Supporting Information for

Facile Synthesis of Alkylphosphonates from 4-Alkyl-1,4-Dihydropyridines via Photoinduced Formal Deformylative Phosphonylation

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Table of Contents

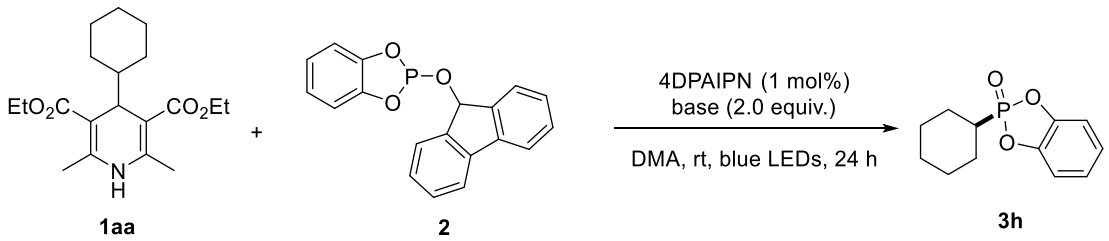
1. General information.....S2
2. Optimization of reaction conditions S2
3. Synthesis and characterizations of substrates S6
4. Synthesis and characterization of products S24
5. ^{1}H, ^{13}C and ^{19}F NMR spectra of new substrates S34
6. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra of new products.....S65
7. Mechanistic studies S89
8. References S1-S12 .....S95

1. General information

All commercially available compounds were purchased from Adamas, Aldrich, Aladdin, Bidepharm, Macklin or TCI. Solvents were purified according to the procedures from "Purification of Laboratory Chemicals". Flash column chromatography was performed on silica gel (particle size 300-400 mesh) and eluted with petroleum ether/ethyl acetate/dichloromethane/methanol. Thin layer chromatography was performed on silica gel 60 F254 plates (250 μm). Nuclear magnetic resonance (NMR) spectra were recorded on a Agilent 400 (or 500) or Bruker 400 (or 500) instrument operating at 400, 100, 376, 162 MHz for ^{1}H, ^{13}C, ^{19}F, ^{31}P respectively. The chemical shifts (δ) were given in parts per million relative to internal standard TMS (0 ppm for ^{1}H) or $CDCl_3$ (77.0 ppm for ^{13}C). ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as outside standard and low field was positive. ^{31}P NMR chemical shifts were determined relative to H_3PO_4 as external standard and low field is positive. Multiplicities were reported using the following abbreviations: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad. Low-resolution and high-resolution mass data were recorded on mass spectrometers in the EI, ESI or DART mode.

2. Optimization of reaction conditions

Table S1. Base screening for the Synthesis of **3h** from **1aa**

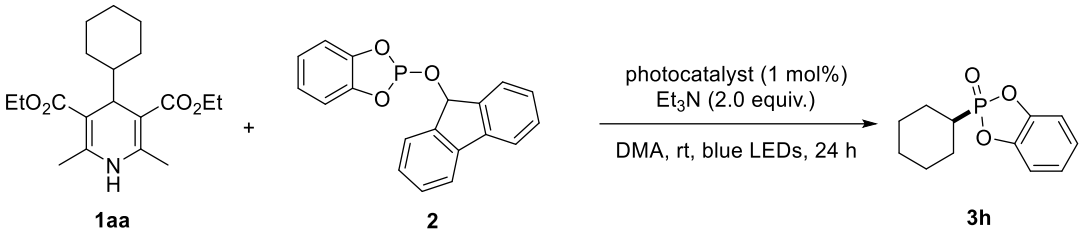


entry[a]	base	yield (%)
1	none	49
2	Et_3N	65

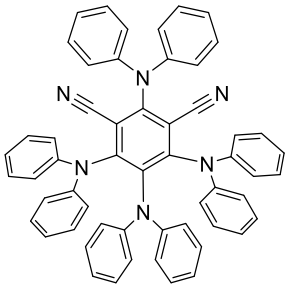
3	DIPEA	21
4	Cy_2NMe	31
5	DABCO	10
6	Na_2CO_3	24

Reaction conditions: **1aa** (0.10 mmol), **2** (0.20 mmol, 2 equiv.), base (0.20 mmol, 2 equiv.), 4DPAIPN (0.001 mmol), DMA (2.0 mL), blue LEDs, rt, 24 h, ^{31}P NMR yield with tributyl phosphate as the internal standard based on **1aa**.

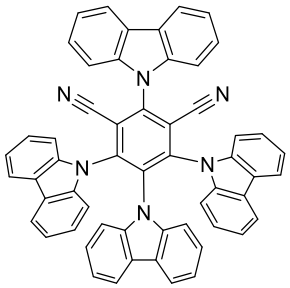
Table S2. Photocatalyst screening for the Synthesis of **3h** from **1aa**



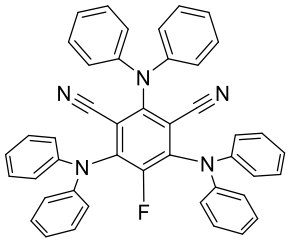
1aa **2** **3h**



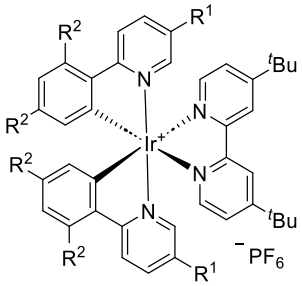
4DPAIPN



4CzIPN



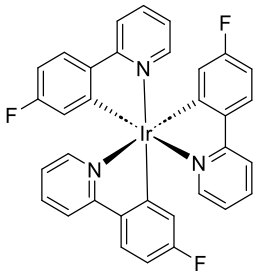
3DPAFIPN



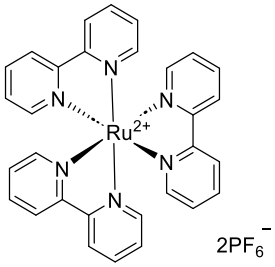
$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$

$R^1 = CF_3$, $R^2 = F$

$Ir(ppy)_2(dtbbpy)PF_6$, R^1, $R^2 = H$



$Ir(p\text{-}Fppy)_3$



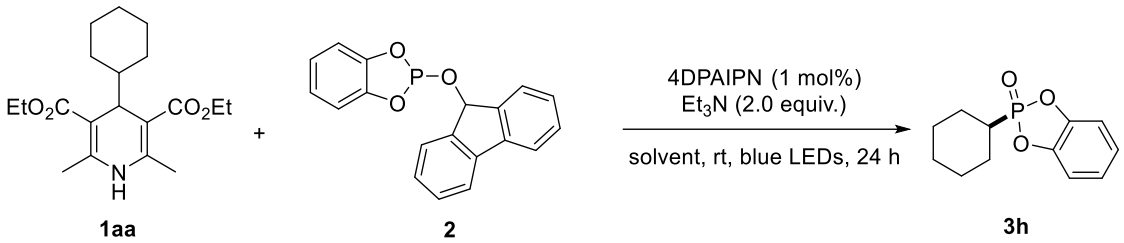
$Ru(bpy)_3(PF_6)_2$

entry	photocatalyst	yield (%)
1	none	0

2	4DPAIPN	65
3	4CzIPN	10
4	3DPAFIPN	59
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	41
6	$Ir(p\text{-}Fppy)_3$	49
7	$Ru(bpy)_3(PF_6)_2$	0
8	$Ir(ppy)_2(dtbbpy)PF_6$	64

Reaction conditions: **1aa** (0.10 mmol), **2** (0.20 mmol, 2 equiv.), Et_3N (0.20 mmol, 2 equiv.), photocatalyst (0.001 mmol, 1 mol%), DMA (2.0 mL), blue LEDs, rt, 24 h, ^{31}P NMR yield with tributyl phosphate as the internal standard based on **1aa**.

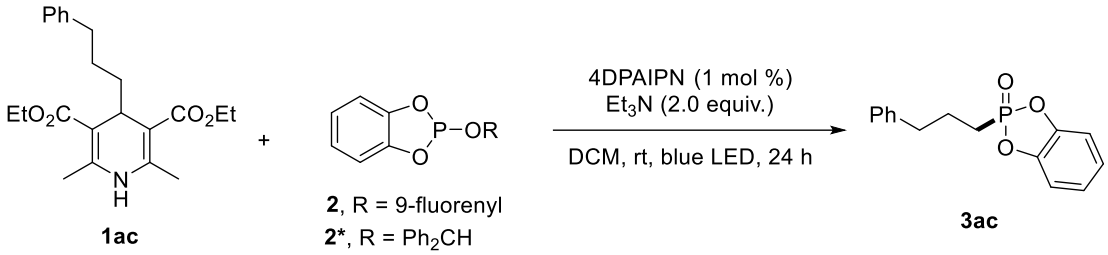
Table S3. Solvent screening for the Synthesis of **3h** from **1aa**



entry[a]	solvent	yield (%)
1	DMF	27
2	DMSO	trace
3	DCM	80
4	DCE	53
5	$PhCF_3$	47
6	PhCl	34
7	MeCN	52
8	NMP	0
9	DME	0
10	EtOAc	0

Reaction conditions: **1aa** (0.10 mmol), **2** (0.20 mmol, 2 equiv.), Et_3N (0.20 mmol, 2 equiv.), 4DPAIPN (0.001 mmol), solvent (2.0 mL), blue LEDs, rt, 24 h, ^{31}P NMR yield with tributyl phosphate as the internal standard based on **1aa**.

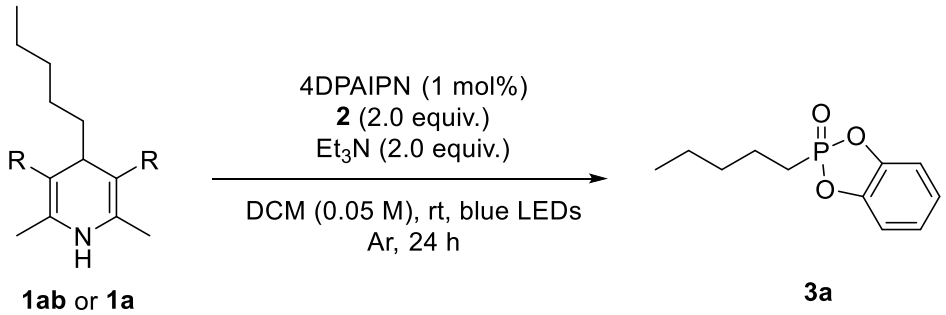
Table S4. Screening of Additives and Solvents for the Synthesis of **4ac** from **1ac**



entry	[P] source	additives	solvent	yield (%)
1	**2**	MeOH	DCM	0
2	**2**	KH_2PO_4	DCM	18
3	**2**	catechol	DCM	0
4	**2**	Et_3N•HCl	DCM	0
5	**2***	none	DCM	0
6	**2***	none	1,4-dioxane	18
7	**2***	none	THF	0
8	**2**	none	DCM	25

Reaction conditions: **1ac** (0.10 mmol), **2** (0.20 mmol, 2 equiv.), Et_3N (0.20 mmol, 2 equiv.), 4DPAIPN (0.001 mmol), solvent (2.0 mL), blue LEDs, rt, 24 h, ^{31}P NMR yield with tributyl phosphate as the internal standard based on **1ac**, entry 8 was performed under the irradiation of 390 ~ 400 nm light.

Table S5. Screening of Substituent Group on 1,4-Dihydropydines

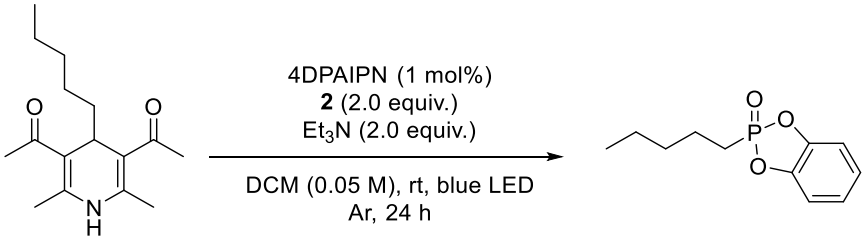


entry	substrate	yield (%)
1	**1ab**, R = CO_2Et	18
5	**1a**, R = COMe	68

Reaction conditions: substrate **1ab** or **1a** (0.10 mmol), **2** (0.20 mmol, 2 equiv.), Et_3N

(0.20 mmol, 2 equiv.), 4DPAIPN (0.001 mmol), DCM (2.0 mL), blue LEDs, rt, 24 h, ^{31}P NMR yield with tributyl phosphate as the internal standard based on **1ab** or **1a**.

Table S6. Variation from optimal conditions



entry	Variation from optimal condition	yield (%)
1	without 4DPAIPN	0
2	without NEt_3	18
3	without light	0
4	in DMA	53
5	in MeCN	22

Optimal reaction conditions: **1a** (0.10 mmol), **2** (0.20 mmol, 2 equiv.), Et_3N (0.20 mmol, 2 equiv.), 4DPAIPN (0.001 mmol), DCM (2.0 mL), blue LEDs, rt, 24 h, ^{31}P NMR yield with tributyl phosphate as the internal standard based on **1a**.

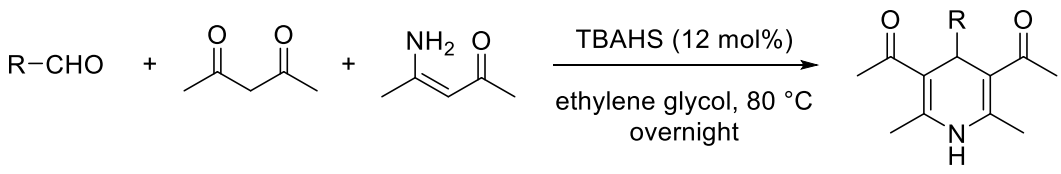
3. Synthesis and Characterizations of Substrates

Synthesis and Characterizations of Phosphite Reagents

The following phosphites were known compounds and prepared according to literature methods: 9-fluorenyl *o*-phenylene phosphite (**2**),[S1] diphenylmethyl *o*-phenylene phosphite (**2***).[S1]

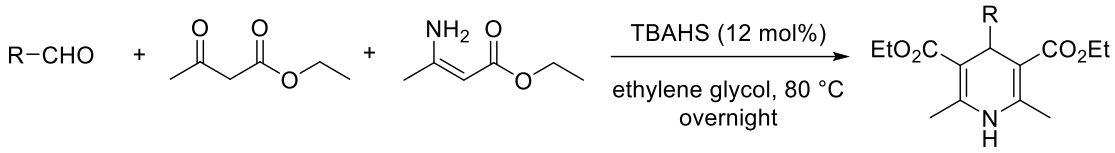
Synthesis and Characterizations of 4-alkyl-1,4-dihydropyridines

Method A:



To a solution of aldehydes (10 mmol, 1.0 equiv.), 4-amino-3-penten-2-one (1.0 g, 10 mmol, 1.0 equiv.) and pentane-2,4-dione (1.0 g, 10 mmol, 1.0 equiv.) in ethylene glycol (5.0 mL) was added *n*-Bu_4NHSO_4 (0.4 g, 1.2 mmol, 12 mol%) in one portion. The vial was sealed and heated overnight at 80 ℃. After the consumption of the aldehyde, the reaction was cooled to rt and diluted with EtOAc. The solution was poured into a separatory funnel and washed with brine three times. The organic phase was dried with anhydrous Na_2SO_4, and the mixture was concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether, ethyl acetate and dichloromethane to give the pure product. Recrystallization from ethyl acetate and petroleum ether were performed if necessary.

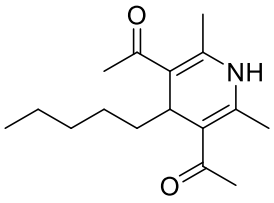
Method B:



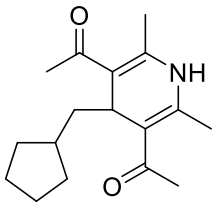
To a solution of aldehydes (10 mmol, 1.0 equiv.), ethyl β-aminocrotonate (1.30 g, 10 mmol, 1.0 equiv.), and ethyl 3-oxobutanoate (1.29 g, 10 mmol, 1.0 equiv.) in ethylene glycol (5.0 mL) was added *n*-Bu_4NHSO_4 (0.4 g, 1.2 mmol, 12 mol%) in one portion. The vial was sealed and overnight heated at 80 ℃. After the consumption of the aldehyde, the reaction was cooled to rt and diluted with EtOAc. The solution was poured into a separatory funnel and washed with brine three times. The organic phase was dried with anhydrous Na2SO4, and the mixture was concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether, ethyl acetate and dichloromethane to give the pure product.

1,1'-(4-Cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1h**) and diethyl 4-((3*r*,5*r*,7*r*)-adamantan-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-

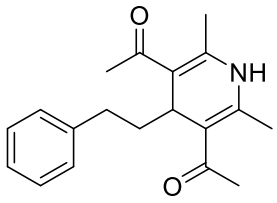
dicarboxylate (**1x**) are known compounds.[S1]



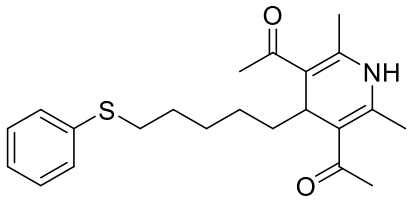
1,1'-(2,6-Dimethyl-4-pentyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1a**). Prepared according to Method A. Yield: 1.85 g (70%), yellow solid; m.p.: 135-136 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.26 (s, 1H), 3.86 (t, *J* = 5.9 Hz, 1H), 2.32 (s, 6H), 2.29 (s, 6H), 1.30-1.11 (m, 8H), 0.84 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.7, 143.3, 113.2, 37.3, 34.9, 32.1, 29.4, 24.7, 22.6, 20.0, 14.0. IR (KBr): ν (cm^{-1}) 3389, 3289, 3169, 3036, 2951, 2922, 2838, 2235, 1657, 1628, 1597, 1375, 1361, 1306, 1232, 1152, 1022, 967, 931, 809, 689, 575. ESI-MS: *m/z* 264.2 (M^++H); HRMS calcd for $C_{16}H_{26}NO_2$ [M+H]: 264.1958, found: 264.1957.



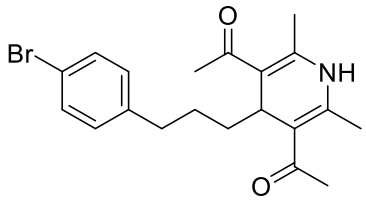
1,1'-(4-(Cyclopentylmethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1b**). Prepared according to Method A. Yield: 1.98 g (72%), yellow solid; m.p.: 164-165 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.28 (s, 1H), 3.86 (t, *J* = 6.8 Hz, 1H), 2.33 (s, 6H), 2.29 (s, 6H), 1.79-1.62 (m, 3H), 1.61-1.41 (m, 4H), 1.23 (t, *J* = 6.7 Hz, 2H), 1.13-1.00 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.5, 143.0, 113.8, 43.6, 35.3, 34.1, 33.3, 29.4, 25.3, 20.0. IR (KBr): ν (cm^{-1}) 3218, 3157, 2990, 2949, 2864, 1641, 1617, 1556, 1458, 1377, 1360, 1330, 1311, 1220, 1113, 1015, 938, 819, 690, 542. ESI-MS: *m/z* 276.2 (M^++H); HRMS calcd for $C_{17}H_{26}NO_2$ [M+H]: 276.1958, found: 276.1959.



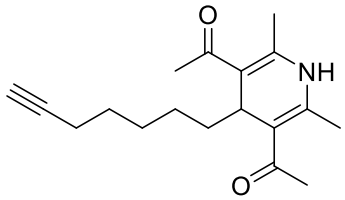
1,1'-(2,6-Dimethyl-4-phenethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1c**). Prepared according to Method A. Yield: 2.0 g (67%), yellow solid; m.p.: 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (m, 2H), 7.10-7.15 (m, 3H), 5.92 (s, 1H), 4.01 (t, *J* = 6.1 Hz, 1H), 2.49-2.53 (m, 2H), 2.31 (s, 6H), 2.30 (s, 6H), 1.57-1.63 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.3, 143.3, 142.1, 128.3, 128.2, 125.7, 113.0, 38.4, 34.6, 31.2, 29.5, 20.2. IR (KBr): ν (cm^{-1}) 3231, 3166, 3025, 2971, 2921, 2846, 1697, 1647, 1617, 1567, 1455, 1376, 1362, 1332, 1307, 1230, 1119, 1017, 963, 926, 805, 731, 696, 543. ESI-MS: *m/z* 298.2 (M^++H); HRMS calcd for $C_{19}H_{24}NO_2$ [M+H]: 298.1802, found: 298.1800.



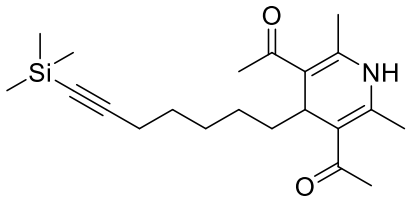
1,1'-(2,6-Dimethyl-4-(5-(phenylthio)pentyl)-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1d**). Prepared according to Method A. Yield: 2.22 g (60%), yellow solid; m.p.: 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.23 (m, 4H), 7.20-7.11 (m, 1H), 5.94 (br, 1H), 3.87 (t, *J* = 5.9 Hz, 1H), 2.86 (t, *J* = 7.3 Hz, 2H), 2.31 (s, 6H), 2.28 (s, 6H), 1.62-1.55 (m, 2H), 1.37-1.30 (m, 2H), 1.28-1.11 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.4, 143.1, 136.9, 128.8, 128.7, 125.6, 113.2, 37.1, 34.7, 33.5, 29.4, 29.2, 29.1, 24.6, 20.1. IR (KBr): ν (cm^{-1}) 3311, 3052, 2930, 2847, 1666, 1589, 1475, 1459, 1381, 1366, 1339, 1298, 1230, 1154, 1009, 957, 936, 918, 743, 732, 688, 677, 566. ESI-MS: *m/z* 372.2 (M^++H); HRMS calcd for $C_{22}H_{30}NO_2S$ [M+H]: 372.1992, found: 372.1991.



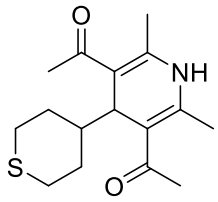
1,1'-(4-(3-(4-Bromophenyl)propyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1e**). Prepared according to Method A. Yield: 2.52g (65%), yellow solid; m.p.: 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 5.93 (s, 1H), 3.92 (t, *J* = 6.1 Hz, 1H), 2.47 (t, *J* = 7.6 Hz, 2H), 2.30 (s, 6H), 2.27 (s, 6H), 1.52-1.41 (m, 2H), 1.33-1.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.3, 143.3, 141.2, 131.3, 130.1, 119.4, 113.1, 36.6, 35.5, 34.5, 29.5, 26.6, 20.2. IR (KBr): ν (cm^{-1}) 3305, 3215, 3058, 2955, 2912, 2840, 1906, 1673, 1610, 1590, 1479, 1424, 1381, 1322, 1232, 1217, 1071, 1020, 924, 810, 737, 676, 626, 569, 498. ESI-MS: *m/z* 390.1 (M^++H); HRMS calcd for $C_{20}H_{25}BrNO_2$ [M+H]: 390.1063, found: 390.1063.



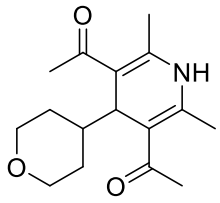
1,1'-(4-(Hept-6-yn-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1f**). Prepared according to Method A. Yield: 1.44 g (50%), yellow solid; m.p.: 104-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.99 (s, 1H), 3.88 (t, *J* = 5.9 Hz, 1H), 2.32 (s, 6H), 2.29 (s, 6H), 2.14 (td, *J* = 7.0, 2.5 Hz, 2H), 1.92 (s, 1H), 1.51-1.41 (m, 2H), 1.35-1.24 (m, 4H), 1.23-1.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.5, 143.2, 113.2, 84.6, 68.2, 37.1, 34.8, 29.4, 29.1, 28.4, 24.5, 20.1, 18.4. IR (KBr): ν (cm^{-1}) 3301, 3231, 3167, 3058, 2926, 2856, 2117, 1645, 1617, 1563, 1458, 1380, 1225, 1120, 1017, 958, 938, 925, 806, 684, 617, 545. ESI-MS: *m/z* 288.2 (M^++H); HRMS calcd for $C_{18}H_{26}NO_2$ [M+H]: 288.1958, found: 288.1952.



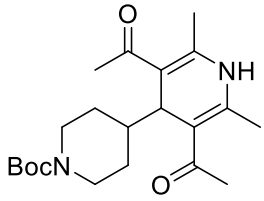
1,1'-(2,6-Dimethyl-4-(7-(trimethylsilyl)hept-6-yn-1-yl)-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1g**). Prepared according to Method A. Yield: 1.26 g (35%), yellow solid; m.p.: 106-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92 (s, 1H), 3.88 (t, *J* = 6.0 Hz, 1H), 2.32 (s, 6H), 2.29 (s, 6H), 2.16 (t, *J* = 7.2 Hz, 2H), 1.51-1.38 (m, 4H), 1.33-1.23 (m, 4H), 1.22-1.11 (m, 2H), 0.14 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.5, 143.1, 113.2, 107.5, 84.3, 37.1, 34.8, 29.4, 29.1, 28.6, 24.5, 20.1, 19.9, 0.2. IR (KBr): ν (cm^{-1}) 3281, 3229, 2929, 2177, 1651, 1578, 1471, 1355, 1224, 1011, 928, 841, 762. ESI-MS: *m/z* 360.2 (M^++H); HRMS calcd for $C_{21}H_{34}NO_2Si$ [M+H]: 360.2353, found: 360.2355.



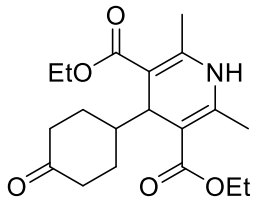
1,1'-(2,6-Dimethyl-4-(tetrahydro-2H-thiopyran-4-yl)-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1i**). Prepared according to Method A. Yield: 1.55 g (53%), yellow solid; m.p.: 207-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.97 (br, 1H), 3.88 (d, *J* = 6.6 Hz, 1H), 2.55-2.49 (m, 4H), 2.33 (s, 6H), 2.31 (s, 6H), 1.85 (d, *J* = 12.9 Hz, 2H), 1.39-1.24 (m, 2H), 1.18-1.06 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.0, 142.6, 111.6, 45.2, 40.6, 30.4, 29.5, 29.0, 20.0. IR (KBr): ν (cm^{-1}) 3327, 3050, 2994, 2939, 2919, 2855, 1661, 1611, 1591, 1474, 1422, 1354, 1221, 1112, 991, 933, 763, 681, 560. ESI-MS: *m/z* 294.2 (M^++H); HRMS calcd for $C_{16}H_{24}NO_2S$ [M+H]: 294.1522, found: 294.1519.



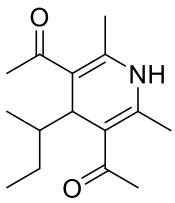
1,1'-(2,6-Dimethyl-4-(tetrahydro-2H-pyran-4-yl)-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1j**). Prepared according to Method A. Yield: 1.16 g (42%), yellow solid; m.p.: 181-183 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.40 (s, 1H), 3.94-3.86 (m, 3H), 3.19 (t, *J* = 10.9 Hz, 2H), 2.34 (s, 6H), 2.31 (s, 6H), 1.42-1.25 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.0, 142.9, 111.5, 68.1, 42.7, 39.8, 29.6, 29.2, 19.9. IR (KBr): ν (cm^{-1}) 3309, 3182, 2930, 2848, 1667, 1592, 1474, 1378, 1227, 1007, 968, 908, 749, 677, 568. ESI-MS: *m/z* 278.2 (M^++H); HRMS calcd for $C_{16}H_{24}NO_3$ [M+H]: 278.1751, found: 278.1751.



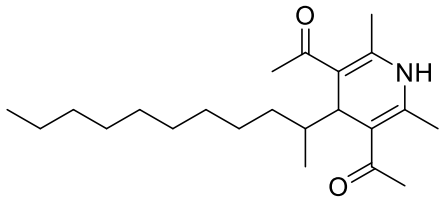
***Tert*-butyl 4-(3,5-diacetyl-2,6-dimethyl-1,4-dihydropyridin-4-yl)piperidine-1-carboxylate** (**1k**). Prepared according to Method A. Yield: 2.55 g (68%), yellow solid; m.p.: 180-182 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (br, 1H), 4.05 (br, 2H), 3.94 (d, *J* = 6.0 Hz, 1H), 2.48 (br, 2H), 2.34 (s, 6H), 2.32 (s, 6H), 1.50-1.39 (m, 2H), 1.44 (s, 9H), 1.32-1.19 (m, 1H), 1.15-1.00 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.9, 154.7, 143.4, 111.3, 79.4, 44.2, 43.8 (br), 39.38, 39.34, 29.6, 28.4, 19.7. IR (KBr): ν (cm^{-1}) 3263, 3210, 3155, 2981, 2951, 2927, 2850, 1694, 1651, 1597, 1466, 1429, 1380, 1364, 1307, 1224, 1190, 1139, 1044, 1015, 944, 931, 869, 820, 761, 561. ESI-MS: *m/z* 377.2 (M^++H); HRMS calcd for $C_{21}H_{33}N_2O_4$ [M+H]: 377.2435, found: 377.2433.



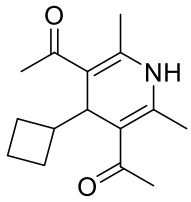
Diethyl 2,6-dimethyl-4-(4-oxocyclohexyl)-1,4-dihydropyridine-3,5-dicarboxylate (**1l**). Prepared according to Method B. Yield: 1.13 g (65%) white solid; m.p.: 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04 (br, 1H), 4.27-4.11 (m, 4H), 4.09 (d, *J* = 5.5 Hz, 1H), 2.49-2.33 (m, 1H), 2.33 (s, 6H), 2.26-2.18 (m, 2H), 2.11-2.08 (m, 1H), 1.92-1.82 (m, 2H), 1.75-1.66 (m, 1H), 1.49-1.30 (m, 2H), 1.30 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 212.7, 168.2, 145.2, 101.3, 59.8, 43.6, 41.1, 37.0, 28.5, 19.5, 14.4. IR (KBr): ν (cm^{-1}) 3342, 3093, 2930, 2863, 2251, 1694, 1487, 1446, 1368, 1299, 1277, 1258, 1216, 1170, 1150, 1107, 1050, 1018, 957, 918, 793, 119, 734, 505, 423. DART-MS: *m/z* 350.2 (M^++H); HRMS calcd for $C_{19}H_{28}NO_5$ [M+H]: 350.1962, found: 350.1964.



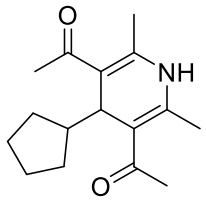
1,1'-(4-(*Sec*-butyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1m**). Prepared according to Method A. Yield: 1.32 g (53%), yellow solid; m.p.: 134-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (br, 1H), 3.83 (d, *J* = 6.1 Hz, 1H), 2.33 (s, 6H), 2.31 (s, 3H), 2.30 (s, 3H), 1.40-1.27 (m, 1H), 1.22-1.11 (m, 1H), 1.00-0.86 (m, 1H), 0.81 (t, *J* = 7.2 Hz, 3H), 0.71 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.8, 199.5, 142.6, 142.3, 112.2, 112.0, 43.0, 40.4, 29.3, 25.1, 19.7, 19.6, 14.7, 12.1. IR (KBr): ν (cm^{-1}) 3278, 2962, 2929, 2874, 1664, 1647, 1574, 1470, 1355, 1312, 1271, 1223, 1138, 1111, 1073, 1011, 931, 758, 673, 632, 565. ESI-MS: *m/z* 250.2 (M^++H); HRMS calcd for $C_{15}H_{24}NO_2$ [M+H]: 250.1801, found: 250.1806.



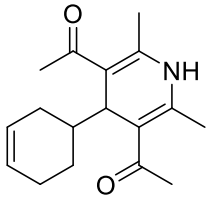
1,1'-(2,6-Dimethyl-4-(undecan-2-yl)-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1n**). Prepared according to Method A. Yield: 1.39 g (40%), yellow solid; m.p.: 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.18 (s, 1H), 3.81 (d, *J* = 5.8 Hz, 1H), 2.32 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H), 2.28 (s, 3H), 1.31-1.09 (m, 16 H), 1.00-0.92 (m, 1 H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.70 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.9, 199.5, 142.5, 142.1, 112.2, 112.1, 41.2, 40.6, 32.4, 31.9, 29.8, 29.64, 19.60, 29.31, 29.29, 29.21, 27.5, 22.6, 19.9, 19.7, 15.2, 14.1. IR (KBr): ν (cm^{-1}) 3270, 2923, 2852, 1686, 1667, 1644, 1574, 1469, 1356, 1311, 1223, 1011, 931, 768, 737, 673, 559. FI-MS: *m/z* 347 (M^+); HRMS calcd for $C_{22}H_{37}NO_2$ [M]: 347.2819, found: 347.2816.



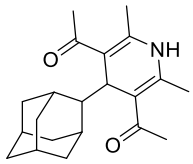
1,1'-(4-Cyclobutyl-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1o**). Prepared according to Method A. Yield: 1.61 g (65%), yellow solid; m.p.: 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78 (s, 1H), 3.87 (d, *J* = 6.7 Hz, 1H), 2.33 (s, 6H), 2.30 (s, 6H), 2.28-2.18 (m, 1H), 1.74-1.66 (m, 2H), 1.66-1.56 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.9, 142.8, 111.6, 42.7, 38.6, 29.5, 24.8, 20.0, 18.4. IR (KBr): ν (cm^{-1}) 3267, 3210, 2980, 2960, 2879, 1660, 1582, 1458, 1380, 1351, 1309, 1272, 1225, 1135, 1103, 1024, 1010, 930, 784, 666, 632, 562. ESI-MS: *m/z* 248.2 (M^++H); HRMS calcd for $C_{15}H_{22}NO_2$ [M+H]: 248.1645, found: 248.1646.



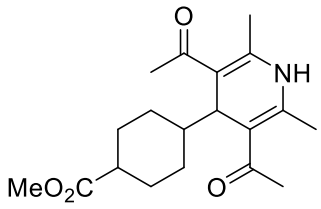
1,1'-(4-Cyclopentyl-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1p**). Prepared according to Method A. Yield: 1.78 g (68%), yellow solid; m.p.: 159-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (s, 1H), 3.91 (d, *J* = 7.1 Hz, 1H), 2.34 (s, 6H), 2.30 (s, 6H), 1.72-1.60 (m, 1H), 1.61-1.45 (m, 4H), 1.45-1.33 (m, 2H), 1.13-0.99 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.2, 142.5, 112.8, 48.5, 38.2, 29.4, 28.5, 24.0, 19.8. IR (KBr): ν (cm^{-1}) 3268, 2955, 2859, 1667, 1640, 1570, 1466, 1357, 1312, 1225, 1166, 1119, 1019, 931, 772, 735, 683, 632, 561. ESI-MS: *m/z* 262.2 (M^++H); HRMS calcd for $C_{16}H_{24}NO_2$ [M+H]: 262.1801, found: 262.1802.



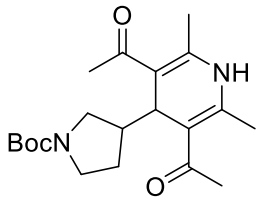
1,1'-(4-(Cyclohex-3-en-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1q**). Prepared according to Method A. Yield: 0.95 g (35%), yellow solid; m.p.: 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.09 (s, 1H), 5.55-5.60 (m, 2H), 3.89 (d, *J* = 6.9 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H), 1.97-2.07 (m, 1H), 1.82-1.94 (m, 2H), 1.65-1.74 (m, 1H), 1.56-1.62 (m, 1H), 1.36-1.48 (m, 1H), 1.12-1.24 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.4, 199.3, 142.7, 142.3, 126.9, 126.3, 112.1, 111.8, 41.5, 40.0, 29.5, 29.4, 27.9, 25.7, 25.1, 20.0, 19.8. IR (KBr): ν (cm^{-1}) 3242, 3169, 3021, 2964, 2918, 2831, 1686, 1648, 1613, 1577, 1459, 1429, 1378, 1362, 1327, 1305, 1229, 1118, 1025, 961, 932, 749, 621, 545. ESI-MS: *m/z* 274.2 (M^++H); HRMS calcd for $C_{17}H_{24}NO_2$ [M+H]: 274.1802, found: 274.1801.



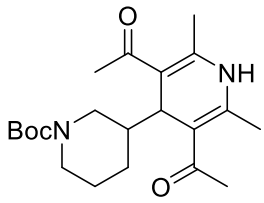
1,1'-(4-(Adamantan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1r**). Prepared according to Method A. Yield: 1.37 g (42%), Yellow solid; m.p.: 244-245 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (s, 1H), 4.27 (d, *J* = 10.9 Hz, 1H), 2.37 (s, 6H), 2.30 (s, 6H), 1.93 (d, *J* = 12.4 Hz, 2H), 1.83 (d, *J* = 15.7 Hz, 2H), 1.74 (d, *J* = 11.9 Hz, 2H), 1.68 (s, 2H), 1.56 (s, 2H), 1.50 (t, *J* = 11.6 Hz, 4H), 1.28 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.3, 140.5, 114.2, 49.0, 39.3, 38.0, 35.6, 32.4, 29.4, 28.9, 28.7, 27.9, 19.7. IR (KBr): ν (cm^{-1}) 3289, 3171, 3022, 2898, 2851, 1661, 1592, 1471, 1449, 1374, 1334, 1293, 1219, 1112, 1016, 953, 762, 687, 568. ESI-MS: *m/z* 328.2 (M^++H); HRMS calcd for $C_{21}H_{30}NO_2$ [M+H]: 328.2271, found: 328.2265.



Methyl 4-(3,5-diacetyl-2,6-dimethyl-1,4-dihydropyridin-4-yl)cyclohexane-1-carboxylate (**1s**). Prepared according to Method A. This compound was isolated as an inseparable mixture of *cis*- and *trans*-isomer in 86:14 ratio determined by ^{1}H NMR (400 MHz). Yield: 1.57 g (47%), yellow solid; m.p.: 136-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.37 (br, 1H), 3.83/3.76 (d, *J* = 6.7 Hz, 1H), 3.68/3.63 (s, 3H), 2.33 (s, 6H), 2.31 (s, 6H), 2.22-2.18 (m, 1H), 2.08/1.91 (d, *J* = 11.4 Hz, 2H), 1.63/1.44 (d, *J* = 11.4 Hz, 2H), 1.36-1.16 (m, 2H), 1.16-1.03 (m, 1H), 1.02-0.80 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, major isomer): δ 199.2, 176.4, 142.5, 111.9, 51.5, 44.7, 43.2, 40.1, 29.5, 28.9, 28.0, 19.9. IR (KBr): ν (cm^{-1}) 3272, 3224, 3030, 2930, 2858, 1732, 1659, 1595, 1465, 1381, 1354, 1223, 1193, 1013, 931, 734, 681, 632, 560. ESI-MS: *m/z* 334.2 (M^++H); HRMS calcd for $C_{19}H_{28}NO_4$ [M+H]: 334.2013, found: 334.2011.

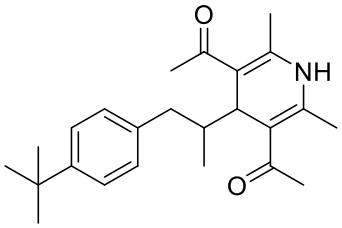


***Tert*-butyl 3-(3,5-diacetyl-2,6-dimethyl-1,4-dihydropyridin-4-yl)pyrrolidine-1-carboxylate** (**1t**). Prepared according to Method A. This compound was isolated as a mixture of two rotamers in 61:39 ratio determined by ^{1}H NMR (400 MHz). Yield: 1.26 g (35%), yellow solid; m.p.: 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61/7.51 (br, 1H), 4.19/4.08 (d, *J* = 5.6 Hz, 1H), 3.46-3.33 (m, 1H), 3.32-3.19 (m, 1H), 3.17-3.06 (m, 1H), 2.91/2.83 (t, *J* = 10.0 Hz, 1H), 2.35-2.31 (m, 12H), 2.14-1.95 (m, 1H), 1.80-1.65 (m, 1H), 1.60-1.40 (m, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.3/198.2, 197.8, 154.6, 144.8/144.6, 144.5/144.3, 112.0/111.7, 111.6/110.5, 79.1, 47.8/47.0, 45.66/45.1, 45.62, 35.2/34.9, 29.9/29.8, 29.7, 28.5, 27.8/27.1, 19.8/19.70, 19.78. IR (KBr): ν (cm^{-1}) 3274, 3225, 3165, 2970, 2885, 1663, 1624, 1596, 1473, 1423, 1352, 1308, 1218, 1168, 1131, 1084, 1004, 927, 878, 775, 687, 557. ESI-MS: *m/z* 363.2 (M^{+}+H); HRMS calcd for $C_{20}H_{31}N_2O_4$ [M+H]: 363.2278, found: 363.2273.

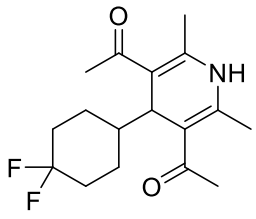


***Tert*-butyl 3-(3,5-diacetyl-2,6-dimethyl-1,4-dihydropyridin-4-yl)piperidine-1-carboxylate** (**1u**). Prepared according to Method A. Yield: 1.73 g (46%), yellow solid; m.p.: 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.67 (br, 1H), 4.10-3.77 (m, 3H), 2.52 (t, *J* = 12.1 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 2.32 (s, 6H), 2.32-2.15 (m, 1H), 1.63 (dd, *J* = 30.7, 12.7 Hz, 2H), 1.41 (s, 9H), 1.35-1.20 (m, 2H), 1.14-1.00 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.4, 198.5, 154.7, 143.4, 143.3, 111.5, 111.4, 79.2, 43.9, 37.6, 29.7, 29.6, 28.4, 27.5, 25.4, 19.9, 19.8. IR (KBr): ν (cm^{-1}) 3293, 2975, 2931, 1657, 1615, 1477, 1432, 1382, 1363, 1289, 1269, 1211, 1174, 1155, 1015, 968,

926, 882, 859, 769, 685, 622. ESI-MS: *m/z* 377.2 (M^++H); HRMS calcd for $C_{21}H_{33}N_2O_4$ [M+H]: 377.2435, found: 377.2437.

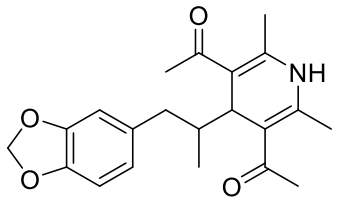


1,1'-(4-(1-(4-(*Tert*-Butyl)phenyl)propan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1v**). Prepared according to Method A. Yield: 2.31 g (63%), yellow solid; m.p.: 167-169 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 5.89 (s, 1H), 3.98 (d, *J* = 5.9 Hz, 1H), 2.67 (dd, *J* = 13.2, 3.5 Hz, 1H), 2.34 (s, 6H), 2.31 (s, 3H), 2.29 (s, 3H), 2.07 (t, *J* = 12.0 Hz, 1H), 1.67-1.54 (m, 1H), 1.28 (s, 9H), 0.66 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.6, 199.2, 148.4, 142.5, 142.2, 138.1, 128.6, 125.0, 112.2, 112.1, 43.2, 40.6, 38.4, 34.3, 31.4, 29.4, 20.0, 19.8, 15.3. IR (KBr): ν (cm^{-1}) 3279, 3179, 3049, 2963, 2868, 1898, 1652, 1614, 1473, 1380, 1362, 1332, 1271, 1224, 1106, 1017, 943, 809, 687, 619, 562. ESI-MS: *m/z* 368.3 (M^++H); HRMS calcd for $C_{24}H_{34}NO_2$ [M + H]$^+$: 368.2584, found: 368.2584.

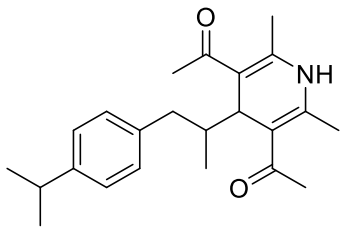


1,1'-(4-(4,4-Difluorocyclohexyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**1w**). Prepared according to Method A. Yield: 1.71 g (55%), yellow solid; m.p.: 197-199 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.27 (s, 1H), 3.91 (d, *J* = 6.2 Hz, 1H), 2.33 (s, 6H), 2.32 (s, 6H), 2.10-2.02 (m, 2H), 1.62-1.40 (m, 4H), 1.28-1.21(m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.9, 142.8, 123.6 (t, $^1J_{C-F}$ =

240.0 Hz), 111.9, 43.3, 39.1, 33.6 (t, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 29.6, 25.2 (d, $^{3}J_{C\text{-}F}$ = 10.0 Hz), 19.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ -91.20 (d, *J* = 234.7 Hz), -102.55 (dt, *J* = 233.3, 34.9 Hz). IR (KBr): ν (cm^{-1}) 3328, 3053, 2993, 2947, 2923, 1662, 1614, 1593, 1475, 1379, 1357, 1327, 1221, 1156, 1115, 962, 935, 687. ESI-MS: *m/z* 312.2 (M^{+}+H); HRMS calcd for $C_{17}H_{24}F_2NO_2$ [M+H]: 312.1769, found: 312.1761.

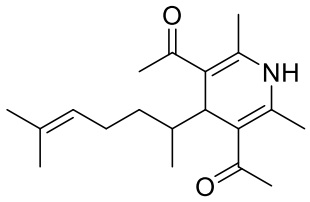


1,1'-(4-(1-(Benzo[d][1,3]dioxol-5-yl)propan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (1-5). Prepared according to Method A. Yield: 2.24 g (63%), yellow solid; m.p.: 161-163 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (s, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.51 (s, 1H), 6.48 (d, *J* = 7.9 Hz, 1H), 5.89 (s, 2H), 3.97 (d, *J* = 6.1 Hz, 1H), 2.64 (dd, *J* = 13.2, 3.3 Hz, 1H), 2.35 (s, 6H), 2.34 (s, 3H), 2.32 (s, 3H), 2.05-1.93 (m, 1H), 1.57-1.46 (m, 1H), 0.63 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.5, 199.2, 147.4, 145.4, 143.2, 142.9, 135.1, 121.7, 112.0, 111.9, 109.2, 107.9, 100.7, 43.3, 40.3, 38.7, 29.54, 29.52, 19.8, 19.7, 15.1. IR (KBr): ν (cm^{-1}) 3307, 2964, 2925, 2771, 1666, 1595, 1475, 1441, 1366, 1335, 1299, 1243, 1224, 1127, 1094, 1039, 961, 939, 887, 866, 799, 761, 735, 674, 625, 601, 567, 544, 491, 447. ESI-MS: *m/z* 356.2 (M^{+}+H); HRMS calcd for $C_{21}H_{26}NO_4$ [M+H]: 356.1856, found: 356.1855.

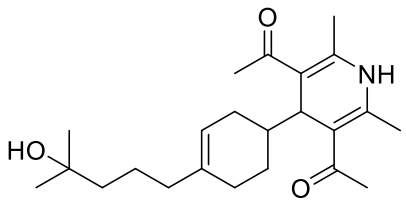


1,1'-(4-(1-(4-Isopropylphenyl)propan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (1-6). Prepared according to Method A. Yield: 2.36 g (67%),

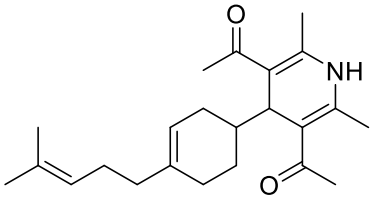
yellow solid; m.p.: 160-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.54 (br, 1H), 3.98 (d, *J* = 6.0 Hz, 1H), 2.91-2.77 (m, 1H), 2.68 (dd, *J* = 13.1, 3.5 Hz, 1H), 2.34 (s, 6H), 2.32 (s, 3H), 2.30 (s, 3H), 2.06 (dd, *J* = 12.9, 11.1 Hz, 1H), 1.66-1.52 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 6H), 0.65 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.6, 199.2, 146.2, 143.0, 142.7, 138.5, 128.8, 126.1, 112.1, 112.0, 43.2, 40.5, 38.5, 33.6, 29.5, 29.4, 24.0, 19.9, 19.7, 15.2. IR (KBr): ν (cm^{-1}) 3304, 2960, 2926, 2869, 1902, 1668, 1593, 1512, 1462, 1381, 1365, 1335, 1299, 1224, 1127, 1017, 958, 938, 854, 811, 760, 727, 674, 642, 561. ESI-MS: *m/z* 354.2 (M^{+}+H); HRMS calcd for $C_{23}H_{32}NO_2$ [M+H]: 354.2427, found: 354.2424.



