Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Nickel-Catalyzed Defluorinative Alkylation of C(sp^2)-F Bonds

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General Information

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an nitrogen atmosphere or in a glovebox under a nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed on Merk TLC silica gel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating using hot air gun.

Proton, carbon and fluorine nuclear magnetic resonance spectra (^1H, ^{13}C, and ^{19}F NMR were recorded on a Bruke-400M Advance III (^1H NMR, 400 MHz; ^{13}C NMR, 101 MHz; ^{19}F NMR, 376 MHz) spectrometer with solvent resonance as the internal standard (^1H NMR, $CDCl_3$ at 7.26 ppm; ^{13}C NMR, 77.0 ppm). NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. GC-MS data was obtained using electron ionization (Agilent 7890B-5977A). GC data was performed on a Nexis GC 2030. High resolution mass spectra were obtained with Waters Xevo G2-Xs QTof (ESI or APCI).

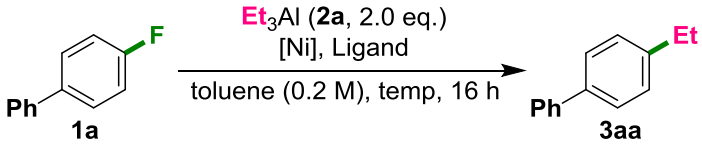
All the commercially available materials were used without further purification. $Ni(COD)_2$ was purchased from Laajoo Chemicals. 1,2-Bis(diphenylphosphino)-benzene (DPPBz), trialkylaluminum reagents and other anhydrous solvents (1,4-dioxane, THF, DMF and DCE) were purchased from Beijing Inno-chem Science & Technology Company Ltd. Anhydrous toluene was distilled from sodium benzophenone ketyl.

Aryl fluorides were purchased from Beijing Inno-chem Science & Technology Company Ltd. and used as received or were prepared by following the literature procedures. All vinyl monofluorides and vinyl *gem*-difluorides were synthesized according to the literature precedents.[1-2]

Flash chromatography was performed with Haiyang Chem silica gel 60 (300-400 mesh). Thin layer chromatography was carried out using CCIS TLC Silica gel 60 F254.

Optimization studies

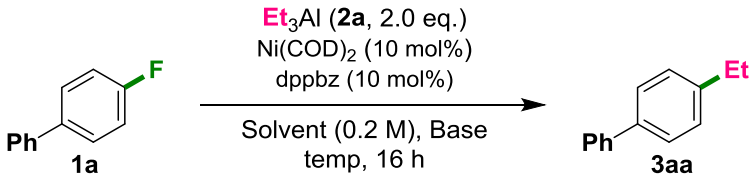
Table S1. Optimization of ligands and nickel catalysts.[a]



Entry	[Ni]	Ligand	temp (°C)[b]	Yield (%) of **3aa**[c]
1	$Ni(COD)_2$	dppm	100	0
2	$Ni(COD)_2$	dppe	100	49
3	$Ni(COD)_2$	dpppr	100	84
4	$Ni(COD)_2$	dppent	100	36
5	$Ni(COD)_2$	dppf	100	69
6	$Ni(COD)_2$	PPh_3	100	17
7	$Ni(COD)_2$	dppbz	100	88(86)[d]
8	$Ni(COD)_2$	*rac*-BINAP	100	75
9	$Ni(COD)_2$	^{t}BuXphos	100	5
10	$Ni(COD)_2$	dcype	100	86
11	$Ni(COD)_2$	PCy_3	100	27
12	$NiCl_2$	dppbz	100	0
13	$Ni(acac)_2$	dppbz	100	0

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Ni(COD)_2$ (10 mol%), dppbz (10 mol%), toluene (0.5 mL; 0.2 M) at 100 °C for 16 h, under N_2. [b] Corrected temperature. [c] GC yields using decane as an internal standard. [d] Isolated yield.

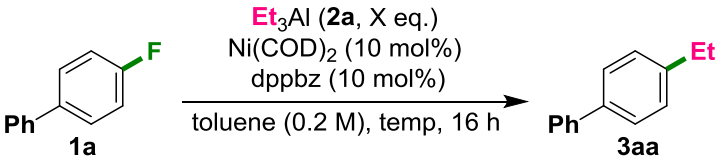
Table S2. Optimization of solvents and additives.[a]



Entry	Solvent	Additive (2.0 eq.)	temp (^{o}C)[b]	Yield (%) of **3aa**[c]
1	toluene	-	100	88(86)[d]
2	1,4-dioxane	-	100	8
3	DMF	-	100	3
4	THF	-	100	3
5	DCE	-	100	0
6	toluene	CsF	100	23
7	toluene	KF	100	26
8	toluene	^{t}BuOK	100	52
9	toluene	Cs_2CO_3	100	0

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Ni(COD)_2$ (10 mol%), dppbz (10 mol%), toluene (0.5 mL; 0.2 M) at 100 ^{o}C for 16 h, under N_2. [b] Corrected temperature. [c] GC yields using decane as an internal standard. DMF = *N*,*N*-Dimethylformamide; THF = Tetrahydrofuran; DCE = 1,2-Dichloroethane. [d] Isolated yield.

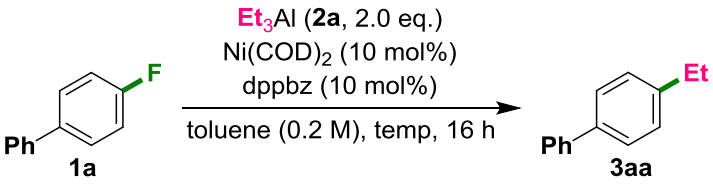
Table S3. Optimization of stoichiometry of reactants 2a and reaction time.[a]



Entry	X	temp (^{o}C)[b]	Yield (%) of **3aa**[c]
1	2.0	100	88(86)[d]
2	1.5	100	76
3	1.0	100	46
4	0.5	100	32
5[e]	2.0	100	67
6[f]	2.0	100	62

[a] Reaction conditions: 1a (0.1 mmol), 2a (0.2 mmol), $Ni(COD)_2$ (10 mol%), dppbz (10 mol%), toluene (0.5 mL; 0.2 M) at 100 ^{o}C for 16 h, under Ar. [b] Corrected temperature. [c] GC yields using decane as an internal standard. [d] Isolated yield. [e] The reaction time is 12 h. [f] The reaction time is 6 h.

Table S4. Optimization of reaction concentration and temperature.[a]



Entry	temp (°C)[b]	Yield (%) of **3aa**[c]
1	100	88(86)[d]
2[e]	100	79
3[f]	100	64
4	90	78
5	110	72

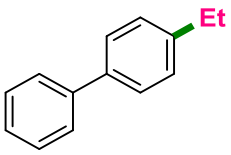
[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Ni(COD)_2$ (10 mol%), dppbz (10 mol%), toluene (0.5 mL; 0.2 M) at 100 °C for 16 h, under N_2. [b] Corrected temperature. [c] GC yields using decane as an internal standard. [d] Isolated yield. [e] 0.25 mL of toluene was used. [e] 1.0 mL of toluene was used.

General Procedure for Nickel catalyzed C–F alkylation with Trialkyl aluminum

An oven dried Schlenk tube containing a stirring bar was charged with aryl fluoride **1** (0.20 mmol, 1.0 eq.). The tube was introduced in nitrogen-filled glovebox and $Ni(COD)_2$ (5.4 mg, 10 mol %), dppbz (8.9 mg, 10 mol %), Toluene (1.0 mL) and Triethylaluminum or Trimethylaluminum **2a** (0.1 mL, 0.40 mmol, 2.0 eq.) were then added. The tube with the mixture was taken out of the glovebox and stirred at 100 ℃ for 16 h. The mixture was then allowed to warm to room temperature, the mixture was diluted with EtOAc (3 mL), concentrated under reduced pressure and purified by column chromatography on silica gel to afford the corresponding final product **3aa**.

Characterization Data

4-Ethyl-1,1'-biphenyl



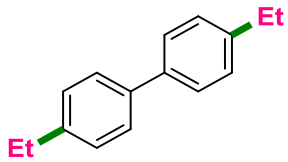
3aa

Isolated yield: 91%

Colorless viscous liquid. This compound is known in the literature.[3] **^{1}H NMR** (400

MHz, $CDCl_3$) δ 7.58 (d, J = 7.9 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.35 – 7.25 (m, 3H), 2.70 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 143.45, 141.26, 138.68, 128.78, 128.37, 127.16, 127.09, 127.04, 28.61, 15.69.

4,4'-Diethylbiphenyl

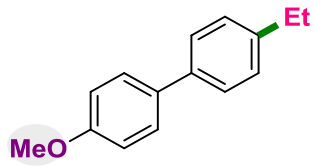


3ba

Isolated yield: 89%

Colorless viscous liquid. This compound is known in the literature.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 4H), 7.28 (d, *J* = 8.1 Hz, 4H), 2.71 (q, *J* = 7.6 Hz, 4H), 1.30 (t, *J* = 7.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.08, 138.61, 128.25, 126.95, 28.53, 15.60.

4-Ethyl-4'-methoxy-1,1'-biphenyl

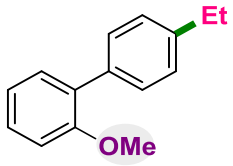


3ca

Isolated yield: 88%

Colorless viscous liquid. This compound is known in the literature.[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 4H), 7.29 – 7.22 (m, 2H) 6.97 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.95, 142.77, 138.25, 133.80, 128.28, 128.02, 126.69, 114.18, 55.35, 28.52, 15.67.

4'-ethyl-2-methoxy-1,1'-biphenyl

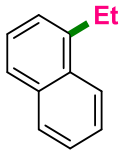


3da

Isolated yield: 84%

Colorless viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.24 (m, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.05 – 6.93 (m, 2H), 3.79 (s, 3H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.53, 142.91, 135.85, 130.88, 129.50, 128.40, 127.58, 120.84, 111.18, 55.56, 28.65, 15.55.
HRMS Calcd for $C_{15}H_{17}O^+$ $[M+H]^+$ 213.1274, found 213.1275.

1-Ethylnaphthalene

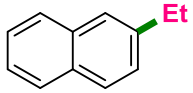


3ea

Isolated yield: 83%

Colorless Liquid. This compound is known in the literature.[6] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.38 (m, 3H), 7.34 (d, *J* = 7.0 Hz, 1H), 3.12 (q, *J* = 7.5 Hz, 2H), 1.38 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.28, 133.81, 131.77, 128.75, 126.39, 125.68, 125.39, 124.85, 123.74, 25.92, 15.07.

2-Ethylnaphthalene

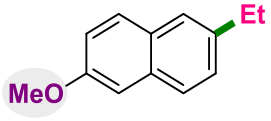


3fa

Isolated yield: 78%

Colorless liquid. This compound is known in the literature.[7] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 3H), 7.61 (s, 1H), 7.46 – 7.31 (m, 3H), 2.80 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.77, 133.69, 131.92, 127.79, 127.60, 127.41, 127.09, 125.83, 125.53, 125.01, 29.06, 15.55.

2-Ethyl-6-methoxynaphthalene

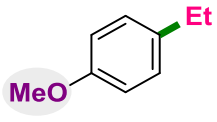


3ga

Isolated yield: 75%

Colorless liquid. This compound is known in the literature.[8] **^{1}H NMR** (400 MHz, $CDCl_3$) 7.70 – 7.64 (m, 2H), 7.55 (s, 1H), 7.31 (d, *J* = 10.0 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 3.90 (s, 3H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.06, 139.45, 132.88, 129.16, 128.90, 127.55, 126.68, 125.42, 118.59, 105.65, 55.29, 28.84, 15.64.

1-ethyl-4-methoxybenzene

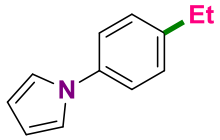


3ha

GC yield: 56%

Colorless liquid. This compound is known in the literature.[9] **^{1}H NMR** (400 MHz, $CDCl_3$) 7.11 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 3.78 (s, 3H), 2.59 (q, J = 7.6 Hz, 2H), 1.21 (t, J= 7.6 Hz, 3H).

1-(4-Ethylphenyl)-1H-pyrrole

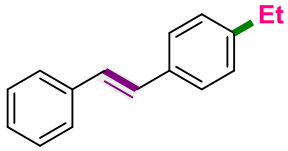


3ia

Isolated yield: 62%

Yellow viscous liquid. This compound is known in the literature.[10] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.06 (t, *J* = 2.1 Hz, 2H), 6.33 (t, *J* = 2.1 Hz, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.78, 138.66, 128.86, 120.65, 119.43, 110.04, 28.28, 15.63.

(E)-1-ethyl-4-styrylbezene

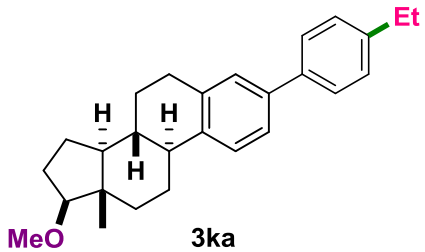


3ja

Isolated yield: 85%

Colorless viscous liquid. This compound is known in the literature.[11] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.10 (m, 3H), 7.01 (d, *J* = 3.2 Hz, 2H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.17 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.96, 137.58, 134.85, 128.67, 128.23, 127.81, 127.42, 126.54, 126.43, 28.67, 15.54.

(8R,9S,13S,14S)-3-(4-ethylphenyl)-17-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene



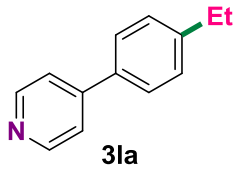
3ka

Isolated yield: 89%

Colorless viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.35 (s, 2H), 7.29 (s, 1H), 7.26 – 7.21 (m, 2H), 3.38 (s, 3H), 3.31 (t, *J* = 8.3 Hz, 1H), 2.97 – 2.89 (m, 2H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.39 – 2.21 (m, 2H), 2.14 – 2.00 (m, 2H), 1.96 – 1.86 (m, 1H), 1.76 – 1.31 (m, 8H), 1.27 (t, *J* = 7.6 Hz, 3H), 0.80 (s, 3H). **^{13}C NMR**

(101 MHz, $CDCl_3$) δ 143.07, 139.28, 138.55, 136.62, 128.68, 128.20, 127.59, 127.04, 126.53, 125.80, 124.31, 90.82, 57.94, 51.50, 44.36, 43.26, 38.46, 37.65, 29.72, 28.53, 27.79, 27.27, 26.30, 23.09, 15.60, 11.58. **HRMS** Calcd for $C_{27}H_{35}O^+$ $[M+H]^+$ 375.2682, found 375.2688.

4-(4-ethylphenyl)pyridine

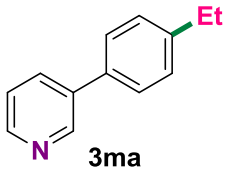


3la

Isolated yield: 80%

Colorless liquid. This compound is known in the literature.[12] **^{1}H NMR** (400 MHz, CDCl3) δ 8.64 (d, *J* = 5.2 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.54 – 7.47 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H).

3-(4-ethylphenyl)pyridine

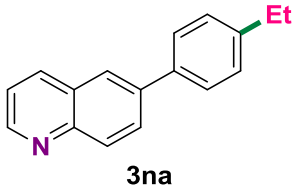


3ma

Isolated yield: 76%

Colorless liquid. This compound is known in the literature.[13] **^{1}H NMR** (400 MHz, CDCl3) δ 8.64 (d, *J* = 5.2 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.54 – 7.47 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H).

6-(4-ethylphenyl)quinoline



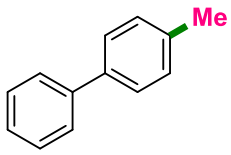
3na

Isolated yield: 89%

Colorless viscous liquid. **^{1}H NMR** (400 MHz, CDCl3) δ 8.64 (d, *J* = 5.2 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.54 – 7.47 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.72 (q, *J* = 7.6 Hz,

2H), 1.28 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.19, 147.61, 144.01, 139.30, 137.66, 136.19, 129.82, 129.22, 128.53, 127.38, 125.11, 121.41, 28.57, 15.58. **HRMS** Calcd for $C_{17}H_{16}N^+$ $[M+H]^+$ 234.1277, found 234.1278.

4-Methyl-1,1'-biphenyl

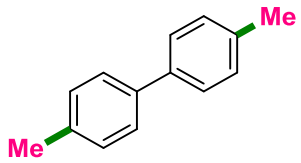


3ab

Isolated yield: 89%

Colorless viscous liquid. This compound is known in the literature.[14] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.0 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.15, 137.34, 135.99, 128.45, 127.68, 125.97, 125.95, 20.06.

4,4'-Dimethylbiphenyl

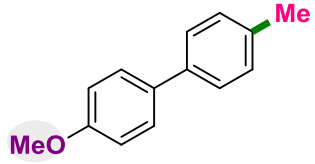


3bb

Isolated yield: 86%

Colorless viscous liquid. This compound is known in the literature.[15] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.59 (d, *J* = 8.1 Hz, 4H), 6.35 (d, *J* = 8.0 Hz, 4H), 1.50 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.31, 136.72, 129.45, 126.83, 21.10.

4-Methyl-4'-methoxy-1,1'-biphenyl

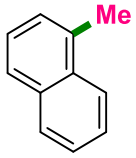


3cb

Isolated yield: 72%

Colorless viscous liquid. This compound is known in the literature.[16] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.95, 137.99, 136.37, 133.77, 129.45, 127.97, 126.60, 114.18, 55.36, 21.06.

1-Methylnaphthalene

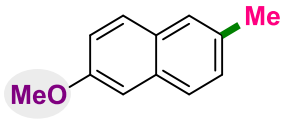


3eb

Isolated yield: 81%

Colorless liquid. This compound is known in the literature.[17] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 9.6 Hz, 1H), 7.92 – 7.85 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.45 – 7.34 (m, 2H), 2.74 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.30, 133.59, 132.66, 128.56, 126.60, 126.41, 125.75, 125.61, 125.58, 124.15, 19.42.

2-Methyl-6-methoxynaphthalene

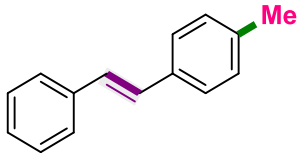


3gb

Isolated yield: 84%

Colorless liquid. This compound is known in the literature.[18] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.9, 3.2 Hz, 2H), 7.58 (s, 1H), 7.31 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.19 – 7.12 (m, 2H), 3.94 (s, 3H), 2.51 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.03, 133.04, 132.67, 129.17, 128.73, 128.60, 126.73, 126.59, 118.64, 105.68, 55.28, 21.47.

(*E*)-1-methyl-4-styrylbezene

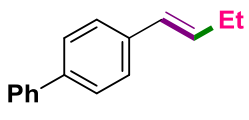


3jb

Isolated yield: 91%

Colorless viscous liquid. This compound is known in the literature.[11] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.49 – 7.43 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.25 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 2.5 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.55, 134.58, 129.42, 128.68, 127.73, 127.43, 126.46, 126.42, 21.28.

(*E*)-4-(But-1-ene-1-yl)-1,1'-biphenyl

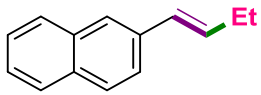


5aa

Isolated yield: 78%

Colorless liquid. This compound is known in the literature.[19] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.1 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.42 (t, *J* = 7.9 Hz, 4H), 7.32 (t, *J* = 7.3 Hz, 1H), 6.41 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.8, 6.2 Hz, 1H), 2.25 (dq, *J* = 8.6, 7.4 Hz, 2H), 1.10 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.90, 139.52, 137.04, 132.88, 128.77, 128.37, 127.20, 127.15, 126.91, 126.34, 26.18, 13.71.

(*E*)-2-(but-1-en-1-yl)naphthalene

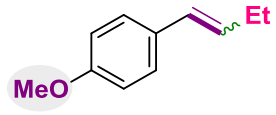


5ba

Isolated yield: 88%

Colorless liquid. This compound is known in the literature.[20] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 3H), 7.67 (s, 1H), 7.58 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.41 (t, *J* = 8.5 Hz, 2H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.40 (dt, *J* = 15.8, 6.4 Hz, 1H), 2.35 – 2.22 (m, 2H), 1.13 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.43, 133.75, 133.16, 132.66, 128.94, 128.05, 127.83, 127.64, 126.11, 125.42, 125.33, 123.60, 26.23, 13.72.

(*Z*/*E*)-1-(but-1-en-1-yl)-4-methoxybenzene



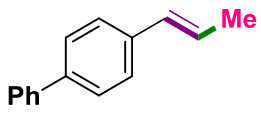
5ca

(*Z*)-/(*E*)- 1:1

Isolated yield: 60%

Colorless liquid. This compound is known in the literature[21]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 2H), 6.89 (dd, *J* = 13.9, 8.7 Hz, 2H), 6.36 (d, *J* = 11.7 Hz, 1H), 6.16 (dt, *J* = 15.8, 6.5 Hz, 1H), 5.60 (dt, *J* = 11.6, 7.2 Hz, 1H), 3.85 (s, 1H), 3.83 (s, 1H), 2.42-2.34 (m, *J* = 7.5, 2.1 Hz, 1H), 2.31 – 2.19 (m, 1H), 1.11 (q, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.63, 158.18, 133.19, 130.82, 130.52, 130.49, 129.92, 128.15, 127.67, 126.97, 113.92, 113.56, 55.25, 26.04, 21.97, 14.54, 13.81.

(*E*)-4-(prop-1-en-1-yl)-1,1'-biphenyl



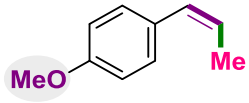
5ab

Isolated yield: 91%

Colorless liquid. This compound is known in the literature.[19] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.33 (q, *J* = 7.8 Hz, 4H), 7.24 (t, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 17.6 Hz, 1H), 6.26 – 6.15 (m, 1H), 1.82 (dd, *J* =

6.6, 1.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.90, 139.51, 137.03, 130.61, 128.78, 127.21, 127.16, 126.91, 126.25, 125.93, 18.61.

(*Z*)-1-Methoxy-4-(prop-1-en-1-yl)benzene

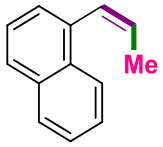


5cb

Isolated yield: 89%

Colorless liquid. This compound is known in the literature.[20] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 2H), 6.91 – 6.78 (m, 2H), 6.36 (dd, *J* = 11.5, 2.0 Hz, 1H), 5.69 (dq, *J* = 11.6, 7.2 Hz, 1H), 3.80 (s, 3H), 1.88 (dd, *J* = 7.2, 1.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.12, 130.35, 130.00, 129.29, 125.10, 113.56, 55.25, 14.60.

(*Z*)-1-(prop-1-en-1-yl)naphthalene

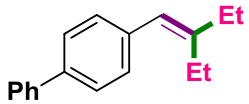


5db

Isolated yield: 93%

Colorless liquid. This compound is known in the literature.[22] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 1H), 7.80 – 7.71 (m, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.43 – 7.31 (m, 3H), 7.27 (d, *J* = 7.0 Hz, 1H), 6.81 (d, *J* = 11.4 Hz, 1H), 5.95 (dq, *J* = 11.4, 7.0 Hz, 1H), 1.66 (dd, *J* = 7.0, 1.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.61, 133.64, 131.96, 128.57, 128.39, 127.94, 127.13, 126.52, 125.79, 125.70, 125.26, 125.08, 14.67.

4-(2-ethyl-1-propen-1-yl)-1,1'-biphenyl

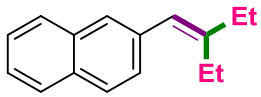


7aa

Isolated yield: 91%

Colorless viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.31 (dd, *J* = 14.5, 7.8 Hz, 3H), 6.26 (s, 1H), 2.32 (q, *J* = 7.5 Hz, 2H), 2.22 (q, *J* = 6.9, 6.4 Hz, 2H), 1.12 (q, *J* = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.97, 141.00, 138.54, 137.77, 129.01, 128.75, 127.07, 126.95, 126.77, 122.82, 29.62, 23.95, 13.13, 12.84. **HRMS** Calcd for $C_{18}H_{21}^{+}$ $[M+H]^{+}$ 237.1643, found 237.1646.

2-(2-ethylbut-1-en-1-yl)naphthalene

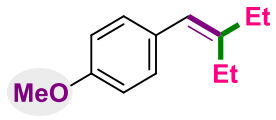


7ba

Isolated yield: 89%

Colorless viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 7.8 Hz, 3H), 7.65 (s, 1H), 7.47 – 7.34 (m, 3H), 6.38 (s, 1H), 2.34 (q, *J* = 7.5 Hz, 2H), 2.29 – 2.22 (m, 2H), 1.13 (dt, *J* = 15.1, 7.5 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.16, 136.31, 133.50, 131.89, 127.83, 127.57, 127.56, 127.47, 126.86, 125.90, 125.33, 123.28, 29.57, 23.97, 13.19, 12.87. **HRMS** Calcd for $C_{16}H_{19}^{+}$ $[M+H]^{+}$ 211.1481, found 211.1478.

1-(2-Ethyl-1-buten-1-yl)-4-methoxybenzene

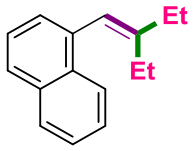


7ca

Isolated yield: 89%

Colorless viscous liquid. This compound is known in the literature.[23] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.17 (s, 1H), 3.80 (s, 3H), 2.25 (q, *J* = 7.5 Hz, 2H), 2.18 (q, *J* = 7.4 Hz, 2H), 1.08 (dt, *J* = 11.4, 7.5 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.70, 145.24, 131.28, 129.64, 122.60, 113.49, 55.24, 29.48, 23.73, 13.09, 12.85.

1-(2-ethylbut-1-en-1-yl)naphthalene

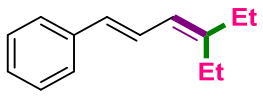


7da

Isolated yield: 72%

Colorless viscous liquid. This compound is known in the literature.[24] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 6.1, 3.5 Hz, 1H), 7.88 (dd, *J* = 6.5, 3.0 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.33 (d, *J* = 7.0 Hz, 1H), 6.64 (s, 1H), 2.37 (q, *J* = 7.4 Hz, 2H), 2.14 (q, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.5 Hz, 3H), 1.01 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.83, 136.26, 133.55, 132.34, 128.26, 126.61, 126.28, 125.60, 125.54, 125.38, 125.35, 121.04, 28.73, 24.20, 13.22, 12.98.

