Supporting Information

Copper-Catalyzed Radical Cascade Cyclization for the Synthesis of Phosphorated Indolines

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Supporting Information

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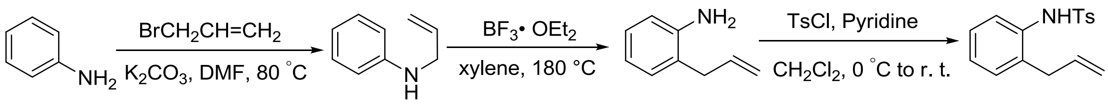
Ⅰ. General Methods and Materials

All reactions involving air- and moisture-sensitive reagents were carried out under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance III 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal standard. ^{31}P and ^{19}F NMR spectra were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, *J*, are reported in hertz. Mass data were measured with Thermo Scientific DSQ II mass spectrometer. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Substrates were prepared according to literature methods A[1] and methods B[2, 3].

Ⅱ. Typical Procedures for the Synthesis of Substrates

Method A



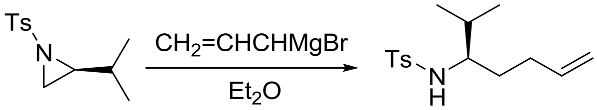
Typical procedure:

Allyl bromide (16.24 mmol) was added dropwise to a solution of commercially available aniline (16.24 mmol) and K_2CO_3 (38.97 mmol) in DMF (37 mL). The solution was heated to 80 ℃ and stirred at this temperature overnight. The reaction mixture was then filtered, washed with H_2O (3x20 mL) and extracted with EtOAc (2x15 mL). The combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography to afford *N*-allyl-aniline.

Next, BF_3 OEt_2 (7.36 mmol) was added to a solution of *N*-allyl-aniline (7.36 mmol) in xylene (4 mL) at 0 ℃ under Ar atmosphere. The mixture was heated to 180 ℃ in a sealed tube and stirred at this temperature for 12 hours. After cooling, the reaction mixture was poured into 10% NaOH (10 mL), and extracted with EtOAc (3x15 mL). The combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography to yield 2-allylaniline as a colorless oil.

Subsequently, 2-allylaniline (4.08 mmol) and pyridine (8.58 mmol, 2.1 equiv) in CH_2Cl_2 (10 mL) was treated sequentially with tosyl chloride (4.49 mmol, 1.1 equiv) at 0 ℃. The solution was allowed to warm to room temperature, and stirring was continued at this temperature overnight. Next, the reaction mixture was washed with a solution of 1 N HCl (20 mL) and extracted with EtOAc (3x20 mL). The combined organic extracts were washed with sat. aq. $NaHCO_3$ (20 mL) and then dried over Na_2SO_4. The solvents were removed in vacuo followed by flash chromatography to obtain the 2-allyl-*N*-tosylaniline as a white solid.

Method B:



(S)-*N*-Tosyl-1-isopropyl-4-pentenyl amine:

Allylmagnesium bromide (1.0 M solution in diethyl ether, 10.5 mmol, 5 equiv) was added dropwise to (S)-2-isopropyl-*N*-tosylaziridine[3] (2.1 mmol, 1 equiv) dissolved in 5 mL Et_2O under Ar(g). The mixture was stirred for an additional 16 h. The reaction was quenched with saturated NH_4Cl(aq) (15 mL), and extracted with EtOAc (2 x10 mL). The crude oil was purified by flash chromatography to give (S)-*N*-tosyl-1-isopropyl-4-pentenyl amine as a white solid.

III. Detailed Reaction Conditions Optimization

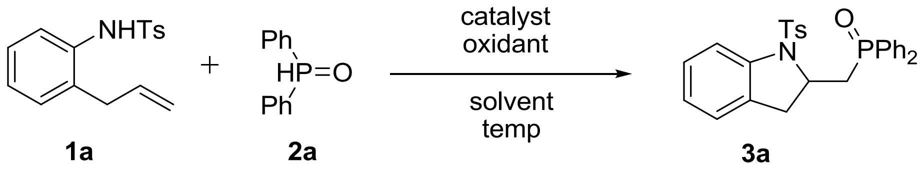


Table S1 Screening Different Catalysts[a]

entry	Cat. (50 mol %)	Oxidant (1.0 equiv)	T (°C)	Solvent	Yield (%)[b]
1	$Cu(ClO_4)_2{\cdot}6H_2O$	$AgNO_3$	80	CH_3CN	16 %
2	$Cu(OAc)_2$	$AgNO_3$	80	CH_3CN	Trace
3	$Cu(OTf)_2$	$AgNO_3$	80	CH_3CN	Trace
4	$CuBr_2$	$AgNO_3$	80	CH_3CN	N.R.
5	$CuCl_2$	$AgNO_3$	80	CH_3CN	N.R.
6	CuO	$AgNO_3$	80	CH_3CN	N.R.
7	$Cu(NO_3)_2{\cdot}3H_2O$	$AgNO_3$	80	CH_3CN	N.R.
8	$Cu(EN)_2$	$AgNO_3$	80	CH_3CN	N.R.
9	CuF_2	$AgNO_3$	80	CH_3CN	N.R.
10	$Cu_2(OH)_2CO_3$	$AgNO_3$	80	CH_3CN	N.R.
11	Cu_2O	$AgNO_3$	80	CH_3CN	N.R.

[a] All reactions were carried out in the presence of 0.2 mmol of **1a** and 0.3 mmol of **2a** in 2.0 mL solvent under Ar atmosphere; N.R. = no reaction. [b] Yield of isolated product.

Table S2 Screening Different Ag Oxidant[a]

entry	Cat. (50 mol %)	Oxidant (1.0 equiv)	T (°C)	Solvent	Yield (%)[b]
1	$Cu(ClO_4)_2{\cdot}6H_2O$	Ag_2O	80	CH_3CN	N.R.
2	$Cu(ClO_4)_2{\cdot}6H_2O$	Ag_2CO_3	80	CH_3CN	Trace
3	$Cu(ClO_4)_2{\cdot}6H_2O$	AgOTf	80	CH_3CN	10 %
4	$Cu(ClO_4)_2{\cdot}6H_2O$	$AgNO_3$	80	CH_3CN	16 %
5	$Cu(ClO_4)_2{\cdot}6H_2O$	$AgBF_4$	80	CH_3CN	N.R.
6	$Cu(ClO_4)_2{\cdot}6H_2O$	AgF	80	CH_3CN	N.R.
7	$Cu(ClO_4)_2{\cdot}6H_2O$	AgTFA	80	CH_3CN	N.R.
8	$Cu(ClO_4)_2{\cdot}6H_2O$	$AgNO_2$	80	CH_3CN	N.R.
9	$Cu(ClO_4)_2{\cdot}6H_2O$	$AgNTf_2$	80	CH_3CN	N.R.
10	$Cu(ClO_4)_2{\cdot}6H_2O$	Ag_3PO_4	80	CH_3CN	37%

[a] All reactions were carried out in the presence of 0.2 mmol of **1a** and 0.3 mmol of **2a** in 2.0 mL solvent under Ar atmosphere; N.R. = no reaction. [b] Yield of isolated product.

Table S3 Screening the Loading of $Cu(ClO_4)_2{\cdot}6H_2O$[a]

entry	$Cu(ClO_4)_2{\cdot}6H_2O$	Oxidant (1.0 equiv.)	T (°C)	Solvent	Yield (%)[b]
1	25 %	Ag_3PO_4	80	CH_3CN	Trace
2	75 %	Ag_3PO_4	80	CH_3CN	41 %
3	100 %	Ag_3PO_4	80	CH_3CN	48 %

4	150 %	Ag_3PO_4	80	CH_3CN	57 %
5	200 %	Ag_3PO_4	80	CH_3CN	65 %
6	250 %	Ag_3PO_4	80	CH_3CN	62 %
7	300 %	Ag_3PO_4	80	CH_3CN	46 %

[a] All reactions were carried out in the presence of 0.2 mmol of **1a** and 0.3 mmol of **2a** in 2.0 mL solvent under Ar atmosphere; N.R. = no reaction. [b] Yield of isolated product.

Table S4 Screening Different Catalysts (200 mol %)[a]

entry	Cat. (200 mol %)	Oxidant (1.0 equiv)	T (°C)	Solvent	Yield (%)[b]
1	$Cu(ClO_4)_2·6H_2O$	Ag_3PO_4	80	CH_3CN	65 %
2	$Cu(OAc)_2$	Ag_3PO_4	80	CH_3CN	Trace
3	$Cu(OTf)_2$	Ag_3PO_4	80	CH_3CN	60 %
4	$CuBr_2$	Ag_3PO_4	80	CH_3CN	N.R.
5	$CuCl_2$	Ag_3PO_4	80	CH_3CN	N.R.
6	CuO	Ag_3PO_4	80	CH_3CN	20 %
7	$Cu(NO_3)_2·3H_2O$	Ag_3PO_4	80	CH_3CN	N.R.
8	$Cu(EN)_2$	Ag_3PO_4	80	CH_3CN	Trace
9	CuF_2	Ag_3PO_4	80	CH_3CN	N.R.
10	$Cu_2(OH)_2CO_3$	Ag_3PO_4	80	CH_3CN	N.R.
11	Cu_2O	Ag_3PO_4	80	CH_3CN	10 %
12	$Cu(CH_3CN)_4PF_6$	Ag_3PO_4	80	CH_3CN	13 %
13	CuI	Ag_3PO_4	80	CH_3CN	N.R.
14	CuBr	Ag_3PO_4	80	CH_3CN	Trace
15	CuCl	Ag_3PO_4	80	CH_3CN	N.R.
16	No	Ag_3PO_4	80	CH_3CN	N.R.

[a] All reactions were carried out in the presence of 0.2 mmol of **1a** and 0.3 mmol of **2a** in 2.0 mL solvent under Ar atmosphere; N.R. = no reaction. [b] Yield of isolated product.

Table S5 Screening Different Temperature[a]

entry	Cat. (200 mol %)	Oxidant (1.0 equiv)	T (°C)	Solvent	Yield (%)[b]
1	$Cu(ClO_4)_2·6H_2O$	Ag_3PO_4	95	CH_3CN	66 %
2	$Cu(ClO_4)_2·6H_2O$	Ag_3PO_4	80	CH_3CN	65 %
3	$Cu(ClO_4)_2·6H_2O$	Ag_3PO_4	65	CH_3CN	68 %
4	$Cu(ClO_4)_2·6H_2O$	Ag_3PO_4	50	CH_3CN	63 %
5	$Cu(ClO_4)_2·6H_2O$	Ag_3PO_4	35	CH_3CN	60 %

[a] All reactions were carried out in the presence of 0.2 mmol of **1a** and 0.3 mmol of **2a** in 2.0 mL solvent under Ar atmosphere; N.R. = no reaction. [b] Yield of isolated product.

Table S6 Screening Different Solvent[a]

entry	Cat. (200 mol %)	Oxidant (1.0 equiv)	T (°C)	Solvent	Yield (%)[b]
1	$Cu(ClO_4)_2·6H_2O$	Ag_3PO_4	65	$ClCH_2CH_2Cl$	Trace
2	$Cu(ClO_4)_2·6H_2O$	Ag_3PO_4	65	$CHCl_3$	Trace
3	$Cu(ClO_4)_2·6H_2O$	Ag_3PO_4	65	CH_2Cl_2	Trace

4	$Cu(ClO_4)_2{\cdot}6H_2O$	Ag_3PO_4	65	toluene	trace
5	$Cu(ClO_4)_2{\cdot}6H_2O$	Ag_3PO_4	65	THF	N.R.
6	$Cu(ClO_4)_2{\cdot}6H_2O$	Ag_3PO_4	65	DME	N.R.
7	$Cu(ClO_4)_2{\cdot}6H_2O$	Ag_3PO_4	65	1,4-dioxane	N.R.
8	$Cu(ClO_4)_2{\cdot}6H_2O$	Ag_3PO_4	65	DMF	N.R.
9	$Cu(ClO_4)_2{\cdot}6H_2O$	Ag_3PO_4	65	DMA	N.R.
10	$Cu(ClO_4)_2{\cdot}6H_2O$	Ag_3PO_4	65	DMSO	N.R.

[a] All reactions were carried out in the presence of 0.2 mmol of **1a** and 0.3 mmol of **2a** in 2.0 mL different solvent under Ar atmosphere; N.R. = no reaction. [b] Yield of isolated product.

Table S7 Screening Different Oxidant[a]

entry	Cat. (200 mol %)	Oxidant (1.0 equiv)	T (°C)	Solvent	Yield (%)[b]
1	$Cu(ClO_4)_2{\cdot}6H_2O$	$K_2S_2O_8$	65	CH_3CN	48 %
2	$Cu(ClO_4)_2{\cdot}6H_2O$	$Na_2S_2O_8$	65	CH_3CN	41 %
3	$Cu(ClO_4)_2{\cdot}6H_2O$	^{t}BuOOH	65	CH_3CN	43 %
4	$Cu(ClO_4)_2{\cdot}6H_2O$	^{t}BuOO^{t}Bu	65	CH_3CN	35 %
5	$Cu(ClO_4)_2{\cdot}6H_2O$	$(NH_4)_2S_2O_8$	65	CH_3CN	36 %
6	$Cu(ClO_4)_2{\cdot}6H_2O$	Dicumyl peroxide	65	CH_3CN	trace
7	$Cu(ClO_4)_2{\cdot}6H_2O$	Dibenzoyl peroxide	65	CH_3CN	trace
8	$Cu(ClO_4)_2{\cdot}6H_2O$	DDQ	65	CH_3CN	N.R.
9	$Cu(ClO_4)_2{\cdot}6H_2O$	BQ	65	CH_3CN	N.R.
10	$Cu(ClO_4)_2{\cdot}6H_2O$	$PhI(OAc)_2$	65	CH_3CN	N.R.
11	$Cu(ClO_4)_2{\cdot}6H_2O$	MnO_2	65	CH_3CN	N.R.

[a] All reactions were carried out in the presence of 0.2 mmol of **1a** and 0.3 mmol of **2a** in 2.0 mL solvent under Ar atmosphere; N.R. = no reaction. [b] Yield of isolated product.

Table S8 Screening the Loading of **2a** and $K_2S_2O_8$[a]

entry	Cat. (200 mol %)	**2a**	$K_2S_2O_8$	T (°C)	Solvent	Yield (%)[b]
1	$Cu(ClO_4)_2{\cdot}6H_2O$	2.0 equiv	1.5 equiv	65	CH_3CN	36 %
2	$Cu(ClO_4)_2{\cdot}6H_2O$	2.0 equiv	2.0 equiv	65	CH_3CN	34 %
3	$Cu(ClO_4)_2{\cdot}6H_2O$	2.0 equiv	2.5 equiv	65	CH_3CN	17 %
4	$Cu(ClO_4)_2{\cdot}6H_2O$	2.0 equiv	3.0 equiv	65	CH_3CN	trace
5	$Cu(ClO_4)_2{\cdot}6H_2O$	3.0 equiv	1.5 equiv	65	CH_3CN	52 %
6	$Cu(ClO_4)_2{\cdot}6H_2O$	3.0 equiv	2.0 equiv	65	CH_3CN	52 %
7	$Cu(ClO_4)_2{\cdot}6H_2O$	3.0 equiv	2.5 equiv	65	CH_3CN	41 %
8	$Cu(ClO_4)_2{\cdot}6H_2O$	3.0 equiv	3.0 equiv	65	CH_3CN	32 %
9	$Cu(ClO_4)_2{\cdot}6H_2O$	4.0 equiv	1.5 equiv	65	CH_3CN	57 %
10	$Cu(ClO_4)_2{\cdot}6H_2O$	4.0 equiv	2.0 equiv	65	CH_3CN	60 %
11	$Cu(ClO_4)_2{\cdot}6H_2O$	4.0 equiv	2.5 equiv	65	CH_3CN	64 %
12	$Cu(ClO_4)_2{\cdot}6H_2O$	4.0 equiv	3.0 equiv	65	CH_3CN	73 %

[a] All reactions were carried out in the presence of 0.2 mmol of **1a** in 2.0 mL solvent under Ar atmosphere; N.R. = no reaction. [b] Yield of isolated product.

Table S9 Screening for Reaction Conditions[a]

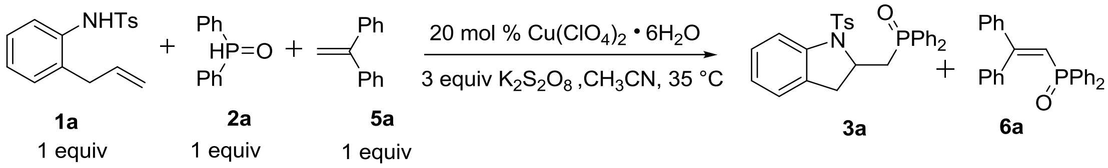
entry	$Cu(ClO_4)_2·6H_2O$	Time	$K_2S_2O_8$	T (°C)	Solvent	Yield (%)[b]
1	20 %	3 hour	3.0 equiv.	65	CH_3CN	35 %
2	20 %	6 hour	3.0 equiv.	65	CH_3CN	58 %
3	20 %	10 hour	3.0 equiv.	65	CH_3CN	40 %
4	20 %	6 hour	3.0 equiv.	50	CH_3CN	62 %
5	20 %	6 hour	3.0 equiv.	35	CH_3CN	74 %
6	25 %	6 hour	3.0 equiv.	35	CH_3CN	74 %
7	15 %	6 hour	3.0 equiv.	35	CH_3CN	60 %

[a] **2a** (0.8 mmol) in solvent (2 mL) was added dropwise *via* an automatic syringe to a mixture of **1a** (0.2 mmol), $Cu(ClO_4)_2·6H_2O$, $K_2S_2O_8$ (0.6 mmol) in solvent (2 mL). [b] Yield of isolated product.

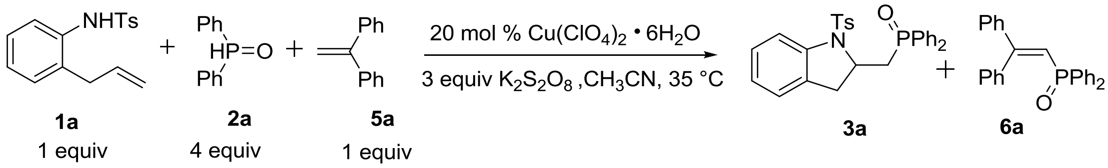
IV. General Procedures for Copper-Catalyzed Radical Cascade Cyclization of Alkenes:

To a Schlenk tube were added **1a** (0.2 mmol), $Cu(ClO_4)_2$ $6H_2O$ (0.04 mmol), $K_2S_2O_8$ (0.6 mmol) and charged with argon for three times. Anhydrous CH_3CN (2.0 mL) was added *via* syringe and the mixture was stirred at 35 ℃ under Ar for 5 min. Then **2a** (0.8 mmol) in CH_3CN (2 mL) was added dropwise *via* an automatic syringe to the mixture in 6 hour at 35 ℃ under Ar atmosphere. The substrate was consumed (monitored by TLC) after the mixture was stirred for an additional hour, and then the reaction was cooled to room temperature. The solvent was removed by rotary and the resulting residue was purified by column chromatography on silica gel (eluent: hexanes/ethylacetate = 4:3) to afford the product **3a** in 74 % yield.

V. Radical Trapping Experiments:

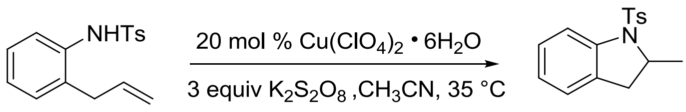


To a Schlenk tube were added **1a** (0.2 mmol), $Cu(ClO_4)_2$ $6H_2O$ (0.04 mmol), $K_2S_2O_8$ (0.6 mmol), **5a** (0.2 mmol) and charged with argon for three times. Anhydrous CH_3CN (2.0 mL) was added *via* syringe and the mixture was stirred at 35 ℃ under Ar for 5 min. Then **2a** (0.2 mmol) in CH_3CN (2 mL) was added dropwise *via* an automatic syringe to the mixture in 6 hour at 35 ℃ under Ar atmosphere. The substrate was consumed (monitored by TLC) after the mixture was stirred for an additional hour, and then the reaction was cooled to room temperature. The solvent was removed by rotary and the resulting residue was purified by column chromatography on silica gel (eluent: hexanes/ethylacetate = 2:1) to afford the product **3a** in 4 % yield and **6a** in 30 % yield.

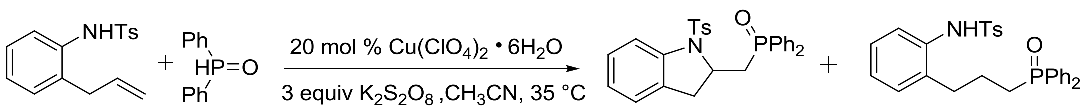


To a Schlenk tube were added **1a** (0.2 mmol), $Cu(ClO_4)_2$ $6H_2O$ (0.04 mmol), $K_2S_2O_8$ (0.6 mmol), **5a** (0.2 mmol) and charged with argon for three times. Anhydrous CH_3CN (2.0 mL) was added *via* syringe and the mixture was stirred at 35 ℃ under Ar for 5 min. Then **2a** (0.8 mmol) in CH_3CN (2 mL) was added dropwise *via* an automatic syringe to the mixture in 6 hour at 35 ℃ under Ar atmosphere. The substrate was consumed (monitored by TLC) after the mixture was stirred for an additional hour, and then the reaction was cooled to room temperature. The solvent was removed by rotary and the resulting residue was purified by column chromatography on silica gel (eluent: hexanes/ethylacetate = 2:1) to afford the product **3a** in 57 % yield and **6a** in 28 % yield.

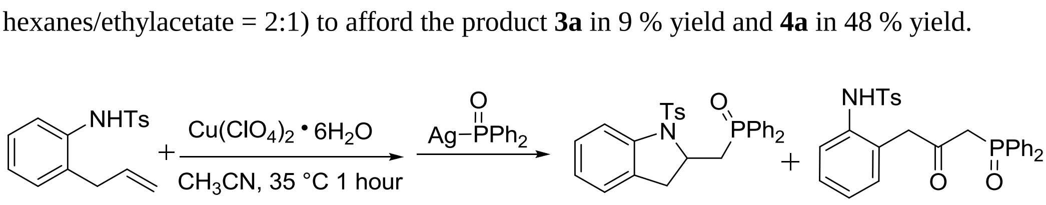
VI. Control Experiments:



To a Schlenk tube were added **1a** (0.2 mmol), $Cu(ClO_4)_2$ $6H_2O$ (0.04 mmol), $K_2S_2O_8$ (0.6 mmol) and charged with argon for three times. Anhydrous CH_3CN (2.0 mL) was added *via* syringe and the mixture was stirred at 35 ℃ under Ar for 6 hour. The reaction was monitored by TLC and no **7a** was detected.



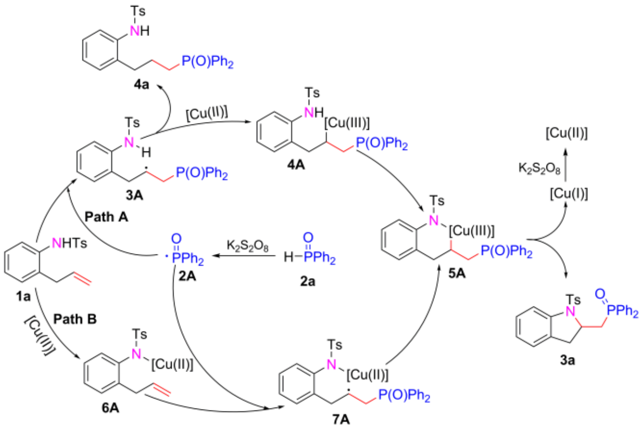
To a Schlenk tube were added **2a** (0.8 mmol), $Cu(ClO_4)_2$ $6H_2O$ (0.04 mmol), $K_2S_2O_8$ (0.6 mmol), and charged with argon for three times. Anhydrous CH_3CN (2.0 mL) was added *via* syringe and the mixture was stirred at 35 ℃ under Ar for 5 min. Then **1a** (0.2 mmol) in CH_3CN (2 mL) was added dropwise *via* an automatic syringe to the mixture in 6 hour at 35 ℃ under Ar atmosphere. The substrate was consumed (monitored by TLC) after the mixture was stirred for an additional hour, and then the reaction was cooled to room temperature. The solvent was removed by rotary and the resulting residue was purified by column chromatography on silica gel (eluent: hexanes/ethylacetate = 2:1) to afford the product **3a** in 9 % yield and **4a** in 48 % yield.



To a Schlenk tube were added **1a** (0.2 mmol), $Cu(ClO_4)_2$ $6H_2O$ (0.2 mmol) and charged with argon for three times. Anhydrous CH_3CN (2.0 mL) was added *via* syringe and the mixture was stirred at 35 ℃ under Ar for 1 hour. Then $Ph_2(O)PAg$ (0.2 mmol) was added and the mixture was stirred for 6 hour. The reaction was cooled to room temperature. The solvent was removed by rotary and the resulting residue was purified by column chromatography on silica gel (eluent: hexanes/ethylacetate = 2:1) to afford the product **3a** in 7 % yield and **8a** in 7 % yield.

VII. Plausible Mechanistic Pathway:

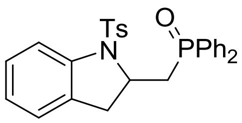
Considering that **2a** is added slowly in order to reduce the byproduct **4a**, we depicted a competitive alternate mechanism in Scheme S1 (Path B). Initially, **1a** reacts with copper salt in order to form the N-chelated copper complex **6A**, which is added by **2A** to give the alkyl radical **7A**. Subsequently, **7A** undergoes an intramolecular oxidative addition providing **5A** followed by reductive elimination to release the product **3a** along with copper (I). Finally, in the presence of $K_2S_2O_8$, the copper (I) is oxidized to copper (II) to complete the catalytic cycle. The slight difference between Path A (Scheme 3 in paper) and Path B is whether copper catalyst is free or coordinated.



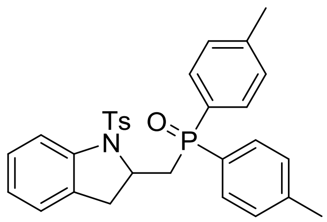
Scheme S1

VIII. Characterization of the Products:

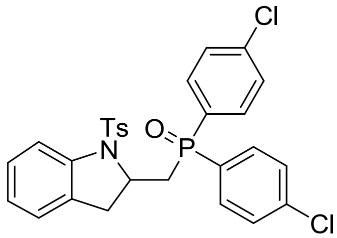
Note: 3e, **3f**, **3g**, **3h**, **3z** and **3aa** are the mixture of diastereoisomers. **3l**, **3n** and **3v** are mixture with trace amount of unknown impurities.



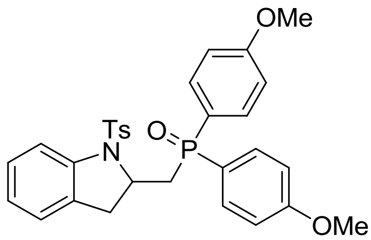
3a: colourless oil; 74 % yield; ^{31}**P NMR** ($CDCl_3$, 162 MHz) δ: 29.38; ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ: 7.99-8.04 (m, 2 H), 7.69-7.76 (m, 2 H), 7.62-7.68 (m, 4 H), 7.44-7.54 (m, 3 H), 7.27-7.29 (m, 2 H), 7.19-7.22 (m, 1 H), 7.07-7.00 (m, 4 H), 4.30-4.39 (m, 1 H), 3.20-3.27 (m, 2 H), 2.91-2.98 (m, 1 H), 2.67-2.77 (m, 1 H), 2.32 (s, 3 H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ: 144.07, 140.66, 134.11, 133.54 (d, J_{C-P} = 101.1 Hz), 132.13 (d, J_{C-P} = 2.5 Hz), 131.97 (d, J_{C-P} = 2.5 Hz), 131.58 (d, J_{C-P} = 98.8 Hz), 131.35 (d, J_{C-P} = 9.5 Hz), 131.26, 130.33 (d, J_{C-P} = 9.6 Hz), 129.58, 128.93 (d, J_{C-P} =11.7 Hz), 128.75 (d, J_{C-P} = 11.7 Hz), 127.76, 126.91, 125.46, 124.75, 116.61, 58.07, 37.18 (d, J_{C-P} = 66.8 Hz), 35.00, 21.47; **MS (ESI)**: found $[M+H]^+$ 488.1.



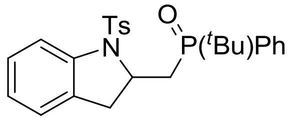
3b: colourless oil; 83 % yield; ^{31}**P NMR** ($CDCl_3$, 162 MHz) δ: 29.88; ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ: 7.84-7.89 (m, 2 H), 7.57-7.66 (m, 3 H), 7.42-7.45 (m, 2 H), 7.24-7.30 (m, 4 H), 7.16-7.21 (m, 1 H), 6.99-7.07 (m, 4 H), 4.31-4.39 (m, 1 H), 3.15-3.26 (m, 2 H), 2.90-2.96 (m, 1 H), 2.63-2.73 (m, 1 H), 2.50 (s, 3 H) , 2.38 (s, 3 H), 2.32 (s, 3 H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ: 144.00, 142.50 (d, $J_{C\text{-}P}$ = 2.7 Hz), 142.37 (d, $J_{C\text{-}P}$ = 2.6 Hz), 140.68, 134.22, 131.37, 131.35 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.51 (d, $J_{C\text{-}P}$ = 103.6 Hz), 130.33 (d, $J_{C\text{-}P}$ = 10.1 Hz),129.66, 129.54, 129.43 (d, $J_{C\text{-}P}$ = 12.2 Hz), 128.37 (d, $J_{C\text{-}P}$ = 101.2 Hz), 127.69, 126.96, 125.46, 124.69, 116.61, 58.20, 37.27 (d, $J_{C\text{-}P}$ = 67.0 Hz), 34.96, 21.66, 21.53, 21.49; **MS (ESI)**: found $[M+H]^+$ 516.2.



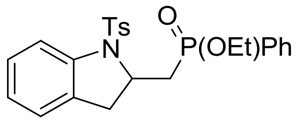
3c: colourless oil; 73 % yield; ^{31}**P NMR** ($CDCl_3$, 162 MHz) δ: 28.61; ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ: 7.89-7.94 (m, 2 H), 7.60-7.67 (m, 5 H), 7.43-7.45 (m, 2 H), 7.29 (d, J = 8.2 Hz, 2 H), 7.18-7.22 (m, 1 H), 7.00-7.10 (m, 4 H), 4.27-4.33 (m, 1 H), 3.16-3.20 (m, 2 H), 2.91-2.98 (m, 1 H), 2.66-2.76 (m, 1 H), 2.33 (s, 3 H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ: 144.29, 140.50, 139.08 (d, $J_{C\text{-}P}$ = 3.4 Hz), 138.87 (d, $J_{C\text{-}P}$ = 3.2 Hz), 134.04, 132.70 (d, $J_{C\text{-}P}$ = 10.3 Hz), 132.01, 131.71 (d, $J_{C\text{-}P}$ = 11.6 Hz),130.97, 130.20, 129.67, 129.40 (d, $J_{C\text{-}P}$ = 12.6 Hz), 129.21 (d, $J_{C\text{-}P}$ = 12.6 Hz), 127.89, 126.87, 125.47, 124.86, 116.57, 57.83, 37.06 (d, $J_{C\text{-}P}$ = 67.8 Hz), 35.00, 21.50; **MS (ESI)**: found $[M+H]^+$ 556.0.



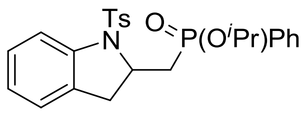
3d: Reaction was carried out in the presence of **1** (0.2 mmol), **2** (0.8 mmol), $Cu(ClO_4)_2$ $6H_2O$ (0.4 mmol), $K_2S_2O_8$ (0.6 mmol) in CH_3CN (2 mL) in 6 hour at 65 ℃ under Ar atmosphere. colourless oil; 53 % yield; ^{31}**P NMR** ($CDCl_3$, 162 MHz) δ: 29.53; ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ: 7.87-7.92 (m, 2 H), 7.59-7.66 (m, 3 H), 7.30 (d, J = 8.2 Hz, 2 H), 7.18-7.21 (m, 1 H), 7.12-7.14 (m, 2 H), 7.00-7.08 (m, 4 H), 6.93-6.96 (m, 2 H), 4.31-4.38 (m, 1 H) , 3.93 (s, 3 H) , 3.83 (s, 3 H), 3.21-3.26 (m, 1 H), 3.11-3.16 (m, 1 H), 2.90-2.96 (m, 1 H), 2.60-2.70 (m, 1 H), 2.32 (s, 3 H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ: 162.62 (d, $J_{C\text{-}P}$ = 2.6 Hz), 162.37 (d, $J_{C\text{-}P}$ = 2.7 Hz), 144.03, 140.68, 134.23, 133.17 (d, $J_{C\text{-}P}$ = 10.7 Hz), 132.15 (d, $J_{C\text{-}P}$ = 11.0 Hz), 131.40, 129.56, 127.70, 126.95, 125.47, 124.69, 116.61, 114.44 (d, $J_{C\text{-}P}$ = 12.8 Hz), 114.24 (d, $J_{C\text{-}P}$ = 12.9 Hz), 58.25, 55.45, 55.34, 37.56 (d, $J_{C\text{-}P}$ = 67.4 Hz), 34.96, 21.48; **MS (ESI)**: found $[M+H]^+$ 548.2.



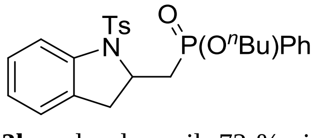
3e: colourless oil; 70 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 48.10, 44.63; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.96-8.01 (m, 1 H), 7.44-7.70 (m, 6 H), 7.17-7.28 (m, 3 H), 6.88-7.07 (m, 3 H), 4.77-4.85 (m, 0.43 H), 4.15-4.22 (m, 0.55 H), 2.62-3.26 (m, 3 H), 2.42-2.52 (m, 1 H), 2.28-2.35 (m, 3 H), 1.12-1.24 (m, 9 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 144.08, 143.99, 140.67, 140.60, 134.66, 134.22, 132.62, 132.54, 131.93, 131.91, 131.64, 131.61, 131.51, 131.47, 131.39, 131.31, 131.05, 129.88, 129.71, 129.52, 129.08, 128.50, 128.39, 128.30, 128.22, 128.19, 127.70, 127.68, 127.03, 126.82, 125.56, 125.34, 124.72, 124.58, 116.69, 116.57, 58.85, 58.30, 34.95, 34.93, 33.86, 33.29, 33.17, 32.59, 31.96, 31.38, 30.57, 29.99, 24.16, 24.12, 21.50, 21.41; **MS (ESI)**: found $[M+H]^+$ 468.2.



3f: colourless oil; 51 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 40.47, 39.91; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.87-7.92 (m, 1 H), 7.76-7.81 (m, 1 H), 7.48-7.70 (m, 5 H), 7.17-7.26 (m, 3 H), 7.00-7.07 (m, 3 H), 4.61-4.70 (m, 0.5 H), 4.06-4.19 (m, 1.5 H) , 3.83-3.98 (m, 1 H), 2.78-3.14 (m, 3 H), 2.25-2.49 (m, 4 H), 1.28-1.38 (m, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 144.04, 143.94, 140.86, 140.72, 134.64, 134.11, 132.58, 132.56, 132.50, 132.48, 131.91, 131.81, 131.69, 131.56, 131.47, 131.32, 131.07, 130.97, 130.45, 129.72, 129.63, 129.51, 128.87, 128.77, 128.74, 128.65, 128.48, 127.76, 127.73, 127.08, 126.99, 125.32, 125.31, 124.69, 124.64, 116.93, 116.70, 60.80, 60.75, 57.89, 57.37, 57.31, 37.82, 37.52, 36.86, 36.57, 34.85, 34.74, 21.51, 21.46, 16.51, 16.45, 16.39; **MS (ESI)**: found $[M+H]^+$ 456.1.

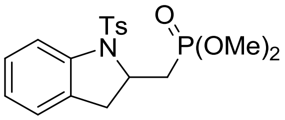


3g: colourless oil; 77 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 39.11, 38.52; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.89-7.94 (m, 1 H), 7.77-7.82 (m, 1 H), 7.64-7.69 (m, 1 H), 7.54-7.62 (m, 3 H), 7.46-7.51 (m, 1 H), 7.15-7.23 (m, 3 H), 7.00-7.07 (m, 3 H), 4.51-4.68 (m, 1.5 H) , 4.04-4.13 (m, 0.5 H), 2.76-3.16 (m, 3 H), 2.23-2.48 (m, 4 H), 1.36-1.44 (m, 3 H), 1.15-1.22 (m, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 144.04, 143.92, 140.87, 140.76, 134.62, 134.07, 132.56, 132.46, 132.44, 132.37, 132.34, 131.94, 131.84, 131.64, 131.56, 131.46, 131.40, 131.31, 131.12, 130.40, 129.77, 129.62, 129.49, 128.77, 128.65, 128.52, 127.73, 127.70, 127.09, 126.98, 125.31, 124.69, 124.62, 116.95, 116.68, 70.10, 70.03, 69.95, 69.89, 57.96, 57.40, 57.33, 38.17, 37.88, 37.21, 36.92, 34.76, 34.65, 24.62, 24.59, 24.54, 24.51, 23.98, 23.96, 23.94, 23.91, 21.52, 21.46; **MS (ESI)**: found $[M+H]^+$ 470.3.

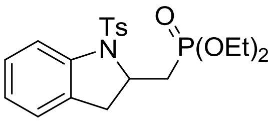


3h: colourless oil; 72 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 40.38, 39.80; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.87-7.92 (m, 1 H), 7.76-7.81 (m, 1 H), 7.48-7.70 (m, 5 H), 7.17-7.26 (m, 3 H), 7.01-7.07 (m, 3 H), 4.62-4.70 (m, 0.43 H), 3.99-4.17 (m, 1.58 H), 3.75-3.84 (m, 1 H), 2.78-3.15 (m, 3 H), 2.25-2.50 (m, 4 H), 1.59-1.74 (m, 2 H), 1.34-1.52 (m, 2 H), 0.88-0.99 (m, 3 H); **^{13}C**

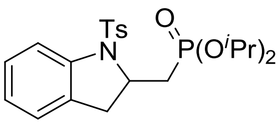
NMR ($CDCl_3$, 100 MHz) δ: 144.05, 143.94, 140.85, 140.73, 134.65, 134.12, 132.58, 132.55, 132.51, 132.48, 131.91, 131.81, 131.59, 131.49, 131.35, 131.08, 130.90, 130.33, 129.62, 129.51, 128.86, 128.77, 128.74, 128.65, 127.76, 127.74, 127.07, 126.99, 126.32, 125.33, 125.31, 124.71, 124.65, 116.96, 116.71, 64.47, 64.41, 64.34, 57.88, 57.39, 57.33, 37.81, 37.46, 36.85, 36.51, 34.84, 34.73, 32.59, 32.51, 32.44, 21.51, 21.46, 18.85, 18.76, 13.65, 13.55; **MS (ESI)**: found $[M+H]^+$ 484.2.



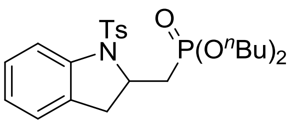
3i: colourless oil; 42 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 29.19; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.67 (d, *J* = 8.1 Hz, 1 H), 7.57 (d, *J* = 8.4 Hz, 2 H), 7.18-7.25 (m, 3 H), 7.03-7.09 (m, 2 H), 4.47-4.55 (m, 1 H), 3.76-3.84 (m, 6 H), 2.98-2.96 (m, 2 H), 2.58-2.68 (m, 1 H), 2.37 (s, 3 H), 2.18-2.26 (m, 1 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 144.13, 140.67, 134.68, 131.04, 129.69, 127.87, 127.04, 125.35, 124.80, 116.88, 57.81, 52.60, 52.42 (d, $J_{C\text{-}P}$ = 6.5 Hz), 34.65, 32.49 (d, $J_{C\text{-}P}$ = 134.5 Hz), 21.50; **MS (ESI)**: found $[M+H]^+$ 396.1.



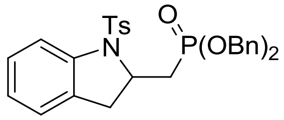
3j: colourless oil; 53 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 26.44; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.67 (d, *J* = 8.1 Hz, 1 H), 7.56 (d, *J* = 8.2 Hz, 2 H), 7.17-7.24 (m, 3 H), 7.02-7.08 (m, 2 H), 4.46-4.55 (m, 1 H), 4.07-4.21 (m, 4 H), 2.91-3.03 (m, 2 H), 2.56-2.66 (m, 1 H), 2.36 (s, 3 H), 2.14-2.24 (m, 1 H) , 1.33-1.41 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 144.10, 140.73, 134.67, 131.17, 129.67, 127.82, 127.03, 125.33, 124.77, 116.92, 61.60 (d, $J_{C\text{-}P}$ = 6.6 Hz), 61.87 (d, $J_{C\text{-}P}$ = 6.3 Hz), 57.96 (d, $J_{C\text{-}P}$ = 2.3 Hz), 34.61, 33.31 (d, $J_{C\text{-}P}$ = 134.4 Hz), 21.50, 16.45, 16.42, 16.39, 16.36; **MS (ESI)**: found $[M+H]^+$ 424.1.



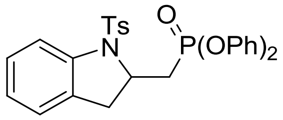
3k: colourless oil; 61 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 24.24; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.67 (d, *J* = 8.1 Hz, 1 H), 7.56 (d, *J* = 8.3 Hz, 2 H), 7.18-7.25 (m, 3 H), 7.02-7.08 (m, 2 H), 4.68-4.80 (m, 2 H), 4.46-4.55 (m, 1 H), 3.03-3.08 (m, 1 H), 2.87-2.93 (m, 1 H), 2.52-2.61 (m, 1 H), 2.37 (s, 3 H), 2.09-2.20 (m, 1 H) , 1.33-1.40 (m, 12 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 144.02, 140.79, 134.80, 131.37, 129.62, 127.77, 127.04, 125.31, 124.74, 117.05, 70.64 (d, $J_{C\text{-}P}$ = 6.8 Hz), 70.61 (d, $J_{C\text{-}P}$ = 6.5 Hz), 58.23 (d, $J_{C\text{-}P}$ = 2.5 Hz), 34.69 (d, $J_{C\text{-}P}$ = 135.9 Hz), 34.42, 24.12, 24.08, 24.04, 24.00, 21.50; **MS (ESI)**: found $[M+H]^+$ 452.1.



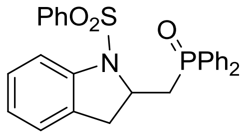
3l: colourless oil; 53 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 26.41; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.67 (d, *J* = 8.0 Hz, 1 H), 7.56 (d, *J* = 7.9 Hz, 2 H), 7.17-7.23 (m, 3 H), 7.03-7.06 (m, 2 H), 4.47-4.54 (m, 1 H), 4.03-4.12 (m, 4 H), 2.90-3.04 (m, 2 H), 2.58-2.66 (m, 1 H), 2.37 (s, 3 H), 2.13-2.24 (m, 1 H), 1.65-1.74 (m, 4 H), 1.39-1.50 (m, 4 H), 0.94-1.01 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 144.05, 140.77, 134.78, 131.20, 129.63, 127.81, 127.03, 125.31, 124.75, 116.95, 65.66 (d, $J_{C\text{-}P}$ = 7.1 Hz), 58.01, 34.57, 33.20 (d, $J_{C\text{-}P}$ = 125.5 Hz), 32.78, 32.48, 21.47, 18.79, 18.75, 13.61, 13.56; **MS (ESI)**: found $[M+H]^+$ 480.1.



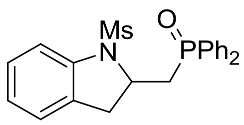
3m: colourless oil; 45 % yield; ^{31}**P NMR** ($CDCl_3$, 162 MHz) δ: 27.55; ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ: 7.66 (d, J = 8.0 Hz, 1 H), 7.47 (d, J = 8.3 Hz, 2 H), 7.32-7.42 (m, 10 H), 7.20-7.24 (m, 1 H), 7.11 (d, J = 8.1 Hz, 2 H), 7.00-7.05 (m, 2 H), 4.98-5.15 (m, 4 H), 4.43-4.52 (m, 1 H), 2.69-2.99 (m, 3 H), 2.35 (s, 3 H), 2.18-2.29 (m, 1 H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ: 144.02, 140.69, 136.18 (d, J_{C-P} = 6.4 Hz), 136.08 (d, J_{C-P} = 6.1 Hz), 134.51, 131.04, 129.62, 128.65, 128.49 (d, J_{C-P} = 4.0 Hz), 127.97 (d, J_{C-P} = 4.6 Hz), 127.83, 127.06, 125.31, 124.75, 116.89, 67.44 (d, J_{C-P} = 6.7 Hz), 67.43 (d, J_{C-P} = 6.7 Hz), 57.82 (d, J_{C-P} = 2.4 Hz), 34.59, 33.67 (d, J_{C-P} = 134.8 Hz), 21.51; **MS (ESI)**: found $[M+H]^+$ 548.1.



3n: colourless oil; 31 % yield; ^{31}**P NMR** ($CDCl_3$, 162 MHz) δ: 19.69; ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ: 7.70 (d, J = 8.1 Hz, 1 H), 7.54 (d, J = 8.3 Hz, 2 H), 7.36-7.42 (m, 2 H), 7.28-7.34 (m, 4 H), 7.22-7.27 (m, 2 H), 7.16-7.20 (m, 5 H), 7.04-7.09 (m, 2 H), 4.64-4.73 (m, 1 H), 3.11-3.16 (m, 2 H), 2.95-3.04 (m, 2 H), 2.48-2.59 (m, 1 H), 2.37 (s, 3 H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ: 150.26 (d, J_{C-P} = 9.0 Hz), 150.00 (d, J_{C-P} = 8.8 Hz), 144.22, 140.62, 134.49, 130.98 129.90 (d, J_{C-P} = 4.4 Hz), 129.71, 127.96, 127.07, 125.40, 124.97, 120.61, 120.58, 120.56, 120.54, 117.11, 57.66 (d, J_{C-P} = 2.9 Hz), 34.68, 33.97 (d, J_{C-P} = 135.0 Hz), 21.52; **MS (ESI)**: found $[M+H]^+$ 520.1.

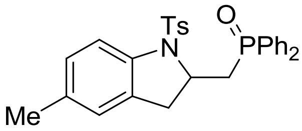


3p: colourless oil; 65 % yield; ^{31}**P NMR** ($CDCl_3$, 162 MHz) δ: 29.58; ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ: 7.98-8.01 (m, 2 H), 7.67-7.74 (m, 2 H), 7.60-7.66 (m, 4 H), 7.42-7.52 (m, 4 H), 7.37-7.39 (m, 2 H), 7.23-7.27 (m, 2 H), 7.17-7.21 (m, 1 H), 6.99-7.04 (m, 2 H), 4.29-4.38 (m, 1 H), 3.17-3.25 (m, 2 H), 2.87-2.93 (m, 1 H), 2.66-2.76 (m, 1 H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ: 140.41, 136.97, 133.75 (d, J_{C-P} = 101.1 Hz), 133.07, 132.07 (d, J_{C-P} = 2.7 Hz), 131.91 (d, J_{C-P} = 2.7 Hz), 131.38 (d, J_{C-P} = 98.7 Hz), 131.25 (d, J_{C-P} = 9.3 Hz), 131.16, 130.24 (d, J_{C-P} = 9.5 Hz), 128.88, 128.86 (d, J_{C-P} =11.7 Hz), 128.68 (d, J_{C-P} = 11.8 Hz), 127.73, 126.77, 125.43, 124.79,116.54, 58.06, 37.01 (d, J_{C-P} = 66.9 Hz), 34.84; **MS (ESI)**: found $[M+H]^+$ 474.1.

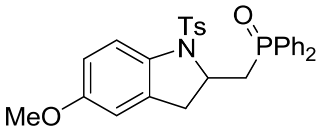


3q: colourless oil; 61 % yield; ^{31}**P NMR** ($CDCl_3$, 162 MHz) δ: 29.38; ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ: 7.92-7.97 (m, 2 H), 7.67-7.72 (m, 2 H), 7.55-7.60 (m, 3 H), 7.40-7.52 (m, 4 H), 7.17-7.21 (m, 2 H), 7.05-7.09 (m, 1 H), 4.53-4.61 (m, 1 H), 3.51-3.42 (m, 2 H), 3.16-3.23 (m, 1 H), 2.75 (s, 3 H), 2.66-2.73 (m, 1 H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ: 140.39, 133.65 (d, J_{C-P} = 101.1 Hz), 132.20 (d, J_{C-P} = 2.8 Hz), 131.93 (d, J_{C-P} = 2.2 Hz), 131.38 (d, J_{C-P} = 99.1 Hz), 131.15 (d, J_{C-P} = 9.4 Hz), 130.69, 130.29 (d, J_{C-P} = 9.6 Hz), 128.95 (d, J_{C-P} =11.9 Hz), 128.74 (d, J_{C-P} = 12.0 Hz), 128.05, 125.79, 124.72, 115.23, 58.93, 37.24 (d, J_{C-P} = 66.7 Hz), 35.82, 35.10; **MS (ESI)**: found $[M+H]^+$

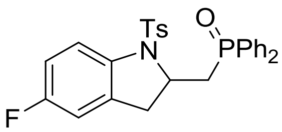
412.1.



