Supporting Information

An air-Stable, well-defined palladium–BIAN–NHC chloro dimer: a fast-activating, highly efficient catalyst for cross-coupling

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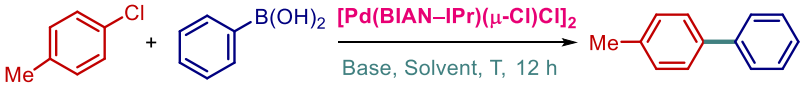
1. Optimization Studies

Table S1. Optimization Studies.[a]



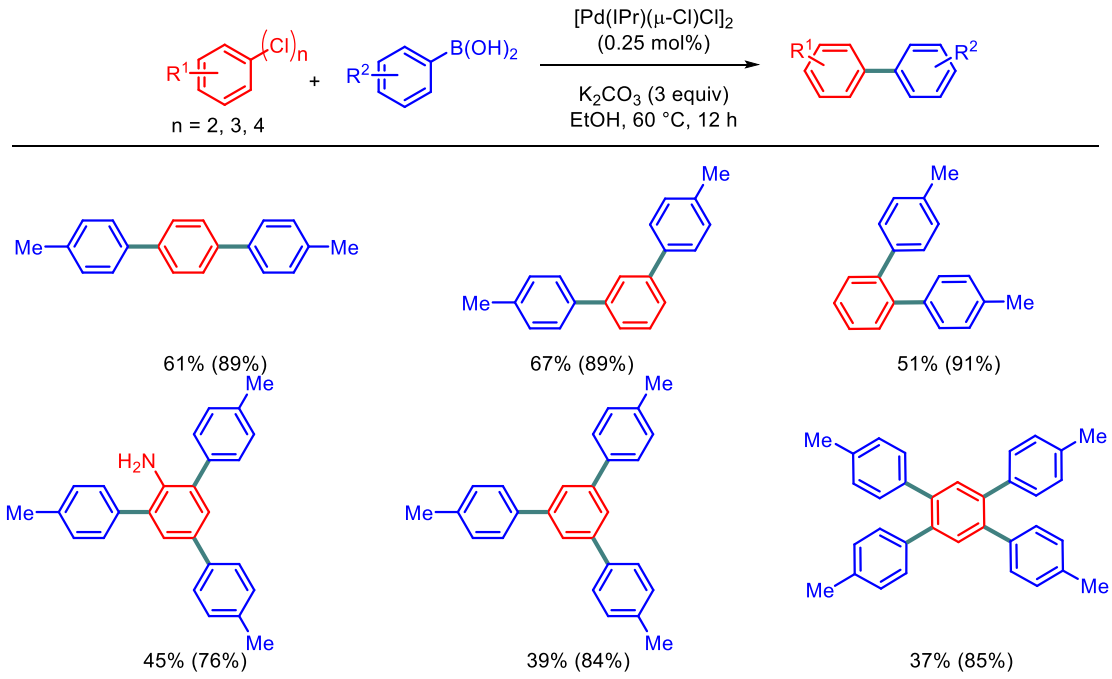
3 4 5

Entry	Base [equiv]	Solvent	T [°C]	Yield [%]
1[b,c]	KO^{t}Bu (1.1)	EtOH	25	95
2[b,d]	KO^{t}Bu (1.1)	EtOH	25	84
3[b]	KO^{t}Bu (1.1)	EtOH	25	52
4	KO^{t}Bu (1.1)	EtOH	25	80
5	KO^{t}Bu (1.1)	^{i}PrOH	25	35
6	KO^{t}Bu (1.1)	THF	25	62
7	KO^{t}Bu (1.1)	1,4-dioxane	25	63
8	KO^{t}Bu (1.1)	MeOH	25	72
9	Cs_2CO_3 (1.5)	EtOH	25	73
10	K_2CO_3 (1.5)	EtOH	25	84
11	K_2CO_3 (3.0)	EtOH	25	87
12	K_2CO_3 (3.0)	EtOH	60	92

[a]Conditions: ArCl (1.0 equiv), Ph-B(OH)$_2$ (2.0 equiv), [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%), base (1.1-3 equiv), solvent (0.5 M), 25-60 °C, 12 h. [b]Ph-B(OH)$_2$ (1.2 equiv.) [c][Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (1.5 mol%). [d][Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.5 mol%).

2. Additional Experiments Referred to from the Main Manuscript

In addition to better kinetics, [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ catalyzes cross-coupling of sterically-hindered substrates and polyhalogenated arenes in much higher yields (Scheme S1). This improvement in catalysis is likely due to the increased bulkiness around the metal facilitating reductive elimination. In agreement with this observed reactivity, the cross-coupling between PhCl and 2-Me-C_6H_4-$B(OH)_2$ proceeds in 95% yield with [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (cf. 68% yield using [Pd(IPr)(μ-Cl)Cl]$_2$) and of 4-MeO-C_6H_4-Cl in 97% yield (cf. 41% yield using [Pd(IPr)(μ-Cl)Cl]$_2$). Studies on the mechanism of the cross-coupling reactions catalyzed by [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ and related catalysts are underway.



*Yields in brackets correspond to the reactions with [Pd(BIAN-IPr)(μ-Cl)Cl]$_2$

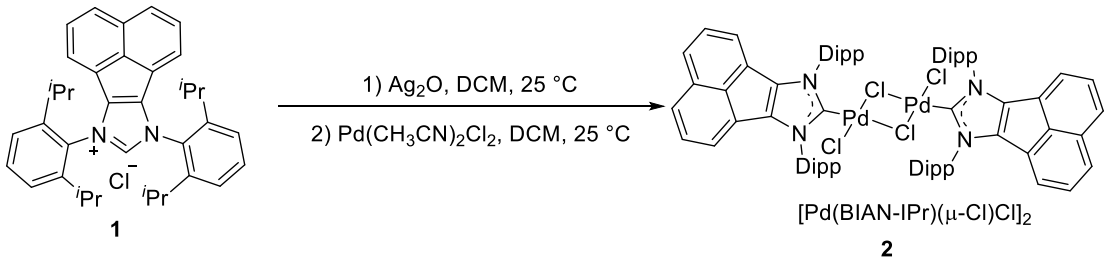
Scheme S1. Cross-Coupling of Polyhalogenated Arenes using [Pd(IPr)(μ-Cl)Cl]$_2$.

3. General Information

All starting materials reported in the manuscript have been previously described in literature. All experiments were performed using standard Schlenk techniques under nitrogen or argon unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All other chemicals were purchased at the highest commercial grade and used as received. All products were identified using ^{1}H NMR and ^{13}C NMR analysis and comparison with authentic samples. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All yields refer to yields determined by ^{1}H NMR using an internal standard (optimization) and isolated yields (scope) unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Ascend spectrometers at 400 (^{1}H NMR) and 100 MHz (^{13}C NMR) or 600 (^{1}H NMR) and 150 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.26 and 77.16 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (J) are reported in Hertz (Hz). Abbreviations are: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet. Dibromomethane was used as an internal standard to determine NMR yields. Powder diffraction data were recorded on a Rigaku SmartLab diffractometer with Cu-K radiation and D/teX Ultra detector covering 3-60° (2θ). All flash chromatography were performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Experimental for characterization purposes.

4. Experimental Procedures and Characterization Data

A. General Procedure for the Synthesis of NHC-Pd Complexes.

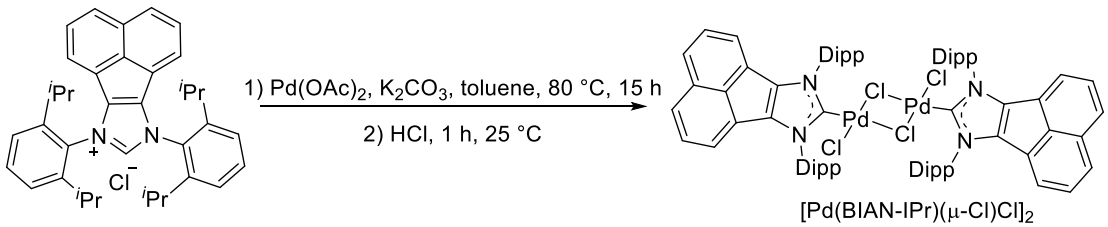


1 2

[Pd(BIAN-IPr)(μ-Cl)Cl]$_2$

The 7,9-bis(2,6-diisopropylphenyl)-6b,9a-dihydro-7*H*-acenaphtho[1,2-*d*]imidazol-9-ium chloride (**1**) has been previously reported and prepared by reported methods[1].

Method A: An oven-dried vial equipped with a stir bar was charged with 7,9-bis(2,6-diisopropylphenyl)-6b,9a-dihydro-7*H*-acenaphtho[1,2-*d*]imidazol-9-ium chloride (**1**) (109.8 mg, 0.2 mmol, 1.0 eq.), Ag_2O (69.5 mg, 0.3 mmol, 1.5 eq.). The reaction mixture was placed under a positive pressure of argon and subjected to three evacuation/backfilling cycles under high vacuum. DCM (5 ml, 0.04 M) was added and the reaction mixture was stirred at room temperature for 48 h in the dark. The reaction mixture was filtered through Celite with DCM as eluent and concentrated under reduced pressure. The resulting solid was added to a freshly prepared solution of $[Pd(CH_3CN)_2Cl_2]$ (104.8 mg, 0.4 mmol, 2.0 eq.) in DCM (5 mL). The reaction mixture was placed under a positive pressure of argon and subjected to three evacuation/backfilling cycles under high vacuum and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was filtered through Celite with DCM as eluent and concentrated under reduced pressure, and dried under high vacuum. The following recrystallisation with CH_2Cl_2/Et_2O afforded the product palladium complex **2** as a yellow solid (107.8 mg, 87%).



1 2

[Pd(BIAN-IPr)(μ-Cl)Cl]$_2$

Method B: An oven-dried vial equipped with a stir bar was charged with 7,9-bis(2,6-diisopropylphenyl)-6b,9a-dihydro-7*H*-acenaphtho[1,2-*d*]imidazol-9-ium chloride (**1**) (109.8 mg, 0.2 mmol, 1.0 eq.), $Pd(OAc)_2$ (53.9 mg, 0.24 mmol, 1.2 eq.) and K_2CO_3 (110.6 mg, 0.8 mmol, 4.0 eq.). The reaction mixture was placed under a positive pressure of argon and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (5 mL, 0.04 M) was added and the reaction mixture was stirred at 80 °C overnight. The reaction mixture was filtered through Celite and washed with DCM. 4M HCl in dioxane (0.4 mL) was added to the filtrate solution, and the mixture was stirred for 1 h. The solution was concentrated under reduced pressure, the products were purified by column chromatography (Silica Gel, n-hexane/ethyl acetate 10:2). After purification the product palladium complex **2** was isolated as a yellow solid (59.5

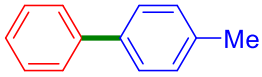
mg, 48%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (t, J = 7.8 Hz, 4H), 7.66 (d, J = 8.2 Hz, 4H), 7.45 – 7.44 (m, 8H), 7.31 – 7.29 (m, 4H), 6.71 (d, J = 7.1 Hz, 4H), 3.17 – 2.81 (m, 8H), 1.27 (d, J = 17.8 Hz, 24H), 0.91 – 0.84 (m, 24H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.0, 147.0, 140.3, 133.3, 130.7, 129.5, 128.9, 128.1, 127.2, 125.9, 124.9, 122.2, 28.8, 25.7, 24.2.

B. General Procedure for the Suzuki-Miyaura Cross-Coupling.

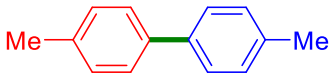
An oven-dried vial equipped with a stir bar was charged with an aryl chloride (neat, 1.0 equiv), potassium carbonate (typically, 3.0 equiv), boronic acid (typically, 2.0 equiv) placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Ethanol (typically, 0.5 M) containing Pd-NHC catalyst (typically, 0.25 mol%) was added with vigorous stirring at the indicated temperature, the reaction mixture was placed in a preheated oil bath and stirred for the indicated time. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2, filtered, and concentrated. The products were purified by column chromatography on silica gel.

4-Methyl-1,1'-biphenyl (5a).



