Supporting Information

One-pot Synthesis of Multisubstituted Propenylbenzenes from Benzyl Chlorides through Relay Catalysis of Palladium

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Table of Contents

1. Experimental Section

General information:

Unless otherwise noted, all reactions were carried out in oven-dried 25-mL Schlenk tubes under a nitrogen atmosphere. An aluminum heating block placed on a stirring plate was used as the heating source. Solvents were purified by standard techniques without special instructions. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker AvanceII-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C); $CDCl_3$ and TMS were used as a solvent and an internal standard, respectively. The NMR yield was determined by ^{1}H NMR using 1,3,5-Trimethoxybenzene as an internal standard. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants *J* are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on either a Q-TOF mass spectrometry or a LTQ Orbitrap XL mass spectrometry. TLC was carried out on SiO_2 (silica gel 60 F254, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 mesh) or basic Al_2O_3 (Al_2O_3 90, 100-200 mesh). Unless otherwise noted, starting materials are commercially available.

Cyclic voltammetry experiments were executed in undivided three-electrode cells. The potentials were measured against Ag/AgCl (3 M KCl) aqueous reference electrode. The working electrode was a 3 mm diameter glassy carbon disk, and the counter electrode was a platinum wire. The glassy carbon working electrode was polished with diamond polishing suspension between each experiment.

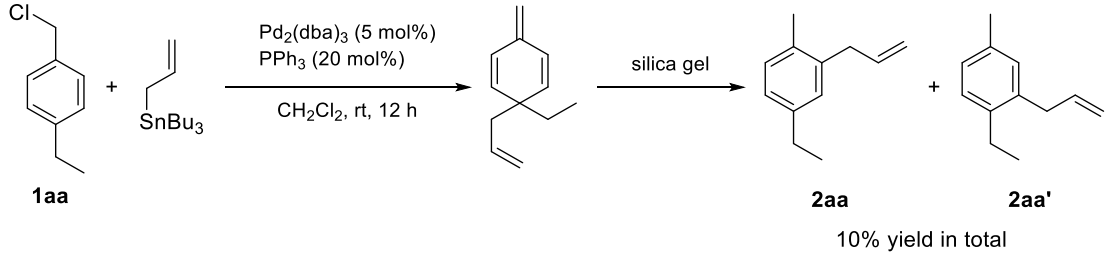
General Procedure：

Benzyl chloride (**1a**, 64.0 mg, 0.3 mmol) and allyltributylstannane (0.3 mmol, 100.0 mg) were added into a mixture of $Pd_2(dba)_3$ (13.7 mg, 0.015 mmol) and PPh_3 (15.7 mg, 0.06 mmol), in dry dichloromethane (2.0 mL). After the reaction mixture was stirred at room temperature for 24 h under N_2 atmosphere, 4-toluenesulfonic acid monohydrate (TsOH·H_2O, 0.6 mmol, 142.0 mg) was subsequently added, and the reaction mixture was stirred at 40 ℃ for 12 h. Purification by basic alumina column chromatography (eluent: hexane) followed by distillation under reduced pressure to give propenylbenzene **2a** as a yellow solid in the yield of 60%.

2. Optimization Studies

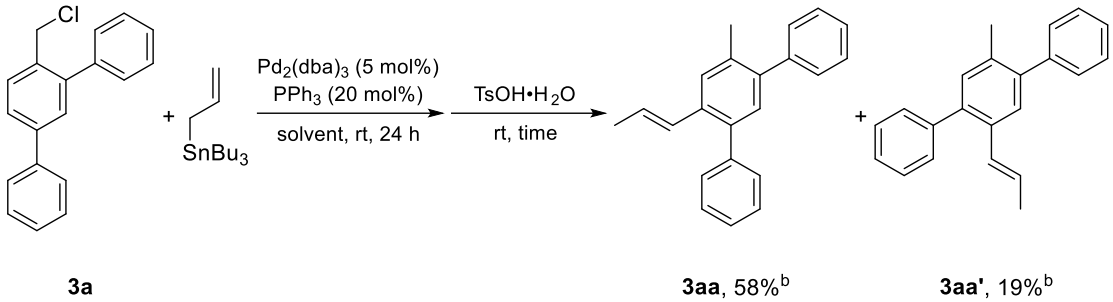
A mixture of *ortho*-allylation product **2aa** and *meta*-allylation product **2aa'** was obtained in 10% yield totally when the mixture of 4-ethylbenzyl chloride **1aa** with allyltributylstannane was purified by silica gel column (Scheme S1).

Scheme S1. Effect of silica gel on dearomatization product



A mixture of 1,2-allylic rearrangement product **3aa** and 1,2-phenyl rearrangement product **3aa'** were obtained under standard reaction conditions when used 2,4-diphenylbenzyl chloride **3a** as substrate (Scheme S2).

Scheme S2. Reactions of 2,4-diphenylbenzyl chloride 3a as substrate[a]

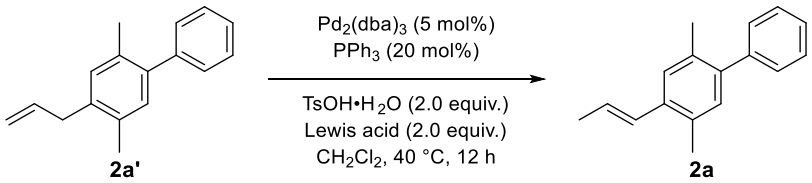


3a **3aa**, 58%[b] **3aa'**, 19%[b]

[a]Reaction conditions: **3a** (0.3 mmol), allyltributylstannane (0.3 mmol), $Pd_2(dba)_3$ (5 mol%) and PPh_3 (20 mol%) in 2.0 mL of solvent at room temperature for 24 h under N_2 atmosphere. TsOH·H_2O (0.6 mmol) was subsequently added, and the reaction mixture was stirred for 12 h. [b]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Different Lewis acids were employed to replace Bu_3SnCl under the standard reaction conditions, the results are shown in Table S1.

Table S1. Optimization of Lewis acid[a]



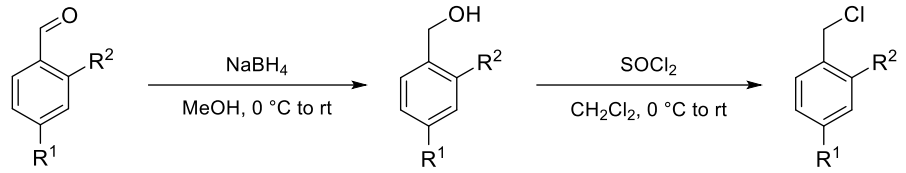
2a' **2a**

entry	Lewis acid	yield (%)[b]
1	-	54
2	Bu_3SnCl	90
3	$AlCl_3$	18
4	$(CH_3)_3SiCl$	trace
5	$TiCl_4$	0
6	$SnCl_4$	0
7	CF_3SO_3La	0
8	$(CH_3)_3SiCl$	0
9	$BF_3{\cdot}O(C_2H_5)_2$	0

[a]Reaction conditions: allylation product **2a'** (0.3 mmol), Lewis acid (0.6 mmol), $Pd_2(dba)_3$ (5 mmol%), PPh_3 (20 mmol%) and TsOH·H_2O (0.6 mmol) in 2.0 mL of CH_2Cl_2 at room temperature for 12 h. [b]Isolated yield.

3. Synthesis of Starting Materials

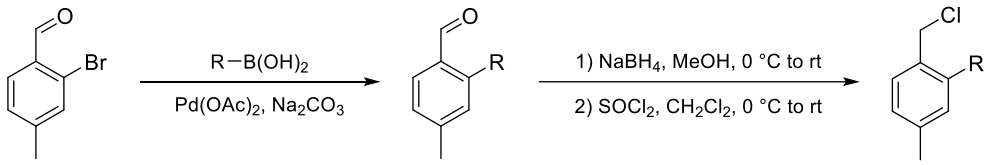
Representative procedure for synthesis of 1a-1o (Method A)



To a solution of aryl aldehyde (5 mmol) in MeOH (20 mL) at 0 ℃, $NaBH_4$ (0.38 g, 10 mmol) was slowly added. The reaction mixture was slowly warmed to room temperature and stirred overnight. The resulting mixture was washed with 5% HCl (aq.), brine, and H_2O, then extracted with EtOAc three times, and the combined organic layers were dried over Na_2SO_4, filtrated, and then concentrated under vacuum. The crude product was washed with hexane to afford the aryl alcohol as a white solid.

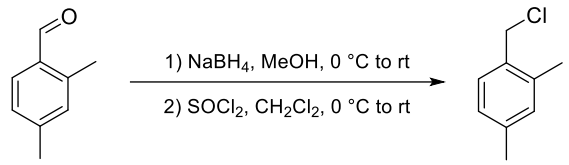
To a solution of the aryl alcohol (5 mmol) in CH_2Cl_2 (20 mL) at 0 ℃, $SOCl_2$ (10 mmol) was slowly added. The reaction mixture was slowly warmed to room temperature and stirred overnight. After washed with saturated $NaHCO_3$ (aq.), brine, and H_2O, the combined organic layers were dried over Na_2SO_4, filtrated, and then concentrated under vacuum to give a crude product. The crude product was purified by silica gel column chromatography (eluent: hexane) to afford the desired benzyl chloride product.

Representative procedure for synthesis of 1a-1l, and 1n-1o[1]



To a solution of 2-bromo-4-methylbenzaldehyde (0.50 g, 5 mmol) and Na_2CO_3 (1.38 g, 10 mmol) in 10 mL DMF/H_2O (v/v = 2:1) was added phenylboronic acid (0.67 g, 5.5 mmol), and stirred for 5 min. After $Pd(OAc)_2$ (56 mg, 0.25 mmol) was added, the resulting mixture was stirred overnight at room temperature under N_2 atmosphere. The resulting mixture was extracted with EtOAc three times, and then the combined organic layers were dried over Na_2SO_4. The Na_2SO_4 was removed through filtration, and the filtrate was concentrated under vacuum to afford a crude product. The crude product was purified by silica gel column chromatography (eluent: hexane/EtOAc = 20/1) to afford the desired 2-phenyl-4-methylbenzaldehyde (0.81 g, 4.15 mmol, 83% yield). The 2-(chloromethyl)-5-methyl-1,1'-biphenyl **1a** was finally obtained by means of Method A as a colorless oil (0.77 g, 71% total yield).

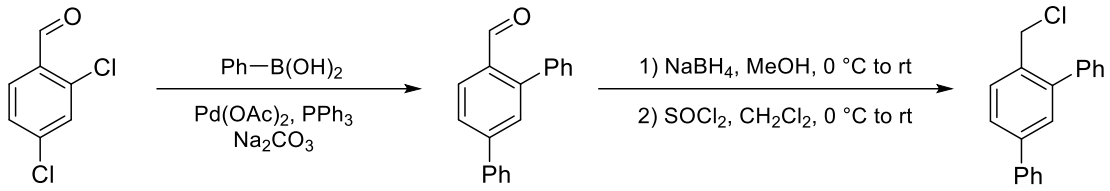
Representative procedure for synthesis of 1m



1m

2,4-dimethylbenzaldehyde (0.67 g, 5 mmol) was used to synthesize 1-(chloromethyl)-2,4-dimethylbenzene **1m** by means of Method A as a colorless oil (1.06 g, 77% total yield).

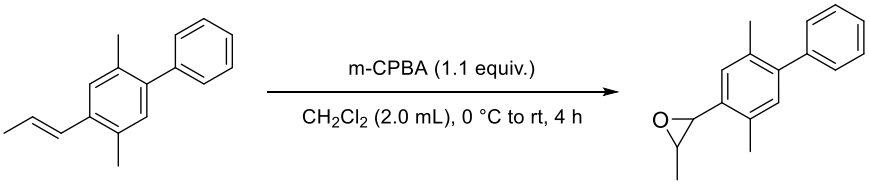
Procedure for synthesis of 3a[2]



3a

A solution of $Pd(OAc)_2$ (68 mg, 0.30 mmol) and PPh_3 (0.39 g, 1.50 mmol) in 5 mL absolute ethanol and 5 mL toluene was stirred at room temperature under N_2 atmosphere for 10 min. After that period, 2,4-dichlorobenzaldehyde (0.87 g, 5 mmol), Na_2CO_3 (2.35 g, 22 mmol) and phenylboronic acid (3.05 g, 25 mmol) were sequentially added. The resulting mixture was stirred at 100 ℃ under N_2 atmosphere for 24 h. The resulting mixture was extracted with EtOAc three times, and then the combined organic layers were dried over Na_2SO_4. The Na_2SO_4 was removed through filtration, and the filtrate was concentrated under vacuum to afford a crude product. The crude product was purified by silica gel column chromatography (eluent: hexane/EtOAc = 20/1) to afford the desired [1,1':3',1"-terphenyl]-4'-carbaldehyde (1.03 g, 4 mmol, 80% yield). The 4'-(chloromethyl)-1,1':3',1"-terphenyl **3a** was finally obtained by means of Method A as a colorless oil (0.89 g, 64% total yield).

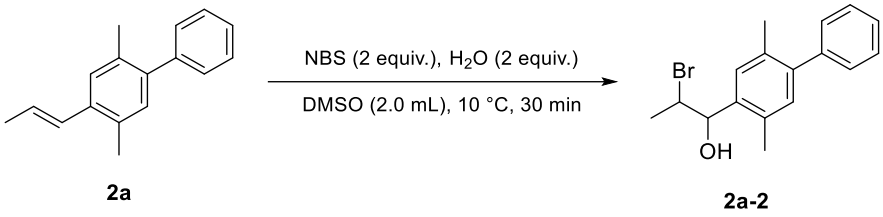
4. General Procedure for Transformation of Products



2a **2a-1**

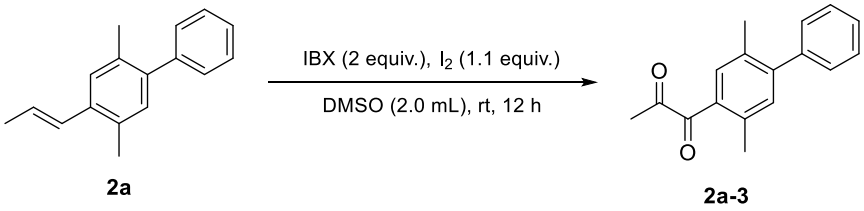
To a solution of **2a** (66.6 mg, 0.3 mmol) in anhydrous CH_2Cl_2 (2.0 mL), *m*-CPBA (56.9 mg, 0.33 mmol) was added at 0 ℃ under nitrogen atmosphere. After stirring for 4 h, the reaction mixture was quenched with a saturated with $NaHCO_3$ and extracted with CH_2Cl_2 three times. The organic phases were collected and dried over Na_2SO_4. The solvent was concentrated in vacuo to yield the epoxide which was directly used without any further purification. The combined organic layers were dried over

Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 100/1 to 50/1) to afford the epoxide product **2a-1** (35.0 mg, 49% yield)[3].



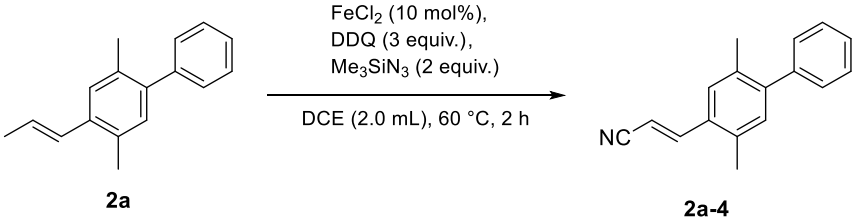
2a **2a-2**

To a solution of **2a** (66.6 mg, 0.3 mmol) in DMSO (2.0 mL), water (10.8 mg, 0.6 mmol) was added under nitrogen atmosphere and cooled to ca. 10 ℃. With stirring, NBS (106.8 mg, 0.6 mmol) was added as one portion. After a short induction period of 2-3 min a yellow color developed and the solution became quite warm. Stirring for an additional 25 min was followed by quenching of the reaction mixture with $NaHCO_3$ and extracted with EtOAc three times. The residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 20/1 to 10/1) to afford the bromohydrin product **2a-2** (61.1 mg, 64% yield)[4].



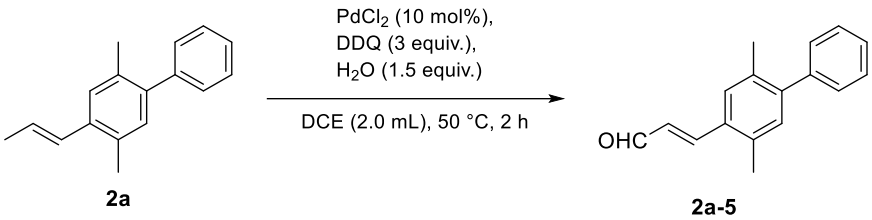
2a **2a-3**

To a solution of IBX (168.0 mg, 0.6 mmol) and iodine (83.8 mg, 0.33 mmol) in dry DMSO (2.0 mL) stirred at room temperature was added **2a** (66.6 mg, 0.3 mmol) in one charge. The reaction mixture was stirred at room temperature overnight. Then it was diluted with CH_2Cl_2 (15 mL) and washed with saturated aqueous $NaHCO_3$–$Na_2S_2O_3$. Then the resulting mixture was extracted with EtOAc three times. The residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 50/1) to afford the diketone product **2a-3** (28.7 mg, 38% yield)[5].



2a **2a-4**

An oven-dried Schlenk tube was charge with $FeCl_2$ (3.8 mg, 0.03 mmol), DDQ (204.6 mg, 0.9 mmol), **2a** (66.6 mg, 0.3 mmol), Me_3SiN_3 (69.1 mg, 0.6 mmol) and DCE (2.0 mL). The reaction mixture was stirred at 60 ℃ under air for 2 h. After cooling down to room temperature and concentrating in vacuum, the residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 50/1) to afford the alkenyl nitriles product **2a-4** (37.8 mg, 54% yield)[6].



An oven-dried Schlenk tube was charge with $PdCl_2$ (5.3 mg, 0.03 mmol), DDQ (204.6 mg, 0.9 mmol), **2a** (66.6 mg, 0.3 mmol), H_2O (8.1 mg, 0.45 mmol) and DCE (2.0 mL). The reaction mixture was stirred at 50 ℃ for 2 h. After cooling down to room temperature and concentrating in vacuum, the residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 50/1 to 20/1) to afford the alkenyl aldehydes product **2a-5** (46.8 mg, 66% yield)[7].

5. Cyclic Voltammetry (CV) Analysis of PPh_3, Bu_3SnCl and $Pd(OAc)_2$

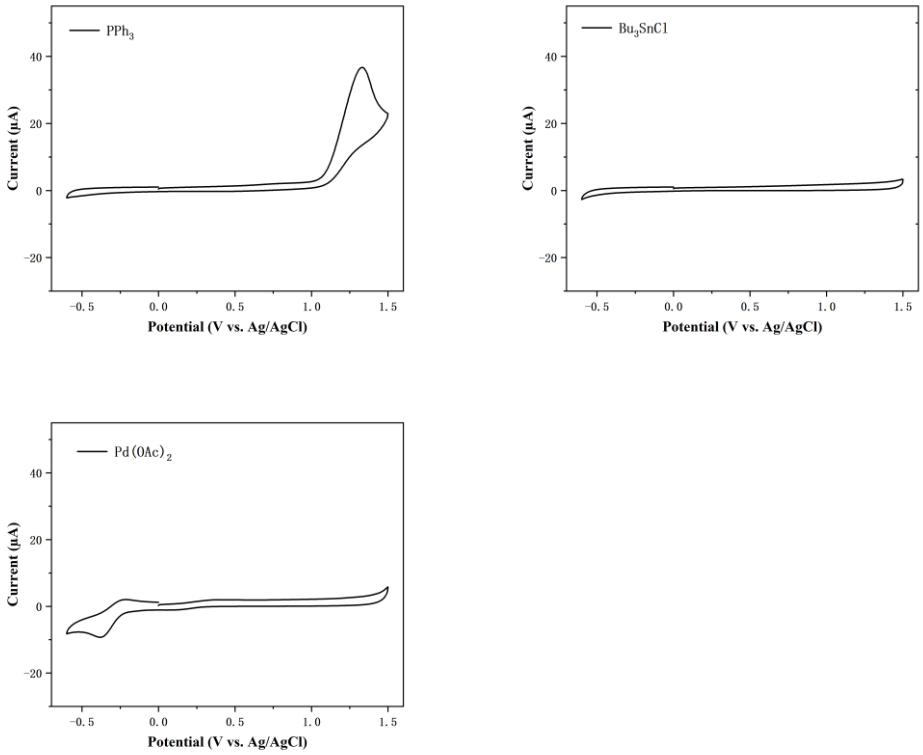
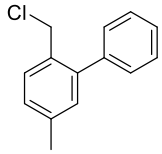


Figure S1. Top left: CV of 2 mM PPh_3 in CH_2Cl_2 with Bu_4NPF_6 (0.1 M) as a supporting electrolyte. Top right: CV of 2 mM Bu_3SnCl in CH_2Cl_2 with Bu_4NPF_6 (0.1 M) as a supporting electrolyte. Bottom left: CV of 1 mM $Pd(OAc)_2$ in CH_2Cl_2 with Bu_4NPF_6 (0.1 M) as a supporting electrolyte. Scan rate = 0.1 V/s. The redox feature of PPh_3 onsets at ca. 1.3 V. No redox features of Bu_3SnCl appears in this voltage range. The redox feature of $Pd(OAc)_2$ onsets at ca. -0.4 V.

6. Characterization Data

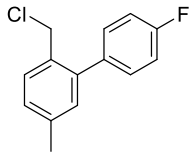
2-(Chloromethyl)-5-methyl-1,1'-biphenyl (1a)



1a

Colorless oil (0.70 g, 59% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.31 (m, 6H), 7.22–7.13 (m, 1H), 7.09 (s, 1H), 4.49 (s, 2H), 2.36 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 142.0, 140.4, 138.5, 132.1, 131.0, 130.5, 129.1, 128.7, 128.3, 127.4, 44.5, 21.2; IR (neat): ν_{max} 3027, 2924, 1611, 1488, 1444, 1262, 824, 780, 737, 701, 668 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{13}Cl$ 216.0706; Found 216.0696.

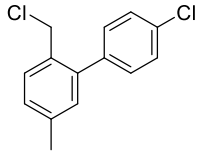
2-(Chloromethyl)-4'-fluoro-5-methyl-1,1'-biphenyl (1b)



1b

Colorless oil (0.62 g, 53% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.39 (m, 3H), 7.28–7.22 (m, 1H), 7.22–7.09 (m, 3H), 4.53 (s, 2H), 2.43 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 246.6 Hz), 141.0, 138.7, 136.3 (d, J = 3.4 Hz), 132.2, 131.1, 130.8, 130.7 (d, J = 5.9 Hz), 128.9, 115.2 (d, J = 21.2 Hz), 44.5, 21.2; IR (neat): ν_{max} 2925, 1611, 1513, 1495, 1445, 1224, 1158, 1093, 1015, 879, 839, 752, 670 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{12}ClF$ 234.0612; Found 234.0604.

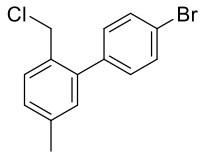
4'-Chloro-2-(chloromethyl)-5-methyl-1,1'-biphenyl (1c)



1c

White solid (0.76 g, 61% yield), M. p. = 60-61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.43 (m, 3H), 7.42–7.34 (m, 2H), 7.26–7.22 (m, 1H), 7.10 (d, J = 1.9 Hz, 1H), 4.51 (s, 2H), 2.42 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 140.8, 138.8, 138.7, 133.6, 132.0, 131.0, 130.7, 130.4, 129.0, 128.5, 44.4, 21.2; IR (KBr): ν_{max} 2924, 1646, 1488, 1263, 1091, 1014, 833, 754, 715, 674 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{12}Cl_2$ 250.0316; Found 250.0309.

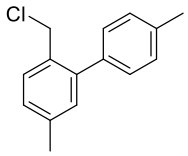
4'-Bromo-2-(chloromethyl)-5-methyl-1,1'-biphenyl (1d)



1d

White solid (0.94 g, 64% yield), M. p. = 70-71 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.43 (m, 2H), 7.36–7.31 (m, 1H), 7.25–7.18 (m, 2H), 7.15–7.10 (m, 1H), 6.98 (d, J = 1.9 Hz, 1H), 4.38 (s, 2H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.8, 139.2, 138.7, 132.0, 131.4, 130.84, 130.82, 130.7, 129.1, 121.7, 44.3, 21.2; IR (KBr): ν_{max} 2923, 2852, 1642, 1488, 1378, 1262, 1183, 1073, 1010, 828, 741, 712, 669 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{12}BrCl$ 293.9811; Found 293.9804.

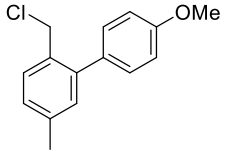
2-(Chloromethyl)-4',5-dimethyl-1,1'-biphenyl (1e)



1e

Colorless oil (0.62 g, 54% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.39 (m, 1H), 7.33–7.27 (m, 2H), 7.26–7.21 (m, 2H), 7.19–7.15 (m, 1H), 7.08 (s, 1H), 4.51 (s, 2H), 2.41 (s, 3H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.0, 138.4, 137.4, 137.1, 132.1, 131.1, 130.5, 129.0, 129.0, 128.5, 44.6, 21.2; IR (neat): ν_{max} 2922, 1610, 1496, 1445, 1378, 1263, 1184, 1110, 1020, 821, 750, 718, 669 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{15}Cl$ 230.0862; Found 230.0854.

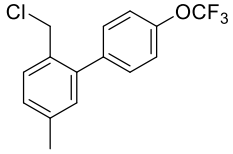
2-(Chloromethyl)-4'-methoxy-5-methyl-1,1'-biphenyl (1f)



1f

White solid (0.76 g, 62% yield), M. p. = 69-70 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.39 (m, 1H), 7.39–7.32 (m, 2H),7.22–7.15 (m, 1H), 7.12 (s, 1H), 7.03–6.94 (m, 2H), 4.53 (s, 2H), 3.87 (s, 3H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.0, 141.7, 138.5, 132.7, 132.2, 131.2, 130.6, 130.2, 128.4, 113.7, 55.3, 44.7, 21.2; IR (KBr): ν_{max} 2925, 1609, 1516, 1496, 1462, 1377, 1245, 1178, 1031, 834, 755, 669 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{15}ClO$ 246.0811; Found 246.0805.

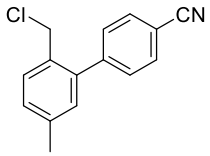
2-(Chloromethyl)-5-methyl-4'-(trifluoromethoxy)-1,1'-biphenyl (1g)



1g

Colorless oil (0.89 g, 59% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.44 (m, 3H), 7.39–7.31 (m, 2H), 7.30–7.23 (m, 1H), 7.14 (s, 1H), 4.53 (s, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.7, 140.6, 139.0, 138.8, 132.1, 131.0, 130.8, 130.6, 129.2, 120.7, 120.6 (q, J = 257.7 Hz) 44.3, 21.2; IR (neat): ν_{max} 2925, 1611, 1513, 1494, 1258, 1104, 1018, 853, 825, 757, 674 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{12}ClF_3O$ 300.0529; Found 300.0520.

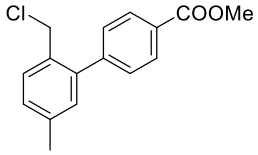
2'-(Chloromethyl)-5'-methyl-[1,1'-biphenyl]-4-carbonitrile (1h)



1h

White solid (0.72 g, 60% yield), M. p. = 84-85 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.68 (m, 2H), 7.67–7.52 (m, 2H), 7.50–7.39 (m, 1H), 7.35–7.20 (m, 1H), 7.16–6.99 (m, 1H), 4.46 (s, 2H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.2, 140.1, 139.0, 132.1, 131.9, 131.0, 130.7, 130.0, 129.8, 118.8, 111.4, 44.1, 21.2; IR (KBr): ν_{max} 2924, 2228, 1607, 1493, 1458, 1378, 1266, 1019, 844, 755, 725, 672 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{12}ClN$ 241.0658; Found 241.0649.

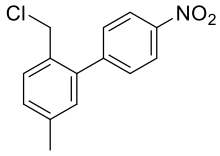
Methyl 2'-(chloromethyl)-5'-methyl-[1,1'-biphenyl]-4-carboxylate (1i)



1i

White solid (0.78 g, 57% yield), M. p. = 75-76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26–8.03 (m, 2H), 7.67–7.37 (m, 2H), 7.33–7.18 (m, 1H), 7.18–7.02 (m, 1H), 7.16–7.09 (m, 1H), 4.50 (s, 2H), 3.98 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.9, 145.1, 141.0, 138.7, 132.0, 130.8, 130.7, 129.6, 129.3, 129.2, 52.2, 44.2, 21.2; IR (KBr): ν_{max} 2924, 1724, 1609, 1435, 1279, 1180, 1112, 1018, 860, 824, 782, 744, 707, 670 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{15}ClO_2$ 274.0761; Found 274.0753.

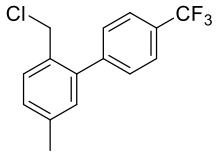
2-(Chloromethyl)-5-methyl-4'-nitro-1,1'-biphenyl (1j)



1j

White solid (0.72 g, 55% yield), M. p. = 65-66 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39–8.22 (m, 2H), 7.67–7.61 (m, 2H), 7.50–7.45 (m, 1H), 7.32–7.27 (m, 1H), 7.14–7.10 (m, 1H), 4.48 (s, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.3, 147.2, 139.8, 139.1, 131.9, 131.0, 130.6, 130.1, 129.9, 123.6, 44.0, 21.2; IR (KBr): ν_{max} 2958, 2924, 1639, 1519, 1456, 1348, 1263, 1106, 1014, 849, 699 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{12}ClNO_2$ 261.0557; Found 261.0549.

2-(Chloromethyl)-5-methyl-4'-(trifluoromethyl)-1,1'-biphenyl (1k)

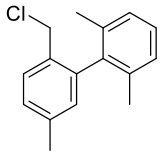


1k

Colorless oil (0.82 g, 58% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.74 (m, 2H), 7.64–7.58 (m, 2H), 7.52–7.48 (m, 1H), 7.30 (dd, J = 8.0, 1.9 Hz, 1H), 7.15 (d, J = 1.9

Hz, 1H), 4.52 (s, 2H), 2.46 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.1, 140.6, 138.9, 132.0, 130.9, 129.7 (q, J = 32.4 Hz), 129.6, 129.5, 125.3 (q, J = 3.8 Hz), 124.3 (q, J = 272.0 Hz), 44.2, 21.2; IR (neat): ν_{max} 2924, 1619, 1450, 1325, 1262, 1167, 1128, 1069, 1017, 847 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{12}ClF_3$ 284.0580; Found 284.0572.

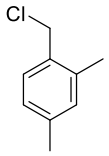
2-(Chloromethyl)-2',5,6'-trimethyl-1,1'-biphenyl (1l)



1l

White solid (0.76 g, 62% yield), M. p. = 58-59 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.44 (m, 1H), 7.21–7.15 (m, 2H), 7.12–7.09 (m, 2H), 6.88 (s, 1H), 4.24 (s, 2H), 2.36 (s, 3H), 1.97 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 140.4, 139.3, 138.8, 136.2, 132.1, 130.1, 130.0, 128.6, 127.5, 127.4, 44.1, 21.2, 20.7; IR (KBr): ν_{max} 2955, 2923, 2853, 1638, 1460, 1377, 1263, 1163, 1029, 821, 768, 676 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{17}Cl$ 244.1019; Found 244.1014.

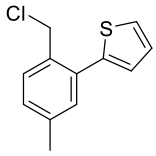
1-(Chloromethyl)-2,4-dimethylbenzene (1m)[7]



1m

Colorless oil (0.63 g, 82% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.22 (m, 1H), 7.09–7.00 (m, 2H), 4.64 (s, 2H), 2.44 (s, 3H), 2.36 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 138.9, 137.1, 132.6, 131.6, 129.8, 127.0, 44.9, 21.1, 18.7;

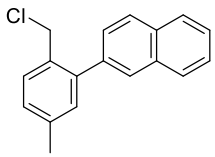
2-(2-(Chloromethyl)-5-methylphenyl)thiophene (1n)



1n

White solid (0.72 g, 65% yield), M. p. = 63-64 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.38 (m, 3H), 7.33–7.26 (m, 1H), 7.26–7.16 (m, 2H), 4.61 (s, 2H), 2.41 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 140.5, 138.7, 136.7, 132.2, 130.9, 130.8, 128.9, 128.8, 125.6, 123.2, 44.9, 21.2; IR (KBr): ν_{max} 2923, 1611, 1445, 1377, 1263, 847, 824, 790, 744, 668 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_{11}ClS$ 222.0270; Found 222.0261.

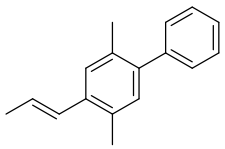
2-(2-(Chloromethyl)-5-methylphenyl)naphthalene (1o)



1o

White solid (0.73 g, 55% yield), M. p. = 66-67 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.83 (m, 4H), 7.55–7.42 (m, 4H), 7.23–7.16 (m, 2H), 4.52 (s, 2H), 2.38 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 142.0, 138.6, 137.9, 133.3, 132.6, 132.4, 131.3, 130.7, 128.9, 128.3, 128.1, 128.0, 127.8, 127.5, 126.5, 126.3, 44.7, 21.3; IR (KBr): ν_{max} 3053, 2922, 1609, 1496, 1444, 1378, 1262, 891, 859, 820, 740 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{15}Cl$ 266.0862; Found 266.0857.

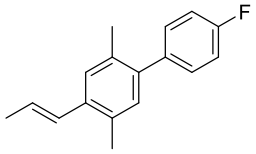
(E)-2,5-Dimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2a)



2a

Yellow solid (40.0 mg, 60% yield), M. p. = 59-60 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.39 (m, 2H), 7.37–7.33 (m, 4H), 7.05 (s, 1H), 6.63 (dd, J = 15.8, 2.0 Hz, 1H), 6.19 (dq, J = 15.4, 6.5 Hz, 1H), 2.36 (s, 3H), 2.28 (s, 3H), 1.96 (dd, J = 6.7, 1.7 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 141.9, 140.4, 136.0, 132.7, 132.2, 131.7, 129.2, 128.6, 128.1, 127.4, 126.9, 126.7, 20.1, 19.3, 18.9; IR (KBr): ν_{max} 2925, 1618, 1447, 1325, 1166, 1127, 1068, 963, 847, 696 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{18}$ 222.1409; Found 222.1402.

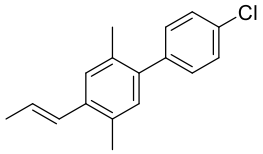
(E)-4'-Fluoro-2,5-dimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2b)



2b

Brown oil (43.2 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.27 (m, 3H), 7.18–7.07 (m, 2H), 7.01 (s, 1H), 6.63 (dd, J = 15.6, 1.8 Hz, 1H), 6.19 (dq, J = 15.6, 6.6 Hz, 1H), 2.36 (s, 3H), 2.25 (s, 3H), 1.96 (dd, J = 6.6, 1.8 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 161.9 (d, J = 245.2 Hz), 139.3, 137.8 (d, J = 3.2 Hz), 136.1, 132.7, 132.3, 131.7, 130.7 (d, J = 7.9 Hz), 128.4, 127.4, 127.0, 114.9 (d, J = 21.2 Hz), 20.0, 19.3, 18.9.; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.34; IR (neat): ν_{max} 2925, 1652, 1605, 1509, 1489, 1447, 1222, 1157, 963, 839, 699 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{17}F$ 240.1314; Found 240.1308.

