Electronic Supplementary Information for

Palladium Polyaniline Complex: A Simple and Efficient Catalyst for Batch and Flow Suzuki-Miyaura Cross-couplings

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General information

Chemicals and solvents were all purchased and used as received. Products were all purified by column chromatography. A ThermoFisher Nicolet iS50 IR spectrometer was used to determine infrared (IR) spectrums. Field emission scanning electron microscopy (FE-SEM) image was determined on Zeiss Supra55 field emission scanning electron microscope. The Agilent 7700X inductively coupled plasma spectrometer was used for the ICP-OES study. The gel permeation chromatography analyses were performed on a Waters1515 GPC system, which was calibrated with polystyrene standards. $CDCl_3$ or DMSO-*d6* as the solvent and Me_4Si as the internal standard were used to record ^1H and ^{13}C NMR spectrums on a QOne Instruments Quantum-I Plus 400M spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C NMR spectroscopy). Chemical shifts for ^1H and ^{13}C NMR were related to Me_4Si (0 ppm) and *J*-values were displayed in Hz. An Agilent 7890B-5977B spectrometer or a Thermo Fisher Trace ISQ were used to record MS spectra. A Waters ACQUITYUPLC H-Class/Xevo G2-XS Qtof spectrometer was used to record HR-MS spectra.

The preparation of Pd@PANI

In 100 mL of aqueous HBr (1 mol/L), aniline (931 mg, 10 mmol) and 160 μL of $PdCl_2$ aqueous solution {$PdCl_2$ (177.3 mg, 1 mmol) was dissolved in 10 mL of aqueous HBr (1 mol/L)} were added at room temperature and stirred for 5 min. Then, 21 mL of H_2O_2 (3.25 wt.%) was added and the mixture was stirred for 8-64 hours at room temperature. The pH of the solution was subsequently adjusted to 7 by adding 1 mol/L of NaOH aqueous solution. Centrifugation was used to isolate the Pd@PANI which was subsequently washed with deionized water and dried in a vacuum at 60 °C for 12 hours.

Catalyst evaluation through Suzuki-Miyaura cross-couplings

In a sealed tube charged with N_2, Pd@PANI catalyst (1.5 mg), iodobenzene (0.5 mmol), 4-tolylboronic acid (0.5 mmol), and K_2CO_3 (1.0 mmol) were added and then added EtOH (2 mL) as solvent. Then, the mixture was stirred for 12 hours at 100 ℃. The tube was cooled to room temperature, and 60 μL of *n*-dodecane was added as an internal standard for GC-MS analysis.

Characterization of Pd@PANI

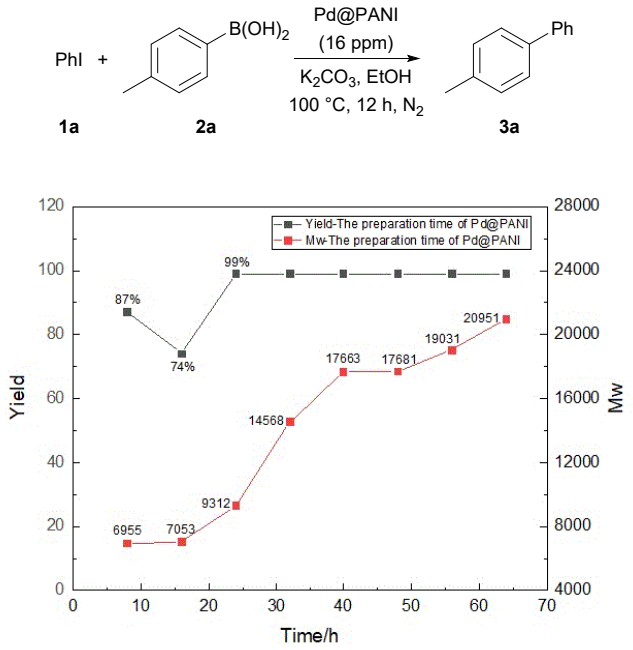


Fig. S1 Dependence of yield for the Suzuki reactions and Mw for polyaniline on the preparation time for Pd@PANI.

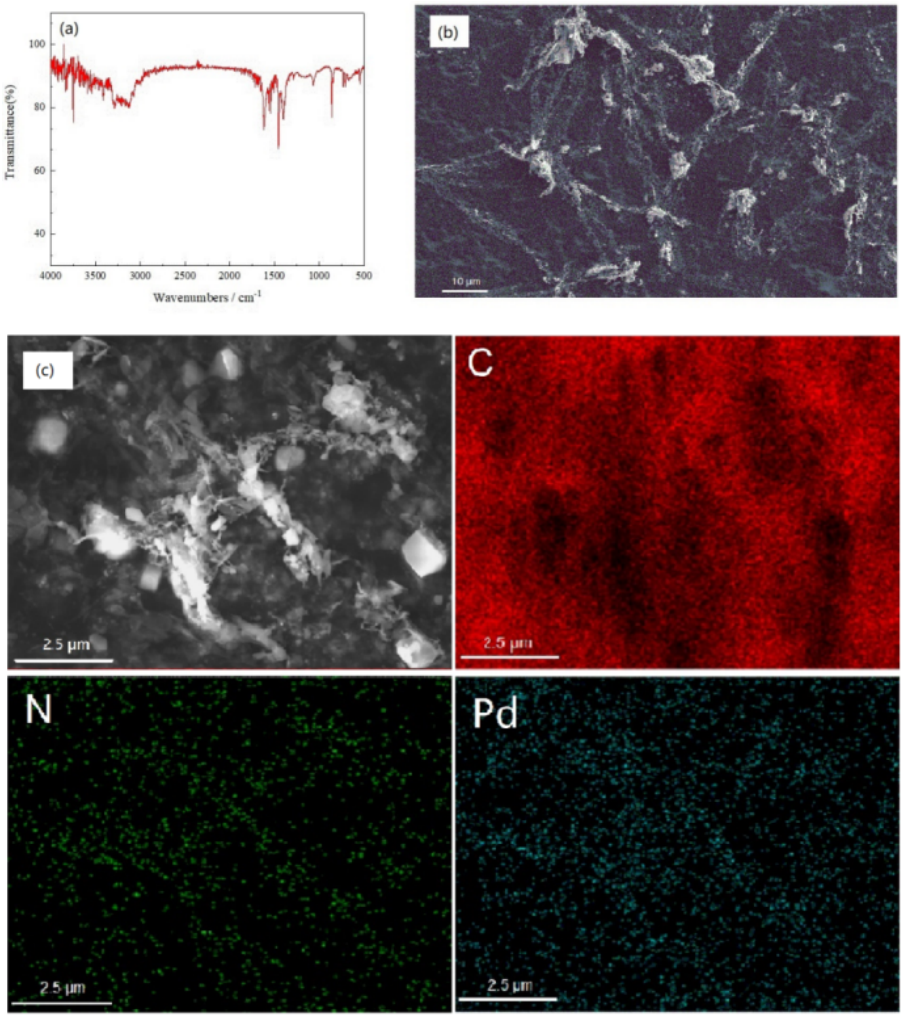
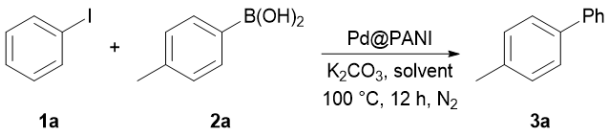


Fig. S2 (a) FT-IR spectrum, (b) FE-SEM image and (c) EDS elemental mapping analysis of Pd@PANI.

Optimization of the reaction conditions in batch

According to the preliminary exploration, our Pd@ PANI showed excellent catalytic activity for Suzuki-Miyaura cross-couplings in the presence of K_2CO_3 in EtOH (Table S1, entry 1). When using ethanol/water (1:1) instead of ethanol as solvent (Table S1, entry 2), the yield of the target product decreased slightly. Satisfactorily, the dosage of K_2CO_3 was reduced to 1 equivalent providing the target product with 99% GC yield and 97% isolated yield (Table S1, entry 3). Further reducing the amount of base (Table S1, entry 4) or using water as the solvent (Table S1, entry 5) resulted in a significant decrease in yield. In addition, we used TMSOK instead of K_2CO_3 as base and the reaction provided the desired product with 86% yield in ethanol/water (1:1) (Table S1, entry 6). Encouragingly, the reaction was performed in the presence of TMSOK as base and *n*-propanol as solvent affording the corresponding product in 99% yield (Table S1, entry 7).

Table S1. Optimization of the reaction conditions in batch[a]



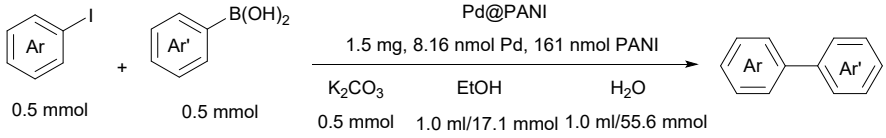
1a **2a** **3a**

Entry	Base/eq.	solvent	Y [%][b]
1	K_2CO_3 (2.0)	EtOH	99
2	K_2CO_3 (2.0)	EtOH/H_2O (1:1)	94
3	K_2CO_3 (1.0)	EtOH/H_2O (1:1)	99(97)[c]
4	K_2CO_3 (0.5)	EtOH/H_2O (1:1)	48
5	K_2CO_3 (1.0)	H_2O	66
6	TMSOK (1.0)	EtOH/H_2O (1:1)	86
7	TMSOK (1.0)	*n*-PrOH	99

[a] 0.5 mmol of **1a**, 0.5 mmol of **2a**, Pd@ PANI (16 ppm, 1.5 mg, 0.0579 wt%), 0.25-1.0 mmol of base and 2 mL of solvent were employed; the reactions were conducted in a sealed tube. [b] GC yield. [c] Isolated yield.

The example calculation for molecular ppm

Scheme S1 Suzuki-Miyaura Cross-coupling Reaction of Aryl Iodides



n(Pd) = (1.5 mg * 579 mg/kg) / (106.4 g/mol) = 8.16 * 10^{-9} mol

Note: The Pd@PANI contained 579 mg/kg of palladium was detected through ICP analysis.

n(PANI) = [1.5 mg - (1.5 mg * 579 mg/kg)] / (9312 g/mol) = 161 * 10^{-9} mol

Note: The molecular weight of polyaniline was detected through GPC analysis.

n(EtOH) = (1.0 ml * 0.789 g/ml) / (46.07 g/mol) = 0.0171 mol

n(H_2O) = (1.0 ml * 0.998 g/ml) / (18.01 g/mol) = 0.0554 mol

The total number of moles was calculated from each species including solvent.

(0.0005 + 0.0005 + 0.0005 + 0.0171 + 0.0554 + 8.16*10^{-9} + 161*10^{-9}) mol = 0.0740 mol

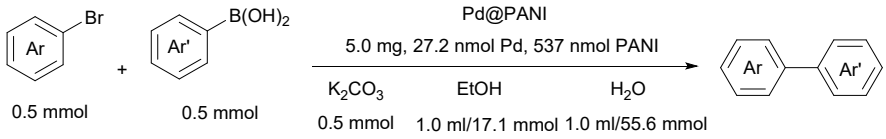
Then, the mole contribution of catalyst compared to the total number of moles was calculated:

(8.16 * 10^{-9} mol) / (0.0740 mol) =110 * 10^{-9} = 1.10 * 10^{-7}

Multiplication by 1 × 10^6 gives the molecular ppm of (pre)catalyst:

1.10 * 10^{-7} × 10^6 = 0.11 ppm

Scheme S2 Suzuki-Miyaura Cross-coupling Reaction of Aryl Bromides



n(Pd) = (5.0 mg * 579 mg/kg) / (106.4 g/mol) = 27.2 * 10^{-9} mol

Note: The Pd@PANI contained 579 mg/kg of palladium was detected through ICP analysis.

n(PANI) = [5.0 mg - (5.0 mg * 579 mg/kg)] / (9312 g/mol) = 537 * 10^{-9} mol

Note: The molecular weight of polyaniline was detected through GPC analysis.

n(EtOH) = (1.0 ml * 0.789 g/ml) / (46.07 g/mol) = 0.0171 mol

n(H_2O) = (1.0 ml * 0.998 g/ml) / (18.01 g/mol) = 0.0554 mol

The total number of moles was calculated from each species including solvent.

(0.0005 + 0.0005 + 0.0005 + 0.0171 + 0.0554 + 27.2 * 10^{-9} + 537 * 10^{-9}) mol = 0.0740 mol

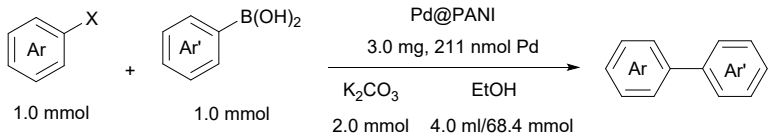
Then, the mole contribution of catalyst compared to the total number of moles was calculated:

(27.2 * 10^{-9} mol) / (0.0740 mol) = 368 * 10^{-9} = 3.68 * 10^{-7}

Multiplication by 1 × 10^6 gives the molecular ppm of (pre)catalyst:

3.68 * 10^{-7} × 10^6 = 0.368 ≈ 0.37 ppm

Scheme S3 Suzuki-Miyaura Cross-coupling Reaction (Previous Report)[1]



n(Pd) = (3.0 mg * 0.75%) / (106.4 g/mol) = 211 * 10^{-9} mol

Note: The Pd@PANI contained 0.75% of Pd (weight ratio) was detected through ICP analysis.

Note: The molecular weight of PANI was not reported in the literature[1], so we had to ignore the moles of polyaniline.

n(EtOH) = (4.0 ml * 0.789 g/ml) / (46.07 g/mol) = 0.0684 mol

The total number of moles was calculated from each species including solvent.

(0.001 + 0.001 + 0.002 + 0.0684 + 211 * 10^{-9}) mol = 0.0724 mol

Then, the mole contribution of catalyst compared to the total number of moles was calculated:

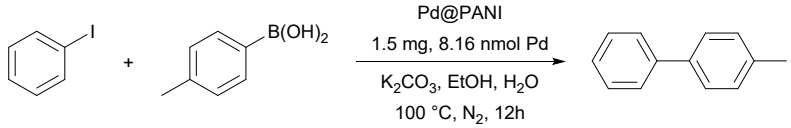
(211 * 10^{-9} mol) / (0.0724 mol) = 2.91 * 10^{-6}

Multiplication by 1 × 10^6 gives the molecular ppm of (pre)catalyst:

2.91 * 10^{-6} × 10^6 = 2.91 ≈ 2.9 ppm

The example calculation for TON and TOF

Scheme S4 Suzuki-Miyaura Cross-coupling Reaction of Iodobenzene with 4-Tolylboronic acid



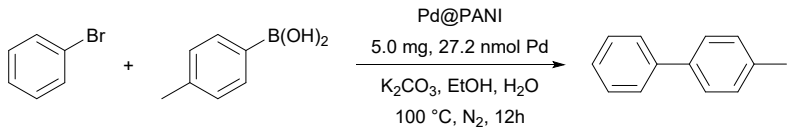
n (Cat.) = n(Pd) = (1.5 mg * 579 mg/kg) / (106.4 g/mol) = 8.16 * 10^{-9} mol

n (Product) = (0.5 mmol) × 97% = 0.485 mmol

TON = n (Product) / n (Cat.) = (0.485 mmol) / (8.16 * 10^{-9} mol) = 5.94 × 10^4

TOF = TON / Time = 5.94 × 10^4 / (12 h) = 4953 h^{-1}

Scheme S5 Suzuki-Miyaura Cross-coupling Reaction of Bromobenzene with 4-Tolylboronic acid



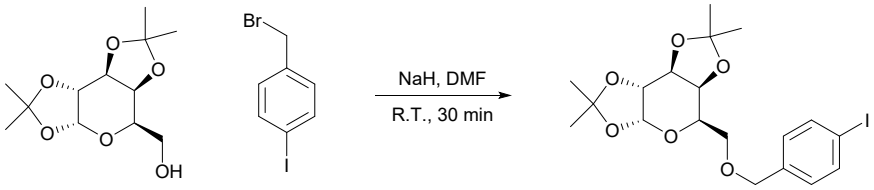
n (Cat.) = n(Pd) = (5.0 mg * 579 mg/kg) / (106.4 g/mol) = 27.2 * 10^{-9} mol

n (Product) = (0.5 mmol) × 88% = 0.44 mmol

TON = n (Product) / n (Cat.) = (0.44 mmol) / (27.2 * 10^{-9} mol) = 1.61 × 10^4

TOF = TON / Time = 1.61 × 10^4 / (12 h) = 1348 h^{-1}

General procedure for peparing iodobenzene derivatives of D-fructose



A flask containing the alcohol (780.9 mg, 1.0 equiv) was purged with nitrogen and charged with DMF (30ml, 10 mL/mmol OH). A nitrogen purge was installed and NaH (132.0 mg, 1.1 equiv, 60% in mineral oil) and the substituted benzyl bromide (979.9 mg, 1.1 equiv) were added. The reaction was stirred at room temperature for 30 min then quenched by dropwise addition of water, diluted with EtOAc and washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in vacuo and purified by flash column chromatography on silica gel.[2]

The Pd@PANI catalyzed Suzuki-Miyaura cross-couplings under batch conditions

In a sealed tube charged with N_2, Pd@PANI catalyst (1.5 mg catalyst for aryl iodide and 5.0 mg catalyst for aryl bromide), 0.5 mmol of aryl halide, 0.5 mmol of boronic acid, and 0.5 mmol of K_2CO_3 were added. Then, EtOH (1 mL) and H_2O (1 mL) were introduced, and the mixture was stirred at 100 °C for 12 hours. After cooling to ambient temperature, the reaction was transferred to a 50 mL separatory funnel with 10 mL of ethyl acetate. The organic layer was washed with brine and 0.1 M aqueous citric acid (3×10 mL). Ethyl acetate was used to extract the aqueous layers (3×10 mL). The organic layers were mixed and dried over anhydrous sodium sulfate before being filtered. Rotary evaporation was used to concentrate the resultant organic layer. After that, the crude material was purified by flash column chromatography to obtain the desired product.

The Pd@PANI catalyzed Suzuki-Miyaura cross-couplings under flow conditions

Pd@PANI was filled in a packed bed reactor (180 mg of catalyst, 5.0 g of glass beads, Column: 4.6×100 mm, 3.7 mL volume, with cotton filling the remaining space). 5 mmol aryl halide, 5 mmol boronic acid, and 5 mmol TMSOK (Potassium trimethylsilanolate) were introduced to a Schlenk tube filled with N_2. 40 mL *n*-propanol was added to the tube, and the mixture was stirred at room temperature for 10 minutes. The prepared solution was pumped into a packed bed reactor with the reaction conditions (reaction temperature = 75 °C, flow rate = 0.1 ml/min, and residence time = 37 mins) set. The sample was collected for 185 minutes after reaching steady state (5 residence times, 185 minutes) and used to calculate the isolated yield. The reaction solution was transferred to a 150 mL separatory funnel with 50 mL of ethyl acetate. The organic layer was then washed with brine and 0.1 M aqueous citric acid (3×50 mL). Ethyl acetate was used to extract the aqueous layers that resulted (3×50 mL). The organic layers were mixed and dried over sodium sulfate before being filtered. Rotary evaporation was used to concentrate the resultant organic layer. After that, the crude material was purified by flash column chromatography to obtain the desired product.

Catalyst lifetime testing under continuous flow

Pd@PANI was filled in a packed bed reactor (180 mg of catalyst, 5.0 g of glass beads, 3.7 mL volume), with cotton filling the remaining space. Iodobenzene (1 eq.), 4-tolylboronic acid (1 eq.), TMSOK (Potassium trimethylsilanolate, 1 eq.) and *n*-dodecane (0.5 eq.) were introduced to a Schlenk tube filled with N_2. In the tube, 1-propanol was added, and the mixture (0.125 mol/L iodobenzene) was stirred for ten minutes at room temperature. The prepared solution was pumped into a packed bed reactor with the reaction parameters established (reaction temperature = 75 ℃, flow rate = 0.1 ml/min, and residence time = 37 mins). The solution was collected and analyzed by GC-MS.

