Supporting Information

Regioselective Coupling of Benzyl Chlorides with Allyl and Allenyl Boronates Catalysed by Bidentate Phosphine Ligand/Palladium Catalyst

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1. General Information

^{1}H , ^{13}C and ^{19}F NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 376 MHz for ^{19}F) or a Bruker Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 376 MHz for ^{19}F); $CDCl_3$ was used as a solvent, while TMS was used as an internal standard. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants *J* are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. TLC was carried out on SiO_2 (silica gel 60 F254, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 meth). GC-MS analysis was performed on an Agilent 7890A GC interfaced to an Agilent 5975C mass-selective detector (30 m × 0.25 mm capillary column, HP-5MS). IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on either a Q-TOF mass spectrometry or a GC-TOF mass spectrometry. All reactions were carried out under nitrogen atmospheric pressure. The starting materials were purchased from Energy Chemicals Co. Ltd.

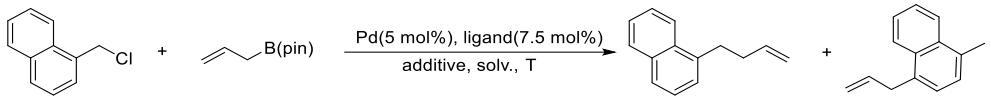
2. General Experimental Procedures

Representative Procedure: A reaction flask was charged with a mixture of benzyl chlorides (0.2 mmol, 28.1 mg), allyl pinacolborate (0.4 mmol, 67.2 mg), $Pd(OAc)_2$ (0.01 mmol, 2.3 mg, 5 mol%), Xantphos （0.015 mmol, 8.7 mg, 7.5 mol%）, CsF（0.6 mmol, 91.1 mg), THF (2.0 mL) under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12 h, and then was cooled to room temperature. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: petroleum ether) to afford corresponding product **3a** in 83% yield.

3. Reaction Condition Screening of 1j

When 1-(Chloromethyl)naphthalene was investigated under the optimized reaction conditions [$Pd(OAc)_2$ (5 mol%), Xantphos (7.5 mol%), and CsF (3.0 equiv.) in THF at 80 °C for 12 h.], the normal coupling product **3j** was obtained in 26% yield along with *para*-allylation product **3ja** in 37% yield (Table S1, Entry 1). The reaction of 1-(Chloromethyl)naphthalene (**1j**) with allyl pinacolborate (**2a**) was selected as a model to optimize the reaction conditions. The results are summarized in Table S1.

Table S1. Reaction Condition Screening[a]

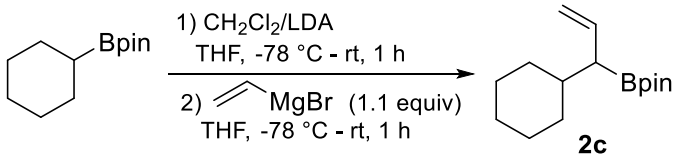


1j 2a 3j 3ja

Entry	Pd/ligand	Additive	Solv.	T (°C)	**3j**(%)[b]	**3ja**(%)[b]
1	$Pd(OAc)_2$/Xantphos	CsF	THF	80	26	37
2	Pd_2dba_3/Xantphos	CsF	THF	80	trace	trace
3	$Pddba_2$/Xantphos	CsF	THF	80	trace	trace
4	$Pd(PPh_3)_4$/Xantphos	CsF	THF	80	trace	trace
5	$Pd(opiv)_2$/Xantphos	CsF	THF	80	35	40
6	$PdCl_2$/Xantphos	CsF	THF	80	trace	trace
7	$Pd(PPh_3)Cl_2$/Xantphos	CsF	THF	80	44	41
8	$Pd(TFA)_2$/Xantphos	CsF	THF	80	18	61
9	$Pd(PPh_3)Cl_2$/Xantphos	CsF	Dioxane	80	51	17
10	$Pd(PPh_3)Cl_2$/Xantphos	CsF	DCE	80	70	0
11	$Pd(PPh_3)Cl_2$/Xantphos	CsF	CH_3CN	80	trace	56
12	$Pd(PPh_3)Cl_2$/Xantphos	CsF	DMSO	80	10	16
13	$Pd(PPh_3)Cl_2$/Xantphos	CsF	Toluene	80	trace	trace
14	$Pd_2(dba)_3/PPh_3$	CsF	DCE	80	64	25
15	$Pd(PPh_3)Cl_2$	CsF	DCE	80	33	26
16	$Pd(PPh_3)Cl_2$/Xantphos	CsF	DCE	100	trace	trace
17	$Pd(PPh_3)Cl_2$/Xantphos	CsF	DCE	120	trace	trace
18[c]	$Pd(PPh_3)Cl_2$/Xantphos	CsF	DCE	80	51	trace

[a] Reaction conditions: benzyl chlorides (**1j**, 0.2 mmol), allyl pinacolborate (**2a**, 0.4 mmol), Pd cat. (5 mol%), ligand (7.5 mol%), and CsF (0.6 mmol) in dry solvent (2.0 mL) at 80 ºC under N_2 atmosphere. [b] NMR yield. [c] ligand (5 mol%)

4. Procedure for the synthesis of 2c.[1]



2c

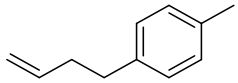
A THF solution of LDA (117 mg, 1.1 mmol) was added to a mixture of 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (210 mg, 1 mmol, 1 equiv) and CH_2Cl_2 (110 mg, 1.3 mmol, 1.3 equiv) in THF (2 mL) at -78 °C under atmosphere of nitrogen. The resulting mixture was stirred for 30 min and warmed to room temperature for another 1 h. The reaction mixture was cooled to -78 °C, and vinylmagnesium bromide (1M in THF, 1.1 mmol, 1.1 equiv) was added dropwise. After stirring for 30 min, the mixture

was warmed to room temperature stirring for 1 h. The reaction was quenched with aqueous NH_4Cl, and extracted with ether. After washing with brine and drying over anhydrous Na_2SO_4, the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel with (PE/EA = 100:1) to afford the title compound as a colorless liquid (154 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73 (dt, J = 17.0, 10.0 Hz, 1H), 5.03–4.86 (m, 2H), 1.77 (d, J = 13.5 Hz, 1H), 1.69–1.60 (m, 5H), 1.56–1.45 (m, 1H), 1.24 (s, 12H), 1.24–1.02 (m, 15H), 1.03–0.95(m, 1H), 0.91–0.77 (m, 1H).

5. The Characterization of Products

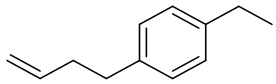
The spectroscopic data of all the products are presented.

1-(but-3-en-1-yl)-4-methylbenzene (3a):[2]



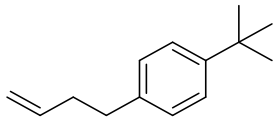
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (s, 4H),5.92–5.80 (m, 1H), 5.08 – 4.94 (m, 2H), 2.67 (t, J = 8.0 Hz, 2H), 2.36 (q, J = 8.0 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 138.2, 135.2, 128.9, 128.3, 114.8, 35.6, 34.9, 21.0.

1-(but-3-en-1-yl)-4-ethylbenzene (3b):[3]



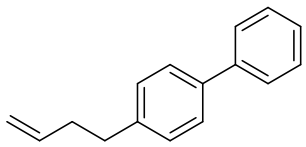
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (s, 4H),5.92–5.90 (m, 1H), 5.09 – 4.95 (m, 2H), 2.68 (t, J = 8.0 Hz, 2H), 2.62 (q, J = 8.0 Hz, 2H), 2.36 (q, J = 8.0 Hz, 2H), 1.22 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 139.1, 138.3, 128.4, 127.8, 114.8, 35.6, 34.9, 28.5, 15.7.

1-(but-3-en-1-yl)-4-(tert-butyl)benzene (3c):[4]



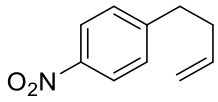
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H),5.98–5.96 (m, 1H), 5.14–4.99 (m, 2H), 2.76–2.69 (t, J = 8.0 Hz, 2H), 2.44–2.39 (m, 2H), 1.36 (s,9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 138.8, 138.3, 128.1, 125.2, 114.8, 35.5, 34.8, 34.4, 31.4.

4-(but-3-en-1-yl)-1,1'-biphenyl (3d):[3]



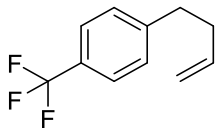
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 7.3 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 5.94–5.84 (m, 1H), 5.09–4.99 (m, 2H), 2.77–2.73 (t, J = 8.0 Hz, 2H), 2.44–2.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 141.0, 138.8, 138.1, 128.9, 128.7, 127.1, 127.0, 115.1, 35.5, 35.0.

1-(but-3-en-1-yl)-4-nitrobenzene (3e):[3]



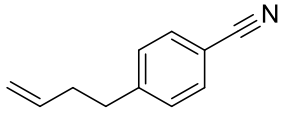
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.97–5.75 (m, 1H), 5.08–4.98 (m, 2H), 2.82 (t, J = 8.0 Hz, 2H), 2.41 (q, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 136.8, 129.8, 129.2, 123.6, 115.8, 35.1, 34.8.

1-(but-3-en-1-yl)-4-(trifluoromethyl)benzene (3f):[3]



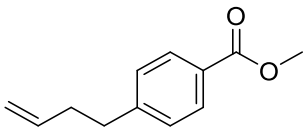
Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, J = 12.0 Hz, 2H), 7.29 (d, J = 12.0 Hz, 2H), 5.86–5.79 (m, 1H), 5.14–4.99 (m, 2H), 2.76–2.69 (t, J = 8.0 Hz, 2H), 2.38 (q, J = 6.0 Hz, 2H), 1.36 (s,9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.9, 137.3, 128.7, 125.4, 125.3, 125.2, 125.1, 115.4, 35.2, 35.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.29 (s).

4-(but-3-en-1-yl)benzonitrile (3g):[3]



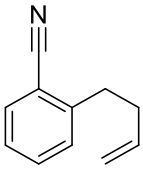
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 7.7 Hz, 2H), 7.28 (d, J = 7.6 Hz, 2H), 5.97–5.75 (m, 1H), 5.07–4.98 (m, 2H), 2.77 (t, J = 6.0 Hz, 2H), 2.38 (q, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 136.9, 132.1, 129.2, 119.1, 115.7, 109.7, 35.4, 34.8.

methyl 4-(but-3-en-1-yl)benzoate (3h):[3]



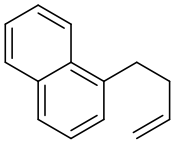
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.5 Hz, 2H), 7.25 (d, J = 7.7 Hz, 2H), 5.89–5.76 (m, 1H), 5.07–4.96 (m, 2H), 3.90 (s, 3H), 2.76 (t, J = 7.7 Hz, 2H), 2.38 (q, J = 7.1, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 147.3, 137.4, 129.6, 128.9, 127.8, 115.3, 51.9, 35.3, 35.0.

2-(but-3-en-1-yl)benzonitrile (3i):[5]



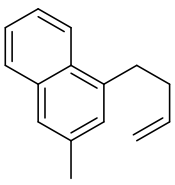
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 7.7 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.36–7.28 (m, 2H), 5.93–5.81 (m, 1H), 5.10–4.99 (m, 2H), 2.97 (t, J = 4.0 Hz, 2H), 2.46 (q, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6 , 136.7 , 132.8 , 132.6 , 129.6 , 126.5 , 118.1 , 115.9 , 112.4 , 34.7 , 33.9 .

1-(but-3-en-1-yl)naphthalene (3j):[6]



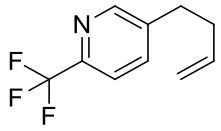
White solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.85 (s, 1H), 7.71 (s, 1H), 7.49 (d, J = 18.5 Hz, 2H), 7.42–7.37 (m, 1H), 7.33 (s, 1H), 6.00–5.90 (m, 1H), 5.06 (dd, J = 47.3, 13.0 Hz, 2H), 3.16 (s, 2H), 2.51 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.2, 137.9, 128.8, 126.6, 125.9, 125.8, 125.5, 125.4, 123.77 , 114.9, 34.8, 32.5.

1-(but-3-en-1-yl)-3-methylnaphthalene (3k):



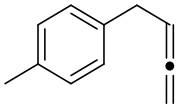
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–7.99 (m, 1H), 7.82–7.78 (m, 2H), 7.54–7.50 (m, 1H), 7.50–7.44 (m, 2H), 7.22 (d, J = 1.7 Hz, 1H), 6.05–5.94 (m, 1H), 5.18–5.04 (m, 2H), 3.22–3.11 (m, 2H), 2.54 (d, J = 11.6 Hz, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 137.7, 135.0, 134.2, 130.0, 128.3, 128.1, 125.5, 125.4, 124.8, 123.5, 114.8, 34.9, 32.4, 21.6; IR (KBr) 2921, 2851, 1639, 1601, 1507, 1440, 1414, 1029, 864 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{16}$: 196.1252 $[M]^+$; found: 196.1255.

5-(but-3-en-1-yl)-2-(trifluoromethyl)pyridine (3l):



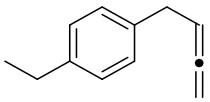
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.72–7.65 (m, 1H), 7.61 (d, J = 8.0 Hz, 1H), 5.81 (ddt, J = 17.1, 10.4, 6.7 Hz, 1H), 5.17–4.92 (m, 2H), 2.81 (t, J = 7.6 Hz, 2H), 2.41 (q, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 150.2, 140.4, 137.1, 136.5, 120.4, 120.1, 116.3, 77.4, 77.0, 76.7, 34.7, 32.2. ^{19}F NMR (376 MHz, CDCl3): δ -67.71; IR (neat) 3081, 2931, 2858, 1643, 1400, 1338, 1258, 1177, 1087, 916, 850 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{10}F_3N$: 201.0765 $[M]^+$; found: 201.0757.

1-methyl-4-(propa-1,2-dien-1-yl)benzene (4a):[7]



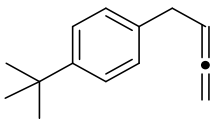
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (s, 4H), 5.31–5.22 (m, 1H), 4.76–4.68 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.9, 137.2, 135.7, 129.1, 128.3, 89.7, 75.1, 34.7, 21.1.

1-ethyl-4-(propa-1,2-dien-1-yl)benzene (4b):



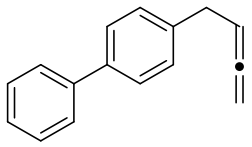
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (s, 4H), 5.36–5.27 (m, 1H), 4.79–4.74 (m, 2H), 3.41–3.35 (m, 2H), 1.28 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.9, 142.1, 135.7, 128.3, 127.9, 89.7, 74.9, 34.7, 28.4, 15.6; IR (neat) 2956, 2923, 2852, 1956, 1633, 1513, 1463, 1261, 1021, 841 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{14}$: 158.1096 $[M]^+$; found: 158.1094.

1-(tert-butyl)-4-(propa-1,2-dien-1-yl)benzene (4c):



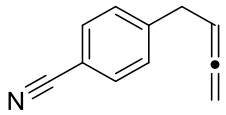
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 8.0 Hz, 2H), δ 7.19 (d, J = 8.0 Hz, 2H), 5.31–5.22 (m, 1H), 4.75–4.69 (m, 2H), 3.36–3.30 (m, 2H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.9, 149.1, 137.3, 128.1, 125.3, 89.5, 74.9, 34.6, 34.4, 31.4; IR (neat) 2962, 2929, 2888, 1948, 1633, 1513, 1463, 1266, 1029, 845 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{18}$: 186.1409 $[M]^+$; found: 186.1411.

4-(propa-1,2-dien-1-yl)-1,1'-biphenyl (4d):



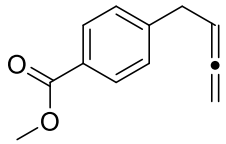
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.57 (m, 4H), 7.51-7.45 (m, 2H), 7.41-7.34 (m, 3H), 5.41–5.32 (m, 1H), 3.48–3.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 139.4, 139.2, 128.8, 127.1, 88.4, 75.2, 34.8; IR (neat) 3027, 2978, 1954, 1600, 1486, 1270, 1008, 842 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{14}$: 206.1096 $[M]^+$; found: 206.1099.

4-(propa-1,2-dien-1-yl)benzonitrile (4g):



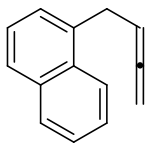
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.32–5.24 (m, 1H), 4.78–4.74 (m, 2H), 3.44–3.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.2, 145.7, 132.2, 129.3, 119.1, 110.1, 88.3, 75.8, 35.1; IR (neat) 2922, 2850, 2227, 1948, 1606, 1503, 1401, 1172, 1020, 846 cm^{-1}; HRMS (EI) calcd for $C_{11}H_9N$: 155.0735 $[M]^+$; found: 155.0730.

methyl 4-(propa-1,2-dien-1-yl)benzoate (4h):



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.0 Hz, 2H), δ 7.32 (d, J = 8.0 Hz, 2H), 5.34–5.25 (m, 1H), 4.77–4.73 (m, 2H), 3.93(s, 3H), 3.45–3.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 171.1, 167.1, 145.6, 129.7, 128.5, 128.2, 88.8, 75.5, 52.0, 35.0; IR (neat) 2951, 2847, 1955, 1721, 1610, 1434, 1279, 1191, 1110, 1020, 847 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{12}O_2$: 188.0837 $[M]^+$; found: 188.0831.