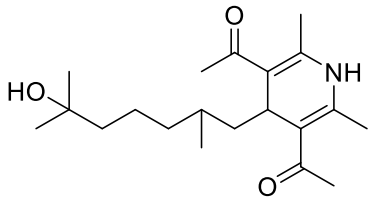
1,1'-(2,6-Dimethyl-4-(6-methylhept-5-en-2-yl)-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (1-7). Prepared according to Method A. Yield: 1.36 g (45%), yellow solid; m.p.: 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (s, 1H), 4.98 (t, *J* = 6.6 Hz, 1H), 3.84 (d, *J* = 5.7 Hz, 1H), 2.33 (s, 6H), 2.32 (s, 3H), 2.30 (s, 3H), 1.93-2.05 (m, 1H), 1.85-1.72 (m, 1H), 1.65 (s, 3H), 1.56 (s, 3H), 1.35-1.21 (m, 2H), 1.04-0.91 (m, 1H), 0.73 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.8, 199.4, 143.2, 142.7, 131.2, 124.5, 111.91, 111.89, 40.8, 40.4, 32.5, 29.4, 29.3, 25.9, 25.7, 19.7, 19.5, 17.6, 15.1. IR (KBr): ν (cm^{-1}) 3312, 3180, 3049, 2999, 2968, 2914, 2851, 1667, 1589, 1537, 1475, 1430, 1380, 1356, 1338, 1322, 1293, 1257, 1229, 1154, 1119, 1056, 1033, 1008, 957, 935, 916, 895, 831, 765, 718, 675, 624, 580, 562. ESI-MS: *m/z* 304.2 (M^{+}+H); HRMS calcd for $C_{19}H_{30}NO_2$ [M+H]: 304.2271, found: 304.2269.



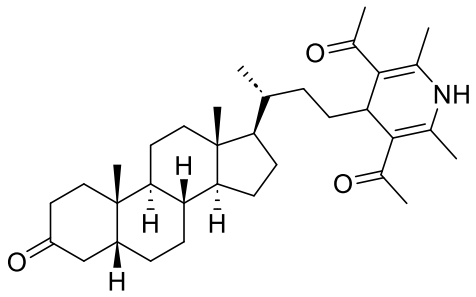
1,1'-(4-(4-(4-Hydroxy-4-methylpentyl)cyclohex-3-en-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (1-8). Prepared according to Method A. This compound was isolated as a mixture of two inseparable diastereoisomers in a ratio of 2:1 determined by ^{1}H NMR. Yield: 1.49 g (40%), yellow solid; m.p.: 145-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.06 (m, 1H), 5.26 (s, 1H), 3.87/3.85 (d, *J* = 7.2 Hz, 1H), 2.40-2.07 (m, 1H), 2.30 (s, 6H), 2.29 (s, 3H), 2.28 (s, 3H), 1.90-1.75 (m, 4H), 1.69-1.51 (m, 2H), 1.42-1.22 (m, 5H), 1.20-1.00 (m, 1H), 1.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 199.4, 143.5, 143.2, 137.4, 137.0, 120.5, 120.2, 111.9, 111.8, 111.6, 71.0, 43.4, 42.0, 41.5, 39.7, 39.5, 38.0, 37.7, 30.9, 29.6, 29.5, 29.4, 29.2, 29.1, 28.5, 27.9, 25.5, 25.4, 25.0, 22.4, 22.3, 19.8, 19.6. IR (KBr): ν (cm^{-1}) 3311, 2969, 2937, 1686, 1655, 1595, 1466, 1379, 1360, 1304, 1262, 1223, 1151, 1119, 1074, 1024, 931, 756, 666, 624, 569. ESI-MS: *m/z* 374.3 (M^{+}+H); HRMS calcd for $C_{23}H_{36}NO_3$ [M+H]: 374.2690, found: 374.2687.



1,1'-(2,6-Dimethyl-4-(4-(4-methylpent-3-en-1-yl)cyclohex-3-en-1-yl)-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (1-9). Prepared according to Method A. Yield: 1.49 g (42%), yellow solid; m.p.: 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.39 (br, 1H), 5.29 (s, 1H), 5.06 (t, *J* = 6.3 Hz, 1H), 3.88 (d, *J* = 6.9 Hz, 1H), 2.34 (s, 6H), 2.32 (s, 3H), 2.30 (s, 3H), 2.05-1.96 (m, 2H), 1.94-1.80 (m, 5H), 1.74-1.50 (m, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.42-1.28 (m, 1H), 1.25-1.10 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.5, 199.4, 143.3, 143.0, 137.6, 131.3, 124.3, 119.9, 111.9, 111.7, 41.6, 39.7, 37.4, 29.5, 29.4, 28.8, 28.0, 26.4, 25.7, 25.4, 19.8, 19.7, 17.6. IR (KBr): ν (cm^{-1}) 3285, 2964, 2914, 2836, 1648, 1582, 1467, 1355, 1305, 1264, 1223, 1121, 1021, 932, 829, 785, 735, 667, 632, 559. ESI-MS: *m/z* 356.3 (M^{+}+H); HRMS calcd for $C_{23}H_{34}NO_2$ [M+H]: 356.2584, found: 356.2577.

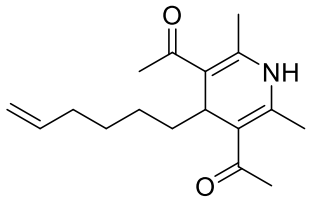


1,1'-(4-(6-Hydroxy-2,6-dimethylheptyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (1-10). Prepared according to Method A. Yield: 1.78 g (53%), yellow solid; m.p.: 135-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.49 (br, 1H), 3.92 (t, *J* = 6.2 Hz, 1H), 2.32 (s, 6H), 2.30 (s, 3H), 2.28 (s, 3H), 1.72 (br, 1H), 1.44-1.31 (m, 3H), 1.30-1.22 (m, 4H), 1.20 (d, *J* = 4.4 Hz, 6H), 1.10-1.00 (m, 1H), 0.99-0.85 (m, 1H), 0.92 (d, *J* = 5.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.8, 198.3, 143.9, 143.3, 114.0, 113.6, 70.9, 44.3, 43.9, 37.8, 32.4, 29.5, 29.4, 29.3, 29.1, 28.1, 21.4, 20.3, 19.9. IR (KBr): ν (cm^{-1}) 3277, 2968, 2905, 2840, 1648, 1599, 1466, 1380, 1356, 1317, 1270, 1222, 1154, 1130, 1103, 1018, 931, 905, 889, 850, 765, 680, 626, 558. ESI-MS: *m/z* 336.3 (M^++H); HRMS calcd for $C_{20}H_{34}NO_3$ [M+H]: 336.2533, found: 336.2529.



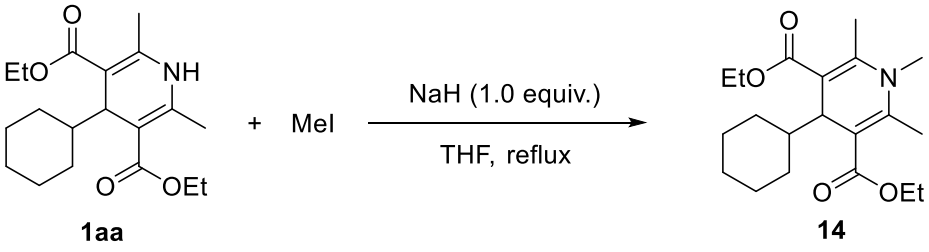
1,1'-(4-((*R*)-3-((5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)butyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (1-11). Prepared according to Method A. Yield: 2.87 g (55%), yellow solid; m.p.: 255-257 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (s, 1H), 3.83 (t, *J* = 5.7 Hz, 1H), 2.69 (t, *J* = 14.2 Hz, 1H), 2.32 (s, 6H), 2.29 (s, 6H), 2.15 (d, *J* = 15.2 Hz, 1H), 2.08-1.93 (m, 3H), 1.93-1.60 (m, 4H), 1.60-1.40 (m, 5H), 1.39-1.20 (m, 6H), 1.20-0.87 (m, 8H), 1.01 (s, 3H), 0.82 (d, *J* = 6.5 Hz, 3H), 0.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 213.6, 198.6, 198.5, 143.2, 143.1, 113.2, 113.1, 56.4, 55.8, 44.3, 42.6, 42.4, 40.7, 40.0, 37.2, 37.0, 35.6, 35.5, 35.2, 34.9, 33.4, 30.9, 29.4, 28.0,

26.6, 25.8, 24.1, 22.6, 21.2, 20.0, 18.6, 12.0. IR (KBr): ν (cm^{-1}) 3324, 2940, 2862, 1712, 1668, 1595, 1468, 1379, 1355, 1322, 1299, 1257, 1222, 1169, 1150, 1120, 1094, 1011, 991, 958, 935, 825, 736, 675, 620, 566, 531. ESI-MS: *m/z* 522.4 (M^++H); HRMS calcd for $C_{34}H_{52}NO_3$ [M+H]: 522.3942, found: 522.3937.



1,1'-(4-(Hex-5-en-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-diyl)bis(ethan-1-one) (**12**). Prepared according to Method A. Yield: 1.1 g (40%) Yellow solid; m.p.: 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46 (br s, 1H), 5.84-5.57 (m, 1H), 4.97-4.89 (m, 2H), 3.87 (t, *J* = 5.8 Hz, 1H), 2.32 (s, 6H), 2.30 (s, 6H), 2.06-1.91 (m, 2H), 1.36-1.11 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.5, 143.3, 138.8, 114.3, 113.1, 37.0, 34.8, 33.7, 29.4, 29.1, 24.5, 20.0. IR (KBr): ν (cm^{-1}) 3408, 3278, 3158, 3028, 2953, 2840, 2247, 1655, 1582, 1463, 1366, 1340, 1305, 1225, 1142, 1089, 1019, 931, 917, 825, 731, 690, 575. ESI-MS: *m/z* 276.2 (M^++H); HRMS calcd for $C_{17}H_{26}NO_2$ [M+H]: 276.1958, found: 276.1952.

Synthesis and Characterizations of Compound 14



1aa **14**

Compound **14** was prepared according to the literature procedure [S3]. To a round-bottom flask equipped with a magnetic stir bar were added sequentially **1aa** (1.0 g, 3.0 mmol, 1.0 equiv.) and NaH (72 mg, 3.0 mmol, 1.0 equiv.) in THF (20.0 mL), the

mixture was stirred at 70 ℃ for 0.5 h. Then MeI (0.71 g, 5.0 mmol, 1.67 equiv.) was added, and the resultant mixture was refluxed for 2 h and then poured into brine and extracted with ethyl acetate. The combined extracts were dried over Na_2SO_4, filtered, and evaporated. The crude residue was purified by flash column chromatography on silica gel with a gradient eluent of ethyl acetate and petroleum ether (1:3) to give the corresponding pure product (**14**) (157 mg, 49% yield). The NMR data are consistent with previous report.

4. Synthesis and Characterization of Products

Typical Procedure for the Deformylative Phosphonylation *via* 4-alkyl-1,4-dihydropyridines (DHPs)

To a 10 mL oven-dried, sealed tube equipped with a Teflon-coated magnetic stir bar were added 4DPAIPN (0.8 mg, 0.001 mmol, 1 mol%), **DHP** (0.1 mmol, 1.0 equiv.) and **2** (64 mg, 0.2 mmol, 2.0 equiv.). The tube was evacuated and backfilled with argon three times. Triethylamine (20 uL, 0.2 mmol, 2.0 equiv.) and DCM (2.0 mL) were added successively. The tube was sealed and placed about 3 cm away from two 30 W blue LEDs. Then the mixture was stirred at room temperature for 24 h under blue light irradiation.

MeOH work up: After completion of the reaction, methanol (1.0 mL) was added to quench the reaction. After stirring at room temperature for 10 min, the solution was concentrated *in vacuo*. The residue was then dissolved in methanol (1.0 mL). 18-crown-6 (1 mg, 0.003 mmol, 3 mol%) and KF (58 mg, 1.0 mmol, 1.0 equiv.) were added. The mixture was stirred at 80 ℃ for 10 min to ensure the complete dissolution of KF. Then the solution was stirred at room temperature for 10 h. The resultant mixture was diluted with EtOAc (5 mL), washed successively with H_2O (3×10 mL) and brine (1×10 mL), dried over Mg_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel with a gradient eluent of ethyl acetate,

dichloromethane and methanol to provide the pure product as dimethyl phosphonate.

Gram-Scale Synthesis of Compound 4k

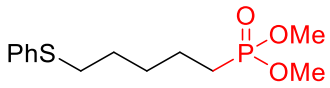
To a 250 mL oven-dried round-bottom flask equipped with a Teflon-coated magnetic stir bar were added 4DPAIPN (48 mg, 0.060 mmol, 1 mol%), **1k** (2.256 g, 6.0 mmol, 1.0 equiv.) and **2** (3.84 g, 12.0 mmol, 2.0 equiv.). The flask was evacuated and backfilled with argon three times. Et_3N (1.212 g, 12.0 mmol, 2.0 equiv.) and DCM (120 mL) were added successively. The tube was sealed and placed about 3 cm away from two 30 W blue LEDs. Then the mixture was stirred at room temperature for 24 h under blue light irradiation. After completion of the reaction, methanol (20.0 mL) was added and the mixture was stirred at room temperature for 1 h. The solution was concentrated in vacuo. The residue was then dissolved in methanol (60.0 mL). 18-crown-6 (0.48 g, 0.18 mmol, 3 mol%) and KF (3.49 g, 60 mmol, 10.0 equiv.) were added. The mixture was stirred at 80 ℃ for 10 min to ensure the complete dissolution of KF. Then the solution was stirred at room temperature for 10 h. The resultant mixture was diluted with EtOAc (50 mL), washed successively with H_2O (3×50 mL) and brine (1×50 mL), dried over Mg_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel with a gradient eluent of ethyl acetate, dichloromethane and methanol to provide the pure product (**4k**) as colorless oil. Yield: 1.21g (69% yield based on **1k**).

The following products are known compounds:

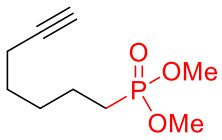
Dimethyl pentylphosphonate (**4a**)[S4], dimethyl (cyclopentylmethyl)phosphonate (**4b**)[S4], dimethyl phenetylphosphonate (**4c**)[S4], diethyl (3-(4-bromophenyl)propyl)phosphonate (**4e**)[S4], dimethyl cyclohexylphosphonate (**4h**)[S4], Dimethyl (tetrahydro-2*H*-pyran-4-yl)phosphonate (**4j**)[S1], *tert*-butyl 4-(dimethoxyphosphoryl)piperidine-1-carboxylateDimethyl (**4k**)[S1], (4-oxocyclohexyl)phosphonate (**4l**)[S1], dimethyl butan-2-ylphosphonate (**4m**)[S1], dimethylcyclobutylphosphonate (**4o**)[S5], dimethyl cyclopentylphosphonate (**4p**)[S4], 2-

adamatylphosphonsaeuremethylester (**4r**)[S4], *tert*-butyl 3-(diethoxyphosphoryl)piperidine-1-carboxylate (**4v**)[S7], diethyl (4,4-difluorocyclohexyl)phosphonate (**4w**)[S7], 2-hydroxyphenyl methyl (adamantan-1-yl)phosphonate (**4x**)[S1].

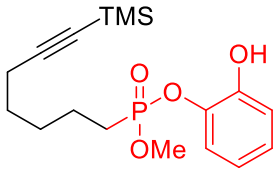
Characterizations of new products



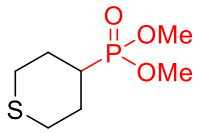
Dimethyl (5-(phenylthio)pentyl)phosphonate (**4d**). Yield: 16 mg (54%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.16 (m, 4H), 7.09-7.05 (m, 1H), 3.63 (dd, *J* = 10.8, 2.2 Hz, 6H), 2.82 (t, *J* = 7.2 Hz, 2H), 1.68-1.51 (m, 6H), 1.47-1.35 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.6, 129.0, 128.8, 125.8, 52.2 (d, *J* = 6.4 Hz), 33.2, 29.5 (d, *J* = 16.6 Hz), 28.6, 24.5 (d, *J* = 140.8 Hz), 21.9 (d, *J* = 5.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.59 (s). IR (neat): ν (cm^{-1}) 3463, 3056, 2950, 2852, 1654, 1584, 1481, 1462, 1438, 1406, 1247, 1184, 1059, 1030, 895, 818, 740, 692, 541, 475. ESI-MS: *m/z* 289.1 (M^++H); HRMS calcd for $C_{13}H_{22}O_3PS$ [M+H]: 289.1022, found: 289.1016.



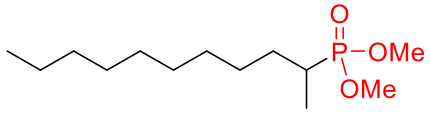
Dimethyl hept-6-yn-1-ylphosphonate (**4f**). Yield: 12 mg (60%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (d, *J* = 10.8 Hz, 6H), 2.24-2.15 (m, 2H), 1.96 (t, *J* = 2.6 Hz, 1H), 1.82-1.72 (m, 2H), 1.69-1.59 (m, 2H), 1.57-1.46 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 84.1, 68.4, 52.2 (d, *J* = 7.0 Hz), 29.5 (d, *J* = 17.0 Hz), 27.8, 24.5 (d, *J* = 140.0 Hz), 21.8 (d, *J* = 5.0 Hz), 18.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.79 (s). IR (neat): ν (cm^{-1}) 3468, 3293, 2950, 2860, 2115, 1647, 1463, 1238, 1185, 1031, 836, 815, 642, 537. ESI-MS: *m/z* 205.1 (M^++H); HRMS calcd for $C_9H_{18}O_3P$ [M+H]: 205.0988, found: 205.0986.



2-Hydroxyphenyl methyl (7-(trimethylsilyl)hept-6-yn-1-yl)phosphonate (**4g**). Yield: 14 mg (40%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (br, 1H), 7.13-6.98 (m, 3H), 6.89-6.82 (m, 1H), 3.79 (d, *J* = 11.0 Hz, 3H), 2.24 (t, *J* = 6.5 Hz, 2H), 2.03-1.93 (m, 2H), 1.78-1.65 (m, 2H), 1.57-1.47 (m, 4H), 0.14 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.7 (d, *J* = 2.7 Hz), 138.8 (d, *J* = 9.9 Hz), 126.6, 121.7 (d, *J* = 4.4 Hz), 120.8, 119.9, 106.9, 84.8, 53.5 (d, *J* = 7.7 Hz), 29.5 (d, *J* = 17.0 Hz), 27.9, 24.4 (d, *J* = 139.4 Hz), 21.7 (d, *J* = 5.4 Hz), 19.6, 0.15. ^{31}P NMR (162 MHz, $CDCl_3$): δ 36.38 (s). IR (neat): ν (cm^{-1}) 3171, 2955, 2862, 2325, 2173, 1595, 1514, 1497, 1460, 1405, 1294, 1249, 1176, 1101, 1039, 988, 942, 841, 757, 698, 554, 523, 459. ESI-MS: *m/z* 355.1 (M^{+}+H); HRMS calcd for $C_{17}H_{28}O_4PSi$ [M+H]: 355.1489, found: 355.1488.

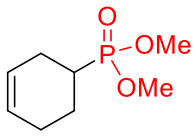


Dimethyl (tetrahydro-2H-thiopyran-4-yl)phosphonate (**4i**). Yield: 18 mg (85%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.61 (d, *J* = 10.6 Hz, 6H), 2.59-2.44 (m, 4H), 2.21-2.05 (m, 2H), 1.78-1.55 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 52.5 (d, *J* = 7.0 Hz), 35.1 (d, *J* = 144.4 Hz), 28.0 (d, *J* = 18.2 Hz), 26.8 (d, *J* = 3.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.90 (s). IR (neat): ν (cm^{-1}) 3467, 2950, 2850, 1445, 1431, 1268, 1233, 1183, 1056, 1027, 965, 865, 823, 794, 720, 574. ESI-MS: *m/z* 211.1 (M^{+}+H); HRMS calcd for $C_7H_{16}O_3PS$ $[M + H]^{+}$: 211.0552, found: 211.0549.

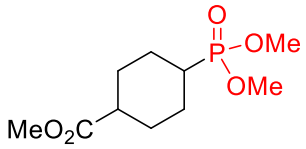


Dimethyl undecan-2-ylphosphonate (**4n**). Yield: 21 mg (81%), brown oil; ^{1}H NMR

(400 MHz, $CDCl_3$): δ 3.75 (d, *J* = 10.0 Hz, 6H), 1.69-1.90 (m, 2H), 1.20-1.52 (m, 15H), 1.16 (dd, *J* = 18.8, 7.1 Hz, 3H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 52.4 (d, *J* = 5.0 Hz), 52.3 (d, *J* = 5.0 Hz), 31.8, 30.3 (d, *J* = 139.0 Hz), 29.8 (d, *J* = 4.0 Hz), 29.5, 29.4, 29.2, 27.2 (d, *J* = 14.0 Hz), 22.6, 14.0, 13.05, 13.00. ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.56 (s). IR (neat): ν (cm^{-1}) 3475, 2925, 2854, 1465, 1378, 1244, 1184, 1061, 1032, 821, 753, 556. ESI-MS: *m/z* 265.2 (M^++H); HRMS calcd for $C_{13}H_{30}O_3P$ [M+H]: 265.1927, found: 265.1928.

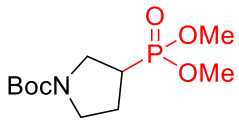


Dimethyl cyclohex-3-en-1-ylphosphonate (**4q**). Yield: 14 mg (38%), brown oil; ^1H NMR (400 MHz, $CDCl_3$): δ 5.70 (s, 2H), 3.78 (s, 3H), 3.75 (s, 3H), 2.26-2.15 (m, 2H), 2.14-1.95 (m, 4H), 1.66-1.56 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 126.8, 125.1 (d, *J* = 15.5 Hz), 52.5 (d, *J* = 5.9 Hz), 31.3 (d, *J* = 145.5 Hz), 24.6, 24.5 (d, *J* = 3.8 Hz), 21.9 (d, *J* = 4.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.33 (s). IR (neat): ν (cm^{-1}) 3463, 3025, 2951, 2924, 2847, 1721, 1653, 1455, 1438, 1270, 1235, 1184, 1058, 1030, 914, 899, 823, 798, 761, 654, 553. ESI-MS: *m/z* 191.1 (M^++H); HRMS calcd for $C_8H_{16}O_3P$ [M+H]: 191.0831, found: 191.0828.

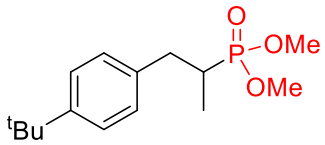


Methyl 4-(dimethoxyphosphoryl)cyclohexane-1-carboxylate (**4s**). This compound was isolated as an inseparable mixture of *cis*- and *trans*-isomer in a ratio of 5:1 determined by ^{31}P NMR. Yield: 20 mg (79%), brown oil; ^1H NMR (400 MHz, $CDCl_3$): δ 3.75/3.74 (d, *J* = 10.6 Hz, 6H), 3.70/3.67 (s, 3H), 2.67-2.59/2.33-2.27 (m, 1H), 2.21-1.98 (m, 5H), 1.88-1.35 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 175.5/174.8, 52.5 (d, *J* = 5.0 Hz)/52.4 (d, *J* = 5.0 Hz), 51.5, 42.3/38.9, 34.2 (d, *J* = 143.0 Hz)/34.0 (d, *J* =

142.0 Hz), 28.3 (d, *J* = 16.4 Hz)/26.5 (d, *J* = 13.7 Hz), 24.7 (d, *J* = 3.0 Hz)/22.5 (d, *J* = 4.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.47 (s)/37.29 (s). IR (neat): ν (cm^{-1}) 3462, 2952, 2863, 1732, 1654, 1453, 1240, 1176, 1031, 822, 574. ESI-MS: *m/z* 251.1 (M^++H); HRMS calcd for $C_{10}H_{20}O_5P$ [M+H]: 251.1043, found: 251.1043.

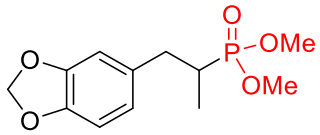


***Tert*-butyl 3-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate** (**4t**). This compound was isolated as a mixture of two inseparable rotamers in a ratio of 42:58 determined by ^{31}P NMR. Yield: 12 mg (42%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (d, *J* = 10.6 Hz, 6H), 3.70-3.40 (m, 3H), 3.35-3.25 (m, 1H), 2.60-2.42 (m, 1H), 2.30-2.00 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.0, 79.4, 52.6 (d, *J* = 7.0 Hz), 45.6 (br), 34.5 (d, *J* = 152.0 Hz)/34.1 (d, *J* = 150.0 Hz), 28.3, 26.5, 25.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.74 (s), 31.62 (s). IR (neat): ν (cm^{-1}) 3484, 2977, 2885, 1697, 1455, 1406, 1366, 1244, 1169, 1121, 1054, 1029, 952, 883, 829, 773, 666, 584, 552. ESI-MS: *m/z* 302.1 (M^++Na); HRMS calcd for $C_{11}H_{23}NO_5P$ [M+H]: 280.1308, found: 280.1303.

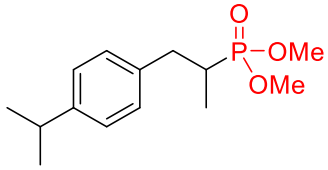


Dimethyl (1-(4-(*tert*-butyl)phenyl)propan-2-yl)phosphonate (**4v**). Yield: 20 mg (69%), brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.77 (d, *J* = 10.5 Hz, 3H), 3.75 (d, *J* = 10.6 Hz, 3H), 3.17 (ddd, *J* = 13.3, 9.5, 3.4 Hz, 1H), 2.55-2.40 (m, 1H), 2.20-2.06 (m, 1H), 1.31 (s, 9H), 1.08 (dd, *J* = 18.6, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 136.0 (d, *J* = 17.2 Hz), 128.7, 125.3, 52.6 (d, *J* = 7.3 Hz), 52.5 (d, *J* = 7.3 Hz), 35.4 (d, *J* = 2.8 Hz), 34.4, 32.4 (d, *J* = 140.2 Hz), 31.4, 12.6 (d, *J* = 4.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 36.60 (s).

IR (neat): ν (cm-1) 3027, 2952, 2851, 1497, 1456, 1238, 1183, 1060, 1035, 926, 911, 823, 732. ESI-MS: *m/z* 285.2 (M^++H); HRMS calcd for $C_{15}H_{26}O_3P$ [M+H]: 285.1614, found: 285.1609.

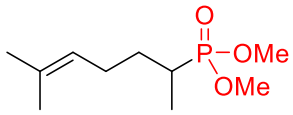


Dimethyl (1-(benzo[d][1,3]dioxol-5-yl)propan-2-yl)phosphonate (5). Yield: 18 mg (69%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (d, *J* = 7.9 Hz, 1H), 6.66 (s, 1H), 6.62 (d, *J* = 7.9 Hz, 1H), 5.93 (s, 2H), 3.77 (dd, *J* = 10.5, 1.2 Hz, 6H), 3.19-3.04 (m, 1H), 2.42 (ddd, *J* = 13.6, 11.3, 8.5 Hz, 1H), 2.12-2.02 (m, 1H), 1.07 (dd, *J* = 18.5, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.6, 146.0, 132.8 (d, *J* = 17.1 Hz), 121.9, 109.1, 108.0, 100.8, 52.5 (d, *J* = 6.8 Hz), 35.7 (d, *J* = 2.5 Hz), 32.5 (d, *J* = 139.9 Hz), 12.4 (d, *J* = 4.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 36.13 (s). IR (neat): ν (cm^{-1}) 3463, 2953, 2881, 2778, 1846, 1609, 1504, 1365, 1247, 1123, 1034, 929, 754, 665, 553. ESI-MS: *m/z* 273.1 (M^++H); HRMS calcd for $C_{12}H_{18}O_5P$ [M+H]: 273.0886, found: 273.0885.

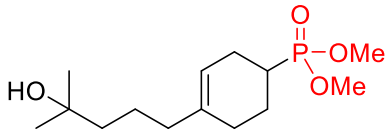


Dimethyl (1-(4-isopropylphenyl)propan-2-yl)phosphonate (6). Yield: 22 mg (81%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.76 (dd, *J* = 10.5, 2.6 Hz, 6H), 3.17 (ddd, *J* = 13.3, 9.5, 3.5 Hz, 1H), 2.92-2.85 (m, 1H), 2.47 (ddd, *J* = 13.6, 11.3, 8.5 Hz, 1H), 2.18-2.07 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.08 (dd, *J* = 18.6, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.9, 136.3 (d, *J* = 16.4 Hz), 128.9, 126.4, 52.5 (d, *J* = 7.3 Hz), 52.4 (d, *J* = 6.4 Hz), 35.5 (d, *J* = 2.8 Hz), 33.6, 32.4 (d, *J* = 139.9 Hz), 23.9, 12.5 (d, *J* = 4.6 Hz). ^{31}P NMR (162

MHz, $CDCl_3$): δ 36.60 (s). IR (neat): ν (cm^{-1}) 3474, 2959, 2873, 1904, 1647, 1513, 1460, 1420, 1382, 1363, 1256, 1228, 1194, 1057, 1031, 904, 874, 824, 750, 695, 580, 525, 490, 421. ESI-MS: *m/z* 271.1 (M^++H); HRMS calcd for $C_{14}H_{24}O_3P$ [M+H]: 271.1458, found: 271.1456.

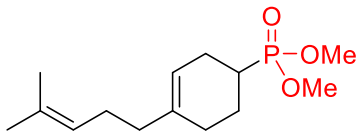


Dimethyl (6-methylhept-5-en-2-yl)phosphonate (7). Yield: 16 mg (73%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.07 (t, *J* = 6.9 Hz, 1H), 3.75 (d, *J* = 10.5 Hz, 6H), 2.19-2.08 (m, 1H), 2.07-1.97 (m, 1H), 1.94-1.72 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.46-1.32 (m, 1H), 1.17 (dd, *J* = 18.7, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 132.4, 123.3, 52.4 (d, *J* = 5.4 Hz), 52.3 (d, *J* = 4.9 Hz), 29.9 (d, *J* = 3.6 Hz), 29.6 (d, *J* = 140.6 Hz), 25.6, 25.5 (d, *J* = 13.8 Hz), 17.6, 12.9 (d, *J* = 5.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.49 (s). IR (neat): ν (cm^{-1}) 3440, 2971, 2854, 2234, 1647, 1457, 1379, 1228, 1058, 1032, 896, 860, 825, 787, 754, 703, 664, 565. ESI-MS: *m/z* 221.1 (M^++H); HRMS calcd for $C_{10}H_{22}O_3P$ [M+H]: 221.0301, found: 221.1299.

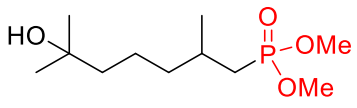


Dimethyl (4-(4-hydroxy-4-methylpentyl)cyclohex-3-en-1-yl)phosphonate (8). This compound was isolated as a mixture of two inseparable diastereoisomers in a ratio of 5:1 determined by ^{31}P NMR. Yield: 22 mg (77%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 (s, 1H), 3.76/3.75 (d, *J* = 10.5 Hz, 6H), 2.26-2.18 (m, 2H), 2.17-1.98 (m, 4H), 198-1.88 (m, 3H), 1.63-1.56 (m, 1H), 1.51-1.40 (m, 4H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.5 (s)/135.9 (d, *J* = 14.9 Hz), 120.5 (d, *J* = 1.4 Hz)/118.9 (d, *J* = 16.1 Hz), 70.6/70.5, 52.5 (d, *J* = 6.5, 7.2 Hz), 52.4 (d, *J* = 6.5, 7.2 Hz), 43.5/43.3, 38.1/37.9, 31.7 (d, *J* = 144.8 Hz)/31.3 (d, *J* = 145.0 Hz), 29.2/29.1, 27.6 (d, *J* = 16.0 Hz)/27.5 (d, *J* = 3.8 Hz), 24.7 (d, *J* = 16.4 Hz)/24.6 (d, *J* = 3.6 Hz),

22.4/22.2, 22.3 (d, J = 4.0 Hz)/21.9 (d, J = 4.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.64 (s), 35.39 (s). IR (neat): ν (cm^{-1}) 3400, 2952, 2848, 2233, 1845, 1670, 1458, 1440, 1377, 1363, 1270, 1228, 1190, 1157, 1060, 1032, 914, 826, 804, 755, 733, 664, 549, 486. ESI-MS: *m/z* 291.2 (M^++H); HRMS calcd for $C_{14}H_{28}O_4P$ [M+H]: 291.1720, found: 291.1719.

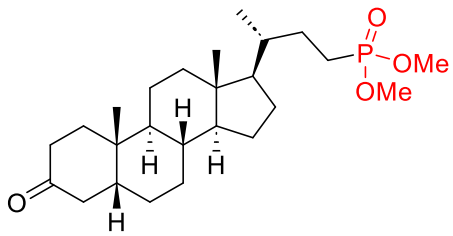


Dimethyl (4-(4-methylpent-3-en-1-yl)cyclohex-3-en-1-yl)phosphonate (9). This compound was isolated as a mixture of two inseparable diastereoisomers in a ratio of 5:1 determined by ^{31}P NMR. Yield: 14 mg (52%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.45-5.36 (m, 1H), 5.08 (t, J = 6.1 Hz, 1H), 3.77/3.76 (d, J = 10.5 Hz, 6H), 2.26-1.89 (m, 10H), 1.68 (s, 3H), 1.64-1.50 (m, 1H), 1.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.5/136.0 (d, J = 14.7 Hz), 131.6/131.5, 124.1/124.0, 120.4 (d, J = 1.4 Hz)/118.8 (d, J = 16.2 Hz), 52.5 (d, J = 6.4 Hz), 52.4 (d, J = 7.2 Hz), 37.6 (d, J = 1.4 Hz)/37.5, 31.8 (d, J = 144.7 Hz)/31.3 (d, J = 145.2 Hz), 27.9 (d, J = 15.8 Hz)/27.7 (d, J = 4.2 Hz), 26.3/26.2, 25.6/24.9, 24.7/24.7 (d, J = 3.6 Hz), 22.4 (d, J = 3.9 Hz)/21.9 (d, J = 4.5 Hz), 17.7/17.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.81 (s), 35.50 (s). IR (neat): ν (cm^{-1}) 3422, 2965, 2924, 2850, 1670, 1454, 1376, 1354, 1271, 1248, 1227, 1190, 1031, 916, 827, 803, 755, 663, 629, 567, 546, 487, 444. ESI-MS: *m/z* 273.2 (M^++H); HRMS calcd for $C_{14}H_{26}O_3P$ [M+H]: 273.1614, found: 273.1613.



Dimethyl (6-hydroxy-2,6-dimethylheptyl)phosphonate (10). Yield: 19 mg (75%), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (d, J = 10.8 Hz, 6H), 1.99-1.88 (m, 1H), 1.85-1.75 (m, 2H), 1.59 (ddd, J = 18.1, 15.4, 8.3 Hz, 1H), 1.50-1.23 (m, 6H), 1.21 (s, 6H), 1.05 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 70.7, 52.1 (d, J

= 6.3 Hz), 52.0 (d, *J* = 6.4 Hz), 43.7, 38.6 (d, *J* = 13.6 Hz), 31.7 (d, *J* = 138.5 Hz), 29.2 (d, *J* = 21.4 Hz), 28.1 (d, *J* = 4.0 Hz), 21.3, 20.8 (d, *J* = 7.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.55 (s). IR (neat): ν (cm^{-1}) 3385, 2970, 1648, 1462, 1405, 1380, 1322, 1220, 1050, 939, 910, 880, 844, 810, 557, 433. ESI-MS: *m/z* 253.2 (M^++H); HRMS calcd for $C_{11}H_{26}O_4P$ [M+H]: 253.1563, found: 253.1563.

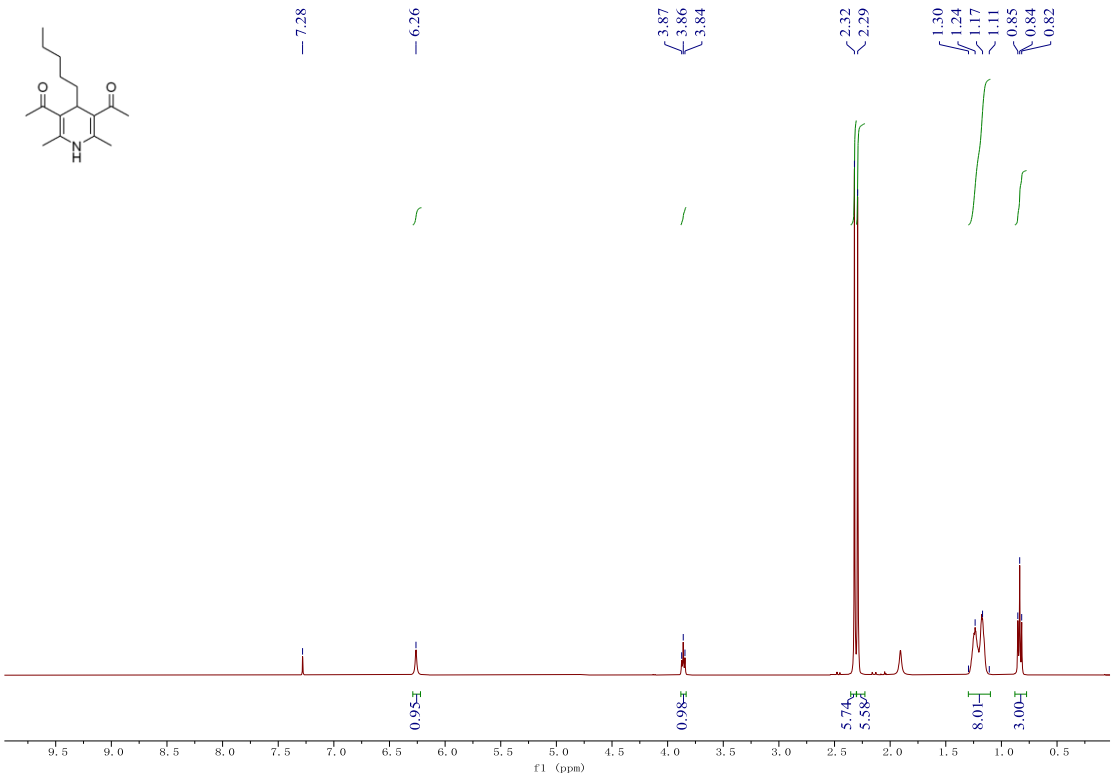


Dimethyl ((*R*)-3-((5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3-oxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)butyl)phosphonate (11). Yield: 38 mg (87%), white solid; m.p.: 204-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (d, *J* = 10.7 Hz, 6H), 2.70 (t, *J* = 14.2 Hz, 1H), 2.34 (td, *J* = 14.6, 5.1 Hz, 1H), 2.16 (d, *J* = 14.4 Hz, 1H), 2.08-1.96 (m, 3H), 1.93-1.76 (m, 4H), 1.76-1.56 (m, 3H), 1.55-1.38 (m, 6H), 1.38-1.17 (m, 5H), 1.17-1.04 (m, 4H), 1.02 (s, 3H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 213.3, 56.4, 55.5, 52.2 (d, *J* = 6.1 Hz), 44.3, 42.7, 42.3, 40.7, 40.0, 37.2, 37.0, 36.1, 36.0, 35.5, 34.8, 28.1, 28.0 (d, *J* = 4.8 Hz), 26.6, 25.7, 24.1, 22.6, 21.2, 21.1 (d, *J* = 140.8 Hz), 18.0, 12.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ 36.11 (s). IR (neat): ν (cm^{-1}) 2989, 2954, 2934, 2865, 2845, 1712, 1467, 1444, 1413, 1382, 1373, 1338, 1294, 1285, 1262, 1238, 1218, 1196, 1107, 1060, 1035, 917, 894, 884, 850, 839, 809, 755, 734, 703, 674, 571, 529, 506, 422. ESI-MS: *m/z* 439.3 (M^++H); HRMS calcd for $C_{25}H_{44}O_4P$ (M+H): 439.2972, found: 439.2970.

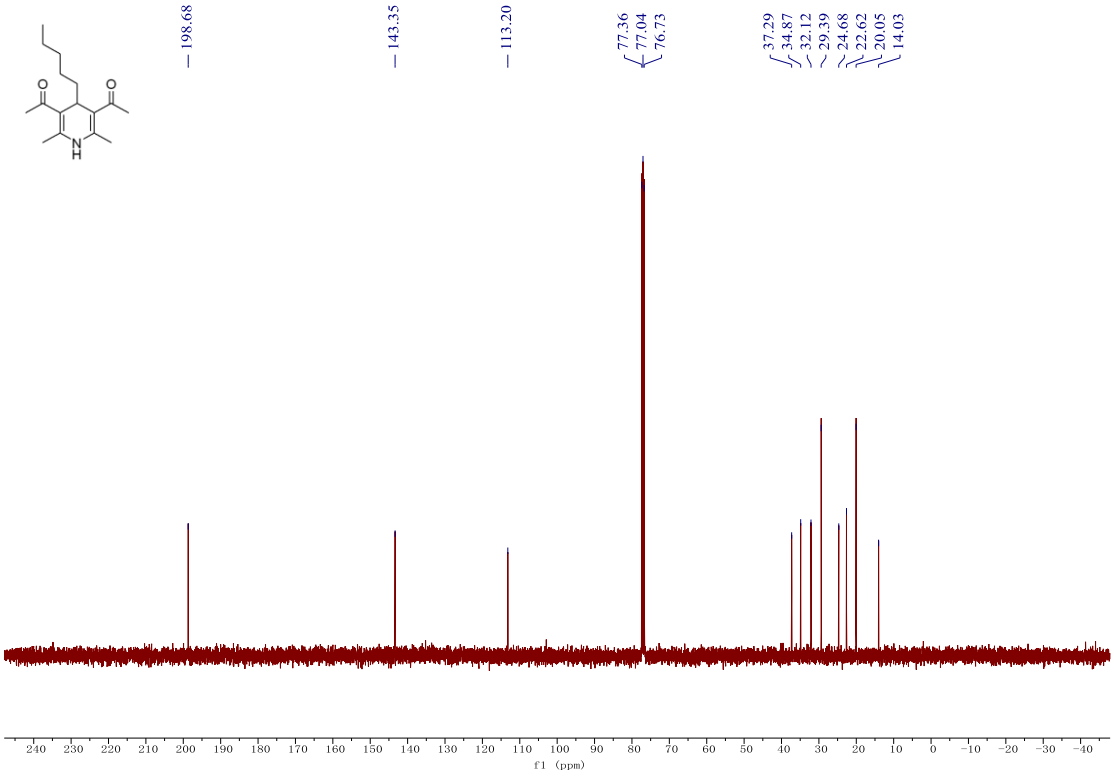
5. ^{1}H, ^{13}C and ^{19}F NMR spectra of new substrates

Compound **1a**

^{1}H NMR (400 MHz, $CDCl_3$):

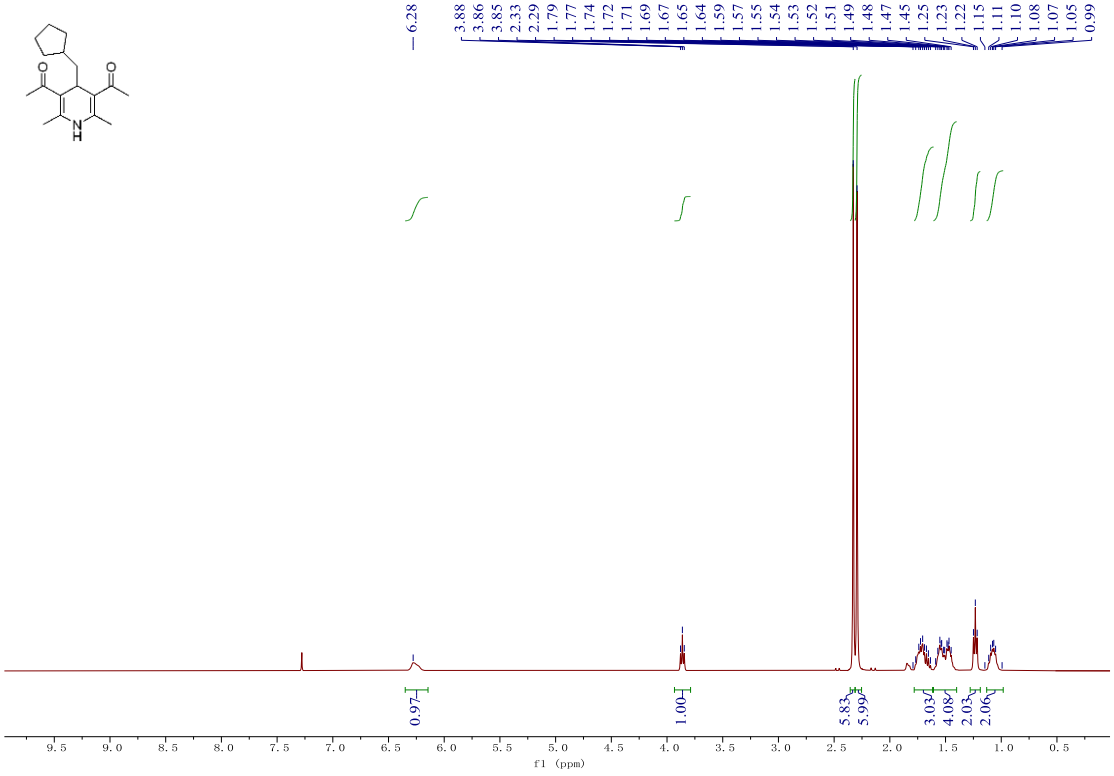


^{13}C NMR (100 MHz, $CDCl_3$):

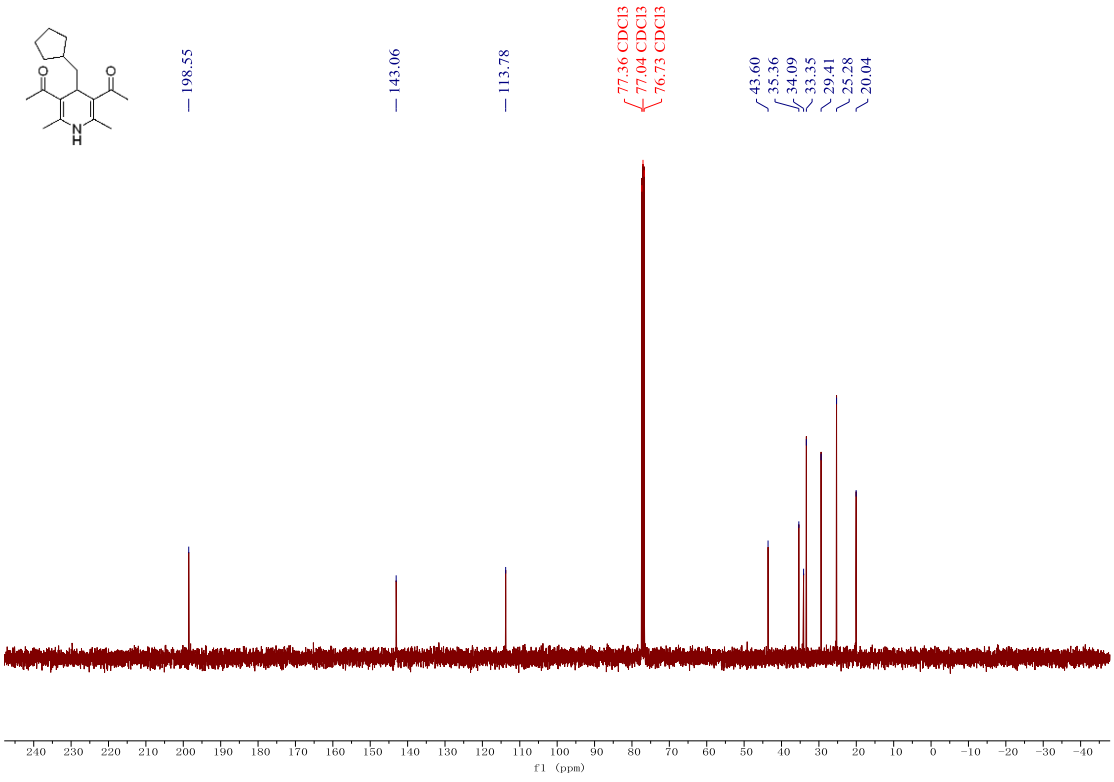


Compound **1b**

^{1}H NMR (400 MHz, $CDCl_3$):

