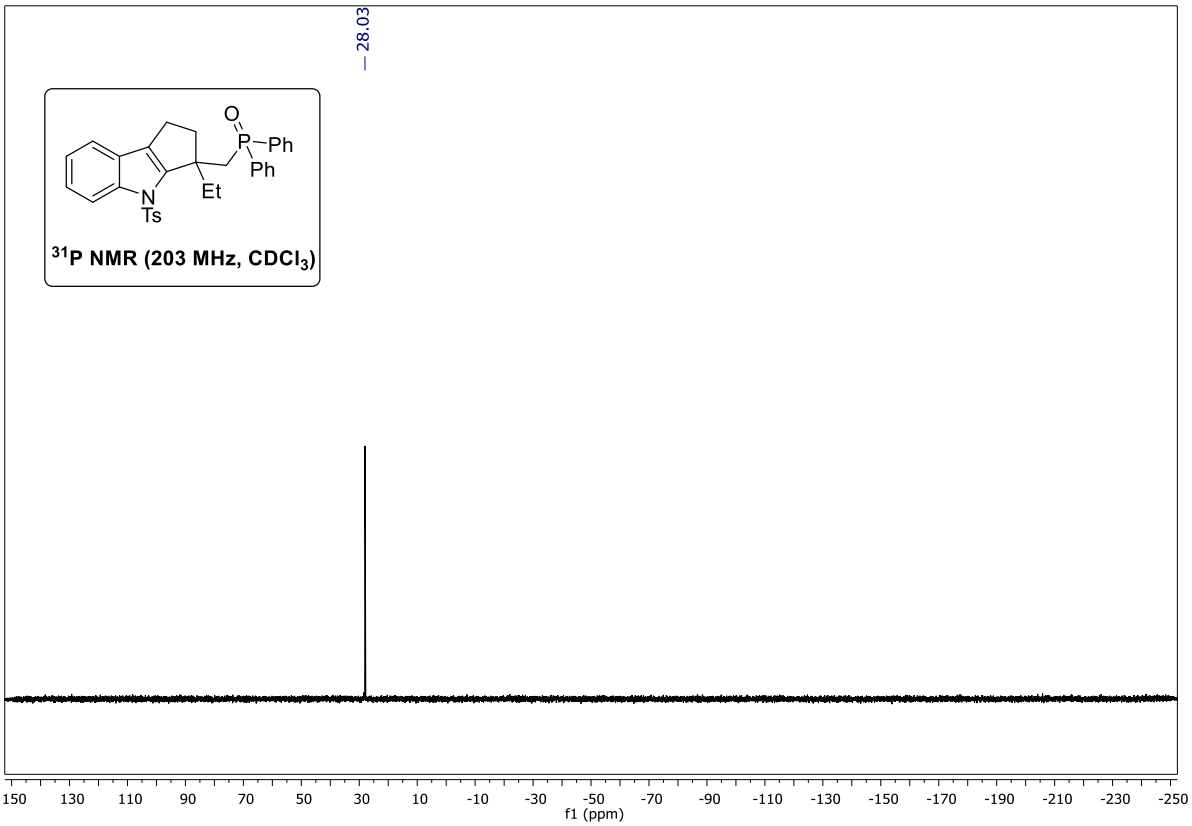

149.649
149.529
144.603
141.223
136.501
134.560
133.721
133.597
132.770
131.900
131.883
131.662
131.649
131.524
131.434
130.912
130.830
129.775
128.947
128.841
128.732
126.377
126.106
125.080
124.959
124.336
123.694
119.259
115.415
53.867
53.159
47.783
29.654
24.525
24.479
24.335
21.638
O
P
Ph
Ph
N
Ts
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


27.636
O
P
Ph
Ph
N
Ts
31P NMR (162 MHz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

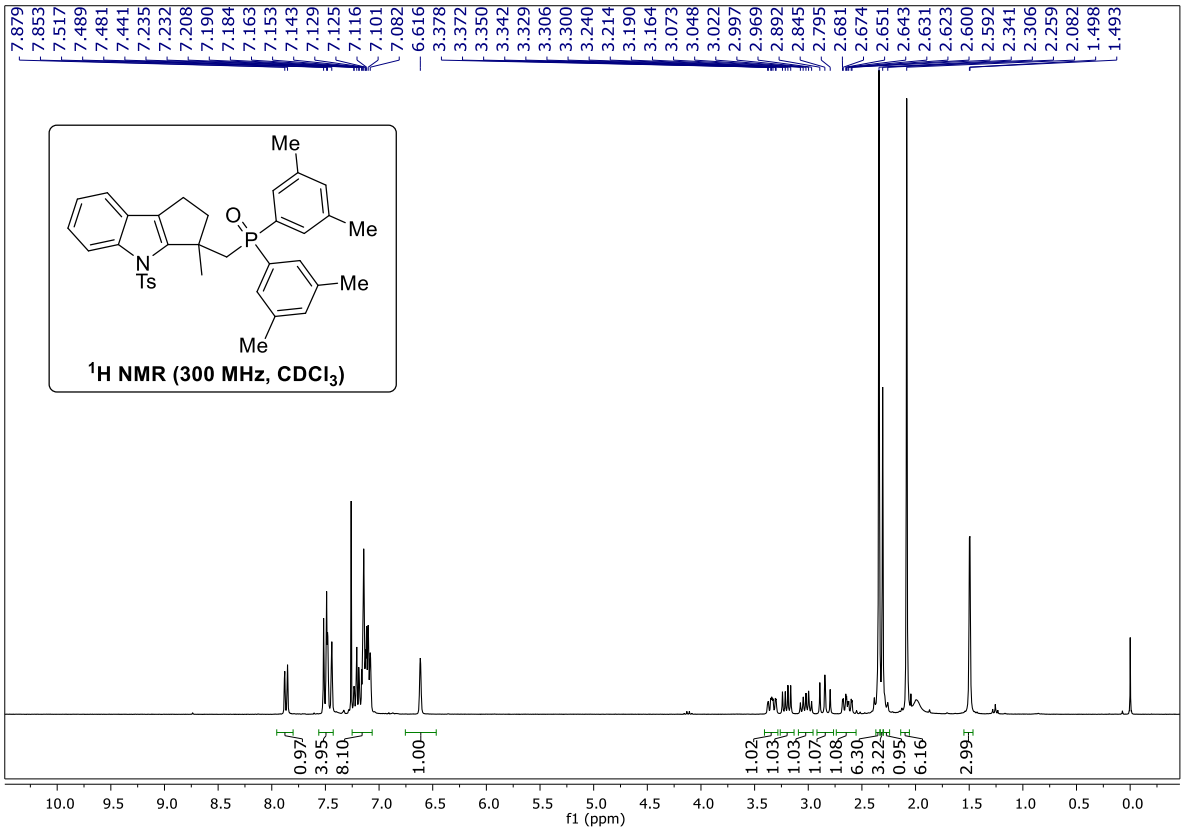
((3-Ethyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)diphenylphosphine oxide (3na):

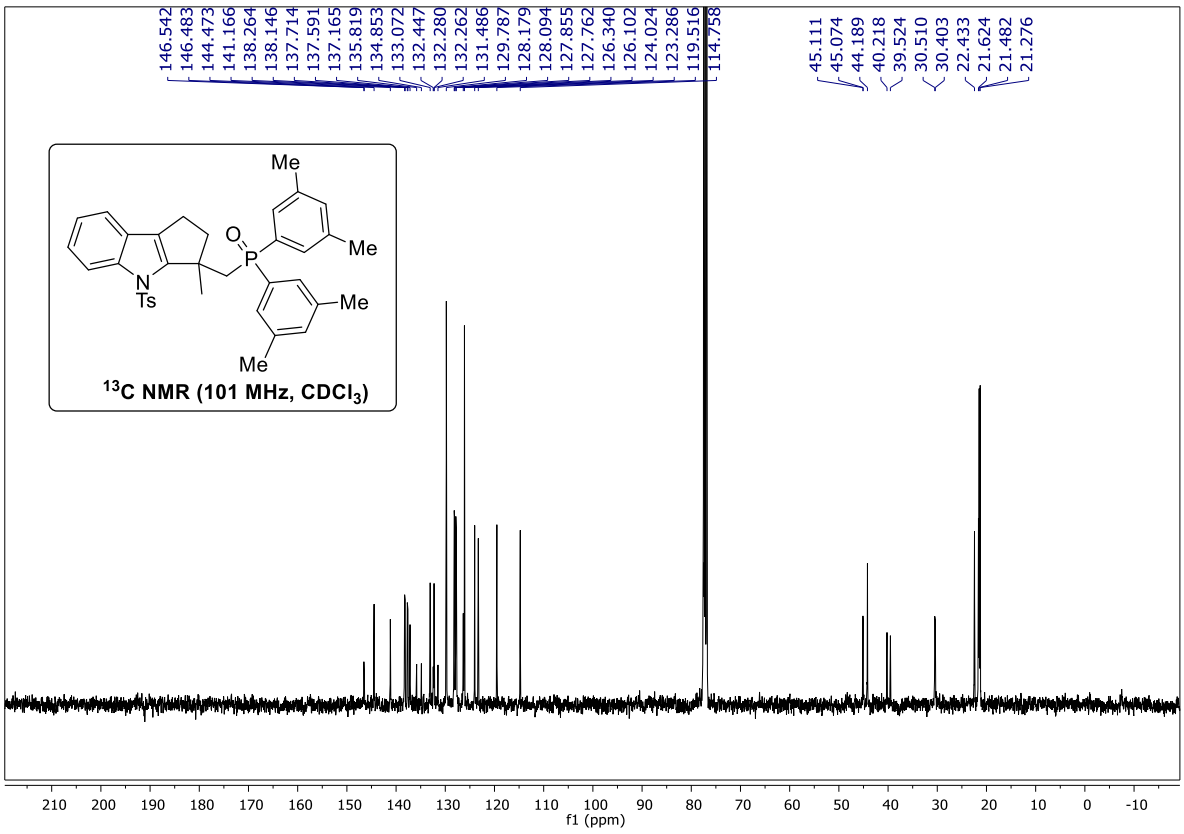


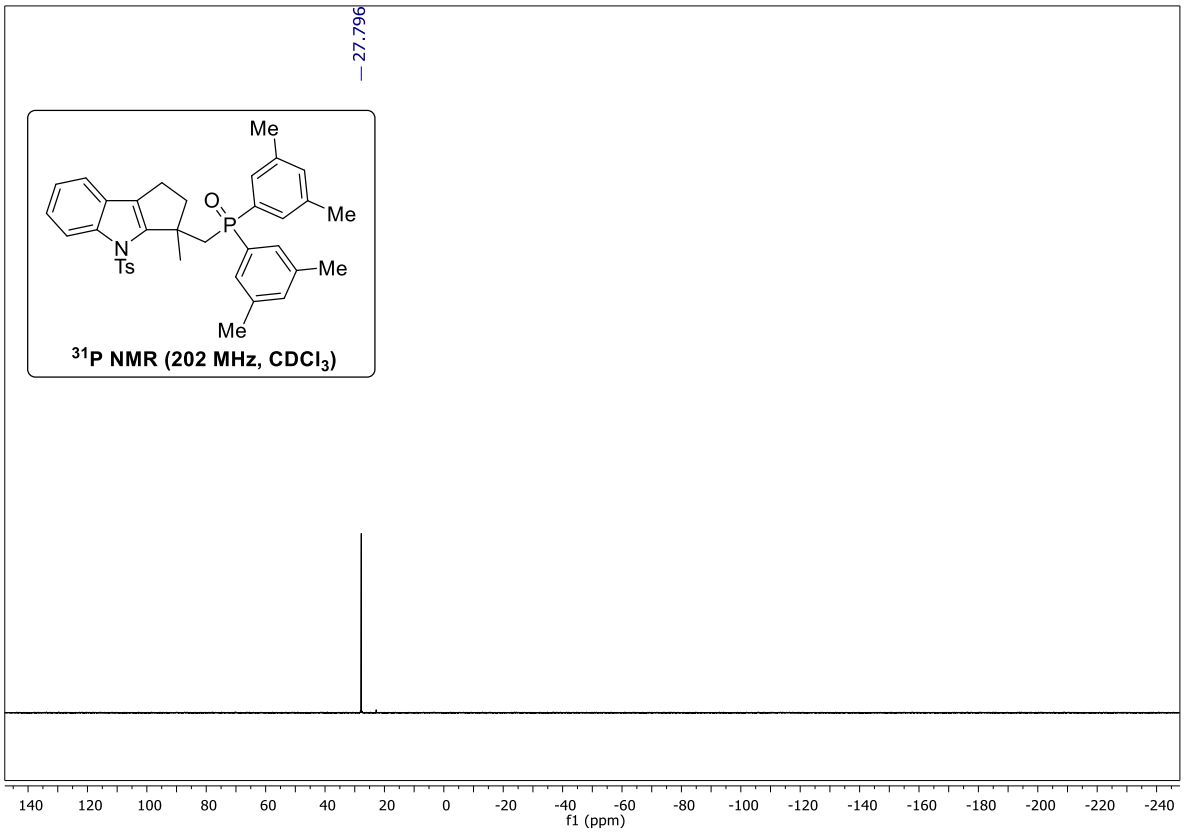



28.03
O
P
Ph
Ph
Et
N
Ts
31P NMR (203 MHz, CDCl3)
150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250
f1 (ppm)

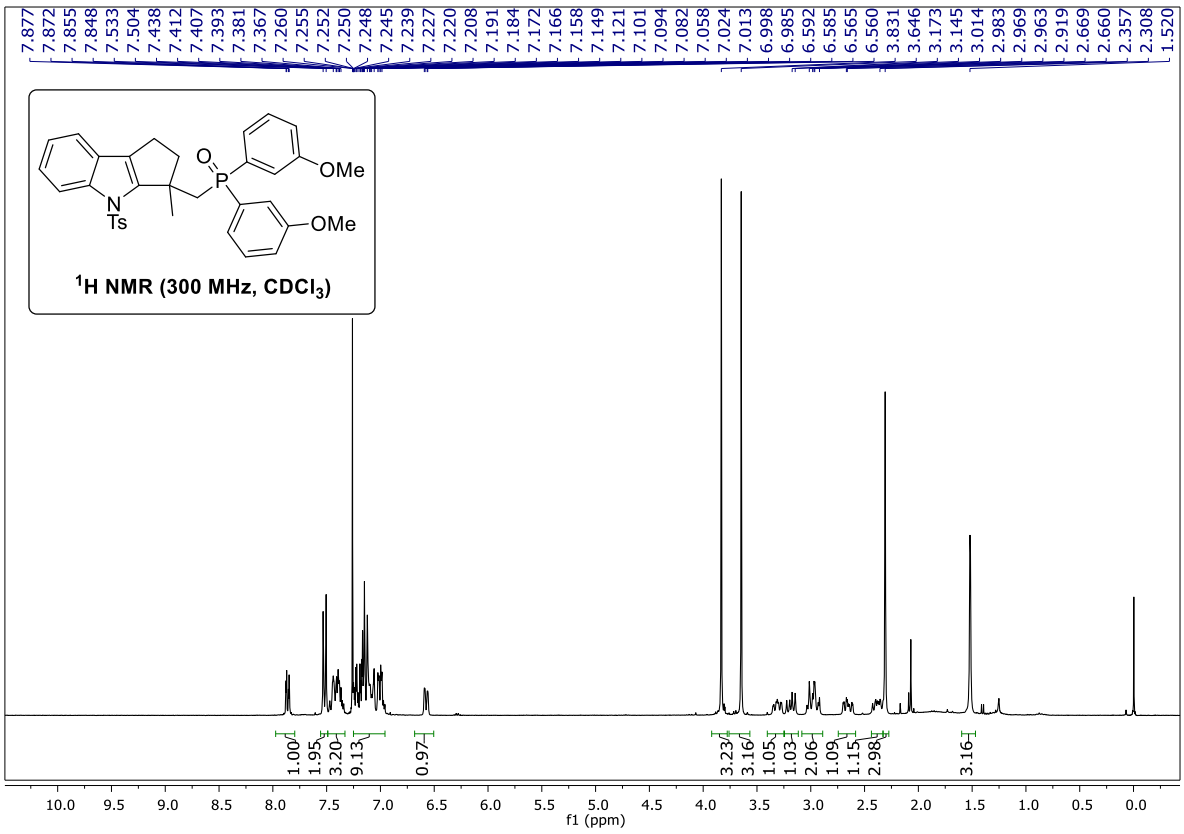
bis(3,5-Dimethylphenyl)((3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)phosphine oxide (3ab):

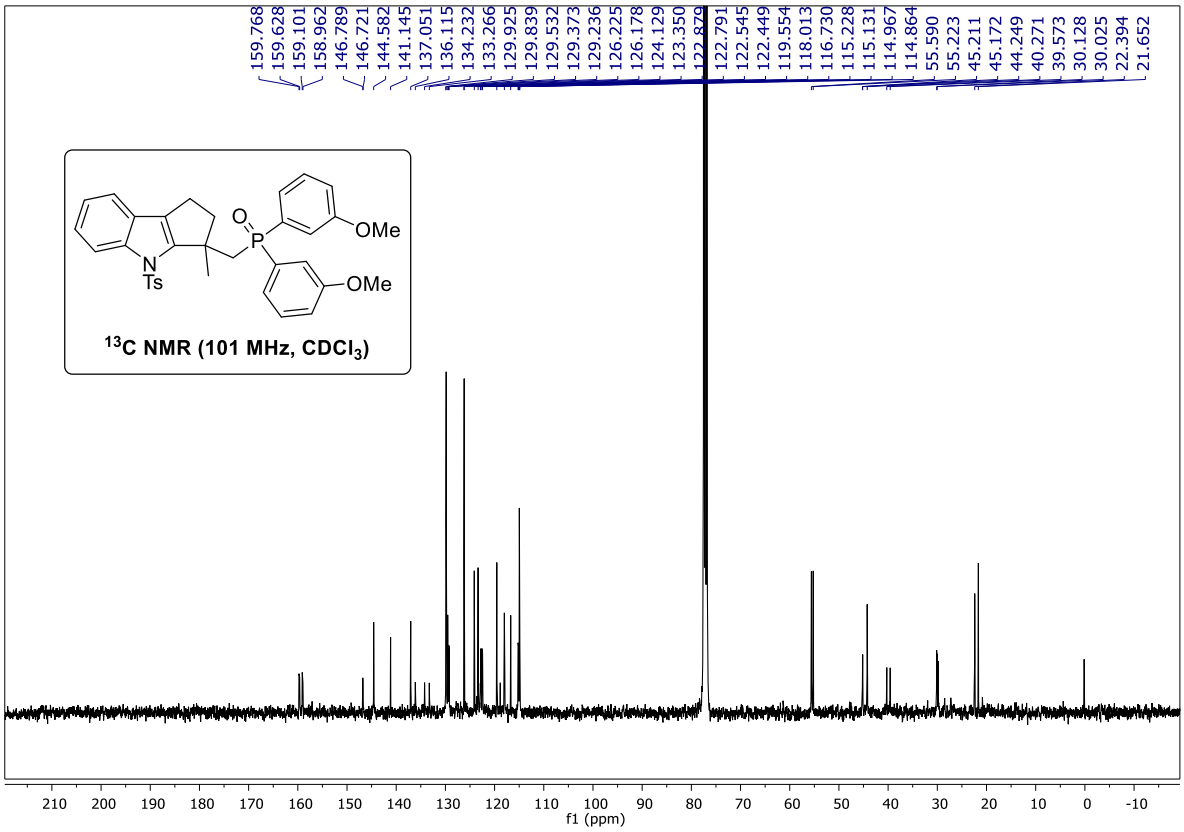




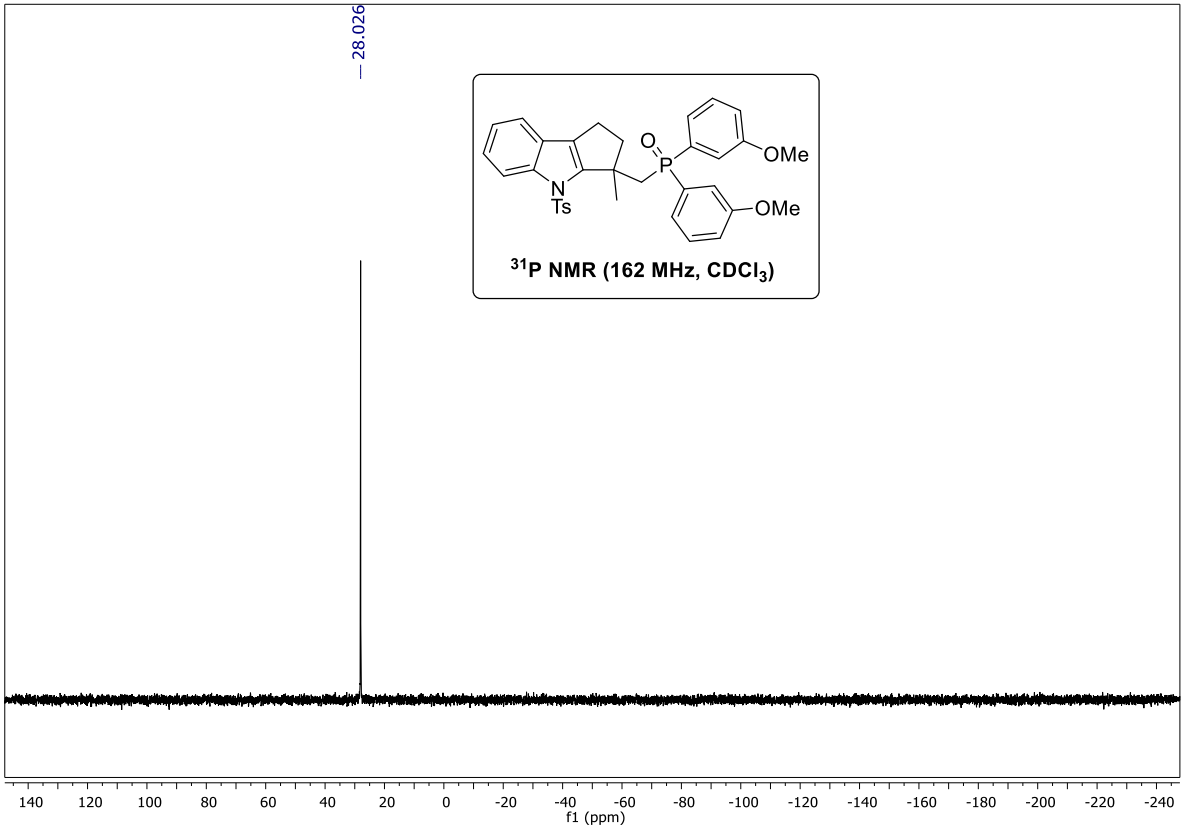


Bis(3-methoxyphenyl)((3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)phosphine oxide (3ac):



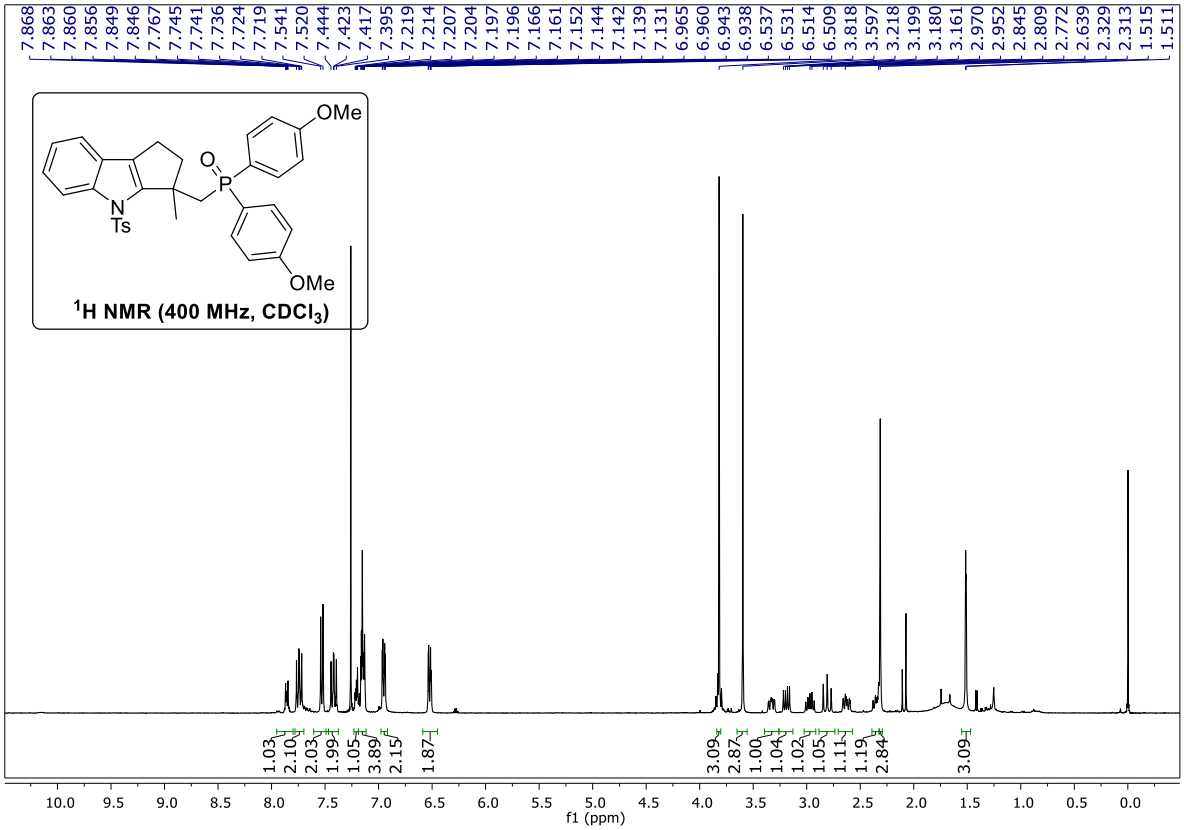


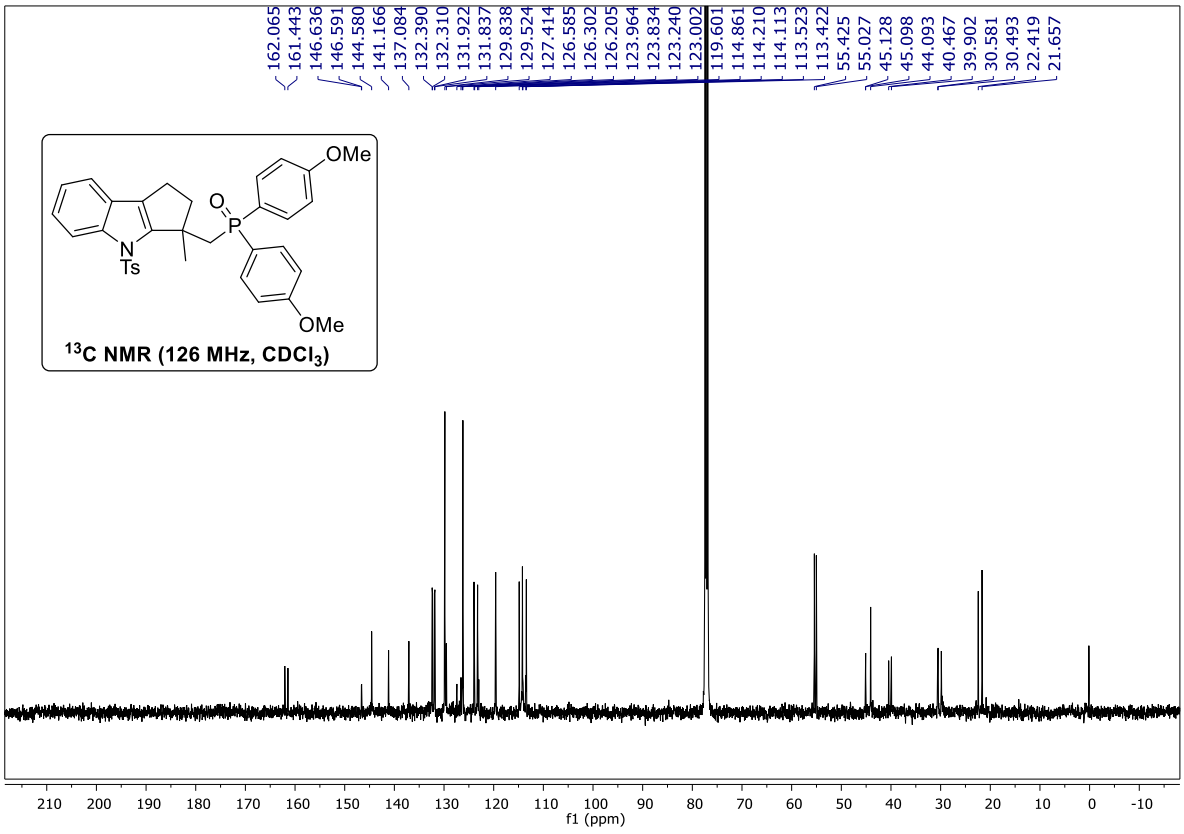
^{13}C NMR (101 MHz, $CDCl_3$)

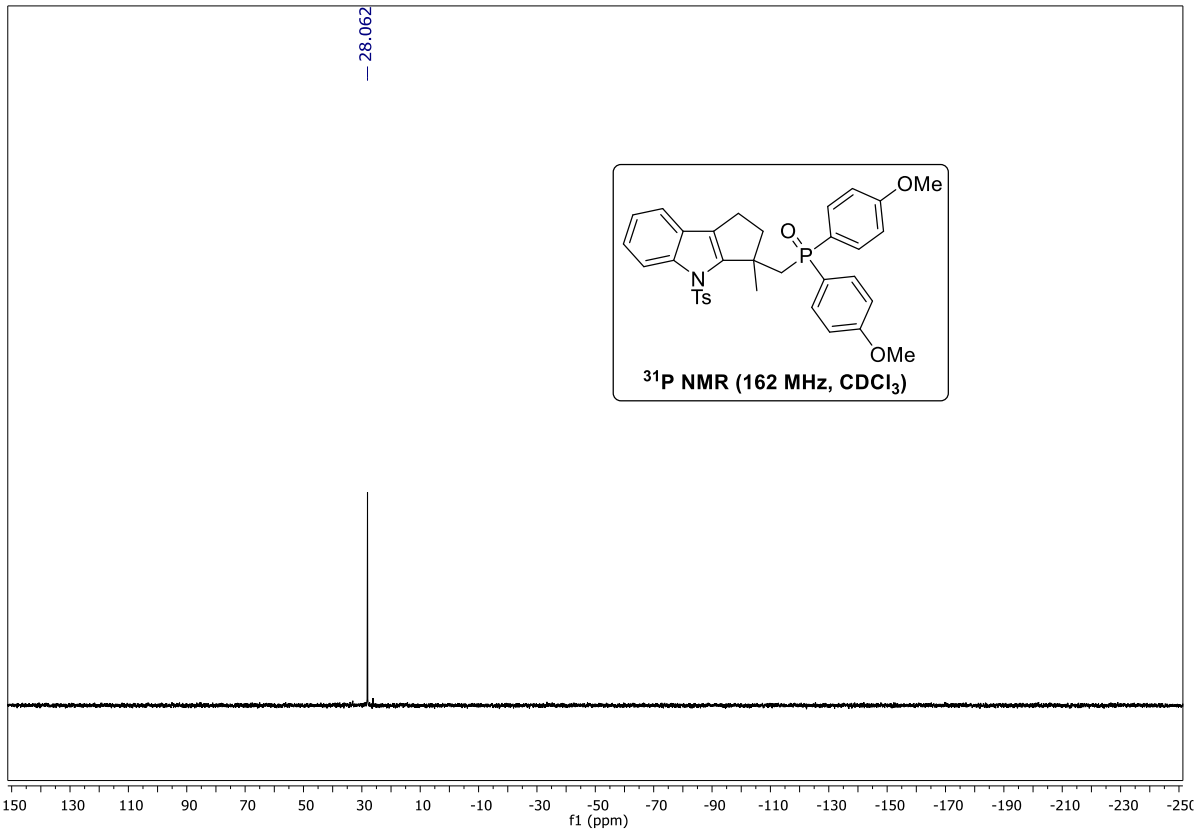


^{31}P NMR (162 MHz, $CDCl_3$)

