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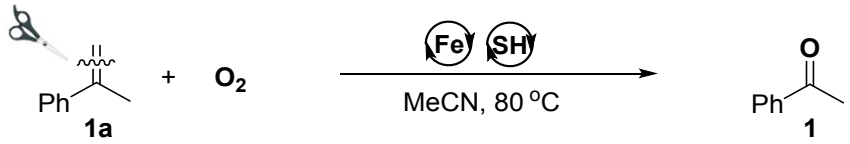
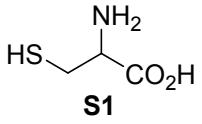
General information: ^{1}H NMR ad ^{13}C NMR spectra were recorded on an Agilent 400MR or 600MR DD2 spectrometer at ambient temperature. Chemical shifts (δ) are reported in ppm, ad coupling constats (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{1}H NMR using mesitylene as an internal standard before working up the reaction.

Materials: All reagents were used as received from commercial sources, unless specified otherwise. MeCN, DCM and Toluene were distilled under reduced pressure from CaH_2. 1,4-Dioxane and THF were distilled from sodium and benzophenone before use.

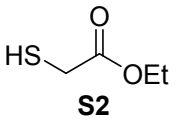
Table S1. Optimization of the Iron-Catalyzed Oxidation of 2-Phenyl-1-propene 1a.[a]



entry	[Fe]	[Thiol]	Temperature	Oxidant	Solvent (mL)	**1** yield (%)[b]
1	$Fe(OTf)_2$	**S1**	80 °C	O_2	MeCN (0.5)	30
2	$Fe(ClO_4)_2$	**S1**	80 °C	O_2	MeCN (0.5)	32
3	$FeCl_2$	**S2**	80 °C	O_2	MeCN (0.5)	19
4	$Fe(ClO_4)_2$	**S2**	80 °C	O_2	MeCN (0.5)	44
5	**Fe1**	**S2**	80 °C	O_2	MeCN (0.5)	44
6	$Fe(OTf)_2$	**S3**	80 °C	O_2	MeCN (0.5)	38
7	$Fe(ClO_4)_2$	**S3**	80 °C	O_2	MeCN (0.5)	31
8	**Fe4**	**S3**	80 °C	O_2	MeCN (0.5)	38
9	***Fe4***	***S3***	*80 °C*	*O_2*	*MeCN (0.5)*	*39*[c]
10	$Fe(OTf)_2$	**S4**	80 °C	O_2	MeCN (0.5)	40
11	**Fe1**	**S4**	80 °C	O_2	MeCN (0.5)	45
12	**Fe2**	**S4**	80 °C	O_2	MeCN (0.5)	67
13	**Fe3**	**S4**	80 °C	O_2	MeCN (0.5)	64
14	***Fe4***	***S4***	*80 °C*	***O_2***	*MeCN (0.5)*	***85 (81)***
15	**Fe1**	**PhSH**	80 °C	O_2	MeCN (0.5)	33
16	**Fe2**	**PhSH**	80 °C	O_2	MeCN (0.5)	67
17	**Fe4**	**PhSH**	80 °C	O_2	MeCN (0.5)	72
18	**Fe4**	**S4**	80 °C	O_2	MeCN (2.0)	71
19	**Fe4**	**S4**	60 °C	O_2	MeCN (0.5)	71
20	**Fe4**	**S4**	40 °C	O_2	MeCN (0.5)	19
21	**Fe4**	**S4**	rt	O_2	MeCN (0.5)	16
22	**Fe4**	**S4**	80 °C	air	MeCN (0.5)	40
23	**Fe4**	**S4**	80 °C	Ar	MeCN (0.5)	nd
24	**Fe4**	**S4**	80 °C	O_2	DCE (0.5)	70
25	**Fe4**	**S4**	80 °C	O_2	Toluene (0.5)	65
26	**Fe4**	**S4**	80 °C	O_2	Acetone (0.5)	53
27	**Fe1**	none	80 °C	O_2	MeCN (0.5)	29
28	**Fe4**	none	80 °C	O_2	MeCN (0.5)	trace
29	$Fe(OTf)_2$	none	80 °C	O_2	MeCN (0.5)	< 5
30	$Fe(ClO_4)_2$	none	80 °C	O_2	MeCN (0.5)	15



S1



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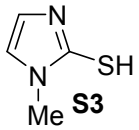
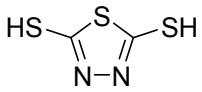
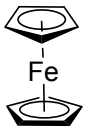


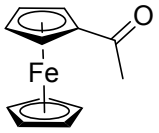
S3



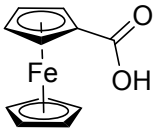
S4



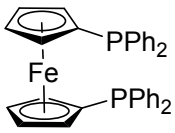
Fe1



Fe2



Fe3

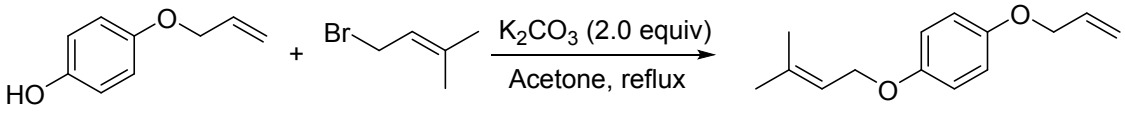


Fe4

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), O_2 (1 atm), [Fe] (0.03 mmol, 0.1 equiv), thiol (0.03 mmol, 0.1 equiv), MeCN (0.5 mL), 80 °C,15 h. [b]Determined by ^{1}H NMR using mesitylene as an internal standard. The isolated yield is shown in parentheses. [c][Fe] (0.03 mmol, 0.1 equiv), thiol (0.06 mmol, 0.2 equiv), MeCN (0.5 mL), 80 °C, 15 h.

Characterization data of alkenes

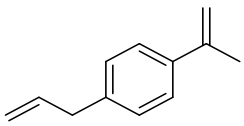
1-(Allyloxy)-4-((3-methylbut-2-en-1-yl)oxy)benzene (29a)



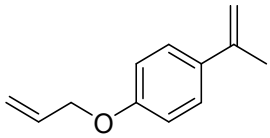
29a

4-(Allyloxy)phenol (1.50 g, 10 mmol, 1.0 equiv) and K_2CO_3 (2.76 g, 20 mmol, 2.0 equiv) was added to a 50 ml of Schlenk tube under N_2, then acetone (10 mL) and 3,3-Dimethylallyl bromide (1.79 g, 12 mmol, 1.2 equiv) was injected by syringe. This mixture was heated to 80 °C and allowed to react for 5 h. The reaction mixture was filtered and the solvents removed in vacuo, the reaction crude was purified with silica gel chromatography (Petroleum ether/EtOAc = 40:1) to provide the product (1.53 g, 70% yield) as a colorless liquid.

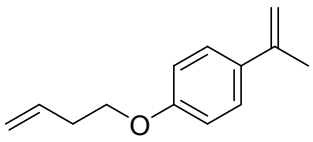
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 4 H), 6.09-5.99 (m, 1 H), 5.51-5.46 (m, 1 H), 5.42-5.36 (m, 1 H), 5.28-5.24 (m, 1 H), 4.49-4.44 (m, 4 H), 1.78 (s, 3 H), 1.72 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 152.7, 137.9, 133.6, 119.9, 117.4, 115.6, 115.5, 69.5, 65.3, 25.8, 18.1. HRMS: Calculated for $C_{14}H_{18}O_2$ $(M+Na)^+$: 241.1199; Found: 241.1203.



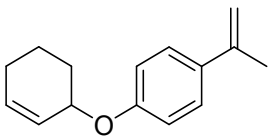
1-Allyl-4-(prop-1-en-2-yl)benzene (30a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 2 H), 6.06-5.96 (m, 1 H), 5.39 (s, 1 H), 5.16-5.11 (m, 1 H), 5.11-5.08 (m, 2 H), 3.43 (d, *J* = 6.8 Hz, 2 H), 2.19 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 139.3, 139.1, 137.3, 128.4, 125.5, 115.8, 111.8, 39.8, 21.8. HRMS: Calculated for $C_{12}H_{14}$ (M^+): 158.1096; Found:158.1092.



1-(Allyloxy)-4-(prop-1-en-2-yl)benzene (31a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.8 Hz, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 6.12-6.03 (m, 1 H), 5.46-5.41 (m, 1 H), 5.32-5.29 (m, 2 H), 5.01-5.00 (m, 1 H), 4.57-4.55 (m, 2 H), 2.15 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 142.5, 133.8, 133.2, 126.5, 117.7, 114.3, 110.7, 68.8, 21.9. HRMS: Calculated for $C_{12}H_{14}O$ $(M+H)^+$: 175.1117; Found: 175.1121.

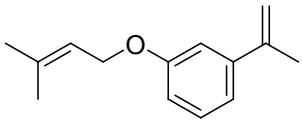


1-(But-3-en-1-yloxy)-4-(prop-1-en-2-yl)benzene (32a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 5.98-5.88 (m, 1 H), 5.31 (s, 1 H), 5.22-5.12 (m, 2 H), 5.01 (s, 1 H), 4.04 (t, *J* = 6.8 Hz, 2 H), 2.60-2.54 (m, 2 H), 2.15 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 142.5, 134.4, 133.7, 126.5, 117.0, 114.2, 110.6, 67.2, 33.6, 21.9. HRMS: Calculated for $C_{13}H_{16}O$ $(M+H)^+$: 189.1273; Found: 189.1277.

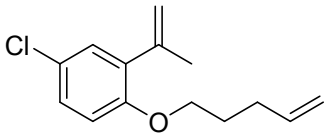


1-(Cyclohex-2-en-1-yloxy)-4-(prop-1-en-2-yl)benzene (33a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 6.00-5.96 (m, 1 H), 5.90-5.86 (m, 1 H), 5.29 (s, 1 H), 4.99

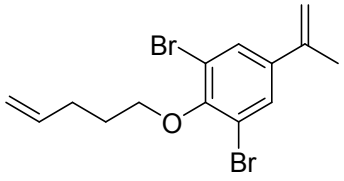
(s, 1 H), 4.83-4.79 (m, 1 H), 2.14 (s, 3 H), 2.08-1.80 (m, 5 H), 1.69-1.60 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 142.5, 133.6, 132.1, 126.6, 126.3, 115.4, 110.5, 70.9, 28.3, 25.1, 21.9, 19.0. HRMS: Calculated for $C_{15}H_{18}O$ $(M+H)^+$: 215.1430; Found: 215.1434.



1-((3-Methylbut-2-en-1-yl)oxy)-3-(prop-1-en-2-yl)benzene (34a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.0 Hz, 1 H), 7.09-7.06 (m, 1 H), 7.04 (m, 1 H), 6.86 (dd, *J* = 8.0, *J* = 2.4 Hz, 1 H), 5.56-5.51 (m, 1 H), 5.38 (s, 1 H), 5.10 (s, 1 H), 4.55 (d, *J* = 6.4 Hz, 2 H), 2.16 (s, 3 H), 1.82 (s, 3 H), 1.78 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 143.2, 142.7, 138.1, 129.1, 119.8, 118.0, 113.3, 112.5, 112.4, 64.7, 25.8, 21.8, 18.2. HRMS: Calculated for $C_{14}H_{18}O$ (M^+): 202.1358; Found: 202.1364.

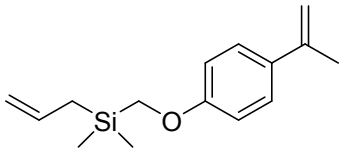


4-Chloro-1-(pent-4-en-1-yloxy)-2-(prop-1-en-2-yl)benzene (35a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 1 H), 7.17-7.15 (m, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 5.90-5.90 (m, 1 H), 5.15 (m, 1 H), 5.08 (m, 1 H), 5.08-5.04 (m, 1 H), 4.99 (d, *J* = 8.4 Hz, 1 H), 3.96 (t, *J* = 6.4 Hz, 2 H), 2.27-2.11 (m, 2 H), 2.11 (s, 3 H), 1.93-1.86 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 143.1, 137.6, 134.4, 129.2, 127.7, 125.1, 115.8, 115.3, 113.0, 67.8, 30.2, 28.4, 23.0. HRMS: Calculated for $C_{14}H_{17}ClO$ (M^+): 236.0968; Found: 236.0977.

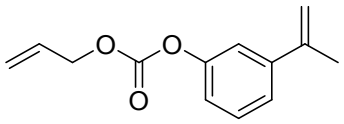


1,3-Dibromo-2-(pent-4-en-1-yloxy)-5-(prop-1-en-2-yl)benzene (36a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 2 H), 5.94-5.84 (m, 1 H), 5.30 (s, 1 H), 5.12-5.07 (m, 1 H), 5.09 (s, 1 H), 5.02-4.99 (d, *J* = 10.0 Hz, 1 H), 4.01 (t, *J* = 6.4 Hz, 2 H), 2.35-2.29 (m, 2 H), 2.07 (s, 3 H), 2.00-1.93 (m, 2 H). ^{13}C

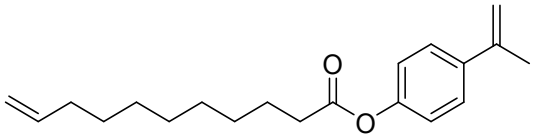
NMR (100 MHz, $CDCl_3$) δ 152.5, 140.4, 139.7, 138.0, 129.7, 118.1, 115.0, 114.0, 72.9, 30.1, 29.3, 21.6. HRMS: Calculated for $C_{14}H_{16}Br_2O$ $(M+Na)^+$: 380.9460; Found: 380.9462.



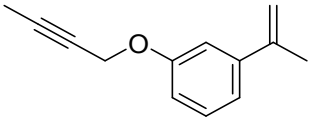
Allyldimethyl((4-(prop-1-en-2-yl)phenoxy)methyl)silae (37a) ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 5.87-5.77 (m, 1 H), 5.28 (s, 1 H), 4.98 (m, 1 H), 4.93-4.85 (m, 2 H), 3.61 (s, 2 H), 2.13 (s, 3 H), 1.70 (d, *J* = 8.0, 2 H), 0.15 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 142.7, 134.2, 133.4, 126.4, 113.7, 113.5, 110.4, 59.6, 21.9, 21.5, -5.1. HRMS: Calculated for $C_{15}H_{22}OSi$ $(M+H)^+$: 247.1512; Found: 247.1518.



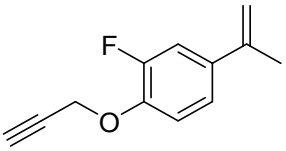
Allyl (3-(prop-1-en-2-yl)phenyl) carbonate (38a) ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 2 H), 7.26 (s, 1 H), 7.12-7.06 (m, 1 H), 6.06-5.96 (m, 1 H), 5.44 (dd, *J* = 17.6, *J* = 1.2 Hz, 1 H), 5.39 (s, 1 H), 5.34 (dd, *J* = 10.4, *J* = 1.2 Hz, 1 H), 5.12 (s, 1 H), 4.75 (d, *J* = 6.0 Hz, 2 H), 2.14 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 151.0, 142.9, 142.1, 131.1, 129.2, 123.2, 119.9, 119.6, 118.2, 113.5, 69.2, 21.7. HRMS: Calculated for $C_{13}H_{14}O_3$ $(M+H)^+$: 219.1015; Found: 219.1019.



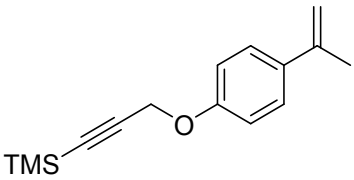
4-(Prop-1-en-2-yl)phenyl undec-10-enoate (39a) ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 5.87-5.76 (m, 1 H), 5.34 (s, 1 H), 5.08 (s, 1 H), 5.01 (d, *J* = 16.4 Hz, 1 H), 4.93 (d, *J* = 10.4 Hz, 1 H), 2.55 (t, *J* = 7.6 Hz, 2 H), 2.14 (s, 3 H), 2.05 (q, *J* = 7.6 Hz, 2 H), 1.79-1.71 (m, 2 H), 1.42-1.25 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 150.0, 142.4, 139.2, 138.8, 126.5, 121.2, 114.1, 112.6, 34.4, 33.8, 29.3, 29.2, 29.1, 29.0, 28.9, 24.9, 21.9. HRMS: Calculated for $C_{20}H_{28}O_2$ $(M+Na)^+$: 323.1981; Found: 323.1985.



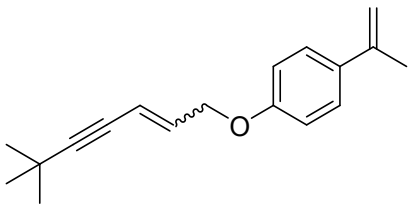
1-(But-2-yn-1-yloxy)-3-(prop-1-en-2-yl)benzene (40a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 8.4, 1 H), 7.10-7.07 (m, 2 H), 6.88 (dd, *J* = 8.4, *J* = 6.0 Hz, 1 H), 5.37 (s, 1 H), 5.08 (s, 1 H), 4.66 (dd, *J* = 4.8, *J* = 2.4 Hz, 2 H), 2.14 (s, 3 H), 1.87 (t, *J* = 2.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 143.0, 142.7, 129.0, 118.6, 113.4, 112.7, 112.6, 83.7, 74.0, 56.4, 21.8, 3.6. HRMS: Calculated for $C_{13}H_{14}O$ $(M+H)^+$: 187.1117; Found: 187.1121.



2-Fluoro-4-(prop-1-en-2-yl)-1-(prop-2-yn-1-yloxy)benzene (41a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.17 (m, 2 H), 7.05 (t, *J* = 8.4 Hz, 2 H), 5.31 (s, 1 H), 5.05 (s, 1 H), 4.77 (d, *J* = 2.4 Hz, 2 H), 2.54 (t, *J* = 2.4 Hz, 1 H), 2.11 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (*J* = 245.0 Hz), 144.6 (*J* = 11.0 Hz), 141.4 (*J* = 2.0 Hz), 135.8 (*J* = 7.0 Hz), 121.0 (*J* = 3.0 Hz), 115.4 (*J* = 2.0 Hz), 113.6 (*J* = 18.0 Hz), 112.2, 78.0, 76.2, 57.1, 21.6. HRMS: Calculated for $C_{12}H_{11}FO$ (M^+): 190.0794; Found: 190.0788.

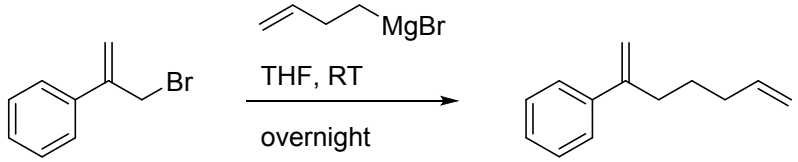


Trimethyl(3-(4-(prop-1-en-2-yl)phenoxy)prop-1-yn-1-yl)silae (42a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 2 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 5.31 (s, 1 H), 5.01 (s, 1 H), 4.68 (s, 2 H), 2.14 (s, 3 H), 0.19 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 142.4, 134.3, 126.5, 114.5, 110.9, 100.0, 92.7, 56.7, 21.9, -0.2. HRMS: Calculated for $C_{15}H_{20}OSi$ $(M+H)^+$: 245.1356; Found: 245.1359.



1-((6,6-Dimethylhept-2-en-4-yn-1-yl)oxy)-4-(prop-1-en-2-yl)benzene (43a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 6.23-6.16 (m, 1 H), 5.87-5.82 (m, 1 H), 5.29 (s, 1 H), 5.00 (m, 1 H), 4.57 (dd, *J* = 5.6, *J* = 1.6 Hz, 2 H), 2.13 (s, 3 H), 1.25 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 142.5, 135.8, 134.0, 126.6, 114.3, 113.3, 110.8, 100.1, 67.8, 30.9, 27.9, 21.9. HRMS: Calculated for $C_{18}H_{22}O$ $(M+H)^+$: 255.1743; Found: 255.1748.

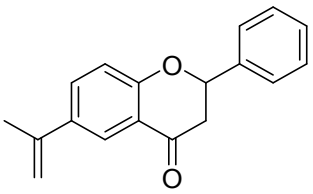
Hepta-1,6-dien-2-ylbenzene (44a)



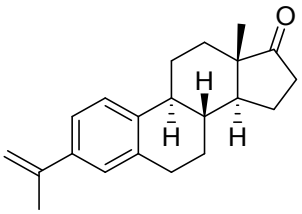
44a

To a solution of the α-bromomethyl styrenes (985 mg, 5 mmol, 1.0 equiv) in THF (20 mL) was added 0.5 M solution of 3-Butenylmagnesium bromide in THF (30 mL, 15 mmol, 3 equiv) at room temperature. The reaction mixture was stirred at room temperature overnight, before it was quenched by adding sat. aq. NH_4Cl solution. Then the aqueous solution was extracted with diethyl ether three times. The combined orgaic phases were washed with sat. aq. $NaHCO_3$ solution and brine, dried over Na_2SO_4, filtered and removed in vacuo. The reaction crude was purified with silica gel chromatography (Petroleum ether/EtOAc = 40:1) to provide the product (440 mg, 51% yield) as a colorless liquid.

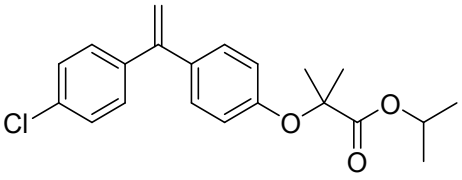
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2 H), 7.40-7.36 (m, 2 H), 7.33-7.29 (m, 1 H), 5.91-5.81 (m, 1 H), 5.33 (m, 1 H), 5.12 (m, 1 H), 5.08-5.04 (m, 1 H), 5.02-5.00 (m, 1 H), 2.57 (t, *J* = 7.6 Hz, 2 H), 2.14 (dd, *J* = 14.8, *J* = 7.2 Hz, 2 H), 1.65-1.57 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 141.3, 138.6, 128.2, 127.3, 126.1, 114.7, 112.3, 34.7, 33.3, 27.4. HRMS: Calculated for $C_{13}H_{16}$ (M^+): 172.1252; Found: 172.1256.



2-Phenyl-6-(prop-1-en-2-yl)chroma-4-one (45a) This compound was synthesized via cross-coupling according to the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.4 Hz, 1 H), 7.68 (dd, *J* = 8.4, *J* = 2.4 Hz, 1 H), 7.51-7.38 (m, 5 H), 7.03 (d, *J* = 8.4 Hz, 1 H), 5.49 (dd, *J* = 13.2, *J* = 2.8 Hz, 1 H), 5.38 (s, 1 H), 5.09 (s, 1 H), 3.10 (dd, *J* = 16.8, *J* = 13.2 Hz, 1 H), 2.91 (dd, *J* = 16.8, *J* = 2.8 Hz, 1 H), 2.16 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 160.9, 141.6, 138.6, 134.6, 133.4, 128.89, 128.85, 126.1, 123.5, 120.2, 118.0, 112.2, 79.6, 44.6, 21.8. HRMS: Calculated for $C_{18}H_{16}O_2$ $(M+H)^+$: 265.1223; Found: 265.1227.



(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(prop-1-en-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenathren-17-one (46a) This compound was synthesized via cross-coupling according to the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 2 H), 7.19 (s, 1 H), 5.32 (s, 1 H), 5.03 (s, 1 H), 2.92 (dd, *J* = 9.2, *J* = 4.4 Hz, 2 H), 2.53-2.40 (m, 2 H), 2.33-2.27 (m, 1 H), 2.18-1.94 (m, 7 H), 1.68-1.40 (m, 6 H), 1.90 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.8, 143.0, 139.0, 138.8, 136.2, 126.1, 125.2, 123.0, 111.8, 50.5, 48.0, 44.4, 38.2, 35.8, 31.6, 29.5, 26.6, 25.7, 21.8, 21.6, 13.8. HRMS: Calculated for $C_{21}H_{26}O$ $(M+Na)^+$:317.1875; Found: 317.1879.



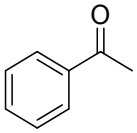
Isopropyl 2-(4-(1-(4-chlorophenyl)vinyl)phenoxy)-2-methylpropaoate (47a) This compound was synthesized via methylenation of the Fenofibrate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.23 (m, 4 H), 7.17 (d, *J* = 8.8 Hz, 2 H), 6.78 (d, *J* = 8.8 Hz, 2 H), 5.38 (s, 1 H), 5.32 (s, 1 H), 5.13-5.03 (m, 1 H),

1.60 (s, 6 H), 1.21 (d, J = 6.0 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 155.4, 148.3, 140.1, 134.3, 133.4, 129.6, 128.8, 128.2, 118.2, 113.6, 79.0, 69.0, 25.3, 21.5. HRMS: Calculated for $C_{21}H_{23}ClO_3$ $(M+H)^+$: 359.1408; Found: 359.1410.

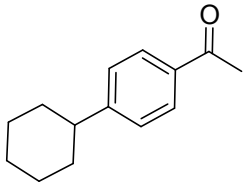
General procedure for the oxidative cleavage of alkenes

To a 25 ml of Schlenk tube was added **1,1'-bis(diphenylphosphino)ferrocene (dppf)** (16.6 mg, 0.03 mmol, 0.1 equiv) and **bismuththiol** (4.5 mg, 0.03 mmol, 0.1 equiv) at room temperature. The reaction tube was degassed with dioxygen gas (1 atm, 3 times), then alkenes (0.30 mmol, 1 equiv) and freshly distilled MeCN (0.5 mL) were added. The reaction mixture was heated to 80 ^{o}C and allowed to react for 15 h. The mixture was concentrated, and the residue was purified with silica gel chromatography to give product.

Characterization data of products

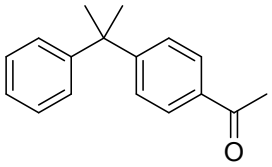


Acetophenone (1) The product (29 mg, 81% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (d, J = 7.6 Hz, 2 H), 7.55(t, J = 7.6 Hz, 1 H), 7.45 (t, J = 8.0 Hz, 2 H), 2.60 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 137.1, 133.0, 128.5, 128.2, 26.5. HRMS Calculated for C_8H_8O (M^+): 120.0575; Found: 120.0574

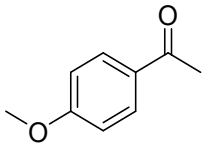


1-(4-Cyclohexylphenyl)etha-1-one (2) The product (46 mg, 76% yield) as a white solid was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.87 (d, J = 8.4 Hz, 2 H), 7.29 (d, J = 8.4 Hz, 2 H), 2.57 (s, 3 H),

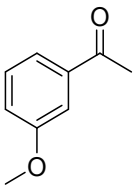
1.90-1.74 (m, 5 H), 1.48-1.23 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 153.7, 135.0, 128.5, 127.0, 44.7, 34.1, 26.7, 26.5, 26.0. HRMS: Calculated for $C_{14}H_{18}O$ $(M+Na)^+$: 225.1249; Found: 225.1248.



1-(4-(2-Phenylpropa-2-yl)phenyl)etha-1-one (3) The product (57 mg, 79% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 6.8, 2 H), 7.33 (d, J = 6.8, 2 H), 7.30-7.25 (m, 2 H), 7.22-7.17 (m, 3 H), 2.57 (s, 3 H), 1.71 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 156.3, 149.6, 134.6, 128.19, 128.15, 127.0, 126.6, 125.9, 43.2, 30.4, 26.5. HRMS: Calculated for $C_{17}H_{18}O$ $(M+H)^+$: 239.1430; Found: 239.1434.

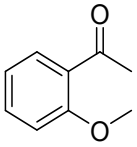


1-(4-Methoxyphenyl)etha-1-one (4) The product (36 mg, 80% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). This compound is known.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2 H), 6.92 (d, J = 8.4 Hz, 2 H), 3.85 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 163.4, 130.5, 130.3, 113.6, 55.4, 26.3. HRMS: Calculated for $C_9H_{10}O_2$ $(M+Na)^+$: 173.0573; Found: 173.0571.

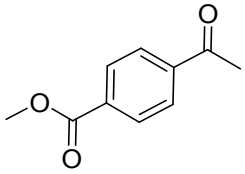


1-(3-Methoxyphenyl)etha-1-one (5) The product (34 mg, 75% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). This compound is known.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 1 H), 7.47 (m, 1 H), 7.36 (t, J = 8.0 Hz, 1 H), 7.12-7.09 (m, 1 H), 3.85 (s, 3 H), 2.59 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 159.8, 138.5,

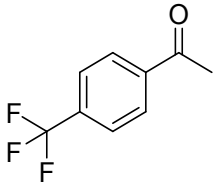
129.5, 121.1, 119.5, 112.3, 55.4, 26.7. HRMS: Calculated for $C_9H_{10}O_2$ $(M+Na)^+$: 173.0573; Found: 173.0576.



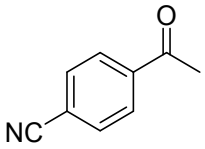
1-(2-Methoxyphenyl)etha-1-one (6) The product (23 mg, 50% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). This compound is known.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 8.0, J = 1.6 Hz, 1 H), 7.48-7.44 (m, 1 H), 7.01-6.96 (m, 2 H), 3.91 (s, 3 H), 2.61 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 158.9, 133.6, 130.3, 128.3, 120.5, 111.5, 55.4, 31.8. HRMS: Calculated for $C_9H_{10}O_2$ $(M+Na)^+$: 173.0573; Found: 173.0575.



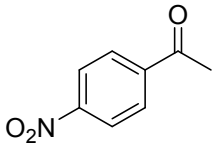
Methyl 4-acetylbenzoate (7) The product (43 mg, 81% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). This compound is known.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4, 2 H), 7.98 (d, J = 8.4, 2 H), 3.93 (s, 3H), 2.62 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 166.1, 140.2, 133.8, 129.7, 128.1, 52.4, 26.8. HRMS: Calculated for $C_{10}H_{10}O_3$ $(M+H)^+$: 179.0702; Found: 179.0706.



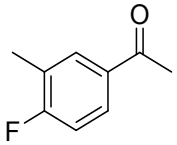
1-(4-(Trifluoromethyl)phenyl)etha-1-one (8) The product (39 mg, 70% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 2 H), 7.72 (d, J = 8.0 Hz, 2 H), 2.64 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 139.7, 134.5 (q, J = 32.0 Hz), 128.6, 125.7 (q, J = 3.6 Hz), 123.6 (q, J = 271.0 Hz), 26.7. HRMS: Calculated for $C_9H_7F_3O$ (M^+): 188.0449; Found: 188.0450



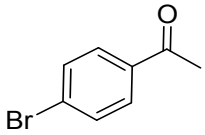
4-Acetylbenzonitrile (9) The product (37 mg, 85% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 12:1). This compound is known.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2 H), 7.77 (d, *J* = 8.8 Hz, 2 H), 2.64 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 139.9, 132.5, 128.7, 117.9, 116.4, 26.7.



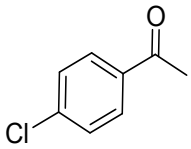
1-(4-Nitrophenyl)etha-1-one (10) The product (35 mg, 71% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). This compound is known.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2 H), 8.11 (d, *J* = 8.8 Hz, 2 H), 2.68 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 150.4, 141.4, 129.3, 123.8, 27.0. HRMS: Calculated for $C_8H_7NO_3$ $(M-H)^-$: 164.0353 ; Found: 164.0359.



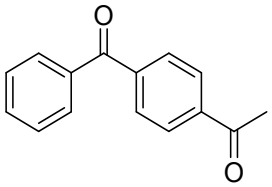
1-(4-Fluoro-3-methylphenyl)etha-1-one (11) The product (37 mg, 82% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.80 (m, 1 H), 7.79-7.75 (m, 1 H), 7.05 (t, *J* = 8.8 Hz, 1 H), 2.57 (s, 3 H), 2.31 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 164.3 (d, *J* = 252.0 Hz), 133.2 (d, *J* = 4.0 Hz), 132.1 (d, *J* = 6.0 Hz), 128.3 (d, *J* = 9.0 Hz), 125.3 (d, *J* = 18.0 Hz), 115.2 (d, *J* = 23.0 Hz), 26.5, 14.5 (d, *J* = 3.0 Hz). HRMS: Calculated for C_9H_9FO (M^+): 152.0637; Found: 152.0535.



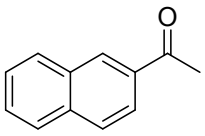
1-(4-Bromophenyl)etha-1-one (12) The product (49 mg, 82% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 2.57 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 135.8, 131.8, 129.8, 128.2, 26.5. HRMS: Calculated for C_8H_7BrO (M^+): 197.9680; Found: 197.9684.



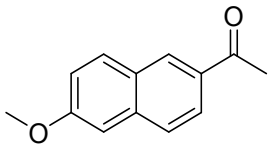
1-(4-Chlorophenyl)etha-1-one (13) The product (42 mg, 91% yield) as a light yellow liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 2 H), 7.42 (*J* = 8.8 Hz, 2 H), 2.57 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 139.5, 135.4, 129.7, 128.8, 26.5. HRMS: Calculated for C_8H_7ClO (M^+): 154.0185; Found: 154.0182.



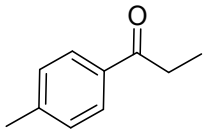
1-(4-Benzoylphenyl)etha-1-one (14) The product (53 mg, 78% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 12:1). This compound is known.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2 H), 7.84 (d, *J* = 8.4 Hz, 2 H), 7.77 (d, *J* = 8.4 Hz, 2 H), 7.59 (t, *J* = 8.4 Hz, 1 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 2.64 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 195.9, 141.2, 139.4, 136.8, 132.9, 130.06, 130.01, 128.4, 128.1, 26.9. HRMS: Calculated for $C_{15}H_{12}O_2$ $(M+H)^+$: 225.0910; Found: 225.0913.



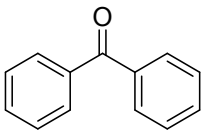
1-(Naphthalen-2-yl)etha-1-one (15) The product (39 mg, 76% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1 H), 8.03 (dd, *J* = 8.8, *J* = 2.0 Hz, 1 H), 7.95 (d *J* = 8.0, 1 H), 7.89-7.85 (m, 2 H), 7.61-7.53 (m, 2 H), 2.72 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 135.5, 134.4, 132.4, 130.1, 129.5, 128.4, 128.3, 127.7, 126.7, 123.8, 26.6. HRMS: Calculated for $C_{12}H_{10}O$ $(M+H)^+$: 171.0804; Found: 171.0806.



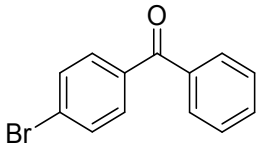
1-(6-Methoxynaphthalen-2-yl)etha-1-one (16) The product (45 mg, 75% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 12:1). This compound is known.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1 H), 8.00 (dd, *J* = 8.8, *J* = 2.0 Hz, 1 H), 7.84 (d, *J* = 8.8 Hz, 1 H), 7.75 (d, *J* = 8.8 Hz, 1 H), 7.20 (dd, *J* = 8.8, *J* = 2.4 Hz, 1 H), 7.14 (d, *J* = 2.4 Hz, 1 H), 3.94 (s, 3 H), 2.69 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 159.7, 137.2, 132.6, 131.0, 130.0, 127.8, 127.0, 124.6, 119.6, 105.7, 55.4, 26.5. HRMS: Calculated for $C_{13}H_{12}O_2(M+H)^+$: 201.0910; Found: 201.0913.



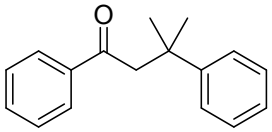
1-(*p*-Tolyl)propa-1-one (17) The product (27 mg, 62% yield) as a light yellow liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 2.97 (q, *J* = 7.2 Hz, 2 H), 2.40 (s, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 143.5, 134.4, 129.2, 128.0, 31.6, 21.6, 8.3. HRMS: Calculated for $C_{10}H_{12}O$ $(M+Na)^+$:171.0780; Found: 171.0785.



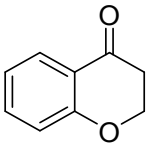
Benzophenone (18) The product (39 mg, 72% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.79 (d, *J* = 7.2 Hz, 4 H), 7.57 (d, *J* = 7.2 Hz, 2 H), 7.47 (t, *J* = 7.6 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 137.5, 132.3, 130.0, 128.2. HRMS: Calculated for $C_{13}H_{10}O$ $(M+Na)^+$: 205.0623; Found: 205.0627.



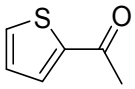
(4-Bromophenyl)(phenyl)methaone (19) The product (56 mg, 72% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2 H), 7.68 (d, *J* = 8.0 Hz, 2 H), 7.63-7.58 (m, 3 H), 7.49 (t, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 137.1, 136.3, 132.6, 131.6, 131.5, 129.9, 128.4, 127.5. HRMS: Calculated for $C_{13}H_9BrO$ $(M+H)^+$: 260.9909; Found: 260.9913.



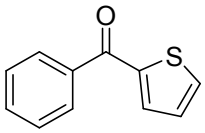
3-Methyl-1,3-diphenylbuta-1-one (20) The product (44 mg, 62% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2 H), 7.51-7.46 (m, 1 H), 7.39-7.35 (m, 4 H), 7.30-7.25 (m, 2 H), 7.17-7.13 (m, 1 H), 3.30 (s, 2 H), 1.50 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 148.8, 138.1, 132.6, 128.3, 128.1, 128.0, 125.7, 125.4, 50.8, 37.5, 29.1. HRMS: Calculated for $C_{17}H_{18}O$ $(M+Na)^+$: 261.1249 ; Found: 261.1254.



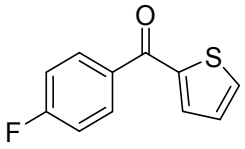
Chroma-4-one (21) The product (29 mg, 66% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). This compound is known.[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1 H), 7.48-7.44 (m, 1 H), 7.03-6.99 (m, 1 H), 6.96 (d, *J* =8.8, 1 H), 4.53 (t, *J* = 6.4 Hz, 2 H), 2.80 (t, *J* = 6.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 161.8, 135.9, 127.1, 121.3, 117.8, 67.0, 37.7. HRMS: Calculated for $C_9H_8O_2$ $(M+MeOH+H)^+$: 181.0859; Found: 181.0864.



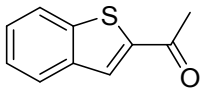
1-(Thiophen-2-yl)etha-1-one (22) The product (25 mg, 66% yield) as a yellow liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 4.4 Hz, 1 H), 7.63 (d, *J* = 5.2 Hz, 1 H), 7.12 (t, *J* = 4.4 Hz, 1 H), 2.56 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 144.5, 133.7, 132.4, 128.1, 26.9. HRMS: Calculated for C_6H_6OS (M^+): 126.0139; Found: 126.0136.



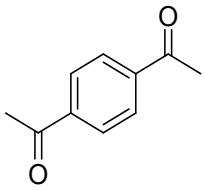
Phenyl(thiophen-2-yl)methaone (23) The product (33 mg, 59% yield) as a yellow solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). This compound is known.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2 H), 7.71 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 1 H), 7.64 (dd, *J* = 4.0 Hz, *J* = 1.2 Hz, 1 H), 7.61-7.57 (m, 1 H), 7.51-7.48 (m, 2 H), 7.16 (dd, *J* = 4.8 Hz, *J* = 4.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 143.6, 138.1, 134.8, 134.1, 132.2, 129.1, 128.4, 127.9. HRMS: Calculated for $C_{11}H_8OS$ $(M+Na)^+$: 211.0188; Found: 211.0191.



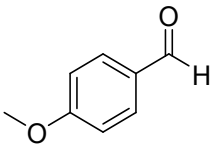
(4-Fluorophenyl)(thiophen-2-yl)methaone (24) The product (33 mg, 53% yield) as a yellow solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). This compound is known.[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 2 H), 7.72 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 1 H), 7.63 (dd, *J* = 4.0 Hz, *J* = 1.2 Hz, 1 H), 7.20-7.15 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.6, 165.5 (d, *J* = 252.0 Hz), 143.3, 134.5, 134.3 (d, *J* = 3.0 Hz), 134.2, 131.7 (d, *J* = 9.0 Hz), 127.9, 115.6 (d, *J* = 21 Hz). HRMS: Calculated for $C_{11}H_7FOS$ $(M+H)^+$: 207.0274; Found: 207.0278.



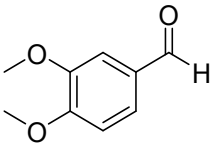
1-(Benzo[b]thiophen-2-yl)etha-1-one (25) The product (43 mg, 82% yield) as a yellow solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). This compound is known.[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1 H), 7.87 (t, *J* = 9.6 Hz, 2 H), 7.48-7.43(m, 1 H), 7.42-7.38 (m, 1 H), 2.66 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 143.9, 142.6, 139.1, 129.6, 127.4, 125.9, 124.9, 122.9, 26.7. HRMS: Calculated for $C_{10}H_8OS$ $(M+H)^+$: 177.0368; Found: 177.0372.



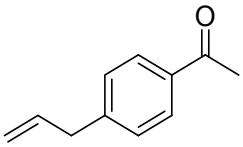
1,1'-(1,4-Phenylene)bis(etha-1-one) (26) The product (29 mg, 60% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). This compound is known.[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 4 H), 2.63 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 140.1, 128.4, 26.8. HRMS: Calculated for $C_{10}H_{10}O_2$ (M^+): 162.0681; Found: 162.0678.



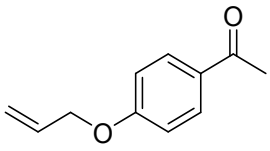
4-Methoxybenzaldehyde (27) The product (25 mg, 60% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1 H), 7.84 (d, *J* = 8.8 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 3.89 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 164.6, 132.0, 130.0, 114.3, 55.6.



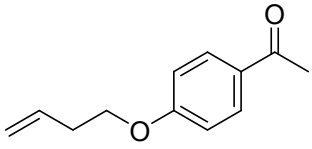
3,4-Dimethoxybenzaldehyde (28) The product (25 mg, 50% yield) as a yellow liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). This compound is known.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1 H), 7.43 (dd, *J* = 8.0, *J* = 2.0 Hz, 1 H), 7.39 (s, 1 H), 6.95 (d, *J* = 8.0 Hz, 1 H), 3.94 (s, 3 H), 3.91 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 154.4, 149.6, 130.1, 126.8, 110.3, 108.9, 56.1, 56.0. HRMS: Calculated for $C_9H_{10}O_3$ $(M+H)^+$: 189.0522; Found: 189.0526.



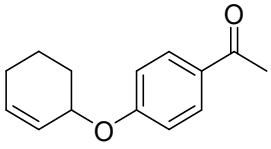
1-(4-allylphenyl)etha-1-one (30) The product (30 mg, 63% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 5.99-5.89 (m, 1 H), 5.11 (s, 1 H), 5.07 (d, *J* = 8.0 Hz, 1 H), 3.43 (d, *J* = 6.8 Hz, 2 H), 2.57 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 145.7, 136.2, 135.3, 128.7, 128.5, 116.6, 40.1, 26.5. HRMS: Calculated for $C_{11}H_{12}O$ $(M+Na)^+$: 183.0780; Found: 183.0785.



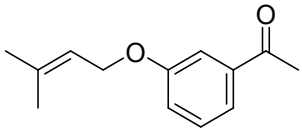
1-(4-(Allyloxy)phenyl)etha-1-one (31) The product (30 mg, 78% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). This compound is known.[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ7.91 (d, *J* = 8.8 Hz, 2 H), 6.93 (d, *J* = 8.8 Hz, 2 H), 6.08-5.99 (m, 1 H), 5.41 (d, *J* = 17.2 Hz, 1 H), 5.30 (d, *J* = 10.4 Hz, 1 H), 4.58 (d, *J* = 4.8 Hz, 2 H), 2.53 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ196.7, 162.4, 132.4, 130.5, 130.3, 118.1, 114.3, 68.8, 26.3. HRMS: Calculated for $C_{11}H_{12}O_2$ $(M+Na)^+$: 199.0729; Found: 199.0735.



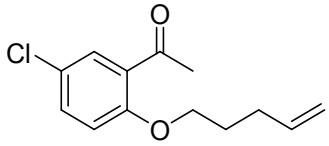
1-(4-(But-3-en-1-yloxy)phenyl)etha-1-one (32) The product (41 mg, 71% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). This compound is known.[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 5.94-5.84 (m, 1 H), 5.19-5.14 (m, 1 H), 5.13-5.09 (m, 1 H), 4.06 (t, *J* = 6.8 Hz, 2 H), 2.58-2.52 (m, 2 H), 2.53 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 162.8, 133.9, 130.5, 130.2, 117.3, 114.1, 67.3, 33.4, 26.2. HRMS: Calculated for $C_{12}H_{14}O_2$ $(M+Na)^+$: 213.0886; Found: 213.0889.



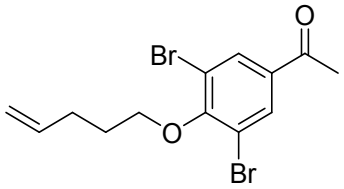
1-(4-(Cyclohex-2-en-1-yloxy)phenyl)etha-1-one (33) The product (39 mg, 60% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 12:1). This compound is known.[24] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 2 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 6.03-5.98 (m, 1 H), 5.85 (m, 1 H), 4.91-4.86 (m, 1 H), 2.54 (s, 3 H), 2.54-1.79 (m, 5 H), 1.70-1.61 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 161.9, 132.8, 130.6, 130.0, 125.4, 115.1, 70.9, 28.2, 26.3, 25.0, 18.8. HRMS: Calculated for $C_{14}H_{16}O_2$ $(M+Na)^+$: 239.1042; Found: 239.1044.



1-(3-((3-Methylbut-2-en-1-yl)oxy)phenyl)etha-1-one (34) The product (38 mg, 62% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). This compound is known.[25] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1 H), 7.50 (m, 1 H), 7.35 (t, *J* = 8.0 Hz, 1 H), 7.11 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1 H), 5.51-5.47 (m, 1 H), 4.56 (d, *J* = 6.8 Hz, 2 H), 2.58 (s, 3 H), 1.80 (s, 3 H), 1.76 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 159.0, 138.6, 138.4, 129.5, 120.9, 120.2, 119.2, 113.2, 64.9, 26.7, 25.8, 18.2. HRMS: Calculated for $C_{13}H_{16}O_2$ $(M+Na)^+$: 227.1042; Found: 227.1043.

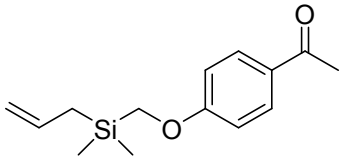


1-(5-Chloro-2-(pent-4-en-1-yloxy)phenyl)etha-1-one (35) The product (36 mg, 50% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 2.8 Hz, 1 H), 7.37 (dd, *J* = 8.8, *J* = 2.8 Hz, 1 H), 6.88 (d, *J* = 8.8 Hz, 1 H), 5.89-5.78 (m, 1 H), 5.09-5.01 (m, 2 H), 4.07-4.03 (t, *J* = 6.4 Hz, 2 H), 2.62 (s, 3 H), 2.29-2.23 (m, 2 H), 1.99-1.92 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 156.9, 137.1, 133.1, 130.0, 129.3, 125.8, 115.7, 113.8, 68.2, 31.9, 30.2, 28.2. HRMS: Calculated for $C_{13}H_{15}ClO_2$ $(M+Na)^+$: 261.0652; Found: 261.0656.

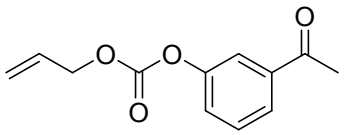


1-(3,5-Dibromo-4-(pent-4-en-1-yloxy)phenyl)etha-1-one (36) The product (74 mg, 68% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 12:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2 H), 5.93-5.83 (m, 1 H), 5.12-5.06 (m, 1 H), 5.03-4.99 (m, 1 H), 4.07 (t, *J* = 6.4 Hz, 2 H), 2.55 (s, 3 H), 2.35-2.29 (m, 2 H), 2.02-1.95 (m, 2 H). ^{13}C NMR (100 MHz,

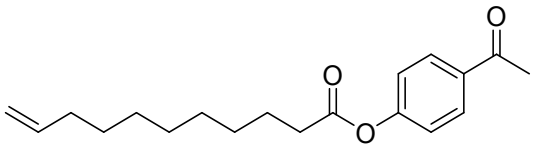
$CDCl_3$) δ 194.5, 157.3, 137.7, 134.8, 132.9, 118.7, 115.2, 73.2, 30.0, 29.2, 26.4. HRMS: Calculated for $C_{13}H_{14}Br_2O_2$ $(M+Na)^+$: 382.9252; Found: 382.9254.



1-(4-((Allyldimethylsilyl)methoxy)phenyl)etha-1-one (37) The product (50 mg, 67% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 5.86-5.75 (m, 1 H), 4.92-4.85 (m, 2 H), 3.67 (s, 2 H), 2.54 (s, 3 H), 1.69 (d, *J* = 8.0 Hz, 2 H), 0.16 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 165.3, 133.8, 130.4, 130.0, 113.8, 113.7, 59.9, 26.2, 21.3, -5.1. HRMS: Calculated for $C_{14}H_{20}O_2Si$ $(M+Na)^+$: 271.1124; Found: 271.1129.

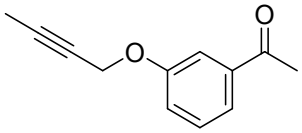


3-Acetylphenyl allyl carbonate (38) The product (47 mg, 71% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H), 7.76 (t, *J* = 1.6 Hz, 1 H), 7.48 (t, *J* = 8.0 Hz, 1 H), 7.40-7.37 (m, 1 H), 6.04-5.95 (m, 1 H), 5.44 (dq, *J* = 13.6 Hz, *J* = 1.6 Hz, 1 H), 5.33 (dq, *J* = 10.4 Hz, *J* = 1.2 Hz, 1 H), 4.74 (dt, *J* = 5.6 Hz, *J* = 1.6 Hz, 2 H), 2.59 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 153.2, 151.3, 138.6, 130.9, 129.7, 125.9, 125.7, 120.9, 119.7, 69.3, 26.6. HRMS: Calculated for $C_{12}H_{12}O_4$ $(M+Na)^+$: 243.0627; Found: 243.0631.

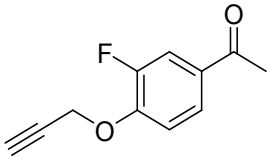


4-Acetylphenyl undec-10-enoate (39) The product (64 mg, 70% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 12:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2 H), 7.18 (d, *J* = 8.8 Hz, 2 H), 5.86-5.76 (m, 1 H), 5.01-4.96 (m, 1 H), 4.94-4.91 (m, 1 H), 2.58 (s, 3 H), 2.56 (d, *J* = 7.6 Hz, 2 H), 2.07-2.01 (m, 2 H), 1.79-1.71 (m, 2 H),

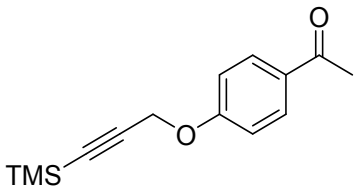
1.45-1.25 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 171.6, 154.4, 139.1, 134.6, 129.9, 121.7, 114.1, 34.3, 33.7, 29.2, 29.1, 29.0, 28.8, 26.5, 24.8. HRMS: Calculated for $C_{19}H_{26}O_3$ $(M+Na)^+$: 325.1774; Found: 325.1780.



1-(3-(But-2-yn-1-yloxy)phenyl)etha-1-one (40) The product (42 mg, 75% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.53 (m, 2 H), 7.37 (t, *J* = 8.0 Hz, 1 H), 7.16 (dd, *J* = 8.4 Hz, 2.8 Hz, 1 H), 4.69 (q, *J* = 2.4 Hz, 2 H), 2.58 (s, 3 H), 1.85 (t, *J* = 2.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 157.9, 138.4, 129.5, 121.4, 120.1, 113.7, 84.1, 73.5, 56.5, 26.7, 3.6. HRMS: Calculated for $C_{12}H_{12}O_2$ $(M+Na)^+$: 211.0729; Found: 211.0732.

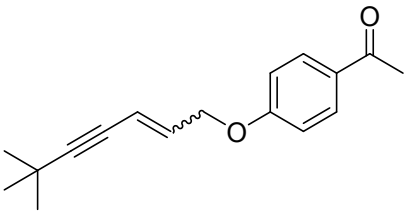


1-(3-Fluoro-4-(prop-2-yn-1-yloxy)phenyl)etha-1-one (41) The product (41 mg, 70% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.68 (m, 2 H), 7.14 (t, *J* = 8.0 Hz, 1 H), 4.83 (d, *J* = 2.4 Hz, 2 H), 2.58 (t, *J* = 2.4 Hz, 1 H), 2.54 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 152.2 (d, *J* = 247.0 Hz), 149.6 (d, *J* = 11.0 Hz), 131.5(d, *J* = 5.0 Hz), 125.3(d, *J* = 4.0 Hz), 116.2(d, *J* = 19.0 Hz), 114.4, 77.2, 76.8, 56.9, 26.3. HRMS: Calculated for $C_{11}H_9FO_2$ $(M+Na)^+$: 215.0478; Found: 215.0480.

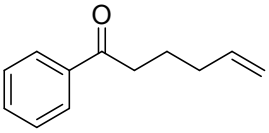


1-(4-((3-(Trimethylsilyl)prop-2-yn-1-yl)oxy)phenyl)etha-1-one (42) The product (54 mg, 73% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 4.72 (s, 2

H), 2.54 (s, 3 H), 0.16 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 161.5, 130.8, 130.4, 114.6, 99.1, 93.5, 56.7, 26.3, -0.3. HRMS: Calculated for $C_{14}H_{18}O_2Si$ $(M+Na)^+$: 269.0968; Found: 269.0973.

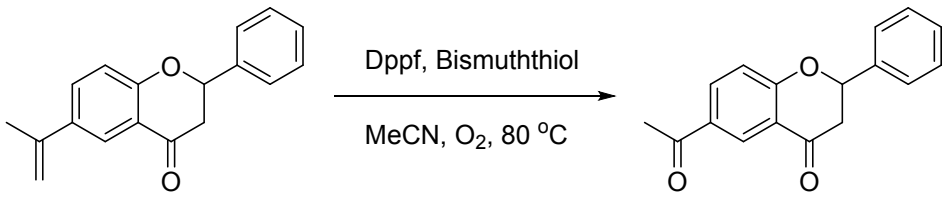


1-(4-((6,6-Dimethylhept-2-en-4-yn-1-yl)oxy)phenyl)etha-1-one (43) The product (44 mg, 57% yield) as a white solid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2 H), 6.99-6.96 (m, 0.4 H), 6.92-6.90 (m, 1.6 H), 6.20-6.14 (m, 0.8 H), 6.01-5.96 (m, 0.2 H), 5.86-5.81 (m, 0.8 H), 5.74-5.71 (m, 0.2 H), 4.85 (dd, *J* = 6.4 Hz, *J* = 1.6 Hz, 0.4 H), 4.61 (dd, *J* = 5.6 Hz, *J* = 1.6 Hz, 1.6 H), 2.54 (s, 3 H), 1.28 (s, 1.8 H), 1.24 (s, 7.2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 162.2, 135.1 (134.7), 130.5, 114.3, 113.9 (113.6), 110.5, 76.4, 67.9 (66.0), 30.9 (30.8), 27.9, 26.3. HRMS: Calculated for $C_{17}H_{20}O_2$ $(M+Na)^+$: 279.1355; Found: 279.1361.



1-Phenylhex-5-en-1-one (44) The product (15 mg, 30% yield) as a colorless liquid, was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1). This compound is known.[26] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2 H), 7.57-7.53 (t, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 5.88-5.77 (m, 1 H), 5.08-4.98 (m, 2 H), 2.98 (t, *J* = 7.2 Hz, 2 H), 2.16 (q, *J* = 7.6 Hz, 2 H), 1.89-1.82 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 138.0, 137.0, 132.9, 128.5, 128.0, 115.3, 37.7, 33.2, 23.3. HRMS: Calculated for $C_{12}H_{14}O$ $(M+Na)^+$: 197.0936; Found: 197.0940.

Synthesis of 6-Acetyl-2-phenylchroma-4-one (45)

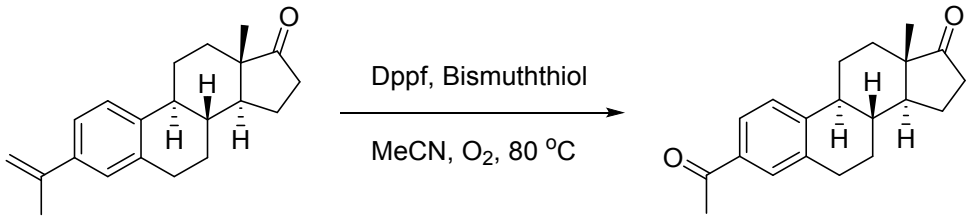


45a **45**

To a 25 ml of Schlenk tube was added dppf (11 mg, 0.02 mmol, 0.1 equiv), bismuththiol (3.0 mg, 0.02 mmol, 0.1 equiv) and **45a** (52.8 mg, 0.20 mmol, 1 equiv) at room temperature. The reaction tube was degassed with dioxygen gas (1 atm, 3 times), then freshly distilled MeCN (0.5 mL) was injected by syringe. The reaction tube was heated to 80 °C and allowed to react for 15 h. The reaction mixture was concentrated and the residual was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1) to provide the product **45** (35 mg, 66% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 2.4 Hz, 1 H), 8.17 (dd, *J* = 8.8 Hz, 2.4 Hz, 1 H), 7.50-7.39 (m, 5 H), 7.12 (d, *J* = 8.8 Hz, 1 H), 5.56 (dd, *J* = 13.2, *J* = 3.2 Hz, 1 H), 3.14 (dd, *J* = 16.8, *J* = 13.2 Hz, 1 H), 2.96 (dd, *J* = 16.8, *J* = 3.2 Hz, 1 H), 2.61 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 191.1, 164.7, 137.8, 135.4, 130.9, 129.0, 128.9, 128.5, 126.1, 120.0, 118.8, 79.9, 44.2, 26.4. HRMS: Calculated for $C_{17}H_{14}O_3$ $(M+H)^+$: 267.1015; Found: 267.1021.

Synthesis of (8*R*,9*S*,13*S*,14*S*)-3-Acetyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenathren-17-one (46)

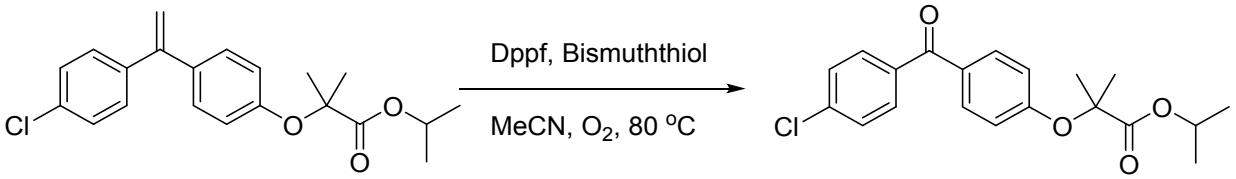


46a **46**

To a 25 ml of Schlenk tube was added dppf (16.6 mg, 0.03 mmol, 0.1 equiv), bismuththiol (4.5 mg, 0.03 mmol, 0.1 equiv) and **46a** (88.3 mg, 0.30 mmol, 1 equiv) at room temperature. The reaction tube was degassed with dioxygen gas (1 atm, 3 times), then freshly distilled MeCN (0.5 mL) was injected by syringe. The reaction tube was heated to 80 °C and allowed to react for 15 h. The reaction mixture was concentrated and the residual was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1) to provide the product **46** (36 mg, 40% yield) as a white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 1 H), 7.68 (s, 1 H), 7.36 (d, *J* = 8.4 Hz, 1 H), 2.97-2.93 (m, 2 H), 2.55 (s, 3 H), 2.53-2.41 (m, 2 H), 2.35-2.29 (m, 1 H), 2.18-1.95 (m, 4 H), 1.68-1.41 (m, 6 H), 0.90 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.3, 198.0, 145.4, 136.9, 134.9, 128.9, 125.8, 125.5, 50.5, 47.8, 44.7, 37.8, 35.8, 31.5, 29.3, 26.5, 26.3, 25.6, 21.6, 13.8. HRMS: Calculated for $C_{20}H_{24}O_2$ $(M+Na)^+$: 319.1668 ; Found: 319.1672.

Synthesis of Isopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropaoate (47)

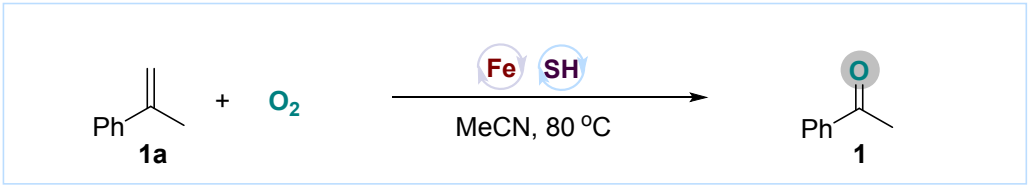


47a **47**

To a 25 ml of Schlenk tube was added dppf (16.6 mg, 0.03 mmol, 0.1 equiv), bismuththiol (4.5 mg, 0.03 mmol, 0.1 equiv) and **47a** (107.6 mg, 0.30 mmol, 1 equiv) at room temperature. The reaction tube was degassed with dioxygen gas (1 atm, 3 times), then freshly distilled MeCN (0.5 mL) was injected by syringe. The reaction tube was heated to 80 °C and allowed to react for 15 h. The reaction mixture was concentrated and the residual was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1) to provide the product **47** (72 mg, 67% yield) as a white solid.This compound is known.[26]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2 H), 7.70 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 5.08 (m, 1 H), 1.66 (s, 6 H), 1.20 (d, *J* = 6.4 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 173.1, 159.7, 138.3, 136.3, 131.9, 131.1, 130.1, 128.5, 117.1, 79.3, 69.3, 25.3, 21.5. HRMS: Calculated for $C_{20}H_{21}ClO_4$ $(M+H)^+$: 361.1201; Found: 361.1202.

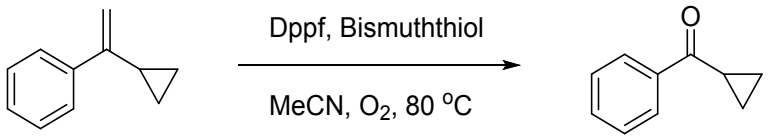
Radical Inhibtion Experiments



Entry	additive	Yield
1	None	85%
2	TEMPO (10 mol%)	76%
3	TEMPO (100 mol%)	11%
4	BHT (10 mol%)	74%
5	BHT (100 mol%)	54%

General Procedure: To a 25 mL of Schlenk tube were added dppf (16.6 mg, 0.03 mmol, 0.1 equiv), bismuththiol (4.5 mg, 0.03 mmol, 0.1 equiv), additive (0.1-1.0 equiv) under air. The mixture was then evacuated and backfilled with O_2 (3 times). 2-phenyl-1-propene **1a** (0.3 mmol), and fresh distilled MeCN (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C (oil bath). After stirring for 15 h, the reaction was cooled to room temperature and mesitylene (0.3 mmol) was added. The yield was determined by ^{1}H NMR.

Radical Clock Experiment



48a **48**

To a 25 ml of Schlenk tube was added dppf (16.6 mg, 0.03 mmol, 0.1 equiv), bismuththiol (4.5 mg, 0.03 mmol, 0.1 equiv) at room temperature. The reaction tube was degassed with dioxygen gas (1 atm, 3 times), then **48a** (0.30 mmol, 1 equiv) and freshly distilled MeCN (0.5 mL) was injected by syringe. The reaction tube was heated to 80 °C and allowed to react for 15 h. The reaction mixture was trasfered to a round bottom flask and the solvents removed in vacuo, the reaction crude was purified with silica gel chromatography (Petroleum ether/EtOAc = 19:1) to provide the product (28 mg, 65% yield) as a light yellow liquid.

Cyclopropyl(phenyl)methaone (48) This compound is known.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (t, *J* = 7.6 Hz, 2 H), 7.56 (t, *J* = 7.6 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 2.71-2.65 (m, 1 H), 1.27-1.23

(m, 2 H), 1.07-1.02 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 138.0, 132.7, 128.5, 128.0, 17.1, 11.6. HRMS: Calculated for $C_{10}H_{10}O$ $(M+Na)^+$: 169.0623; Found: 169.0628.

Cyclic Voltammetry Studies

The cyclic voltammograms were recorded in an electrolyte of nBu_4NClO_4 (0.1 M) in MeCN using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. The scan rate is 100 mV/s. The electrode potential of ferrocene: $E_{p/2}$ =+ 0.52 V vs. Ag/AgCl; and bismuththiol: E_p =+ 0.44 V vs. Ag/AgCl.

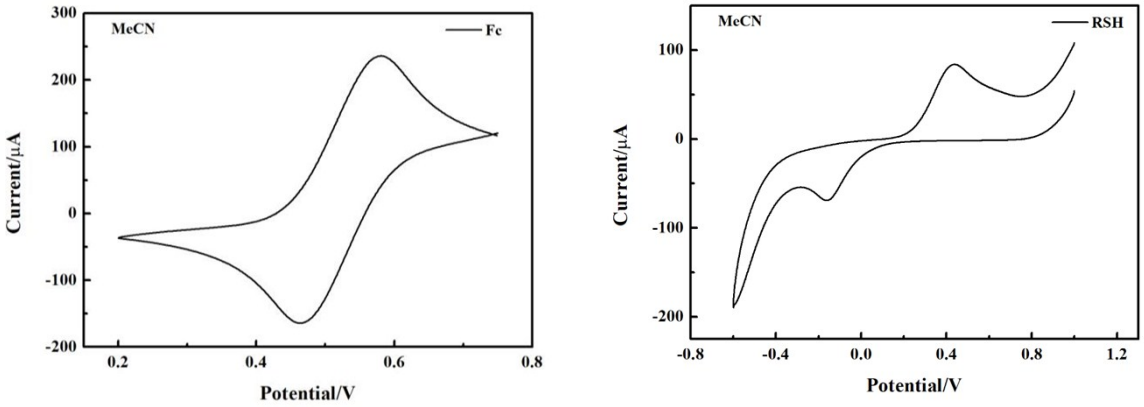
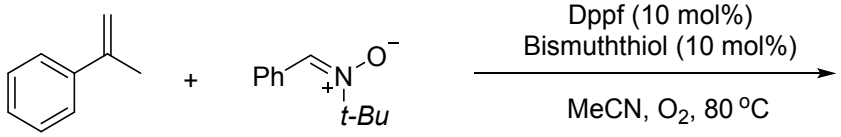


Figure S2. Cyclic voltammograms of ferrocene or bismuththiol in 0.1 M nBu_4ClO_4/MeCN

Electron Paramagnetic Resonance (EPR) Experiments.



1a **PBN**

To a 25 ml of Schlenk tube was added dppf (16.6 mg, 0.03 mmol, 0.1 equiv), bismuththiol (4.5 mg, 0.03 mmol, 0.1 equiv) at room temperature. The reaction tube was degassed with dioxygen gas (1 atm, 3 times), then **1a** (0.30 mmol, 1 equiv), PBN (0.30 mmol) and freshly distilled MeCN (0.5 mL) was injected by syringe. The reaction tube was heated to 80 °C and allowed to react for 3 h. The resulting mixture was then analyzed by EPR at 80 °C.

The EPR showed a broad EPR triplet spectrum of nitroxide (g = 2.0056, a = 16.15 G), indicating that a free radical must be involved in this reaction.

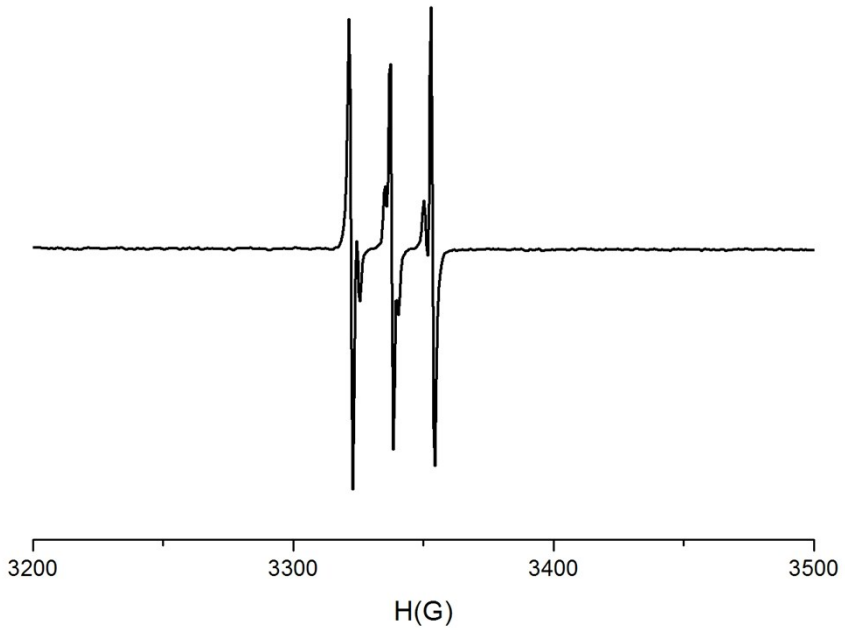
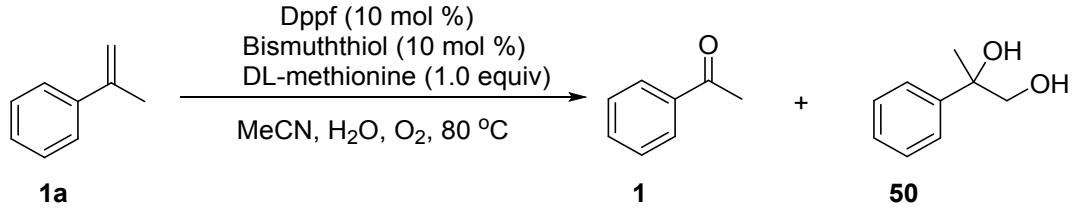


Figure S1. The Electron Paramagnetic Resonance (EPR) Spectrum of our reaction mixture in the presence of PBN

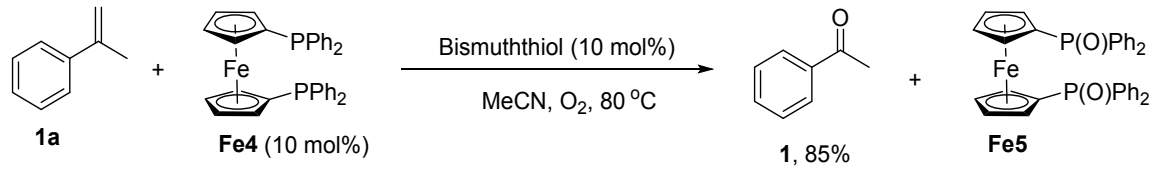
Mechaistic studies



To a 25 ml of Schlenk tube was added dppf (16.6 mg, 0.03 mmol, 0.1 equiv), bismuththiol (4.5 mg, 0.03 mmol, 0.1 equiv) and DL-methionine (49.7 mg, 0.3 mmol, 1.0 equiv) at room temperature. The reaction tube was degassed with dioxygen gas (1 atm, 3 times), then 2-phenyl-1-propene **1a** (0.30 mmol, 1 eq) and freshly distilled MeCN (0.4 mL) and H_2O (0.2 mL) was injected by syringe. The reaction tube was heated to 80 °C and allowed to react for 15 h. The reaction mixture was trasfered to a round bottom flask and the solvents removed in vacuo, the reaction crude was purified with silica gel chromatography provide product **50** (10% yield) as a white solid.