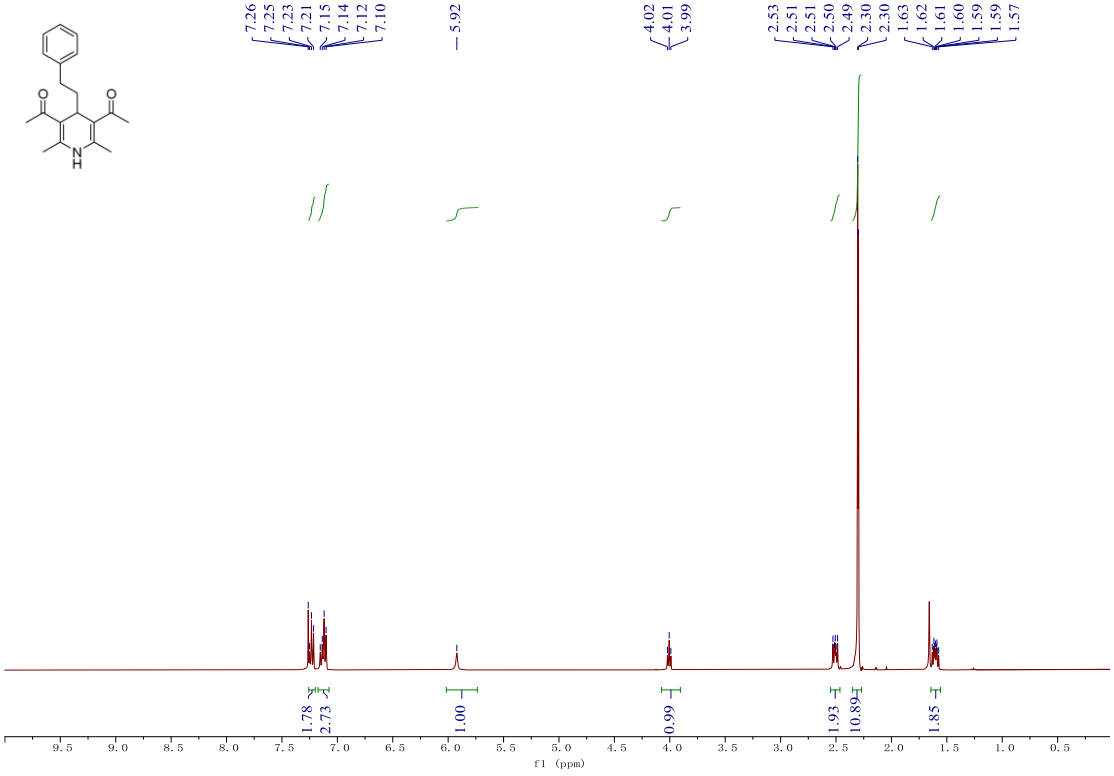


^{13}C NMR (100 MHz, $CDCl_3$):

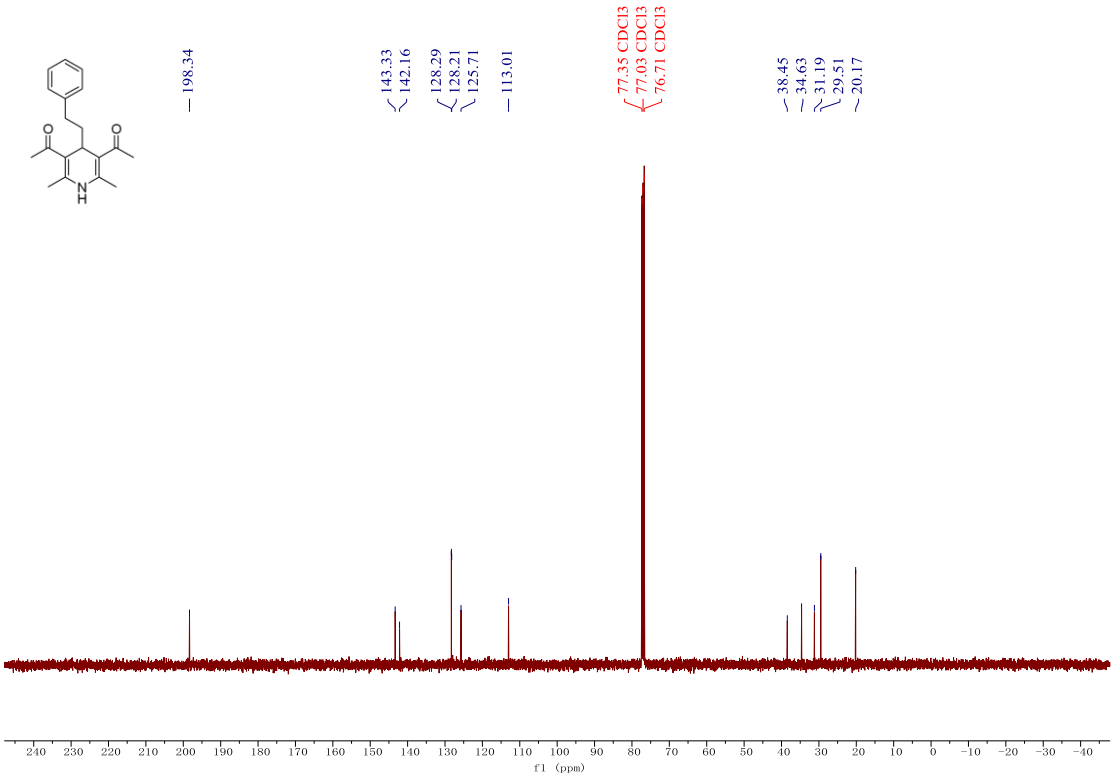


Compound **1c**

^{1}H NMR (400 MHz, $CDCl_3$):

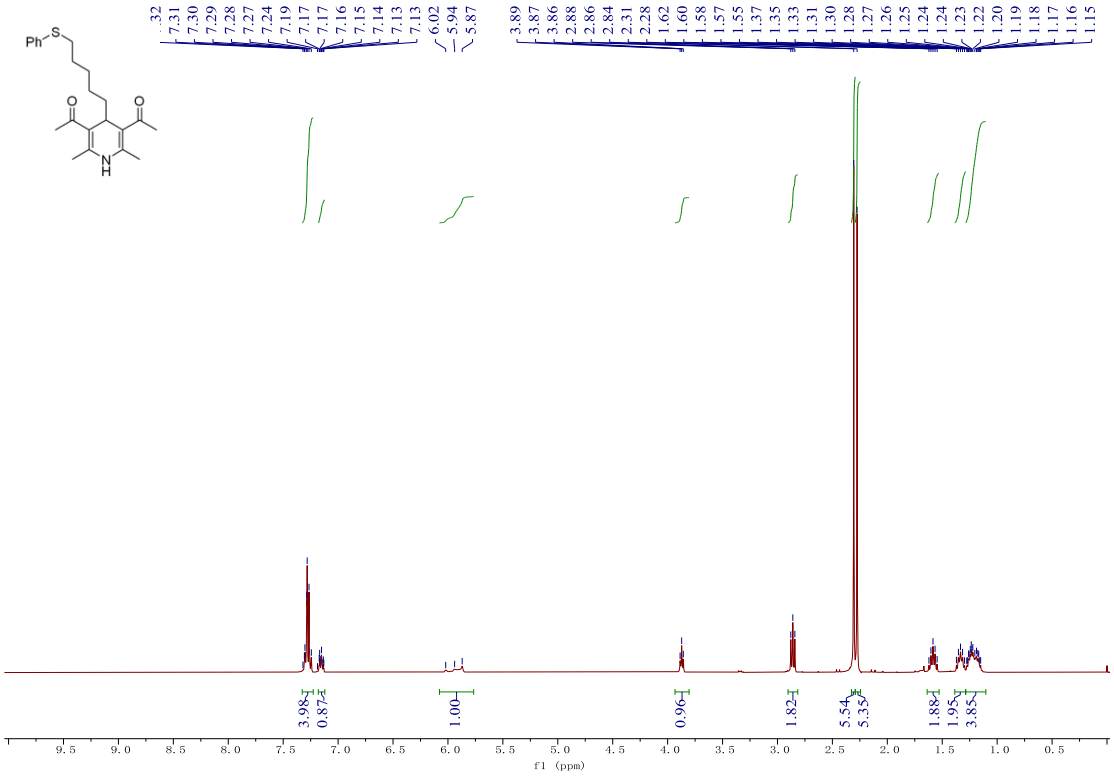


^{13}C NMR (100 MHz, $CDCl_3$):

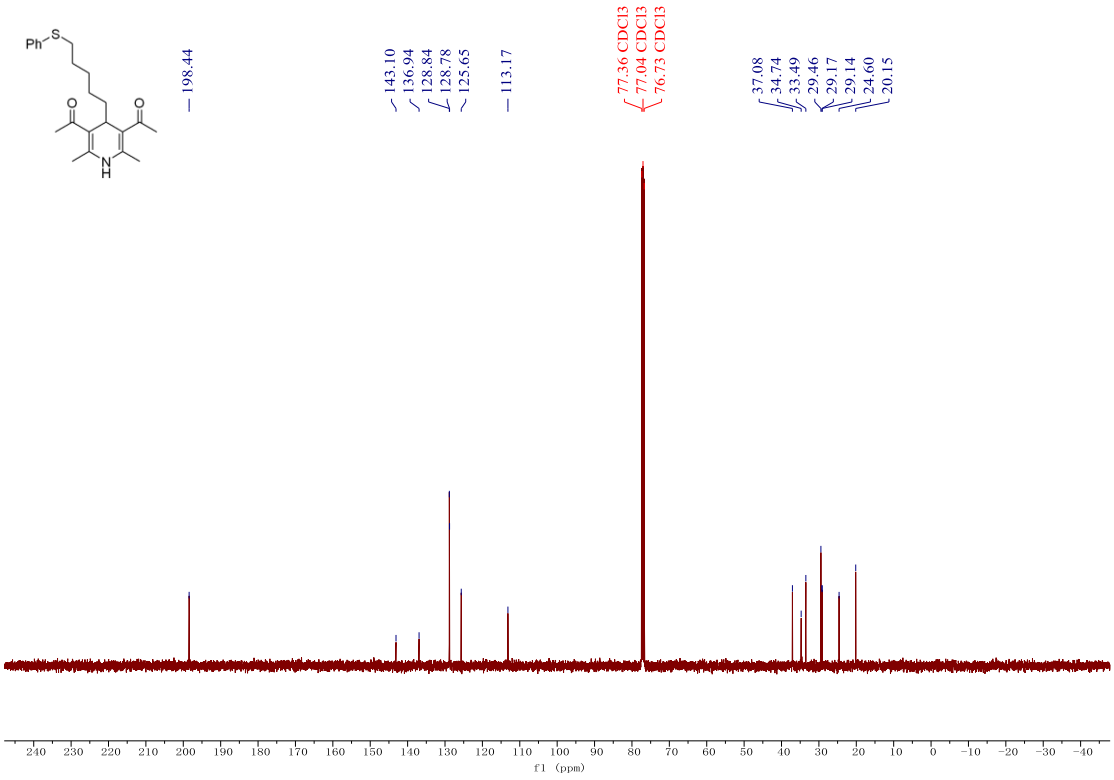


Compound **1d**

^{1}H NMR (400 MHz, $CDCl_3$):

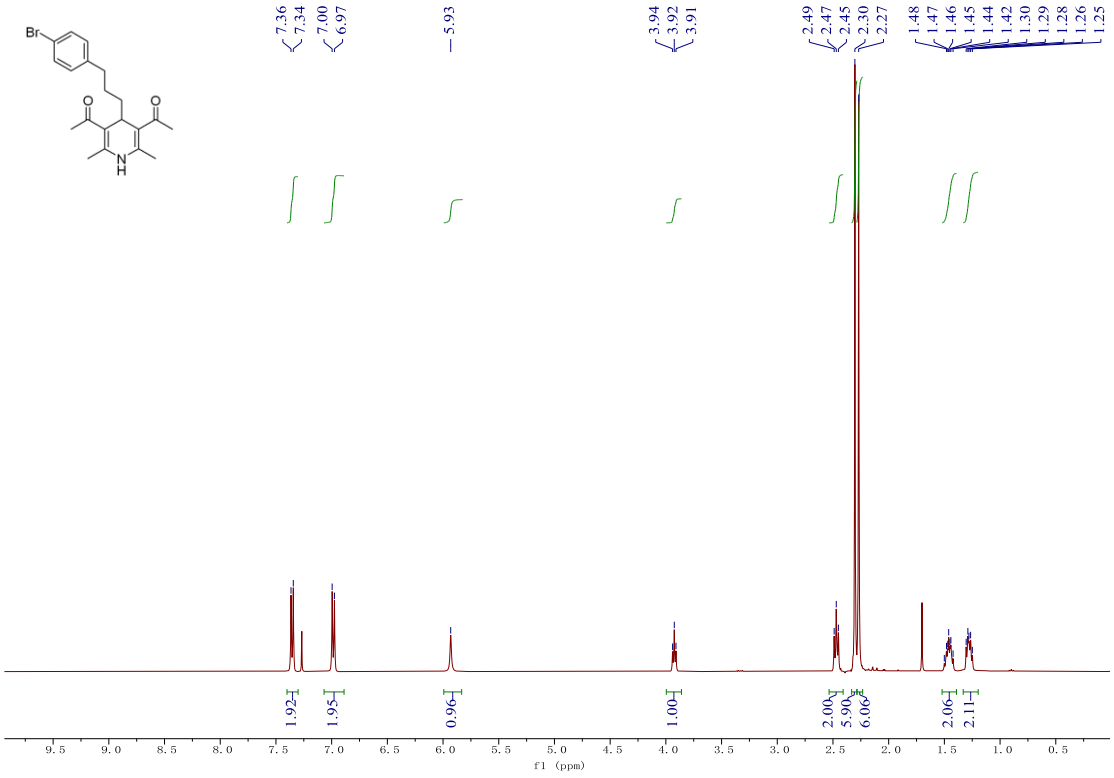


^{13}C NMR (100 MHz, $CDCl_3$):

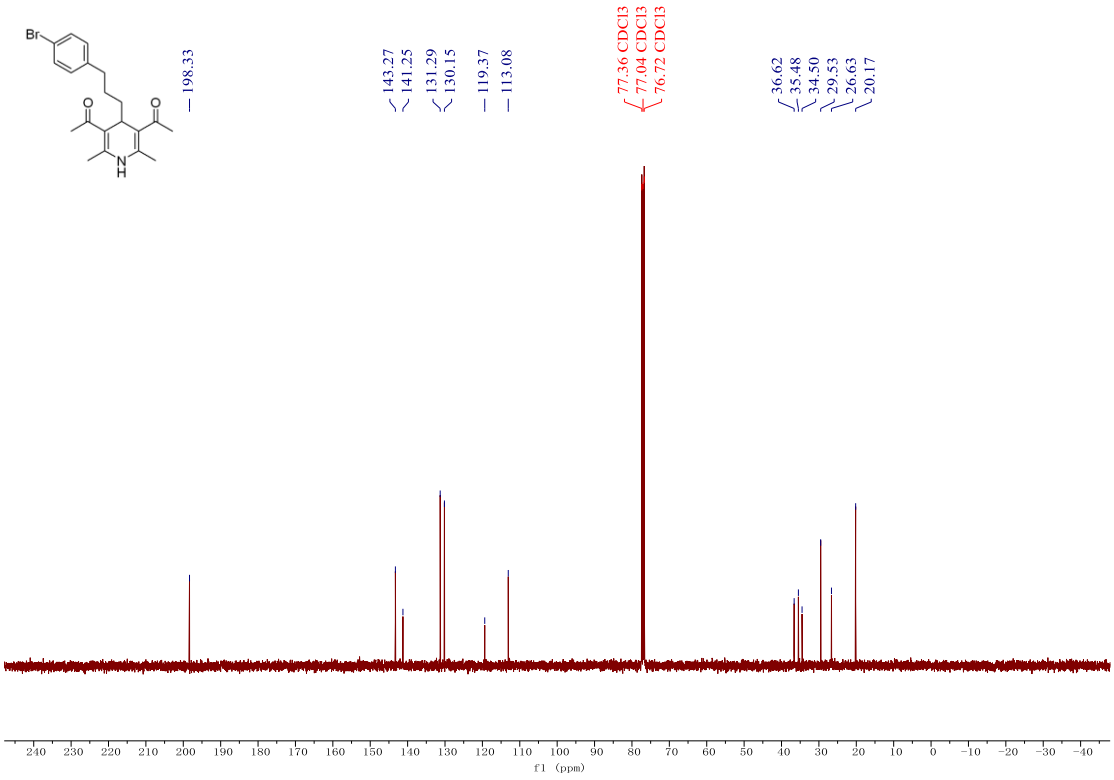


Compound **1e**

^{1}H NMR (400 MHz, $CDCl_3$):

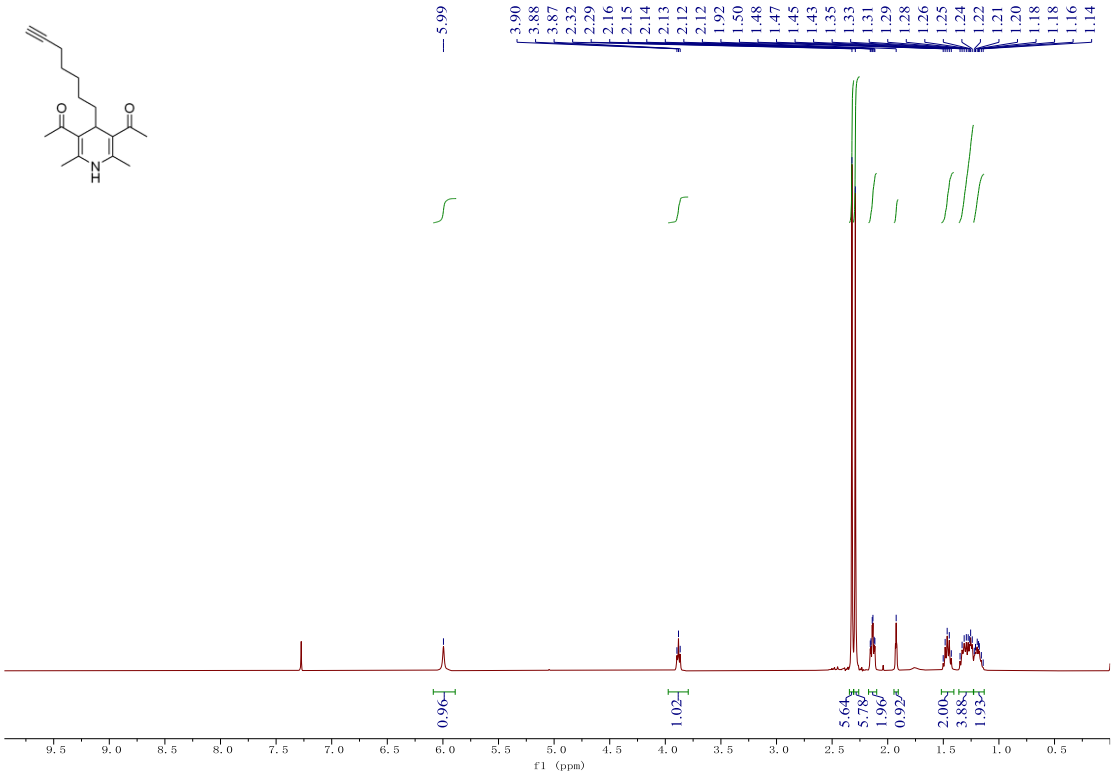


^{13}C NMR (100 MHz, $CDCl_3$):

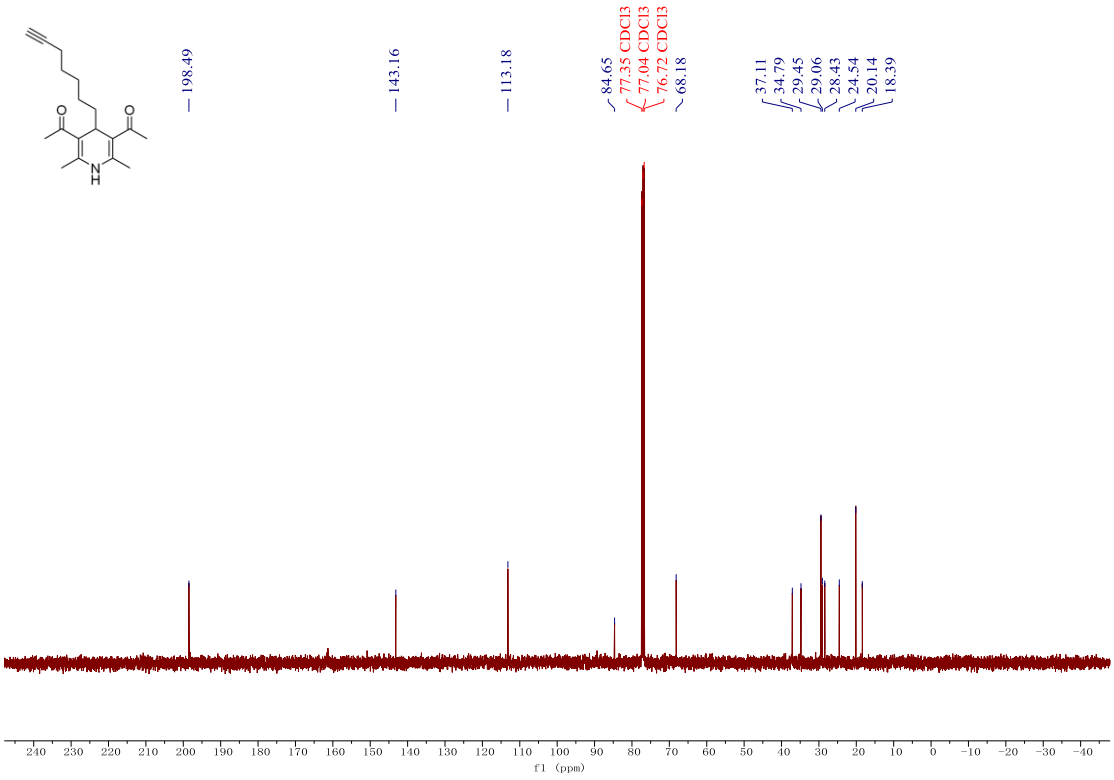


Compound **1f**

^{1}H NMR (400 MHz, $CDCl_3$):

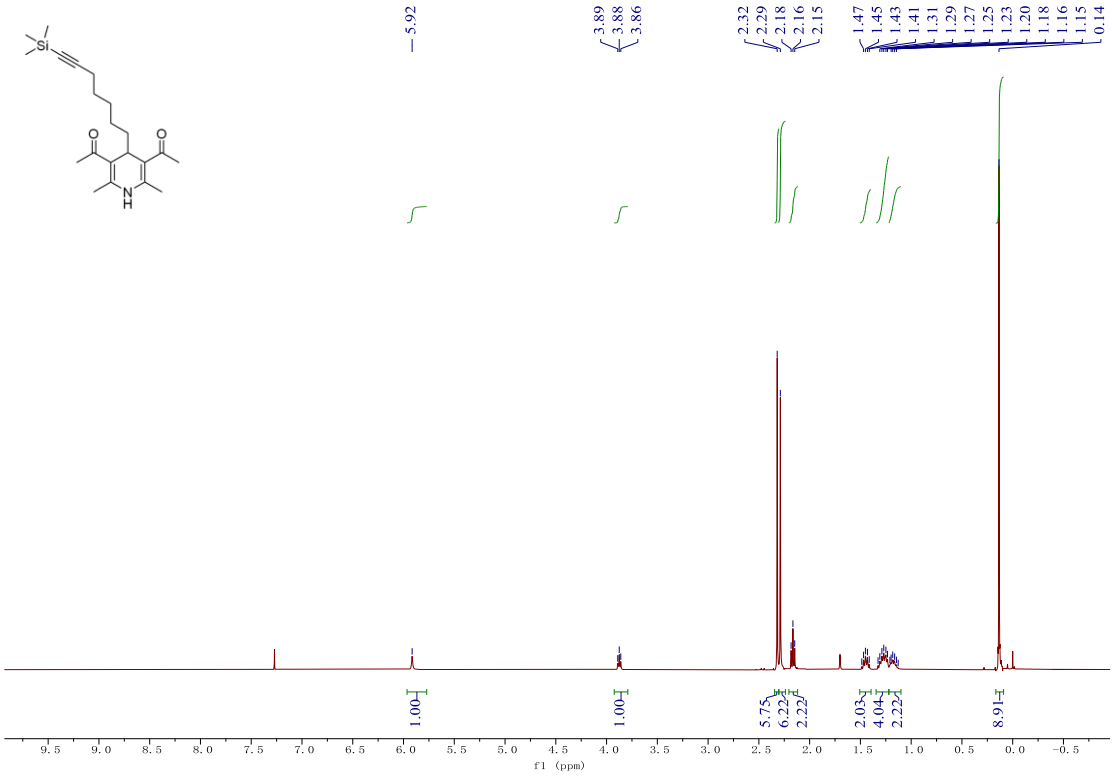


^{13}C NMR (100 MHz, $CDCl_3$):

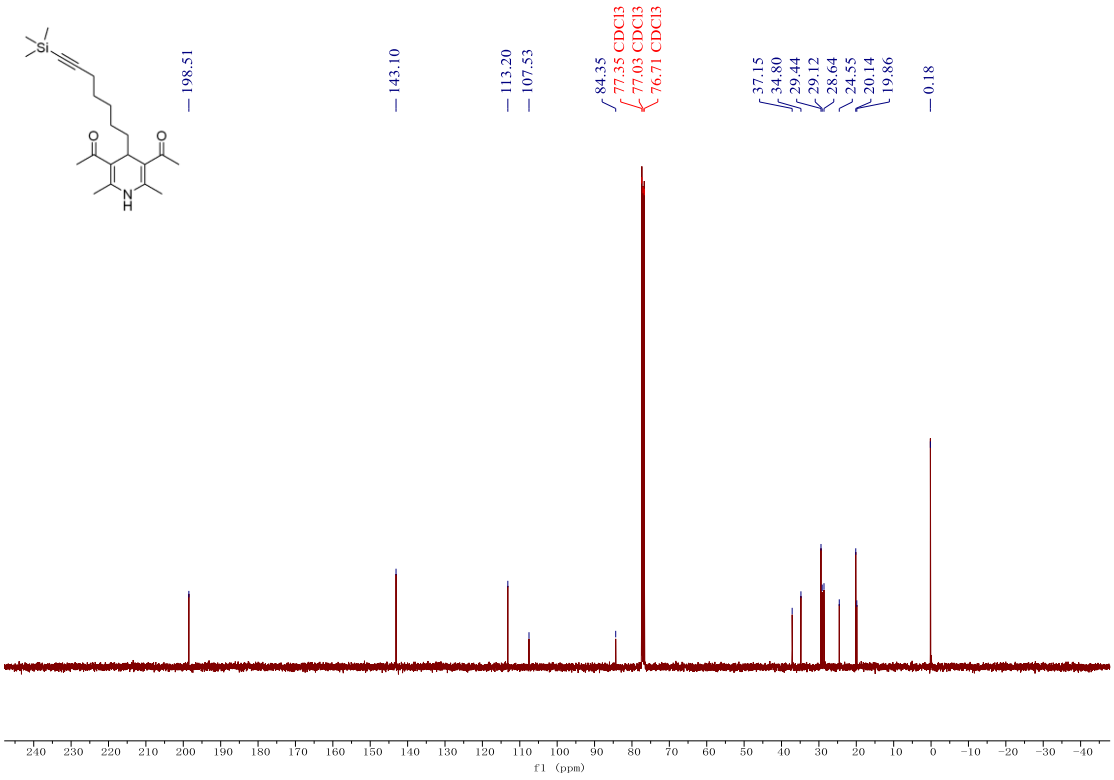


Compound **1g**

^{1}H NMR (400 MHz, $CDCl_3$):

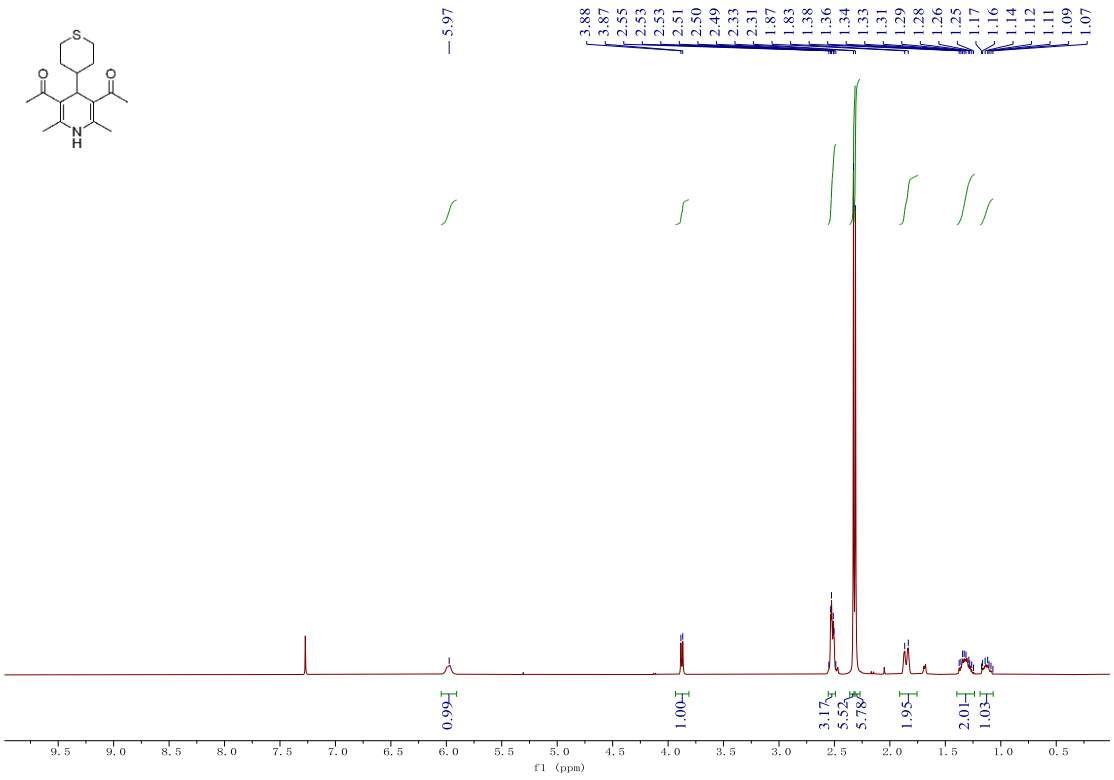


^{13}C NMR (100 MHz, $CDCl_3$):

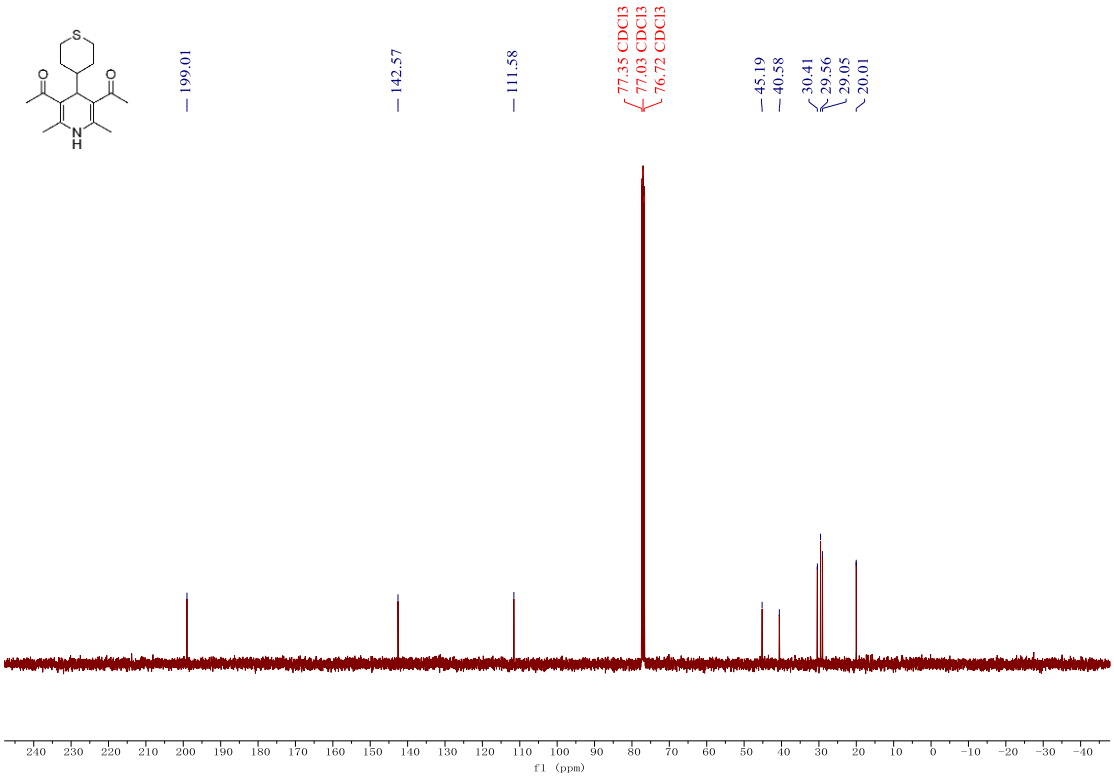


Compound **1i**

^{1}H NMR (400 MHz, $CDCl_3$):

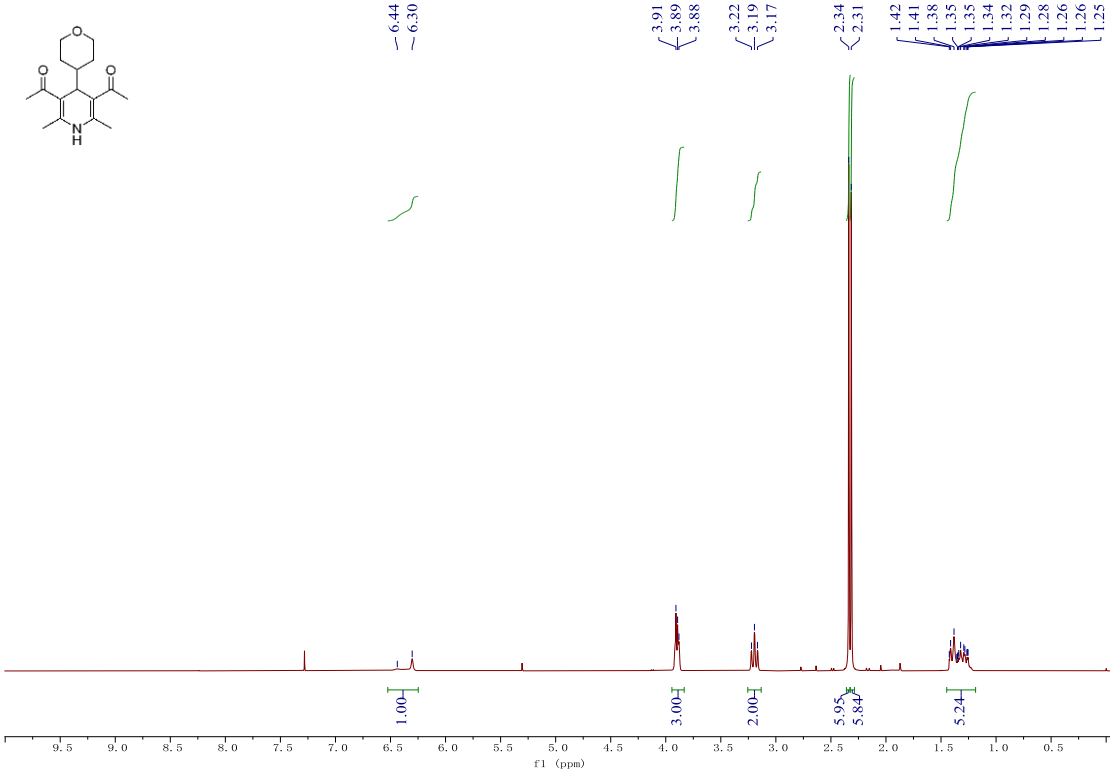


^{13}C NMR (100 MHz, $CDCl_3$):

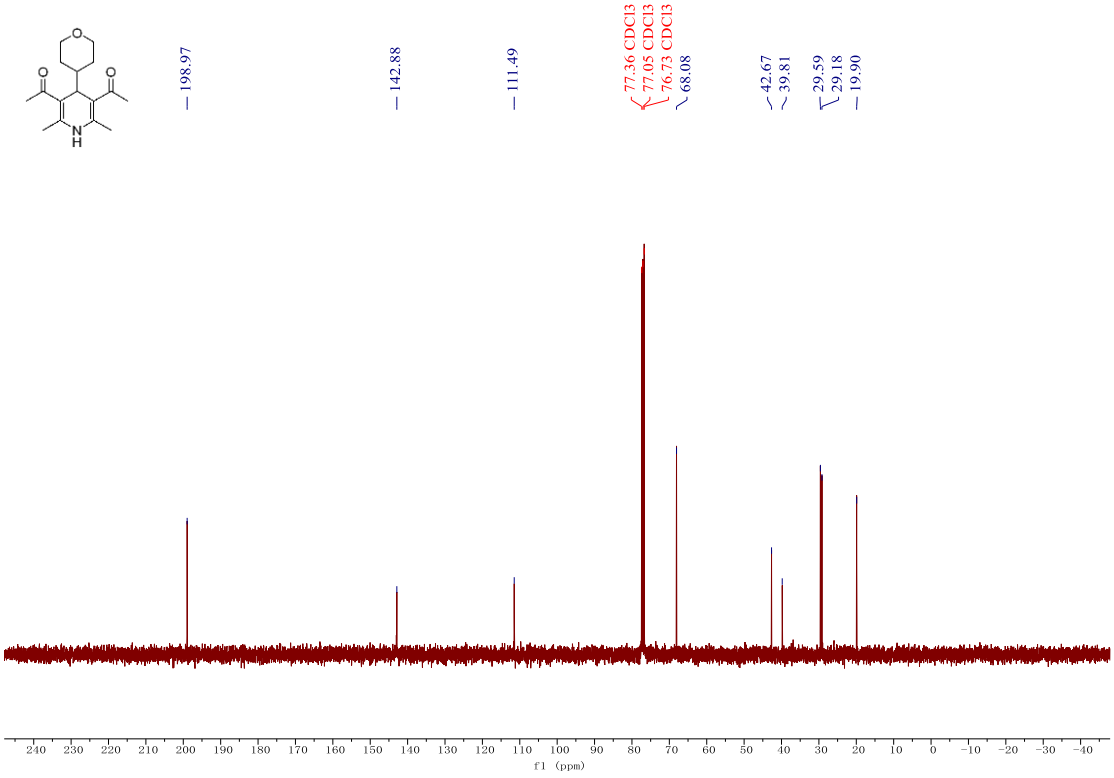


Compound **1j**

^{1}H NMR (400 MHz, $CDCl_3$):

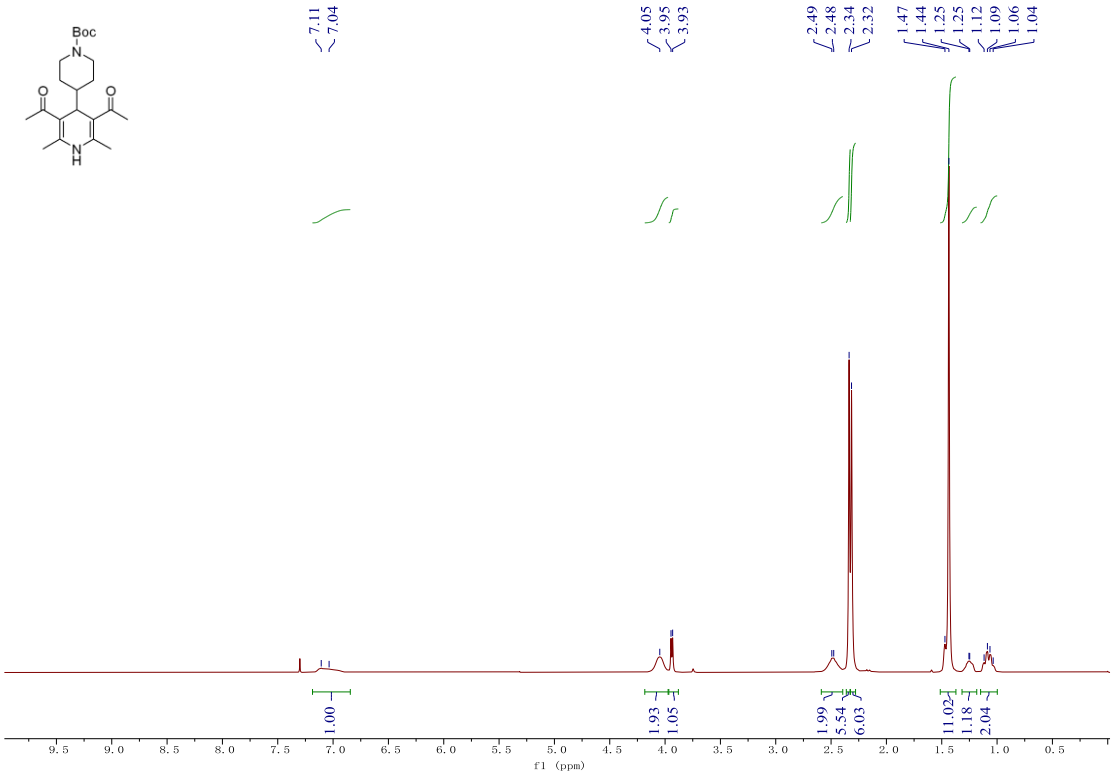


^{13}C NMR (100 MHz, $CDCl_3$):

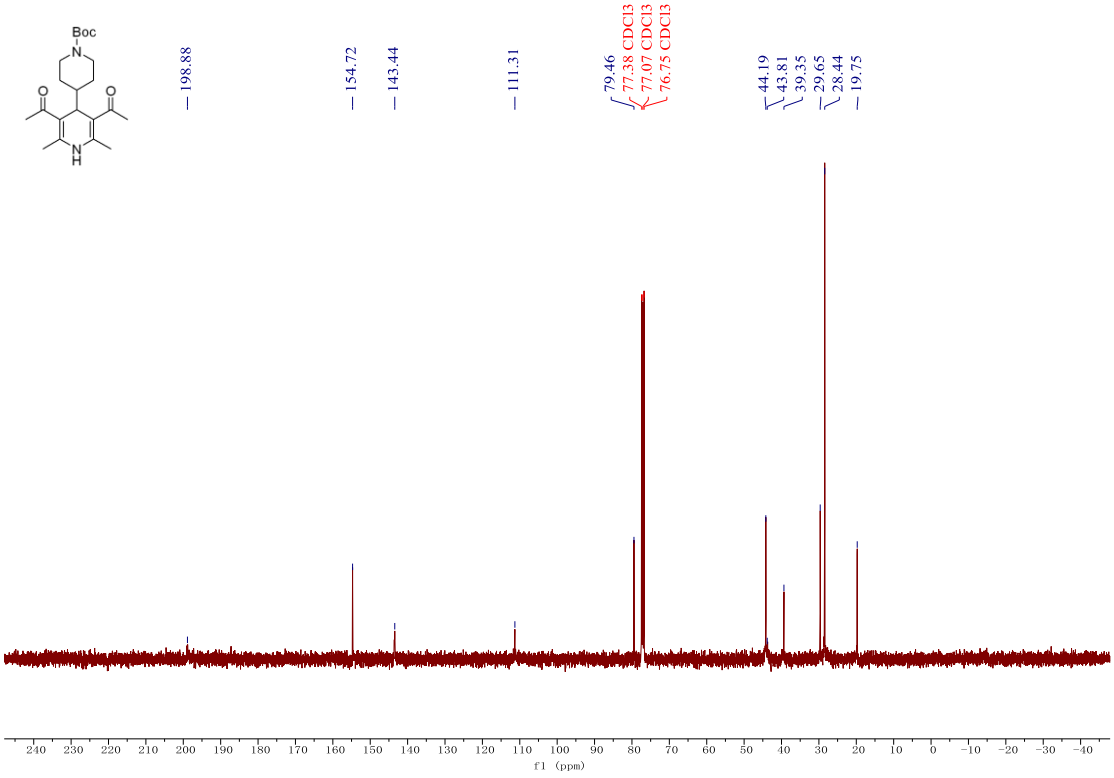


Compound **1k**

^{1}H NMR (400 MHz, $CDCl_3$):

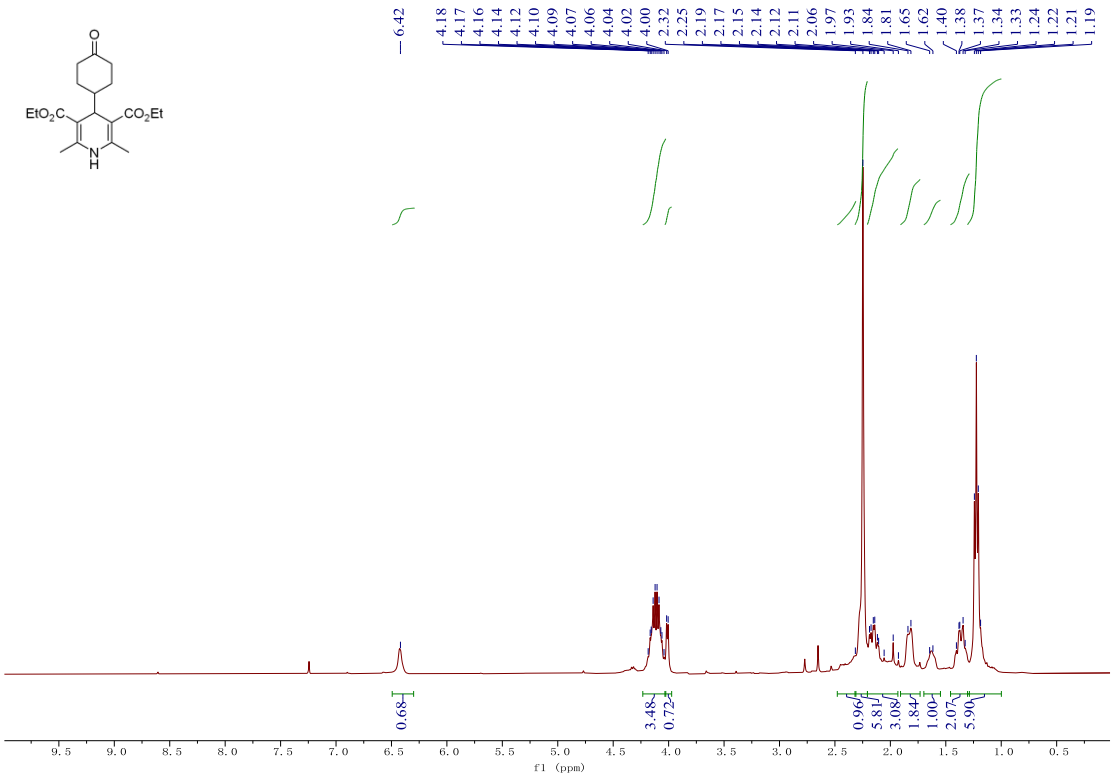


^{13}C NMR (100 MHz, $CDCl_3$):

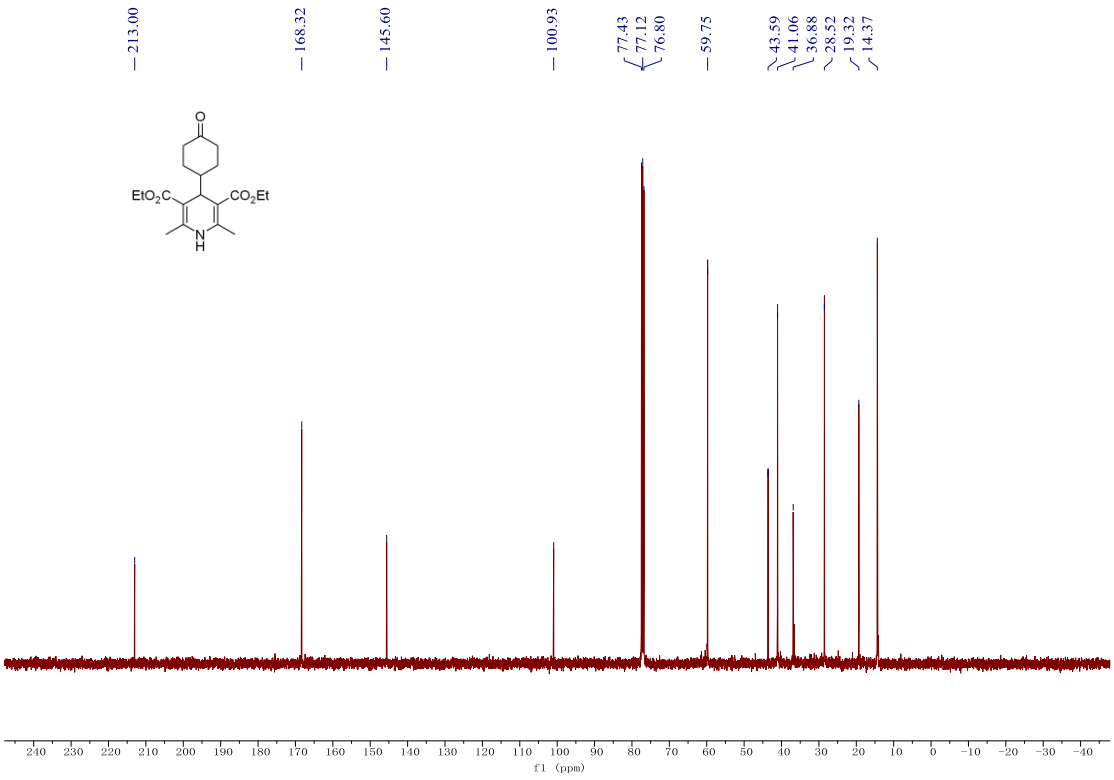


Compound **1l**

^{1}H NMR (400 MHz, $CDCl_3$):