(E)-4'-Chloro-2,5-dimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2c)

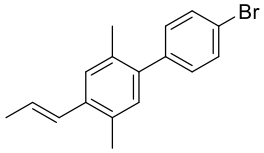


2c

White solid (44.6 mg, 58% yield), M. p. = 60-61 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.33 (m, 2H), 7.29 (s, 1H), 7.26–7.20 (m, 2H), 6.96 (s, 1H), 6.58 (dd, J = 15.7, 1.9 Hz, 1H), 6.15 (dq, J = 15.6, 6.6 Hz, 1H), 2.31 (s, 3H), 2.21 (s, 3H), 1.92 (dd, J = 6.6, 1.8 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 140.3, 139.1, 136.3, 132.7, 132.6, 132.3, 131.5, 130.5, 128.5, 128.2, 127.5, 127.1, 20.0, 19.2, 18.8; IR (KBr): ν_{max}

2922, 2069, 1652, 1483, 1445, 1266, 1090, 1013, 962, 834, 747, 692 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{17}Cl$ 256.1019; Found 256.1012.

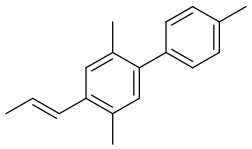
(E)-4'-Bromo-2,5-dimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2d)



2d

White solid (51.3 mg, 57% yield); M. p. = 73-74 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58–7.51 (m, 2H), 7.33 (s, 1H), 7.24–7.18 (m, 2H), 6.99 (s, 1H), 6.61 (dd, J = 15.6, 1.8 Hz, 1H), 6.19 (dq, J = 15.6, 6.6 Hz, 1H), 2.34 (s, 3H), 2.25 (s, 3H), 1.95 (dd, J = 6.6, 1.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.7, 139.0, 136.3, 132.5, 132.3, 131.4, 131.2, 130.9, 128.4, 127.5, 127.2, 120.8, 20.0, 19.2, 18.9; IR (KBr): ν_{max} 2925, 1646, 1480, 1442, 1267, 1070, 1011, 962, 698 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{17}Br$ 300.0514; Found 300.0506.

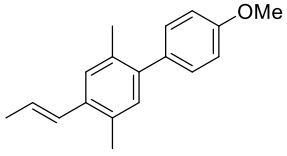
(E)-2,4',5-Trimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2e)



2e

White solid (43.9 mg, 62% yield); M. p. = 59-60 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.25–7.19 (m, 4H), 7.02 (s, 1H), 6.62 (dd, J = 15.7, 2.0 Hz, 1H), 6.17 (dq, J = 15.6, 6.6 Hz, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 2.26 (s, 3H), 1.94 (dd, J = 6.6, 1.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.3, 138.9, 136.2, 135.8, 132.7, 132.1, 131.7, 129.1, 128.7, 128.6, 127.4, 126.8, 21.2, 20.1, 19.3, 18.9; IR (KBr): ν_{max} 3020, 2922, 2853, 1650, 1489, 1446, 1377, 962, 889, 815 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{20}$ 236.1565; Found 236.1556.

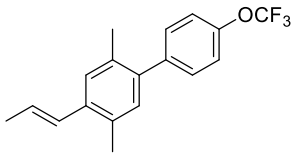
(E)-4'-Methoxy-2,5-dimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2f)



2f

Brown oil (31.8 mg, 42% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.26–7.22 (m, 2H), 6.99 (s, 1H), 6.96–6.90 (m, 2H), 6.58 (dd, J = 15.5, 1.8 Hz, 1H), 6.14 (dq, J = 15.6, 6.6 Hz, 1H), 3.84 (s, 3H), 2.31 (s, 3H), 2.24 (s, 3H), 1.91 (dd, J = 6.6, 1.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.4, 140.0, 135.7, 134.3, 132.8, 132.2, 131.8, 130.2, 128.6, 127.4, 126.7, 113.5, 113.4, 55.3, 20.1, 19.3, 18.9; IR (neat): ν_{max} 2954, 1609, 1518, 1489, 1460, 1287, 1247, 1175, 1038, 965, 835 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{20}O$ 252.1514; Found 252.1505.

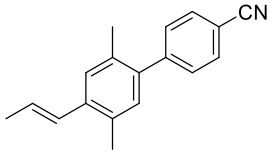
(E)-2,5-Dimethyl-4-(prop-1-en-1-yl)-4'-(trifluoromethoxy)-1,1'-biphenyl (2g)



2g

Brown oil (50.5 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.29 (m, 3H), 7.25–7.21 (m, 2H), 6.98 (s, 1H), 6.59 (dd, J = 15.6, 1.9 Hz, 1H), 6.16 (dq, J = 15.6, 6.6 Hz, 1H), 2.32 (s, 3H), 2.22 (s, 3H), 1.92 (dd, J = 6.6, 1.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.1, 140.6, 138.9, 136.4, 132.6, 132.3, 131.6, 130.5, 128.4, 127.5, 127.2, 120.5, 19.9, 19.2, 18.8.; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.79; IR (neat): ν_{max} 2923, 2855, 1636, 1490, 1444, 1258, 1222, 1165, 964, 750, 696 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{17}F_3O$ 306.1231; Found 306.1222.

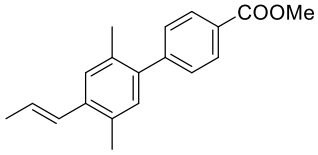
(E)-2',5'-Dimethyl-4'-(prop-1-en-1-yl)-[1,1'-biphenyl]-4-carbonitrile (2h)



2h

White solid (25.9 mg, 35% yield); M. p. = 82-83 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.68 (m, 2H), 7.50–7.42 (m, 2H), 7.35 (s, 1H), 7.00 (s, 1H), 6.62 (dd, J = 15.6, 2.2 Hz, 1H), 6.21 (dq, J = 13.1, 6.3 Hz, 1H), 2.36 (s, 3H), 2.25 (s, 3H), 1.96 (dd, J = 6.7, 1.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.7, 138.3, 137.0, 132.6, 132.4, 131.9, 131.3, 130.0, 128.2, 127.7, 119.1, 110.5, 19.9, 19.3, 18.9; IR (KBr): ν_{max} 2226, 1652, 1488, 1446, 1390, 1262, 1035, 964, 688 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{17}N$ 247.1361; Found 247.1354.

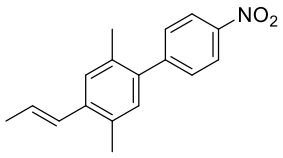
Methyl (E)-2',5'-Dimethyl-4'-(prop-1-en-1-yl)-[1,1'-biphenyl]-4-carboxylate (2i)



2i

White solid (49.6 mg, 59% yield); M. p. = 74-75 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.3 Hz, 2H), 7.34–7.29 (m, 2H), 7.24 (s, 1H), 6.92 (s, 1H), 6.51 (dd, J = 15.6, 1.8 Hz, 1H), 6.09 (dq, J = 15.7, 6.6 Hz, 1H), 3.86 (s, 3H), 2.25 (s, 3H), 2.15 (s, 3H), 1.85 (dd, J = 6.6, 1.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.1, 146.7, 139.2, 136.6, 132.5, 132.4, 131.4, 129.5, 129.4, 129.3, 128.4, 127.6, 127.3, 52.1, 20.0, 19.2, 18.9.; IR (KBr): ν_{max} 2950, 1719, 1608, 1435, 1276, 1178, 1102, 963, 860, 777, 712, 701 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{20}O_2$ 280.1463; Found 280.1455.

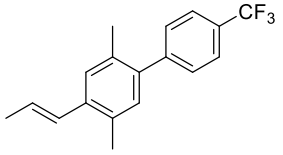
(E)-2,5-Dimethyl-4'-nitro-4-(prop-1-en-1-yl)-1,1'-biphenyl (2j)



2j

Yellow solid (38% yield); M. p. = 63-64 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33–8.24 (m, 2H), 7.54–7.47 (m, 2H), 7.37 (s, 1H), 7.02 (s, 1H), 6.62 (dd, J = 15.6, 1.8 Hz, 1H), 6.22 (dq, J = 15.6, 6.6 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 1.96 (dd, J = 6.6, 1.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.8, 146.7, 137.9, 137.2, 132.6, 132.4, 131.3, 130.1, 128.2, 127.8, 127.7, 123.4, 20.0, 19.3, 18.9; IR (KBr): ν_{max} 2923, 2852, 1646, 1515, 1484, 1447, 1343, 1106, 964, 854, 703 cm^{-1}; HRMS (EI) m/z: [M]$^{+}$ Calcd for $C_{17}H_{17}NO_2$ 267.1259; Found 267.1253.

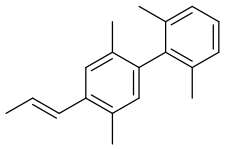
(E)-2,5-Dimethyl-4-(prop-1-en-1-yl)-4'-(trifluoromethyl)-1,1'-biphenyl (2k)



2k

Brown oil (37.4 mg, 43% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.35 (s, 1H), 7.01 (s, 1H), 6.62 (dd, J = 15.6, 1.8 Hz, 1H), 6.20 (dq, J = 15.6, 6.6 Hz, 1H), 2.36 (s, 3H), 2.26 (s, 3H), 1.96 (dd, J = 6.6, 1.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.6, 138.9, 136.7, 132.6, 132.4, 131.5, 129.5, 128.8 (q, J = 32.4 Hz), 128.4, 127.6, 127.4, 125.0 (q, J = 3.8 Hz), 124.37 (q, J = 272.1 Hz), 77.3, 77.0, 76.7, 19.9, 19.2, 18.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.33; IR (neat): ν_{max} 2956, 2921, 1635, 1485, 1443, 1377, 1261, 1011, 963, 698 cm^{-1}; HRMS (EI) m/z: [M]$^{+}$ Calcd for $C_{18}H_{17}F_3$ 290.1282; Found 290.1275.

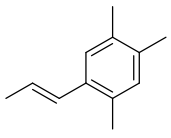
(E)-2,2',5,6'-Tetramethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2l)



2l

Brown oil (45.8 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.28 (s, 1H), 7.21–7.07 (m, 3H), 6.81 (s, 1H), 6.65 (dd, J = 15.6, 2.0 Hz, 1H), 6.21 (dq, J = 15.7, 6.5 Hz, 1H), 2.34 (s, 3H), 1.99 (s, 6H), 1.95 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.1, 139.1, 136.0, 135.4, 133.0, 132.3, 130.6, 128.7, 127.1, 126.8, 126.2, 77.2, 20.4, 19.4, 19.0, 18.9; IR (neat): ν_{max} 3018, 2922, 2854, 1650, 1462, 1377, 1093, 1032, 963, 885, 768 cm^{-1}; HRMS (EI) m/z: [M]$^{+}$ Calcd for $C_{19}H_{22}$ 250.1722; Found 250.1714.

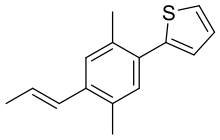
(E)-1,2,4-Trimethyl-5-(prop-1-en-1-yl)benzene (2m)



2m

Brown oil (26.9 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 1H), 6.89 (s, 1H), 6.53 (dd, J = 15.6, 1.9 Hz, 1H), 6.06 (dq, J = 15.6, 6.6 Hz, 1H), 2.26 (s, 3H), 2.21 (s, 3H), 2.20 (s, 3H), 1.88 (dd, J = 6.6, 1.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.0, 134.4, 133.9, 132.1, 131.5, 128.7, 126.7, 125.8, 19.31, 19.27, 19.1, 18.8. IR (neat): ν_{max} 2919, 2862, 1647, 1502, 1459, 1377, 963, 870, 840, 803 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{12}H_{16}$ 160.1252; Found 160.1243.

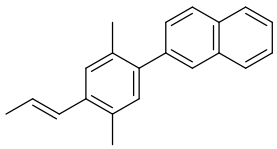
(E)-2-(2,5-Dimethyl-4-(prop-1-en-1-yl)phenyl)thiophene (2n)



2n

Brown oil (39.0 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.25 (m, 1H), 7.22 (s, 1H), 7.14–7.10 (m, 1H), 7.09–7.06 (m, 1H), 7.01 (s, 1H), 6.50 (dd, *J* = 15.6, 1.8 Hz, 1H), 6.07 (dq, *J* = 15.8, 6.7 Hz, 1H), 2.23 (d, *J* = 3.2 Hz, 6H), 1.84 (dd, *J* = 6.6, 1.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.1, 136.0, 134.9, 133.0, 132.2, 131.5, 129.0, 128.5, 127.5, 126.9, 124.8, 122.3, 20.4, 19.2, 18.9; IR (neat): ν_{max} 2923, 1691, 1607, 1448, 1377, 1080, 1035, 964, 889, 857, 789, 723 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{15}H_{16}S$ 228.0973; Found 228.0966.

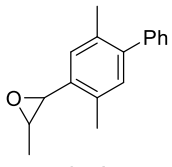
(E)-2-(2,5-Dimethyl-4-(prop-1-en-1-yl)phenyl)naphthalene (2o)



2o

Brown oil (50.6 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.82 (m, 3H), 7.76 (s, 1H), 7.50–7.44 (m, 3H), 7.34 (s, 1H), 7.10 (s, 1H), 6.62 (dd, *J* = 15.6, 1.8 Hz, 1H), 6.17 (dq, *J* = 15.6, 6.6 Hz, 1H), 2.34 (s, 3H), 2.27 (s, 3H), 1.93 (dd, *J* = 6.6, 1.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.3, 139.5, 136.1, 133.4, 132.9, 132.3, 131.9, 128.6, 128.0, 127.8, 127.73, 127.69, 127.5, 127.4, 127.0, 126.1, 125.8, 77.3, 20.1, 19.3, 18.9; IR (neat): ν_{max} 3053, 3016, 2923, 2852, 1631, 1495, 1445, 1377, 1267, 1131, 963, 857, 820, 749 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{21}H_{20}$ 272.1565; Found 272.1558.

2-(2,5-Dimethyl-[1,1'-biphenyl]-4-yl)-3-methyloxirane (2a-1)

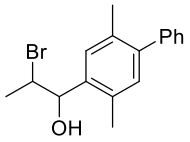


2a-1

White solid (35.0 mg, 49% yield); M. p. = 68-69 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.38 (d, *J* = 6.9 Hz, 1H), 7.39–7.36 (m, 2H), 7.09 (s, 1H), 7.02 (s, 1H), 3.78 (s, 1H), 2.98 (qd, *J* = 5.3, 2.2 Hz, 1H), 2.35 (s, 3H), 2.26 (s, 3H), 1.53 (d, *J* = 5.1 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 142.2, 141.9, 136.6, 135.2, 130.02, 129.97, 129.4, 128.1, 126.8, 124.1, 58.2, 58.0, 21.0, 18.0, 15.7; IR (neat): ν_{max} 2957,

2924, 2854, 1642, 1466, 1377, 1260, 1073, 1033, 860, 774, 702 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{18}O$ 238.1358; Found 238.1351.

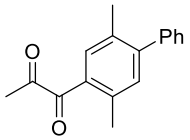
2-Bromo-1-(2,5-dimethyl-[1,1'-biphenyl]-4-yl)propan-1-ol (2a-2)



2a-2

Orange oil (61.1 mg, 64% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.47–7.40 (m, 3H), 7.39–7.35 (m, 1H), 7.35–7.31 (m, 2H), 7.06 (s, 1H), 5.29 (t, J = 3.2 Hz, 1H), 4.46 (qd, J = 6.8, 3.5 Hz, 1H), 2.47 (d, J = 3.0 Hz, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 1.70 (d, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.54, 141.46, 136.7, 133.1, 132.0, 129.1, 128.1, 127.9, 126.8, 74.4, 54.4, 20.2, 18.8, 18.7; IR (neat): ν_{max} 2931, 1601, 1487, 1444, 1376, 1191, 1127, 1073, 1020, 886, 770, 704 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{19}BrO$ 318.0619; Found 318.0615.

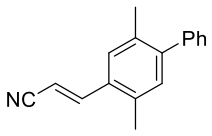
1-(2,5-Dimethyl-[1,1'-biphenyl]-4-yl)propane-1,2-dione (2a-3)



2a-3

Orange oil (28.7 mg, 38% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.38–7.34 (m, 2H), 7.33–7.30 (m, 1H), 7.25–7.23 (m, 1H), 7.23–7.21 (m, 1H), 7.10 (s, 1H), 2.48 (s, 3H), 2.47 (s, 3H), 2.19 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.3, 194.6, 147.1, 140.6, 138.2, 134.0, 133.8, 133.0, 129.8, 128.8, 128.3, 127.6, 26.2, 21.0, 19.9; IR (neat): ν_{max} 2927, 2854, 1708, 1669, 1610, 1542, 1486, 1443, 1187, 1129, 956, 863, 760, 702 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{16}O_2$ 252.1150; Found 252.1145.

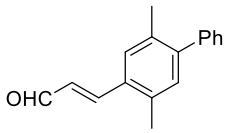
(E)-3-(2,5-Dimethyl-[1,1'-biphenyl]-4-yl)acrylonitrile (2a-4)



2a-4

Orange oil (37.7 mg, 54% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 16.6 Hz, 1H), 7.46–7.39 (m, 2H), 7.38–7.34 (m, 2H), 7.32–7.26 (m, 2H), 7.09 (s, 1H), 5.83 (d, J = 16.5 Hz, 1H), 2.39 (s, 3H), 2.25 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.2, 144.8, 140.8, 134.6, 133.7, 132.5, 131.4, 128.9, 128.2, 127.5, 127.3, 118.6, 96.7, 20.0, 19.0; IR (neat): ν_{max} 3058, 3023, 2954, 2924, 2215, 1602, 1484, 1443, 963, 769, 703 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{15}N$ 233.1204; Found 233.1198.

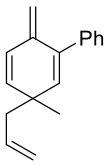
(E)-3-(2,5-Dimethyl-[1,1'-biphenyl]-4-yl)acrylaldehyde (2a-5)



2a-5

Orange oil (46.7 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (d, J = 7.7 Hz, 1H), 7.70 (d, J = 15.8 Hz, 1H), 7.43 (s, 1H), 7.38–7.32 (m, 2H), 7.31–7.27 (m, 1H), 7.26–7.21 (m, 2H), 7.05 (s, 1H), 6.64 (dd, J = 15.8, 7.7 Hz, 1H), 2.40 (s, 3H), 2.20 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.8, 150.1, 144.9, 141.0, 135.4, 133.7, 132.6, 131.7, 129.3, 128.9, 128.8, 128.2, 127.3, 20.0, 19.2; IR (neat): ν_{max} 2924, 1681, 1606, 1485, 1442, 1394, 1283, 1127, 970, 892, 769, 703, 692 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{16}O$ 236.1201; Found 236.1196.

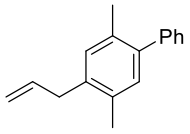
5-Methyl-2-methylene-5-(prop-1-en-1-yl)-2,5-dihydro-1,1'-biphenyl (C)



C

Colorless oil (0.62 g, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.29 (m, 5H), 6.36 (d, J = 9.8 Hz, 1H), 5.86–5.74 (m, 1H), 5.72 (d, J = 9.8 Hz, 1H), 5.67–5.62 (m, 1H), 5.09 (s, 1H), 5.06 (dq, J = 9.2, 1.5 Hz, 1H), 4.98 (s, 1H), 4.87 (s, 1H), 2.26 (s, 2H), 1.23 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.7, 138.6, 137.33, 137.29, 136.2, 134.8, 129.1, 128.0, 127.4, 127.0, 117.2, 112.7, 77.4, 77.1, 76.7, 47.2, 40.2, 28.1; IR (neat): ν_{max} 2926, 1689, 1604, 1488, 1259, 1073, 991, 921, 822, 770, 701; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{18}$ 222.1409; Found 222.1402.

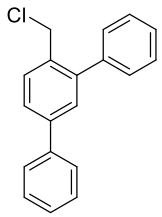
4-Allyl-2,5-dimethyl-1,1'-biphenyl (2a')



2a'

Colorless oil (60 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, J = 7.4 Hz, 2H), 7.31 (d, J = 7.2 Hz, 3H), 7.04 (d, J = 4.3 Hz, 2H), 6.04–5.92 (m, 1H), 5.19–4.98 (m, 2H), 3.38 (d, J = 6.4 Hz, 2H), 2.28 (s, 3H), 2.22 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.0, 139.9, 137.1, 136.7, 133.6, 132.8, 131.7, 131.2, 129.3, 128.0, 126.6, 115.8, 77.4, 77.1, 76.8, 37.5, 19.9, 18.8; IR (neat): ν_{max} 2921, 1637, 1601, 1487, 1442, 1072, 1031, 993, 912, 884, 765, 702; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{18}$ 222.1409; Found 222.1402.

4'-(chloromethyl)-1,1':3',1''-terphenyl (3a)

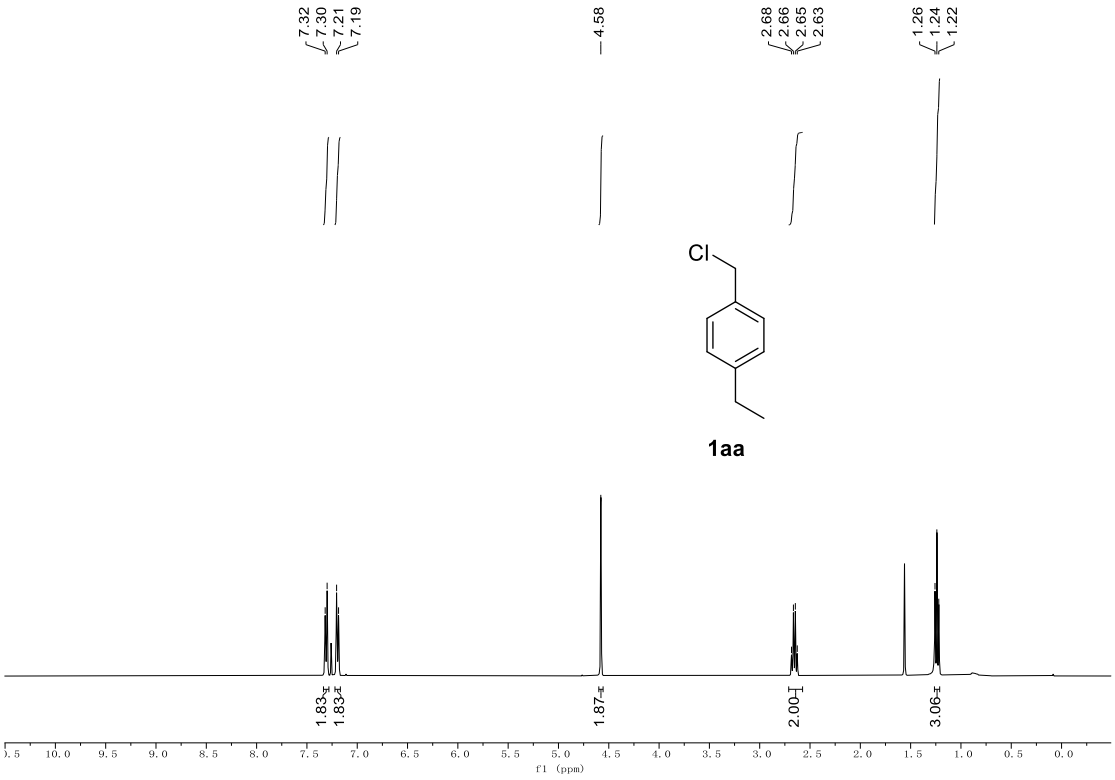


White solid (0.89 g, 64% yield); M. p. = 91-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.62 (m, 4H), 7.56 (s, 1H), 7.53–7.48 (m, 4H), 7.48–7.42 (m, 3H), 7.42–7.35 (m, 1H), 4.61 (s, 2H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 142.5, 141.5, 140.3, 140.2, 133.9, 131.1, 129.2, 129.1, 128.9, 128.4, 127.7, 127.6, 127.2, 126.6, 44.3; IR (neat): ν_{max} 3058, 3028, 1600, 1442, 1263, 1027, 896, 853, 776, 753, 698, 672 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{15}Cl$ 278.0862; Found 278.0857.

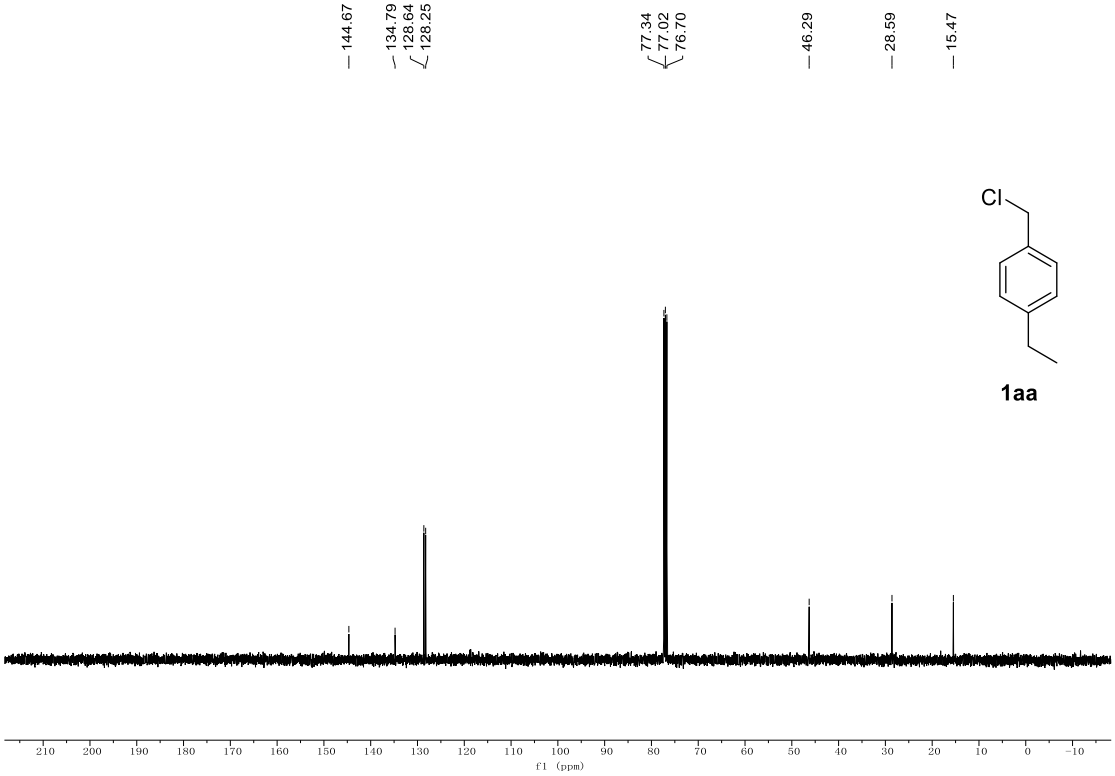
7. Copies of ^{1}H and ^{13}C NMR Spectra

1-(Chloromethyl)-4-ethylbenzene (1aa)

^{1}H NMR, 400 MHz, $CDCl_3$

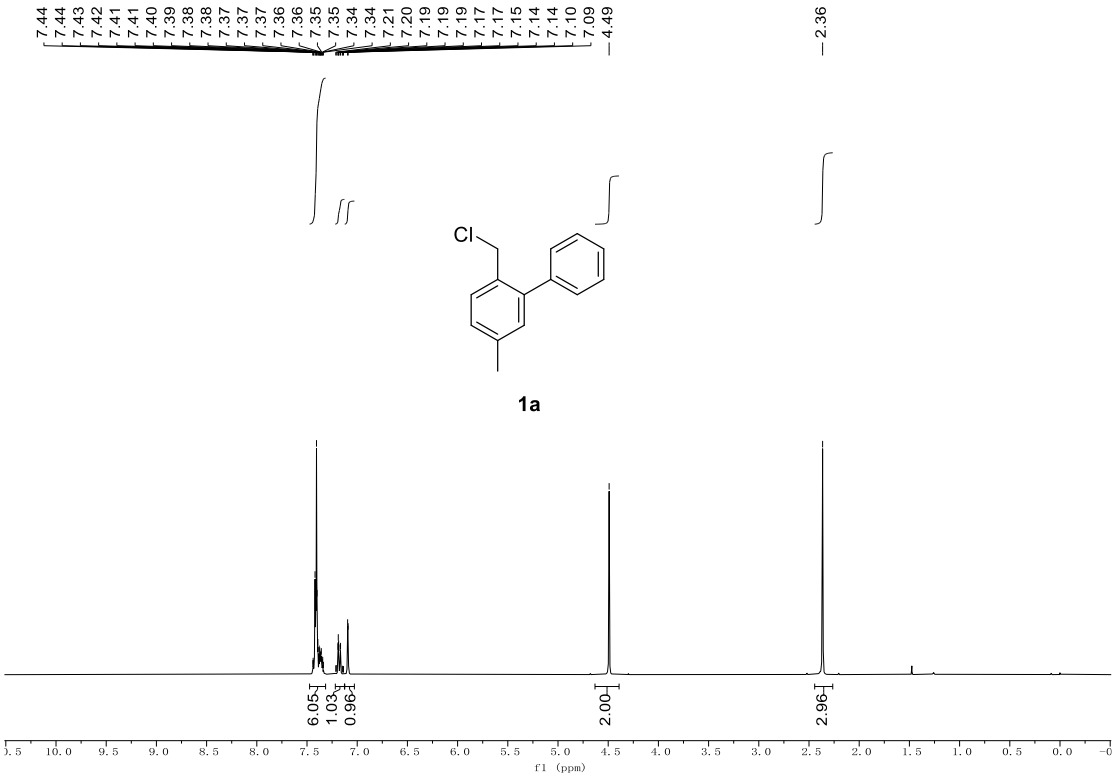


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

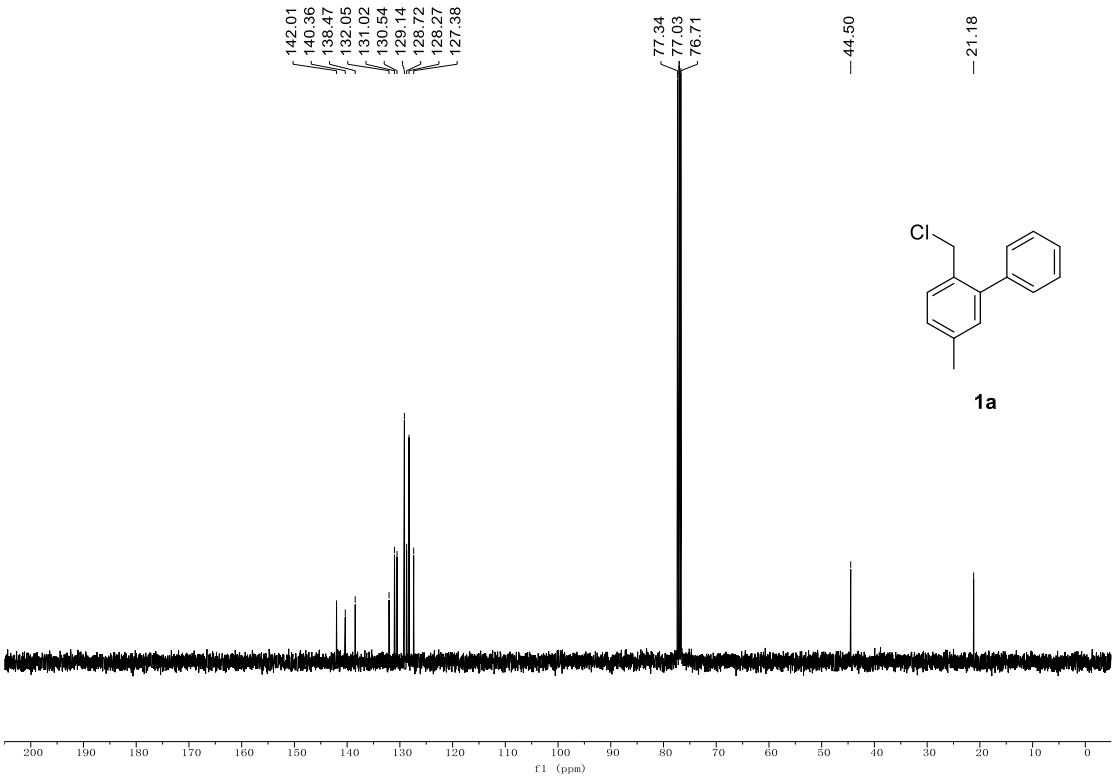


2-(Chloromethyl)-5-methyl-1,1'-biphenyl (1a)

^{1}H NMR, 400 MHz, $CDCl_3$

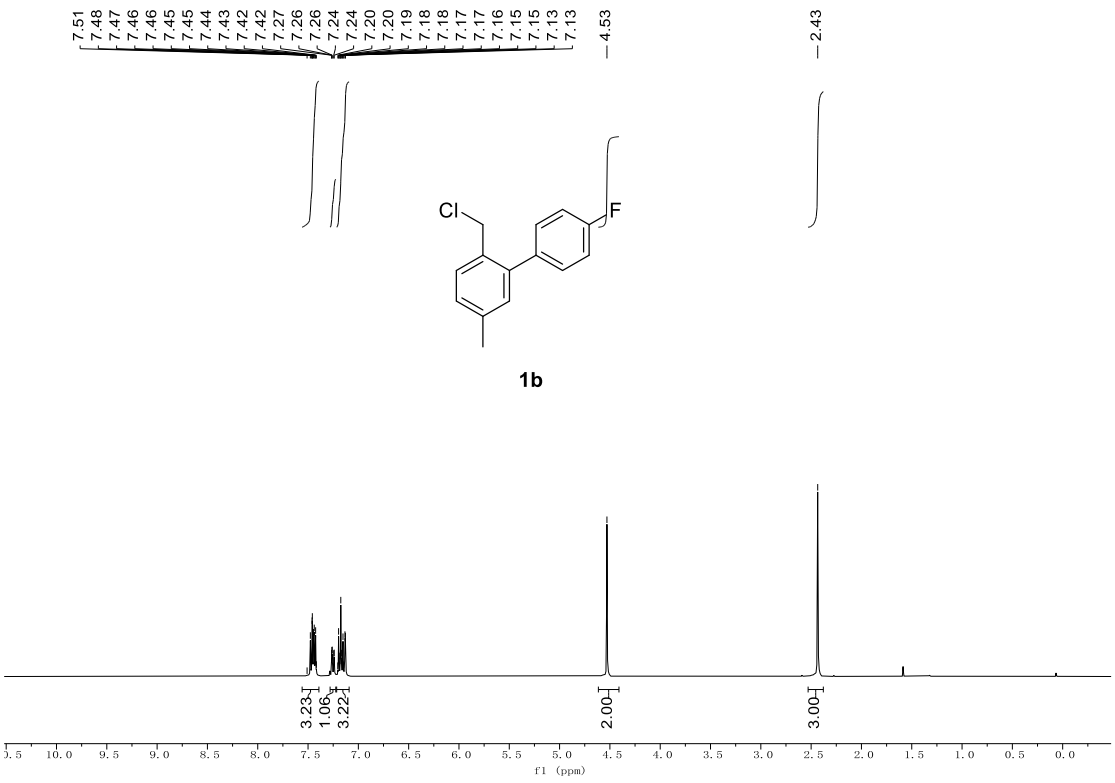


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

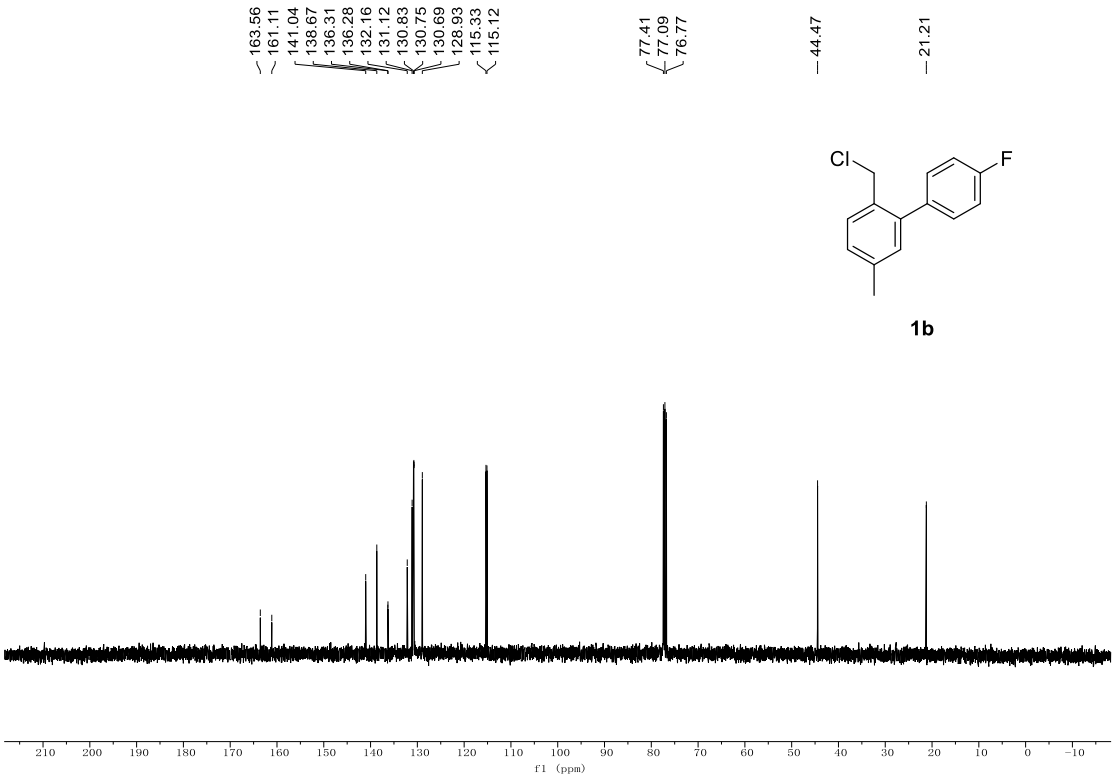


2-(Chloromethyl)-4'-fluoro-5-methyl-1,1'-biphenyl (1b)