(*E*)-(4-Ethylhexa-1,3-dien-1-yl)benzene

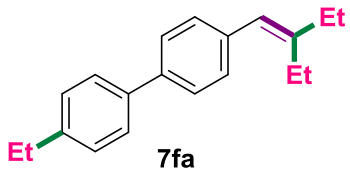


7ea

Isolated yield: 90%

Colorless viscous liquid. This compound is known in the literature.[25] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.03 (dd, *J* = 15.5, 11.0 Hz, 1H), 6.47 (d, *J* = 15.5 Hz, 1H), 5.97 (d, *J* = 11.0 Hz, 1H), 2.30 (q, *J* = 7.6 Hz, 2H), 2.16 (q, *J* = 7.4 Hz, 2H), 1.07 (td, *J* = 7.5, 2.5 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.10, 138.17, 129.99, 128.55, 126.90, 126.10, 125.44, 123.17, 29.78, 24.17, 13.70, 12.70.

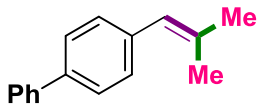
4-ethyl-4'-(2-ethylbut-1-en-1-yl)-1,1'-biphenyl



7fa

Isolated yield: 92%
Colorless viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.1, 3.7 Hz, 4H), 7.30 – 7.22 (m, 4H), 6.25 (s, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.31 (q, *J* = 7.5 Hz, 2H), 2.21 (qd, *J* = 7.4, 1.4 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.11 (q, *J* = 7.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.83, 143.24, 138.58, 138.44, 137.51, 129.03, 128.34, 126.92, 126.67, 122.97, 29.69, 28.60, 15.67, 13.18, 12.90. **HRMS** Calcd for $C_{20}H_{25}^+$ $[M+H]^+$ 265.1951, found 265.1950.

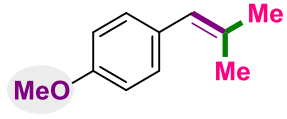
4-(2-methyl-1-propen-1-yl)-1,1'-biphenyl



7ab

Isolated yield: 89%
Colorless viscous liquid. This compound is known in the literature.[26] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.24 (dd, *J* = 12.0, 8.2 Hz, 3H), 6.22 (s, 1H), 1.85 (dd, *J* = 6.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.01, 138.52, 137.78, 135.85, 129.14, 128.75, 127.09, 126.97, 126.75, 124.76, 27.03, 19.56.

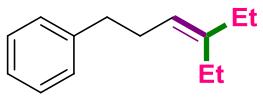
1-Methoxy-4(2-Methylprop-1-en-1-yl)benzene



7cb

Isolated yield: 82%
Colorless viscous liquid. This compound is known in the literature.[23] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.20 (s, 1H), 3.78 (s, 3H), 1.88 (s, 3H), 1.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.68, 133.94, 131.38, 129.81, 124.55, 113.49, 55.22, 26.83, 19.34.

(4-ethylhex-3-en-1-yl)benzene

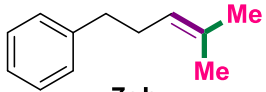


7ga

Isolated yield: 65%

Colorless liquid. This compound is known in the literature.[27] **^{1}H NMR** (400 MHz, CDCl3) δ 7.30 – 7.23 (m, 2H), 7.18 (m, J = 8.3, 2.3 Hz, 3H), 5.13 (t, J = 7.2 Hz, 1H), 2.64 (dd, J = 9.0, 6.7 Hz, 2H), 2.35 – 2.27 (m, 2H), 2.00 (dq, J = 7.5, 0.9 Hz, 4H), 0.98 (t, J = 7.4 Hz, 3H), 0.90 (t, J = 7.6 Hz, 3H).

(4-methylpent-3-en-1-yl)benzene



7gb

Isolated yield: 58%

Colorless liquid. This compound is known in the literature.[28] **^{1}H NMR** (400 MHz, CDCl3) δ 7.30 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 5.25 – 5.06 (m, 1H), 2.68 – 2.58 (m, 2H), 2.29 (dd, J = 14.3, 8.6 Hz, 2H), 1.69 (s, 3H), 1.56 (s, 3H).

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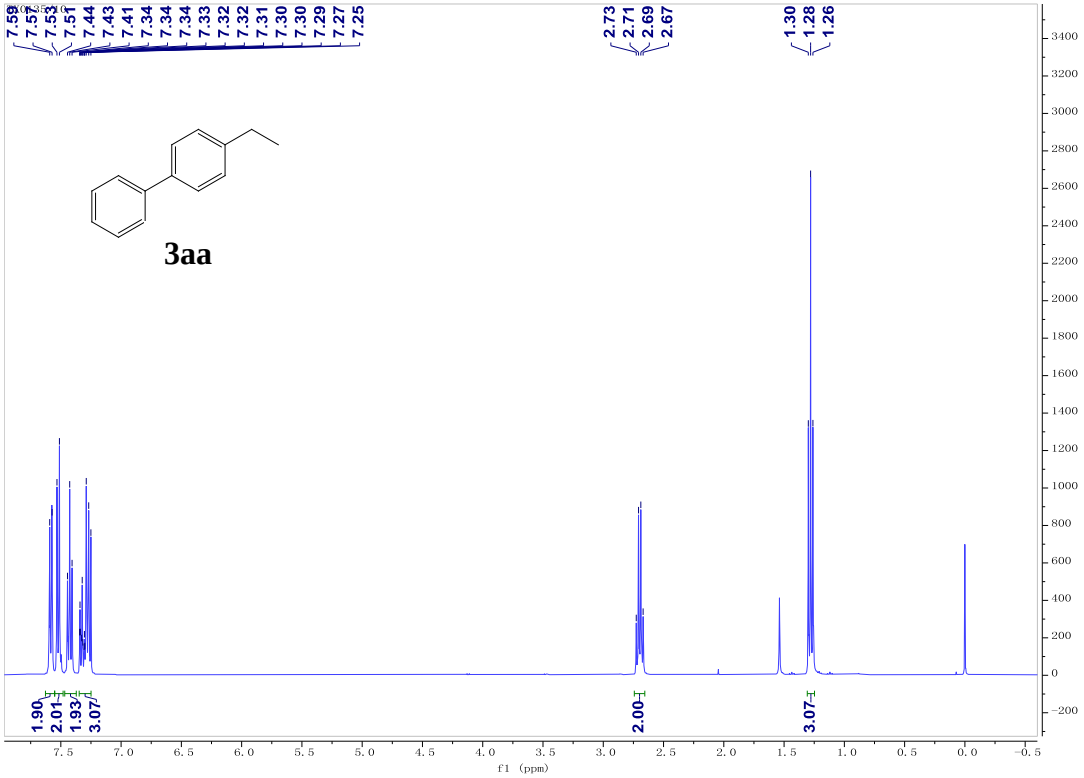
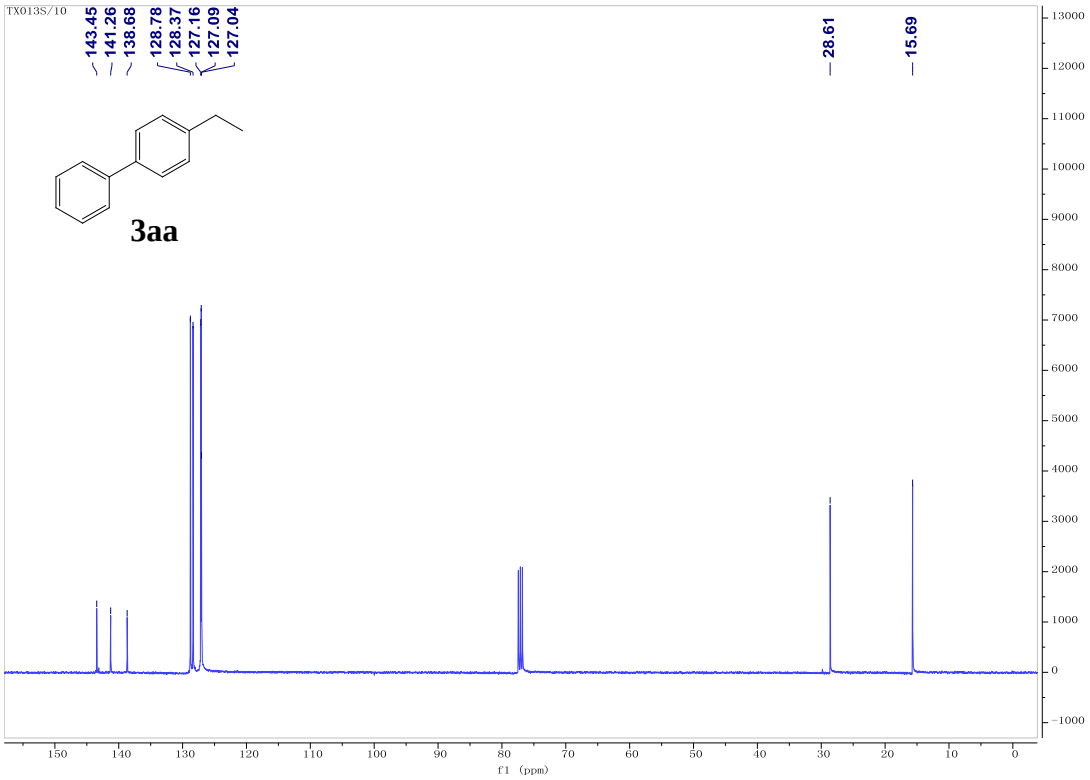
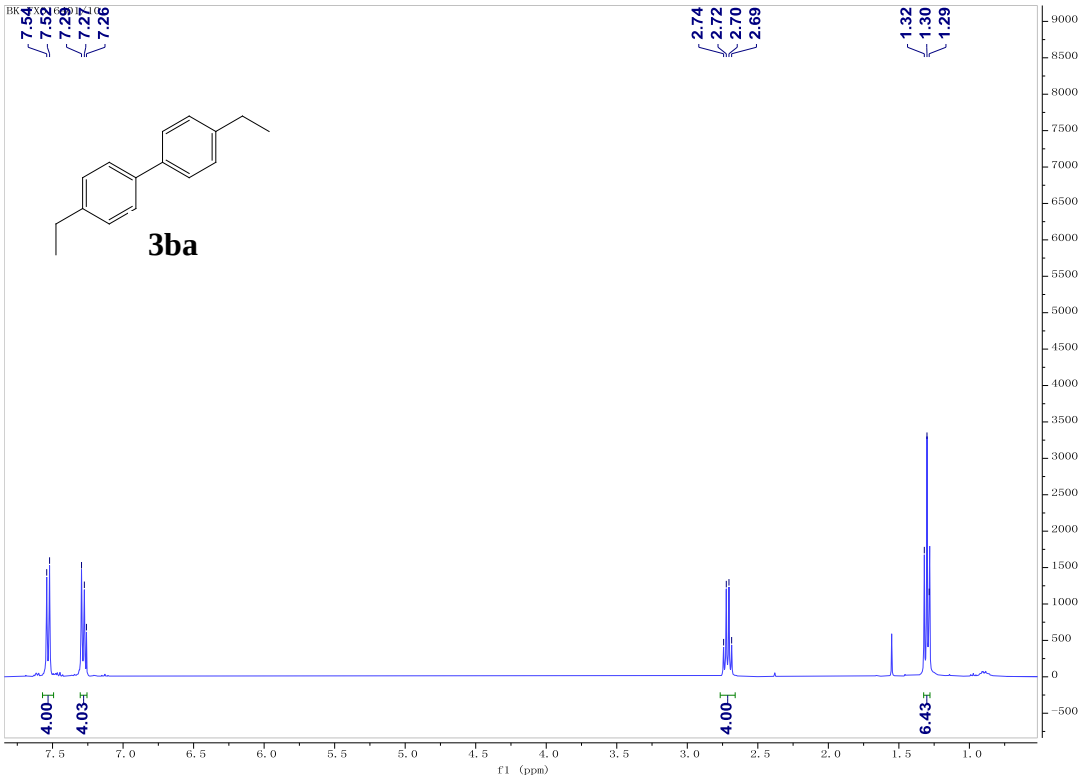
^{1}H and ^{13}C NMR spectra