2-Phenylpropae-1,2-diol (50) This compound is known.[27] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 2 H), 7.37 (t, *J* = 7.6 Hz, 2 H), 7.28 (t, *J* = 7.6 Hz, 1 H), 3.81 (d, *J* = 11.2 Hz, 1 H), 3.64

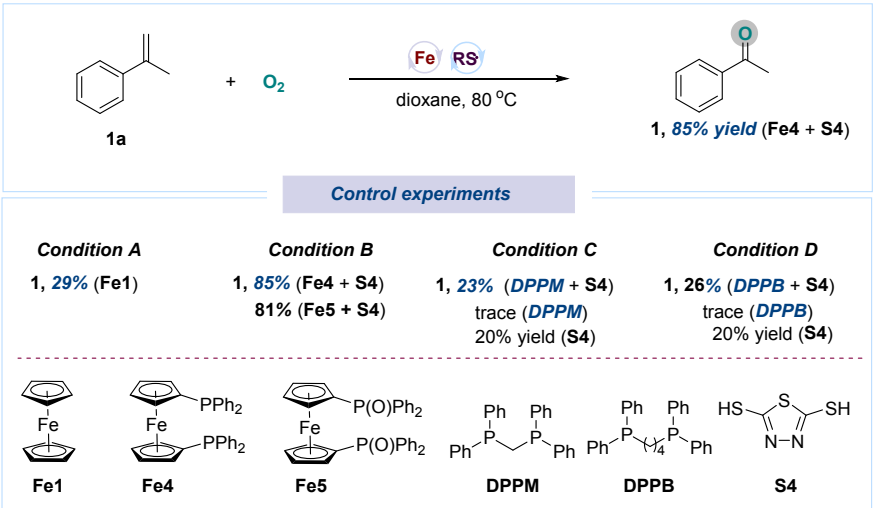
(m, 1 H), 2.61 (s, 1 H), 1.86 (s, 1 H), 1.54 (s, 3 H). HRMS: Calculated for $C_9H_{12}O_2$ $(M+Na)^+$: 175.0729; Found: 175.0733.



To a 25 mL of Schlenk tube were added dppf (16.6 mg, 0.03 mmol, 0.1 equiv), bismuththiol (4.5 mg, 0.03 mmol, 0.1 equiv) under air. The mixture was then evacuated and backfilled with O_2 (3 times). 2-phenyl-1-propene **1a** (0.3 mmol), and fresh distilled MeCN (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C (oil bath). After stirring for 15 h, the reaction was cooled to room temperature and mesitylene (0.3 mmol) was added. The yield was determined by ^{1}H NMR, and we found that **Fe5** was obtained as well.

Bis(2-(diphenylphosphoryl)cyclopenta-2,4-dien-1-yl)iron (Fe5) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.55 (m, 8 H), 7.50-7.46 (m, 4 H), 7.41-7.39 (m, 8 H), 4.67 (s, 4 H), 4.26 (s, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 133.0, 131.7, 131.6, 131.3, 131.2, 128.3, 128.2, 74.7, 74.0, 73.9, 73.5, 73.4, 73.3. HRMS: Calculated for $C_{34}H_{29}FeO_2P_2$ $(M+H)^+$: 587.0987; Found: 587.0986.

To dertmine the real catalysts in this reaction, we conducted the control experiments (as shown, below)



When we monitored this reaction by ^{1}H NMR, we found that a new iron species, **Fe5** was generated, which was successfully isolated as well. The dppf analogue **Fe5** could be synthesized

through the oxidation of dppf using H_2O_2 as oxidant. Furthermore, 81% yield of desired product was obtained when dppf analogue **Fe5** was used as catalyst. To rule out phosphine moieties on the dppf might promote this trasnformation, the control experiments were conducted. As shown, when DPPM, and DPPB were used as catalysts in the absence of thiols, this transformation was totally shut down. In addition, 23%-26% yiled were obtained using phospine and thiol as co-catalysts, which is similar with the thiol as sole catalyst. What's more, ferrocene **Fe1** without any phosphine moieties could also promote this transformation, providing ketone in 29% yield. These result demonstrats that phospine might not promote this transformation, so we still think that this reaction was promoted by iron species, not phosphine species.

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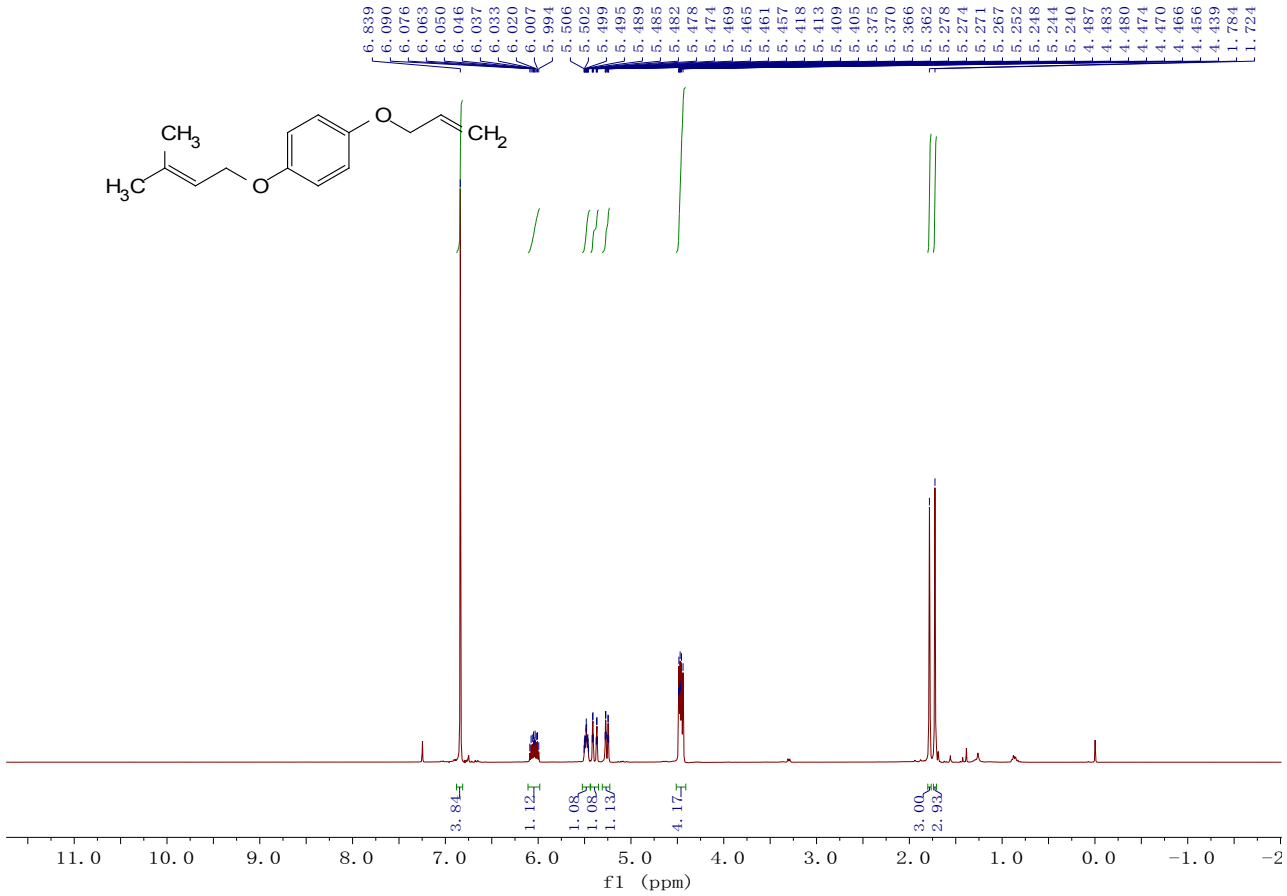
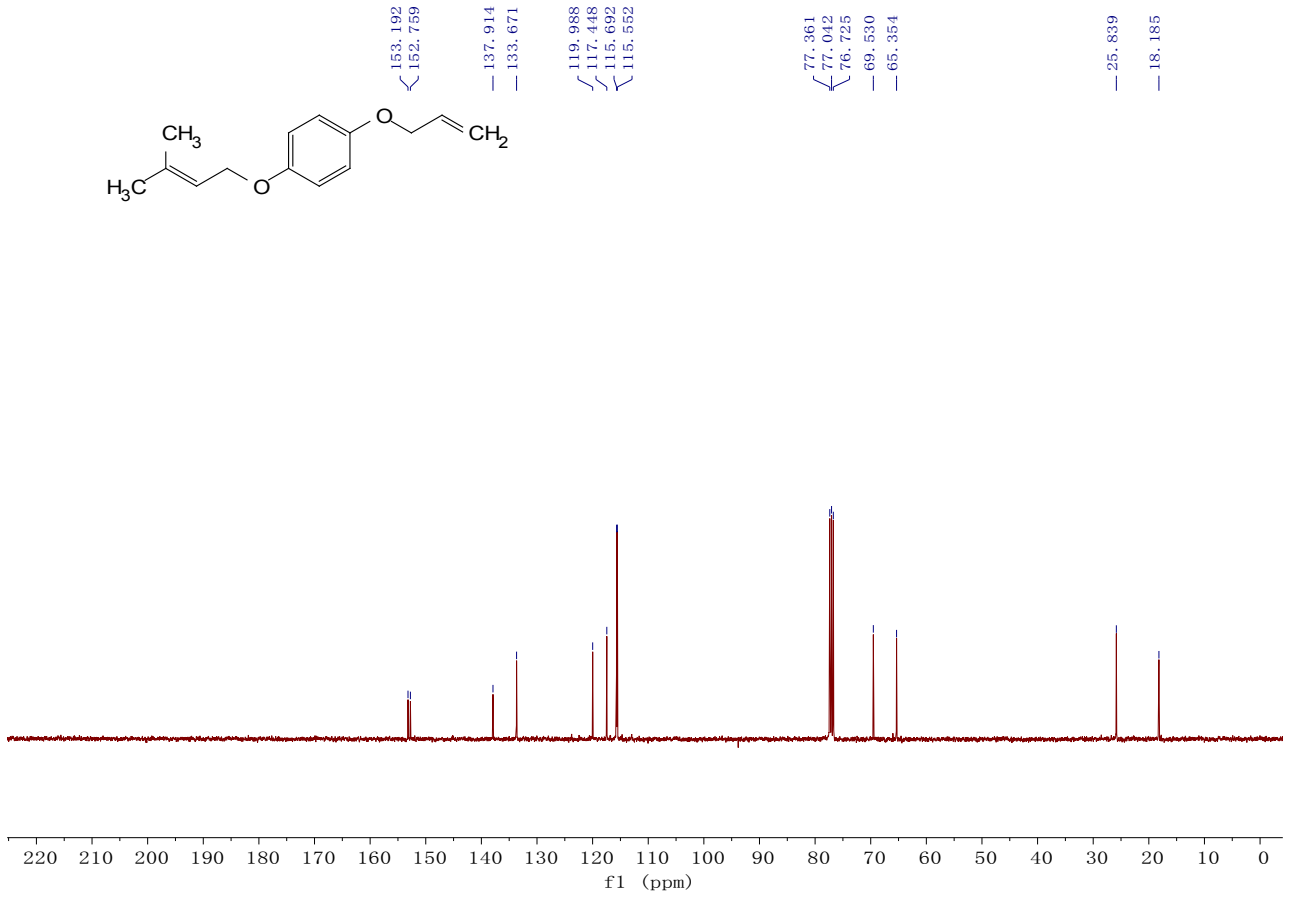
1-(Allyloxy)-4-((3-methylbut-2-en-1-yl)oxy)benzene (29a)





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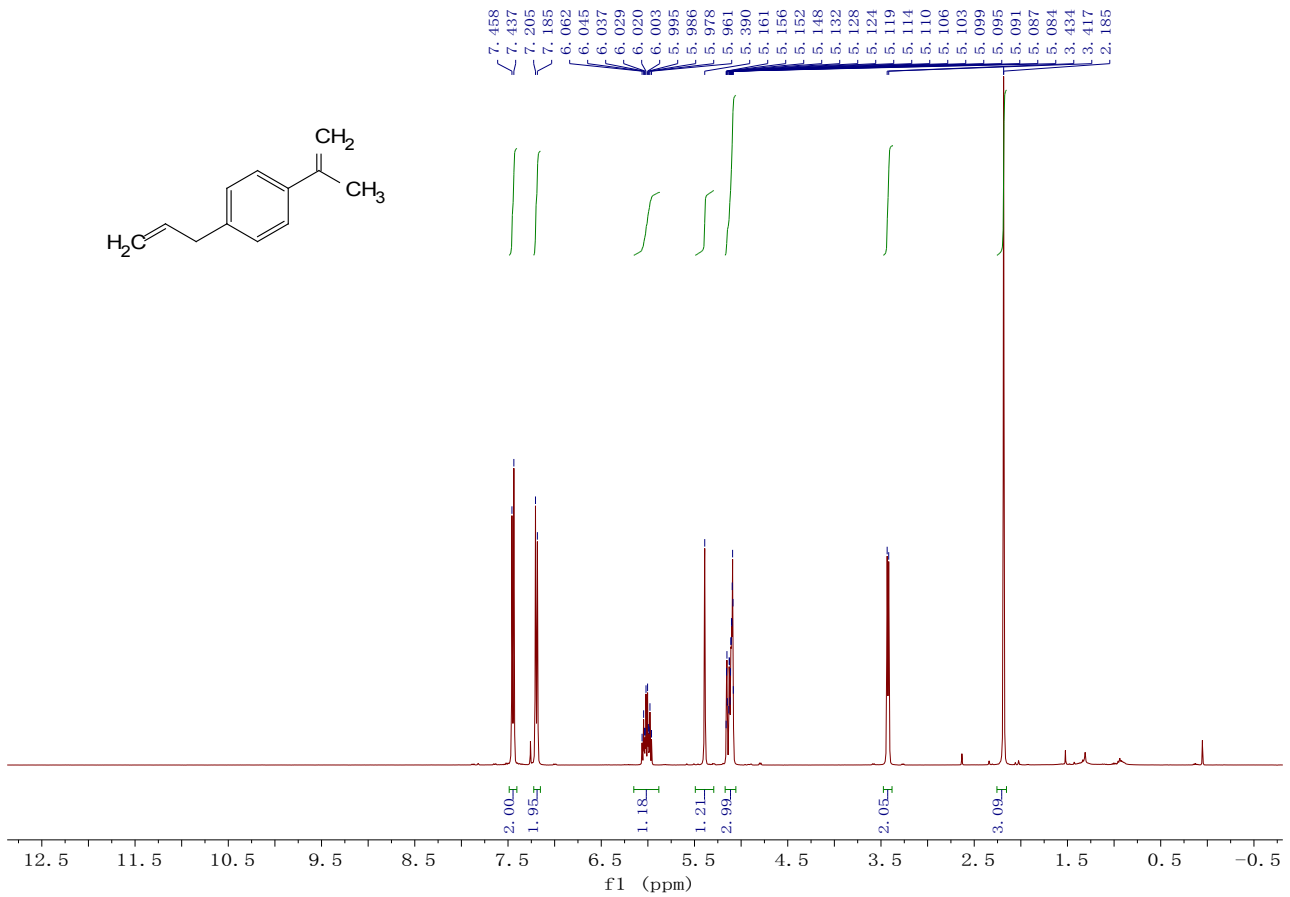

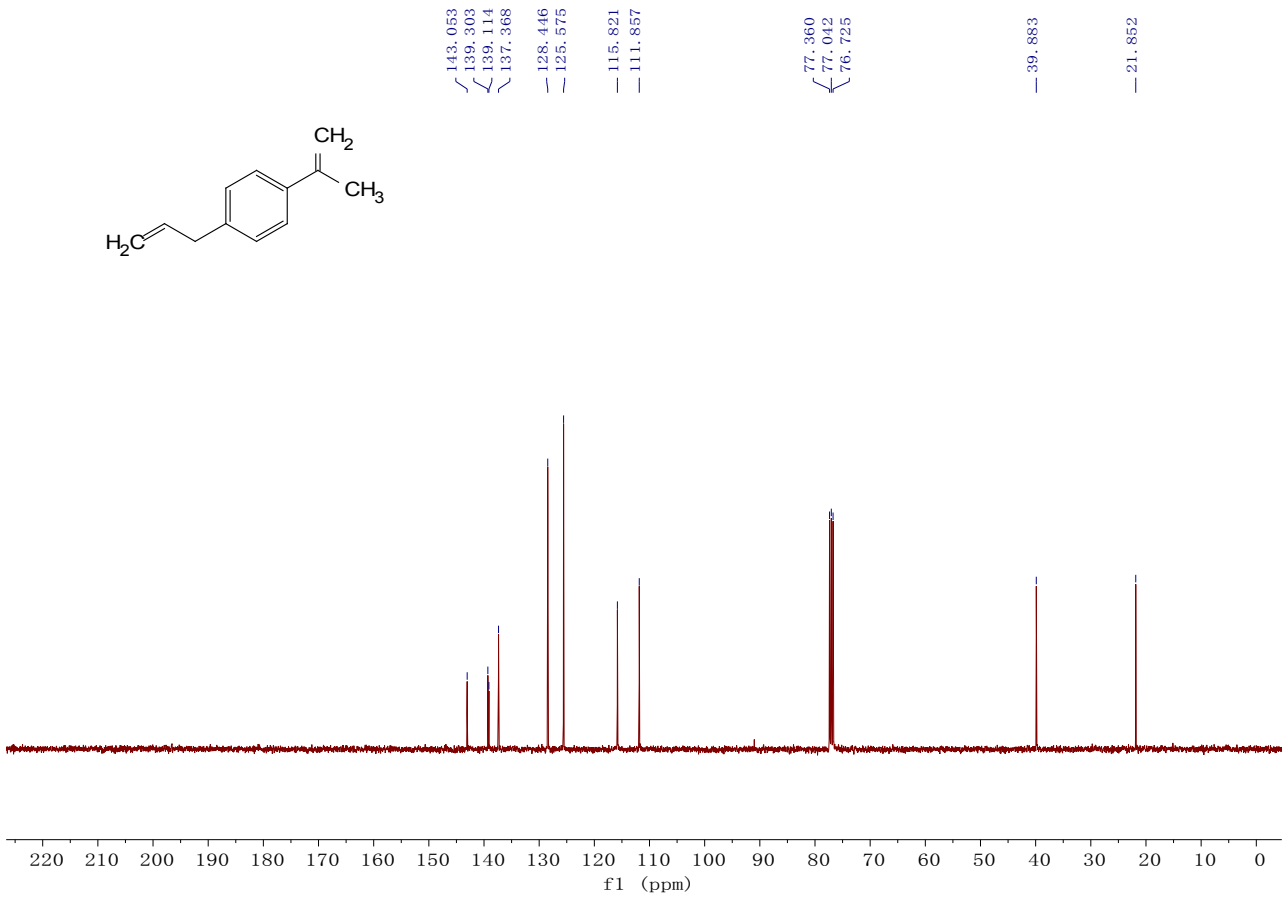

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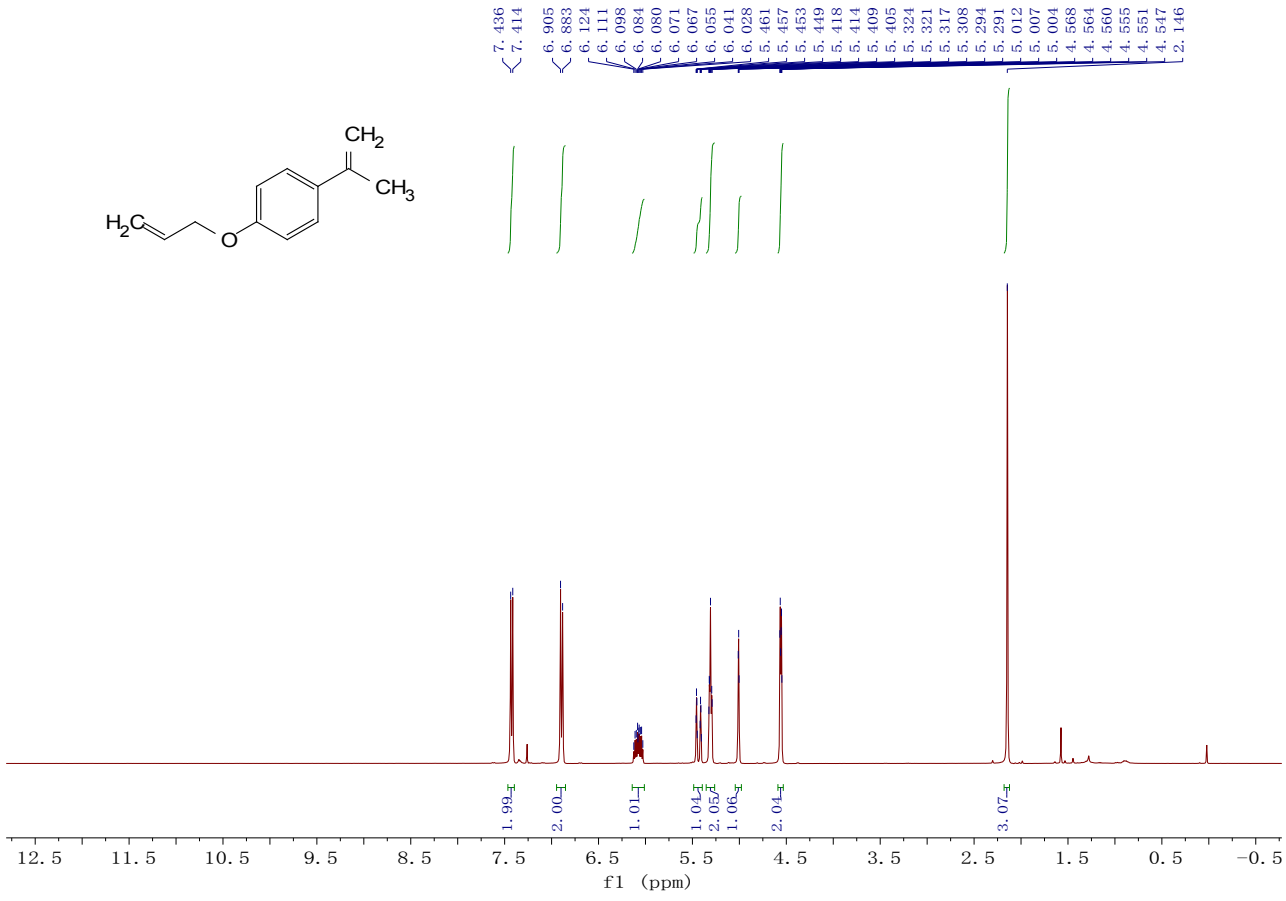
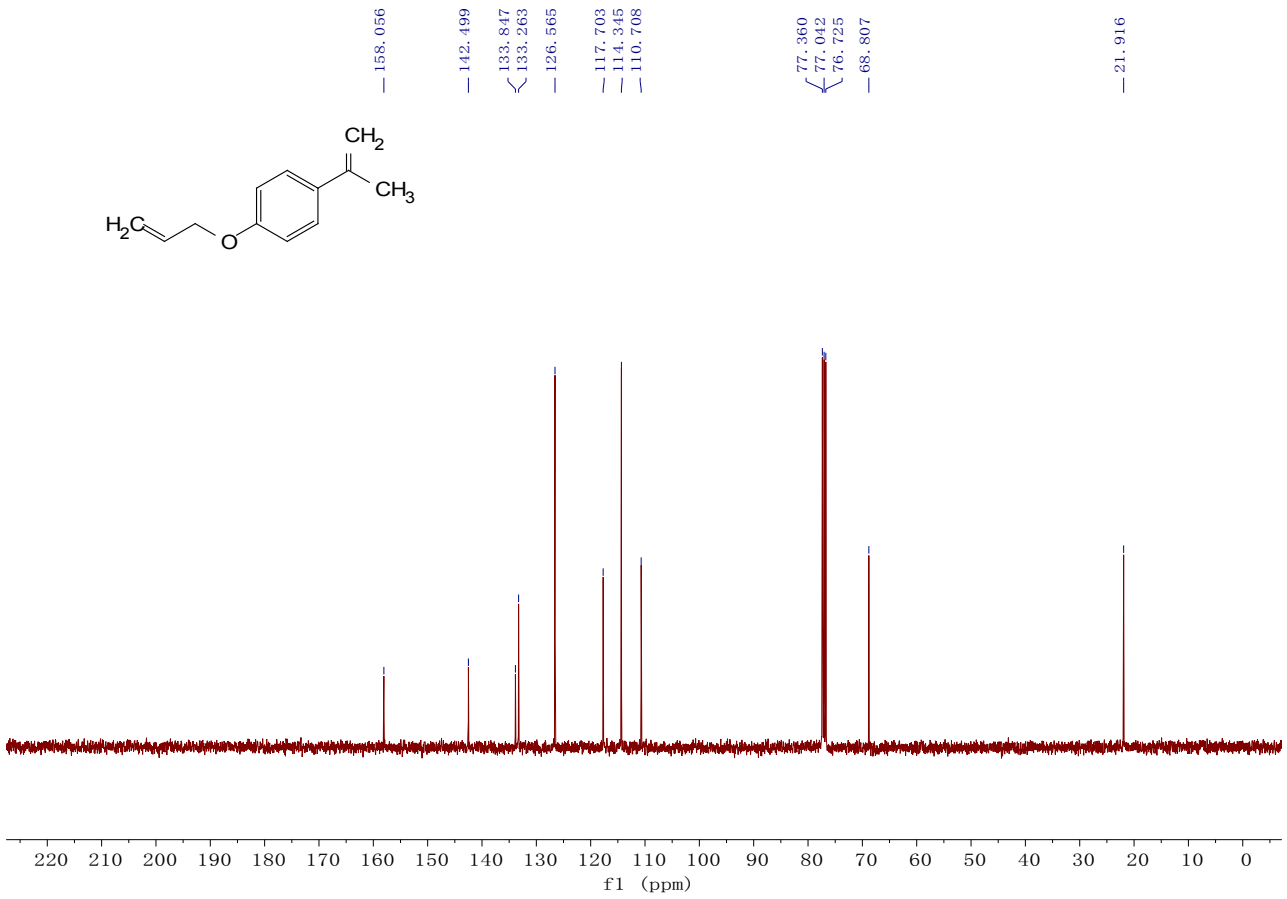
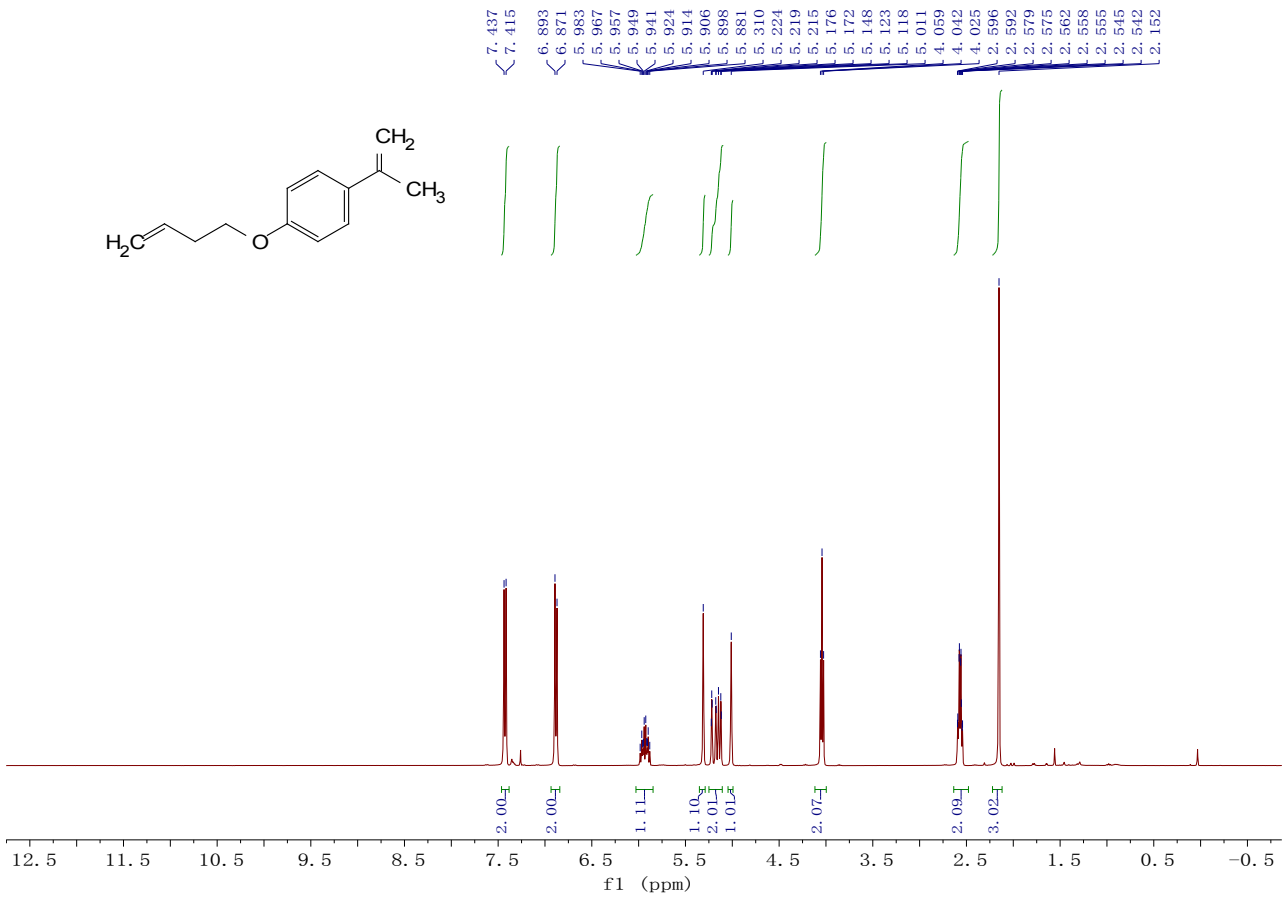
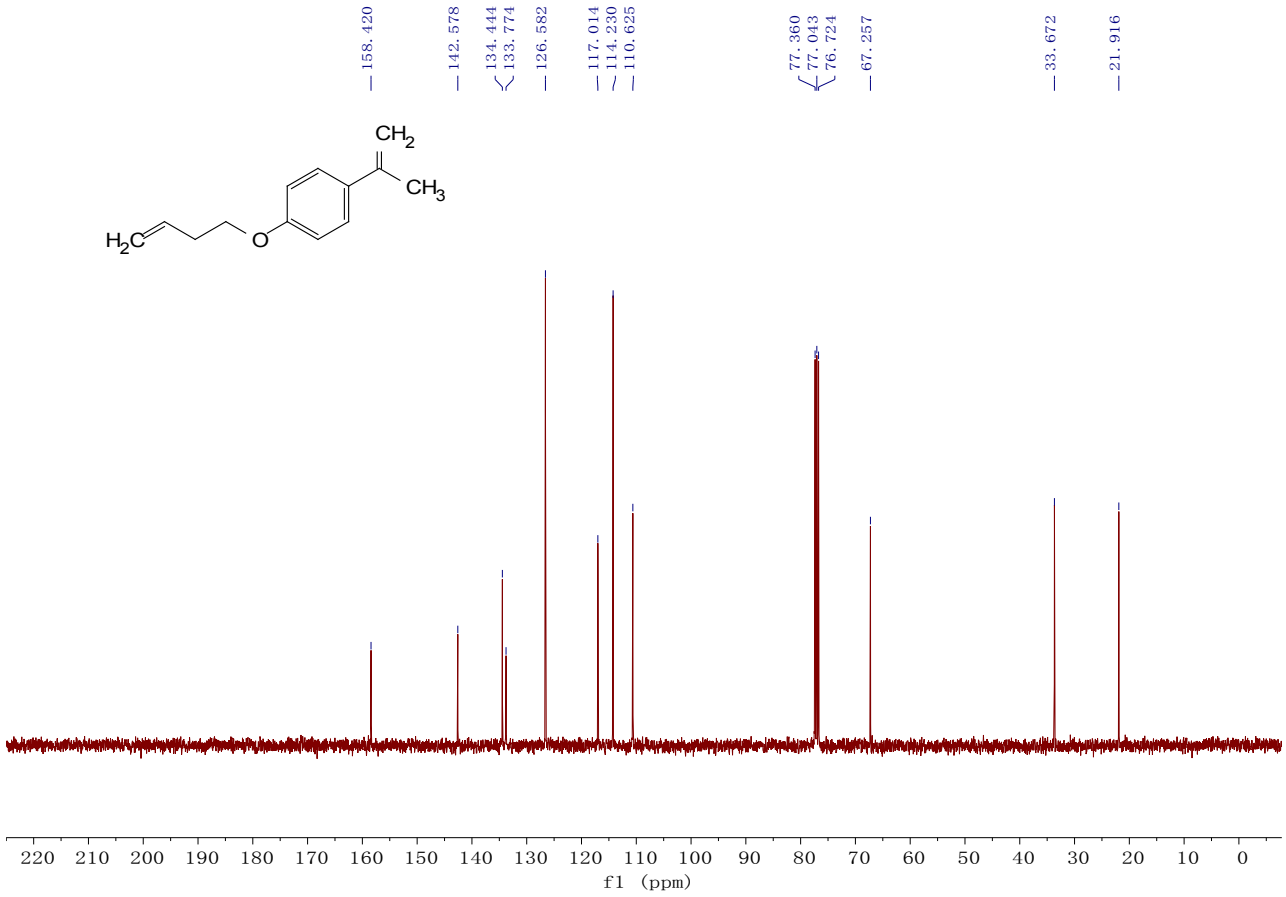


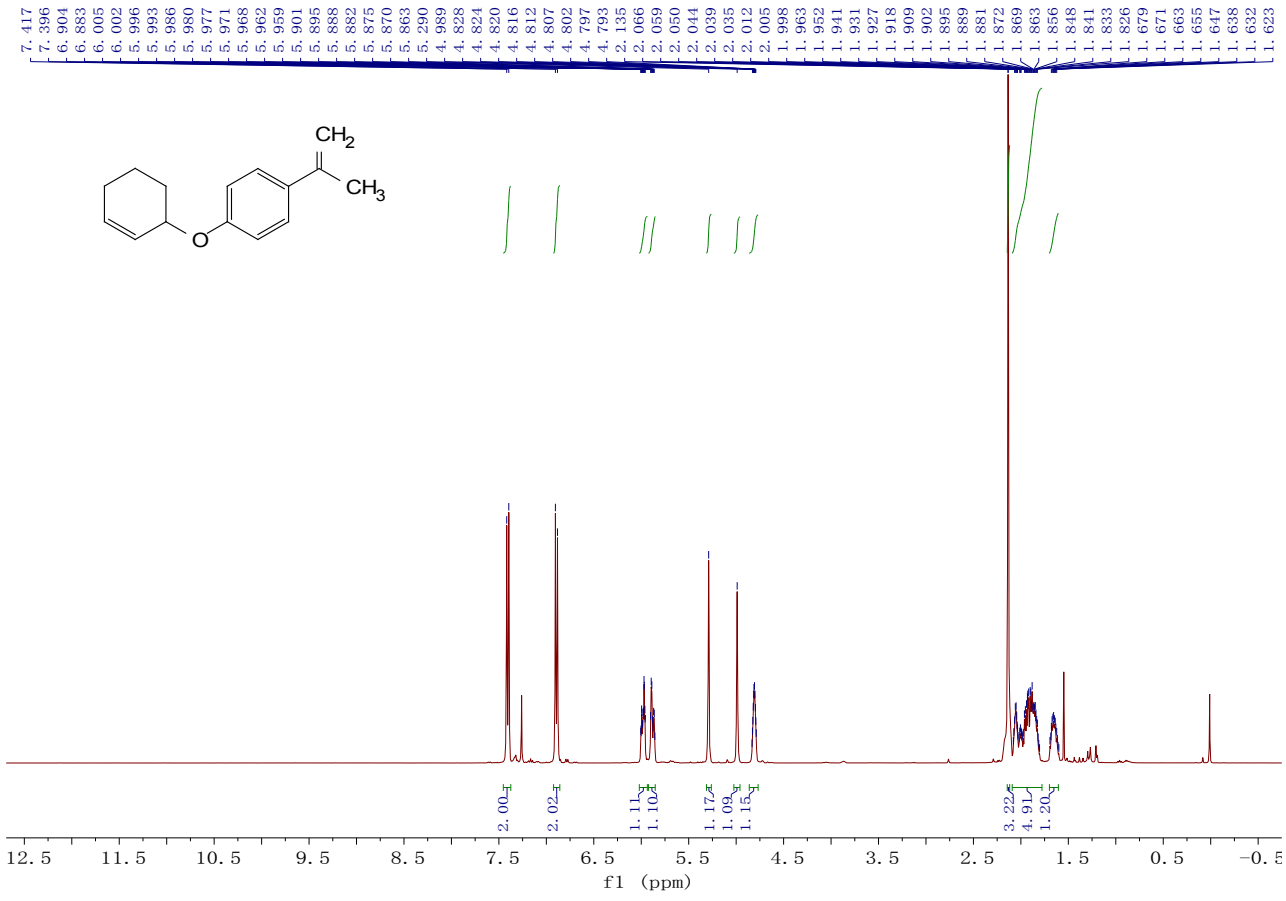


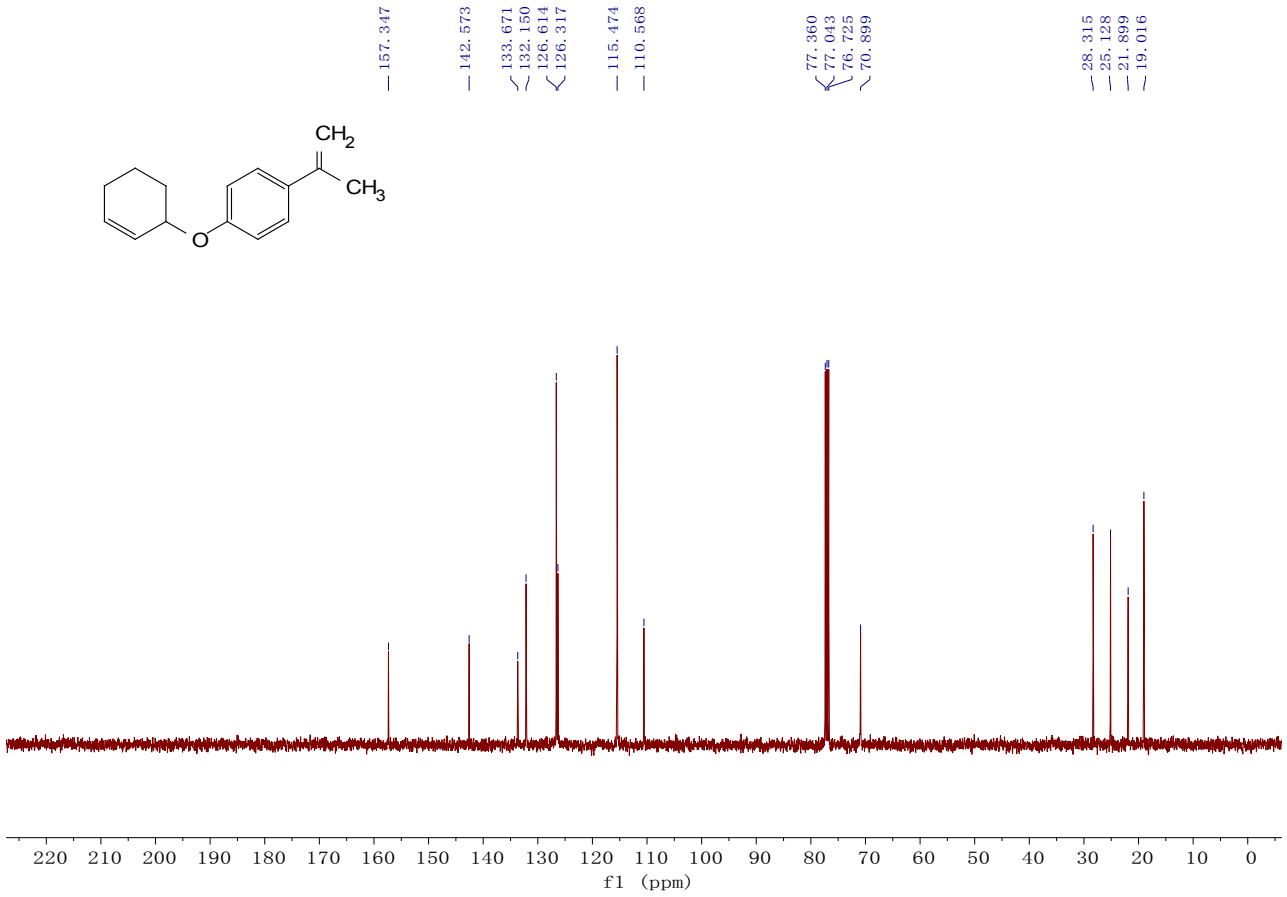
1-(But-3-en-1-yloxy)-4-(prop-1-en-2-yl)benzene (32a)





1-(Cyclohex-2-en-1-yloxy)-4-(prop-1-en-2-yl)benzene (33a)





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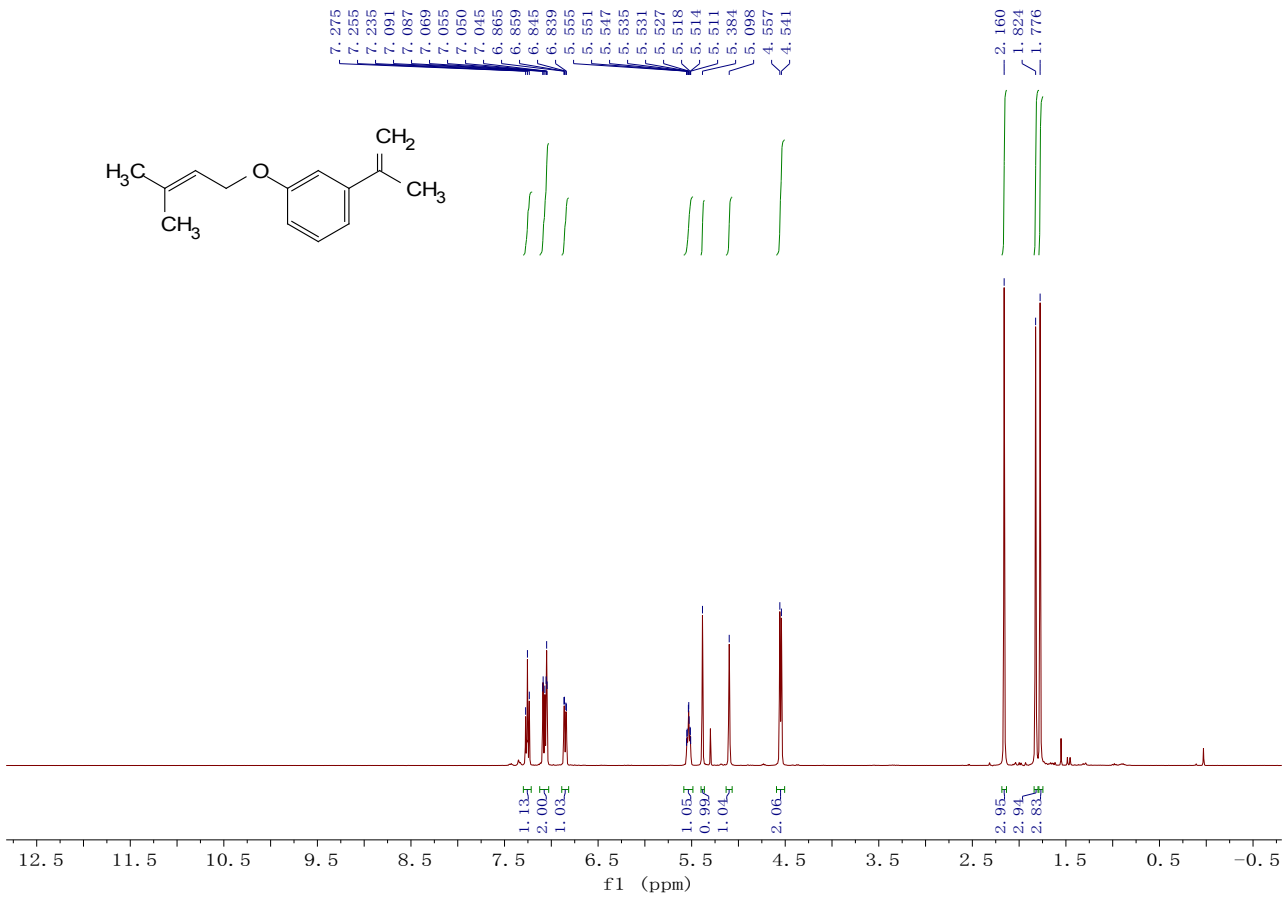
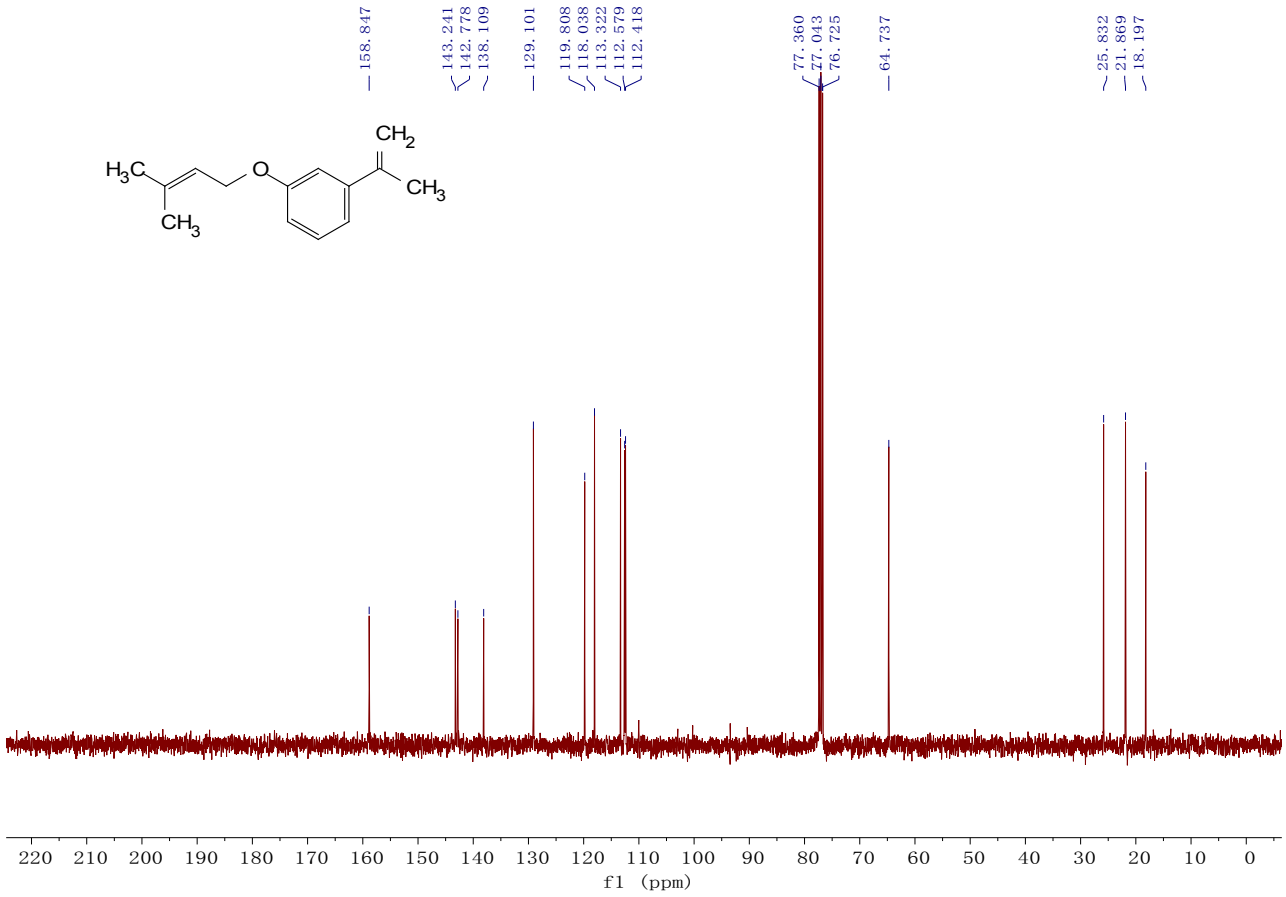
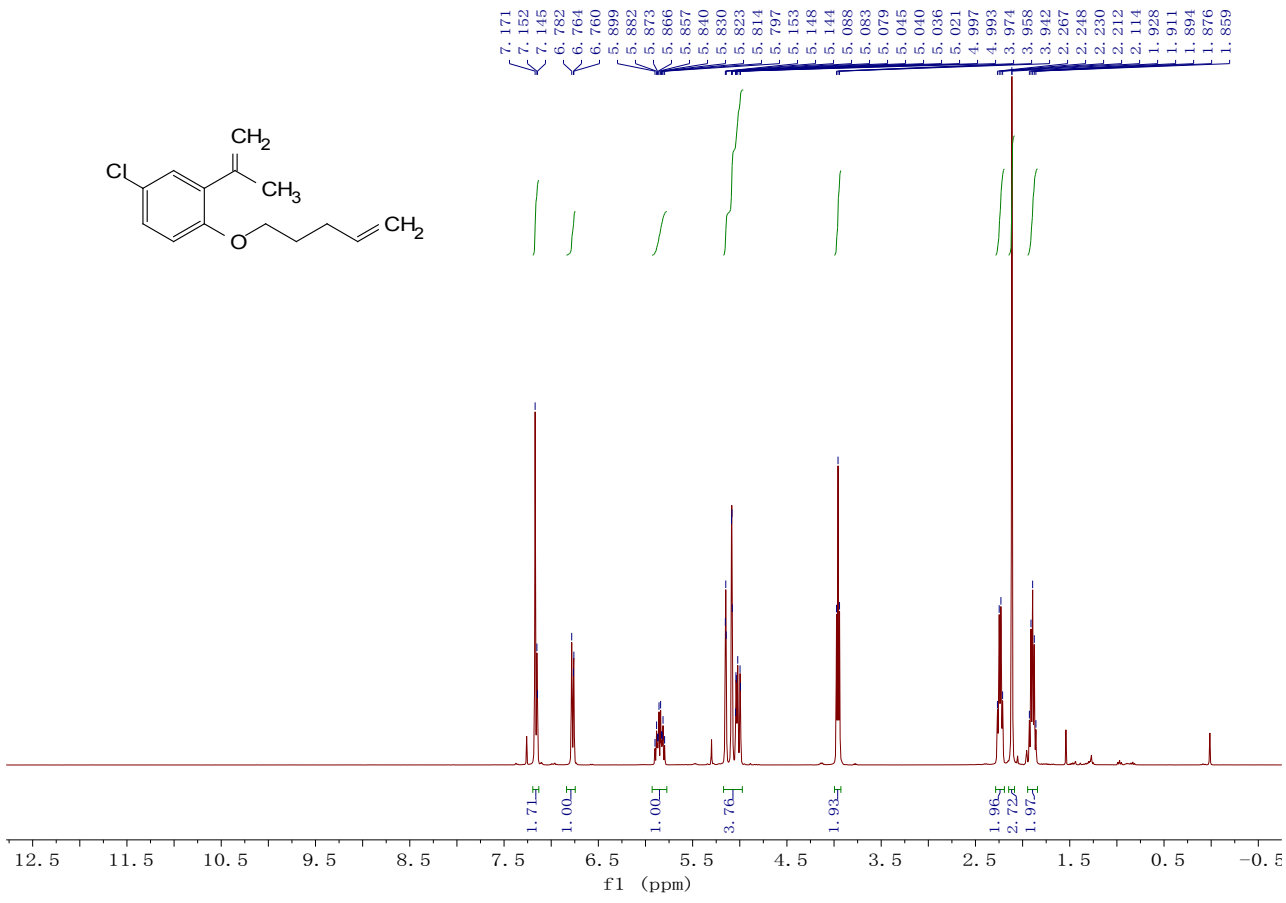
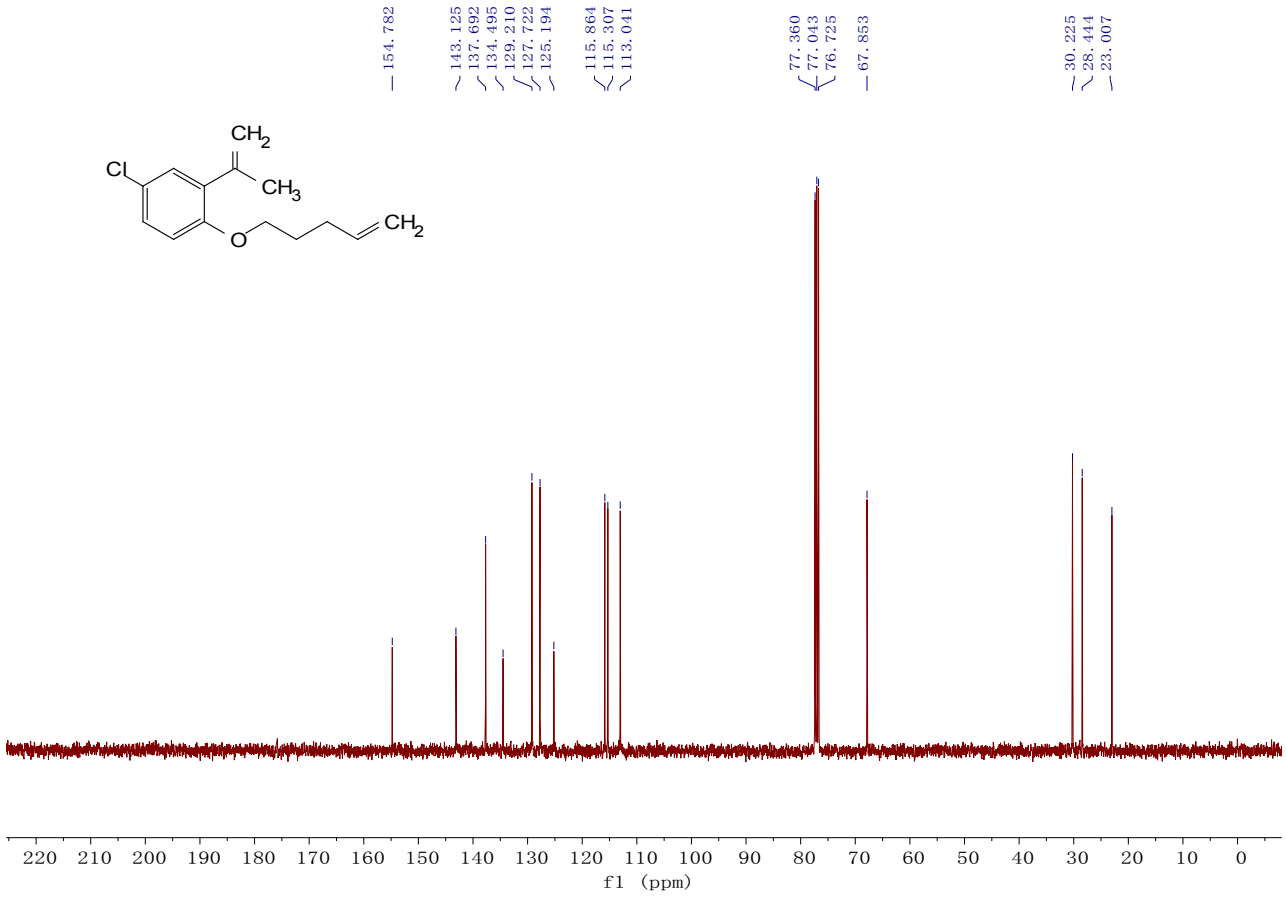


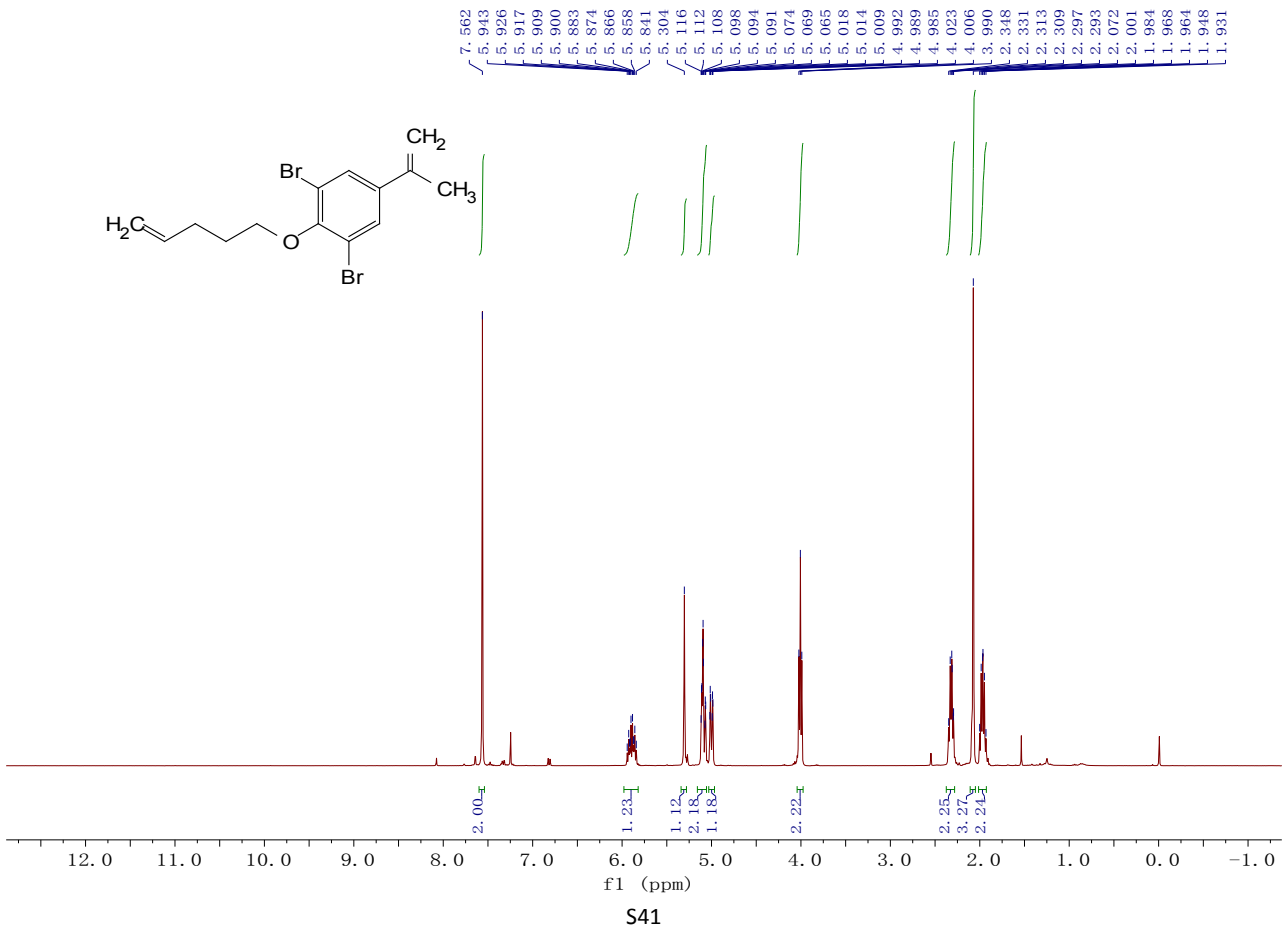


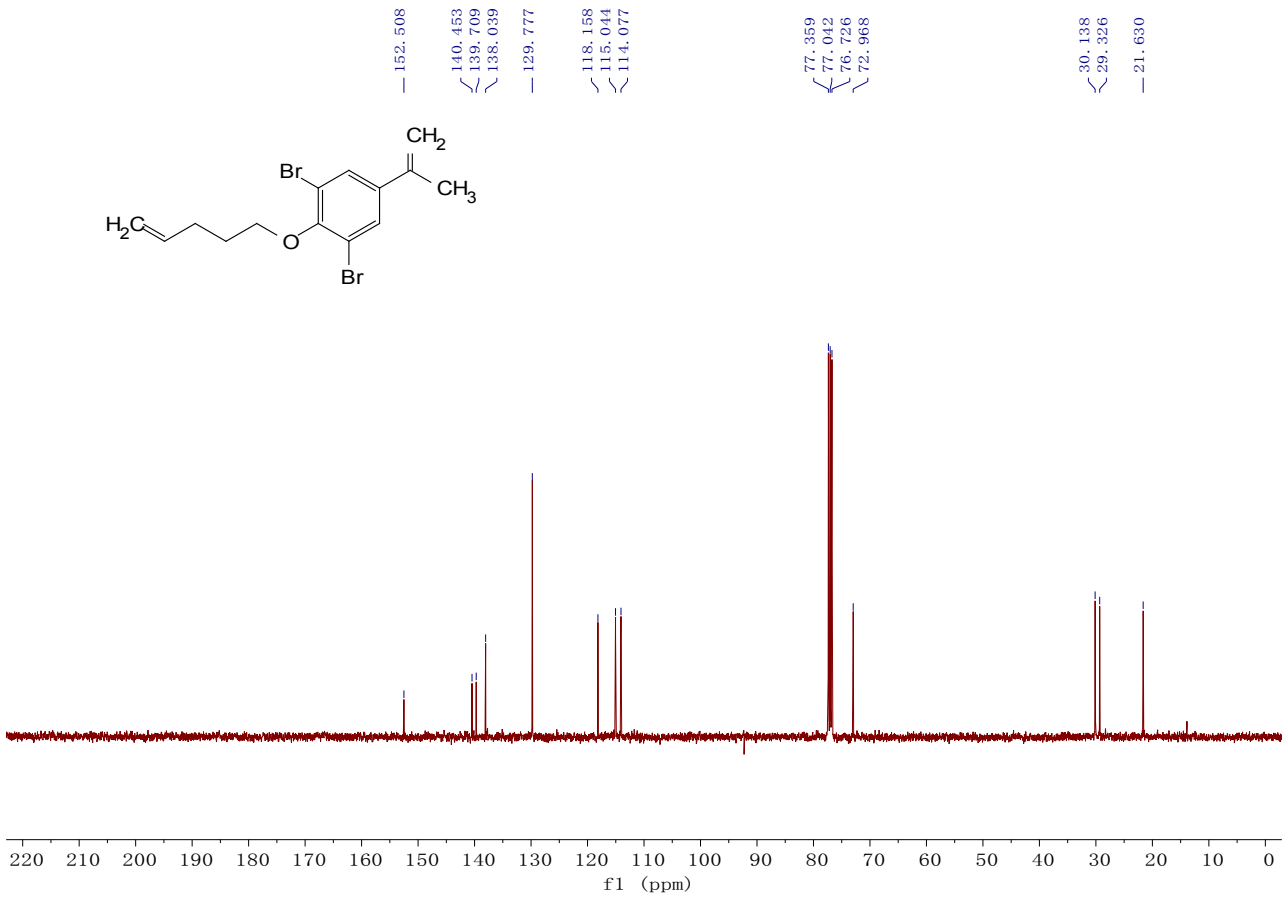
4-Chloro-1-(pent-4-en-1-yloxy)-2-(prop-1-en-2-yl)benzene (35a)



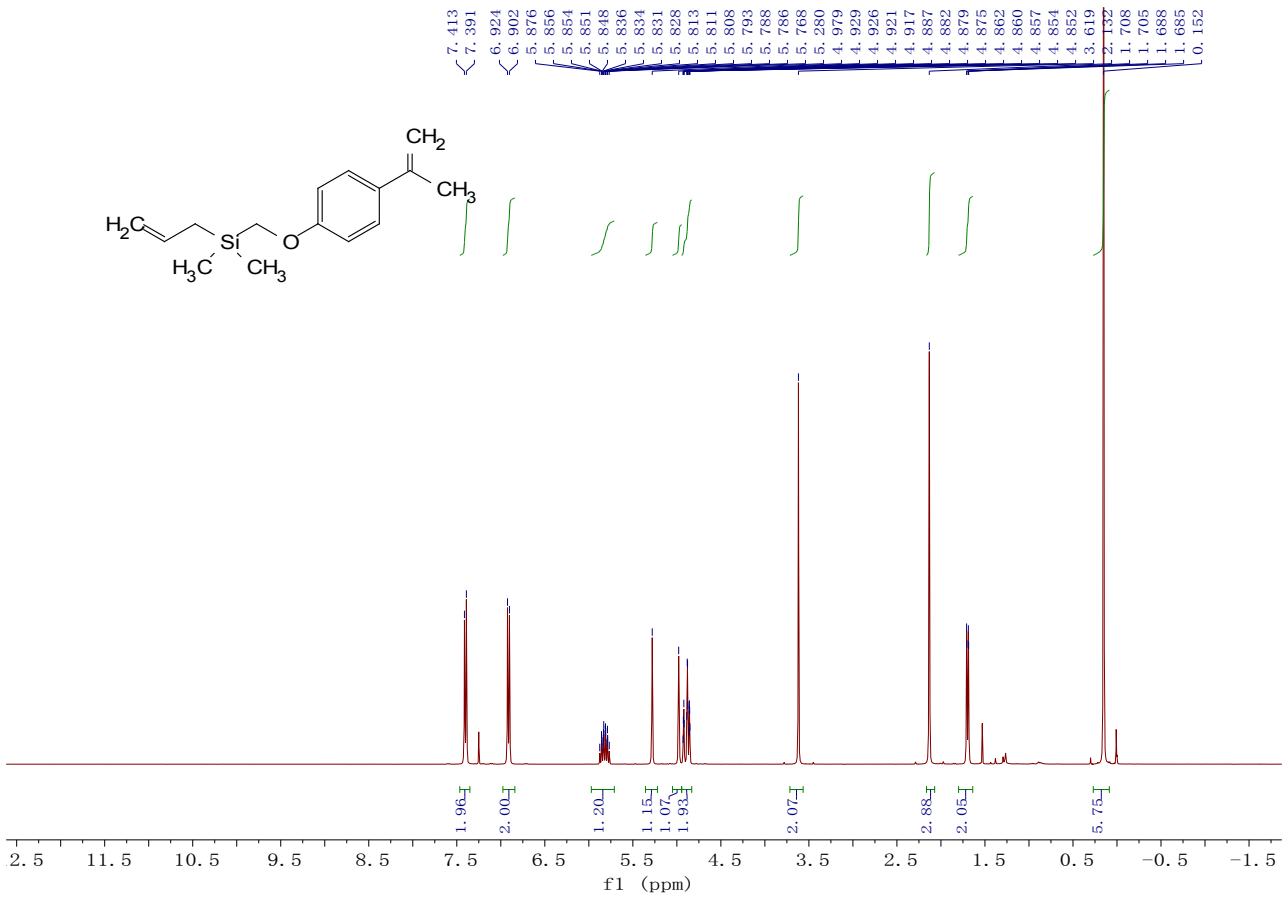


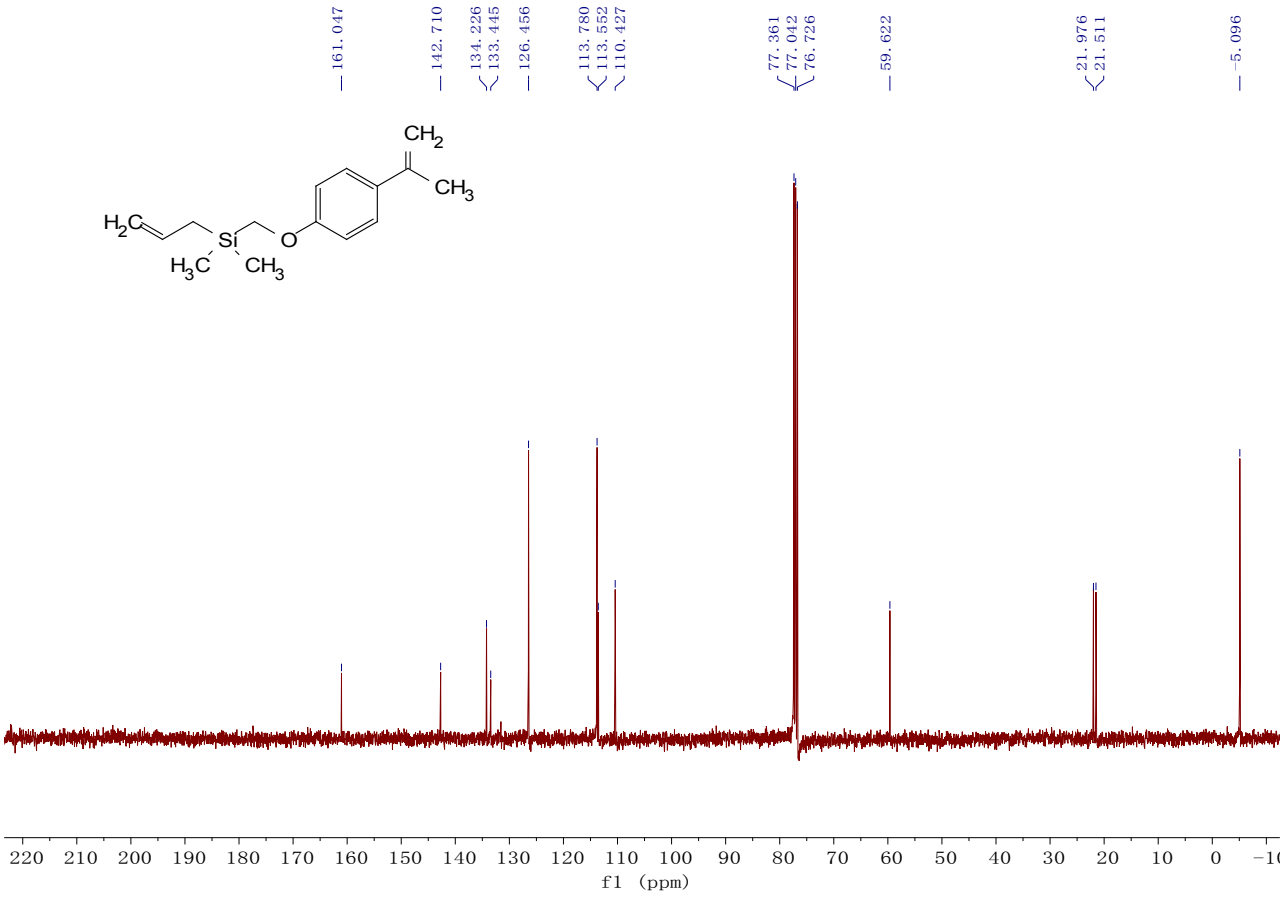
1,3-Dibromo-2-(pent-4-en-1-yloxy)-5-(prop-1-en-2-yl)benzene (36a)