^{1}H NMR, 400 MHz, $CDCl_3$

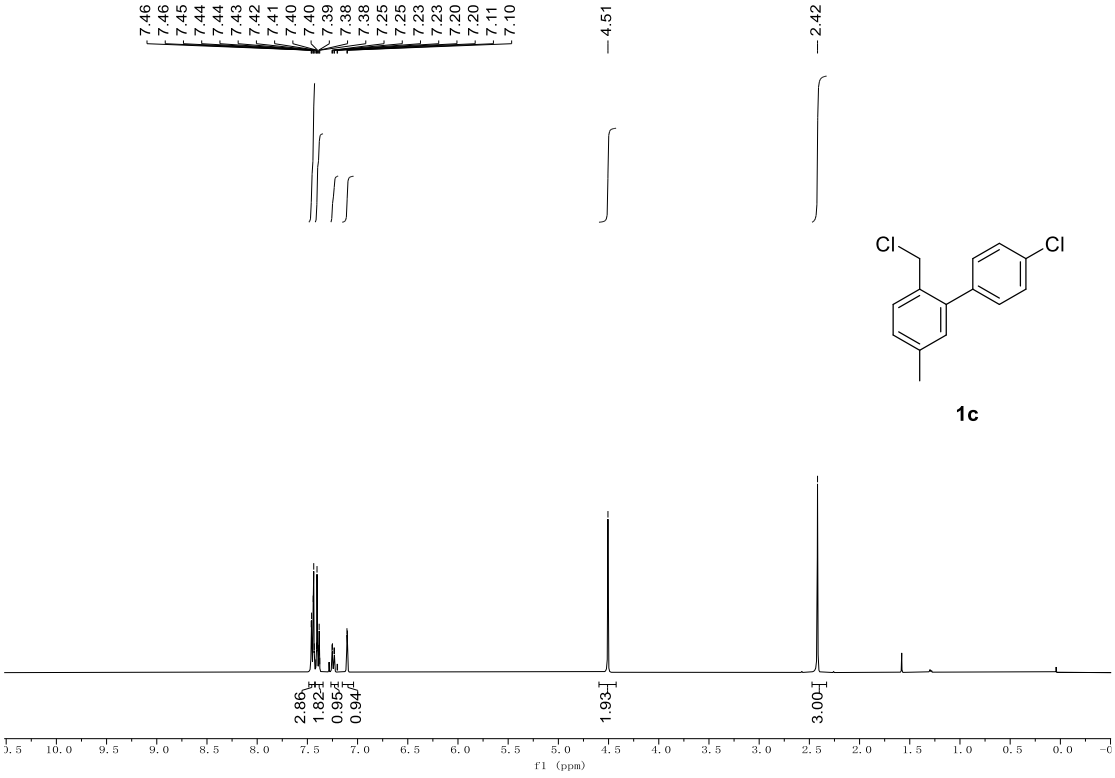


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

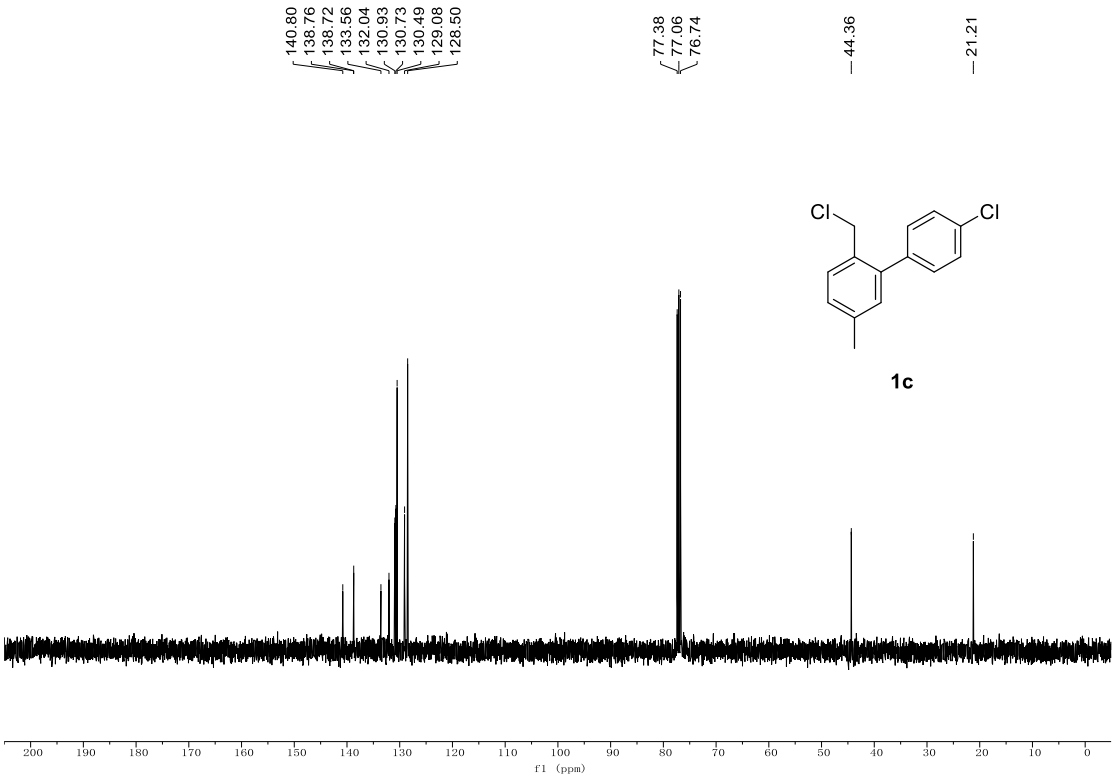


4'-Chloro-2-(chloromethyl)-5-methyl-1,1'-biphenyl (1c)

^{1}H NMR, 400 MHz, $CDCl_3$

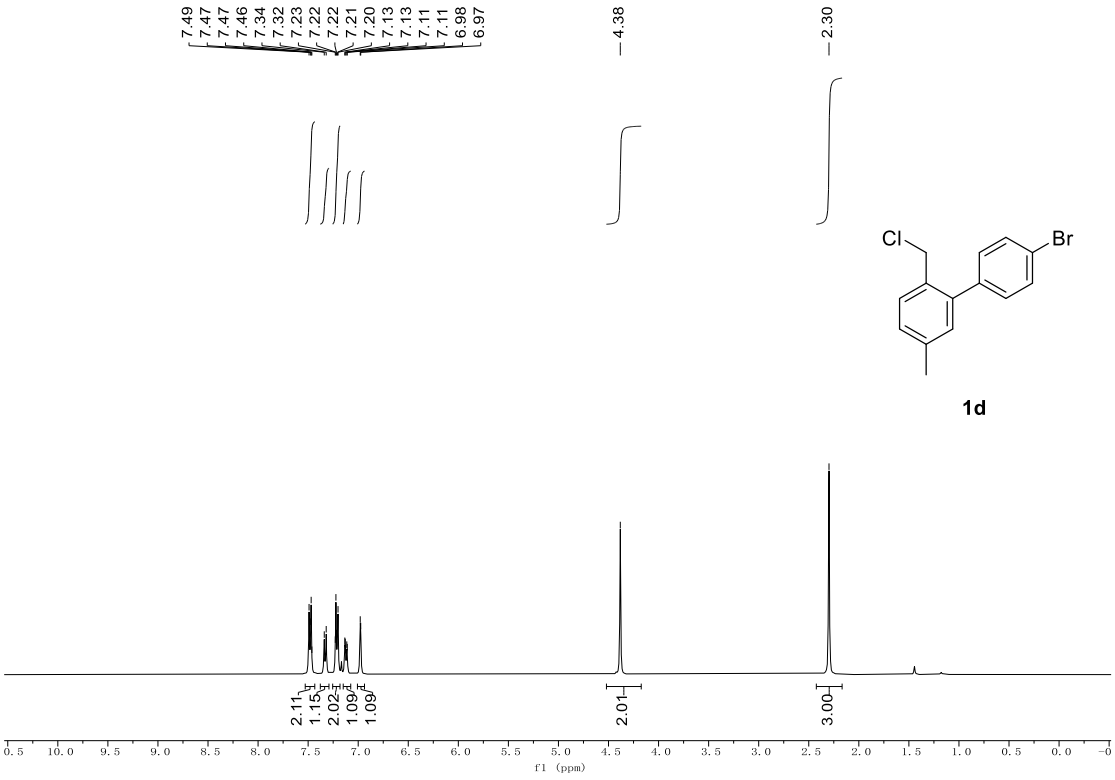


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

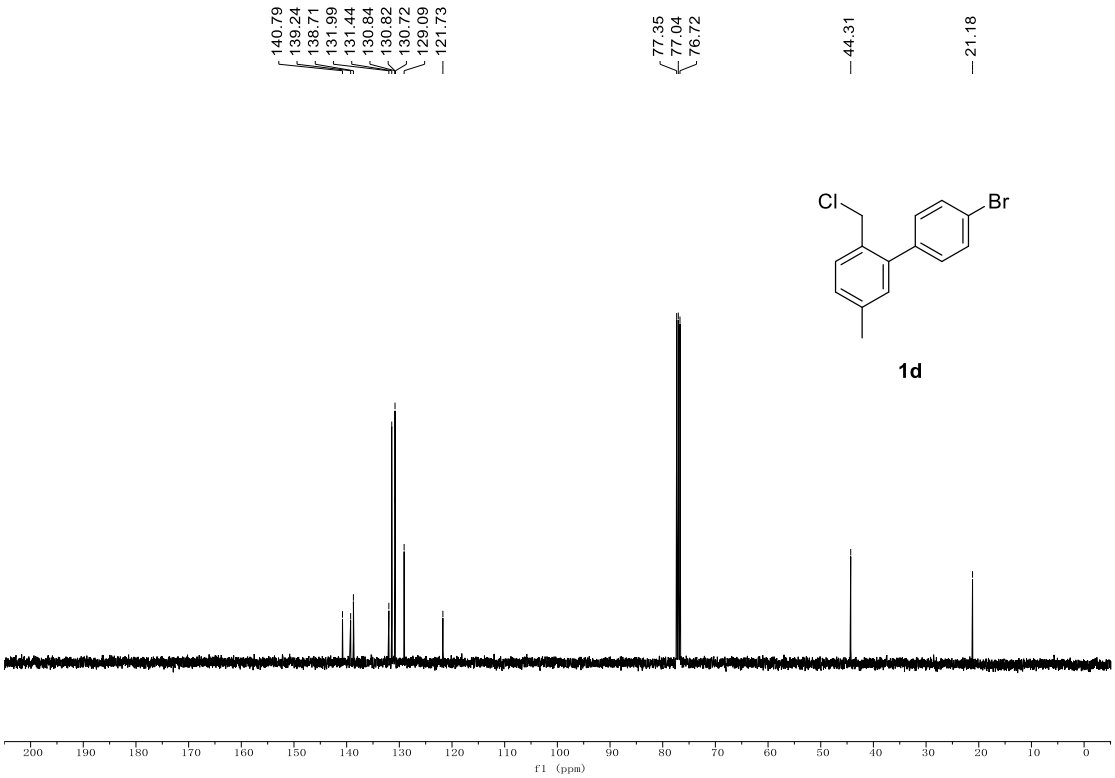


4'-Bromo-2-(chloromethyl)-5-methyl-1,1'-biphenyl (1d)

^{1}H NMR, 400 MHz, $CDCl_3$

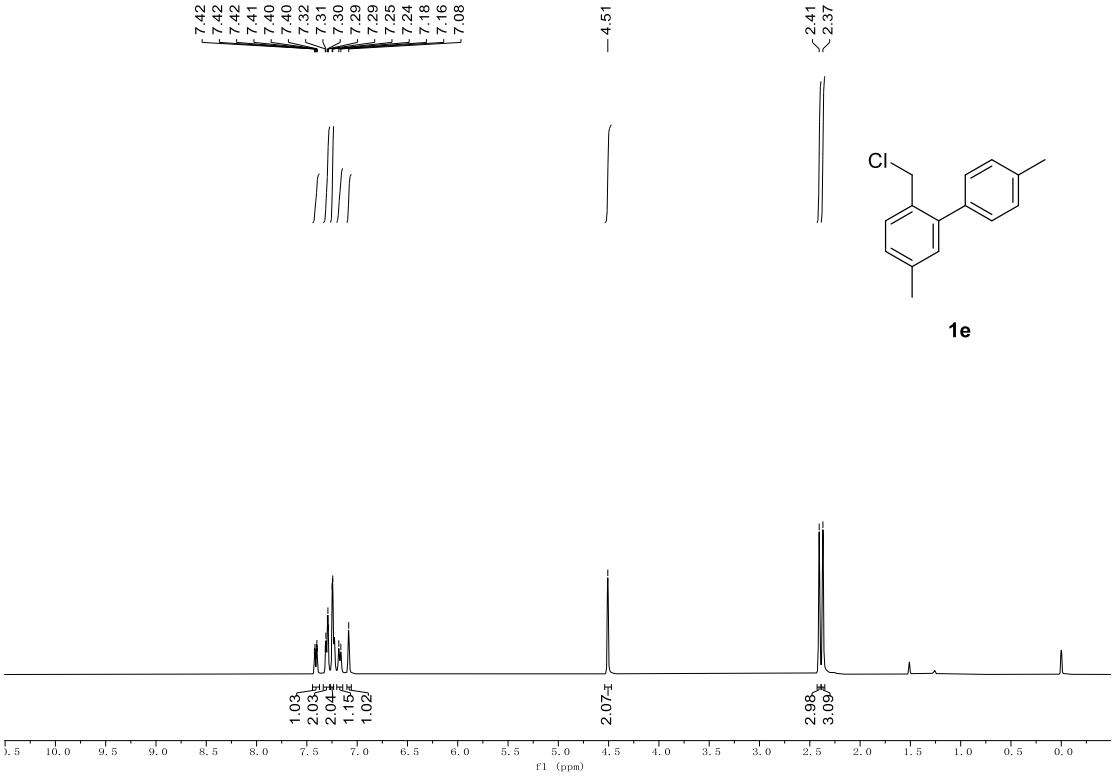


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

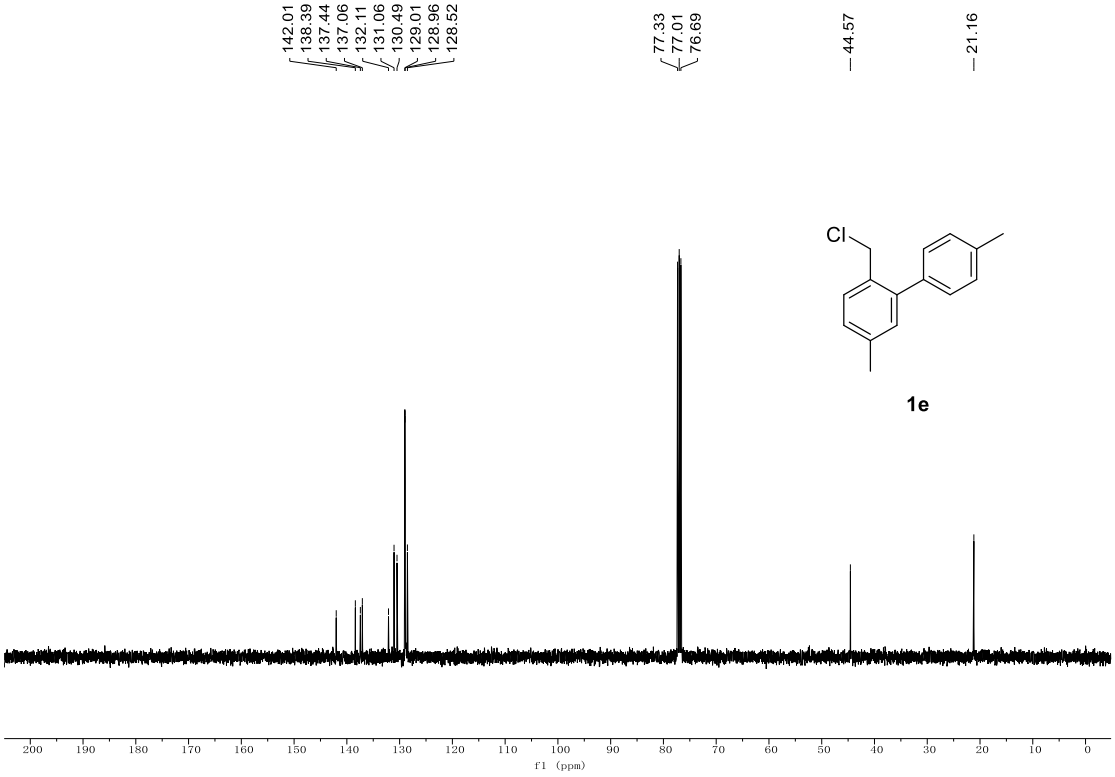


2-(Chloromethyl)-4',5-dimethyl-1,1'-biphenyl (1e)

^{1}H NMR, 400 MHz, $CDCl_3$

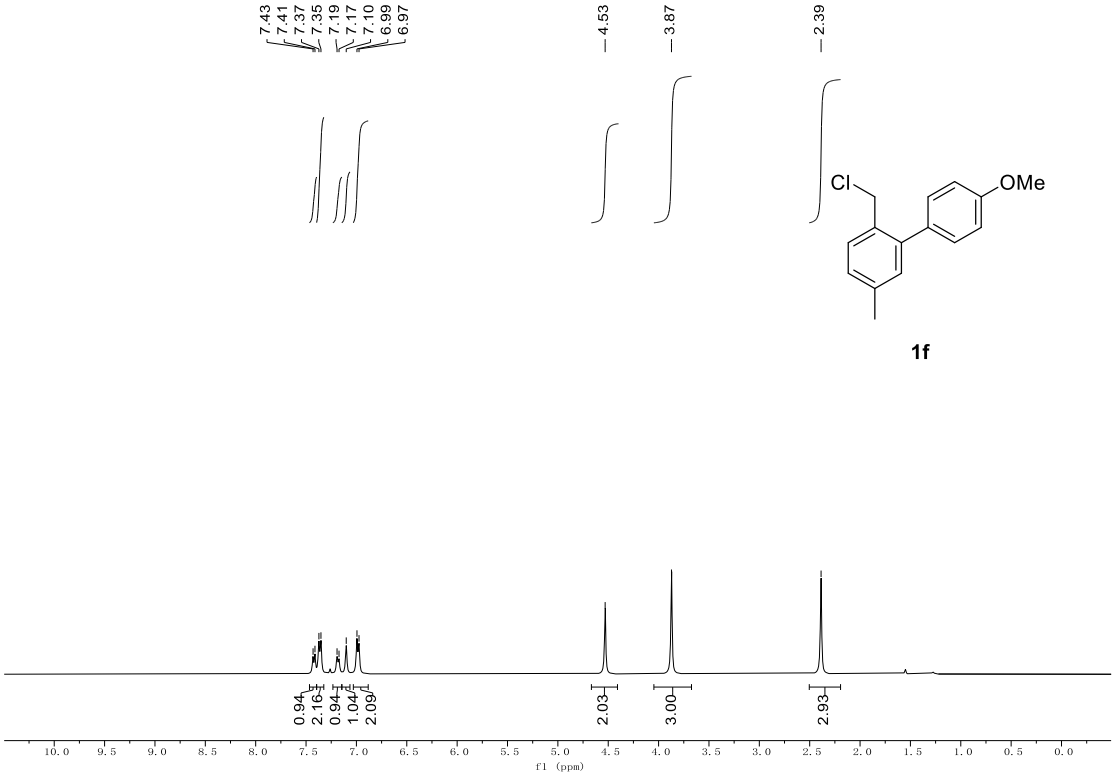


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

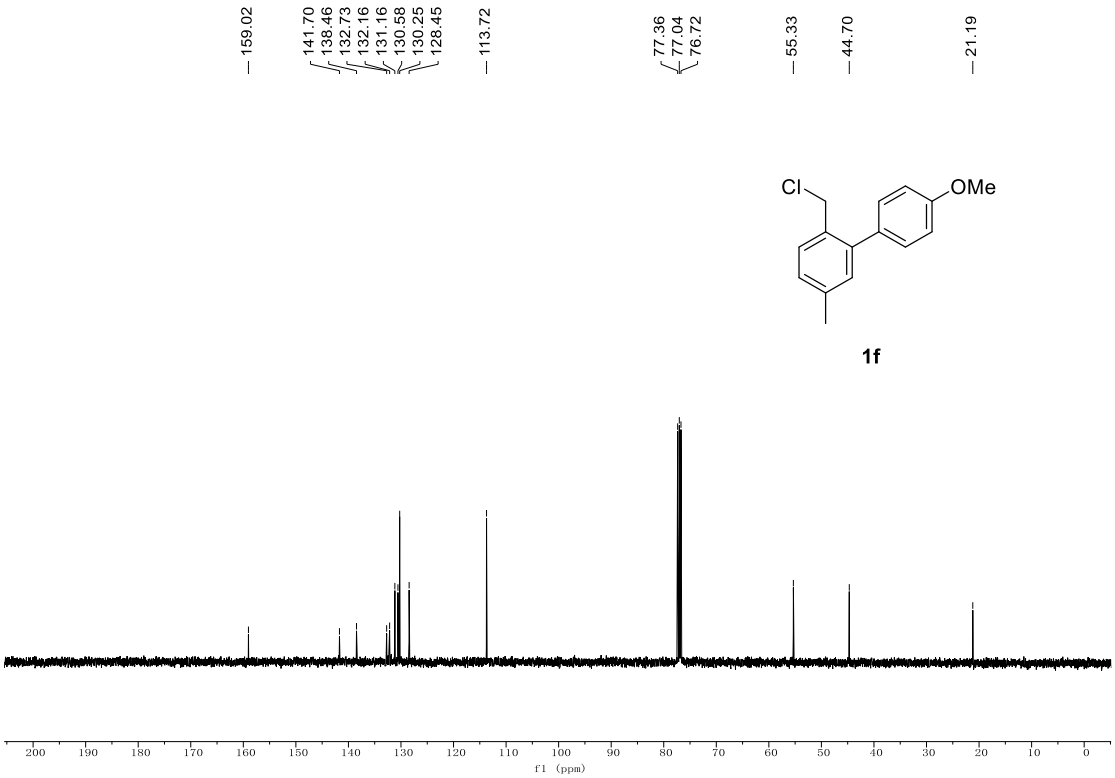


2-(Chloromethyl)-4'-methoxy-5-methyl-1,1'-biphenyl (1f)

^{1}H NMR, 400 MHz, $CDCl_3$

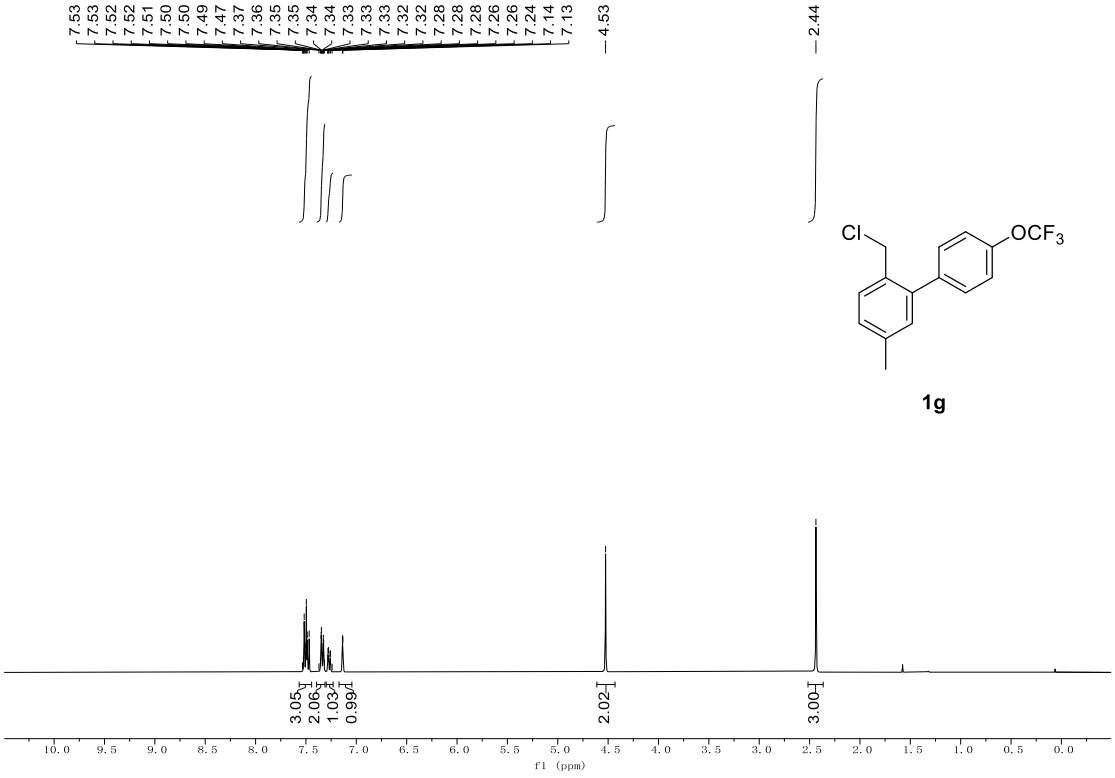


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

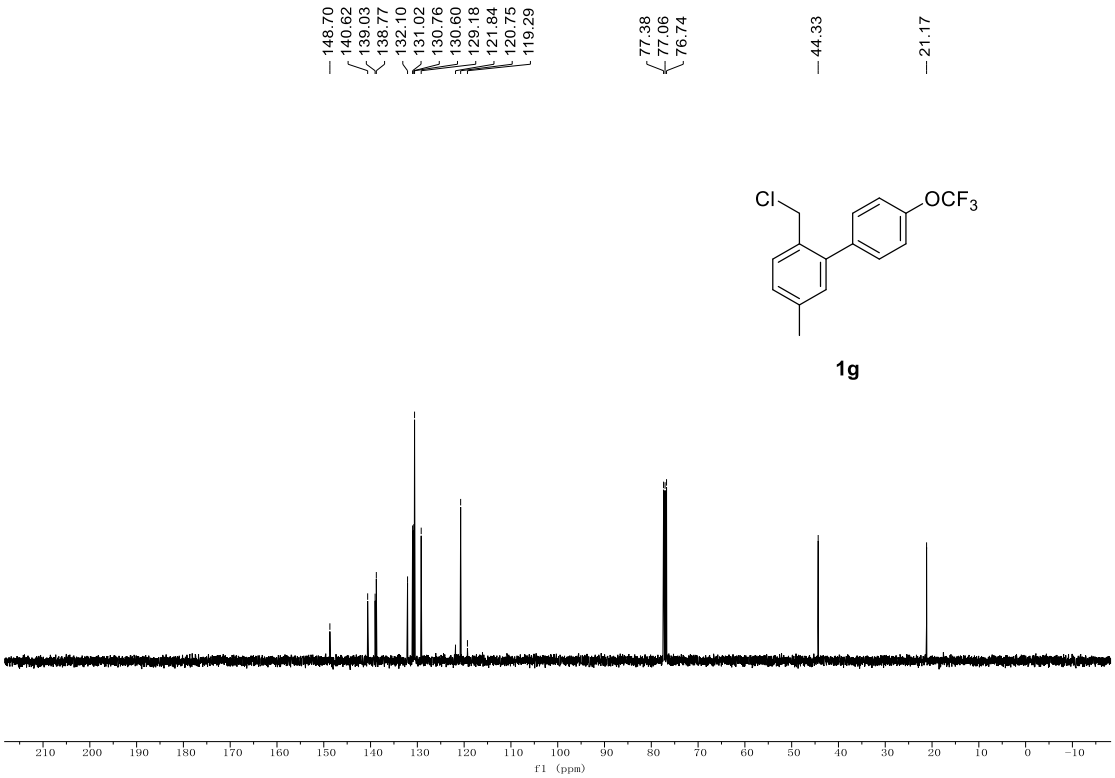


2-(Chloromethyl)-5-methyl-4'-(trifluoromethoxy)-1,1'-biphenyl (1g)

^{1}H NMR, 400 MHz, $CDCl_3$

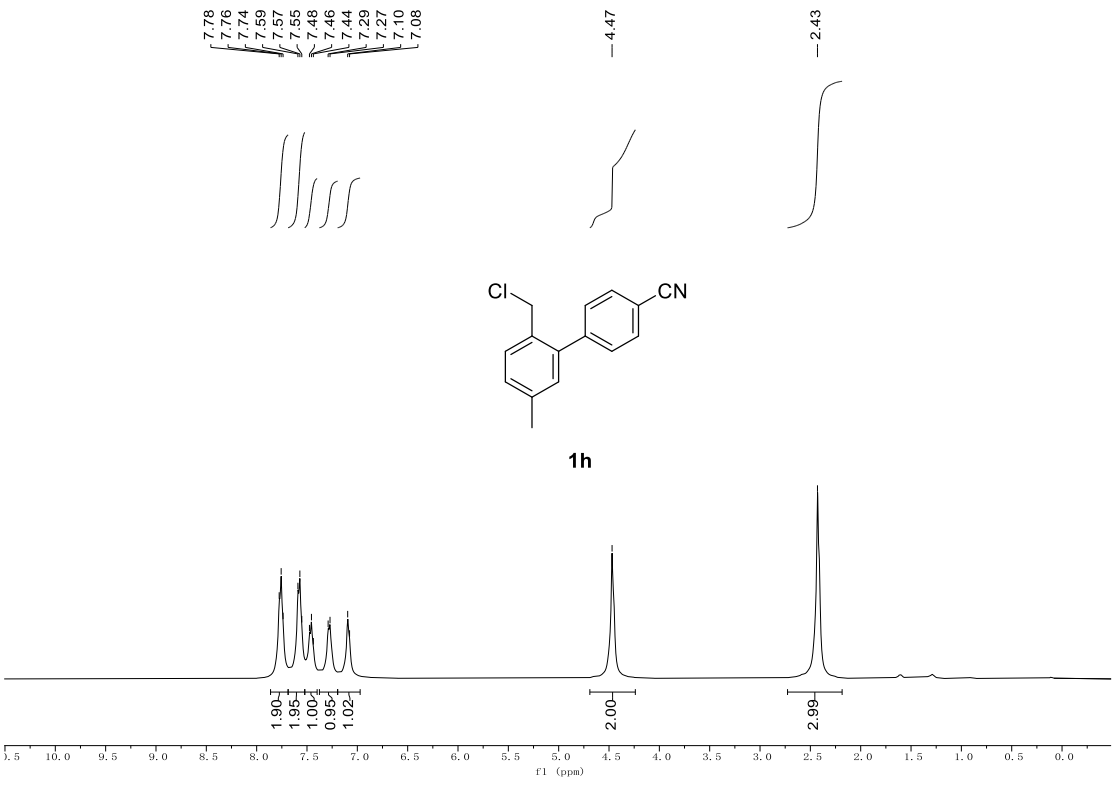


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

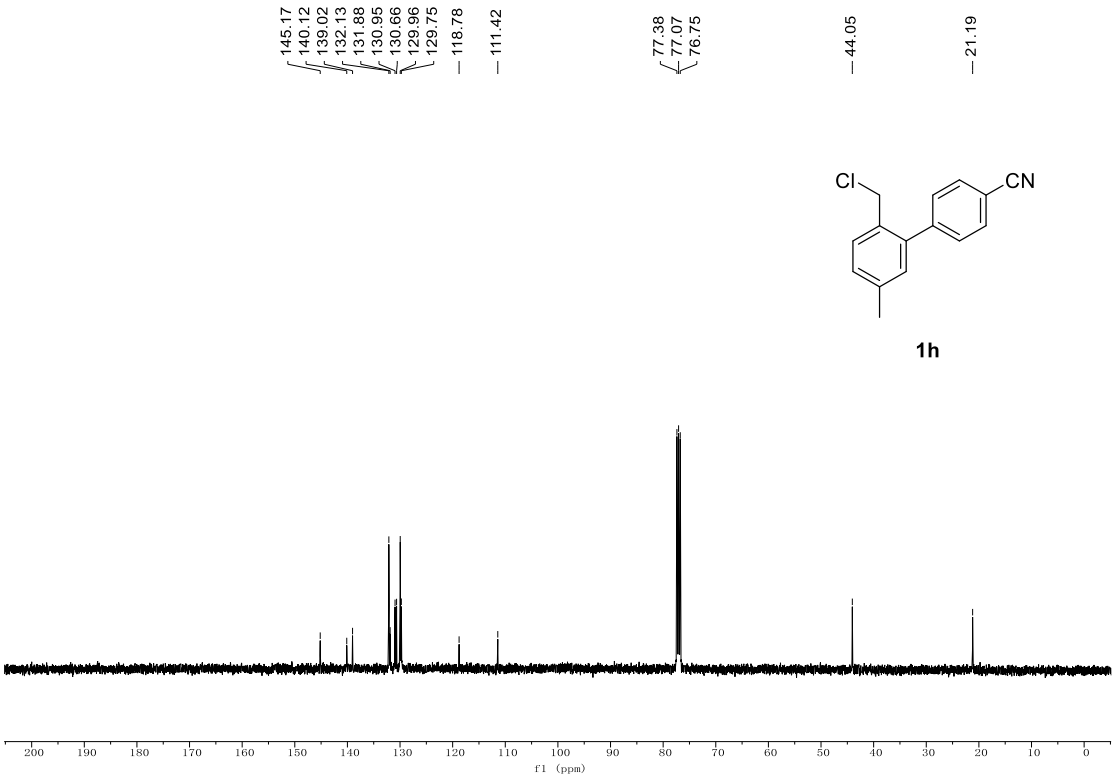


2'-(Chloromethyl)-5'-methyl-[1,1'-biphenyl]-4-carbonitrile (1h)