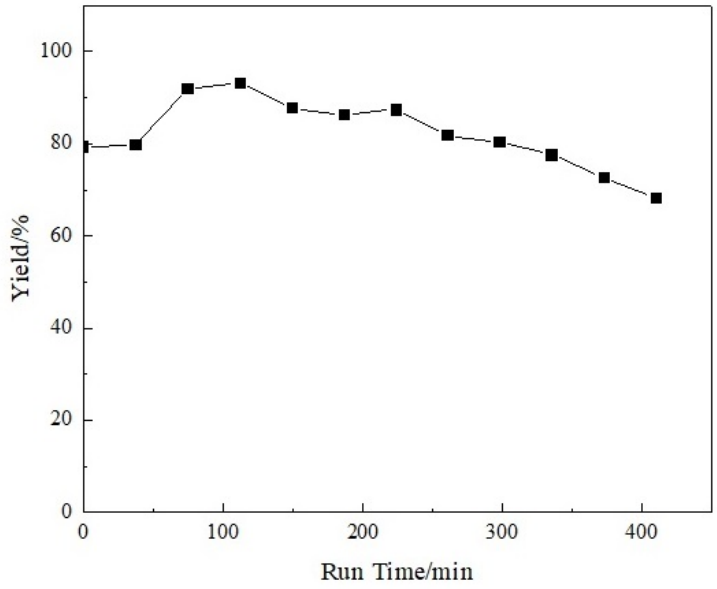
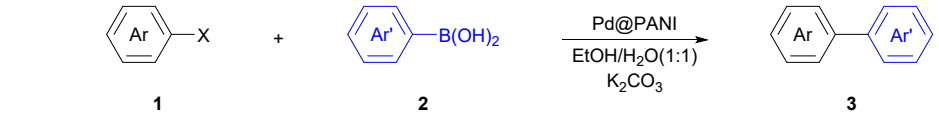


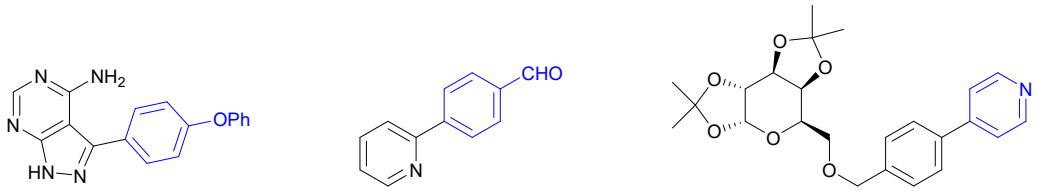
Fig. S3 Catalyst lifetime testing of Pd@PANI under continuous flow

Failed examples

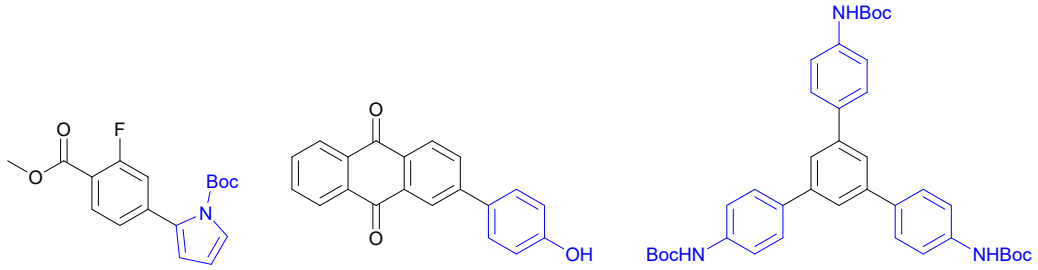
Table S2. Some failed examples under standard batch conditions



1 2 3



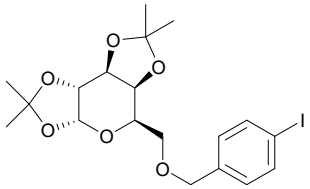
X = I X = I X = I



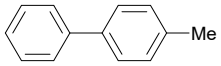
X = Br X = Br X = Br

Reaction conditions: 0.5 mmol of **1**, 0.5 mmol of **2**, Pd@ PANI (1.5 mg for aryl iodide and 5.0 mg for aryl bromide), 0.5 mmol of K_2CO_3, 2 mL of EtOH/H_2O (1:1), 100 ℃ for 12h; the reactions were conducted in sealed tubes.

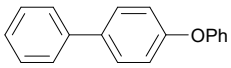
Characterization data of the products



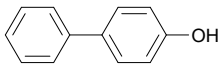
(3aR,5R,5aS,8aS,8bR)-5-(((4-iodobenzyl)oxy)methyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (1w): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.54 (d, *J* = 4.8 Hz, 1H), 4.63-4.43 (m, 3H), 4.34-4.20 (m, 2H), 4.03-3.94 (m, 1H), 3.72-3.57 (m, 2H), 1.53 (s, 3H), 1.43 (s, 3H), 1.33 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 137.90, 137.19, 129.39, 109.04, 108.35, 96.18, 92.84, 72.40, 71.01, 70.47, 70.37, 68.91, 66.78, 25.96, 25.86, 24.82, 24.33 ppm. **HRMS** (ESI) *m*/*z* calcd for $C_{19}H_{25}O_6INa$ $[M+Na]^+$: 499.05880, found: 499.05792. **IR** (ATR) ν (cm^{-1}, KBr): 2987, 2933, 1484, 1382, 1372, 1255, 1212, 1168, 1104, 1071, 1007, 891, 800.



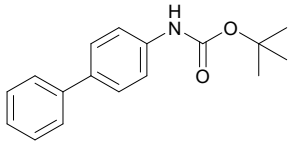
4-Methylbiphenyl(3a): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.648 (d, *J* = 7.8 Hz, 2H), 7.564 (d, *J* = 8.4 Hz, 2 H), 7.487 (t, *J* = 7.8 Hz, 2 H), 7.384 (t, *J* = 7.2 Hz, 1 H), 7.313 (d, *J* = 8.0 Hz, 2 H), 2.461 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.15, 138.35, 136.97, 129.45, 128.68, 126.97, 126.94, 21.06. **MS** (EI) *m*/z calcd for $C_{13}H_{12}$ $[M]^+$: 168.1, found: 168.1. **IR** (ATR) ν (cm^{-1}, KBr): 3055, 3030, 2925, 2855, 1601, 1568, 1488, 1445, 1403, 1129, 910, 823, 755, 690. [3]



4-phenoxy-1,1'-biphenyl (3b): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.646-7.552 (m, 4 H), 7.465 (t, *J* = 7.6 Hz, 2 H), 7.426-7.330 (m, 3 H), 7.197-7.063 (m, 5 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.10, 156.81, 140.51, 136.23, 129.76, 128.75, 128.40, 127.00, 126.87, 123.35, 119.00 ppm. **MS** (EI) *m*/z calcd for $C_{18}H_{14}O$ $[M]^+$: 246.1, found: 246.1. **IR** (ATR) ν (cm^{-1}, KBr): 3056, 3036, 1590, 1520, 1485, 1271, 1258, 1072, 876, 842, 751, 722, 689. [4]

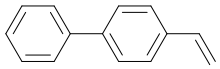


4-Hydroxybiphenyl (3c): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.570-7.515 (m, 2 H), 7.510-7.459 (m, 2 H), 7.447-7.383 (m, 2 H), 7.337-7.277 (m, 1 H), 6.942-6.869 (m, 2 H), 4.774 (s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.06, 140.73, 133.99, 128.69, 128.36, 126.69, 115.62 ppm. **MS** (EI) *m*/z calcd for $C_{12}H_{10}O$ $[M]^+$: 170.1, found: 170.1. **IR** (ATR) ν (cm^{-1}, KBr): 3413, 3038, 1652, 1610, 1597, 1523, 1488, 1461, 1259, 1242, 1114, 833, 758. [5]

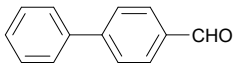


***tert*-butyl [1,1'-biphenyl]-4-ylcarbamate (3d):** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.602-7.529 (m, 4 H), 7.485-7.405 (m, 4 H), 7.333 (t, *J* = 7.4 Hz, 1 H), 6.646 (s, 1H), 1.565 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.73,

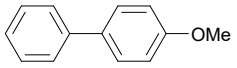
140.57, 137.63, 135.84, 128.68, 127.54, 126.86, 126.70, 118.79, 80.56, 28.31 ppm. **HRMS** (ESI) *m*/*z* calcd for $C_{17}H_{20}NO_2$ $[M+H]^+$: 270.1489, found: 270.1498. **IR** (ATR) ν (cm^{-1}, KBr): 3368, 3065, 3006, 2979, 2934, 1702, 1589, 1529, 1507, 1405, 1319, 1264, 1233, 1161, 1057, 836, 755, 689. [6]



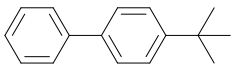
4-vinyl-1,1'-biphenyl (3e): ^1H NMR (400 MHz, $CDCl_3$) δ: 7.644–7.562 (m, 4H), 7.521–7.425 (m, 4H), 7.390–7.332 (m, 1H), 6.777 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.812 (d, *J* = 17.6 Hz, 1H), 5.293 (d, *J* = 10.0 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 140.72, 140.57, 136.58, 136.39, 128.76, 127.30, 127.21, 126.95, 126.62, 113.87 ppm. **MS** (EI) *m*/z calcd for $C_{14}H_{12}$ $[M]^+$: 180.1, found: 180.1. **IR** (ATR) ν (cm^{-1}, KBr): 3085, 3056, 3033, 2923, 1626, 1486, 1401, 993, 905, 844, 770, 734, 690. [7]



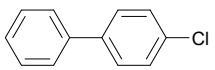
4-Carboxaldehydebiphenyl (3f): ^1H NMR (400 MHz, $CDCl_3$) δ: 10.054 (s, 1H), 7.948 (d, *J* = 8.4 Hz, 2H), 7.746 (d, *J* = 8.4 Hz, 2H), 7.637 (d, *J* = 6.8 Hz, 2H), 7.528-7.387 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.75, 147.05, 139.60, 135.13, 130.15, 128.92, 128.38, 127.56, 127.26 ppm. **MS** (EI) *m*/z calcd for $C_{13}H_{10}O$ $[M]^+$: 182.1, found: 182.1. **IR** (ATR) ν (cm^{-1}, KBr): 3031, 2847, 2738, 1701, 1604, 1214, 1168, 837, 762, 696. [5]



4-Methoxybiphenyl (3g): ^1H NMR (400 MHz, $CDCl_3$) δ: 7.629-7.534 (m, 4 H), 7.453 (t, *J* = 7.4 Hz, 2 H), 7.341 (t, *J* = 7.2 Hz, 1 H), 7.018(d, *J* = 8.0 Hz, 2 H), 3.880 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.11, 140.78, 133.72, 128.69, 128.11, 126.69, 126.62, 114.16, 55.28 ppm. **MS** (EI) *m*/z calcd for $C_{13}H_{12}O$ $[M]^+$: 184.1, found: 184.1. **IR** (ATR) ν (cm^{-1}, KBr): 3056, 3001, 2961, 2926, 2836, 1605, 1581, 1521, 1486, 1462, 1365, 1308, 1287, 1270, 1250, 909, 833, 759. [3,8]

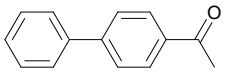


4-(tert-butyl)-1,1'-biphenyl (3h): ^1H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 1.48 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.19, 141.04, 138.30, 128.67, 126.99, 126.95, 126.77, 125.68, 34.49, 31.36 ppm. **MS** (EI) *m*/z calcd for $C_{16}H_{18}$ $[M]^+$: 210.1, found: 210.2. **IR** (ATR) ν (cm^{-1}, KBr): 3034, 2961, 1637, 1485, 1405, 835, 765, 729, 690. [9]

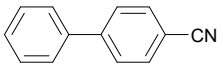


4-Chloridebiphenyl (3i): ^1H NMR (400 MHz, $CDCl_3$) δ: 7.601-7.509 (m, 4 H), 7.499-7.348 (m, 5 H) ppm. ^{13}C

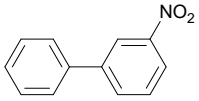
NMR (101 MHz, $CDCl_3$) δ: 139.95, 139.63, 133.35, 128.88, 128.85, 128.36, 127.56, 126.95 ppm. **MS** (EI) *m*/z calcd for $C_{12}H_9Cl$ $[M]^+$: 188.0, found: 188.0. **IR** (ATR) ν (cm^{-1}, KBr): 3058, 3032, 1583, 1478, 1449, 1399, 1261, 1098, 1004, 832, 758, 688. [5]



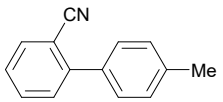
4-Acetylbiphenyl (3j): ^1H NMR (400 MHz, $CDCl_3$) δ: 8.039 (d, *J* = 8.4 Hz, 2H), 7.690 (d, *J* = 8.8 Hz, 2H), 7.633 (d, *J* = 7.2 Hz, 2H), 7.479 (t, *J* = 7.4 Hz, 2H), 7.407 (d, *J* = 7.2 Hz, 1H), 2.643 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.74, 145.71, 139.79, 135.76, 128.91, 128.87, 128.19, 127.21, 127.16, 26.64 ppm. **MS** (EI) *m*/z calcd for $C_{14}H_{12}O$ $[M]^+$: 196.1, found: 196.1. **IR** (ATR) ν (cm^{-1}, KBr): 3030, 2918, 1680, 1602, 1404, 1356, 1263, 961, 833, 765, 691. [5]



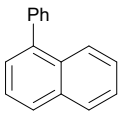
[1,1'-biphenyl]-4-carbonitrile (3k): ^1H NMR (400 MHz, $CDCl_3$) δ: 7.745-7.662 (m, 4H), 7.619-7.572 (m, 2H), 7.525-7.409 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.55, 139.05, 132.50, 129.03, 128.58, 127.63, 127.13, 118.87, 110.80 ppm. **MS** (EI) *m*/z calcd for $C_{13}H_9N$ $[M]^+$: 179.1, found: 179.1. **IR** (ATR) ν (cm^{-1}, KBr): 3076, 2226, 1605, 1483, 1396, 1077, 770, 723, 697. [5]



3-Nitrobiphenyl (3l): ^1H NMR (400 MHz, $CDCl_3$) δ: 8.453 (s, 1H), 8.202 (d, *J* = 8.4 Hz, 1H), 7.918 (d, *J* = 8.0 Hz, 1H), 7.650-7.587 (m, 3H), 7.526-7.414 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.68, 142.82, 138.61, 132.99, 129.66, 129.12, 128.50, 127.11, 121.98, 121.89 ppm. **MS** (EI) *m*/z calcd for $C_{12}H_9NO_2$ $[M]^+$: 199.1, found: 199.1. **IR** (ATR) ν (cm^{-1}, KBr): 3081, 1530, 1501, 1351, 1080, 898, 875, 768, 732, 695. [5]

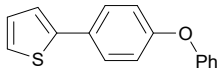


4'-methyl-[1,1'-biphenyl]-2-carbonitrile (3m): ^1H NMR (400 MHz, $CDCl_3$) δ: 7.751 (d, *J* = 7.6 Hz, 1H), 7.626 (t, *J* = 7.6 Hz, 1H), 7.506 (d, *J* = 8.0 Hz, 1H), 7.469 (d, *J* = 8.4 Hz, 2H), 7.425 (t, *J* = 7.6 Hz, 1H), 7.307 (d, *J* = 8.4 Hz, 2H), 2.428 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.51, 138.65, 135.25, 133.67, 132.71, 129.94, 129.40, 128.57, 127.23, 118.81, 111.18, 21.20 ppm. **MS** (EI) *m*/z calcd for $C_{14}H_{11}N$ $[M]^+$: 193.1, found: 193.1. **IR** (ATR) ν (cm^{-1}, KBr): 3058, 3022, 2922, 2854, 2225, 1595, 1562, 1479, 813, 764, 745. [10,11]

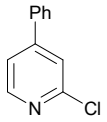


1-phenylnaphthalene (3n): ^1H NMR (400 MHz, $CDCl_3$) δ: 8.047-7.906 (m, 3H), 7.645-7.466 (m, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 140.73, 140.23, 133.77, 131.59, 130.04, 128.22, 127.60, 127.19, 126.89, 125.99,

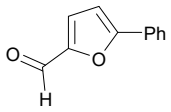
125.72, 125.34 ppm. **MS** (EI) *m*/z calcd for $C_{16}H_{12}$ $[M]^+$: 204.1, found: 204.1. **IR** (ATR) ν (cm^{-1}, KBr): 3057, 1637, 1617, 1592, 1507, 1493, 1395, 802, 778, 703. [12]



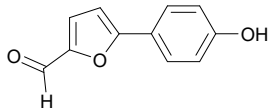
2-(4-phenoxyphenyl) thiophene (3o): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 - 7.52 (m, 2H), 7.38 - 7.30 (m, 2H), 7.25 - 7.20 (m, 2H), 7.16 - 6.97 (m, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.97, 156.77, 143.81, 129.78, 129.63, 127.99, 127.34, 124.39, 123.42, 122.67, 119.12, 118.94 ppm. **MS** (EI) *m*/z calcd for $C_{16}H_{12}OS$ $[M]^+$: 252.1, found: 251.9. **IR** (ATR) ν (cm^{-1}, KBr): 3056, 2924, 2854, 1589, 1531, 1498, 1490, 1281, 1258, 841, 821, 785, 747, 700, 692, 682. [13]



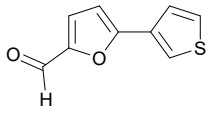
2-chloro-4-phenylpyridine (3p): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.433 (d, *J* = 5.2 Hz, 1 H), 7.640-7.595 (m, 2 H), 7.551 (d, *J* = 1.2 Hz, 1 H), 7.532-7.463 (m, 3 H), 7.436 (dd, *J* = 5.2, 1.6 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.19, 151.55, 149.97, 136.83, 129.66, 129.24, 127.02, 122.04, 120.47 ppm. **MS** (EI) *m*/z calcd for $C_{11}H_8ClN$ $[M]^+$: 189.0, found: 189.0. **IR** (ATR) ν (cm^{-1}, KBr): 3058, 3023, 1605, 1590, 1534, 1503, 1458, 1375, 1089, 859, 802, 756, 728, 708, 690. [14]



5-Phenylfuran-2-carbaldehyde (3q): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.633 (s, 1H), 7.850-7.770 (m, 2H), 7.470-7.350 (m, 3H), 7.309 (d, *J* = 3.6 Hz, 1H), 6.831 (d, *J* = 3.6 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 177.16, 159.35, 151.96, 129.61, 128.88, 125.22, 123.48, 107.62 ppm. **MS** (EI) *m*/z calcd for $C_{11}H_8O_2$ $[M]^+$: 172.1, found: 172.1. **IR** (ATR) ν (cm^{-1}, KBr): 1675, 1522, 1474, 1451, 1398, 765. [15]

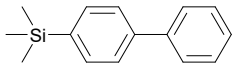


5-(4-hydroxyphenyl) furan-2-carbaldehyde (3r): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.04 (s, 1H), 9.52 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 3.8 Hz, 1H), 7.05 (d, *J* = 3.7 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ: 177.07, 159.29, 159.16, 151.05, 126.98, 126.19, 119.80, 116.08, 106.59 ppm. **MS** (EI) *m*/z calcd for $C_{11}H_8O_3$ $[M]^+$: 188.0, found: 188.0. **IR** (ATR) ν (cm^{-1}, KBr): 3413, 1640, 1608, 1591, 1491, 1447, 1390, 1239, 830. [16]

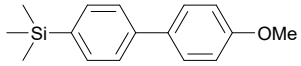


5-(thiophen-3-yl) furan-2-carbaldehyde (3s): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.595 (s, 1H), 7.806-7.733 (m, 1H), 7.453-7.347 (m, 2H), 7.285 (d, *J* = 4.0 Hz, 1H), 6.657 (d, *J* = 3.6 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 176.89, 155.96, 151.27, 130.68, 126.89, 124.92, 123.86, 123.29, 107.44 ppm. **MS** (EI) *m*/z calcd for $C_9H_6O_2S$

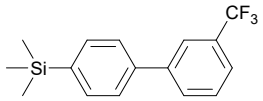
[M]$^+$: 178.0, found: 178.0. **IR** (ATR) ν (cm^{-1}, KBr): 3079, 1672, 1587, 1541, 1400, 1371, 1339, 1281, 1207, 1089, 1028, 961. [17]



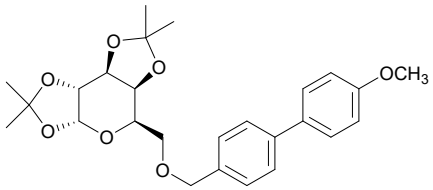
[1,1'-biphenyl]-4-yltrimethylsilane (3t): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 – 7.67 (m, 6H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 0.42 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.59, 141.15, 139.16, 133.81, 128.74, 127.30, 127.15, 126.49, -1.07 ppm. **MS** (EI) *m*/z calcd for $C_{15}H_{18}Si$ [M]$^+$: 226.1, found: 226.2. **IR** (ATR) ν (cm^{-1}, KBr): 3026, 2951, 2892, 1596, 1486, 1386, 1248, 1118, 840, 828, 753, 698, 657. [18]



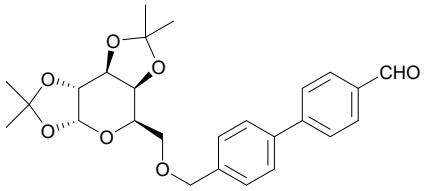
(4'-methoxy-[1,1'-biphenyl]-4-yl) trimethylsilane (3u): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 – 7.55 (m, 6H), 7.06 – 6.99 (m, 2H), 3.88 (s, 3H), 0.35 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.17, 141.17, 138.40, 133.78, 133.63, 128.13, 126.05, 114.17, 55.28, -1.08 ppm. **MS** (EI) *m*/z calcd for $C_{16}H_{20}OSi$ [M]$^+$: 256.1, found: 256.1. **IR** (ATR) ν (cm^{-1}, KBr): 2955, 1604, 1522, 1490, 1459, 1387, 1284, 1251, 1208, 1181, 1114, 1035, 845, 814, 757. [19]



Trimethyl(3'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl) silane (3v): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.72 – 7.56 (m, 6H), 0.38 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.97, 140.35, 140.07, 134.02, 131.17(q, *J* = 32.3 Hz), 130.39, 129.23, 126.49, 124.22(q, *J* = 273.4 Hz), 124.17 -123.74 (m), -1.16 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.50 ppm. **HRMS** (ESI) *m*/*z* calcd for $C_{16}H_{18}F_3Si$ [M+H]$^+$: 295.1124, found: 295.1119. **IR** (ATR) ν (cm^{-1}, KBr): 2957, 2928, 2856, 1597, 1400, 1335, 1265, 1251, 1167, 1129, 841, 797.