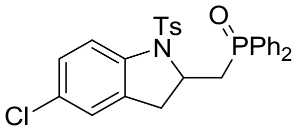
3r: colourless oil; 45 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 29.61; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.95-8.00 (m, 2 H), 7.68-7.73 (m, 2 H), 7.60-7.65 (m, 3 H), 7.48-7.52 (m, 2 H), 7.41-7.46 (m, 2 H), 7.24 (d, *J* = 8.3 Hz, 2 H), 7.04 (d, *J* = 8.1 Hz, 2 H), 6.98 (d, *J* = 7.7 Hz, 1 H), 6.83 (s, 1 H), 4.26-4.33 (m, 1 H), 3.16-3.22 (m, 2 H), 2.83-2.90 (m, 1 H), 2.66-2.76 (m, 1 H), 2.30 (s, 3 H), 2.25 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 143.93, 138.24, 134.54, 134.07, 133.60 (d, $J_{C\text{-}P}$ = 101.1 Hz), 132.09 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.94 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.54 (d, $J_{C\text{-}P}$ = 98.8 Hz), 131.41, 131.36 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.32 (d, $J_{C\text{-}P}$ = 9.5 Hz), 129.54, 128.91 (d, $J_{C\text{-}P}$ =11.8 Hz), 128.73 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.36, 126.95, 126.02, 116.47, 58.16 (d, $J_{C\text{-}P}$ = 0.8 Hz), 37.14 (d, $J_{C\text{-}P}$ = 66.8 Hz), 34.98, 21.47, 20.93; **MS (ESI)**: found $[M+H]^+$ 502.1.



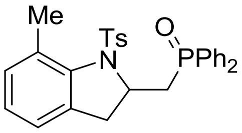
3s: Reaction was carried out in the presence of **1** (0.2 mmol), **2** (0.8 mmol), $Cu(ClO_4)_2$ $6H_2O$ (0.4 mmol), $K_2S_2O_8$ (0.6 mmol) in CH_3CN (2 mL) in 6 hour at 65 ℃ under Ar atmosphere. colourless oil; 55 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 29.46; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.96-8.01 (m, 2 H), 7.69-7.74 (m, 2 H), 7.61-7.66 (m, 3 H), 7.43-7.56 (m, 4 H), 7.24 (d, *J* = 7.9 Hz, 2 H), 7.05 (d, *J* = 8.2 Hz, 2 H), 6.73-6.76 (m, 1 H), 6.59 (d, *J* = 1.9 Hz, 1 H), 4.29-4.36 (m, 1 H), 3.74 (s, 3 H), 3.13-3.18 (m, 2 H), 2.78-2.85 (m, 1 H), 2.64-2.74 (m, 1 H), 2.31 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 157.48, 143.92, 133.95, 133.90, 133.22, 133.61 (d, $J_{C\text{-}P}$ = 100.9 Hz), 132.09 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.93 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.57 (d, $J_{C\text{-}P}$ = 98.8 Hz), 131.33 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.32 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.52, 128.93 (d, $J_{C\text{-}P}$ = 12.8 Hz), 128.73 (d, $J_{C\text{-}P}$ = 11.9 Hz), 126.99, 117.90, 113.17, 110.89, 58.39 (d, $J_{C\text{-}P}$ = 1.1 Hz), 55.57, 37.01 (d, J = 66.9 Hz), 35.11, 21.47; **MS (ESI)**: found $[M+H]^+$ 518.1.



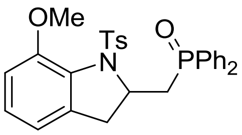
3t: colourless oil; 75 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 29.30; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.96-8.00 (m, 2 H), 7.69-7.74 (m, 2 H), 7.55-7.64 (m, 4 H), 7.42-7.52 (m, 3 H), 7.21 (d, *J* = 8.2 Hz, 2 H), 7.06 (d, *J* = 8.1 Hz, 2 H), 7.85-7.90 (m, 1 H), 6.73 (d, *J* = 8.0 Hz, 1 H), 4.31-4.38 (m, 1 H), 3.14-3.24 (m, 2 H), 2.83-2.90 (m, 1 H), 2.65-2.75 (m, 1 H), 2.31 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 160.37 (d, $J_{C\text{-}F}$ = 243.3 Hz), 144.24, 136.71 (d, $J_{C\text{-}F}$ = 2.1 Hz), 133.75, 133.64 (d, $J_{C\text{-}F}$ = 8.7 Hz), 133.41 (d, $J_{C\text{-}P}$ = 101.2 Hz), 132.16 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.01 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.47 (d, $J_{C\text{-}P}$ = 98.7 Hz), 131.30 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.32 (d, $J_{C\text{-}P}$ = 9.7 Hz), 129.64, 128.98 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.76 (d, $J_{C\text{-}P}$ = 11.9 Hz), 126.94, 117.80 (d, $J_{C\text{-}F}$ = 8.6 Hz), 114.41 (d, $J_{C\text{-}F}$ = 23.5 Hz), 112.56 (d, $J_{C\text{-}F}$ = 23.9 Hz), 58.57 (d, $J_{C\text{-}P}$ = 1.0 Hz), 37.04 (d, J = 66.8 Hz), 34.92, 21.47; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ : -118.08; **MS (ESI)**: found $[M+H]^+$ 506.1.



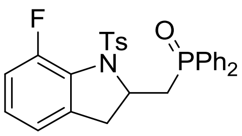
3u: colourless oil; 70 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 29.35; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.95-8.00 (m, 2 H), 7.68-7.74 (m, 2 H), 7.60-7.67 (m, 3 H), 7.49-7.56 (m, 2 H), 7.43-7.47 (m, 2 H), 7.24 (d, *J* = 8.3 Hz, 2 H), 7.13-7.16 (m, 1 H), 7.07 (d, *J* = 8.1 Hz, 2 H), 7.00 (s, 1 H), 4.28-4.36 (m, 1 H), 3.17-3.24 (m, 2 H), 2.87-2.93 (m, 1 H), 2.64-2.74 (m, 1 H), 2.32 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 144.38, 139.43, 133.75, 133.35 (d, J_{C-P} = 101.3 Hz), 133.27, 132.18 (d, J_{C-P} = 2.7 Hz), 132.06 (d, J_{C-P} = 2.7 Hz), 131.42 (d, J_{C-P} = 98.9 Hz), 131.32 (d, J_{C-P} = 9.3 Hz), 131.12 (d, J_{C-P} = 9.6 Hz), 120.00, 129.73, 129.75 (d, J_{C-P} = 11.7 Hz), 129.58 (d, J_{C-P} = 11.9 Hz), 128.65, 127.68, 126.34, 118.24, 58.77, 37.35 (d, J_{C-P} = 66.7 Hz), 35.02, 21.64; **MS (ESI)**: found $[M+H]^+$ 522.1.



3v: colourless oil; 73 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 29.99; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.87-7.92 (m, 2 H), 7.59-7.65 (m, 5 H), 7.44-7.46 (m, 1 H), 7.37-7.42 (m, 2 H), 7.08-7.15 (m, 3 H), 7.02-7.06 (m, 3 H), 6.85 (d, *J* = 9.2 Hz, 1 H), 4.51-4.58 (m, 1 H), 2.71-2.77 (m, 2 H), 2.53 (s, 3 H), 2.37-2.48 (m, 1 H) , 2.33 (s, 3 H), 2.07-2.13 (m, 1 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 143.98, 139.77, 135.81, 134.13, 133.45 (d, J_{C-P} = 101.0 Hz), 132.64, 132.11 (d, J_{C-P} = 2.3 Hz), 131.83 (d, J_{C-P} = 2.4 Hz), 131.27 (d, J_{C-P} = 99.2 Hz), 131.13 (d, J_{C-P} = 9.3 Hz) , 130.31, 130.22 (d, J_{C-P} = 9.7 Hz) , 129.35, 128.91 (d, J_{C-P} =11.8 Hz), 128.61 (d, J_{C-P} = 12.0 Hz), 127.35, 126.66, 122.74, 59.69, 35.18 (d, J_{C-P} = 67.7 Hz), 34.38, 21.47, 19.90; **MS (ESI)**: found $[M+H]^+$ 502.1.

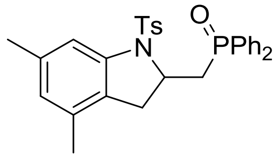


3w: colourless oil; 60 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 29.70; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.86-7.91 (m, 2 H), 7.57-7.66 (m, 5 H), 7.39-7.48 (m, 3 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.07-7.10 (m, 3 H), 6.82 (d, *J* = 9.2 Hz, 1 H), 6.68 (d, *J* = 7.4 Hz, 1 H), 4.67-4.73 (m, 1 H), 3.86 (s, 3 H), 2.95 (d, *J* = 16.4 Hz, 1 H), 2.79-2.86 (m, 1 H), 2.43-2.56 (m, 2 H), 2.35 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 152.56, 143.78, 137.11, 135.27, 133.62 (d, J_{C-P} = 100.9 Hz), 132.15, 131.88, 131.14 (d, J_{C-P} = 9.4 Hz), 130.90, 130.26 (d, J_{C-P} = 9.6 Hz), 129.33, 128.97 (d, J_{C-P} = 12.8 Hz), 128.68 (d, J_{C-P} = 12.9 Hz), 127.70, 127.36, 117.88, 112.06, 60.22, 56.08, 35.48 (d, J = 67.2 Hz), 34.86, 21.52; **MS (ESI)**: found $[M+H]^+$ 518.1.

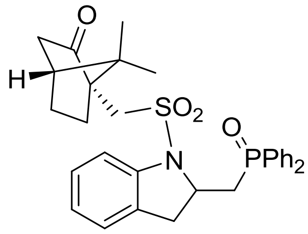


3x: colourless solid; 66 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 29.50; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.89-7.95 (m, 2 H), 7.60-7.68 (m, 5 H), 7.47-7.51 (m, 1 H), 7.41-7.45 (m, 2 H), 7.31 (d, *J* = 8.3 Hz, 2 H), 7.04-7.11 (m, 3 H), 6.97-7.01 (m, 1 H), 6.86 (d, *J* = 7.3 Hz, 1 H), 4.58-4.64 (m, 1

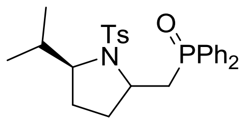
H), 3.10 (d, J = 16.6 Hz, 1 H), 2.84-2.90 (m, 1 H), 2.48-2.61 (m, 2 H), 2.35 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 155.11 (d, J_{C-F} = 255.2 Hz), 144.29, 137.86, 134.43, 133.41 (d, J_{C-P} = 101.7 Hz), 132.26 (d, J_{C-P} = 2.4 Hz), 132.01 (d, J_{C-P} = 2.4 Hz), 131.22 (d, J_{C-P} = 99.2 Hz), 131.17 (d, J_{C-P} = 9.3 Hz), 130.25 (d, J_{C-P} = 9.7 Hz), 129.63, 129.03 (d, J_{C-P} = 11.8 Hz), 128.75 (d, J_{C-P} = 12.0 Hz), 127.75 (d, J_{C-F} = 10.4 Hz), 127.50 (d, J_{C-F} = 6.8 Hz), 127.29, 121.20 (d, J_{C-F} = 3.4 Hz), 116.00 (d, J_{C-F} = 20.3 Hz), 60.40, 36.66 (d, J = 67.0 Hz), 34.75, 21.54; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ : -118.75; **MS (ESI)**: found $[M+H]^+$ 506.1.



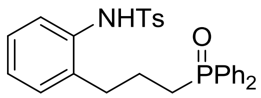
3y: colourless oil; 64 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 29.42; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.98-8.03 (m, 2 H), 7.71-7.76 (m, 2 H), 7.62-7.66 (m, 3 H), 7.43-7.53 (m, 3 H), 7.33 (s, 1 H), 7.26 (d, J = 8.2 Hz, 2 H), 7.06 (d, J = 8.2 Hz, 2 H), 6.66 (s, 1 H), 4.29-4.37 (m, 1 H), 3.23-3.29 (m, 1 H), 3.05-3.10 (m, 1 H), 2.67-2.86 (m, 2 H) , 2.31-2.32 (m, 6 H), 2.05 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 143.80, 140.40, 137.73, 134.48, 134.10, 133.57 (d, J_{C-P} = 100.7 Hz), 131.96 (d, J_{C-P} = 2.7 Hz), 131.82 (d, J_{C-P} = 2.7 Hz), 131.60 (d, J_{C-P} = 98.5 Hz), 131.29 (d, J_{C-P} = 9.4 Hz), 130.24 (d, J_{C-P} = 9.5 Hz), 129.45, 128.78 (d, J_{C-P} =11.9 Hz), 128.64 (d, J_{C-P} = 11.9 Hz), 126.86, 126.81, 126.46, 114.31, 58.07, 37.38 (d, J_{C-P} = 66.9 Hz), 33.71, 21.43, 21.39, 18.57; **MS (ESI)**: found $[M+H]^+$ 516.1.



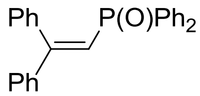
3z: colourless solid; 63 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 29. 67; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.92-7.97 (m, 2 H), 7.65-7.71 (m, 2 H), 7.50-7.56 (m, 3 H), 7.39-7.45 (m, 4 H), 7.16-7.19 (m, 2 H), 7.01-7.05 (m, 1 H), 4.57-4.63 (m, 1 H), 3.46-3.50 (m, 2 H), 3.19-3.32 (m, 2 H), 2.64-2.82 (m, 2 H), 2.42-2.54 (m, 1 H), 2.30-2.34 (m, 1 H), 2.03-2.07 (m, 2 H), 1.86-1.91 (m, 1 H), 1.54-1.60 (m, 1 H), 1.37-1.42 (m, 1 H), 1.11-1.12 (m, 3 H), 0.77-0.80 (m, 3 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 214.70, 214.63, 140.55, 140.42, 132.14, 131.93, 131.26, 131.17, 130.76, 130.62, 130.36, 130.26, 130.23, 129.07, 128.97, 128.85, 128.79, 128.75, 128.68, 128.63, 128.05, 127.89, 125.89, 125.79, 124.33, 114.65, 114.42, 58.86, 58.28, 58.26, 47.92, 47.73, 45.73, 45.68, 42.98, 42.88, 42.48, 42.45, 37.74, 37.43, 37.07, 36.77, 35.04, 34.91, 26.89, 26.83, 25.52, 25.33, 20.09, 20.04, 19.76, 19.73; **MS (ESI)**: found $[M+H]^+$ 548.2.



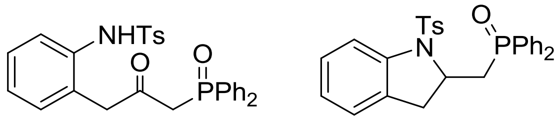
3aa: colourless oil; 49 % yield; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 29. 29, 29.73; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.94-8.037 (m, 2 H), 7.73-7.79 (m, 2 H), 7.56-7.65 (m, 3 H), 7.42-7.52 (m, 4 H), 7.28-7.32 (m, 1 H), 7.12-7.16 (m, 2 H), 4.05-4.10 (m, 0.46 H), 3.89-3.92 (m, 0.46 H), 3.48-3.62 (m, 1 H), 3.30-3.382 (m, 1 H), 2.28-2.48 (m, 5 H), 1.98-2.06 (m, 1.13 H), 1.88-1.957 (m, 0.63 H), 1.71-1.83 (m, 1.49 H), 1.62-1.68 (m, 0.63 H), 1.11-1.17 (m, 0.59 H), 0.98-1.00 (m, 1.64 H), 0.91-0.93 (m, 1.71 H), 0.79-0.81 (m, 1.44 H), 0.24-0.25 (m, 1.34 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 143.37, 142.77, 139.00, 134.52, 134.19, 133.75, 133.52, 133.19, 132.15, 132.08, 131.93, 131.91, 131.87, 131.81, 131.79, 131.53, 131.47, 131.44, 131.37, 131.17, 131.11, 130.43, 130.35, 130.33, 130.26, 129.54, 129.36, 128.88, 128.80, 128.77, 128.69, 128.65, 127.46, 126.56, 67.36, 65.04, 57.07, 57.05, 56.77, 38.14, 37.48, 35.24, 34.59, 31.68, 31.18, 31.01, 29.03, 25.60, 23.08, 21.45, 21.43, 20.10, 19.89, 17.70, 15.38; **MS (ESI)**: found $[M+H]^+$ 482.2.



4a: colourless oil; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 34.68; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 9.45(s), 7.71-7.76 (m, 4 H), 7.66 (d, *J* = 8.2 Hz, 2 H), 7.39-7.53 (m, 7 H), 7.01-7.13 (m, 5 H), 2.46-2.50 (m, 2 H), 2.33 (s, 3 H), 2.05-2.11 (m, 2 H), 1.75-1.87 (m, 2 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 142.83, 137.79, 135.51, 134.79, 132.31 (d, J_{C-P} = 99.1 Hz), 131.91 (d, J_{C-P} = 2.5 Hz), 130.90, 130.81, 129.44, 129.26, 128.80, 128.69, 127.25, 126.96, 125.98 (d, J_{C-P} = 6.9 Hz), 29.22 (d, J_{C-P} = 5.5 Hz), 26.83 (d, J_{C-P} = 4.3 Hz), 23.20 (d, J_{C-P} = 71.0 Hz), 21.50; **MS (ESI)**: found $[M+H]^+$ 490.1.



6a: white solid; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 18.75,18.66; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.68-7.74 (m, 4 H), 7.29-7.39 (m, 11 H), 7.24-7.27 (m, 2 H), 7.07-7.16 (m, 3 H), 6.82 (d, *J* = 18.2 Hz, 2 H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ:162.00 (d, J_{C-P} = 2.6 Hz), 141.88 (d, J_{C-P} = 16.3 Hz), 138.03 (d, J_{C-P} = 6.6 Hz), 134.40 (d, J_{C-P} = 108.8 Hz), 131.08 (d, J_{C-P} = 2.6 Hz), 130.87 (d, J_{C-P} = 9.4 Hz), 130.32, 129.09 (d, J_{C-P} = 90.4 Hz), 128.36 (d, J_{C-P} = 5.0 Hz), 128.26 (d, J_{C-P} = 6.4 Hz), 127.59, 120.55 (d, J_{C-P} = 103.7 Hz); **MS (ESI)**: found $[M+H]^+$ 381.2.

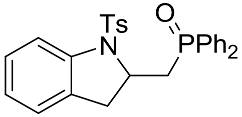


8a:3a = 1:1: colourless oil; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ: 29.49, 28.55; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 9.56 (s, 1 H), 7.97-8.01 (m, 2 H), 7.43-7.77 (m, 23 H), 7.00-7.24 (m, 11 H), 4.28-4.35 (m, 1 H), 3.53 (s, 2 H), 3.48 (d, J_{H-P} = 14.2 Hz, 2 H), 3.18-3.25 (m, 2 H), 2.89-2.96 (m, 1 H), 2.65-2.75 (m, 1 H), 2.36 (s, 3 H) , 2.30 (s, 3 H); **MS (ESI)**: found $[M+H]^+$ 488.1, 504.1.

IX. References:

1. Correa, A.; Tellitu, I.; Dom ńguez, E.; SanMartin, R. *J. Org. Chem.* **2006**, *71*, 8316.
2. Sherman, E. S.; Fuller, P. H.; Kasi, D.; Chemler, S. R. *J. Org. Chem.* **2007**, *72*, 3896.
3. Berry, M. B.; Craig, D. *Synlett* **1992**, 41.

X. NMR Charts



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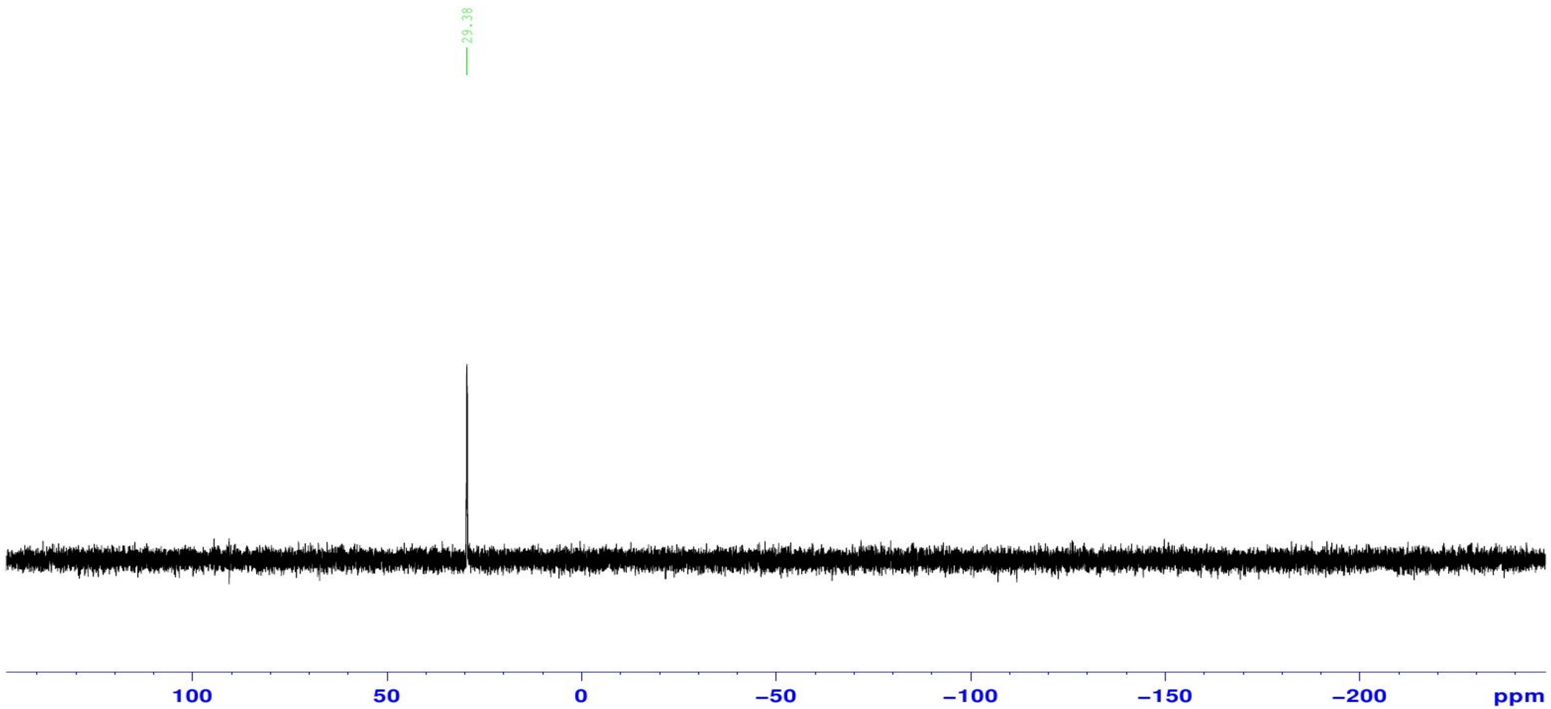

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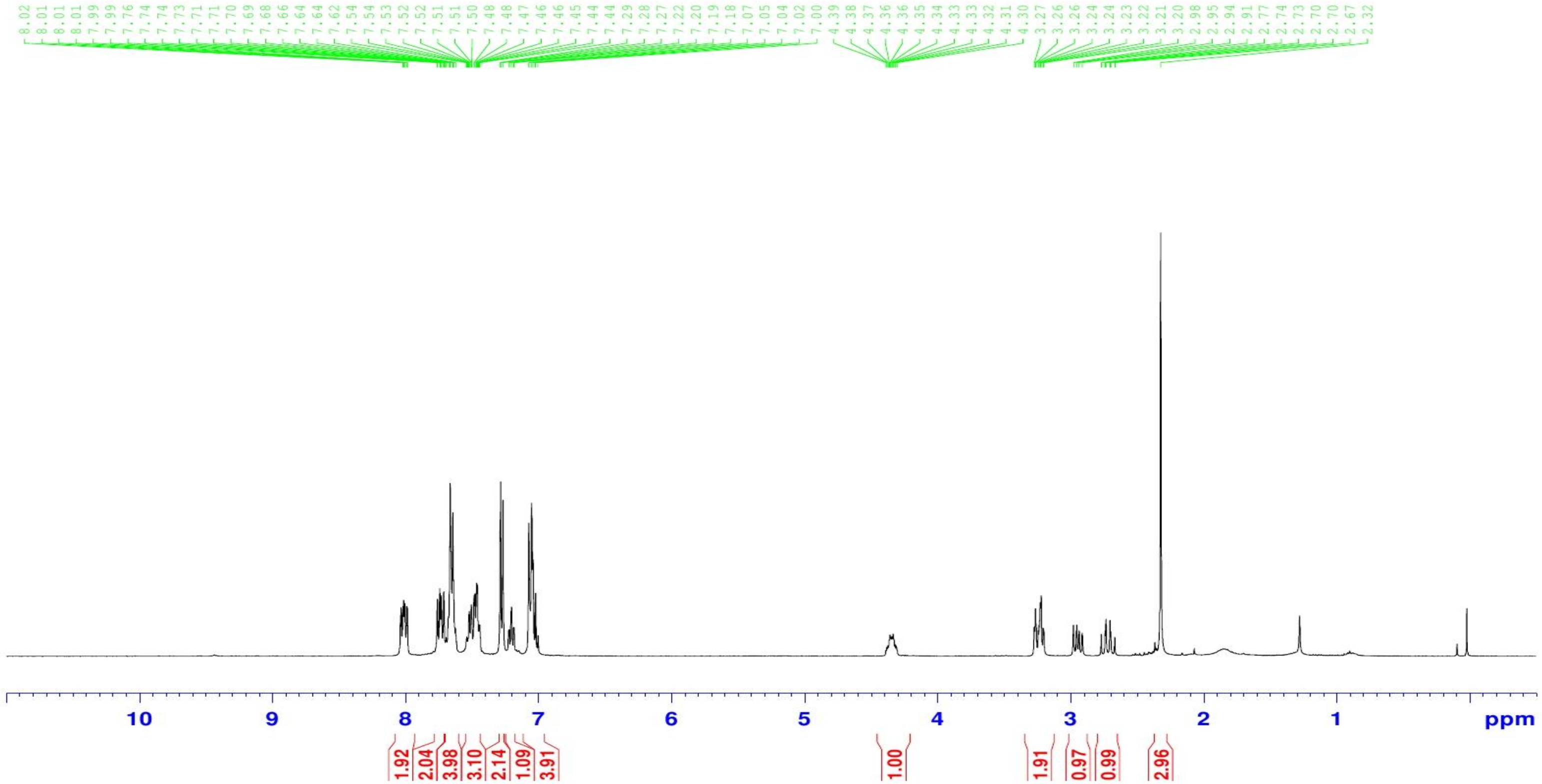
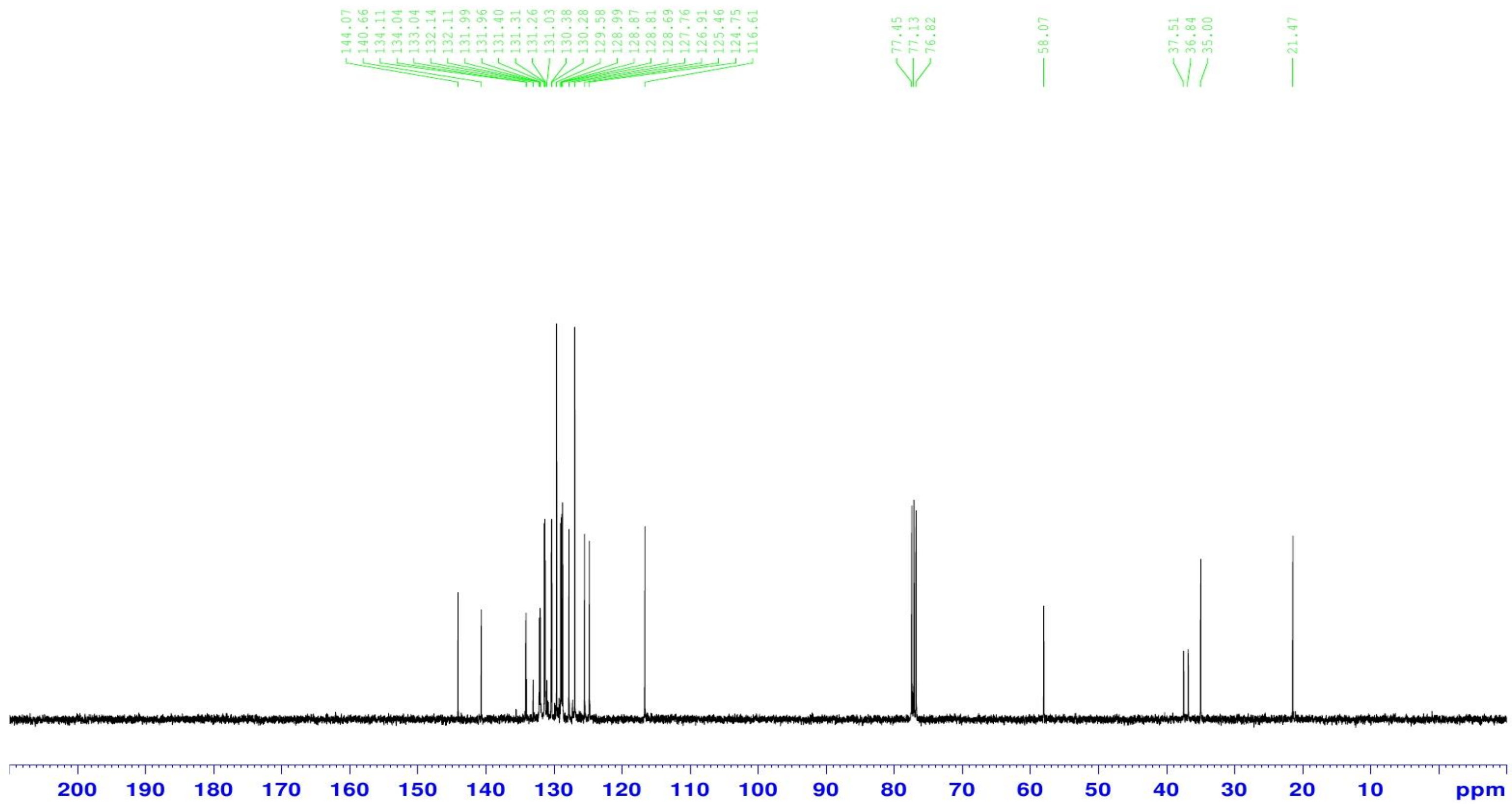


a1-C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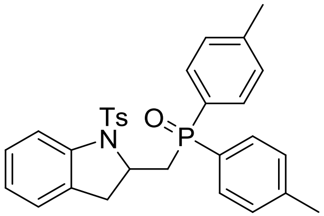

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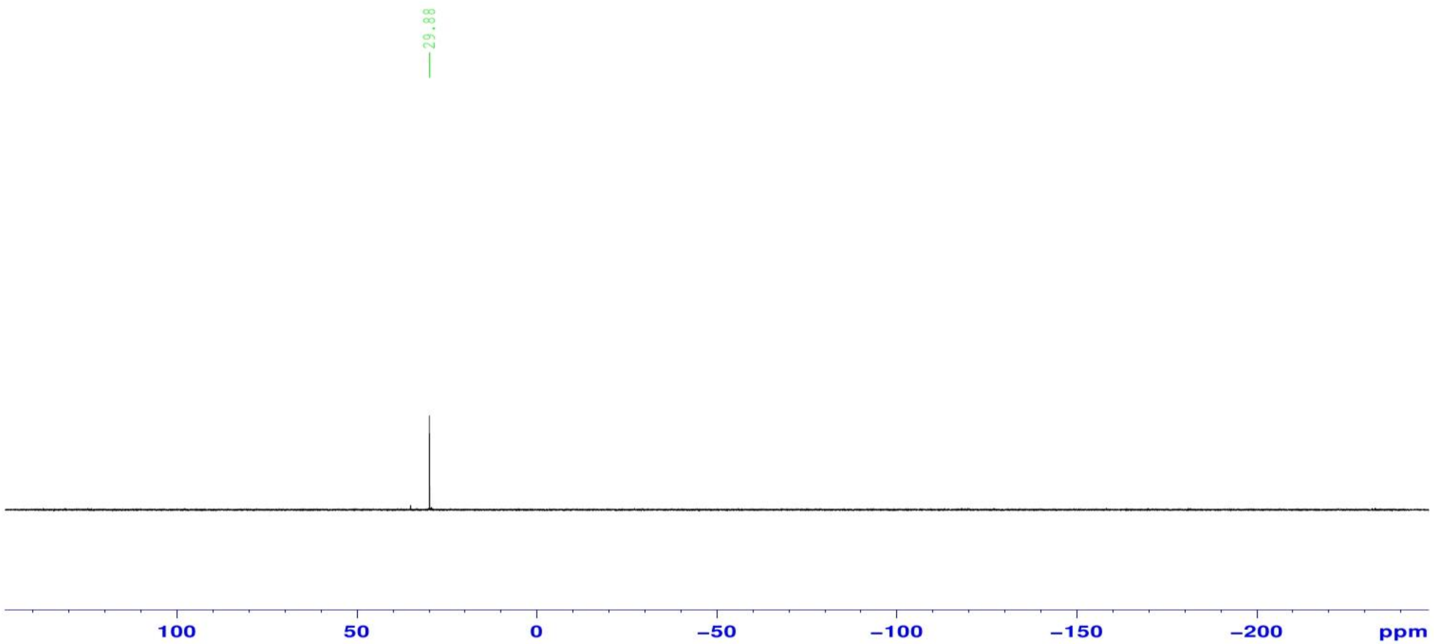

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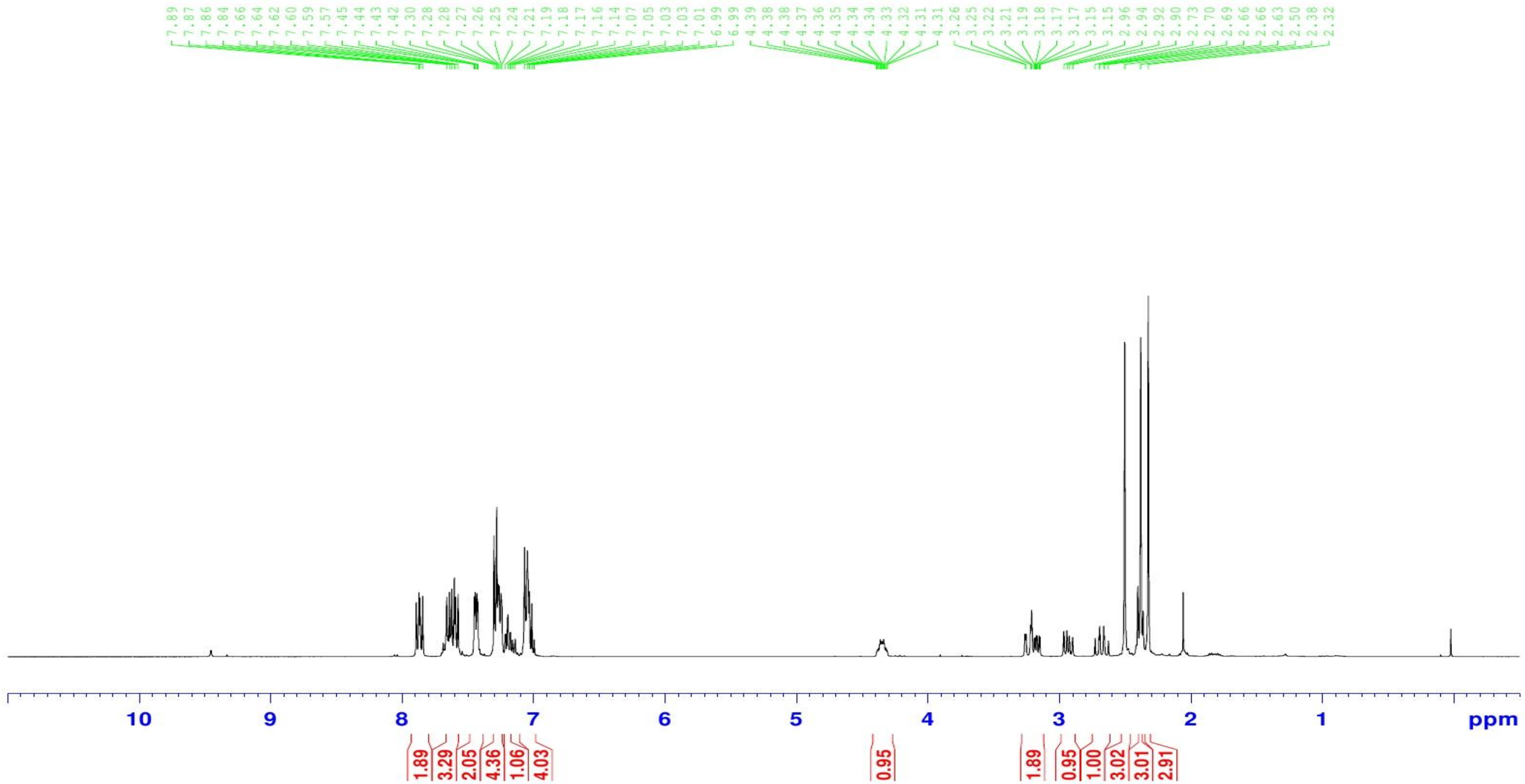

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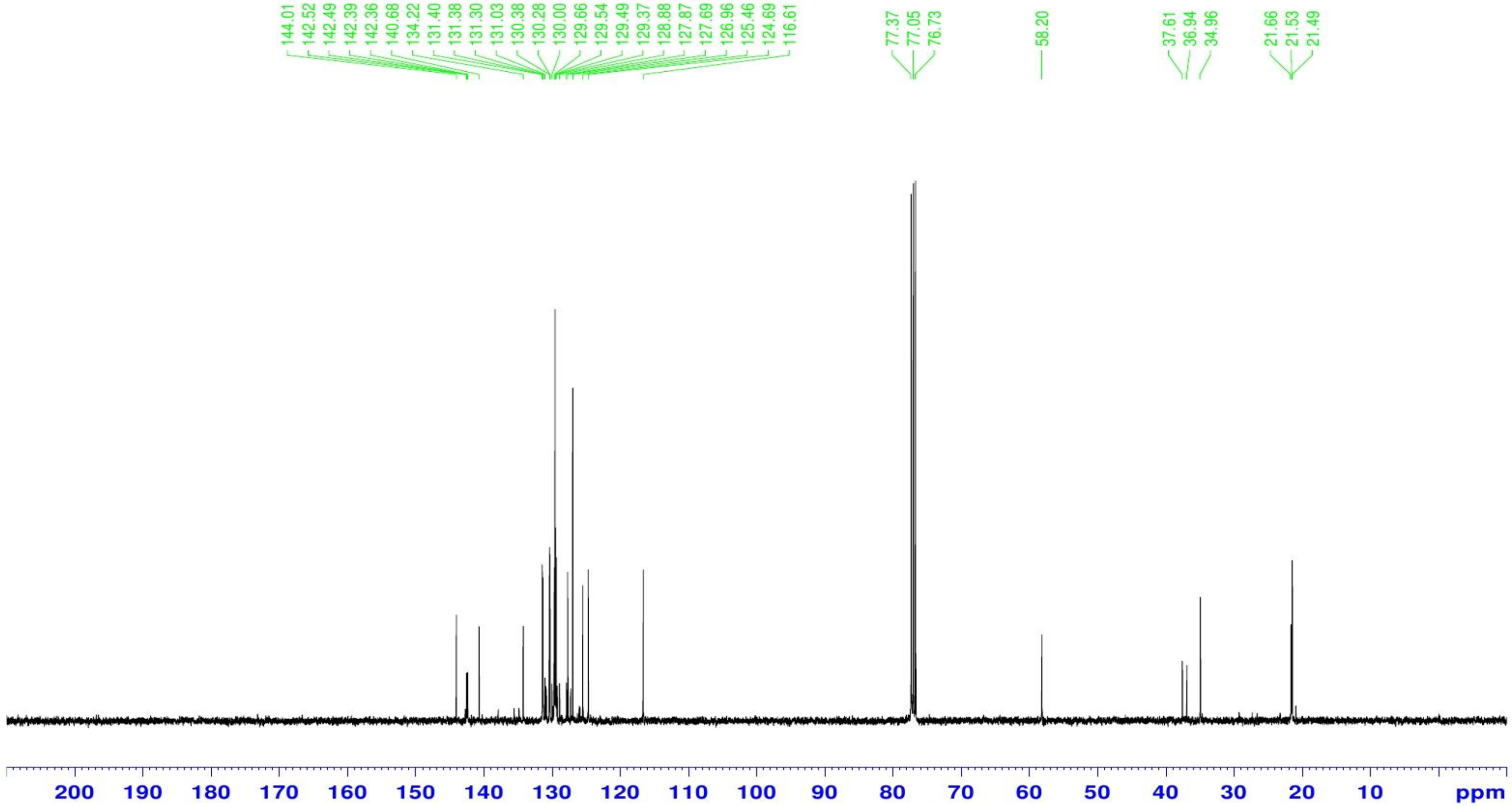

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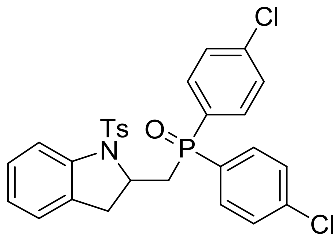

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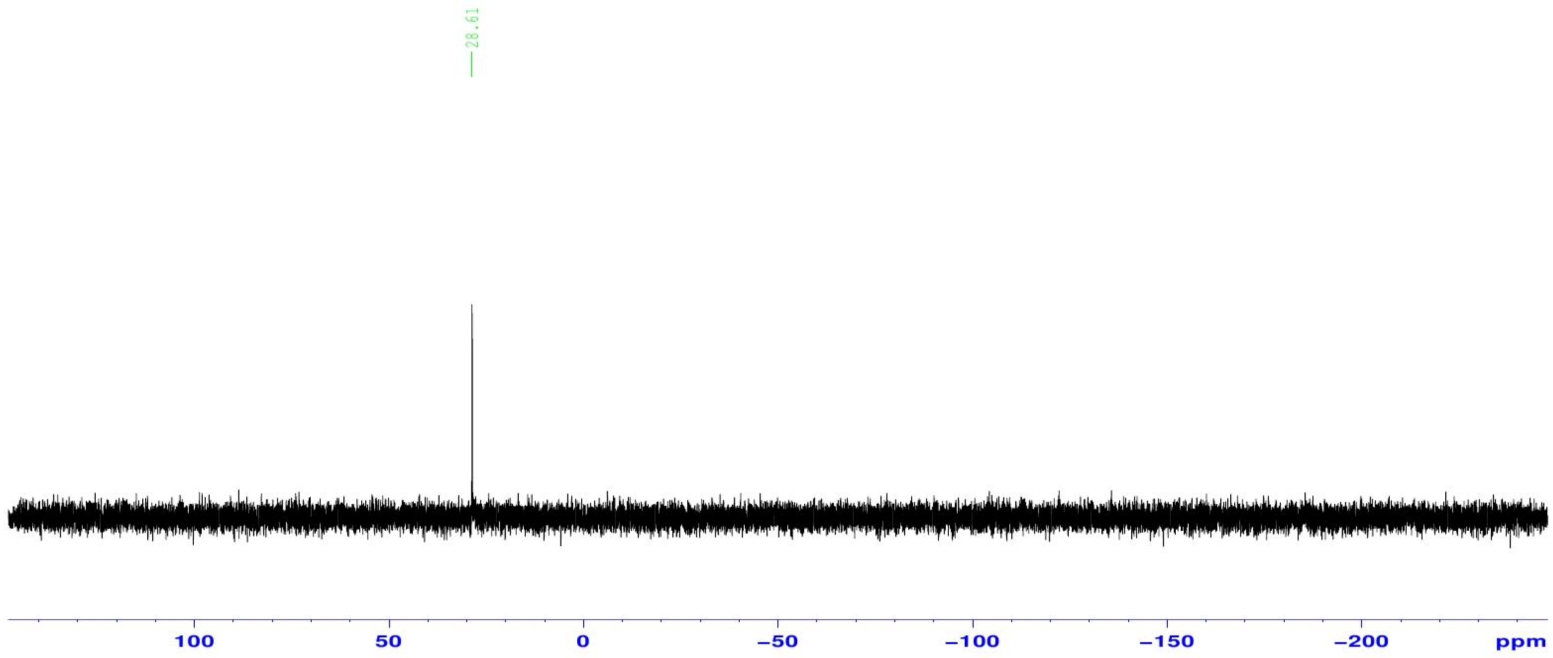

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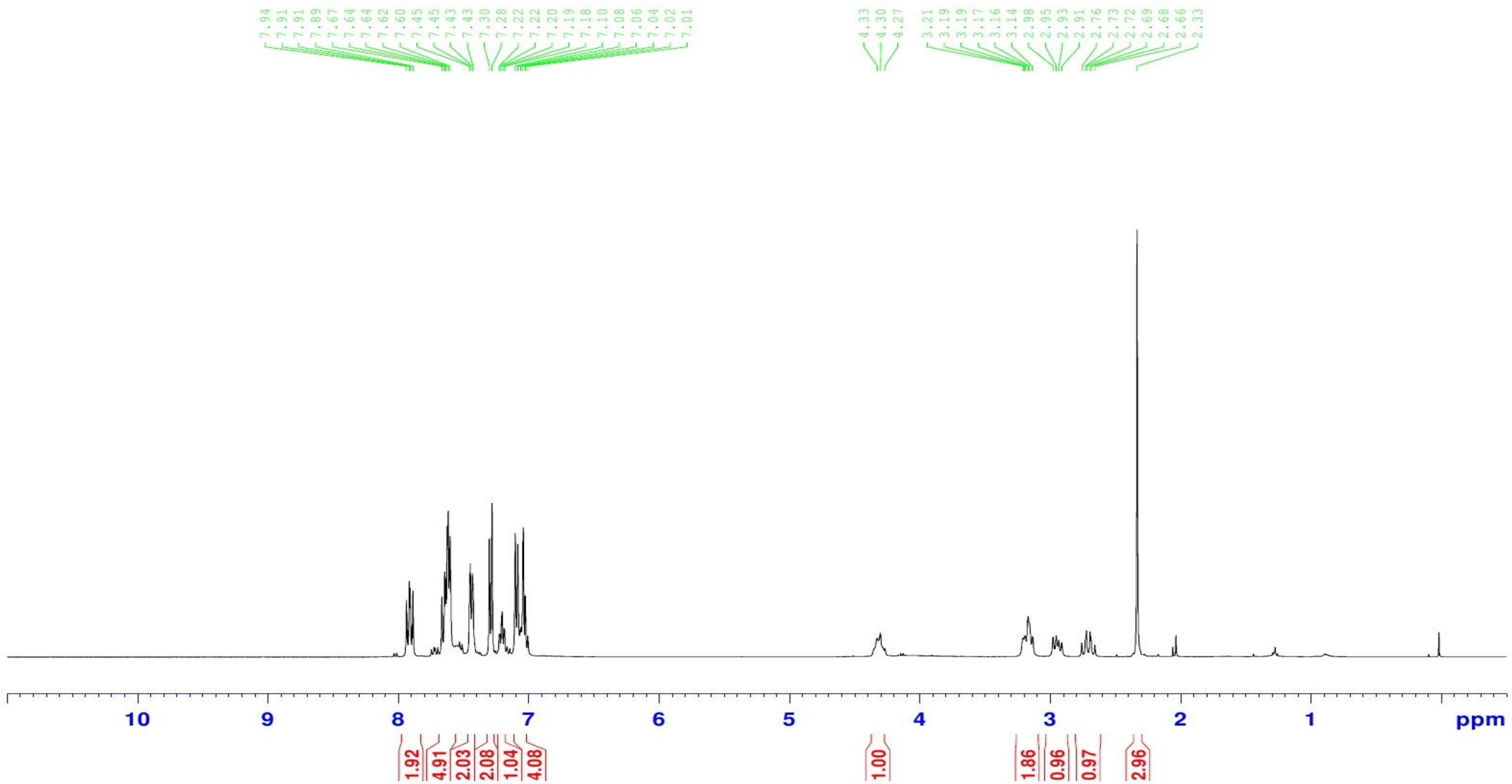