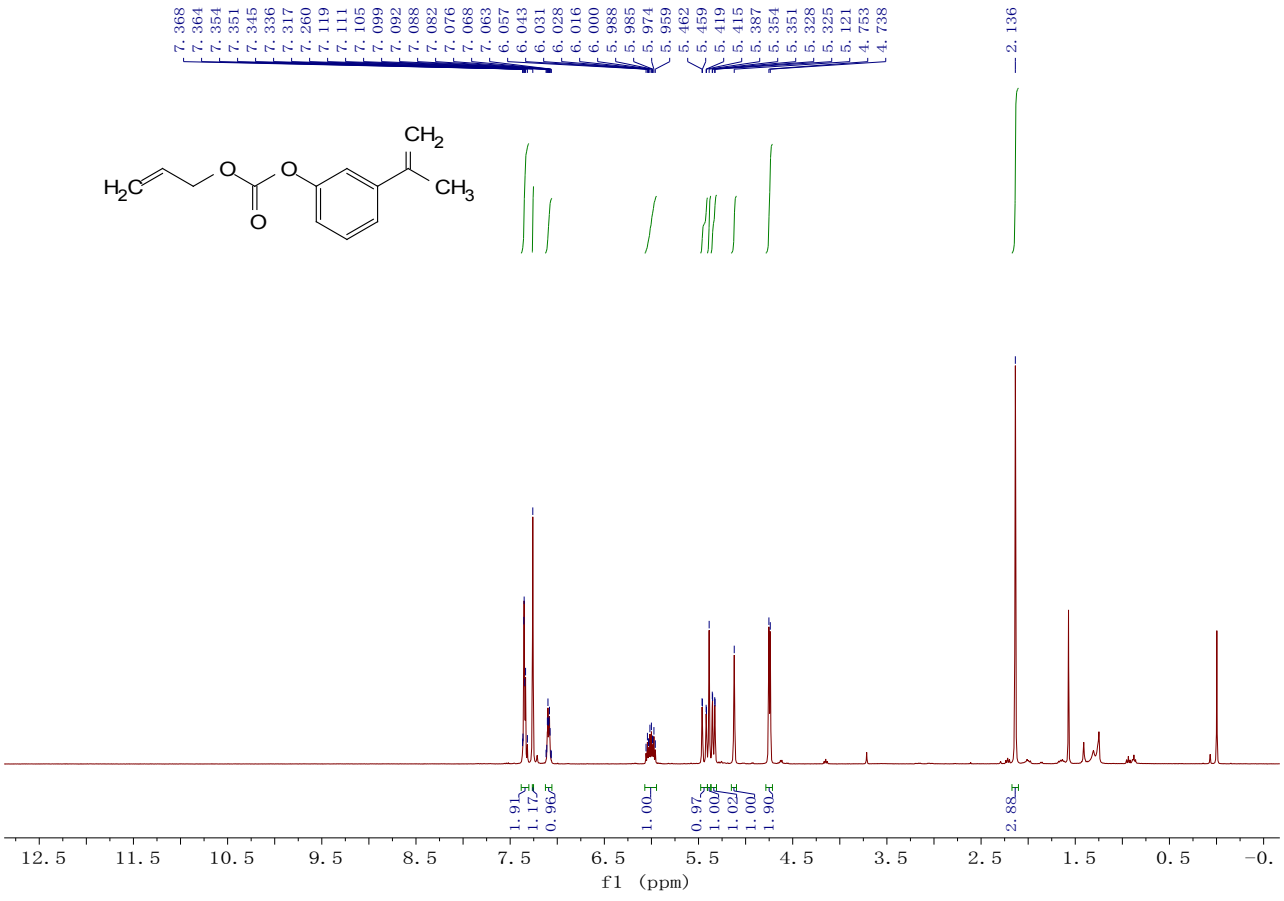


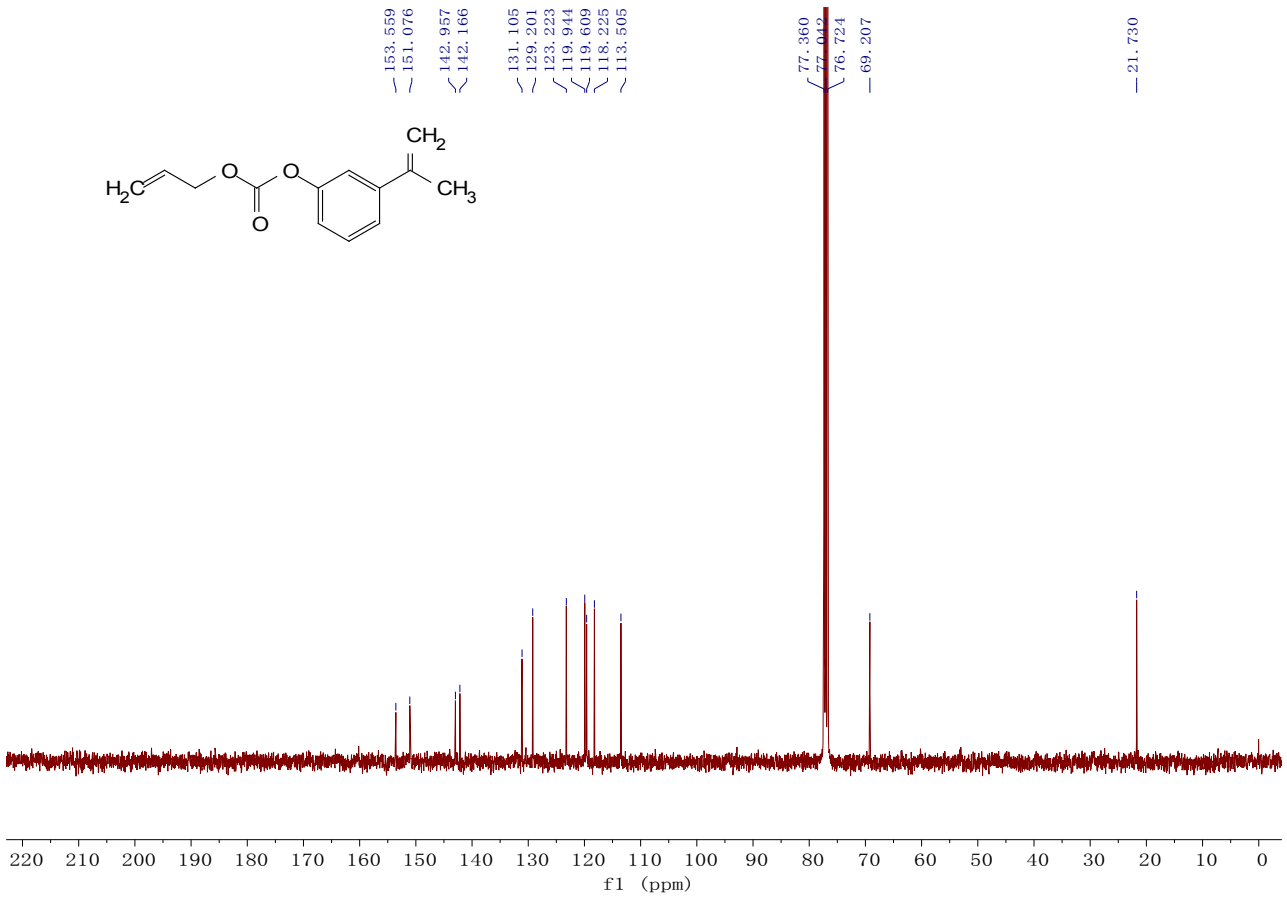
Allyldimethyl((4-(prop-1-en-2-yl)phenoxy)methyl)silane (37a)



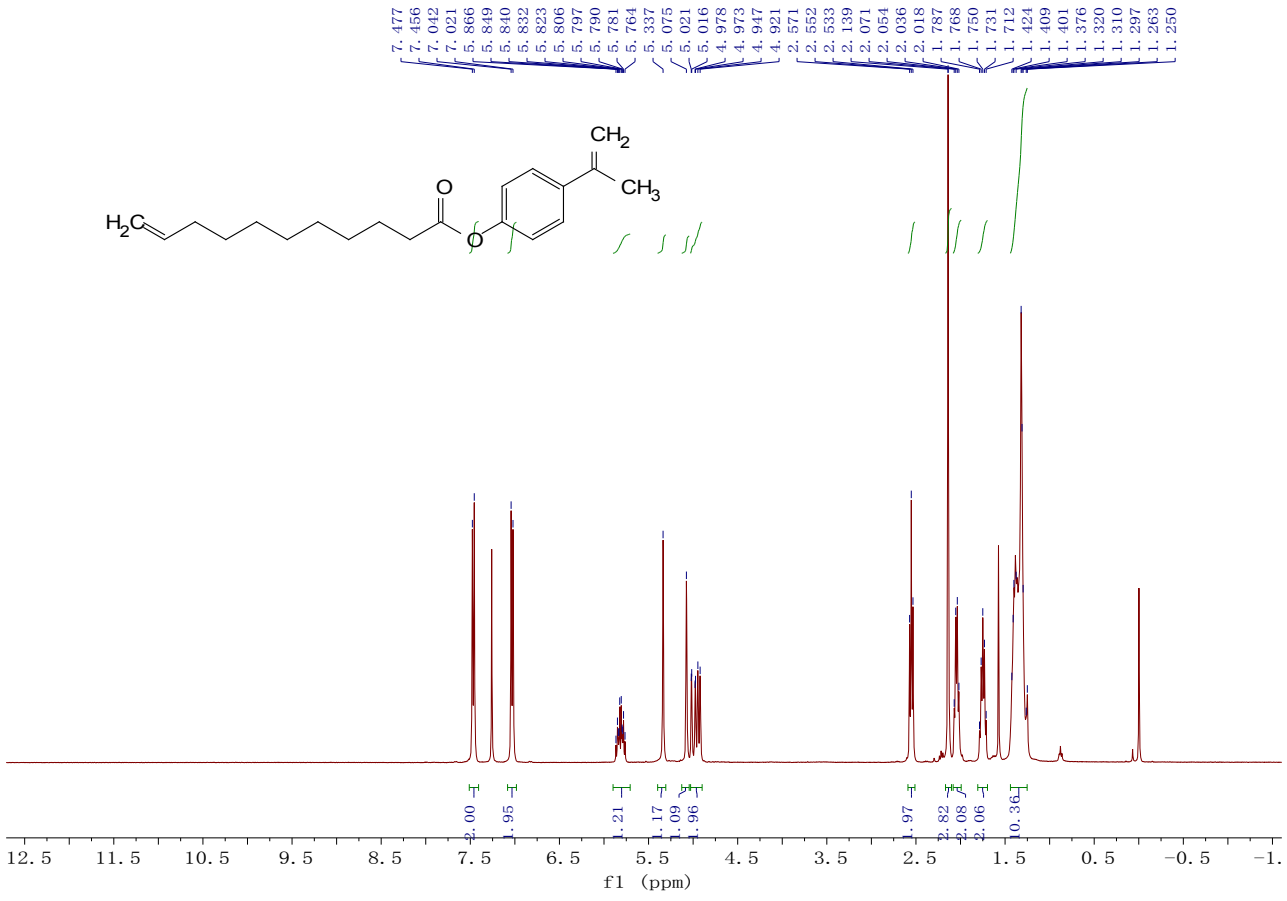


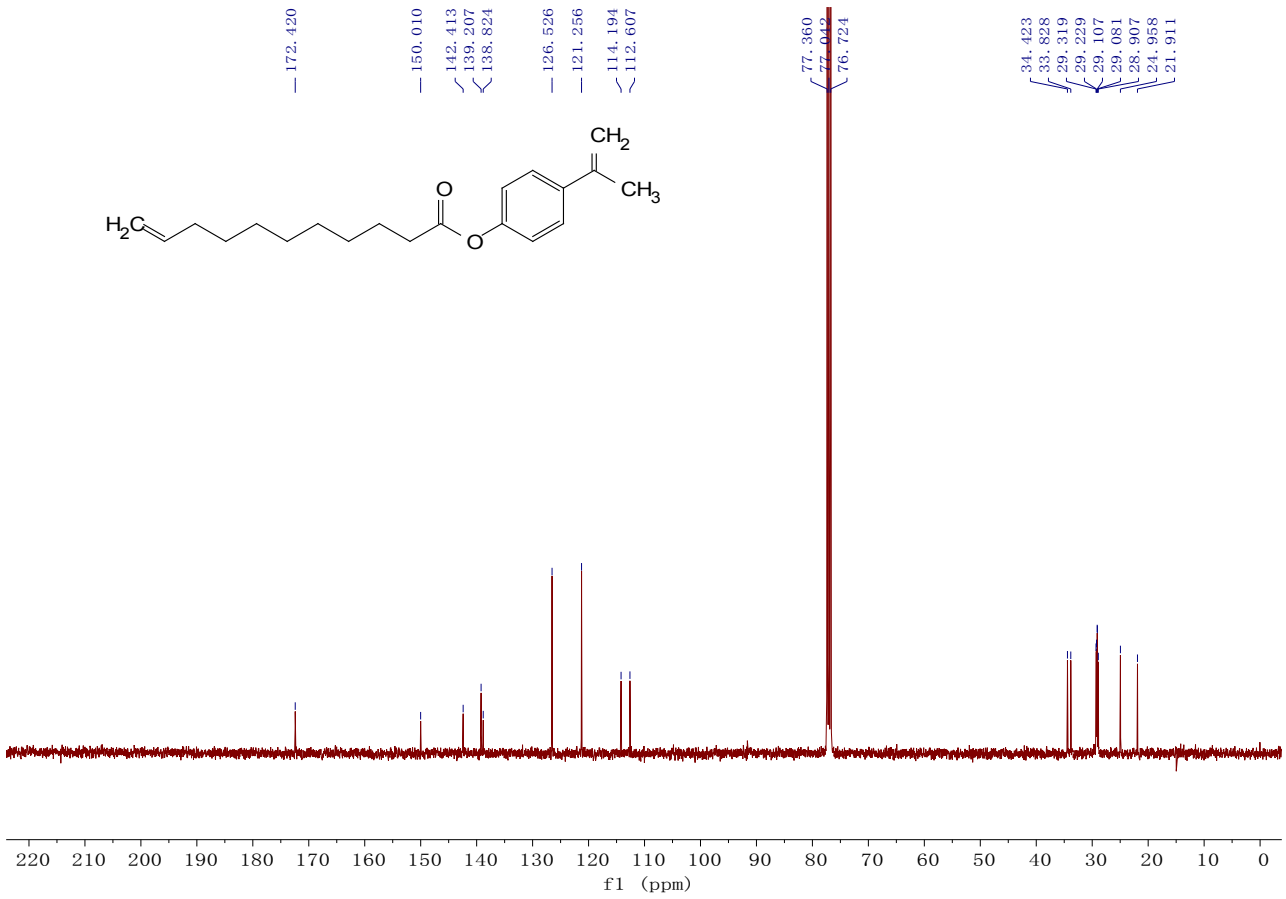
Allyl (3-(prop-1-en-2-yl)phenyl) carbonate (38a)



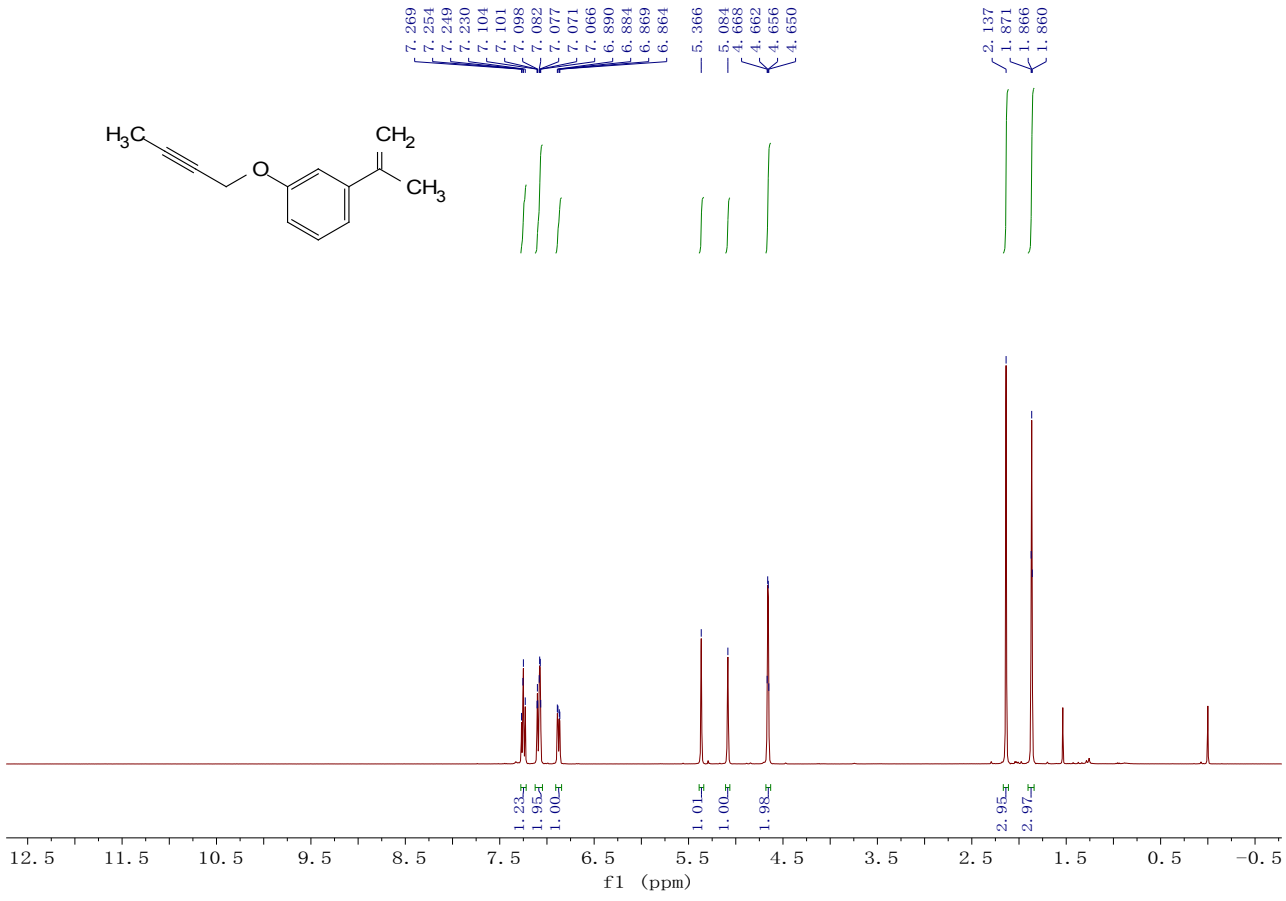


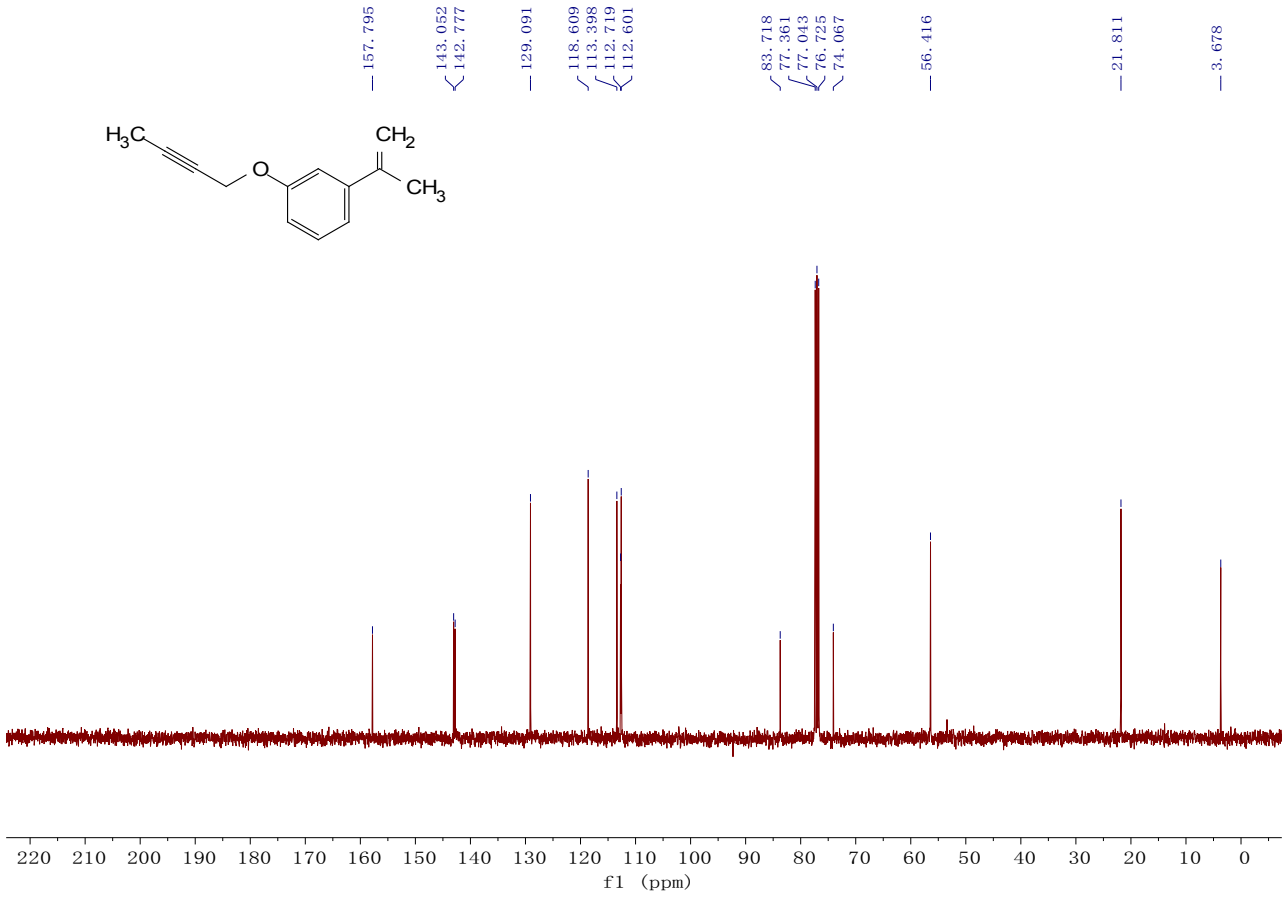
4-(Prop-1-en-2-yl)phenyl undec-10-enoate (39a)



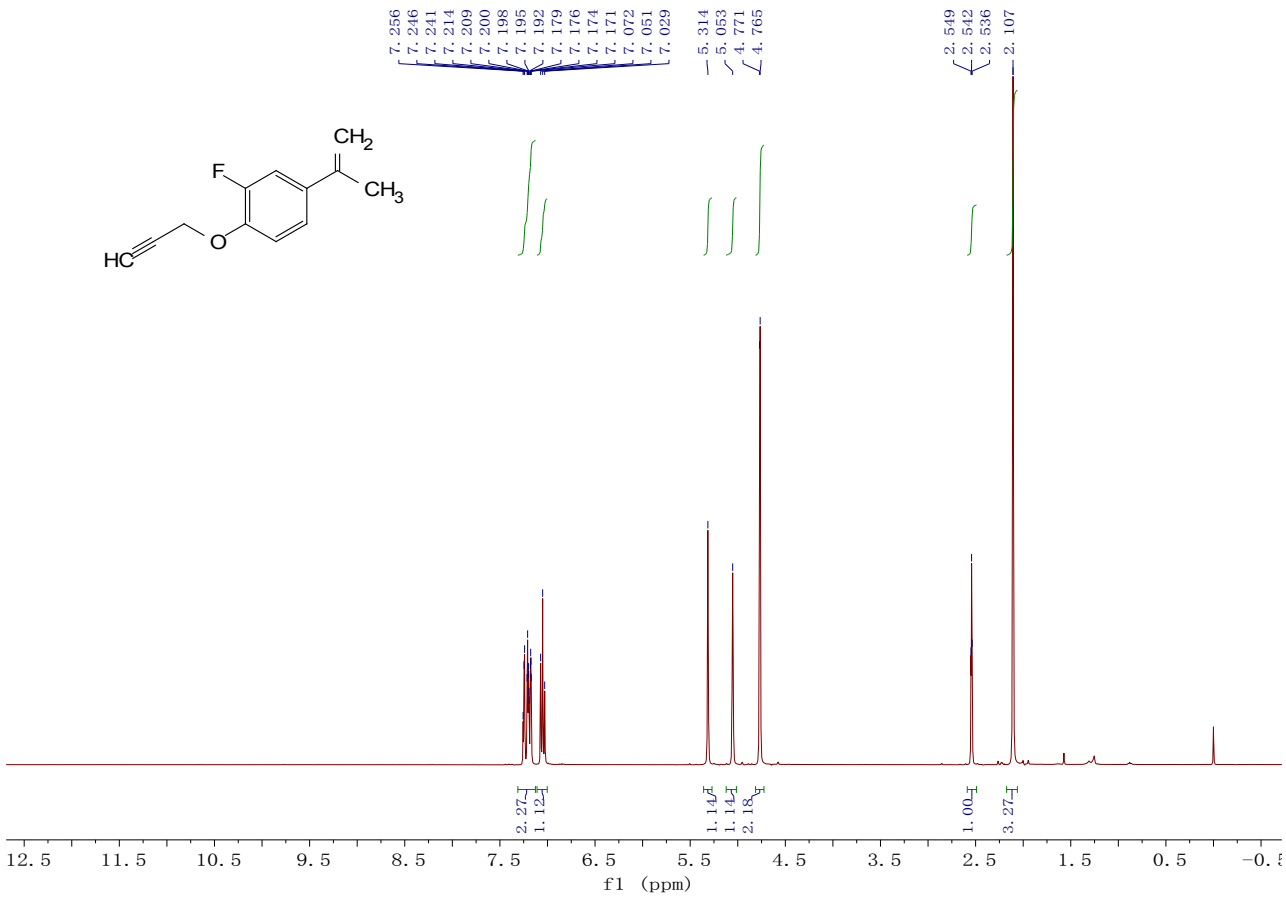


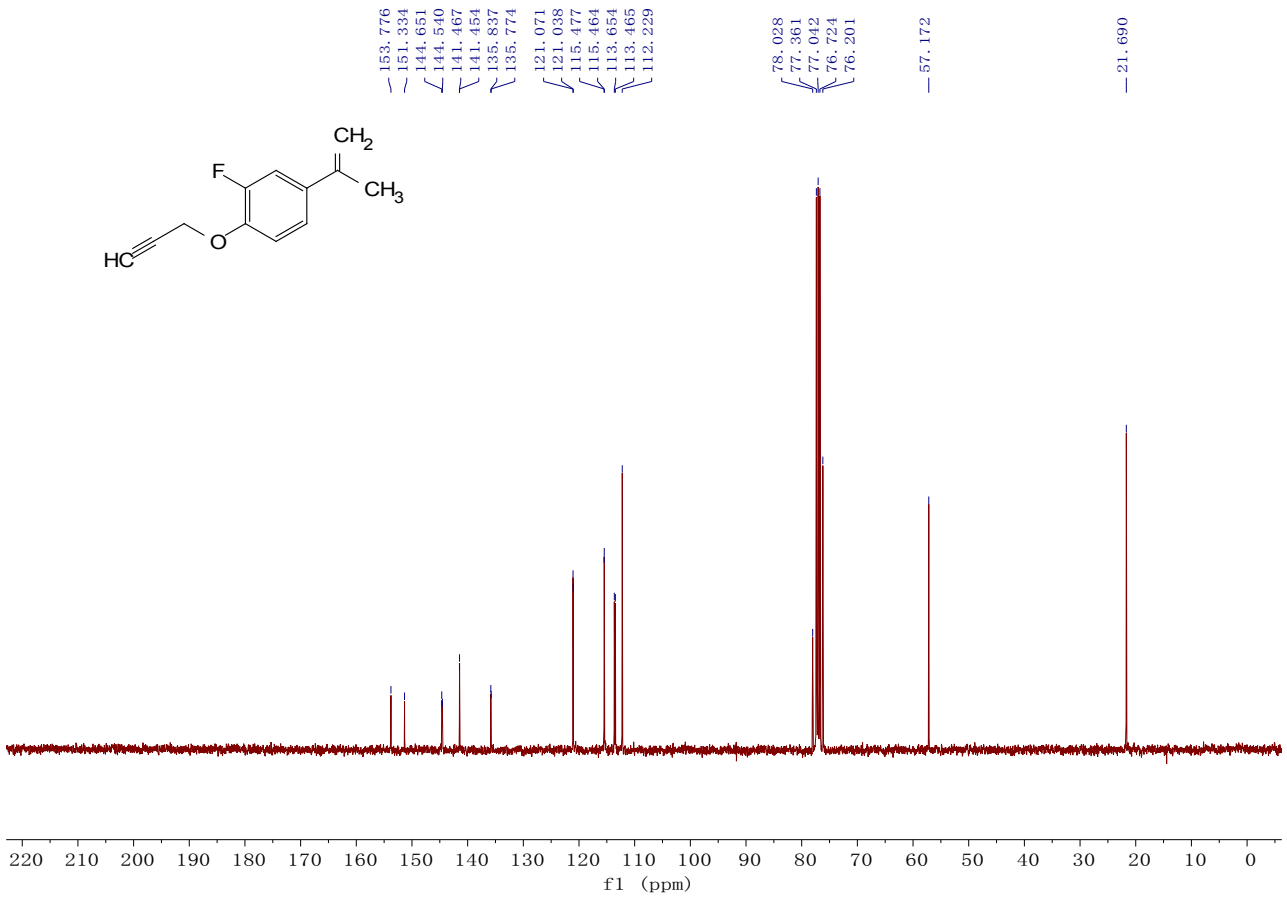
1-(But-2-yn-1-yloxy)-3-(prop-1-en-2-yl)benzene (40a)



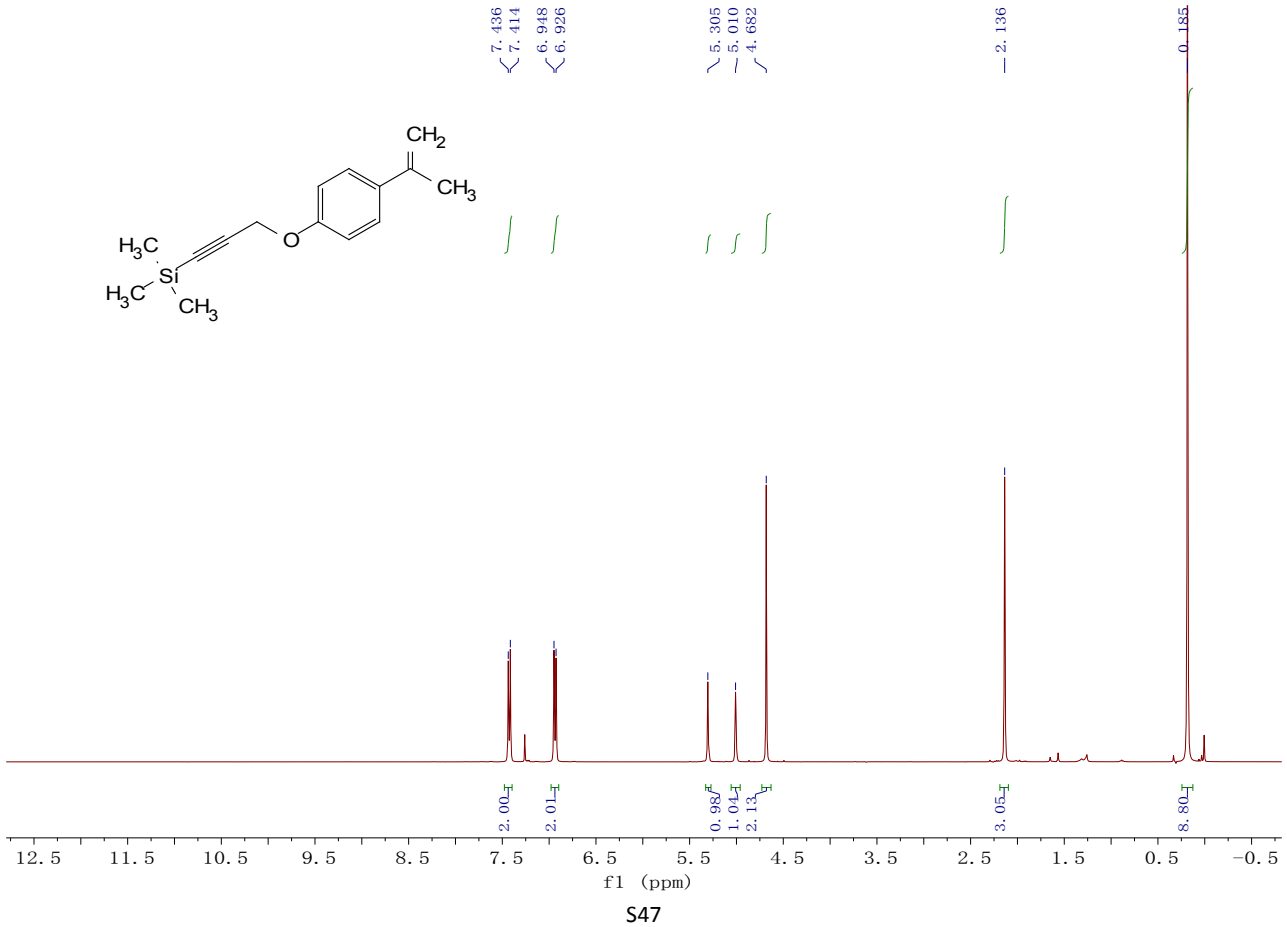


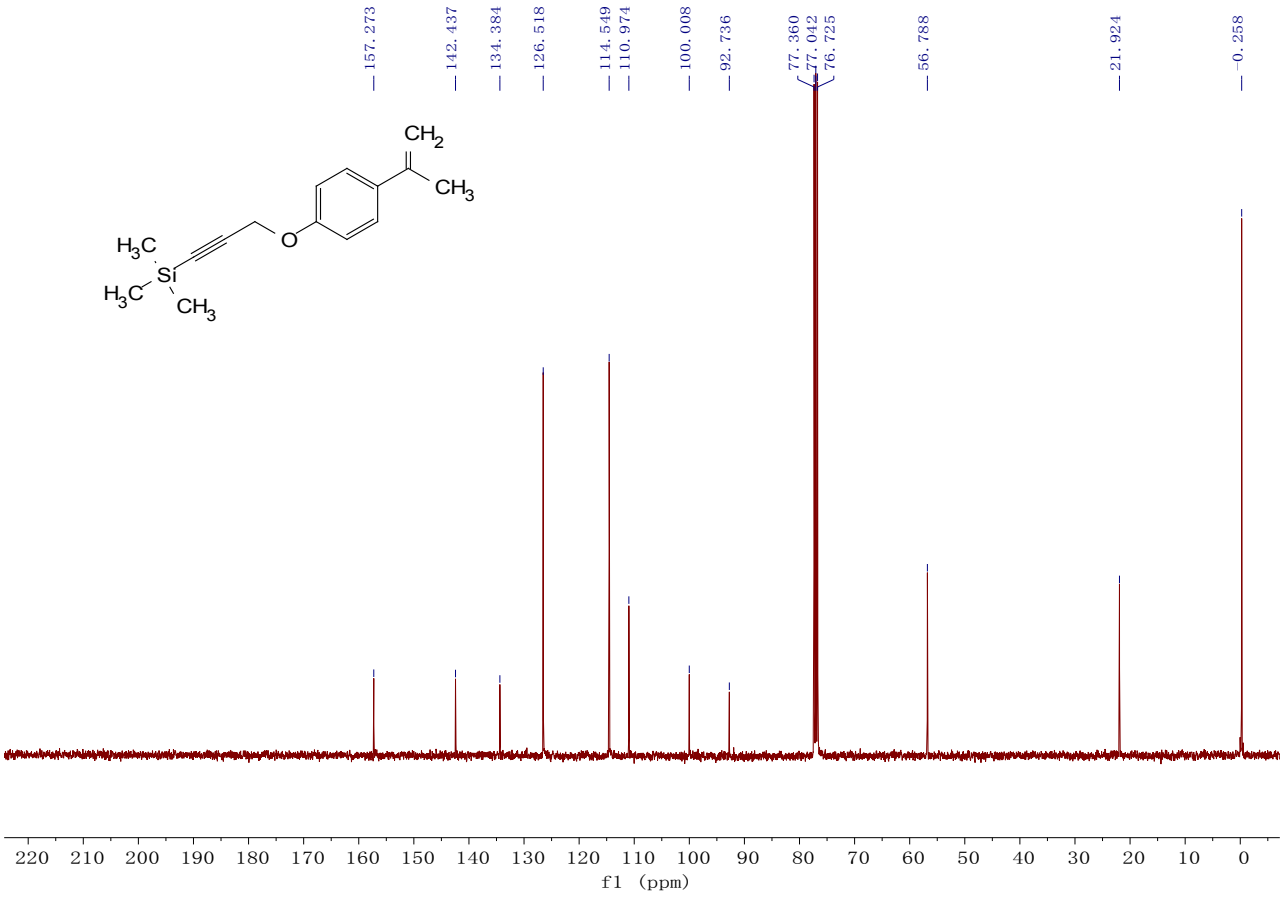
2-Fluoro-4-(prop-1-en-2-yl)-1-(prop-2-yn-1-yloxy)benzene (41a)



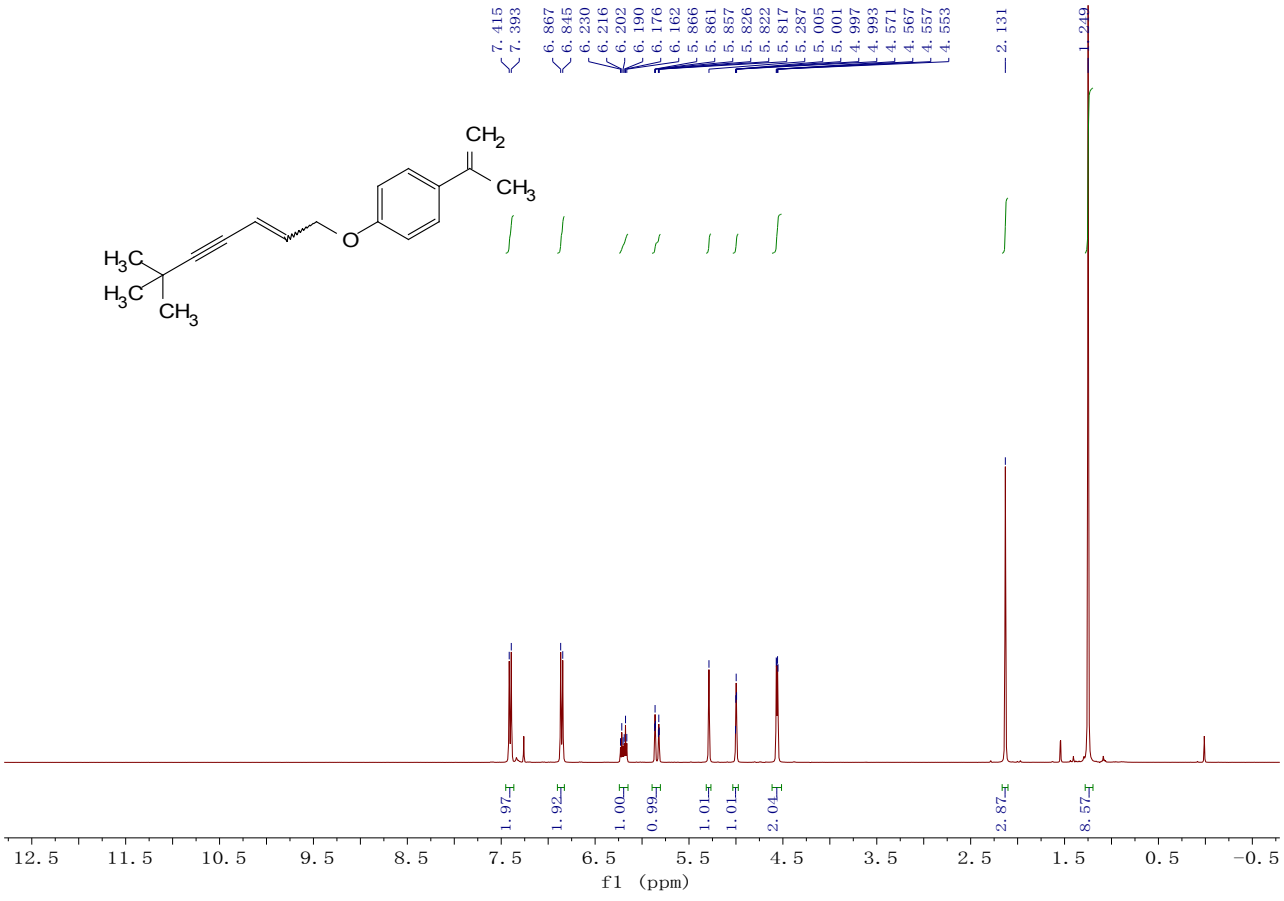


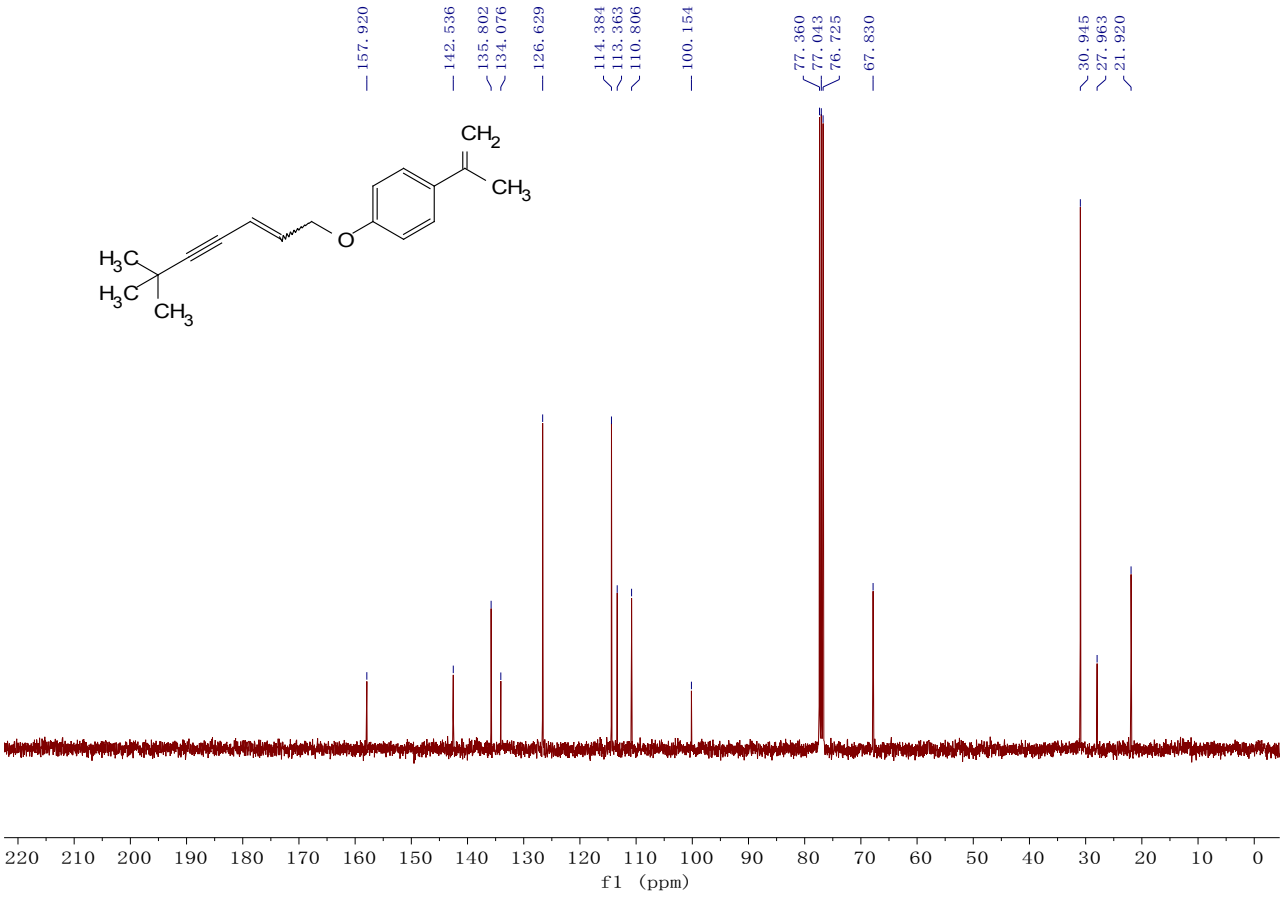
Trimethyl(3-(4-(prop-1-en-2-yl)phenoxy)prop-1-yn-1-yl)silane (42a)



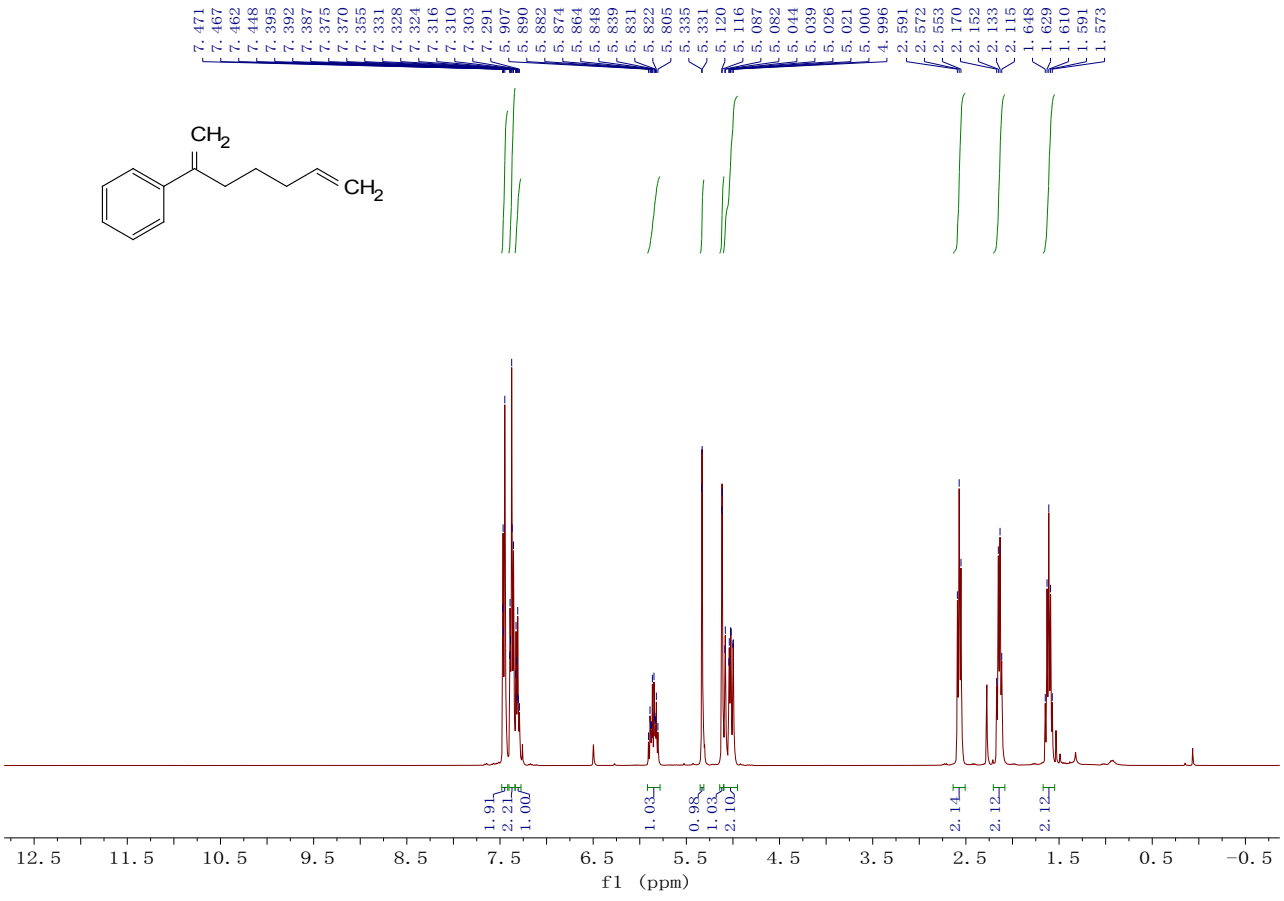


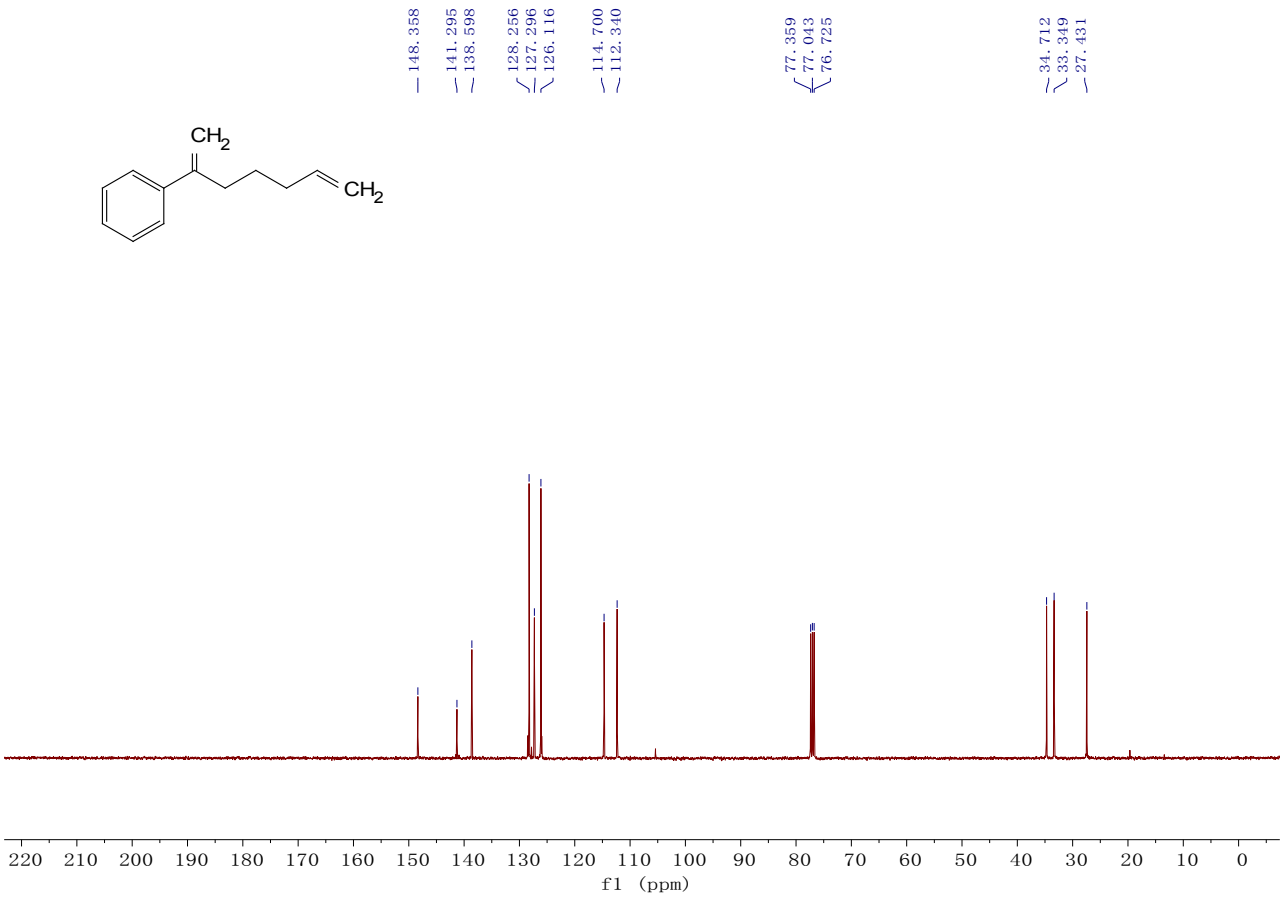
1-((6,6-Dimethylhept-2-en-4-yn-1-yl)oxy)-4-(prop-1-en-2-yl)benzene (43a)



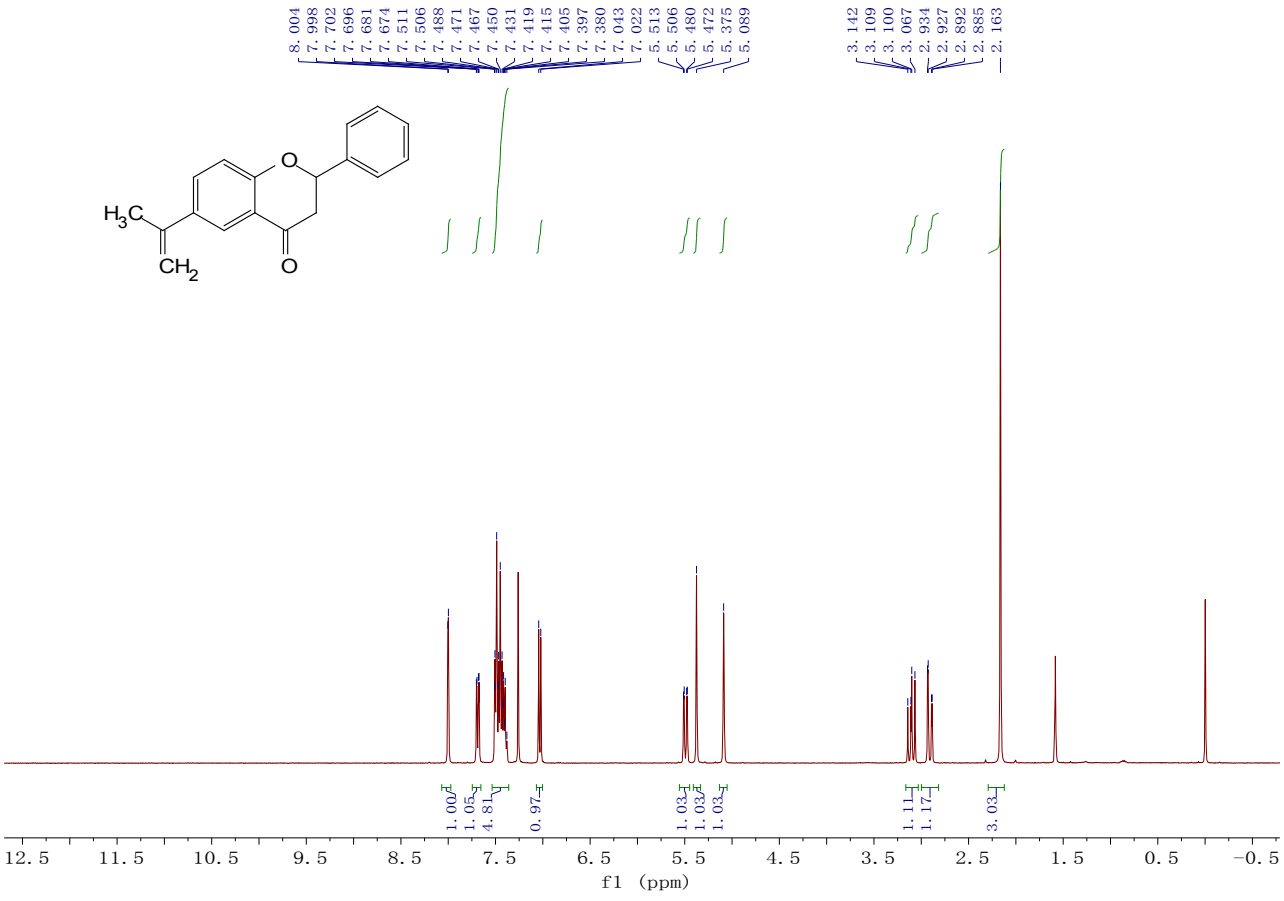


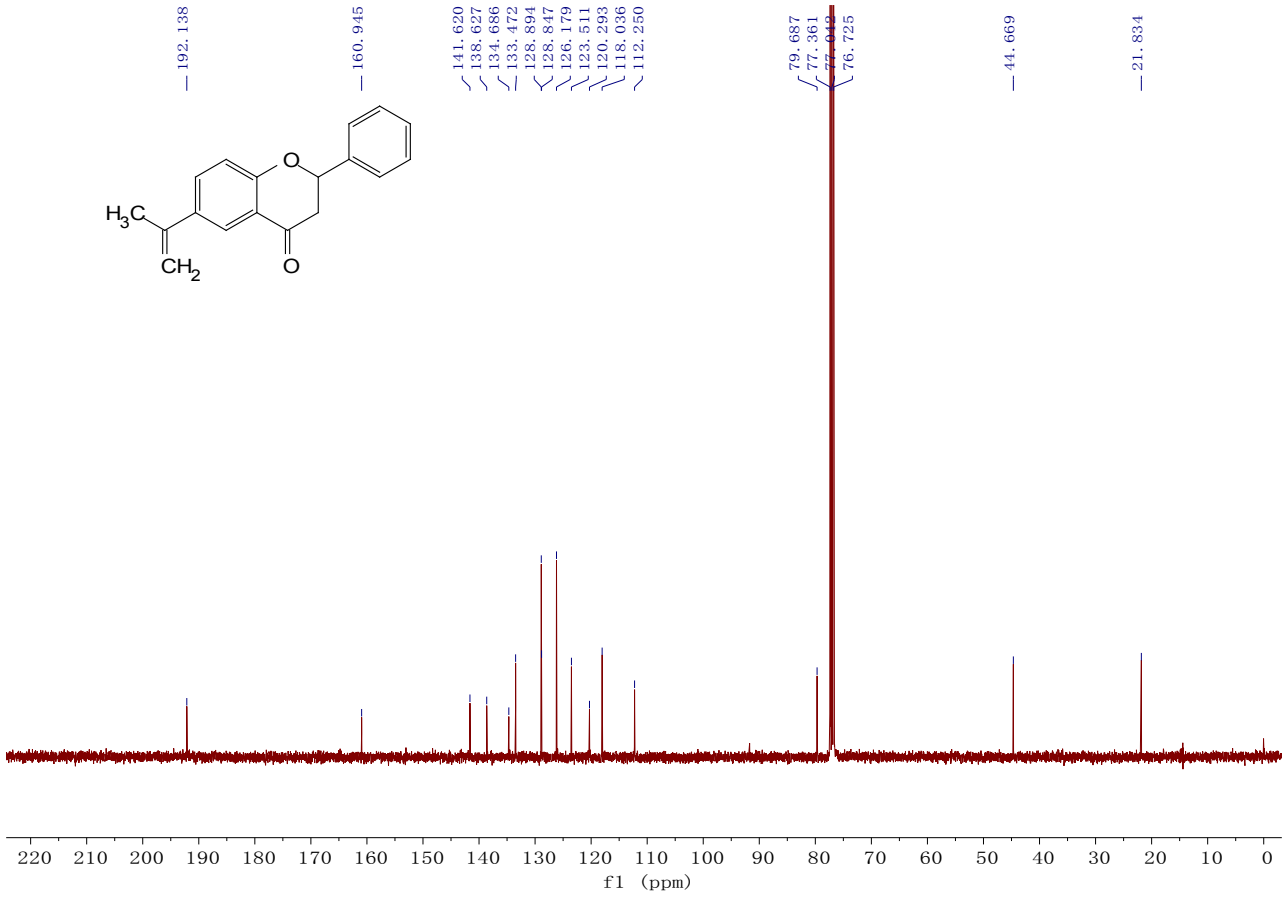
Hepta-1,6-dien-2-ylbenzene (44a)



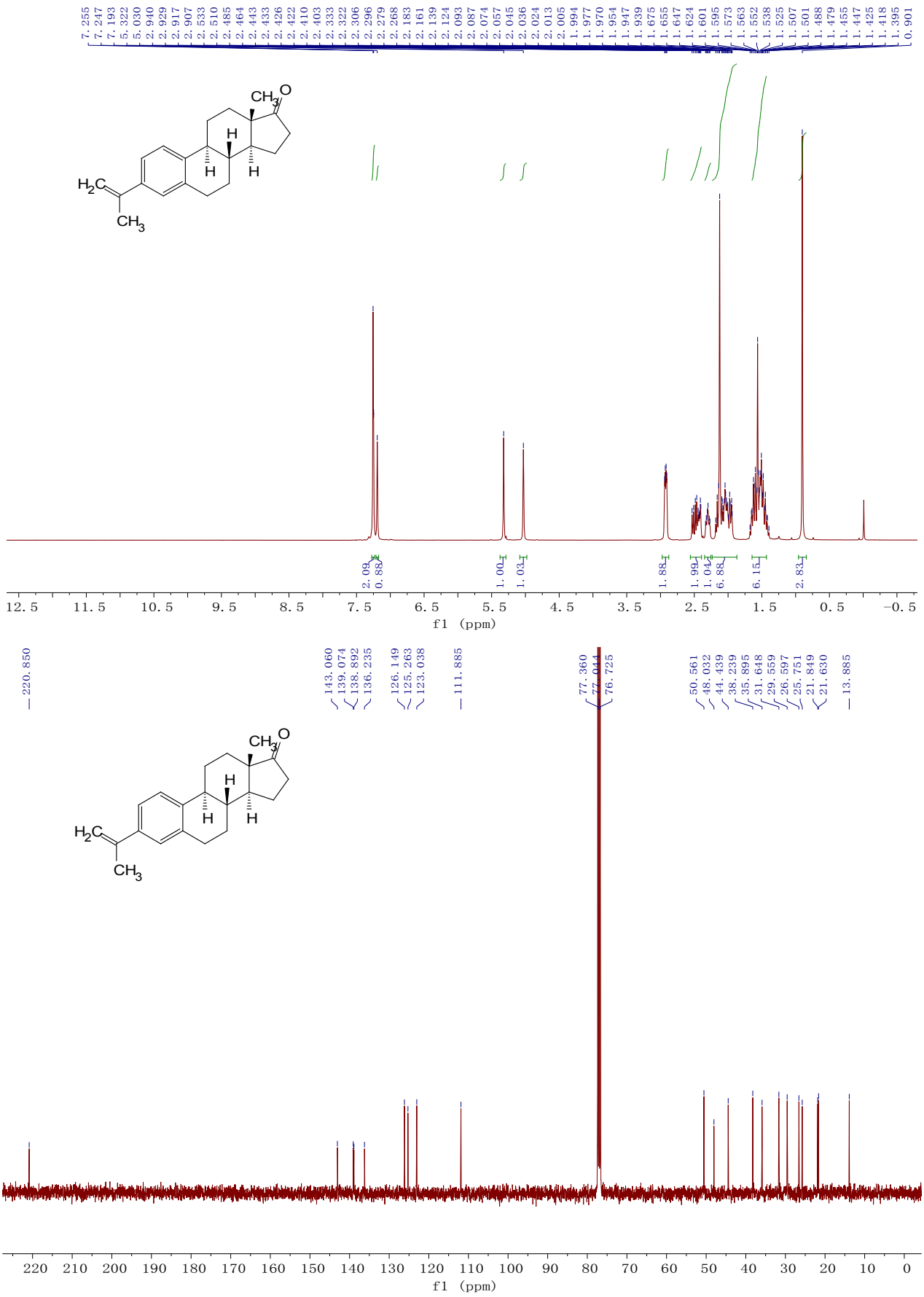


2-Phenyl-6-(prop-1-en-2-yl)chroman-4-one (45a)

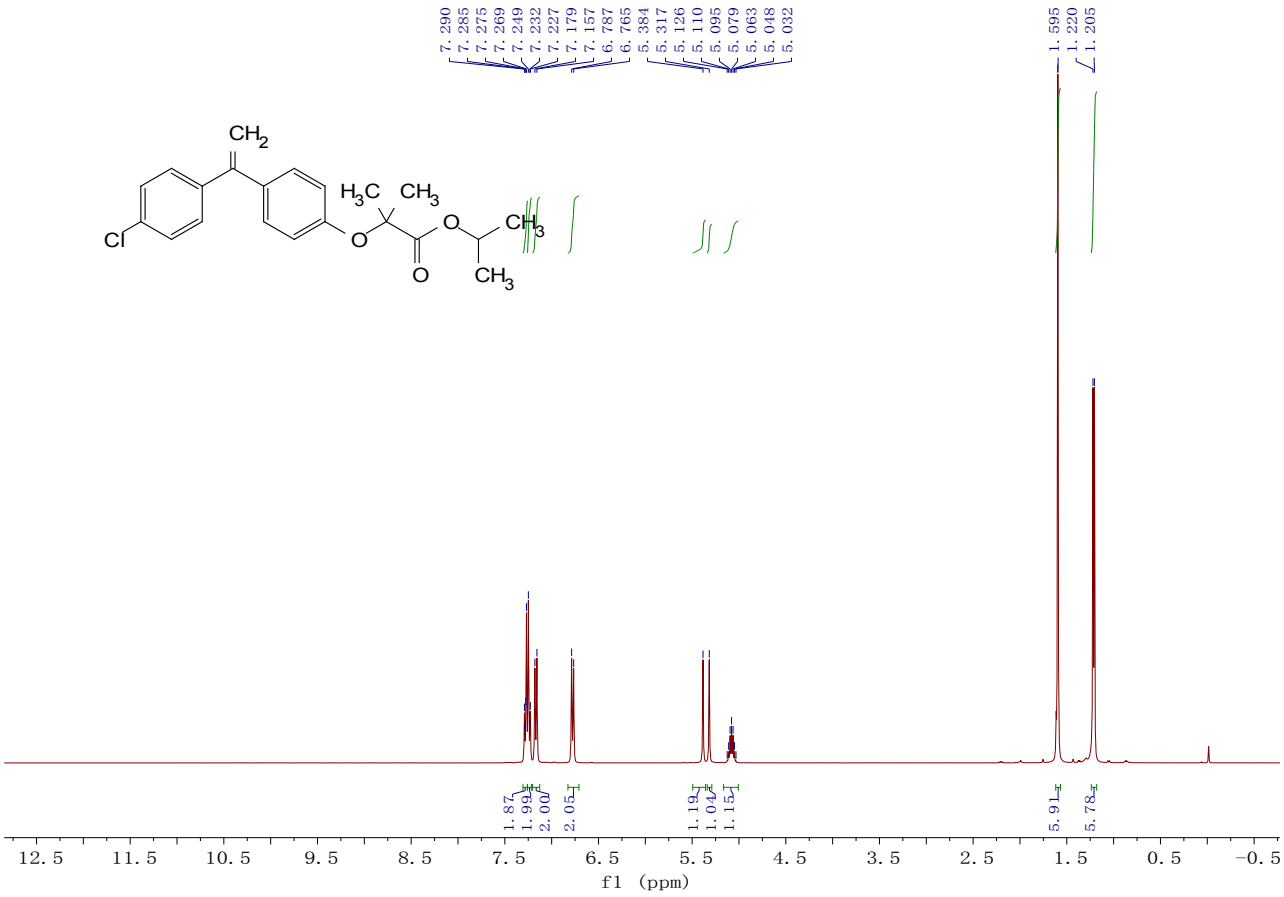




(8R,9S,13S,14S)-13-Methyl-3-(prop-1-en-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (46a)