(3aR,5R,5aS,8aS,8bR)-5-(((4'-methoxy-[1,1'-biphenyl]-4-yl)methoxy)methyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (3w): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 8.0 Hz, 4H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.56 (d, *J* = 5.2 Hz, 1H), 4.70-4.56 (m, 3H), 4.35-4.27 (m, 2H), 4.03 (td, *J* = 10.4, 6.0 Hz, 1H), 3.85 (s, 3H), 3.76-3.64 (m, 2H), 1.55 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.08, 140.09, 136.67, 133.47, 128.18, 128.04, 126.62, 114.15, 109.17, 108.50, 96.34, 73.04, 71.14, 70.61, 70.56, 68.83, 66.87, 55.28, 26.05, 25.95, 24.90, 24.40 ppm. **HRMS** (ESI) *m*/*z* calcd for $C_{26}H_{32}O_7Na$ [M+Na]$^+$: 479.20402, found: 479.20340. **IR** (ATR) ν (cm^{-1}, KBr): 2993, 2961, 2912, 1608, 1503, 1254, 1212, 1169, 1087, 1075, 1034, 1009, 810.



4'-((((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)methyl)-[1,1'-biphenyl]-4-carbaldehyde (3x): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.05 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 5.56 (d, *J* = 4.8 Hz, 1H), 4.73-4.57 (m, 3H), 4.36-4.25 (m, 2H), 4.08-4.00 (m, 1H), 3.78-3.64 (m, 2H), 1.55 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.87, 146.93, 138.90, 138.82, 135.14, 130.25, 128.27, 127.57, 127.30, 109.23, 108.54, 96.36, 72.84, 71.19, 70.64, 70.55, 69.08, 66.94, 26.07, 25.97, 24.91, 24.43 ppm. **HRMS** (ESI) *m*/*z* calcd for $C_{26}H_{30}O_7Na$ $[M+Na]^+$: 477.18837, found: 477.18793. **IR** (ATR) ν (cm^{-1}, KBr): 3029, 2988, 2934, 1702, 1605, 1382, 1255, 1211, 1170, 1103, 1070, 1005, 808.

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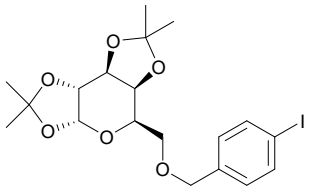
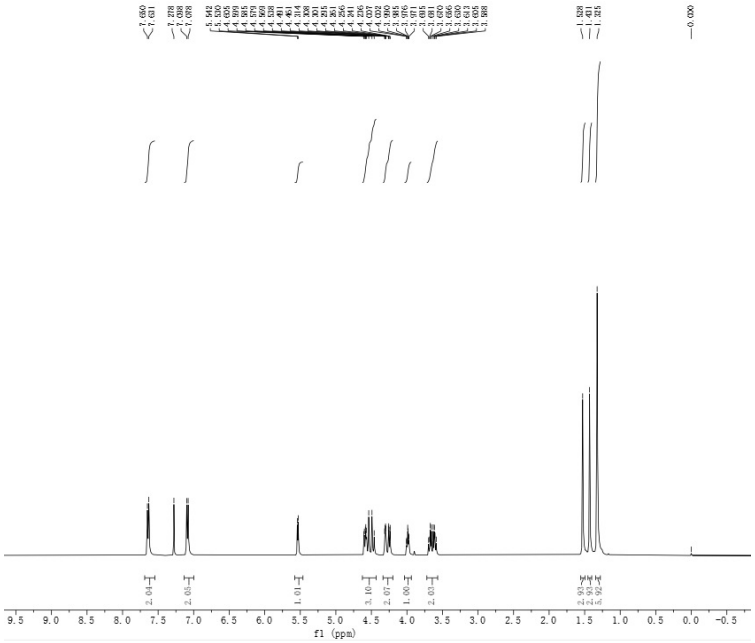
Copies of ^{1}H NMR ^{13}C Spectra of the Products

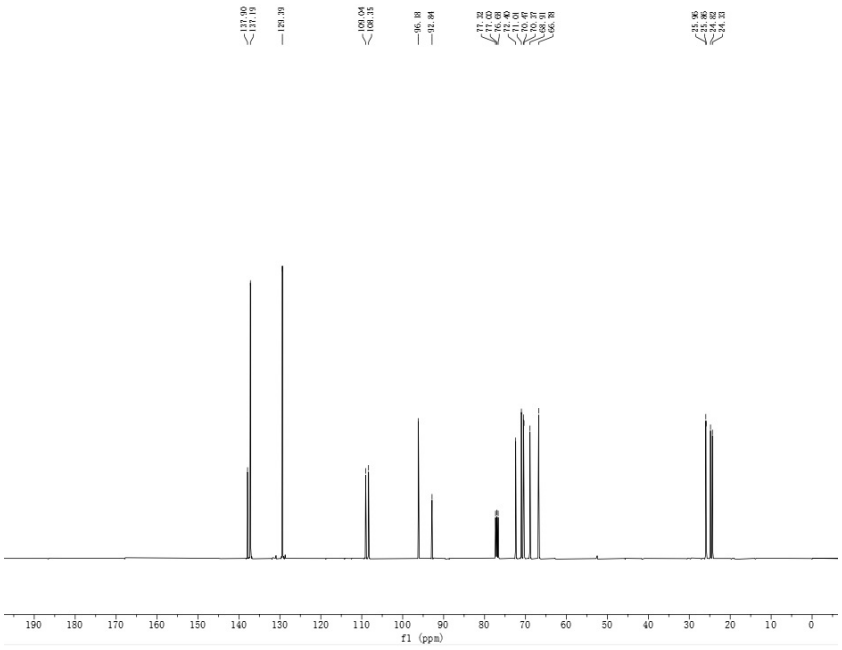
(3aR,5R,5aS,8aS,8bR)-5-(((4-iodobenzyl)oxy)methyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (1w)



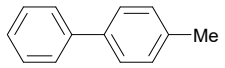
^{1}H NMR (400 MHz, $CDCl_3$)



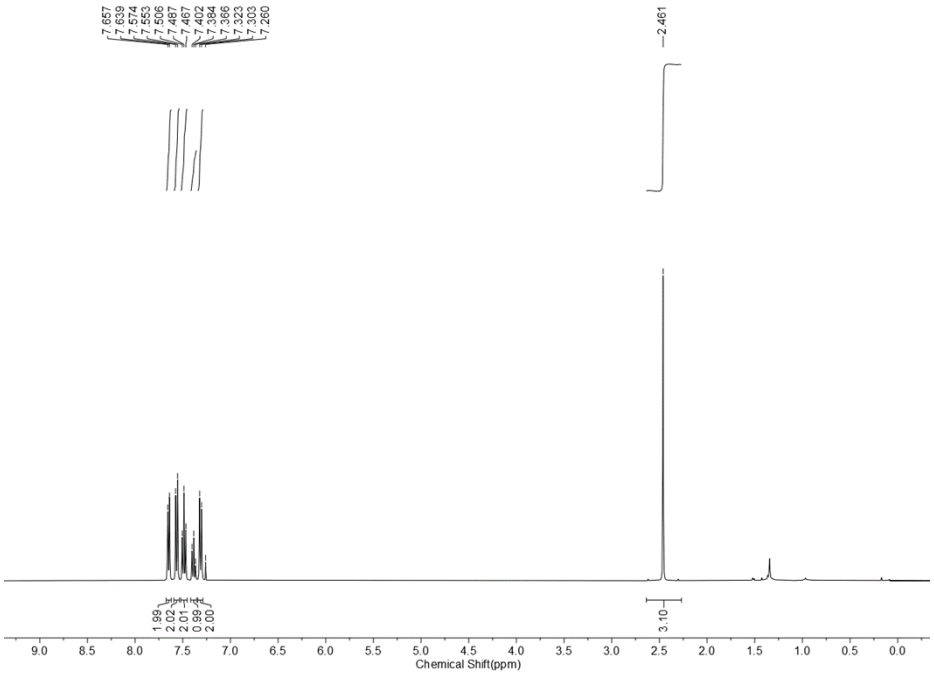
^{13}C NMR, $CDCl_3$, 101 MHz



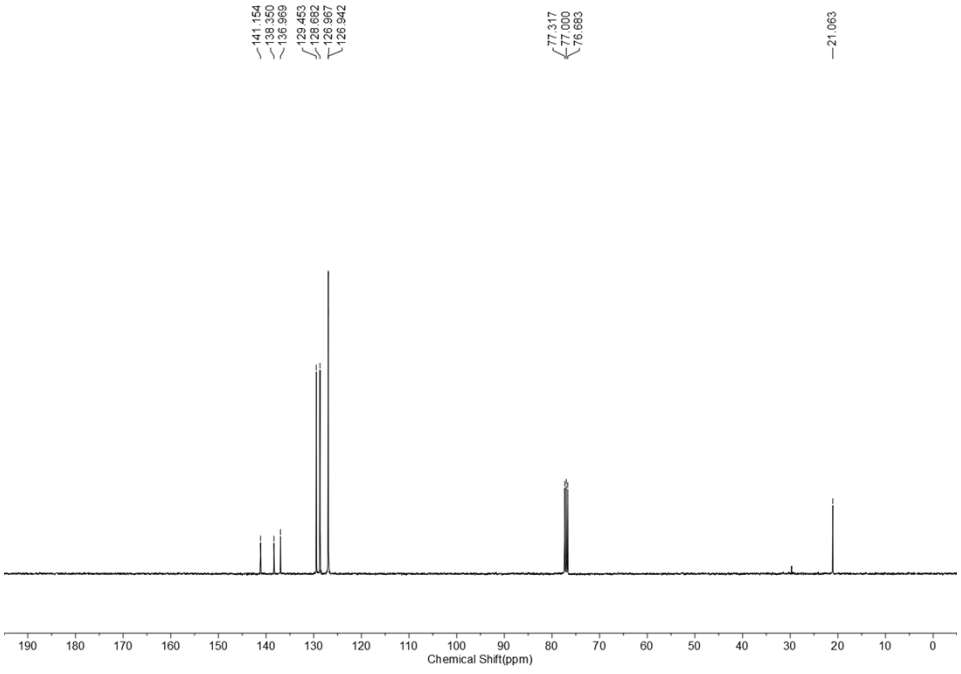
4-Methylbiphenyl(3a)



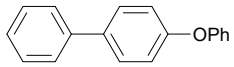
^{1}H NMR, $CDCl_3$, 400 MHz



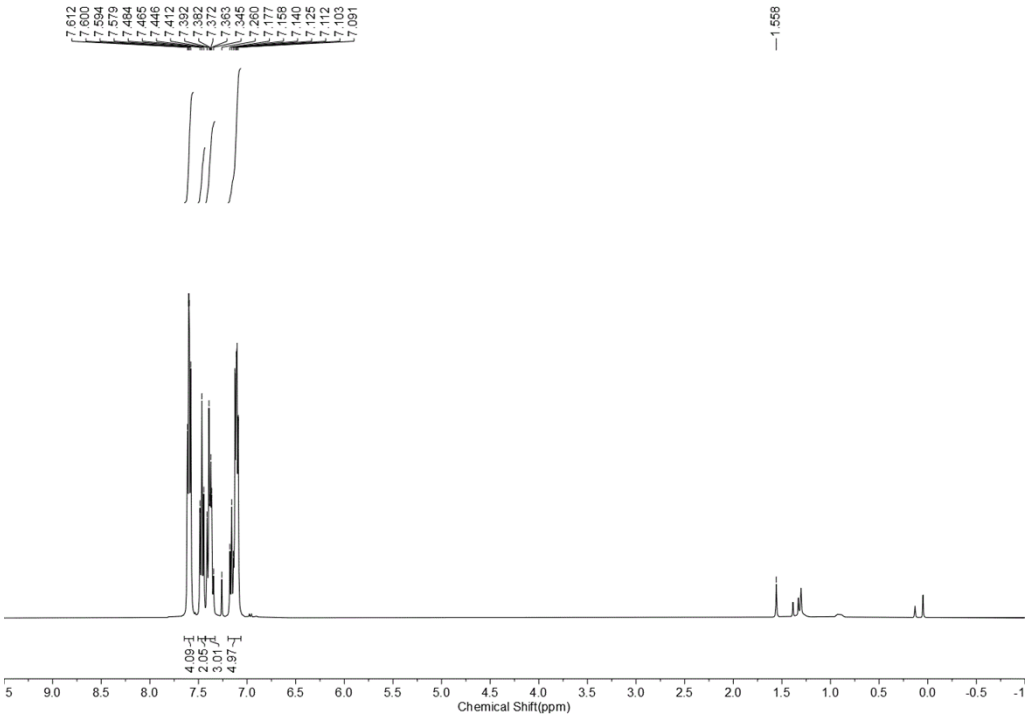
^{13}C NMR, $CDCl_3$, 101 MHz



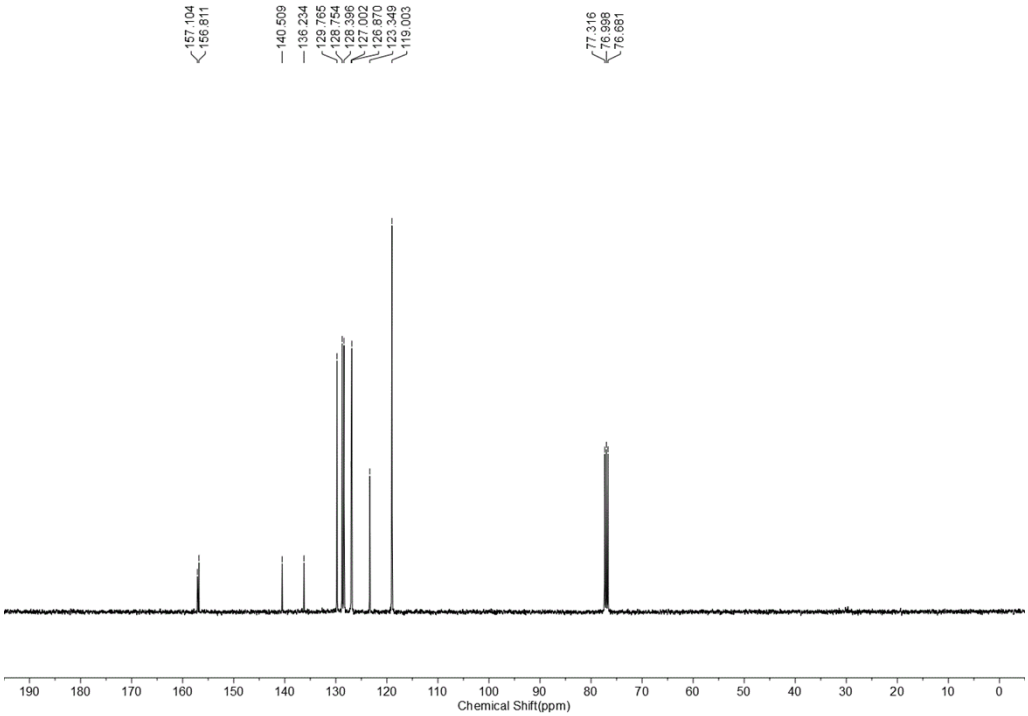
4-phenoxy-1,1'-biphenyl (3b)



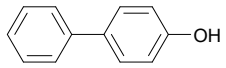
^{1}H NMR, $CDCl_3$, 400 MHz



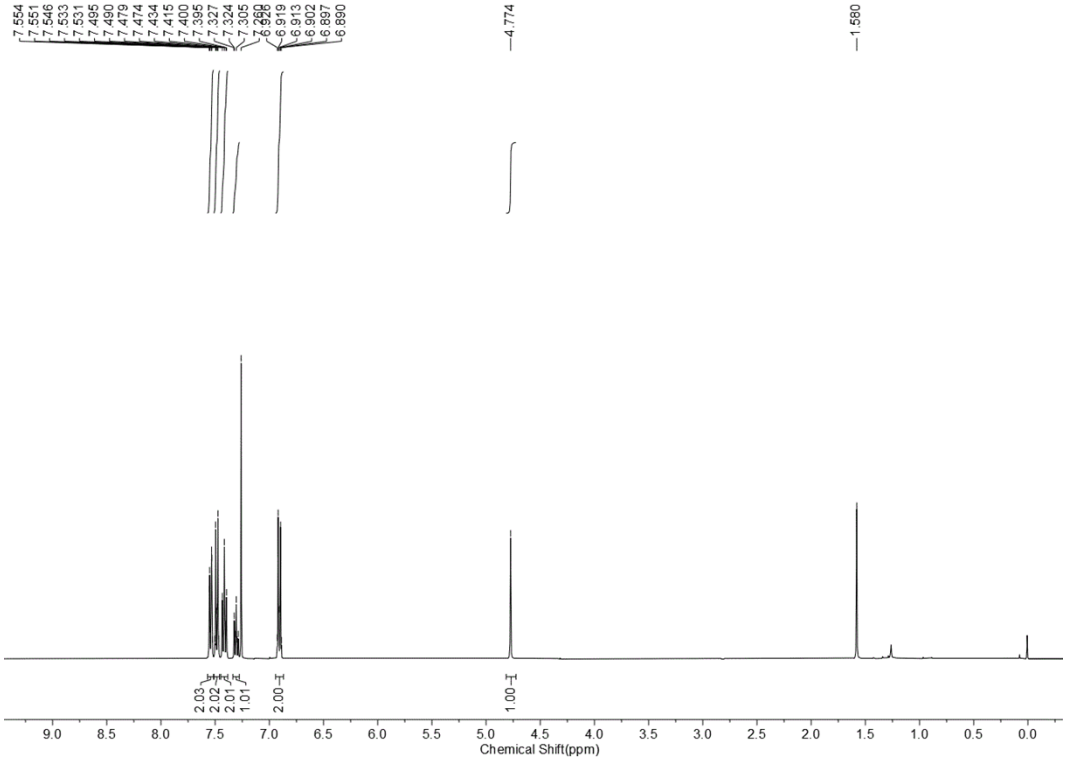
^{13}C NMR, $CDCl_3$, 101 MHz



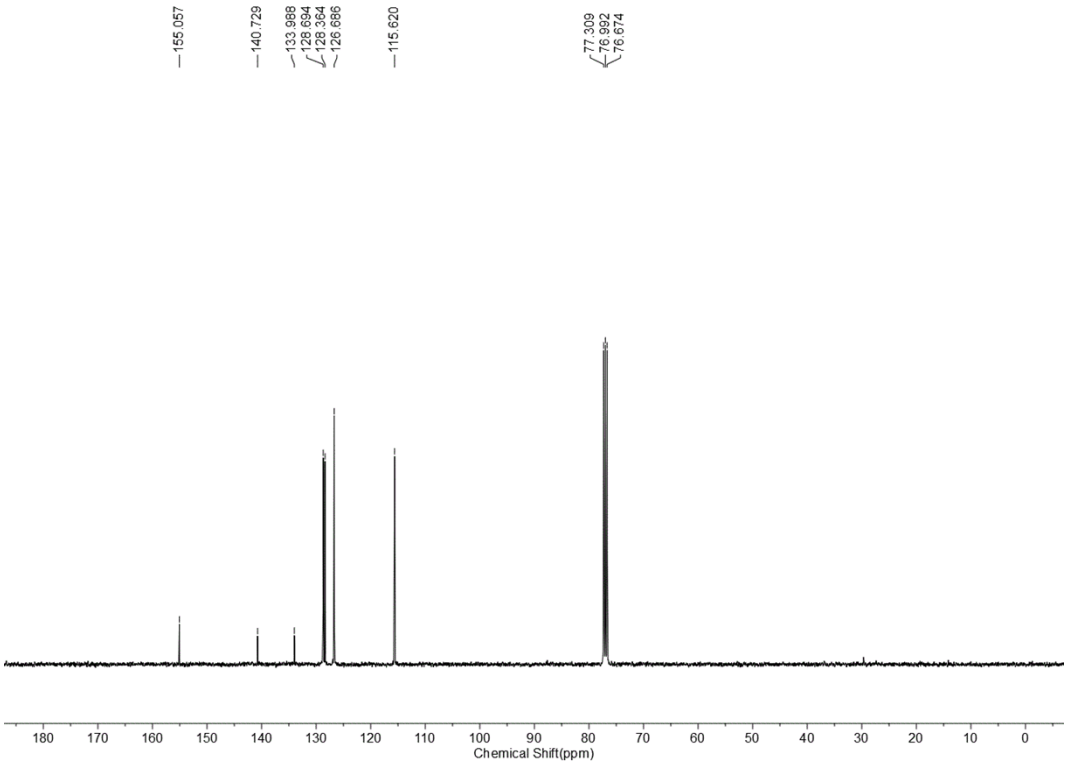
4-Hydroxybiphenyl (3c)