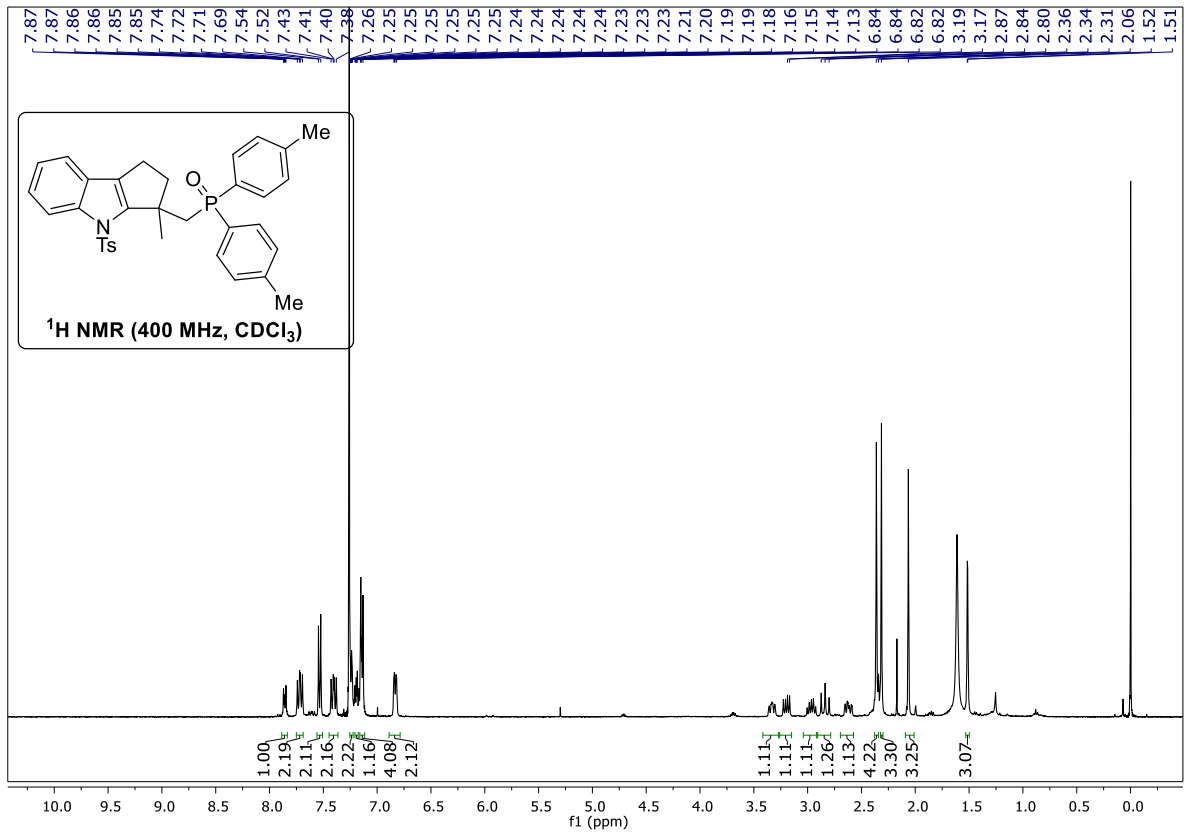
Bis(4-methoxyphenyl)((3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)phosphine oxide (3ad):

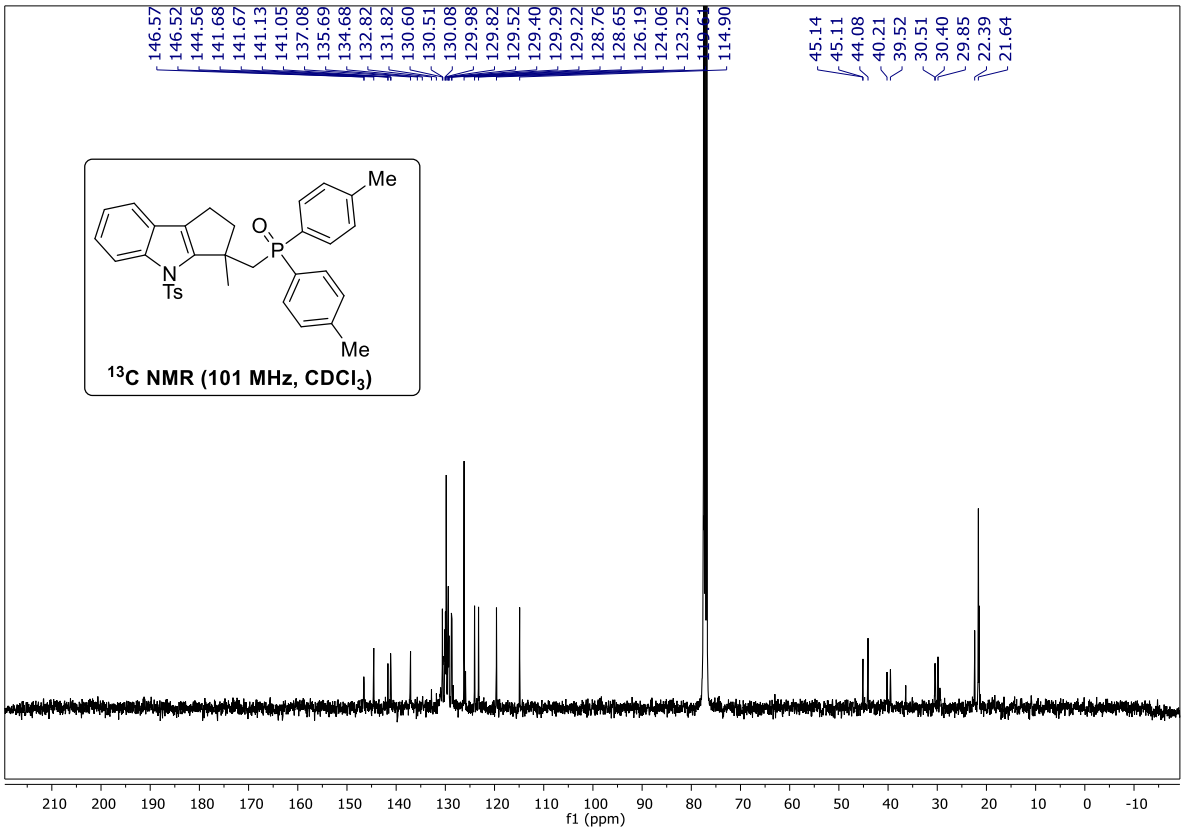


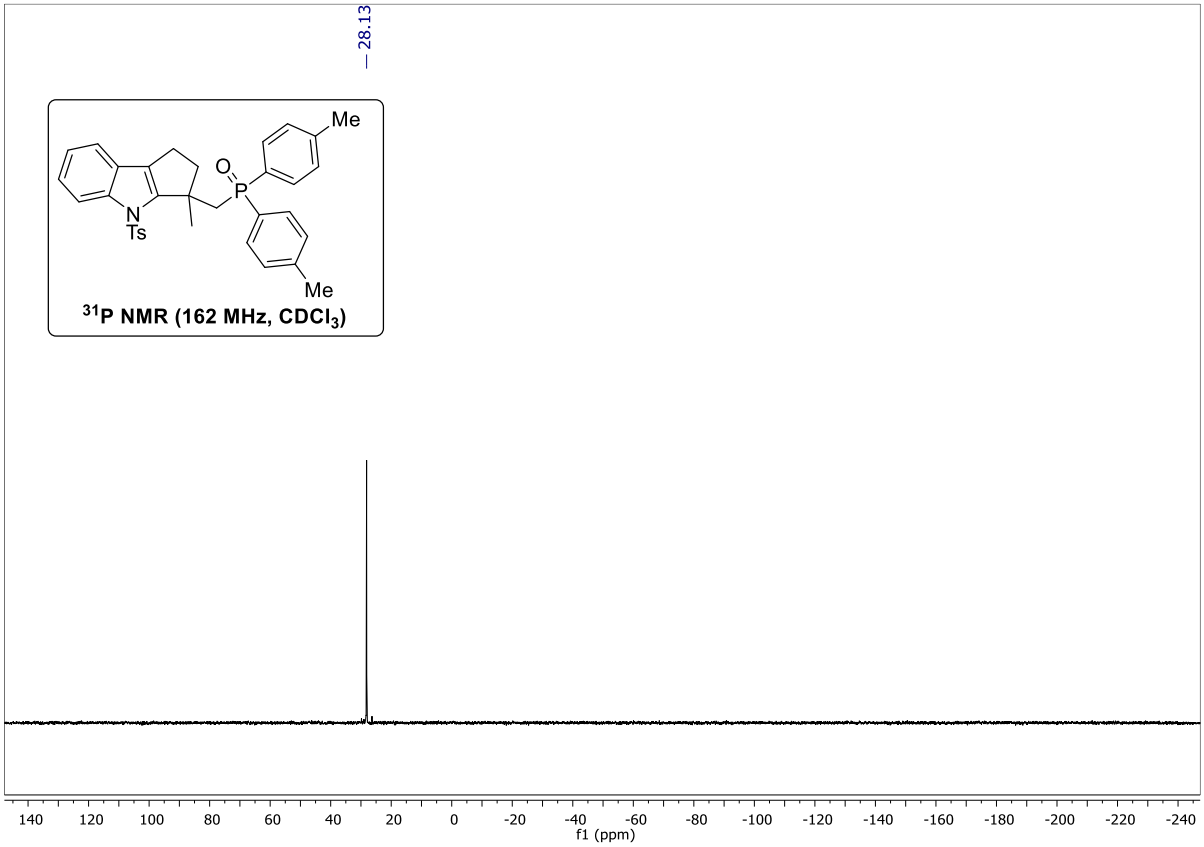




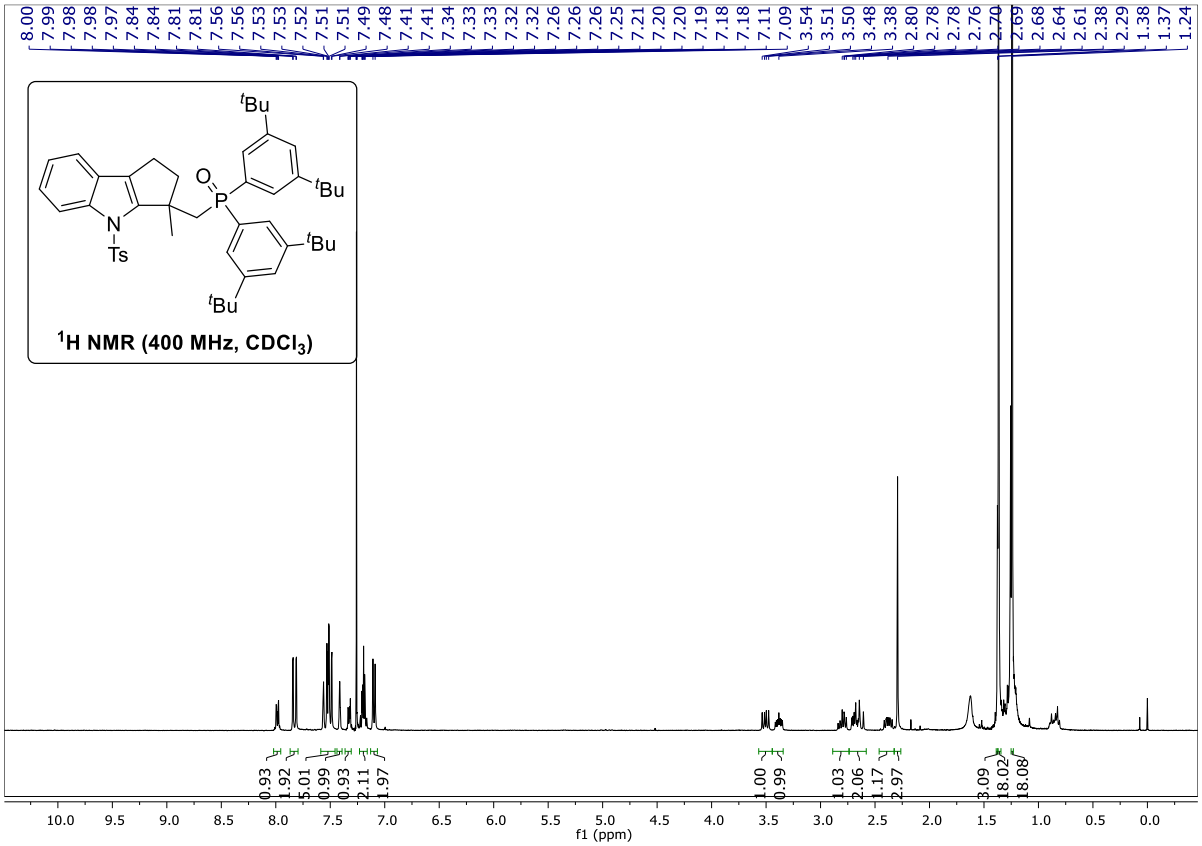
((3-Methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-3-yl)methyl)di-*p*-tolylphosphine oxide (3ae):

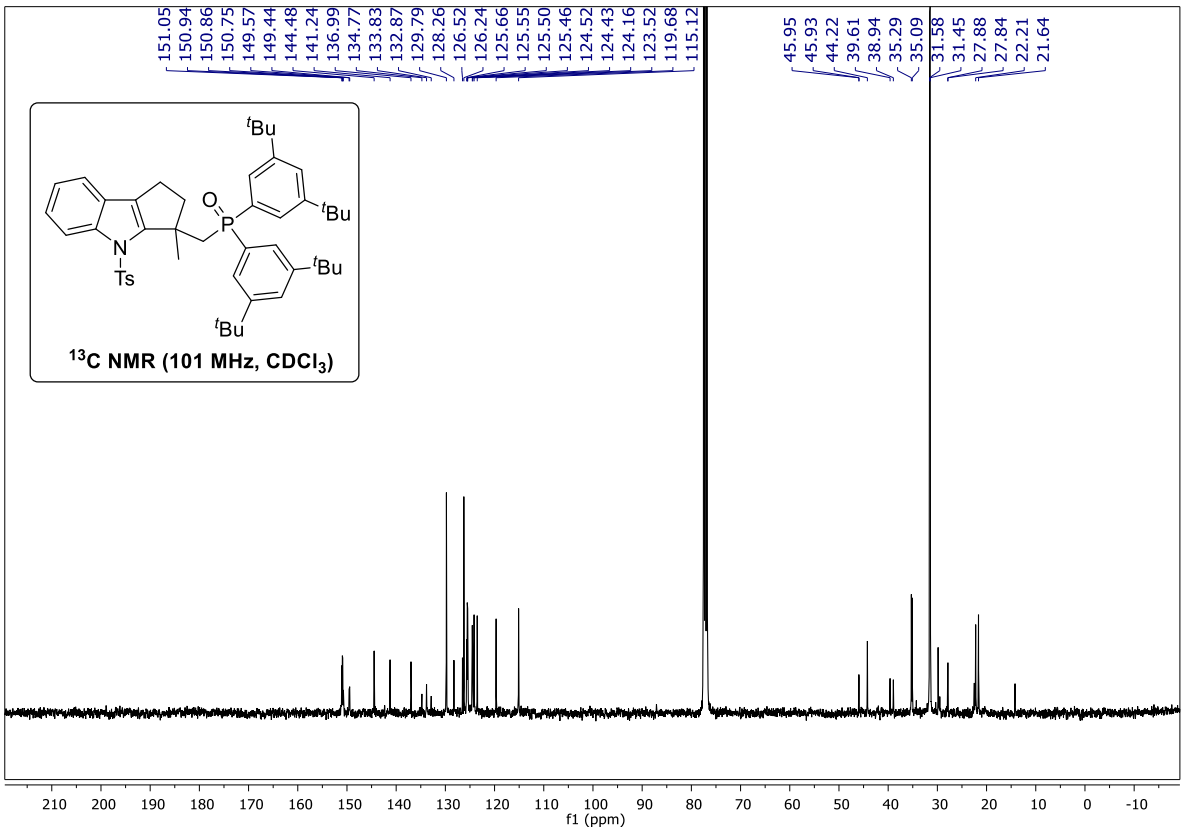


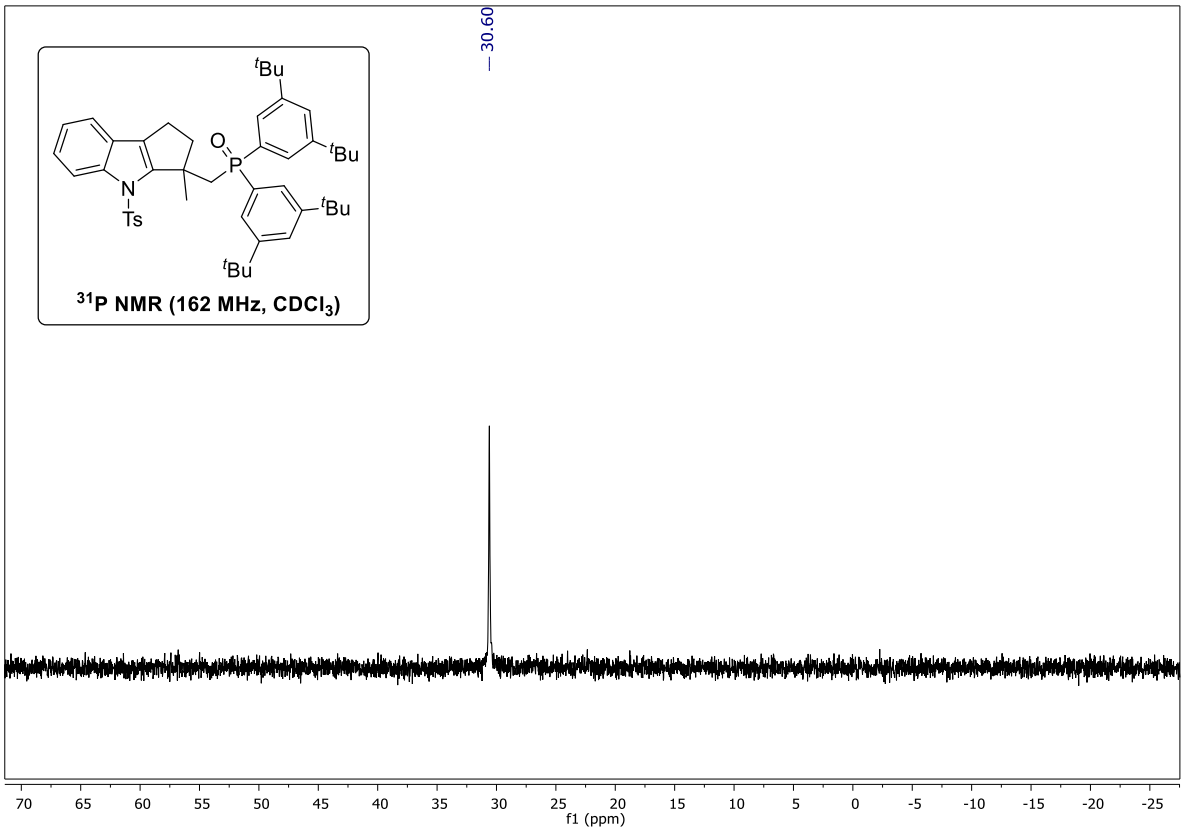

146.57
146.52
144.56
141.68
141.67
141.13
141.05
137.08
135.69
134.68
132.82
131.82
130.60
130.51
130.08
129.98
129.82
129.52
129.40
129.29
129.22
128.76
128.65
126.19
124.06
123.25
119.64
114.90
45.14
45.11
44.08
40.21
39.52
30.51
30.40
29.85
22.39
21.64
Me
O
P
N
Ts
Me
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


28.13
Me
O
P
N
Ts
Me
31P NMR (162 MHz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

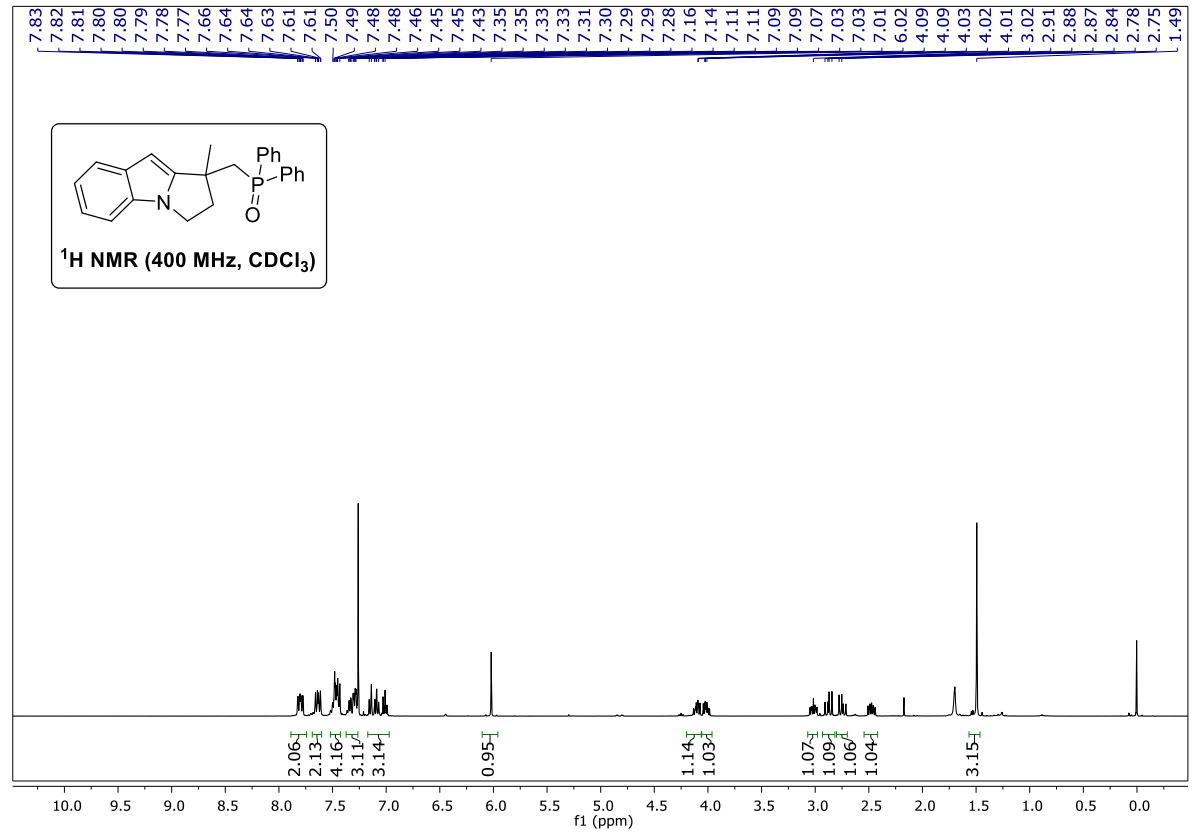
bis(3,5-di-*tert*-Butylphenyl)((3-methyl-4-tosyl-1,2,3,4-tetrahydrocyclopenta[b]indol-3-yl)methyl)phosphine oxide (3af):

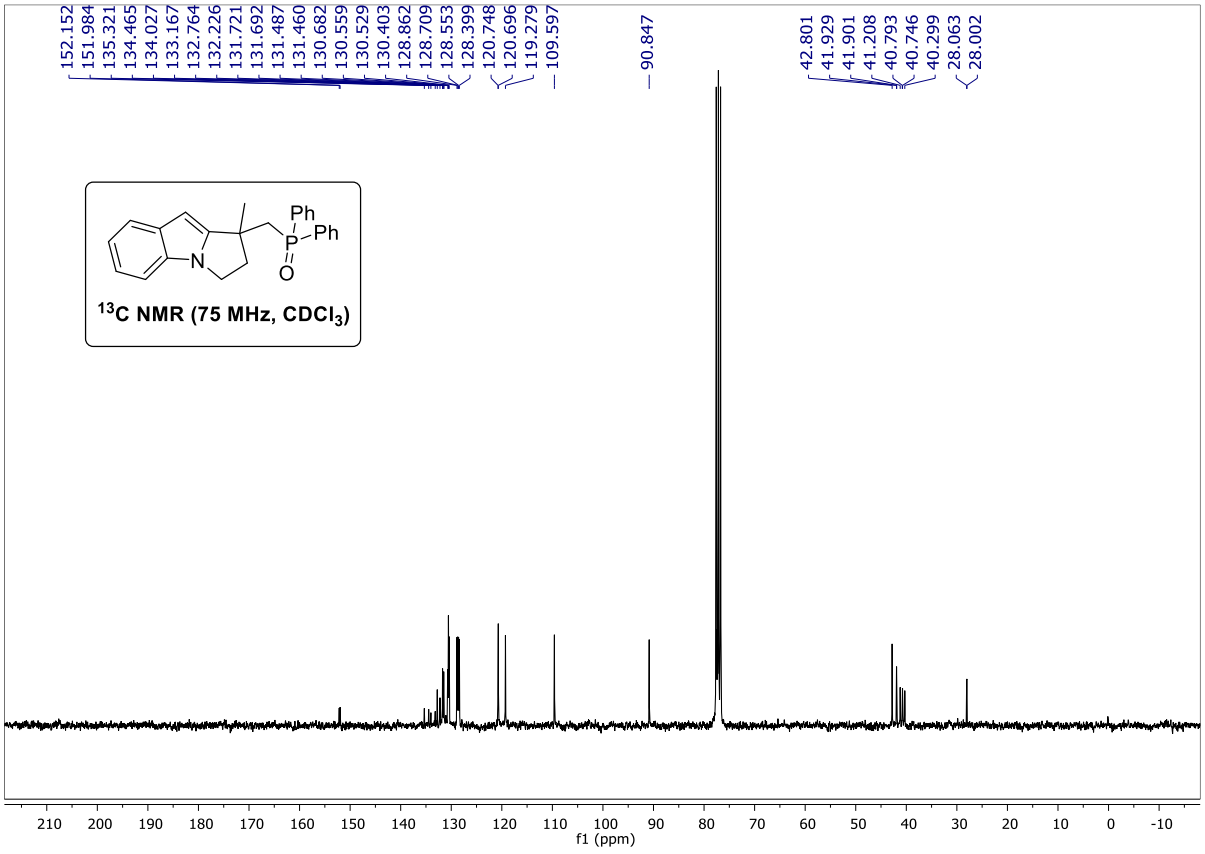


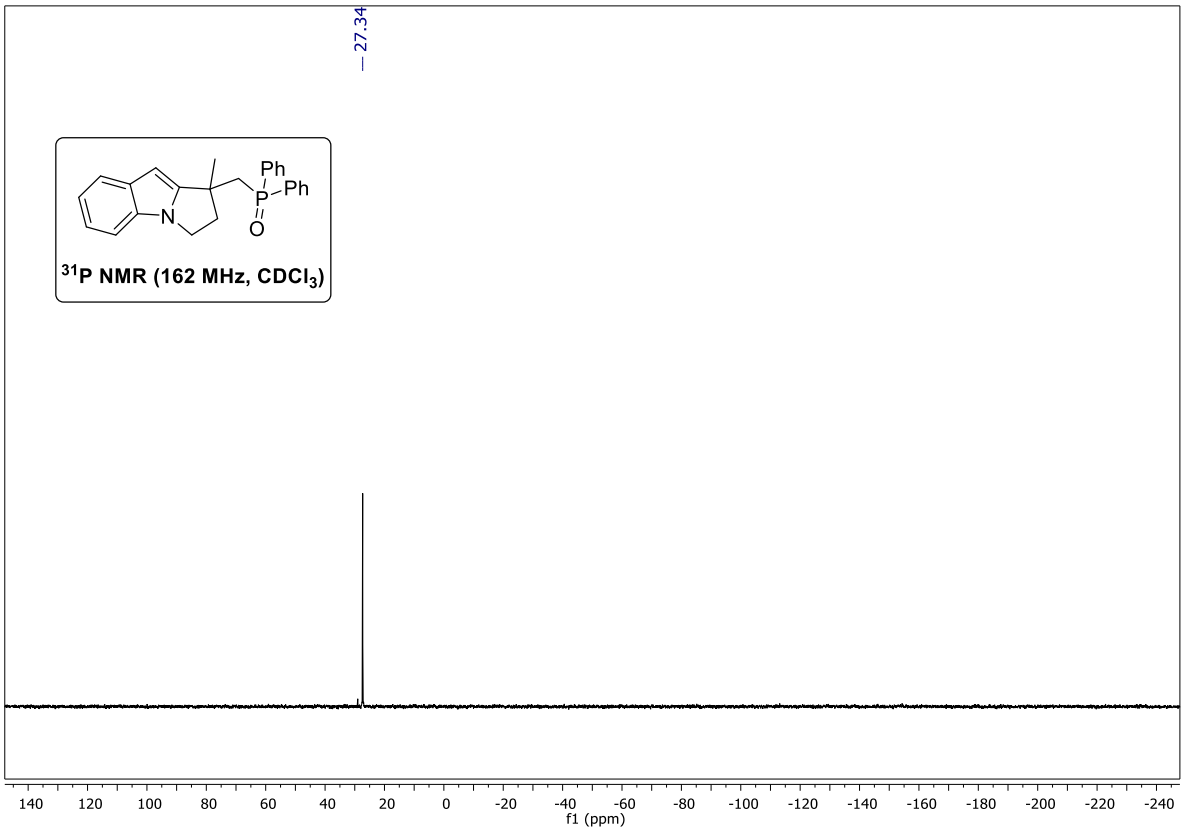



30.60
tBu
tBu
tBu
tBu
O
P
N
Ts
31P NMR (162 MHz, CDCl3)
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

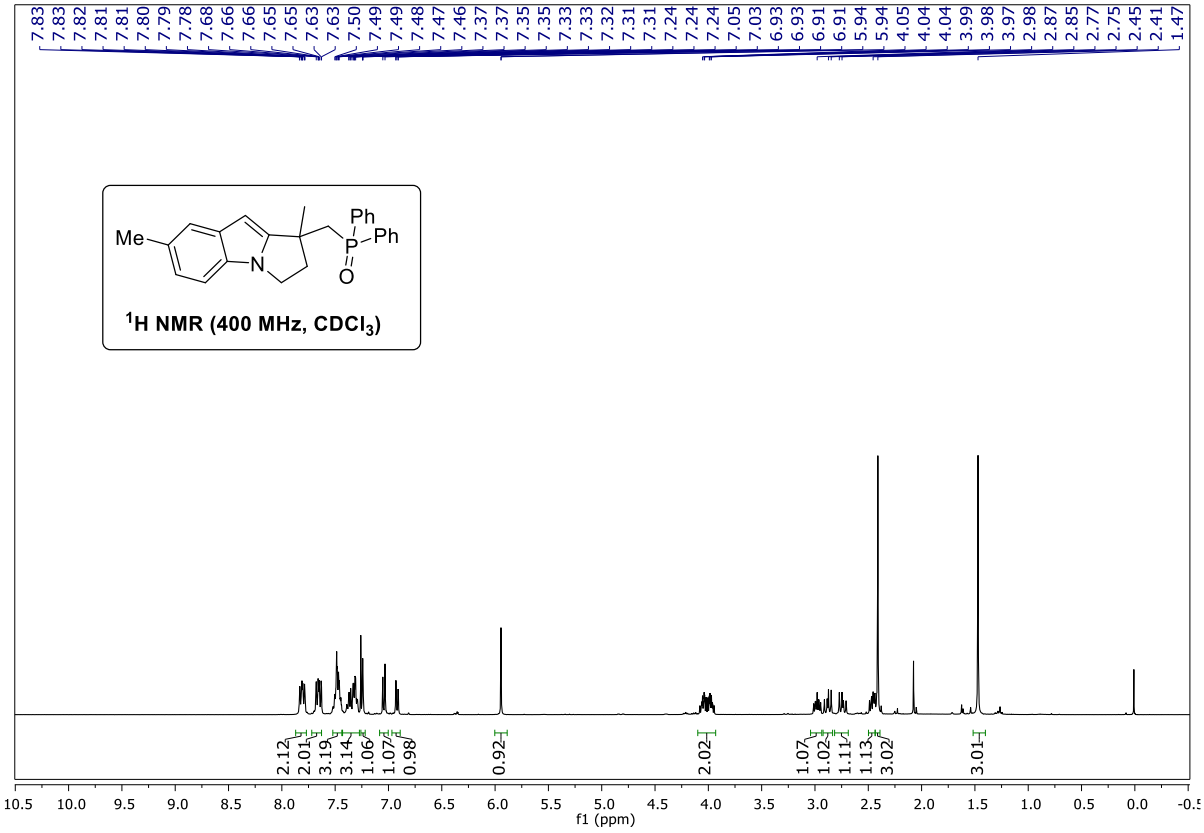
((1-Methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5aa).