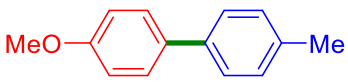
According to the general procedure, the reaction of chlorobenzene (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 76 % yield (25.6 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$ δ 7.56 (d, J = 7.2 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.2, 138.4, 137.1, 129.6, 128.8, 127.1, 127.0, 21.2. This compound showed identical spectroscopic properties to those reported previously[2].

4,4'-Dimethyl-1,1'-biphenyl (5b).



According to the general procedure, the reaction of 1-chloro-4-methylbenzene (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 25 °C, afforded after work-up and chromatography the title compound in 97 % yield (35.4 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.1 Hz, 4H), 7.20 (d, J = 8.0 Hz, 4H), 2.36 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.4, 136.8, 129.6, 126.9, 21.2. This compound showed identical spectroscopic properties to those reported previously[3].

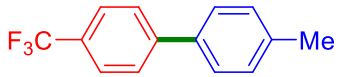
4-Methoxy-4'-methyl-1,1'-biphenyl (5c).



According to the general procedure, the reaction of 1-chloro-4-methoxybenzene (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and

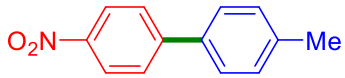
chromatography the title compound in 67 % yield (26.3 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.0, 138.0, 136.4, 133.8, 129.5, 128.0, 126.7, 114.2, 55.4, 21.1. This compound showed identical spectroscopic properties to those reported previously[4].

4-Methyl-4'-(trifluoromethyl)-1,1'-biphenyl (5d).



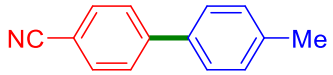
According to the general procedure, the reaction of 1-chloro-4-(trifluoromethyl)benzene (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 25 °C, afforded after work-up and chromatography the title compound in 97 % yield (45.8 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 4H), 7.43 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.7, 138.2, 136.9, 129.8, 129.1 (q, J = 32.4 Hz), 127.2, 127.1, 125.7 (q, J = 3.8 Hz), 124.5 (q, J = 270.1 Hz), 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.2. This compound showed identical spectroscopic properties to those reported previously[5].

4-Methyl-4'-nitro-1,1'-biphenyl (5e).



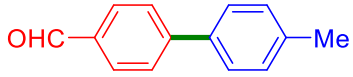
According to the general procedure, the reaction of 1-chloro-4-nitrobenzene (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 25 °C, afforded after work-up and chromatography the title compound in 98 % yield (41.8 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, J = 8.7 Hz, 2H), 7.71 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 146.8, 139.1, 135.8, 129.9, 127.5, 127.2, 124.1, 21.2. This compound showed identical spectroscopic properties to those reported previously[6].

4-Isocyano-4'-methyl-1,1'-biphenyl (5f).



According to the general procedure, the reaction of 4-chlorobenzonitrile (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 25 °C, afforded after work-up and chromatography the title compound in 98 % yield (37.9 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.6, 138.8, 136.3, 132.6, 129.9, 127.5, 127.1, 119.1, 110.5, 21.2. This compound showed identical spectroscopic properties to those reported previously[7].

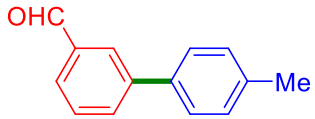
4'-Methyl-[1,1'-biphenyl]-4-carbaldehyde (5g).



According to the general procedure, the reaction of 4-chlorobenzaldehyde (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25

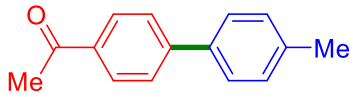
mol%) in EtOH (0.5 M) for 12 h at 25 °C, afforded after work-up and chromatography the title compound in 96 % yield (37.7 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.91 (d, J = 7.9 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.9, 147.1, 138.5, 136.8, 135.0, 130.3, 129.8, 127.4, 127.2, 21.2. This compound showed identical spectroscopic properties to those reported previously[8].

4'-Methyl-[1,1'-biphenyl]-3-carbaldehyde (5h).



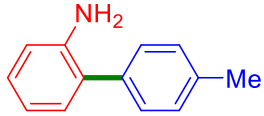
According to the general procedure, the reaction of 3-chlorobenzaldehyde (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 25 °C, afforded after work-up and chromatography the title compound in 95 % yield (37.3 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.07 (s, 1H), 7.82 (t, J = 6.2 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.52 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.4, 142.0, 137.9, 136.9, 136.7, 132.8, 129.7, 129.4, 128.3, 127.9, 126.9, 21.1. This compound showed identical spectroscopic properties to those reported previously[9].

1-(4'-Methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (5i).



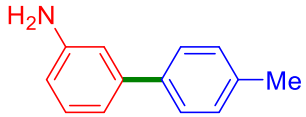
According to the general procedure, the reaction of 1-(4-chlorophenyl)ethan-1-one (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 98 % yield (41.2 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.26 (d, J = 8.0 Hz, 2H), 2.61 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.7, 145.7, 138.2, 136.9, 135.6, 129.7, 128.9, 127.1, 126.9, 26.6, 21.2. This compound showed identical spectroscopic properties to those reported previously[10].

4'-Methyl-[1,1'-biphenyl]-2-amine (5j).



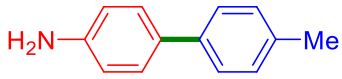
According to the general procedure, the reaction of 2-chloroaniline (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 83 % yield (30.4 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.3 Hz, 2H), 7.40 (d, J = 7.5 Hz, 2H), 7.29 (s, 2H), 6.97 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 7.9 Hz, 1H), 3.83 (s, 2H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 136.9, 136.6, 130.5, 129.5, 129.0, 128.3, 127.7, 118.7, 115.6, 21.2. This compound showed identical spectroscopic properties to those reported previously[7].

4'-Methyl-[1,1'-biphenyl]-3-amine (5k).



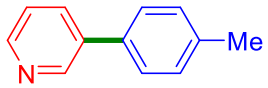
According to the general procedure, the reaction of 3-chloroaniline (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 73 % yield (26.8 mg). Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.0 Hz, 2H), 7.20 (dd, J = 14.3, 7.8 Hz, 3H), 6.97 (d, J = 7.6 Hz, 1H), 6.87 (s, 1H), 6.63 (d, J = 7.9 Hz, 1H), 3.53 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.7, 142.4, 138.5, 137.0, 129.7, 129.4, 127.0, 117.6, 113.9, 113.8, 21.1. This compound showed identical spectroscopic properties to those reported previously[11].

4'-Methyl-[1,1'-biphenyl]-4-amine (5l).



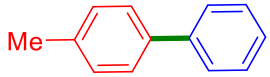
According to the general procedure, the reaction of 4-chloroaniline (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 79 % yield (29.0 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 14.0, 8.2 Hz, 4H), 7.20 (d, J = 7.9 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H), 3.70 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 138.3, 135.9, 131.6, 129.4, 127.8, 126.3, 115.4, 21.0. This compound showed identical spectroscopic properties to those reported previously[7].

3-(*p*-Tolyl)pyridine (5m).



According to the general procedure, the reaction of 3-chloropyridine (0.20 mmol), *p*-tolylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 98 % yield (33.2 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.53 (d, J = 4.8 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 8.1 Hz, 2H), 7.28 – 7.26 (m, 1H), 7.23 (d, J = 8.3 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.1, 138.0, 136.5, 134.9, 134.0, 129.8, 126.9, 123.5, 21.1. This compound showed identical spectroscopic properties to those reported previously[7].

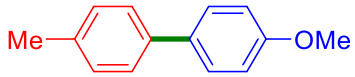
4-Methyl-1,1'-biphenyl (5n).



According to the general procedure, the reaction of 1-chloro-4-methylbenzene (0.20 mmol), phenylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 25 °C, afforded after work-up and chromatography the title compound in 87 % yield (29.3 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$ δ 7.56 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.8 Hz, 1H), 7.22 (d, J = 8.3 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.3, 138.5, 137.1, 129.6, 128.8, 127.1, 127.1, 21.2. This compound

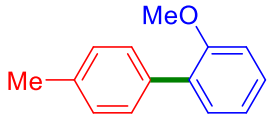
showed identical spectroscopic properties to those reported previously[8].

4-Methoxy-4'-methyl-1,1'-biphenyl (5o).



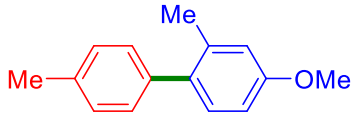
According to the general procedure, the reaction of 1-chloro-4-methylbenzene (0.20 mmol), (4-methoxyphenyl)boronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 61 % yield (24.3 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.0, 138.1, 136.4, 133.8, 129.5, 128.0, 126.7, 114.3, 55.4, 21.1. This compound showed identical spectroscopic properties to those reported previously[4].

2-Dethoxy-4'-methyl-1,1'-biphenyl (5p).



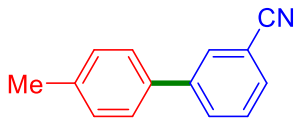
According to the general procedure, the reaction of 1-chloro-4-methylbenzene (0.20 mmol), (2-methoxyphenyl)boronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 25 °C, afforded after work-up and chromatography the title compound in 73 % yield (28.9 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.0 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.01 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.5 Hz, 1H), 3.80 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 136.6, 135.6, 130.8, 130.7, 129.4, 128.7, 128.4, 120.8, 111.2, 55.5, 21.2. This compound showed identical spectroscopic properties to those reported previously[12].

4-Methoxy-2,4'-dimethyl-1,1'-biphenyl (5q).



According to the general procedure, the reaction of 1-chloro-4-methylbenzene (0.20 mmol), (4-methoxy-2-methylphenyl)boronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 64 % yield (27.2 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.6 Hz, 2H), 7.36 (s, 2H), 7.21 (d, J = 7.6 Hz, 2H), 6.90 – 6.85 (m, 1H), 3.86 (s, 3H), 2.37 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 138.3, 136.3, 133.5, 129.5, 129.5, 127.0, 126.7, 125.3, 110.3, 55.6, 21.2, 16.5. This compound showed identical spectroscopic properties to those reported previously.

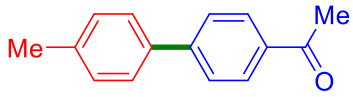
4'-Methyl-[1,1'-biphenyl]-3-carbonitrile (5r).



According to the general procedure, the reaction of 1-chloro-4-methylbenzene (0.20 mmol), (3-cyanophenyl)boronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–

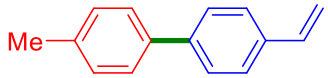
IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 25 °C, afforded after work-up and chromatography the title compound in 71 % yield (27.4 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.80 (d, J = 7.7 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.46 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 7.7 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 138.4, 136.0, 131.3, 130.5, 130.4, 129.8, 129.5, 126.9, 119.0, 112.9, 21.2. This compound showed identical spectroscopic properties to those reported previously[13].

1-(4'-Methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (5s).



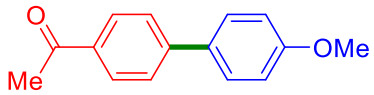
According to the general procedure, the reaction of 1-chloro-4-methylbenzene (0.20 mmol), (4-acetylphenyl)boronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 25 °C, afforded after work-up and chromatography the title compound in 74 % yield (31.1 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.02 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 2.63 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 145.7, 138.3, 137.0, 135.6, 129.7, 128.9, 127.1, 127.0, 26.7, 21.2. This compound showed identical spectroscopic properties to those reported previously[14].

4-Methyl-4'-vinyl-1,1'-biphenyl (5t).



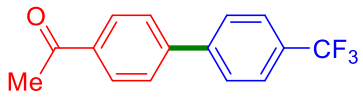
According to the general procedure, the reaction of 1-chloro-4-methylbenzene (0.20 mmol), (4-vinylphenyl)boronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 64 % yield (24.9 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H), 7.52 – 7.45 (m, 4H), 7.28 – 7.19 (m, 2H), 6.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.78 (d, J = 17.6 Hz, 1H), 5.26 (d, J = 10.9 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 138.0, 137.3, 136.6, 136.5, 129.7, 127.2, 126.9, 126.8, 113.8, 21.3. This compound showed identical spectroscopic properties to those reported previously[15].

1-(4'-Methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one (5u).