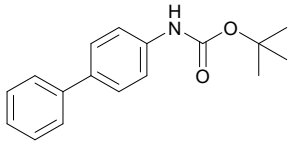
^{1}H NMR, $CDCl_3$, 400 MHz



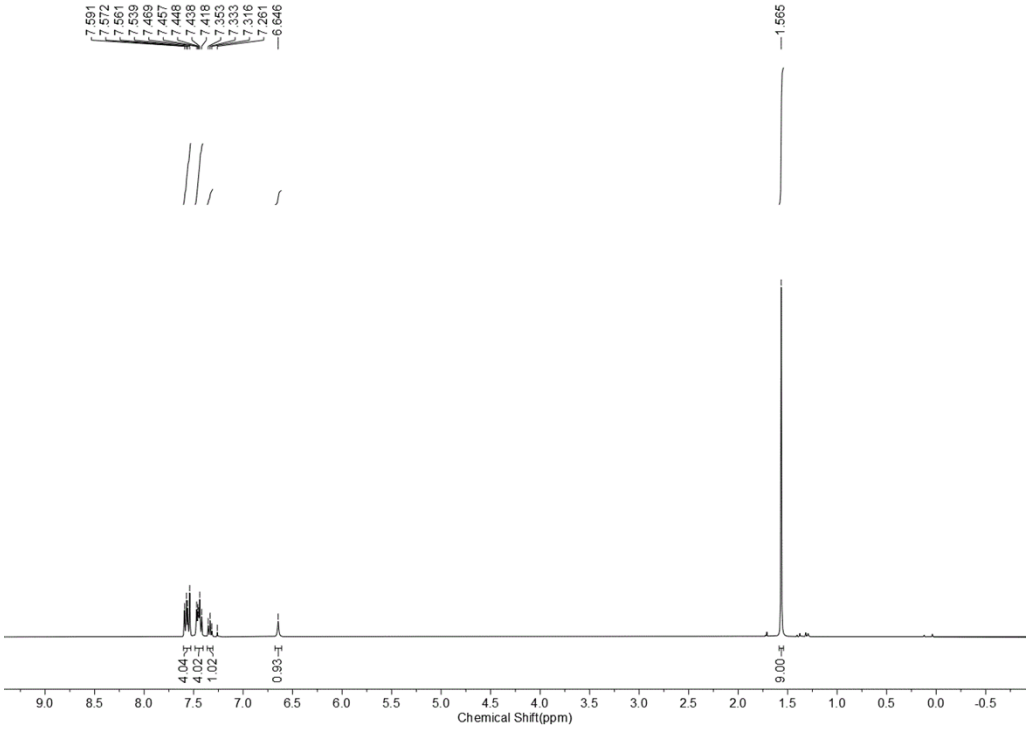
^{13}C NMR, $CDCl_3$, 101 MHz



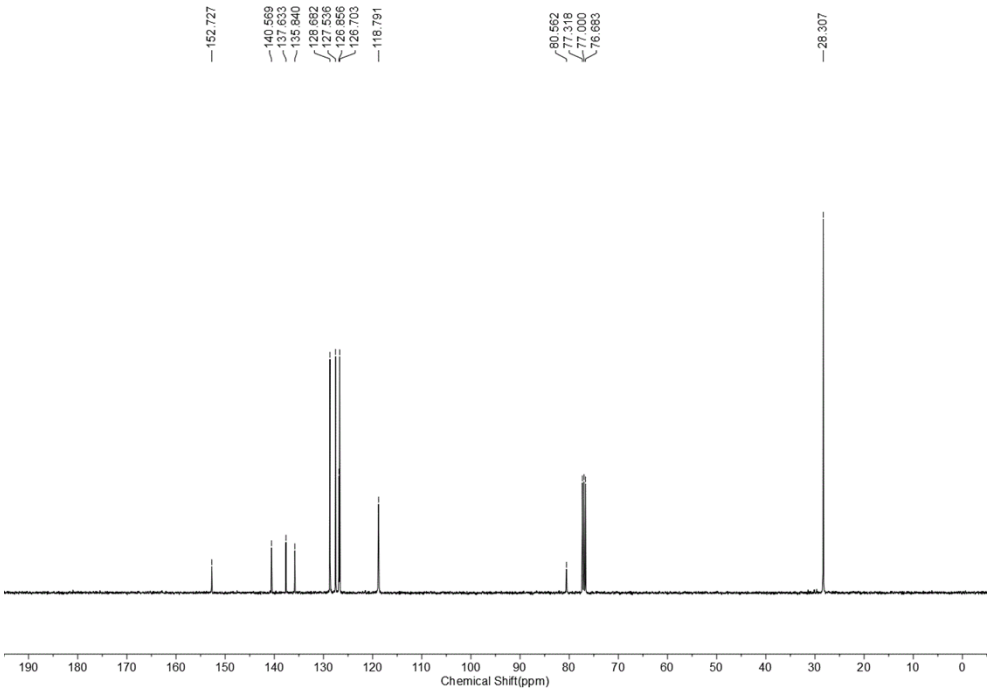
***tert*-butyl [1,1'-biphenyl]-4-ylcarbamate (3d)**



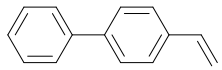
^{1}H NMR, $CDCl_3$, 400 MHz



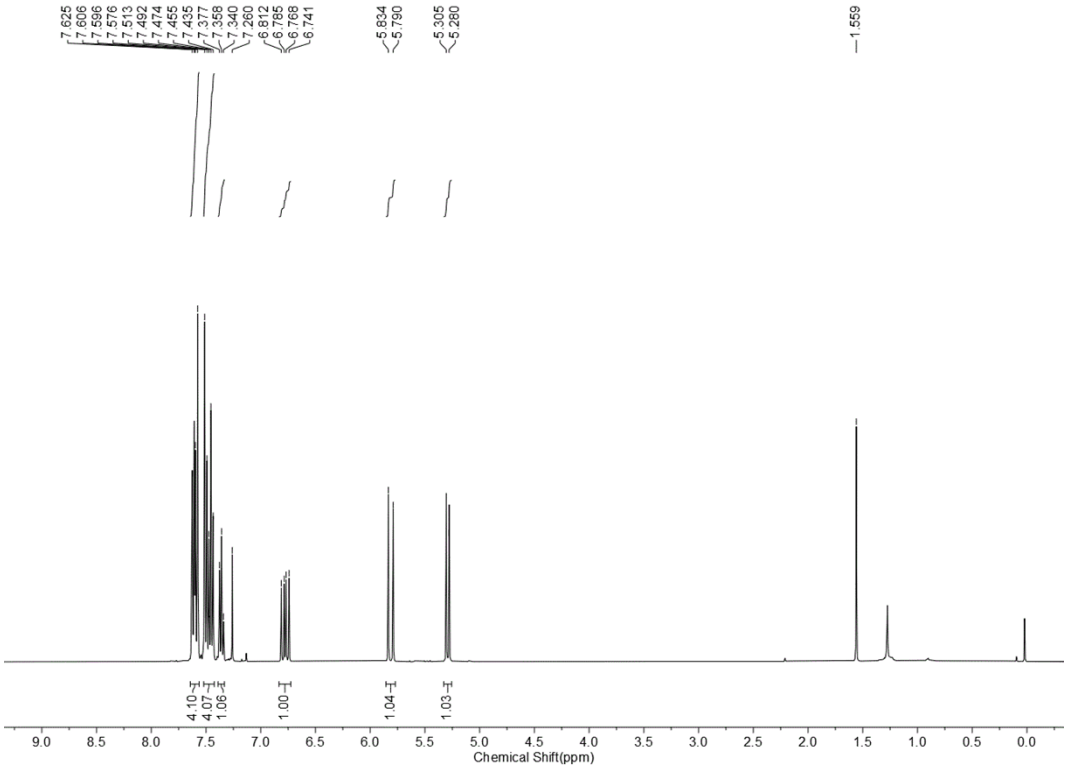
^{13}C NMR, $CDCl_3$, 101 MHz



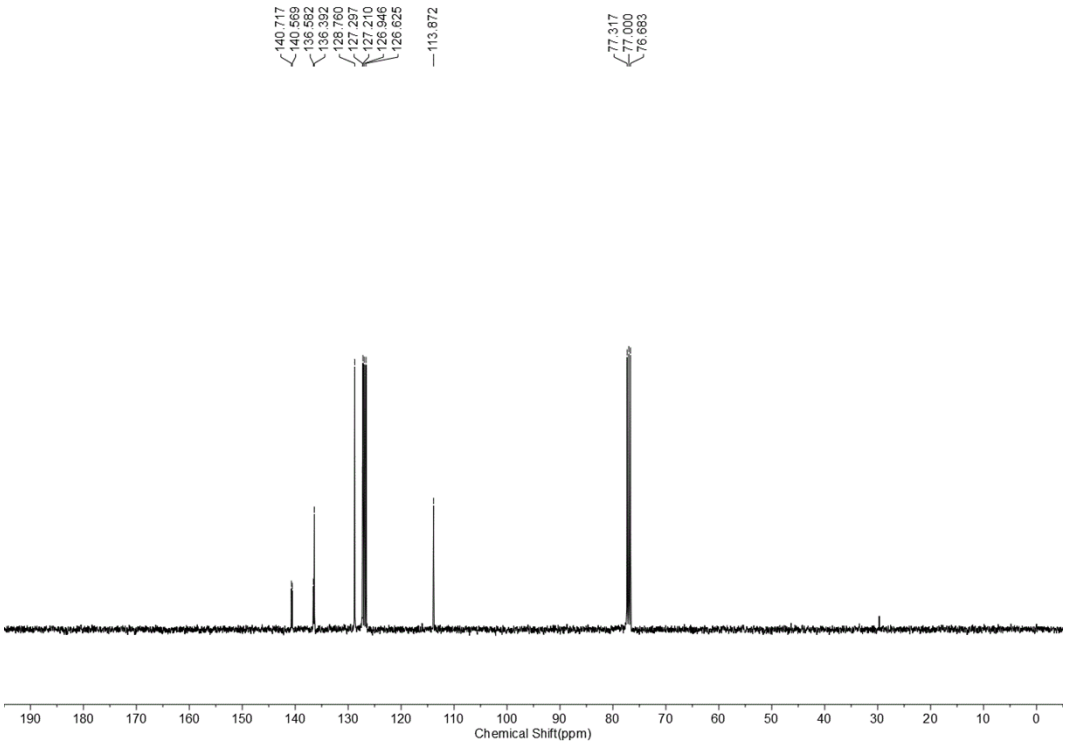
4-vinyl-1,1'-biphenyl (3e)



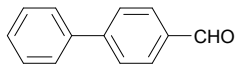
^{1}H NMR, $CDCl_3$, 400 MHz



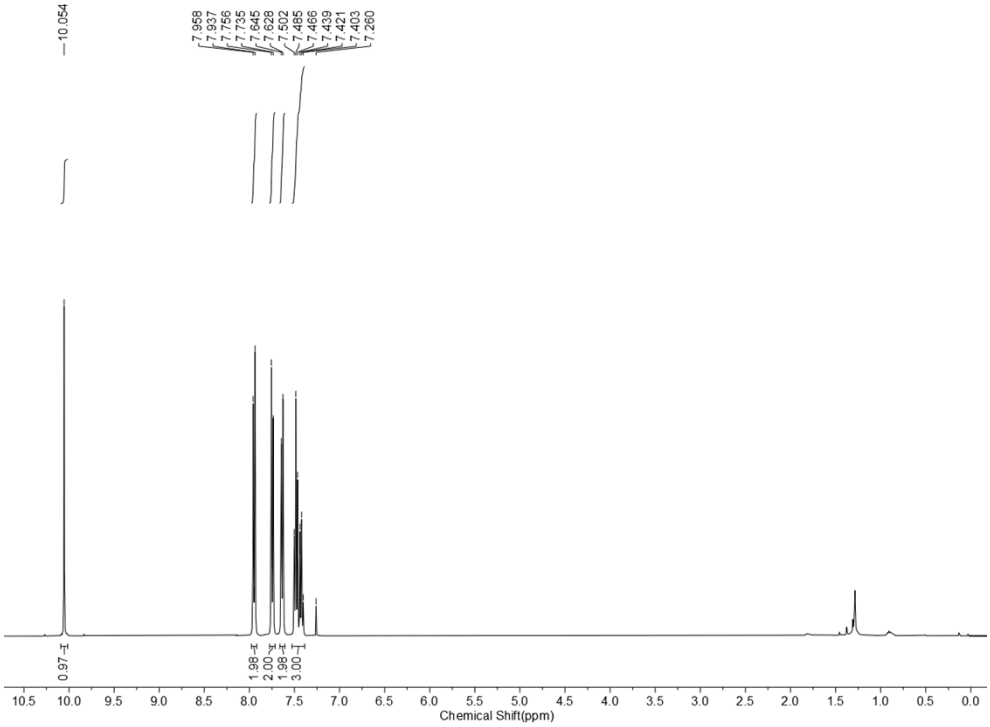
^{13}C NMR, $CDCl_3$, 101 MHz



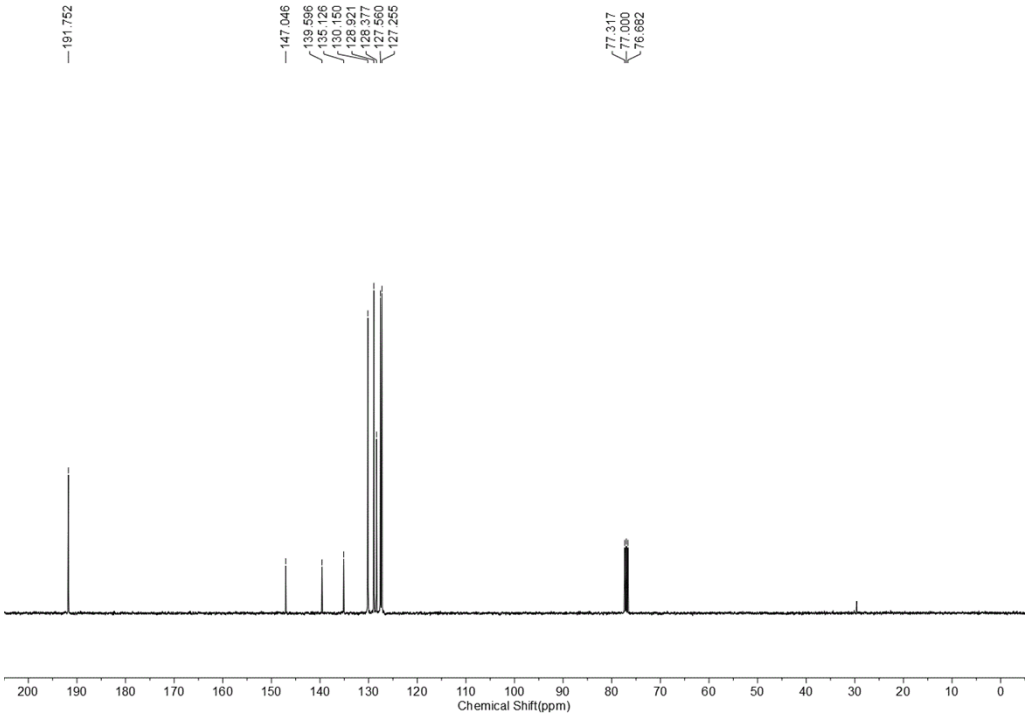
4-Carboxaldehydebiphenyl (3f)



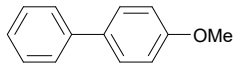
^{1}H NMR, $CDCl_3$, 400 MHz



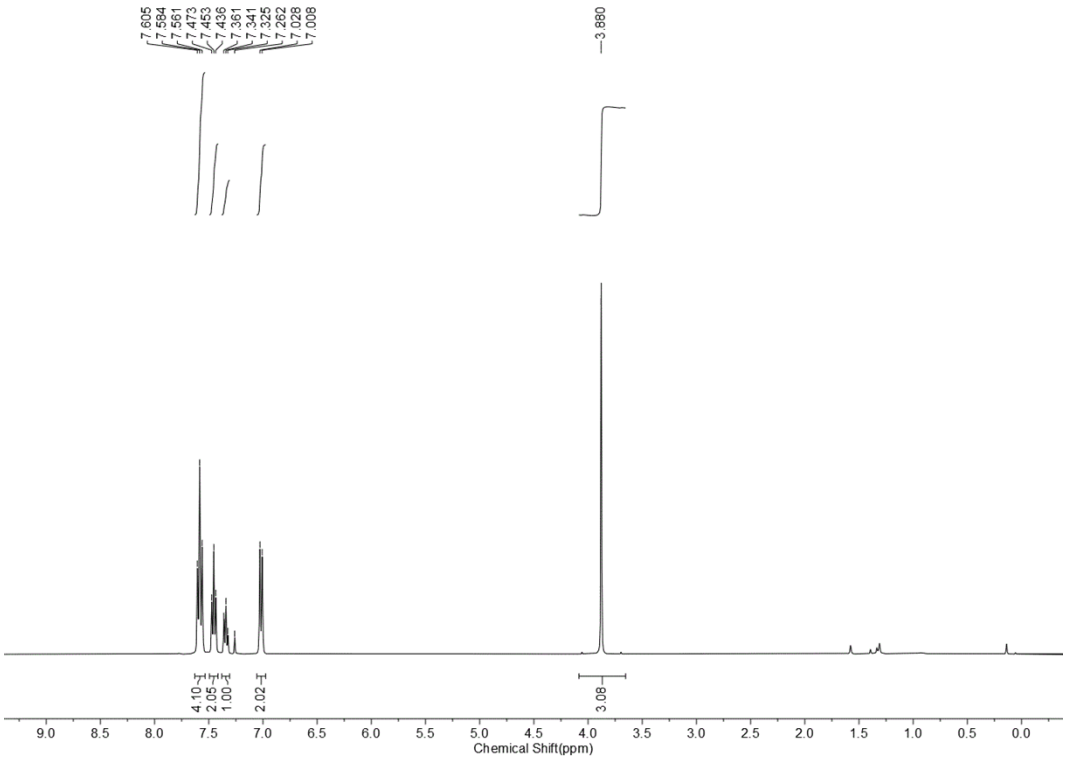
^{13}C NMR, $CDCl_3$, 101 MHz



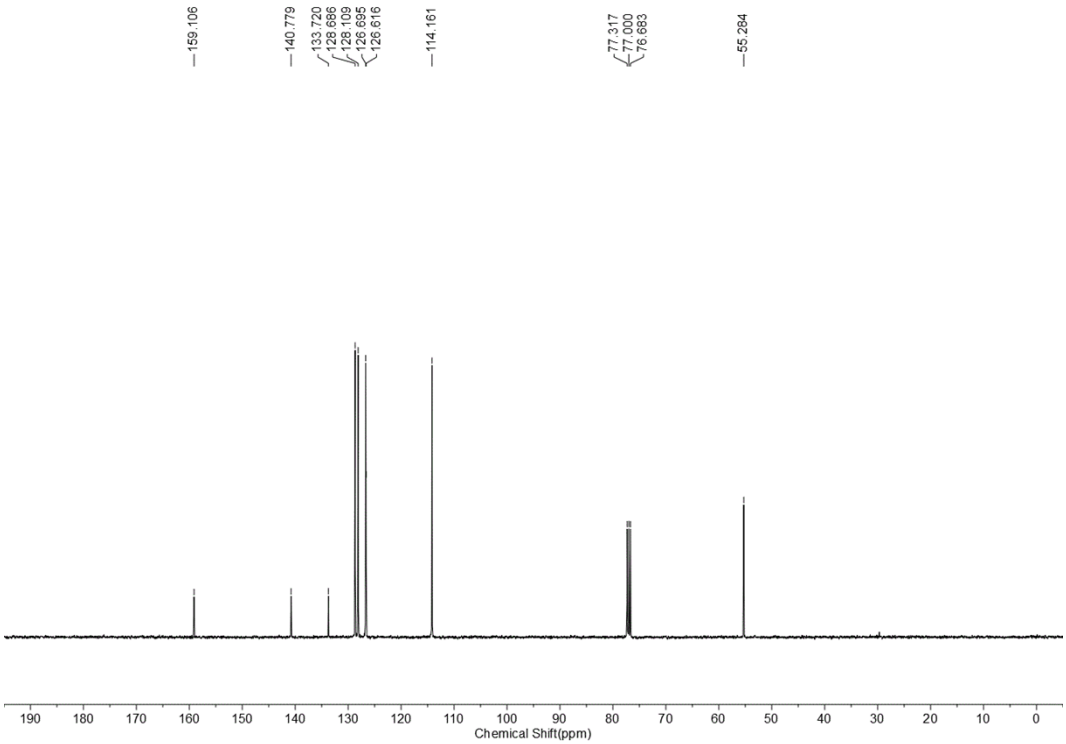
4-Methoxybiphenyl (3g)