Isopropyl 2-(4-(1-(4-chlorophenyl)vinyl)phenoxy)-2-methylpropanoate (47a)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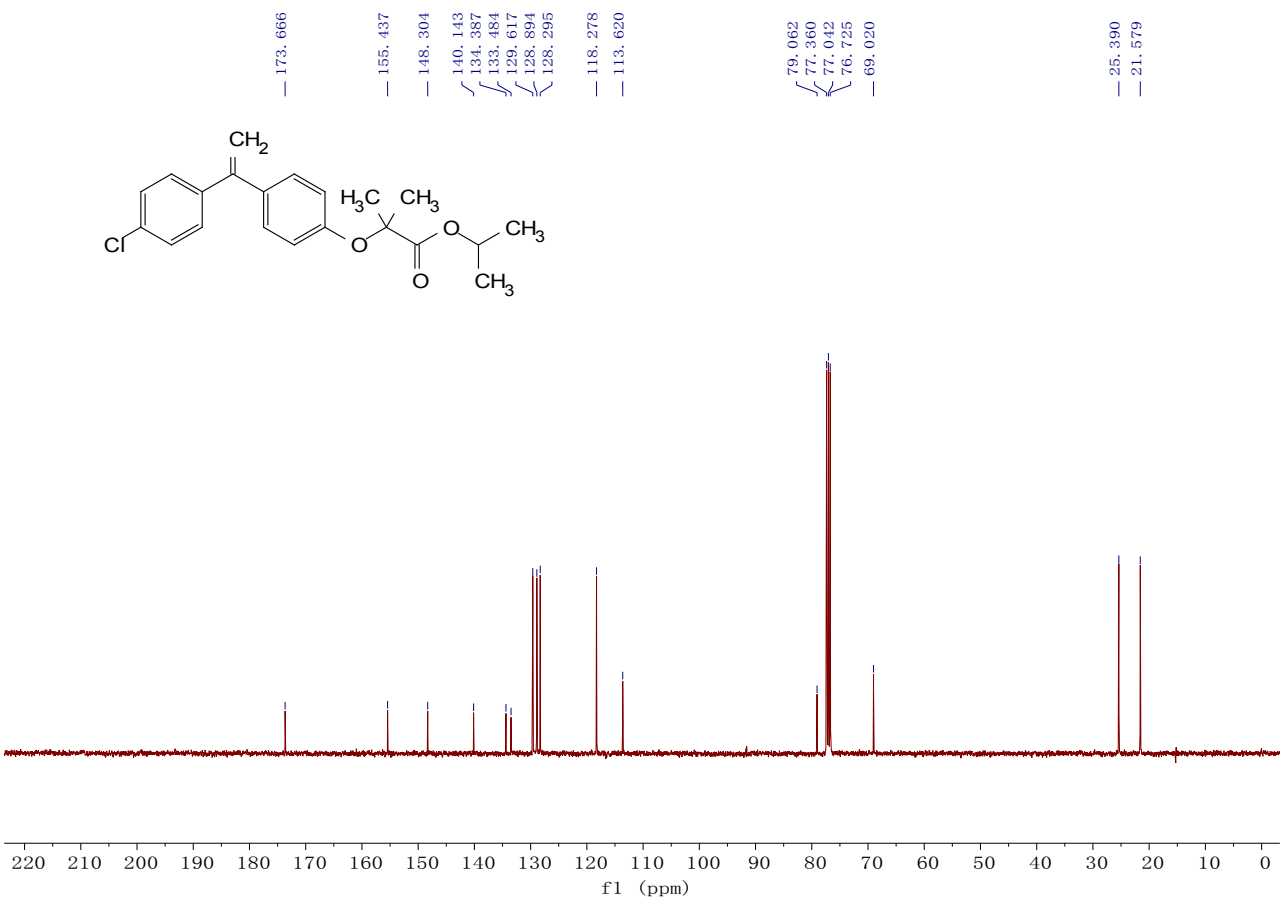
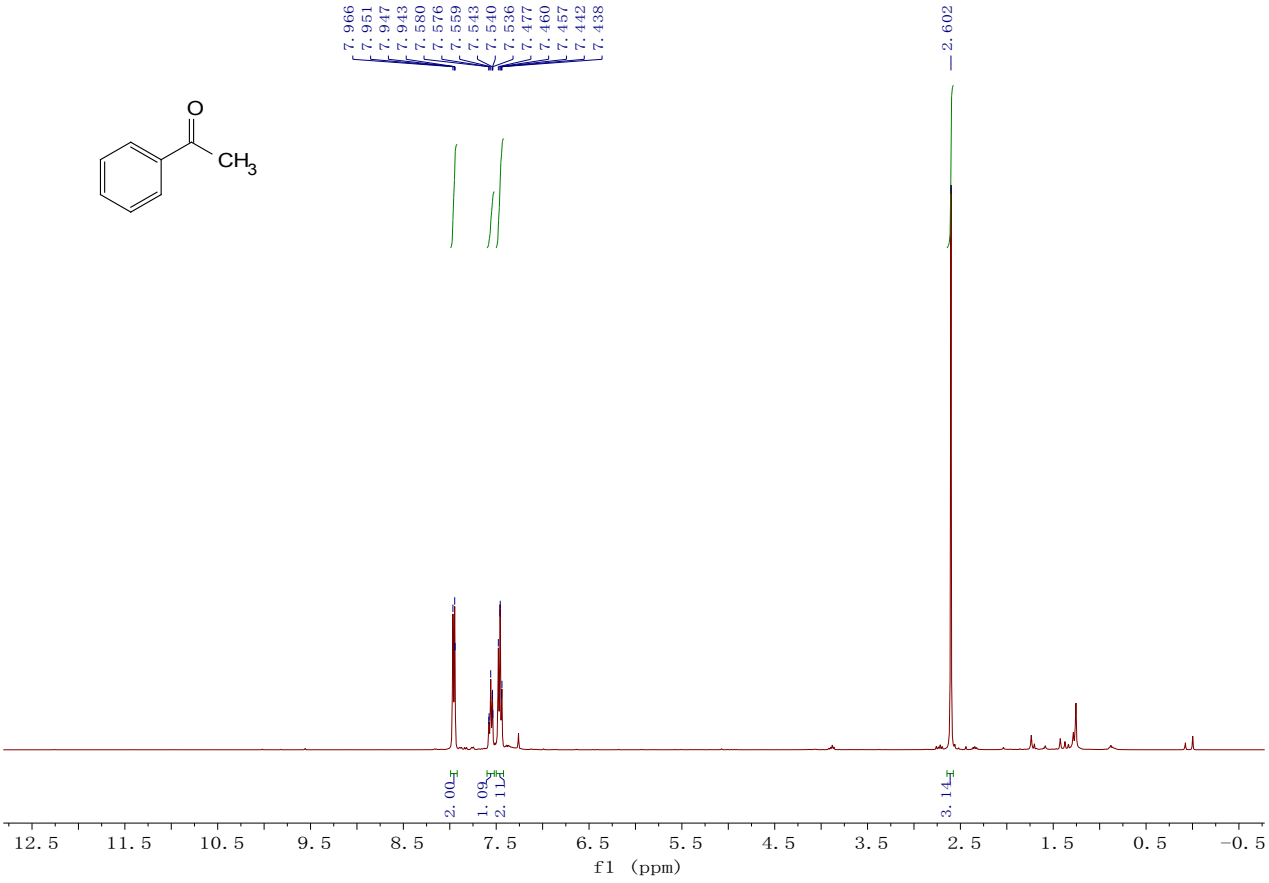
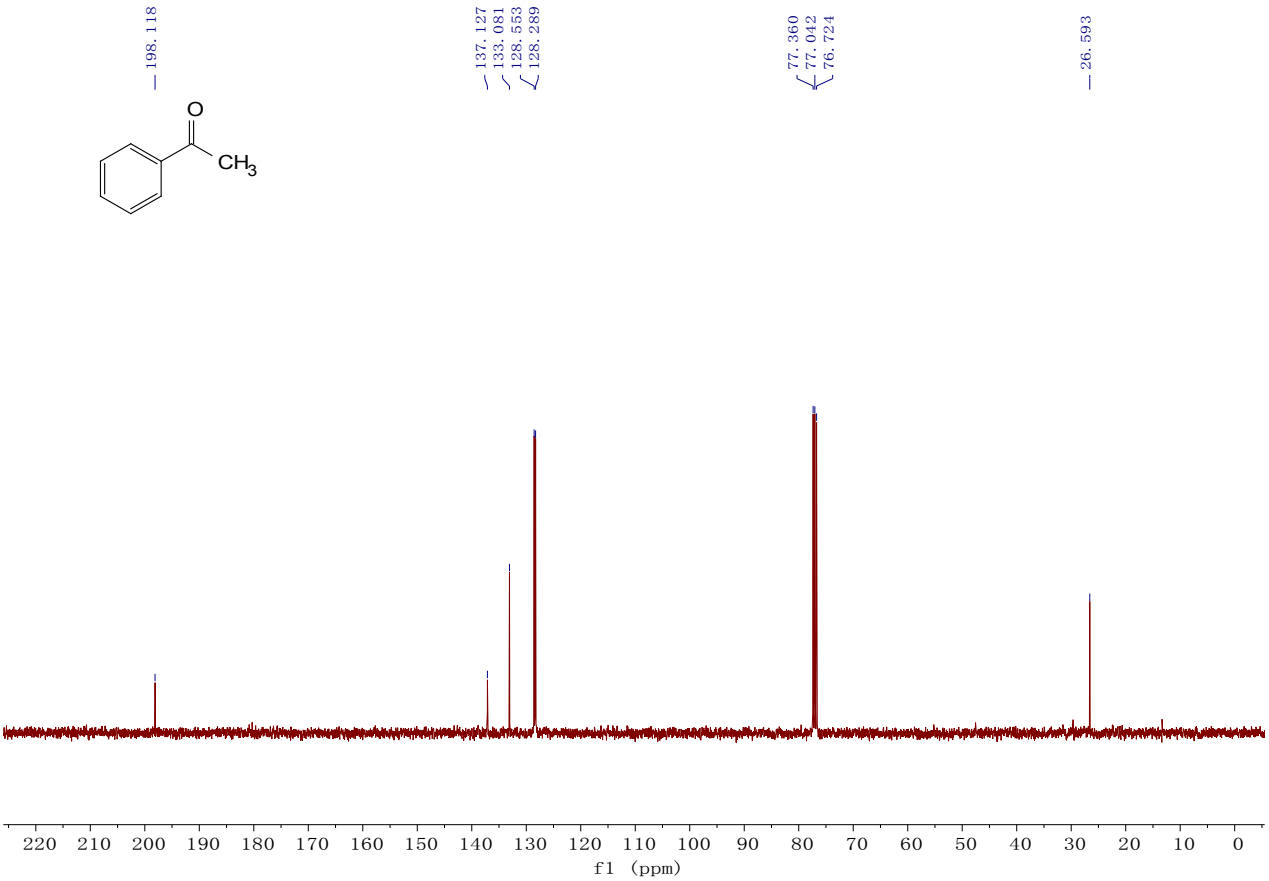
7.285
7.275
7.269
7.249
7.232
7.227
7.179
7.157
6.787
6.765
5.384
5.317
5.126
5.110
5.095
5.079
5.063
5.048
5.032
1.595
1.220
1.205
CH2
Cl
H3C
CH3
O
O
CH3
O
CH3
1.87
1.99
2.00
2.05
1.19
1.04
1.15
5.91
5.78
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

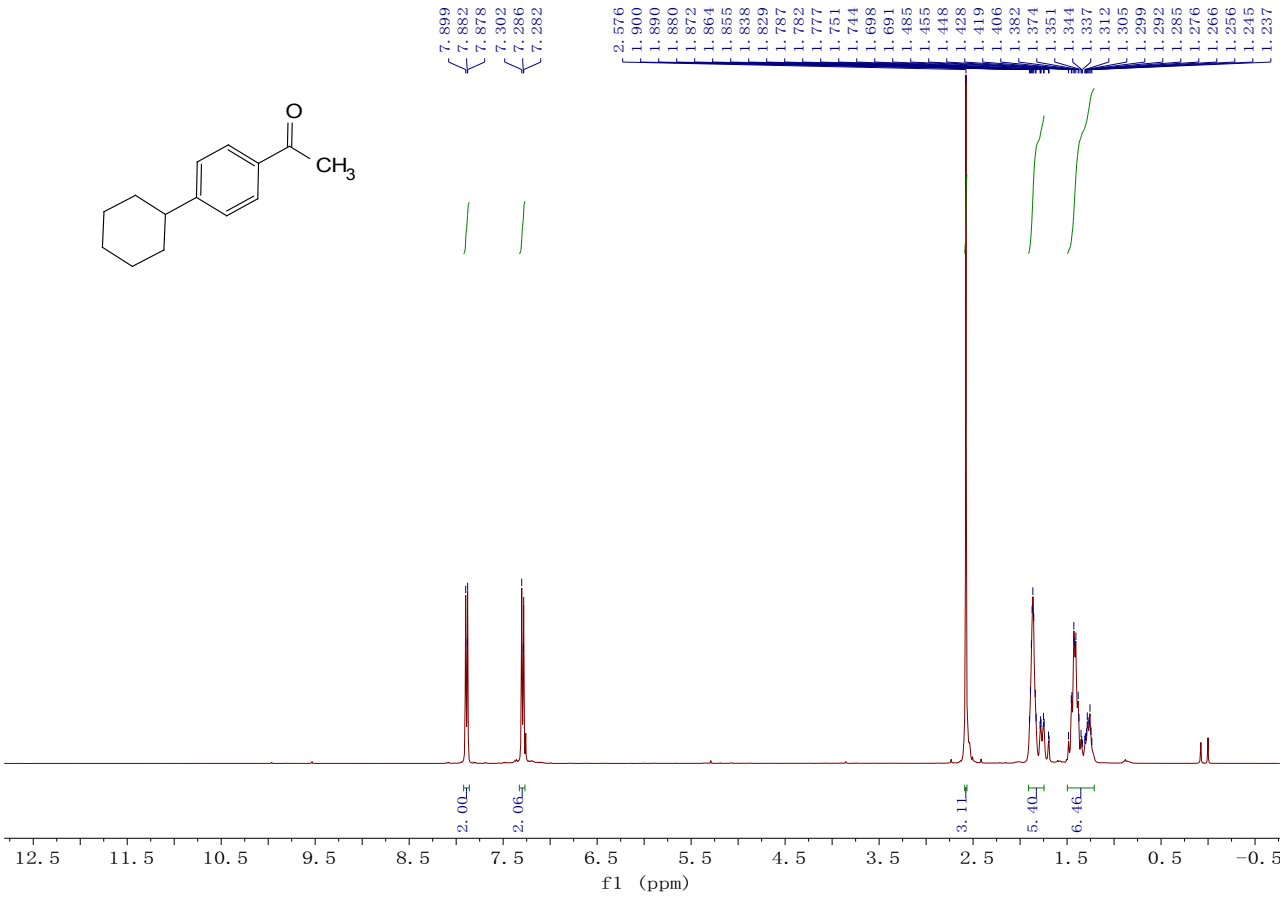

173.666
155.437
148.304
140.143
134.387
133.484
129.617
128.894
128.295
118.278
113.620
79.062
77.360
77.042
76.725
69.020
25.390
21.579
CH2
Cl
H3C
CH3
O
O
CH3
O
CH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

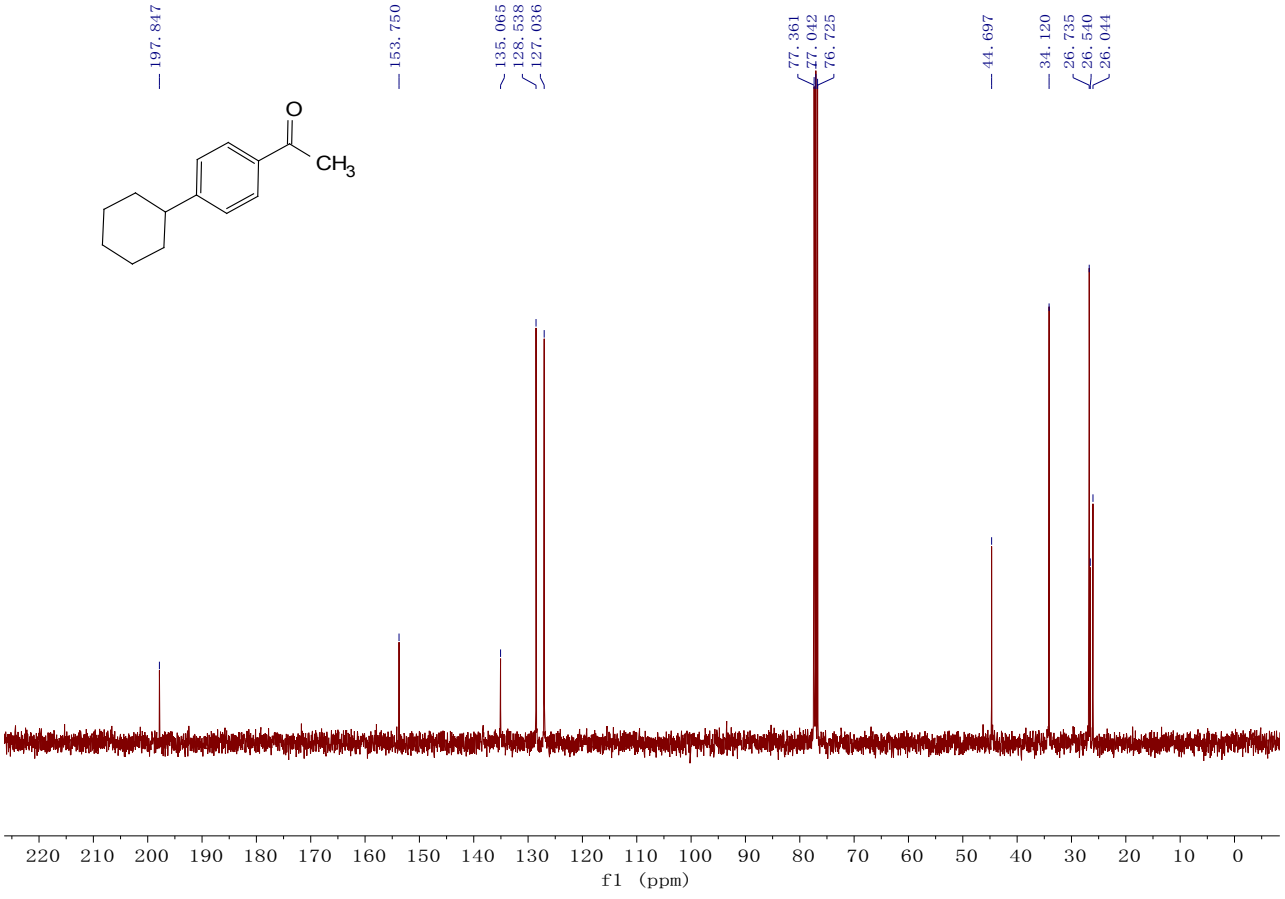
Acetophenone (1)



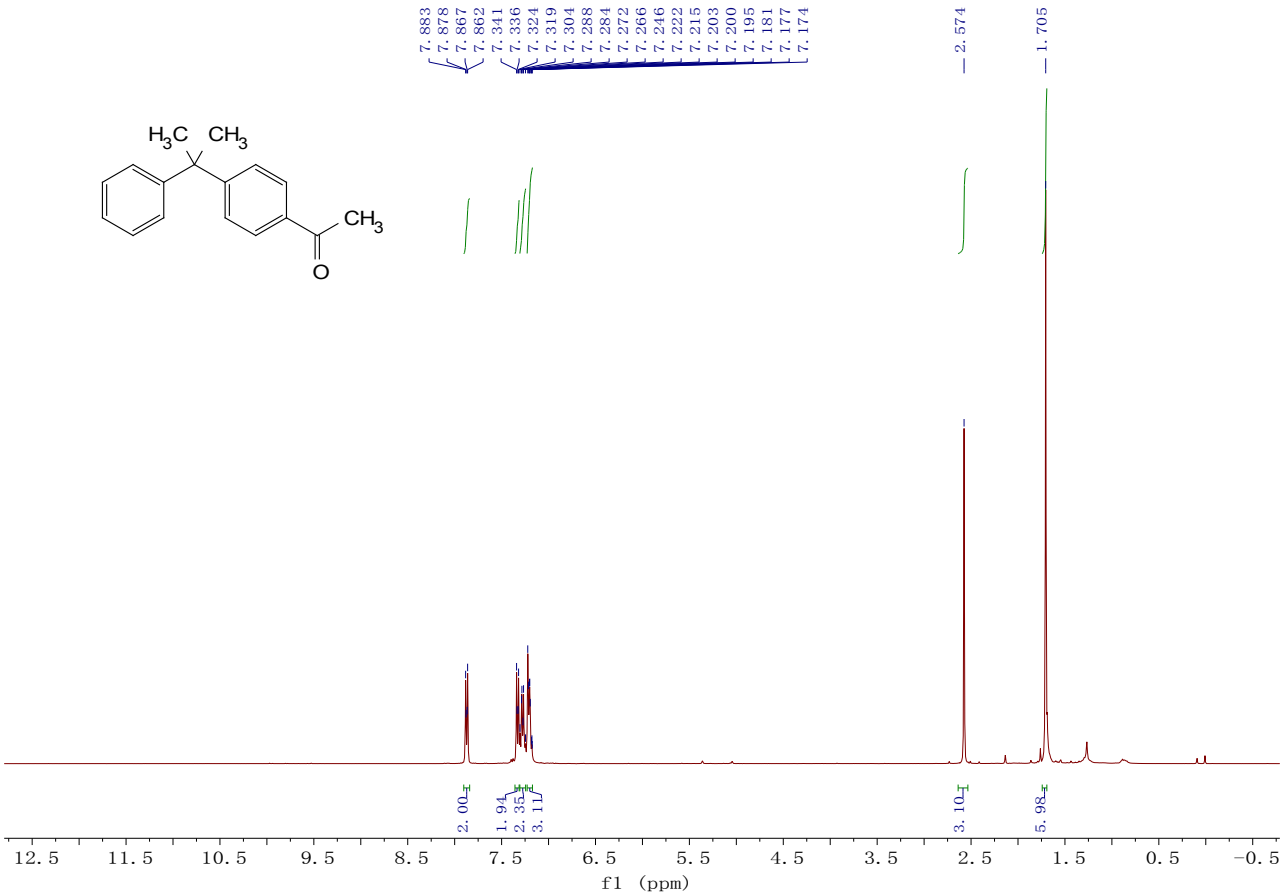


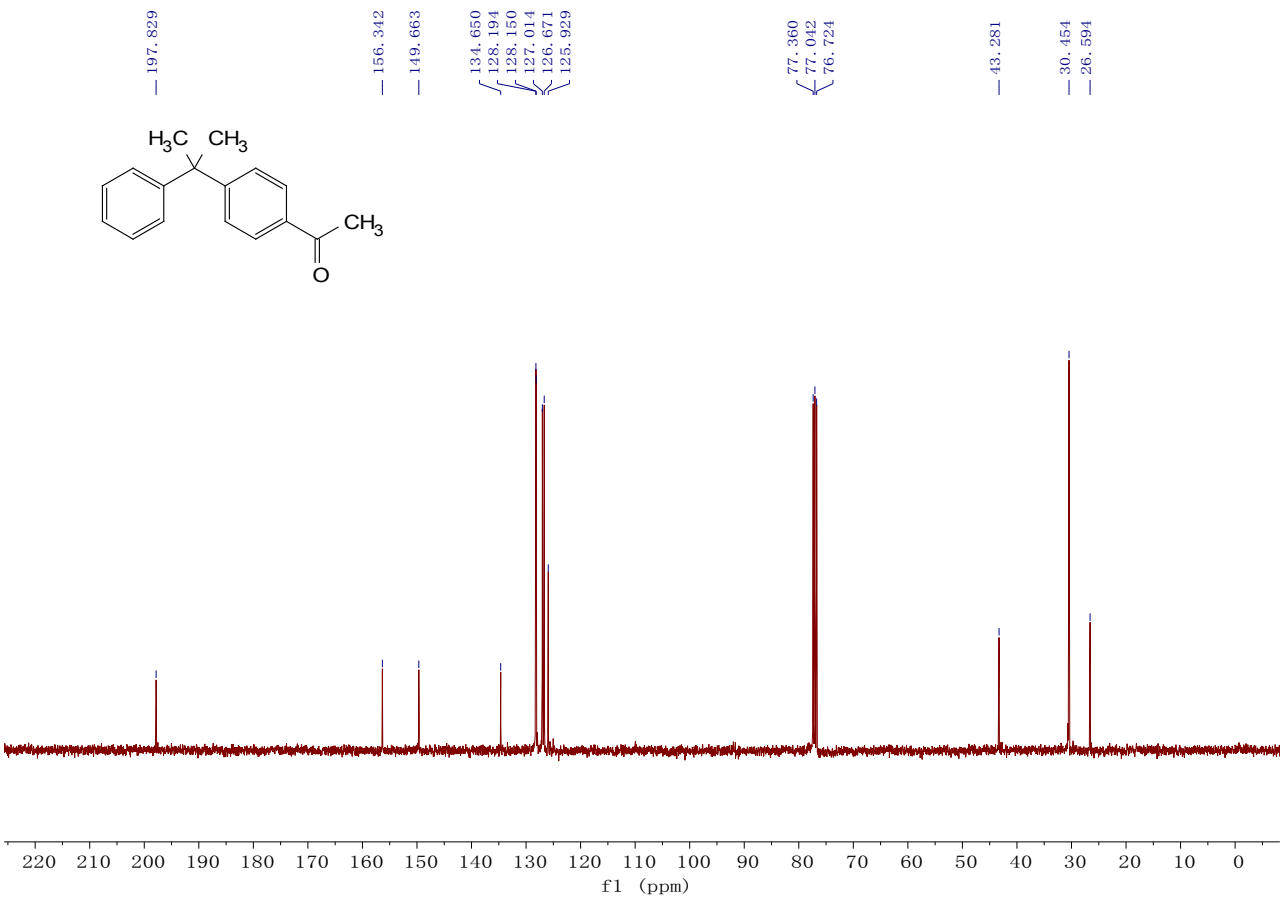
1-(4-Cyclohexylphenyl)ethan-1-one (2)



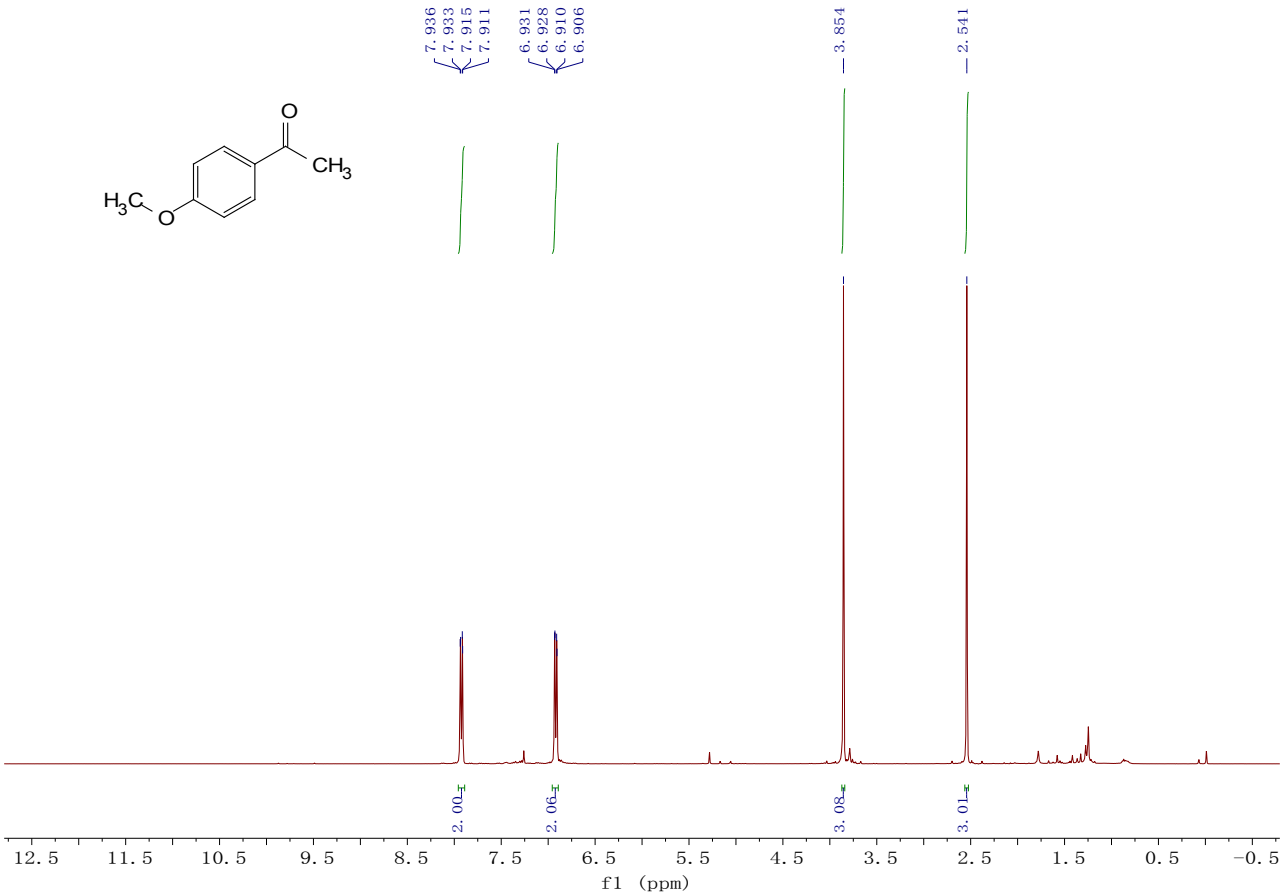


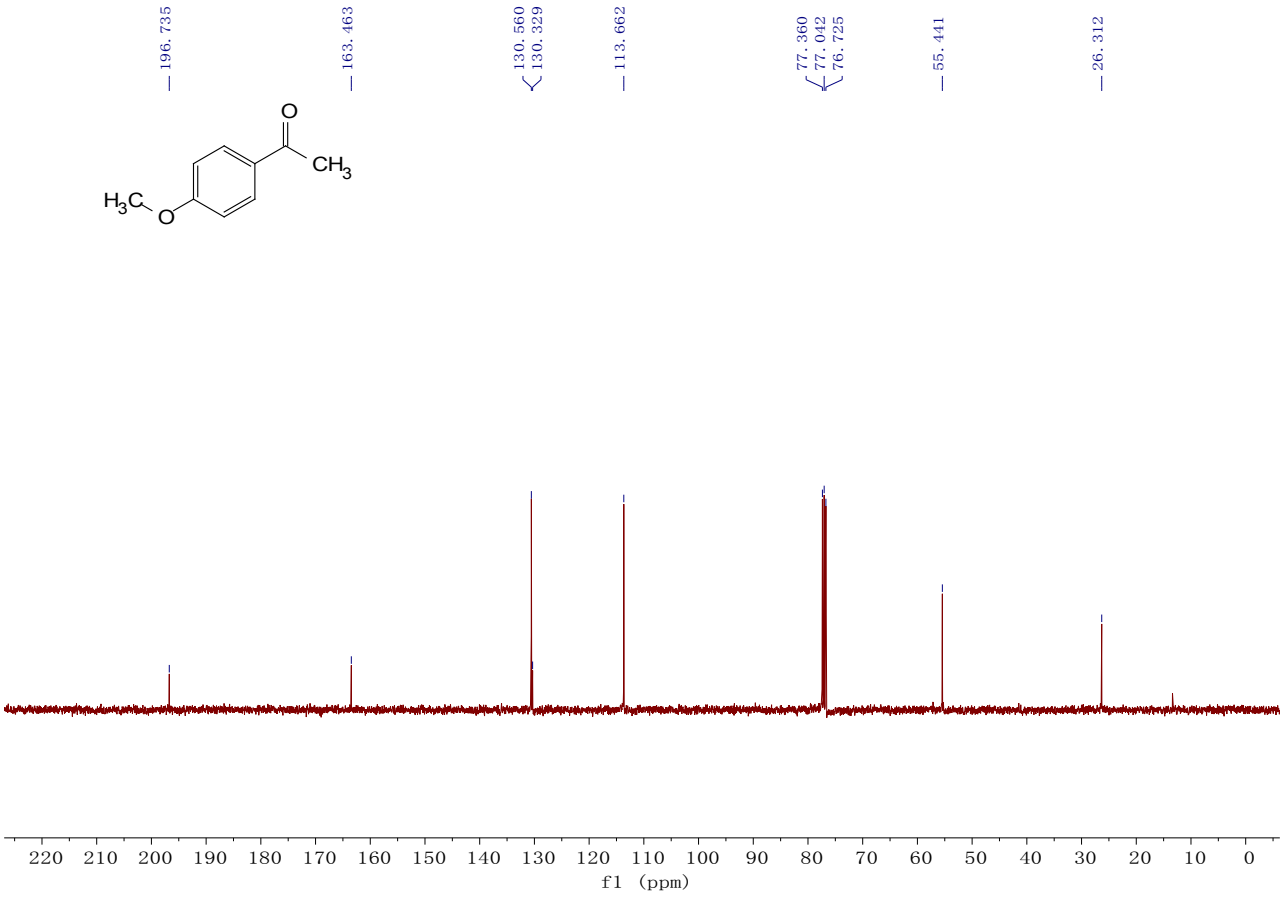
1-(4-(2-Phenylpropan-2-yl)phenyl)ethan-1-one (3)



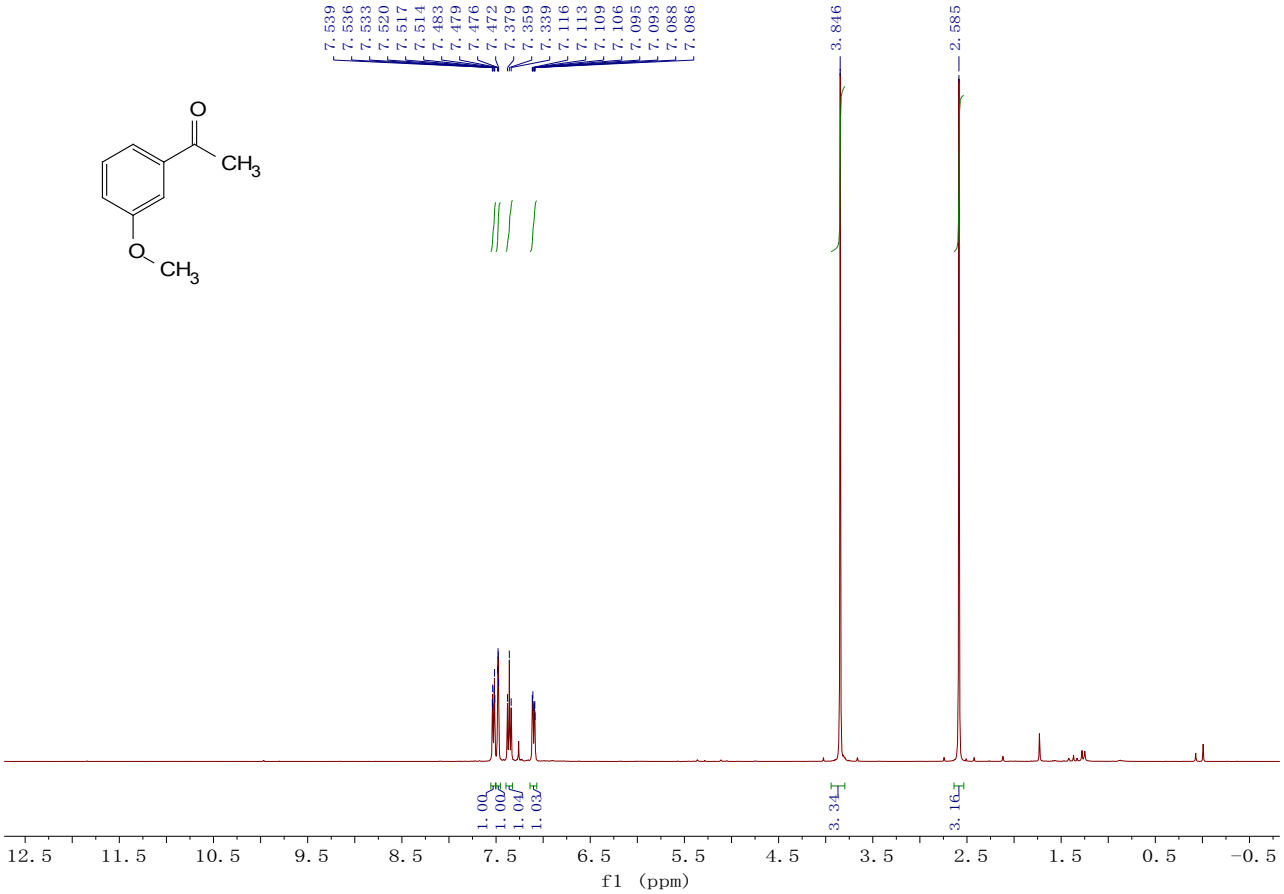


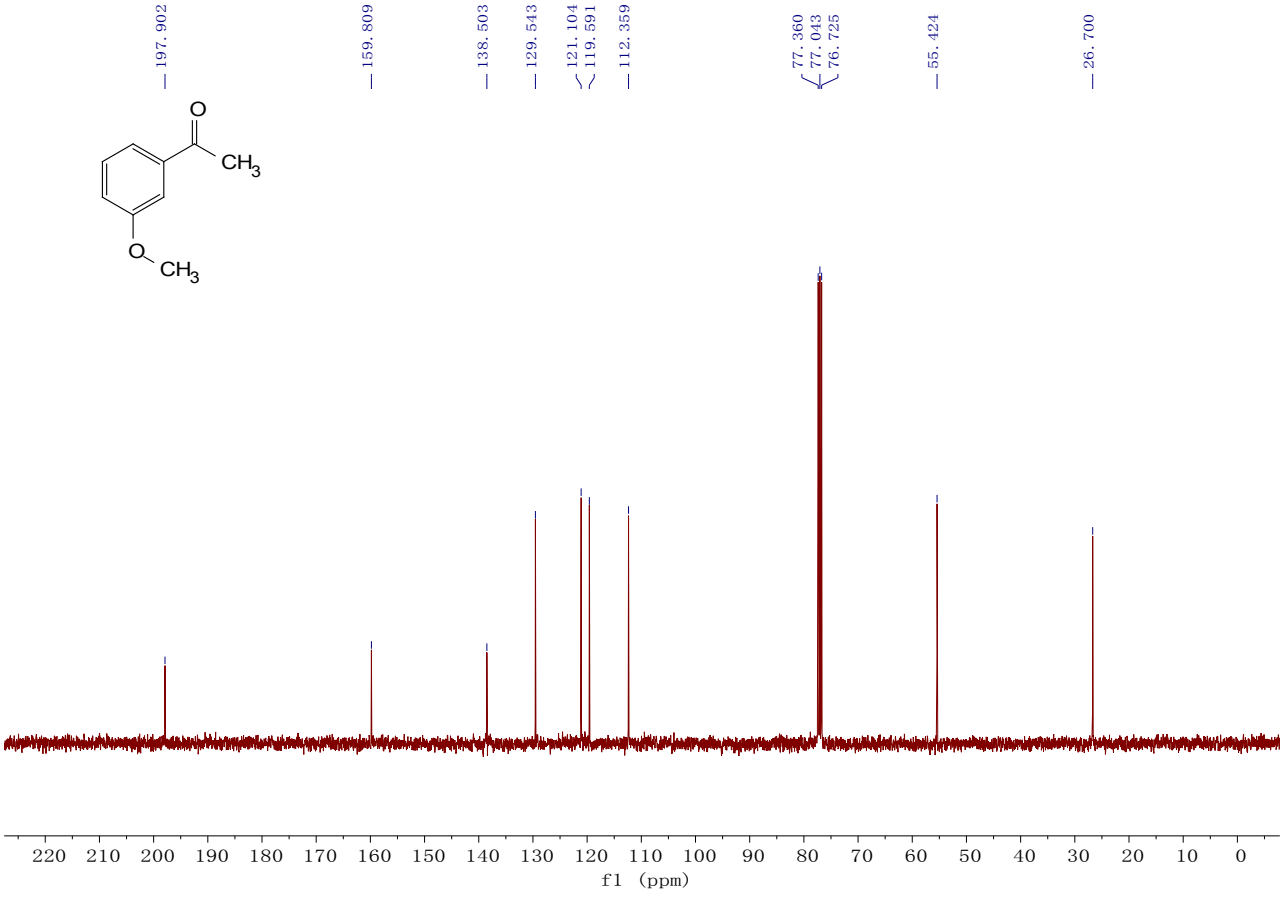
1-(4-Methoxyphenyl)ethan-1-one (4)



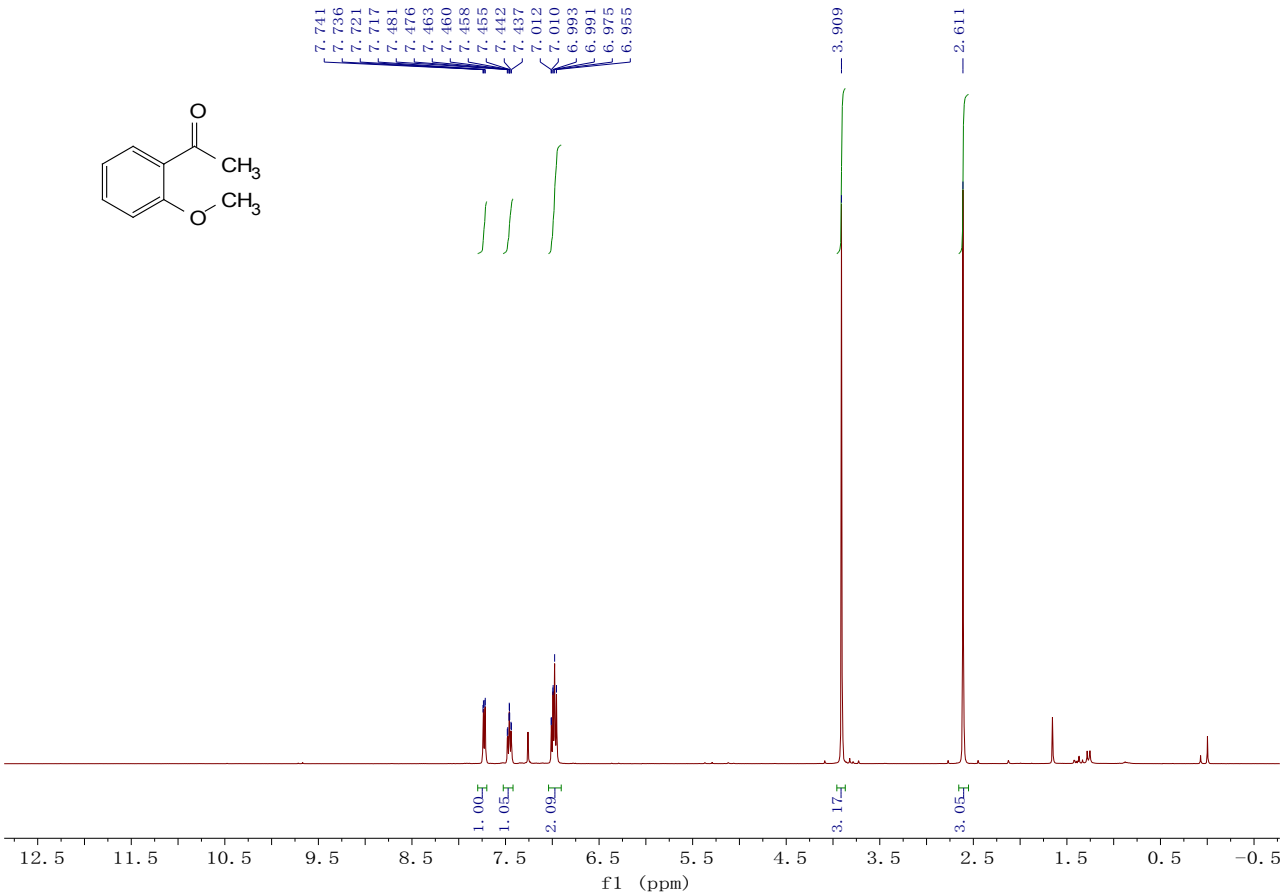


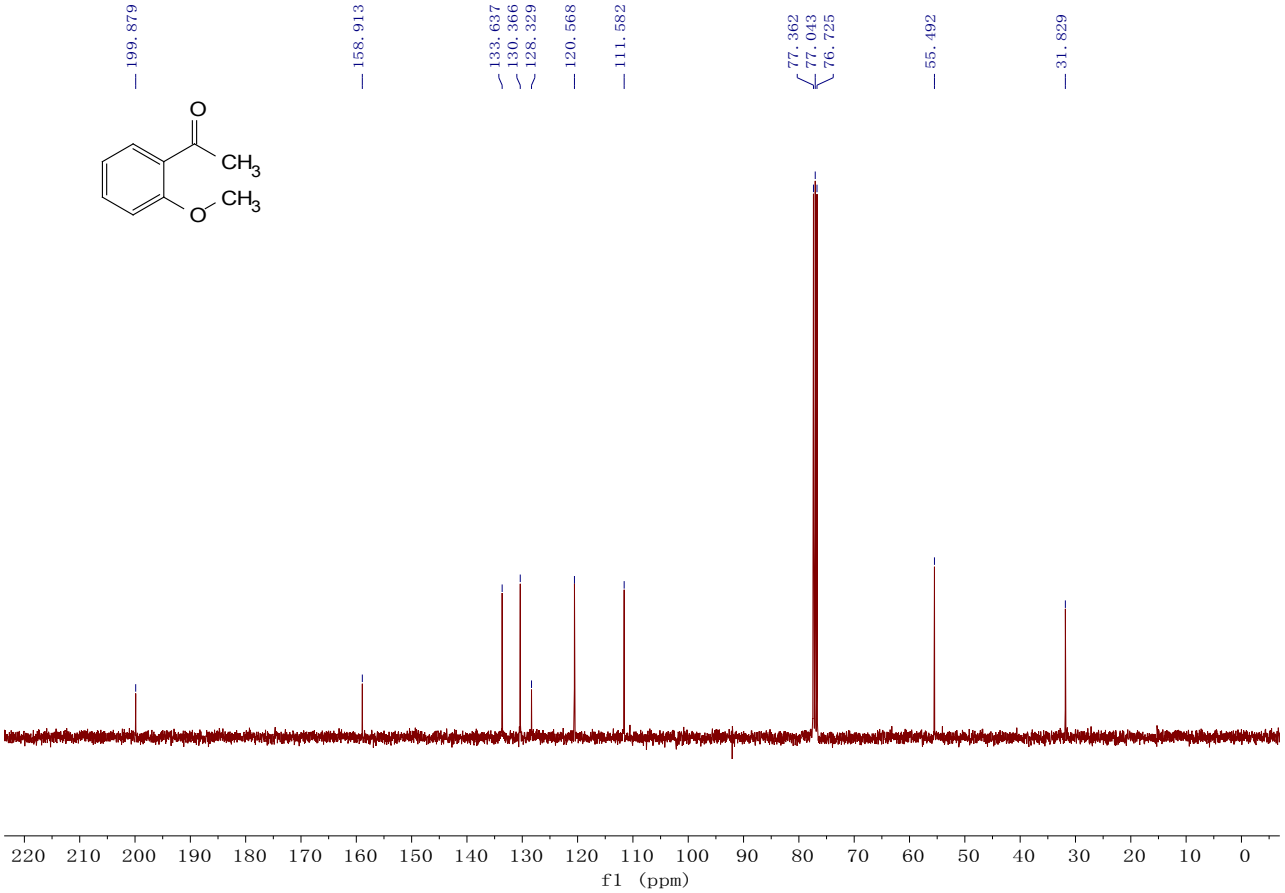
1-(3-Methoxyphenyl)ethan-1-one (5)



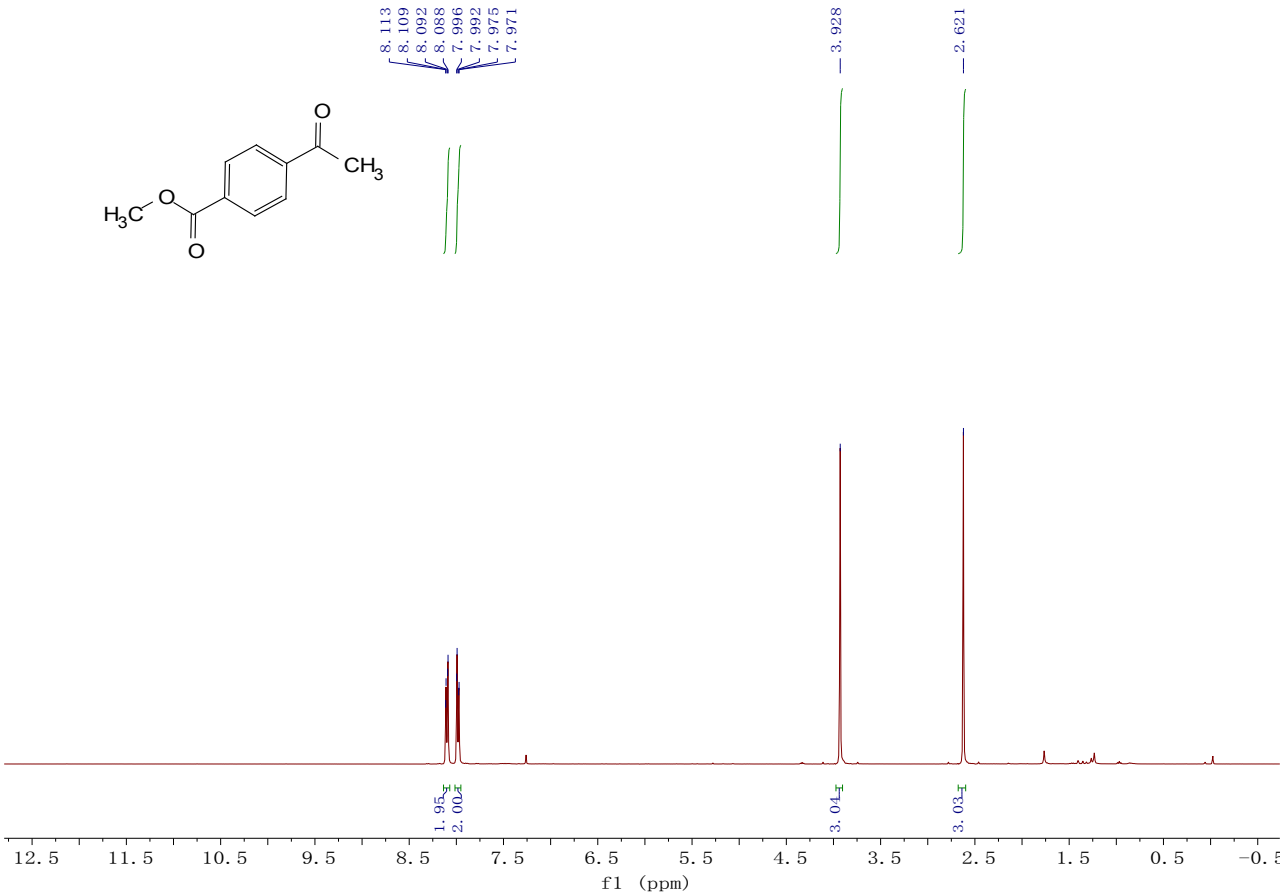


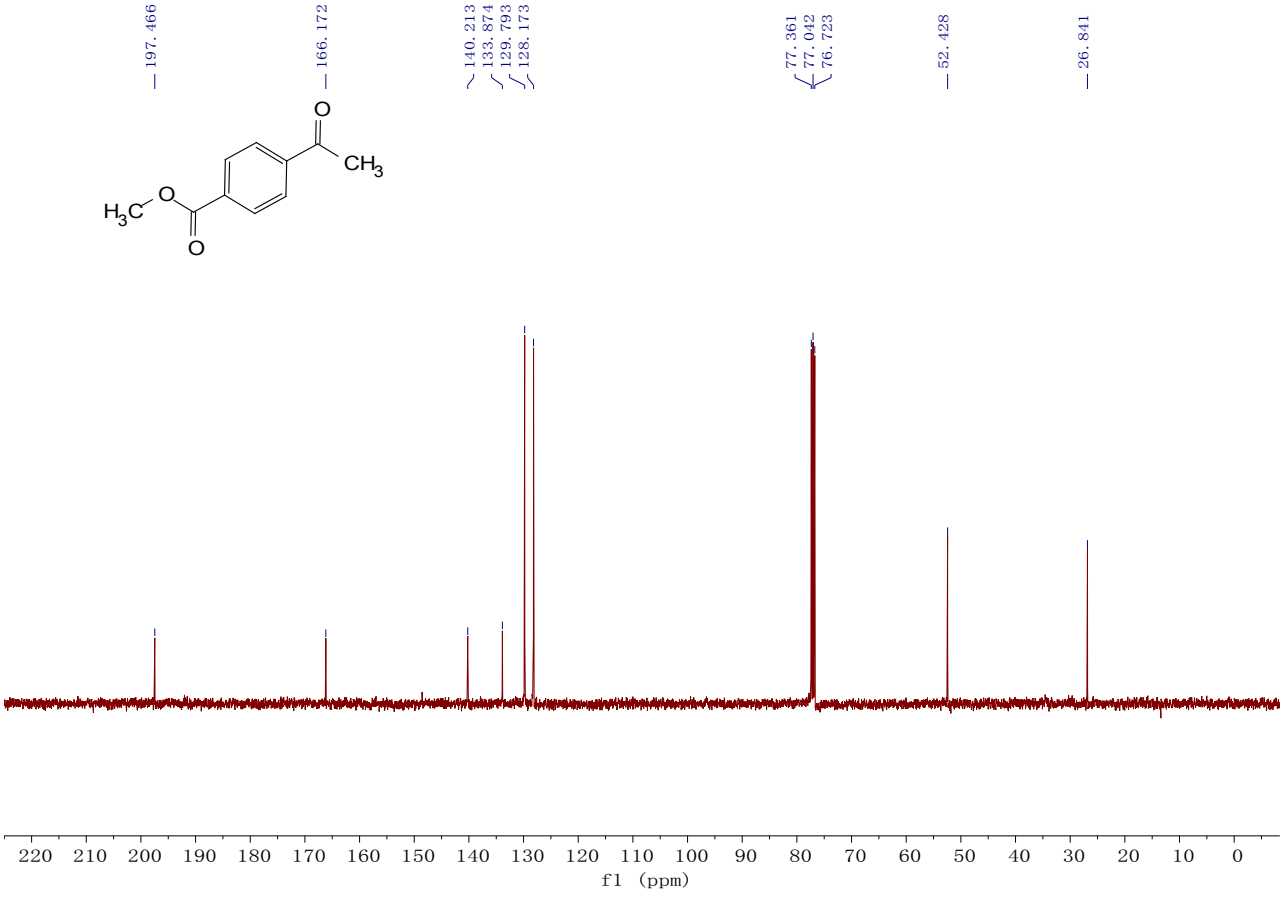
1-(2-Methoxyphenyl)ethan-1-one (6)



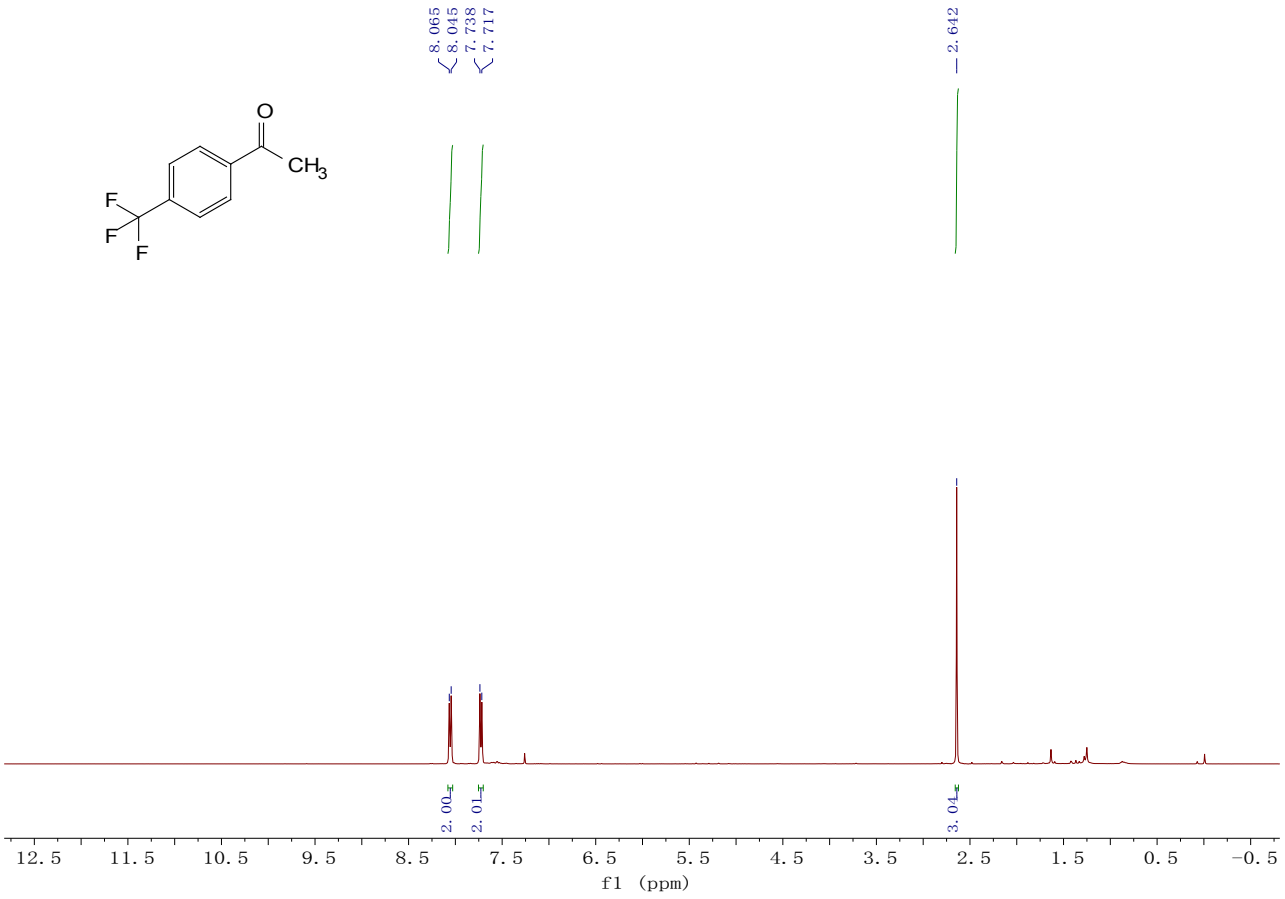


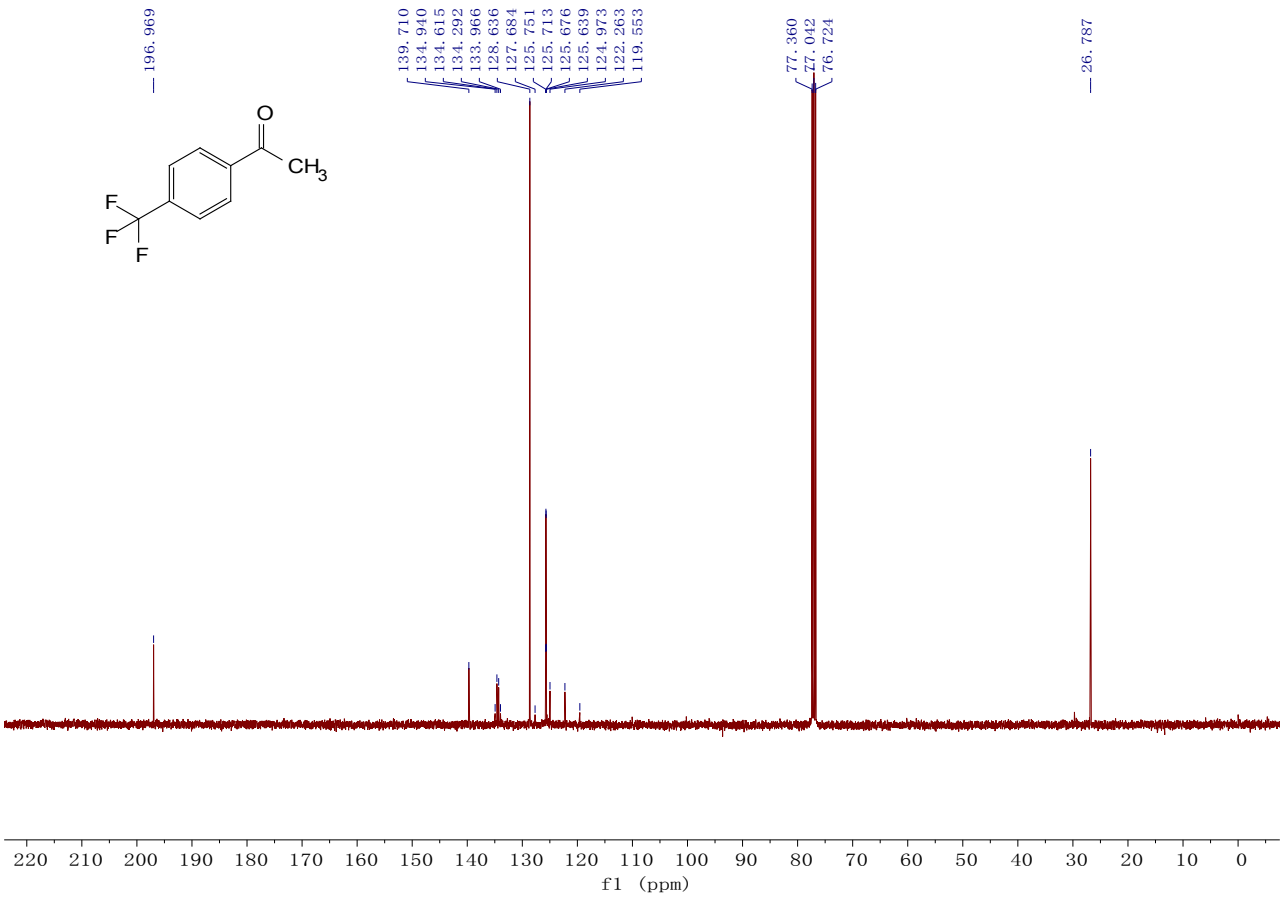
Methyl 4-acetylbenzoate (7)



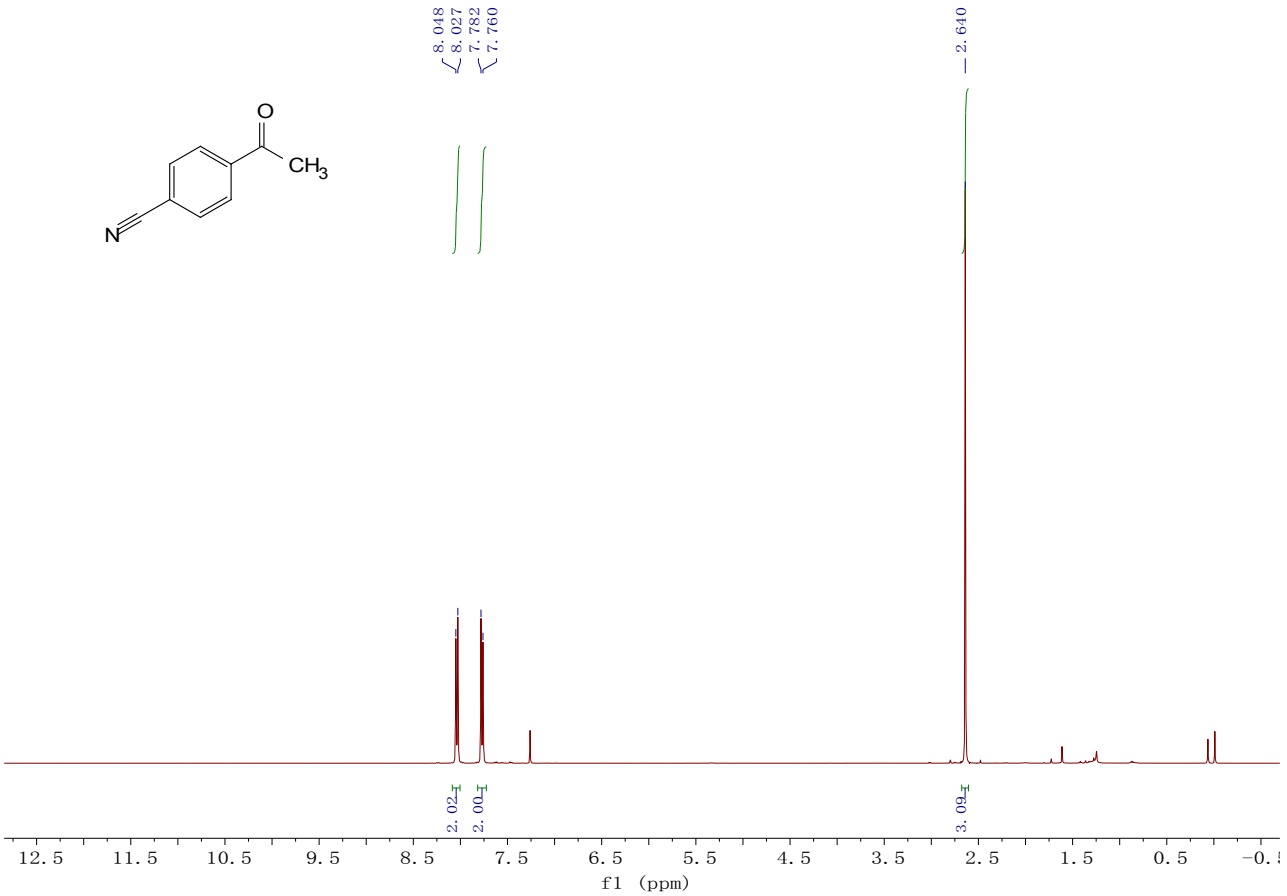


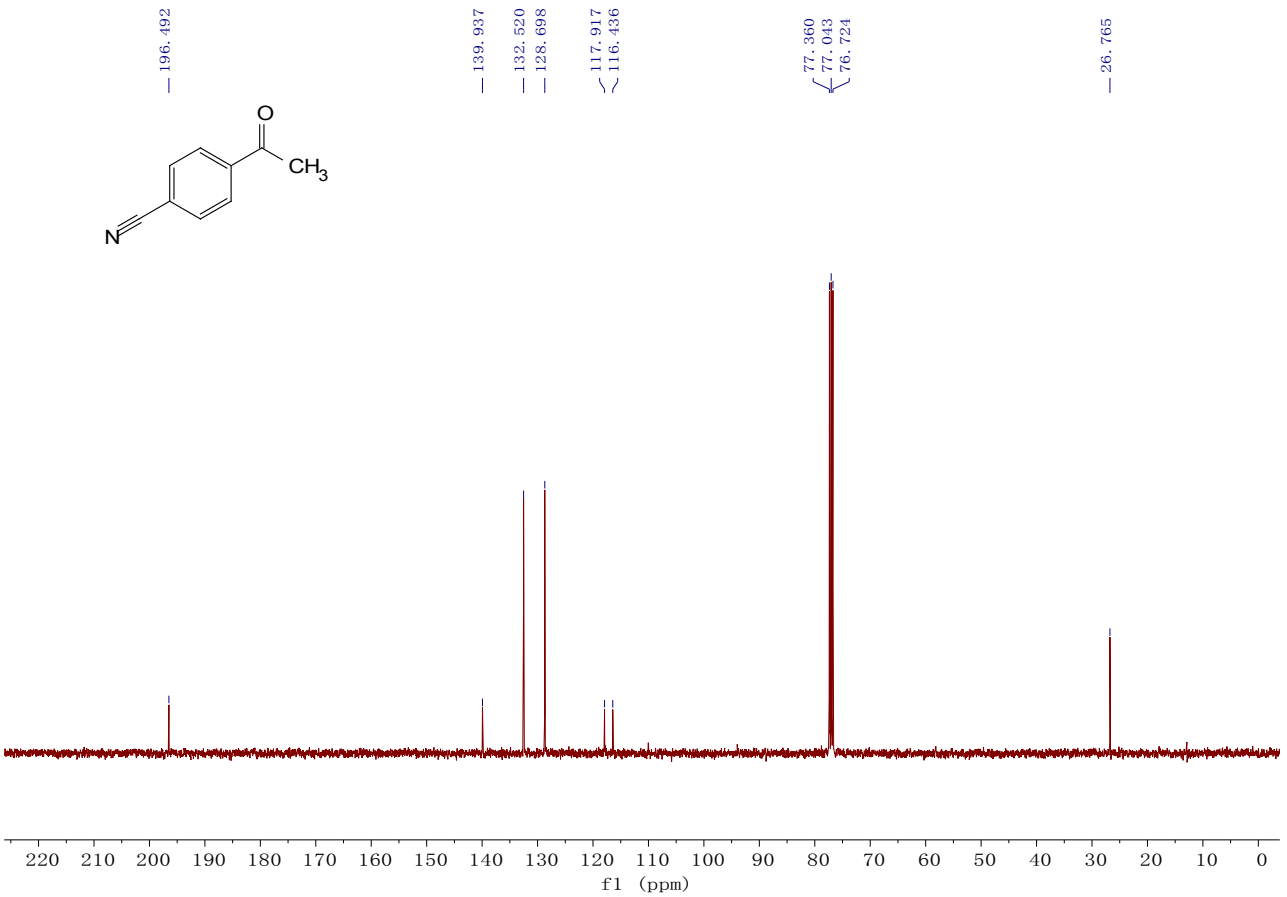
1-(4-(Trifluoromethyl)phenyl)ethan-1-one (8)