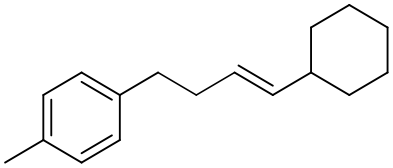
1-(buta-2,3-dien-1-yl)naphthalene (4j):



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25–8.18 (m, 1H), 8.05–7.98 (m, 1H), 7.57–7.50 (m, 2H), 7.48 (d, J = 7.3 Hz, 1H), 7.29 (d, J = 7.3 Hz, 1H), 6.84 (t, J = 6.9 Hz, 1H), 5.18 (d, J = 6.9 Hz, 2H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 210.9, 133.7, 133.0, 130.8, 128.3, 126.6, 125.7, 125.6, 125.1, 124.8, 124.1, 90.5, 77.7, 77.4,

77.0, 76.7, 19.6. IR (neat) 3040, 2924, 2854, 1940, 1688, 1515, 1392, 1262, 1096, 830, 753 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{12}$: 180.0939 $[M]^+$; found: 180.0930.

(E)-1-(4-cyclohexylbut-3-en-1-yl)-4-methylbenzene (5a):



Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.07 (s, 4H), 5.38 (d, J = 4.5 Hz, 2H), 2.61 (t, J = 7.9 Hz, 2H), 2.31 (s, 3H), 2.26 (dd, J = 8.8, 5.3 Hz, 2H), 1.88 (tt, J = 11.3, 3.9 Hz, 1H), 1.76–1.65 (m, 4H), 1.32–0.94 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.2, 137.1, 135.1, 128.9, 128.4, 126.9, 77.4, 77.1, 76.8, 40.7, 35.9, 34.8, 33.3, 26.3, 26.2, 21.0. IR (neat) 3018, 2924, 2851, 1515, 1448, 1348, 1259, 1108, 1022, 968, 891, 807 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{24}$: 228.1878. $[M]^+$; found: 228.1871.

6. Computational Details

All of the calculations reported here were performed with the Gaussian16 program[7]. The molecular geometries were optimized using B3LYP exchange-correlation functional. The 6-31G(d, p) basis set was used for all atoms except for Pd, for which LANL2DZ is used. During the calculation, analytical vibration frequencies were calculated to determine the nature of the located stationary point. Then, the electronic energies were further refined with single point energy calculations with M06-2X functional and higher basis sets SDD for Pd and 6-311G(d, p) for other atoms. Solvent effects were taken into account using SMD model[9] for the single point energy calculations. Total free energy is the sum of the single point energy in the liquid phase, thermal correction to gibbs free energy with the correction factor 0.9838[10] for zero-point energy and a concentration correction which is 1.89 kcal/mol from P = 1 atm to C = 1 mol/L condition in the solvent at 298.15K.

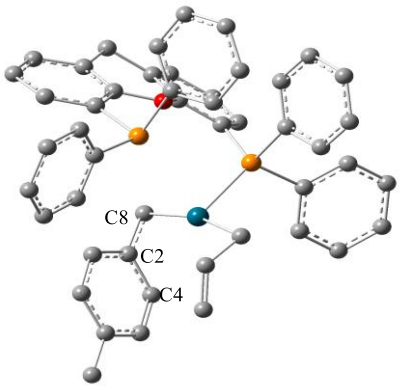


Table S2 The calculated bond order of **B'**.

Bond	Mayer bond order	Wiberg bond order	Fuzzy bond order
Pd-C2	0.03	0.17	0.23
Pd-C4	0.04	0.29	0.46
Pd-C8	0.38	0.72	0.89

7. Cartesian Coordinates of the Computed Structures

B

C	0.95840900	5.03970000	0.14445100
C	1.04014000	3.77865200	0.72720200
C	-0.27933500	5.64518100	-0.11659000
C	-0.11837200	3.05123700	1.08952600
C	-1.36046700	3.67619700	0.82728700
C	-1.43522700	4.93653600	0.24430600
H	-2.41097900	5.38607400	0.07080400
C	-0.03656500	1.70171800	1.66495600
H	-0.90285400	1.41652000	2.25887300
Pd	-0.00867800	0.66077900	-0.25122200
P	2.17836500	-0.23861500	0.06832800
P	-2.10414300	-0.44770100	0.12693100
C	-3.71265400	0.38396600	-0.25080800
C	-3.68164100	1.49350600	-1.10865800
C	-4.94750300	-0.03257200	0.27863000
C	-4.86176100	2.16371100	-1.44151600
H	-2.73424700	1.83151000	-1.51784400
C	-6.12258000	0.64255600	-0.05104200
H	-4.98923100	-0.87952800	0.95637800
C	-6.08180900	1.74150100	-0.91381300
H	-4.82079800	3.01967400	-2.10898200
H	-7.06945800	0.31202600	0.36696600
H	-6.99805100	2.26740900	-1.16758200
C	-2.19718500	-2.02944600	-0.84423400
C	-3.37007600	-2.44691400	-1.49240100
C	-1.05211900	-2.82671900	-1.02429900
C	-3.39866700	-3.59821100	-2.27907500
H	-4.27074600	-1.85293200	-1.39449900
C	-1.06231400	-3.99364500	-1.79605300
C	-2.24699600	-4.36746200	-2.43081700
H	-4.31980000	-3.89022500	-2.77403300
H	-2.26196100	-5.26643500	-3.04180600
C	3.67194200	0.74200200	-0.41834900
C	4.96541900	0.49018800	0.07230900
C	3.48923000	1.79352100	-1.32866600
C	6.04608600	1.26657400	-0.34699700
H	5.12703700	-0.30852400	0.78932300
C	4.57274900	2.56545900	-1.75311100
H	2.49043400	2.01162100	-1.69266700
C	5.85244400	2.30371300	-1.26306600
H	7.03934700	1.06206100	0.04293300
H	4.41249200	3.37551400	-2.45872600
H	6.69511400	2.90803600	-1.58688600
C	2.58667300	-0.75798000	1.79775000
C	2.34042800	-2.06178900	2.25352300
C	3.06735900	0.19156300	2.71690300
C	2.57492800	-2.40776600	3.58504400
H	1.96688000	-2.81574200	1.56999600
C	3.30412600	-0.15715500	4.04664100
H	3.27465100	1.20630300	2.39189100
C	3.05794300	-1.45868700	4.48649700
H	2.38271800	-3.42481500	3.91540300
H	3.68091600	0.59142000	4.73787300
H	3.24133100	-1.73022700	5.52206900
H	0.87692000	1.50942600	2.22465800
H	-2.27680400	3.16075300	1.10269400
C	-2.36117100	-1.02773700	1.86877200
C	-2.90697400	-0.14877300	2.82112500
C	-1.94239700	-2.29627400	2.29756600
C	-3.03717800	-0.53118200	4.15634400
H	-3.24937200	0.83562500	2.51821600
C	-2.07167100	-2.67642800	3.63423400
H	-1.51487500	-2.99707200	1.58997600
C	-2.61914600	-1.79717300	4.56897800
H	-3.46661200	0.16330600	4.87293000
H	-1.74634800	-3.66622300	3.94257400
H	-2.72017200	-2.09538700	5.60854300
C	2.38599300	-1.81875500	-0.89211900
C	3.58149400	-2.13633600	-1.55610100
C	1.31415700	-2.71769500	-1.04619200
C	3.70095200	-3.28546100	-2.33685100
H	4.42763300	-1.46466200	-1.47716000
C	1.41633800	-3.88251400	-1.81582800
C	2.61899000	-4.15309900	-2.46831600
H	4.63692300	-3.49774200	-2.84437700
H	2.70324100	-5.04980900	-3.07701600
O	0.12262200	-2.44297600	-0.39544800
C	0.21482600	-4.79725100	-1.88017600
H	0.25352100	-5.51303500	-1.04340300
H	0.23474900	-5.39544000	-2.79691700
H	2.01719200	3.34620700	0.92701500
H	1.87453600	5.57113100	-0.10616000
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H	-1.25364500	7.55149700	-0.44583800
H	-0.42554300	6.91734300	-1.86773100
H	0.51269800	7.61471500	-0.54680200
C	0.01376200	0.21522500	-2.41935000
H	0.99107700	-0.21581800	-2.64872900
C	-0.17251400	1.52440100	-3.06048100
H	-0.76743800	-0.49822100	-2.69246400
C	-1.26048100	1.96399200	-3.72567300
H	-1.30770300	2.96496900	-4.14453200
H	-2.12466400	1.32333600	-3.88717100
H	0.66446400	2.22254500	-2.97820400

TSB

C	5.66420100	-1.66621600	0.05365300
C	4.58666000	-1.38545800	-0.77623800

C	5.59565500	-2.67326100	1.03069300	H	-1.24296500	-2.08510700	5.54011300
C	3.36955100	-2.10410700	-0.67067100	H	2.39107200	-3.69026000	0.42767700
C	3.30886000	-3.11674100	0.31874800	C	1.55275900	1.38360400	1.55308500
C	4.39260000	-3.38800200	1.14576700	C	2.31662100	0.28122100	1.97304800
H	4.31009800	-4.17282300	1.89494800	C	1.24648600	2.38530700	2.48500800
C	2.25473500	-1.83705800	-1.53900600	C	2.77622300	0.19474500	3.28654600
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P	-2.26398300	-0.92461800	0.00683700	C	1.69224300	2.28675800	3.80550600
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C	2.55157100	1.87791700	-1.11180600	C	2.46095200	1.19511800	4.20929800
C	2.56646400	1.72943800	-2.50876400	H	3.37843600	-0.65883000	3.58487400
C	3.70384500	2.36160000	-0.47532600	H	1.44168200	3.07008200	4.51571400
C	3.69817800	2.06571700	-3.25134200	H	2.81181600	1.12380300	5.23510300
H	1.68600100	1.33567800	-3.01067800	C	-3.58486200	0.37898600	0.06999300
C	4.84198700	2.68741600	-1.21814000	C	-4.95576600	0.15728100	-0.13443500
H	3.71682500	2.48185800	0.60274300	C	-3.17995000	1.70718800	0.27325200
C	4.84255900	2.54261900	-2.60604400	C	-5.85924700	1.22115300	-0.17819900
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H	5.72825700	3.05527000	-0.70833600	C	-4.05949700	2.79120100	0.22146600
H	5.72864600	2.79530300	-3.18154900	C	-5.41071700	2.53191000	-0.01682600
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C	-0.10864000	5.39718000	-0.88650200	C	-3.49235800	4.17609800	0.44421500
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C	-2.05548000	4.24152700	-0.02810300	H	-4.10123800	4.92894300	-0.06766300
C	-1.45388800	5.40150600	-0.51871200	H	4.66878900	-0.59698400	-1.51911300
H	0.35594700	6.30458500	-1.26033000	H	6.58193700	-1.09149500	-0.05268500
H	-2.04273900	6.31151500	-0.60314300	C	6.78472000	-2.99511600	1.90326800
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C	-3.26810900	-3.59274400	0.24600300	H	7.35697300	-2.09496600	2.15129400
C	-3.84942100	-2.42228300	-1.78189300	H	7.47555200	-3.68621000	1.40206600
C	-3.91615600	-4.73380100	-0.23212100	C	-0.70934600	-1.92377500	-2.85970500
H	-2.79504700	-3.62042200	1.22153900	C	0.41678800	-1.90188900	-3.72189800
C	-4.50682700	-3.55829300	-2.25249500	C	1.45431100	-2.81596000	-3.70118200
H	-3.82840900	-1.52912800	-2.39941900	H	0.52987600	-1.02695100	-4.36417100
C	-4.54087100	-4.72082500	-1.47936600	H	-0.96791800	-2.87475200	-2.39512300
H	-3.93605700	-5.63267900	0.37803100	H	-1.57816900	-1.34737700	-3.17528100
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H	-5.04684200	-5.60839800	-1.84821200	H	2.30304300	-2.71416400	-4.36901400
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C	-2.96998700	-1.10454800	2.77534900	H	1.34719500	-2.39960700	-1.40730700
C	-0.70227600	-1.71012600	2.20050000	**3a**			
C	-2.70856800	-1.40018700	4.11314900	C	-2.78964800	-0.08724700	0.14438300
H	-3.95518500	-0.75119100	2.48699700	C	-2.02465700	-1.22139900	-0.15643300
C	-0.44363000	-2.01256400	3.53895900	C	-0.66909100	-1.11499100	-0.46692200
H	0.08279800	-1.80914700	1.45608100	C	-0.02746700	0.12990400	-0.49084700
C	-1.44552100	-1.85745000	4.49723900	C	-0.79393200	1.26486100	-0.19508500
H	-3.49147800	-1.27327600	4.85589300	C	-2.14916600	1.15848300	0.11547100
H	0.54525300	-2.35271300	3.83124100	H	-2.49767700	-2.20081500	-0.15382300

H	-0.10199000	-2.01259700	-0.70370200
H	-0.32587200	2.24671500	-0.21776600
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H	2.14848900	-0.77436100	1.00238400
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C	3.79647300	0.32706700	0.18685800
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H	5.77845200	-0.41924800	0.20082300
H	4.48836600	-1.53606700	0.91481300

C

Pd	0.00000300	-0.60232300	-1.17443700
P	-2.15630600	-0.26447500	-0.41521000
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C	3.49291400	0.15627300	-2.82718500
C	4.91845500	-0.75611900	-1.10357200
C	4.56593800	0.15869800	-3.71782400
H	2.51184600	0.49060100	-3.15567500
C	5.98973100	-0.76566400	-2.00008900
H	5.06443500	-1.11888500	-0.09099600
C	5.81786600	-0.30460500	-3.30620000
H	4.42166400	0.50942200	-4.73596400
H	6.95882700	-1.13547600	-1.67614600
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C	2.29011300	1.40533800	0.39661600
C	3.47188700	2.16358500	0.35073200
C	1.18279100	1.98925100	1.04484500
C	3.54600500	3.43996200	0.90862700
H	4.34313000	1.75191000	-0.14646800
C	1.24000300	3.26534100	1.61775500
C	2.42962200	3.98968000	1.53588800
H	4.47233800	4.00331500	0.84865800
H	2.47734500	4.98459800	1.97158200
C	-3.65766200	-0.28897900	-1.50497800
C	-4.91859900	-0.75603700	-1.10319600
C	-3.49315000	0.15587400	-2.82714500
C	-5.98998300	-0.76561100	-1.99958300
H	-5.06449200	-1.11862600	-0.09054200
C	-4.56627800	0.15826600	-3.71765800
H	-2.51207300	0.49001900	-3.15579200
C	-5.81821400	-0.30480500	-3.30579600
H	-6.95908500	-1.13524600	-1.67545900
H	-4.42209000	0.50878000	-4.73588300
H	-6.65237200	-0.31482000	-4.00177100
C	-2.62498100	-1.42332600	0.95064500
C	-3.31826700	-1.02757700	2.10431700
C	-2.26363400	-2.77312300	0.81000500
C	-3.64833800	-1.96166800	3.08921300
H	-3.59805900	0.01265300	2.23820200
C	-2.60346100	-3.70694400	1.78833400
H	-1.70170500	-3.08196100	-0.06744600
C	-3.29563100	-3.30266100	2.93224600
H	-4.18080400	-1.63891900	3.97978400
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TSB'

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3aa

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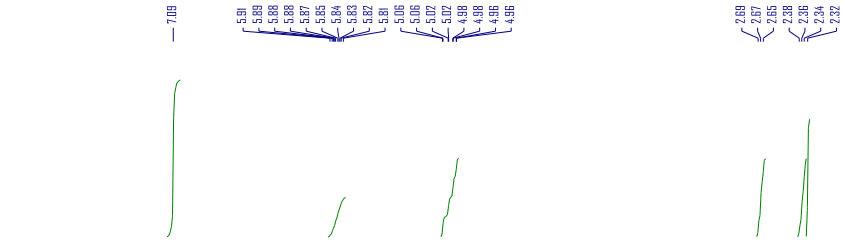
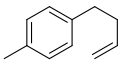
9. Copies of ^{1}H , ^{13}C and ^{19}F NMR Spectra of Products





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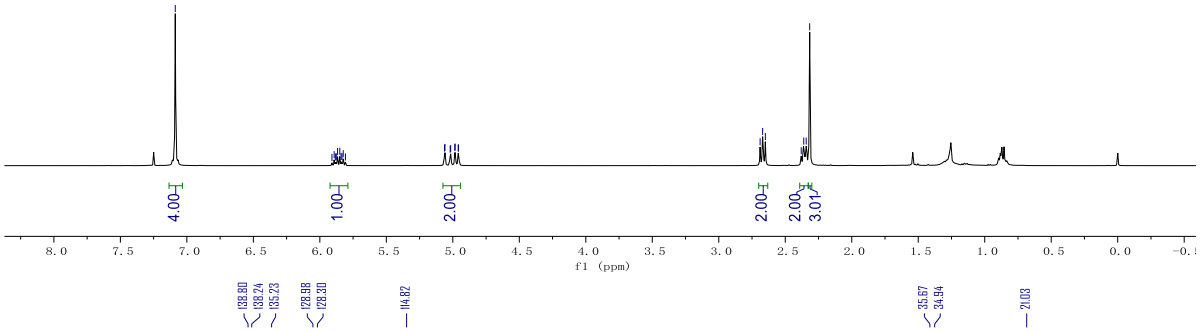