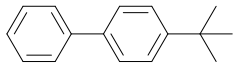
^{1}H NMR, $CDCl_3$, 400 MHz



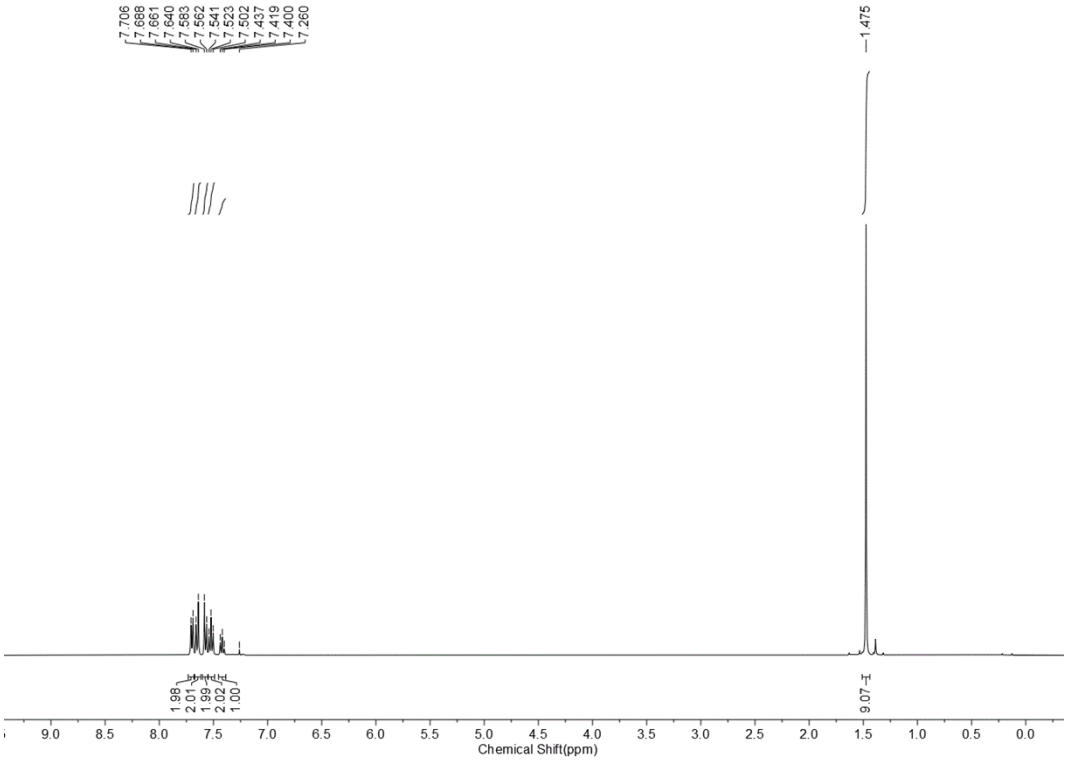
^{13}C NMR, $CDCl_3$, 101 MHz



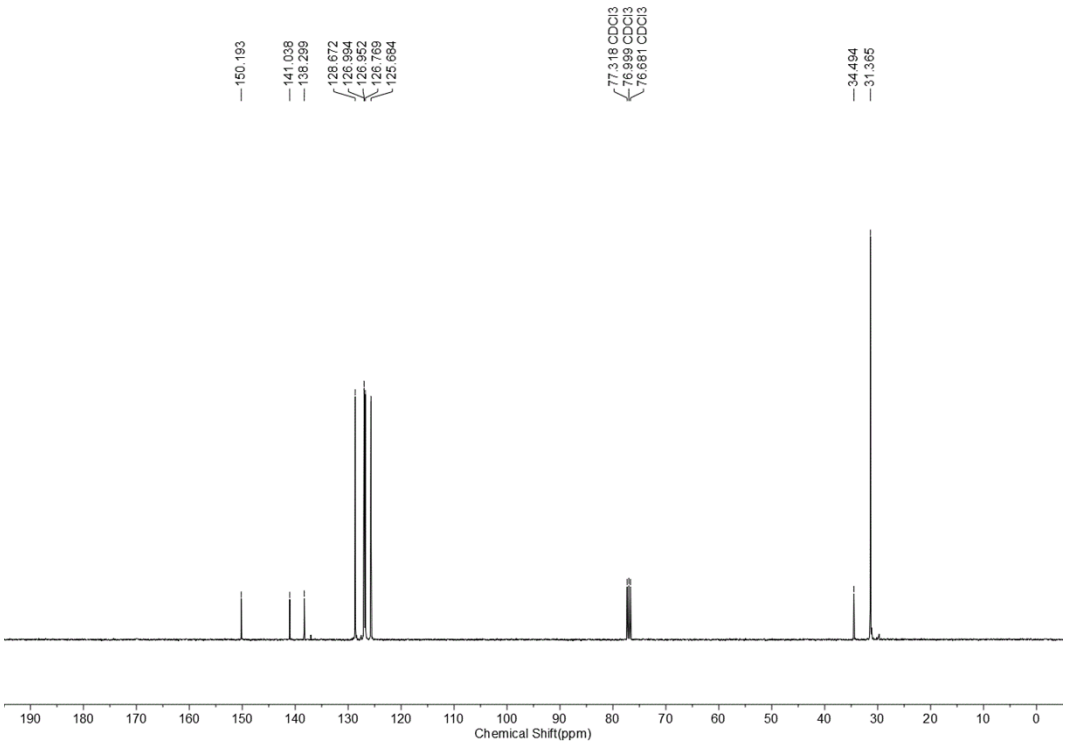
4-(tert-butyl)-1,1'-biphenyl (3h)



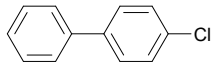
^{1}H NMR, $CDCl_3$, 400 MHz



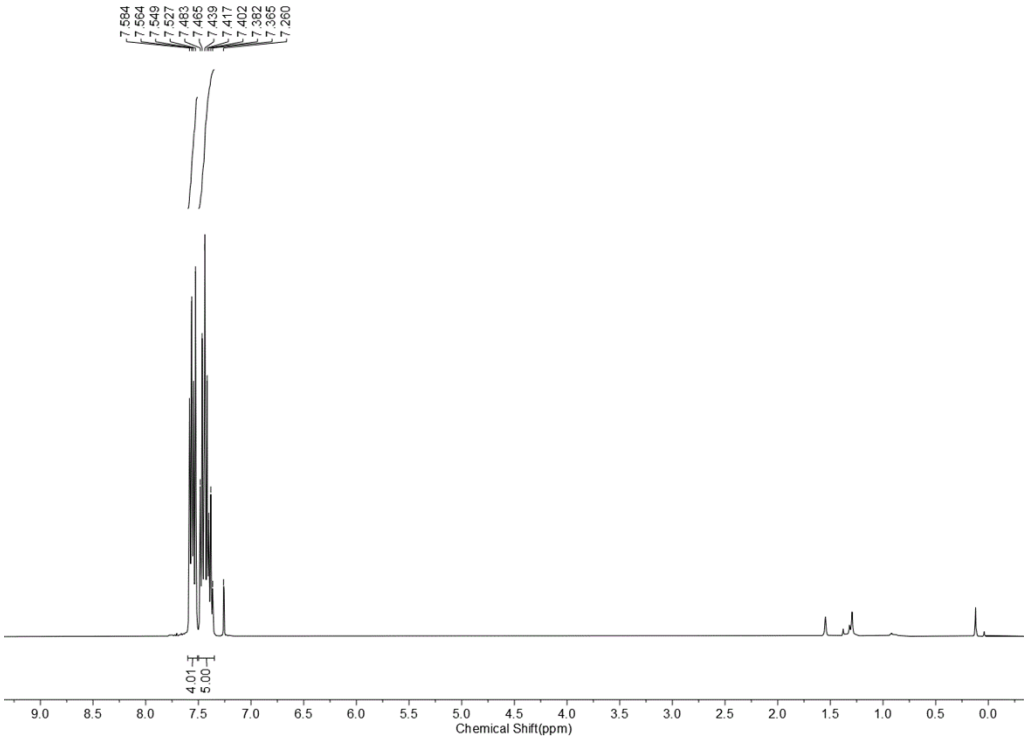
^{13}C NMR, $CDCl_3$, 101 MHz



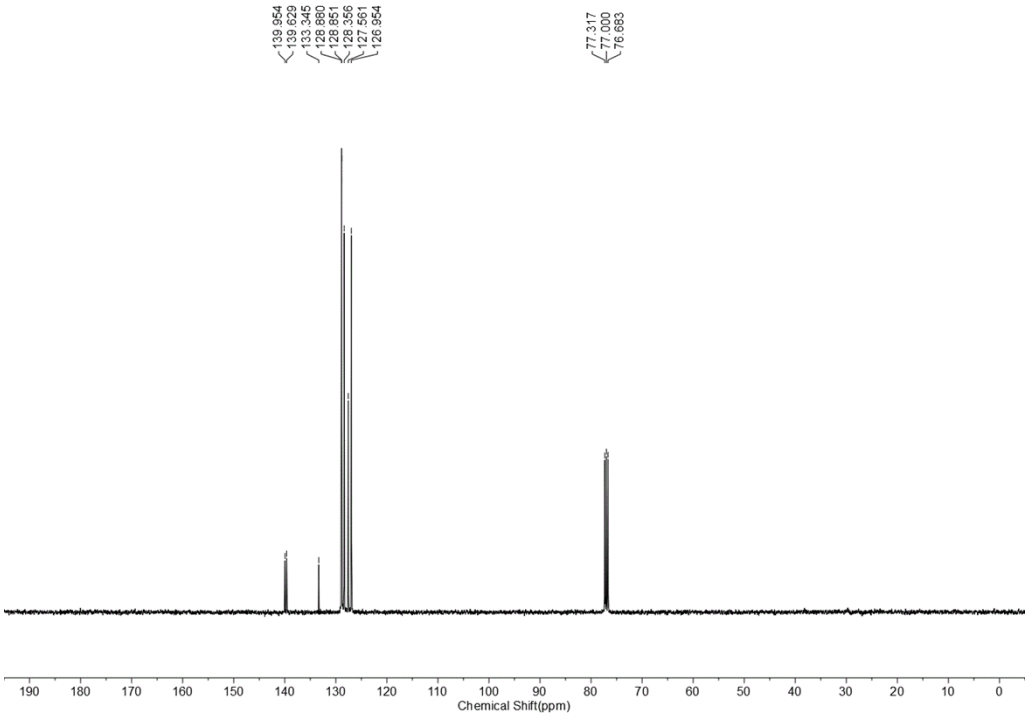
4-Chloridebiphenyl (3i)



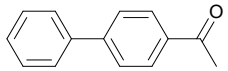
^{1}H NMR, $CDCl_3$, 400 MHz



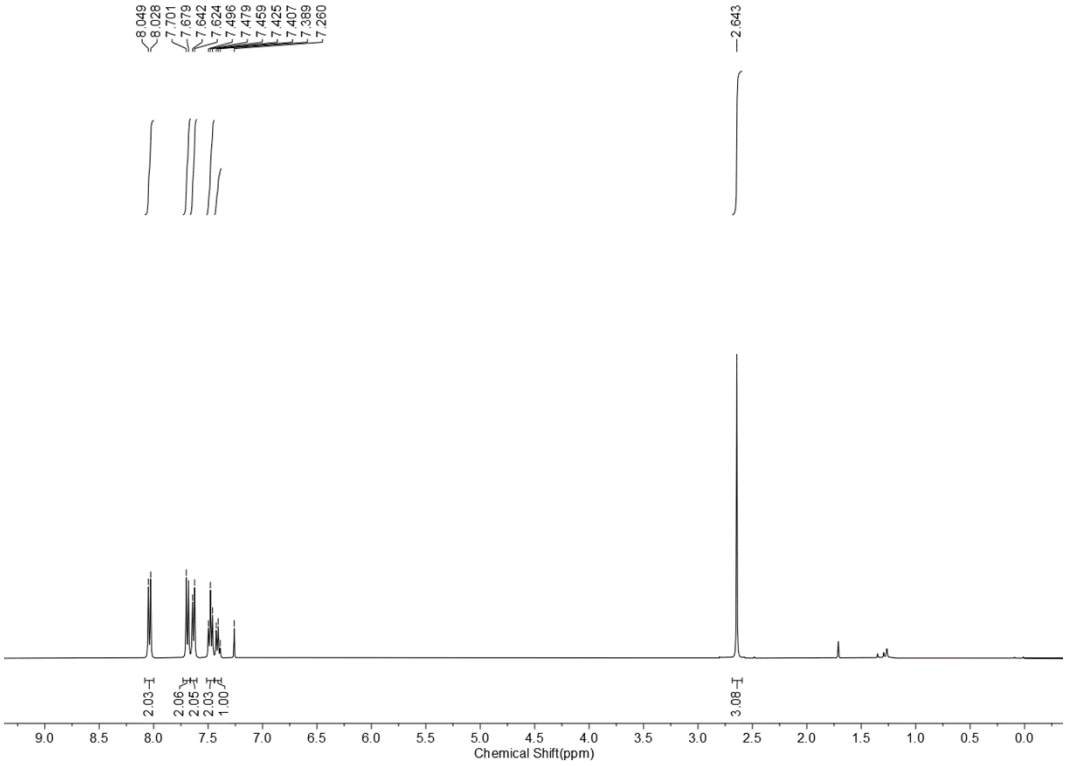
^{13}C NMR, $CDCl_3$, 101 MHz



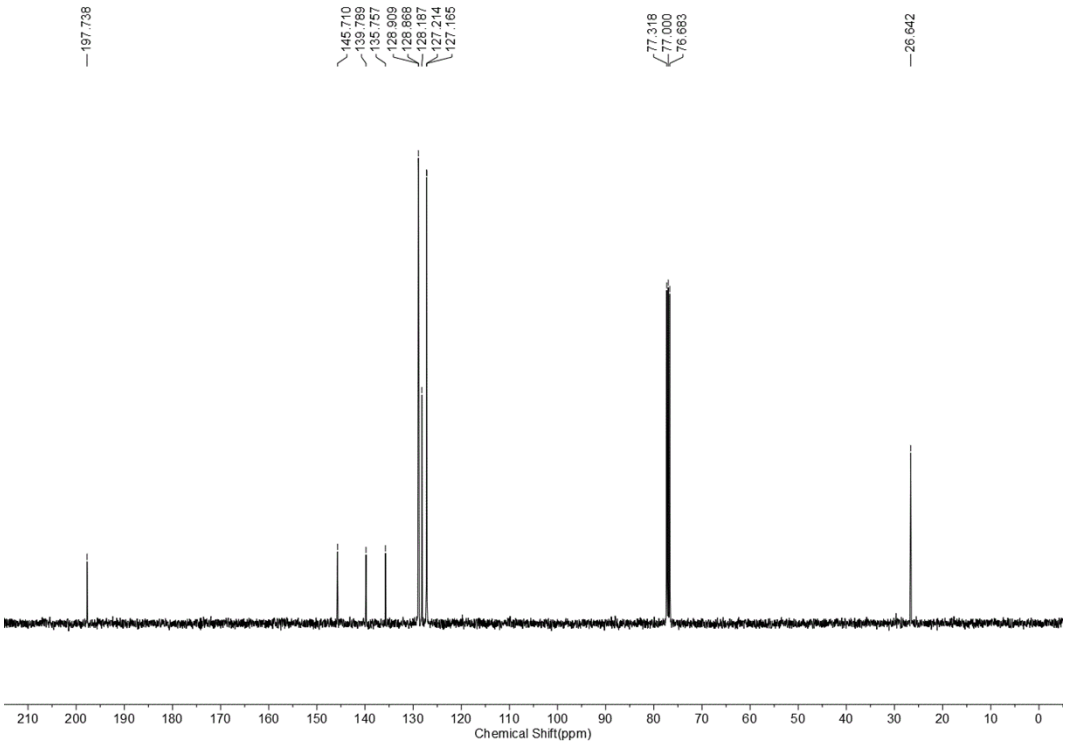
4-Acetylbiphenyl (3j)



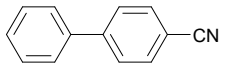
^{1}H NMR, $CDCl_3$, 400 MHz



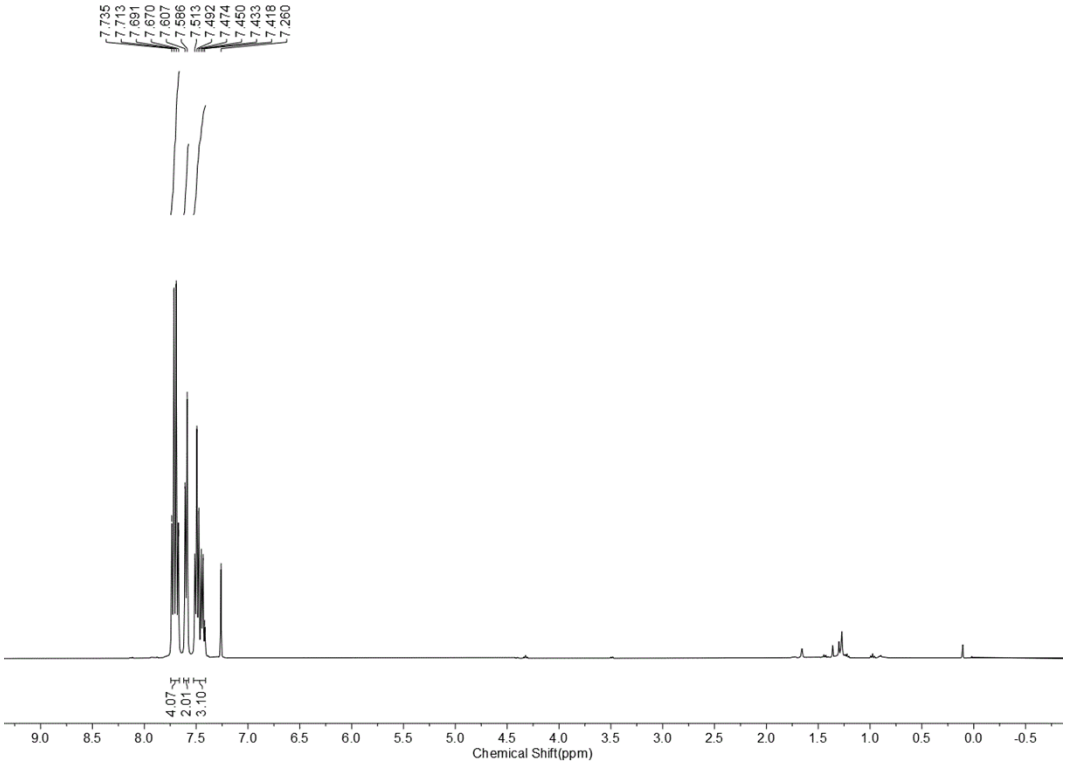
^{13}C NMR, $CDCl_3$, 101 MHz



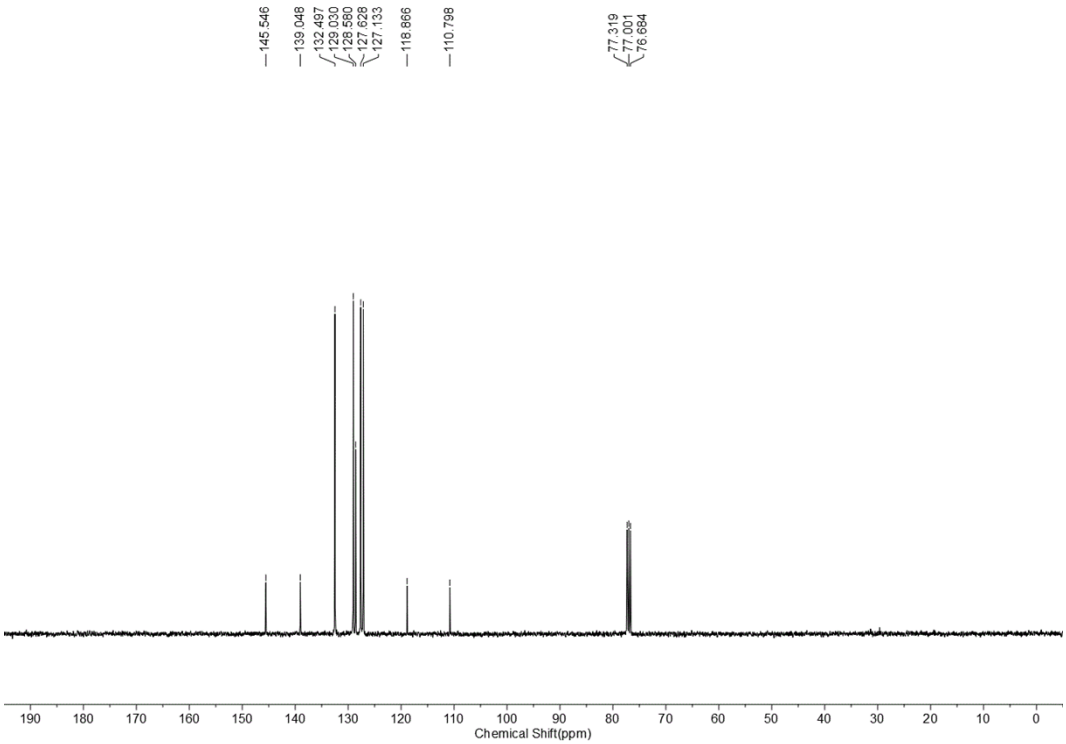
[1,1'-biphenyl]-4-carbonitrile (3k)