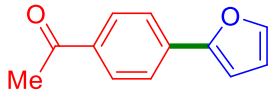
According to the general procedure, the reaction of 1-(4-chlorophenyl)ethan-1-one (0.20 mmol), (4-methoxyphenyl)boronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 96 % yield (43.4 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.7, 159.9, 145.4, 135.3, 132.2, 128.9, 128.4, 126.6, 114.4, 55.4, 26.6. This compound showed identical spectroscopic properties to those reported previously[16].

1-(4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (5v).



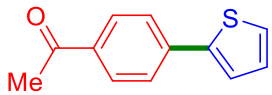
According to the general procedure, the reaction of 1-(4-chlorophenyl)ethan-1-one (0.20 mmol), (4-(trifluoromethyl)phenyl)boronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 96 % yield (50.7 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 2H), 7.72 (s, 4H), 7.68 (d, J = 8.3 Hz, 2H), 2.6 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.5, 144.1, 143.4, 136.6, 130.2 (q, J = 32.6 Hz), 129.0, 127.6, 127.4, 125.9 (q, J = 3.7 Hz), 124.1 (q, J = 270.4 Hz), 26.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.5. This compound showed identical spectroscopic properties to those reported previously[17].

1-(4-(Furan-2-yl)phenyl)ethan-1-one (5w).



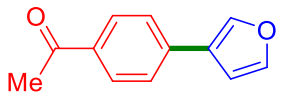
According to the general procedure, the reaction of 1-(4-chlorophenyl)ethan-1-one (0.20 mmol), furan-2-ylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 96 % yield (35.8 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H), 7.52 – 7.50 (m, 1H), 6.79 (d, J = 3.4 Hz, 1H), 6.51 (dd, J = 3.4, 1.8 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.3, 152.8, 143.3, 135.6, 134.9, 128.9, 123.5, 112.1, 107.5, 26.5. This compound showed identical spectroscopic properties to those reported previously[18].

1-(4-(Thiophen-2-yl)phenyl)ethan-1-one (5x).



According to the general procedure, the reaction of 1-(4-chlorophenyl)ethan-1-one (0.20 mmol), thiophen-2-ylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 98 % yield (39.6 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J = 8.6 Hz, 2H), 7.82 – 7.80 (m, 1H), 7.56 (d, J = 8.6 Hz, 2H), 7.50 (t, J = 1.7 Hz, 1H), 6.74 (dd, J = 1.8, 0.9 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.4, 144.1, 139.6, 137.2, 135.6, 129.0, 125.7, 125.6, 108.6, 26.5. This compound showed identical spectroscopic properties to those reported previously[19].

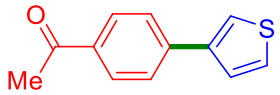
1-(4-(Furan-3-yl)phenyl)ethan-1-one (5y).



According to the general procedure, the reaction of 1-(4-chlorophenyl)ethan-1-one (0.20 mmol), furan-3-ylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–

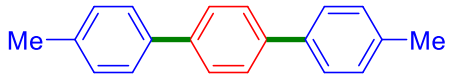
IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 95 % yield (35.4 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 3.6 Hz, 1H), 7.36 (d, J = 5.0 Hz, 1H), 7.11 (t, J = 4.3 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.3, 142.9, 138.8, 135.8, 129.1, 128.4, 126.5, 125.7, 124.6, 26.6. This compound showed identical spectroscopic properties to those reported previously[20].

1-(4-(Thiophen-3-yl)phenyl)ethan-1-one (5z).



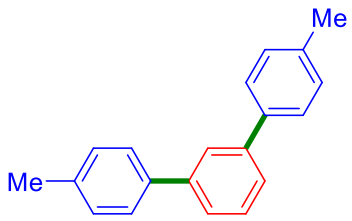
According to the general procedure, the reaction of 1-(4-chlorophenyl)ethan-1-one (0.20 mmol), thiophen-3-ylboronic acid (2.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 98 % yield (39.6 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.57 (dd, J = 2.7, 1.5 Hz, 1H), 7.42 (qd, J = 5.0, 2.1 Hz, 2H), 2.61 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.5, 141.1, 140.2, 135.7, 129.1, 126.8, 126.4, 126.2, 122.0, 26.6. This compound showed identical spectroscopic properties to those reported previously[21].

4,4''-Dimethyl-1,1':4',1''-terphenyl (5aa).



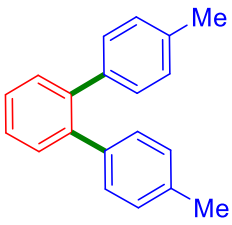
According to the general procedure, the reaction of 1,4-dichlorobenzene (0.20 mmol), *p*-tolylboronic acid (4.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 89 % yield (46.0 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 4H), 7.54 (d, J = 7.8 Hz, 4H), 7.26 (d, J = 7.2 Hz, 4H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 137.9, 137.1, 129.5, 127.3, 126.9, 21.1. This compound showed identical spectroscopic properties to those reported previously[22].

4,4''-Dimethyl-1,1':3',1''-terphenyl (5ab).



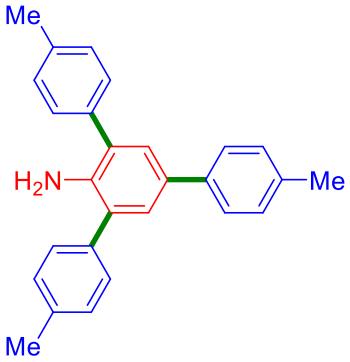
According to the general procedure, the reaction of 1,3-dichlorobenzene (0.20 mmol), *p*-tolylboronic acid (4.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 89 % yield (46.0 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.53 (d, J = 8.2 Hz, 6H), 7.47 (ddd, J = 8.5, 6.1, 1.8 Hz, 1H), 7.26 (d, J = 7.4 Hz, 4H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 138.4, 137.2, 129.5, 129.1, 127.1, 125.8, 125.7, 21.1. This compound showed identical spectroscopic properties to those reported previously[23].

4,4''-Dimethyl-1,1':2',1''-terphenyl (5ac).



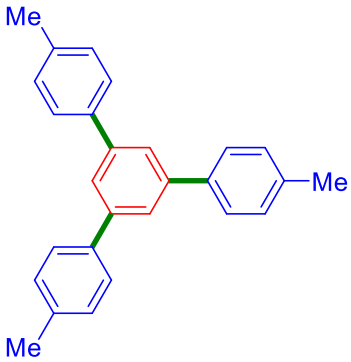
According to the general procedure, the reaction of 1,2-dichlorobenzene (0.20 mmol), *p*-tolylboronic acid (4.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 91 % yield (47.0 mg). White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (q, J = 5.1 Hz, 4H), 7.04 (d, J = 8.5 Hz, 8H), 2.31 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.4, 138.7, 136.0, 130.6, 129.7, 128.6, 127.2, 21.1. This compound showed identical spectroscopic properties to those reported previously[24].

4,4''-Dimethyl-5'-(*p*-tolyl)-[1,1':3',1''-terphenyl]-2'-amine (5ad).



According to the general procedure, the reaction of 2,4,6-trichloroaniline (0.20 mmol), *p*-tolylboronic acid (6.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 76 % yield (55.3 mg). Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.0 Hz, 4H), 7.36 (s, 2H), 7.28 (d, J = 7.9 Hz, 4H), 7.19 (d, J = 8.0 Hz, 2H), 3.88 (s, 2H), 2.41 (s, 6H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.2, 138.1, 137.0, 136.8, 135.9, 131.0, 129.6, 129.4, 129.2, 128.2, 128.0, 126.2, 21.2, 21.0. HRMS calcd for $C_{27}H_{26}N^+$ $[M+H]^+$ 364.2060, found 364.2058.

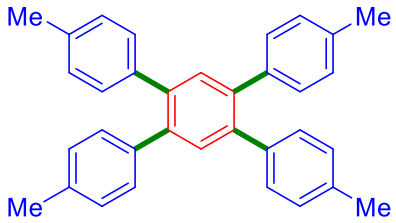
4,4''-Dimethyl-5'-(*p*-tolyl)-1,1':3',1''-terphenyl (5ae).



According to the general procedure, the reaction of 1,3,5-trichlorobenzene (0.20 mmol), *p*-tolylboronic acid (6.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography

the title compound in 84 % yield (58.5 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 3H), 7.59 (d, J = 6.8 Hz, 6H), 7.32 – 7.26 (m, 6H), 2.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 138.5, 137.4, 129.7, 127.3, 124.7, 21.3. This compound showed identical spectroscopic properties to those reported previously[25].

4,4''-Dimethyl-4',5'-di-*p*-tolyl-1,1':2',1''-terphenyl (5af).



According to the general procedure, the reaction of 1,2,4,5-tetrachlorobenzene (0.20 mmol), *p*-tolylboronic acid (8.0 equiv), K_2CO_3 (3.0 equiv) and [Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (0.25 mol%) in EtOH (0.5 M) for 12 h at 60 °C, afforded after work-up and chromatography the title compound in 85 % yield (74.6 mg). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 2H), 7.12 (d, J = 7.8 Hz, 8H), 7.04 (d, J = 7.8 Hz, 8H), 2.31 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 138.5, 137.4, 129.7, 127.3, 124.7, 21.3. This compound showed identical spectroscopic properties to those reported previously[26].

5. Crystallographic Studies

Crystal Structure of 2.

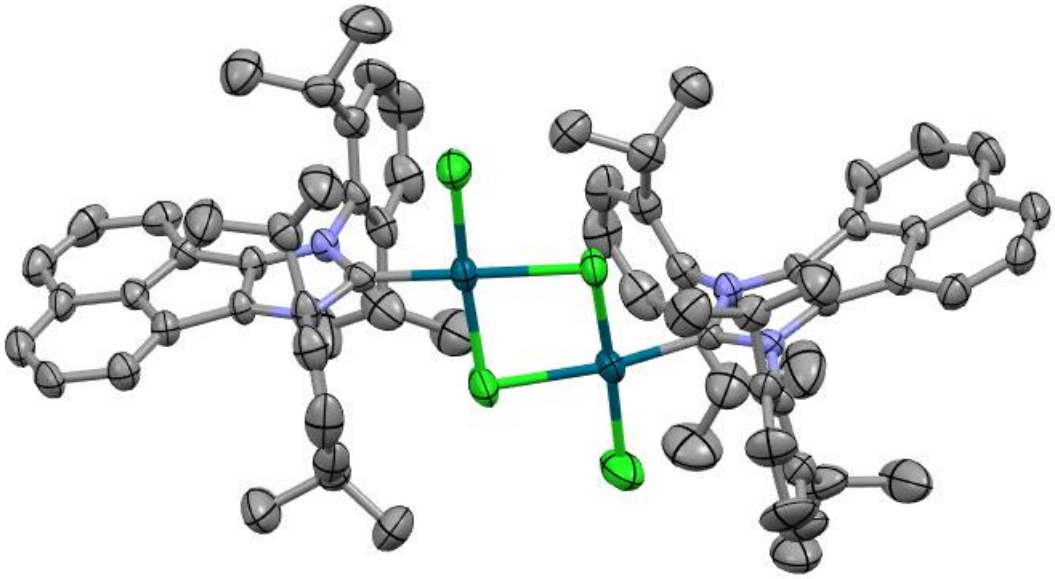


Figure S1. Crystal structure of **2** *(50% ellipsoids)*. (Crystallographic data has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2159737.)

