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Supporting Information

Silver-Catalyzed Radical Ring-Opening of Cycloalkanols for the Synthesis of distal acylphosphine oxides

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Contents

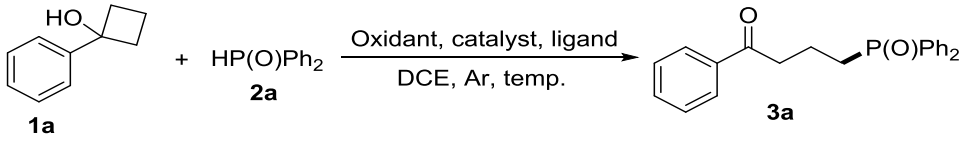
1. General Information

All reactions were performed under argon atmosphere. ^{1}H NMR (400 MHz or 300 MHz) and ^{13}C NMR (150, 100 or 75 MHz) spectra were determined on a Varian-Inova 300 MHz or 400 MHz spectrometer with $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard or 85% H_3PO_4 as external standard for ^{31}P NMR (162 MHz). Chemical shifts were reported in ppm from internal TMS (δ), all coupling constants (J values) were reported in Hertz (Hz). High resolution mass spectra were recorded on a microTOF-Q III (ESI). Column chromatography was performed with 300-400 mesh silica gel using flash column techniques. All of the reagents were used directly as obtained commercially unless otherwise noted.

2. Optimization of Reaction Conditions

2.1 Optimization of Reaction Conditions for 3a

Table S1. Screening of Reaction Conditions[a]

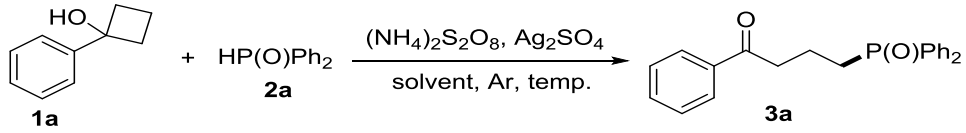


Entry	Oxidant	Catalyst (20 mol %)	Ligand	Temp. (^{o}C)	Yield (%)
1	$Mn(OAc)_3$	--	--	60	N.D.[b]
2	$CuCl_2$	--	--	60	N.D.[b]
3	CuCl	--	--	60	N.D.[b]
4	TBHP	--	--	60	N.D.[b]
5	DTBP	--	--	60	N.D.[b]
6	PIDA	--	--	60	N.D.[b]
7	$AgNO_3$	--	--	60	24
8	AgOAc	--	--	60	trace
9	Ag_2CO_3	--	--	60	23
10	Ag_2O	--	--	60	22
11	AgOTf	--	--	60	trace
12	$AgNO_2$	--	--	60	12
13	Ag_2SO_4	--	--	60	35
14	Ag_2SO_4	--	--	80	42
15	Ag_2SO_4	CuCl	bipy	80	N.D.[b]
16	Ag_2SO_4	CuI	bipy	80	N.D.[b]
17	Ag_2SO_4	CuOAc	bipy	80	N.D.[b]
18	Ag_2SO_4	CuTc	bipy	80	N.D.[b]
19	Ag_2SO_4	$Cu(OTf)_2$	bipy	80	N.D.[b]

20	$Na_2S_2O_8$	Ag_2SO_4	--	80	33
21	$K_2S_2O_8$	Ag_2SO_4	--	80	48
22	$K_2S_2O_8$	Ag_2SO_4	bipy	80	24
23	$K_2S_2O_8$	Ag_2SO_4	1,10-phen	80	22
24	$K_2S_2O_8$	Ag_2SO_4	TMEDA	80	25
25	$(NH_4)_2S_2O_8$	Ag_2SO_4	--	80	61
26	$Mg(NO_3)_2$	Ag_2SO_4	--	80	N.D.[b]
27	LPO	Ag_2SO_4	--	80	N.D.[b]

[a] Conditions: **1a** (0.1 mmol), $Ph_2P(O)H$ (0.2 mmol), catalyst (0.02 mmol), oxidant (0.3 mmol), DCE (1 mL) under argon atmosphere for 12 h. [b] N.D. means not detected.

Table S2. Screening of Solvents and Temperature[a]

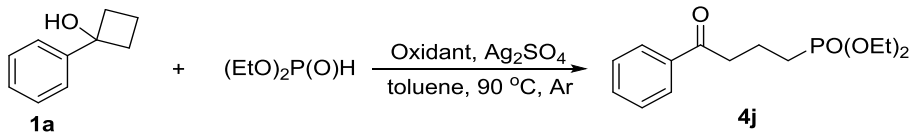


Entry	Oxidant	Catalyst (20 mol %)	Solvent	Temp. (^oC)	Yield (%)
1	$(NH_4)_2S_2O_8$	Ag_2SO_4	DCE	80	61
2	$(NH_4)_2S_2O_8$	Ag_2SO_4	MeCN	80	46
3	$(NH_4)_2S_2O_8$	Ag_2SO_4	PhH	80	52
4	$(NH_4)_2S_2O_8$	Ag_2SO_4	PhF	80	54
5	$(NH_4)_2S_2O_8$	Ag_2SO_4	Toluene	80	67
6	$(NH_4)_2S_2O_8$	Ag_2SO_4	DMF	80	trace
7	$(NH_4)_2S_2O_8$	Ag_2SO_4	DMSO	80	N.D.[b]
8	$(NH_4)_2S_2O_8$	Ag_2SO_4	DME	80	41
9	$(NH_4)_2S_2O_8$	Ag_2SO_4	THF	80	trace
10	$(NH_4)_2S_2O_8$	Ag_2SO_4	1,4-Dioxane	80	23
11	$(NH_4)_2S_2O_8$	Ag_2SO_4	EtOAc	80	14
12	$(NH_4)_2S_2O_8$	Ag_2SO_4	Cyclohexane	80	16
13	$(NH_4)_2S_2O_8$	Ag_2SO_4	$CHCl_3$	80	N.D.[b]
14	$(NH_4)_2S_2O_8$	Ag_2SO_4	PhCl	80	66
15	$(NH_4)_2S_2O_8$	Ag_2SO_4	Toluene	60	44
16	$(NH_4)_2S_2O_8$	Ag_2SO_4	Toluene	70	59
17	$(NH_4)_2S_2O_8$	Ag_2SO_4	Toluene	90	76
18	$(NH_4)_2S_2O_8$	Ag_2SO_4	DMF	90	19
19	$(NH_4)_2S_2O_8$	Ag_2SO_4	MeCN	90	52
20	$(NH_4)_2S_2O_8$	Ag_2SO_4	Toluene/H_2O	90	44
21	$(NH_4)_2S_2O_8$	Ag_2SO_4	PhH	90	60
22	$(NH_4)_2S_2O_8$	Ag_2SO_4	PhF	90	59
23	$(NH_4)_2S_2O_8$	Ag_2SO_4	PhCl	90	69

[a] Conditions: **1a** (0.1 mmol), $Ph_2P(O)H$ (0.2 mmol), catalyst (0.02 mmol), oxidant (0.3 mmol), solvent (1 mL) under argon atmosphere for 12 h. [b] N.D. means not detected.

2.2 Optimization of Reaction Conditions for 4j

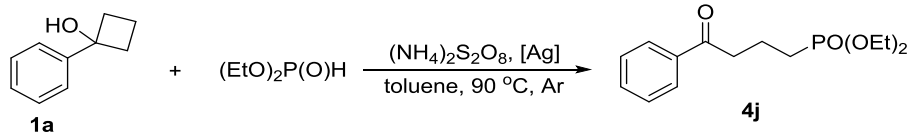
Table S3. Screening of oxidant[a]



Entry	Oxidant	Yield (%)
1	TBHP	N.D.[b]
2	DTBP	N.D.[b]
3	BPO	N.D.[b]
4	$K_2S_2O_8$	N.D.[b]
5	$Na_2S_2O_8$	N.D.[b]
6	$(NH_4)_2S_2O_8$	N.D.[b]
7	PIDA	N.D.[b]

[a] Conditions: **1a** (0.1 mmol), $(EtO)_2P(O)H$ (0.2 mmol), Ag_2SO_4 (0.02 mmol), oxidant (0.3 mmol), toluene (1 mL) under argon atmosphere at 90 °C for 12 h. [b] N.D. means not detected.

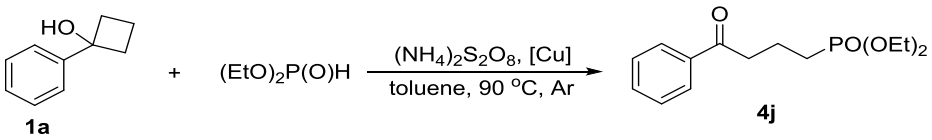
Table S4. Screening of silver catalyst[a]



Entry	[Ag]	Yield (%)
1	$AgNO_3$	N.D.[b]
2	AgOAc	N.D.[b]
3	Ag_2CO_3	N.D.[b]
4	Ag_2O	N.D.[b]
5	AgOTf	N.D.[b]
6	$AgNO_2$	N.D.[b]
7	AgTFA	N.D.[b]
8	AgOTs	N.D.[b]
9	$AgBF_4$	N.D.[b]
10	$AgSbF_6$	N.D.[b]

[a] Conditions: **1a** (0.1 mmol), $(EtO)_2P(O)H$ (0.2 mmol), [Ag] (0.02 mmol), $(NH_4)_2S_2O_8$ (0.3 mmol), toluene (1 mL) under argon atmosphere at 90 °C for 12 h. [b] N.D. means not detected.

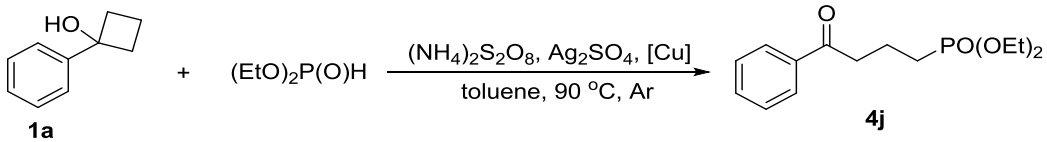
Table S5. Screening of copper catalyst[a]



Entry	[Cu]	Yield (%)
1	CuBr	N.D.[b]
2	CuI	Trace
3	CuOAc	Trace
4	CuTc	N.D.[b]
5	$Cu(OTf)_2$	Trace
6	$Cu(acac)_2$	Trace
7	$CuSO_4$	N.D.[b]
8	$Cu(OAc)_2$	N.D.[b]
9	$CuBr_2$	N.D.[b]
10	CuBr	N.D.[b]

[a] Conditions: **1a** (0.1 mmol), $(EtO)_2P(O)H$ (0.2 mmol), Cu salt (0.02 mmol), $(NH_4)_2S_2O_8$ (0.3 mmol), toluene (1 mL) under argon atmosphere at 90 °C for 12 h. [b] N.D. means not detected.

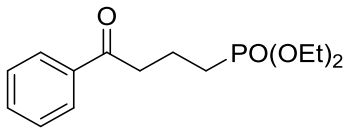
Table S6. Screening of Ag_2SO_4/[Cu] co-catalyst[a]



Entry	[Cu]	Yield (%)
1	CuBr	Trace
2	CuI	Trace
3	CuOAc	Trace
4	CuTc	Trace
5	$Cu(OTf)_2$	Trace
6	$Cu(acac)_2$	Trace
7	$CuSO_4$	Trace
8	$Cu(OAc)_2$	Trace
9	$CuBr_2$	N.D.[b]

[a] Conditions: **1a** (0.1 mmol), $(EtO)_2P(O)H$ (0.2 mmol), Ag_2SO_4 (0.02 mmol), Cu salt (0.02 mmol), $(NH_4)_2S_2O_8$ (0.3 mmol), toluene (1 mL) under argon atmosphere at 90 °C for 12 h. [b] N.D. means not detected.

Diethyl (4-oxo-4-phenylbutyl)phosphonate (4j)



HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{22}O_4P$ 285.1256, found 285.1255; $[M+Na]^+$ Calcd for $C_{14}H_{21}NaO_4P$ 307.1075, found 307.1093.

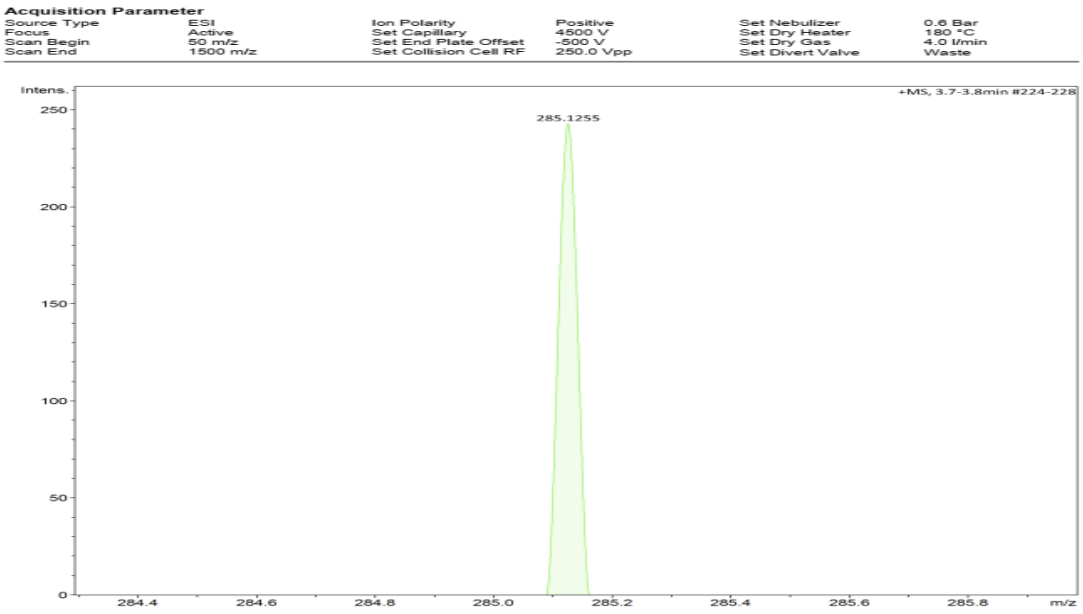


Figure S1. HRMS of compound **4j** (*m/z*: $[M+H]^+$ Calcd for $C_{14}H_{22}O_4P$ 285.1256, found 285.1255)

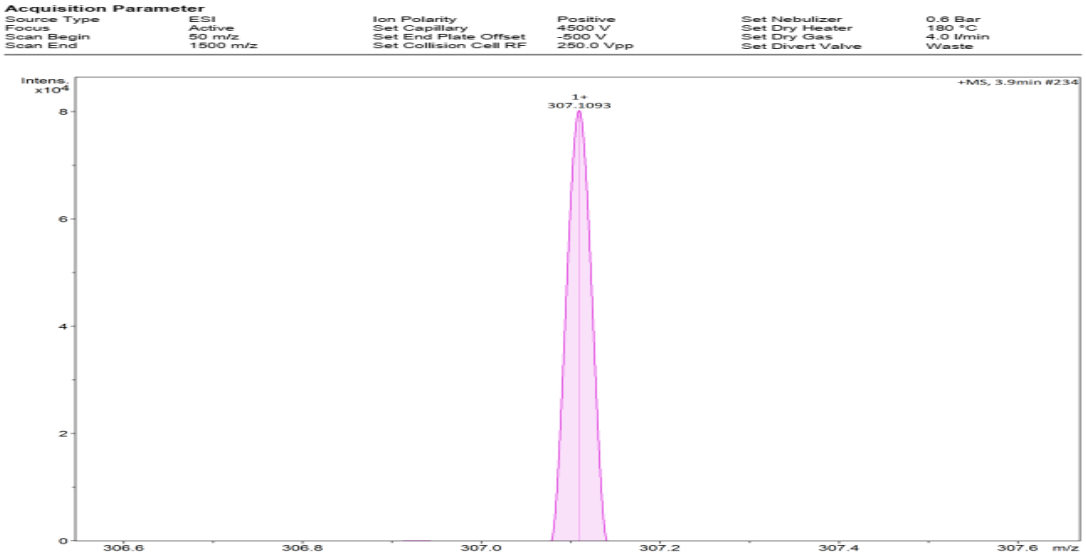
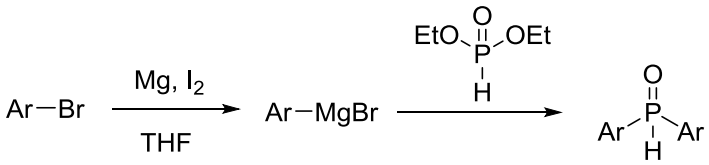


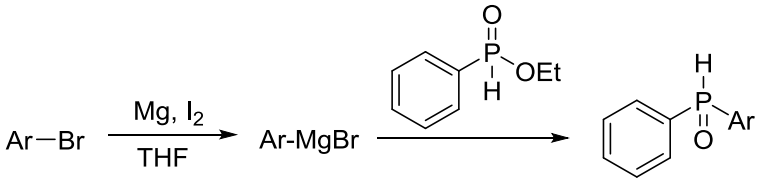
Figure S2. HRMS of compound **4j** (*m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{21}NaO_4P$ 307.1075, found 307.1093)

3. General Procedure for the Preparation of Diarylphosphine Oxides (GP1)

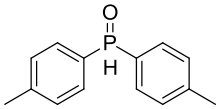
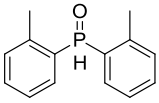
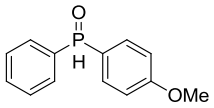


Arylmagnesium bromide was prepared from the corresponding aryl bromide (22 mmol), a grain of iodine and magnesium (57.6 mg, 24 mmol) in dry THF. Then, diethyl phosphite (1.29 mL, 10.0 mmol) was added drop-wise to a 2.5 M solution of the prepared arylmagnesium bromide at 0 ^{o}C. The mixture was cooled at 0 ^{o}C for 30 minutes, and then stirred at ambient temperature for 2-12 hours. Afterwards, the mixture was allowed to cool to 0 ^{o}C, followed by the slow addition of 30 mL aqueous NH_4Cl. The mixture was extracted with ethyl acetate, dried over with Mg_2SO_4, and the solvent was completely removed under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v : v = 1 : 1) as eluent to give the product.[1,2]

4. General Procedure for the Synthesis of Aryl-phenylphosphine Oxides (GP2)



Arylmagnesium bromide was prepared from the corresponding aryl bromide (22 mmol), a grain of iodine and magnesium (57.6 mg, 24 mmol) in dry THF. Afterwards, ethyl phenylphosphinate (1701 mg, 10.0 mmol) was added in a drop-wise manner to a solution of the prepared arylmagnesium bromide at 0 ^{o}C. The mixture was allowed to cool at 0 ^{o}C for 30 minutes, and then stirred at ambient temperature for 2-12 hours. Afterwards, the mixture was allowed to cool to 0 ^{o}C, followed by the slow addition of 30 mL aqueous NH_4Cl. The mixture was extracted with ethyl acetate, dried over with Mg_2SO_4, and the solvent was completely removed under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v : v = 1 : 1) as eluent to give the product.[3,4]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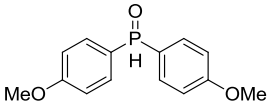	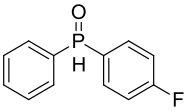	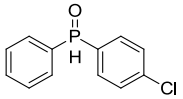
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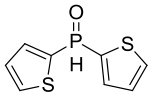
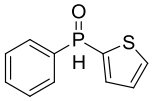
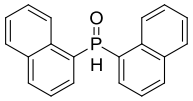
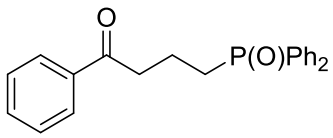
		
Ref. 1	Ref. 3	Ref. 2

5. General Procedure for the Preparation of Compounds 3 and 4 (GP3)

To a Schlenk tube was successively added cycloalkanol **1** (0.1 mmol), phosphine oxide **2** (0.2 mmol, 2 equiv), Ag_2SO_4 (6.2 mg, 0.02 mmol), $(NH_4)_2S_2O_8$ (68.5 mg, 0.3 mmol), and toluene (1 mL). The tube was sealed and then backfilled thrice with argon. The mixture was allowed to stir at 90 ℃ for 12 hours. Afterwards, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtered. The filtrate was concentrated under vacuum, and the residue was purified by column chromatography on silica gel using acetone/petroleum ether (v : v = 1 : 1.86) as eluent to give pure products **3** or **4**.

6. Characterization Data for Products 3, 4, 7 and 8

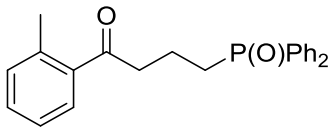
4-(Diphenylphosphoryl)-1-phenylbutan-1-one (3a)



According to the general procedure (**GP3**) using 1-phenylcyclobutanol **1a** (14.9 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3a** was obtained as colorless oil (26.5 mg, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92–7.87 (m, 2H), 7.81–7.72 (m, 4H), 7.57–7.38 (m, 9H), 3.15 (t, J = 6.6 Hz, 2H), 2.45–2.36 (m, 2H), 2.16–2.04 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.5, 136.8, 133.5, 133.3, 132.5, 131.89, 131.87, 131.0, 130.9, 128.9, 128.8, 128.7,

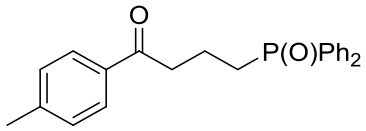
128.1, 38.8 (d, J = 12.2 Hz), 29.0 (d, J = 71.9 Hz), 16.6 (d, J = 3.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 33.0. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{22}O_2P$ 349.1357, found 349.1360.

4-(Diphenylphosphoryl)-1-(*o*-tolyl)butan-1-one (3b)



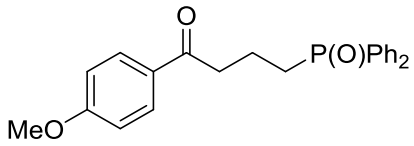
According to the general procedure (**GP3**) using 1-(*o*-tolyl)cyclobutanol **1b** (16.3 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3b** was obtained as colorless oil (29.4 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81–7.70 (m, 4H), 7.58–7.53 (m, 1H), 7.50–7.40 (m, 6H), 7.33 (td, J = 7.4, 1.4 Hz, 1H), 7.24–7.16 (m, 2H), 3.05 (t, J = 6.8 Hz, 2H), 2.45 (s, 3H), 2.42 – 2.28 (m, 2H), 2.13 – 1.96 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.3, 138.0, 137.6, 133.5, 132.6, 132.0, 131.79, 131.77, 131.4, 130.9, 130.8, 128.8, 128.7, 128.6, 125.8, 41.6 (d, J = 12.1 Hz), 29.0 (d, J = 71.8 Hz), 21.4, 16.8 (d, J = 3.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.5. **HRMS (ESI-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{23}NaO_2P$ 385.1333, found 385.1338.

4-(Diphenylphosphoryl)-1-(*p*-tolyl)butan-1-one (3c)



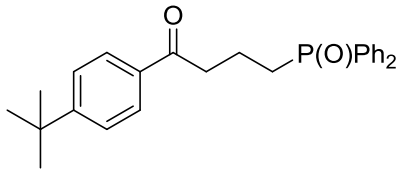
According to the general procedure (**GP3**) using 1-(*p*-tolyl)cyclobutanol **1c** (16.3 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3c** was obtained as colorless oil (30.8 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82–7.74 (m, 4H), 7.70 (d, J = 8.4 Hz, 2H), 7.55–7.40 (m, 6H), 7.38-7.27 (m, 2H), 3.14 (t, J = 6.7 Hz, 2H), 2.48–2.33 (m, 5H), 2.19–2.03 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.6, 138.4, 136.8, 134.0, 133.6, 132.6, 131.78, 131.75, 130.9, 130.8, 128.8, 128.7, 128.6, 128.5, 125.3, 38.8 (d, J = 12.2 Hz), 28.9 (d, J = 71.9 Hz), 21.4, 16.6 (d, J = 3.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.6. **HRMS (ESI-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{23}NaO_2P$ 385.1333, found 385.1340.

4-(Diphenylphosphoryl)-1-(4-methoxyphenyl)butan-1-one (3d)



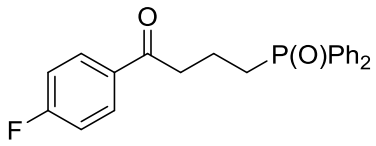
According to the general procedure (**GP3**) using 1-(4-methoxyphenyl)cyclobutanol **1d** (17.9 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3d** was obtained as colorless oil (26.1 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91–7.86 (m, 2H), 7.82–7.73 (m, 4H), 7.54–7.40 (m, 6H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.09 (t, *J* = 6.6 Hz, 2H), 2.55–2.30 (m, 2H), 2.15–2.01 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.1, 163.6, 133.7, 132.7, 131.83, 131.81, 131.0, 130.9, 130.4, 130.0, 128.9, 128.7, 113.9, 55.6, 38.5 (d, *J* = 12.2 Hz), 29.1 (d, *J* = 71.9 Hz), 16.9 (d, *J* = 3.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.7. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{24}O_3P$ 379.1463, found 379.1456.

1-(4-(*tert*-Butyl)phenyl)-4-(diphenylphosphoryl)butan-1-one (3e)



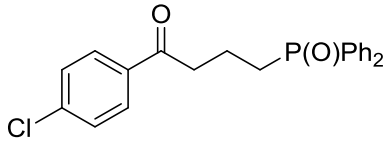
According to the general procedure (**GP3**) using 1-(4-(*tert*-butyl)phenyl)cyclobutanol **1e** (20.5 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3e** was obtained as colorless oil (34.3 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.81–7.73 (m, 4H), 7.50–7.42 (m, 8H), 3.12 (t, *J* = 6.6 Hz, 2H), 2.48–2.32 (m, 2H), 2.15–2.01 (m, 2H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.2, 157.1, 134.3, 131.9, 131.1, 128.9, 128.1, 125.7, 38.8, 35.2, 31.2, 16.7; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.7. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{30}O_2P$ 405.1983, found 405.1977.

4-(Diphenylphosphoryl)-1-(4-fluorophenyl)butan-1-one (3f)



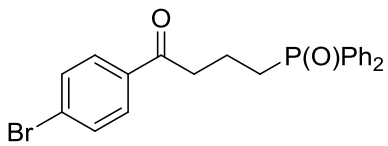
According to the general procedure (**GP3**) using 1-(4-fluorophenyl)cyclobutanol **1f** (16.7 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3f** was obtained as colorless oil (23.8 mg, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98–7.89 (m, 2H), 7.83–7.70 (m, 4H), 7.55–7.42 (m, 6H), 7.10 (t, *J* = 8.6 Hz, 2H), 3.13 (t, *J* = 6.7 Hz, 2H), 2.48–2.33 (m, 2H), 2.20–2.01 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.9, 165.9 (d, *J* = 254.8 Hz), 133.6, 133.3(d, *J* = 3.2 Hz), 132.6, 131.90 131.88, 131.0, 130.9, 130.8, 130.7, 128.9, 128.8, 115.9, 115.7, 38.7 (d, *J* = 11.5 Hz), 28.9 (d, *J* = 71.9 Hz), 16.7 (d, *J* = 3.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.6. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{21}FO_2P$ 367.1263, found 367.1267.

1-(4-Chlorophenyl)-4-(diphenylphosphoryl)butan-1-one (3g)



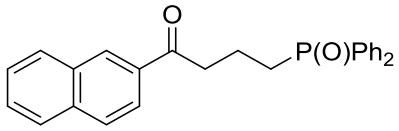
According to the general procedure (**GP3**) using 1-(4-chlorophenyl)cyclobutanol **1g** (18.3 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3g** was obtained as colorless oil (26.7 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86–7.81 (m, 2H), 7.80–7.71 (m, 4H), 7.53–7.42 (m, 6H), 7.41–7.37 (m, 2H), 3.13 (t, *J* = 6.7 Hz, 2H), 2.44–2.34 (m, 2H), 2.10–2.03 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.2, 139.7, 135.1, 133.5, 132.6, 131.89, 131.87, 130.9, 130.8, 129.5, 129.0, 128.9, 128.8, 38.7 (d, *J* = 11.4 Hz), 28.8 (d, *J* = 71.9 Hz), 16.6 (d, *J* = 3.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.6. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{21}ClO_2P$ 383.0968, found 383.0960.

1-(4-Bromophenyl)-4-(diphenylphosphoryl)butan-1-one (3h)



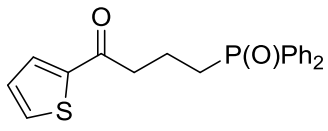
According to the general procedure (**GP3**) using 1-(4-bromophenyl)cyclobutanol **1h** (22.6 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3h** was obtained as colorless oil (32.8 mg, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78–7.71 (m, 6H), 7.56–7.52 (m, 2H), 7.5 –7.40 (m, 6H), 3.10 (t, J = 6.7 Hz, 2H), 2.43–2.33 (m, 2H), 2.14–1.99 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.3, 135.3, 133.4, 132.5, 131.8, 130.7, 129.5, 128.7, 128.3, 38.5, 28.7 (d, J = 71.6 Hz), 16.5; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.5. **HRMS (ESI-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{20}BrNaO_2P$ 449.0282, found 449.0280.

4-(Diphenylphosphoryl)-1-(naphthalen-2-yl)butan-1-one (3i)



According to the general procedure (**GP3**) using 1-(naphthalen-2-yl)cyclobutanol **1i** (19.9 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3i** was obtained as colorless oil (29.8 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.58 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.88–7.85 (m, 1H), 7.82 (dd, J = 7.2, 0.9 Hz, 1H), 7.79–7.73 (m, 4H), 7.61–7.42 (m, 9H), 3.23 (t, J = 6.7 Hz, 2H), 2.50–2.41 (m, 2H), 2.23–2.09 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.7, 135.6, 134.1, 132.9, 131.92, 131.89, 131.0, 130.9, 130.2, 128.9, 128.8, 128.6, 128.1, 128.0, 126.6, 125.8, 124.5, 42.1 (d, J = 12.2 Hz), 29.0 (d, J = 71.3 Hz), 17.2 (d, J = 3.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.9. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{24}O_2P$ 399.1514, found 399.1510.

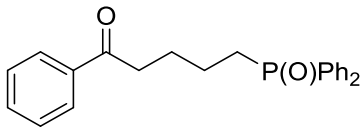
4-(Diphenylphosphoryl)-1-(thiophen-2-yl)butan-1-one (3j)



According to the general procedure (**GP3**) using 1-(thiophen-2-yl)cyclobutanol **1j** (15.5 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3j** was obtained as colorless oil (18.1 mg, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81–7.72 (m, 4H), 7.66 (d, J = 3.8

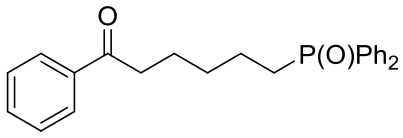
Hz, 1H), 7.61 (d, *J* = 4.9 Hz, 1H), 7.54–7.41 (m, 6H), 7.10 (t, *J* = 4.4 Hz, 1H), 3.08 (t, *J* = 6.7 Hz, 2H), 2.45–2.35 (m, 2H), 2.17–2.04 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.5, 144.2, 133.8, 133.5, 132.6, 132.2, 131.90, 131.87, 131.0, 130.9, 128.9, 128.8, 128.3, 39.5, 29.0 (d, *J* = 71.9 Hz), 17.0 (d, *J* = 3.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.6. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{20}O_2PS$ 355.0922, found 355.0919.