^{1}H NMR, 400 MHz, $CDCl_3$

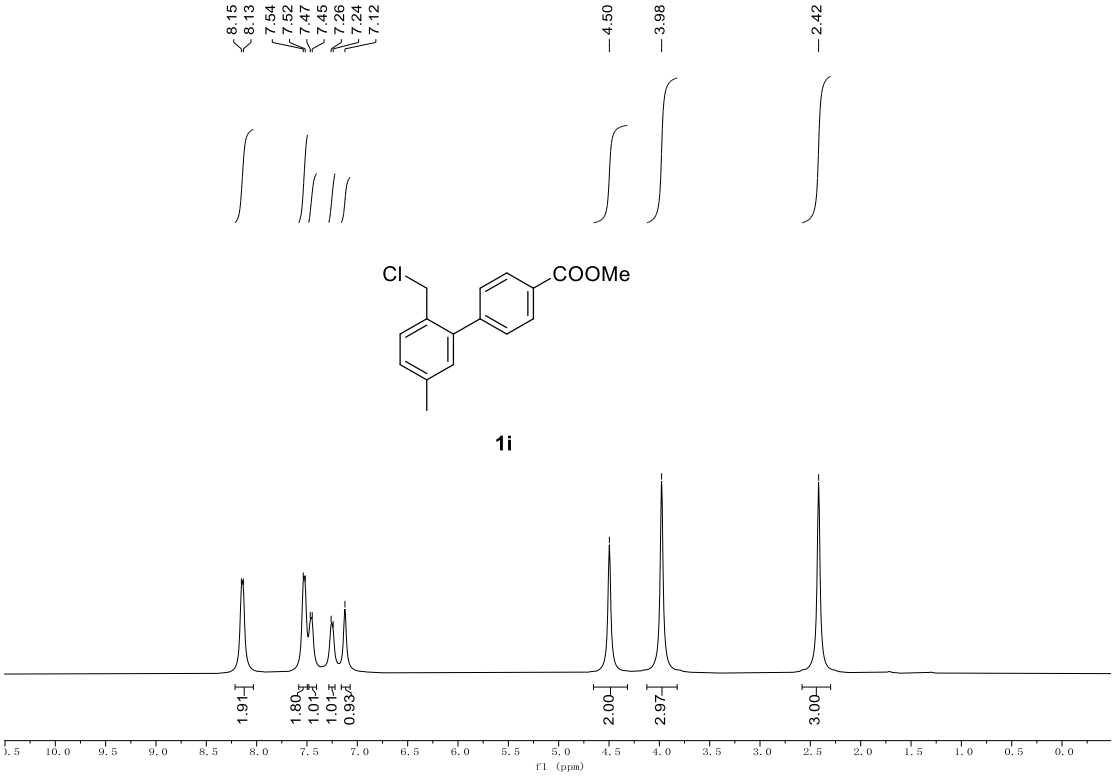


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

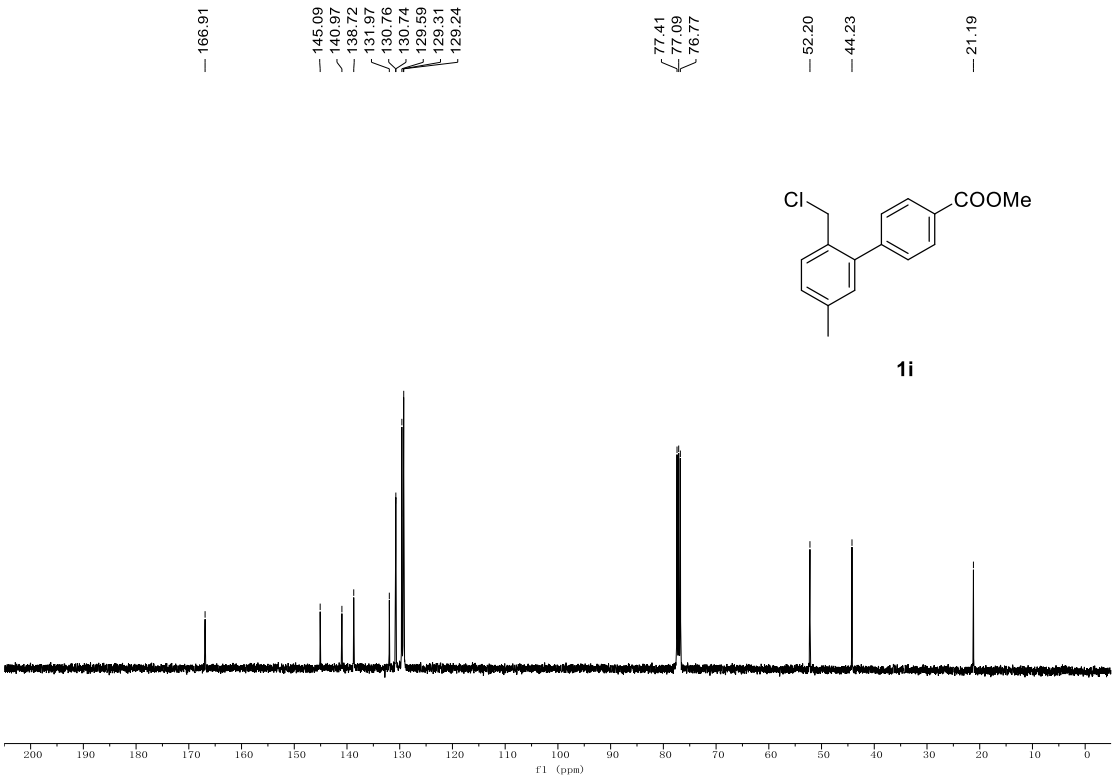


Methyl 2'-(chloromethyl)-5'-methyl-[1,1'-biphenyl]-4-carboxylate (1i)

^{1}H NMR, 400 MHz, $CDCl_3$

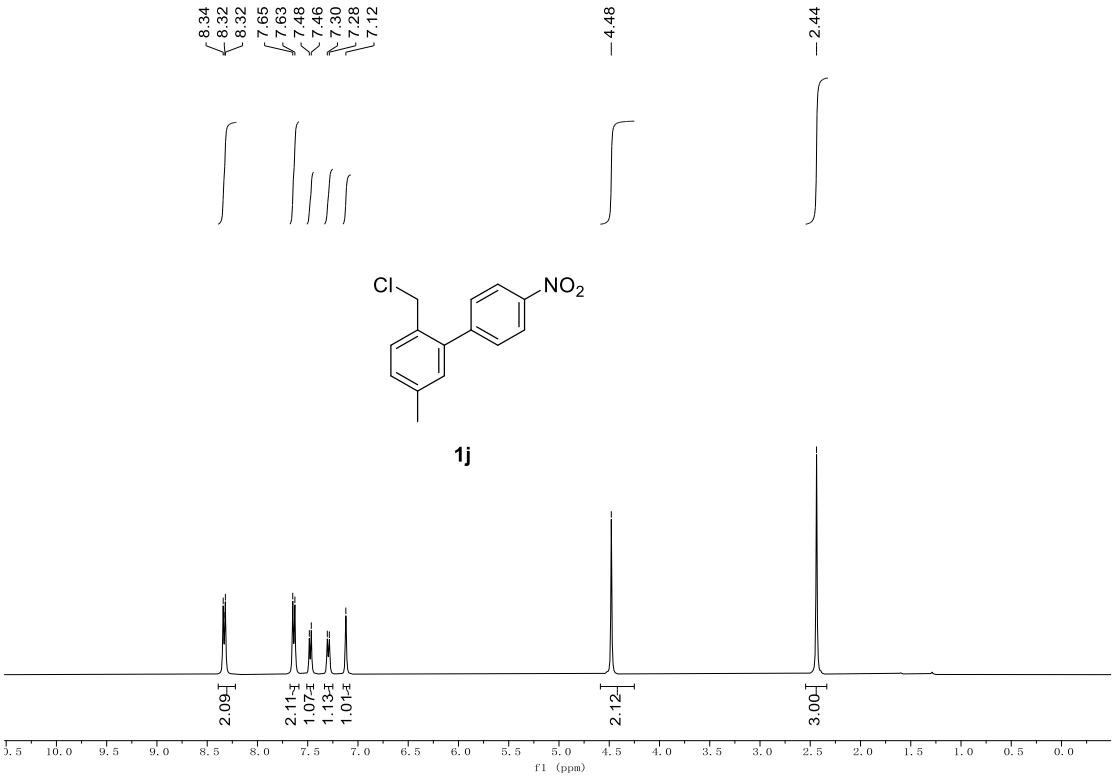


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

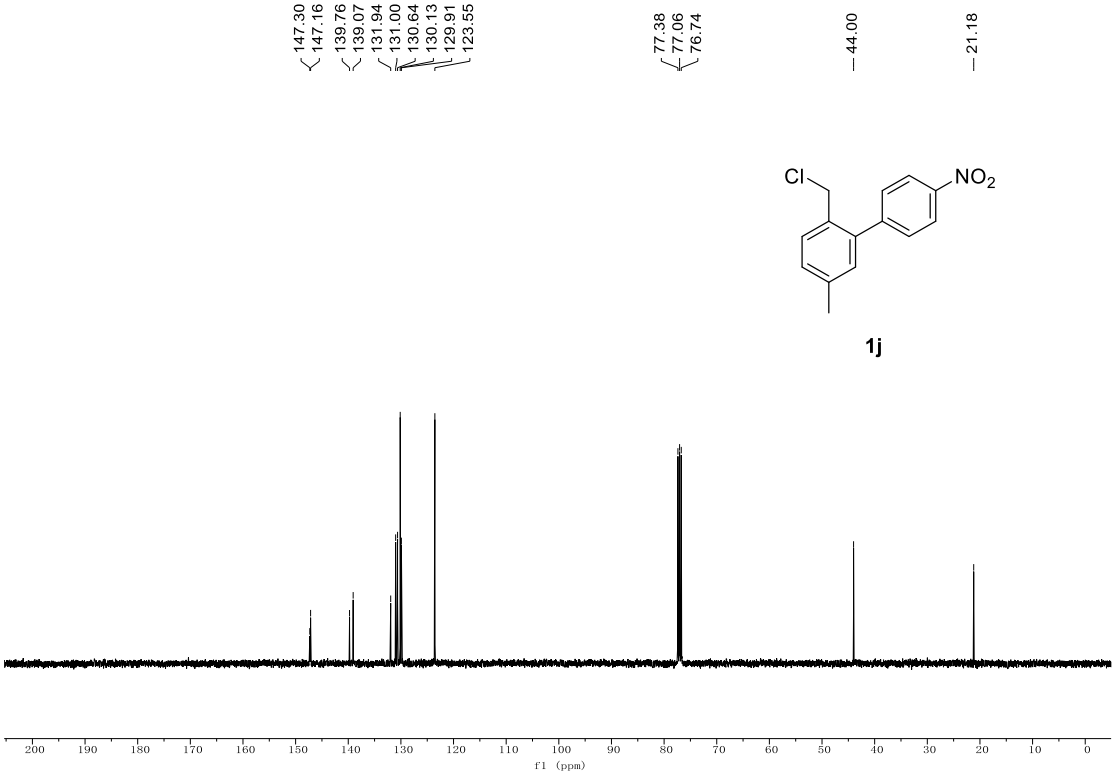


2-(Chloromethyl)-5-methyl-4'-nitro-1,1'-biphenyl (1j)

^{1}H NMR, 400 MHz, $CDCl_3$

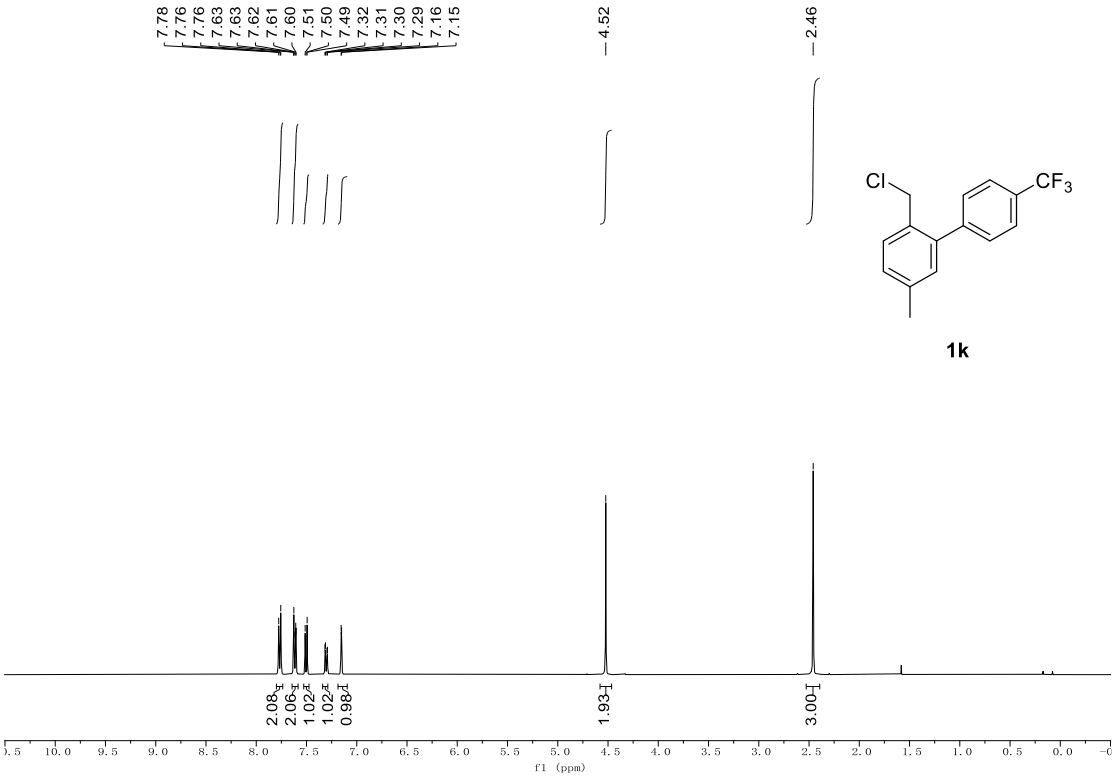


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

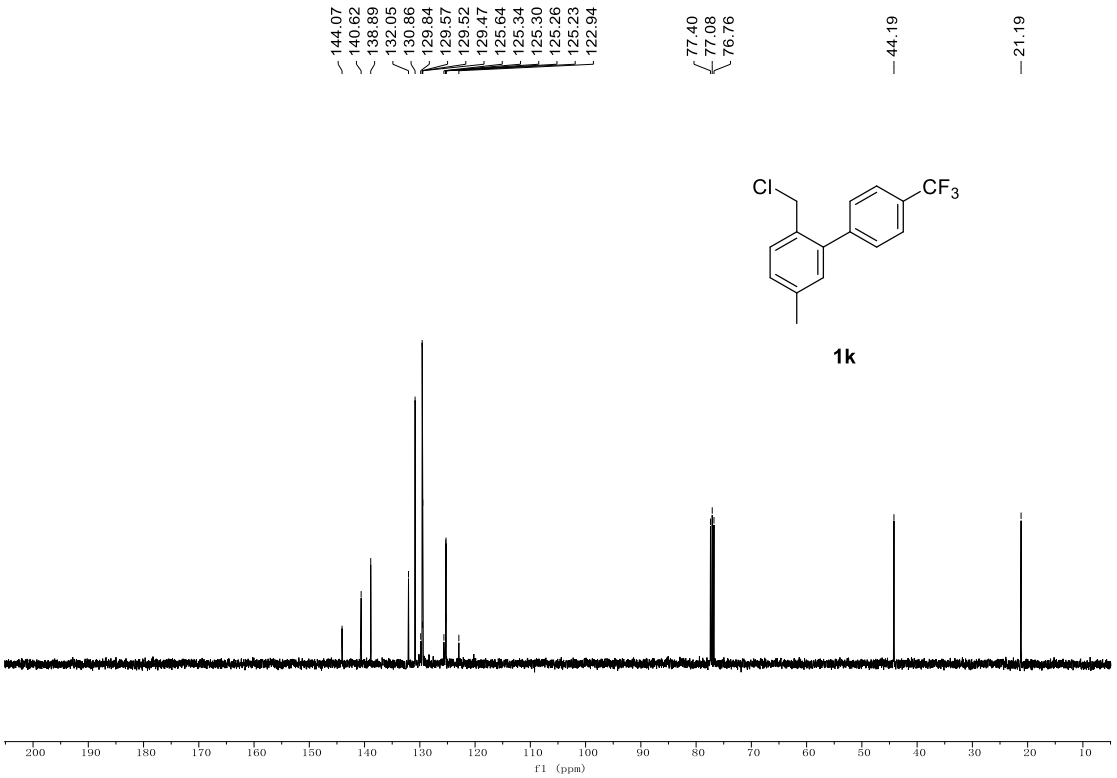


2-(Chloromethyl)-5-methyl-4'-(trifluoromethyl)-1,1'-biphenyl (1k)

^{1}H NMR, 400 MHz, $CDCl_3$

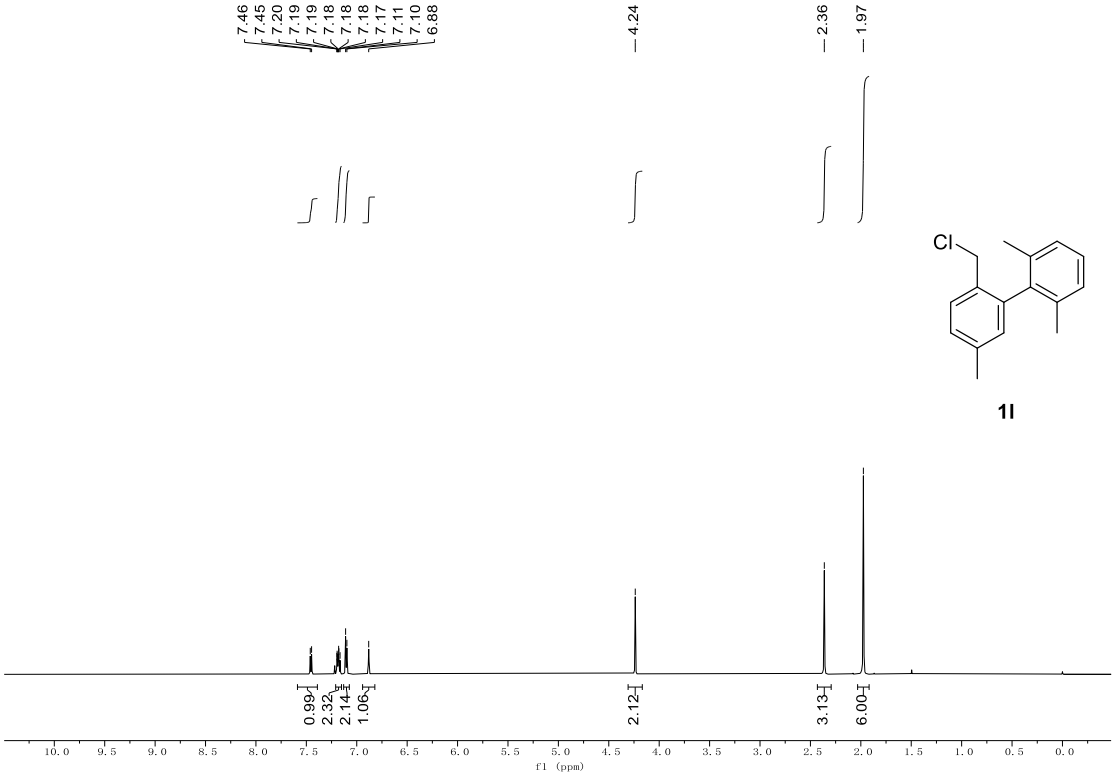


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

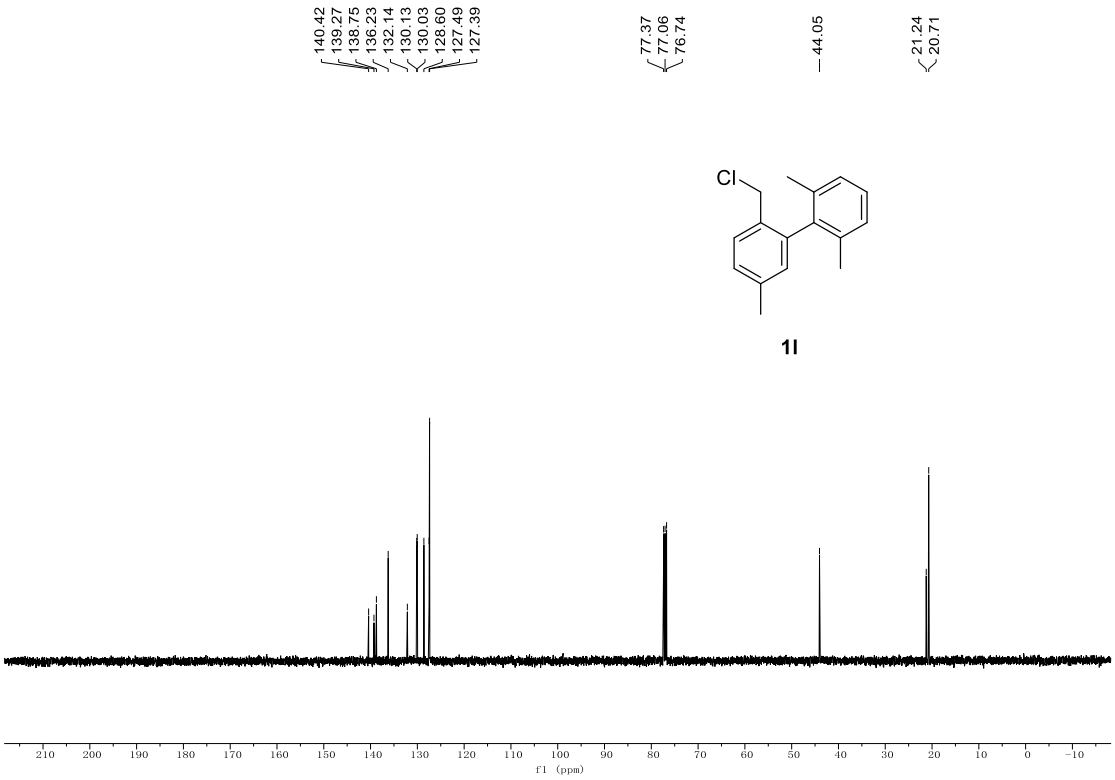


2-(Chloromethyl)-2',5,6'-trimethyl-1,1'-biphenyl (1l)

^{1}H NMR, 400 MHz, $CDCl_3$

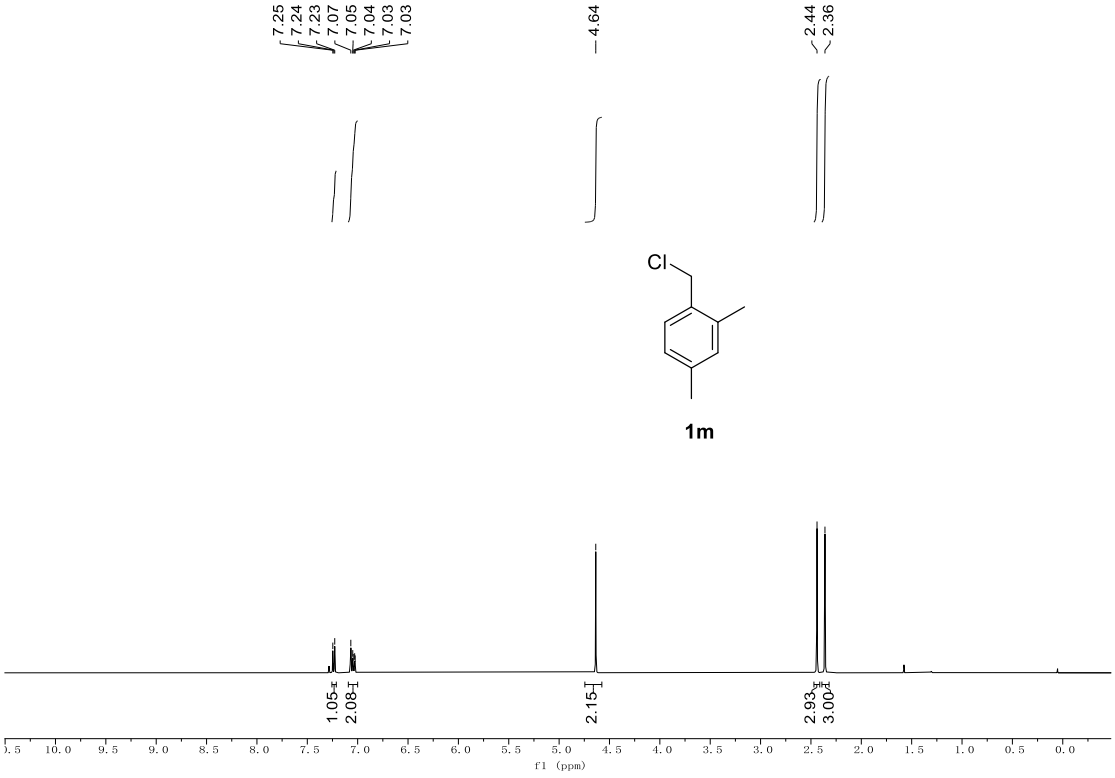


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

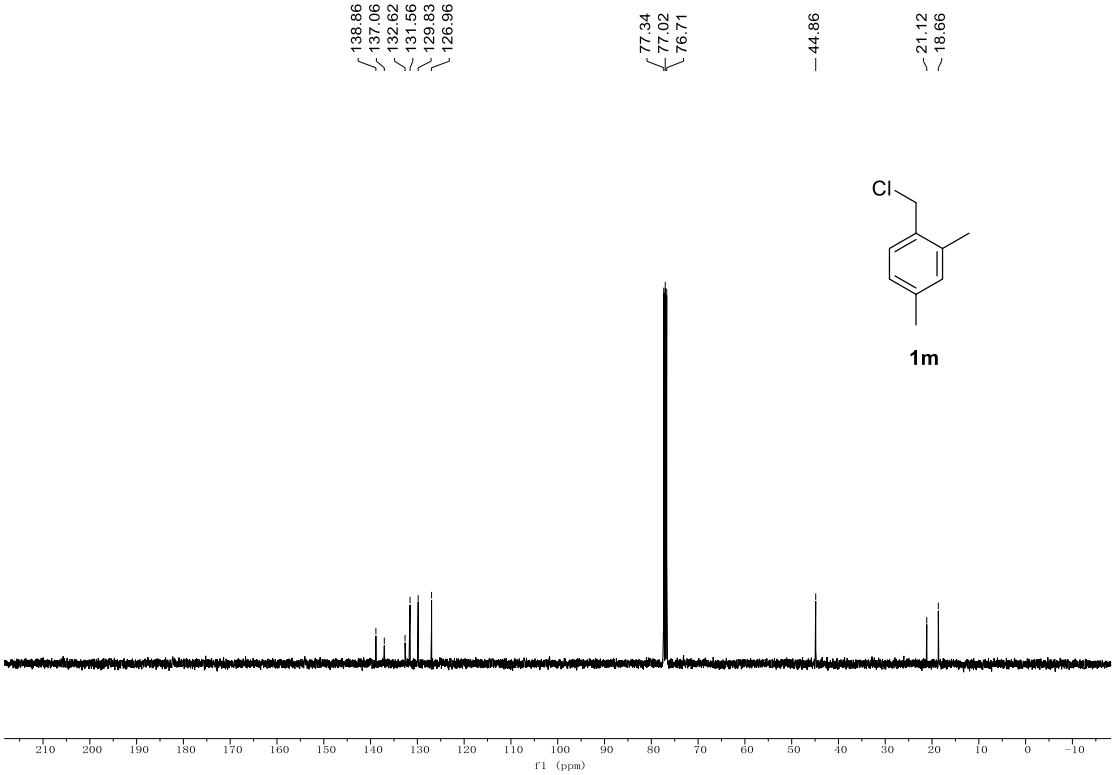


1-(Chloromethyl)-2,4-dimethylbenzene (1m)

^{1}H NMR, 400 MHz, $CDCl_3$

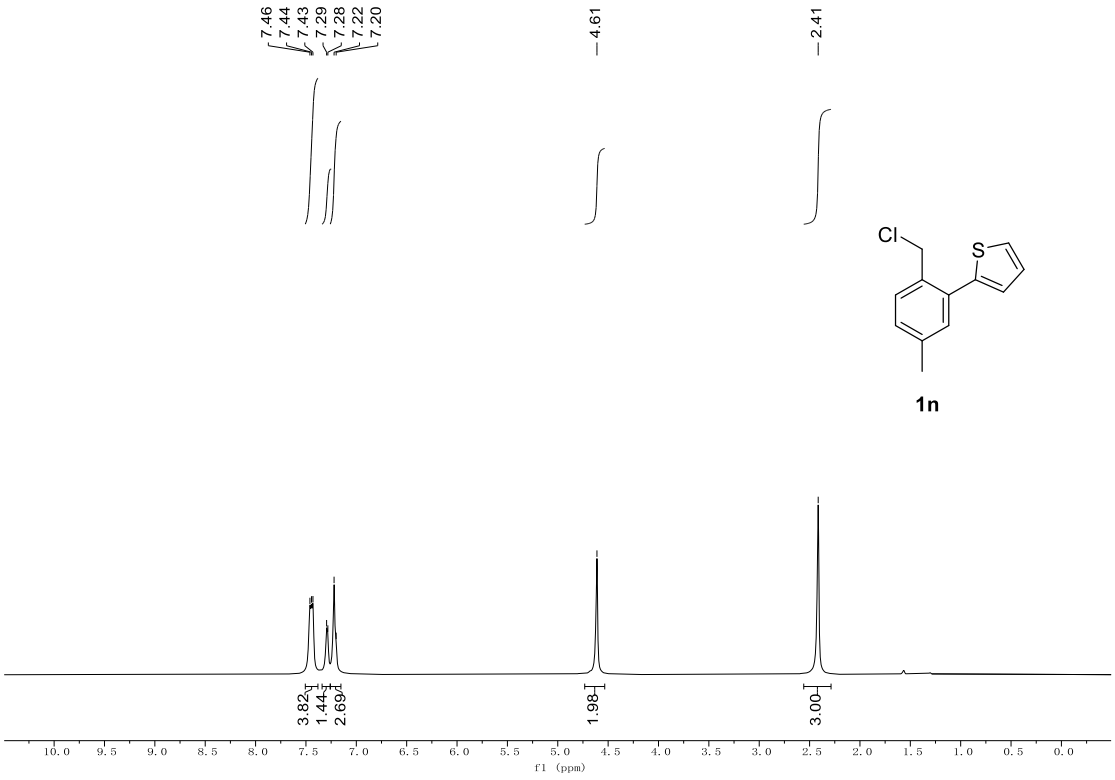


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

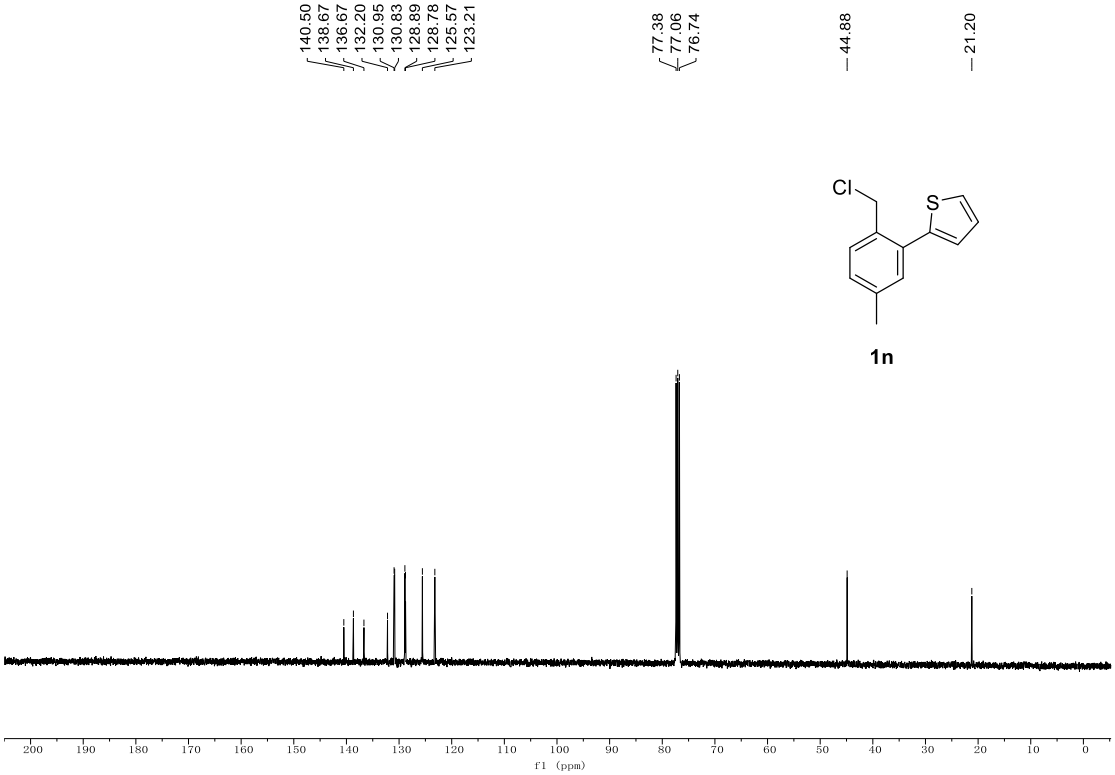


2-(2-(Chloromethyl)-5-methylphenyl)thiophene (1n)