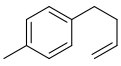

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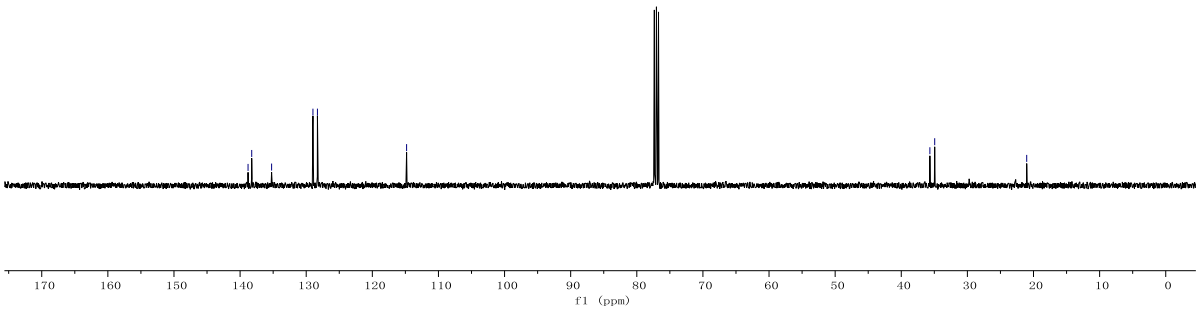

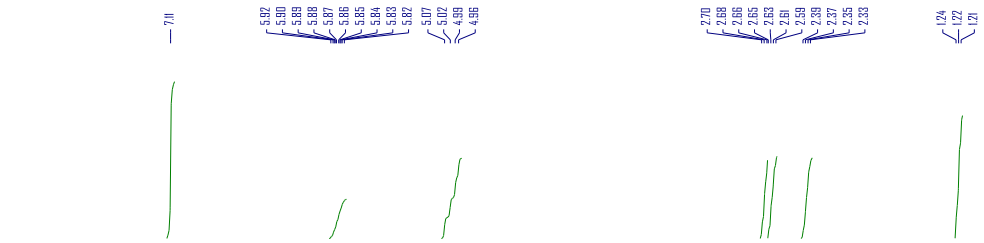
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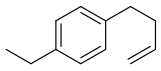

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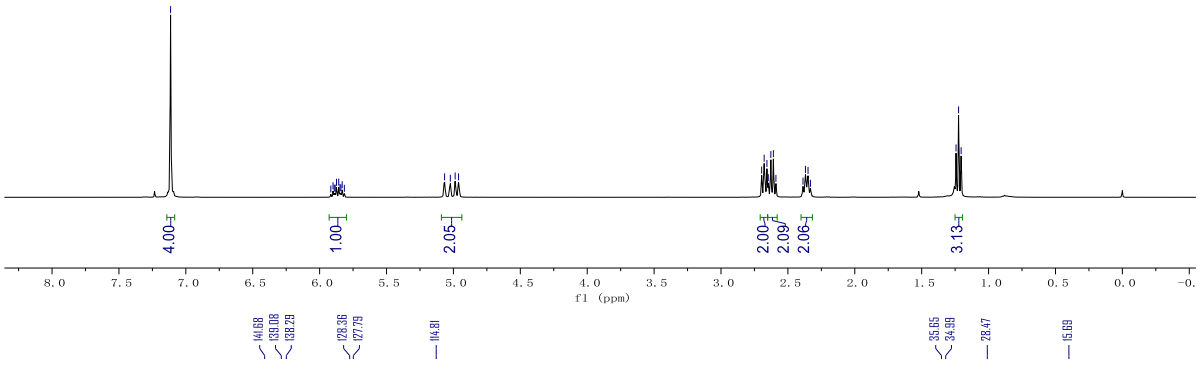
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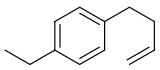

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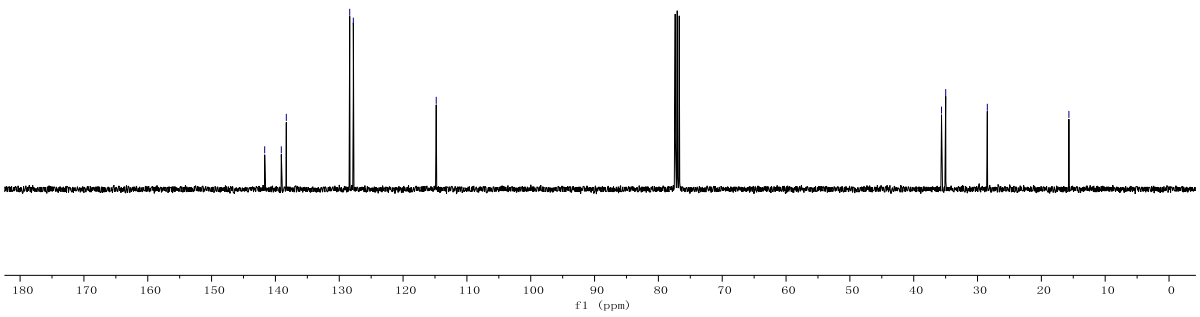
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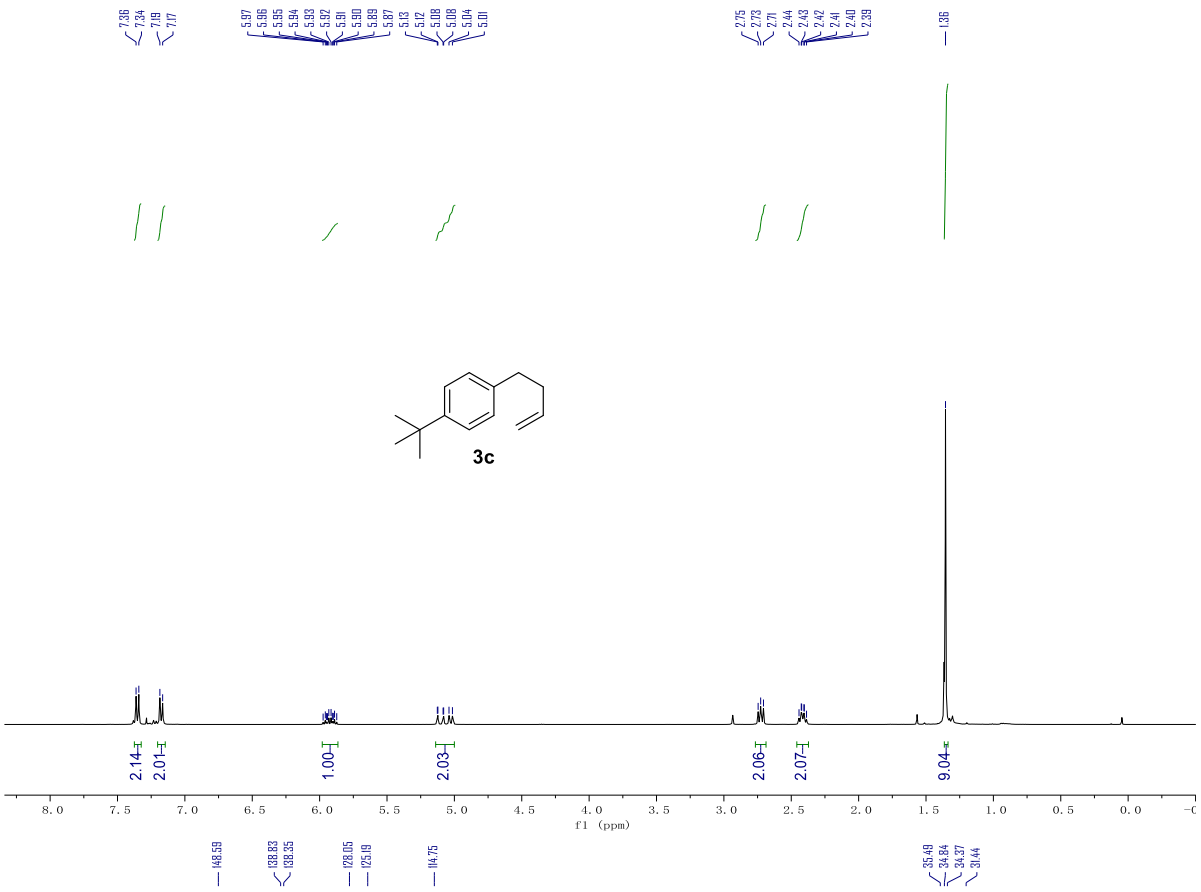
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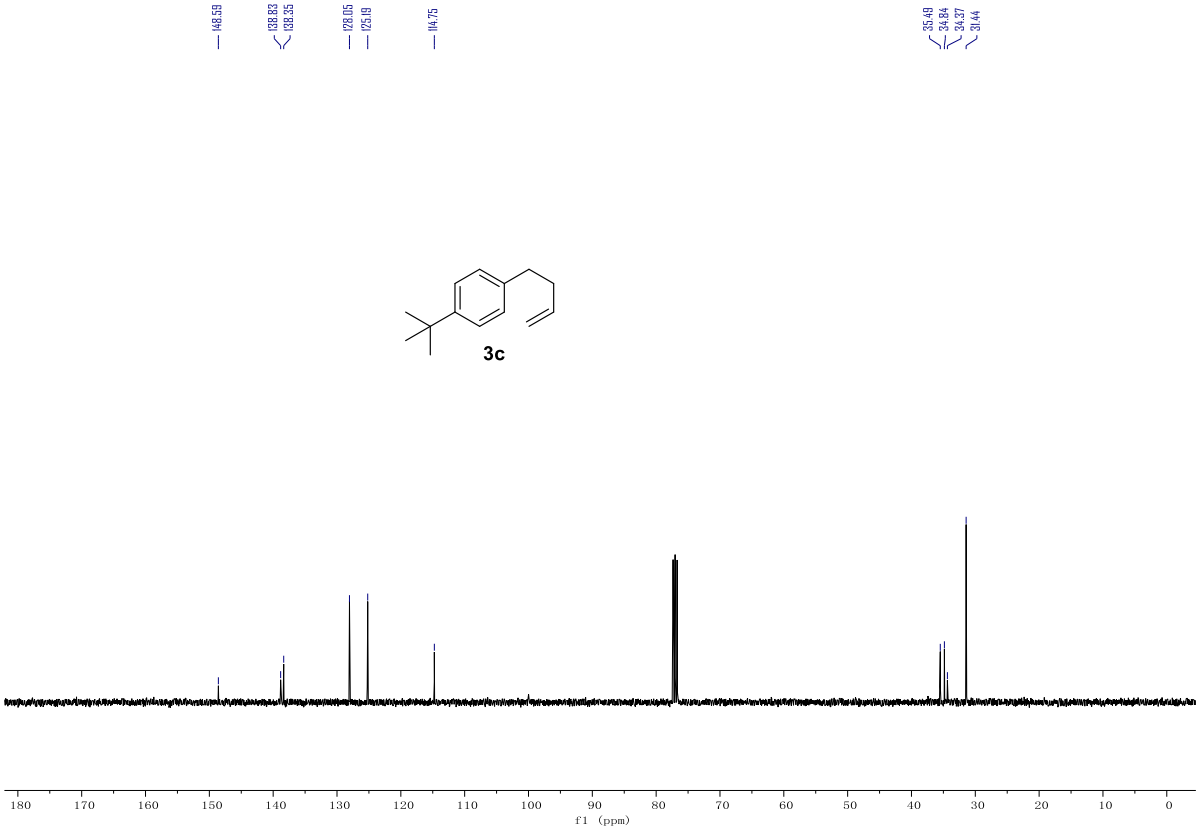
f1 (ppm)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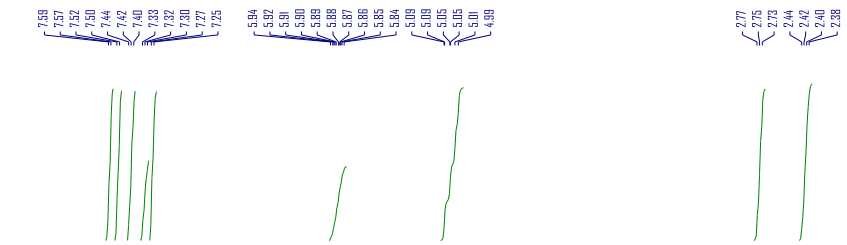
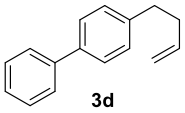
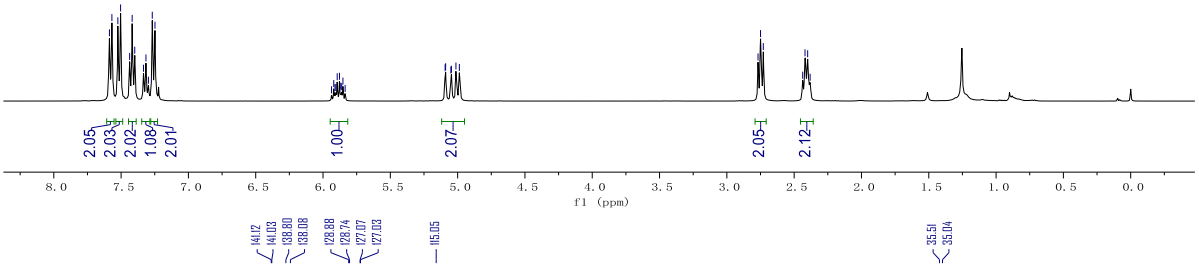
138.83
138.35
128.05
125.18
114.75
35.48
34.84
34.37
31.44
3c
f1 (ppm)

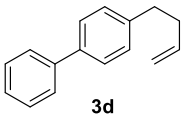

7.59
7.57
7.52
7.50
7.44
7.42
7.40
7.33
7.32
7.30
7.27
7.25
5.94
5.92
5.91
5.90
5.89
5.88
5.87
5.86
5.85
5.84
5.09
5.05
5.05
5.01
4.99
2.77
2.75
2.73
2.44
2.42
2.40
2.38



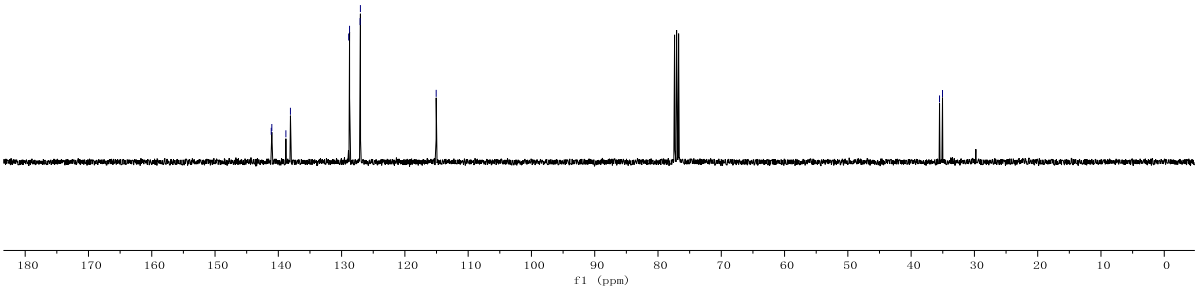
3d

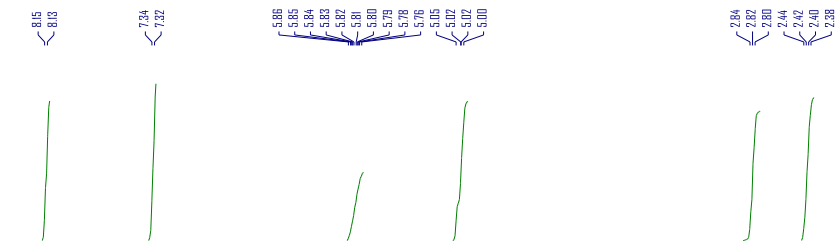

2.05
2.03
2.02
1.08
2.01
1.00
2.07
2.05
2.12
f1 (ppm)

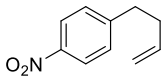
141.12
141.03
138.80
138.08
129.88
129.74
127.07
127.03
115.05
35.51
35.04



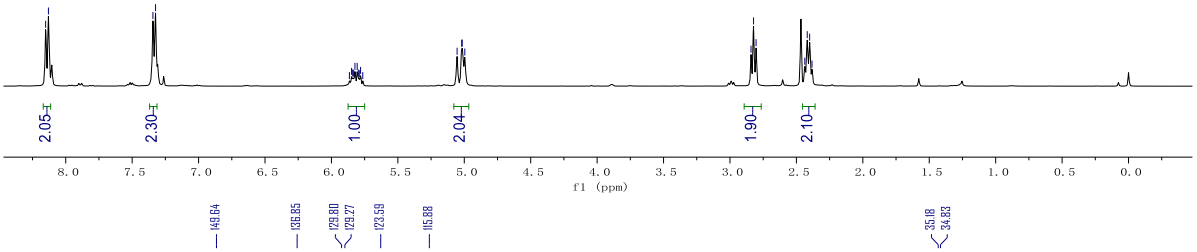
3d

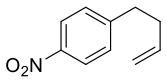

f1 (ppm)


8.15
8.13
7.34
7.32
5.86
5.85
5.84
5.83
5.82
5.81
5.80
5.79
5.78
5.76
5.05
5.02
5.02
5.00
2.84
2.82
2.80
2.44
2.42
2.40
2.38

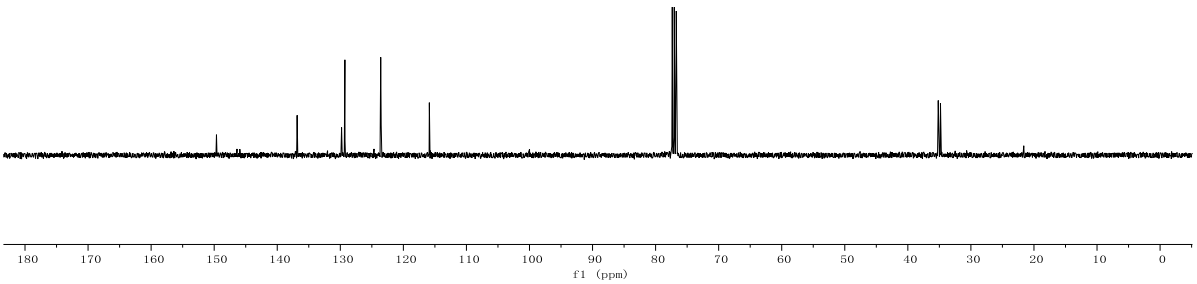

O2N

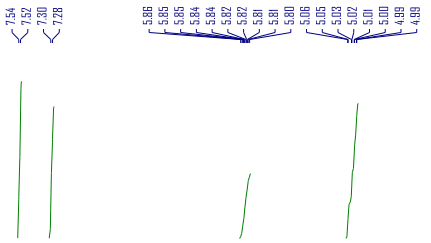
3e

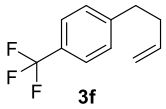

2.05
2.30
1.00
2.04
1.90
2.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
149.64
135.85
129.80
129.27
123.59
115.88
35.18
34.83