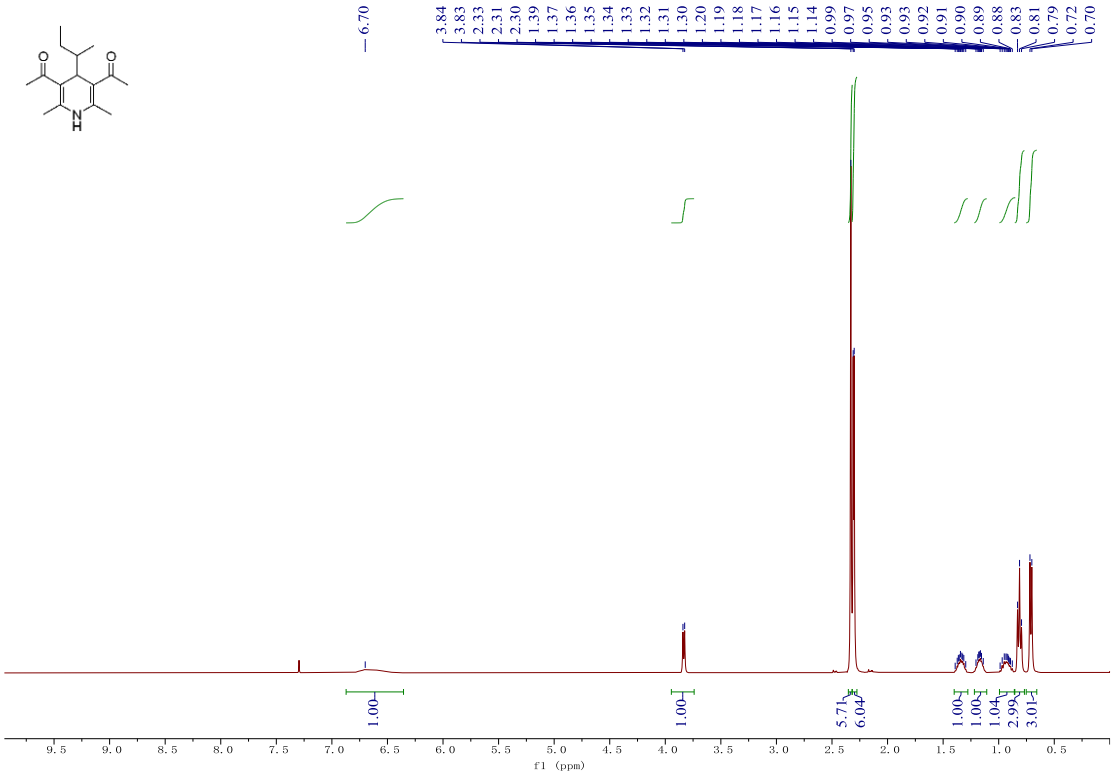


^{13}C NMR (100 MHz, $CDCl_3$):

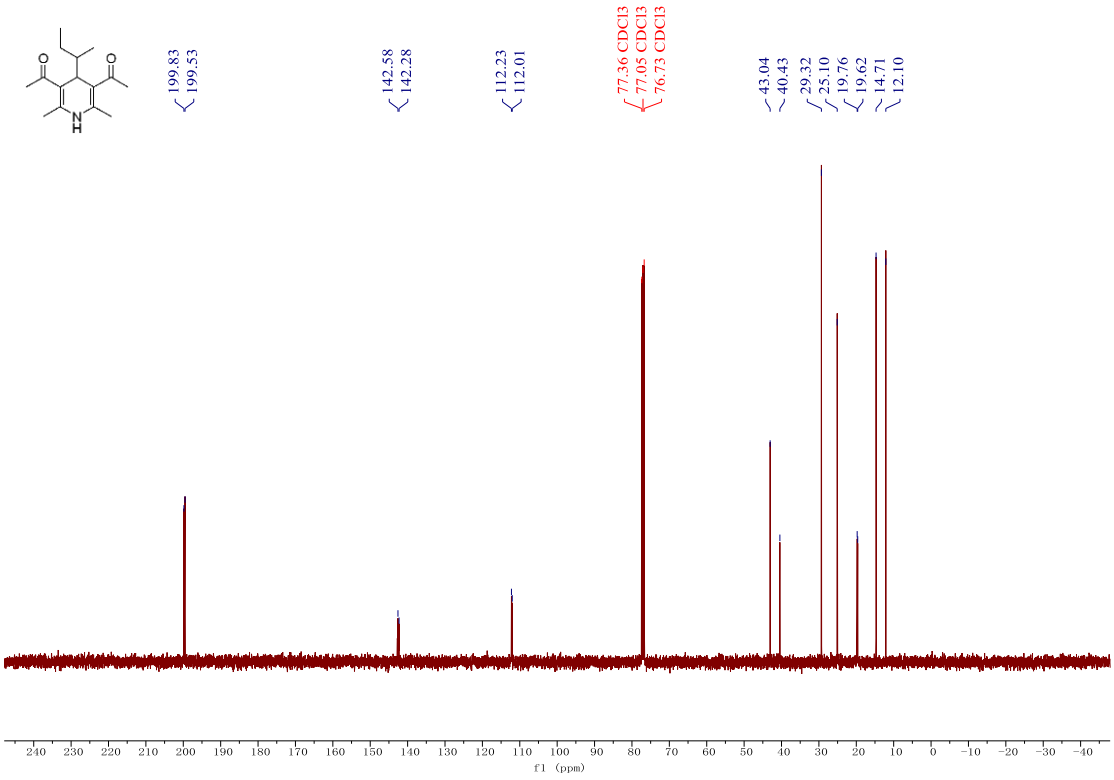


Compound **1m**

^{1}H NMR (400 MHz, $CDCl_3$):

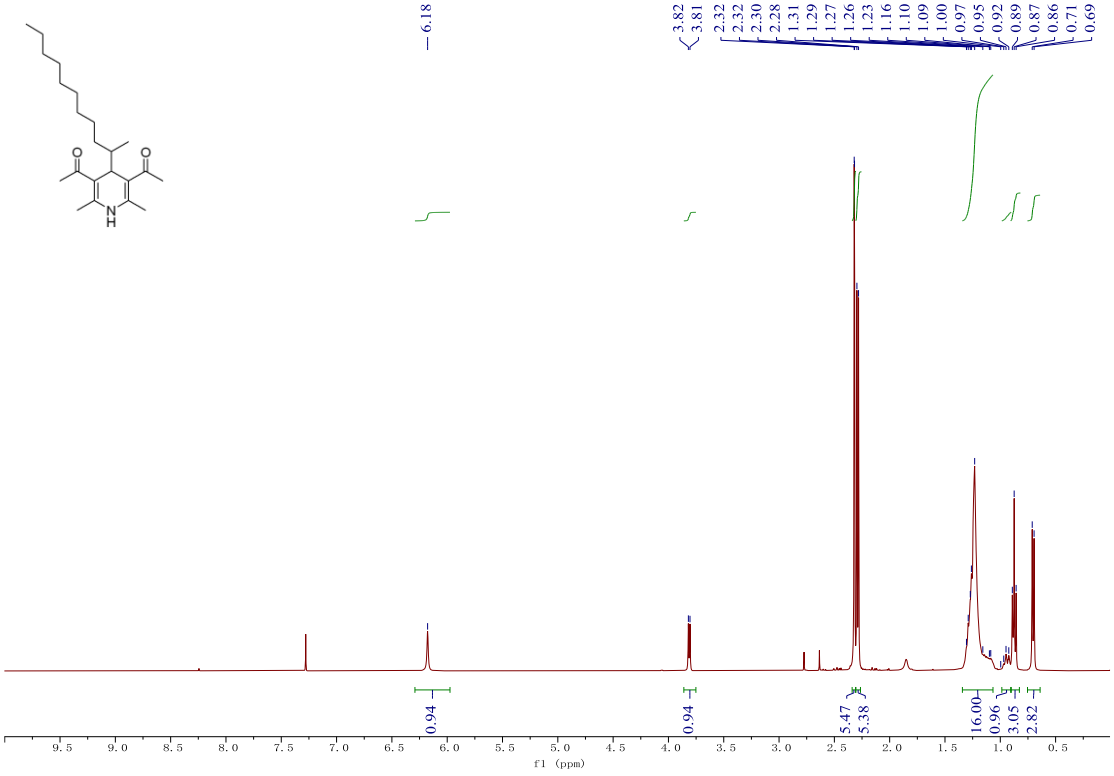


^{13}C NMR (100 MHz, $CDCl_3$):

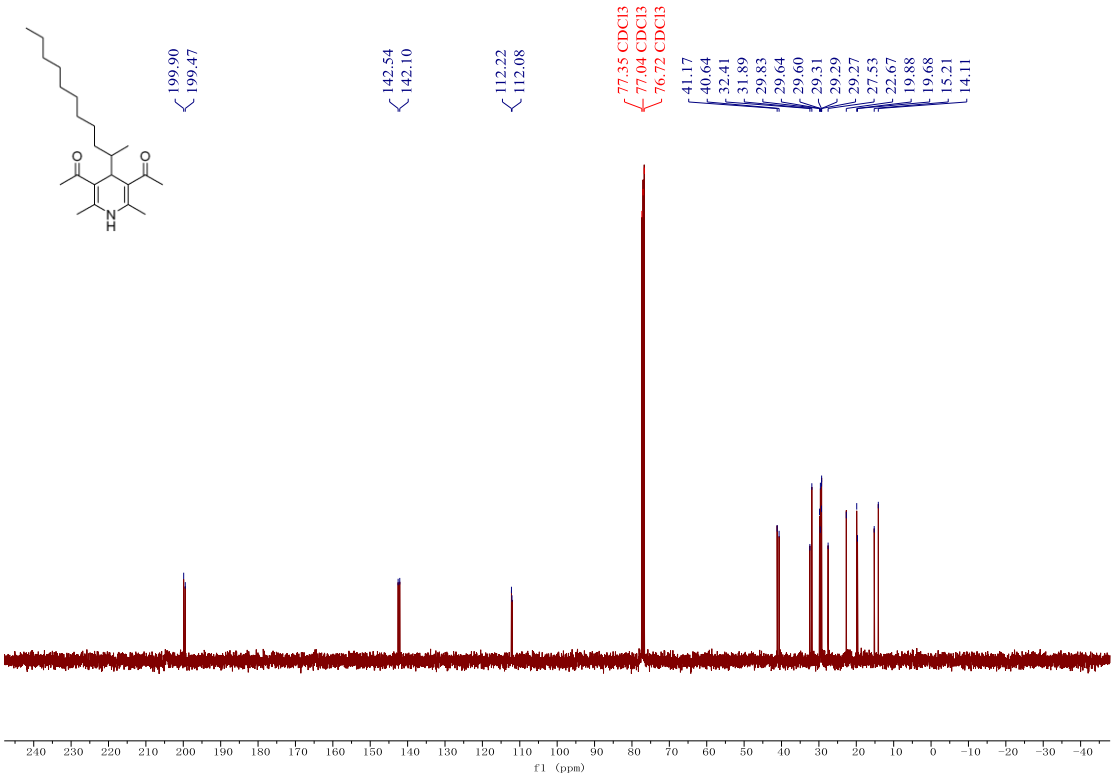


Compound **1n**

^{1}H NMR (400 MHz, $CDCl_3$):

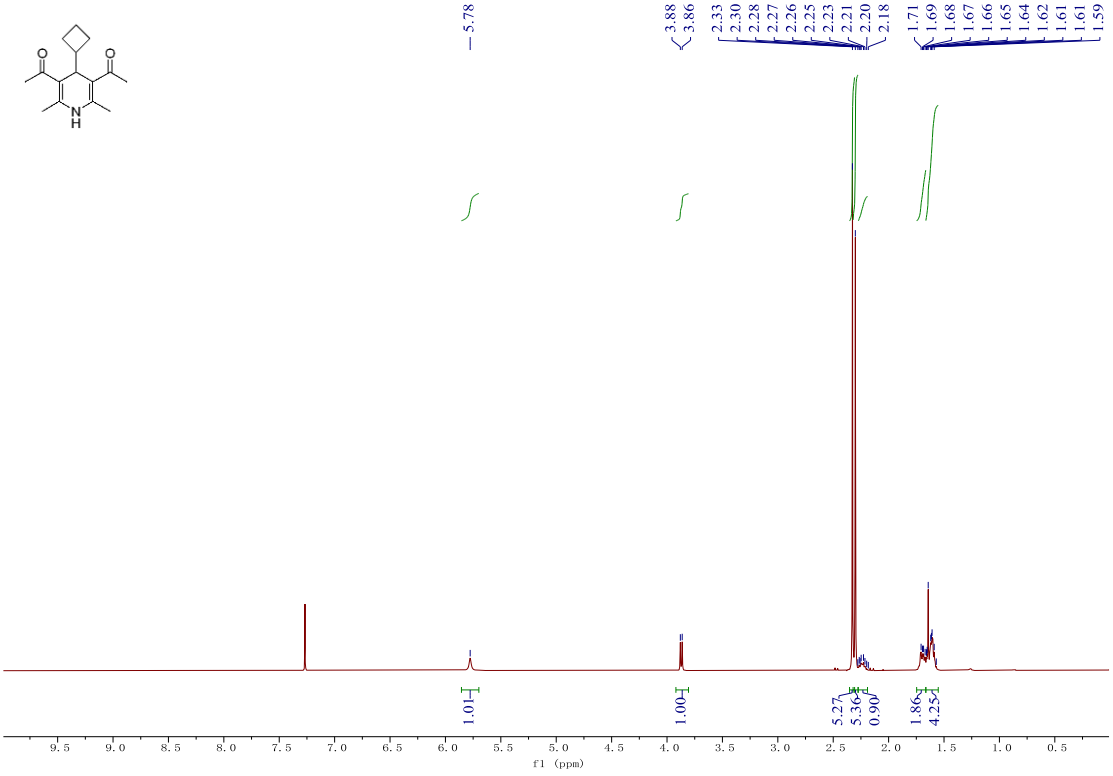


^{13}C NMR (100 MHz, $CDCl_3$):

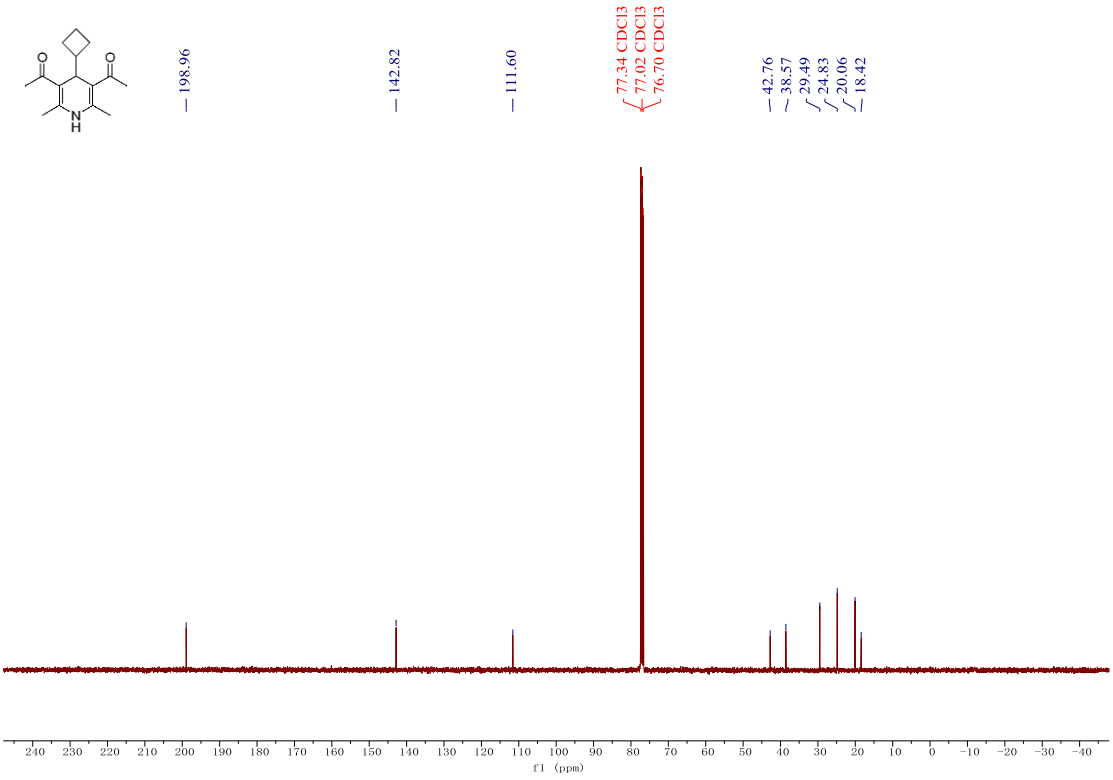


Compound **1o**

^{1}H NMR (400 MHz, $CDCl_3$):

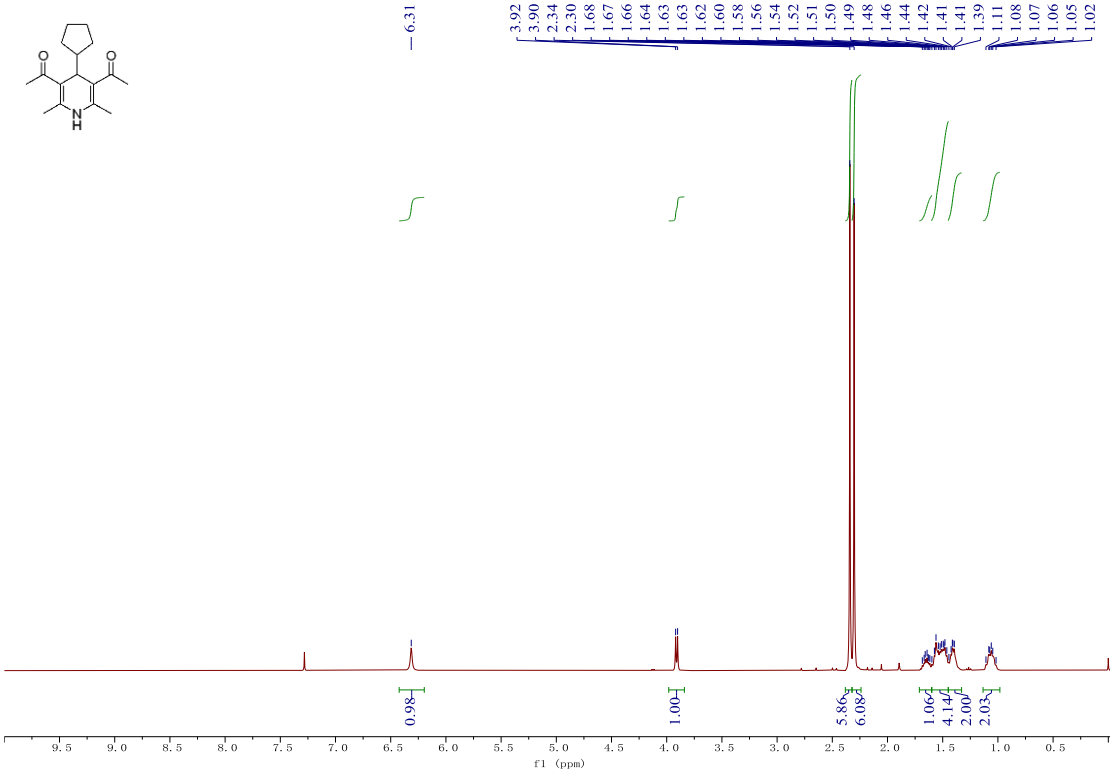


^{13}C NMR (100 MHz, $CDCl_3$):

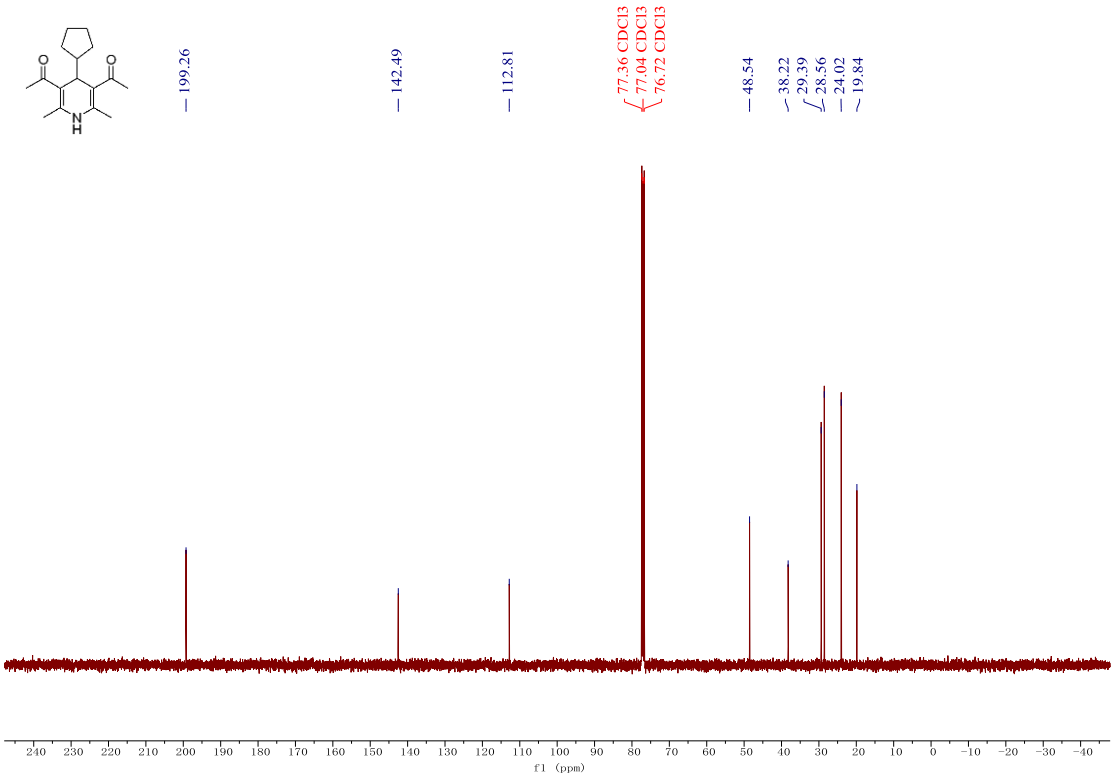


Compound **1p**

^{1}H NMR (400 MHz, $CDCl_3$):

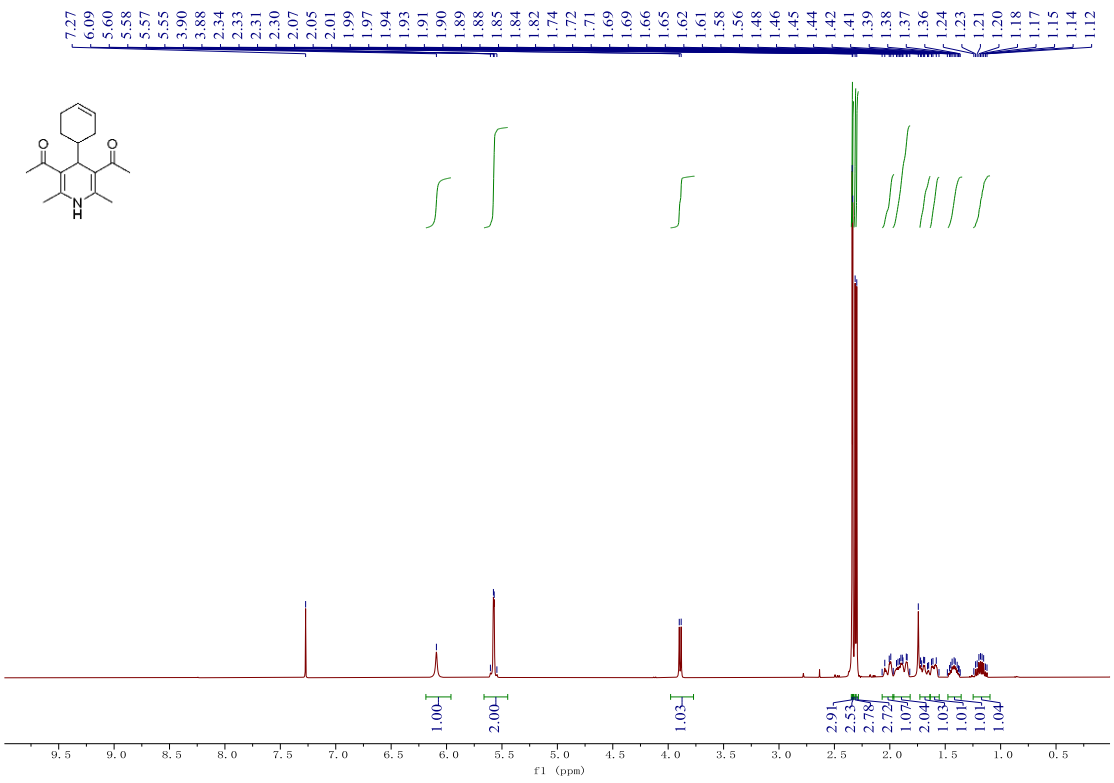


^{13}C NMR (100 MHz, $CDCl_3$):

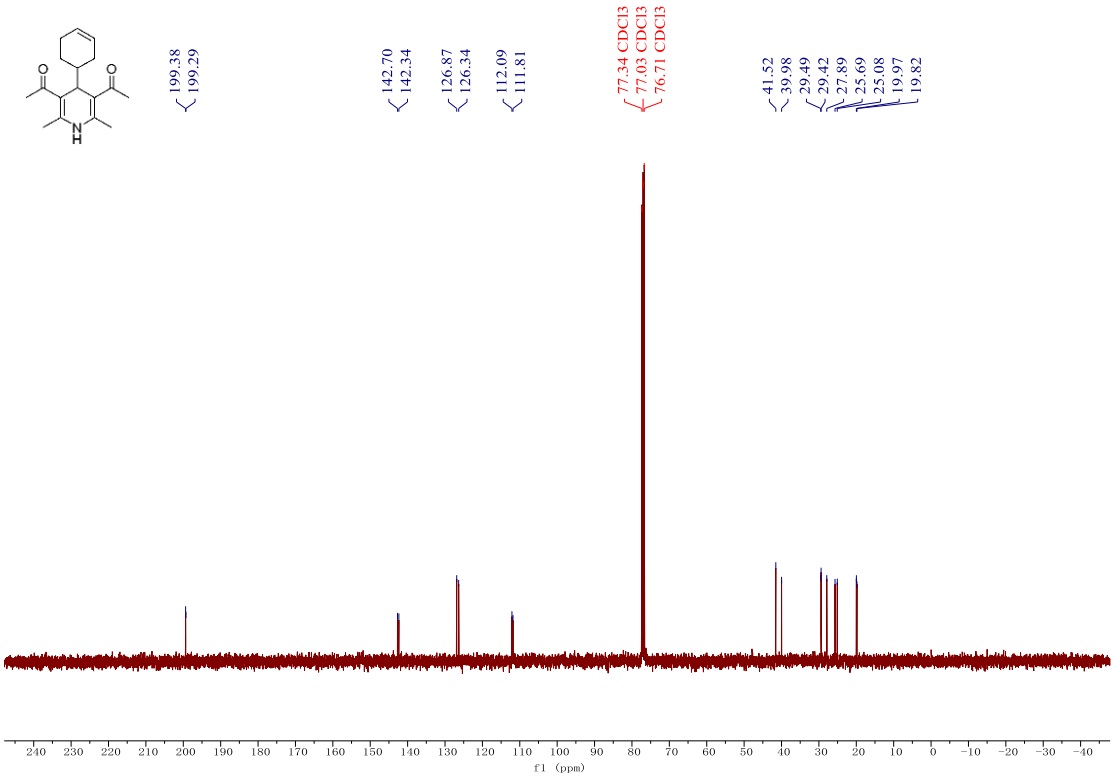


Compound **1q**

^{1}H NMR (400 MHz, $CDCl_3$):

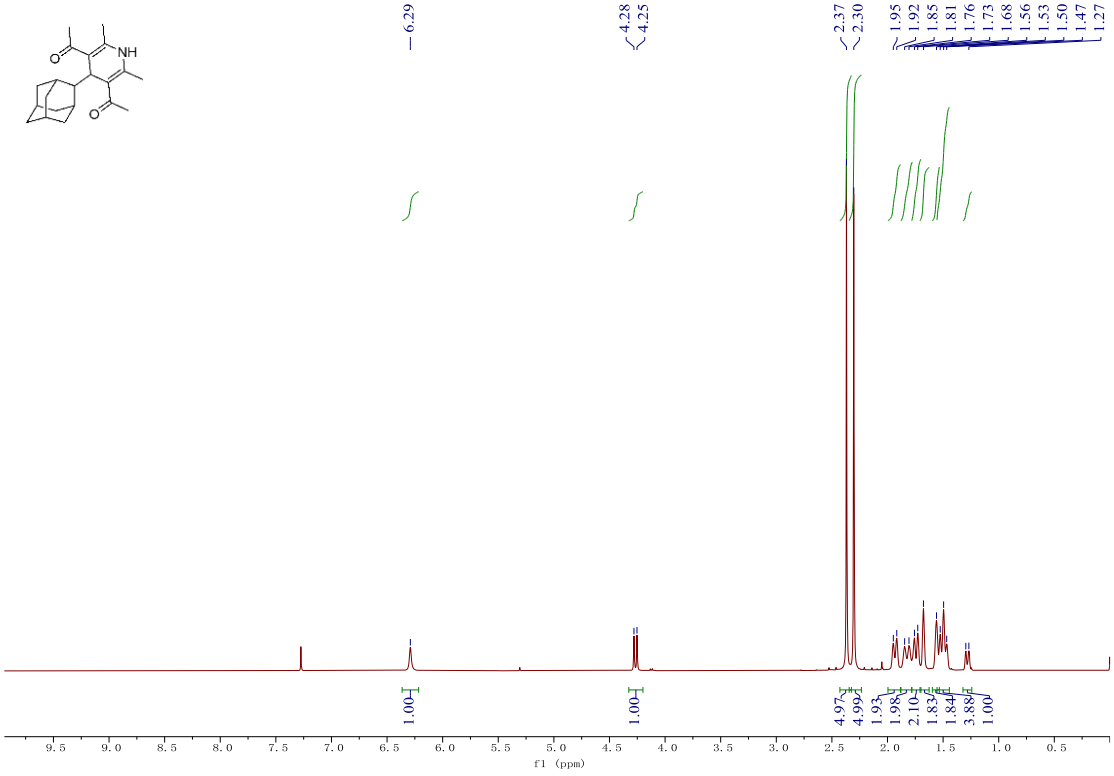


^{13}C NMR (100 MHz, $CDCl_3$):

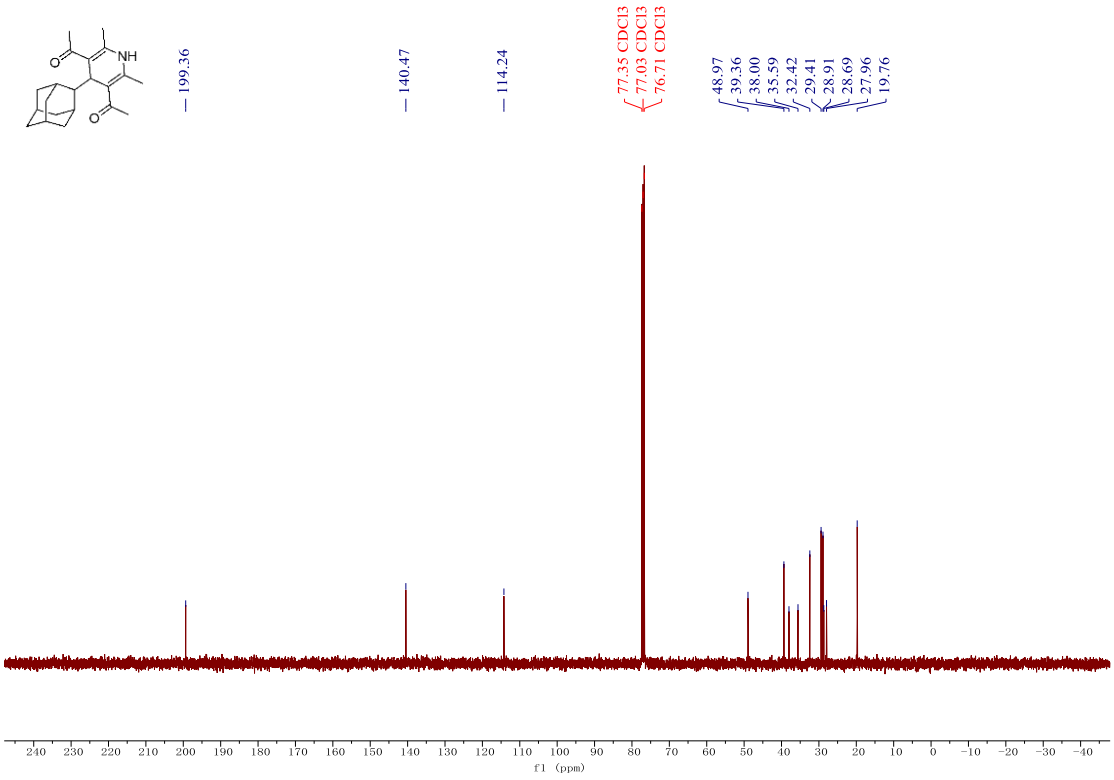


Compound **1r**

^{1}H NMR (400 MHz, $CDCl_3$):

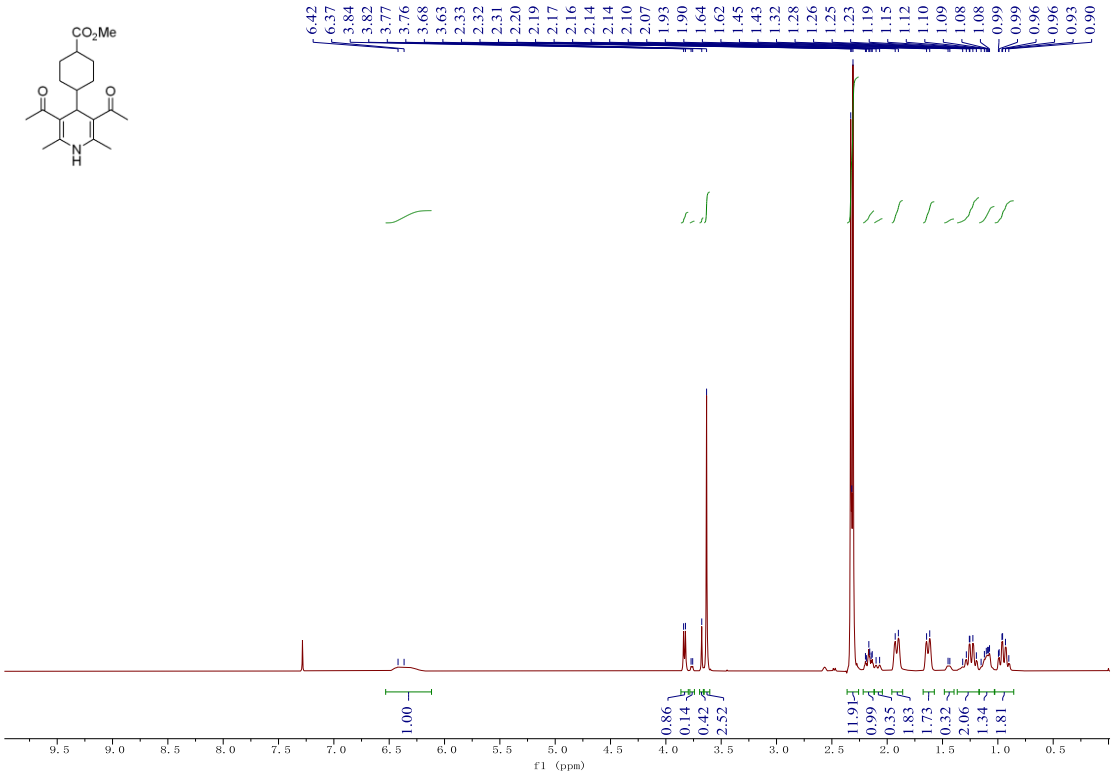


^{13}C NMR (100 MHz, $CDCl_3$):

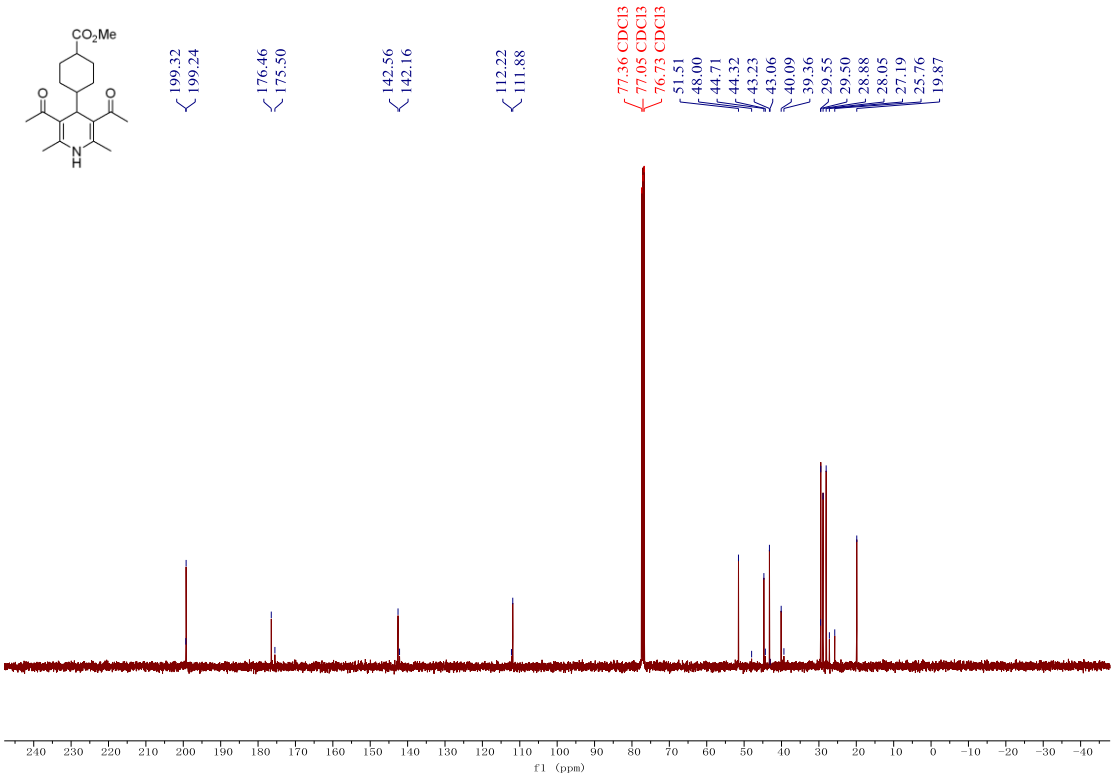


Compound **1s**

^{1}H NMR (400 MHz, $CDCl_3$):

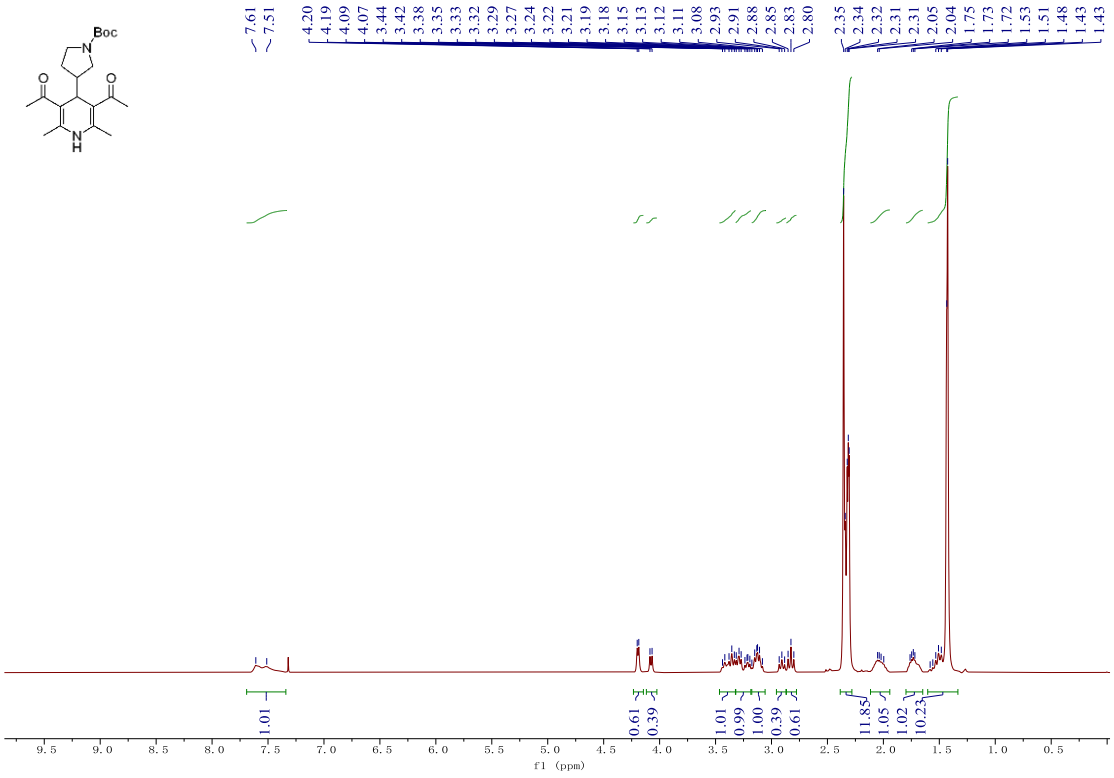


^{13}C NMR (100 MHz, $CDCl_3$):

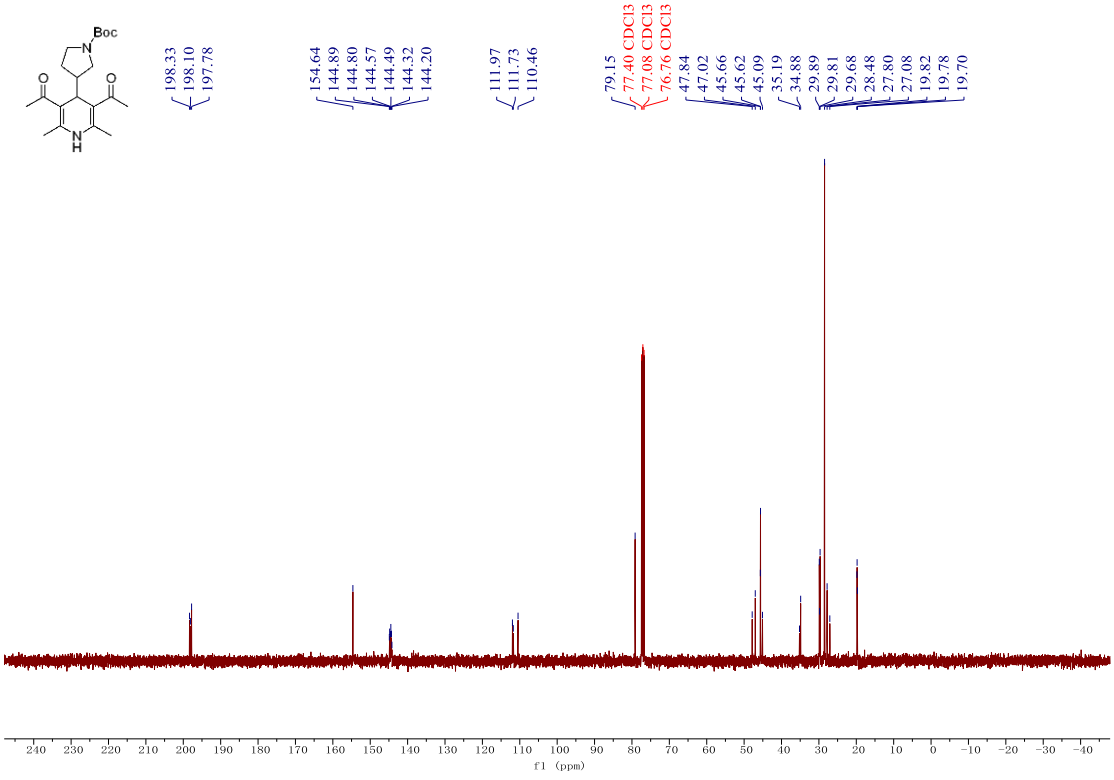


Compound **1t**

^{1}H NMR (400 MHz, $CDCl_3$):

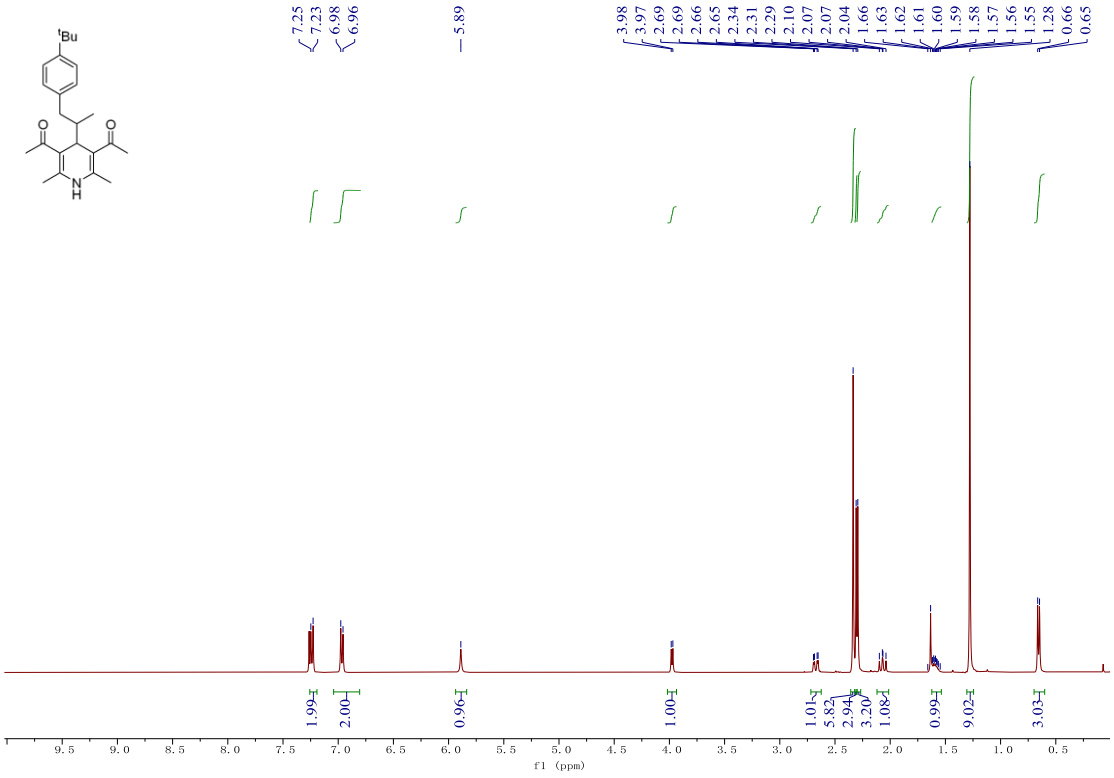


^{13}C NMR (100 MHz, $CDCl_3$):