^{1}H NMR, 400 MHz, $CDCl_3$

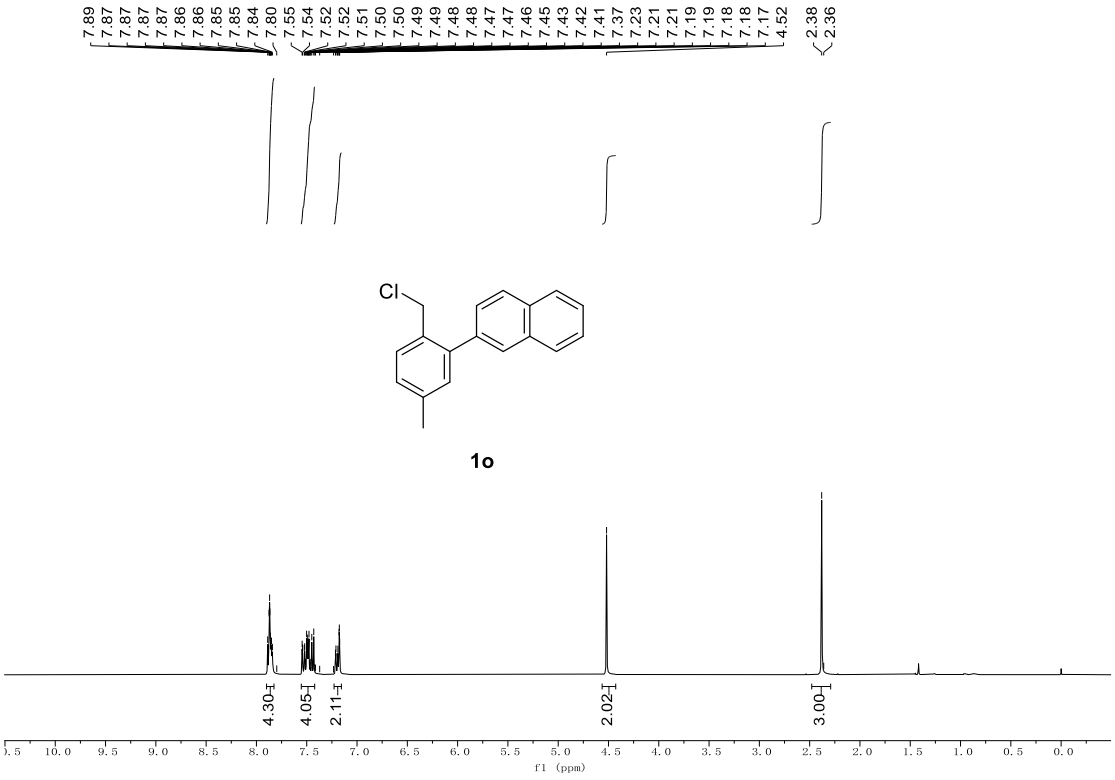


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

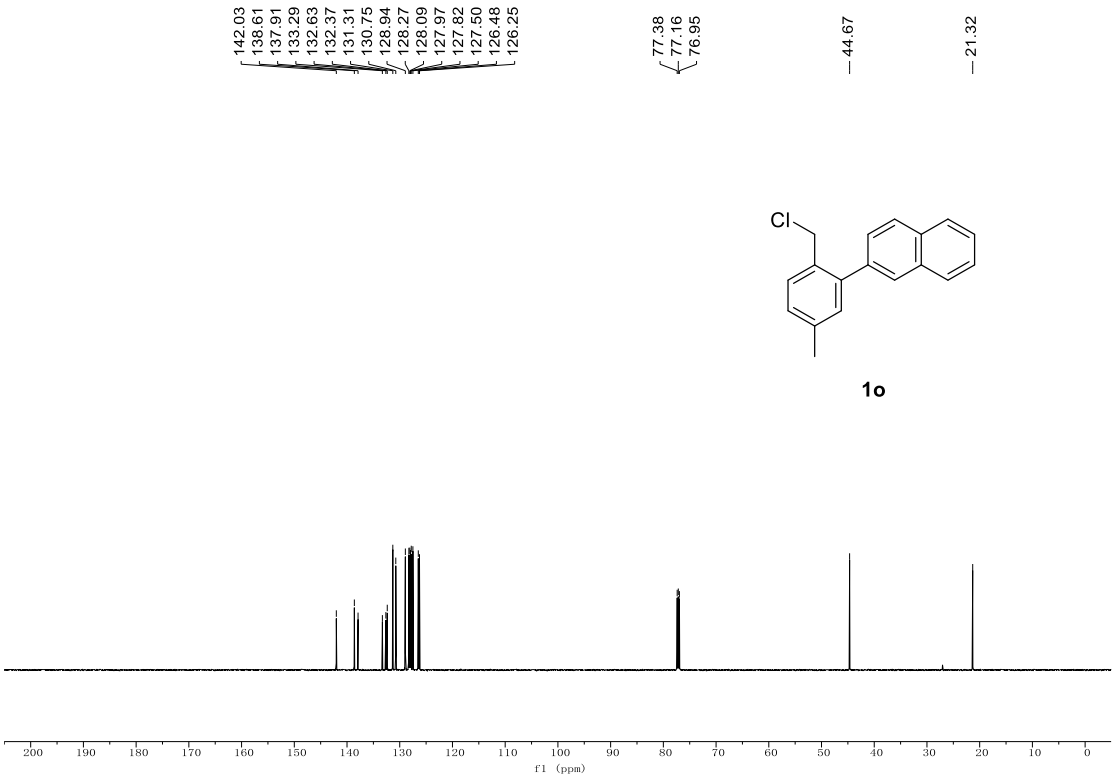


2-(2-(Chloromethyl)-5-methylphenyl)naphthalene (1o)

^{1}H NMR, 400 MHz, $CDCl_3$

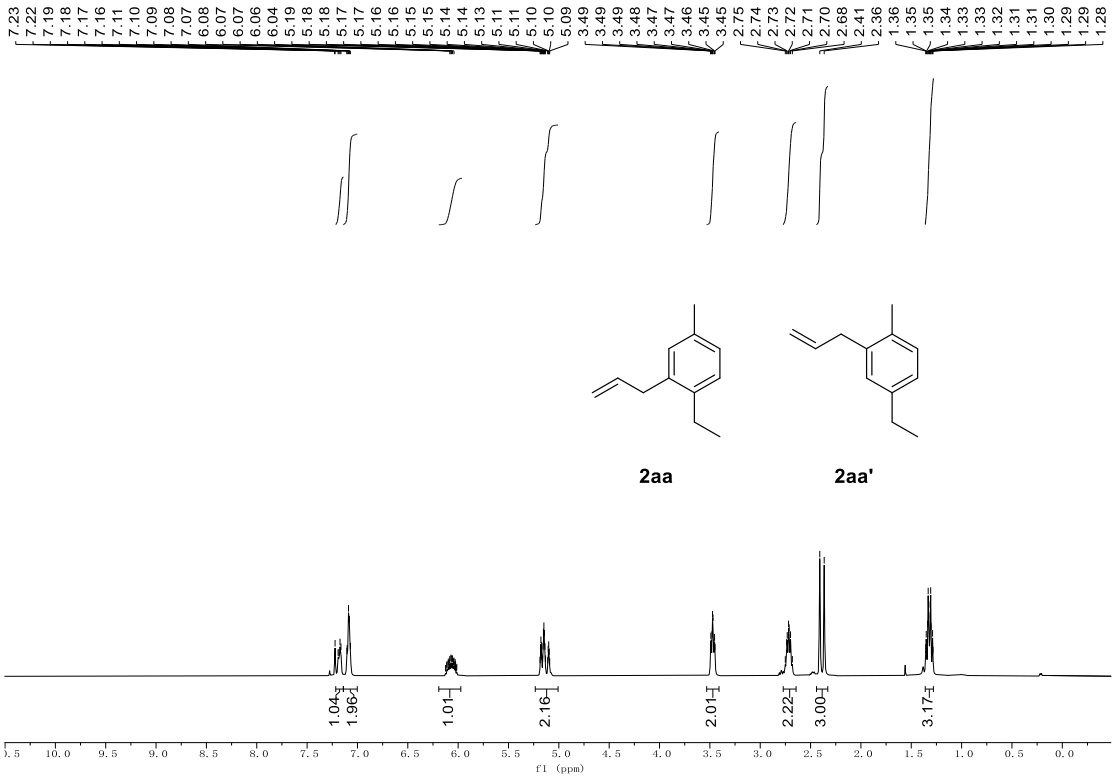


^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$



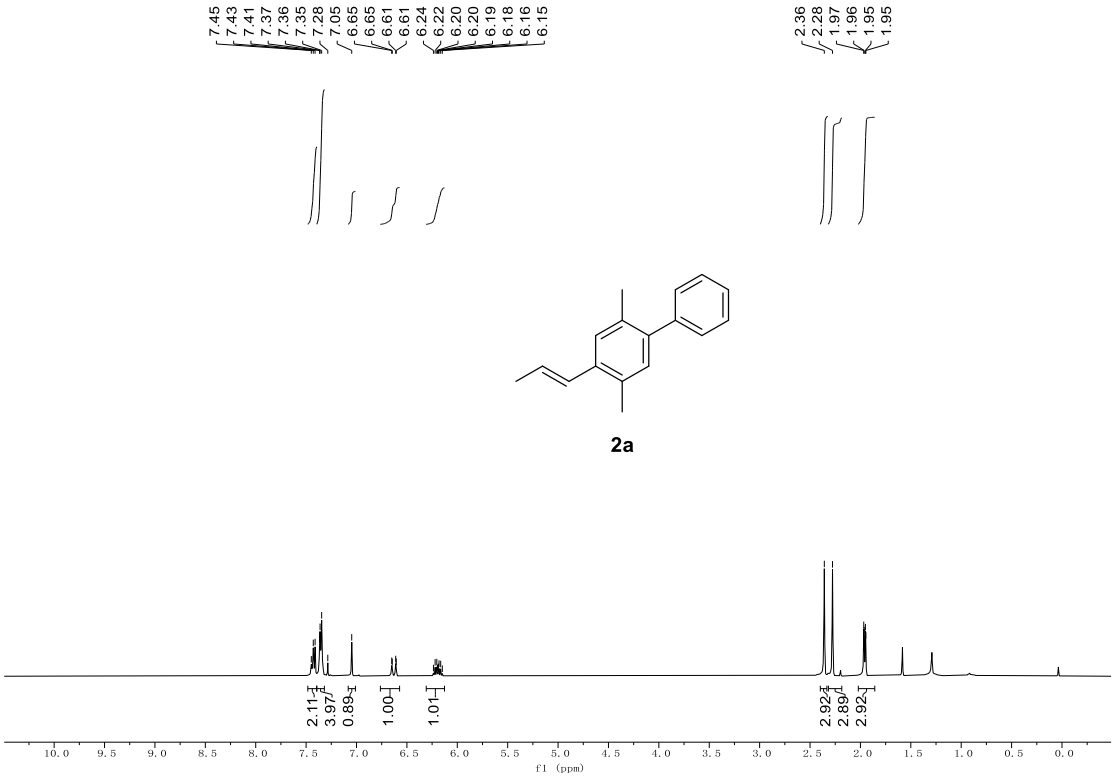
(E)-1-Ethyl-4-methyl-2-(prop-1-en-1-yl)benzene (2aa) and (E)-4-ethyl-1-methyl-2-(prop-1-en-1-yl)benzene (2aa')

^{1}H NMR, 400 MHz, $CDCl_3$

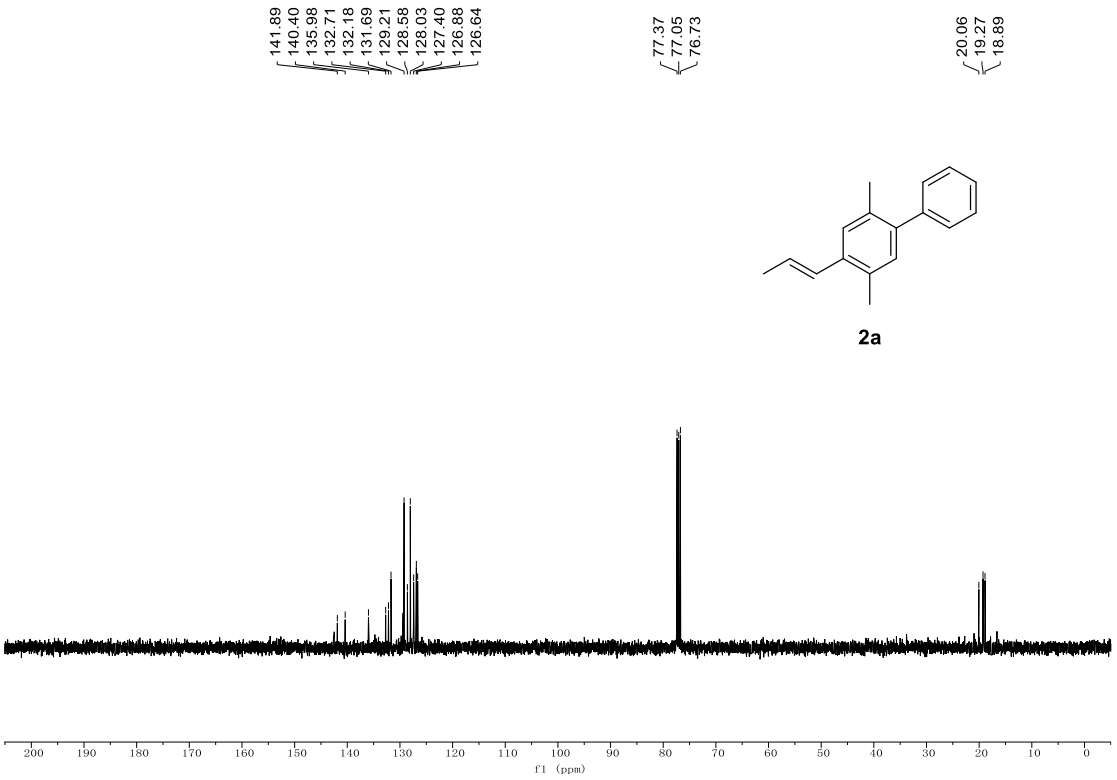


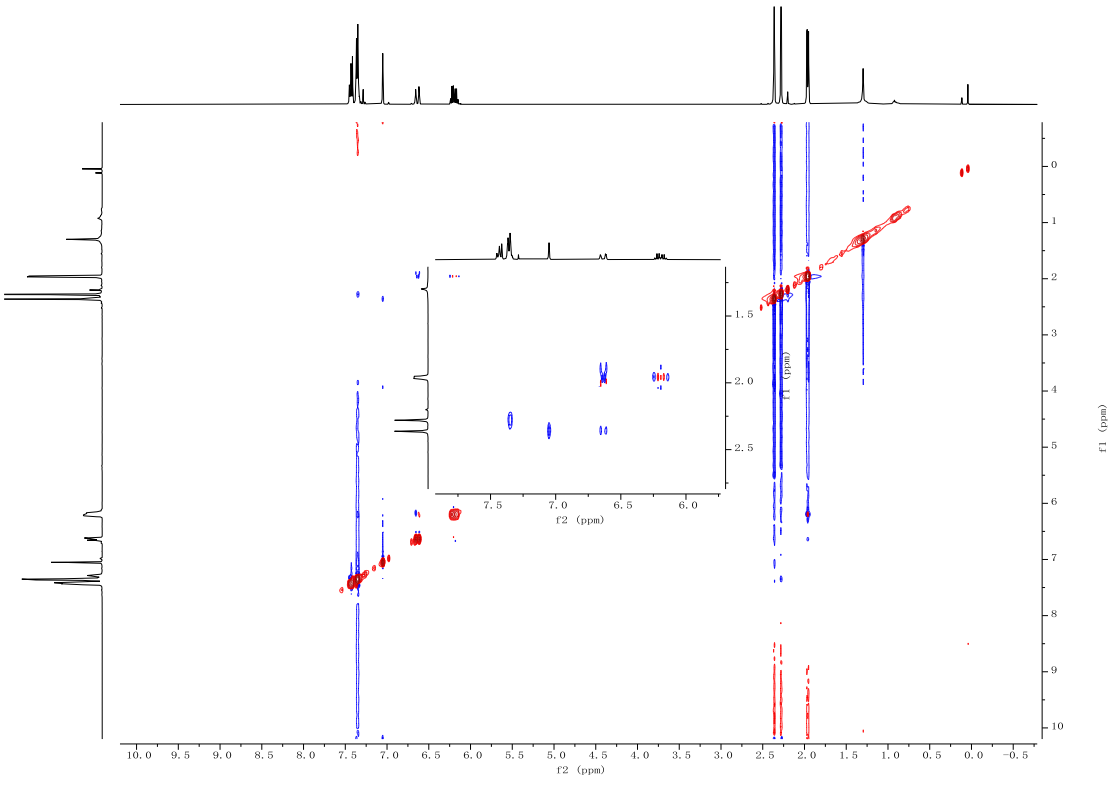
(E)-2,5-Dimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2a)

^{1}H NMR, 400 MHz, $CDCl_3$



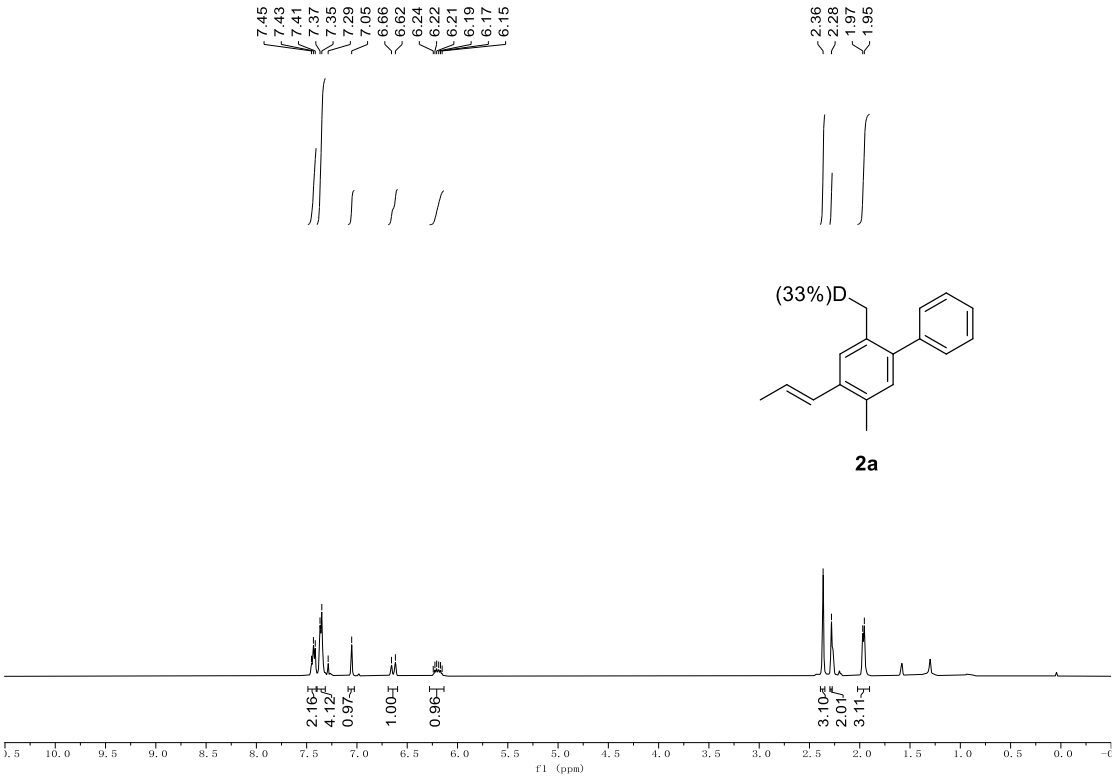
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$



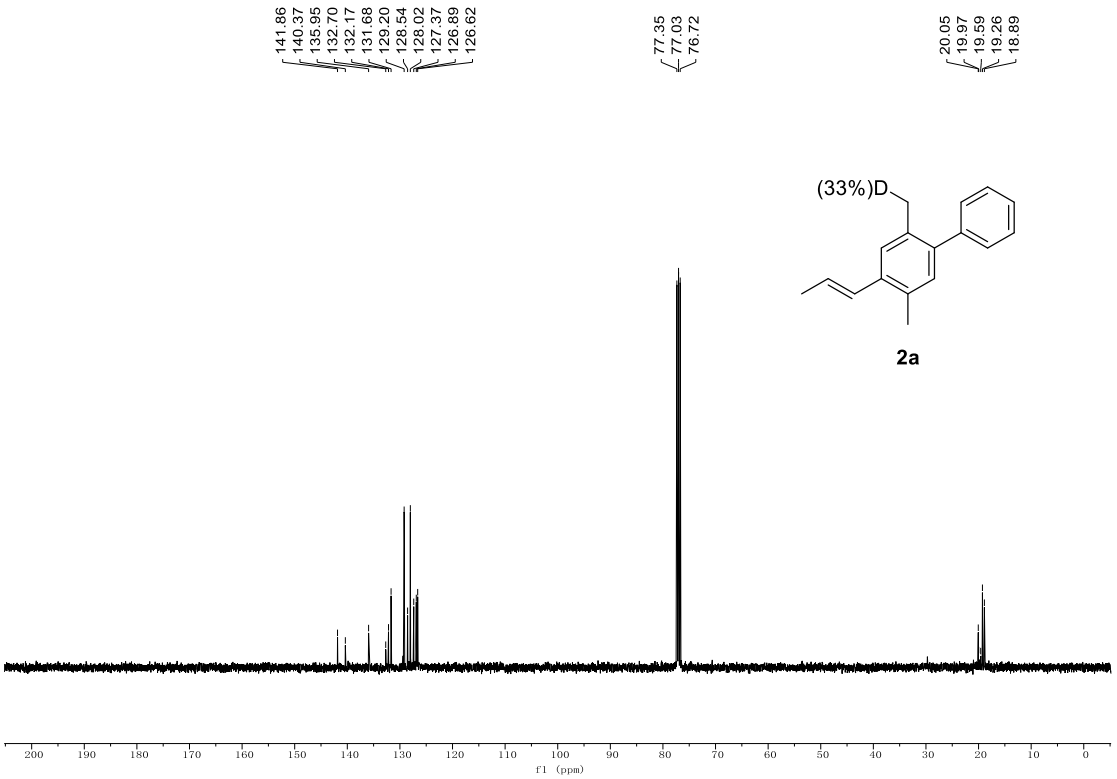


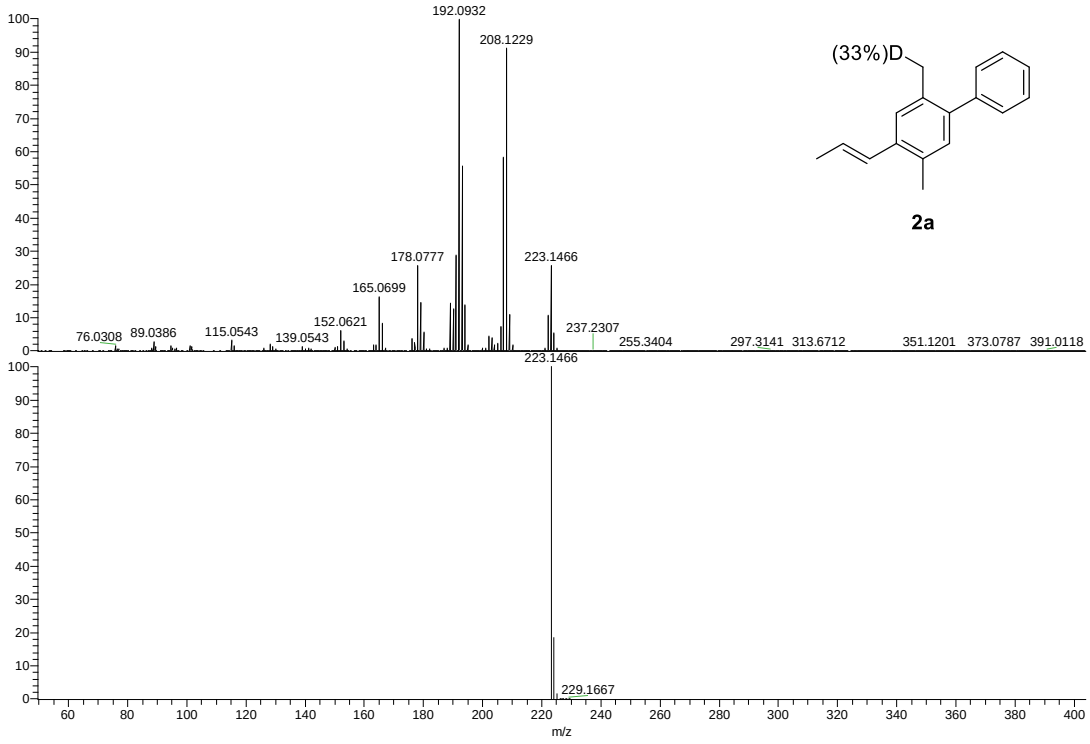
(E)-2,5-Dimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl-*d* (2a-*d*)

^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C{^{1}H} NMR, 100 MHz, $CDCl_3$

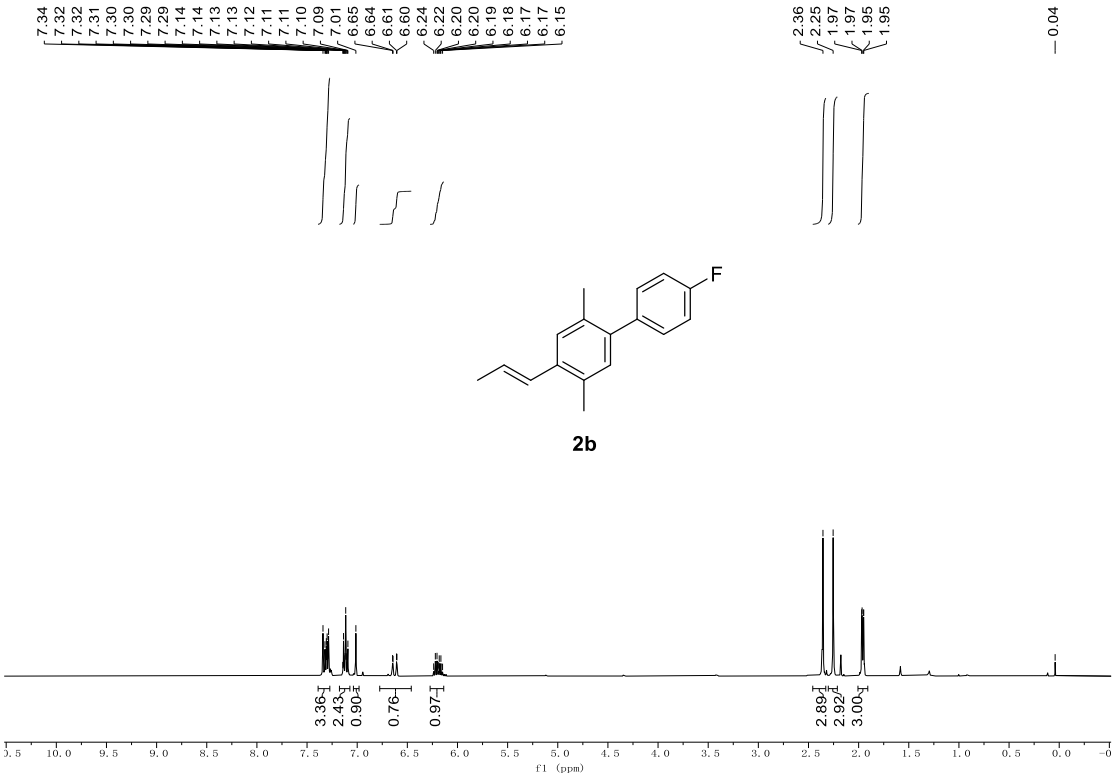




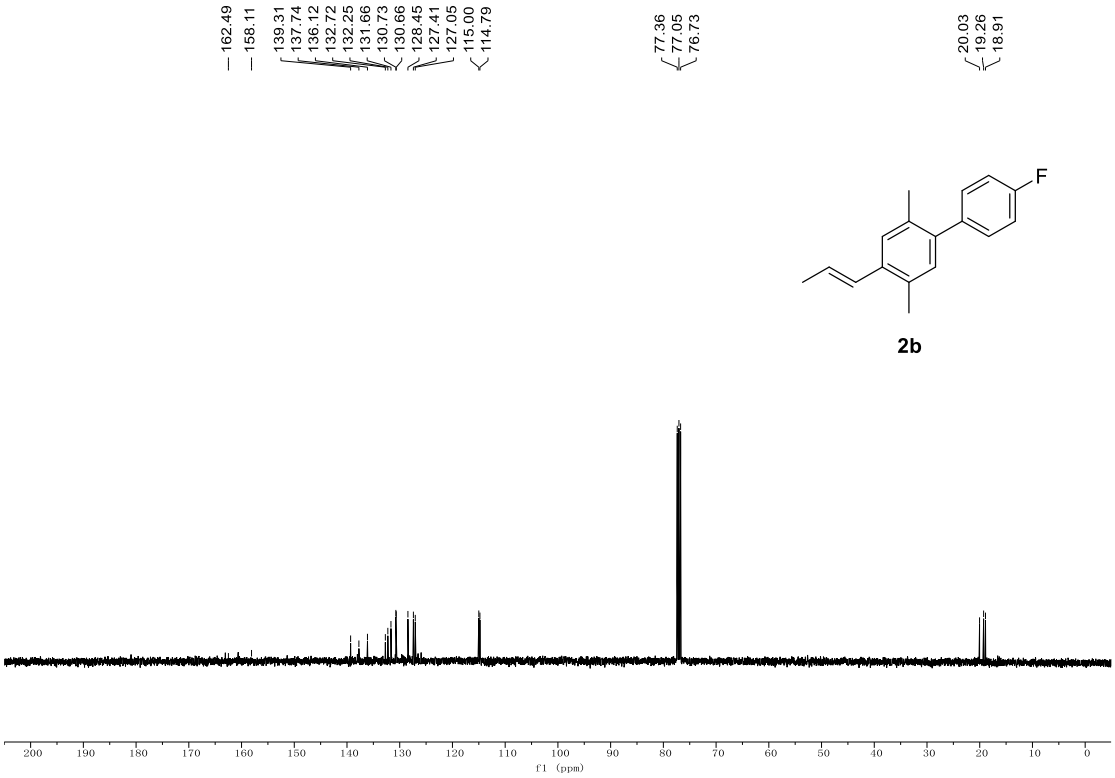
HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{17}D$ 223.1471; Found 223.1466.

(E)-4'-Fluoro-2,5-dimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2b)

^1H NMR, 400 MHz, $CDCl_3$

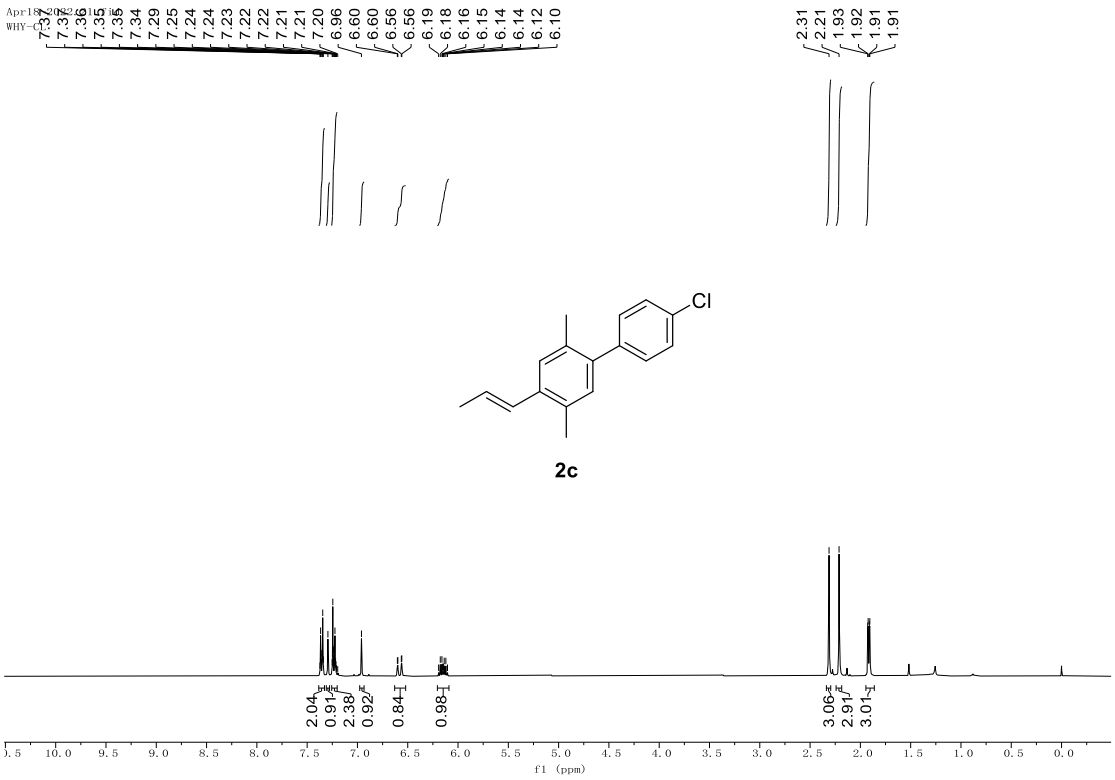


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

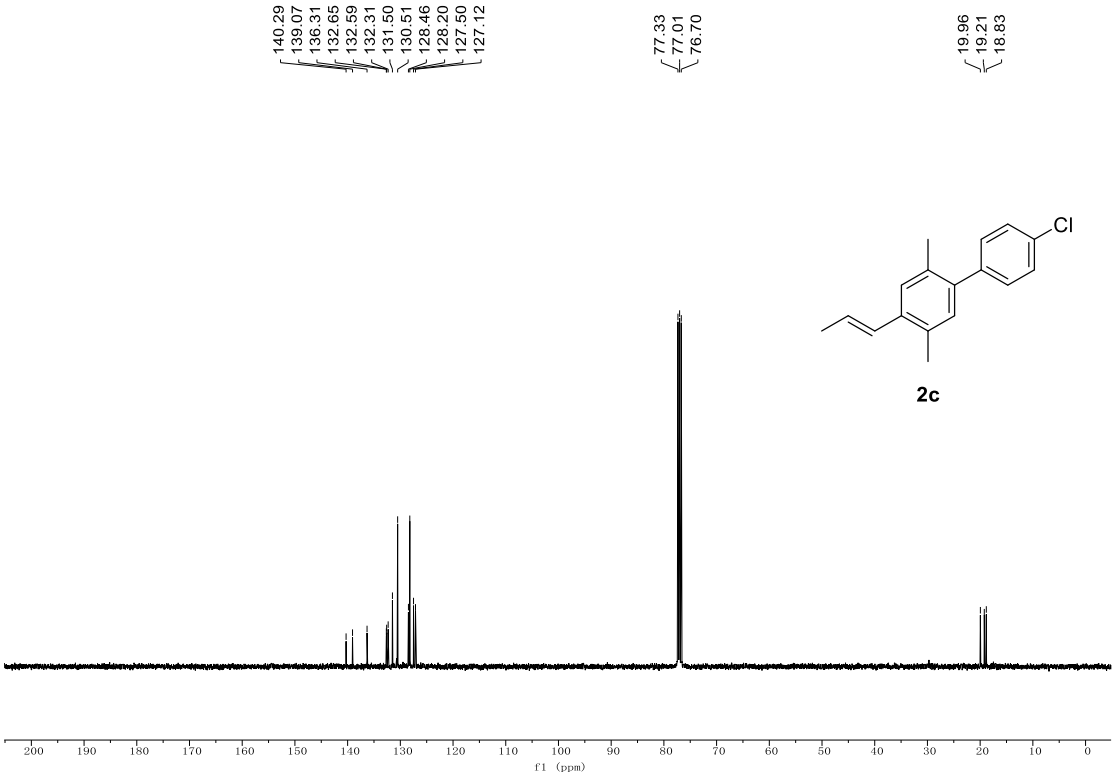


(E)-4'-Chloro-2,5-dimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2c)

