Supporting Information

Selective Synthesis of Secondary Benzylic (*Z*)-Allylboronates by Fe-Catalyzed 1,4-Hydroboration of 1-Aryl-substituted 1,3-Dienes

Yanchun Cao, Yanlu Zhang, Lei Zhang, Dan Zhang, Xuebing Leng and Zheng Huang*
State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 345 Lingling Road, Shanghai 200032, People's Republic of China

huangzh@sioc.ac

Table of Contents

1. General Information…………………………………………………………....S2
2. Procedure for Preparation of Fe(II) complexs...S3
3. Preparation of 1,3-Dienes...S16
4. Hydroboration of 1,3-Dienes……….…..………………..……………….........S19
5. Suzuki-Miyaura Cross–Couplings of Secondary Benzylic and Allylic Boronic Esters……………………………………………………………..………S31
6. Crystallographic Data of Complexes **4, 5** and **7e**…...…………………….....…S41
7. References……………………………………………...……….……... S44

NMR Spectra………………………………………………..…….......S45

NOESY Spectra……………………………………………………………..S97

1. General Information

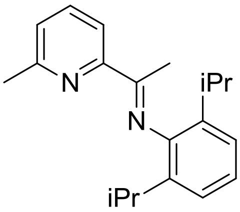
a. Materials

All manipulations were carried out using standard Schlenk, high-vacuum and glovebox techniques. All solvents were purified and dried according to standard methods prior to use. Tetrahydrofuran (THF), Et_2O was distilled from sodium benzophenone ketyl prior to use. The following chemicals were purchased and used as received: $FeCl_2$ (98%, Strem), $NaBEt_3H$ (1.0 M in toluene) (Aldrich), Chlorodiphenylphosphine (98+%, Acros), α,β-unsaturated aldehydes (Adams-beta), 2,6-dimethylaniline (TCI), 2,6-diethylaniline (TCI), 2,6-diisopropylaniline (J&K), acrolein diethyl acetal (TCI), methyltriphenylphosphonium bromide(J&K), ethyltriphenylphosphonium bromide (TCI), (1-hexyl)triphenylphosphonium bromid (J&K), trans-1,3-hexadiene (TCI), Pd $(dba)_2$ (J&K), $Pd(PPh_3)_4$ (J&K), 1-((*E*)-buta-1,3-dienyl)-3-fluorobenzene. Pinacolborane (97%) was purchased from TCI and purified according to reported procedure.[1] 1,2-dimethoxyethane (DME) were dried with CaH_2 and distilled prior to use. Iron complex 7c was prepared according to reported procedure.[2] All other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

b. Analytical Methods

NMR spectra were recorded on Agilent 400 MHz or Varian Mercury 400 MHz. ^1H NMR chemical shifts were referenced to residual protio solvent peaks or tetramethylsilane signal (0 ppm), and ^{13}C NMR chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). ^{31}P NMR chemical shifts were referenced to an external H_3PO_4 standard. Data for ^1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). The carbon bearing the boron is missing for all hydroboration products in the ^{13}C NMR spectra. GC-MS analysis was performed on Agilent 7890A gas chromatograph coupled to an Agilent 5975C inert mass selective detector. Elemental analyses and high resolution mass spectrometer (HR-MS) were carried out by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS).

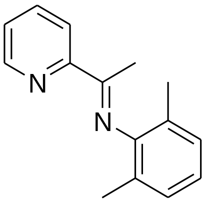
2. Procedure for Preparation of Fe(II) complexs



2,6-diisopropyl-*N*-(1-(6-methylpyridin-2-yl)ethylidene)aniline (1)

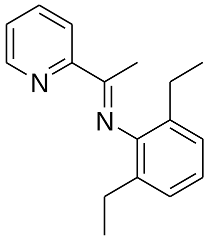
To a 100 mL single-neck flask, 1-(6-methylpyridin-2-yl)ethanone (2.5 g, 18.5 mmol, 1.0 equiv), 2,6-diisopropylaniline (2.5 g, 15.3 mmol, 0.77 equiv), *p*-tosyl acid (141.0 mg, 741 μmol, 4 mol %) and toluene (30 mL) were added. After refluxing for 48 h with azeotropic removal of water using a Dean-Stark trap, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel eluting with ethyl acetate/n-hexane (1 : 100) (v/v) to afford the title compound as a yellow solid (3.6 g, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (d, J = 7.6 Hz, 1H, Ar-H), 7.68 (t, J = 7.6 Hz, 1H, Ar-H), 7.24-7.22 (m, 1H, Ar-H), 7.16-7.15 (m, 2H, Ar-H), 7.10-7.06 (m, 1H, Ar-H), 2.79-2.72 (m, 2H, $Ar(CH(CH_3)_2)_2$), 2.62 (s, 3H, $ArCH_3$), 2.21 (s, 3H, $NCCH_3$), 1.14 (d, J = 7.2 Hz, 12H, $Ar(CH(CH_3)_2)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.5, 157.5, 156.0, 146.7, 136.7, 136.0, 124.4, 123.5, 123.1, 118.4, 28.3, 24.7, 23.4, 23.1, 17.5. Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.30; H, 8.93; N, 9.46.



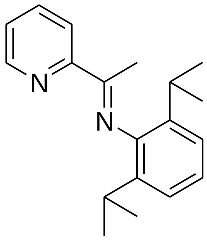
2,6-dimethyl-*N*-(1-(pyridin-2-yl)ethylidene)benzenamine (6d)

To a 100 mL single-neck flask, 1-(pyridin-2-yl)ethanone (3.6 g, 30.0 mmol, 1.0 equiv), 2,6-dimethylbenzenamine (2.6 g, 21.4 mmol, 0.71 equiv), *p*-tosyl acid (285.0 mg, 1.5 mmol, 5 mol %) and toluene (40 mL) were added. After refluxing for 48 h with azeotropic removal of water using a Dean-Stark trap, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel eluting with ethyl acetate/n-hexane (1 : 100) (v/v) to afford the title compound as a yellow oil (3.9g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68-8.66 (m, 1H, Ar-*H*), 8.38-8.36 (m, 1H, Ar-*H*), 7.82-7.78 (m, 1H, Ar-*H*), 7.39-7.36 (m, 1H, Ar-*H*), 7.06 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 6.93 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 2.19 (s, 3H, $NCCH_3$), 2.04 (s, 6H, Ar-$(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.3, 156.5, 148.7, 136.6, 128.0, 125.5, 125.0, 123.1, 121.4, 18.0, 16.7. HRMS (ESI) m/z ($M+H^+$) calcd for $C_{15}H_{17}N_2$: 225.1392, found: 225.1385.



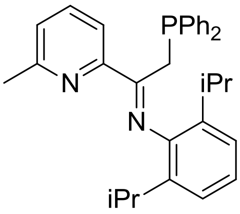
2,6-diethyl-*N*-(1-(pyridin-2-yl)ethylidene)benzenamine (6e)

To a 100 mL single-neck flask, 1-(pyridin-2-yl)ethanone (3.6 g, 30.0 mmol, 1.0 equiv), 2,6-diethylbenzenamine (3.7 g, 25 mmol, 0.83 equiv), *p*-tosyl acid (285.0 mg, 1.5 mmol, 5 mol %) and toluene (40 mL) were added. After refluxing for 48 h with azeotropic removal of water using a Dean-Stark trap, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel eluting with ethyl acetate/n-hexane (1 : 100) (v/v) to afford the title compound as a yellow solid (5.5 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68-8.66 (m, 1H, Ar-*H*), 8.38-8.36 (m, 1H, Ar-*H*), 7.82-7.78 (m, 1H, Ar-*H*), 7.39-7.36 (m, 1H, Ar-*H*), 7.11 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.05-7.01 (m, 1H, Ar-*H*), 2.46-2.29 (m, 4H, $Ar(CH_2CH_3)_2$), 2.02 (s, 3H, $NCCH_3$), 1.14 (t, *J* = 7.6 Hz, 6H, $Ar(CH_2CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.0, 156.5, 148.7, 147.8, 136.6, 131.3, 126.0, 124.9, 123.4, 121.4, 24.7, 17.1, 13.8. HRMS (ESI) m/z ($M+H^+$) calcd for $C_{17}H_{21}N_2$: 253.1705, found: 253.1699.



2,6-diisopropyl-*N*-(1-(pyridin-2-yl)ethylidene)benzenamine (6f)

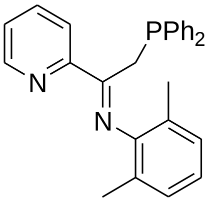
To a 100 mL single-neck flask, 1-(pyridin-2-yl)ethanone (3.6 g, 30.0 mmol, 1.0 equiv), 2,6-diisopropylaniline (4.1 g, 23 mmol, 0.77 equiv), *p*-tosyl acid (285.0 mg, 1.5 mmol, 5 mol %) and toluene (40 mL) were added. After refluxing for 48 h with azeotropic removal of water using a Dean-Stark trap, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel eluting with ethyl acetate/n-hexane (1 : 100) (v/v) to afford the title compound as a yellow solid (5.5 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.69-8.67 (m, 1H, Ar-*H*), 8.37-8.35 (m, 1H, Ar-*H*), 7.83-7.78 (m, 1H, Ar-*H*), 7.40-7.37 (m, 1H, Ar-*H*), 7.16 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.11-7.08 (m, 1H, Ar-*H*), 2.78-2.72 (m, 2H, $Ar(CH(CH_3)_2)_2$), 2.22 (s, 3H, $NCCH_3$), 1.15 (d, *J* = 7.2, 12H, $Ar(CH(CH_3)_2)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.1, 156.6, 148.7, 146.5, 136.6, 135.9, 124.9, 123.7, 123.1, 121.4, 28.4, 23.3, 23.0, 17.5. HRMS (ESI) m/z ($M+H^+$) calcd for $C_{19}H_{25}N_2$: 281.2018, found: 281.2006.



N-(2-(diphenylphosphino)-1-(6-methylpyridin-2-yl)ethylidene)-2,6-diisopropylaniline (3)

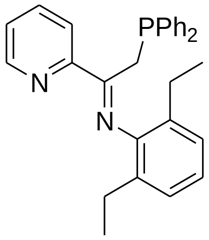
An oven-dried 100 mL Schlenk flask equipped with an argon inlet, a stirring bar, dropping funnel and one rubber septum was cooled under a stream of argon. The flask was then charged with **1** (1.1 g, 3.6 mmol) in 30 mL THF. The solution was cooled to -78 ℃ and 2.0 mL of a 2.0 M solution of commercial lithium diisopropylamide (LDA) in n-heptane/THF/ethylbenzene (28% : 26% : 13%) (4.0 mmol) was added dropwise via syringe for 10 minutes. The resulting brown colored mixture was stirred for 1 hr at 0 ℃ and then cooled to –78 ℃ and a solution of chlorodiphenylphosphine (8.8 g, 4.0 mmol) was added dropwise to it. The mixture was allowed to slowly warm up to room temperature and stirred for 12 h. The solvent was removed under vacuum to get yellow oil. The crude product was purified by column chromatography in a nitrogen glove box (basic alumina; hexane: ether (20 : 1) as eluent) to yield **3** (1.1 g, 64%) as a yellow solid. ^{1}H NMR (400 MHz, C_6D_6) δ = 8.39 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.36-7.32 (m, 4H, Ar-*H*), 7.26-7.18 (m, 4H, Ar-*H*), 7.09-7.03 (m, 6H, Ar-*H*), 6.65 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 4.03 (d, *J* = 2.8 Hz, 2H, $NCCH_2P$), 3.18-3.11 (m, 2H, $CH(CH_3)_2$), 2.17 (s, 3H, $ArCH_3$), 1.29 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.20 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR (101 MHz, C_6D_6) δ = 167.9 (d, *J* = 13.8 Hz), 157.2, 155.7, 147.3, 140.4 (d, *J* = 17.6

Hz), 136.7, 136.0 (d, *J* = 1.6 Hz), 133.1 (d, *J* = 20.0 Hz), 128.6, 128.5, 128.4, 124.2 (d, *J* = 4.6 Hz), 123.5, 119.2, 31.1 (d, *J* = 23.7 Hz), 29.2 (d, *J* = 1.5 Hz), 23.8, 23.7, 21.8. ^{31}P{^{1}H}NMR (C_6D_6, 162 MHz) δ = - 13.4. Anal. Calcd for $C_{31}H_{33}N_2P$: C, 80.30; H, 7.37; N, 5.85. Found: C, 80.01; H, 7.34; N, 5.98.



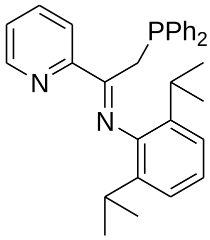
2,6-dimethyl-*N*-(2-(diphenylphosphino)-1-(pyridin-2-yl)ethylidene)benzenamine (6g)

An oven-dried 100 mL Schlenk flask equipped with an argon inlet, a stirring bar, dropping funnel and one rubber septum was cooled under a stream of argon. The flask was then charged with **6d** (1.2 g, 5.35 mmol) in 30 mL THF. The solution was cooled to -78 ℃ and 4.0 mL of a 2.0 M solution of commercial lithium diisopropylamide (LDA) in n-heptane/THF/ethylbenzene (28% : 26% : 13%) (8.0 mmol) was added dropwise via syringe for 10 minutes. The resulting brown colored mixture was stirred for 1 hr at 0 ℃ and then cooled to –78 ℃ and a solution of chlorodiphenylphosphine (1.78 g, 8.0 mmol) was added dropwise to it. The mixture was allowed to slowly warm up to room temperature and stirred for 12 h. The solvent was removed under vacuum to get yellow oil. The crude product was purified by column chromatography in a nitrogen glove box (basic alumina; hexane: ether (20 : 1) as eluent) to yield **6g** (1.64 g, 75 %) as a yellow solid. ^{1}H NMR (400 MHz, C_6D_6) δ = 8.42 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 8.35-8.34 (m, 1H, Ar-*H*), 7.35-7.30 (m, 4H, Ar-*H*), 7.14-7.10 (m, 1H, Ar-*H*), 7.00-6.98 (m, 6H, Ar-*H*), 6.92 (s, 3H, Ar-*H*), 6.68-6.45 (m, 1H, Ar-*H*), 3.89 (d, *J* = 3.6 Hz, 2H, NCCH_2P), 1.98 (s, 6H, Ar-(CH_3)$_2$). ^{13}C NMR (101 MHz, C_6D_6) δ = 167.9 (d, *J* = 13.0 Hz), 156.3, 149.2, 148.4, 139.7 (d, *J* = 17.7 Hz), 136.2, 133.3, 133.1, 128.6 (d, *J* = 2.3 Hz), 128.5 (d, *J* = 3.1 Hz), 126.0 (d, *J* = 1.5 Hz), 124.7, 123.4, 122.1, 31.5, 31.3, 18.6 (d, *J* = 2.3 Hz). ^{31}P{^{1}H}NMR (C_6D_6, 162 MHz) δ = - 12.2. Anal. Calcd for $C_{27}H_{25}N_2P$: C, 79.39; H, 6.17; N, 6.86. Found: C, 79.37; H, 6.18; N, 6.80.



2,6-diethyl-*N*-(2-(diphenylphosphino)-1-(pyridin-2-yl)ethylidene)benzenamine (6h)

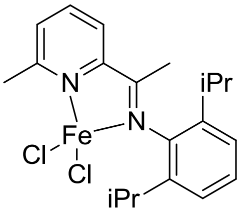
An oven-dried 100 mL Schlenk flask equipped with an argon inlet, a stirring bar, dropping funnel and one rubber septum was cooled under a stream of argon. The flask was then charged with **6e** (2.02 g, 8.0 mmol) in 40 mL THF. The solution was cooled to -78 ℃ and 5.2 mL of a 2.0 M solution of commercial lithium diisopropylamide (LDA) in n-heptane/THF/ethylbenzene (28% : 26% : 13%) (10.4 mmol) was added dropwise via syringe for 15 minutes. The resulting brown colored mixture was stirred for 1 h at 0 ℃ and then cooled to –78 ℃ and a solution of chlorodiphenylphosphine (2.3 g, 10.4 mmol) was added dropwise to it. The mixture was allowed to slowly warm up to room temperature and stirred for 12 h. The solvent was removed under vacuum to get yellow oil. The crude product was purified by column chromatography in a nitrogen glove box (basic alumina; hexane: ether (20 : 1) as eluent) to yield **6h** (2.86g, 82%) as a yellow solid. ^{1}H NMR (400 MHz, C_6D_6) δ = 8.55 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 8.46-8.45 (m, 1H, Ar-*H*), 7.47-7.43 (m, 4H, Ar-*H*), 7.27-7.23 (m, 1H, Ar-*H*), 7.15-7.08 (m, 9H, Ar-*H*), 6.80-6.76 (m, 1H, Ar-*H*), 4.01 (d, *J* = 4.0 Hz, 2H, NCCH_2P), 2.70-2.61 (m, 2H, CH_2CH$_3$) , 2.35-2.26 (m, 2H, CH_2CH$_3$), 1.23 (t, *J* = 7.2 Hz, 6H, CH$_2$CH_3). ^{13}C NMR (101 MHz, C_6D_6) δ = 167.6 (d, *J* = 13.8 Hz), 156.2, 148.4, 148.2, 139.9 (d, *J* = 17.7 Hz), 136.3, 133.3, 133.1, 131.5 (d, *J* = 1.5 Hz), 128.6, 128.5 (d, *J* = 3.0 Hz), 126.2, 124.7, 123.8, 122.1, 31.5 (d, *J* = 23.0 Hz), 25.5 (d, *J* = 1.5 Hz), 13.5. ^{31}P{^{1}H}NMR (C_6D_6, 162 MHz) δ = - 12.6. Anal. Calcd for $C_{29}H_{29}N_2P$: C, 79.79; H, 6.70; N, 6.42. Found: C, 79.51; H, 6.71; N, 6.66.



2,6-diisopropyl-*N*-(2-(diphenylphosphino)-1-(pyridin-2-yl)ethylidene)benzenamine (6i)

An oven-dried 100 mL Schlenk flask equipped with an argon inlet, a stirring bar, dropping funnel and one rubber septum was cooled under a stream of argon. The flask was then charged with 6f (0.9 g, 3.2 mmol) in 25 mL THF. The solution was cooled to -78 ℃ and 2.4 mL of a 2.0 M solution of commercial lithium diisopropylamide (LDA) in n-heptane/THF/ethylbenzene (28% : 26% : 13%) (4.8 mmol) was added dropwise via syringe for 7 minutes. The resulting brown colored mixture was stirred for 1 h at 0 ℃ and then cooled to –78 ℃ and a solution of chlorodiphenylphosphine (1.0 g, 4.8 mmol) was added dropwise to it. The mixture was allowed to slowly warm up to room temperature and stirred for 12 h. The solvent was removed under vacuum to get yellow oil. The crude product was purified by column chromatography in the nitrogen glove box (basic alumina; hexane: ether (20 : 1) as eluent) to yield **6i** (1.13g, 76 %) as a yellow solid. ^{1}H NMR (400 MHz, C_6D_6) δ = 8.48 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 8.29-8.28 (m, 1H, Ar-*H*), 7.40-7.35 (m, 4H, Ar-*H*), 7.21-7.15 (m, 4H, Ar-*H*), 7.08-7.04 (m, 6H, Ar-*H*), 6.70-6.67 (m, 1H, Ar-*H*), 4.03 (d, *J* = 2.8 Hz, 2H, NCCH_2P), 3.11-3.04 (m, 2H, C*H*(CH_3)$_2$) , 1.27 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.16 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (101 MHz, C_6D_6) δ = 167.7 (d, *J* = 13.0 Hz), 156.2, 148.2, 147.1, 140.2 (d, *J* = 17.6 Hz), 136.3, 136.0 (d, *J* = 1.5 Hz), 133.2 (d, *J* = 19.2 Hz), 128.6, 128.5, 124.6, 124.3, 123.5, 122.1, 31.1 (d, *J* = 23.7 Hz), 29.2 (d, *J* = 1.5 Hz), 23.7, 21.8. ^{31}P{^{1}H}NMR (C_6D_6, 162 MHz) δ = - 13.1. Anal. Calcd for $C_{31}H_{33}N_2P$: C, 80.14; H, 7.16; N, 6.03. Found: C, 80.13; H, 7.18; N, 6.02.

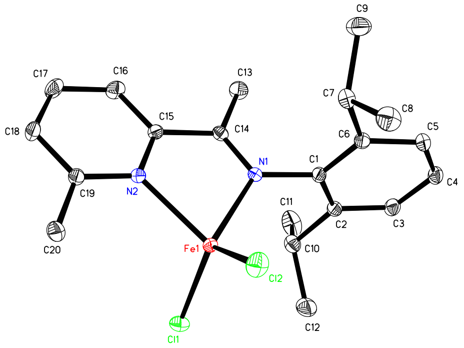
(NN)FeCl$_2$:



4

In a nitrogen filled glovebox, $FeCl_2$ (133 mg, 1.0 mmol, 1.0 equiv) , THF (35 mL) were added to a 50 mL Schlenk tube. After stirring for 2.5 hr, a solution of **1** (324 mg, 1.1 mmol, 1.05 equiv) in THF (10 mL) was added. The reaction mixture stirred for 24 h. The resulting solution was concentrated under vacuum to about 1 mL, and 5 mL pentane was added to cause precipitation of a blue solid, which was filtered and washed with pentane (3 × 10 mL), then dried under vacuum. The product was obtained as a blue powder (370 mg, 84 %). Anal. Calcd for $C_{20}H_{26}Cl_2FeN_2$: C, 57.03; H, 6.22; N, 6.65. Found: C, 56.85; H, 6.18; N, 6.72.

Crystal structure for 4.

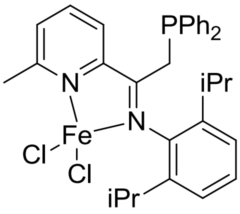


Selected Bond Length for 4

Selected Bond Length	Distance(Å)
Fe(1)-N(1)	2.1111(16)
Fe(1)-N(2)	2.1160(17)
Fe(1)-Cl(2)	2.2289(7)
Fe(1)-Cl(1)	2.2309(7)

Selected Bond Angles for 4

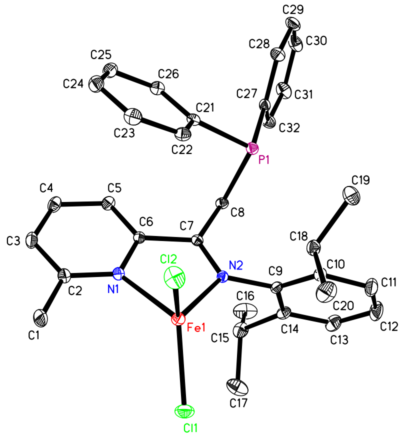
Selected Bond Angles	(deg)
N(1)-Fe(1)-N(2)	77.32(6)
N(1)-Fe(1)-Cl(2)	113.00(5)
N(2)-Fe(1)-Cl(2)	119.45(5)
N(1)-Fe(1)-Cl(1)	113.79(5)
N(2)-Fe(1)-Cl(1)	104.66(5)
Cl(2)-Fe(1)-Cl(1)	120.71(3)
C(14)-N(1)-Fe(1)	115.85(13)
C(1)-N(1)-Fe(1)	124.27(12)
C(19)-N(2)-Fe(1)	126.49(14)
C(15)-N(2)-Fe(1)	113.63(13)



5

In a nitrogen filled glovebox, $FeCl_2$ (52 mg, 0.4 mmol, 1.0 equiv), THF (25 mL) were added to a 50 mL Schlenk tube. After stirring for 2.5 hr, a solution of **3** (216 mg, 1.1 mmol, 1.1 equiv) in THF (10 mL) was added. The reaction mixture stirred for 24 h. The resulting solution was concentrated under vacuum to about 1 mL, and 5 mL pentane was added to cause precipitation of a blue solid, which was filtered and washed with pentane (3 × 10 mL), then dried under vacuum. The product was obtained as a blue powder (210 mg, 85 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 78.77, 74.83, 60.69, 13.15, 11.28, 10.70, 2.96, 2.58, 1.96, -7.17, -15.61, -16.43, -32.52. ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 244.8. Anal. Calcd for $C_{32}H_{35}Cl_2FeN_2P$: C, 63.49; H, 5.83; N, 4.63 Found: C, 63.49; H, 5.87; N, 4.52.

Crystal structure for 5

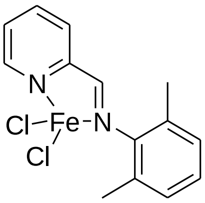


Selected Bond Length for 5

Selected Bond Length	Distance(Å)
Fe(1)-N(2)	2.1032(11)
Fe(1)-N(1)	2.1098(11)
Fe(1)-Cl(1)	2.2306(4)
Fe(1)-Cl(2)	2.2447(5)

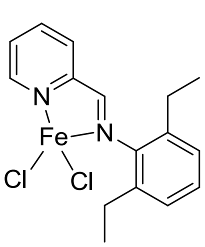
Selected Bond Angles for 5

Selected Bond Angles	(deg)
N(2)-Fe(1)-N(1)	77.37(4)
N(2)-Fe(1)-Cl(1)	113.71(3)
N(1)-Fe(1)-Cl(1)	122.07(3)
N(2)-Fe(1)-Cl(2)	115.77(3)
N(1)-Fe(1)-Cl(2)	100.77(4)
Cl(1)-Fe(1)-Cl(2)	119.636(18)
C(2)-N(1)-Fe(1)	125.36(9)
C(6)-N(1)-Fe(1)	114.14(8)
C(7)-N(2)-Fe(1)	115.83(9)
C(9)-N(2)-Fe(1)	124.74(8)



7a

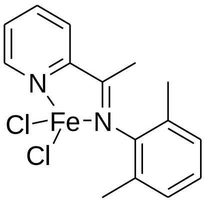
In a nitrogen filled glovebox, $FeCl_2$ (292.0 mg, 2.31 mmol, 1.0 equiv), THF (35 mL) were added to a 50 mL Schlenk tube. After stirring for 2.5 hr, a solution of 2,6-dimethyl-N-((pyridin-2-yl)methylene)benzenamine (**6a**) (510.0 mg, 2.43 mmol, 1.05 equiv) in THF (5 mL) was added. The reaction mixture stirred for 24 h. The resulting solution was concentrated under vacuum to about 1 mL, and 5 mL pentane was added to cause precipitation of a blue-brown solid, which was filtered and washed with pentane (3 × 10 mL), then dried under vacuum. The product was obtained as a blue-brown powder (714 mg, 92 %). Anal. Calcd for $C_{14}H_{14}Cl_2FeN_2$: C, 49.89; H, 4.19; N, 8.31. Found: C, 49.71; H, 4.28; N, 8.56.



7b

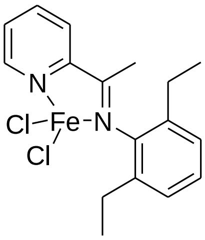
In a nitrogen filled glovebox, $FeCl_2$ (126.8 mg, 1.0 mmol, 1.0 equiv), THF (30 mL) were added to a 50 mL Schlenk tube. After stirring for 2.5 hr, a solution of 2,6-diethyl-N-(pyridin-2-ylmethylene)aniline (**6b**)

(262.0 mg, 1.1 mmol, 1.1 equiv) in THF (5 mL) was added. The reaction mixture stirred for 24 h. The resulting solution was concentrated under vacuum to about 1 mL, and 5 mL pentane was added to cause precipitation of a blue-brown solid, which was filtered and washed with pentane (3 × 10 mL), then dried under vacuum. The product was obtained as a blue powder (331.0 mg, 91%). Anal. Calcd for $C_{16}H_{18}Cl_2FeN_2$: C, 52.64; H, 4.97; N, 7.67. Found: C, 52.94; H, 4.88; N, 7.88.



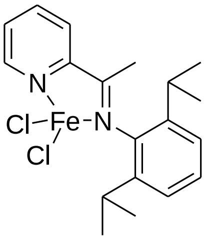
7d

In a nitrogen filled glovebox, $FeCl_2$ (196.0 mg, 1.55 mmol, 1.0 equiv), THF (35 mL) were added to a 100 mL Schlenk tube. After stirring for 2 h, a solution of ligand **6d** (359.0 mg, 1.6 mmol, 1.05 equiv) in THF (10 mL) was added. The reaction mixture stirred for 24 h. The resulting solution was concentrated under vacuum to about 1 mL, and 5 mL pentane was added to cause precipitation of a red solid, which was filtered and washed with pentane (3 × 10 mL), then dried under vacuum. The product was obtained as a red powder (490 mg, 90 %). ^1H NMR (400 MHz, CD_2Cl_2) δ 102.21, 71.89, 47.97, 8.94, 3.60, 1.31, -0.47, -0.85, -1.65, -20.09, -20.59. Anal. Calcd for $C_{15}H_{16}Cl_2FeN_2$: C, 51.32; H, 4.59; N, 7.98. Found: C,51.29; H, 4.73; N, 8.22.



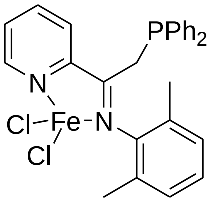
7e

In a nitrogen filled glovebox, $FeCl_2$ (144.0 mg, 1.14 mmol, 1.0 equiv), THF (30 mL) were added to a 50 mL Schlenk tube. After stirring for 2 h, a solution of **6e** ligand (303.0 mg, 1.2 mmol, 1.05 equiv) in THF (5 mL) was added. The reaction mixture stirred for 24 h. The resulting solution was concentrated under vacuum to about 1 mL, and 5 mL pentane was added to cause precipitation of a blue-brown solid, which was filtered and washed with pentane (3 × 10 mL), then dried under vacuum. The product was obtained as a blue powder (379 mg, 88 %). Anal. Calcd for $C_{17}H_{20}Cl_2FeN_2$: C, 53.86; H, 5.32; N, 7.39. Found: C, 53.85; H, 5.29; N, 7.69.



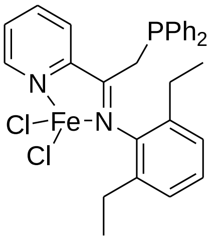
7f

In a nitrogen filled glovebox, $FeCl_2$ (154.0 mg, 1.22 mmol, 1.0 equiv), CH_2Cl_2 (30 mL) were added to a 50 mL Schlenk tube. After stirring for 2 h, a solution of **6f** ligand (359.0 mg, 1.28 mmol, 1.05 equiv) in CH_2Cl_2 (10 mL) was added. The reaction mixture stirred for 24 h. The resulting solution was concentrated under vacuum to about 1 mL, and 5 mL pentane was added to cause precipitation of a purple-brown solid, which was filtered and washed with pentane (3 × 10 mL), then dried under vacuum. The product was obtained as a purple powder (411 mg, 83 %). Anal. Calcd for $C_{19}H_{24}Cl_2FeN_2$: C, 56.05; H, 5.94; N, 6.88. Found: C, 55.98; H, 5.88; N, 7.06.



7g

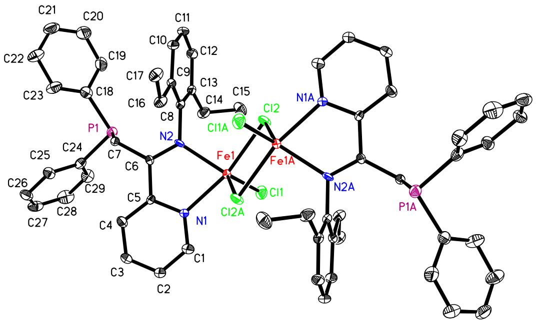
In a nitrogen filled glovebox, $FeCl_2$ (68.6 mg, 0.54 mmol, 1.0 equiv), THF (20 mL) were added to a 50 mL Schlenk tube. After stirring for 2 h, a solution of **6g** ligand (230.0 mg, 0.56 mmol, 1.05 equiv) in THF (5 mL) was added. The reaction mixture stirred for 24 h. The resulting solution was concentrated under vacuum to about 2 mL, and 5 mL pentane was added to cause precipitation of a blue-brown solid, which was filtered and washed with pentane (3 × 10 mL), then dried under vacuum. The product was obtained as a blue powder (274 mg, 95 %). ^{1}H NMR (400 MHz, CDCl3) δ 81.85, 73.93, 46.65, 8.23, 6.95, 6.15, 5.54, 2.79, -0.23, -1.28, -1.67, -2.46, -20.97, -21.30. Anal. Calcd for $C_{27}H_{25}Cl_2FeN_2P$: C, 60.59; H, 4.71; N, 5.23. Found: C, 60.46; H, 4.84; N, 5.51.



7h

In a nitrogen filled glovebox, $FeCl_2$ (56.0 mg, 0.44 mmol, 1.0 equiv), THF (25 mL) were added to a 50 mL Schlenk tube. After stirring for 2 h, a solution of **6h** ligand (201.0 mg, 0.46 mmol, 1.05 equiv) in THF (5 mL) was added. The reaction mixture stirred for 24 h. The resulting solution was concentrated under vacuum to about 1 mL, and 5 mL pentane was added to cause precipitation of a blue-brown solid, which was filtered and washed with pentane (3 × 10 mL), then dried under vacuum. The product was obtained as a blue powder (230 mg, 93%). The product (50 mg) was dissolved in CH_2Cl_2 (5 mL). Slow diffusion of *n*-pentane into the above solution resulted in the formation of red crystals of **7b** suitable for single crystal X-ray analysis. Anal. Calcd for $C_{29}H_{29}Cl_2FeN_2P$: C, 61.84; H, 5.19; N, 4.97. Found: C, 61.62; H, 5.44; N, 5.14.

Crystal structure for 7h.

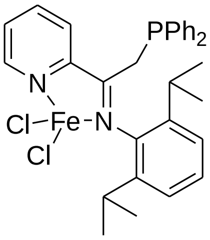


Selected Bond Length for 7h

Selected Bond Length	Distance(Å)
Fe(1)-N(2)	2.127(5)
Fe(1)-N(1)	2.157(5)
Fe(1)-Cl(1)	2.262(2)
Fe(1)-Cl(2)#1	2.386(2)
Fe(1)-Cl(2)	2.4730(19)
Cl(2)-Fe(1)#1	2.386(2)

Selected Bond Angles for 7h

Selected Bond Angles	(deg)
N(2)-Fe(1)-N(1)	74.66(19)
N(2)-Fe(1)-Cl(1)	119.90(15)
N(1)-Fe(1)-Cl(1)	96.30(16)
N(2)-Fe(1)-Cl(2)#1	19.74(14)
N(1)-Fe(1)-Cl(2)#1	89.40(15)
Cl(1)-Fe(1)-Cl(2)#1	119.41(8)
N(2)-Fe(1)-Cl(2)	95.28(14)
N(1)-Fe(1)-Cl(2)	164.91(16)
Cl(1)-Fe(1)-Cl(2)	98.49(7)
Cl(2)#1-Fe(1)-Cl(2)	85.91(6)
Fe(1)#1-Cl(2)-Fe(1)	94.09(6)
C(1)-N(1)-Fe(1)	125.6(5)
C(5)-N(1)-Fe(1)	116.4(4)
C(6)-N(2)-Fe(1)	118.8(4)
C(8)-N(2)-Fe(1)	121.9(4)

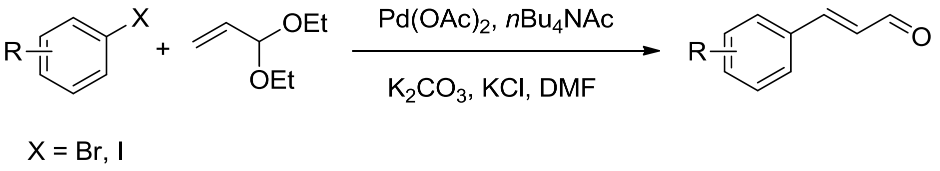


7i

In a nitrogen filled glovebox, $FeCl_2$ (62.0 mg, 0.49 mmol, 1.0 equiv), THF (25 mL) were added to a 50 mL Schlenk tube. After stirring for 2 hr, a solution of **6i** ligand (242.0 mg, 0.52 mmol, 1.07 equiv) in THF (5 mL) was added. The reaction mixture stirred for 24 h. The resulting solution was concentrated under vacuum to about 1 mL, and 5 mL pentane was added to cause precipitation of a blue-brown solid, which was filtered and washed with pentane (3 × 10 mL), then dried under vacuum. The product was obtained as a blue powder (272 mg, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 79.52, 78.02, 52.65, 11.20, 9.49, 8.81, 5.33, 3.37, 1.24, 1.12, 0.85, 0.23, -9.79, -16.67, -18.92. Anal. Calcd for $C_{31}H_{33}Cl_2FeN_2P$: C, 62.96; H, 5.62; N, 4.74. Found: C, 62.75; H, 5.62; N, 4.74.

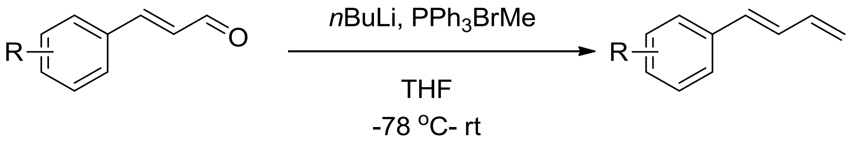
3. Preparation of 1,3-Dienes.

A.

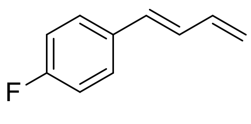


The following α,β-unsaturated aldehydes were prepared by Heck-type coupling of aryl bromides and acrolein diethyl acetale: (*E*)-3-(naphthalen-3-yl)acrylaldehyde, (*E*)-3-(benzo[*d*][1,3]dioxol-6-yl)acrylaldehyde, (*E*)-3-(m-tolyl)acrylaldehyde, (*E*)-3-(3-methoxyphenyl)acrylaldehyde, (*E*)-3-(3,5-dimethylphenyl)acrylaldehyde Spectral data are in accordance with the literature reference.[3]

B.



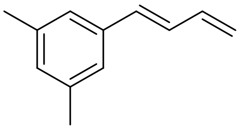
The following dienes were prepared by Wittig olefination of the reported α,β-unsaturated aldehydes with methyltriphenylphosphonium bromide and *n*-BuLi in THF: 1-((*E*)-buta-1,3-dienyl)benzene (**8a**),[4] 1-((*E*)-buta-1,3-dienyl)-4-methoxybenzene (**8b**), [4] 1-bromo-4-((*E*)-buta-1,3-dienyl)benzene (**8c**),[4] 1-((*E*)-buta-1,3-dienyl)-4-chlorobenzene (**8d**),[4] 1-((*E*)-buta-1,3-dienyl)-4-fluorobenzene (**8e**),[4] (*E*)-1-(buta-1,3-dien-1-yl)-3-methylbenzene (**8g**),[5] (*E*)-1-(buta-1,3-dien-1-yl)-3,5-dimethylbenzene (**8h**), (*E*)-1-(buta-1,3-dien-1-yl)-3-methoxybenzene (**8i**)[4], (*E*)-2-(buta-1,3-dien-1-yl)naphthalene (**8j**),[5] (*E*)-5-(buta-1,3-dien-1-yl)-3a,7a-dihydrobenzo[d][1,3]dioxole (**8k**), [6] Spectral data are in accordance with the literature reference.



(*E*)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene (8e)

^{1}H NMR (400 MHz, CDCl$_3$) δ = 6.94-6.91 (m, 2H, Ar-*H*), 6.76-6.72 (m, 2H, Ar-*H*), 6.51-6.45 (m, 1H, ArC*H*CHCH), 6.39-6.30 (m, 1H, ArCHC*H*CH), 6.22 (d, *J* = 15.6 Hz , 1H, ArCHCHC*H*), 5.19 (d, *J* = 16.8 Hz, 1H, CHCHC*H$_2$*), 5.06 (d, *J* = 10.0 Hz, 1H, CHCHC*H$_2$*). ^{13}C NMR (101 MHz, CDCl$_3$) δ 162.8 (d, *J* = 247.9 Hz), 137.5, 133.6 (d, *J* = 3.3 Hz), 132.0 (d, *J* = 1.1 Hz), 129.7 (d, *J* = 2.3 Hz), 128.4, 117.5, 115.7 (d, *J*

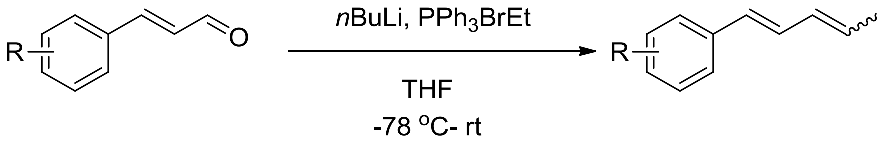
= 21.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.0. HRMS-EI (*m/z*): Calcd for [$C_{10}H_9F+$], 148.0689; found: 148.0688.



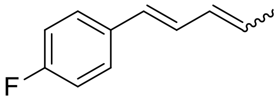
(*E*)-1-(buta-1,3-dien-1-yl)-3,5-dimethylbenzene (8h)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.03 (s, 2H, Ar-*H*), 6.88 (s, 1H, Ar-*H*), 6.80-6.74 (m, 1H, ArC*H*CHCH), 6.54-6.45 (m, 2H, ArCHC*H*C*H*), 5.31 (d, *J* = 17.6 Hz , 1H, CHCHC*H*$_2$), 5.15 (d, *J* = 10.0 Hz, 1H, CHCHC*H*$_2$), 2.31 (s, 6H, Ar(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.5, 137.1, 133.2, 129.6, 129.4, 124.5, 117.4, 21.4. HRMS-EI (*m/z*): Calcd for [$C_{12}H_{14}+$], 158.1096; found: 158.1093.

C.



The following dienes were prepared by Wittig olefination of the commercially available α,β-unsaturated aldehydes with ethyltriphenylphosphonium bromide and *n*-BuLi in THF: 1-(penta-1,3-dienyl)benzene (**10a**),[7] 1-fluoro-4-(penta-1,3-dienyl)benzene (**10c**), 2-(penta-1,3-dienyl)furan (**10d**).

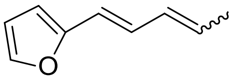


***E,E* : *E, Z* = 49 : 51**

fluoro-4-((*1E*)-penta-1,3-dien-1-yl)benzene (10c)

NMR data for the mixture of *E,E* and *E, Z isomers*: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42-7.36 (m, 1H, Ar-*H*), 7.36-7.31 (m, 1H, Ar-*H*), 7.05-7.00 (m, 1H, Ar-*H*), 7.04-6.98 (m, 1H, Ar-*H*), 7.00-6.98 (m, 0.5H, ArCHC*H*CHCH), 6.70-6.53 (m, 0.5H, ArCHC*H*CHCH), 6.49 (d, *J* = 16.0 Hz, 0.5H, ArC*H*CHCHCH), 6.39 (d, *J* = 16.0 Hz, 0.5H, ArC*H*CHCHCH), 6.24-6.21 (m, 0.5H, ArCHCHC*H*CH), 6.18-6.15 (m, 0.5H, ArCHCHC*H*CH), 5.89-5.79 (m, 0.5H, ArCHCHCHC*H*), 5.66-5.57 (m, 0.5H, ArCHCHCHC*H*), 1.87 (d, *J* = 8.0 Hz, 1.5H, CHCHC*H*$_3$), 1.83 (d, *J* = 8.0 Hz, 1.5H, CHCHC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 162.1 (d, *J* = 246.8 Hz), 161.9 (d, *J* = 246.4 Hz), 133.83 (d, *J* = 1.7 Hz), 133.80 (d, *J* = 1.7 Hz), 131.64 (d, *J* = 0.6 Hz), 130.5 (d, *J* = 1.0 Hz), 130.3 (d, *J* = 1.1 Hz), 129.4 (d, *J* = 0.8 Hz), 129.0 (d, *J* = 2.4 Hz), 128.4 (d, *J* = 1.0

Hz), 127.7 (d, J = 7.9 Hz), 127.5 (d, J = 7.9 Hz), 127.2 (d, J = 1.1 Hz), 123.9 (d, J = 2.4 Hz), 115.5 (d, J = 21.6 Hz), 115.4 (d, J = 21.6 Hz), 18.3, 13,6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.7, -115.1. HRMS-EI (m/z): Calcd for [$C_{11}H_{11}F+$], 162.0845; found: 162.0847.

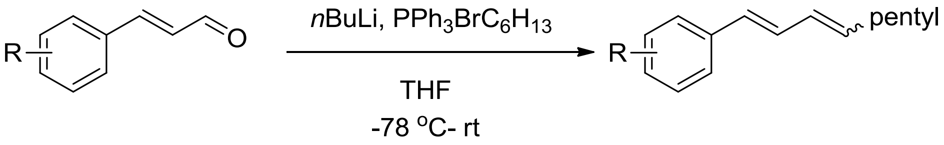


***E,E* : *E, Z* = 47 : 53**

2-((*1E*)-penta-1,3-dien-1-yl)furan

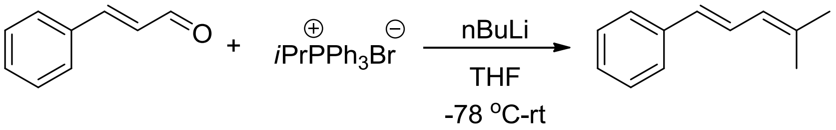
NMR data for the mixture of *E,E* and *E, Z isomers*: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.33 (m, 1H), 7.06-6.97 (m, 0.53H), 6.74-6.64 (m, 0.47H), 6.42-6.08 (m, 4H), 5.90-5.79 (m, 0.47H), 0.66-0.56 (m, 0.53H), 1.90-1.80 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 153.5, 142.0, 141.8, 131.6, 130.7, 129.4, 128.2, 127.6, 123.0, 119.6, 117.7, 111.7, 111.6, 108.2, 107.5, 18.5, 13.7. HRMS-EI (m/z): Calcd for [$C_{10}H_{10}+$], 134.0732; found: 134.0526.

D.



1-(nona-1,3-dienyl)benzene (**10b**) were prepared by Wittig olefination of the commercially available cinnamaldehyde with (1-Hexyl)triphenylphosphonium bromide and *n*BuLi in THF, Spectral data are in accordance with the literature reference.[8]

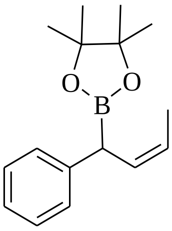
E.



(*E*)-(4-methylpenta-1,3-dien-1-yl)benzene (**10e**) were prepared by Wittig olefination of the commercially available cinnamaldehyde with isopropyltriphenylphosphonium bromide and *n*BuLi in THF, Spectral data are in accordance with the literature reference.[9]

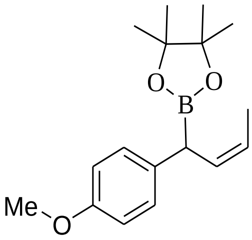
4. Hydroboration of 1, 3-Dienes

Substrate Scope for Fe-Catalyzed 1, 4-Hydroboration of 1,3-Dienes



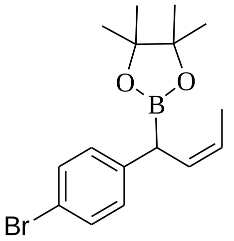
4,4,5,5-tetramethyl-2-((*Z*)-1-phenylbut-2-enyl)-1,3,2-dioxaborolane (9a)

In a nitrogen glovebox, **7h** (1.4 mg, 2.5 μmol, 1 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (6.25 μmol, 2.5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 1 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9a** and **9a’** (**9a : 9a’** = 95 : 5) as colorless oil (92 %). NMR data for compound **9a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.24 (m, 4H, Ar-*H*), 7.17-7.11 (m, 1H, Ar-*H*), 5.76-5.71 (m, 1H, CHC*H*CH), 5.58-5.52 (m, 1H, CHCHC*H*), 3.51 (d, *J* = 9.6 Hz , 1H, C*H*B), 1.67 (dd, *J* = 6.8, 1.6 Hz , 3H, CHCHCH_3), 1.21 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 130.7, 128.6, 128.2, 125.4, 123.8, 83.6, 24.7, 24.6, 13.2. HRMS-EI (*m/z*): Calcd for [$C_{16}H_{23}BO_2$+], 257.1827; found: 257.1831.



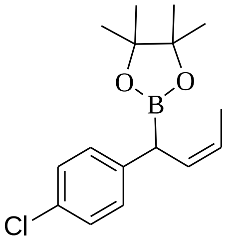
2-((*Z*)-1-(4-methoxyphenyl)but-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9b)

In a nitrogen glovebox, **7h** (1.4 mg, 2.5 μmol, 1 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (6.25 μmol, 2.5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 1 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9b** and **9b'** (**9b : 9b'** = 95 : 5) as colorless oil (92 %). NMR data for compound **9b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18-7.16 (m, 2H, Ar-*H*), 6.83-6.81 (m, 2H, Ar-*H*), 5.72-5.67 (m, 1H, CHC*H*CH), 5.60-5.50 (m, 1H, CHCHC*H*), 3.77 (s, 3H, OC*H*$_3$), 3.44 (d, *J* = 9.6 Hz , 1H, C*H*B), 1.67-1.65 (m, 3H, CHCHC*H*$_3$), 1.21 (s, 12H, C(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 134.4, 131.1, 129.1, 123.5, 114.0, 83.6, 55.3, 24.7, 24.6, 13.2. HRMS-EI (*m/z*): Calcd for [$C_{17}H_{25}BO_3$+], 287.1933; found: 287.1930.



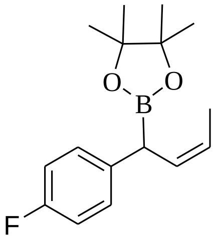
2-((*Z*)-1-(4-bromophenyl)but-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9c)

In a nitrogen glovebox, **7h** (5.6 mg, 10.0 μmol, 4 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (25 μmol, 10 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 2 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9c** and **9c'** (**9c : 9c'** = 94 : 6) as colorless oil (82 %). NMR data for compound **9c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41-7.36 (m, 2H, Ar-*H*), 7.21-7.12 (m, 2H, Ar-*H*), 5.70-5.65 (m, 1H, CHC*H*CH), 5.60-5.54 (m, 1H, CHCHC*H*), 3.45 (d, *J* = 9.6 Hz , 1H, C*H*B), 1.66-1.64 (m, 3H, CHCHC*H*$_3$), 1.21 (s, 12H, C(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 131.6, 130.0, 129.9, 124.5, 119.2, 83.8, 24.7, 24.6, 13.2. HRMS-EI (*m/z*): Calcd for [$C_{16}H_{22}BBrO_2$+], 335.0936; found: 335.0933.



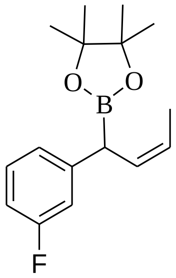
2-((*Z*)-1-(4-chlorophenyl)but-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9d)

In a nitrogen glovebox, **7h** (5.6 mg, 10.0 μmol, 4 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (25 μmol, 10 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 2 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9d** and **9d'** (**9d : 9d'** = 94 : 6) as colorless oil (84 %). NMR data for compound **9d**: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.25-7.17 (m, 4H, Ar-*H*), 5.70-5.65 (m, 1H, CHC*H*CH), 5.60-5.54 (m, 1H, CHCHC*H*), 3.47 (d, *J* = 9.6 Hz, 1H, C*H*B), 1.65 (dd, *J* = 6.4, 1.2 Hz, 3H, $CHCHCH_3$), 1.21 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 131.1, 130.0, 129.5, 128.6, 124.4, 83.7, 24.7, 24.6, 13.2. HRMS-EI (*m/z*): Calcd for [$C_{16}H_{22}BClO_2$+], 291.1438; found: 291.1436.



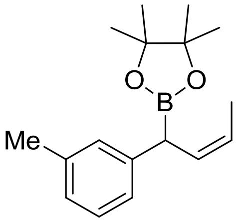
2-((*Z*)-1-(4-fluorophenyl)but-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9e)

In a nitrogen glovebox, **7h** (5.6 mg, 10.0 μmol, 4 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (25 μmol, 10 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 2 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9e** and **9e'** (**9e : 9e'** = 94 : 6) as colorless oil (89 %). NMR data for compound **9e**: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.25-7.18 (m, 2H, Ar-*H*), 6.98-6.92 (m, 2H, Ar-*H*), 5.71-5.65 (m, 1H, CHC*H*CH), 5.59-5.51 (m, 1H, CHCHC*H*), 3.47 (d, *J* = 9.2 Hz , 1H, C*H*B), 1.66 (dd, *J* = 6.8, 2.0 Hz, 3H, $CHCHCH_3$), 1.21 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1 (d, *J* = 244.5 Hz), 137.9 (d, *J* = 3.0 Hz), 130.5, 129.5 (d, *J* = 7.7 Hz), 124.1, 115.3 (d, *J* = 21.5 Hz), 83.7, 24.7, 24.6, 13.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.6. HRMS-EI (*m/z*): Calcd for [$C_{16}H_{22}BFO_2$+], 275.1733; found: 275.1728.



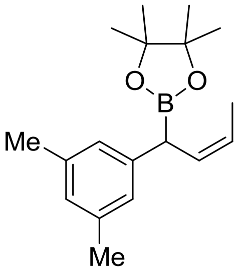
2-((*Z*)-1-(3-fluorophenyl)but-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9f)

In a nitrogen glovebox, **7h** (2.8 mg, 5.0 μmol, 2 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (12.5 μmol, 5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 2 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9f** and **9f’** (**9f : 9f’** = 94 : 6) as colorless oil (80 %). NMR data for compound **9f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24-7.17 (m, 1H, Ar-*H*), 7.01-6.95 (m, 2H, Ar-*H*), 6.84-6.79 (m, 1H, Ar-*H*), 5.70-5.65 (m, 1H, CHC*H*CH), 5.60-5.54 (m, 1H, CHCHC*H*), 3.49 (d, *J* = 9.6 Hz , 1H, C*H*B), 1.64 (dd, *J* = 6.8, 1.2 Hz, 3H, $CHCHCH_3$), 1.20 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, *J* = 245.9 Hz), 145.0 (d, *J* = 28.0 Hz), 129.9 (d, *J* = 9.8 Hz), 129.8, 124.5, 123.9 (d, *J* = 2.6 Hz), 115.1 (d, *J* = 21.4 Hz), 112.3 (d, *J* = 21.4 Hz), 83.8, 24.7, 24.6, 13.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.7. HRMS-EI (*m/z*): Calcd for [$C_{16}H_{22}BFO_2$+], 275.1733; found: 275.1736.



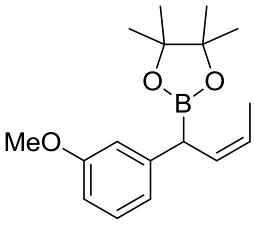
(*Z*)-4,4,5,5-tetramethyl-2-(1-(m-tolyl)but-2-en-1-yl)-1,3,2-dioxaborolane (9g)

In a nitrogen glovebox, **7h** (2.8 mg, 5.0 μmol, 2 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (12.5 μmol, 5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 1 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9g** and **9g'** (**9g : 9g'** = 96 : 4) as colorless oil (78 %). NMR data for compound **9g**: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.18-7.14 (m, 1H, Ar-*H*), 7.06-7.05 (m, 2H, Ar-*H*), 6.96 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 5.75-5.70 (m, 1H, CHC*H*CH), 5.58-5.51 (m, 1H, CHCHC*H*), 3.47 (d, *J* = 9.6 Hz , 1H, C*H*B), 2.31 (s, 3H, Ar-C*H$_3$*), 1.67 (dd, *J* = 6.8, 1.6 Hz, 3H, CHCHC*H$_3$*), 1.22 (s, 12H, C(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.2, 138.1, 130.9, 129.1, 128.5, 126.2, 125.3, 123.6, 83.6, 24.7, 24.6, 21.6, 13.2. HRMS-EI (*m/z*): Calcd for [$C_{17}H_{25}BO_2$+], 271.1984; found: 271.1981.



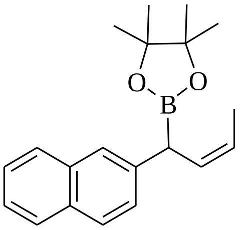
(*Z*)-2-(1-(3,5-dimethylphenyl)but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9h)

In a nitrogen glovebox, **7h** (2.8 mg, 5.0 μmol, 2 mol %), Et$_2$O (1 mL), diene (250 μmol, 1.0 equiv), NaBEt$_3$H (1M in toluene) (12.5 μmol, 5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 1 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9h** and **9h'** (**9h : 9h'** = 94 : 6) as colorless oil (73 %). NMR data for compound **9h**: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 6.87 (s, 2H, Ar-*H*), 6.78 (s, 1H, Ar-*H*), 5.74-5.68 (m, 1H, CHC*H*CH), 5.54-5.50 (m, 1H, CHCHC*H*), 3.43 (d, *J* = 10.0 Hz , 1H, C*H*B), 2.27 (s, 6H, Ar-(C*H$_3$*)$_2$), 1.66 (dd, *J* = 6.8, 1.6 Hz, 3H, CHCHC*H$_3$*), 1.22 (s, 12H, C(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.1, 138.0, 131.0, 127.2, 126.1, 123.4, 83.6, 24.7, 24.6, 21.5, 13.2. HRMS-EI (*m/z*): Calcd for [$C_{18}H_{27}BO_2$+], 285.2140; found: 285.2138.



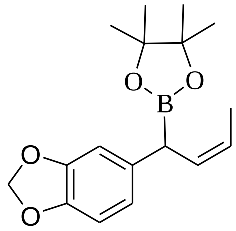
(*Z*)-2-(1-(3-methoxyphenyl)but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9i)

In a nitrogen glovebox, **7h** (2.8 mg, 5.0 μmol, 2 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (12.5 μmol, 5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 1 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9i** and **9i'** (**9i : 9i'** = 94 : 6) as colorless oil (78 %). NMR data for compound **9i**: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.20-7.16 (m, 1H, Ar-*H*), 6.86-6.83 (m, 2H, Ar-*H*), 6.71-6.69 (m, 1H, Ar-*H*), 5.75-5.70 (m, 1H, CHC*H*CH), 5.57-5.53 (m, 1H, CHCHC*H*), 3.79 (s, 3H, Ar-OCH_3), 3.49 (d, *J* = 9.6 Hz , 1H, C*H*B), 1.67 (dd, *J* = 6.8, 1.6 Hz, 3H, CHCHCH_3), 1.22 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 143.9, 130.5, 129.5, 123.9, 120.7, 113.8, 111.0, 83.6, 55.2, 24.9, 24.7, 24.6, 13.2. HRMS-EI (*m/z*): Calcd for [$C_{17}H_{25}BO_3$+], 287.1933; found: 287.1930.



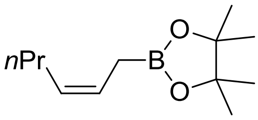
4,4,5,5-tetramethyl-2-((*Z*)-1-(naphthalen-3-yl)but-2-enyl)-1,3,2-dioxaborolane (9j)

In a nitrogen glovebox, **7h** (2.8 mg, 5.0 μmol, 2 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (12.5 μmol, 5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 2 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9j** and **9j'** (**9j : 9j'** = 94 : 6) as colorless oil (92 %). NMR data for compound **9j**: ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81-7.77 (m, 3H, Ar-*H*), 7.71 (s, 1H, Ar-*H*), 7.46-7.39 (m, 3H, Ar-*H*), 5.92-5.86 (m, 1H, CHC*H*CH), 5.66-5.61 (m, 1H, CHCHC*H*), 3.70 (d, *J* = 10.0 Hz , 1H, C*H*B), 1.73 (dd, *J* = 9.6, 1.6 Hz, 3H, CHCHCH_3), 1.24 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 134.0, 131.9, 130.4, 128.0, 127.6, 127.4, 126.0, 125.8, 125.0, 124.2, 83.7, 24.7, 24.6, 13.3. HRMS-EI (*m/z*): Calcd for [$C_{20}H_{25}BO_2$+], 307.1984; found: 307.1986.



2-((*Z*)-1-(benzo[d][1,3]dioxol-6-yl)but-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9k)

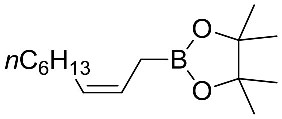
In a nitrogen glovebox, **7h** (1.4 mg, 2.5 μmol, 1 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (6.25 μmol, 2.5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 1 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9k** and **9k'** (**9k : 9k'** = 94 : 6) as colorless oil (93 %). NMR data for compound **9k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.78-6.77 (m, 1H, Ar-*H*), 6.73-6.68 (m, 2H, Ar-*H*), 5.89 (s, 2H, OCH_2O), 5.68-5.63 (m, 1H, CHC*H*CH), 5.56-5.48 (m, 1H, CHCHC*H*), 3.42 (d, *J* = 9.6 Hz, 1H, C*H*B), 1.65 (dd, *J* = 6.8, 1.6 Hz, 3H, $CHCHCH_3$), 1.22 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 145.4, 136.2, 130.8, 123.7, 120.9, 108.9, 108.4, 100.8, 83.6, 24.7, 24.6, 13.1. HRMS-EI (*m/z*): Calcd for [$C_{17}H_{23}BO_4$+], 301.1726; found: 301.1725.



(*Z*)-2-(hex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9l')

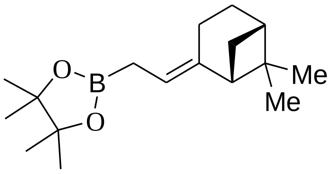
In a nitrogen glovebox, **7h** (1.4 mg, 2.5 μmol, 1 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (6.25 μmol, 2.5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 1 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9l** and **9l'** (**9l : 9l'** = 20 : 80) as colorless oil (80 %). NMR data for compound **9l'**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.53-5.31 (m, 2H, $CH_2CHCHCH_2$), 2.02-1.96 (m, 2H, CH_2CH_2CH), 1.67 (d, *J* = 8.0 Hz, 2H, CH_2B), 1.44-1.32 (m, 2H, CH_2CH_2CH), 1.24 (s, 12H, $C(CH_3)_2$), 0.92-0.87 (m, 3H, CH_3). ^{13}C NMR (101

MHz, $CDCl_3$) δ 129.9, 124.3, 83.3, 29.2, 24.9, 22.8, 13.9. These spectroscopic data correspond to reported data.[10]



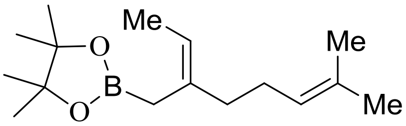
(*Z*)-2-(dec-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9m’)

In a nitrogen glovebox, **7h** (1.4 mg, 2.5 μmol, 1 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (6.25 μmol, 2.5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 1 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9m** and **9m’** (**9m : 9m’** = 25 : 75) as colorless oil (72 %). NMR data for compound **9m’**: ^1H NMR (400 MHz, $CDCl_3$) δ = 5.49-5.36 (m, 2H, $CH_2C\mathit{H}C\mathit{H}CH_2$), 2.03-1.97 (m, 2H, $CH_2C\mathit{H}_2CHCH$), 1.67-1.58 (m, 2H, $C\mathit{H}_2B$), 1.42-1.22 (m, 20H, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_2CH$, $C(C\mathit{H}_3)_2$), 0.88-0.85 (m, 3H, $C\mathit{H}_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.2, 124.1, 83.3, 32.1, 29.7, 29.4, 27.2, 24.9, 22.8, 14.2. HRMS-EI (*m/z*): Calcd for $[C_{16}H_{31}BO_2+]$, 265.2453; found: 265.2452.



