Supplementary Information for:

Catalytic Cross Deoxygenative and Dehydrogenative Coupling of Aldehydes and Alkenes: Redox-Neutral Process to Skipped Dienes

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1. General experimental details

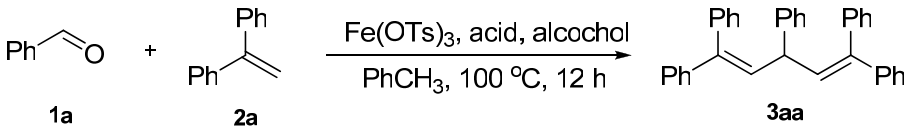
All non-aqueous reactions and manipulations were performed under argon atmosphere using flame-dried Young-type tube. All solvents before used were dried and degassed by standard methods and stored under argon. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER AVANCE III (400M). Chemical shifts are reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications.

High resolution mass spectra (HRMS) were recorded on Waters Micromass GCT Premier (EI+). GC analysis were performed on Agilent 7890 with Hp-5 column. GS-MS analysis were performed with Agilent 7890A/5975C GC-MS system. 1,1-Diphenylethylene, substituted styrenes and aldehydes used here were known compounds and purchased from Alfa Aesar except 1-fluoro-4-vinylbenzene which was purchased from Acros. 1-Fluoro-4-(1-phenylvinyl)benzene, 1-bromo-4-(1-phenylvinyl)benzene, 1-methyl-4-(1-phenylvinyl)benzene, 1-methoxy-4-(1-phenylvinyl)benzene and 2-(1-phenylvinyl)thiophene used here were known compounds and synthesized according to the reported methods.[1] Benzaldehyde dimethyl acetal and (*E*)-(3-methoxyprop-1-ene-1,3-diyl)dibenzene used here were known compounds and synthesized according to the known literature.[2, 3]

2. Optimization of the reaction conditions

Benzaldehyde **1a** (42.4 mg, 0.4 mmol, 1.0 equiv), 1,1-diphenylethylene **2a** (216.0 mg, 1.2 mmol, 3.0 equiv), Lewis acid (0.02 mmol, 5 mol%), Brønsted acid (0.08 mmol, 20 mol%), alcohol (0.1 mmol, 25 mol%) and dry solvent (2.0 mL) were added to a 25 mL flame-dried Young-type tube under argon atmosphere. The reaction mixture was stirred at designed temperature for 12 hours, and then cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel and eluted with petroleum ethers (PE) to afford the desired product **3aa**.

Table 1. Screening of Brønsted acids and alcohols[a]

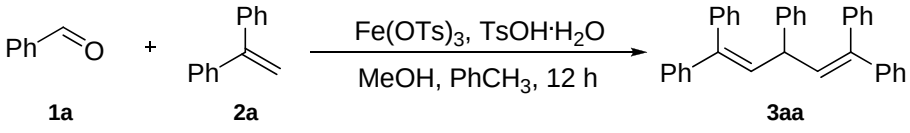


1a 2a 3aa

Entry	Brønsted acid	Alcohol	Yield (%)[b]
1	NH_2SO_3H	MeOH	34
2	4-NsOH	MeOH	18
3	$H_2C_2O_4{\cdot}2H_2O$	MeOH	10
4	4-NO_2-$PhCO_2H$	MeOH	11
5	CCl_3CO_2H	MeOH	26
6	$TsOH{\cdot}H_2O$	MeOH	60
7	$TsOH{\cdot}H_2O$	^{i}PrOH	49
8	$TsOH{\cdot}H_2O$	EtOH	53
9	$TsOH{\cdot}H_2O$	^{n}BuOH	55
10	$TsOH{\cdot}H_2O$	^{t}BuOH	24

[a] Reaction conditions: benzaldehyde **1a** (42.4 mg, 0.4 mmol, 1.0 equiv), 1,1-diphenylethylene **2a** (216.0 mg, 1.2 mmol, 3.0 equiv), $Fe(OTs)_3$ (11.4 mg, 0.02 mmol, 5 mol%), Brønsted acid (0.08 mmol, 20 mol%), alcohol (0.1 mmol, 25 mol%), $PhCH_3$ (2.0 mL), 100 °C, 12 h, under argon atmosphere. [b] Yield determined by GC analysis with *n*-tetradecane as internal standard.

Table 2. Screening of reaction additives and temperature[a]

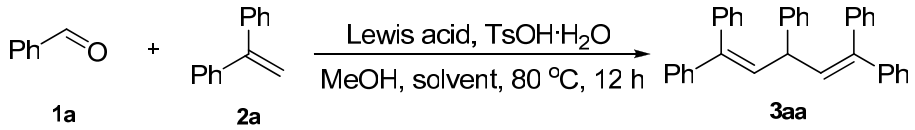


1a 2a 3aa

Entry	Temperature (°C)	Yield (%)[b]
1	100	60
2	80	91(88)
3	80	72(67)[c]
4	80	11[d]
5	80	NR[e]
6	80	17[f]
7	60	18

[a] Reaction conditions: benzaldehyde **1a** (42.4 mg, 0.4 mmol, 1.0 equiv), 1,1-diphenylethylene **2a** (216.0 mg, 1.2 mmol, 3.0 equiv), $Fe(OTs)_3$ (11.4 mg, 0.02 mmol, 5 mol%), $TsOH{\cdot}H_2O$ (15.2 mg, 0.08 mmol, 20 mol%), MeOH (3.2 mg, 0.1 mmol, 25 mol%), $PhCH_3$ (2.0 mL), 12 h, under argon atmosphere. [b] Yield determined by GC analysis with *n*-tetradecane as internal standard (isolated yield in parentheses). [c] Without $Fe(OTs)_3$. [d] Without $TsOH{\cdot}H_2O$. [e] Without $Fe(OTs)_3$ and $TsOH{\cdot}H_2O$. [f] Without MeOH, isolated yield.

Table 3. Screening of Lewis acids and solvents[a]



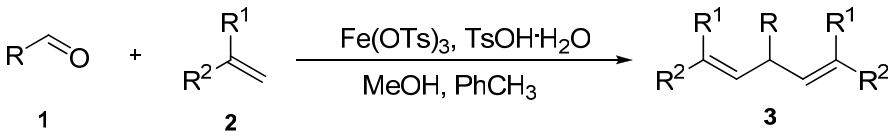
Entry	Lewis acid	Solvent	Yield (%)[b]
1	$ZnCl_2$	$PhCH_3$	46
2	$Zn(OTs)_2$	$PhCH_3$	65
3	$Cu(OAc)_2$	$PhCH_3$	21
4	CuF_2	$PhCH_3$	40
5	$Ni(OAc)_2$	$PhCH_3$	28
6	$NiSO_4$	$PhCH_3$	49
7	$Ni(acac)_2$	$PhCH_3$	29
8	$MnCl_2$	$PhCH_3$	63
9	$CeCl_3$	$PhCH_3$	20
10	$AlCl_3$	$PhCH_3$	4
11	$FeCl_3$	$PhCH_3$	37
12	$FeBr_3$	$PhCH_3$	56
13	$Fe(acac)_3$	$PhCH_3$	5
14	$Fe(OTs)_3$	$PhCH_3$	91(88)
15	$Fe(OTs)_3$	dioxane	4
16	$Fe(OTs)_3$	MeCN	8
17	$Fe(OTs)_3$	CH_2Cl_2	48
18	$Fe(OTs)_3$	THF	4

19	$Fe(OTs)_3$	xylene	62
20	$Fe(OTs)_3$	mesitylene	48
21	$Fe(OTs)_3$	$PhCH(CH_3)_2$	29
22	$Fe(OTs)_3$	$PhCF_3$	38
23	$Fe(OTs)_3$	MTBE	9
24	$Fe(OTs)_3$	DCE	59
25	$Fe(OTs)_3$	DMF	NR
26	$Fe(OTs)_3$	DMSO	NR

[a] Reaction conditions: benzaldehyde **1a** (42.4 mg, 0.4 mmol, 1.0 equiv), 1,1-diphenylethylene **2a** (216.0 mg, 1.2 mmol, 3.0 equiv), Lewis acid (0.02 mmol, 5 mol%), $TsOH·H_2O$ (0.08 mmol, 20 mol%), MeOH (3.2 mg, 0.1 mmol, 25 mol%), solvent (2.0 mL), 80 ^oC, 12 h, under argon atmosphere. [b] Yield determined by GC analysis with *n*-tetradecane as internal standard (isolated yield in parentheses).

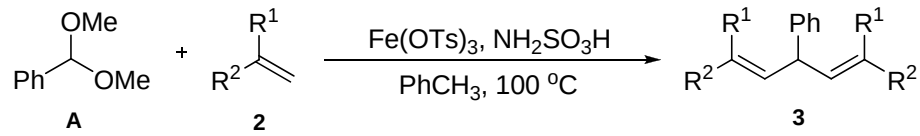
3. General procedure for redox-neutral process to skipped dienes

Method I:



Aldehydes **1** (0.4 mmol, 1.0 equiv), alkenes **2** (1.2 mmol, 3.0 equiv), $Fe(OTs)_3$ (11.4 mg, 0.02 mmol, 5 mol%), $TsOH·H_2O$ (15.2 mg, 0.08 mmol, 20 mol%), MeOH (3.2 mg, 0.1 mmol, 25 mol%) and dry $PhCH_3$ (2.0 mL) were added to a 25 mL flame-dried Young-type tube under argon atmosphere. The reaction mixture was stirred at 80 ^oC for 12 hours, and then cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel and eluted with PE/EtOAc (100/0 to 100/1) to afford the desired product **3**.

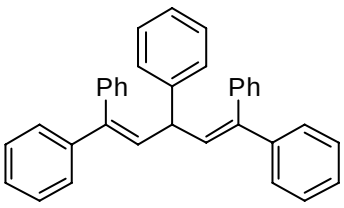
Method II:



Benzaldehyde dimethyl acetal **A** (60.8 mg, 0.4 mmol, 1.0 equiv), alkenes **2** (1.2 mmol, 3.0 equiv), $Fe(OTs)_2$ (11.4 mg, 0.02 mmol, 5 mol%), NH_2SO_3H (7.8 mg, 0.08 mmol, 20 mol%) and dry $PhCH_3$ (2.0 mL) were added to the a 25 mL flame-dried Young-type tube under argon atmosphere. The reaction mixture was stirred at 100 ^oC for 12 hours, and then cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel and eluted with PE/EtOAc (100/0 to 100/1) to afford the desired product **3**.

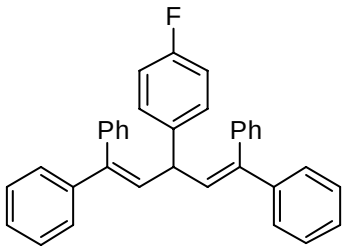
4. Experimental characterization data for products

Penta-1,4-diene-1,1,3,5,5-pentaylpentabenzene (3aa)



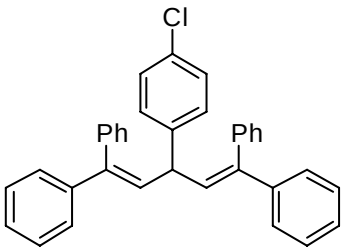
The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (158.1 mg, 88% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 4.53 (t, J = 10.0 Hz, 1H), 6.24 (dd, J_1 = 2.0 Hz, J_2 = 10.0 Hz, 2H), 6.94-6.96 (m, 4H), 7.09-7.32 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.1, 126.4, 127.1, 127.3, 127.7, 127.8, 128.2, 128.3, 128.7, 129.7, 130.2, 139.5, 141.7, 142.9. 144.3; HRMS (EI+) calcd for $C_{35}H_{28}$ [M]: 448.2191, found: 448.2190.

(3-(4-Fluorophenyl)penta-1,4-diene-1,1,5,5-tetrayl)tetrabenzene (3ba)



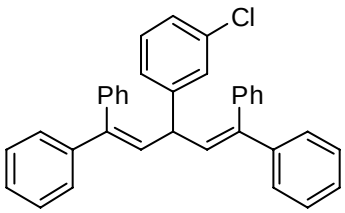
The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (165.1 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.48 (t, J = 10.0 Hz, 1H), 6.20 (dd, J_1 = 1.2 Hz, J_2 = 10.0 Hz, 2H), 6.92-7.00 (m, 6H), 7.09-7.13 (m, 4H), 7.16-7.20 (m, 4H), 7.24-7.28 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.3, 115.2, 115.4, 127.1, 127.3, 127.7, 128.1, 128.2, 128.9, 129.0, 129.5, 129.8, 139.3, 139.9, 141.8, 142.6, 160.3, 162.7; ^{19}F NMR (376 MHz, $CDCl_3$): -116.91, -116.90; HRMS (EI+) calcd for $C_{35}H_{27}F$ [M]: 466.2097, found: 466.2101.

(3-(4-Chlorophenyl)penta-1,4-diene-1,1,5,5-tetrayl)tetrabenzene (3ca)



The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (167.4 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.47 (t, J = 10.0 Hz, 1H), 6.19 (d, J = 10.4 Hz, 2H), 6.91-6.93 (m, 4H), 7.10-7.28 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.5, 127.1, 127.4, 127.7, 128.1, 128.2, 128.7, 128.9, 129.4, 129.5, 132.1, 139.2, 142.0, 142.5, 142.7; HRMS (EI+) calcd for $C_{35}H_{27}Cl$ [M]: 482.1801, found: 482.1798.

(3-(3-Chlorophenyl)penta-1,4-diene-1,1,5,5-tetrayl)tetrabenzene (3da)



The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (184.0 mg, 95% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 4.71 (t, J = 10.0 Hz, 1H), 6.19 (d, J = 10.4 Hz, 2H), 6.84-7.02 (m, 12H), 7.05-7.11 (m, 7H), 7.22-7.26 (m, 4H), 7.45 (s, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ 45.4, 126.0, 126.8, 127.3, 127.6, 127.7, 128.1, 128.4, 128.4, 129.5, 129.8, 130.3, 135.0, 139.6, 142.7, 142.7, 147.0; HRMS (EI+) calcd for $C_{35}H_{27}Cl$ [M]: 482.1801, found: 482.1805.

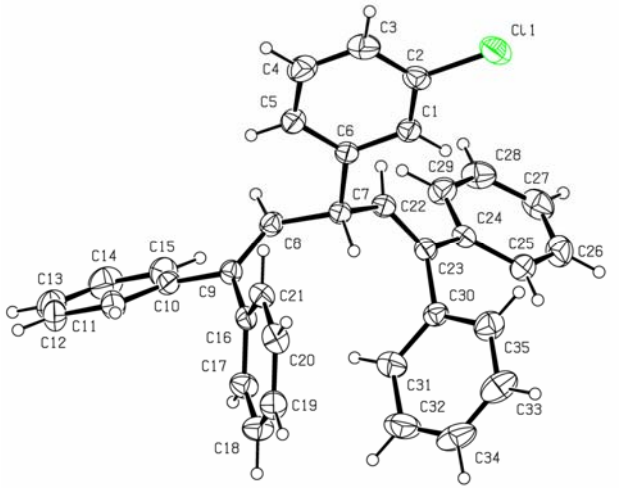
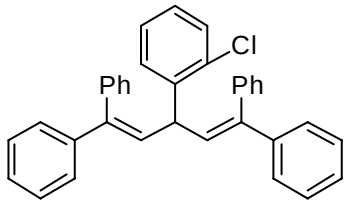


Figure 1. X-ray Crystal Structure of **3da**

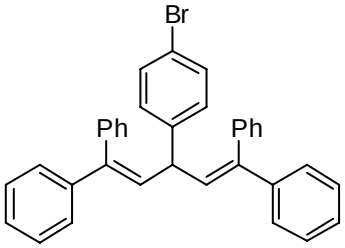
(3-(2-Chlorophenyl)penta-1,4-diene-1,1,5,5-tetrayl)tetrabenzene (3ea)



The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (188.2 mg, 97% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 5.08 (t, J = 10.0 Hz, 1H), 6.36 (d, J = 9.6 Hz, 2H), 6.76-6.80 (m, 1H), 6.91-7.10 (m, 17H), 7.18-7.27 (m, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ 43.7, 127.3, 127.4, 127.5, 127.7, 127.8, 128.4, 129.5, 129.9, 130.1, 130.2,

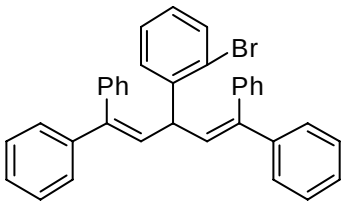
133.9, 139.8, 142.7, 143.1, 143.3; HRMS (EI+) calcd for $C_{35}H_{27}Cl$ [M]: 482.1801, found: 482.1804.

(3-(4-Bromophenyl)penta-1,4-diene-1,1,5,5-tetrayl)tetrabenzene (3fa)



The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (176.7 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.45 (t, *J* = 10.0 Hz, 1H), 6.18 (d, *J* = 10.0 Hz, 2H), 6.91-6.93 (m, 4H), 7.08-7.29 (m, 18H), 7.39-7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.5, 120.2, 127.1, 127.4, 127.7, 128.1, 128.2, 129.3, 129.4, 129.5, 131.6, 139.2, 142.0, 142.5, 143.3; HRMS (EI+) calcd for $C_{35}H_{27}Br$ [M]: 526.1296, found: 526.1300.

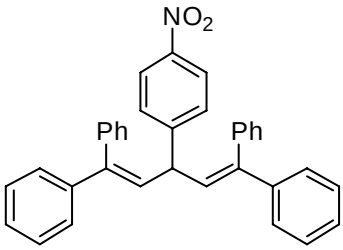
(3-(2-Bromophenyl)penta-1,4-diene-1,1,5,5-tetrayl)tetrabenzene (3ga)



The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (153.4 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.63 (t, *J* = 9.6 Hz, 1H), 6.19 (d, *J* = 9.6 Hz, 2H), 6.83-7.08 (m, 14H), 7.12-7.38 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.5, 123.9, 127.1, 127.4, 127.8, 127.9, 128.1, 128.2, 129.6, 129.9, 130.1, 133.4, 139.4, 142.3, 142.8, 144.7; HRMS (EI+) calcd for $C_{35}H_{27}Br$ [M]: 526.1296, found: 526.1302.

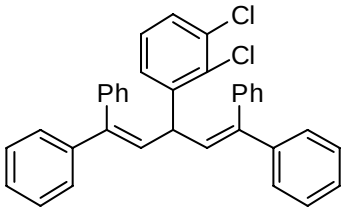
(3-(4-Nitrophenyl)penta-1,4-diene-1,1,5,5-tetrayl)tetrabenzene (3ha)

The title compound was prepared according to the general procedure of method I and



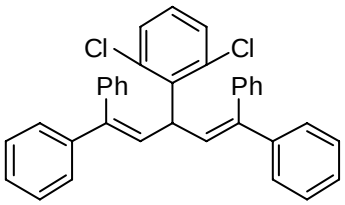
purified by column chromatography to give a yellow solid (193.7mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.59 (t, *J* = 10.0 Hz, 1H), 6.22 (d, *J* = 10.0 Hz, 2H), 6.91 (d, *J* = 7.2 Hz, 4H), 7.12-7.16 (m, 4H), 7.19-7.30 (m, 12H), 7.32 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.2, 123.9, 127.4, 127.6, 127.7, 128.3, 128.4, 129.4, 139.0, 142.1, 143.0, 146.6, 152.1; HRMS (EI+) calcd for $C_{35}H_{27}NO_2$ [M]: 493.2042, found: 493.2045.

(3-(2,3-Dichlorophenyl)penta-1,4-diene-1,1,5,5-tetrayl)tetrabenzene (3ia)



The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (193.1 mg, 93% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 5.06 (t, *J* = 9.6 Hz, 1H), 6.25 (d, *J* = 9.6 Hz, 2H), 6.68 (t, *J* = 8.0 Hz, 1H), 6.92-7.00 (m, 11H), 7.04-7.09 (m, 7H), 7.21-7.25 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6): δ 44.4, 127.4, 127.5, 127.6, 127.8, 128.3, 128.4, 128.5, 129.3, 129.9, 132.3, 133.8, 139.6, 142.8, 143.2, 145.7; HRMS (EI+) calcd for $C_{35}H_{26}Cl_2$ [M]: 516.1412, found: 516.1414.

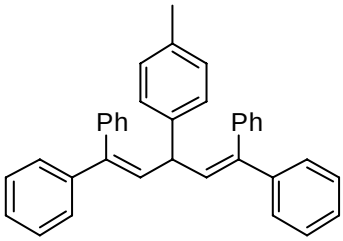
(3-(2,6-Dichlorophenyl)penta-1,4-diene-1,1,5,5-tetrayl)tetrabenzene (3ja)



The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (150.3 mg, 73% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 5.44 (t, *J* = 8.4 Hz, 1H), 6.36 (t, *J* = 8.0 Hz, 1H),

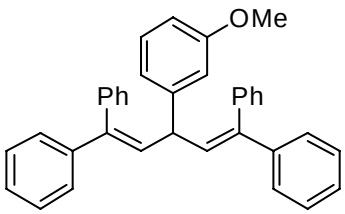
6.83 (d, J = 8.0 Hz, 2H), 6.97-7.09 (m, 18H), 7.32 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.5, 127.0, 127.3, 127.6, 128.2, 128.2, 128.8, 129.0, 129.7, 135.5, 139.4, 140.0, 142.1, 142.7; HRMS (EI+) calcd for $C_{35}H_{26}Cl_2$ [M]: 516.1412, found: 516.1416.

(3-*p*-Tolylpenta-1,4-diene-1,1,5,5-tetrayl)tetrabenzene (3ka)



The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (129.3 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 4.50 (t, J = 10.0 Hz, 1H), 6.22 (d, J = 10.0 Hz, 2H), 6.94-6.96 (m, 4H), 7.07-7.25 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 44.6, 127.0, 127.3, 127.6, 127.8, 128.1, 128.2, 129.4, 129.7, 130.3, 135.9, 139.5, 141.2, 141.5, 142.9; HRMS (EI+) calcd for $C_{36}H_{30}$ [M]: 462.2348, found: 462.2344.

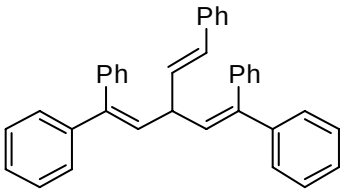
(3-(3-Methoxyphenyl)penta-1,4-diene-1,1,5,5-tetrayl)tetrabenzene (3la)



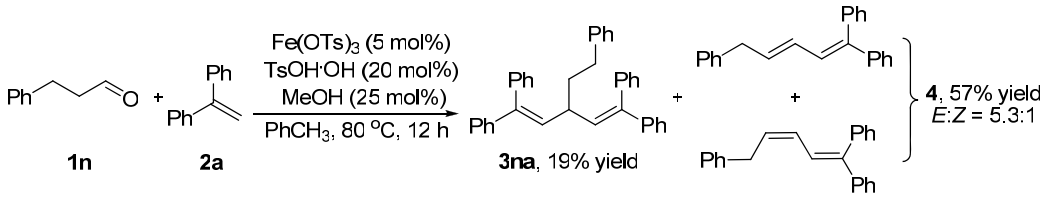
The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (174.8 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.75 (s, 3H), 4.51 (t, J = 10.0 Hz, 1H), 6.21 (dd, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 2H), 6.73-7.24 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.0, 55.3, 111.3, 111.4, 113.7, 113.8, 120.0, 120.0, 127.0, 127.1, 127.3, 127.4, 127.7, 127.8, 128.1, 128.1, 128.2, 128.2, 129.6, 129.6, 129.7, 129.9, 130.0, 139.4, 139.5, 141.7, 141.7, 142.8, 142.8, 145.9, 145.9, 159.8, 159.9; HRMS (EI+)

calcd for $C_{36}H_{30}O$ [M]: 478.2297, found: 478.2292.

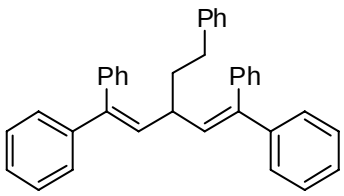
(*E*)-(5-phenyl-3-styrylpenta-1,4-diene-1,1,5-triyl)tribenzene (3ma)



The title compound was prepared according to the general procedure of method I and purified by column chromatography to give colorless oil (85.5 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17-4.21 (m, 1H), 6.03-6.28 (m, 3H), 6.71 (d, *J* = 10.8 Hz, 1H), 7.14-7.24 (m, 15 H), 7.27-7.38 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.3, 126.4, 127.1, 127.2, 127.3, 127.4, 127.5, 127.6, 127.9, 128.1, 128.2, 128.2, 128.3, 128.6, 128.9, 129.8, 130.1, 130.5, 137.5, 139.8, 139.9, 141.7, 141.9, 142.3, 142.4, 143.6; HRMS (EI+) calcd for $C_{37}H_{30}$ [M]: 474.2348, found: 474.2345.

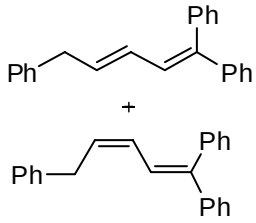


(3-Phenethyl-5-phenylpenta-1,4-diene-1,1,5-triyl)tribenzene (3na)



The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (36.2 mg, 19% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.81-1.87 (m, 2H), 2.52 (t, *J* = 8.0 Hz, 2H), 3.30-3.39 (m, 1H), 5.97 (d, *J* = 10.4 Hz, 2H), 6.84-6.91 (m, 6H), 7.07-7.28 (m, 19H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.1, 38.5, 39.1, 125.6, 126.7, 127.1, 127.5, 128.1, 128.1, 128.2, 128.4, 129.7, 131.9, 139.7, 141.2, 142.1, 143.1; HRMS (EI+) calcd for $C_{37}H_{32}$ [M]: 476.2504, found: 476.2503.

Penta-1,3-diene-1,1,5-triyltribenzene (4)



The title compound was prepared according to the general procedure of method I and purified by column chromatography to give colorless oil (67.9 mg, 57% yield, *E:Z* = 5.3:1 (determined by ^{1}H NMR)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.39 (d, *J* = 7.2 Hz, 1.65H), 3.67 (d, *J* = 8.0 Hz, 0.31H), 5.62-5.69 (m, 0.16H), 5.97-6.05 (m, 0.83H), 6.19-6.29 (m, 1H), 6.68 (d, *J* = 10.8 Hz, 0.82H), 7.06 (d, *J* = 10.8 Hz, 0.16H), 7.16-7.42 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.3, 39.5, 122.9, 126.2, 127.3, 127.4, 127.5, 127.6, 127.8, 128.0, 128.3, 128.3, 128.4, 128.6, 128.7, 129.6, 130.6, 130.7, 131.8, 135.0, 139.8, 140.0, 140.4, 140.6, 141.4, 142.5, 142.7, 143.5; GC-MS [m/z]: 296.1.

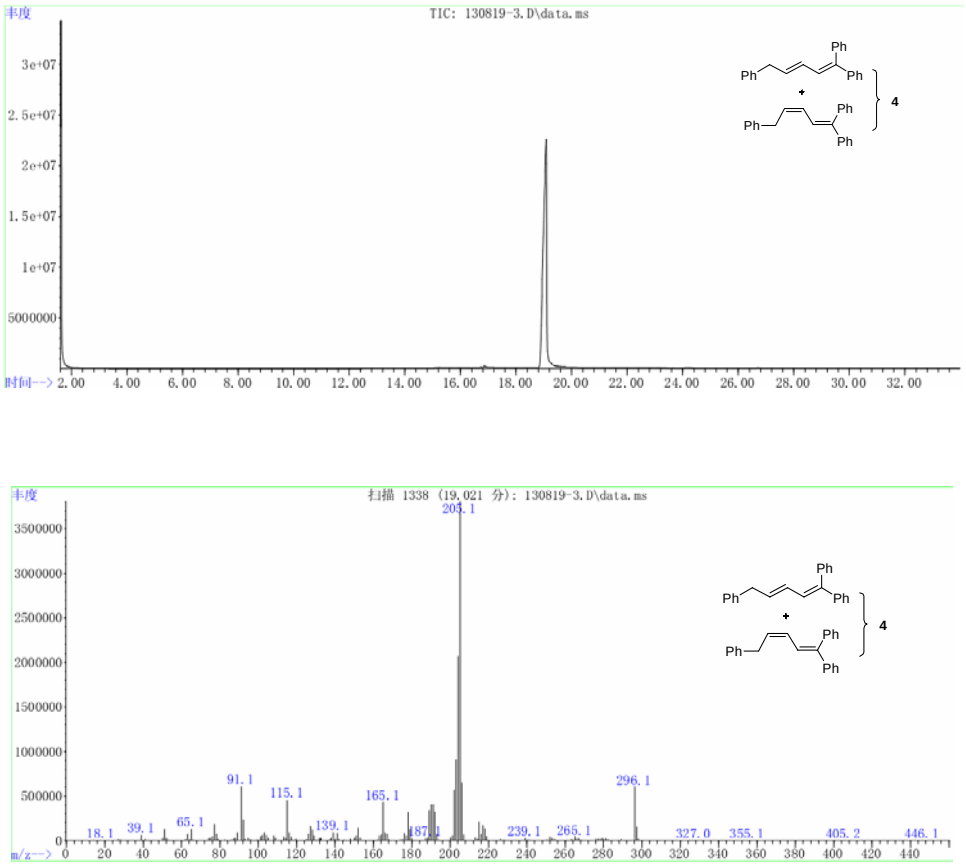
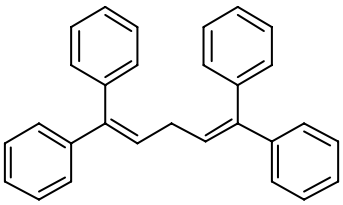


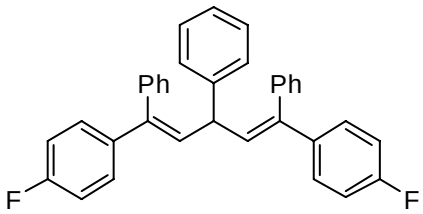
Figure 2. GC-MS spectra of penta-1,3-diene-1,1,5-triyltribenzene

1,1,5,5-Tetraphenylpenta-1,4-diene (3oa)



The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (94.9 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95 (t, *J* = 7.6 Hz, 2H), 6.07 (t, *J* = 7.6 Hz, 2H), 7.09-7.12 (m, 4H), 7.19-7.31 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.8, 127.1, 127.1, 127.4, 127.5, 128.2, 128.3, 130.0, 139.9, 142.4, 142.8; HRMS (EI+) calcd for $C_{29}H_{24}$ [M]: 372.1878, found: 372.1874.

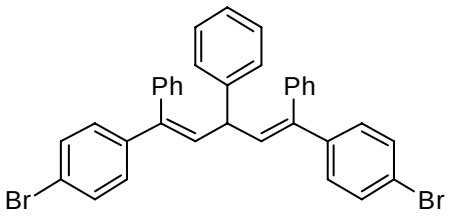
1,5-Bis(4-fluorophenyl)penta-1,4-diene-1,3,5-triyl)tribenzene (3ab)



The title compound was prepared according to the modified procedure of method I (1-fluoro-4-(1-phenylvinyl)benzene (198 mg, 1.0 mmol, 2.5 equiv)) and purified by column chromatography to give a white solid to give a white solid (123.2 mg, 64% yield, *E/Z:E/E:Z/Z* = 28:52:20 (determined by GC analysis)). Product **3ab** could also be prepared through the general procedure of method II to give a white solid (169.8 mg, 88% yield, *E/E:E/Z:Z/Z* = 31:53:16 (determined by ^{1}HNMR)). ^{1}H NMR (400 MHz, C_6D_6): δ, 4.58 (t, *J* = 10.0 Hz, 0.16H), 4.66 (t, *J* = 10 Hz, 0.53H), 4.74 (t, *J* = 10.0 Hz, 0.31H), 6.14-6.29 (m, 2H), 6.56-6.61 (m, 2H), 6.73-6.83 (m, 4H), 6.91-7.27 (m, 17H); ^{13}C NMR (100 MHz, C_6D_6): δ 45.5, 115.1, 115.3, 126.7, 126.8, 127.3, 127.4, 127.8, 128.4, 128.4, 128.5, 129.0, 129.1, 129.1, 129.6, 129.6, 129.7, 129.8, 130.0, 130.3, 130.4, 130.5, 131.4, 131.5, 131.6, 135.5, 135.6, 139.0, 139.0, 139.1, 139.1,

139.5, 139.6, 140.9, 141.0, 141.0, 141.1, 142.6, 142.7, 144.3, 144.4, 144.5, 161.0, 161.4, 163.4, 163.9; ^{19}F (376 MHz, $CDCl_3$): δ -114.65, -114.58, -114.32; HRMS (EI+) calcd for $C_{35}H_{26}F_2$ [M]: 484.2003, found:. 484.2007.