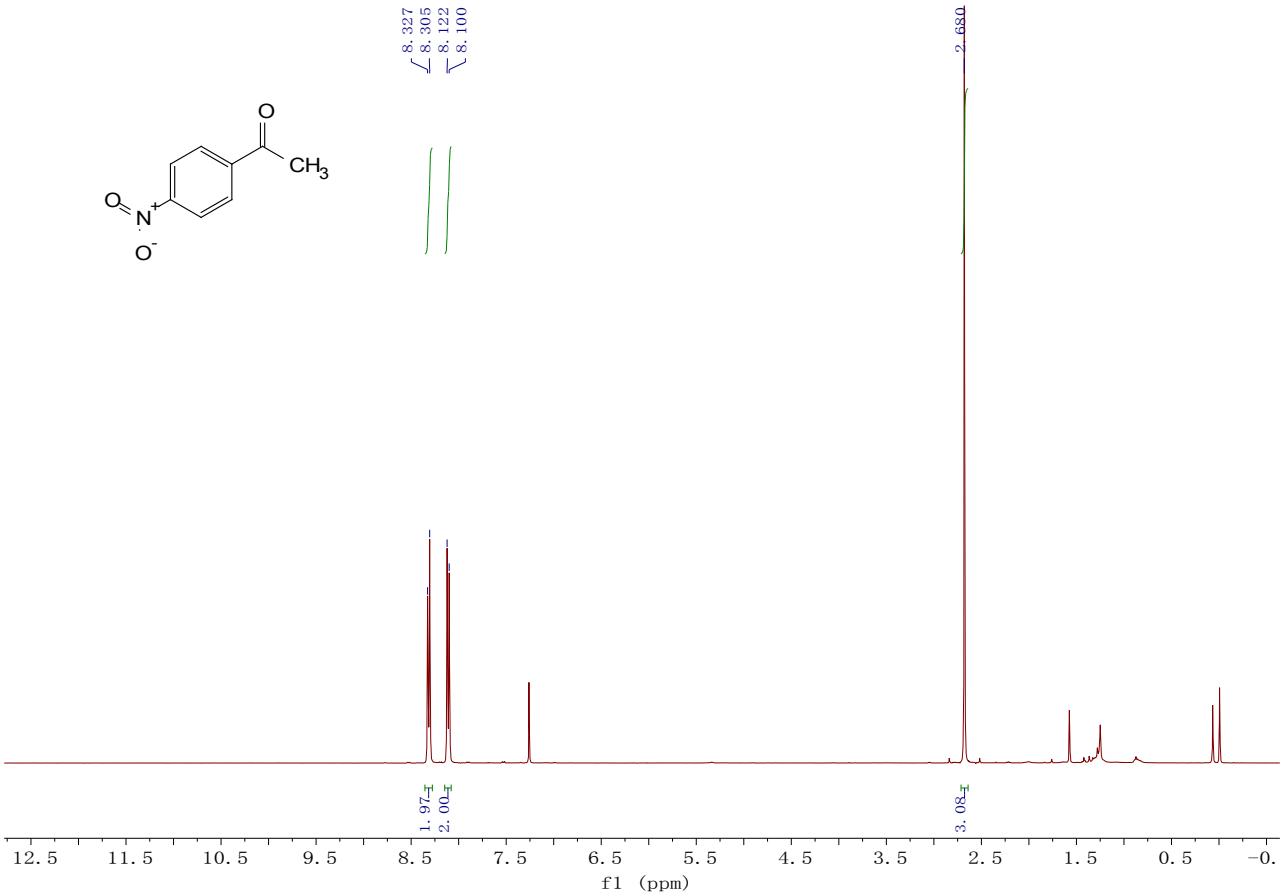


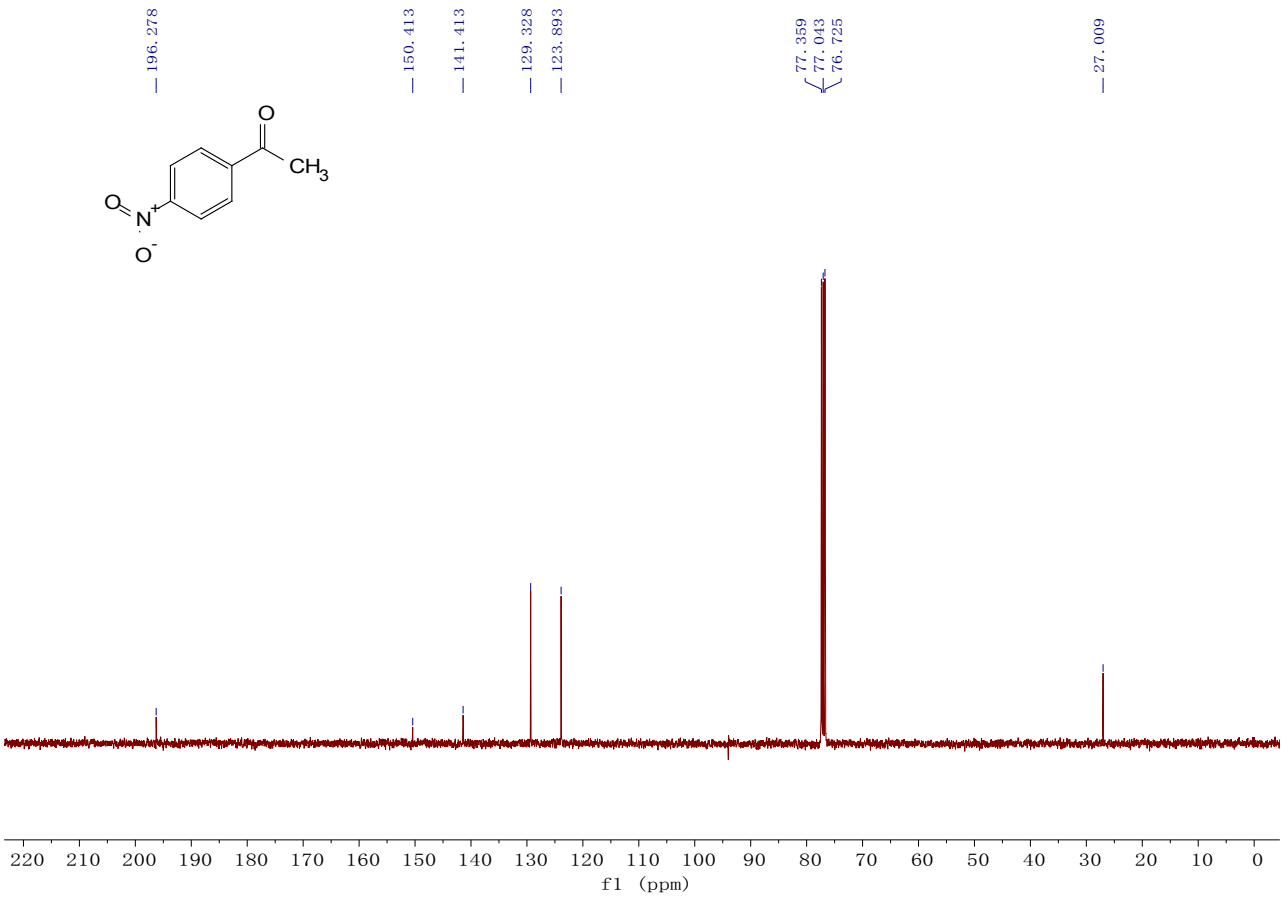
4-Acetylbenzonitrile (9)



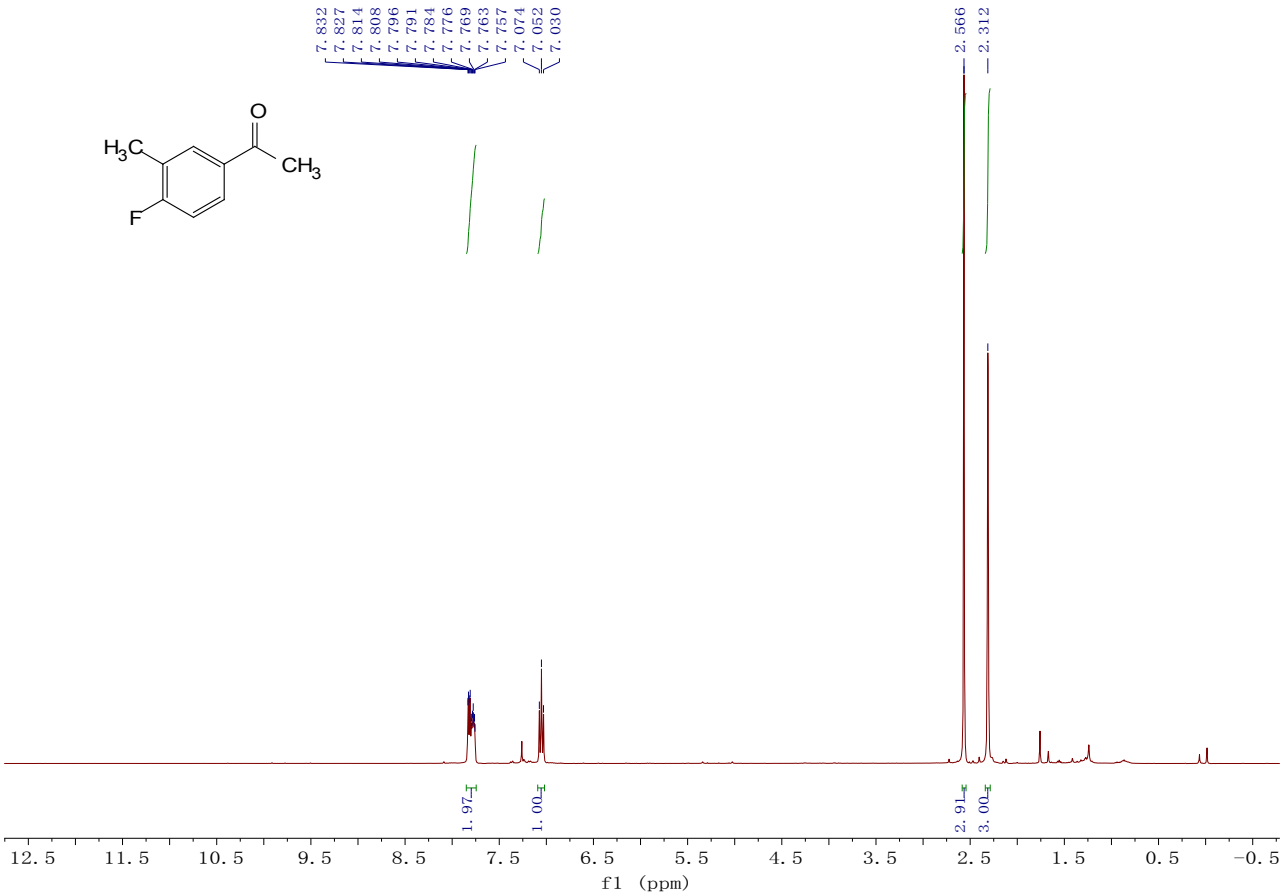


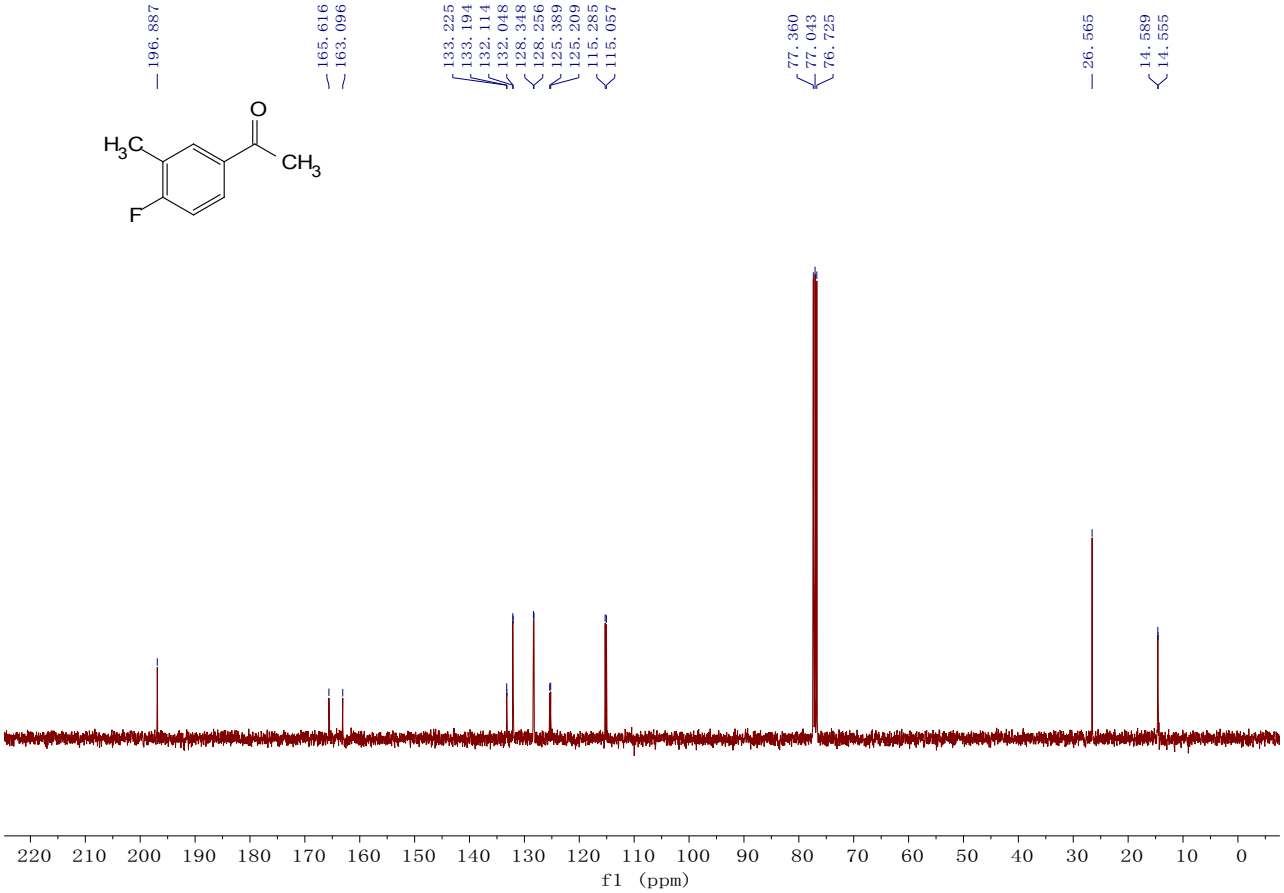
1-(4-Nitrophenyl)ethan-1-one (10)



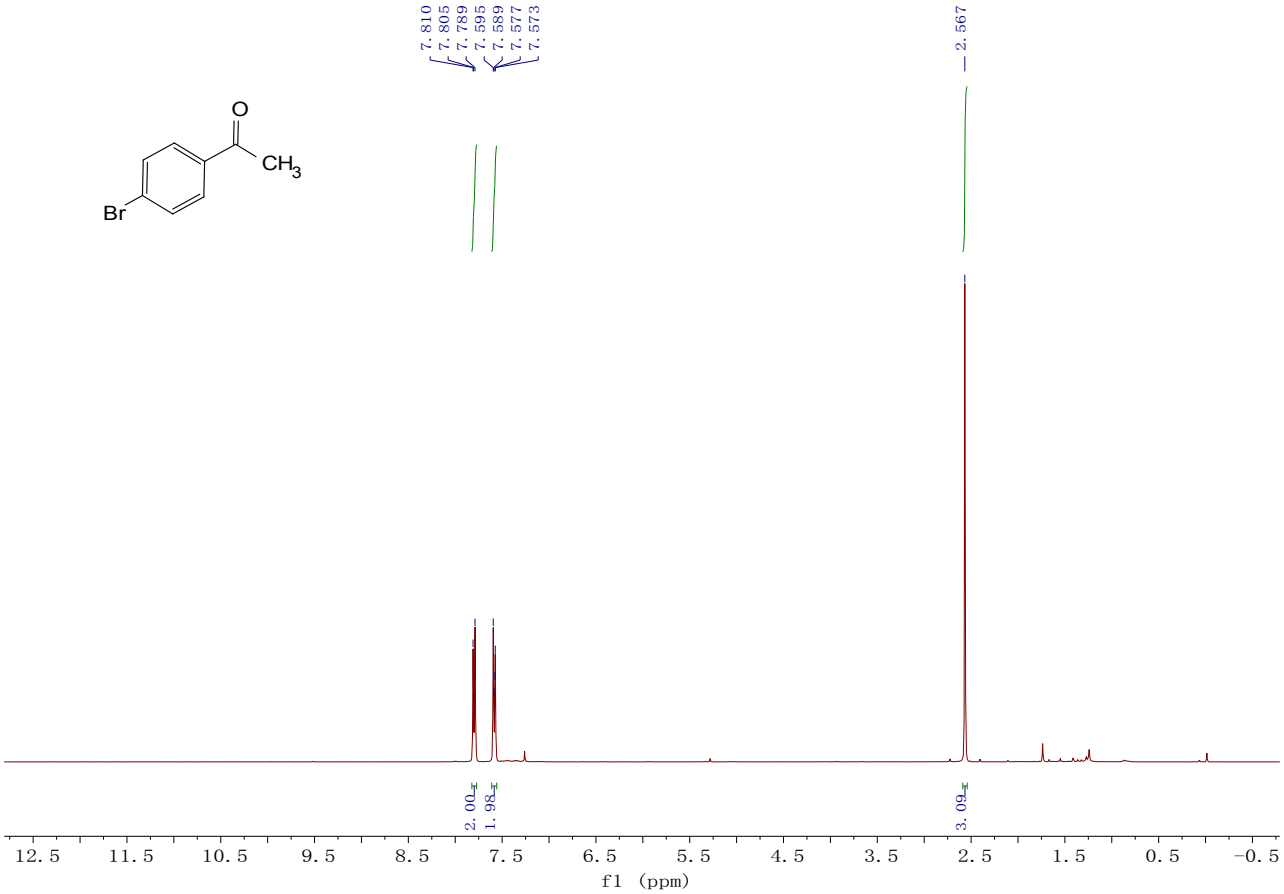


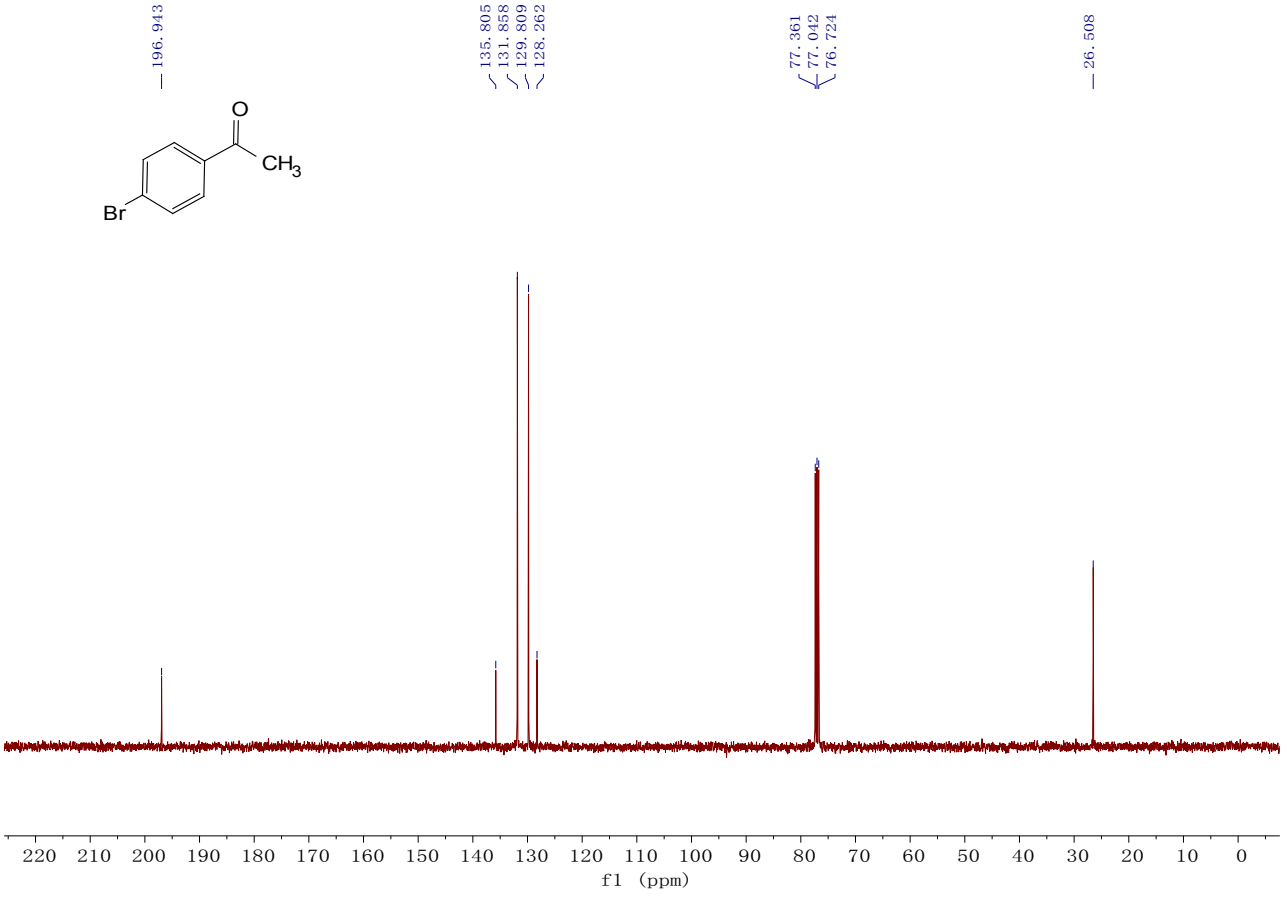
1-(4-Fluoro-3-methylphenyl)ethan-1-one (11)



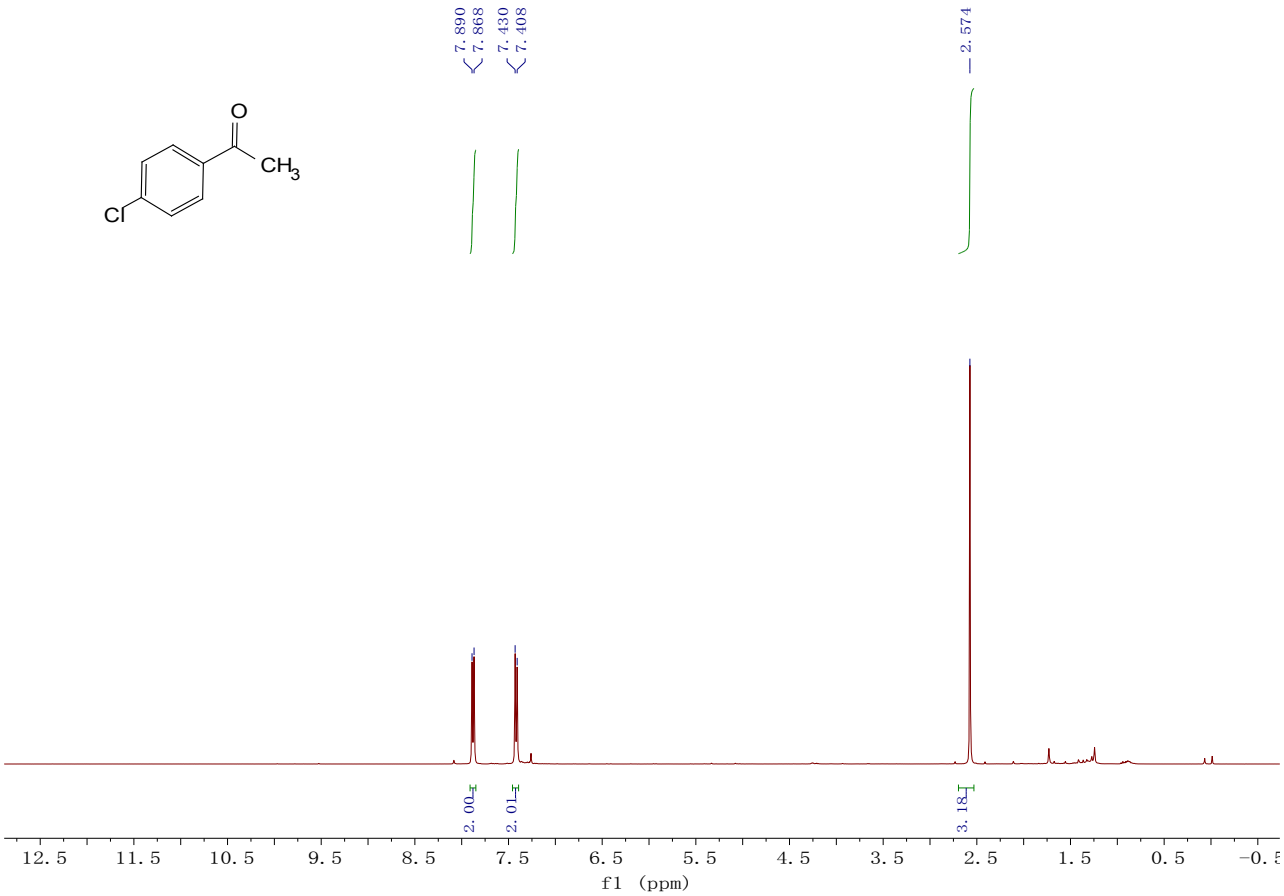


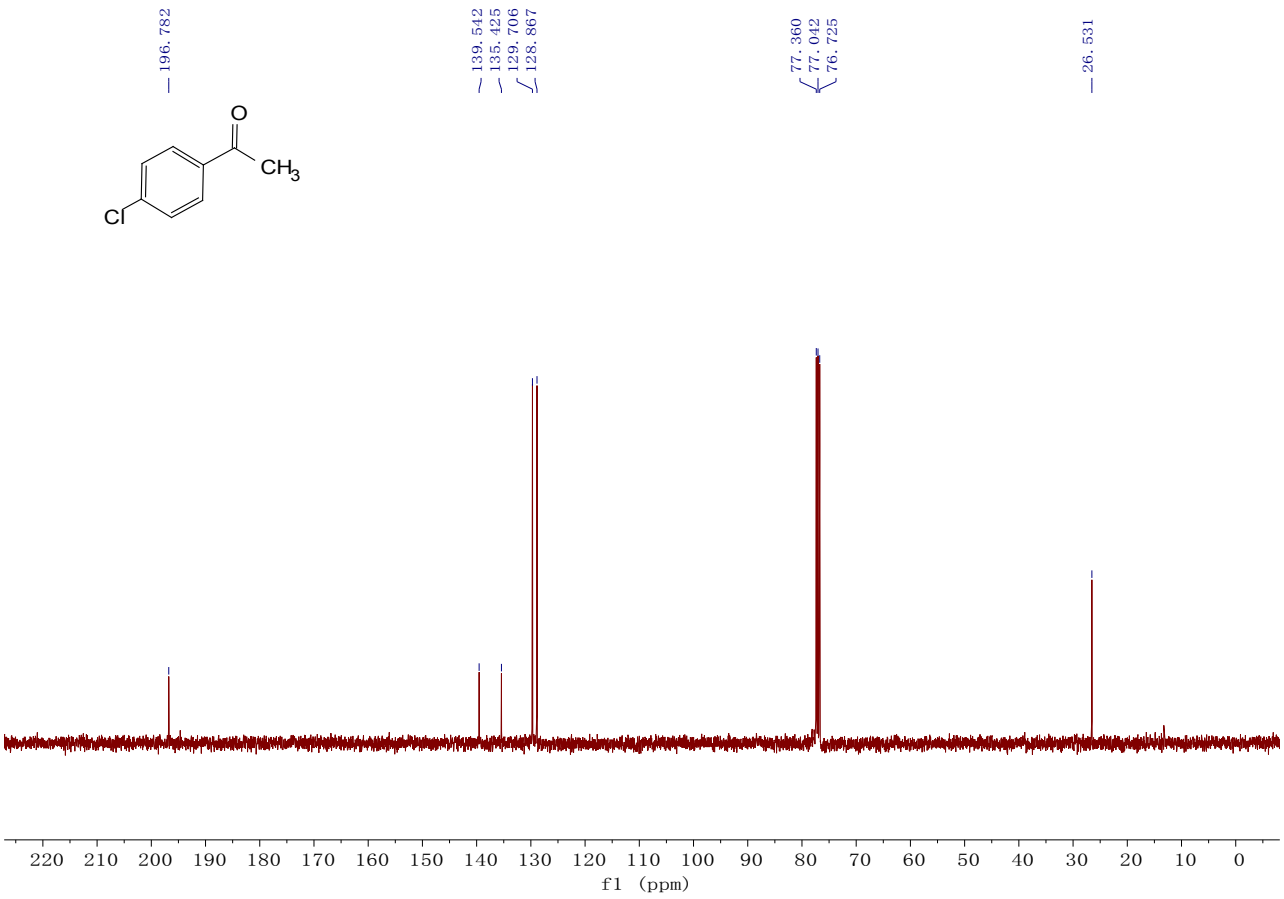
1-(4-Bromophenyl)ethan-1-one (12)



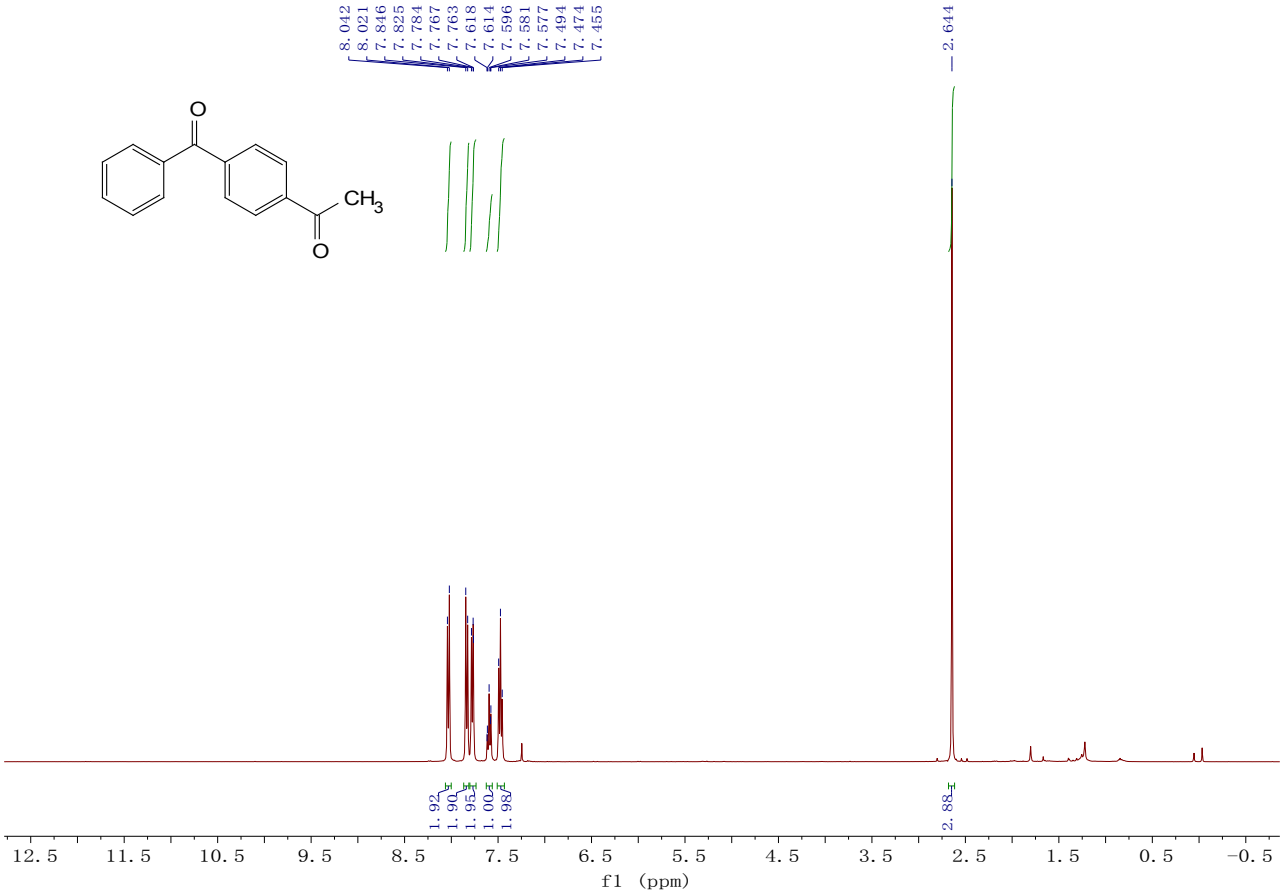


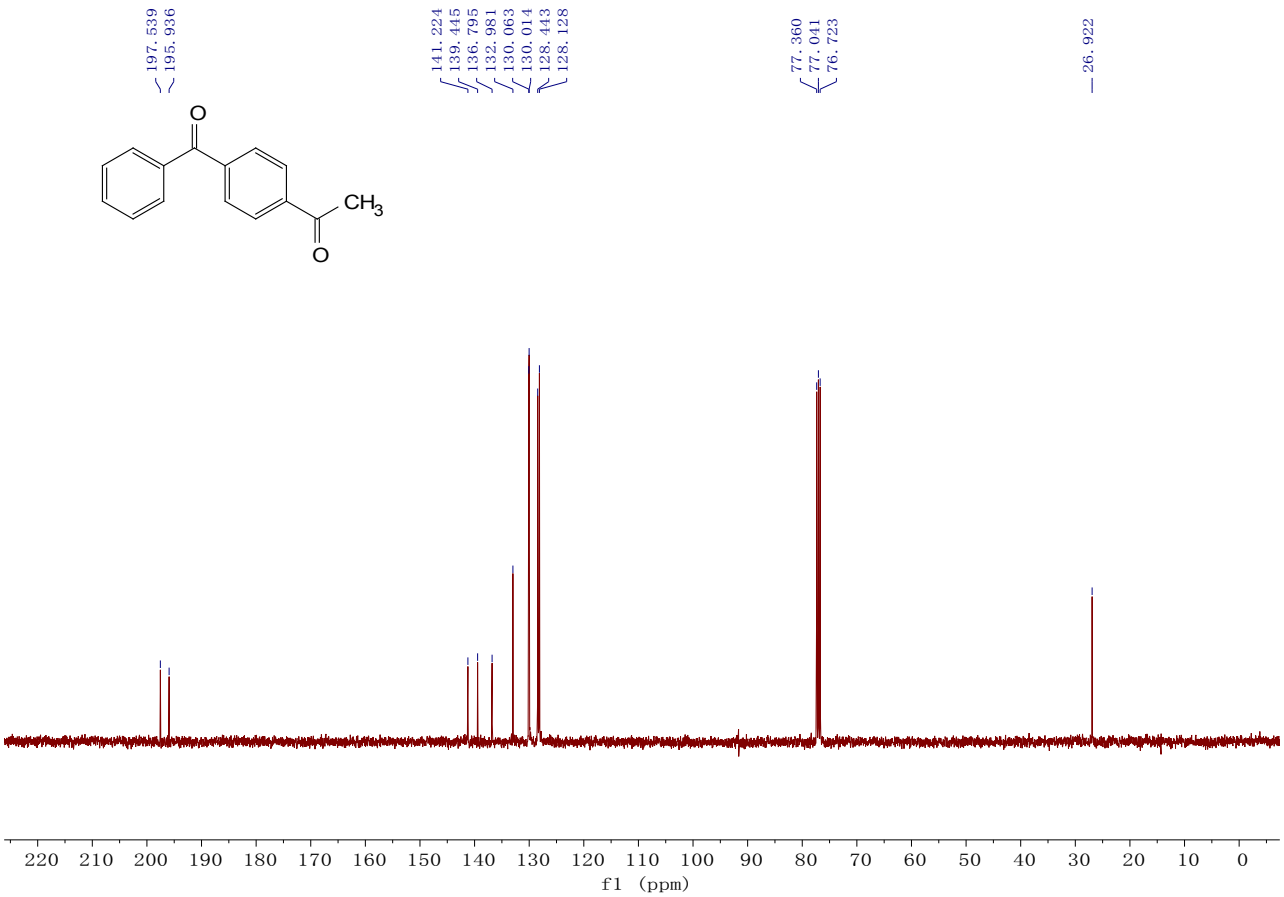
1-(4-Chlorophenyl)ethan-1-one (13)



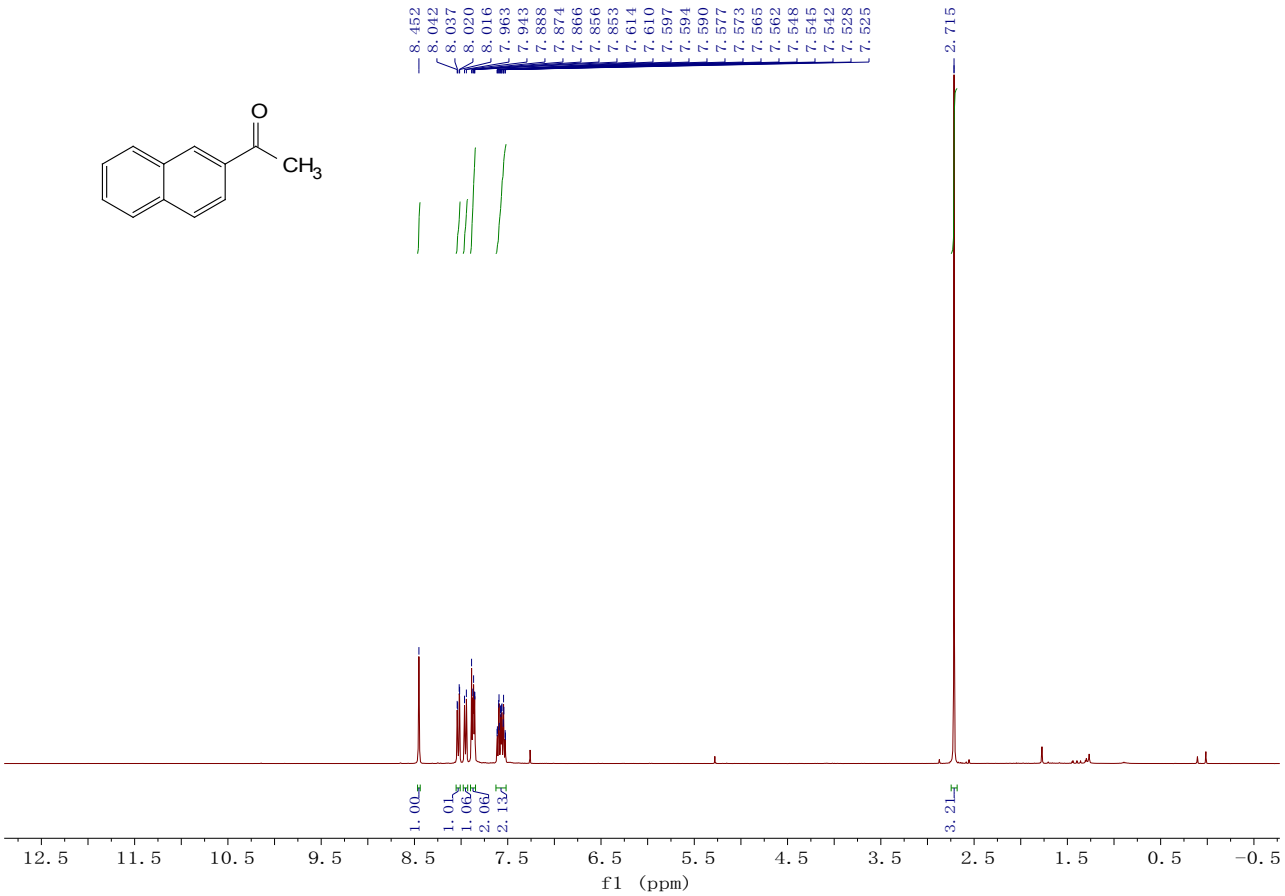


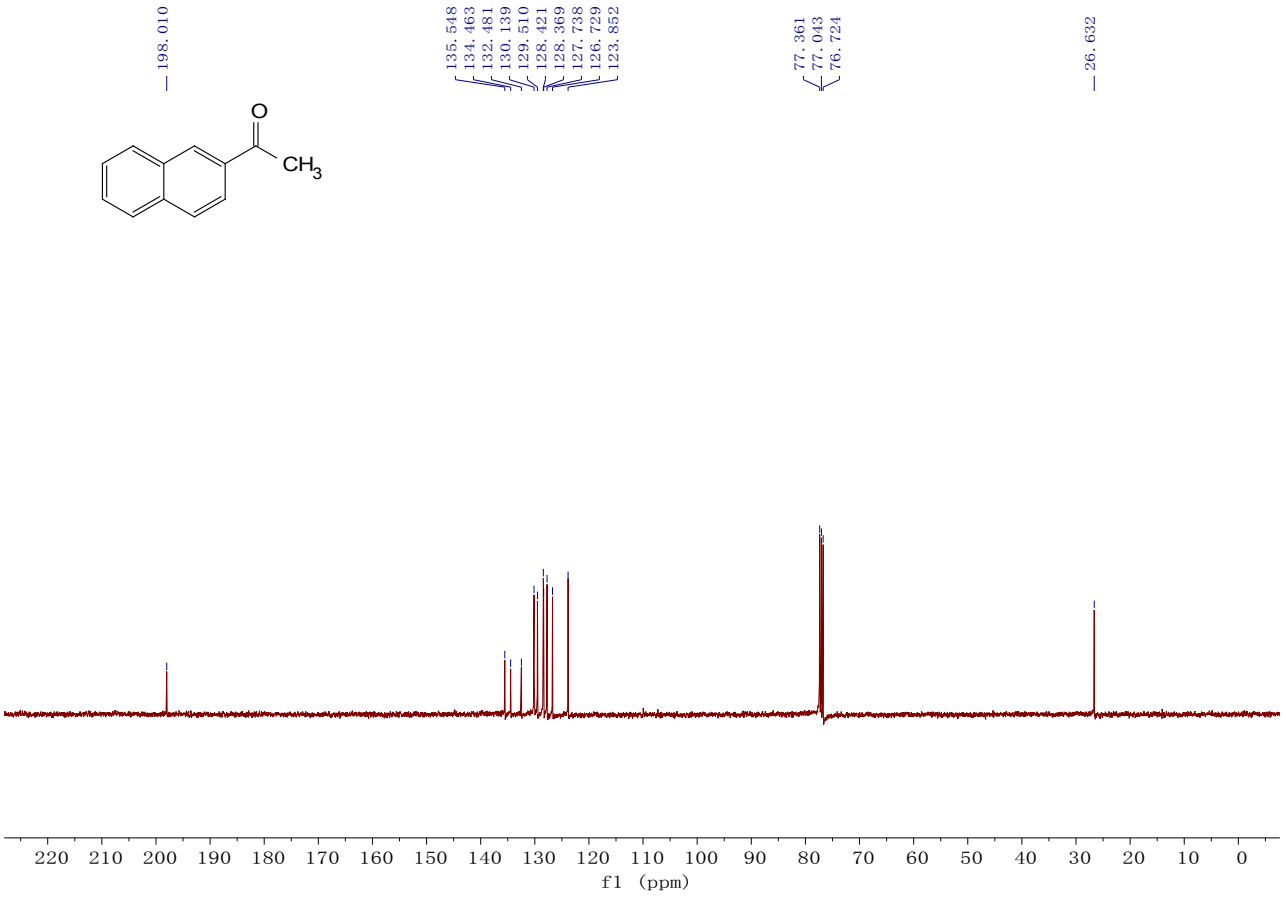
1-(4-Benzoylphenyl)ethan-1-one (14)



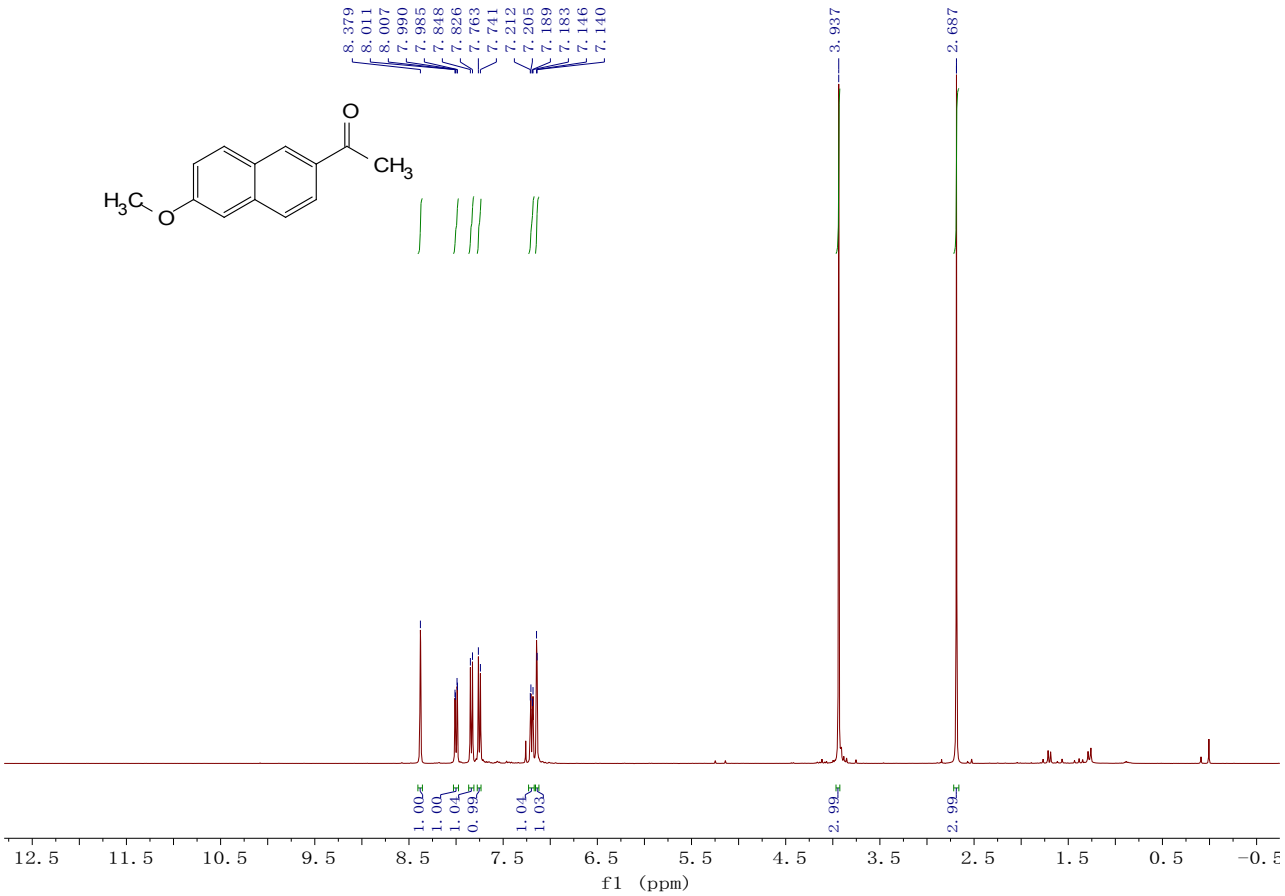


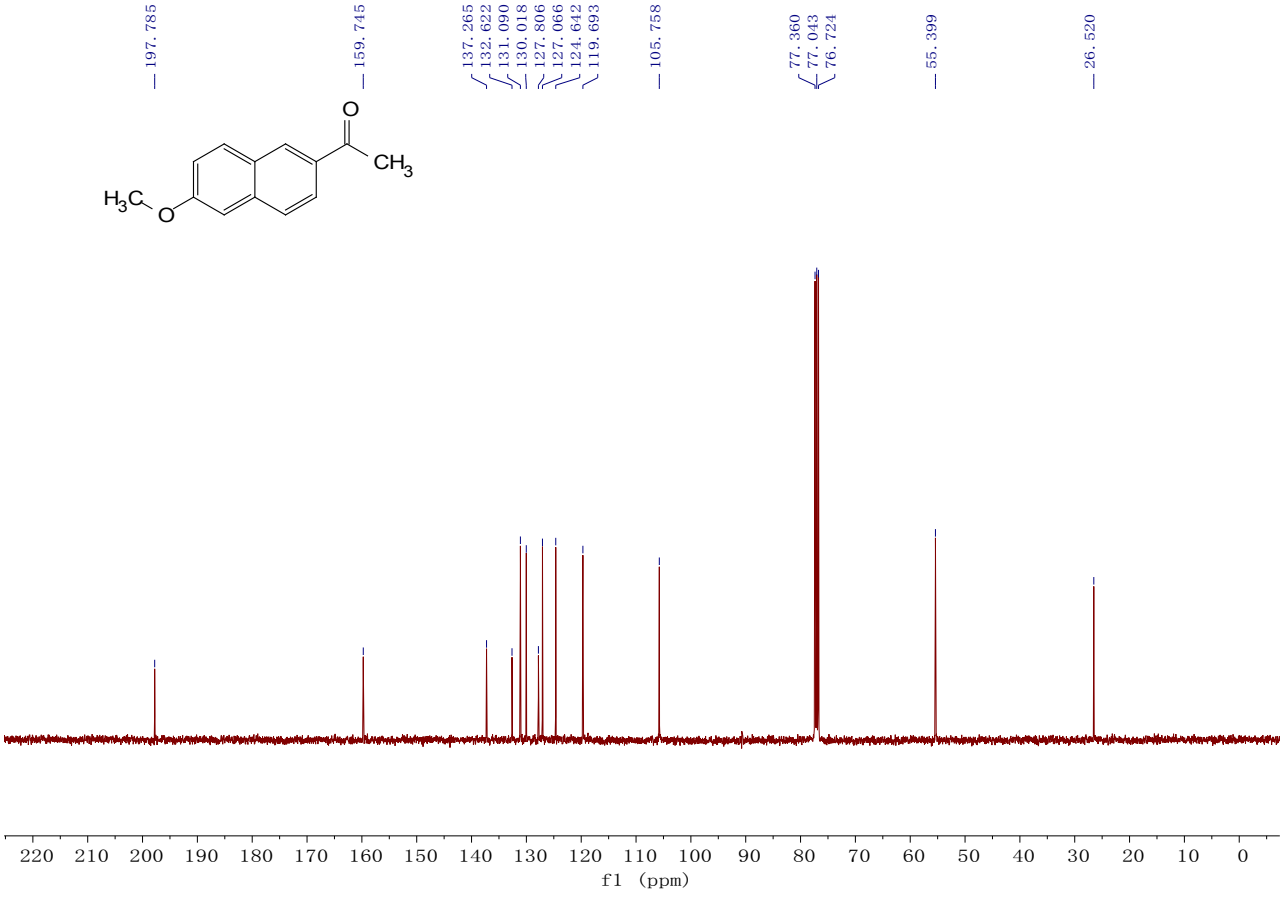
1-(Naphthalen-2-yl)ethan-1-one (15)



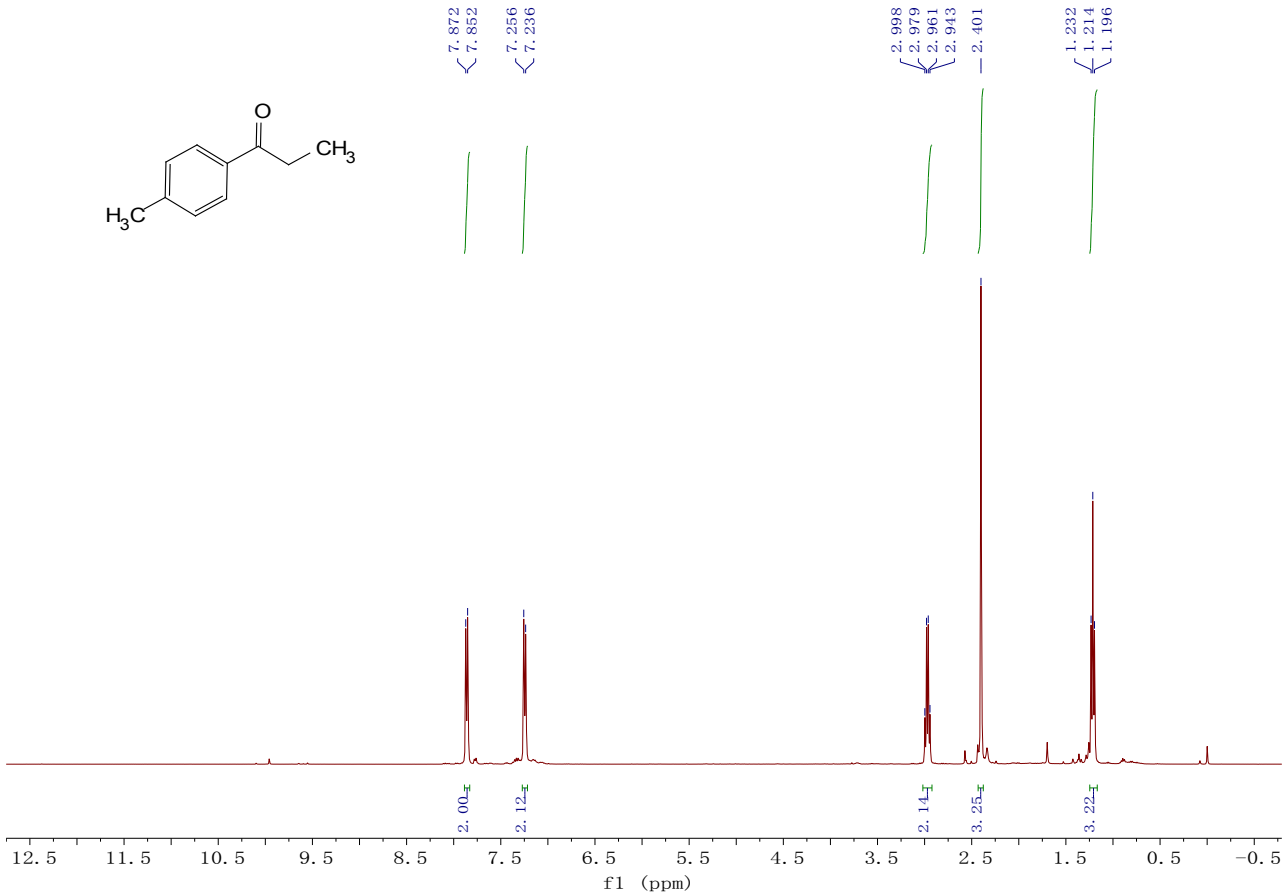


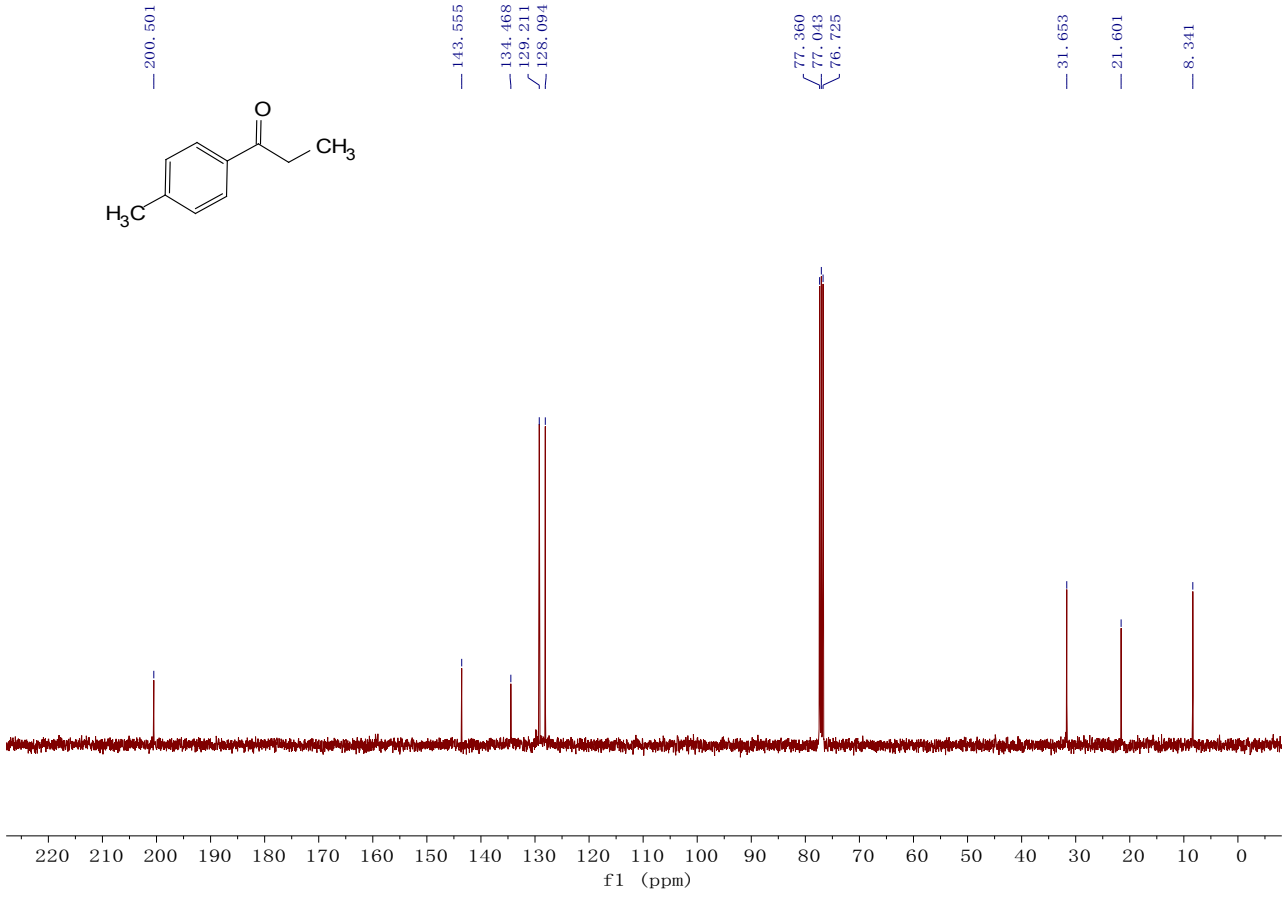
1-(6-Methoxynaphthalen-2-yl)ethan-1-one (16)



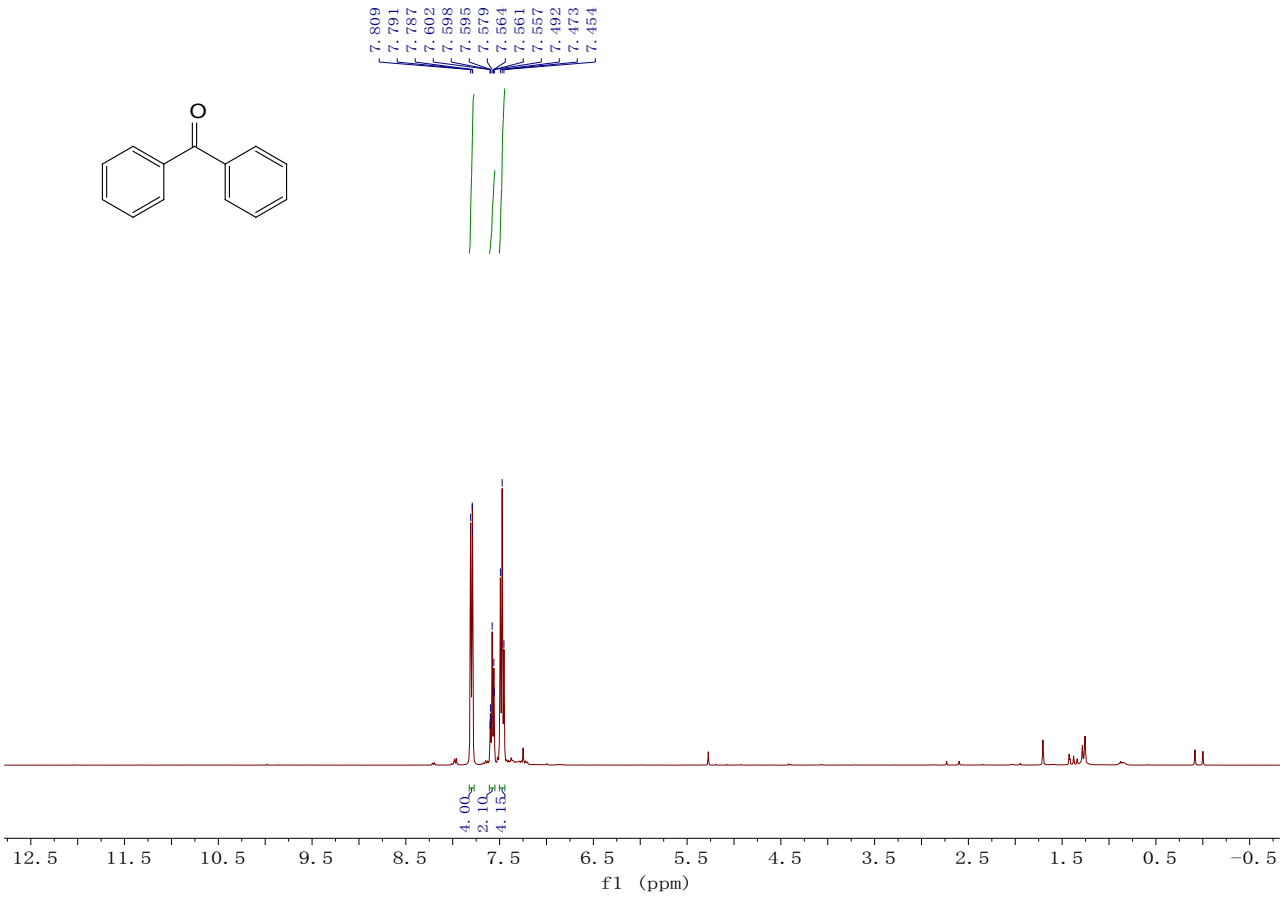


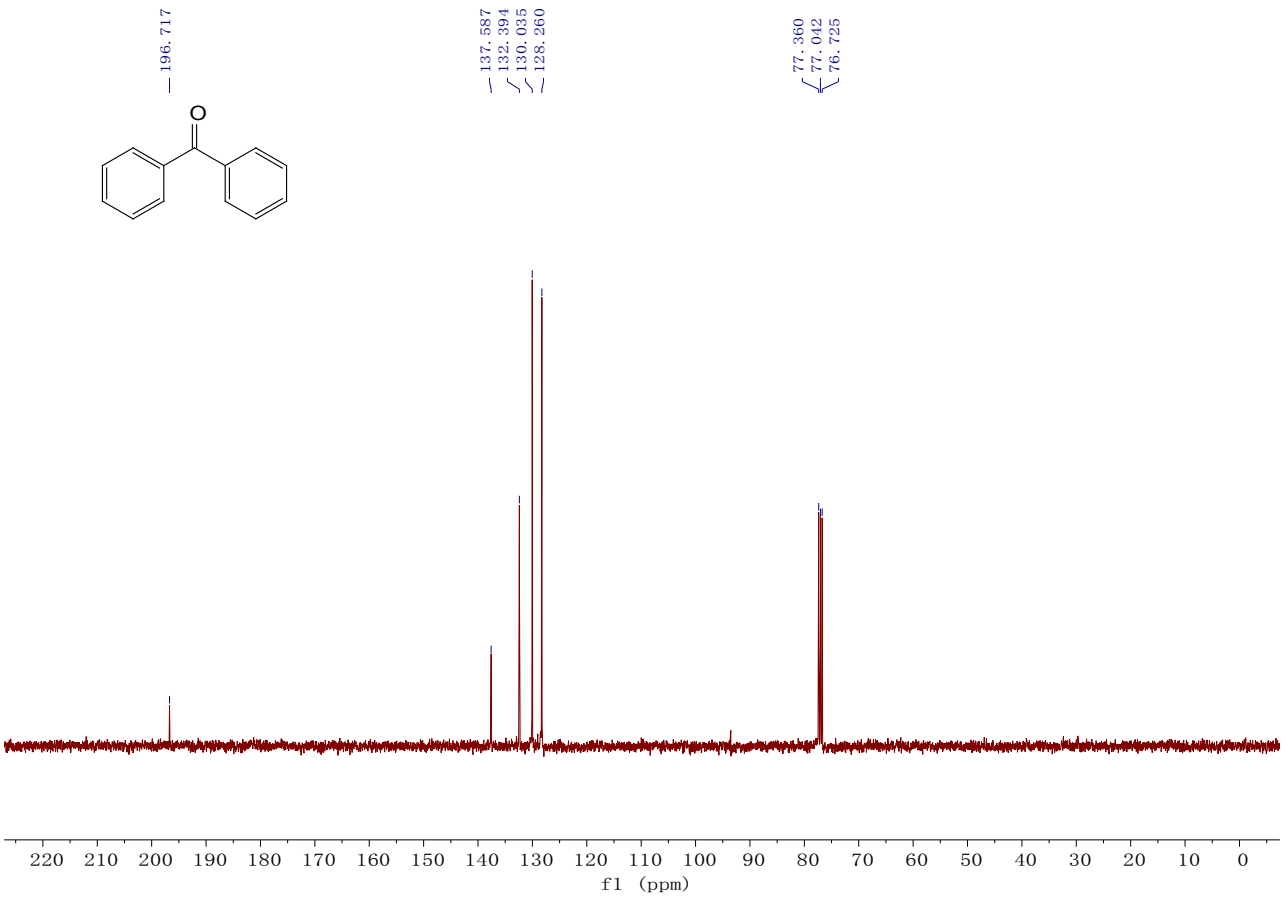
1-(*p*-Tolyl)propan-1-one (17)



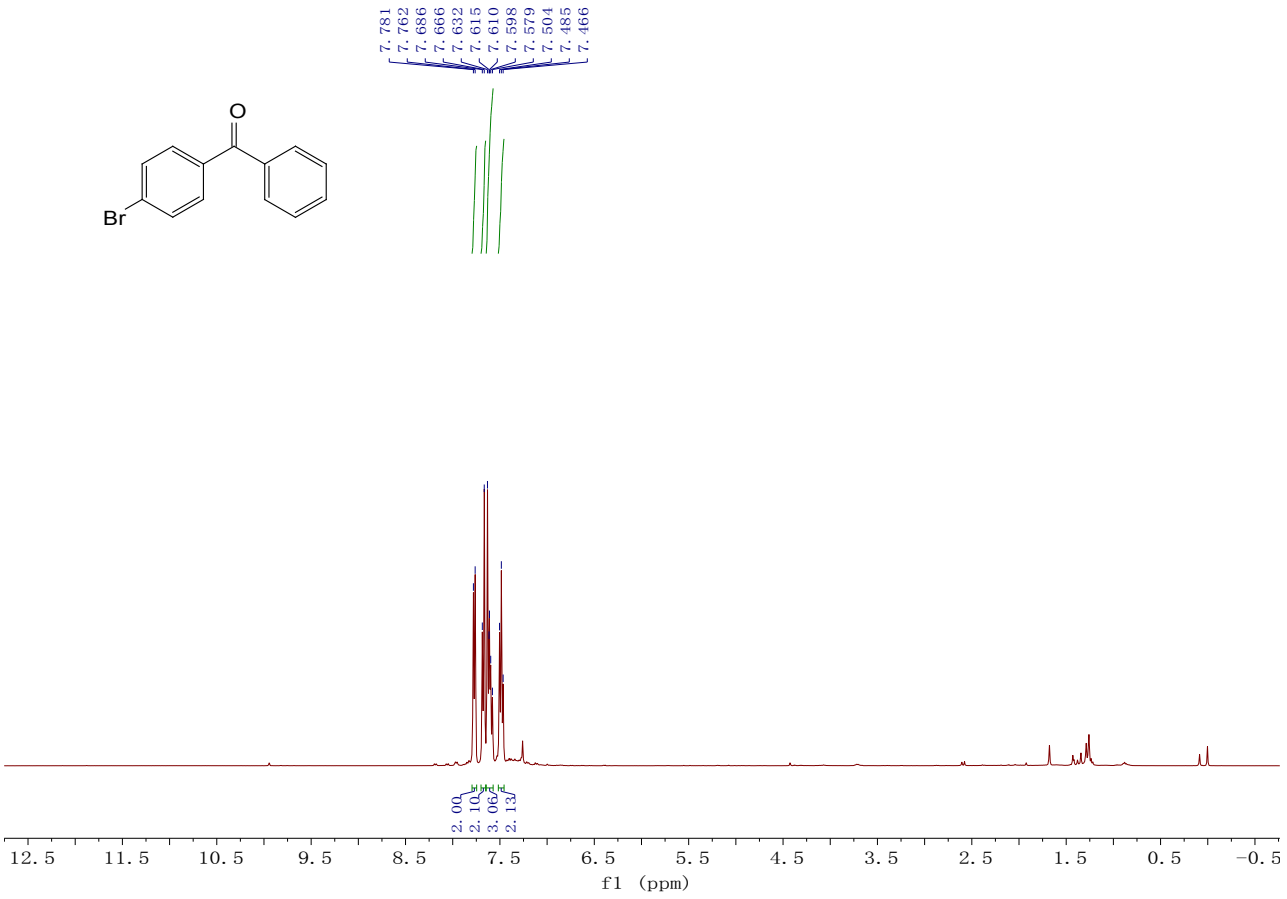


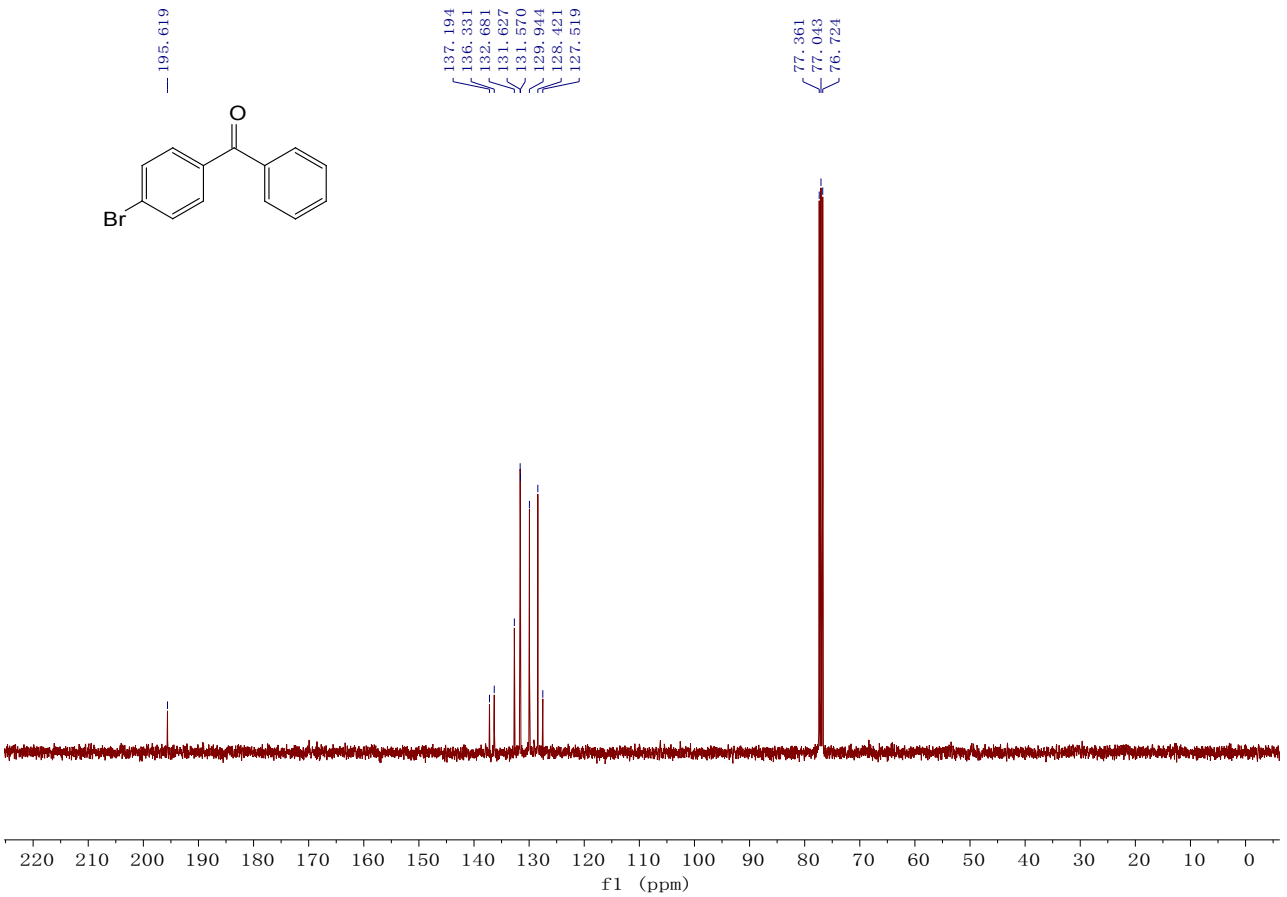
Benzophenone (18)