^{1}H NMR, 400 MHz, $CDCl_3$

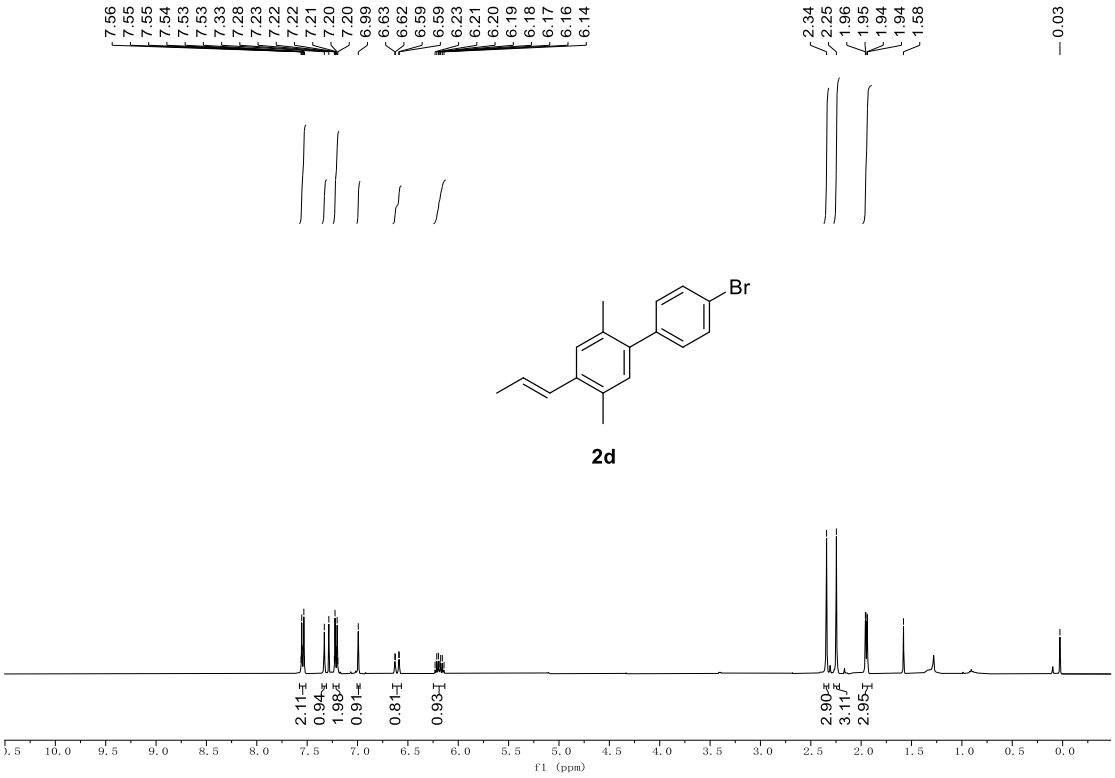


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

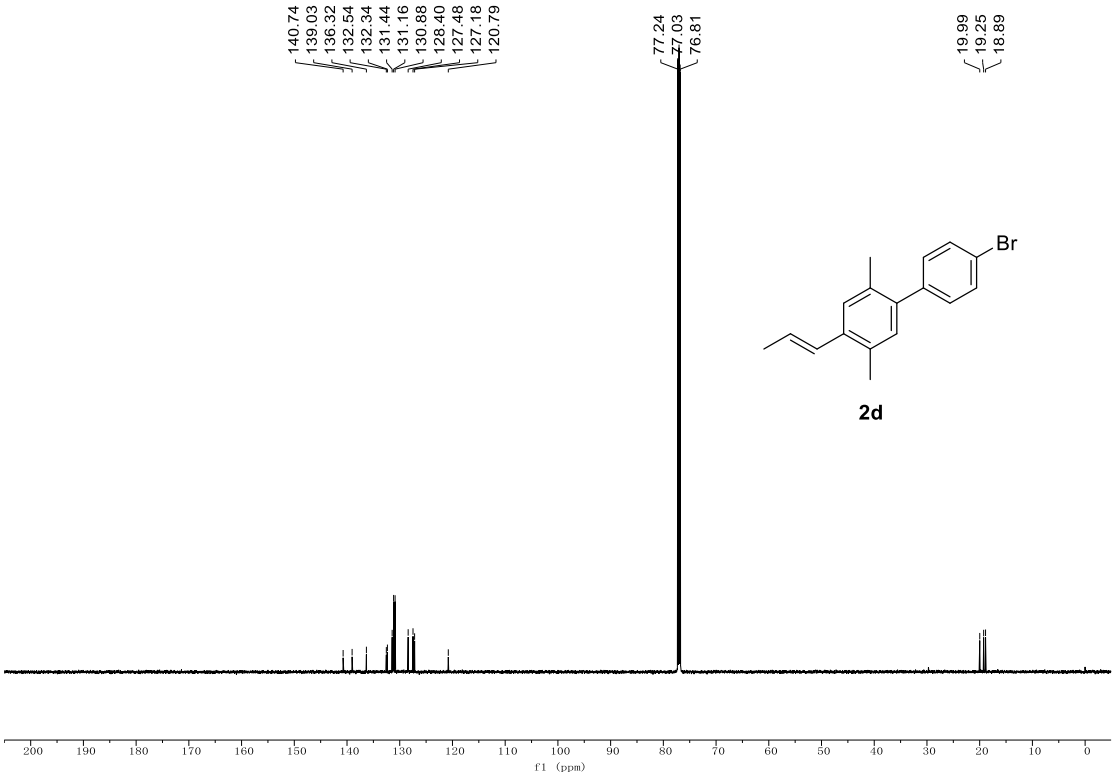


(E)-4'-Bromo-2,5-dimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2d)

^{1}H NMR, 400 MHz, $CDCl_3$



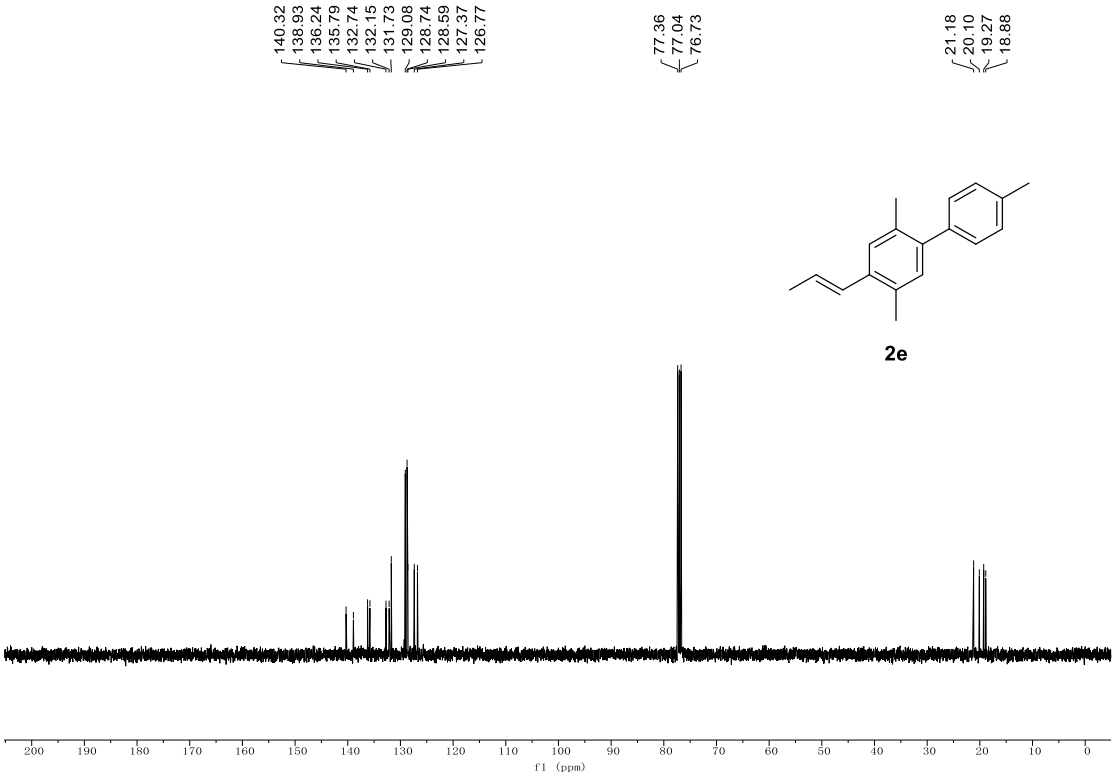
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$



(E)-2,4',5-Trimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2e)

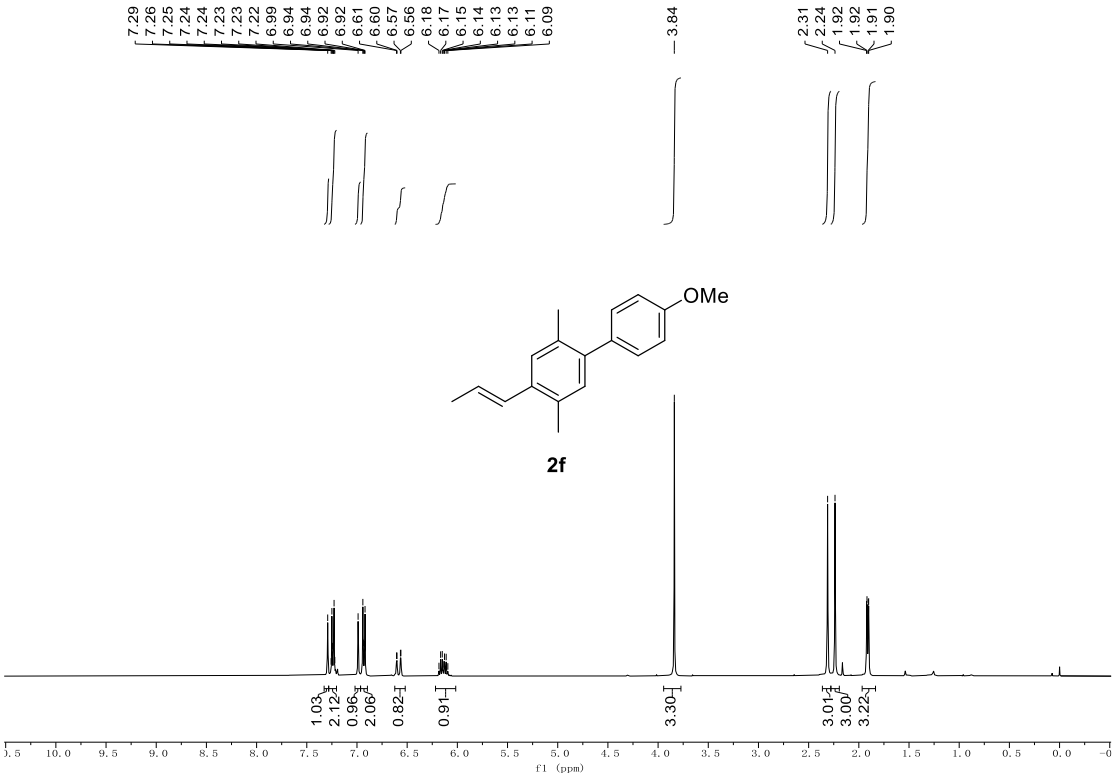
^{1}H NMR, 400 MHz, $CDCl_3$

$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

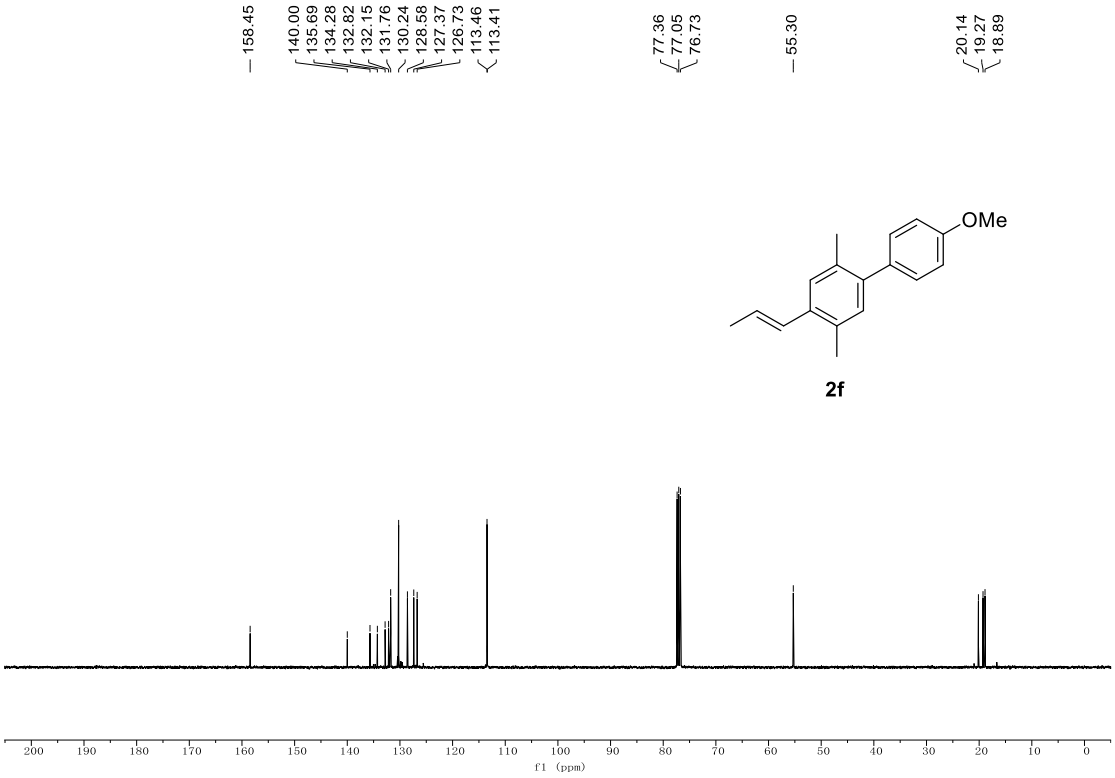


(E)-4'-Methoxy-2,5-dimethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2f)

^{1}H NMR, 400 MHz, $CDCl_3$

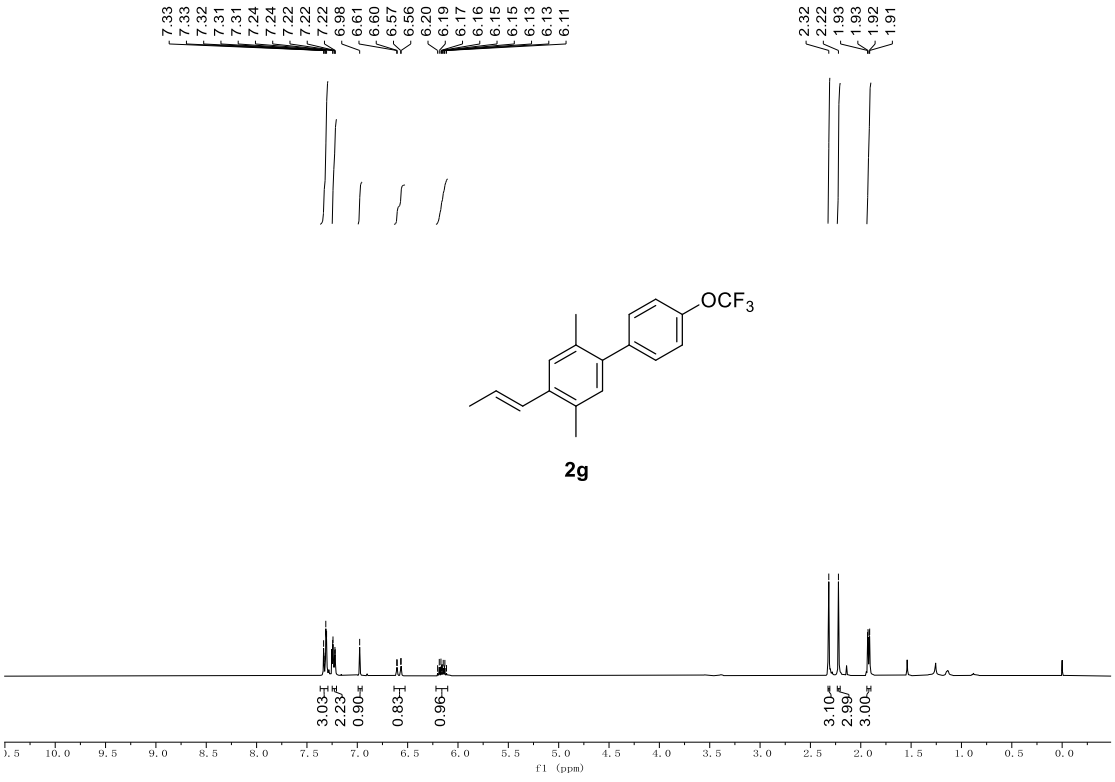


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

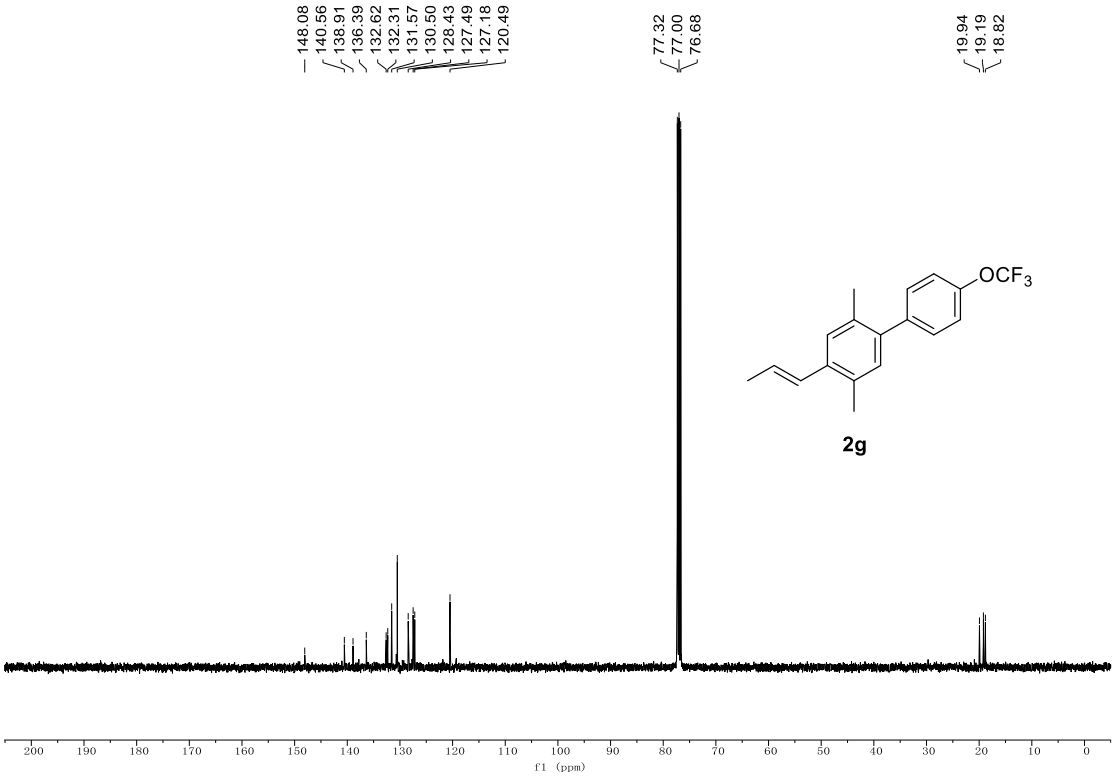


(E)-2,5-Dimethyl-4-(prop-1-en-1-yl)-4'-(trifluoromethoxy)-1,1'-biphenyl (2g)

^{1}H NMR, 400 MHz, $CDCl_3$

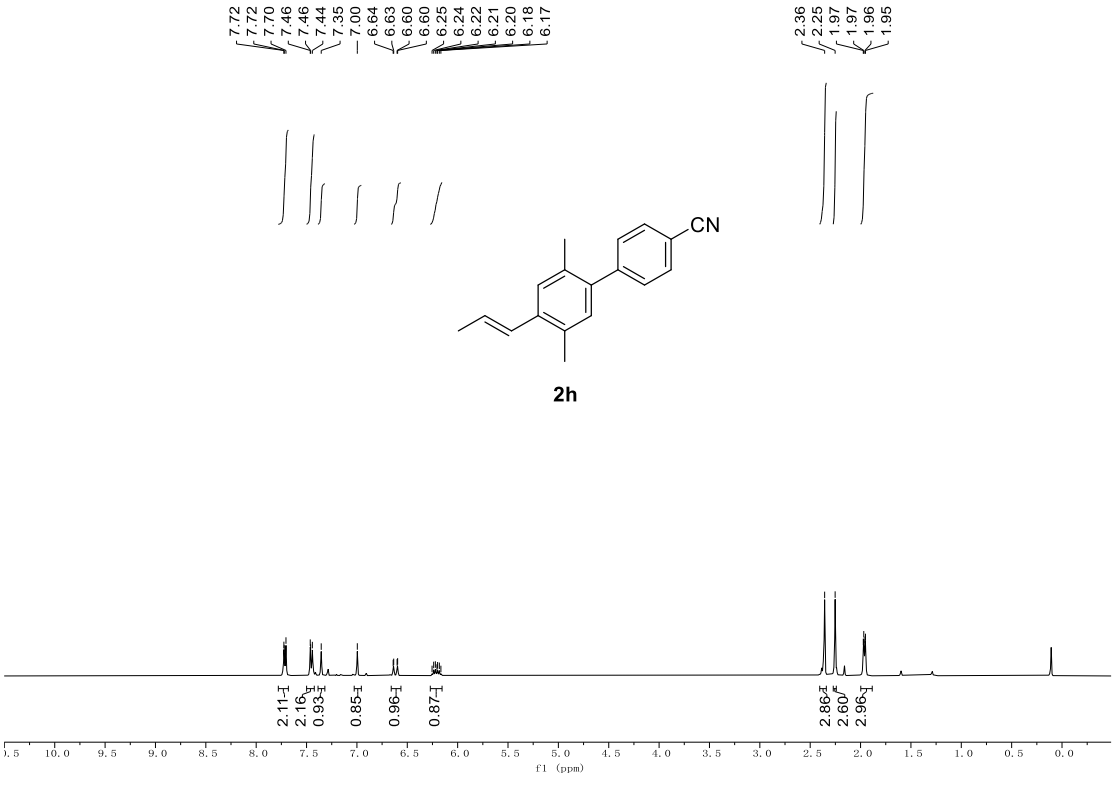


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

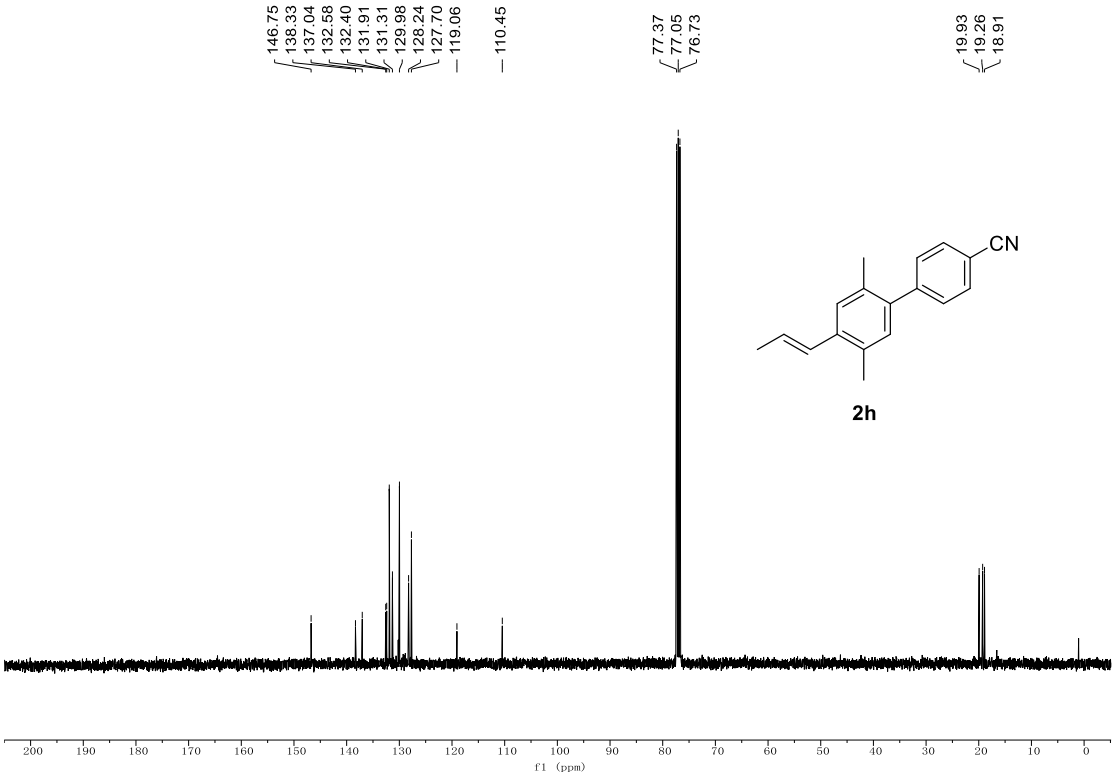


(E)-2',5'-Dimethyl-4'-(prop-1-en-1-yl)-[1,1'-biphenyl]-4-carbonitrile (2h)

^{1}H NMR, 400 MHz, $CDCl_3$

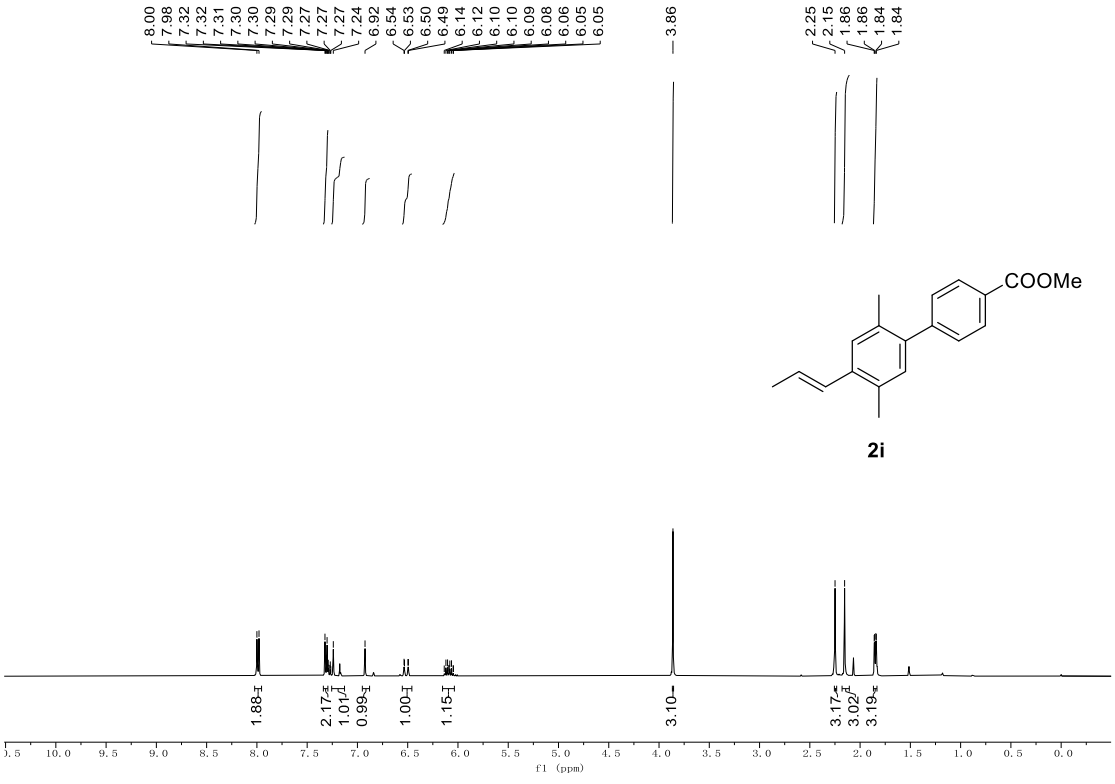


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

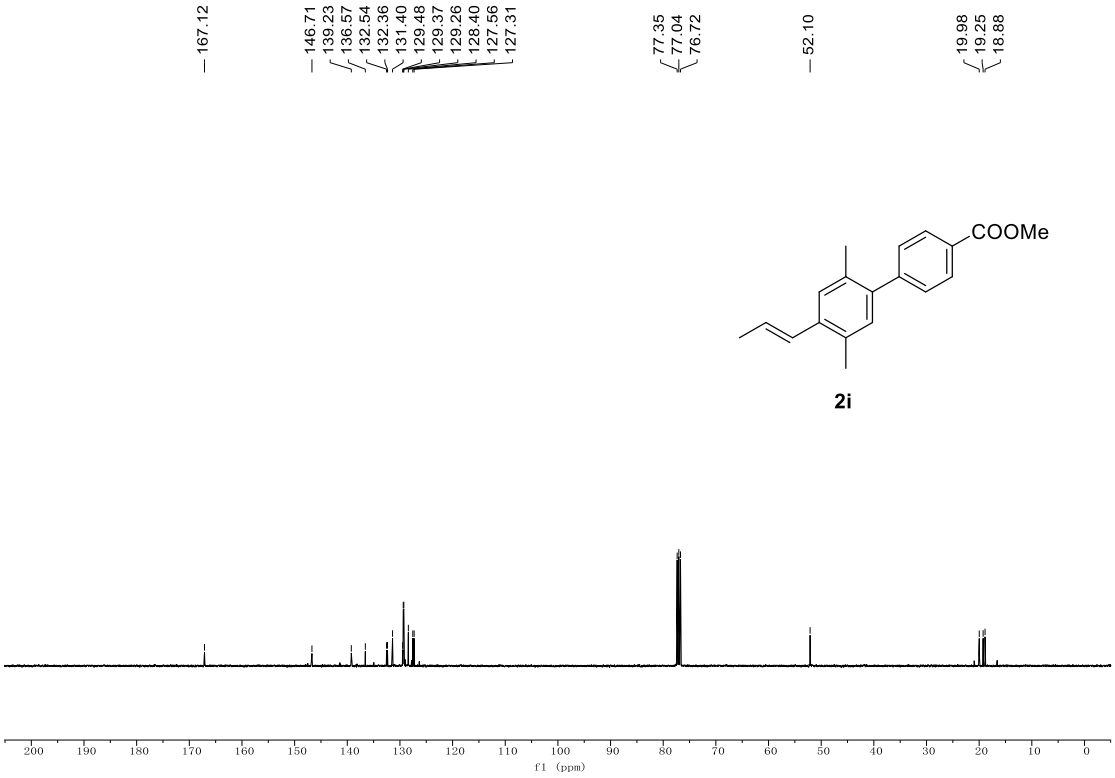


Methyl (E)-2',5'-dimethyl-4'-(prop-1-en-1-yl)-[1,1'-biphenyl]-4-carboxylate (2i)

^{1}H NMR, 400 MHz, $CDCl_3$

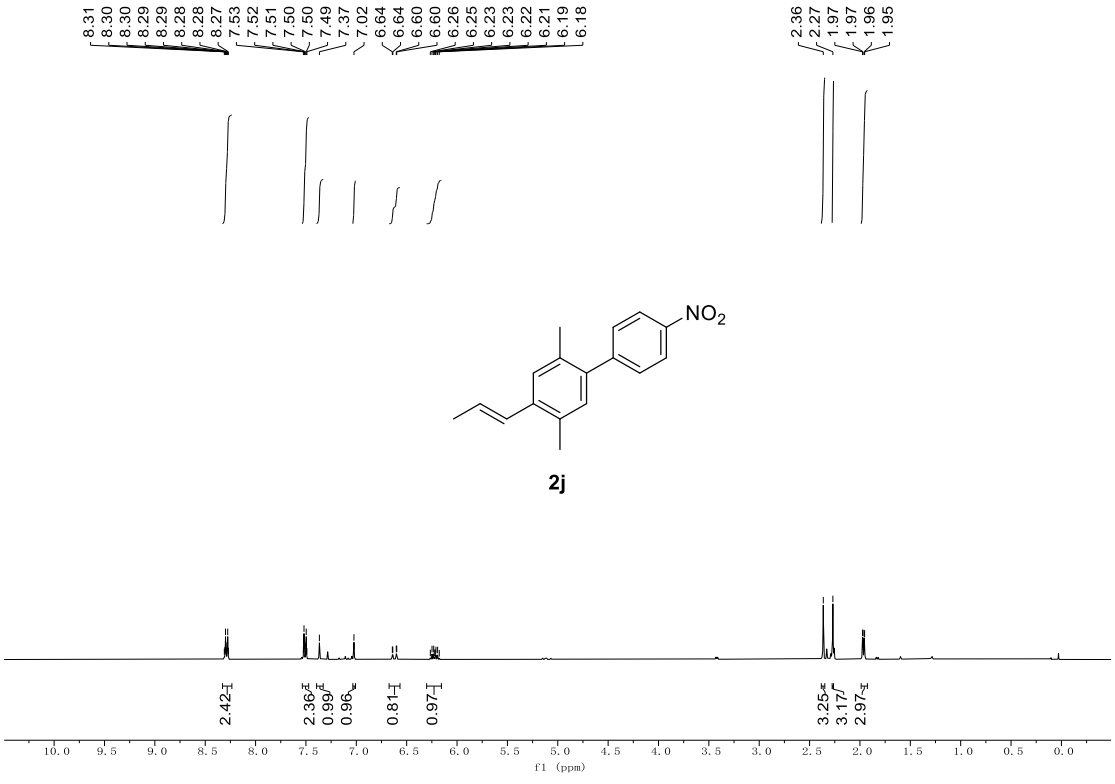


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

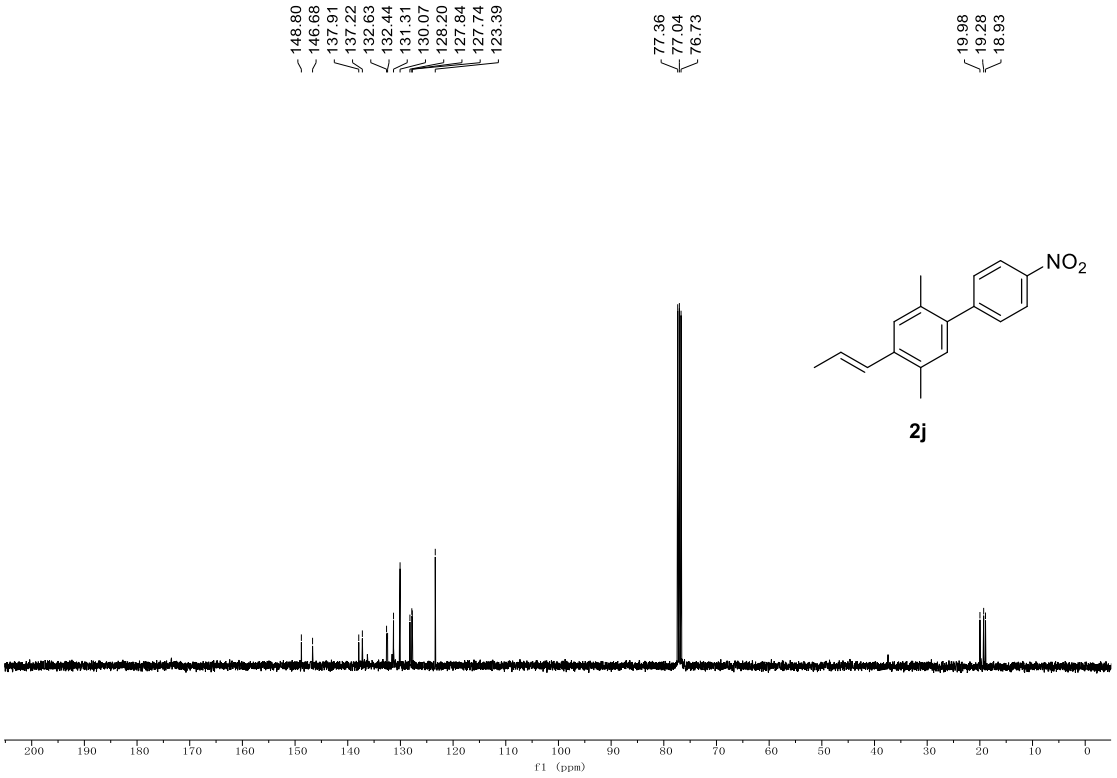


(E)-2,5-Dimethyl-4'-nitro-4-(prop-1-en-1-yl)-1,1'-biphenyl (2j)