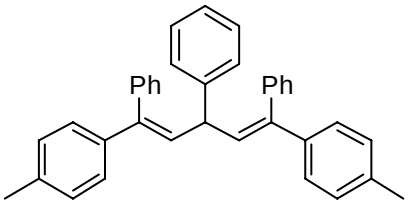
1,5-Bis(4-bromophenyl)penta-1,4-diene-1,3,5-triyl)tribenzene (3ac)



The title compound was prepared according to the modified procedure of method I (1-bromo-4-(1-phenylvinyl)benzene (258 mg, 1.0 mmol, 2.5 equiv)) and purified by column chromatography to give a white solid (73.3 mg, 30% yield, *E/Z:E/E:Z/Z* = 25:58:17 (determined by ^{1}H NMR)). Product **3ac** could also be prepared through the general procedure of method II to give a white solid (205.5 mg, 85% yield, *E/Z:E/E:Z/Z* = 27:51:22 (determined by ^{1}HNMR)). ^{1}H NMR (400 MHz, C_6D_6): δ 4.52 (t, J = 10.0 Hz, 0.22H), 4.62 (t, J = 10.0 Hz, 0.51H), 4.72 (t, J = 10.0 Hz, 0.27H), 6.15-6.27 (m, 2H), 6.62 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 2H), 6.87-7.14 (m, 13H), 7.17-7.26 (m, 8H); ^{13}C NMR (100 MHz, C_6D_6): δ 45.5, 121.5, 121.7, 121.8, 126.9, 127.5, 127.6, 127.8, 127.9, 128.5, 128.5, 128.5, 129.1, 129.1, 129.7, 129.7, 129.8, 130.2, 130.4, 130.4, 130.7, 131.4, 131.5, 131.5, 131.6, 138.4, 138.5, 139.0, 139.1, 141.1, 141.1, 141.1, 141.7, 141.8, 142.1, 142.2, 143.9, 144.0, 144.2; HRMS (EI+) calcd for $C_{35}H_{26}Br_2$ [M]: 604.0401, found: 604.0403.

1,5-Dip-tolylpenta-1,4-diene-1,3,5-triyl)tribenzene (3ad)

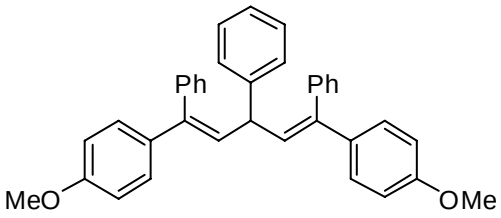
The title compound was prepared according to the general procedure of method I and purified by column chromatography to give a white solid (182.4 mg, 96% yield,



E/E:E/Z:Z/Z = 34:52:14 (determined by GC analysis)). ^{1}H NMR (400 MHz, C_6D_6): δ 2.11 (s, 4.31H), 2.13 (s, 1.67H), 4.82-4.90 (m, 1H), 6.32-6.38 (m, 2H), 6.75-6.78 (m, 2H), 6.94-7.03 (m, 7H), 7.06-7.22 (m, 8H), 7.26-7.28 (m, 2H), 7.33-7.37 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6): δ 21.1, 21.1, 21.2, 45.5, 45.6, 45.7, 126.5, 126.9, 127.1, 127.4, 127.9, 127.9, 128.1, 128.3, 128.3, 128.4, 129.0, 129.1, 129.1, 129.8, 129.9, 129.9, 130.0, 130.0, 130.3, 130.4, 136.3, 136.5, 137.0, 137.0, 140.1, 140.1, 140.5, 141.9, 142.0, 143.3, 143.3, 144.9, 145.0; HRMS (EI+) calcd for $C_{37}H_{32}$ [M]: 476.2504, found: 476.2501.

1,5-Bis(4-methoxyphenyl)penta-1,4-diene-1,3,5-triyl)tribenzene (3ae)

The title compound was prepared according to the modified procedure of method I

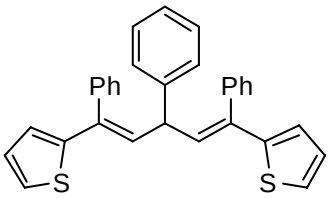


(1-methoxy-4-(1-phenylvinyl)benzene (210 mg, 1.0 mmol, 2.5 equiv)) and purified by column chromatography to give a white solid (201.7 mg, 99% yield, *E/E:E/Z:Z/Z* = 38:33:29 (determined by ^{1}H NMR)). ^{1}H NMR (400 MHz, C_6D_6): δ 3.29 (s, 2.62), 3.31 (s, 0.97), 3.33 (s, 2.41), 4.81 (t, *J* = 10 Hz, 0.29H), 4.88 (t, *J* = 10 Hz, 0.33H), 4.95 (t, *J* = 10.0 Hz, 0.38H), 6.29-6.34 (m, 2H), 6.53 (m, 2H), 6.73-6.75 (m, 2H), 6.96-7.26 (m, 15H), 7.34-7.41 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6): δ 45.5, 45.6, 45.7, 54.5, 54.6, 54.7, 113.8, 113.8, 126.5, 126.5, 126.6, 127.0, 127.1, 127.4, 128.2, 128.2, 128.3, 128.4, 128.9, 128.9, 129.0, 129.3, 129.3, 130.0, 130.0, 130.1, 130.3, 131.1, 131.1, 132.1, 135.7, 140.3, 141.3, 141.5, 141.6, 141.7, 143.5, 143.5, 144.9, 145.1, 145.2, 159.1, 159.1, 159.6, 159.6;

HRMS (EI+) calcd for calcd for $C_{37}H_{32}O_2$ [M]: 508.2402, found: 508.2399.

2,2'-(1,3,5-Triphenylpenta-1,4-diene-1,5-diyl)dithiophene (3af)

The title compound was prepared according to the modified procedure of method I

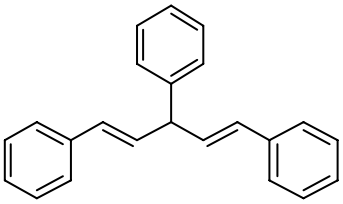


(2-(1-phenylvinyl)thiophene (186 mg, 1.0 mmol, 2.5 equiv)) and purified by column chromatography to give a yellowish solid (90.0 mg, 49% yield, *E/E:E/Z:Z/Z* =18:30:52 (determined by ^{1}H NMR)). Product **3af** could also be prepared through the general procedure of method II to give a yellowish solid (137.2 mg, 75% yield, *E/E:E/Z:Z/Z* = 10:42:48 (determined by ^{1}HNMR)). ^{1}H NMR (400 MHz, C_6D_6): δ 4.88 (t, *J* = 10.0 Hz, 0.48H), 4.95 (t, *J* = 10.0 Hz, 0.42H), 5.37(t, *J* = 10.0 Hz, 0.10H), 6.18-6.52 (m, 2H), 6.58-7.22 (m, 17H), 7.29-7.36 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6): δ 44.9, 45.5, 46.1, 124.5, 125.9, 126.0, 126.1, 126.3, 126.6, 126.7, 126.7, 126.8, 127.4, 127.4, 127.4, 127.5, 127.7, 127.8, 127.8, 128.1, 128.3, 128.5, 128.8, 129.0, 129.0, 129.1, 129.5, 129.6, 132.1, 132.4, 135.3, 135.7, 136.3, 136.6, 138.8, 138.9, 141.2, 141.3, 143.0, 143.1, 144.0, 144.1, 147.0, 147.1; HRMS (EI+) calcd for $C_{31}H_{24}S_2$ [M]: 460.1319, found: 460.1315.

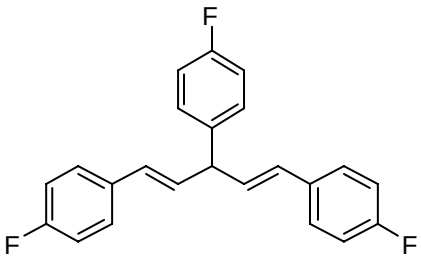
Penta-1,4-diene-1,3,5-triyltribenzene (3ag)

The title compound was prepared according to the modified procedure of method I (MeOH (32.0 mg, 1.0 mmol, 2.5 equiv), styrene (249.6 mg, 2.4 mmol, 6.0 equiv), 120 ^{o}C) and purified by column chromatography to give colorless oil (107.8 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.39 (t, *J* = 2.8 Hz, 1H), 6.48 (d, *J* = 2.8 Hz, 4H), 7.20-7.41 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.8, 126.4, 126.8,

127.5, 128.3, 128.7, 128.8, 130.9, 132.0, 137.4, 142.9; HRMS (EI+) calcd for $C_{23}H_{20}$ [M]: 296.1565, found: 296.1562.

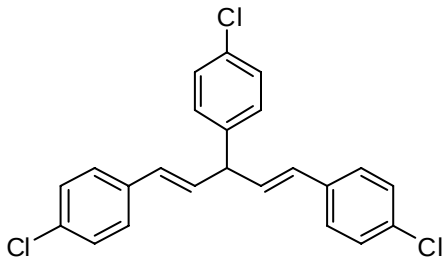


4,4',4''-(Penta-1,4-diene-1,3,5-triyl)tris(fluorobenzene) (3ph)



The title compound was prepared according to the modified procedure of method I (MeOH (32.0 mg, 1.0 mmol, 2.5 equiv), 1-fluoro-4-vinylbenzene (292.8 mg, 2.4 mmol, 6.0 equiv), 120 ^{o}C) and purified by column chromatography to give colorless oil (71.5 mg, 51% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 4.07 (t, J = 6.8 Hz, 1H), 6.11-6.17 (m, 2H), 6.24 (d, J = 16.0 Hz, 2H), 6.77-6.81 (m, 4H), 6.89-6.94 (m, 2H), 6.98-7.04 (m, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ 50.9, 115.5, 115.5, 115.7, 115.7, 127.8, 128.0, 128.1, 129.8, 129.9, 130.1, 131.4, 133.5, 133.6, 138.6, 138.6, 160.9, 161.3, 163.3, 163.8; ^{19}F NMR (376 MHz, C_6D_6): δ-116.20, -114.59; HRMS (EI+) calcd for $C_{23}H_{17}F_3$ [M]: 350.1282, found: 350.1280.

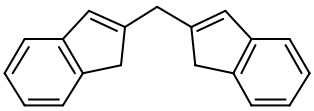
4,4',4''-(Penta-1,4-diene-1,3,5-triyl)tris(chlorobenzene) (3qi)



The title compound was prepared according to the modified procedure of method I (MeOH (32.0 mg, 1.0 mmol, 2.5 equiv), 1-chloro-4-vinylbenzene (336 mg, 2.4 mmol, 6.0 equiv), 120 ^{o}C) and purified by column chromatography to give colorless oil (130.3 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.34 (t, J = 4.0 Hz, 1H),

6.39-6.40 (m, 4H), 7.21-7.33 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.9, 127.5, 128.8, 128.9, 129.5, 130.2, 131.7, 132.7, 133.2, 135.5, 140.7; HRMS (EI+) calcd for $C_{23}H_{17}Cl_3$ [M]: 398.0396, found: 398.0392.

Di(1*H*-inden-2-yl)methane (3oj)



The title compound was prepared according to the modified procedure of method I (without MeOH, 70 °C) and purified by column chromatography to give a white solid (58.7 mg, 60% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 2.96 (s, 4H), 3.25 (s, 2H), 6.38 (s, 2H), 7.09-7.13 (m, 2H), 7.21-7.27 (m, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ 33.1, 41.0, 120.5, 123.7, 124.3, 126.6, 128.2, 143.6, 145.7, 147.9; HRMS (EI+) calcd for $C_{19}H_{16}$: [M]: 244.1252, found: 244.1254.

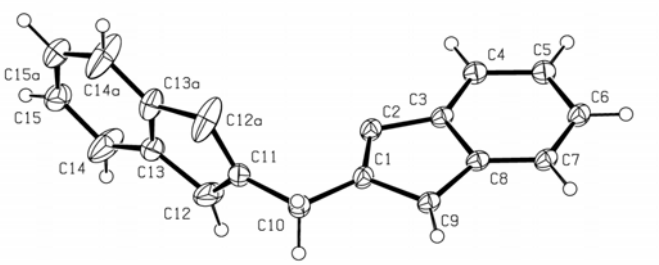
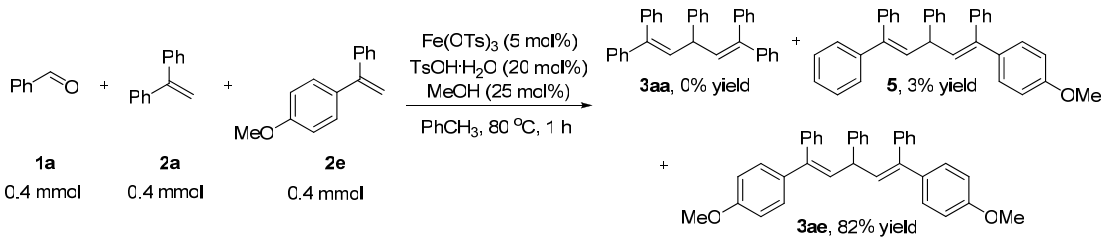


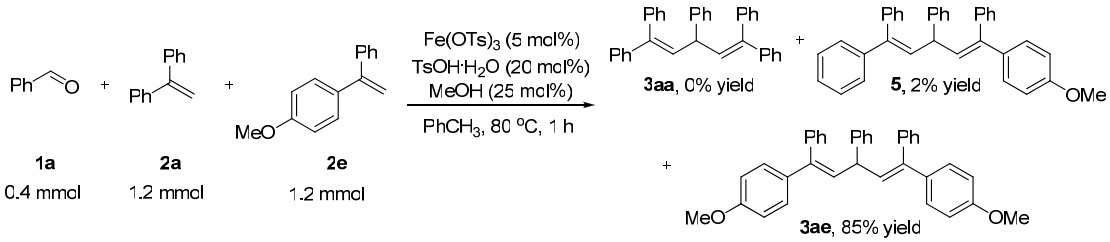
Figure 3. X-ray crystal structure of **3oj**

5. Mechanistic studies

5.1 Crossover reaction with different alkenes for examining the substituent effect.

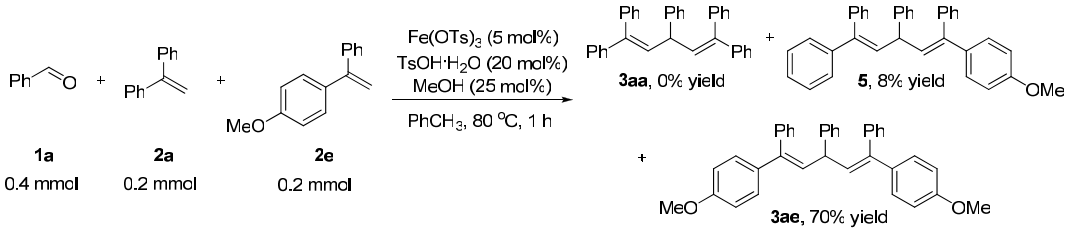


Benzaldehyde **1a** (42.4 mg, 0.4 mmol, 1.0 equiv), 1,1-diphenylethylene **2a** (72.0 mg, 0.4 mmol, 1.0 equiv), 1-methoxy-4-(1-phenylvinyl)benzene **2e** (84.0 mg, 0.4 mmol, 1.0 equiv), $Fe(OTs)_3$ (11.4 mg, 0.02 mmol, 5 mol%), $TsOH{\cdot}H_2O$ (15.2 mg, 0.08 mmol, 20 mol%), MeOH (3.2 mg, 0.1 mmol, 25 mol%) and dry $PhCH_3$ (2.0 mL) were added to a 25 mL flame-dried Young-type tube under argon atmosphere. The reaction mixture was stirred at 80 °C for 1 hour, and then cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel and eluted with PE/EtOAc (100/0 to 100/1) to afford the product **3aa** (0 mg, 0% yield), **5** (6.0 mg, 3% yield) and **3ae** (83.2mg, 82% yield).



Benzaldehyde **1a** (42.4 mg, 0.4 mmol, 1.0 equiv), 1,1-diphenylethylene **2a** (216.0 mg, 1.2 mmol, 3.0 equiv), 1-methoxy-4-(1-phenylvinyl)benzene **2e** (252.0 mg, 1.2 mmol, 3.0 equiv), $Fe(OTs)_3$ (11.4 mg, 0.02 mmol, 5 mol%), $TsOH{\cdot}H_2O$ (15.2 mg, 0.08 mmol, 20 mol%), MeOH (3.2 mg, 0.1 mmol, 25 mol%) and dry $PhCH_3$ (2.0 mL) were added to a 25 mL flame-dried Young-type tube under argon atmosphere. The reaction mixture was stirred at 80 °C for 1 hour, and then cooled to room

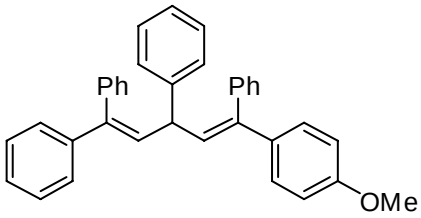
temperature. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel and eluted with PE/EtOAc (100/0 to 100/1) to afford the product **3aa** (0 mg, 0% yield), **5** (4.7 mg, 2% yield) and **3ae** (173.3 mg, 85% yield).



Benzaldehyde **1a** (42.4 mg, 0.4 mmol, 1.0 equiv), 1,1-diphenylethylene **2a** (36.0 mg, 0.2 mmol, 0.5 equiv), 1-methoxy-4-(1-phenylvinyl)benzene **2e** (42.0 mg, 0.2 mmol, 0.5 equiv), $Fe(OTs)_3$ (11.4 mg, 0.02 mmol, 5 mol%), $TsOH{\cdot}H_2O$ (15.2 mg, 0.08 mmol, 20 mol%), MeOH (3.2 mg, 0.1 mmol, 25 mol%) and dry $PhCH_3$ (2.0 mL) were added to a 25 mL flame-dried Young-type tube under argon atmosphere. The reaction mixture was stirred at 80 ^oC for 1 hour, and then cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel and eluted with PE/EtOAc (100/0 to 100/1) to afford the product **3aa** (0 mg, 0% yield), **5** (7.6 mg, 8% yield) and **3ae** (35.8 mg, 70% yield).

The above results demonstrated that the 1,4-skipped diene **3ae** was formed as the major product and the unsymmetric 1,4-skipped diene was obtained in lower yield, which indicated that the cationic intermediate was most likely involved in this reaction.

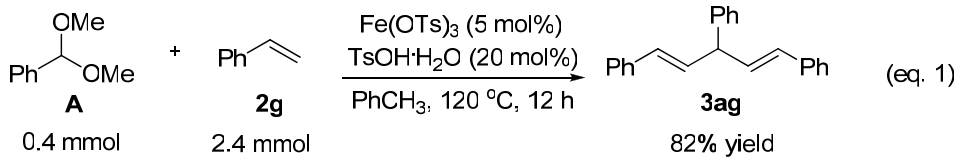
(5-(4-Methoxyphenyl)penta-1,4-diene-1,1,3,5-tetrayl)tetrabenzene (5)



A white solid (*E*:*Z* = 55:45 (determined by ^{1}H NMR)). ^{1}H NMR (400 MHz, C_6D_6): δ 3.27 (s, 1.32H), 3.29 (s, 1.68H), 4.81 (t, *J* = 10.0 Hz, 0.45H), 4.88 (t, *J* = 10.0 Hz, 0.55H), 6.27-6.36 (m, 2H), 6.51-6.53 (m, 1H), 6.72-6.74 (m, 1H), 6.91-7.14 (m, 14H), 7.17-7.36 (m, 8H); ^{13}C NMR (100 MHz, C_6D_6): δ 45.5, 45.6, 54.6, 54.7, 113.8, 126.5, 126.5, 127.1, 127.1, 127.4, 127.8, 128.0, 128.3, 128.4, 128.8, 128.9, 129.0, 129.3, 129.9, 130.0, 130.0, 130.6, 130.7, 131.1, 132.0, 135.7, 139.9, 140.2, 141.5, 141.8, 141.8, 141.9, 143.2, 143.5, 144.8, 144.9.

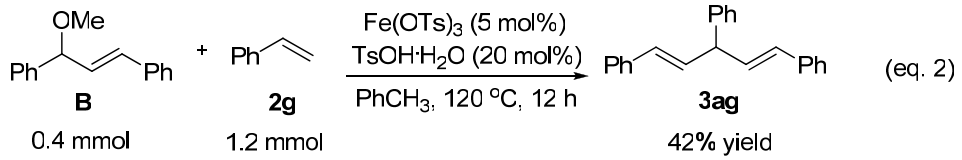
5.2 Control experiments:

To get some preliminary understanding of the mechanism, a series of control experiments were conducted. First, dimethyl acetal **A** instead of benzaldehyde was introduced into the catalytic system, which led to give raise to the desired skipped diene **3ag** in 82% yield, indicating that dimethyl acetal **A** was indeed the intermediate of the coupling reaction (eq. 1). Subsequently, allylic ether **B** was successfully converted to the diene **3ag** under the standard reaction conditions, which provided strong evidence that allylic ether **B** might be also involved in this transformation (eq. 2).



Benzaldehyde dimethyl acetal **A** (60.8 mg, 0.4 mmol, 1.0 equiv), styrene **2g** (249.6 mg, 2.4 mmol, 6.0 equiv), $Fe(OTs)_3$ (11.4 mg, 0.02 mmol, 5 mol%),

$TsOH{\cdot}H_2O$ (15.2 mg, 0.08 mmol, 20 mol%), and dry $PhCH_3$ (2.0 mL) were added to the a 25 mL flame-dried Young-type tube under argon atmosphere. The reaction mixture was stirred at 120 °C for 12 hours, and then cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel and eluted with PE to afford the desired product **3ag** (97.1 mg, 82% yield).



Allylic ether **B** (89.6 mg, 0.4 mmol, 1.0 equiv), styrene **2g** (124.8 mg, 1.2 mmol, 3.0 equiv), $Fe(OTs)_3$ (11.4 mg, 0.02 mmol, 5 mol%), $TsOH{\cdot}H_2O$ (15.2 mg, 0.08 mmol, 20 mol%), and dry $PhCH_3$ (2.0 mL) were added to a 25 mL flame-dried Young-type tube under argon atmosphere. The reaction mixture was stirred at 120 °C for 12 hours, and then cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel and eluted with PE to afford the desired product **3ag** (50.1 mg, 42% yield).

On the basis of above results and previous work,[4] a plausible mechanism was proposed in **Figure 4**. The dimethyl acetal **A** is formed in situ by the reaction of aldehyde **1** with methanol in the presence of Brønsted acid, which then interacts with Lewis acid $Fe(OTs)_3$ to afford oxocarbenium cation **C**. Species **C** reacts with alkene **2** to form carbocation **D**, which produces allylic ether **B** via deprotonation. Allylic ether **B** is activated by Lewis acid $Fe(OTs)_3$ and Brønsted acid to generate

oxocarbenium cation **E**, which can be further transformed to carbocation **F** through reacting with alkene **2,** regenerating $Fe(OTs)_3$. Finally, deprotonation of species **F** leads to the formation of 1,4-skipped diene **3**.

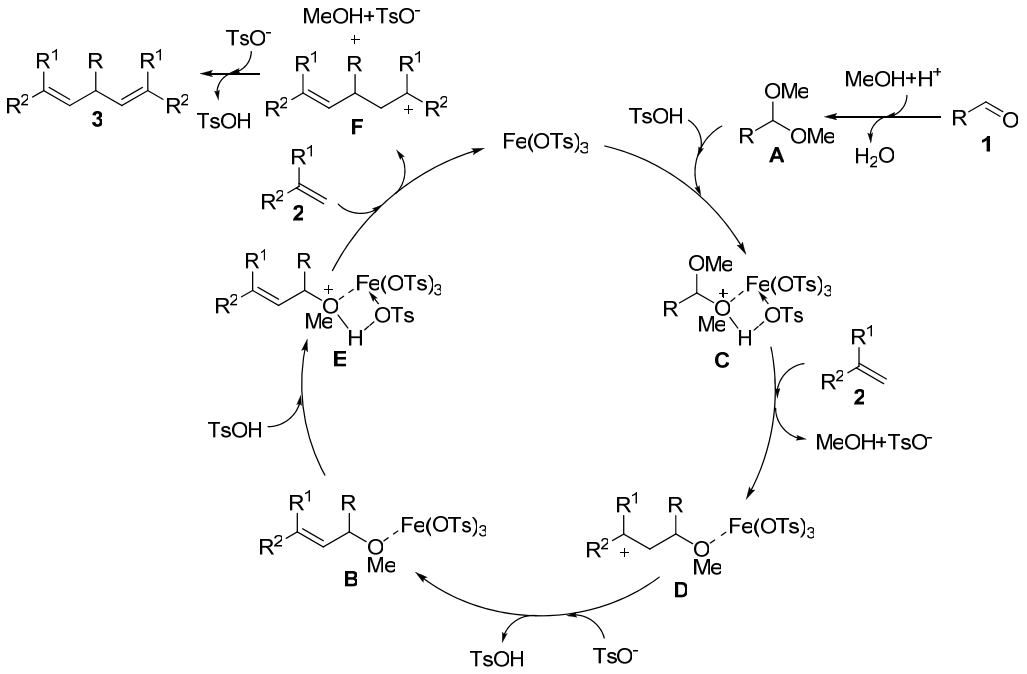


Figure 4. Proposed mechanism

Reference

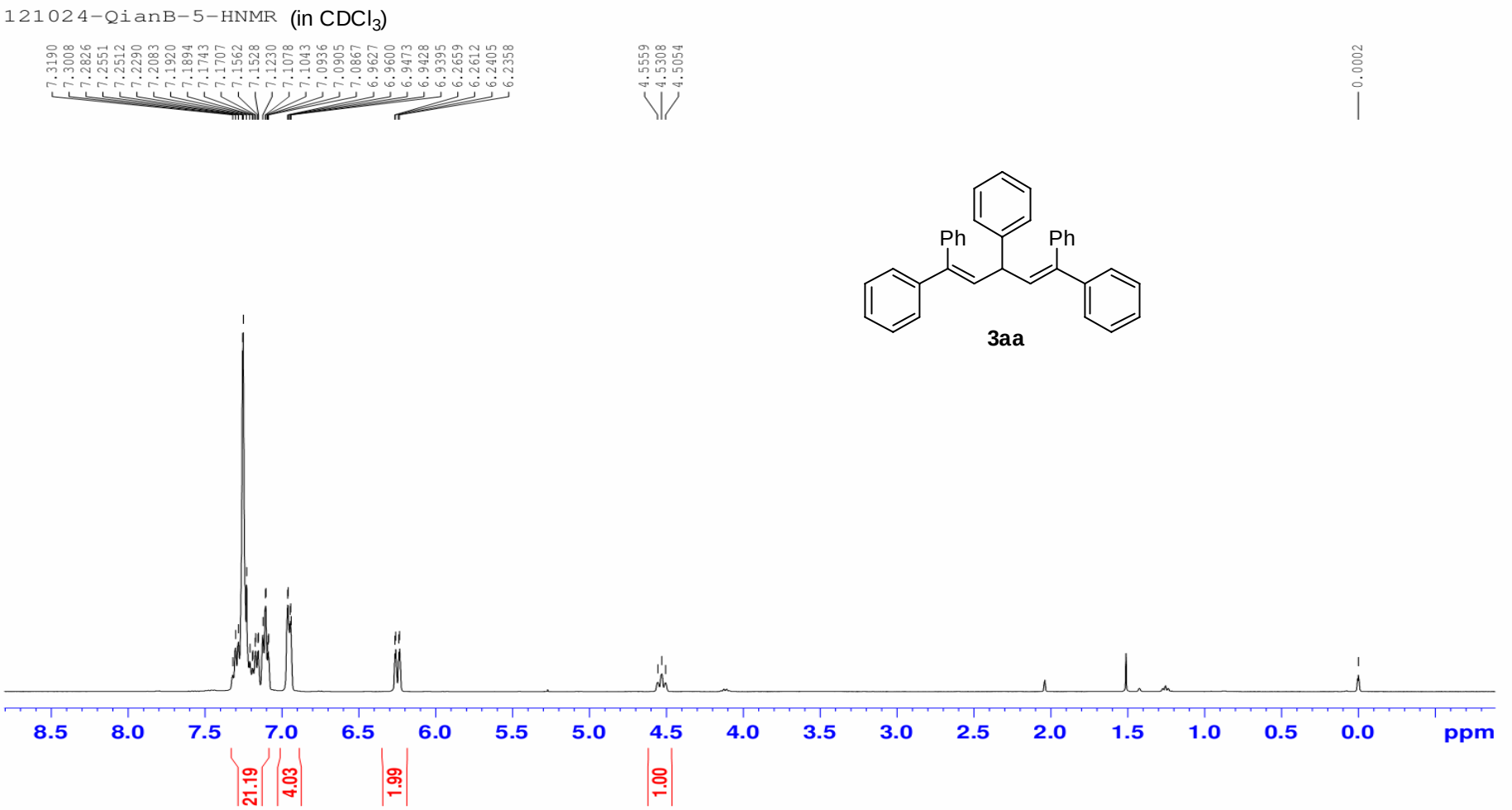
[1] T. Wang, Y. Hu and S. A. Zhang, *Org. Biomol. Chem.*, 2010, **8**, 2312.

[2] A. Ladepeche, E. Tam, J.-E. Ancel and L. Ghosez, *Synthesis.*, 2004, 1375.

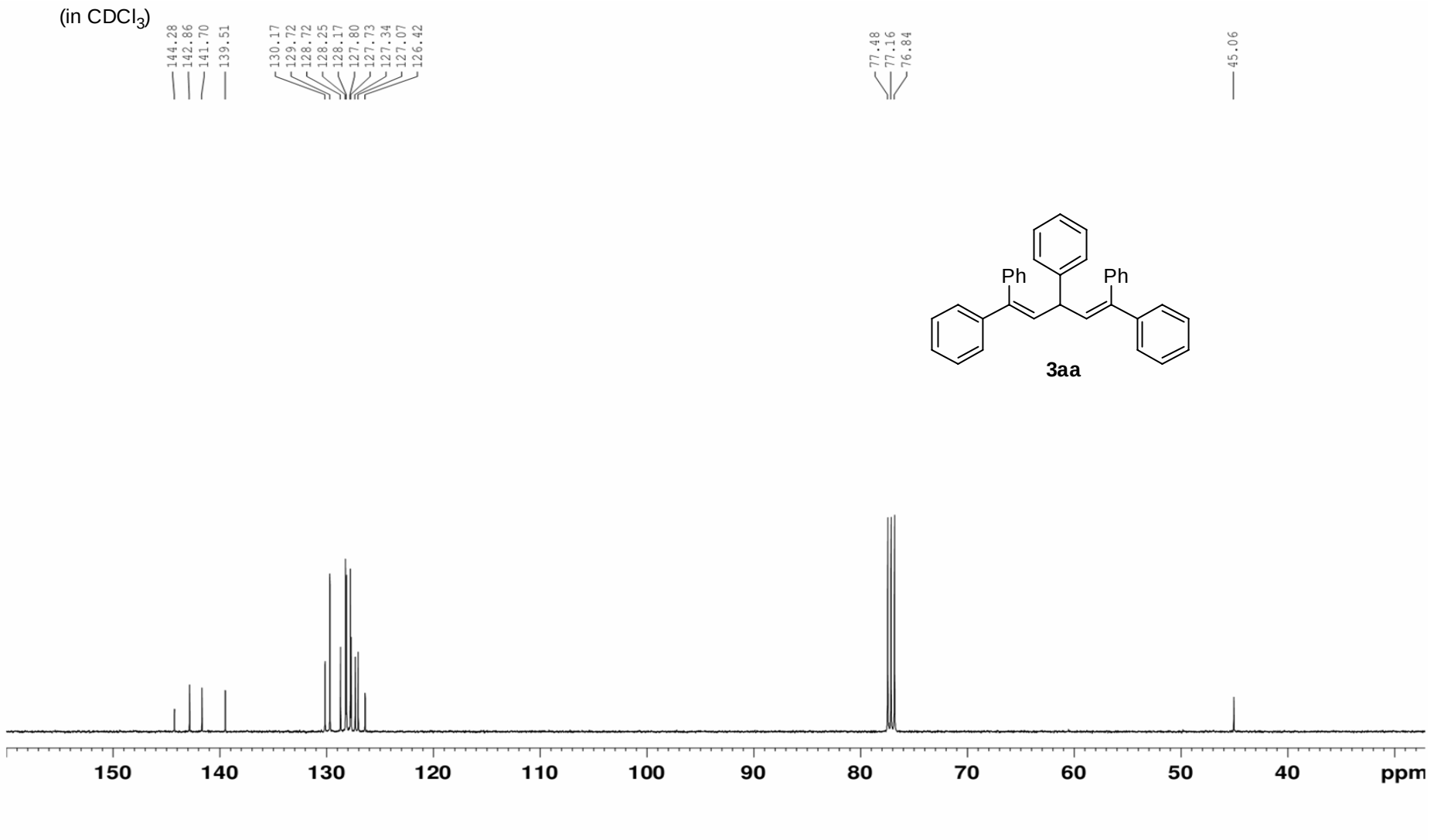
[3] Y. Hamada, N. Seto, Y. Takayanagi, T. Nakano and O. Hara, *Tetrahedron Lett.*, 1999**, 40**, 7791.