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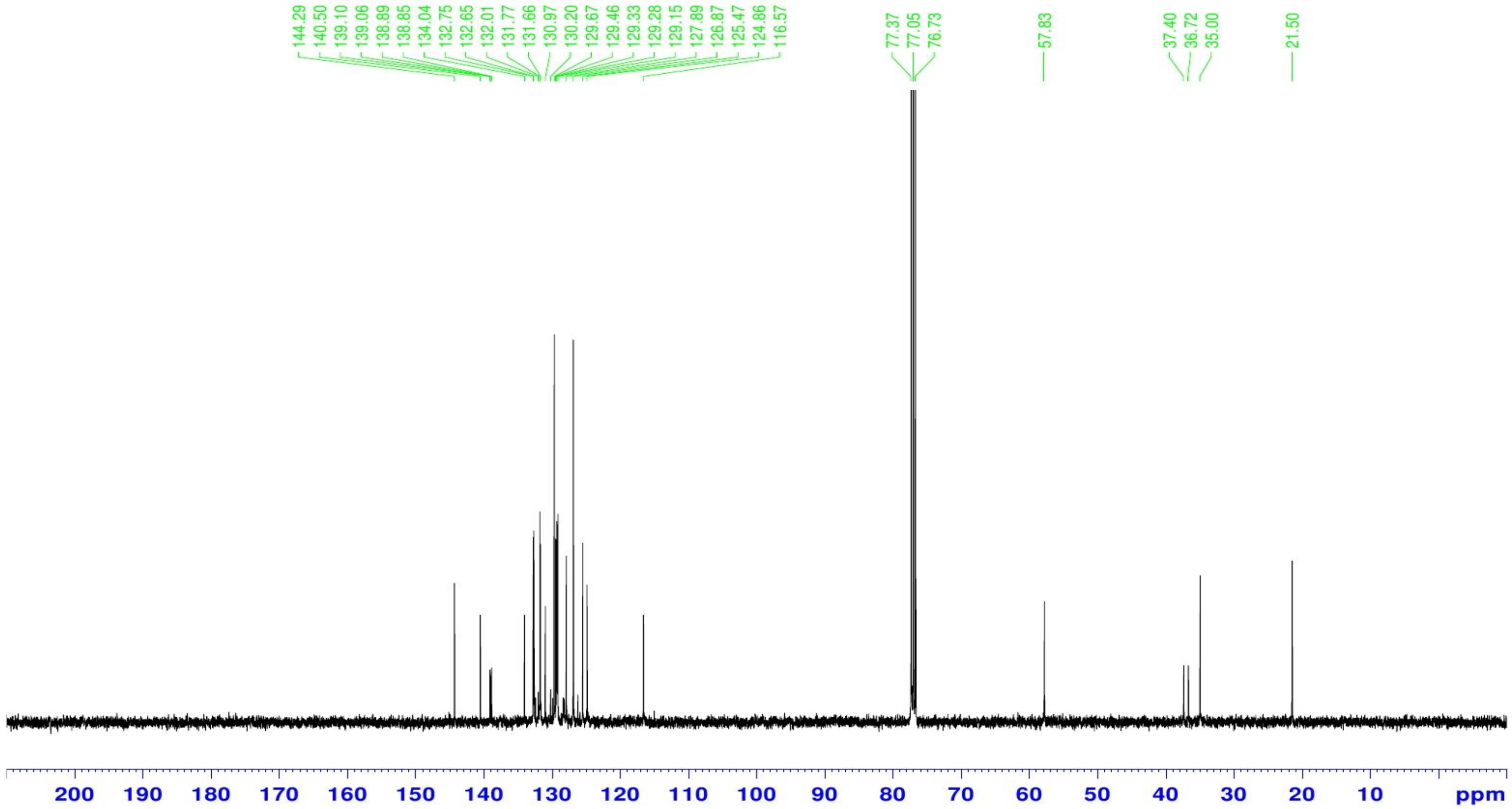
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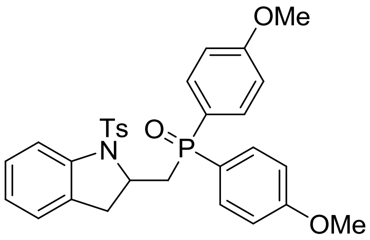

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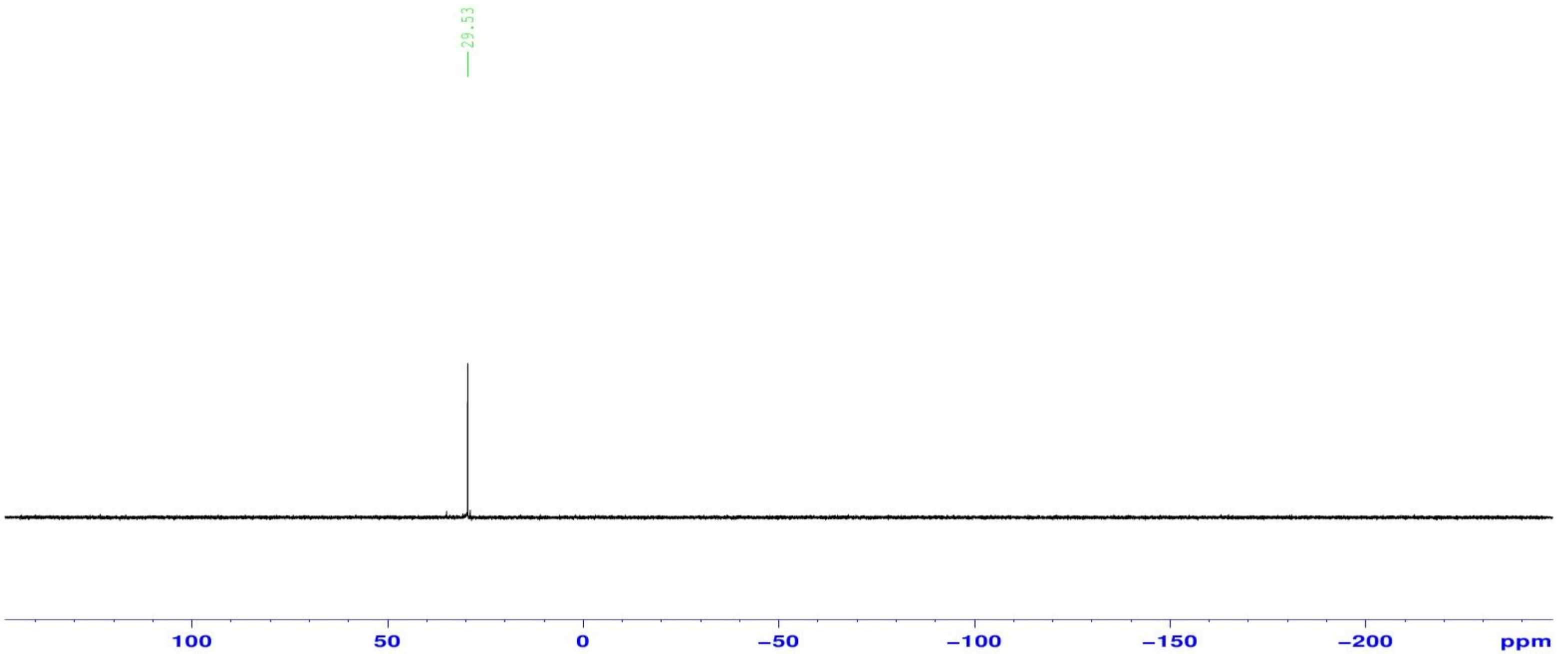

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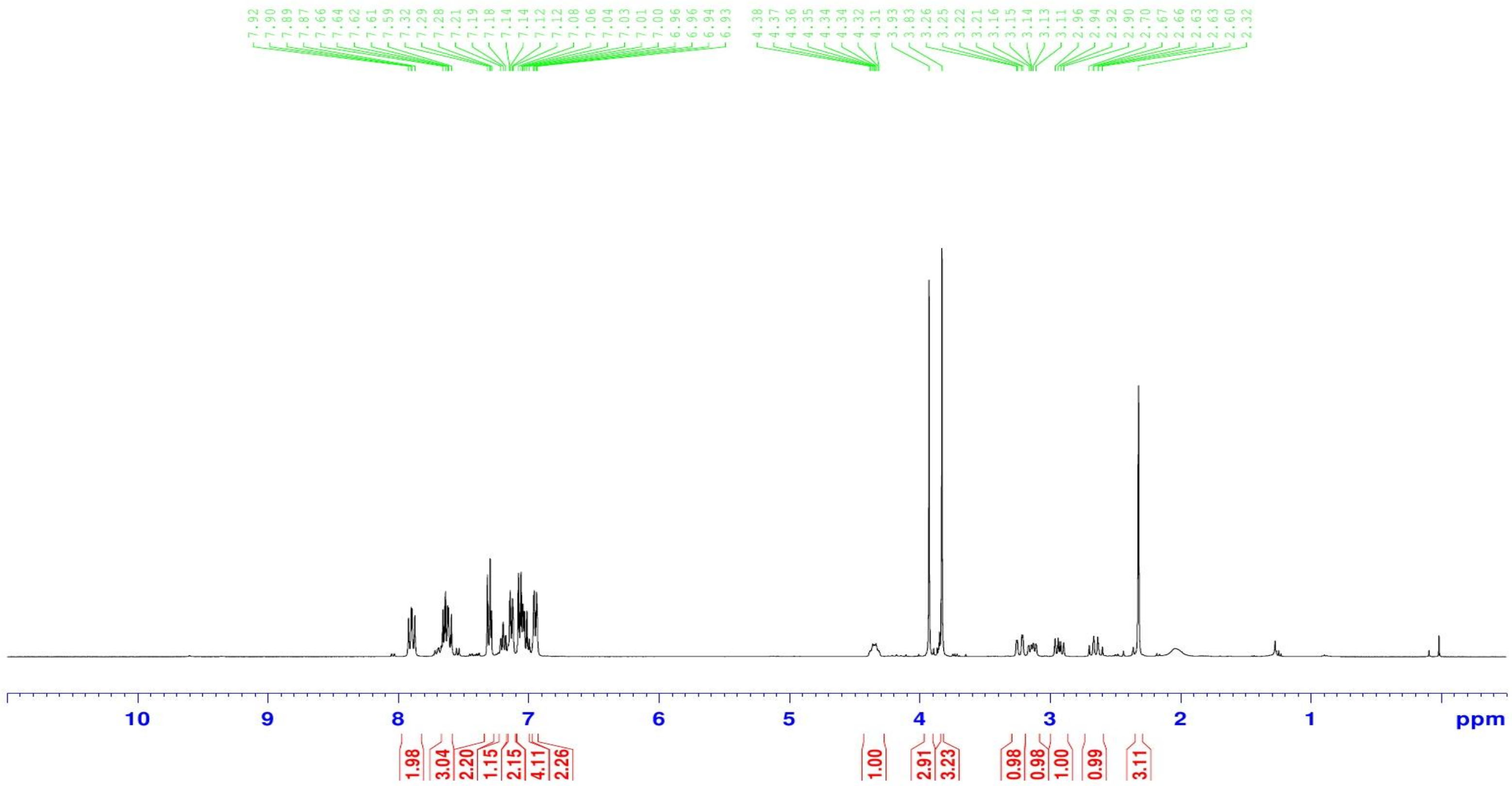

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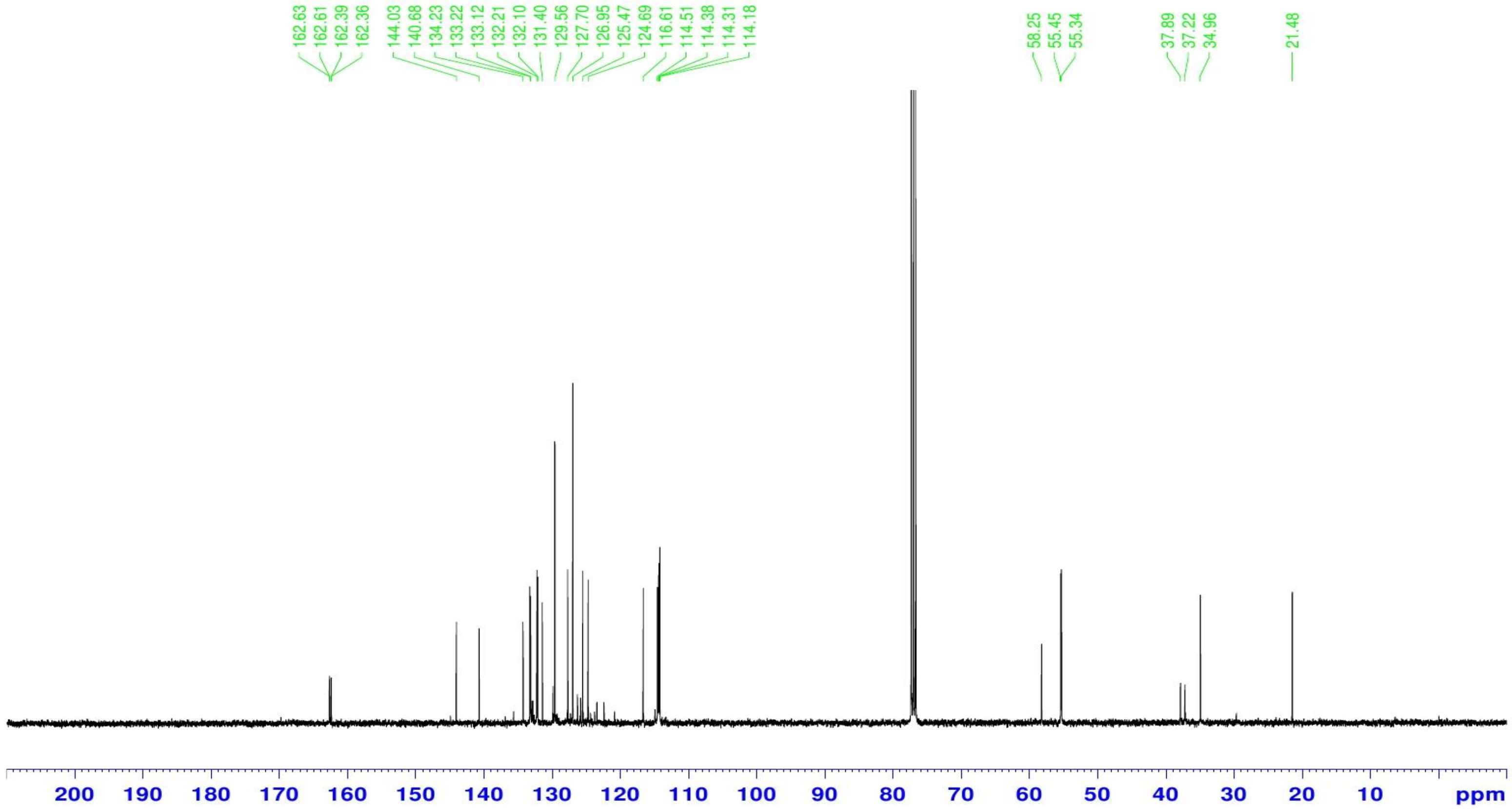

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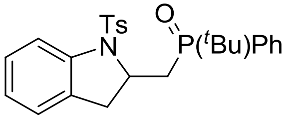

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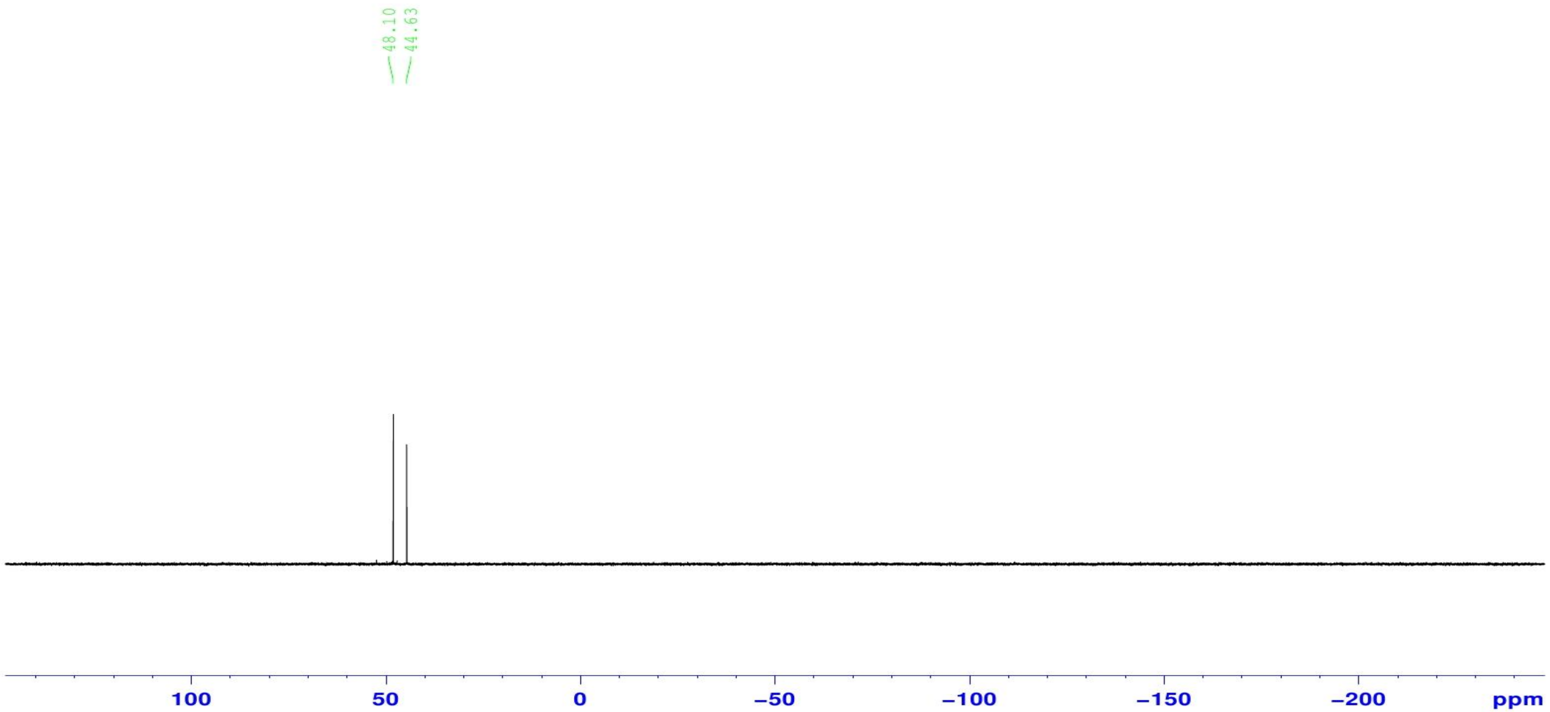

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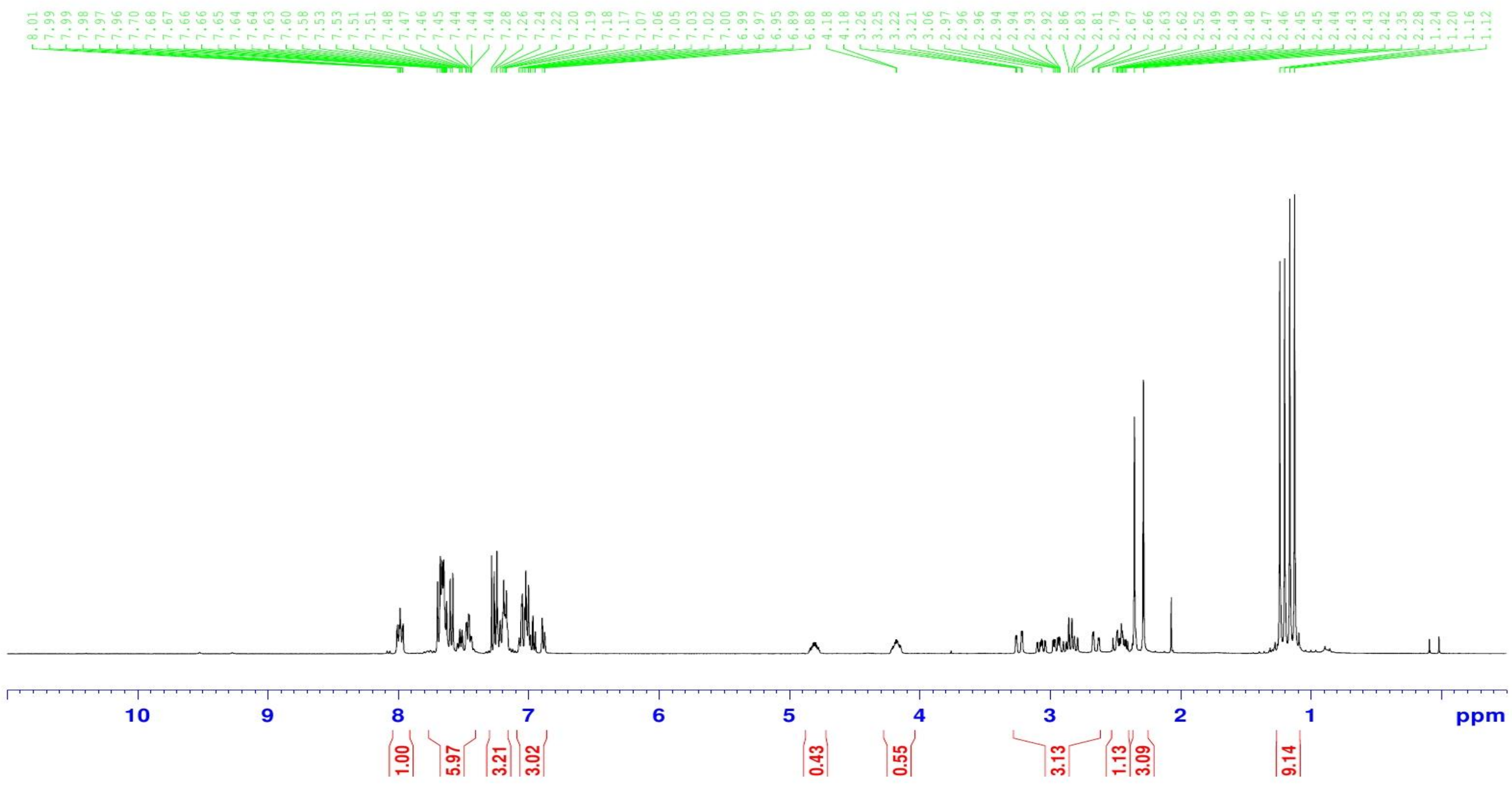

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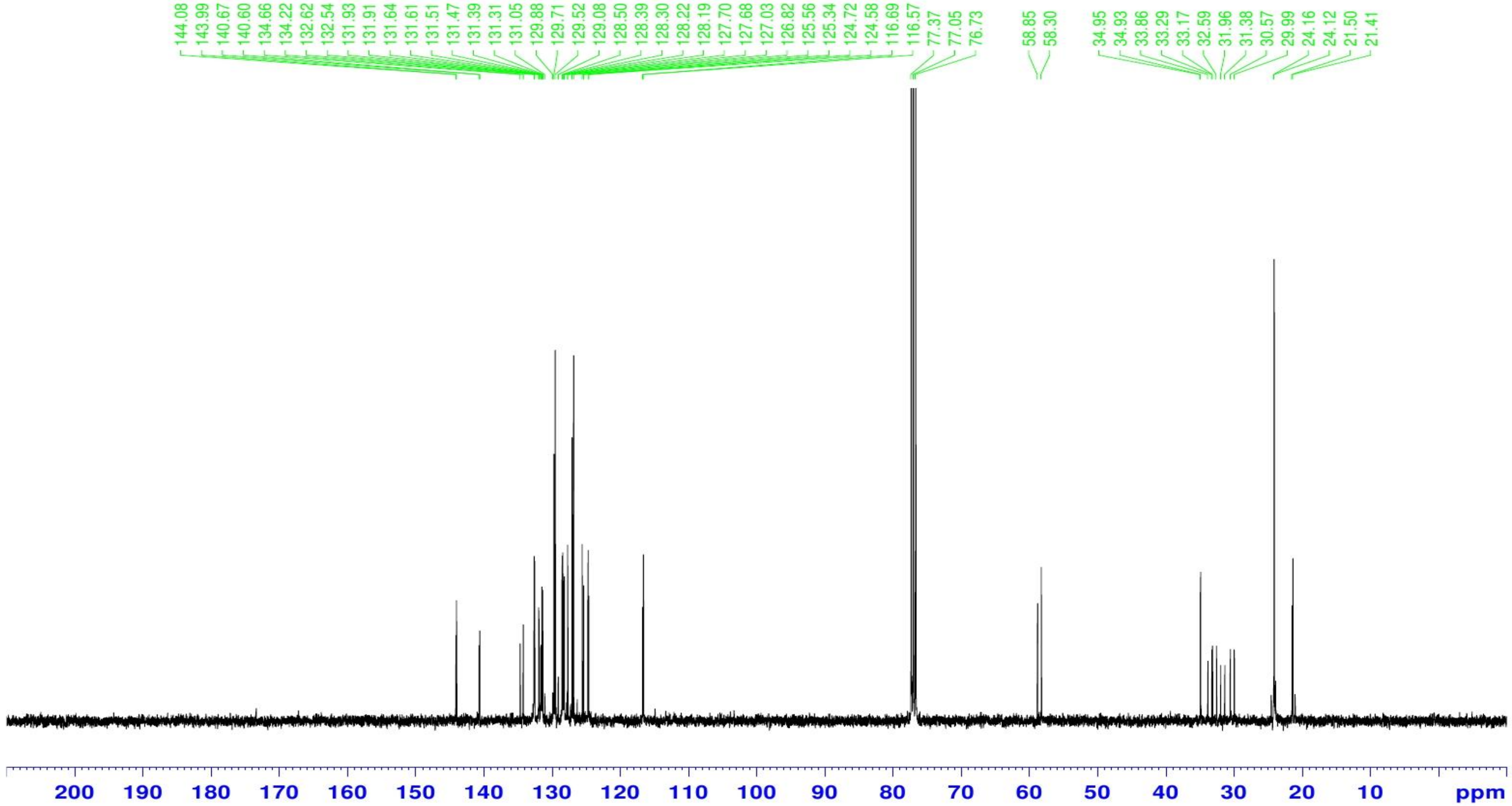
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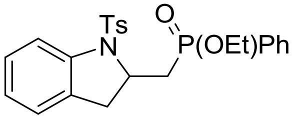

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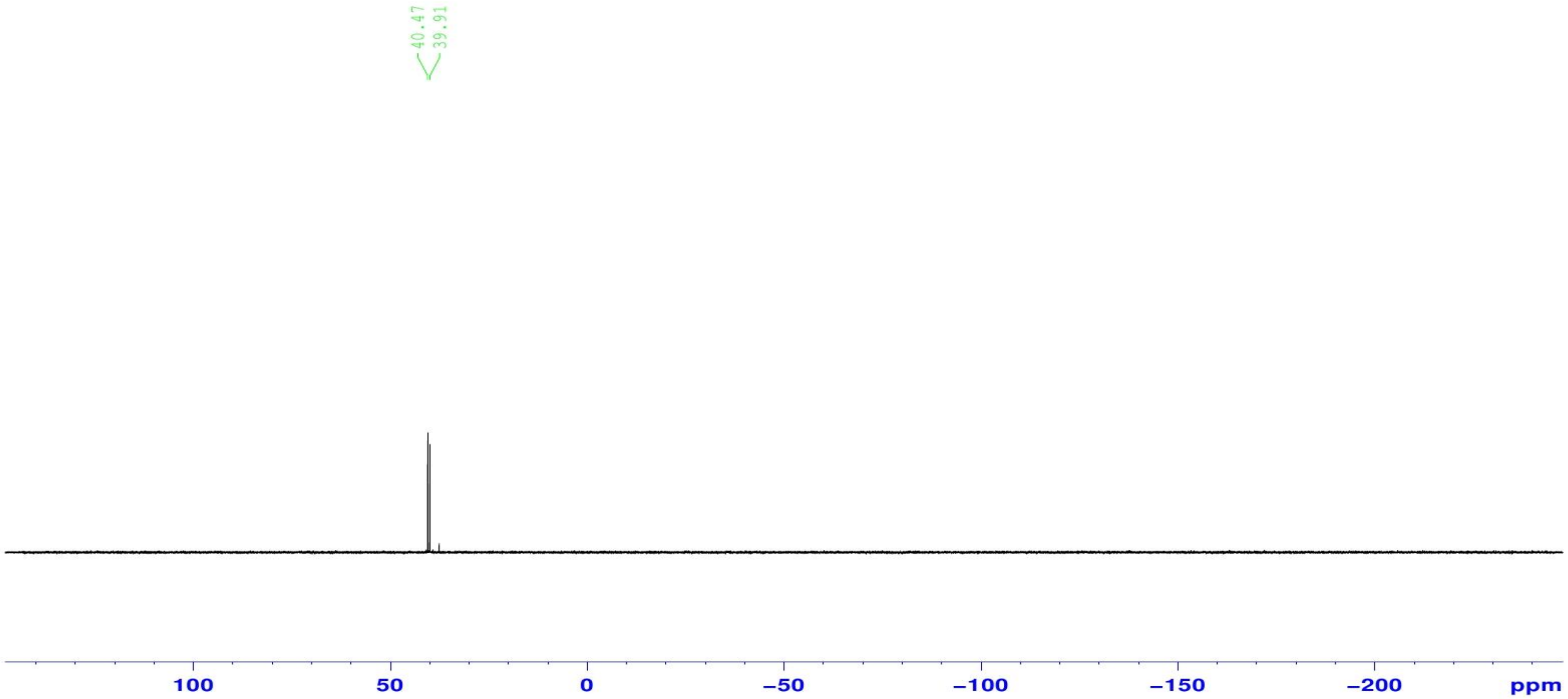

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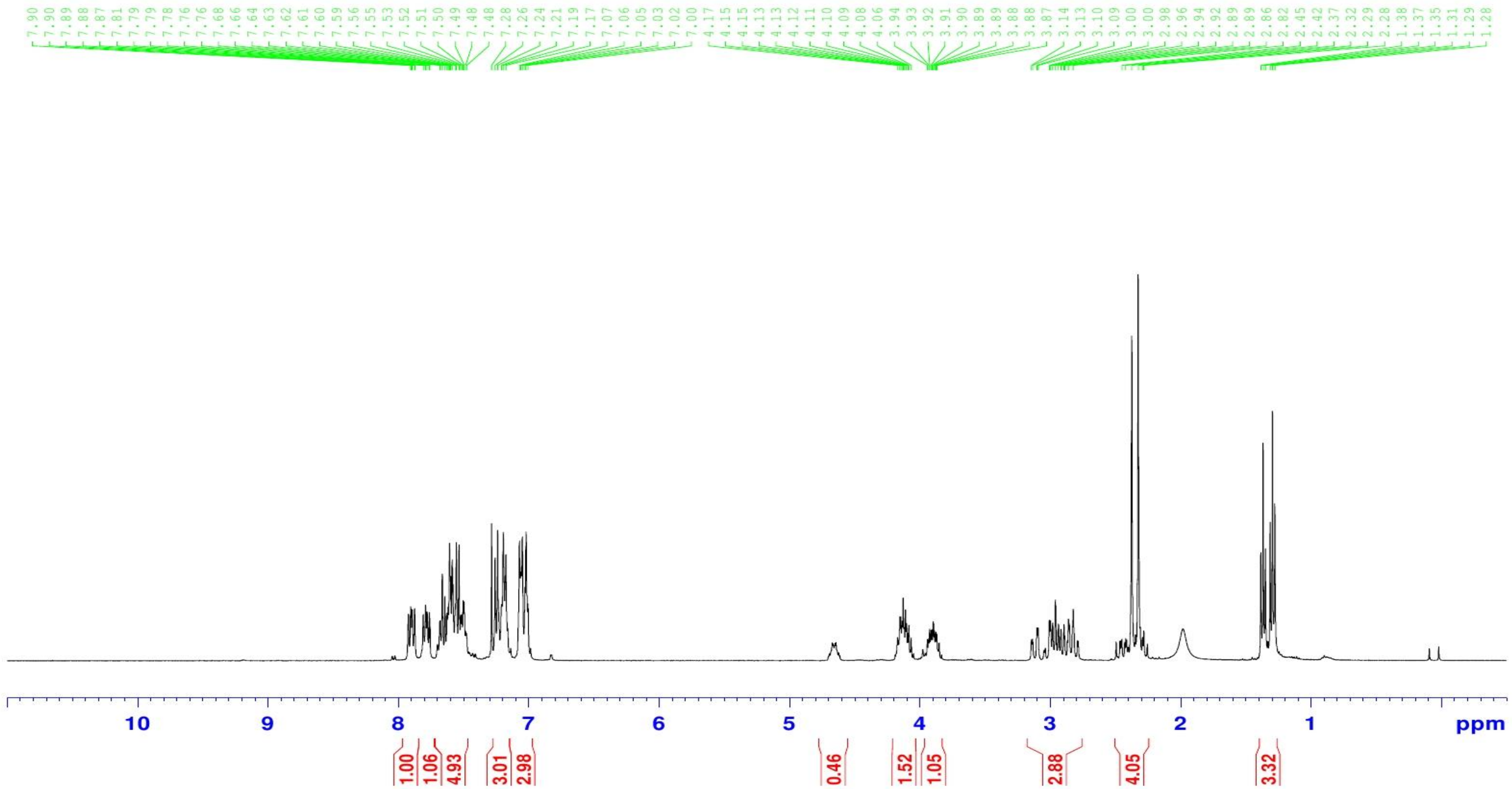

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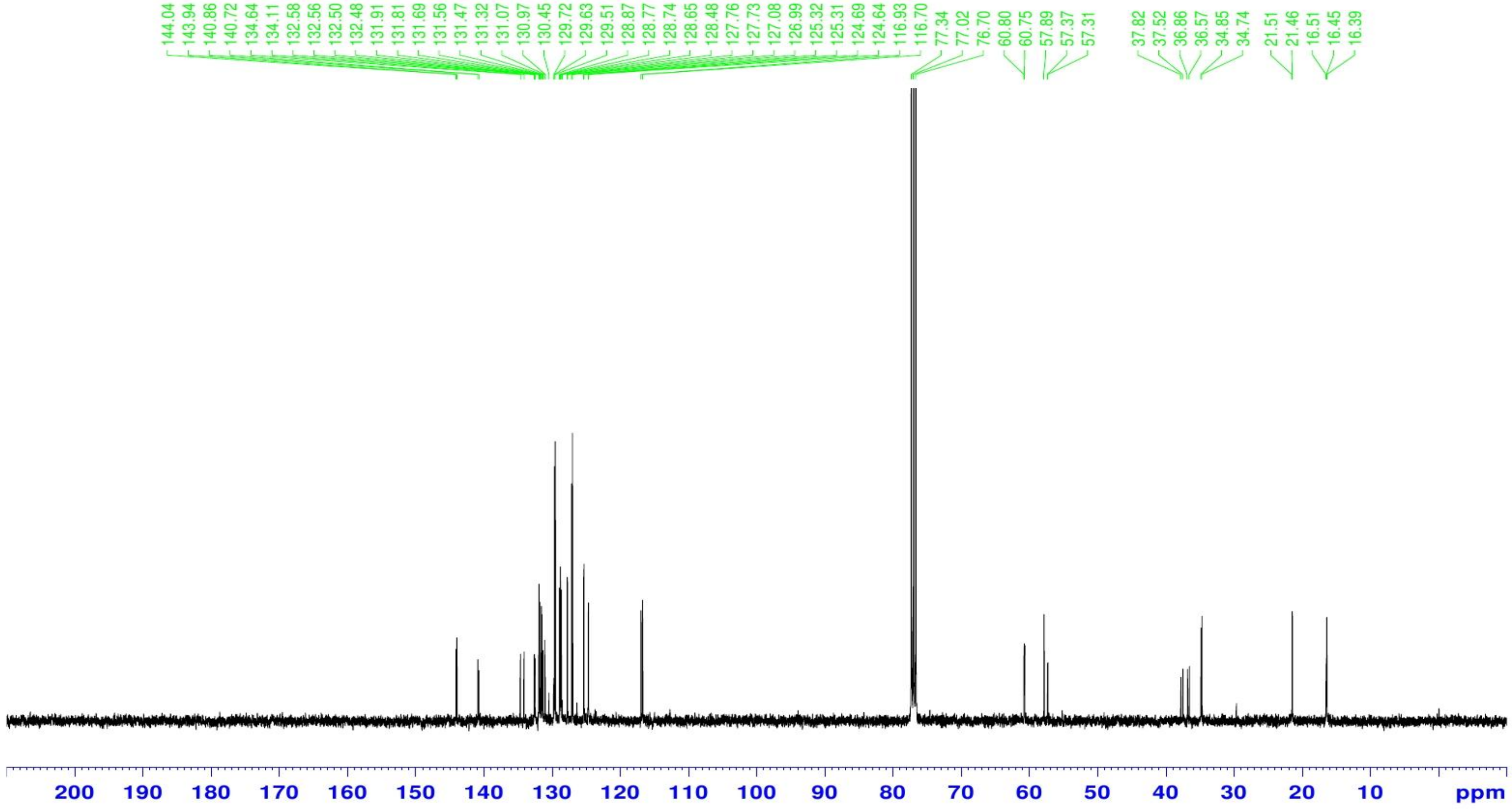
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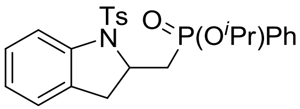

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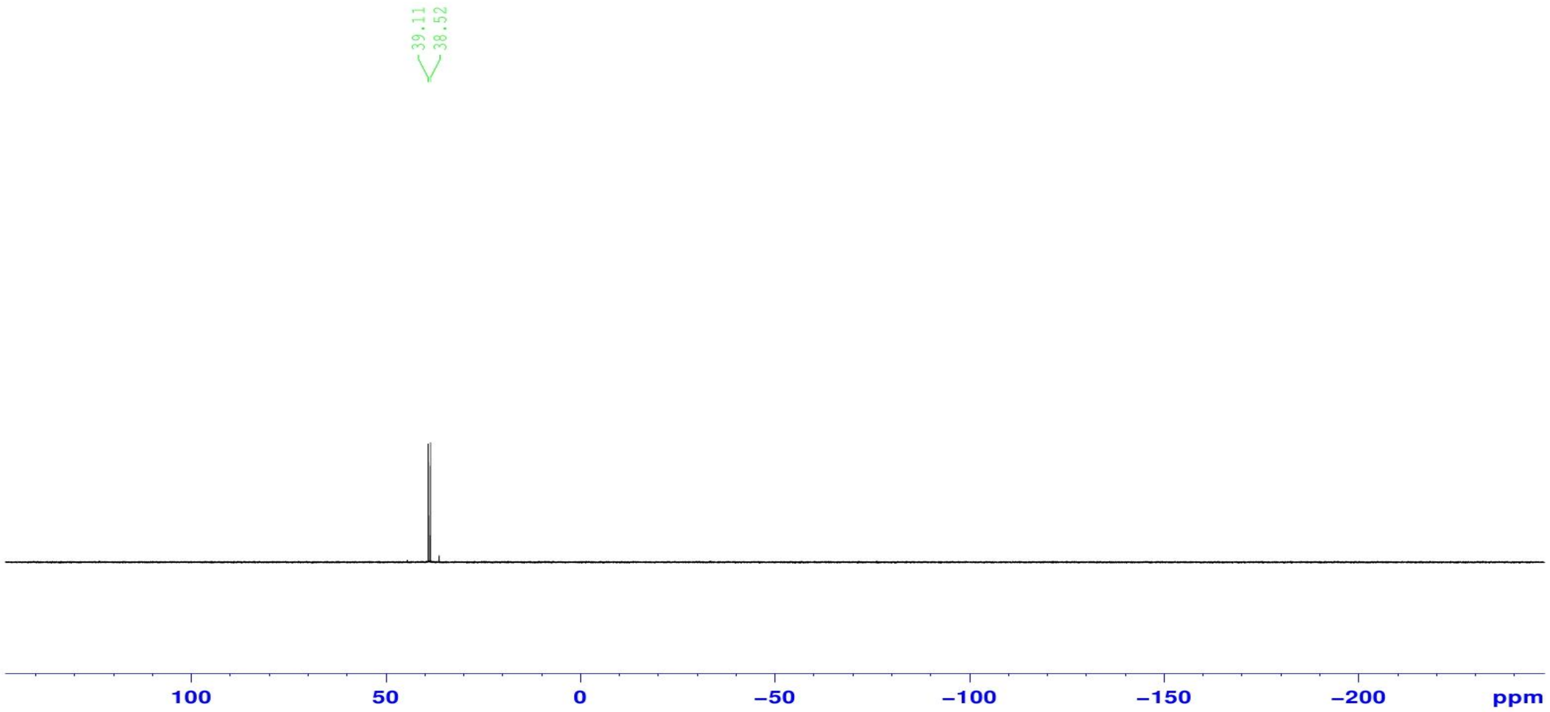

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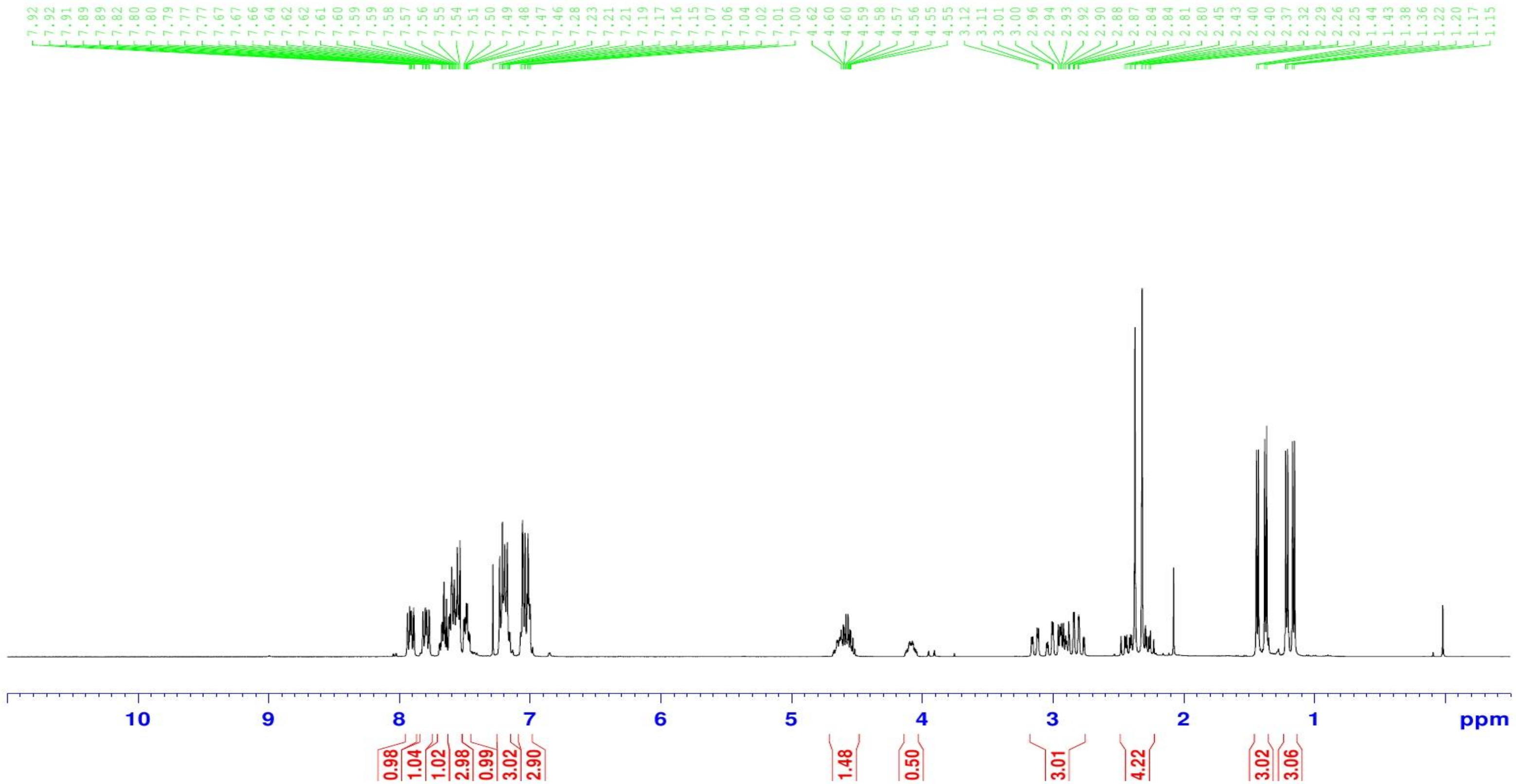

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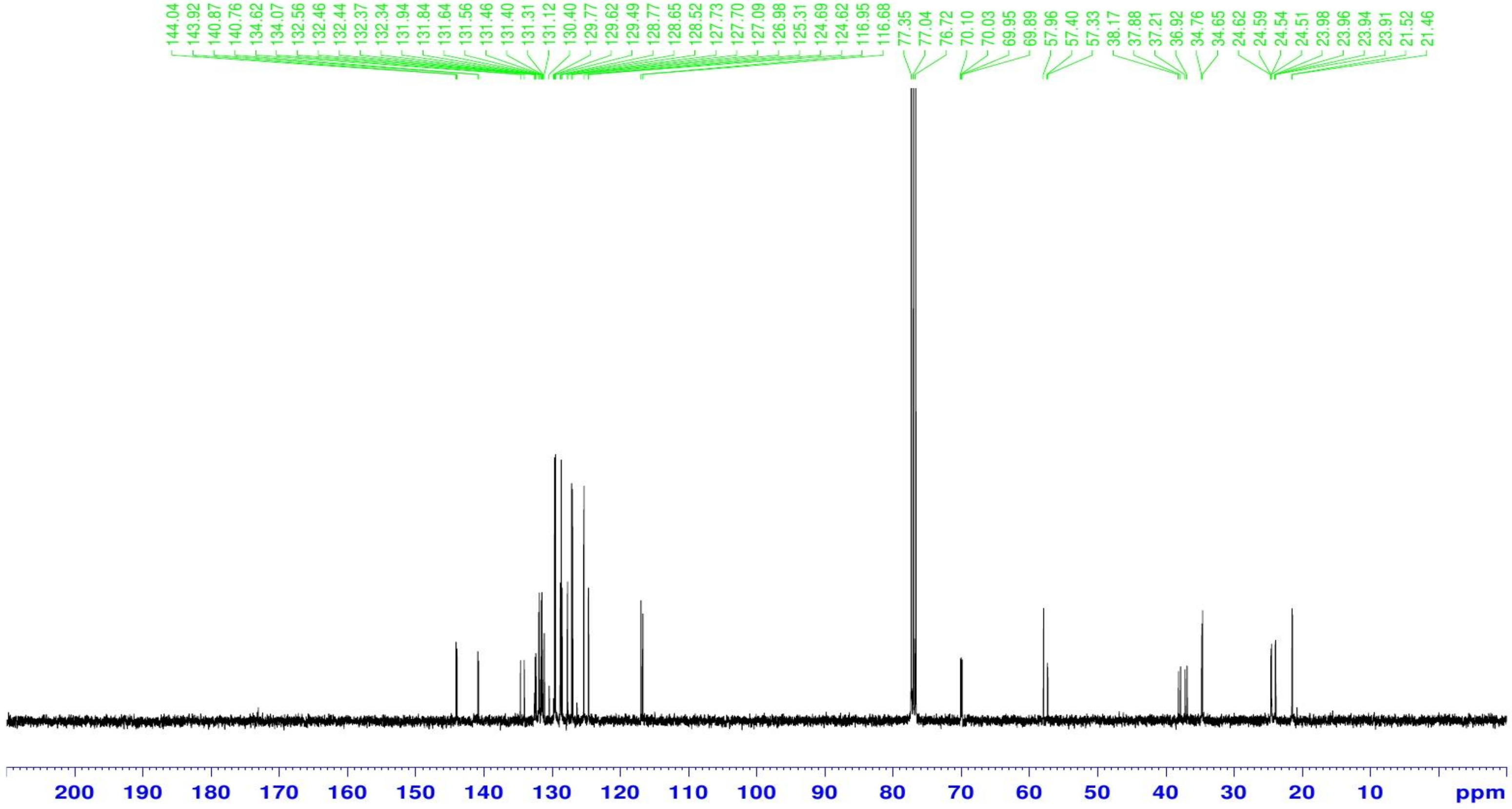