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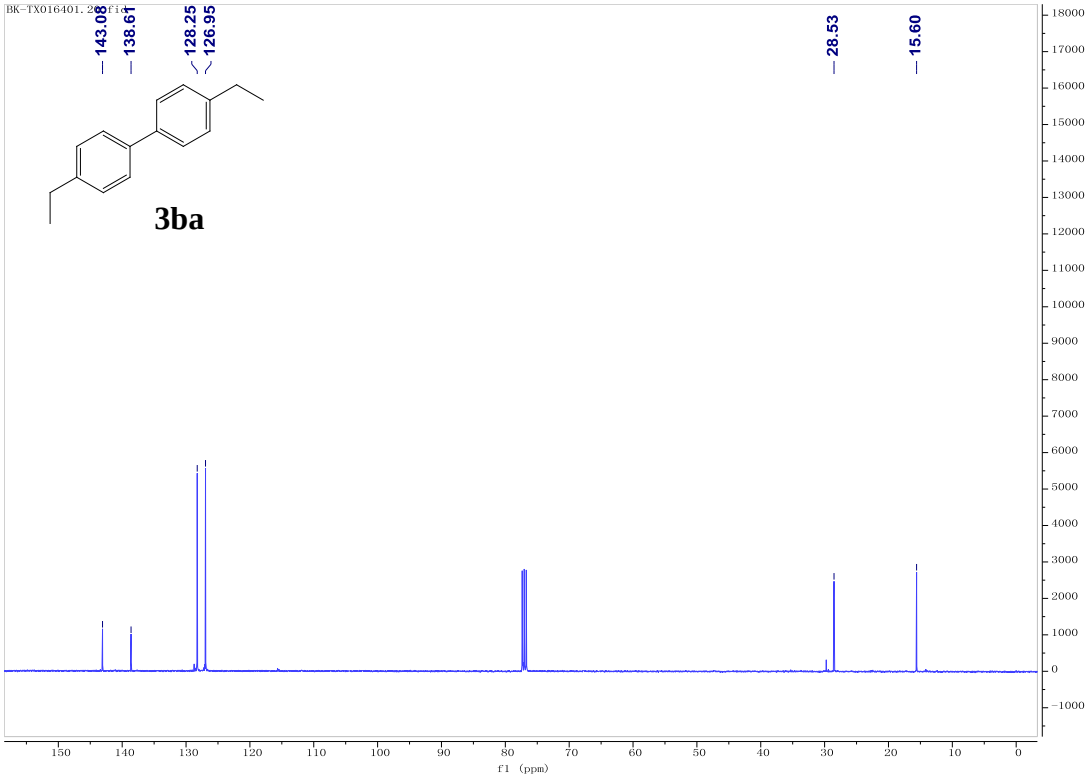
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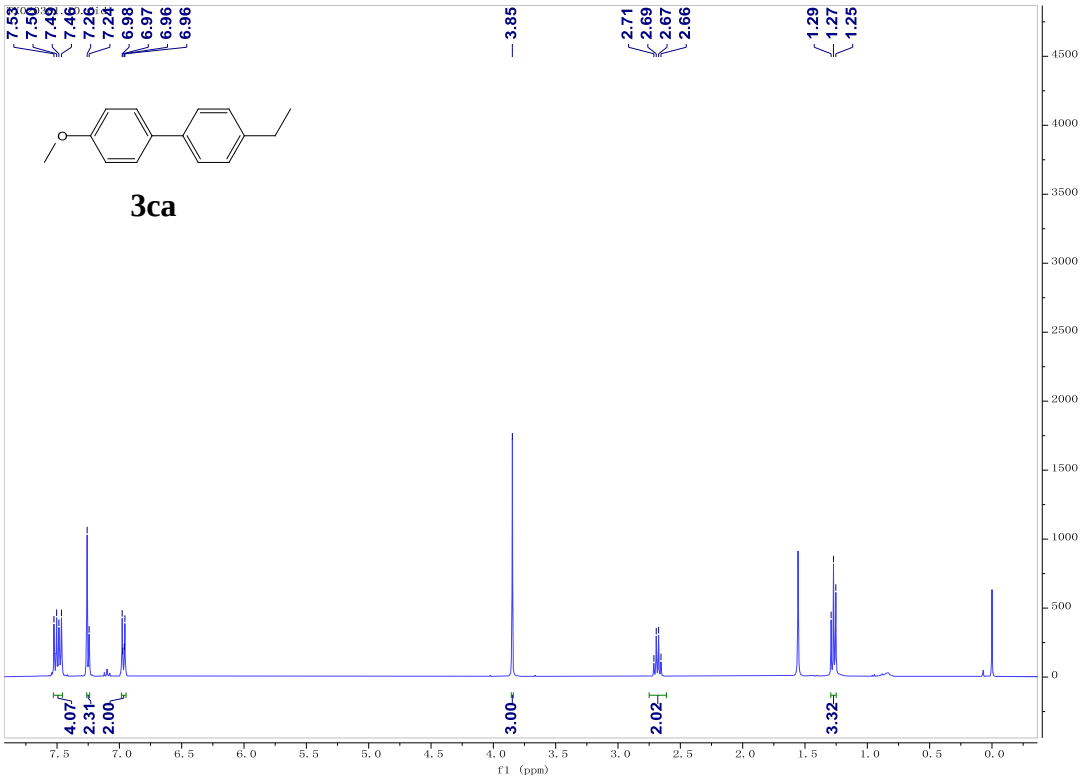
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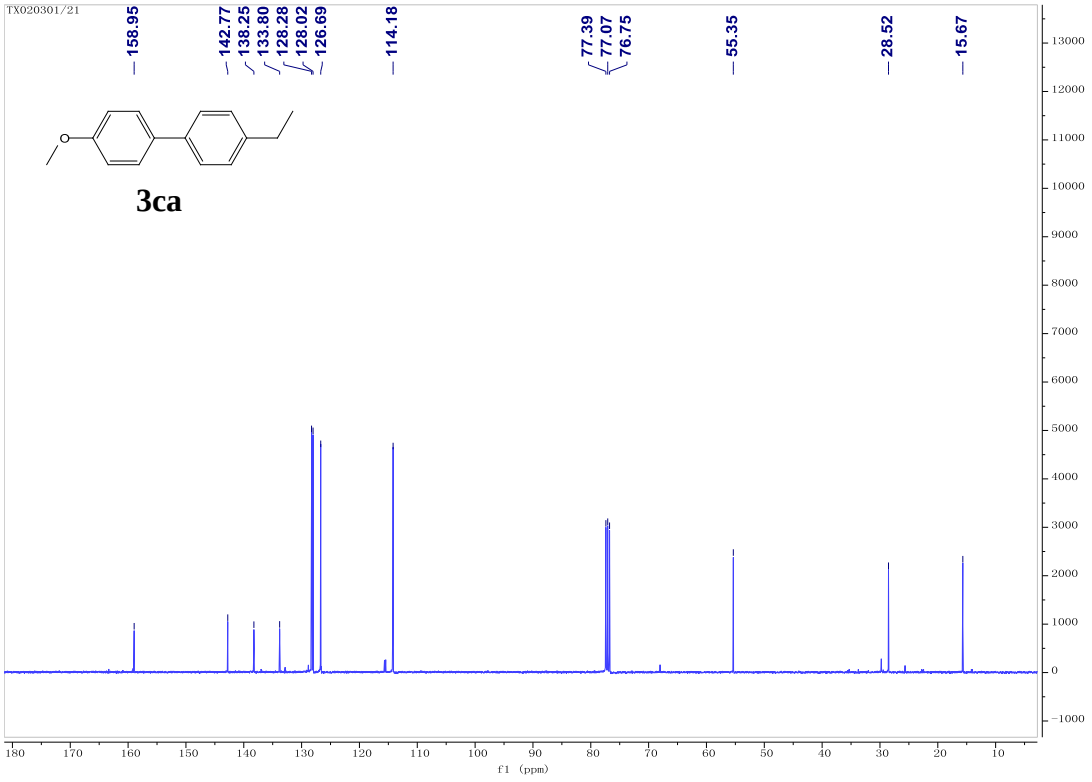
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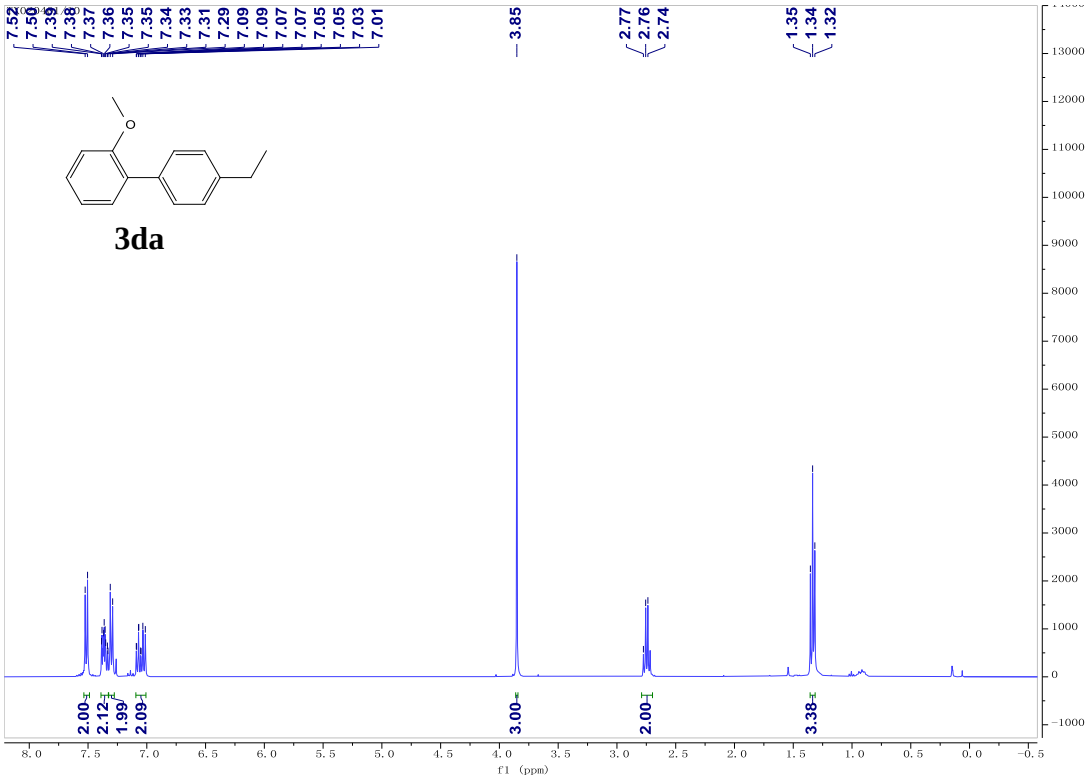
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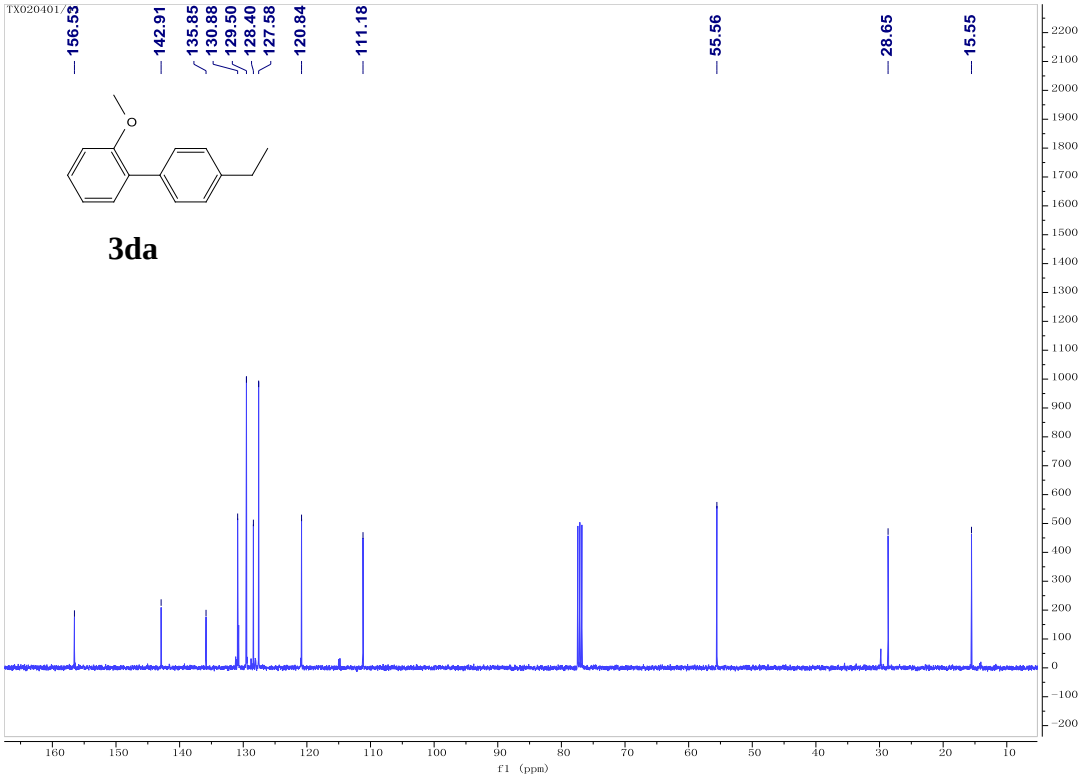
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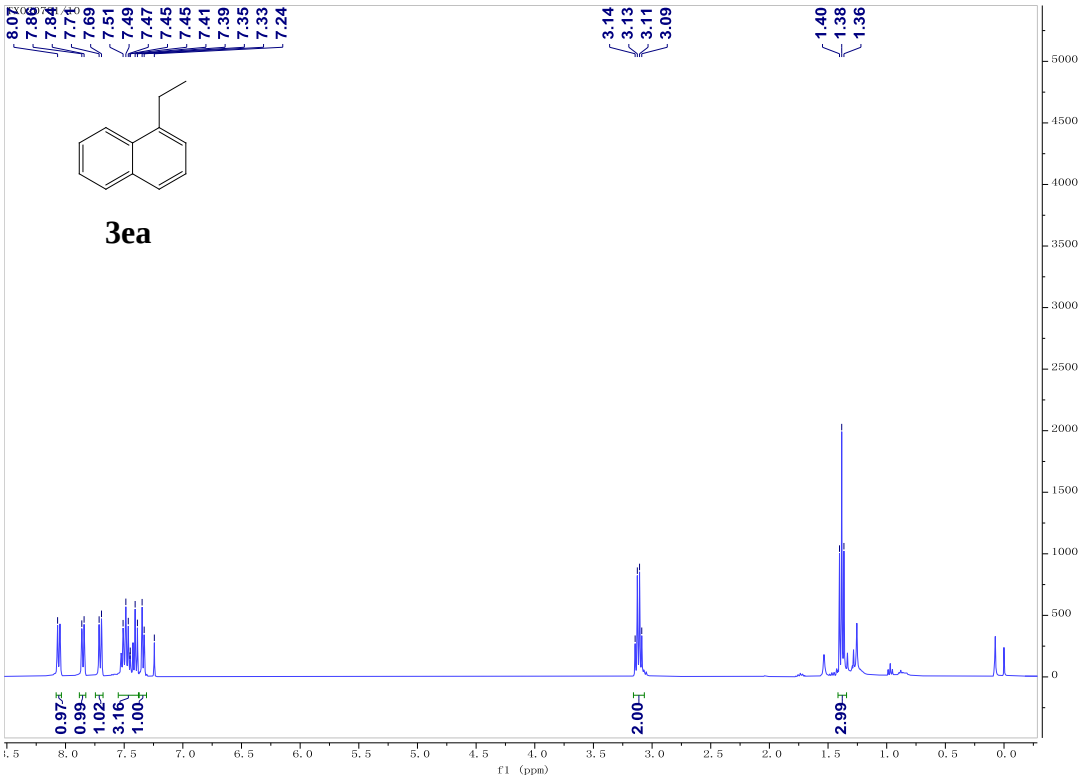
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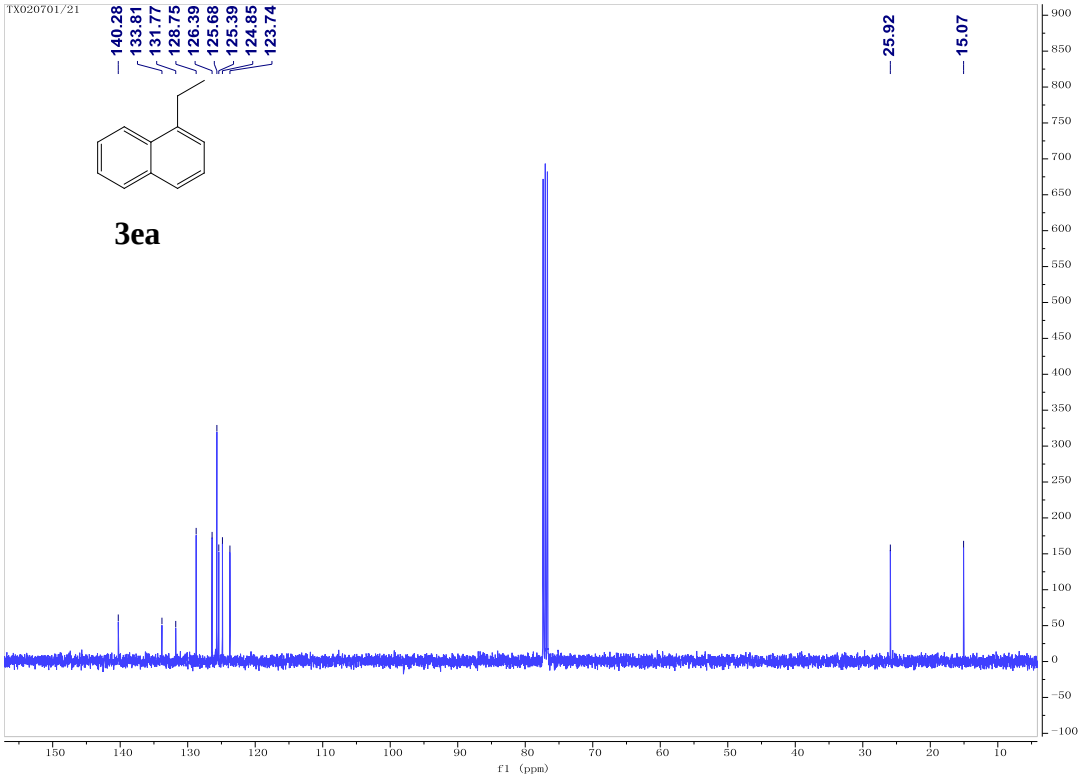
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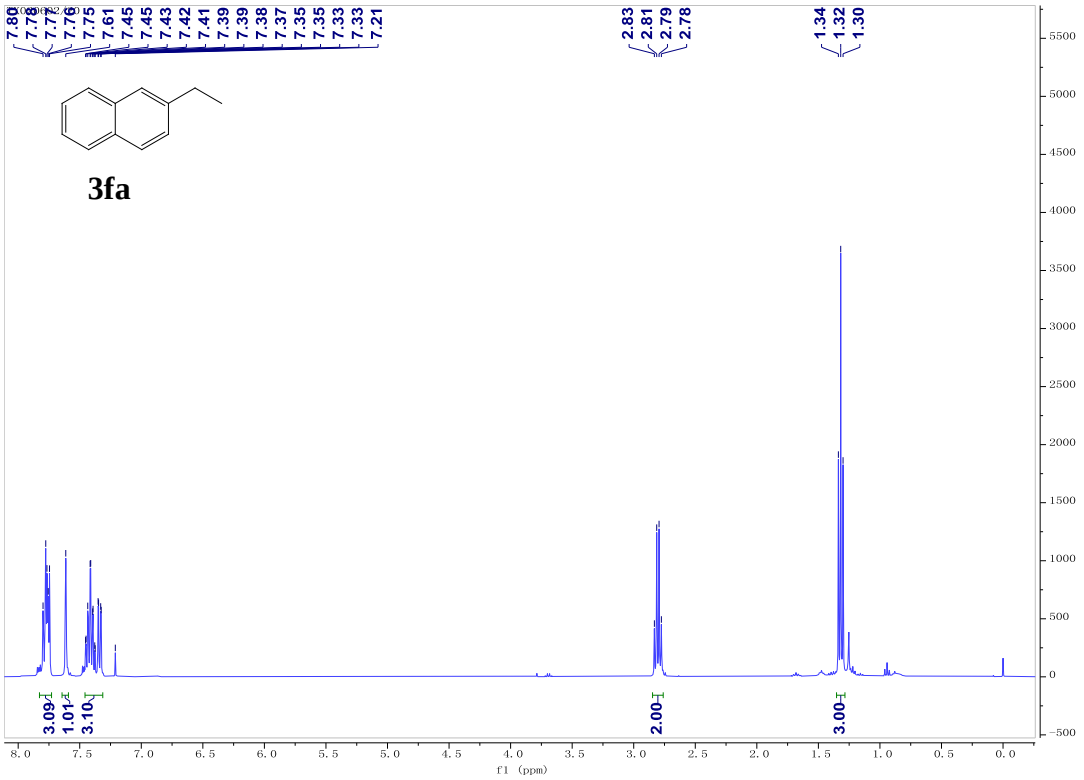
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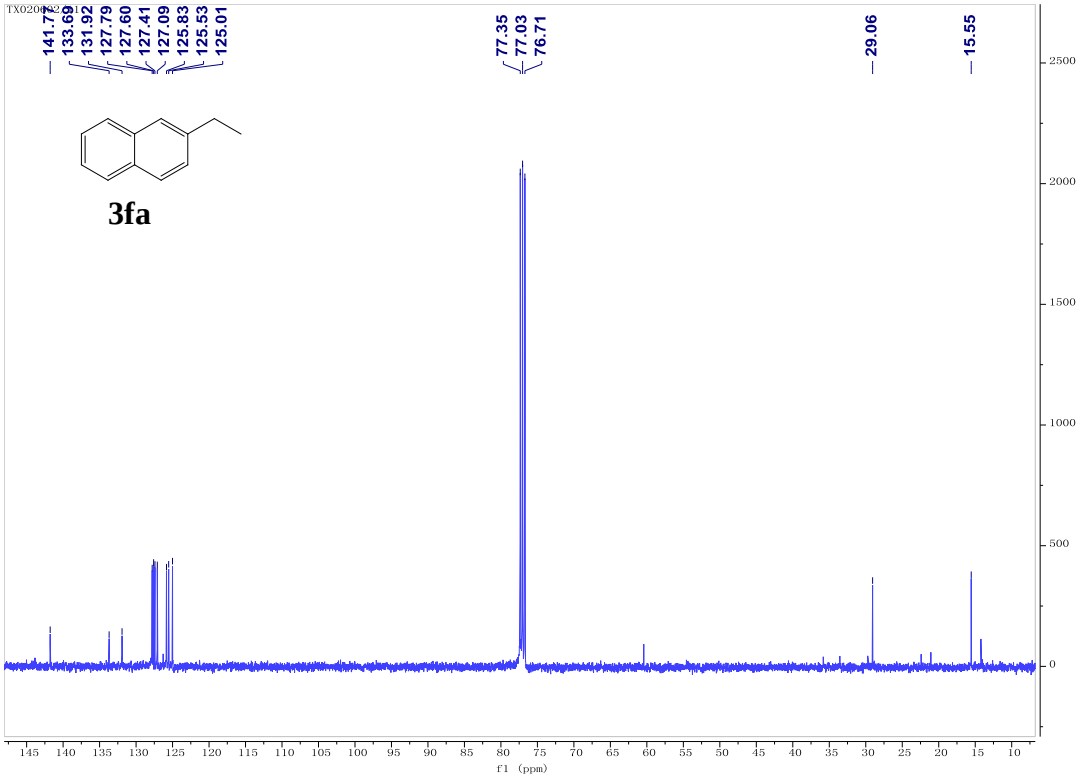
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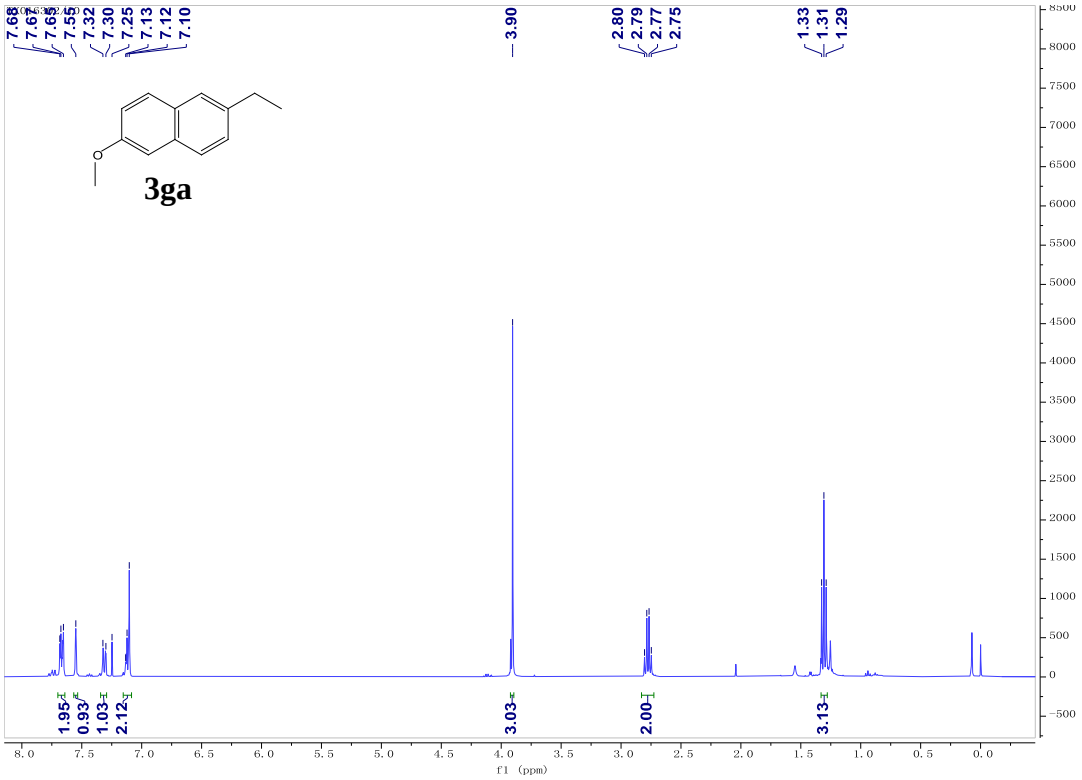
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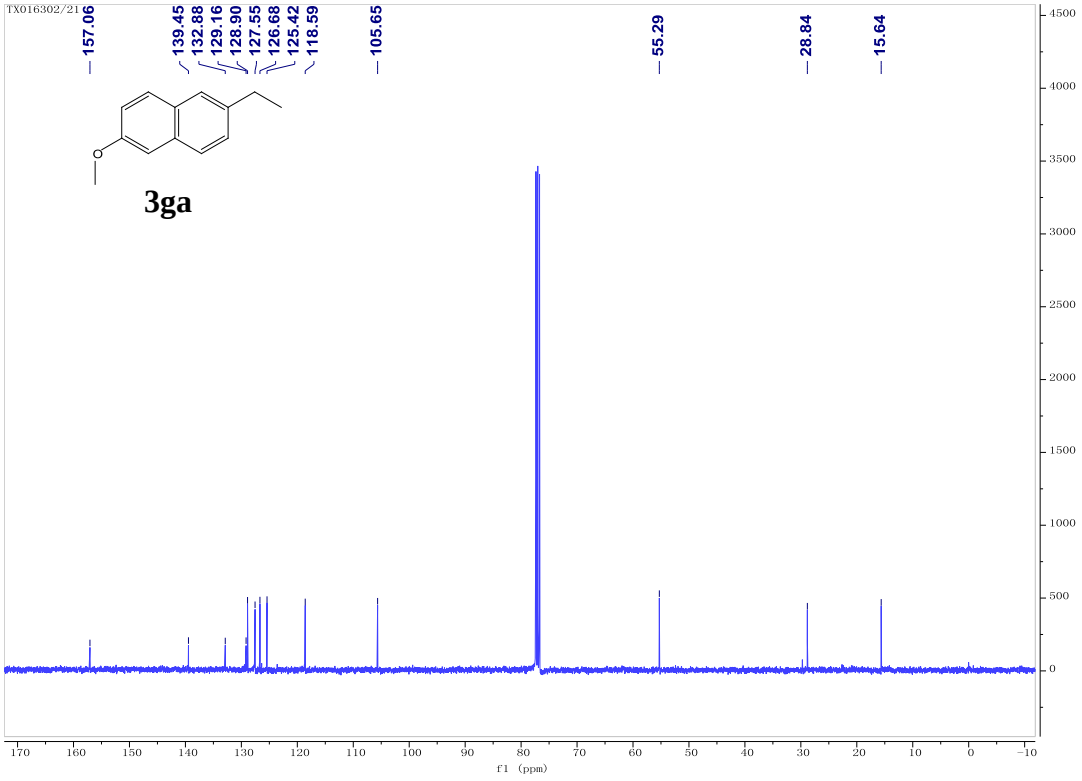
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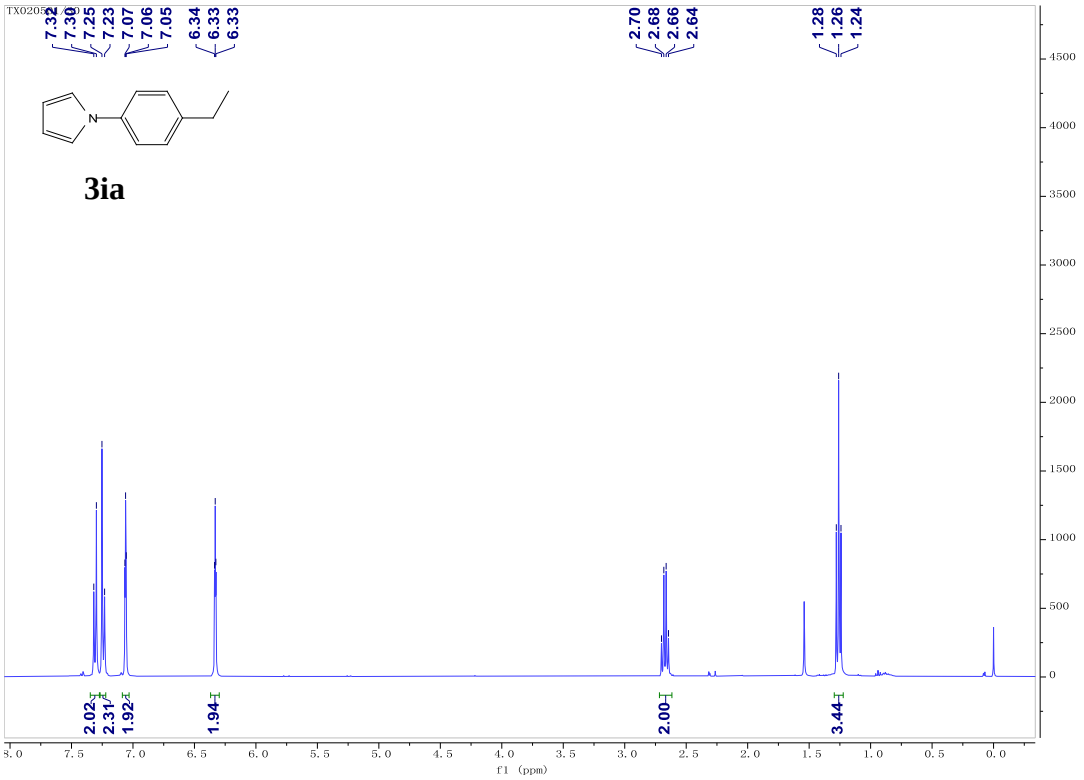
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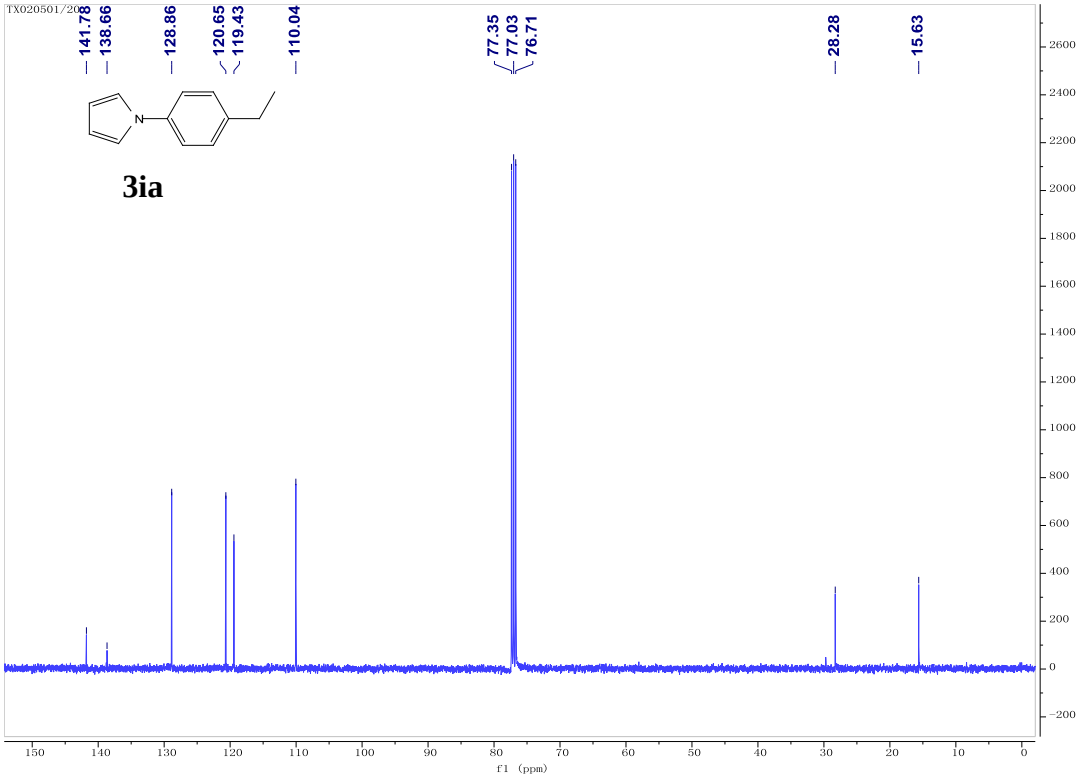