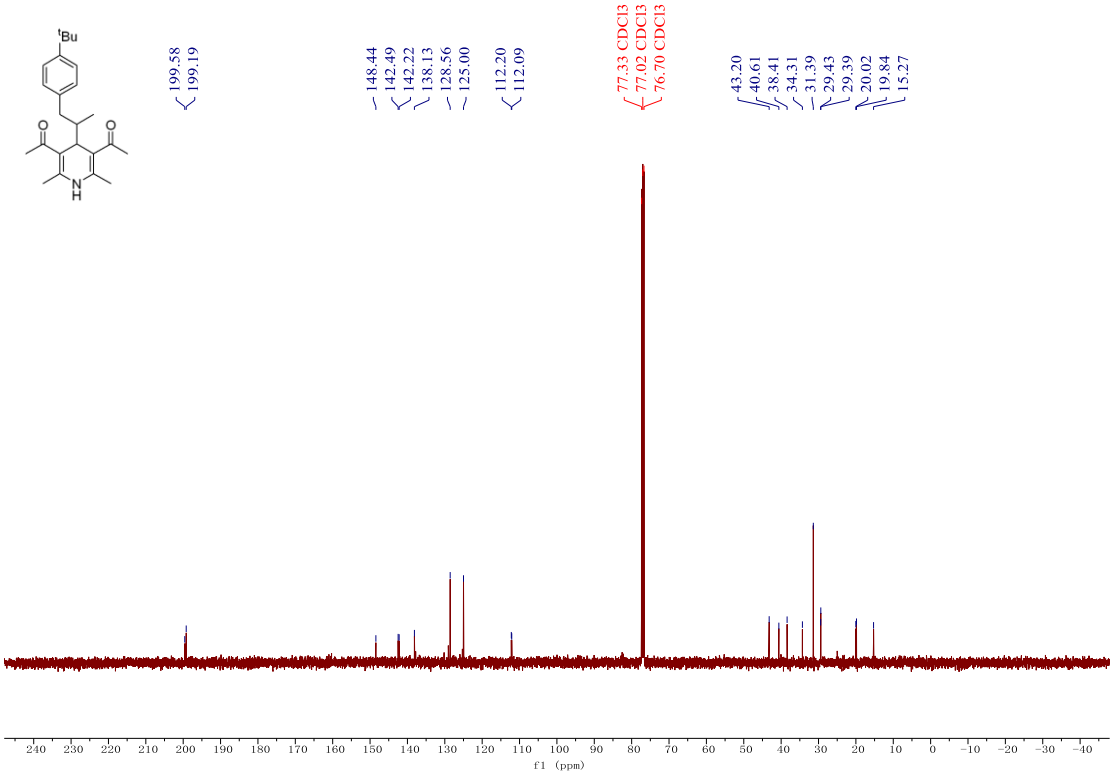


Compound **1u**

^{1}H NMR (400 MHz, $CDCl_3$):

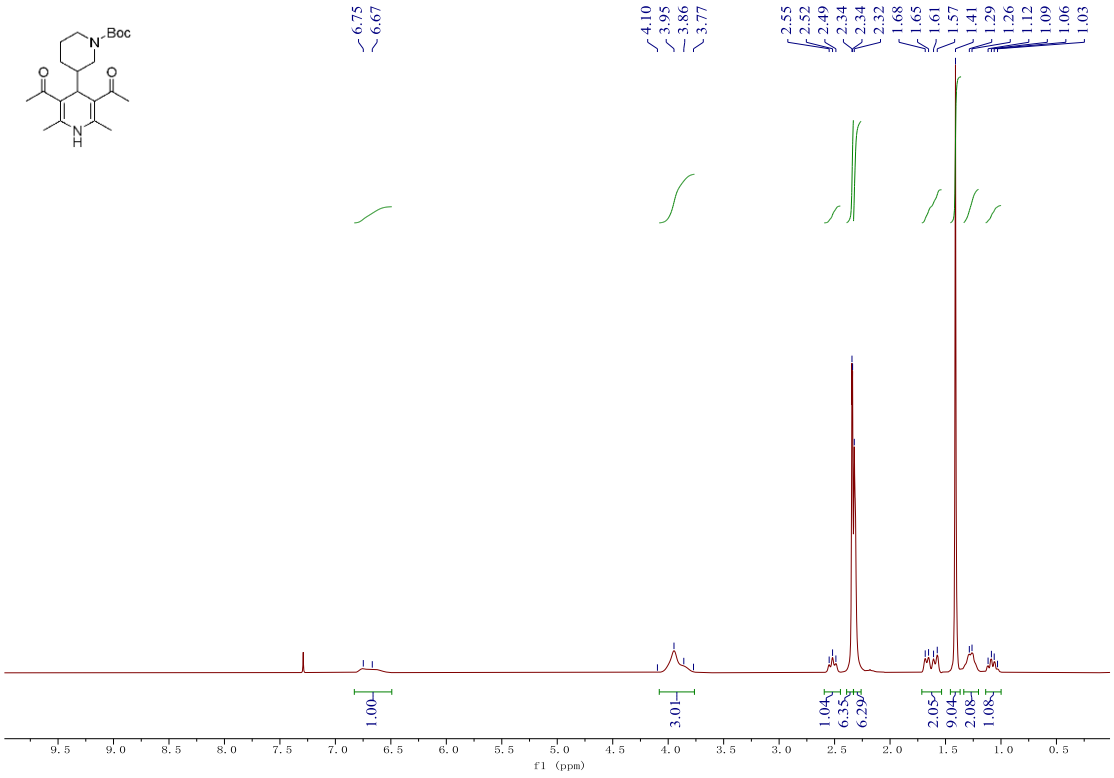


^{13}C NMR (100 MHz, $CDCl_3$):

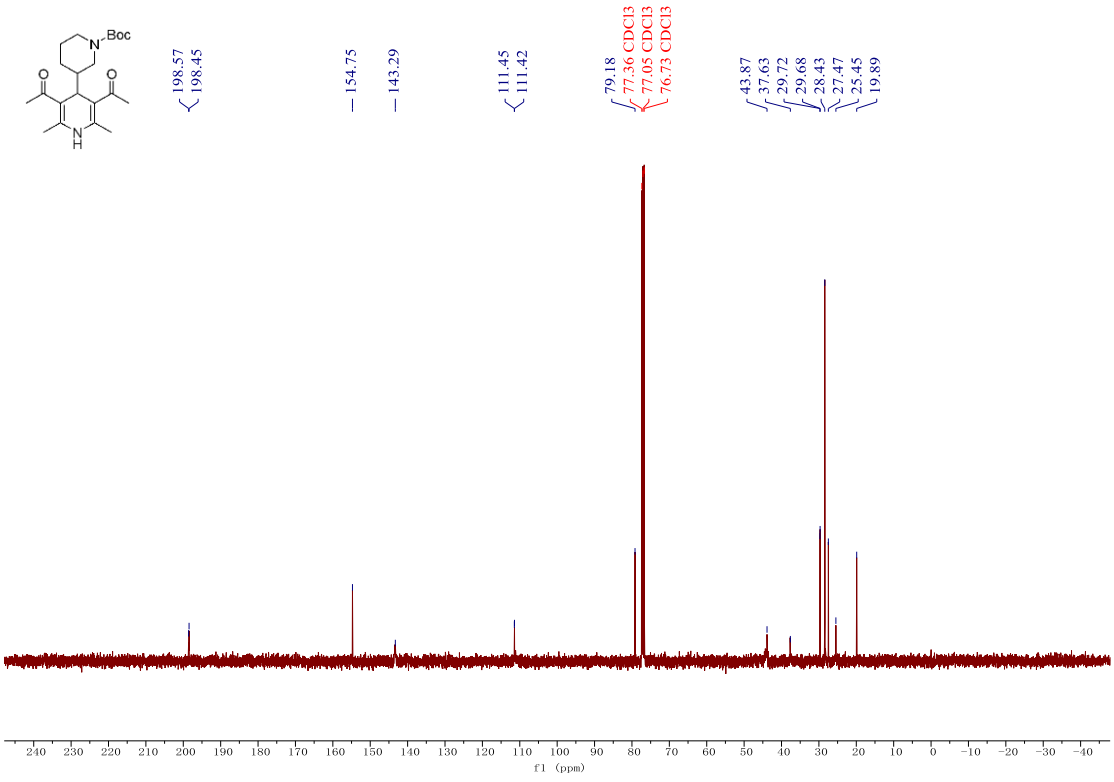


Compound **1v**

^{1}H NMR (400 MHz, $CDCl_3$):

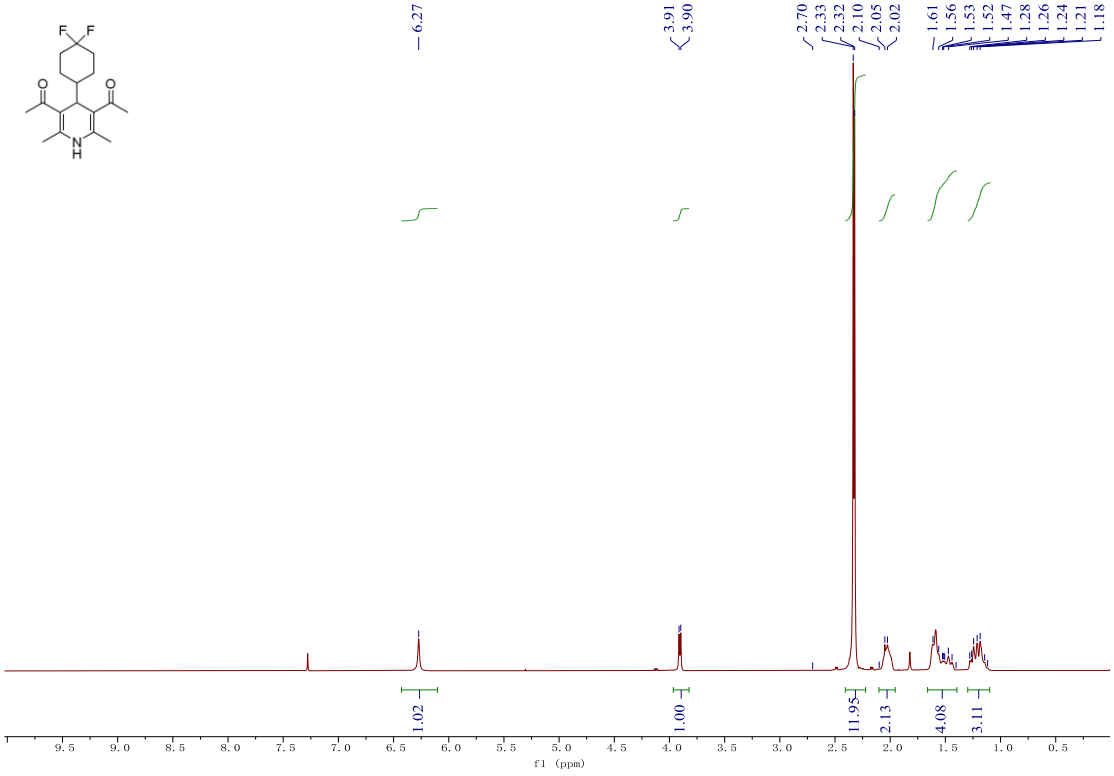


^{13}C NMR (100 MHz, $CDCl_3$):

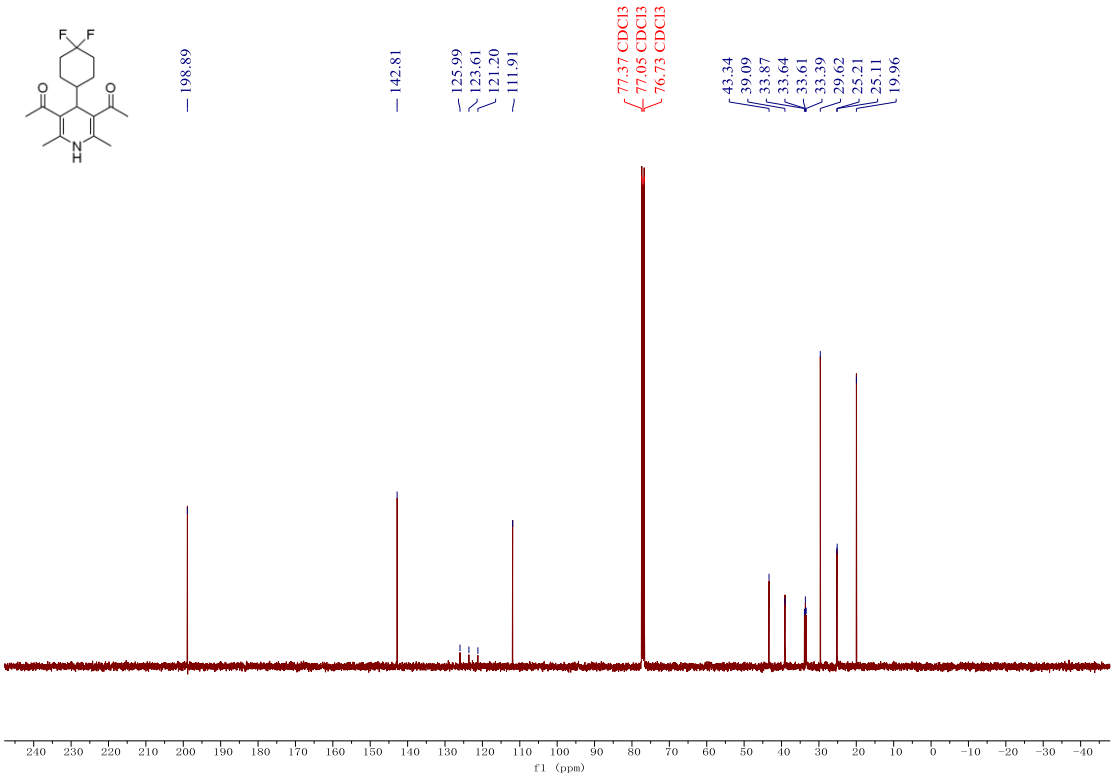


Compound **1w**

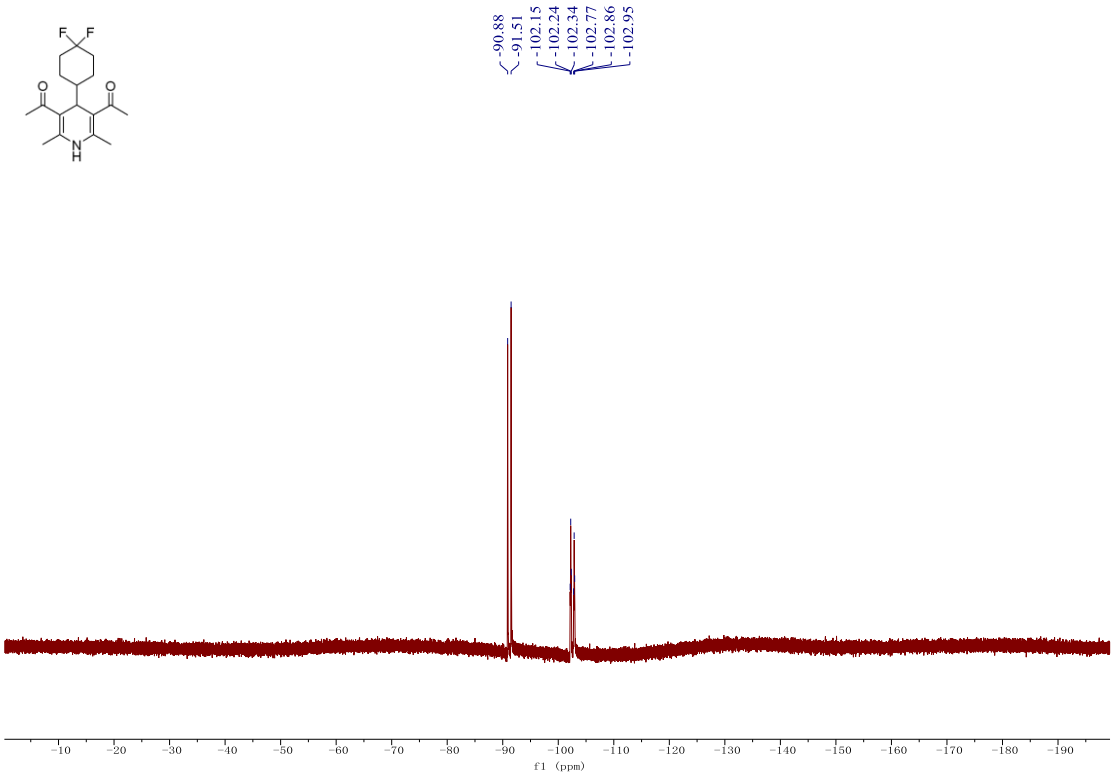
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

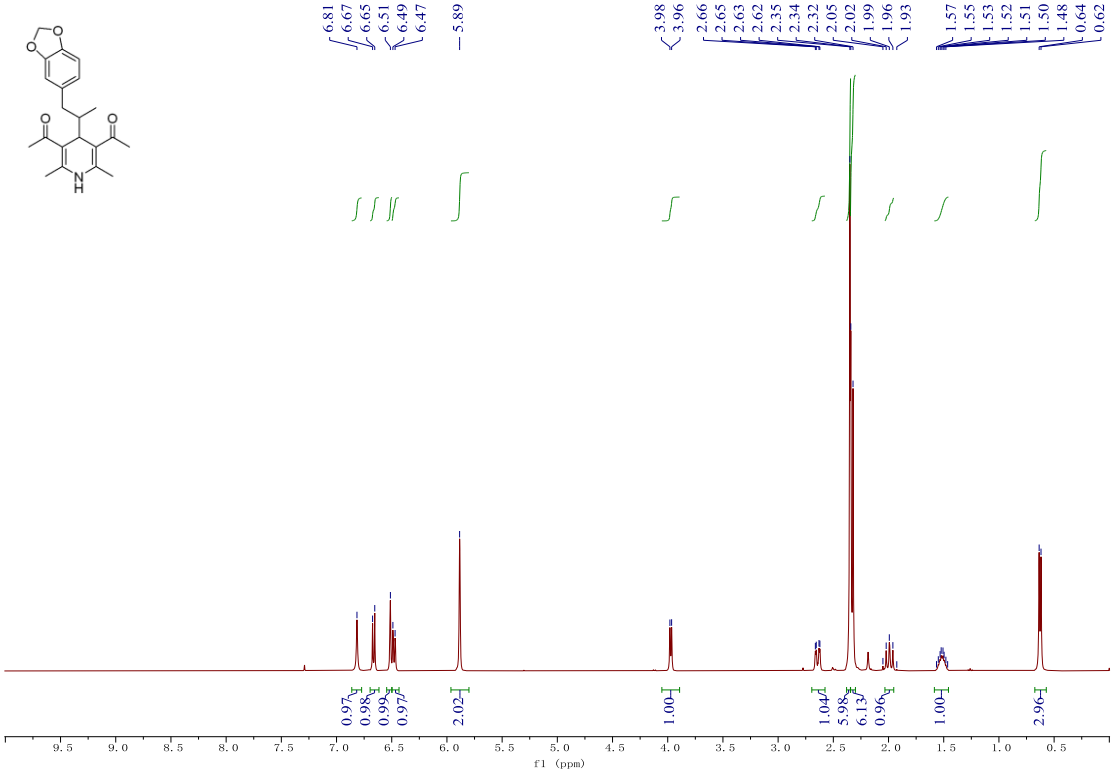


^{19}F NMR (376 MHz, $CDCl_3$):

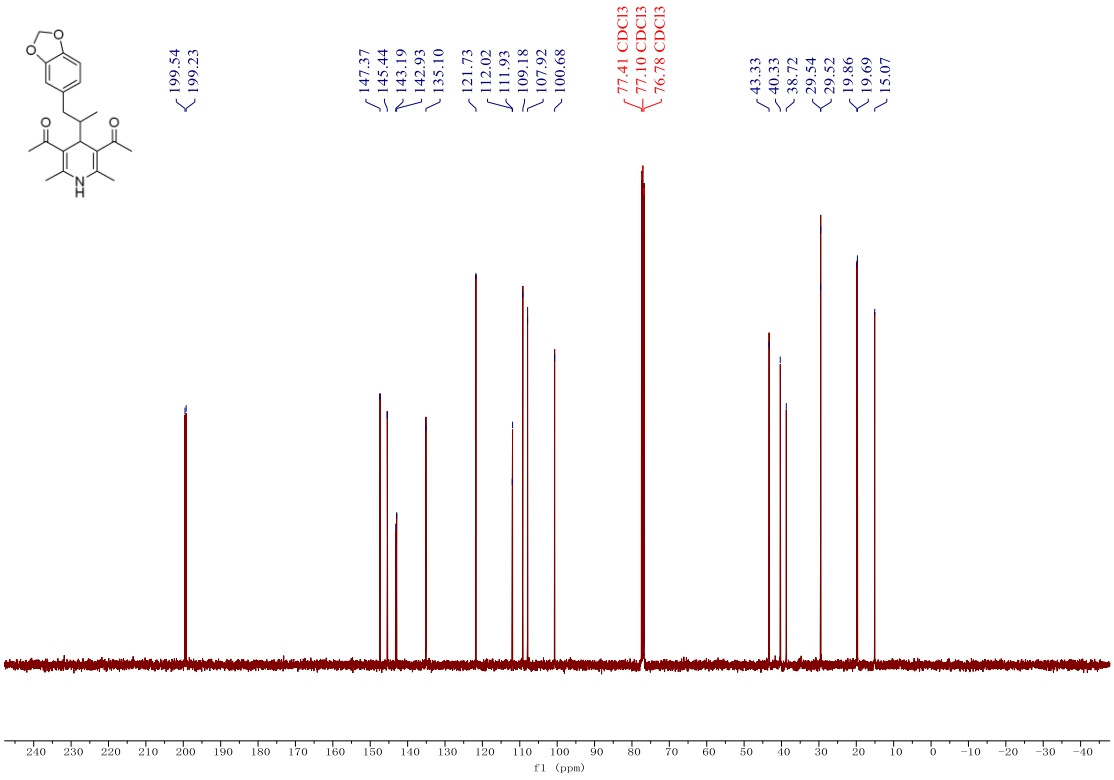


Compound **1-5**

^{1}H NMR (400 MHz, $CDCl_3$):

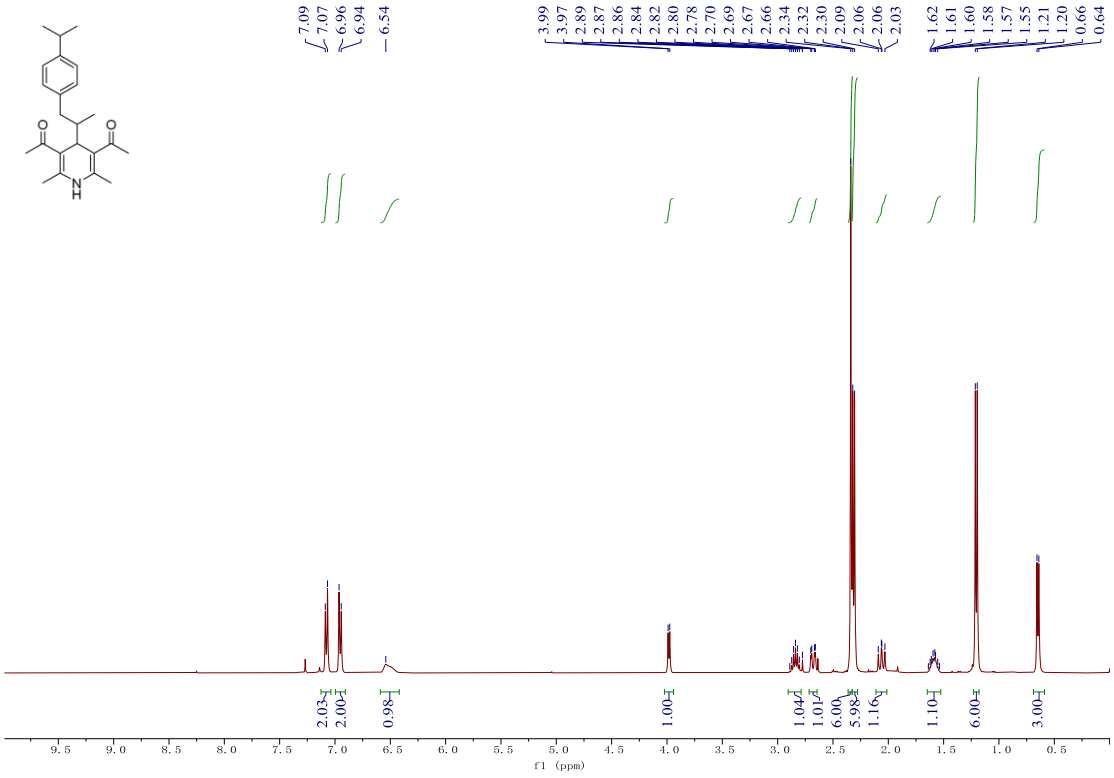


^{13}C NMR (100 MHz, $CDCl_3$):

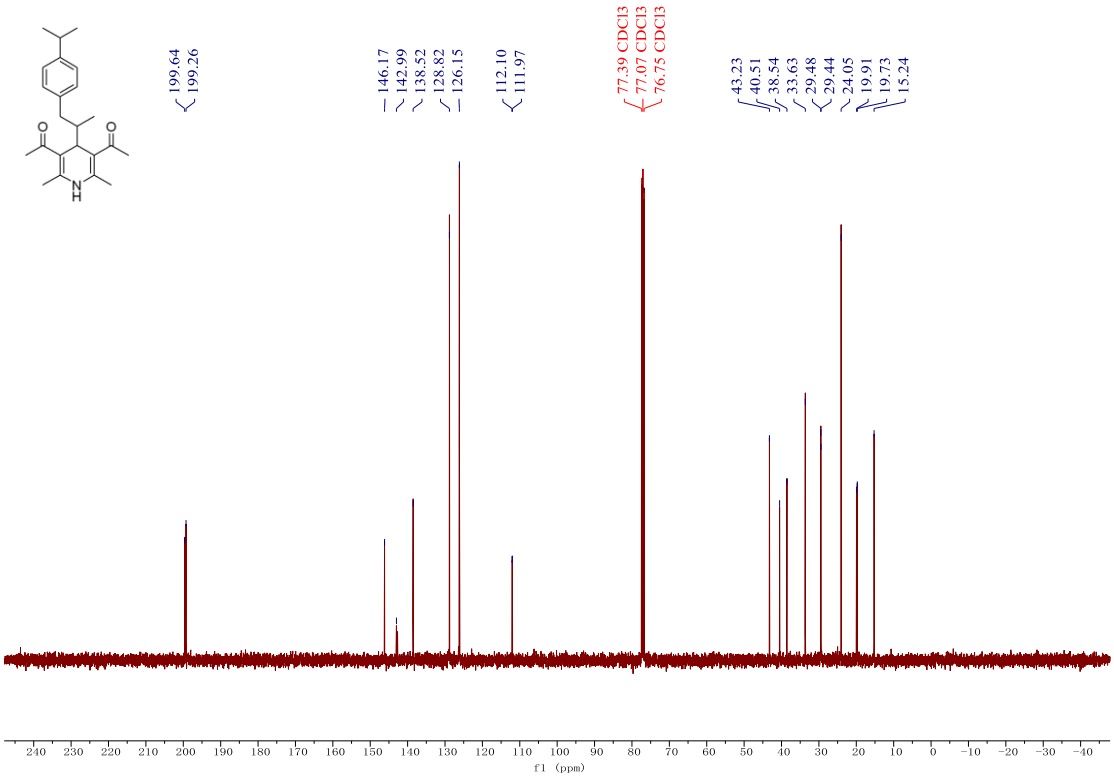


Compound **1-6**

^{1}H NMR (400 MHz, $CDCl_3$):

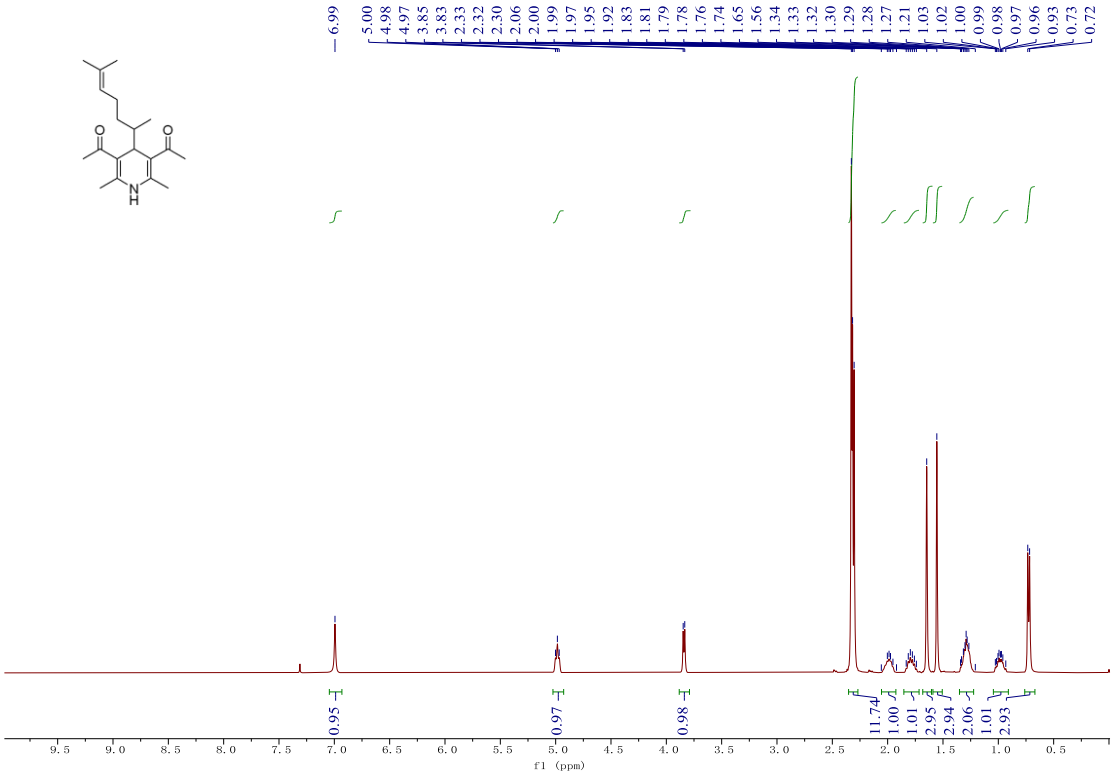


^{13}C NMR (100 MHz, $CDCl_3$):

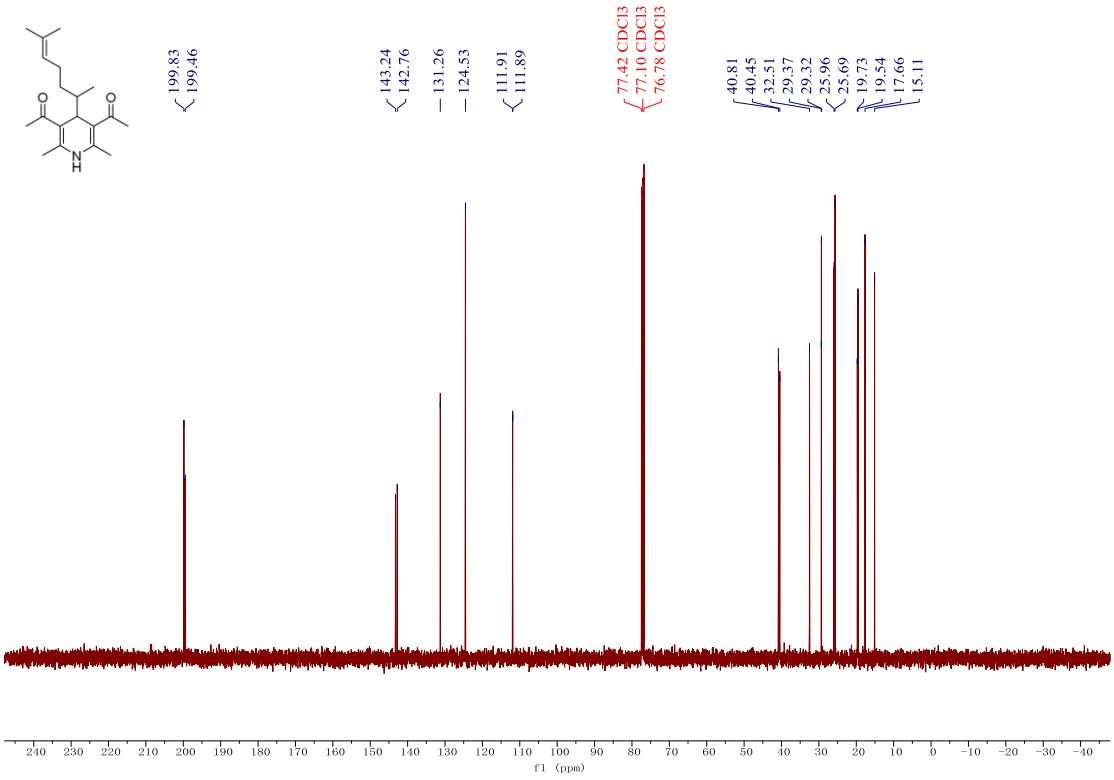


Compound **1-7**

^{1}H NMR (400 MHz, $CDCl_3$):

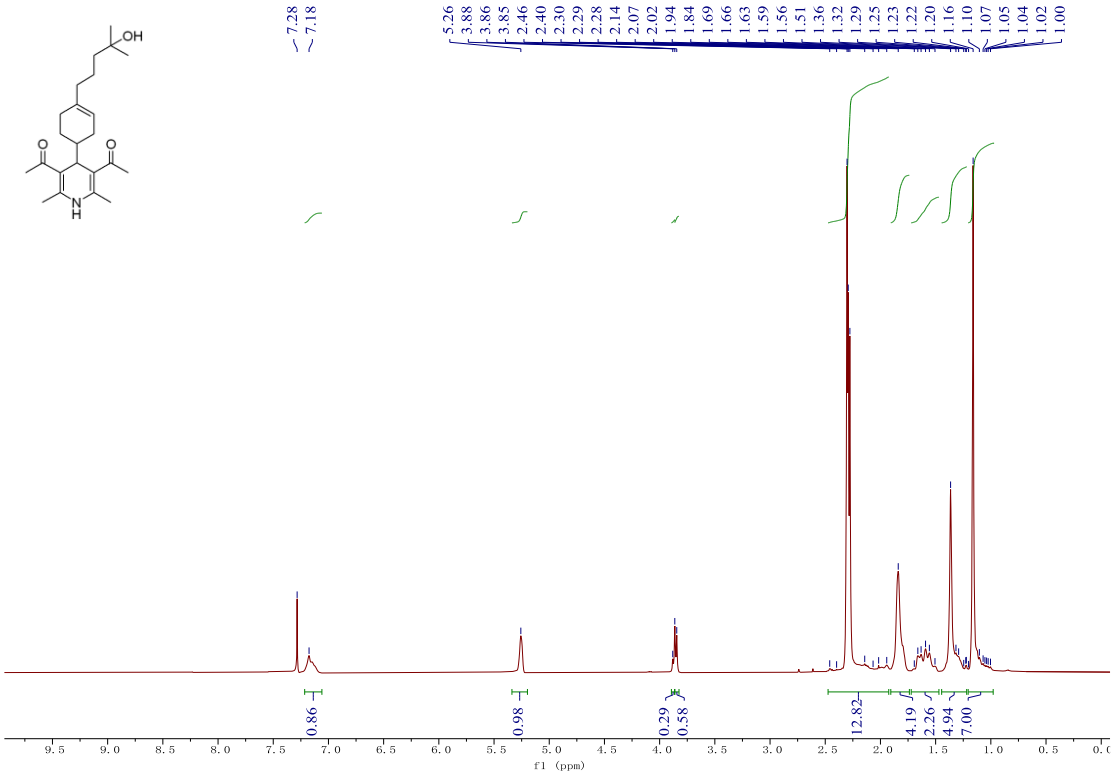


^{13}C NMR (100 MHz, $CDCl_3$):

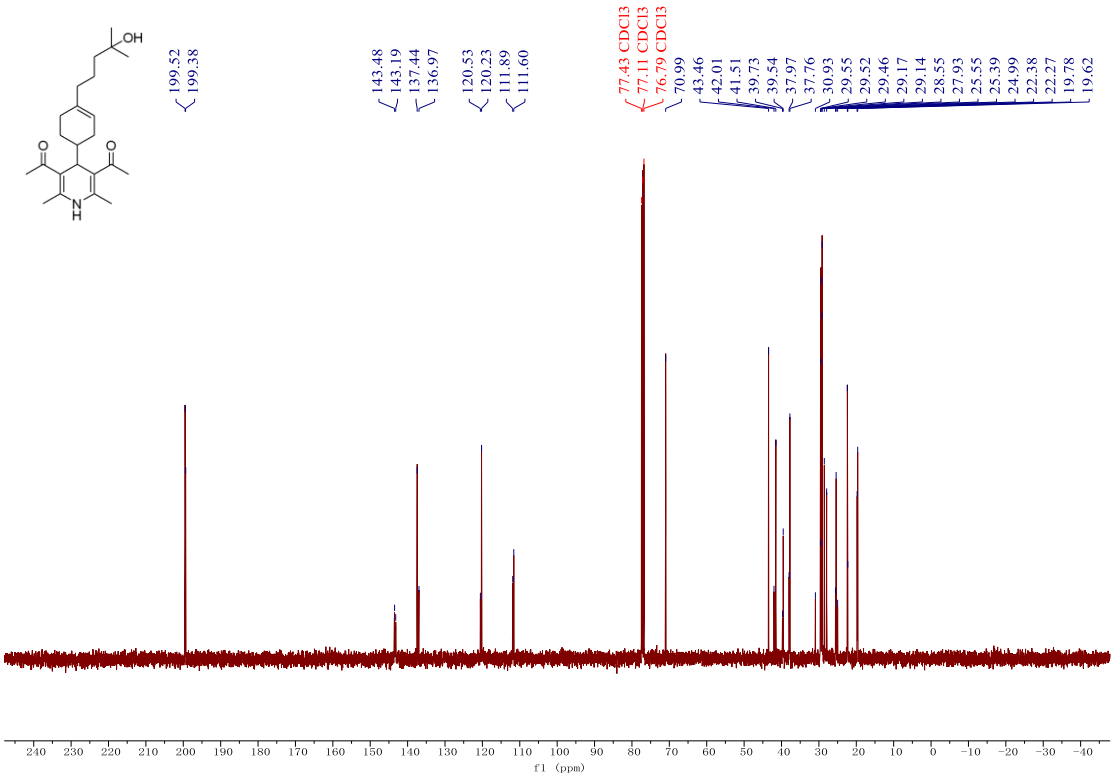


Compound **1-8**

^{1}H NMR (400 MHz, $CDCl_3$):

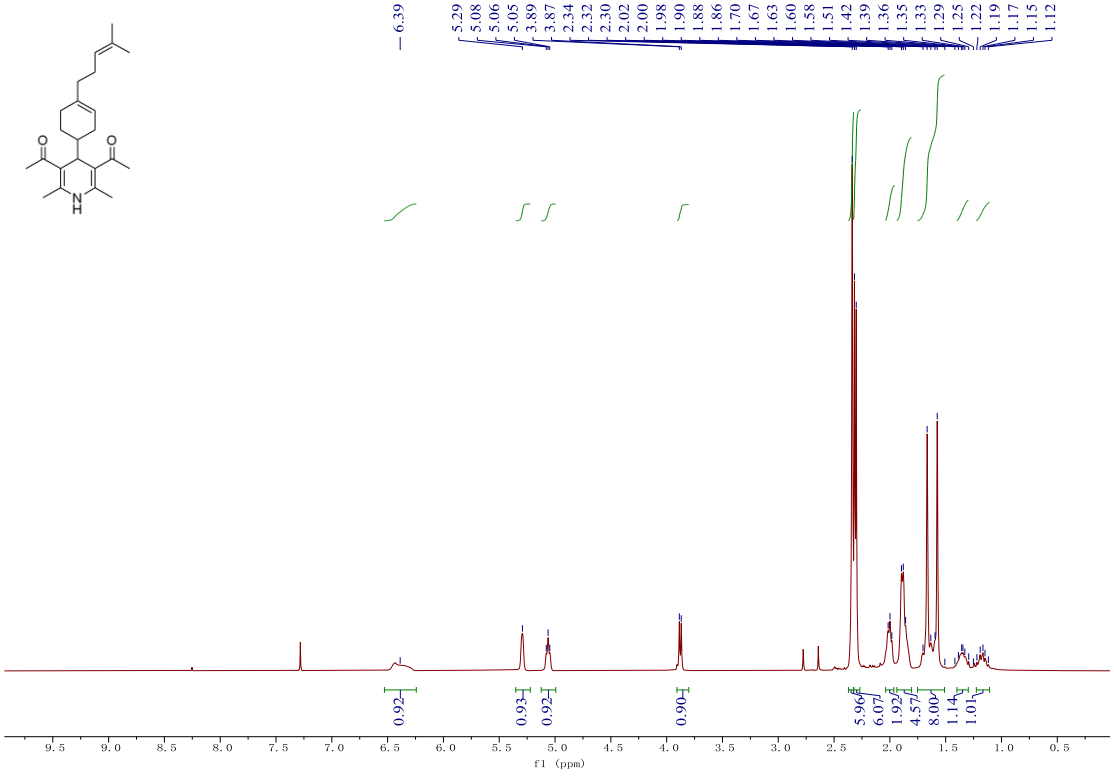


^{13}C NMR (100 MHz, $CDCl_3$):

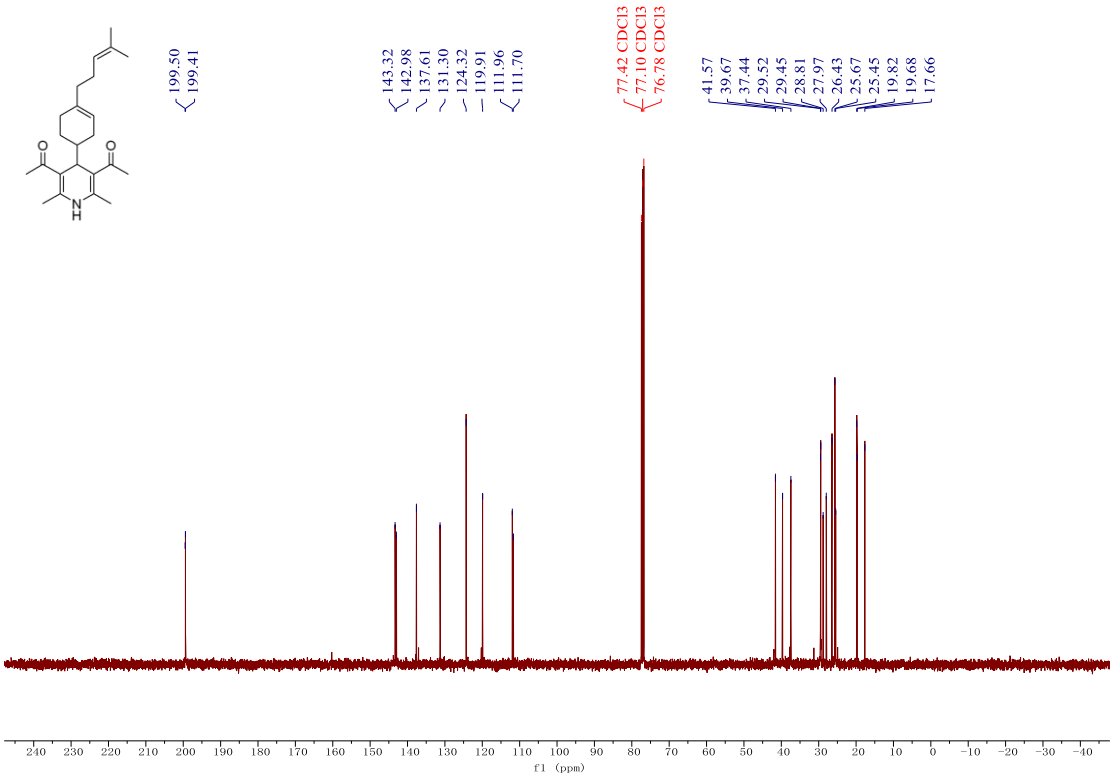


Compound **1-9**

^{1}H NMR (400 MHz, $CDCl_3$):

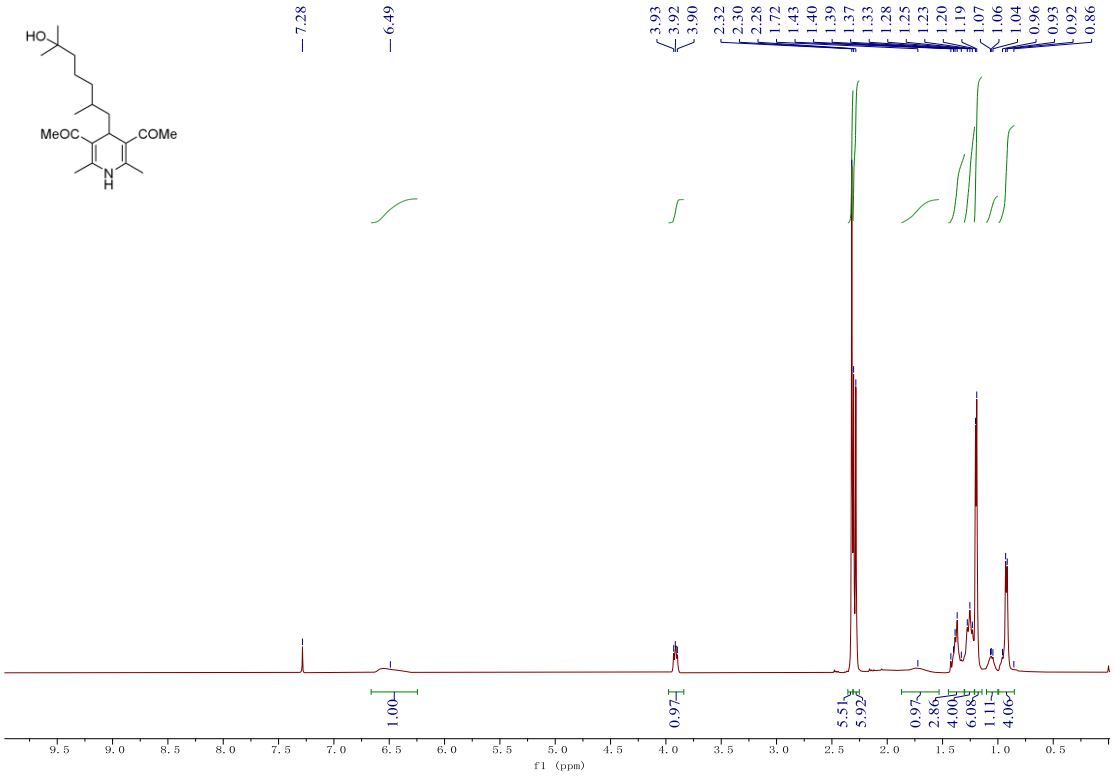


^{13}C NMR (100 MHz, $CDCl_3$):

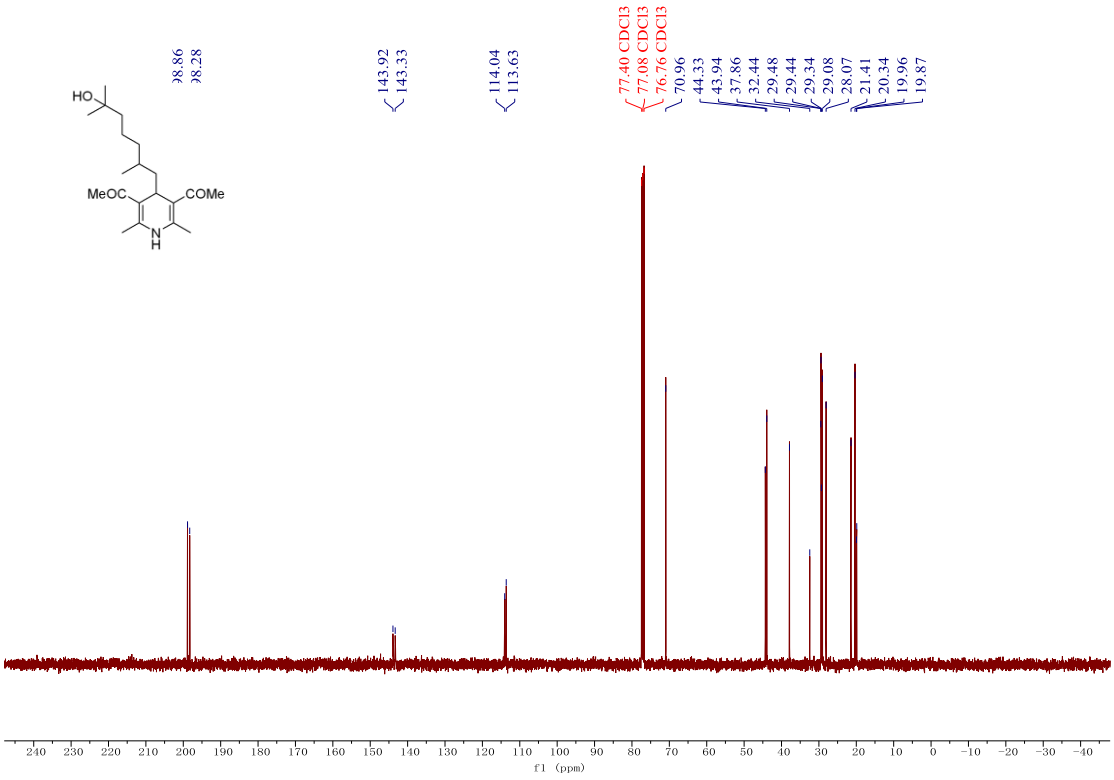


Compound **1-10**

^{1}H NMR (400 MHz, $CDCl_3$):