O2N

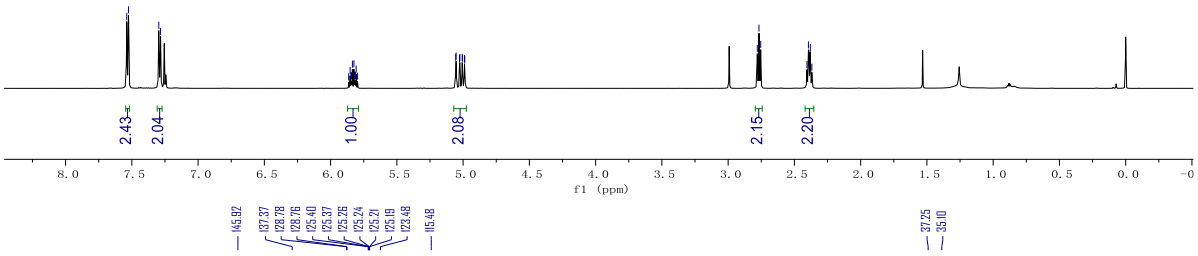
3e


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

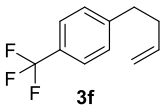

7.54
7.52
7.30
7.28
5.86
5.85
5.85
5.84
5.84
5.82
5.82
5.81
5.81
5.80
5.06
5.05
5.03
5.02
5.01
5.00
4.99
4.99
2.78
2.77
2.75
2.41
2.39
2.38
2.37


F
F
F

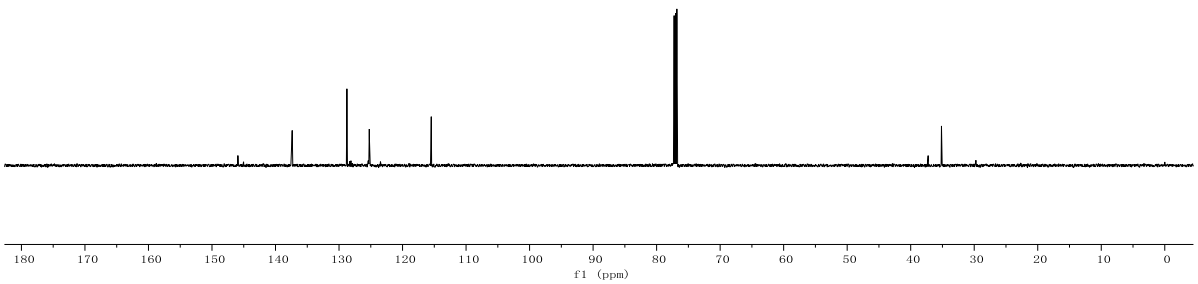
3f

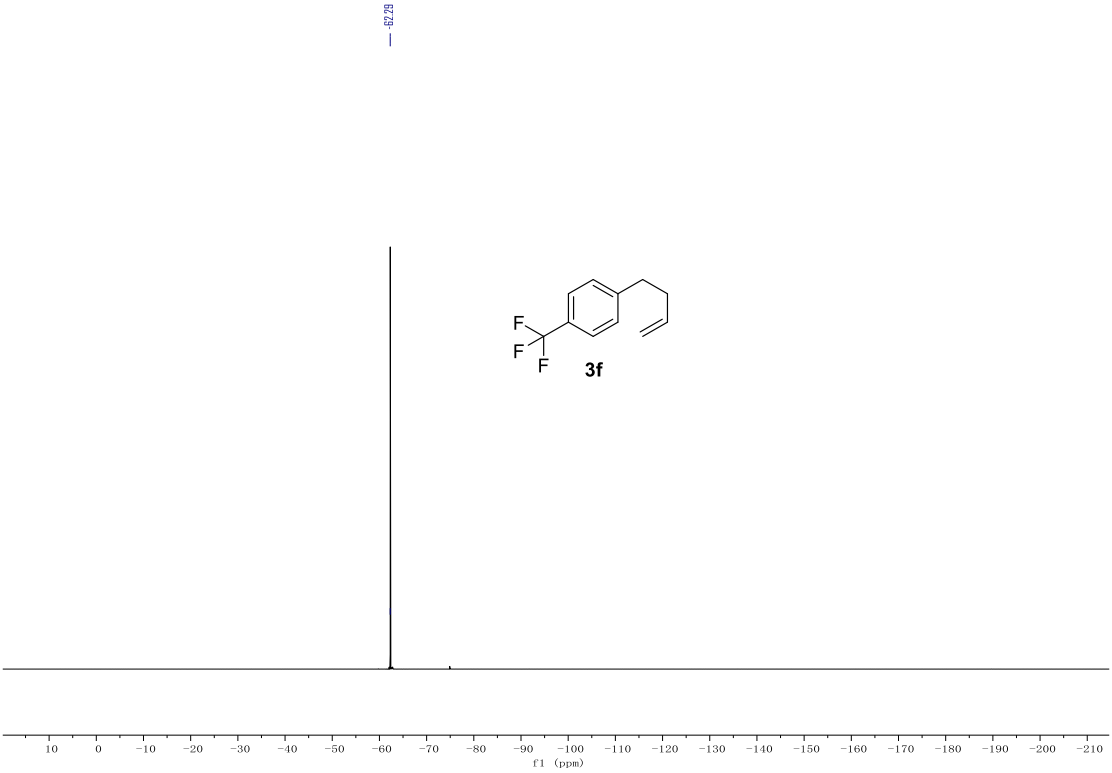

2.43
2.04
1.00
2.08
2.15
2.20
f1 (ppm)

145.92
137.37
128.78
128.76
125.40
125.37
125.26
125.24
125.21
125.19
123.48
115.48
37.25
35.10

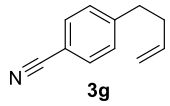

F
F
F

3f

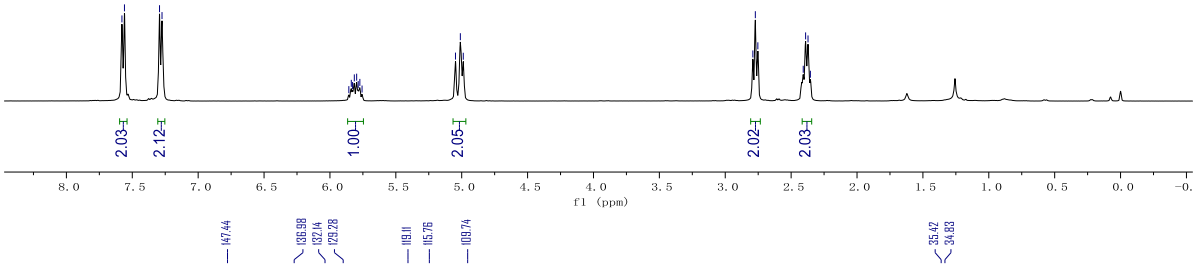

f1 (ppm)


-62.78
F
F
F
3f
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

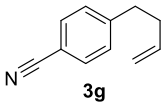

7.58
7.56
7.29
7.27
5.86
5.84
5.83
5.81
5.80
5.79
5.77
5.76
5.05
5.01
4.99
2.79
2.77
2.75
2.44
2.39
2.37
2.35


N

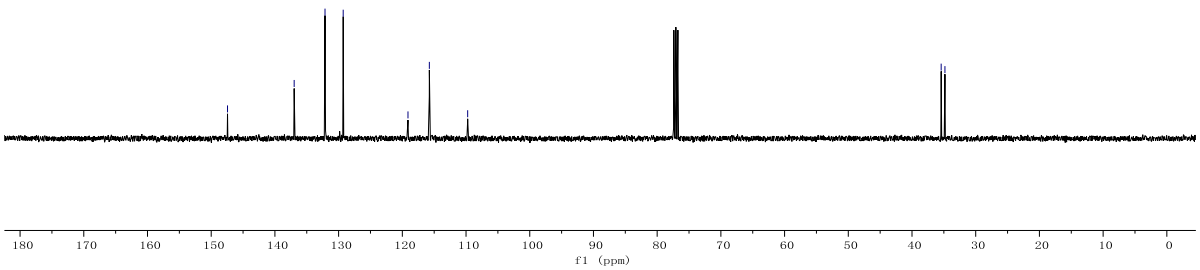
3g

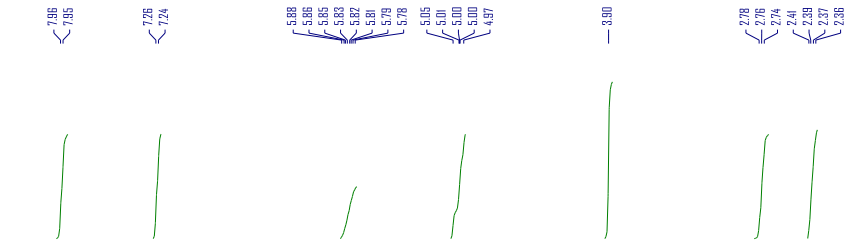

2.03
2.12
1.00
2.05
2.02
2.03
f1 (ppm)

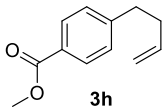
147.44
138.88
132.14
129.28
119.11
115.76
109.74
35.42
34.83


N

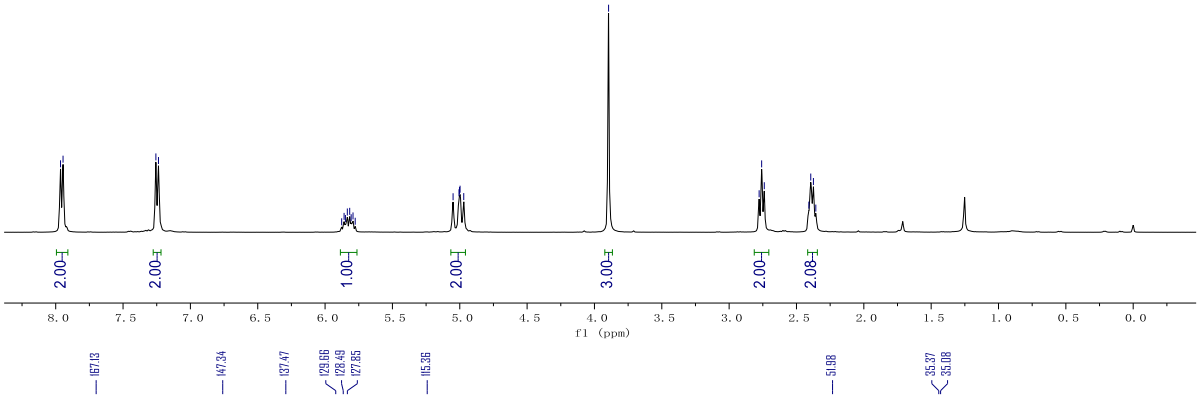
3g


f1 (ppm)

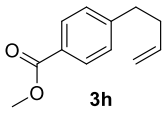

7.96
7.95
7.26
7.24
5.88
5.86
5.85
5.83
5.82
5.81
5.79
5.78
5.05
5.01
5.00
5.00
4.97
3.90
2.78
2.76
2.74
2.41
2.38
2.37
2.36


O
O

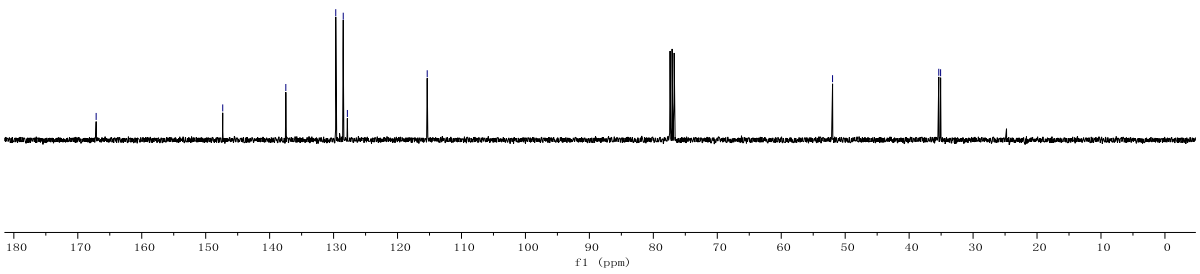
3h


2.00
2.00
1.00
2.00
3.00
2.00
2.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

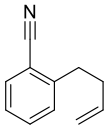
167.13
147.34
137.47
129.66
128.49
127.85
115.36
51.98
35.37
35.08


O
O

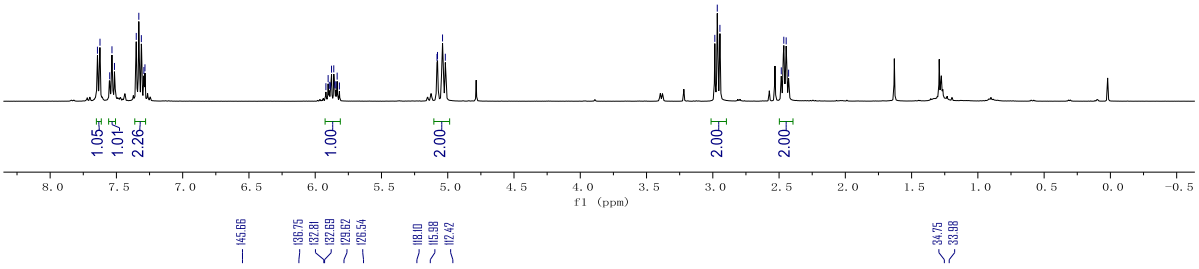
3h


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

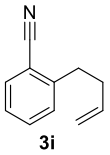

7.64
7.62
7.55
7.53
7.51
7.35
7.33
7.31
7.29
7.28
5.92
5.90
5.89
5.88
5.86
5.85
5.84
5.83
5.82
5.08
5.04
5.02
2.98
2.97
2.95
2.48
2.46
2.45
2.43


N

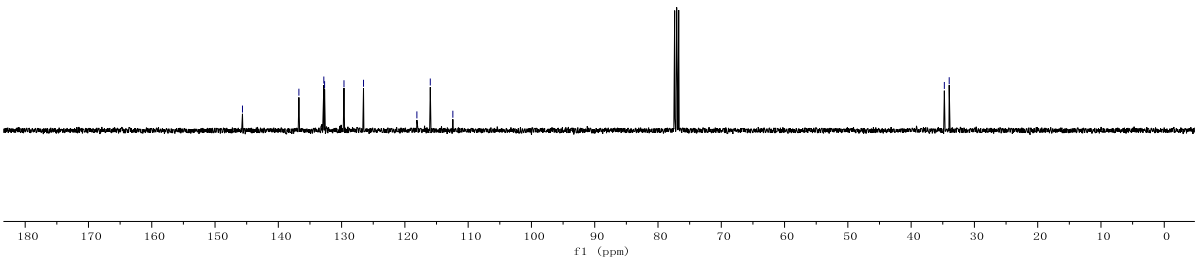
3i

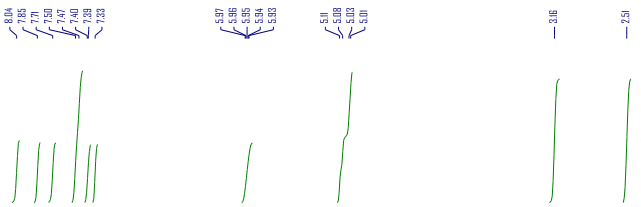

1.05
1.01
2.26
1.00
2.00
2.00
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

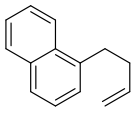
145.66
136.75
132.81
132.63
129.62
126.54
118.10
115.98
112.42
34.75
33.98