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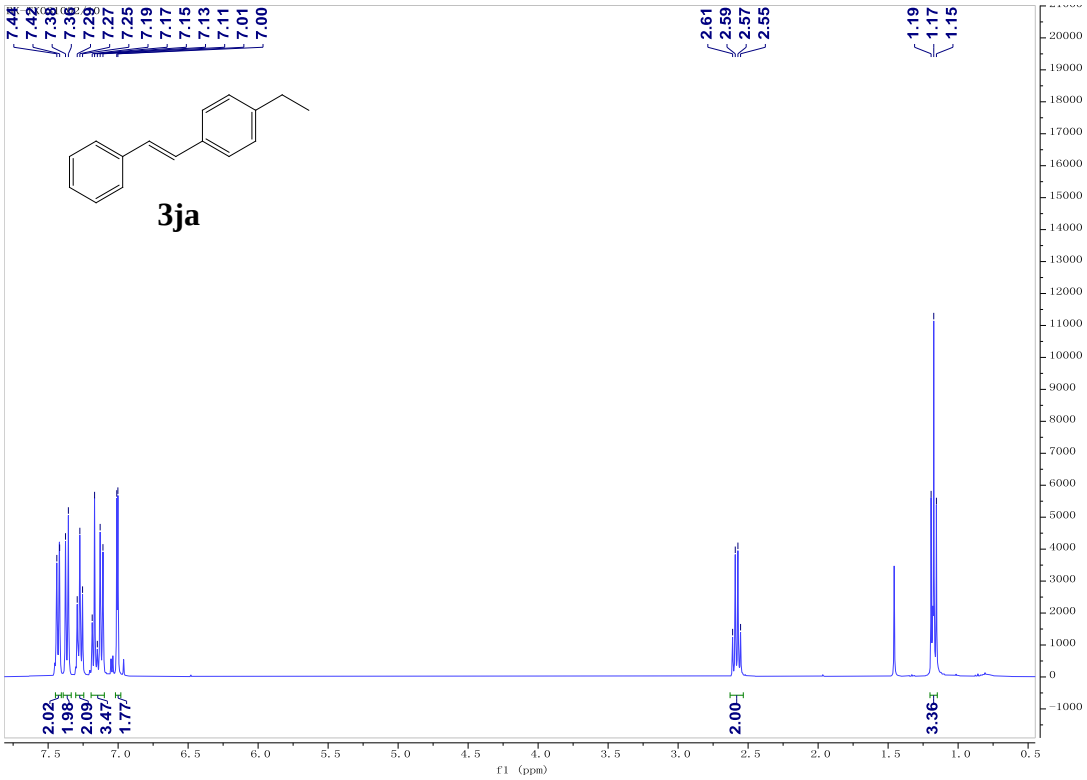
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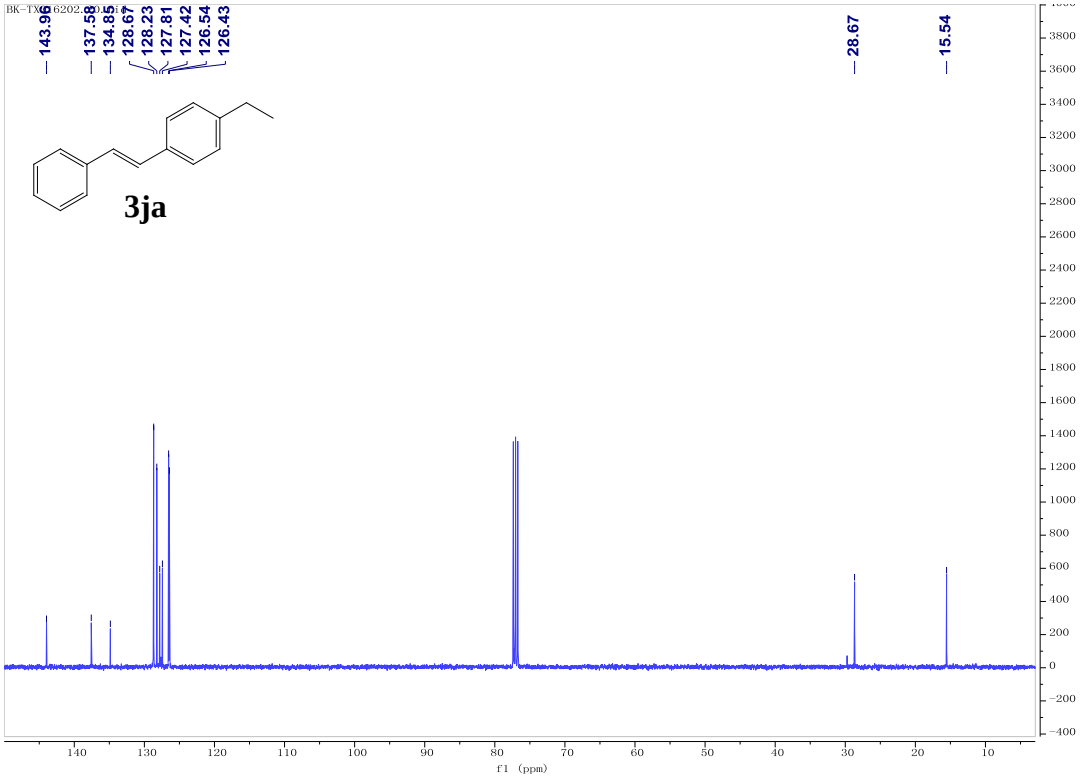
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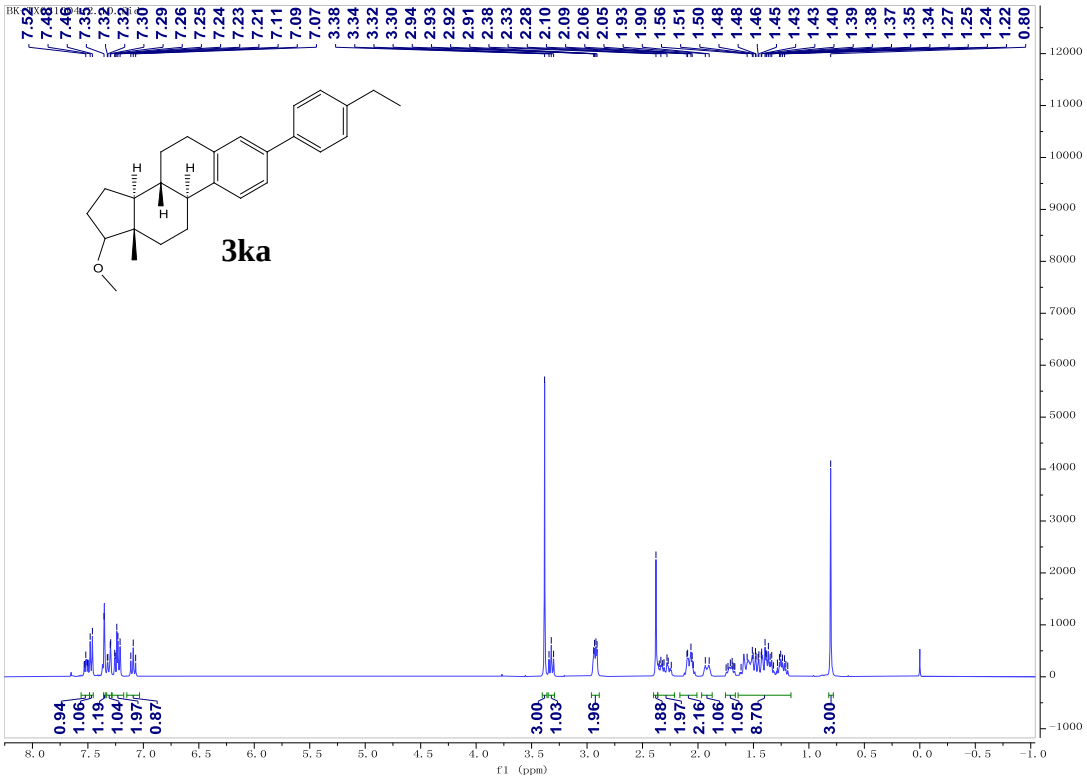
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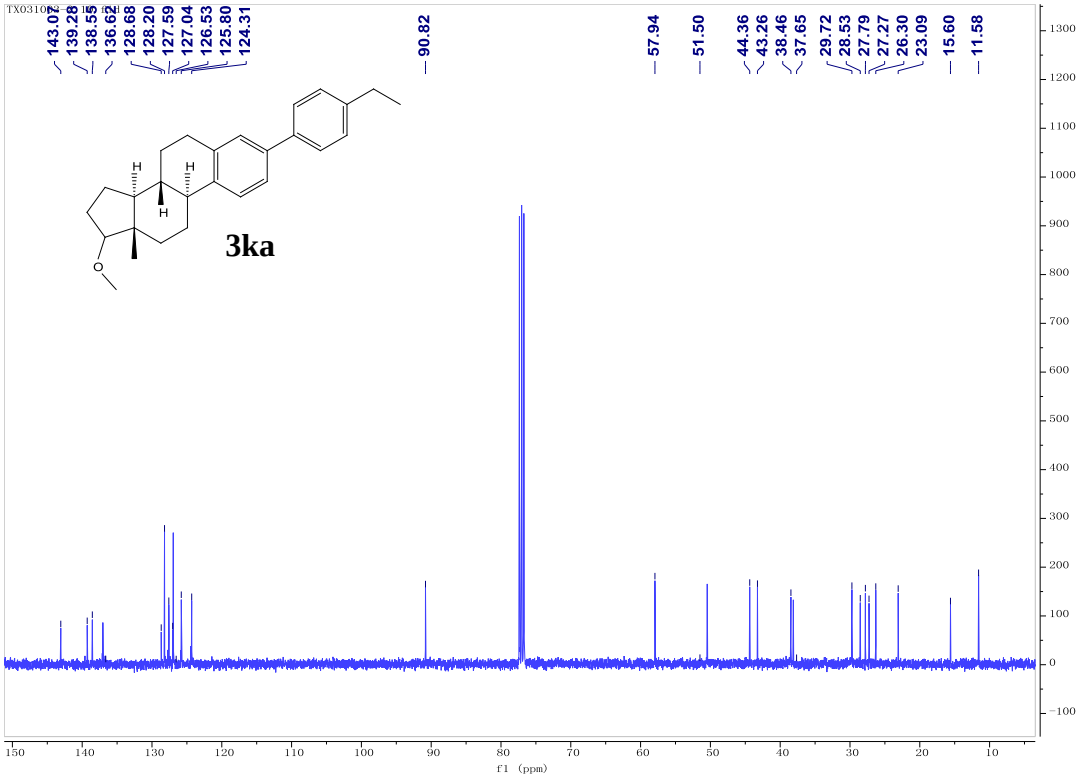
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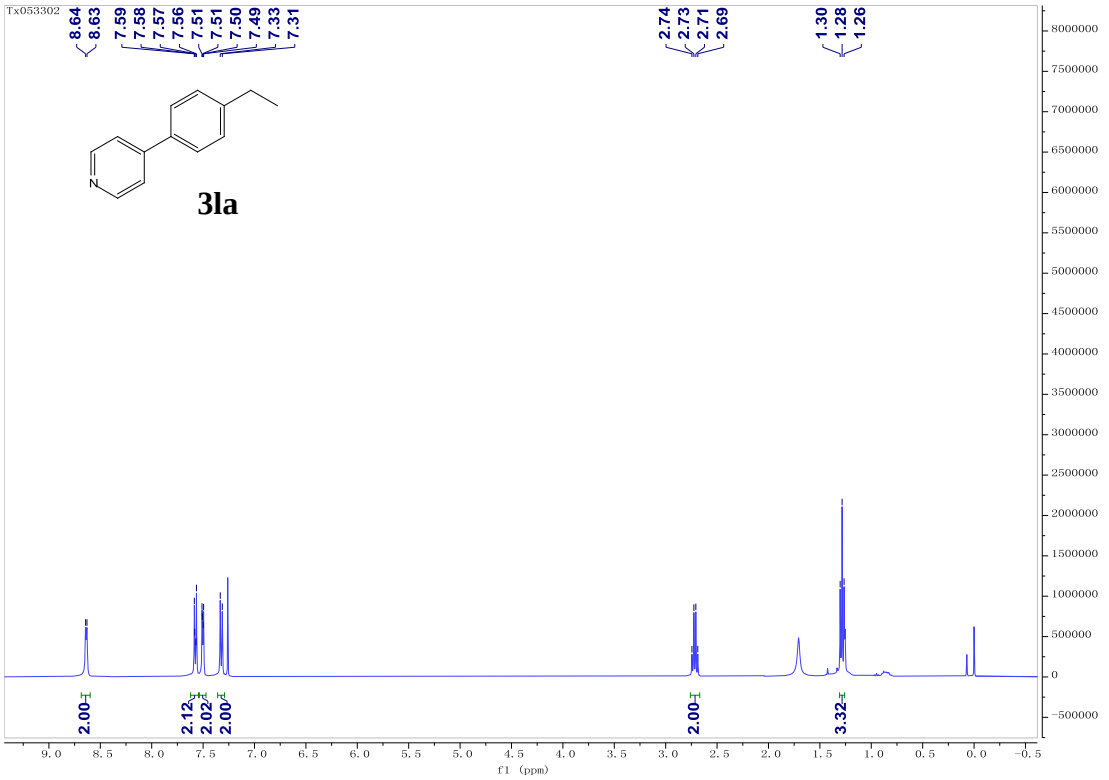
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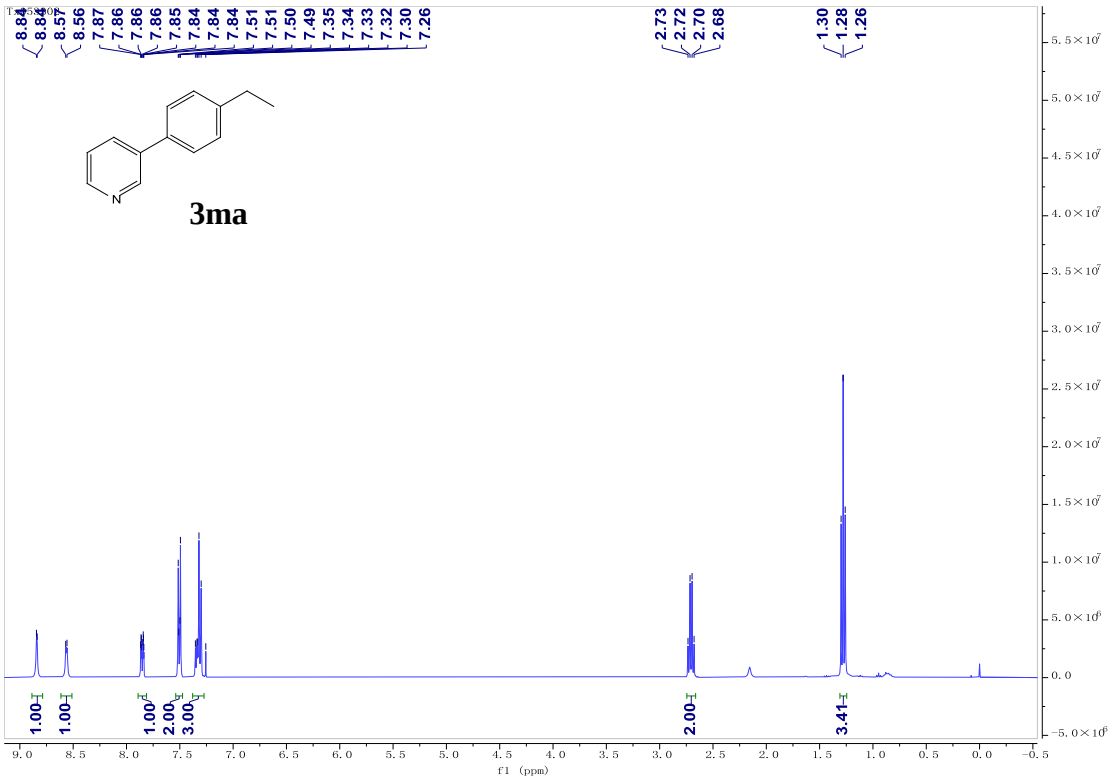
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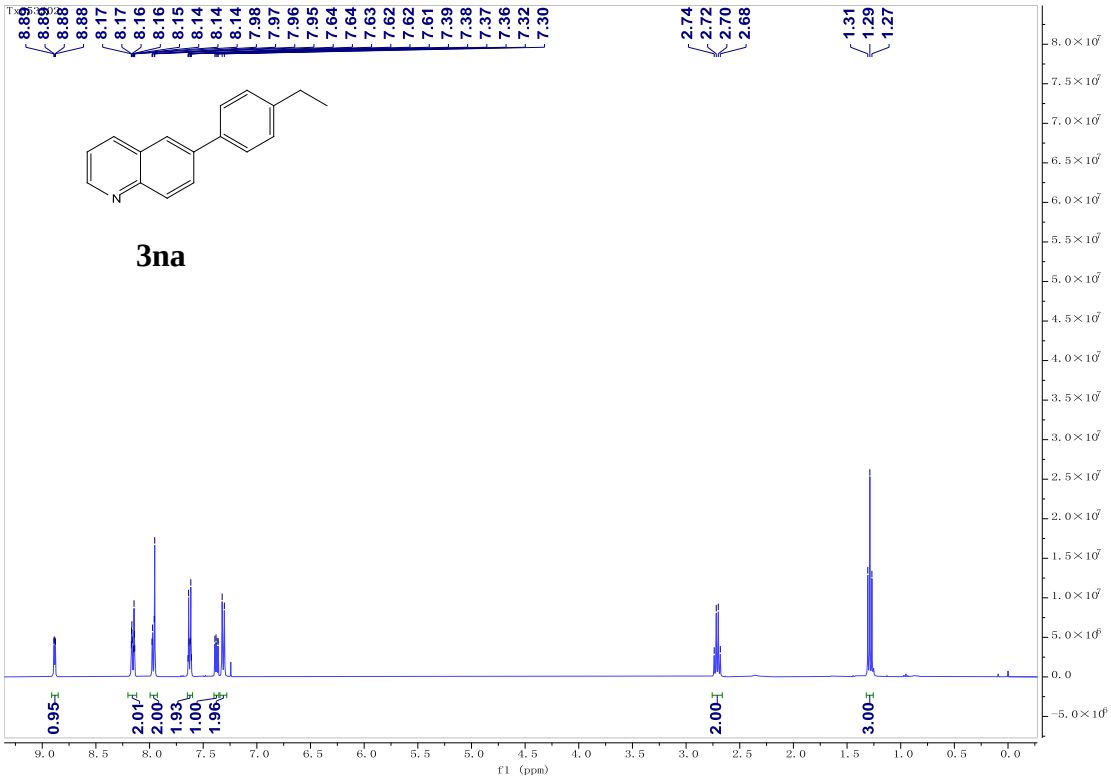
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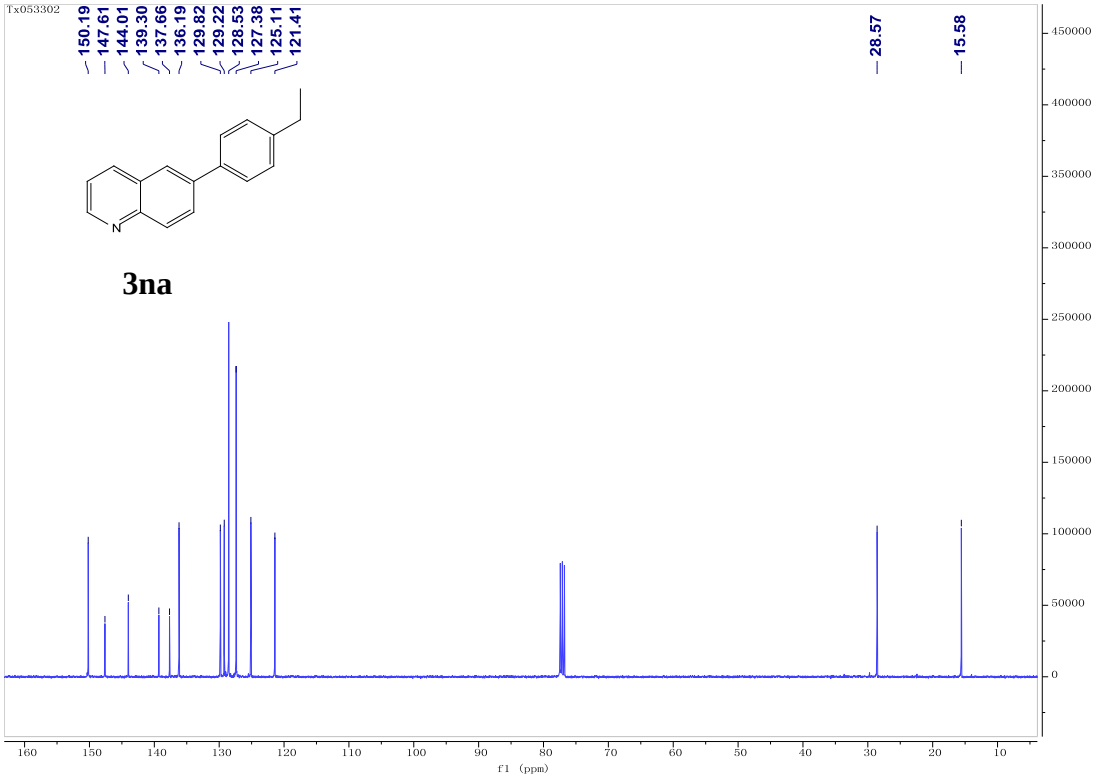
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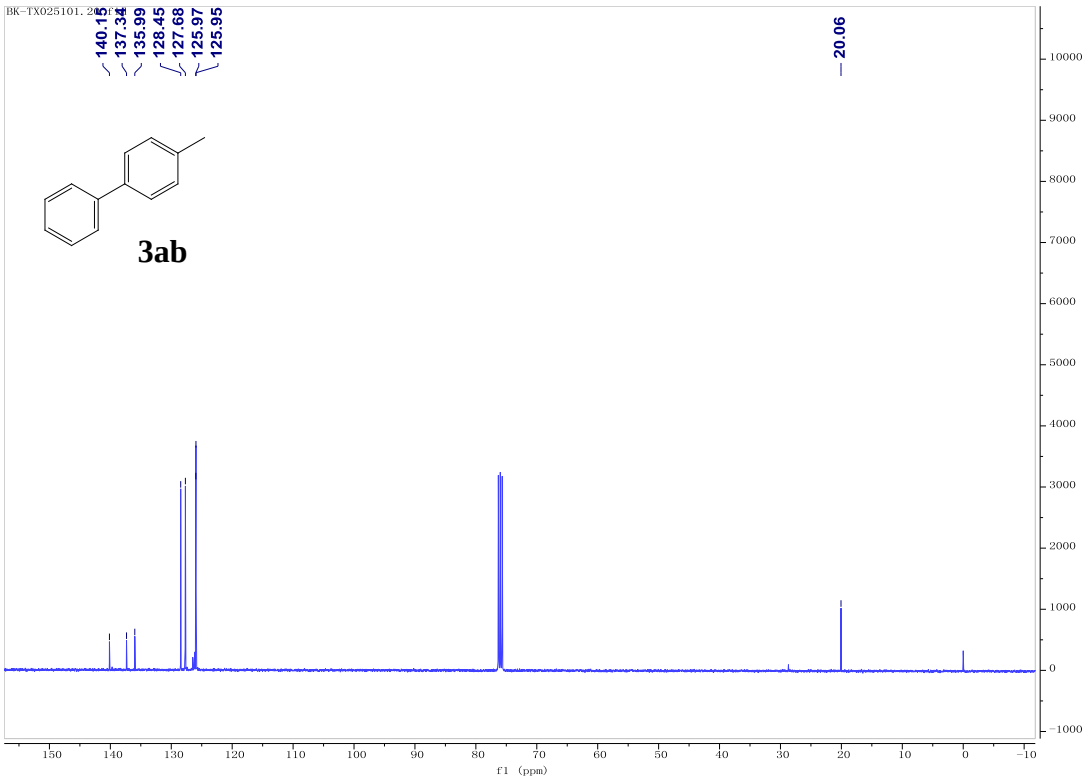
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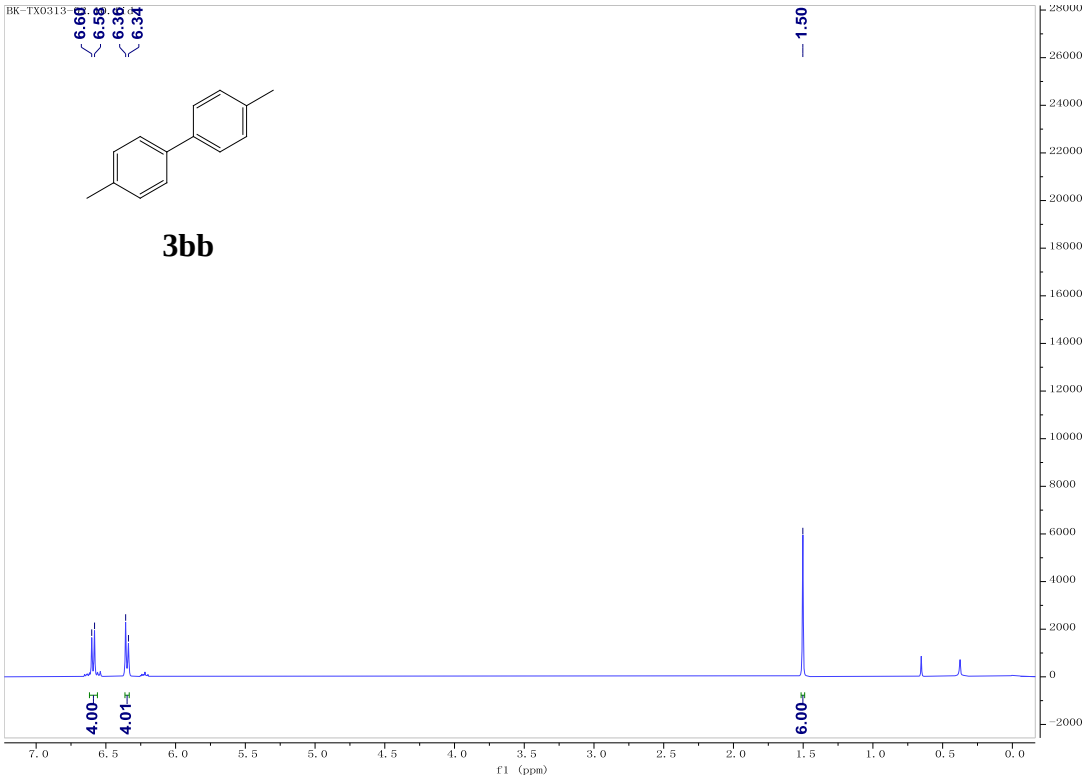
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6.36
6.34
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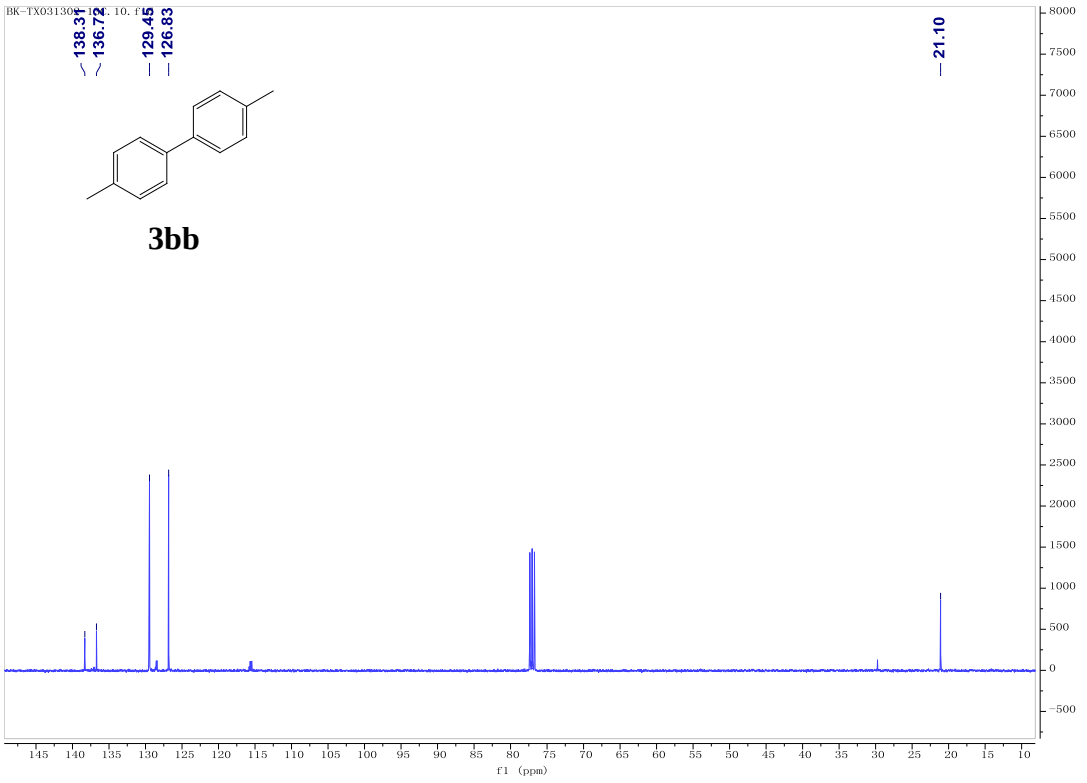
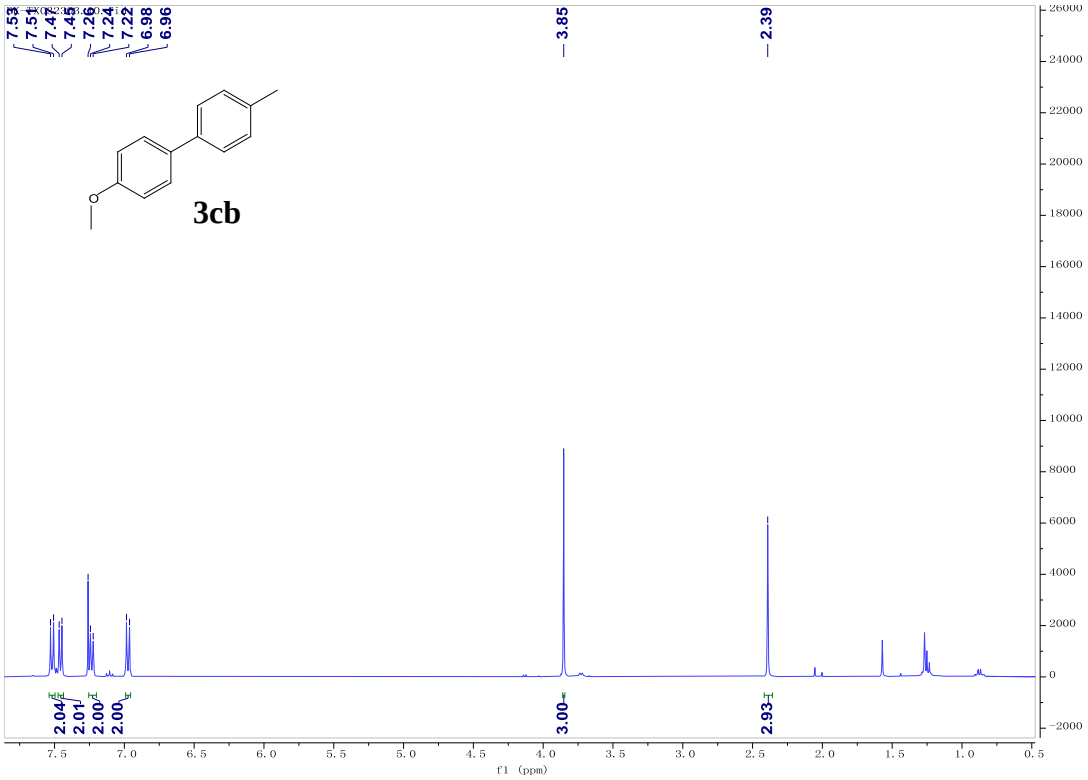
4.01
6.00
f1 (ppm)