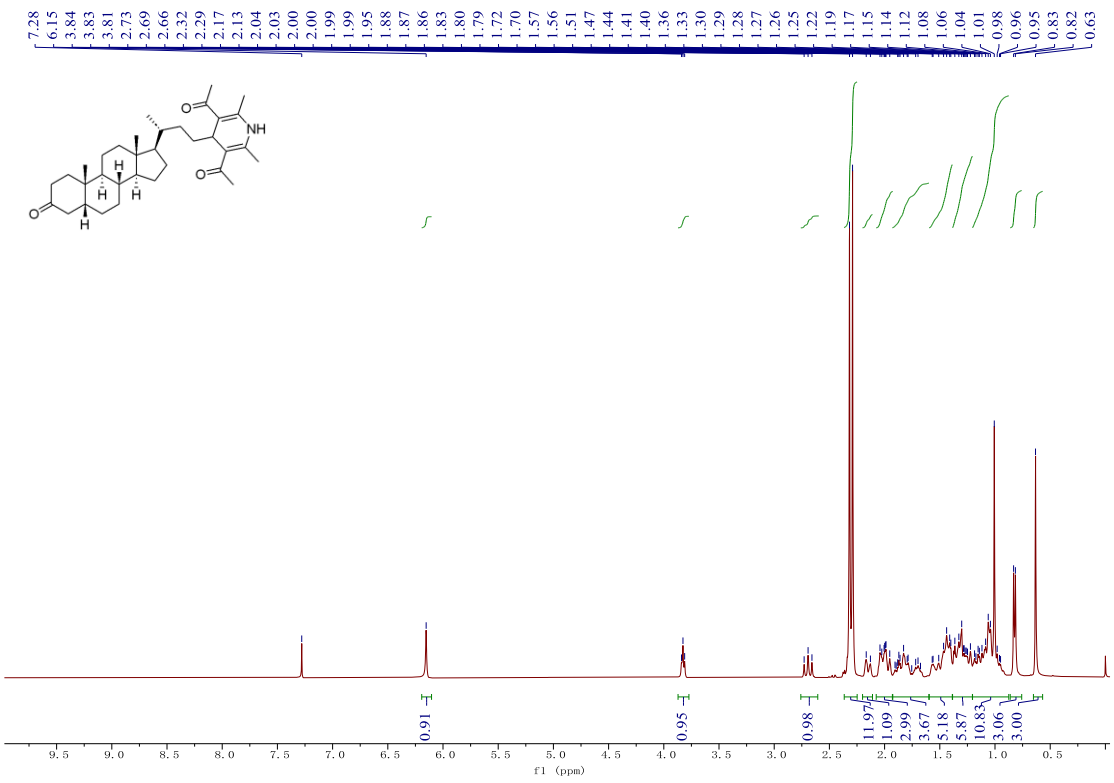


^{13}C NMR (100 MHz, $CDCl_3$):

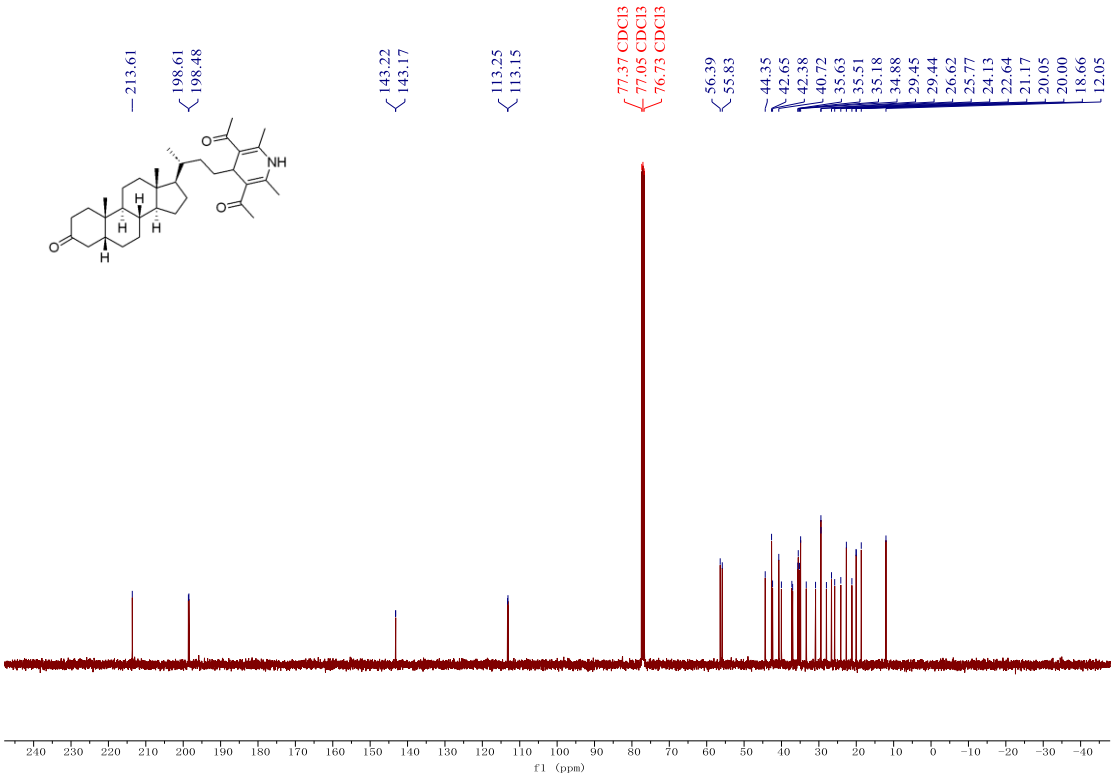


Compound **1-11**

^{1}H NMR (400 MHz, $CDCl_3$):

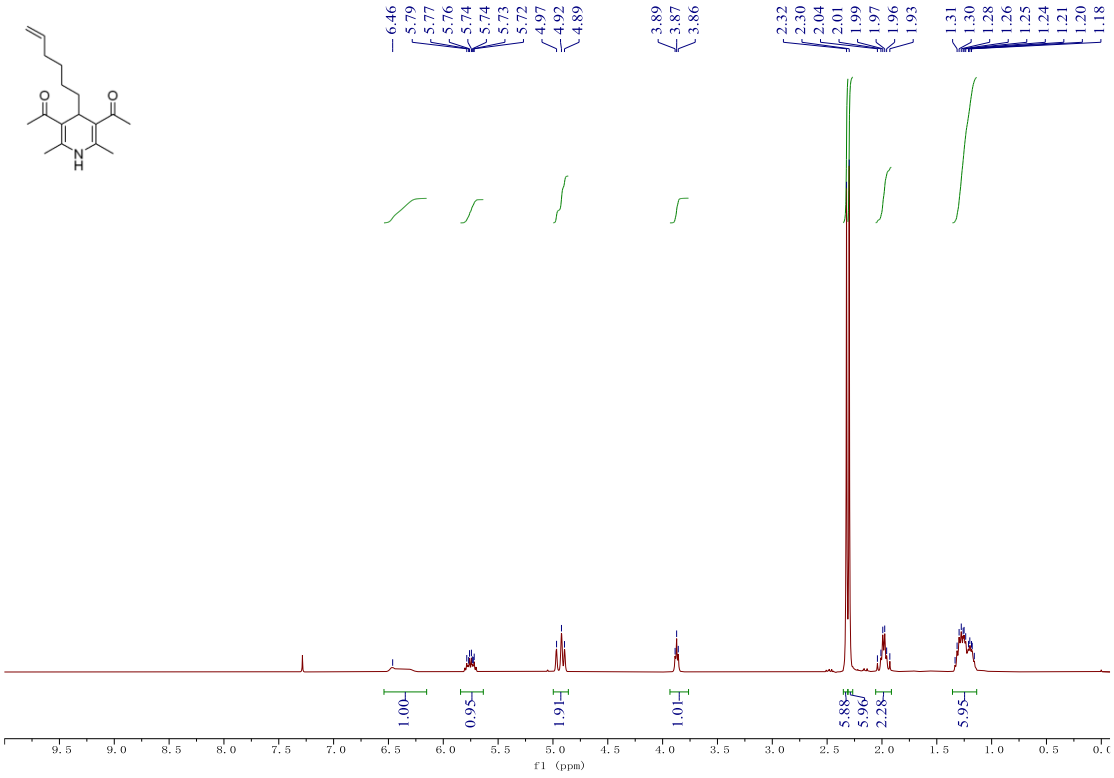


^{13}C NMR (100 MHz, $CDCl_3$):

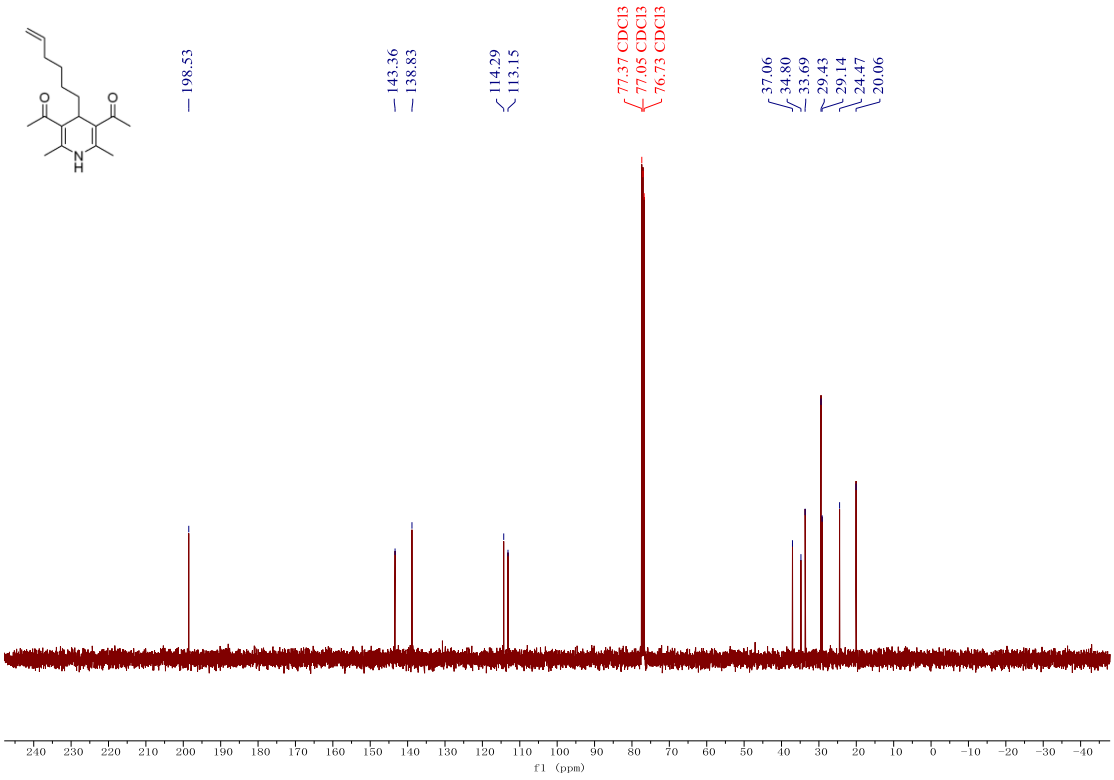


Compound **12**

^{1}H NMR (400 MHz, $CDCl_3$):



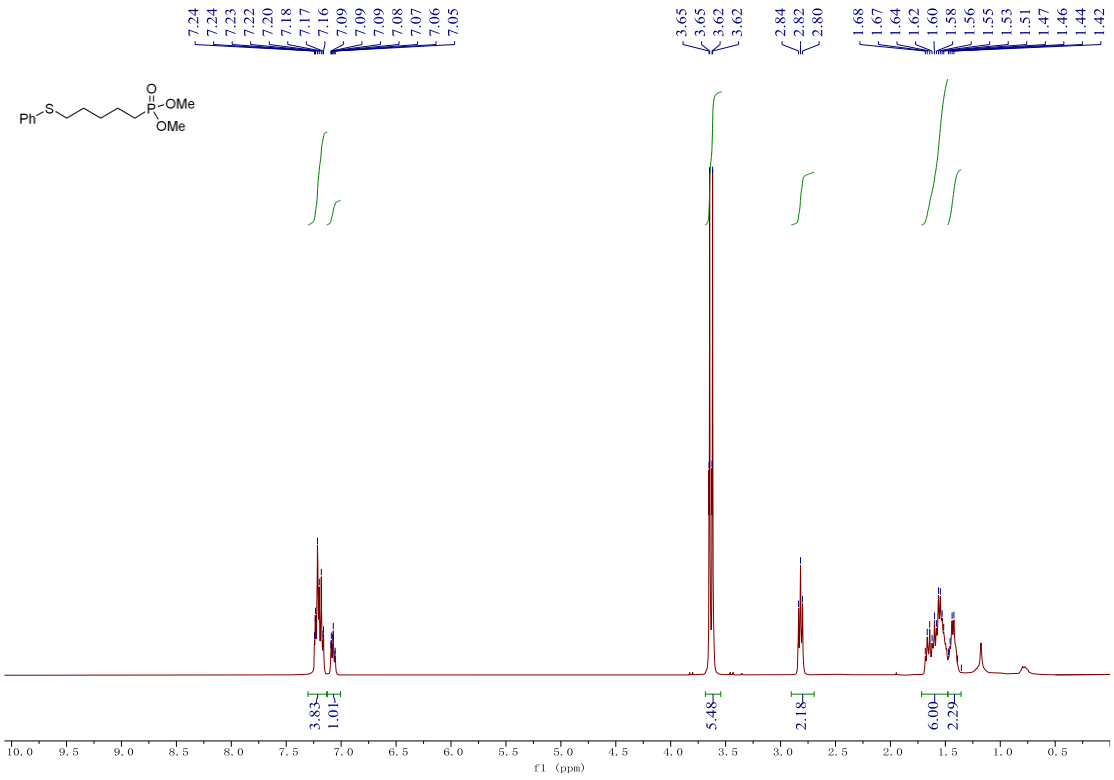
^{13}C NMR (100 MHz, $CDCl_3$):



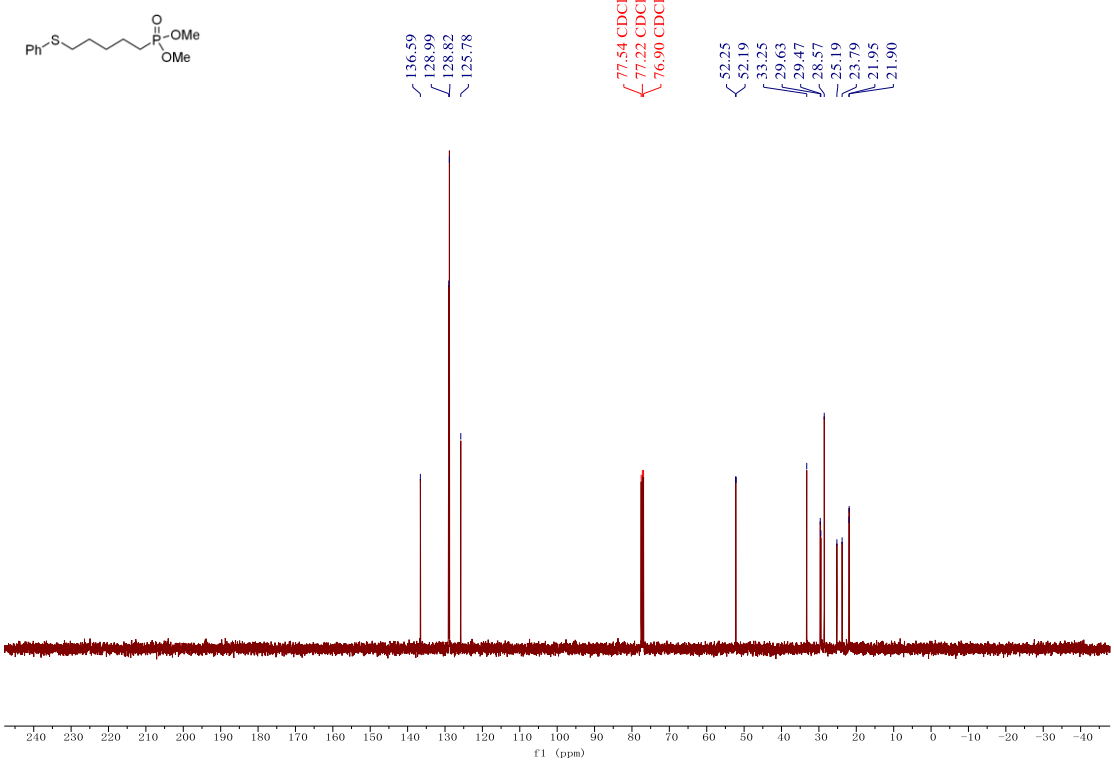
6. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra of new products

Compound **4d**

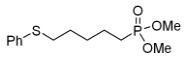
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

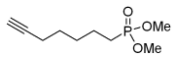


^{31}P NMR (162 MHz, $CDCl_3$):

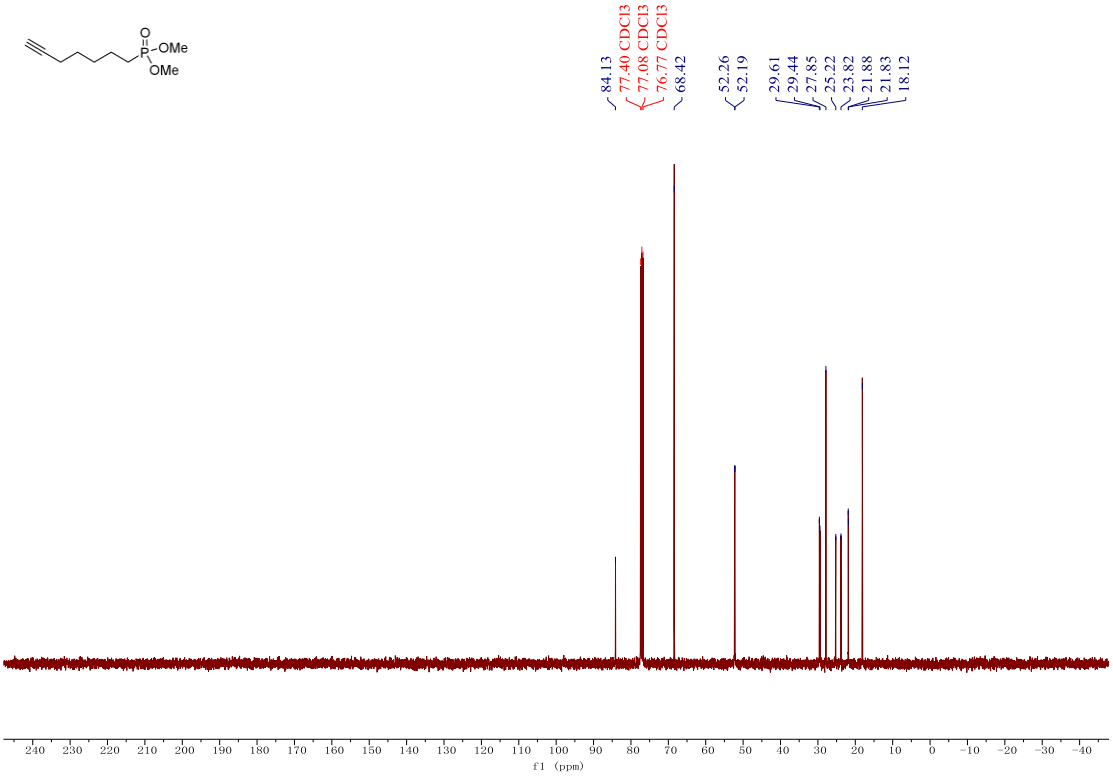


Compound **4f**

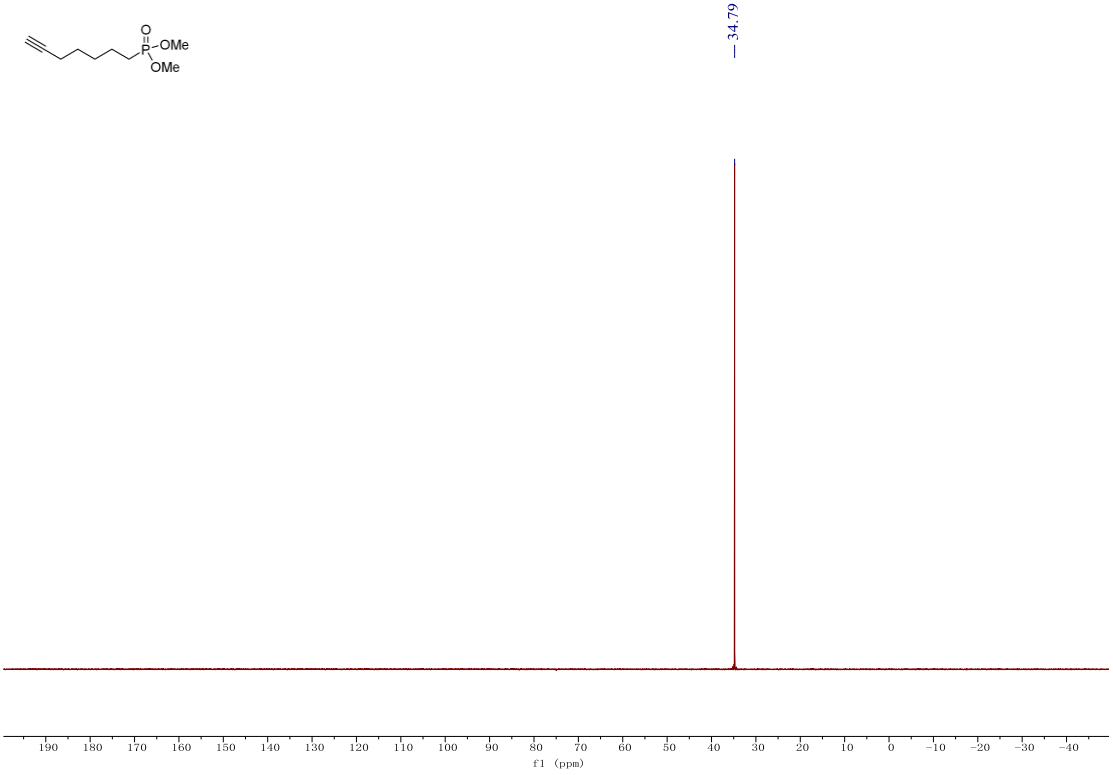
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

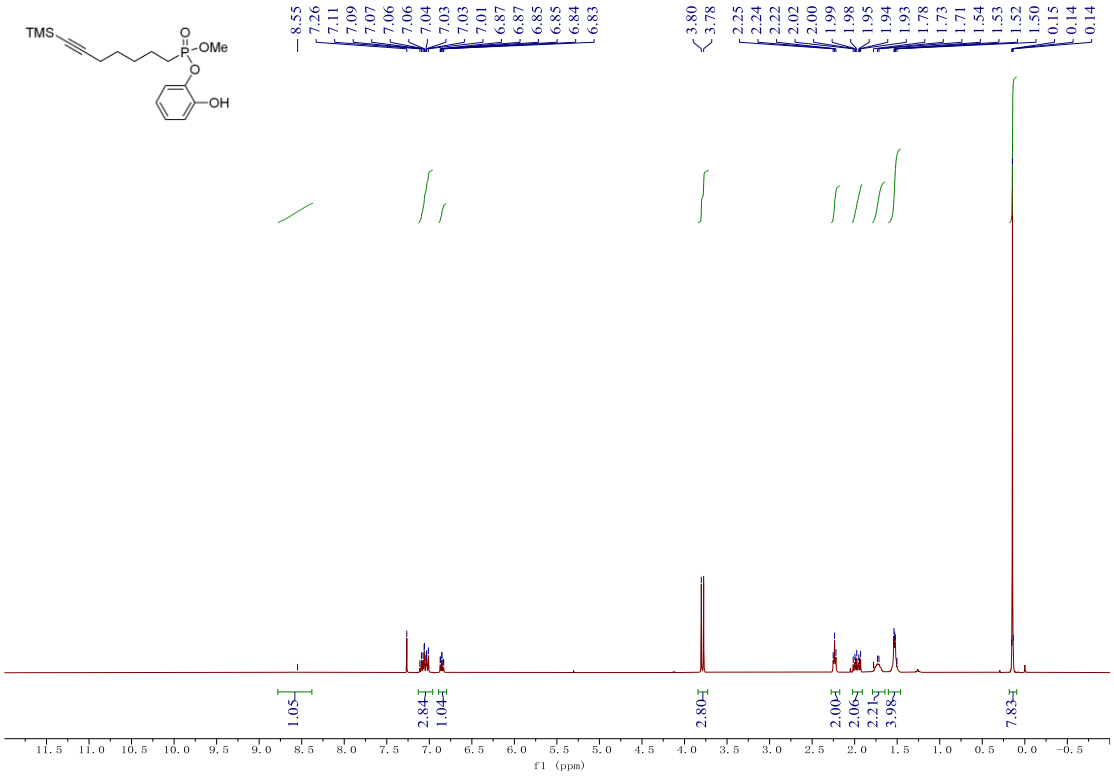


^{31}P NMR (162 MHz, $CDCl_3$):

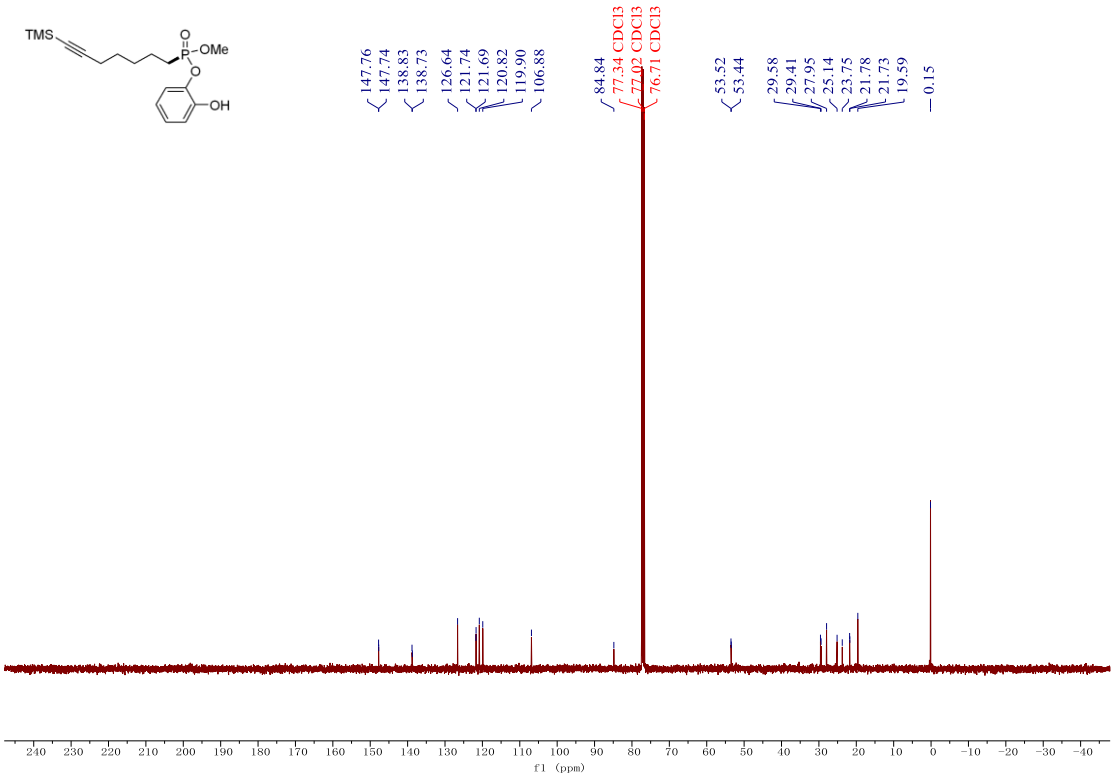


Compound **4g**

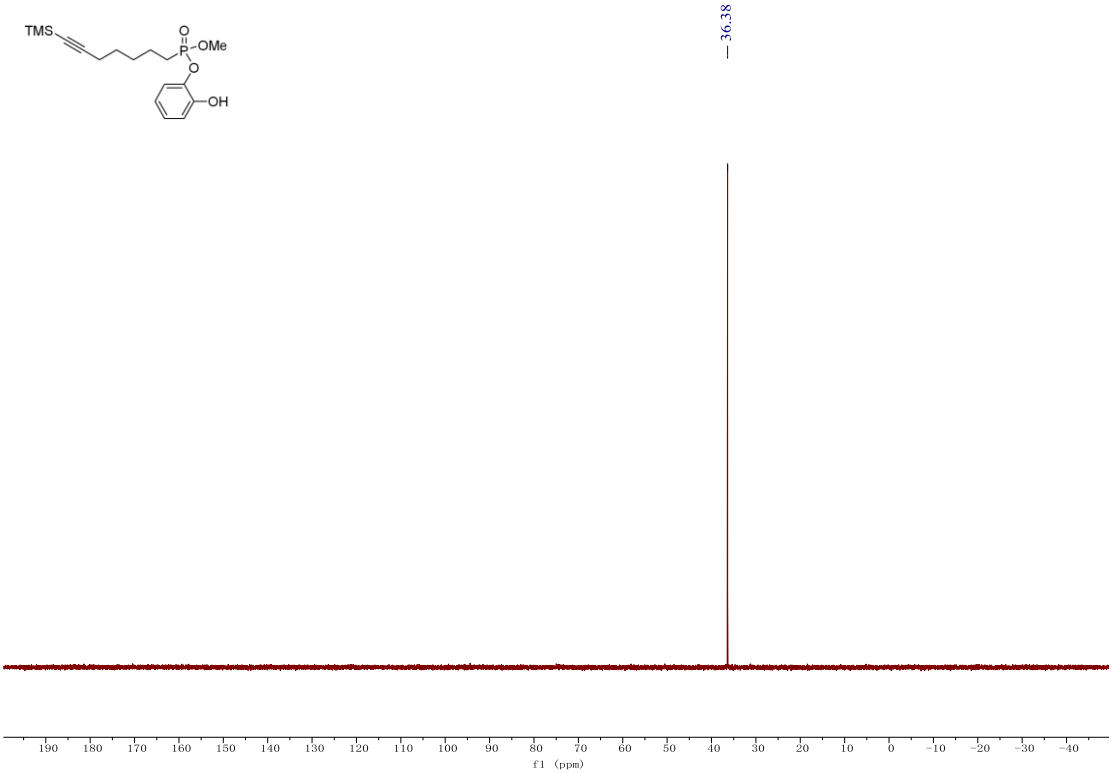
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

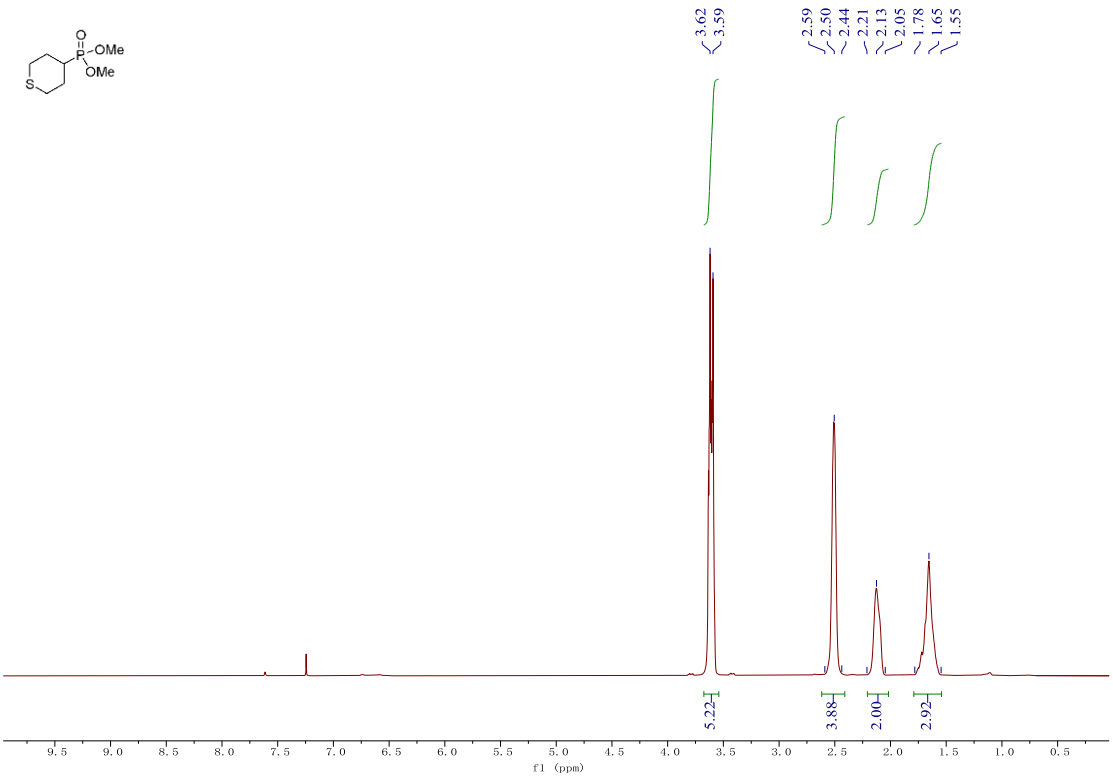


^{31}P NMR (162 MHz, $CDCl_3$):

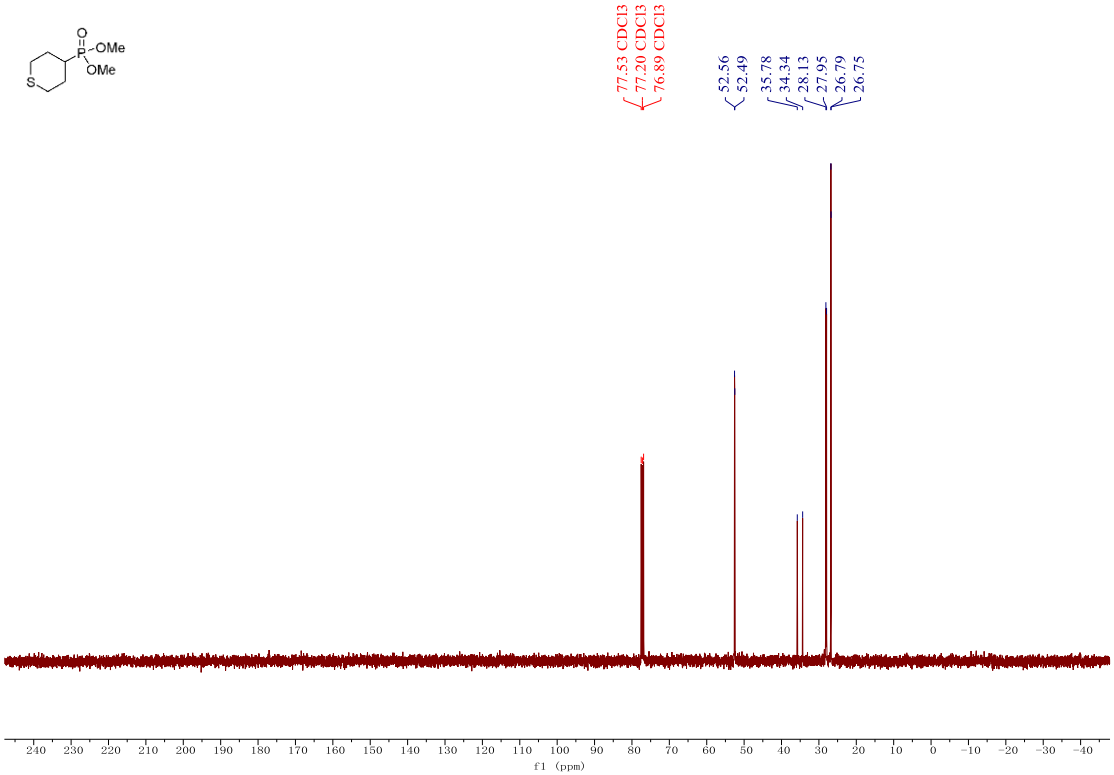


Compound **4i**

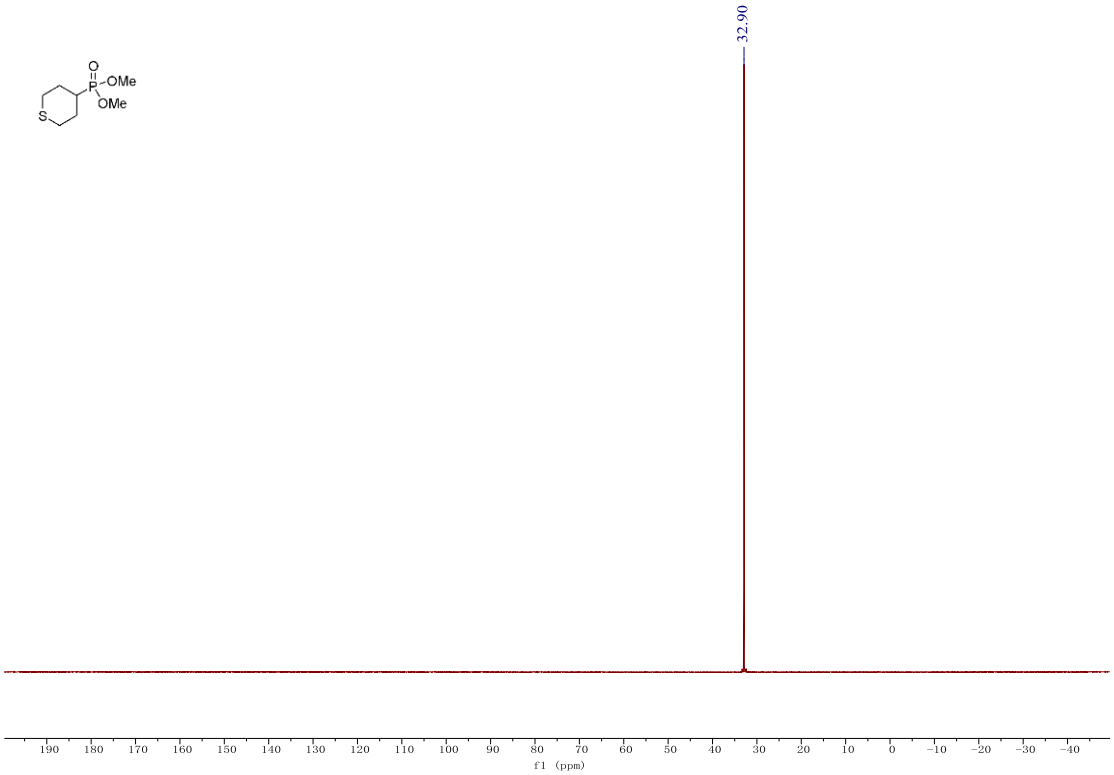
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

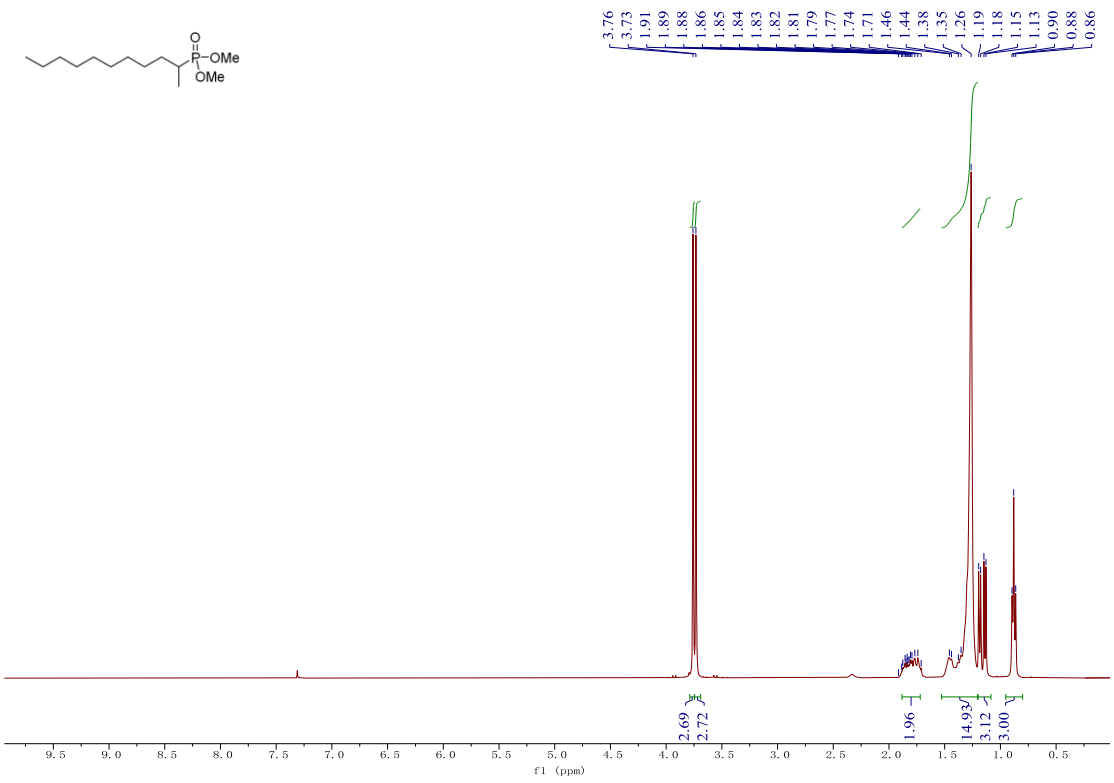


^{31}P NMR (162 MHz, $CDCl_3$):

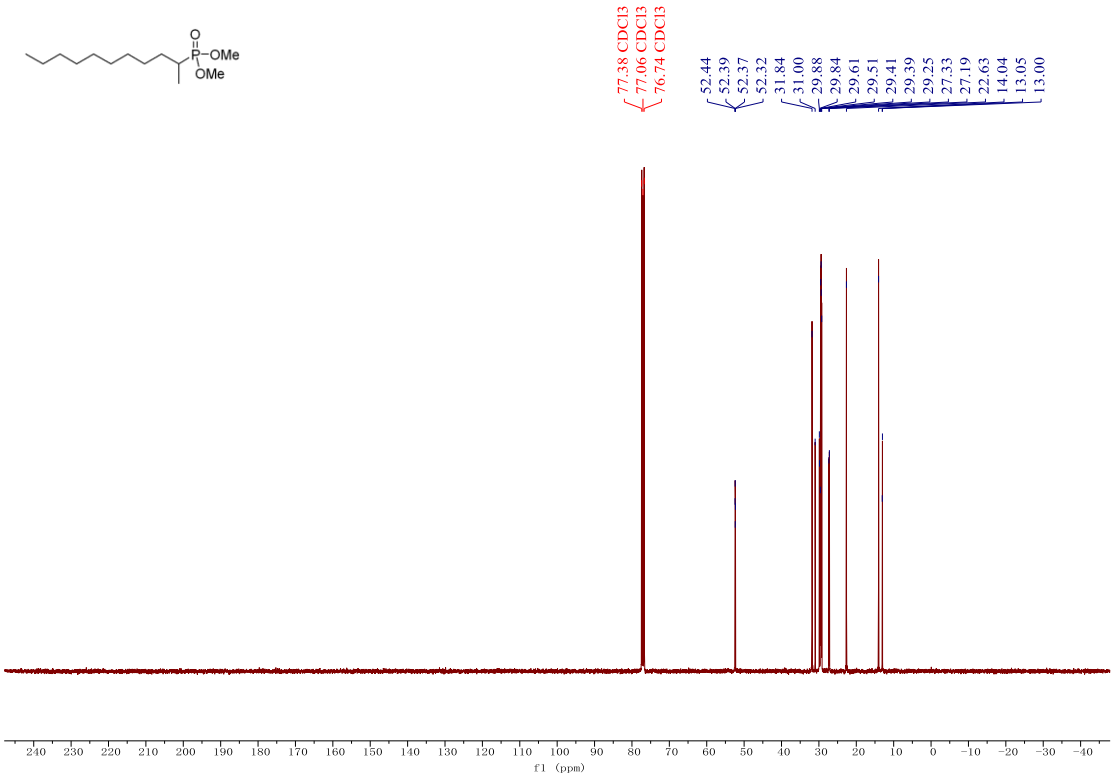


Compound **4n**

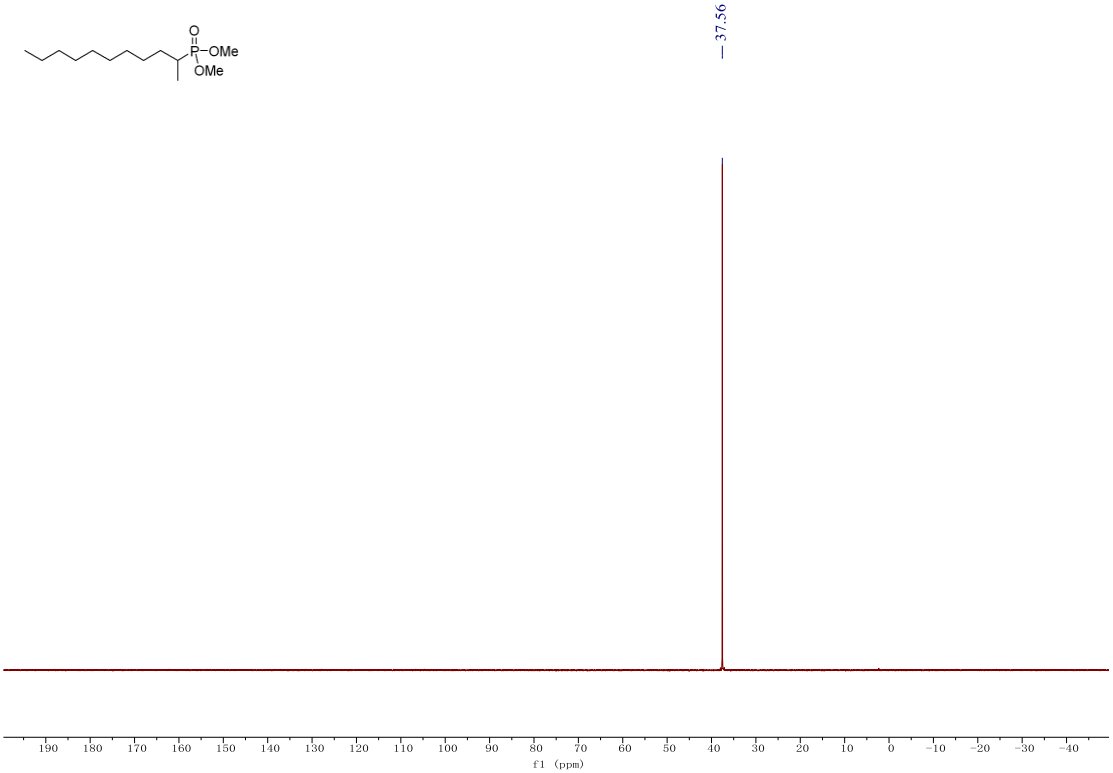
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

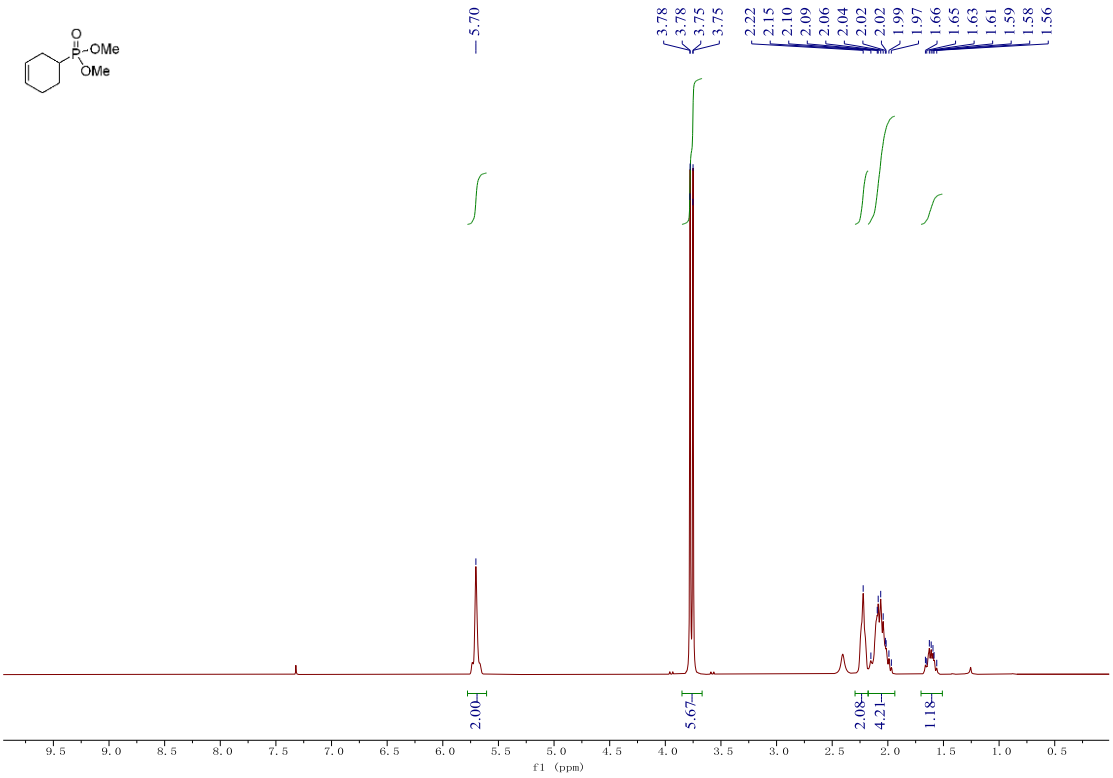


^{31}P NMR (162 MHz, $CDCl_3$):