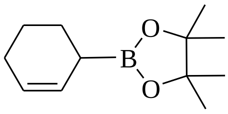
4,4,5,5-tetramethyl-2-((*E*)-2-((*1R,5S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-ylidene)ethyl)-1,3,2-dioxaborolane (9n’)

In a nitrogen glovebox, **7h** (2.8 mg, 5.0 μmol, 2 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (12.5 μmol, 5.0 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 2 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9n** and **9n’** (**9n : 9n’** = 2 : 98) as colorless oil (90 %). NMR data for compound **9n’**: ^1H NMR (400 MHz, $CDCl_3$) δ = 5.07-5.03 (m, 1H, $CH_2C\mathit{H}C$), 2.37-2.34 (m, 1H), 2.31-2.27 (m, 3H), 1.94-1.92 (m, 1H), 1.86-1.82 (m, 2H), 1.58-1.51 (m, 2H), 1.28 (d, *J* = 9.6 Hz, 1H), 1.22 (s, 12H, C(C*H*$_3$)$_2$), 1.18 (s, 3H), 0.68 (s, 3H) . ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.5, 115.2, 83.1, 52.4, 41.0, 40.8, 28.3, 26.2, 24.9, 24.8, 23.9, 22.1, 19.9. HRMS-EI (*m/z*): Calcd for [$C_{17}H_{29}BO_2$+]: 275.2297; found: 275.2295. These spectroscopic data correspond to reported data.^{2}



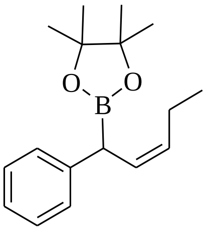
2-((*E*)-3-ethylidene-7-methyloct-6-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9o)

In a nitrogen glovebox, **7h** (2.8 mg, 5.0 μmol, 2 mol %), Et$_2$O (1 mL), diene (250 μmol, 1.0 equiv), NaBEt$_3$H (1M in toluene) (12.5 μmol, 5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 2 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **9o** and **9o'** (**9o : 9o'** = 85 : 15) as colorless oil (90 %). NMR data for compound **9o**: ^{1}H NMR (400 MHz, CDCl$_3$) δ =5.25-5.21 (m, 1H, C*H*CCH$_2$B), 5.11 (m, 1H, C*H*C(CH$_3$)$_2$), 2.06-2.01 (m, 4H), 1.67 (s, 5H), 1.60-1.55 (m, 6H), 1.23 (s, 12H, C(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.8, 131.3, 124.7, 117.4, 83.2, 39.7, 26.9, 25.8, 24.8, 17.8, 13.7. These spectroscopic data correspond to reported data.^{2}



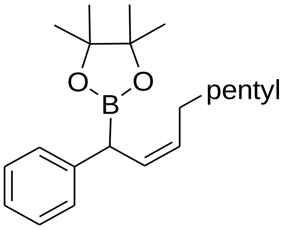
2-(cyclohex-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9p)

In a nitrogen glovebox, **7h** (1.4 mg, 2.5 μmol, 1 mol %), Et$_2$O (1 mL), diene (250 μmol, 1.0 equiv), NaBEt$_3$H (1M in toluene) (6.25 μmol, 2.5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 1 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the product **9p** as colorless oil (78 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 5.73-5.67 (m, 2H, C*H*C*H*), 2.00 (s, 2H), 1.78-1.69 (m, 2H), 1.67-1.57 (m, 3H), 1.24 (s, 12H, C(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 127.7, 126.2, 83.3, 25.1, 24.9, 24.8, 24.2, 22.7. HRMS-EI (*m/z*): Calcd for [$C_{12}H_{21}BO_2$+], 207.1671; found: 207.1669. These spectroscopic data correspond to reported data.[2]



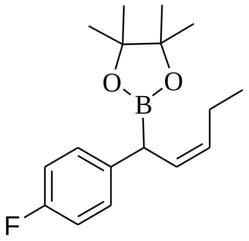
4,4,5,5-tetramethyl-2-((*Z*)-1-phenylpent-2-enyl)-1,3,2-dioxaborolane (11a)

In a nitrogen glovebox, **7e** (4.74 mg, 12.5 μmol, 5 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), magnesium (0.76 mg, 31.25 μmol, 12.5 equiv) and pinacolborane (63.99 mg, 73.4 μL, 0.263 mmol, 2.0 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 3 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **11a** and **11a'** (**11a : 11a'** = 88 : 12) as colorless oil (74 %). NMR data for compound **11a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28-7.22 (m, 4H, Ar-*H*), 7.16-7.12 (m, 1H, Ar-*H*), 5.70-5.64 (m, 1H, CHC*H*CH), 5.49-5.45 (m, 1H, CHCHC*H*), 3.49 (d, *J* = 10.0 Hz , 1H, C*H*B), 2.13- 2.07 (m, 2H, CHCH_2CH_3), 1.21 (s, 12H, C(CH_3)$_2$), 0.99-0.95 (m, 3H, CHCH_2CH_3),. ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 131.5, 129.1, 128.6, 128.2, 125.4, 83.6, 24.7, 24.6, 21.0, 14.4. HRMS-EI (*m/z*): Calcd for [$C_{17}H_{25}BO_2$+], 271.1984; found: 271.1981.



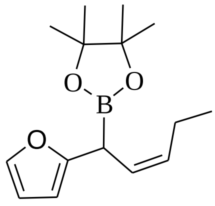
4,4,5,5-tetramethyl-2-((*Z*)-1-phenylnon-2-enyl)-1,3,2-dioxaborolane (11b)

In a nitrogen glovebox, **7e** (4.74 mg, 12.5 μmol, 5 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), magnesium (0.76 mg, 31.25 μmol, 12.5 equiv) and pinacolborane (63.99 mg, 73.4 μL, 0.263 mmol, 2.0 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 3 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **11b** and **11b'** (**11b : 11b'** = 83 : 17) as colorless oil (85 %). NMR data for compound **11b**: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.33-7.25 (m, 4H, Ar-*H*), 7.16-7.14 (m, 1H, Ar-*H*), 5.72-5.67 (m, 1H, CHC*H*CH), 5.49-5.43 (m, 1H, CHCHC*H*), 3.50 (d, *J* = 10.0 Hz, 1H, C*H*B), 2.11-2.06 (m, 2H, CHCH_2CH$_2$), 1.34-1.21 (m, 20H, CH$_2$(CH_2)$_4$CH$_3$, C(CH_3)$_2$), 0.89-0.86 (m, 3H, CH$_2$(CH$_2$)$_4$CH_3),. ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.4, 129.8, 129.6, 128.6, 128.2, 125.4, 83.6, 31.9, 29.7, 29.1, 27.6, 24.7, 24.6, 22.8, 14.3. HRMS-EI (*m/z*): Calcd for [$C_{21}H_{33}BO_2$+], 327.2610; found: 327.2609.



2-((*Z*)-1-(4-fluorophenyl)pent-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11c)

In a nitrogen glovebox, **7e** (4.74 mg, 12.5 μmol, 5 mol %), Et$_2$O (1 mL), diene (250 μmol, 1.0 equiv), magnesium (0.76 mg, 31.25 μmol, 12.5 equiv) and pinacolborane (63.99 mg, 73.4 μL, 0.263 mmol, 2.0 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 3 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1:20) to give the products **11c** and **11c'** (**11c : 11c'** = 88 : 12) as colorless oil (88 %). NMR data for compound **11c**: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.22-7.19 (m, 2H, Ar-*H*), 6.97-6.93 (m, 2H, Ar-*H*), 5.64-5.59 (m, 1H, CHC*H*CH), 5.50-5.44 (m, 1H, CHCHC*H*), 3.46 (d, *J* = 9.2 Hz , 1H, C*H*B), 2.13-2.06 (m, 2H, CHCH_2CH$_3$), 1.21 (s, 12H, C(CH_3)$_2$), 0,99-0.95 (m, 3H, CHCH$_2$CH_3),. ^{13}C NMR (101 MHz, CDCl$_3$) δ 161.1 (d, *J* = 244.5 Hz), 138.0 (d, *J* = 3.0 Hz), 131.7, 129.5 (d, *J* = 8.4 Hz), 128.9, 115.3 (d, *J* = 21.4 Hz), 83.7, 24.7, 24.6, 20.9, 14.3. ^{19}F NMR (376 MHz, CDCl$_3$) δ -116.1. HRMS-EI (*m/z*): Calcd for [$C_{17}H_{24}BFO_2$+], 289.1890; found: 289.1889.

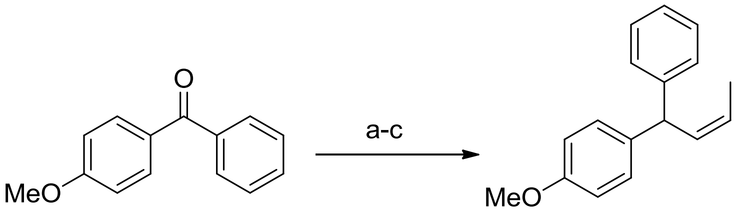


2-((*Z*)-1-(furan-2-yl)pent-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11d)

In a nitrogen glovebox, **7e** (4.74 mg, 12.5 μmol, 5 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), magnesium (0.76 mg, 31.25 μmol, 12.5 equiv) and pinacolborane (63.99 mg, 73.4 μL, 0.263 mmol, 2.0 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 3 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/*n*-hexane (1 : 20) to give the products **11d** and **11d'** (**11d : 11d'** = 95 : 5) as colorless oil (62 %). NMR data for compound **11d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.28 (m, 1H, Ar-*H*), 6.28-6.27 (m, 1H, Ar-*H*), 6.05-6.04 (m, 1H, Ar-*H*), 5.56-5.47 (m, 2H, CHC*H*C*H*), 3.57 (d, *J* = 8.4 Hz , 1H, C*H*B), 2.15- 2.08 (m, 2H, $CHCH_2CH_3$), 1.26 (s, 12H, $C(CH_3)_2$), 0.99 (t, *J* = 15.2 Hz, 7.6 Hz, 3H, $CHCH_2CH_3$),. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 141.1, 132.5, 125.5, 110.3, 104.8, 83.8, 24.7, 24.6, 20.9, 14.3. HRMS-EI (*m/z*): Calcd for $[C_{15}H_{23}BO_3+]$, 261.1777; found: 261.1772.

5. Suzuki-Miyaura Cross–Couplings of Secondary Benzylic and Allylic Boronic Esters

Synthesis of (*Z*)-1-methoxy-4-(1-phenylbut-2-en-1-yl)benzene (14b’) [11]



Reagents and conditions

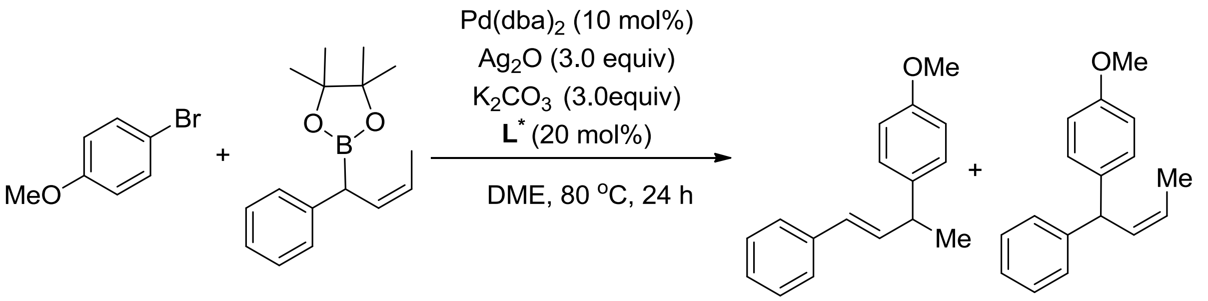
a) (methoxymethyl)triphenylphosphonium chloride, THF, -78 °C then LDA, then 4-methoxybenzophenone

b) NaI, H_2SO_4, 1,4-dioxane, △

c) ethyltriphenylphosphonium bromine, THF, -78 °C then *n*BuLi, then (4-methoxyphenyl)phenylacetaldehyde

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33-7.29 (m, 2H, Ar-*H*), 7.23-7.19 (m, 3H, Ar-*H*), 7.15-7.11 (m, 2H, Ar-*H*), 6.87-6.84 (m, 2H, Ar-*H*), 5.92-5.86 (m, 1H, ArCHC*H*CH), 5.70-5.66 (m, 1H, ArCHCHC*H*), 4.99 (d, *J* = 9.6 Hz, 1H, ArC*H*CHCH), 3.80 (s, 3H, Ar-OC*H*$_3$), 1.75 (dd, *J* = 6.8, 1.6 Hz, 3H, CHCHC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 145.1, 136.9, 133.3, 129.3, 128.5, 128.3, 126.2, 124.5, 113, 9, 55.4, 47.3, 13.2. HRMS-EI (*m/z*): Calcd for [$C_{17}H_{18}O$], 238.1358; found: 238.1357.

Table S2. Evaluation of Ligands for Pd-Catalyzed Suzuki couping reaction.[a]

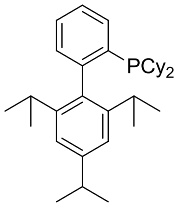
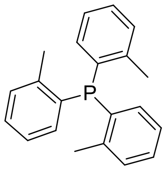
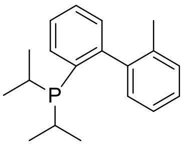
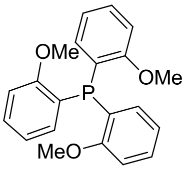
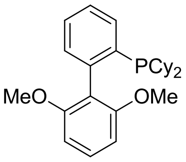
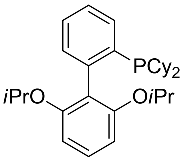
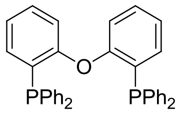
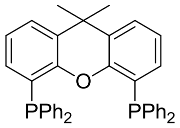


13b 1.0 equiv

9a 1.5 equiv

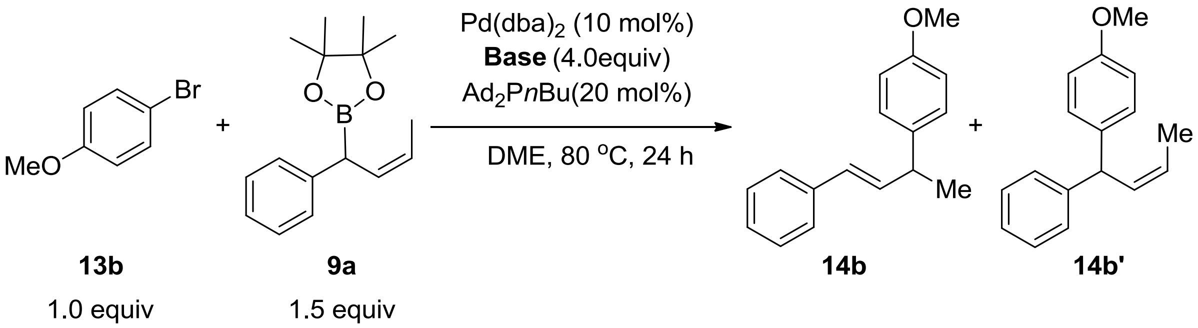
14b

14b'

Entry	L*	**14b'**/**14b**	Yield of **14b** (%)^b	Yield of **14b'** (%)^b
1		15 : 75	23	4
2		7 : 93	25	2
3	**Ad_2PnBu**	**12 : 88**	**44**	**6**
4		15 : 85	11	2
5	$(tBu)_3\overset{\oplus}{P}H\overset{\ominus}{B}F_4$	< 1 :99	23	< 1
6	$P(tBu)_3$	< 1 :99	15	< 1
7		< 1 :99	17	< 1
8		7 : 93	14	1
9		19 : 71	17	4
10	PPh_3	< 1 :99	12	< 1
11		8 : 92	23	2
12		< 1 :99	14	< 1
13	BINAP	22 : 88	7	2
14	dppp	< 1 :99	15	< 1
15	dppe	6 : 94	15	1

[a] Conditions : 1mL DME, substrate : 1-bromo-4-methoxybenzene (101.4 μmol), 10 mol % $Pd(dba)_2$, 20 mol % L*. T = 80 ^oC. [b] Yield of **14b** and **14b'** determined relative to Mesitylene as external standard by ^1H NMR.

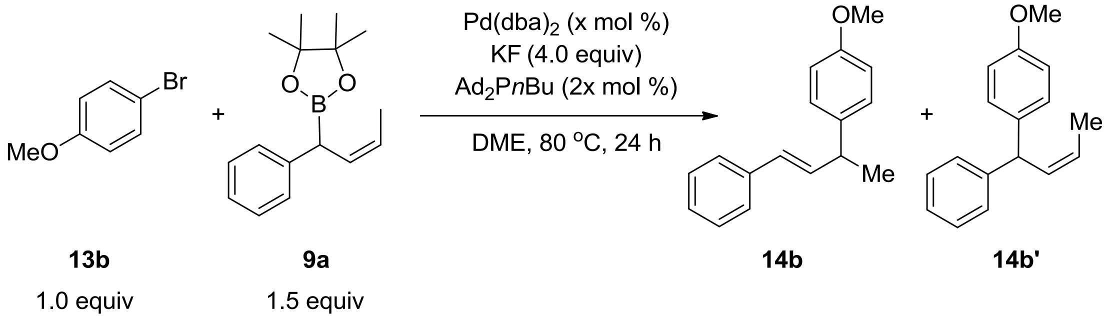
Table S3. Evaluation of Bases for Pd-Catalyzed Suzuki couping reaction.[a]



Entry	**Base**	**14b'/14b**	Yield of **14b** (%)[b]	Yield of **14b'** (%)[b]
1	K_2CO_3	< 1 : 99	30	< 1
2	K_3PO4	17 : 83	29	6
3	CsF	< 1 : 99	20	< 1
4	Cs_2CO_3	< 1 : 99	30	< 1
5	KOH	9 : 91	10	1
6	**KF**	< 1 : 99	**90**	< 1
7	$NaHCO_3$	--	< 10	< 1
8	$NaCOOF_3$	--	< 10	< 1
9	Ag_2O	13 : 87	39	6
10	NaOH	< 1 : 99	15	< 1
11	Ag_2CO_3	15 : 85	45	8
12	$AgNO_3$	--	< 10	< 1
13	K_2HPO_4	--	< 10	< 1

[a] Conditions : 1mL DME, substrate : 1-bromo-4-methoxybenzene (101.4 μmol), 10 mol% $Pd(dba)_2$,20 mol% Ad_2P*n*Bu. T = 80 °C. [b] Yield of **14b** and **14b'** determined relative to Mesitylene as external standard by ^1H NMR.

Table S4. Evaluation of Catalyst loading for Pd-Catalyzed Suzuki couping reaction.[a]

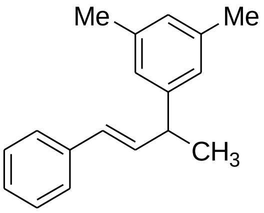


Entry	$Pd(dba)_2$ (x mol%)	Ad_2PnBu (2x mol%)	**14b'/14b**	Yield of **14b** (%)[b]	Yield of **14b'** (%)[b]
1	10	20	< 1 : 99	89	< 1
2	5	10	< 1 : 99	88	< 1
3	**2**	**4**	< 1 : 99	88	< 1

[a] Conditions : 1 mL DME, substrate : 1-bromo-4-methoxybenzene (101.4 μmol). T = 80 °C.

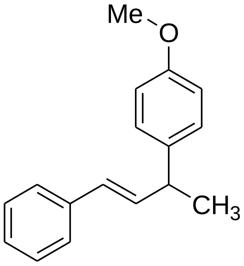
Yield of **14b** and **14b'** determined relative to Mesitylene as external standard by ^{1}H NMR.

Substrate Scope for Pd-Catalyzed Suzuki couping reaction



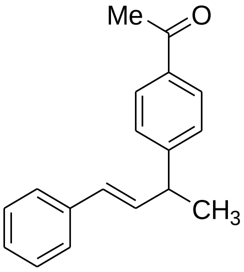
1,3-dimethyl-5-((*E*)-4-phenylbut-3-en-2-yl)benzene (14a)

In a nitrogen-atmosphere glovebox, $Pd(dba)_2$ (2.4 mg, 0.004 mmol, 2 mol %.), Ad_2P*n*Bu (3.0 mg, 0.008 mmol, 4mol %.), KF (47.2 mg, 0.405 mmol, 4.0 equiv.), 1-bromo-3,5-dimethylbenzene (37.54 mg, 0.203 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-2-((*Z*)-1-phenylbut-2-enyl)-1,3,2-dioxaborolane (**9a**, 78.4 mg, 0.304 mmol, 1.5 equiv.) and DME (1.0 mL) were added to a 5 mL Schlenk tube. The tube was sealed with a teflon plug, and then heated at 80 ℃ for 24 h. Once cooled, the reaction solution was concentrated in vacuum. The crude mixture was purified by silica gel chromatography (v/v, EA : PE = 1 : 100) to give the product **14a** as colorless oil (44 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43-7.42 (m, 2H, Ar-*H*), 7.42-7.40 (m, 2H, Ar-*H*), 7.35-7.31 (m, 1H, Ar-*H*), 7.26-7.22 (m, 3H, Ar-*H*), 6.93-6.40 (m, 2H, C*H*C*H*CHCH$_3$), 3.63-3.58 (m, 1H, CHCHC*H*CH$_3$), 2.35 (s, 6H, Ar-(C*H*$_3$)$_2$), 1.49 (d, *J* = 7.2 Hz, 3H, CHCHCHC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.8, 138.1, 137.8, 135.5, 128.6, 128.3, 128.0, 127.1, 126.3, 125.2, 42.6, 21.5, 21.4. HRMS-EI (*m/z*): Calcd for [$C_{18}H_{20}$], 236.1556; found: 236.1562.



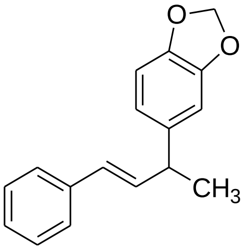
1-methoxy-4-((*E*)-4-phenylbut-3-en-2-yl)benzene (14b)

In a nitrogen-atmosphere glovebox, Pd(dba)$_2$ (2.4 mg, 0.004 mmol, 2 mol %.), Ad$_2$P*n*Bu (3.0 mg, 0.008 mmol, 4mol %.), KF (47.2 mg, 0.405 mmol, 4.0 equiv.), 1-bromo-4-methoxybenzene (37.92 mg, 0.203 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-2-((*Z*)-1-phenylbut-2-enyl)-1,3,2-dioxaborolane (**9a**, 78.4 mg, 0.304 mmol, 1.5 equiv.) and DME (1.0 mL) were added to a 5 mL Schlenk tube. The tube was sealed with a teflon plug, and then heated at 80 ℃ for 24 h. Once cooled, the reaction solution was concentrated in vacuum. The crude mixture was purified by silica gel chromatography (v/v, EA : PE = 1 : 100) to give the product **14b** as colorless oil (44 mg, 90 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.37-7.35 (m, 2H, Ar-*H*), 7.31-7.27 (m, 2H, Ar-*H*), 7.22-7.18 (m, 3H, Ar-*H*), 6.89-6.86 (m, 2H, Ar-*H*), 6.43-6.34 (m, 2H, C*H*C*H*CHCH$_3$), 3.80 (s, 3H, OC*H*$_3$), 3.64-3.58 (m, 1H, CHCHC*H*CH$_3$), 1.46-1.44 (d, *J* = 6.8 Hz, 3H, CHCHCHC*H*$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ = 158.1, 137.8, 137.7, 135.7, 128.6, 128.4, 127.1, 126.3, 114.0, 55.4, 41.8, 21.4. These spectroscopic data correspond to reported data.[12]



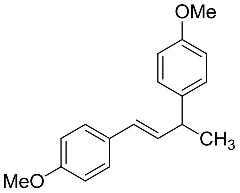
(*E*)-1-(4-(4-phenylbut-3-en-2-yl)phenyl)ethanone (14c)

In a nitrogen-atmosphere glovebox, Pd(dba)$_2$ (2.4 mg, 0.004 mmol, 2 mol %.), Ad$_2$P*n*Bu (3.0 mg, 0.008 mmol, 4mol %), KF (47.2 mg, 0.405 mmol, 4.0 equiv.), 1-(4-bromophenyl)ethanone (41.2 mg, 0.203 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-2-((*Z*)-1-phenylbut-2-enyl)-1,3,2-dioxaborolane (**9a**, 78.4 mg, 0.304 mmol, 1.5 equiv.) and DME (1.0 mL) were added to a 5 mL Schlenk tube. The tube was sealed with a teflon plug, and then heated at 80 ℃ for 24 h. Once cooled, the reaction solution was concentrated in vacuum. The crude mixture was purified by silica gel chromatography (v/v, EA : PE = 1 : 100) to give the product **14c** as colorless oil (46 mg, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95-7.92 (m, 2H, Ar-*H*), 7.39-7.35 (m, 4H, Ar-*H*), 7.32-7.29 (m, 2H, Ar-*H*), 7.24-7.20 (m,1H, Ar-*H*), 6.44 (d, *J* = 16.0 Hz, 1H, C*H*CHCHCH$_3$), 6.36 (dd, *J* = 15.6, 6.4 Hz, 1H, CHC*H*CHCH$_3$), 3.73-3.70 (m, 1H, CHCHC*H*CH$_3$), 2.60 (s, 3H, OCC*H*$_3$), 1.49 (d, *J* = 6.8 Hz, 3H, CHCHCHC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 198.0, 151.4, 137.3, 135.5, 134.1, 129.4, 128.8, 128.7, 127.7, 127.4, 126.3, 42.7, 26.7, 21.1. These spectroscopic data correspond to reported data.[13]



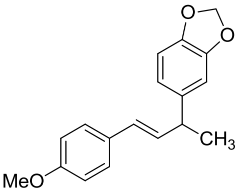
(*E*)-5-(4-phenylbut-3-en-2-yl)benzo[*d*][1,3]dioxole (14d)

In a nitrogen-atmosphere glovebox, Pd(dba)$_2$ (2.4 mg, 0.004 mmol, 2 mol %.), Ad$_2$P*n*Bu (3.0 mg, 0.008 mmol, 4mol %.), KF (47.2 mg, 0.405 mmol, 4.0 equiv.), 5-bromobenzo[*d*][1,3]dioxole (41.6 mg, 0.203 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-2-((*Z*)-1-phenylbut-2-enyl)-1,3,2-dioxaborolane (**9a**, 78.4 mg, 0.304 mmol, 1.5 equiv.) and DME (1.0 mL) were added to a 5 mL Schlenk tube. The tube was sealed with a teflon plug, and then heated at 80 ℃ for 24 h. Once cooled, the reaction solution was concentrated in vacuum. The crude mixture was purified by silica gel chromatography (v/v, EA : PE = 1 : 100) to give the product **14d** as colorless oil (44 mg, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37-7.35 (m, 2H, Ar-*H*), 7.31-7.27 (m, 2H, Ar-*H*), 7.22-7.18 (m, 1H, Ar-*H*), 6.78-6.76 (m, 2H, Ar-*H*), 6.74-6.71 (m, 1H, Ar-*H*), 6.40 (d, *J* = 16.0 Hz, 1H, C*H*CHCHCH$_3$), 6.36-6.30 (m, 1H, CHC*H*CHCH$_3$), 5.93 (s, 2H, OC*H*$_2$O), 3.59-3.54 (m, 1H, CHCHC*H*CH$_3$), 1.43 (d, *J* = 6.8 Hz, 3H, CHCHCHC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.8, 146.0, 139.8, 137.6, 135.4, 128.6, 126.5, 127.2, 126.3, 120.2, 108.3, 108.0, 101.0, 42.4, 21.5. HRMS-EI (*m/z*): Calcd for [$C_{17}H_{16}O_2$+], 252.1150; found: 252.1152.



(*E*)-1,3-bis(4-methoxyphenyl)but-1-ene (14e)

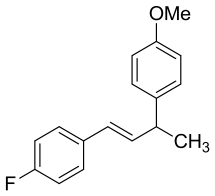
In a nitrogen-atmosphere glovebox, Pd(dba)$_2$ (2.4 mg, 0.004 mmol, 2 mol %.), Ad$_2$P*n*Bu (3.0 mg, 0.008 mmol, 4 mol %.), KF (47.2 mg, 0.405 mmol, 4.0 equiv.), 1-bromo-4-methoxybenzene (37.92 mg, 0.203 mmol, 1.0 equiv.), 2-((*Z*)-1-(4-methoxyphenyl)but-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9b**, 78.4 mg, 0.304 mmol, 1.5 equiv.) and DME (1.0 mL) were added to a 5 mL Schlenk tube. The tube was sealed with a teflon plug, and then heated at 80 ℃ for 24 h. Once cooled, the reaction solution was concentrated in vacuum. The crude mixture was purified by silica gel chromatography (v/v, EA : PE = 1 : 100) to give the product **14e** as colorless oil (47 mg, 86 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.30-7.28 (m, 2H, Ar-*H*), 7.21-7.18 (m, 2H, Ar-*H*), 6.88-6.82 (m, 4H, Ar-*H*), 6.34 (d, *J* = 16.0 Hz, 1H, C*H*CHCHCH$_3$), 6.22 (dd, *J* = 16.0, 6.4 Hz, 1H, CHC*H*CHCH$_3$), 3.80 (s, 6H, OC*H*$_3$, OC*H*$_3$), 3.60-3.56 (m, 1H, CHCHC*H*CH$_3$), 1.43 (d, *J* = 7.2 Hz, 3H, CHCHCHC*H$_3$*). ^{13}C NMR (101 MHz, CDCl$_3$) δ = 158.9, 158.1, 138.1, 133.6, 130.5, 128.3, 127.7, 127.3, 114.0, 113.9, 55.4, 41.8, 21.6. These spectroscopic data correspond to reported data.[14]



***(E)*-5-(4-(4-methoxyphenyl)but-3-en-2-yl)benzo[d][1,3]dioxole (14f)**

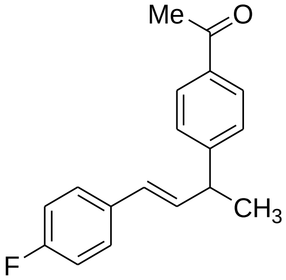
In a nitrogen-atmosphere glovebox, Pd(dba)$_2$ (2.4 mg, 0.004 mmol, 2 mol %), Ad$_2$P*n*Bu (3.0 mg, 0.008 mmol, 4 mol %), KF (47.2 mg, 0.405 mmol, 4.0 equiv.), 5-bromobenzo[*d*][1,3]dioxole (41.6 mg, 0.203 mmol, 1.0 equiv.), 2-((Z)-1-(4-methoxyphenyl)but-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9b**, 78.4 mg, 0.304 mmol, 1.5 equiv.) and DME (1.0 mL) were added to a 5 mL Schlenk tube. The tube was sealed with a teflon plug, and then heated at 80 ℃ for 24 h. Once cooled, the reaction solution was concentrated in vacuum. The crude mixture was purified by silica gel chromatography (v/v, EA : PE = 1 :

100) to give the product **14f** as colorless oil (48.1 mg, 84 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.31-7.28 (m, 2H, Ar-*H*), 6.86-6.82 (m, 2H, Ar-*H*), 6.78-6.72 (m, 3H, Ar-*H*), 6.36-6.32 (m, 1H, C*H*CHCHCH$_3$), 6.23-6.17 (dd, 1H, *J* = 16.0, 6.8 Hz, CHC*H*CHCH$_3$), 5.93 (s, 2H, OC*H*$_2$O), 3.80 (s, 3H, OC*H*$_3$), 3.57-3.53 (m, 1H, CHCHC*H*CH$_3$), 1.42 (d, *J* = 6.8 Hz, 3H, CHCHCHC*H*$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ = 158.9, 147.8, 145.9, 140.1, 133.3, 130.4, 127.9, 127.4, 120.2, 114.0, 108.3, 108.0, 101.0, 55.4, 42.3, 21.6. HRMS-EI (*m/z*): Calcd for [$C_{18}H_{18}O_3$+], 282.1256; found: 282.1260.



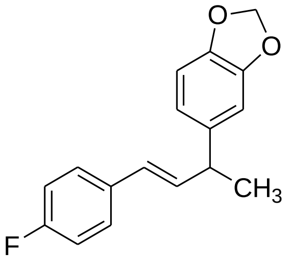
(*E*)-1-fluoro-4-(3-(4-methoxyphenyl)but-1-en-1-yl)benzene (14g)

In a nitrogen-atmosphere glovebox, Pd(dba)$_2$ (2.4 mg, 0.004 mmol, 2 mol %.), Ad$_2$P*n*Bu (3.0 mg, 0.008 mmol, 2 mol %.), KF (47.2 mg, 0.405 mmol, 4.0 equiv.), 1-bromo-4-methoxybenzene (37.92 mg, 0.203 mmol, 1.0 equiv), 2-((*Z*)-1-(4-fluorophenyl)but-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4e**, 84.0 mg, 0.304 mmol, 1.5 equiv.) and DME (1.0 mL) were added to a 5 mL Schlenk tube. The tube was sealed with a teflon plug, and then heated at 80 ℃ for 24 h. Once cooled, the reaction solution was concentrated in vacuum. The crude mixture was purified by silica gel chromatography (v/v, EA : PE = 4 : 100) to give the product **14g** as colorless oil (43 mg, 83 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.33-7.28 (m, 2H, Ar-*H*), 7.20-7.18 (m, 2H, Ar-*H*), 7.00-6.95 (m, 2H, Ar-*H*), 6.89-6.85 (m, 2H, Ar-*H*), 6.35 (d, *J* = 16.0 Hz, 1H, C*H*CHCHCH$_3$), 6.27 (dd, 1H, *J* = 16.0, 6.4 Hz, CHC*H*CHCH$_3$), 3.80 (s, 3H, Ar-OC*H*$_3$), 3.62-3.55 (m, 1H, CHCHC*H*CH$_3$), 1.44 (d, *J* = 6.8 Hz, 3H, CHCHCHC*H*$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ = 162.0 (d, *J* = 246.9 Hz), 158.0, 137.6, 135.4 (d, *J* = 2.3 Hz), 133.7 (d, *J* = 3.4 Hz), 128.2, 127.5 (d, *J* = 7.9 Hz), 127.0, 115.3 (d, *J* = 21.4 Hz), 113.9, 55.3, 41.7, 21.3. ^{19}F NMR (376 MHz, CDCl$_3$) δ -115.6. HRMS-EI (*m/z*): Calcd for [$C_{17}H_{17}FO$+], 256.1263; found: 256.1259.



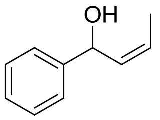
(E)-1-(4-(4-(4-fluorophenyl)but-3-en-2-yl)phenyl)ethanone (14h)

In a nitrogen-atmosphere glovebox, Pd(dba)$_2$ (2.4 mg, 0.004 mmol, 2 mol %.), Ad$_2$P*n*Bu (3.0 mg, 0.008 mmol, 2 mol %.), KF (47.2 mg, 0.405 mmol, 4.0 equiv.), 5-bromobenzo[*d*][1,3]dioxole (41.6 mg, 0.203 mmol, 1.0 equiv), 2-((*Z*)-1-(4-fluorophenyl)but-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9e**, 84.0 mg, 0.304 mmol, 1.5 equiv.) and DME (1.0 mL) were added to a 5 mL Schlenk tube. The tube was sealed with a teflon plug, and then heated at 80 ℃ for 24 h. Once cooled, the reaction solution was concentrated in vacuum. The crude mixture was purified by silica gel chromatography (v/v, EA : PE = 4 : 100) to give the product **14h** as colorless oil (48 mg, 88 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.94-7.91 (m, 2H, Ar-*H*), 7.37-7.35 (m, 2H, Ar-*H*), 7.34-7.29 (m, 2H, Ar-*H*), 7.01-6.95 (m, 2H, Ar-*H*), 6.39 (d, *J* = 16.0 Hz, 1H, C*H*CHCHCH$_3$), 6.26 (dd, 1H, *J* = 15.6, 6.4Hz, CHC*H*CHCH$_3$), 3.73-3.66 (m, 1H, CHCHC*H*CH$_3$), 2.59 (s, 3H, OCC*H*$_3$), 1.48 (d, *J* = 6.8 Hz, 3H, CHCHCHC*H*$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ = 197.9, 162.2 (d, *J* = 247.2 Hz), 151.3, 135.5, 133.9 (d, *J* = 2.6 Hz), 133.5 (d, *J* = 3.3 Hz), 128.8, 128.2, 127.7 (d, *J* = 7.9 Hz), 127.6, 115.5 (d, *J* = 21.8 Hz), 42.7, 26.7, 21.1. ^{19}F NMR (376 MHz, CDCl$_3$) δ -115.0. HRMS-EI (*m/z*): Calcd for [$C_{18}H_{17}FO$+], 268.1263; found: 268.1262.



(*E*)-5-(4-(4-fluorophenyl)but-3-en-2-yl)benzo[d][1,3]dioxole (14i)

In a nitrogen-atmosphere glovebox, Pd(dba)$_2$ (2.4 mg, 0.004 mmol, 2 mol %.), Ad$_2$P*n*Bu (3.0 mg, 0.008 mmol, 2 mol %.), KF (47.2 mg, 0.405 mmol, 4.0 equiv.), 5-bromobenzo[*d*][1,3]dioxole (41.6 mg, 0.203 mmol, 1.0 equiv.), 2-((*Z*)-1-(4-fluorophenyl)but-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9e**, 84.0 mg, 0.304 mmol, 1.5 equiv.) and DME (1.0 mL) were added to a 5 mL Schlenk tube. The tube was sealed with a teflon plug, and then heated at 80 ℃ for 24 h. Once cooled, the reaction solution was concentrated in vacuum. The crude mixture was purified by silica gel chromatography (v/v, EA : PE = 1 : 100) to give the product **14i** as colorless oil (47 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33-7.28 (m, 2H, Ar-*H*), 7.00-6.95 (m, 2H, Ar-*H*), 6.78-6.76 (m, 2H, Ar-*H*), 6.73-6.70 (m, 1H, Ar-*H*), 6.35 (d, *J* = 16.0 Hz, 1H, C*H*CHCHCH$_3$), 6.27-6.22 (m, 1H, CHC*H*CHCH$_3$), 5.93 (s, 2H, OC*H*$_2$O), 3.59-3.52 (m, 1H, CHCHC*H*CH$_3$), 1.42 (d, *J* = 6.8 Hz, 3H, CHCHCHC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.1 (d, *J* = 246.8 Hz), 147.8, 146.0, 139.7, 135.2 (d, *J* = 2.2 Hz), 133.8 (d, *J* = 3.3 Hz), 127.7 (d, *J* = 7.9 Hz), 127.4, 120.2, 115.4 (d, *J* = 21.8 Hz), 108.3, 107.9, 101.0, 42.4, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.4. HRMS-EI (*m/z*): Calcd for [$C_{17}H_{15}FO_2$+], 270.1056; found: 270.1055.



(*Z*)-1-phenylbut-2-en-1-ol (12)

In a nitrogen glovebox, **7h** (1.4 mg, 2.5 μmol, 1 mol %), Et_2O (1 mL), diene (250 μmol, 1.0 equiv), $NaBEt_3H$ (1M in toluene) (6.25 μmol, 2.5 mol %) and pinacolborane (33.6 mg, 38 μL, 263 μmol, 1.05 equiv) were charged in a vial (8 mL). Then the reaction mixture was stirred at 23 ℃ for 1 h and was quenched by exposing the solution to air. In air, NaOH (3.0 M in H_2O, 1.15 mL), H_2O_2 (30% in H_2O, 0.87 mL) and THF (2 ml) at 0 ^{o}C (ice/water) was added to the reaction. The reaction mixture was stirred at 25 ℃ for 4 h, at which time the vial was cooled to 0 ℃ (ice/water) and was added saturated aqueous $Na_2S_2O_3$(1.16 mL). The aqueous layer was extracted with EA (2 x 5 mL) and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (v/v, EA : PE = 1: 10) to give the title compound as a colorless oil (80 % over 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 4H, Ar-*H*), 7.27-7.23 (m, 1H, Ar-*H*), 5.68-5.58 (m, 2H, CHC*H*C*H*CH$_3$), 5.54 (d, *J* = 7.2 Hz, 1H, C*H*CHCHCH$_3$), 2.19 (s, 1H, CHO*H*), 1.77 (dd, *J* = 5.2, 0.8 Hz, 3H, CHCHCHC*H*$_3$). These spectroscopic data correspond to reported data.[15]

6. Crystallographic Data

Table S5-1. Crystal data and structure refinement for $C_{20}H_{26}Cl_2FeN_2$ (Complex 4)

Empirical formula	$C_{20}H_{26}Cl_2FeN_2$	Formula weight	421.18
Temperature	140(2) K	Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2 (1)/n		
Unit cell dimensions	a = 9.0055(13) A	alpha = 90 deg.	
	b = 15.940(2) A	beta = 90.178(3) deg.	
	c = 14.422(2) A	gamma = 90 deg.	
Volume	2070.3(5) A^3	Z, Calculated density	4, 1.351 Mg/m^3
Absorption coefficient	0.991 mm^-1	F (000)	880
Crystal size	0.18 x 0.13 x 0.02 mm	Theta range for data collection	1.90 to 33.11 deg.
Limiting indices	-12<=h<=13, -24<=k<=24, -16<=l<=21		
Reflections collected / unique	23426 / 7729 [R(int) = 0.0750]		
Completeness to theta = 33.11	98.2 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.9804 and 0.8417		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	7729 / 0 / 232		
Goodness-of-fit on F^2	1.074		
Final R indices [I>2sigma(I)]	R1 = 0.0521, wR2 = 0.1000		
R indices (all data)	R1 = 0.0996, wR2 = 0.1152		
Largest diff. peak and hole	0.627 and -0.744 e.A^-3		

Table S5-2. Crystal data and structure refinement for $C_{32} H_{35} Cl_2 Fe N_2 P$ (Complex 5)

Empirical formula	C32 H35 Cl2 Fe N2 P		
Formula weight	605.34	Temperature	140(2) K
Wavelength	0.71073 A	Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 12.5511(10) A alpha = 90 deg.		
	b = 14.2462(12) A beta = 98.210(2) deg.		
	c = 17.4859(14) A gamma = 90 deg.		
Volume	3094.5(4) A^3	Z, Calculated density	4, 1.299 Mg/m^3
Absorption coefficient	0.735 mm^-1	F (000)	1264
Crystal size	0.26 x 0.16 x 0.08 mm	Theta range for data collection	1.64 to 31.31 deg.
Limiting indices	-13<=h<=18, -20<=k<=20, -25<=l<=24		
Reflections collected / unique	31842 / 10097 [R(int) = 0.0373]		
Completeness to theta = 31.31	99.7 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.9436 and 0.8319		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	10097 / 0 / 348		
Goodness-of-fit on F^2	1.082		
Final R indices [I>2sigma(I)]	R1 = 0.0342, wR2 = 0.0842		
R indices (all data)	R1 = 0.0546, wR2 = 0.0926		
Largest diff. peak and hole	0.437 and -0.268 e.A^-3		

Table S5-3. Crystal data and structure refinement for $C_{29}H_{29}Cl_2FeN_2P$ (Complex 7e)

Empirical formula	C29 H29 Cl2 Fe N2 P		
Formula weight	563.26	Temperature	173(2) K
Wavelength	0.71073 A	Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 17.631(5) A alpha = 90 deg.		
	b = 10.038(3) A beta = 111.334(5) deg.		
	c = 16.442(4) A gamma = 90 deg.		
Volume	2710.6(12) A^3		
Z, Calculated density	4, 1.380 Mg/m^3		
Absorption coefficient	0.833 mm^-1	F (000)	1168
Crystal size	0.165 x 0.134 x 0.048 mm		
Theta range for data collection	2.38 to 25.50 deg.		
Limiting indices	-21<=h<=21, -12<=k<=12, -19<=l<=19		
Reflections collected / unique	17978 / 5022 [R(int) = 0.1228]		
Completeness to theta = 25.50	99.4 %		
Absorption correction	Multi_scan		
Max. and min. transmission	0.7456 and 0.5898		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	5022 / 10 / 336		
Goodness-of-fit on F^2	1.093		
Final R indices [I>2sigma(I)]	R1 = 0.0744, wR2 = 0.1682		
R indices (all data)	R1 = 0.1291, wR2 = 0.1931		
Largest diff. peak and hole	1.114 and -0.504 e.A^-3		

7. References

(1) Shimada, S.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Angew. Chem. Int. Ed.* **2001**, *40*, 2168.

(2) Wu, J. Y.; Moreau, B. t.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 12915.

(3) Battistuzzi, G.; Cacchi, S.; Fabrizi, G. *Org. Lett.* **2003**, *5*, 777.

(4) Mundal, D. A.; Lutz, K. E.; Thomson, R. J. *Org. Lett.* **2008**, *11*, 465.

(5) Preuß, T.; Saak, W.; Doye, S. *Chem. Eur. J.* **2013**, *19*, 3833.

(6) Bohn, M. A.; Schmidt, A.; Hilt, G.; Dindaroğlu, M.; Schmalz, H.-G. *Angew. Chem. Int. Ed.* **2011**, *50*, 9689.

(7) Chen, J.; Che, C.-M. *Angew. Chem. Int. Ed.* **2004**, *43*, 4950.

(8) Dong, D.-J.; Li, Y.; Wang, J.-Q.; Tian, S.-K. *Chem. Commun.* **2011**, *47*, 2158.

(9) Tamura, R.; Saegusa, K.; Kakihana, M.; Oda, D. *J. Org. Chem.* **1988**, *53*, 2723.

(10) Zhang, P.; Roundtree, I. A.; Morken, J. P. *Org. Lett.* **2012**, *14*, 1416.

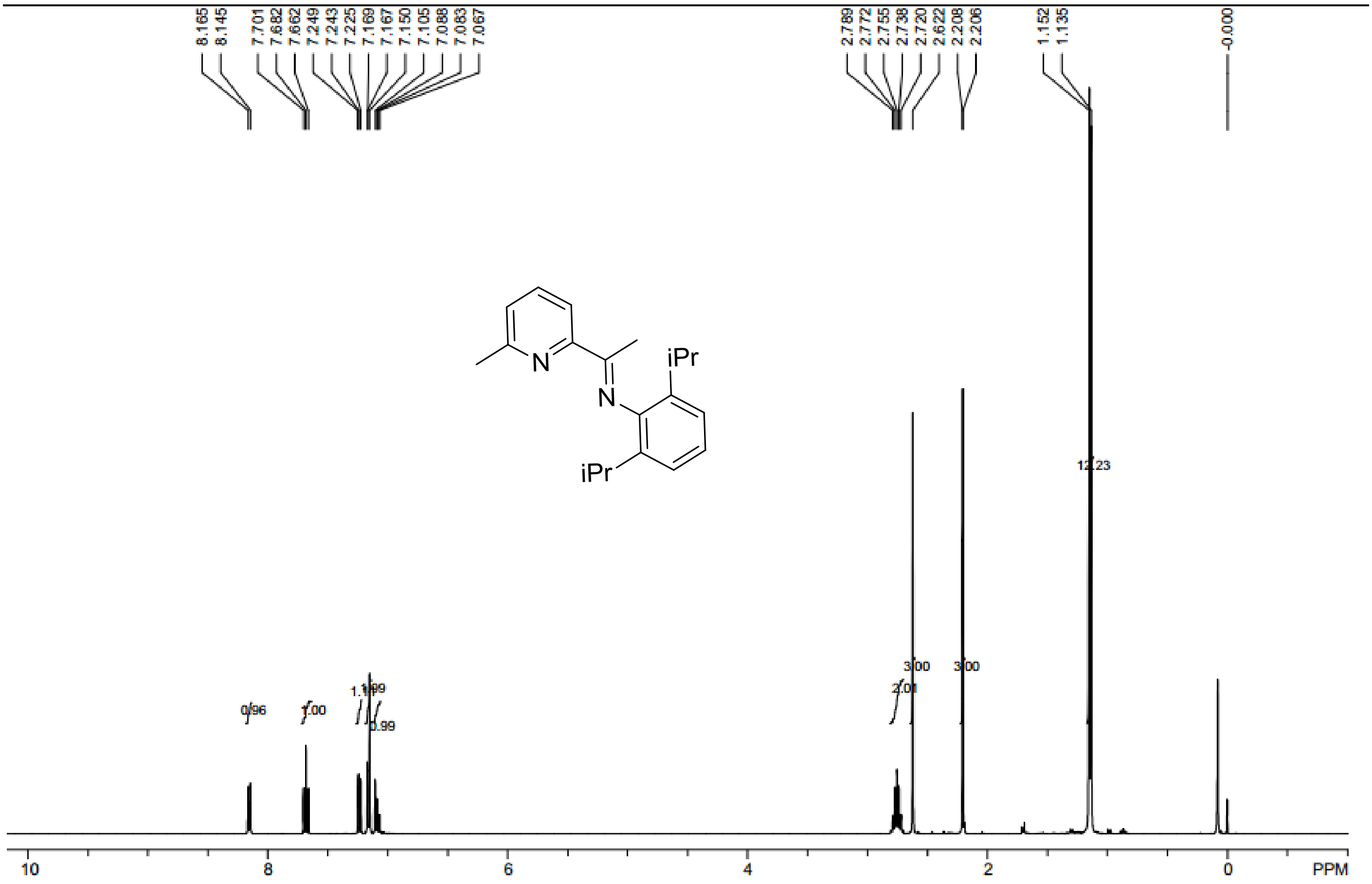
(11) Seiders, J. R.; Wang, L.; Floreancig, P. E. *J. Am. Chem. Soc.* **2003**, *125*, 2406.

(12) Liao, L.; Sigman, M. S. *J. Am. Chem. Soc.* **2010**, *132*, 10209.

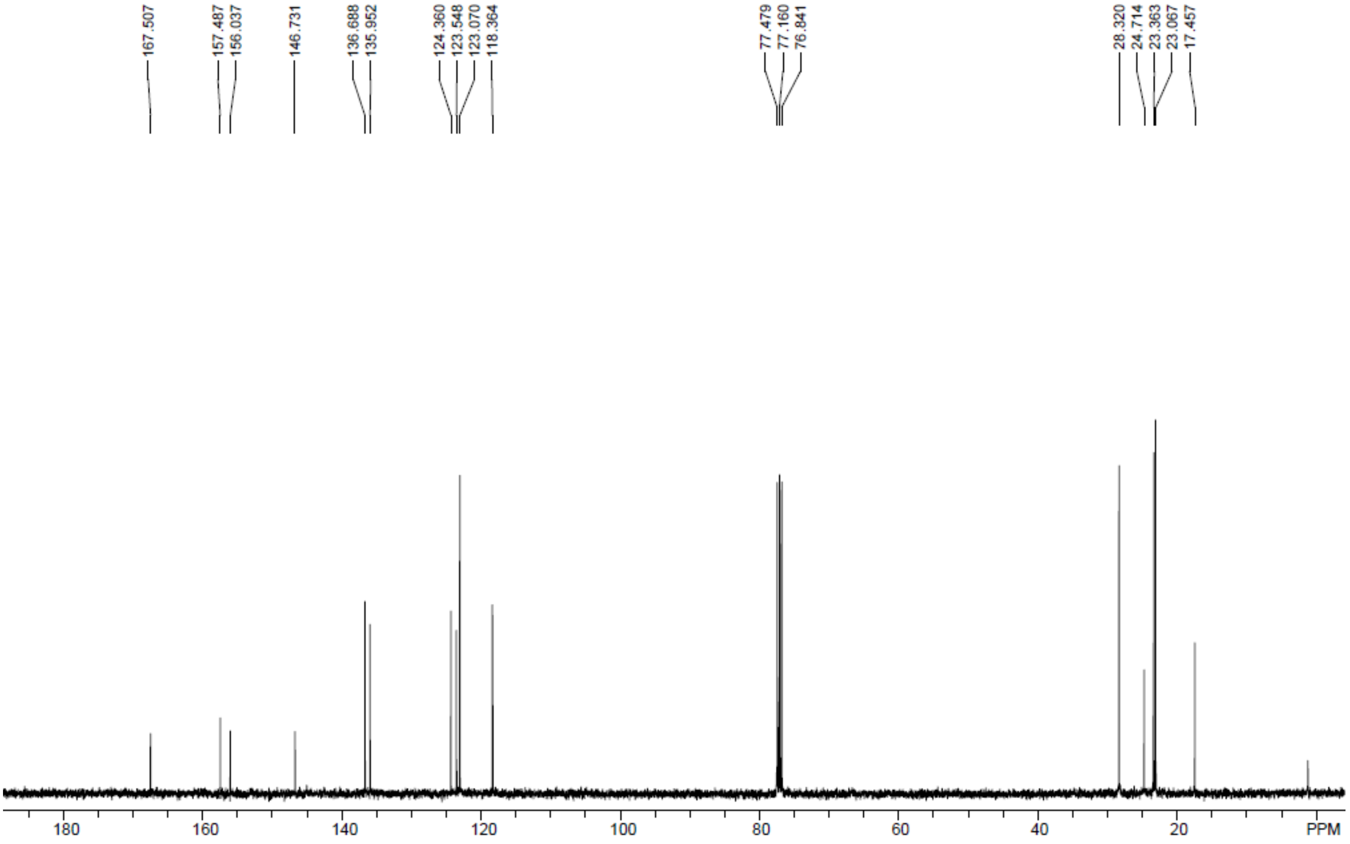
(13) Glasspoole, B. W.; Ghozati, K.; Moir, J. W.; Crudden, C. M. *Chem. Commun.* **2012**, *48,* 1230.

(14) Colbon, P.; Barnard, J. H.; Purdie, M.; Mulholland, K.; Kozhevnikov, I.; Xiao, J. *Adv. Synth. Catal.* **2012**, *354*, 1395.

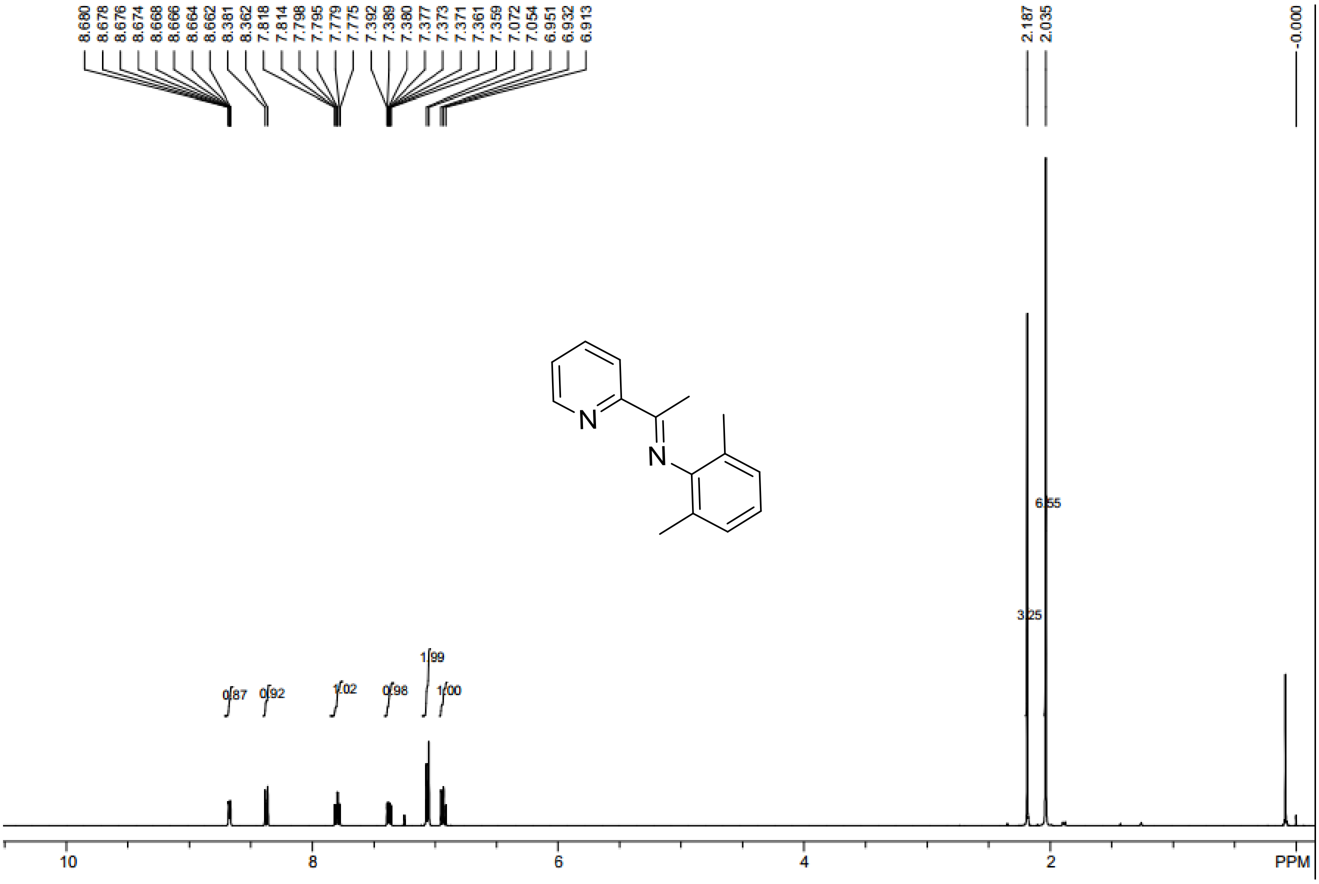
(15) Feldman, K. S.; Selfridge, B. R. *Tetrahedron Lett.* **2012**, *53*, 825.