3bb


138.31
136.72
129.45
126.83
21.10
f1 (ppm)

3bb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7.45
7.26
7.24
7.22
6.98
6.96
3.85
2.39
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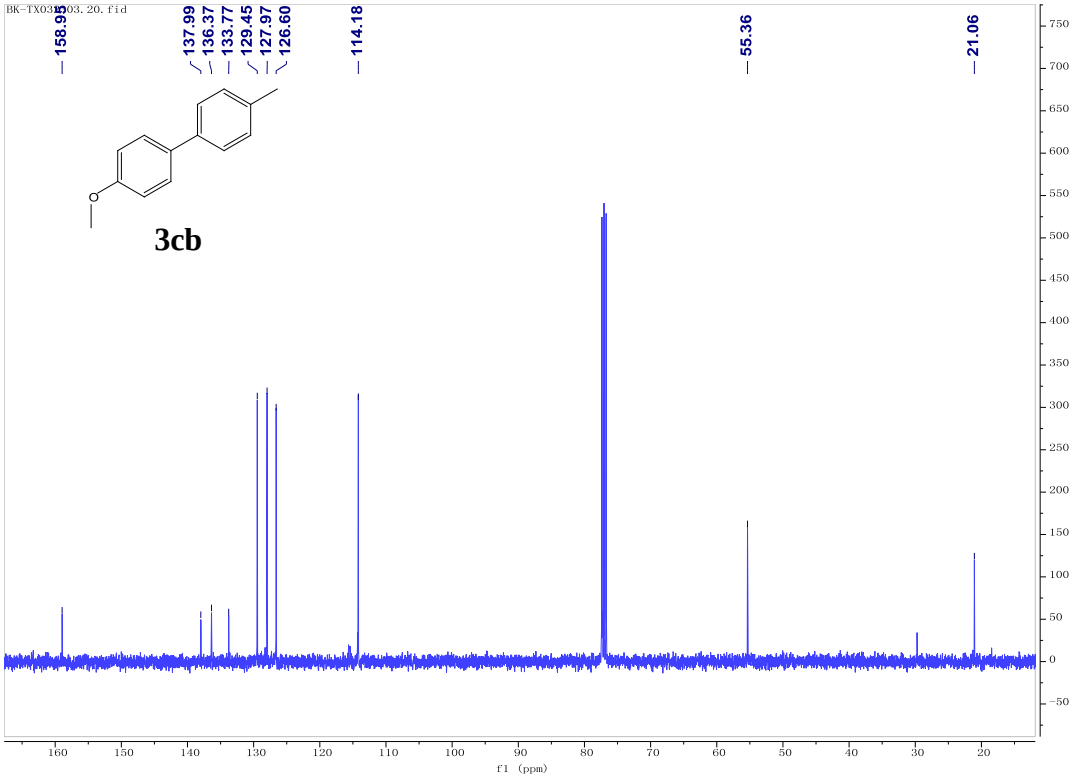
2.04
2.01
2.00
2.00
3.00
2.93
f1 (ppm)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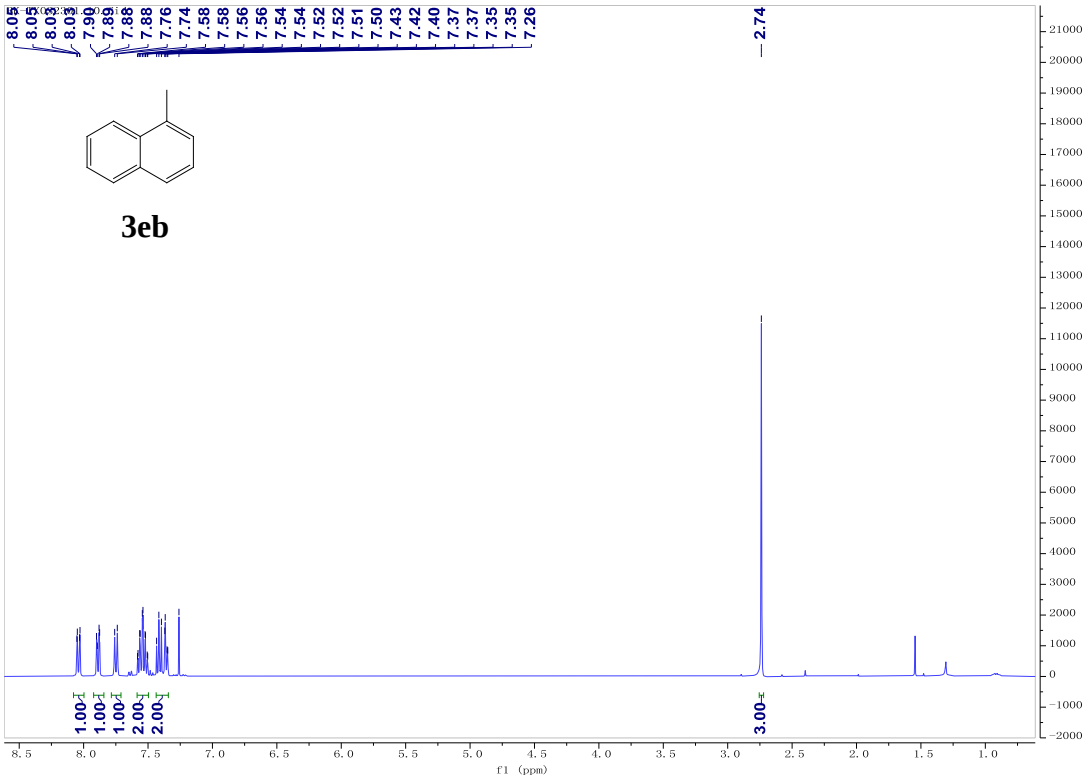
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7.88
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7.58
7.58
7.56
7.56
7.54
7.54
7.52
7.52
7.51
7.50
7.43
7.42
7.40
7.37
7.37
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7.35
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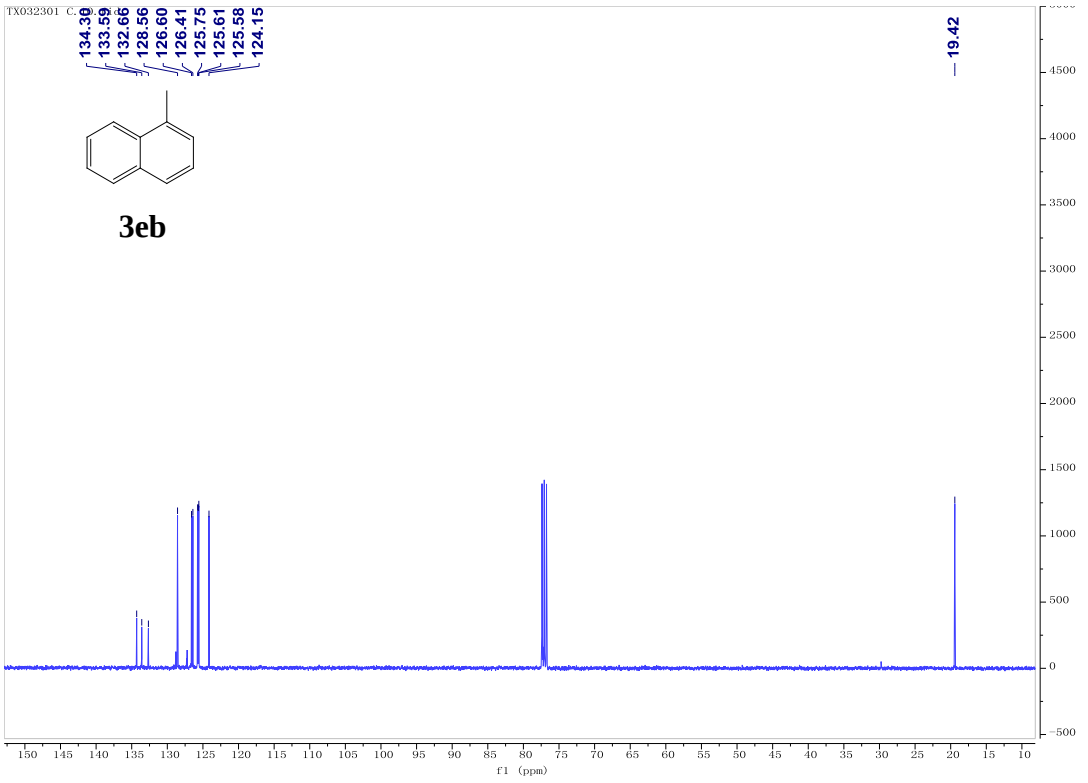
1.00
1.00
2.00
2.00
3.00
f1 (ppm)


134.30
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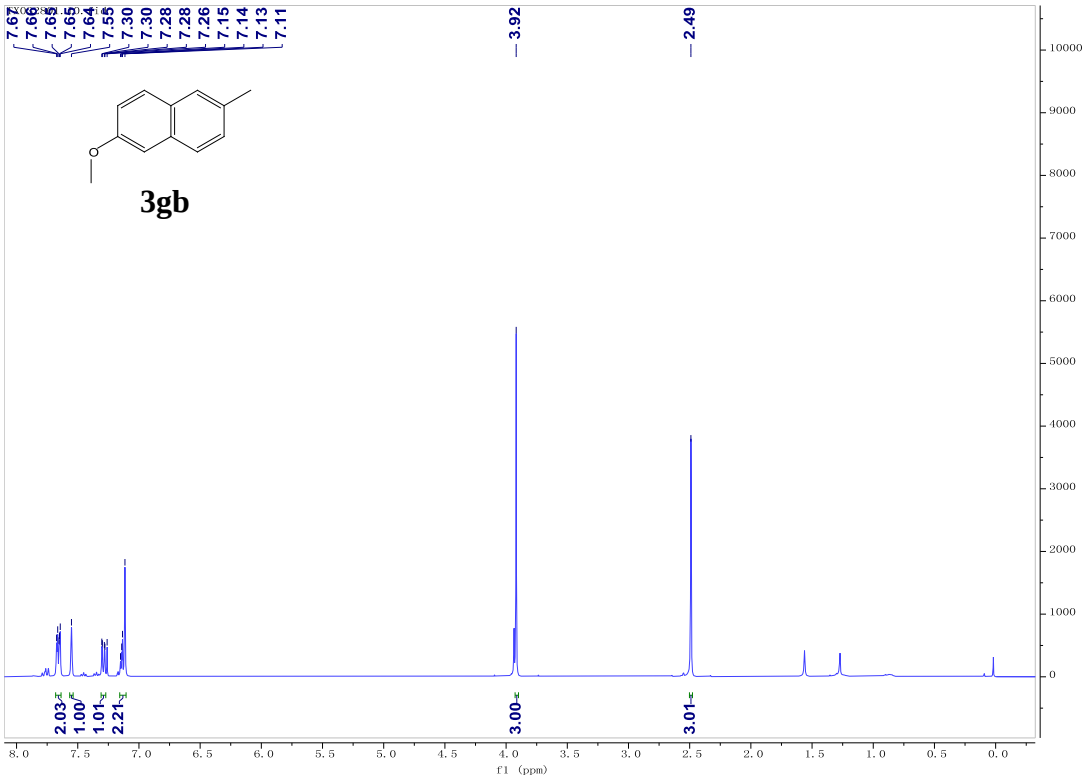
126.41
125.75
125.61
125.58
124.15
19.42
3eb
f1 (ppm)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7.28
7.26
7.15
7.14
7.13
7.11
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2.03
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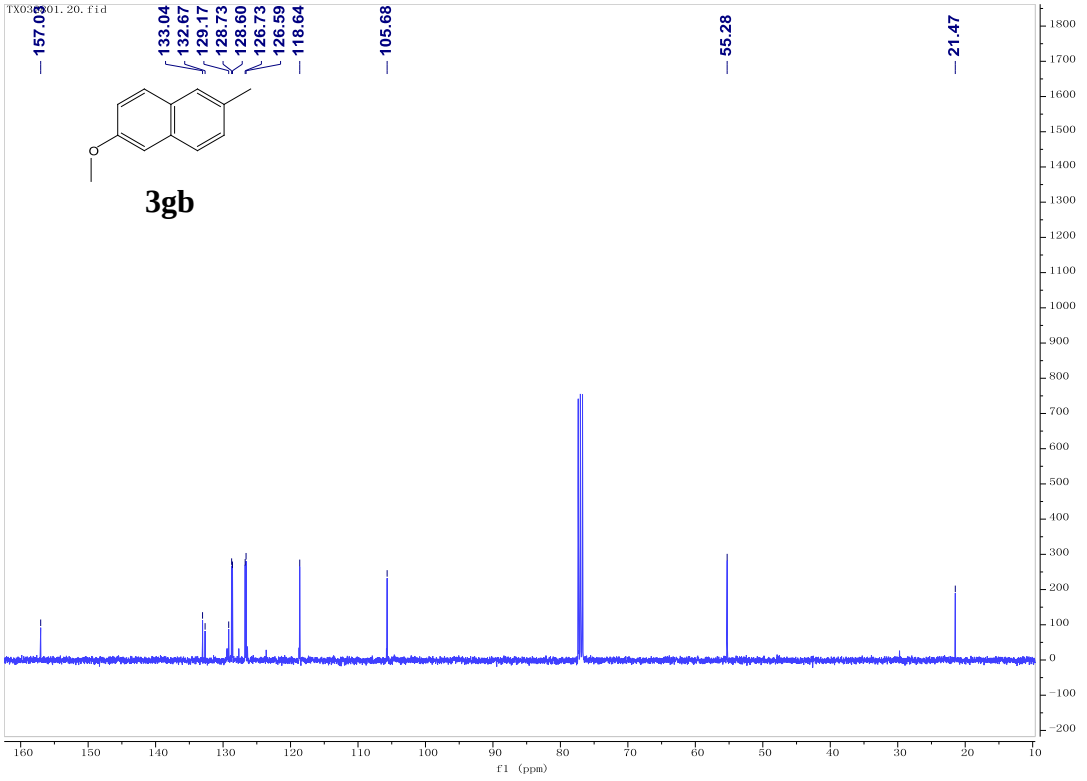
1.01
2.21
3.00
3.01
f1 (ppm)

3gb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126.59
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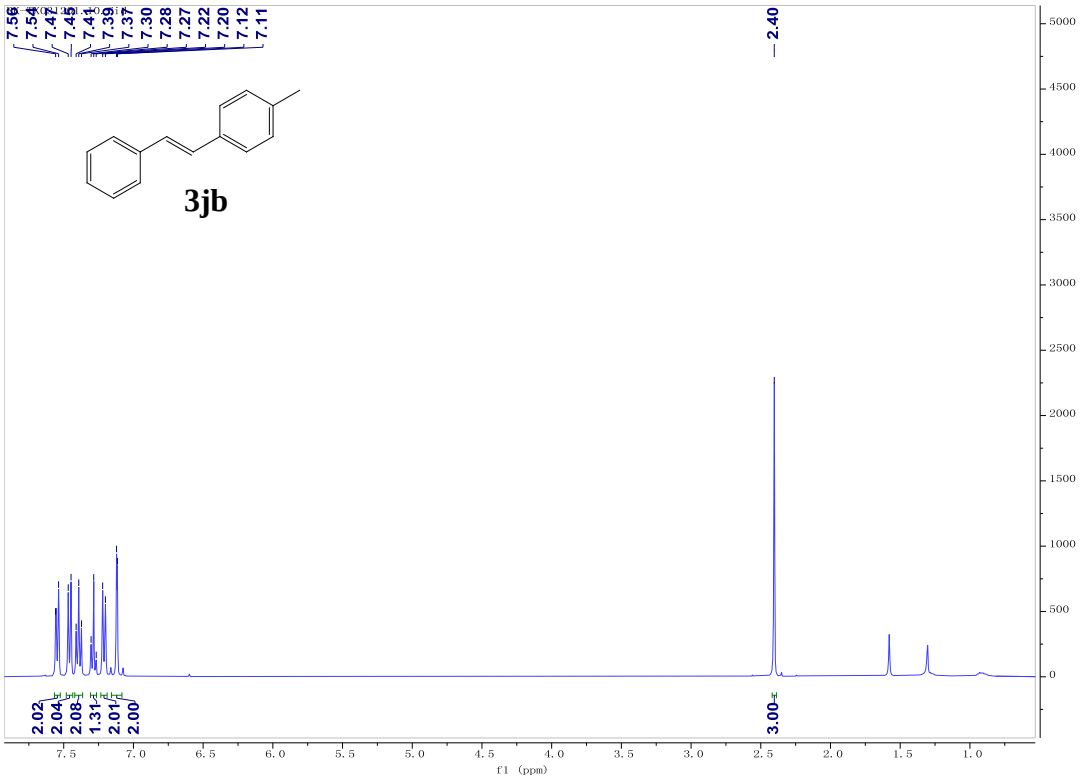
55.28
21.47
f1 (ppm)