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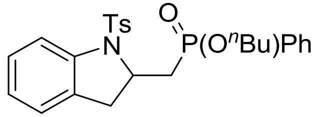
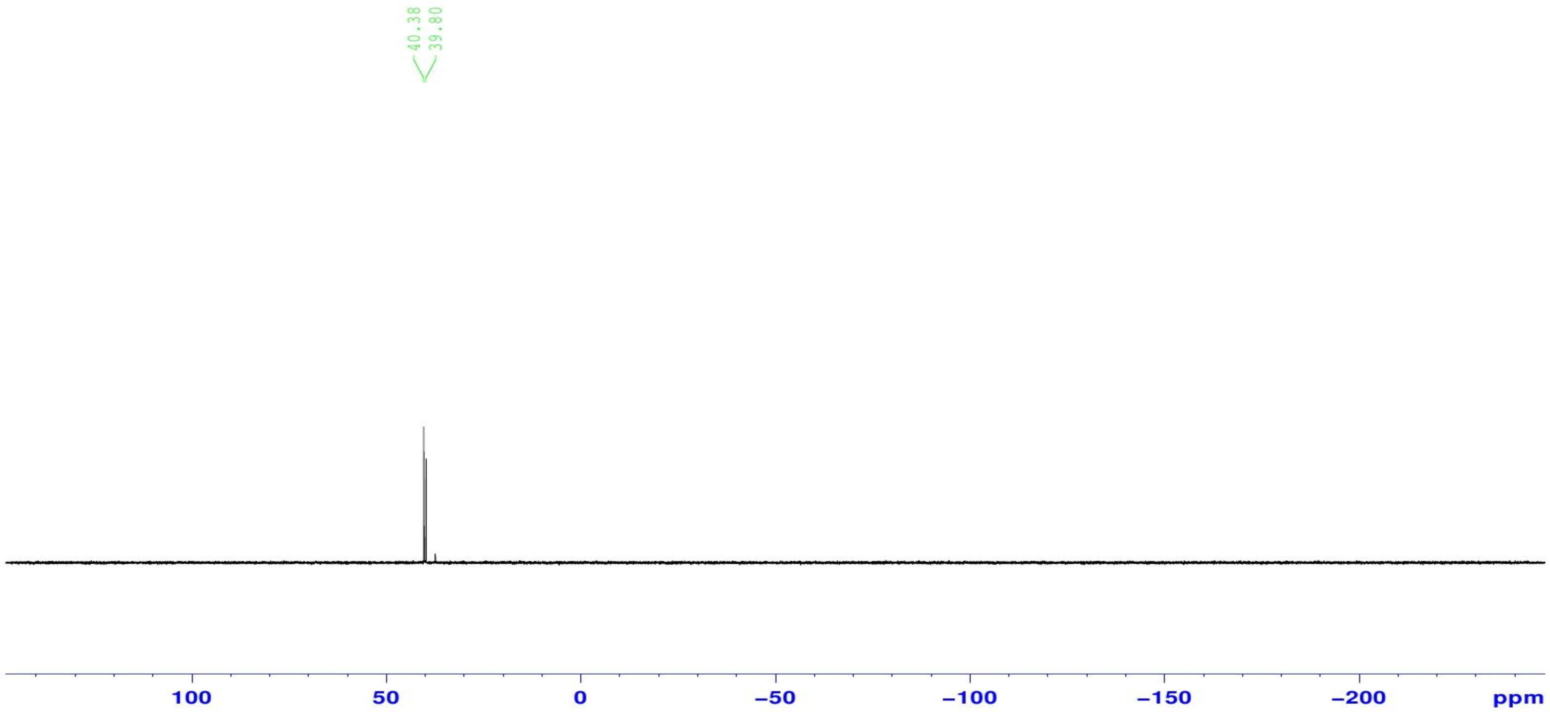


3h-P



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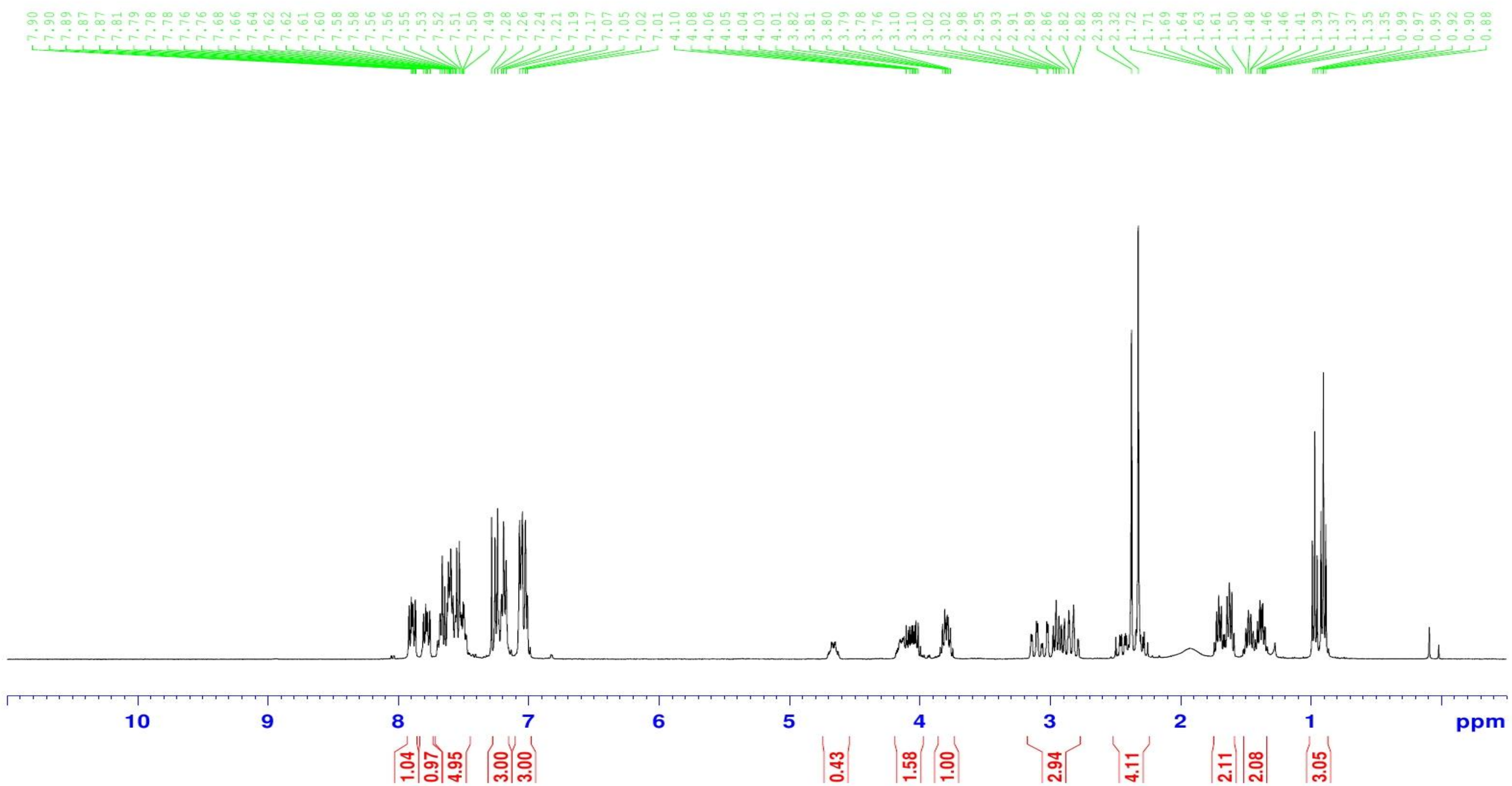
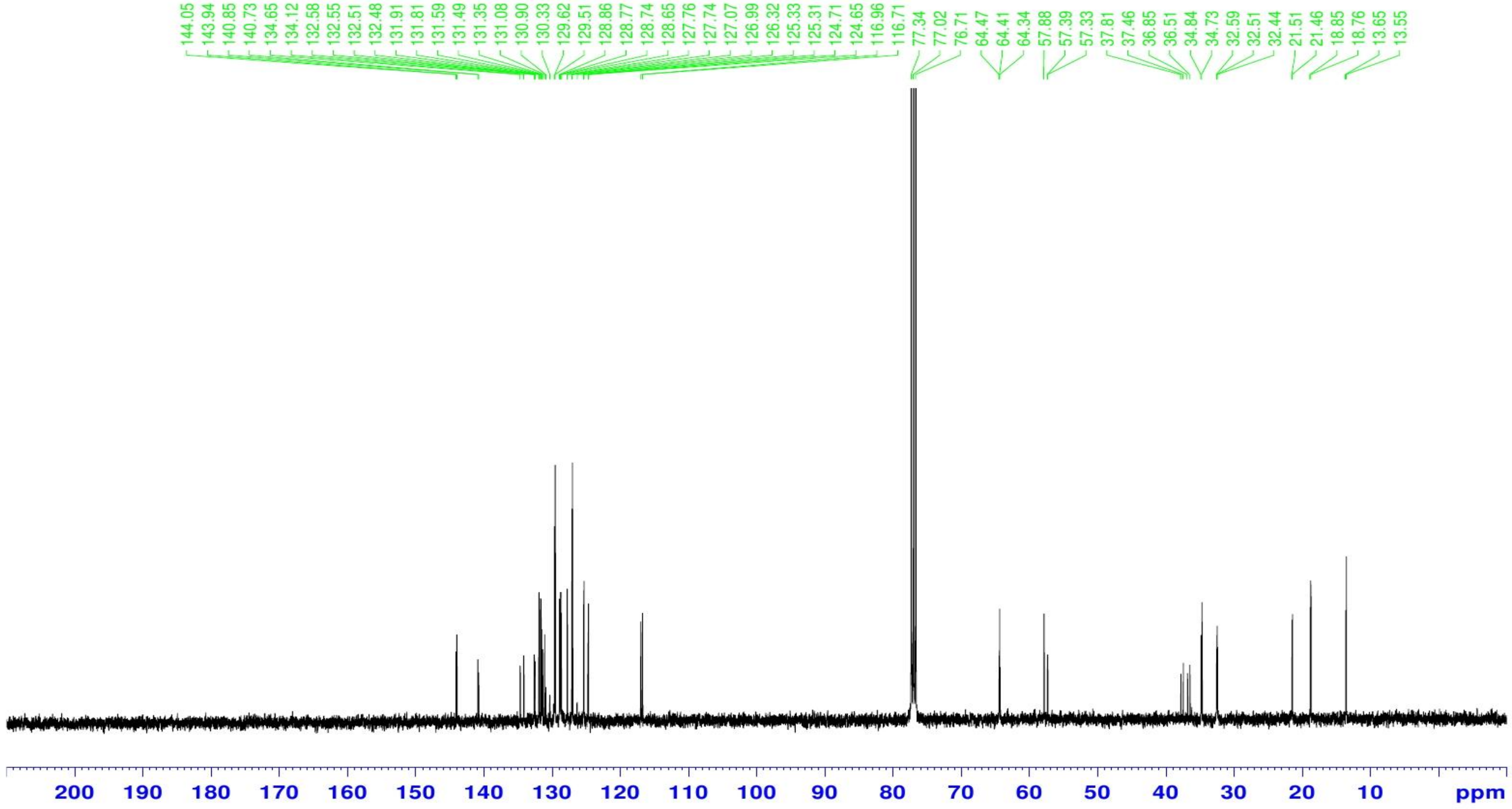


3h-C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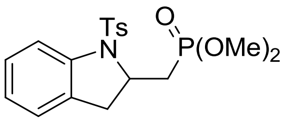
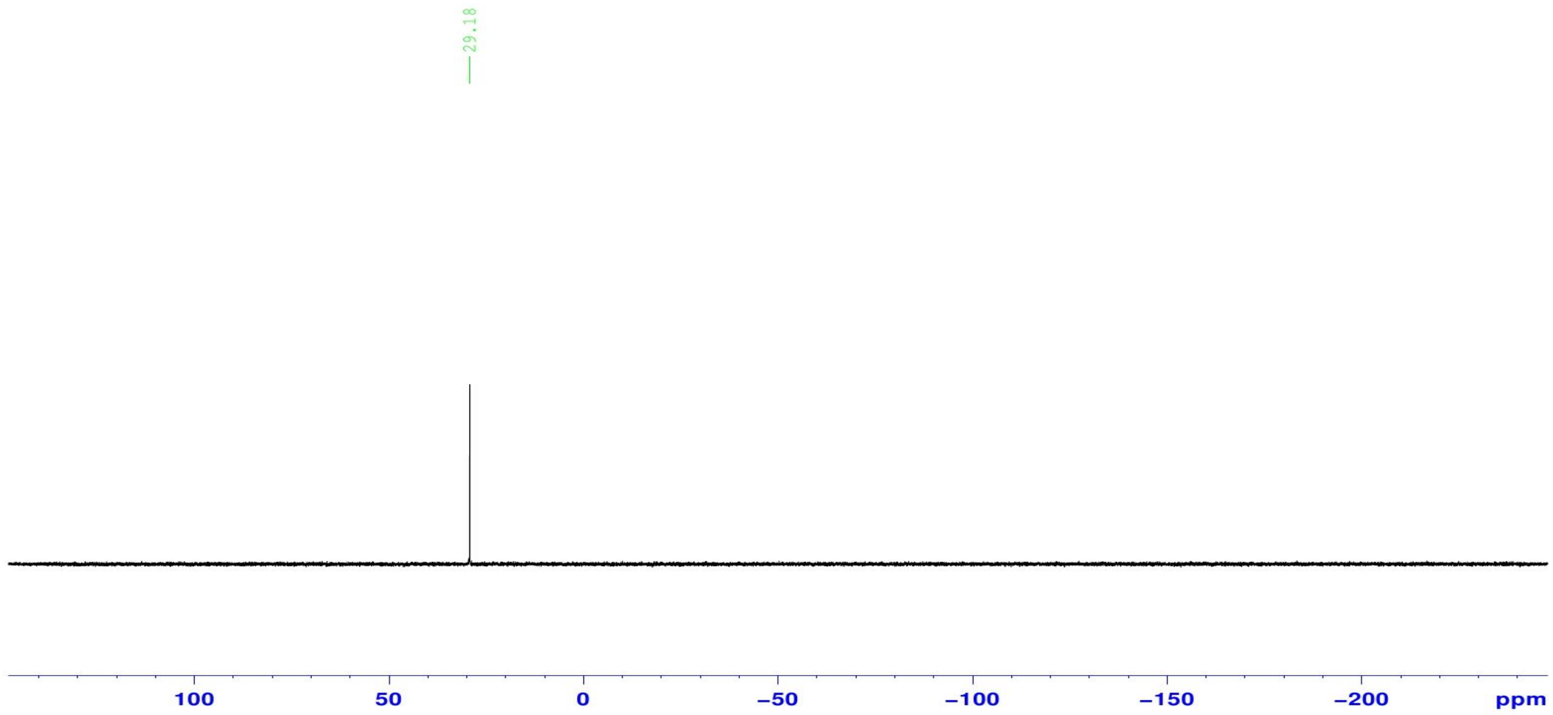
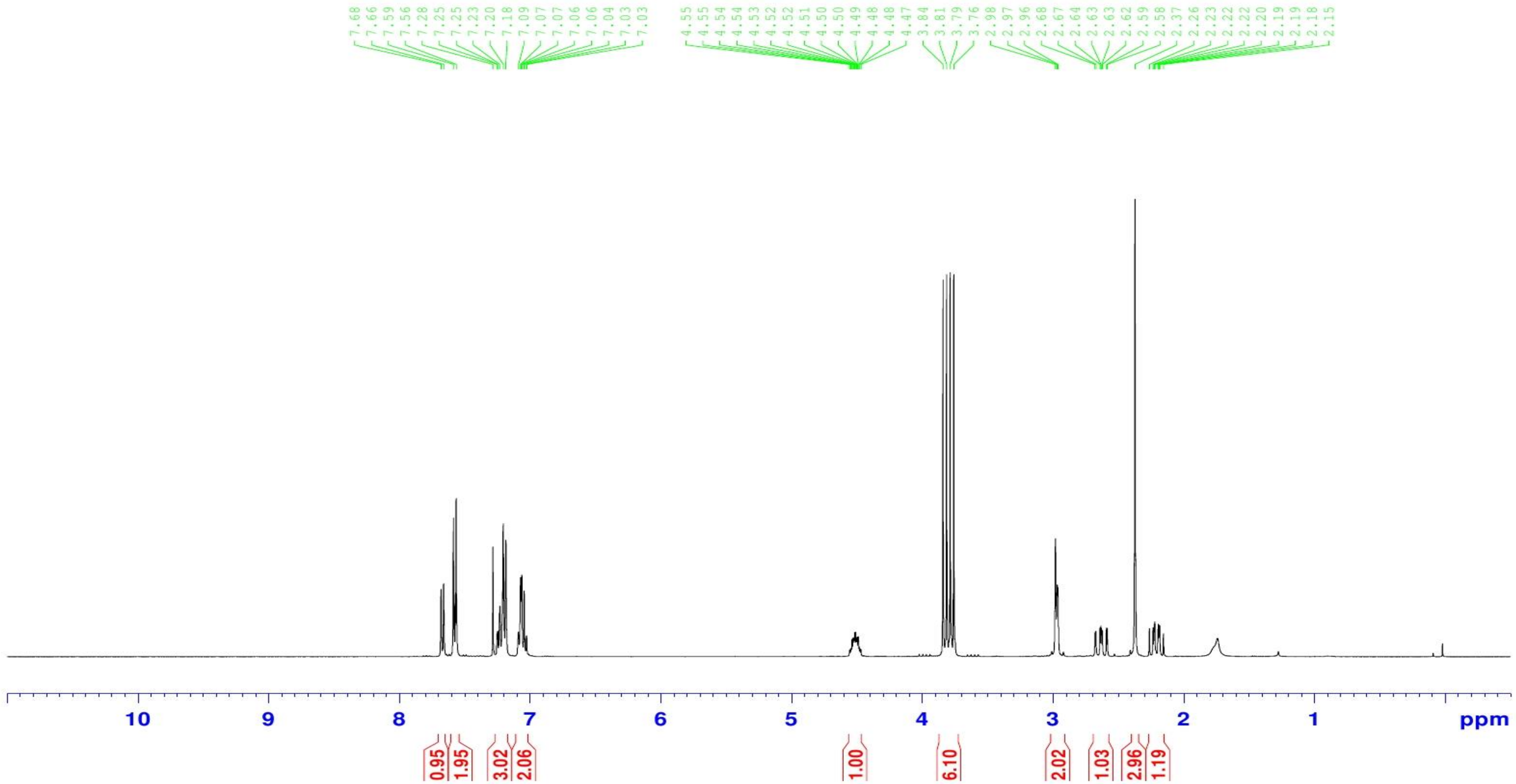


3i-P



3i-H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7.66
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7.25
7.25
7.23
7.20
7.18
7.09
7.07
7.06
7.06
7.04
7.03
7.03
4.55
4.55
4.54
4.54
4.53
4.52
4.52
4.51
4.50
4.50
4.49
4.48
4.48
4.47
3.84
3.81
3.79
3.76
2.98
2.97
2.96
2.68
2.67
2.64
2.63
2.63
2.62
2.59
2.58
2.37
2.26
2.23
2.22
2.22
2.20
2.19
2.18
2.15
10
9
8
7
6
5
4
3
2
1
ppm
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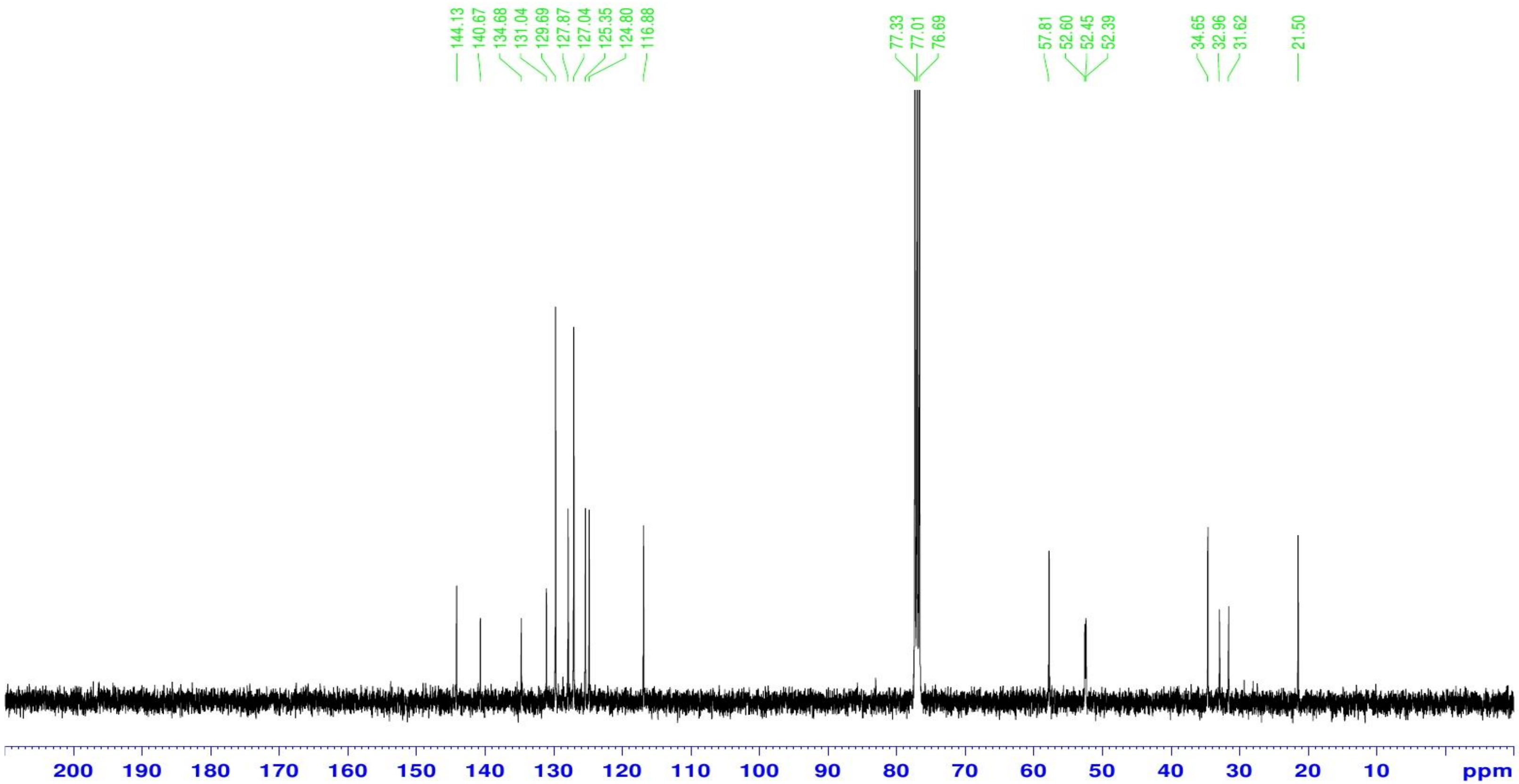
3.02
2.06
1.00
6.10
2.02
1.03
2.96
1.19

3i-C



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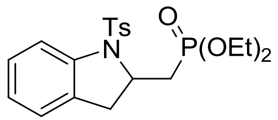
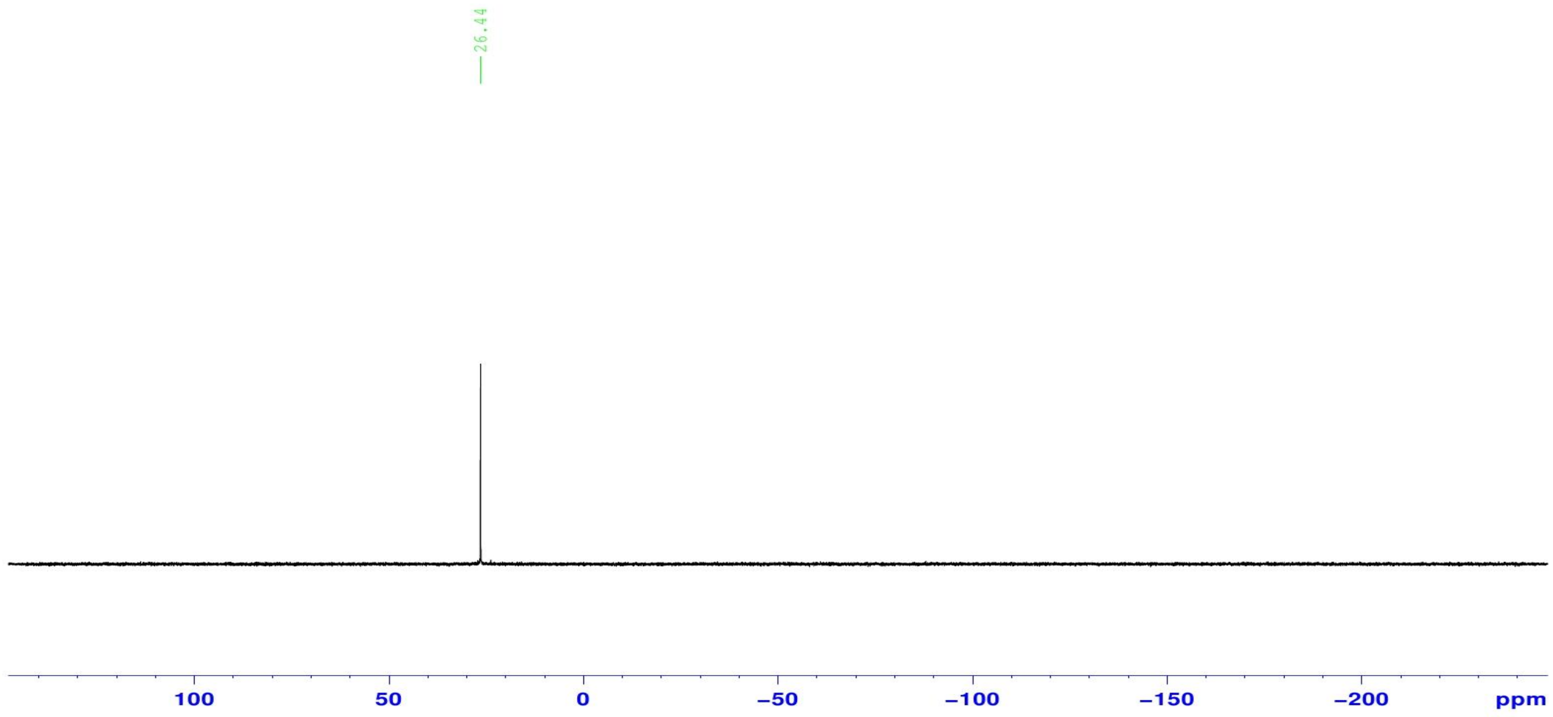
140.67
134.68
131.04
129.69
127.87
127.04
125.35
124.80
116.88
77.33
77.01
76.69
57.81
52.60
52.45
52.39
34.65
32.96
31.62
21.50
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



3j-P



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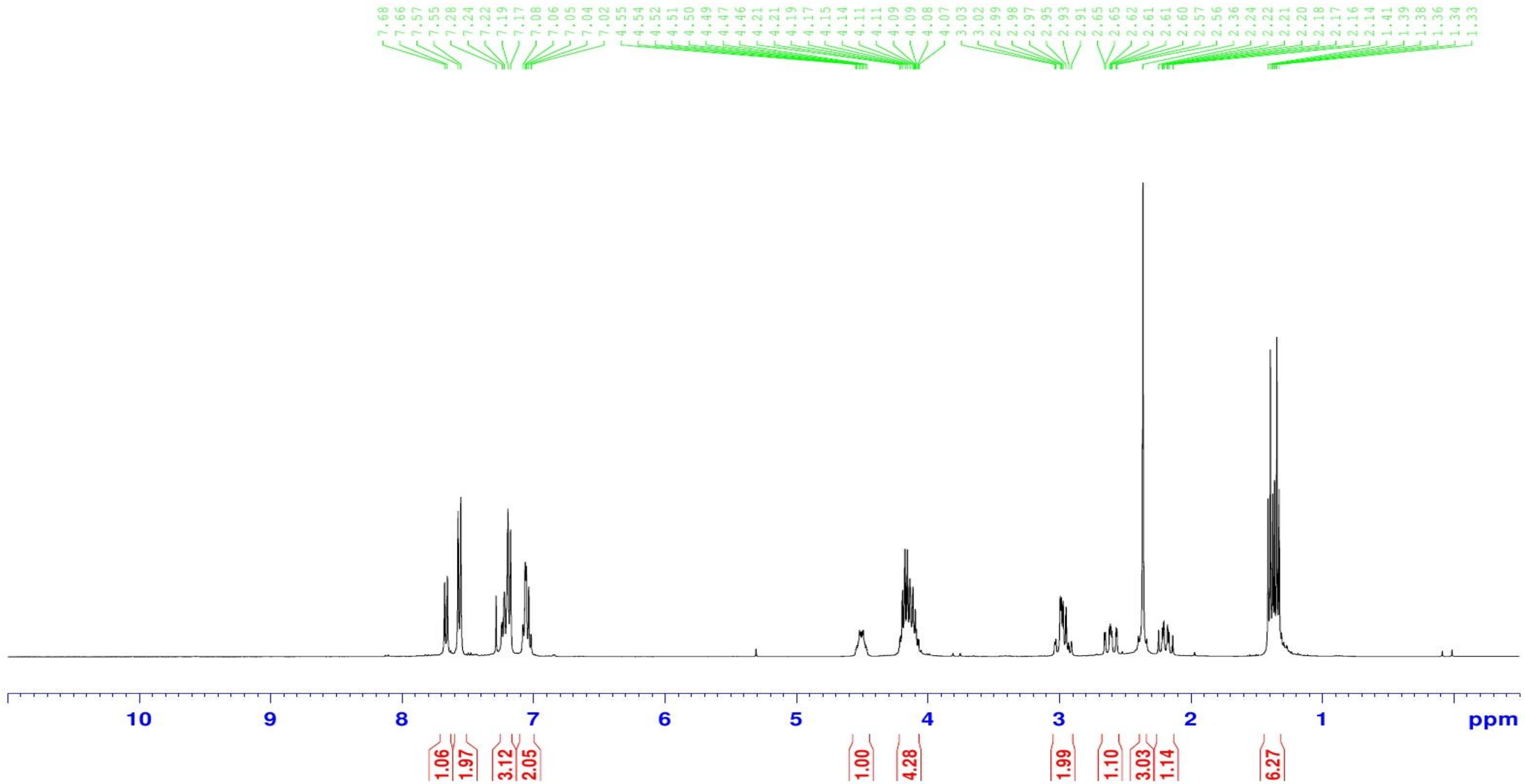
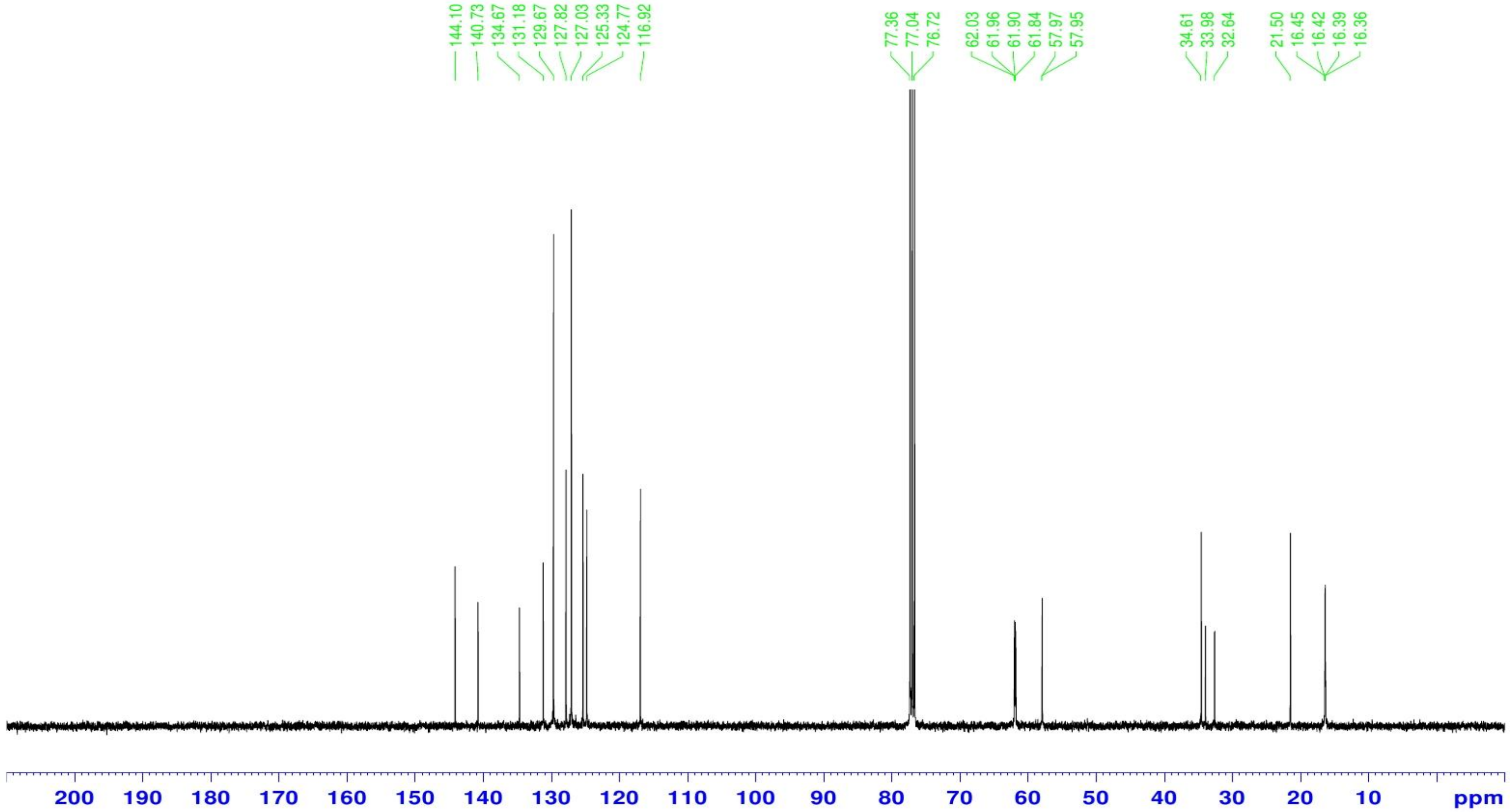


3j-C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140.73
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131.18
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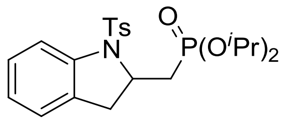
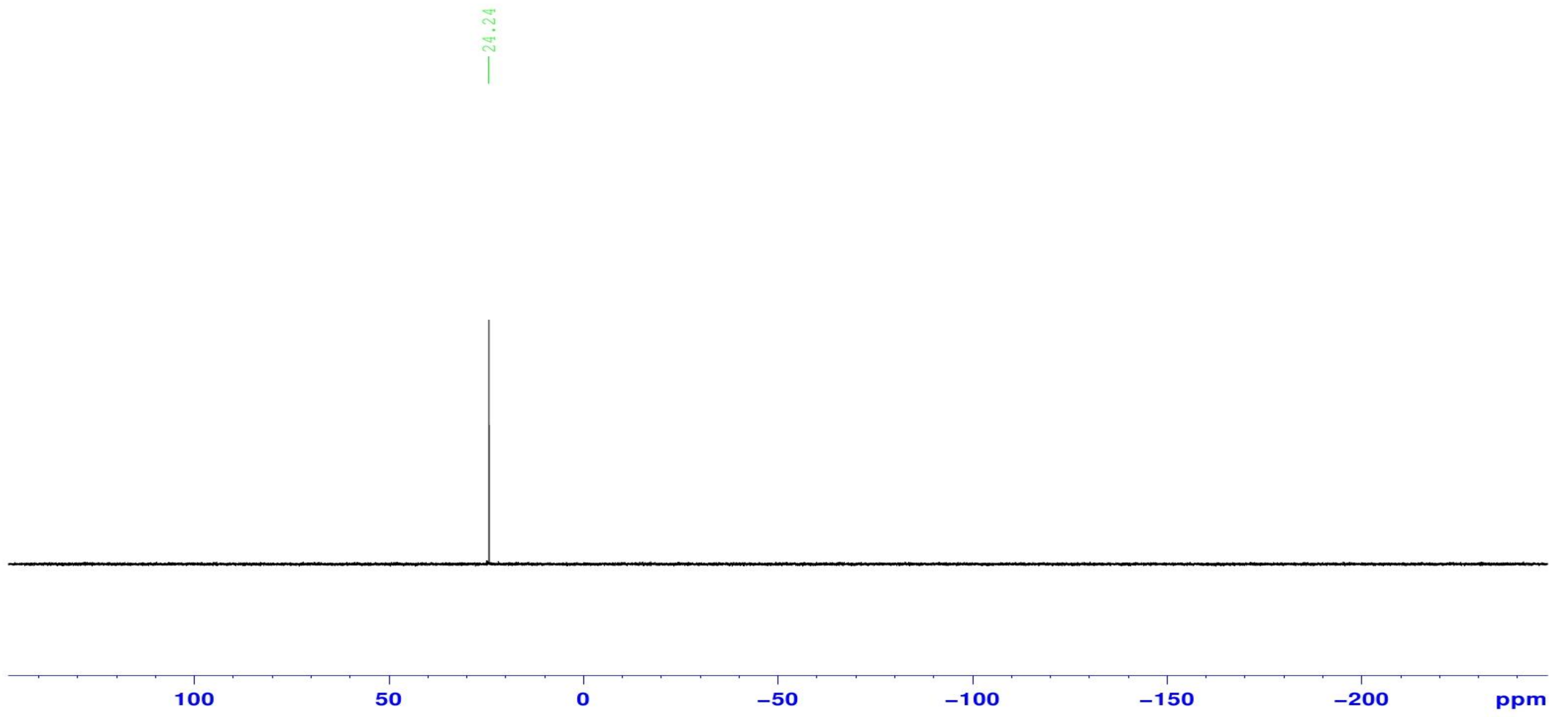
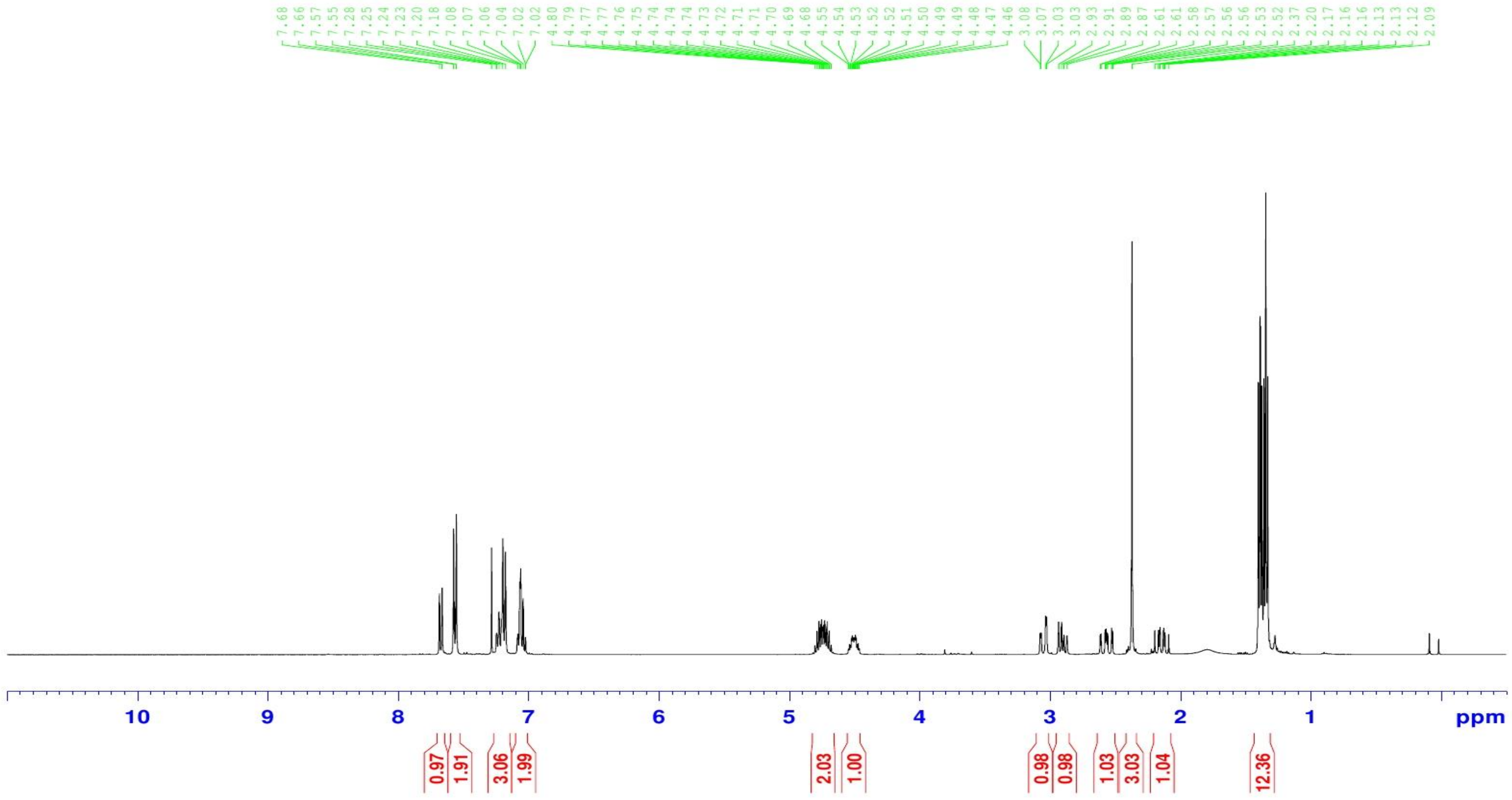
127.03
125.33
124.77
116.92
77.36
77.04
76.72
62.03
61.96
61.90
61.84
57.97
57.95
34.61
33.98
32.64
21.50
16.45
16.42
16.39
16.36
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



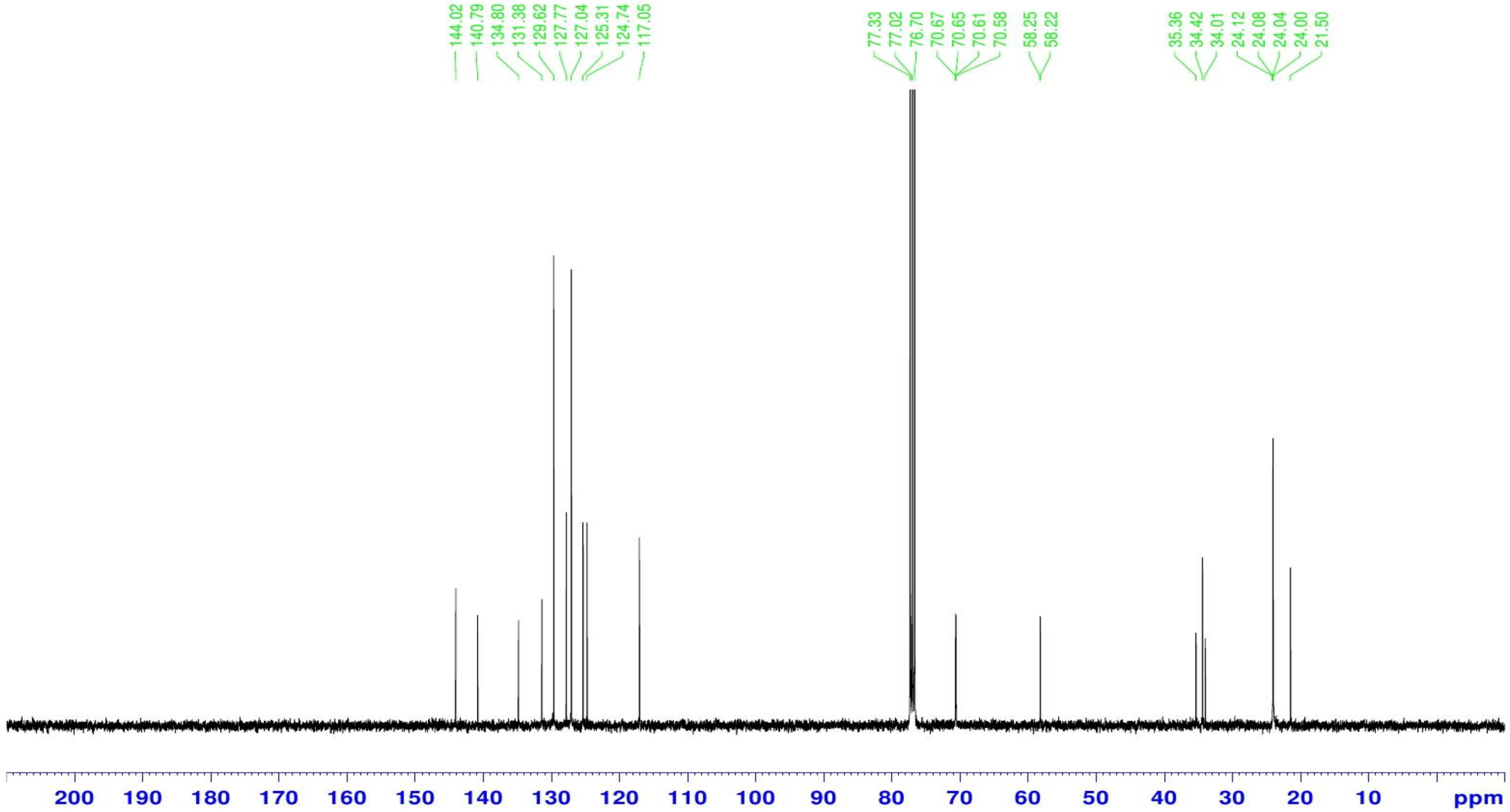
3k-P



3k-H



3k-C



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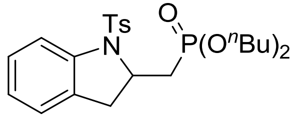
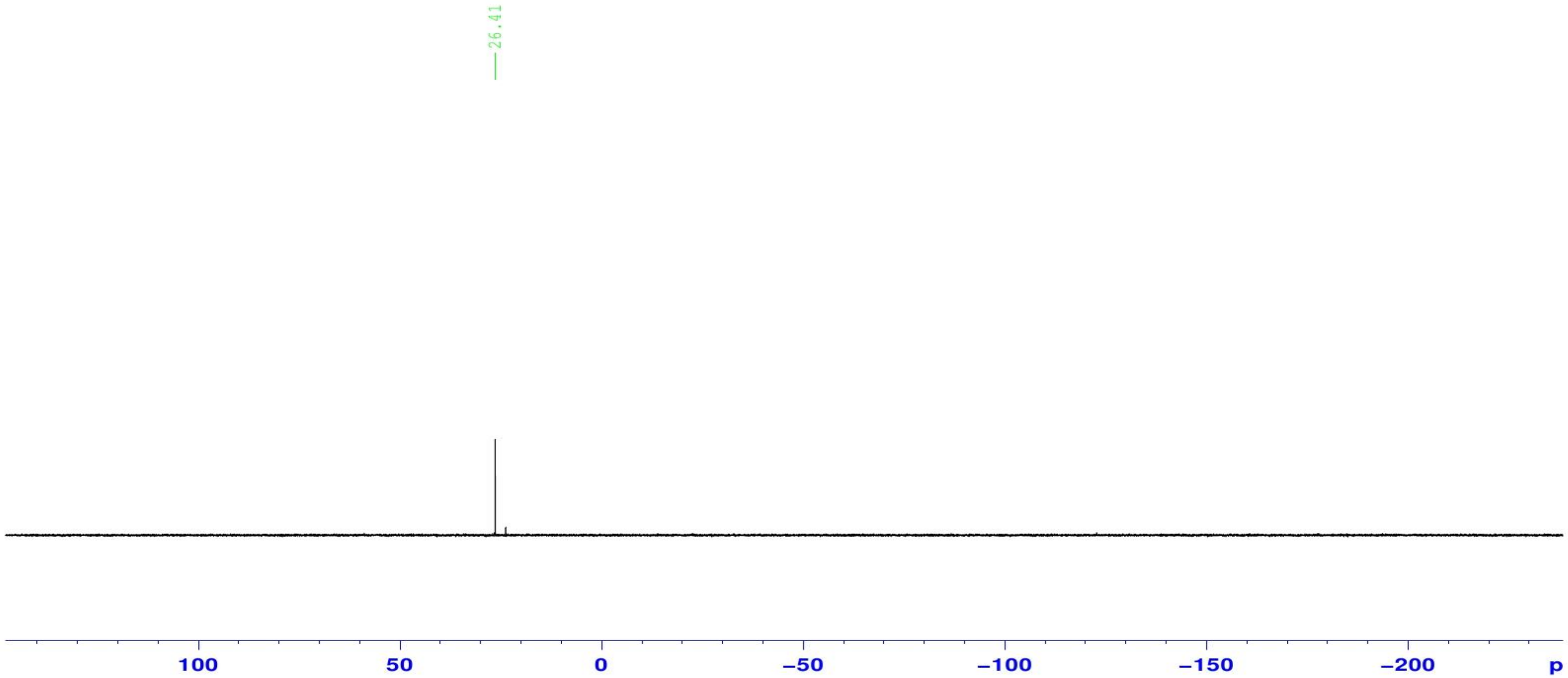
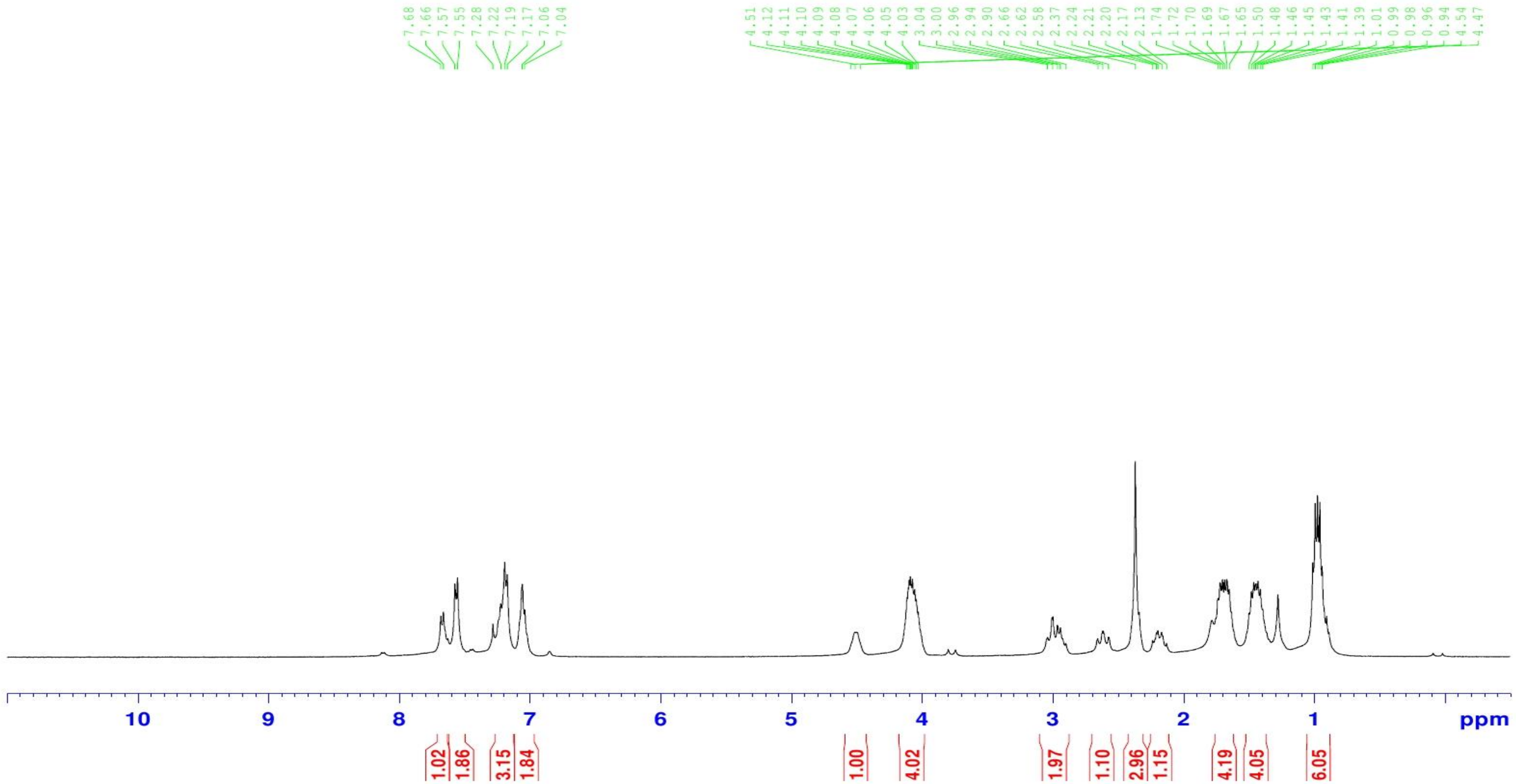
140.79
134.80
131.38
129.62
127.77
127.04
125.31
124.74
117.05
77.33
77.02
76.70
70.67
70.65
70.61
70.58
58.25
58.22
35.36
34.42
34.01
24.12
24.08
24.04
24.00
21.50
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