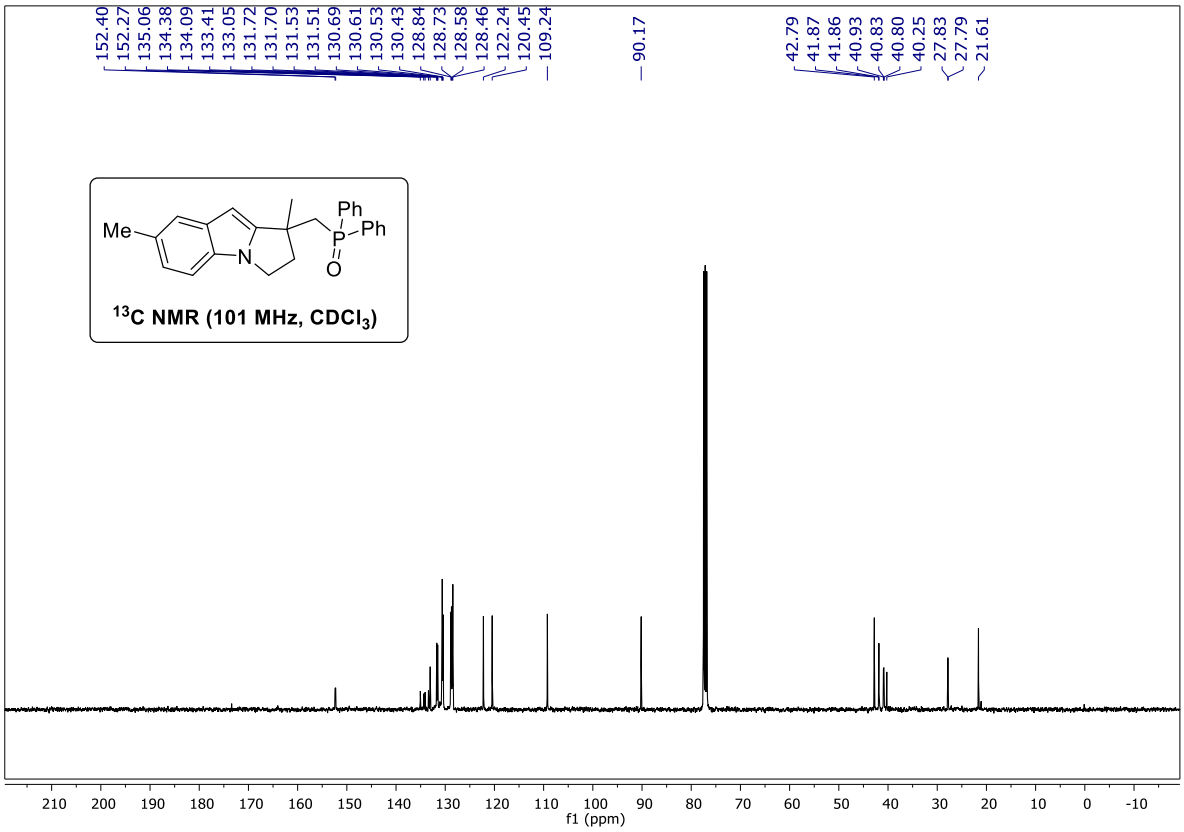


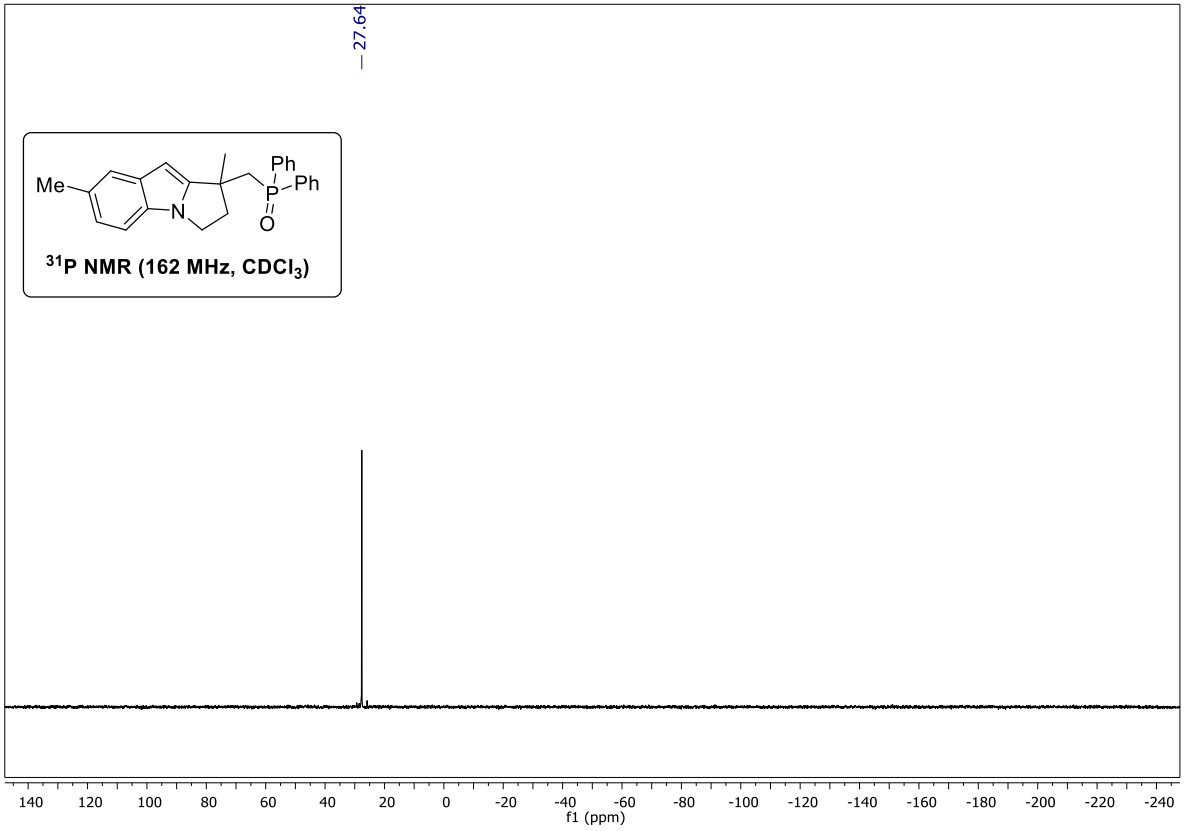




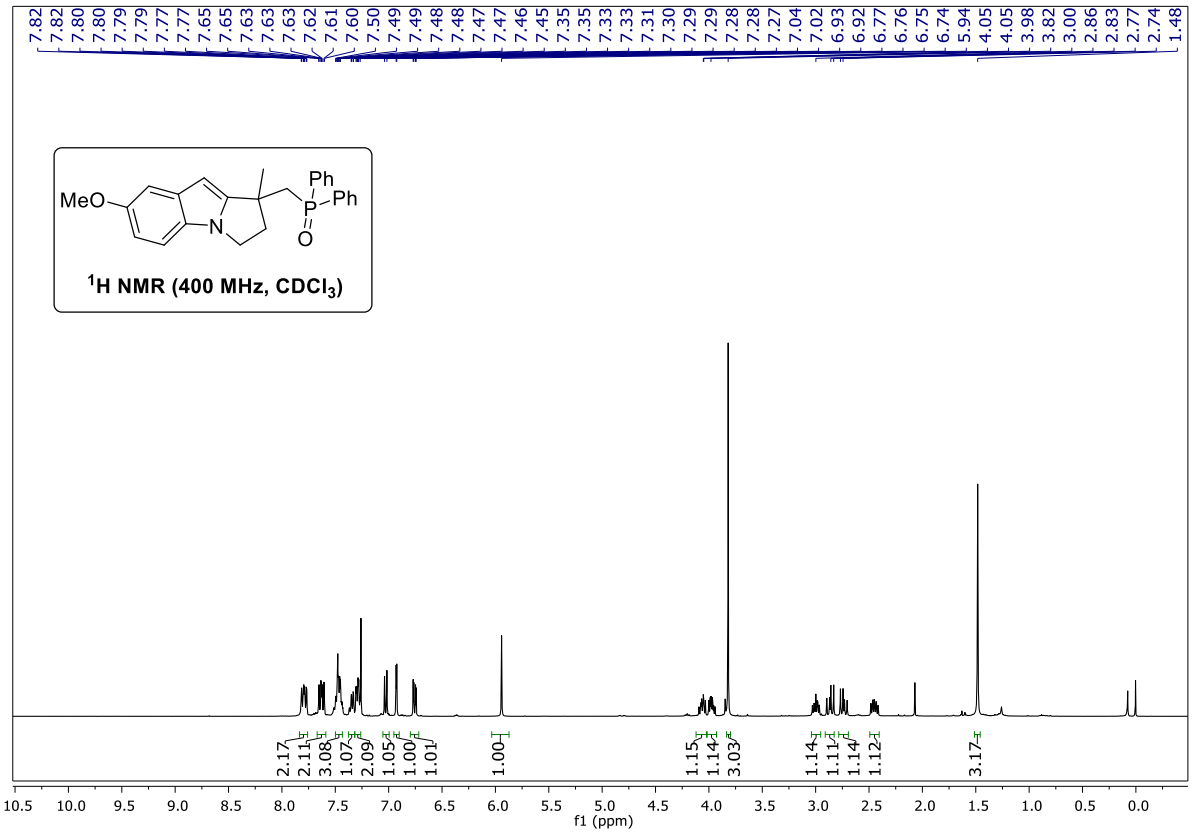
((1,7-Dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5ba):

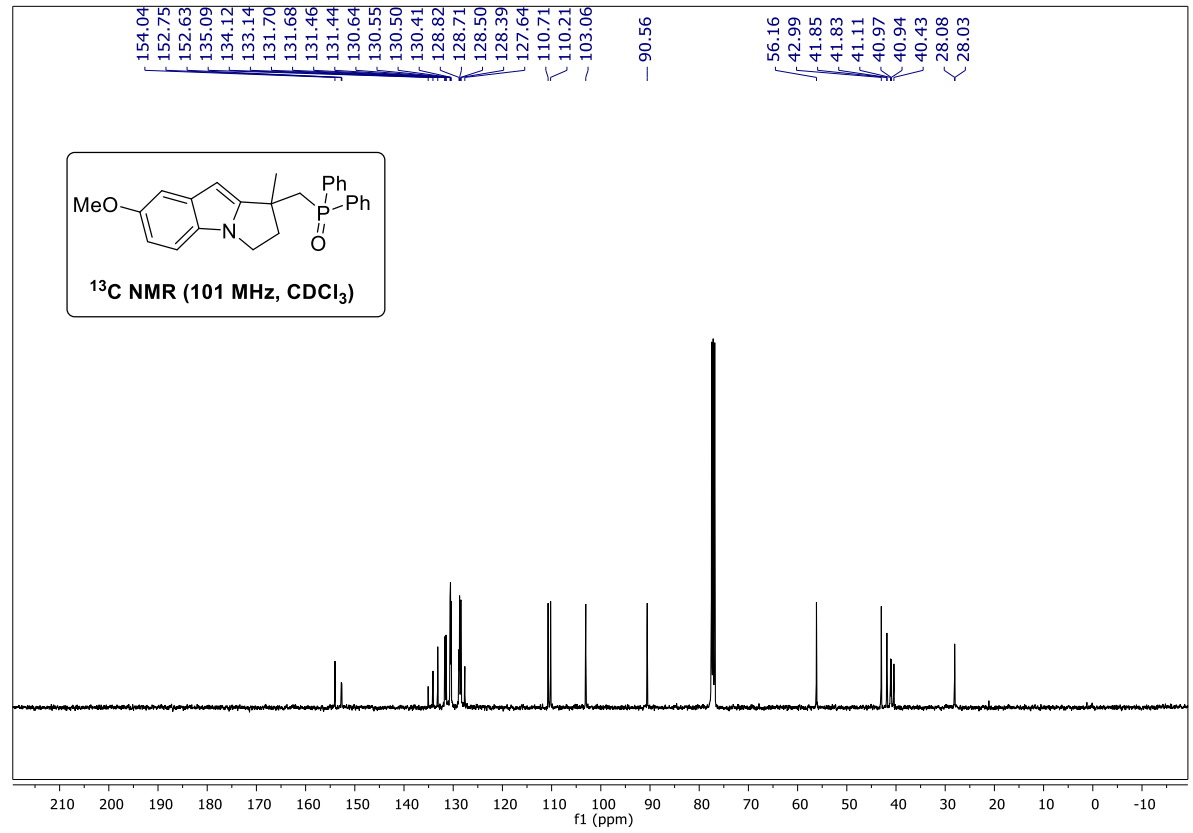


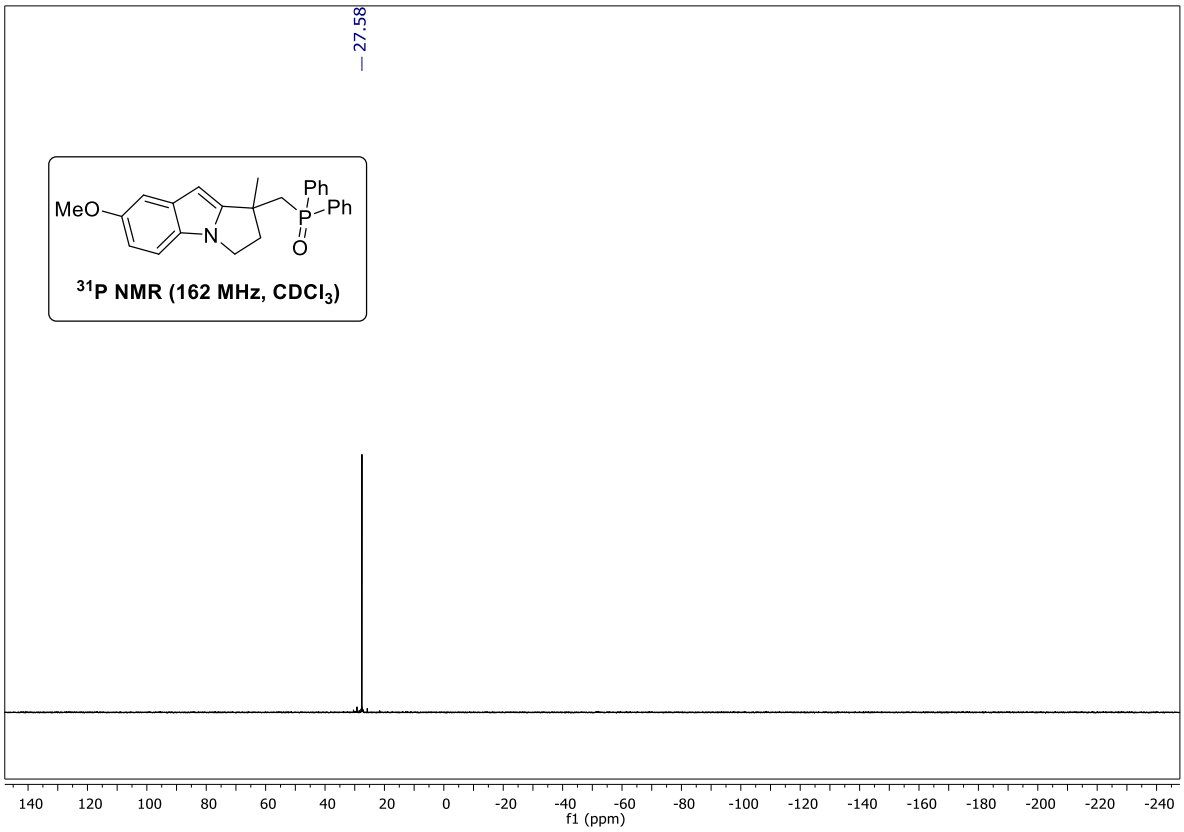

152.40
152.27
135.06
134.38
134.09
133.41
133.05
131.72
131.70
131.53
131.51
130.69
130.61
130.53
130.43
128.84
128.73
128.58
128.46
122.24
120.45
109.24
90.17
42.79
41.87
41.86
40.93
40.83
40.80
40.25
27.83
27.79
21.61
Me
Ph
Ph
P
O
N
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


27.64
Me
Ph
Ph
P
O
N
31P NMR (162 MHz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

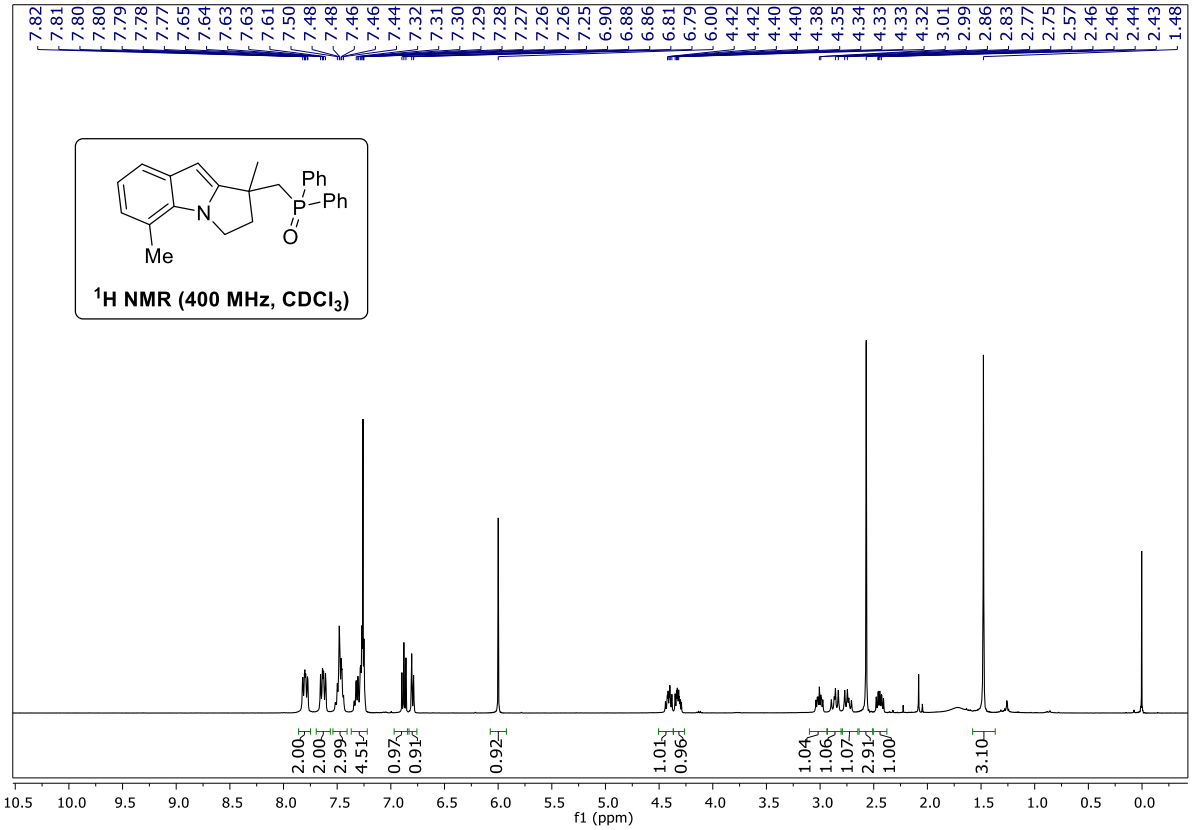
((7-Methoxy-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenyl phosphine oxide (5ca):

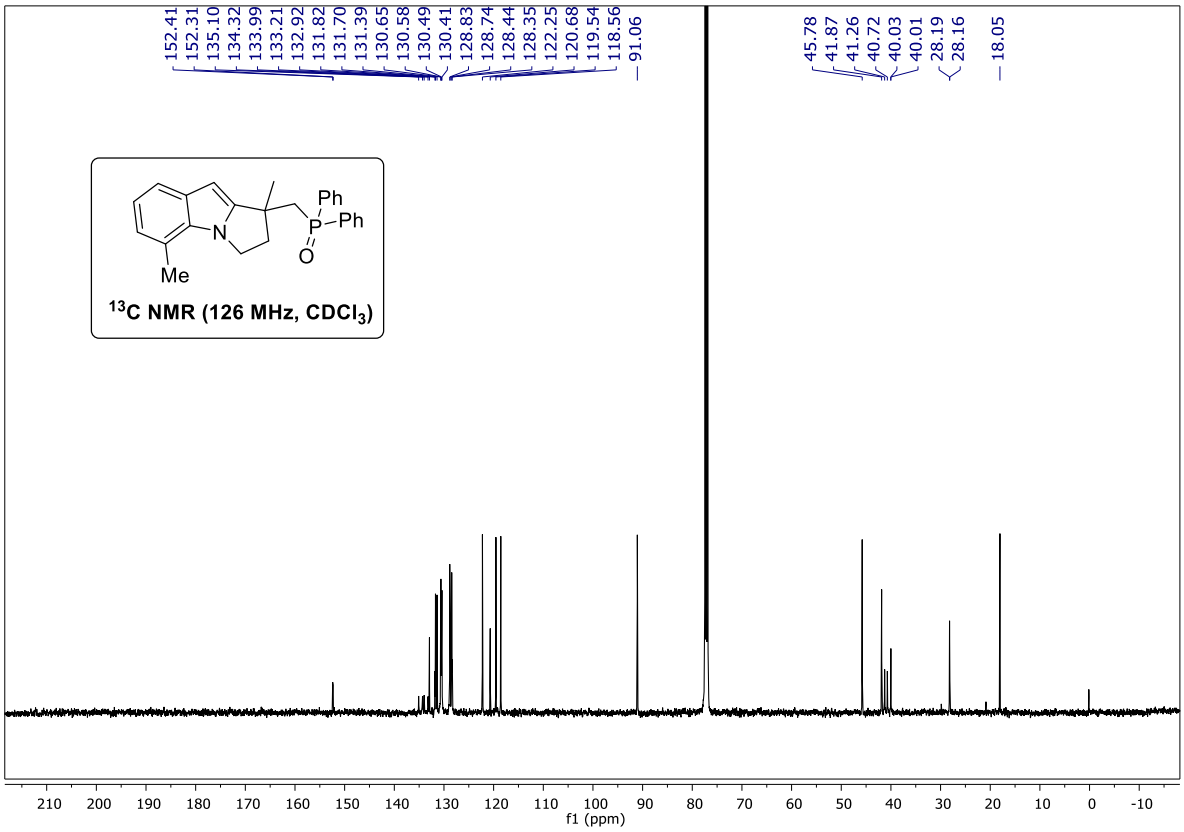


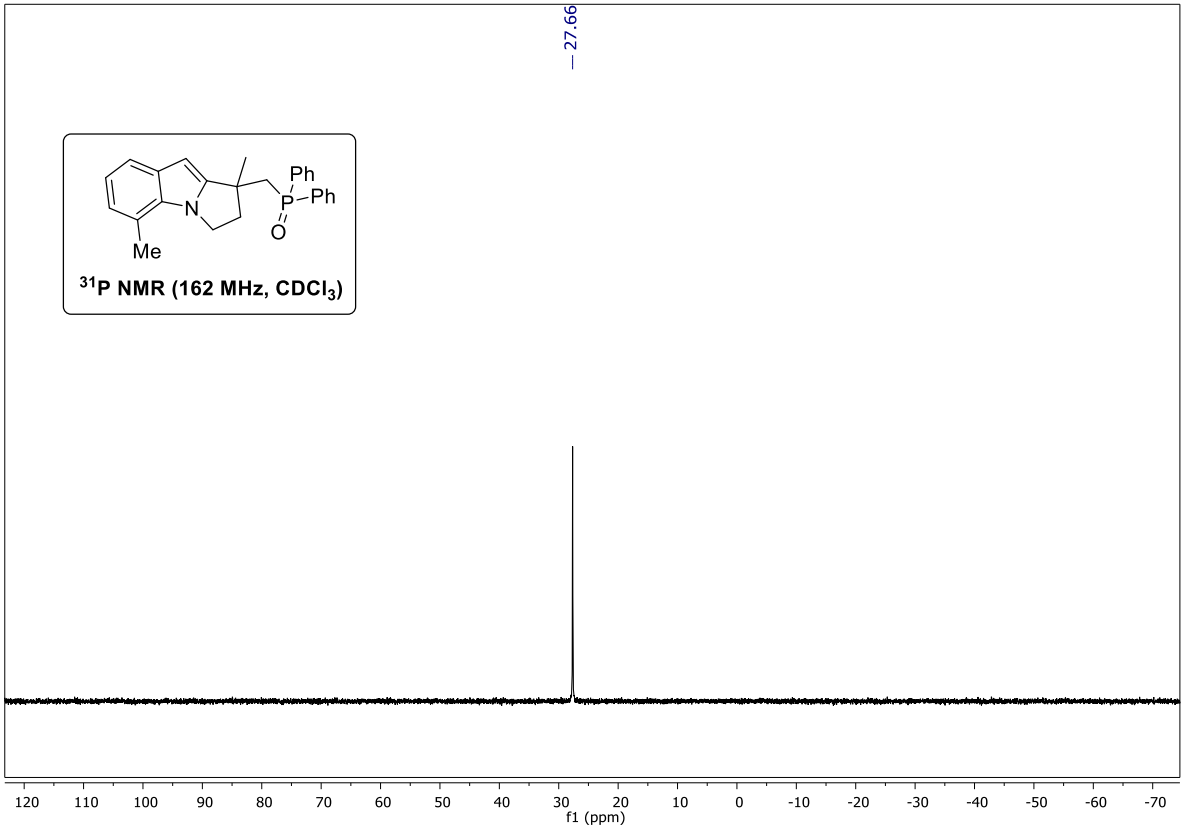




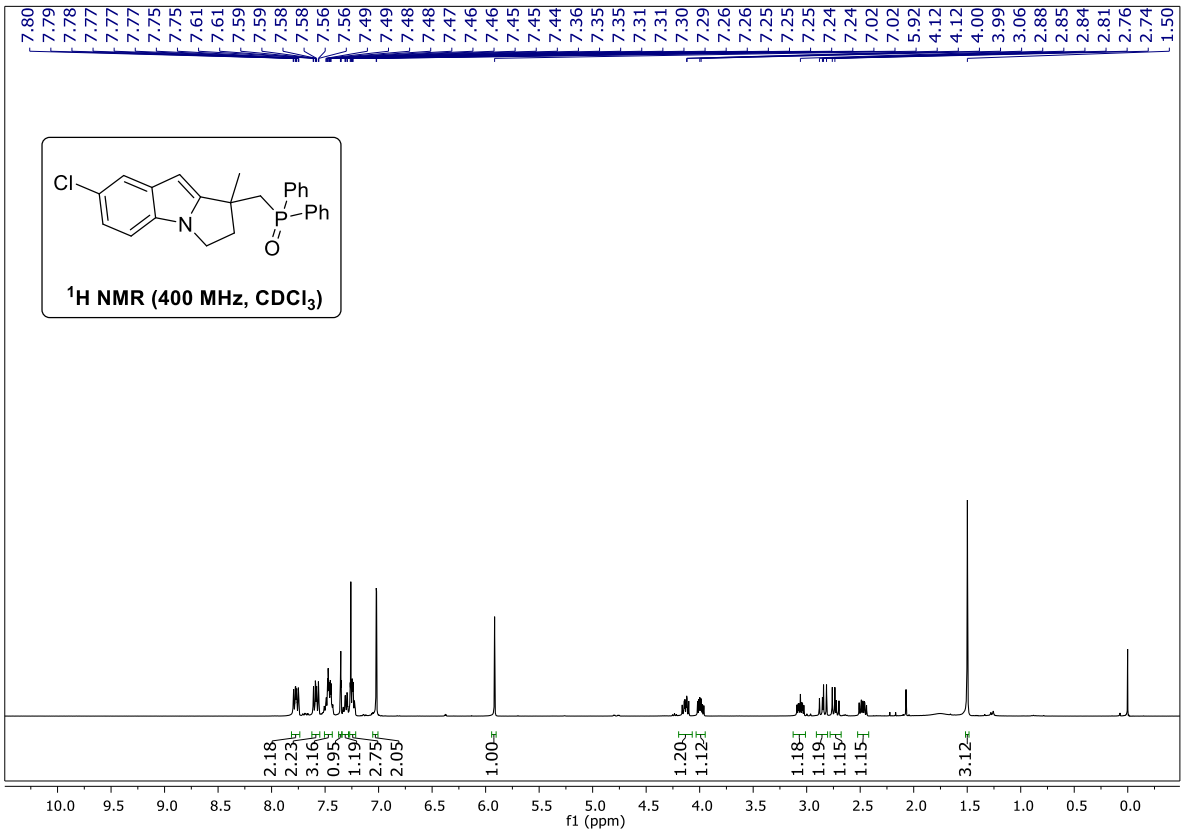
((1,5-Dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5da):

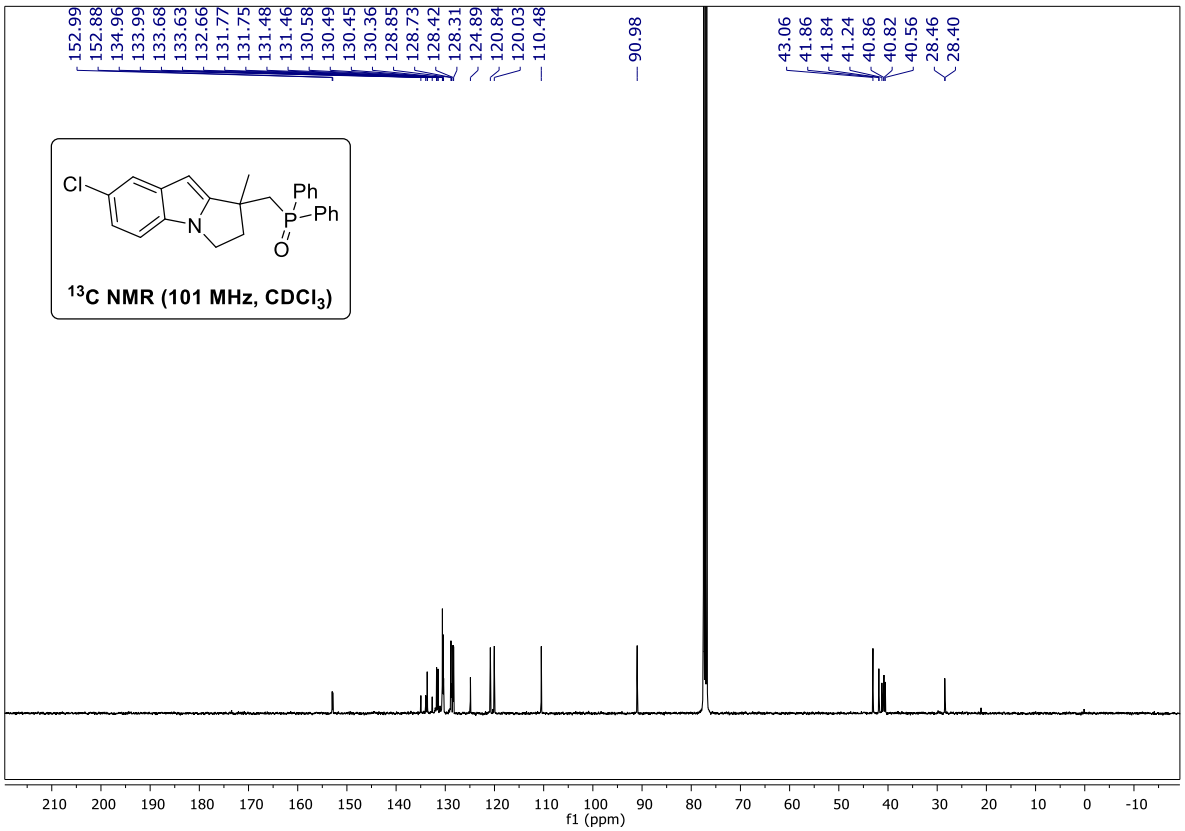


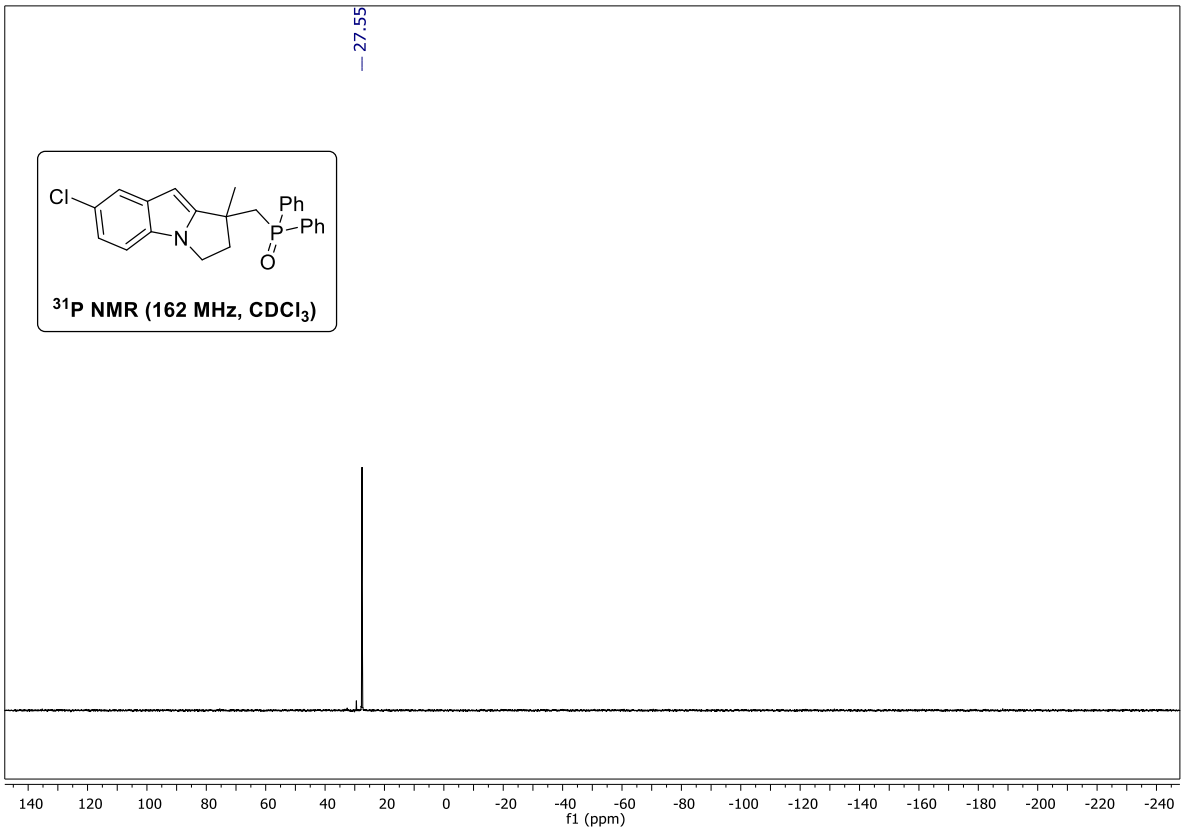

152.41
152.31
135.10
134.32
133.99
133.21
132.92
131.82
131.70
131.39
130.65
130.58
130.49
130.41
128.83
128.74
128.44
128.35
122.25
120.68
119.54
118.56
91.06
45.78
41.87
41.26
40.72
40.03
40.01
28.19
28.16
18.05
Ph
Ph
P
O
N
Me
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