3gb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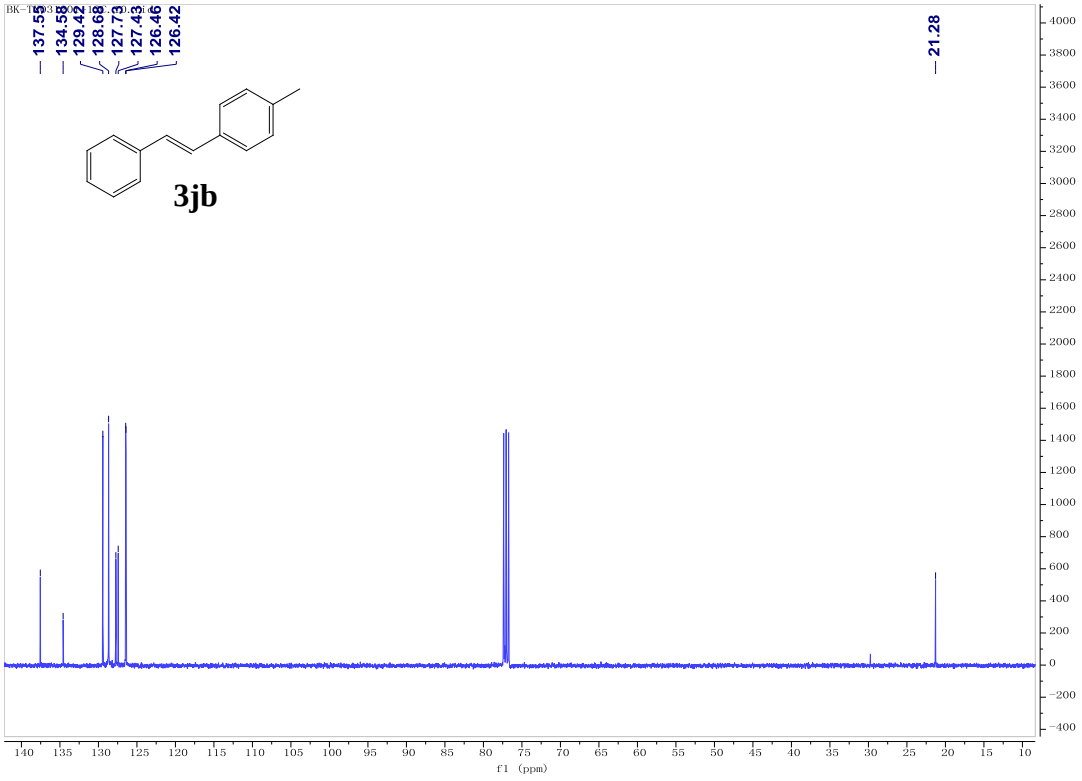
2.04
2.08
1.31
2.01
2.00
3.00
f1 (ppm)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126.42
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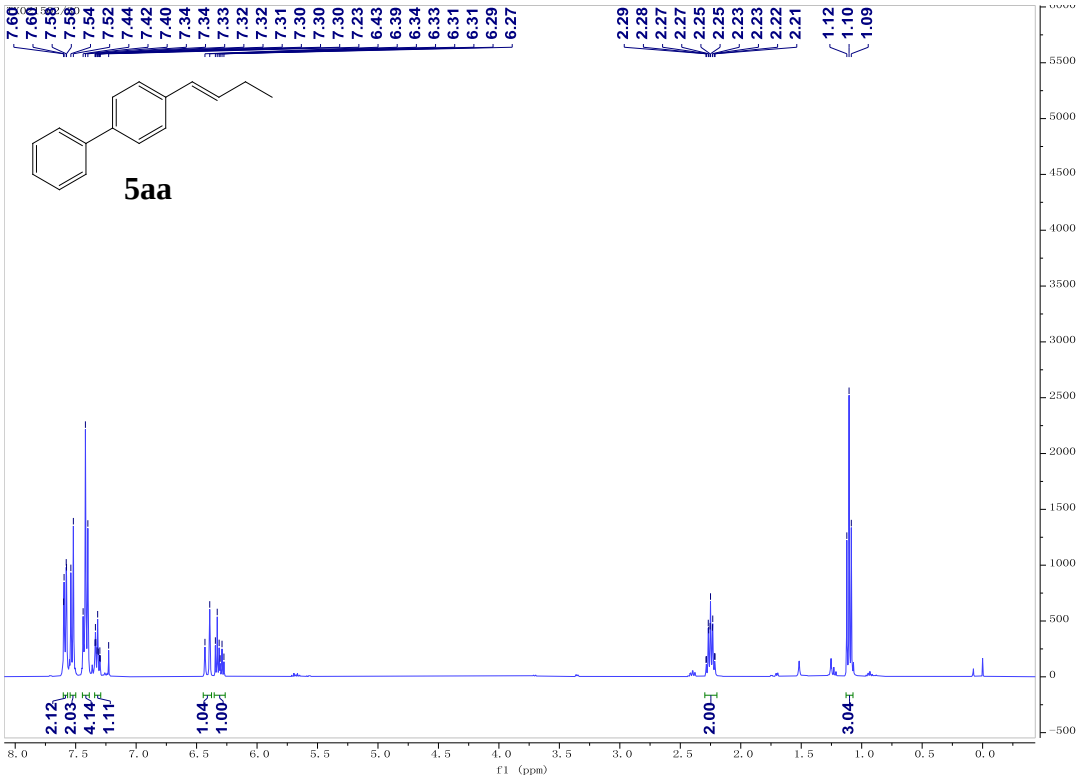
3jb
f1 (ppm)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6.33
6.31
6.31
6.29
6.27
2.29
2.28
2.27
2.27
2.25
2.25
2.23
2.23
2.22
2.21
1.12
1.10
1.09
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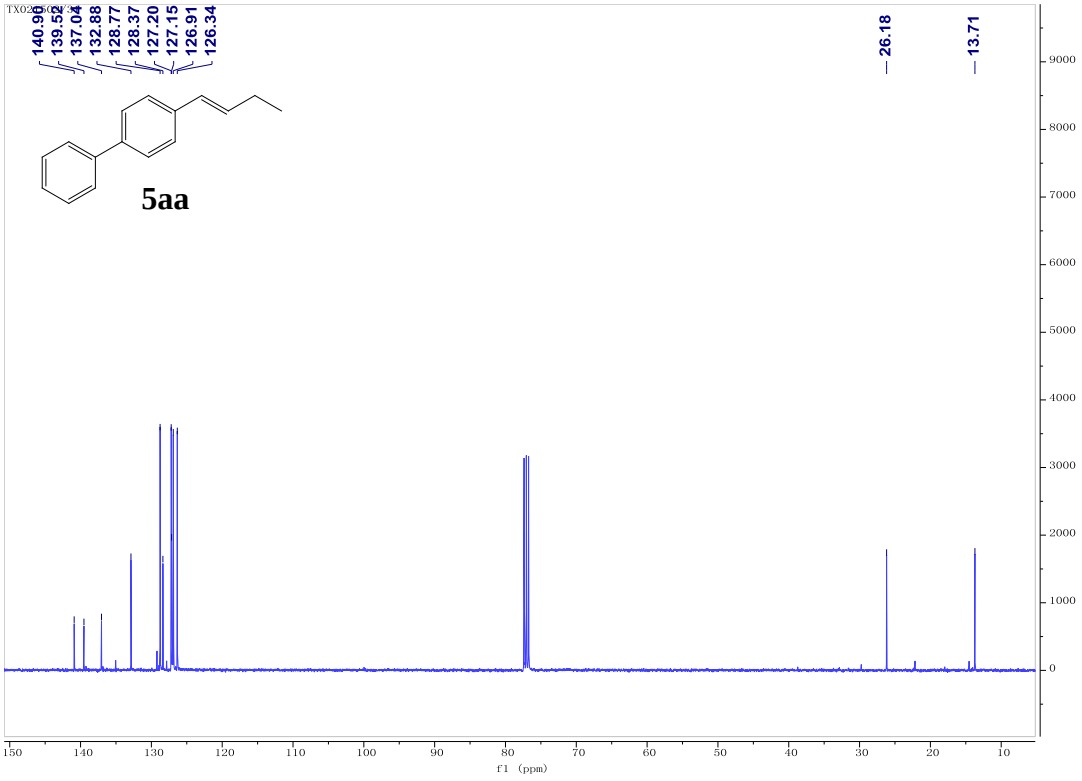
2.12
2.03
4.14
1.11
1.04
1.00
2.00
3.04
f1 (ppm)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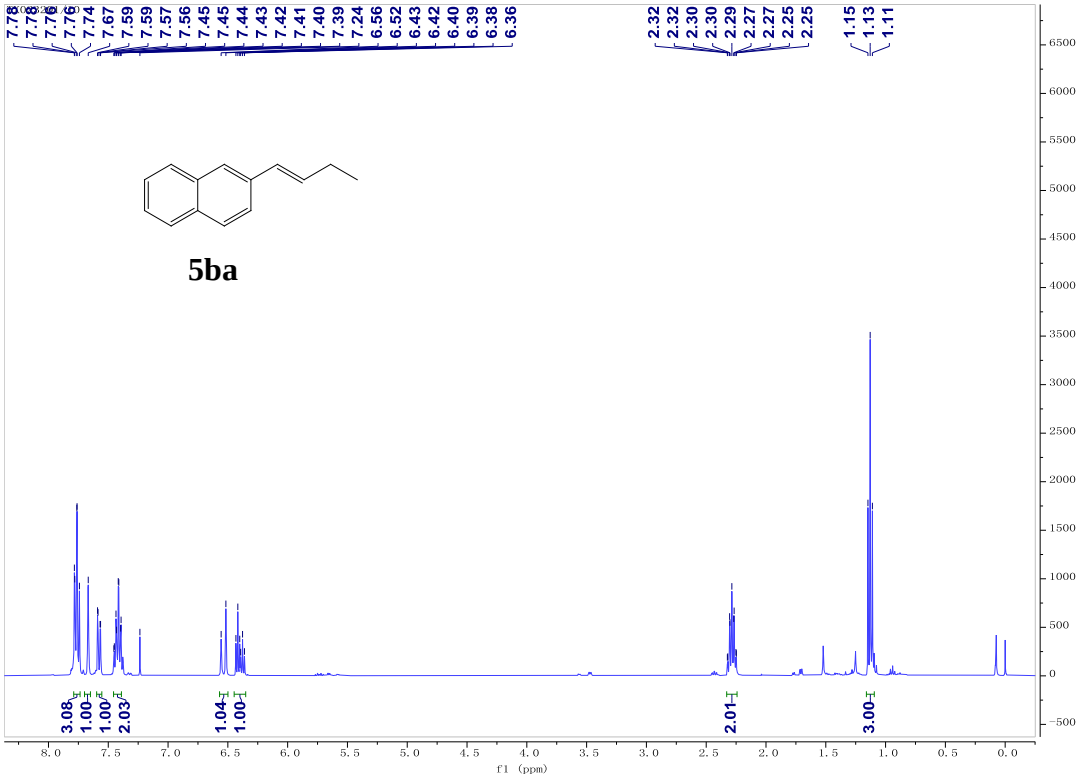
127.15
126.91
126.34
26.18
13.71
5aa
f1 (ppm)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7.41
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7.39
7.24
6.56
6.52
6.43
6.42
6.40
6.39
6.38
6.36
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2.29
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2.25
1.15
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1.11
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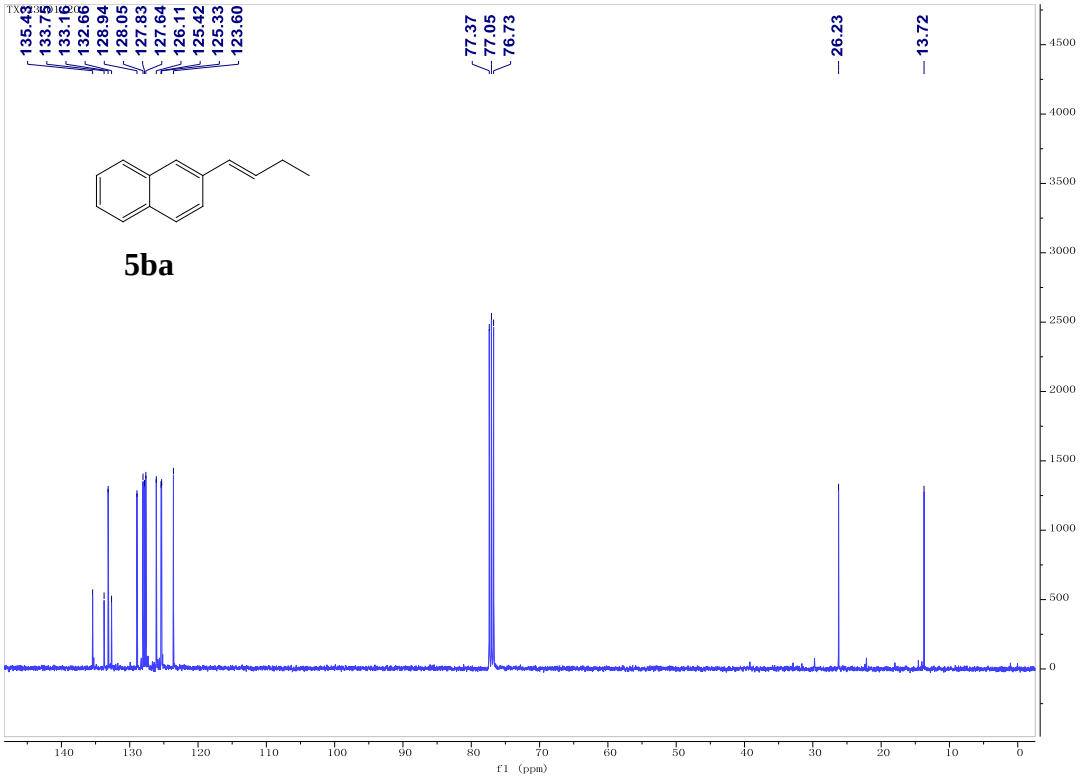
1.00
2.03
1.04
1.00
2.01
3.00
f1 (ppm)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125.33
123.60
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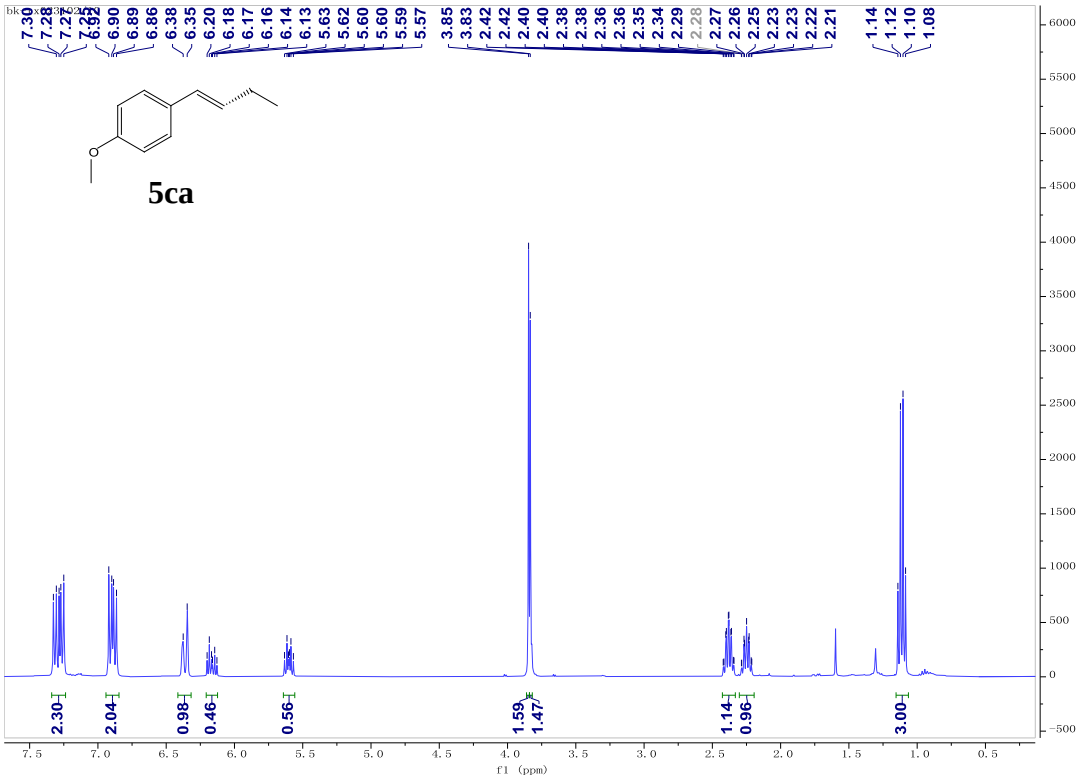
77.05
76.73
26.23
13.72
5ba
f1 (ppm)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6.86
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6.35
6.20
6.18
6.17
6.16
6.14
6.13
5.63
5.62
5.60
5.60
5.59
5.57
3.85
3.83
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2.42
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2.40
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2.25
2.23
2.23
2.22
2.21
1.14
1.12
1.10
1.08
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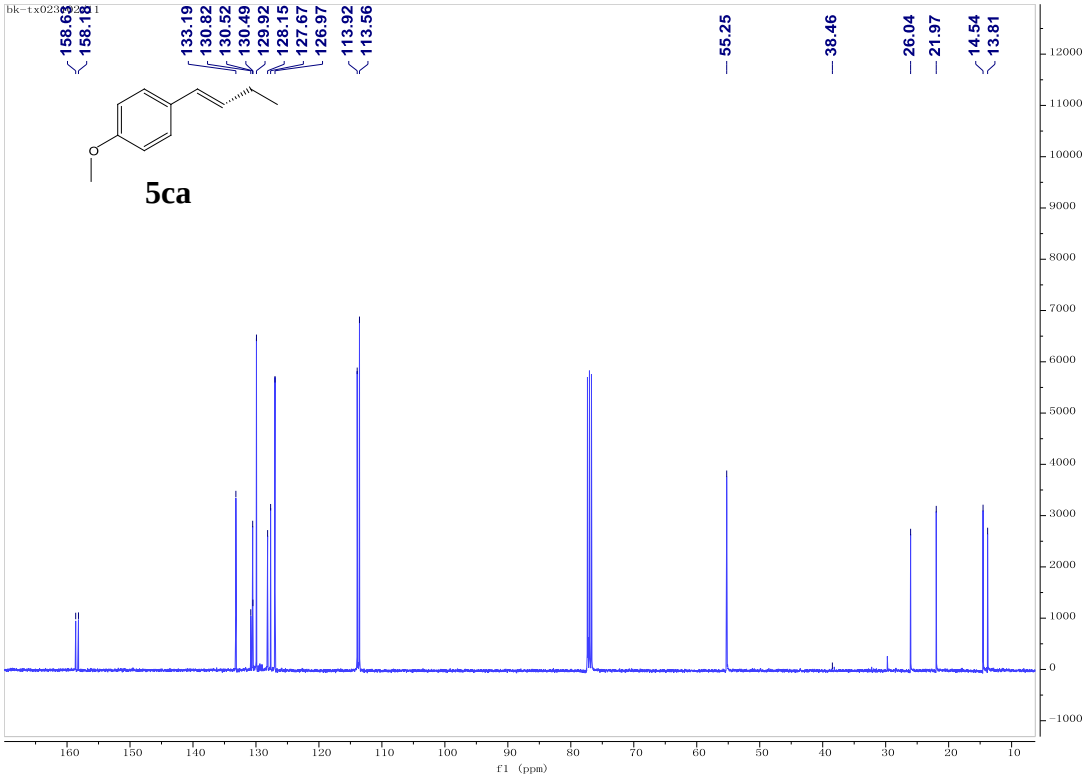
1.47
1.14
0.96
3.00
f1 (ppm)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113.56
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38.46
26.04
21.97
14.54
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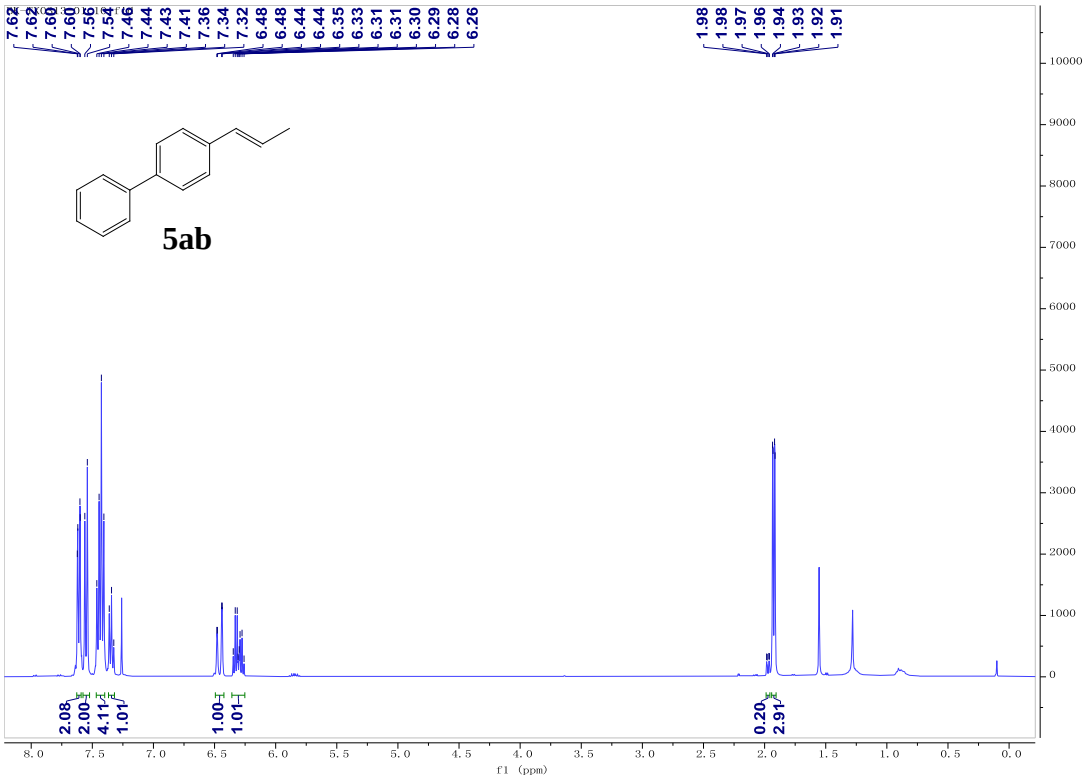
5ca
f1 (ppm)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6.48
6.44
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6.35
6.33
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6.30
6.29
6.28
6.26
1.98
1.98
1.97
1.96
1.94
1.93
1.92
1.91
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4.11
1.01
1.00
1.01
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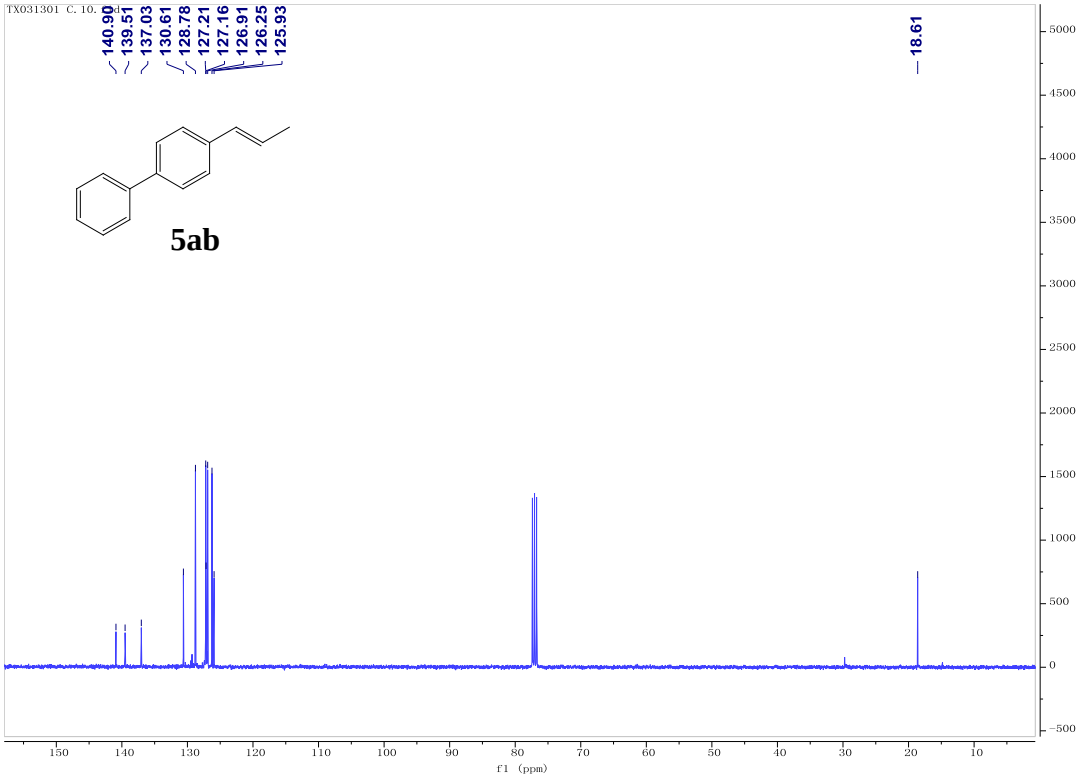
2.91
f1 (ppm)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127.16
126.91
126.25
125.93
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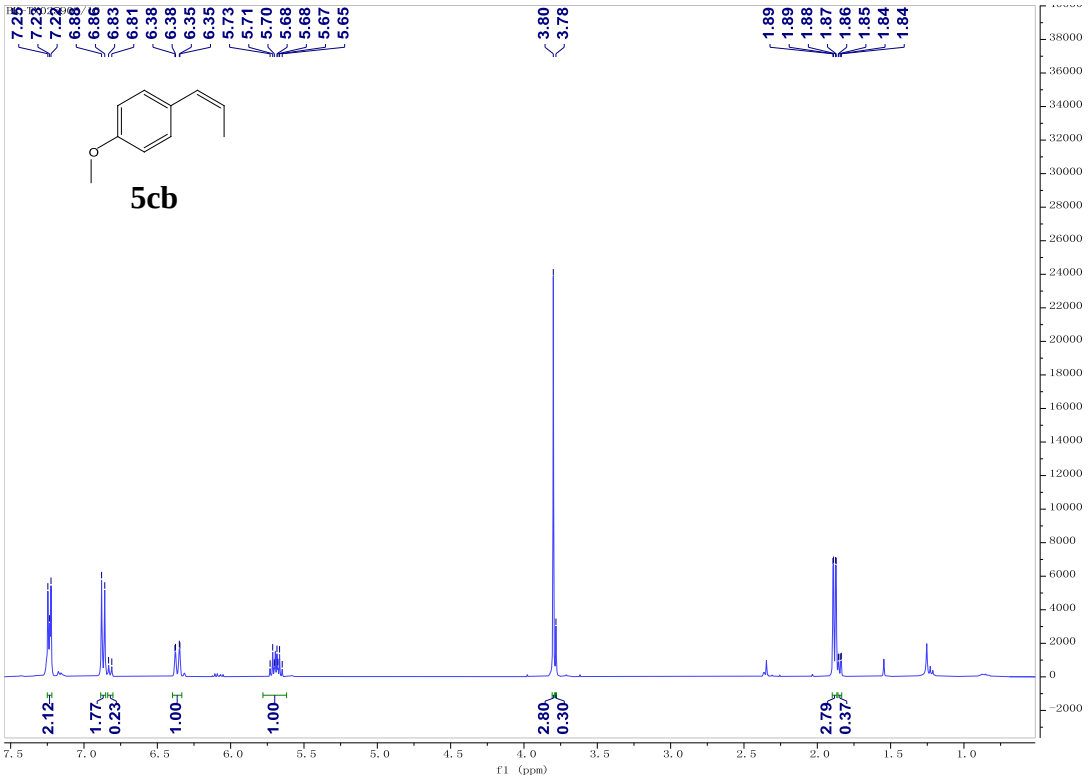
5ab
f1 (ppm)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5.68
5.67
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3.78
1.89
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1.88
1.87
1.86
1.85
1.84
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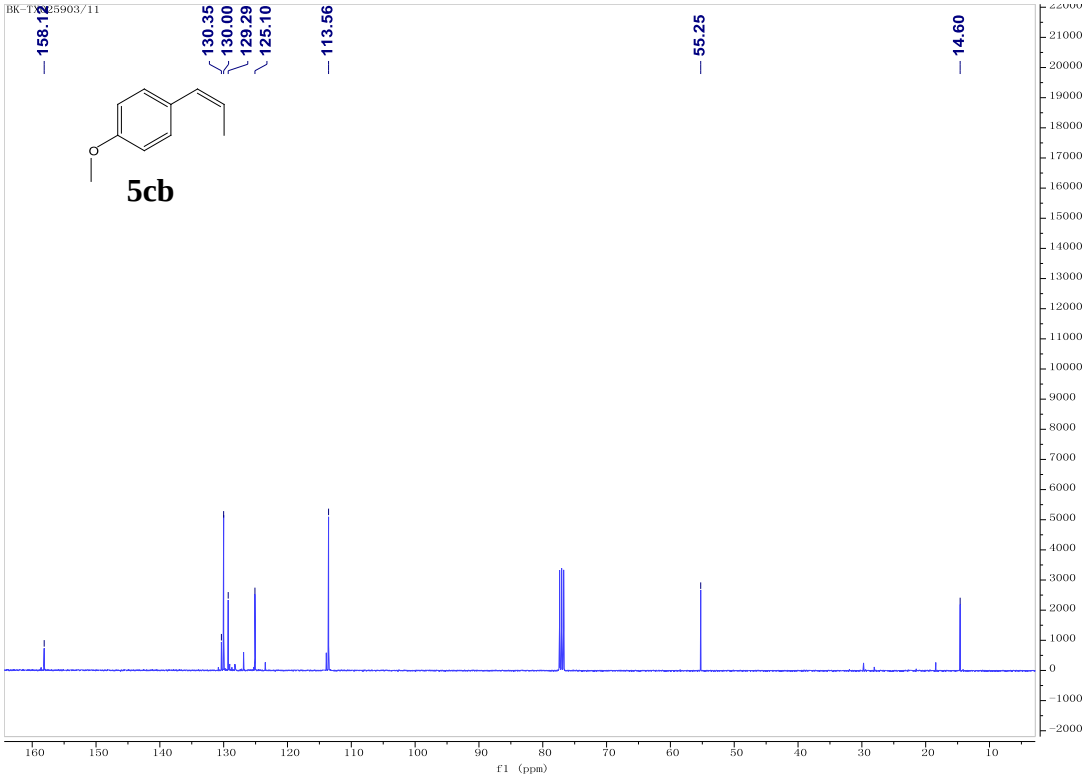
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5cb
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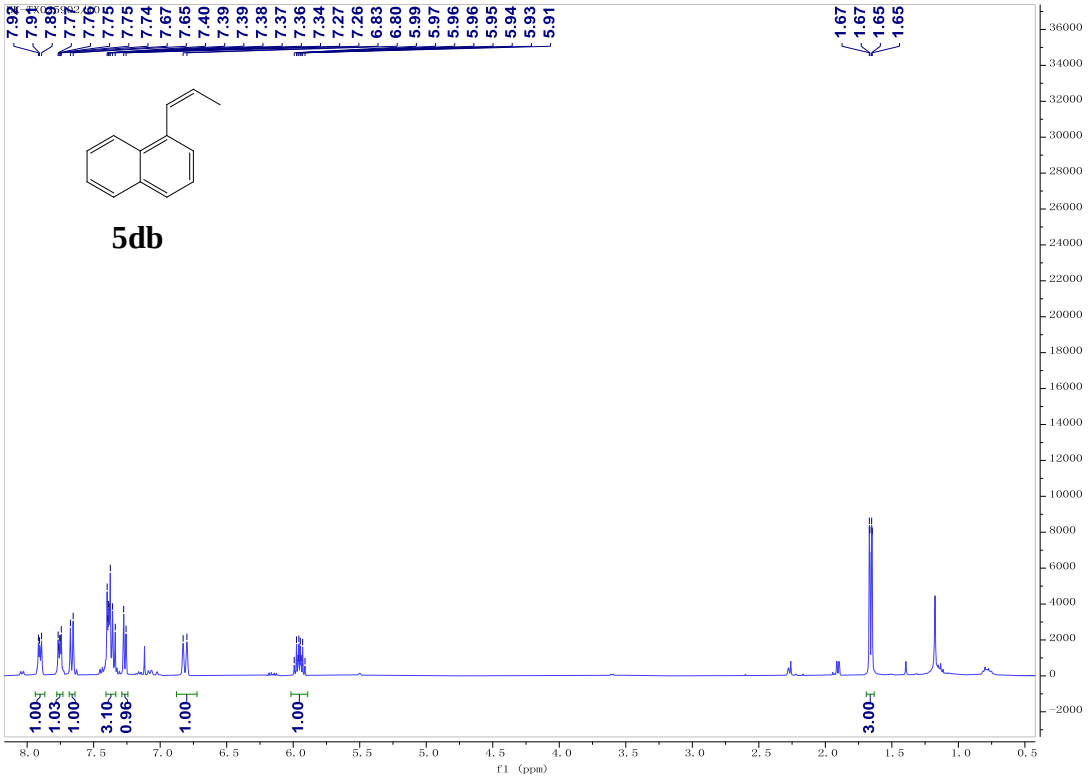
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7.39
7.38
7.37
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7.34
7.27
7.26
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6.80
5.99
5.97
5.96
5.96
5.95
5.94
5.93
5.91
1.67
1.67
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1.65
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1.03
1.00
3.10
0.96
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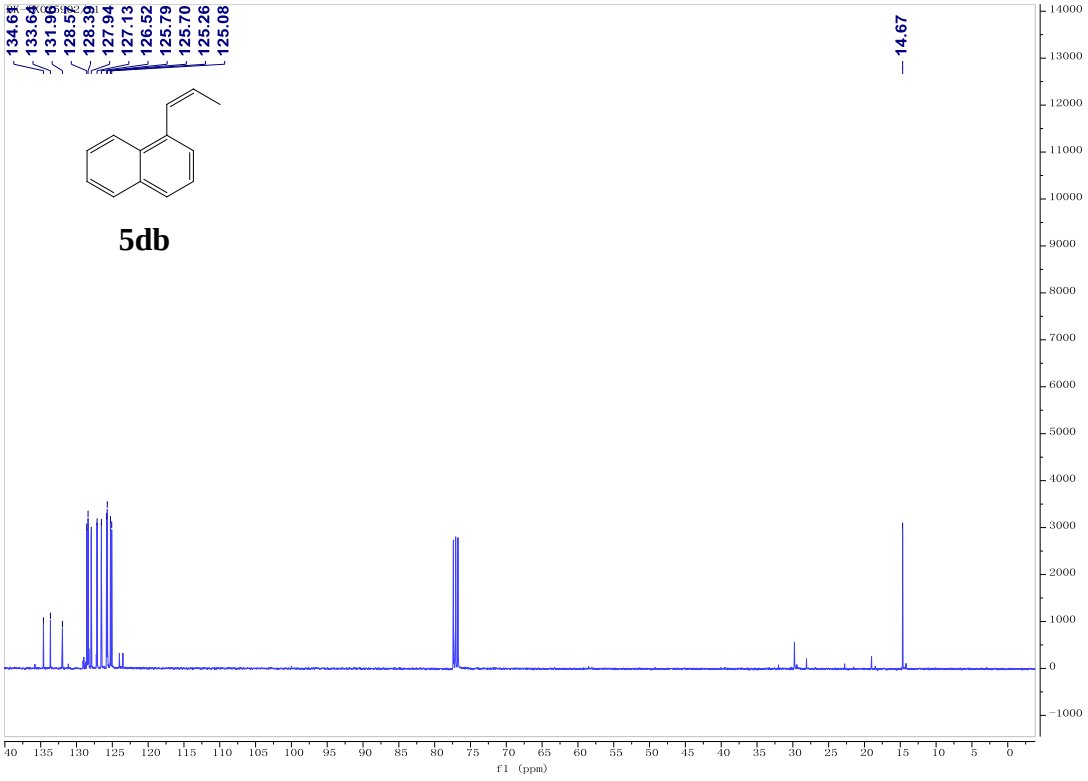
1.00
3.00
f1 (ppm)