5-(Diphenylphosphoryl)-1-phenylpentan-1-one (3m)



According to the general procedure (**GP3**) using 1-phenylcyclopentanol **1m** (16.3 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3m** was obtained as colorless oil (21.5 mg, 58%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92–7.88 (m, 2H), 7.77–7.70 (m, 4H), 7.58–7.40 (m, 9H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.37–2.28 (m, 2H), 1.91–1.81 (m, 2H), 1.79–1.68 (m, 2H); **^{13}C NMR** (100 MHz, DMSO): δ 199.9, 137.0, 133.6, 133.2, 132.6, 131.9, 131.9, 131.0, 130.9, 128.9, 128.8, 128.7, 128.1, 38.2, 29.9 (d, *J* = 71.8 Hz), 25.6 (d, *J* = 15.3 Hz), 21.5 (d, *J* = 3.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.2. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{24}O_2P$ 363.1514，found 363.1510.

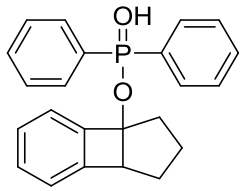
6-(Diphenylphosphoryl)-1-phenylhexan-1-one (3n)



According to the general procedure (**GP3**) using 1-phenylcyclohexanol **1n** (17.7 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3n** was obtained as colorless oil (19.5 mg, 52%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95–7.89 (m, 2H), 7.78–7.68 (m, 4H), 7.59–7.39 (m, 9H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.33–2.22 (m, 2H), 1.7–1.62 (m, 4H), 1.56–1.45 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.2, 137.1, 133.7, 133.1, 132.7, 131.80, 131.77, 130.9, 130.8, 128.8, 128.70, 128.69, 128.1, 38.2, 30.6 (d, *J* = 14.5 Hz), 29.7 (d, *J* = 72.1 Hz), 23.7, 21.4 (d, *J* = 3.8 Hz);

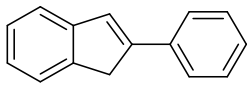
^{31}P NMR (162 MHz, $CDCl_3$): δ 32.4. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{26}O_2P$ 377.1670, found 377.1664.

1,2,3,7b-Tetrahydro-*3aH*-cyclopenta[3,4]cyclobuta[1,2]benzen-*3a*-yl diphenylphosphinate (3p')



According to the general procedure (**GP3**) using 1,2,3,7b-tetrahydro-3a*H*-cyclopenta[3,4]-cyclobuta[1,2]benzen-3a-ol **1p'** (16.0 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3p'** was obtained as colorless oil (29.9 mg, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83–7.70 (m, 4H), 7.51–7.31 (m, 6H), 7.20 (td, *J* = 7.5, 1.0 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.93– 6.87 (m, 1H), 3.97 (d, *J* = 6.7 Hz, 1H), 2.26 (dd, *J* = 12.6, 6.1 Hz, 1H), 2.06–1.96 (m, 1H), 1.85–1.68 (m, 3H), 1.10–0.96 (tt, *J* = 12.3, 6.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 144.5 (d, *J* = 4.8 Hz), 142.8, 134.1 (d, *J* = 12.9 Hz), 132.7 (d, *J* = 13.6 Hz), 131.9 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 2.9 Hz), 131.73, 131.66, 131.62, 131.56, 130.0, 128.5, 128.40, 128.35, 128.3, 127.9, 122.8, 122.5, 93.4 (d, *J* = 8.6 Hz), 55.8 (d, *J* = 5.2 Hz), 36.7 (d, *J* = 3.2 Hz), 28.2, 24.4. **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.2. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{22}O_2P$ 361.1357, found 361.1356.

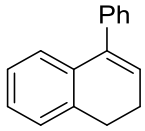
2-Phenyl-1*H*-indene (3q')



According to the general procedure (**GP3**) using 2-phenyl-2,3-dihydro-1H-inden-2-ol **1q'** (21.0 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3q'** was obtained as colorless oil (17.5 mg, 91%).[7] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73–7.66 (m, 2H), 7.57–7.51 (m, 1H), 7.49–7.41 (m, 3H), 7.39–7.30 (m, 2H), 7.32–7.21 (m, 2H), 3.85 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 146.5, 145.5, 143.3, 136.1, 128.8, 127.6, 126.8, 126.6, 125.8, 124.9,

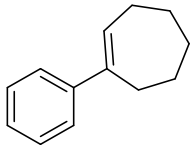
123.8, 121.1, 39.1. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{13}$ 193.1017, found 193.1022.

4-Phenyl-1,2-dihydronaphthalene (3r')



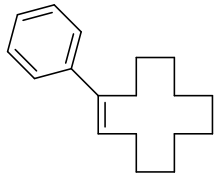
According to the general procedure (**GP3**) using 1-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol **1r'** (22.4 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3r'** was obtained as colorless oil (17.5 mg, 85%).[8] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39–7.24 (m, 5H), 7.20–7.04 (m, 3H), 7.00 (d, J = 7.7 Hz, 1H), 6.06 (t, J = 4.8 Hz, 1H), 2.82 (t, J = 8.0 Hz, 2H), 2.42–2.33 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.1, 140.2, 137.1, 135.4, 129.1, 128.5, 127.93, 127.9, 127.4, 127.3, 126.5, 125.8, 28.6, 23.9. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{15}$ 207.1174, found 207.1176.

1-Phenylcyclohept-1-ene (3s')



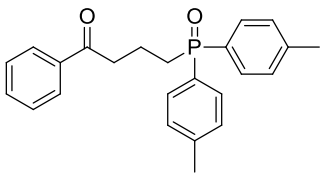
According to the general procedure (**GP3**) using 1-phenylcycloheptan-1-ol **1s'** (19.0 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3s'** was obtained as colorless oil (15.3 mg, 89%).[5] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27–7.18 (m, 4H), 7.15–7.08 (m, 1H), 6.02 (t, J = 6.8 Hz, 1H), 2.58–2.51 (m, 2H), 2.29–2.17 (m, 2H), 1.82–1.72 (m, 2H), 1.63–1.53 (m, 2H), 1.53–1.44 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 145.1 (d, J = 2.7 Hz), 130.5, 128.2, 126.4, 125.8, 32.9, 29.0, 27.1, 27.0. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{17}$ 173.1330, found 173.1327.

1-Phenylcyclododec-1-ene (3t')



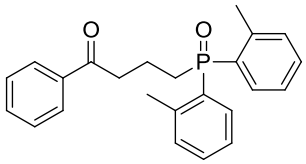
According to the general procedure (**GP3**) using 1-phenylcyclododecan-1-ol **1t'** (26.0 mg, 0.1 mmol) and diphenylphosphine oxide **2a** (40.5 mg, 0.2 mmol), compound **3t'** was obtained as colorless oil (22.3 mg, 92%).[6] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 – 7.27 (m, 4H), 7.24 – 7.15 (m, 1H), 5.58 (t, J = 7.8 Hz, 1H), 2.59 (t, J = 6.8 Hz, 2H), 2.26 (q, J = 7.1 Hz, 2H), 1.60 – 1.52 (m, 2H), 1.46 – 1.30 (m, 12H), 1.22 – 1.15 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.6, 140.5, 130.5, 128.2, 126.9, 126.5, 29.8, 27.5, 25.7, 25.6, 25.5, 25.0, 24.9, 24.5, 24.4, 22.6, 22.6. **HRMS (ESI-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{26}Na$ 265.1932, found 265.1933.

4-(Di-*p*-tolylphosphoryl)-1-phenylbutan-1-one (4a)



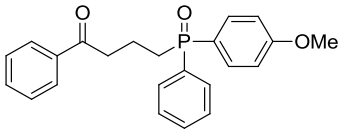
According to the general procedure (**GP3**) using 1-phenylcyclobutanol **1a** (14.9 mg, 0.1 mmol) and di-*p*-tolylphosphine oxide **2b** (46.2 mg, 0.2 mmol), compound **4a** was obtained as colorless oil (29.3 mg, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.1 Hz, 2H), 7.64 (dd, J = 11.3, 7.8 Hz, 4H), 7.54 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.27–7.23 (m, 4H), 3.14 (t, J = 6.6 Hz, 2H), 2.41–2.32 (m, 8H), 2.16–2.02 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.6, 142.2, 142.2, 136.9, 133.2, 131.0, 130.9, 130.6, 129.6, 129.5, 128.7, 128.1, 38.8 (d, J = 11.8 Hz), 29.2 (d, J = 71.9 Hz), 21.7, 16.8 (d, J = 3.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.9. **HRMS (ESI-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{25}NaO_2P$ 399.1490, found 399.1495.

4-(Di-*o*-tolylphosphoryl)-1-phenylbutan-1-one (4b)



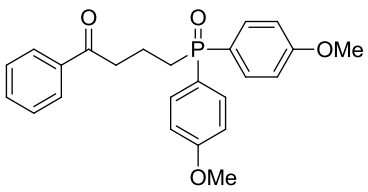
According to the general procedure (**GP3**) using 1-phenylcyclobutanol **1a** (14.9 mg, 0.1 mmol) and di-*o*-tolylphosphine oxide **2c** (46.2 mg, 0.2 mmol), compound **4b** was obtained as colorless oil (27.1 mg, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (d, J = 7.4 Hz, 2H), 7.84–7.75 (m, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.47–7.34 (m, 4H), 7.31–7.24 (m, 2H), 7.20–7.14 (m, 2H), 3.17 (t, J = 6.4 Hz, 2H), 2.55–2.44 (m, 2H), 2.31 (s, 6H), 2.16–2.03 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.6, 141.7, 141.6, 136.9, 133.3, 132.2, 132.1, 132.0, 131.9, 128.7, 128.1, 125.9, 125.7, 38.9 (d, J = 12.4 Hz), 28.3 (d, J = 71.8 Hz), 21.3 (d, J = 4.2 Hz), 16.8; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 34.5. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{26}O_2P$ 377.1670, found 377.1668.

4-((4-Methoxyphenyl)(phenyl)phosphoryl)-1-phenylbutan-1-one (4c)



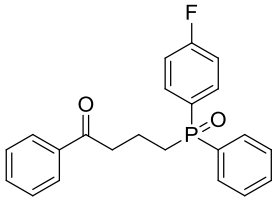
According to the general procedure (**GP3**) using 1-phenylcyclobutanol **1a** (14.9 mg, 0.1 mmol) and (4-methoxyphenyl)(phenyl)phosphine oxide **2d** (46.6 mg, 0.2 mmol), compound **4c** was obtained as colorless oil (23.8 mg, 63%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92–7.87 (m, 2H), 7.79–7.65 (m, 4H), 7.54 (t, J = 7.4 Hz, 1H), 7.50–7.39 (m, 5H), 6.95 (dd, J = 8.8, 2.0 Hz, 2H), 3.81 (s, 3H), 3.13 (t, J = 6.6 Hz, 2H), 2.42–2.32 (m, 2H), 2.14–2.01 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.6, 162.5, 136.8, 133.3, 132.9, 132.8, 131.7, 130.9, 130.8, 128.8, 128.7, 128.1, 114.5, 114.3, 55.4, 38.8 (d, J = 12.5 Hz), 29.2 (d, J = 72.5 Hz), 16.7 (d, J = 2.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.7. **HRMS (ESI-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{23}NaO_3P$ 401.1283, found 401.1280.

4-(Bis(4-methoxyphenyl)phosphoryl)-1-phenylbutan-1-one (4d)



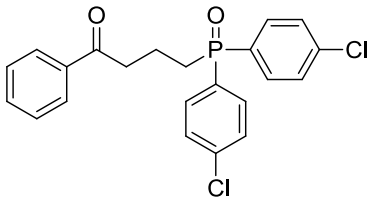
According to the general procedure (**GP3**) using 1-phenylcyclobutanol **1a** (14.9 mg, 0.1 mmol) and bis(4-methoxyphenyl)phosphine oxide **2e** (52.6 mg, 0.2 mmol), compound **4d** was obtained as colorless oil (22.4 mg, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.5 Hz, 2H), 7.67 (t, J = 9.3 Hz, 4H), 7.54 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 6.95 (d, J = 7.6 Hz, 4H), 3.82 (s, 6H) 3.14 (t, J = 6.3 Hz, 2H), 2.40–2.28 (m, 2H), 2.15–2.04 (m, 2H); **^{13}C NMR** (100 MHz, DMSO): δ 199.5, 161.7, 136.5, 133.2, 132.3, 132.2, 128.7, 127.8, 125.8, 124.8, 114.3, 114.2, 55.3, 38.4 (d, J = 13.0 Hz), 28.2 (d, J = 72.6 Hz), 16.5 (d, J = 3.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.1. **HRMS (ESI-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{25}NaO_4P$ 431.1388, found 431.1388.

4-((4-Fluorophenyl)(phenyl)phosphoryl)-1-phenylbutan-1-one (4e)



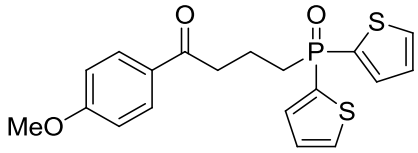
According to the general procedure (**GP3**) using 1-phenylcyclobutanol **1a** (14.9 mg, 0.1 mmol) and (4-fluorophenyl)(phenyl)phosphine oxide **2f** (44.1 mg, 0.2 mmol), compound **4e** was obtained as colorless oil (17.9 mg, 49%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93–7.88 (m, 2H), 7.82–7.72 (m, 4H), 7.58–7.41 (m, 6H), 7.15 (td, J = 8.7, 2.0 Hz, 2H), 3.16 (t, J = 6.5 Hz, 2H), 2.44–2.34 (m, 2H), 2.15–2.04 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.4, 163.8 (d, J = 3.1 Hz), 136.8, 133.6–133.3 (m), 132.0, 132.0, 130.9, 130.8, 129.0, 128.9, 128.8, 128.1, 116.4, 116.24, 116.16, 116.0, 38.7 (d, J = 12.4 Hz), 29.1 (d, J = 72.4 Hz), 16.6 (d, J = 3.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.2. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{21}FO_2P$ 367.1263, found 367.1259.

4-(Bis(4-chlorophenyl)phosphoryl)-1-phenylbutan-1-one (4f)



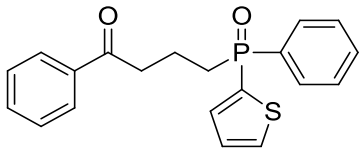
According to the general procedure (**GP3**) using 1-phenylcyclobutanol **1a** (14.9 mg, 0.1 mmol) and bis(4-chlorophenyl)phosphine oxide **2g** (54.0 mg, 0.2 mmol), compound **4f** was obtained as colorless oil (32.9 mg, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94–7.86 (m, 2H), 7.69 (dd, J = 10.9, 8.2 Hz, 4H), 7.60–7.52 (m, 1H), 7.49–7.41 (m, 6H), 3.15 (t, J = 6.4 Hz, 2H), 2.45–2.31 (m, 2H), 2.17–2.00 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.3, 138.8, 138.7, 136.7, 133.4, 132.3, 132.2, 131.8, 130.8, 129.4, 129.3, 128.8, 128.1, 38.5 (d, J = 12.7 Hz), 28.8 (d, J = 72.8 Hz), 16.5 (d, J = 3.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.6. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{20}Cl_2O_2P$ 417.0578, found 417.0579.

4-(Di(thiophen-2-yl)phosphoryl)-1-phenylbutan-1-one (4g)



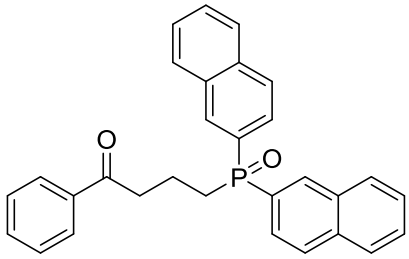
According to the general procedure (**GP3**) using 1-phenylcyclobutanol **1a** (14.9 mg, 0.1 mmol) and bis(4-chlorophenyl)phosphine oxide **2h** (54.0 mg, 0.2 mmol), compound **4g** was obtained as colorless oil (20.7 mg, 53%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 77.95–7.87 (m, 2H), 7.74–7.67 (m, 2H), 7.67–7.59 (m, 2H), 7.22–7.15 (m, 2H), 6.95–6.87 (m, 2H), 3.86 (s, 3H), 3.12 (t, J = 6.7 Hz, 2H), 2.48–2.36 (m, 2H), 2.22–2.08 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.8, 163.7, 135.6, 135.5, 133.6, 133.5, 133.4, 130.4, 129.9, 128.6, 128.4, 113.9, 55.6, 38.3 (d, J = 12.9 Hz), 33.3 (d, J = 79.8 Hz), 17.0 (d, J = 3.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 22.5. **HRMS (ESI-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{19}NaO_3PS_2$ 413.0411, found 413.0409.

1-Phenyl-4-(phenyl(thiophen-2-yl)phosphoryl)butan-1-one (4h)



According to the general procedure (**GP3**) using 1-phenylcyclobutanol **1a** (14.9 mg, 0.1 mmol) and phenyl(thiophen-2-yl)phosphine oxide **2i** (41.7 mg, 0.2 mmol), compound **4h** was obtained as colorless oil (21.9 mg, 62%). **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.03–7.99 (m, 1H), 7.93–7.89 (m, 2H), 7.84–7.76 (m, 2H), 7.68–7.64 (m, 1H), 7.61 (dt, J = 2.6, 1.6 Hz, 1H), 7.58–7.48 (m, 5H), 7.29–7.26 (m, 1H), 3.19 (t, J = 7.1 Hz, 2H), 2.48–2.38 (m, 2H), 1.91–1.72 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6): δ 199.4, 136.5, 135.5, 134.7, 134.6, 133.8 (d, J = 4.4 Hz), 131.8 (d, J = 2.7 Hz), 130.3, 130.2, 128.8, 128.71, 128.67, 127.8, 38.3 (d, J = 13.8 Hz), 29.8 (d, J = 74.8 Hz), 16.4 (d, J = 3.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ 27.9. **HRMS (ESI-TOF)** *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{19}NaO_2PS$ 377.0741, found 377.0744.

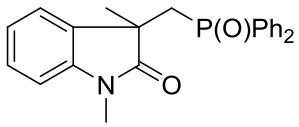
4-(Di(naphthalen-1-yl)phosphoryl)-1-phenylbutan-1-one (4i)



According to the general procedure (**GP3**) using 1-phenylcyclobutanol **1a** (14.9 mg, 0.1 mmol) and di(naphthalen-1-yl)phosphine oxide **2j** (60.6 mg, 0.2 mmol), compound **4i** was obtained as colorless oil (28.7 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (dd, J = 13.2, 1.5 Hz, 2H), 7.97–7.82 (m, 8H), 7.78–7.70 (m, 2H), 7.61–7.48 (m, 5H), 7.44–7.35 (m, 2H), 3.19 (t, J = 6.6 Hz, 2H), 2.66–2.55 (m, 2H), 2.27–2.12 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.5, 136.8, 134.8, 133.3, 132.9, 132.8, 132.7, 130.7, 129.7, 129.0, 128.8, 128.7, 128.2, 128.1, 128.0, 127.1, 125.8, 125.7, 38.7 (d, J = 12.5 Hz), 28.8 (d, J = 72.1 Hz), 16.8. **^{31}P NMR** (162 MHz, $CDCl_3$): δ 33.0. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{26}O_2P$ 449.1670, found 449.1666.

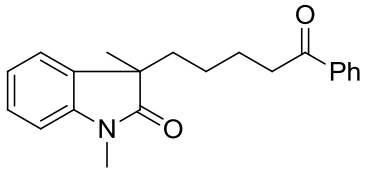
Detection of Radical Intermediates

3-((Diphenylphosphoryl)methyl)-1,3-dimethylindolin-2-one (7)



To a Schlenk tube was successively added diphenylphosphine oxide **2a** (40.4 mg, 0.2 mmol), *N*-methyl-*N*-phenylmethacrylamide **6** (35.4 mg, 0.2 mmol), Ag_2SO_4 (6.2 mg, 0.02 mmol), $(NH_4)_2S_2O_8$ (68.5 mg, 0.3 mmol) and toluene (1 mL). The tube was sealed and then backfilled thrice with argon. The reaction mixture was stirred at 90 ℃ for 12 hours, and then allowed to cool to room temperature. Afterwards, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtered. The filtrate was concentrated under vacuum, and the residue was purified by column chromatography on silica gel (acetone/petroleum ether = 1.86:1) to afford compound **7** as colorless oil (31.4 mg, 42%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58–7.51 (m, 2H), 7.50–7.44 (m, 2H), 7.43–7.27 (m, 6H), 7.17–7.10 (m, 2H), 6.76 (td, *J* = 7.6, 0.8 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 3.07 (dd, *J* = 15.2, 10.3 Hz, 1H), 3.00 (s, 3H), 2.84 (dd, *J* = 15.2, 10.7 Hz, 1H), 1.41 (d, *J* = 1.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 179.6 (d, *J* = 4.0 Hz), 143.1, 134.3, 133.6, 133.3, 132.6, 131.5 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 2.5 Hz), 130.8 (d, *J* = 9.4 Hz), 130.6 (d, *J* = 9.0 Hz), 128.5, 128.4, 128.3, 128.2, 128.0, 124.9, 122.3, 107.9, 45.6 (d, *J* = 3.8 Hz), 37.6 (d, *J* = 71.4 Hz), 27.0 (d, *J* = 11.9 Hz), 26.4; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 26.0. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{23}NO_2P$ 376.1466, found 376.1470.

1,3-Dimethyl-3-(5-oxo-5-phenylpentyl)indolin-2-one (8)



To a Schlenk tube was successively added 1-phenylcyclobutanol **1a** (14.9 mg，0.1 mmol), *N*-methyl-*N*-phenylmethacrylamide **6** (35.4 mg, 0.2 mmol), Ag_2SO_4 (6.2 mg, 0.02 mmol), $(NH_4)_2S_2O_8$ (68.5 mg, 0.3 mmol) and toluene (1 mL). The tube was sealed and then backfilled

thrice with argon. The reaction mixture was stirred at 90 ℃ for 12 hours, and then allowed to cool to room temperature. Afterwards, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtered. The filtrate was concentrated under vacuum, and the residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 10:1) to afford compound **8** as colorless oil (10.3 mg, 32%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92–7.87 (m, 2H), 7.55–7.50 (m, 1H), 7.47–7.40 (m, 2H), 7.30–7.23 (m, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 3.21 (s, 3H), 2.93–2.75 (m, 2H), 2.02–1.91 (m, 1H), 1.84–1.72 (m, 1H), 1.68–1.54 (m, 2H), 1.26 (s, 3H), 1.12–1.03 (m, 1H), 1.01–0.93 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.2, 180.8, 143.4, 137.0, 134.2, 133.0, 128.7, 128.1, 127.8, 122.7, 122.6, 108.1, 48.5, 38.43, 38.37, 26.3, 24.40, 24.38, 24.0. **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{24}NO_2$ 322.1807, found 322.1812.

7. References

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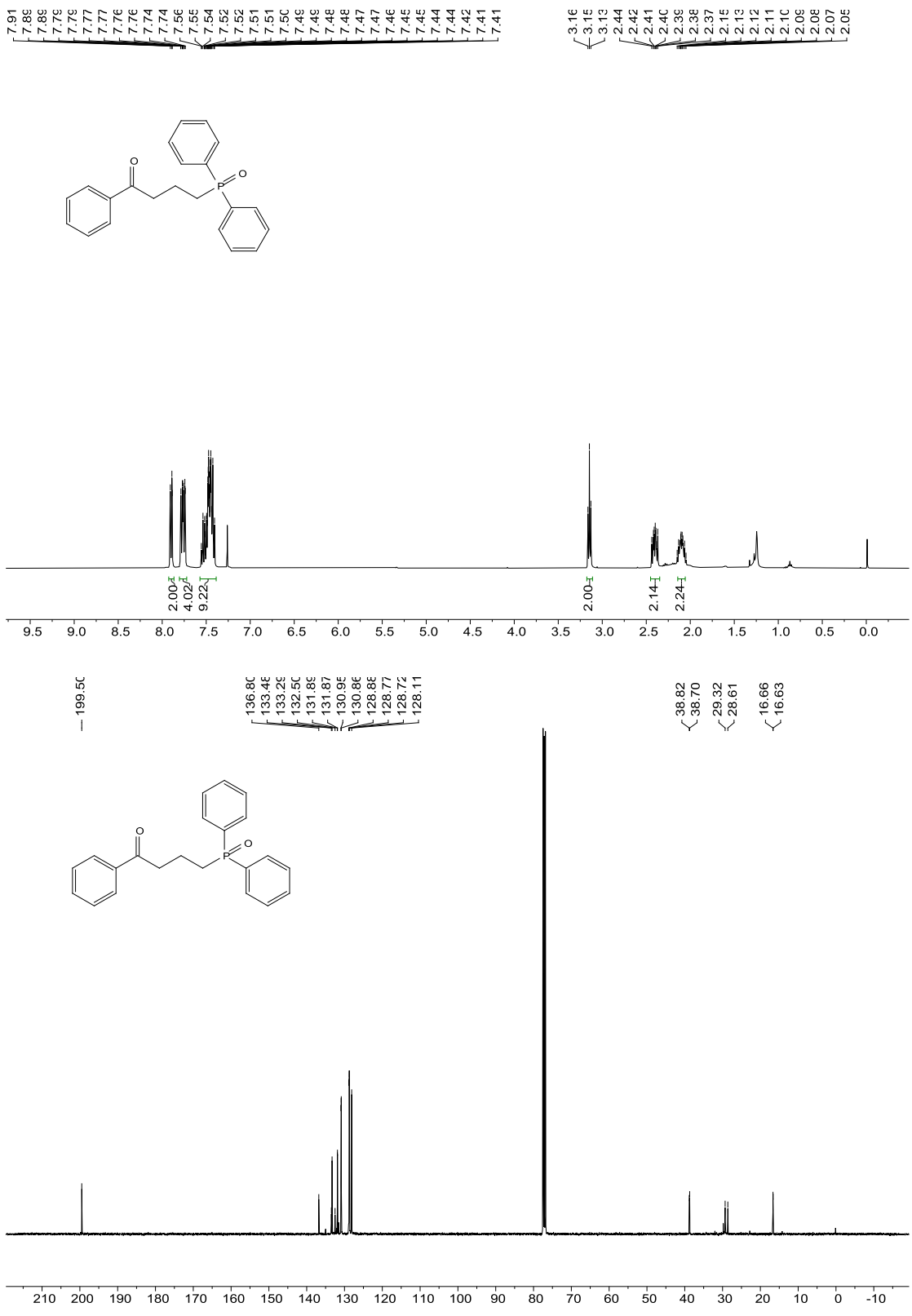
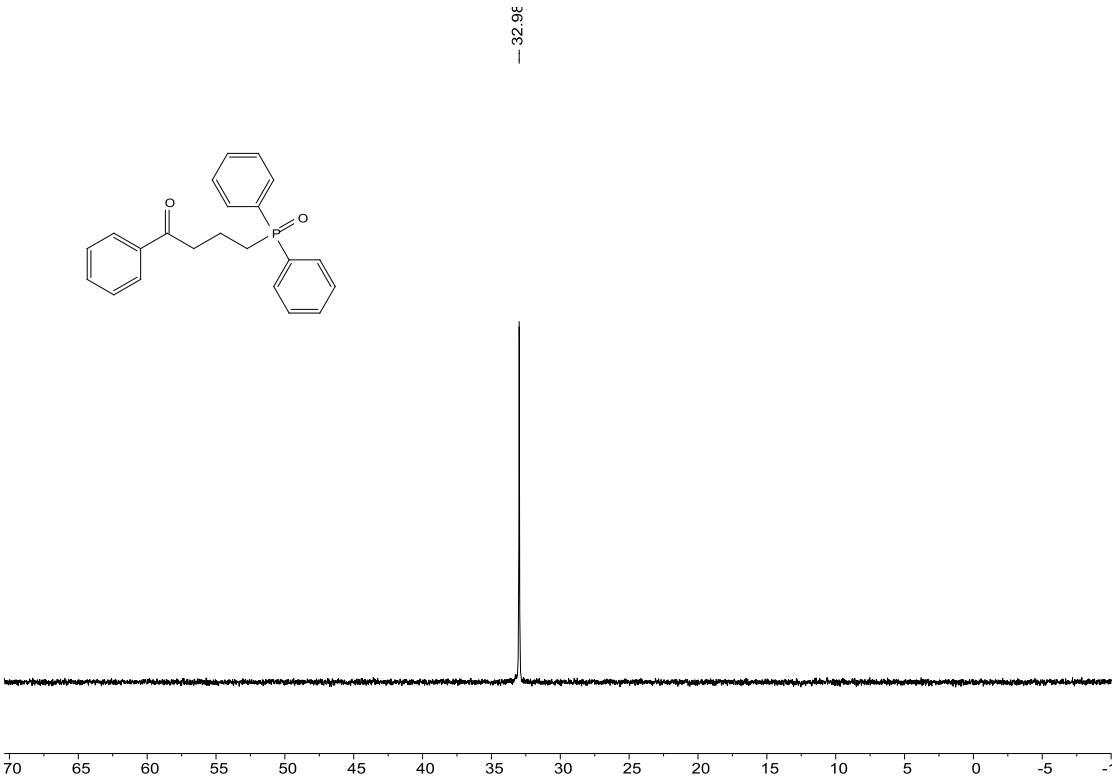
8. ^{1}H, ^{13}C and ^{31}P NMR Spectra of Products 3, 4, 7 and 8