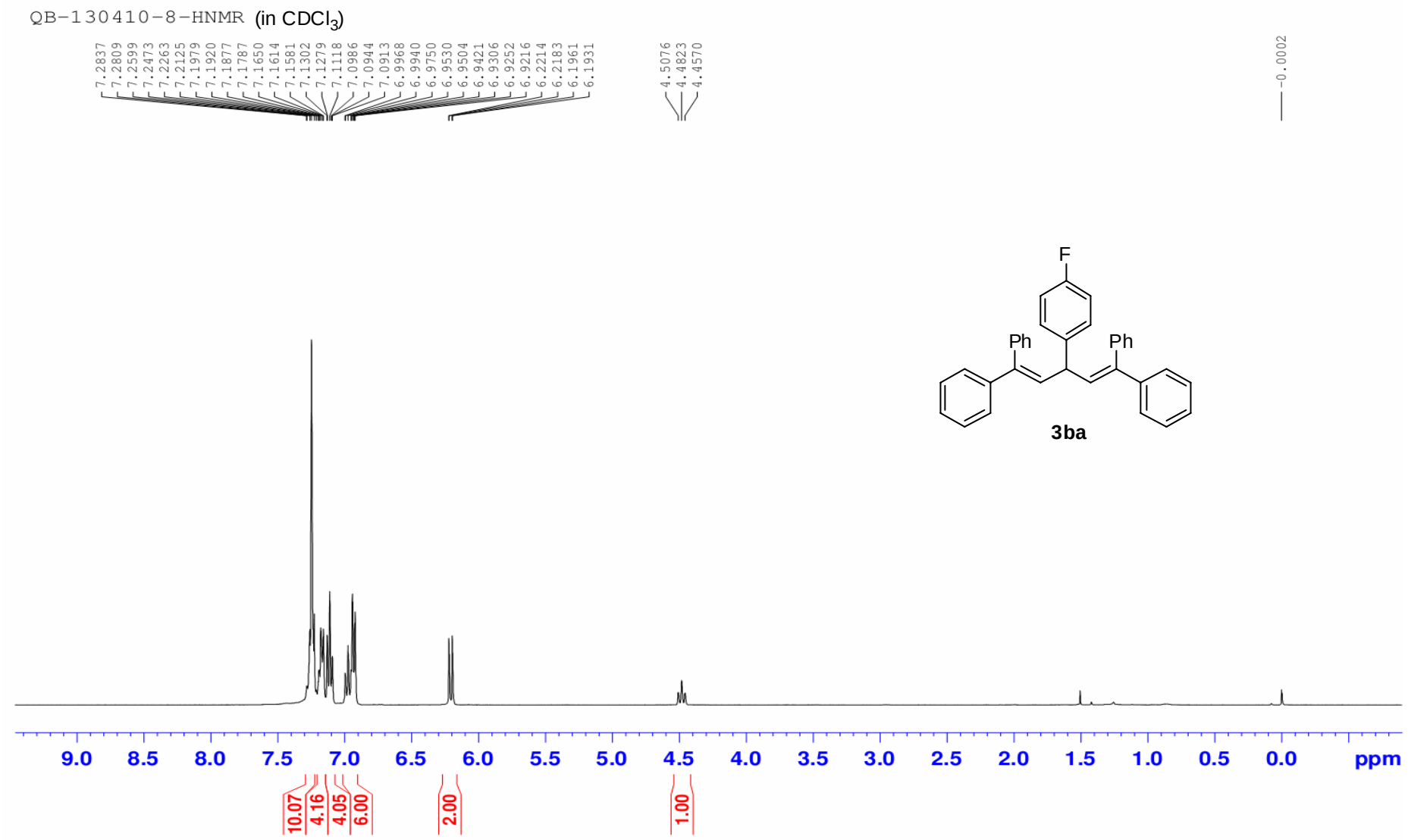
[4] (a) H. Yamamoto and K. Futatsugi, *Angew. Chem. Int. Ed.*, 2005, **44** , 1924; (b) H. Ishibashi, K. Ishihara, H. Yamamoto, *Chem. Rec.*, 2002, **2** , 177; (c) S. Nakamura, M. Kaneeda, K. Ishihara and H. Yamamoto, *J. Am. Chem. Soc.*, 2000, **122**, 8120.

6. Copies of product ^{1}H NMR and ^{13}C NMR

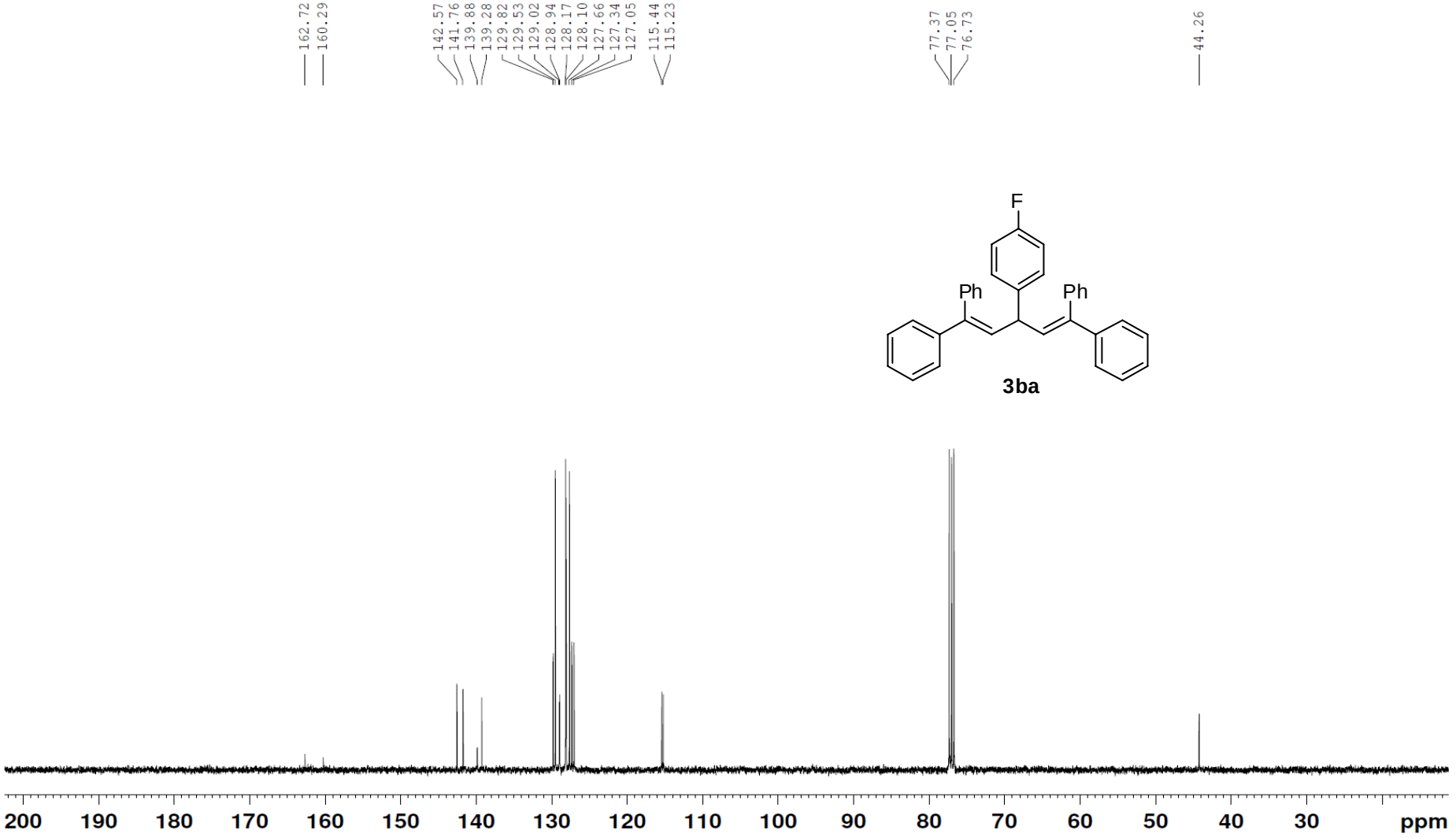

121024-QianB-5-HNMR (in CDCl3)
7.3190
7.3008
7.2826
7.2551
7.2512
7.2290
7.2083
7.1920
7.1894
7.1743
7.1707
7.1562
7.1528
7.1230
7.1078
7.1043
7.0936
7.0905
7.0867
6.9627
6.9600
6.9473
6.9428
6.9395
6.2659
6.2612
6.2405
6.2358
4.5559
4.5308
4.5054
0.0002
Ph
Ph
3aa
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
21.19
4.03
1.99
1.00

(in $CDCl_3$)


144.28
142.86
141.70
139.51
130.17
129.72
128.72
128.25
128.17
127.80
127.73
127.34
127.07
126.42
77.48
77.16
76.84
45.06
Ph
Ph
3aa
150
140
130
120
110
100
90
80
70
60
50
40
ppm


QB-130410-8-HNMR (in CDCl3)
7.2837
7.2809
7.2599
7.2473
7.2263
7.2125
7.1979
7.1920
7.1877
7.1787
7.1650
7.1614
7.1581
7.1302
7.1279
7.1118
7.0986
7.0944
7.0913
6.9968
6.9940
6.9750
6.9530
6.9504
6.9421
6.9306
6.9252
6.9216
6.2214
6.2183
6.1961
6.1931
4.5076
4.4823
4.4570
-0.0002
F
Ph
Ph
3ba
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
10.07
4.16
4.05
6.00
2.00
1.00

QB-130506-2-CNMR (in $CDCl_3$)



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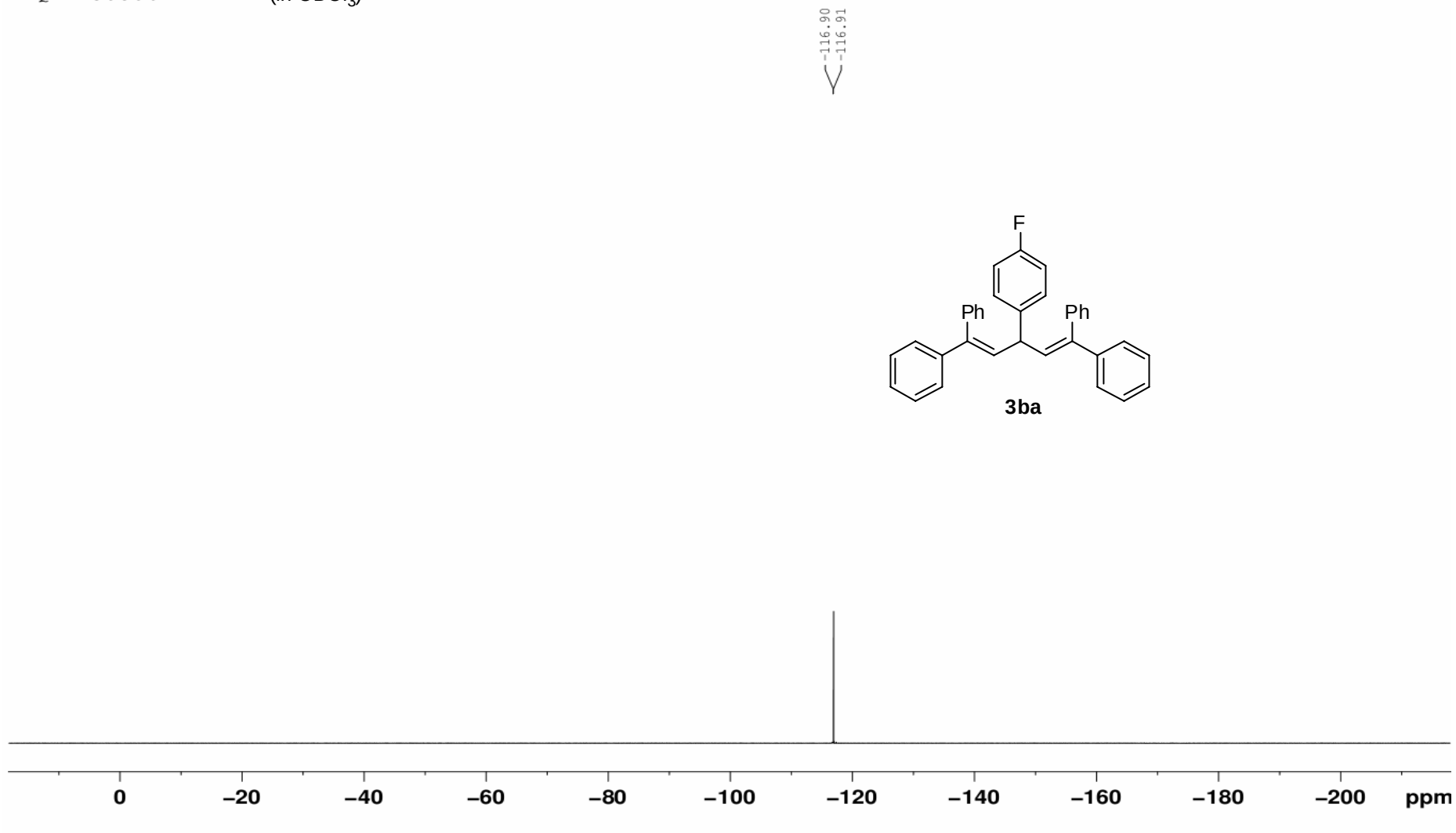
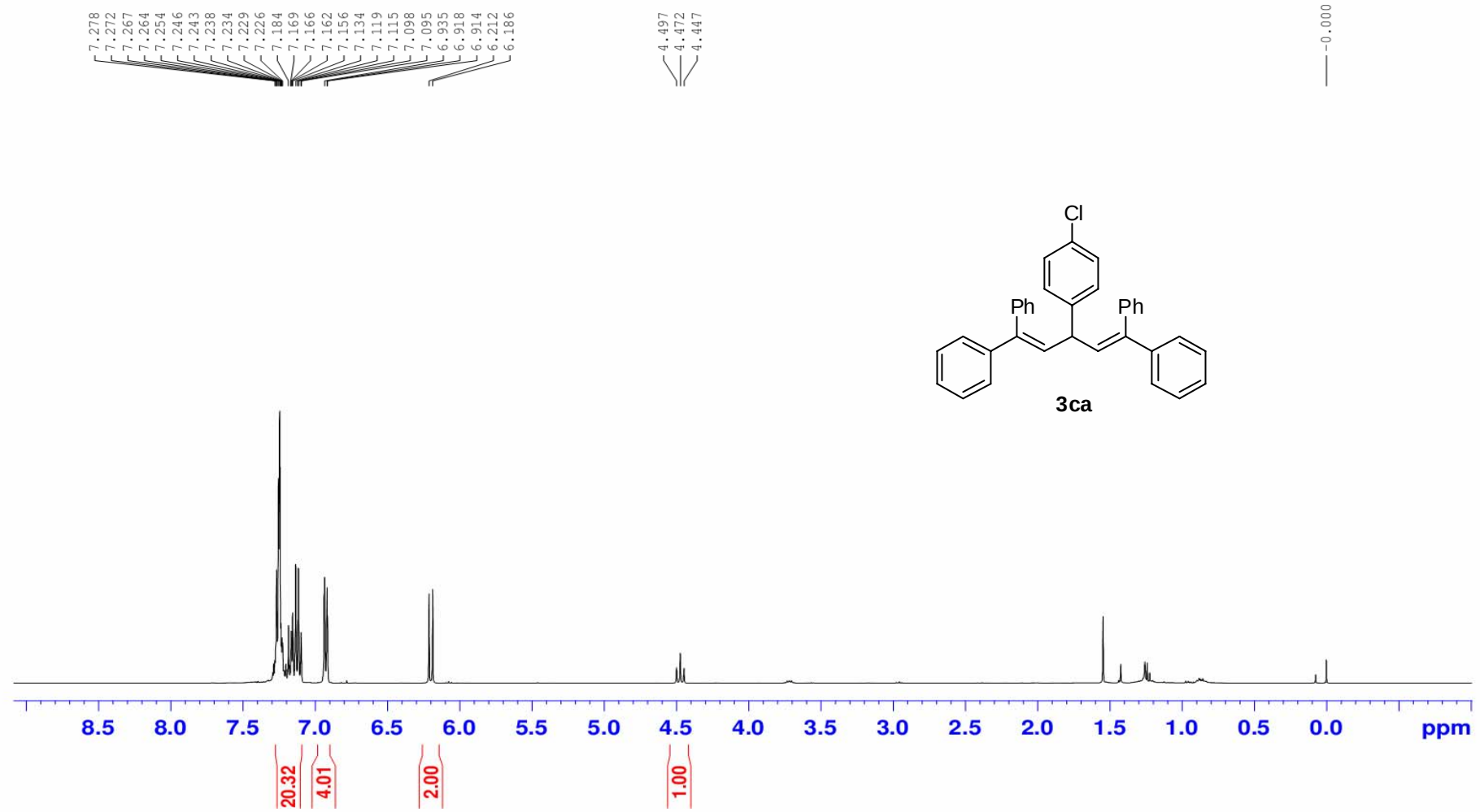
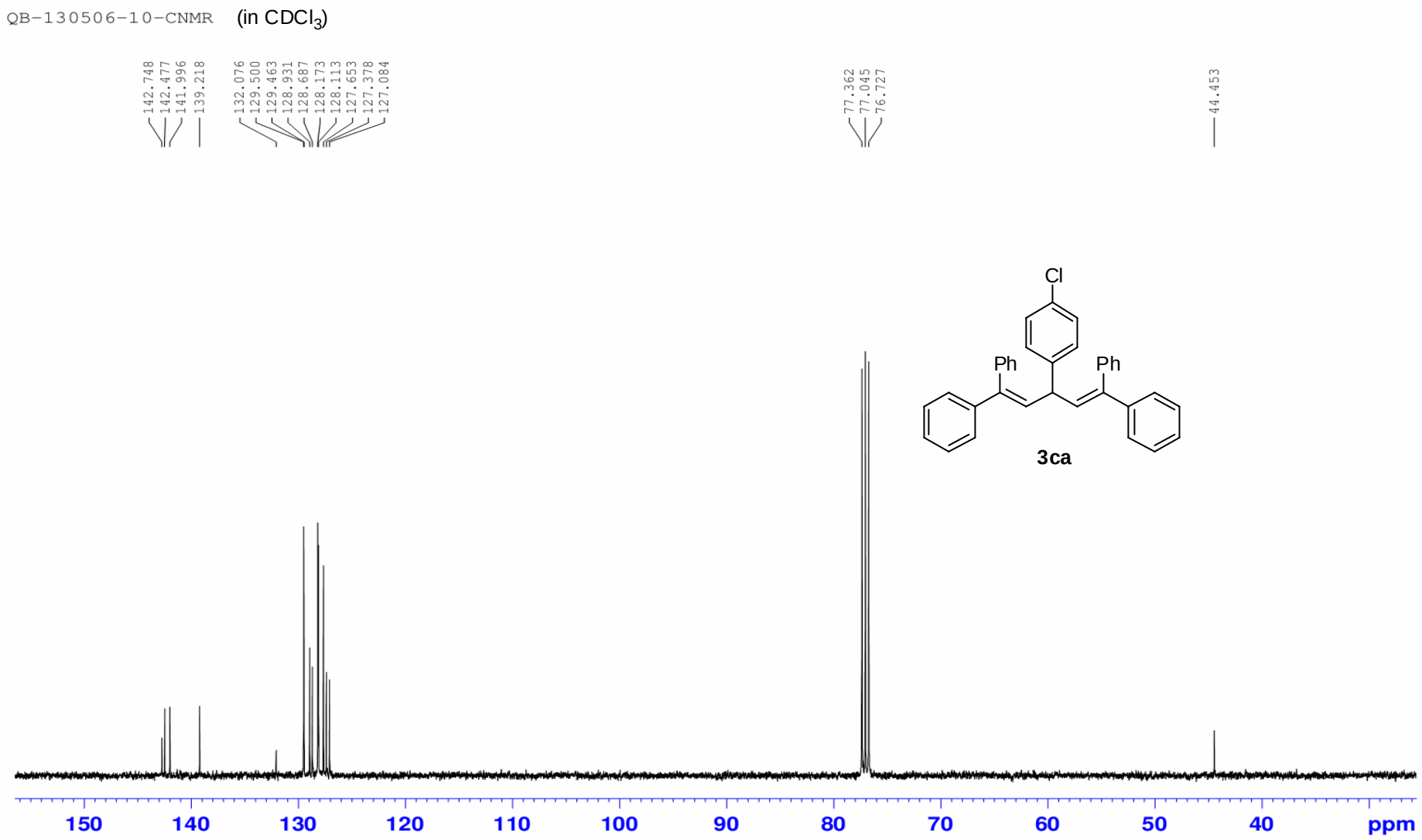
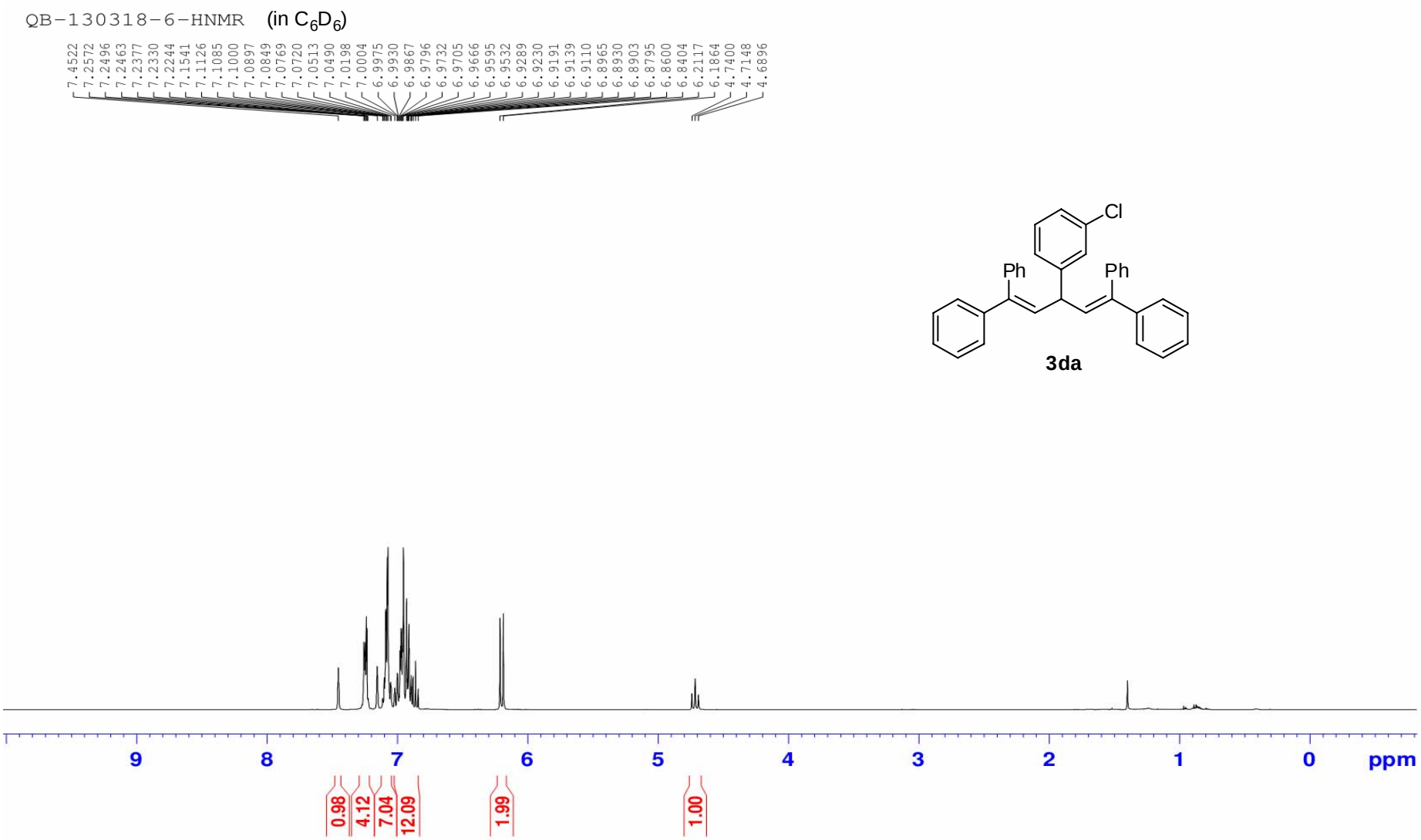


3ba

QB-130506-10-HNMR (in $CDCl_3$)




QB-130506-10-CNMR (in $CDCl_3$)
142.748
142.477
141.996
139.218
132.076
129.500
129.463
128.931
128.687
128.173
128.113
127.653
127.378
127.084
77.362
77.045
76.727
44.453
Cl
Ph
Ph
3ca
150
140
130
120
110
100
90
80
70
60
50
40
ppm


QB-130318-6-HNMR (in C_6D_6)
7.4522
7.2572
7.2496
7.2463
7.2377
7.2330
7.2244
7.1541
7.1126
7.1085
7.1000
7.0897
7.0849
7.0769
7.0720
7.0513
7.0490
7.0198
7.0004
6.9975
6.9930
6.9867
6.9796
6.9732
6.9705
6.9666
6.9595
6.9532
6.9289
6.9230
6.9191
6.9139
6.9110
6.8965
6.8930
6.8903
6.8795
6.8600
6.8404
6.2117
6.1864
4.7400
4.7148
4.6896
Cl
Ph
Ph
3da
9
8
7
6
5
4
3
2
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ppm
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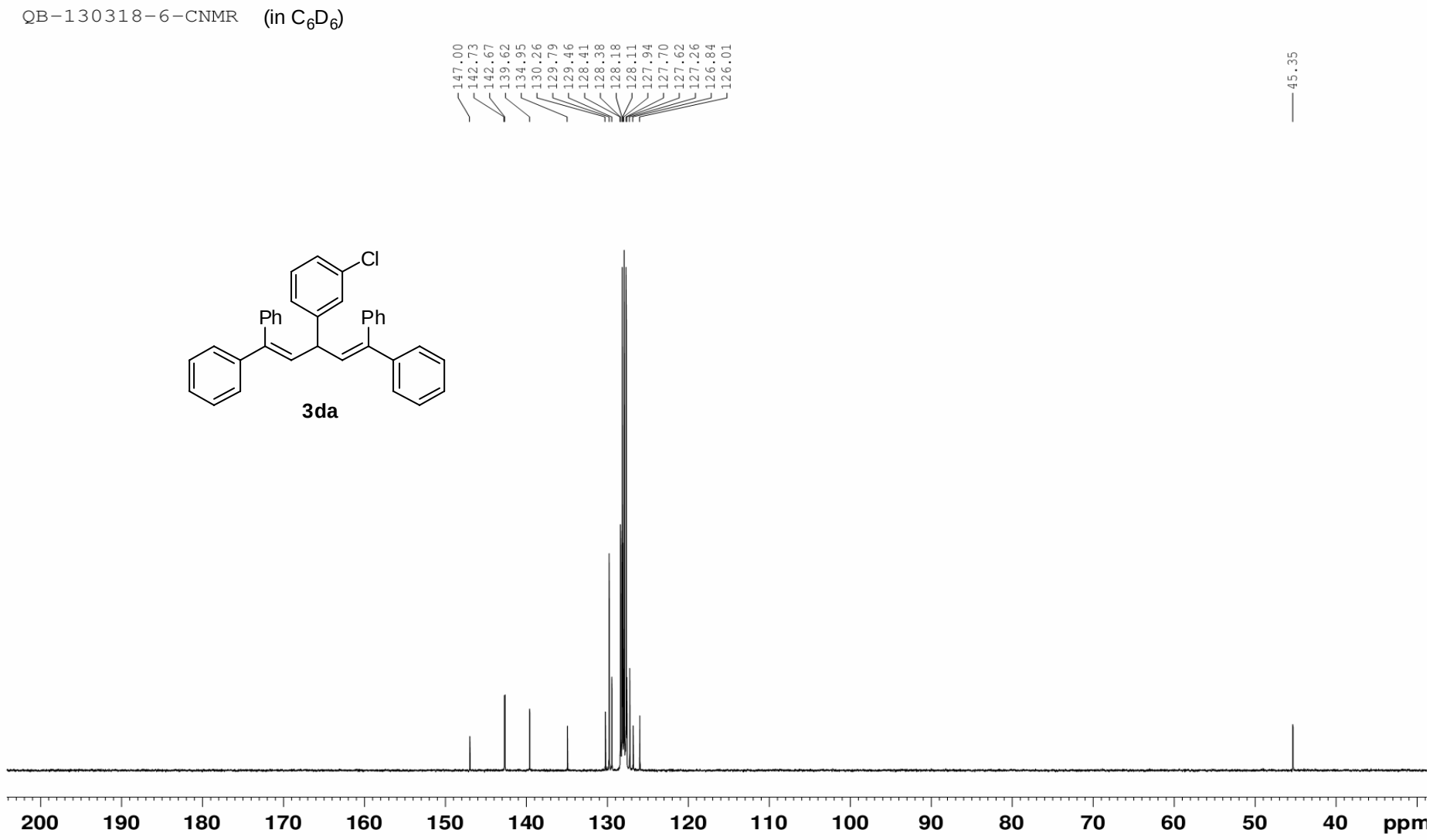
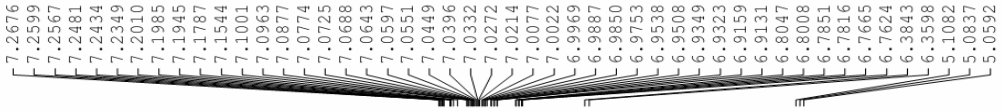
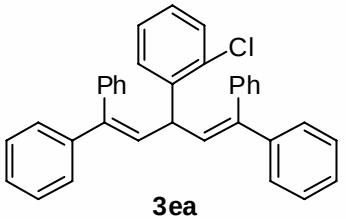
7.04
12.09
1.99
1.00

QB-130318-6-CNMR (in C_6D_6)

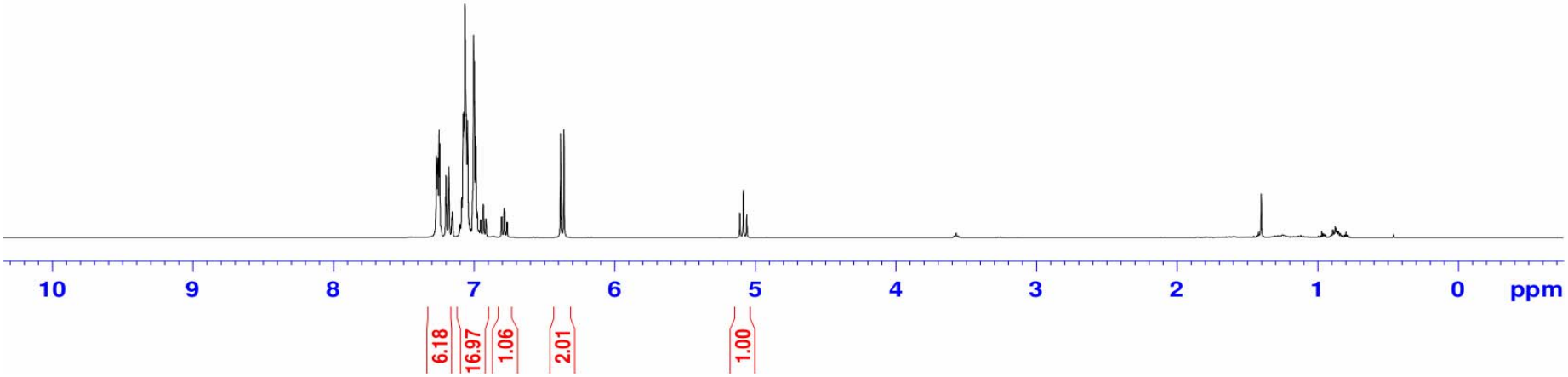


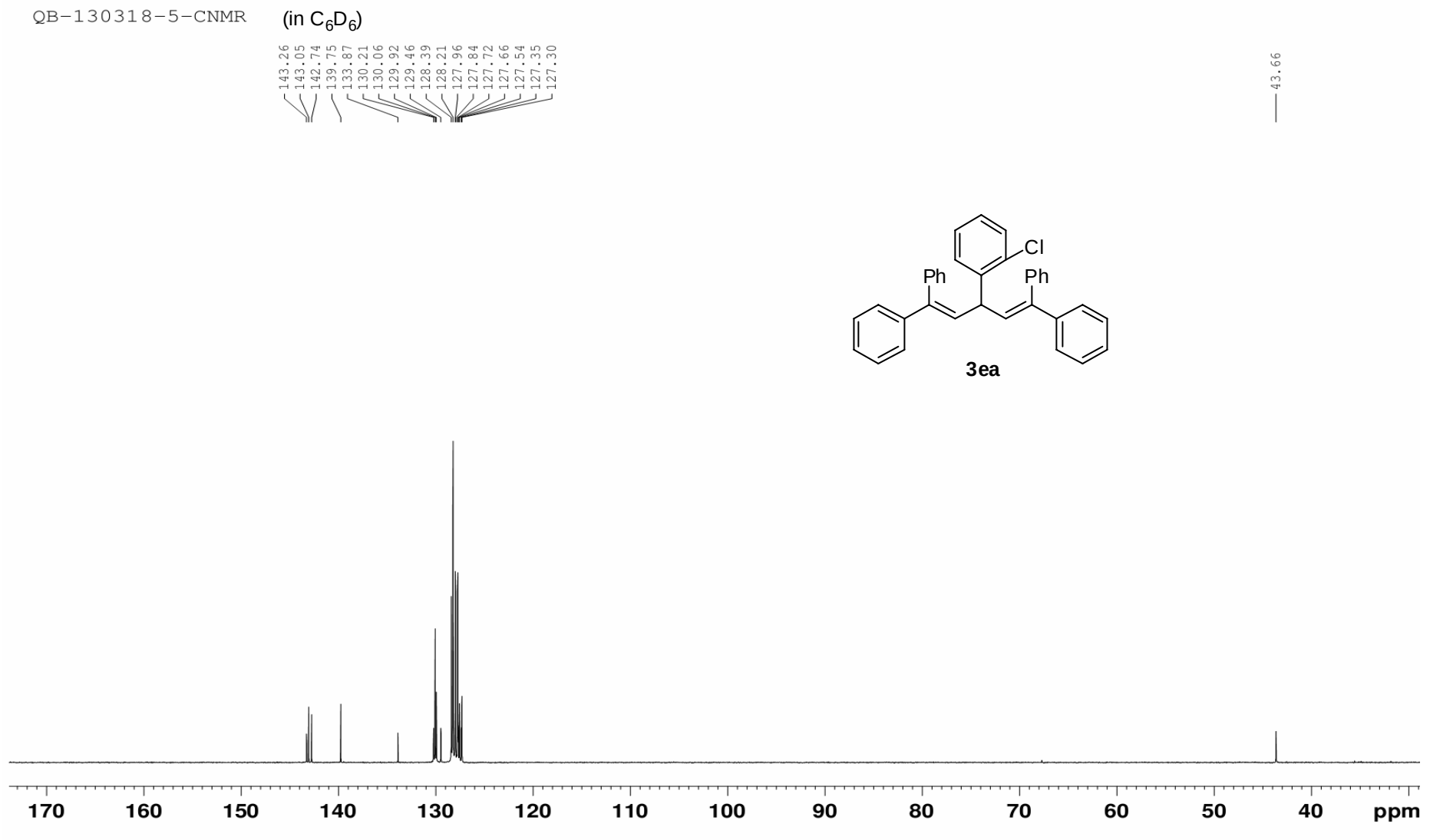
QB-130318-5-HNMR (in C_6D_6)