N

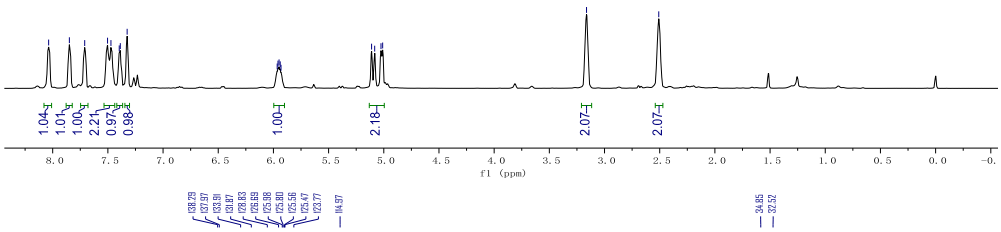
3i

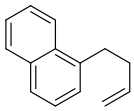

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



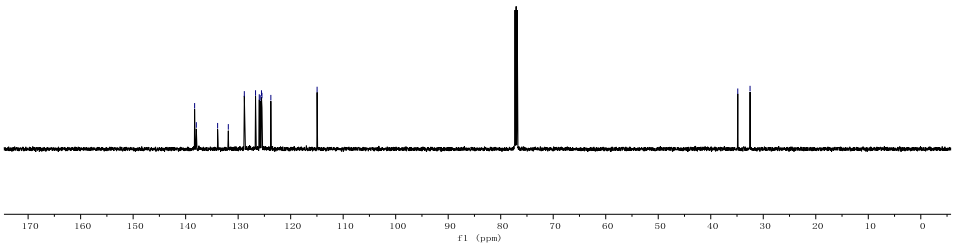


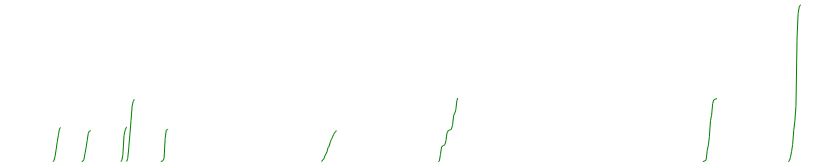
3j

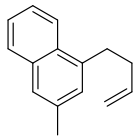




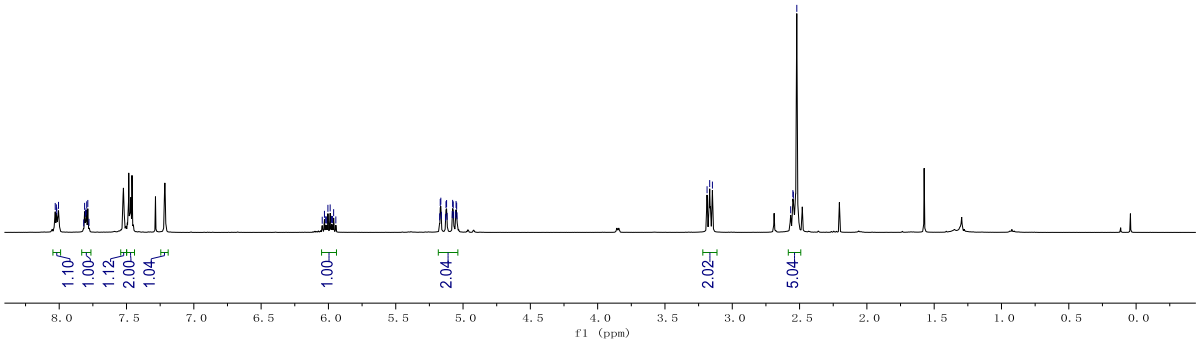
3j

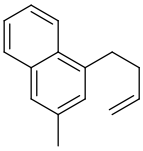




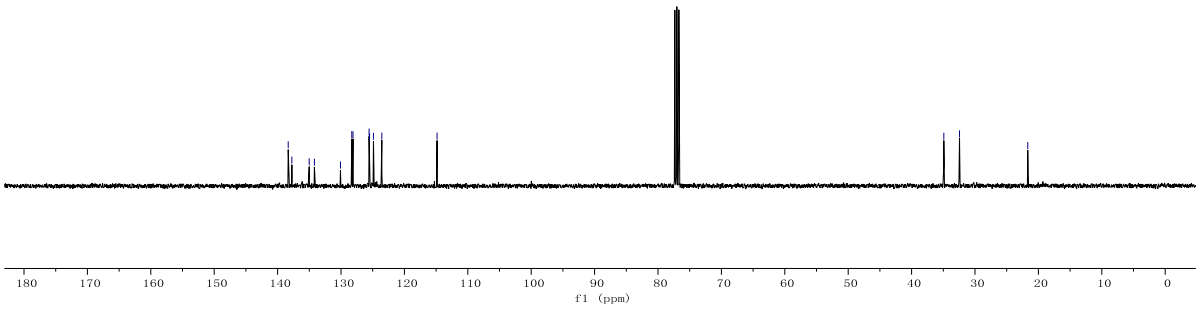


3k

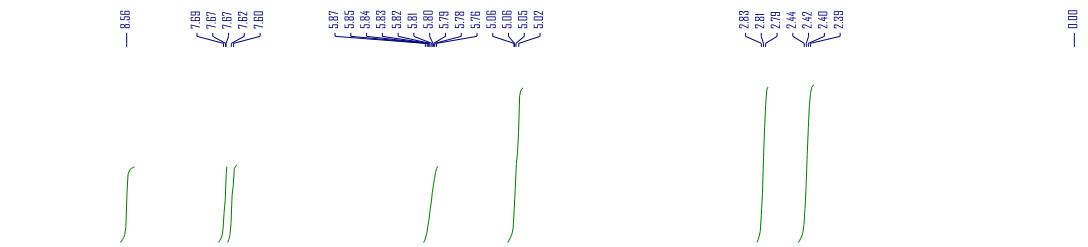


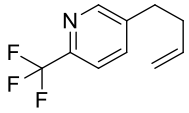


3k

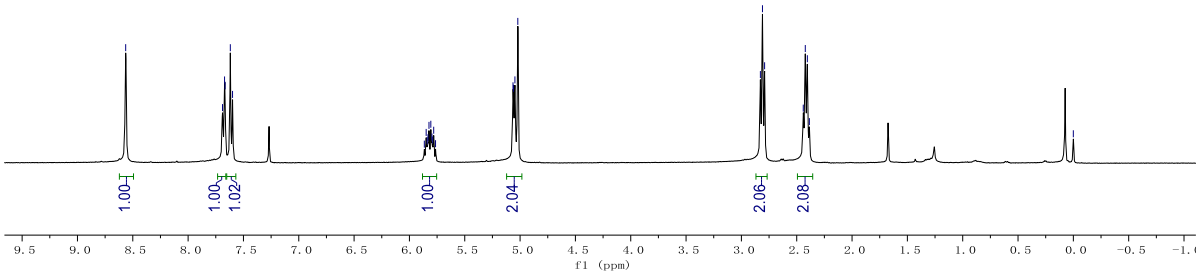


S28

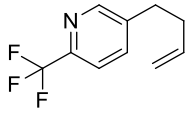

8.56
7.69
7.67
7.67
7.62
7.60
5.87
5.85
5.84
5.83
5.82
5.81
5.80
5.79
5.78
5.76
5.06
5.06
5.05
5.02
2.83
2.81
2.79
2.44
2.42
2.40
2.39
0.00


N
F
F
F

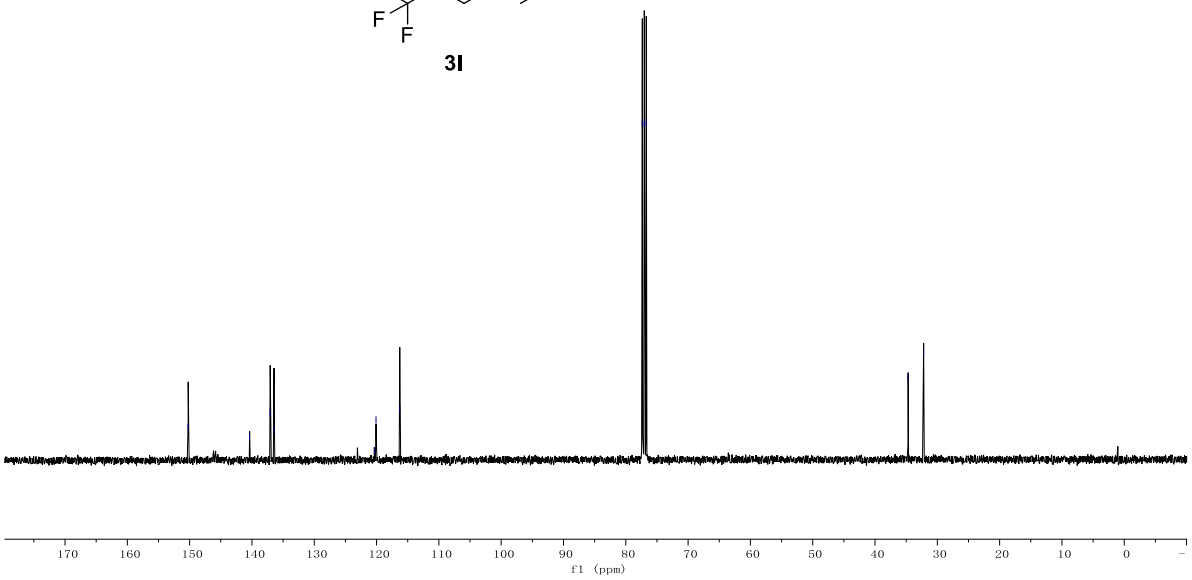
3l

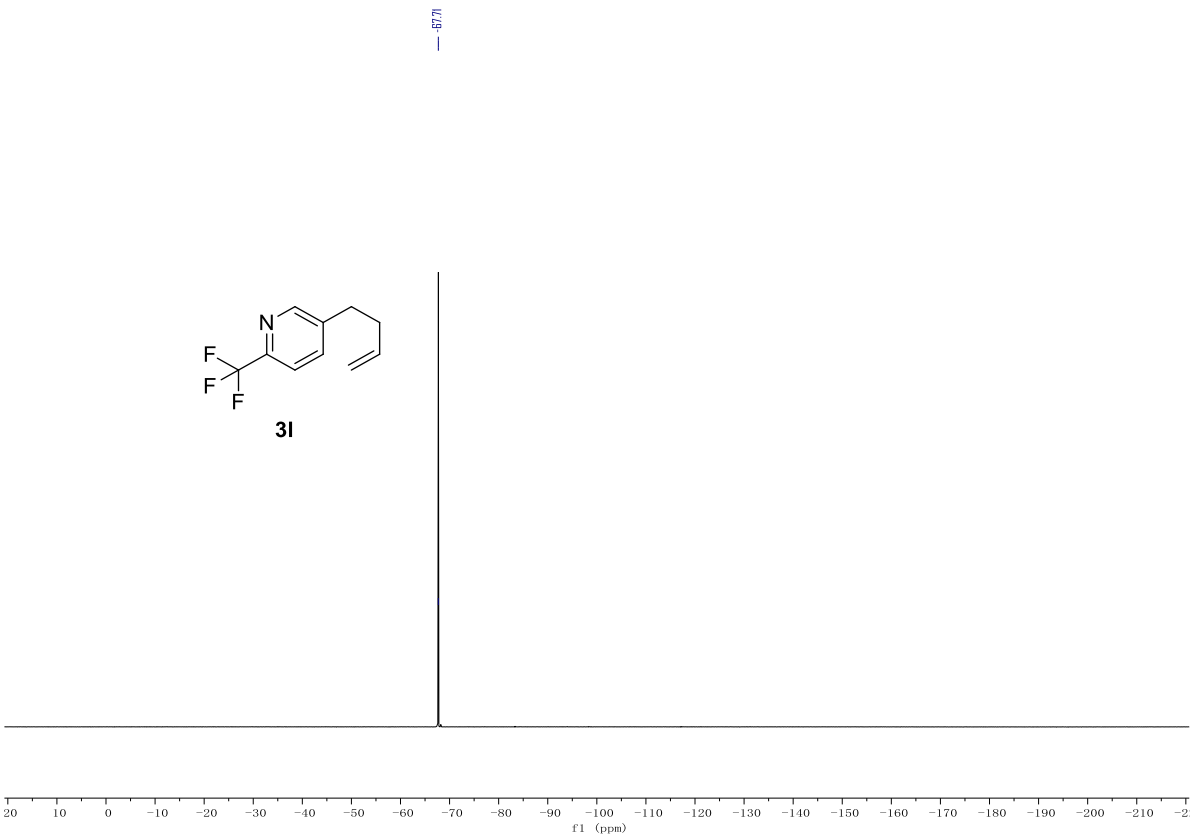

1.00
1.00
1.02
1.00
2.04
2.06
2.08
f1 (ppm)

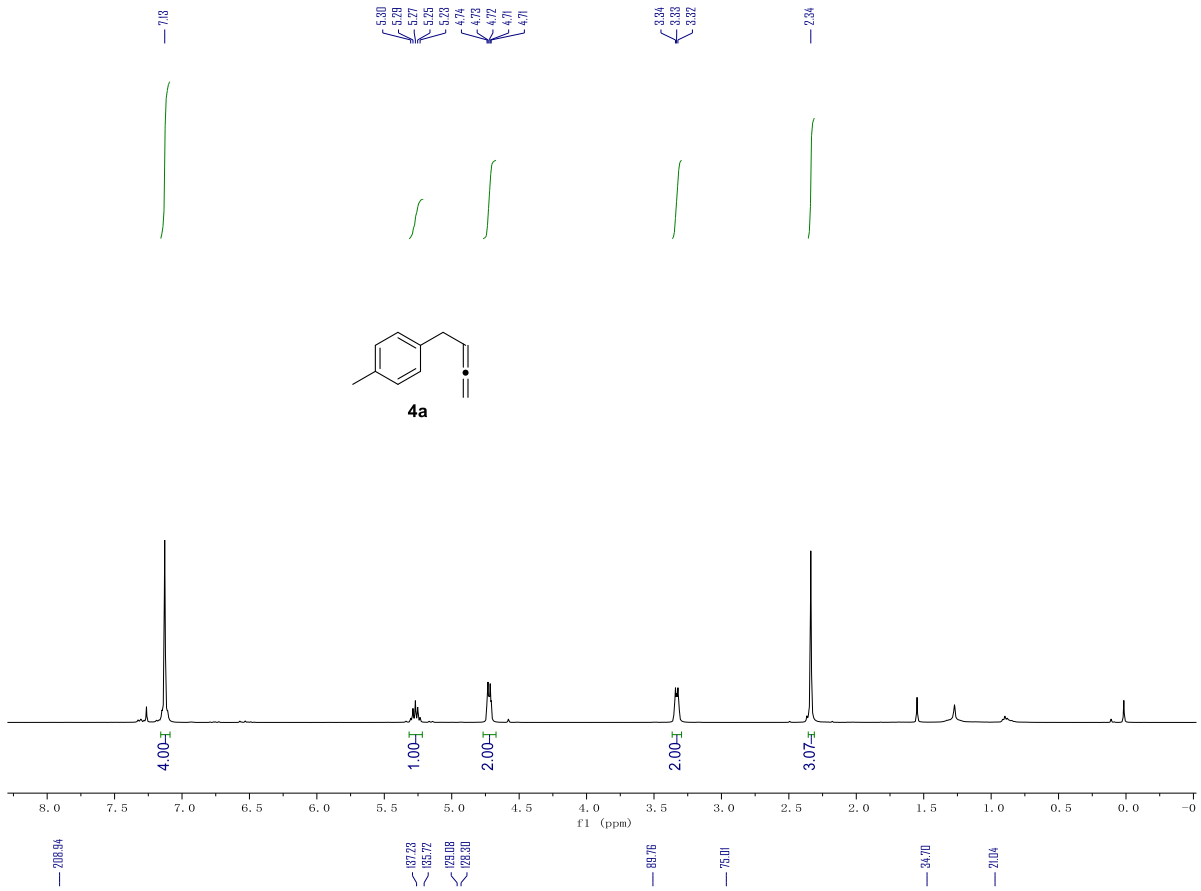

150.25
140.39
137.09
136.47
120.36
120.09
116.29
77.36
77.04
76.72
34.69
32.20


N
F
F
F

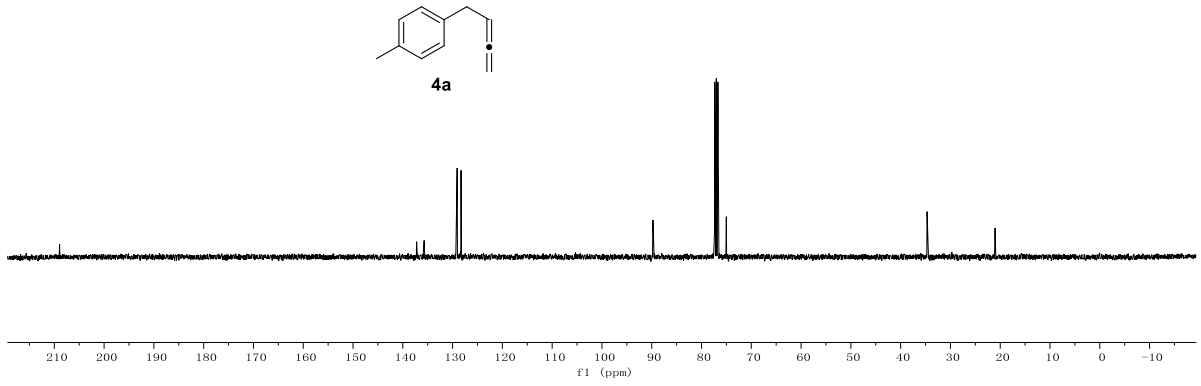
3l

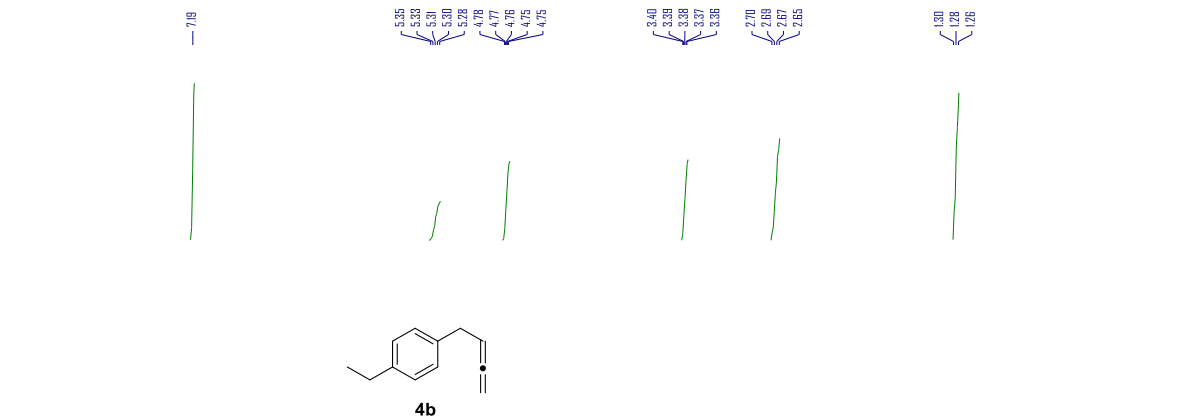

f1 (ppm)