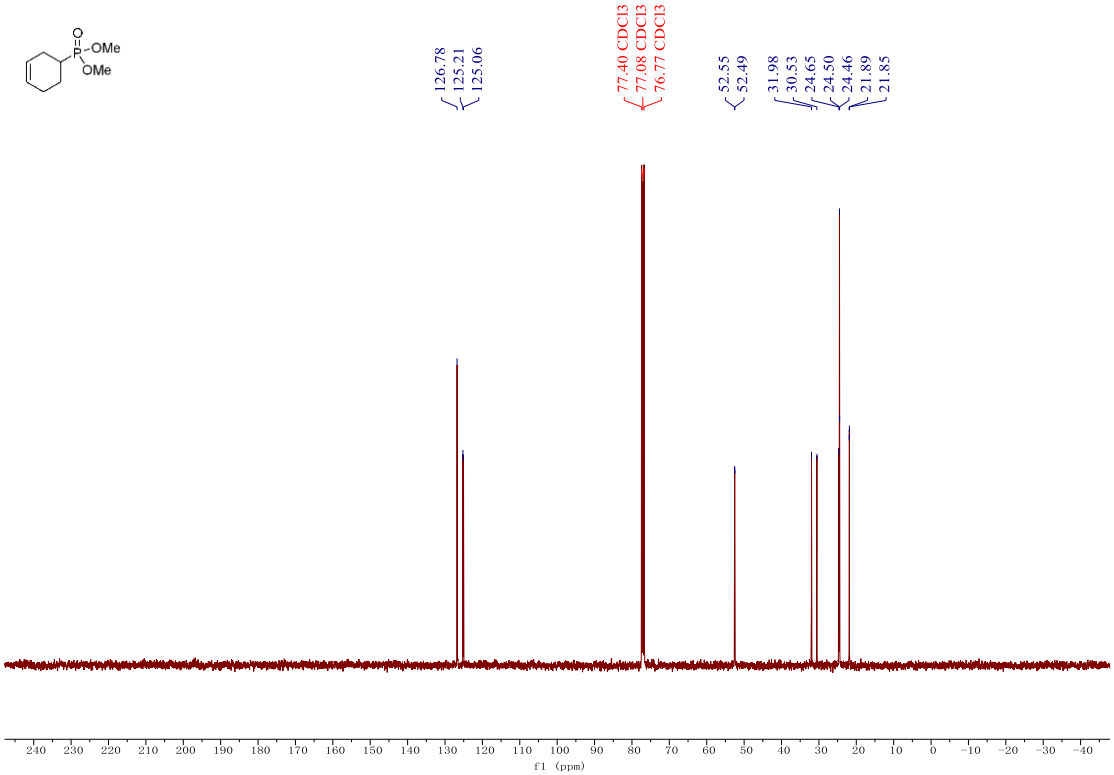


Compound **4q**

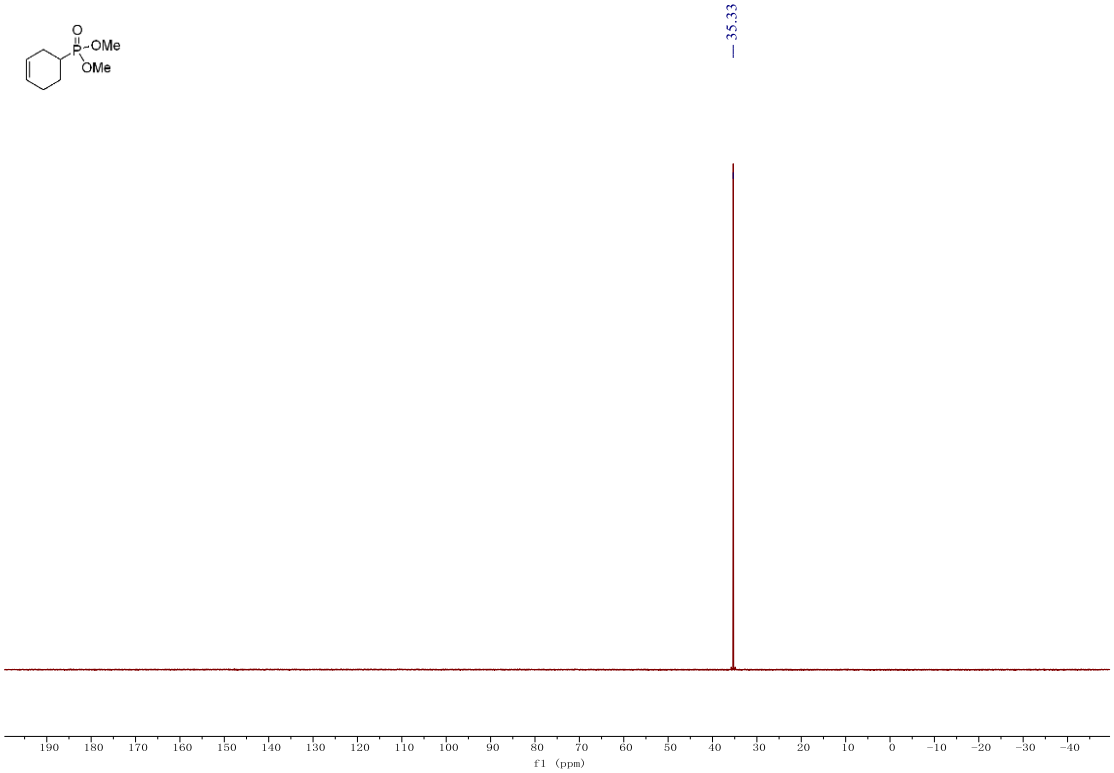
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

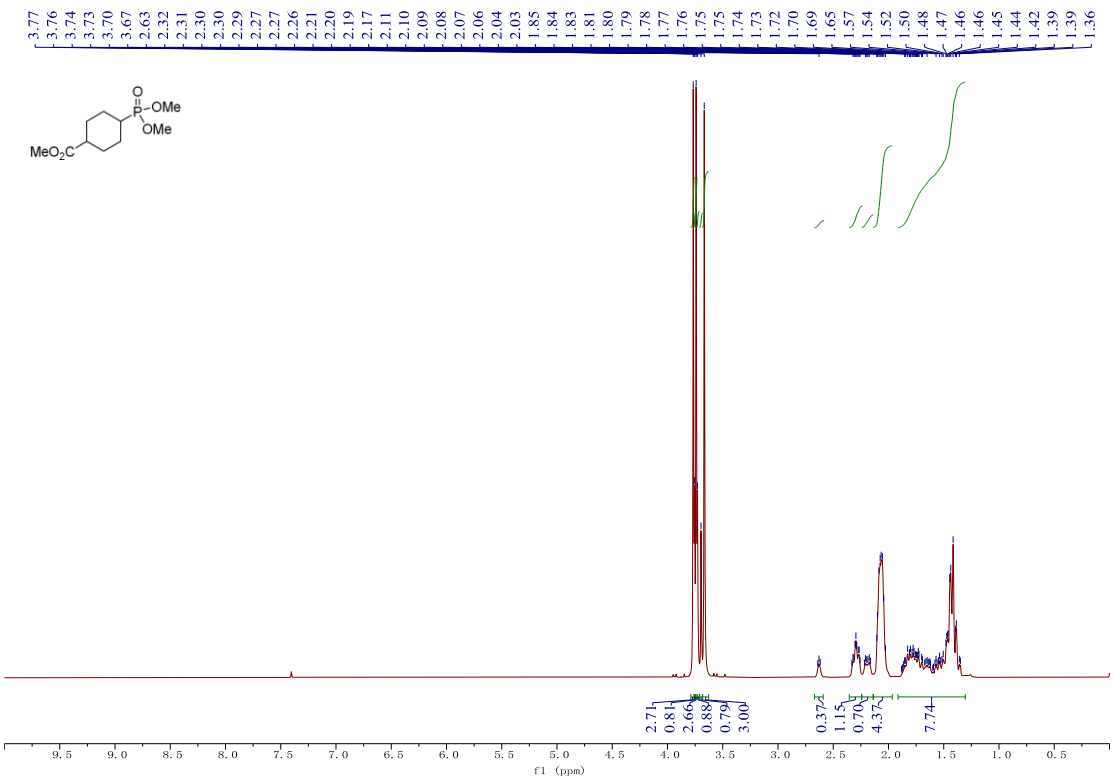


^{31}P NMR (162 MHz, $CDCl_3$):

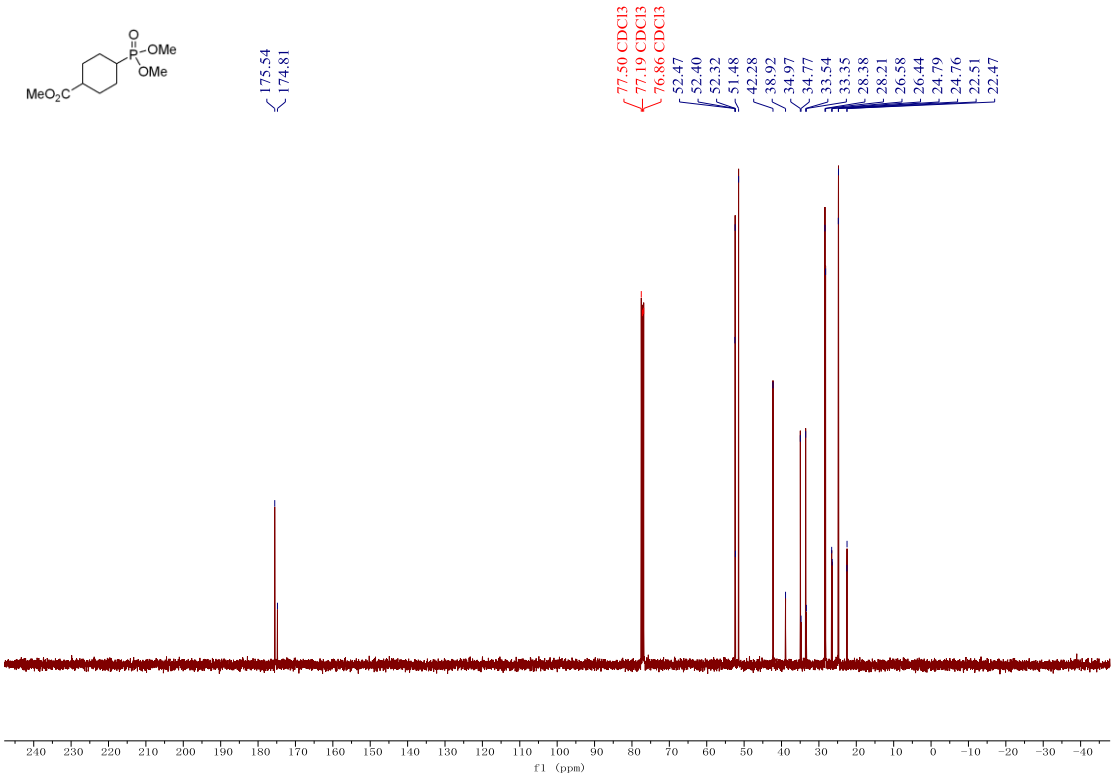


Compound **4s**

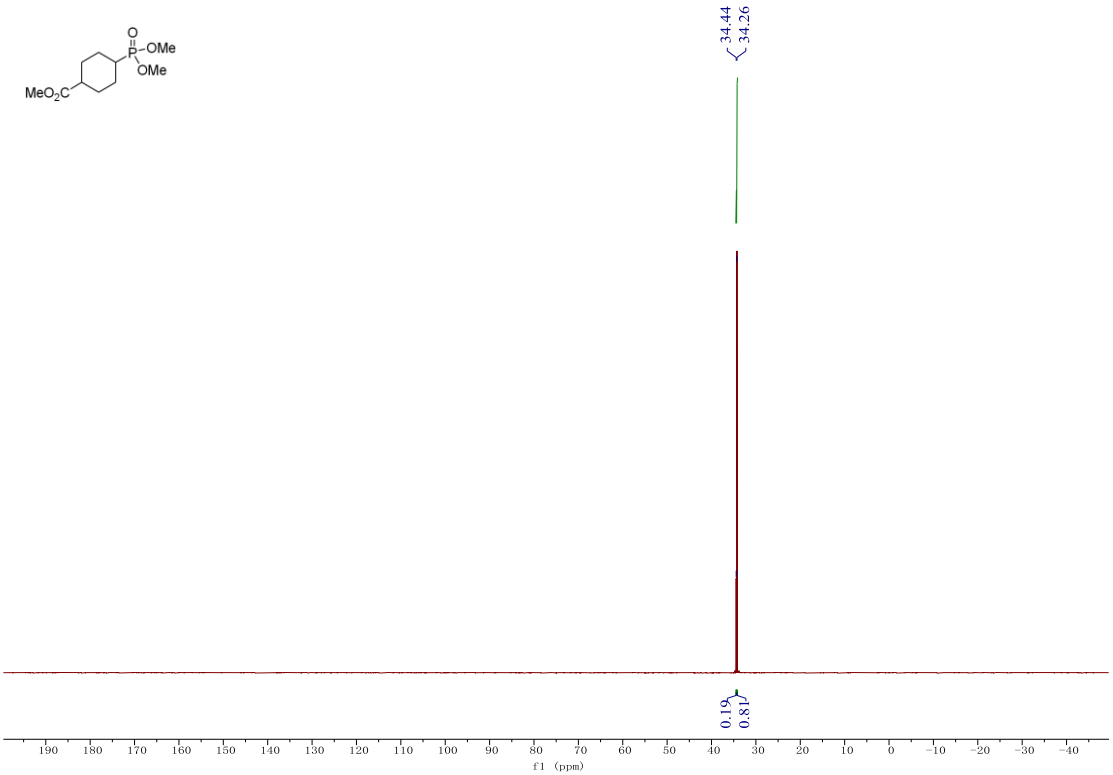
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

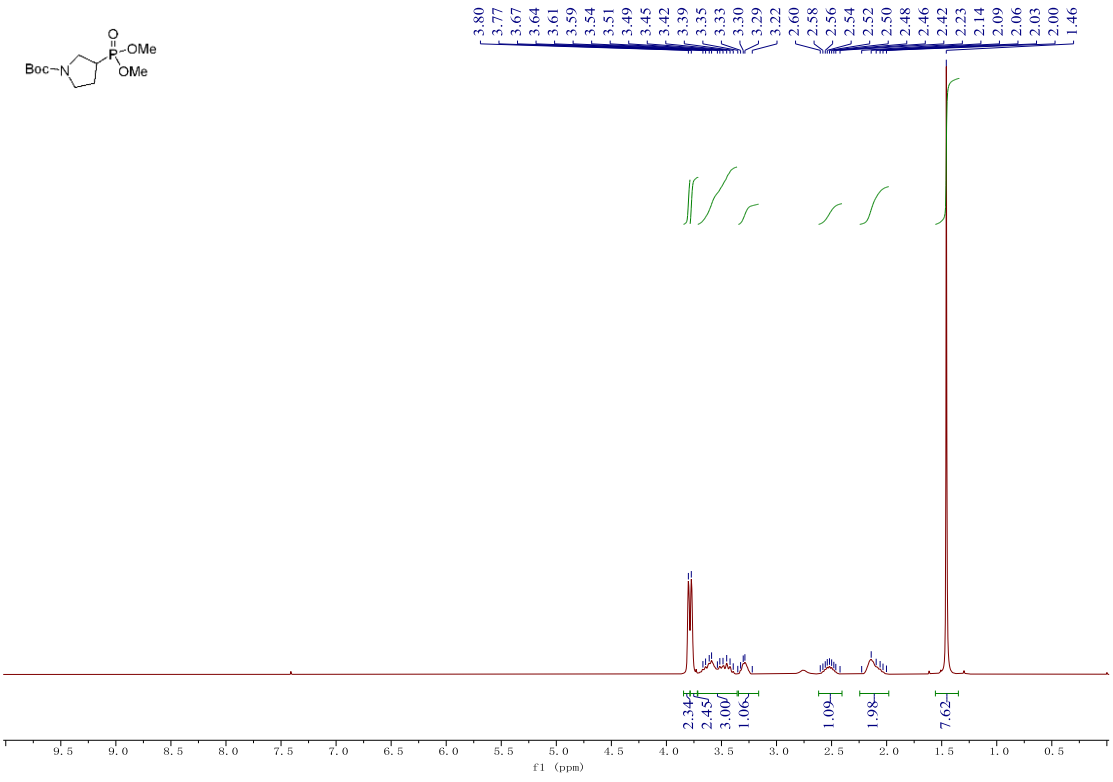


^{31}P NMR (162 MHz, $CDCl_3$):

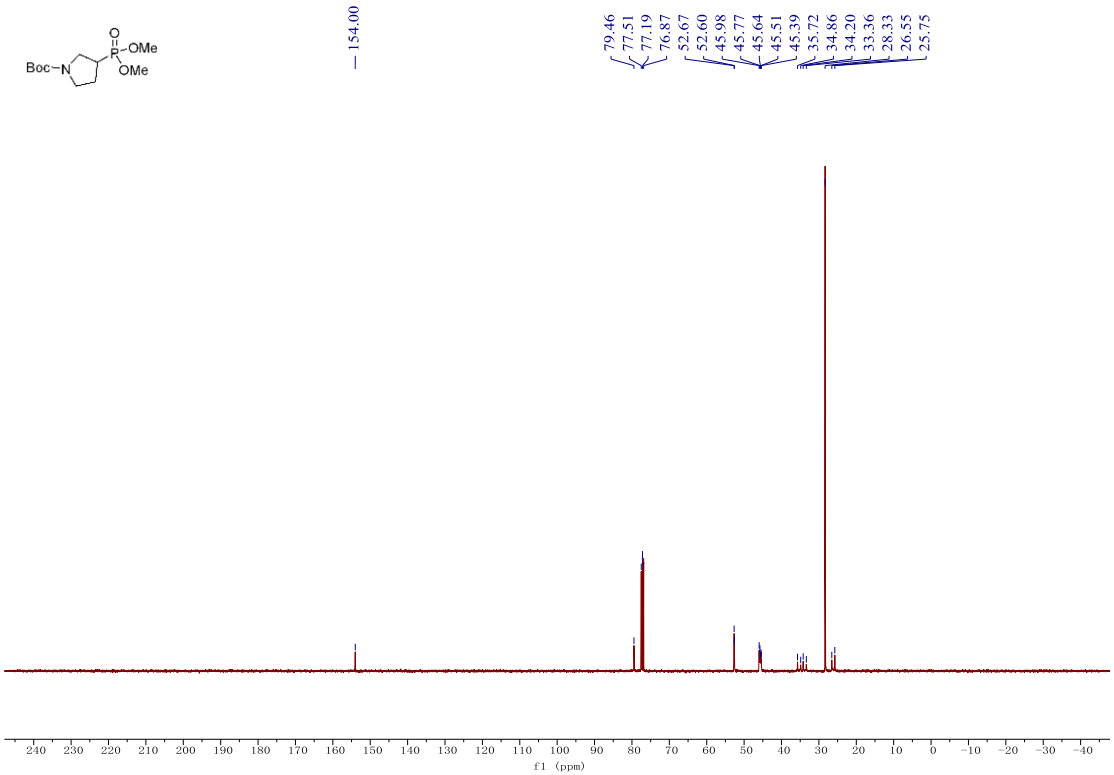


Compound **4t**

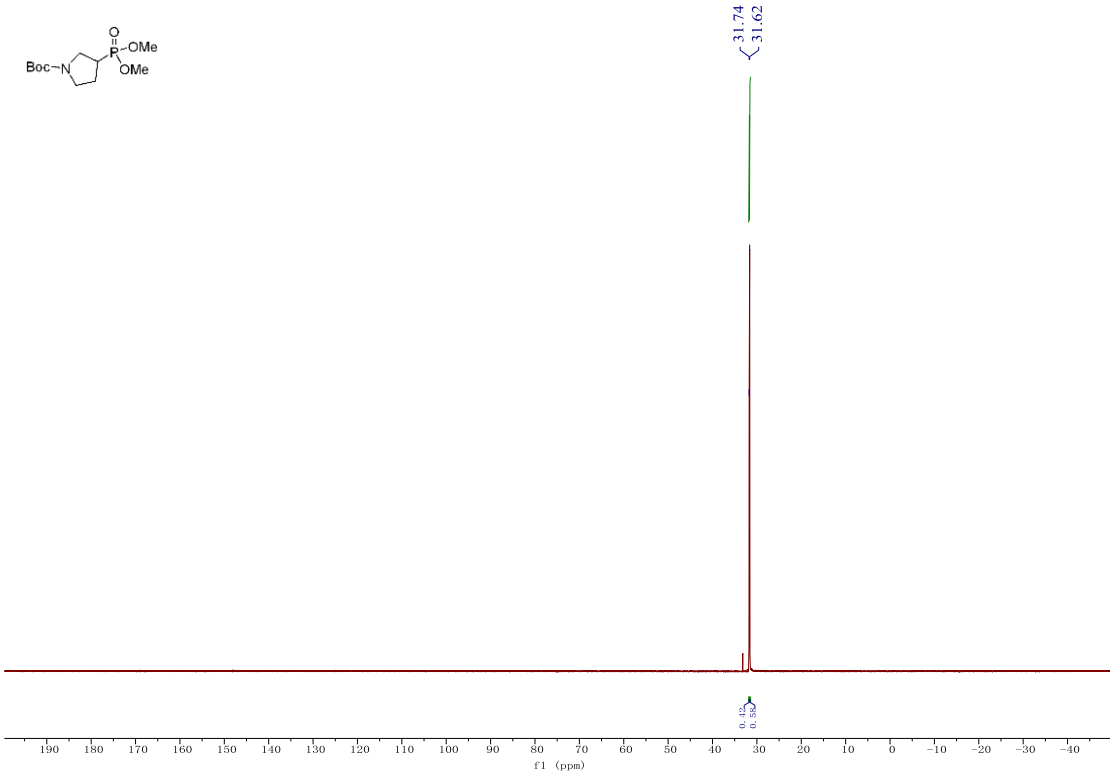
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

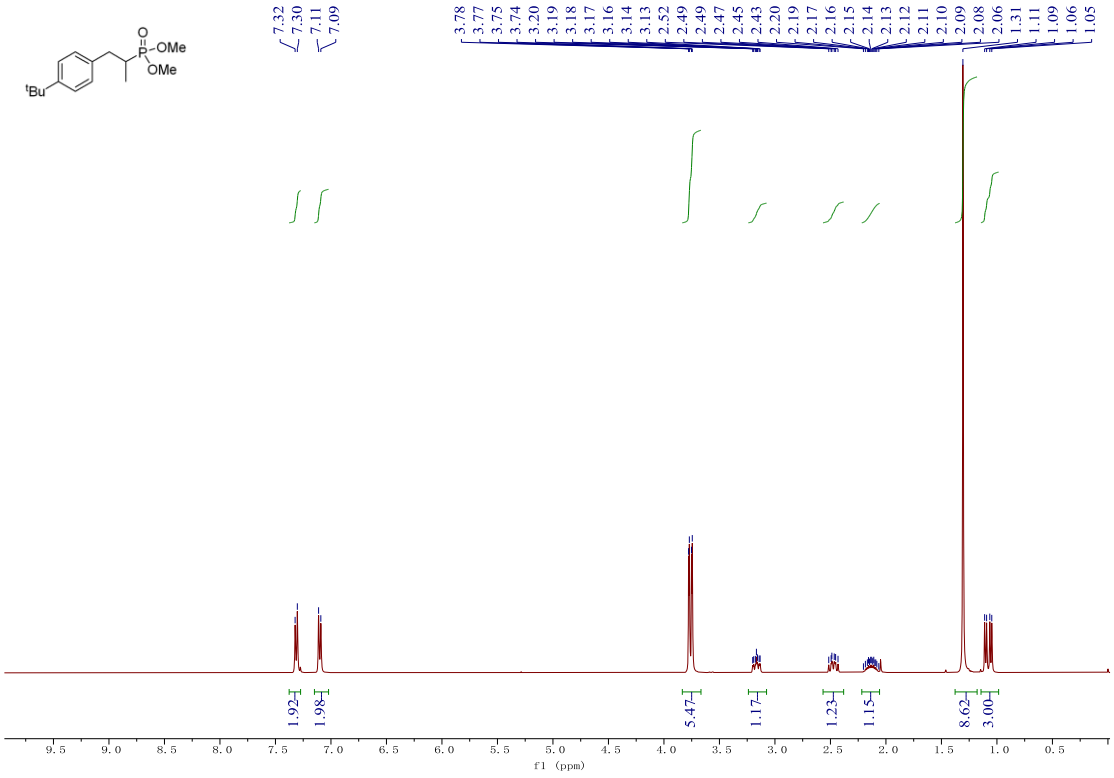


^{31}P NMR (162 MHz, $CDCl_3$):

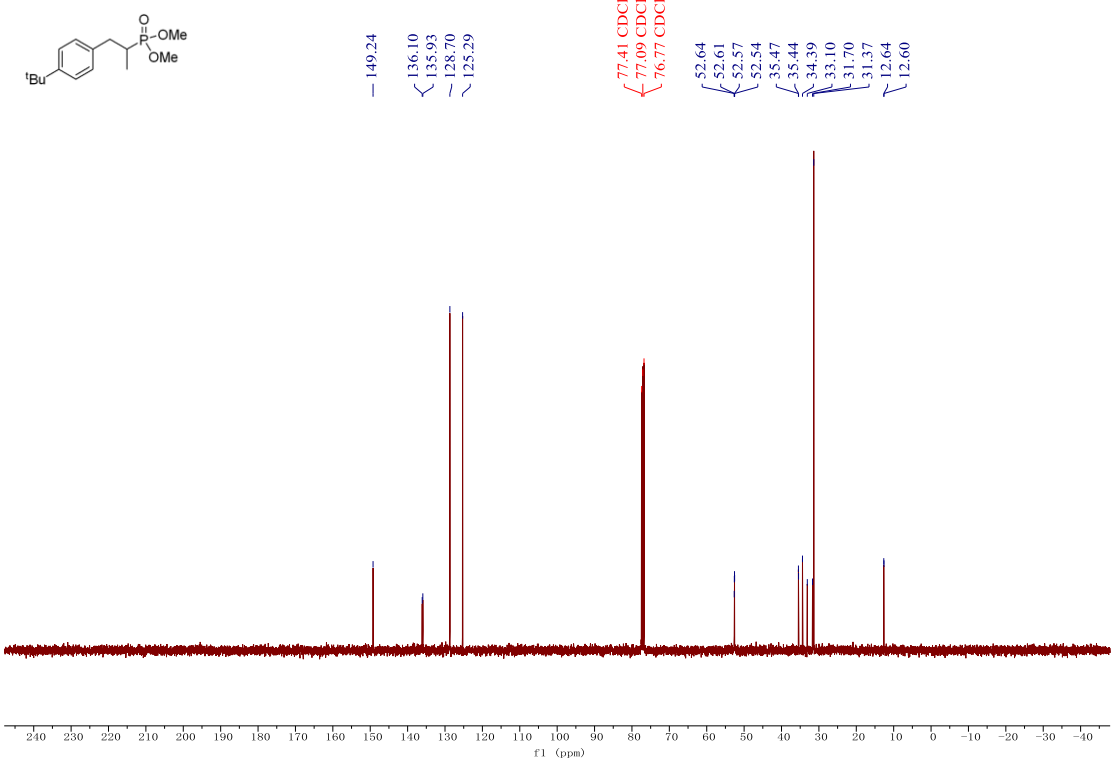


Compound **4u**

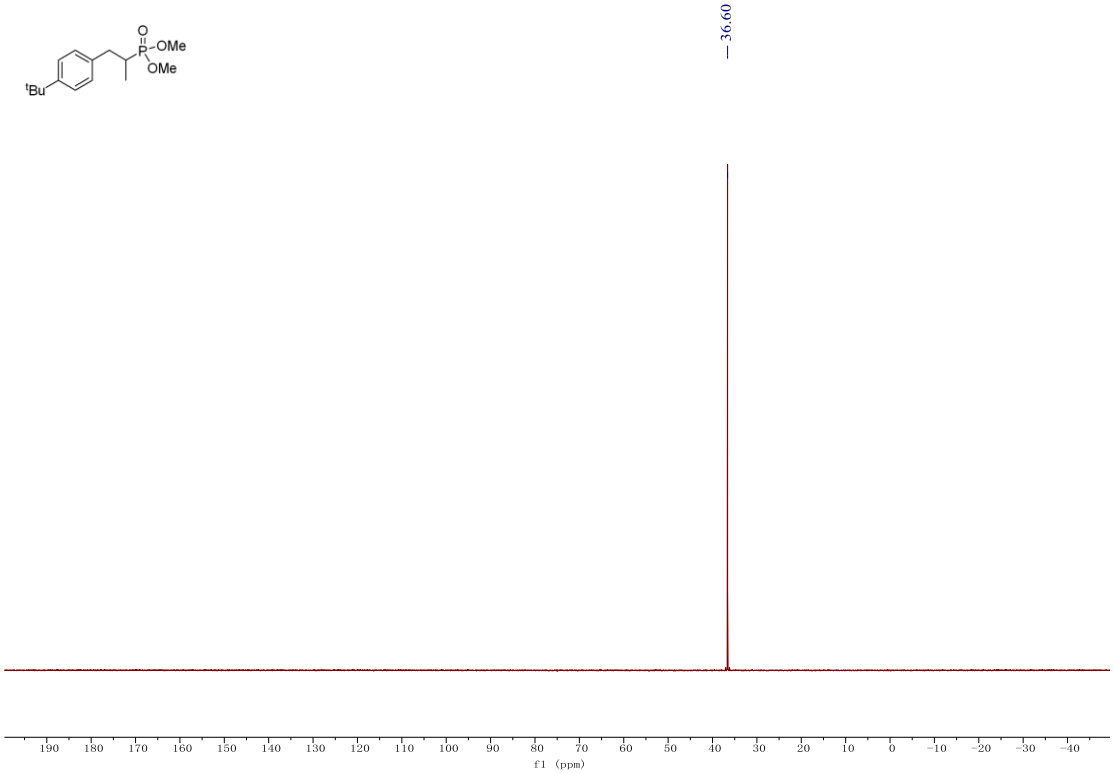
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

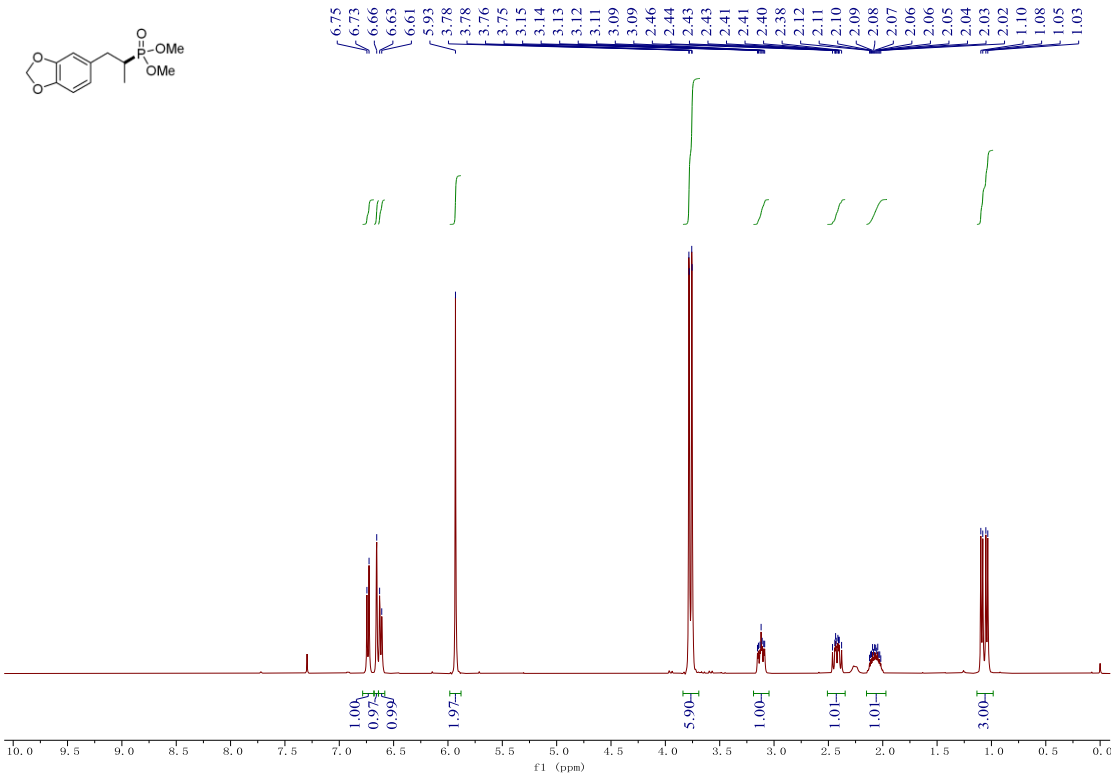


^{31}P NMR (162 MHz, $CDCl_3$):

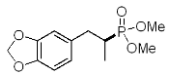


Compound **5**

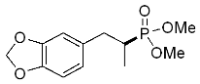
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

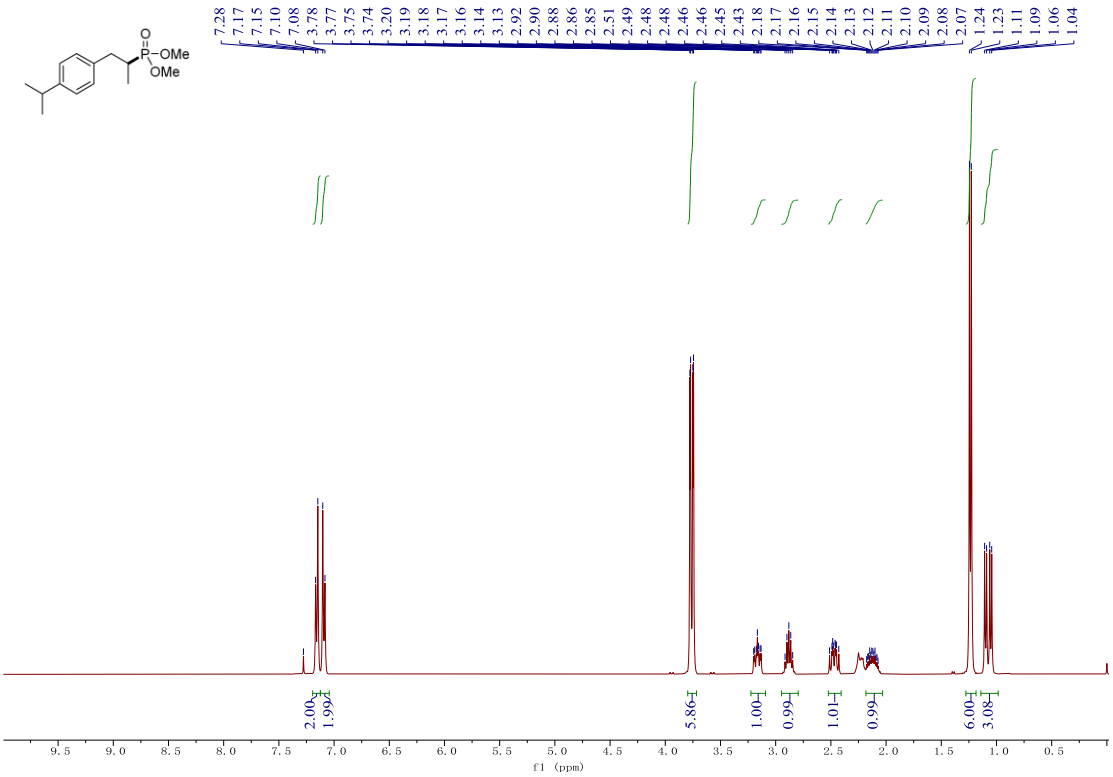


^{31}P NMR (162 MHz, $CDCl_3$):

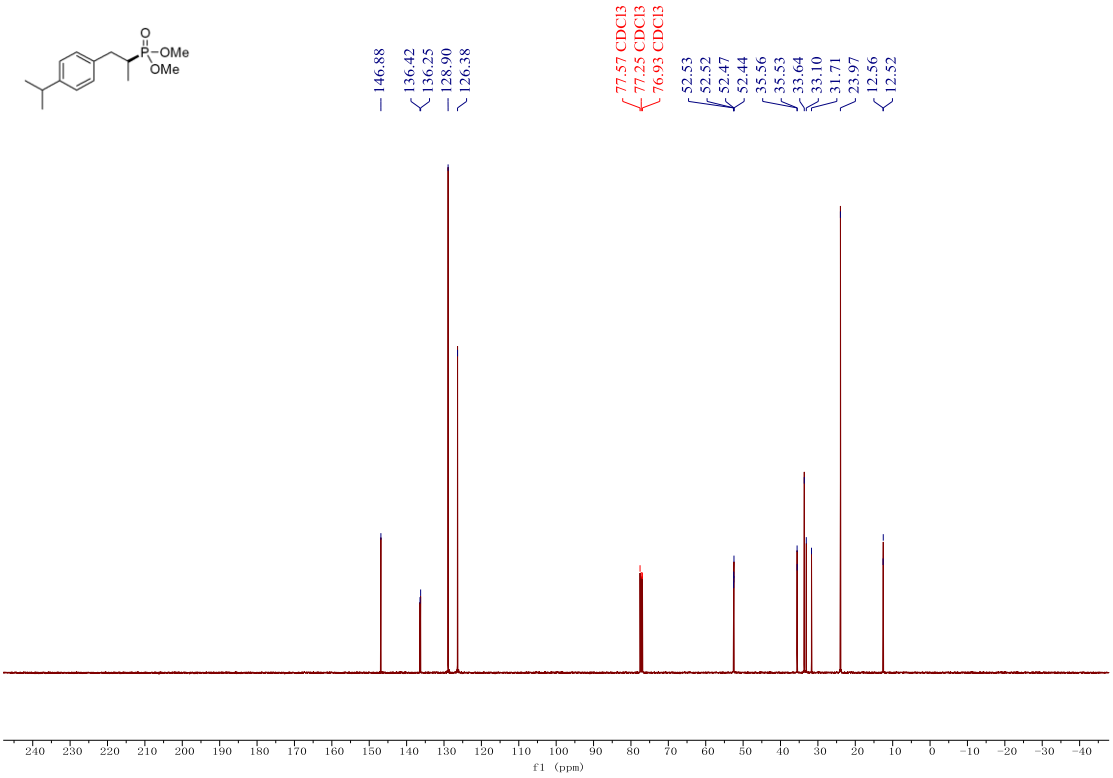


Compound **6**

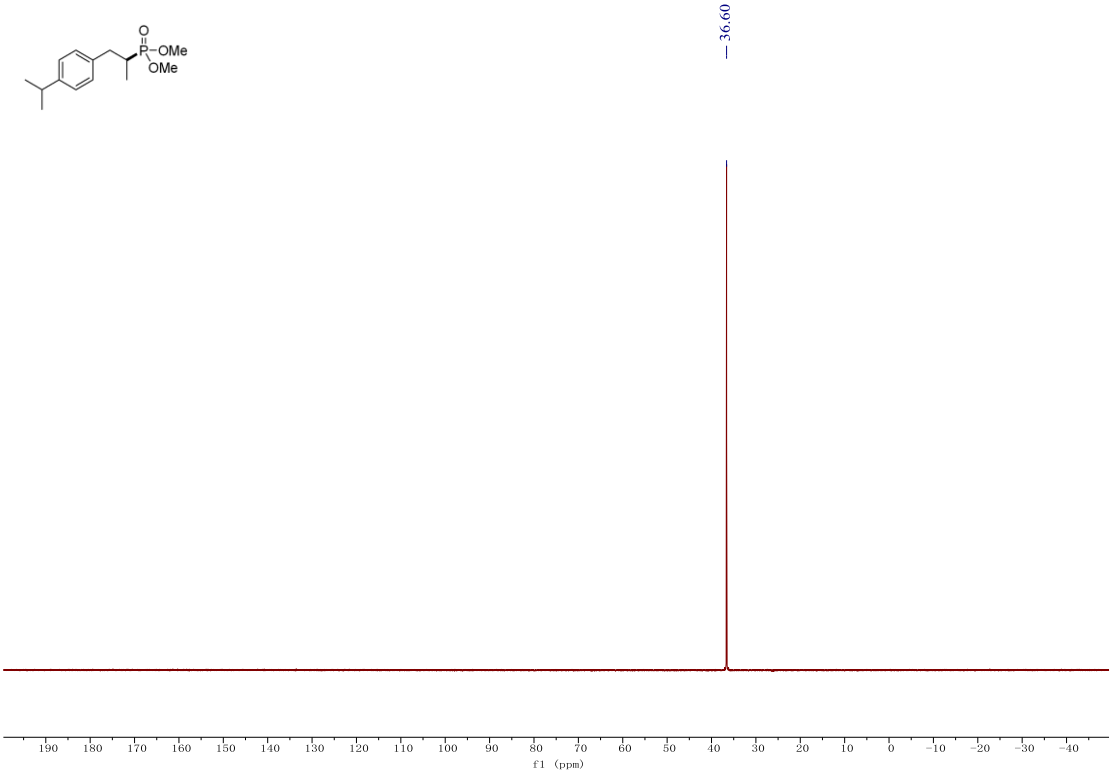
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

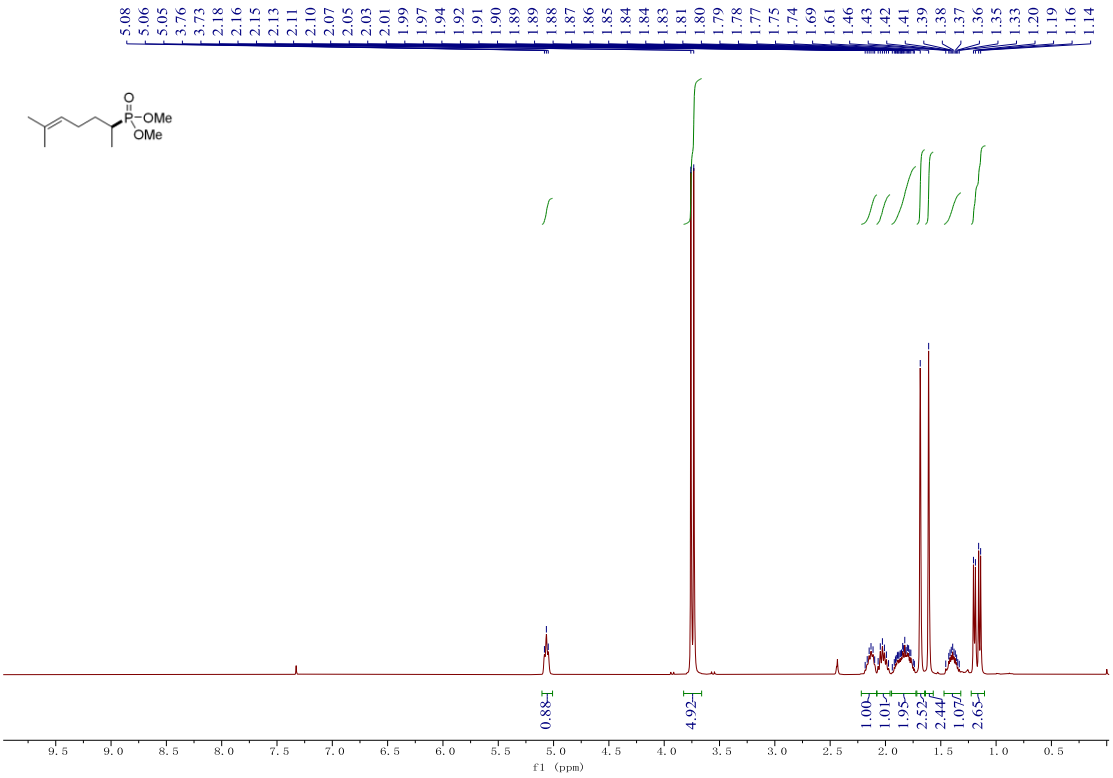


^{31}P NMR (162 MHz, $CDCl_3$):

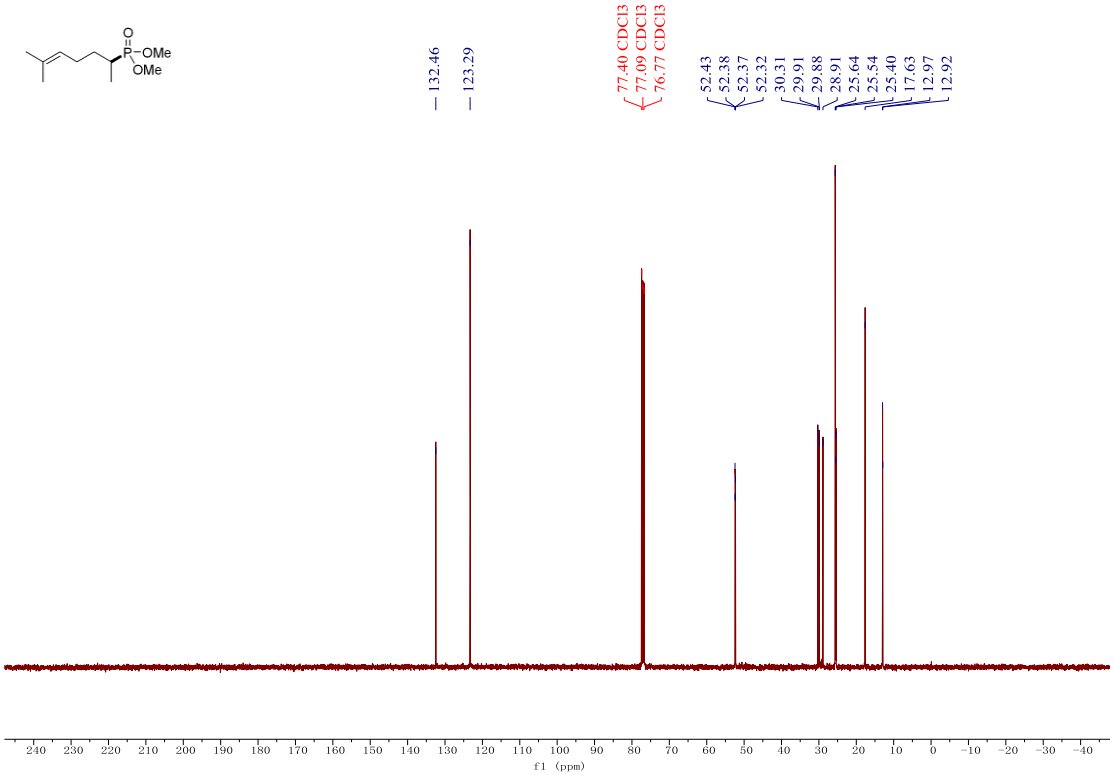


Compound **7**

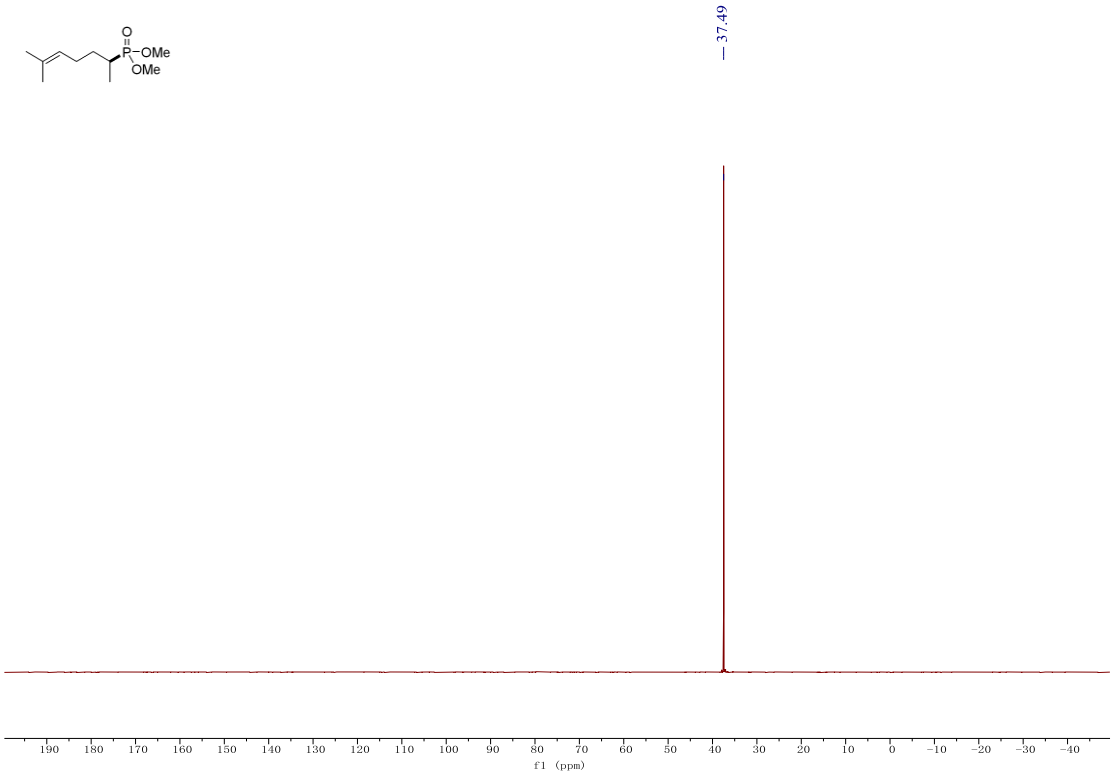
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