3ea




QB-130318-5-CNMR
(in C_6D_6)
143.26
143.05
142.74
139.75
133.87
130.21
130.06
129.92
129.46
128.39
128.21
127.96
127.84
127.72
127.66
127.54
127.35
127.30
43.66
Cl
Ph
Ph
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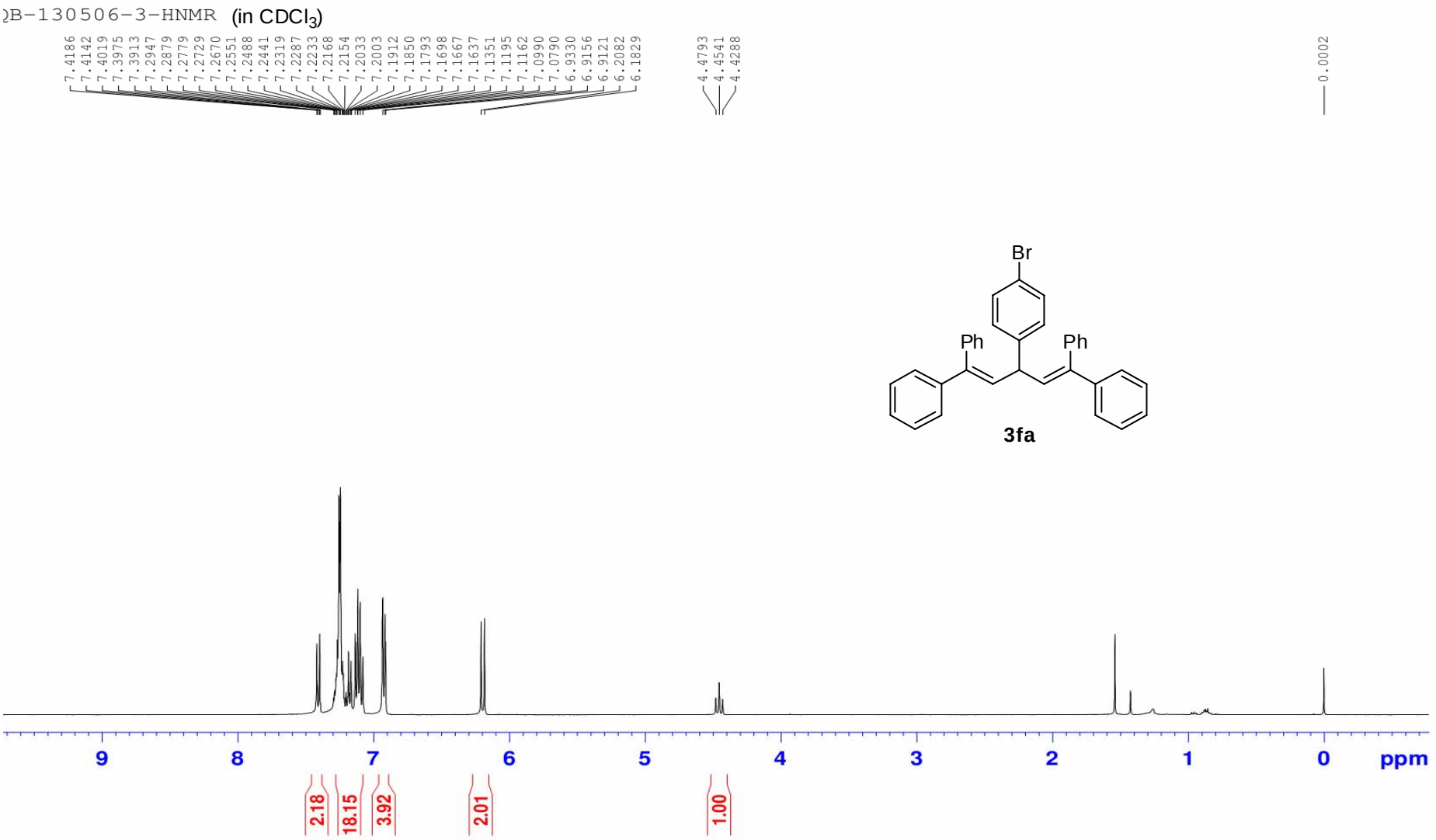
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm


)B-130506-3-HNMR (in CDCl3)
7.4186
7.4142
7.4019
7.3975
7.3913
7.2947
7.2879
7.2779
7.2729
7.2670
7.2551
7.2488
7.2441
7.2319
7.2287
7.2233
7.2168
7.2154
7.2033
7.2003
7.1912
7.1850
7.1793
7.1698
7.1667
7.1637
7.1351
7.1195
7.1162
7.0990
7.0790
6.9330
6.9156
6.9121
6.2082
6.1829
4.4793
4.4541
4.4288
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Br
Ph
Ph
3fa
9
8
7
6
5
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ppm
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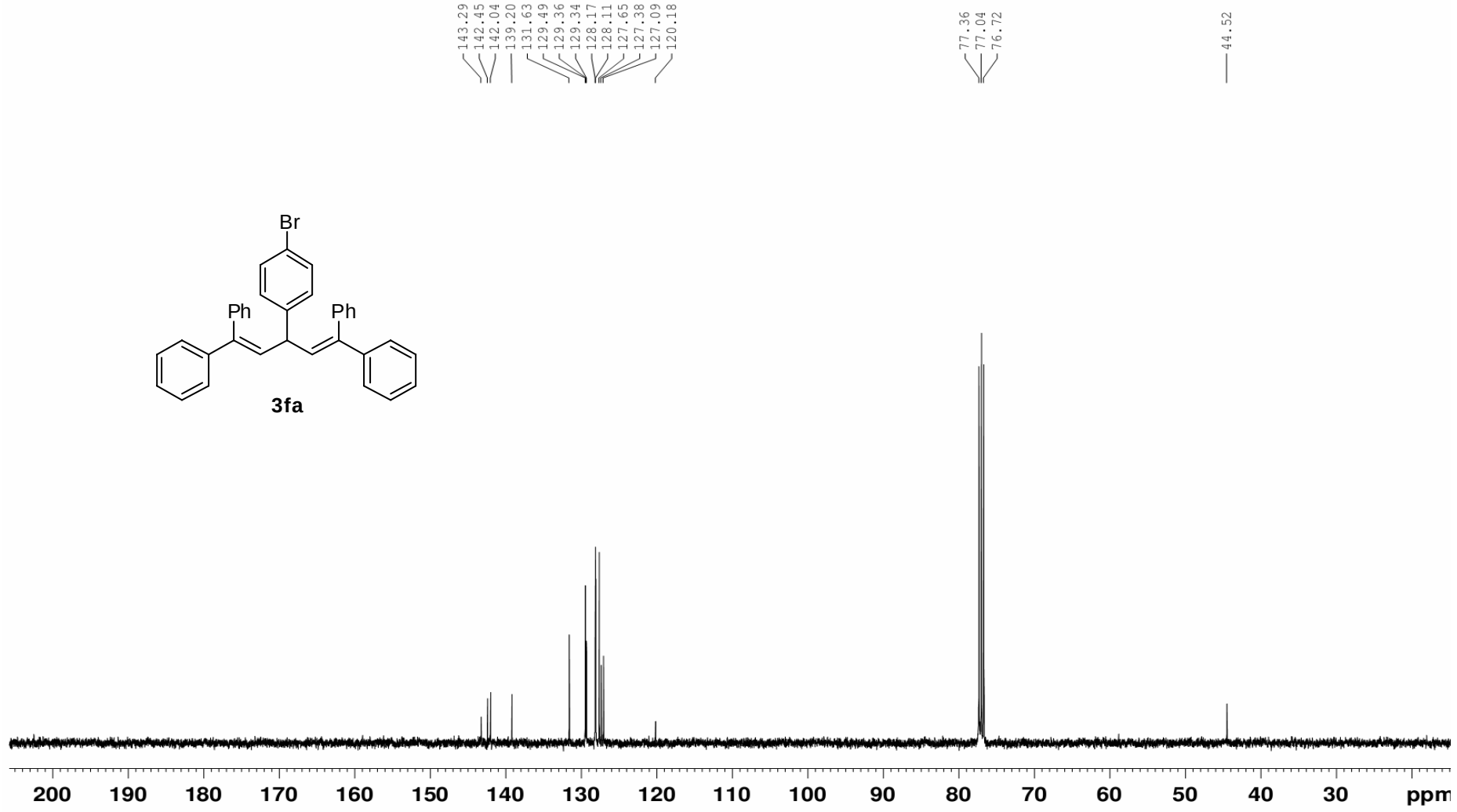
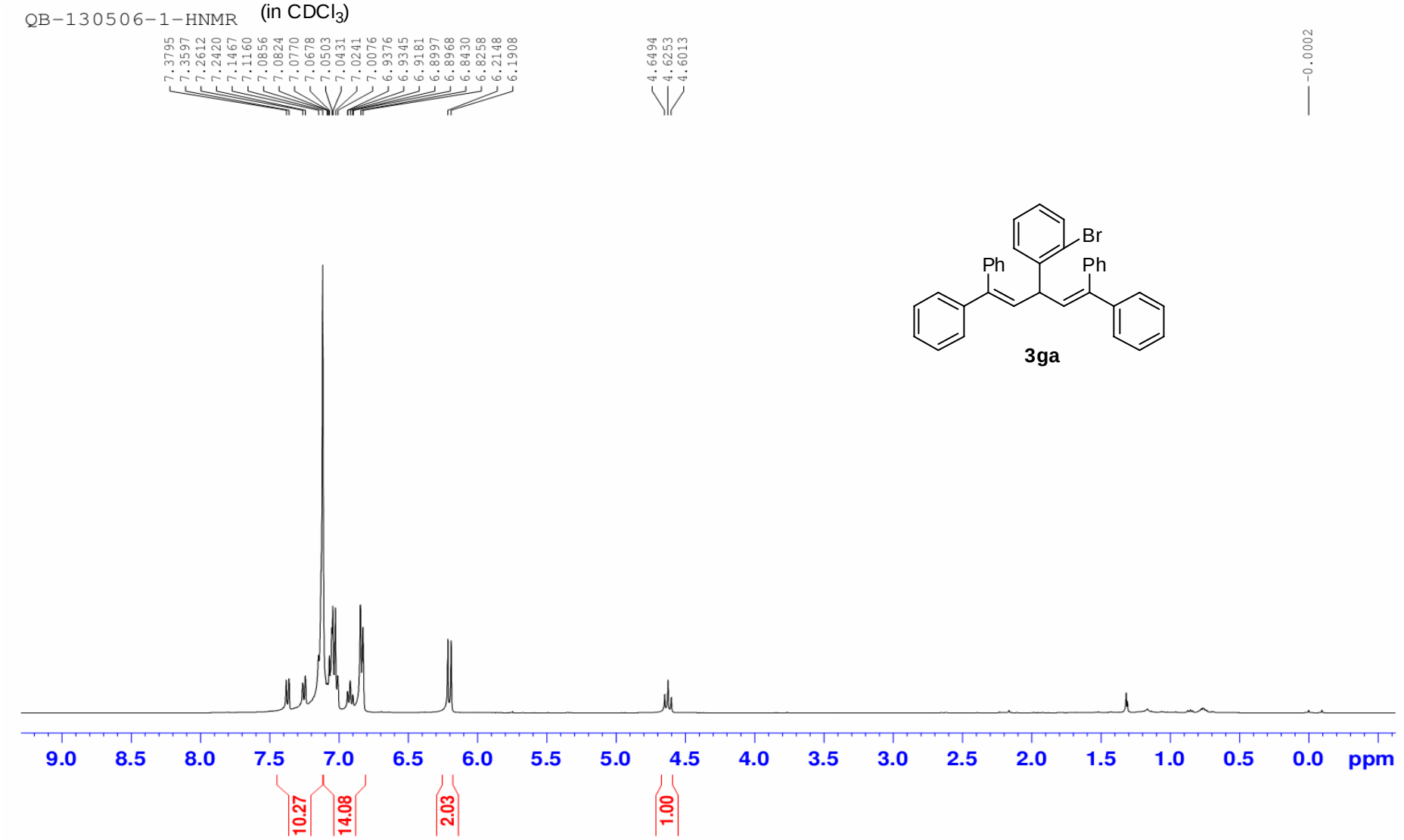
2.01
1.00

QB-130506-3-CNMR (in $CDCl_3$)

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(in CDCl3)
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7.0678
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7.0431
7.0241
7.0076
6.9376
6.9345
6.9181
6.8997
6.8968
6.8430
6.8258
6.2148
6.1908
4.6494
4.6253
4.6013
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Br
Ph
Ph
3ga
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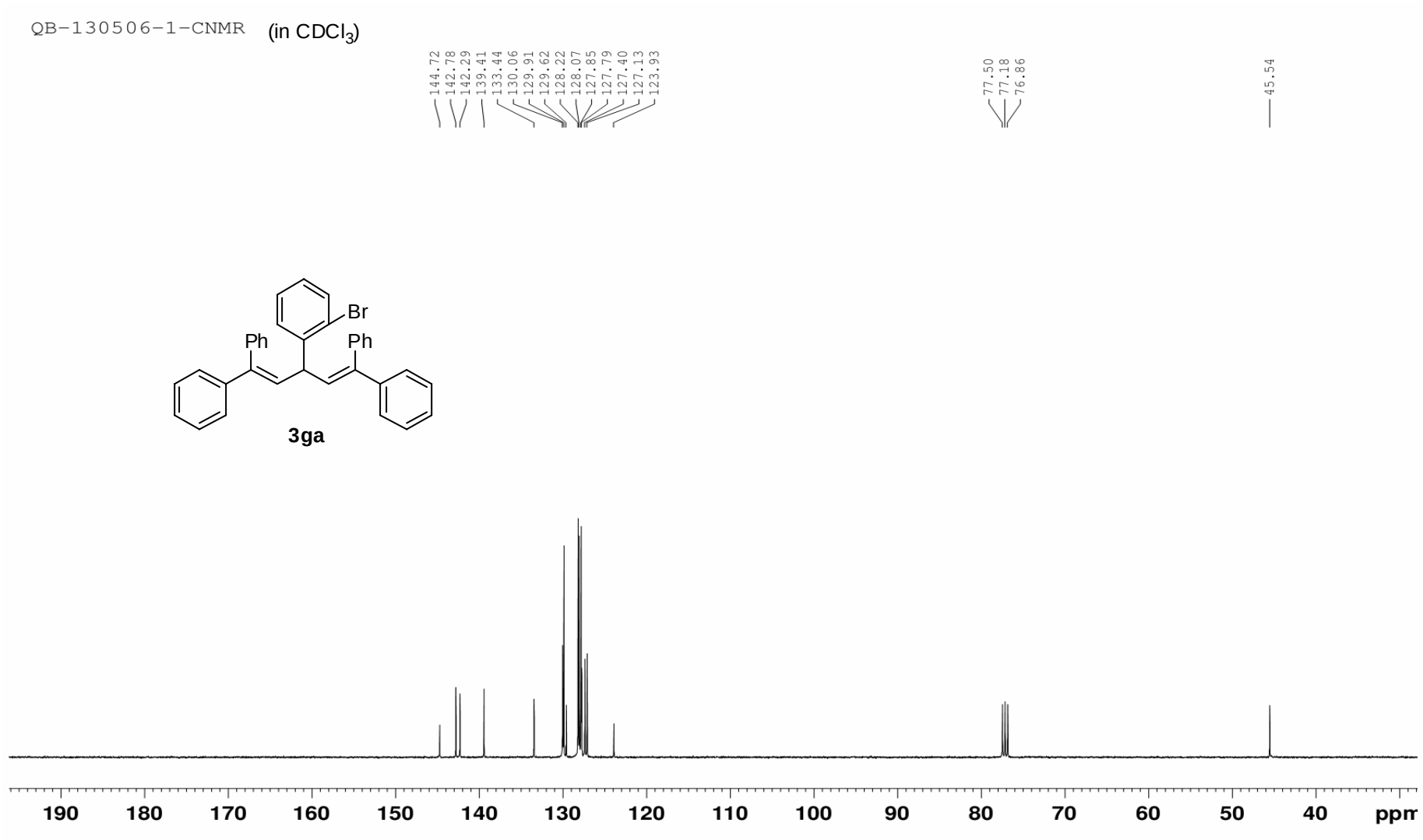
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
10.27
14.08
2.03
1.00


QB-130506-1-CNMR (in $CDCl_3$)
144.72
142.78
142.29
139.41
133.44
130.06
129.91
129.62
128.22
128.07
127.85
127.79
127.40
127.13
123.93
77.50
77.18
76.86
45.54
Br
Ph
Ph
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170
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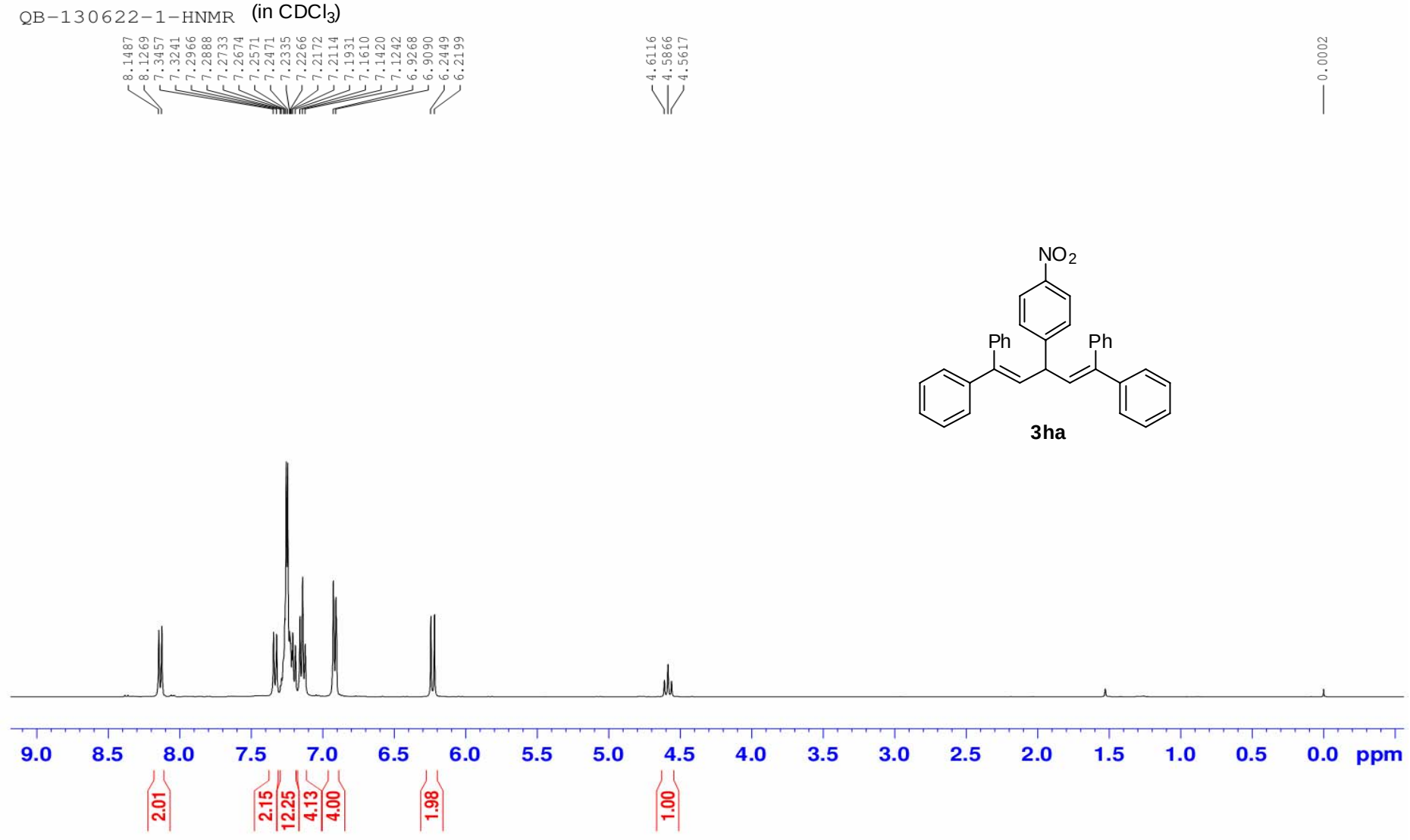
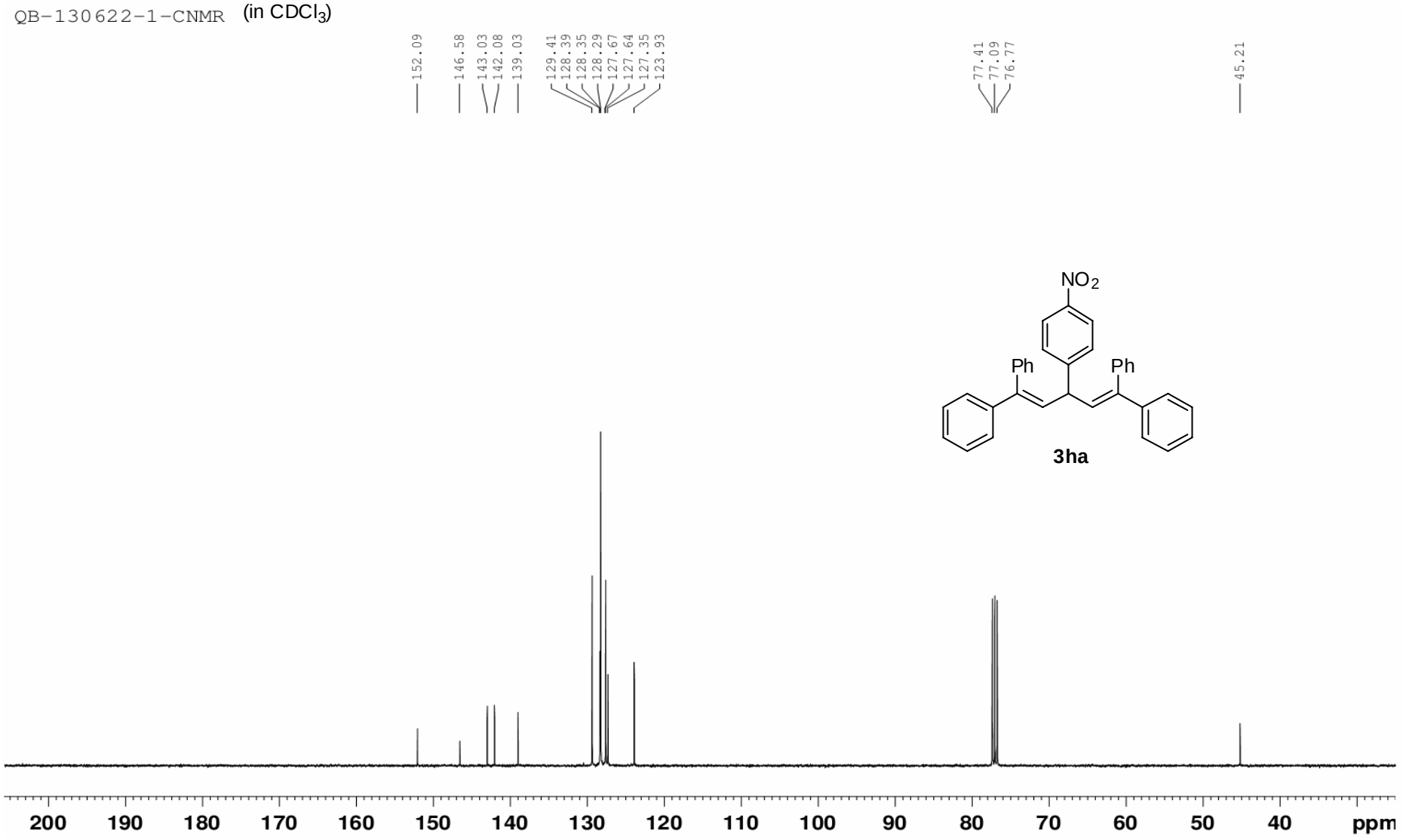
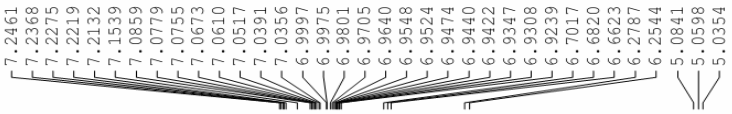
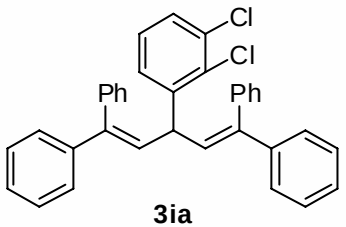
150
140
130
120
110
100
90
80
70
60
50
40
ppm



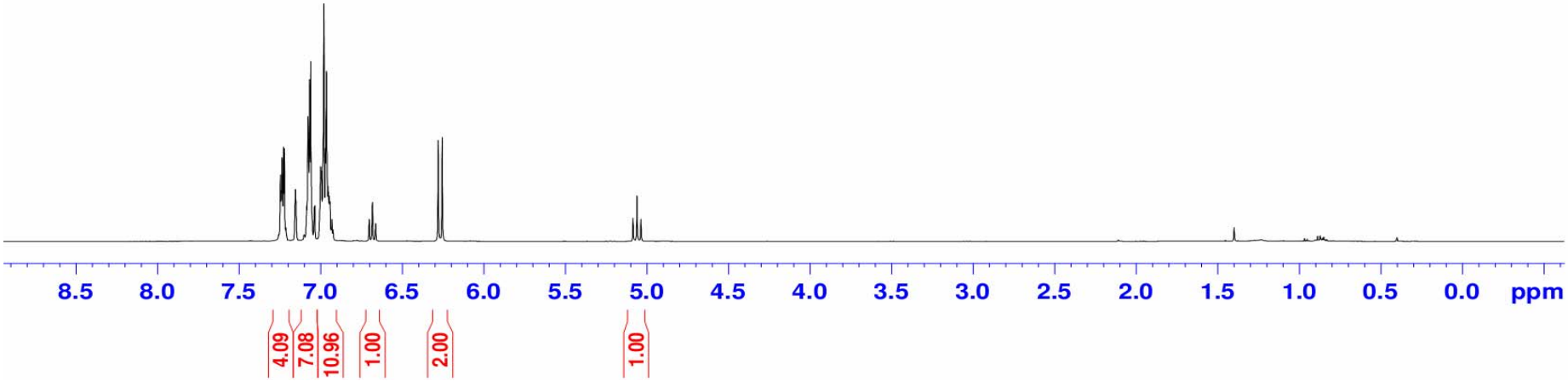

QB-130622-1-CNMR (in CDCl3)
152.09
146.58
143.03
142.08
139.03
129.41
128.39
128.35
128.29
127.67
127.64
127.35
123.93
77.41
77.09
76.77
45.21
NO2
Ph
Ph
3ha
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

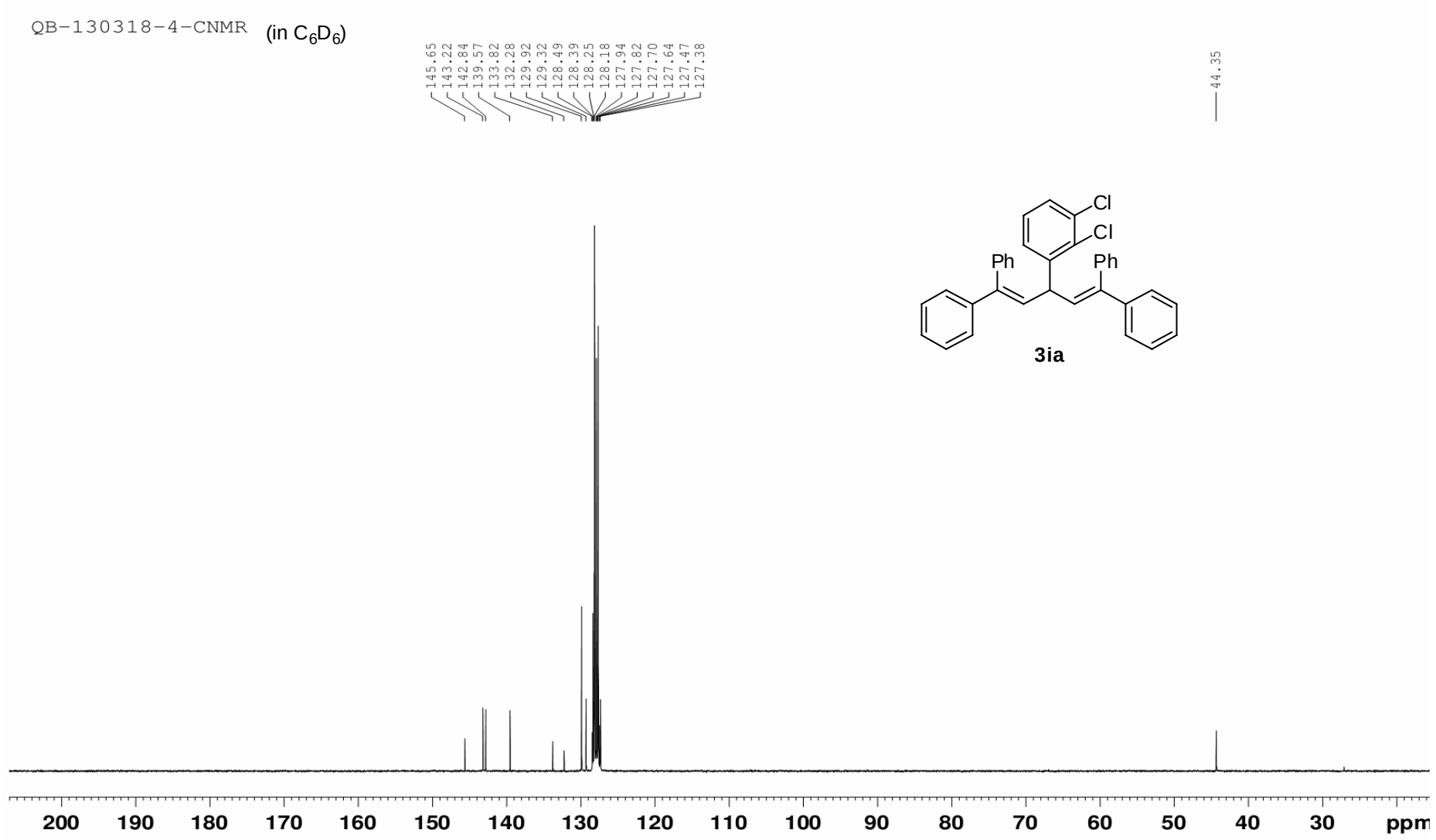
QB-130318-4-HNMR (in C_6D_6)