Table S2. *Crystal Data and Structure Refinement Summary for **2**.*

Crystal data

$C_{74}H_{80}Cl_4N_4Pd_2$	$F(000)$ = 2848
M_r = 1380.02	D_x = 1.365 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 18.932 (5) Å	Cell parameters from 6289 reflections
b = 15.475 (4) Å	θ = 2.4–27.4°
c = 22.985 (6) Å	μ = 0.74 mm^{-1}
β = 94.362 (14)°	T = 273 K
V = 6714 (3) Å^3	Block
Z = 4	0.11 × 0.1 × 0.09 mm

Data collection

Bruker APEX-II CCD diffractometer	R_{int} = 0.083
ϕ and ω scans	θ_{max} = 25.0°, θ_{min} = 2.2°

44065 measured reflections	h = -22→18
11815 independent reflections	k = -18→18
7822 reflections with $I > 2\sigma(I)$	l = -27→27

Refinement

Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.054$	H-atom parameters constrained
$wR(F^2) = 0.149$	$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
11815 reflections	$\Delta\rangle_{max} = 0.65$ e Å^{-3}
773 parameters	$\Delta\rangle_{min} = -0.91$ e Å^{-3}
0 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2) for (**2**).*

	x	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.21176 (2)	1.02085 (3)	0.10950 (2)	0.04064 (14)
Pd2	0.34002 (2)	0.86841 (3)	0.09042 (2)	0.03781 (14)
Cl1	0.11915 (11)	1.07277 (15)	0.05143 (8)	0.0873 (7)
Cl2	0.25286 (10)	0.93839 (12)	0.03096 (7)	0.0674 (5)
Cl3	0.31548 (8)	0.97539 (10)	0.16171 (6)	0.0474 (4)
Cl4	0.43250 (9)	0.81762 (11)	0.14966 (7)	0.0590 (4)
N1	0.3195 (2)	0.6975 (3)	0.03470 (18)	0.0344 (10)
N2	0.3849 (2)	0.7784 (3)	-0.01664 (18)	0.0324 (10)

N3	0.1973 (2)	1.1484 (3)	0.20658 (18)	0.0336 (10)
N4	0.1388 (2)	1.0285 (3)	0.21688 (18)	0.0373 (11)
C1	0.2979 (4)	0.9998 (4)	-0.1028 (3)	0.079 (2)
H1A	0.3098	1.0291	-0.0666	0.118*
H1B	0.2473	0.9964	-0.1097	0.118*
H1C	0.3171	1.0311	-0.1341	0.118*
C2	0.3289 (3)	0.9090 (4)	-0.0999 (3)	0.0519 (16)
H2	0.3006	0.8749	-0.0743	0.062*
C3	0.3199 (5)	0.8681 (5)	-0.1607 (3)	0.088 (3)
H3A	0.3470	0.9001	-0.1870	0.132*
H3B	0.2708	0.8691	-0.1745	0.132*
H3C	0.3363	0.8094	-0.1586	0.132*
C4	0.4052 (3)	0.9061 (4)	-0.0741 (2)	0.0453 (15)
C5	0.4536 (4)	0.9654 (4)	-0.0923 (3)	0.0594 (19)
H5	0.4389	1.0079	-0.1191	0.071*
C6	0.5229 (4)	0.9617 (4)	-0.0708 (3)	0.071 (2)
H6	0.5540	1.0038	-0.0823	0.085*
C7	0.5483 (4)	0.8991 (5)	-0.0335 (3)	0.0569 (18)
H7	0.5962	0.8980	-0.0209	0.068*
C8	0.5037 (3)	0.8378 (4)	-0.0145 (2)	0.0433 (15)
C9	0.4327 (3)	0.8443 (3)	-0.0346 (2)	0.0349 (13)
C10	0.5907 (4)	0.7910 (5)	0.0705 (3)	0.080 (2)
H10A	0.6325	0.8080	0.0524	0.120*
H10B	0.6015	0.7432	0.0963	0.120*
H10C	0.5738	0.8387	0.0923	0.120*
C11	0.5337 (3)	0.7641 (4)	0.0238 (3)	0.0506 (16)
H11	0.4943	0.7405	0.0441	0.061*
C12	0.5608 (4)	0.6915 (5)	-0.0129 (3)	0.083 (2)
H12A	0.5245	0.6750	-0.0422	0.124*
H12B	0.5732	0.6428	0.0117	0.124*
H12C	0.6018	0.7109	-0.0313	0.124*
C13	0.3745 (3)	0.7017 (3)	-0.0459 (2)	0.0336 (12)
C14	0.3918 (3)	0.6553 (3)	-0.0989 (2)	0.0378 (13)

C15	0.4272 (3)	0.6715 (4)	-0.1468 (2)	0.0468 (15)
H15	0.4509	0.7235	-0.1509	0.056*
C16	0.4270 (4)	0.6066 (5)	-0.1906 (3)	0.0571 (18)
H16	0.4514	0.6169	-0.2236	0.069*
C17	0.3928 (3)	0.5310 (4)	-0.1862 (3)	0.0550 (17)
H17	0.3938	0.4904	-0.2159	0.066*
C18	0.3559 (3)	0.5128 (4)	-0.1372 (3)	0.0443 (15)
C19	0.3170 (3)	0.4377 (4)	-0.1273 (3)	0.0559 (17)
H19	0.3149	0.3931	-0.1545	0.067*
C20	0.2827 (3)	0.4304 (4)	-0.0782 (3)	0.0586 (18)
H20	0.2581	0.3795	-0.0724	0.070*
C21	0.2819 (3)	0.4958 (4)	-0.0346 (3)	0.0476 (15)
H21	0.2567	0.4888	-0.0017	0.057*
C22	0.3199 (3)	0.5693 (3)	-0.0433 (2)	0.0408 (14)
C23	0.3338 (3)	0.6511 (3)	-0.0140 (2)	0.0345 (13)
C24	0.3567 (3)	0.5763 (3)	-0.0944 (2)	0.0359 (13)
C25	0.3516 (3)	0.7767 (4)	0.0337 (2)	0.0361 (13)
C26	0.4194 (4)	0.5198 (4)	0.0976 (3)	0.076 (2)
H26A	0.4024	0.4695	0.1166	0.114*
H26B	0.4702	0.5184	0.0992	0.114*
H26C	0.4007	0.5204	0.0576	0.114*
C27	0.3950 (3)	0.6017 (4)	0.1286 (3)	0.0523 (16)
H27	0.4150	0.6514	0.1091	0.063*
C28	0.4270 (4)	0.6019 (5)	0.1921 (3)	0.085 (3)
H28A	0.4065	0.6481	0.2130	0.127*
H28B	0.4773	0.6099	0.1927	0.127*
H28C	0.4170	0.5477	0.2101	0.127*
C29	0.3147 (3)	0.6131 (4)	0.1239 (2)	0.0440 (15)
C30	0.2785 (3)	0.6627 (4)	0.0799 (2)	0.0382 (13)
C31	0.2053 (3)	0.6741 (4)	0.0743 (3)	0.0479 (15)
C32	0.1673 (4)	0.6328 (5)	0.1156 (3)	0.0634 (19)
H32	0.1183	0.6391	0.1139	0.076*
C33	0.2000 (4)	0.5835 (5)	0.1585 (3)	0.072 (2)

H33	0.1729	0.5564	0.1852	0.086*
C34	0.2720 (4)	0.5730 (4)	0.1634 (3)	0.066 (2)
H34	0.2929	0.5388	0.1932	0.079*
C35	0.1336 (4)	0.6641 (7)	-0.0209 (3)	0.120 (4)
H35A	0.1702	0.6334	-0.0390	0.181*
H35B	0.1059	0.6967	-0.0499	0.181*
H35C	0.1037	0.6235	-0.0029	0.181*
C36	0.1672 (3)	0.7255 (5)	0.0255 (3)	0.067 (2)
H36	0.2023	0.7611	0.0073	0.080*
C37	0.1109 (4)	0.7853 (5)	0.0473 (3)	0.086 (3)
H37A	0.0742	0.7514	0.0627	0.129*
H37B	0.0910	0.8199	0.0155	0.129*
H37C	0.1321	0.8222	0.0773	0.129*
C38	0.3766 (4)	1.2399 (5)	0.2708 (3)	0.078 (2)
H38C	0.4002	1.2910	0.2587	0.117*
H38A	0.4089	1.2058	0.2955	0.117*
H38B	0.3368	1.2560	0.2919	0.117*
C39	0.3509 (3)	1.1871 (4)	0.2171 (3)	0.0461 (15)
H39	0.3284	1.1345	0.2305	0.055*
C40	0.4149 (3)	1.1605 (5)	0.1859 (3)	0.072 (2)
H40A	0.3997	1.1341	0.1492	0.109*
H40B	0.4426	1.1198	0.2095	0.109*
H40C	0.4431	1.2105	0.1791	0.109*
C41	0.2964 (3)	1.2362 (4)	0.1786 (2)	0.0436 (14)
C42	0.3181 (4)	1.3060 (4)	0.1453 (3)	0.069 (2)
H42	0.3661	1.3189	0.1453	0.083*
C43	0.2696 (5)	1.3558 (5)	0.1127 (4)	0.088 (3)
H43	0.2853	1.4005	0.0899	0.105*
C44	0.1996 (4)	1.3404 (5)	0.1135 (3)	0.072 (2)
H44	0.1676	1.3757	0.0920	0.086*
C45	0.1748 (3)	1.2745 (4)	0.1451 (3)	0.0501 (16)
C46	0.2244 (3)	1.2219 (3)	0.1762 (2)	0.0373 (13)
C47	0.0731 (4)	1.3324 (6)	0.1927 (3)	0.108 (3)

H47A	0.1014	1.3258	0.2289	0.163*
H47B	0.0241	1.3240	0.1992	0.163*
H47C	0.0796	1.3894	0.1775	0.163*
C48	0.0956 (3)	1.2657 (5)	0.1490 (3)	0.069 (2)
H48	0.0862	1.2081	0.1644	0.083*
C49	0.0509 (4)	1.2767 (6)	0.0913 (3)	0.093 (3)
H49A	0.0547	1.3352	0.0780	0.140*
H49B	0.0023	1.2639	0.0970	0.140*
H49C	0.0677	1.2380	0.0628	0.140*
C50	0.1783 (3)	1.0720 (3)	0.1797 (2)	0.0331 (12)
C51	0.1710 (3)	1.1508 (3)	0.2606 (2)	0.0322 (12)
C52	0.1691 (3)	1.2036 (3)	0.3137 (2)	0.0359 (13)
C53	0.1966 (3)	1.2806 (4)	0.3351 (3)	0.0471 (15)
H53	0.2235	1.3156	0.3123	0.056*
C54	0.1832 (3)	1.3053 (4)	0.3922 (3)	0.0530 (17)
H54	0.2037	1.3559	0.4074	0.064*
C55	0.1415 (3)	1.2581 (4)	0.4260 (3)	0.0554 (17)
H55	0.1325	1.2783	0.4629	0.066*
C56	0.1118 (3)	1.1786 (4)	0.4056 (2)	0.0462 (15)
C57	0.1275 (3)	1.1533 (4)	0.3498 (2)	0.0371 (13)
C58	0.0678 (4)	1.1203 (5)	0.4353 (3)	0.064 (2)
H58	0.0554	1.1338	0.4726	0.076*
C59	0.0444 (4)	1.0467 (5)	0.4100 (3)	0.066 (2)
H59	0.0156	1.0103	0.4300	0.079*
C60	0.0623 (3)	1.0227 (4)	0.3535 (3)	0.0559 (17)
H60	0.0457	0.9709	0.3372	0.067*
C61	0.1036 (3)	1.0750 (4)	0.3232 (2)	0.0391 (13)
C62	0.1348 (3)	1.0780 (4)	0.2668 (2)	0.0368 (13)
C63	-0.0500 (4)	1.0285 (6)	0.1004 (4)	0.104 (3)
H63A	-0.0223	1.0070	0.0703	0.155*
H63B	-0.0681	1.0847	0.0898	0.155*
H63C	-0.0889	0.9898	0.1052	0.155*
C64	-0.0043 (4)	1.0345 (5)	0.1570 (3)	0.073 (2)

H64	0.0322	1.0781	0.1517	0.088*
C65	-0.0495 (5)	1.0676 (6)	0.2055 (4)	0.117 (4)
H65A	-0.0875	1.0278	0.2104	0.175*
H65B	-0.0687	1.1233	0.1948	0.175*
H65C	-0.0205	1.0722	0.2415	0.175*
C66	0.0335 (3)	0.9516 (4)	0.1766 (3)	0.0535 (17)
C67	-0.0015 (4)	0.8733 (5)	0.1672 (3)	0.065 (2)
H67	-0.0467	0.8727	0.1482	0.078*
C68	0.0296 (4)	0.7965 (5)	0.1856 (3)	0.065 (2)
H68	0.0054	0.7447	0.1787	0.078*
C69	0.1345 (3)	0.8719 (4)	0.2251 (2)	0.0442 (15)
C70	0.1018 (3)	0.9479 (4)	0.2052 (2)	0.0388 (14)
C71	0.0956 (3)	0.7961 (4)	0.2138 (3)	0.0568 (18)
H71	0.1155	0.7435	0.2259	0.068*
C72	0.1988 (4)	0.8483 (5)	0.3220 (3)	0.072 (2)
H72A	0.1752	0.8959	0.3390	0.108*
H72B	0.2450	0.8411	0.3416	0.108*
H72C	0.1716	0.7965	0.3260	0.108*
C73	0.2059 (3)	0.8662 (4)	0.2581 (3)	0.0495 (16)
H73	0.2293	0.9223	0.2550	0.059*
C74	0.2520 (3)	0.7985 (4)	0.2323 (3)	0.0660 (19)
H74A	0.2355	0.7419	0.2419	0.099*
H74B	0.3001	0.8055	0.2480	0.099*
H74C	0.2497	0.8049	0.1907	0.099*

6. ^{1}H and ^{13}C Spectra

7,9-Bis(2,6-diisopropylphenyl)-7H-acenaphtho[1,2-d]imidazol-9-ium chloride (1).