^{1}H NMR, 400 MHz, $CDCl_3$

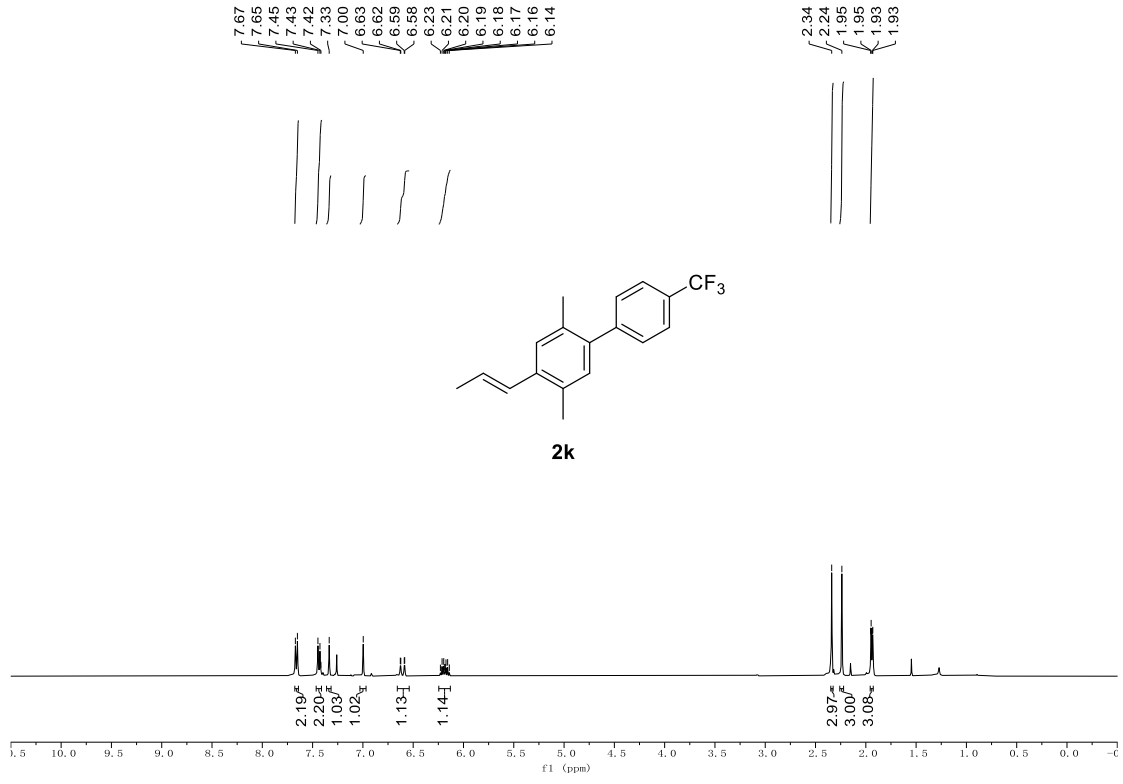


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

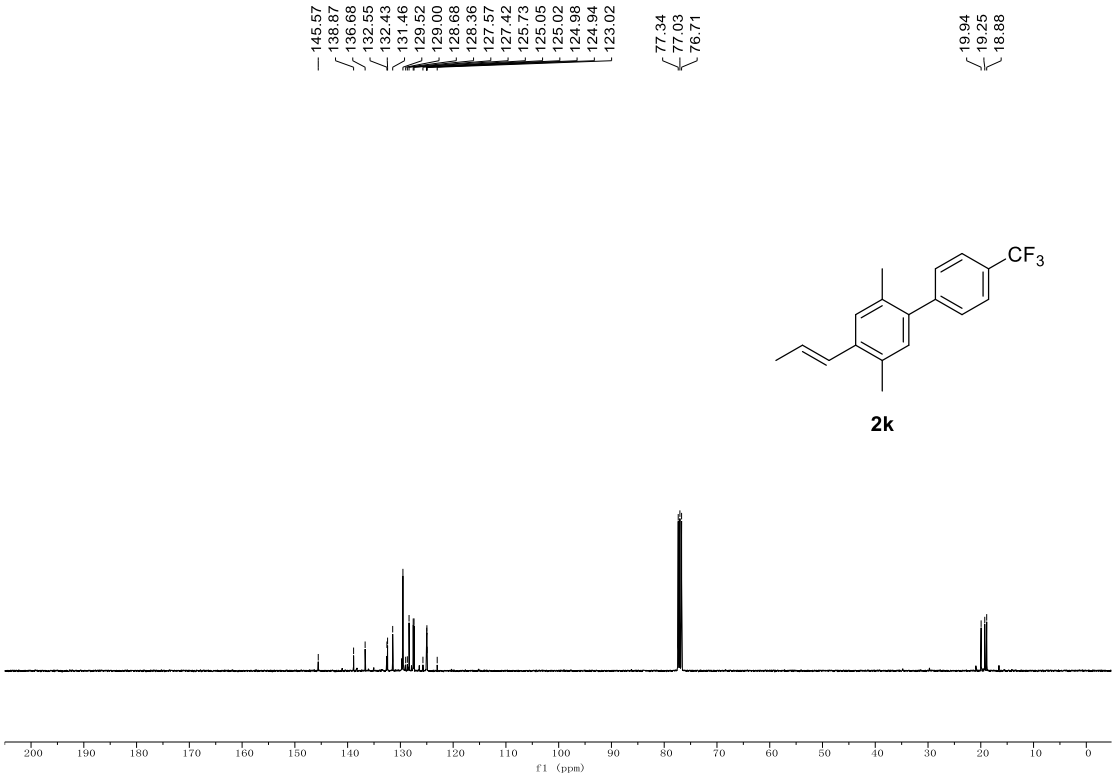


(E)-2,5-Dimethyl-4-(prop-1-en-1-yl)-4'-(trifluoromethyl)-1,1'-biphenyl (2k)

^{1}H NMR, 400 MHz, $CDCl_3$

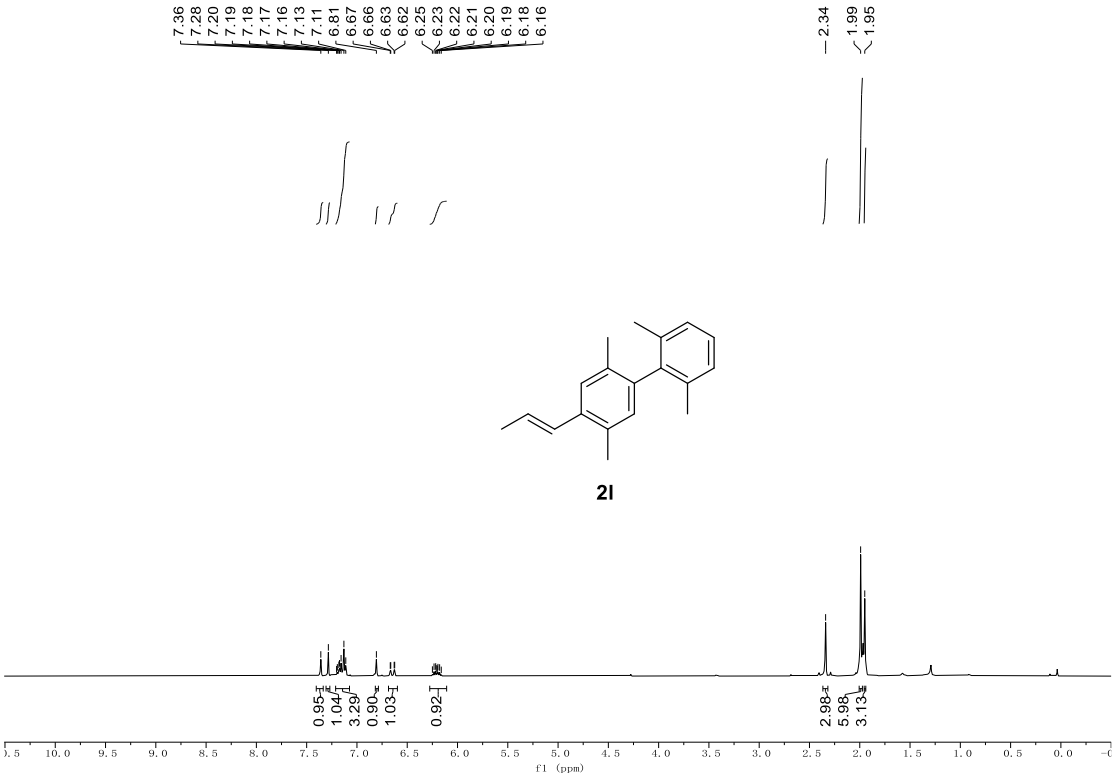


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

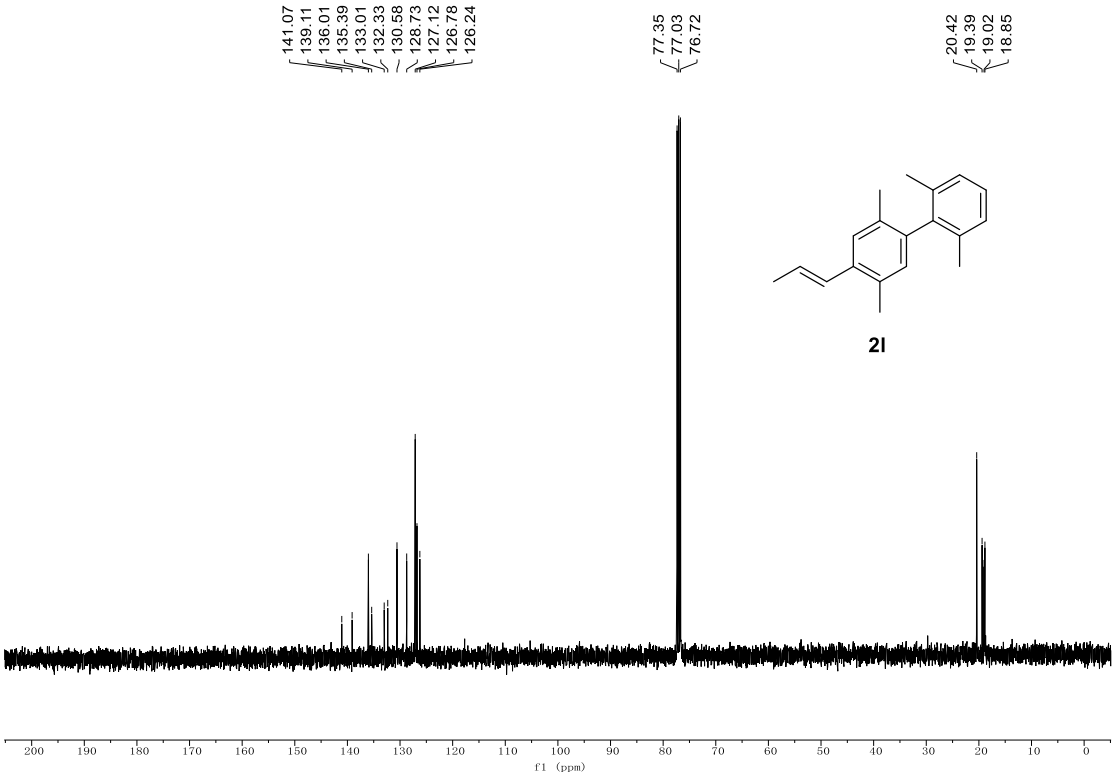


(E)-2,2',5,6'-Tetramethyl-4-(prop-1-en-1-yl)-1,1'-biphenyl (2l)

^{1}H NMR, 400 MHz, $CDCl_3$

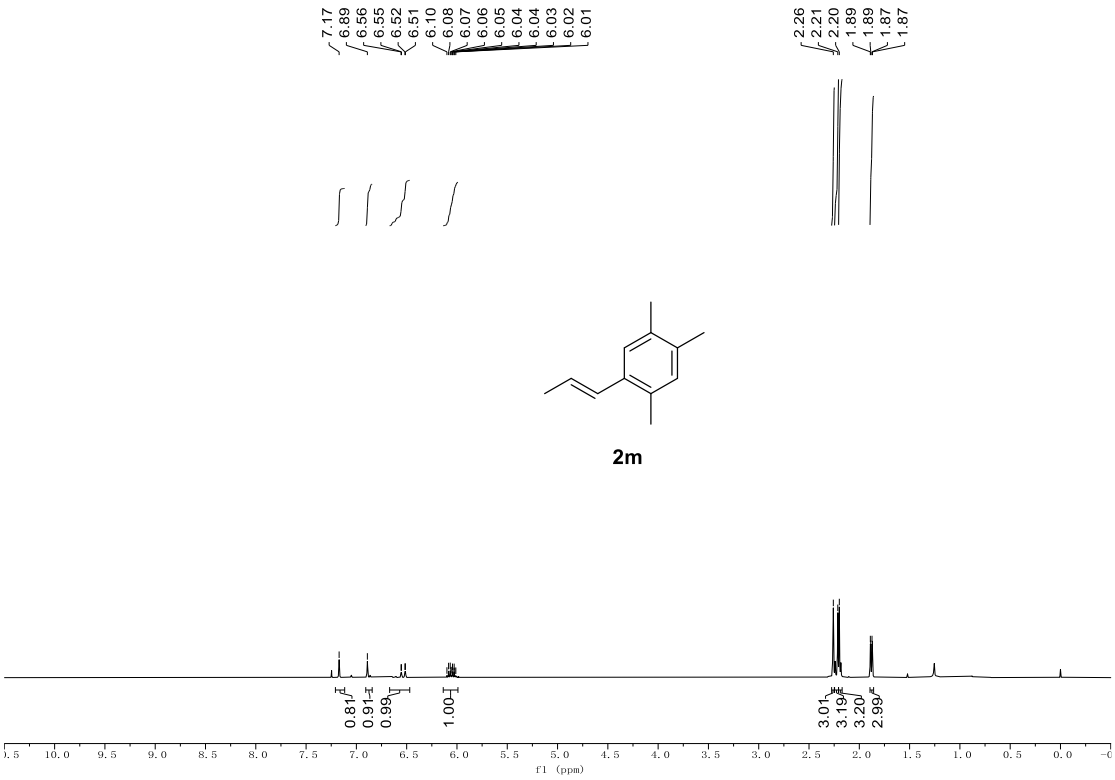


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

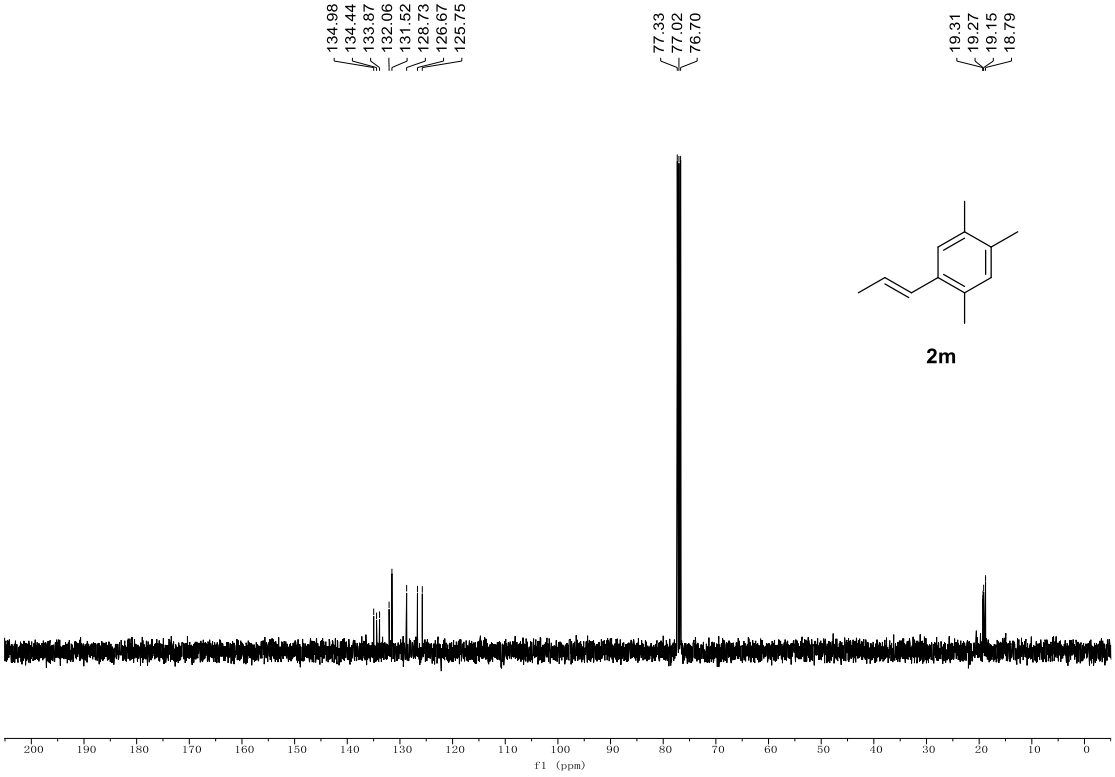


(E)-1,2,4-Trimethyl-5-(prop-1-en-1-yl)benzene (2m)

^{1}H NMR, 400 MHz, $CDCl_3$

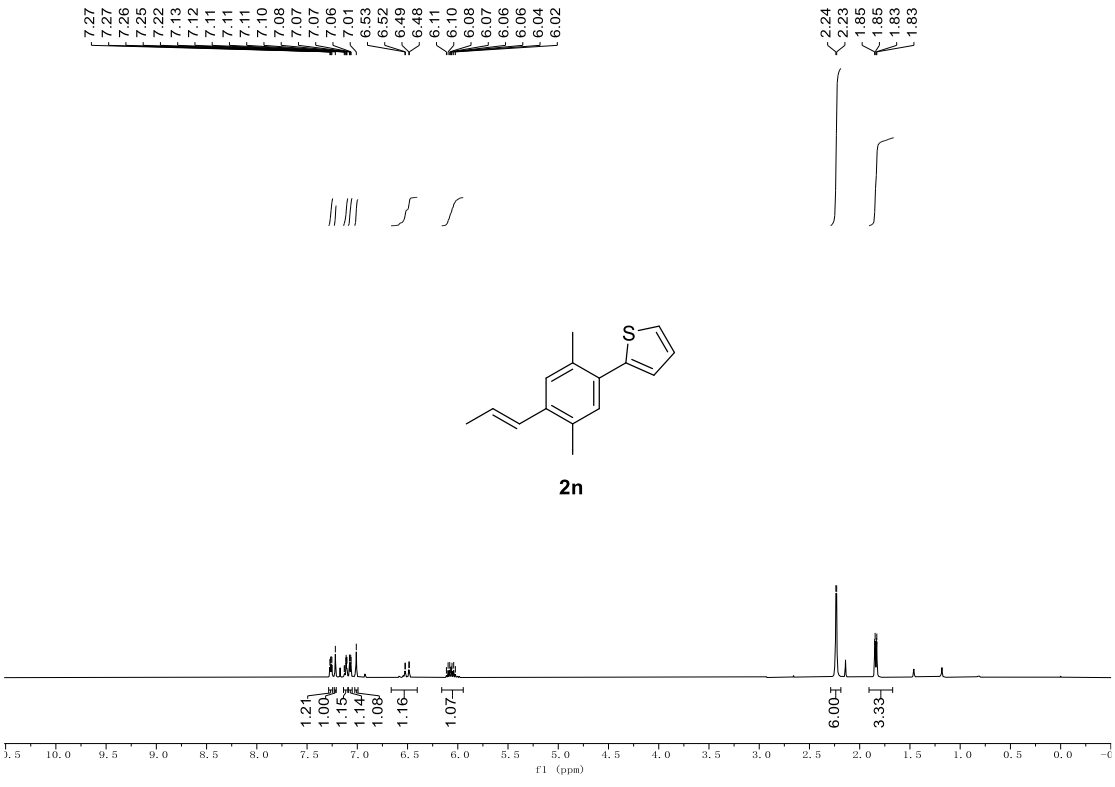


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

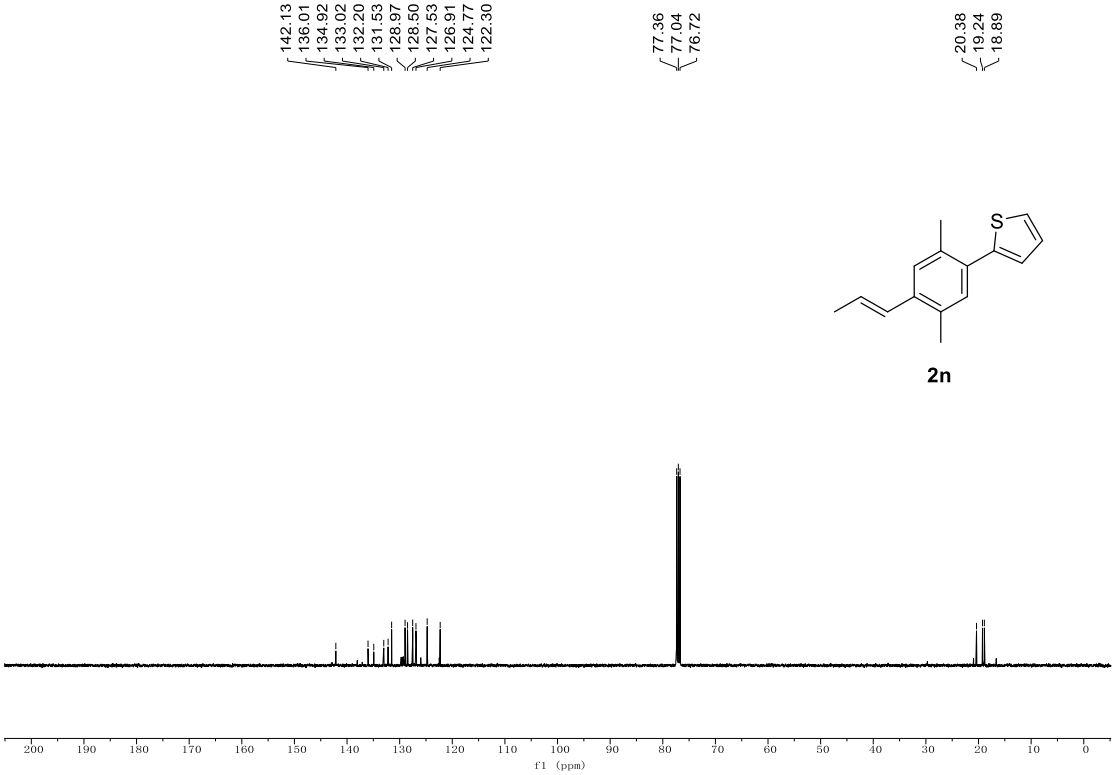


(E)-2-(2,5-Dimethyl-4-(prop-1-en-1-yl)phenyl)thiophene (2n)

^{1}H NMR, 400 MHz, $CDCl_3$



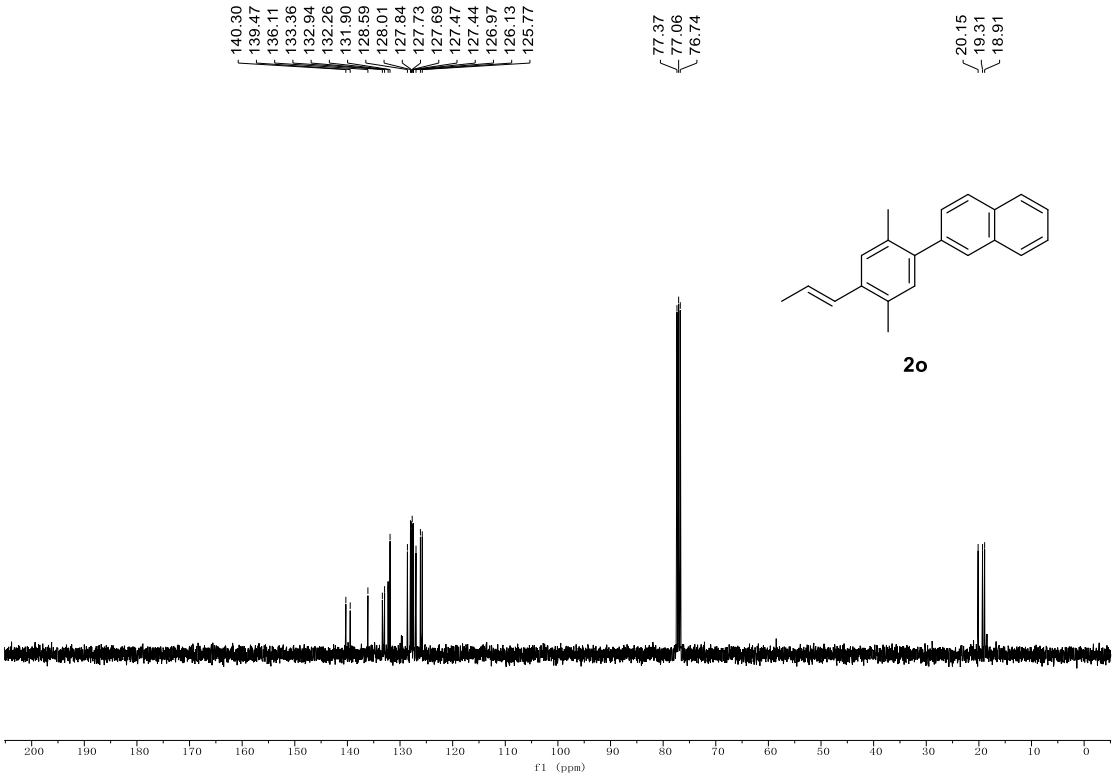
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$



(E)-2-(2,5-Dimethyl-4-(prop-1-en-1-yl)phenyl)naphthalene (2o)

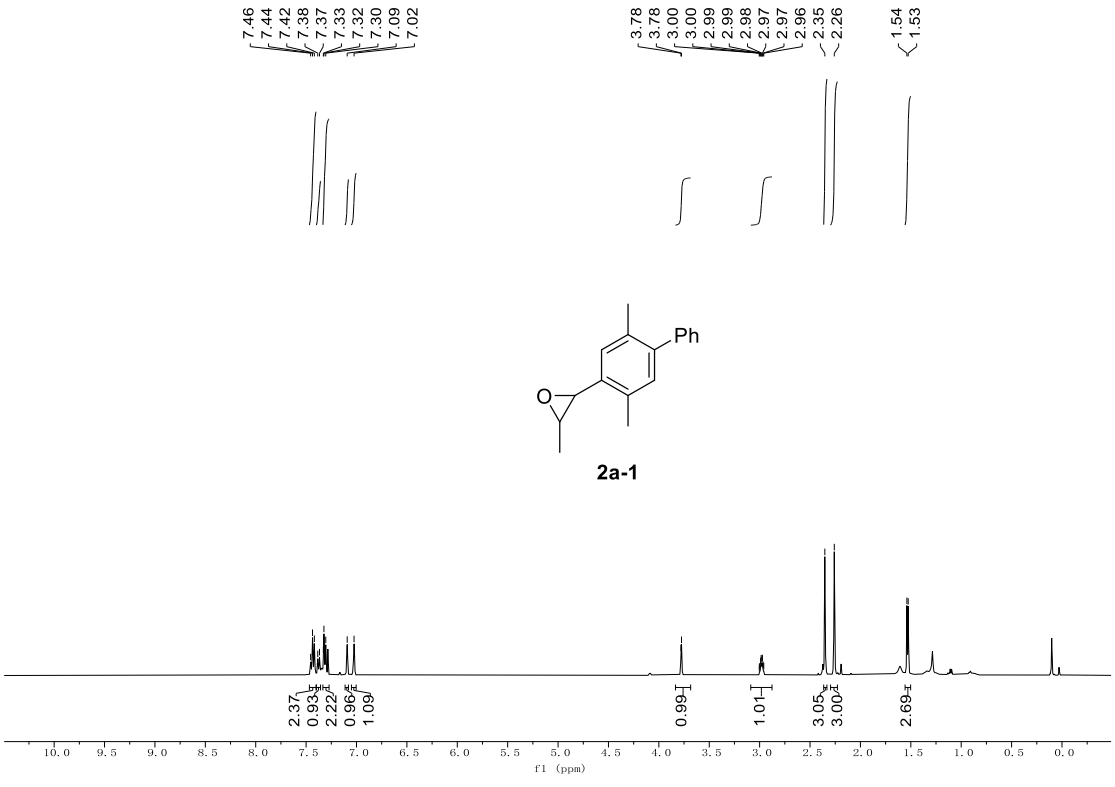
^{1}H NMR, 400 MHz, $CDCl_3$

$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

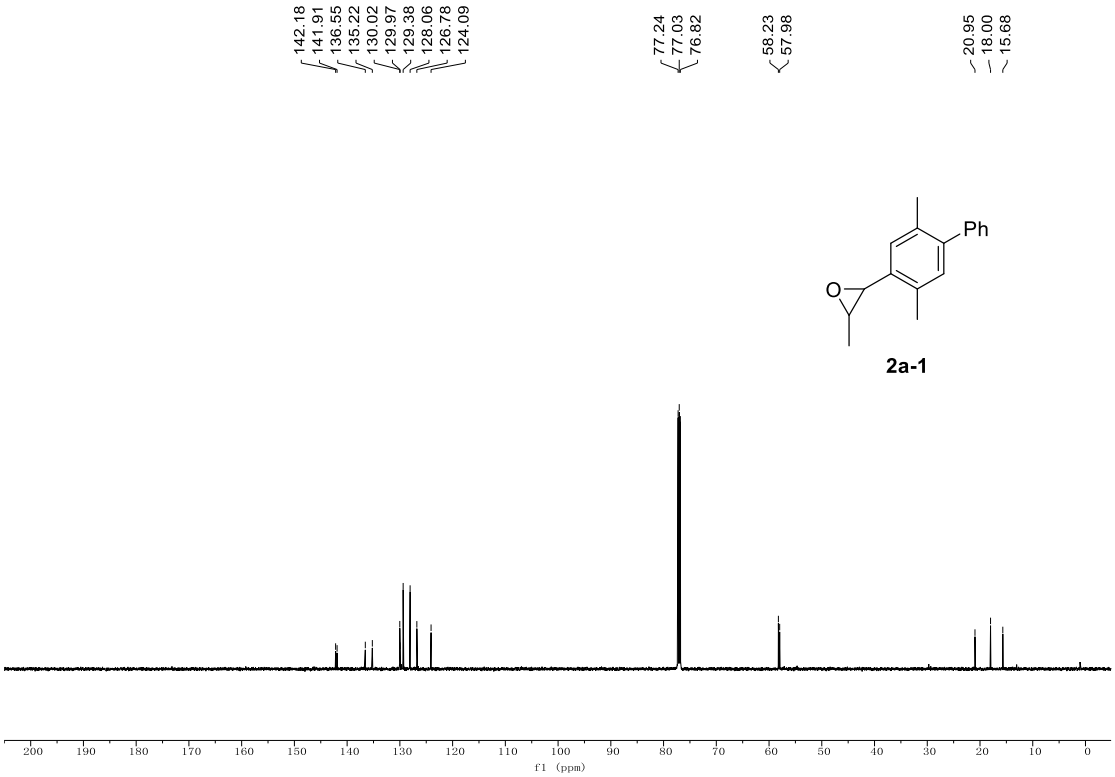


2-(2,5-Dimethyl-[1,1'-biphenyl]-4-yl)-3-methyloxirane (2a-1)

^{1}H NMR, 400 MHz, $CDCl_3$

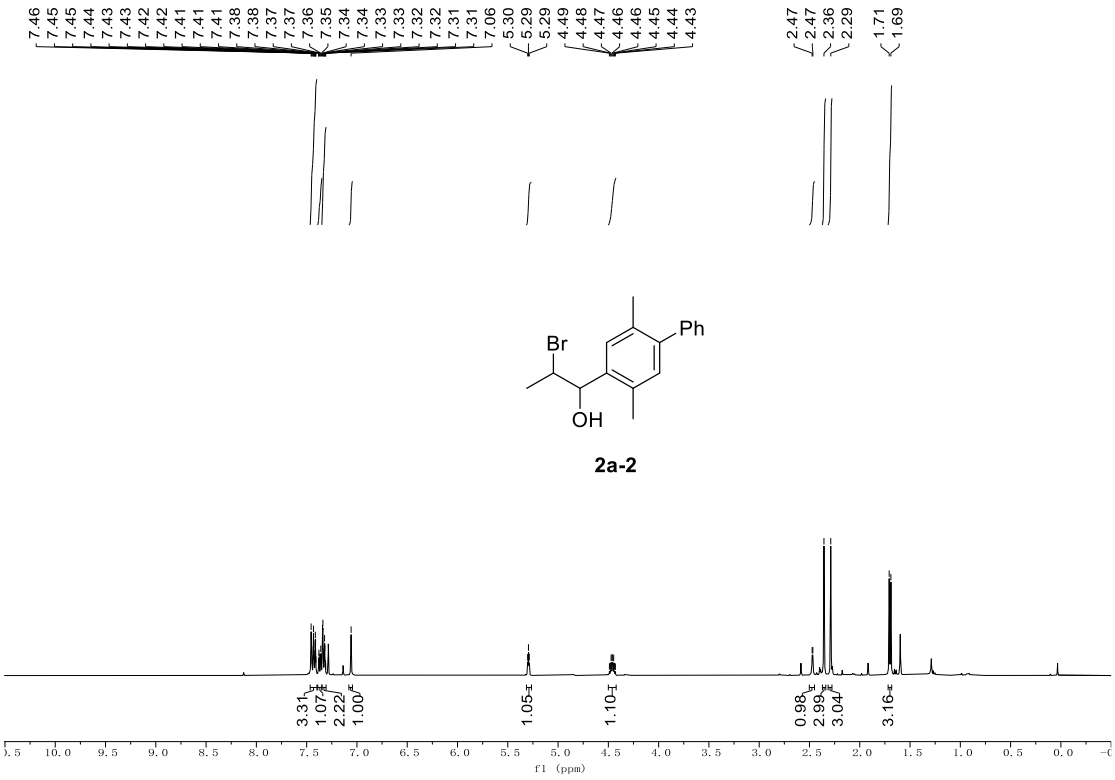


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

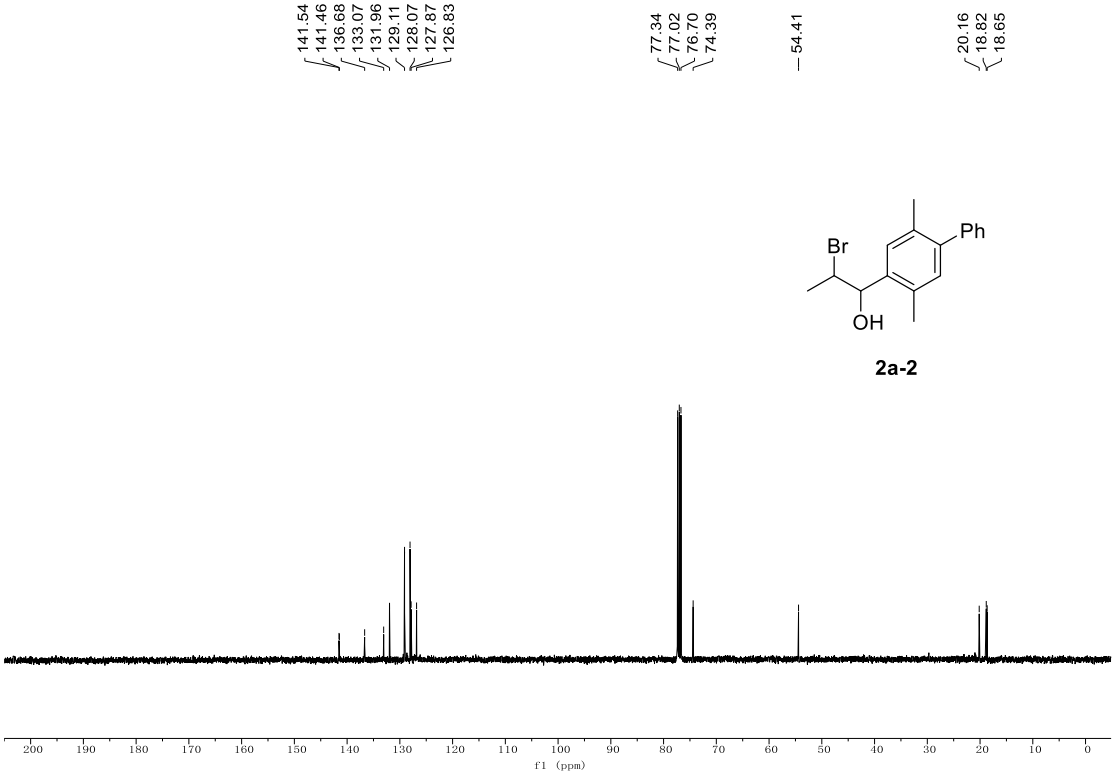


2-Bromo-1-(2,5-dimethyl-[1,1'-biphenyl]-4-yl)propan-1-ol (2a-2)