27.66
Ph
Ph
P
O
N
Me
31P NMR (162 MHz, CDCl3)
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

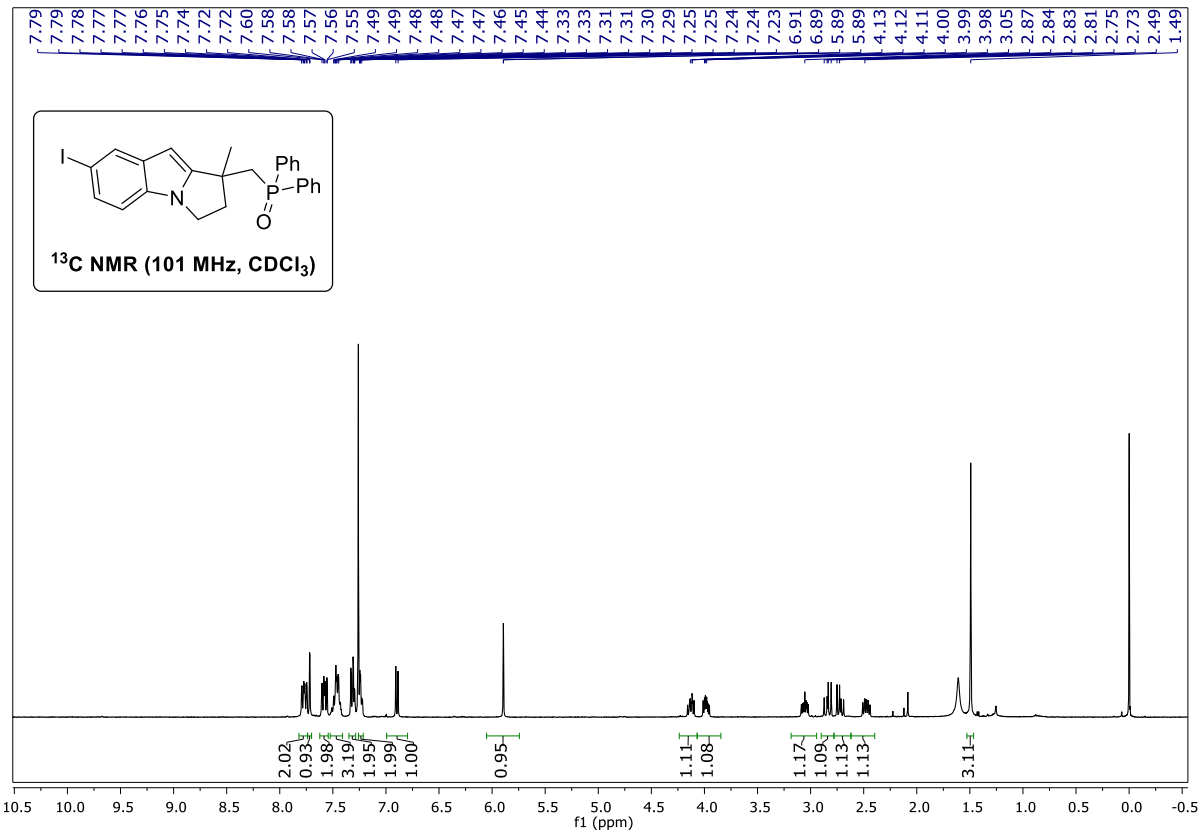
((7-Chloro-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenyl phosphine oxide (5ea):

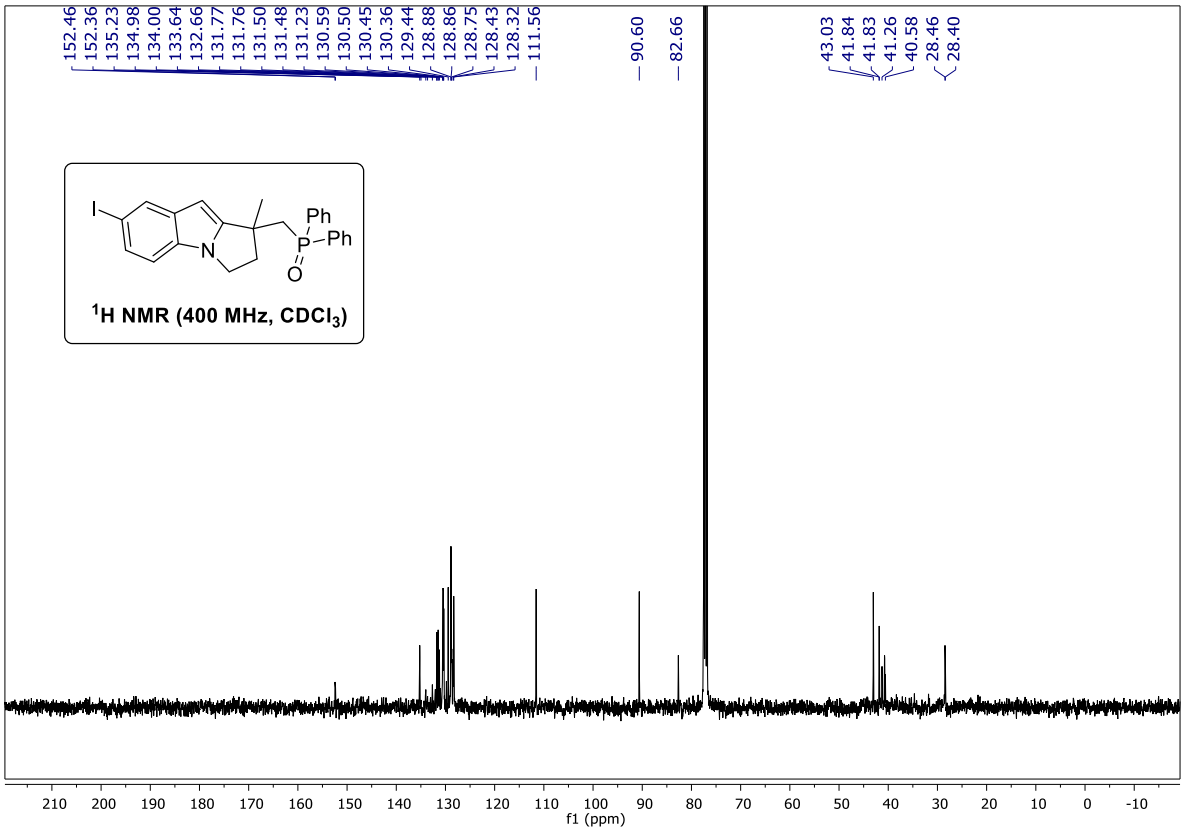


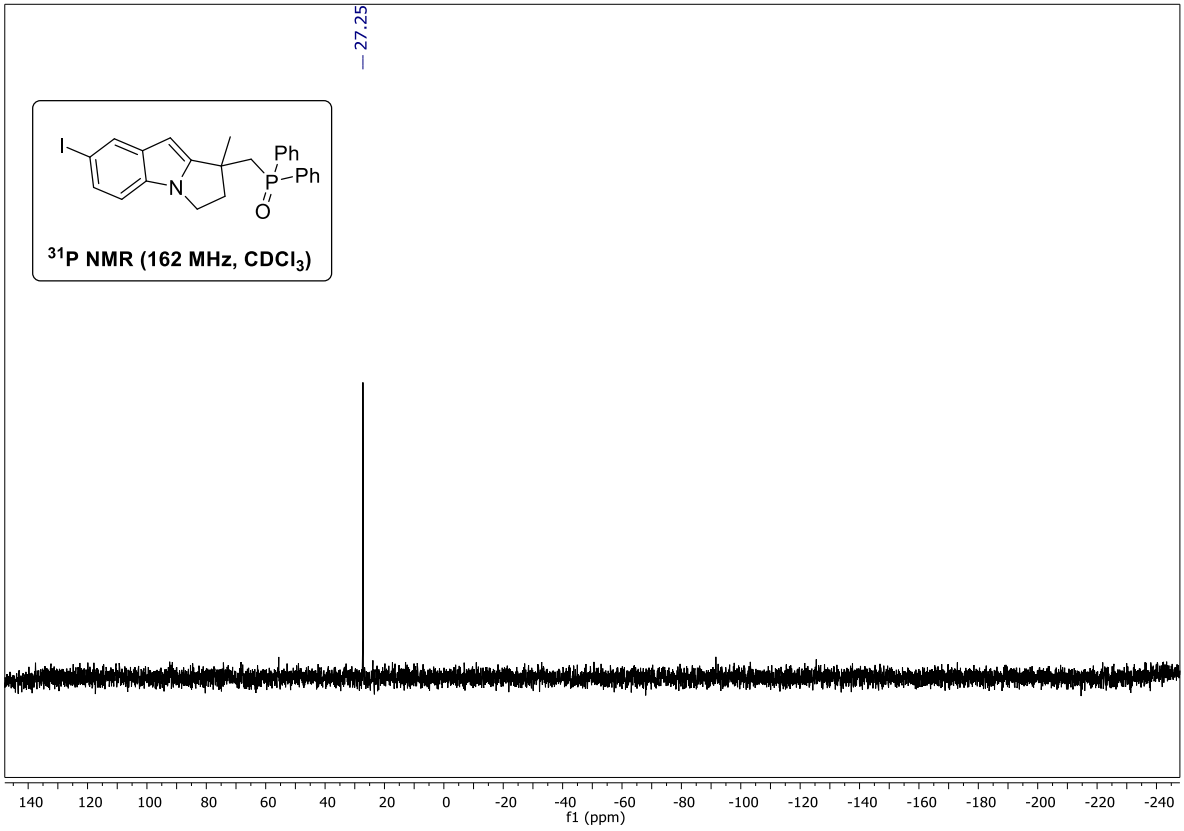




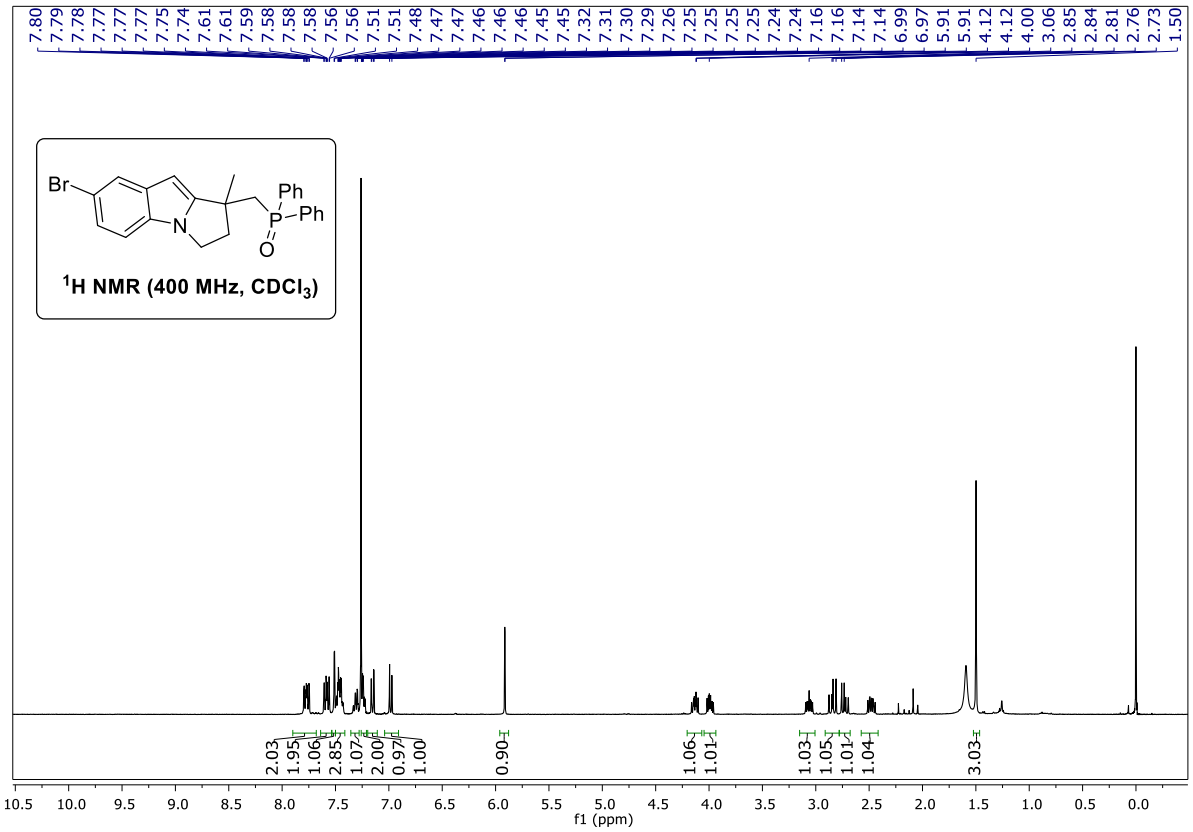
((7-Iodo-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5fa):

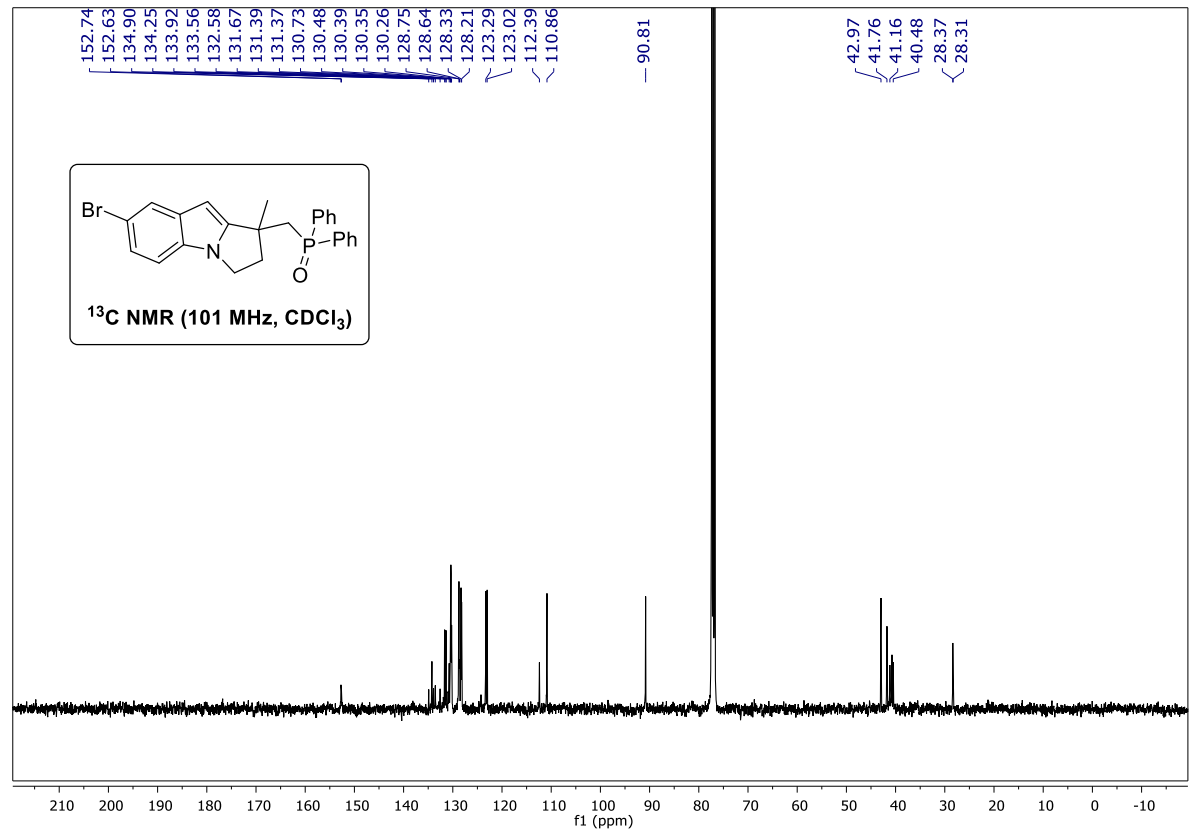


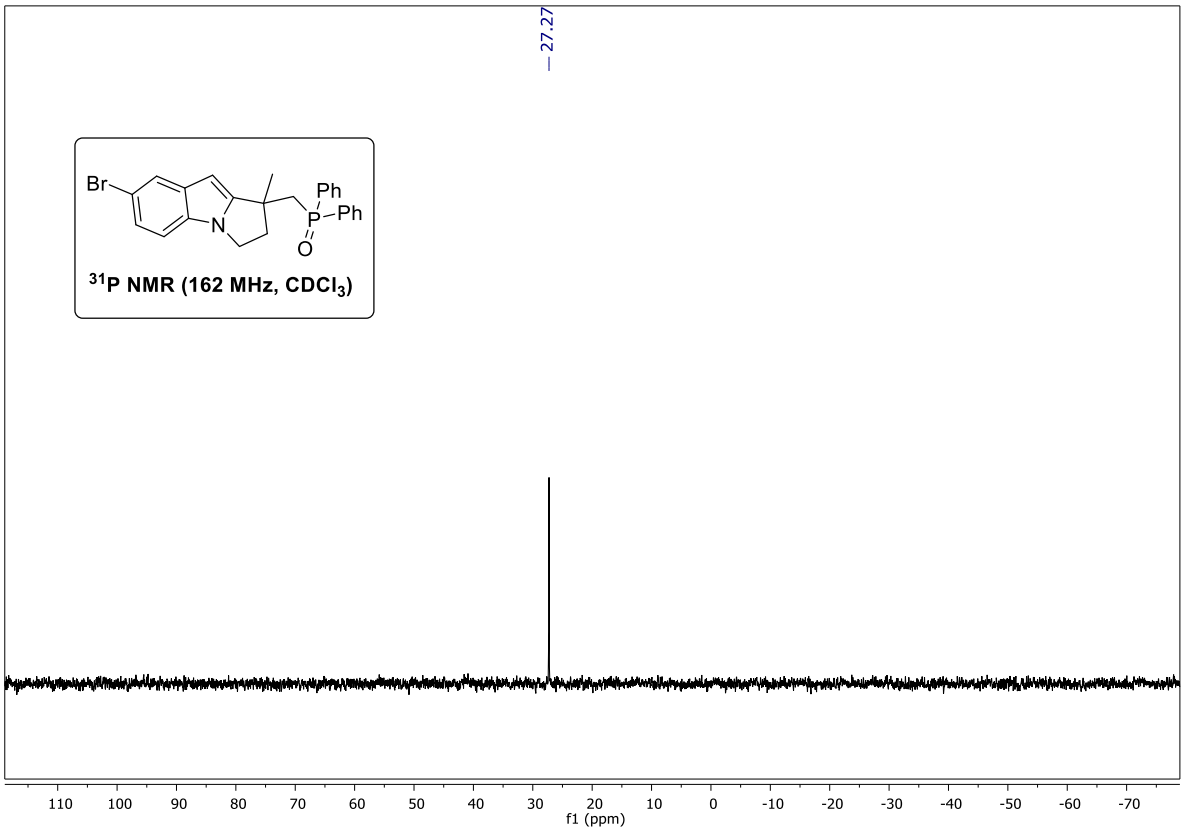

152.46
152.36
135.23
134.98
134.00
133.64
132.66
131.77
131.76
131.50
131.48
131.23
130.59
130.50
130.45
130.36
129.44
128.88
128.86
128.75
128.43
128.32
111.56
90.60
82.66
43.03
41.84
41.83
41.26
40.58
28.46
28.40
I
N
Ph
P
Ph
O
^{1}H NMR (400 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


27.25
I
N
Ph
P
Ph
O
^{31}P NMR (162 MHz, CDCl$_3$)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

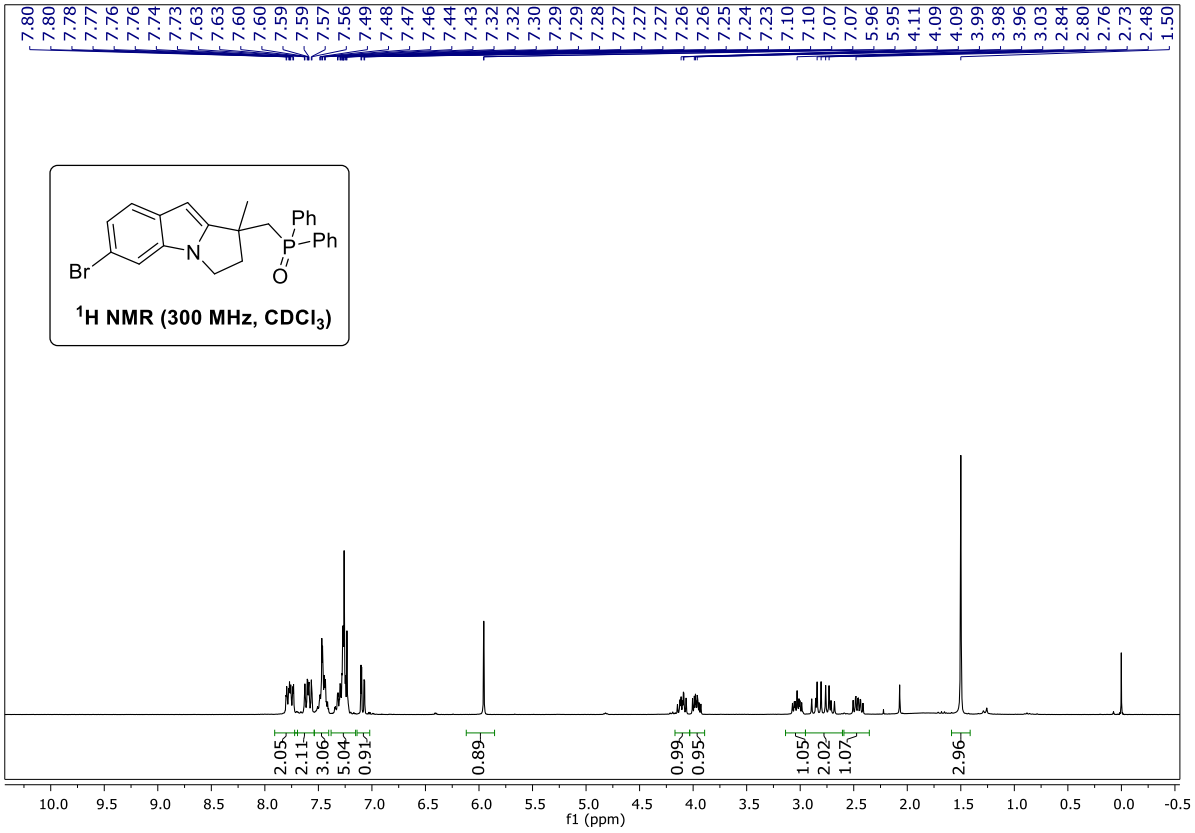
((7-Bromo-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5ga):

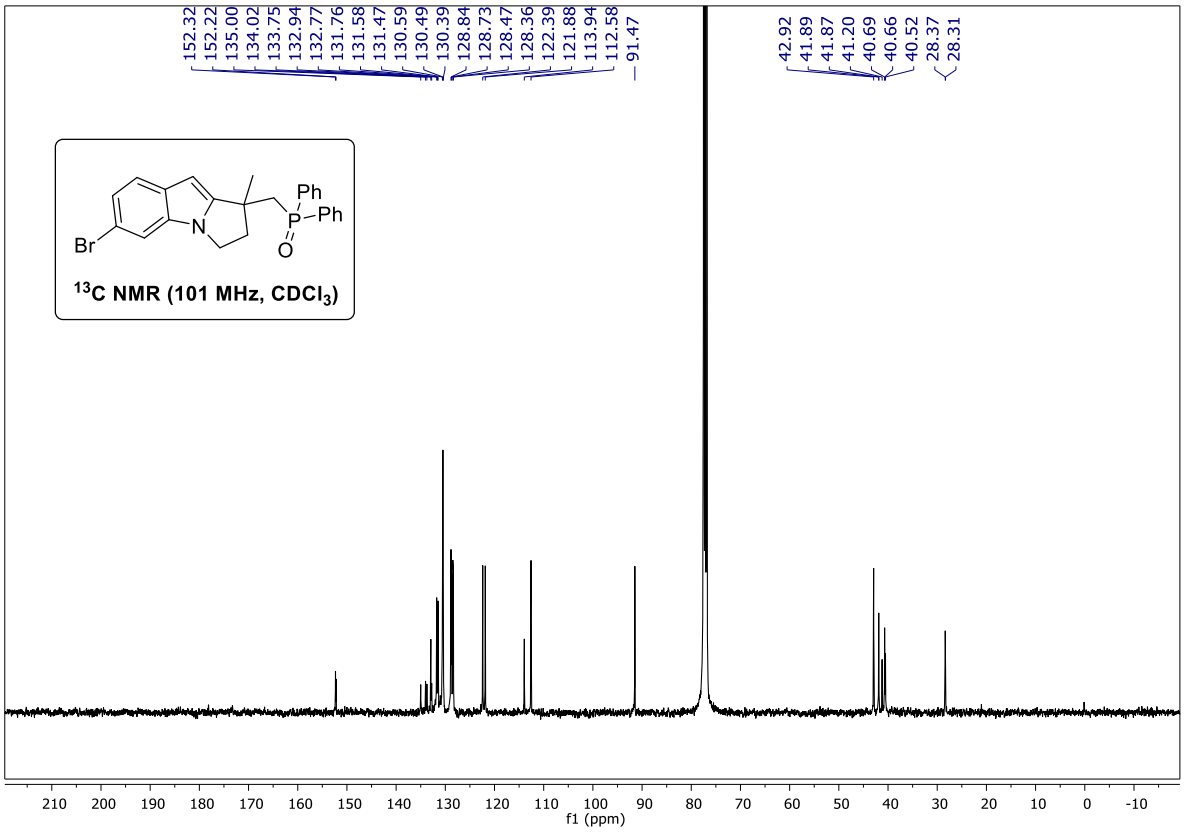


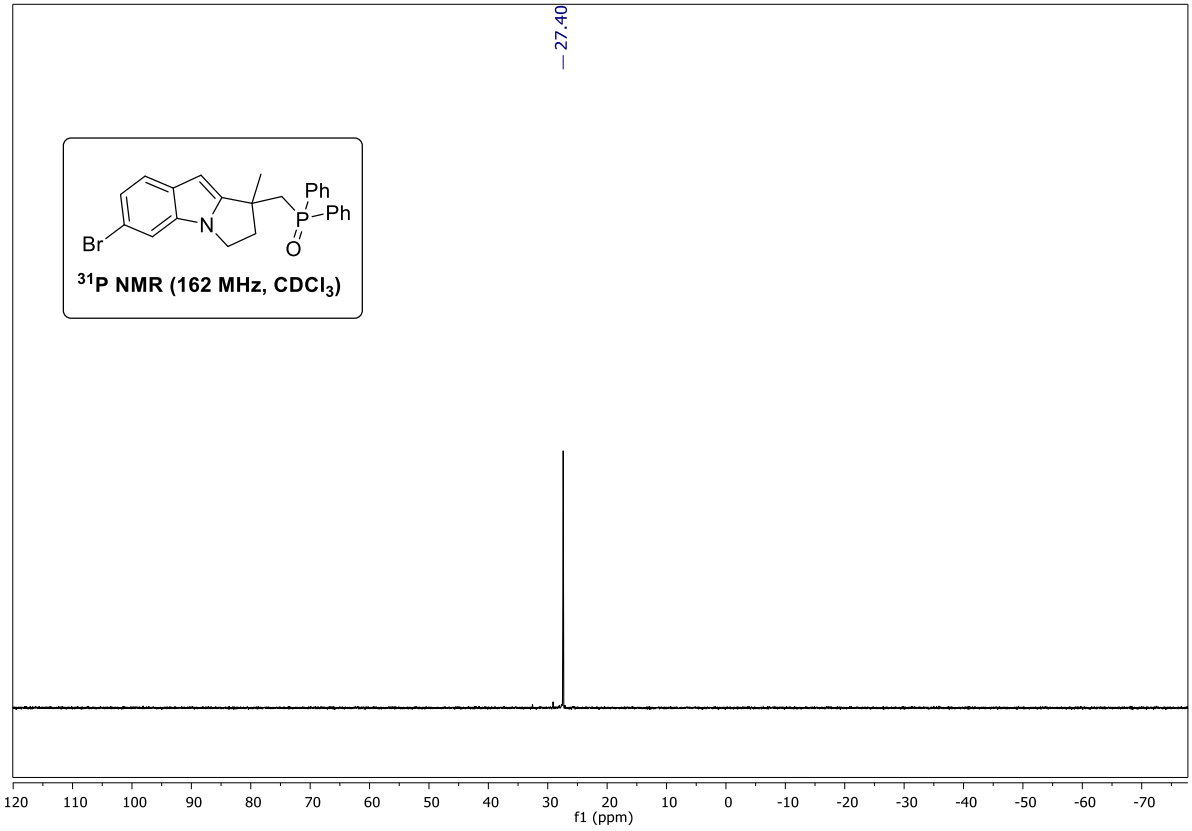




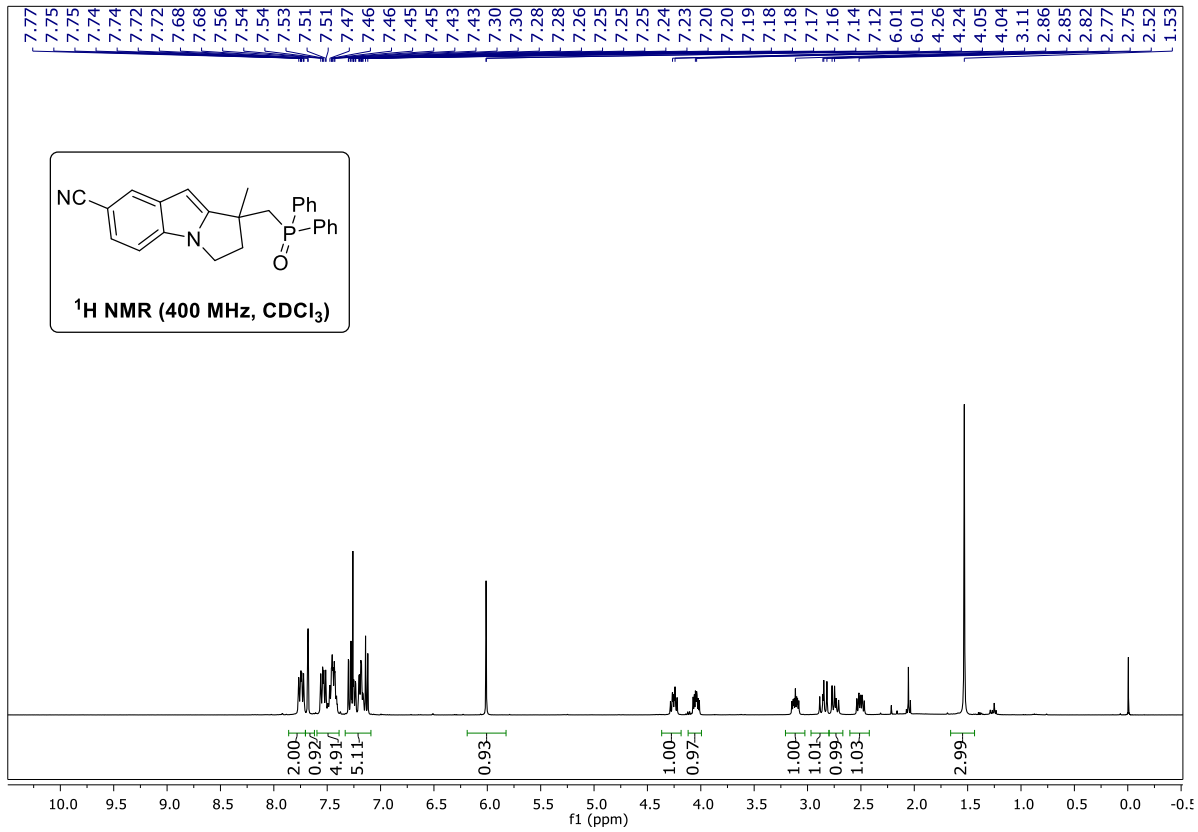
((6-Bromo-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5ha):