3a

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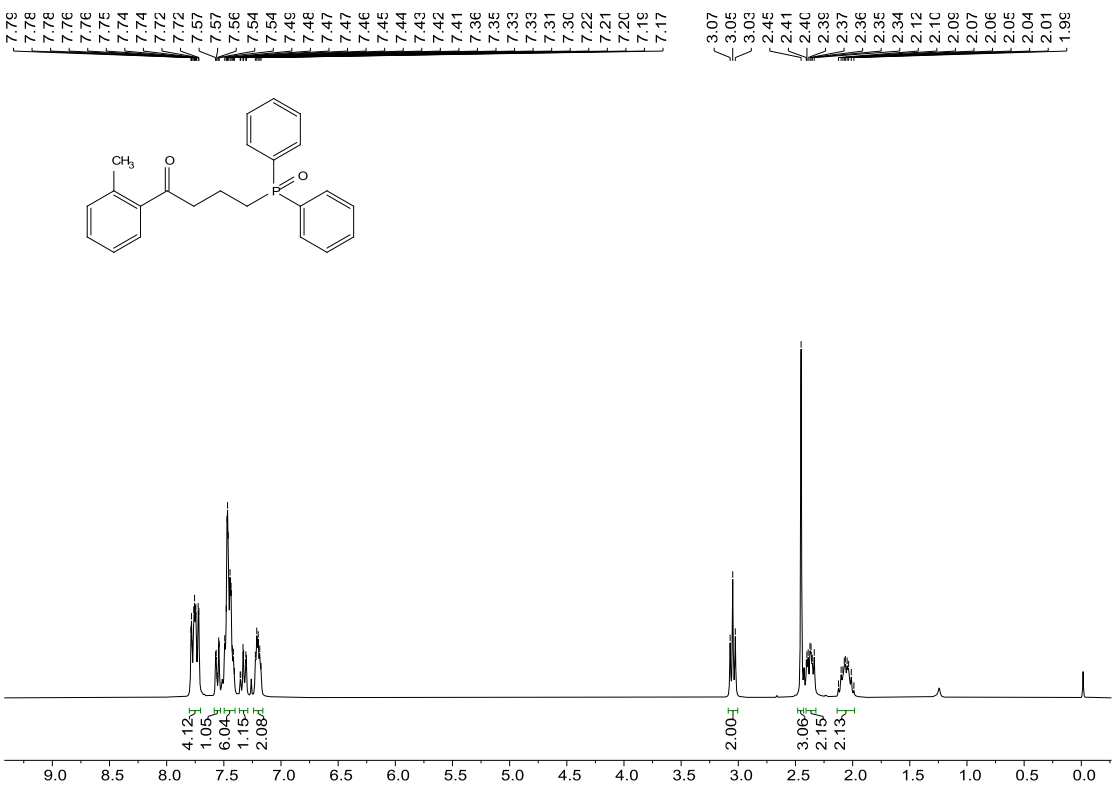
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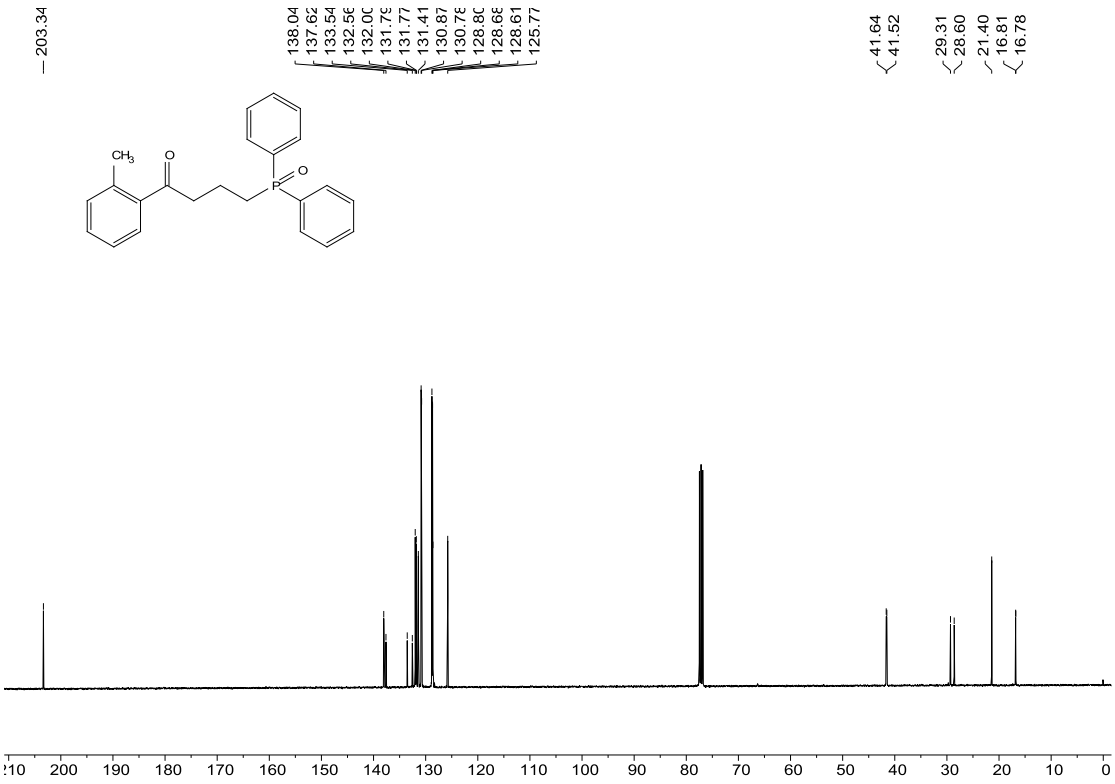
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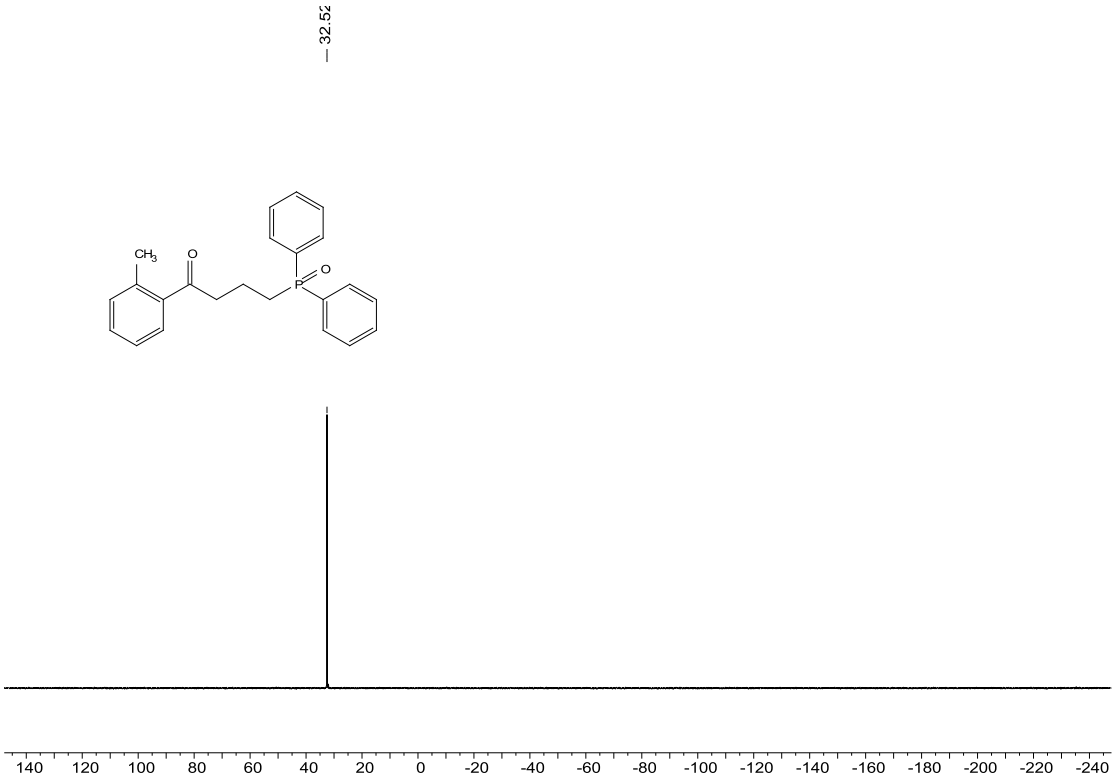
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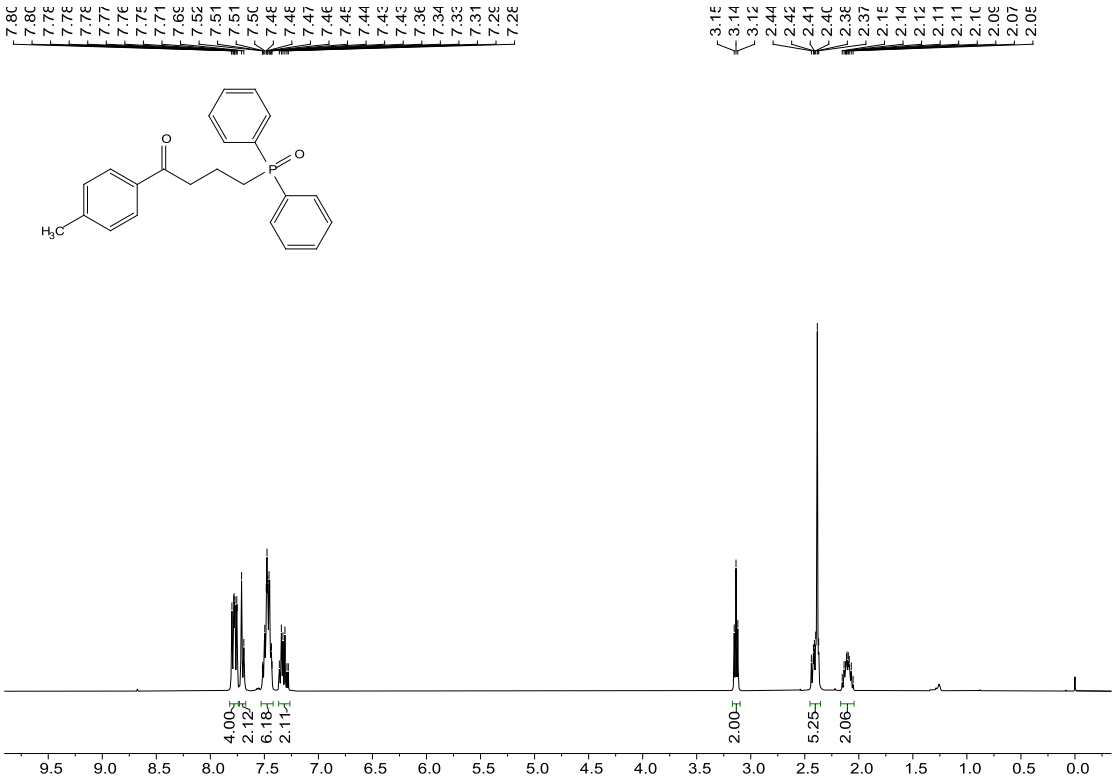
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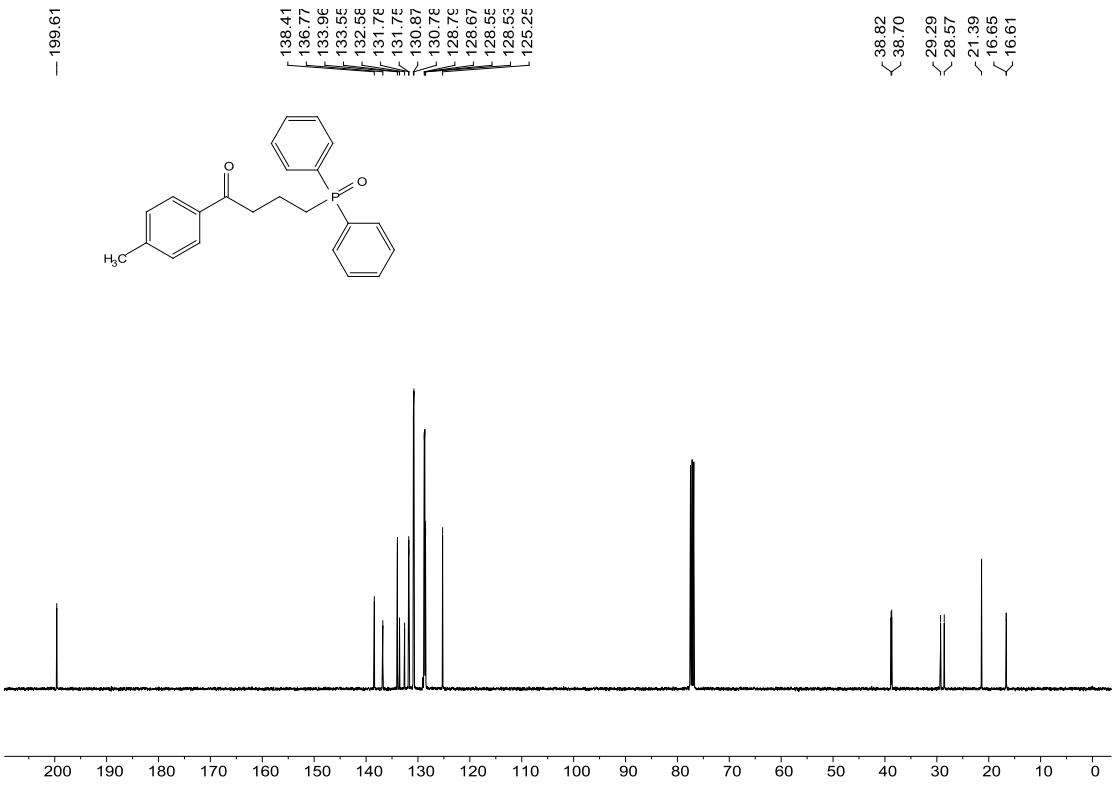
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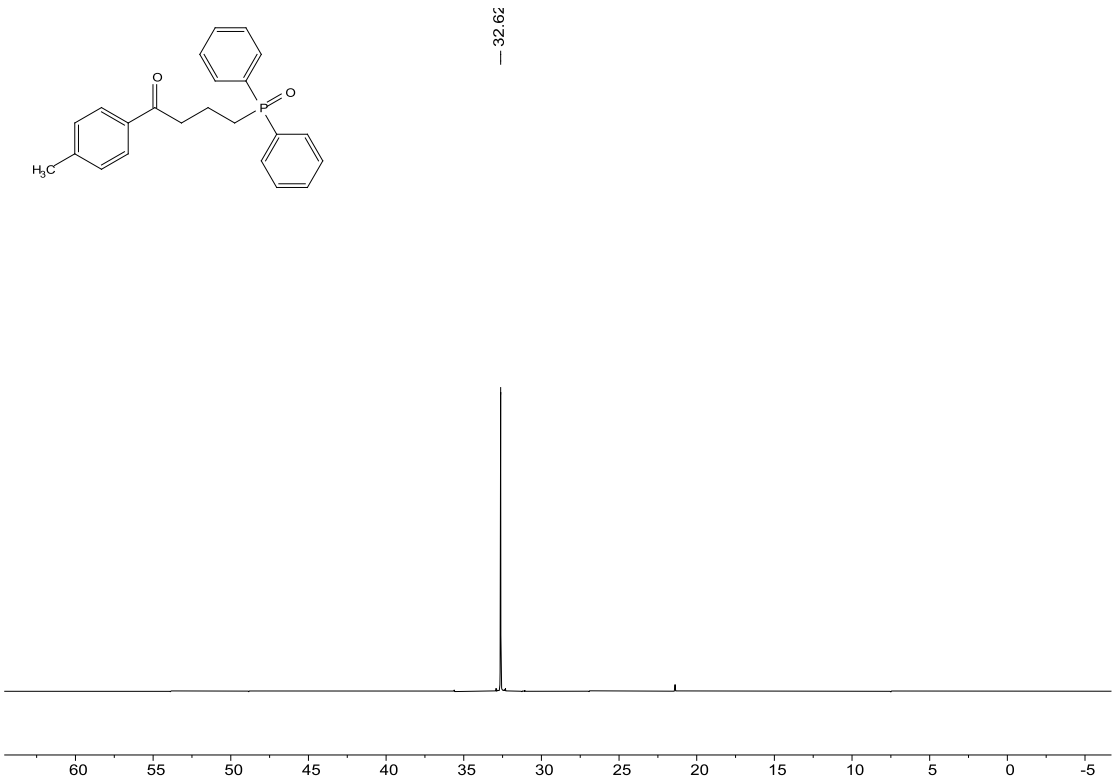
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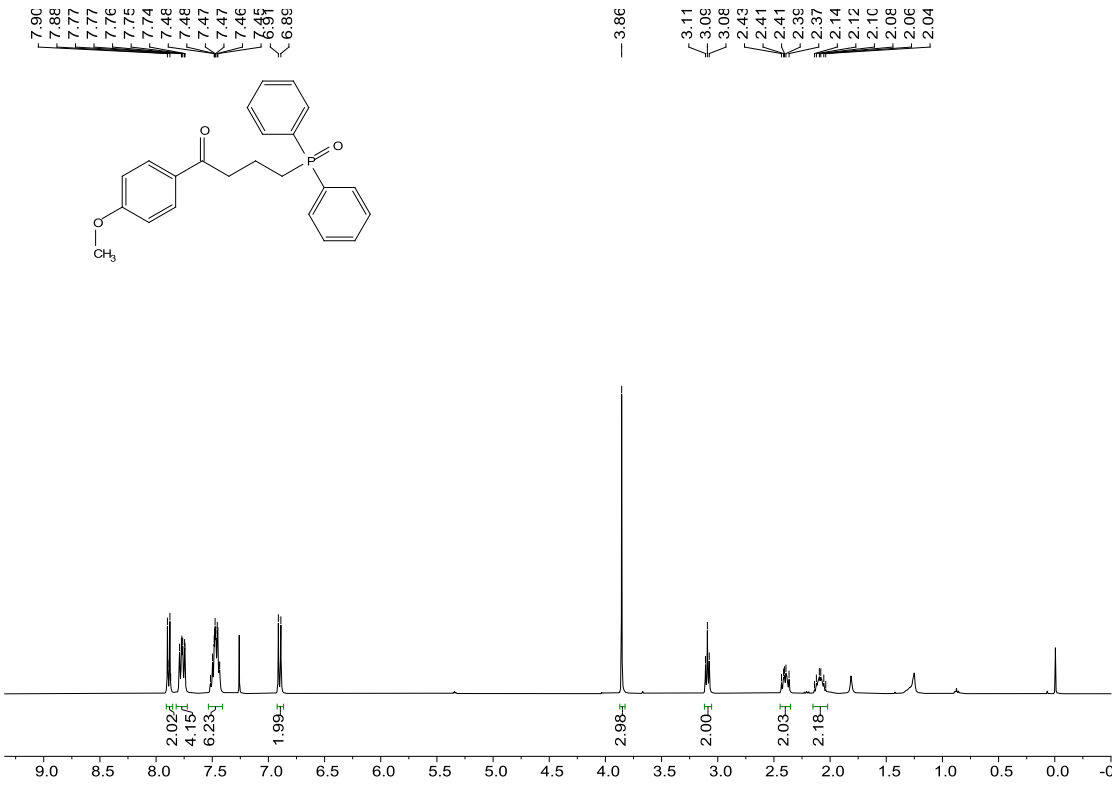
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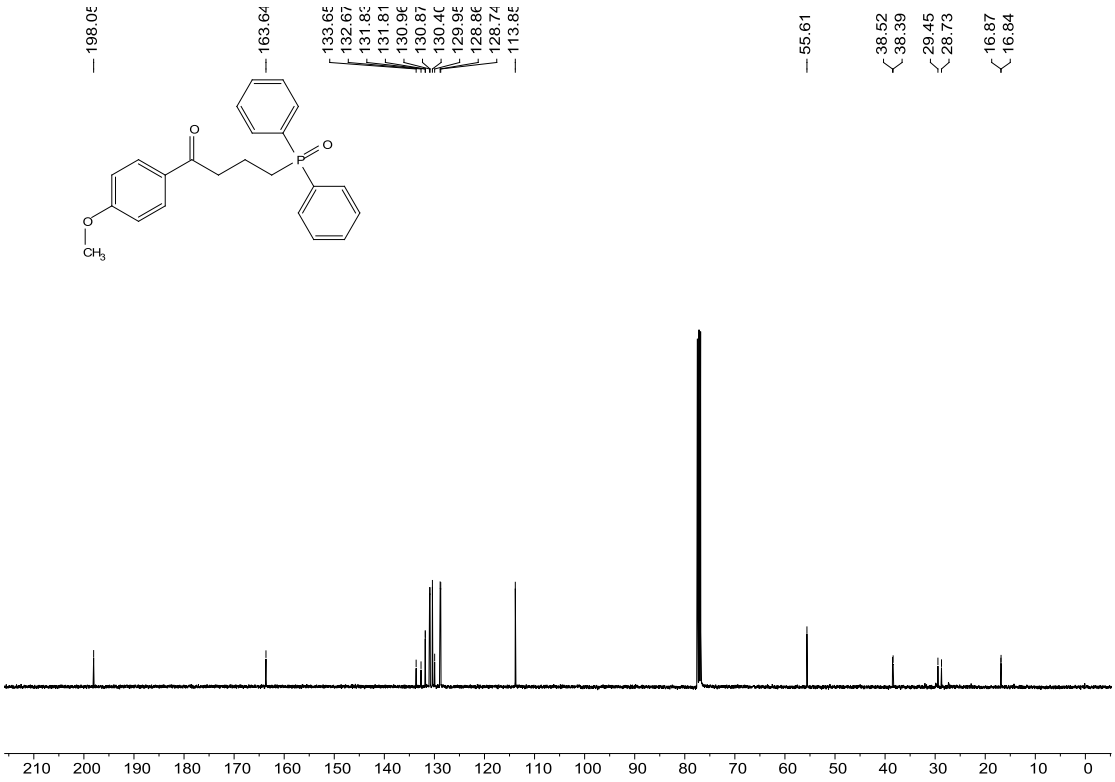
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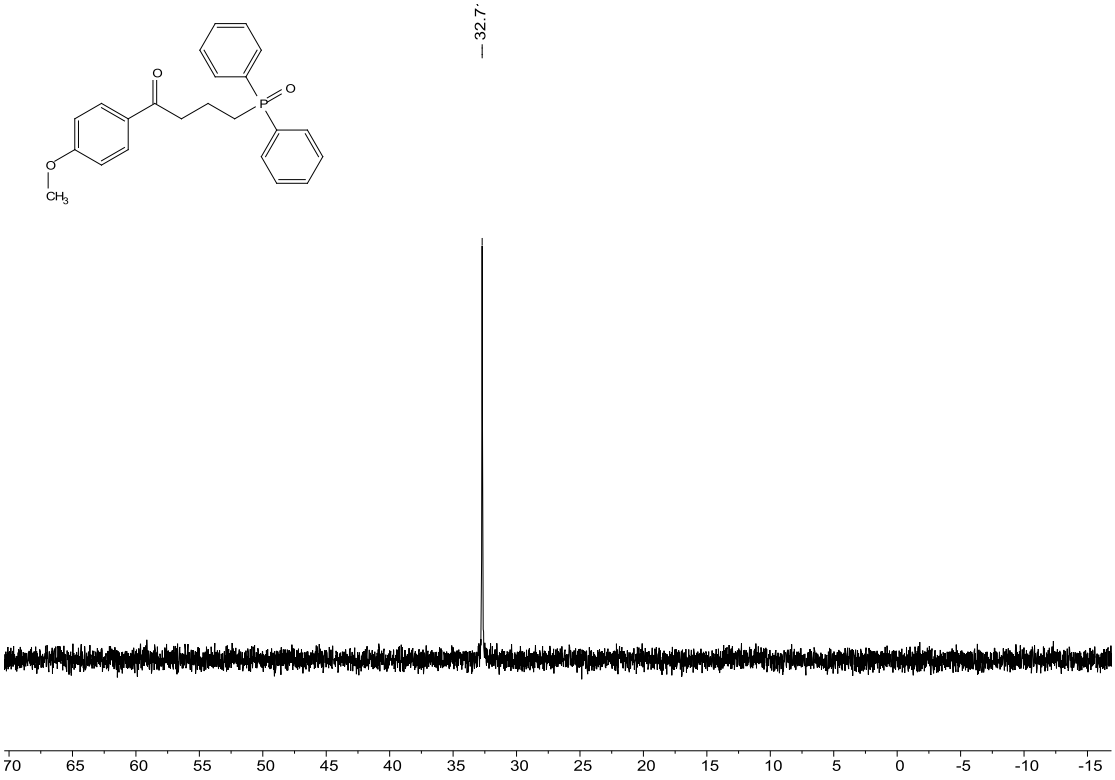
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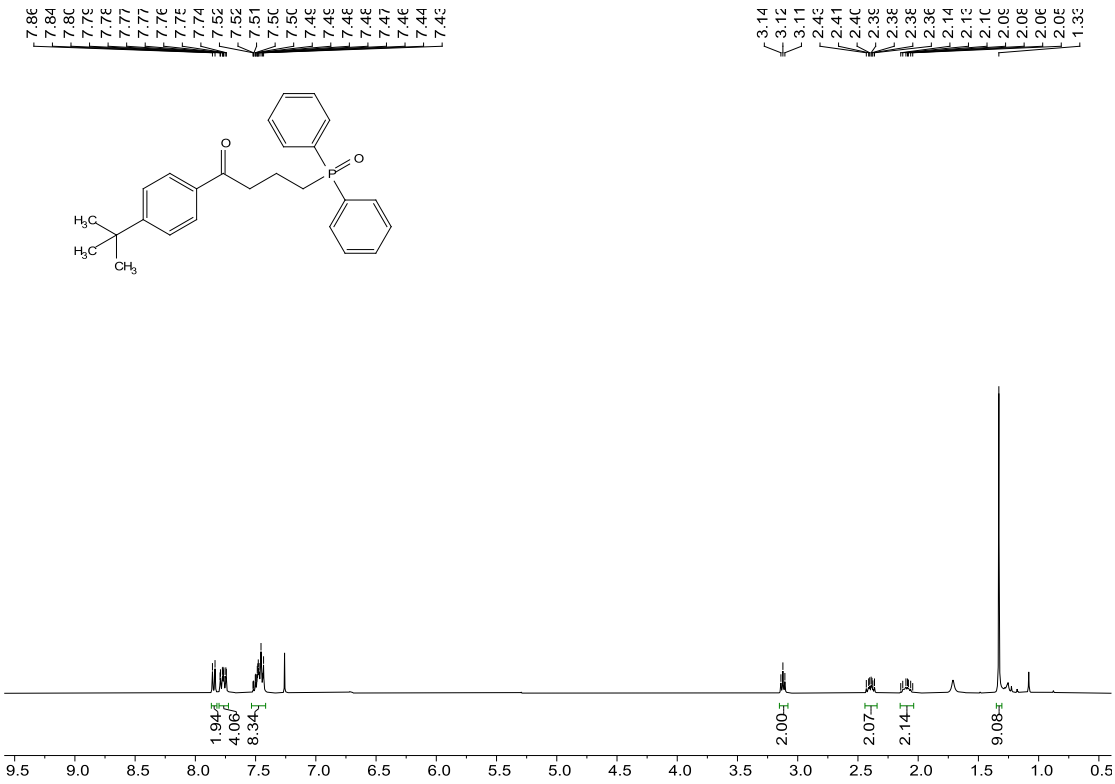