-67.71
N
F
F
F
3l
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

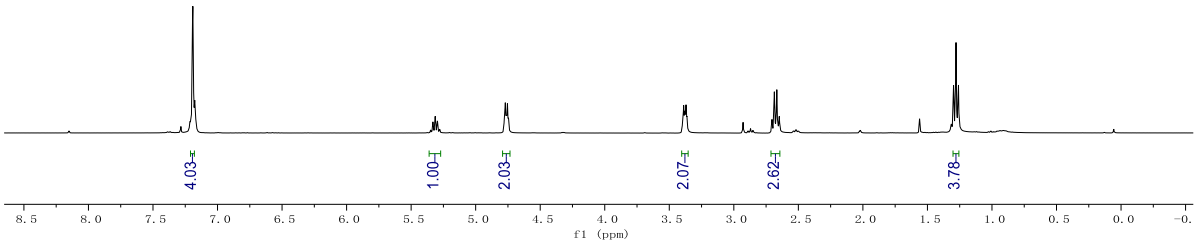

7.18
5.30
5.29
5.27
5.25
5.23
4.74
4.73
4.72
4.71
4.71
3.34
3.33
3.32
2.34
4a
4.00
1.00
2.00
2.00
3.07
f1 (ppm)

208.94
137.23
135.72
129.08
128.30
89.76
75.01
34.70
21.04

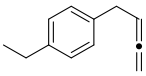

4a
f1 (ppm)


7.19
5.35
5.33
5.31
5.30
5.28
4.78
4.77
4.76
4.75
4.75
3.40
3.39
3.38
3.37
3.36
2.70
2.69
2.67
2.65
1.30
1.28
1.26

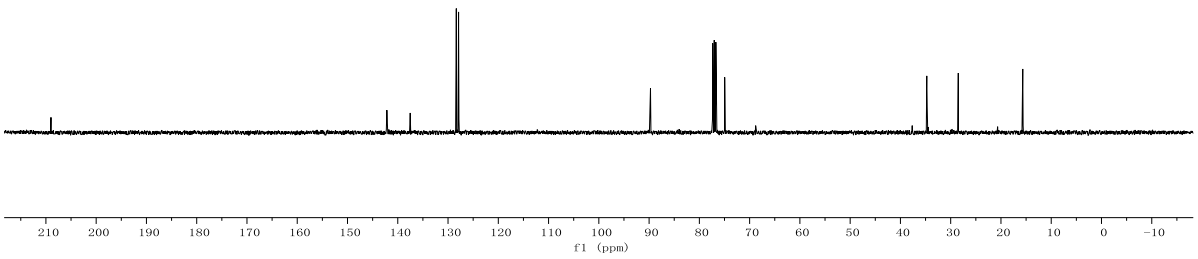
4b

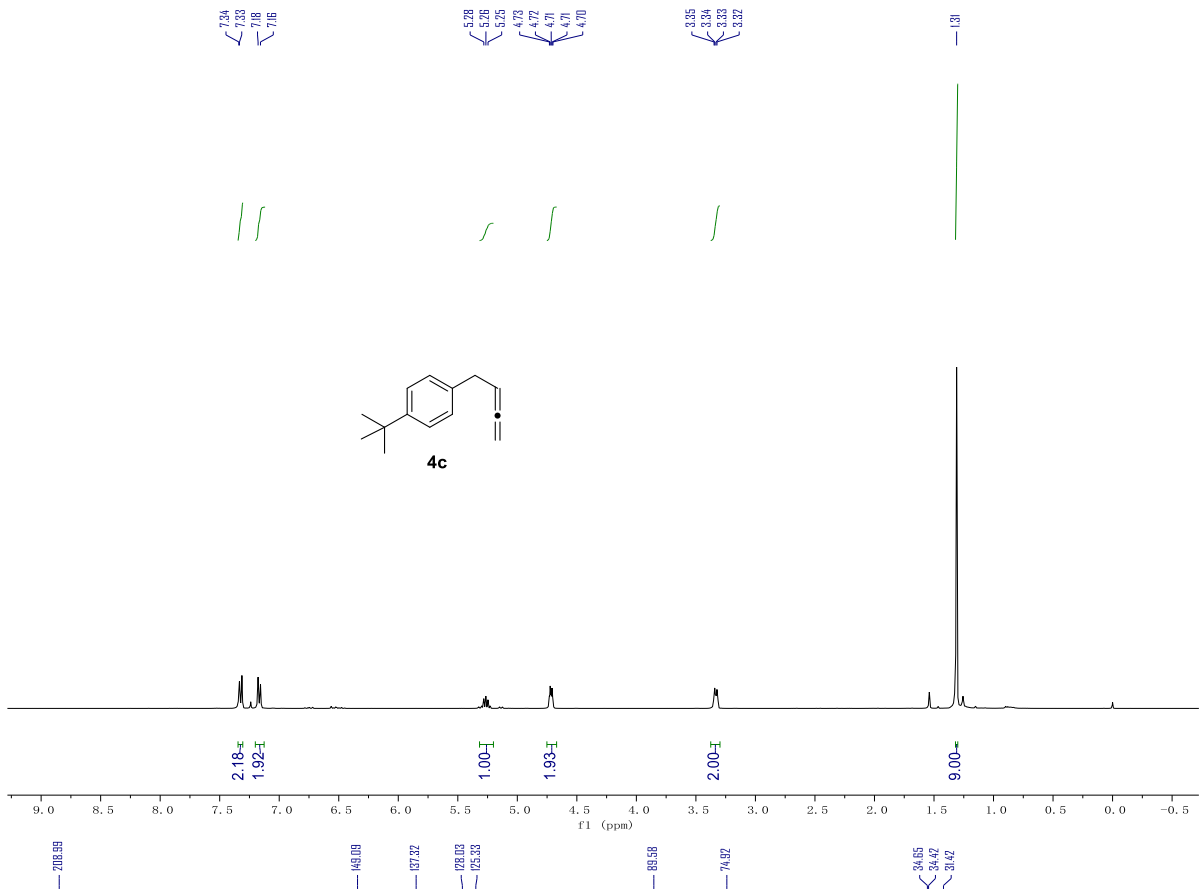

4.03
1.00
2.03
2.07
2.62
3.78
f1 (ppm)

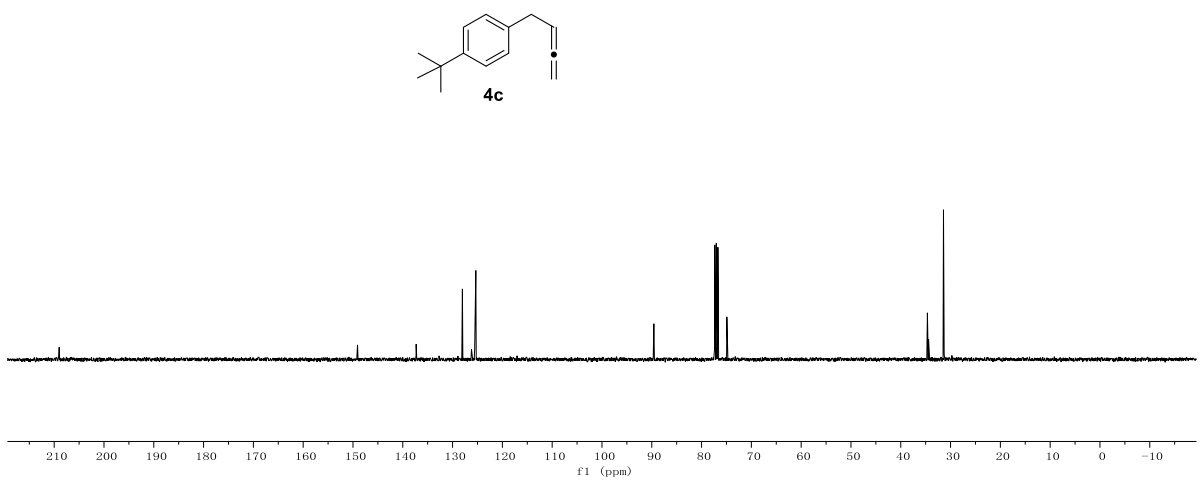

208.89
142.17
137.53
128.35
127.90
89.72
74.96
34.76
28.49
15.66

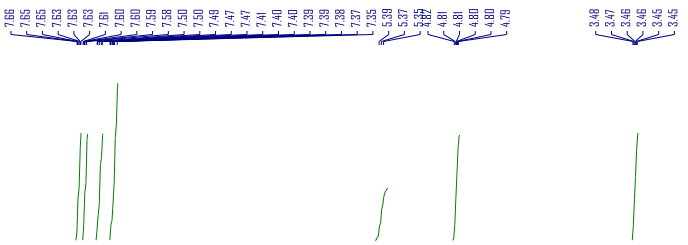


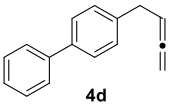
4b


f1 (ppm)

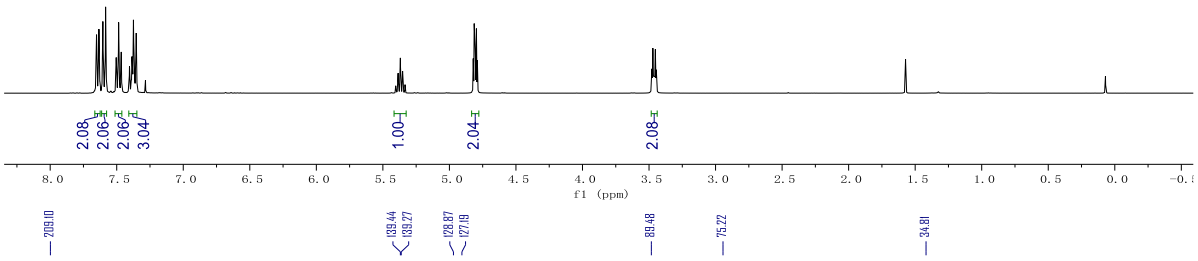

7.34
7.33
7.18
7.16
5.28
5.26
5.25
4.73
4.72
4.71
4.71
4.70
3.35
3.34
3.33
3.32
1.31
4c
2.18
1.92
1.00
1.93
2.00
9.00
f1 (ppm)

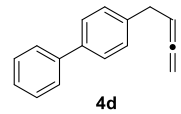

208.99
149.09
137.32
128.03
125.33
89.58
74.92
34.65
34.42
31.42
4c
f1 (ppm)



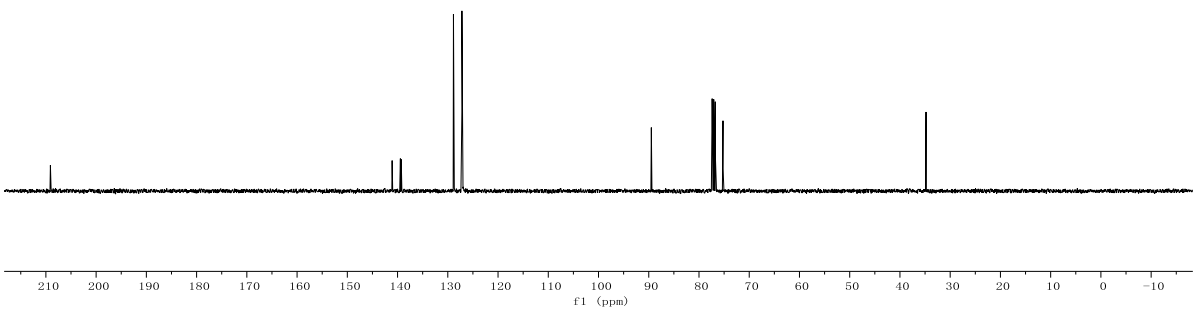


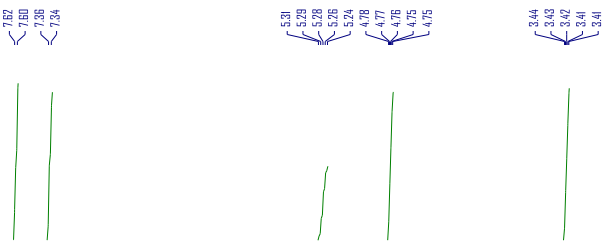
4d

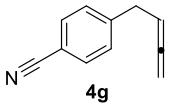




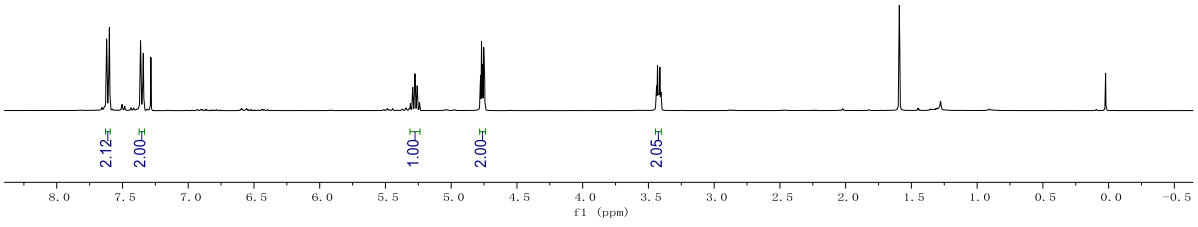
4d



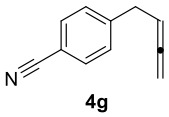

7.82
7.80
7.36
7.34
5.31
5.29
5.28
5.26
5.24
4.78
4.77
4.76
4.75
4.75
3.44
3.43
3.42
3.41
3.41



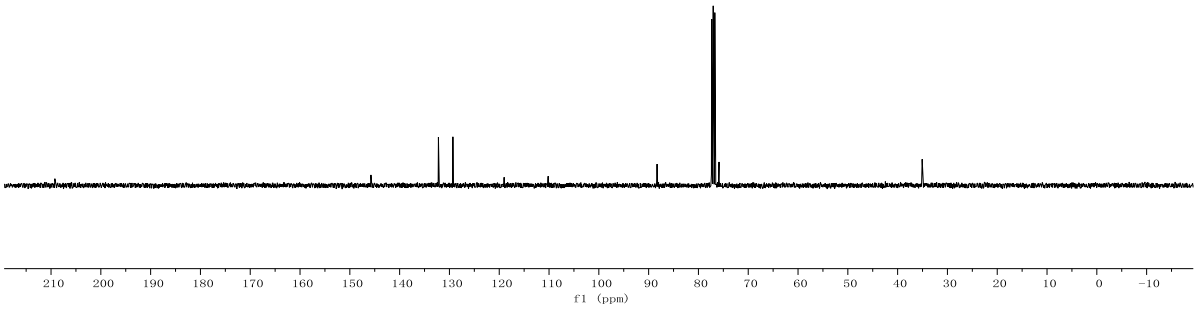
4g

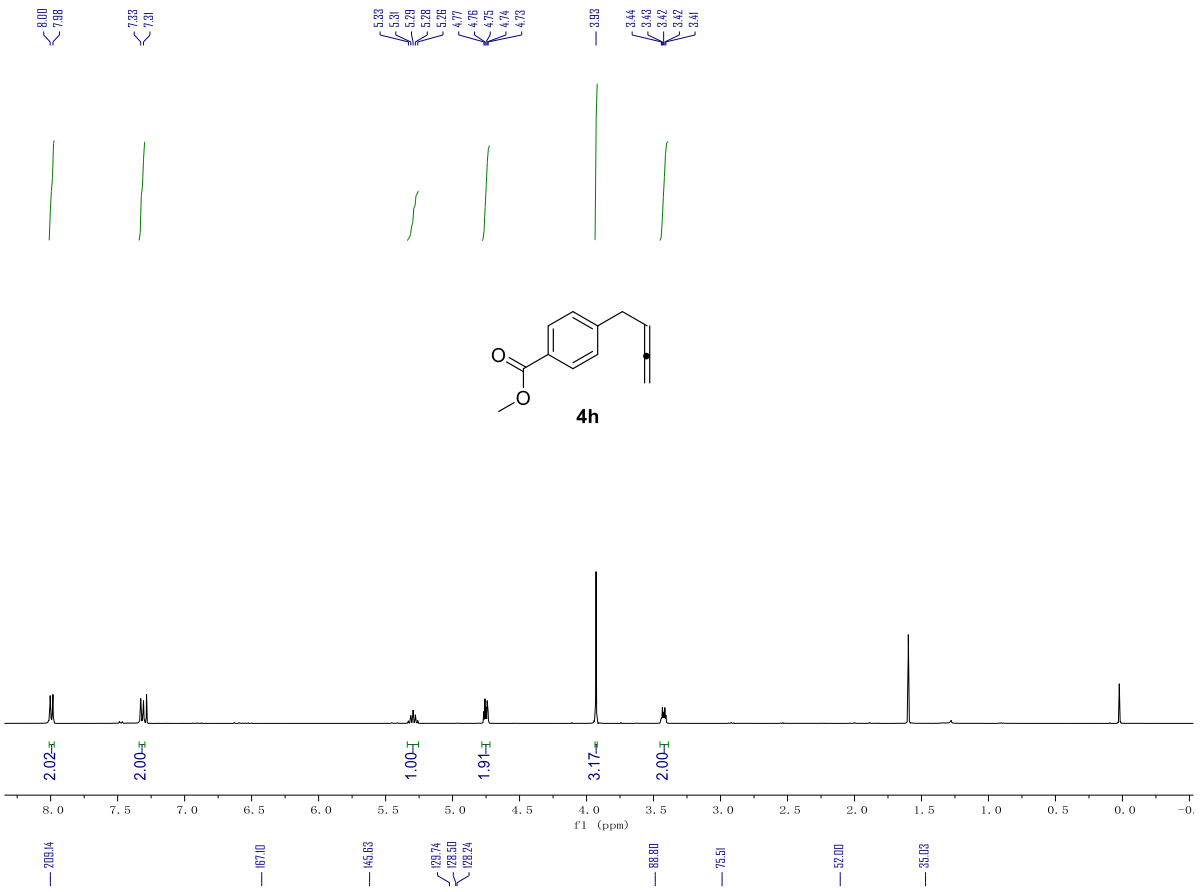

2.12
2.00
1.00
2.00
2.05
f1 (ppm)