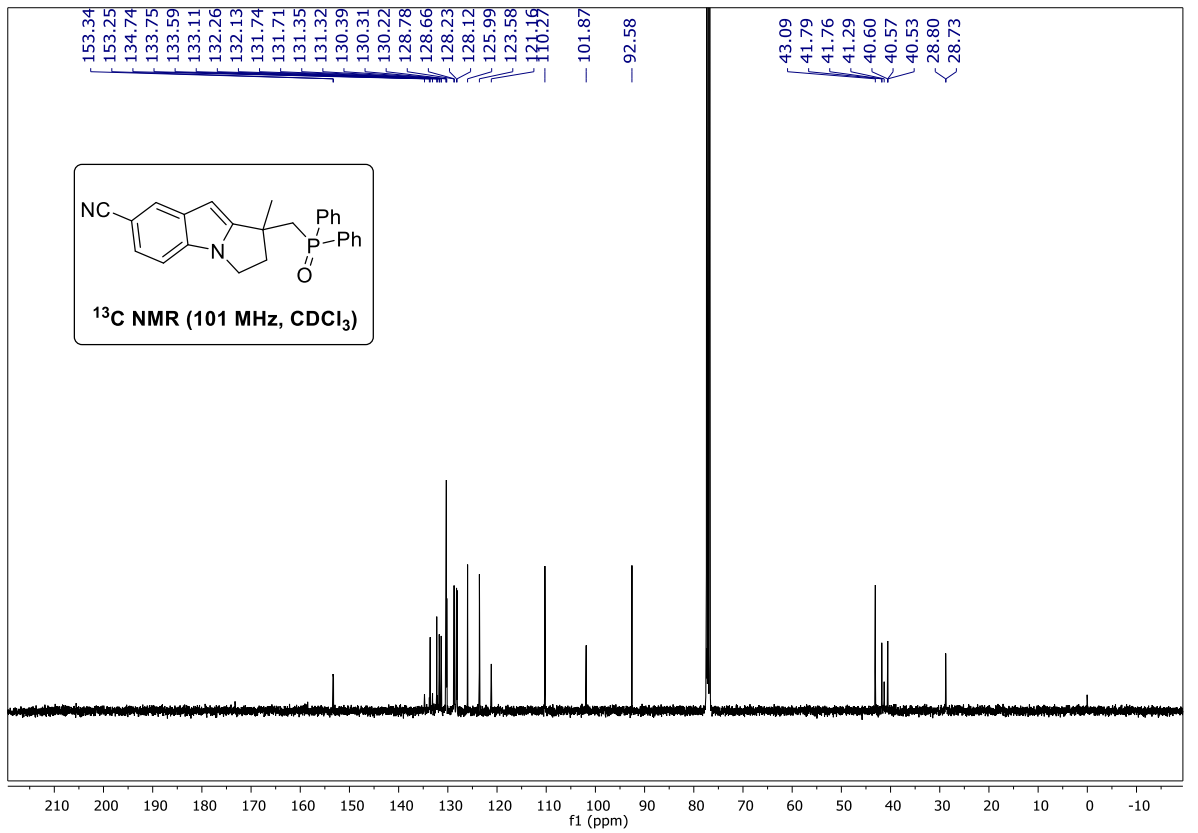


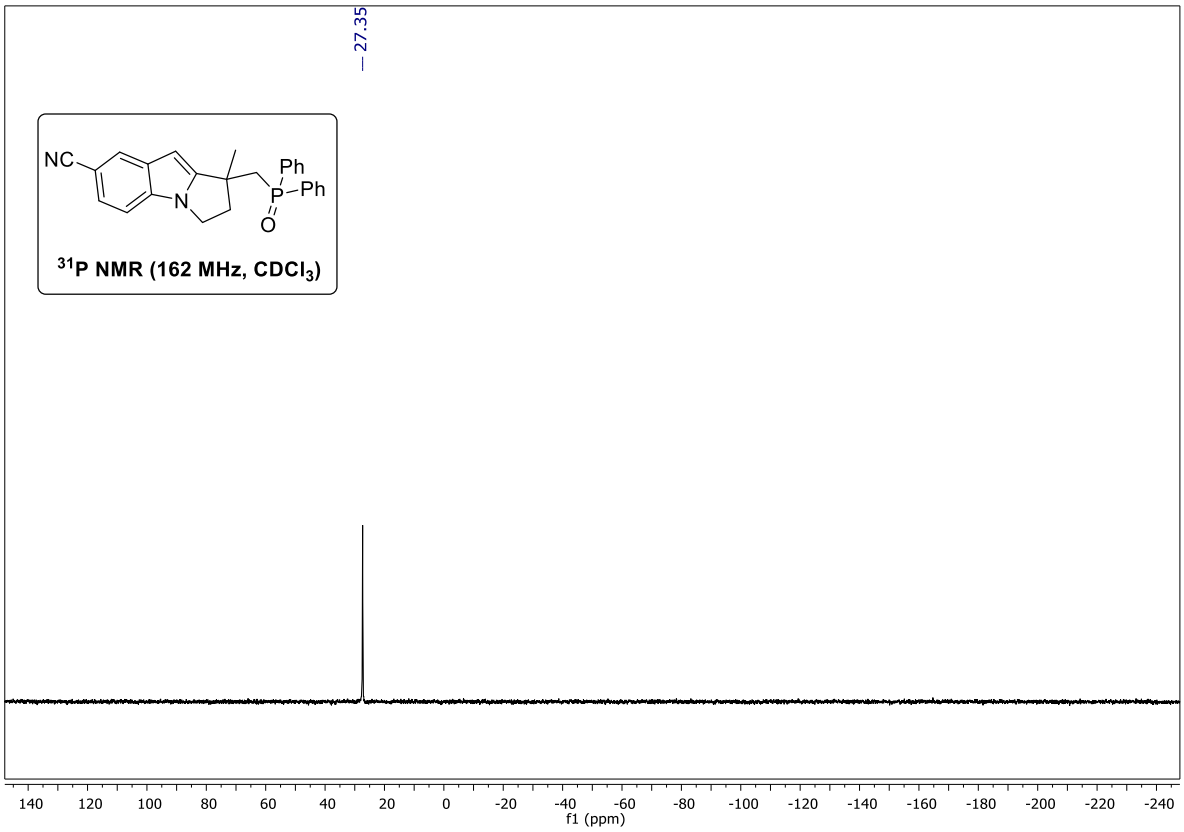

152.32
152.22
135.00
134.02
133.75
132.94
132.77
131.76
131.58
131.47
130.59
130.49
130.39
128.84
128.73
128.47
128.36
122.39
121.88
113.94
112.58
91.47
42.92
41.89
41.87
41.20
40.69
40.66
40.52
28.37
28.31
Ph
Ph
P
O
N
Br
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


27.40
Ph
Ph
P
O
N
Br
31P NMR (162 MHz, CDCl3)
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

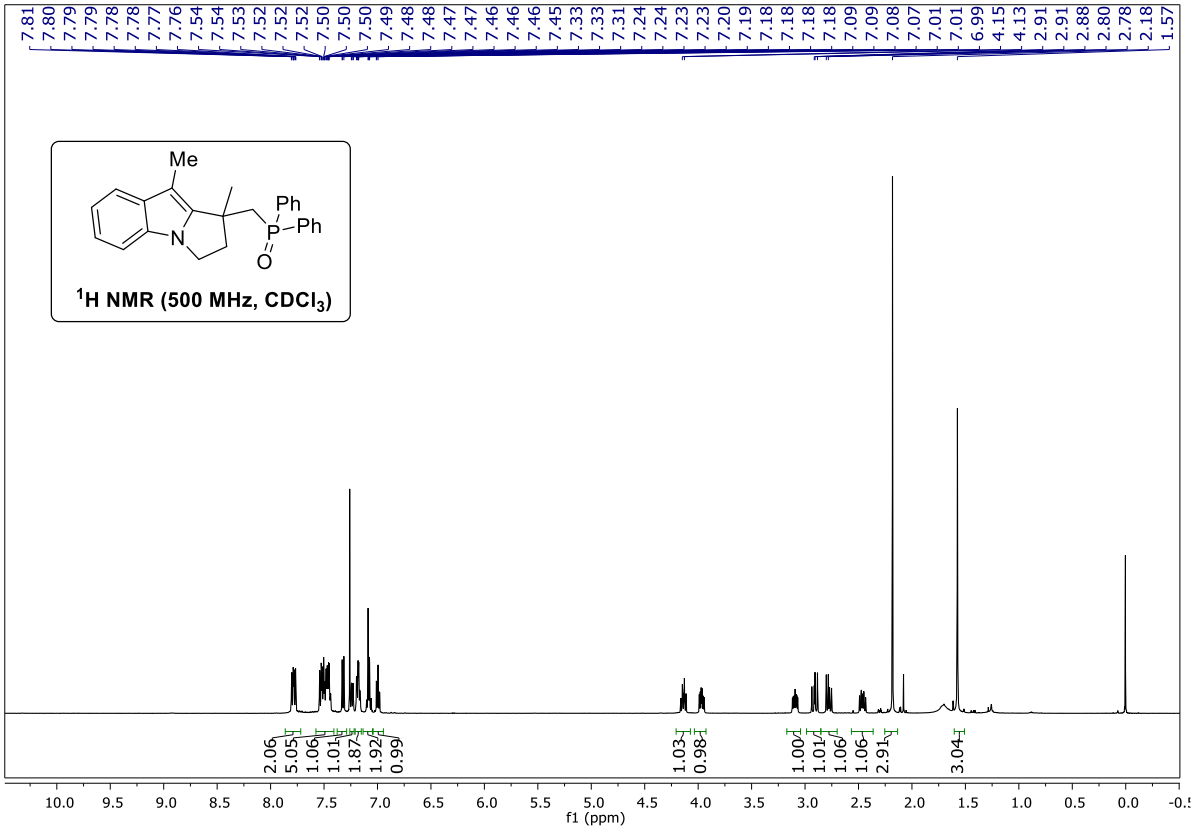
1-((Diphenylphosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-7-carbonitrile (5ia):

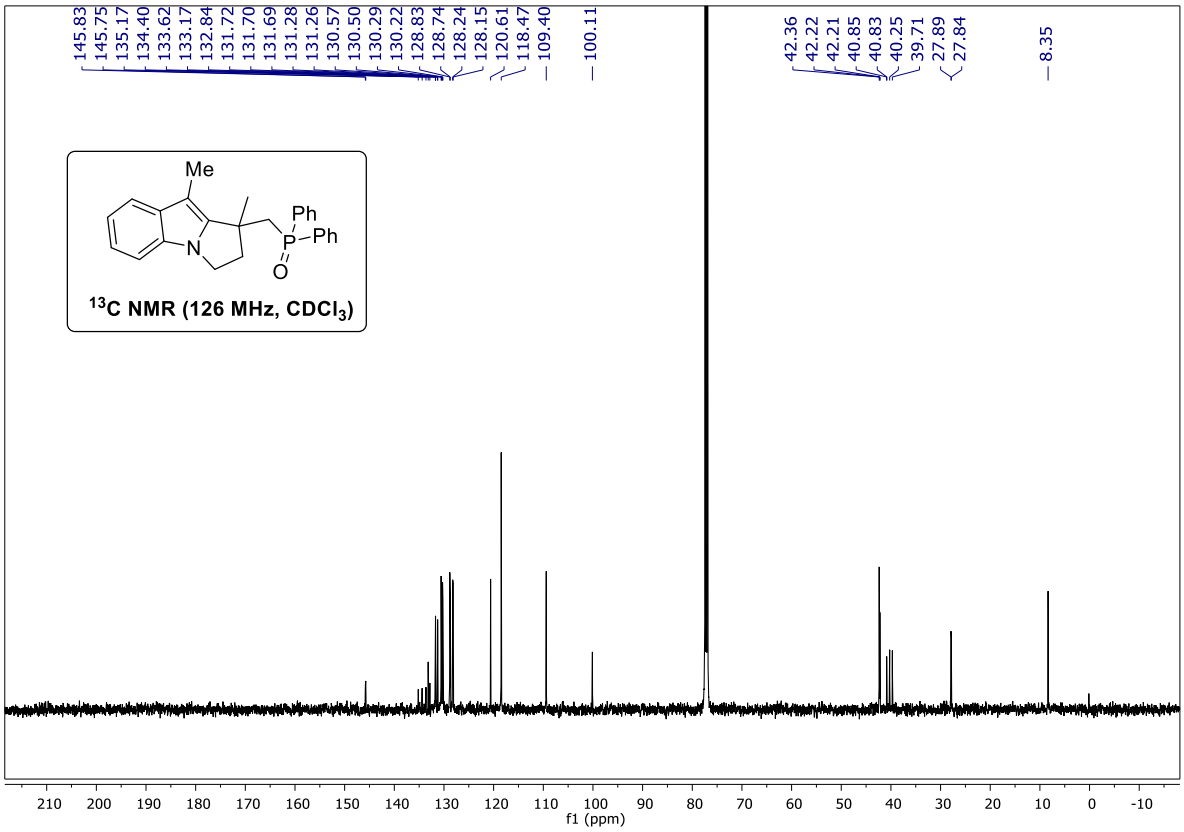


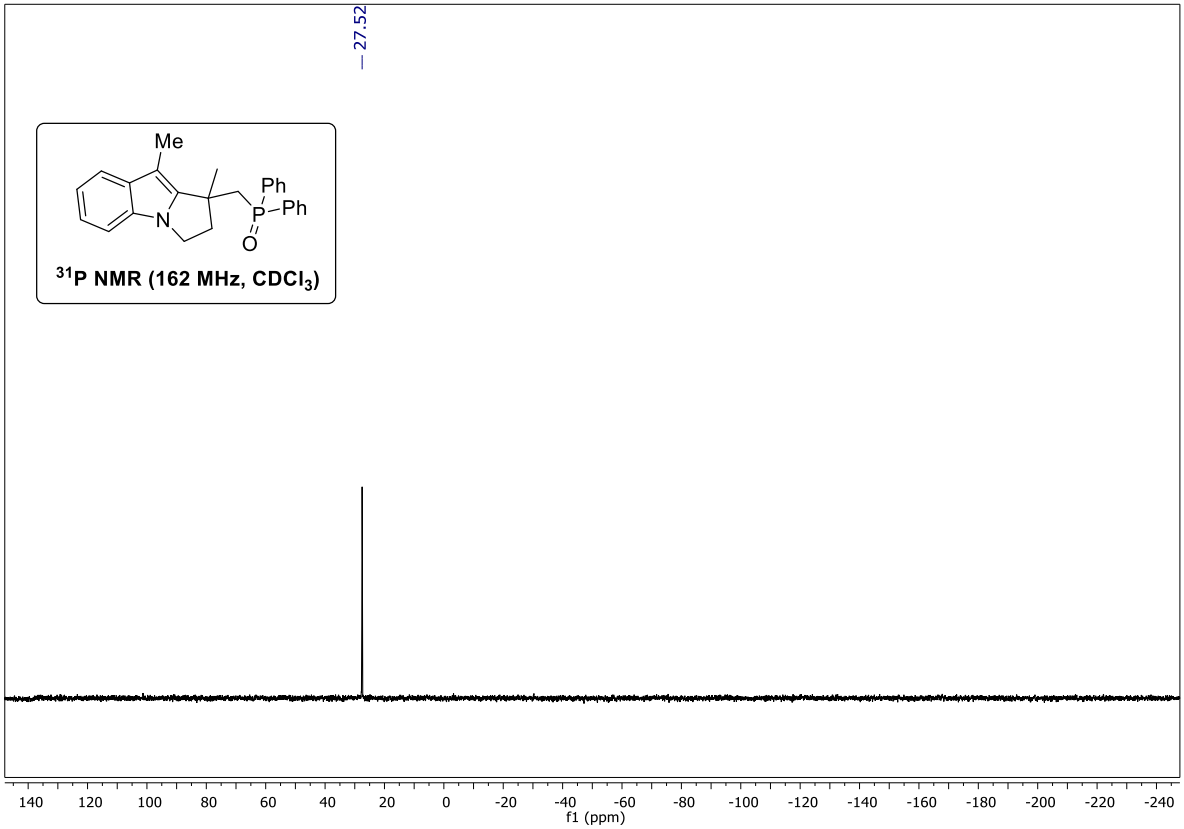




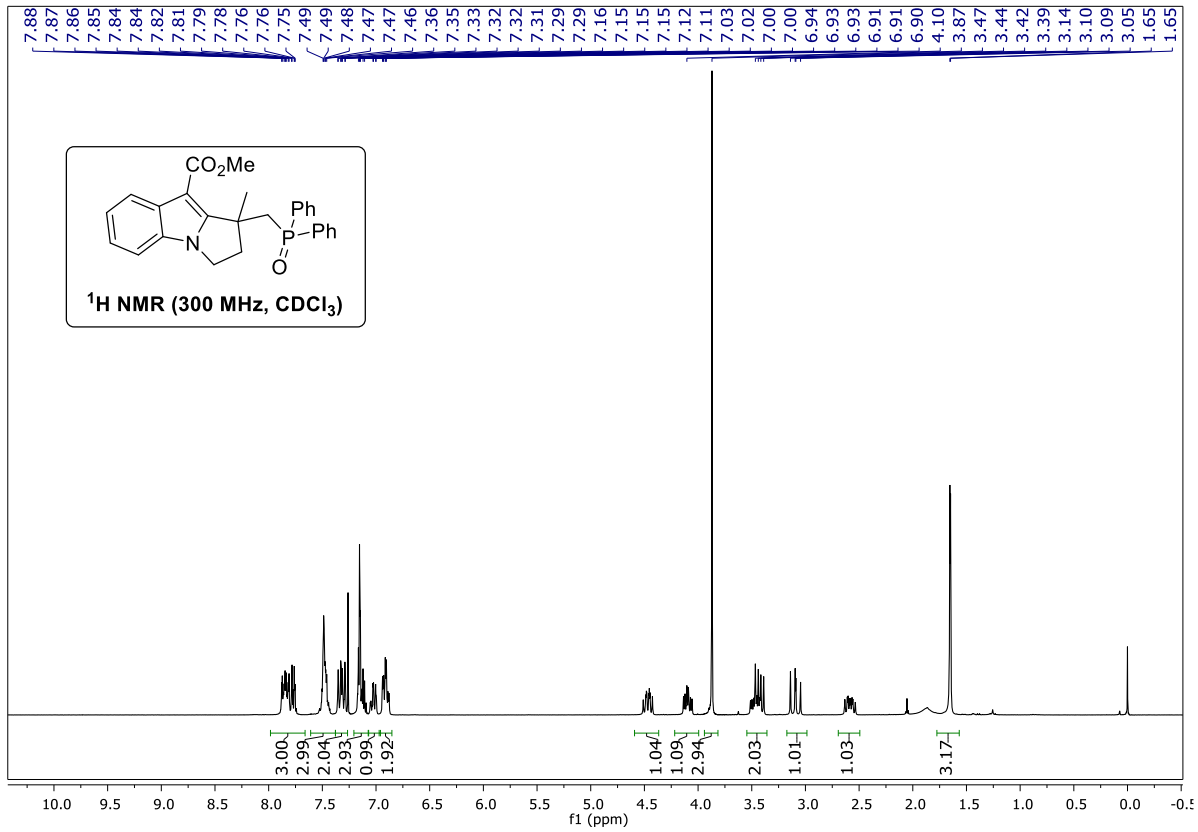
((1,9-Dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)methyl)diphenylphosphine oxide (5ka):

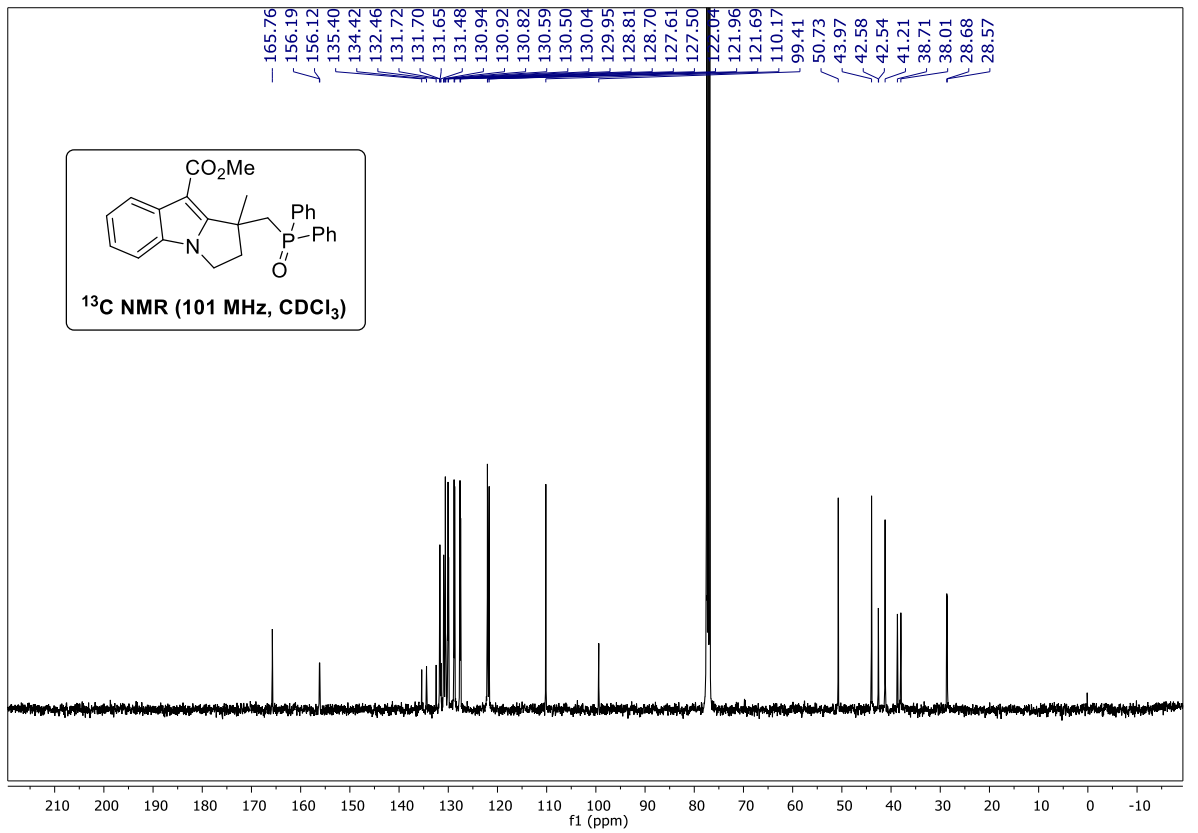


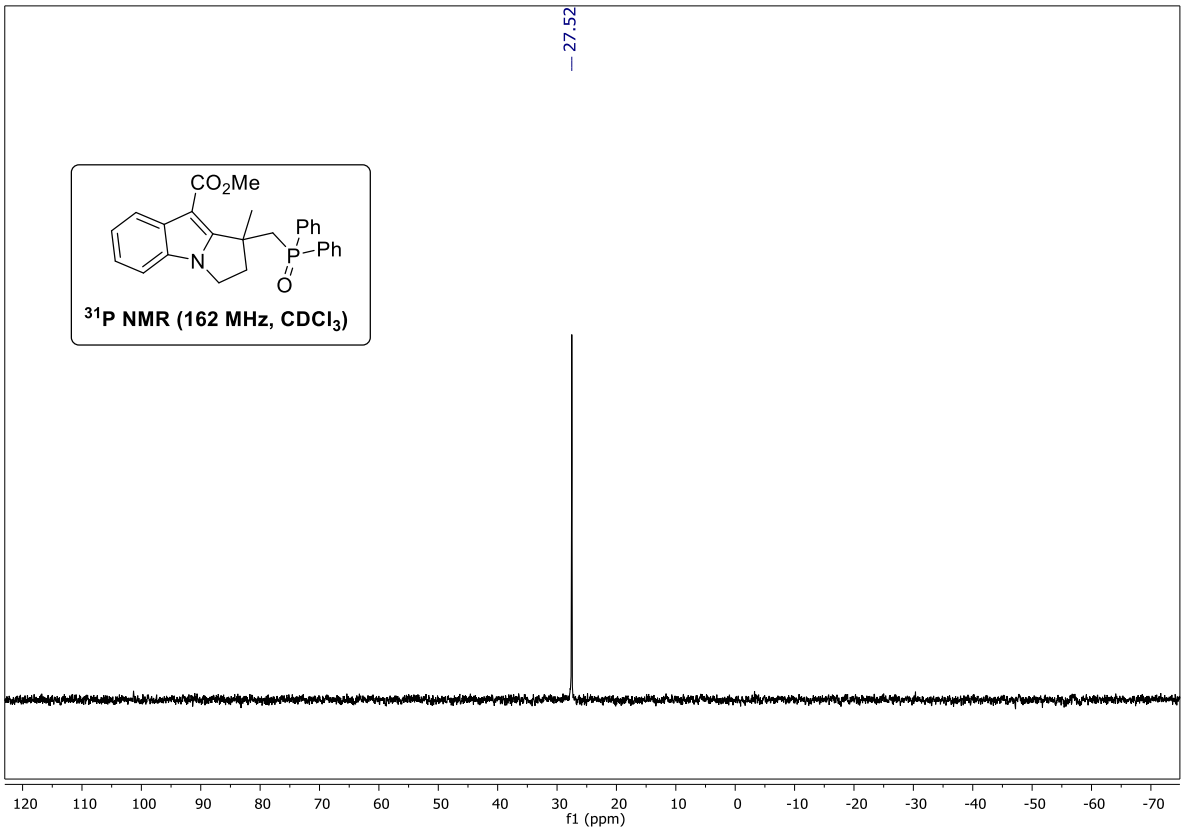

145.83
145.75
135.17
134.40
133.62
133.17
132.84
131.72
131.70
131.69
131.28
131.26
130.57
130.50
130.29
130.22
128.83
128.74
128.24
128.15
120.61
118.47
109.40
100.11
42.36
42.22
42.21
40.85
40.83
40.25
39.71
27.89
27.84
8.35
Me
Ph
P
Ph
O
N
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


27.52
Me
Ph
P
Ph
O
N
31P NMR (162 MHz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

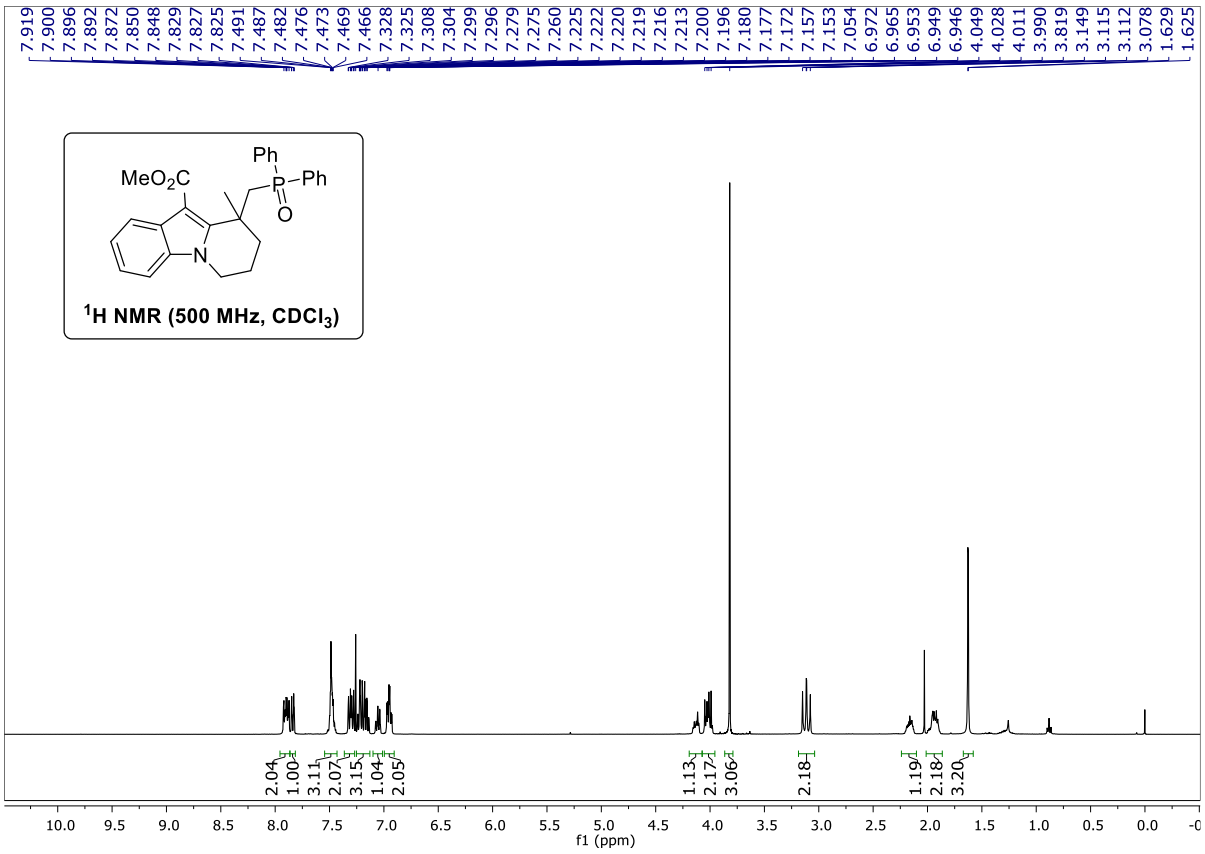
Methyl 1-((diphenylphosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5la):