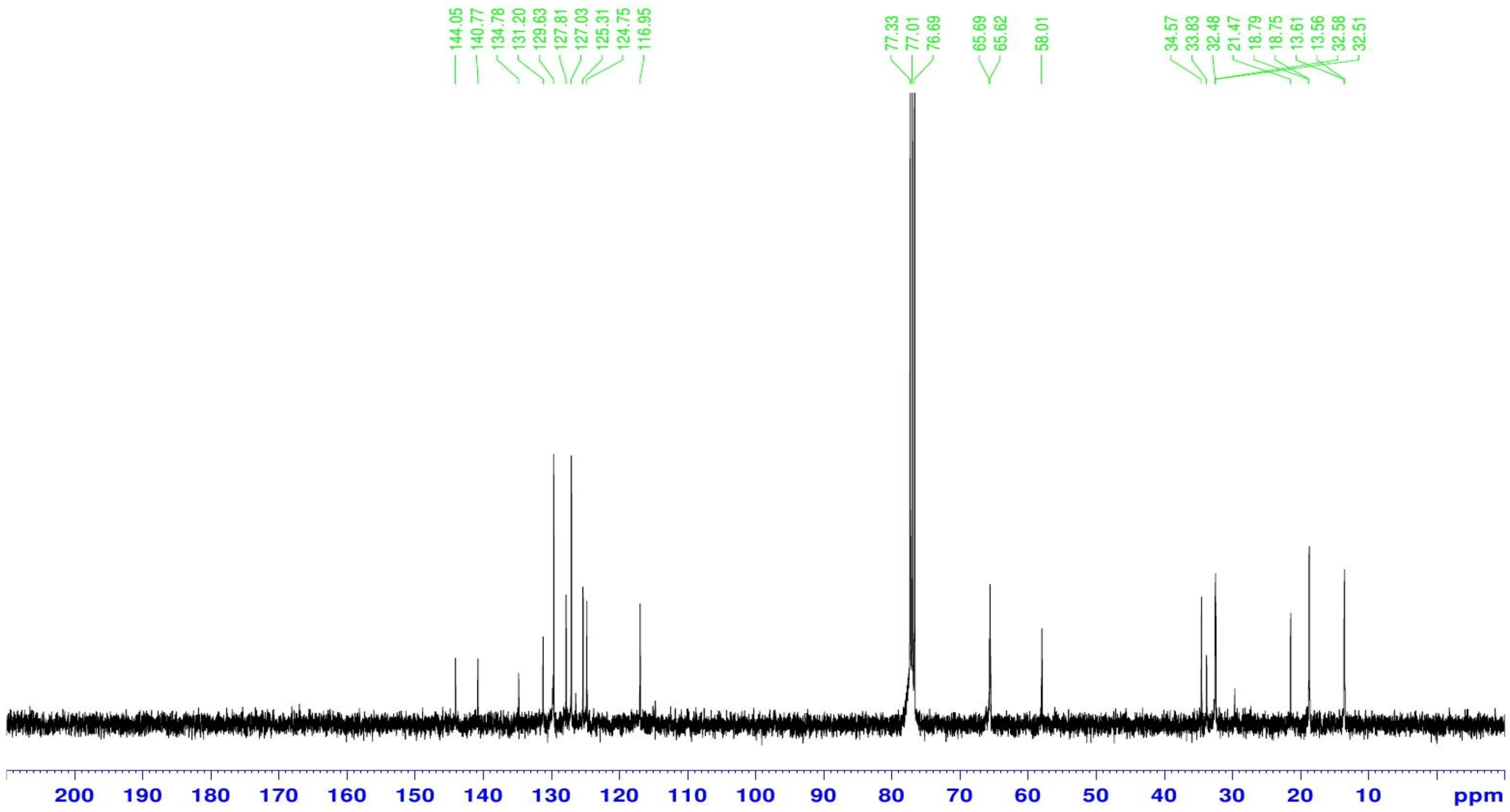
3l-P



3l-H



3l-C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127.81
127.03
125.31
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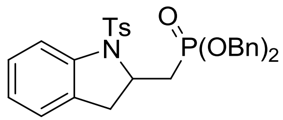
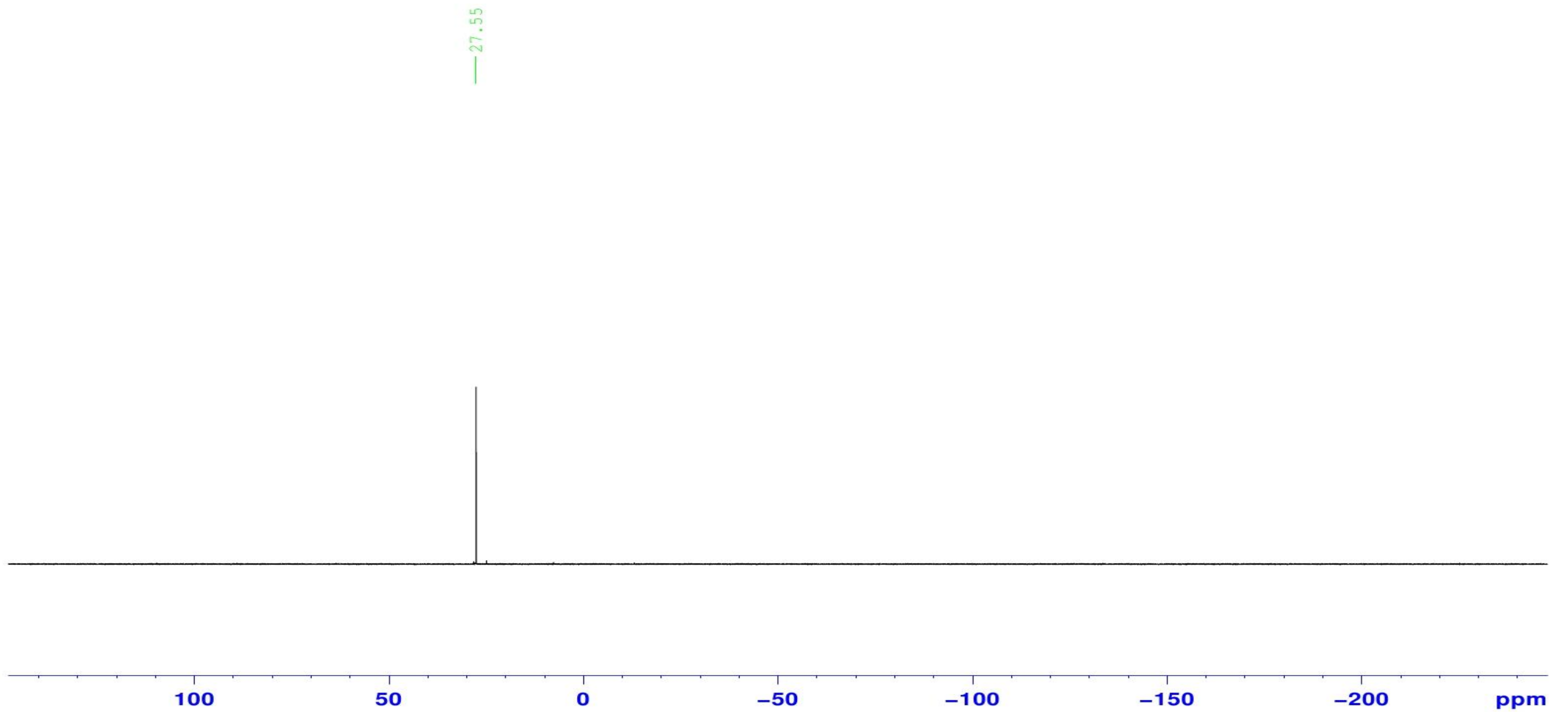
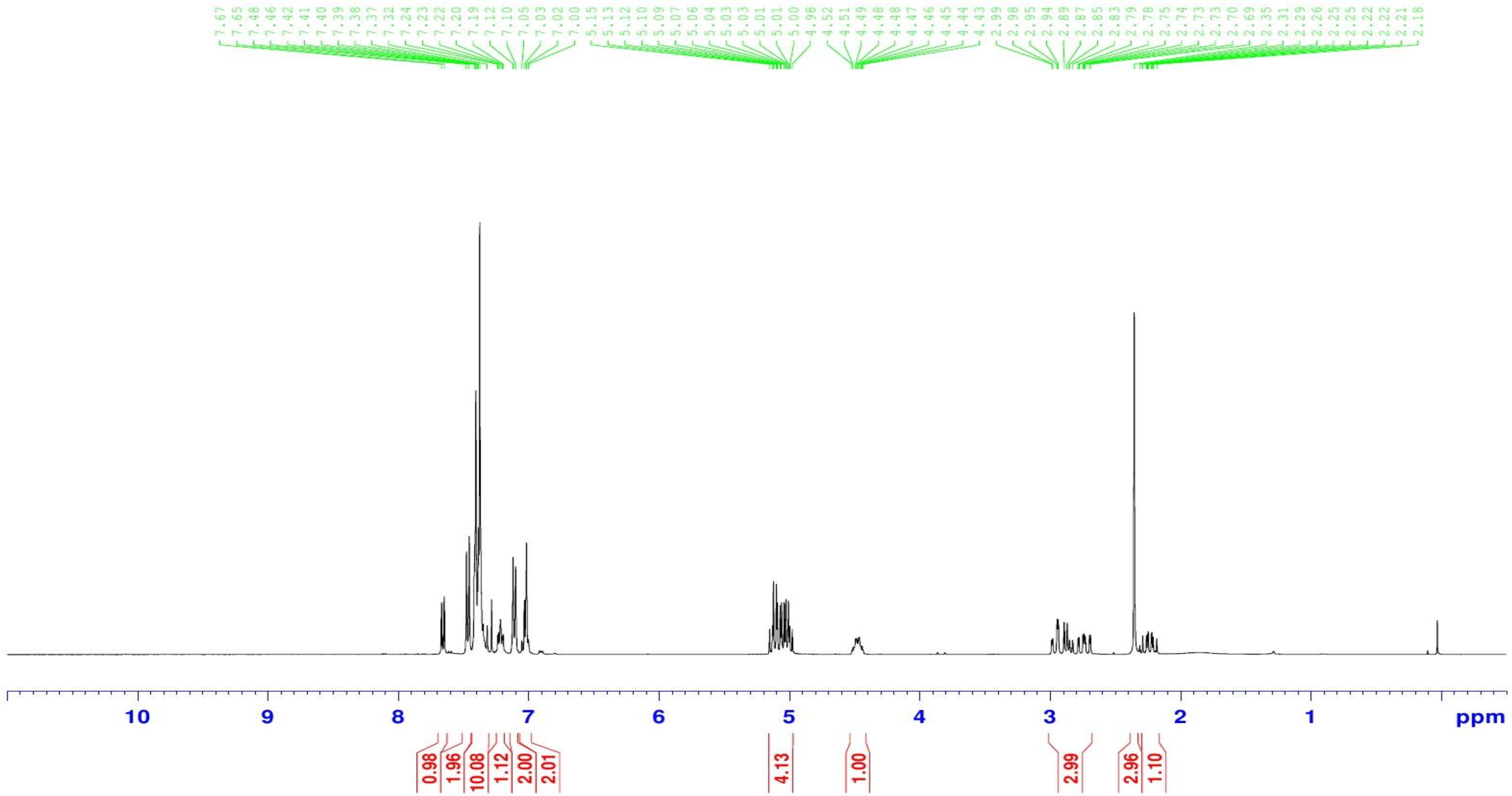
116.95
77.33
77.01
76.69
65.69
65.62
58.01
34.57
33.83
32.48
21.47
18.79
18.75
13.61
13.56
32.58
32.51
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



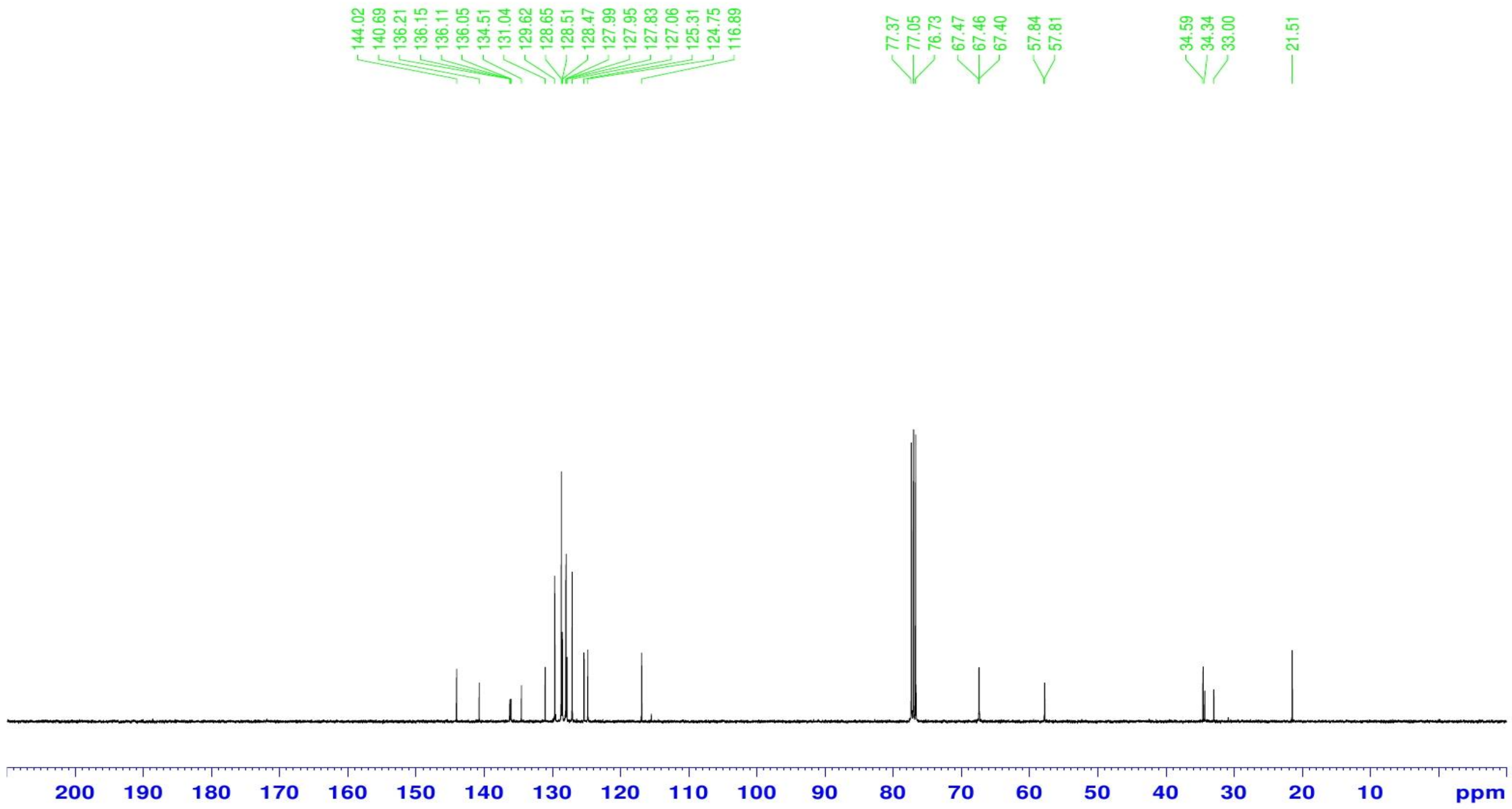
3m-P



3m-H



3m-C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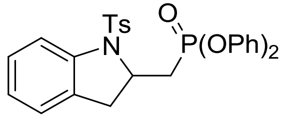
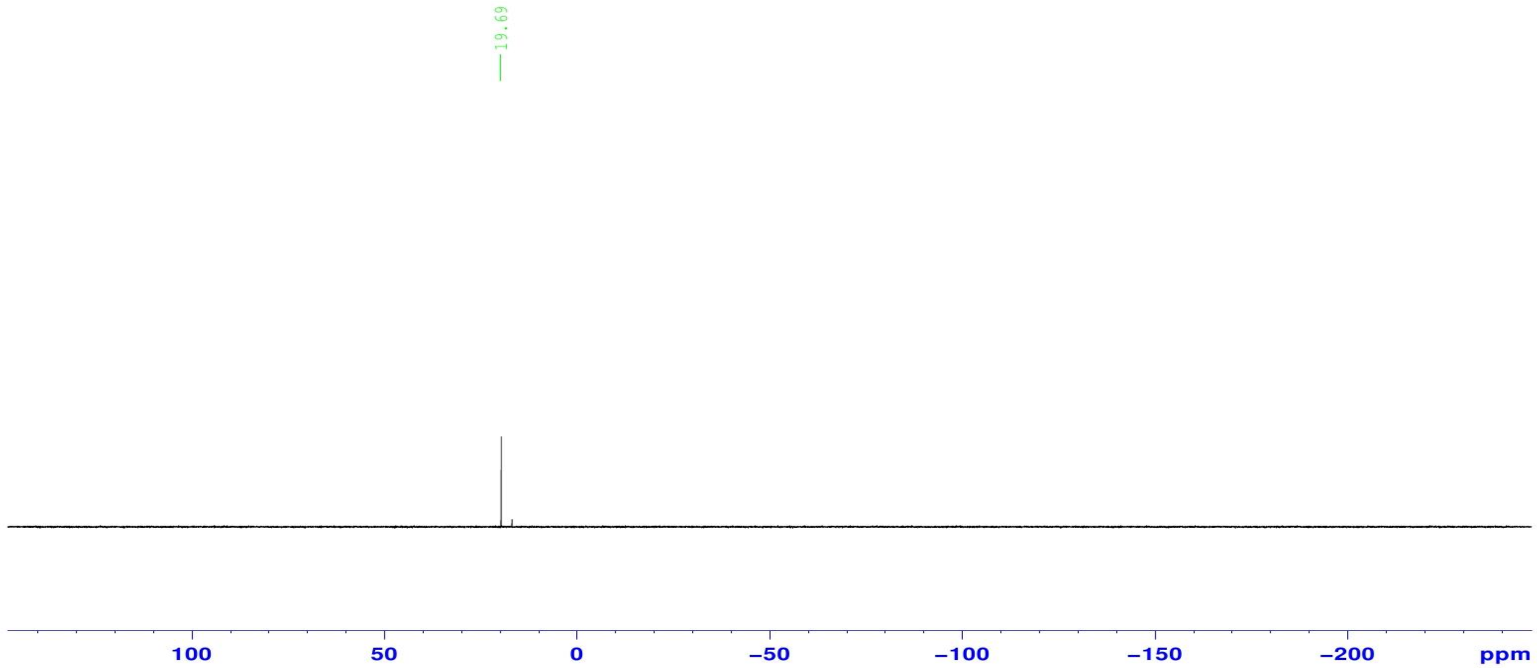
136.15
136.11
136.05
134.51
131.04
129.62
128.65
128.51
128.47
127.99
127.95
127.83
127.06
125.31
124.75
116.89
77.37
77.05
76.73
67.47
67.46
67.40
57.84
57.81
34.59
34.34
33.00
21.51
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



3n-P



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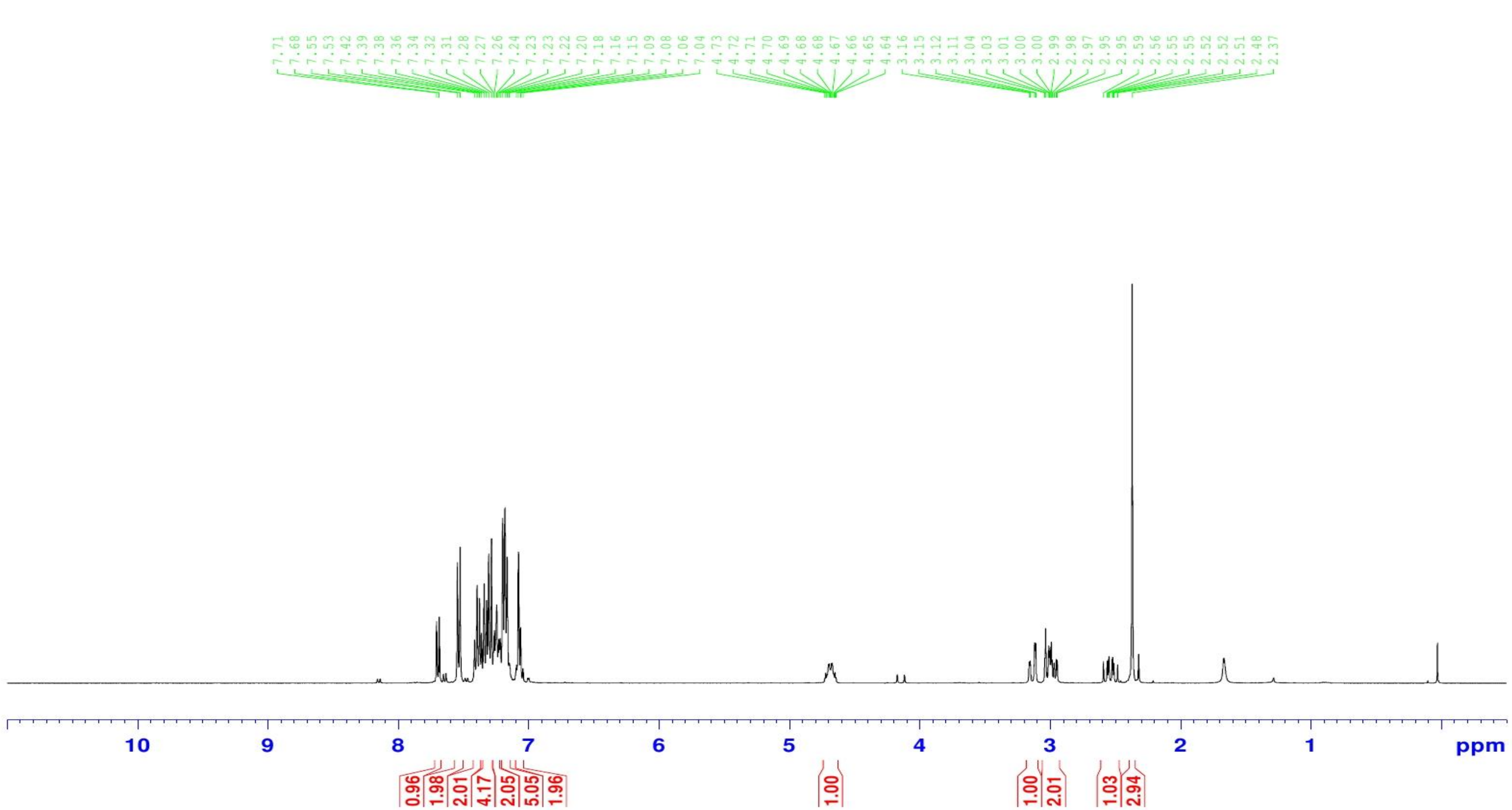
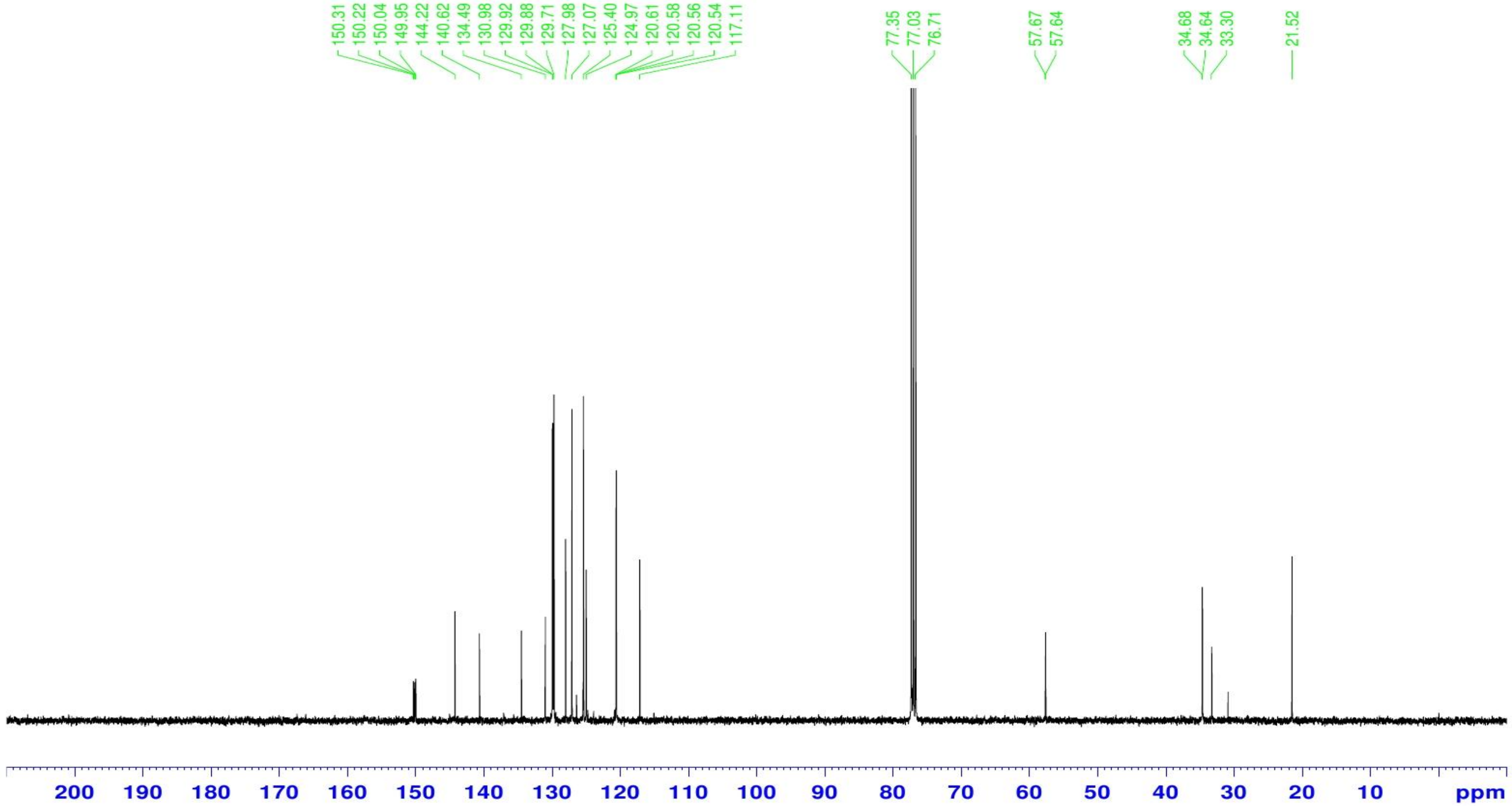


3n-C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150.04
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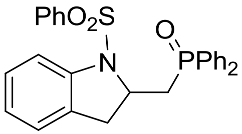
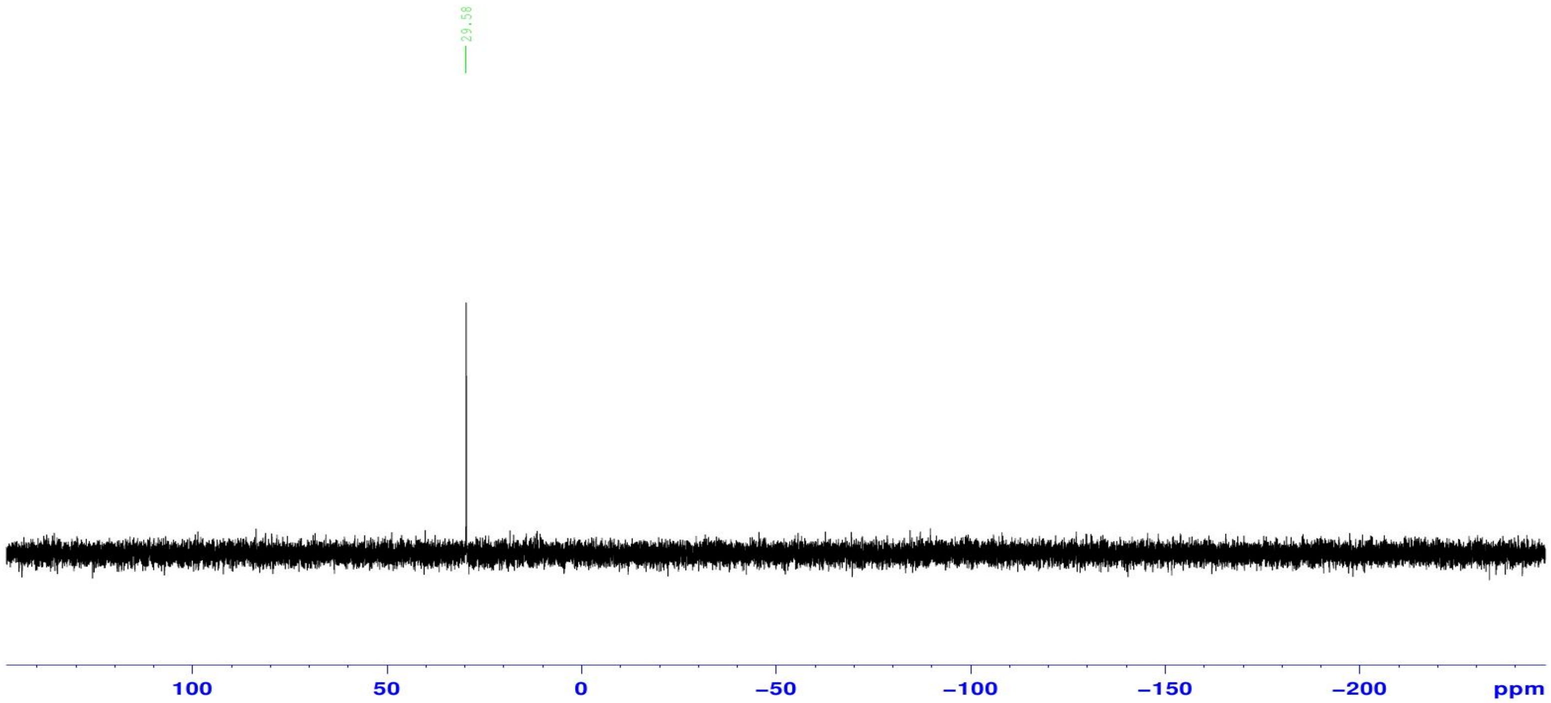
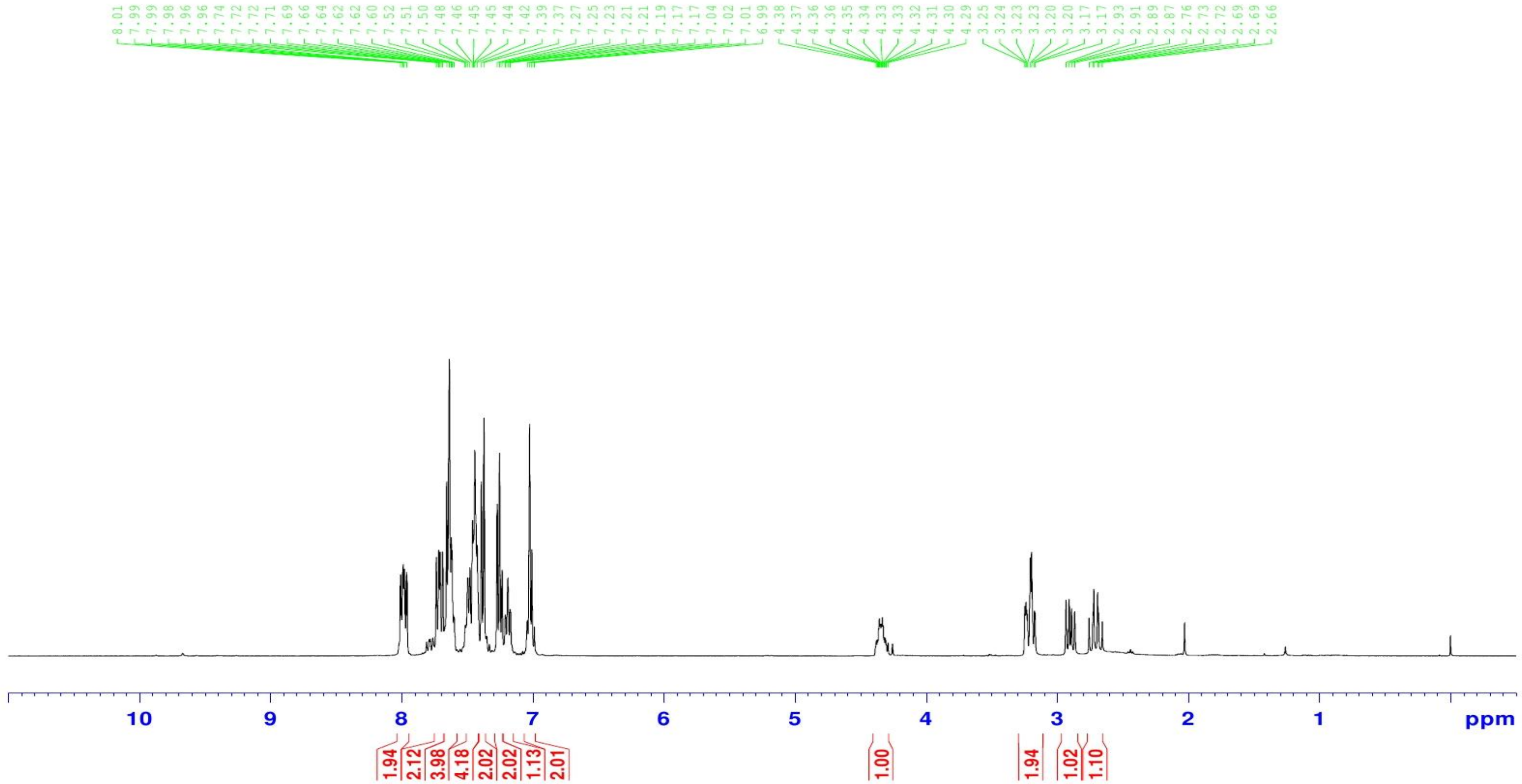
144.22
140.62
134.49
130.98
129.92
129.88
129.71
127.98
127.07
125.40
124.97
120.61
120.58
120.56
120.54
117.11
77.35
77.03
76.71
57.67
57.64
34.68
34.64
33.30
21.52
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



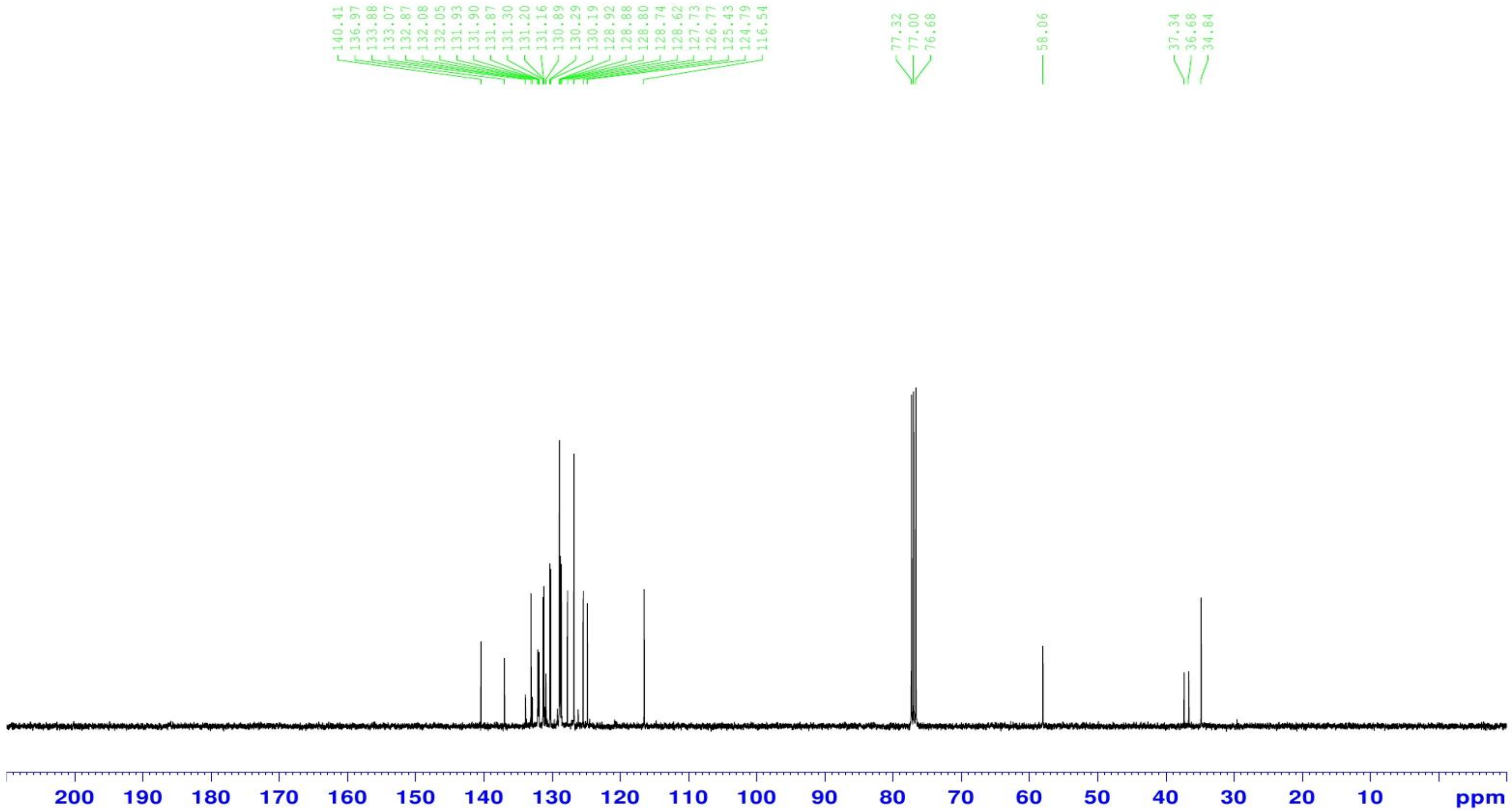
3p-P



3p-H



3p-C


140.41
136.97
133.88
133.07
132.87
132.08
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131.93
131.90
131.87
131.30
131.20
131.16
130.89
130.29
130.19
128.92
128.88
128.80
128.74
128.62
127.73
126.77
125.43
124.79
116.54
77.32
77.00
76.68
58.06
37.34
36.68
34.84
200
190
180
170
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150
140
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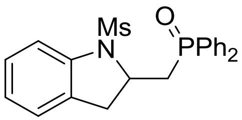
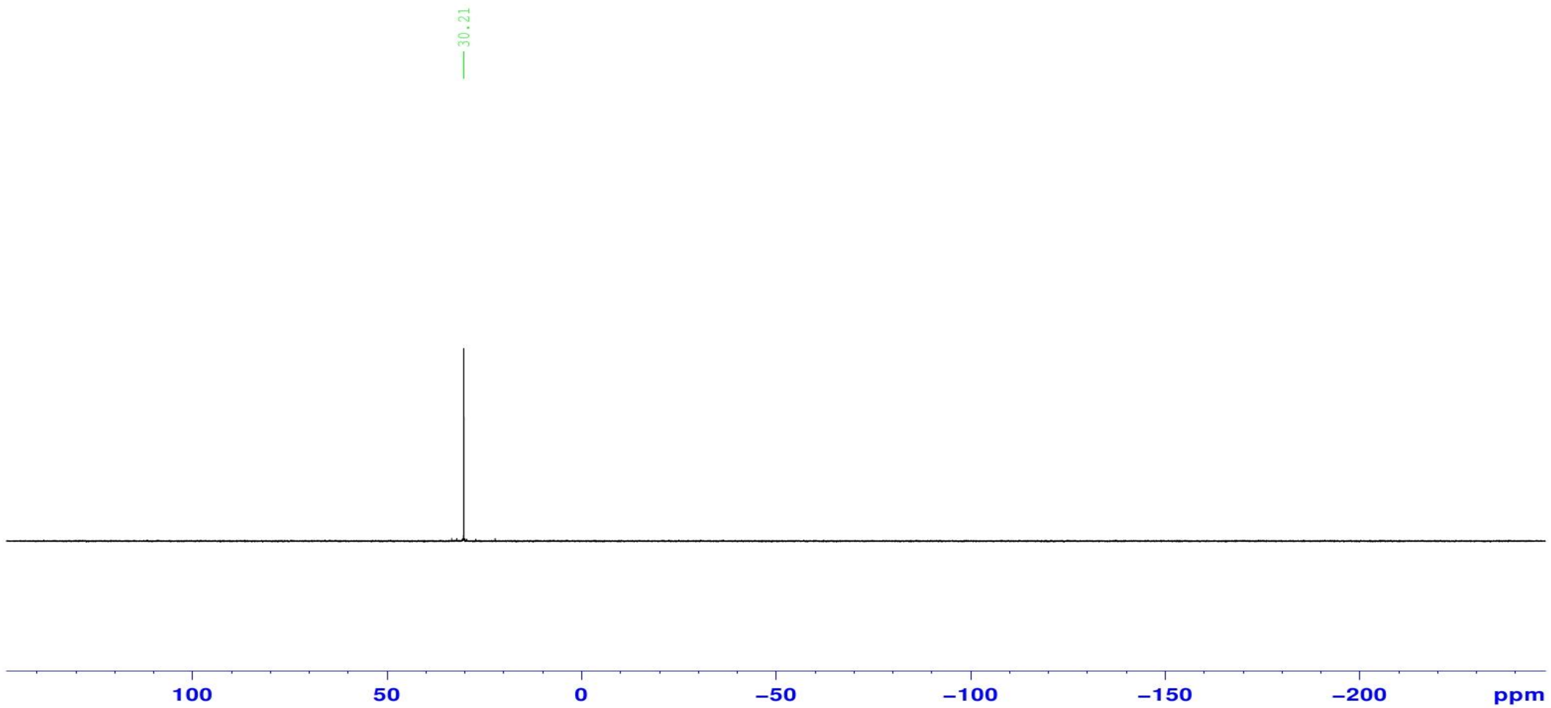
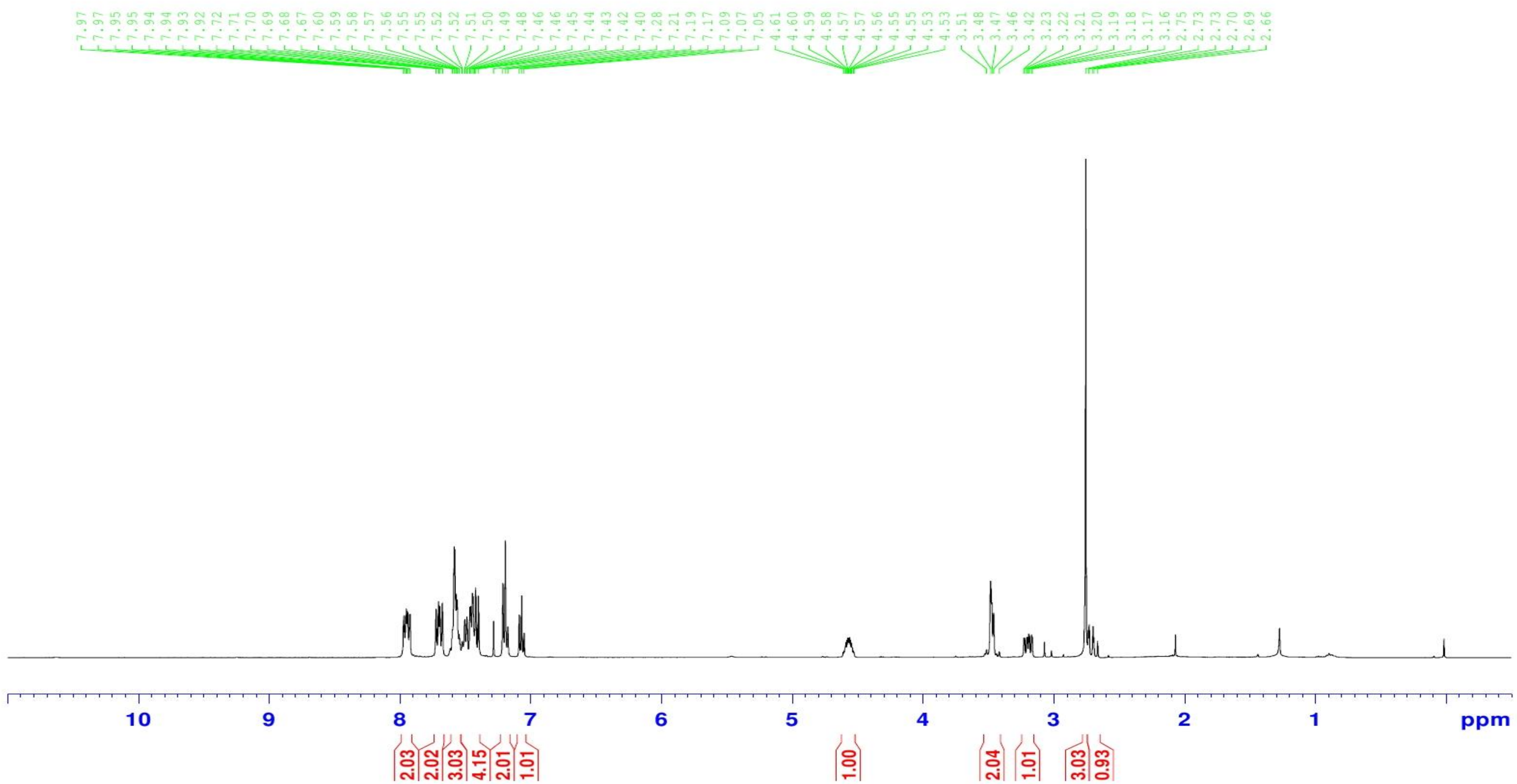
40
30
20
10
ppm