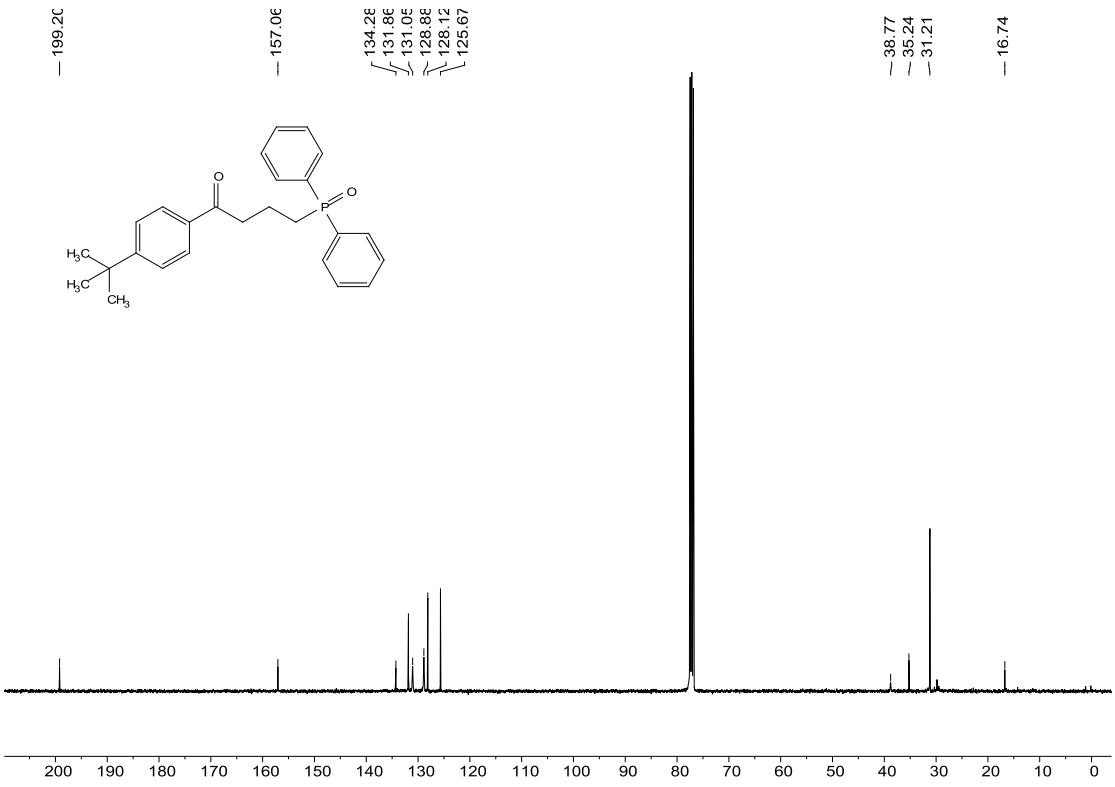

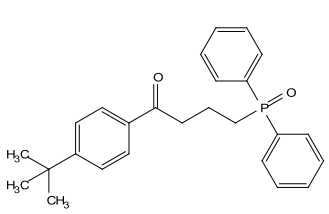
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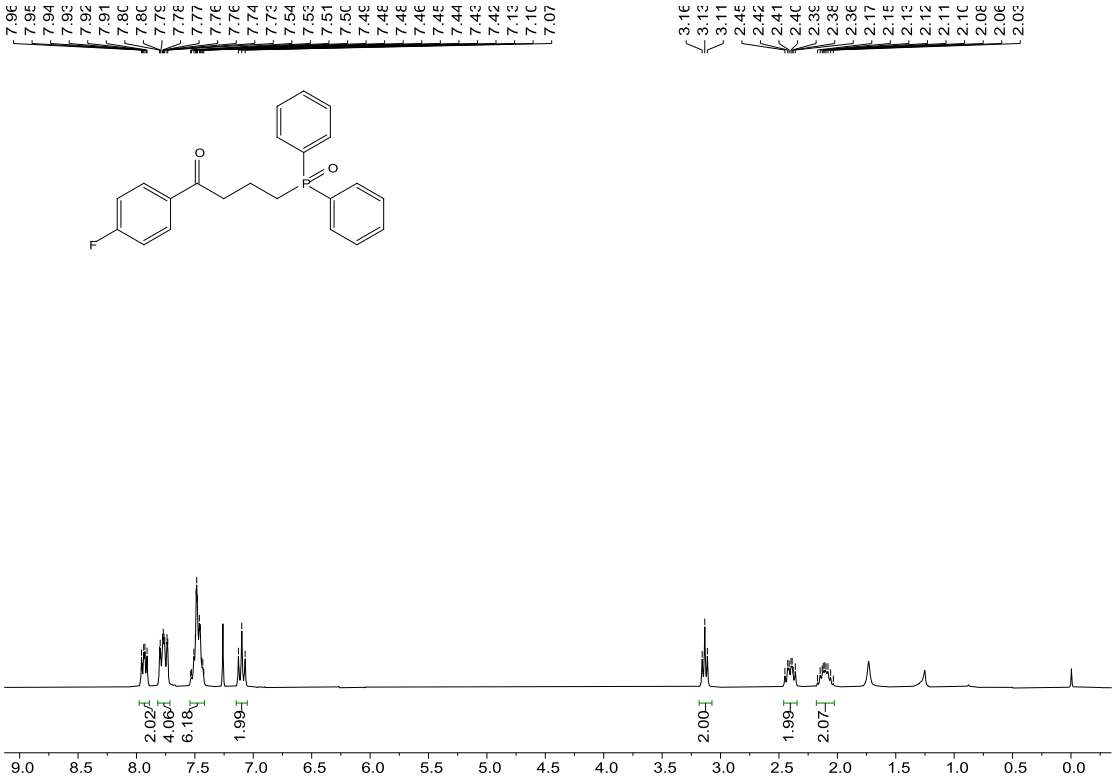
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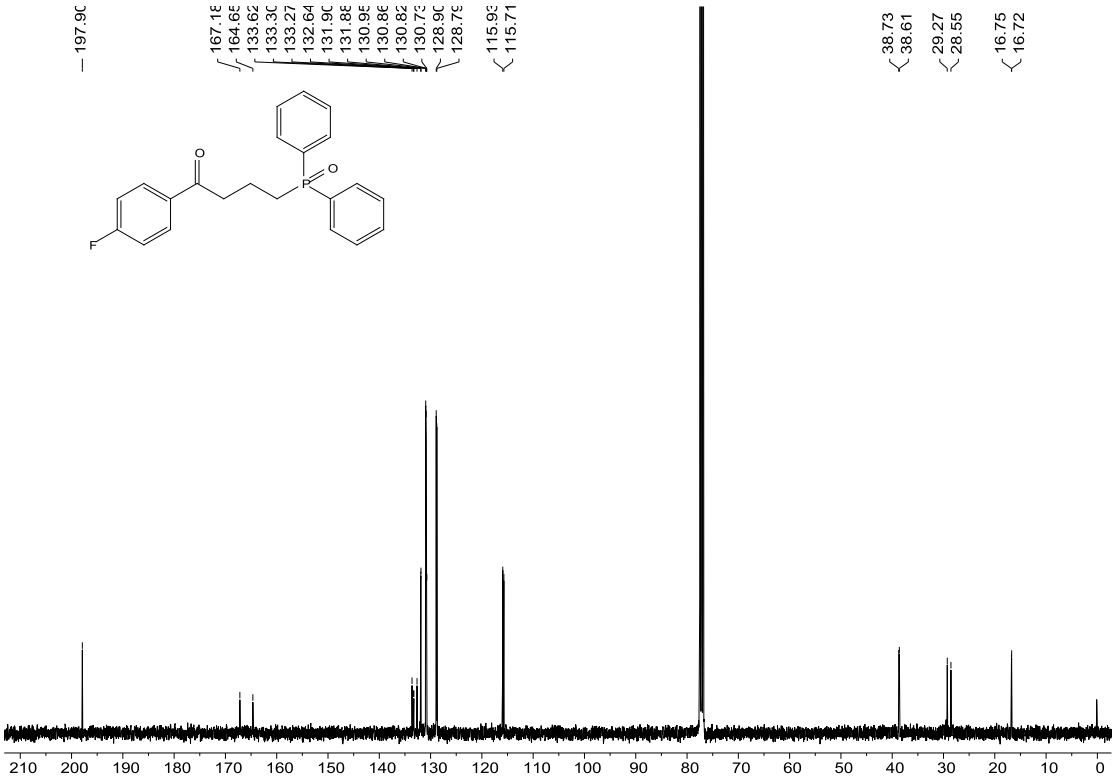
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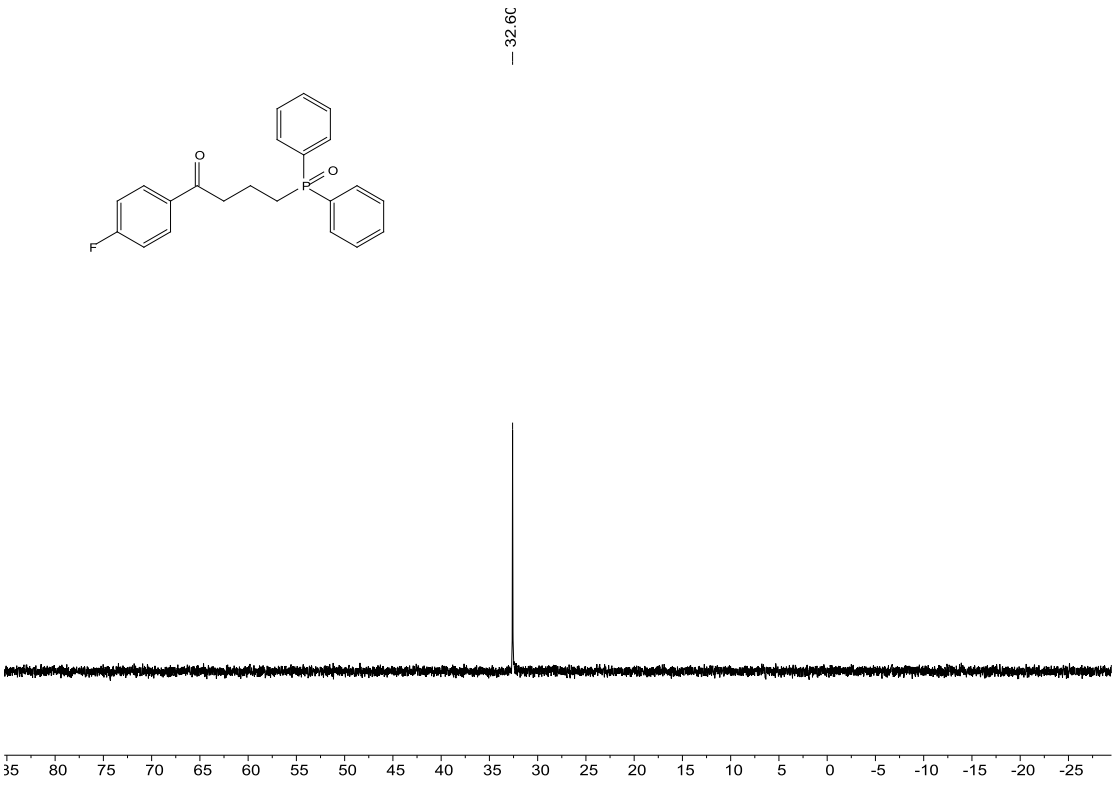
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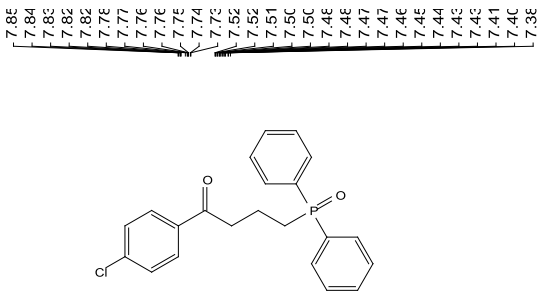

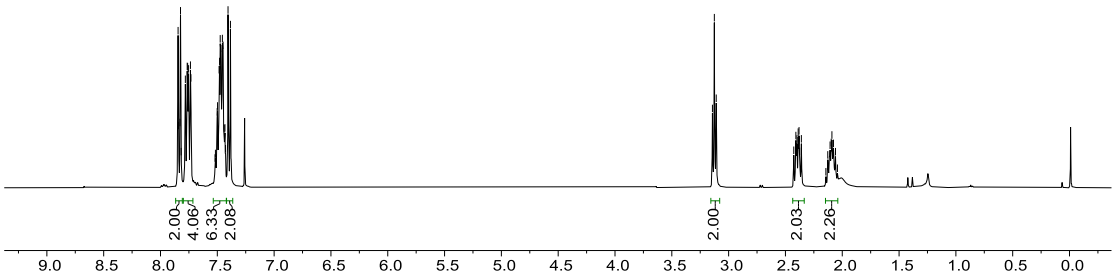
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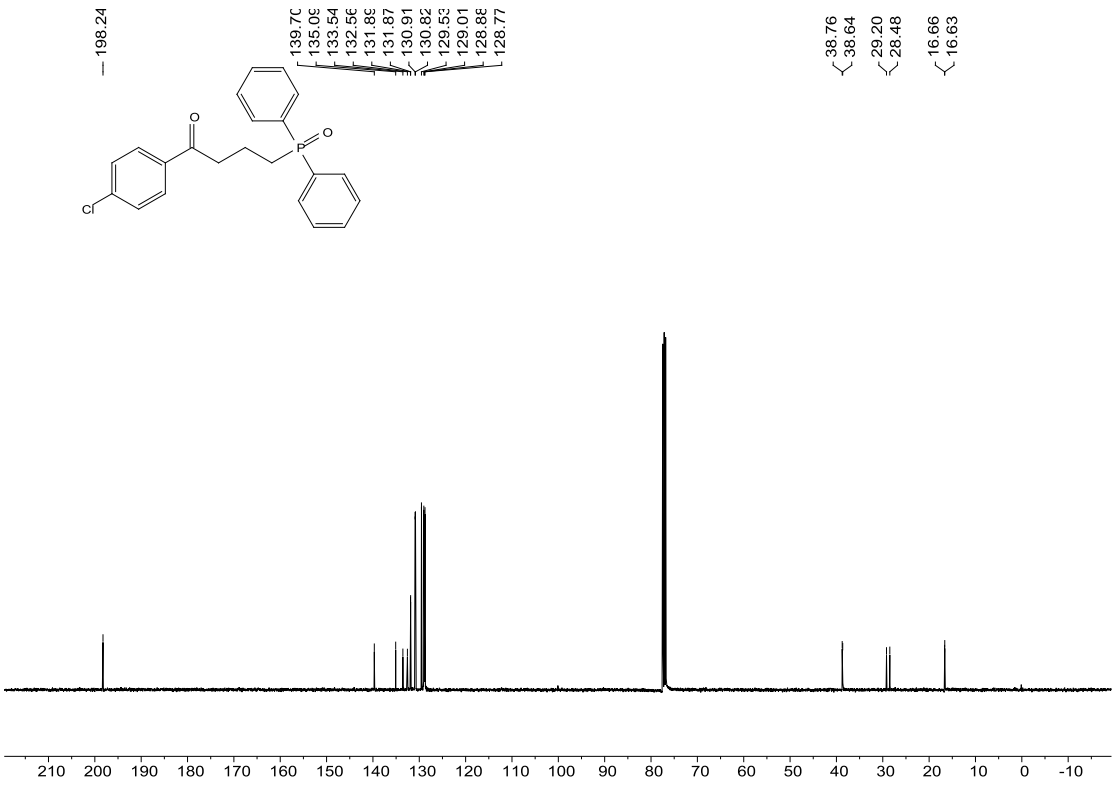
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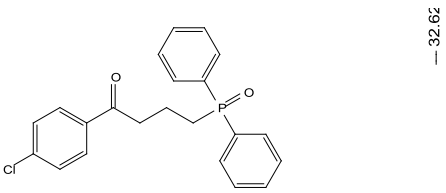
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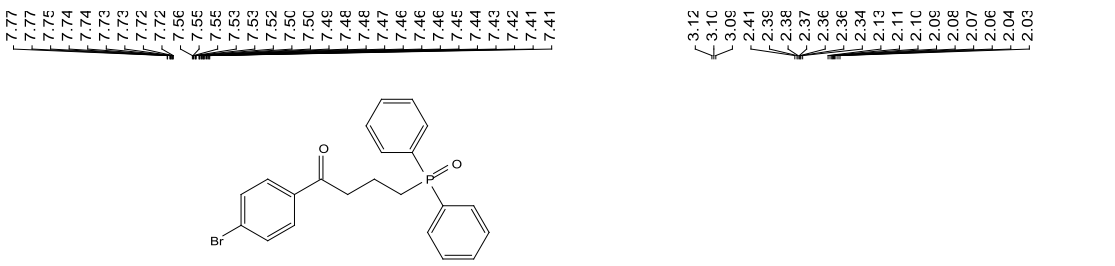
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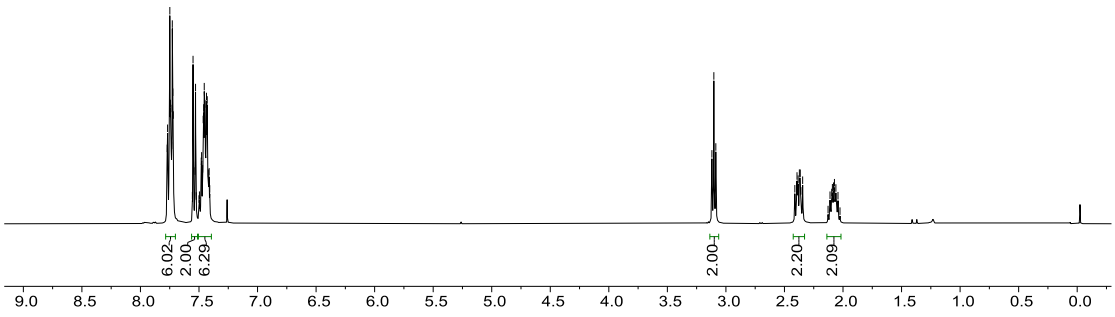
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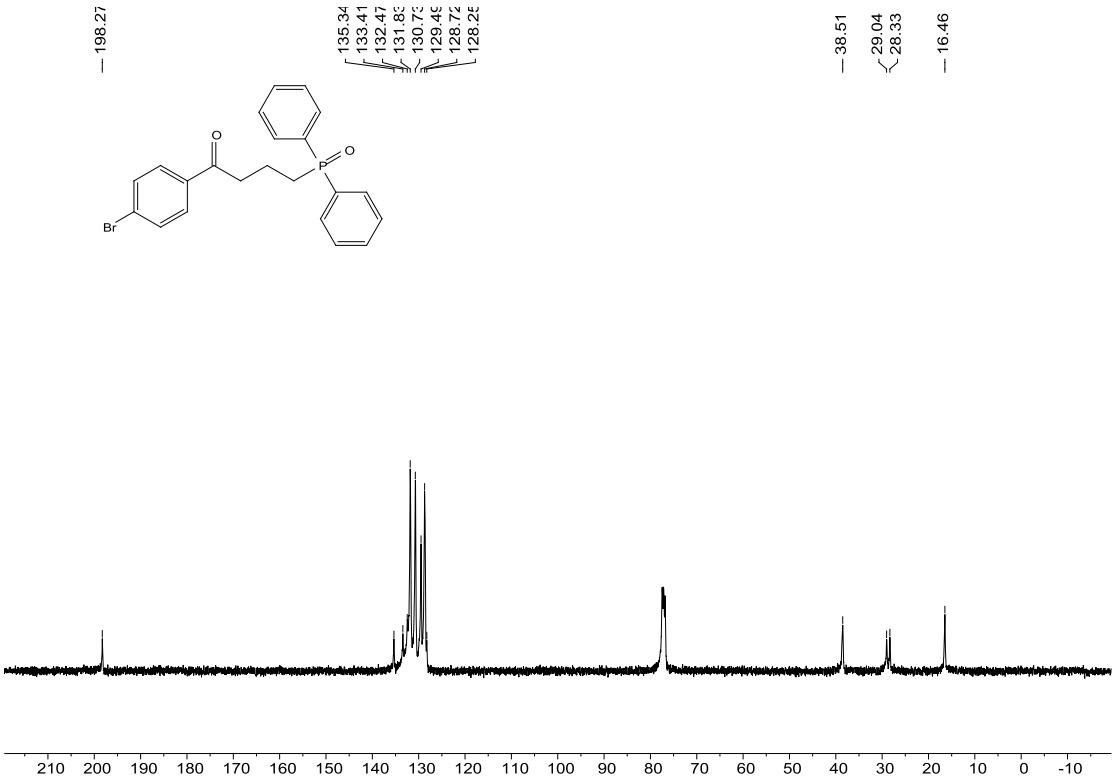
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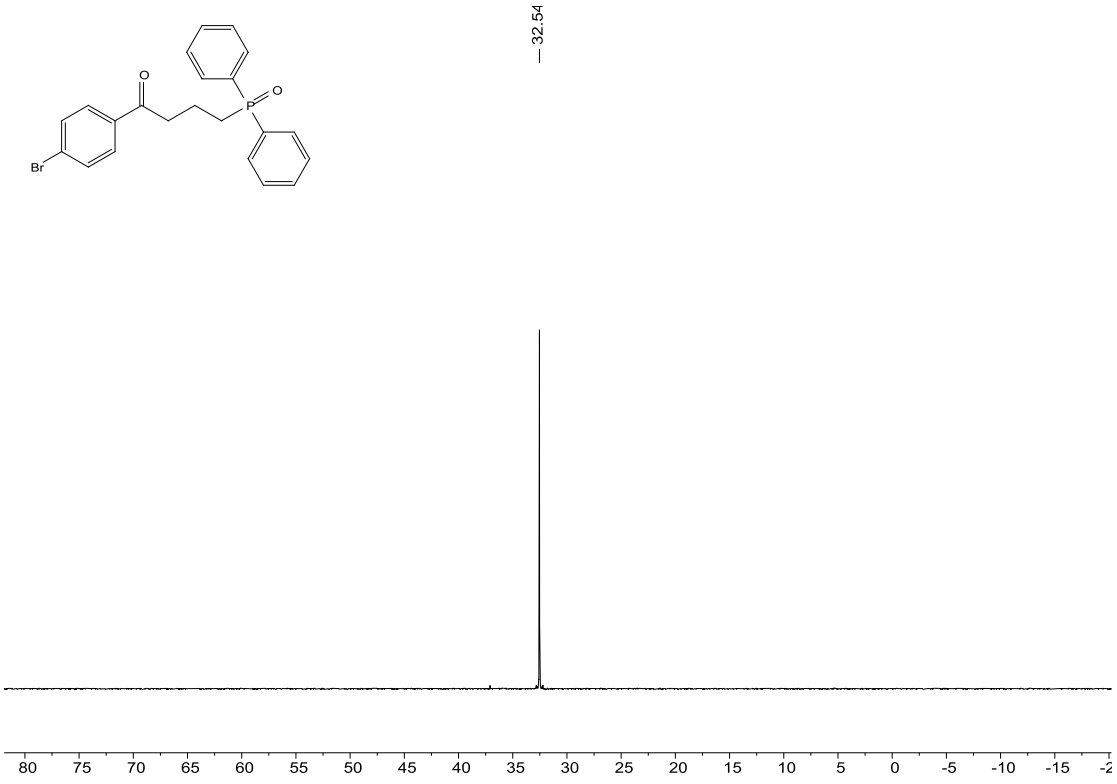
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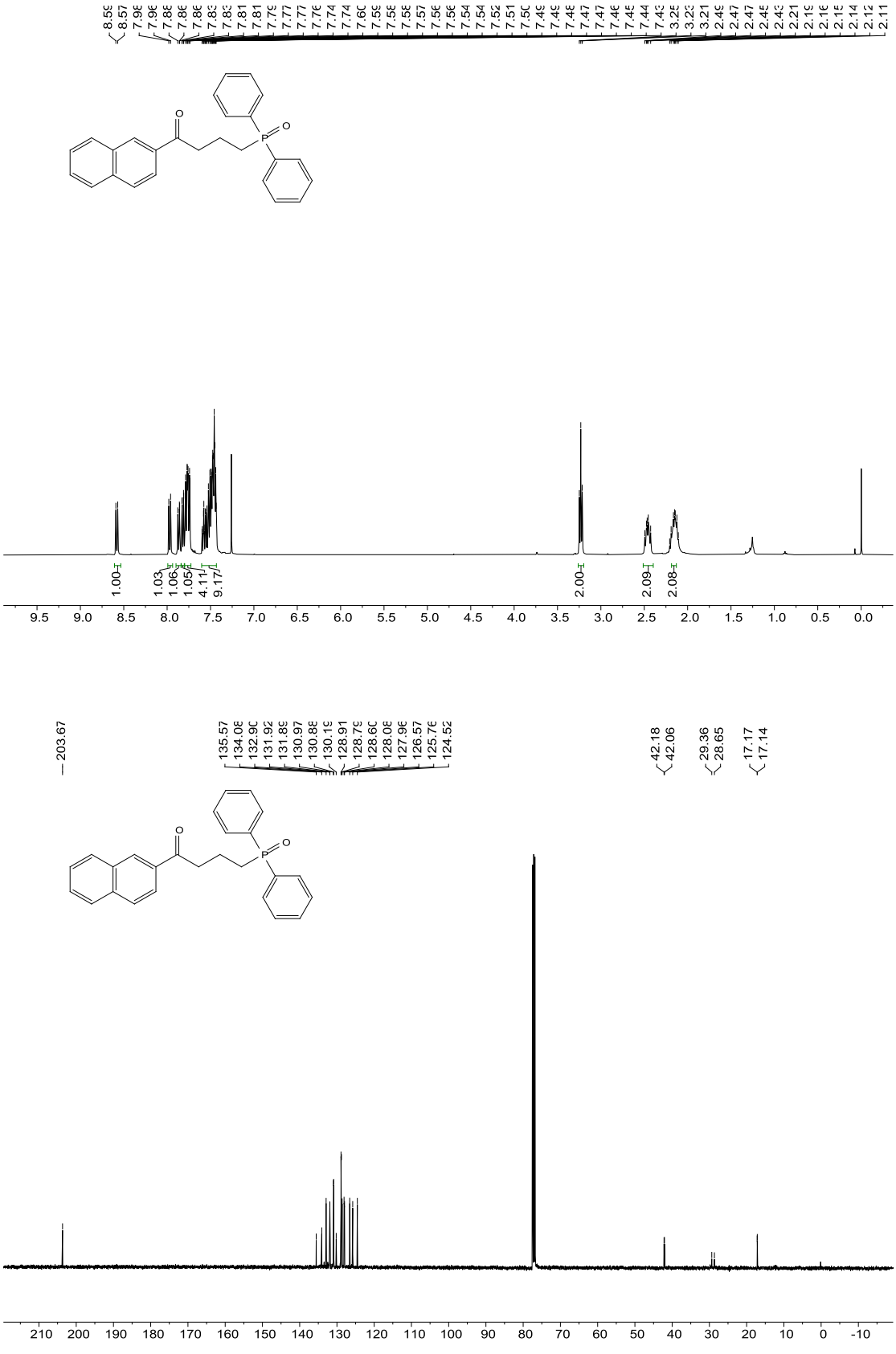

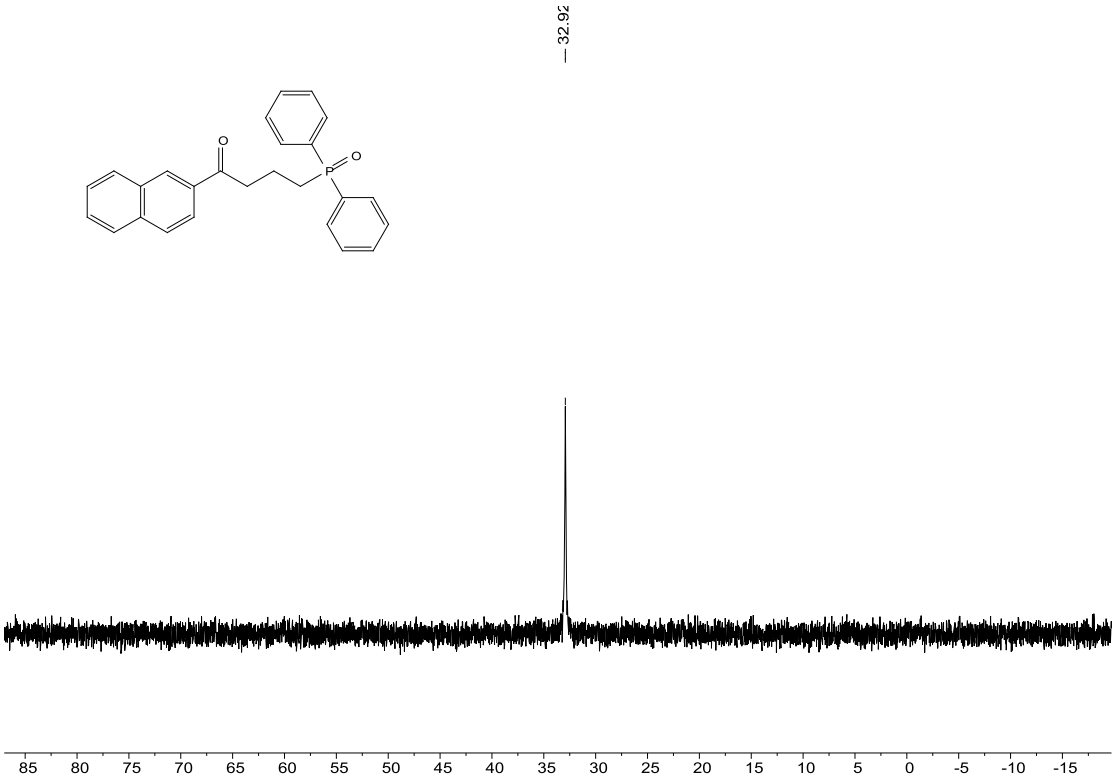
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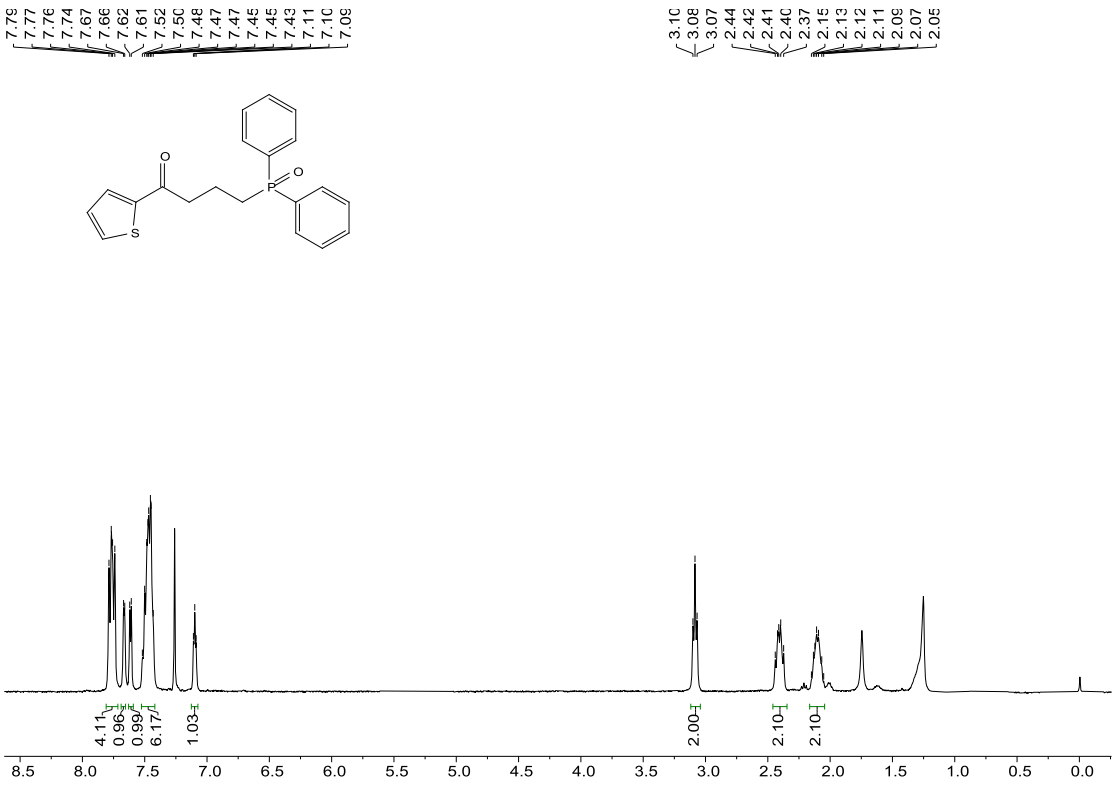
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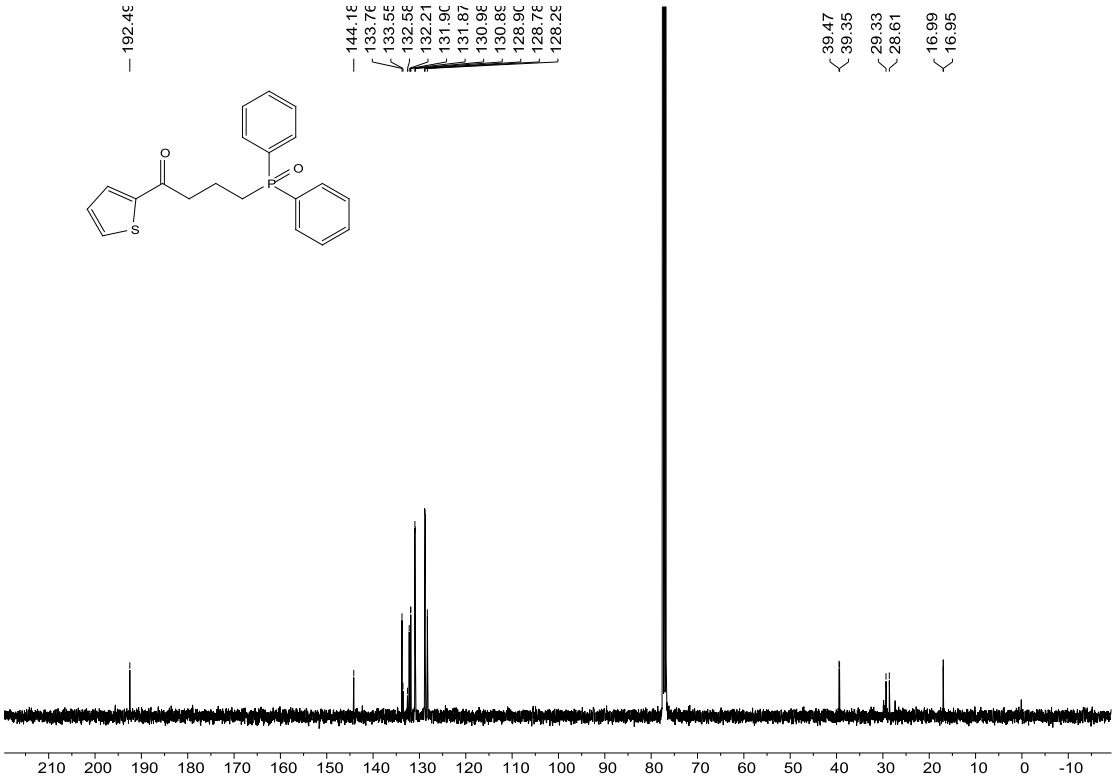
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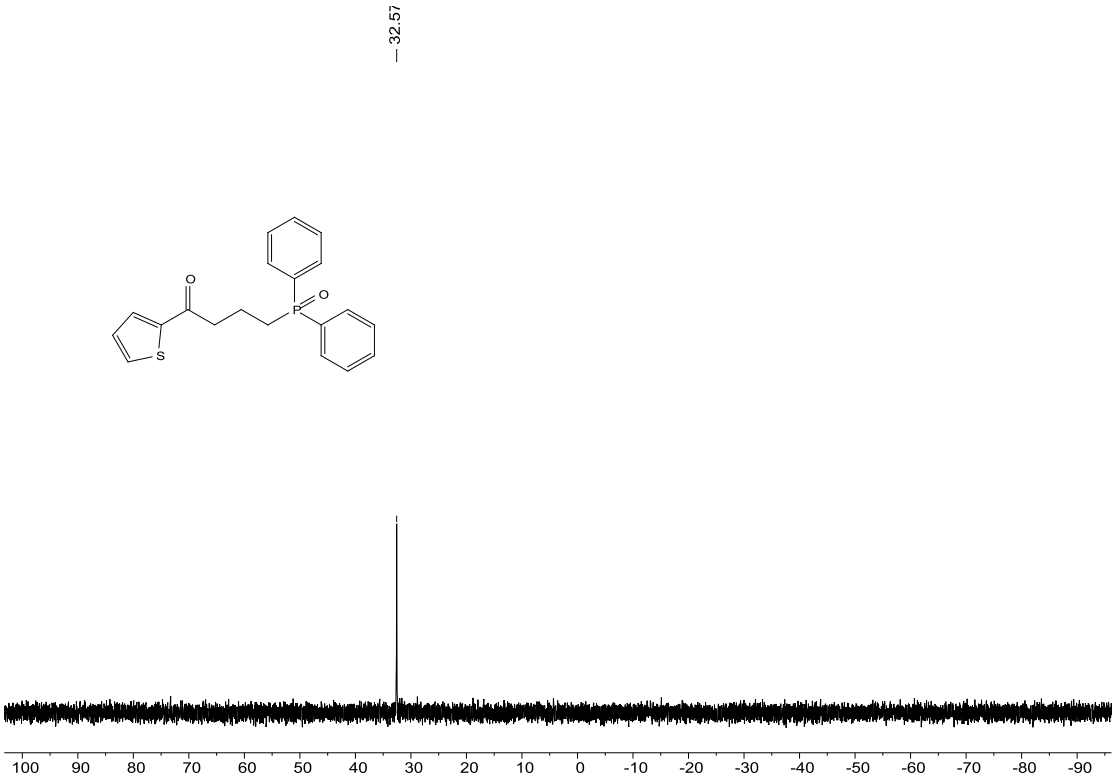
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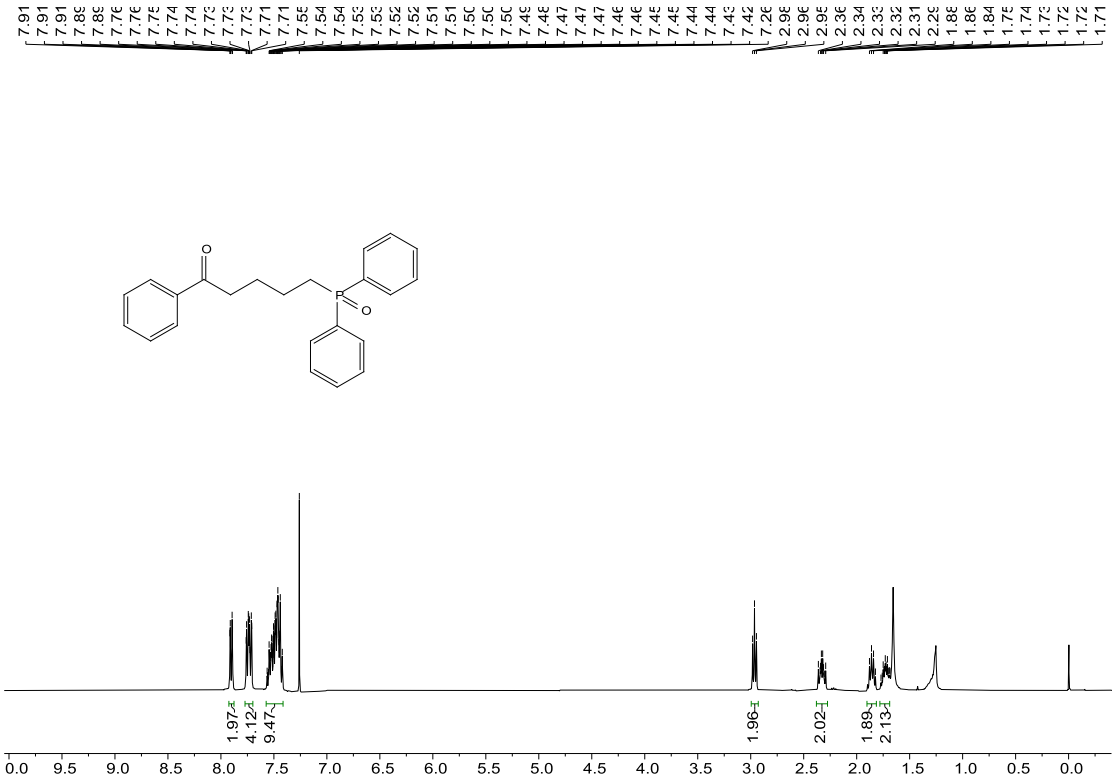