^{1}H NMR, 400 MHz, $CDCl_3$

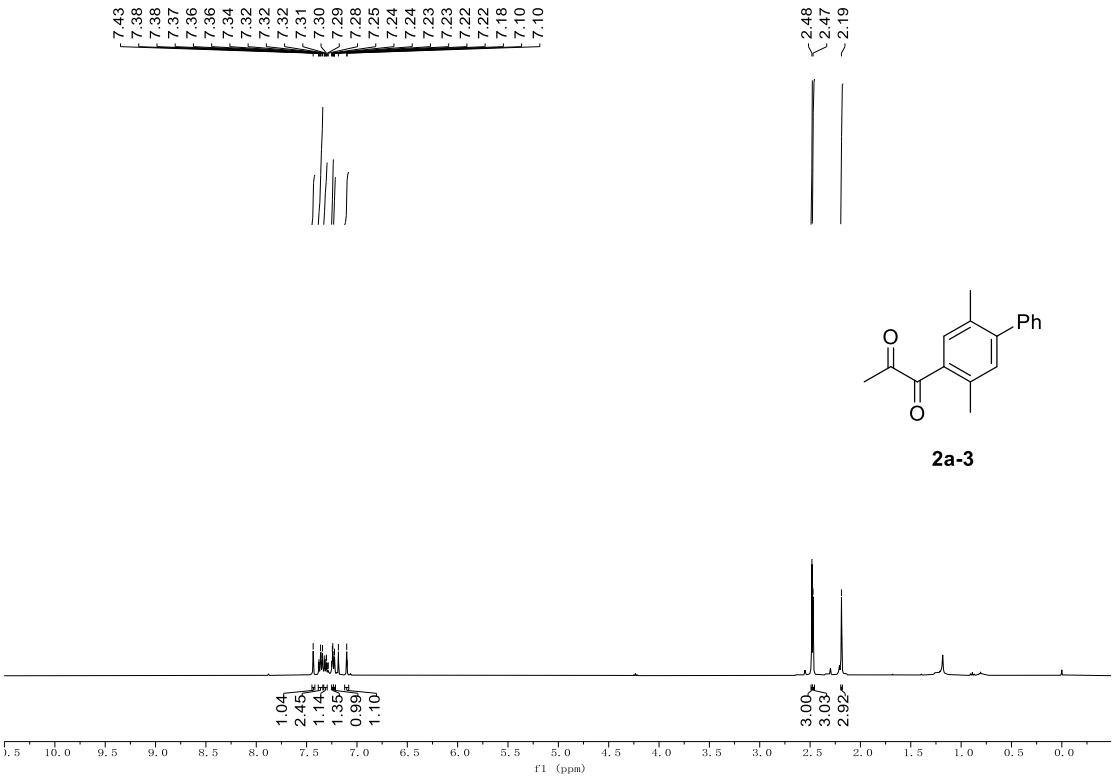


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

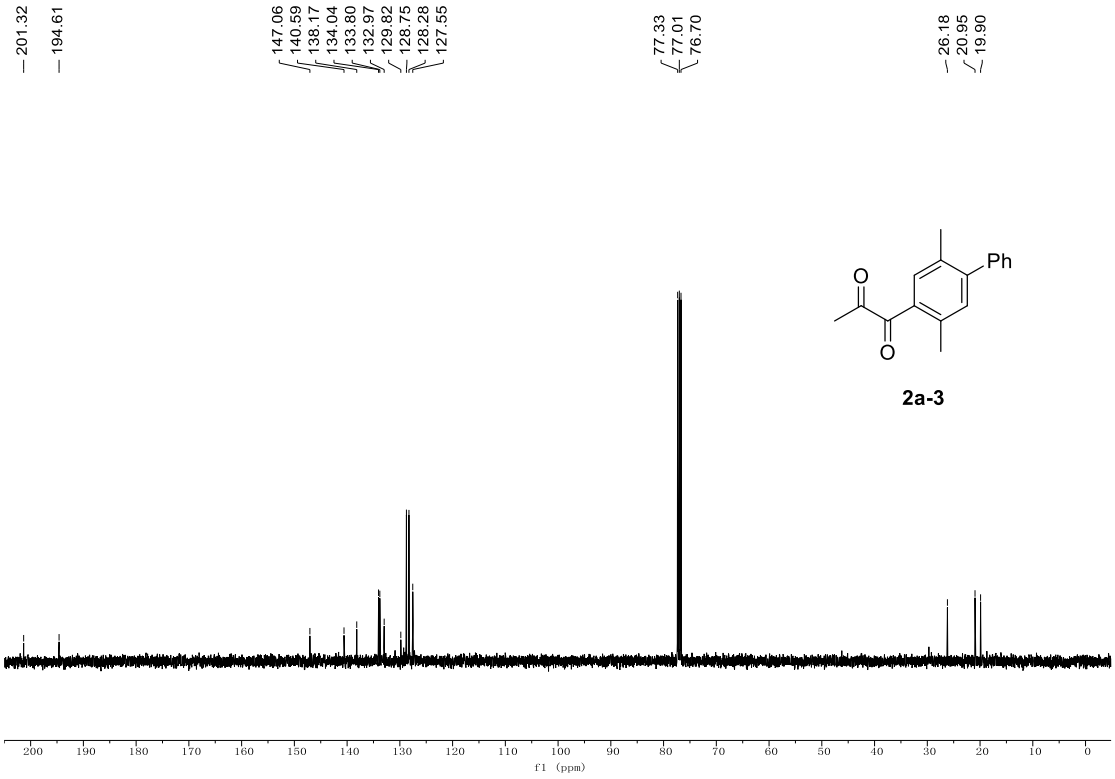


1-(2,5-Dimethyl-[1,1'-biphenyl]-4-yl)propane-1,2-dione (2a-3)

^{1}H NMR, 400 MHz, $CDCl_3$

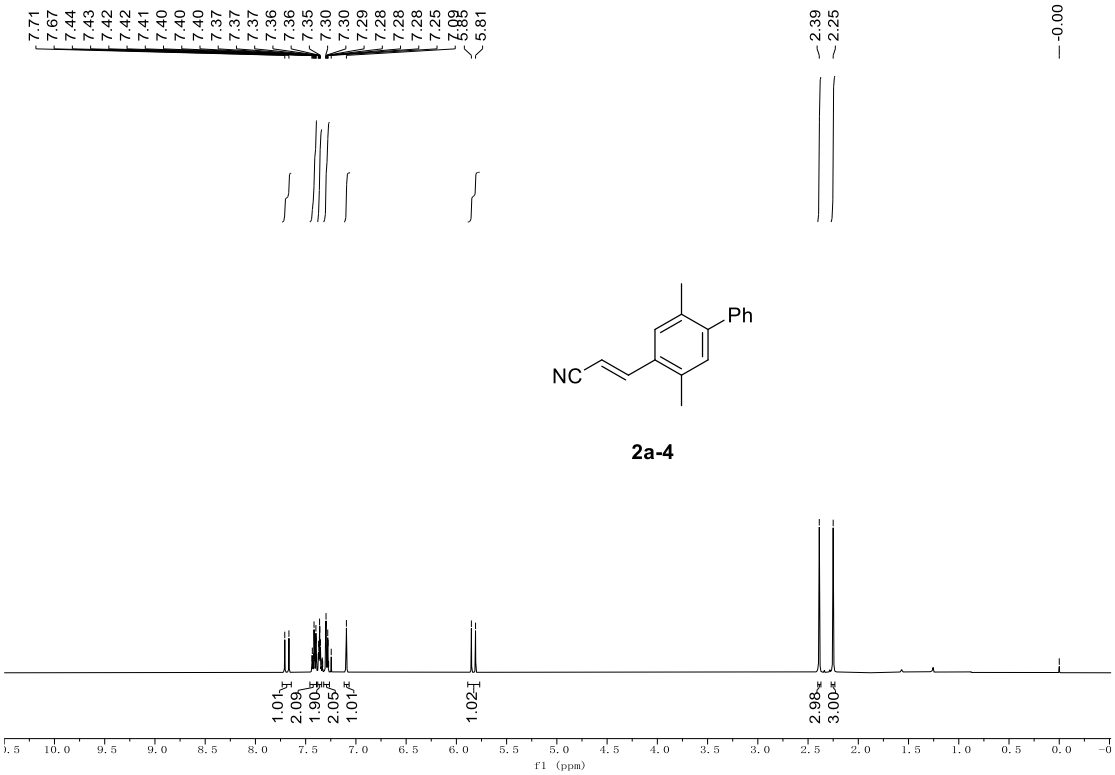


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

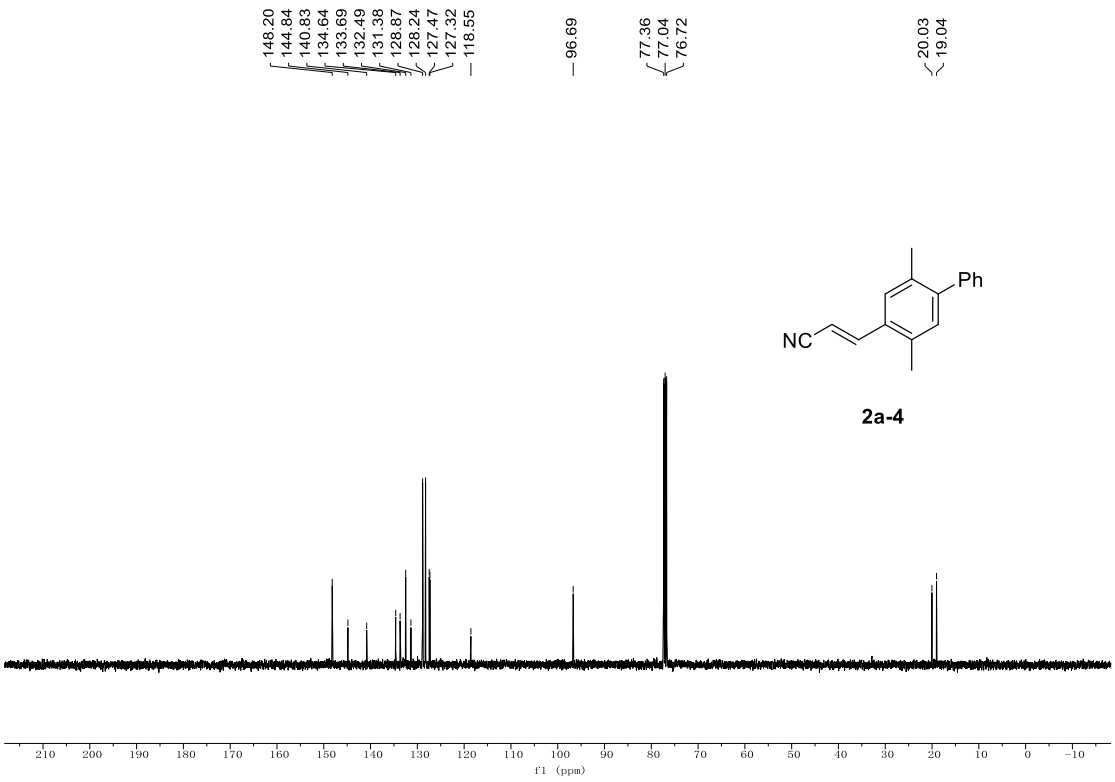


(E)-3-(2,5-Dimethyl-[1,1'-biphenyl]-4-yl)acrylonitrile (2a-4)

^{1}H NMR, 400 MHz, $CDCl_3$

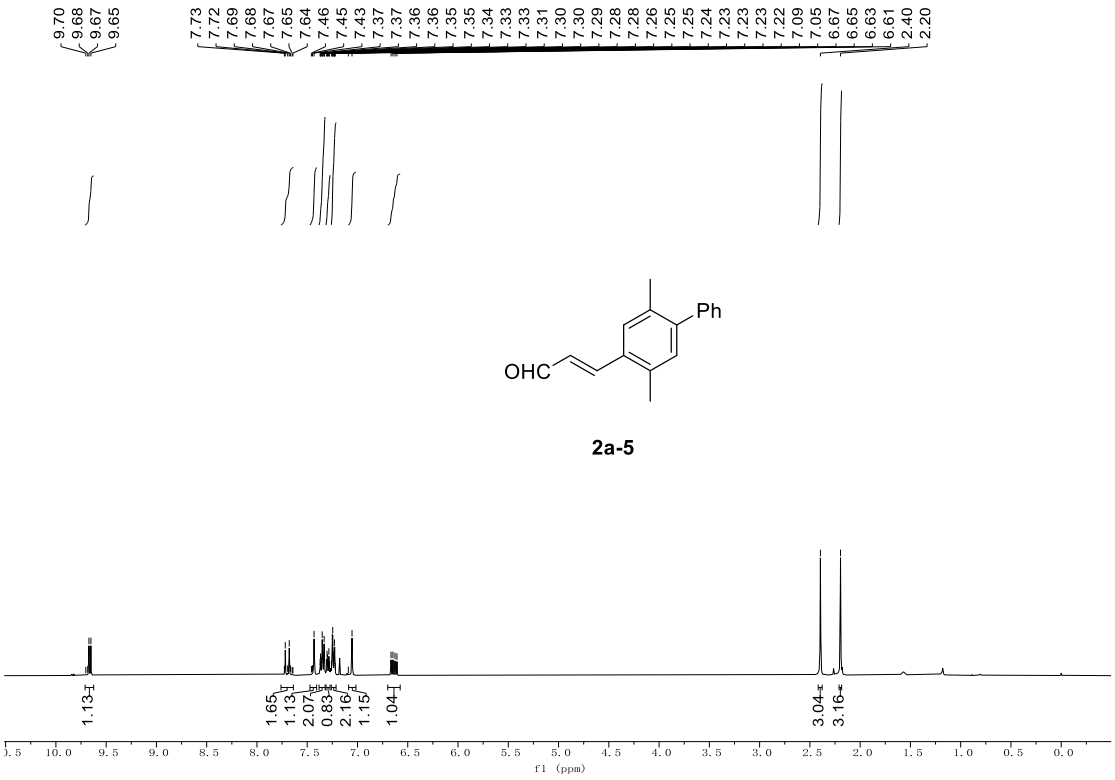


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

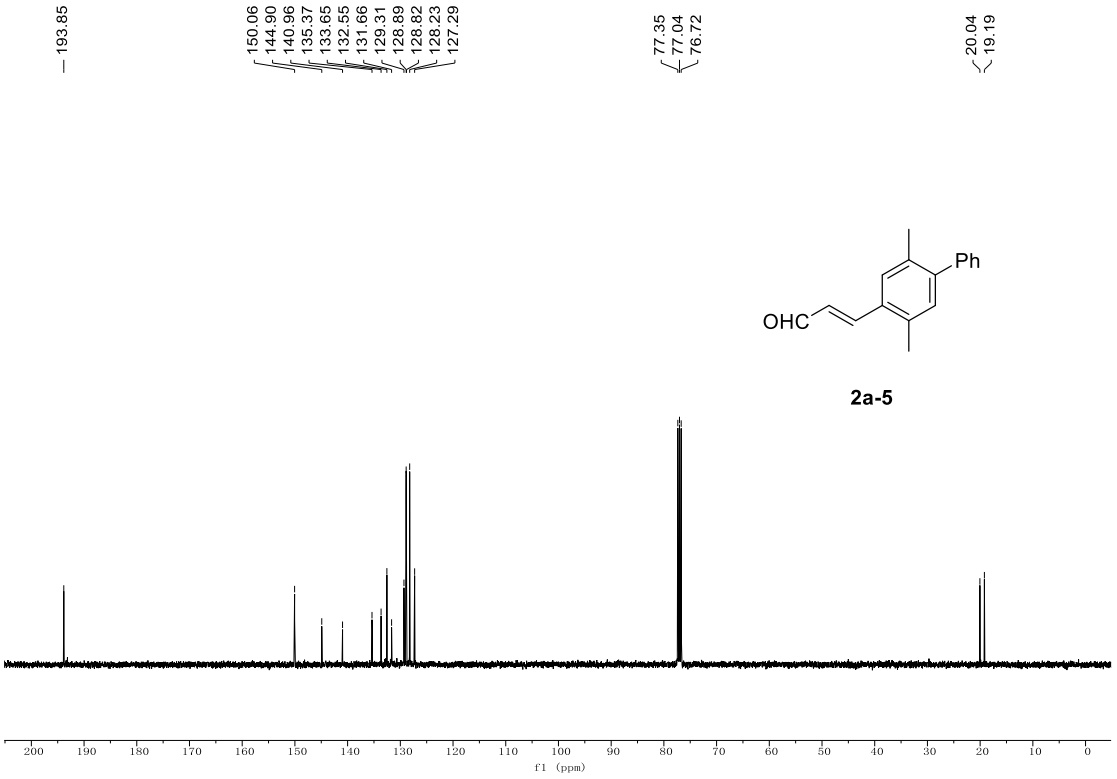


(E)-3-(2,5-Dimethyl-[1,1'-biphenyl]-4-yl)acrylaldehyde (2a-5)

^{1}H NMR, 400 MHz, $CDCl_3$



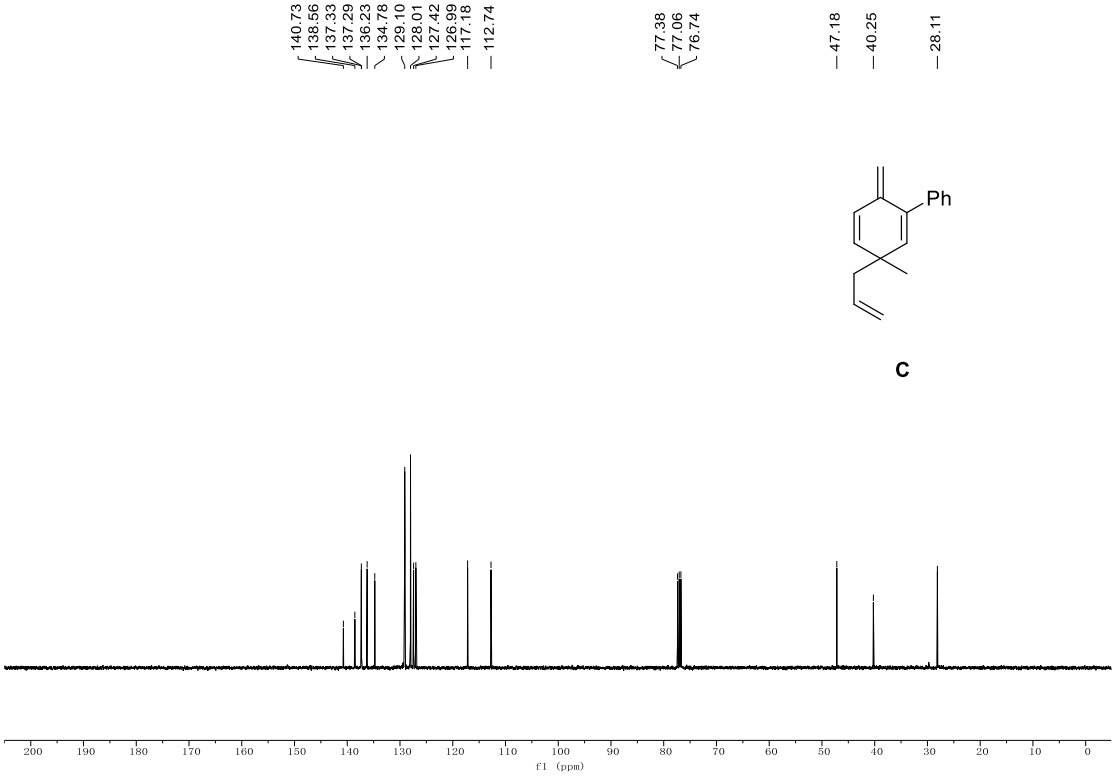
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$



5-Methyl-2-methylene-5-(prop-1-en-1-yl)-2,5-dihydro-1,1'-biphenyl (C)

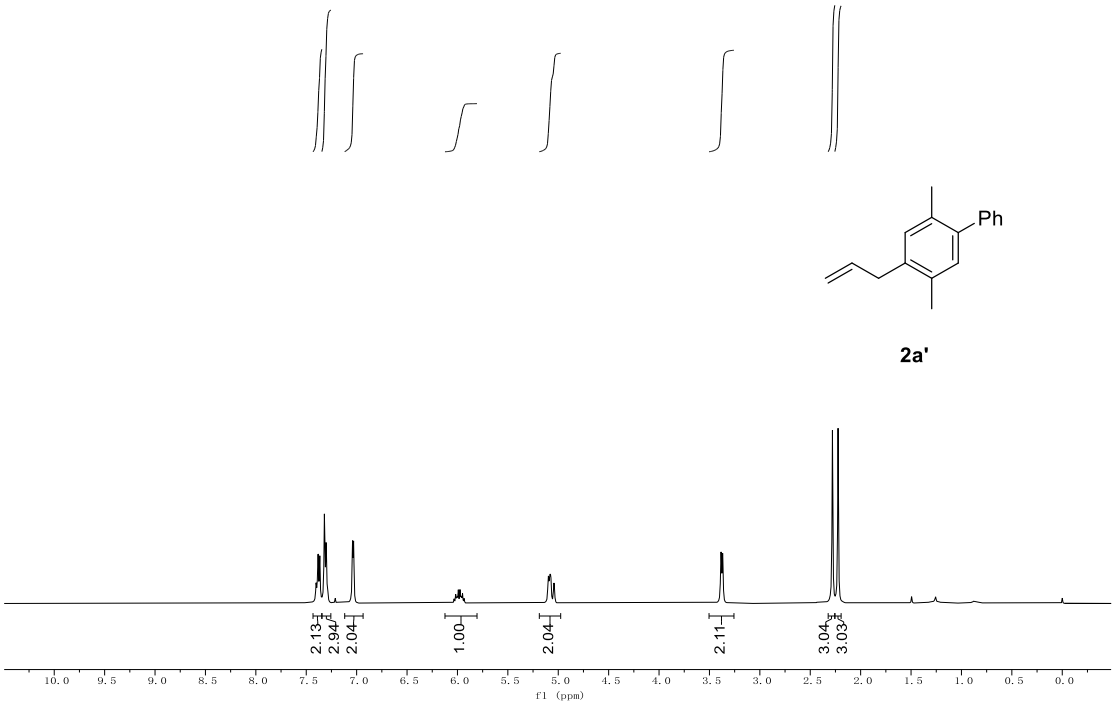
^{1}H NMR, 400 MHz, $CDCl_3$

$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

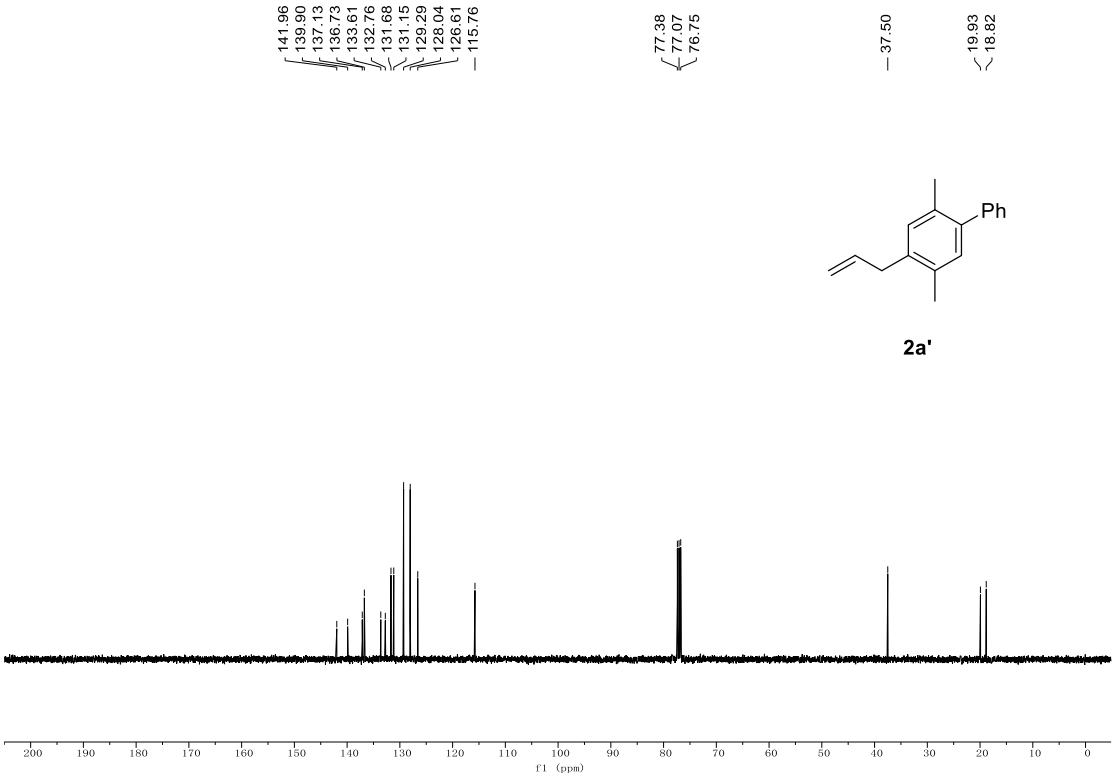


4-Allyl-2,5-dimethyl-1,1'-biphenyl (2a')

^{1}H NMR, 400 MHz, $CDCl_3$

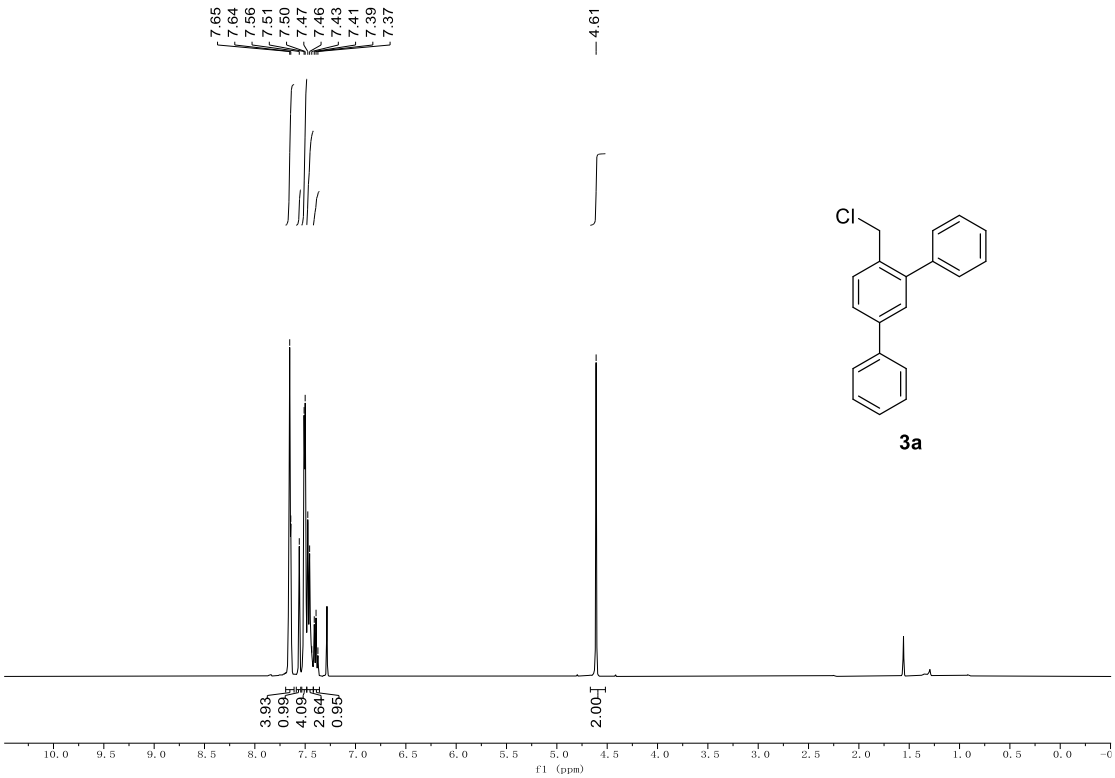


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

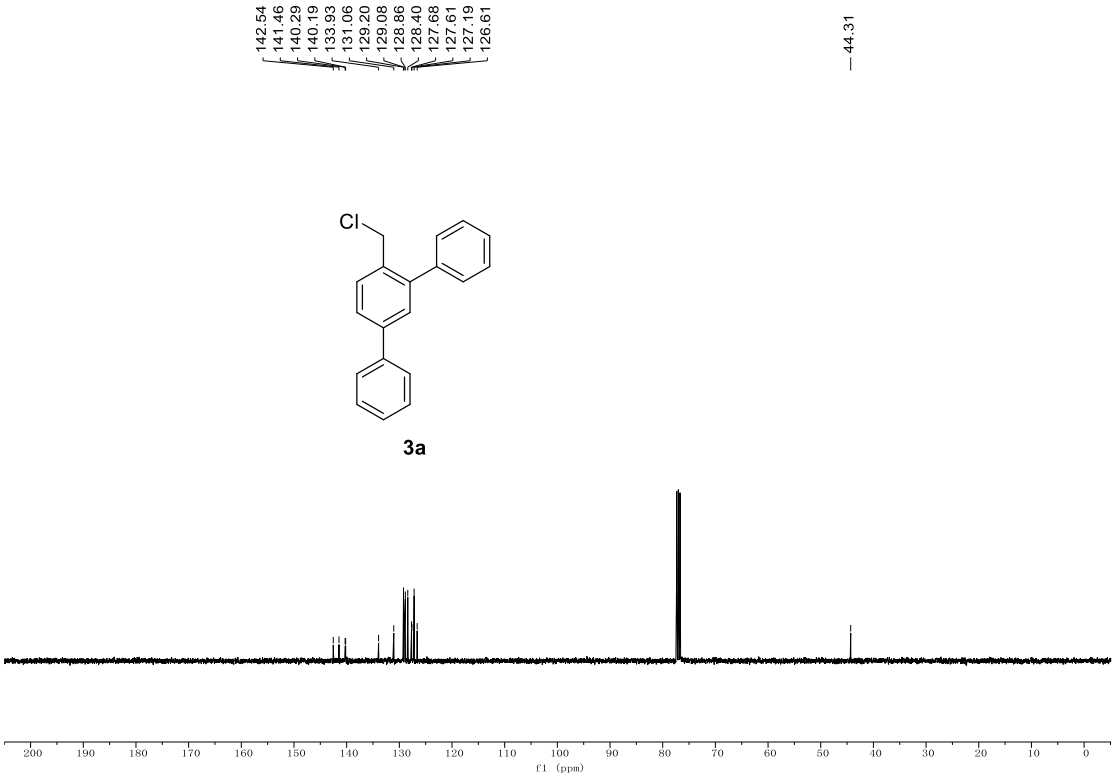


4'-(chloromethyl)-1,1':3',1''-terphenyl (3a)

^{1}H NMR, 400 MHz, $CDCl_3$

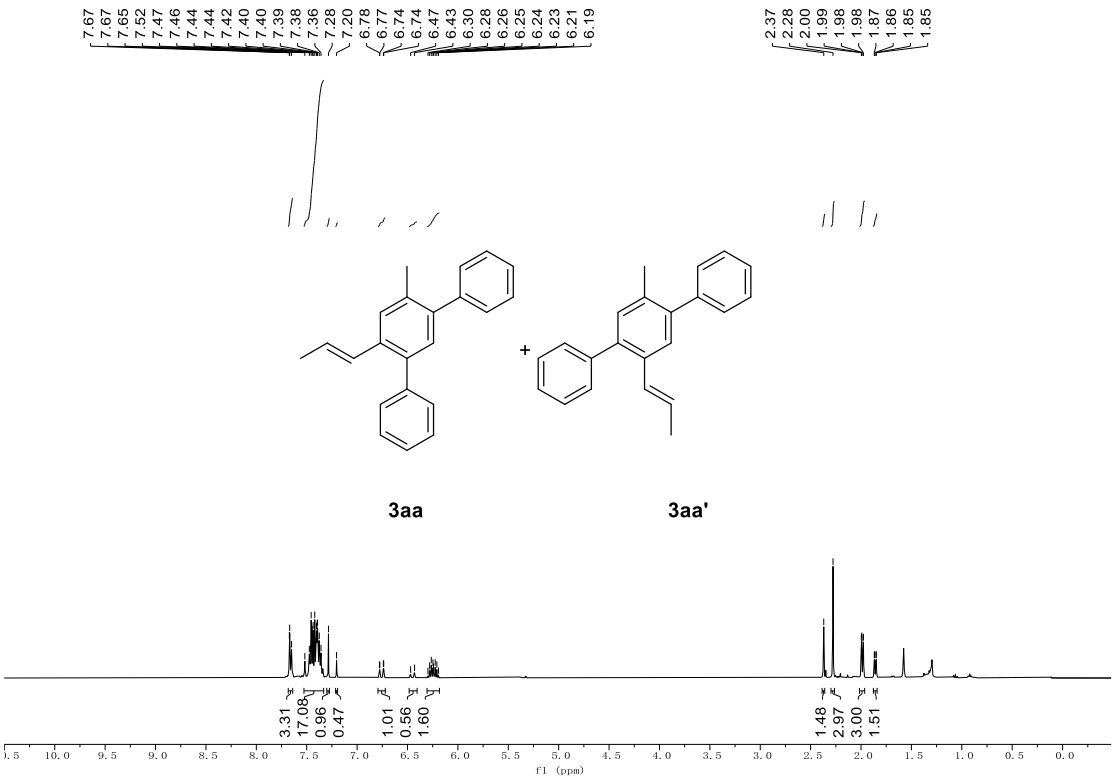


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$

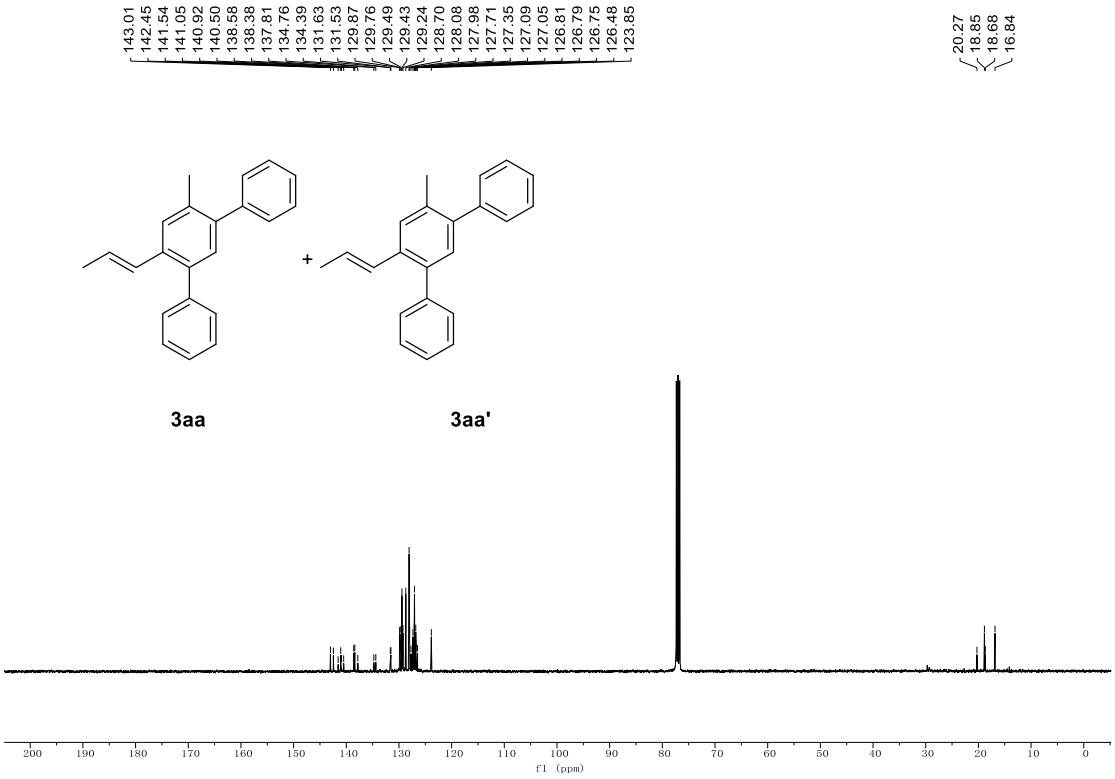


(E)-4'-methyl-6'-(prop-1-en-1-yl)-1,1':3',1''-terphenyl (3aa) and (E)-3-(6'-methyl-[1,1':3',1''-terphenyl]-4'-yl)allylium (3aa')

^{1}H NMR, 400 MHz, $CDCl_3$



$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$



8. References

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