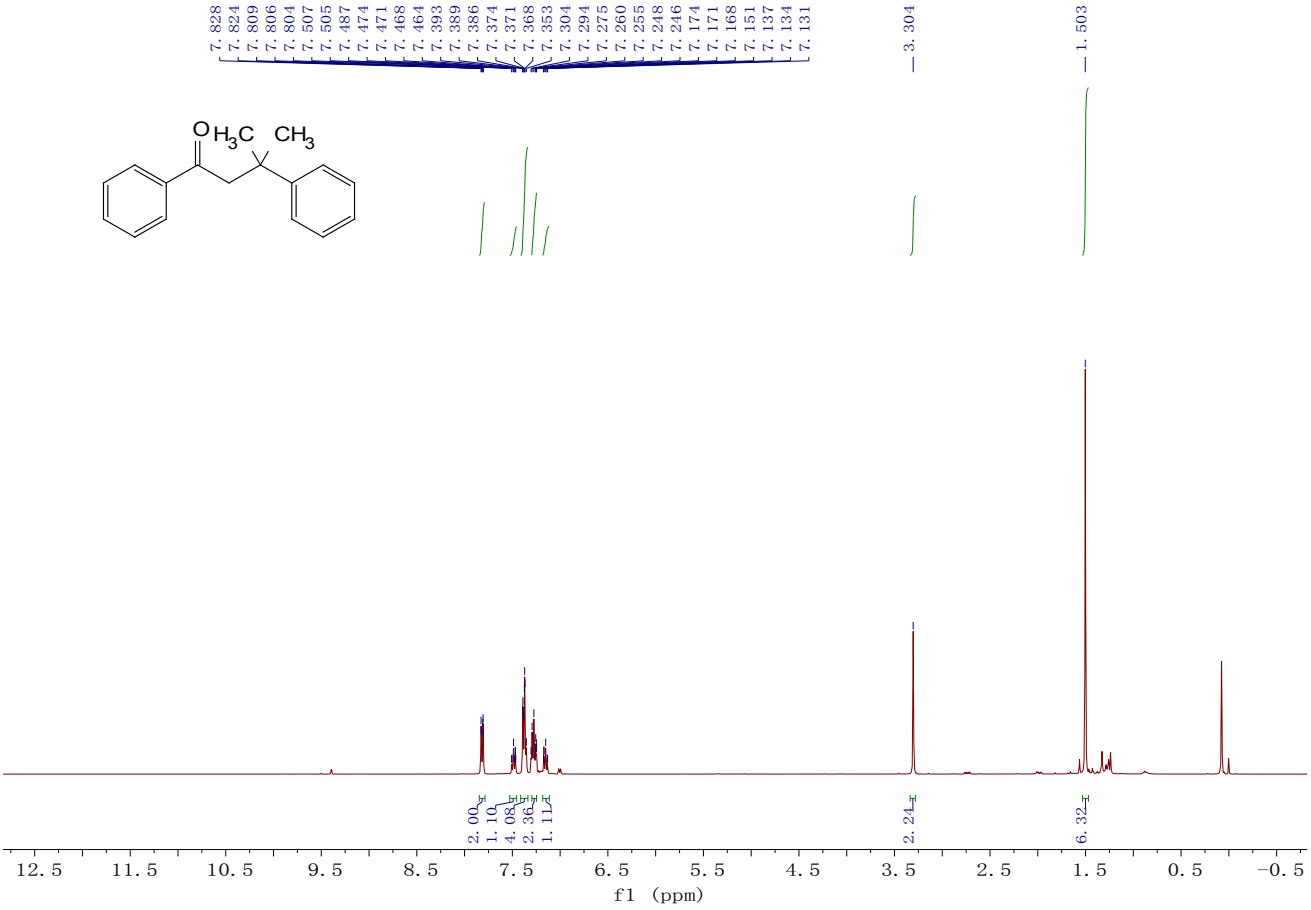


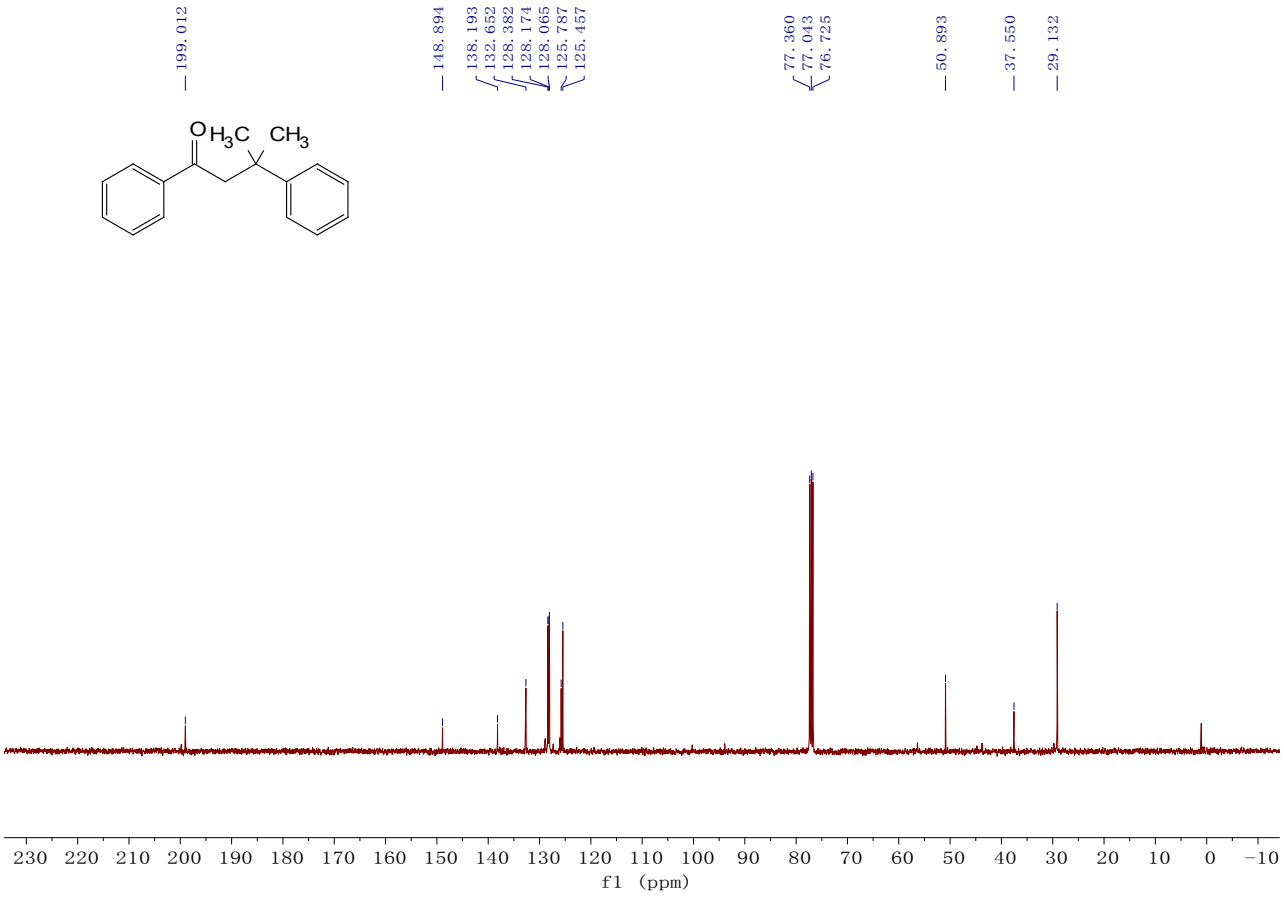
(4-Bromophenyl)(phenyl)methanone (19)



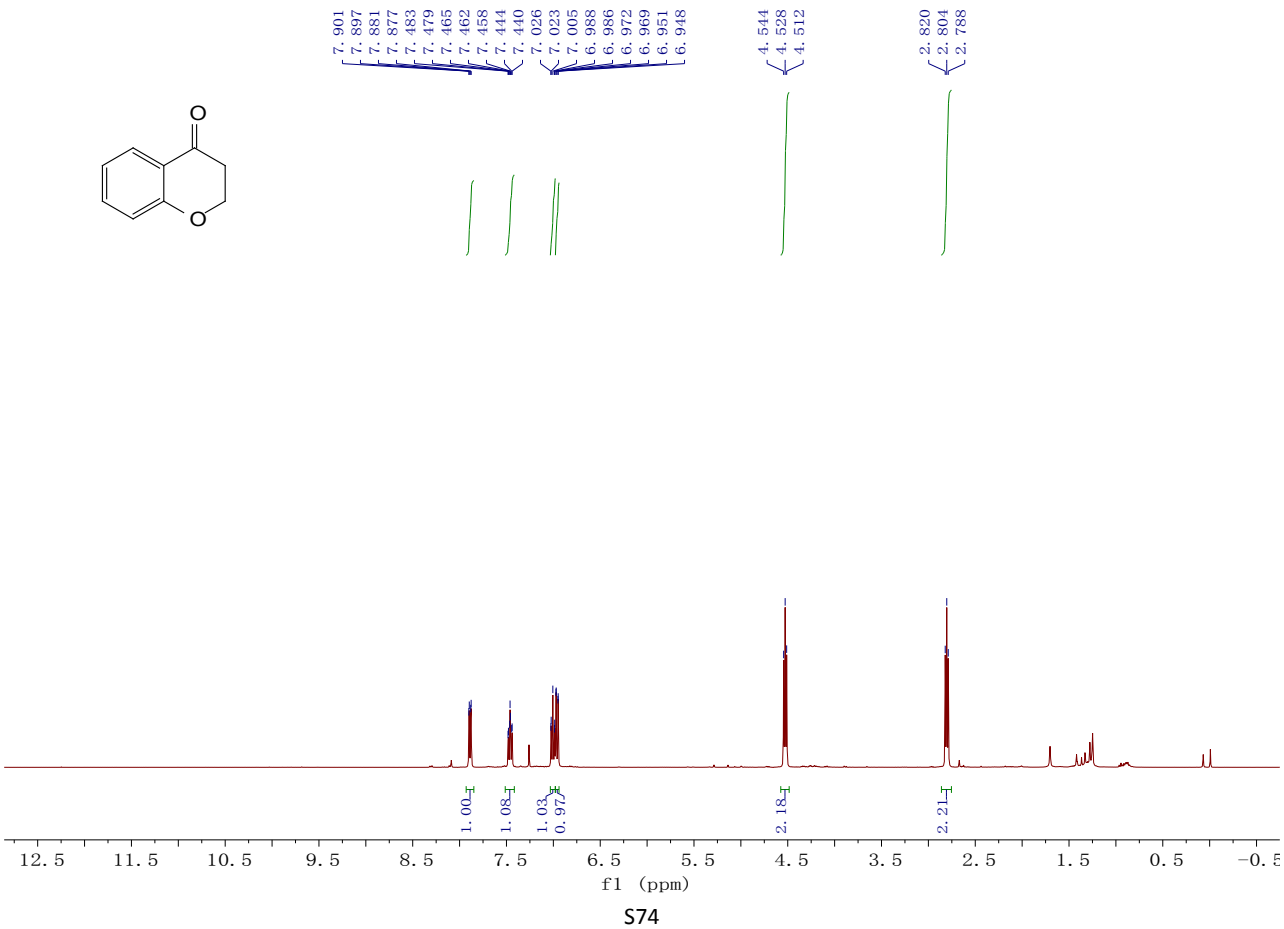


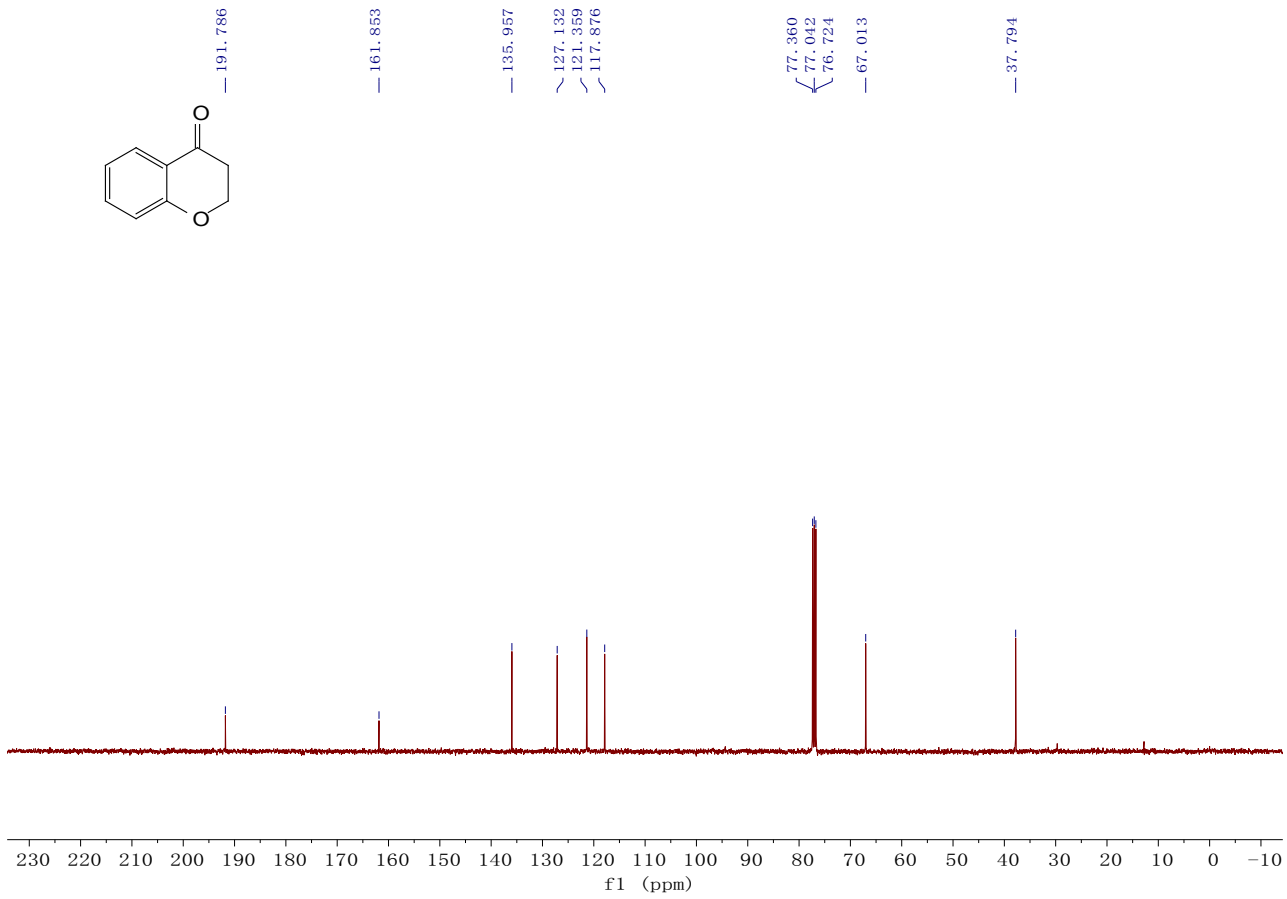
3-Methyl-1,3-diphenylbutan-1-one (20)



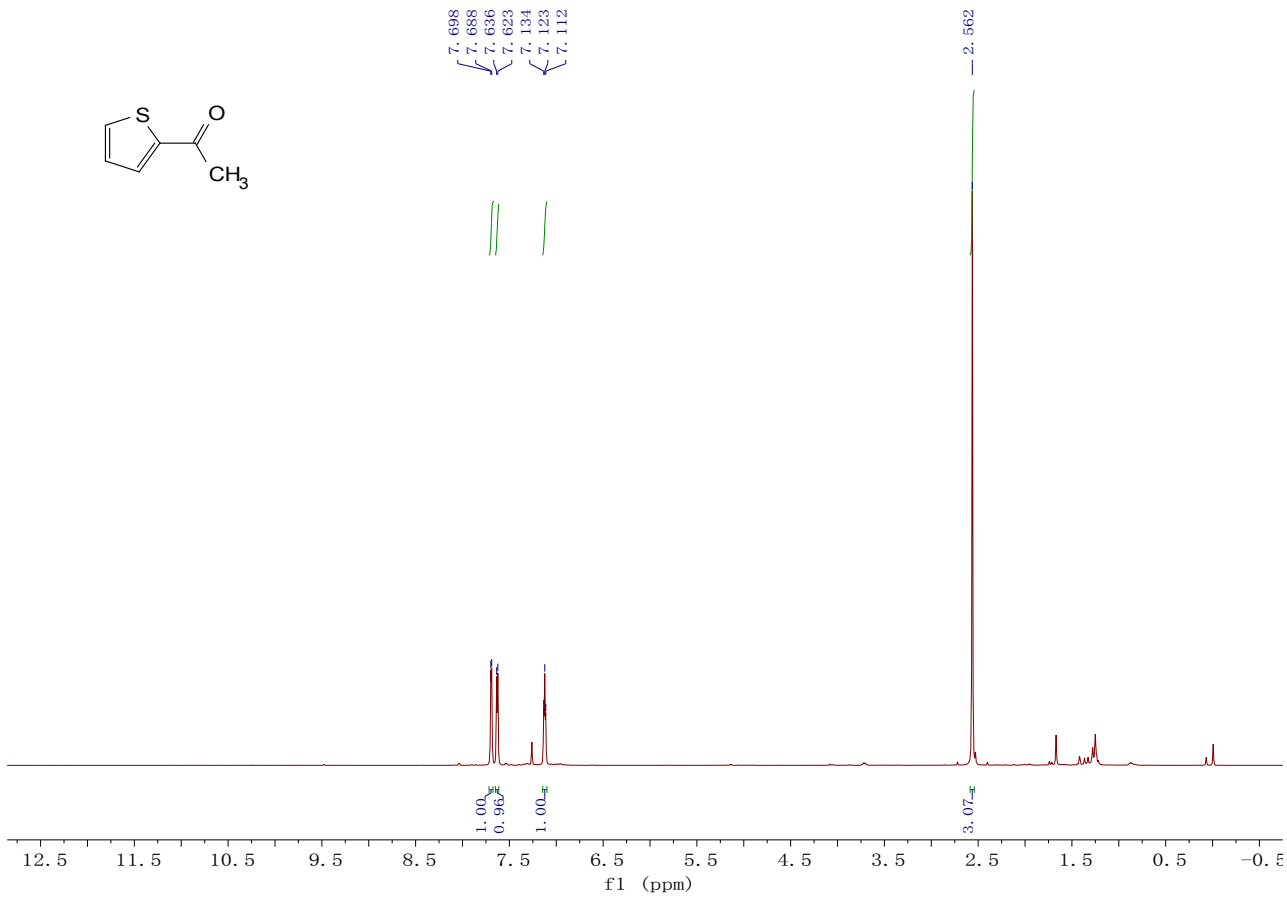


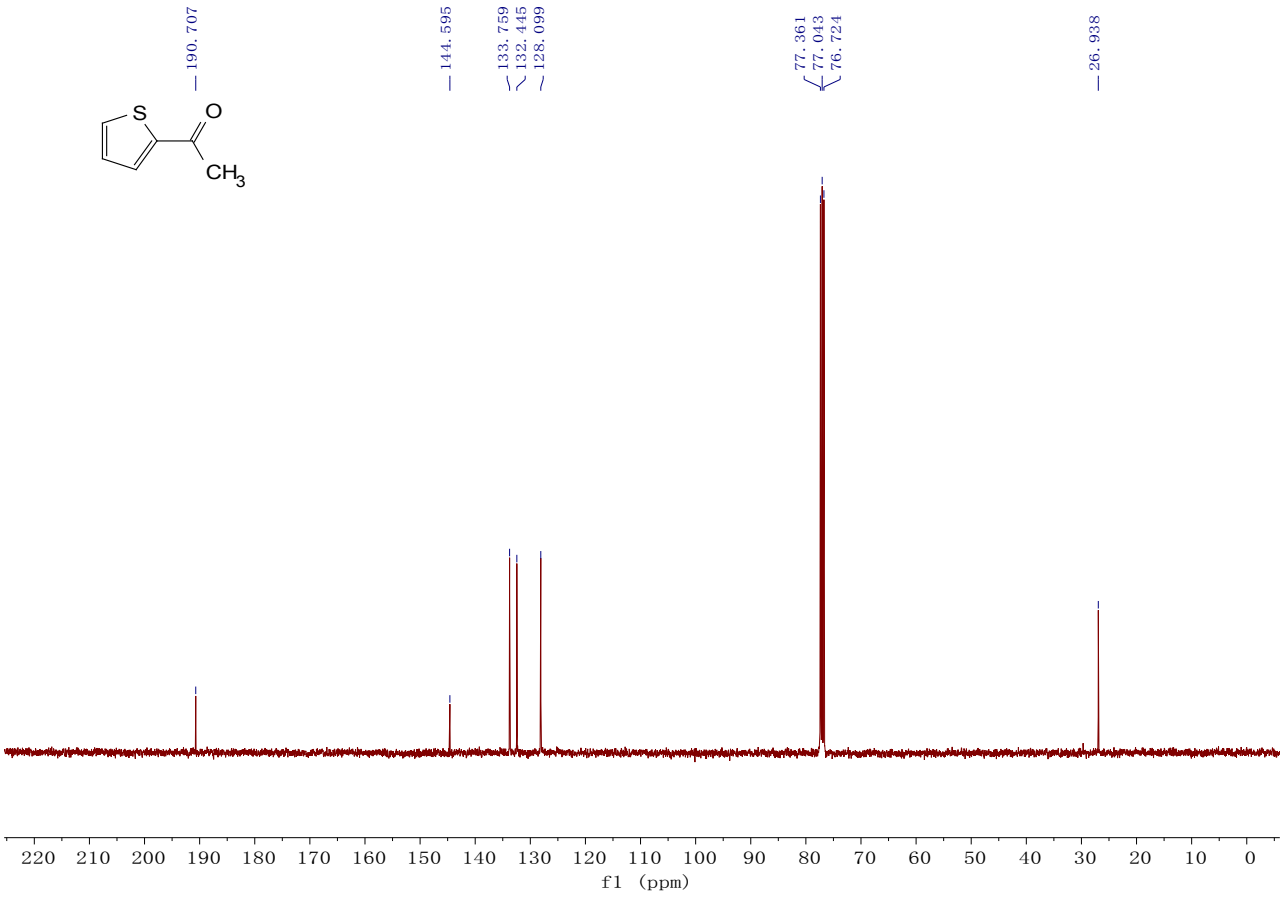
Chroman-4-one (21)



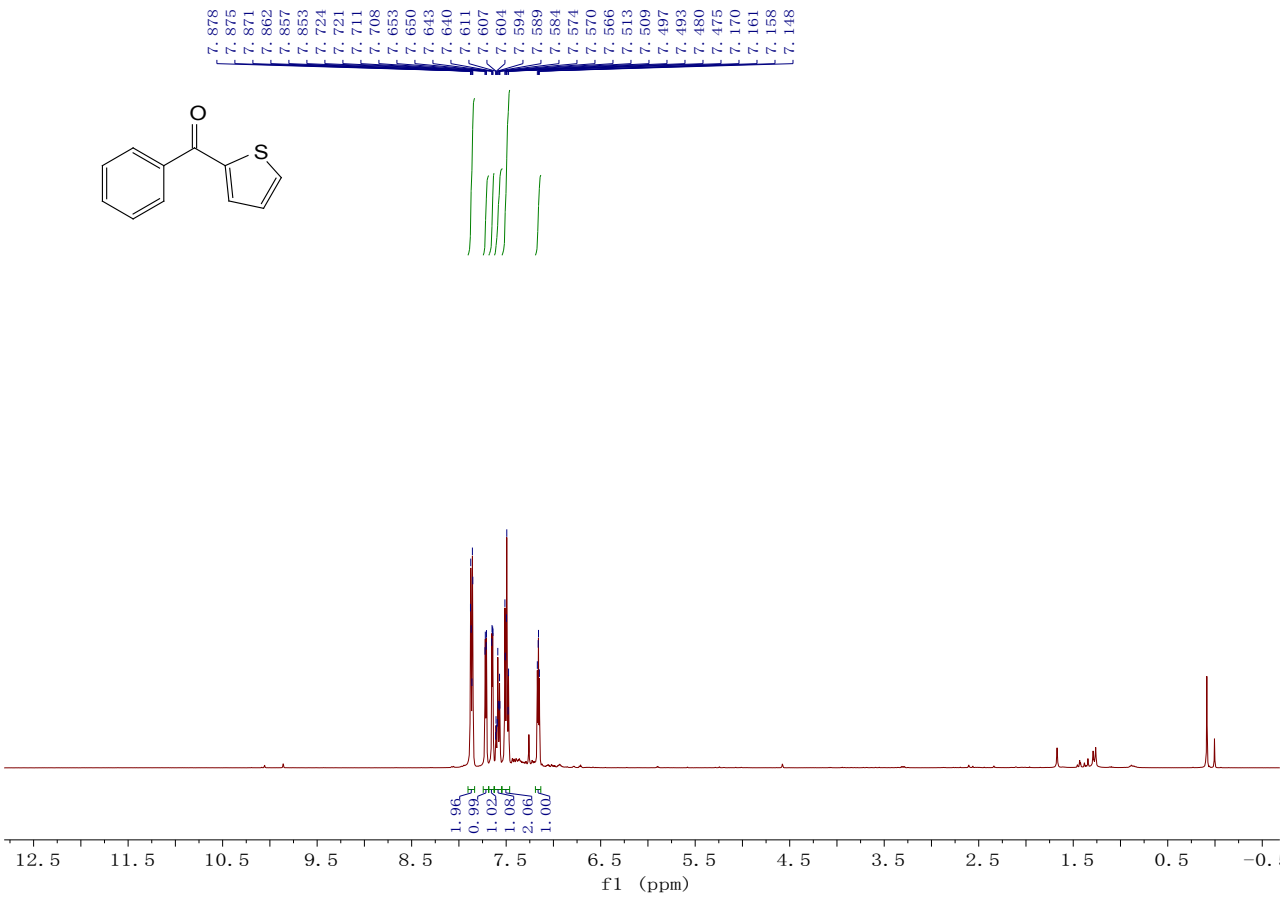


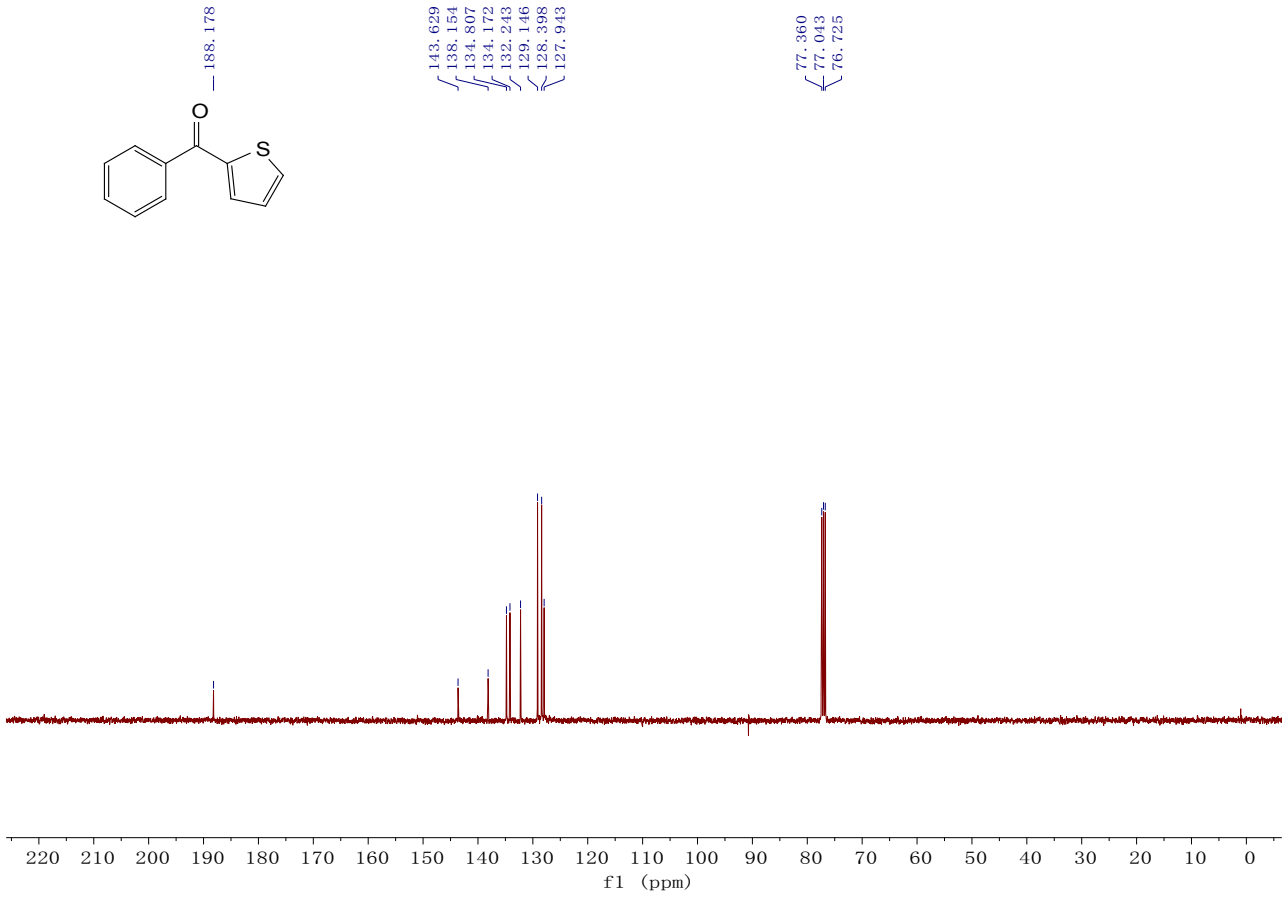
1-(Thiophen-2-yl)ethan-1-one (22)



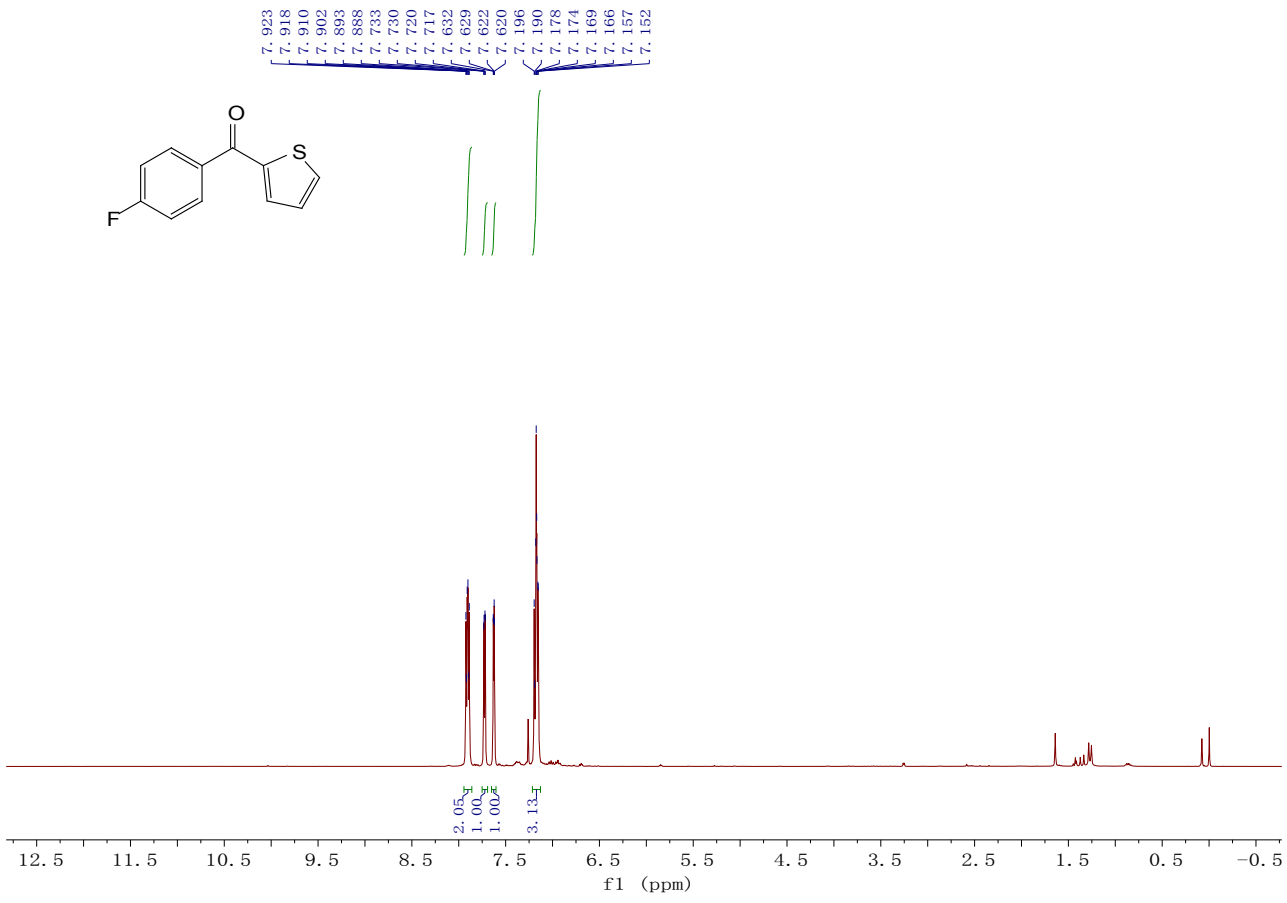


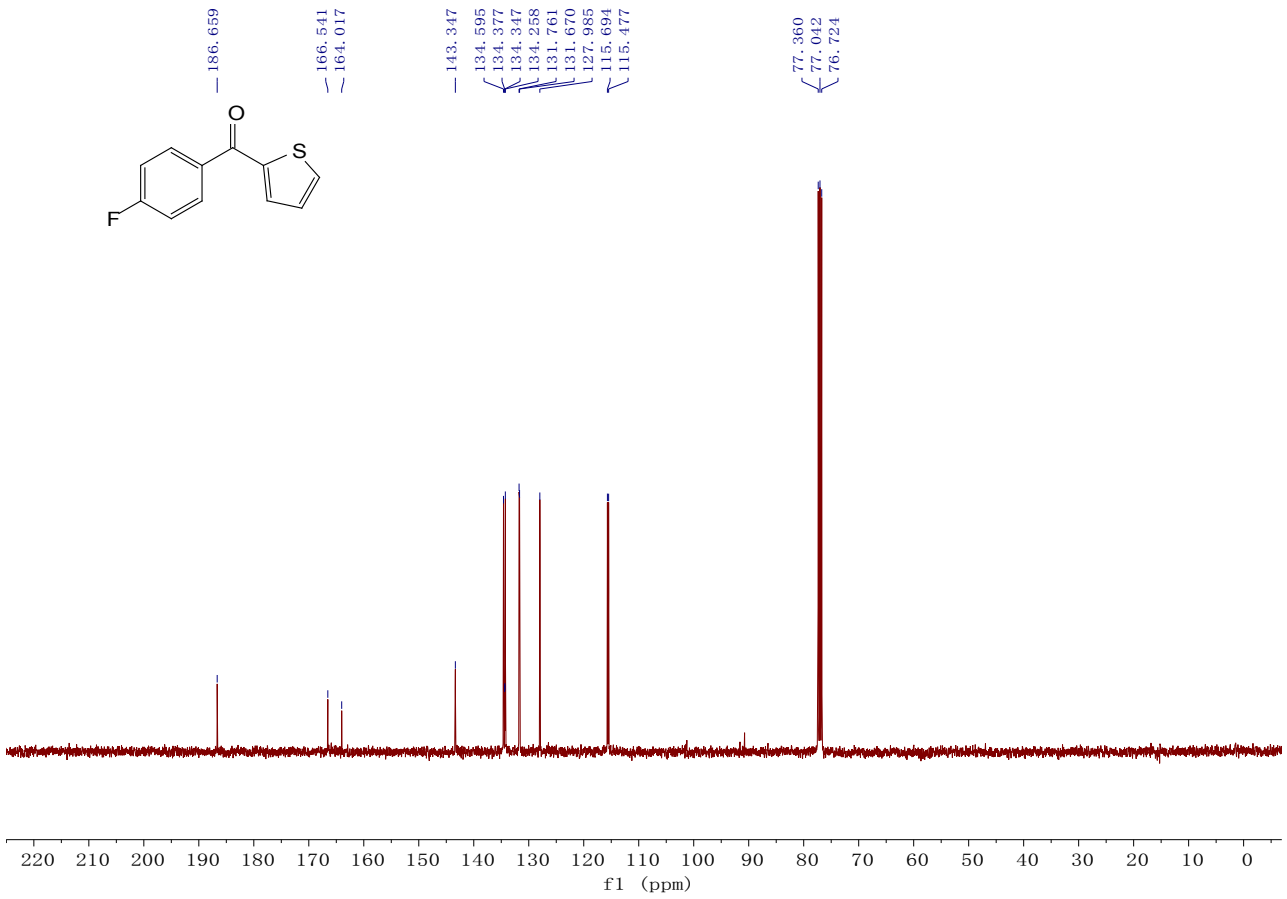
Phenyl(thiophen-2-yl)methanone (23)



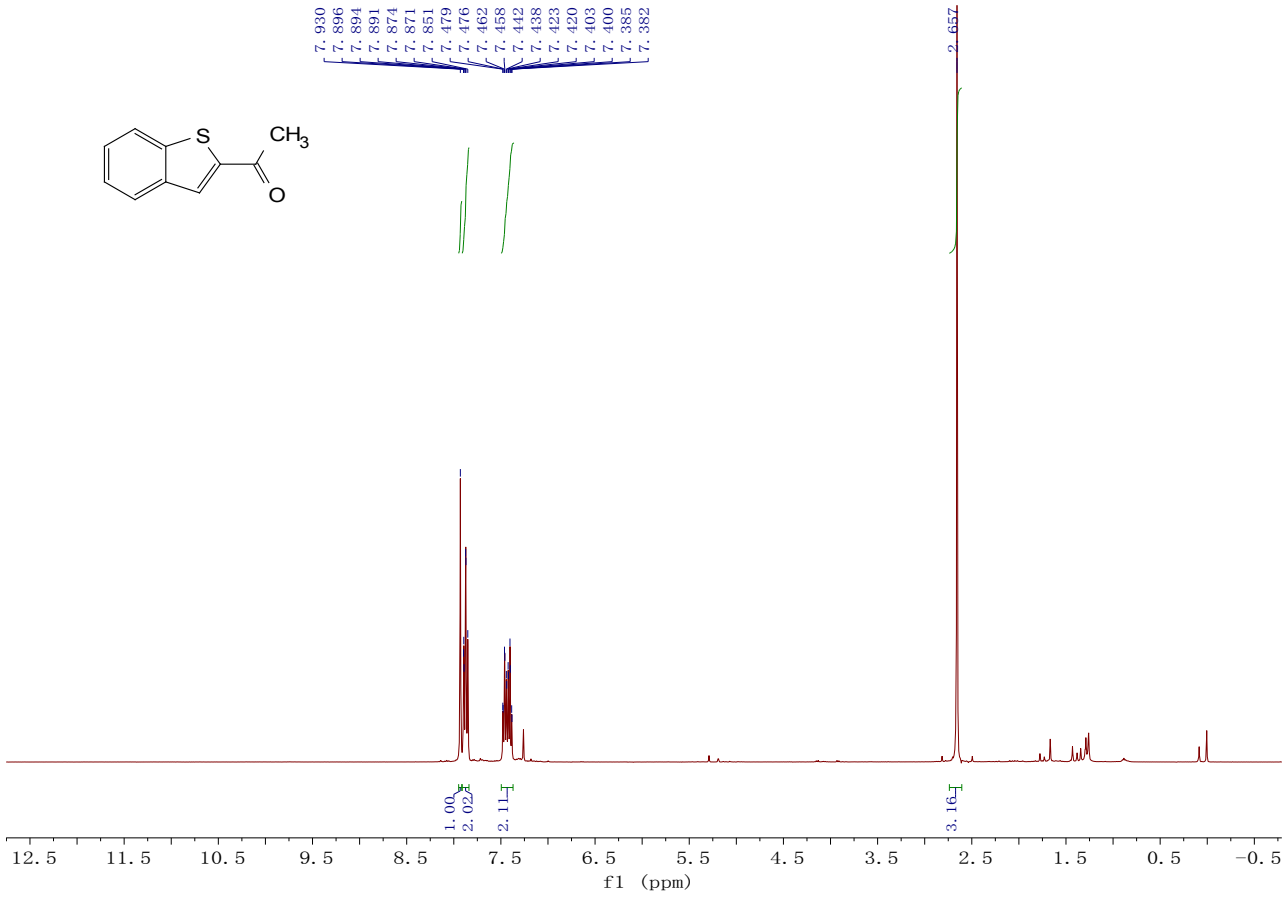


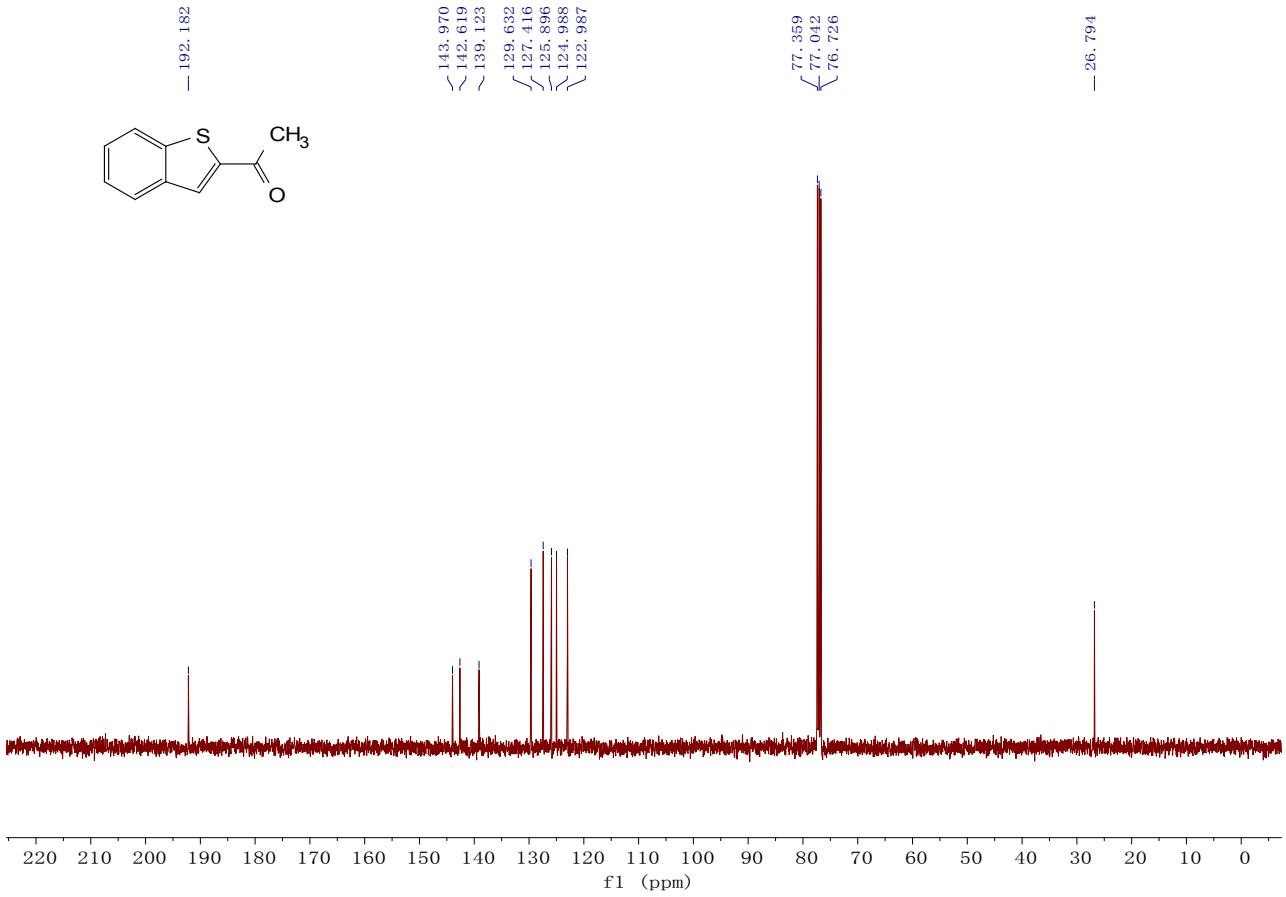
(4-Fluorophenyl)(thiophen-2-yl)methanone (24)



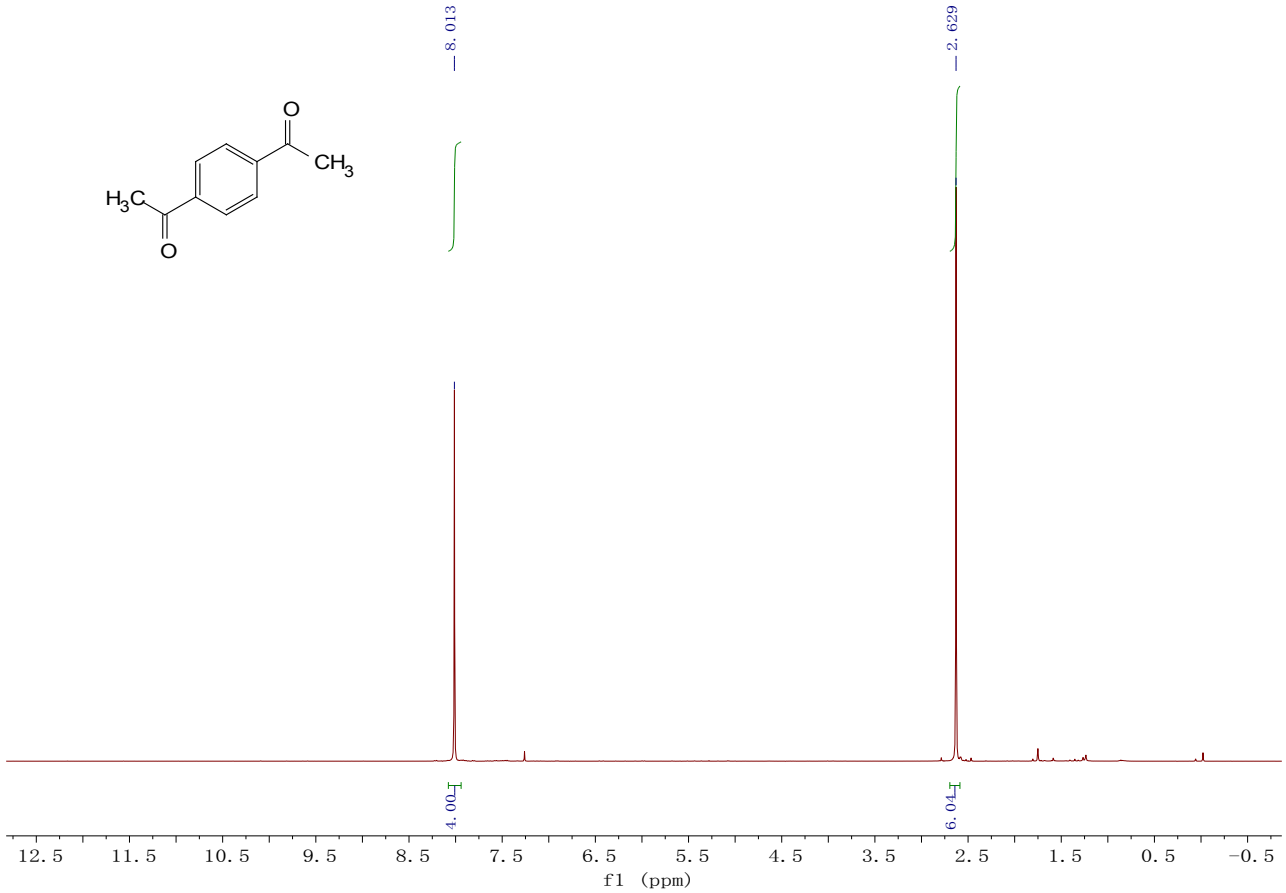


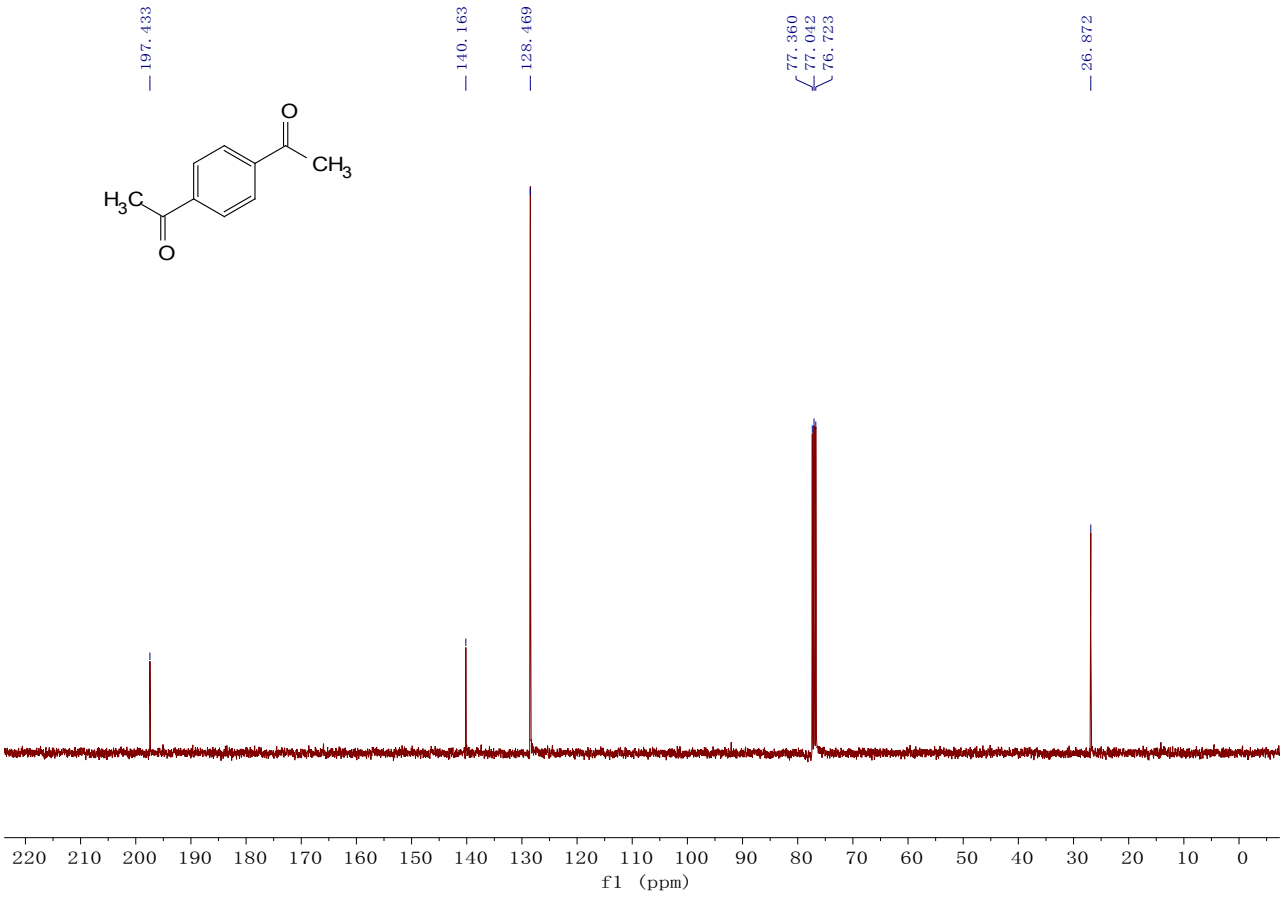
1-(Benzo[b]thiophen-2-yl)ethan-1-one (25)



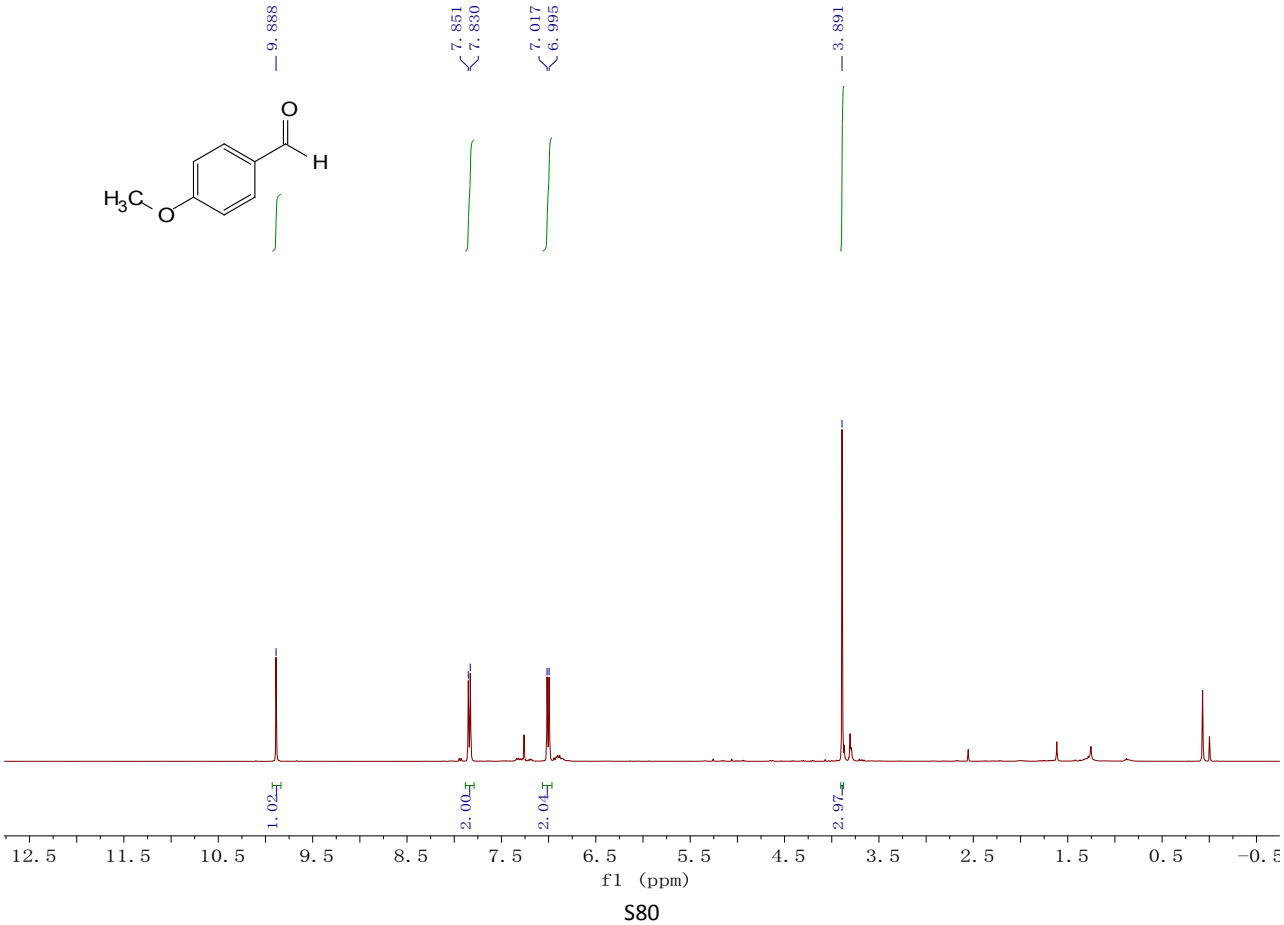


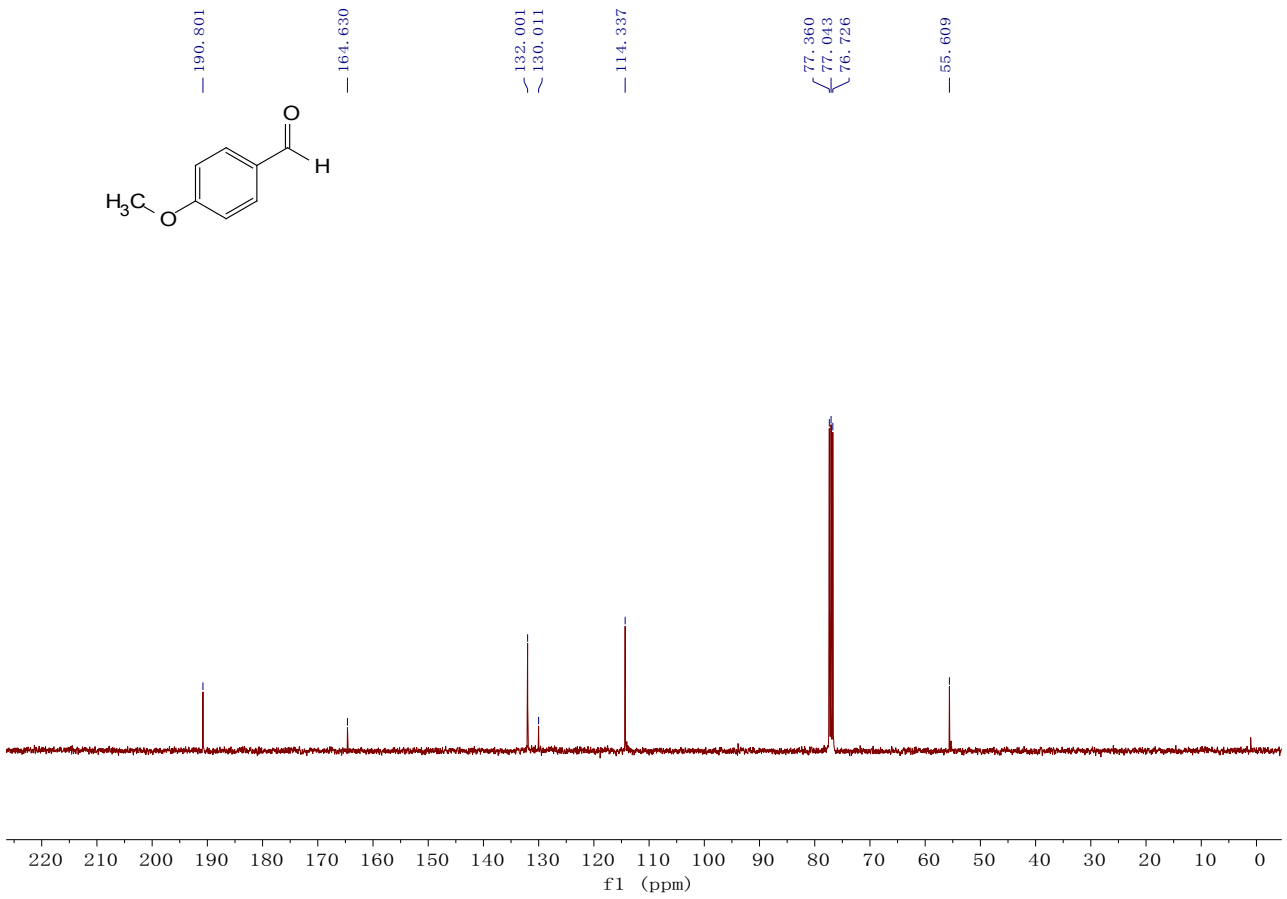
1,1'-(1,4-Phenylene)bis(ethan-1-one) (26)



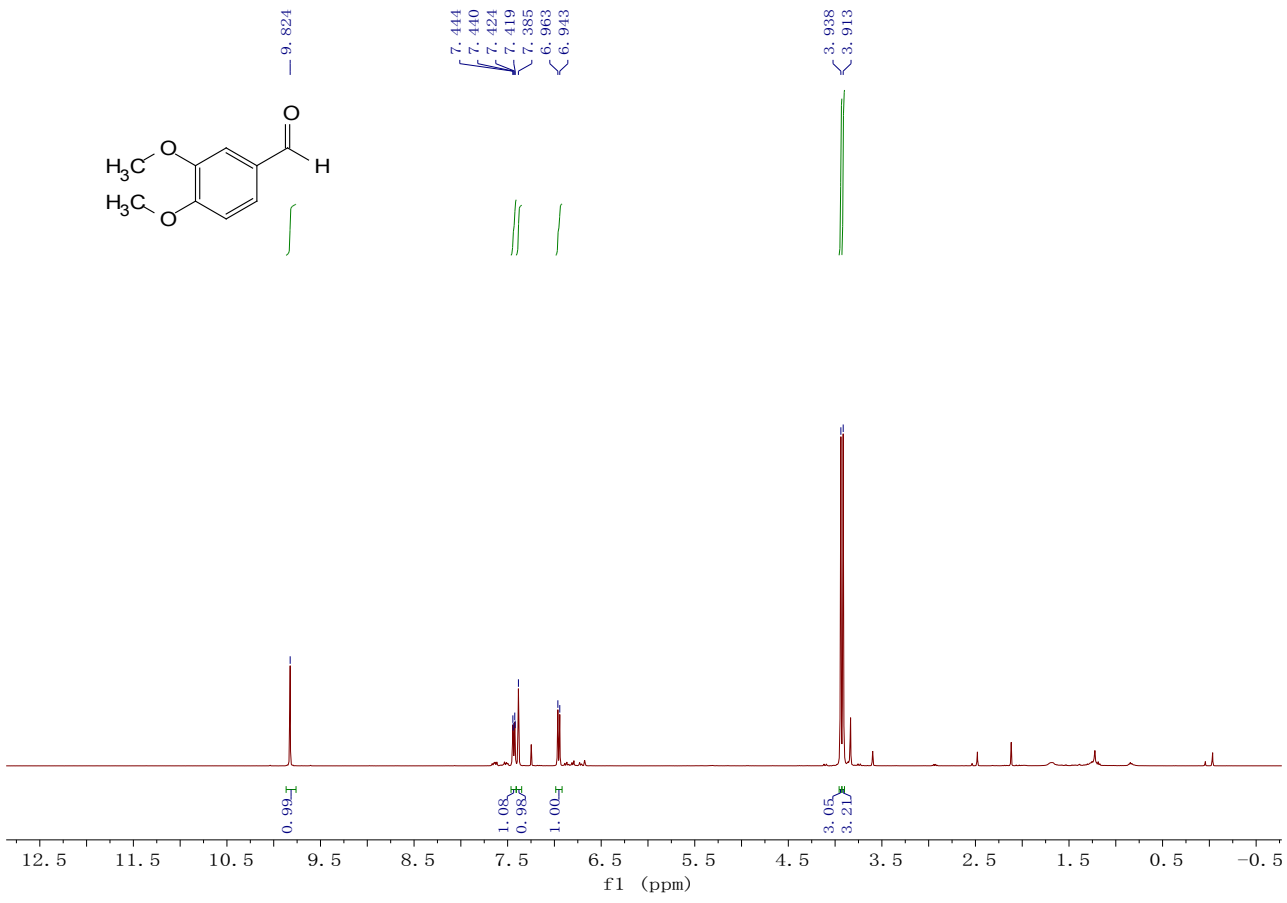


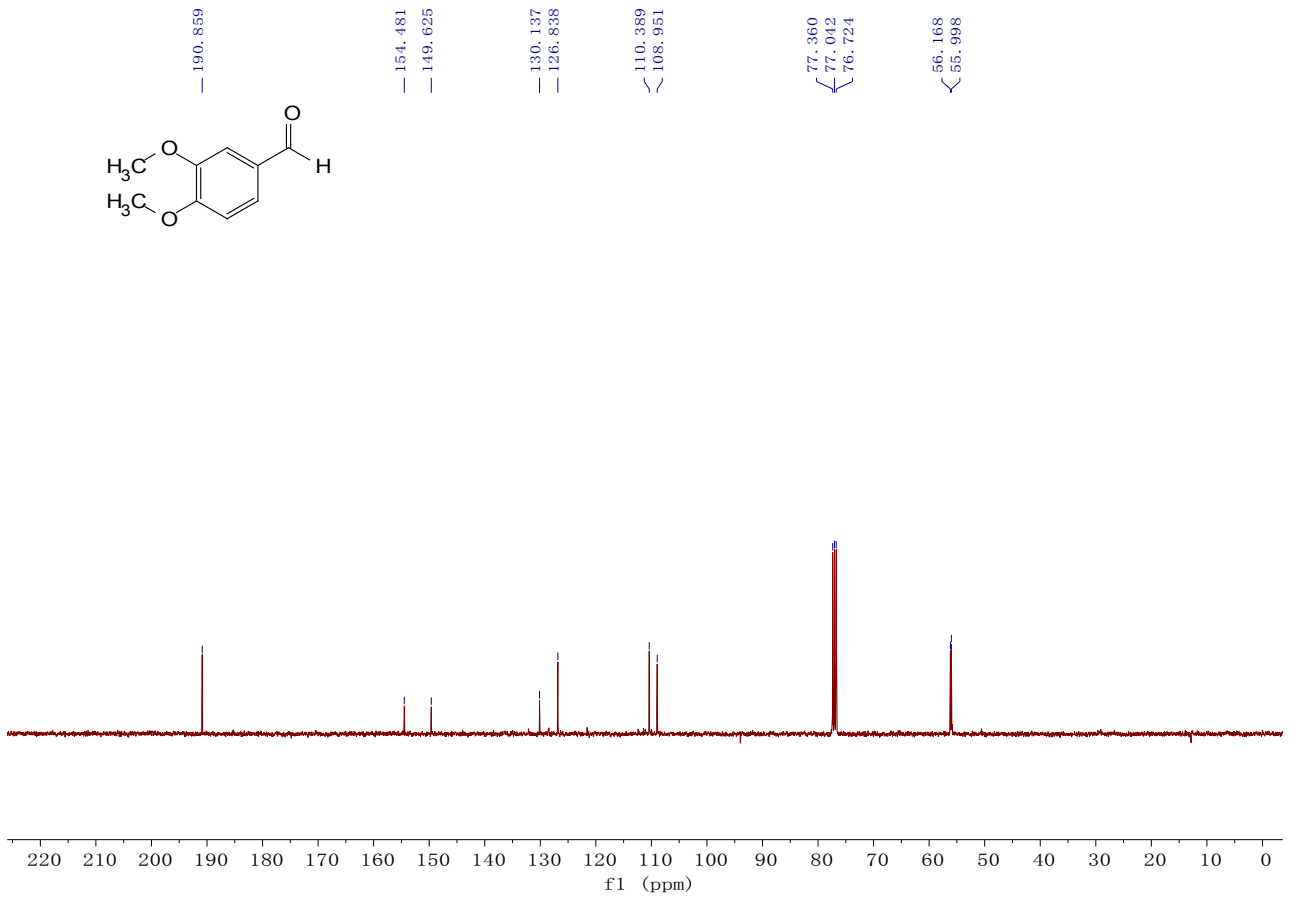
4-Methoxybenzaldehyde (27)