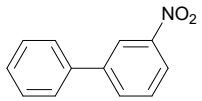
^{1}H NMR, $CDCl_3$, 400 MHz



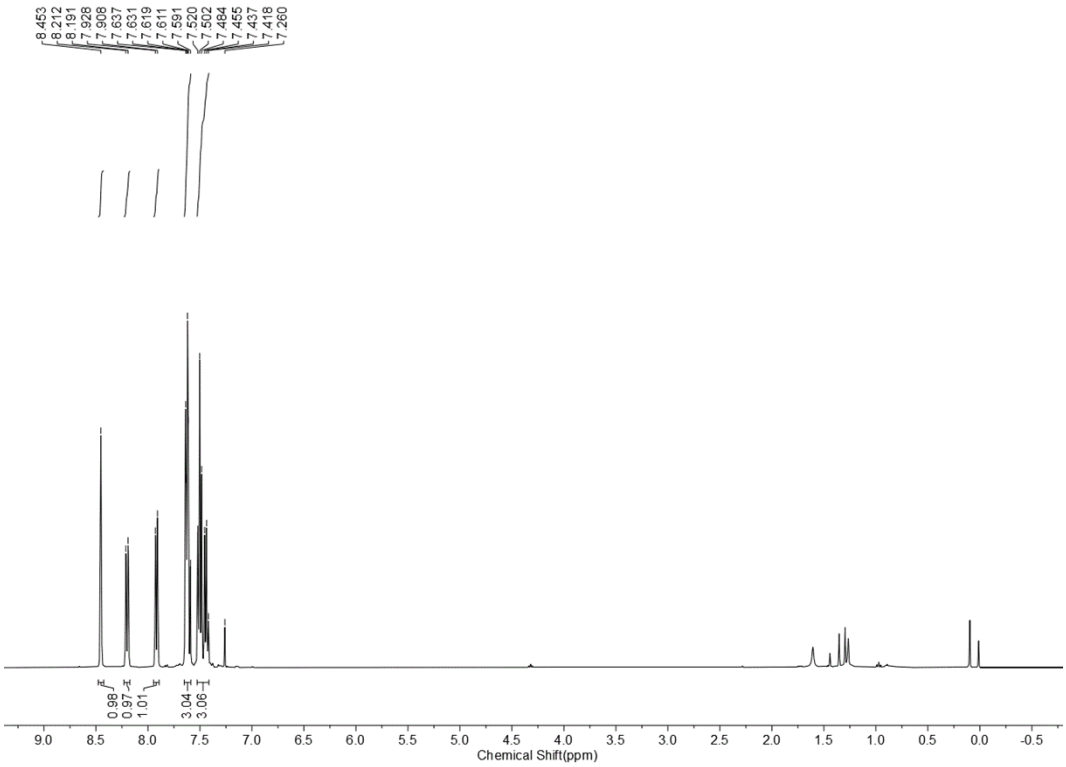
^{13}C NMR, $CDCl_3$, 101 MHz



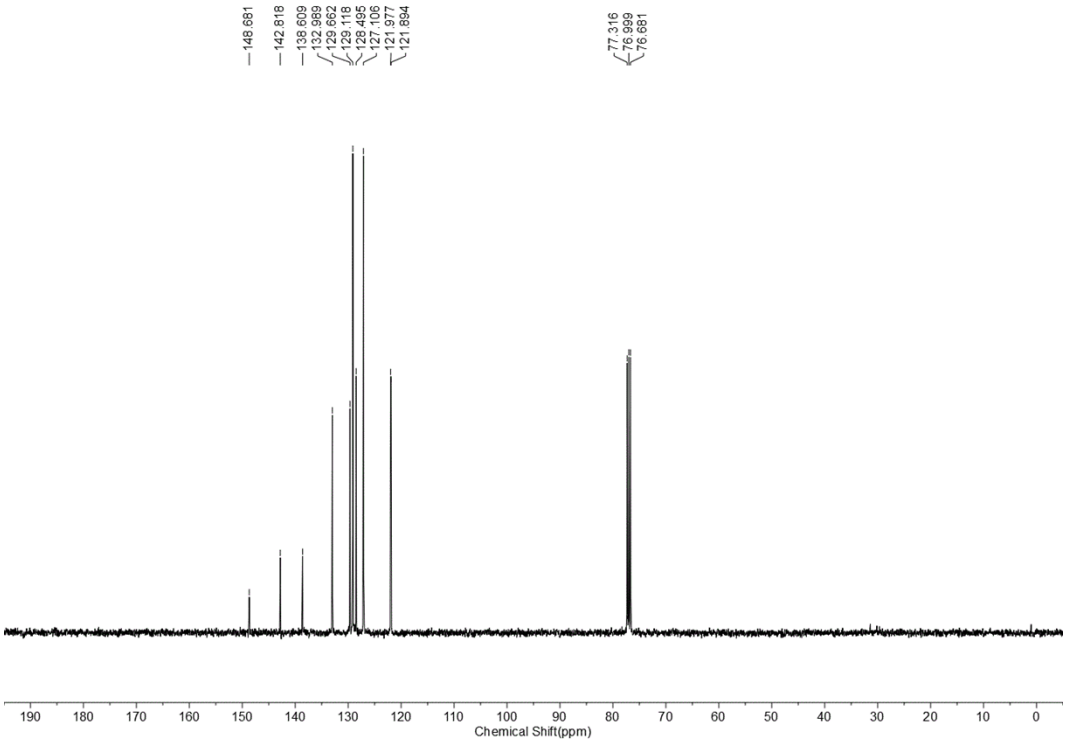
3-Nitrobiphenyl (3l)



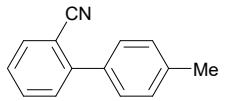
^{1}H NMR, $CDCl_3$, 400 MHz



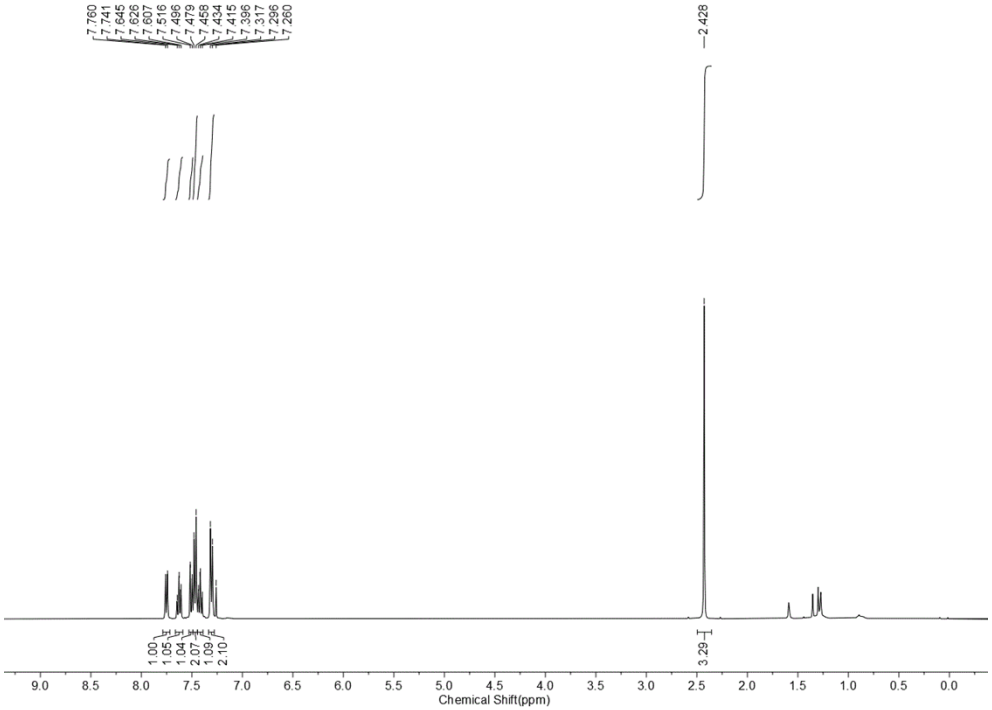
^{13}C NMR, $CDCl_3$, 101 MHz



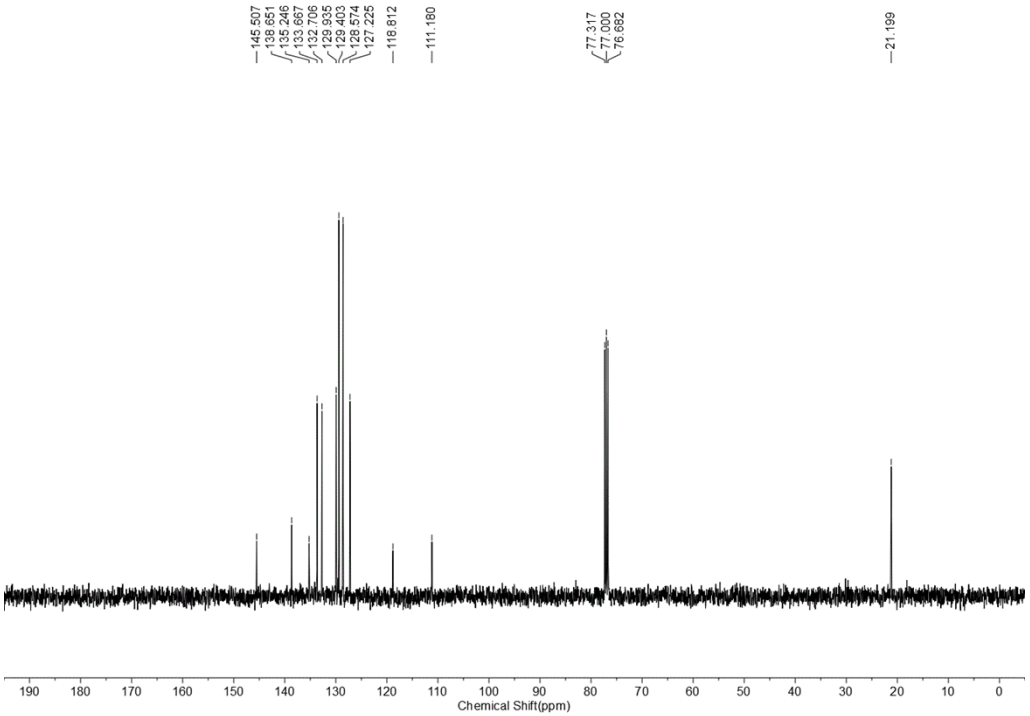
4'-methyl-[1,1'-biphenyl]-2-carbonitrile (3m)



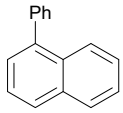
^{1}H NMR, $CDCl_3$, 400 MHz



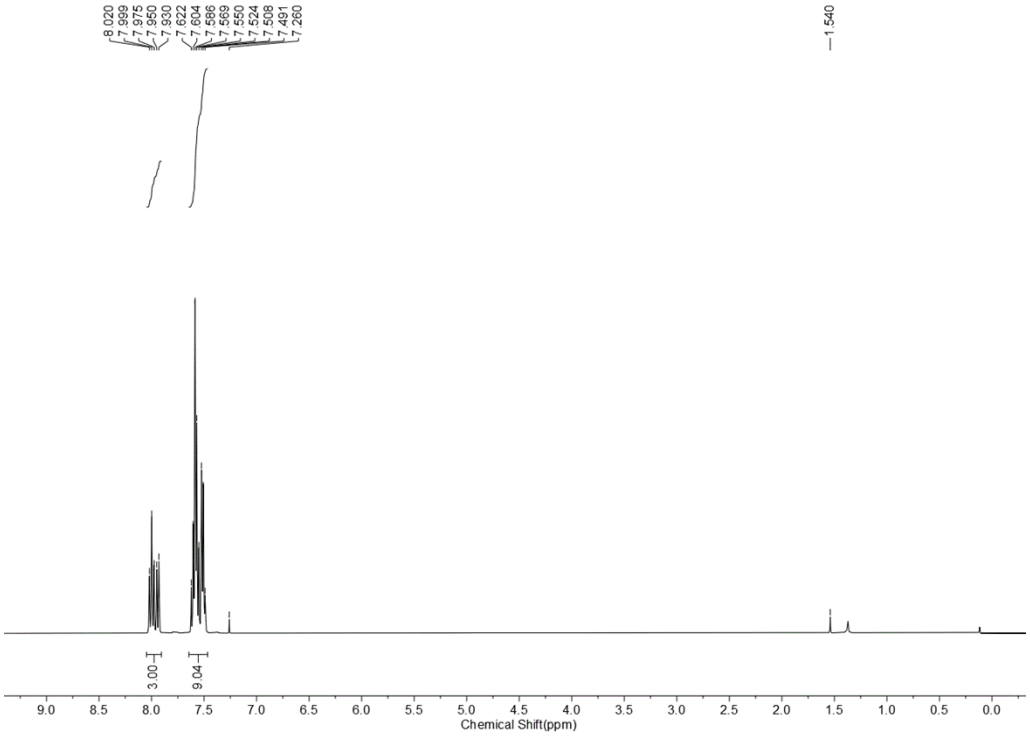
^{13}C NMR, $CDCl_3$, 101 MHz



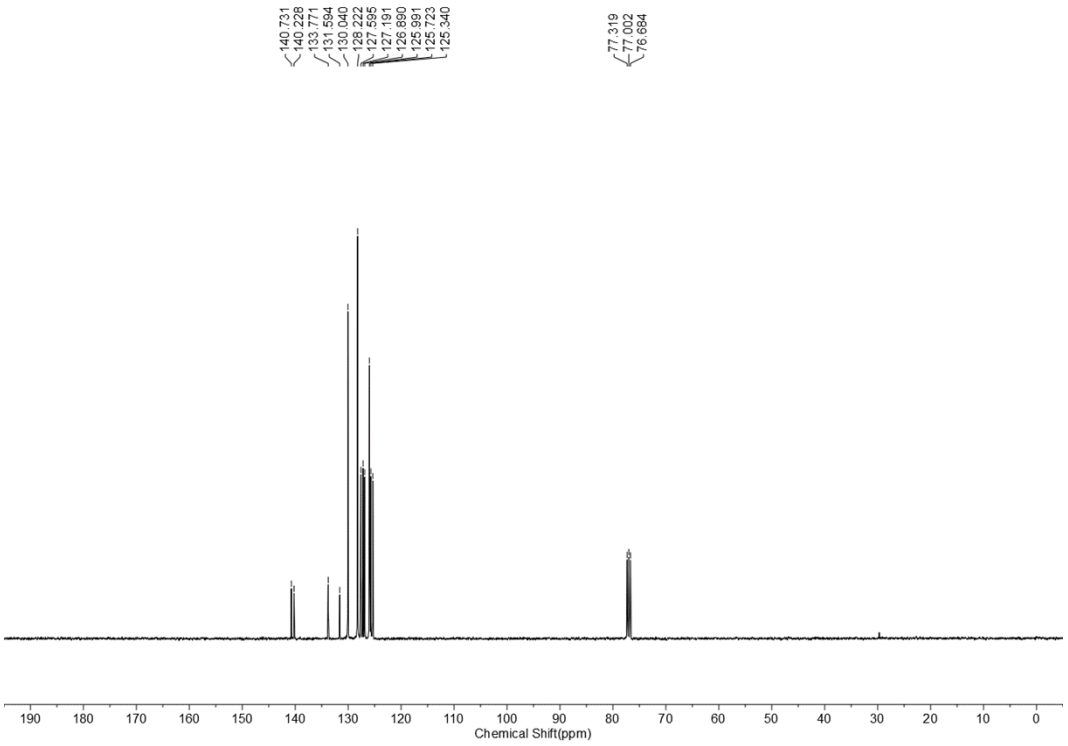
1-phenylnaphthalene (3n)



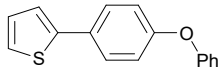
^{1}H NMR, $CDCl_3$, 400 MHz



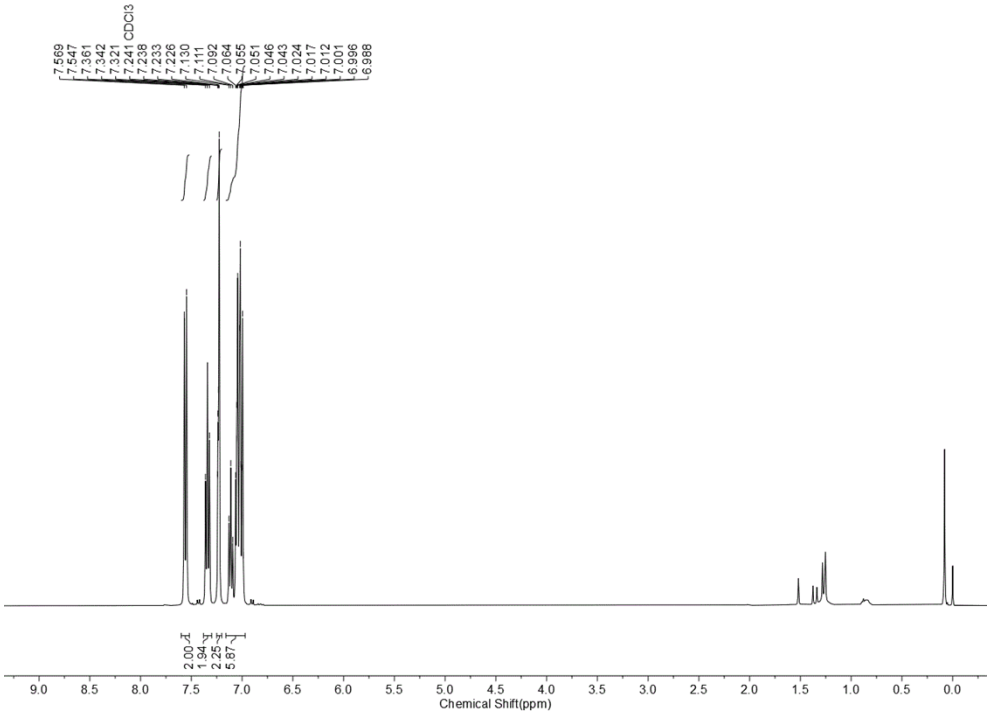
^{13}C NMR, $CDCl_3$, 101 MHz



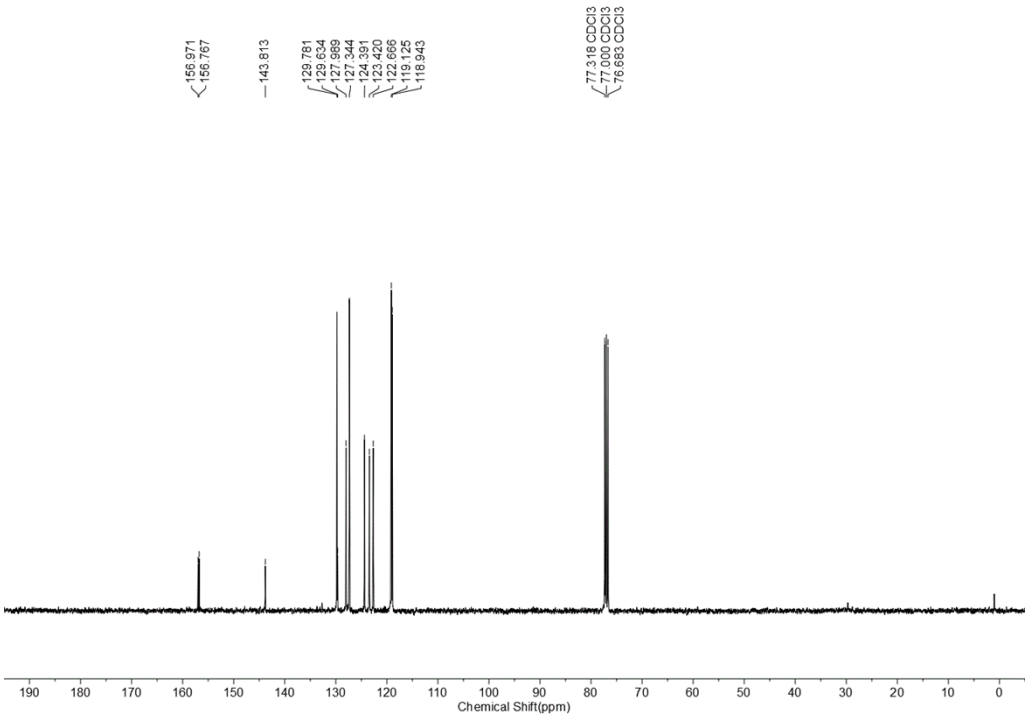
2-(4-phenoxyphenyl)thiophene (3o)