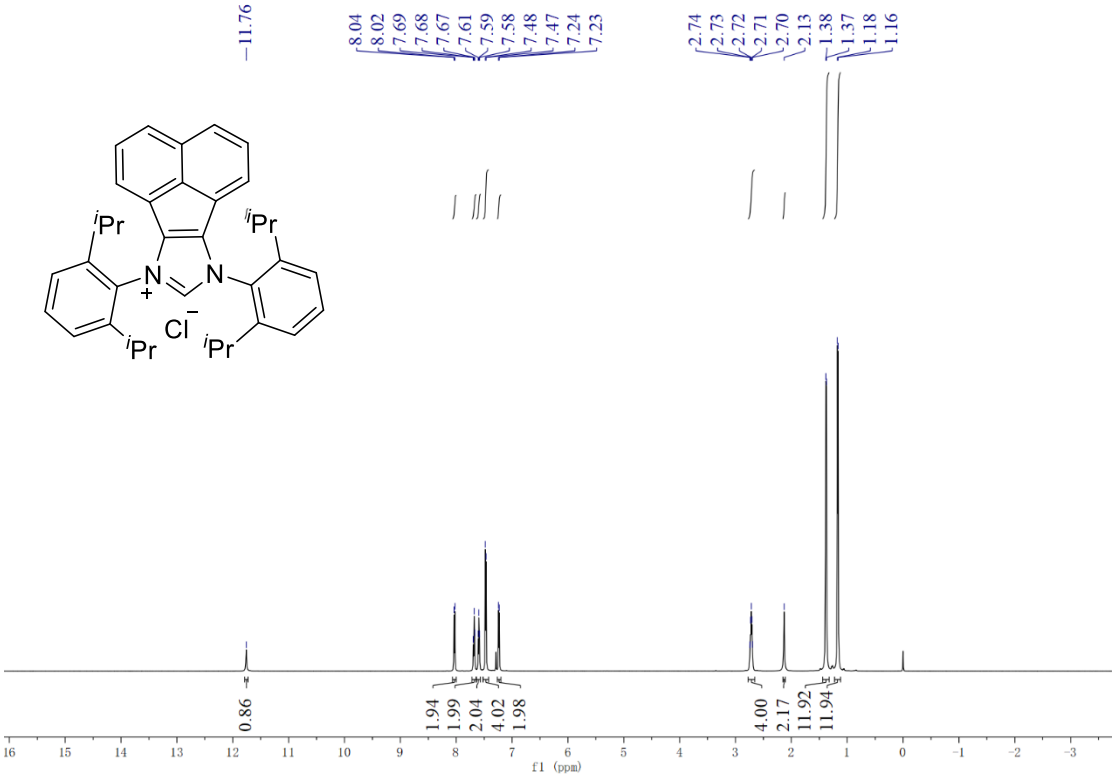


Figure S2. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **1**

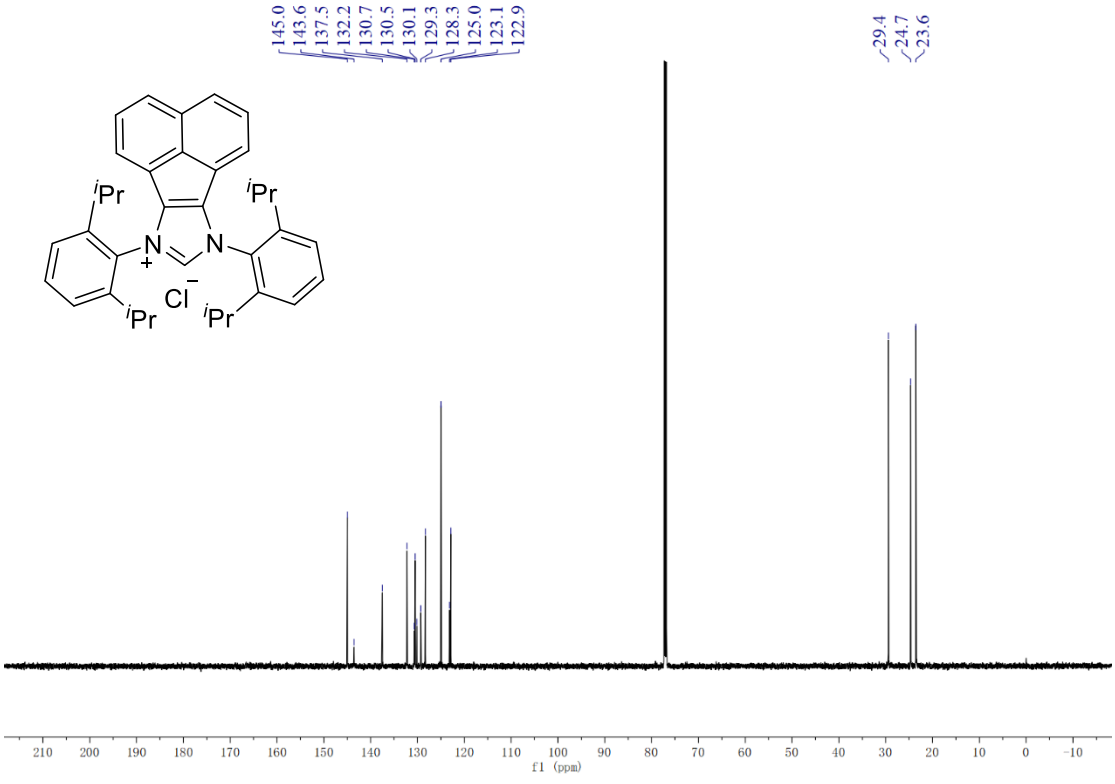


Figure S3. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **1**

[Pd(BIAN–IPr)(μ-Cl)Cl]$_2$ (2).

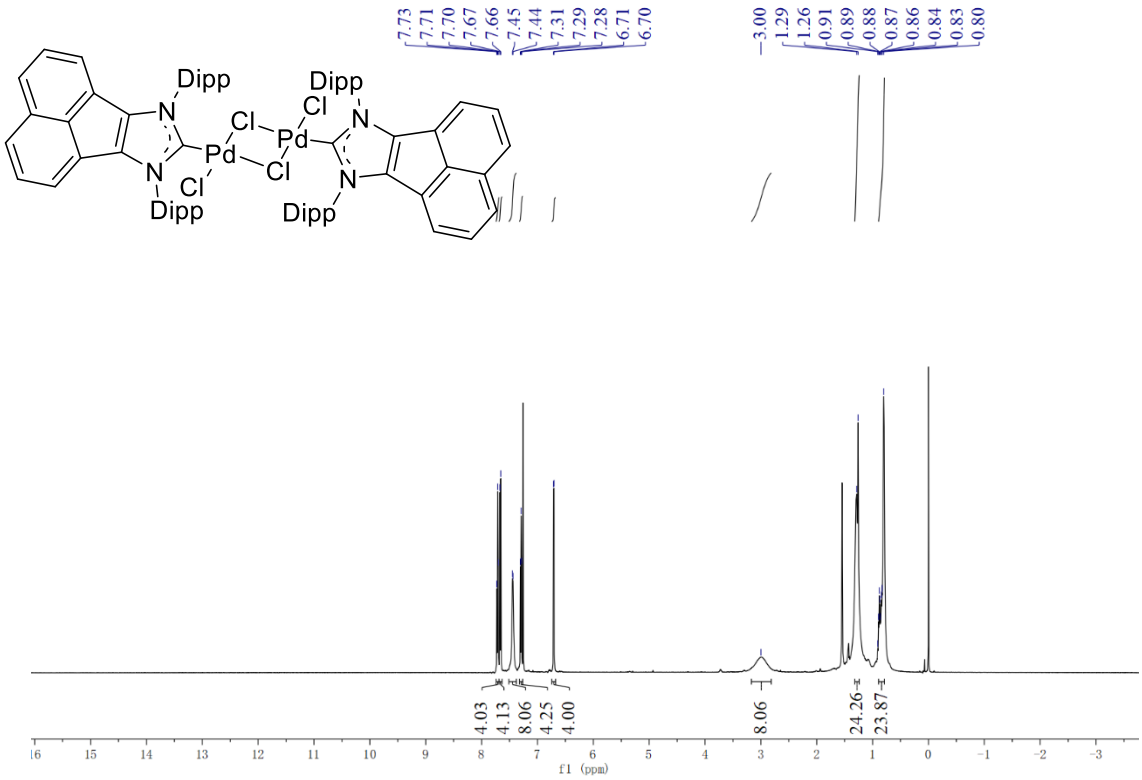


Figure S4. ^{1}H NMR (600 MHz, CDCl$_3$) Spectrum of Compound **2**

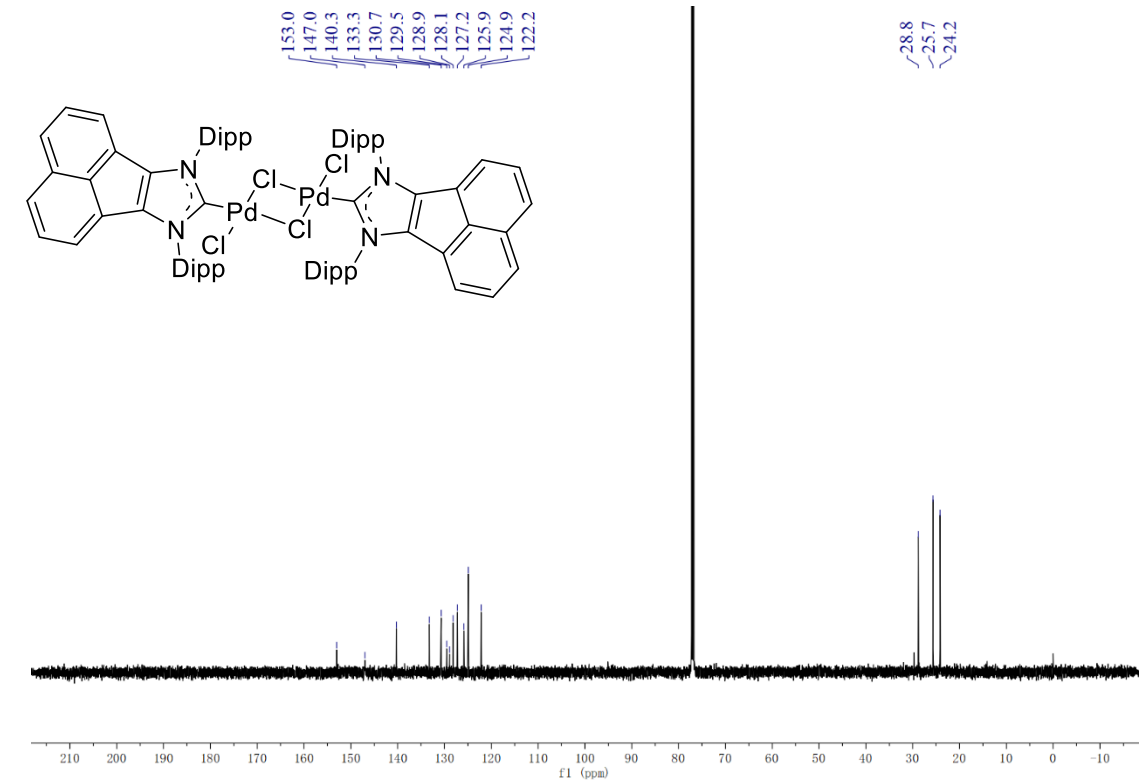


Figure S5. ^{13}C NMR (150 MHz, CDCl$_3$) Spectrum of Compound **2**

4-Methyl-1,1'-biphenyl (5a).