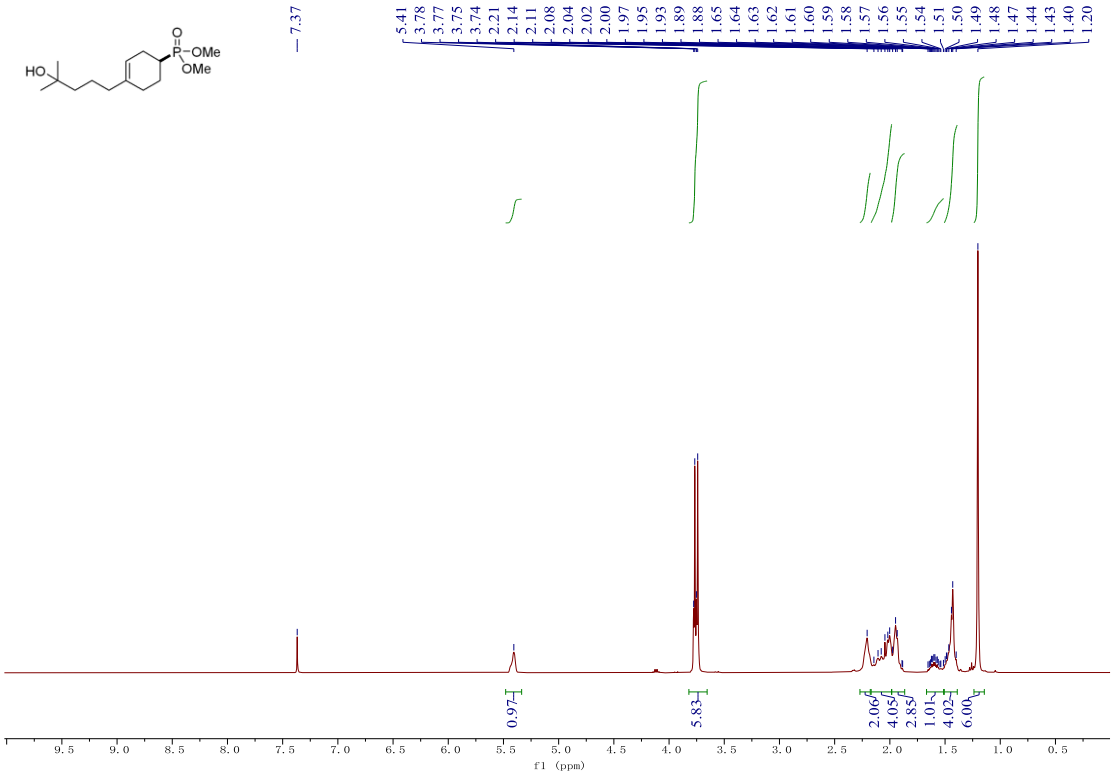


^{31}P NMR (162 MHz, $CDCl_3$):

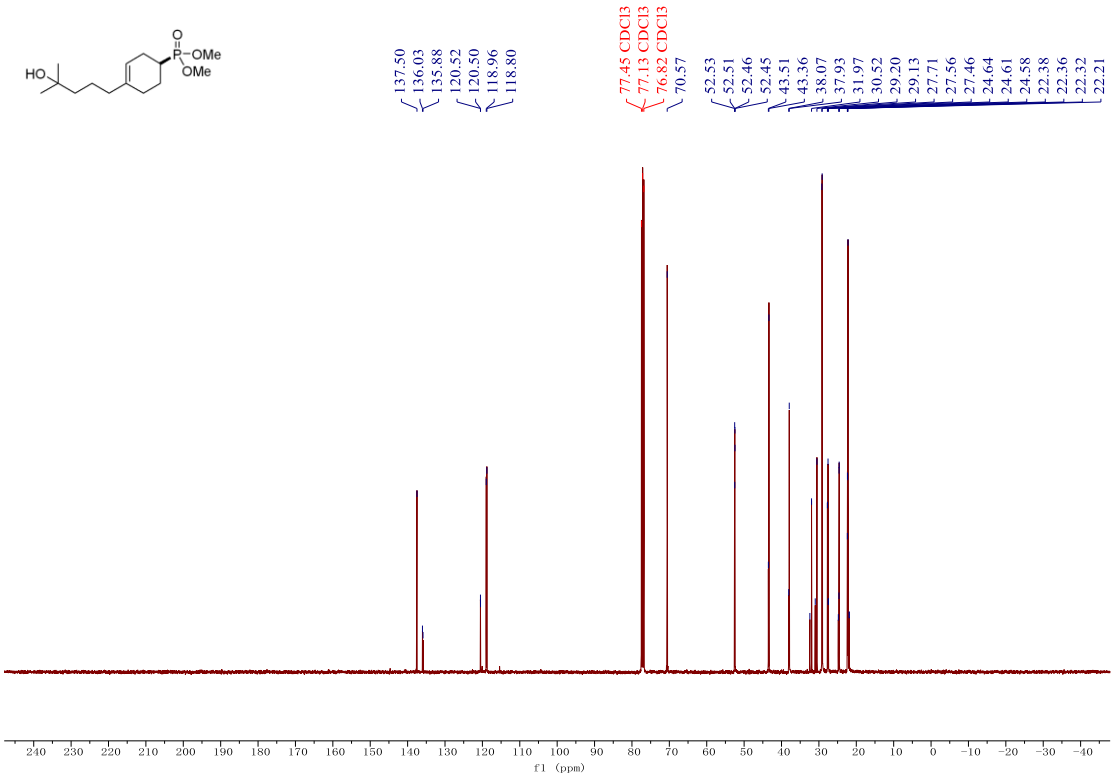


Compound **8**

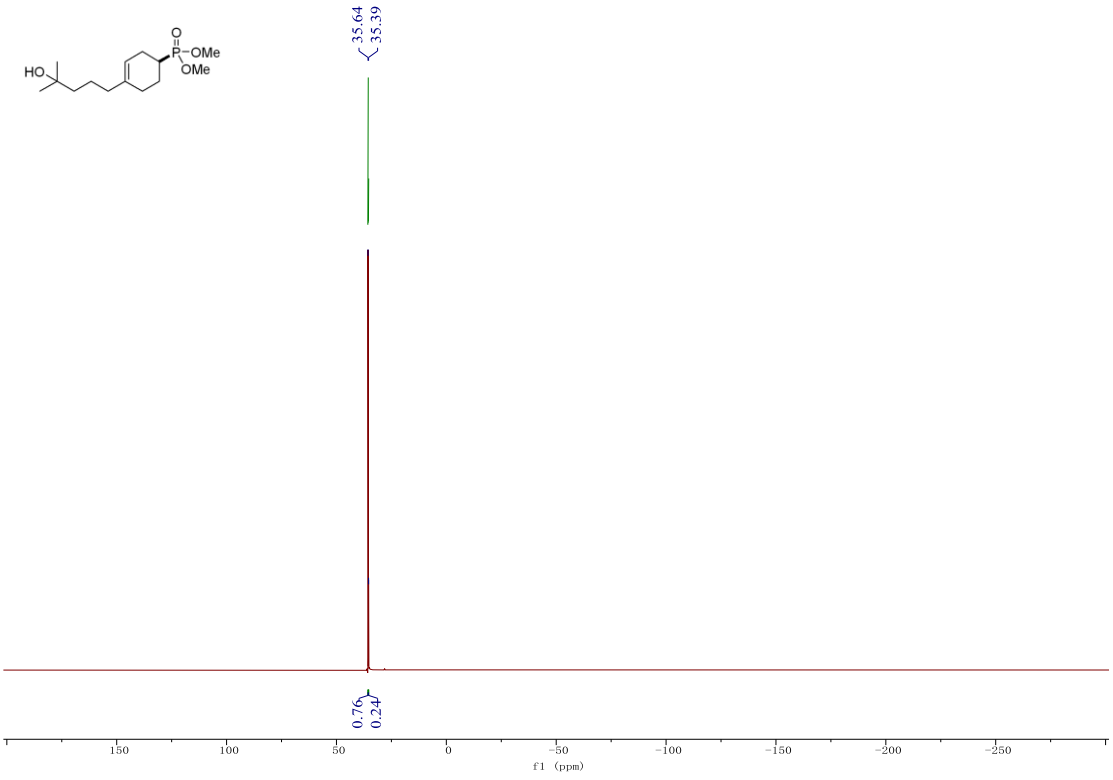
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

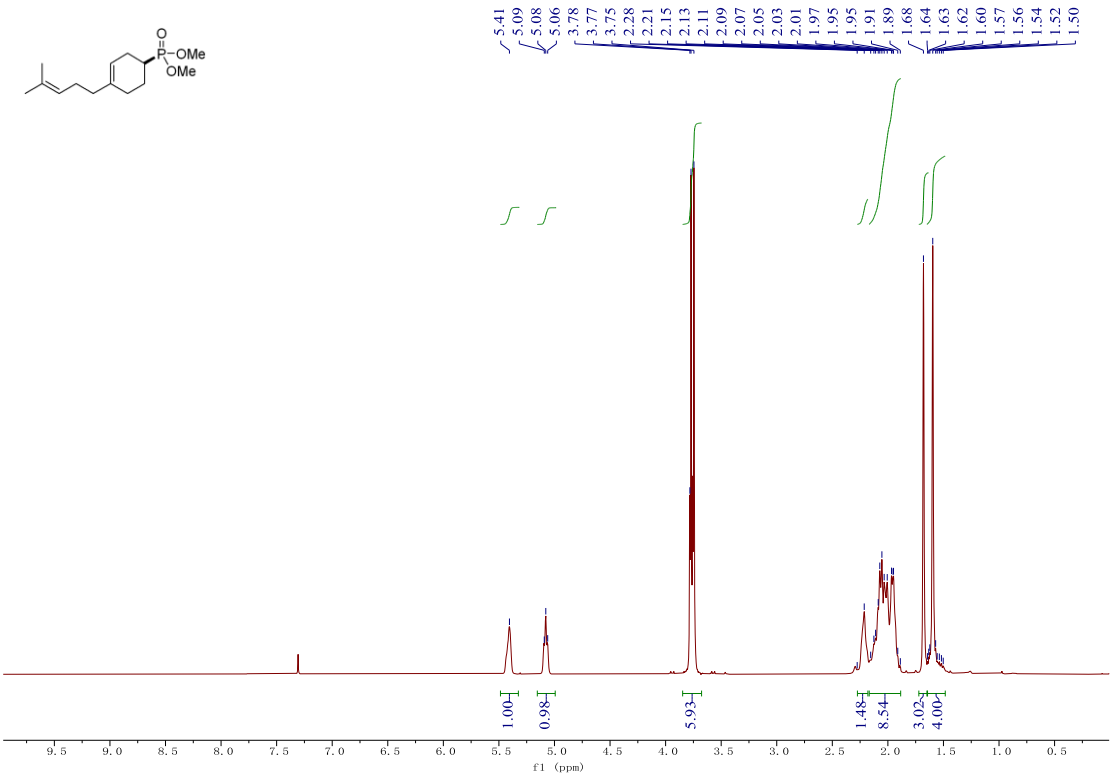


^{31}P NMR (162 MHz, $CDCl_3$):

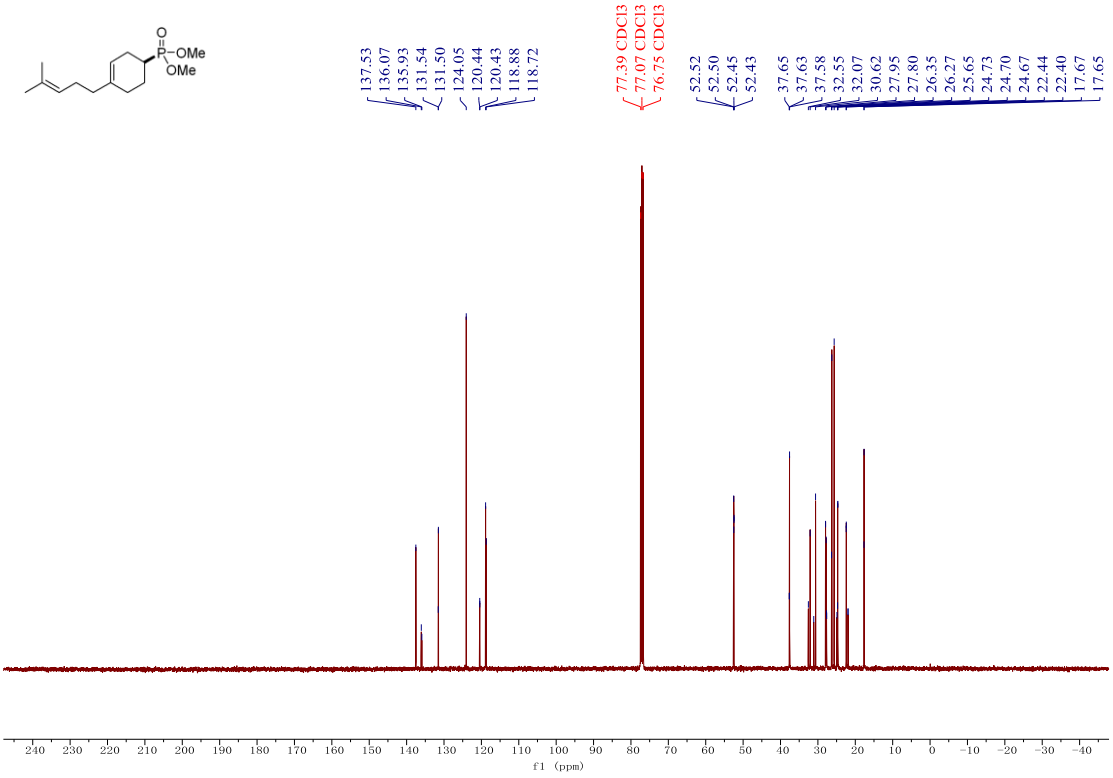


Compound **9**

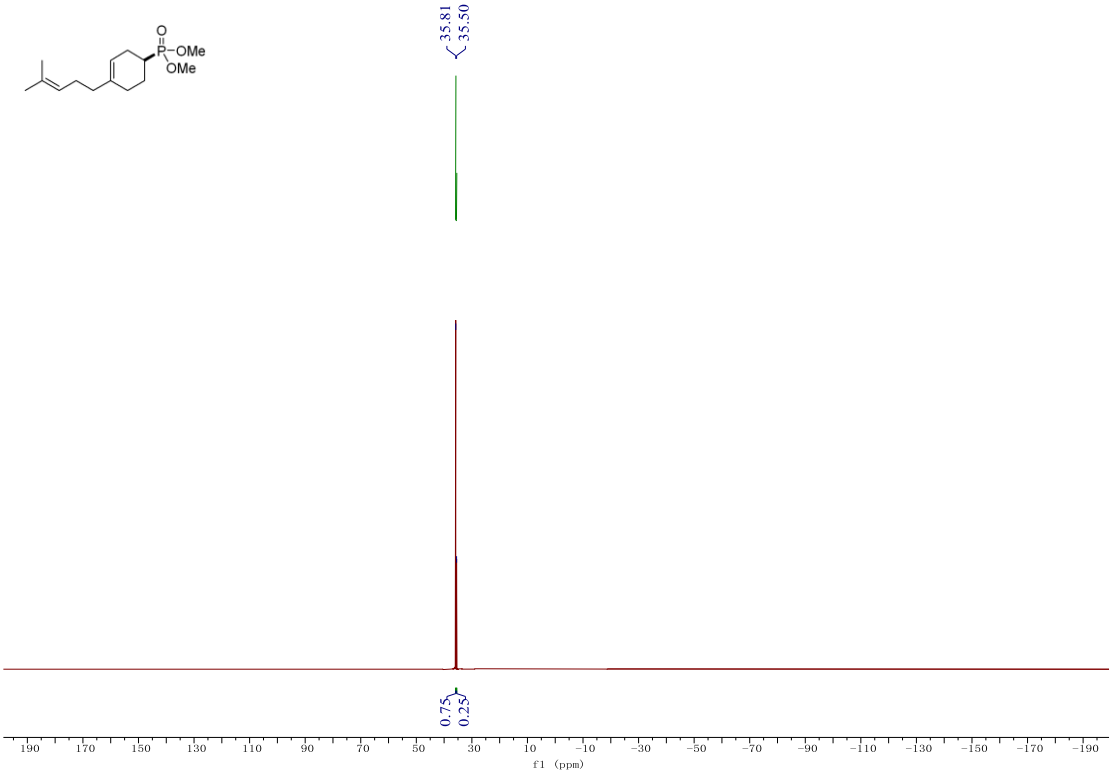
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

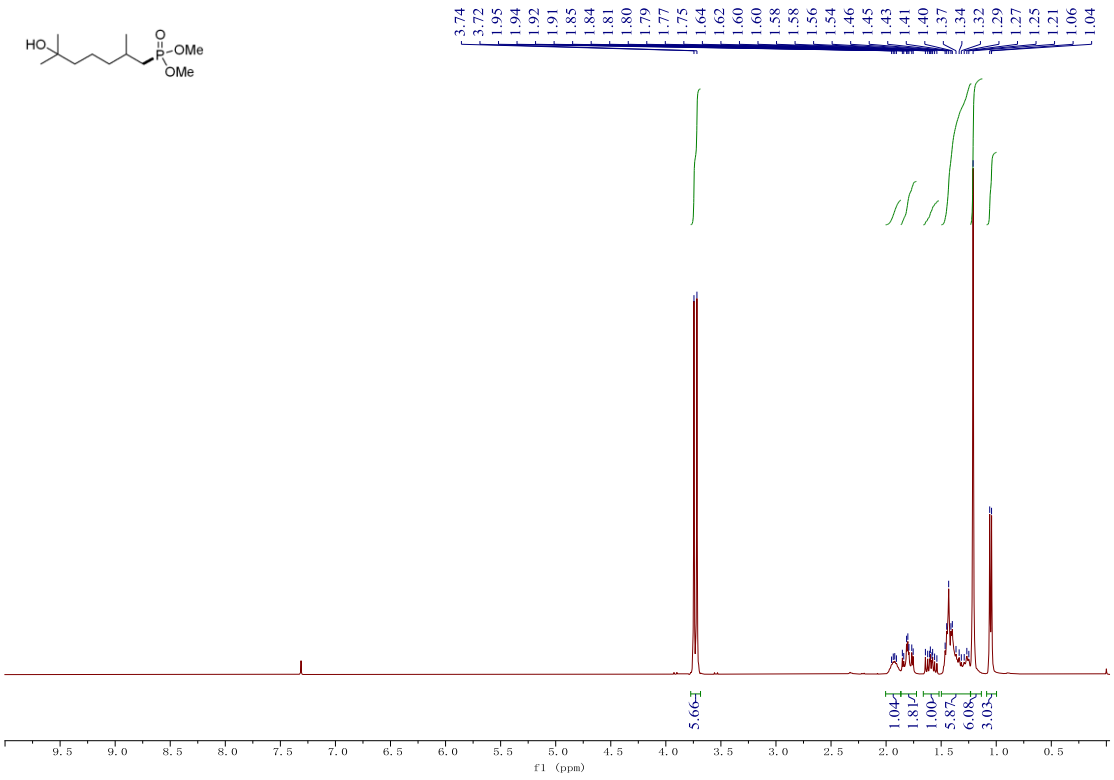


^{31}P NMR (162 MHz, $CDCl_3$):

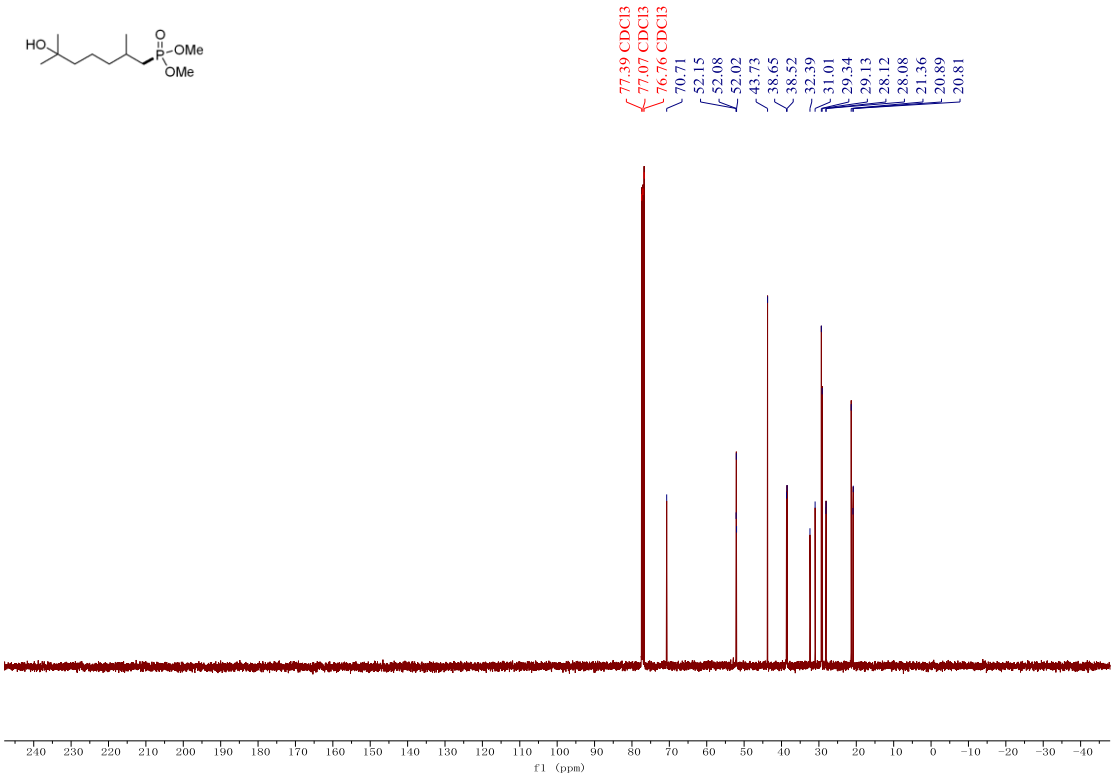


Compound **10**

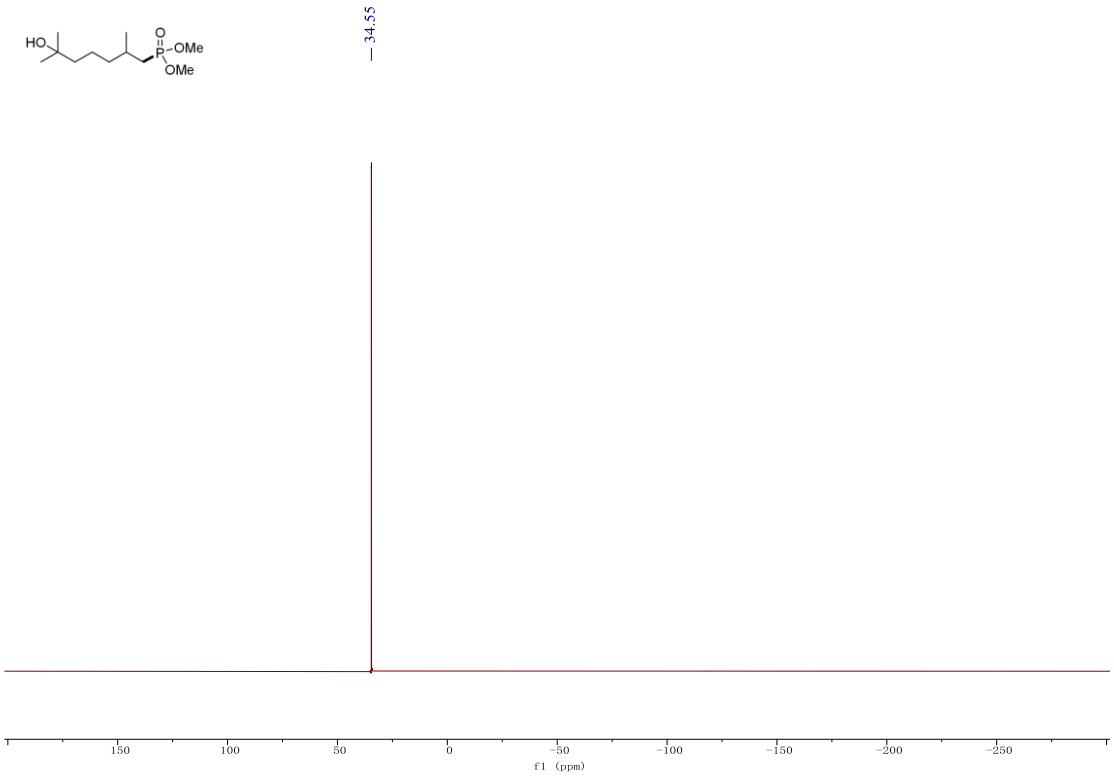
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

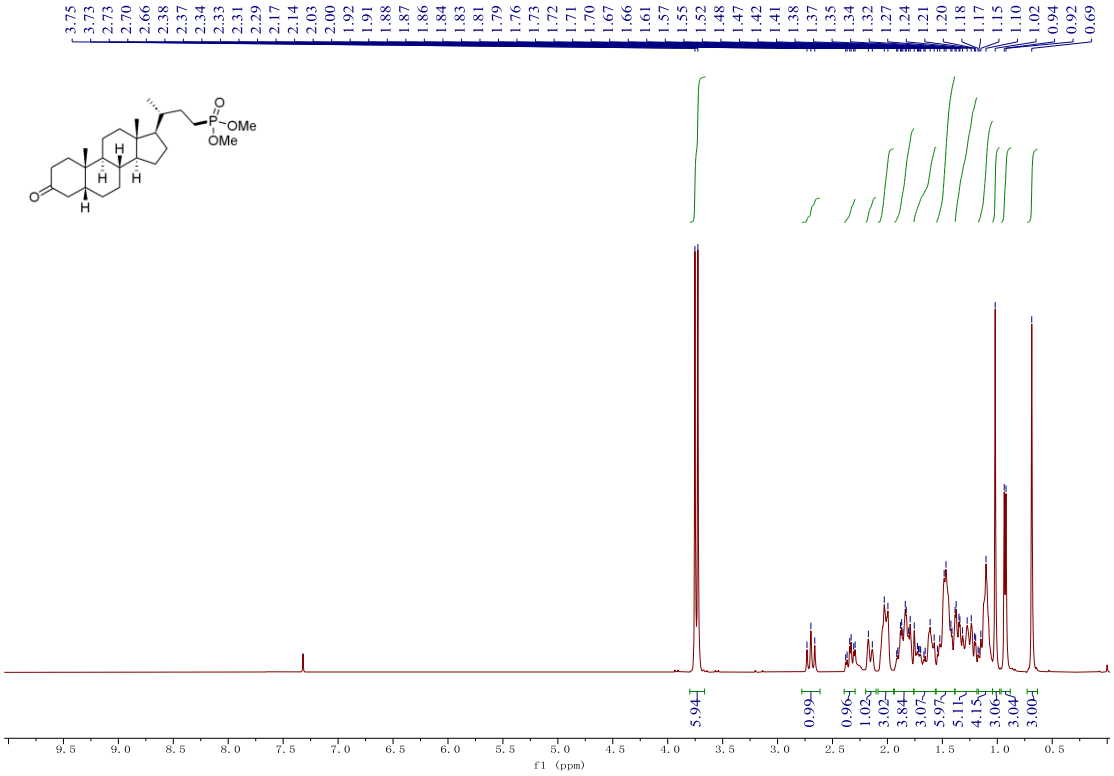


^{31}P NMR (162 MHz, $CDCl_3$):

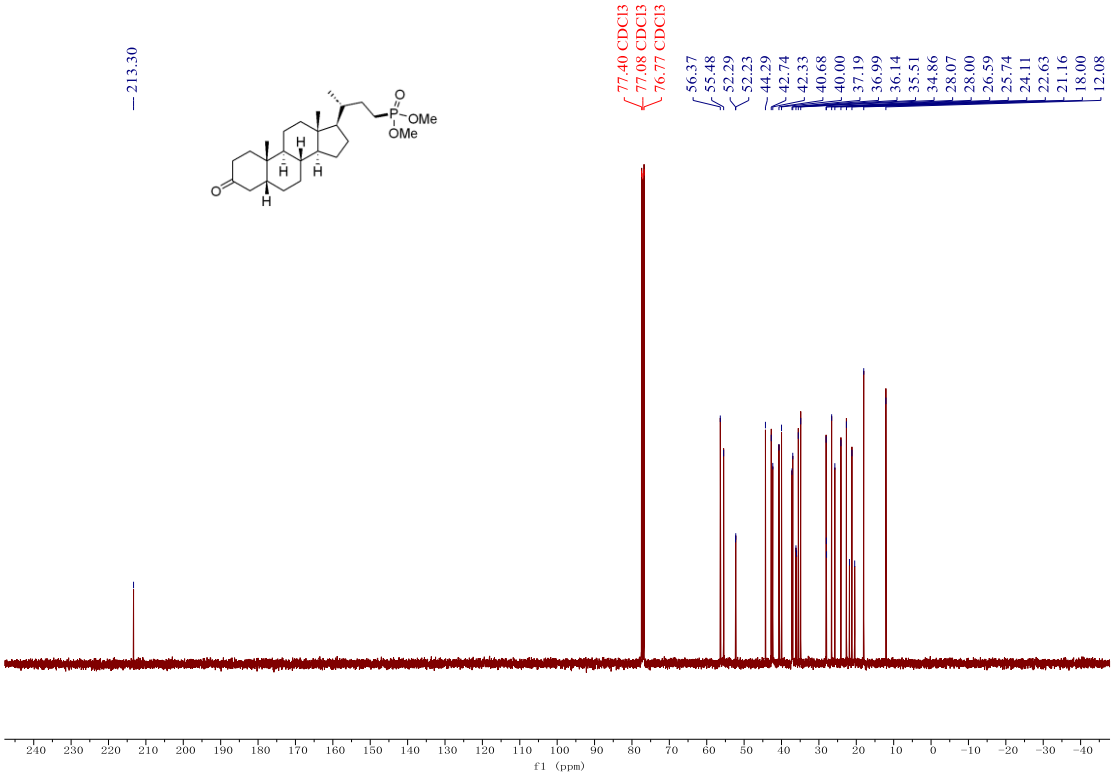


Compound **11**

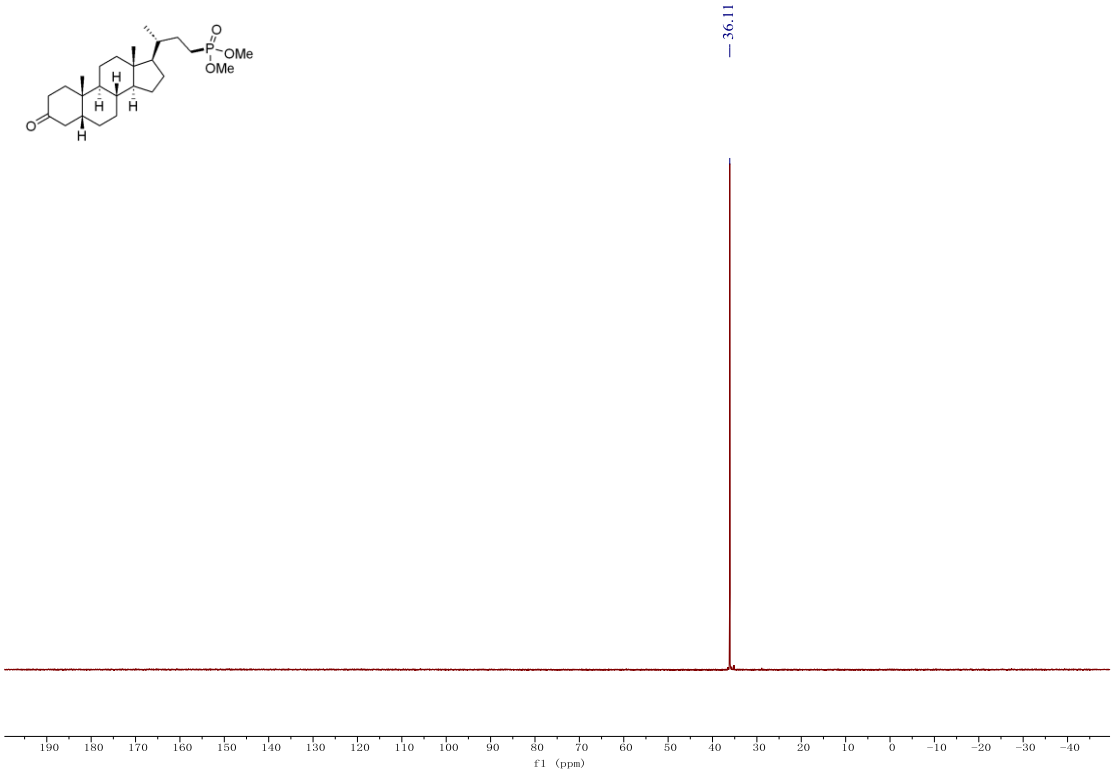
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

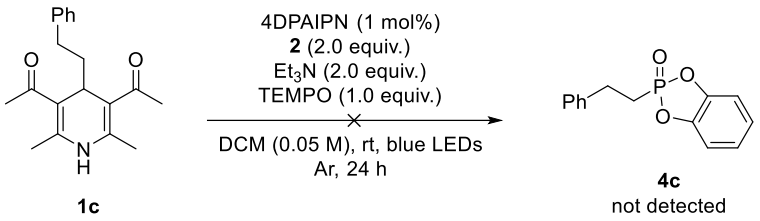


^{31}P NMR (162 MHz, $CDCl_3$):



7. Mechanistic studies

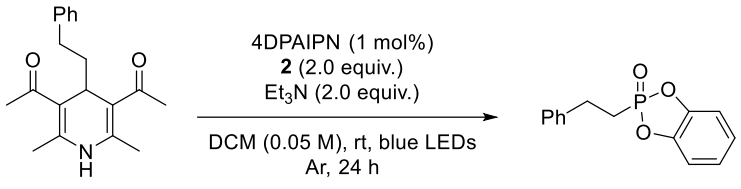
7-1. TEMPO Experiment



1c **4c** not detected

To a 10 mL oven-dried, sealed tube equipped with a Teflon-coated magnetic stir bar were added 4DPAIPN (0.8 mg, 0.001 mmol, 1 mol%), **1c** (30 mg, 0.1 mmol, 1.0 equiv.), 2,2,6,6-tetramethylpiperidinyloxyl (16 mg, 0.1 mmol, 1.0 equiv.) and **2** (64 mg, 0.2 mmol, 2.0 equiv.). The tube was evacuated and backfilled with argon three times. Triethylamine (20 uL, 0.2 mmol, 2.0 equiv.) and DCM (2.0 mL) were added successively. The tube was sealed and the mixture was stirred at room temperature for 24 h under blue light irradiation. The expected product formation was inhibited completely, as indicated by ^{31}P NMR analysis with tributyl phosphate (27 uL, 0.1 mmol) as internal standard.

7-2. Light On/off Experiment



1c **4c**

Eight parallel reactions were conducted. To a 10 mL oven-dried, sealed tube equipped with a Teflon-coated magnetic stir bar were added 4DPAIPN (0.8 mg, 0.001 mmol, 1 mol%), **1c** (30 mg, 0.1 mmol, 1.0 equiv.) and **2** (64 mg, 0.2 mmol, 2.0 equiv.). The tube was evacuated and backfilled with argon three times. Triethylamine (20 uL, 0.2 mmol, 2.0 equiv.) and DCM (2.0 mL) were added successively. The tube was sealed and the mixture was stirred at room temperature for indicated time under blue light irradiation. The light was turned on and off every 5 h. The crude mixture was

analyzed by ^{31}P NMR with tributyl phosphate (27 uL, 0.1 mmol) as internal standard to determine the yield of **4c**.

Table S7. Data of light ON/OFF experiment

time (h)	yield of **4c** (%)	light
0	0	/
5	12	on
10	12	off
15	16	on
20	16	off
25	28	on
30	28	off
35	43	on
40	43	off

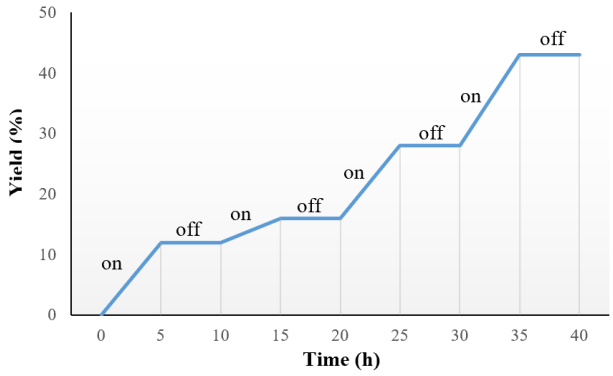
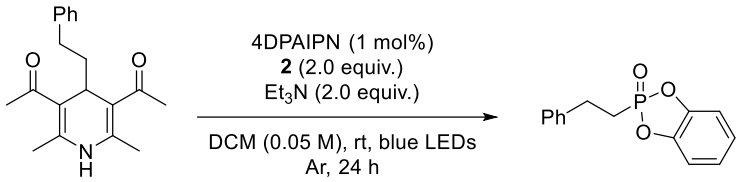


Figure S2. Light ON/OFF experiment

7-3. Quantum Yield Calculations

The quantum yield of the reaction was determined using the procedure reported previously.[s11] 1,4-Dihydropyridine compound **1c** and 9-fluorenyl *o*-phenylene phosphite **2** were used as model substrates to determinate the quantum yield of this transformation. Blue LED (λ_{max} = 440 nm) was used for measurement of quantum yield.



1c **4c**

7-3-1. Incident light absorbed by 4DPAIPN.

The fraction of light, f, absorbed was determined according to equation S:

$$F = 1 - 10^{-A} \quad \text{(eq S)}$$

Where A is the absorbance of 4DPAIPN in DCM at 440 nm, The absorbance (A) of 4DPAIPN in DCM (1 mol%) was determined to be 1.55, thus indicating the fraction of light absorbed is 0.97.

7-3-2. Photon flux at 440 nm

The following solutions were prepared in the dark (flasks were wrapped in aluminum foil) and stored in the dark at rt:

Ferrioxalate solution (0.15 M Ferrioxalate/0.05 M H_2SO_4): Potassium ferrioxalate hydrate (1.13 g, 3.0 mmol) was added to a flask wrapped in aluminum foil containing H_2SO_4 (20 mL, 0.05 M). The flask was stirred for complete solvation of the green solid in complete darkness. It is noteworthy that the solution should not be exposed to any incident light.

Developer solution: 1,10-Phenanthroline (50 mg) and NaOAc (11.25 g) were added to a flask containing H_2SO_4 (50 mL, 0.5 M) and sonicated until completely solvated.

7-3-3. The absorbance of the non-irradiated sample. The developer solution (350 μL) was added to a ferrioxalate solution (2.0 mL) in a vial that had been covered with aluminum foil. The vial was capped and allowed to rest for 1 h and then transferred to a cuvette. The absorbance of the non-irradiated solution was measured to be 0.32 at 510 nm.

7-3-4. The absorbance of the irradiated sample. In a cuvette equipped with a stir bar was added the ferrioxalate solution (2.0 mL), and the stirred solution was irradiated for 90 s at λ = 440 nm. After irradiation, the developer solution (350 μL) was added to the cuvette and allowed to rest for 1 h in the dark to allow the ferrous ions to coordinate completely to 1,10-phenanthroline. The absorbance was measured

at 510 nm to be 2.10 (90 s).

Photon flux sample calculation:

$$\text{mol}\,(Fe^{+2}) = \frac{\text{V} \cdot \Delta\text{A}}{l \cdot \epsilon}$$

Where V is the total volume (0.00235 L) of the solution after addition of 1,10-phenanthroline, Δ A is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions (2.10-0.32 = 1.78), *l* is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11100 L mol^{-1} cm^{-1}).

The photon flux can be calculated as follows:

$$\text{photon flux} = \frac{mol\,(Fe^{2+})}{\Phi \cdot t \cdot f}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (approximated with the literature known value of 1.01 for a 0.15 M solution at λ = 436 nm), *t* is the irradiation time, and *f* is the fraction of light absorbed (approximated with the literature known value of 0.997 at λ = 436 nm). Photon flux = 4.16×10^{-9} Einstein s^{-1}.

7-3-5. Determination of quantum yield of phosphonylation of 1c with 2

The photoredox transformation was developed using the typical procedure for 5 h, tributyl phosphate (27 uL, 0.1 mmol) was added as internal standard. The yield of the reaction was determined by ^{31}P NMR, where 0.012 mmol (12%) of the desired compound were obtained.

The quantum yield was calculated as follows:

$$\Phi = \frac{mol\ product}{flux \cdot t \cdot f}$$

where *flux* is the photon flux determined by ferrioxalate actinometry (4.16×10^{-9} Einstein s^{-1}), *t* is the time (5 h = 18000 s), and *f* is the fraction of light absorbed by 4DPAIPN at 440 nm (0.97).

The quantum yield of the reaction was determined to be: Φ = 0.0018

7-4. Cyclic Voltammograms for DHP 1c and 2

Cyclic voltammetry experiments were carried out using a 3-electrode system consisting of a glassy carbon working electrode, a platinum counter electrode, and a

Ag/AgCl (in sat. KCl) electrode as the reference electrode. The scan rate was 0.1 V/s. All samples were prepared from spectrophotometric grade dichloromethane and 0.1 M tetrabutylammonium perchlorate ($TBAClO_4$) was used as the supporting electrolyte. The CVs taken were as follows: (a) 5 mM compound **2**; (b) 5 mM compound **1c**.

As shown in the figure below, the oxidation potential of the compound **1c** is around +1.19 V (peak) in DCM (+0.97 V vs SCE), the oxidation potential of the compound **2** is around +2.20 V (peak) in DCM (+1.98 V vs SCE). According to the reported literature,[s12] $E_{1/2}(PC^*/PC^{-\bullet})$ = +1.10 V vs SCE, indicating that the triplet-excited photocatalyst was reduced by **1c**.

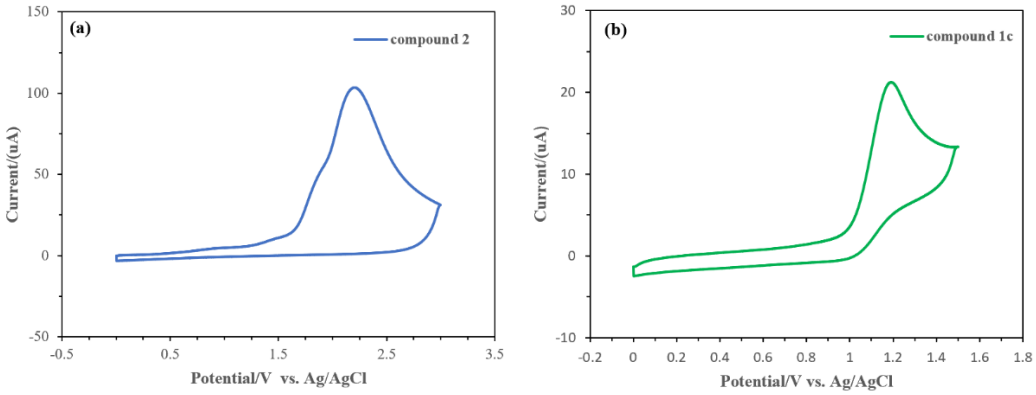


Figure S4. CV spectrum of (a) compound **2** in DCM and (b) compound **1c** in DCM.

7-5. Stern-Volmer Quenching Studies

Preparation of stock solutions:

A stock solution of photocatalyst was prepared by dissolving 4DPAIPN (8 mg, 0.01 mmol) in DCM (1.0 mL). Of this solution, 20 uL were further diluted with DCM to give a total volume of 2.0 mL. Concentration of [4DPAIPN] = 1.0×10^{-4} M.

A stock solution of compound **1c** was prepared by dissolving **1c** (15 mg, 0.05 mmol) in DCM (1.0 mL). Of this solution, 30 uL were further diluted with DCM to give a total volume of 3.0 mL. Concentration of [**1c**] = 5.0×10^{-4} M.

A stock solution of compound Et_3N was prepared by dissolving Et_3N (10 mg, 0.1 mmol) in DCM (2.0 mL). Of this solution, 30 uL were further diluted with DCM to give a total volume of 3.0 mL. Concentration of [Et_3N] = 5.0×10^{-4} M.

A stock solution of compound **2** was prepared by dissolving **2** (16 mg, 0.05 mmol) in DCM (1.0 mL). Of this solution, 30 uL were further diluted with DCM to give a total volume of 3.0 mL. Concentration of [**2**] = 5.0×10^{-4} M.

All 4DPAIPN solutions were excited at 388 nm and the emission intensity was collected at 535 nm. In a typical experiment, quartz cuvettes (3.5 mL, Teflon cap) were filled with 4DPAIPN stock solution (10 uL) and DCM (3.0 mL), the emission of the blank sample was collected (I_0). Then **1c** stock solution (20 uL) was added as quencher and recorded the emission spectra (I). Different amounts of stock solution **1c**, Et_3N and **2** were added to obtain a total volume of 3.0 mL, the emission of the sample was collected.

Stern-Volmer analysis indicated that this reaction proceeded through an oxidative quenching mechanism of 4DPAIPN by **1c**.

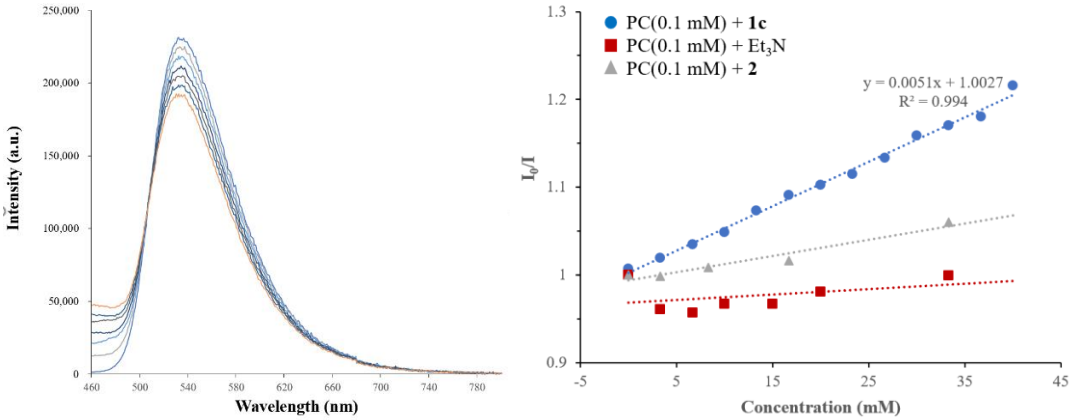


Figure S5. Fluorescence quenching experiments of 4DPAIPN with **1c**, Et_3N or **2** in DCM: (*left*) Phosphorescence of 4DPAIPN at different concentrations of **1c** and (*right*) Stern-Volmer plot for quenching of **1c**, Et_3N and **2**.

8. References S1-S12

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