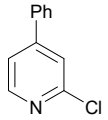
^{1}H NMR, $CDCl_3$, 400 MHz



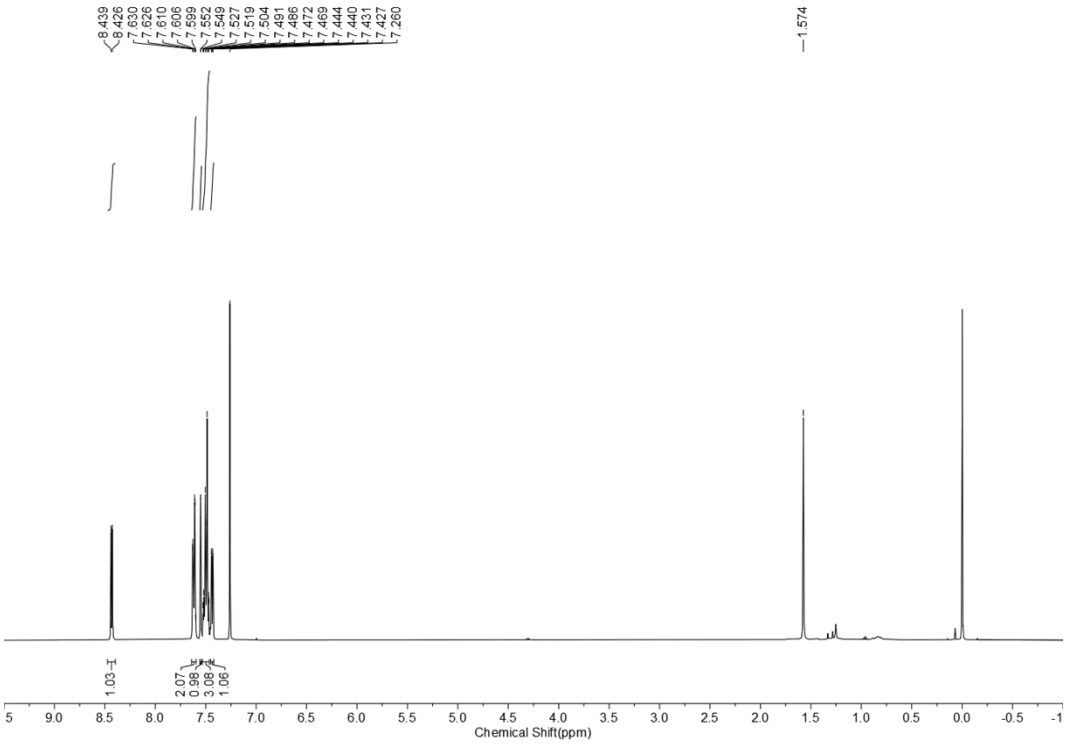
^{13}C NMR, $CDCl_3$, 101 MHz



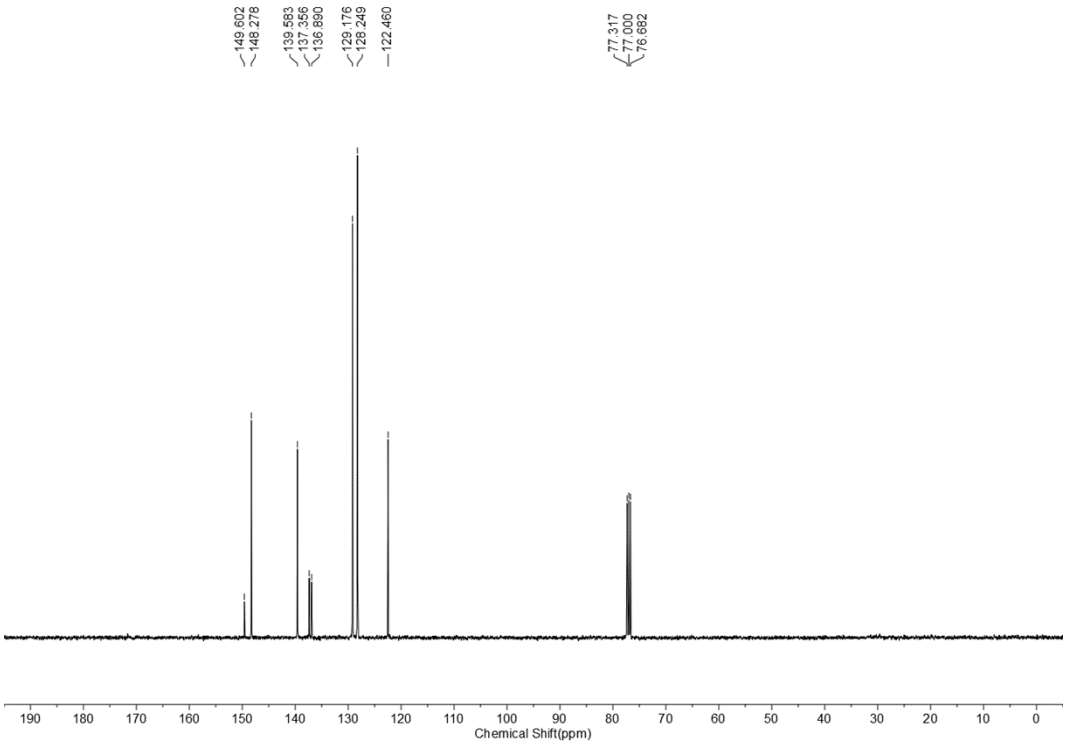
2-chloro-4-phenylpyridine (3p)



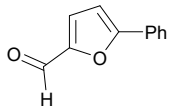
^{1}H NMR, $CDCl_3$, 400 MHz



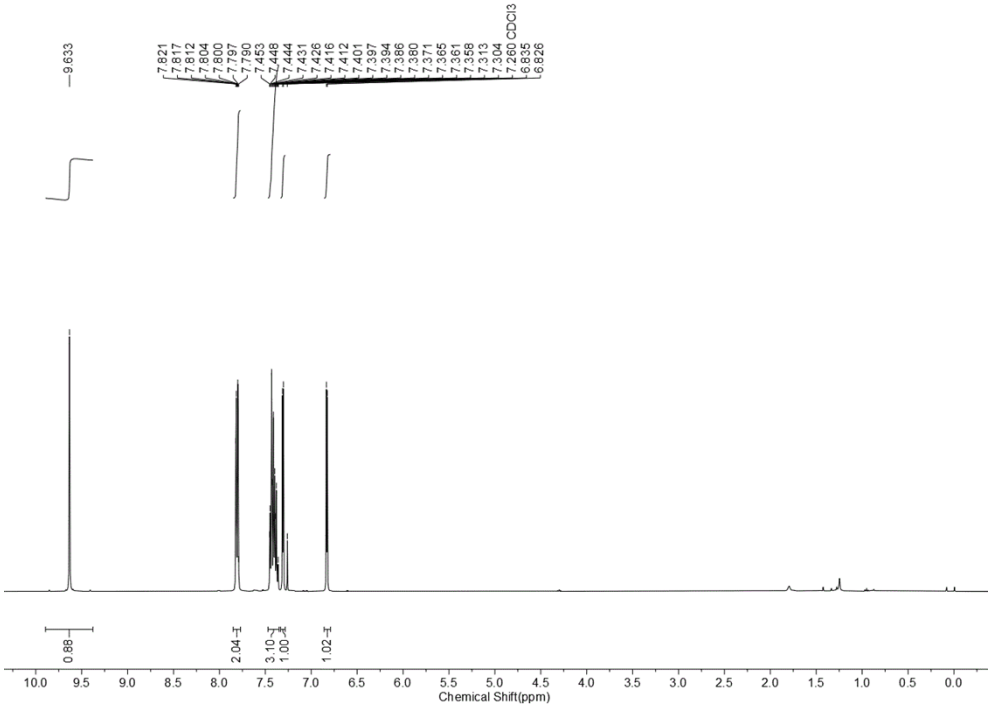
^{13}C NMR, $CDCl_3$, 101 MHz



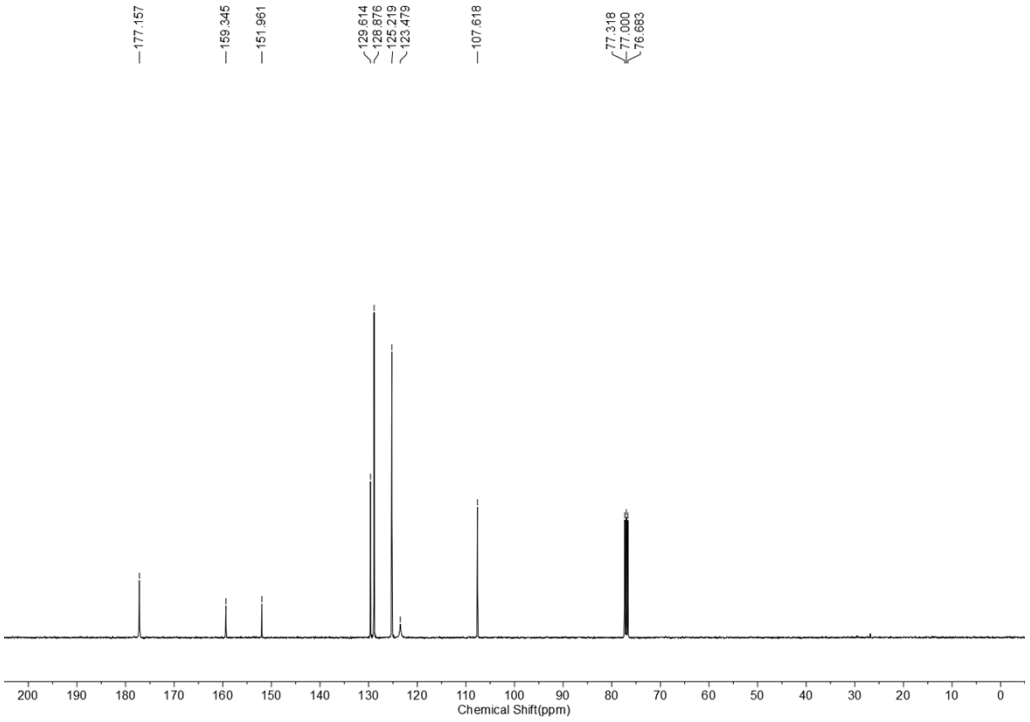
5-Phenylfuran-2-carbaldehyde (3q)



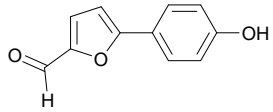
^{1}H NMR, $CDCl_3$, 400 MHz



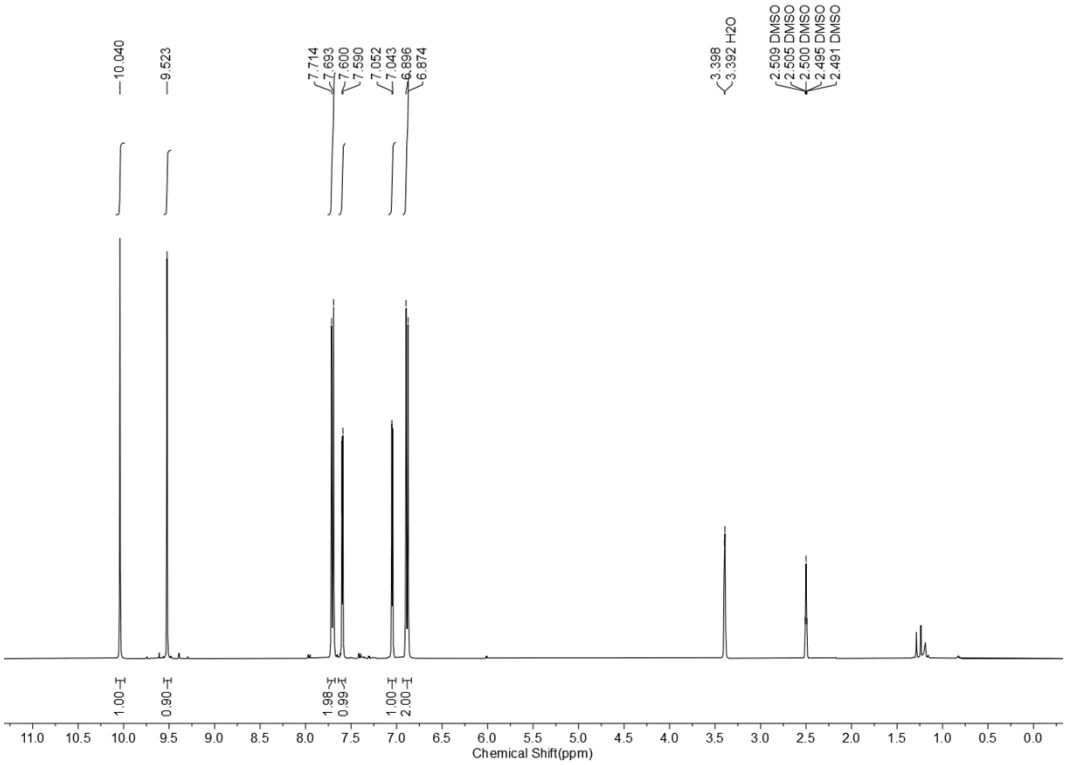
^{13}C NMR, $CDCl_3$, 101 MHz



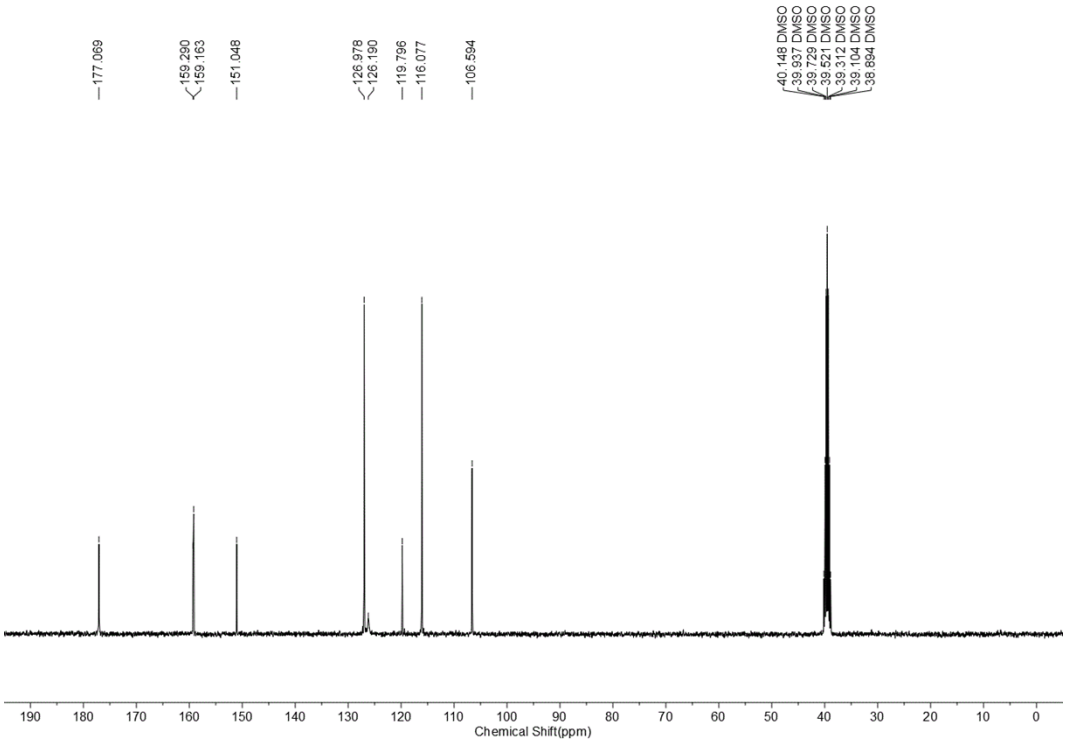
5-(4-hydroxyphenyl)furan-2-carbaldehyde (3r)



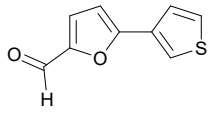
^{1}H NMR, DMSO-d_6, 400 MHz



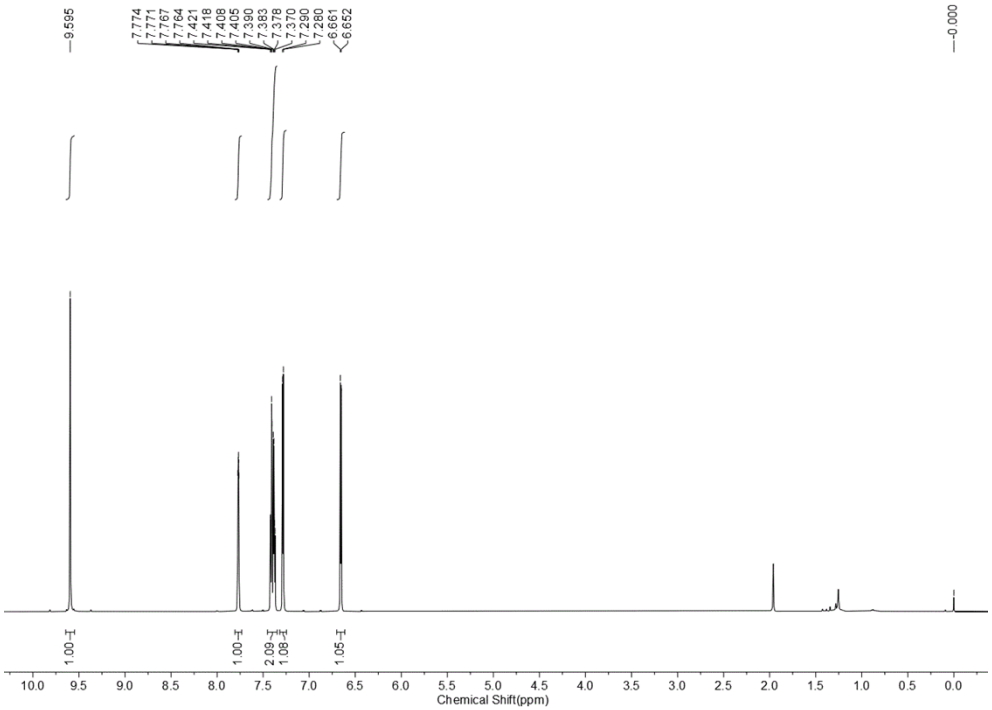
^{13}C NMR, DMSO-d_6, 101 MHz



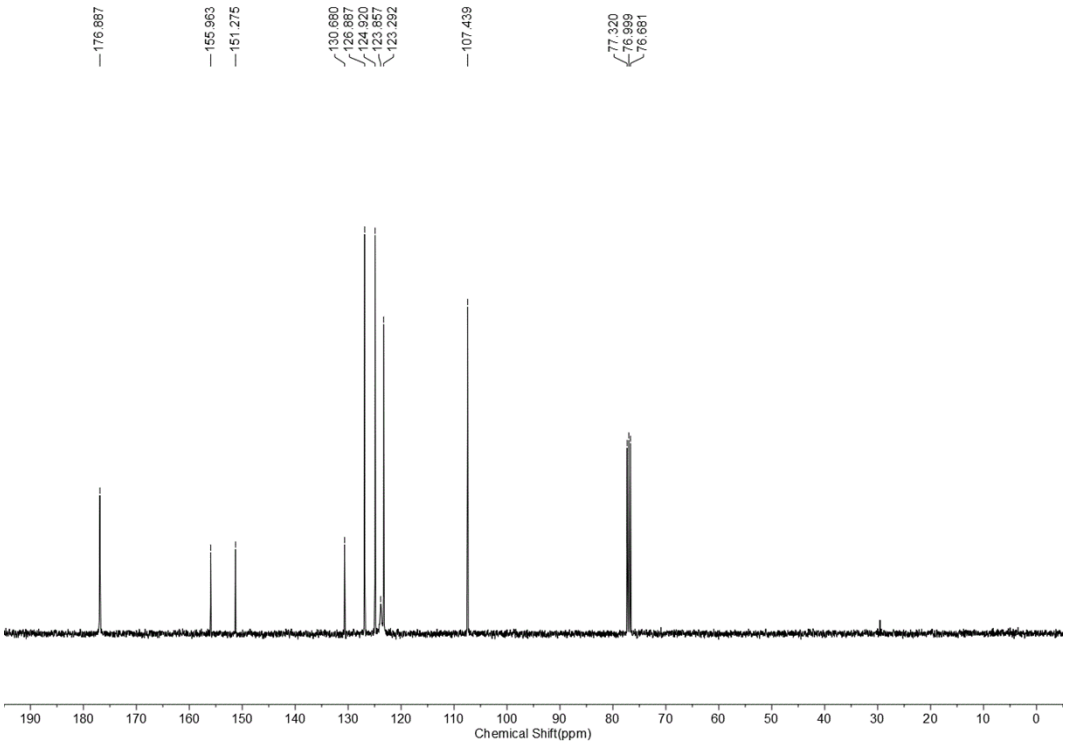
5-(thiophen-3-yl)furan-2-carbaldehyde (3s)



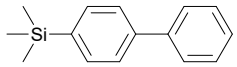
^{1}H NMR, $CDCl_3$, 400 MHz



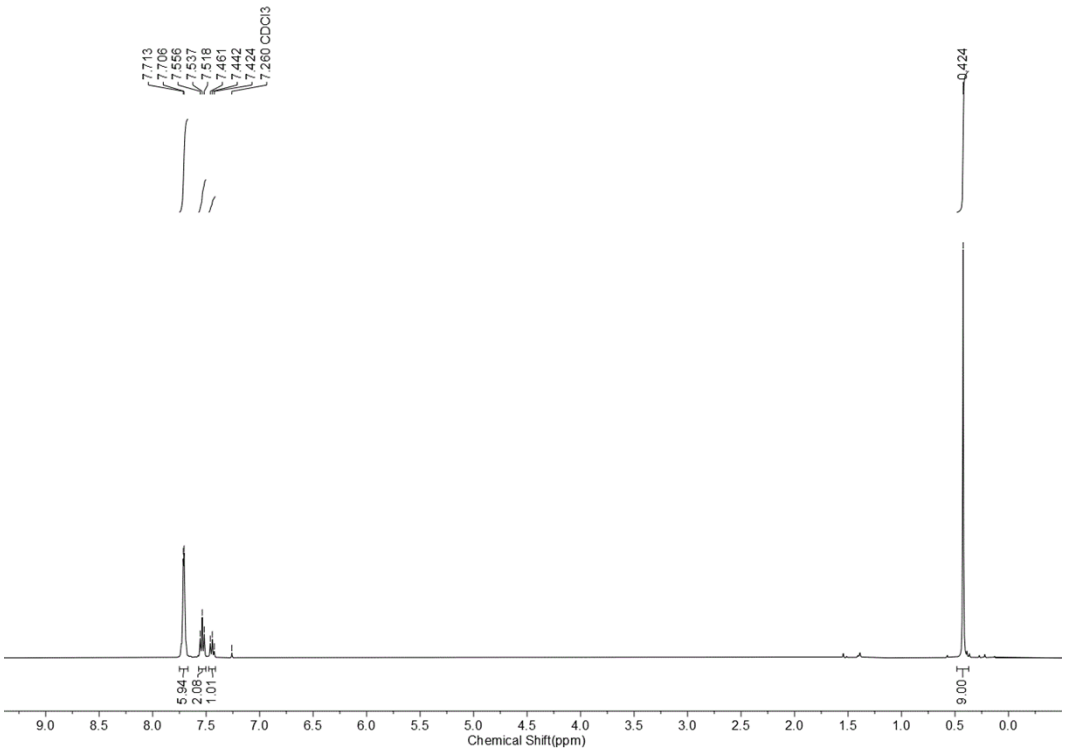
^{13}C NMR, $CDCl_3$, 101 MHz



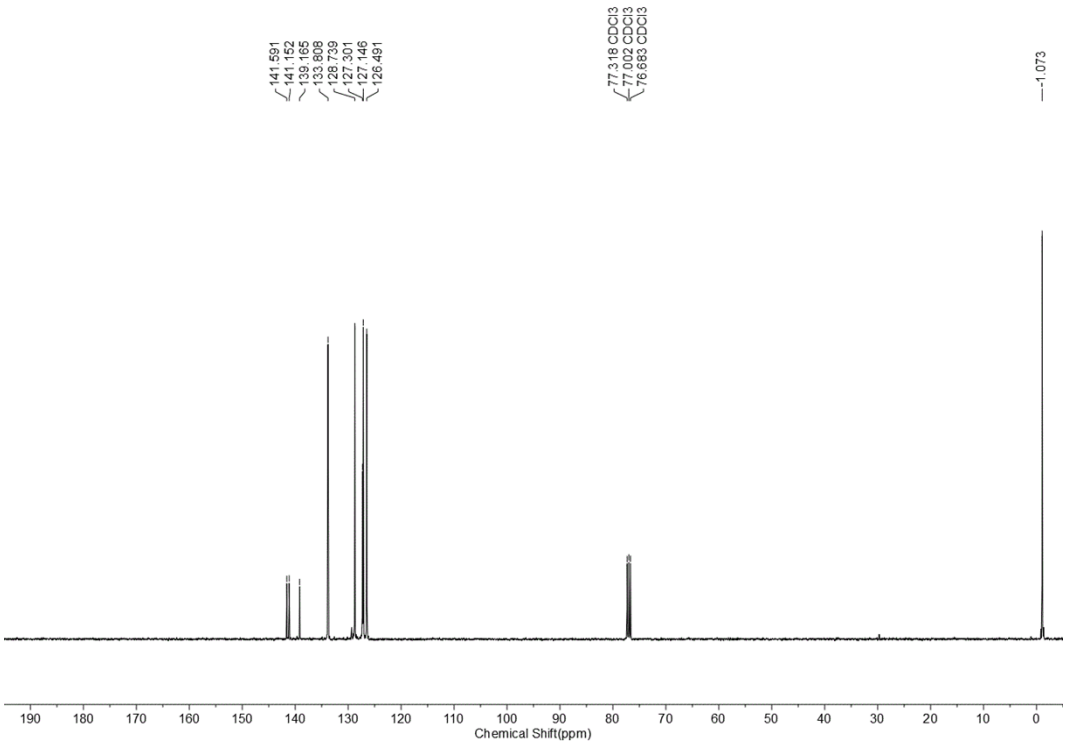
[1,1'-biphenyl]-4-yltrimethylsilane (3t)