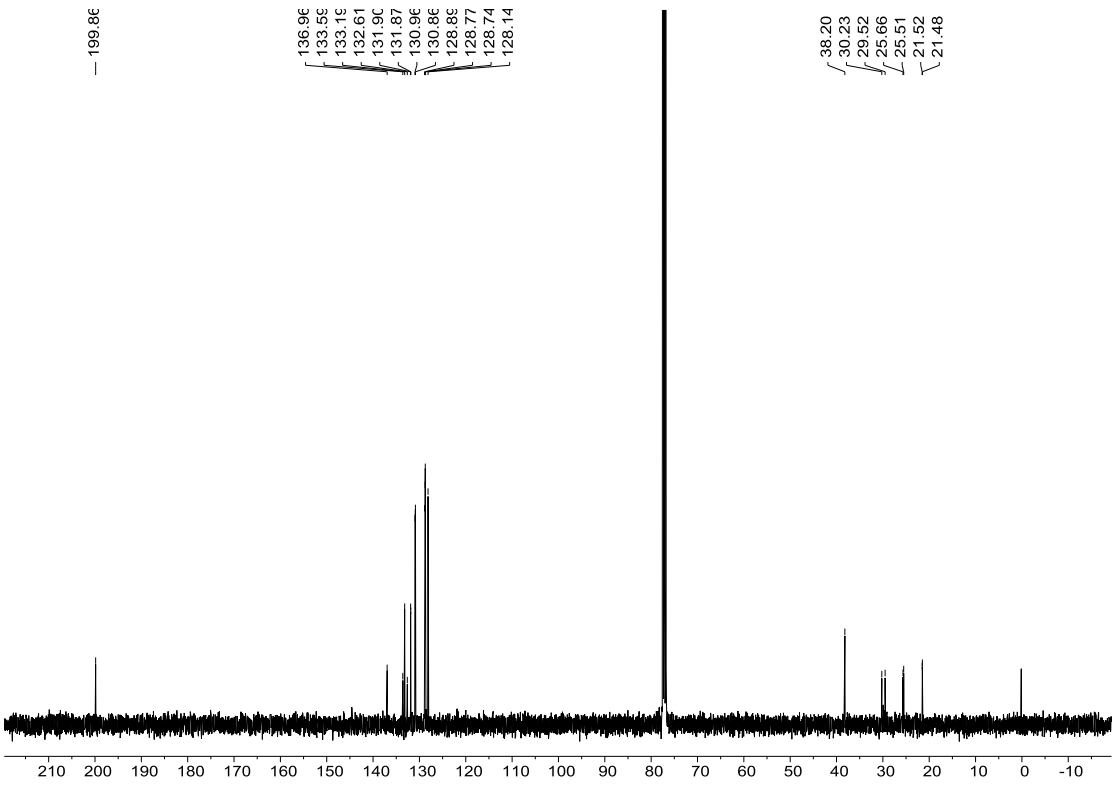

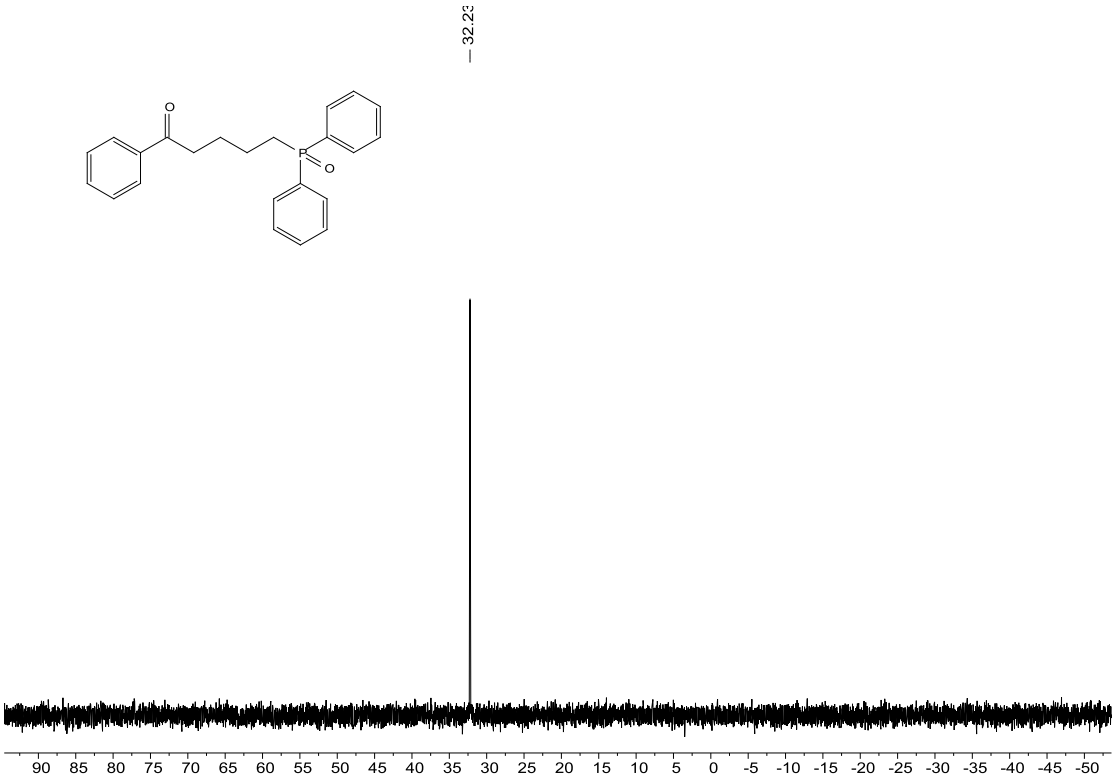
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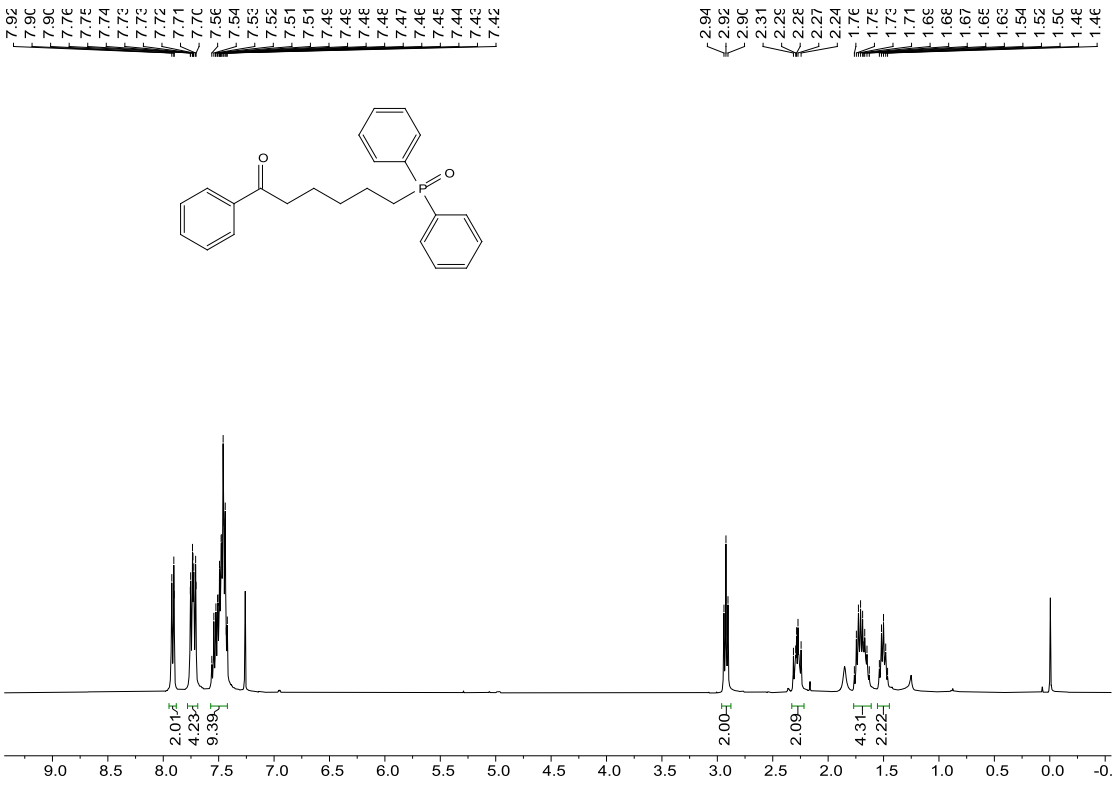
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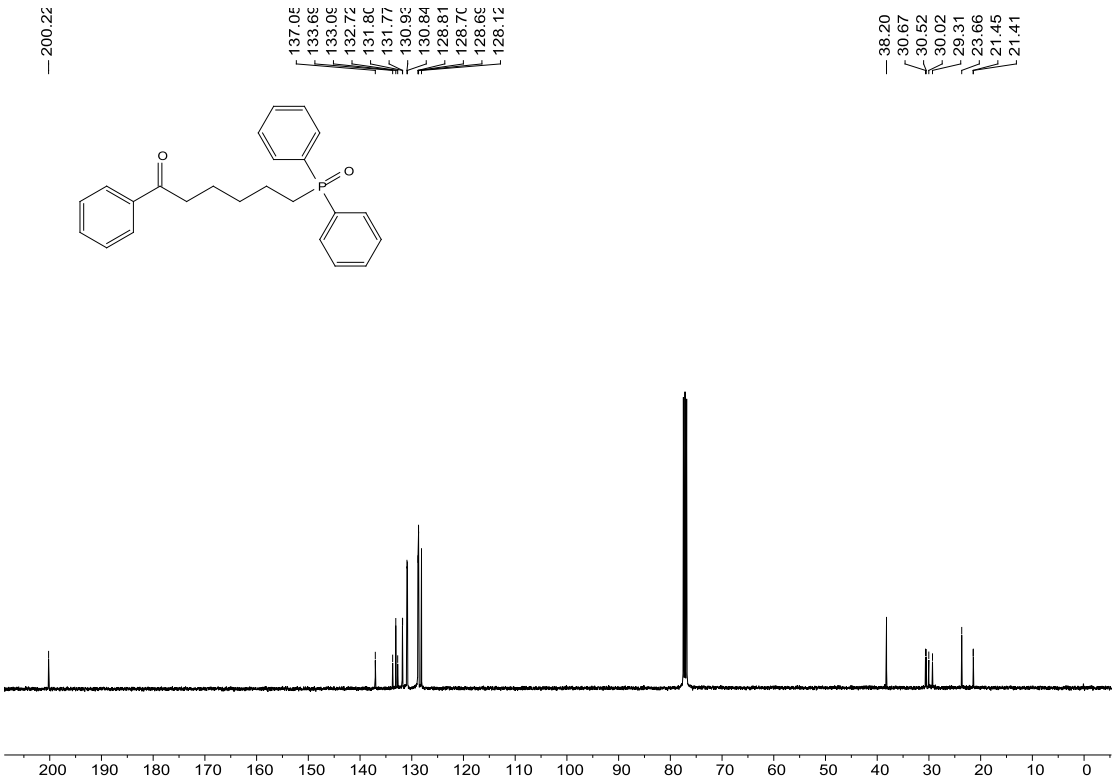
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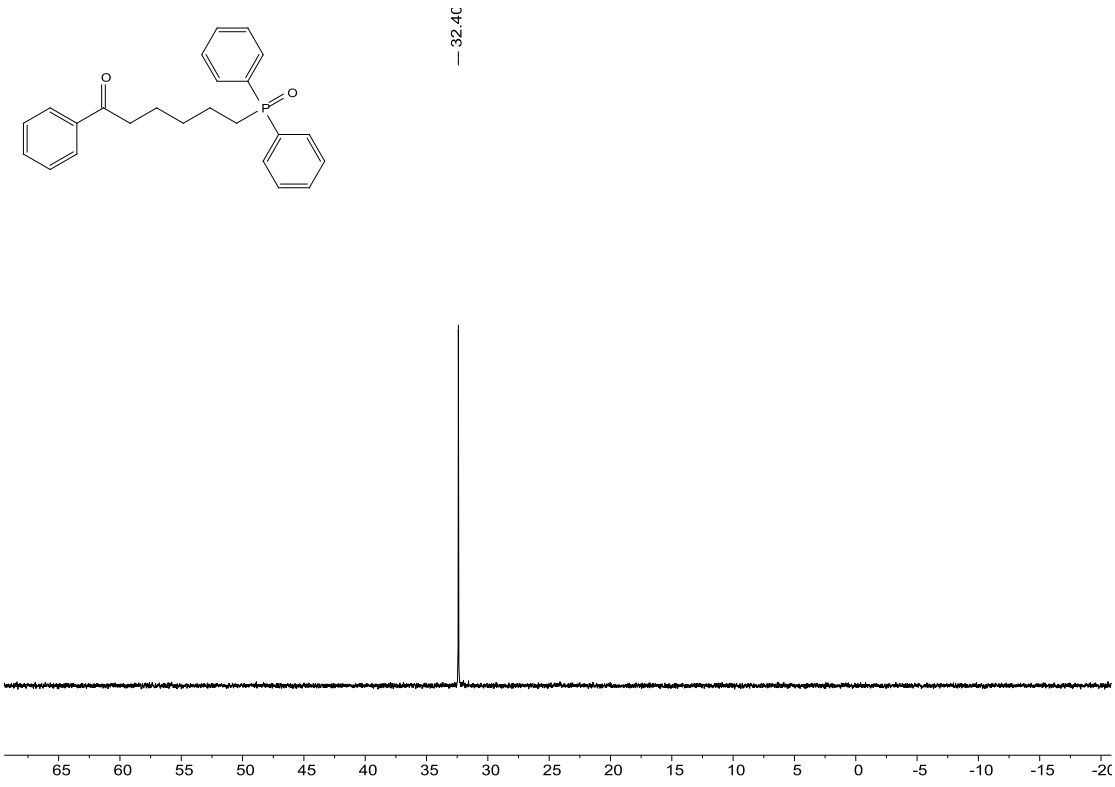
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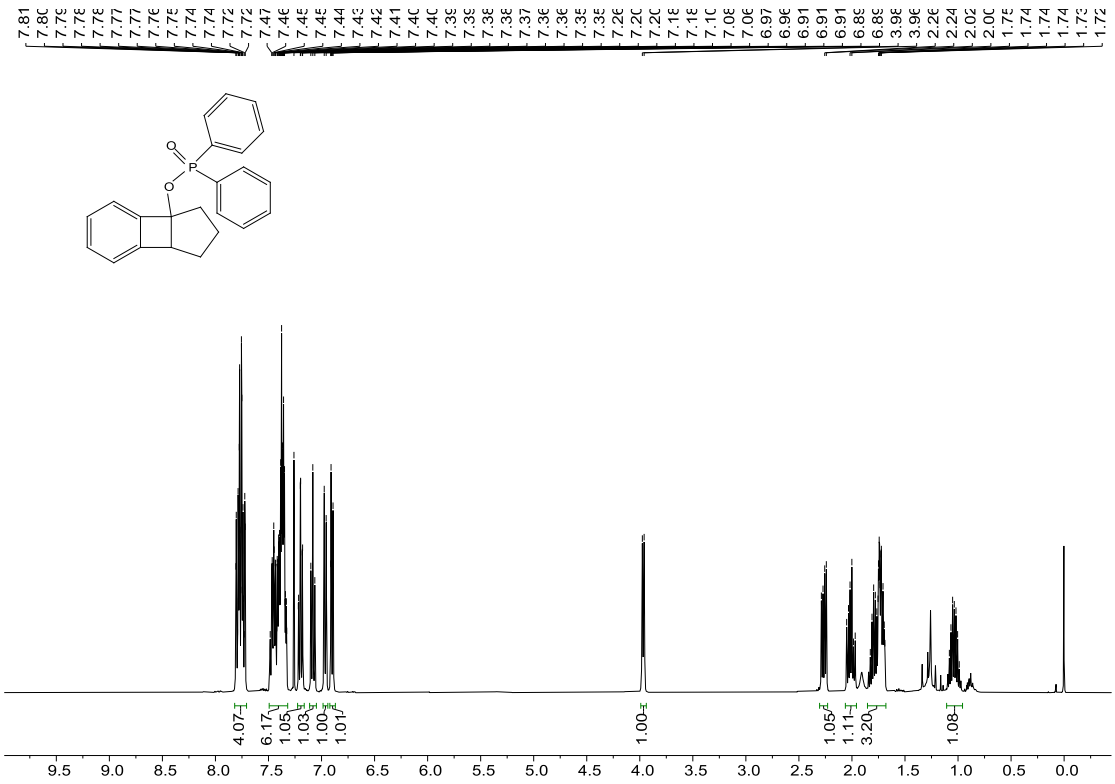