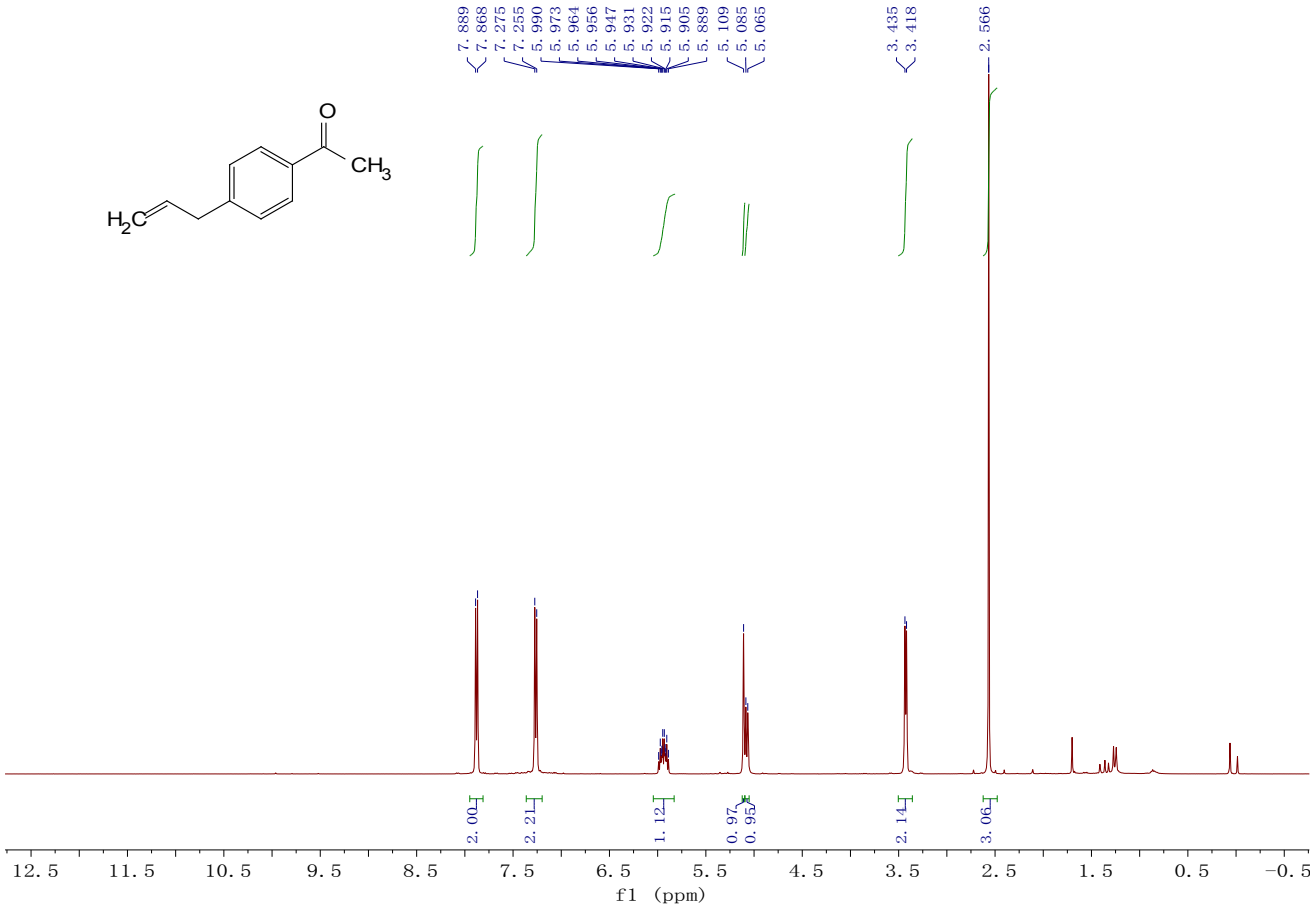


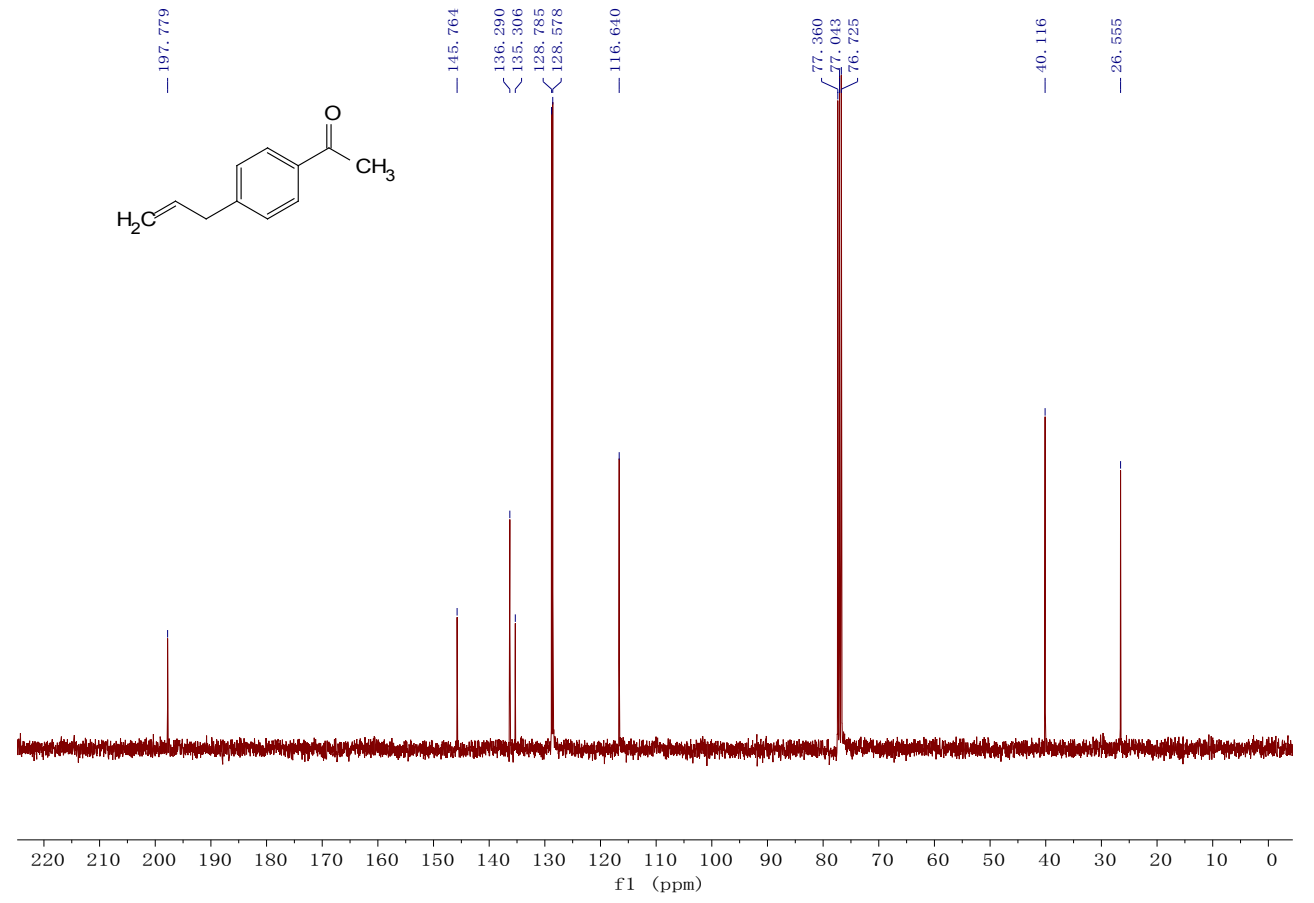
3,4-Dimethoxybenzaldehyde (28)



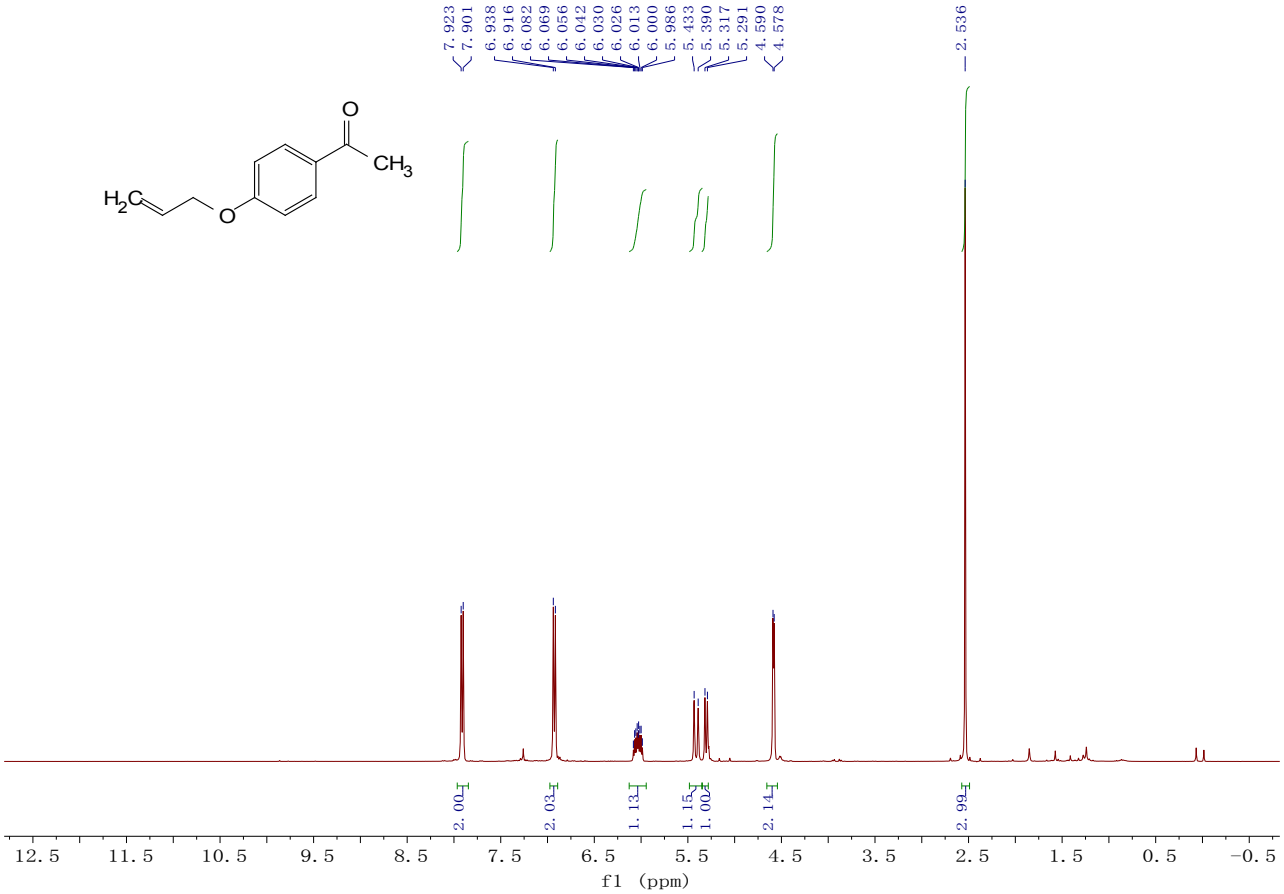


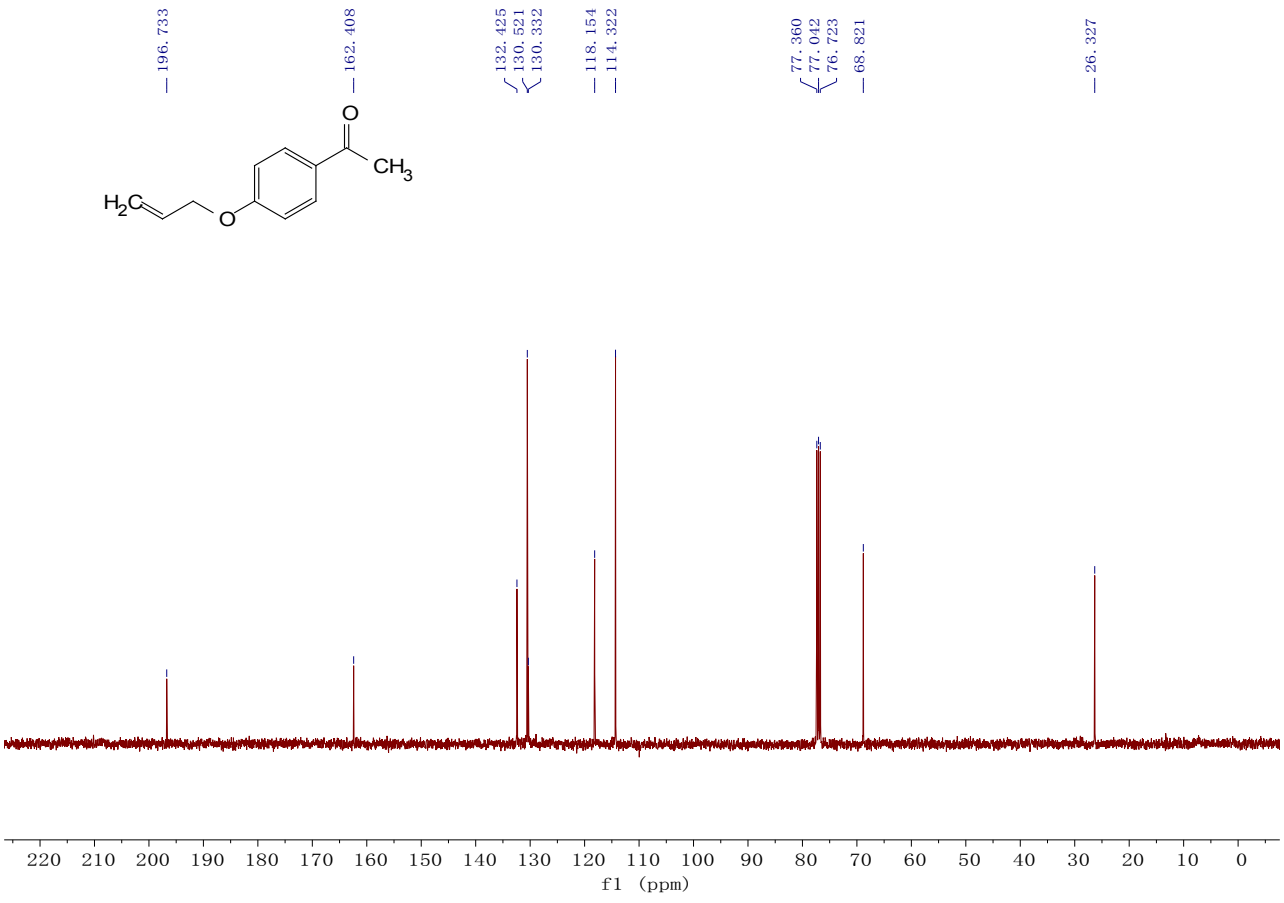
1-(4-Allylphenyl)ethan-1-one (30)


7.889
7.868
7.275
7.255
5.990
5.973
5.964
5.956
5.947
5.931
5.922
5.915
5.905
5.889
5.109
5.085
5.065
3.435
3.418
2.566
O
CH3
H2C
2.00
2.21
1.12
0.97
0.95
2.14
3.06
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)

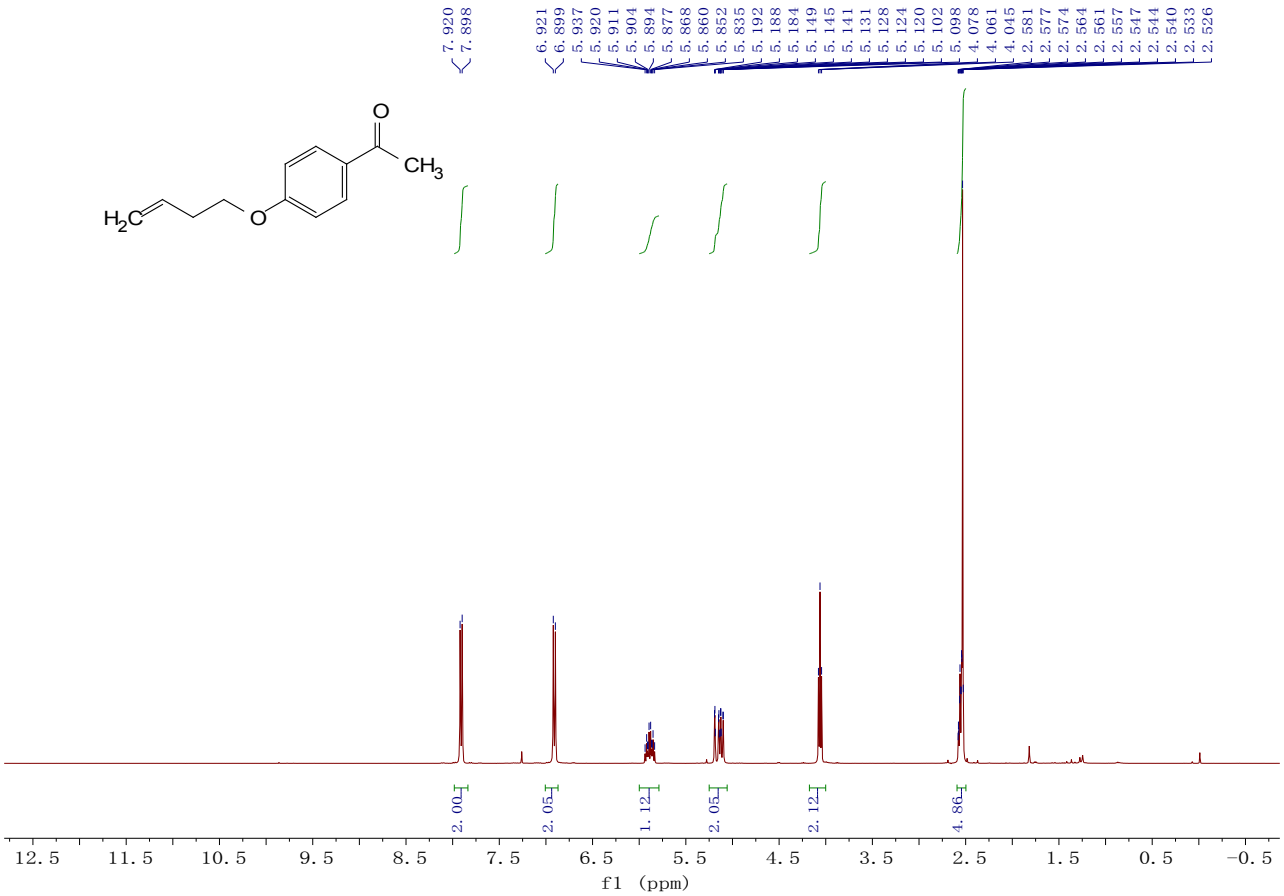

197.779
145.764
136.290
135.306
128.785
128.578
116.640
77.360
77.043
76.725
40.116
26.555
O
CH3
H2C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

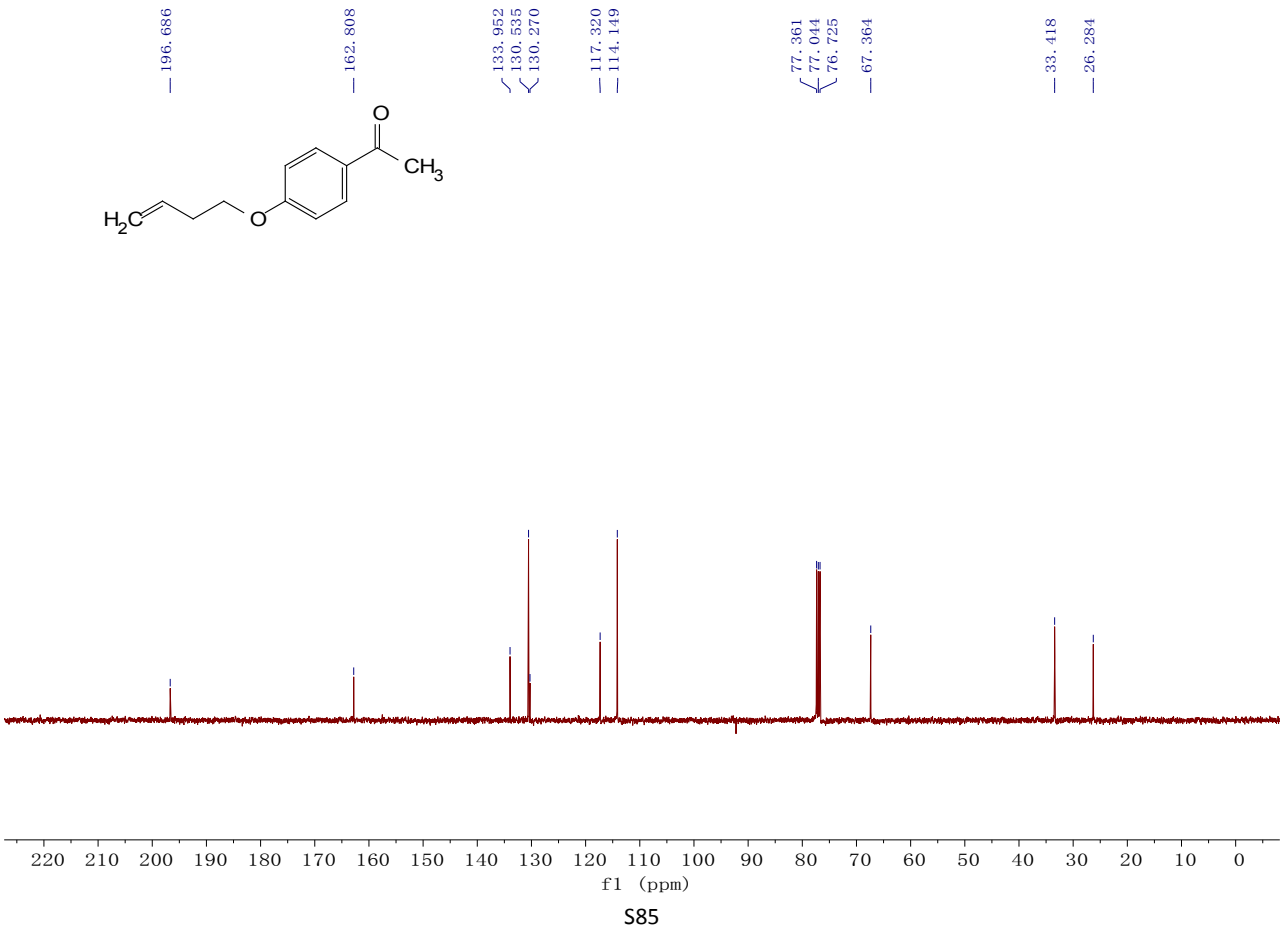
1-(4-(Allyloxy)phenyl)ethan-1-one (31)



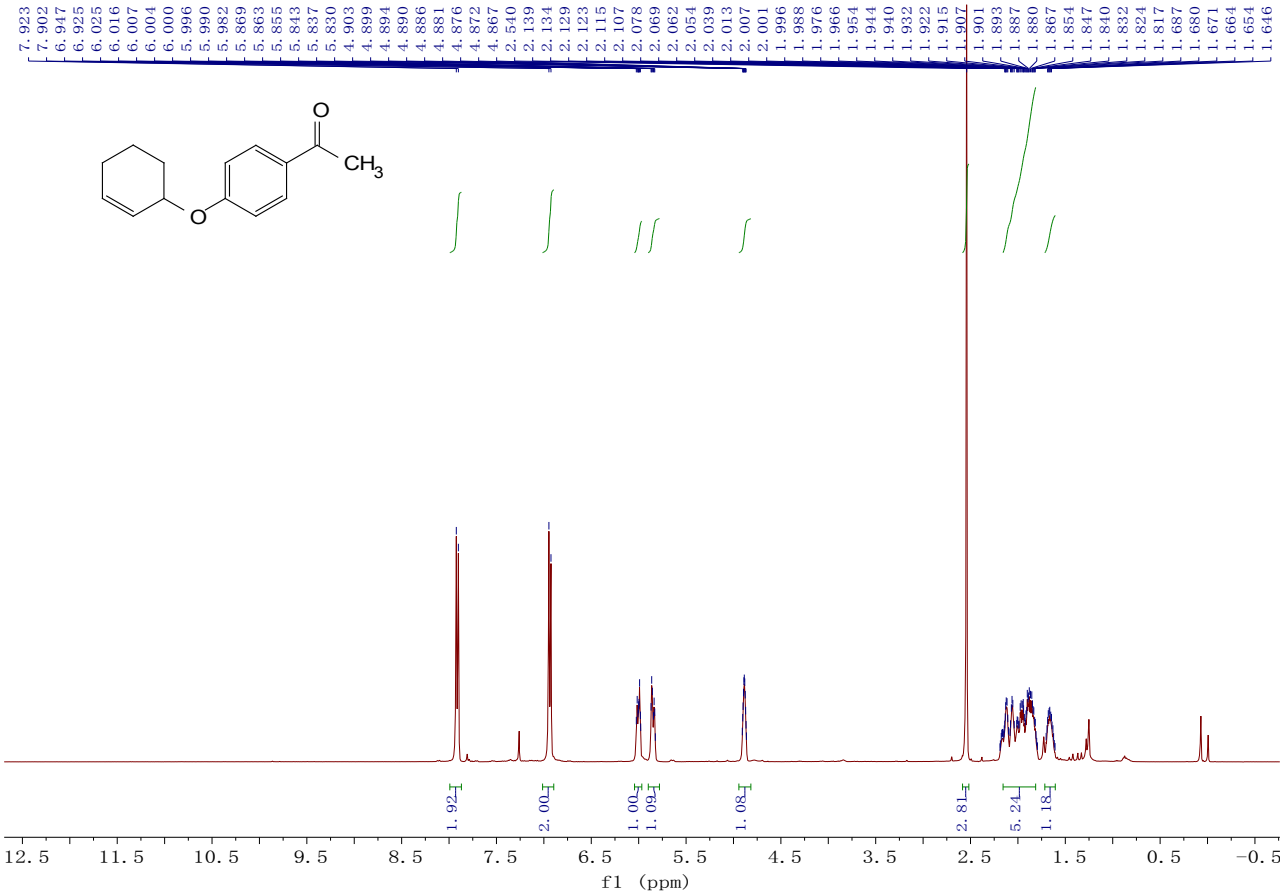


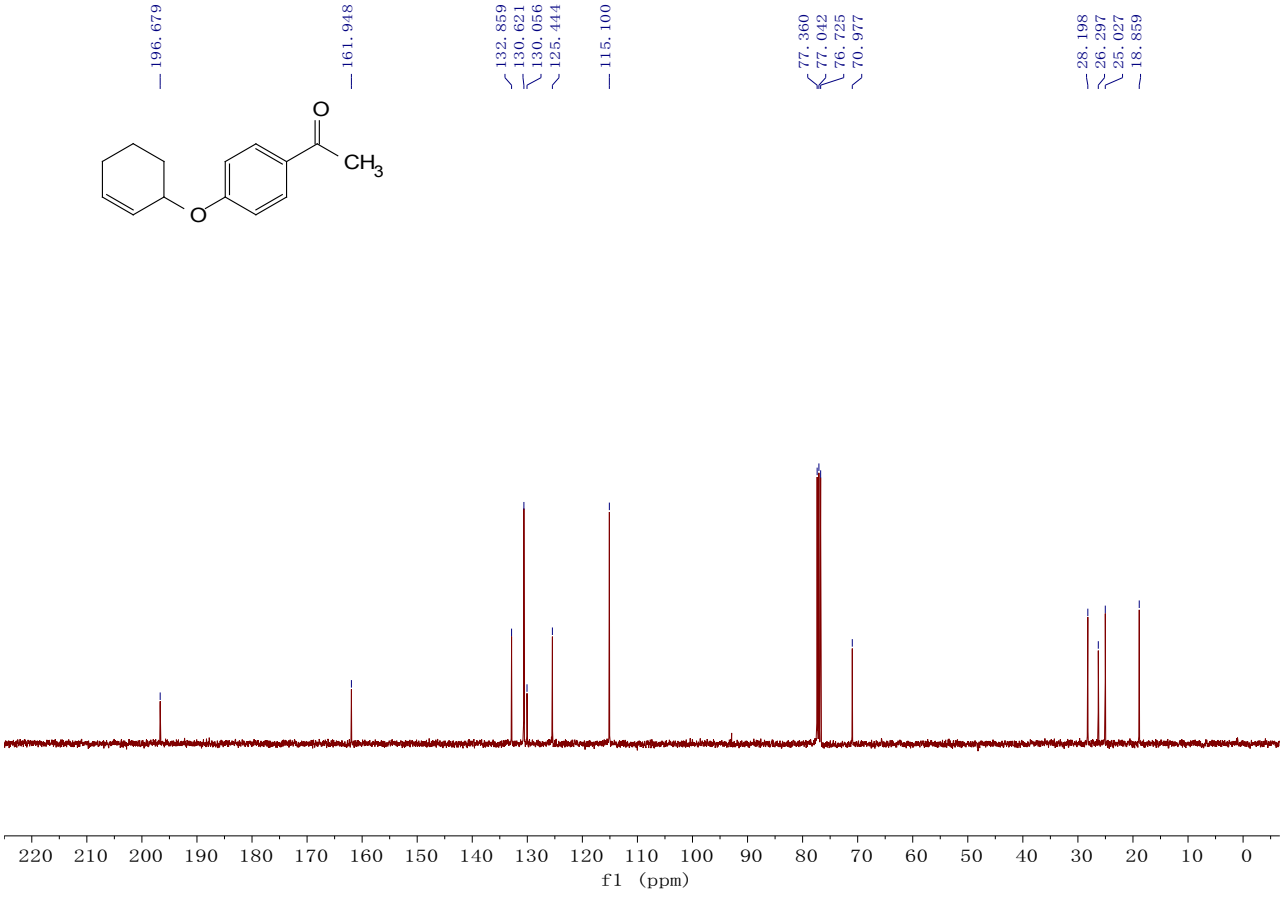
1-(4-(But-3-en-1-yloxy)phenyl)ethan-1-one (32)



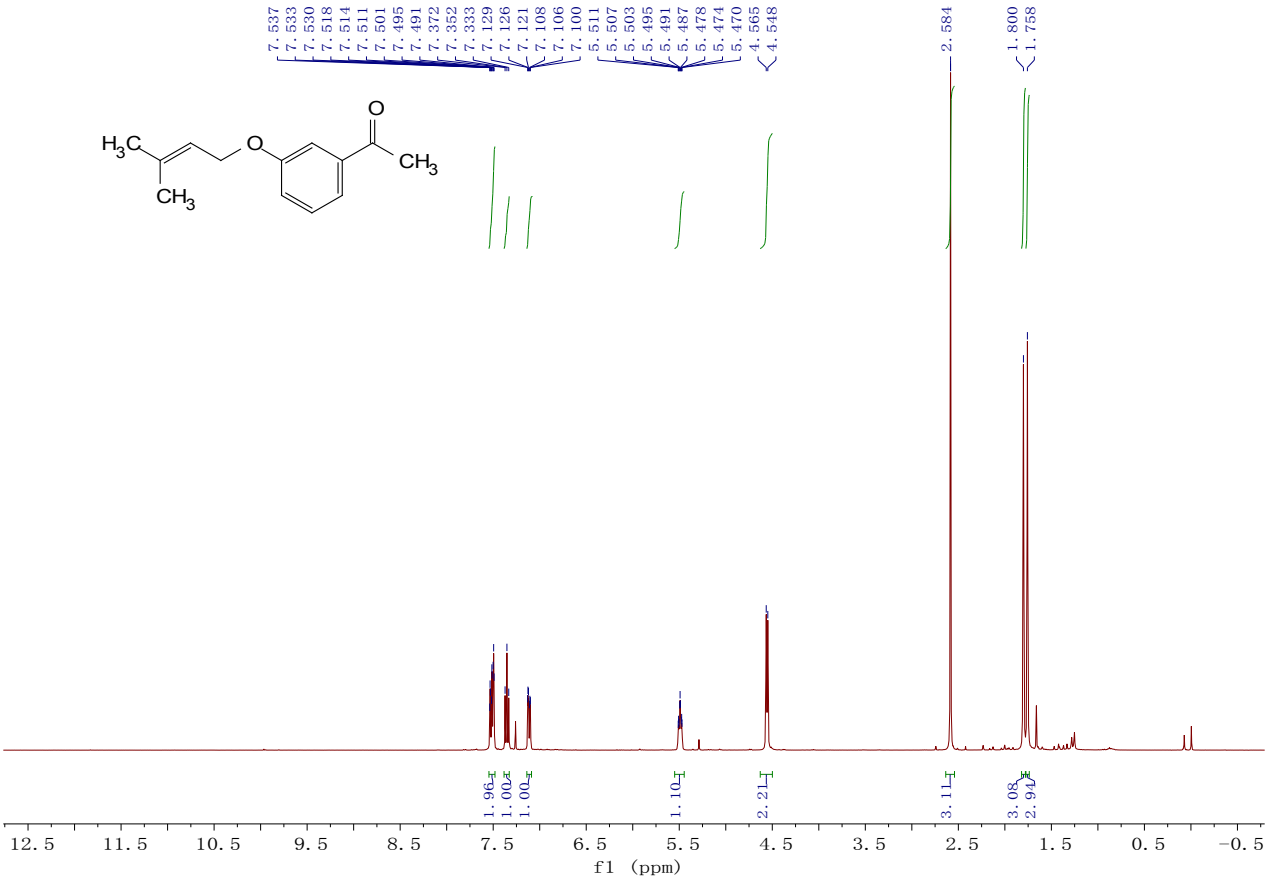


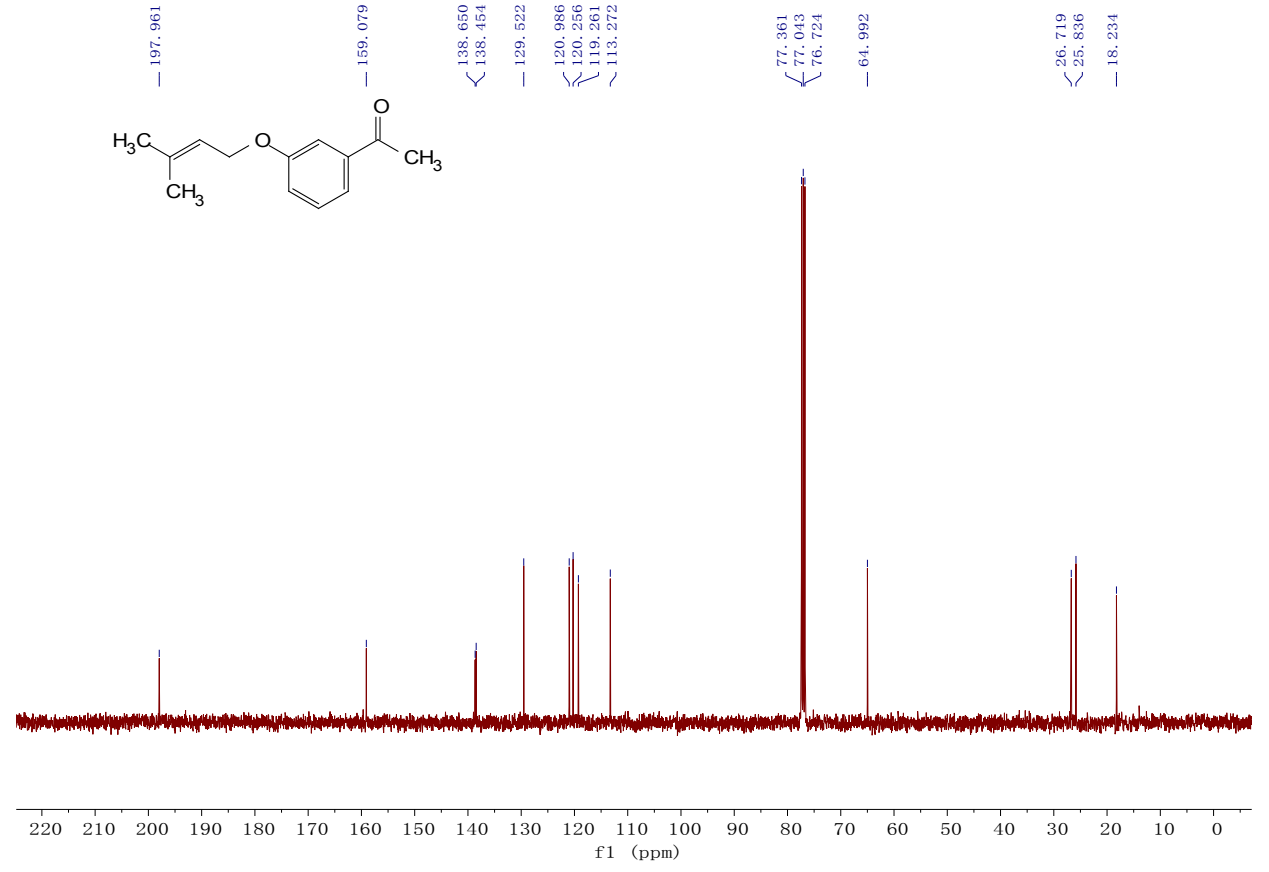
1-(4-(Cyclohex-2-en-1-yloxy)phenyl)ethan-1-one (33)



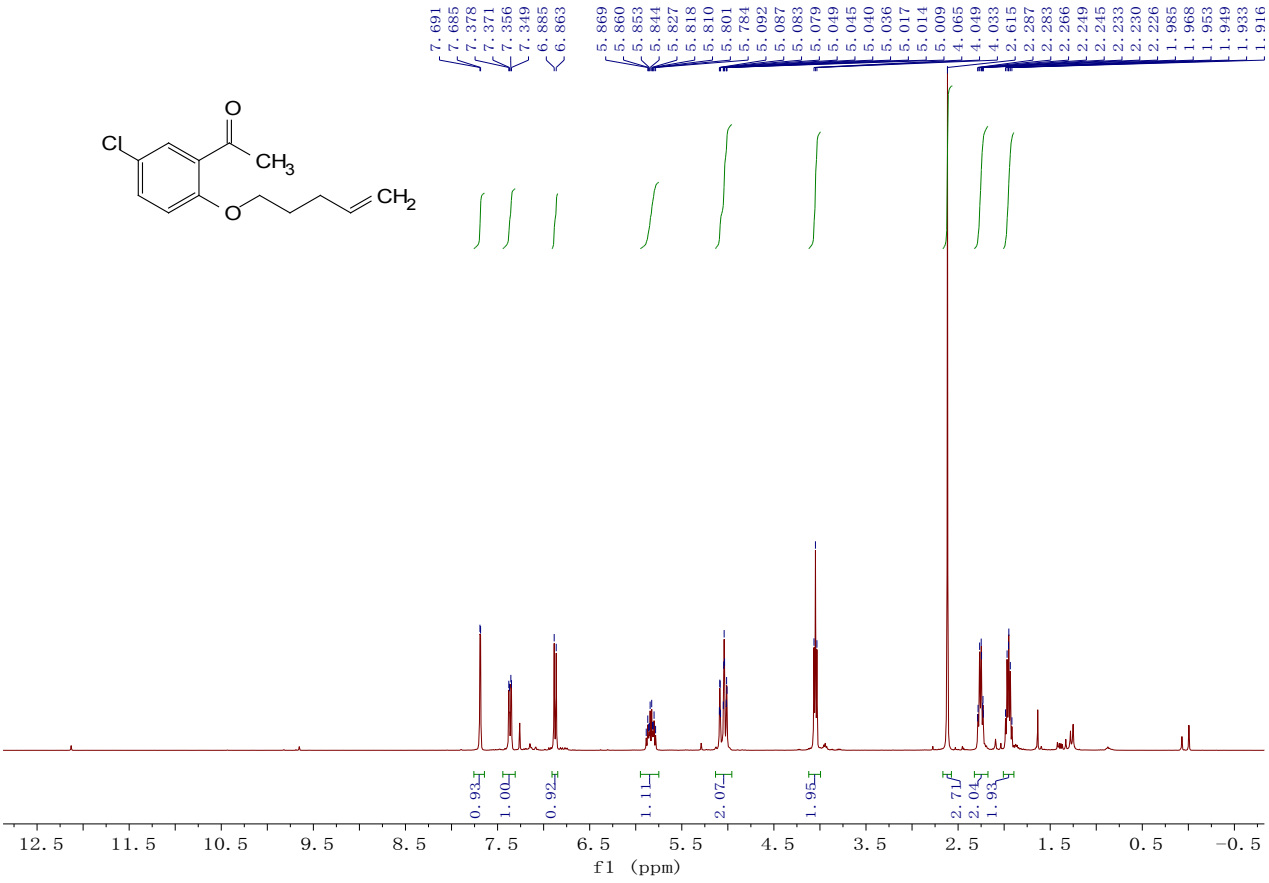


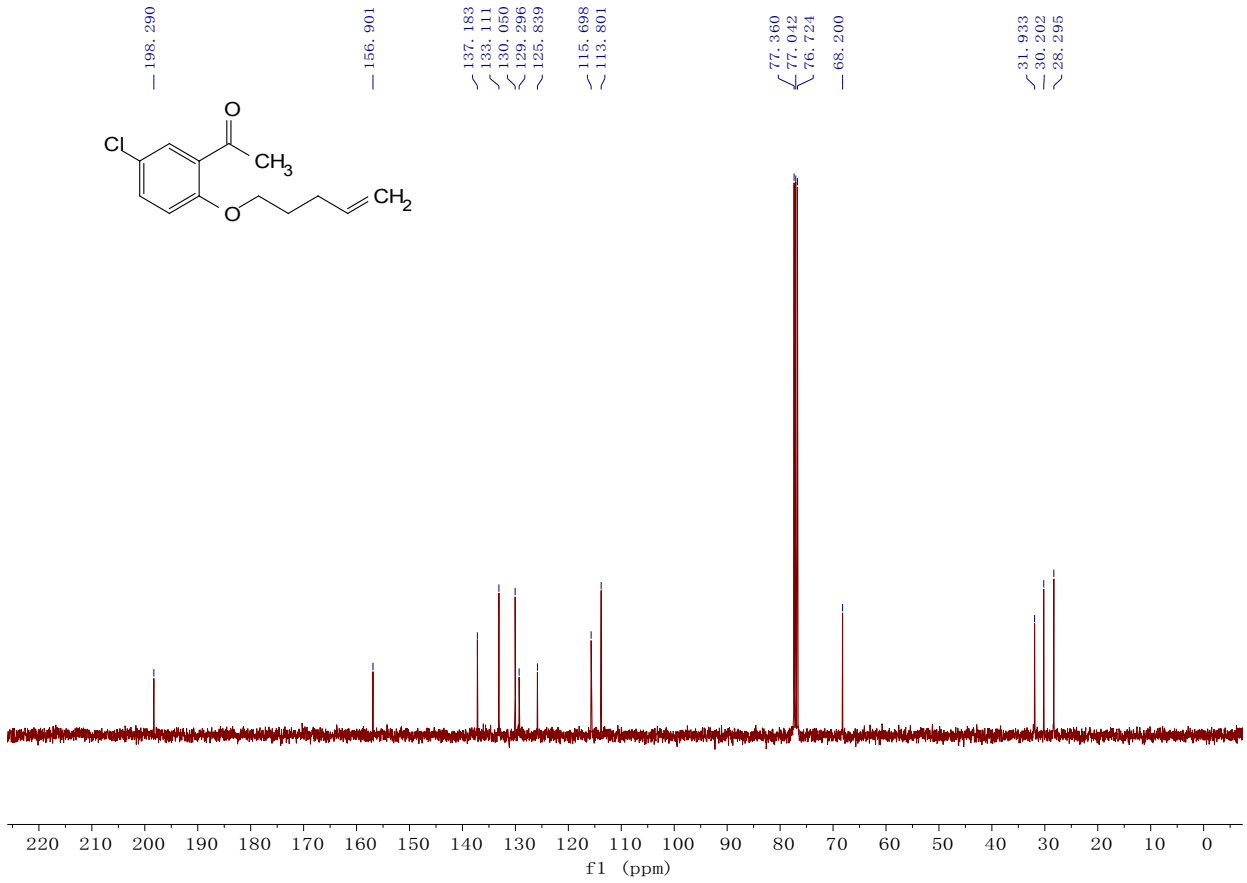
1-(3-((3-Methylbut-2-en-1-yl)oxy)phenyl)ethan-1-one (34)



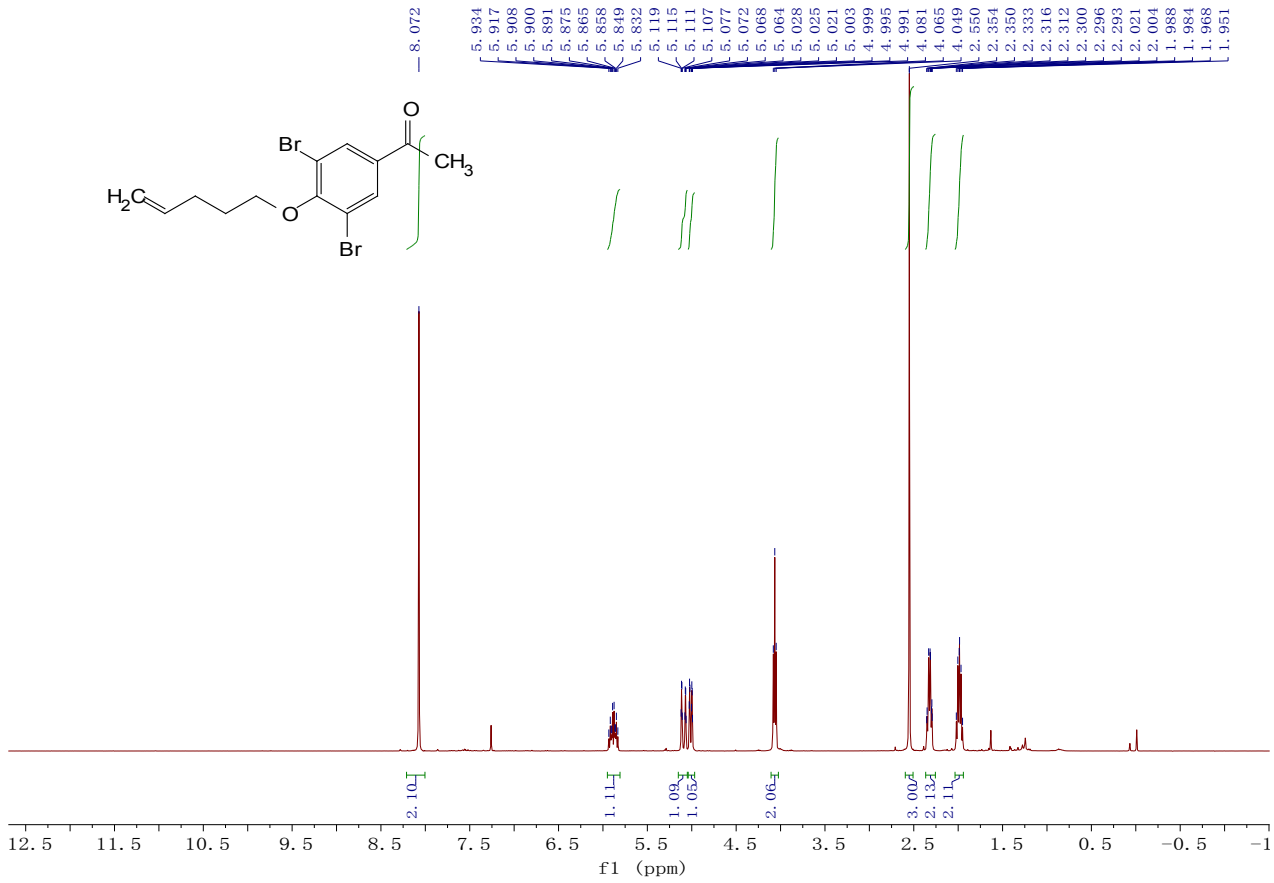


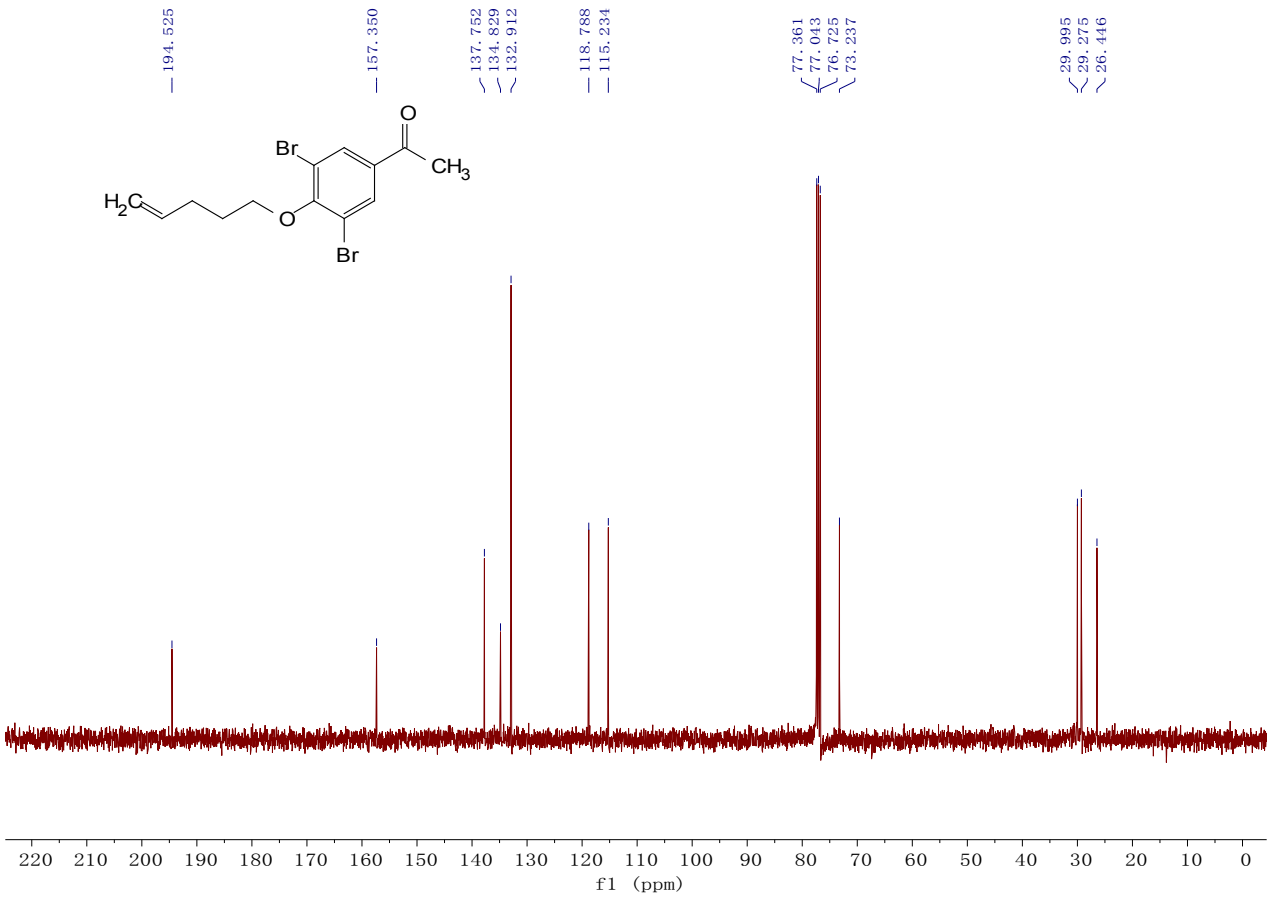
1-(5-Chloro-2-(pent-4-en-1-yloxy)phenyl)ethan-1-one (35)



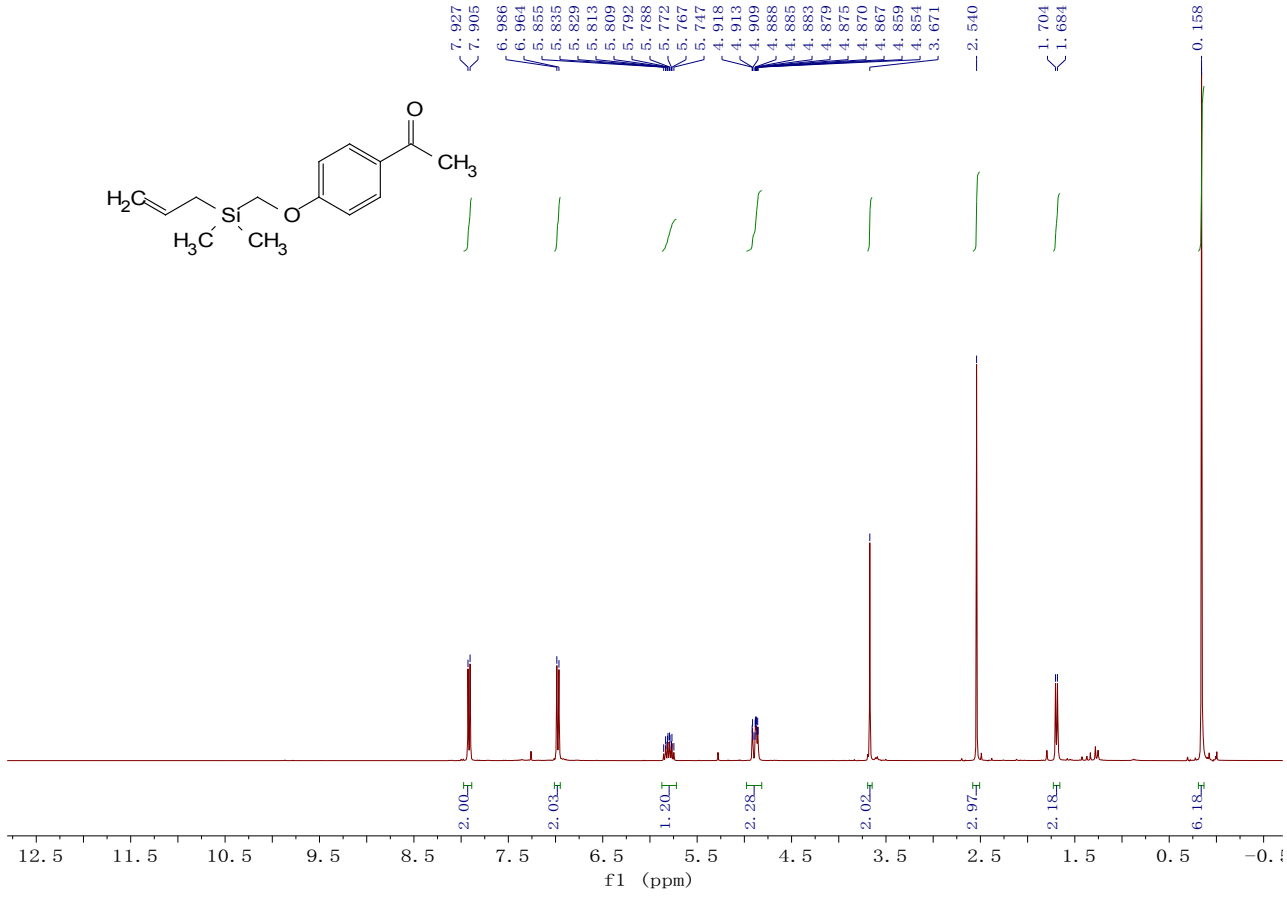


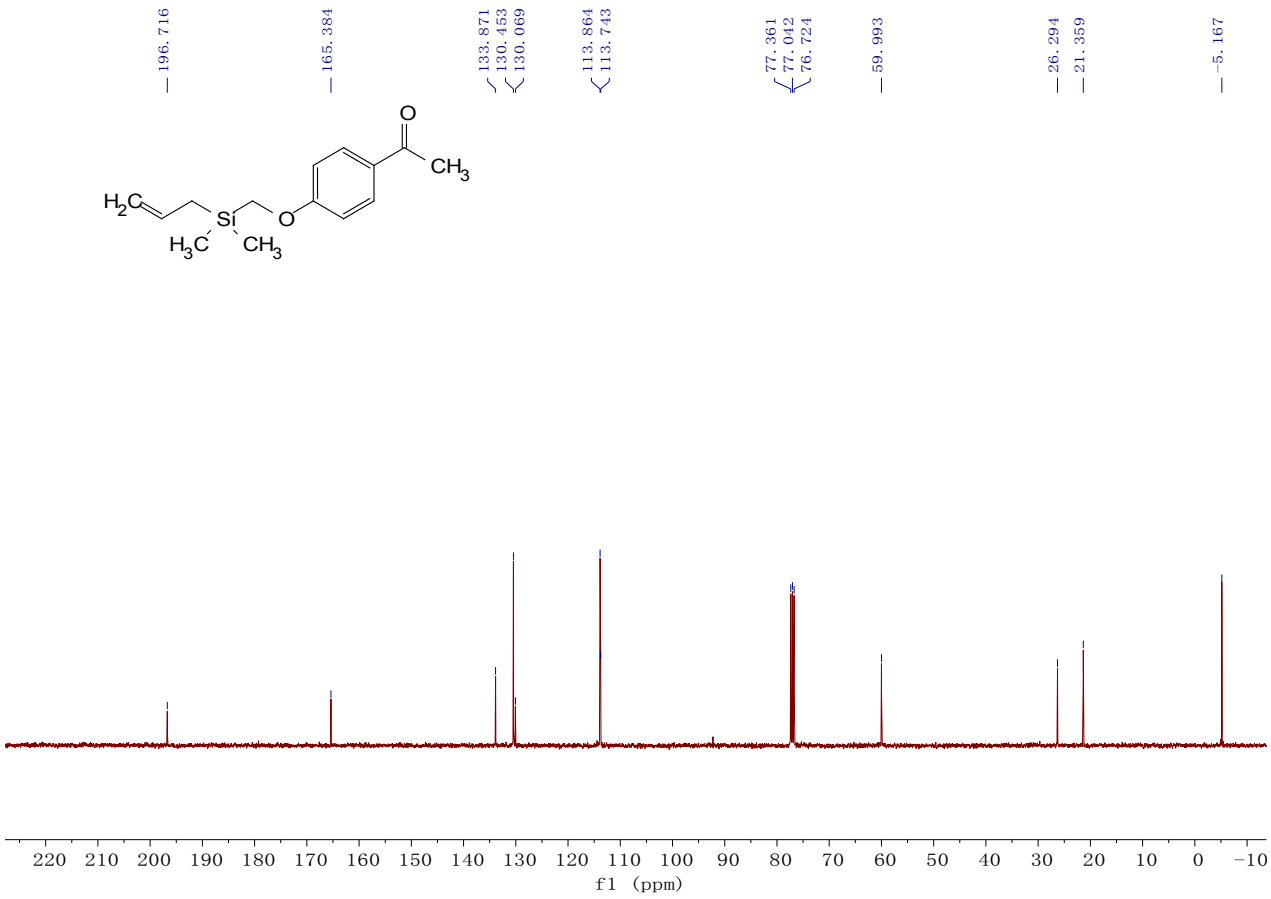
1-(3,5-Dibromo-4-(pent-4-en-1-yloxy)phenyl)ethan-1-one (36)



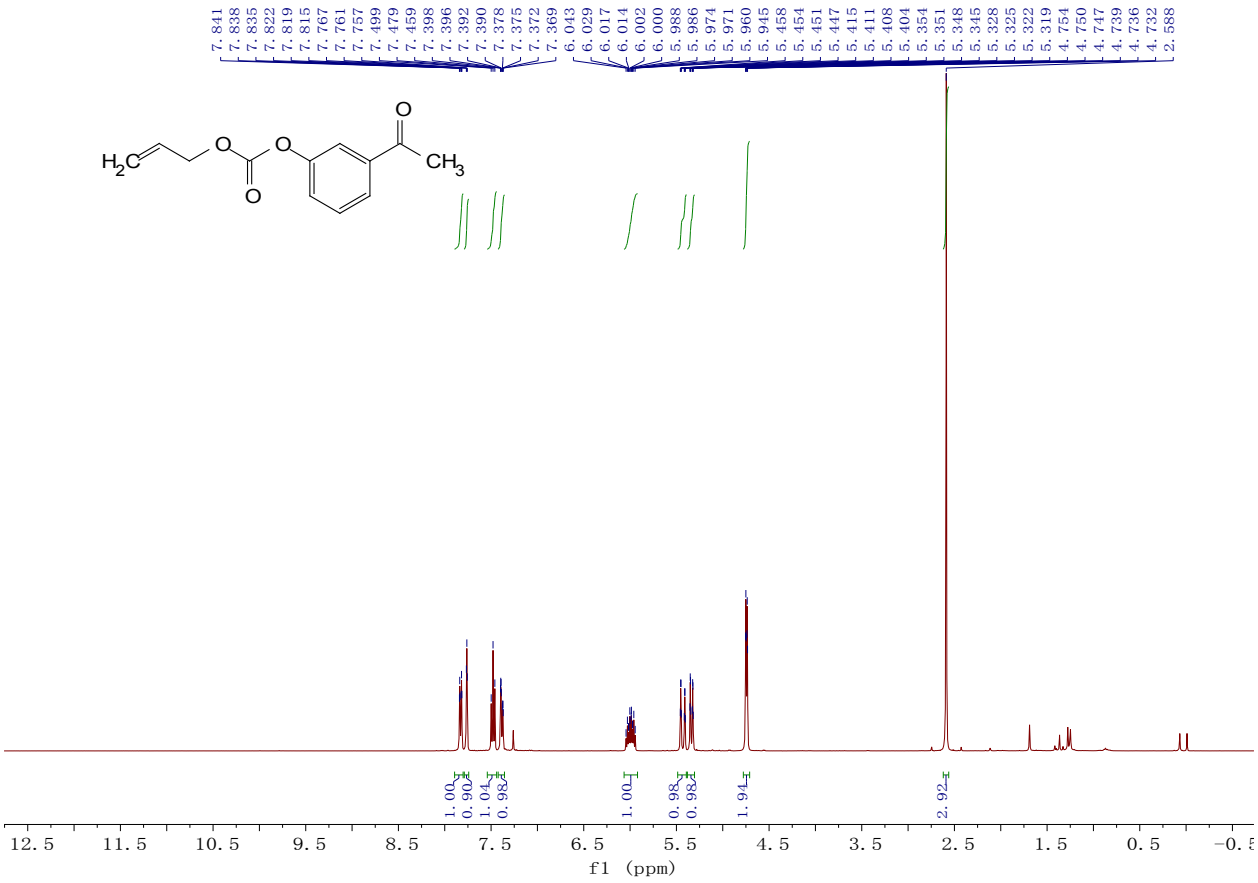


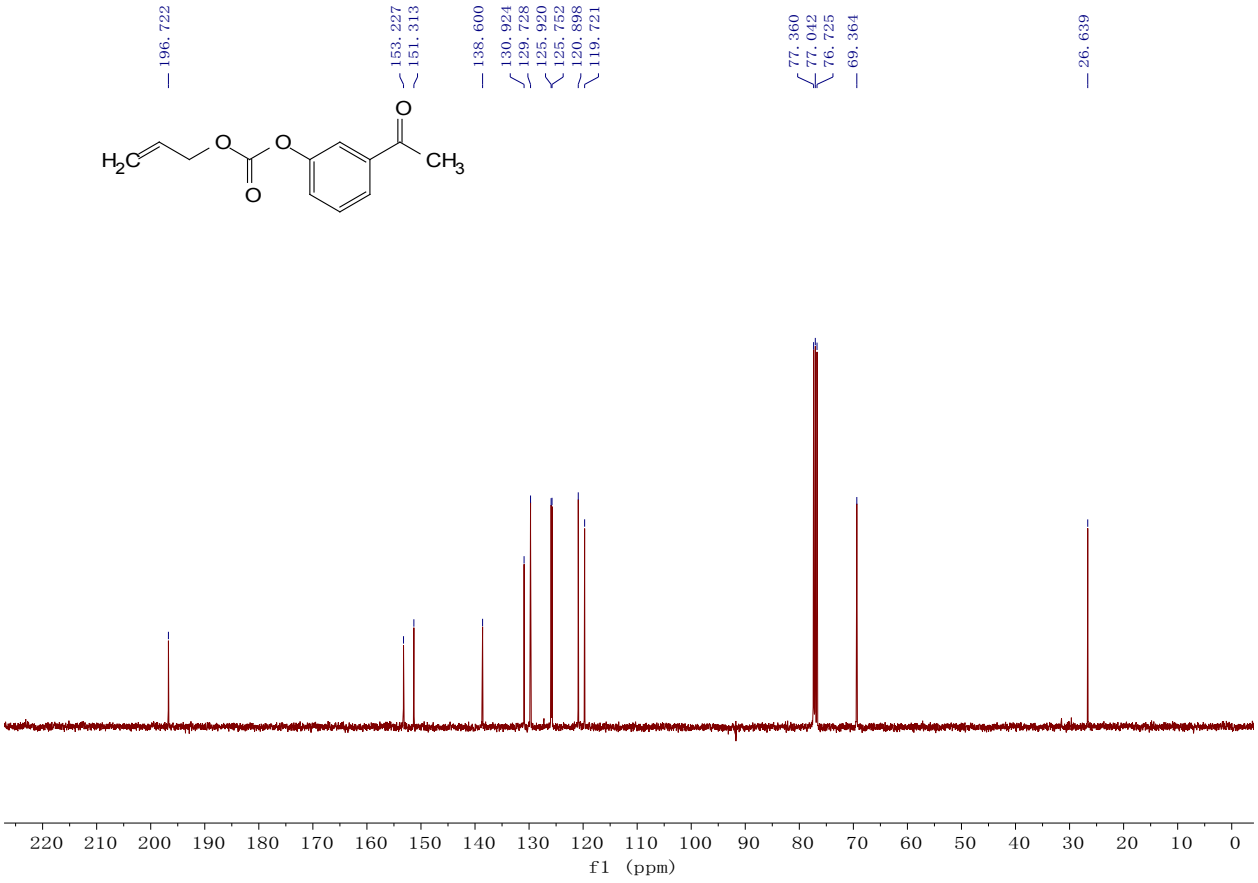
1-(4-((Allyldimethylsilyl)methoxy)phenyl)ethan-1-one (37)



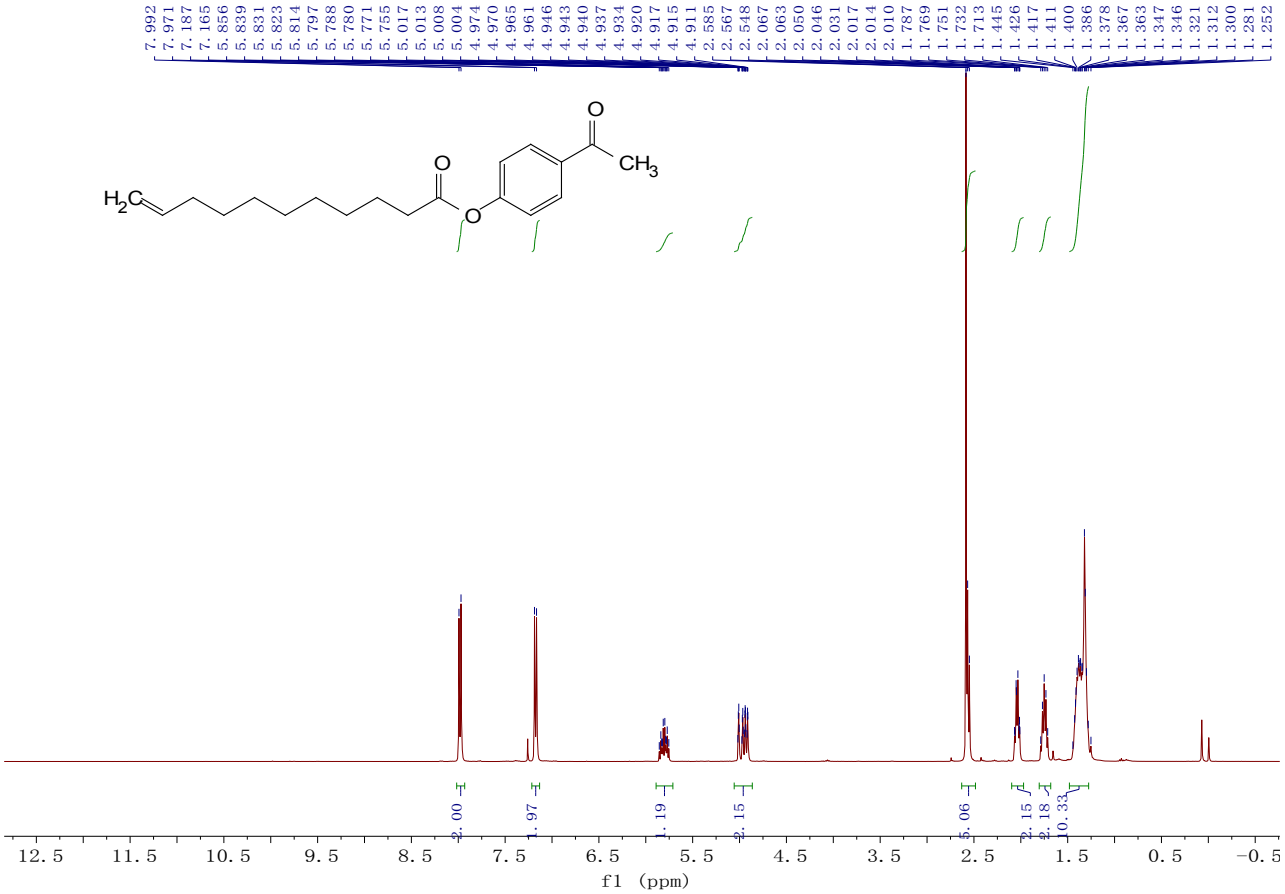


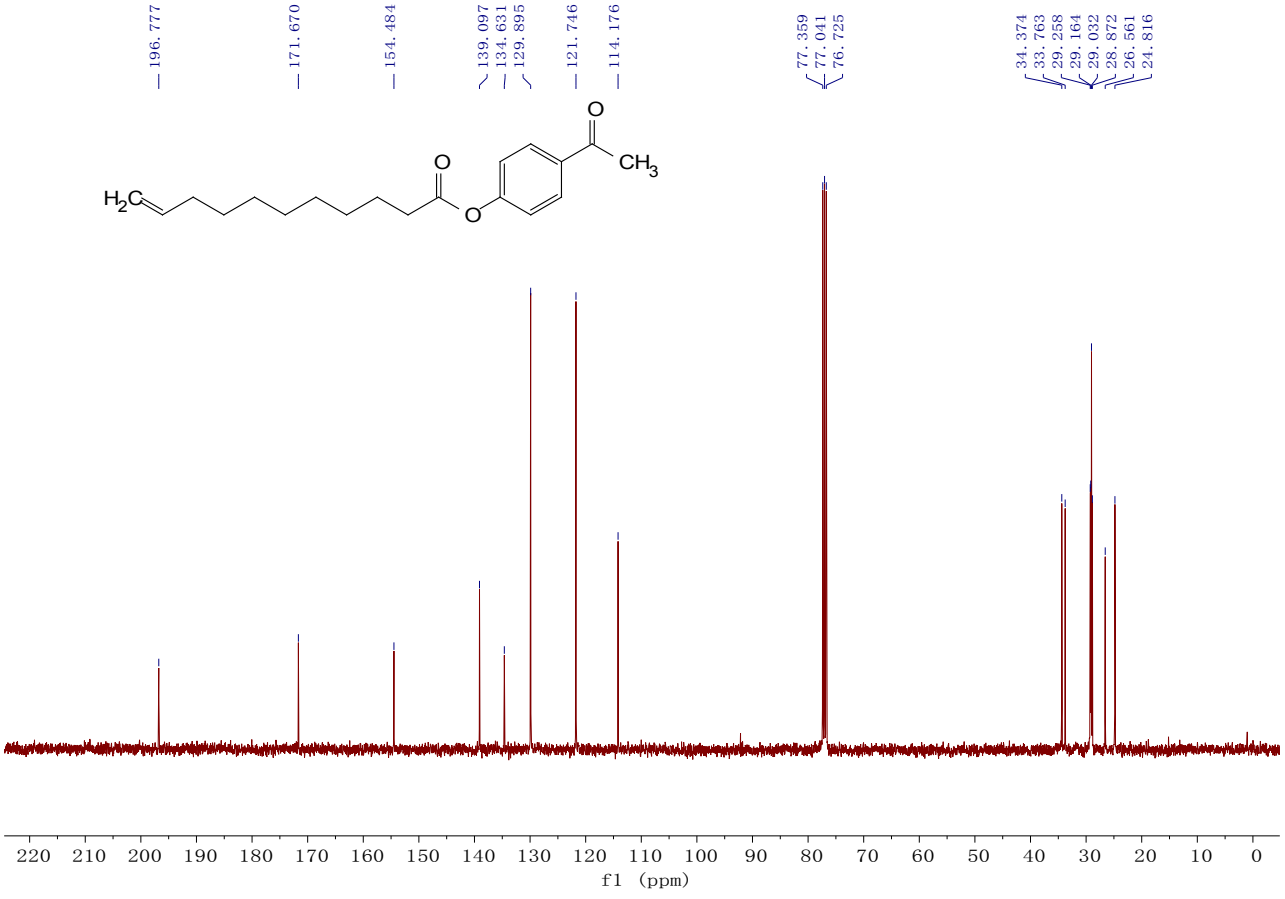
3-Acetylphenyl allyl carbonate (38)