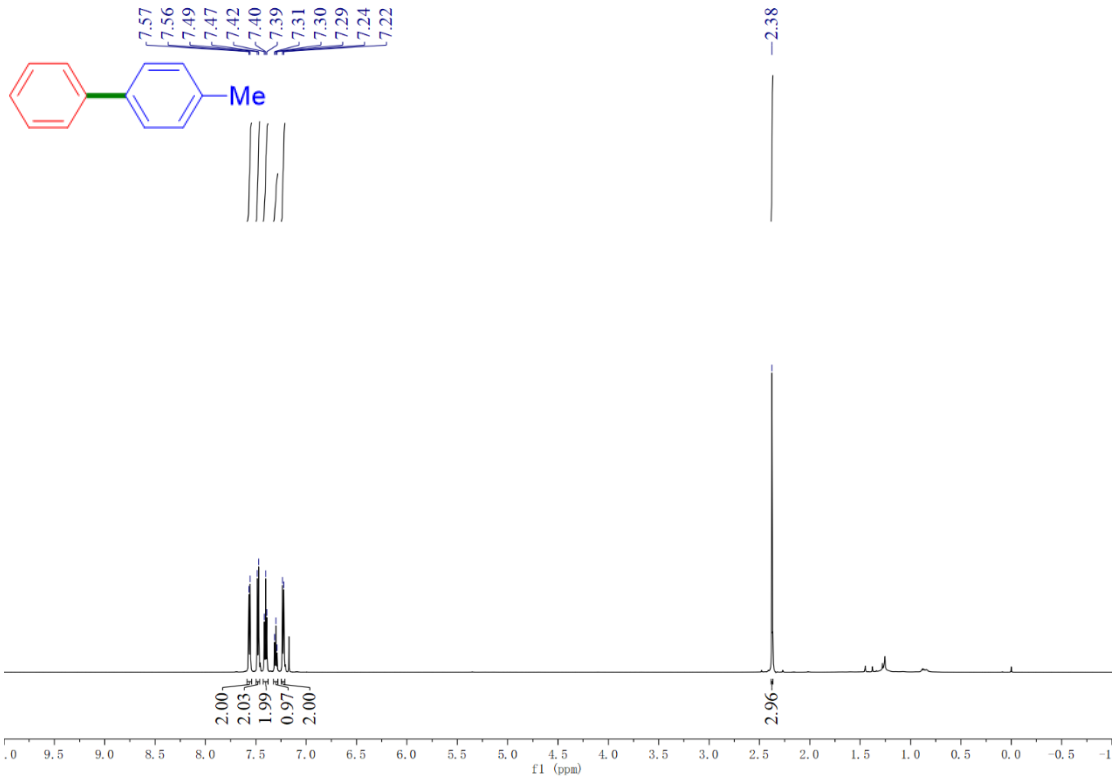


Figure S6. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5a**

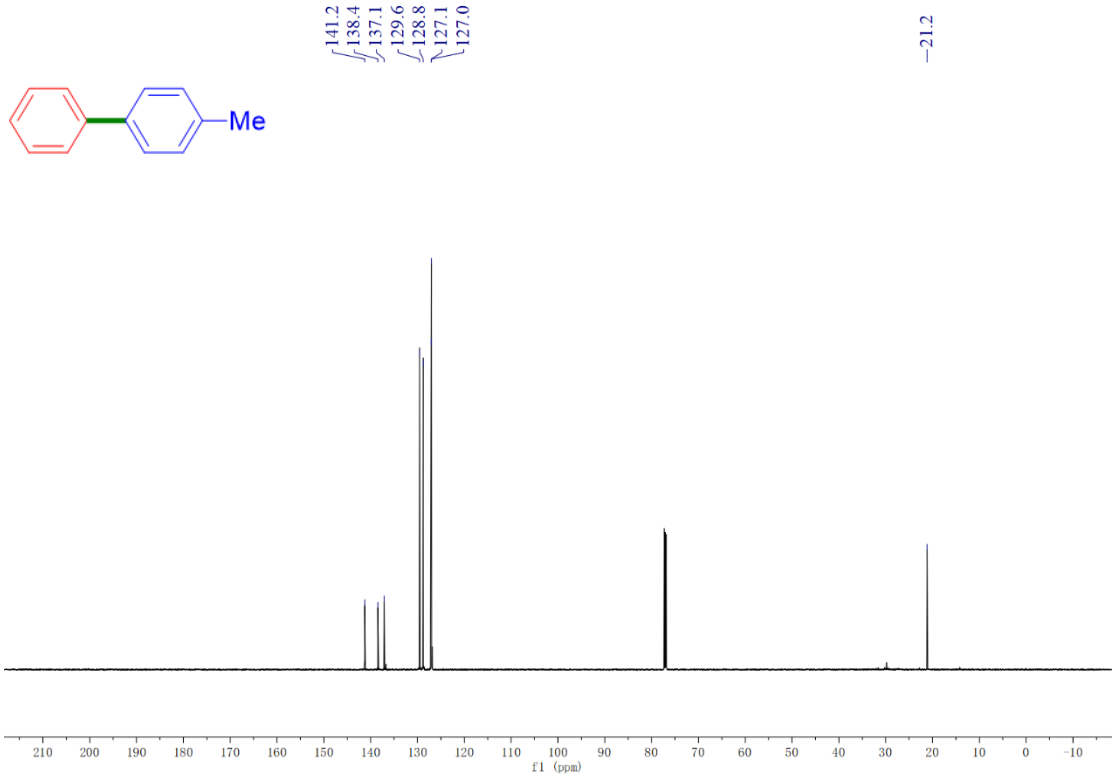


Figure S7. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5a**

4,4'-Dimethyl-1,1'-biphenyl (5b).

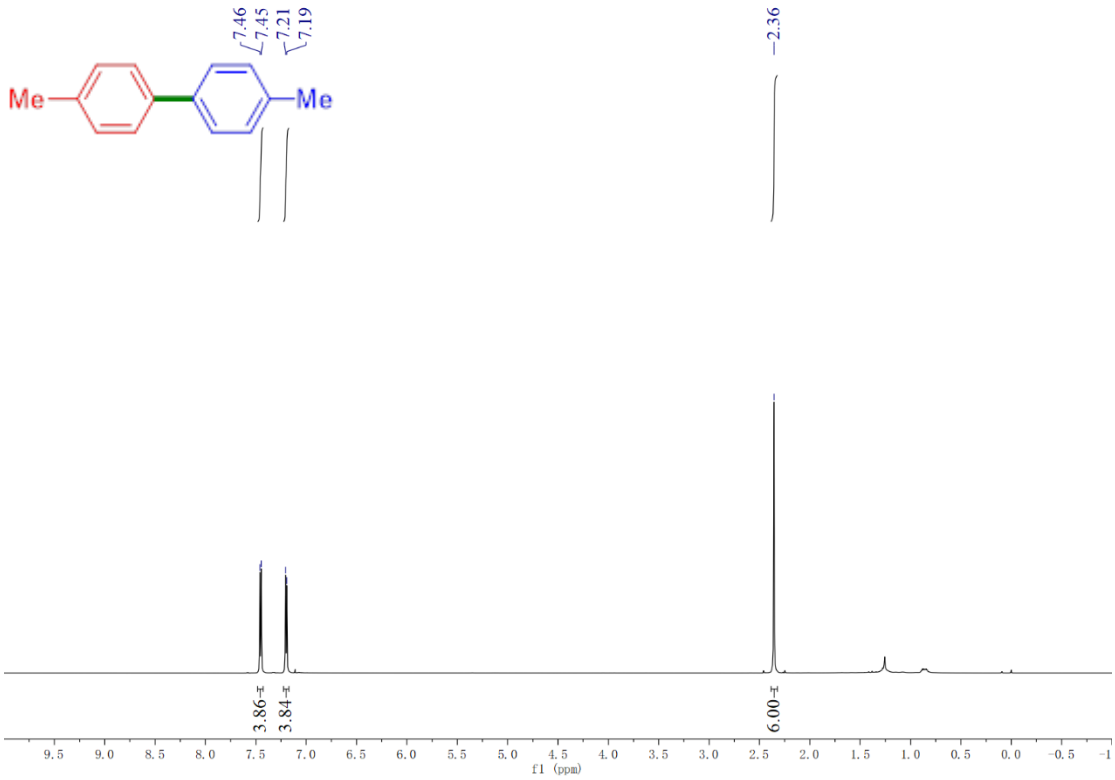


Figure S8. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5b**

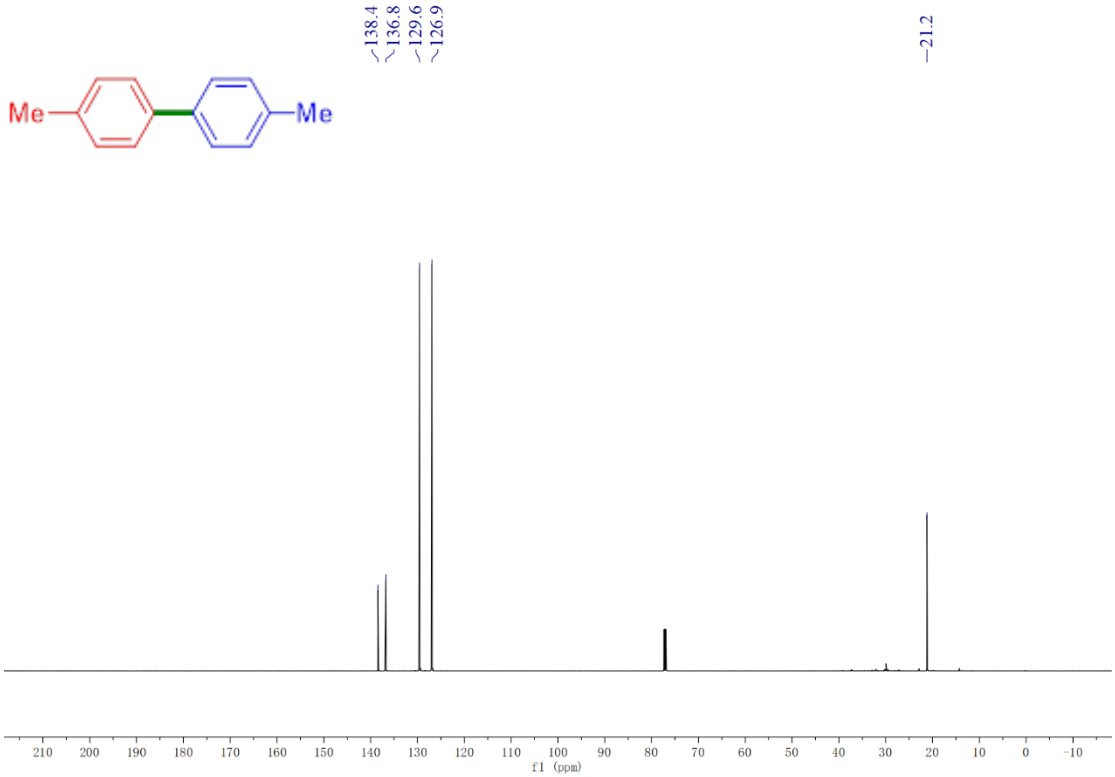


Figure S9. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5b**

4-Methoxy-4'-methyl-1,1'-biphenyl (5c).