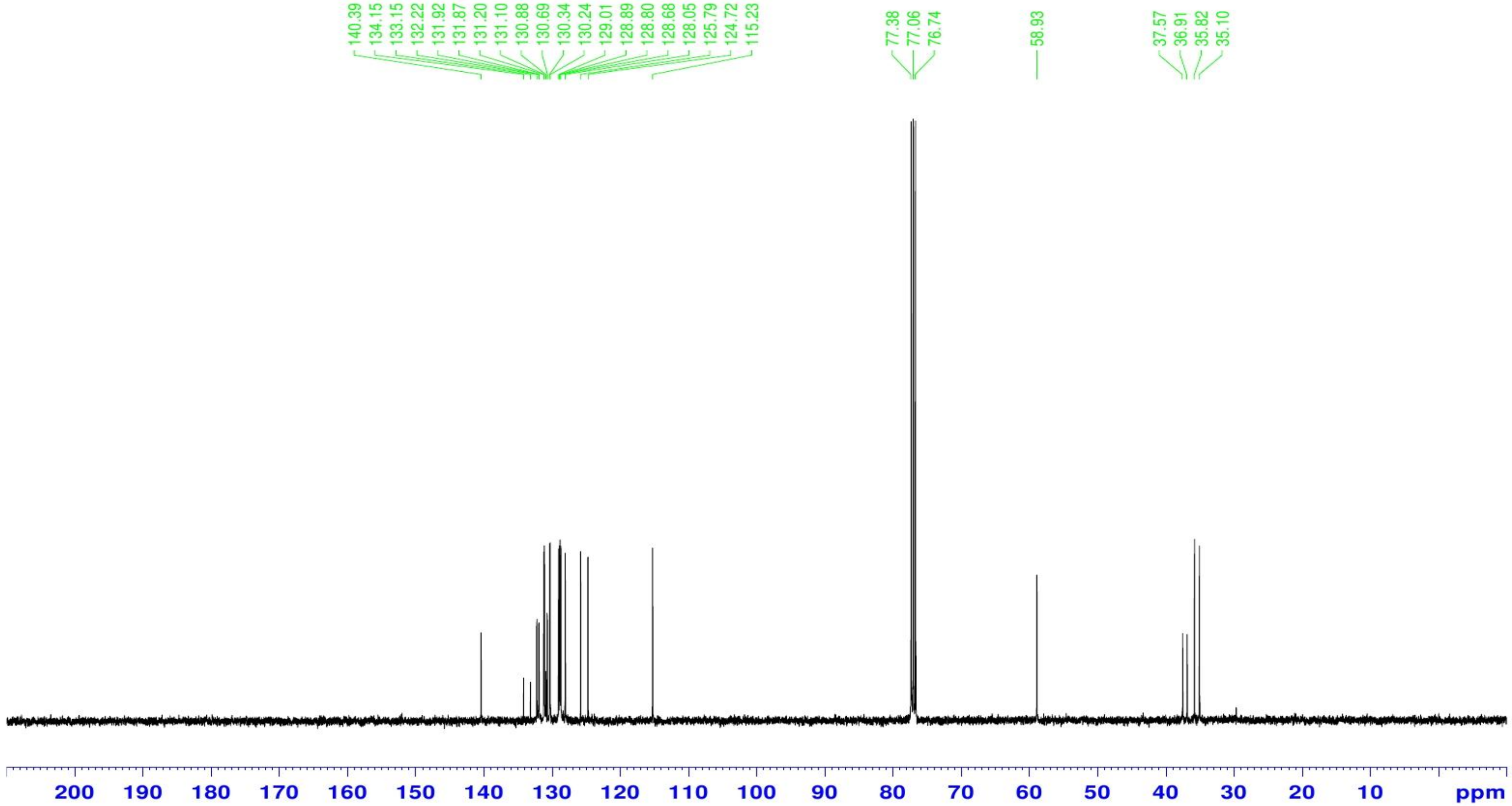
3q-P



3q-H



3q-C


140.39
134.15
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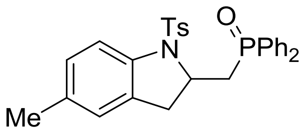
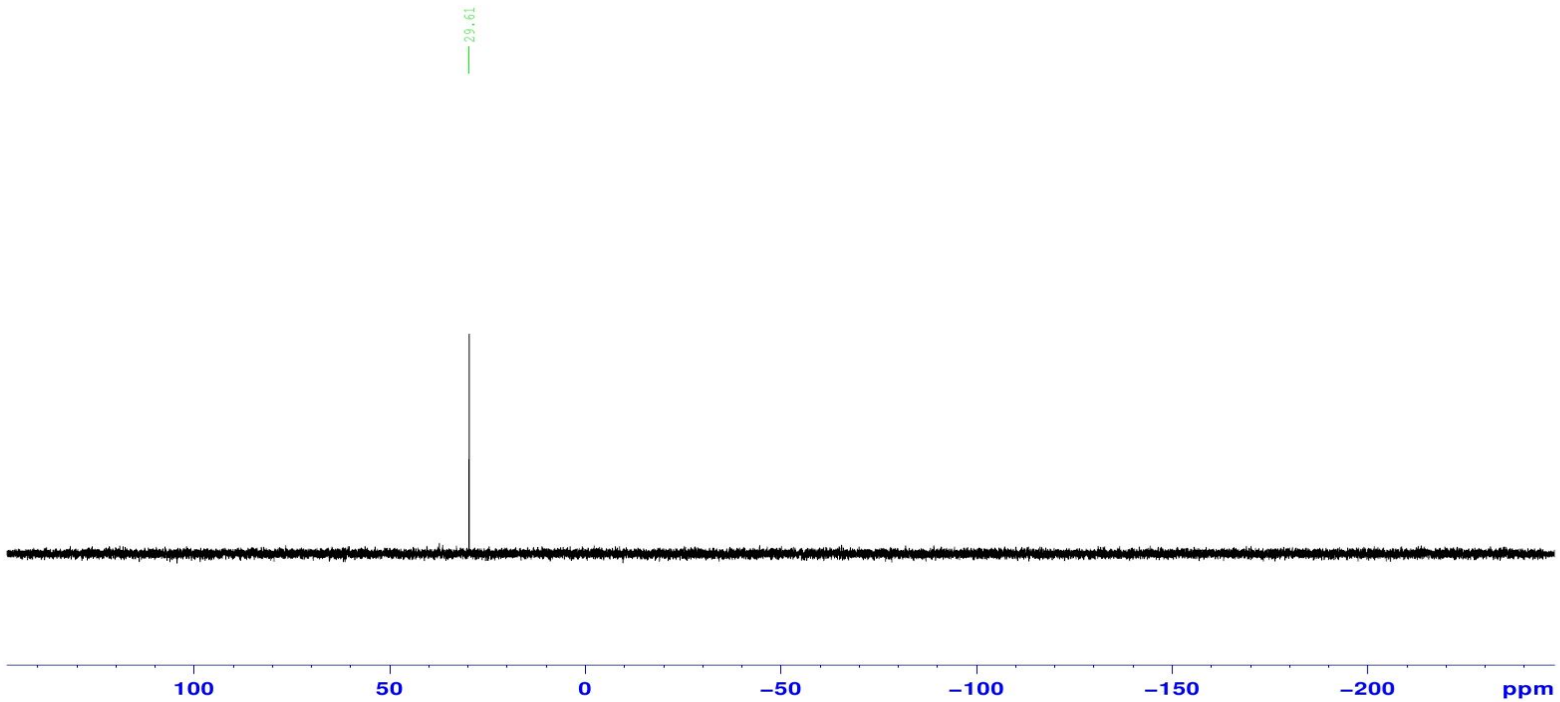
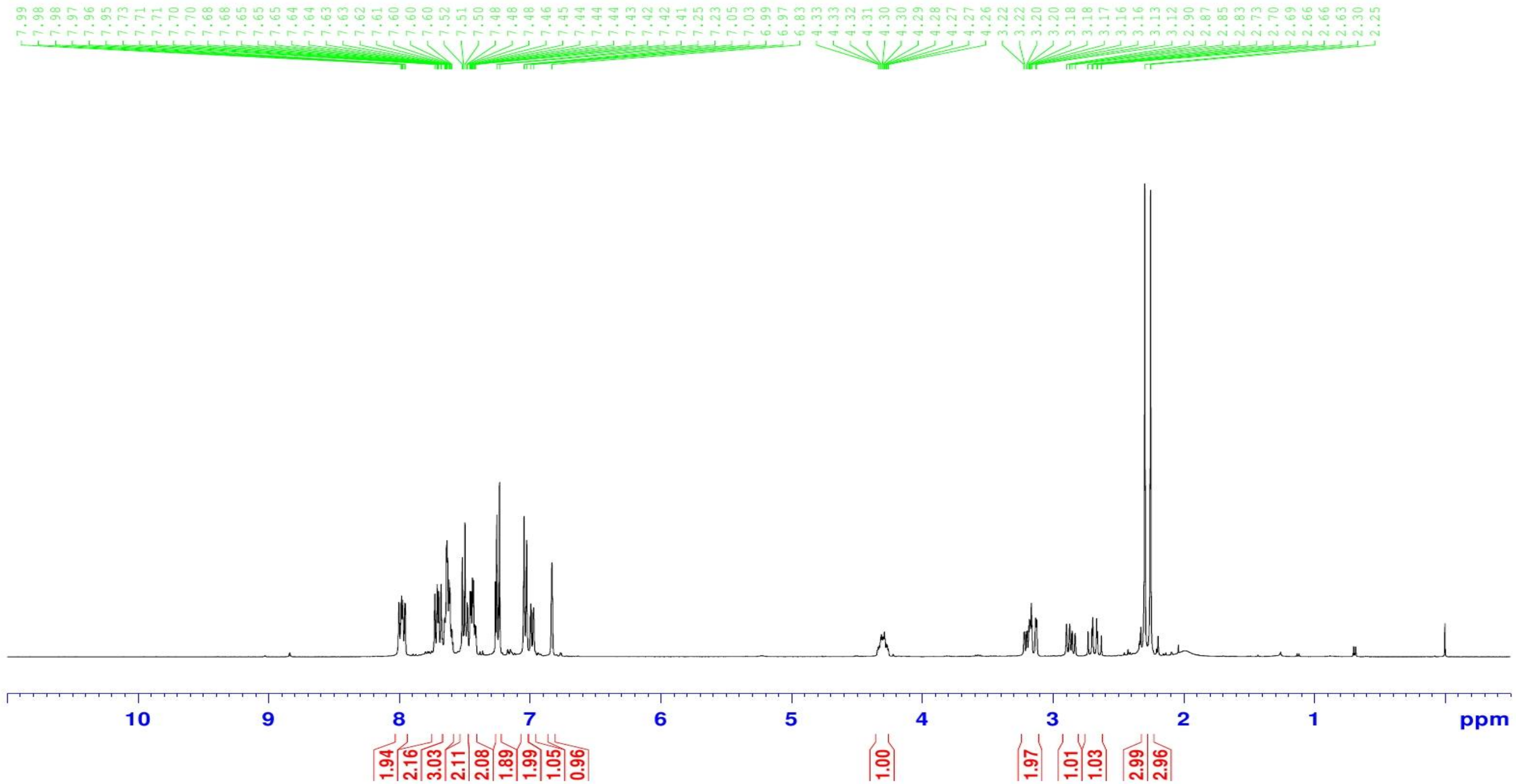
132.22
131.92
131.87
131.20
131.10
130.88
130.69
130.34
130.24
129.01
128.89
128.80
128.68
128.05
125.79
124.72
115.23
77.38
77.06
76.74
58.93
37.57
36.91
35.82
35.10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



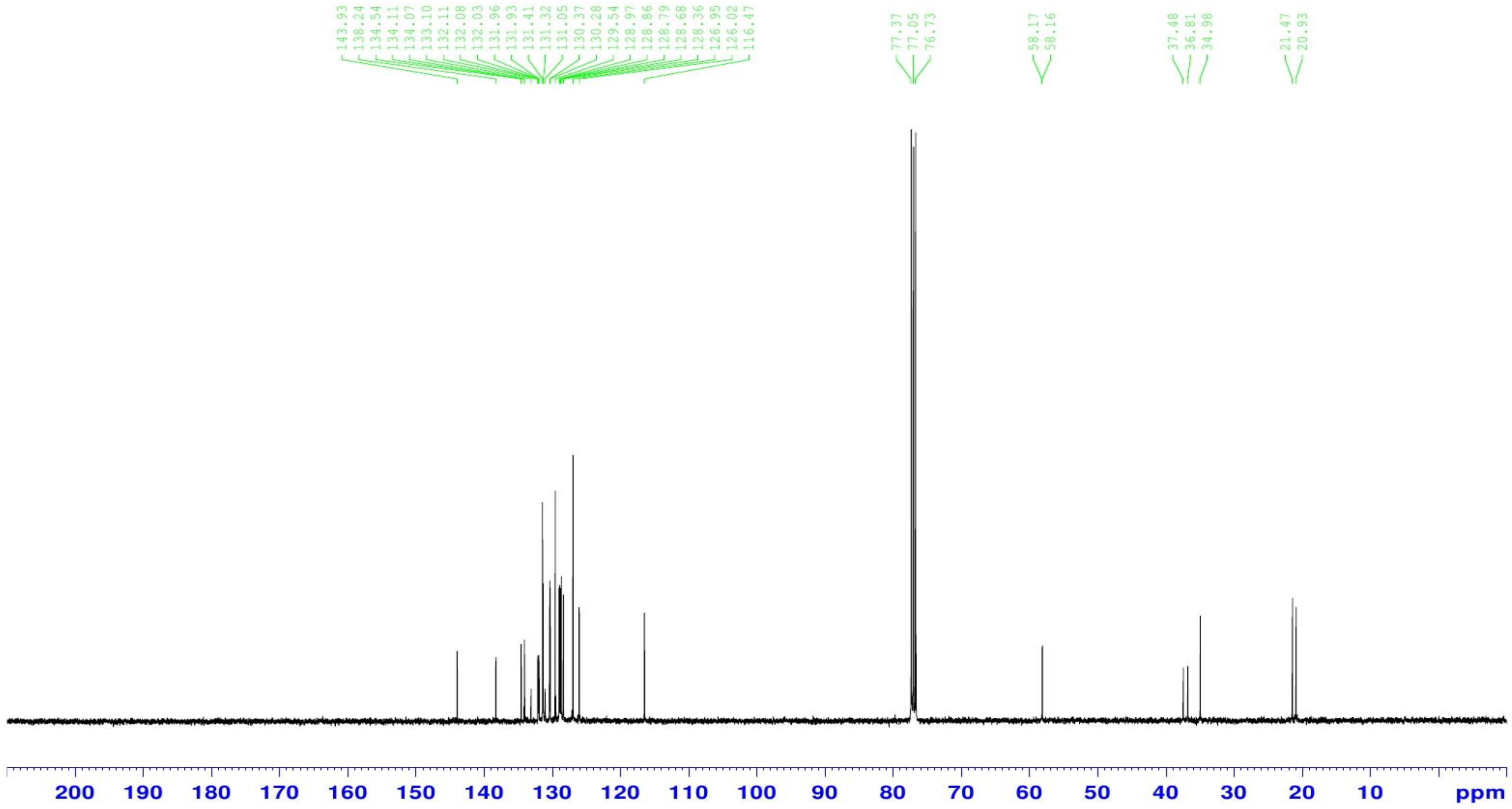
3r-P



3r-H


7.99 7.98 7.97 7.96 7.95 7.73 7.71 7.71 7.70 7.70 7.68 7.68 7.65 7.65 7.64 7.63 7.63 7.62 7.61 7.60 7.60 7.52 7.51 7.50 7.48 7.48 7.46 7.45 7.44 7.44 7.43 7.42 7.41 7.25 7.23 7.05 7.03 6.99 6.97 6.83
4.33 4.33 4.32 4.31 4.30 4.30 4.29 4.28 4.27 4.27 4.26
3.22 3.22 3.20 3.20 3.18 3.17 3.16 3.16 3.13 3.12 2.90 2.87 2.85 2.83 2.73 2.70 2.69 2.66 2.66 2.63 2.30 2.25
10 9 8 7 6 5 4 3 2 1 ppm
1.94 2.16 3.03 2.11 2.08 1.89 1.99 1.05 0.96
1.00
1.97 1.01 1.03 2.99 2.96

3r-C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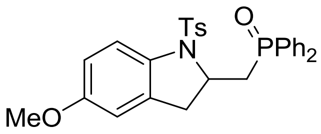
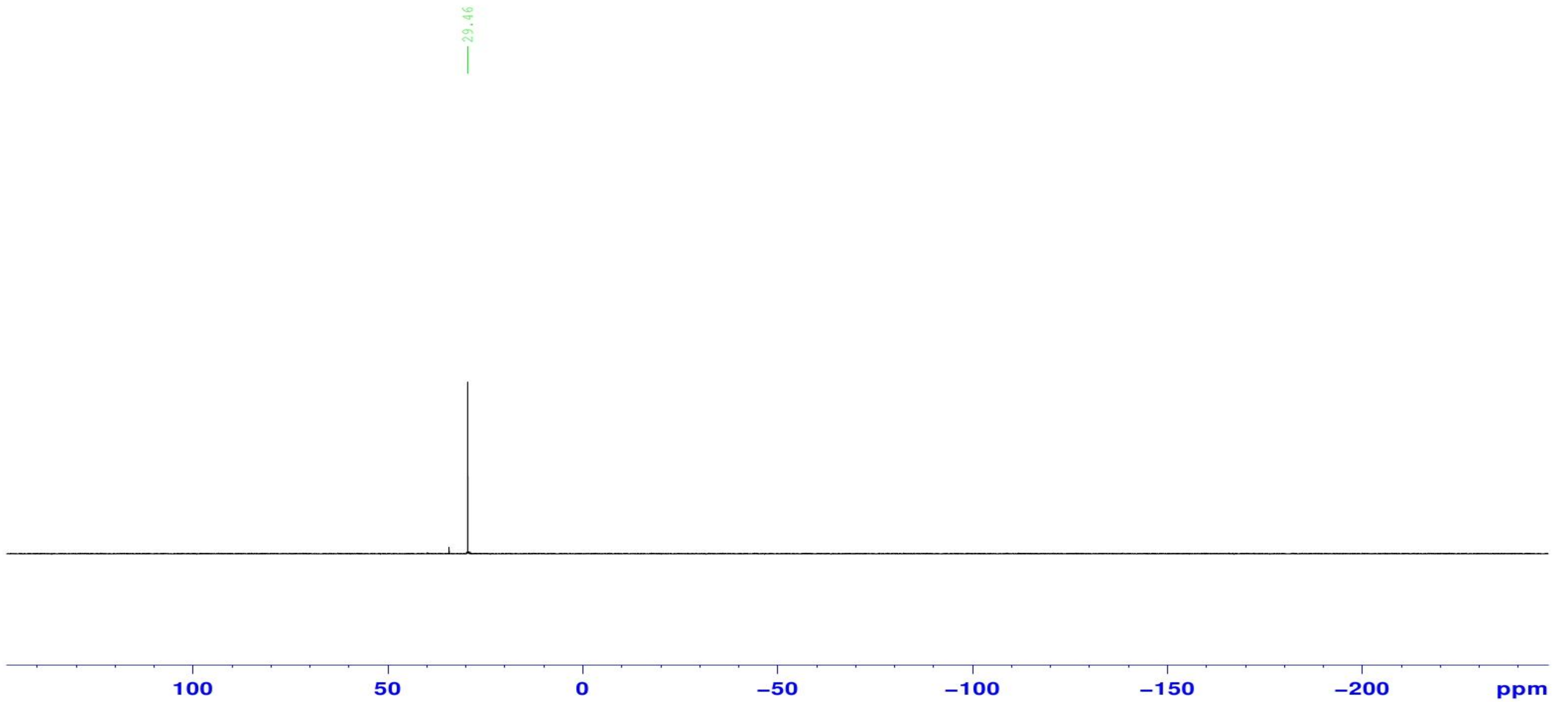
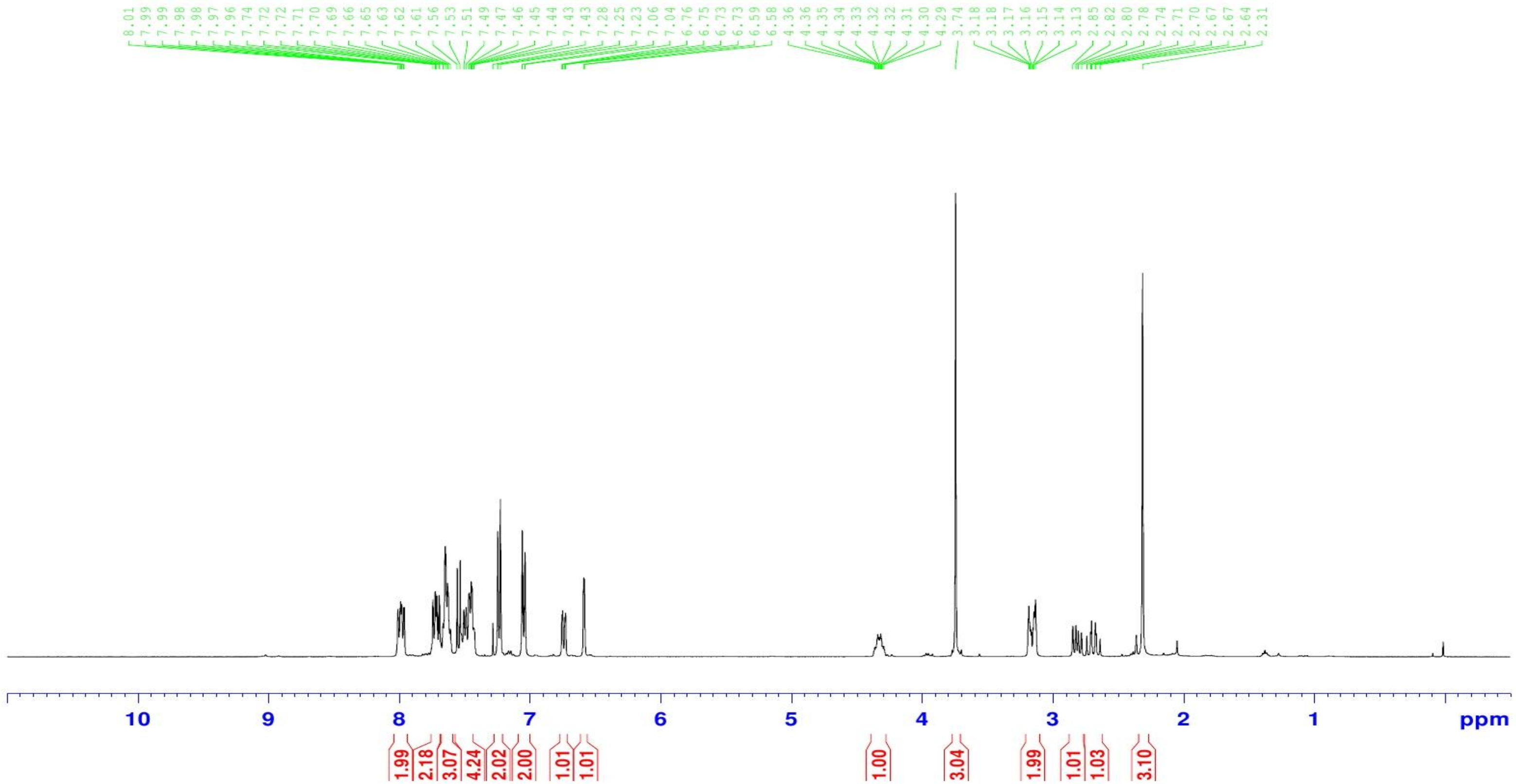
132.11
132.08
132.03
131.96
131.93
131.41
131.32
131.05
130.37
130.28
129.54
128.97
128.86
128.79
128.68
128.36
126.95
126.02
116.47
77.37
77.05
76.73
58.17
58.16
37.48
36.81
34.98
21.47
20.93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



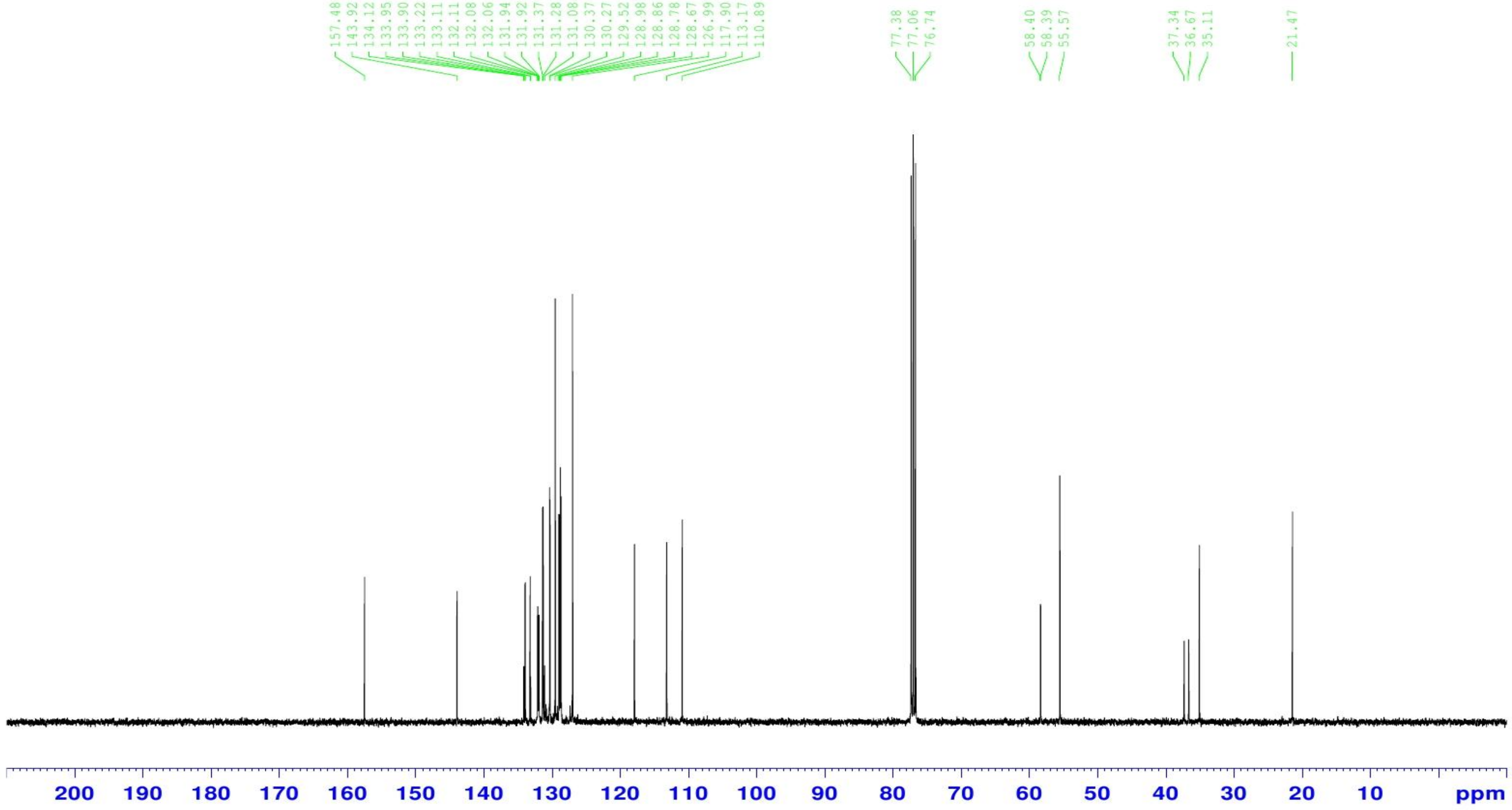
3s-P



3s-H



3s-C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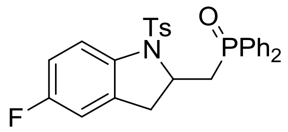
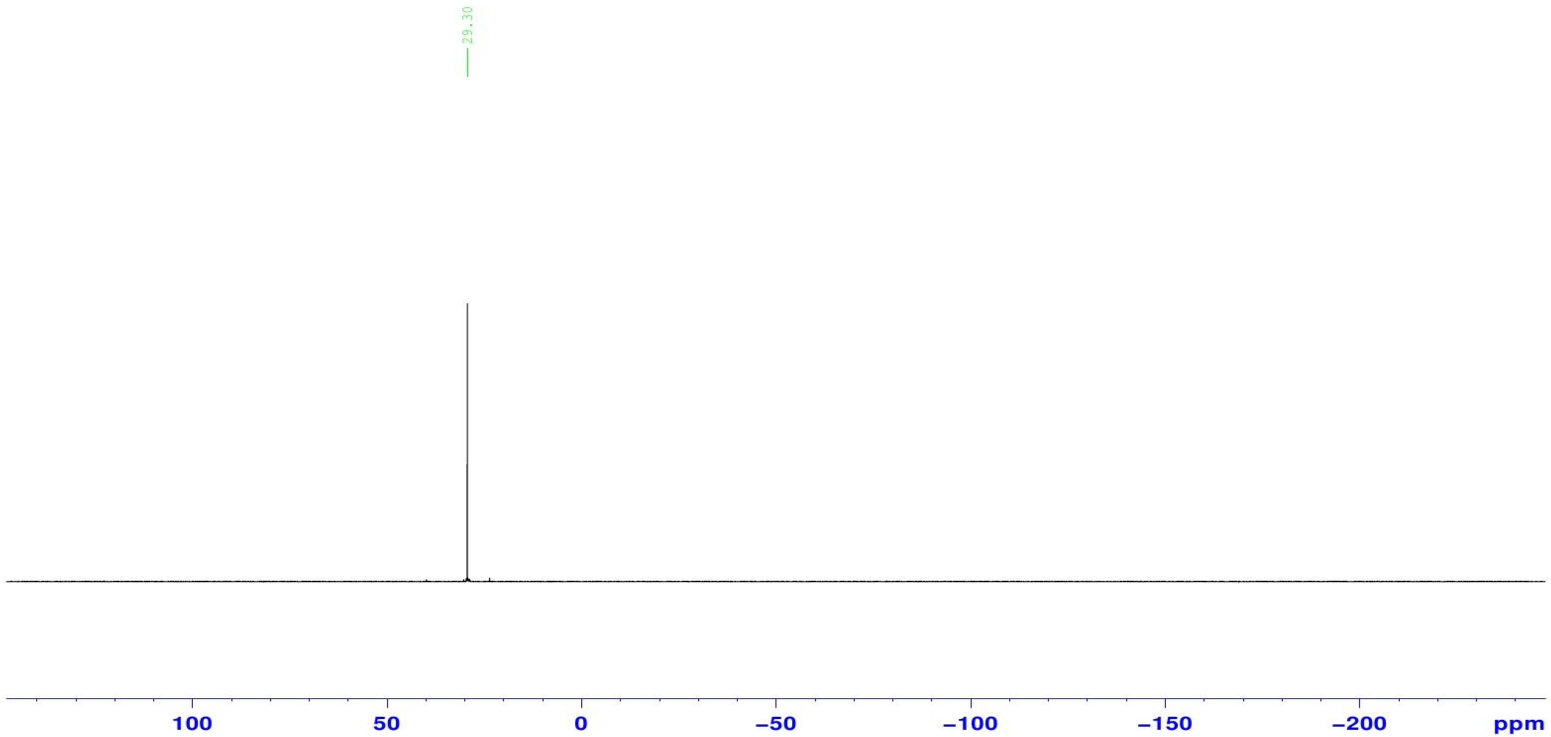
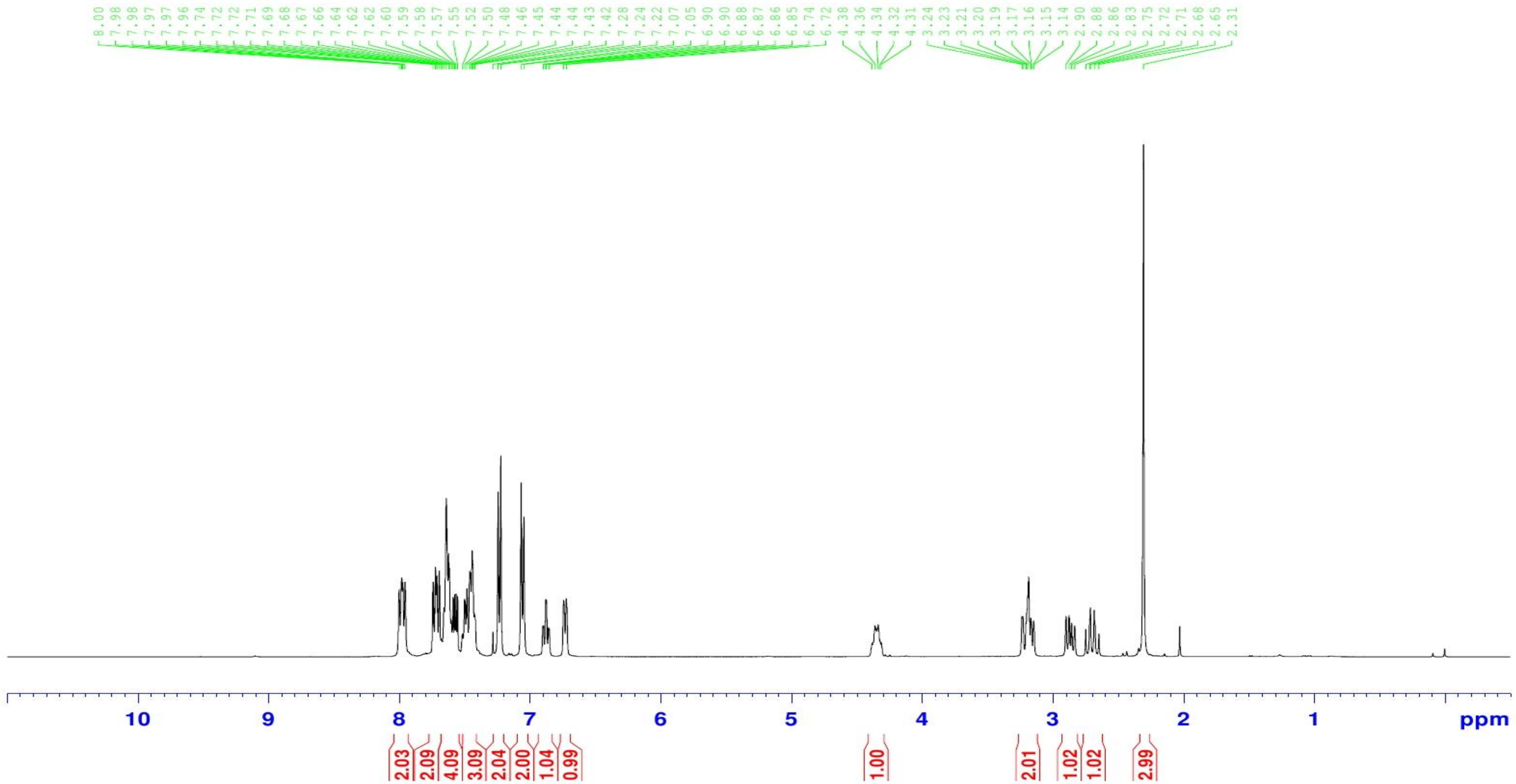
134.12
133.95
133.90
133.22
133.11
132.11
132.08
132.06
131.94
131.92
131.37
131.28
131.08
130.37
130.27
129.52
128.98
128.86
128.78
128.67
126.99
117.90
113.17
110.89
77.38
77.06
76.74
58.40
58.39
55.57
37.34
36.67
35.11
21.47
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



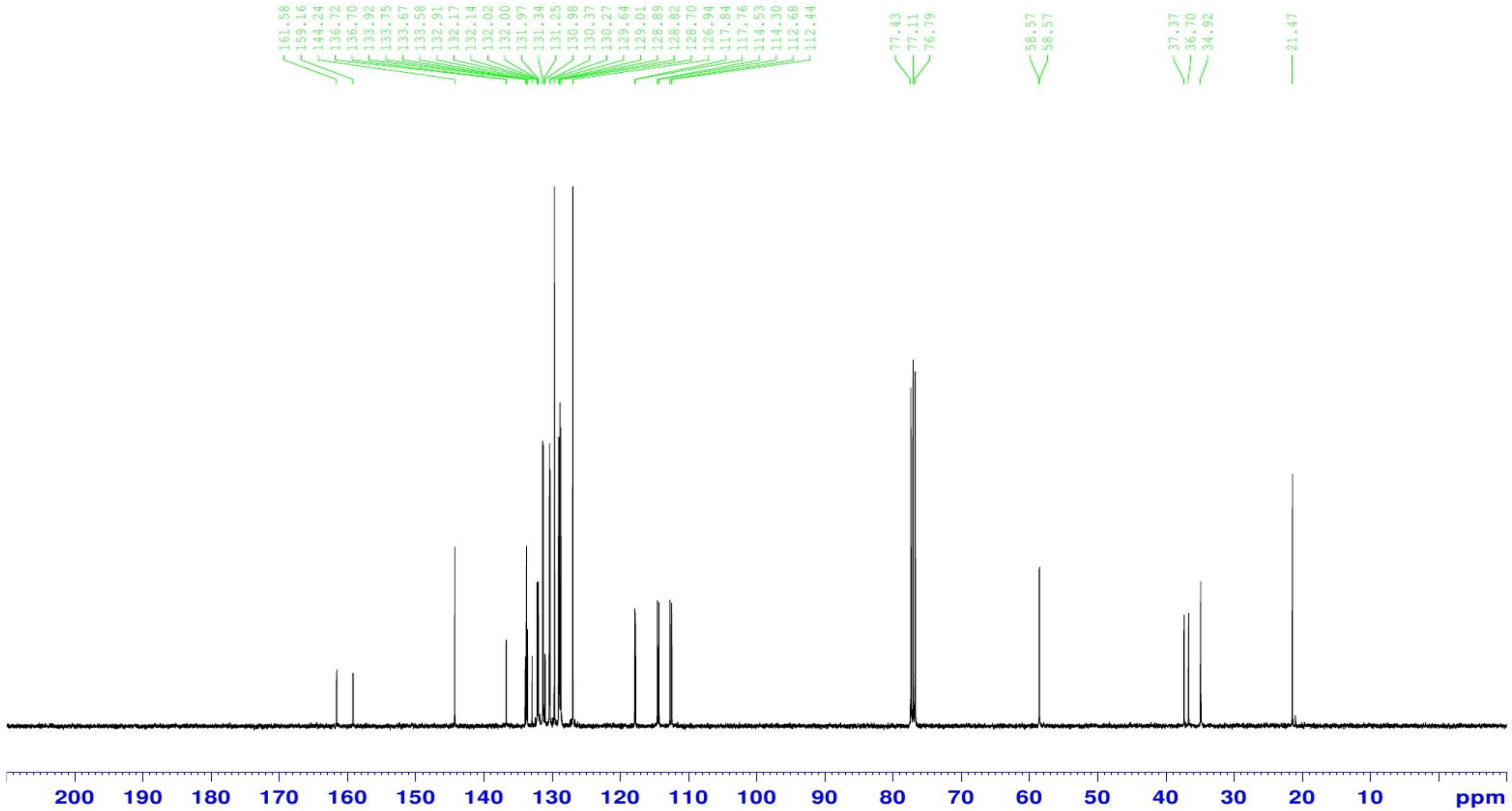
3t-P



3t-H



3t-C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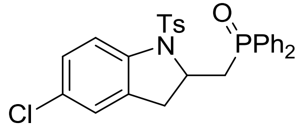
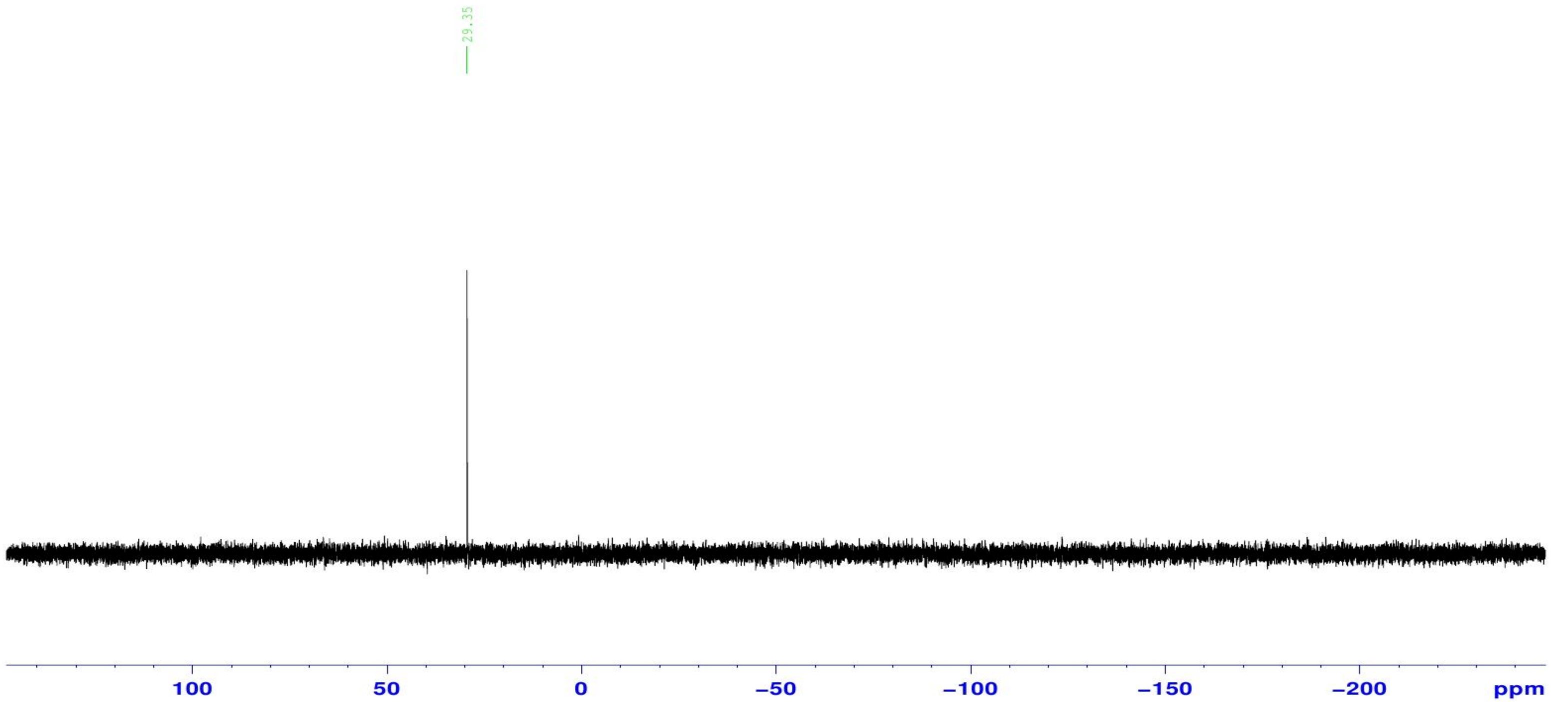
136.72
136.70
133.92
133.75
133.67
133.58
132.91
132.17
132.14
132.02
132.00
131.97
131.34
131.25
130.98
130.37
130.27
129.64
129.01
128.89
128.82
128.70
126.94
117.84
117.76
114.53
114.30
112.68
112.44
77.43
77.11
76.79
58.57
58.57
37.37
36.70
34.92
21.47
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