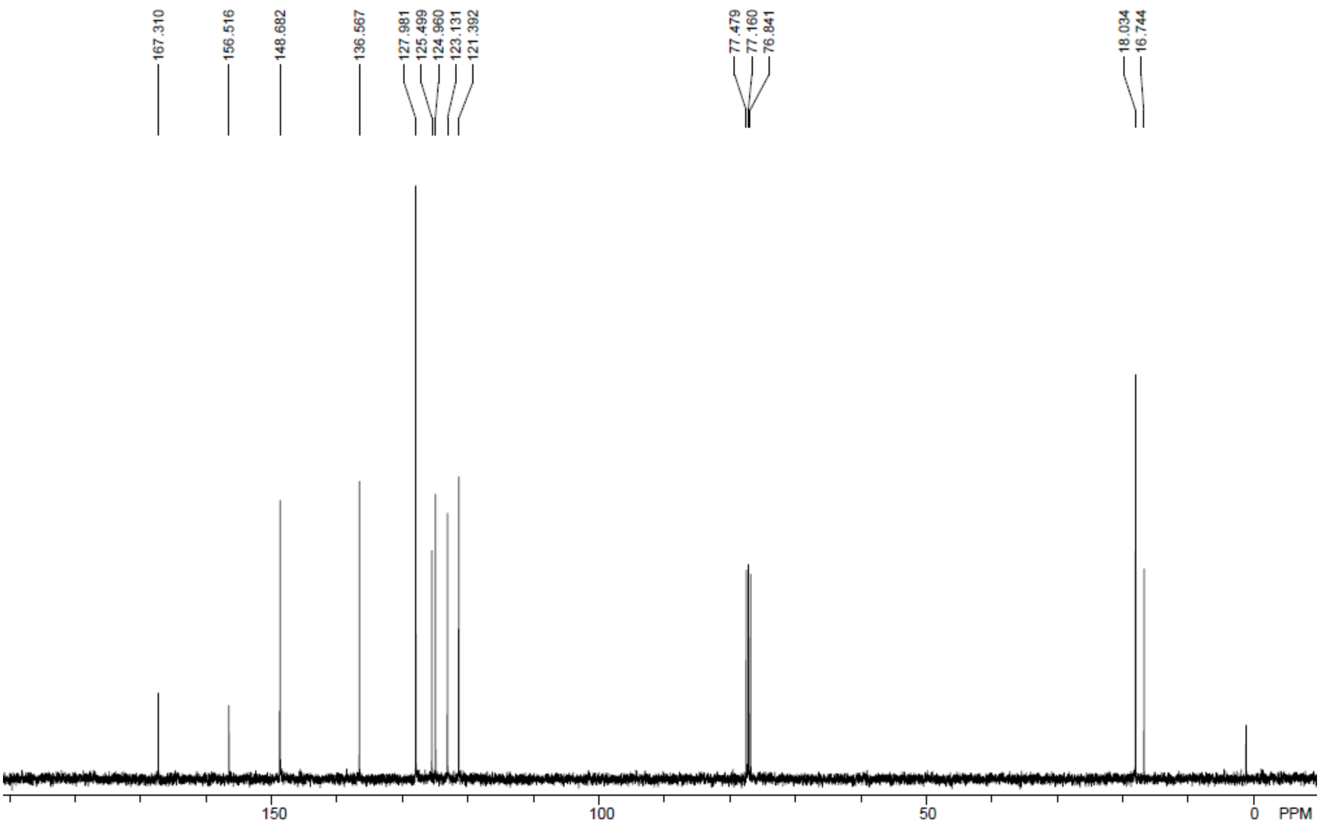
^{1}H NMR spectrum of **1**



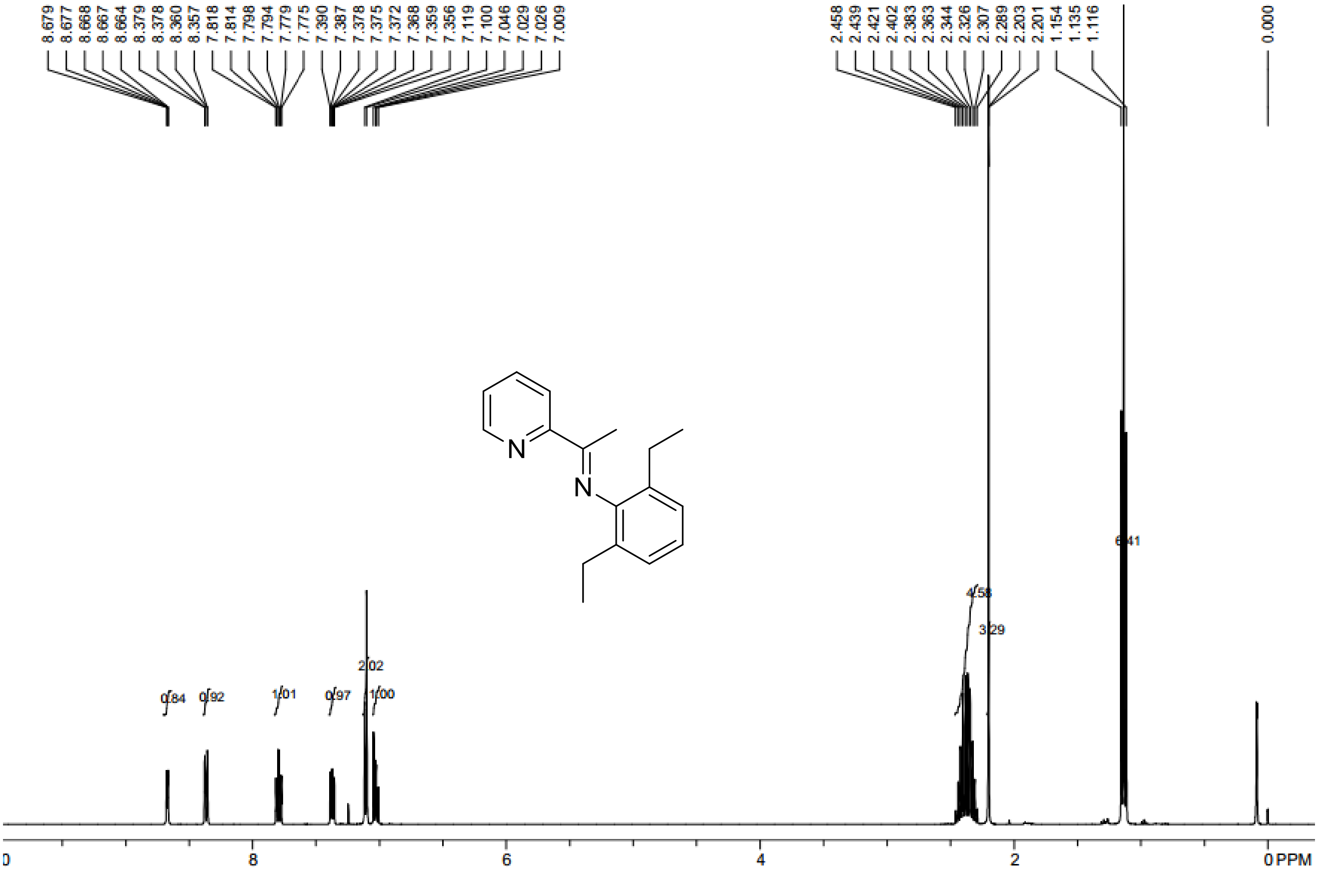
^{13}C NMR spectrum of **1**



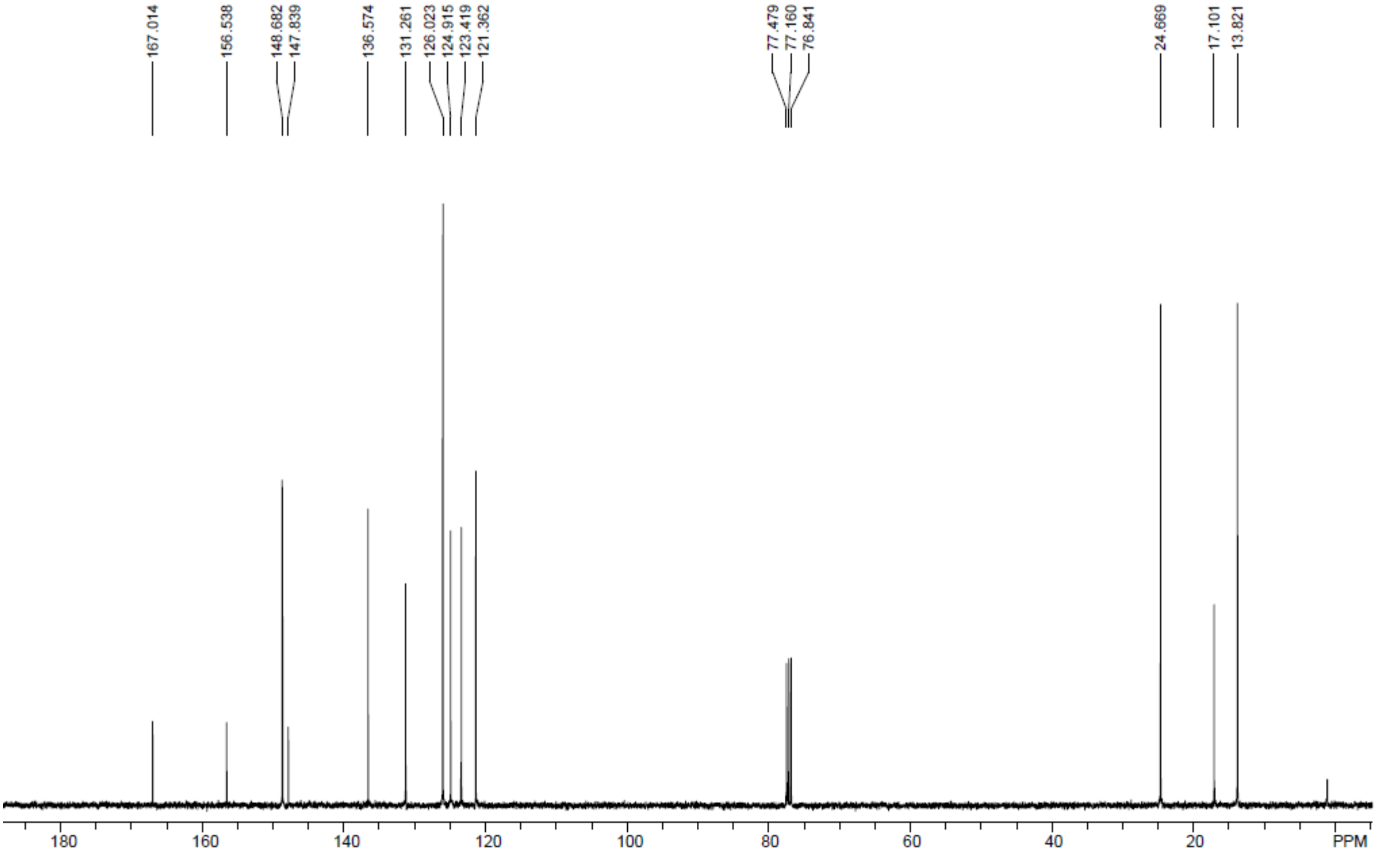
^{1}H NMR spectrum of **6d**



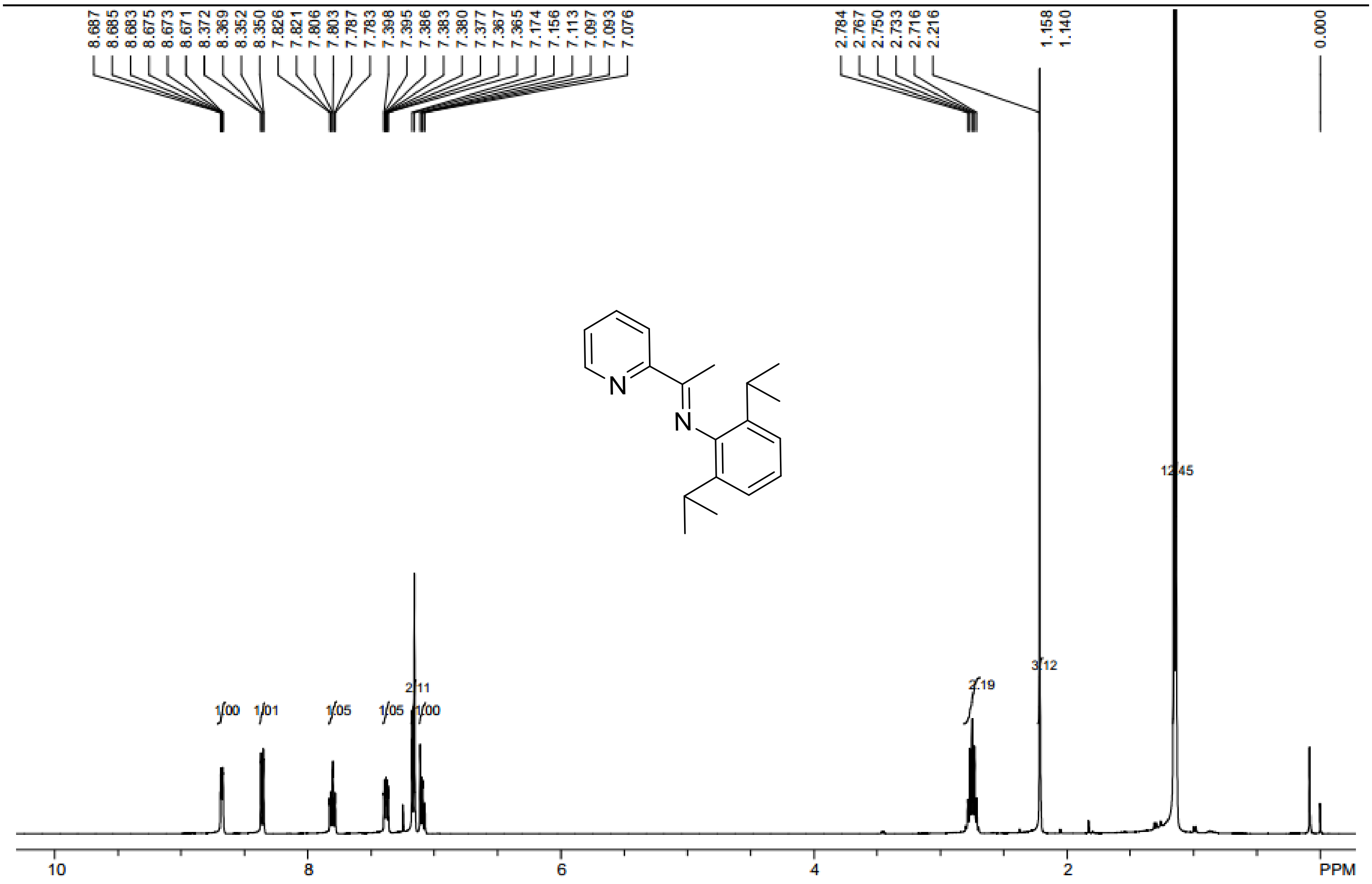
^{13}C NMR spectrum of **6d**



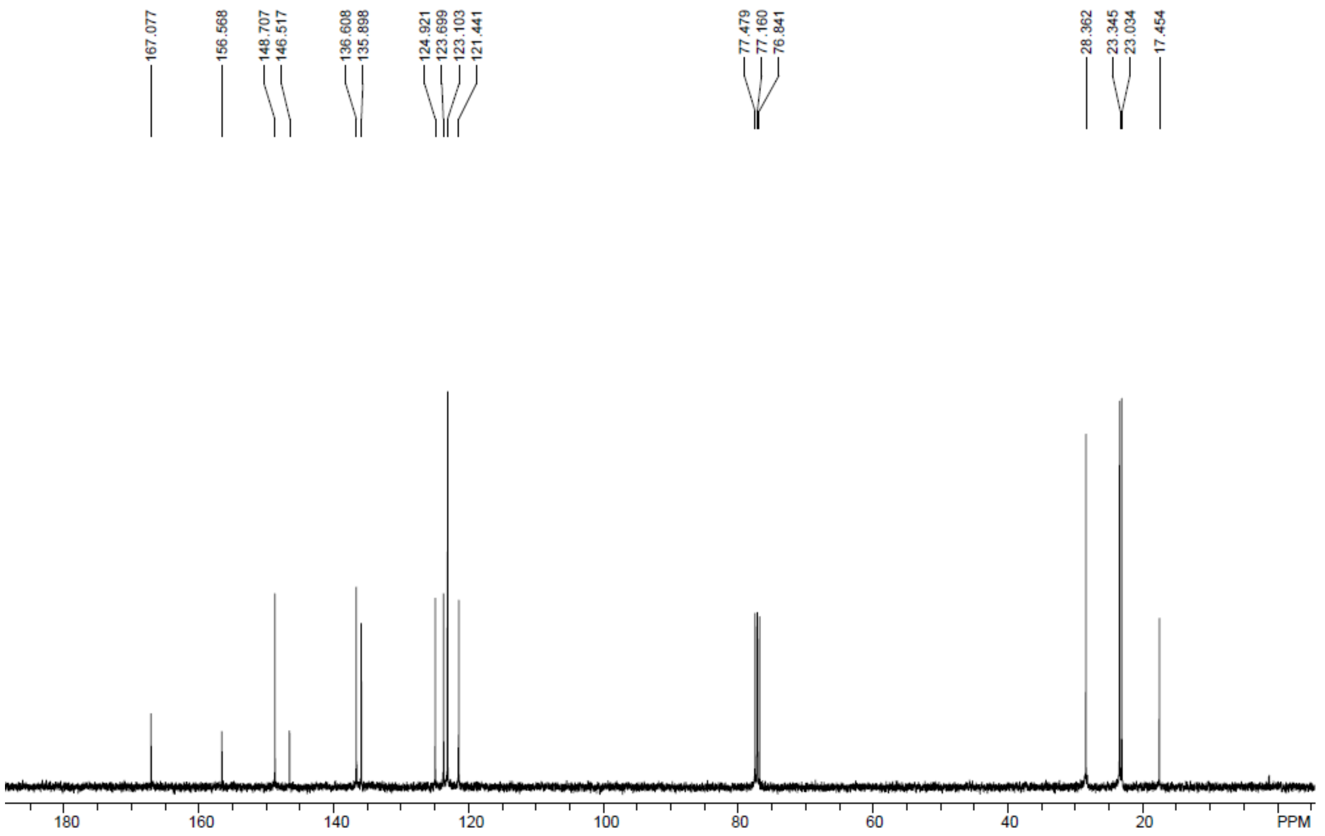
^{1}H NMR spectrum of **6e**



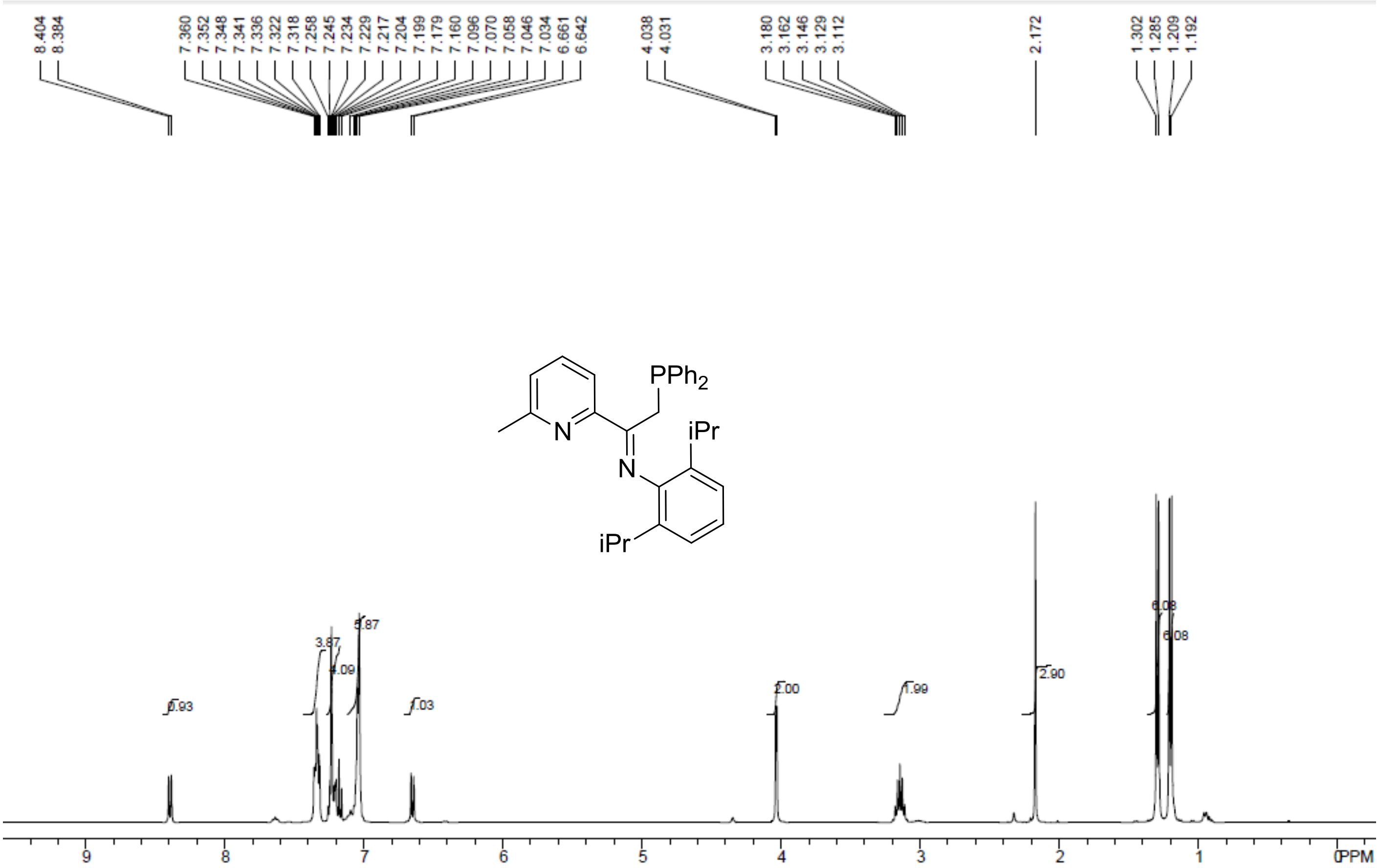
^{13}C NMR spectrum of **6e**



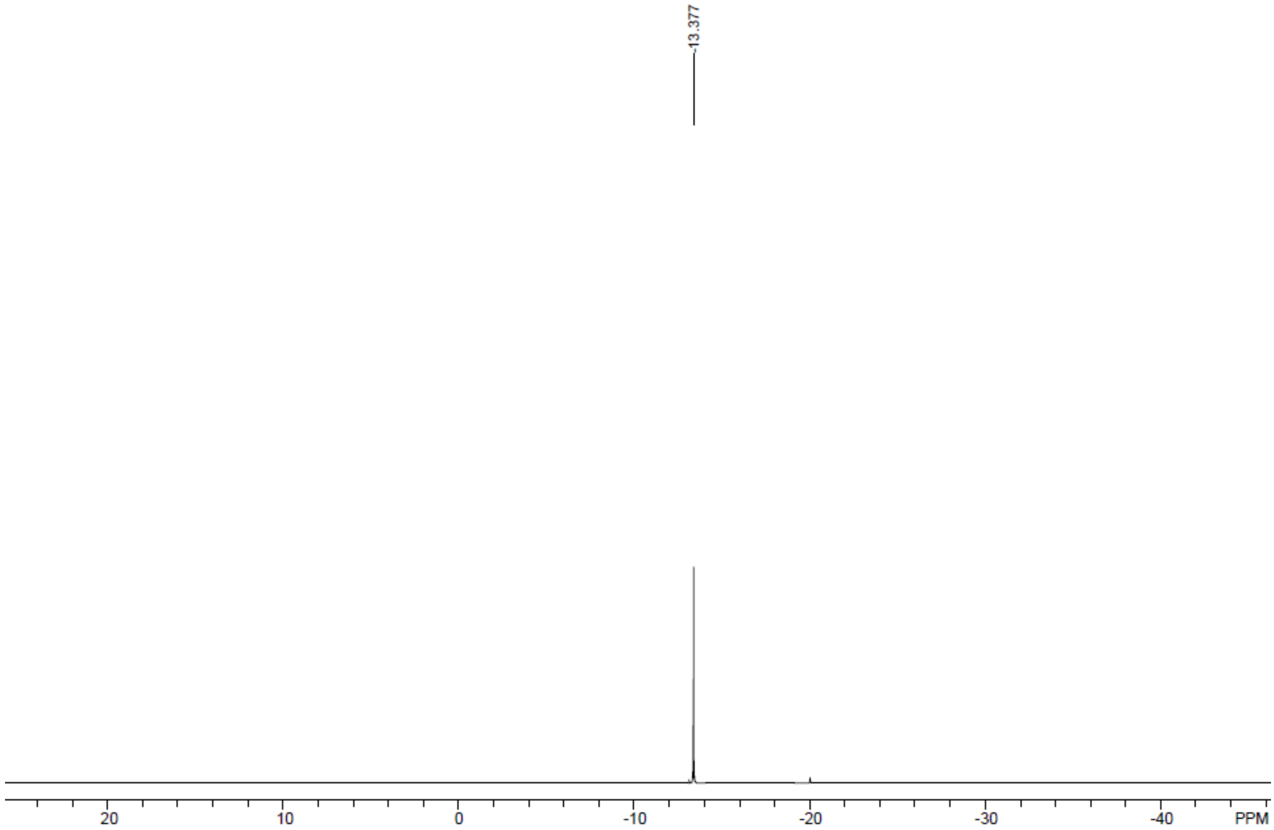
^{1}H NMR spectrum of **6f**



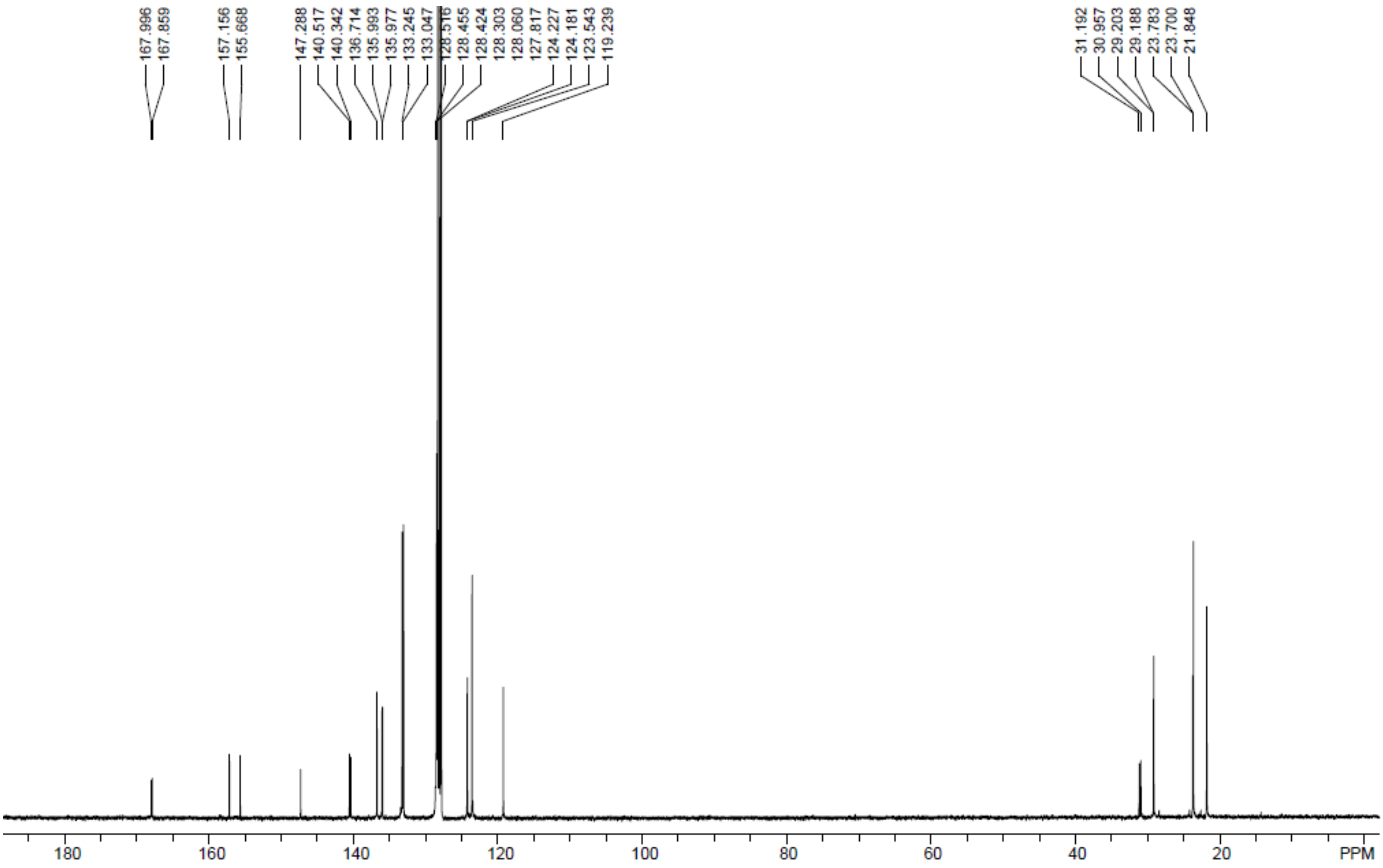
^{13}C NMR spectrum of **6f**



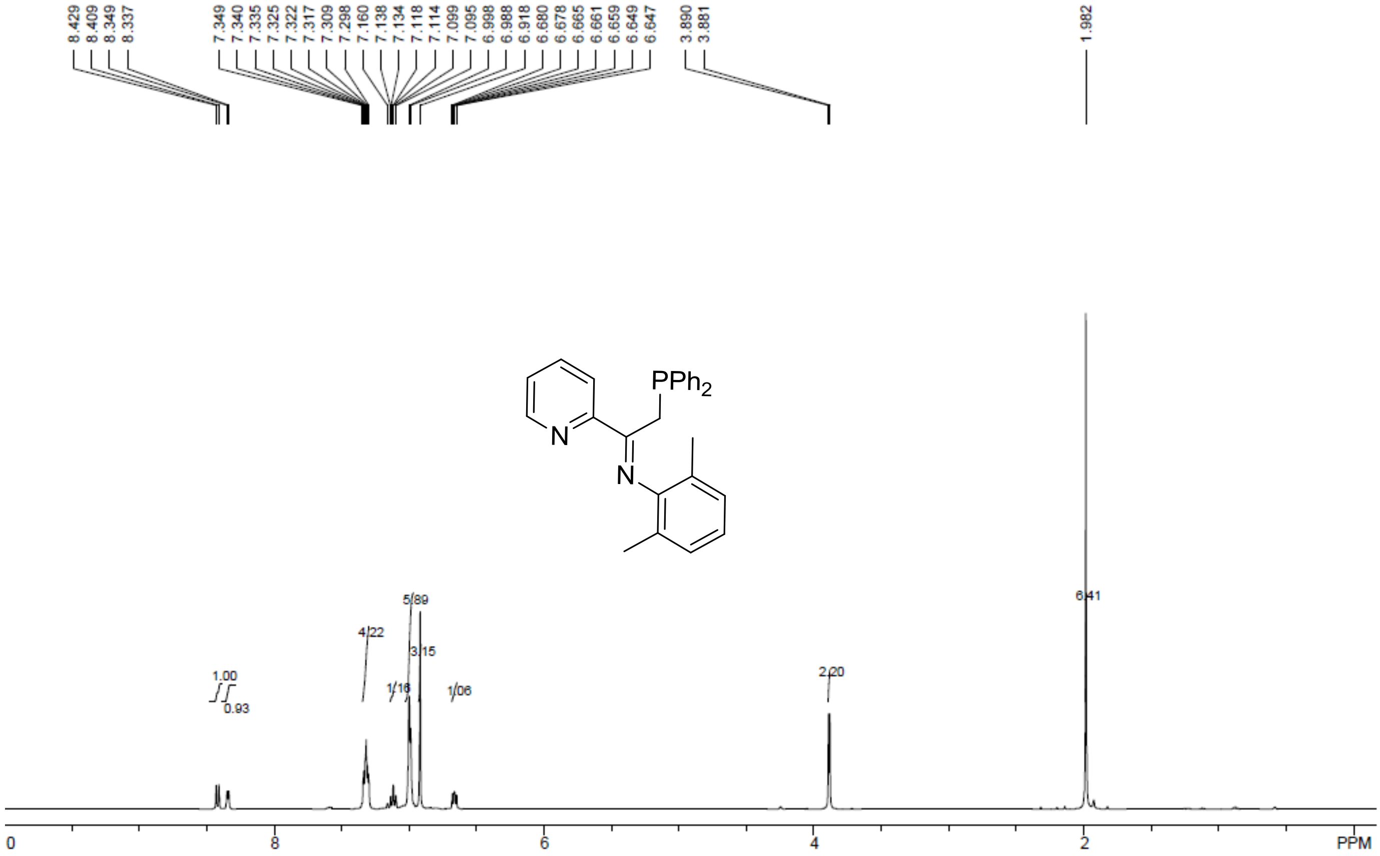
^{1}H NMR spectrum of **3**



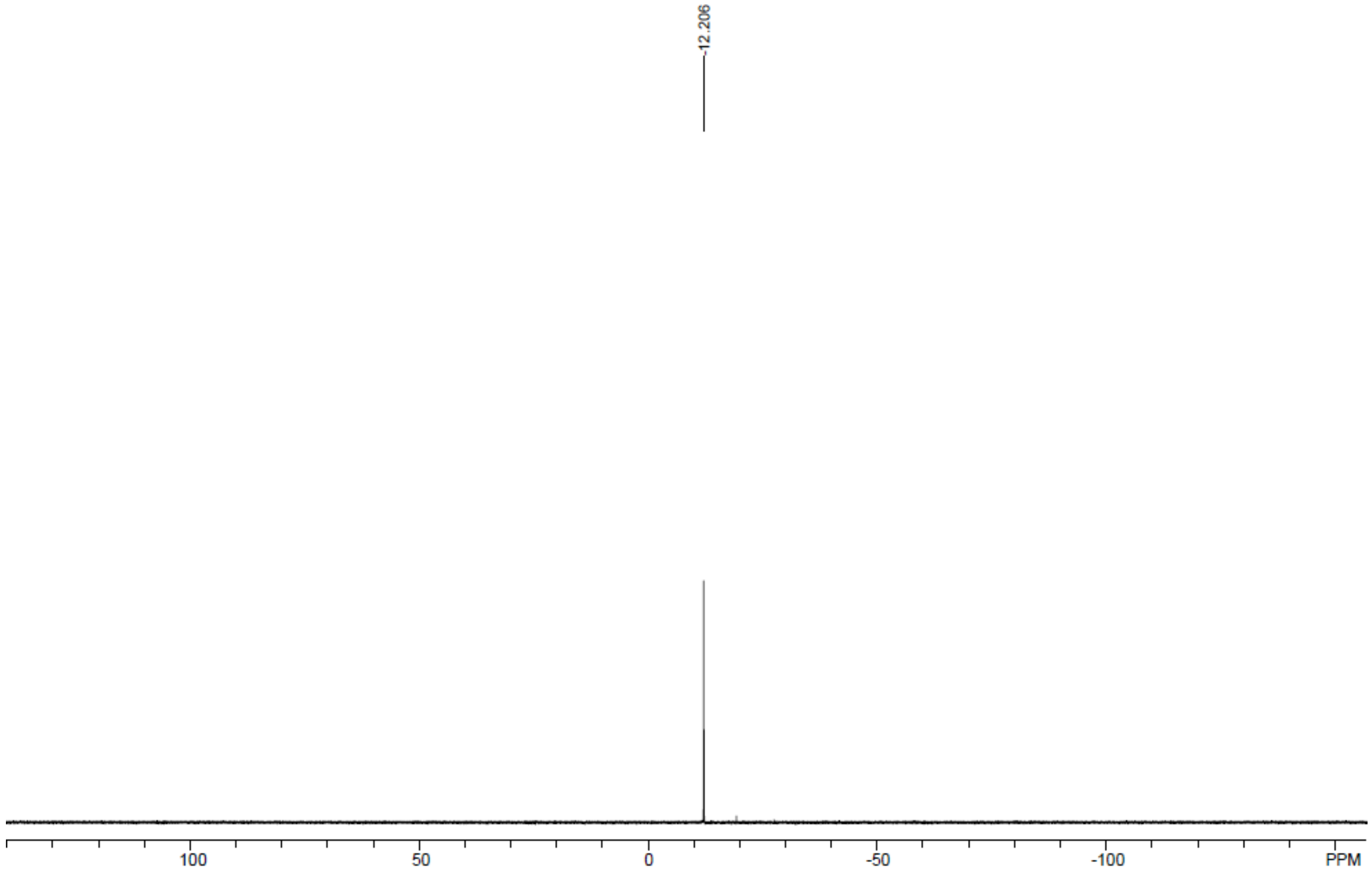
^{31}P NMR spectrum of **3**



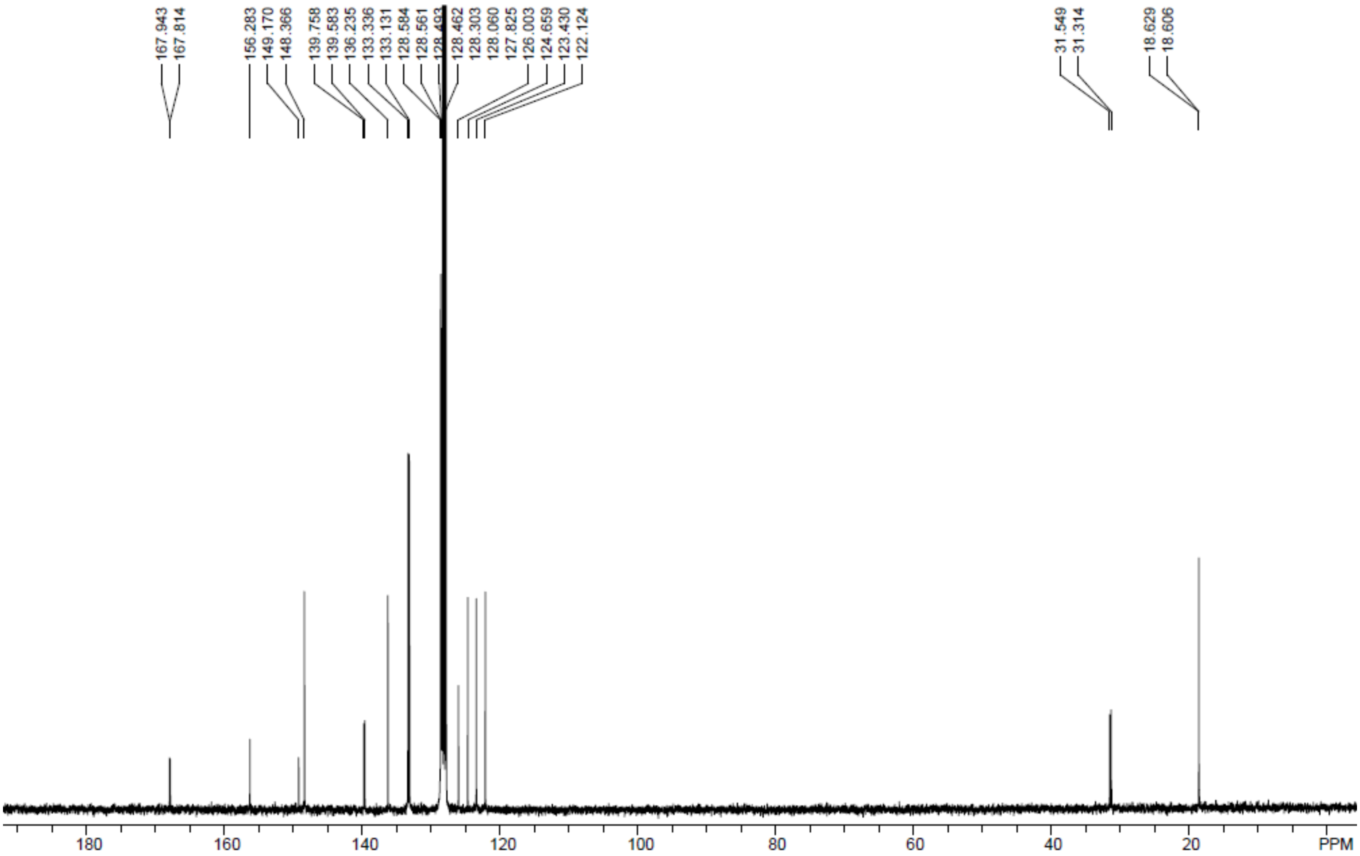
^{13}C NMR spectrum of **3**



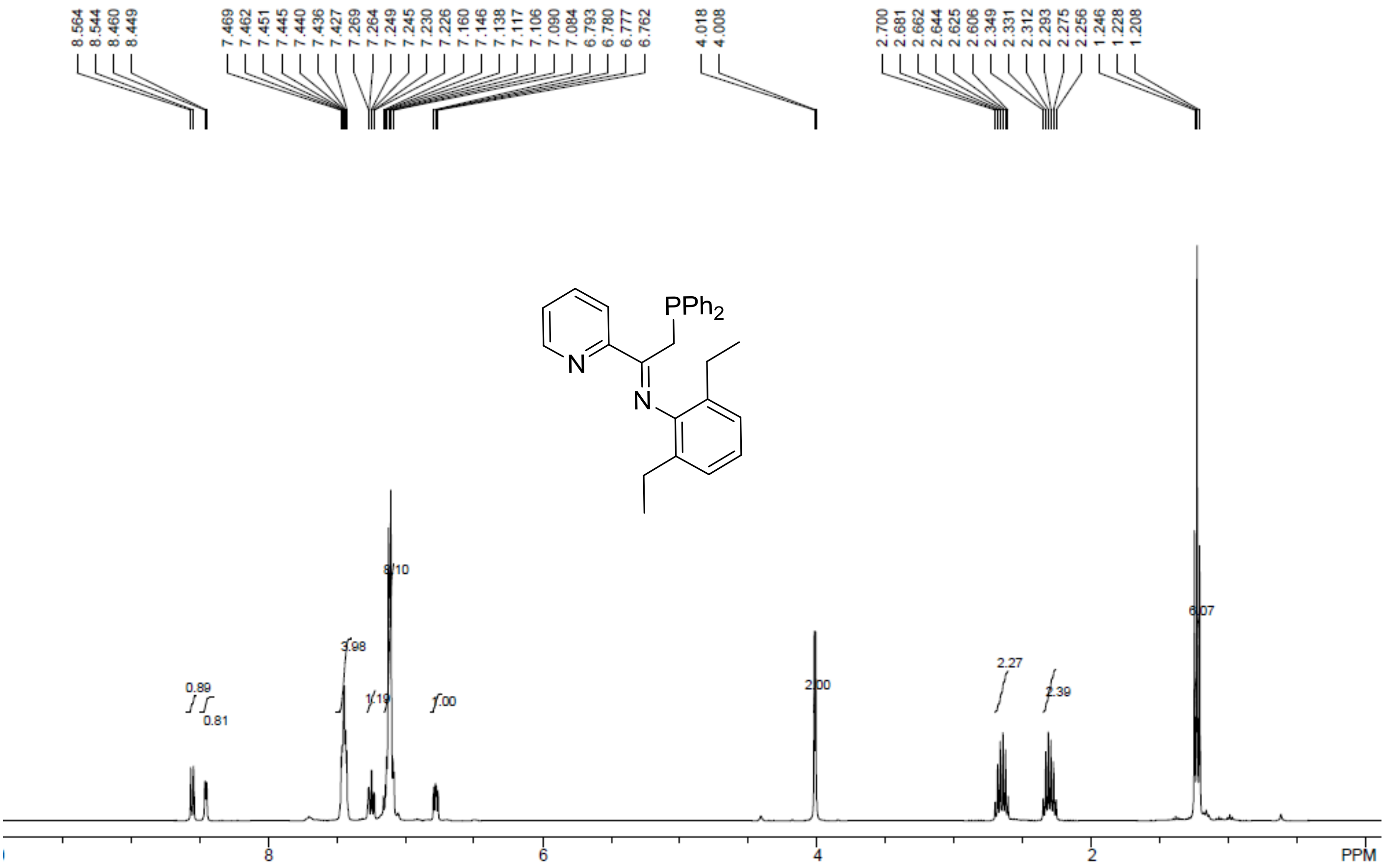
^{1}H NMR spectrum of **6g**



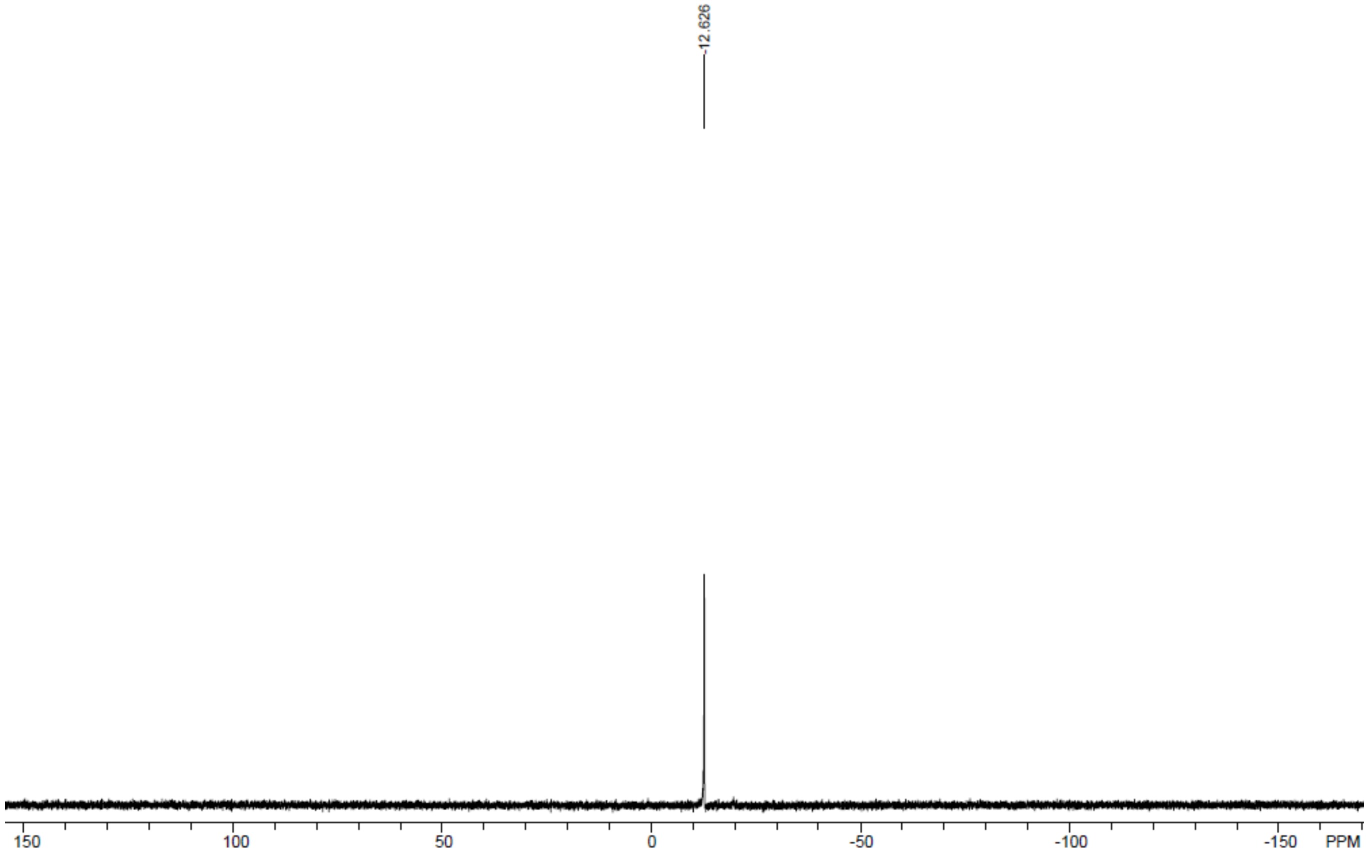
^{31}P NMR spectrum of **6g**



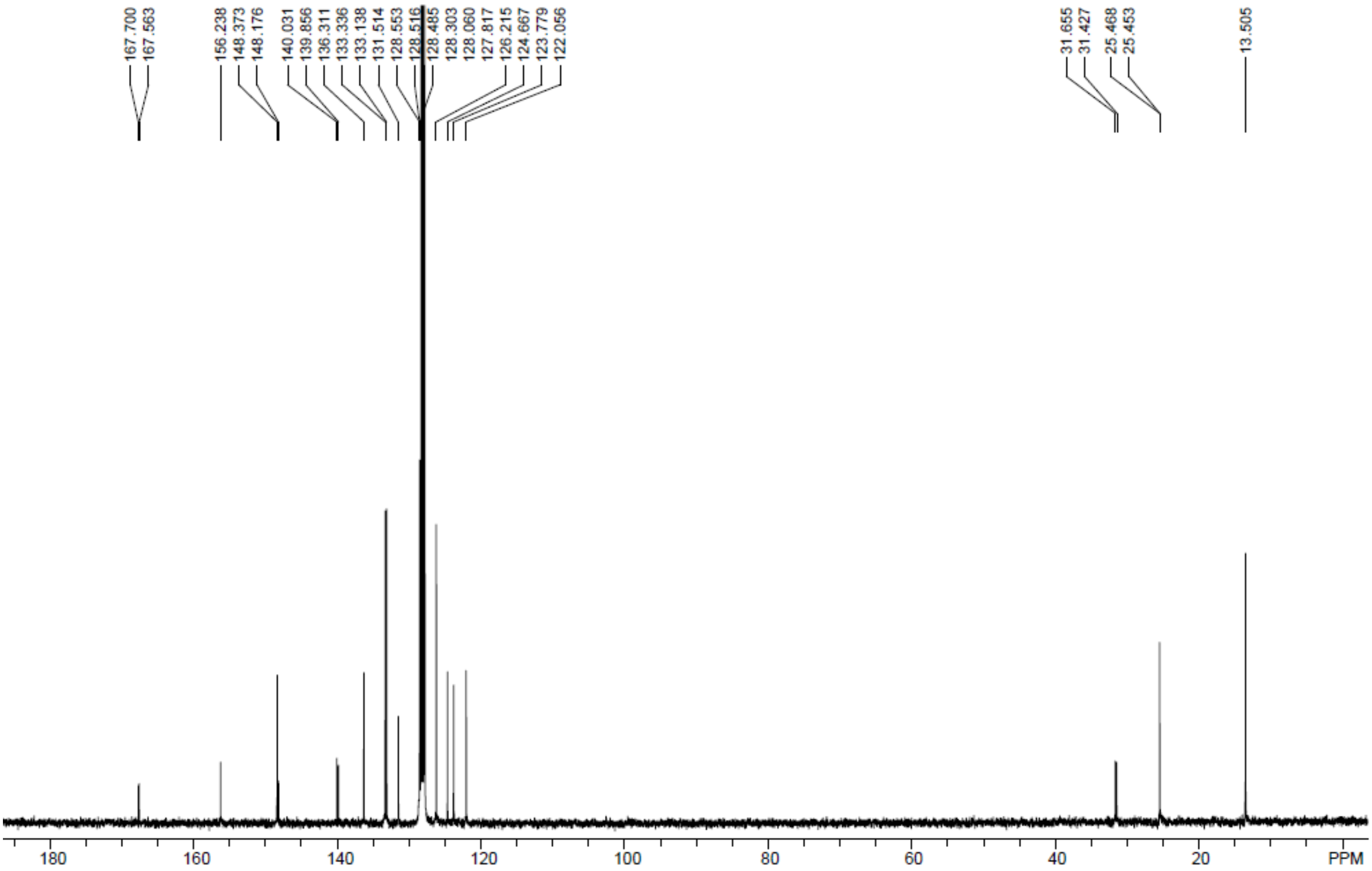
^{13}C NMR spectrum of **6g**



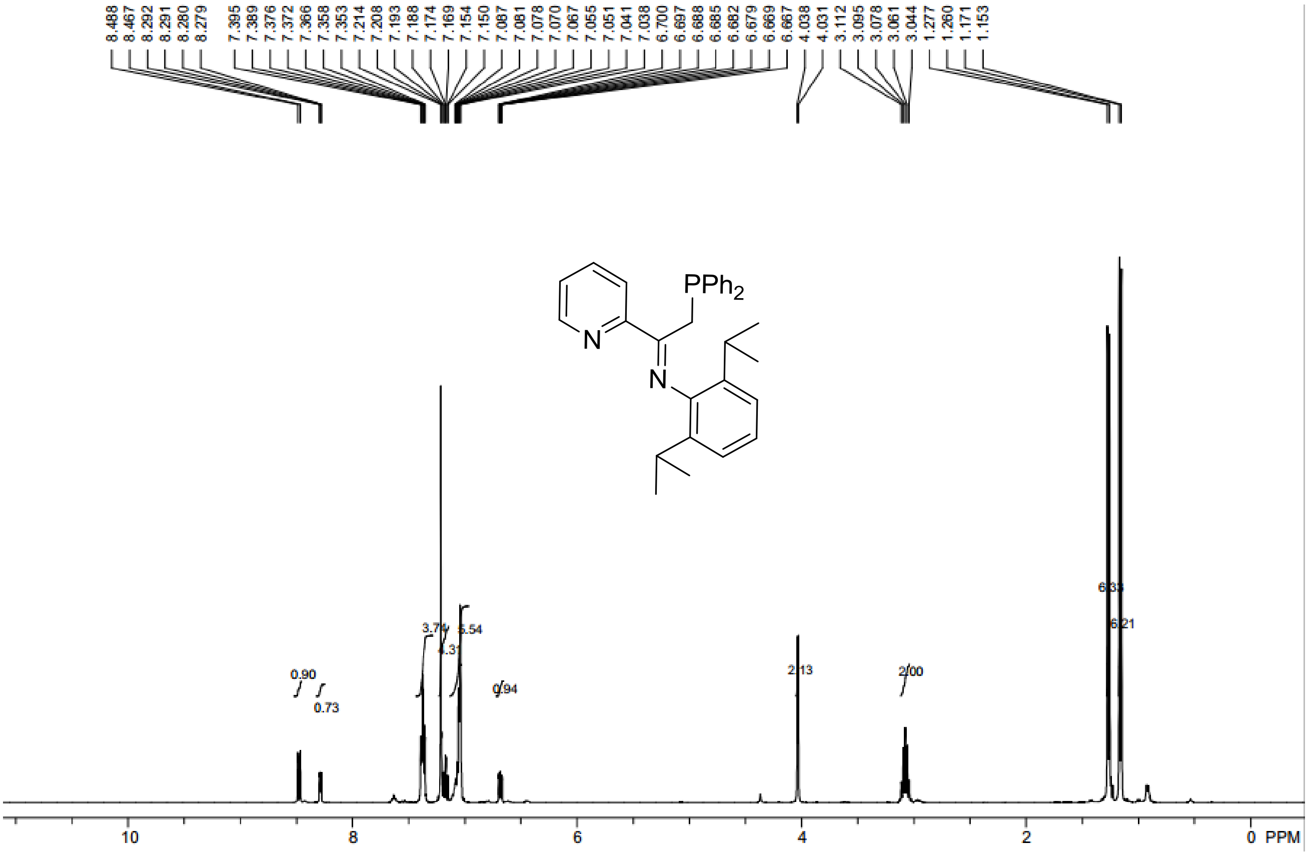
^{1}H NMR spectrum of **6h**



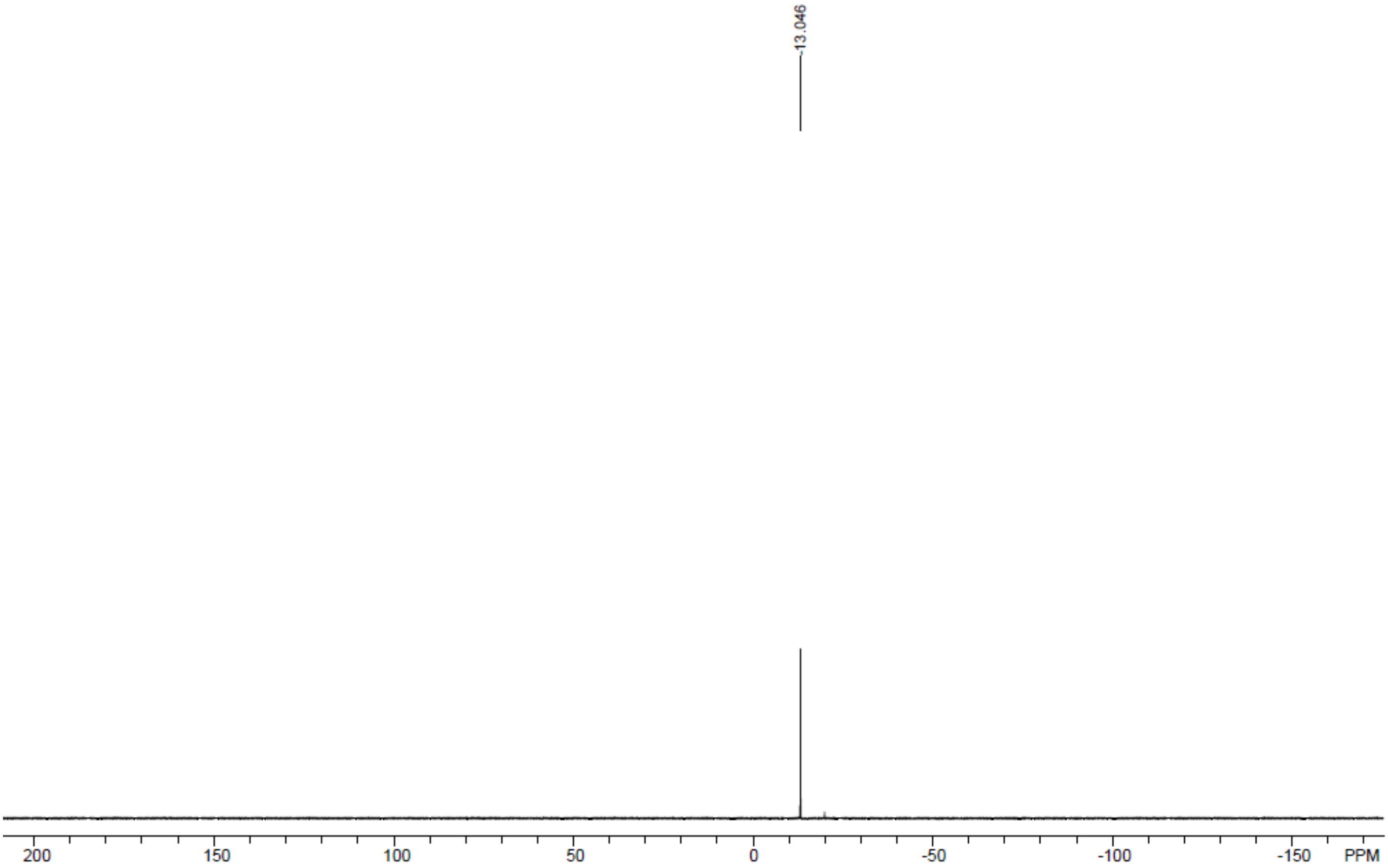
^{31}P NMR spectrum of **6h**



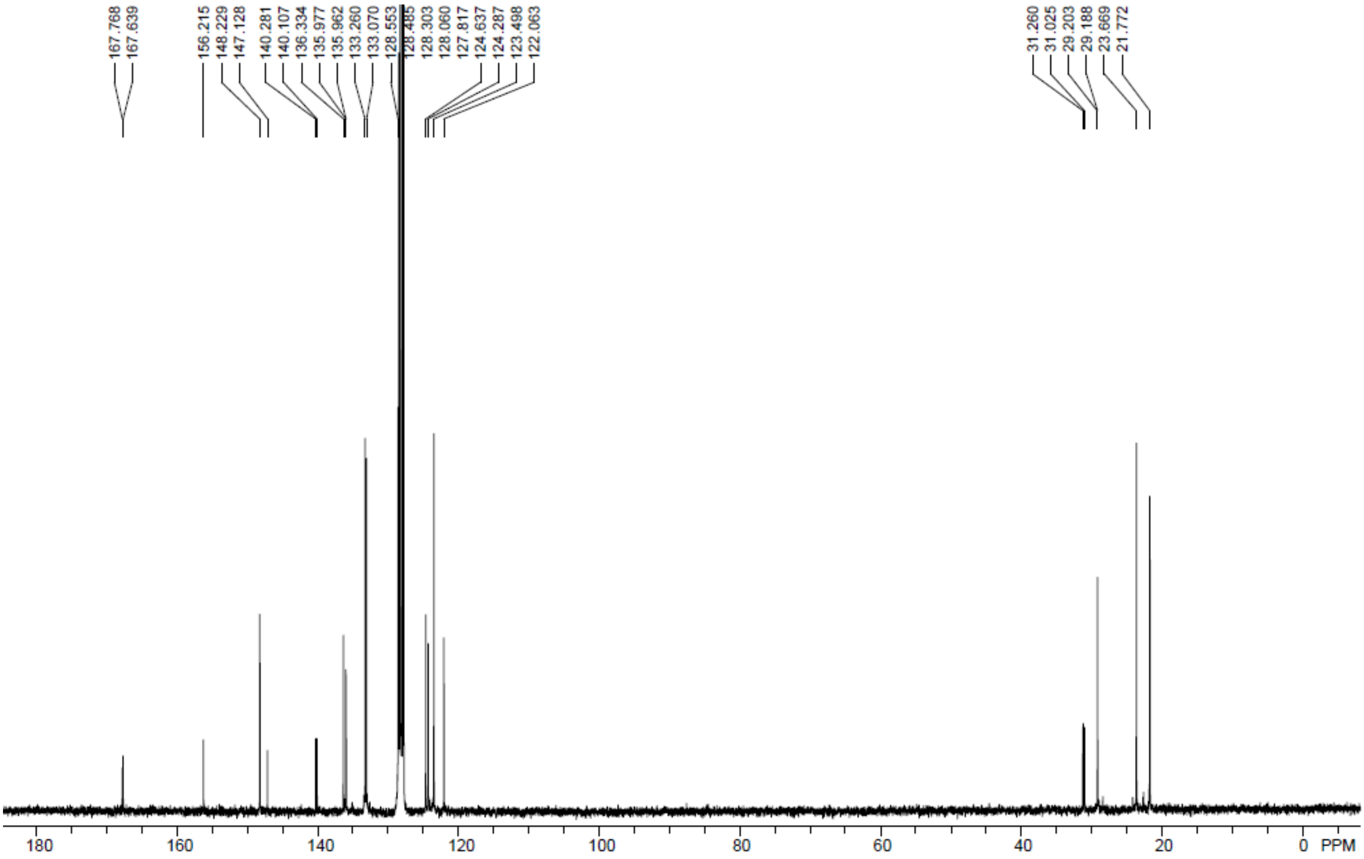
^{13}C NMR spectrum of **6h**



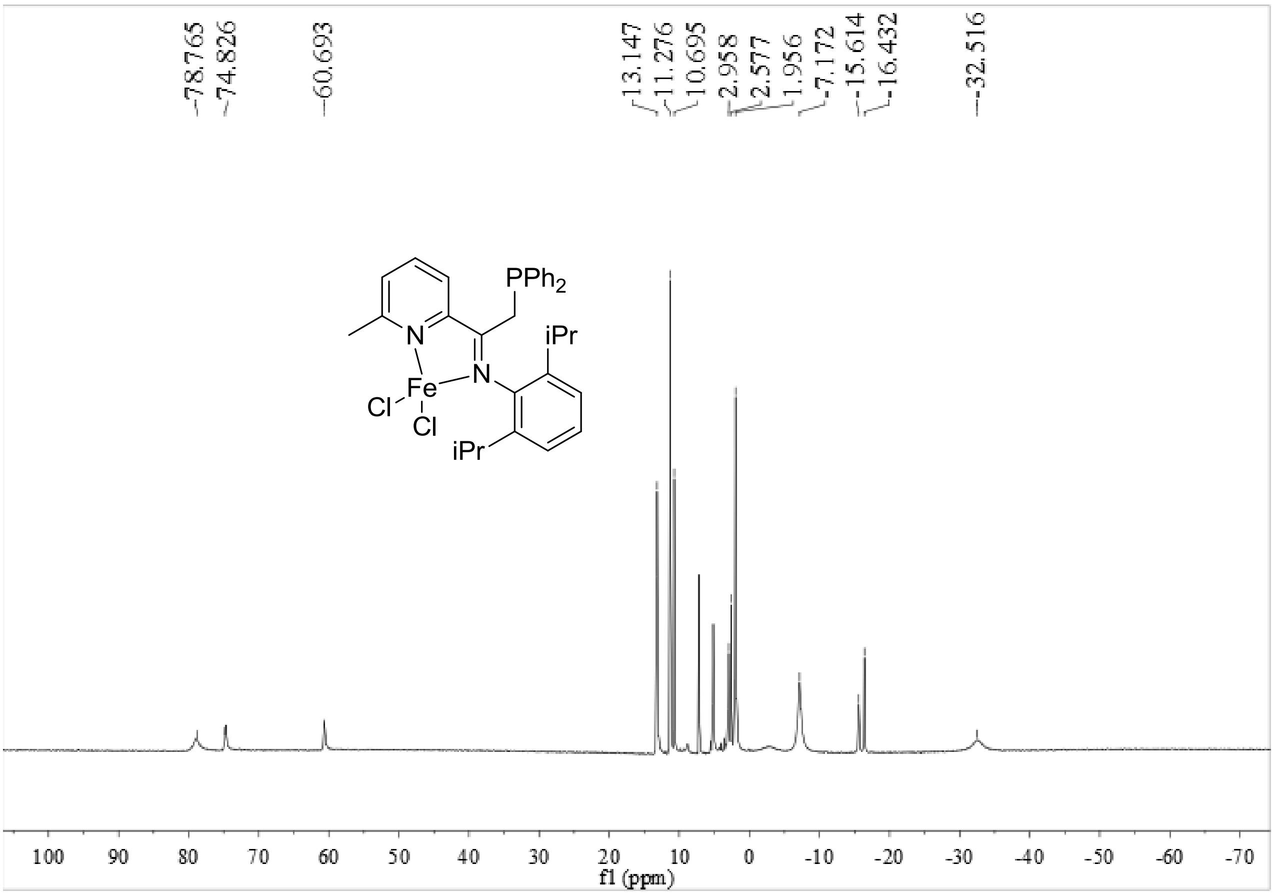
^{1}H NMR spectrum of **6i**