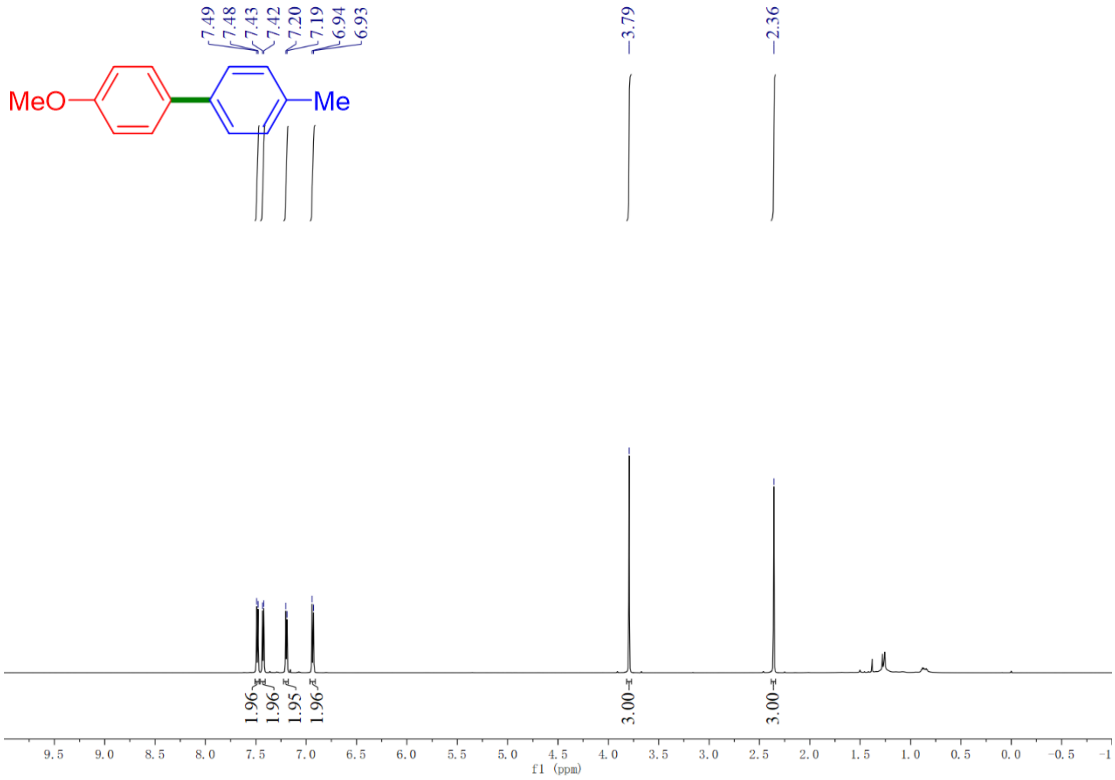


Figure S10. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5c**

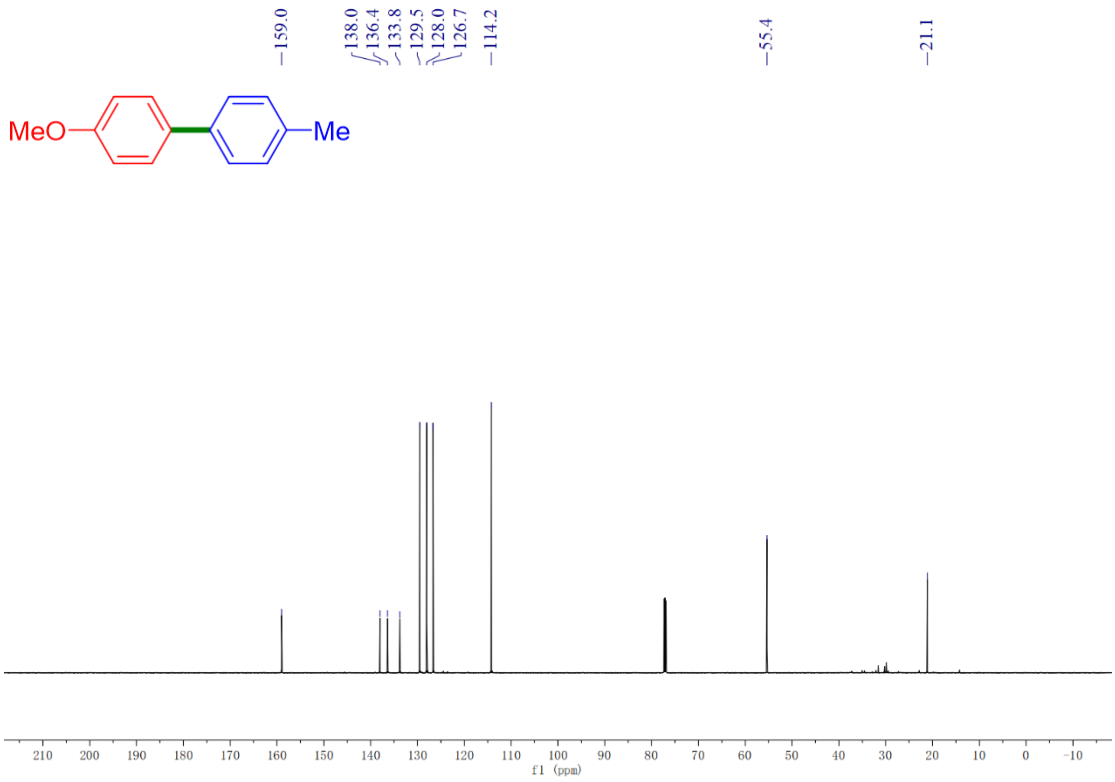


Figure S11. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5c**

4-Methyl-4'-(trifluoromethyl)-1,1'-biphenyl (5d).

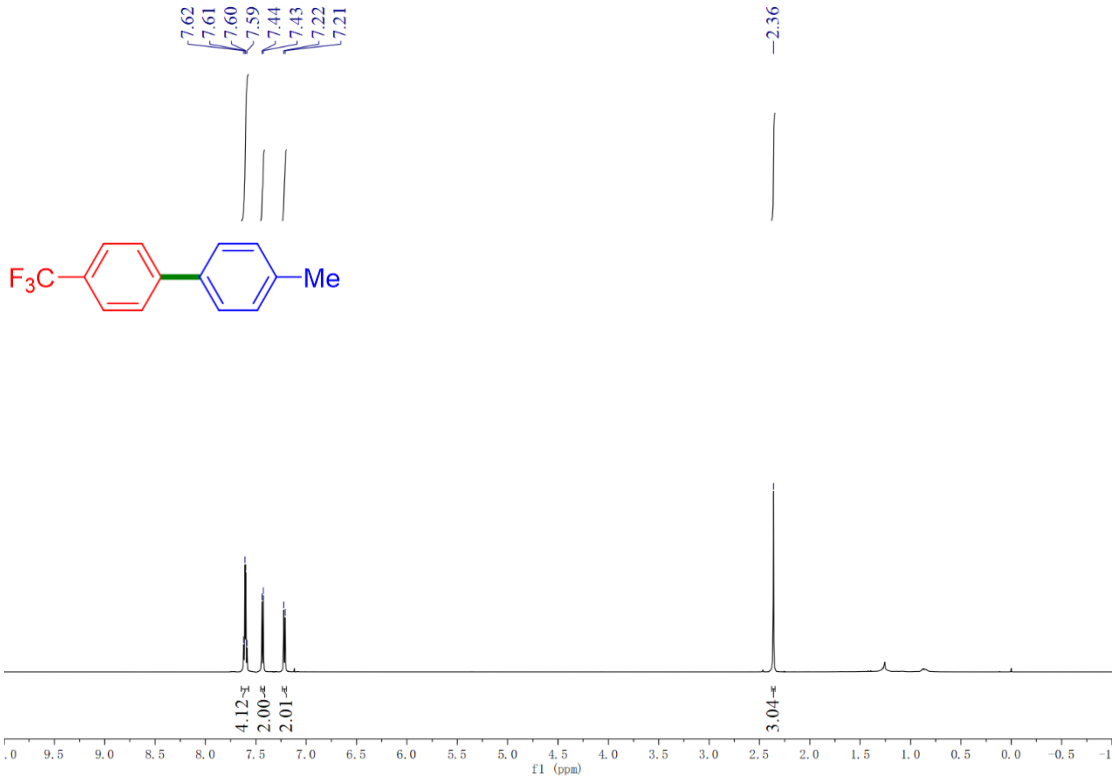


Figure S12. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5d**

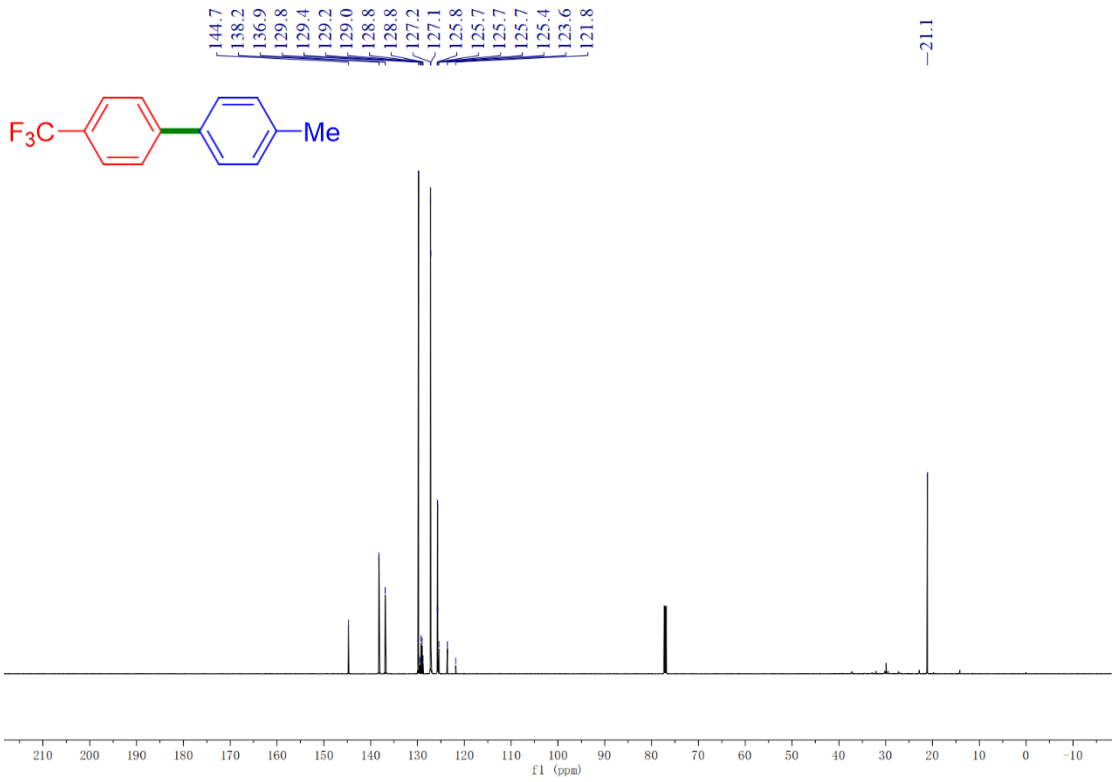


Figure S13. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5d**

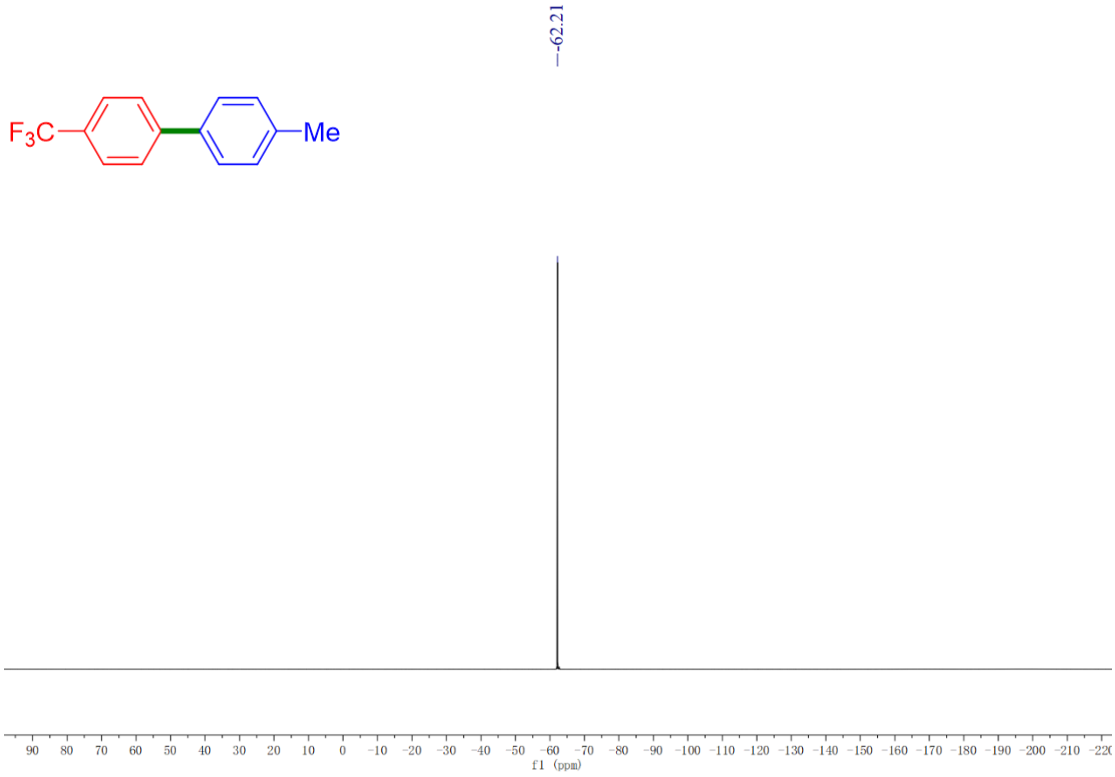


Figure S14. ^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **5d**

4-Methyl-4'-nitro-1,1'-biphenyl (5e).