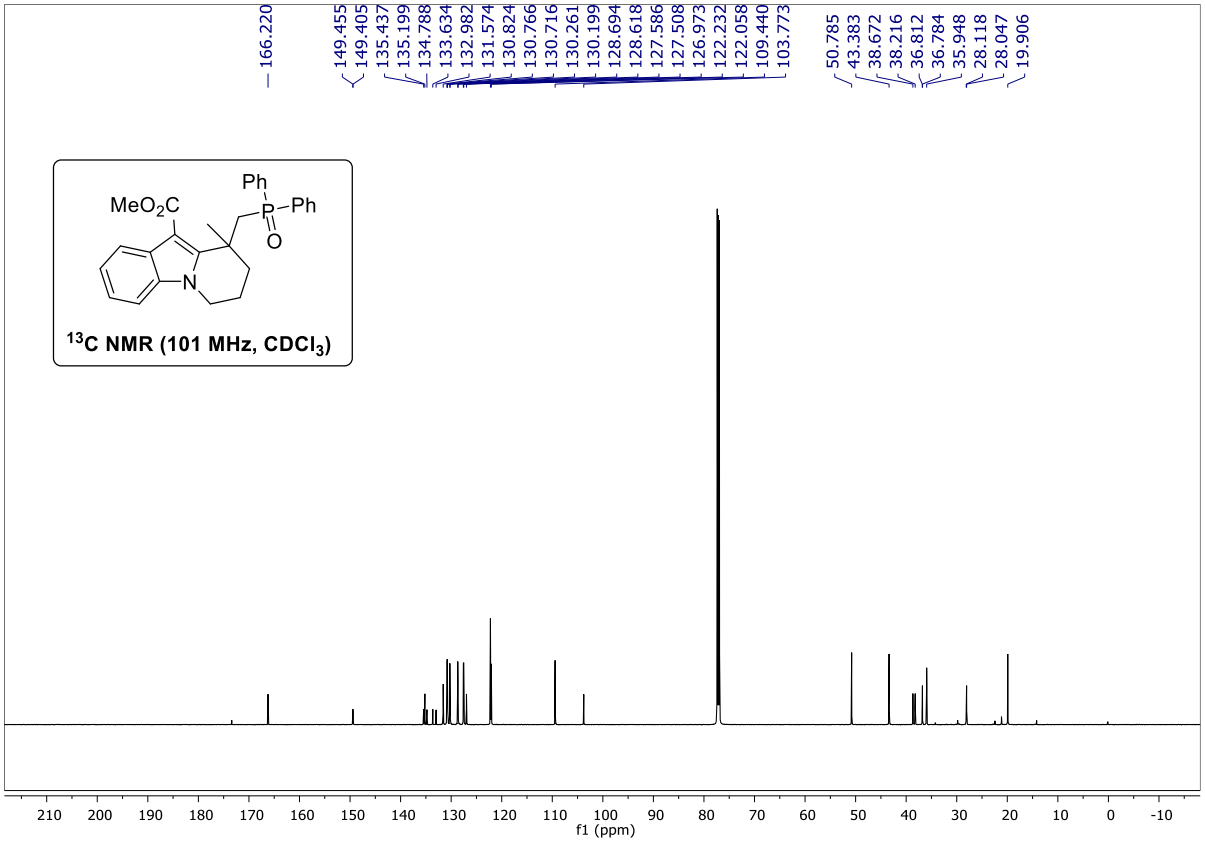


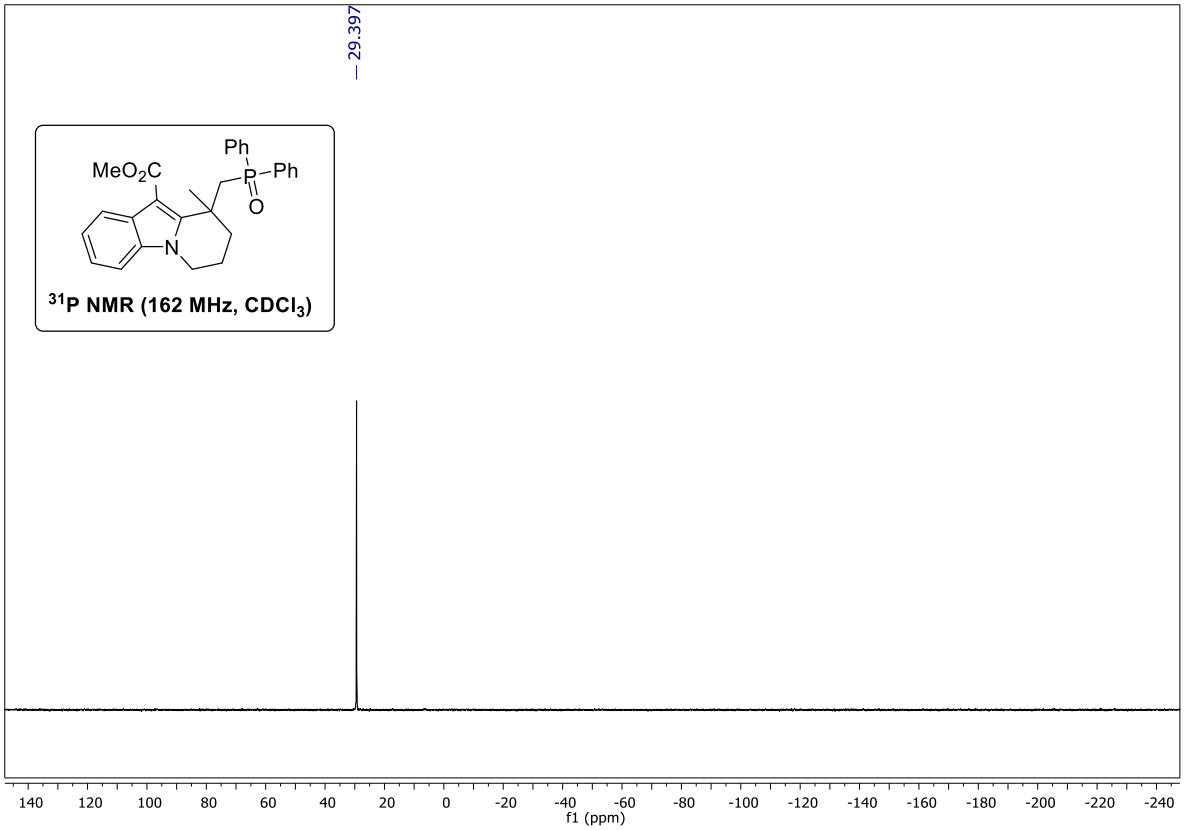




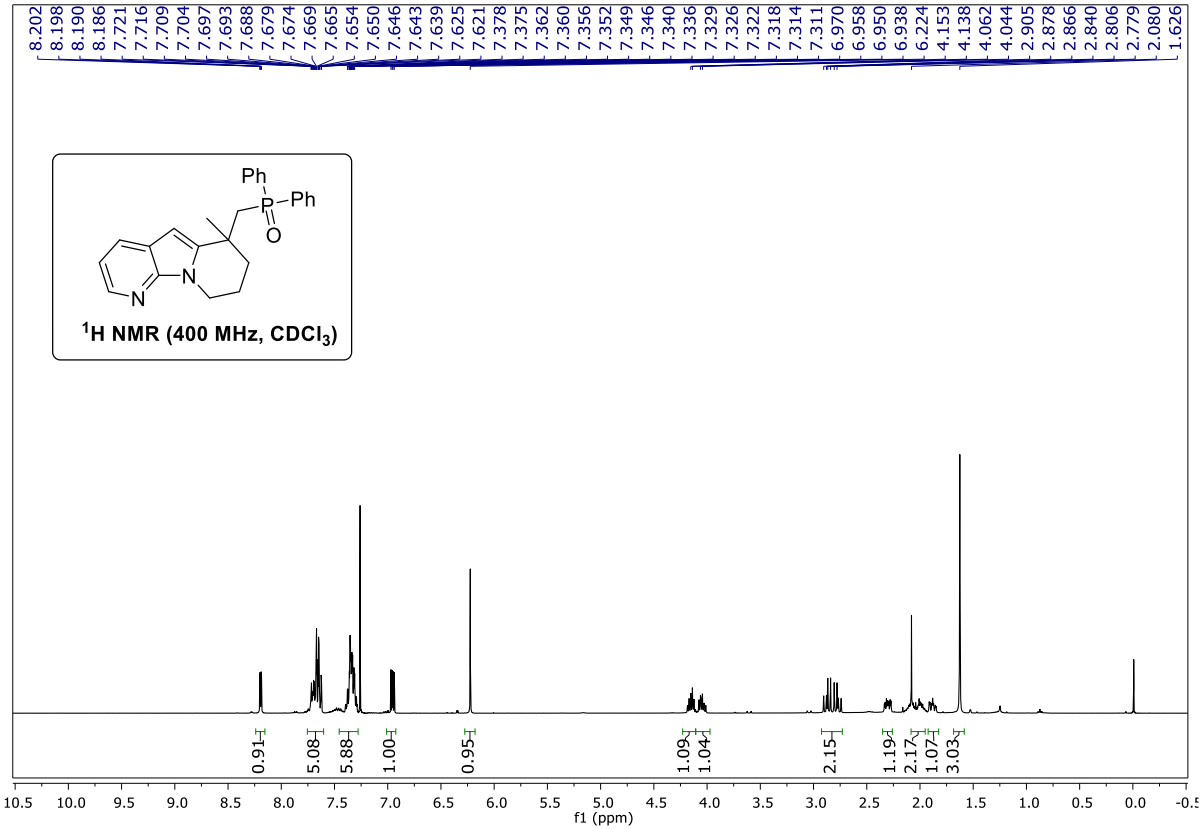
Methyl 9-((diphenylphosphoryl)methyl)-9-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole- 10-carboxylate (5ma):

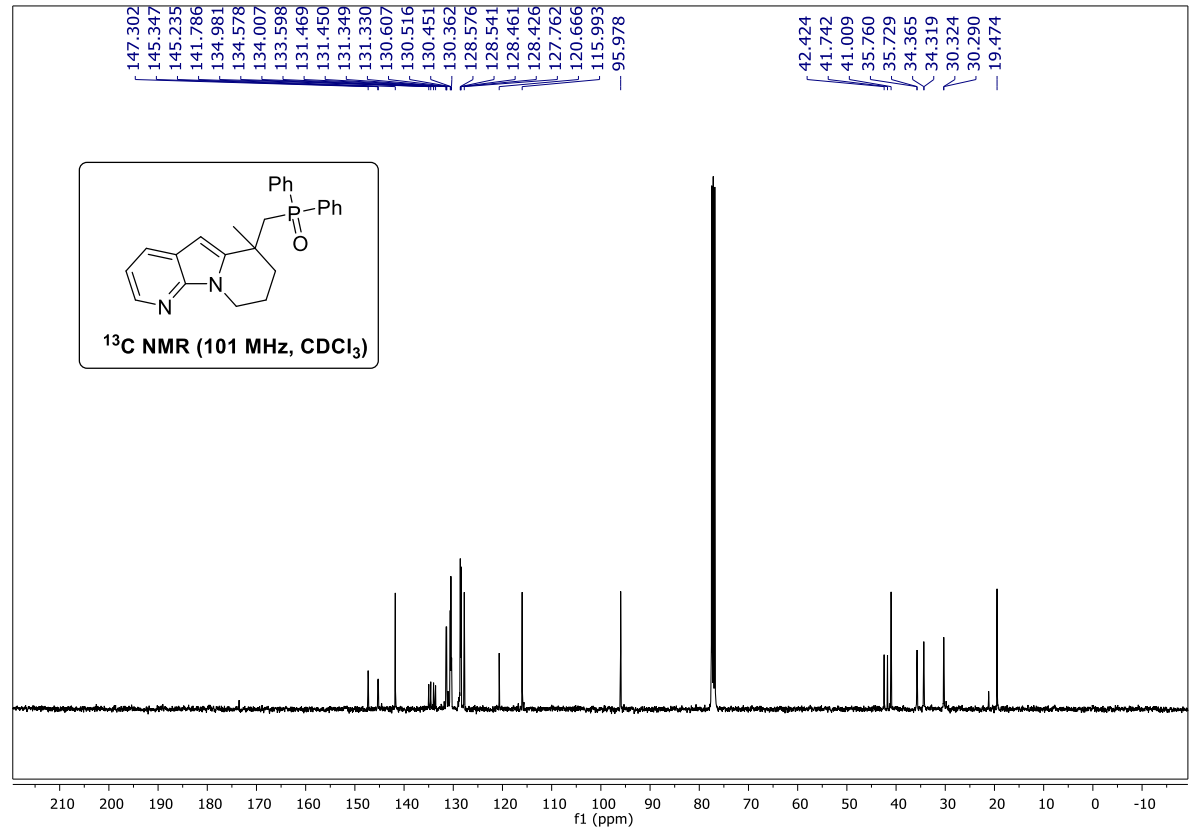


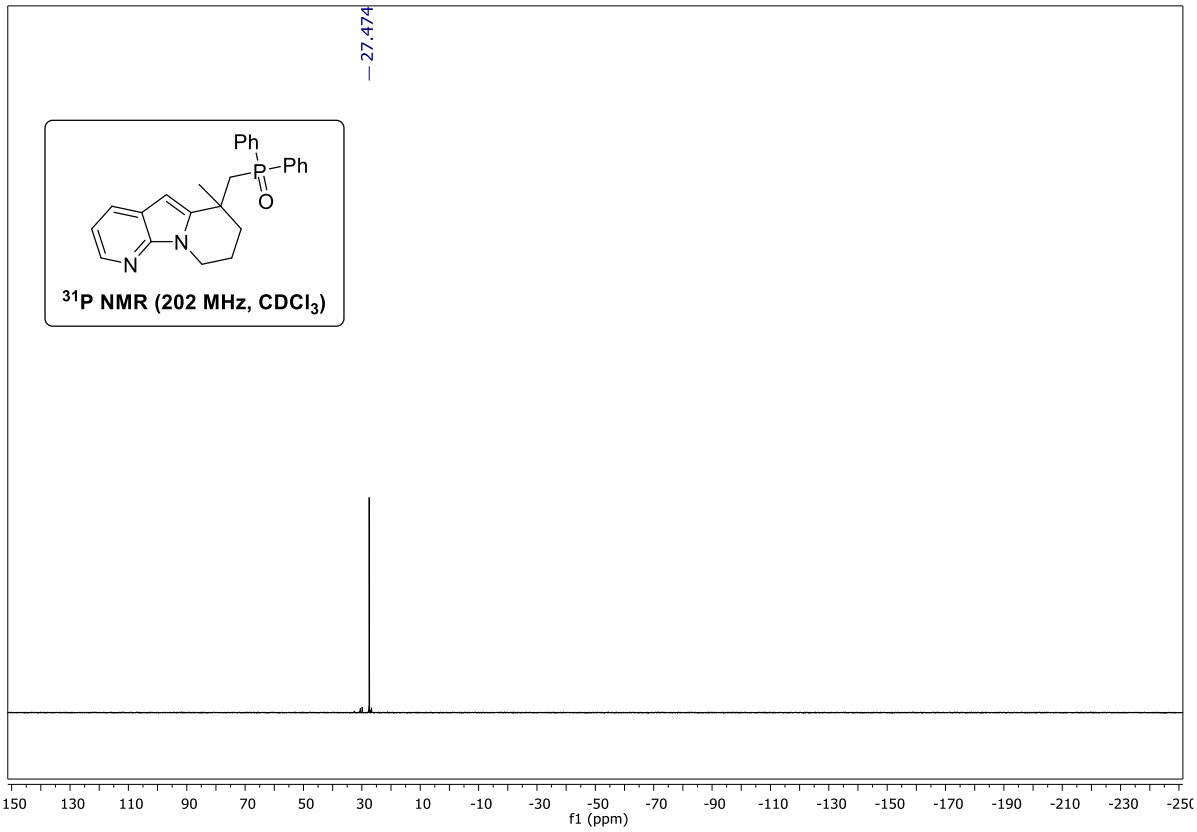

166.220
149.455
149.405
135.437
135.199
134.788
133.634
132.982
131.574
130.824
130.766
130.716
130.261
130.199
128.694
128.618
127.586
127.508
126.973
122.232
122.058
109.440
103.773
50.785
43.383
38.672
38.216
36.812
36.784
35.948
28.118
28.047
19.906
MeO2C
Ph
P
Ph
O
N
13C NMR (101 MHz, CDCl3)
f1 (ppm)


29.397
MeO2C
Ph
P
Ph
O
N
31P NMR (162 MHz, CDCl3)
f1 (ppm)

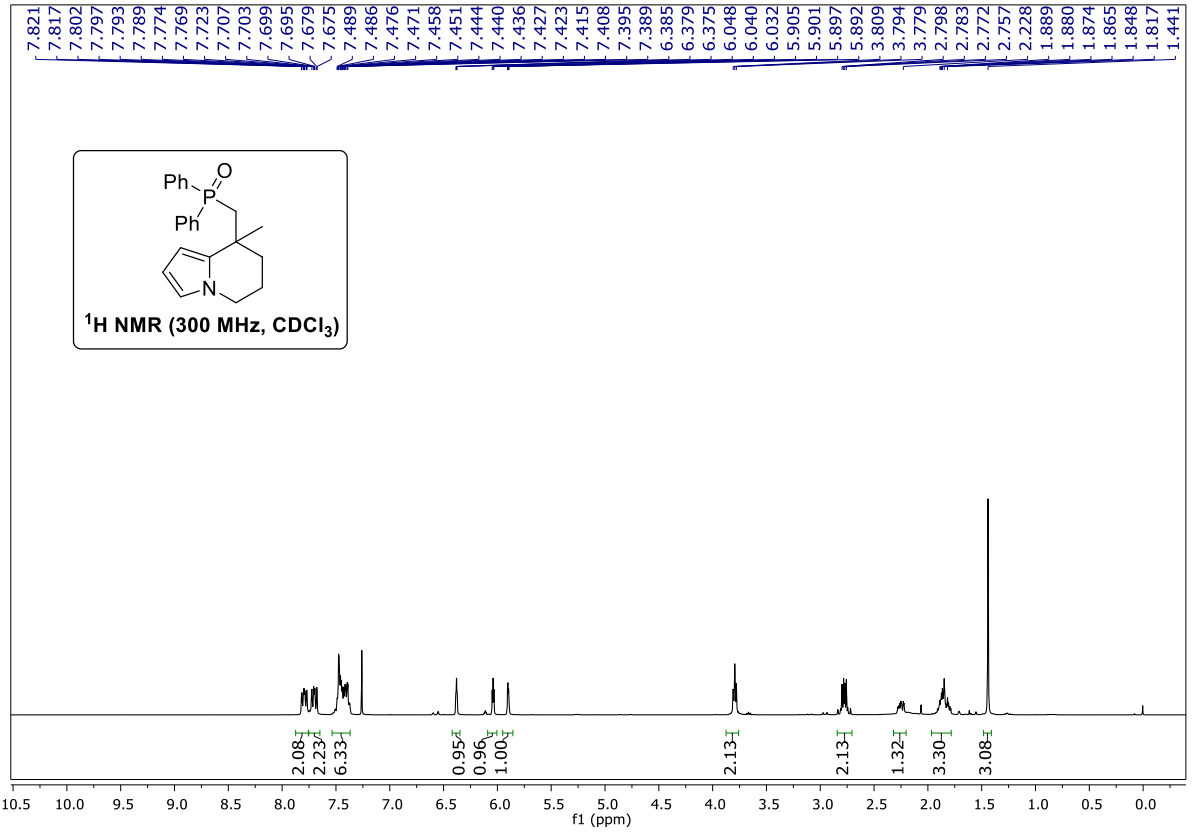
((6-Methyl-6,7,8,9-tetrahydropyrido[3,2-*b*]indolizin-6-yl)methyl)diphenylphosphine oxide (5na):

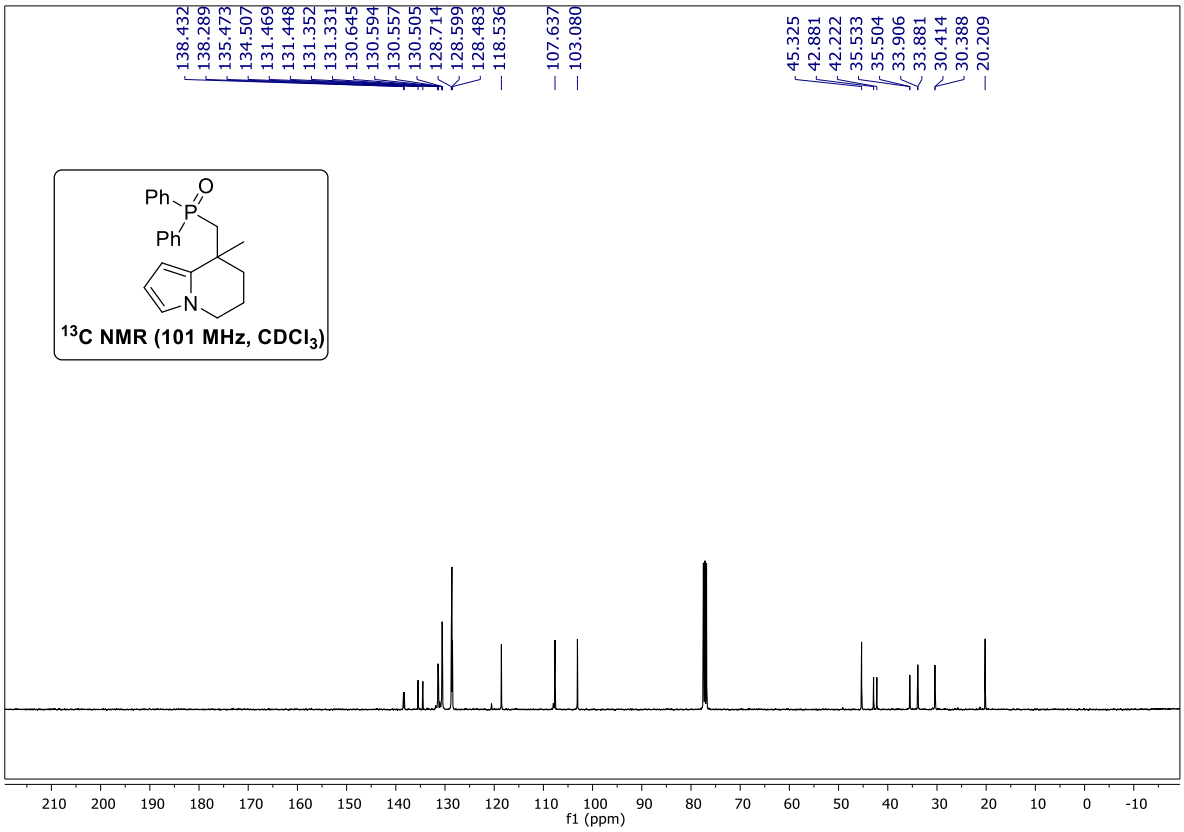


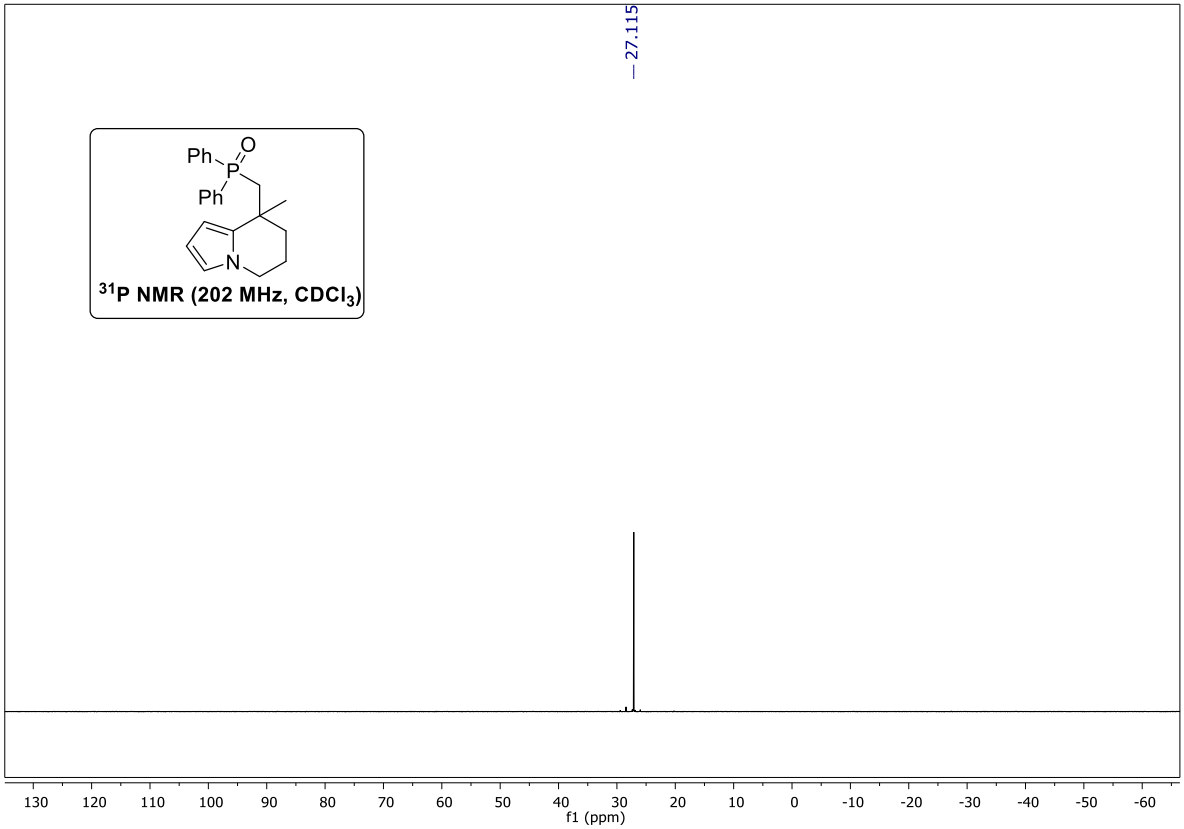




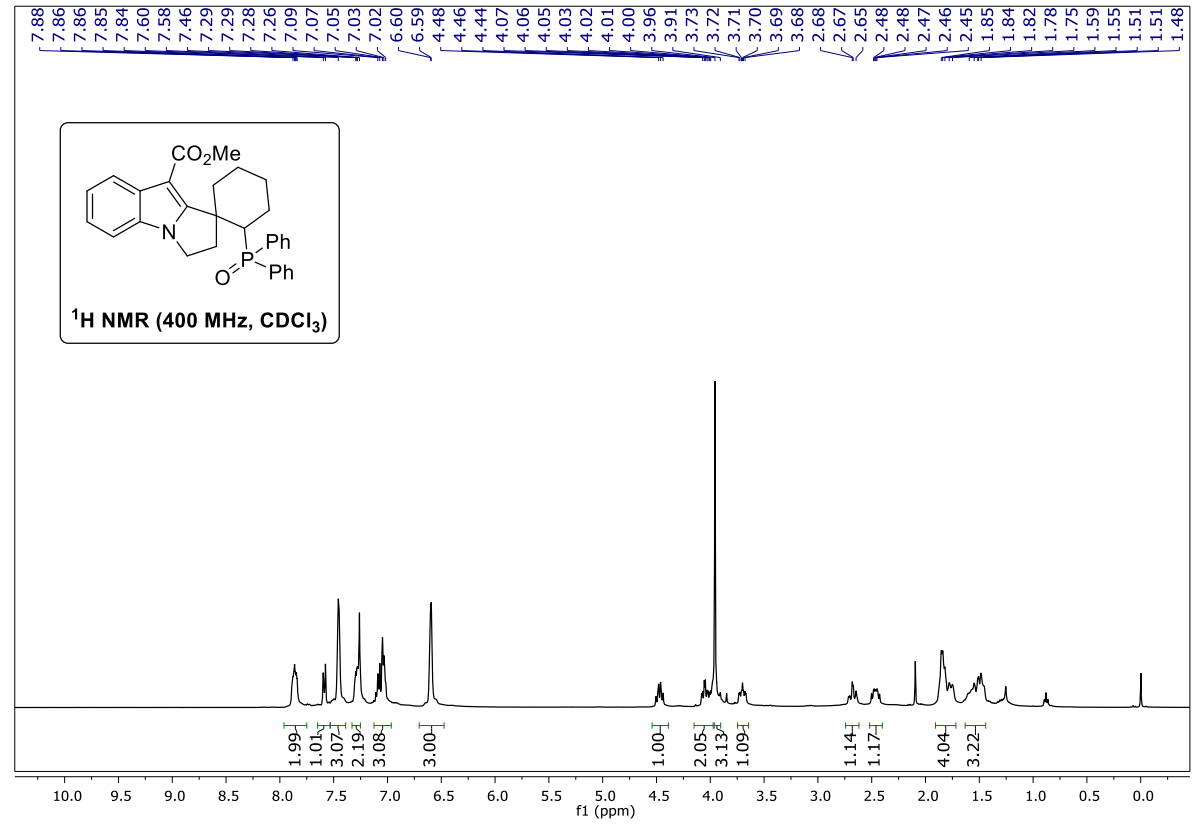
((8-Methyl-5,6,7,8-tetrahydroindolizin-8-yl)methyl)diphenylphosphine oxide (5oa):

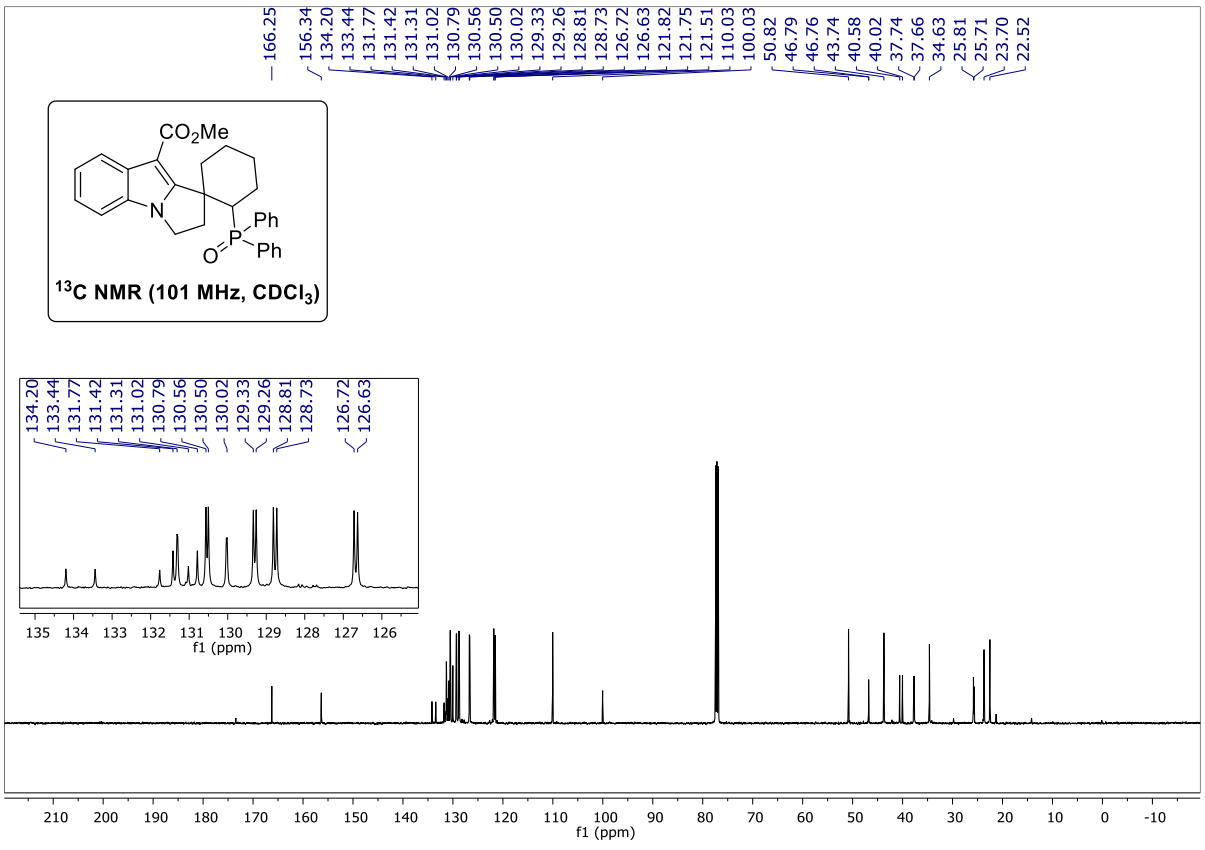


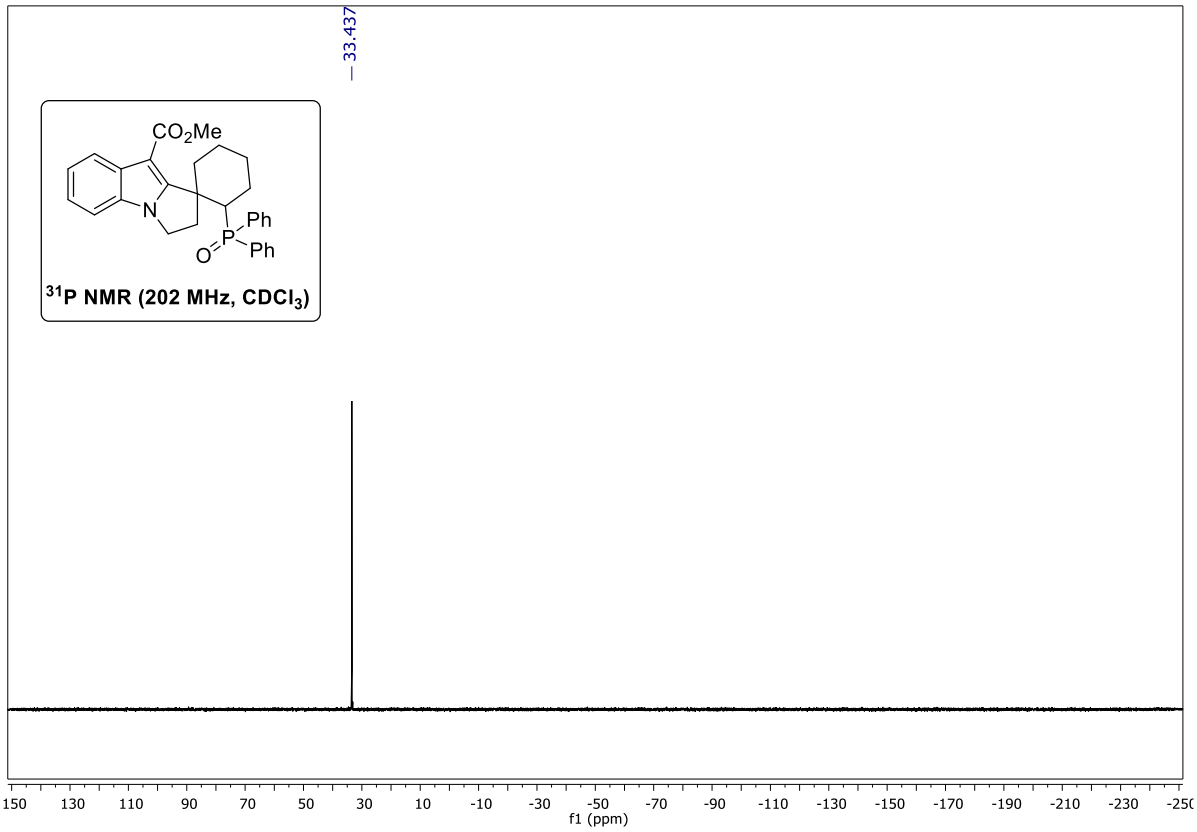

138.432
138.289
135.473
134.507
131.469
131.448
131.352
131.331
130.645
130.594
130.557
130.505
128.714
128.599
128.483
118.536
107.637
103.080
45.325
42.881
42.222
35.533
35.504
33.906
33.881
30.414
30.388
20.209
Ph
P
O
Ph
N
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


27.115
Ph
P
O
Ph
N
31P NMR (202 MHz, CDCl3)
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

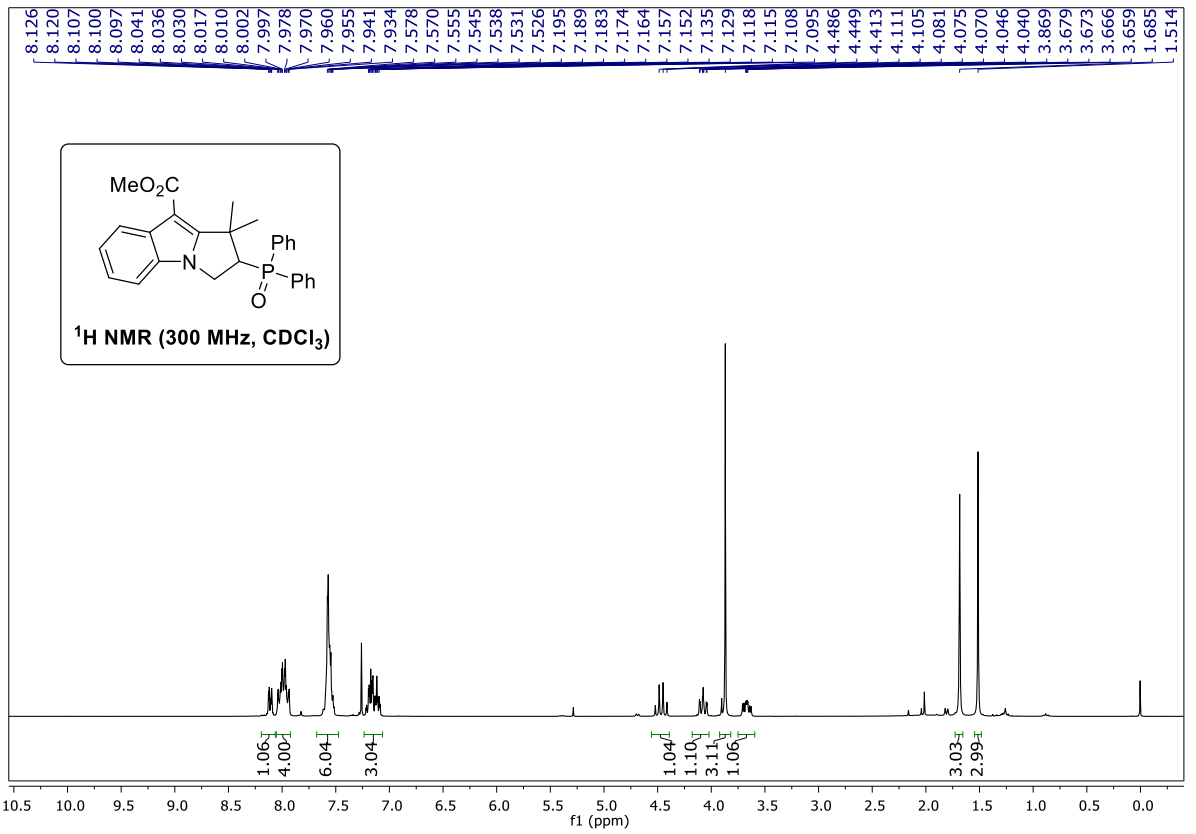
Methyl 2-(diphenylphosphoryl)-2',3'-dihydrospiro[cyclohexane-1,1'-pyrrolo[1,2-*a*]indole]-9'-carboxylate (5pa):