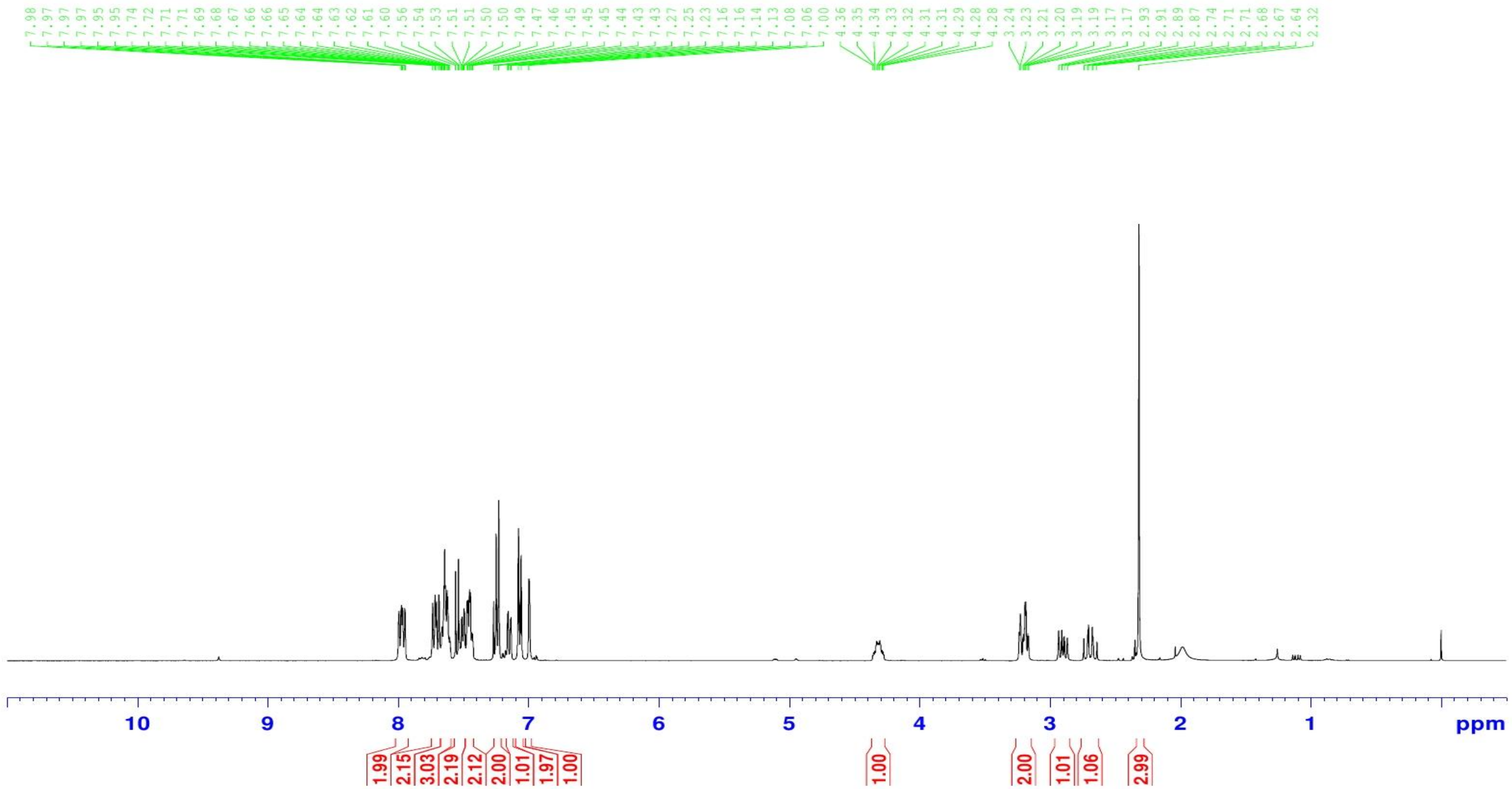
3t-F



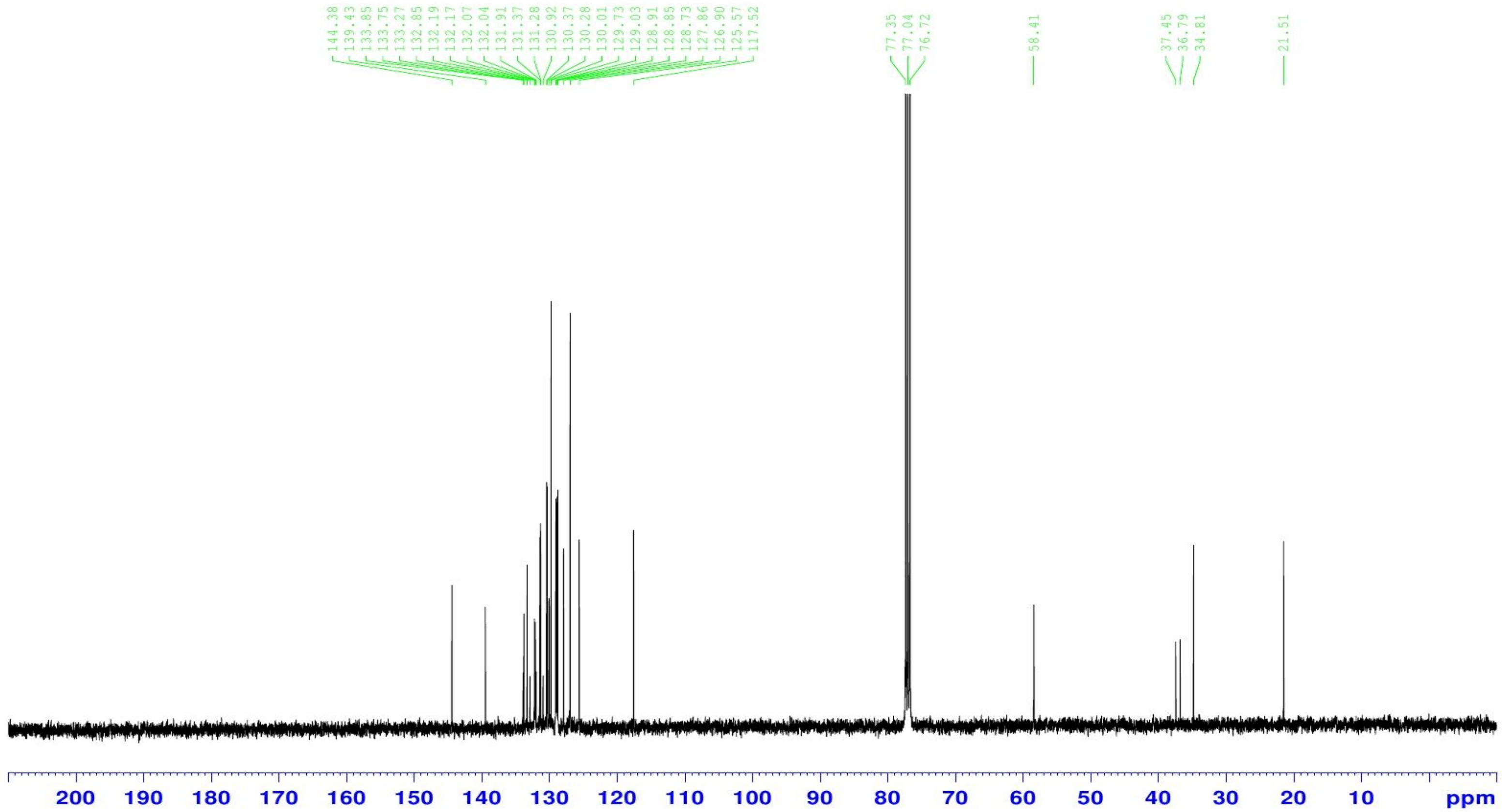
3u-P



3u-H



3u-C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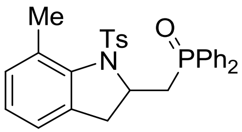
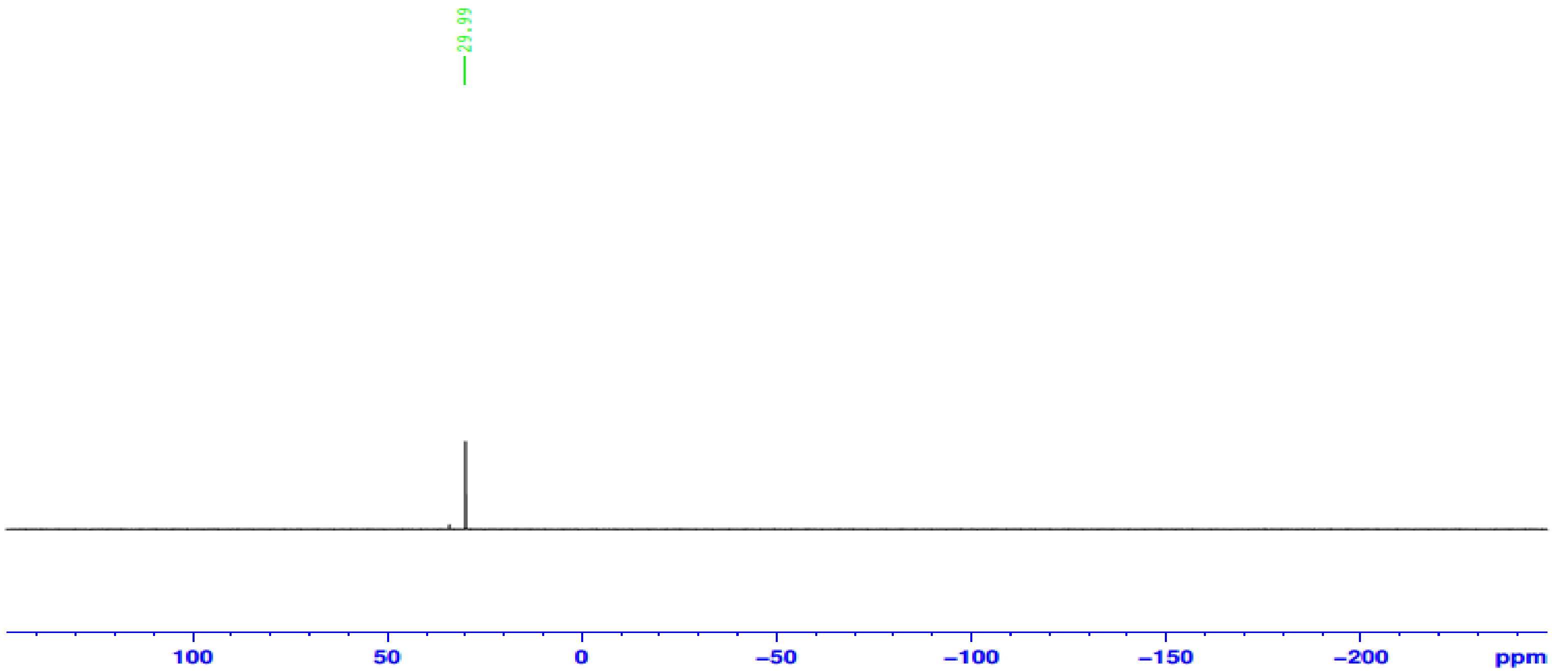
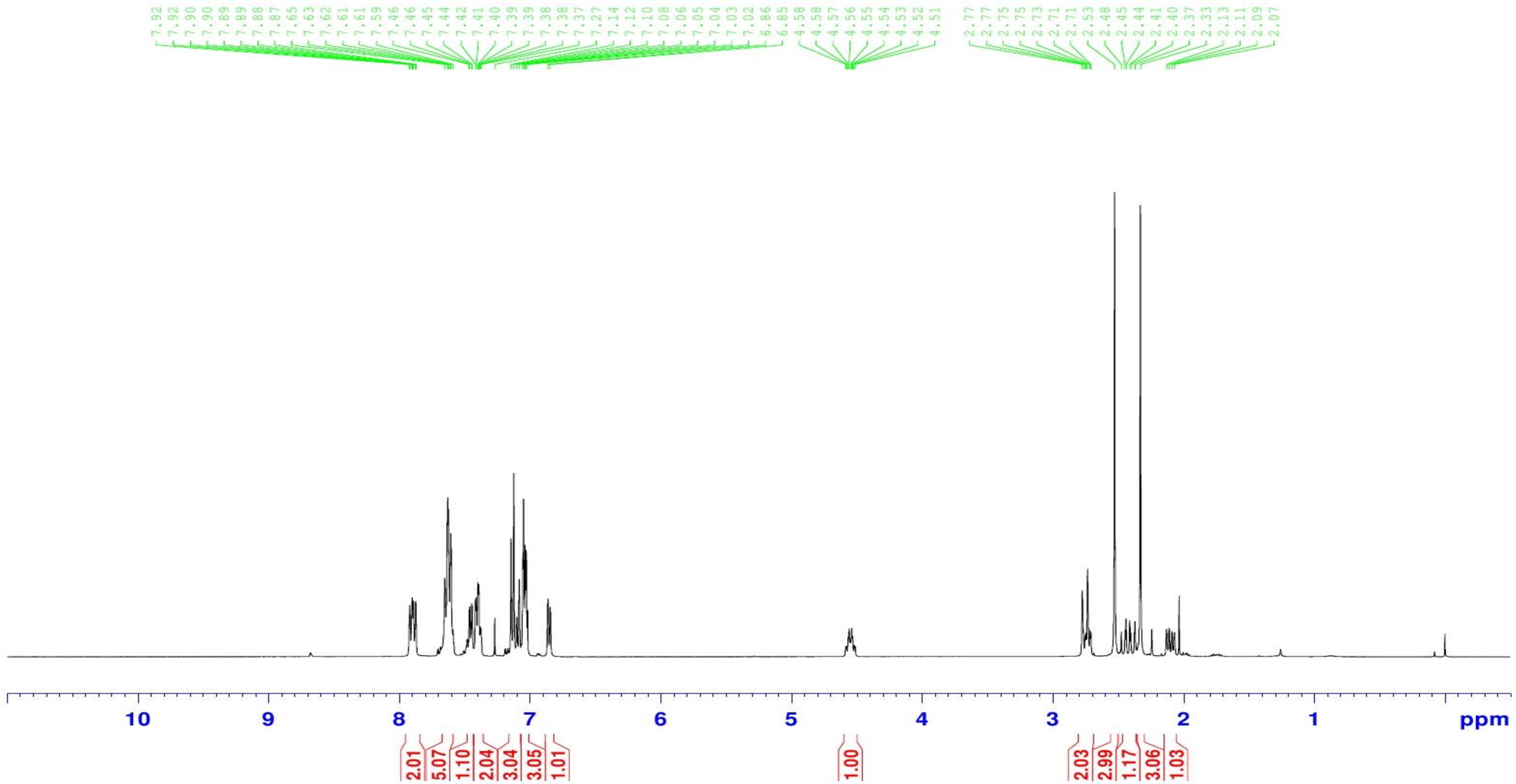
139.43
133.85
133.75
133.27
132.85
132.19
132.17
132.07
132.04
131.91
131.37
131.28
130.92
130.37
130.28
130.01
129.73
129.03
128.91
128.85
128.73
127.86
126.90
125.57
117.52
77.35
77.04
76.72
58.41
37.45
36.79
34.81
21.51
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



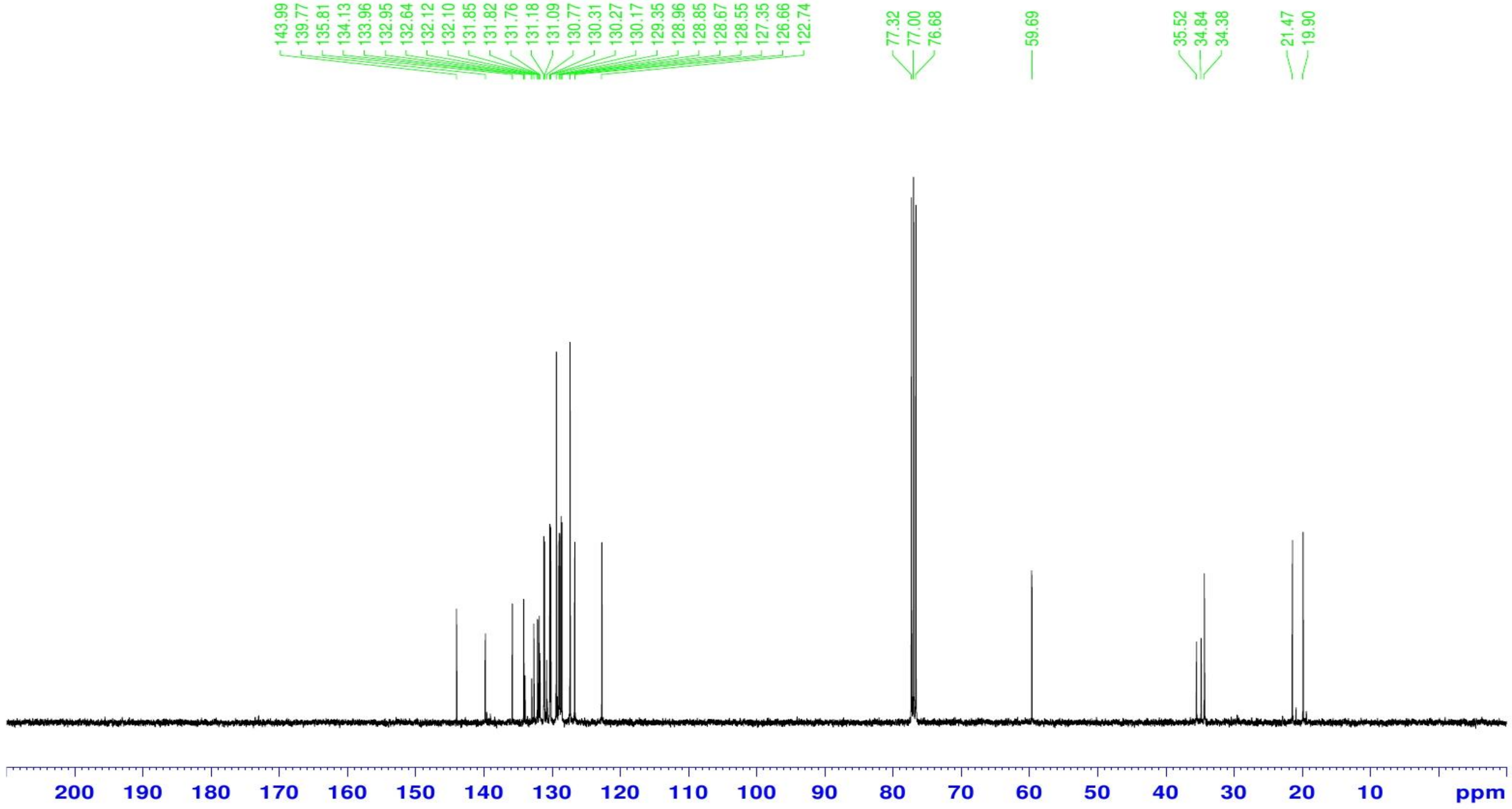
3v-P

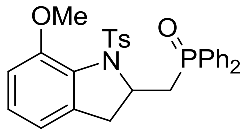


3v-H

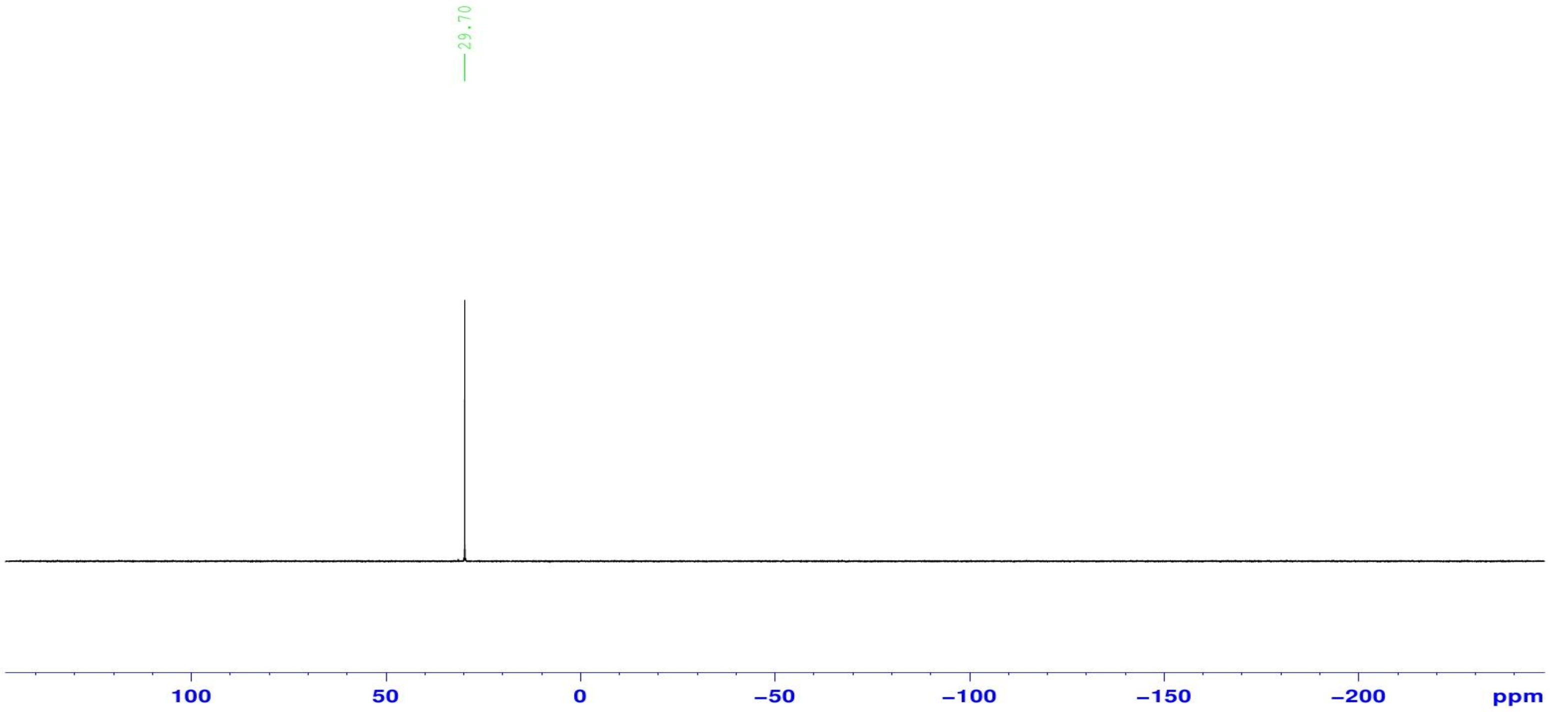


3v-C

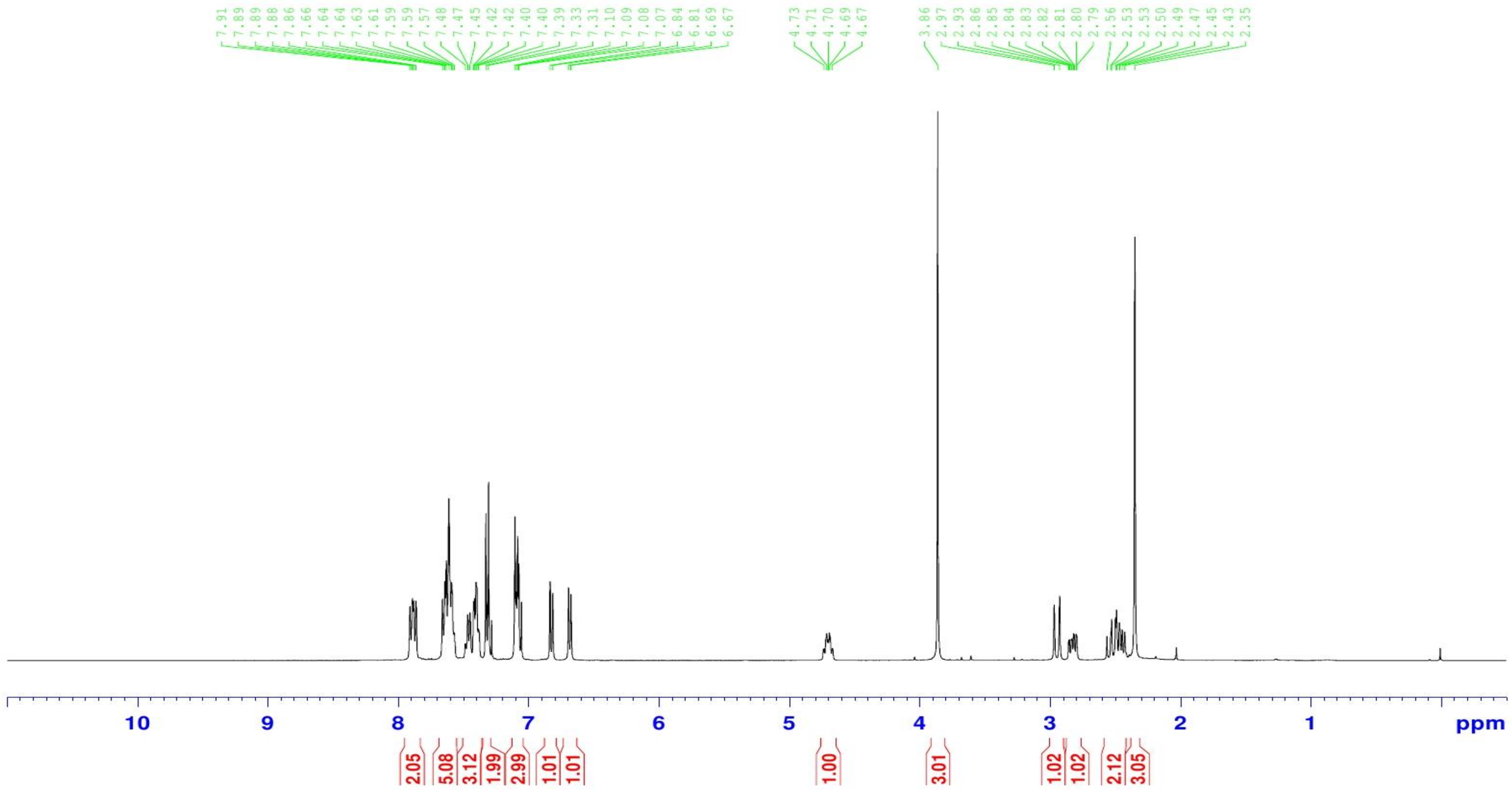

143.99
139.77
135.81
134.13
133.96
132.95
132.64
132.12
132.10
131.85
131.82
131.76
131.18
131.09
130.77
130.31
130.27
130.17
129.35
128.96
128.85
128.67
128.55
127.35
126.66
122.74
77.32
77.00
76.68
59.69
35.52
34.84
34.38
21.47
19.90
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



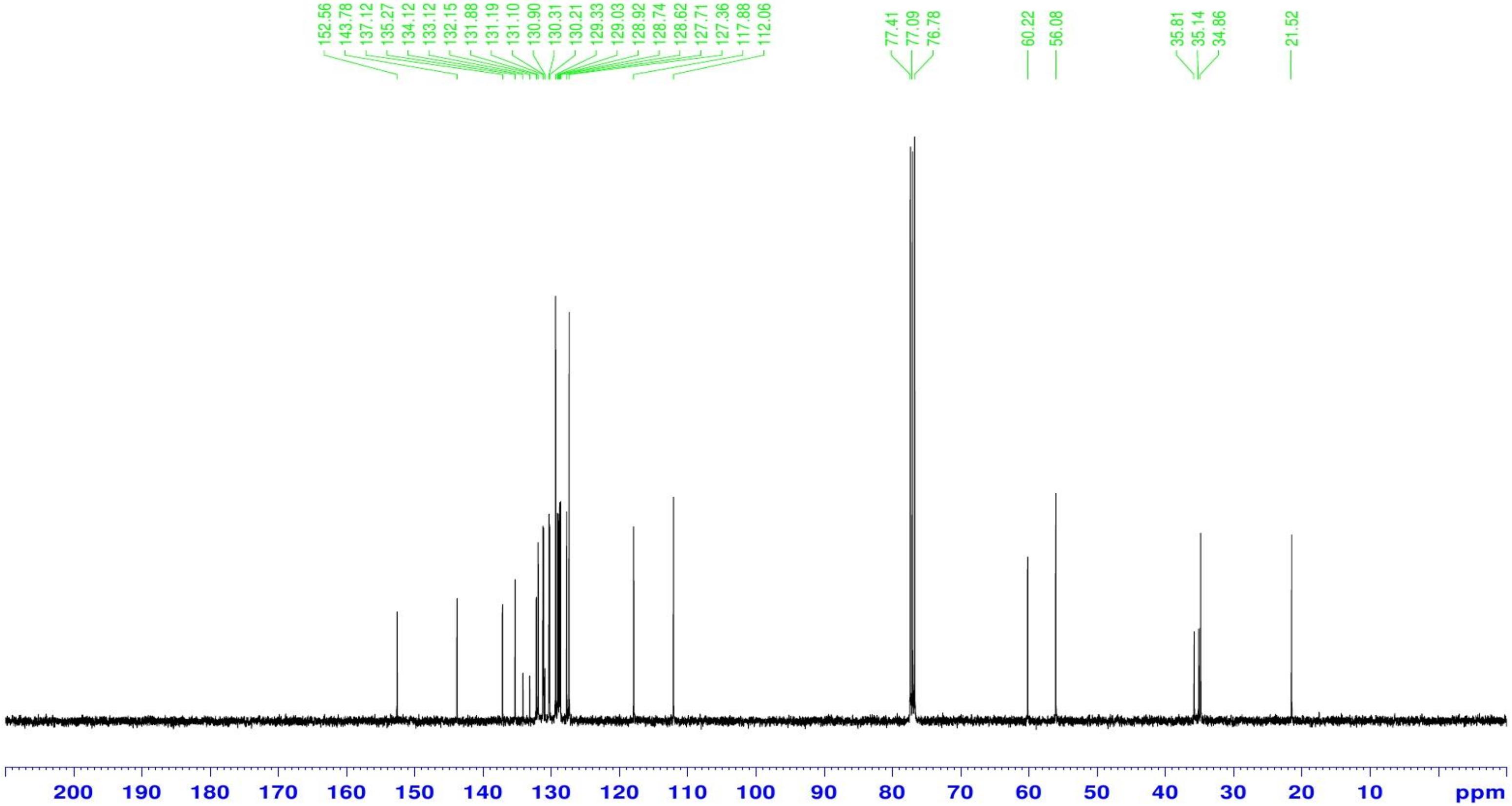
3w-P

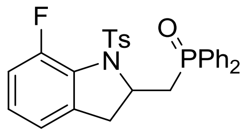


3w-H

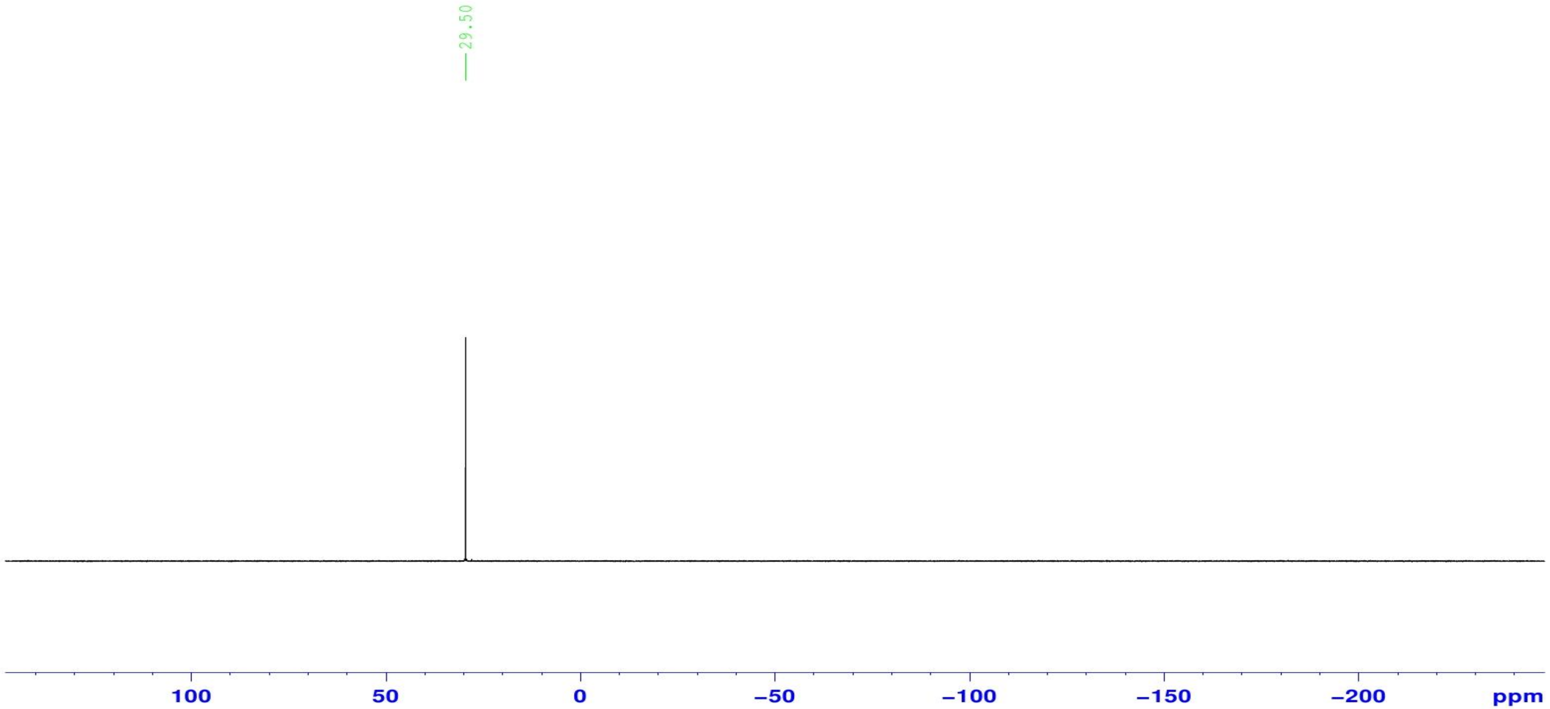


3w-C

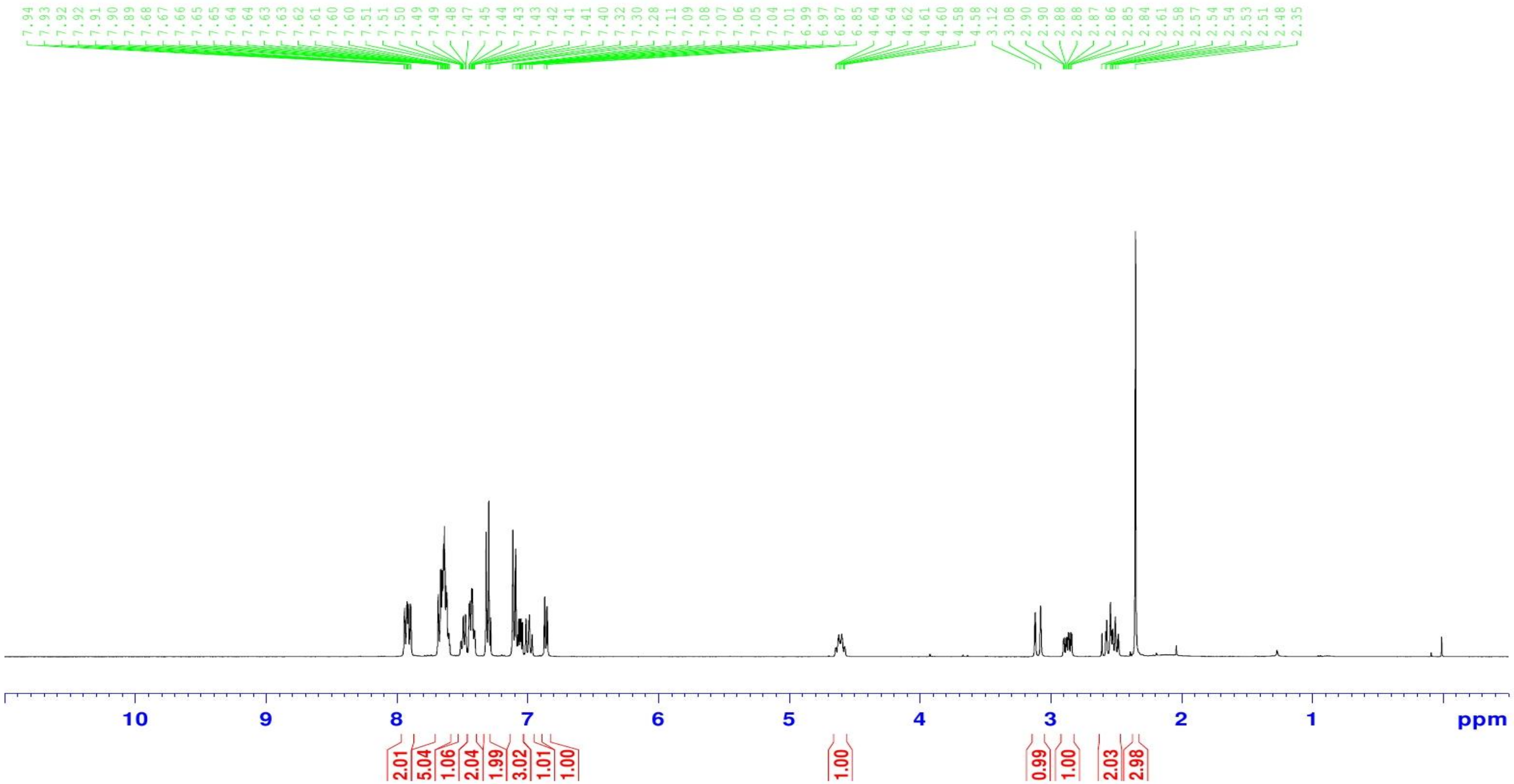

152.56
143.78
137.12
135.27
134.12
133.12
132.15
131.88
131.19
131.10
130.90
130.31
130.21
129.33
129.03
128.92
128.74
128.62
127.71
127.36
117.88
112.06
77.41
77.09
76.78
60.22
56.08
35.81
35.14
34.86
21.52
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



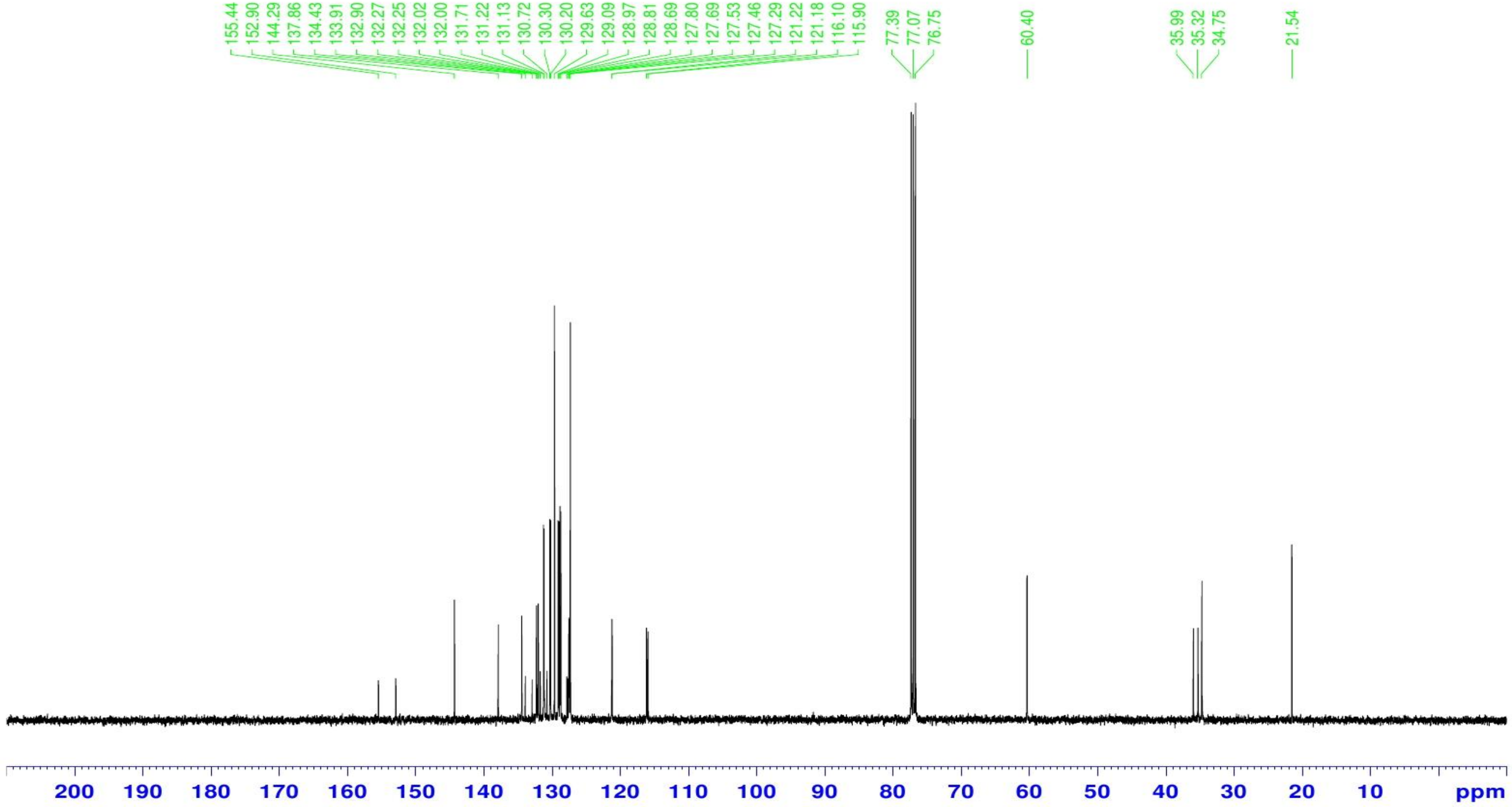
3x-P



3x-P

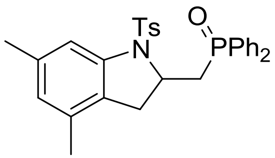


3x-C

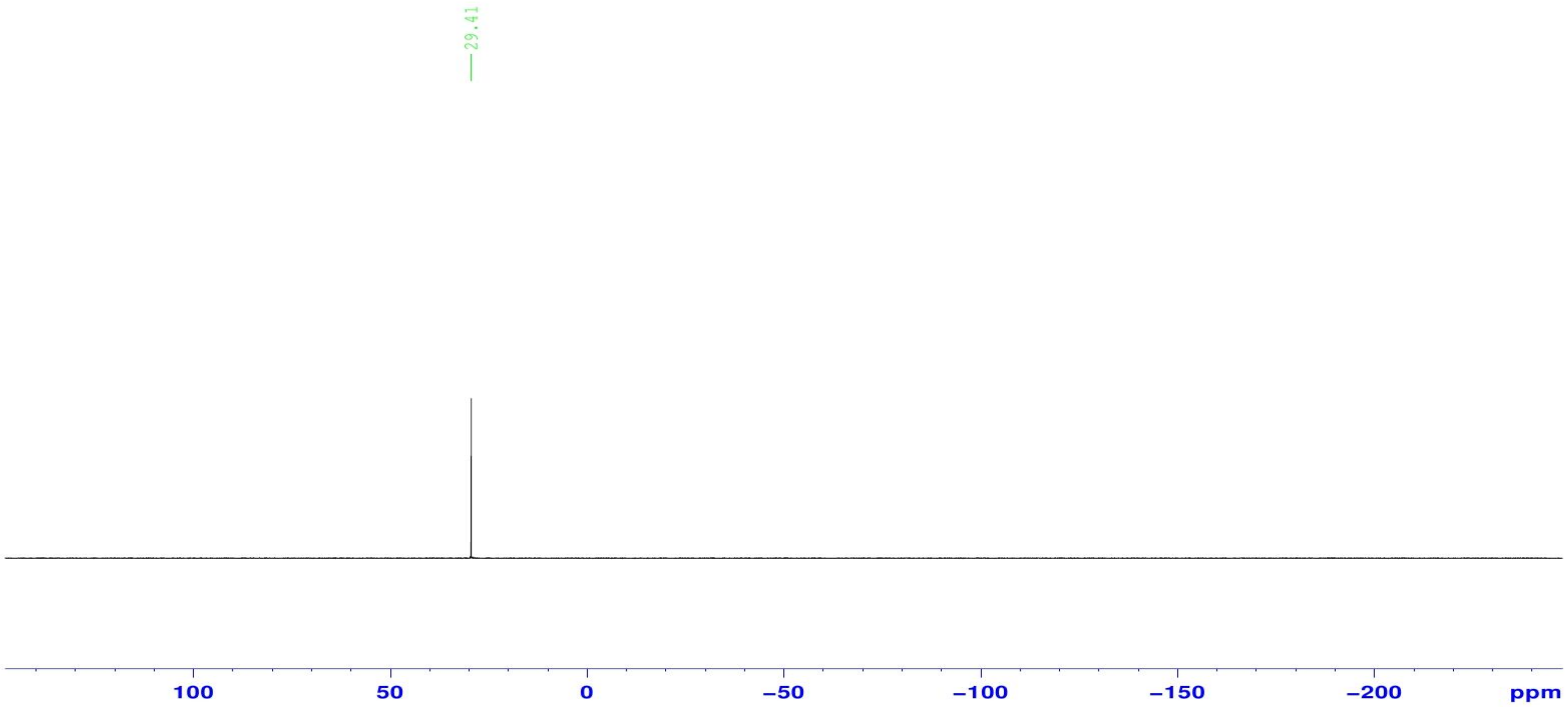


155.44
152.90
144.29
137.86
134.43
133.91
132.90
132.27
132.25
132.02
132.00
131.71
131.22
131.13
130.72
130.30
130.20
129.63
129.09
128.97
128.81
128.69
127.80
127.69
127.53
127.46
127.29
121.22
121.18
116.10
115.90
77.39
77.07
76.75
60.40
35.99
35.32
34.75
21.54
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

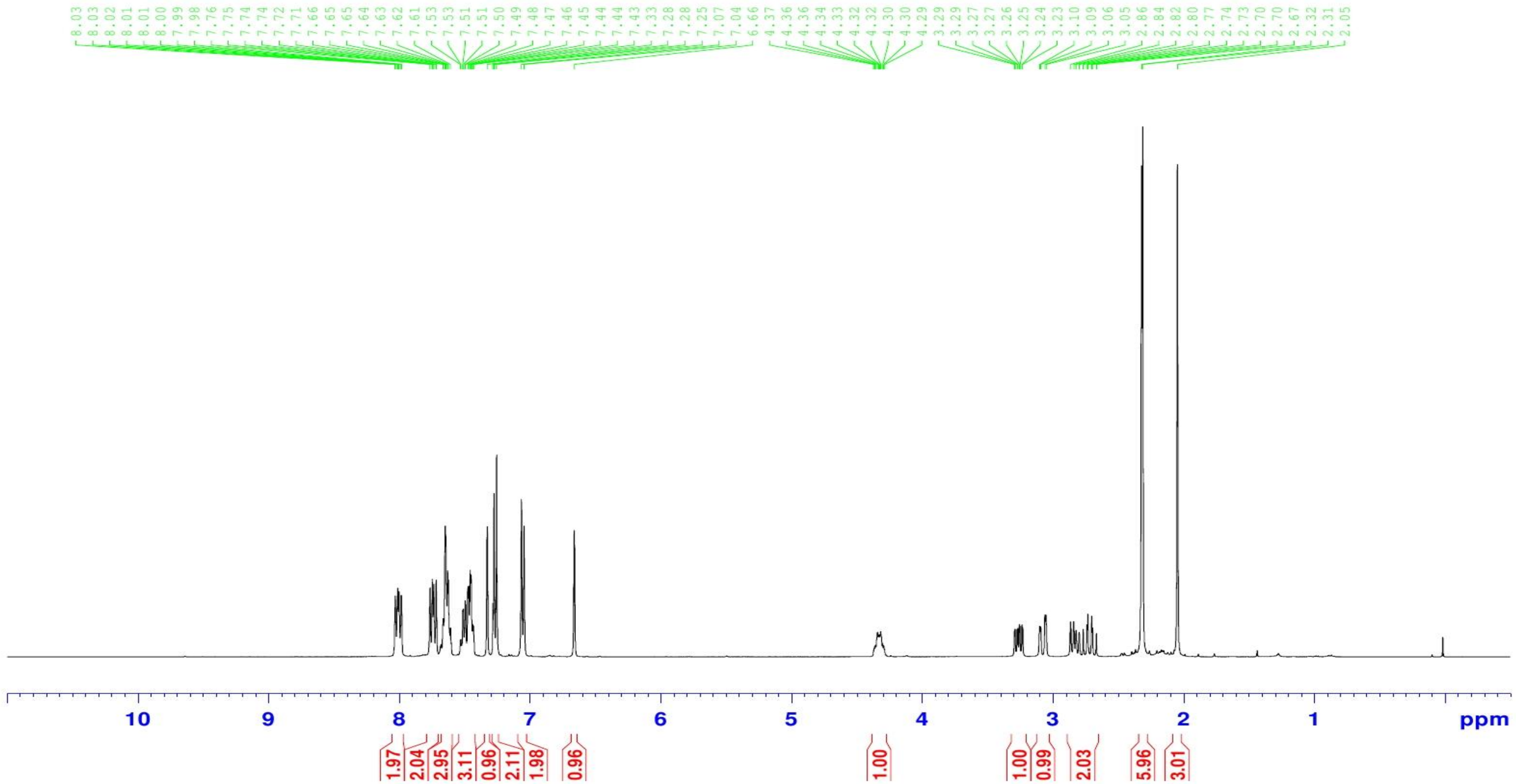
3x-F



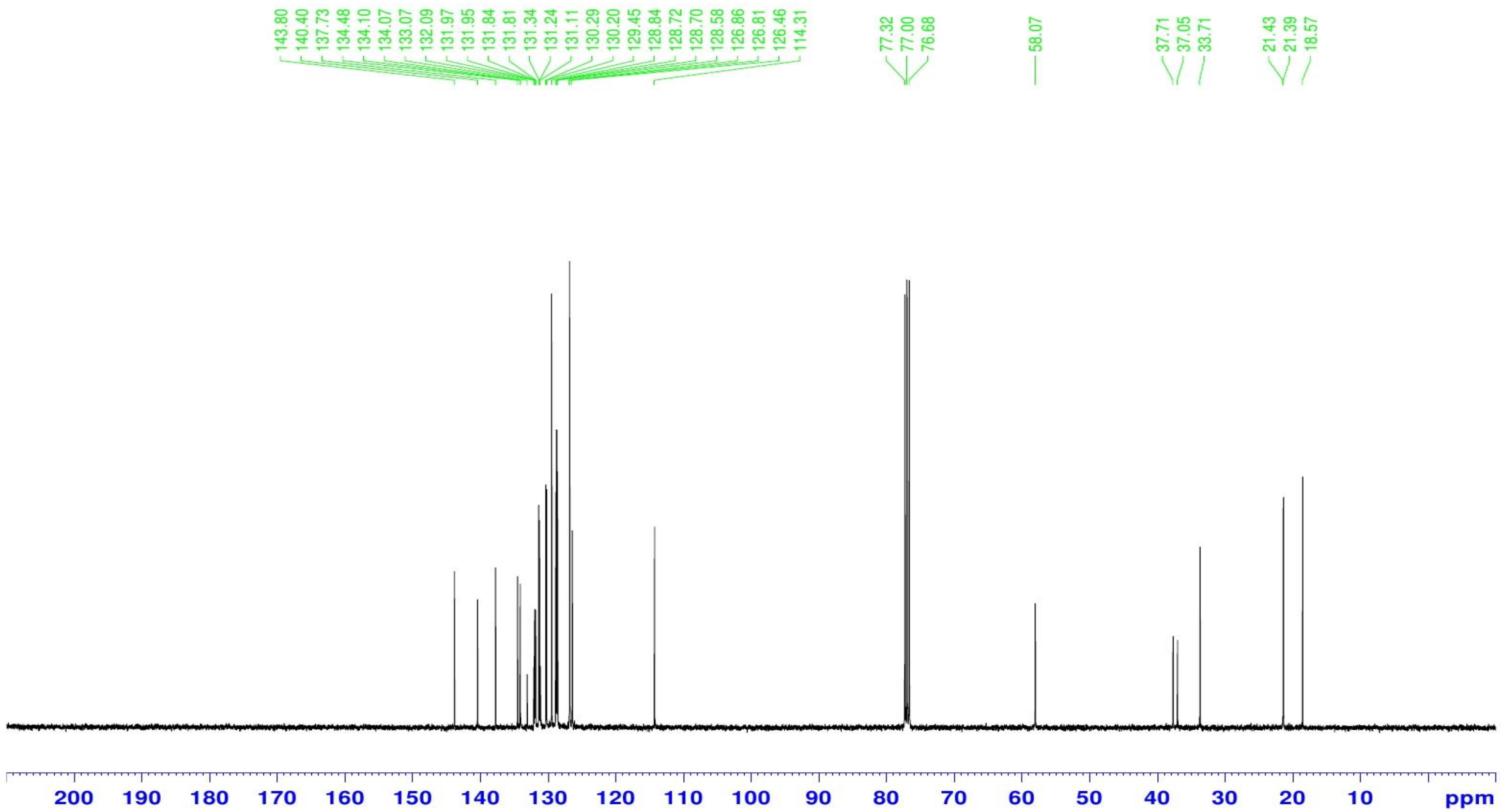
3y-P

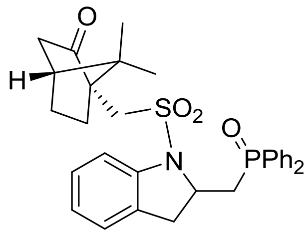


3y-H

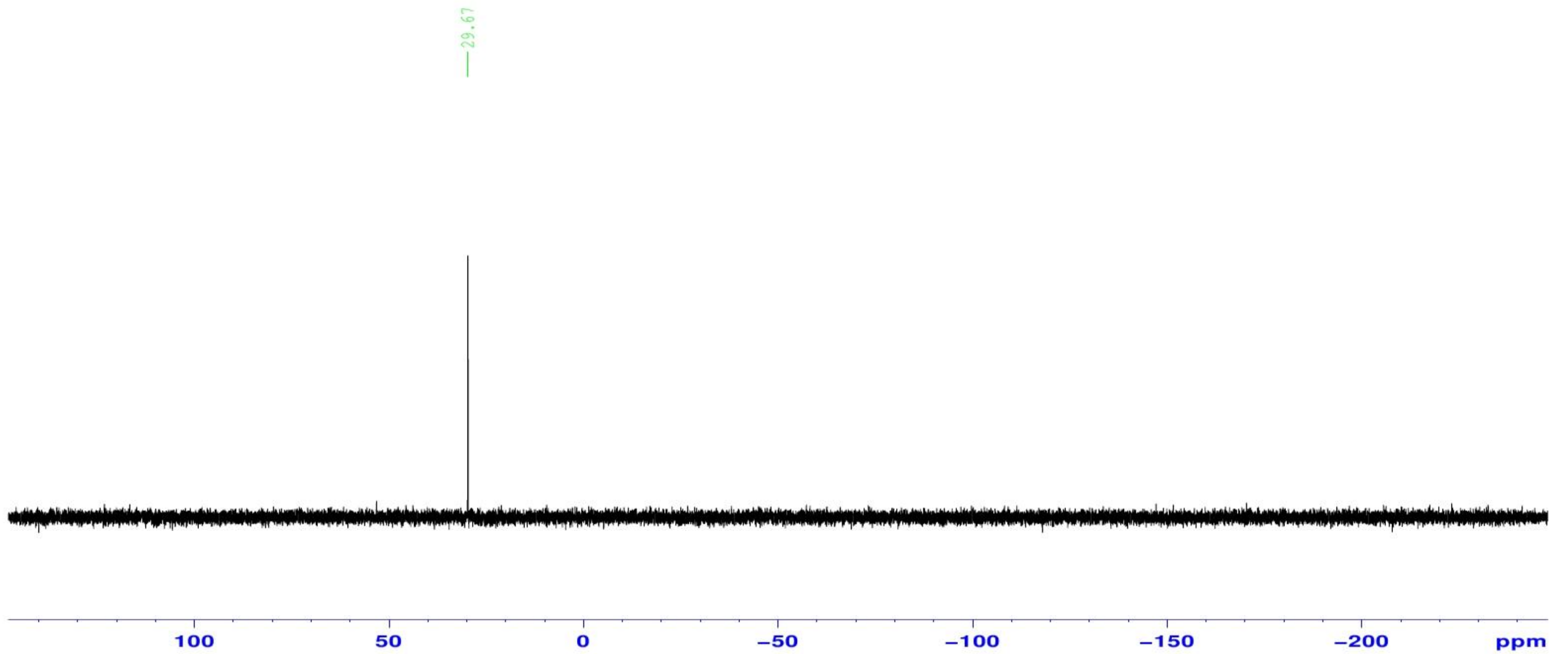


3y-C

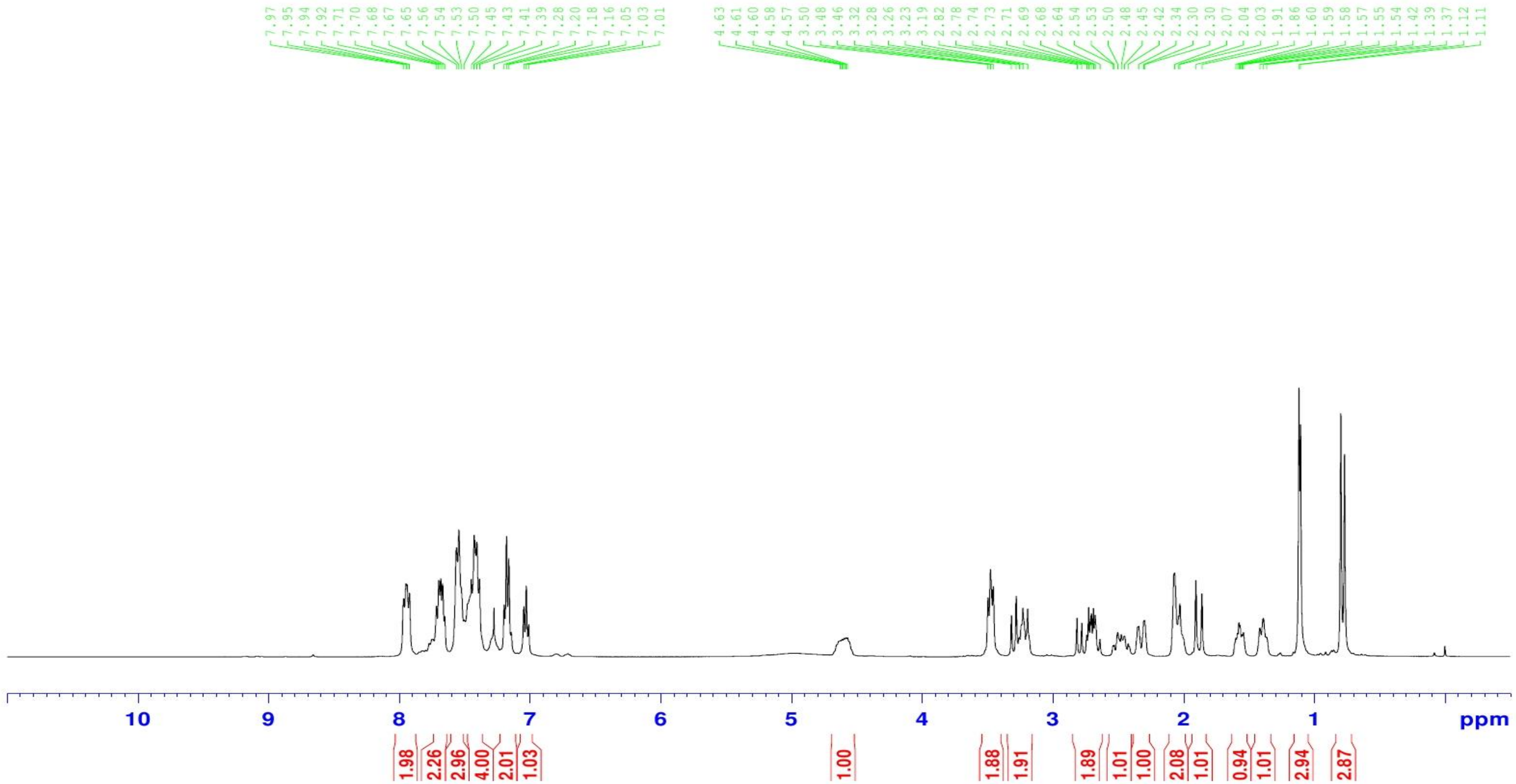

143.80
140.40
137.73
134.48
134.10
134.07
133.07
132.09
131.97
131.95
131.84
131.81
131.34
131.24
131.11
130.29
130.20
129.45
128.84
128.72
128.70
128.58
126.86
126.81
126.46
114.31
77.32
77.00
76.68
58.07
37.71
37.05
33.71
21.43
21.39
18.57
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