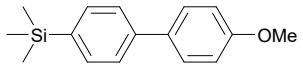
^{1}H NMR, $CDCl_3$, 400 MHz



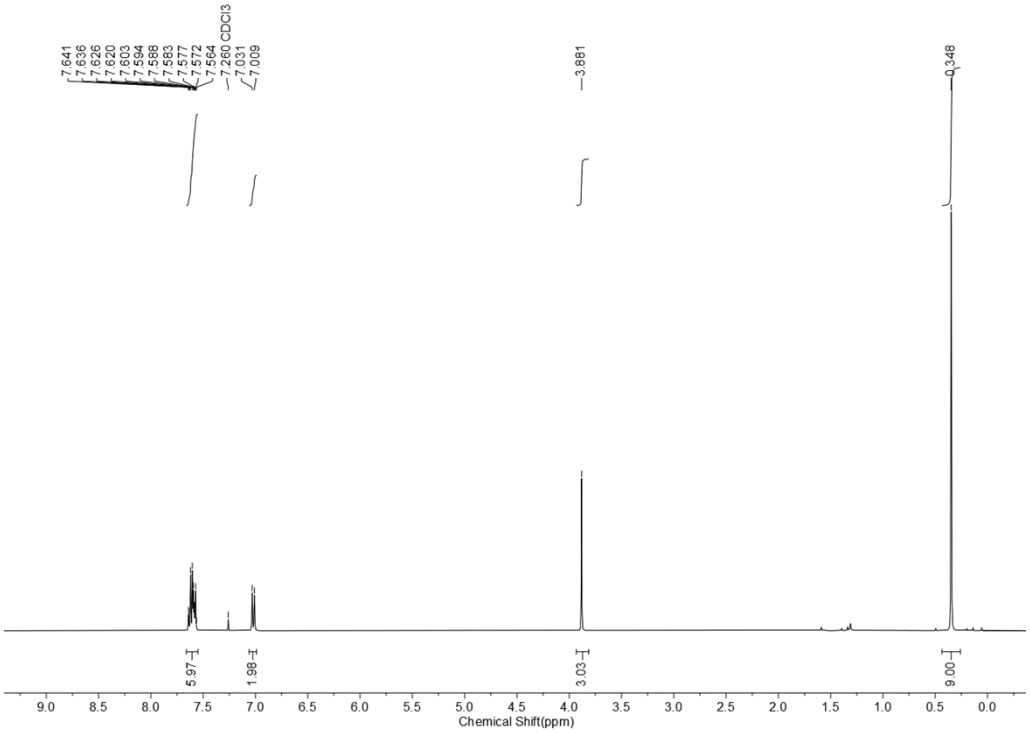
^{13}C NMR, $CDCl_3$, 101 MHz



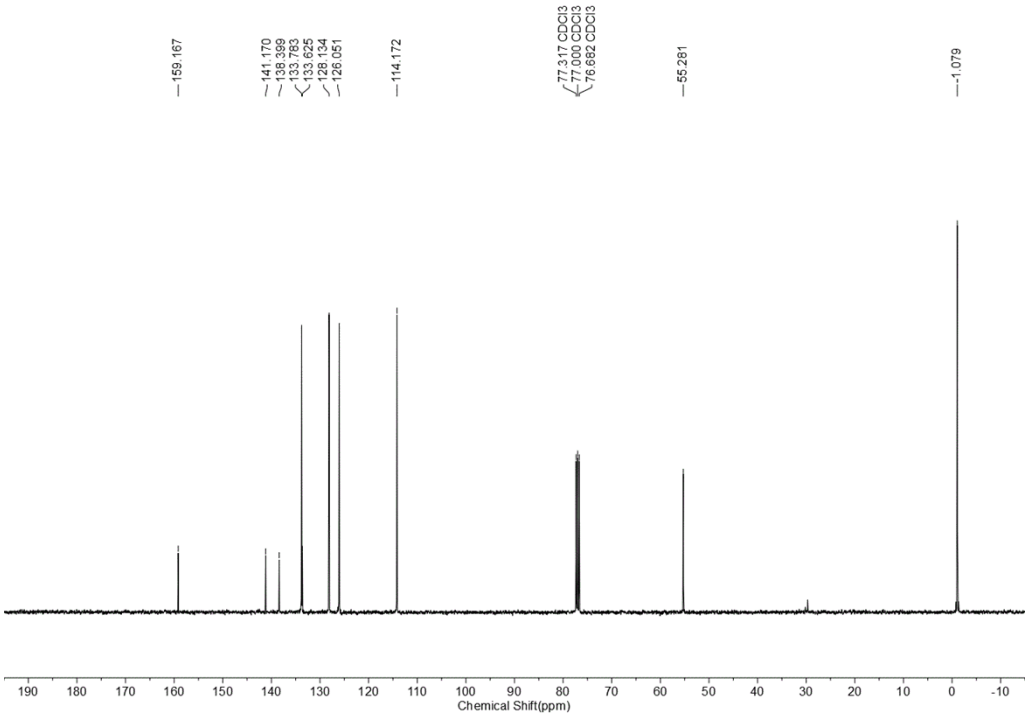
(4'-methoxy-[1,1'-biphenyl]-4-yl)trimethylsilane (3u)



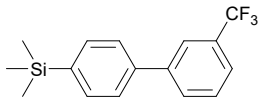
^{1}H NMR, $CDCl_3$, 400 MHz



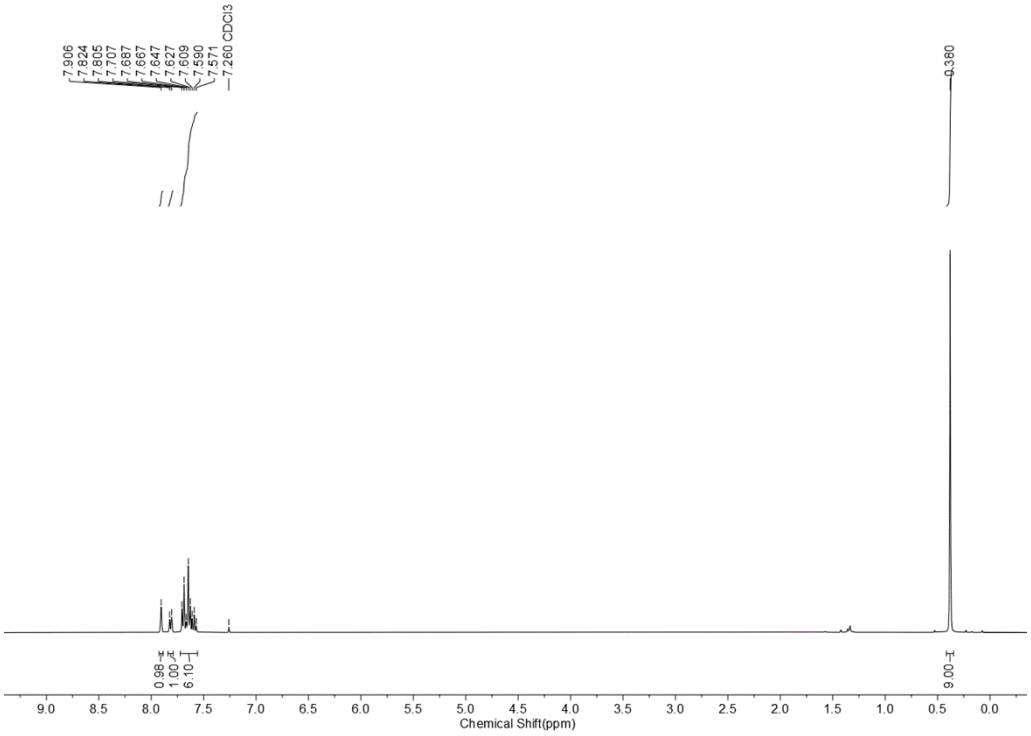
^{13}C NMR, $CDCl_3$, 101 MHz



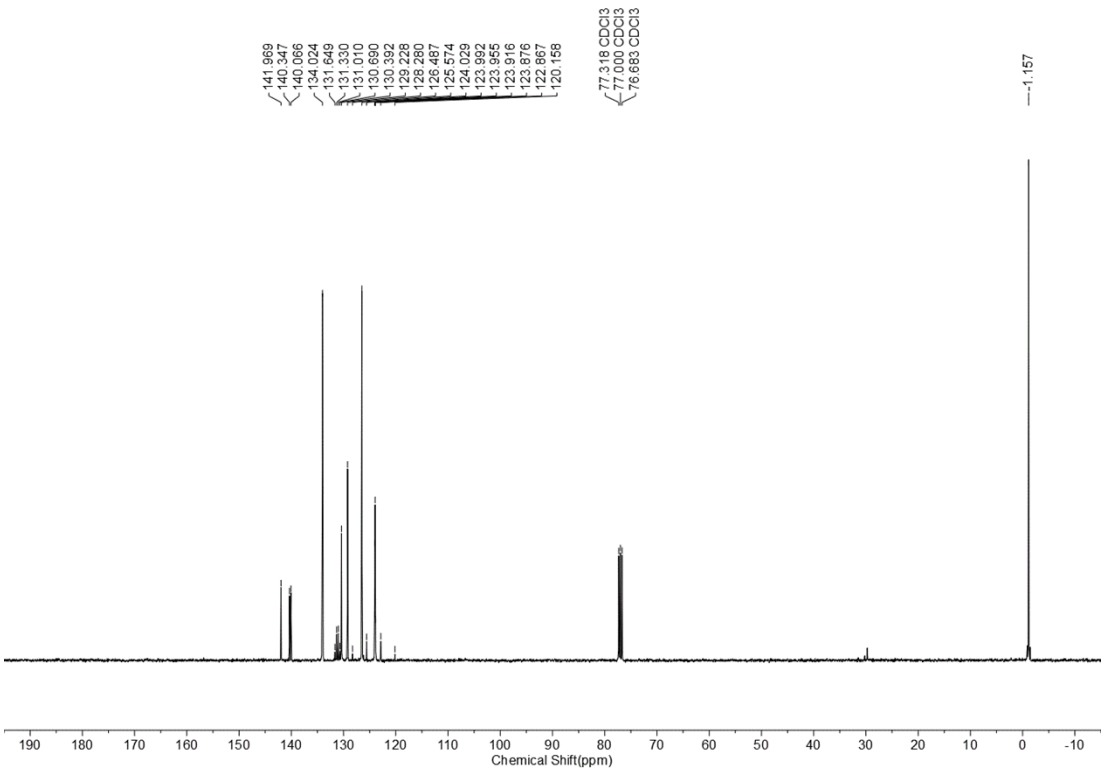
Trimethyl(3'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)silane (3v)



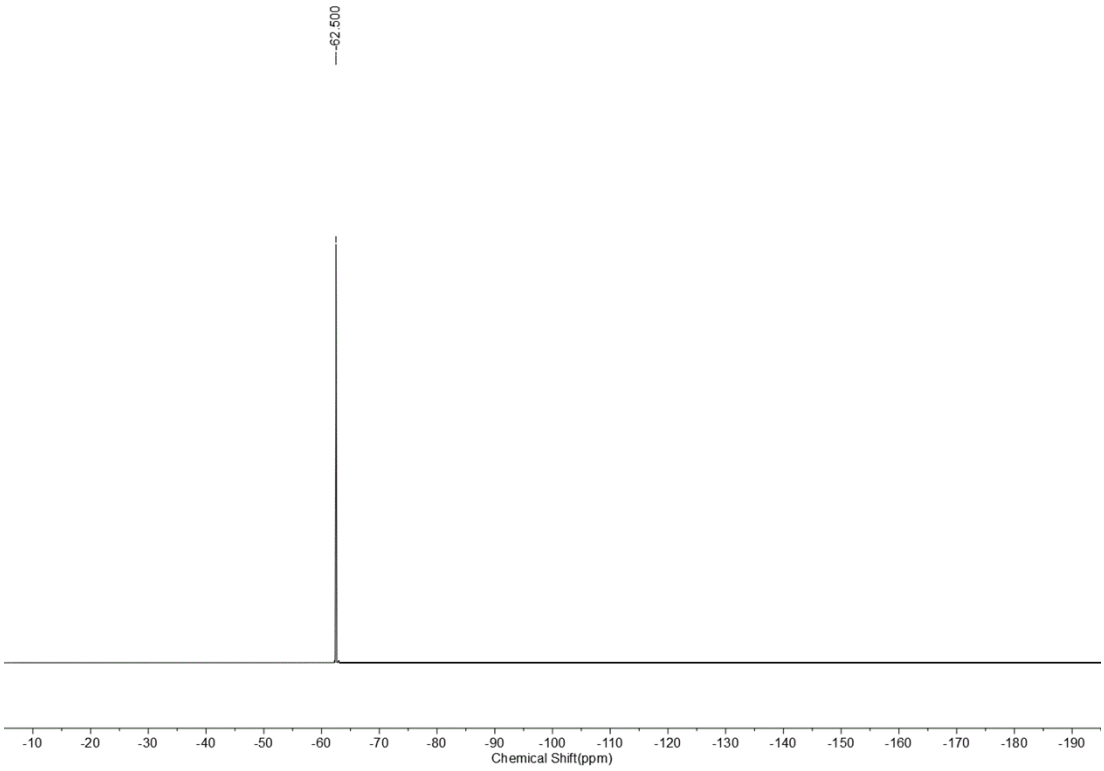
^{1}H NMR, $CDCl_3$, 400 MHz



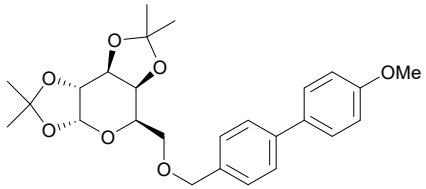
^{13}C NMR, $CDCl_3$, 101 MHz



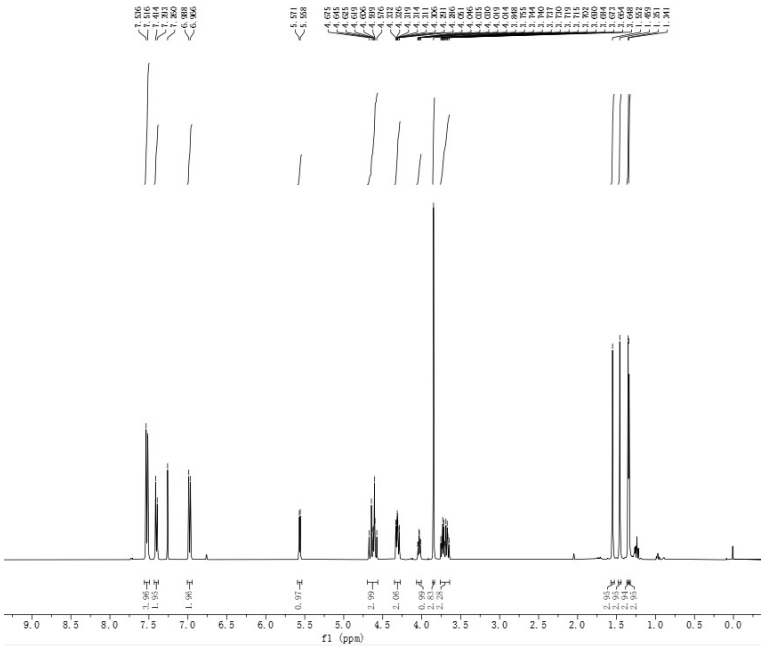
^{19}F NMR, $CDCl_3$, 376 MHz



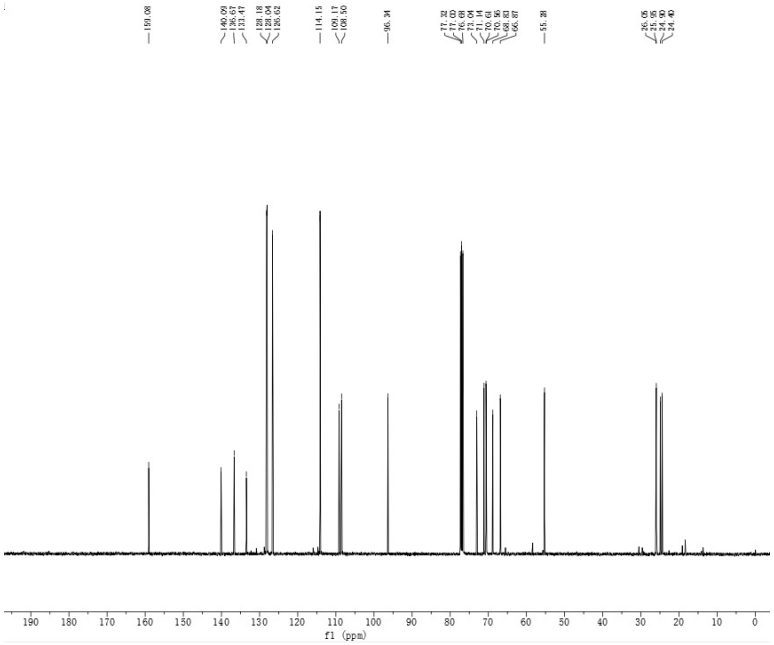
(3aR,5R,5aS,8aS,8bR)-5-(((4'-methoxy-[1,1'-biphenyl]-4-yl)methoxy)methyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (3w)



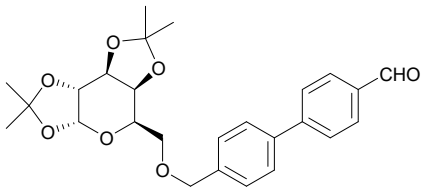
^{1}H NMR, $CDCl_3$, 400 MHz



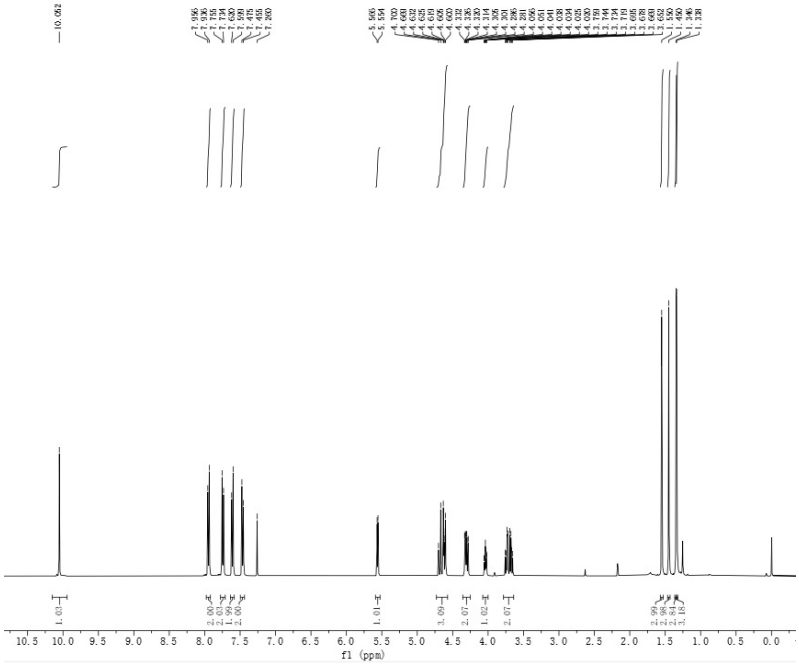
^{13}C NMR, $CDCl_3$, 101 MHz



4'-((((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)methyl)-[1,1'-biphenyl]-4-carbaldehyde (3x)



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



^{13}C NMR, $CDCl_3$, 101 MHz