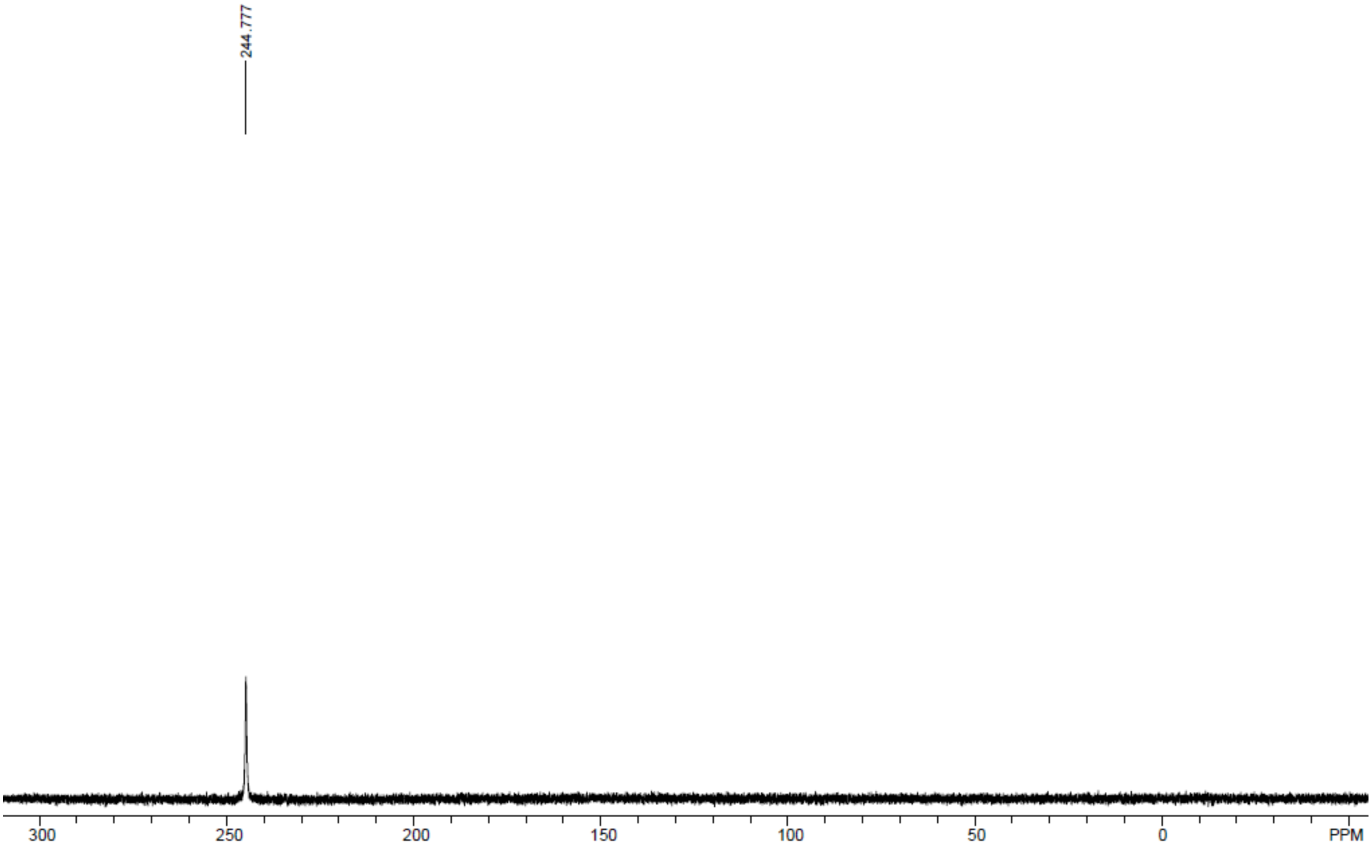
^{31}P NMR spectrum of **6i**



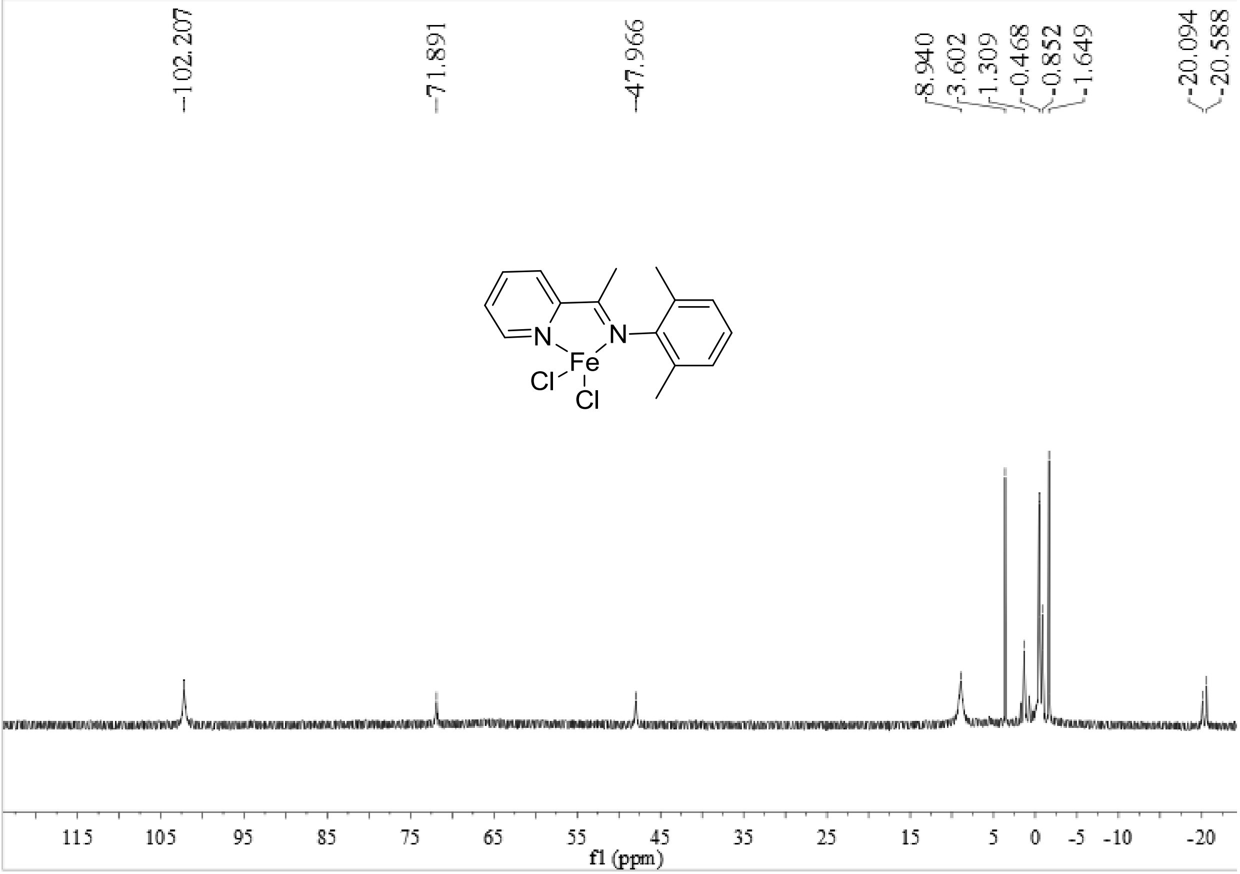
^{13}C NMR spectrum of **6i**



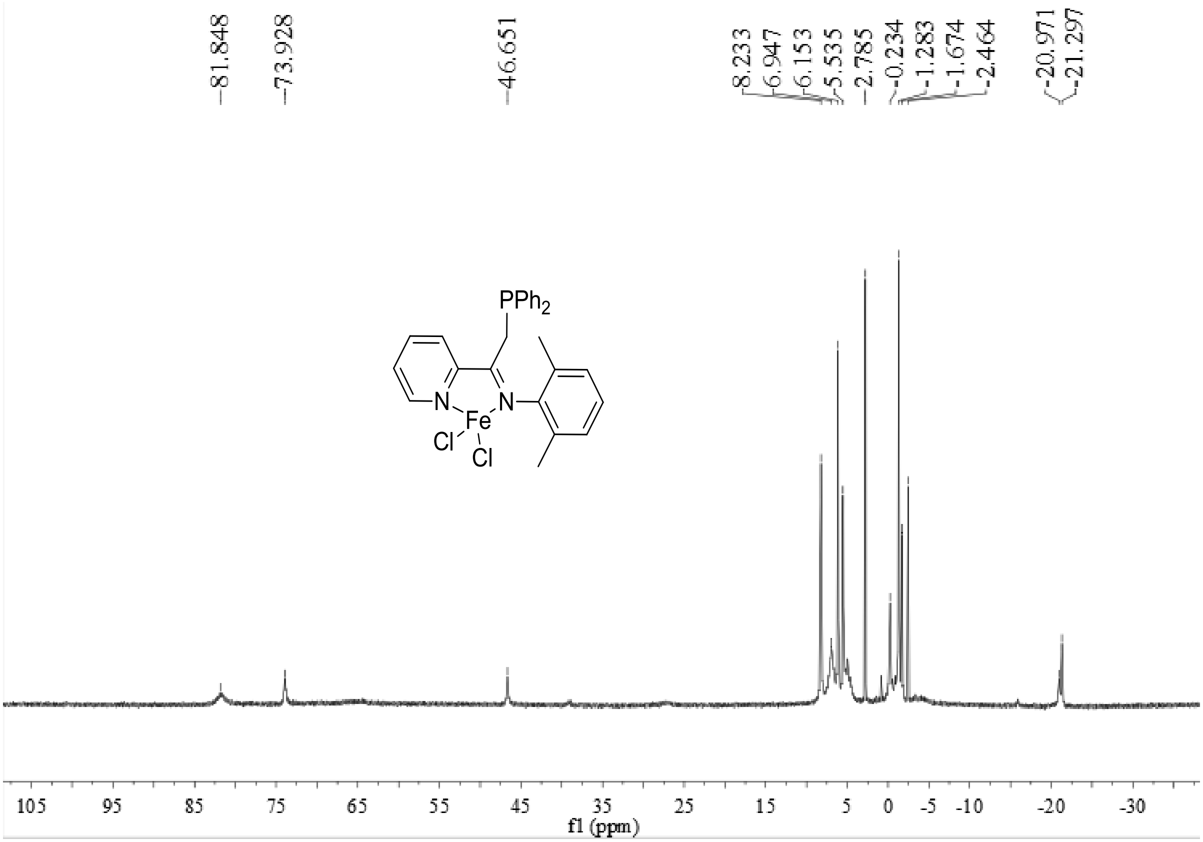
^{1}H NMR spectrum of **5**



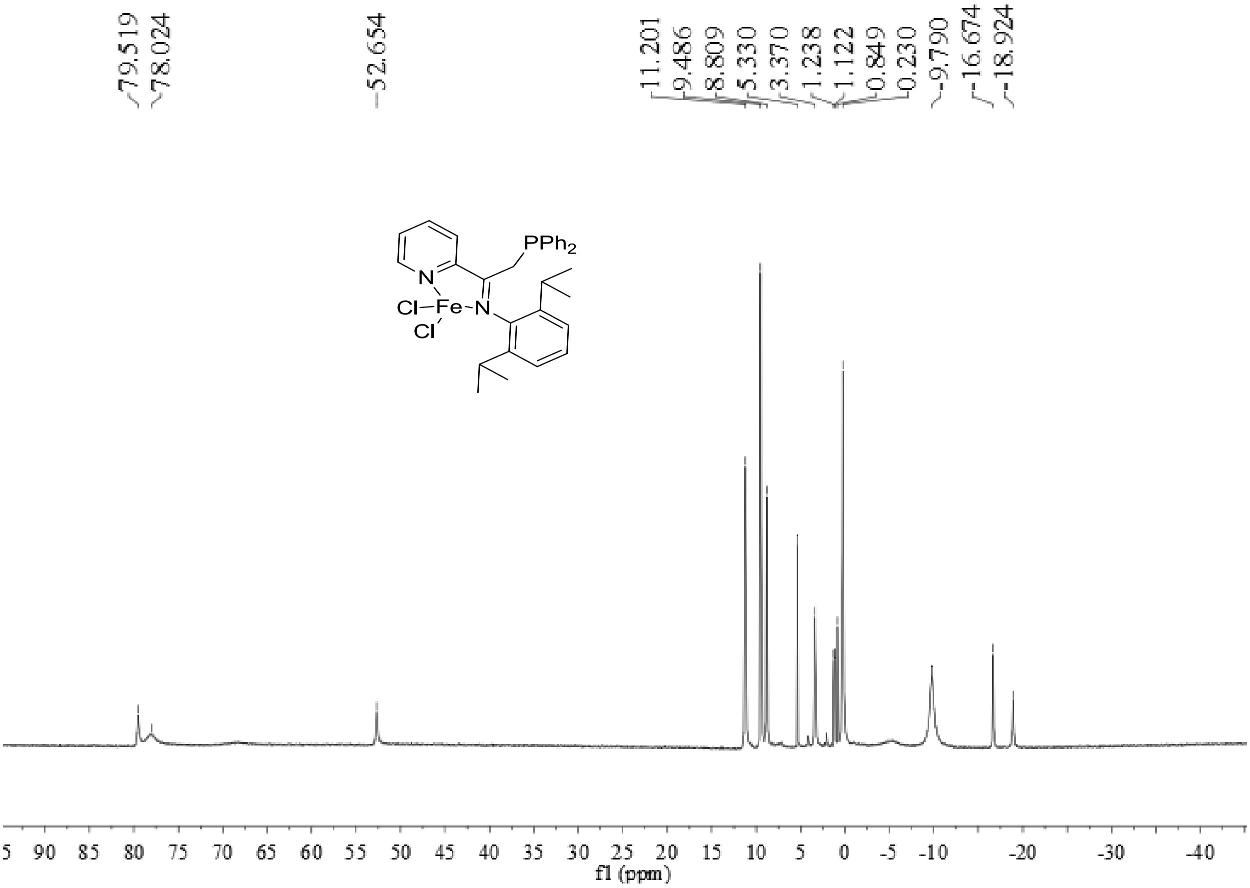
^{31}P NMR spectrum of **5**



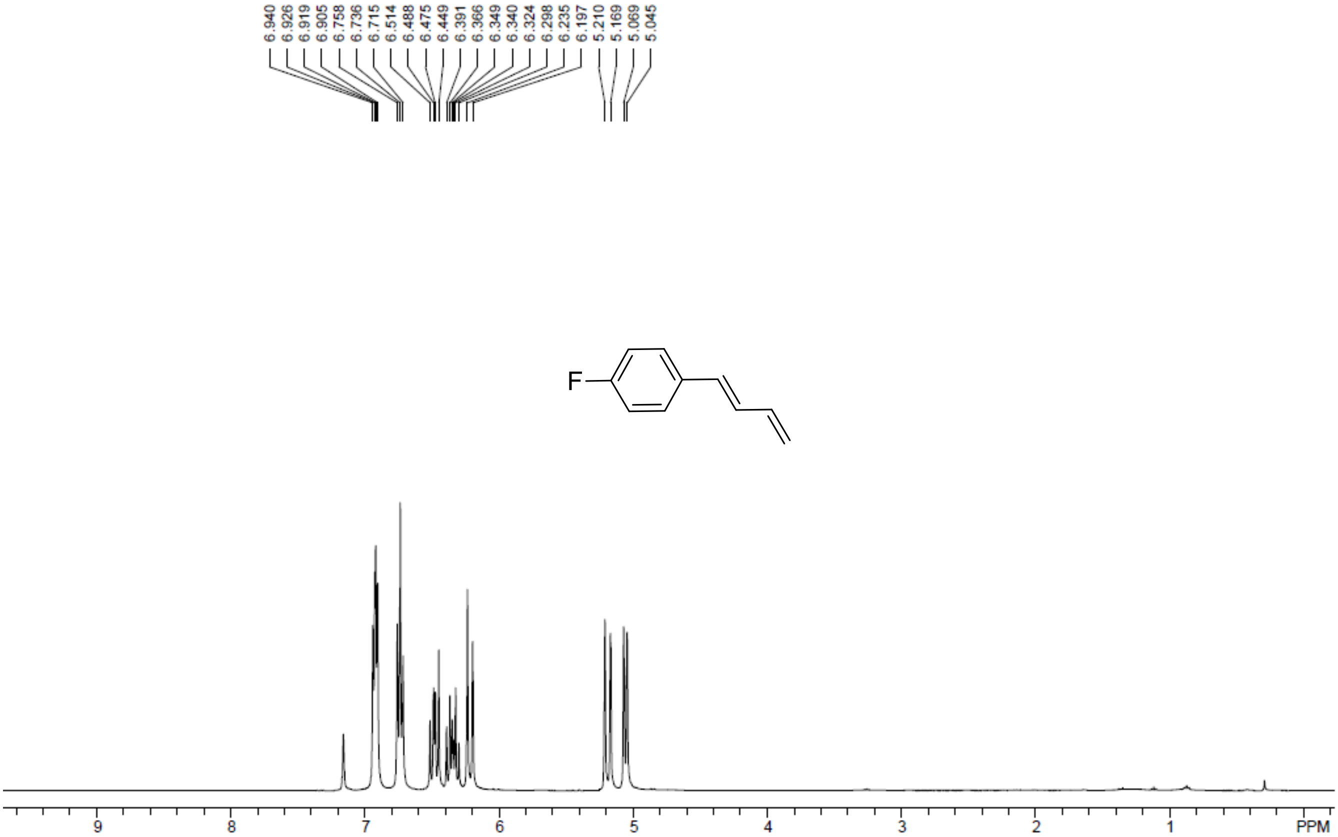
^{1}H NMR spectrum of **7d**



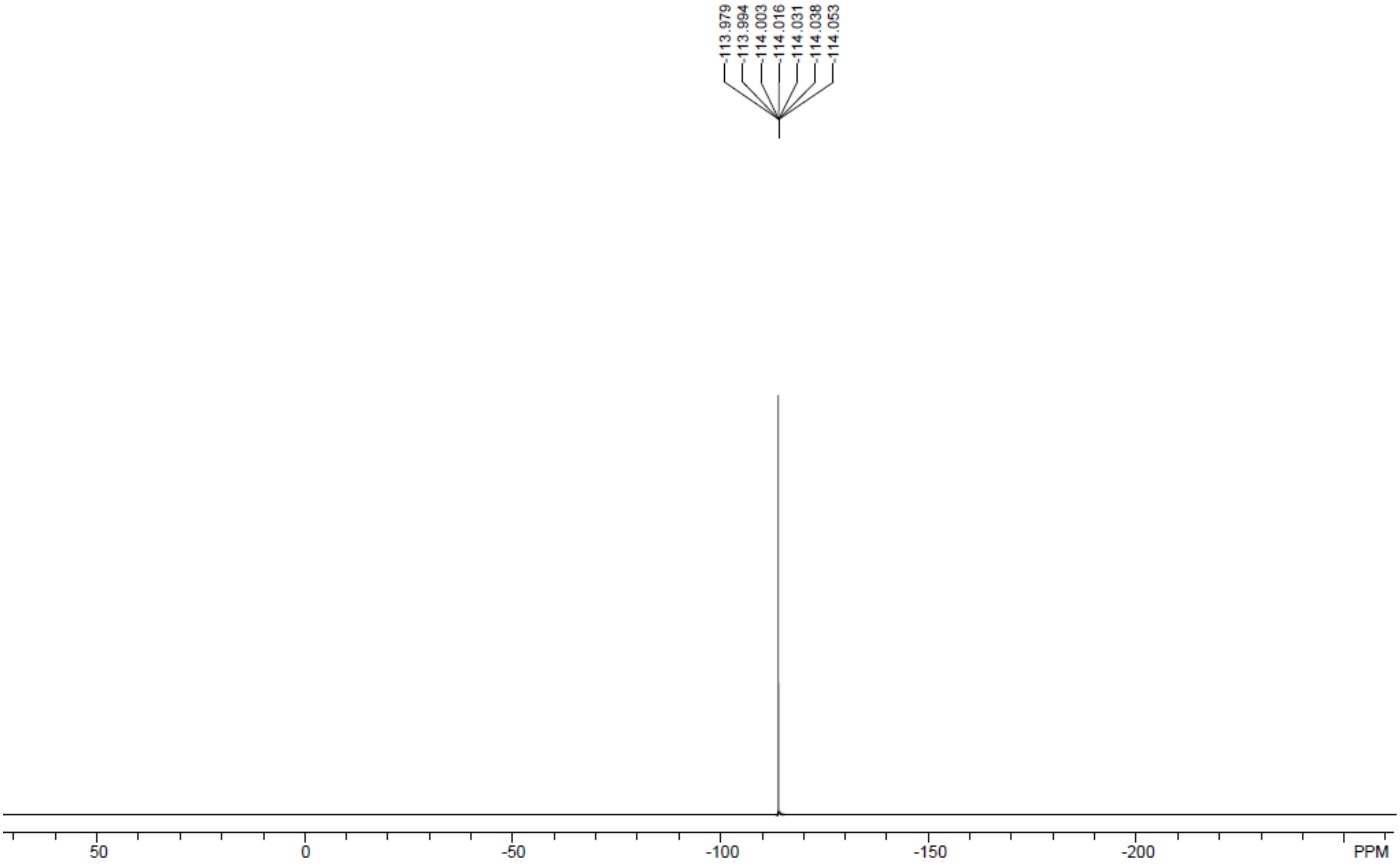
^{1}H NMR spectrum of **7g**



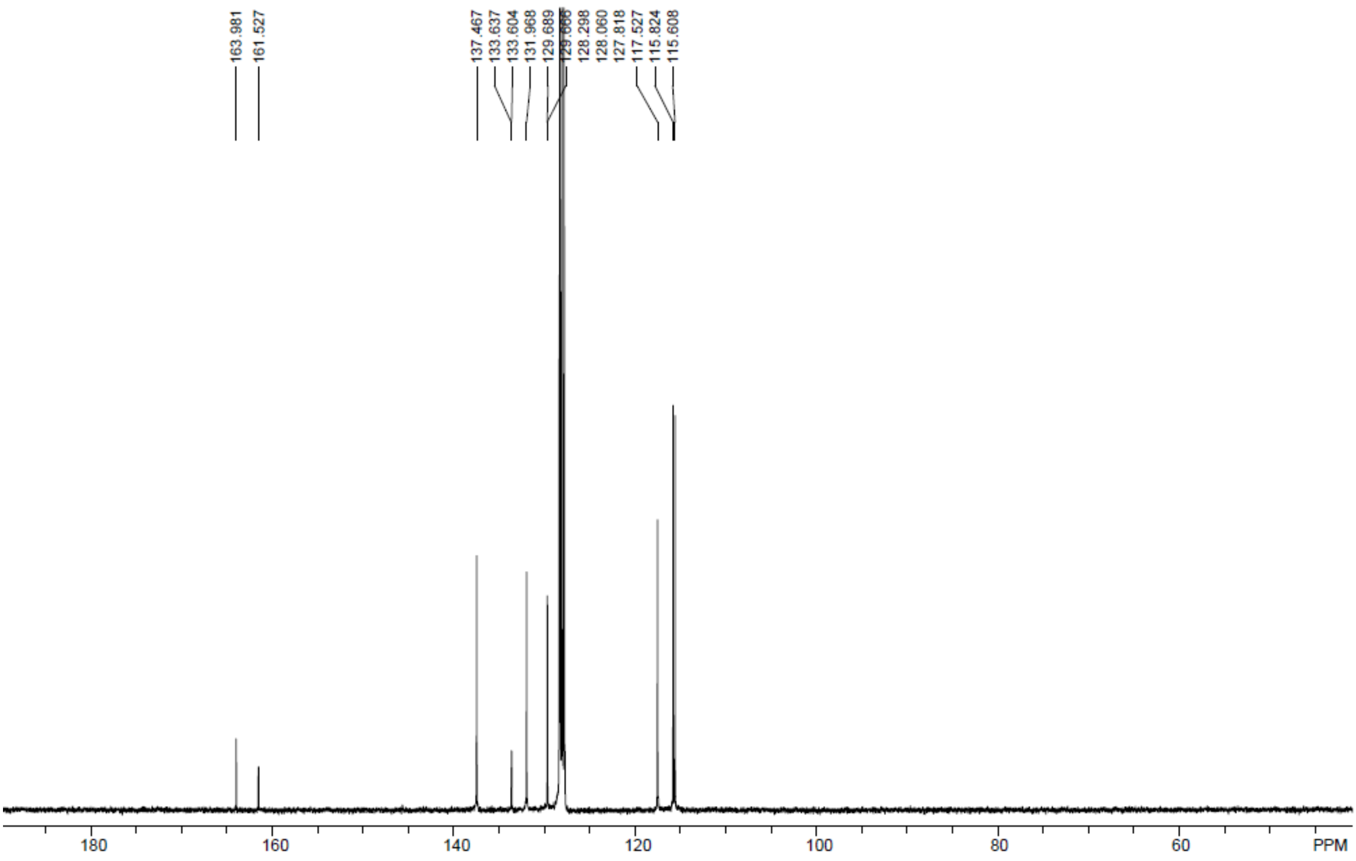
^{1}H NMR spectrum of **7i**



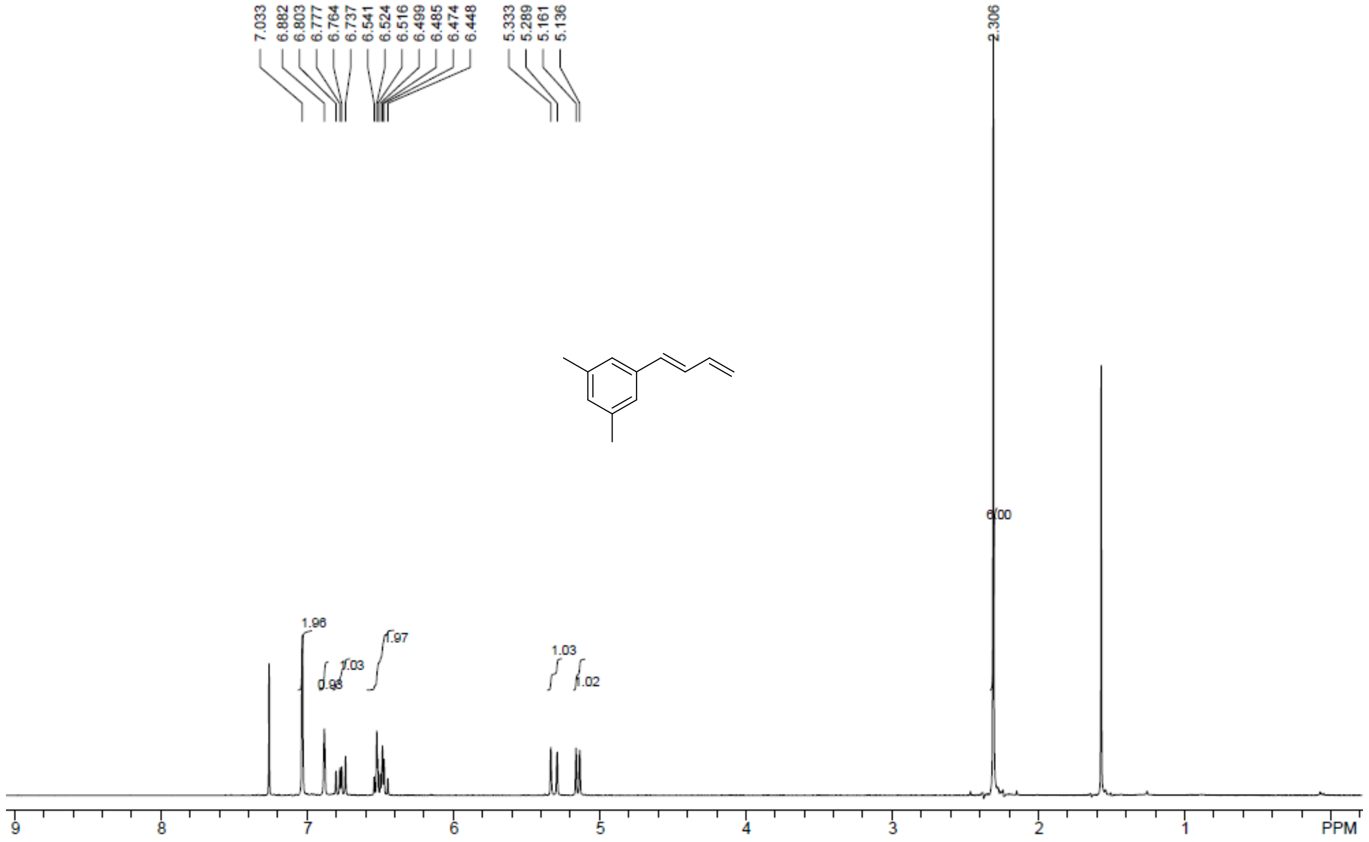
^{1}H NMR spectrum of **8e**



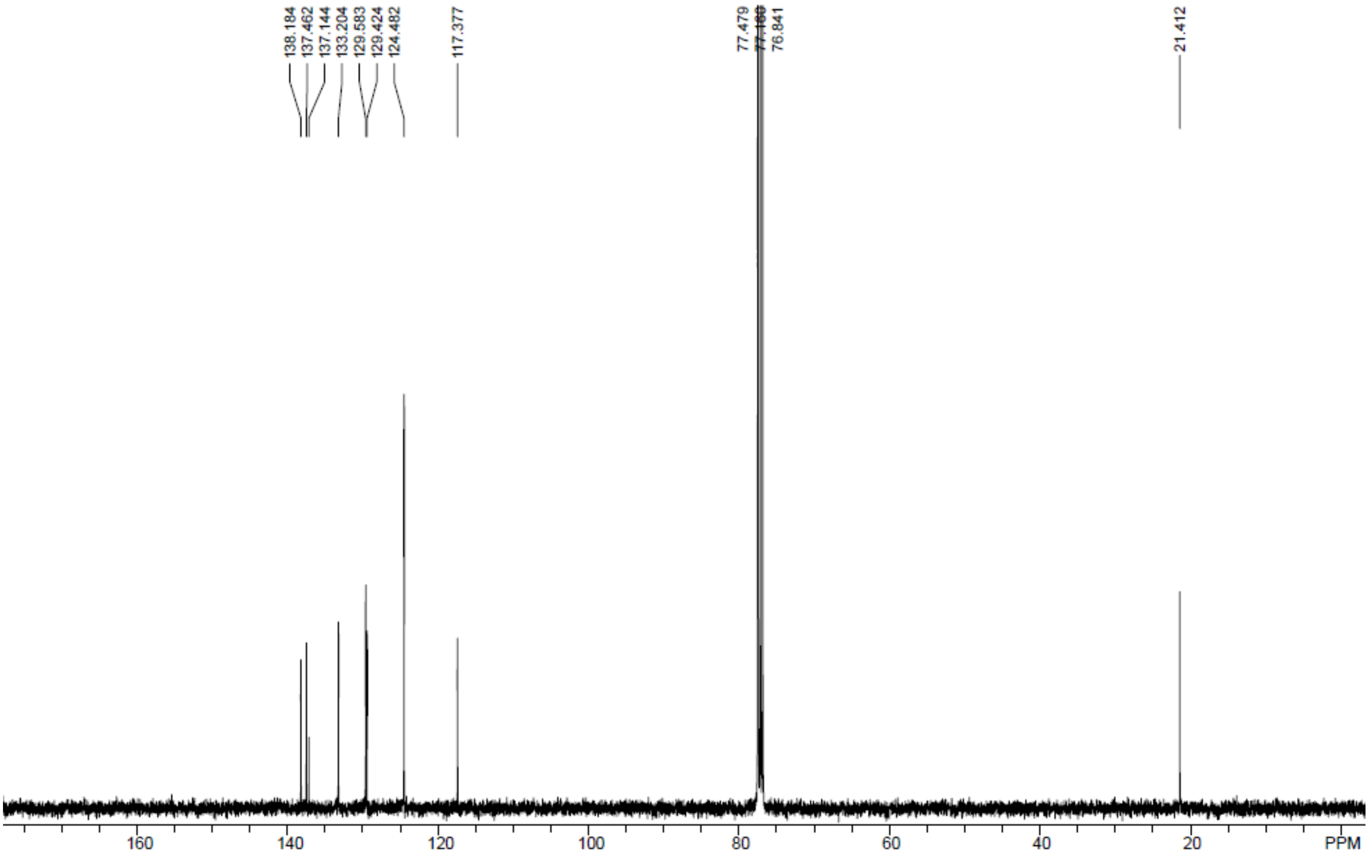
^{19}F NMR spectrum of **8e**



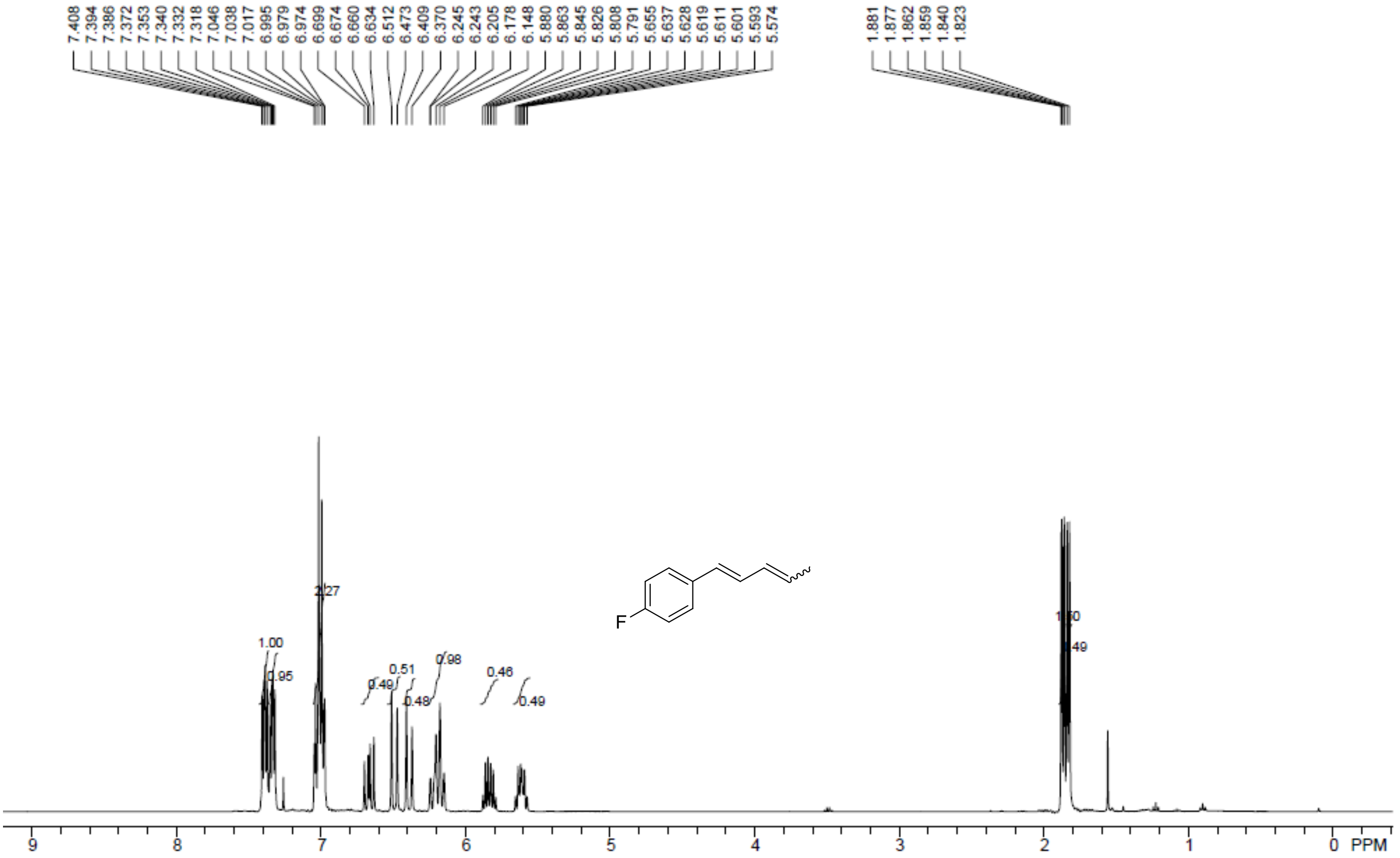
^{13}C NMR spectrum of **8e**



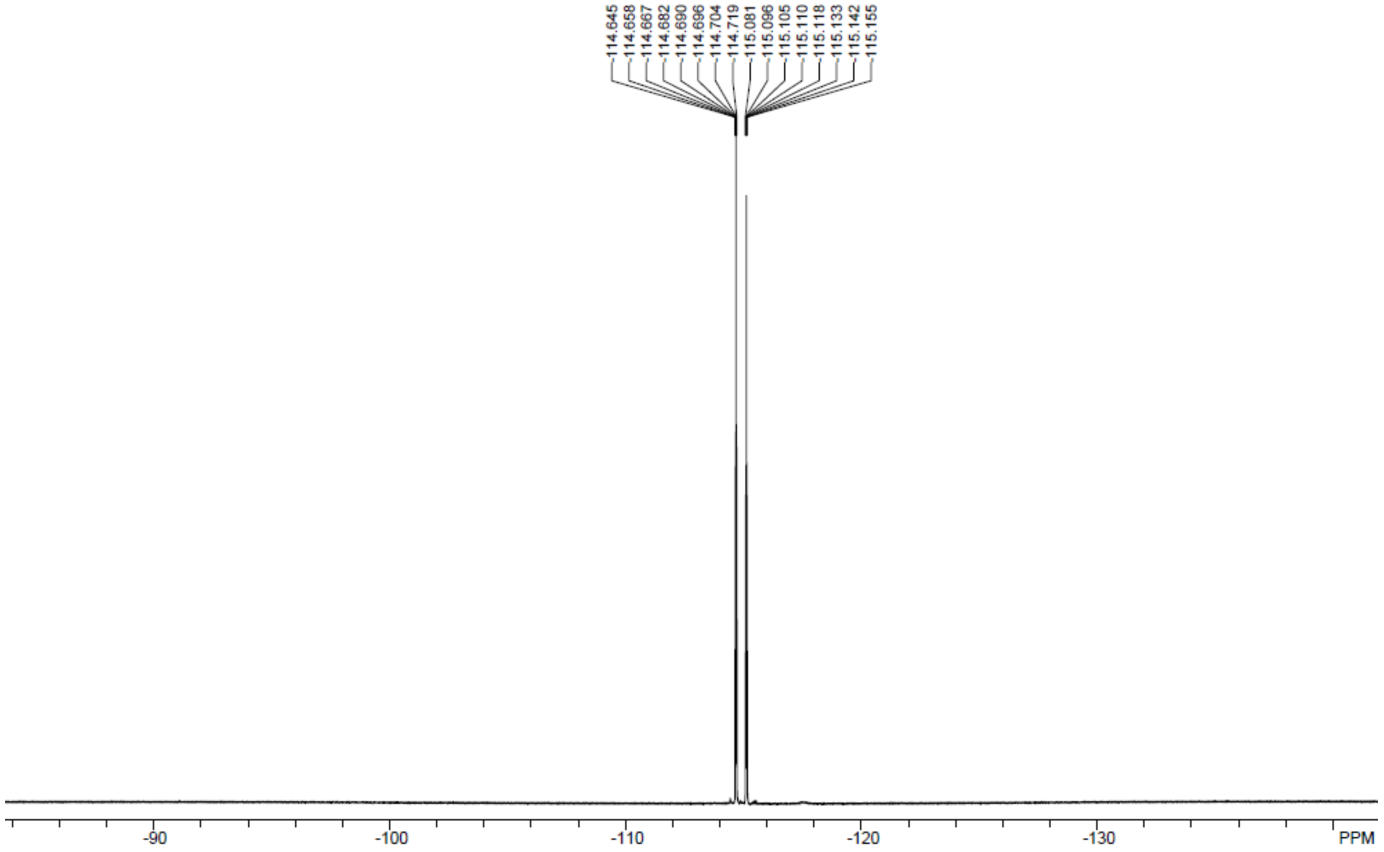
^{1}H NMR spectrum of **8h**



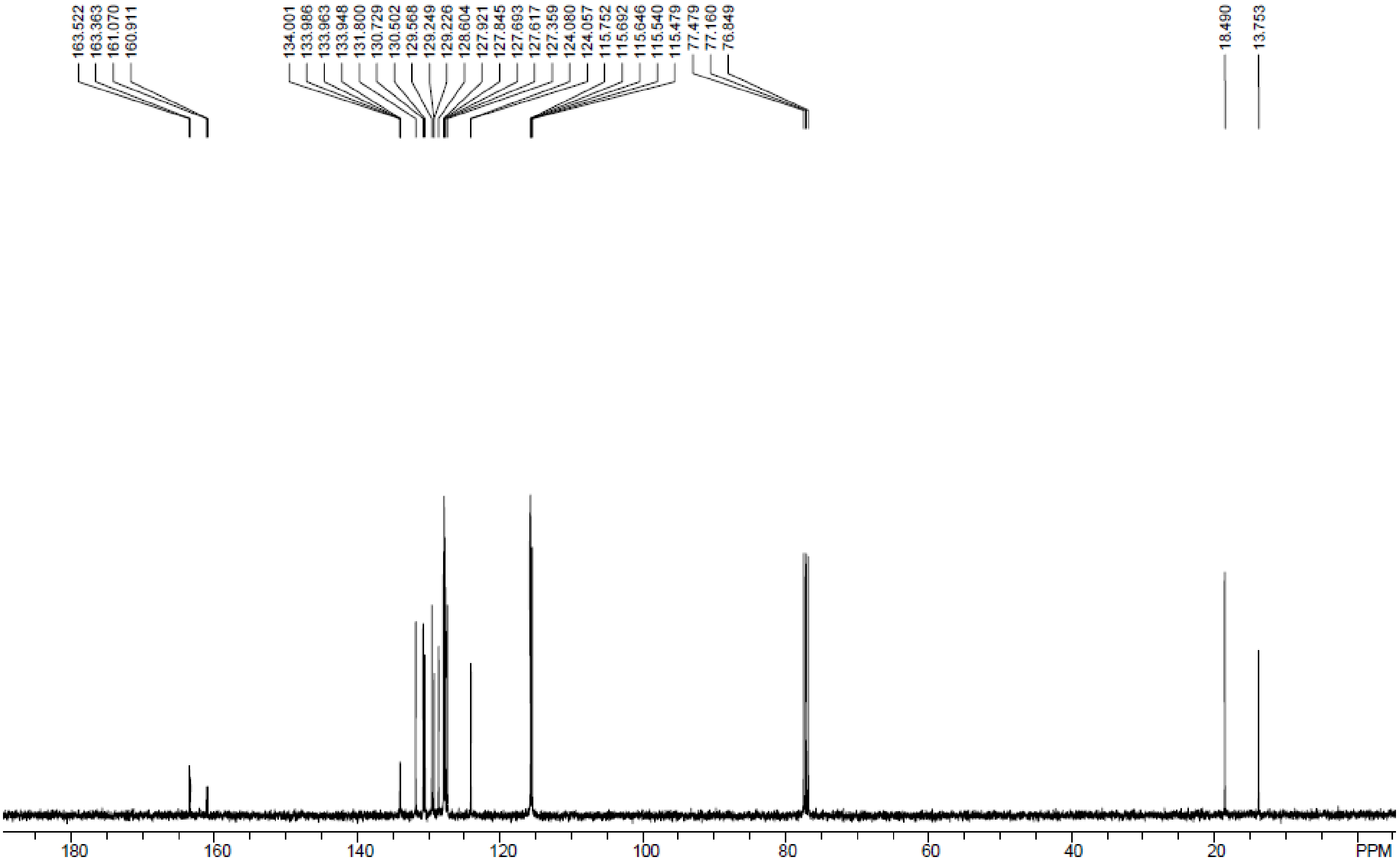
^{13}C NMR spectrum of **8h**



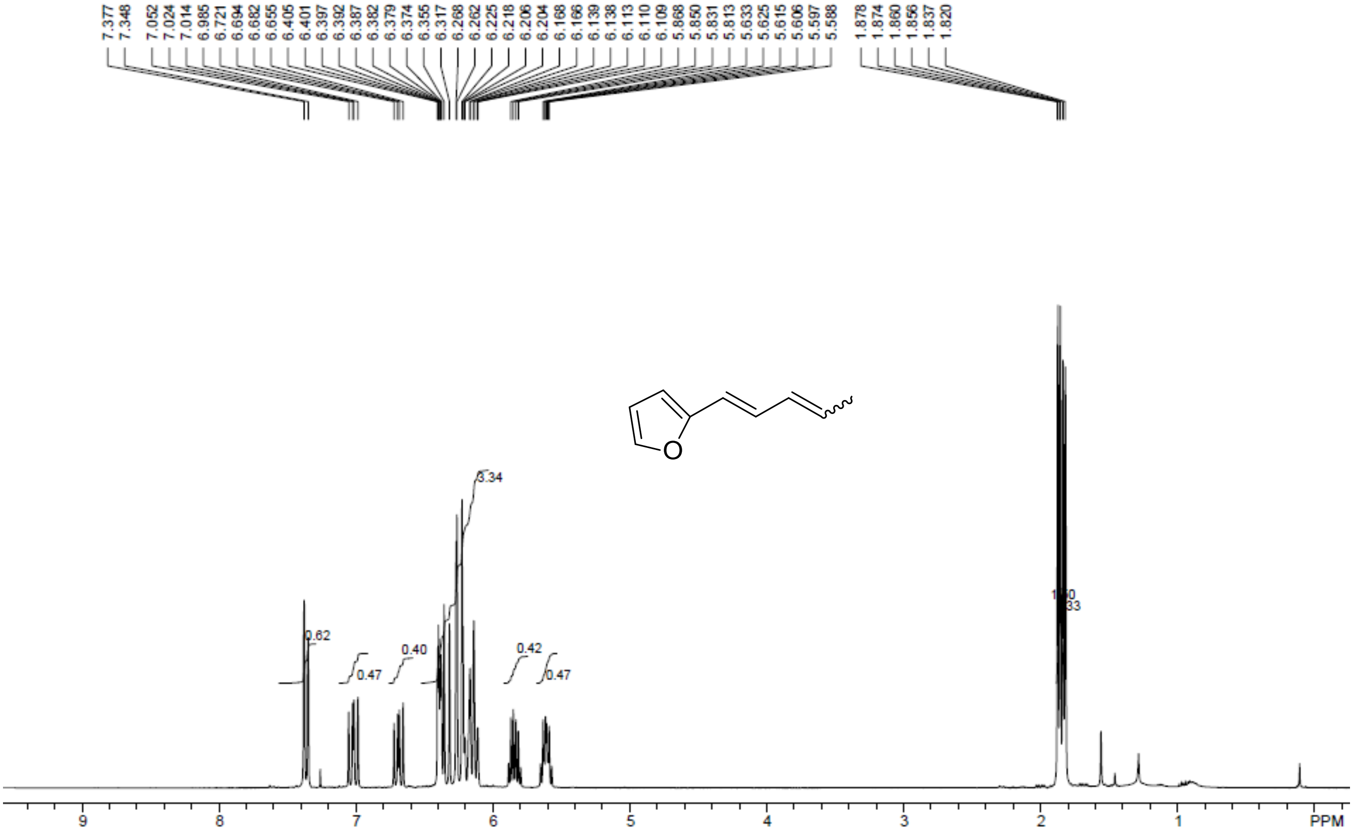
^{1}H NMR spectrum of **10c**



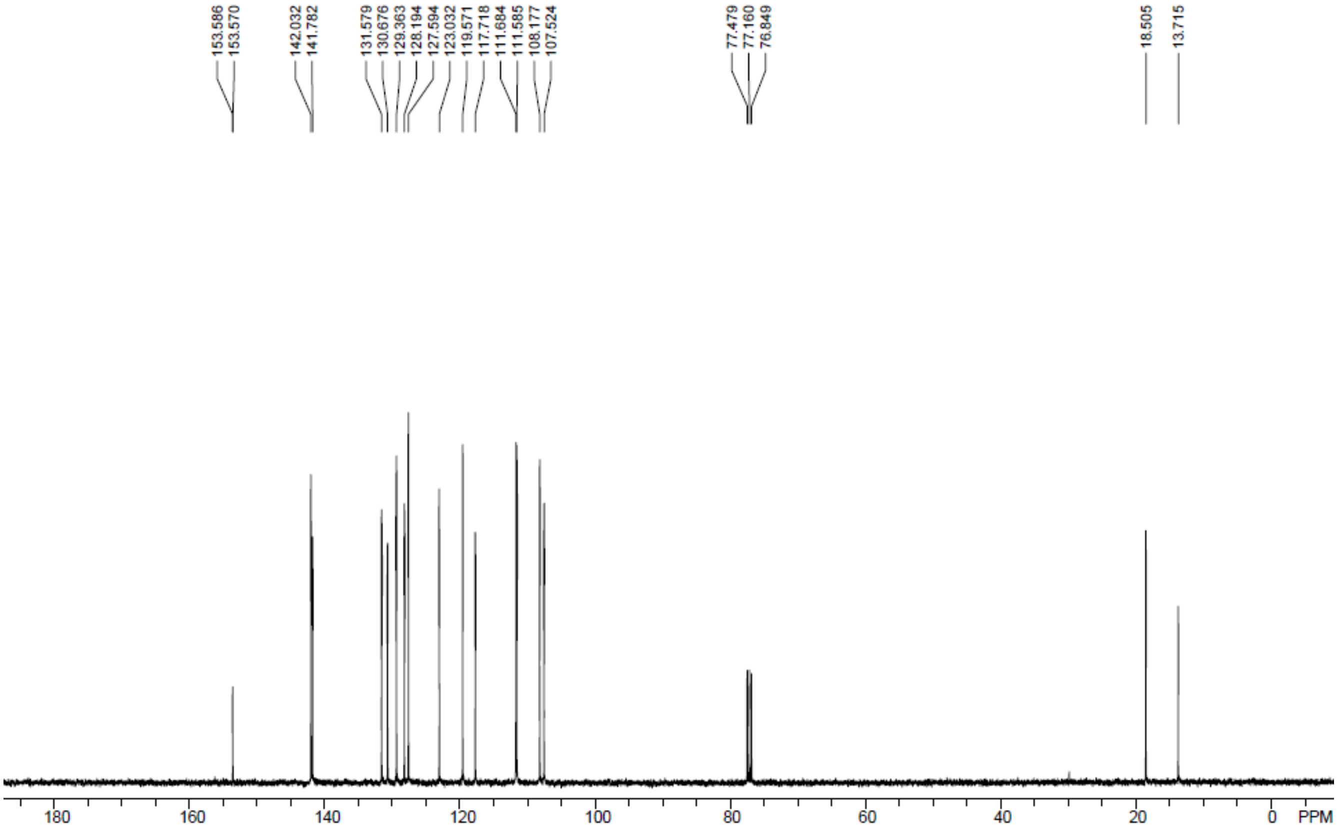
^{19}F NMR spectrum of **10c**



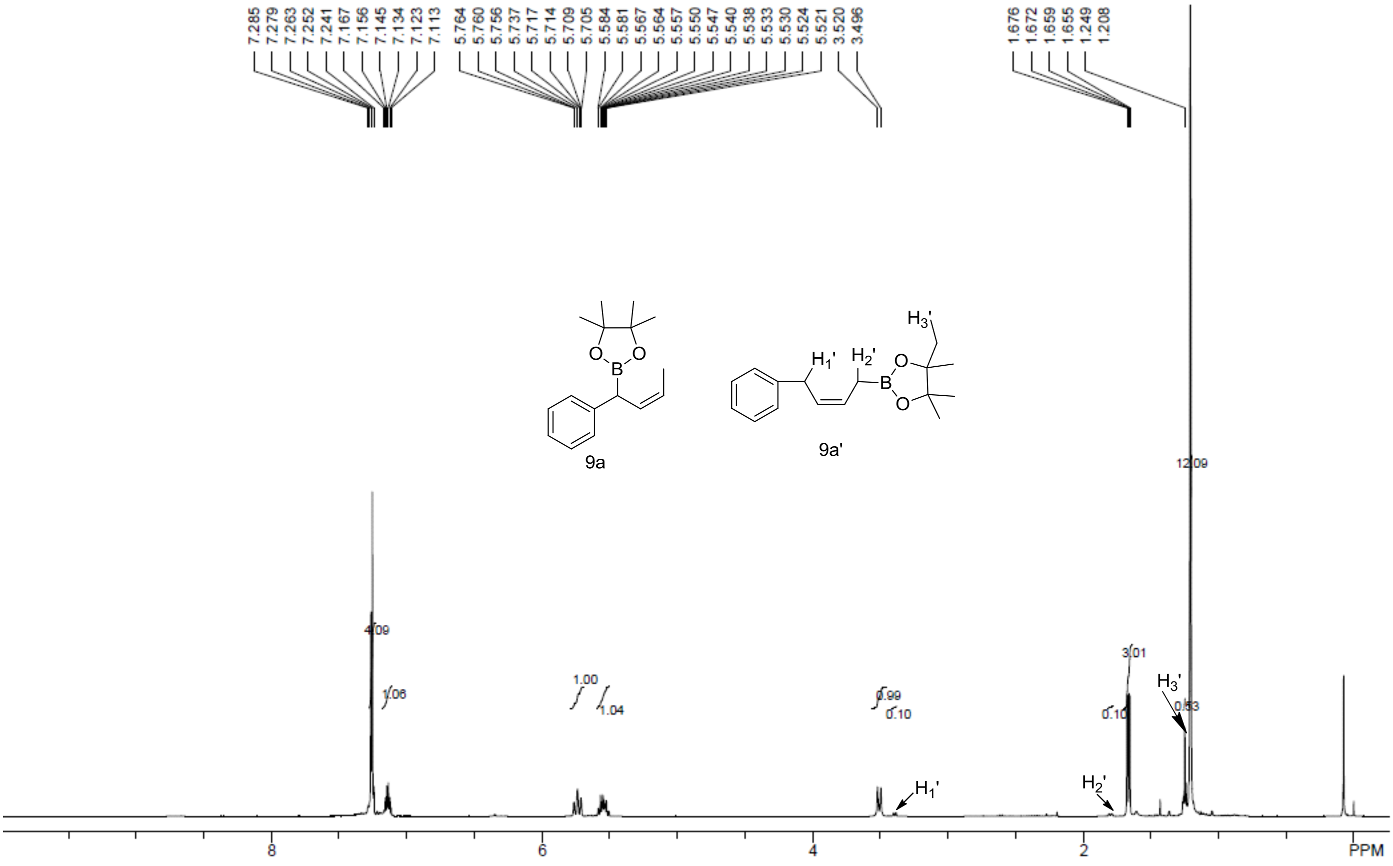
^{13}C NMR spectrum of **10c**



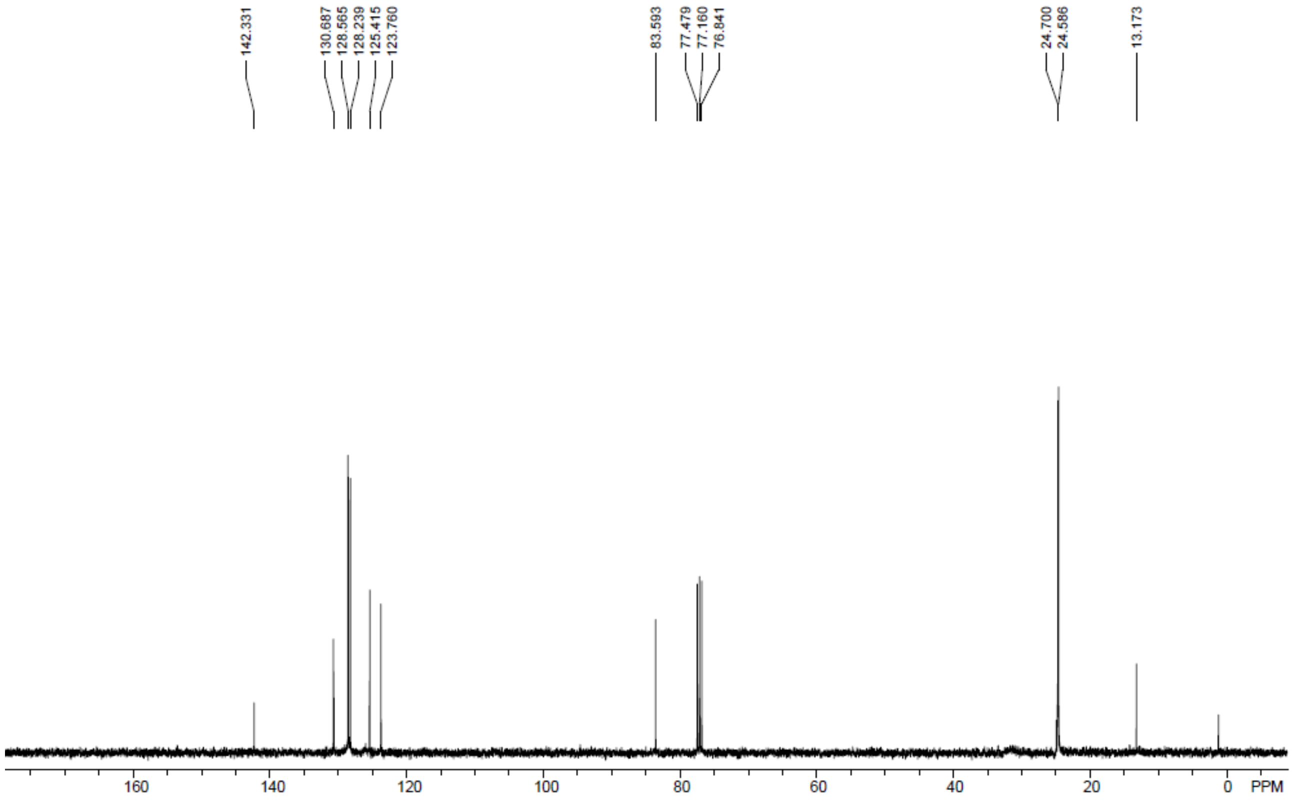
^{1}H NMR spectrum of **10d**



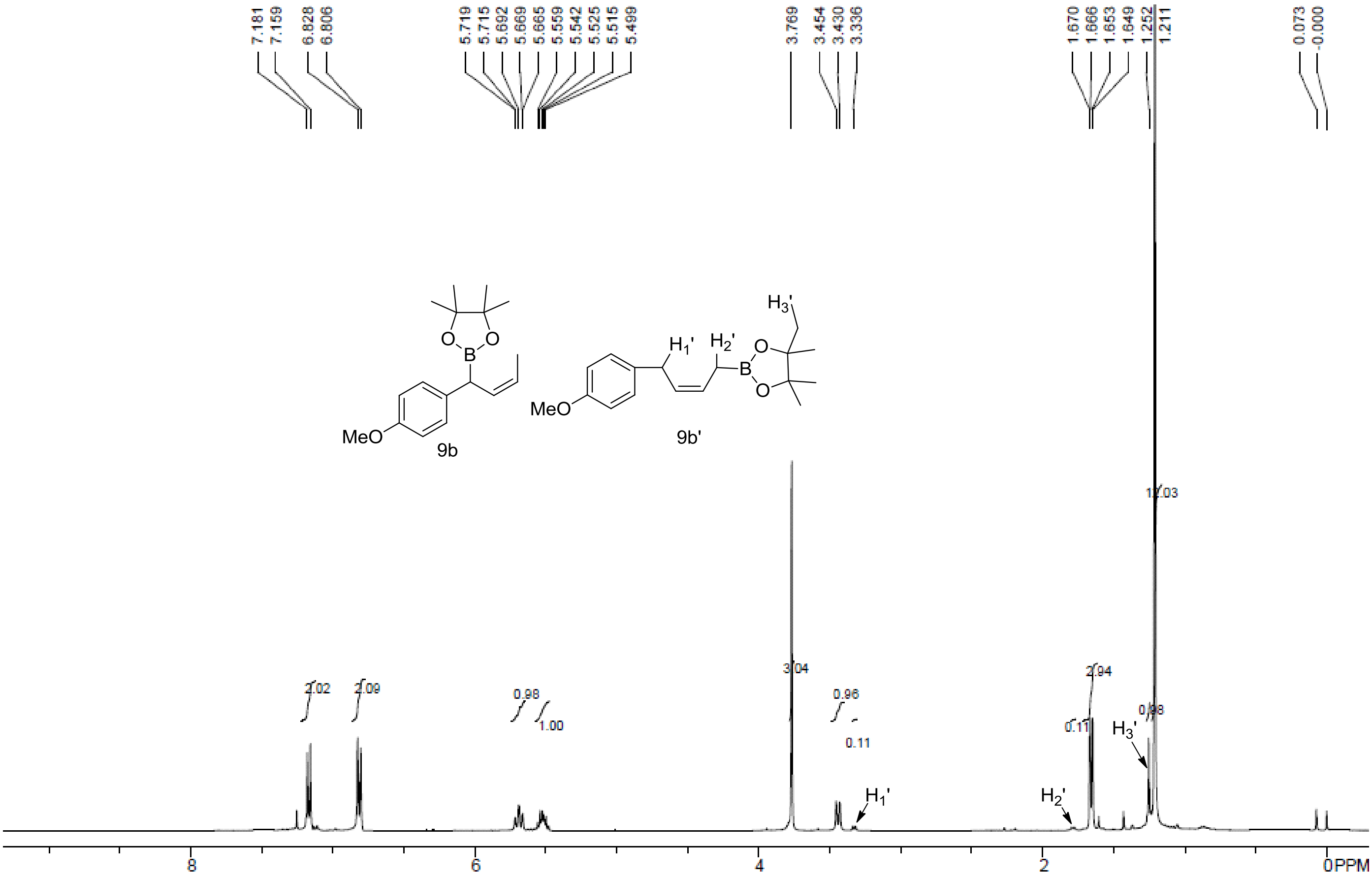
^{13}C NMR spectrum of **10d**



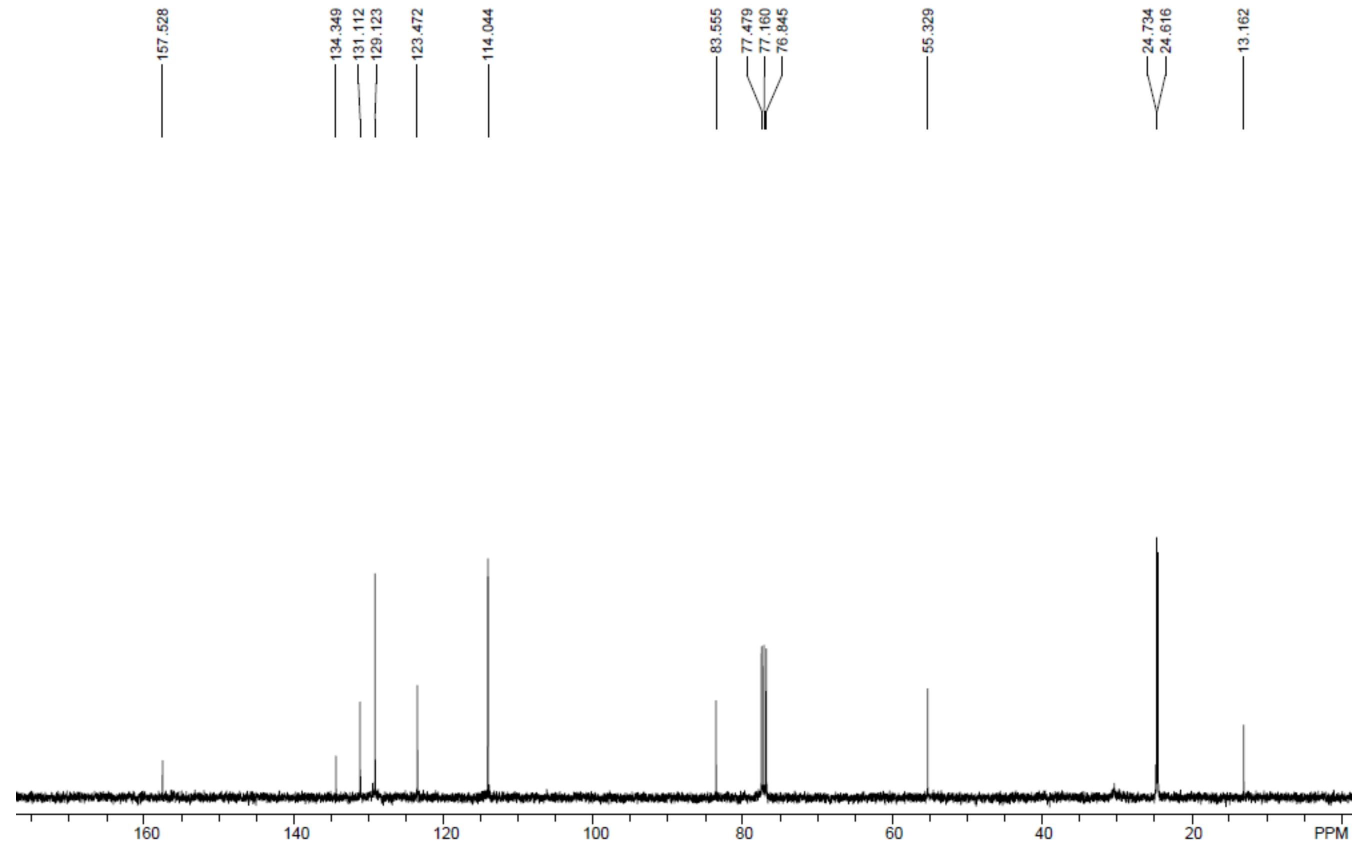
^{1}H NMR spectrum of **9a + 9a’**



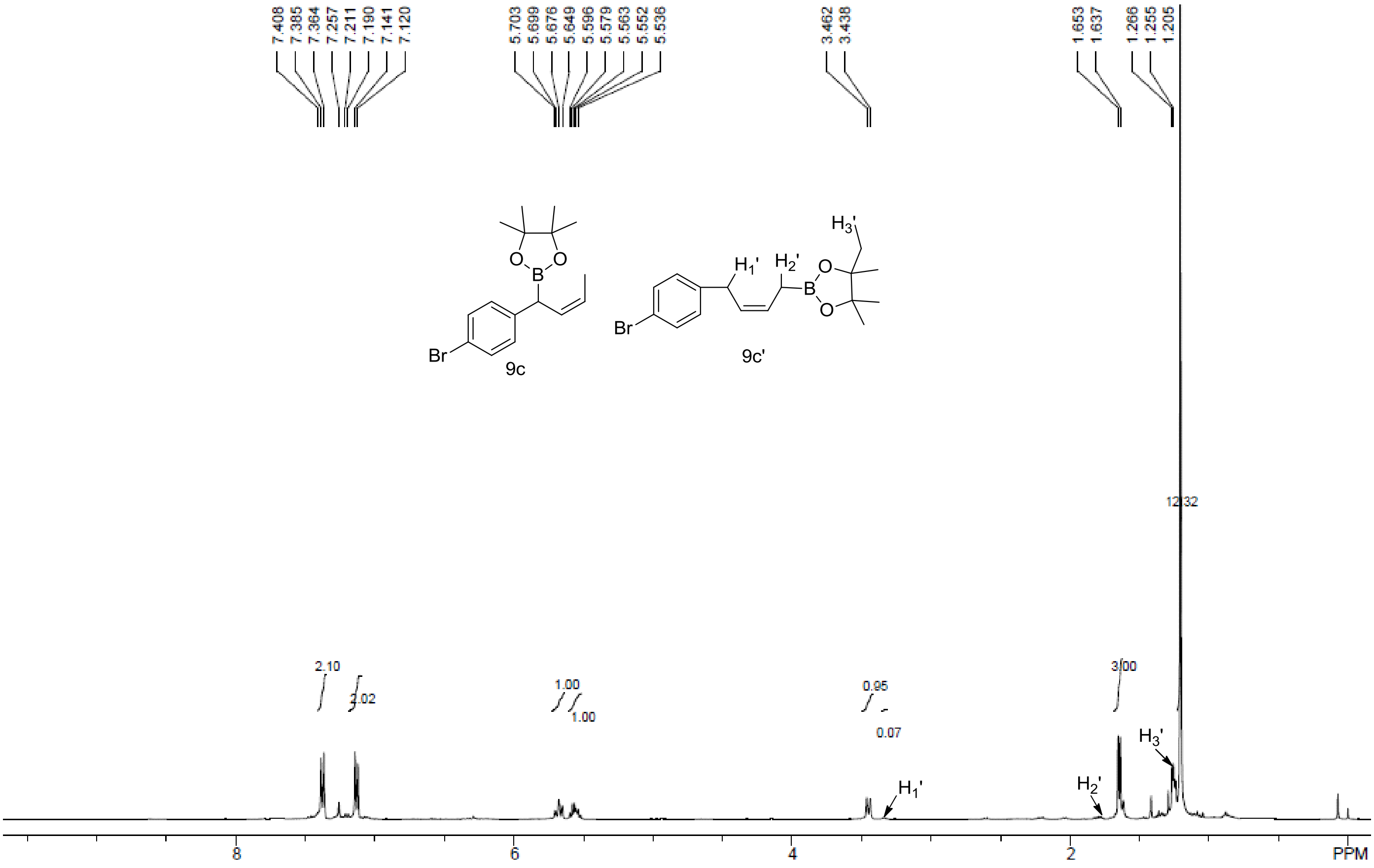