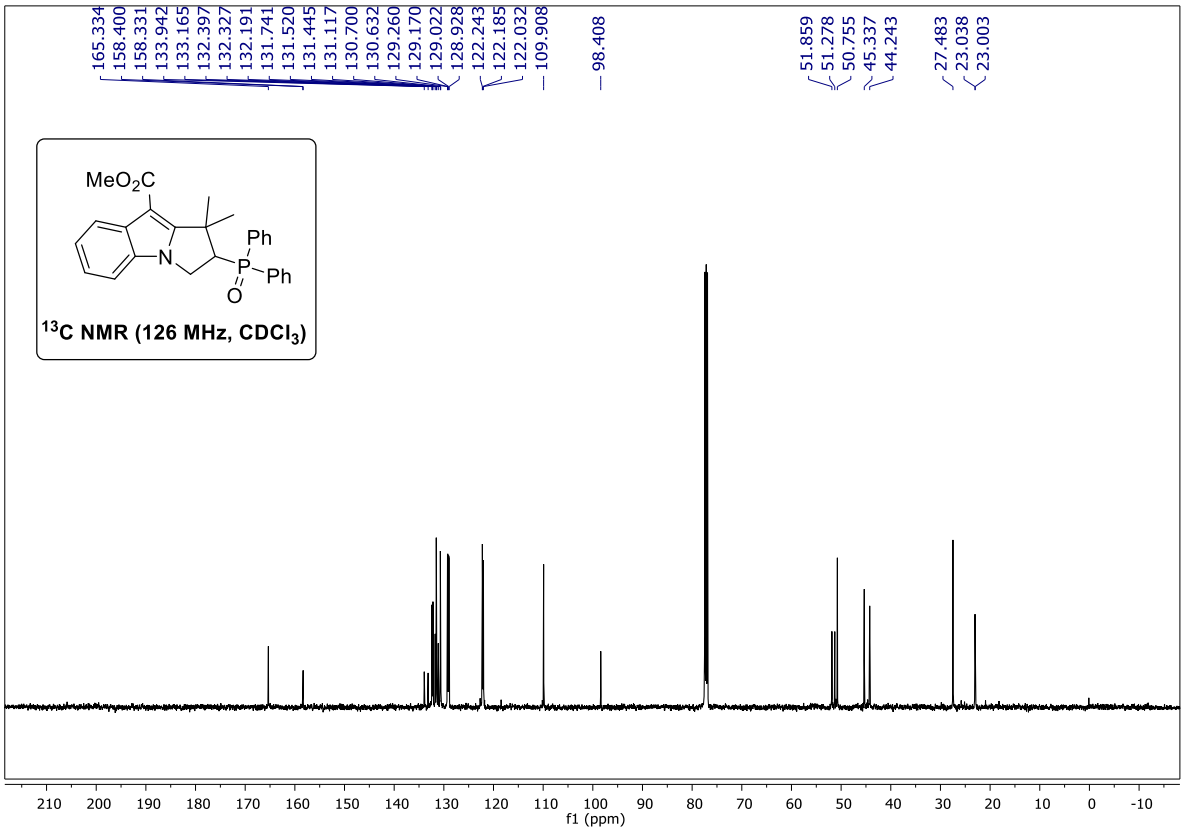


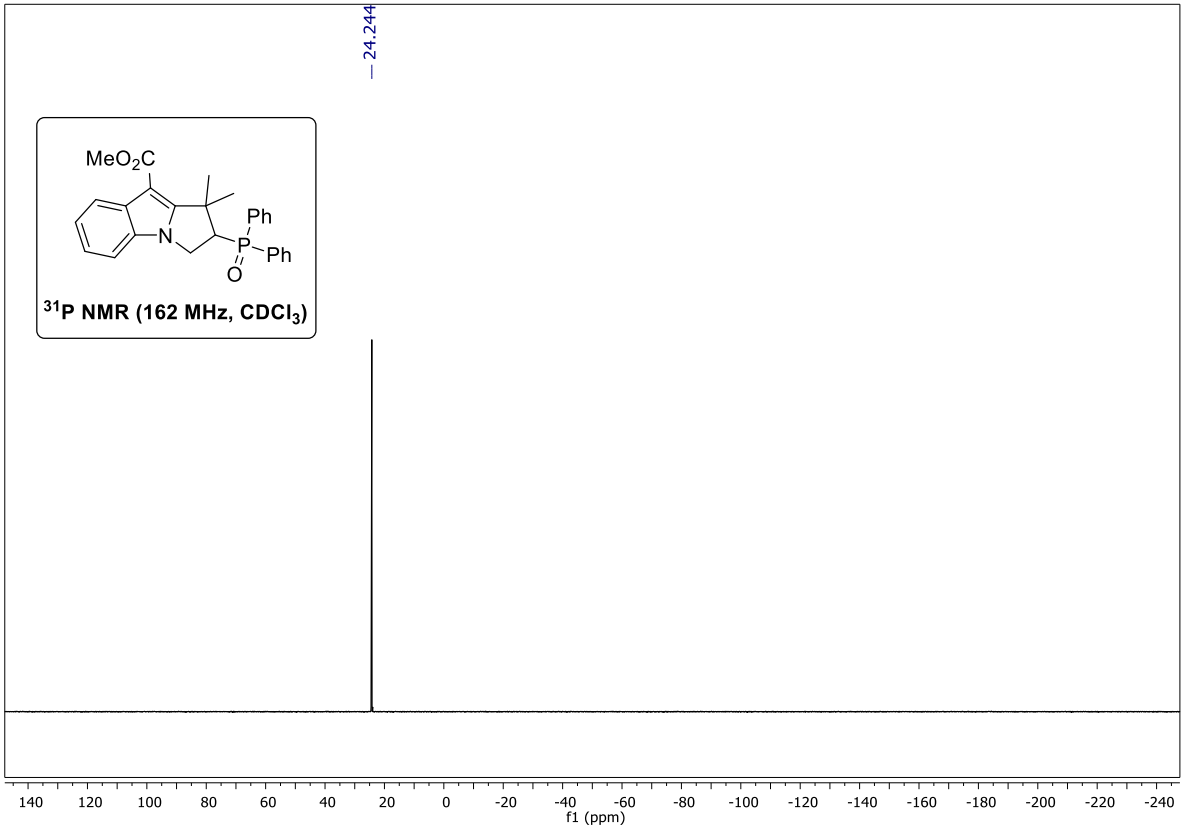




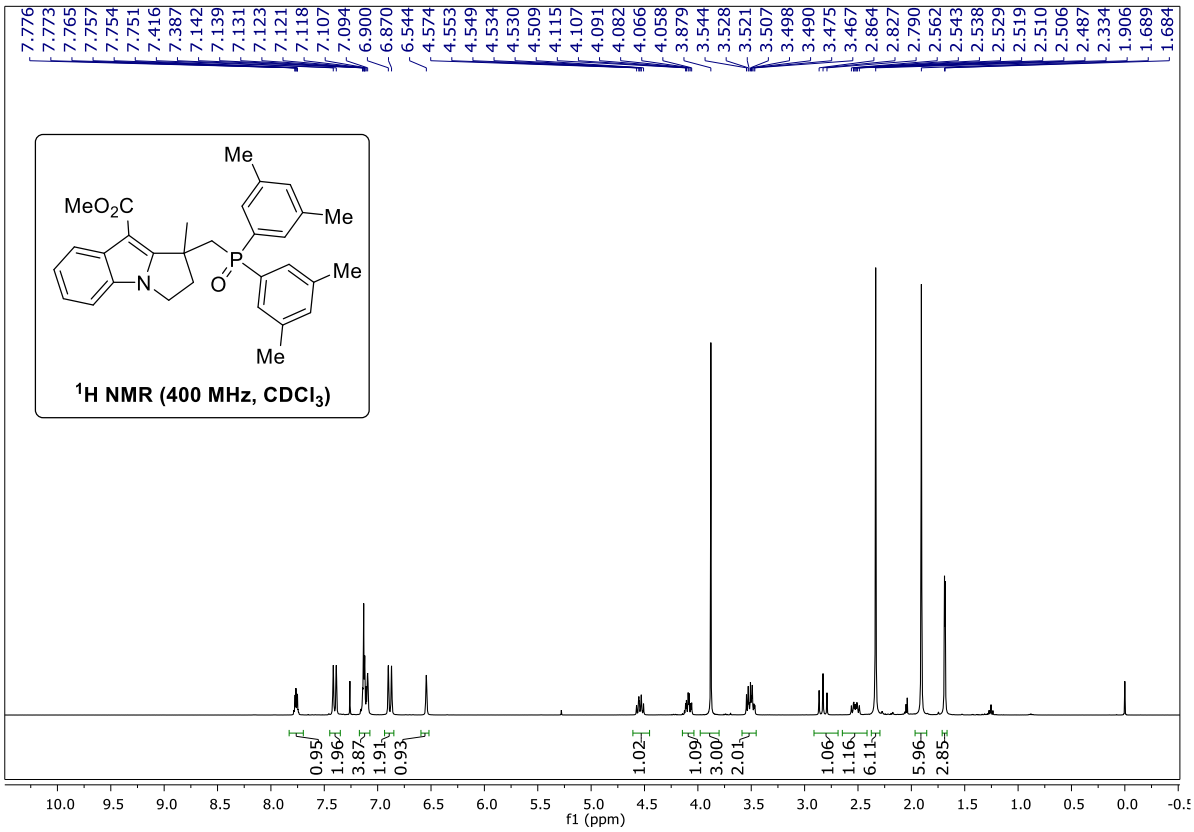
Methyl 2-(diphenylphosphoryl)-1,1-dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5qa):

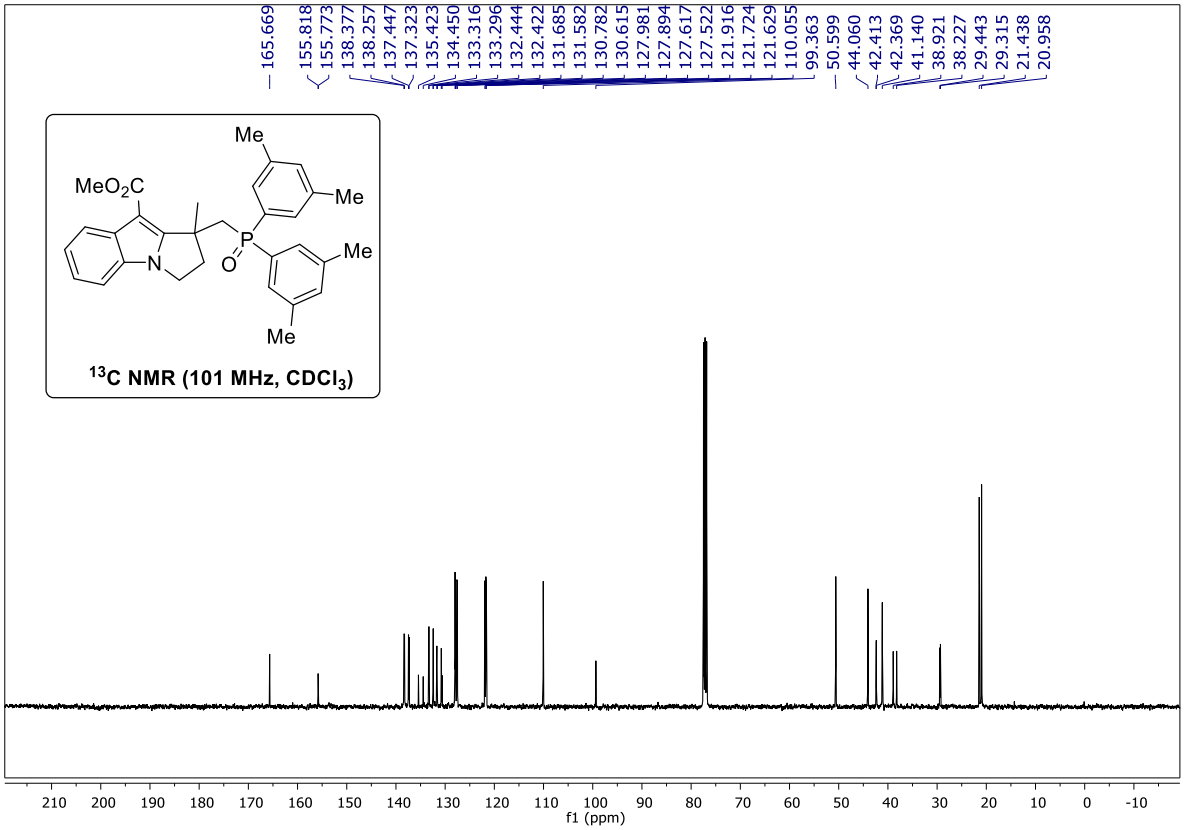


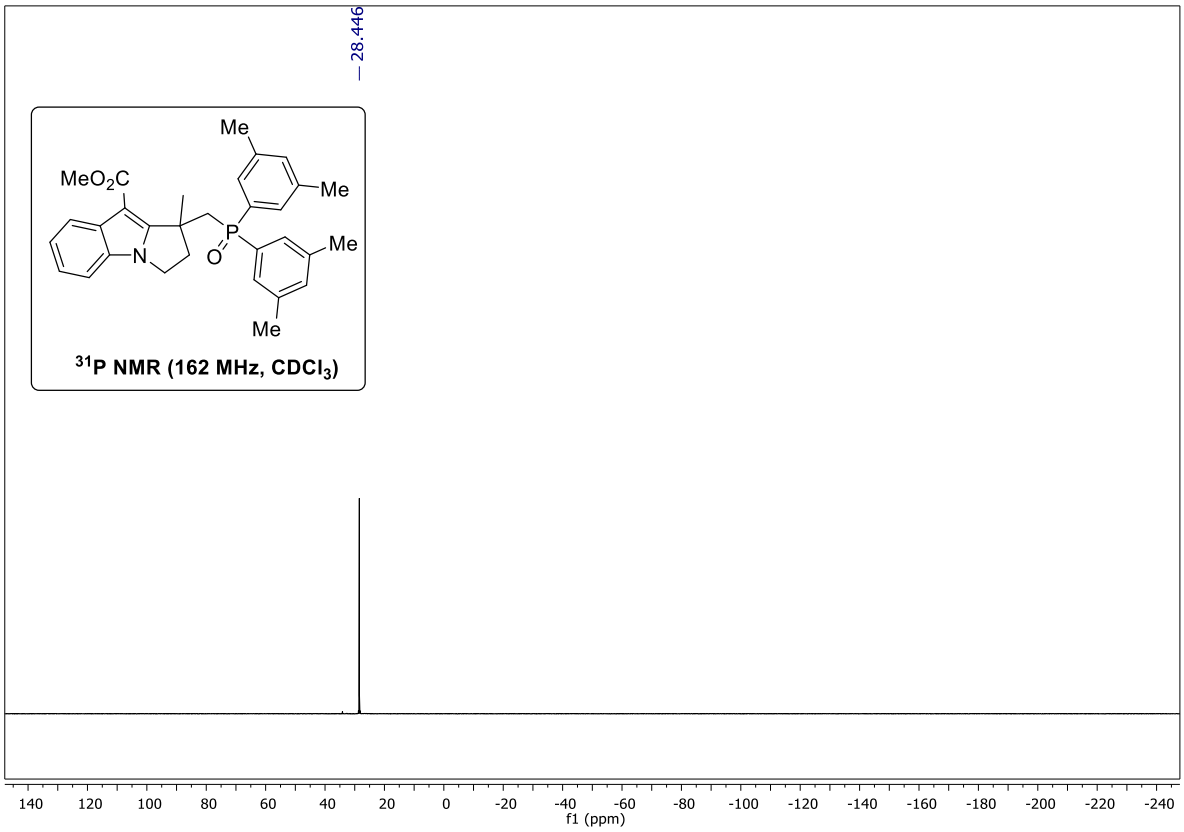

165.334
158.400
158.331
133.942
133.165
132.397
132.327
132.191
131.741
131.520
131.445
131.117
130.700
130.632
129.260
129.170
129.022
128.928
122.243
122.185
122.032
109.908
98.408
51.859
51.278
50.755
45.337
44.243
27.483
23.038
23.003
MeO2C
Ph
N
P
Ph
O
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


24.244
MeO2C
Ph
N
P
Ph
O
31P NMR (162 MHz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

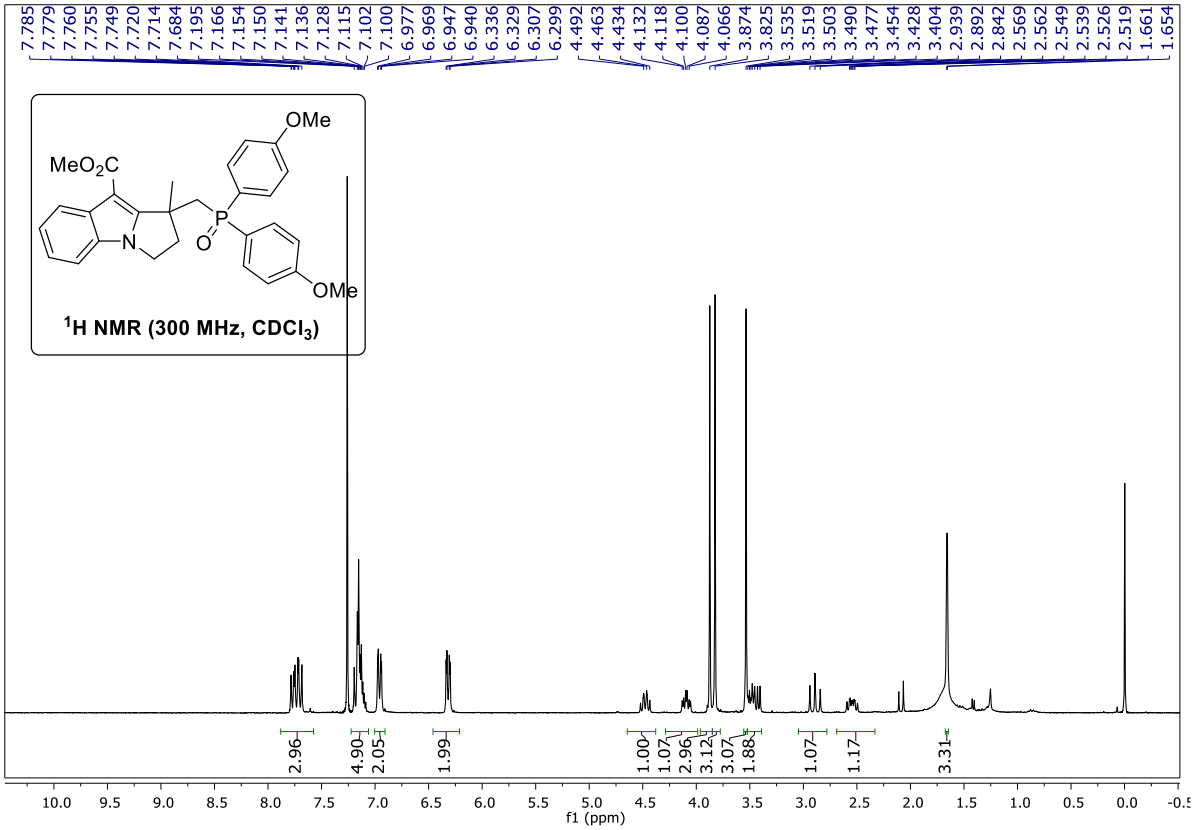
Methyl 1-((bis(3,5-dimethylphenyl)phosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5lb):

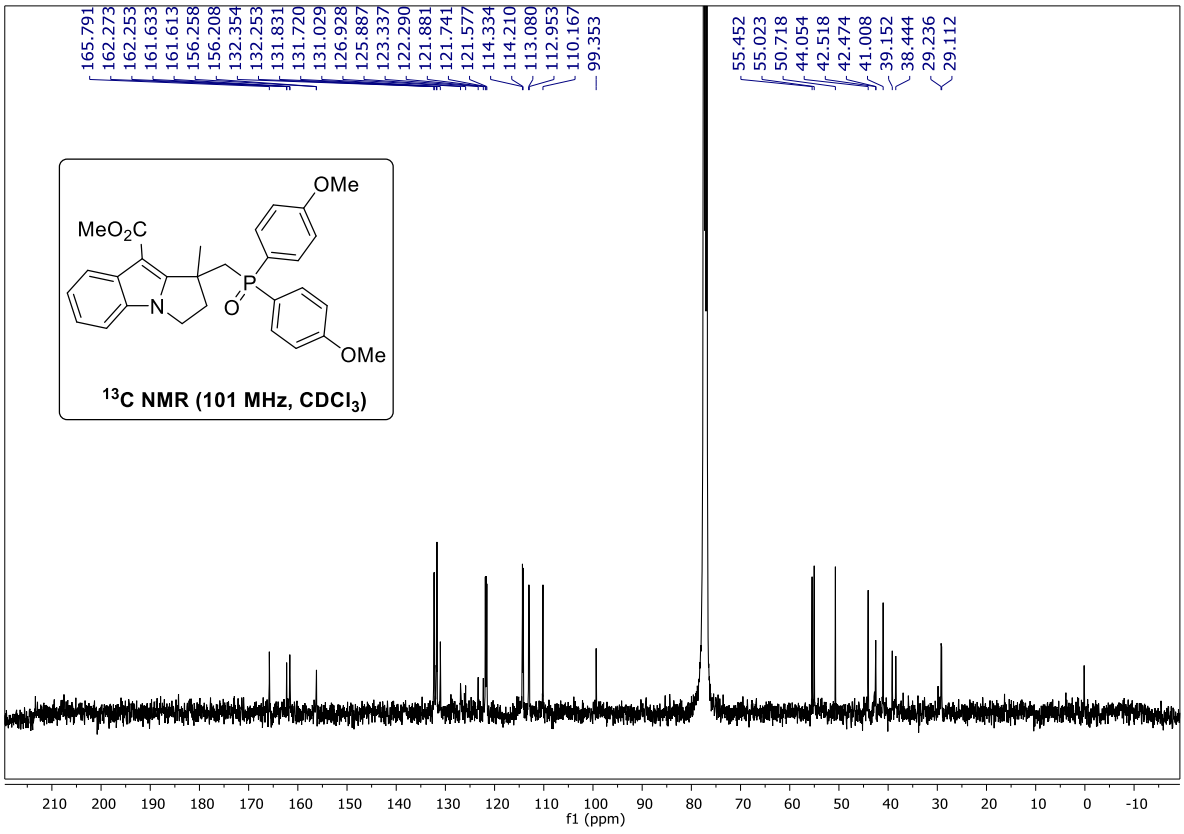


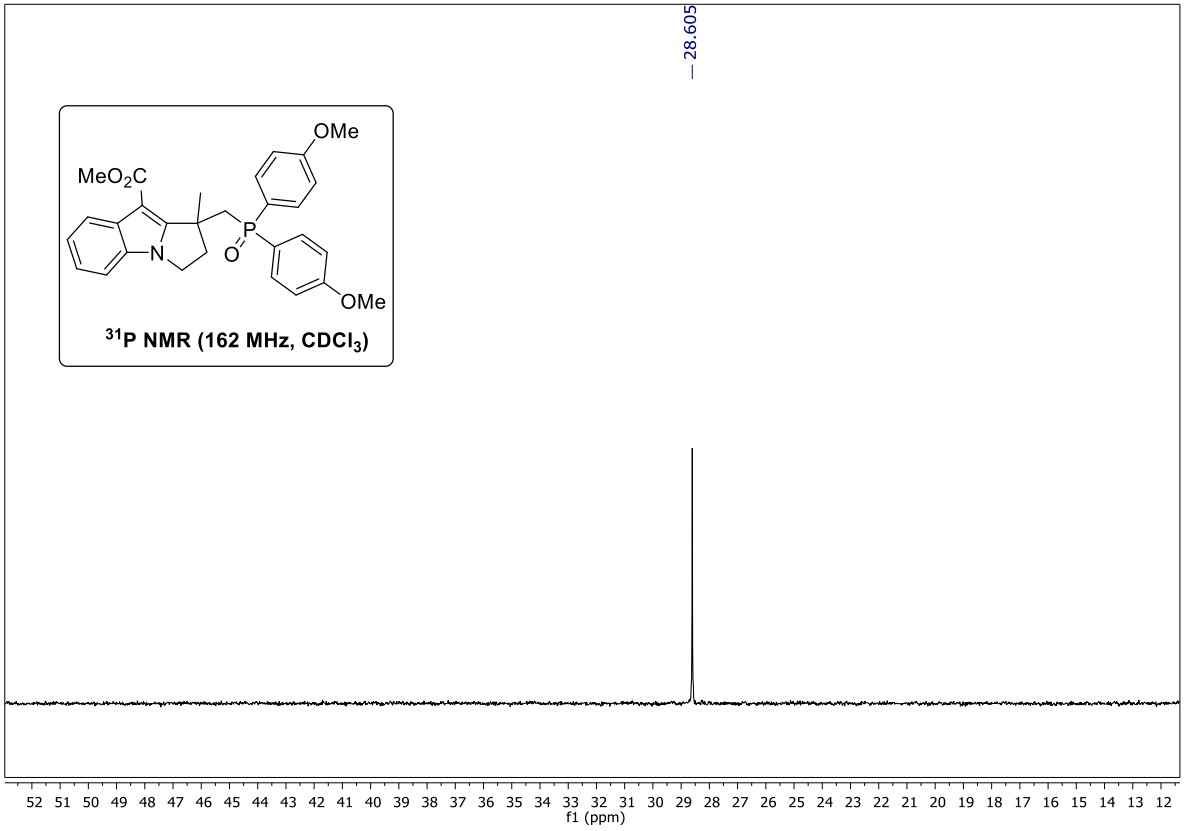




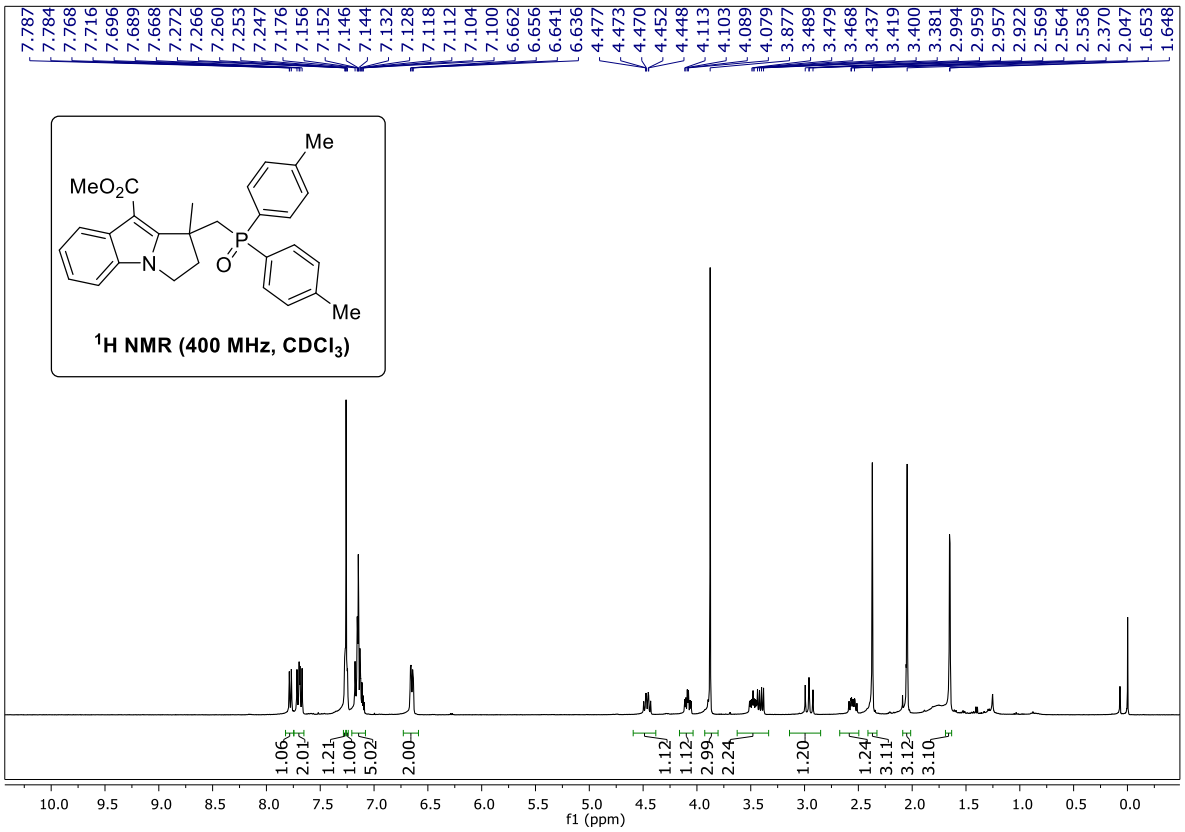
Methyl 1-((bis(4-methoxyphenyl)phosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5ld):