7.841
7.838
7.835
7.822
7.819
7.815
7.767
7.761
7.757
7.499
7.479
7.459
7.398
7.396
7.392
7.390
7.378
7.375
7.372
7.369
6.043
6.029
6.017
6.014
6.002
6.000
5.988
5.986
5.974
5.971
5.960
5.945
5.458
5.454
5.451
5.447
5.415
5.411
5.408
5.404
5.354
5.351
5.348
5.345
5.328
5.325
5.322
5.319
4.754
4.750
4.747
4.739
4.736
4.732
2.588
O
O
O
H2C
CH3
1.00
0.90
1.04
0.98
1.00
0.98
0.98
1.94
2.92
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

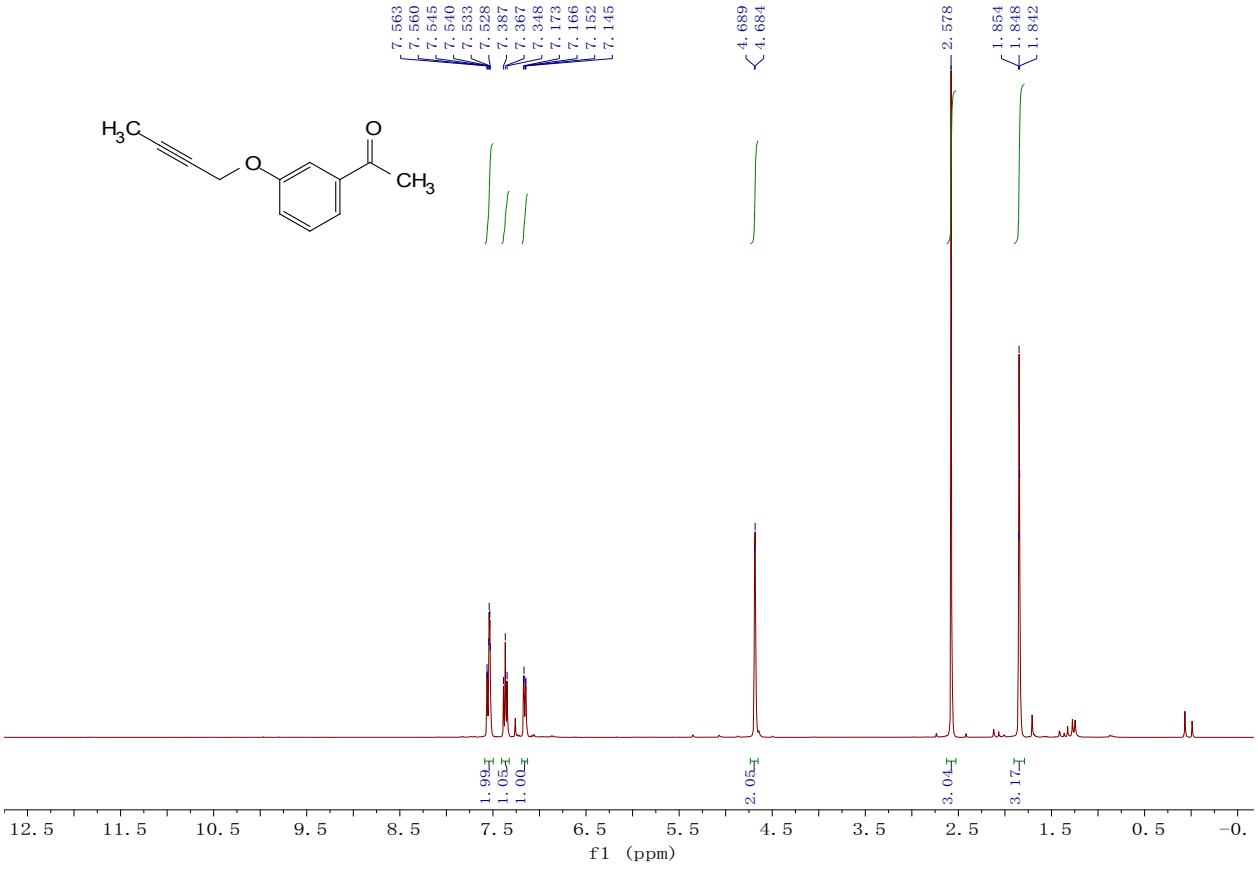

196.722
153.227
151.313
138.600
130.924
129.728
125.920
125.752
120.898
119.721
77.360
77.042
76.725
69.364
26.639
O
O
O
H2C
CH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

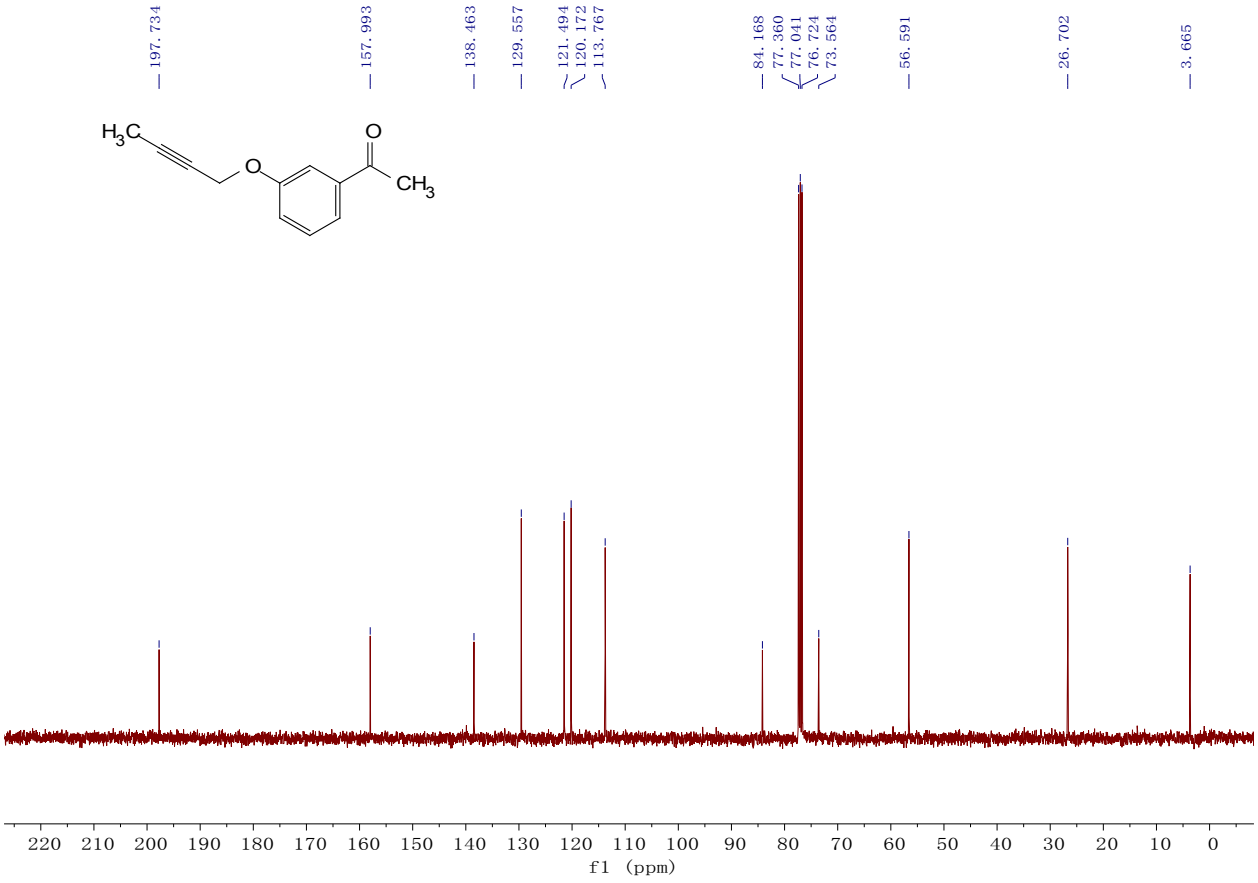
4-Acetylphenyl undec-10-enoate (39)



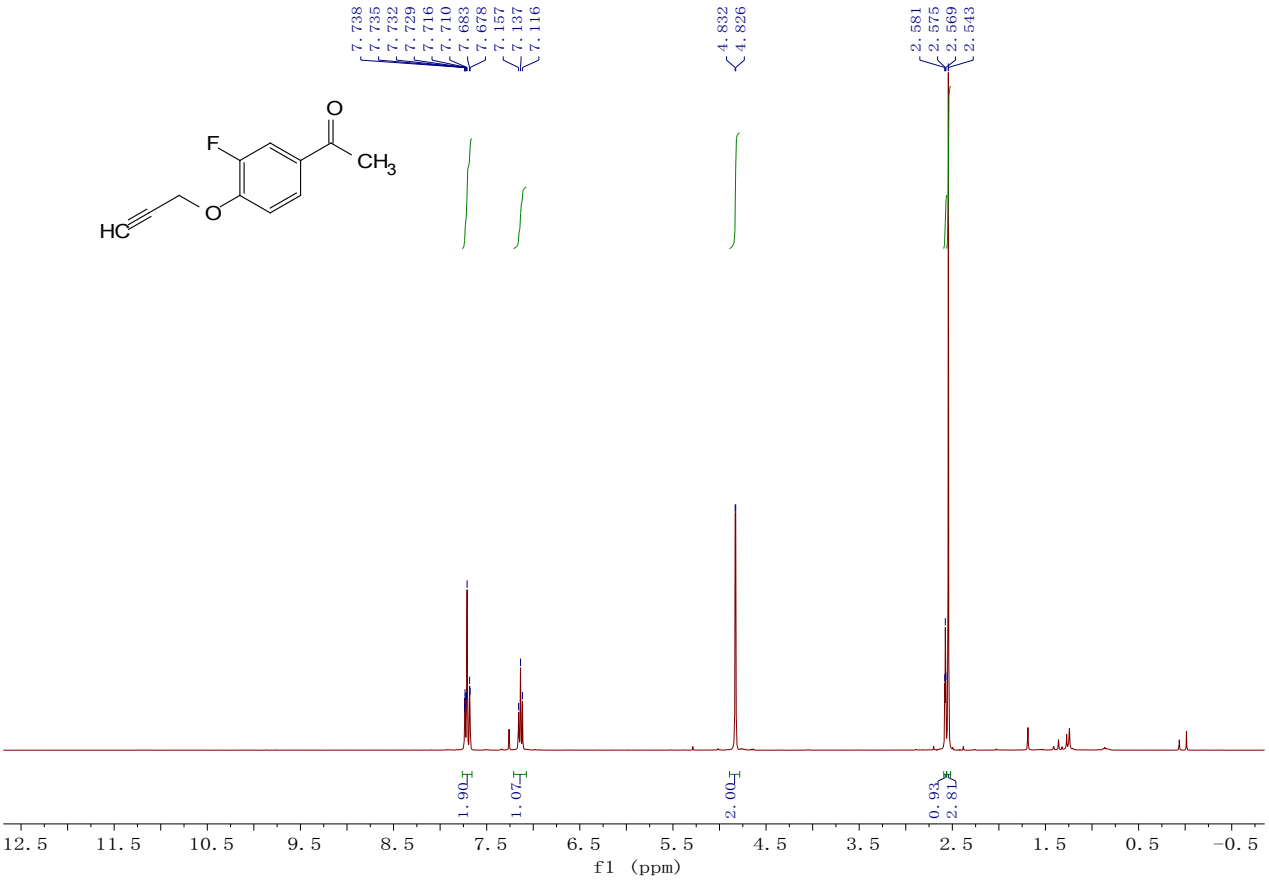


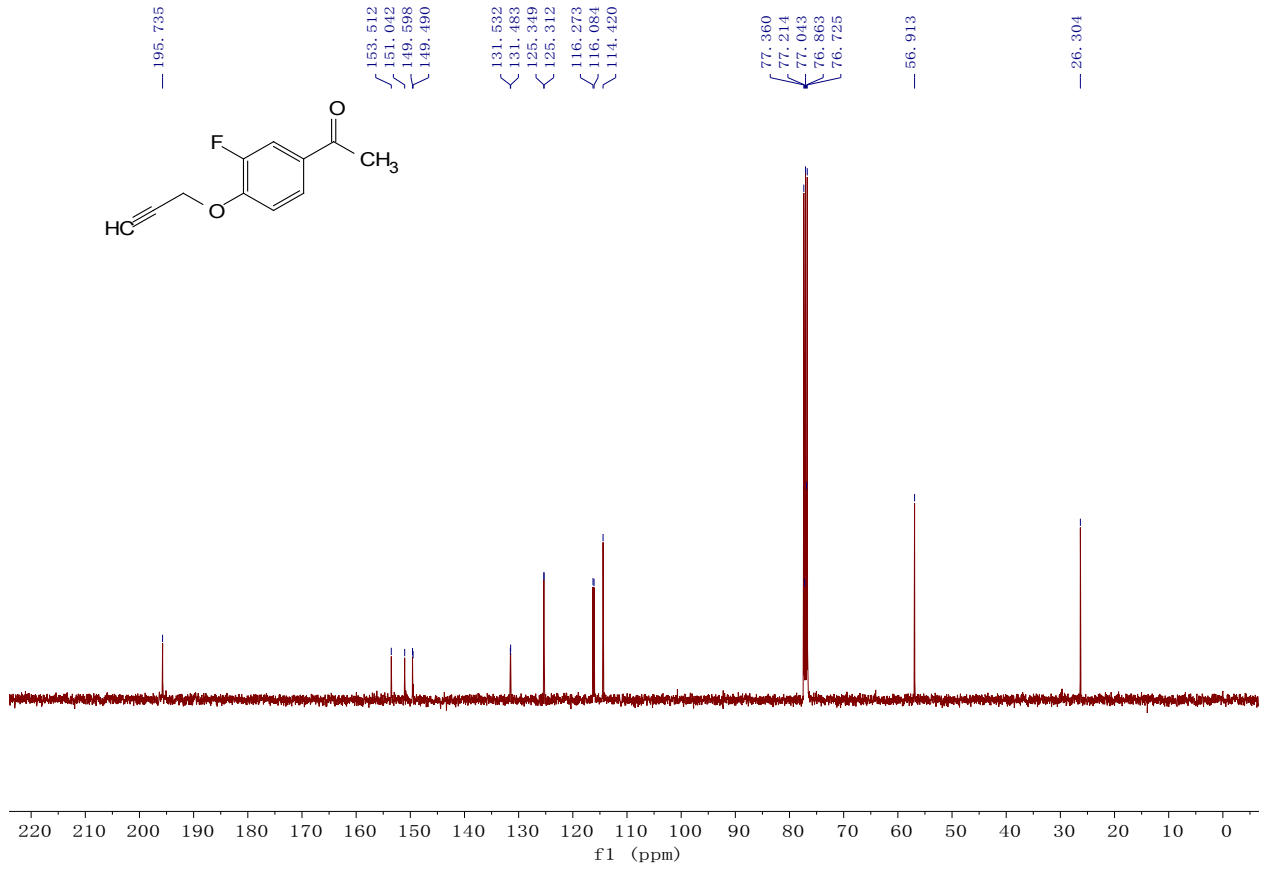
1-(3-(But-2-yn-1-yloxy)phenyl)ethan-1-one (40)



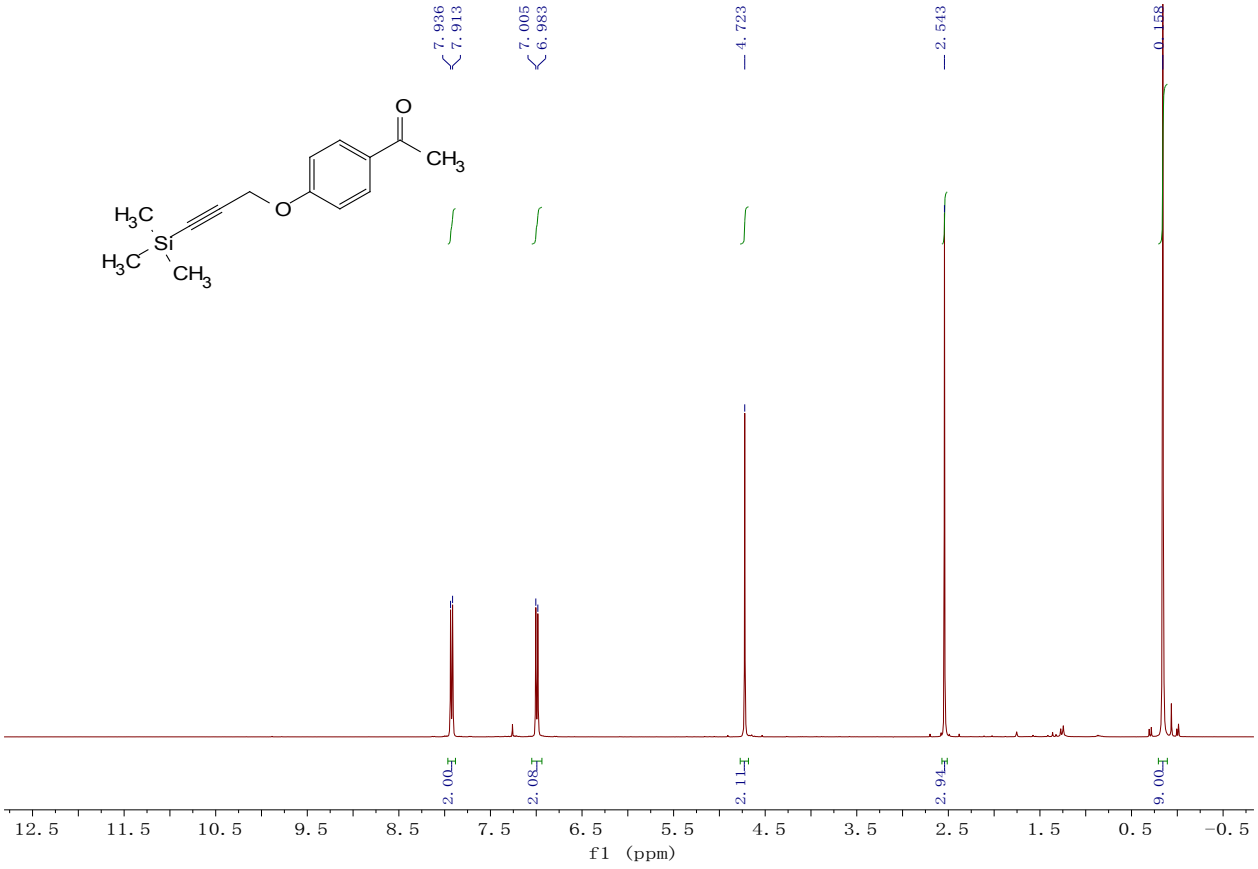


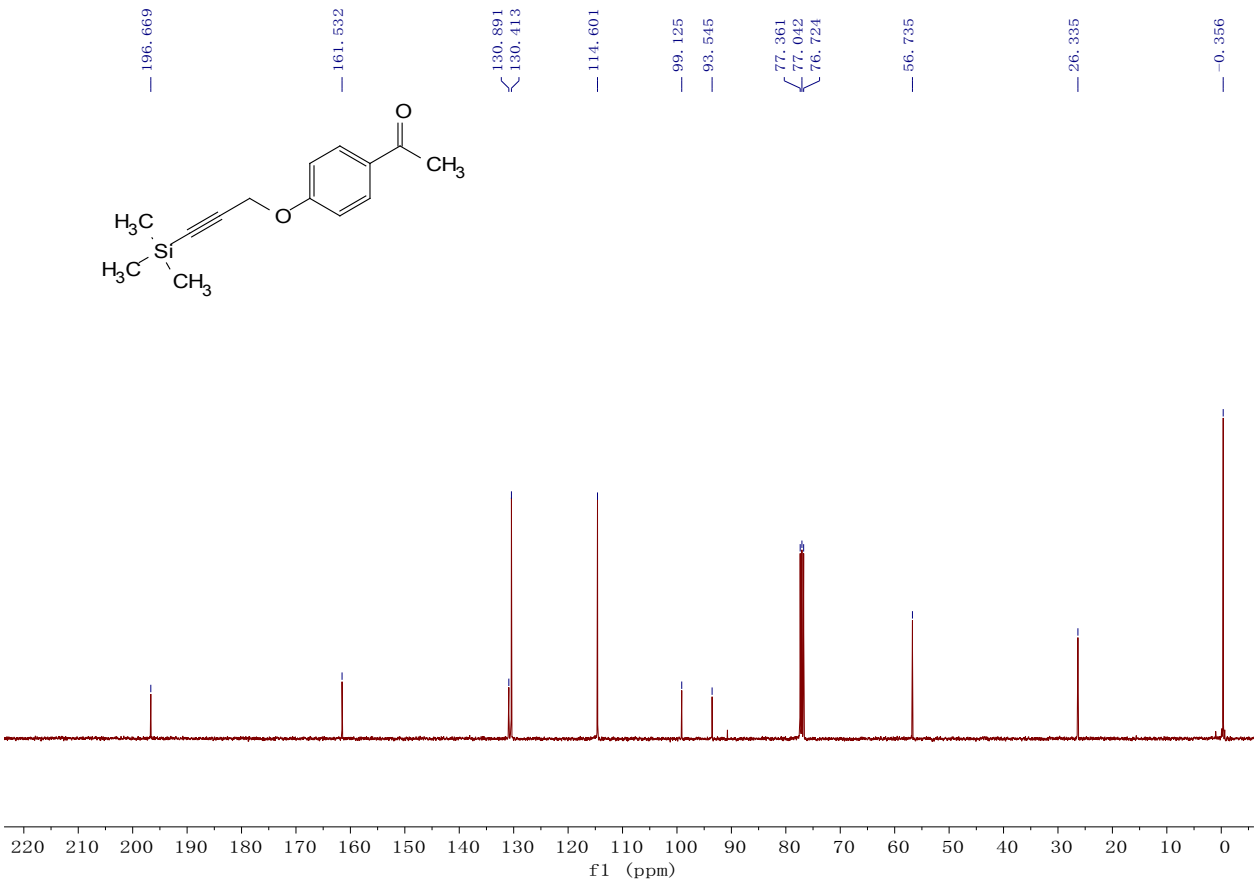
1-(3-Fluoro-4-(prop-2-yn-1-yloxy)phenyl)ethan-1-one (41)



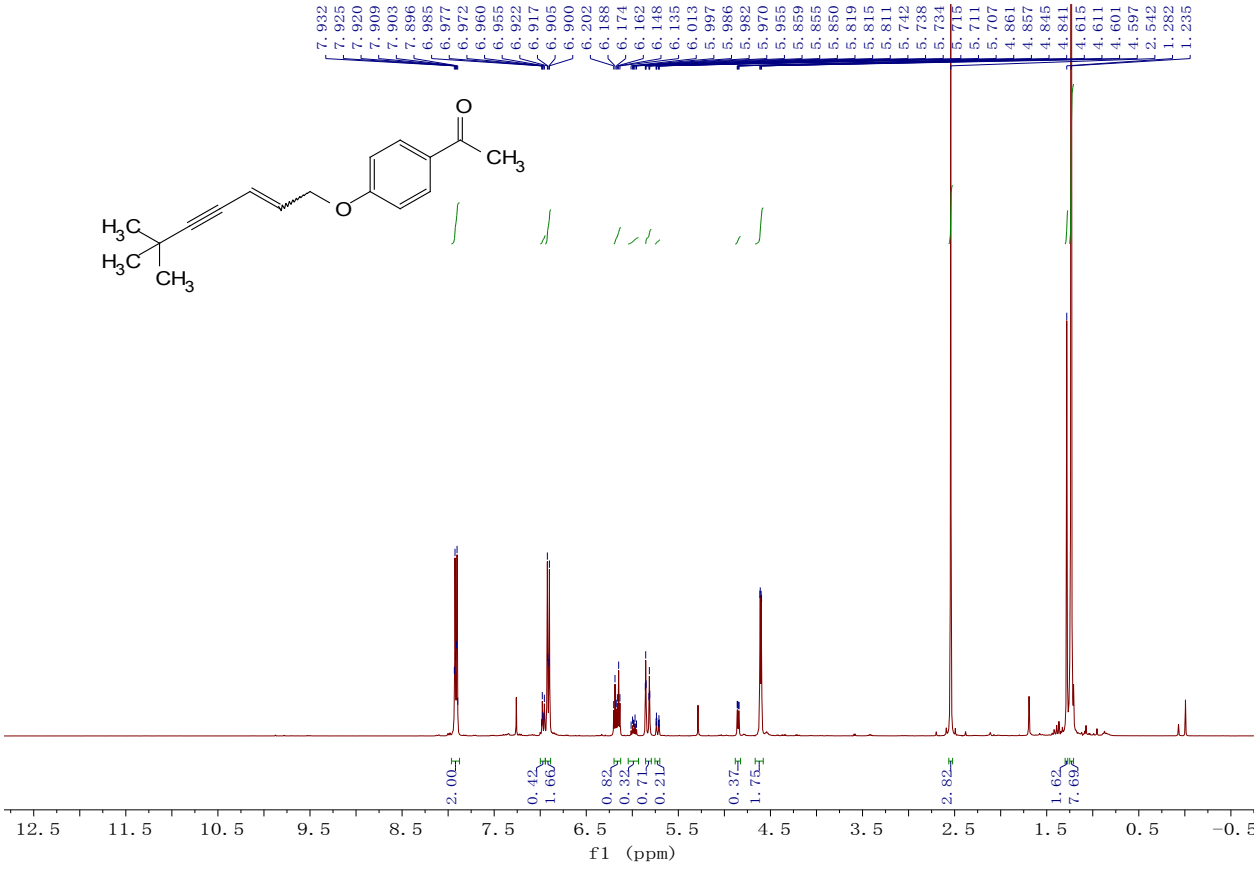


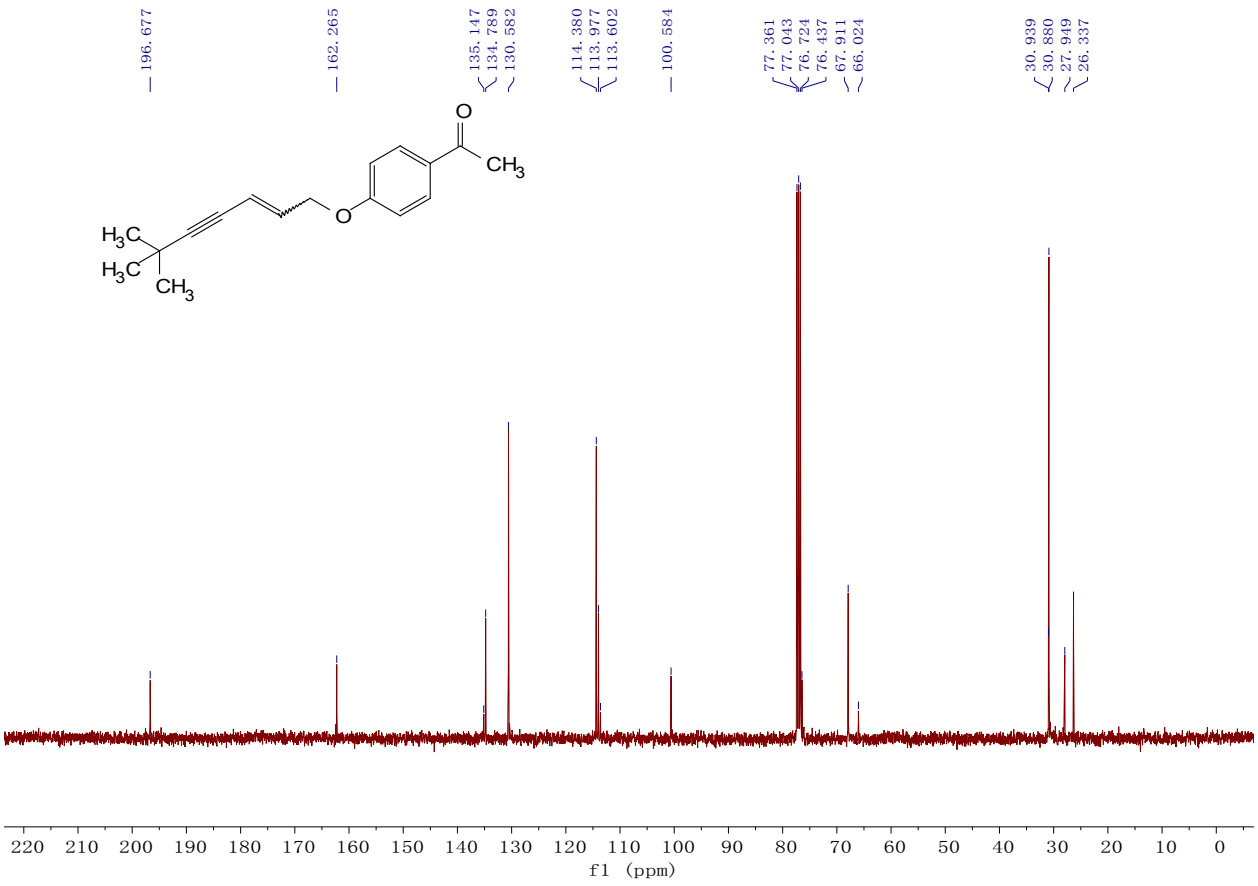
1-(4-((3-(Trimethylsilyl)prop-2-yn-1-yl)oxy)phenyl)ethan-1-one (42)



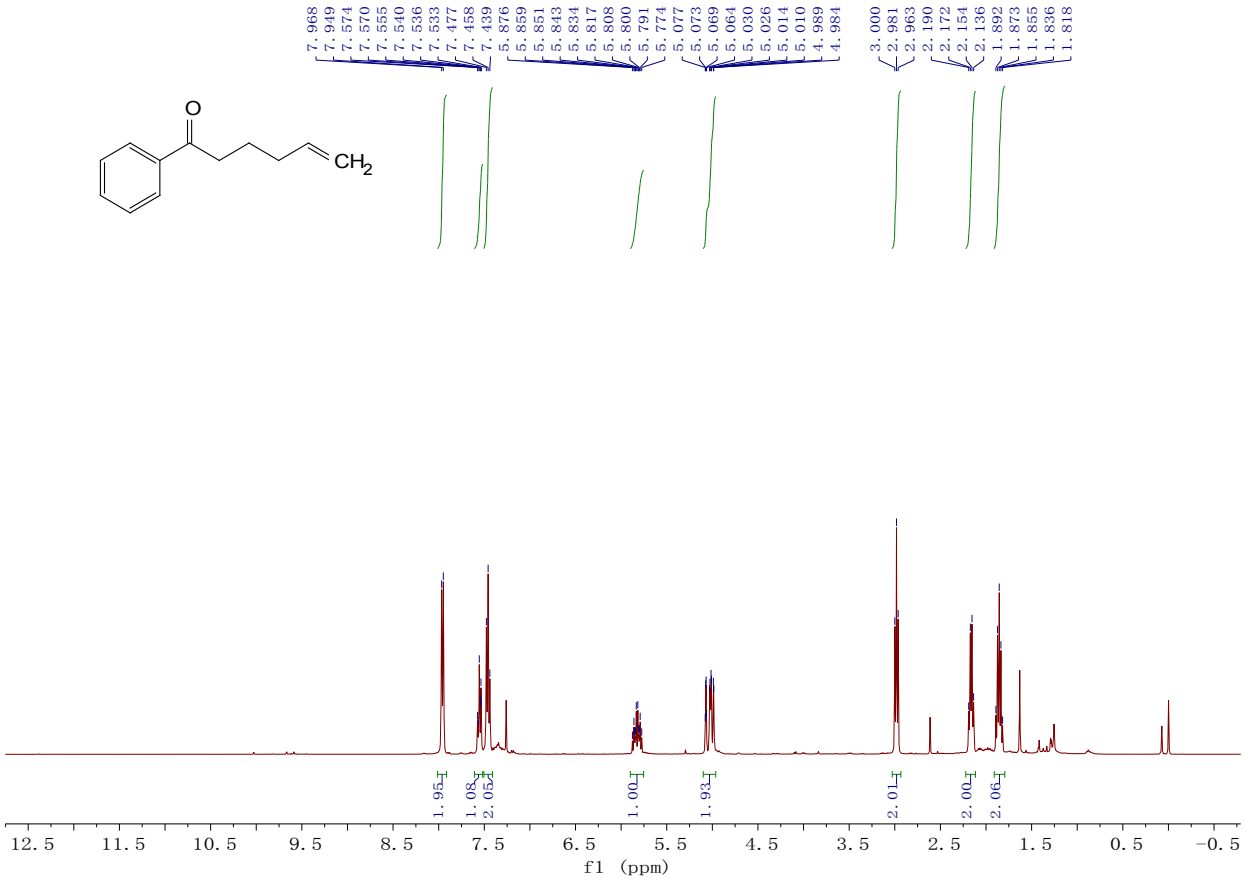


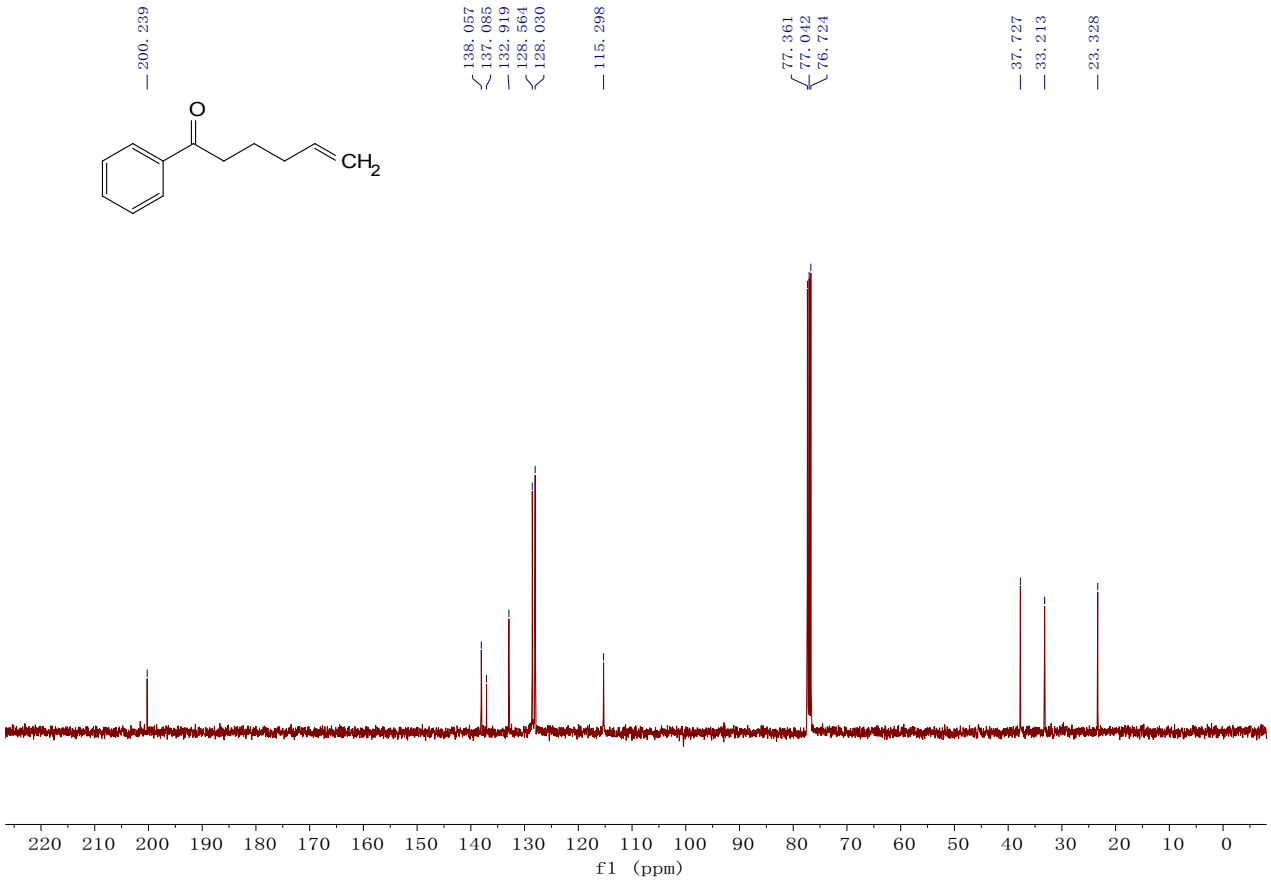
1-(4-((6,6-Dimethylhept-2-en-4-yn-1-yl)oxy)phenyl)ethan-1-one (43)



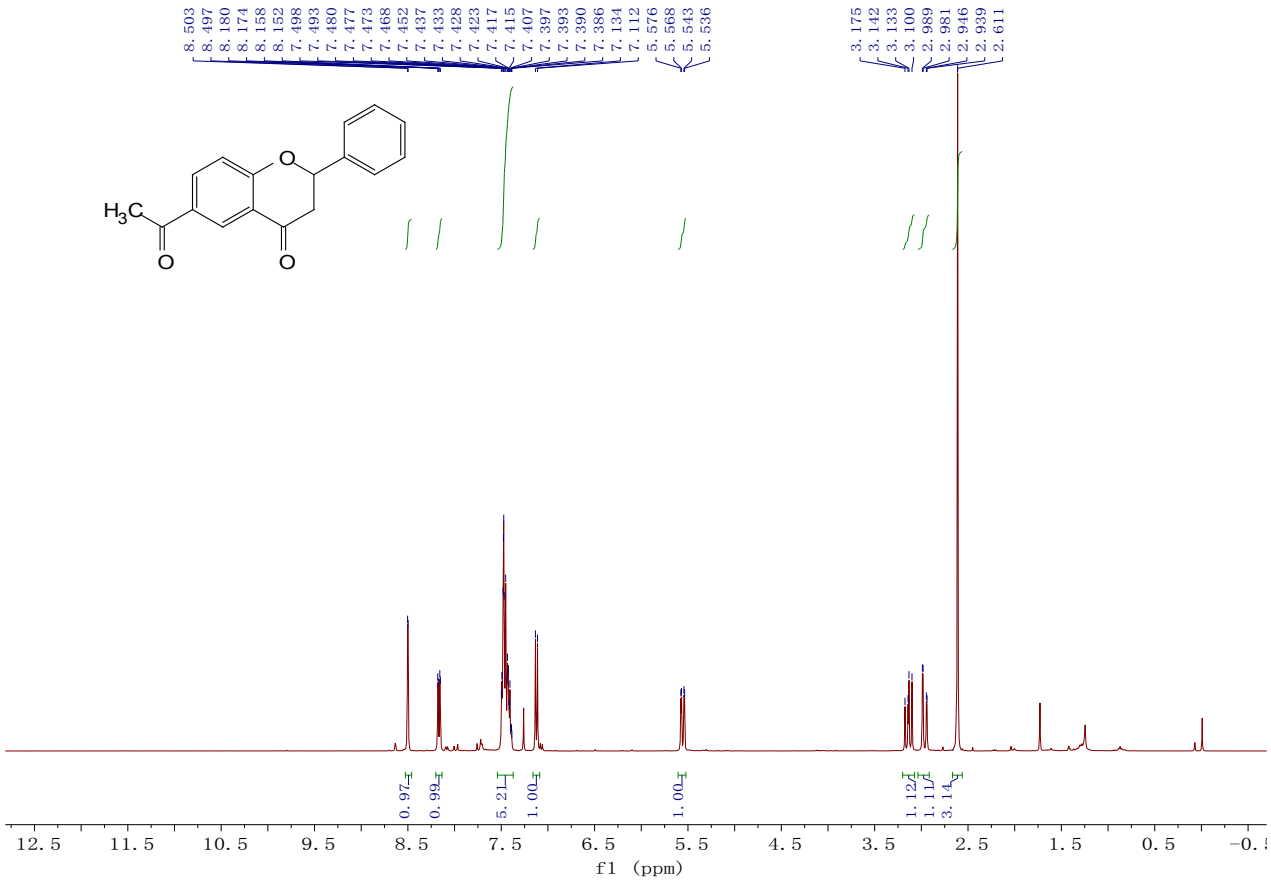


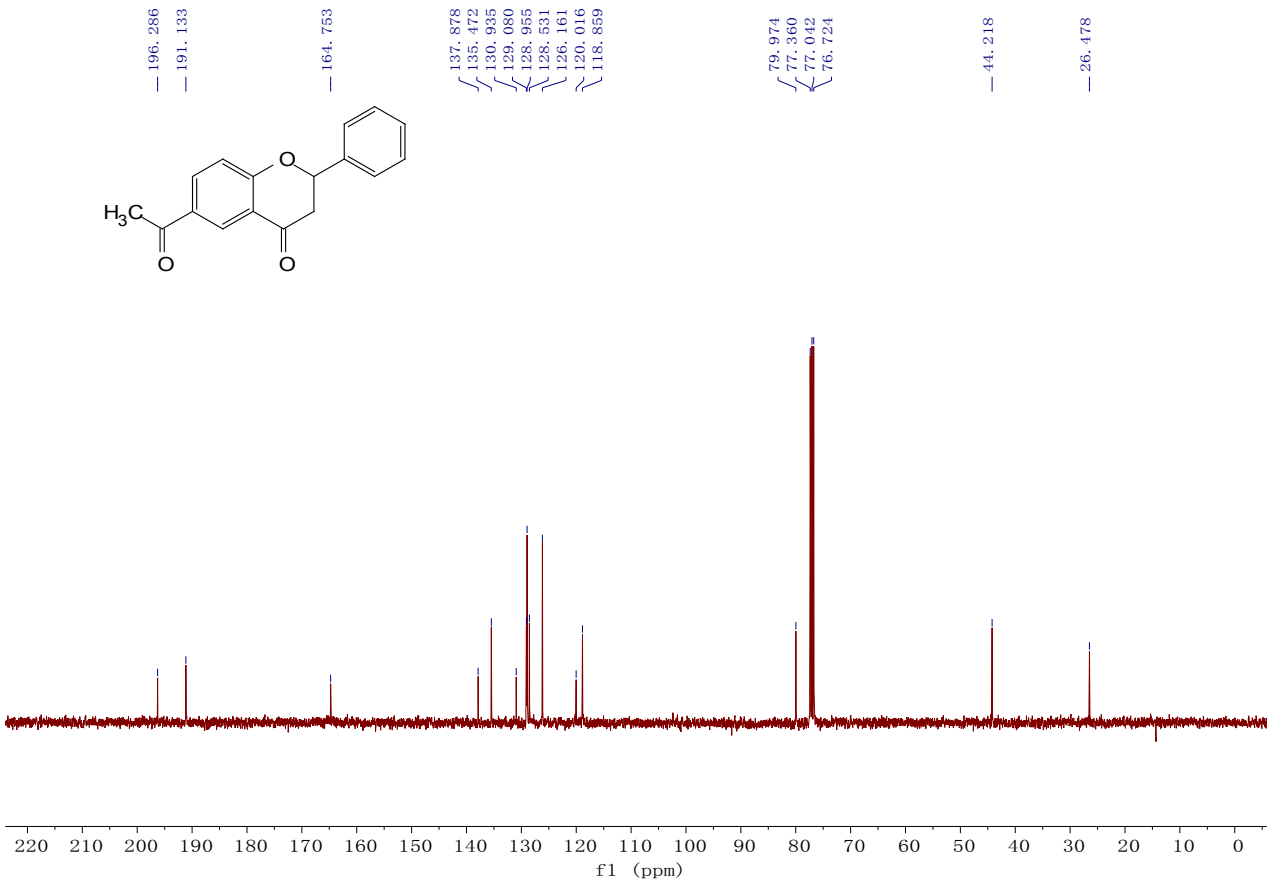
1-Phenylhex-5-en-1-one (44)



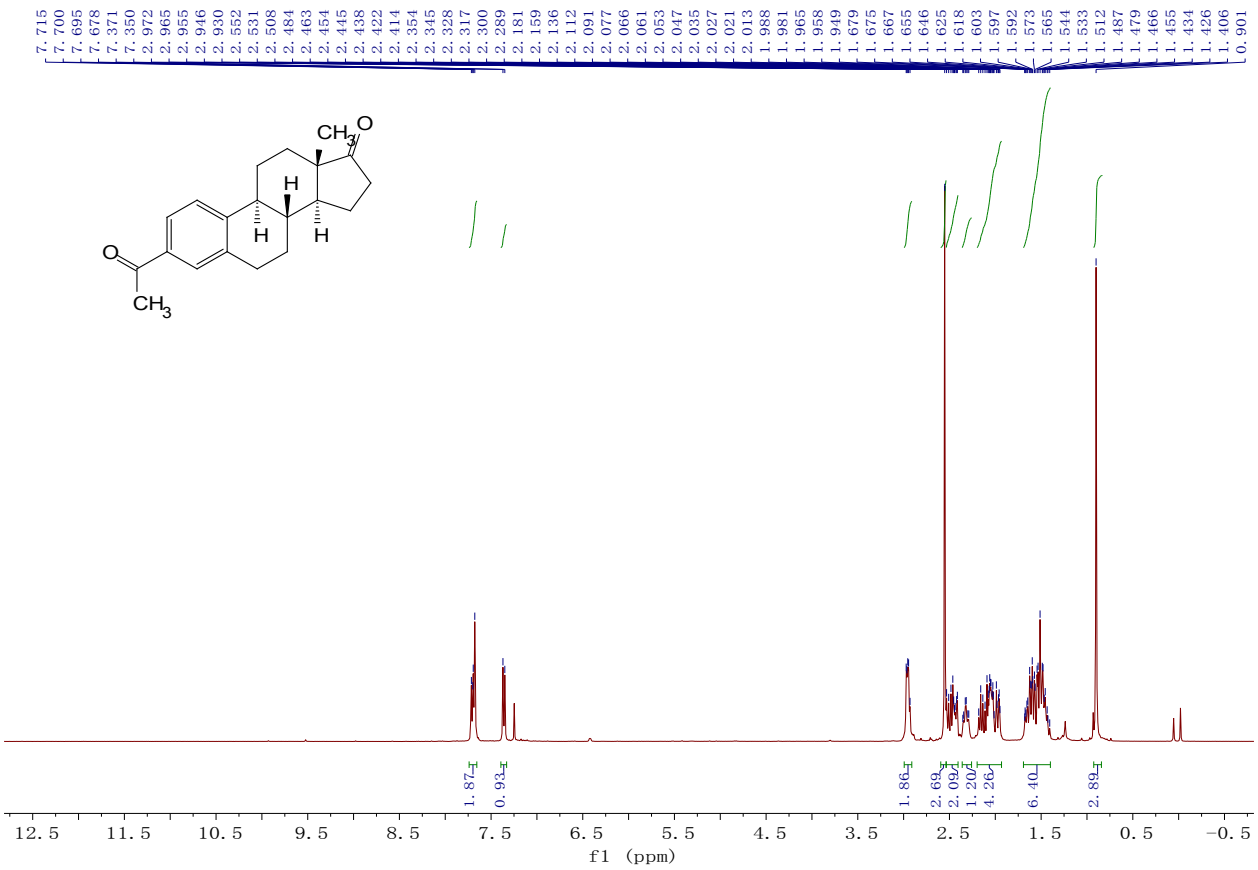


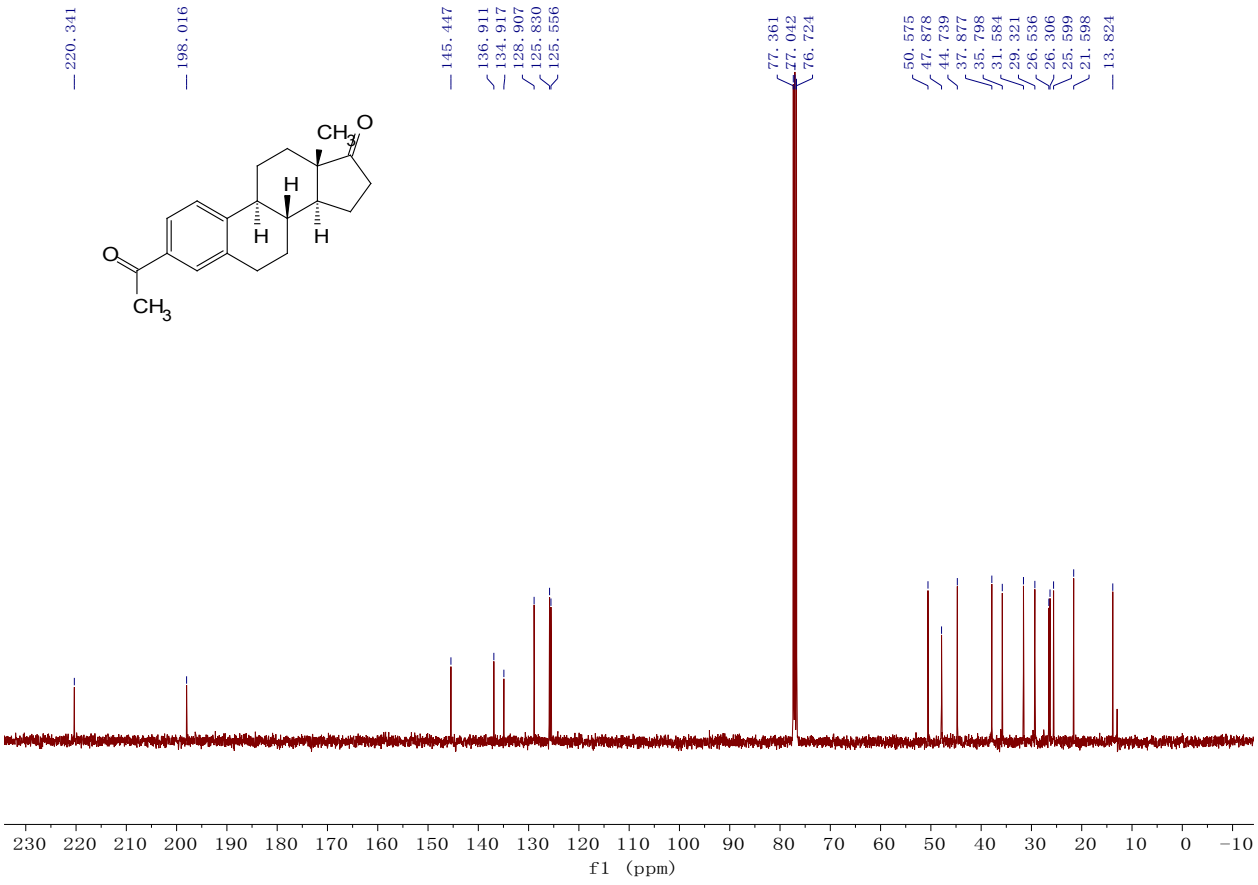
6-Acetyl-2-phenylchroman-4-one (45)



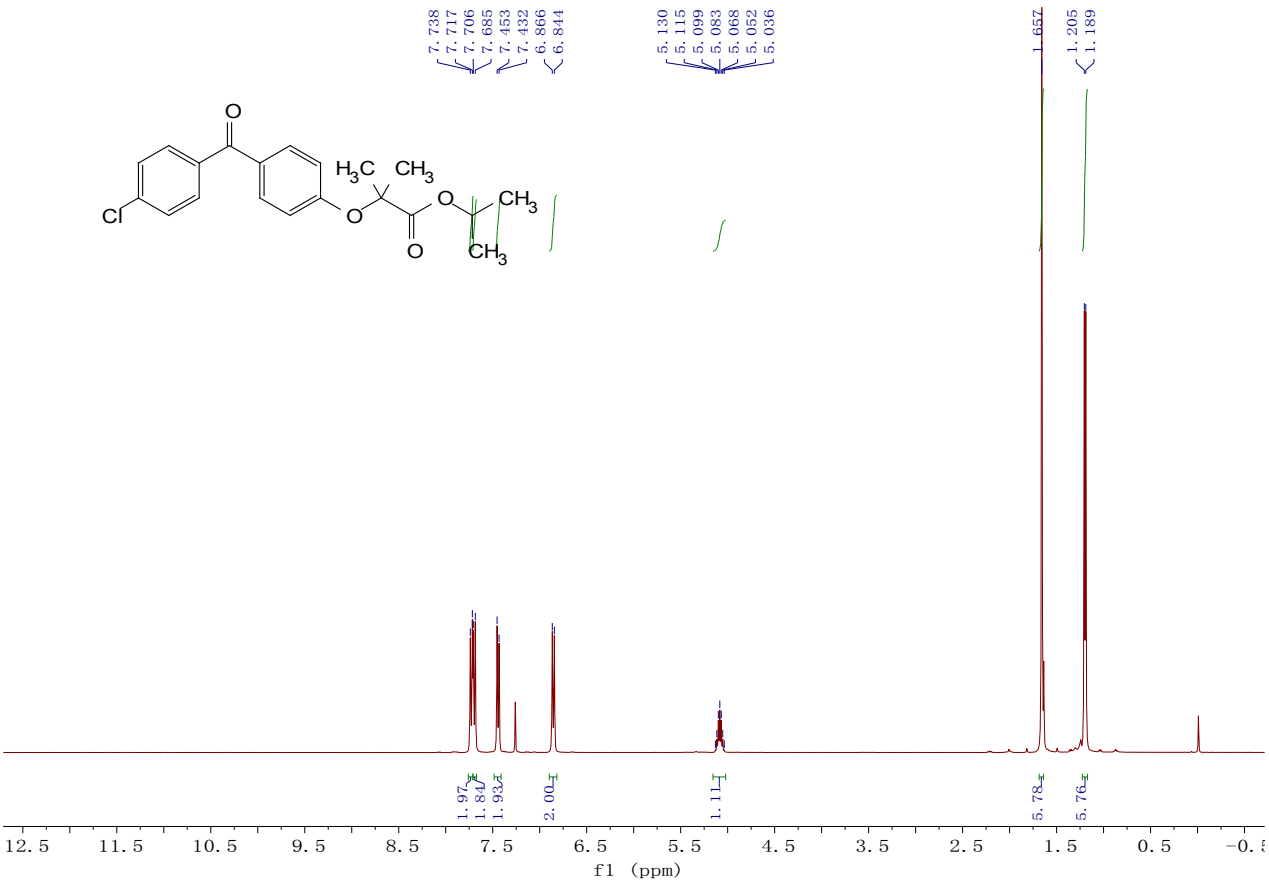


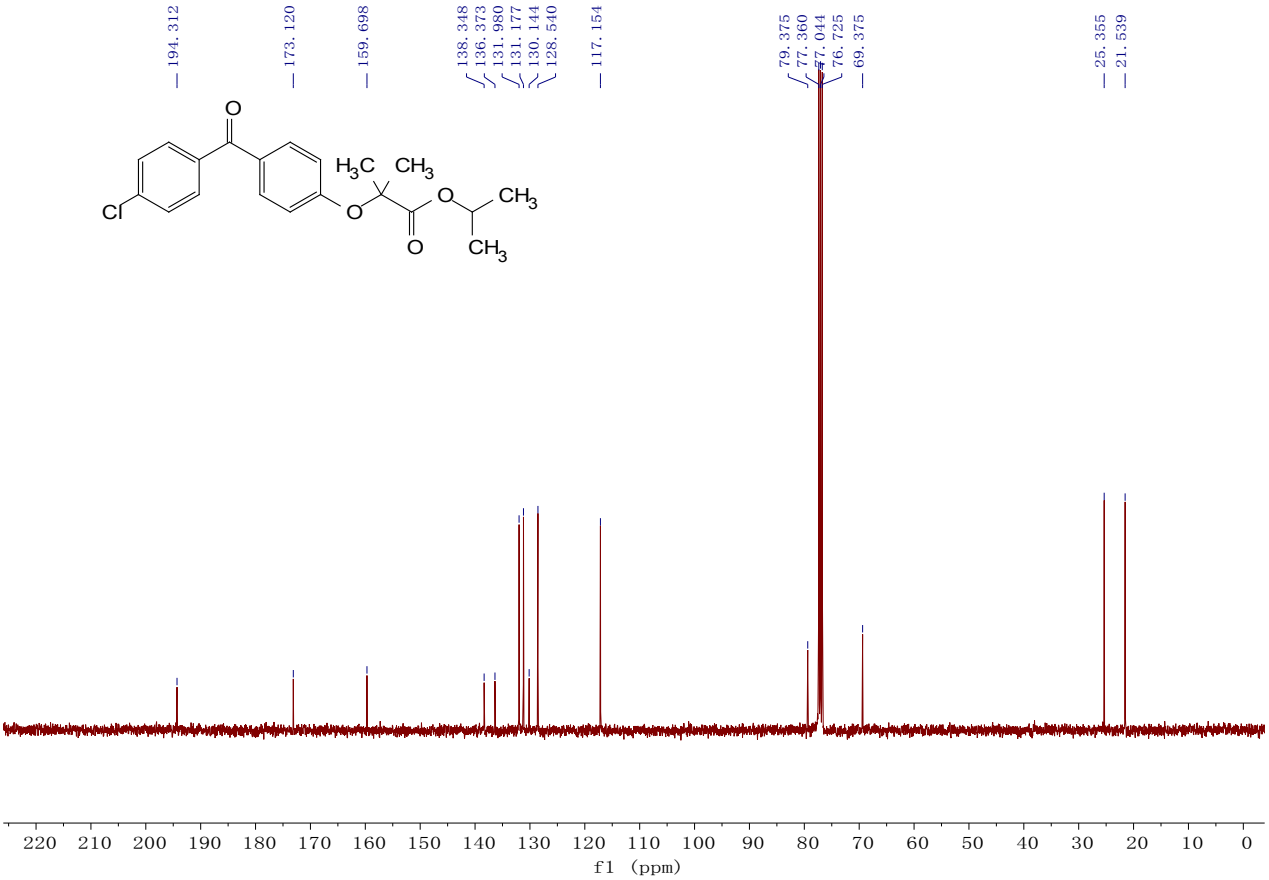
(8R,9S,13S,14S)-3-Acetyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (46)



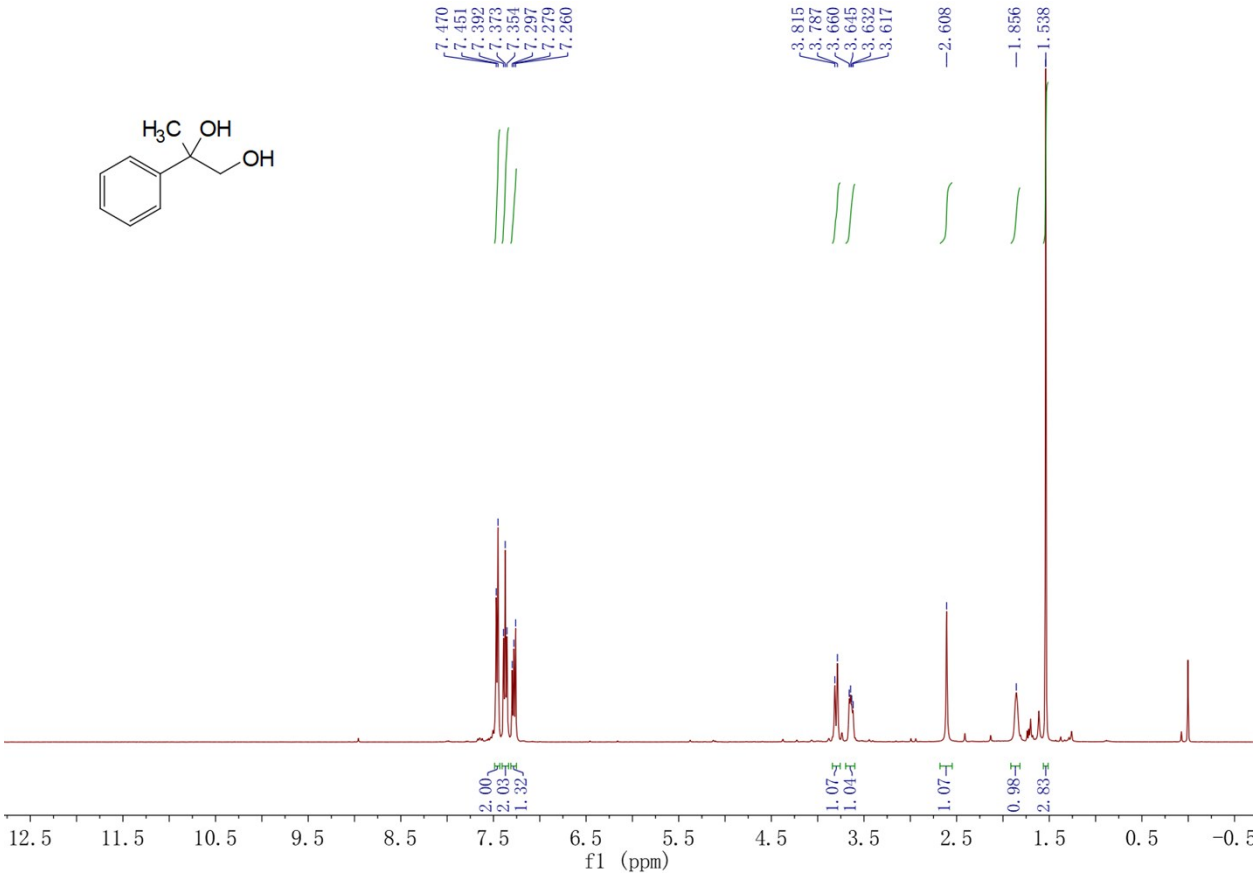


Isopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (47)

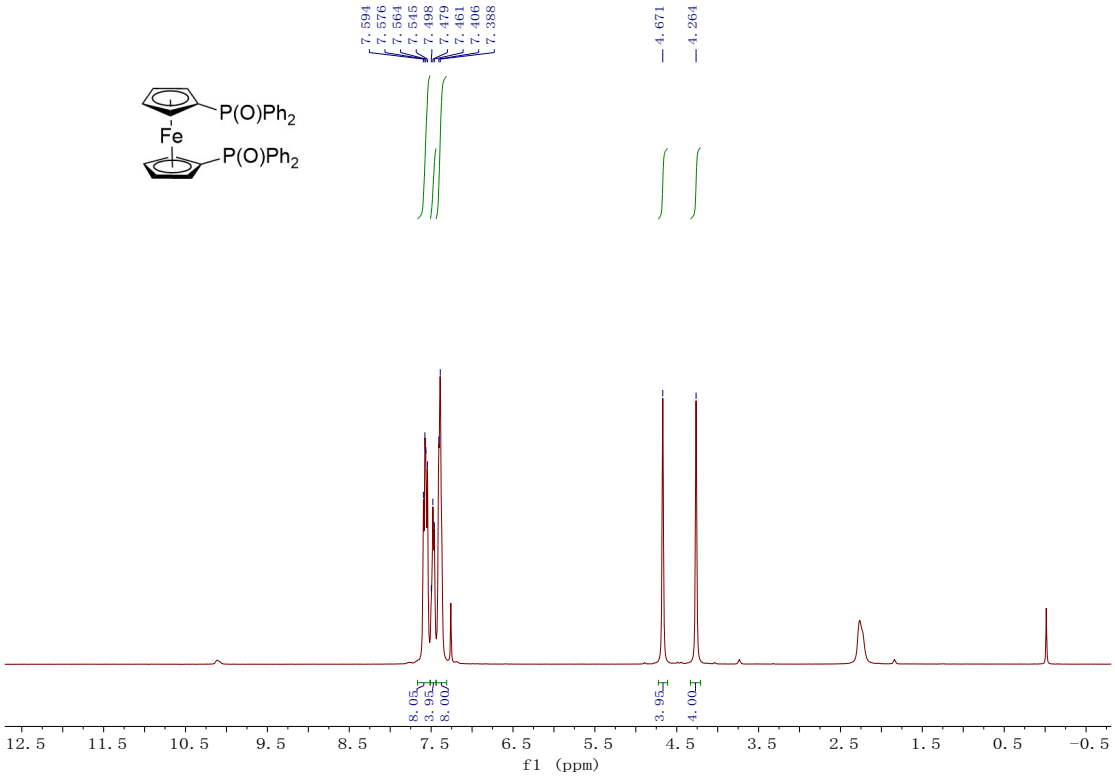

7.738
7.717
7.706
7.685
7.453
7.432
6.866
6.844
5.130
5.115
5.099
5.083
5.068
5.052
5.036
1.657
1.205
1.189
O
Cl
H3C
CH3
O
O
CH3
O
CH3
1.97
1.84
1.93
2.00
1.11
5.78
5.76
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

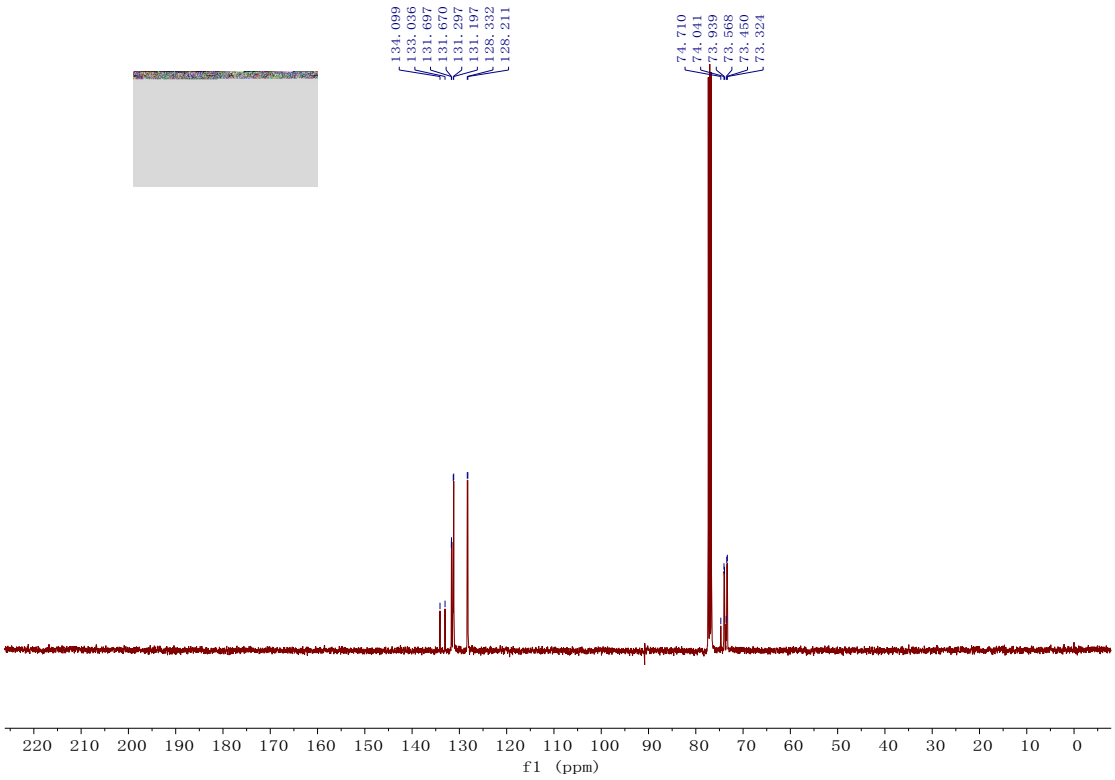

194.312
173.120
159.698
138.348
136.373
131.980
131.177
130.144
128.540
117.154
79.375
77.360
77.044
76.725
69.375
25.355
21.539
O
Cl
H3C
CH3
O
O
CH3
O
CH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-Phenylpropane-1,2-diol (50)



Bis(2-(diphenylphosphoryl)cyclopenta-2,4-dien-1-yl)iron (Fe5)




134.099
133.036
131.697
131.670
131.297
131.197
128.332
128.211
74.710
74.041
73.939
73.568
73.450
73.324
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)