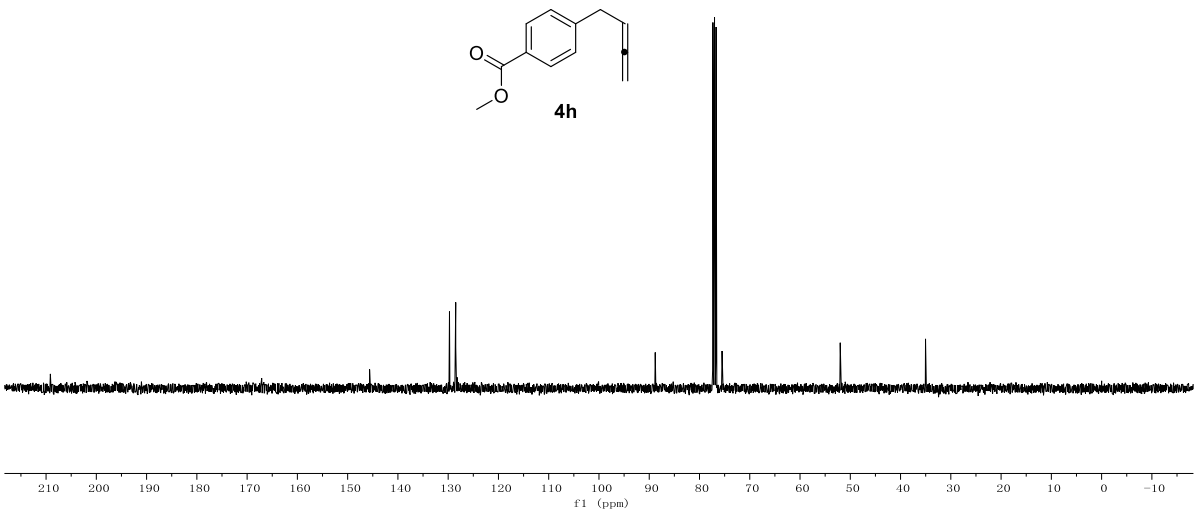

209.23
145.76
132.21
129.58
119.02
110.18
88.31
75.87
35.07

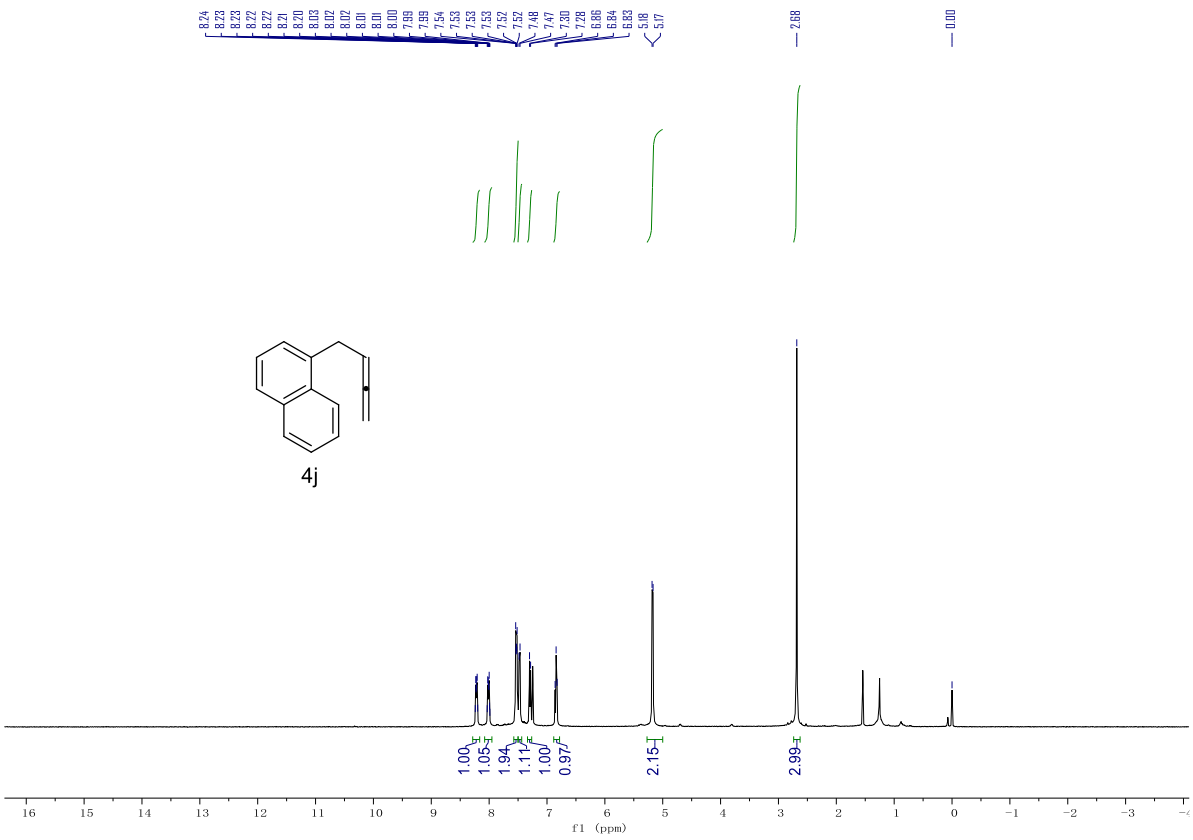


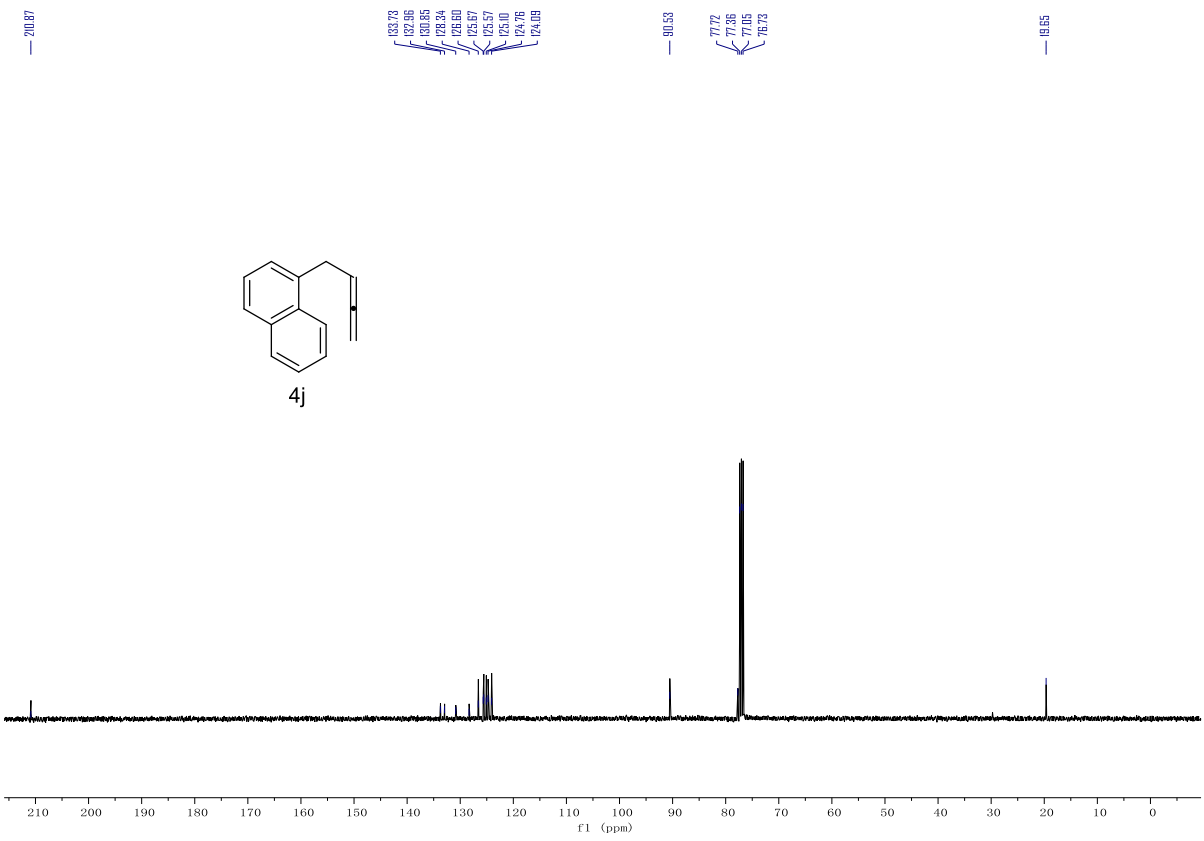
4g

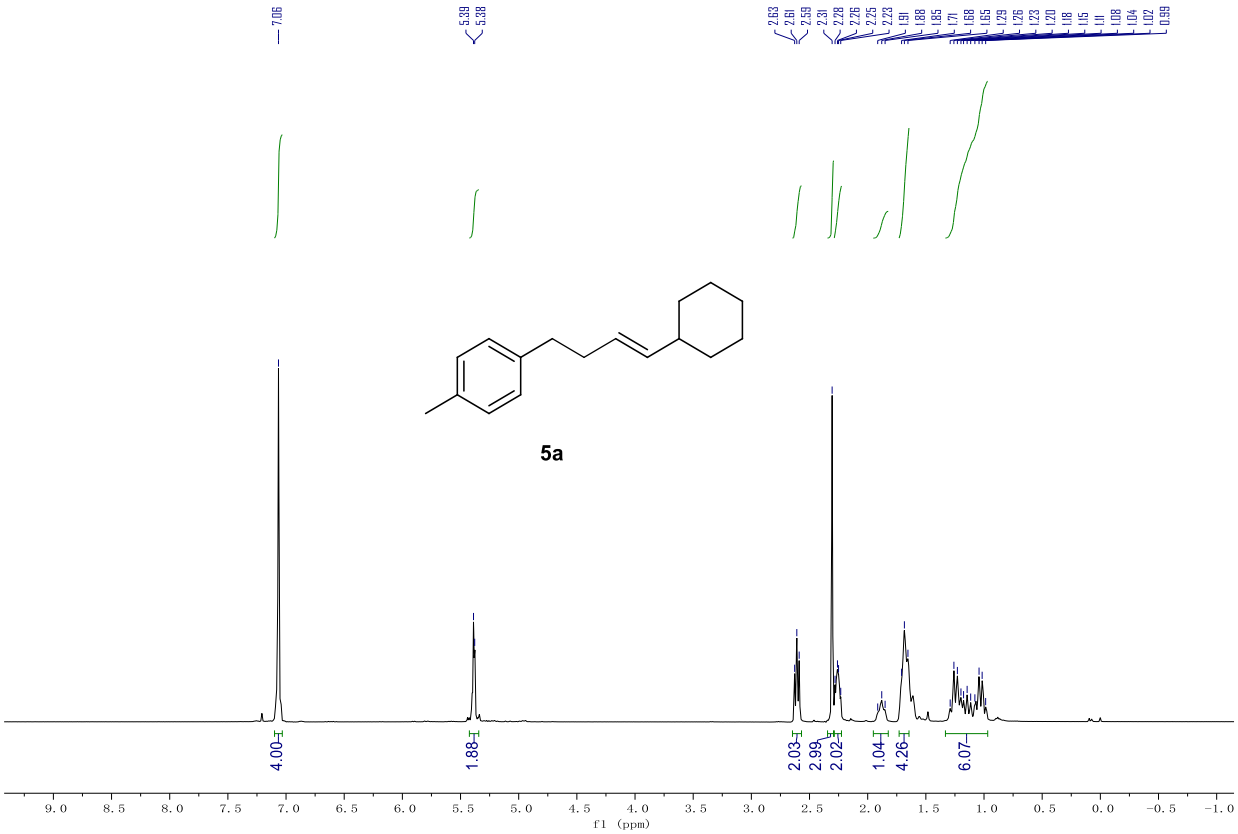

f1 (ppm)


8.00
7.98
7.33
7.31
5.33
5.31
5.29
5.28
5.26
4.77
4.76
4.75
4.74
4.73
3.43
3.42
3.41
O
O
4h
2.02
2.00
1.00
1.91
3.17
2.00
f1 (ppm)

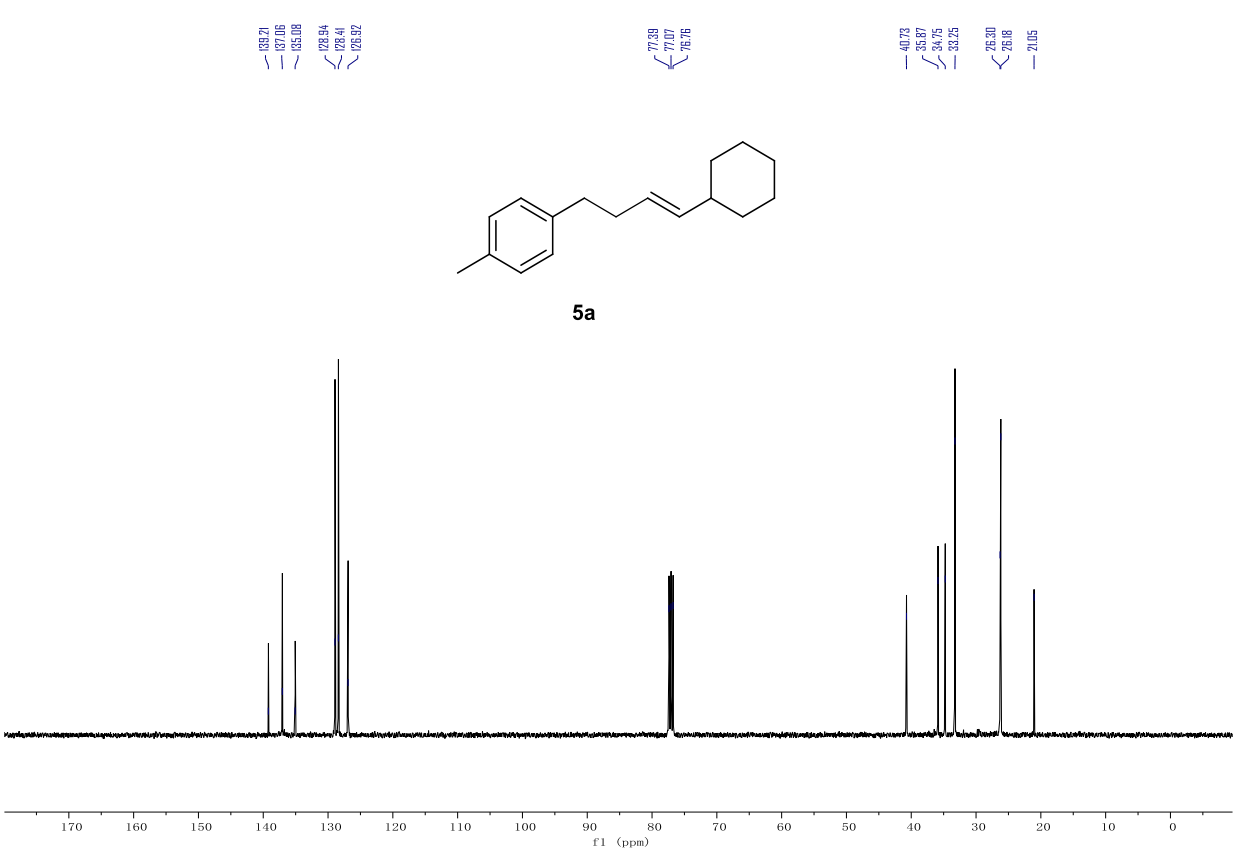

O
O
4h
f1 (ppm)


8.24
8.23
8.23
8.22
8.22
8.21
8.20
8.013
8.012
8.012
8.011
8.011
8.010
7.919
7.919
7.554
7.553
7.553
7.553
7.552
7.552
7.548
7.547
7.330
7.328
6.836
6.834
6.833
5.18
5.17
2.88
0.00
4j
1.00
1.05
1.94
1.11
1.00
0.97
2.15
2.99
f1 (ppm)


210.87
133.73
132.96
130.85
128.34
126.60
125.67
125.57
125.10
124.76
124.09
90.53
77.72
77.36
77.05
76.73
19.65
4j
f1 (ppm)