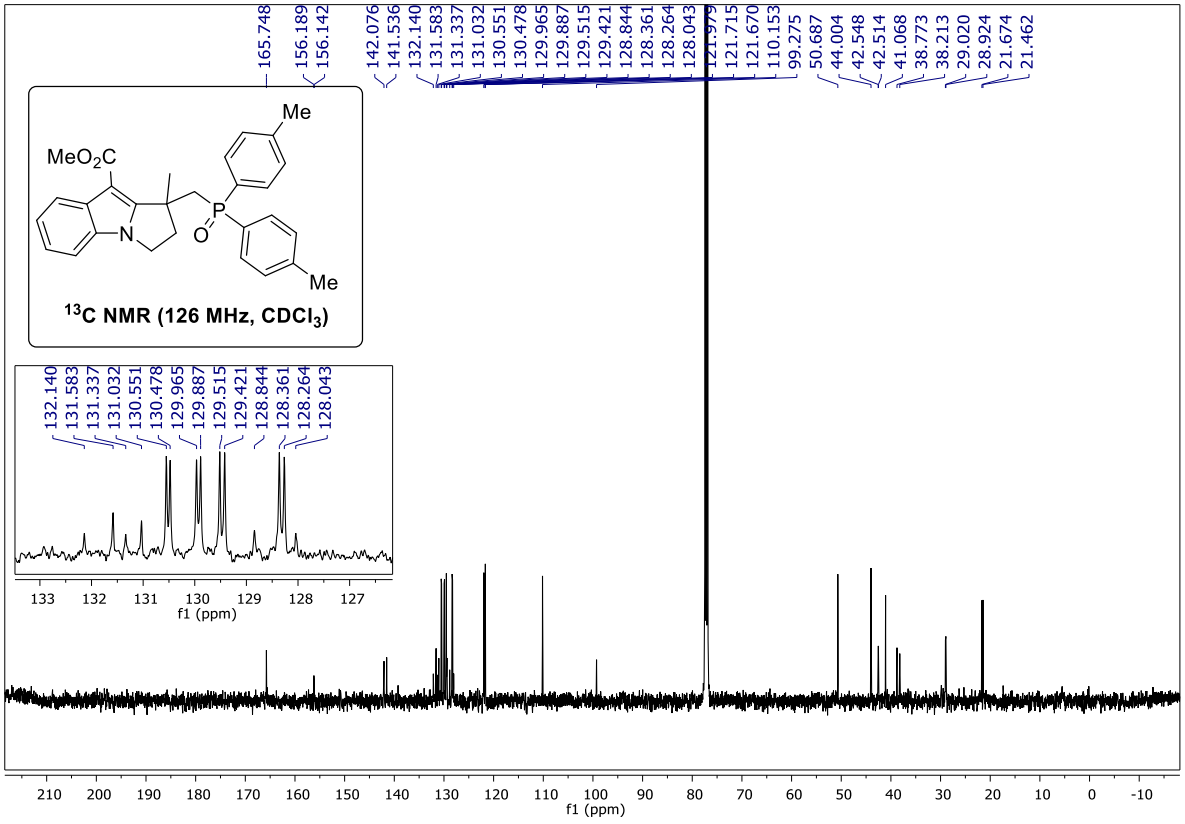


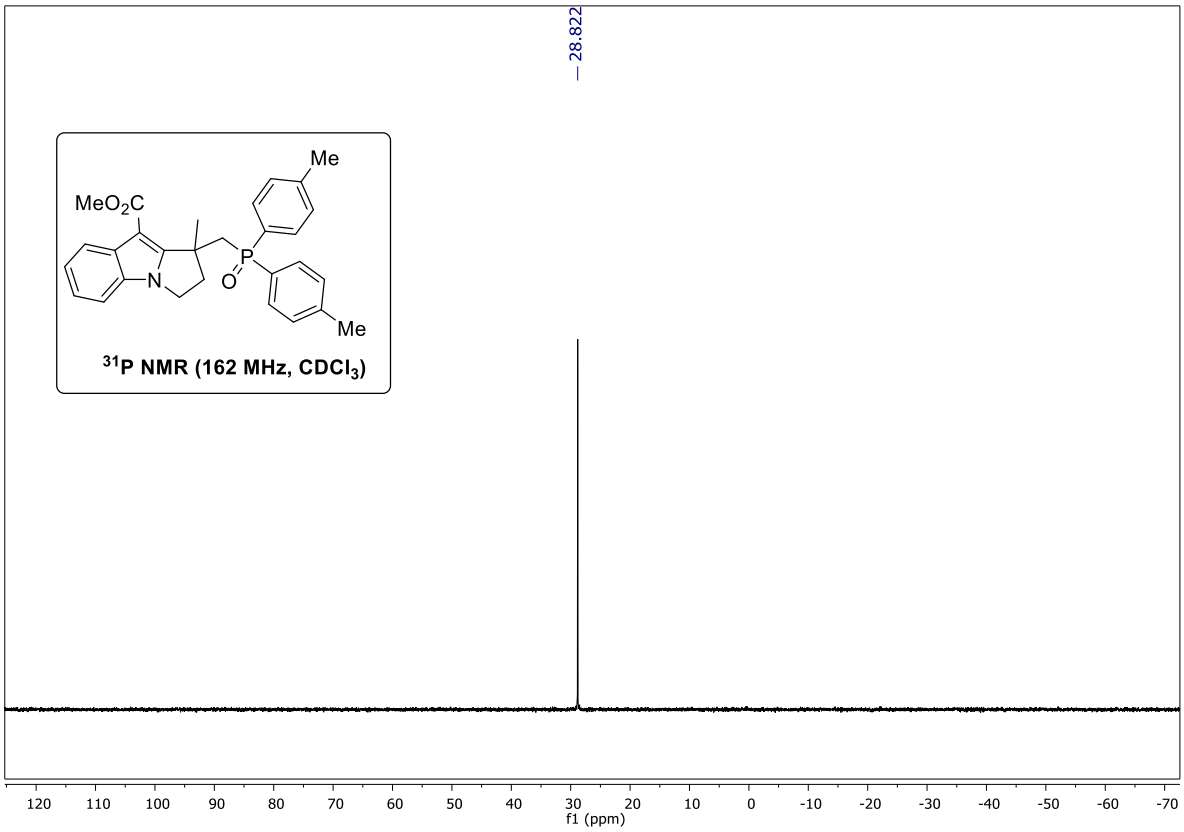

165.791
162.273
162.253
161.633
161.613
156.258
156.208
132.354
132.253
131.831
131.720
131.029
126.928
125.887
123.337
122.290
121.881
121.741
121.577
114.334
114.210
113.080
112.953
110.167
99.353
55.452
55.023
50.718
44.054
42.518
42.474
41.008
39.152
38.444
29.236
29.112
OMe
MeO2C
P
O
N
OMe
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


28.605
OMe
MeO2C
P
O
N
OMe
31P NMR (162 MHz, CDCl3)
52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12
f1 (ppm)

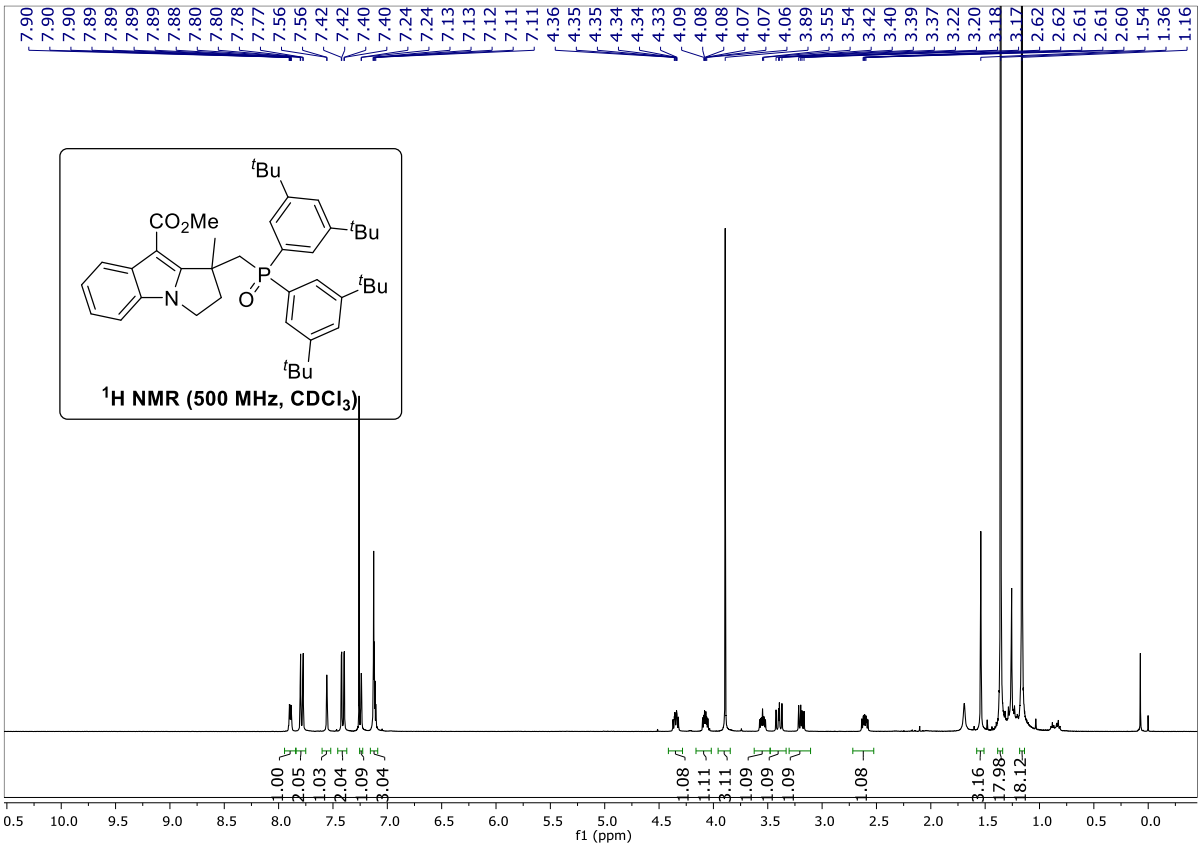
Methyl 1-((di-*p*-tolylphosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5le):

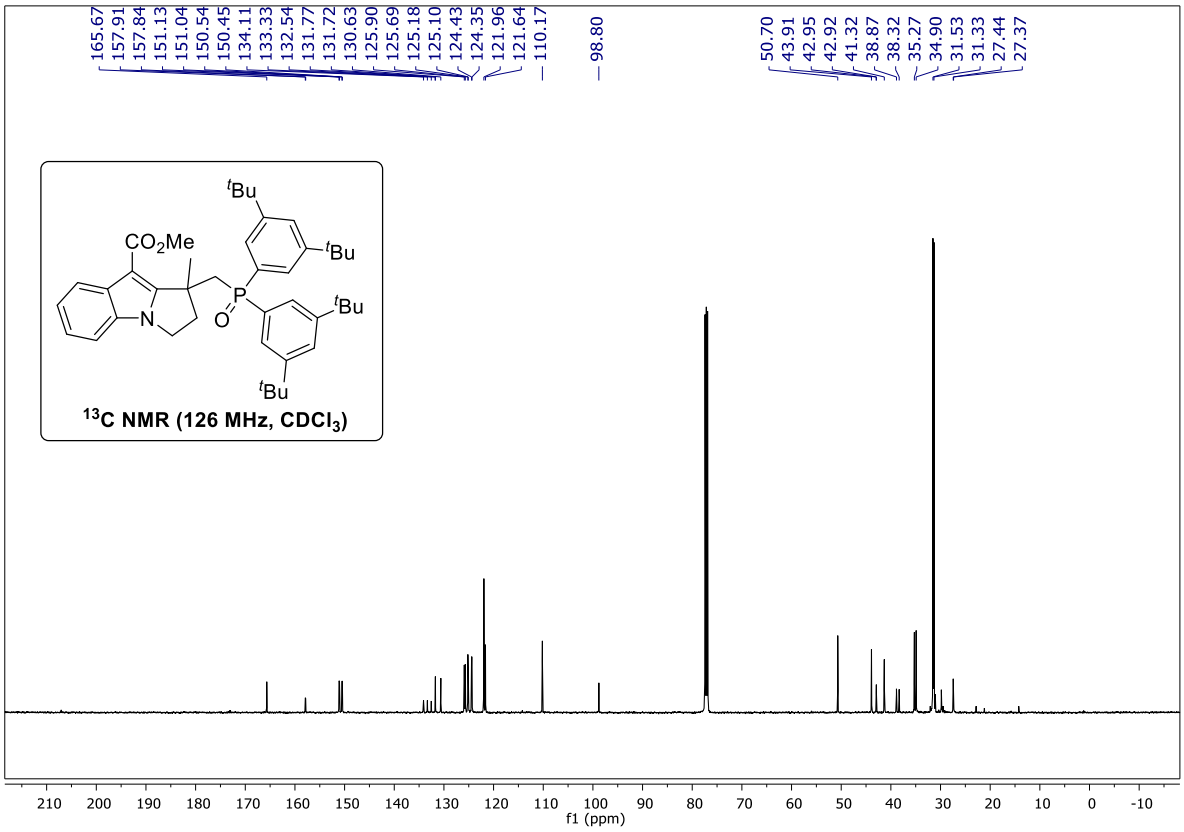


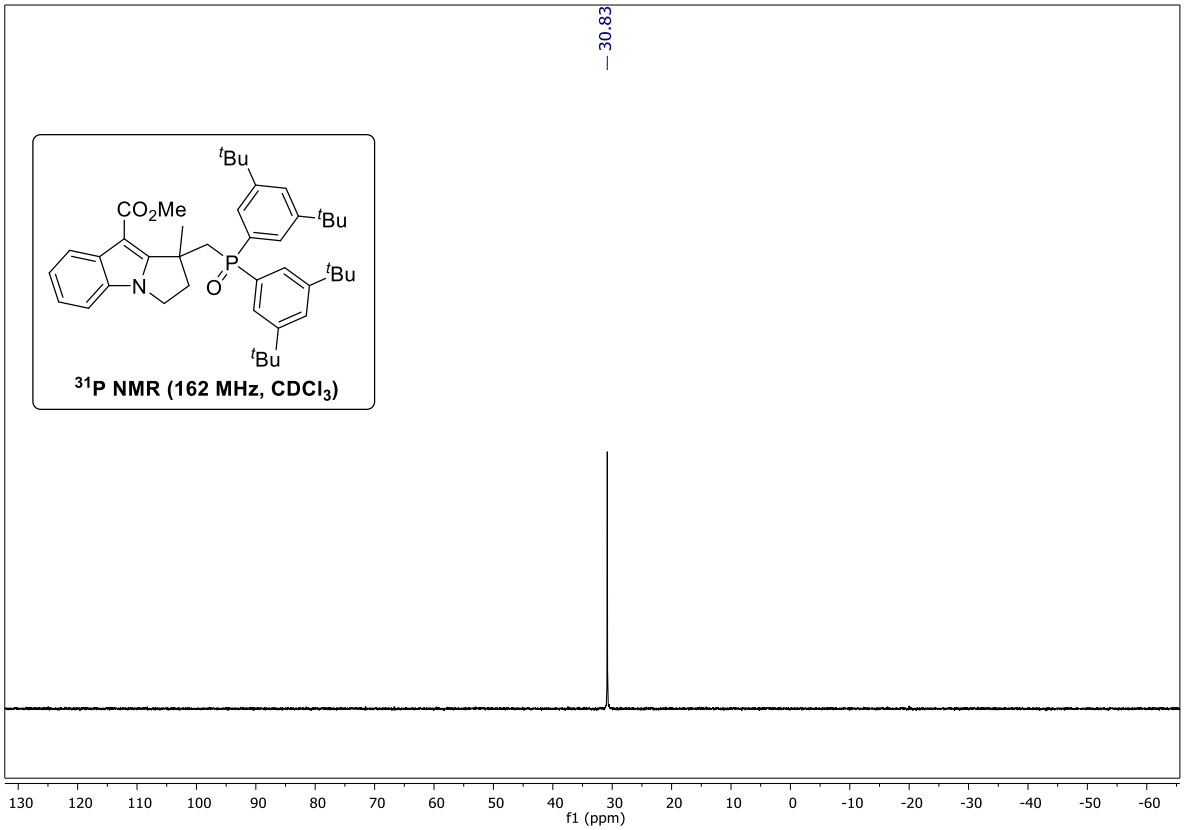




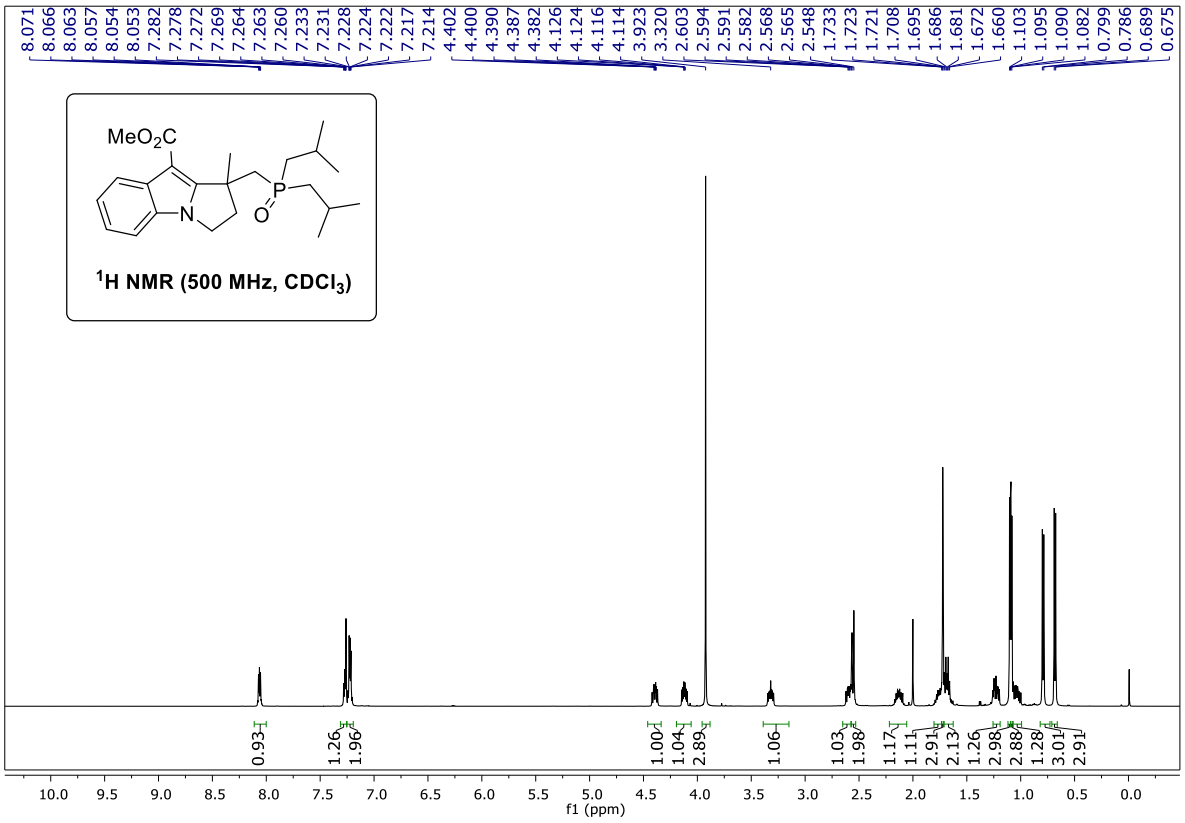
Methyl 1-((bis(3,5-di-*tert*-butylphenyl)phosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5lf):

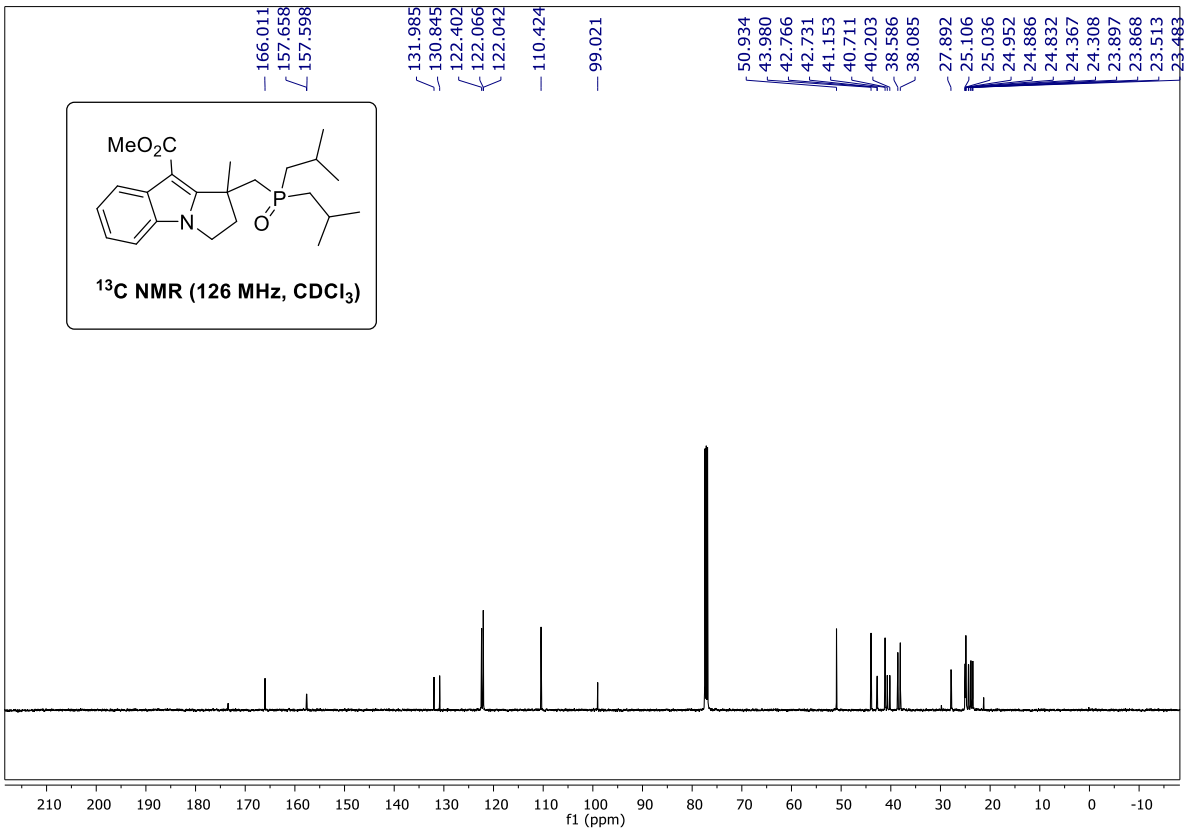


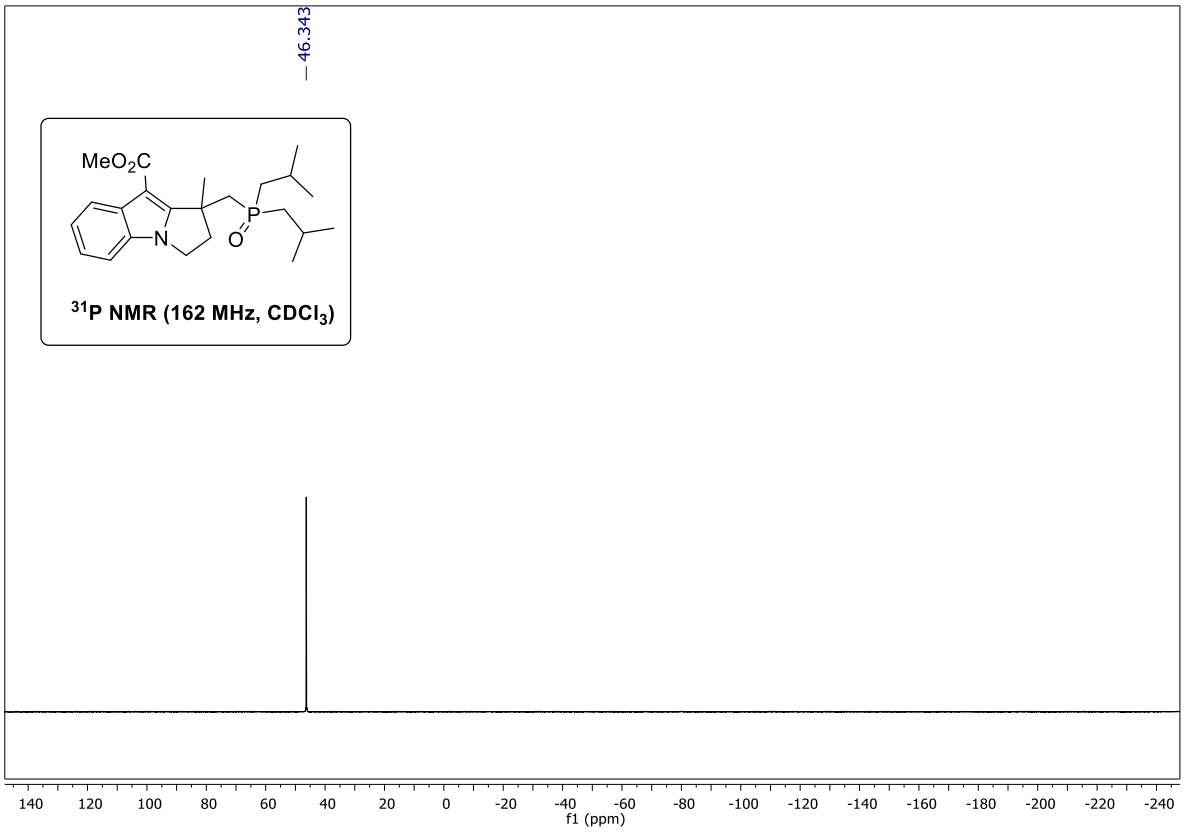

165.67
157.91
157.84
151.13
151.04
150.54
150.45
134.11
133.33
132.54
131.77
131.72
130.63
125.90
125.69
125.18
125.10
124.43
124.35
121.96
121.64
110.17
98.80
50.70
43.91
42.95
42.92
41.32
38.87
38.32
35.27
34.90
31.53
31.33
27.44
27.37
tBu
CO2Me
tBu
tBu
P
O
N
tBu
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


30.83
tBu
CO2Me
tBu
tBu
P
O
N
tBu
31P NMR (162 MHz, CDCl3)
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

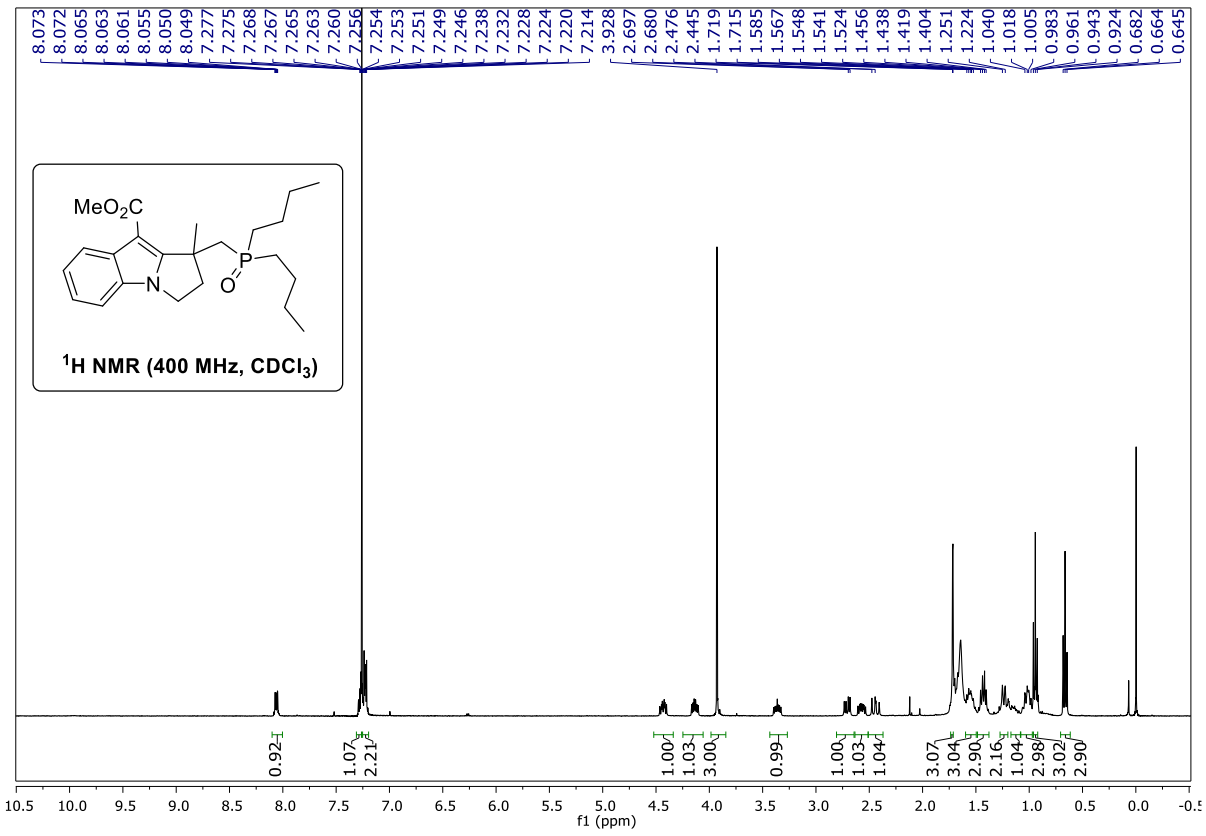
Methyl 1-((diisobutylphosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5lg):

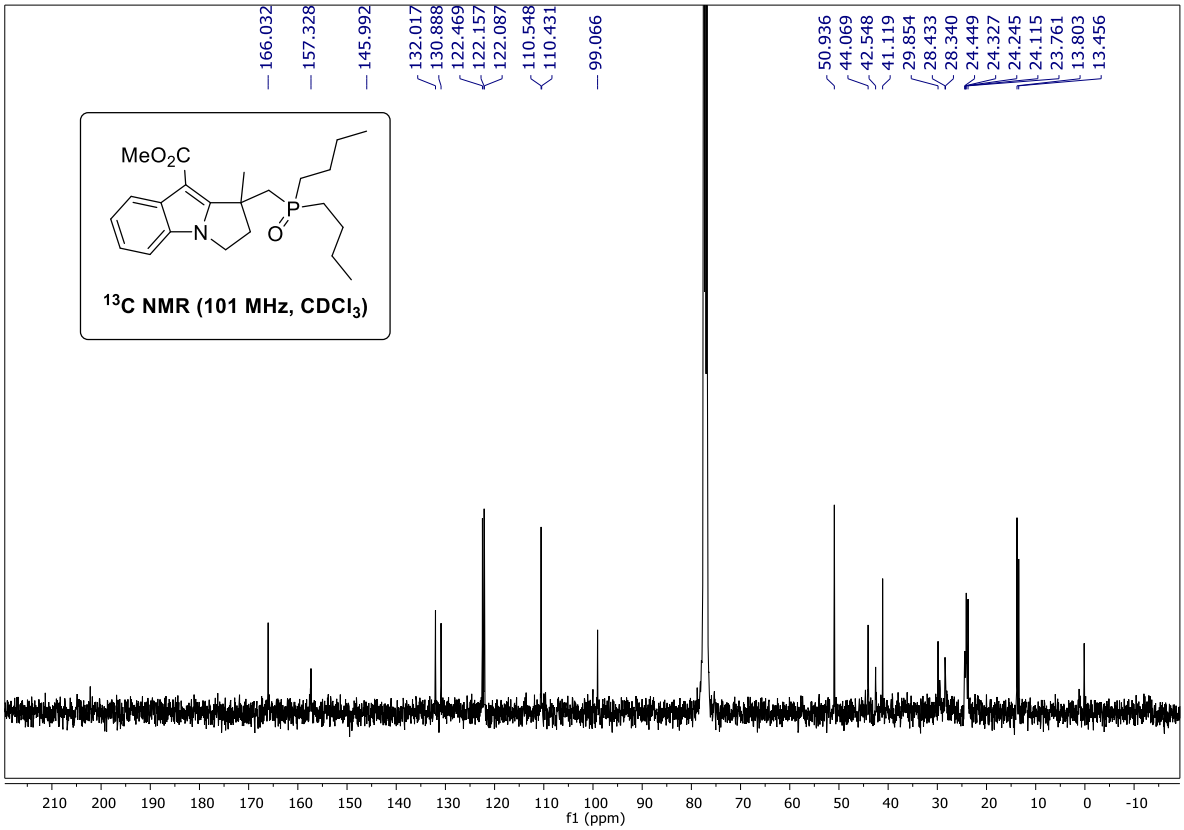


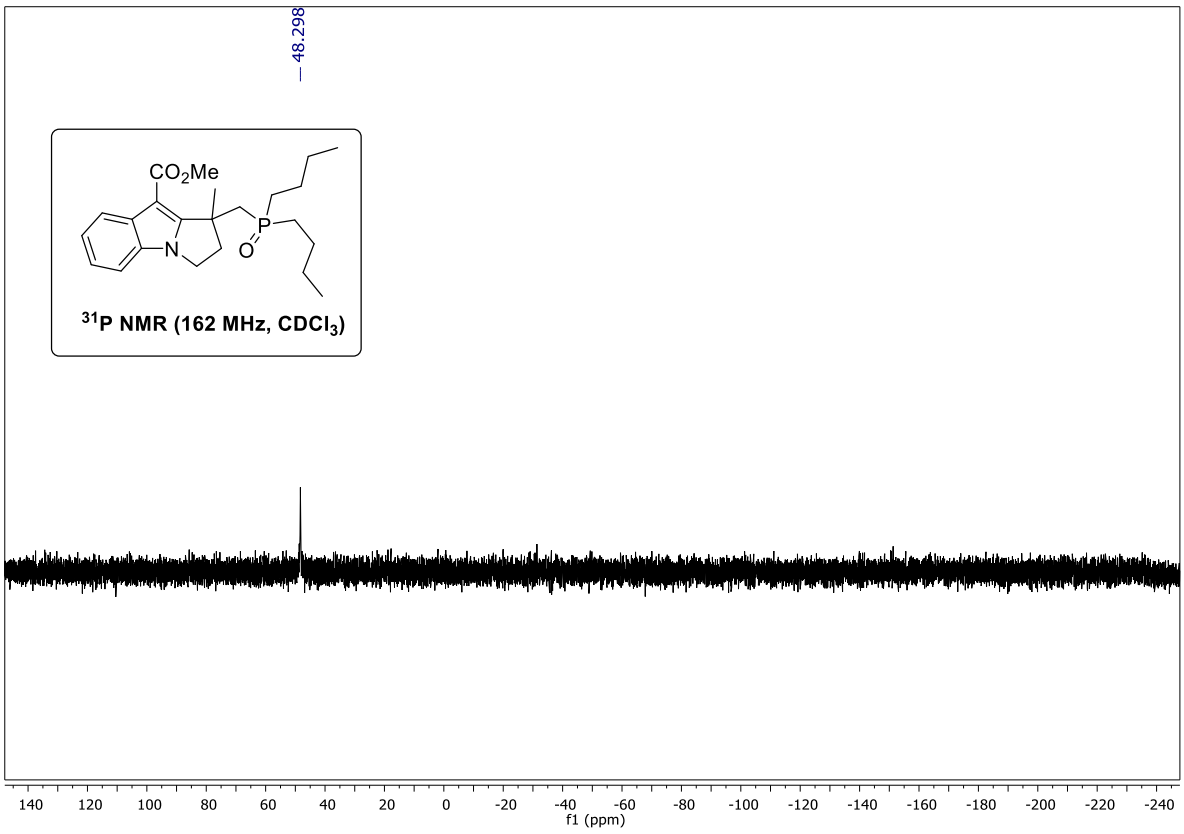




Methyl 1-((dibutylphosphoryl)methyl)-1-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5lh):




166.032
157.328
145.992
132.017
130.888
122.469
122.157
122.087
110.548
110.431
99.066
50.936
44.069
42.548
41.119
29.854
28.433
28.340
24.449
24.327
24.245
24.115
23.761
13.803
13.456
MeO2C
N
P
O
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


48.298
CO2Me
N
P
O
31P NMR (162 MHz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)