^{13}C NMR spectrum of **9a**



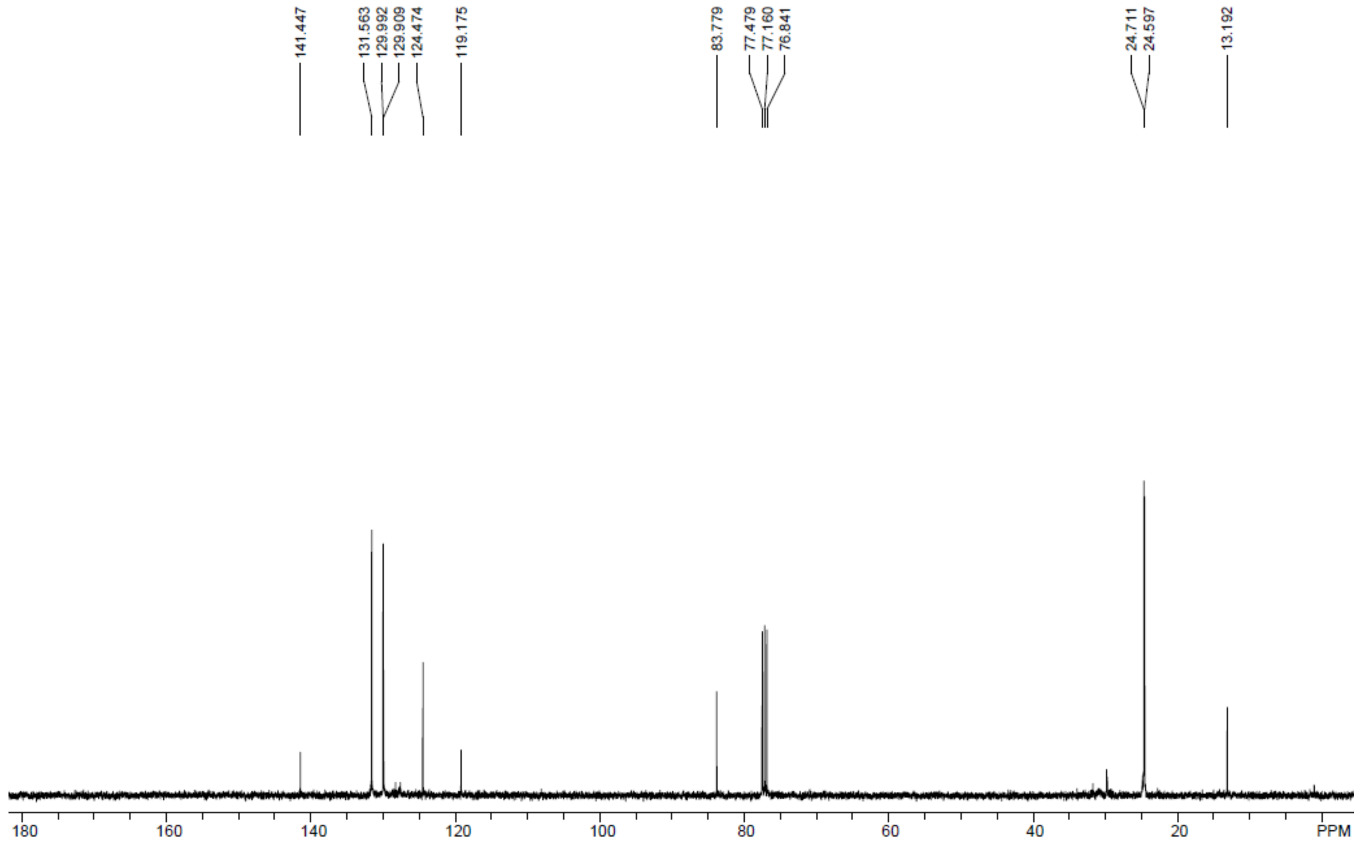
^{1}H NMR spectrum of **9b + 9b'**



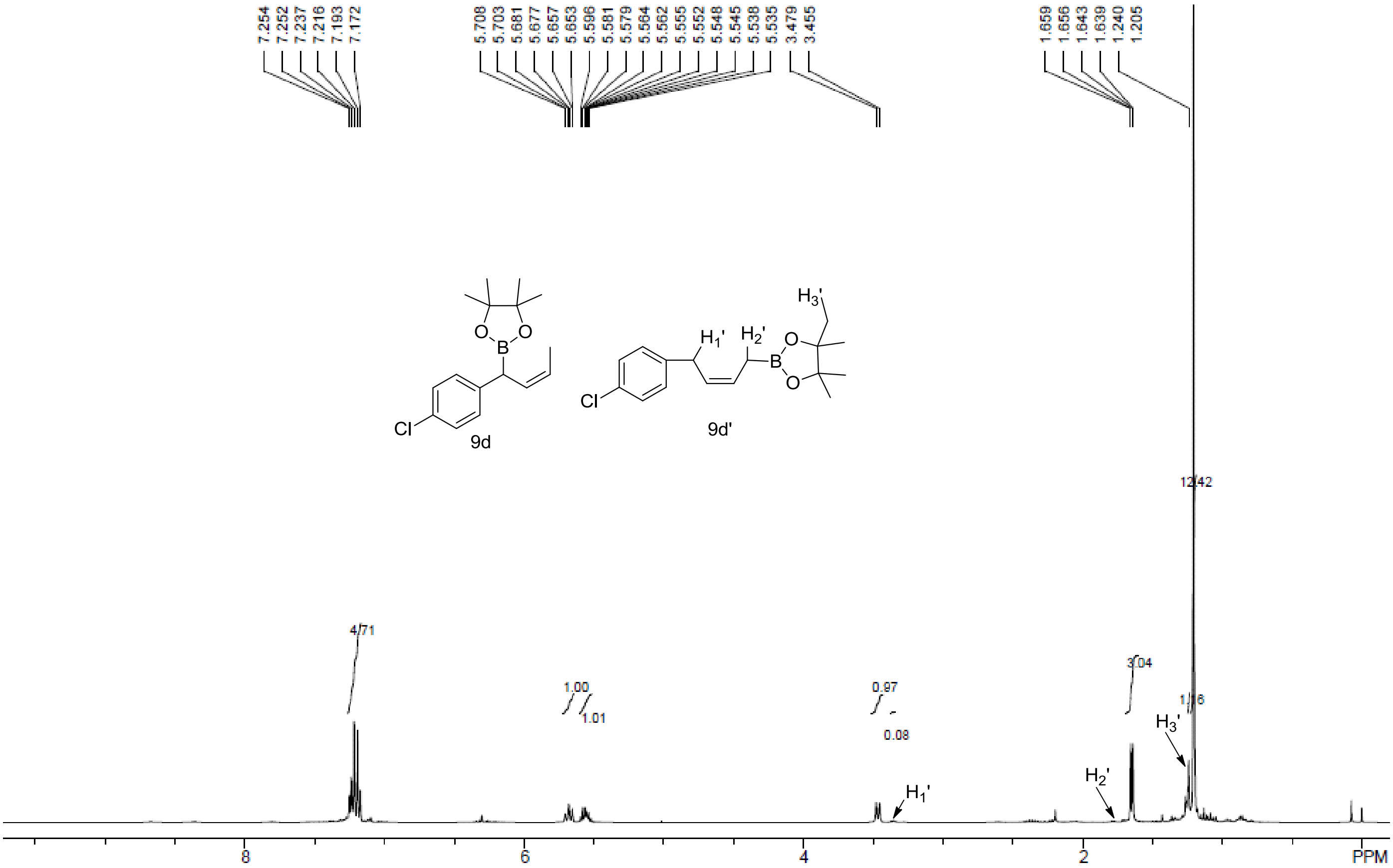
^{13}C NMR spectrum of **9b**



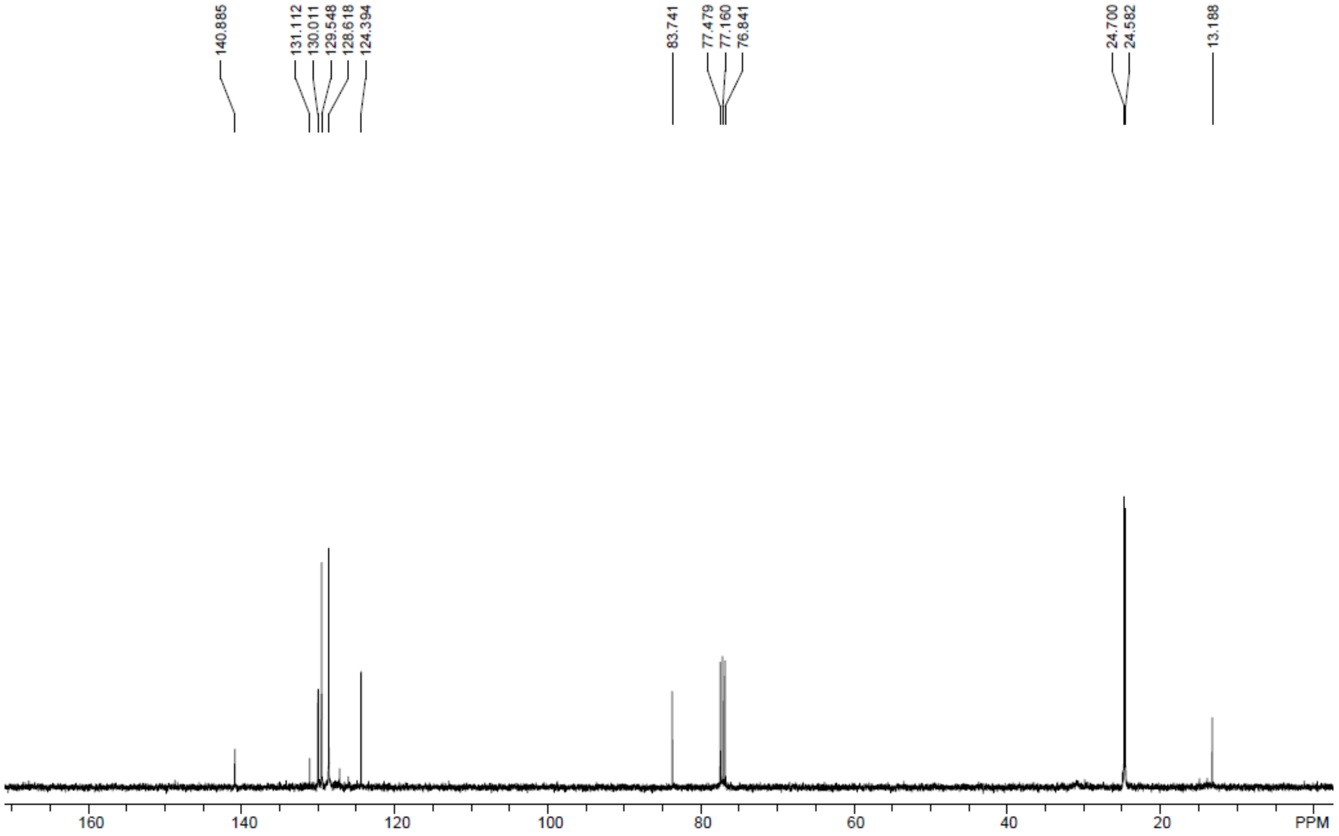
^{1}H NMR spectrum of **9c + 9c’**



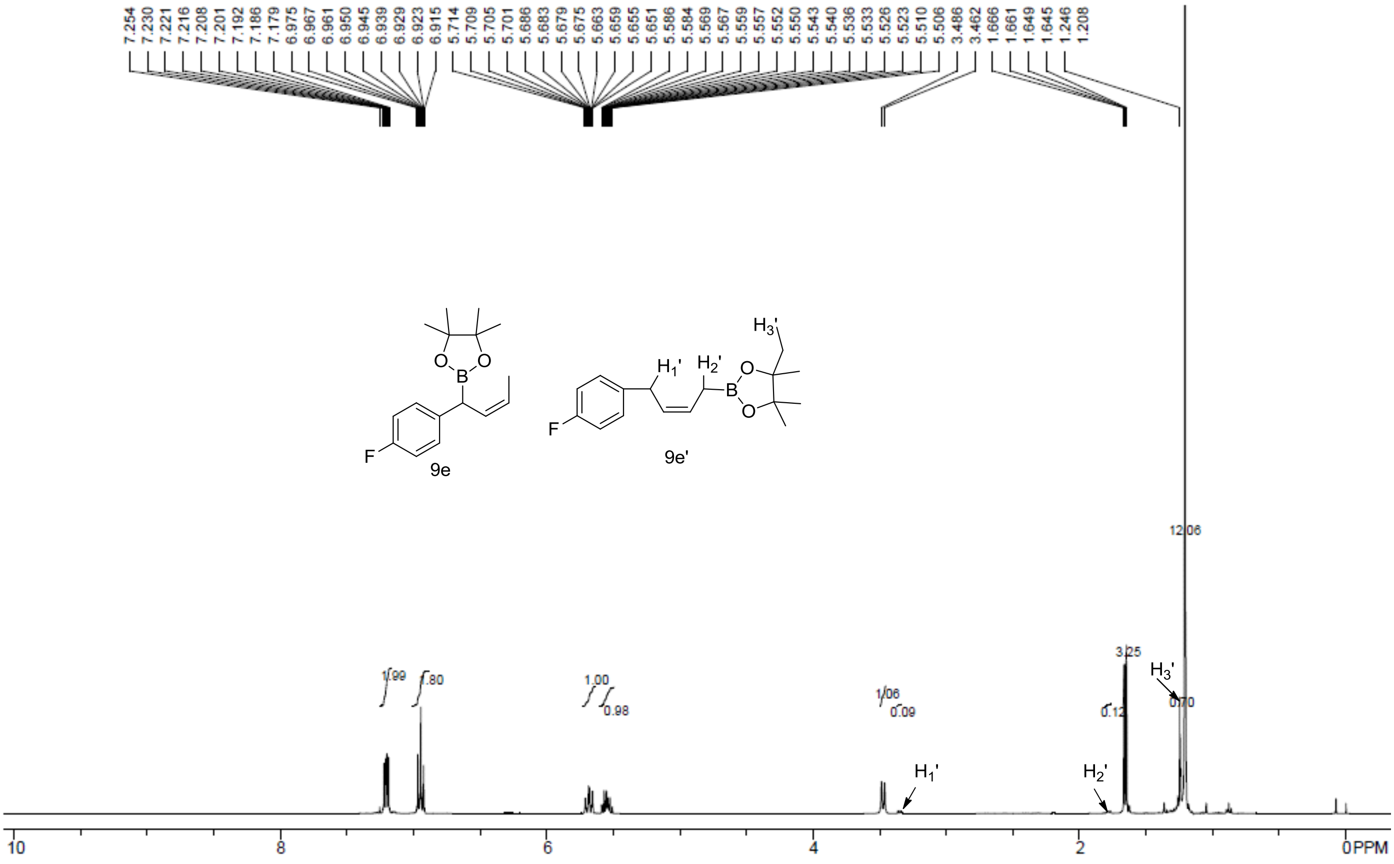
^{13}C NMR spectrum of **9c**



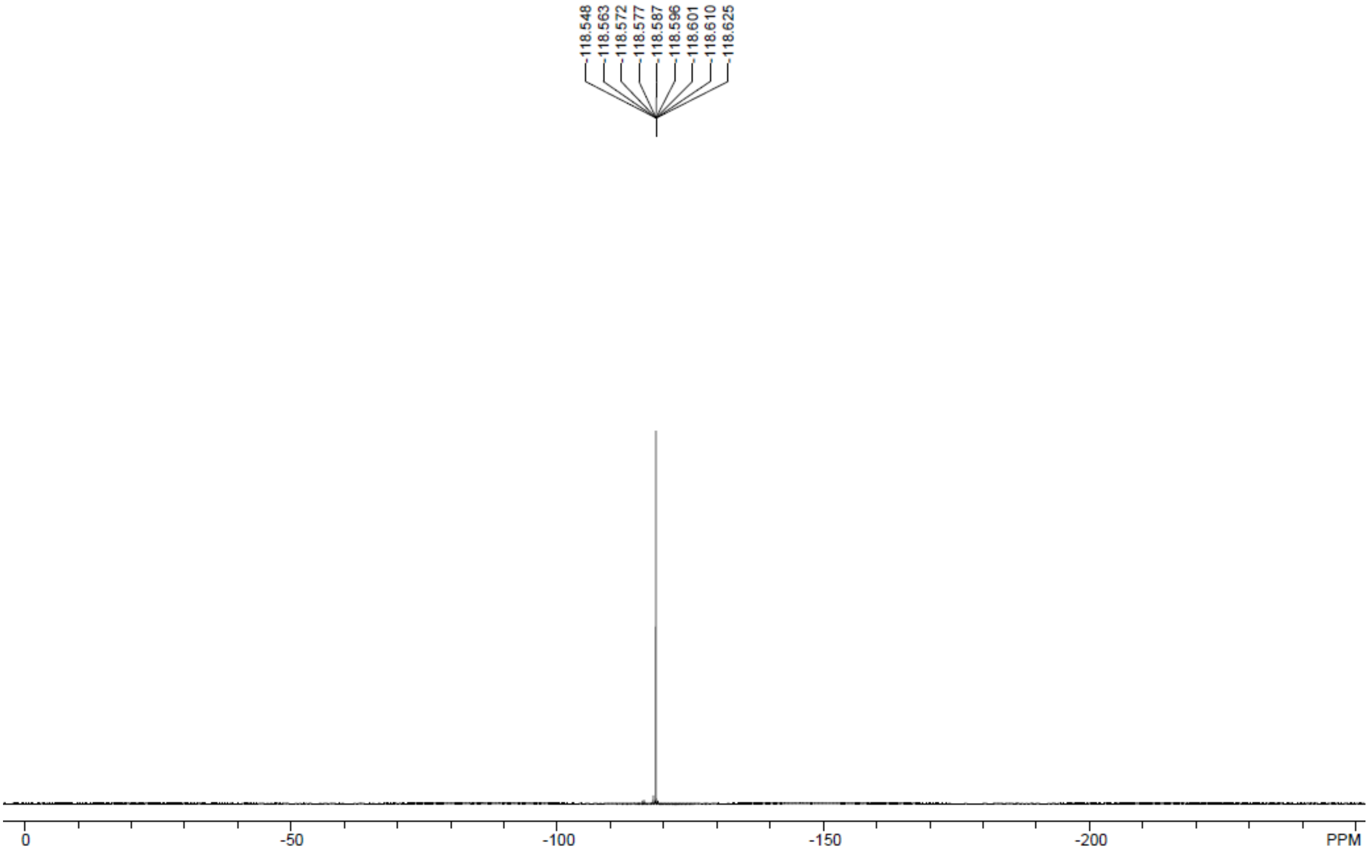
^{1}H NMR spectrum of **9d + 9d’**



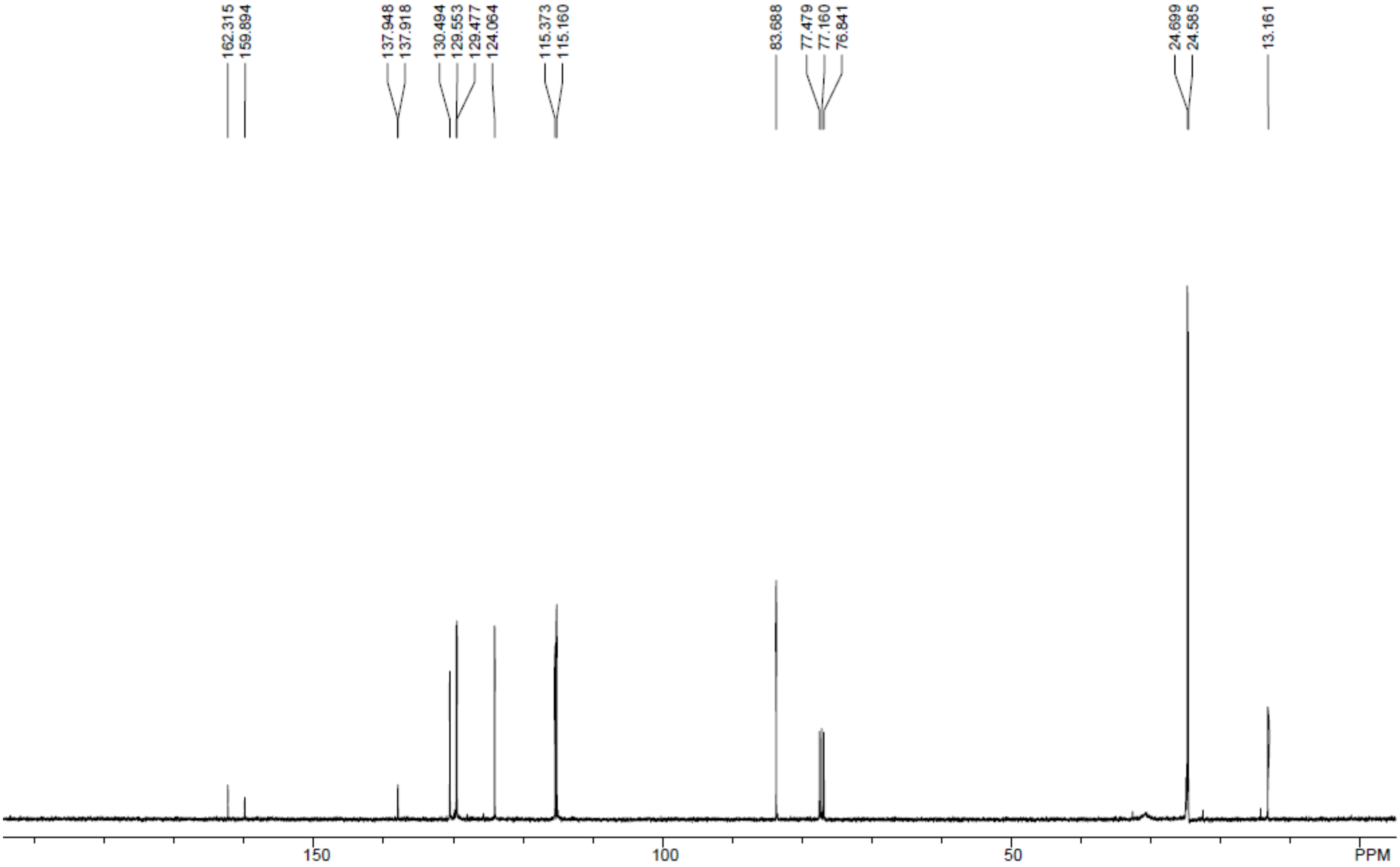
^{13}C NMR spectrum of **9d**



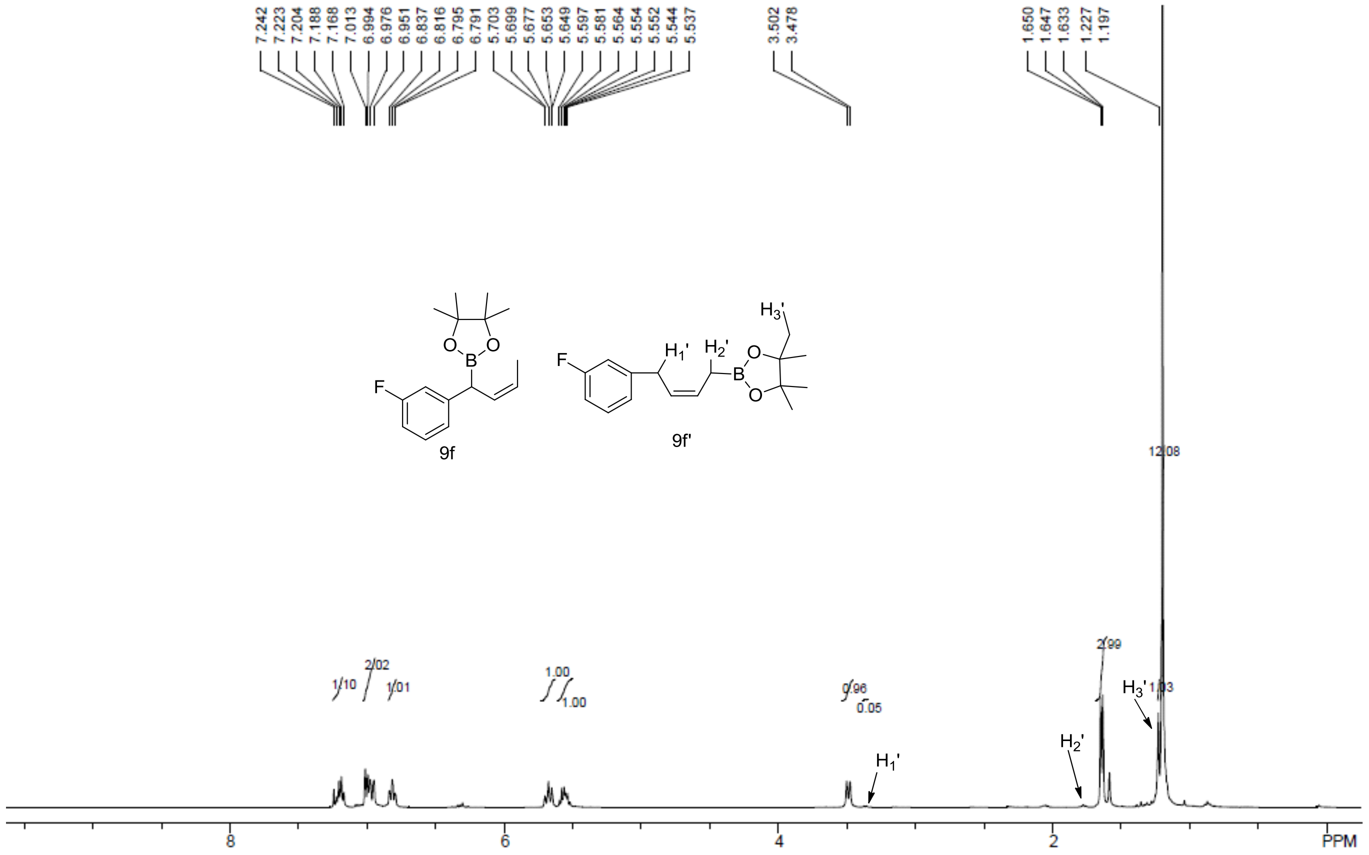
^{1}H NMR spectrum of **9e + 9e'**



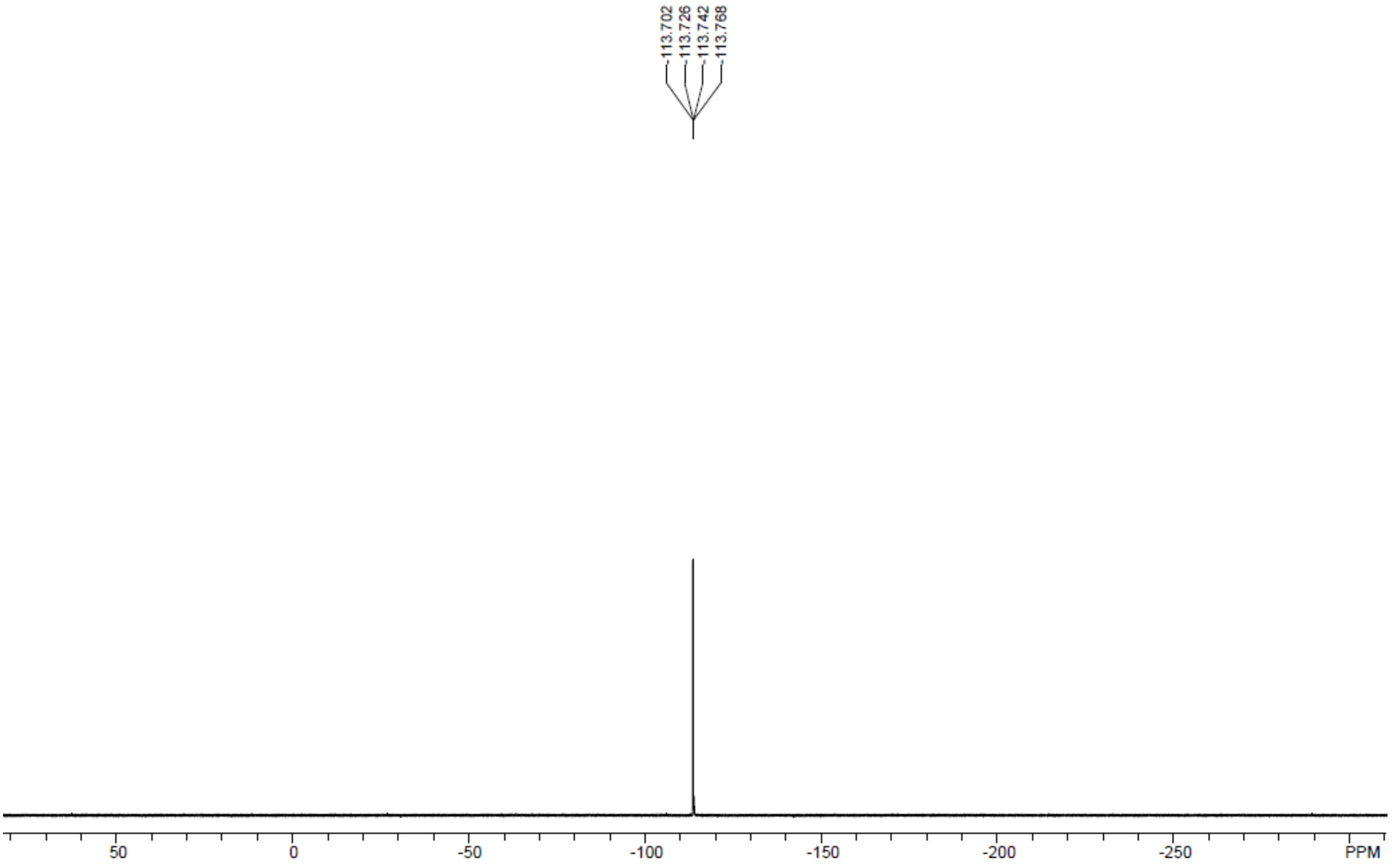
^{19}F NMR spectrum of **9e**



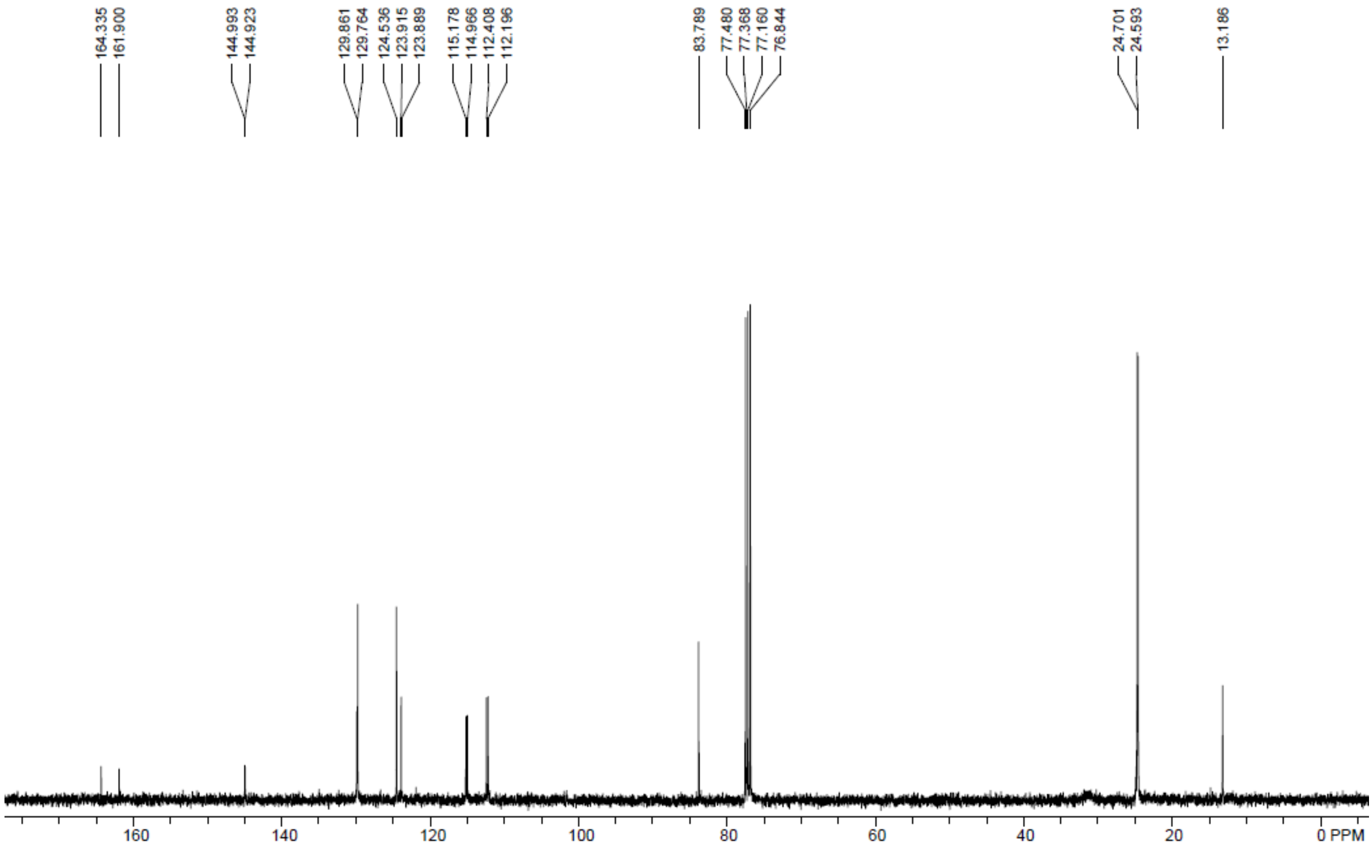
^{13}C NMR spectrum of **9e + 9e’**



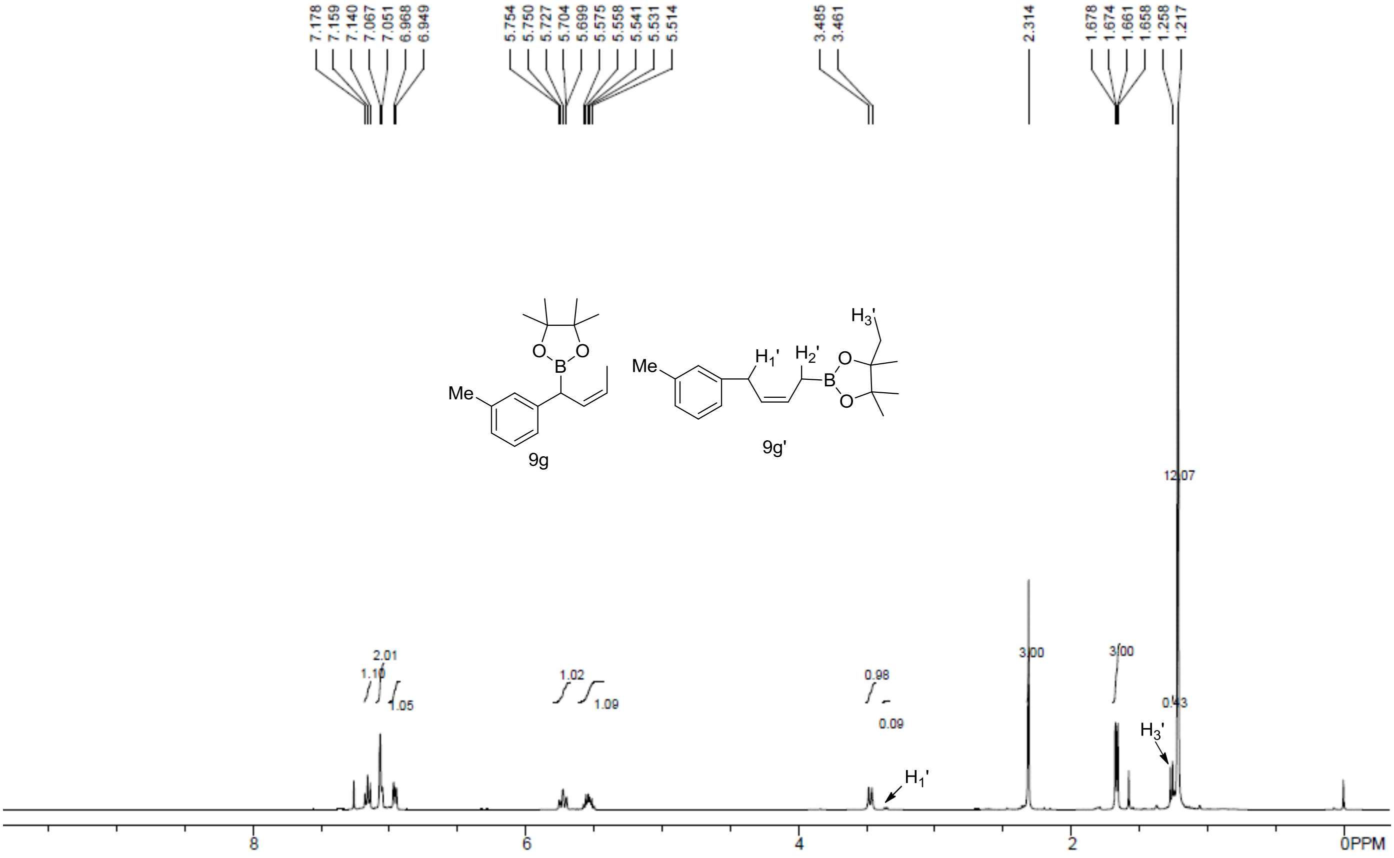
^{1}H NMR spectrum of **9f + 9f'**



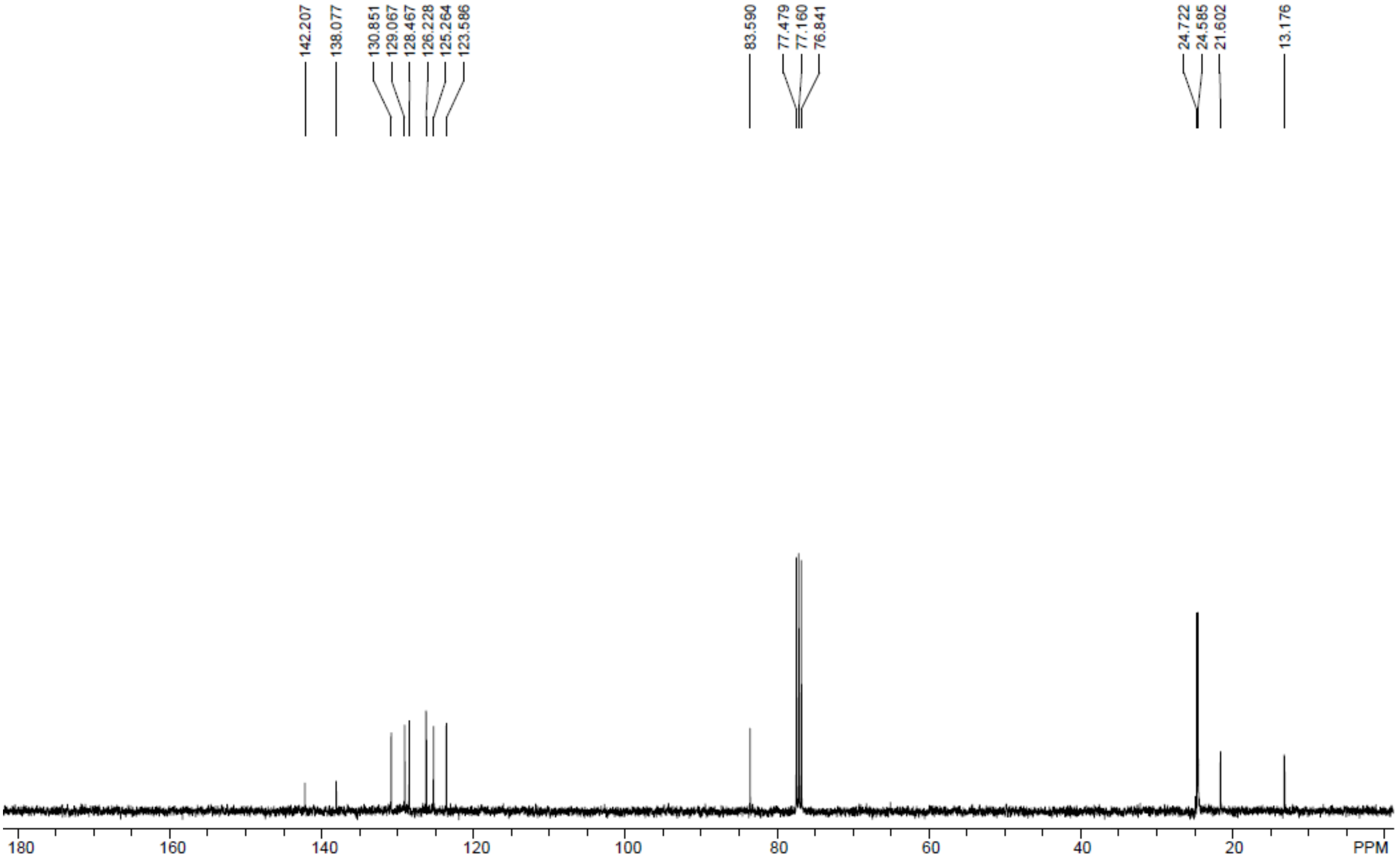
^{19}F NMR spectrum of **9f**



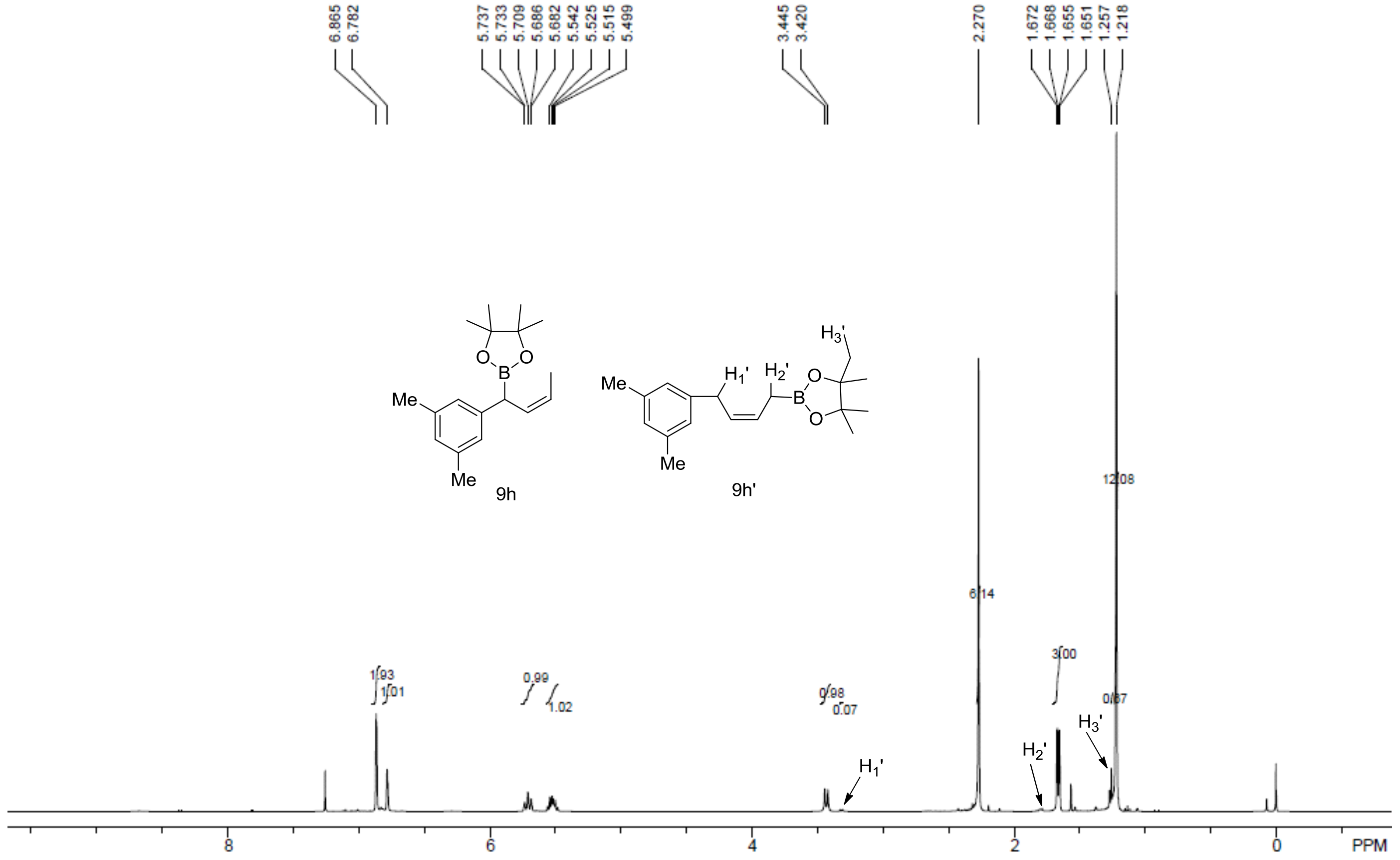
^{13}C NMR spectrum of **9f**



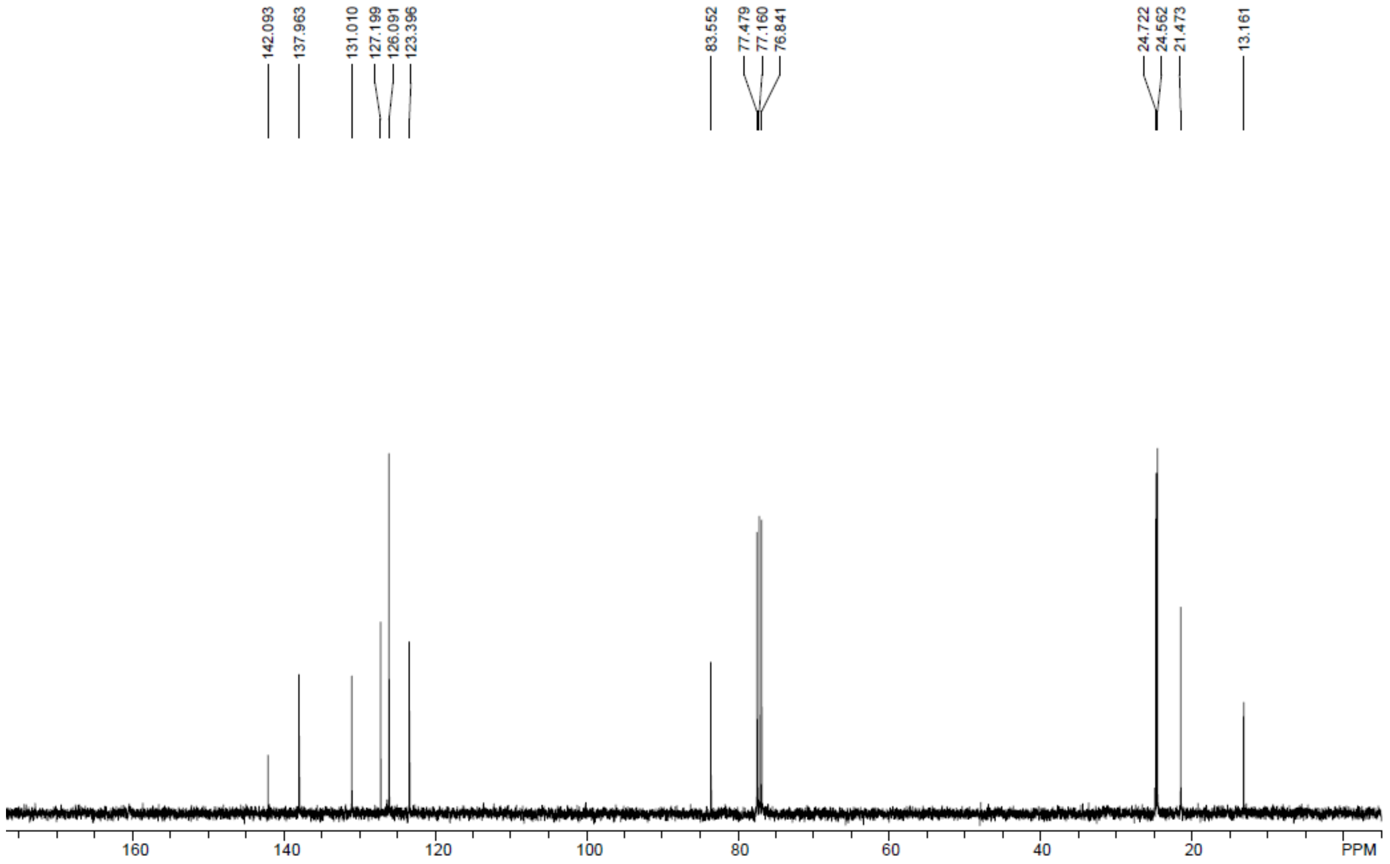
^{1}H NMR spectrum of **9g + 9g’**



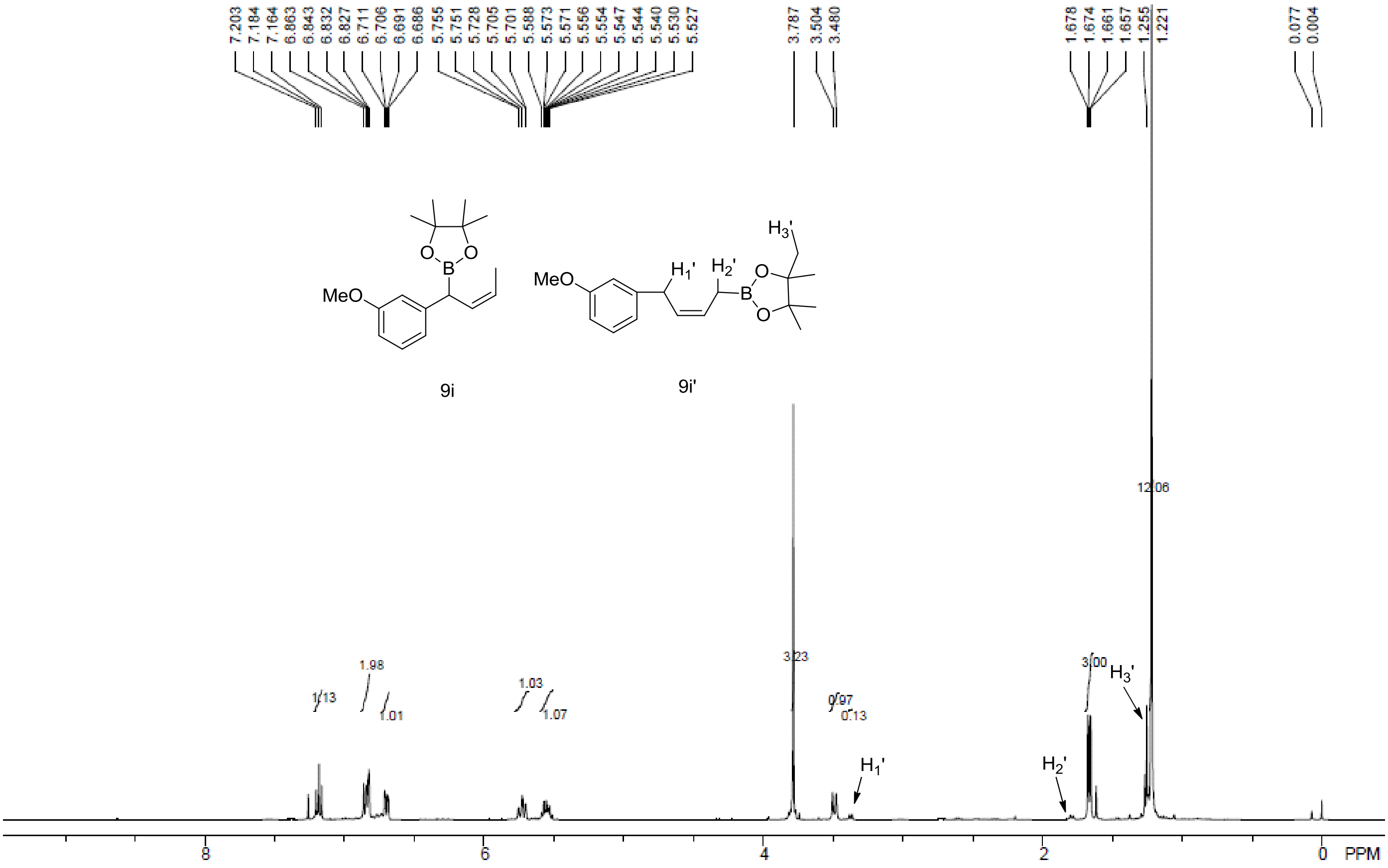
^{13}C NMR spectrum of **9g**



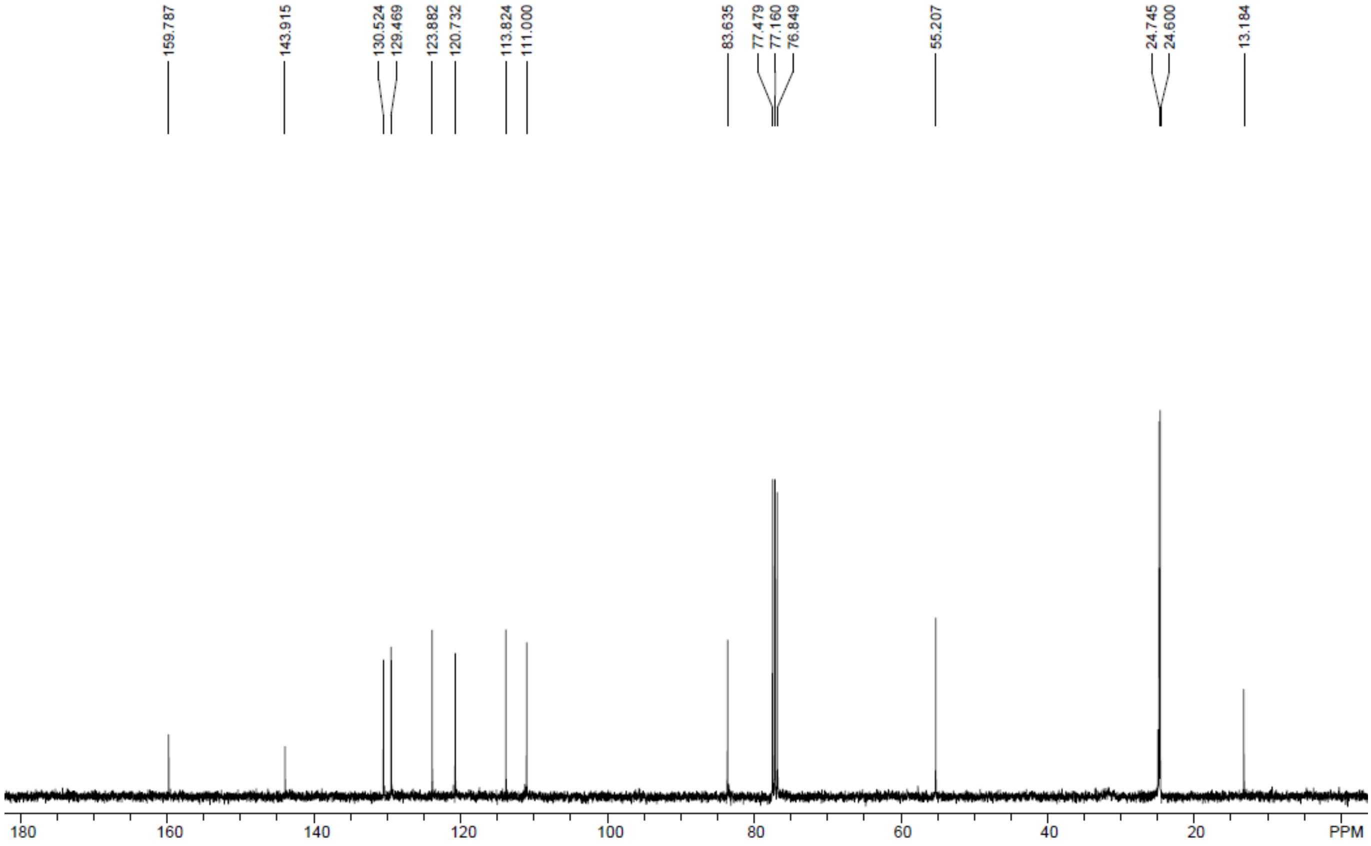
^{1}H NMR spectrum of **9h + 9h'**



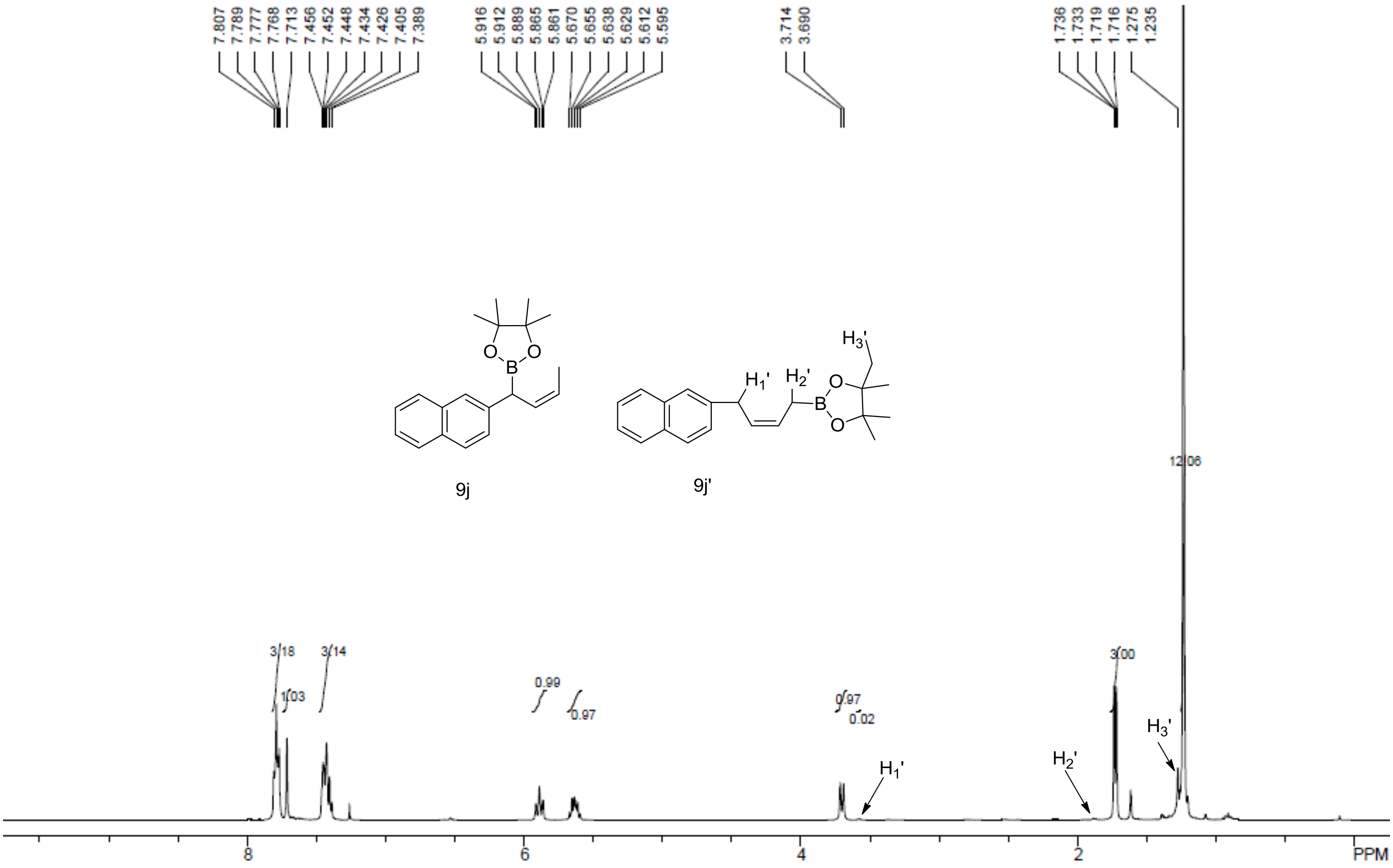
^{13}C NMR spectrum of **9h**



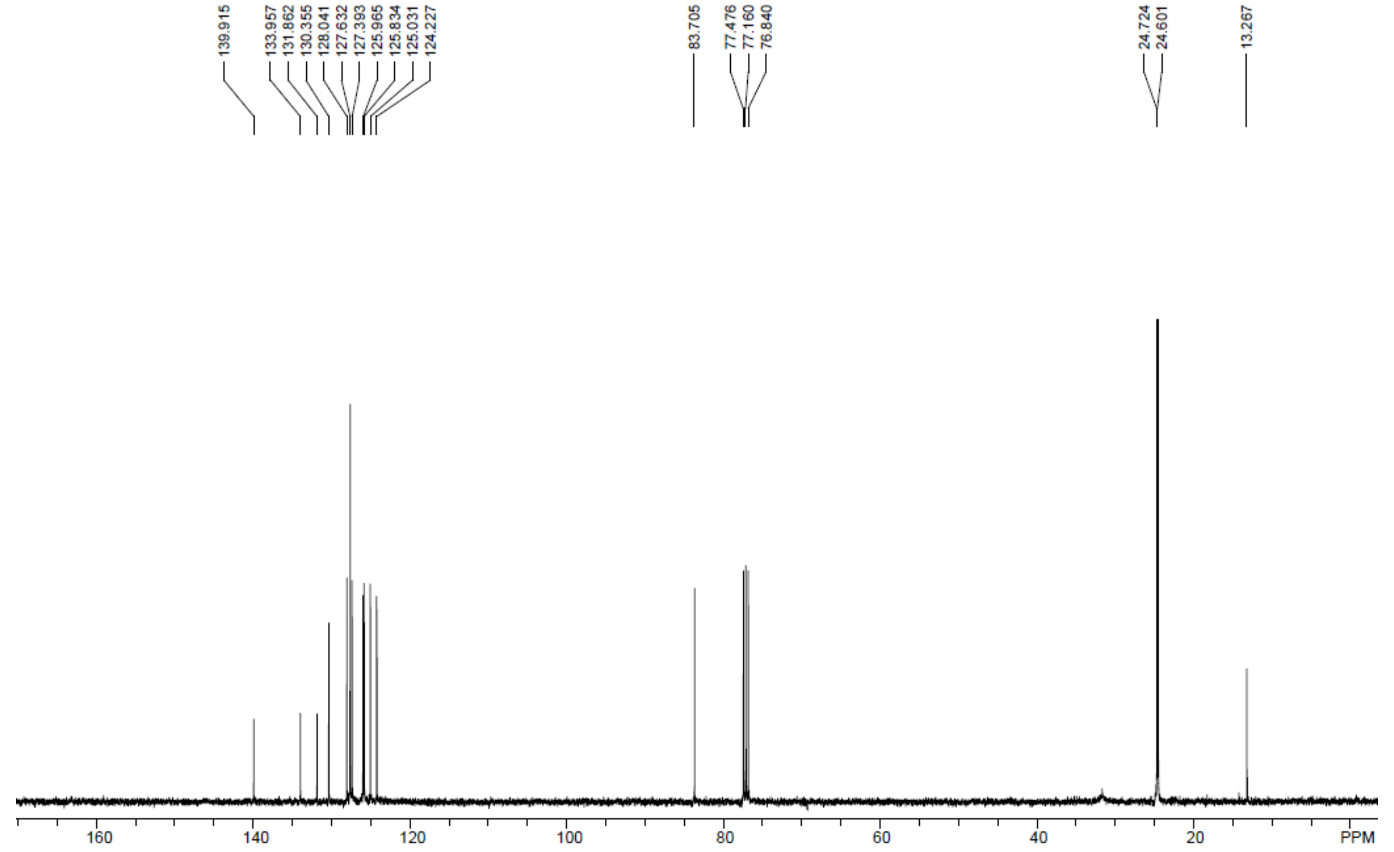
^{1}H NMR spectrum of **9i + 9i’**