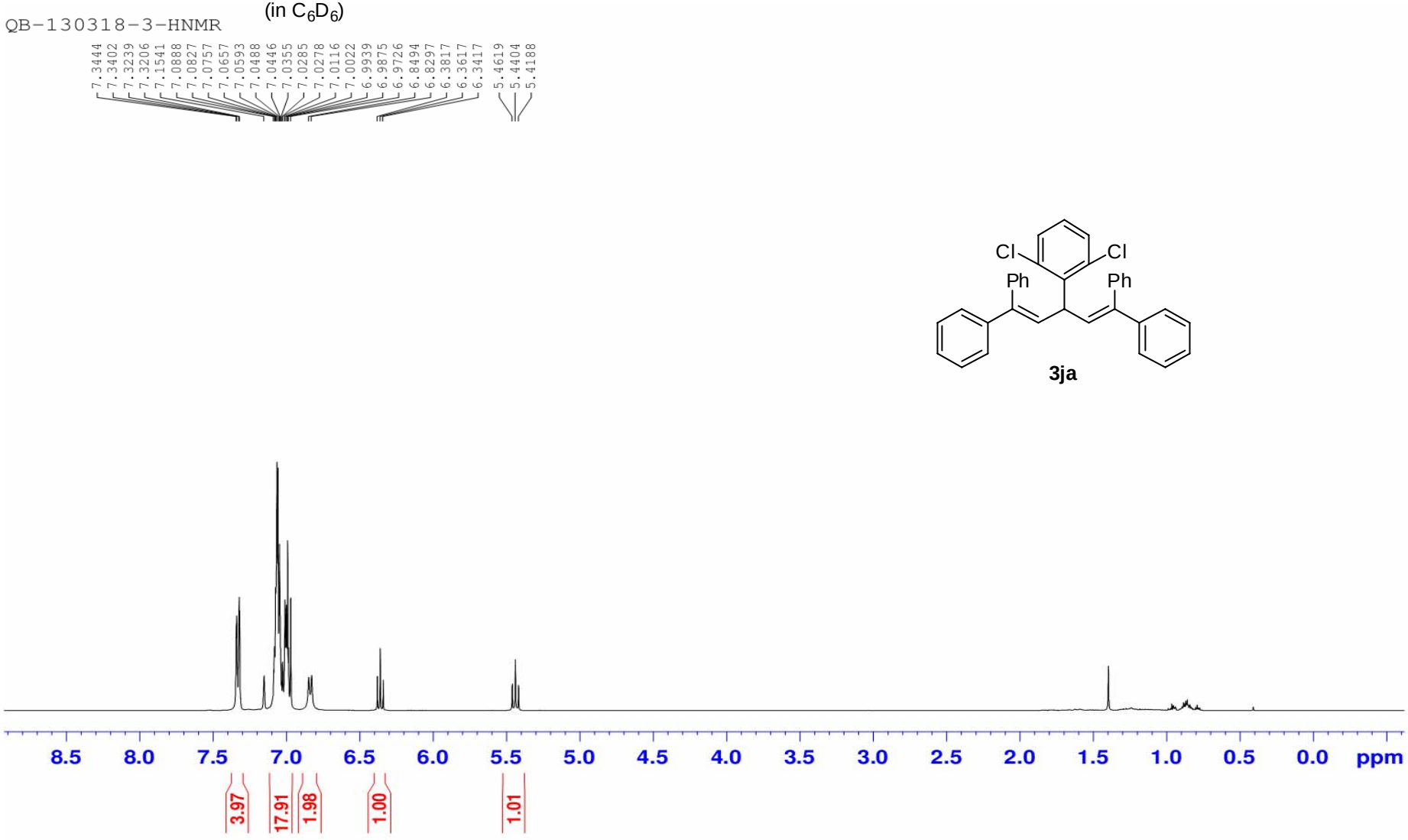


3ia

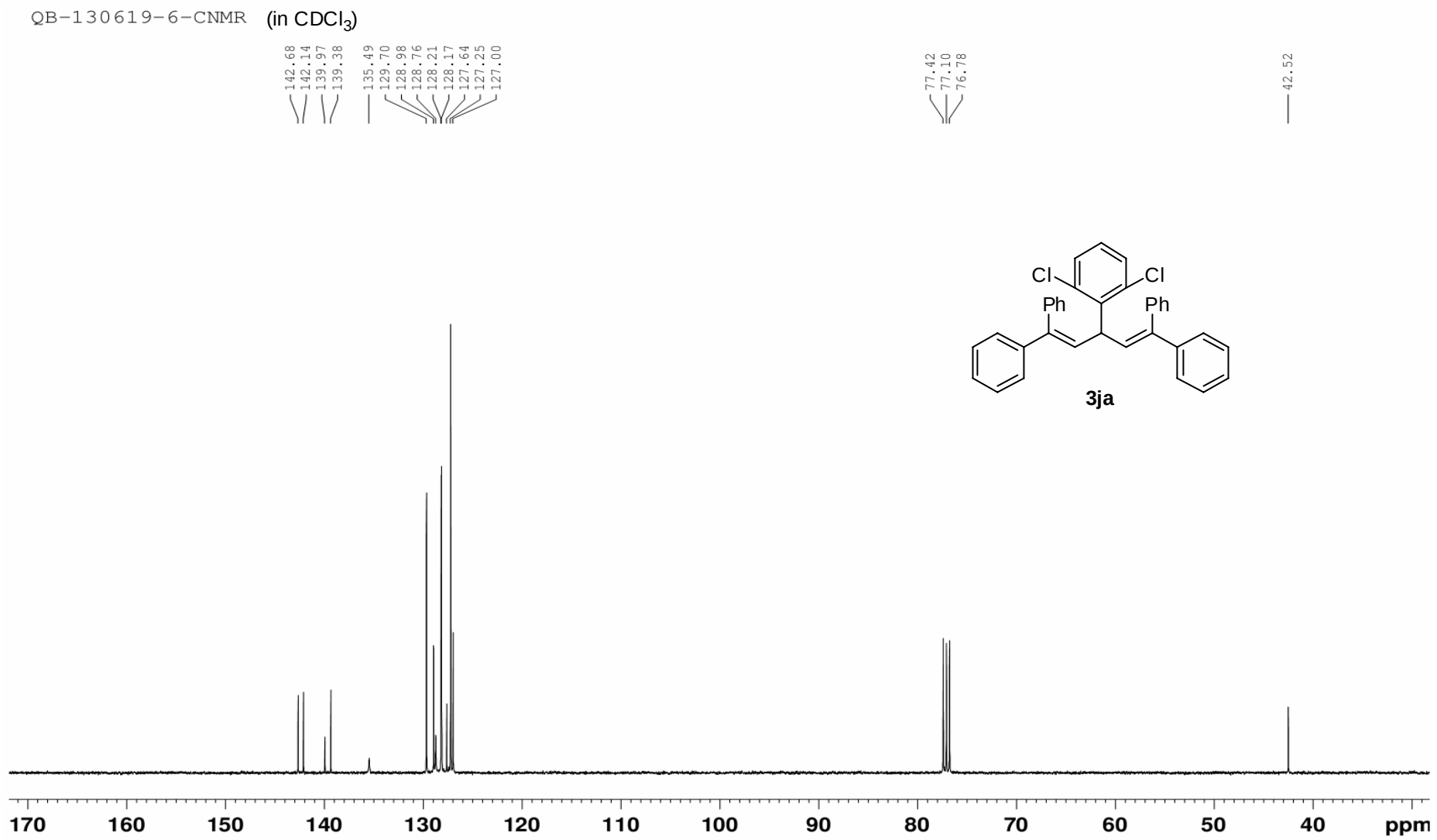


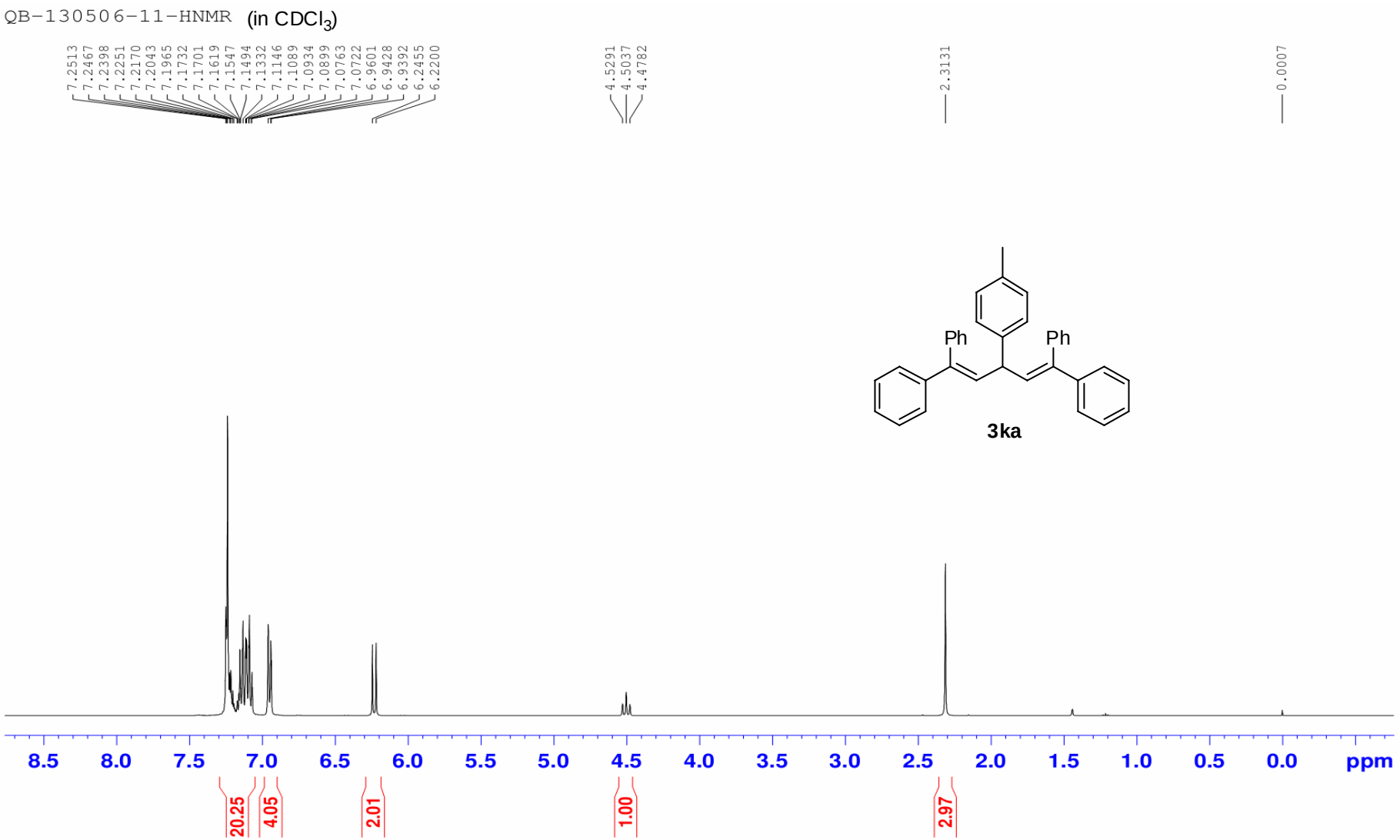

QB-130318-4-CNMR (in C_6D_6)
145.65
143.22
142.84
139.57
133.82
132.28
129.92
129.32
128.49
128.39
128.25
128.18
127.94
127.82
127.70
127.64
127.47
127.38
44.35
Cl
Cl
Ph
Ph
3ia
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

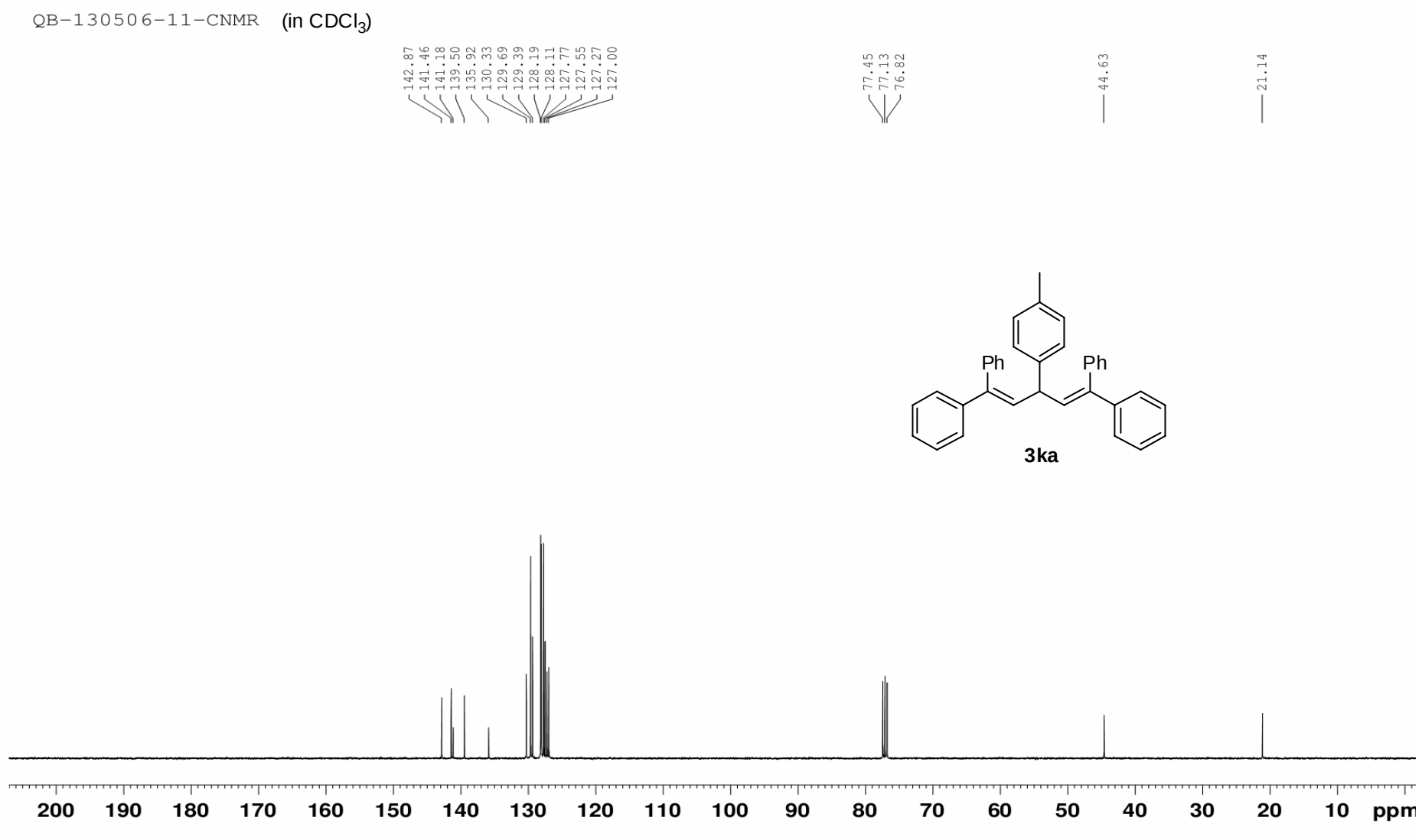
(in C_6D_6)

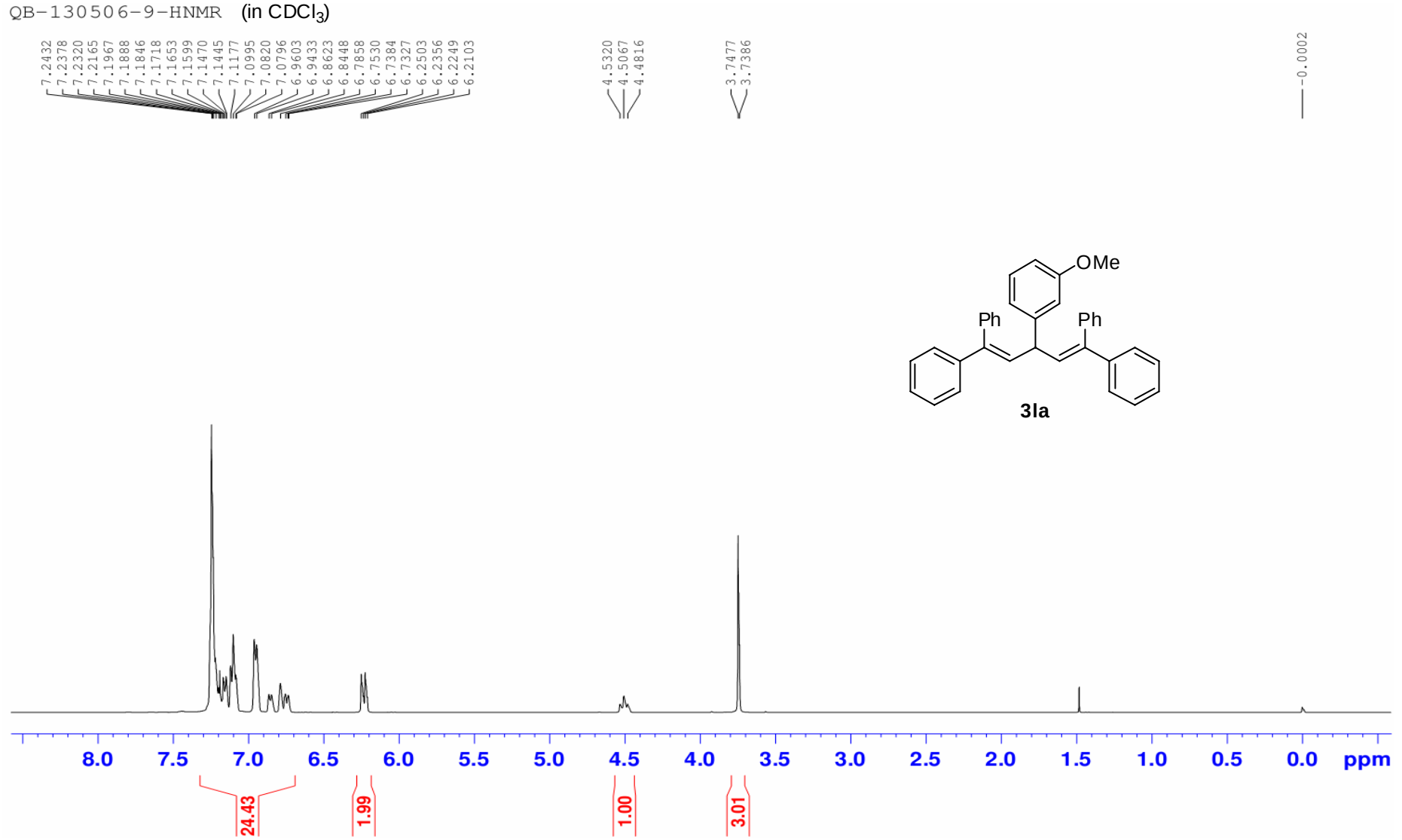

QB-130318-3-HNMR
7.3444
7.3402
7.3239
7.3206
7.1541
7.0888
7.0827
7.0757
7.0657
7.0593
7.0488
7.0446
7.0355
7.0285
7.0278
7.0116
7.0022
6.9939
6.9875
6.9726
6.8494
6.8297
6.3817
6.3617
6.3417
5.4619
5.4404
5.4188
Cl
Cl
Ph
Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.97
17.91
1.98
1.00
1.01

3ja


QB-130619-6-CNMR (in CDCl3)
142.68
142.14
139.97
139.38
135.49
129.70
128.98
128.76
128.21
128.17
127.64
127.25
127.00
77.42
77.10
76.78
42.52
Cl
Cl
Ph
Ph
3ja
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

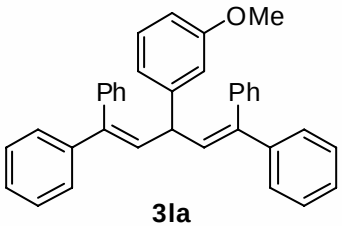

QB-130506-11-HNMR (in $CDCl_3$)
7.2513
7.2467
7.2398
7.2251
7.2170
7.2043
7.1965
7.1732
7.1701
7.1619
7.1547
7.1494
7.1332
7.1146
7.1089
7.0934
7.0899
7.0763
7.0722
6.9601
6.9428
6.9392
6.2455
6.2200
4.5291
4.5037
4.4782
2.3131
0.0007
Ph
Ph
3ka
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
20.25
4.05
2.01
1.00
2.97


QB-130506-11-CNMR (in $CDCl_3$)
142.87
141.46
141.18
139.50
135.92
130.33
129.69
129.39
128.19
128.11
127.77
127.55
127.27
127.00
77.45
77.13
76.82
44.63
21.14
Ph
Ph
3ka
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

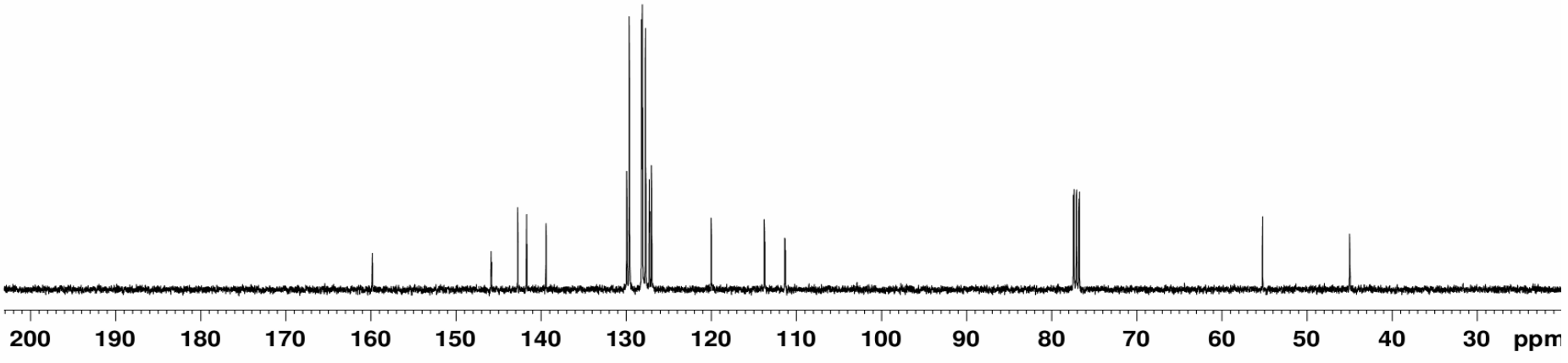

QB-130506-9-HNMR (in CDCl3)
7.2432
7.2378
7.2320
7.2165
7.1967
7.1888
7.1846
7.1718
7.1653
7.1599
7.1470
7.1445
7.1177
7.0995
7.0820
7.0796
6.9603
6.9433
6.8623
6.8448
6.7858
6.7530
6.7384
6.7327
6.2503
6.2356
6.2249
6.2103
4.5320
4.5067
4.4816
3.7477
3.7386
-0.0002
OMe
Ph
Ph
3la
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
24.43
1.99
1.00
3.01

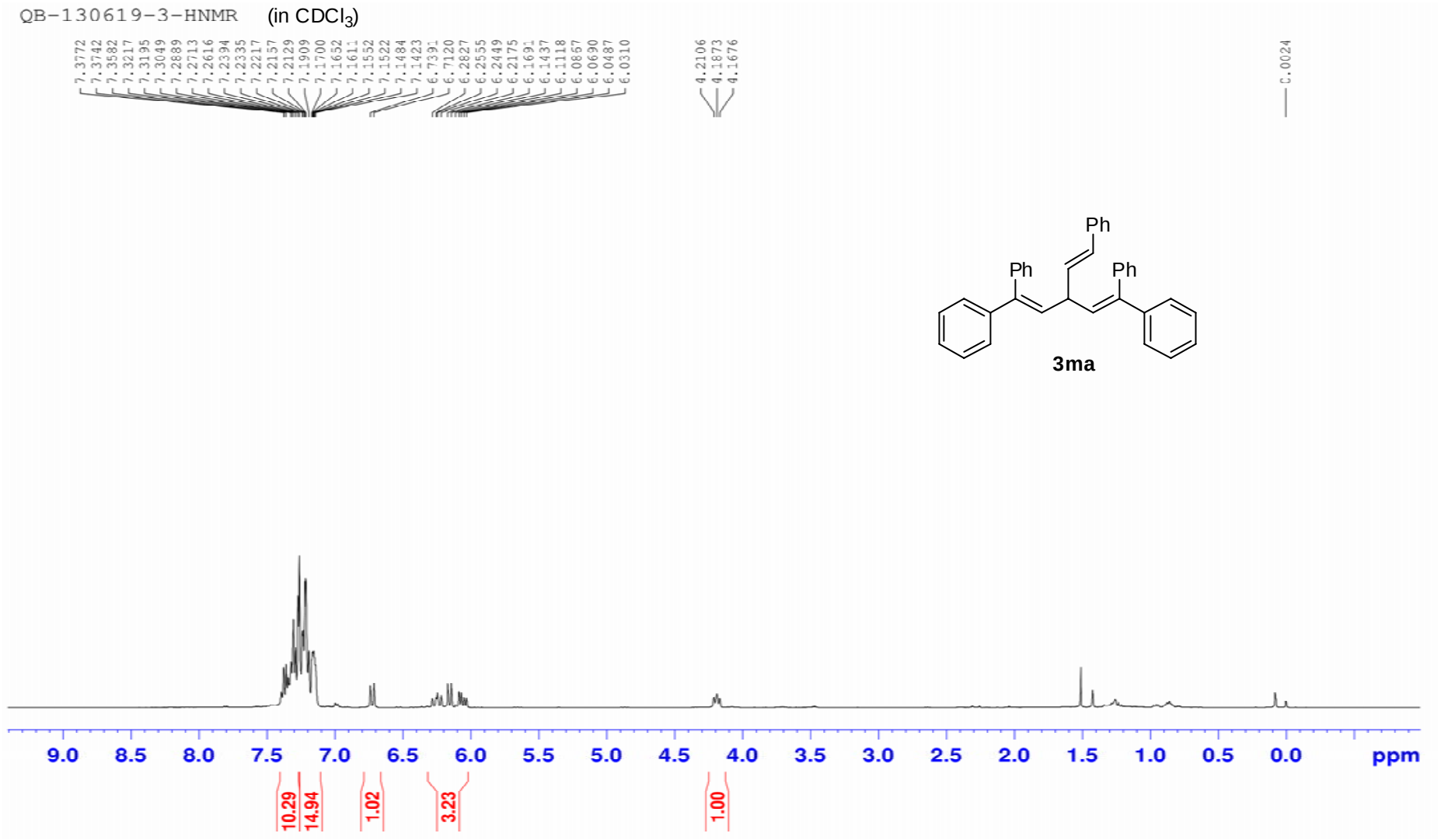
QB-130428-1-CNMR (in $CDCl_3$)

159.88
159.83
145.91
145.86
142.79
142.75
141.74
141.69
139.46
139.41
129.97
129.93
129.69
129.64
129.58
128.21
128.16
128.14
128.09
127.77
127.73
127.32
127.28
127.05
127.00
120.04
120.01
113.79
113.74
111.37
111.32
77.41
77.09
76.77
55.25
45.02

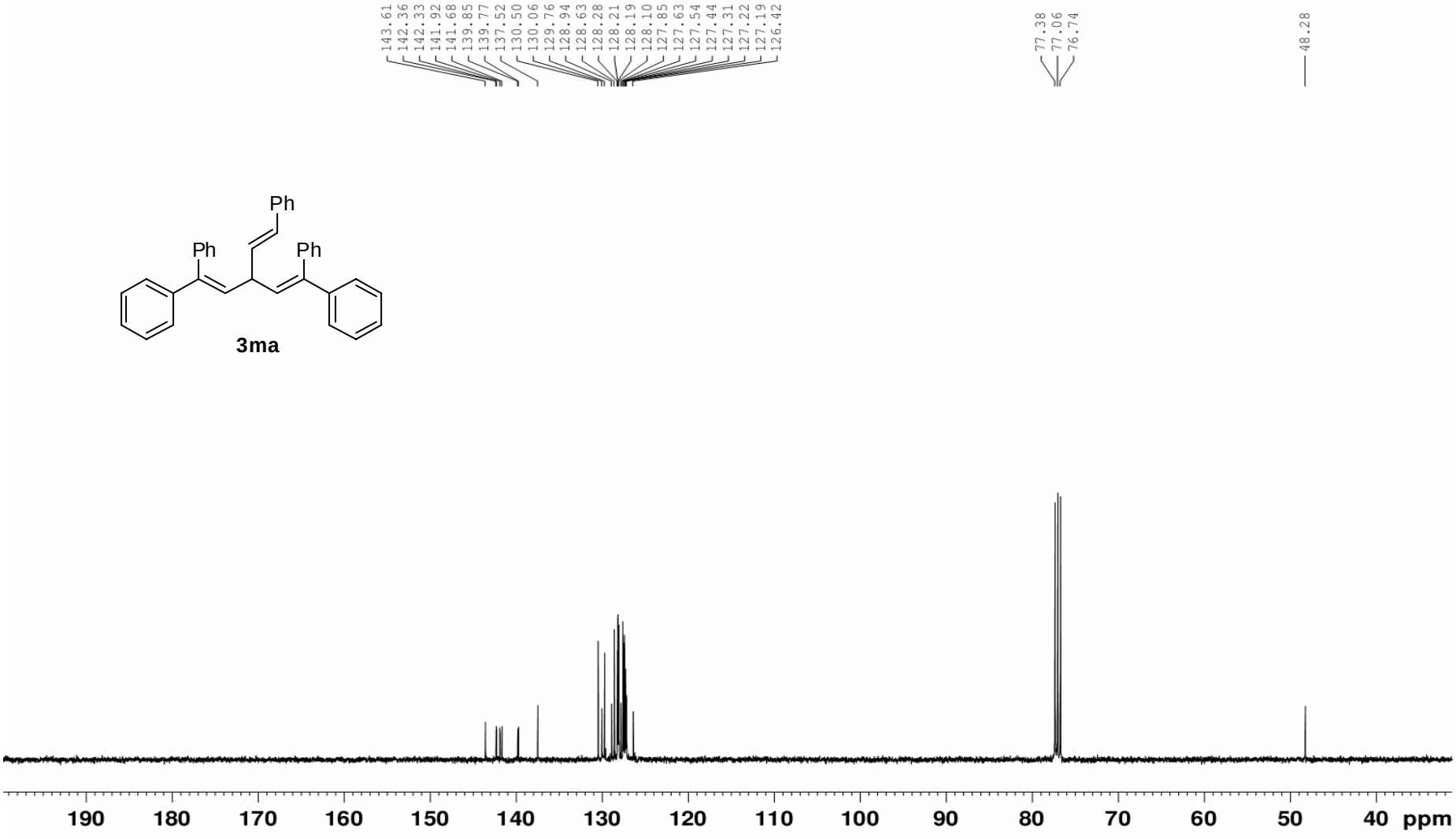


3Ia

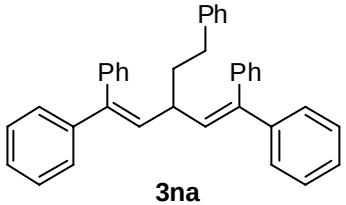



QB-130619-3-HNMR (in $CDCl_3$)
7.3772
7.3742
7.3582
7.3217
7.3195
7.3049
7.2889
7.2713
7.2616
7.2394
7.2335
7.2217
7.2157
7.2129
7.1909
7.1700
7.1652
7.1611
7.1552
7.1522
7.1484
7.1423
6.7391
6.7120
6.2827
6.2555
6.2449
6.2175
6.1691
6.1437
6.1118
6.0857
6.0690
6.0487
6.0310
4.2106
4.1873
4.1676
0.0024
Ph
Ph
Ph
3ma
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
10.29
14.94
1.02
3.23
1.00

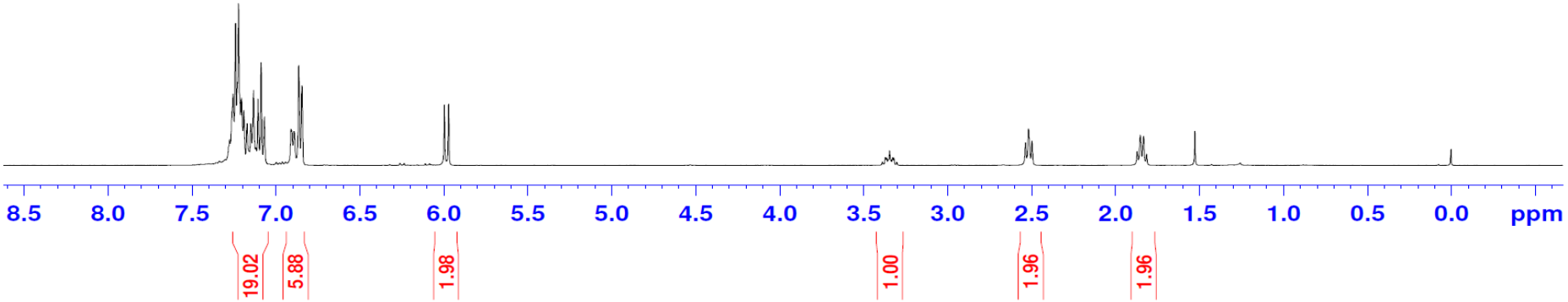
QB-130619-3-CNMR (in $CDCl_3$)



QB-130403-4-HNMR (in $CDCl_3$)