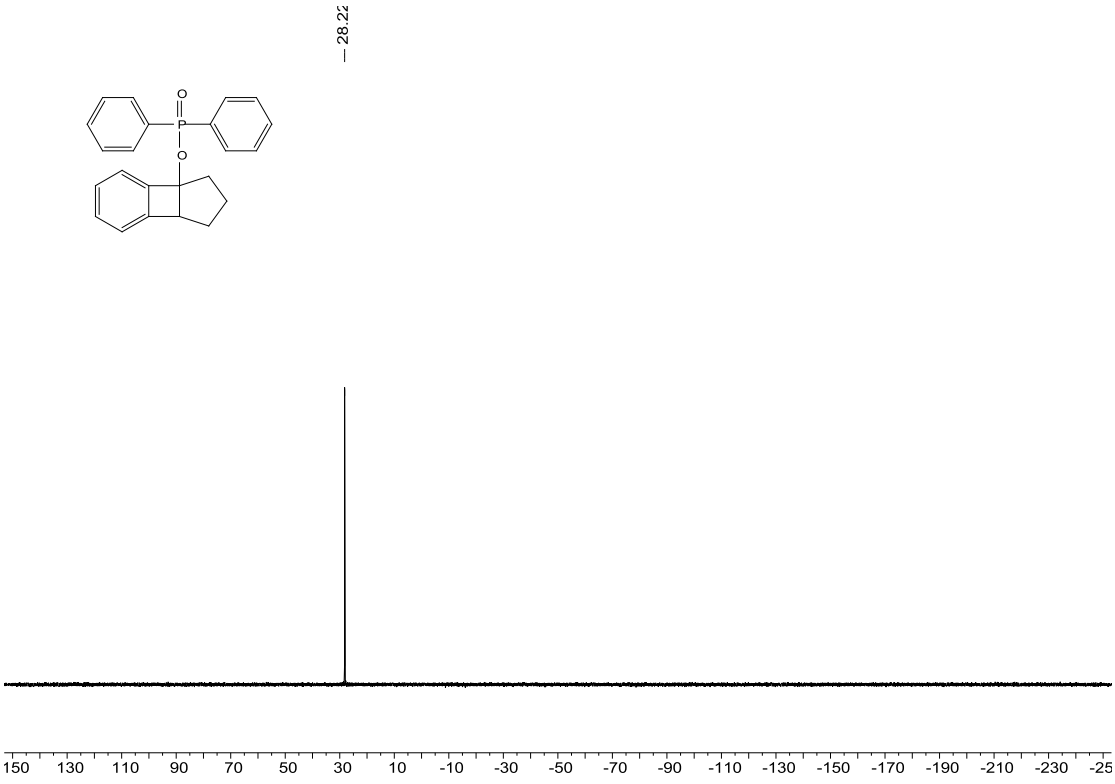

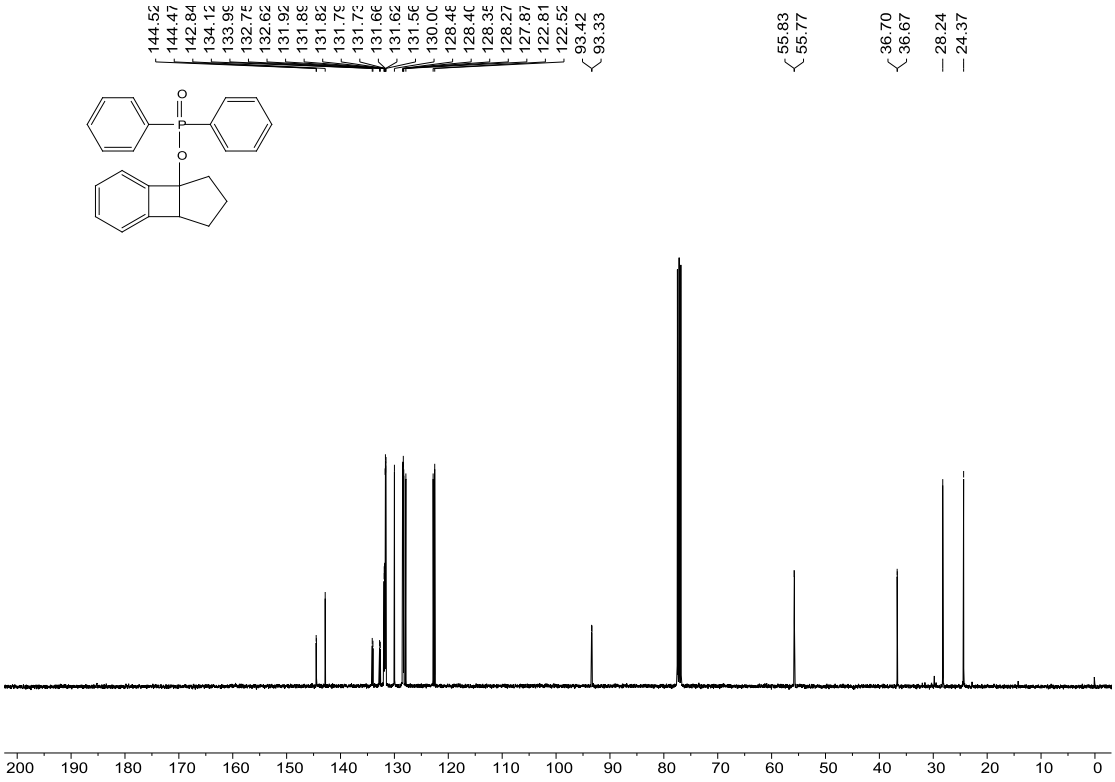
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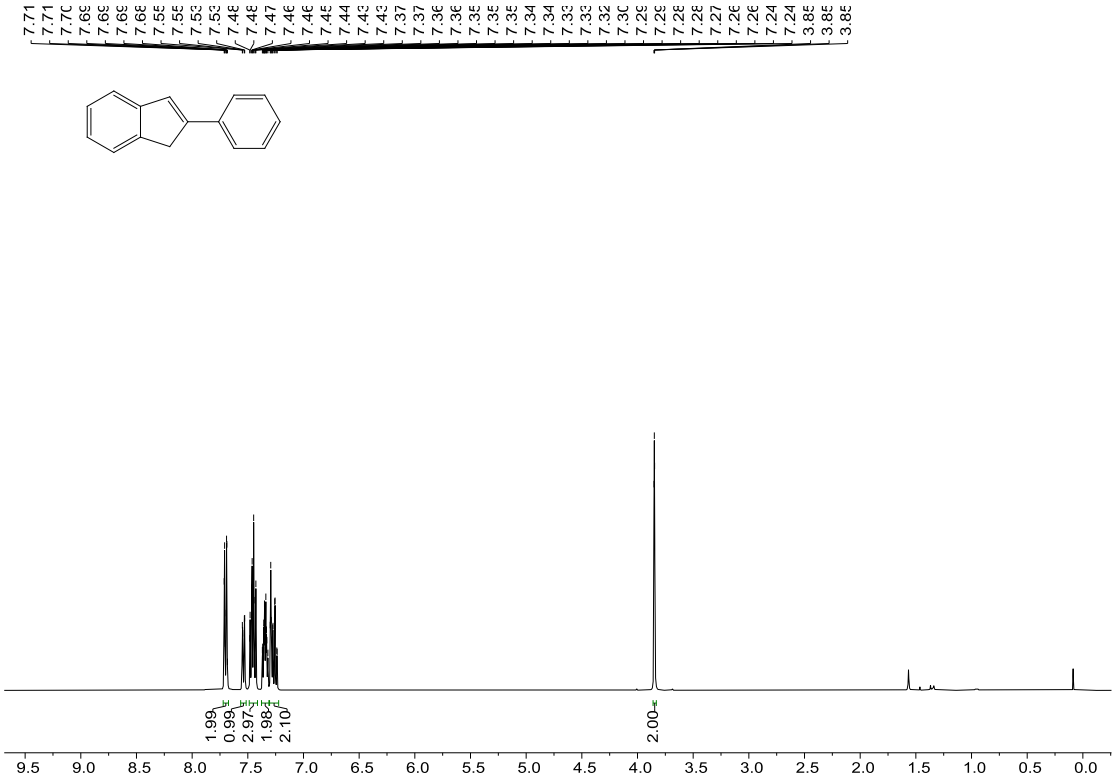
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1.98
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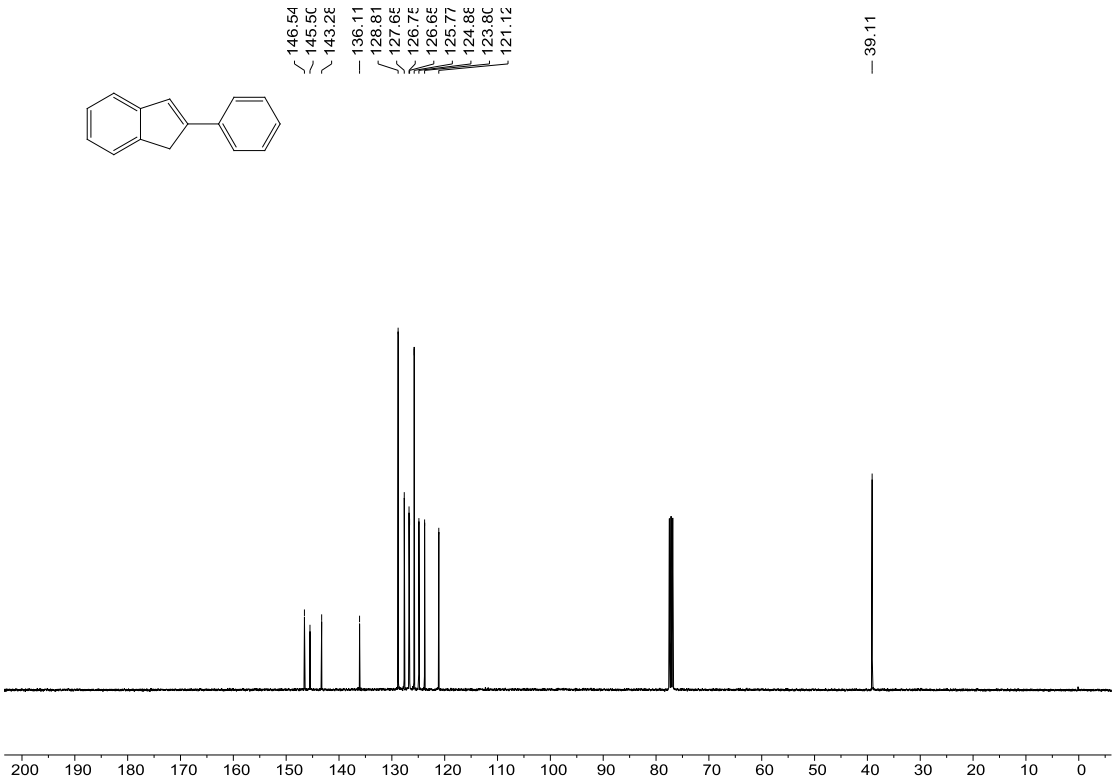
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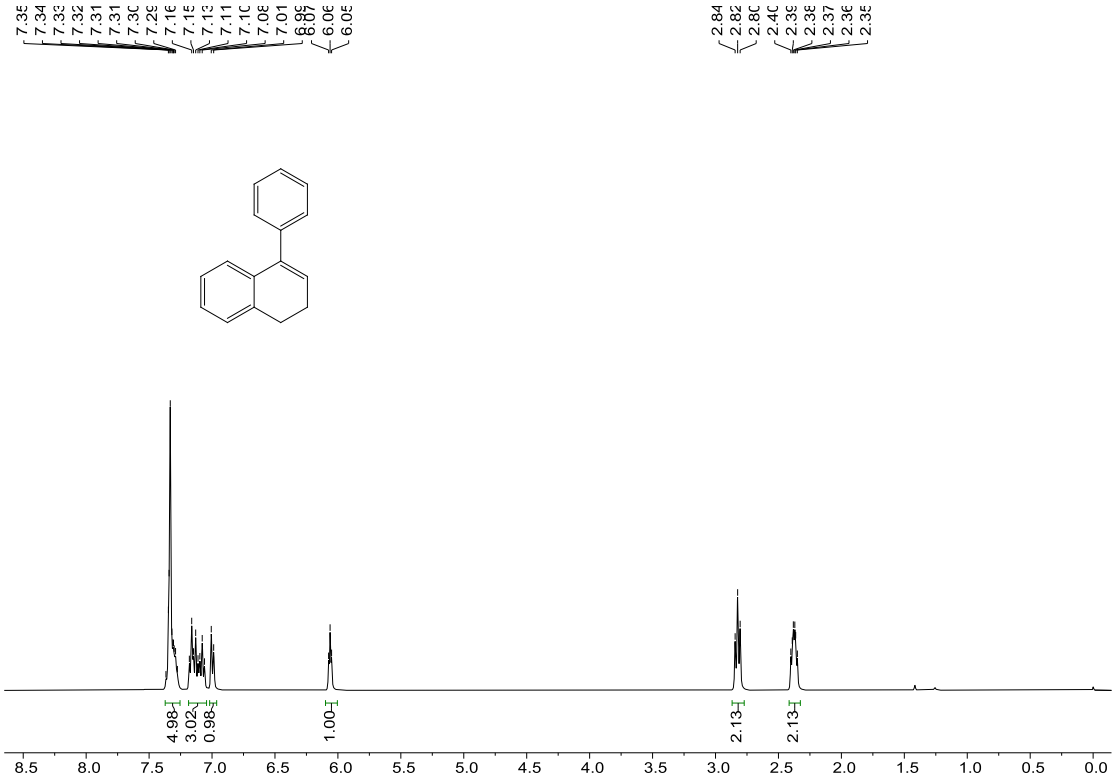
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1.00
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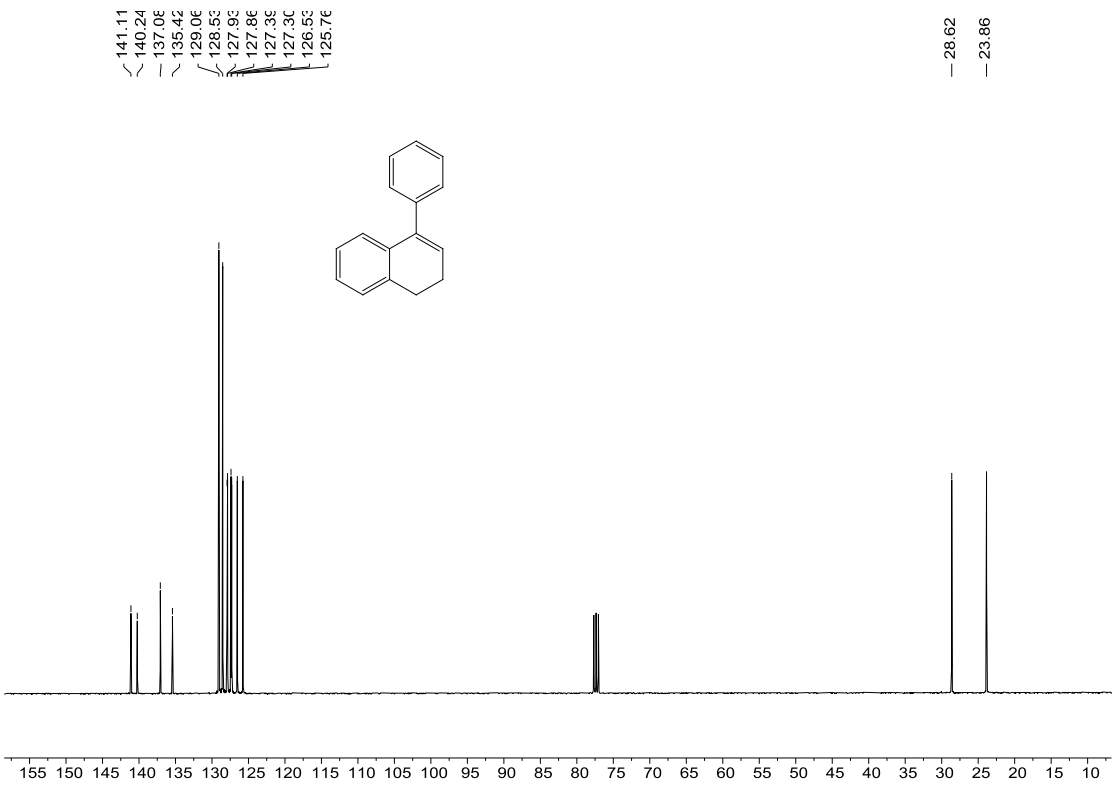
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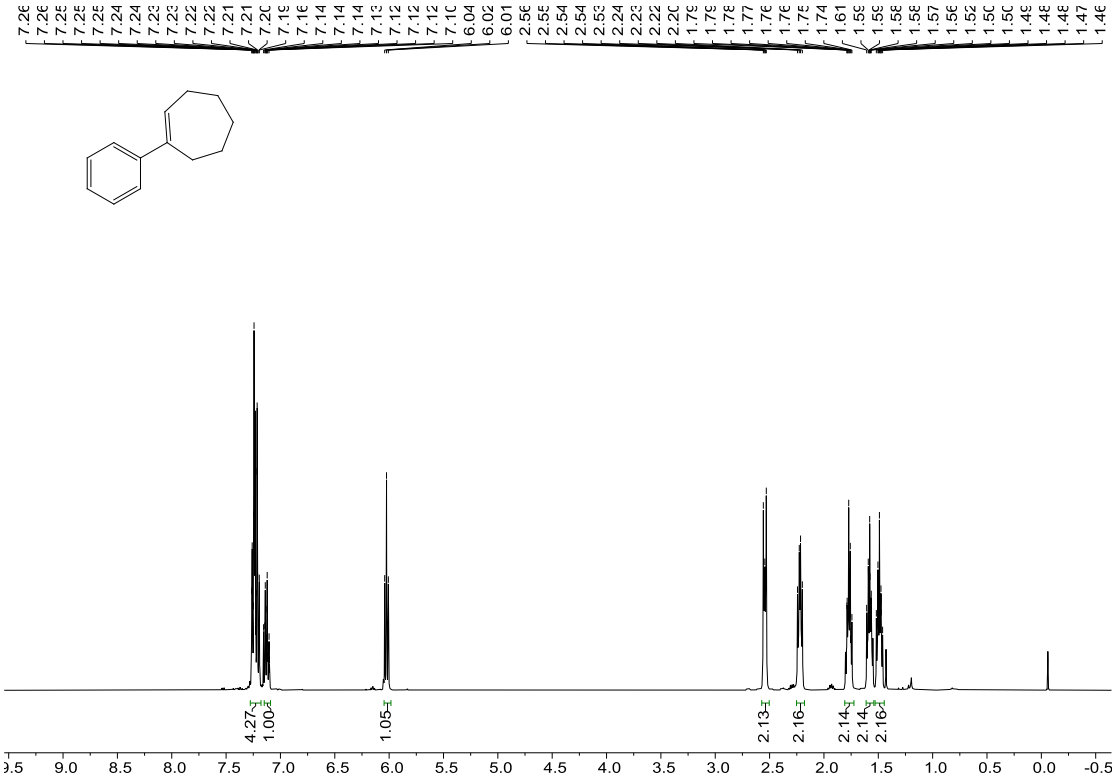
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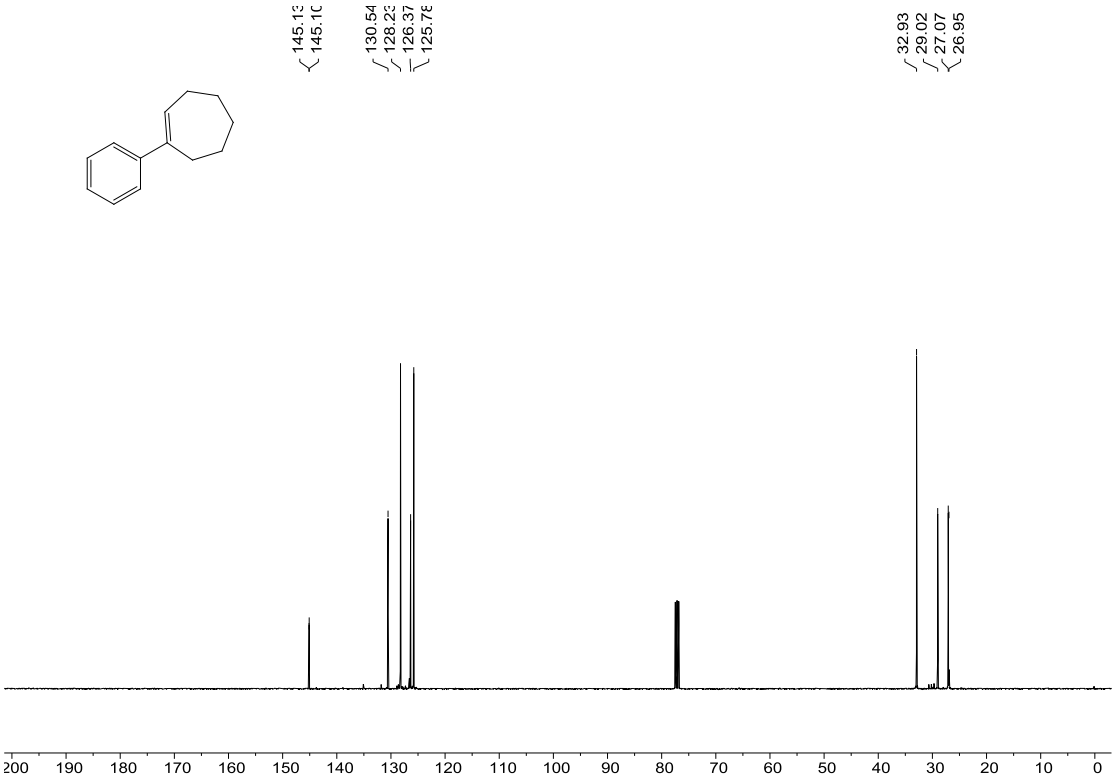

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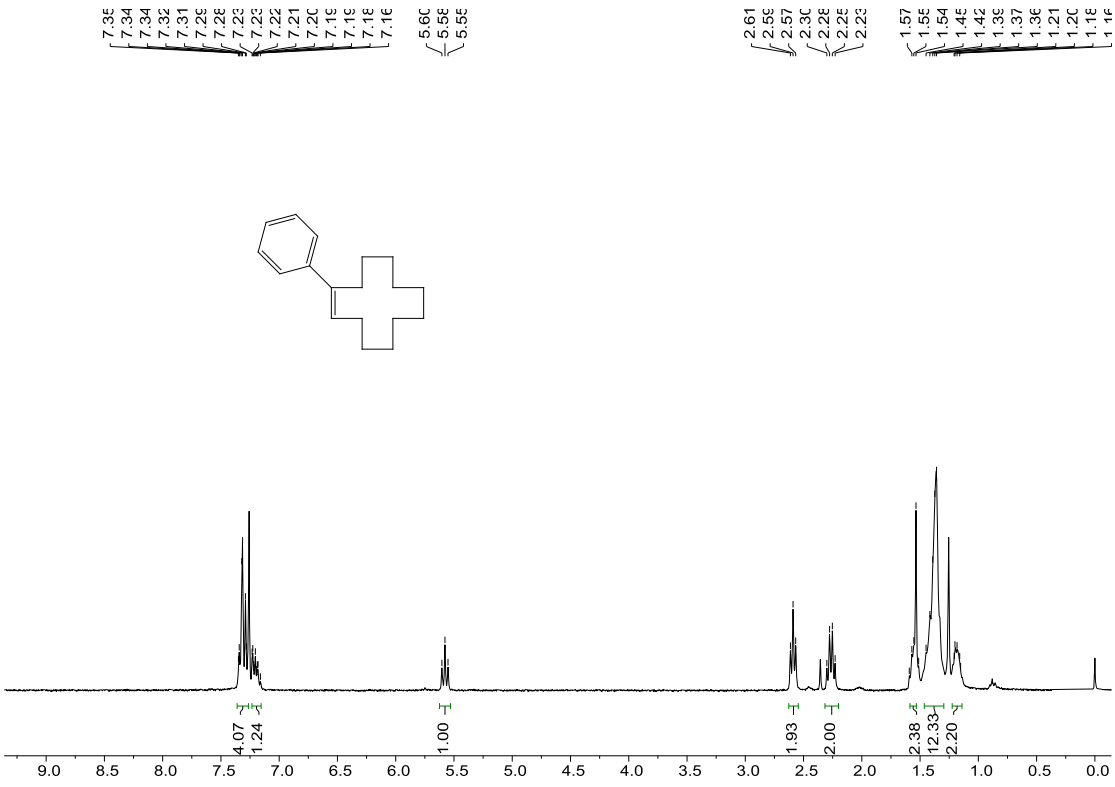

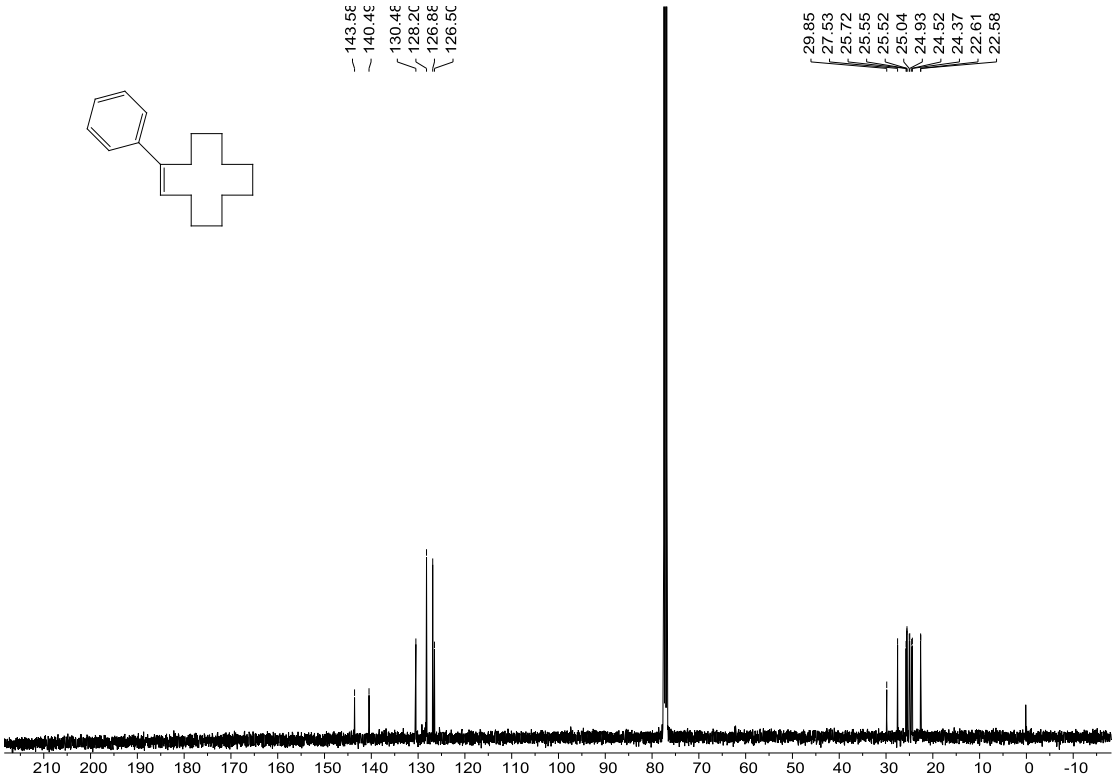
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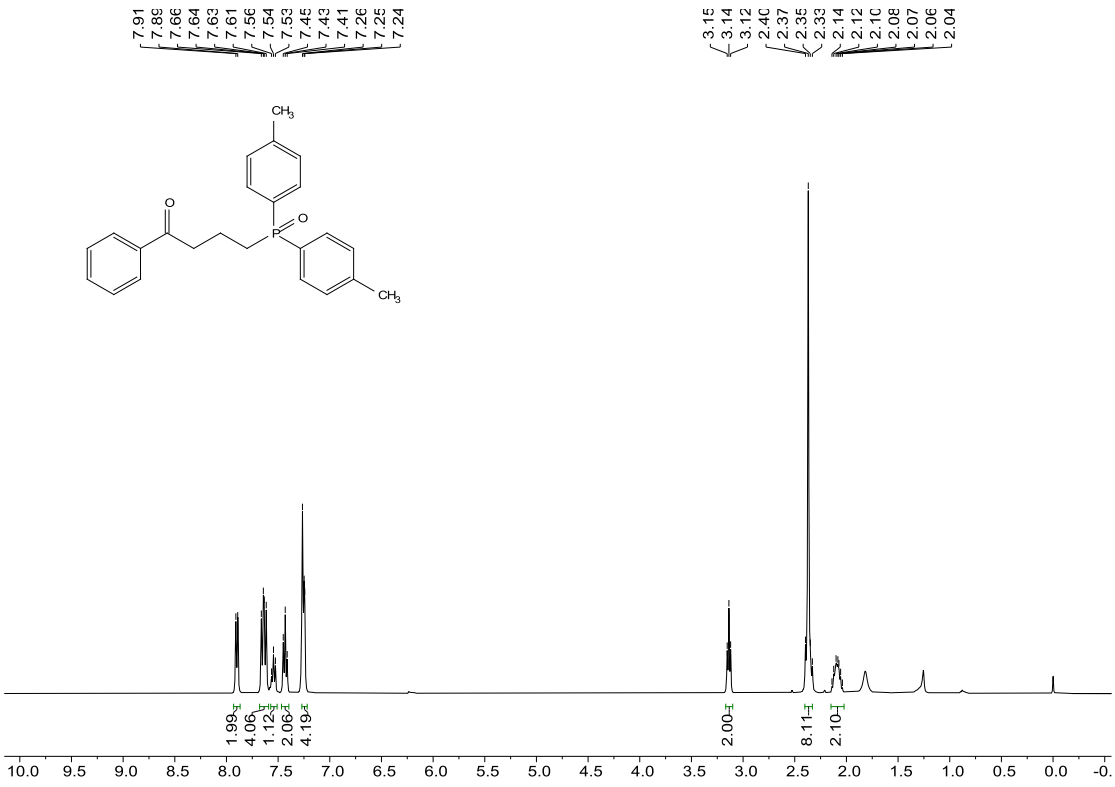
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2.08
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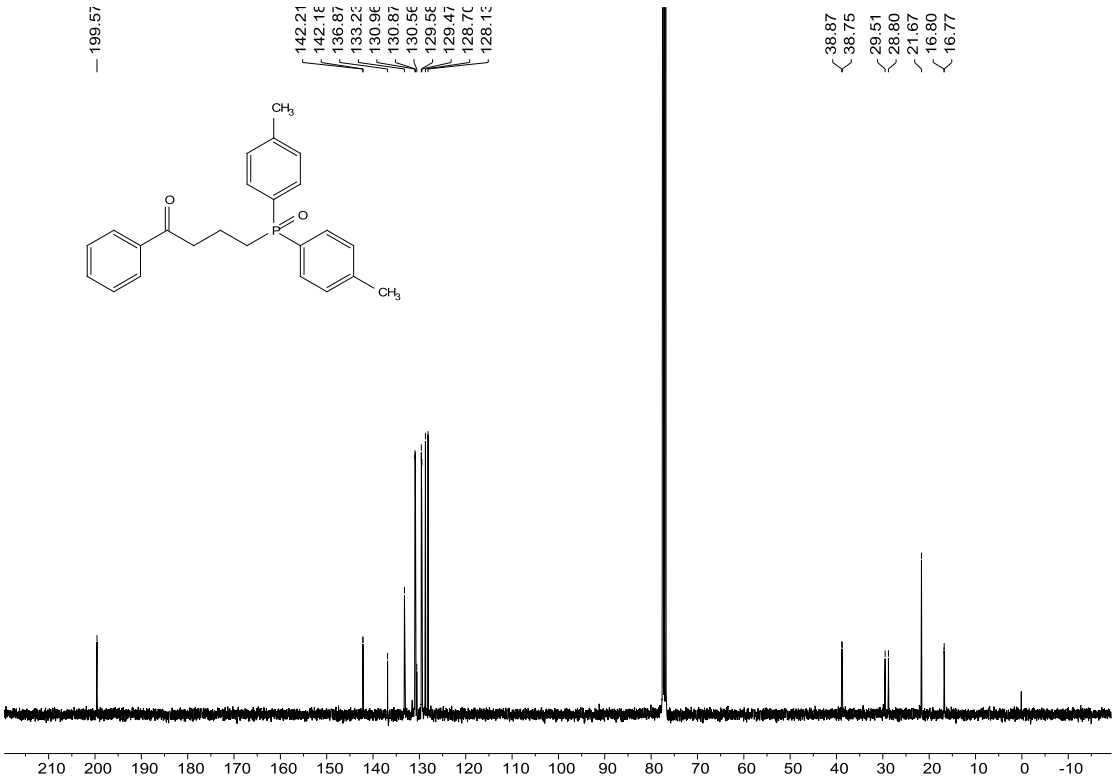
2.06
2.04
CH3
O
P
O
CH3
1.99
4.06
1.12
2.06
4.19
2.00
8.11
2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.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29.51
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O
P
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CH3
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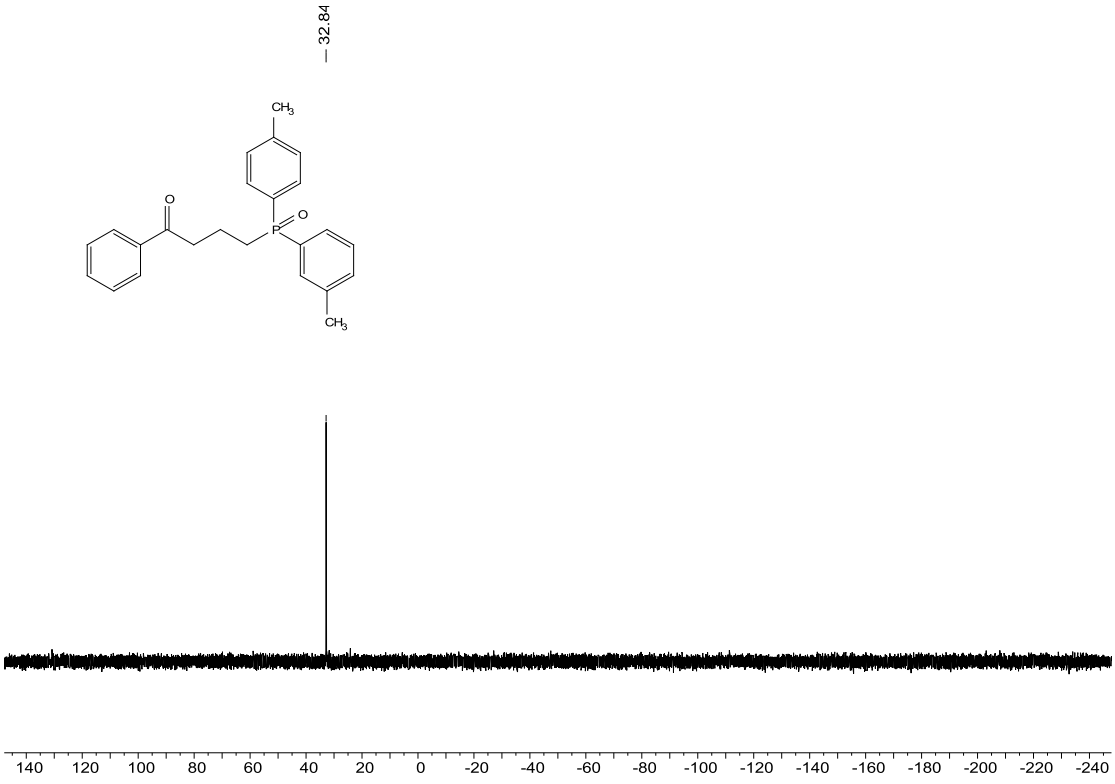
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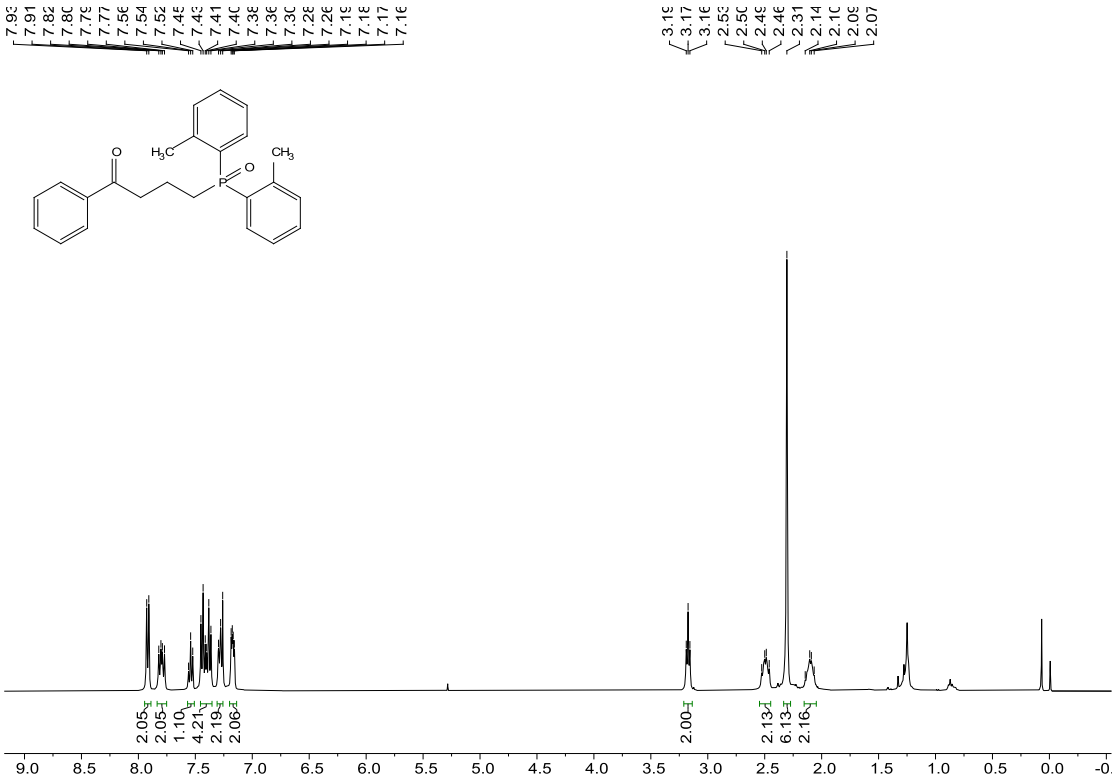
4b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4.21
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2.06
2.00
2.13
6.13
2.16
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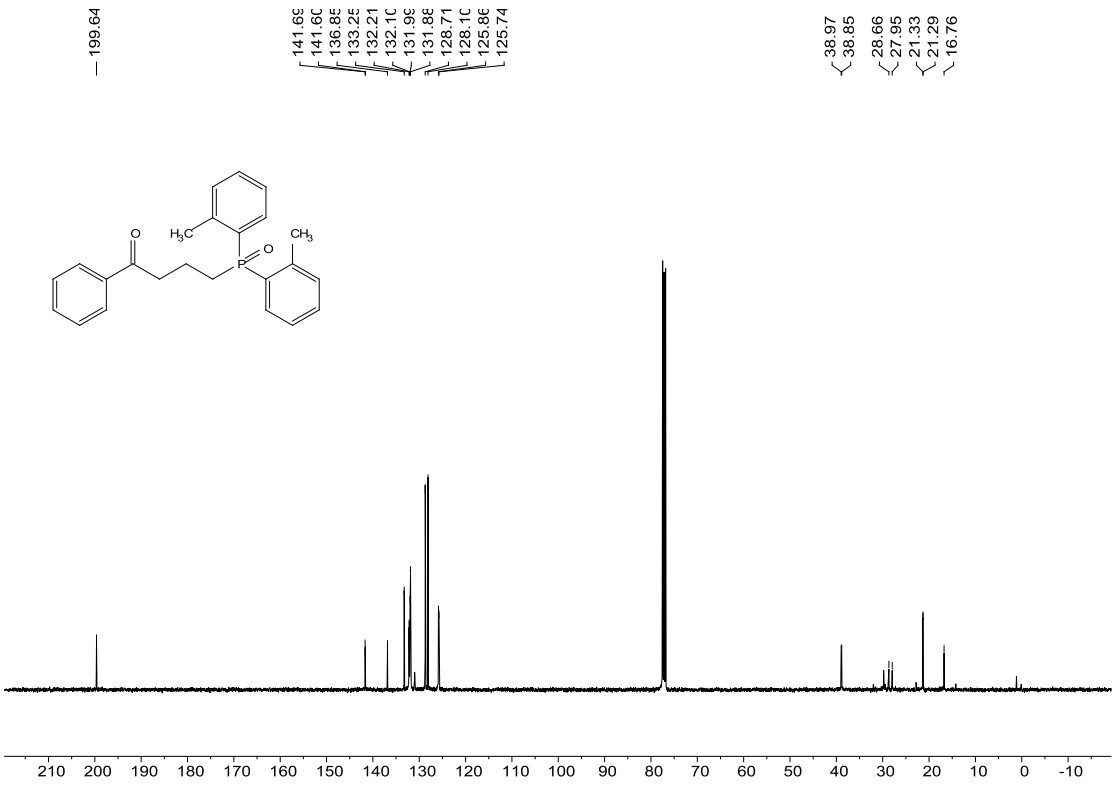
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CH3
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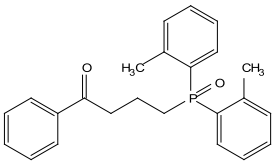
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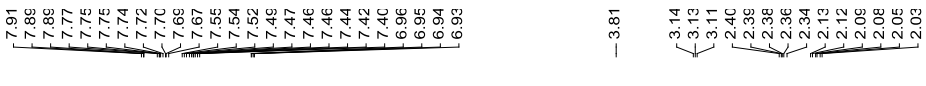
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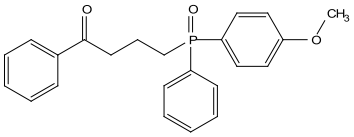
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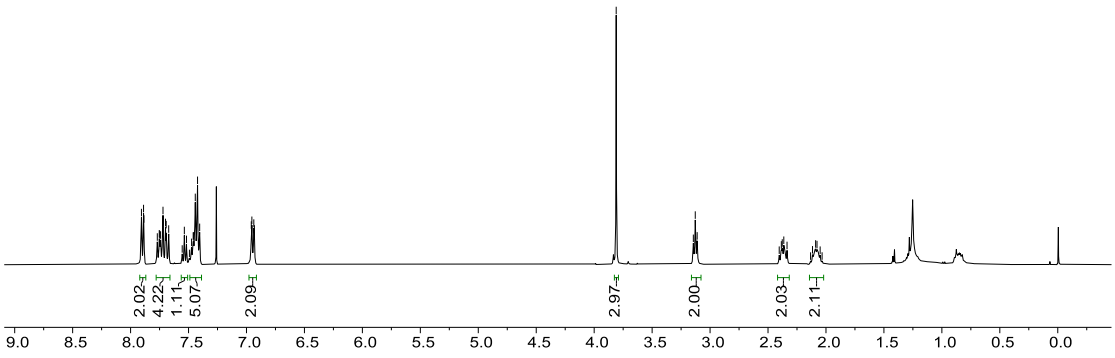
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2.11
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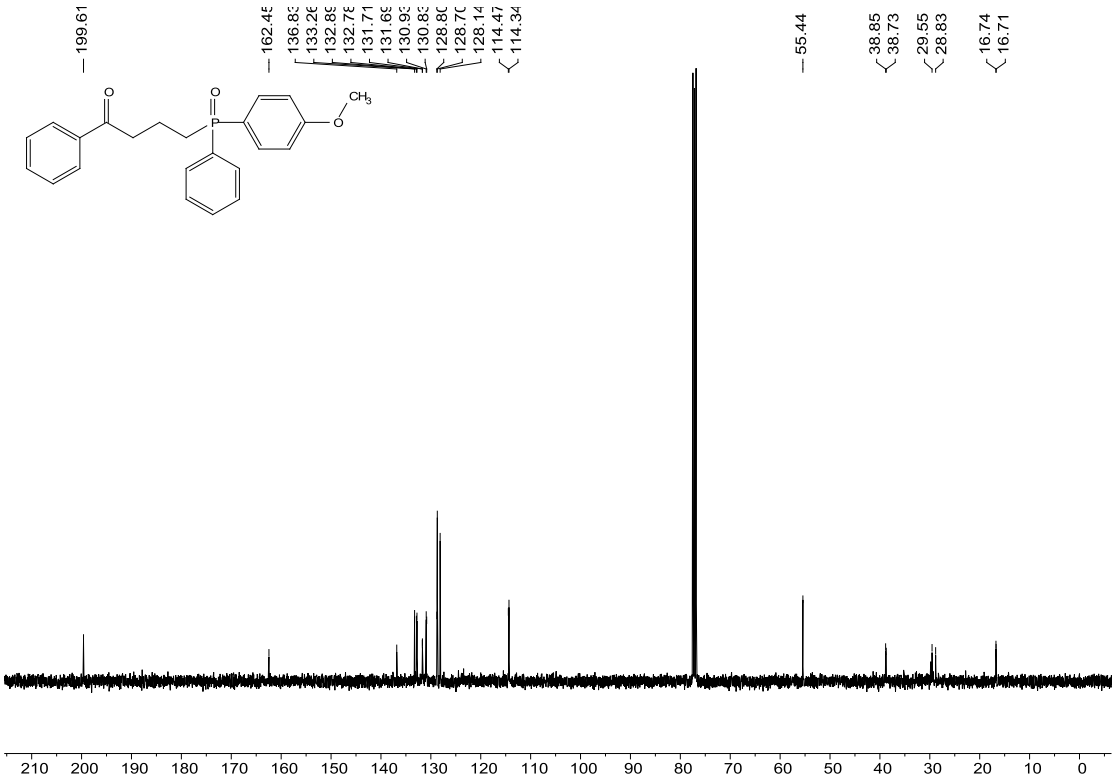
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128.14
114.47
114.34
55.44
38.85
38.73
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16.71
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O
P
O
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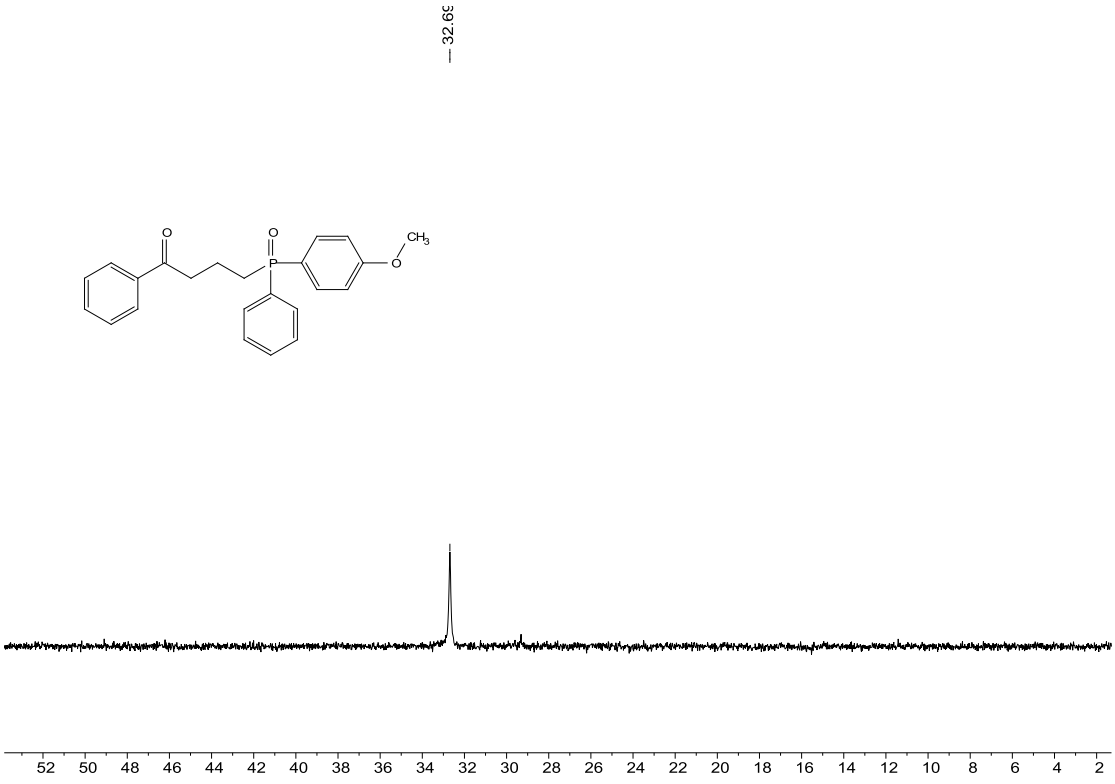
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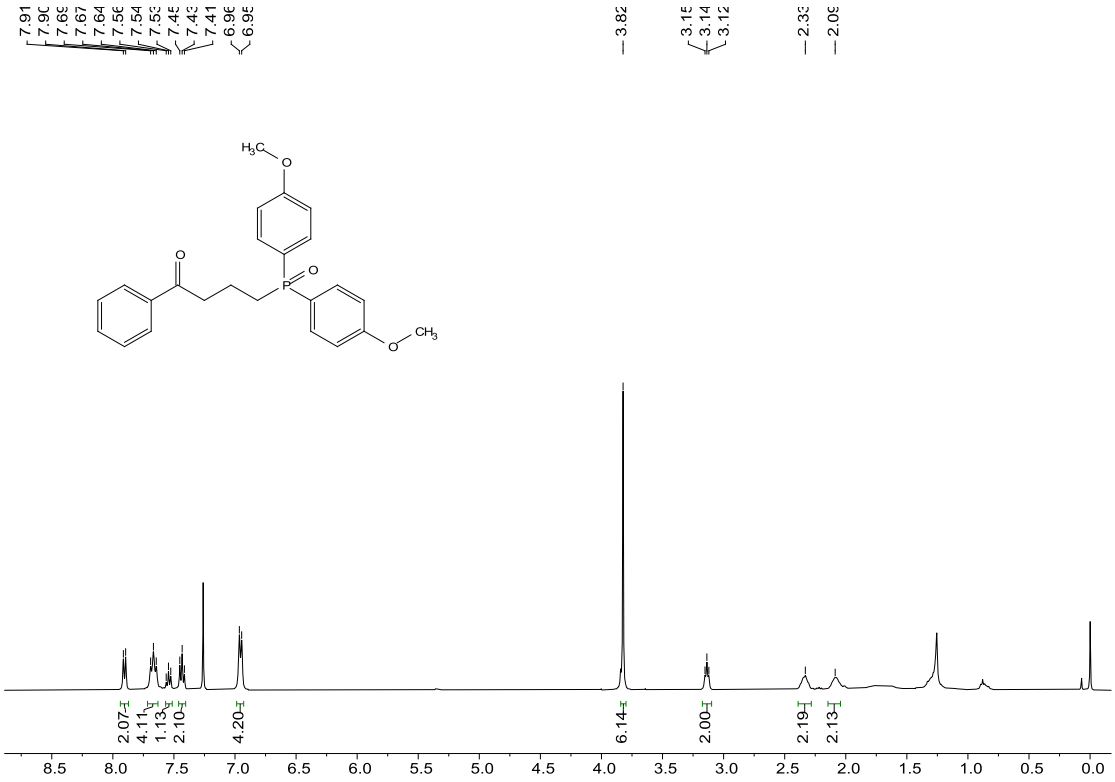