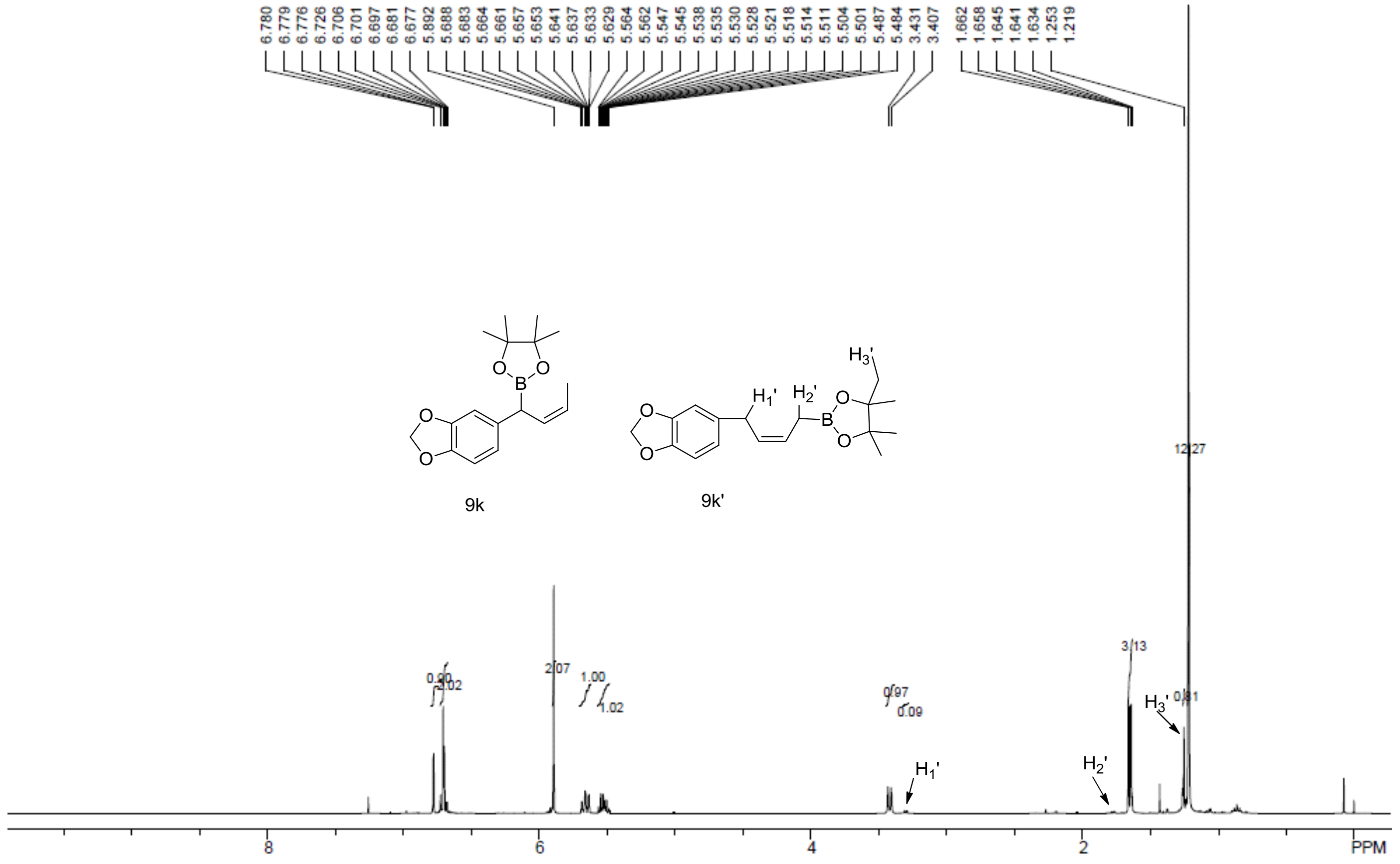
^{13}C NMR spectrum of **9i**



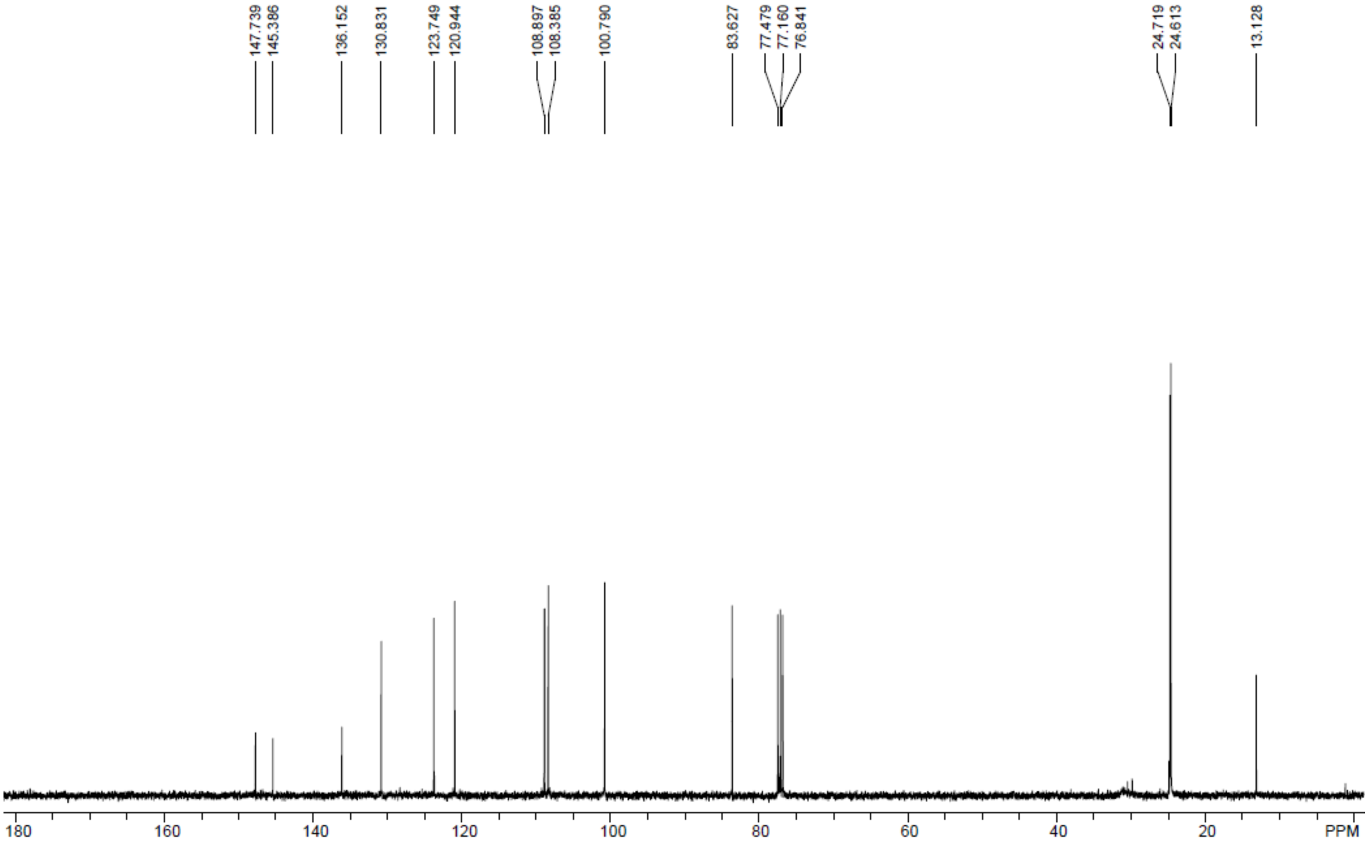
^{1}H NMR spectrum of **9j + 9j'**



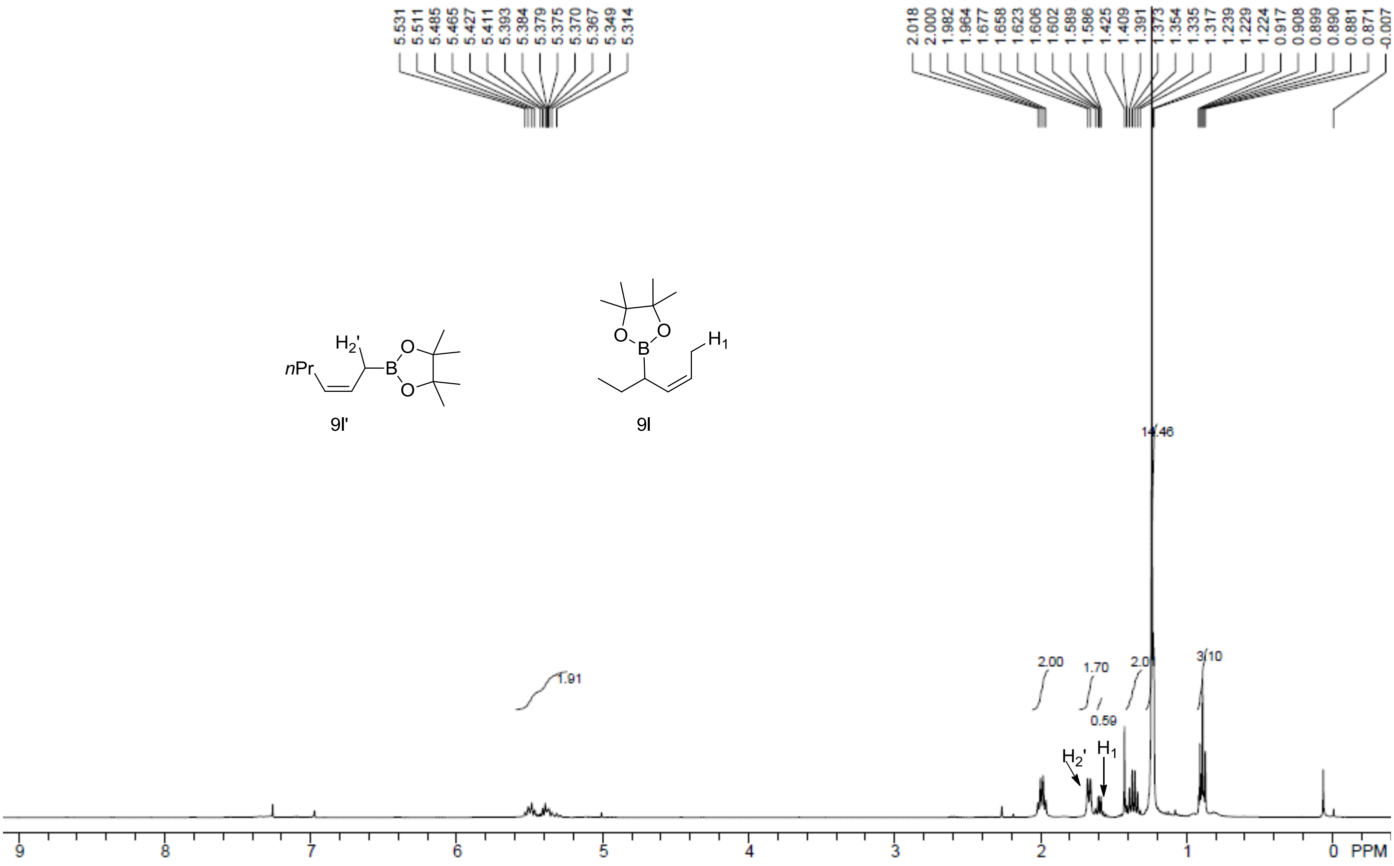
^{13}C NMR spectrum of **9j**



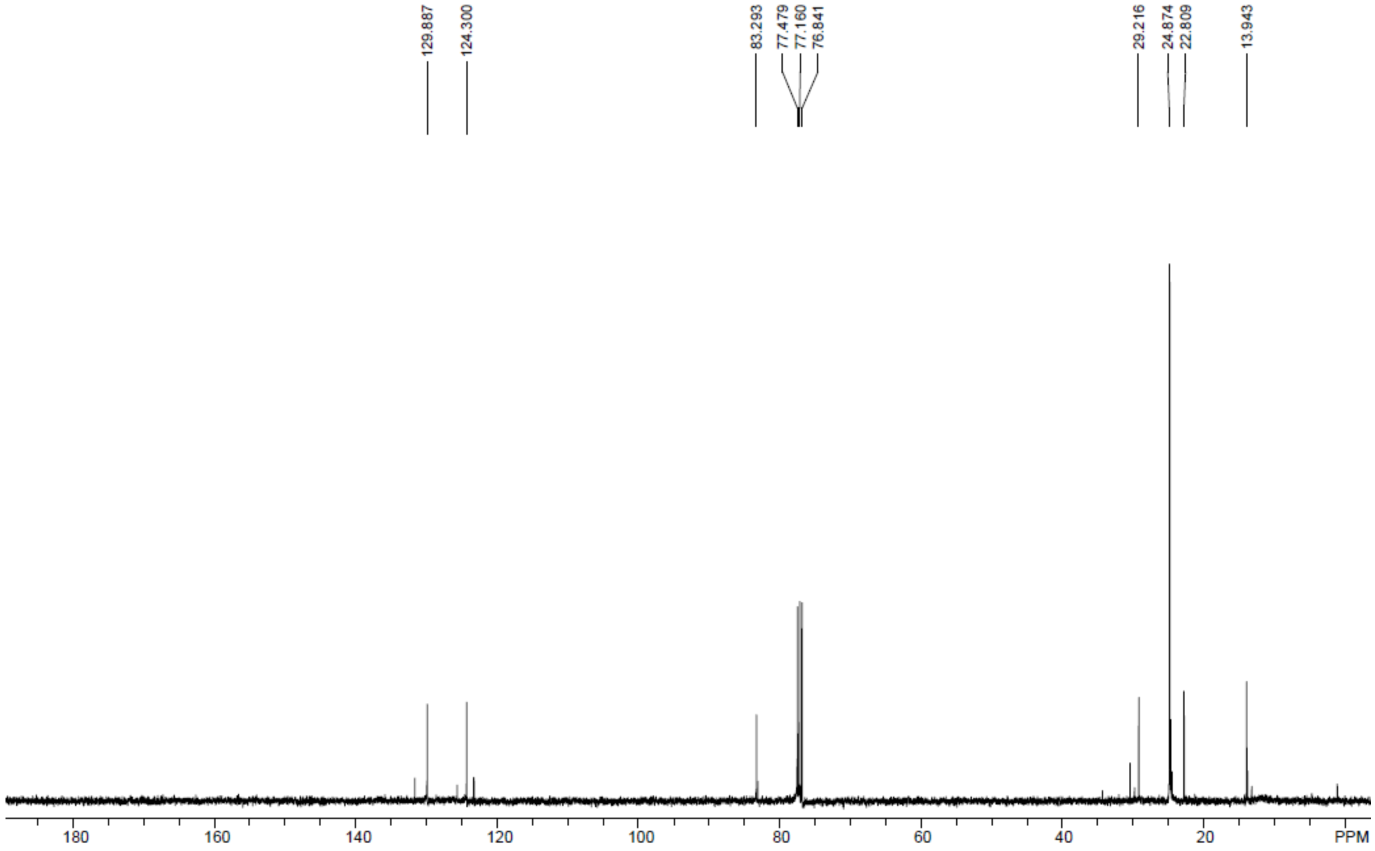
^{1}H NMR spectrum of **9k + 9k’**



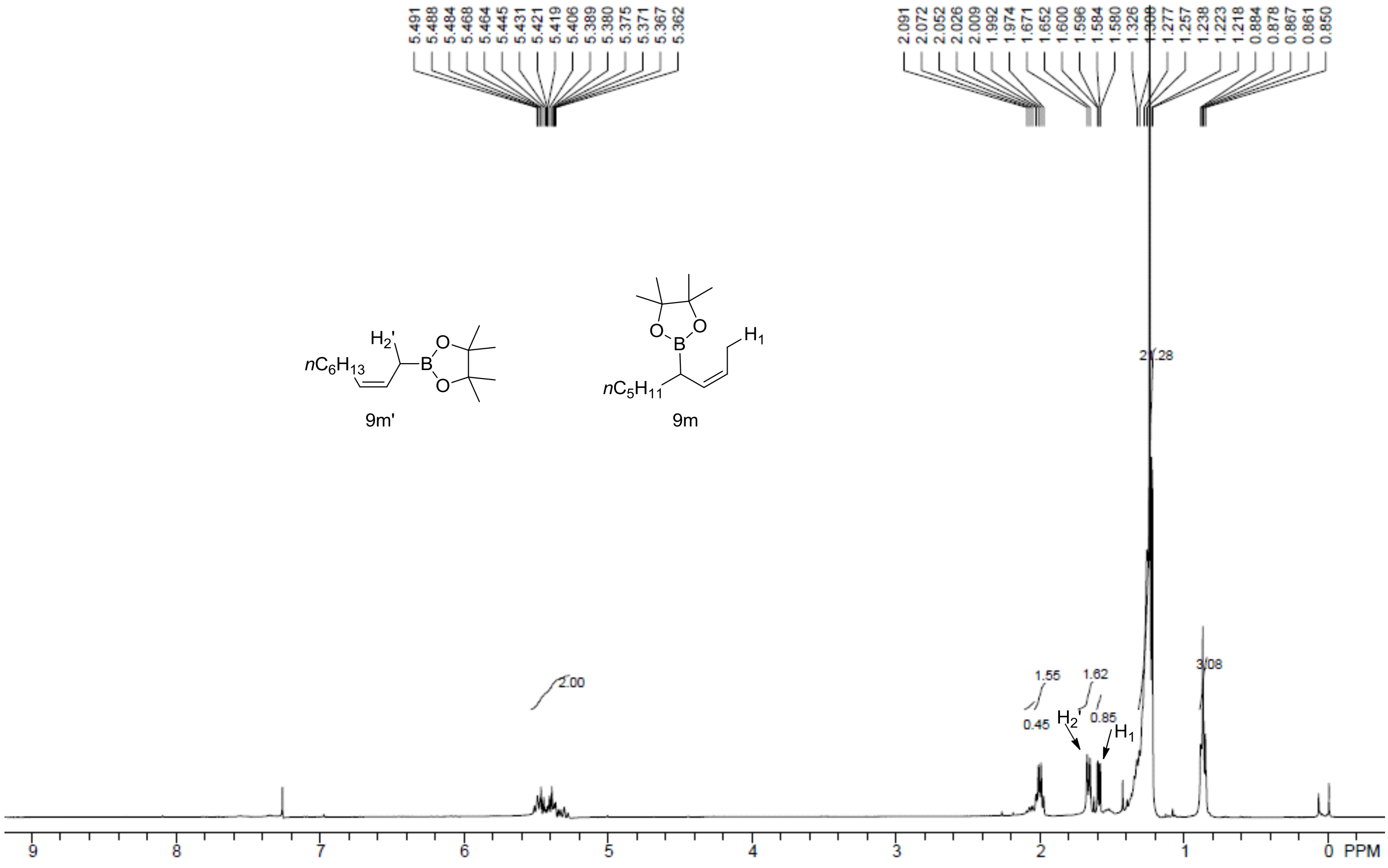
^{13}C NMR spectrum of **9k**



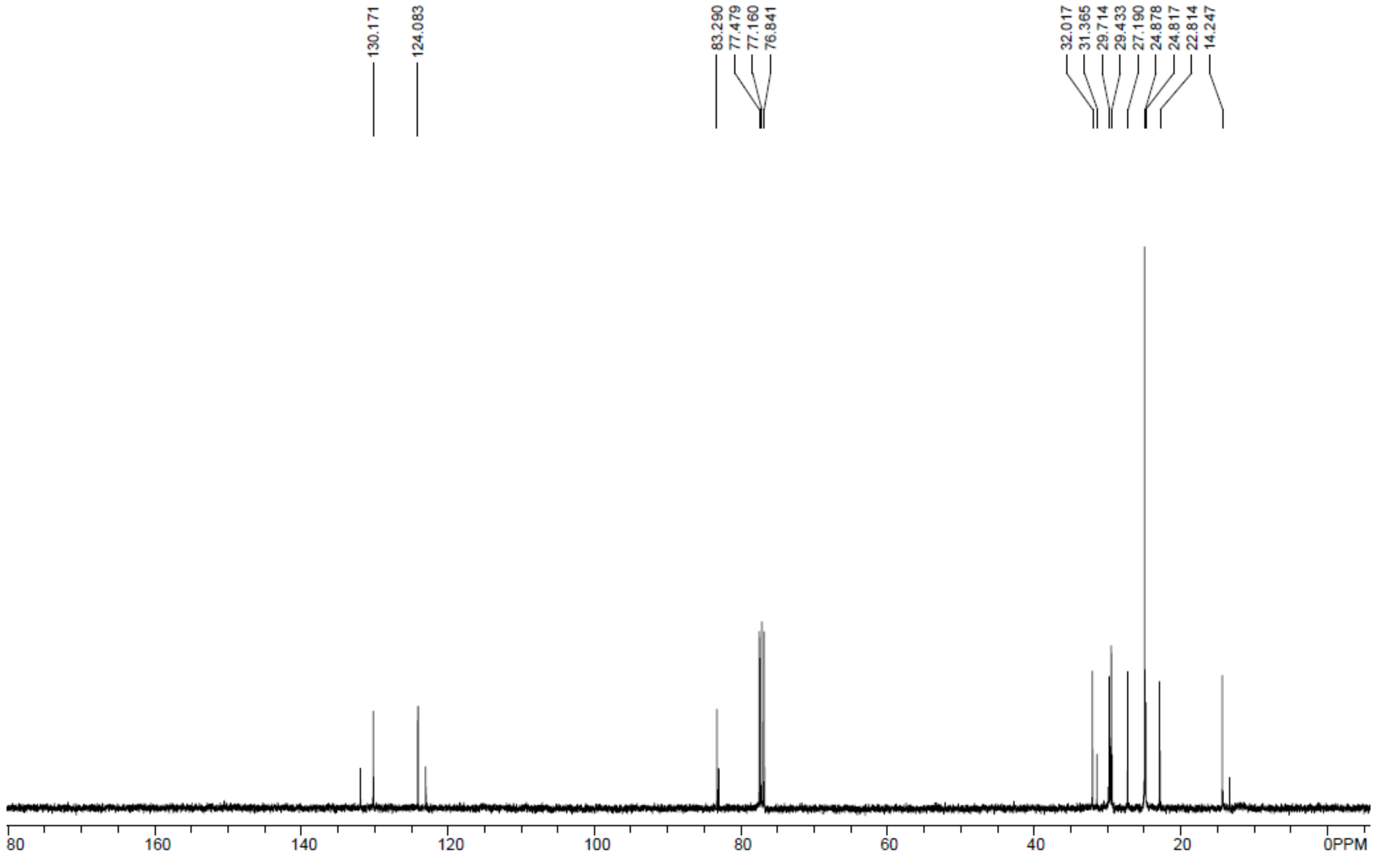
^{1}H NMR spectrum of **9l’ + 9l**



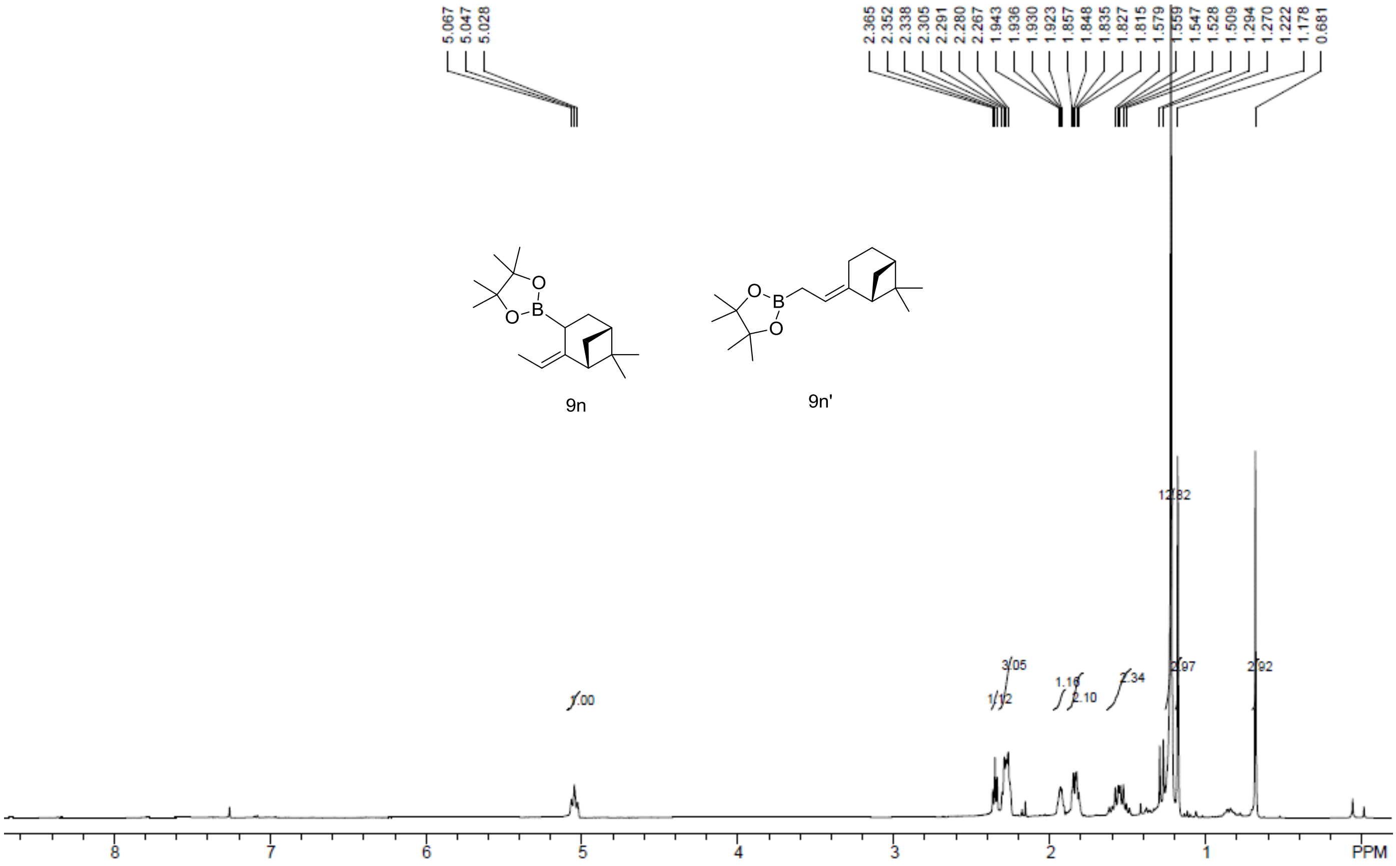
^{13}C NMR spectrum of **9l’ + 9l**



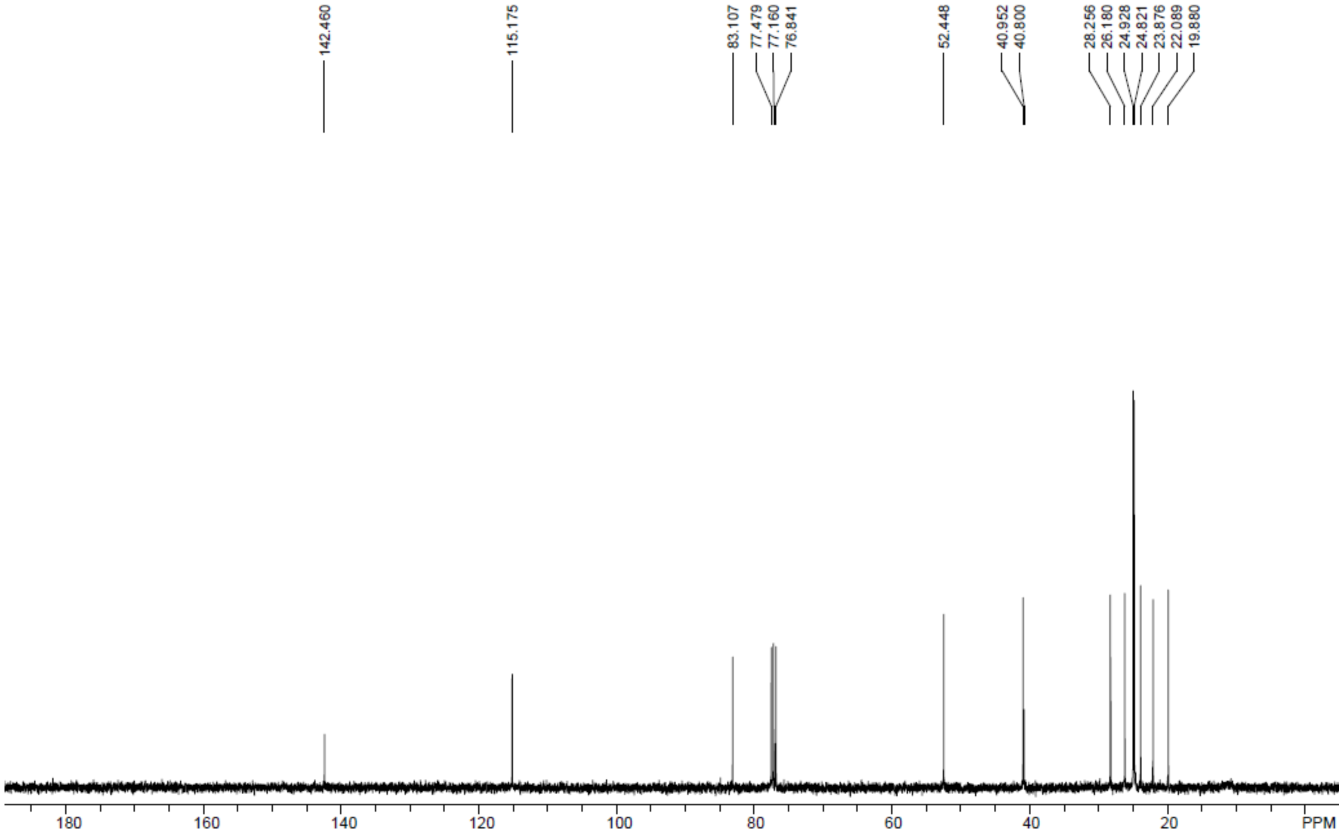
^{1}H NMR spectrum of **9m’ + 9m**



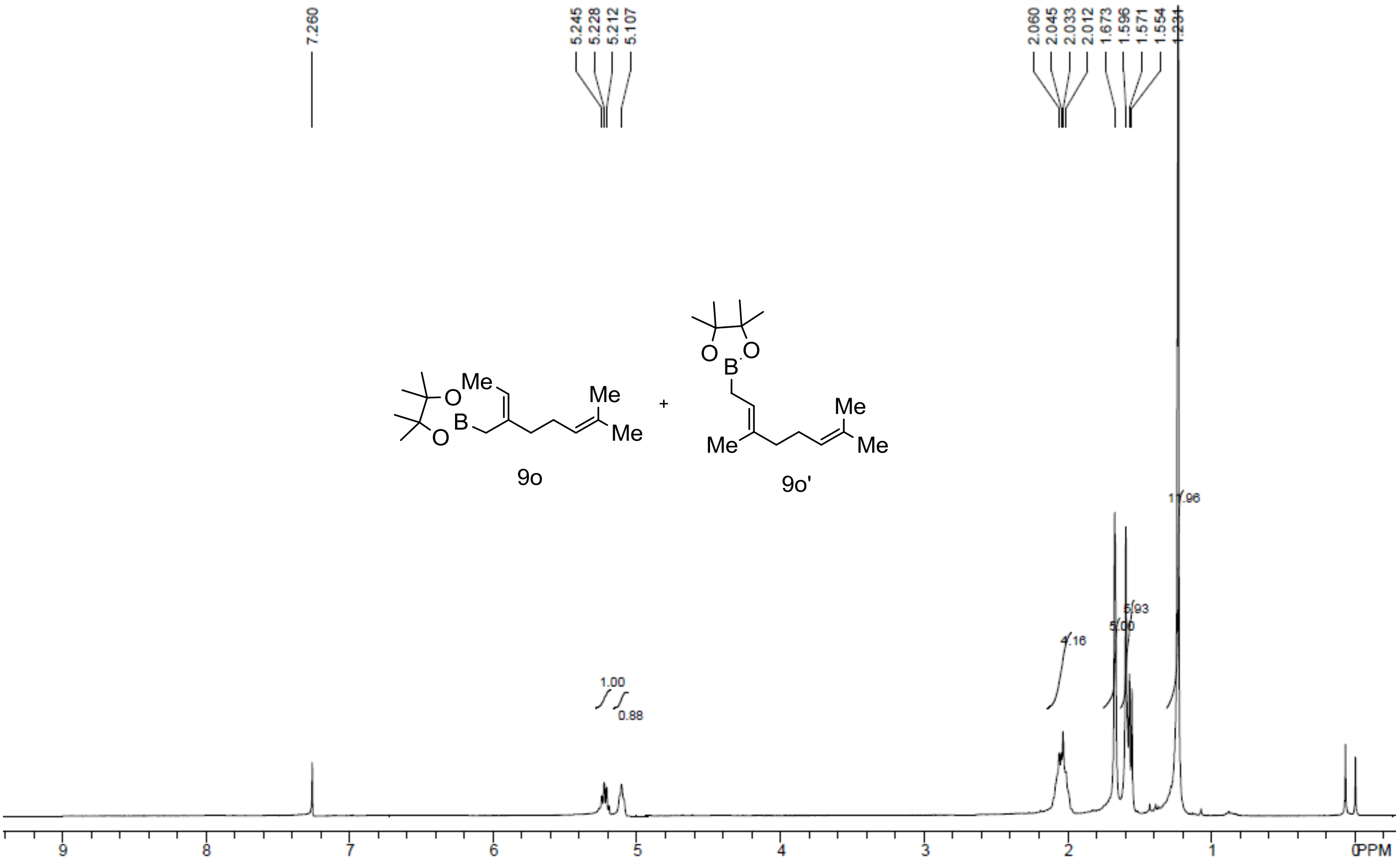
^{13}C NMR spectrum of **9m' + 9m**



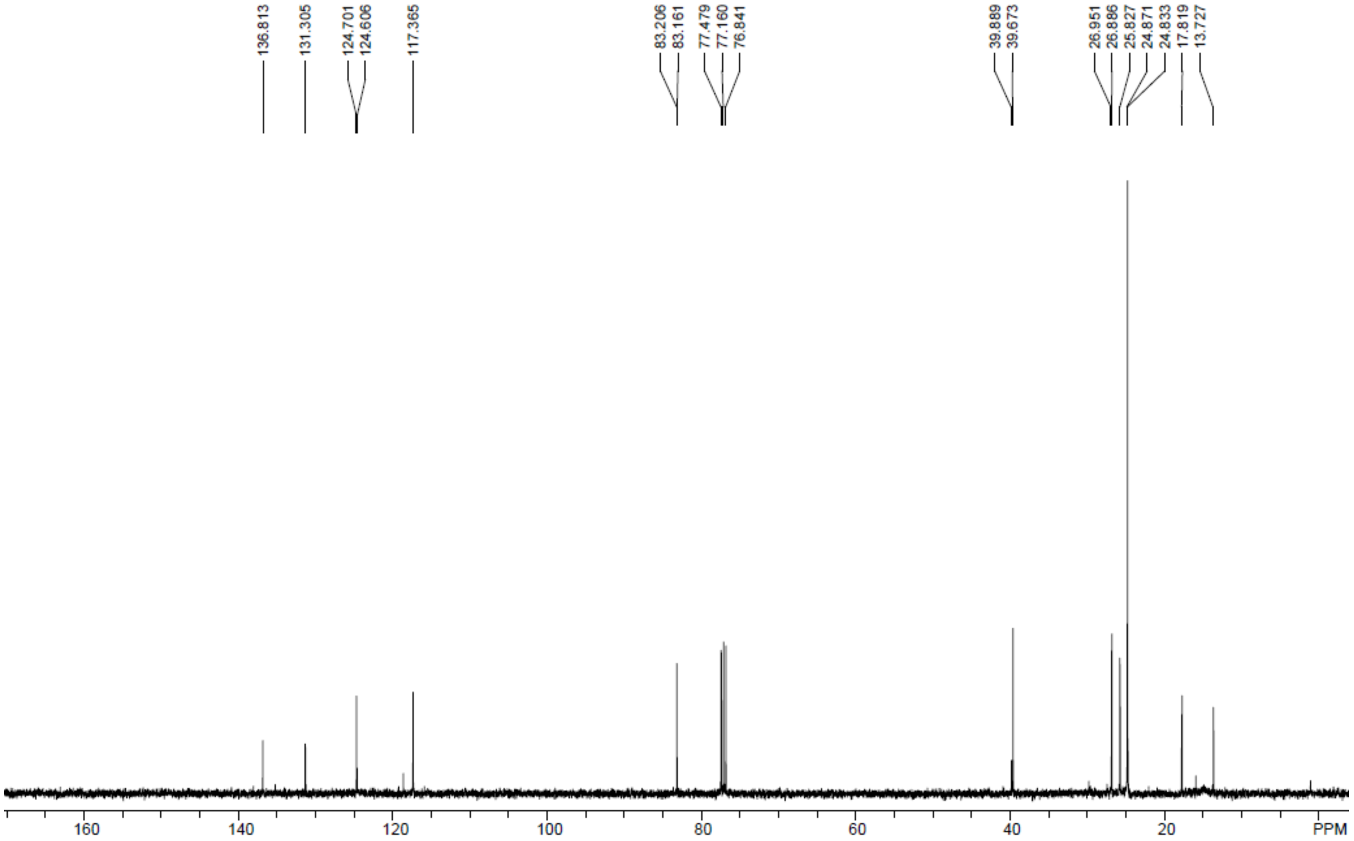
^{1}H NMR spectrum of **9n' + 9n**



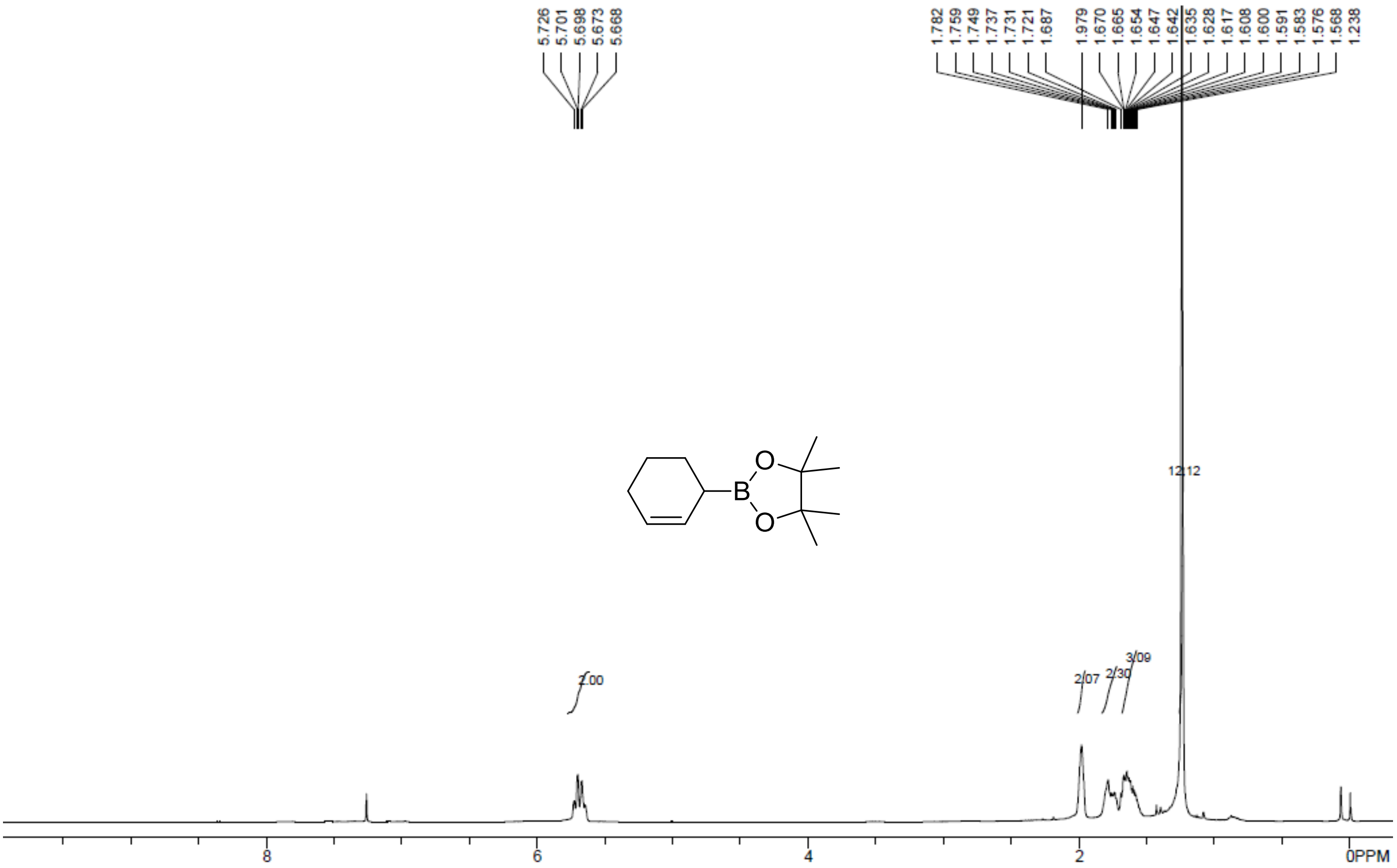
^{13}C NMR spectrum of **9n’ + 9n**



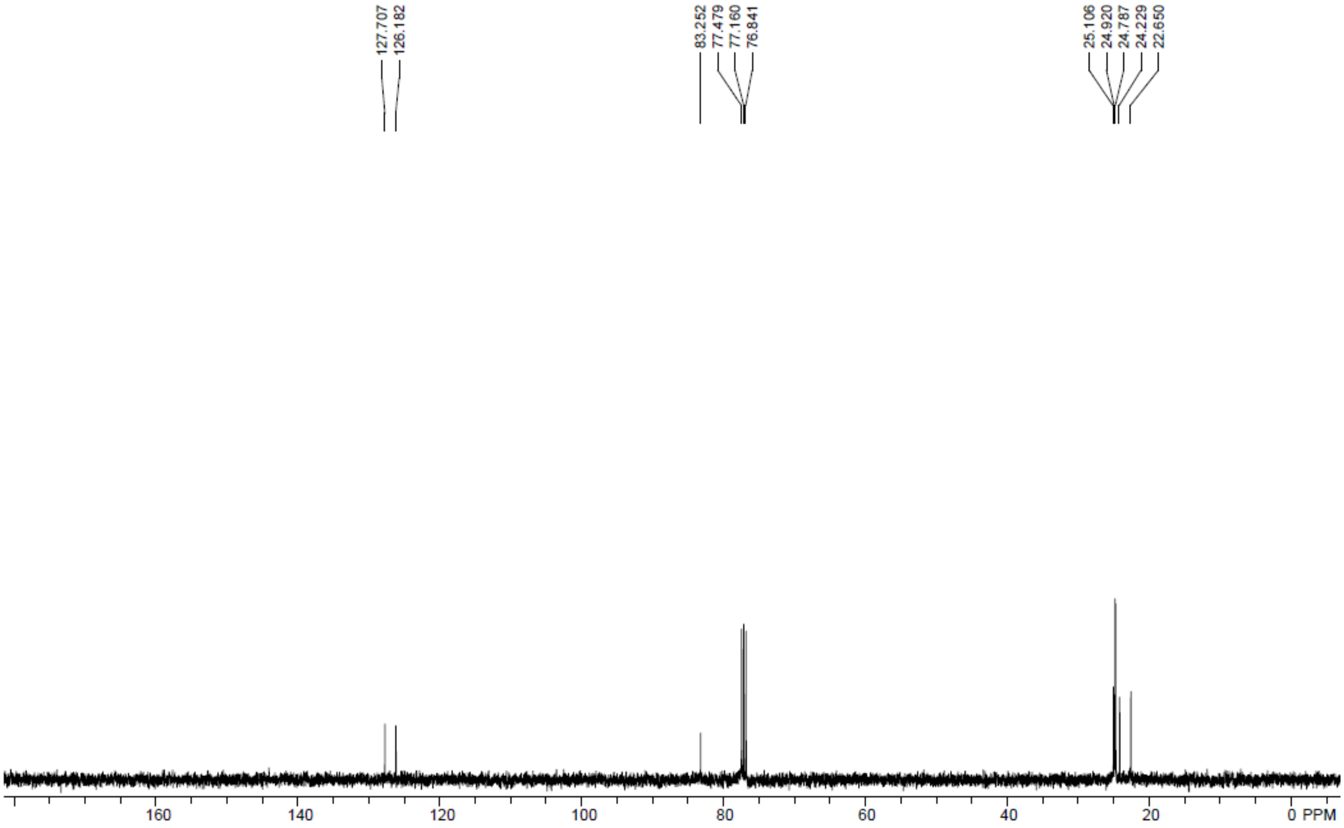
^{1}H NMR spectrum of **9o + 9o’**



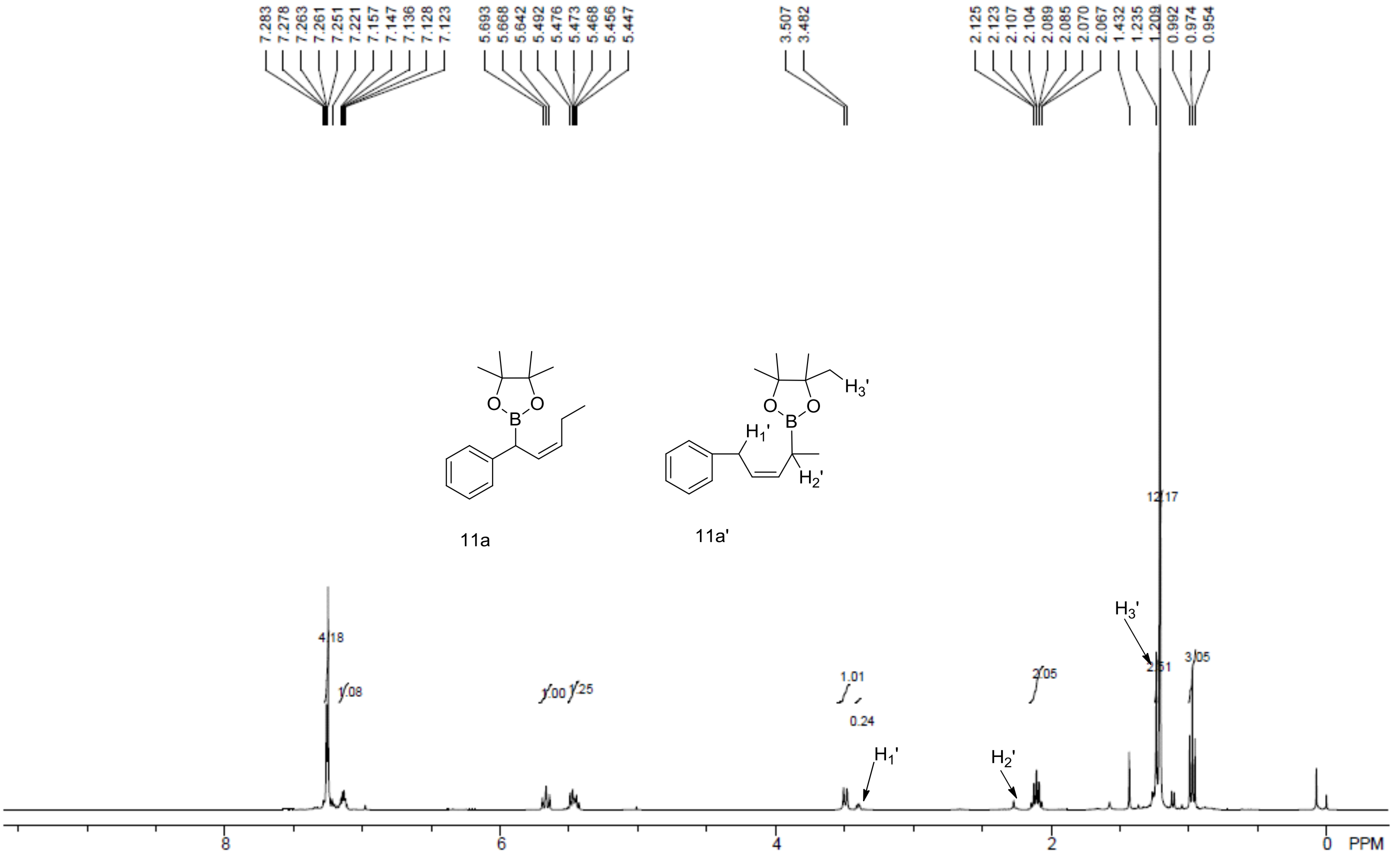
^{13}C NMR spectrum of **9o + 9o'**



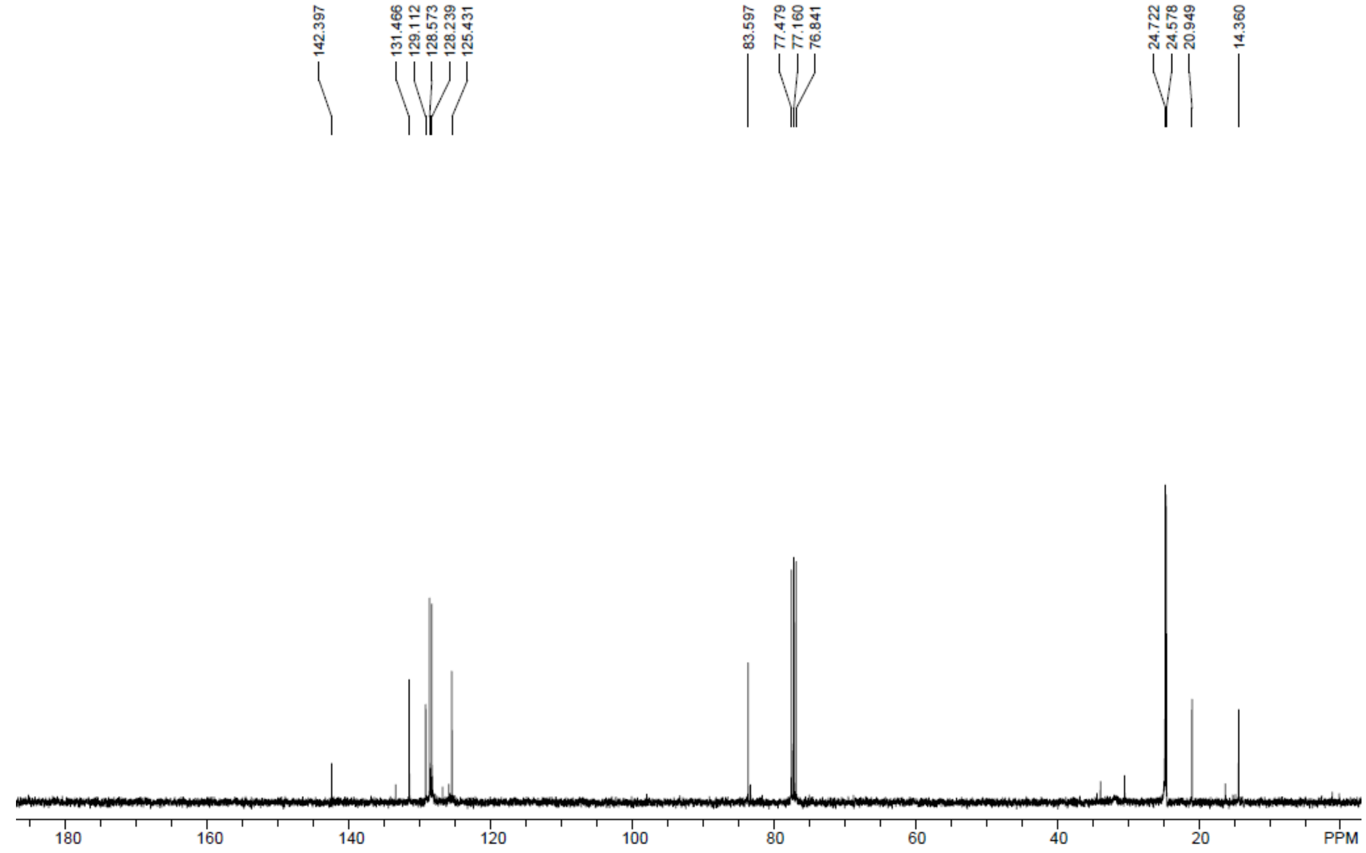
^{1}H NMR spectrum of **9p**



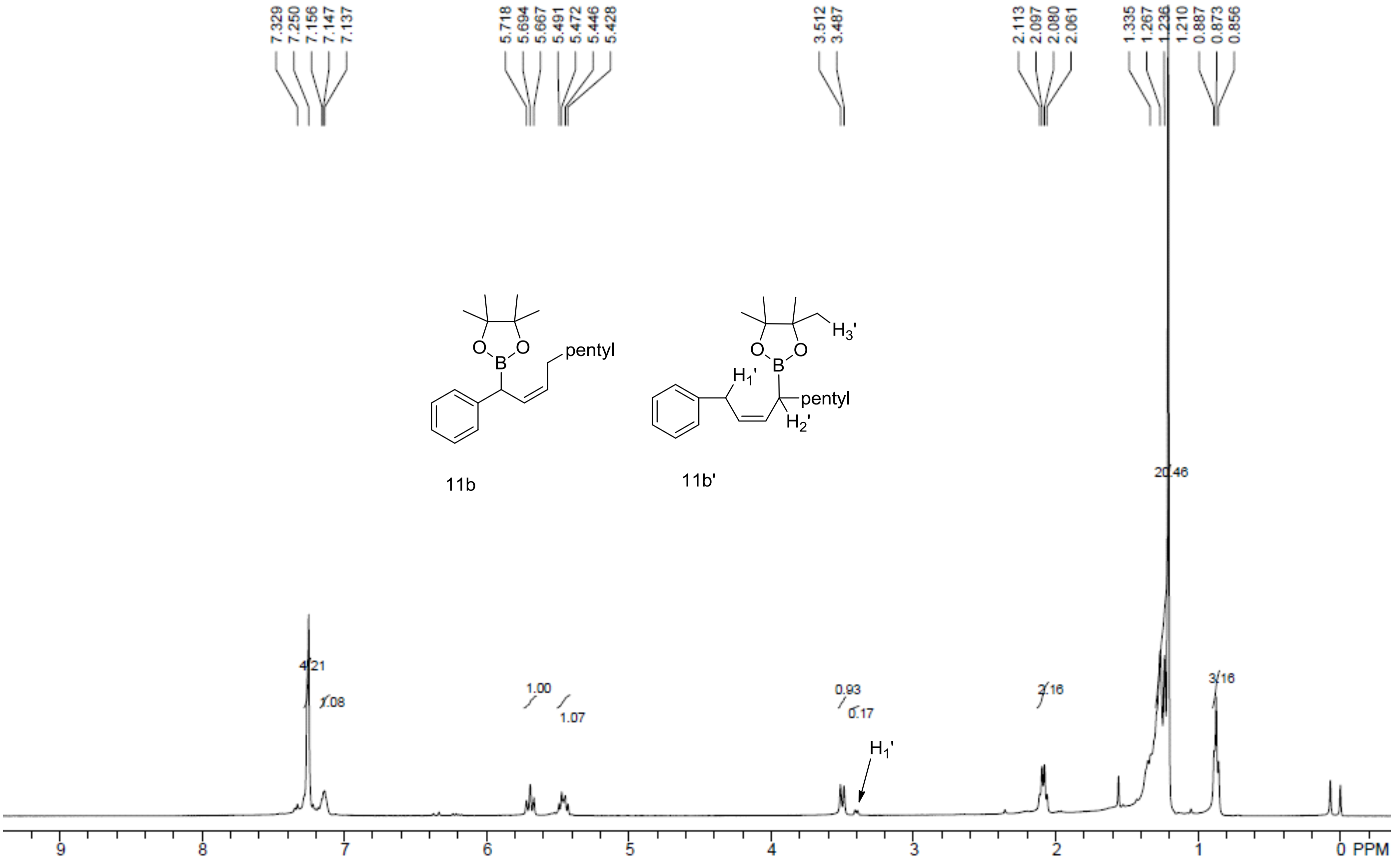
^{13}C NMR spectrum of **9p**



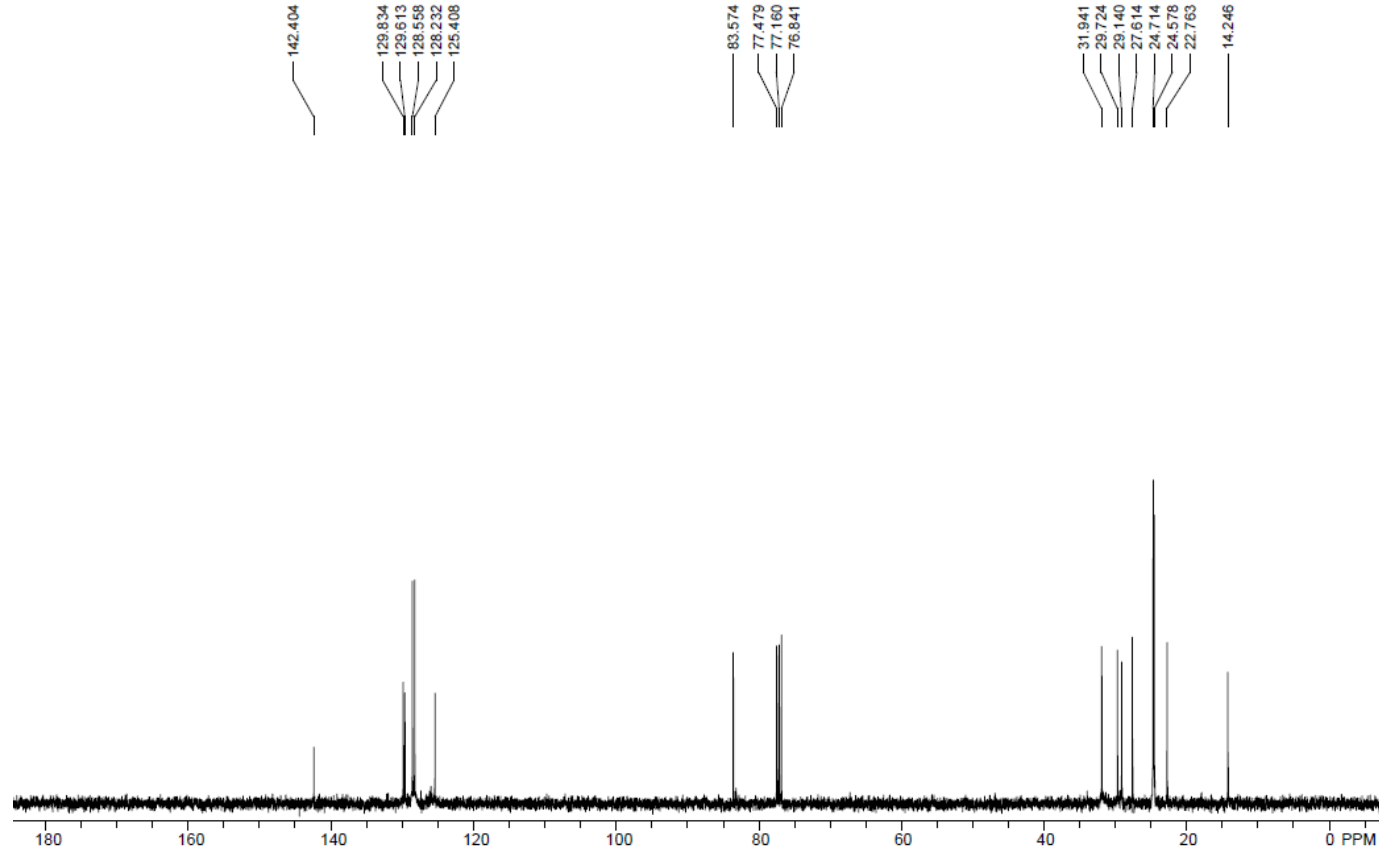
^{1}H NMR spectrum of **11a + 11a’**



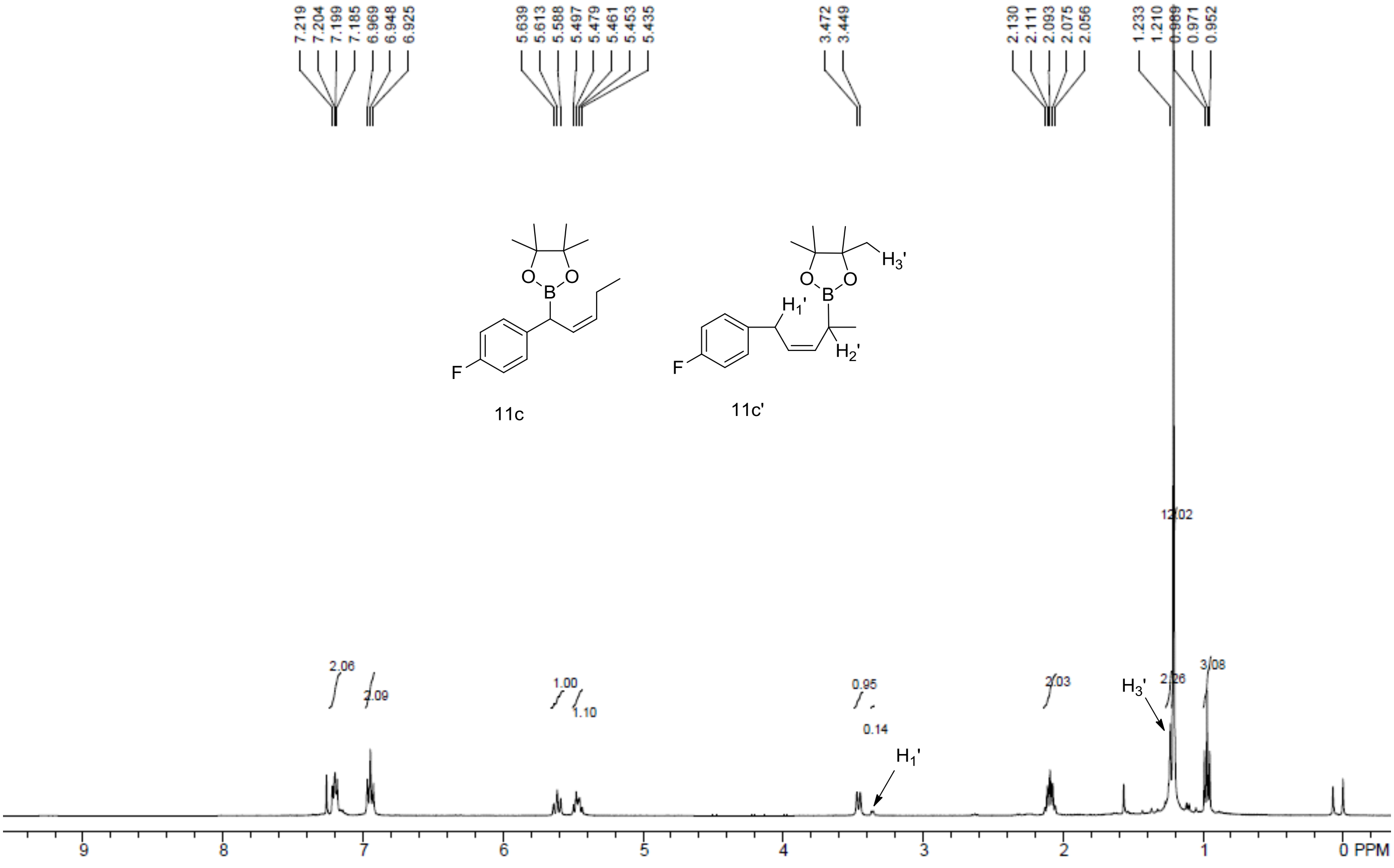
^{13}C NMR spectrum of **11a + 11a'**