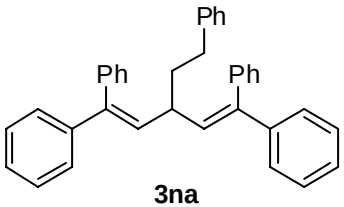


3na

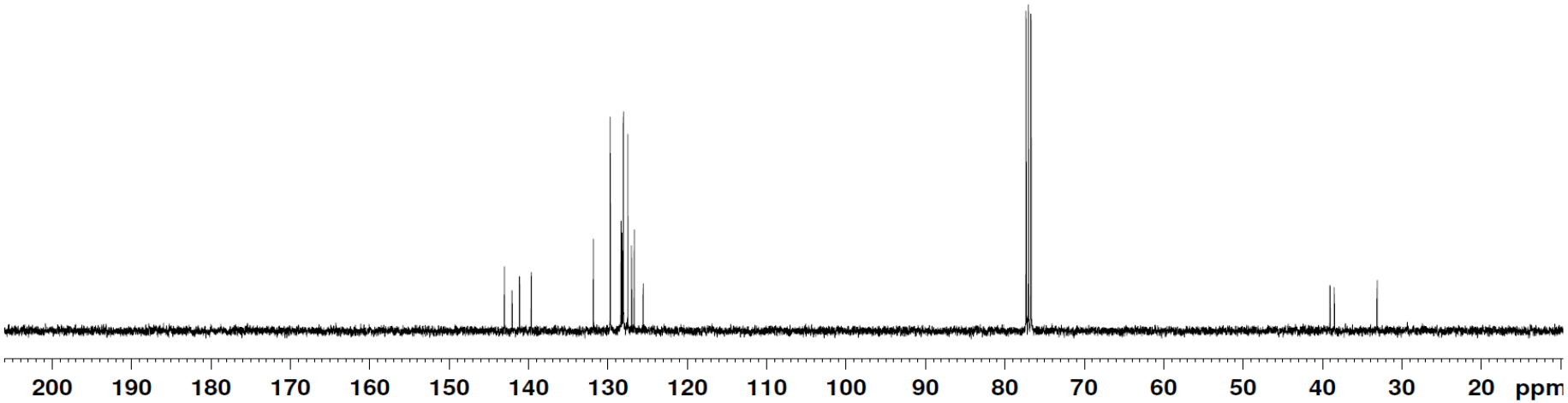


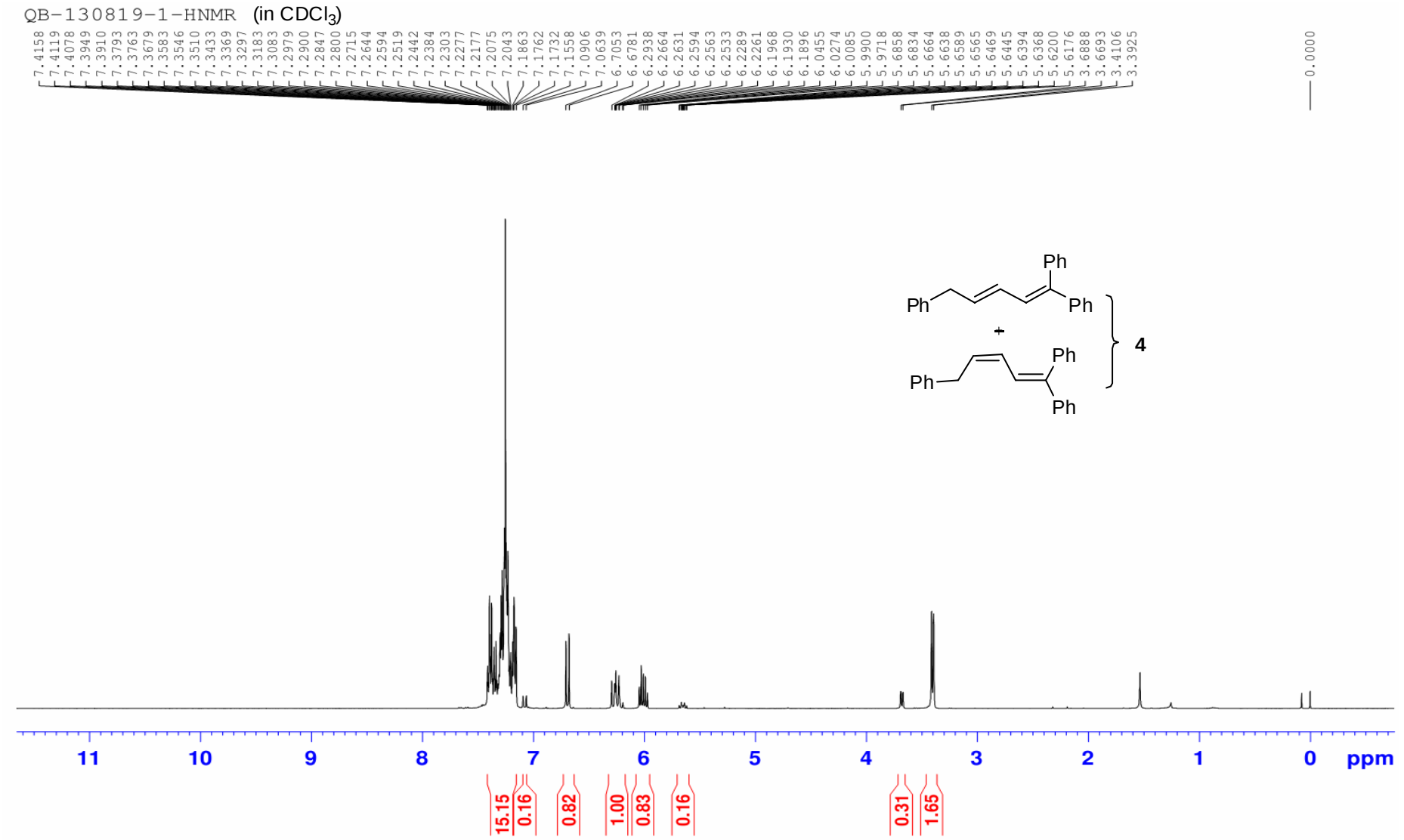
QB-130428-7-CNMR (in $CDCl_3$)

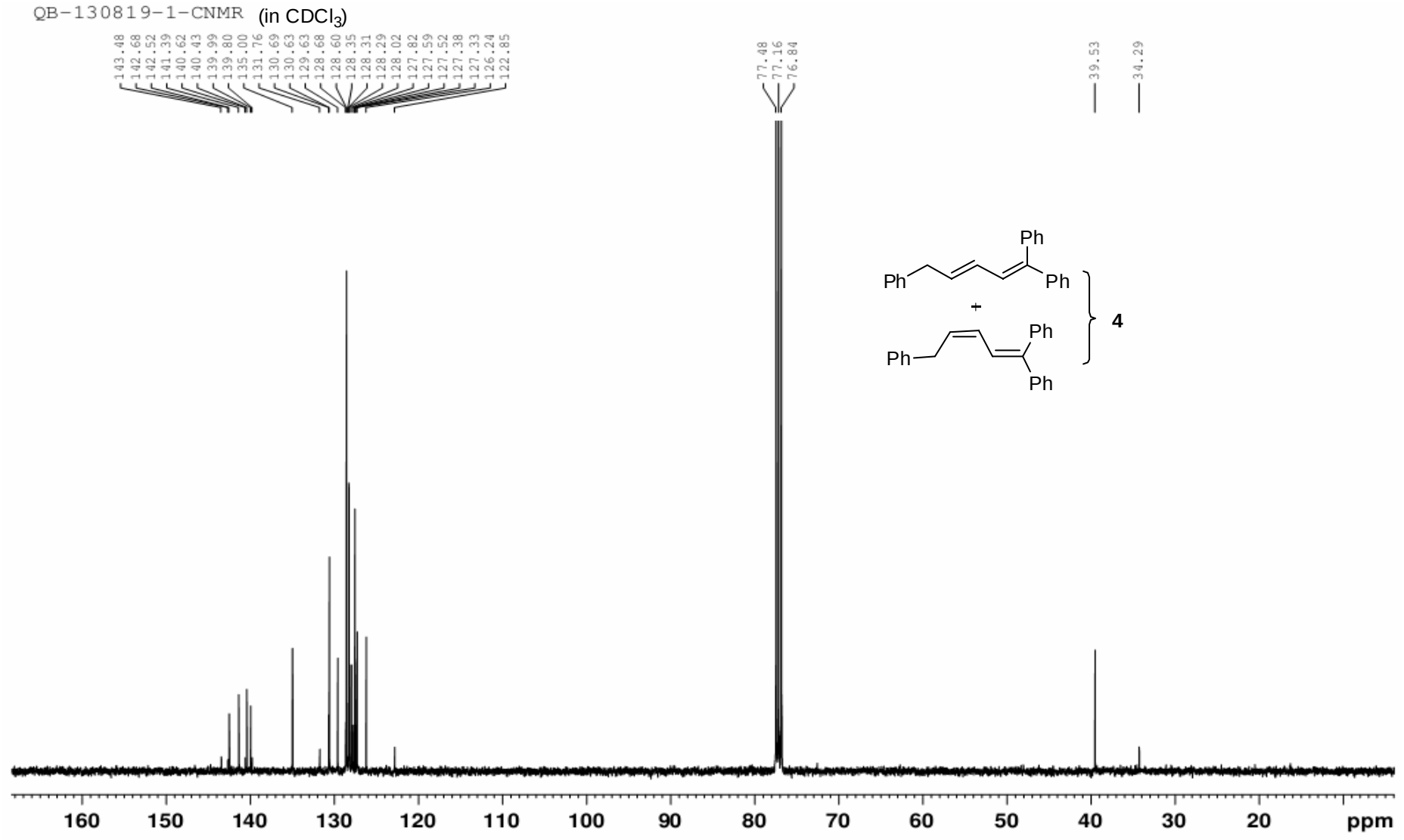
143.06
142.09
141.16
139.68
131.85
129.74
128.37
128.24
128.10
128.05
127.52
127.05
126.72
125.59
77.36
77.05
76.73
39.07
38.54
33.13



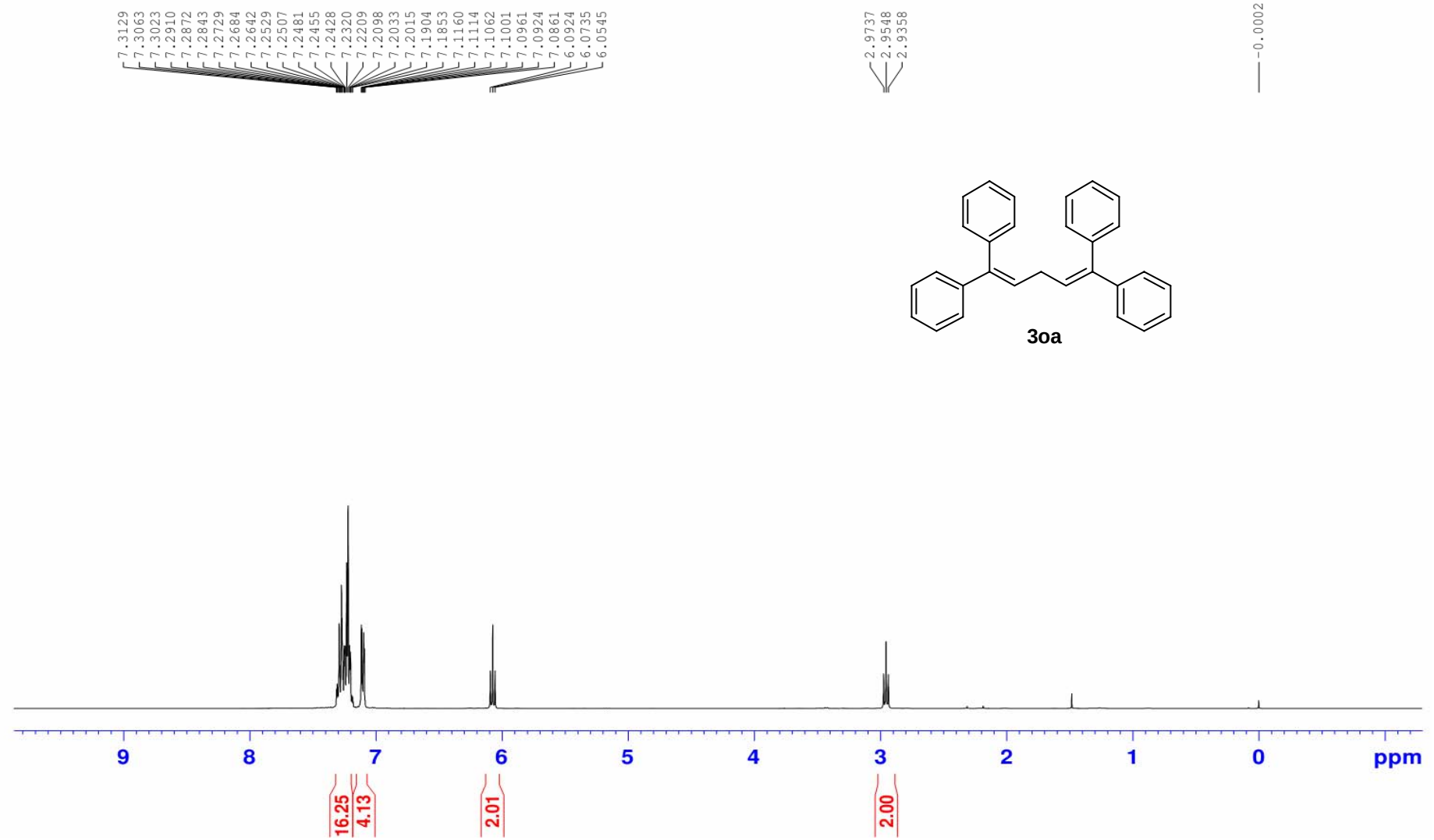
3na




QB-130819-1-HNMR (in CDCl3)
7.4158 7.4119 7.4078 7.3949 7.3910 7.3793 7.3763 7.3679 7.3583 7.3546 7.3510 7.3433 7.3369 7.3297 7.3183 7.3083 7.2979 7.2900 7.2847 7.2800 7.2715 7.2644 7.2594 7.2519 7.2442 7.2384 7.2303 7.2277 7.2177 7.2075 7.2043 7.1863 7.1762 7.1732 7.1558 7.0906 7.0639 6.7053 6.6781 6.2938 6.2664 6.2631 6.2594 6.2563 6.2533 6.2289 6.2261 6.1968 6.1930 6.1896 6.0455 6.0274 6.0085 5.9900 5.9718 5.6858 5.6834 5.6664 5.6638 5.6589 5.6565 5.6469 5.6445 5.6394 5.6368 5.6200 5.6176 3.6888 3.6693 3.4106 3.3925
0.0000
Ph
Ph
Ph
+
Ph
Ph
Ph
4
11 10 9 8 7 6 5 4 3 2 1 0 ppm
15.15 0.16 0.82 1.00 0.83 0.16 0.31 1.65

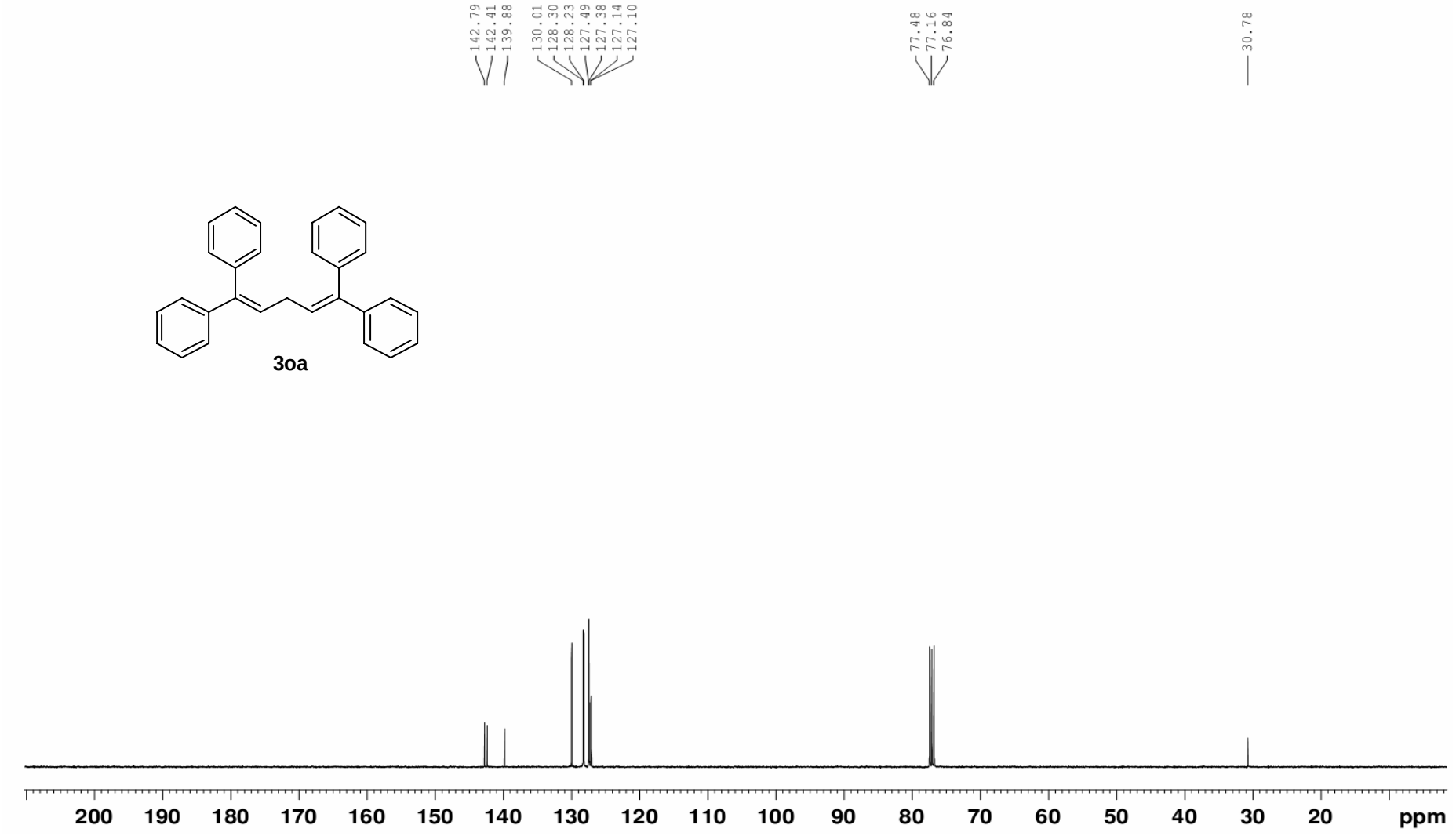

QB-130819-1-CNMR (in CDCl3)
143.48
142.68
142.52
141.39
140.62
140.43
139.99
139.80
135.00
131.76
130.69
130.63
129.63
128.68
128.60
128.35
128.31
128.29
128.02
127.82
127.59
127.52
127.38
127.33
126.24
122.85
77.48
77.16
76.84
39.53
34.29
Ph
Ph
Ph
+
Ph
Ph
Ph
4
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

121217-QianB-1-HNMR (in $CDCl_3$)

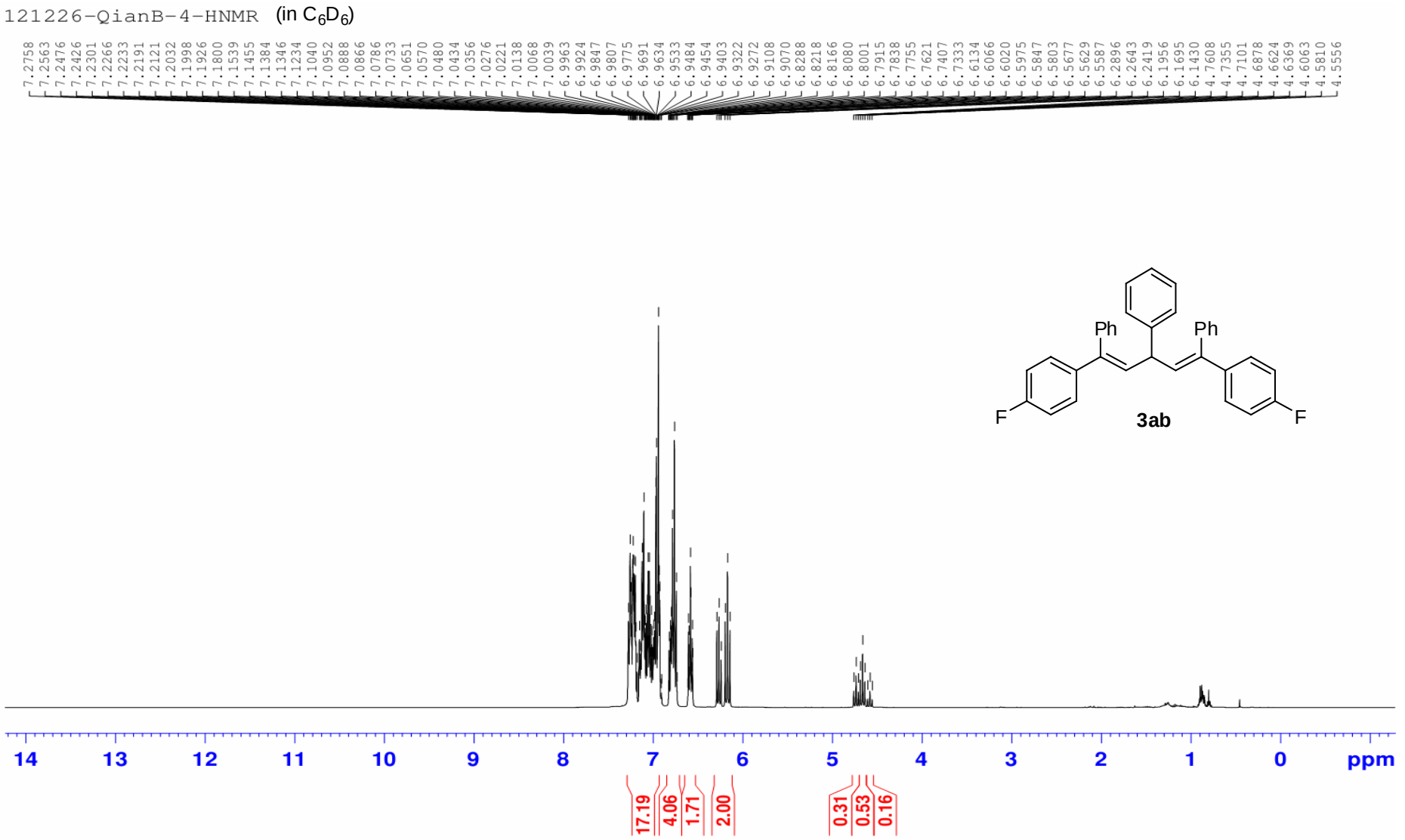


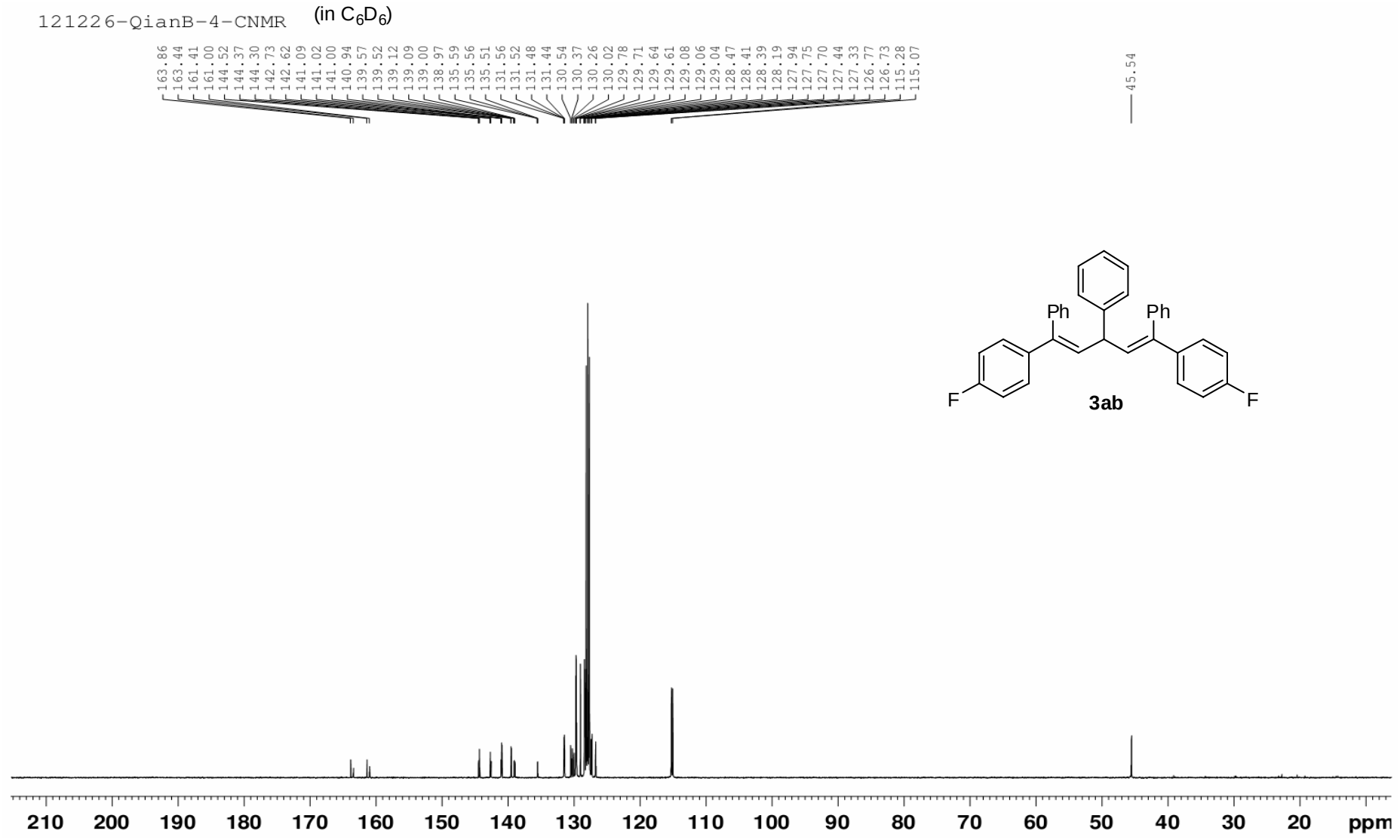
3oa

121217-QianB-1-CNMR (in $CDCl_3$)

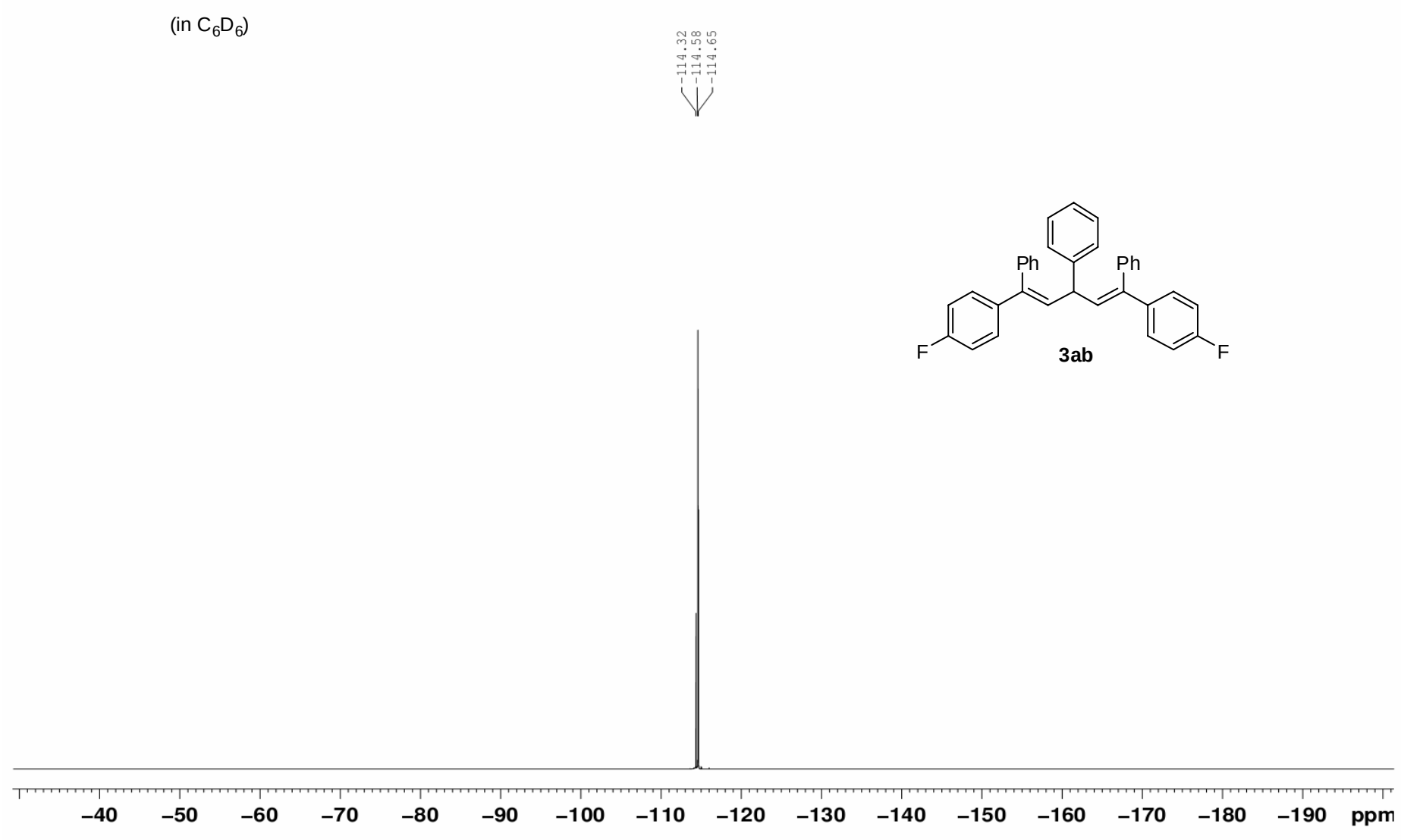


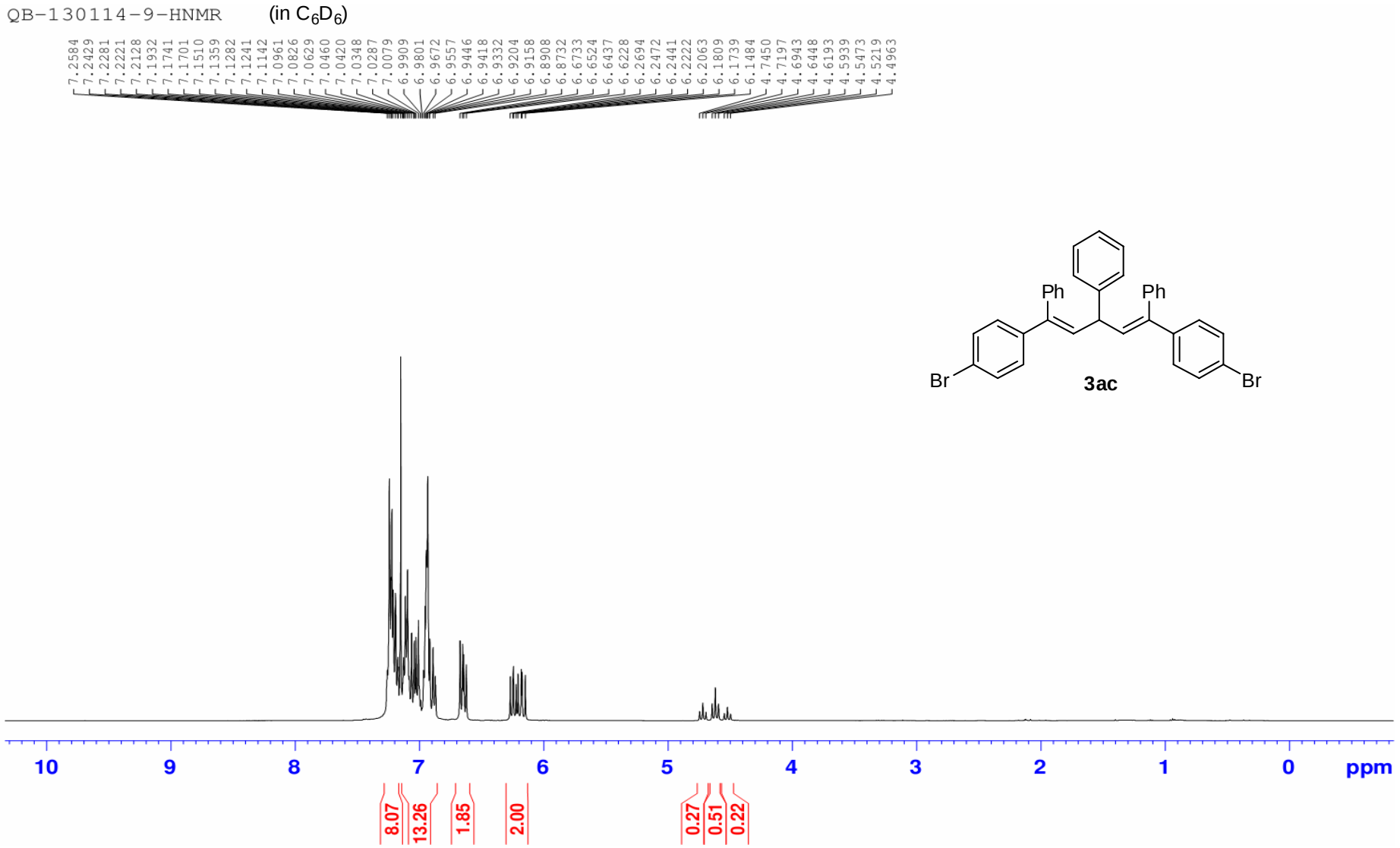
3oa

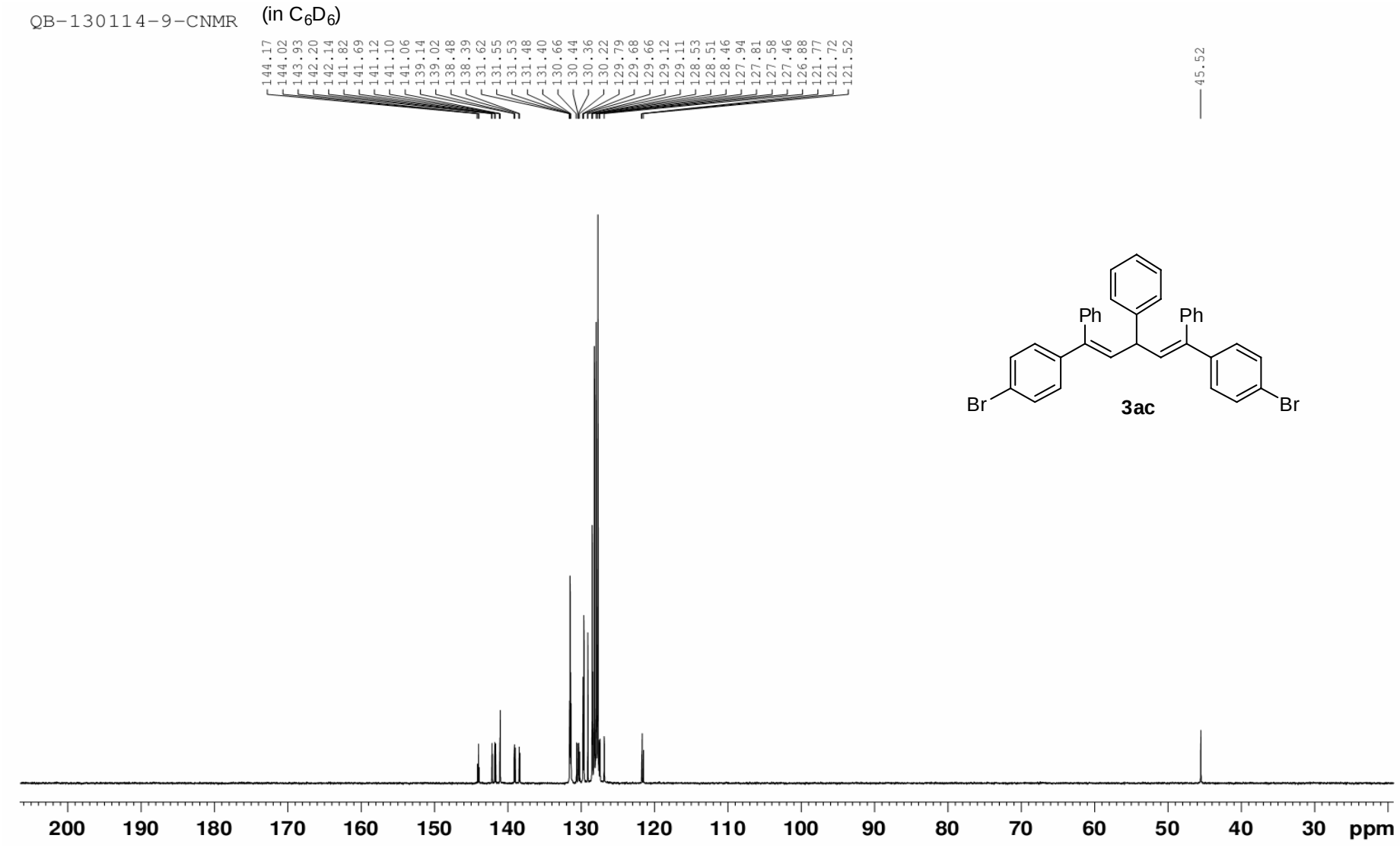

121226-QianB-4-HNMR (in C_6D_6)
7.2758 7.2563 7.2476 7.2426 7.2301 7.2266 7.2233 7.2191 7.2121 7.2032 7.1998 7.1926 7.1800 7.1539 7.1455 7.1384 7.1346 7.1234 7.1040 7.0952 7.0888 7.0866 7.0786 7.0733 7.0651 7.0570 7.0480 7.0434 7.0356 7.0276 7.0221 7.0138 7.0068 7.0039 6.9963 6.9924 6.9847 6.9807 6.9775 6.9691 6.9634 6.9533 6.9484 6.9454 6.9403 6.9322 6.9272 6.9108 6.9070 6.8288 6.8218 6.8166 6.8080 6.8001 6.7915 6.7838 6.7755 6.7621 6.7407 6.7333 6.6134 6.6066 6.6020 6.5975 6.5847 6.5803 6.5677 6.5629 6.5587 6.2896 6.2643 6.2419 6.1956 6.1695 6.1430 4.7608 4.7355 4.7101 4.6878 4.6624 4.6369 4.6063 4.5810 4.5556
Ph
Ph
F
F
3ab
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
17.19
4.06
1.71
2.00
0.31
0.53
0.16