5db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126.52
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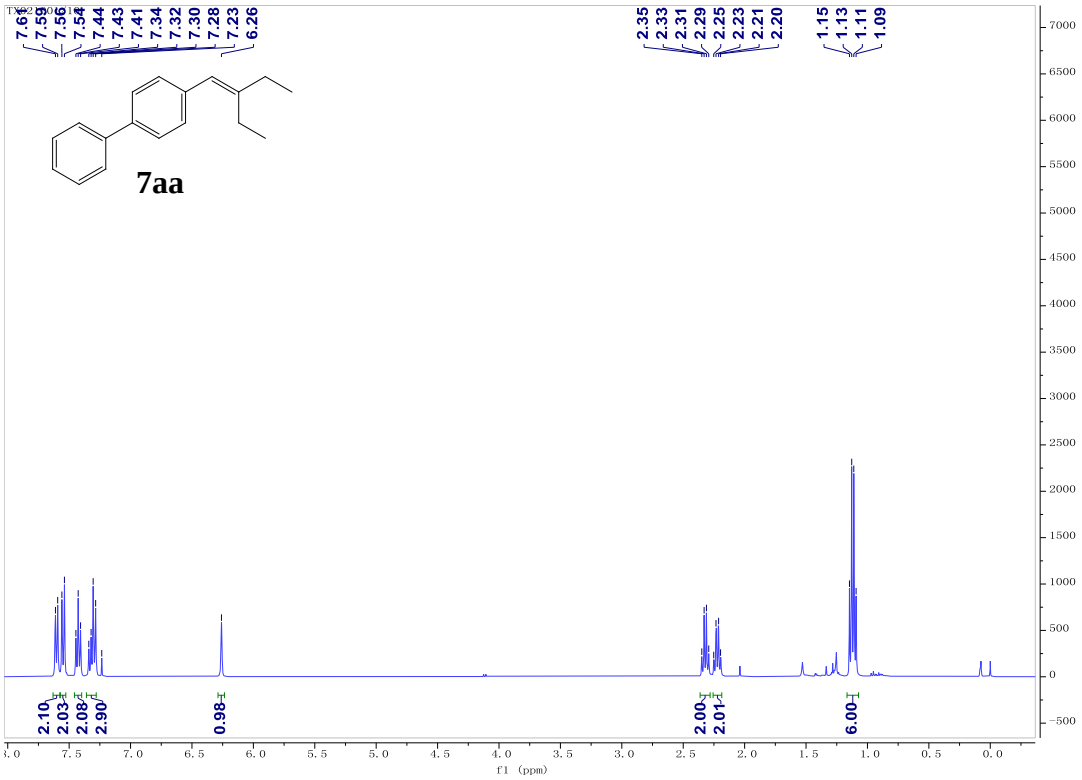
125.26
125.08
14.67
f1 (ppm)

5db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7.34
7.32
7.30
7.28
7.23
6.26
2.35
2.33
2.31
2.29
2.25
2.23
2.21
2.20
1.15
1.13
1.11
1.09
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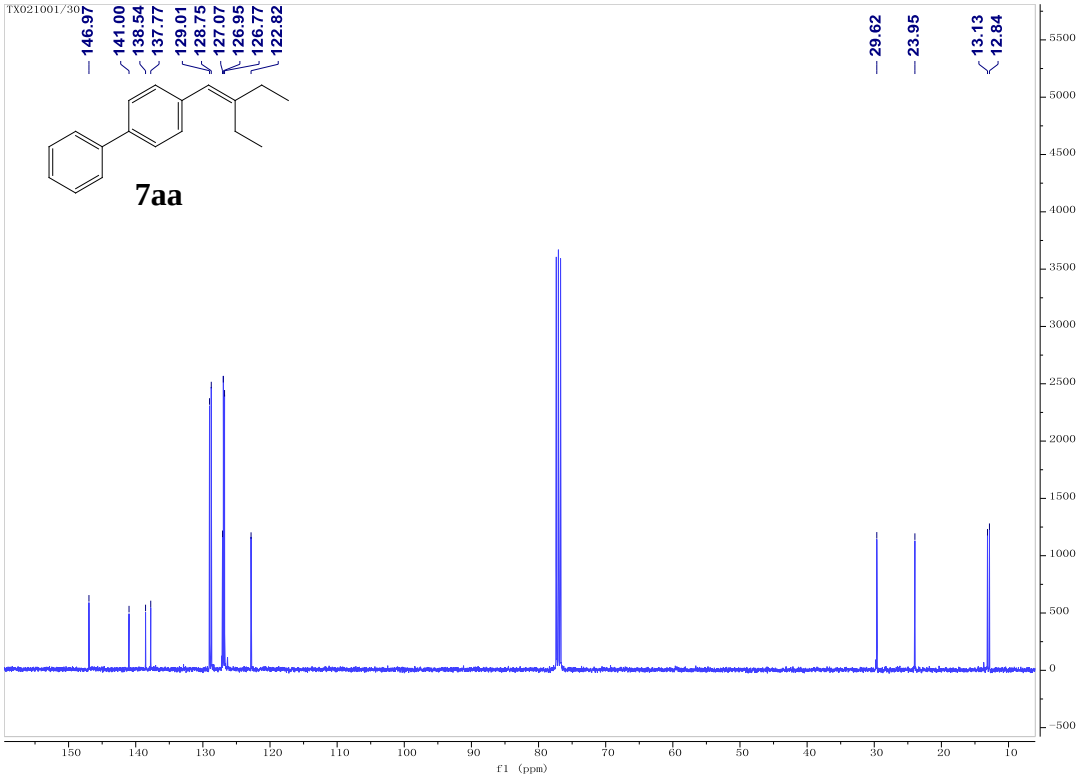
2.10
2.03
2.08
2.90
0.98
2.00
2.01
6.00
f1 (ppm)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23.95
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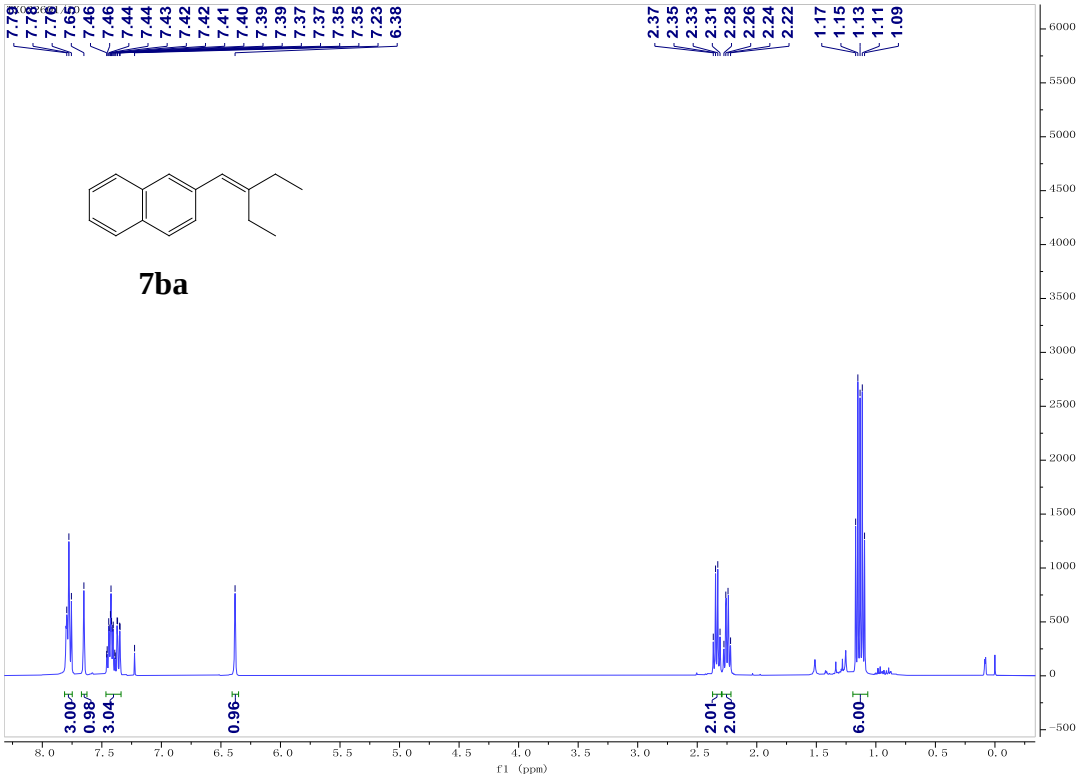
7aa
f1 (ppm)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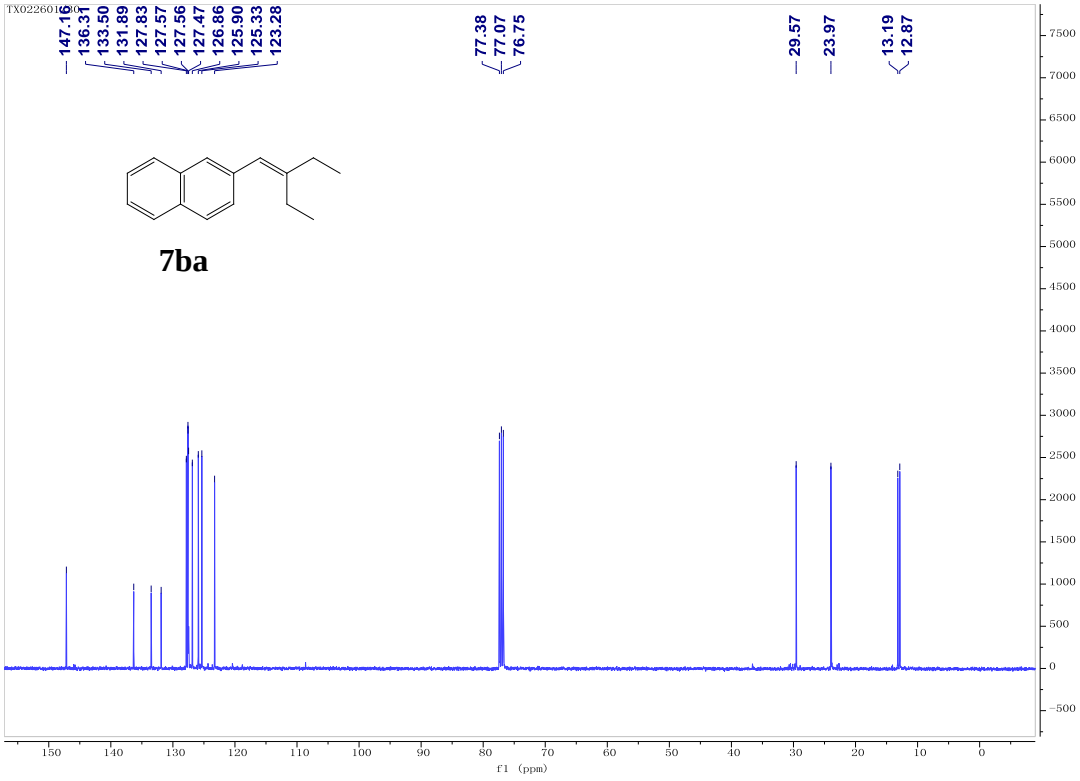
7.37
7.37
7.35
7.35
7.23
6.38
2.37
2.35
2.33
2.31
2.28
2.26
2.24
2.22
1.17
1.15
1.13
1.11
1.09
7ba
3.00
0.98
3.04
0.96
2.01
2.00
6.00
f1 (ppm)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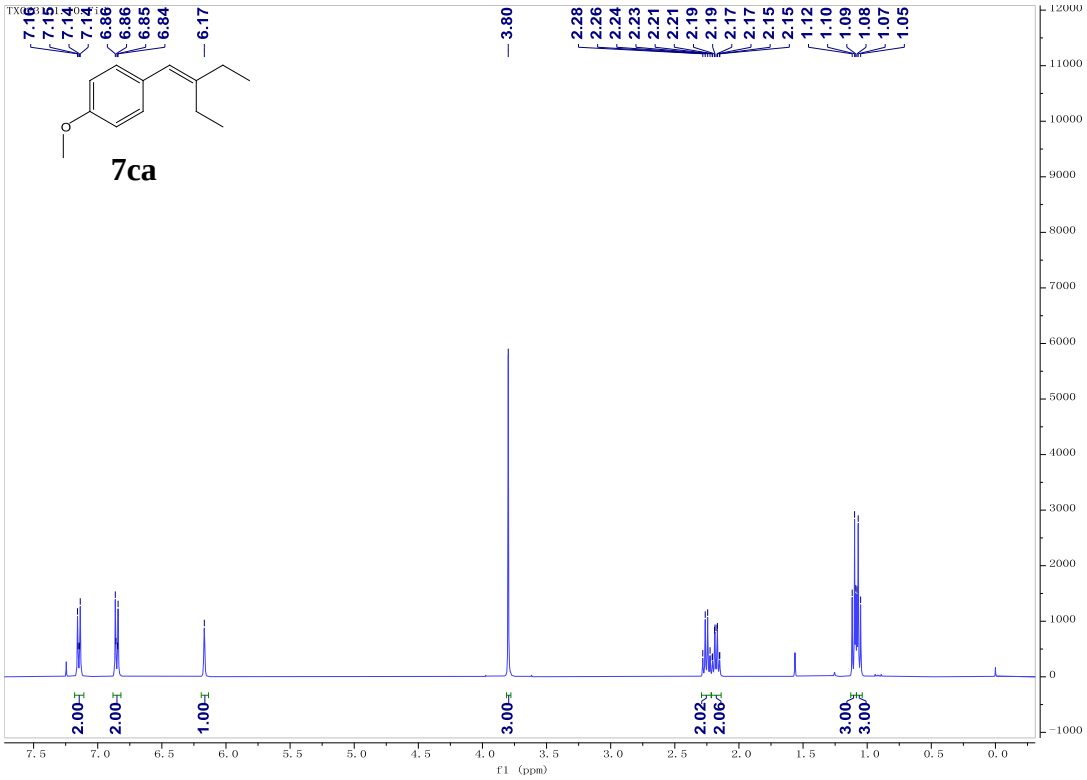
77.07
76.75
29.57
23.97
13.19
12.87
7ba
f1 (ppm)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7.14
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6.86
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6.17
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2.24
2.23
2.21
2.21
2.19
2.19
2.17
2.17
2.15
2.15
1.12
1.10
1.09
1.08
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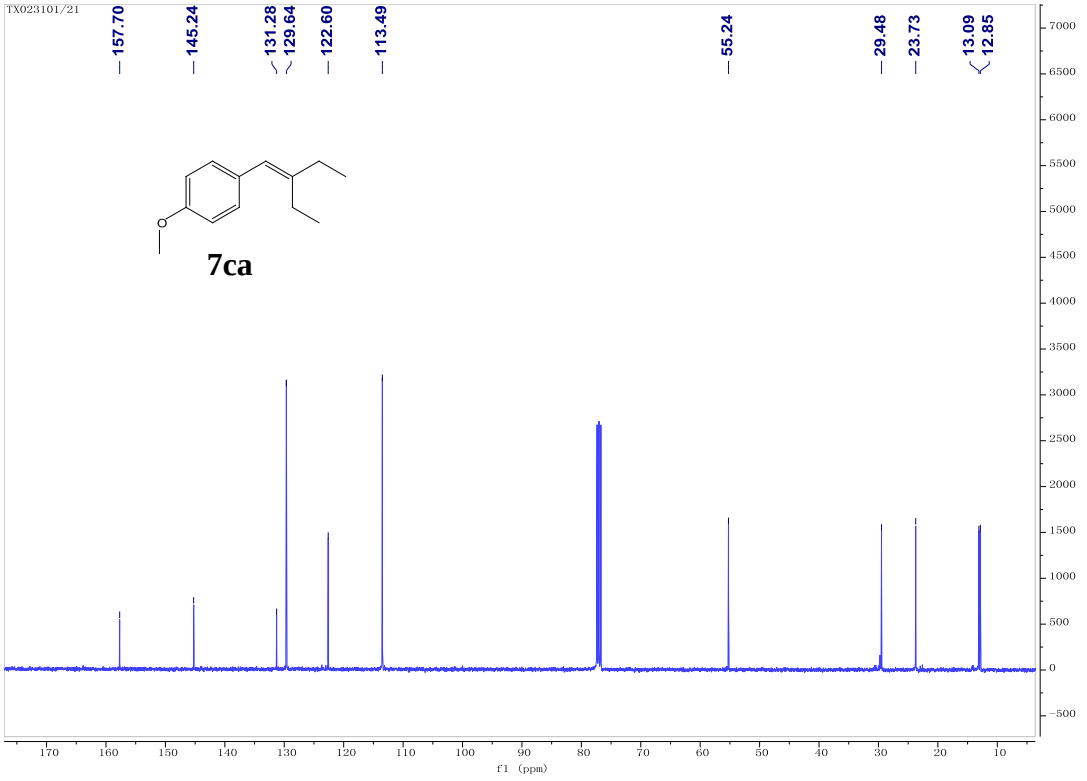
2.02
2.06
3.00
3.00
f1 (ppm)


TX023101/21
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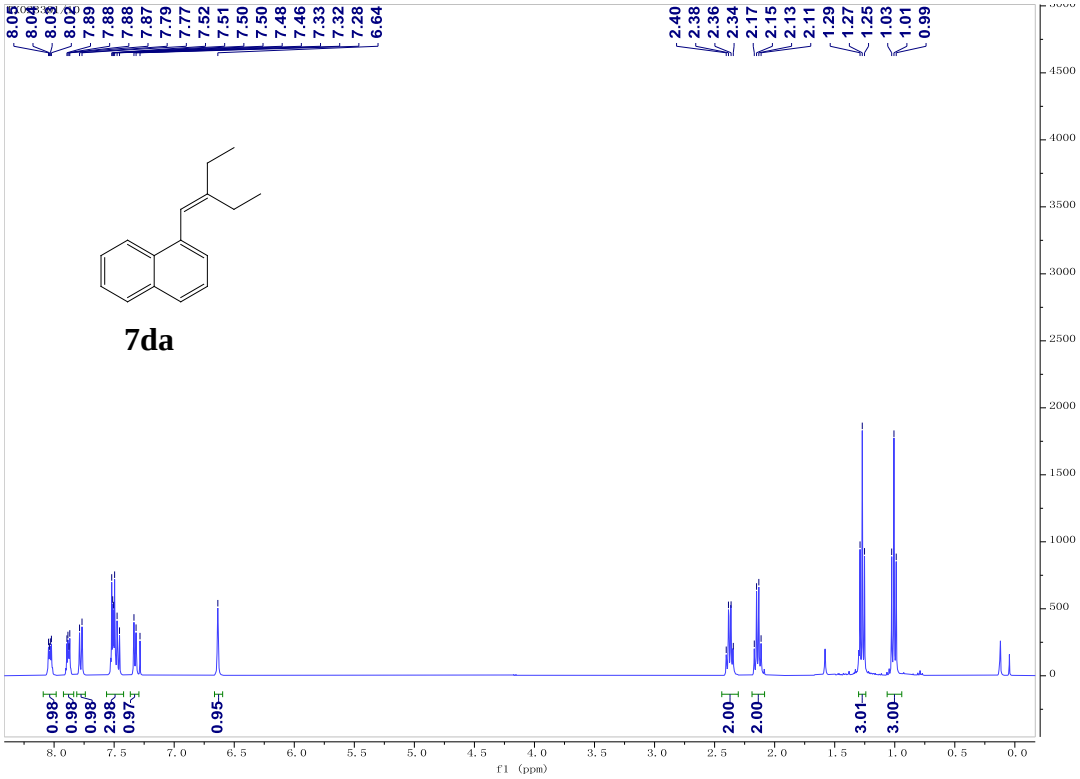
23.73
13.09
12.85
7ca
f1 (ppm)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7.50
7.50
7.48
7.46
7.33
7.32
7.28
6.64
2.40
2.38
2.36
2.34
2.17
2.15
2.13
2.11
1.29
1.27
1.25
1.03
1.01
0.99
0.98
0.98
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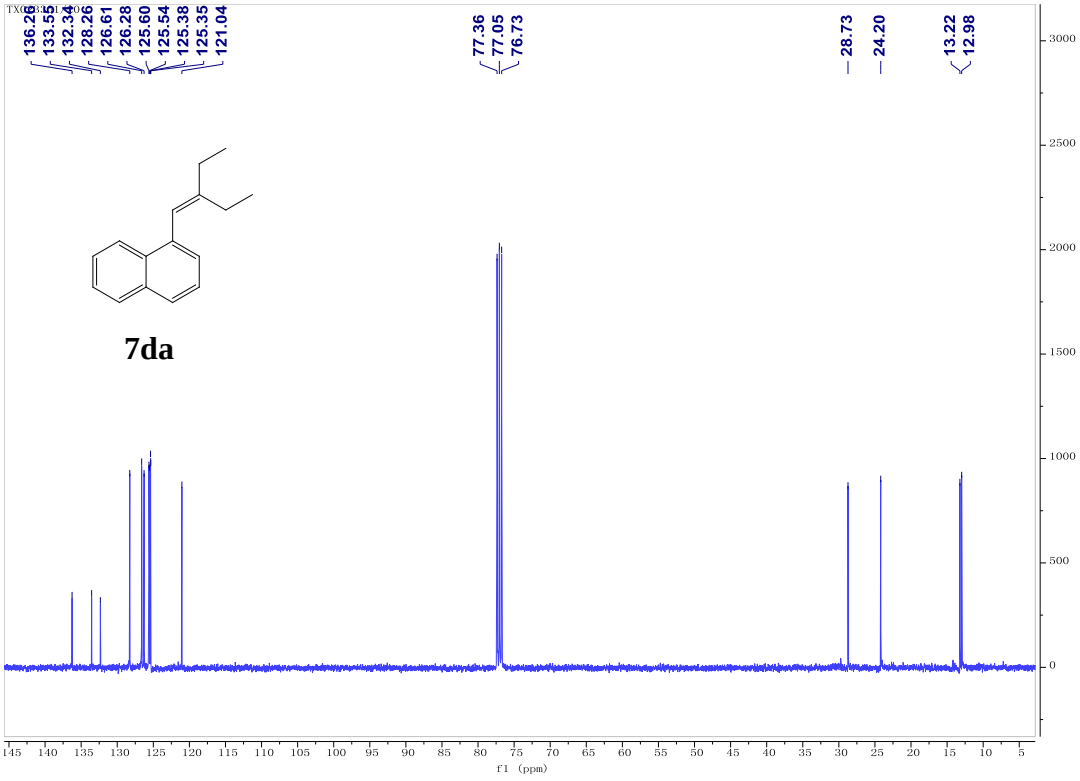
2.98
0.97
0.95
2.00
2.00
3.01
3.00
f1 (ppm)

7da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125.54
125.38
125.35
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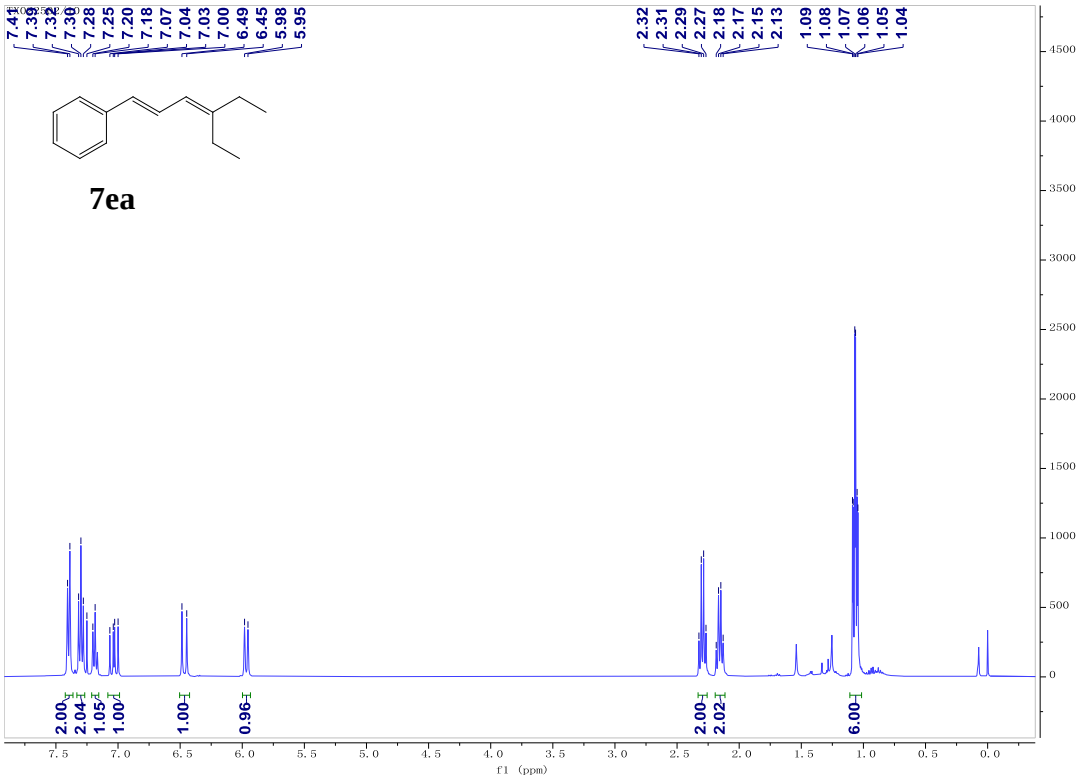
77.05
76.73
28.73
24.20
13.22
12.98
f1 (ppm)