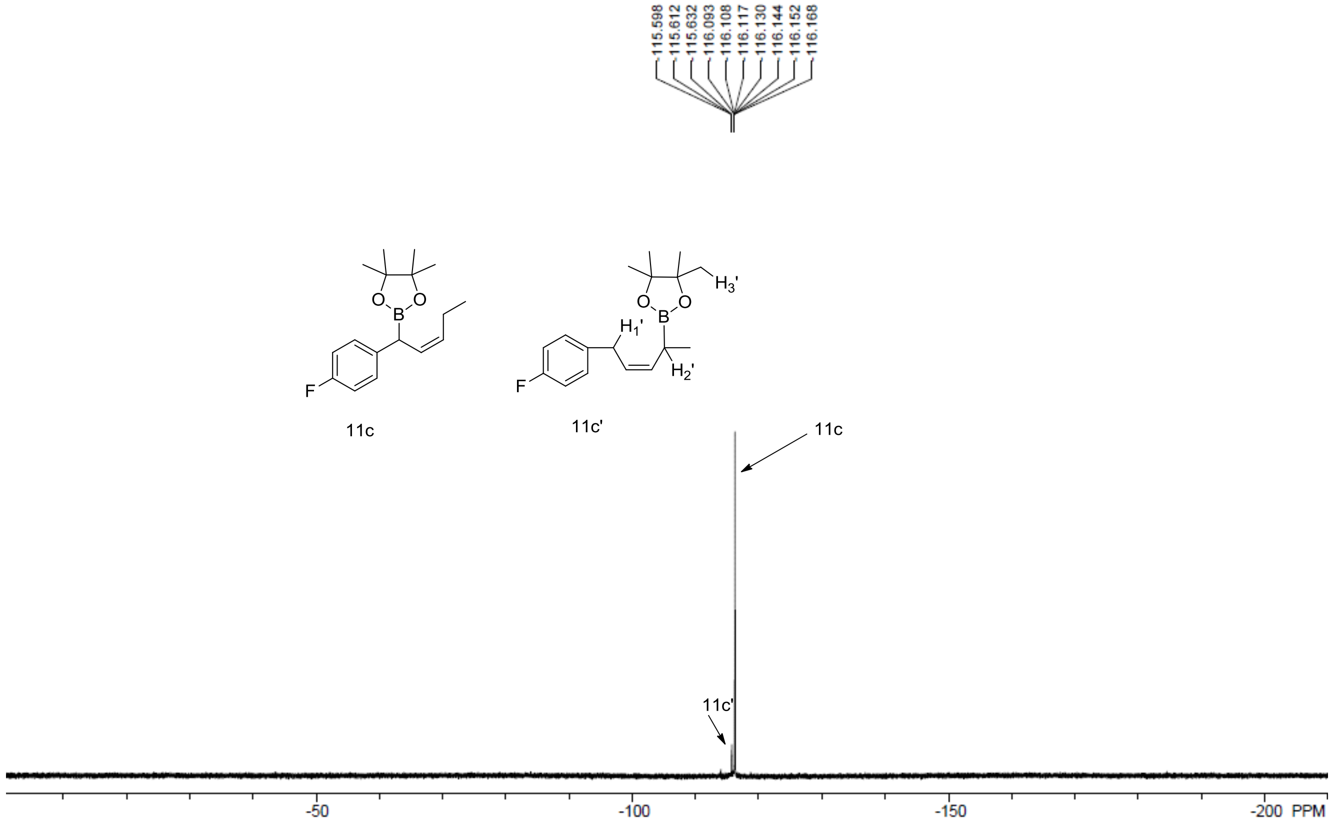
^{1}H NMR spectrum of **11b + 11b'**



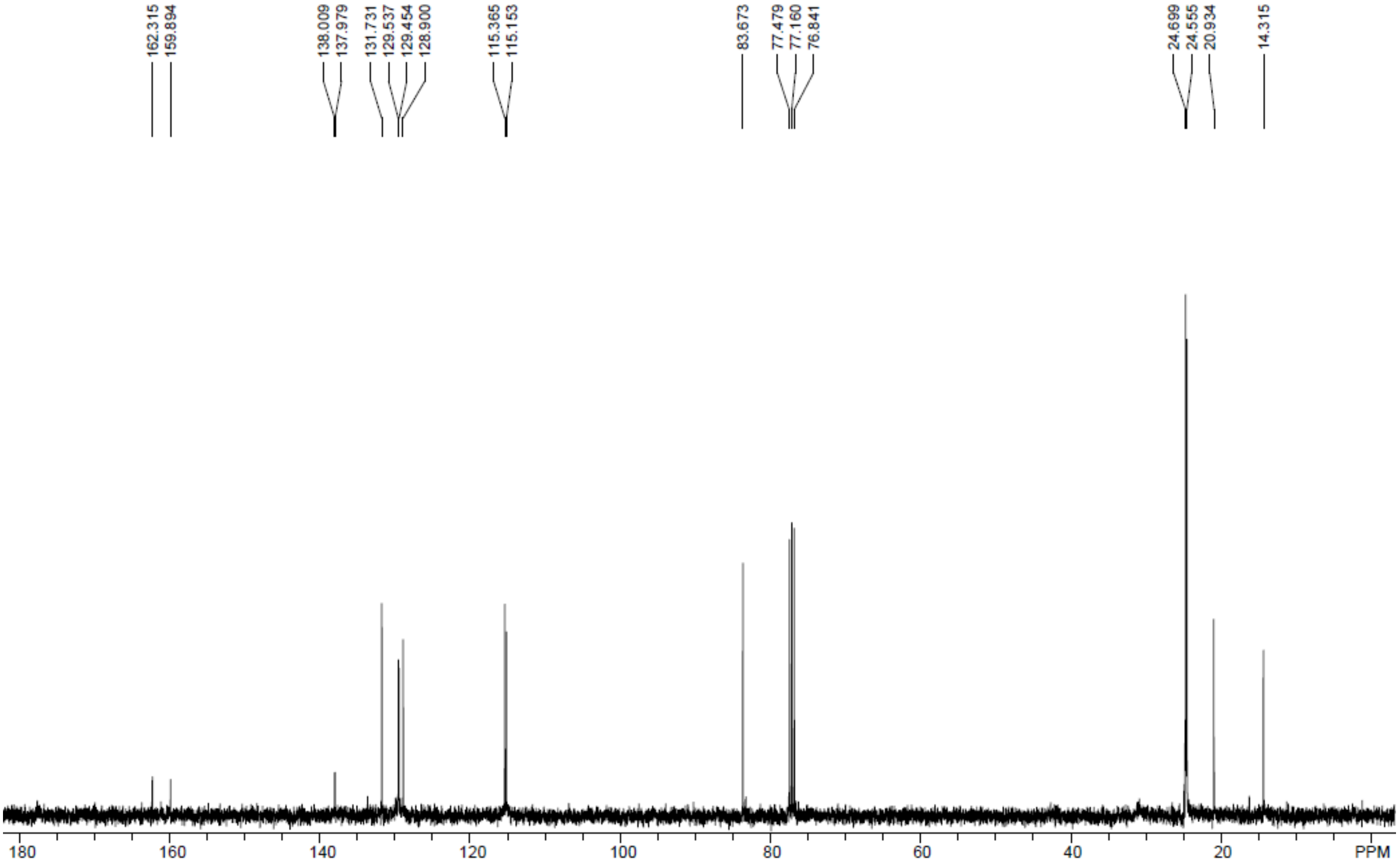
^{13}C NMR spectrum of **11b + 11b'**



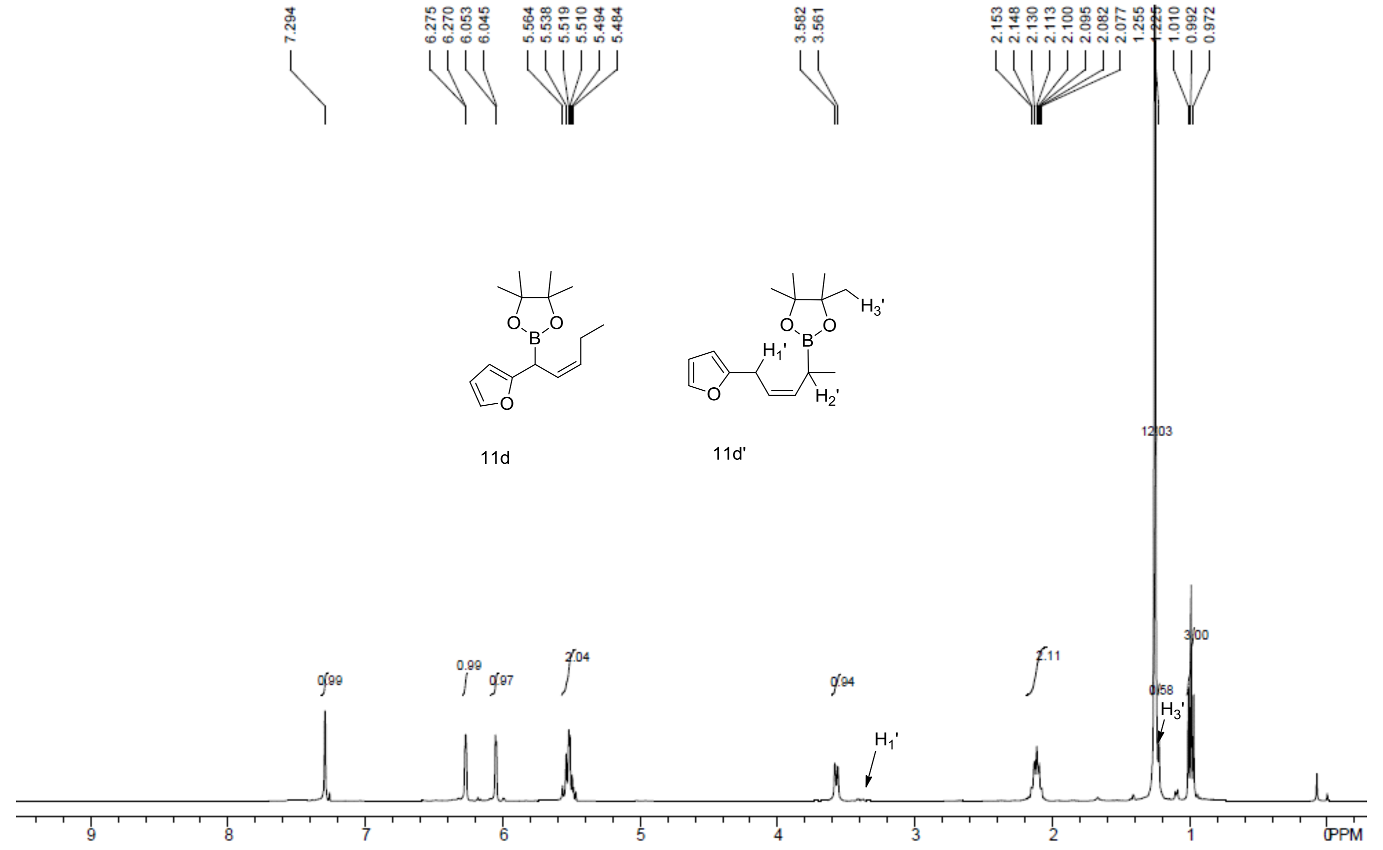
^{1}H NMR spectrum of **11c + 11c'**



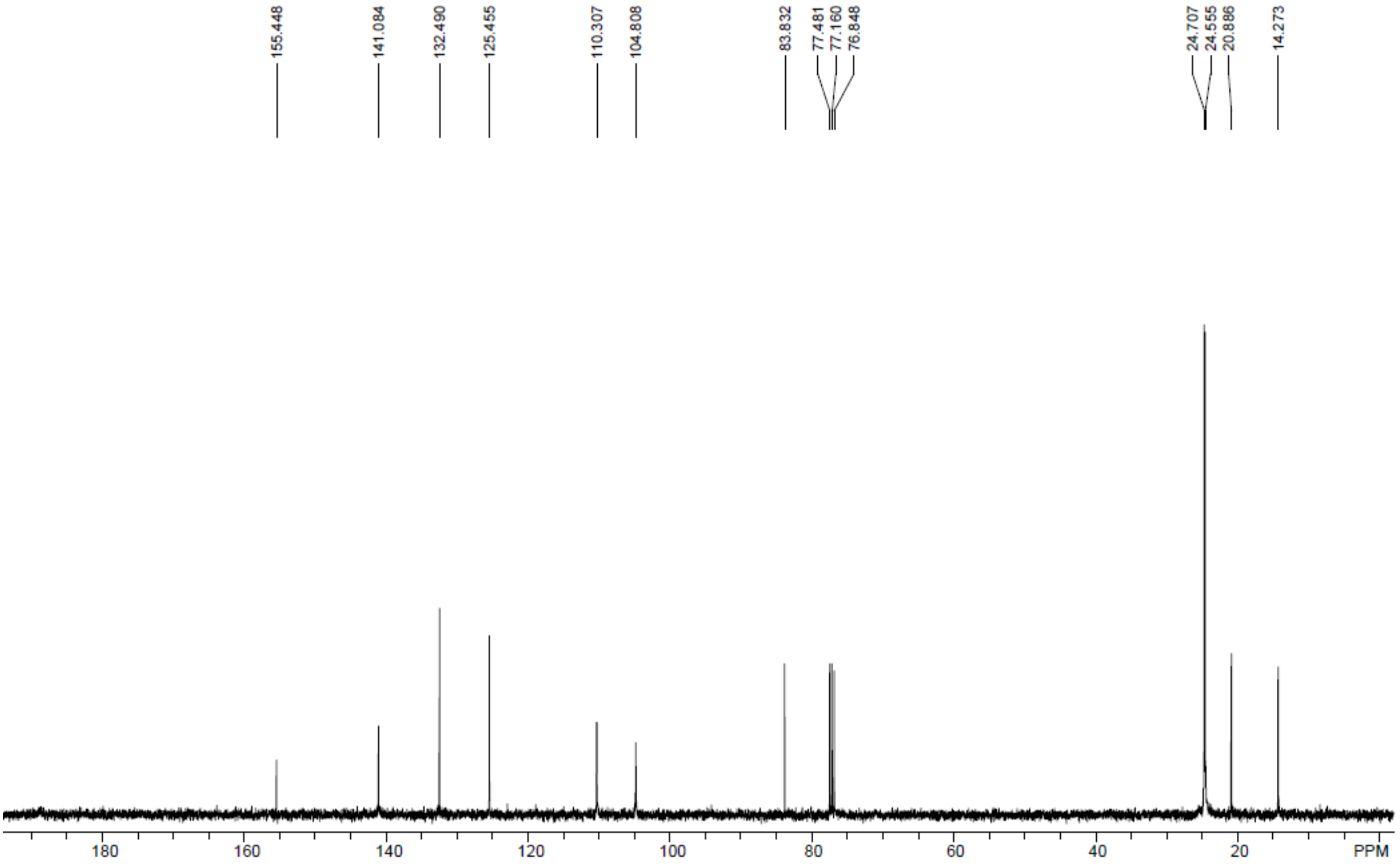
^{19}F NMR spectrum of **11c +11c'**



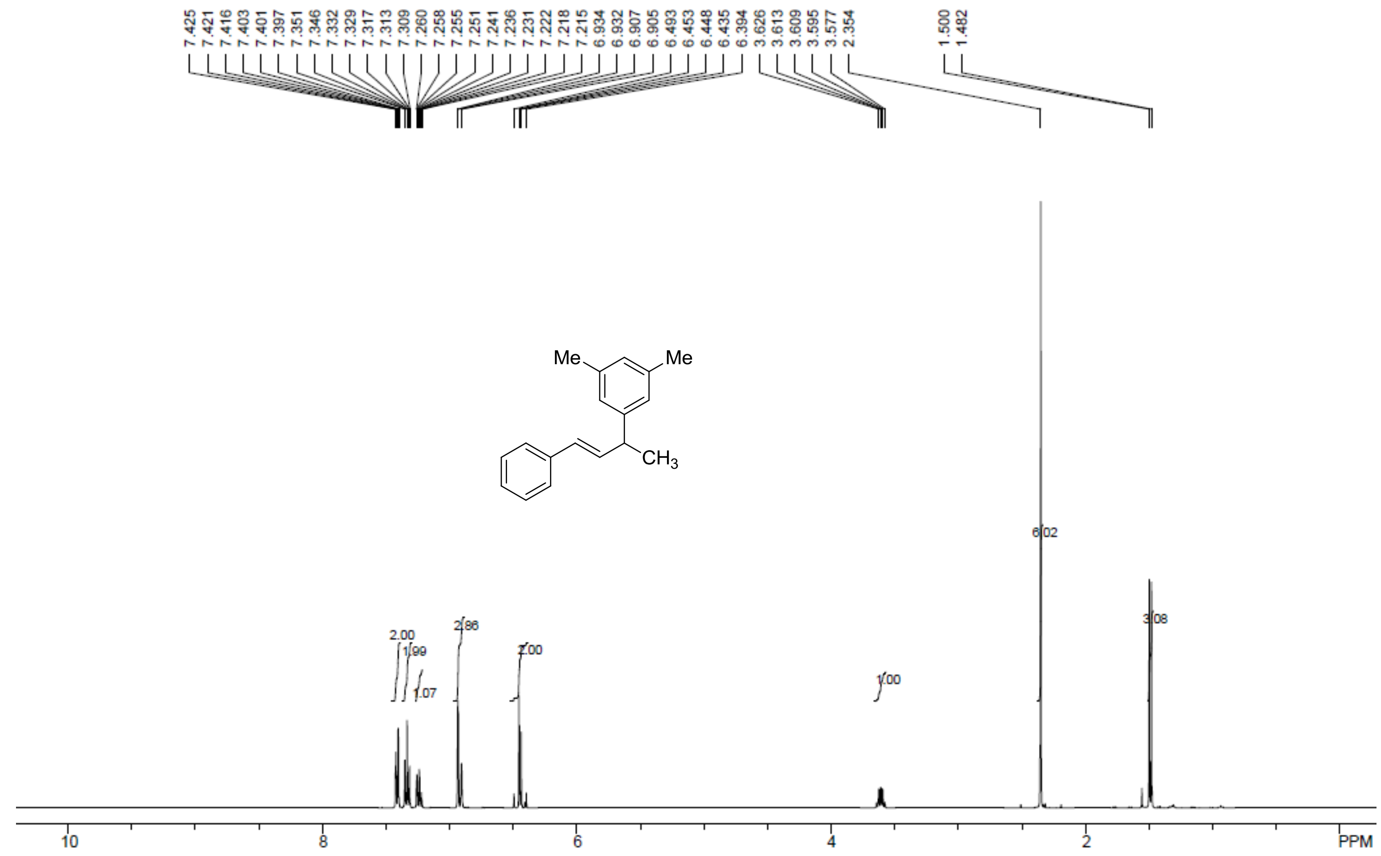
^{13}C NMR spectrum of **11c + 11c'**



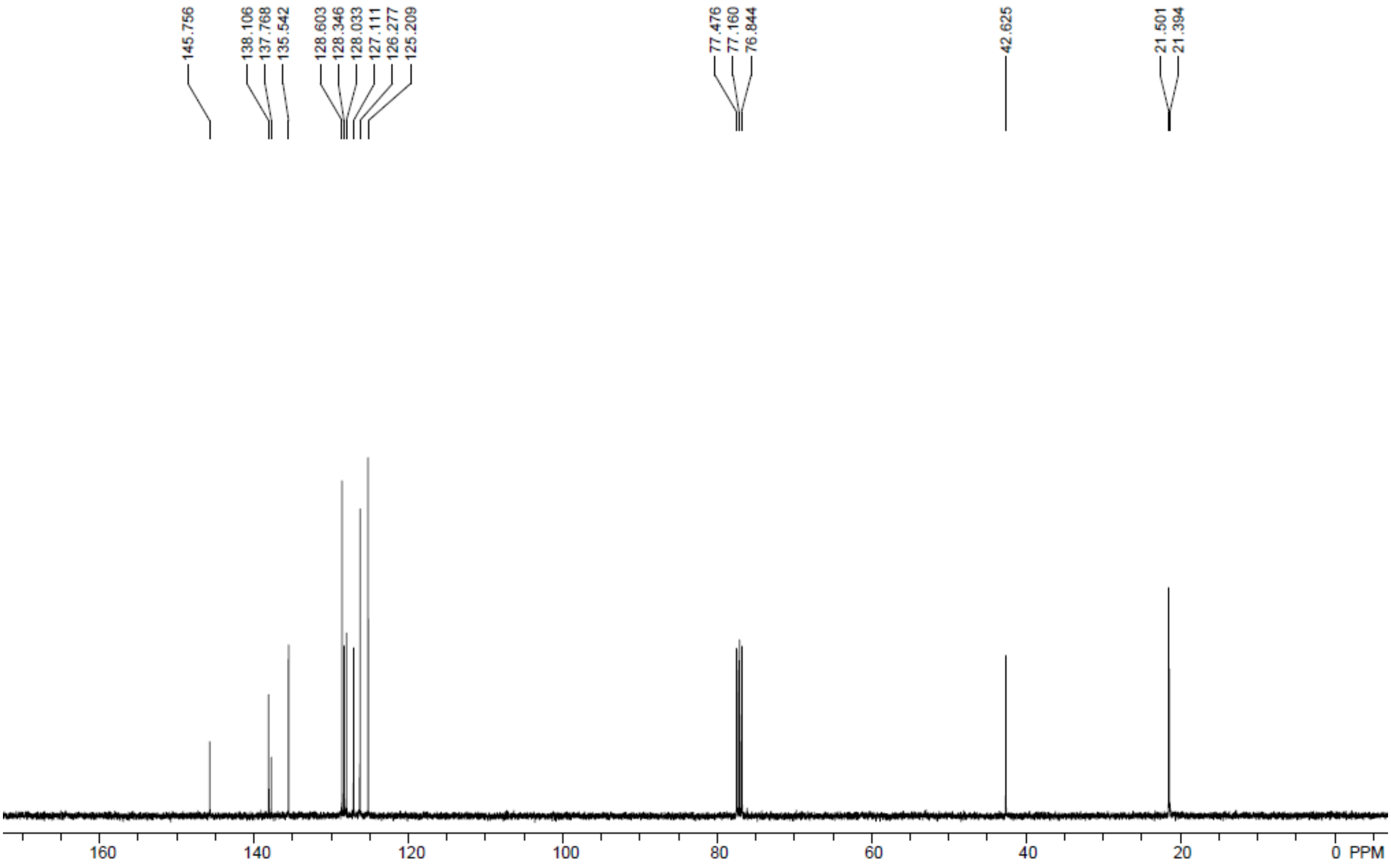
^{1}H NMR spectrum of **11d + 11d'**



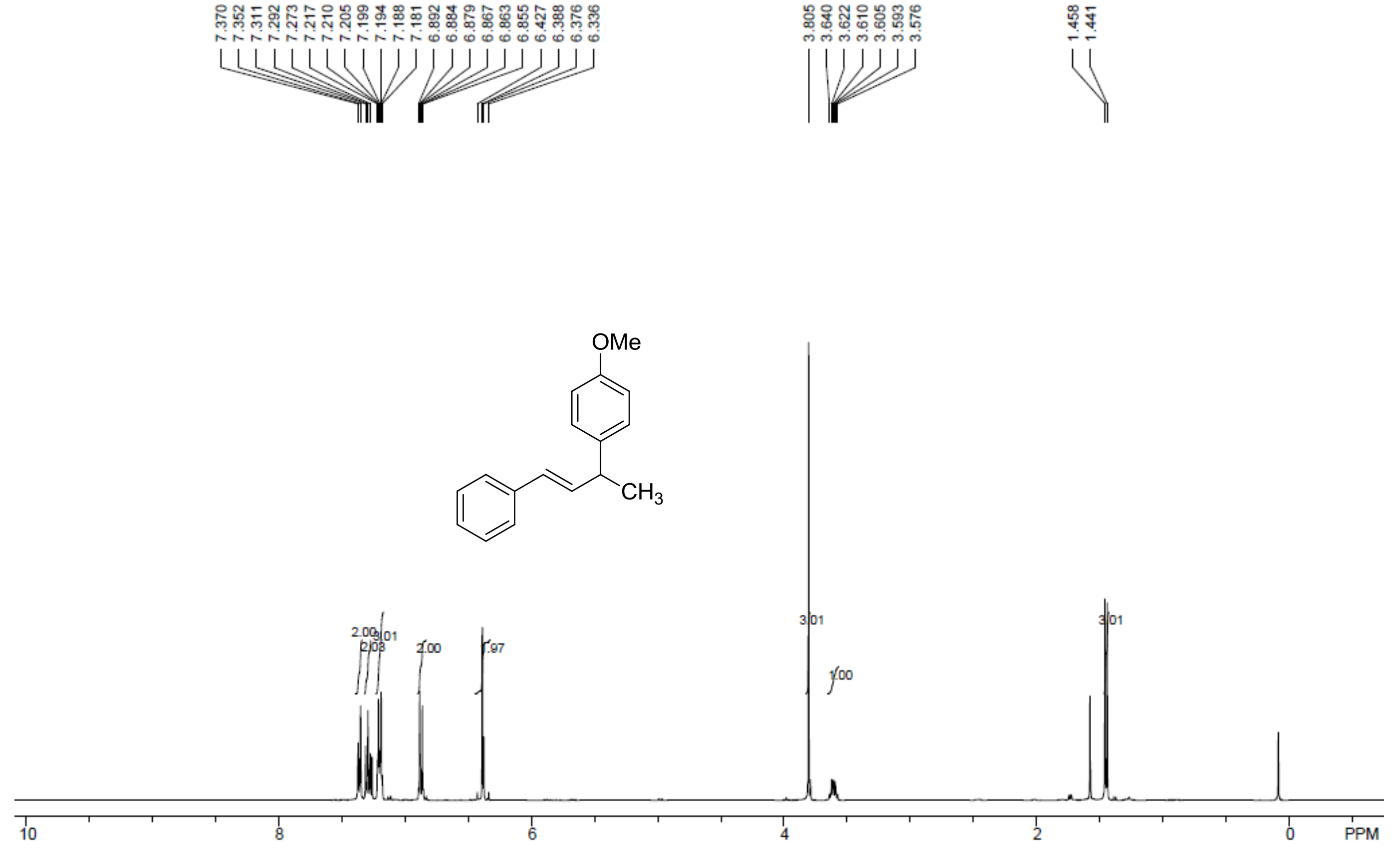
^{13}C NMR spectrum of **11d**



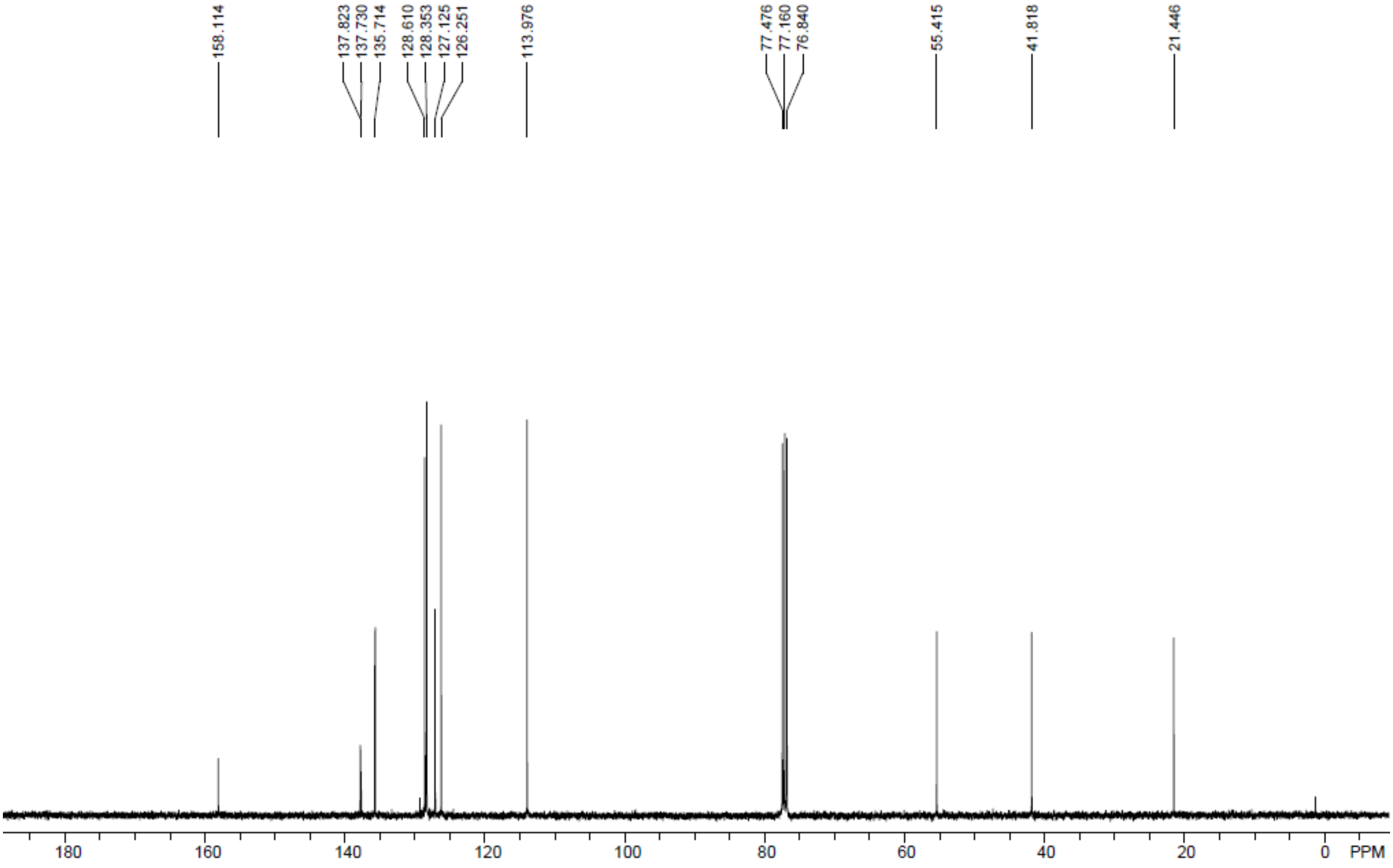
^{1}H NMR spectrum of **14a**



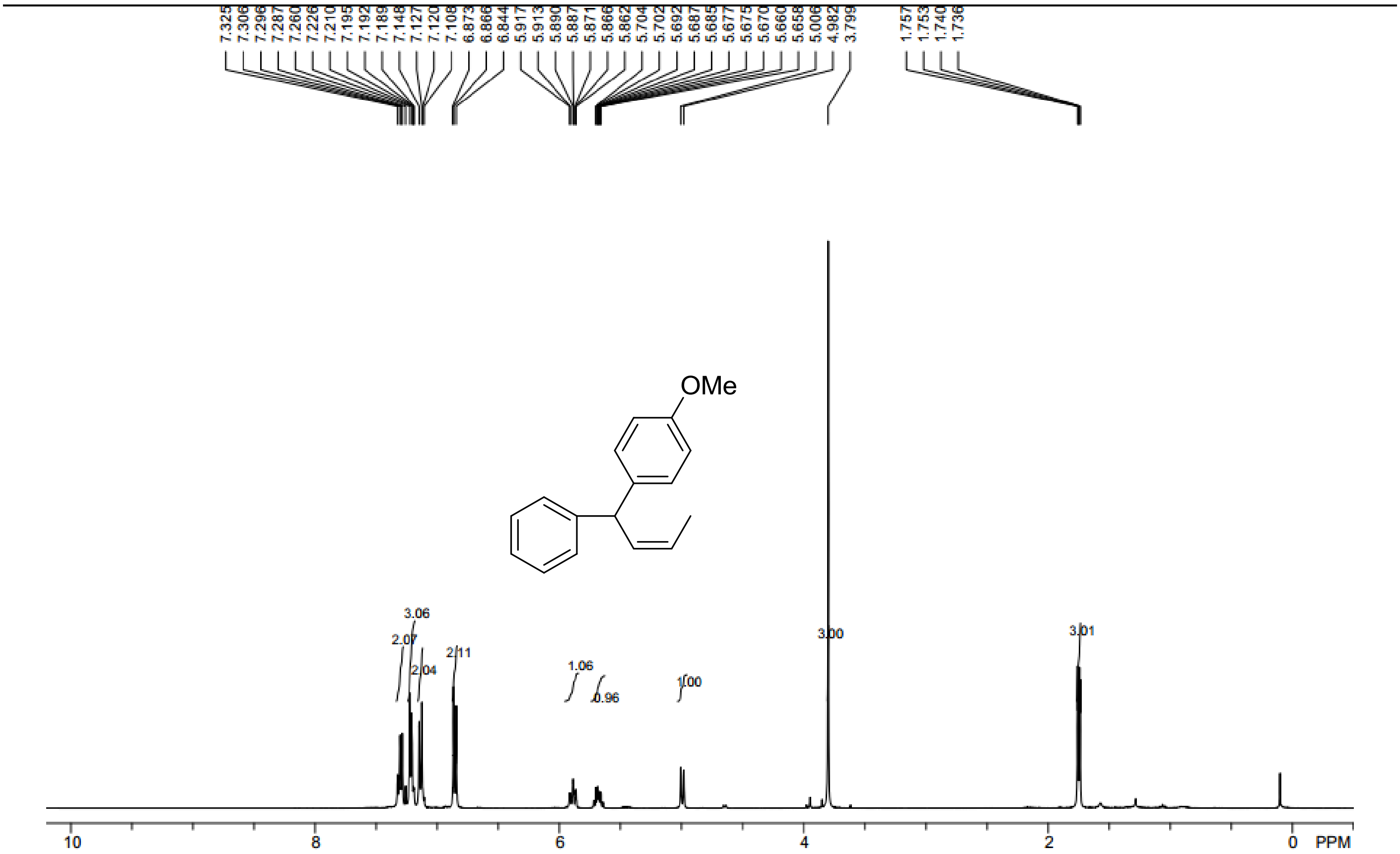
^{13}C NMR spectrum of **14a**



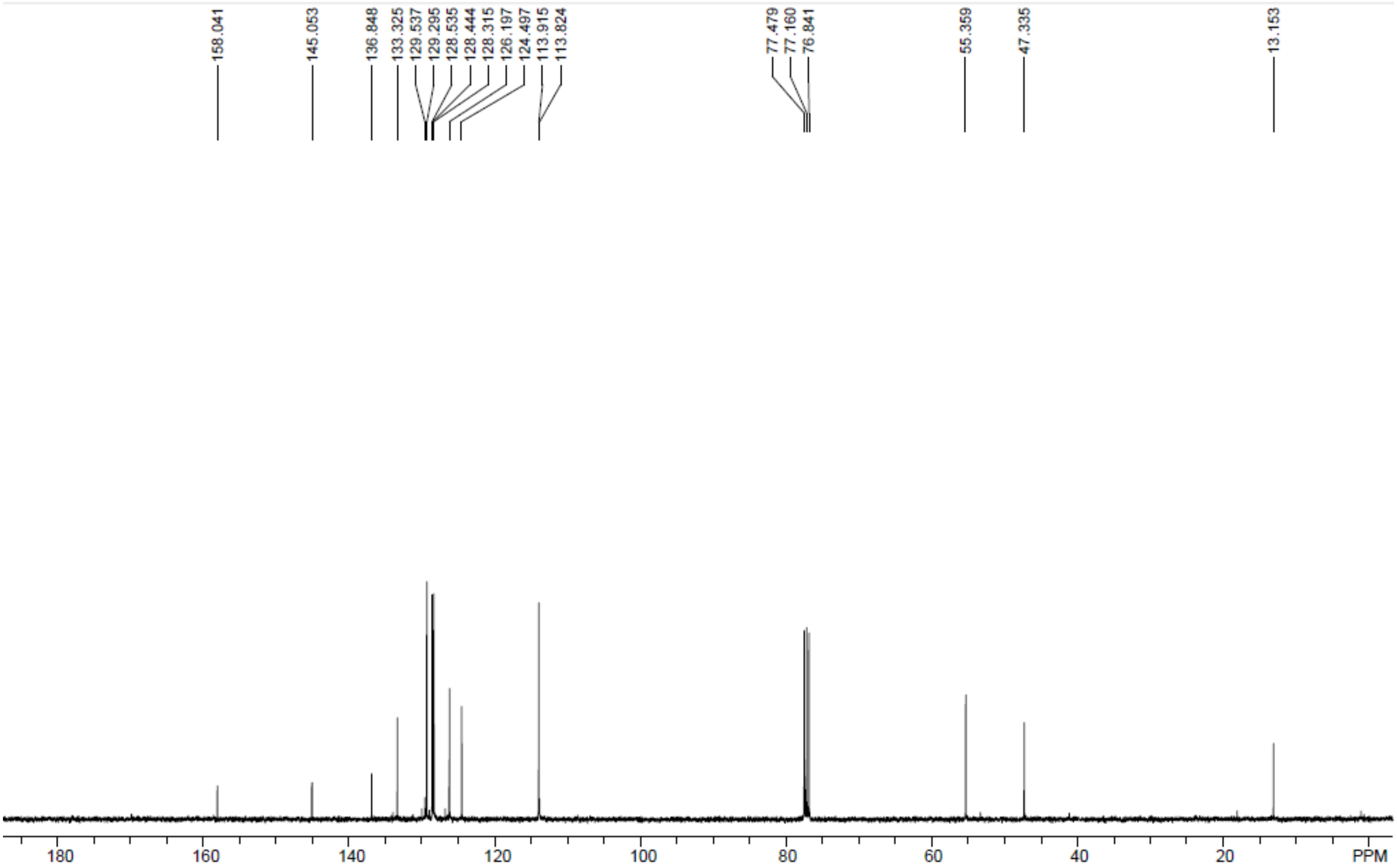
^{1}H NMR spectrum of **14b**



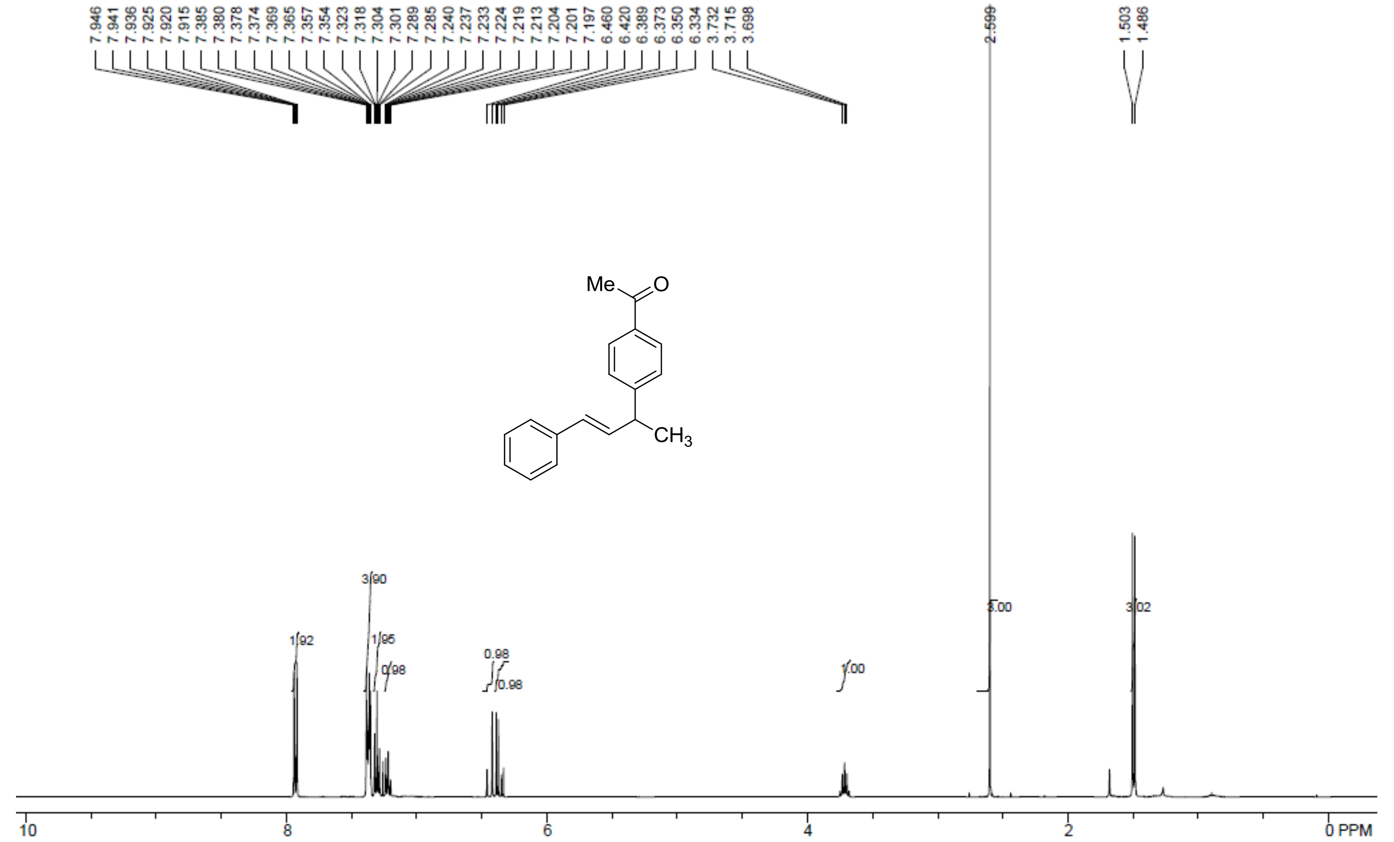
^{13}C NMR spectrum of **14b**



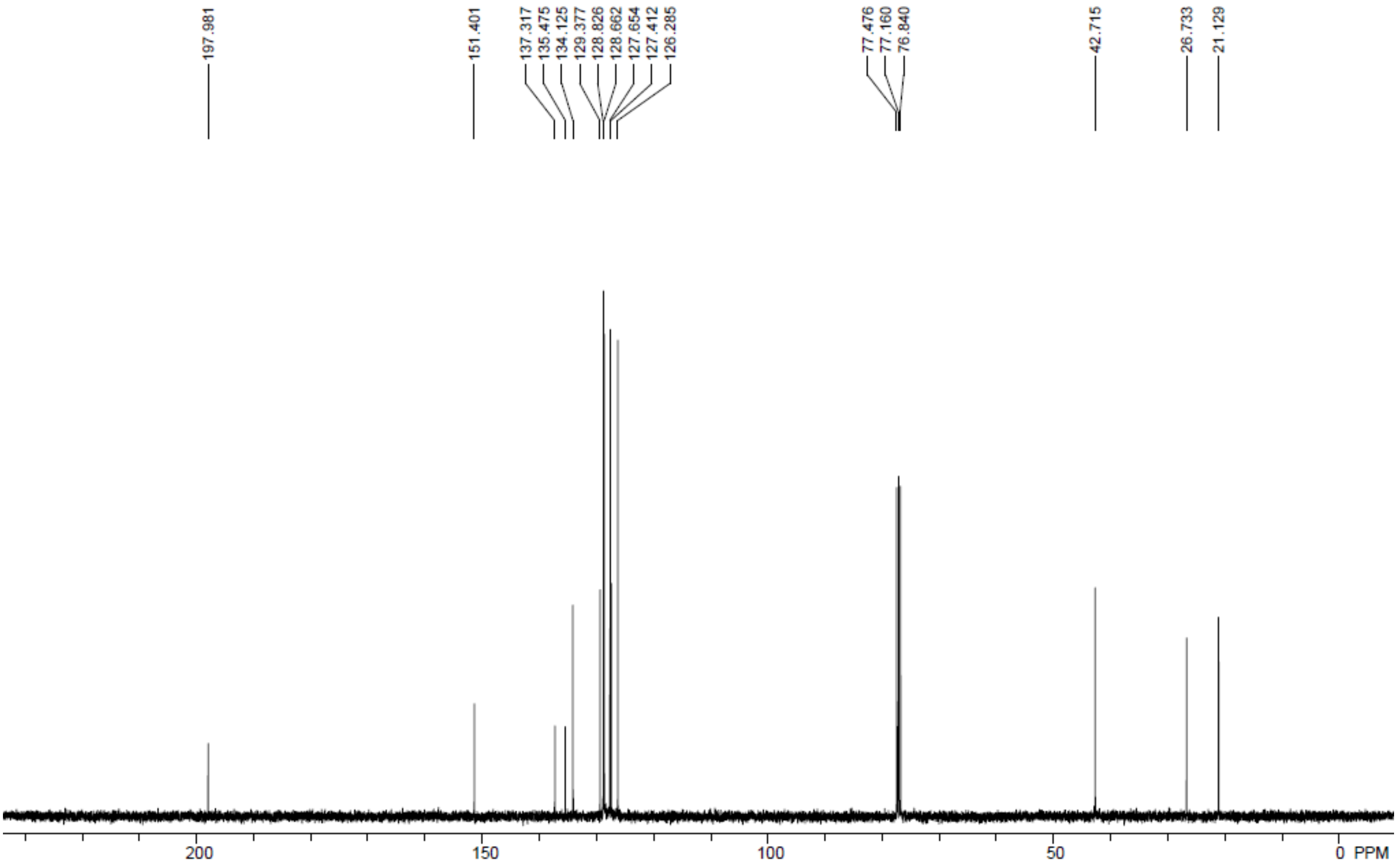
^{1}H NMR spectrum of **14b’**



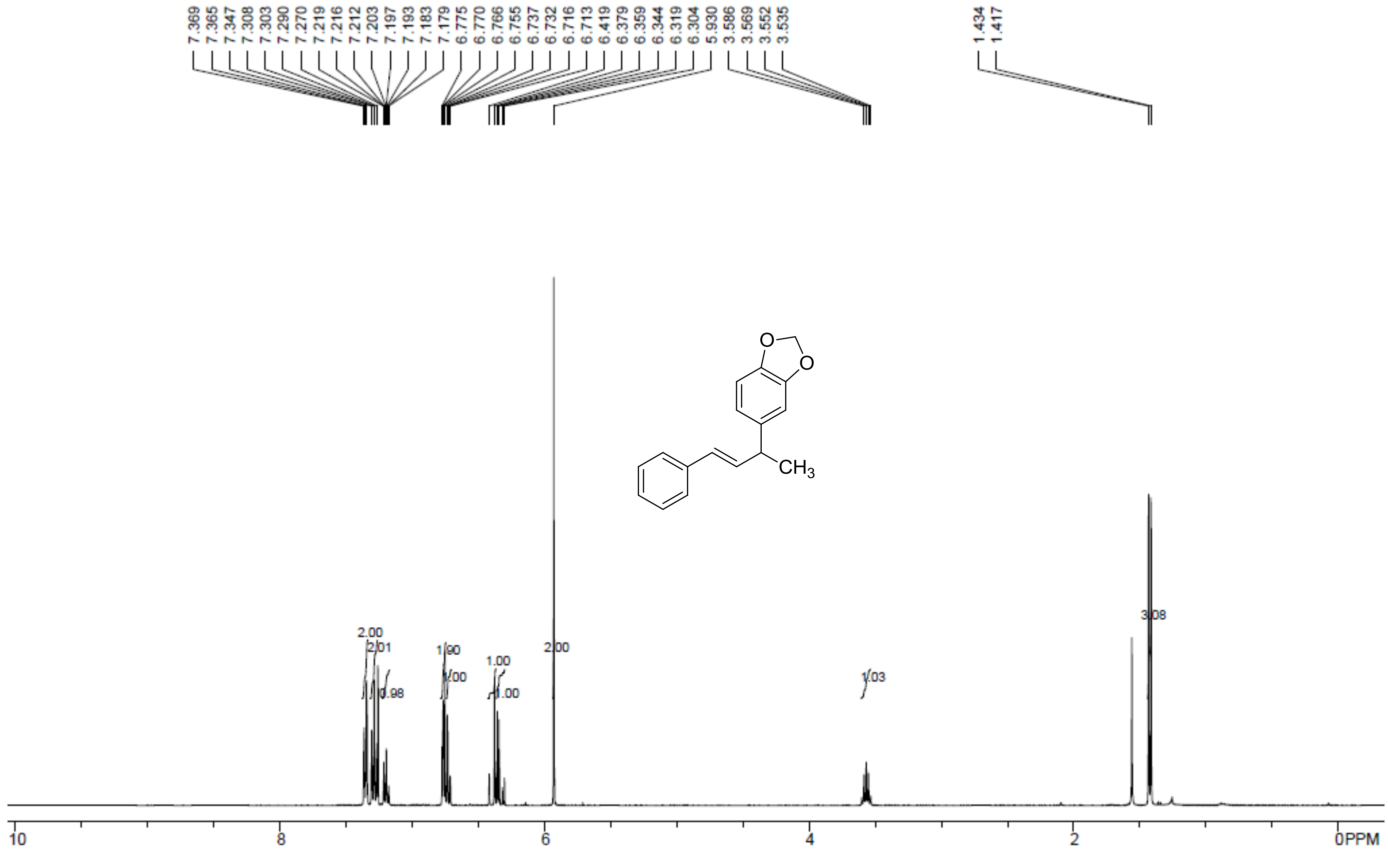
^{13}C NMR spectrum of **14b’**



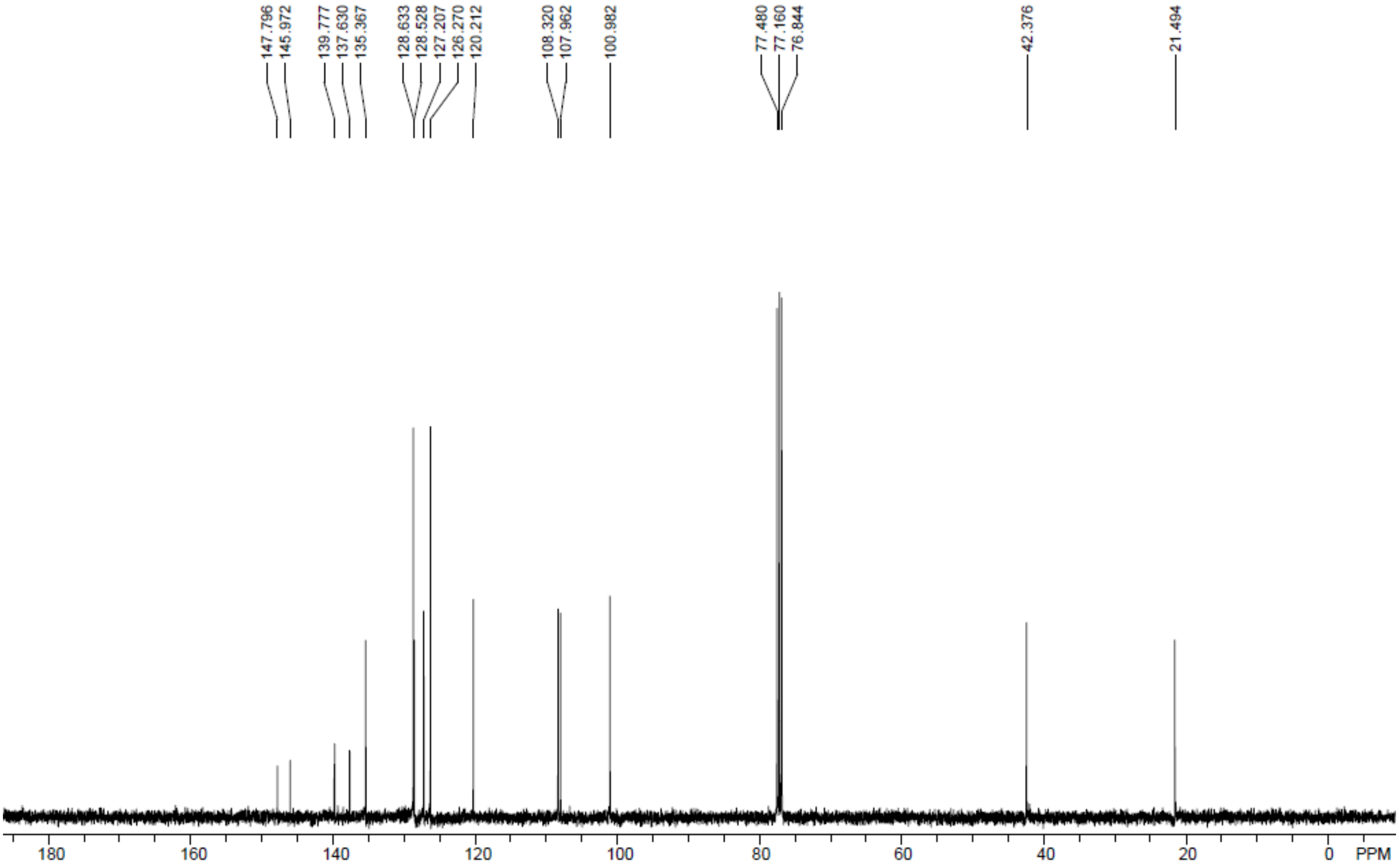
^{1}H NMR spectrum of **14c**



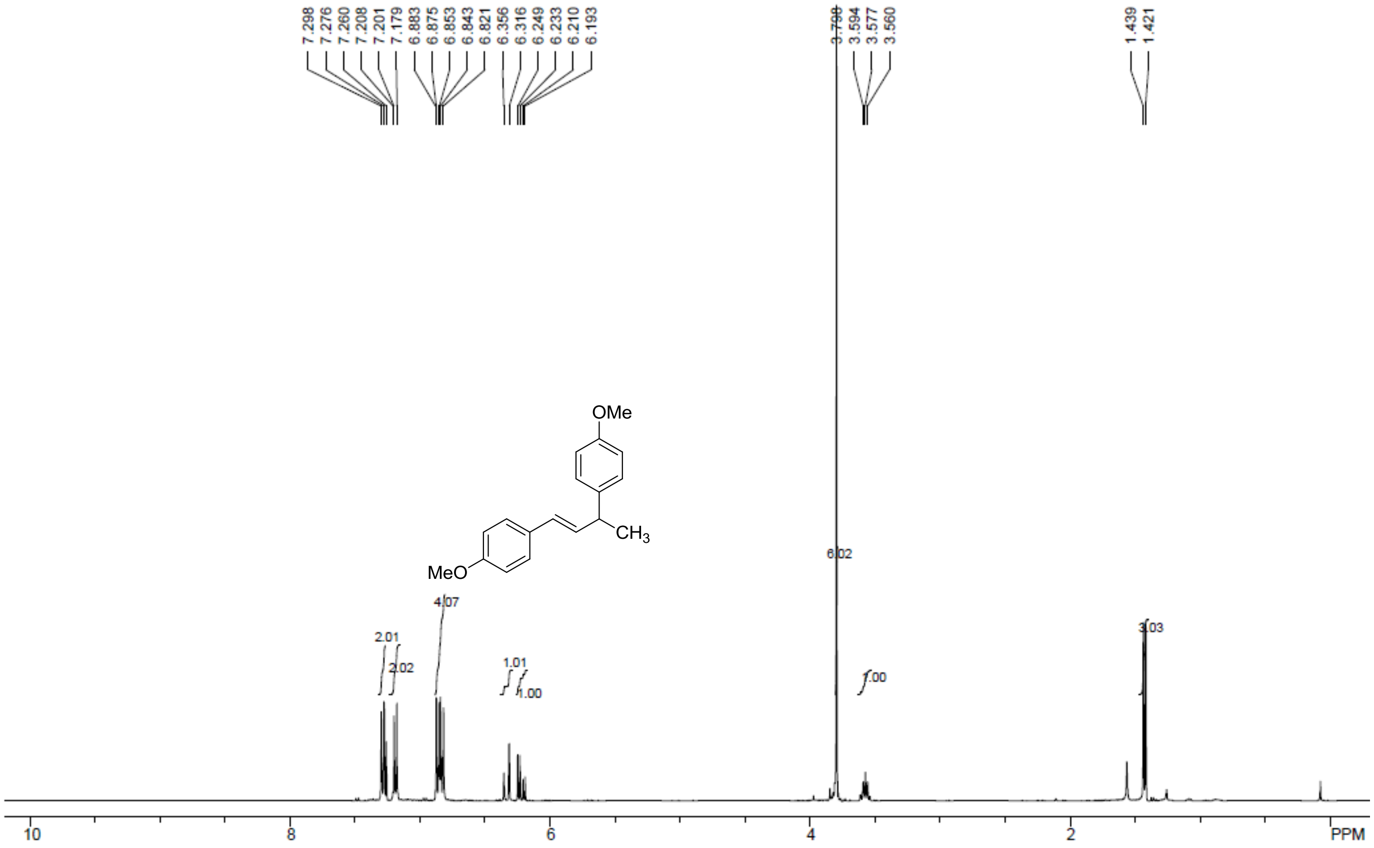
^{13}C NMR spectrum of **14c**



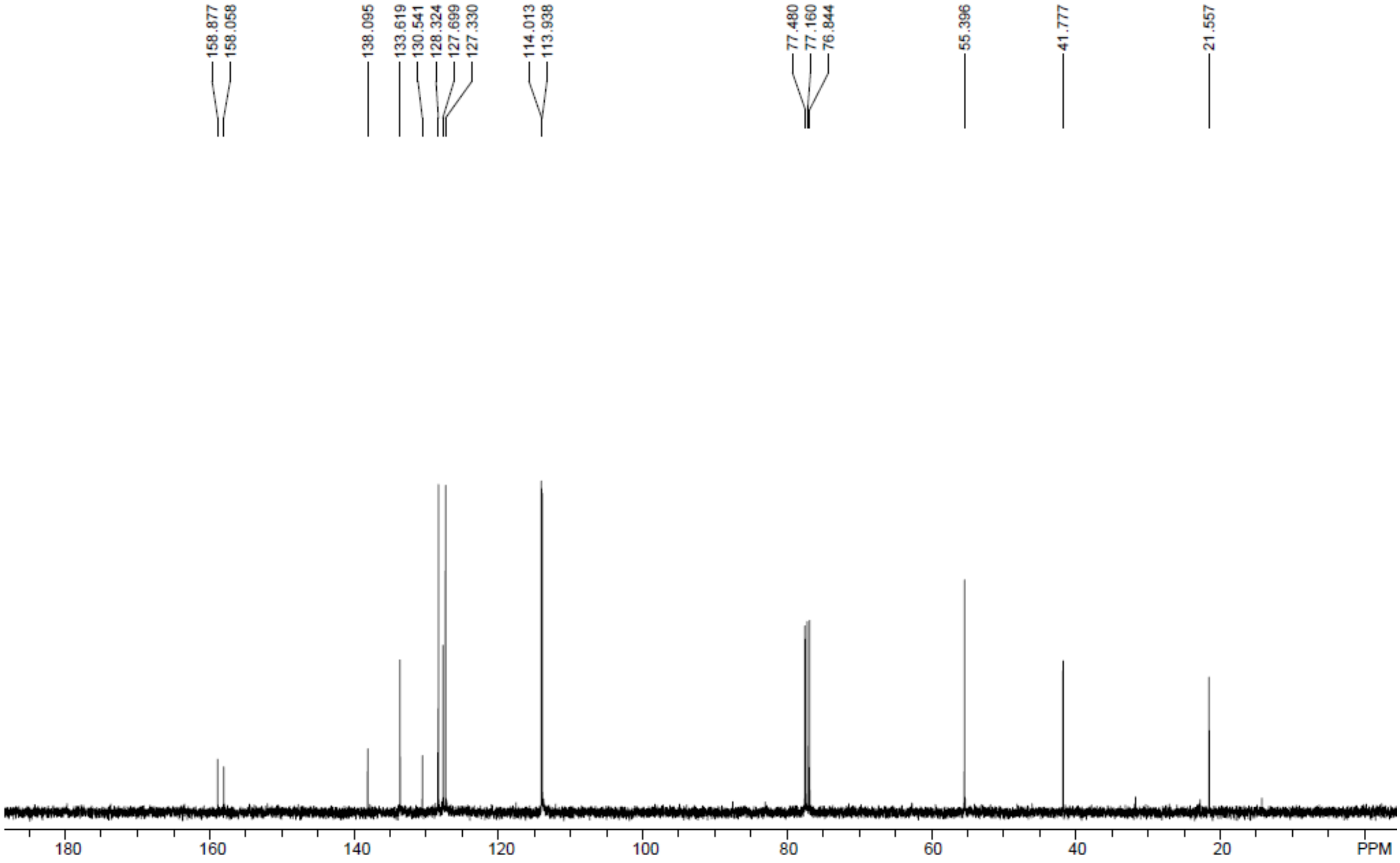
^{1}H NMR spectrum of **14d**



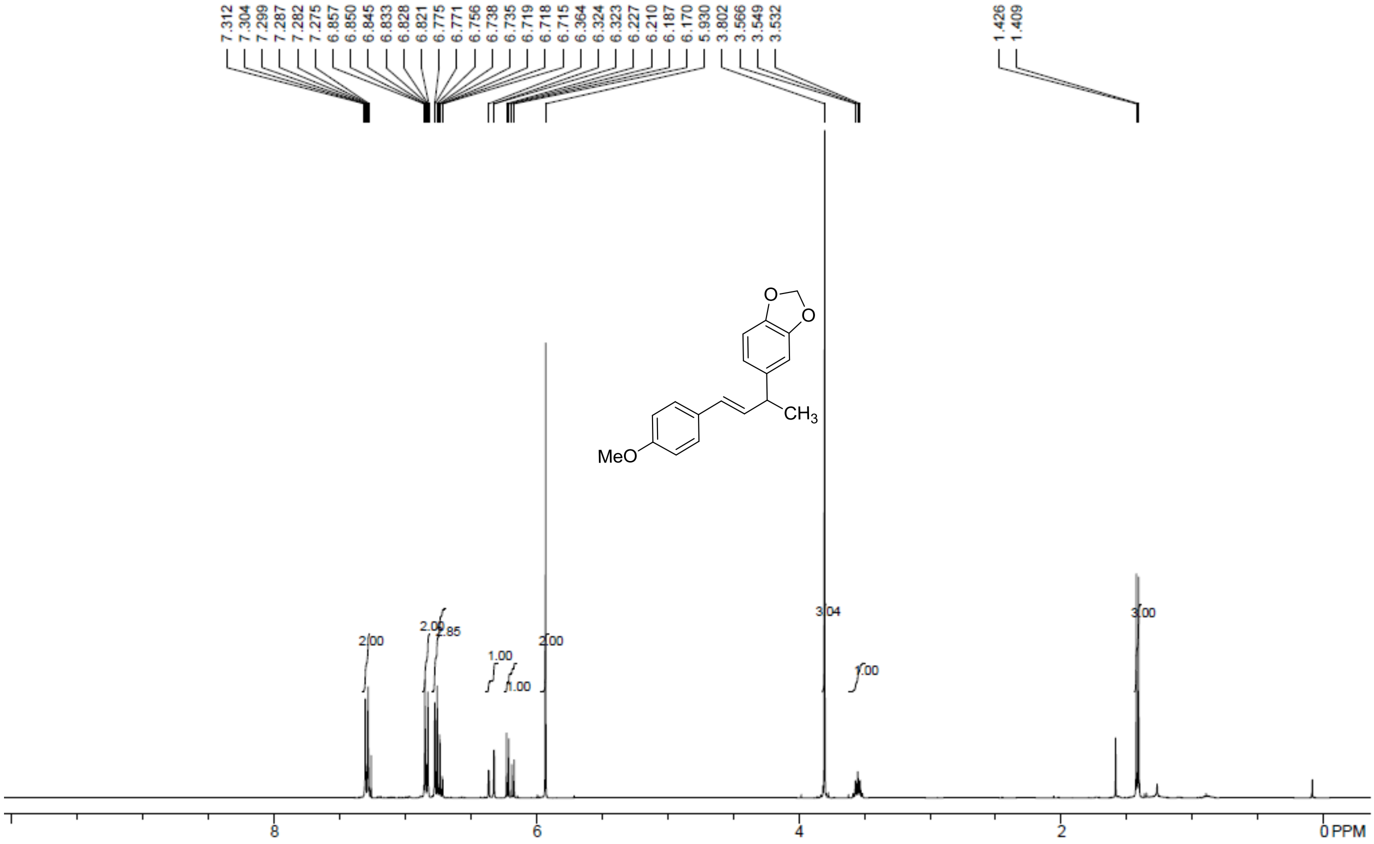
^{13}C NMR spectrum of **14d**



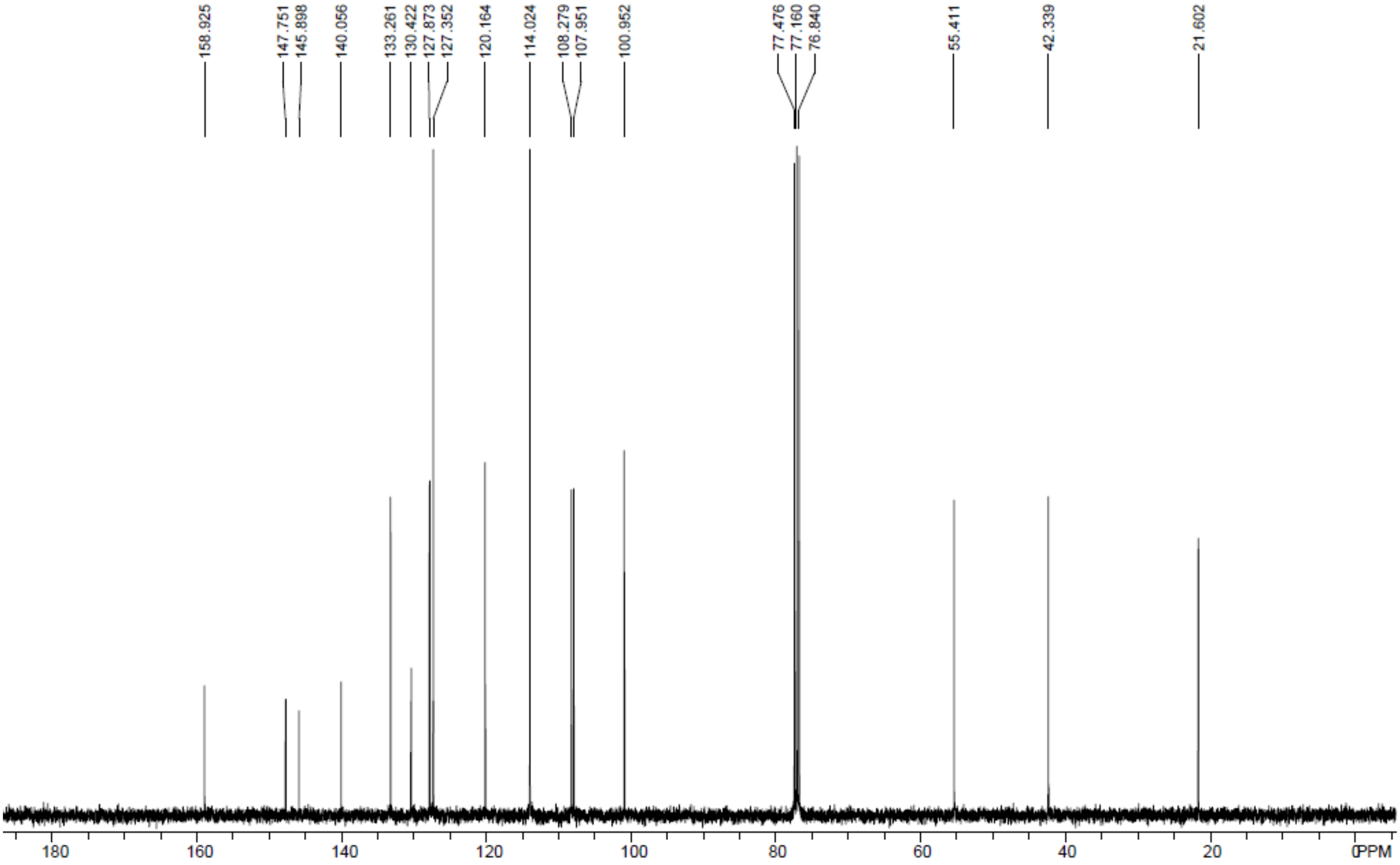