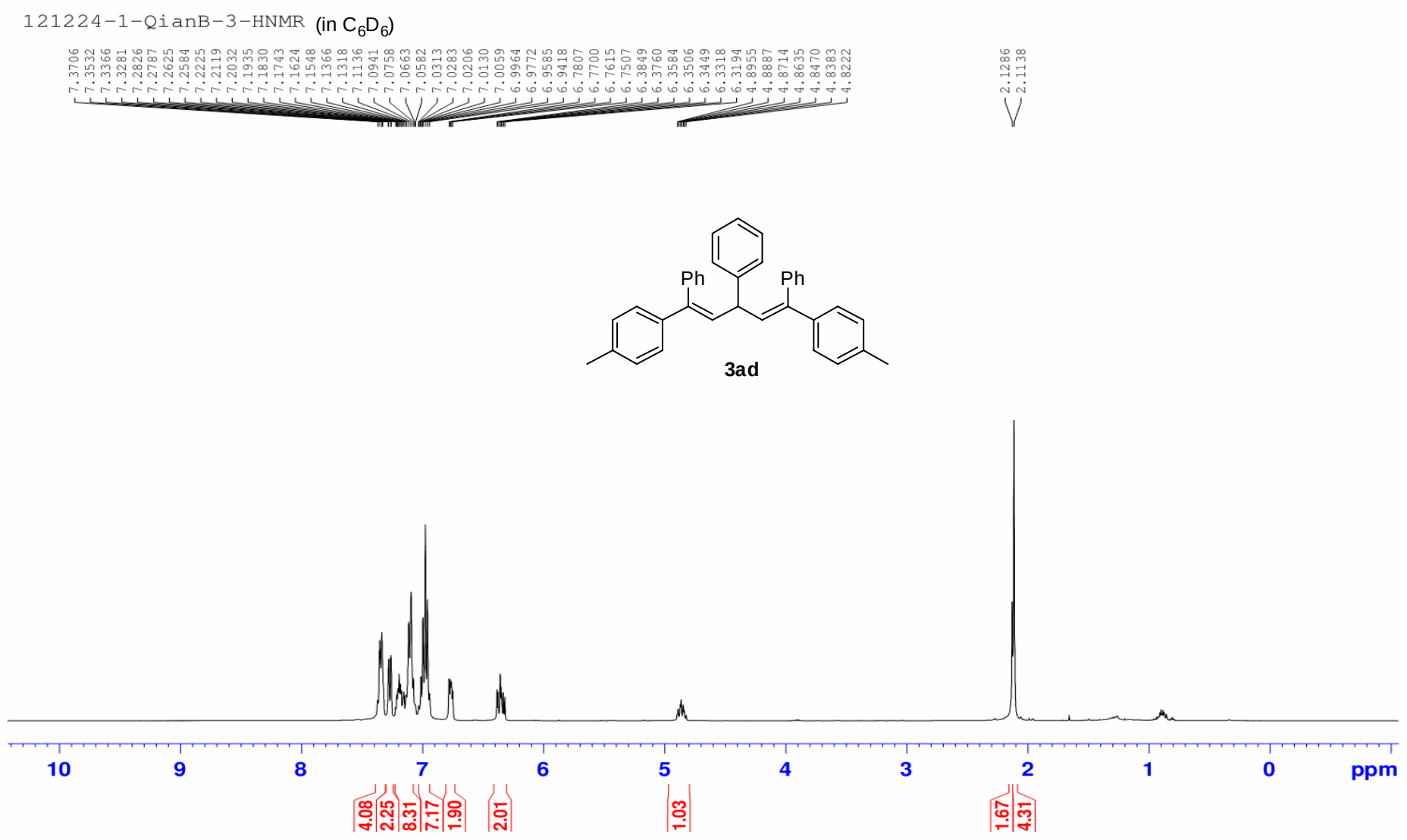

121226-QianB-4-CNMR
(in C_6D_6)
163.86
163.44
161.41
161.00
144.52
144.37
144.30
142.73
142.62
141.09
141.02
141.00
140.94
139.57
139.52
139.12
139.09
139.00
138.97
135.59
135.56
135.51
131.56
131.52
131.48
131.44
130.54
130.37
130.26
130.02
129.78
129.71
129.64
129.61
129.08
129.06
129.04
128.47
128.41
128.39
128.19
127.94
127.75
127.70
127.44
127.33
126.77
126.73
115.28
115.07
45.54
Ph
Ph
F
F
3ab
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

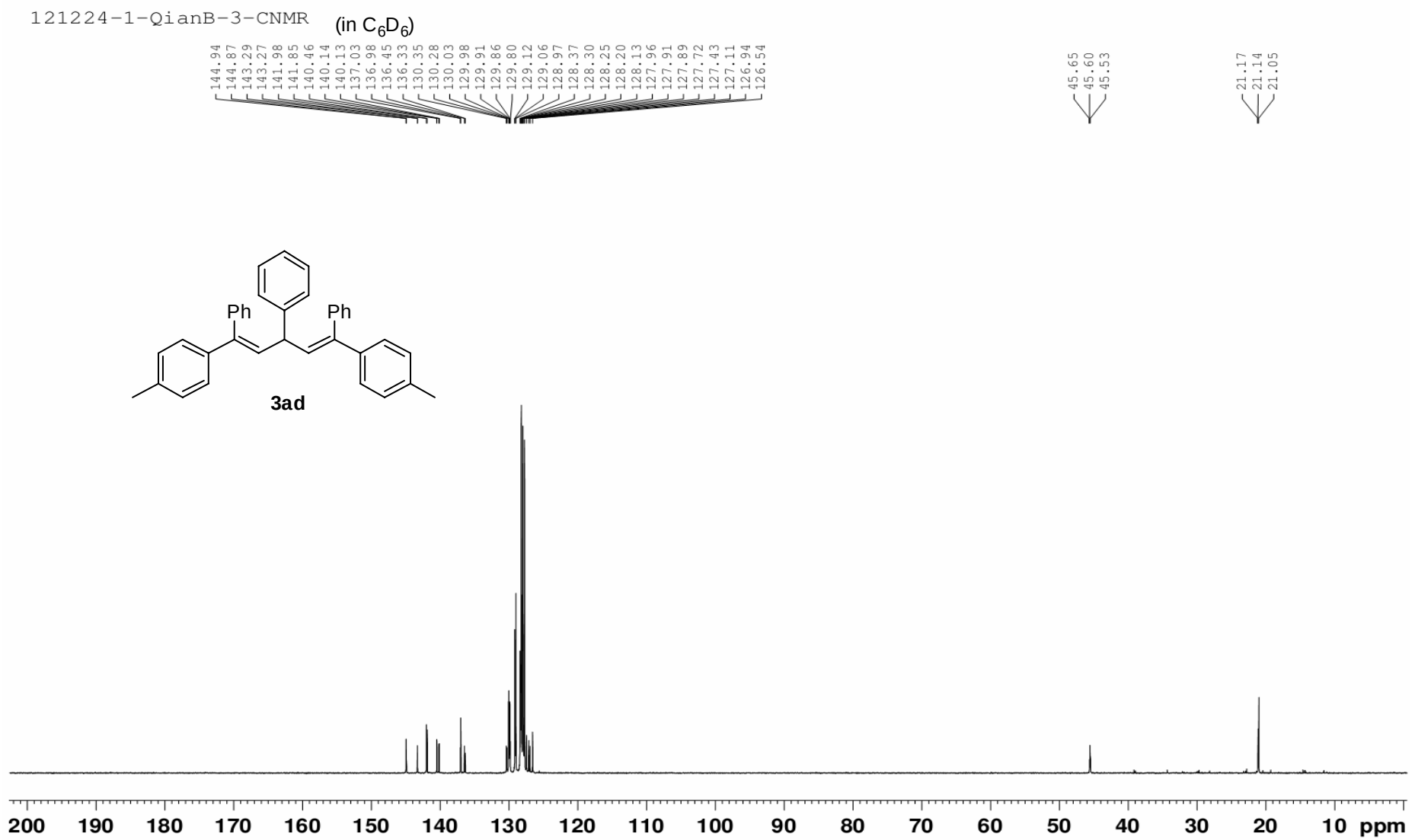
(in C_6D_6)

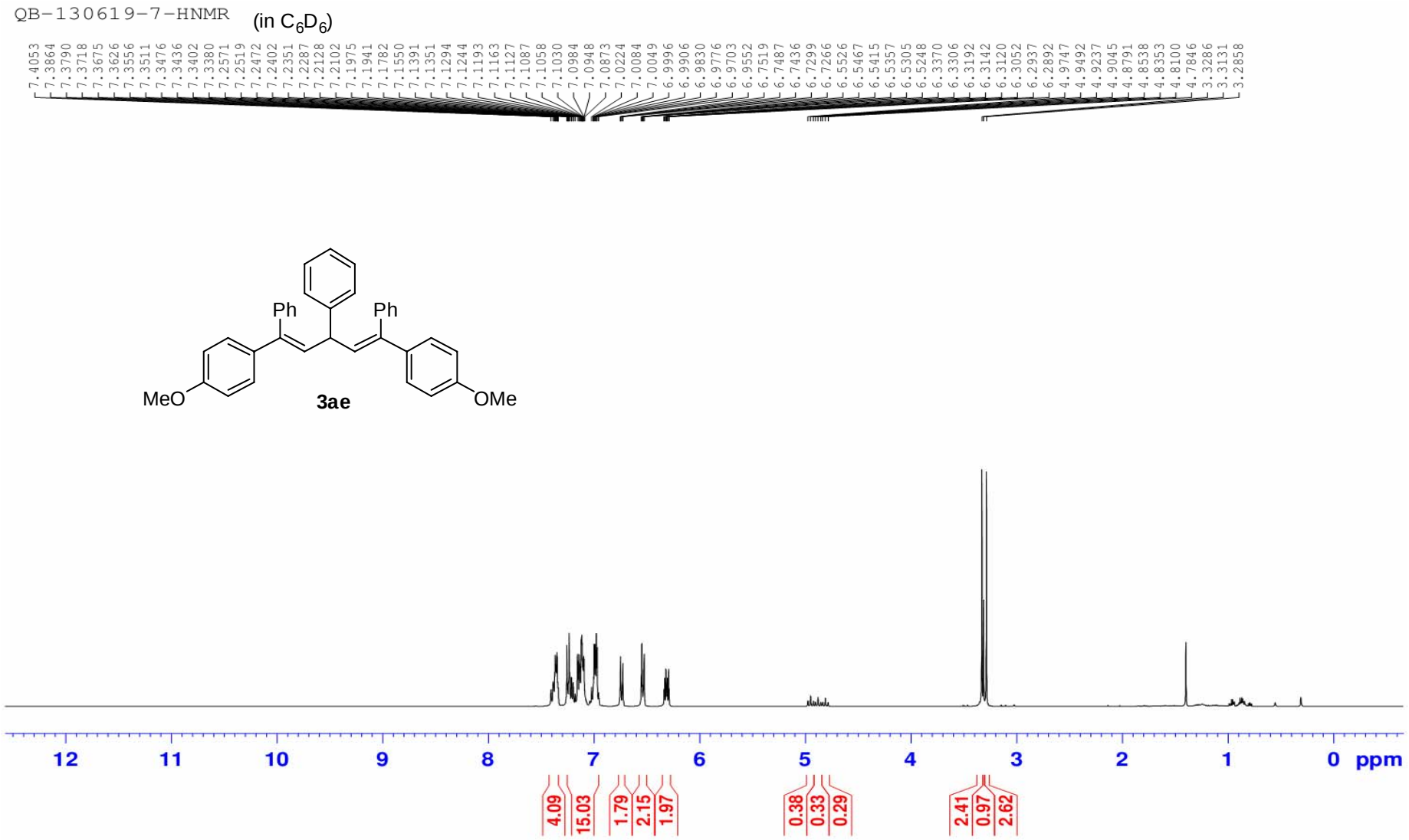


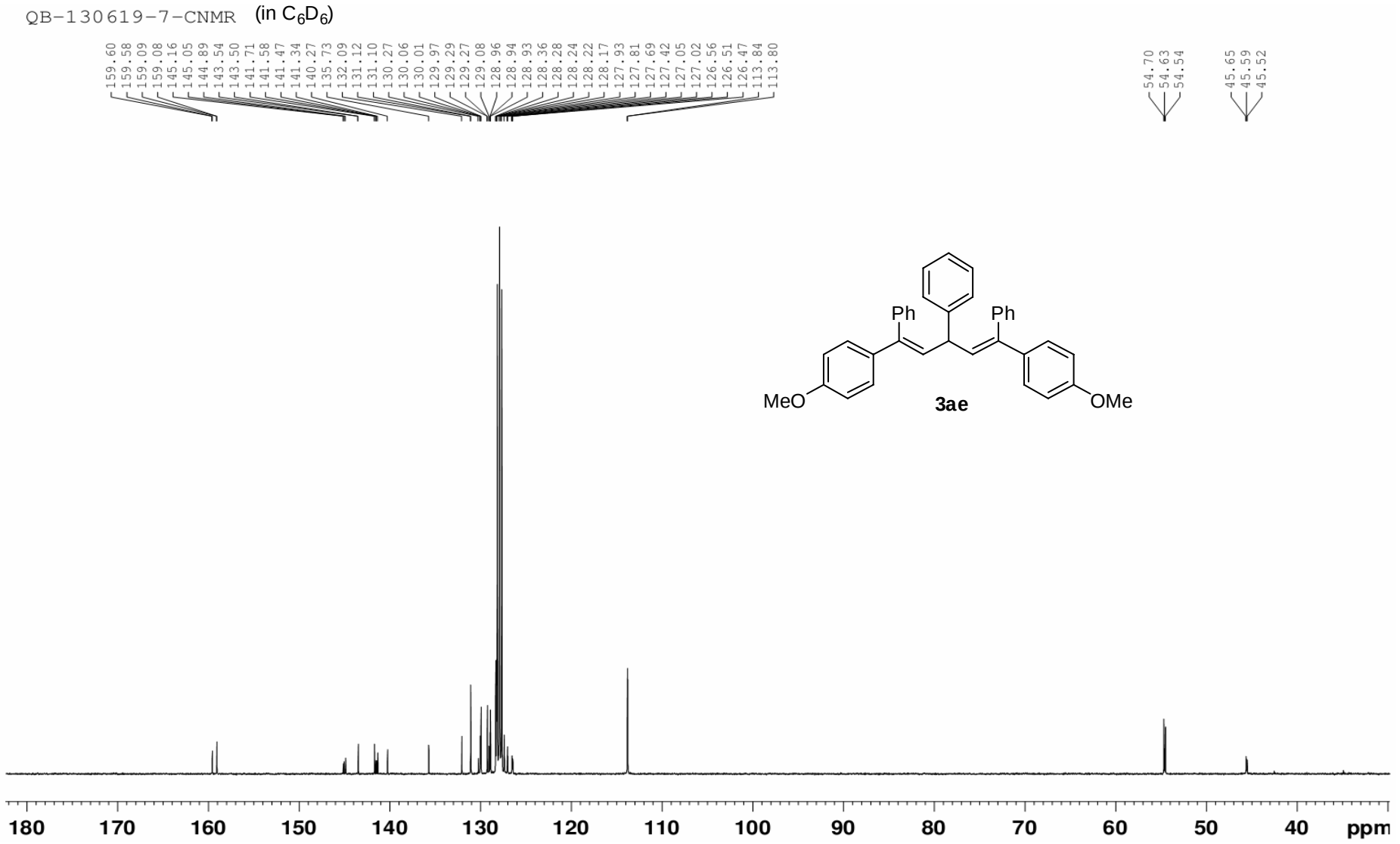

QB-130114-9-HNMR
(in C_6D_6)
7.2584
7.2429
7.2281
7.2221
7.2128
7.1932
7.1741
7.1701
7.1510
7.1359
7.1282
7.1241
7.1142
7.0961
7.0826
7.0629
7.0460
7.0420
7.0348
7.0287
7.0079
6.9909
6.9801
6.9672
6.9557
6.9446
6.9418
6.9332
6.9204
6.9158
6.8908
6.8732
6.6733
6.6524
6.6437
6.6228
6.2694
6.2472
6.2441
6.2222
6.2063
6.1809
6.1739
6.1484
4.7450
4.7197
4.6943
4.6448
4.6193
4.5939
4.5473
4.5219
4.4963
Ph
Ph
Br
Br
3ac
10
9
8
7
6
5
4
3
2
1
0
ppm
8.07
13.26
1.85
2.00
0.27
0.51
0.22

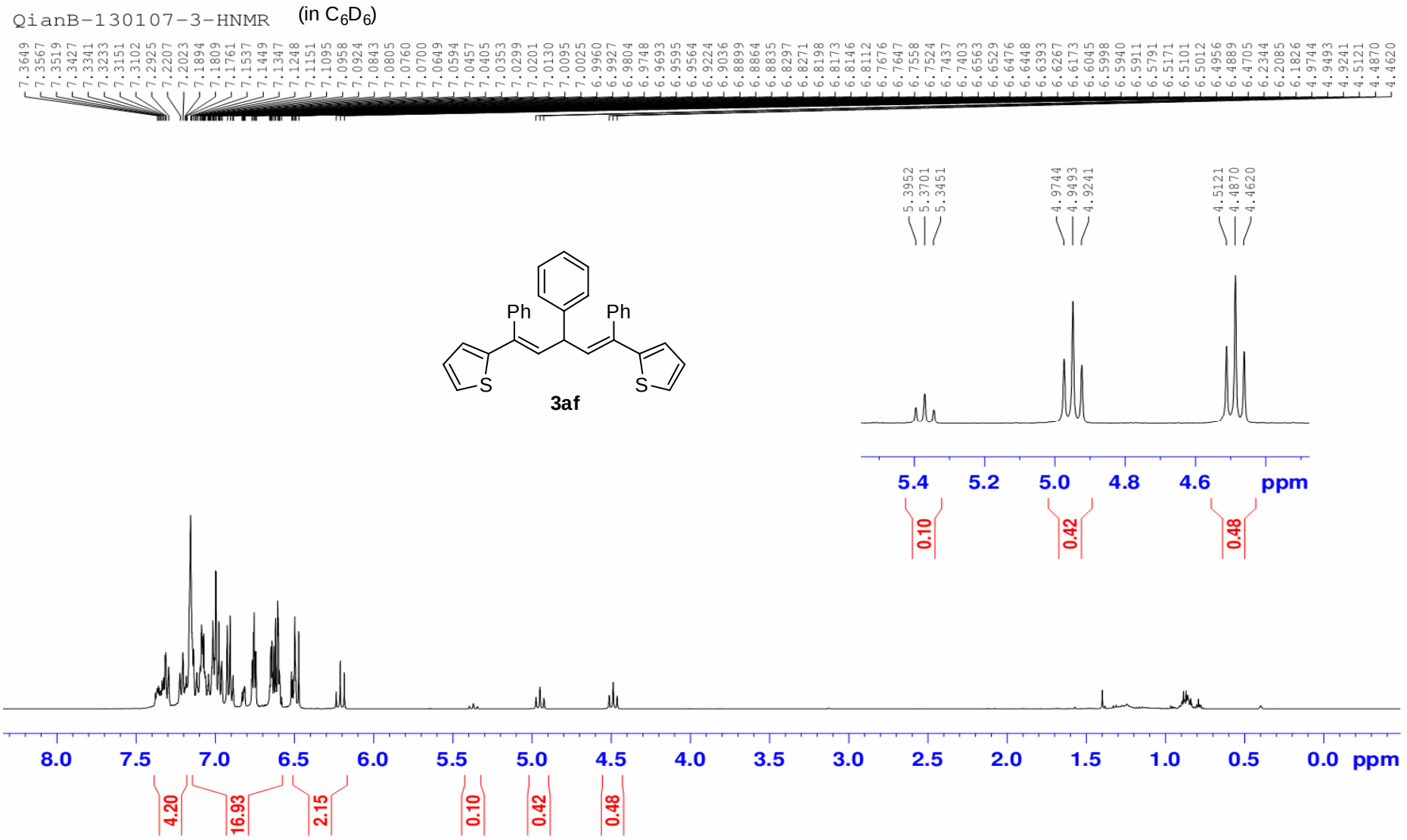

QB-130114-9-CNMR
(in C_6D_6)
144.17
144.02
143.93
142.20
142.14
141.82
141.69
141.12
141.10
141.06
139.14
139.02
138.48
138.39
131.62
131.55
131.53
131.48
131.40
130.66
130.44
130.36
130.22
129.79
129.68
129.66
129.12
129.11
128.53
128.51
128.46
127.94
127.81
127.58
127.46
126.88
121.77
121.72
121.52
45.52
Ph
Ph
Br
Br
3ac
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

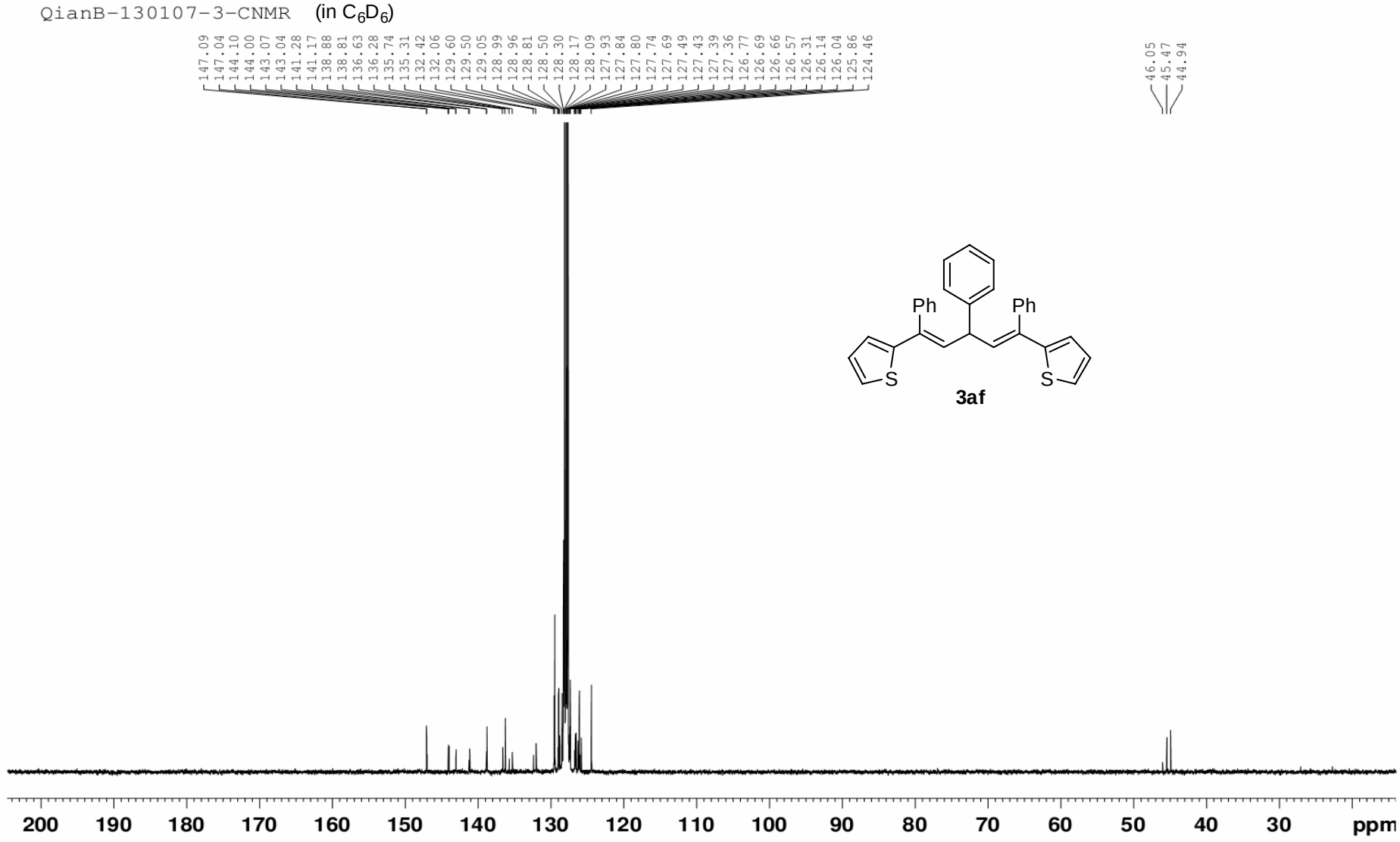

121224-1-QianB-3-HNMR (in C_6D_6)
7.3706
7.3532
7.3366
7.3281
7.2826
7.2787
7.2625
7.2584
7.2225
7.2119
7.2032
7.1935
7.1830
7.1743
7.1624
7.1548
7.1366
7.1318
7.1136
7.0941
7.0758
7.0663
7.0582
7.0313
7.0283
7.0206
7.0130
7.0059
6.9964
6.9772
6.9585
6.9418
6.7807
6.7700
6.7615
6.7507
6.3849
6.3760
6.3584
6.3506
6.3449
6.3318
6.3194
4.8955
4.8887
4.8714
4.8635
4.8470
4.8383
4.8222
2.1286
2.1138
Ph
Ph
3ad
10
9
8
7
6
5
4
3
2
1
0
ppm
4.08
2.25
8.31
7.17
1.90
2.01
1.03
1.67
4.31

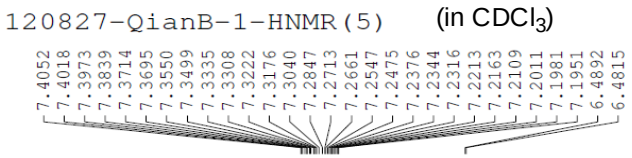

121224-1-QianB-3-CNMR
(in C_6D_6)
144.94
144.87
143.29
143.27
141.98
141.85
140.46
140.14
140.13
137.03
136.98
136.45
136.33
130.35
130.28
130.03
129.98
129.91
129.86
129.80
129.12
129.06
128.97
128.37
128.30
128.25
128.20
128.13
127.96
127.91
127.89
127.72
127.43
127.11
126.94
126.54
45.65
45.60
45.53
21.17
21.14
21.05
Ph
Ph
3ad
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

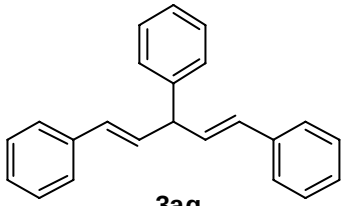

QB-130619-7-HNMR
(in C_6D_6)
7.4053
7.3864
7.3790
7.3718
7.3675
7.3626
7.3556
7.3511
7.3476
7.3436
7.3402
7.3380
7.2571
7.2519
7.2472
7.2402
7.2351
7.2287
7.2128
7.2102
7.1975
7.1941
7.1782
7.1550
7.1391
7.1351
7.1294
7.1244
7.1193
7.1163
7.1127
7.1087
7.1058
7.1030
7.0984
7.0948
7.0873
7.0224
7.0084
7.0049
6.9996
6.9906
6.9830
6.9776
6.9703
6.9552
6.7519
6.7487
6.7436
6.7299
6.7266
6.5526
6.5467
6.5415
6.5357
6.5305
6.5248
6.3370
6.3306
6.3192
6.3142
6.3120
6.3052
6.2937
6.2892
4.9747
4.9492
4.9237
4.9045
4.8791
4.8538
4.8353
4.8100
4.7846
3.3286
3.3131
3.2858
Ph
Ph
MeO
OMe
3ae
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.09
15.03
1.79
2.15
1.97
0.38
0.33
0.29
2.41
0.97
2.62


QB-130619-7-CNMR (in C_6D_6)
159.60
159.58
159.09
159.08
145.16
145.05
144.89
143.54
143.50
141.71
141.58
141.47
141.34
140.27
135.73
132.09
131.12
131.10
130.27
130.06
130.01
129.97
129.29
129.27
129.08
128.96
128.94
128.93
128.36
128.28
128.24
128.22
128.17
127.93
127.81
127.69
127.42
127.05
127.02
126.56
126.51
126.47
113.84
113.80
54.70
54.63
54.54
45.65
45.59
45.52
Ph
Ph
MeO
OMe
3ae
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

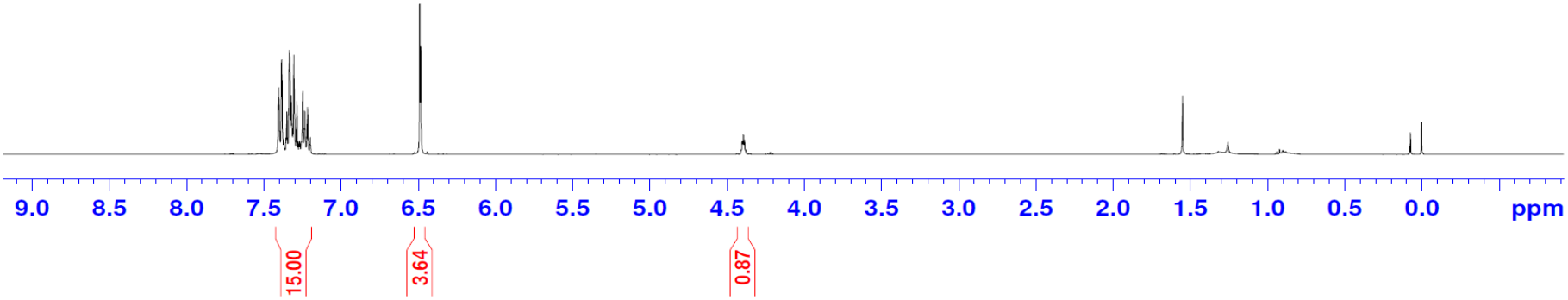

QianB-130107-3-HNMR
(in C_6D_6)
Ph
Ph
S
S
3af
ppm
ppm


QianB-130107-3-CNMR (in C_6D_6)
147.09
147.04
144.10
144.00
143.07
143.04
141.28
141.17
138.88
138.81
136.63
136.28
135.74
135.31
132.42
132.06
129.60
129.50
129.05
128.99
128.96
128.81
128.50
128.30
128.17
128.09
127.93
127.84
127.80
127.74
127.69
127.49
127.43
127.39
127.36
126.77
126.69
126.66
126.57
126.31
126.14
126.04
125.86
124.46
46.05
45.47
44.94
Ph
Ph
S
S
3af
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