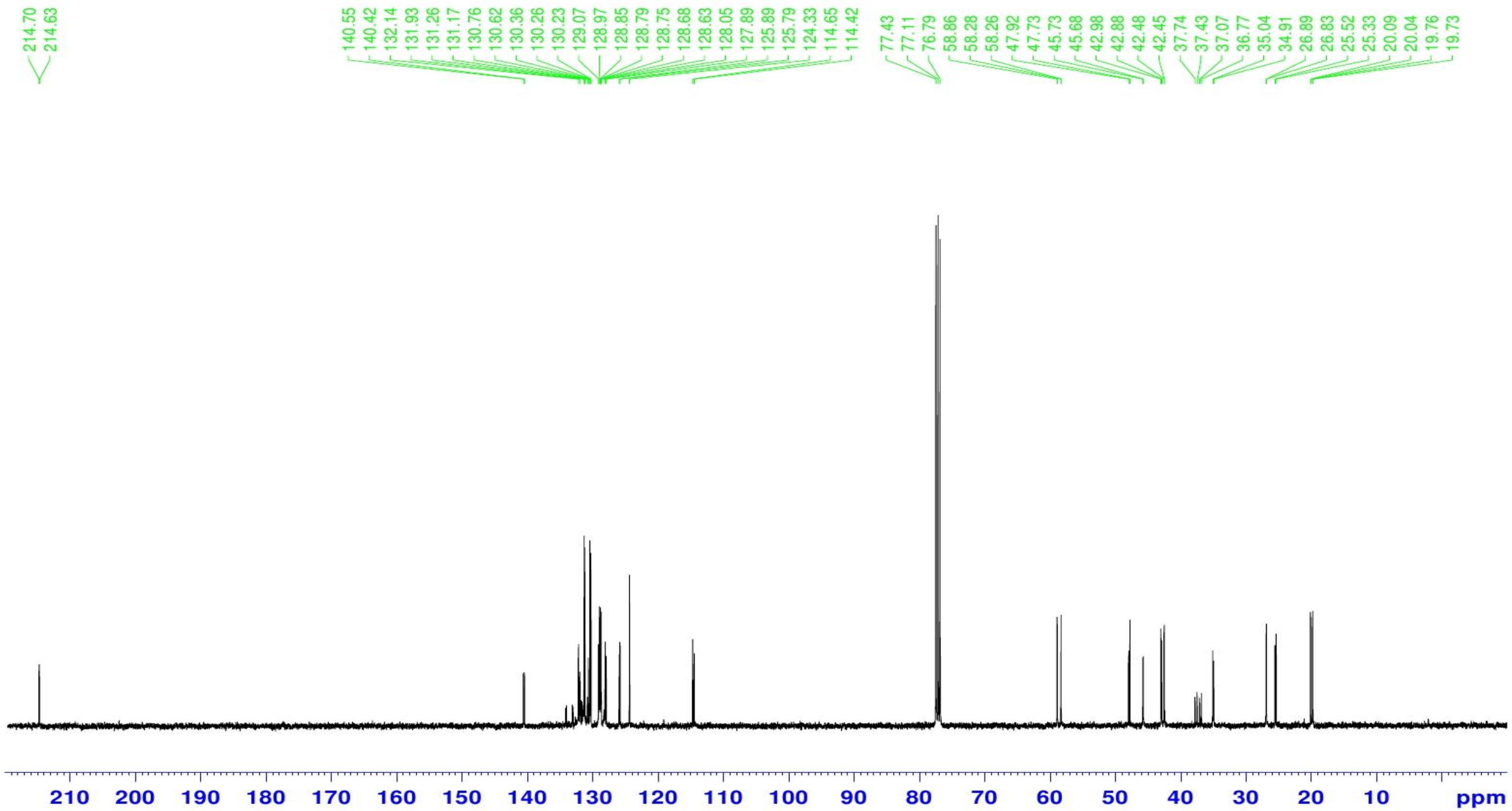
3z-P

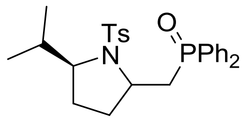


3z-H

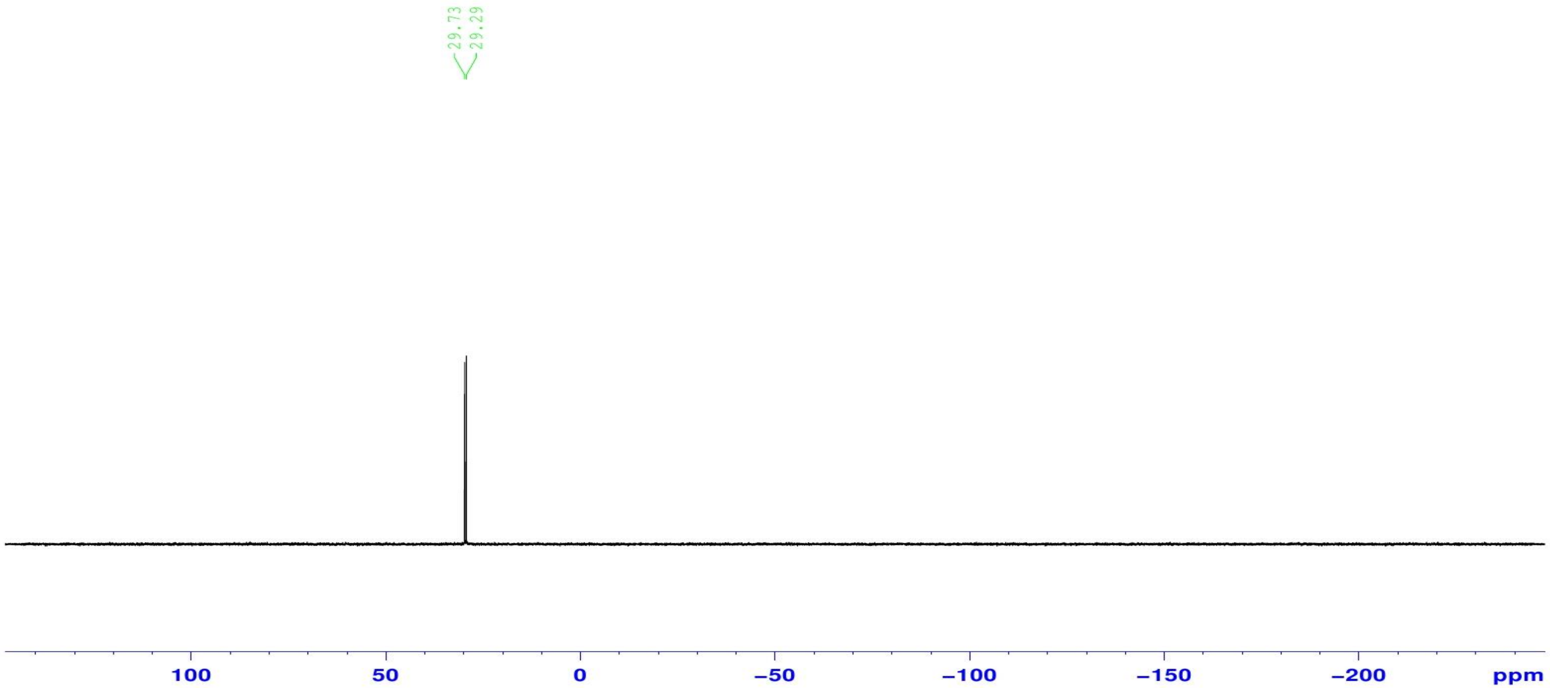


3z-C


214.70
214.63
140.55
140.42
132.14
131.93
131.26
131.17
130.76
130.62
130.36
130.26
130.23
129.07
128.97
128.85
128.79
128.75
128.68
128.63
128.05
127.89
125.89
125.79
124.33
114.65
114.42
77.43
77.11
76.79
58.86
58.28
58.26
47.92
47.73
45.73
45.68
42.98
42.88
42.48
42.45
37.74
37.43
37.07
36.77
35.04
34.91
26.89
26.83
25.52
25.33
20.09
20.04
19.76
19.73
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



3aa-P



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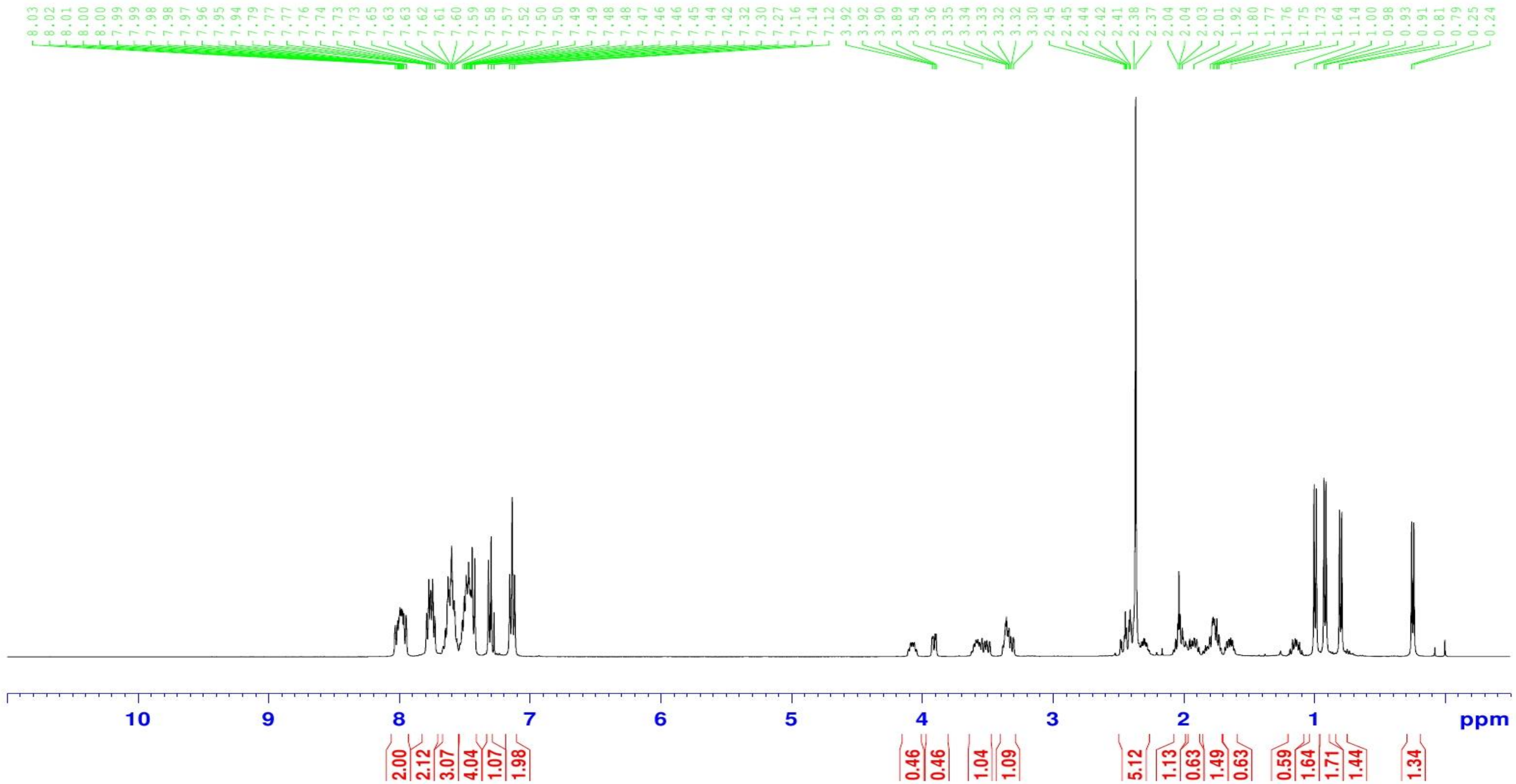
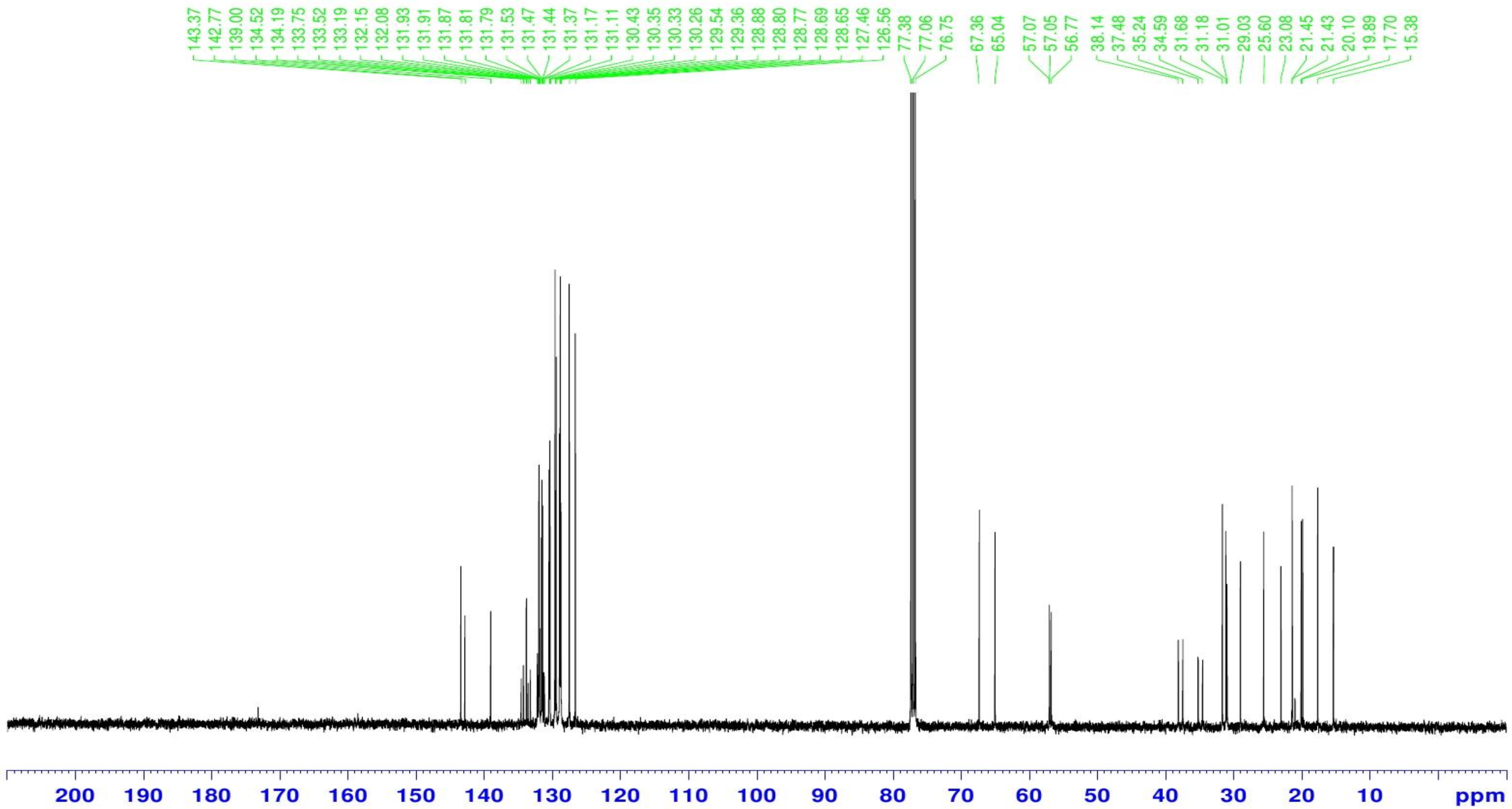
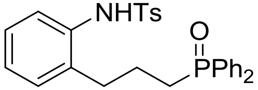
3aa-H

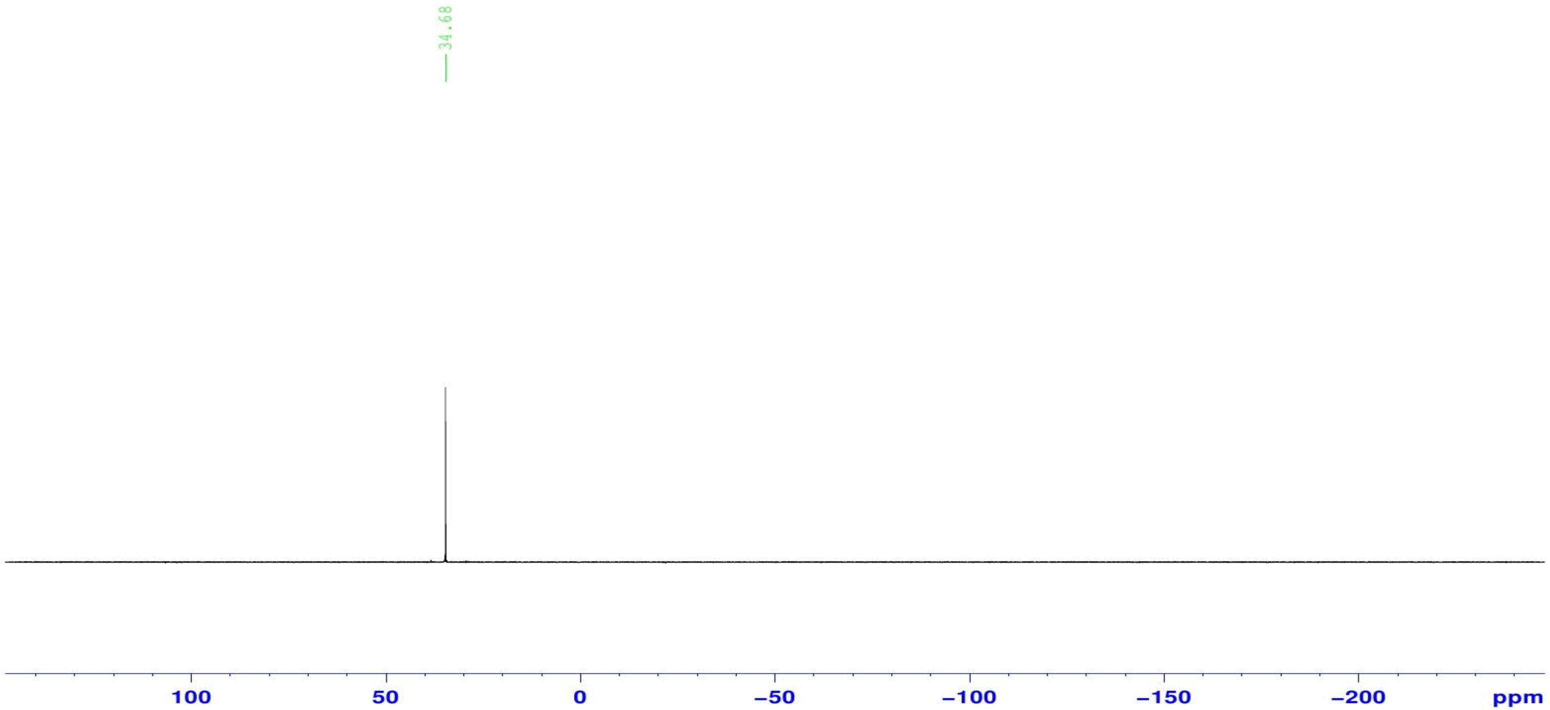


3aa-C

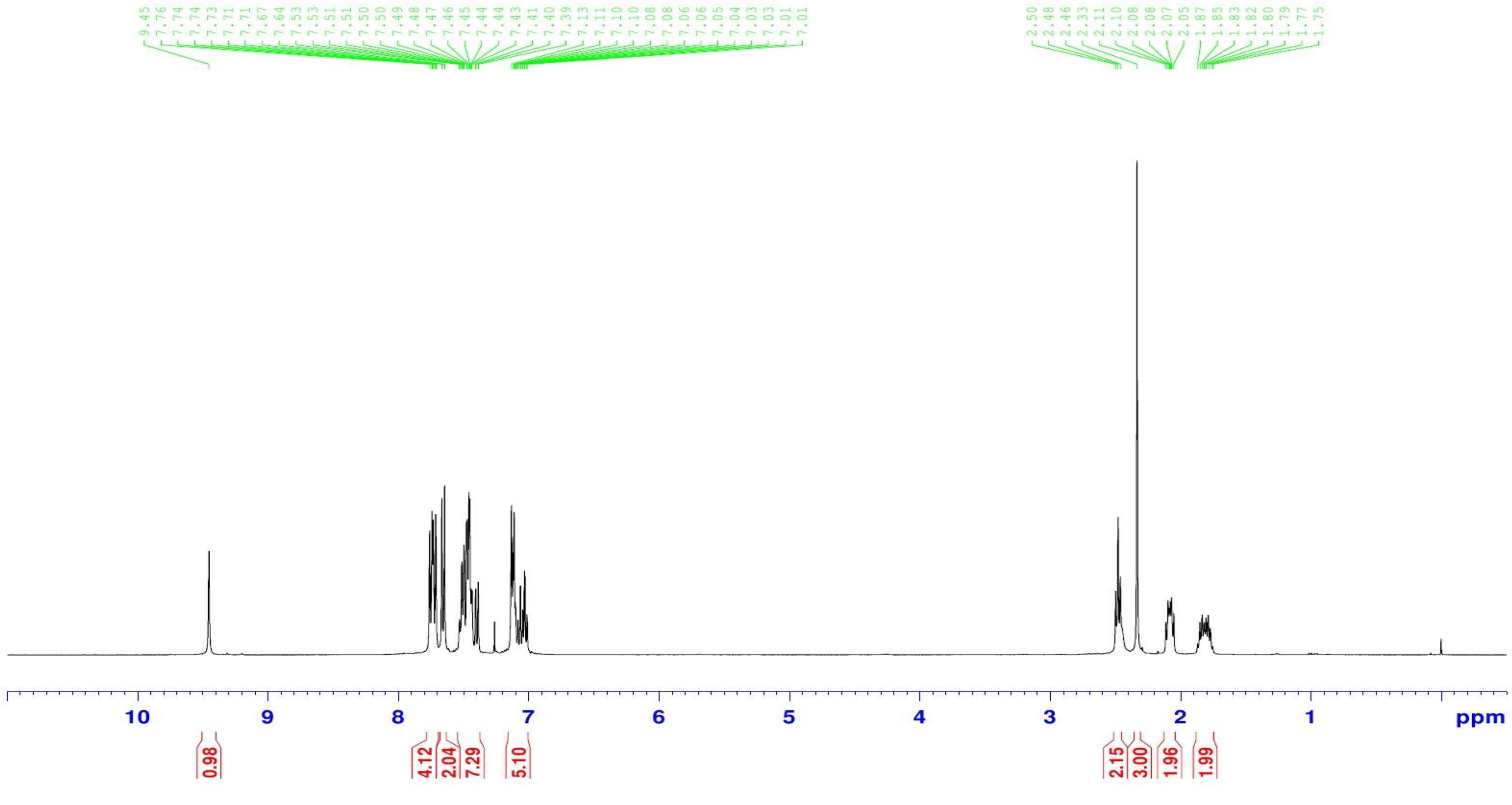

143.37
142.77
139.00
134.52
134.19
133.75
133.52
133.19
132.15
132.08
131.93
131.91
131.87
131.81
131.79
131.53
131.47
131.44
131.37
131.17
131.11
130.43
130.35
130.33
130.26
129.54
129.36
128.88
128.80
128.77
128.69
128.65
127.46
126.56
77.38
77.06
76.75
67.36
65.04
57.07
57.05
56.77
38.14
37.48
35.24
34.59
31.68
31.18
31.01
29.03
25.60
23.08
21.45
21.43
20.10
19.89
17.70
15.38
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



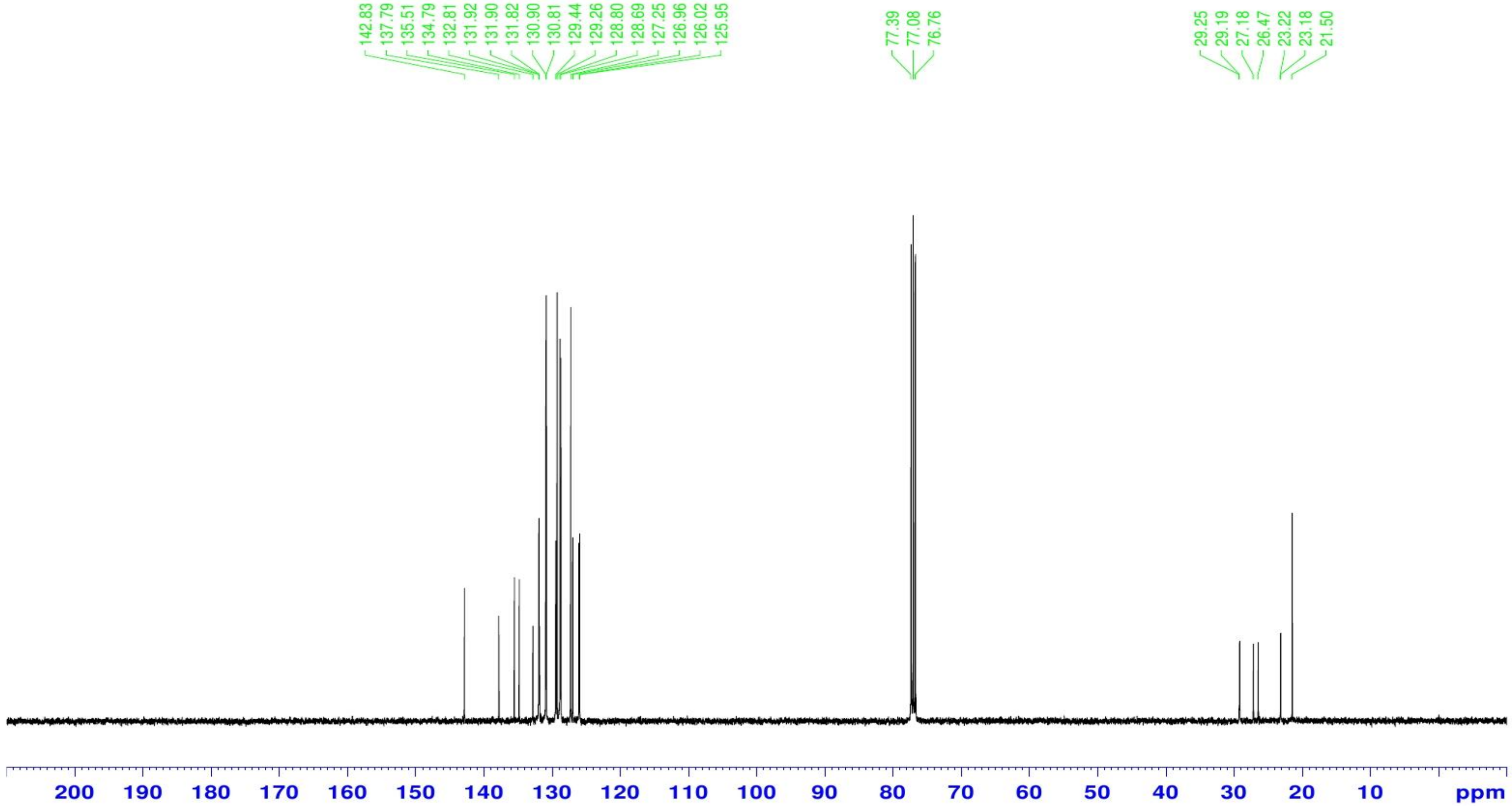
4a-P



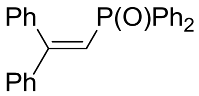
4a-H


9.45
7.76
7.74
7.74
7.73
7.71
7.71
7.67
7.64
7.53
7.53
7.51
7.51
7.50
7.50
7.49
7.48
7.47
7.46
7.45
7.44
7.44
7.43
7.41
7.40
7.39
7.13
7.11
7.10
7.10
7.08
7.08
7.06
7.06
7.05
7.04
7.03
7.03
7.01
7.01
2.50
2.48
2.46
2.33
2.11
2.10
2.08
2.08
2.07
2.05
1.87
1.85
1.83
1.82
1.80
1.79
1.77
1.75
10
9
8
7
6
5
4
3
2
1
ppm
0.98
4.12
2.04
7.29
5.10
2.15
3.00
1.96
1.99

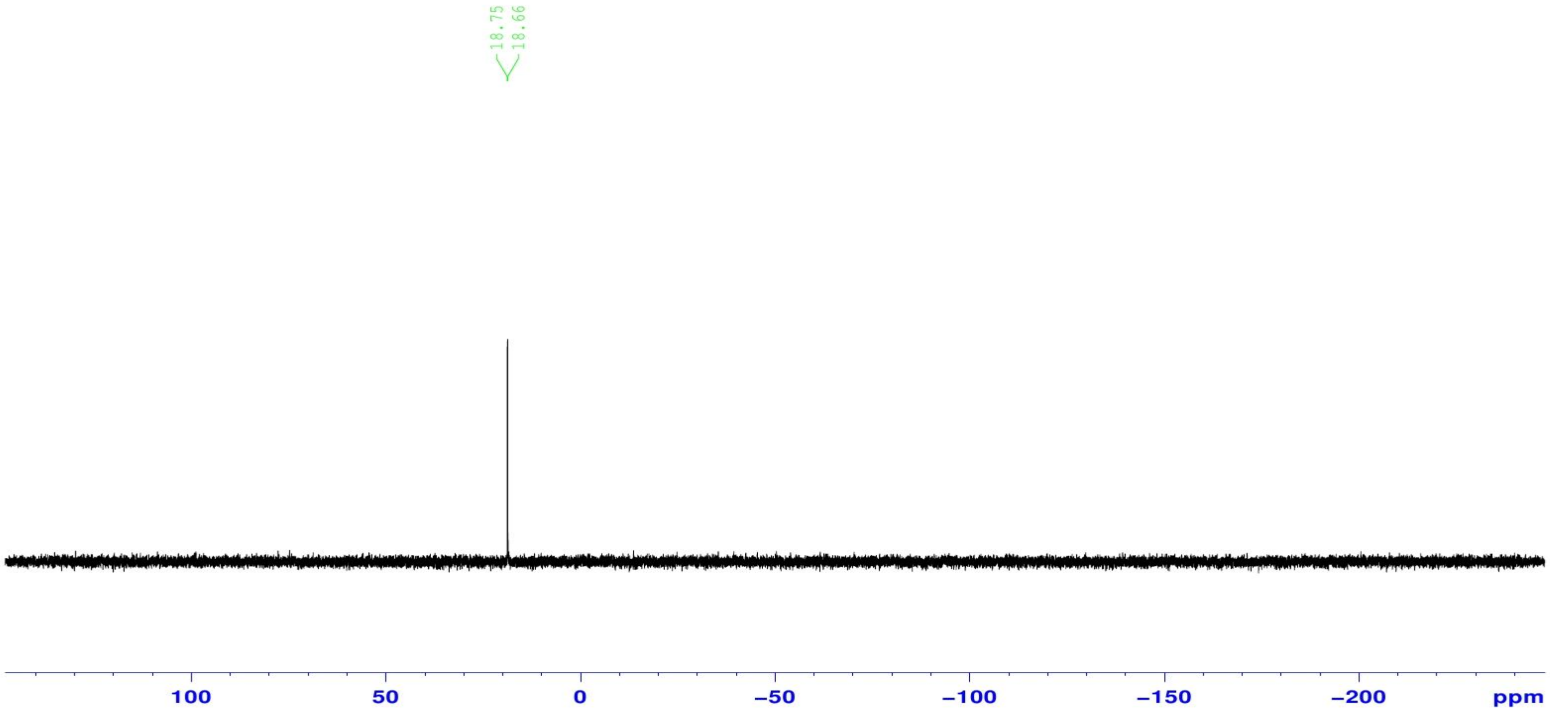
4a-C



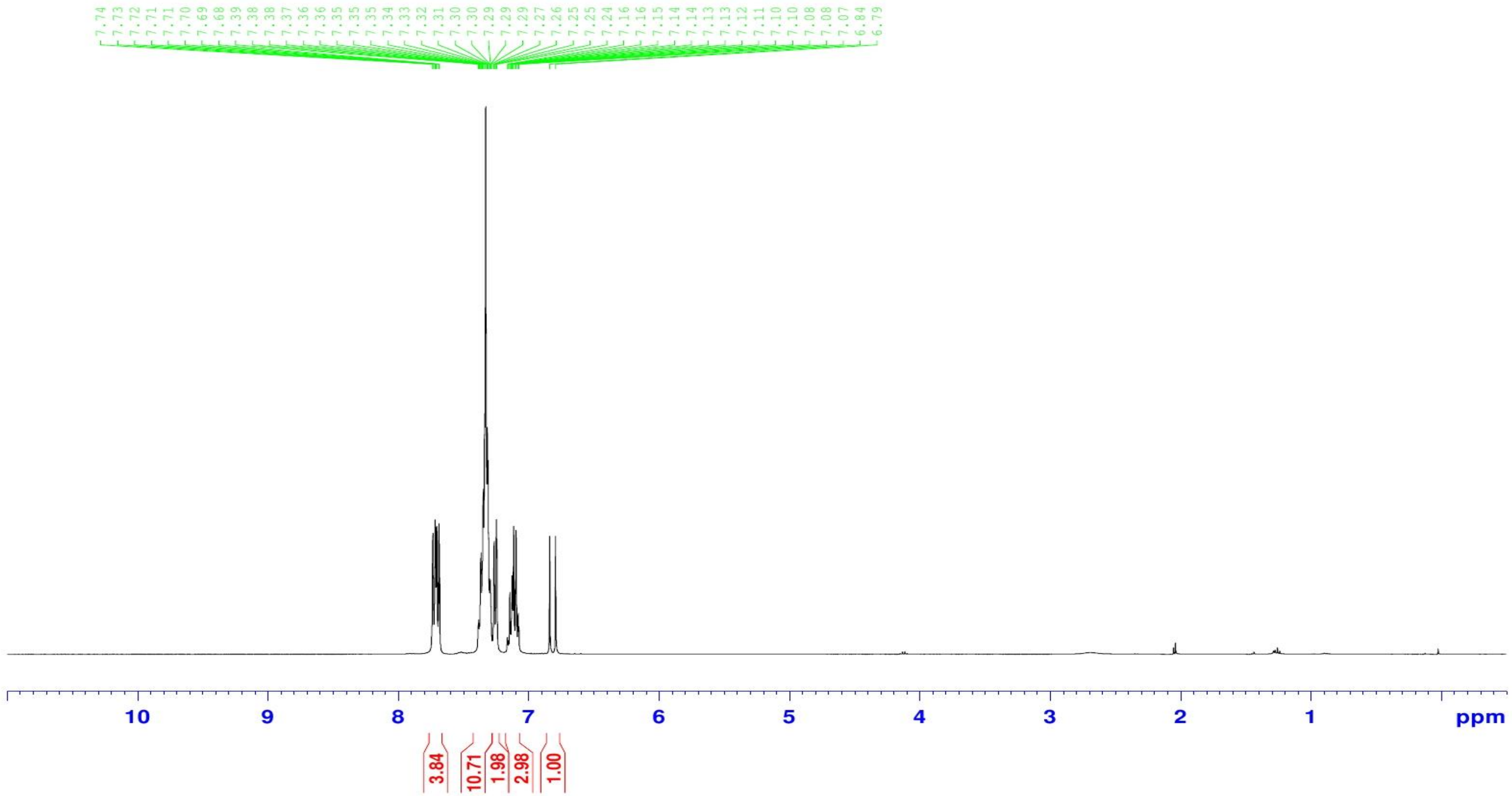
142.83
137.79
135.51
134.79
132.81
131.92
131.90
131.82
130.90
130.81
129.44
129.26
128.80
128.69
127.25
126.96
126.02
125.95
77.39
77.08
76.76
29.25
29.19
27.18
26.47
23.22
23.18
21.50
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



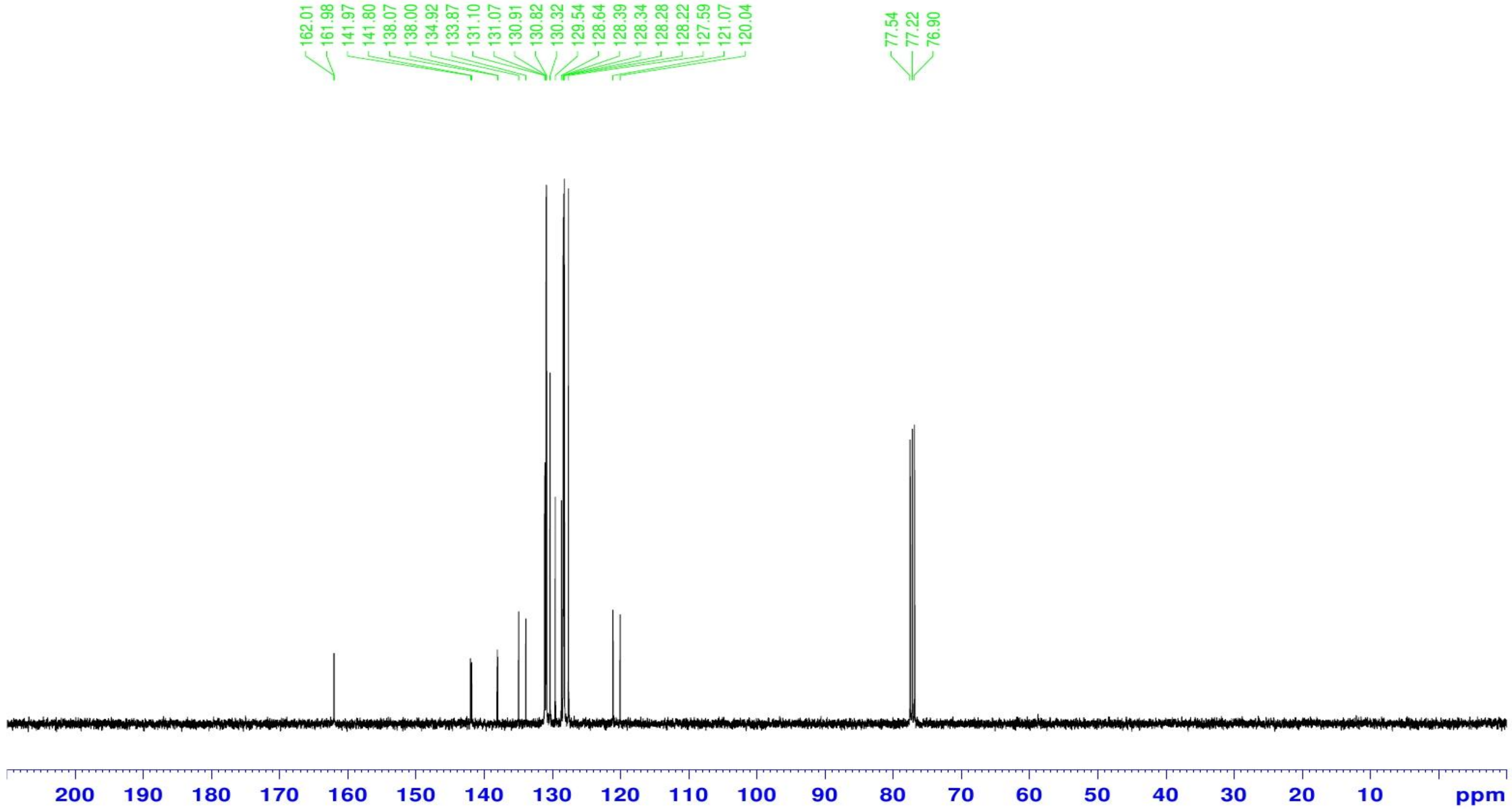
6a-P

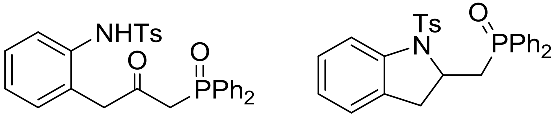


6a-H

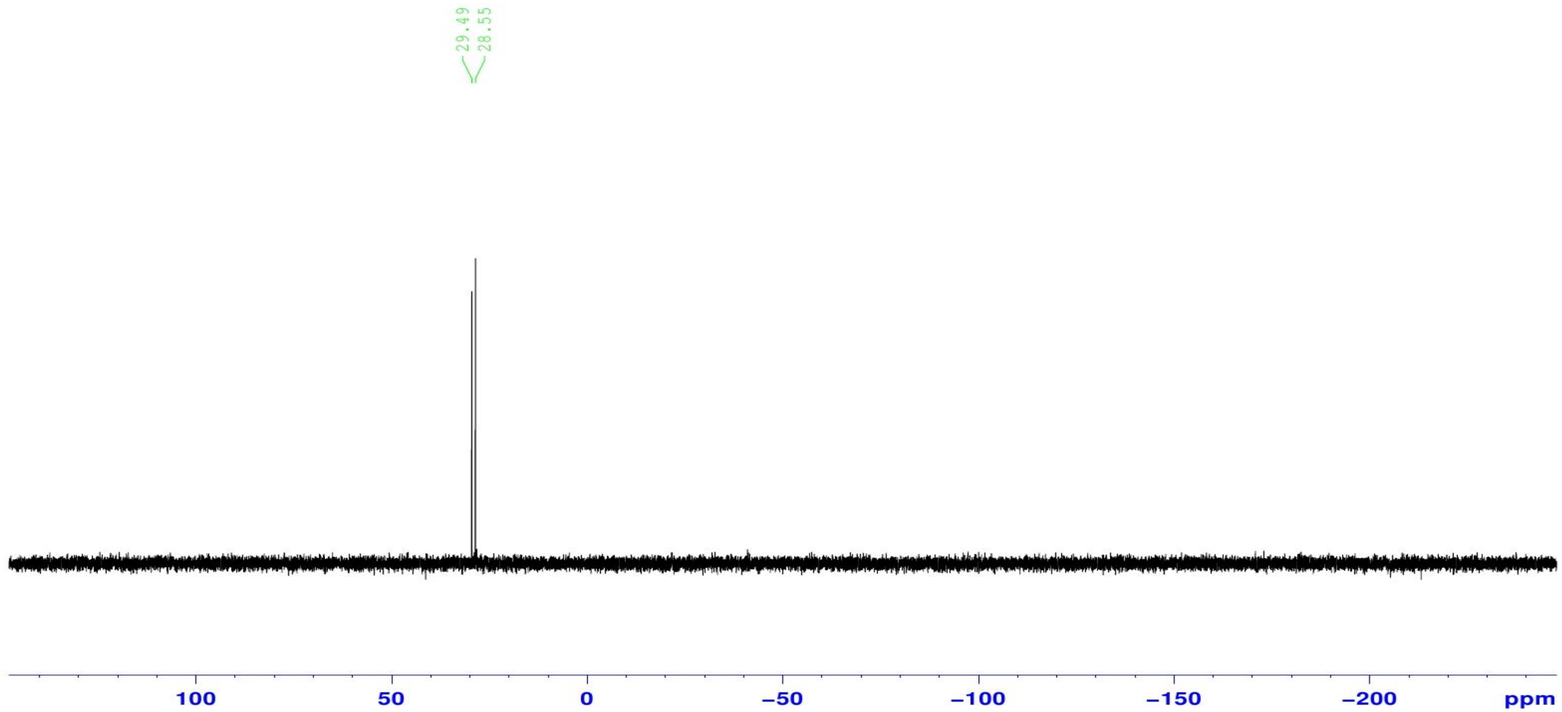


6a-C


162.01
161.98
141.97
141.80
138.07
138.00
134.92
133.87
131.10
131.07
130.91
130.82
130.32
129.54
128.64
128.39
128.34
128.28
128.22
127.59
121.07
120.04
77.54
77.22
76.90
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



8a:3a = 1:1-P



8a:3a = 1:1-H