^{1}H NMR spectrum of **14e**



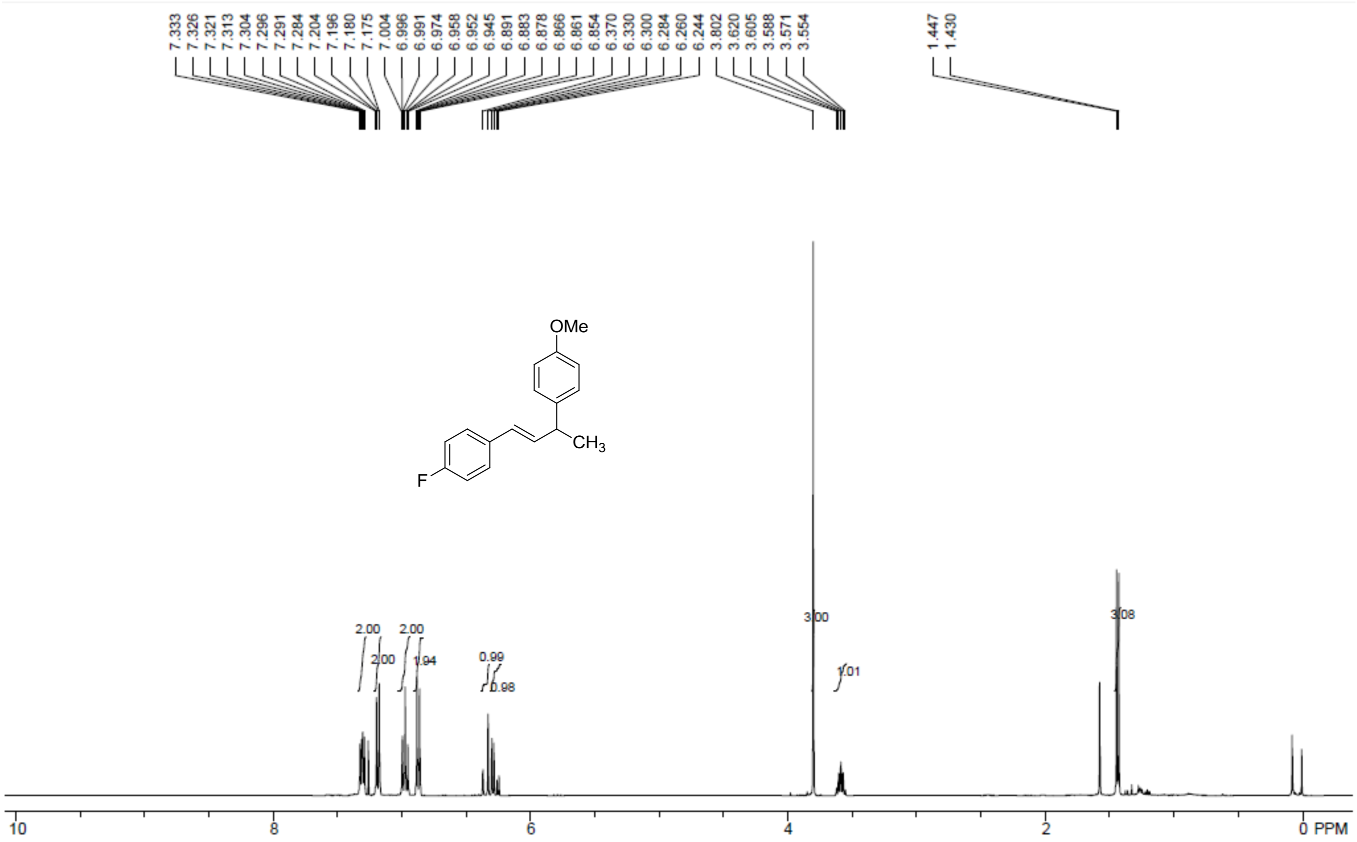
^{13}C NMR spectrum of **14e**



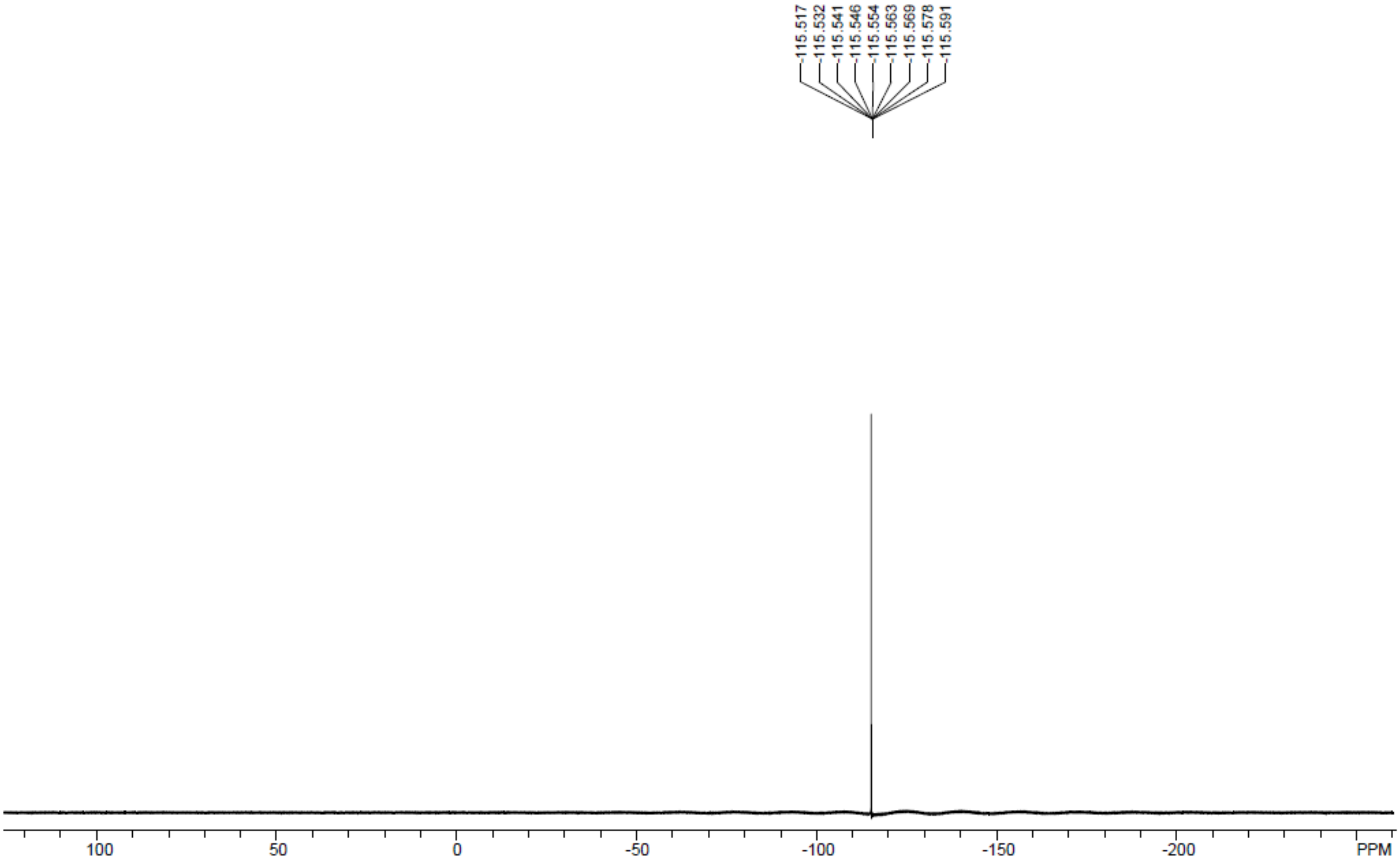
^{1}H NMR spectrum of **14f**



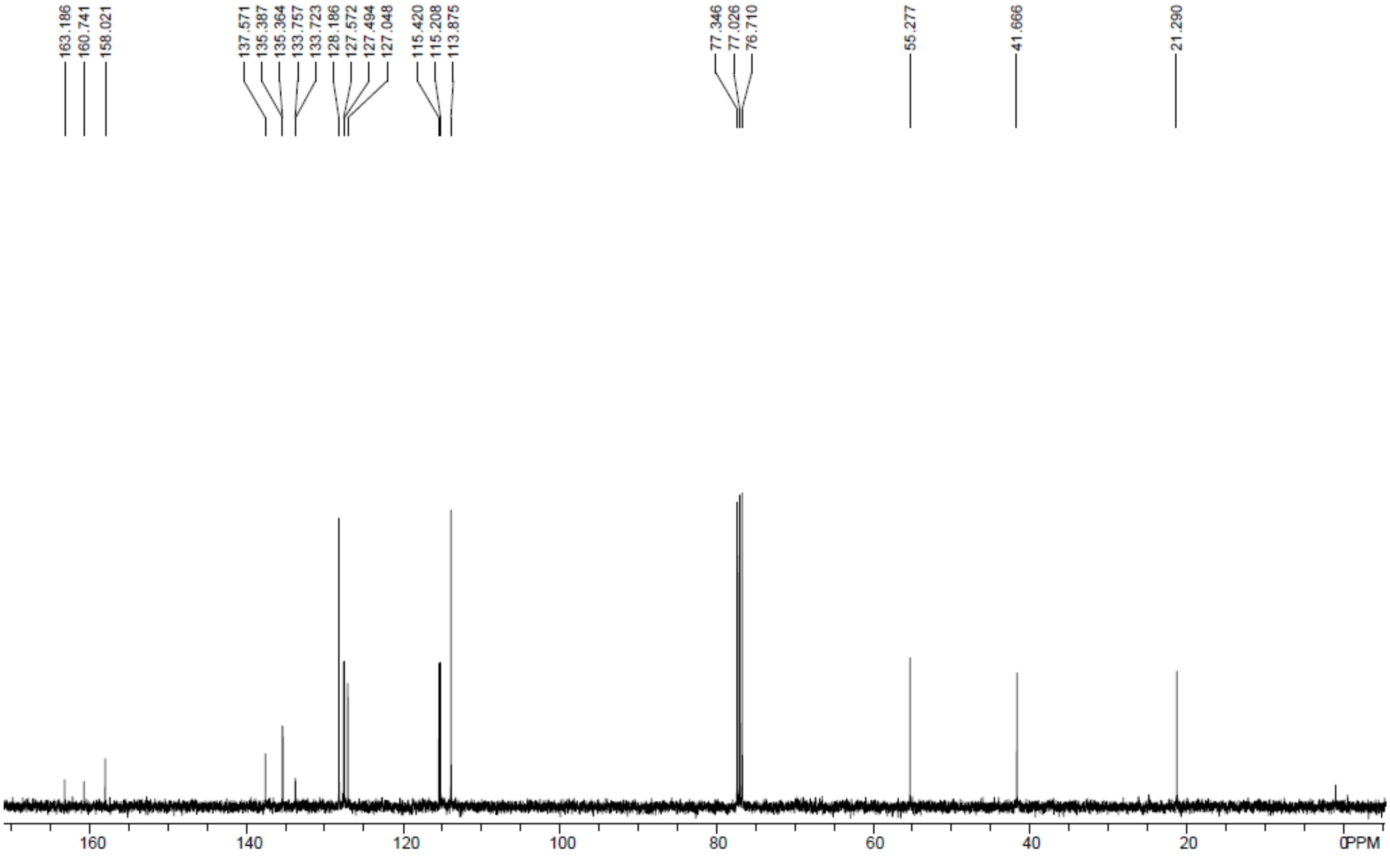
^{13}C NMR spectrum of **14f**



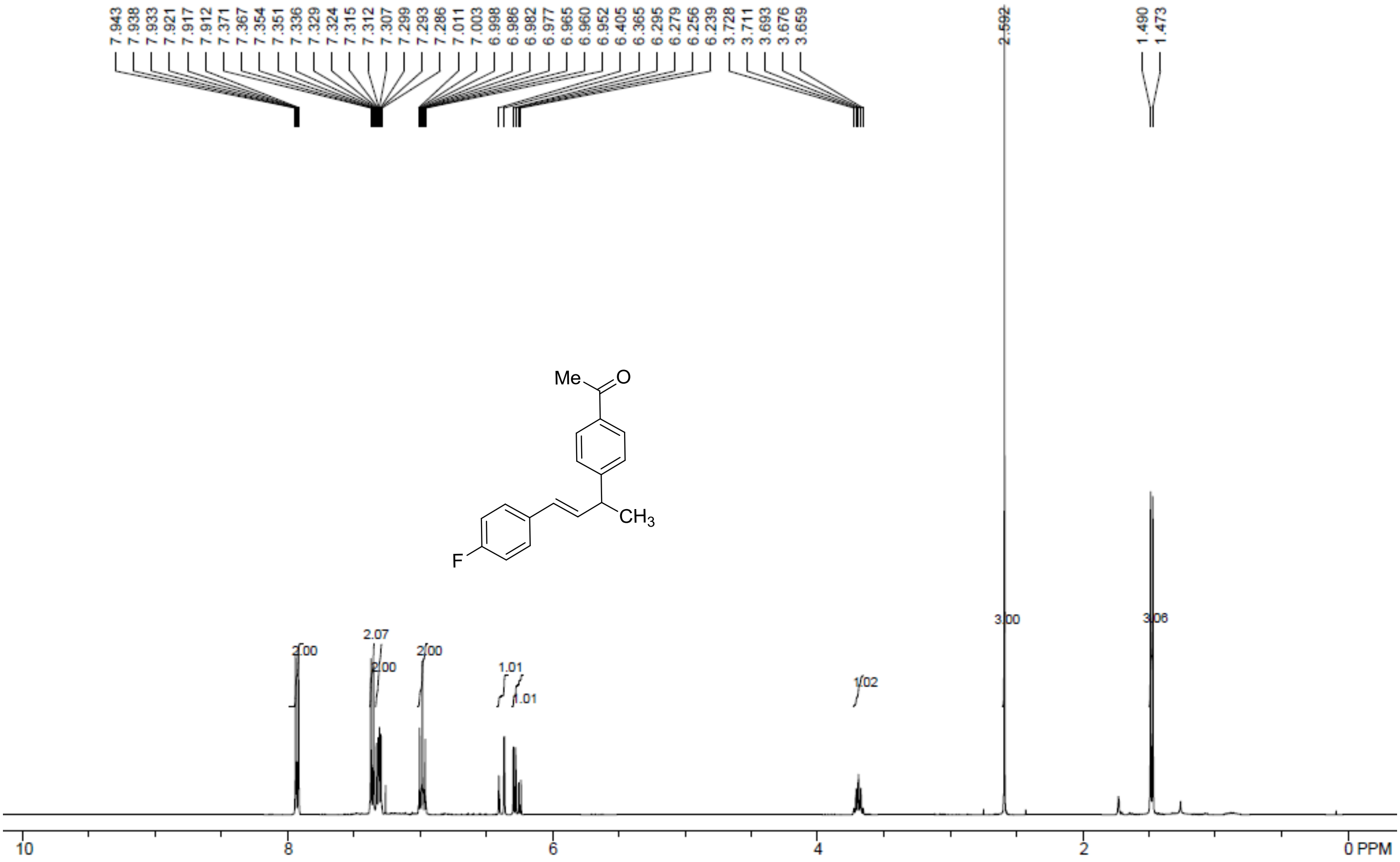
^{1}H NMR spectrum of **14g**



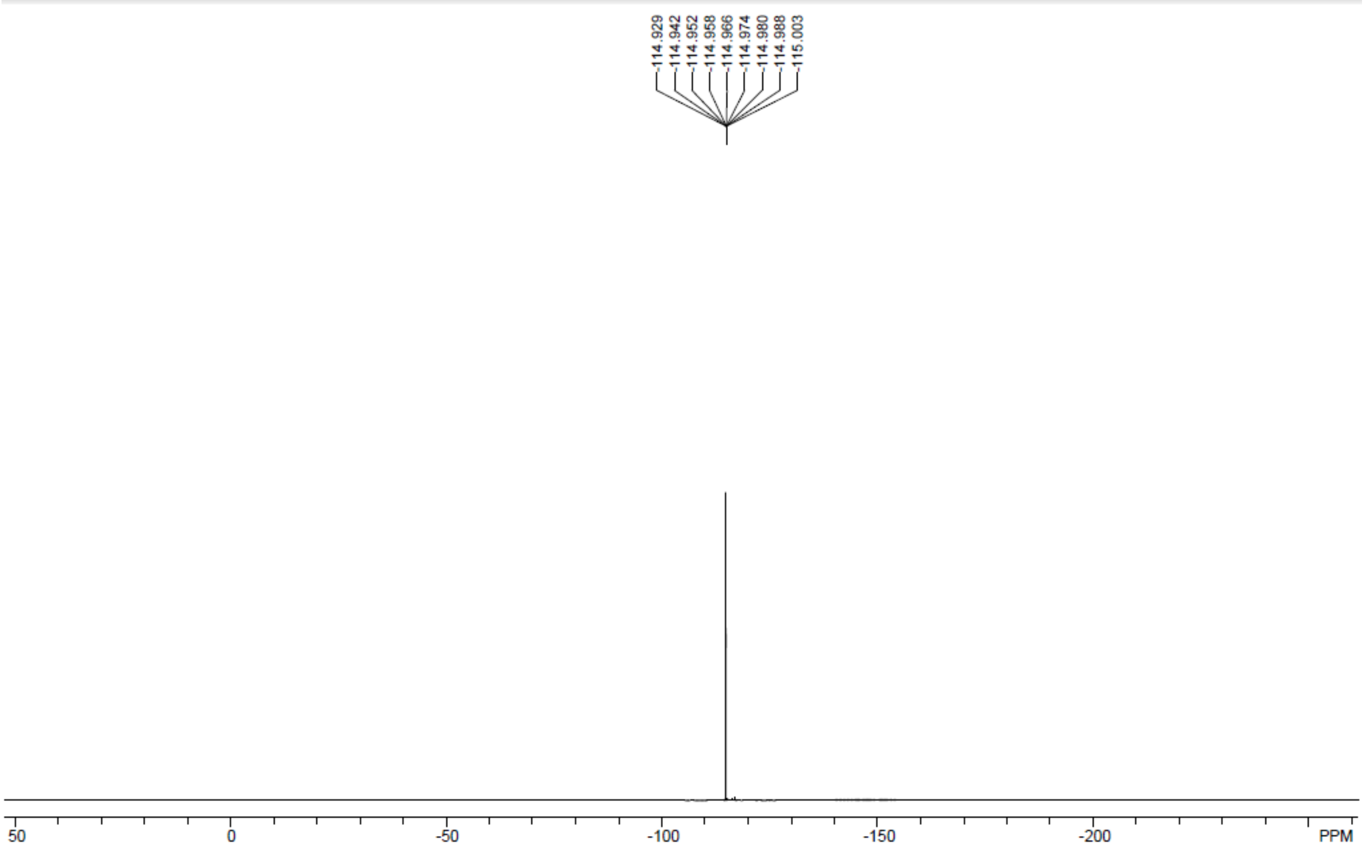
^{19}F NMR spectrum of **14g**



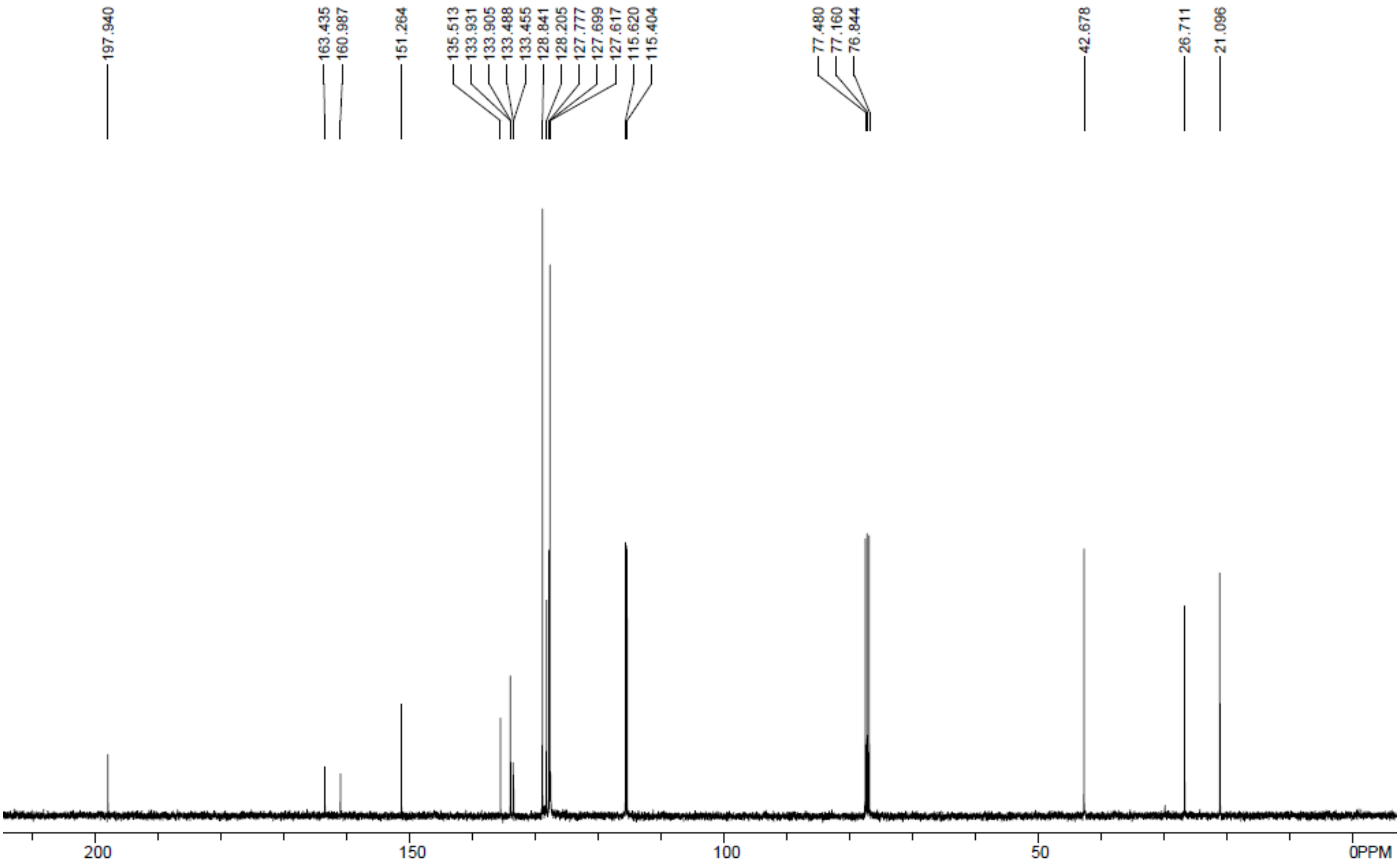
^{13}C NMR spectrum of **14g**



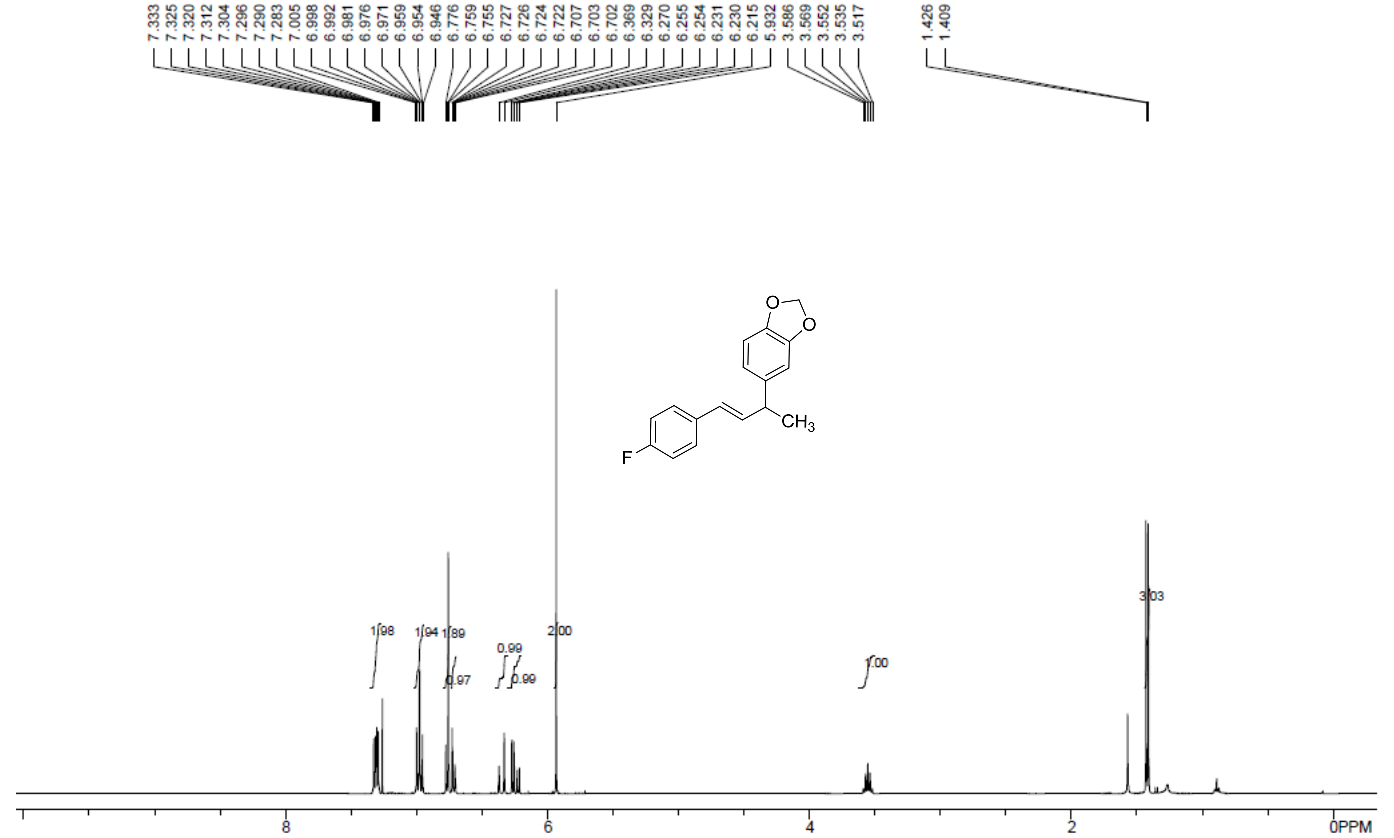
^{1}H NMR spectrum of **14h**



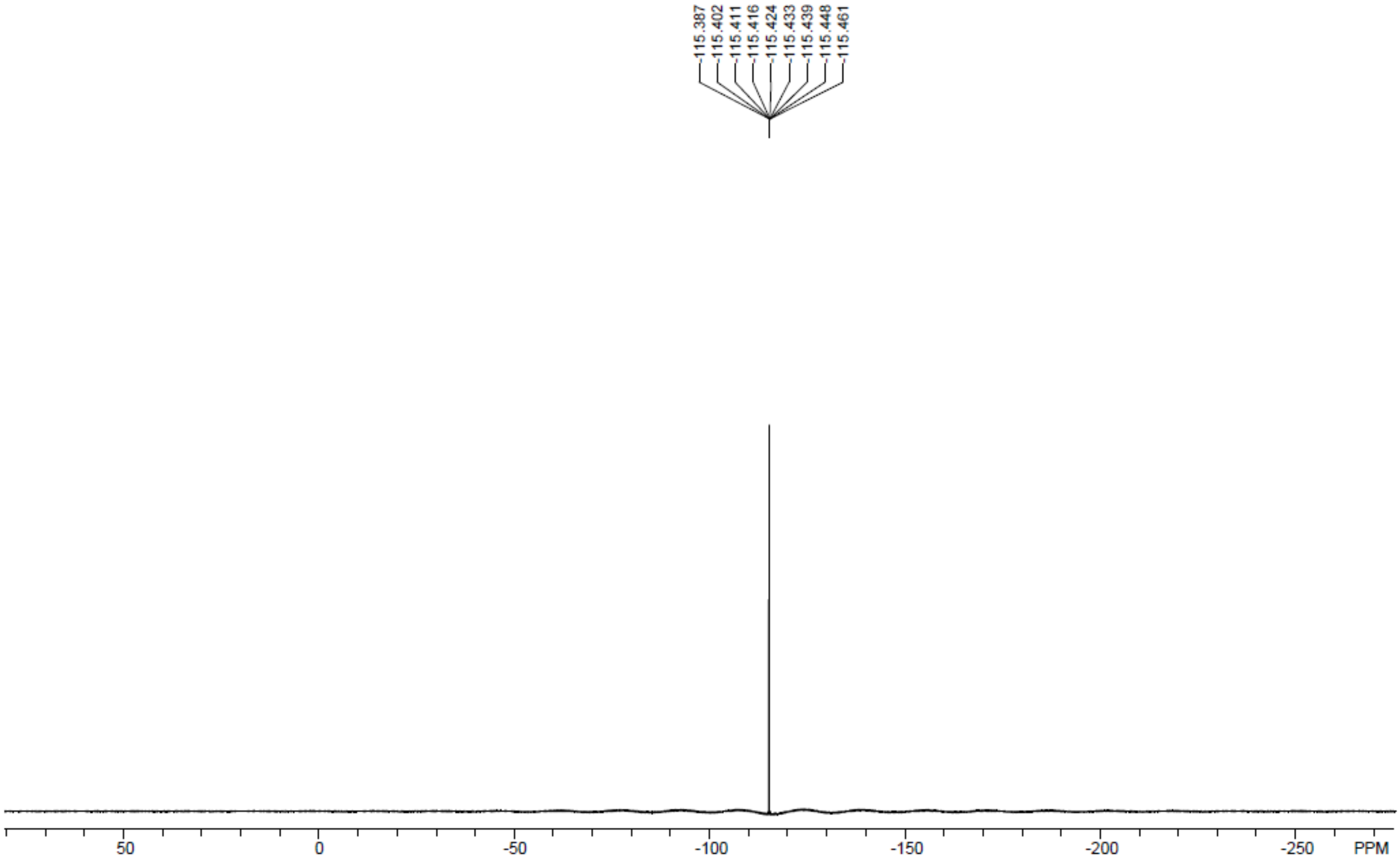
^{19}F NMR spectrum of **14h**



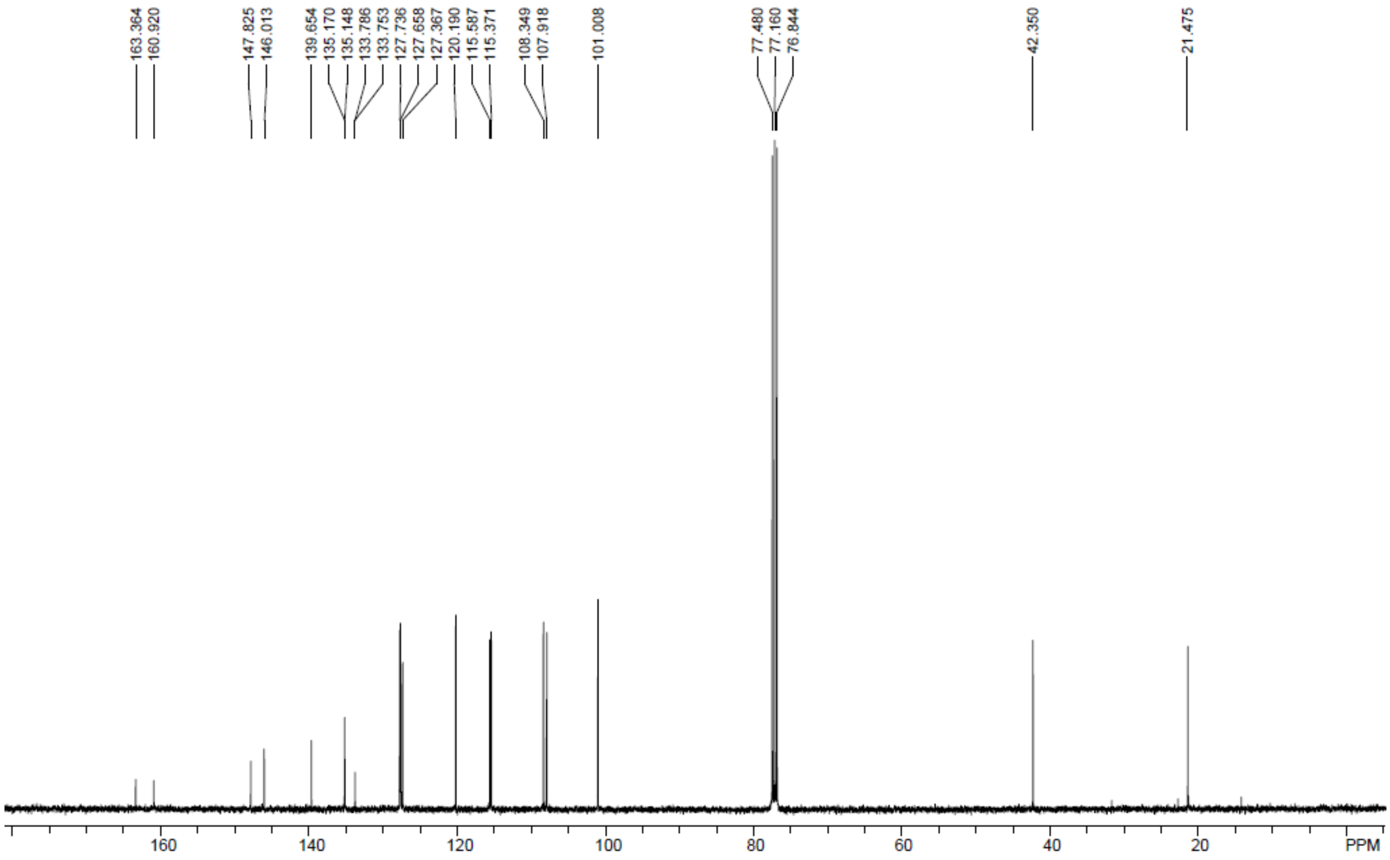
^{13}C NMR spectrum of **14h**



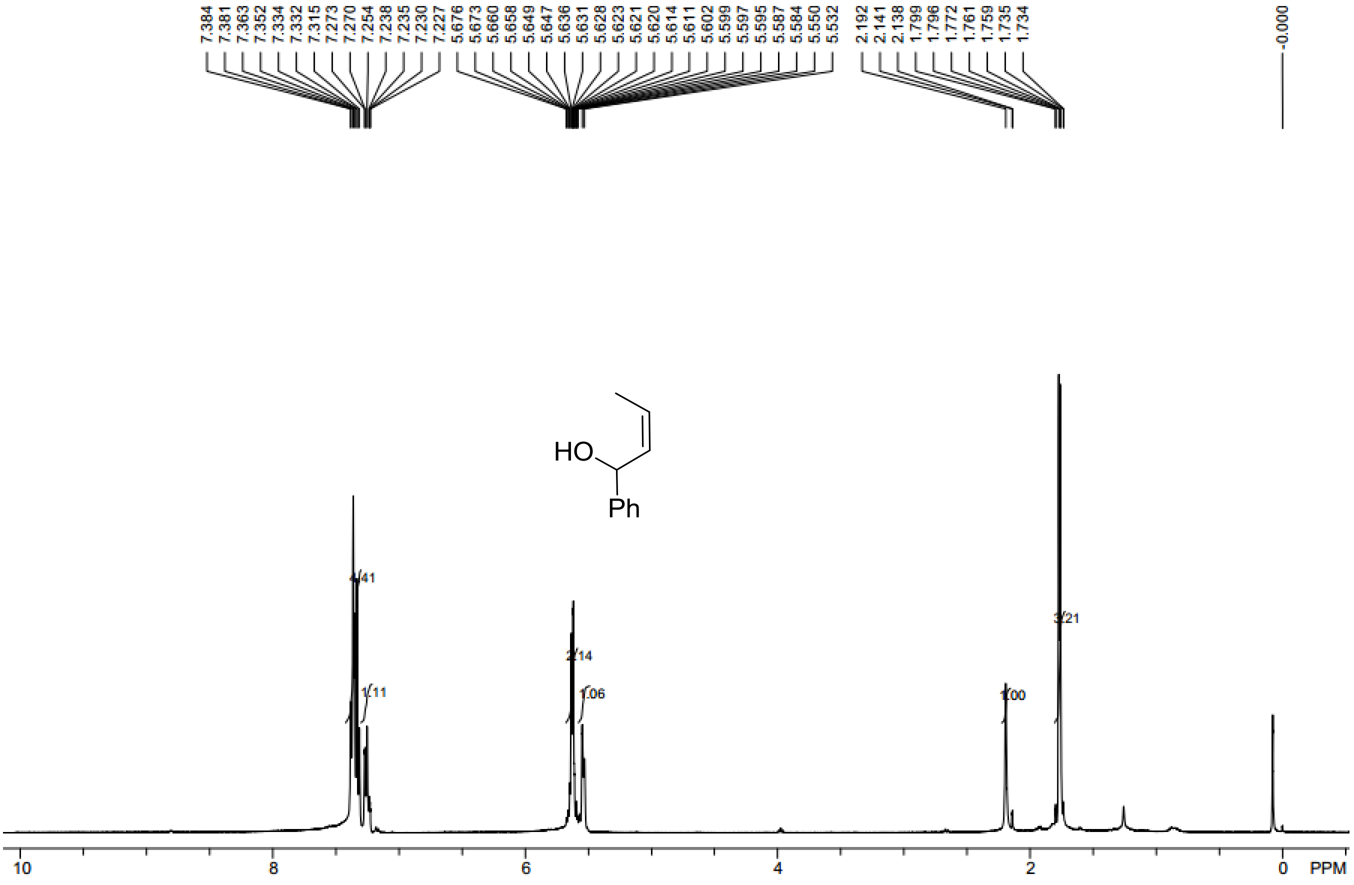
^{1}H NMR spectrum of **14i**



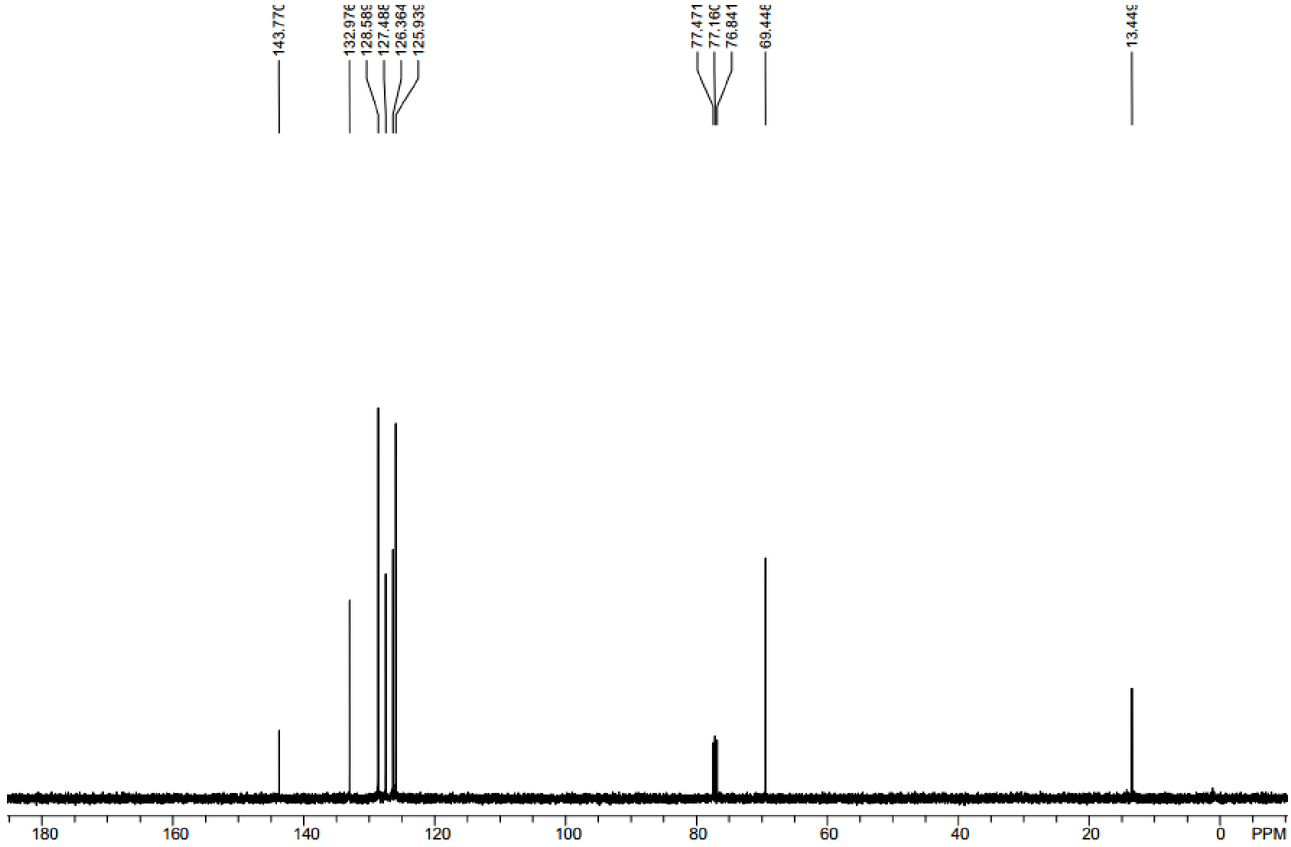
^{19}F NMR spectrum of **14i**



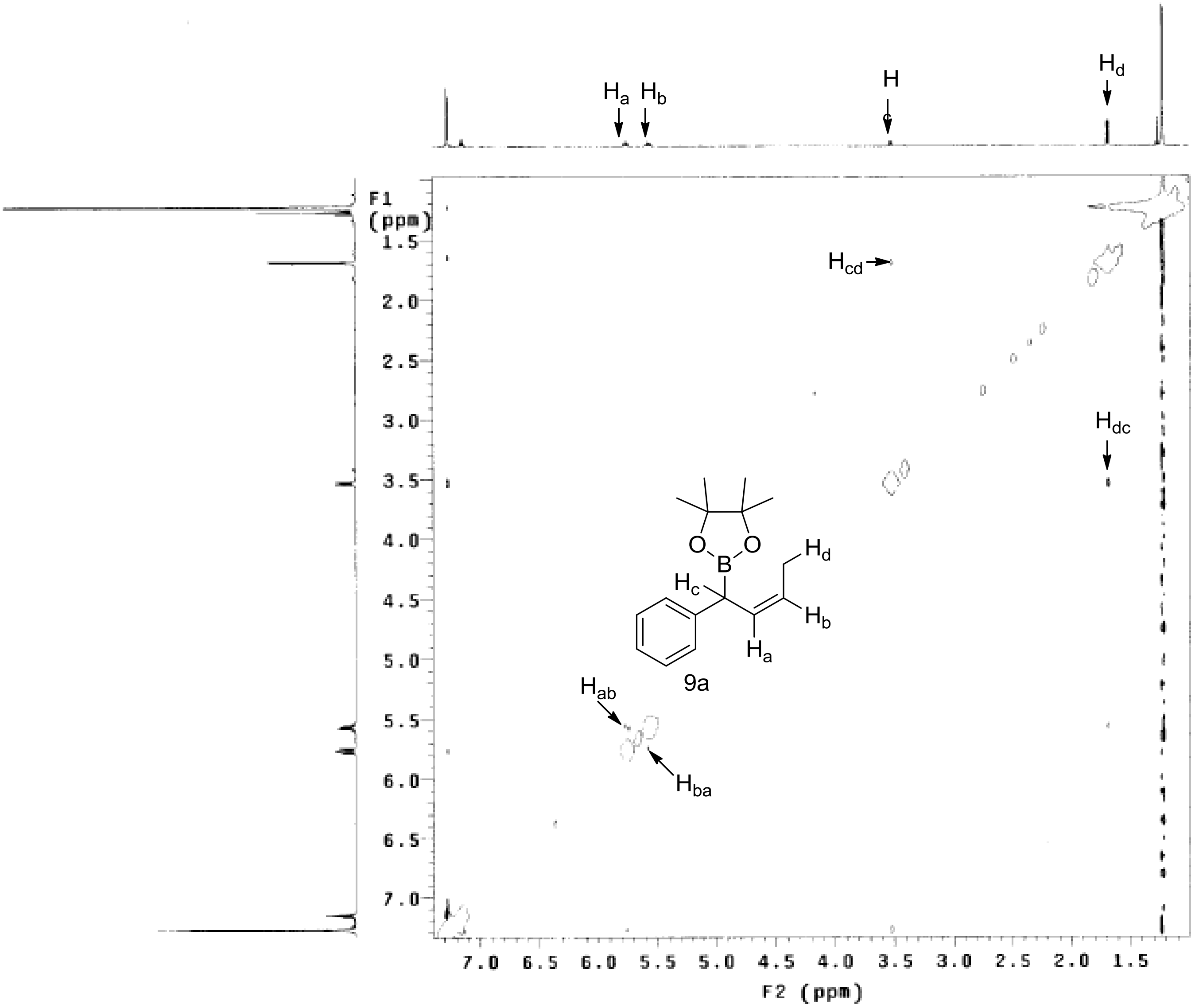
^{13}C NMR spectrum of **14i**



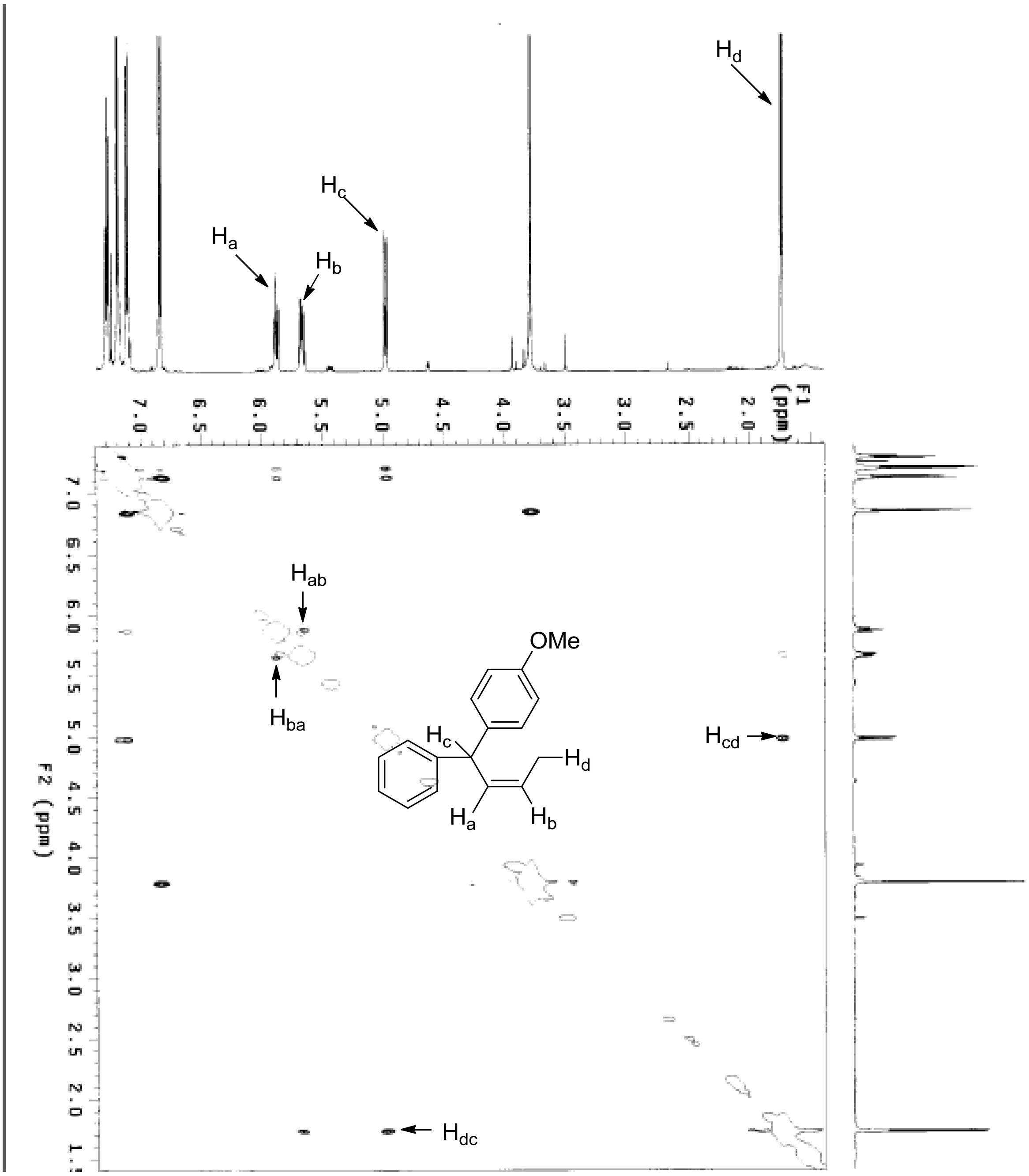
^{1}H NMR spectrum of **12**



^{13}C NMR spectrum of **12**


H_a
H_b
H_c
H_d
H_{cd}
H_{dc}
H_{ab}
H_{ba}
F1 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
F2 (ppm)
O
B
O
H_d
H_c
H_b
H_a
9a

NOESY of **9a**


Hd
Hc
Ha
Hb
F1 (ppm)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
F2 (ppm)
1.5
Hab
Hba
Hcd
Hdc
OMe
Hc
Hd
Ha
Hb

NOESY of **14b'**