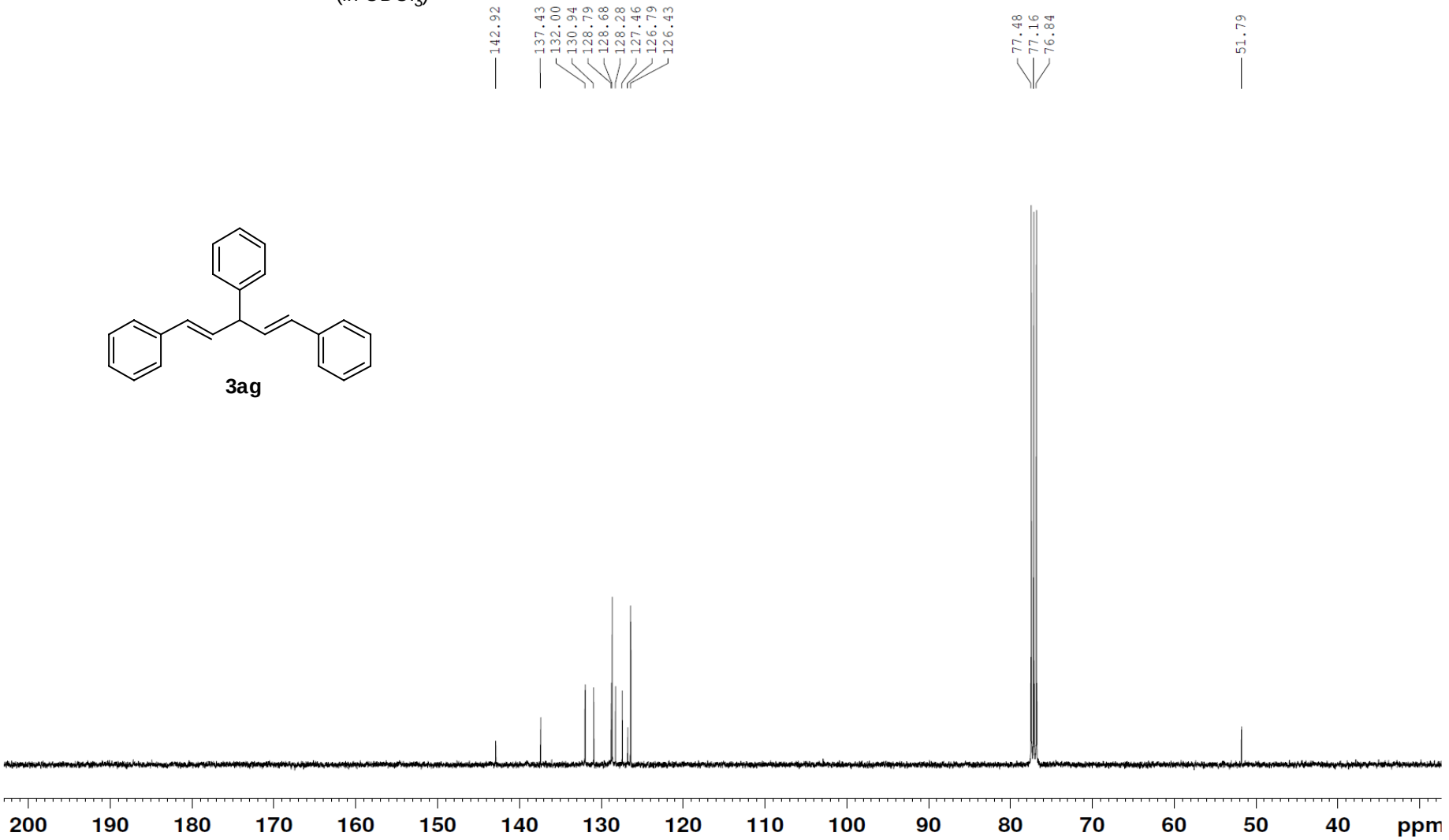

120827-QianB-1-HNMR(5)
(in $CDCl_3$)
7.4052
7.4018
7.3973
7.3839
7.3714
7.3695
7.3550
7.3499
7.3335
7.3308
7.3222
7.3176
7.3040
7.2847
7.2713
7.2661
7.2547
7.2475
7.2376
7.2344
7.2316
7.2213
7.2163
7.2109
7.2011
7.1981
7.1951
6.4892
6.4815
4.3996
4.3927
4.3857
0.0000



3ag

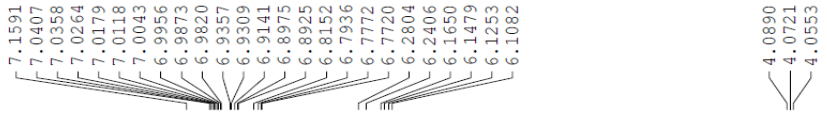

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
15.00
3.64
0.87

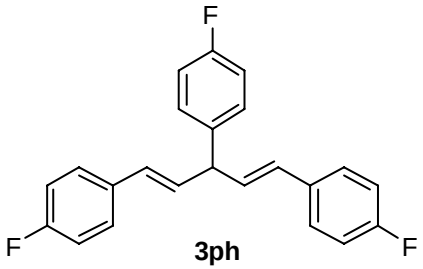
120827-QianB-1-CNMR(6) (in $CDCl_3$)



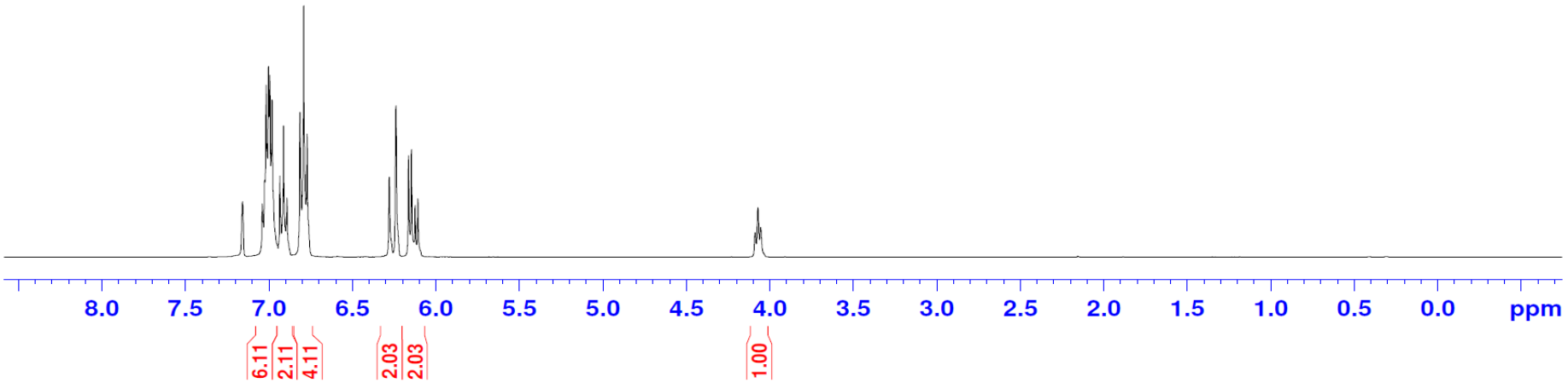
3ag

QB-130225-1-HNMR (in C_6D_6)

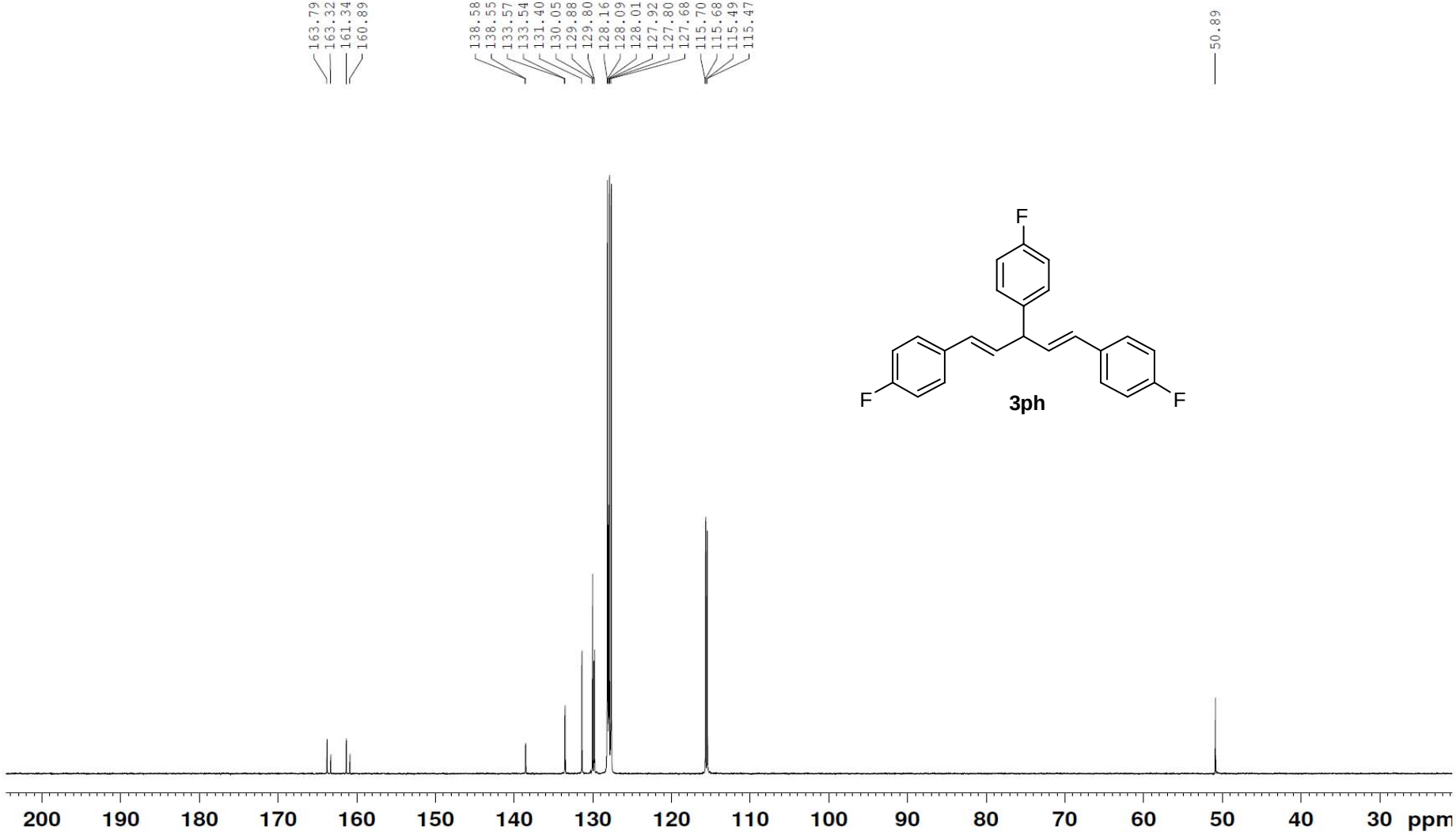




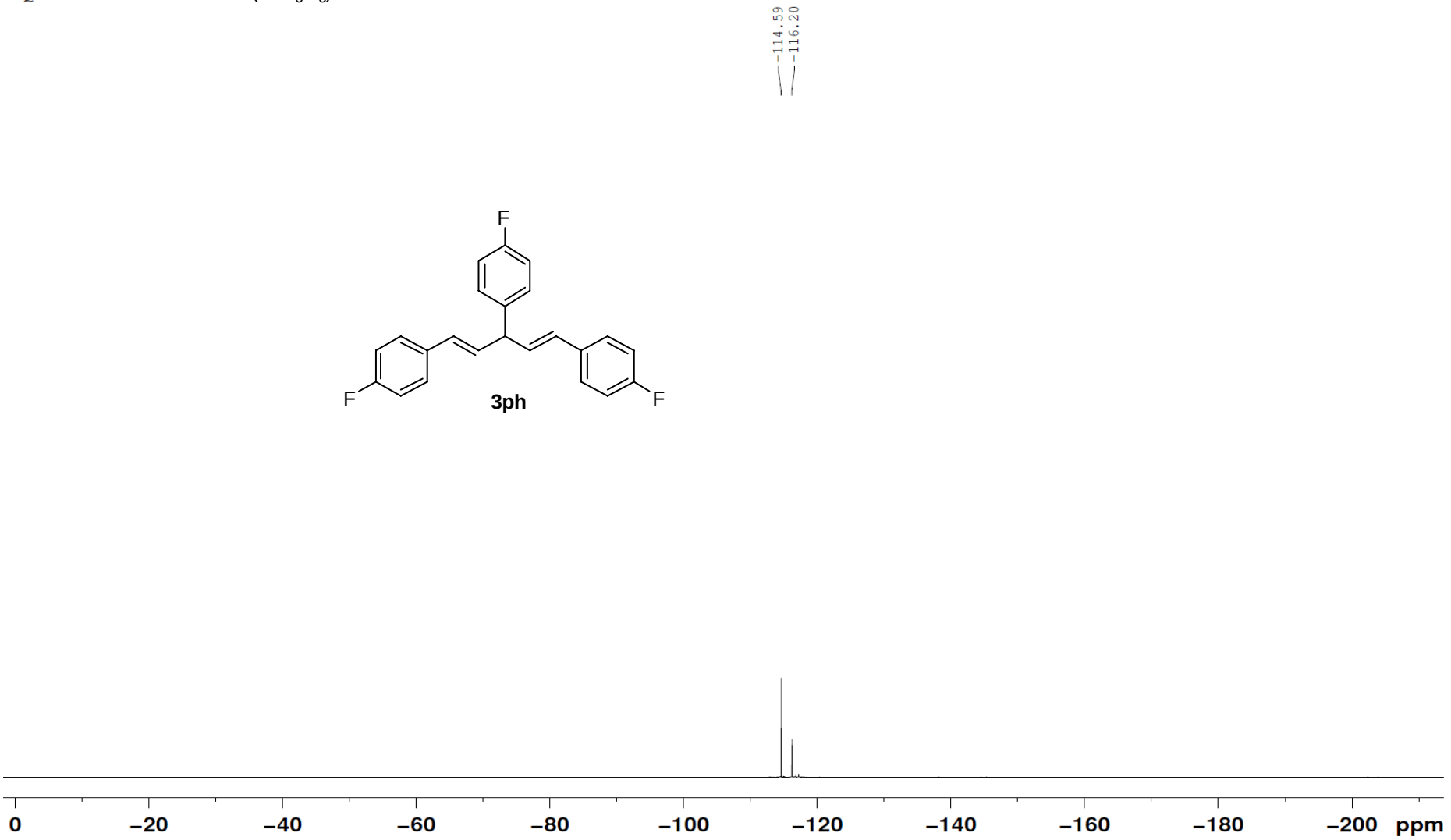
3ph

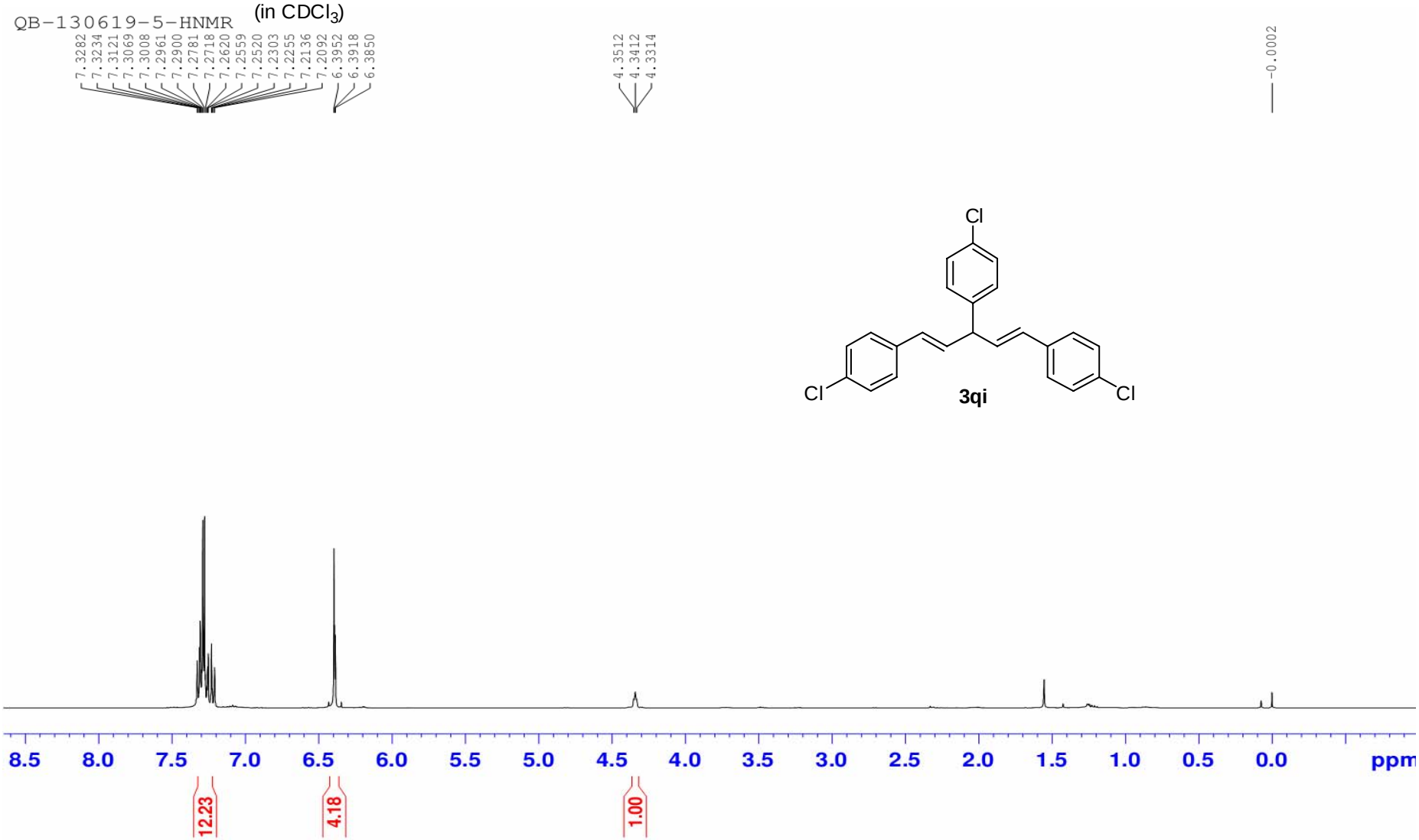


QB-130225-1-CNMR (in C_6D_6)

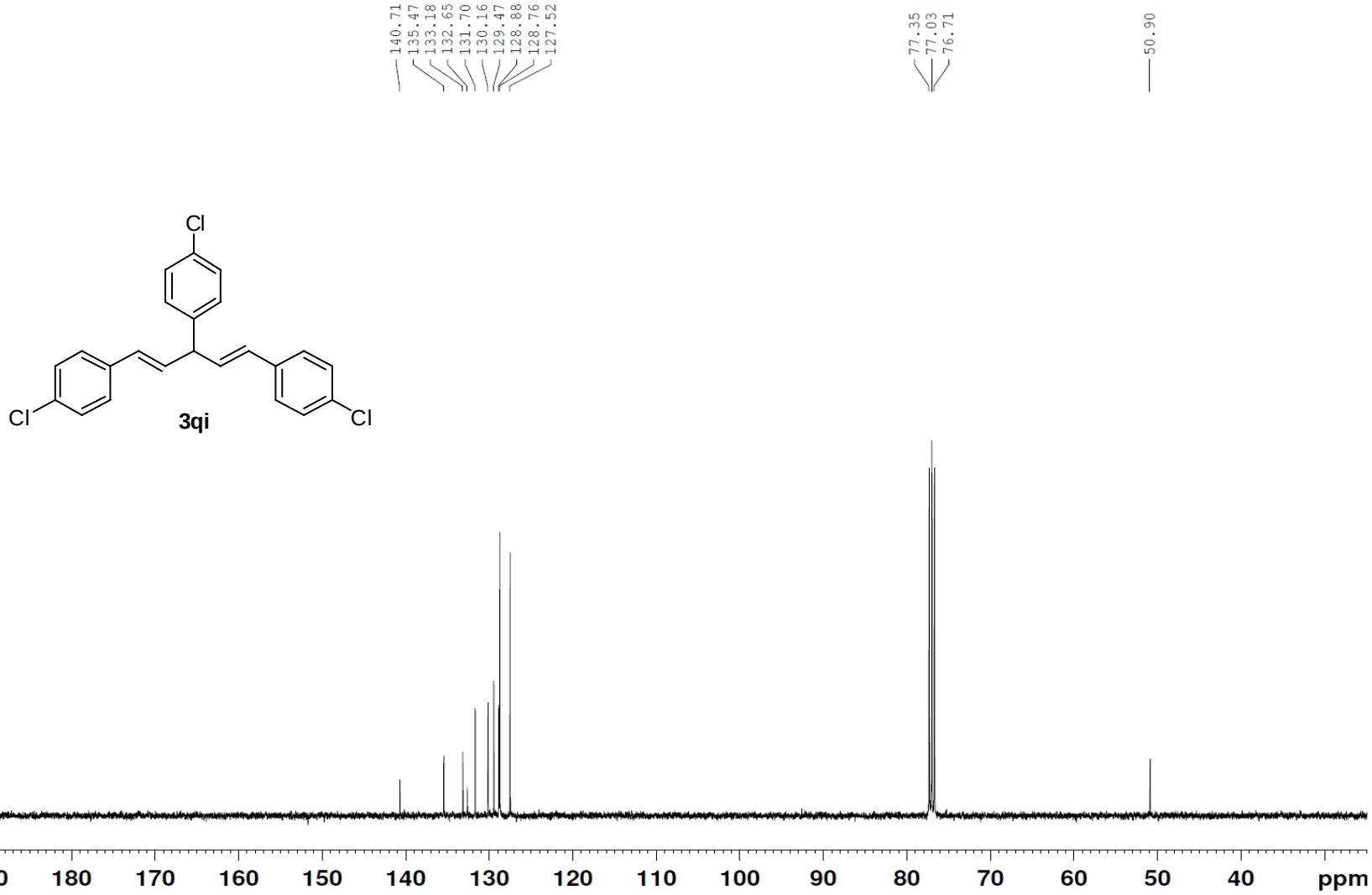


QB-130428-4-FNMR (in C_6D_6)

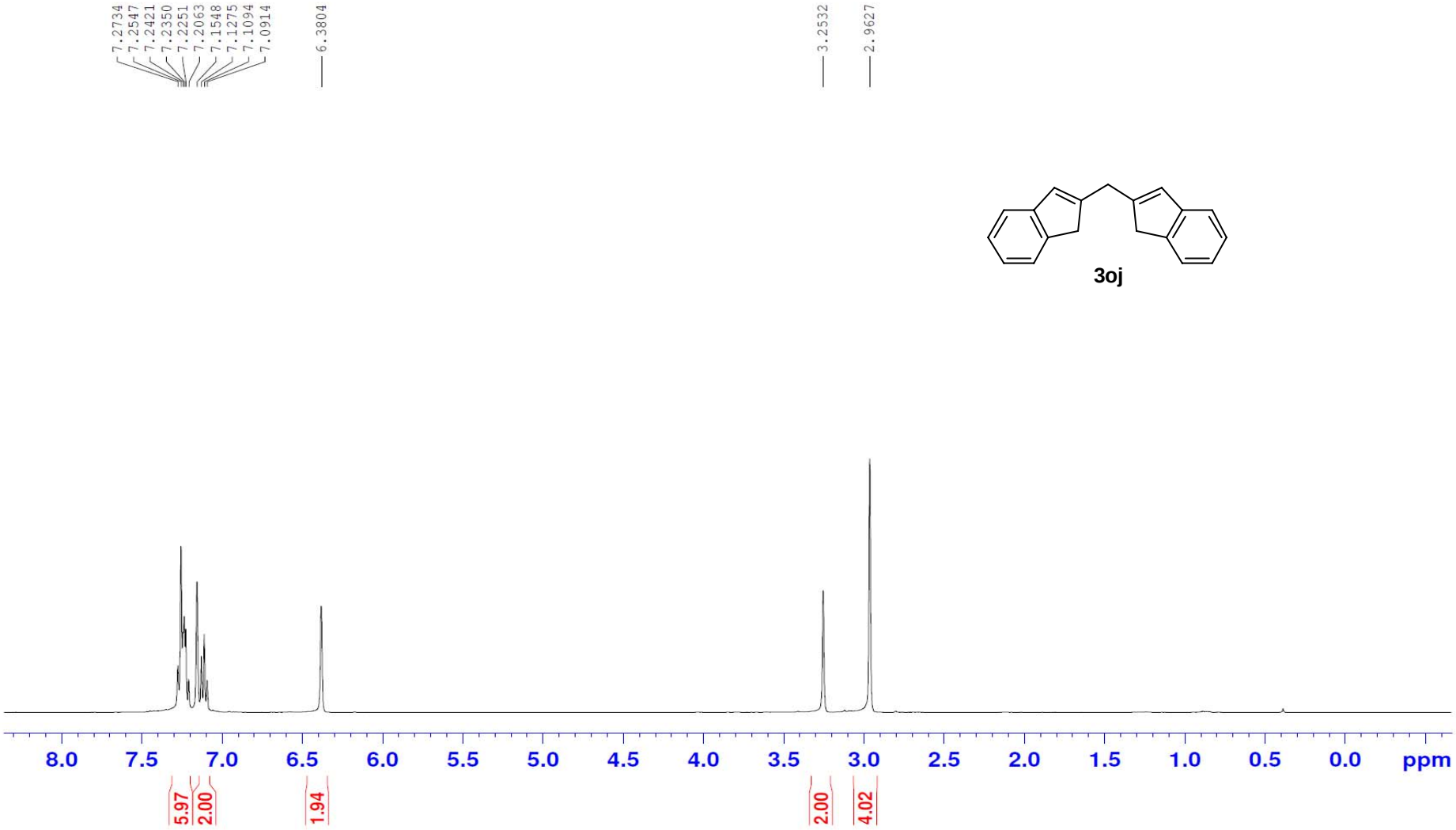



QB-130619-5-HNMR
(in $CDCl_3$)
7.3282
7.3234
7.3121
7.3069
7.3008
7.2961
7.2900
7.2781
7.2718
7.2620
7.2559
7.2520
7.2303
7.2255
7.2136
7.2092
6.3952
6.3918
6.3850
4.3512
4.3412
4.3314
0.0002
Cl
Cl
Cl
3qi
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
12.23
4.18
1.00

QB-130619-5-CNMR (in $CDCl_3$)

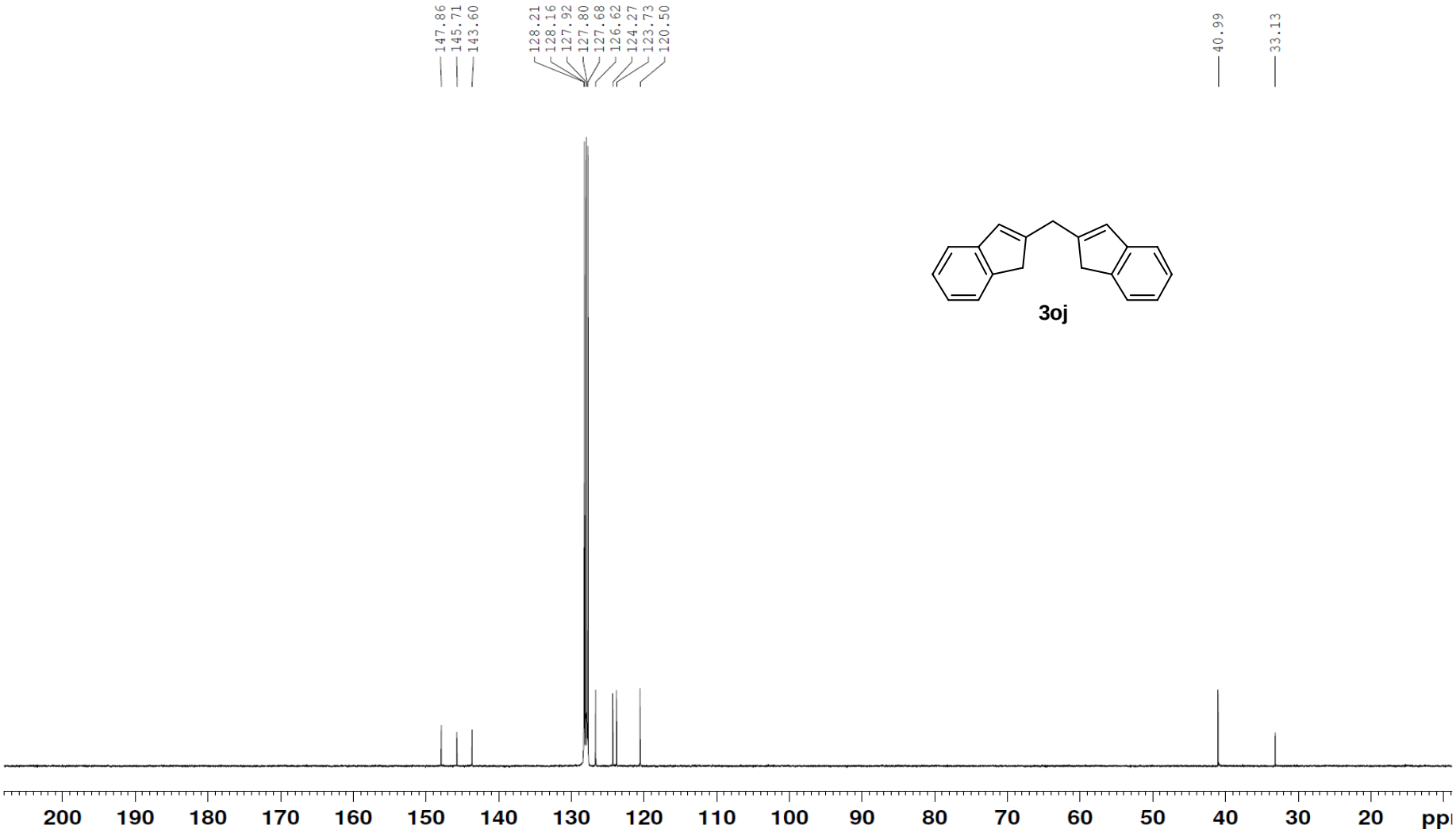


QianB-121229-6-HNMR (in C_6D_6)



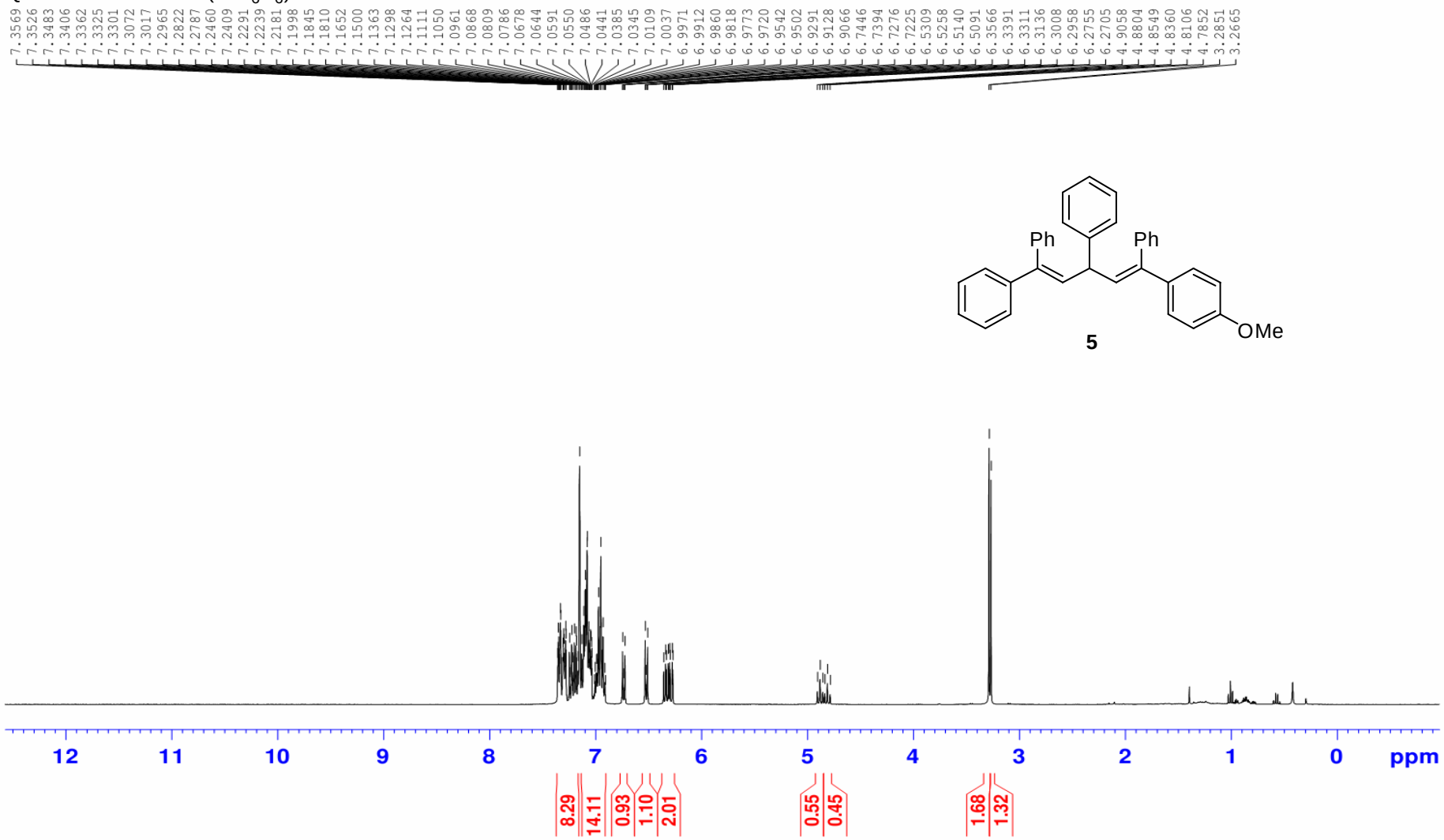
3oj

QianB-121229-6-CNMR (in C_6D_6)



3oj

QB-130814-1-HNMR (in C_6D_6)



QB-130814-1-CNMR (in C_6D_6)