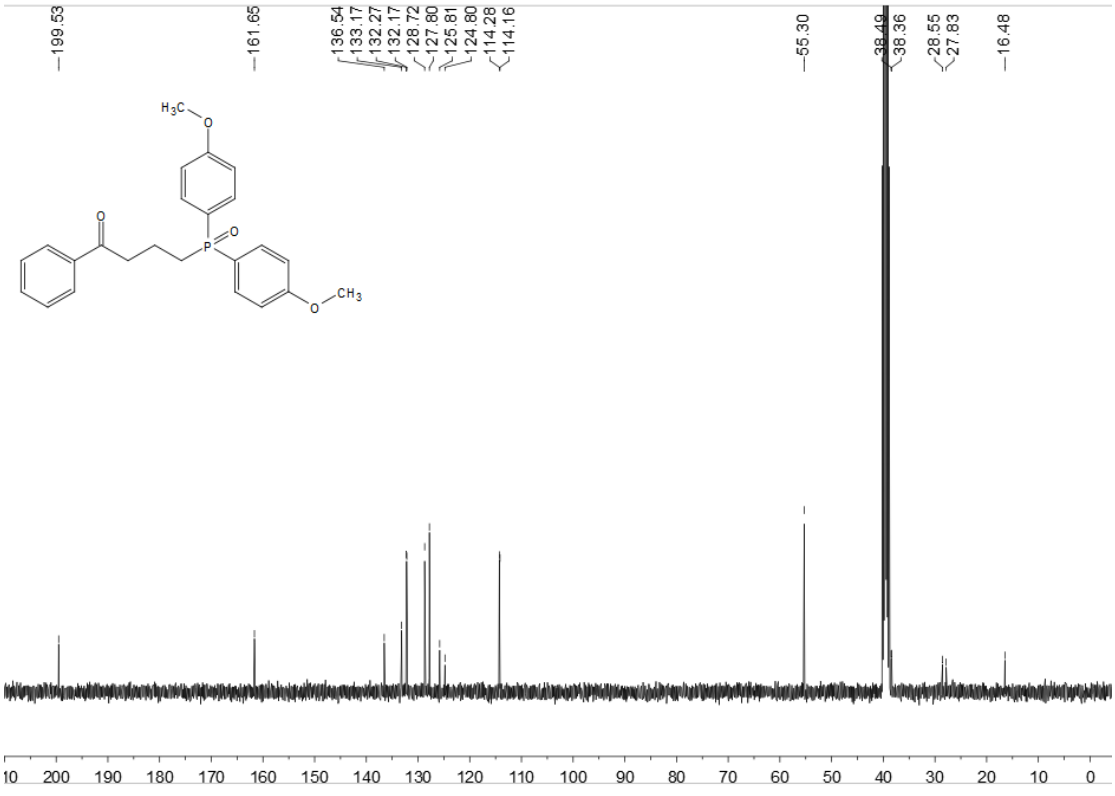

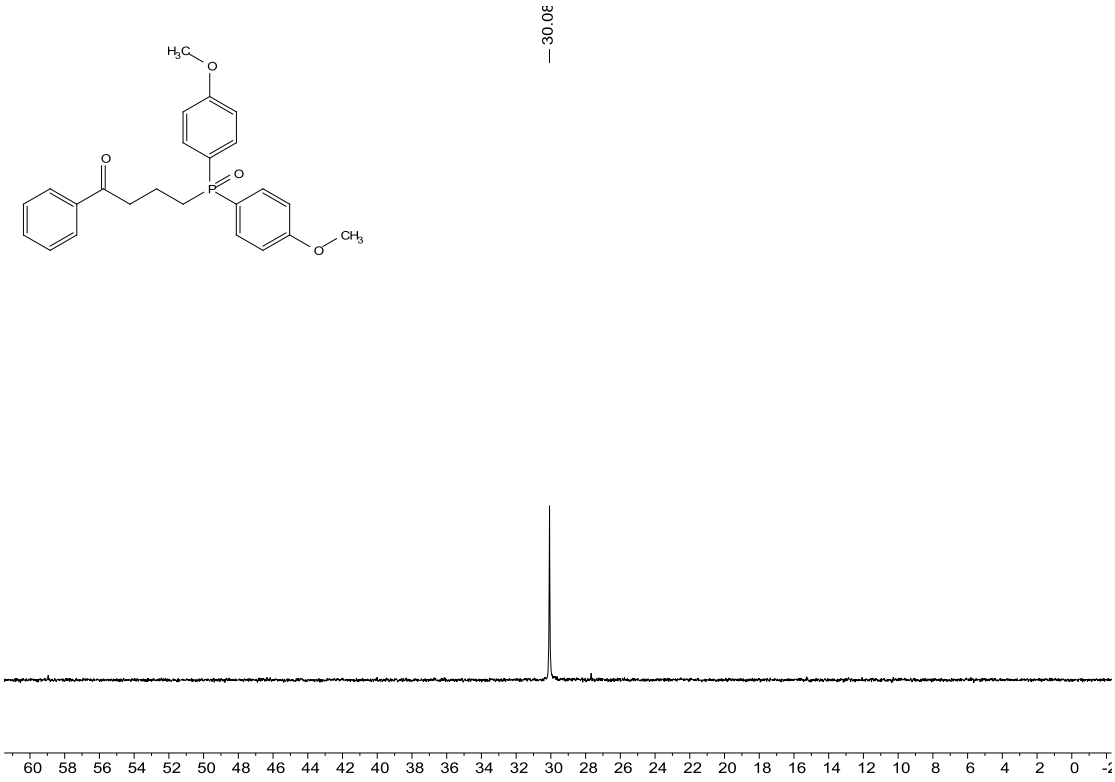
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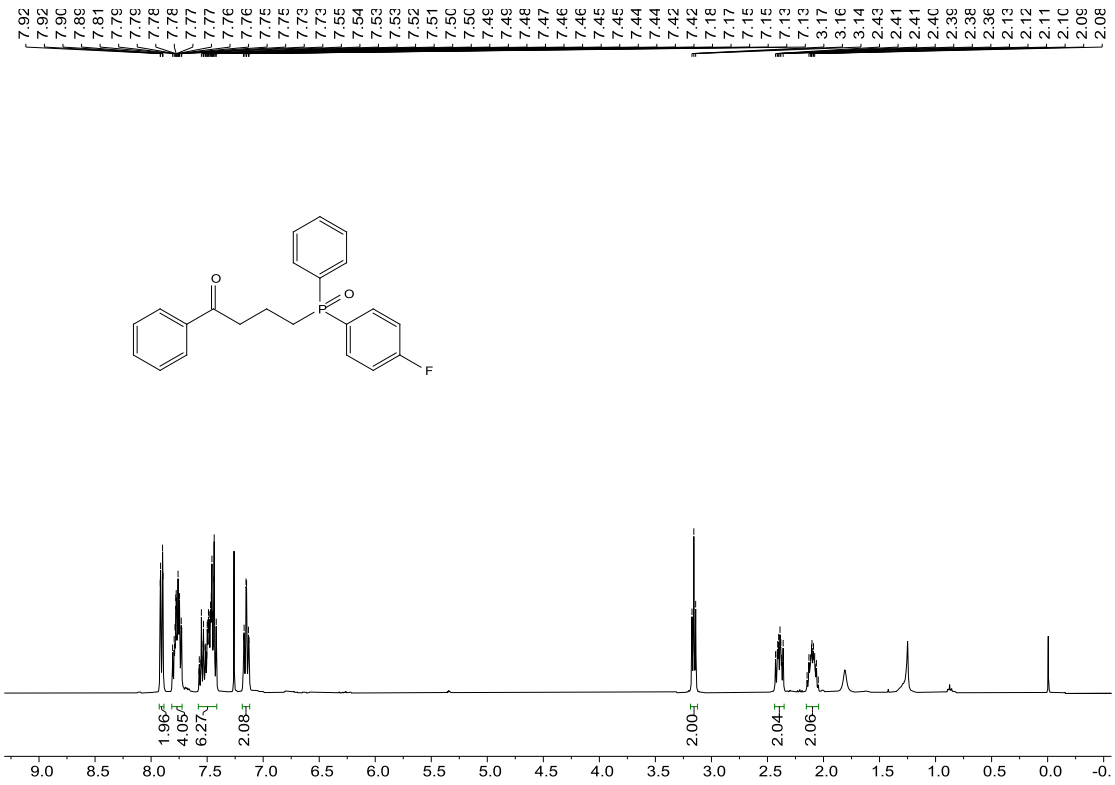
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2.06
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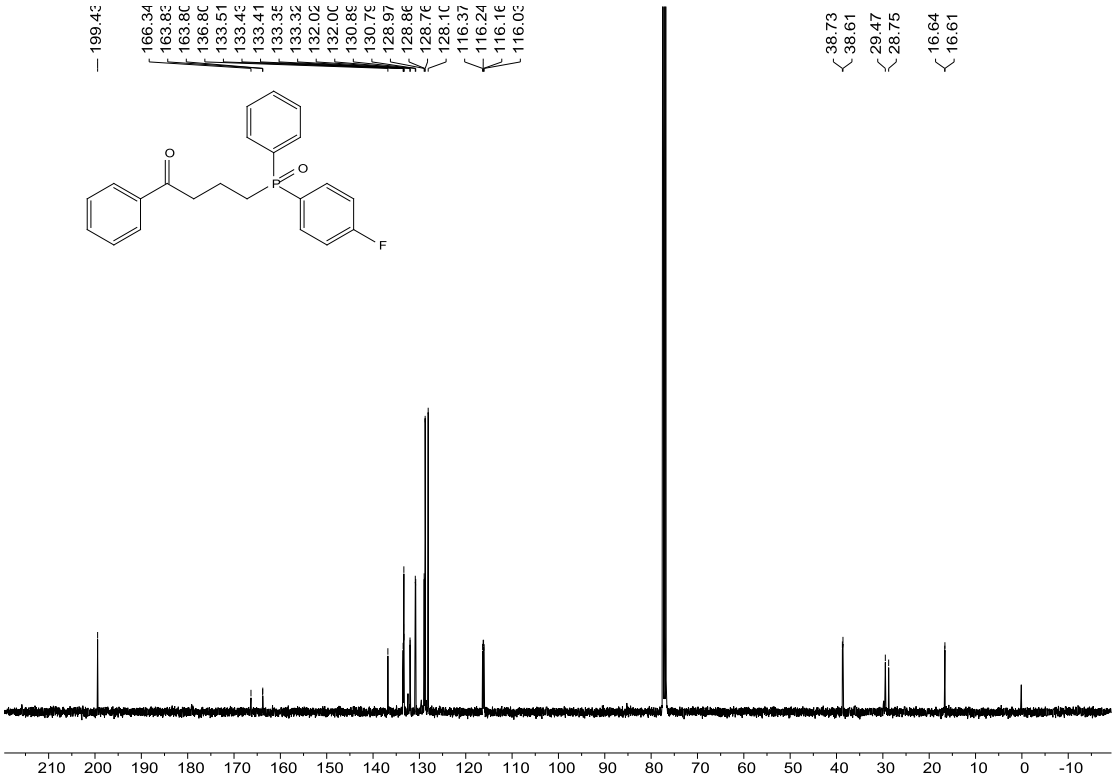
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128.76
128.10
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116.16
116.03
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P
O
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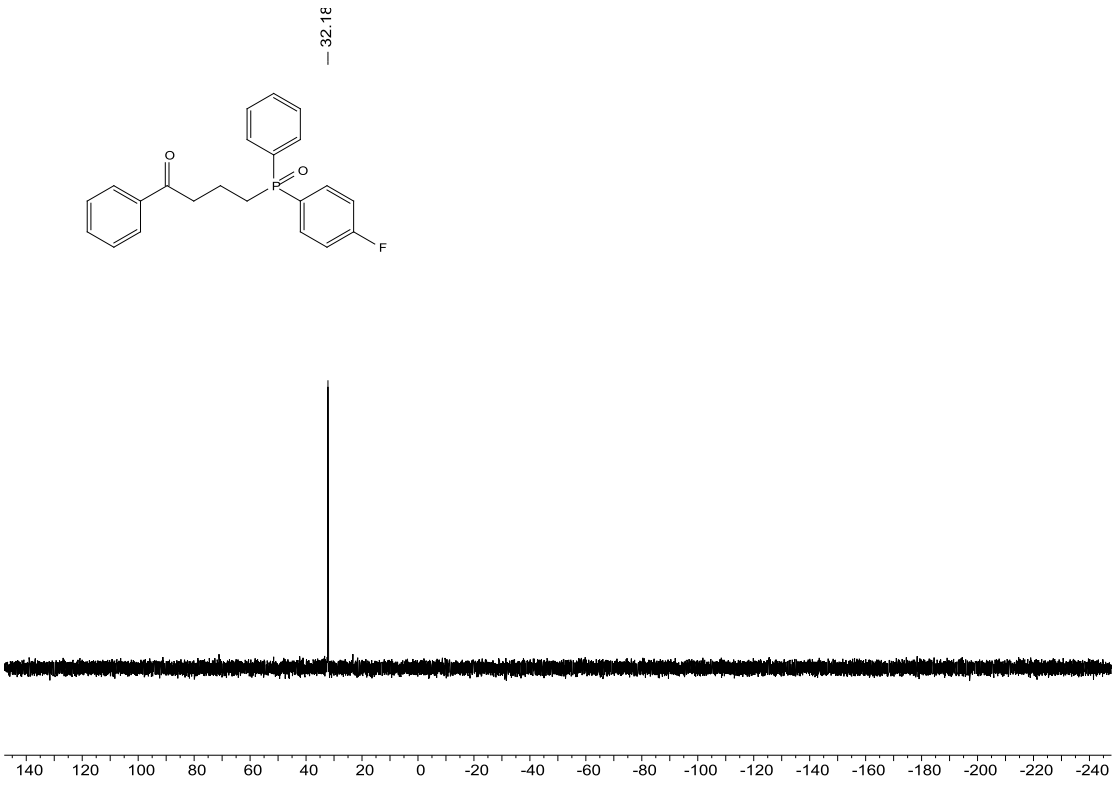
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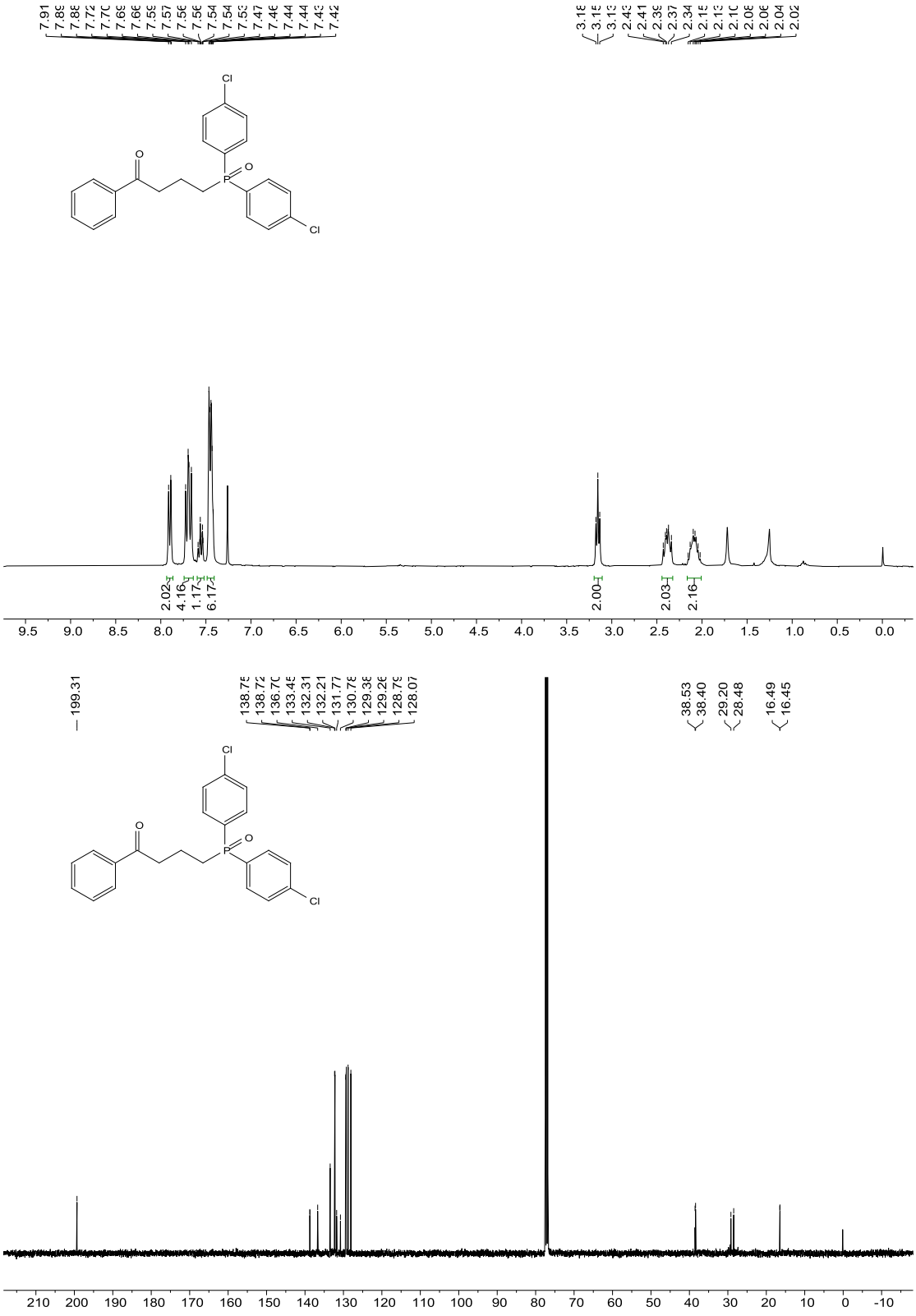
4f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O
Cl
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2.16
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38.40
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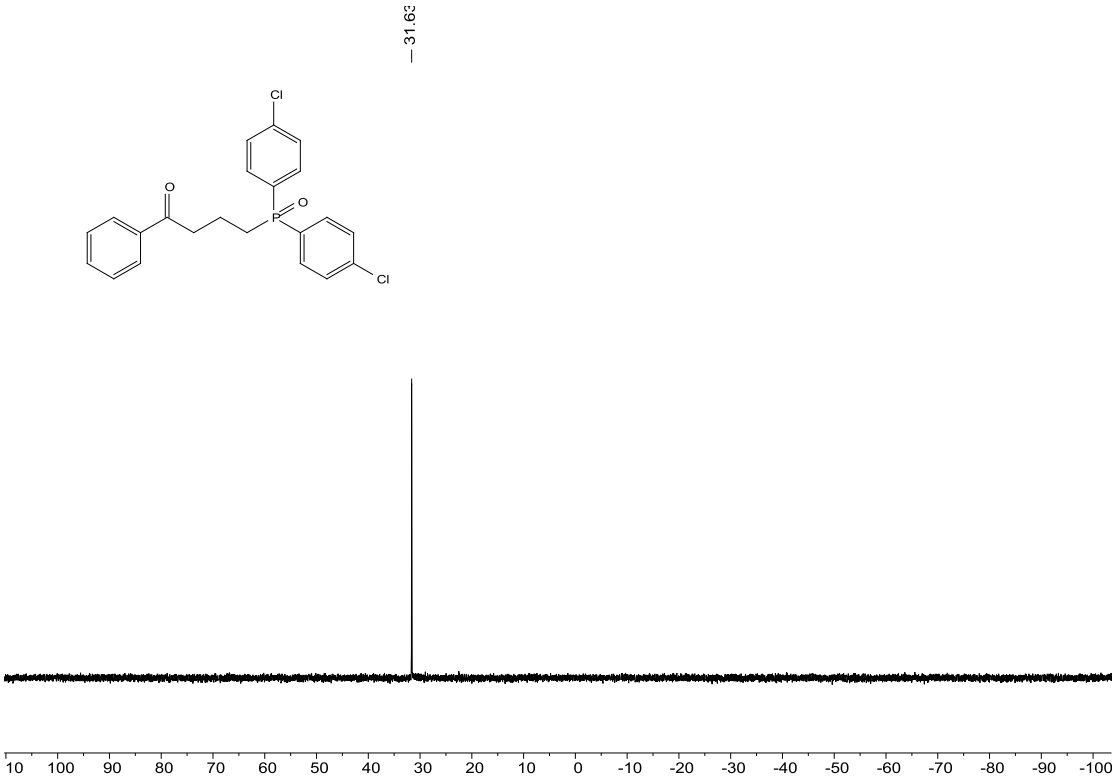
28.48
16.49
16.45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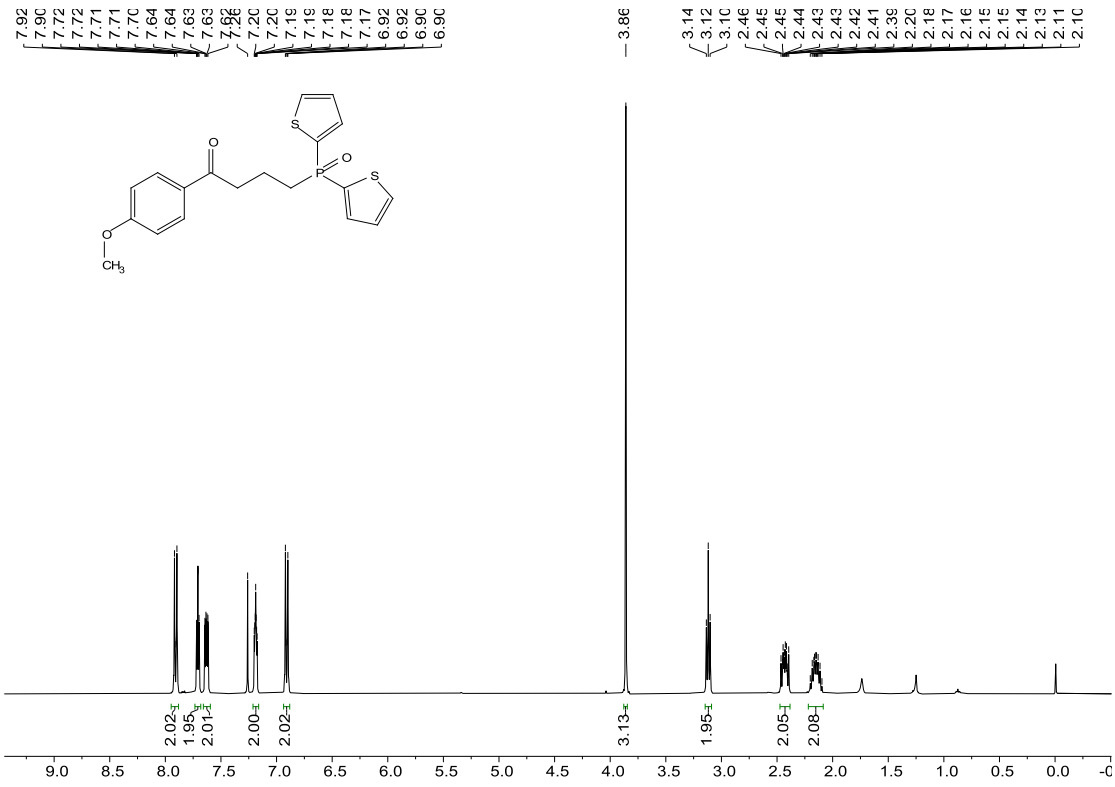
4g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3.86
3.14 3.12 3.10 2.46 2.45 2.45 2.44 2.43 2.43 2.42 2.41 2.39 2.20 2.18 2.17 2.16 2.15 2.15 2.14 2.13 2.11 2.10
S
O
P
O
S
O
CH3
2.02 1.95 2.01 2.00 2.02 3.13 1.95 2.05 2.08
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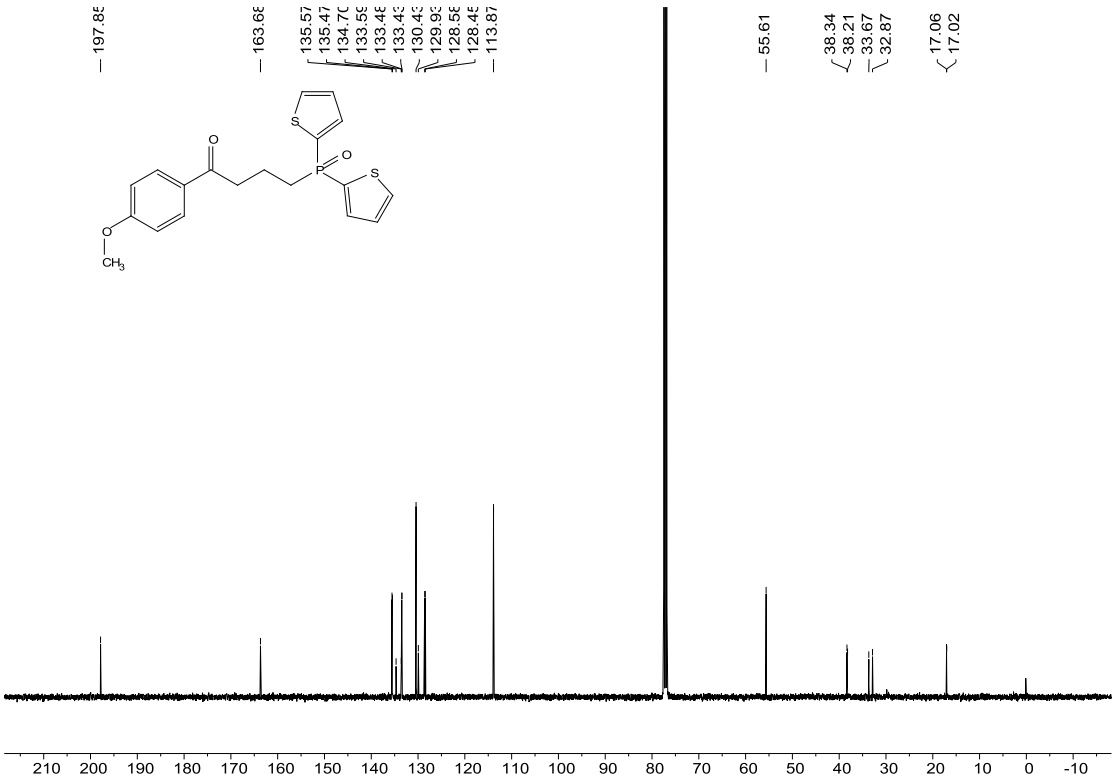
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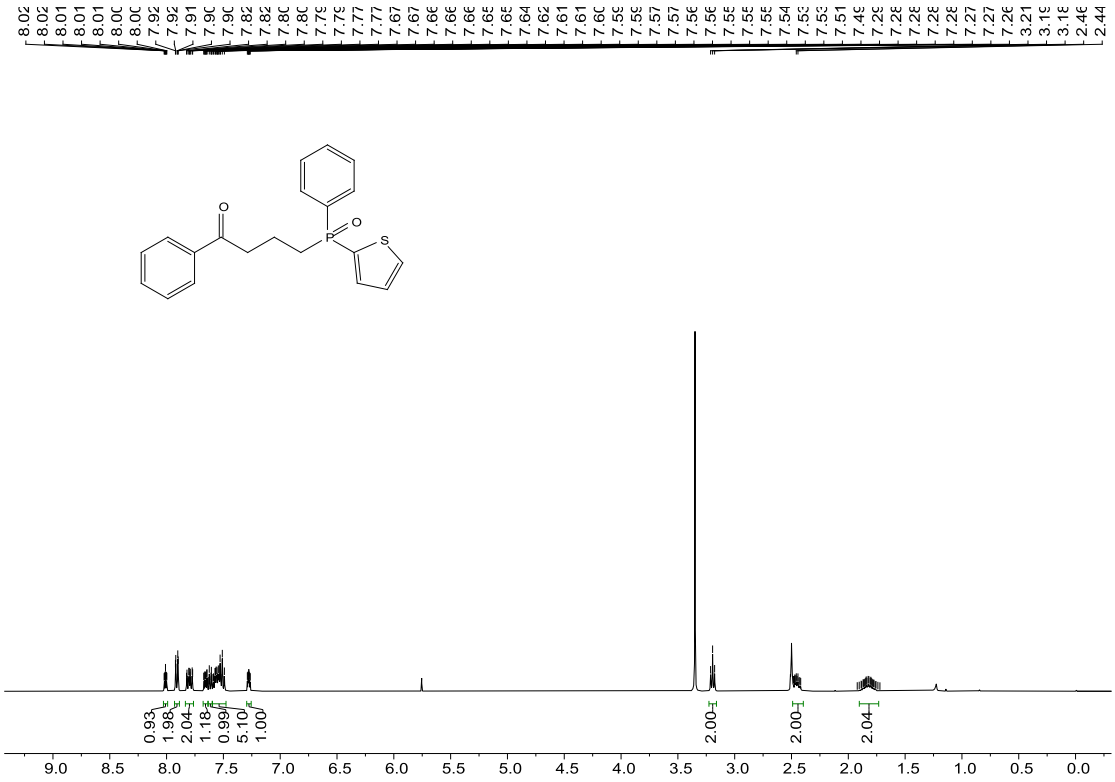
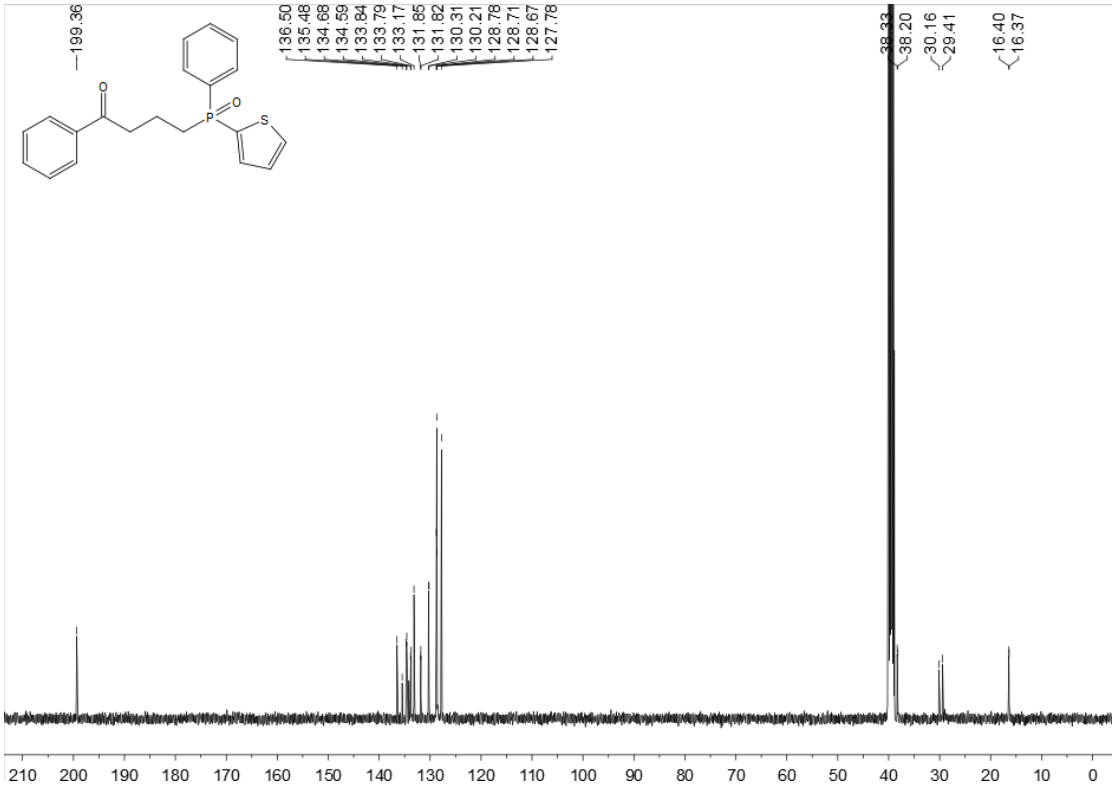
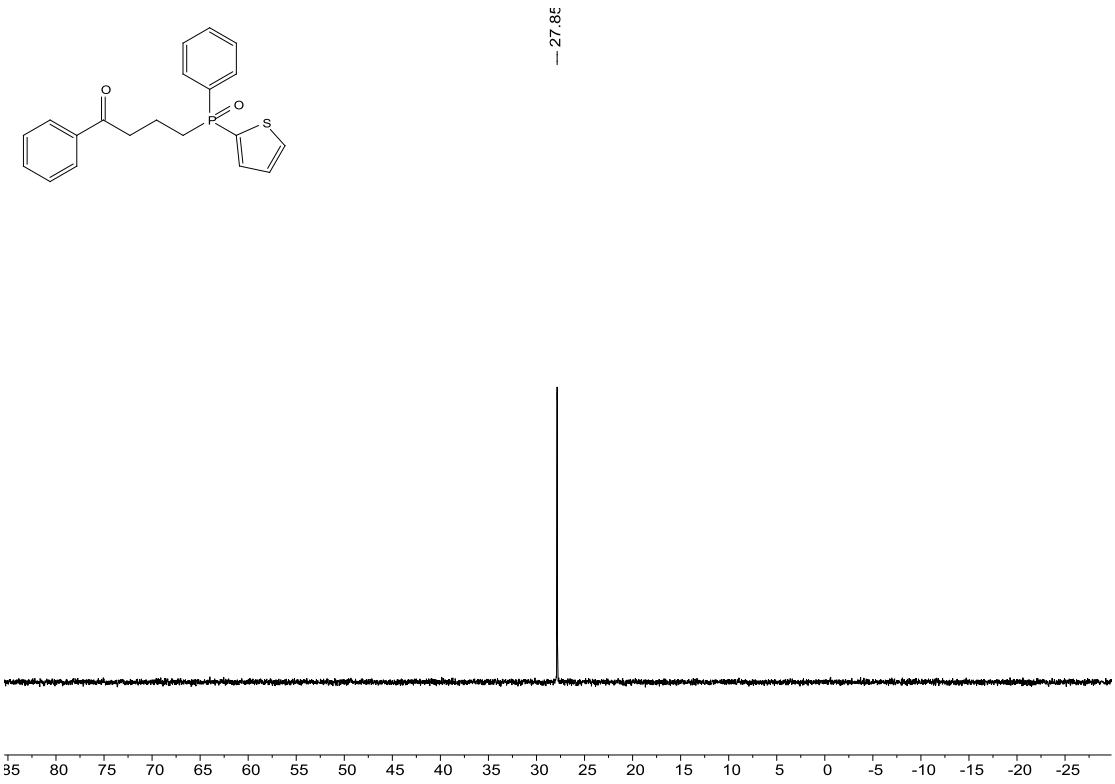
S
S
O
CH3