7da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5.98
5.95
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2.31
2.29
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2.17
2.15
2.13
1.09
1.08
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1.04
7ea
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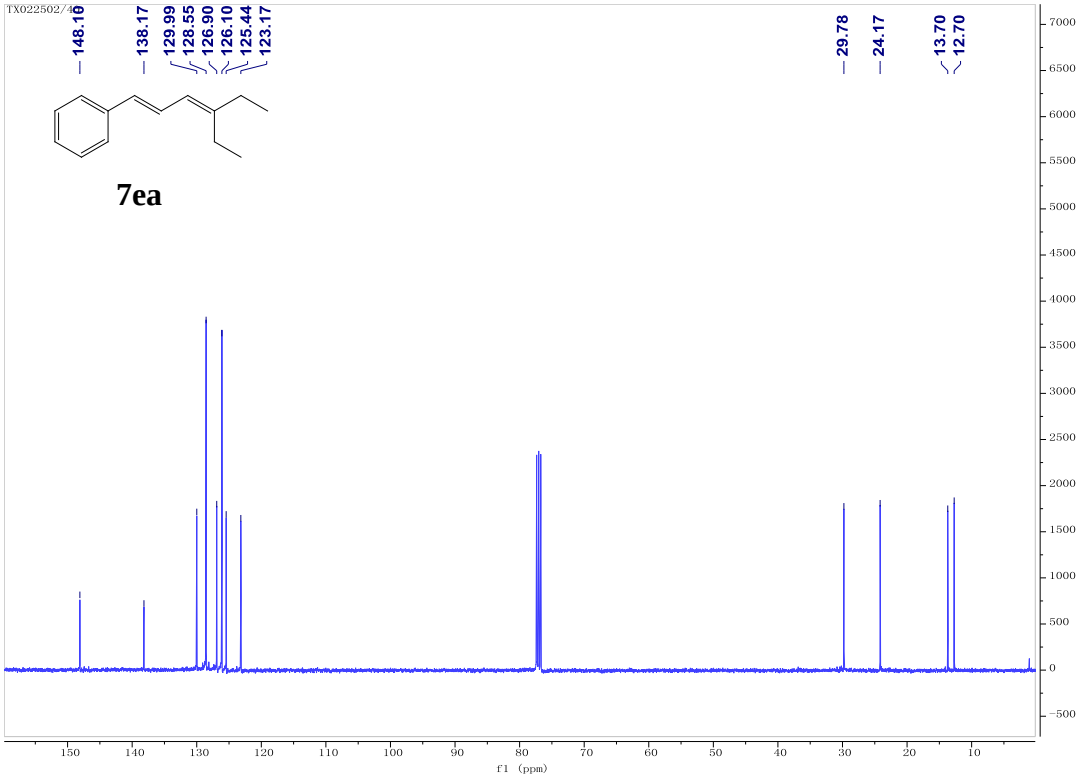
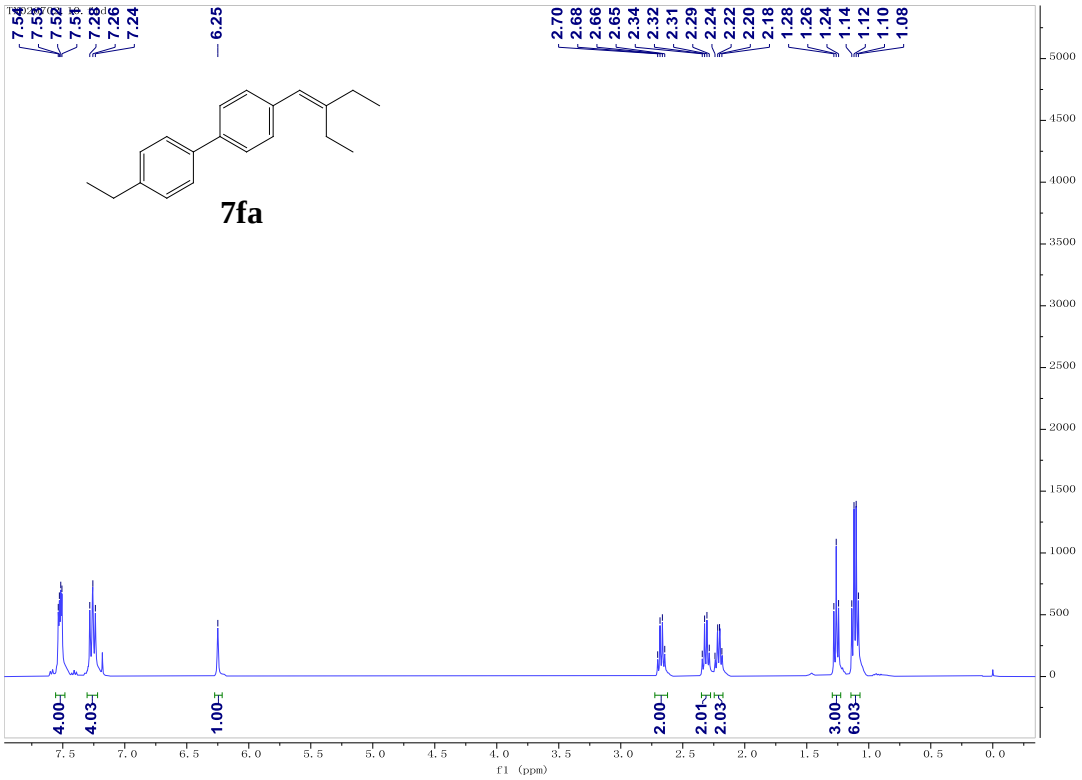
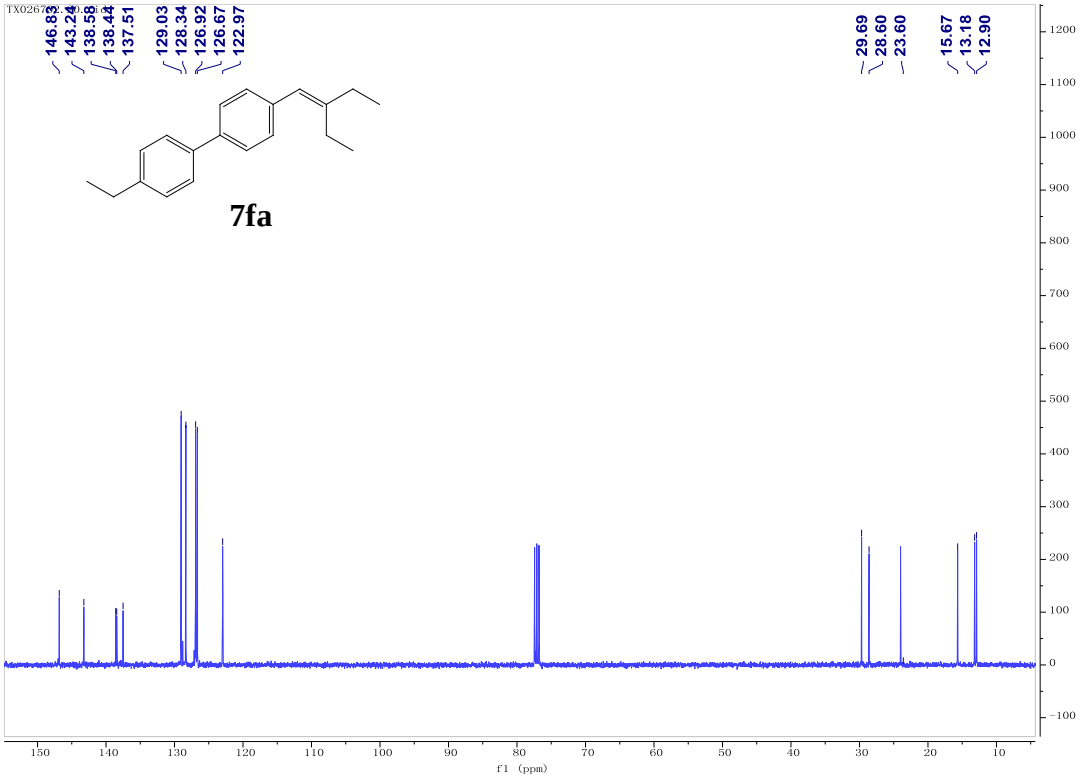
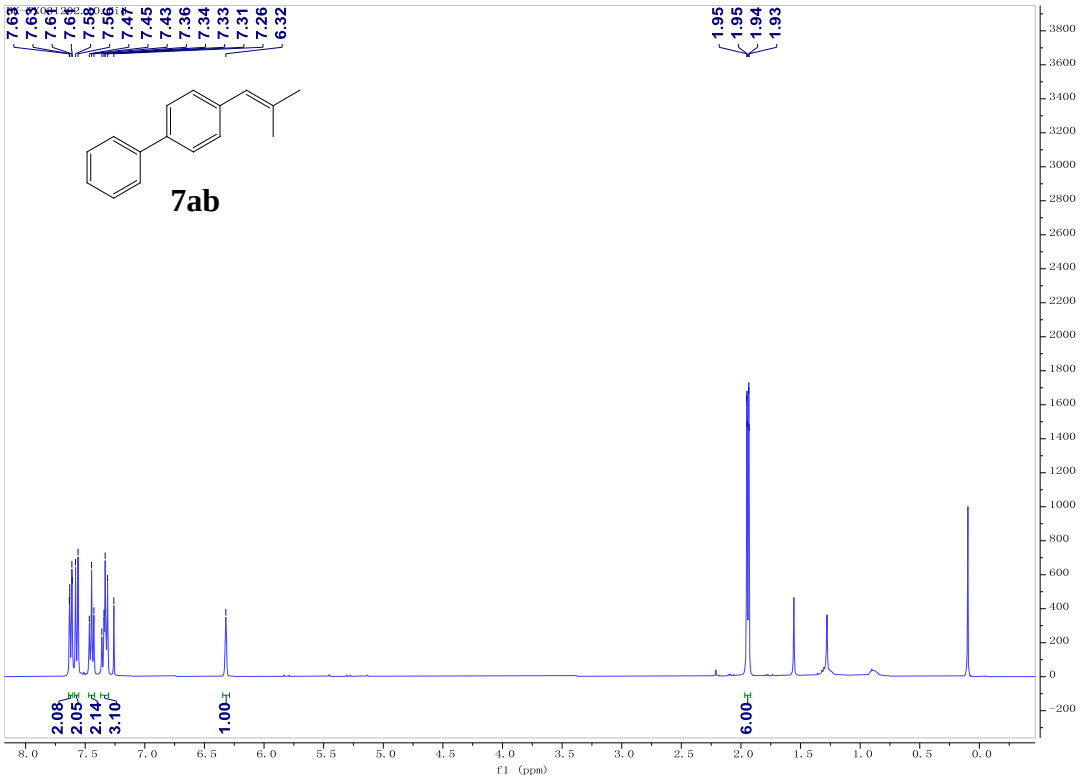
1.05
1.00
1.00
0.96
2.00
2.02
6.00
f1 (ppm)


148.16
138.17
129.99
128.55
126.90
126.10
125.44
123.17
29.78
24.17
13.70
12.70
7ea
f1 (ppm)


7.54
7.53
7.52
7.51
7.28
7.26
7.24
6.25
2.70
2.68
2.66
2.65
2.34
2.32
2.31
2.29
2.24
2.22
2.20
2.18
1.28
1.26
1.24
1.14
1.12
1.10
1.08
7fa
4.00
4.03
1.00
2.00
2.01
2.03
3.00
6.03
f1 (ppm)


146.83
143.24
138.58
138.44
137.51
129.03
128.34
126.92
126.67
122.97
29.69
28.60
23.60
15.67
13.18
12.90
7fa
f1 (ppm)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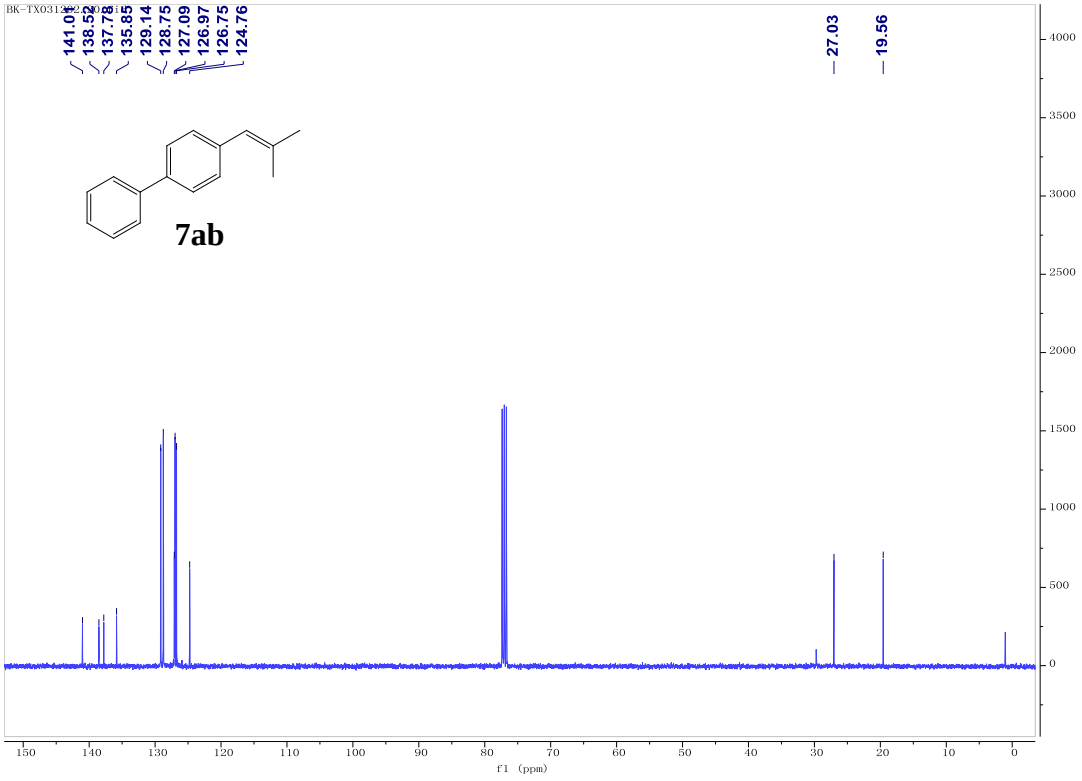
7.63
7.61
7.61
7.58
7.56
7.47
7.45
7.43
7.36
7.34
7.33
7.31
7.26
6.32
1.95
1.95
1.94
1.93
7ab
2.08
2.05
2.14
3.10
1.00
6.00
f1 (ppm)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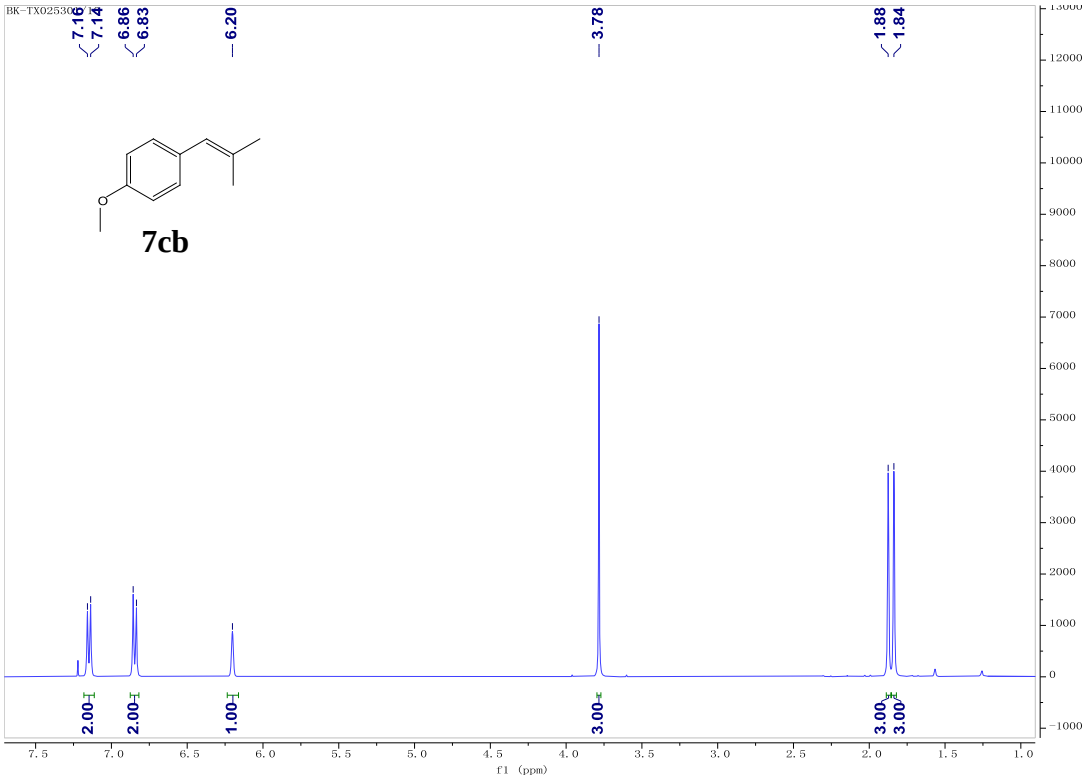
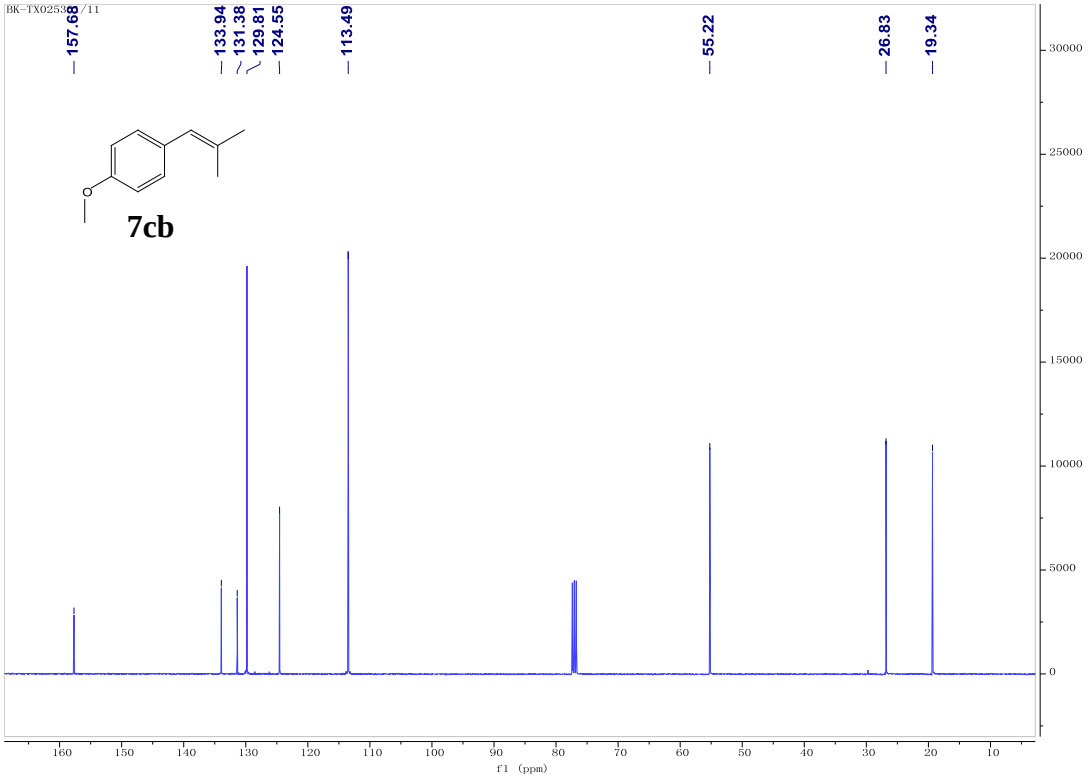
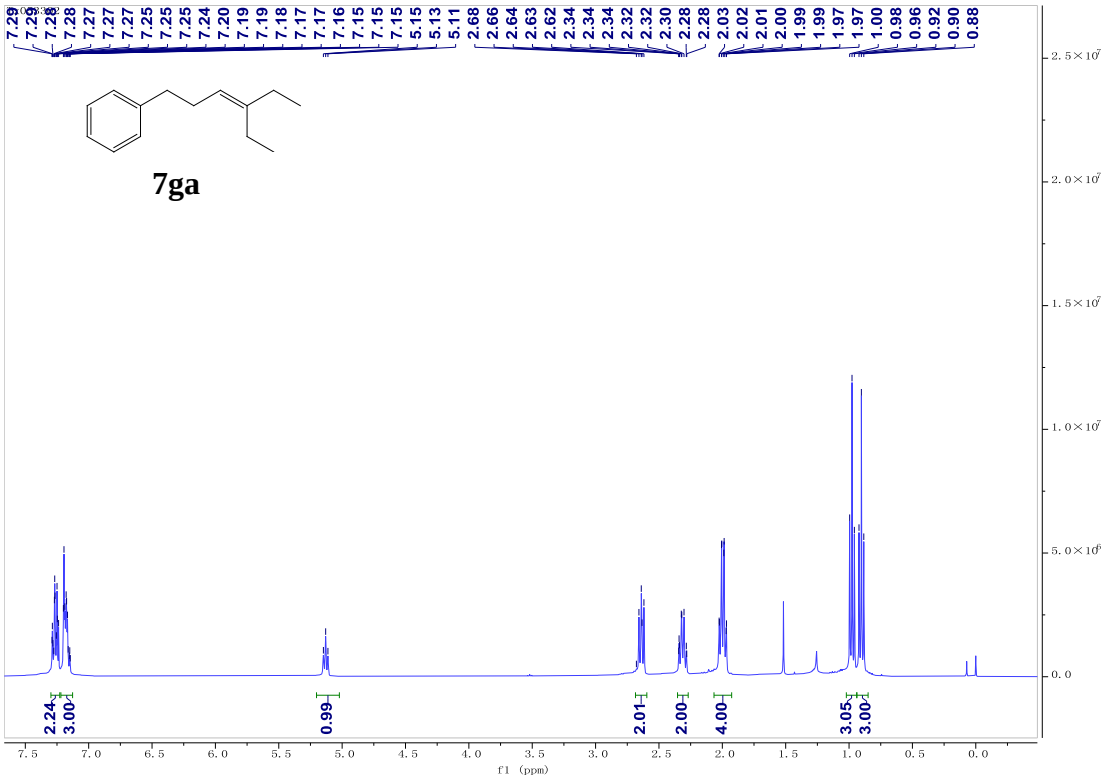
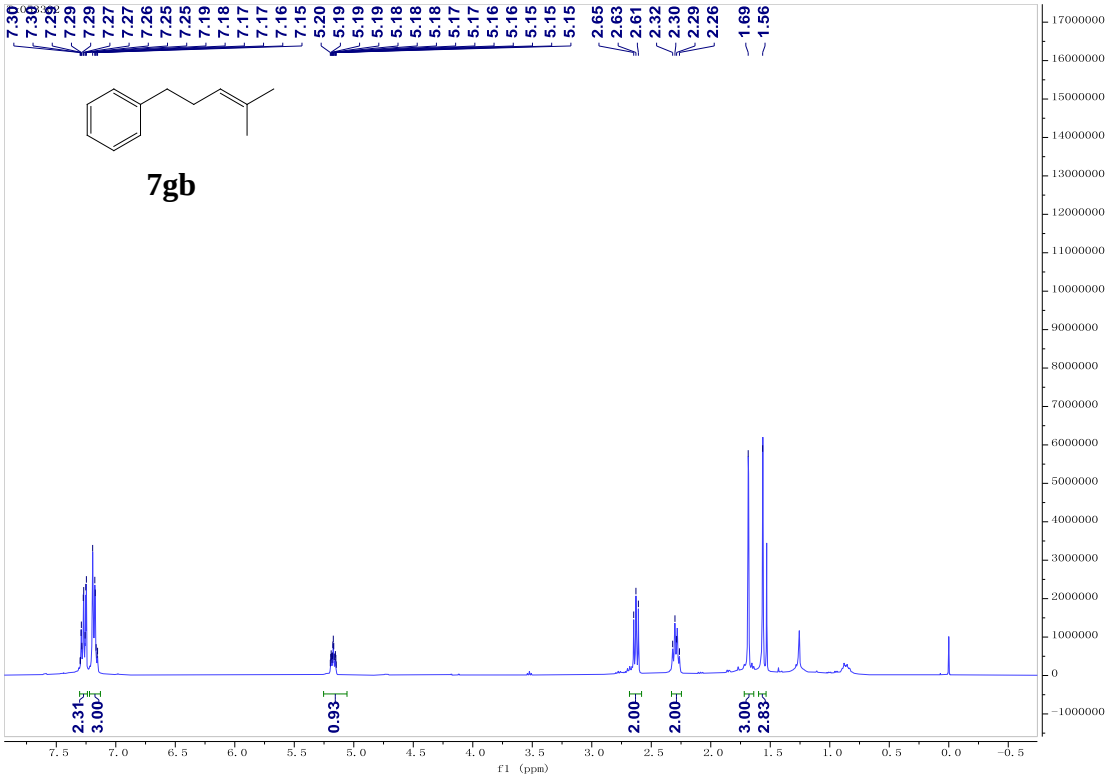
138.52
137.78
135.85
129.14
128.75
127.09
126.97
126.75
124.76
27.03
19.56
7ab
f1 (ppm)


7.16
7.14
6.86
6.83
6.20
3.78
1.88
1.84
7cb
2.00
2.00
1.00
3.00
3.00
3.00
f1 (ppm)


157.68
133.94
131.38
129.81
124.55
113.49
55.22
26.83
19.34
7cb
f1 (ppm)



7ga



7gb