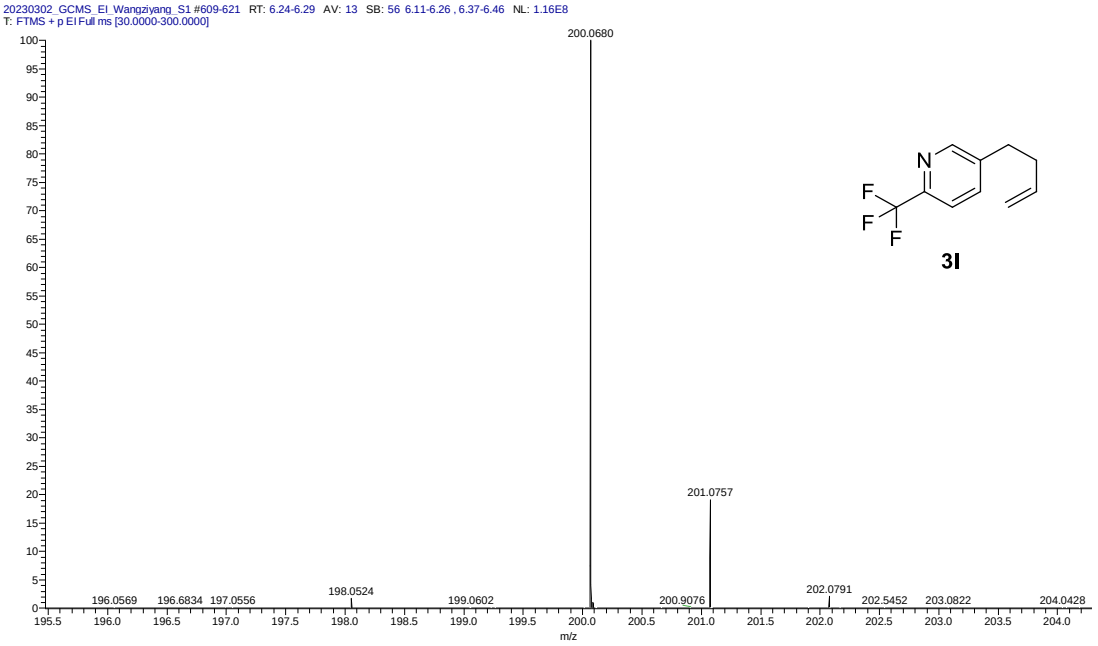

7.06
5.39
5.38
2.63
2.61
2.59
2.31
2.28
2.26
2.25
2.23
1.91
1.88
1.85
1.71
1.68
1.65
1.29
1.26
1.23
1.21
1.18
1.15
1.11
1.08
1.04
1.02
0.99
4.00
1.88
2.03
2.99
2.02
1.04
4.26
6.07
f1 (ppm)

5a

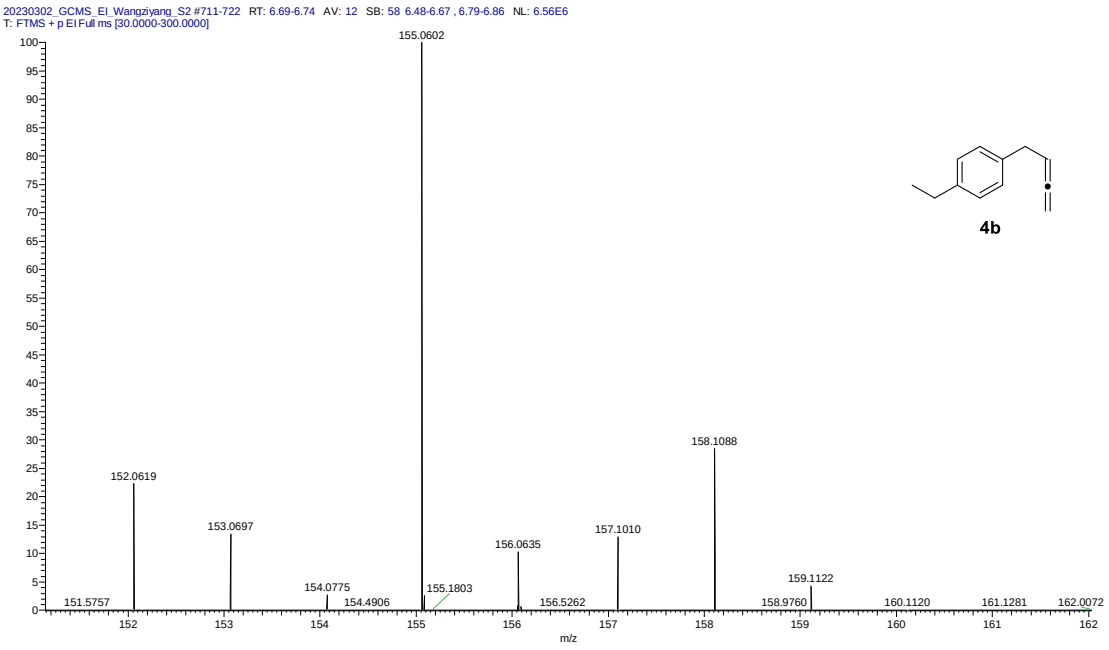

139.21
137.06
135.08
128.94
128.41
126.92
77.39
77.07
76.76
40.73
35.87
34.75
33.25
26.30
26.18
21.05
f1 (ppm)

5a

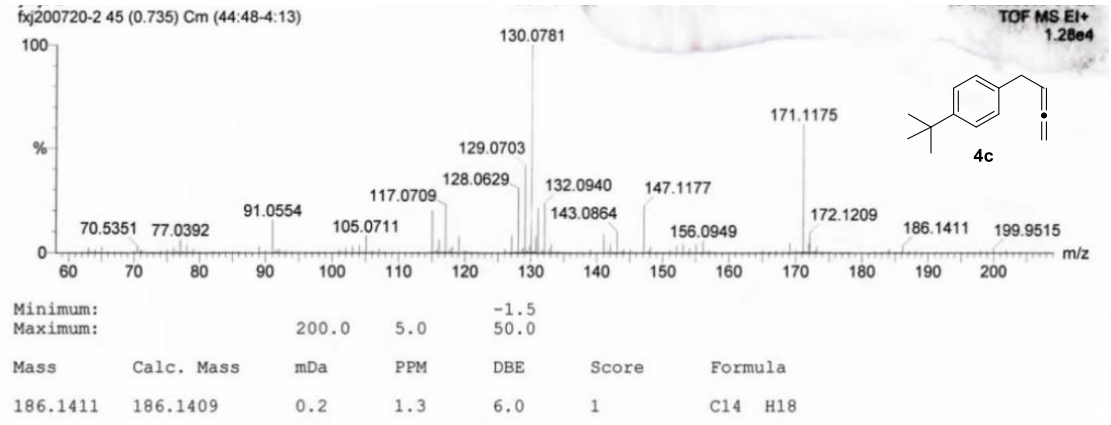
10. Copies of HR MS of Products



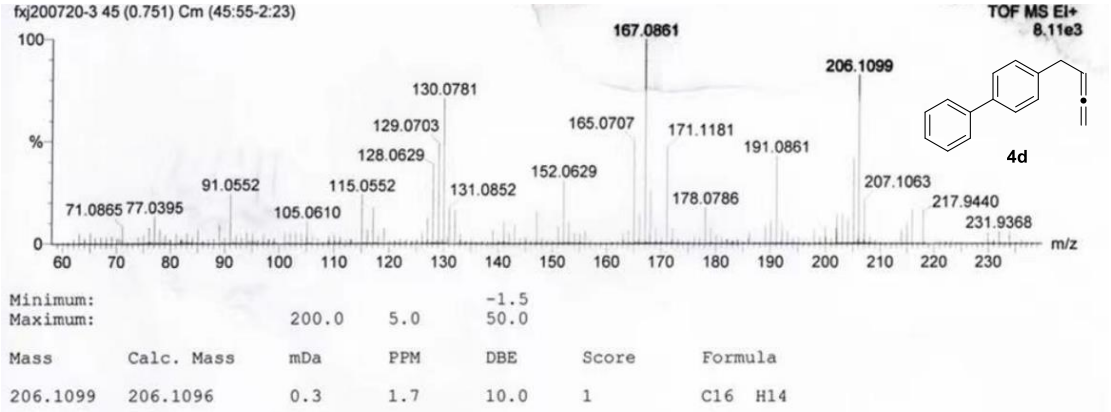
HRMS (EI) calcd for $C_{10}H_{10}F_3N$: 201.0765 $[M]^+$; found: 201.0757.



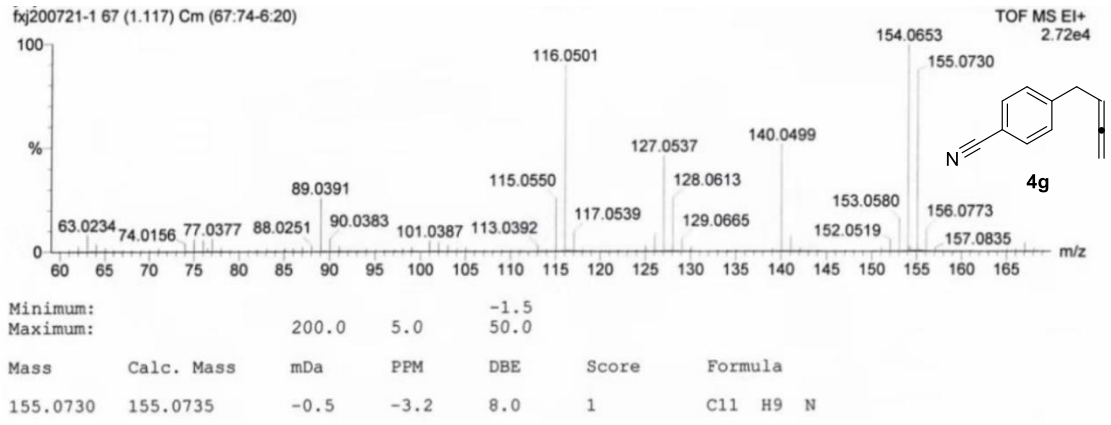
HRMS (EI) calcd for $C_{12}H_{14}$: 158.1096 $[M]^+$; found: 158.1094.



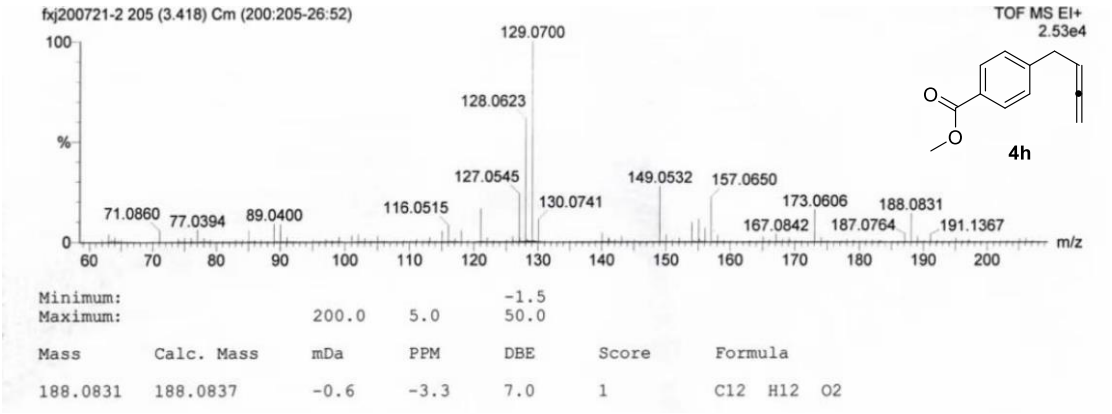
HRMS (EI) calcd for $C_{14}H_{18}$: 186.1409 $[M]^+$; found: 186.1411.



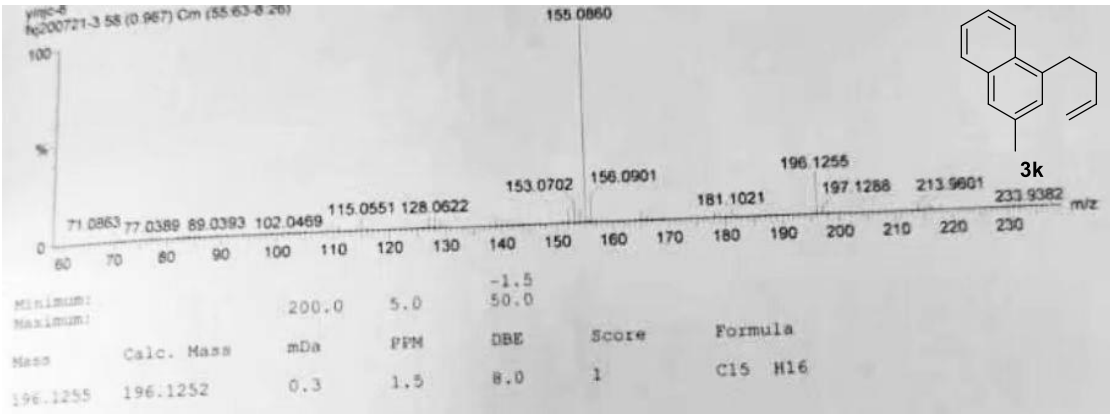
HRMS (EI) calcd for $C_{16}H_{14}$: 206.1096 $[M]^+$; found: 206.1099.



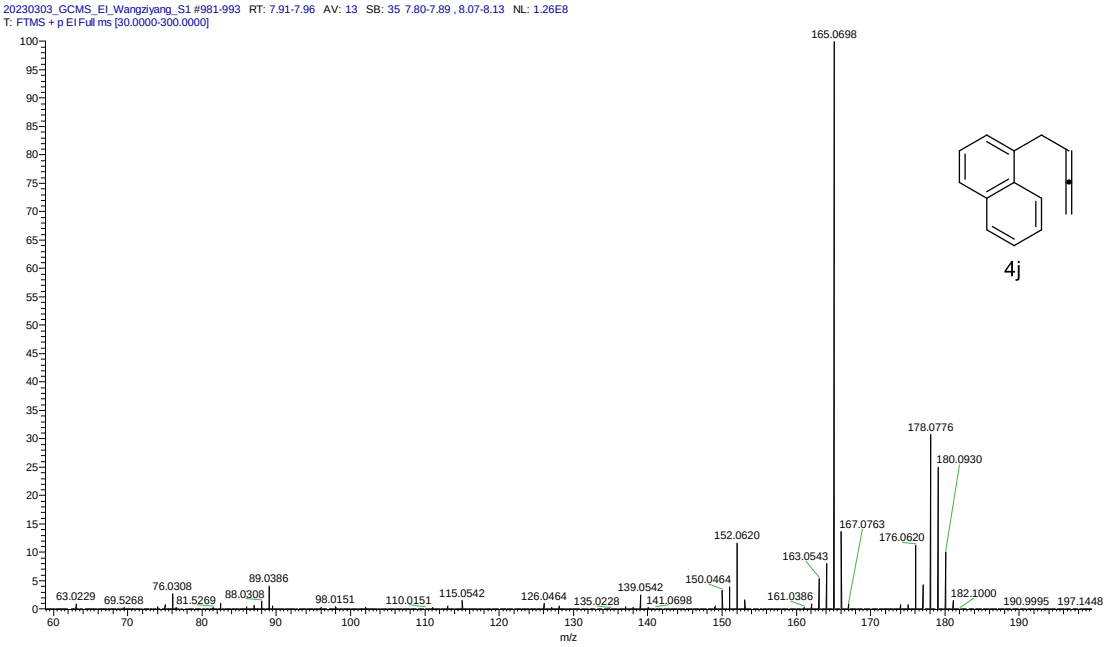
HRMS (EI) calcd for $C_{11}H_9N$: 155.0735 $[M]^+$; found: 155.0730.



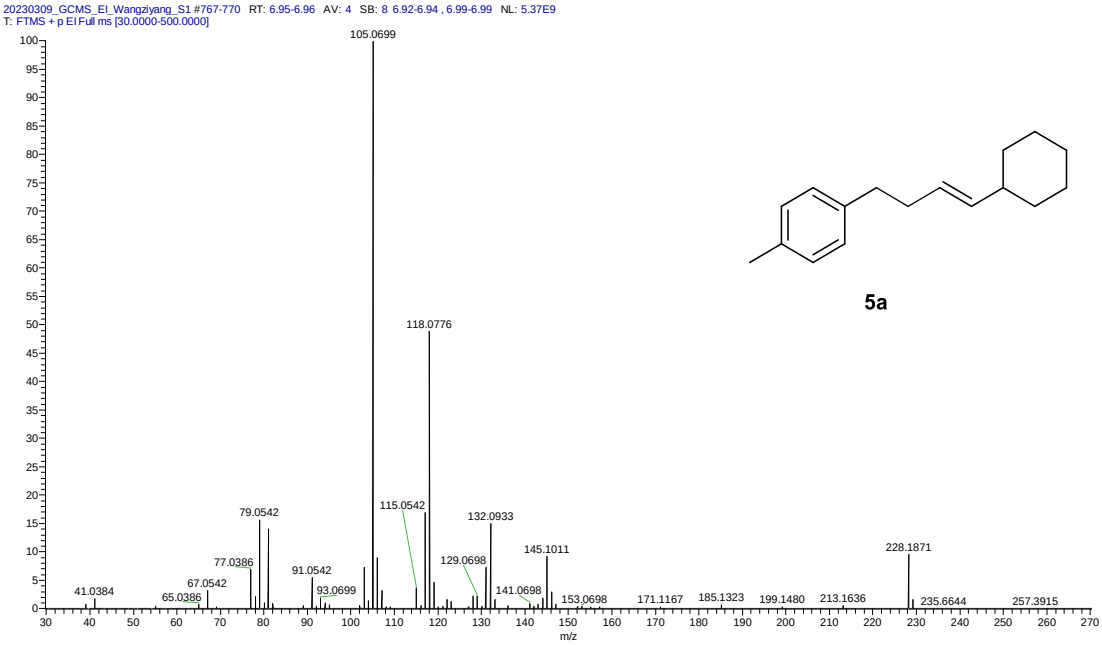
HRMS (EI) calcd for $C_{12}H_{12}O_2$: 188.0837 $[M]^+$; found: 188.0831.



HRMS (EI) calcd for $C_{15}H_{16}$: 196.1252 $[M]^+$; found: 196.1255.



HRMS (EI) calcd for $C_{14}H_{12}$: 180.0939 $[M]^+$; found: 180.0930.



HRMS (EI) calcd for $C_{17}H_{24}$: 228.1878. $[M]^+$; found: 228.1871.