O
P
O
S
S
O
CH3

4h



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O
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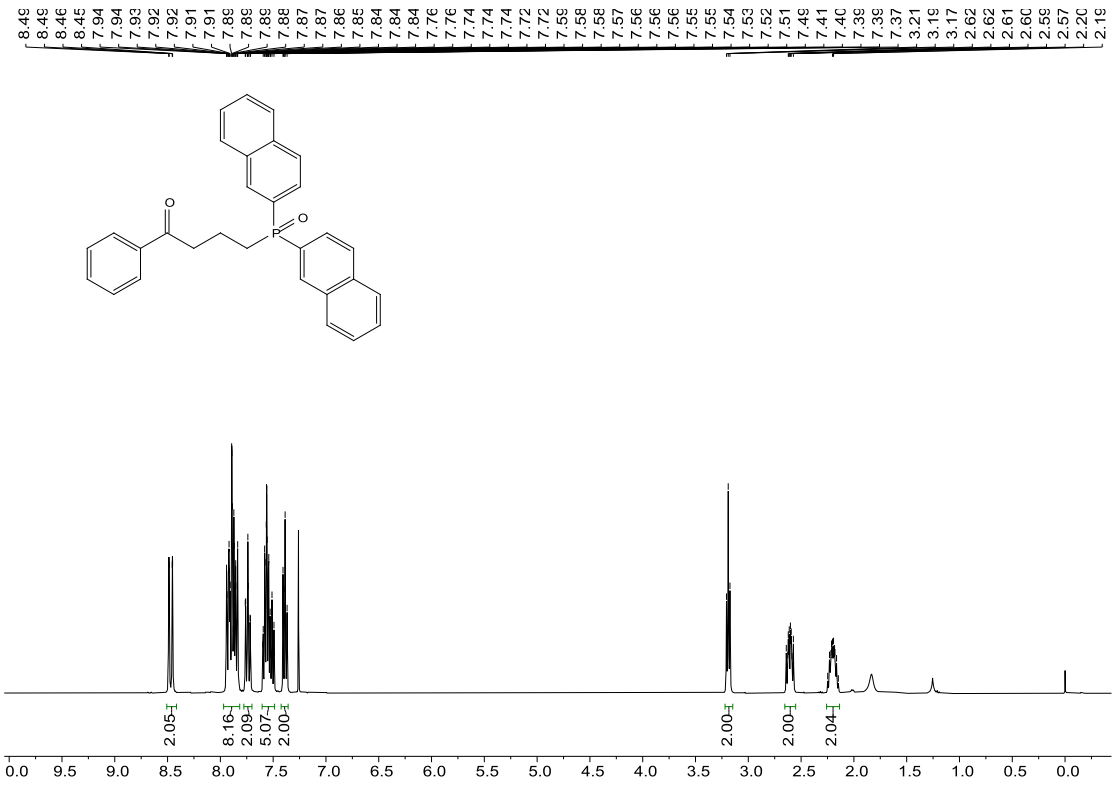
4i


O
O
P
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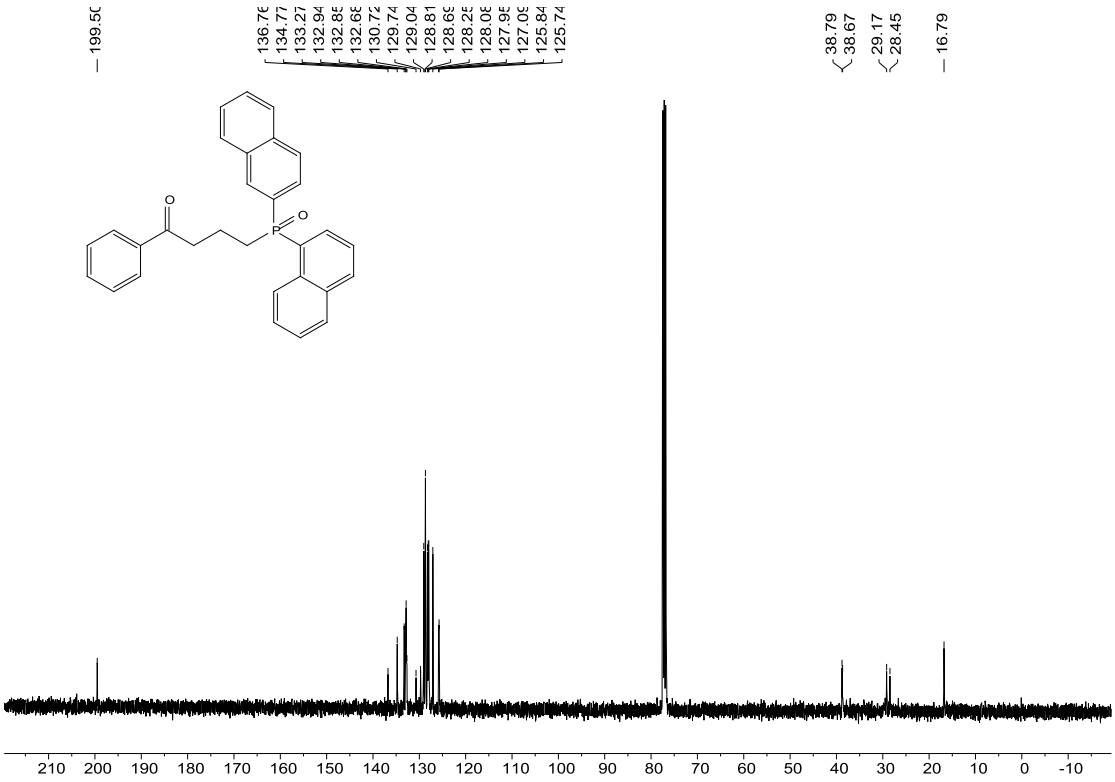
8.16
2.09
5.07
2.00
2.00
2.00
2.04
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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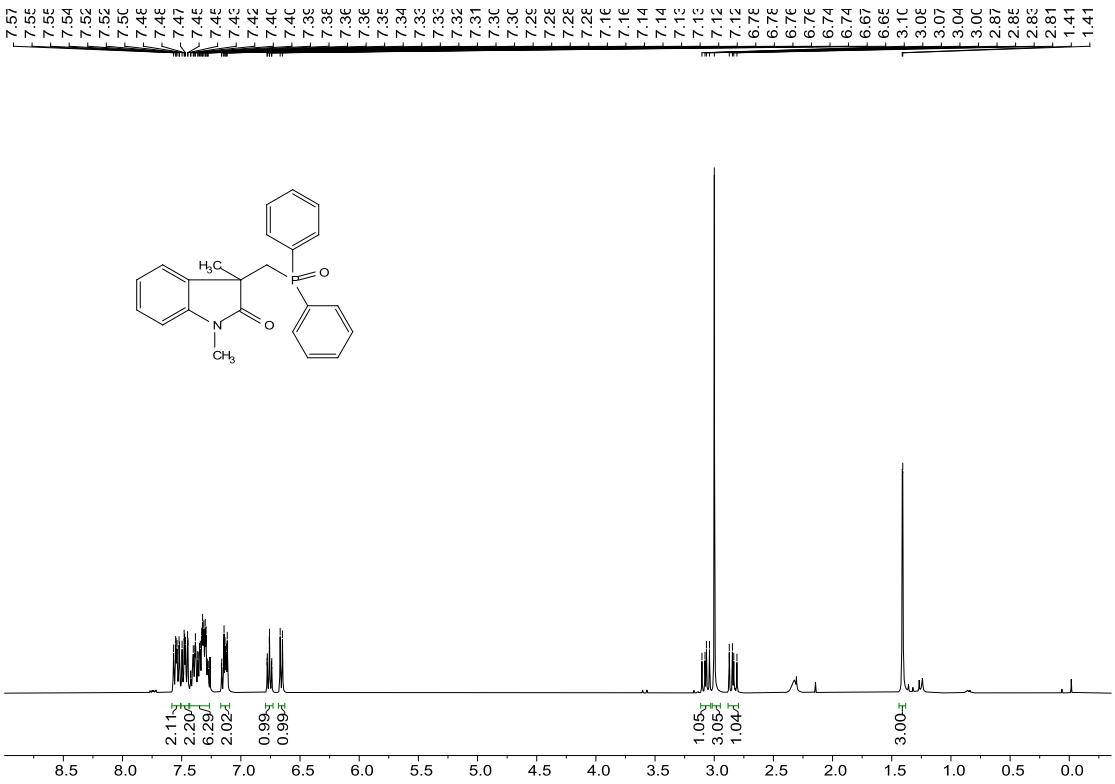
7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1.04
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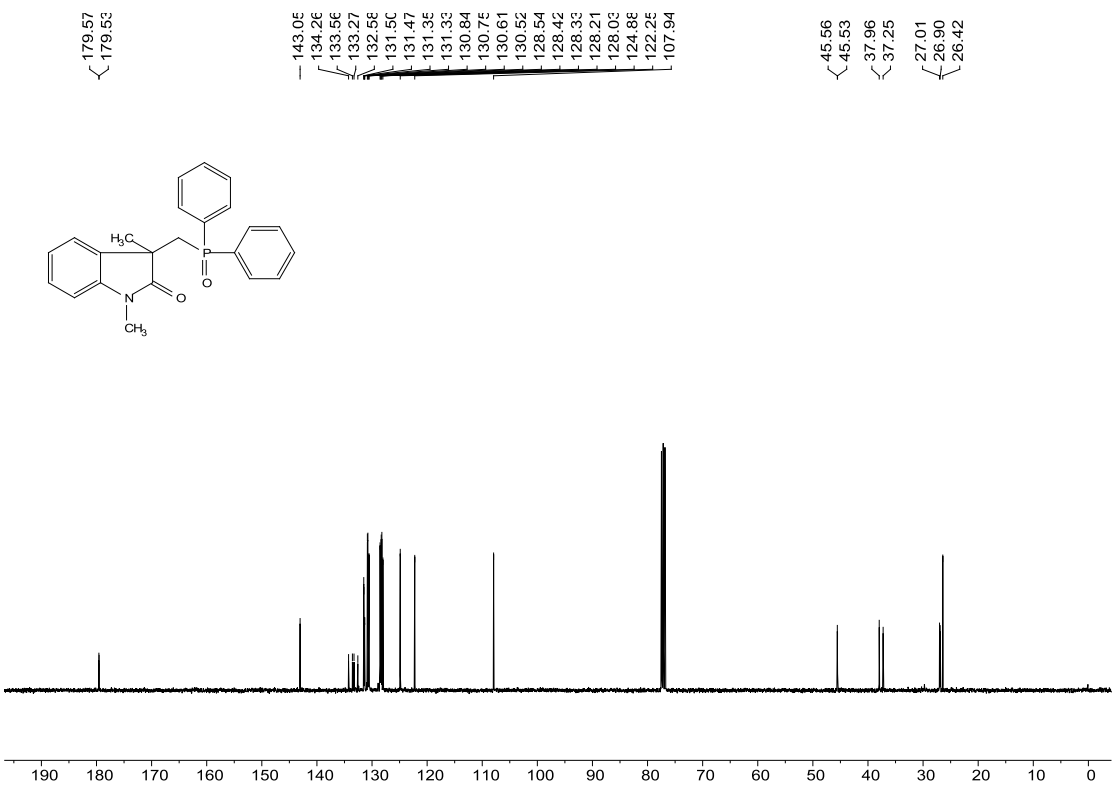
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130.75
130.61
130.52
128.54
128.42
128.33
128.21
128.03
124.88
122.25
107.94
45.56
45.53
37.96
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N
O
CH3
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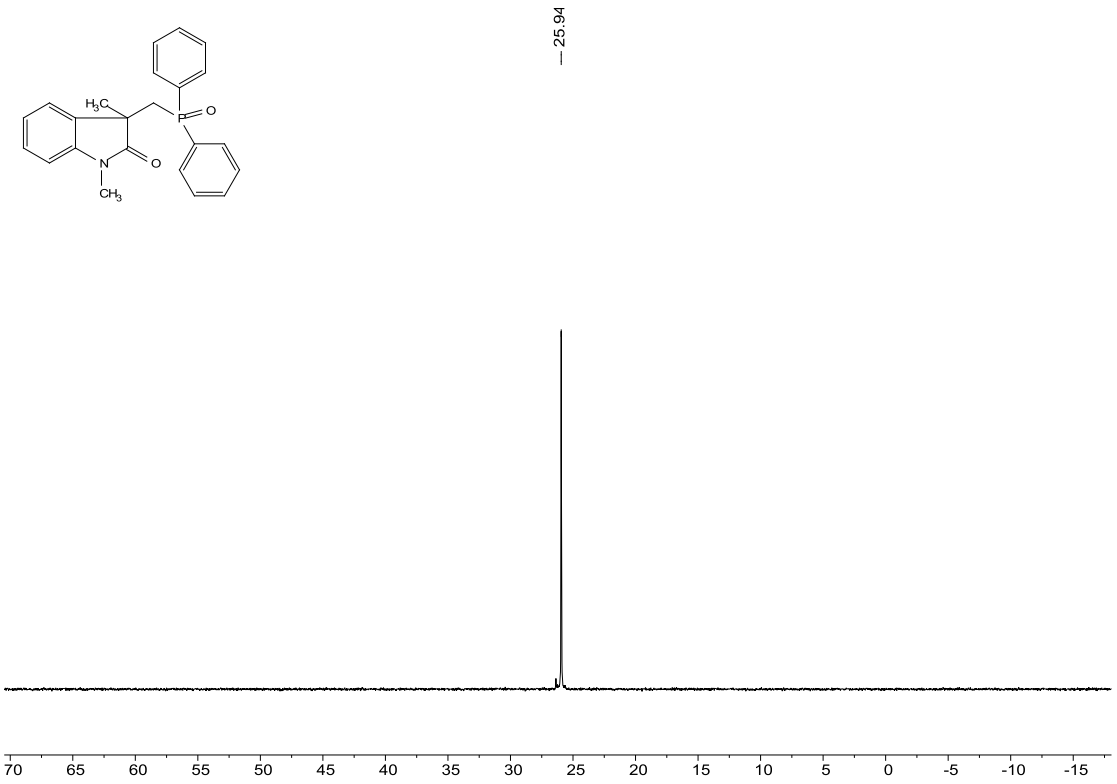
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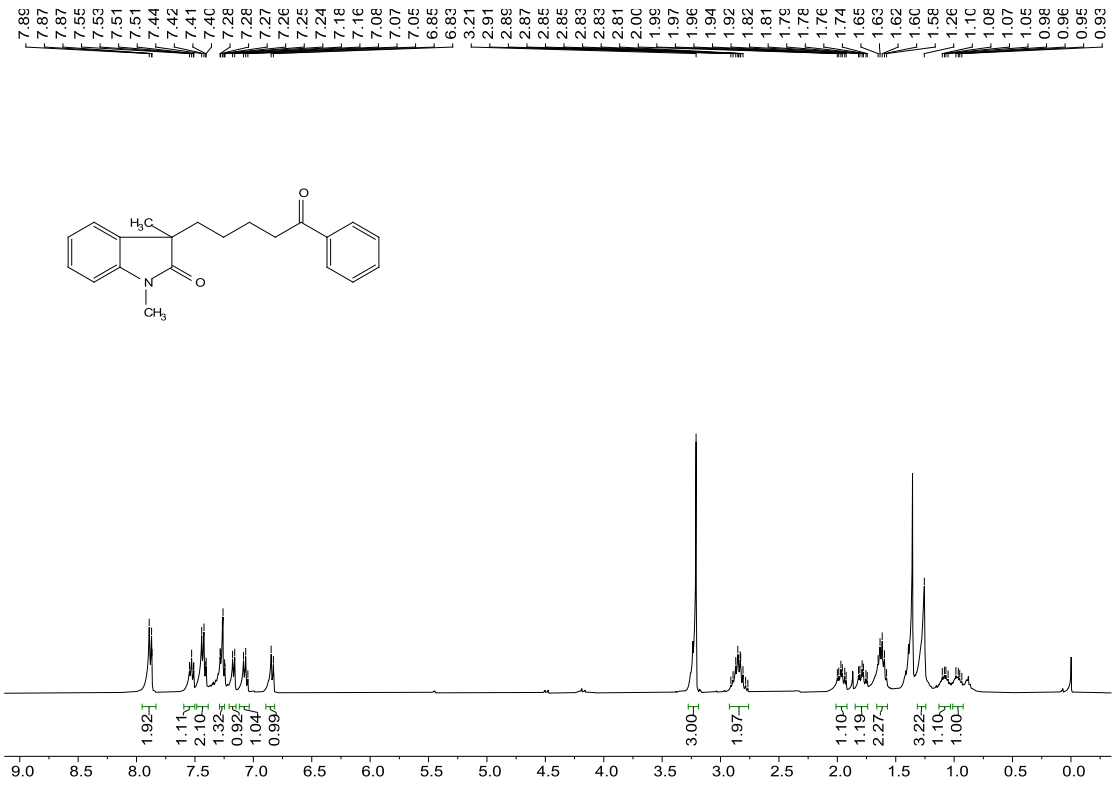
8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3.21 2.91 2.89 2.87 2.85 2.85 2.83 2.83 2.81 2.00 1.99 1.97 1.96 1.94 1.92 1.82 1.81 1.79 1.78 1.76 1.74 1.65 1.63 1.62 1.60 1.58 1.26 1.10 1.08 1.07 1.05 0.98 0.96 0.95 0.93
O
H3C
N
O
CH3
1.92 1.11 2.10 1.32 0.92 1.04 0.99 3.00 1.97 1.10 1.19 2.27 3.22 1.10 1.00
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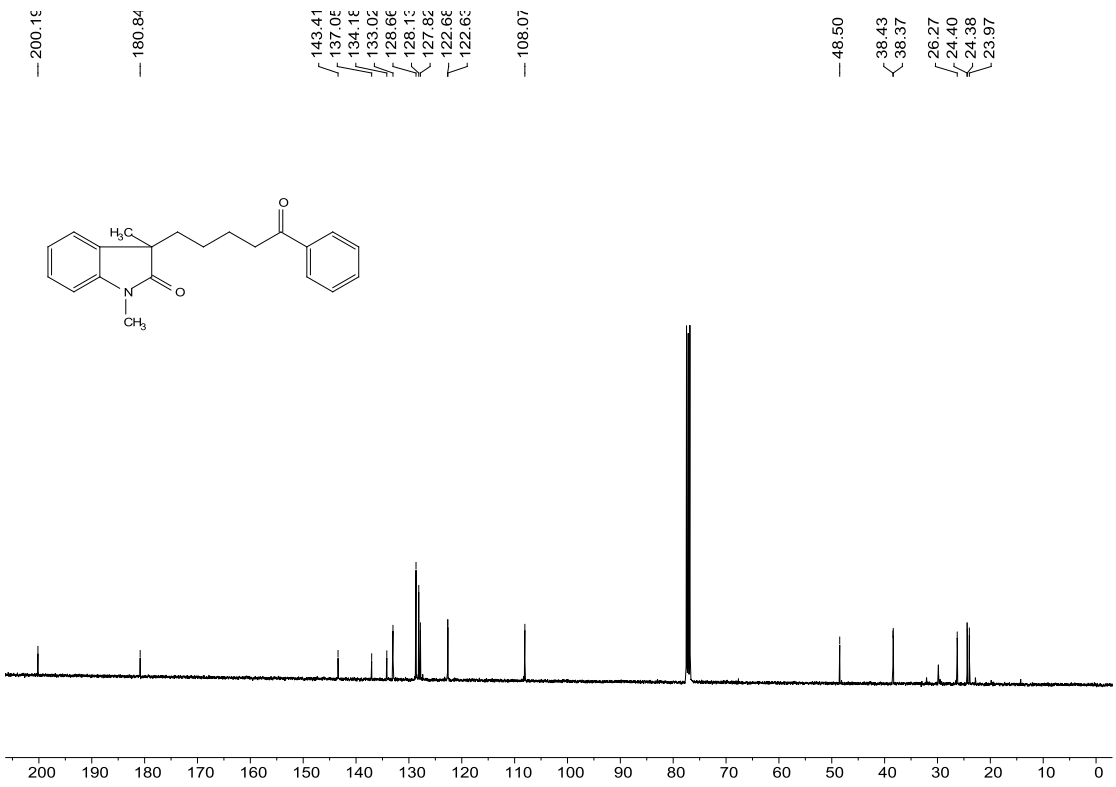
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38.43
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24.40
24.38
23.97
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O
CH3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
20
10
0