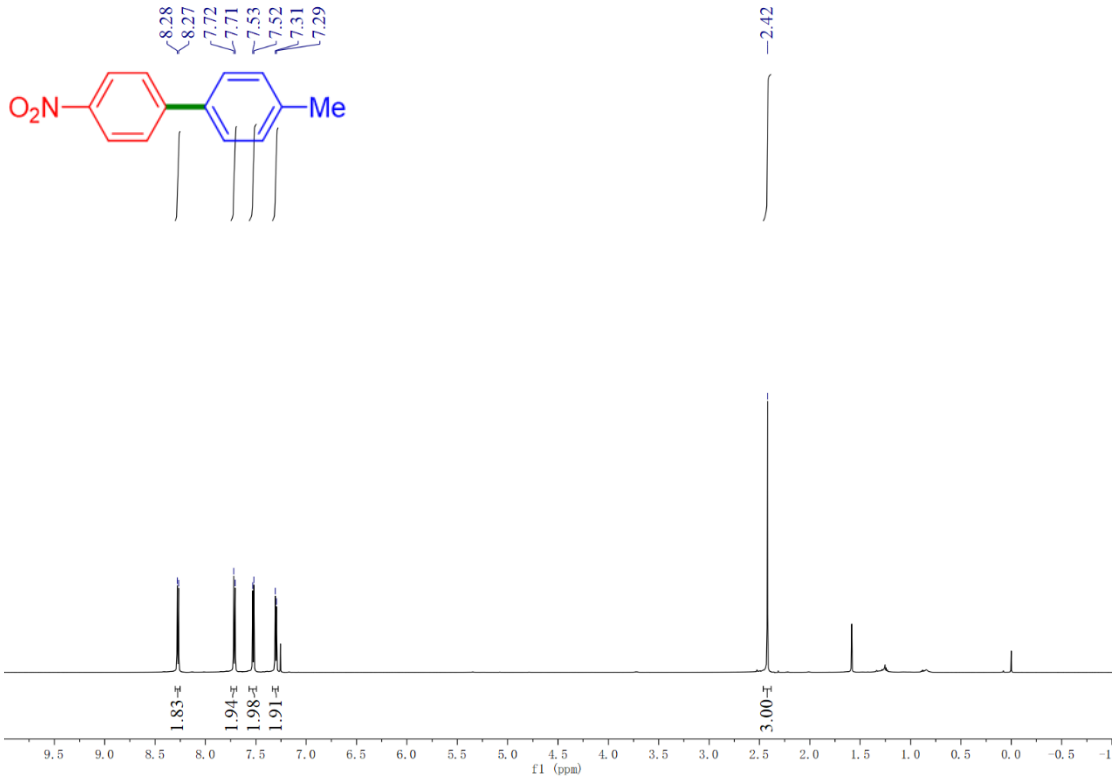


Figure S15. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5e**

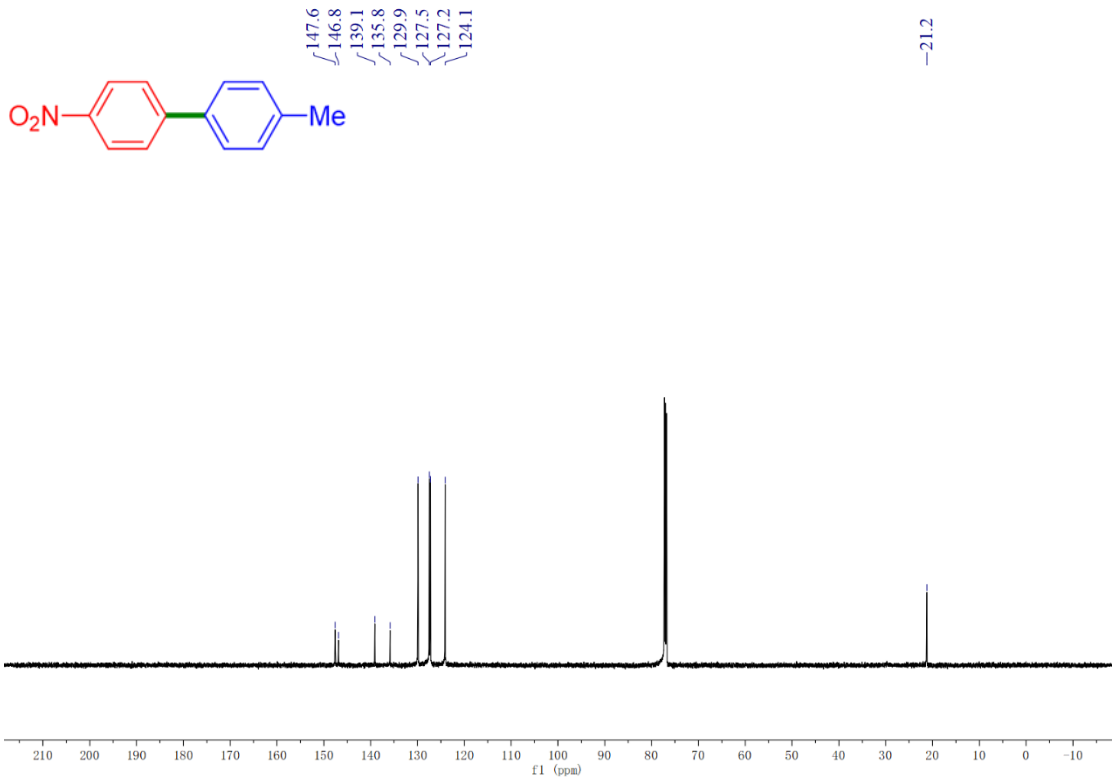


Figure S16. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5e**

4-Isocyano-4'-methyl-1,1'-biphenyl (5f).

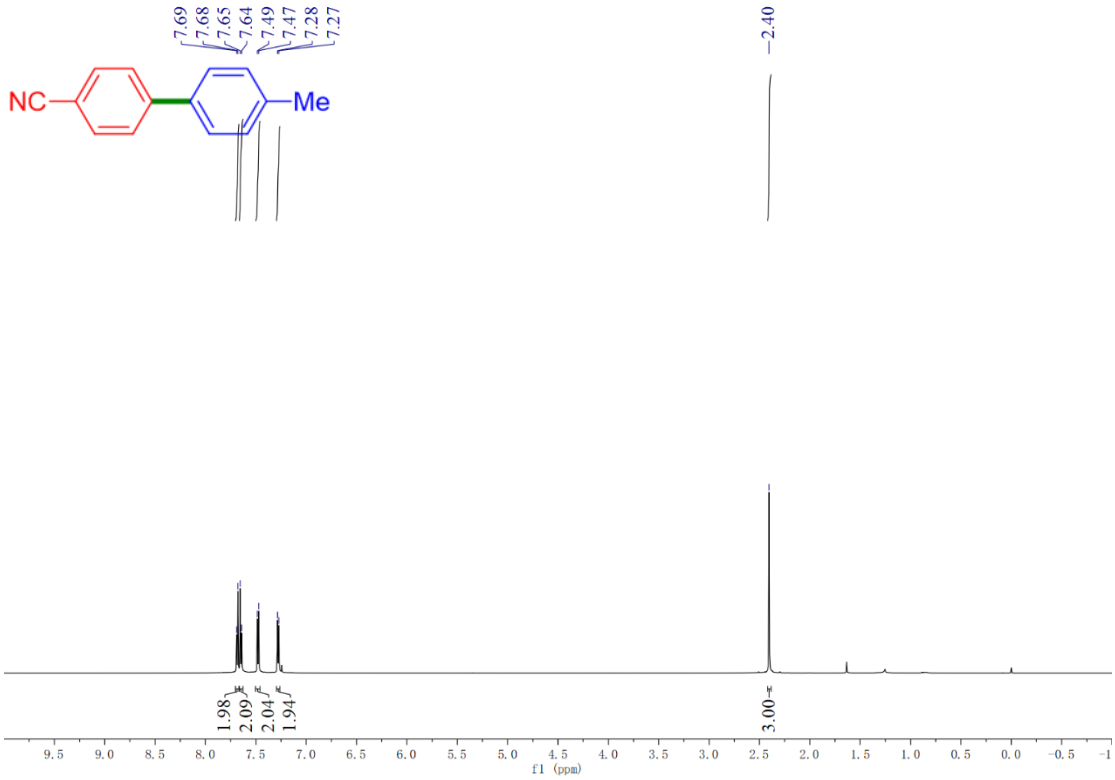


Figure S17. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5f**

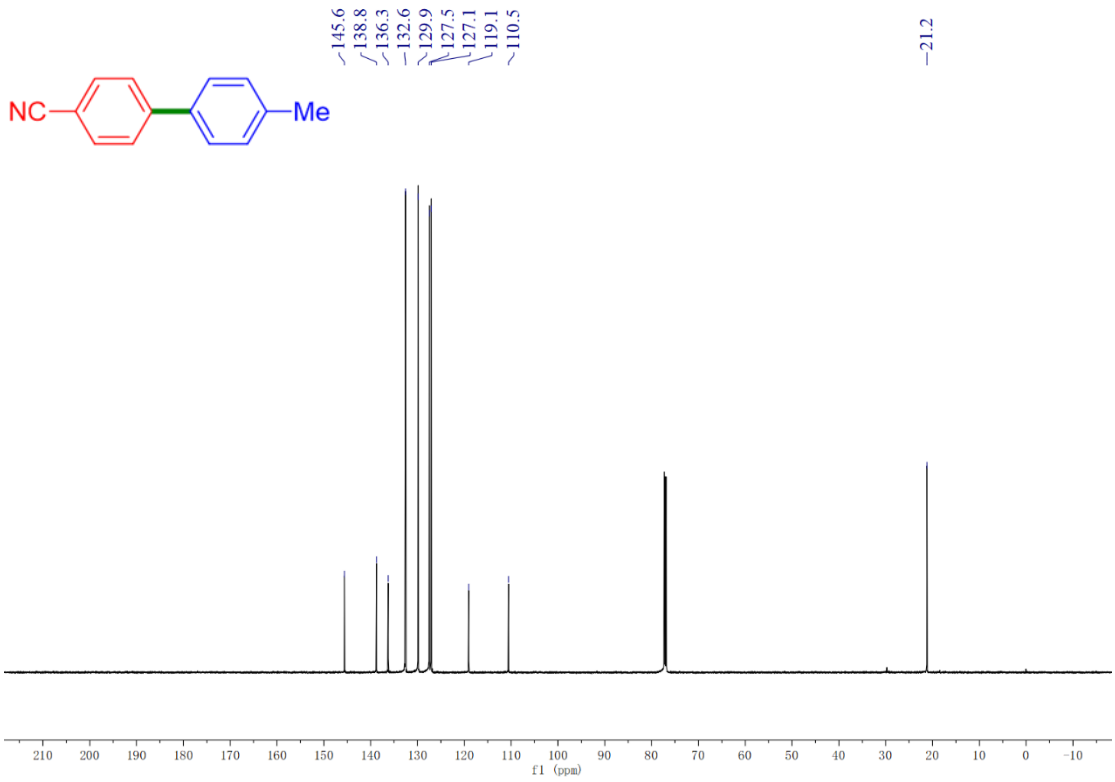


Figure S18. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5f**

4'-Methyl-[1,1'-biphenyl]-4-carbaldehyde (5g).

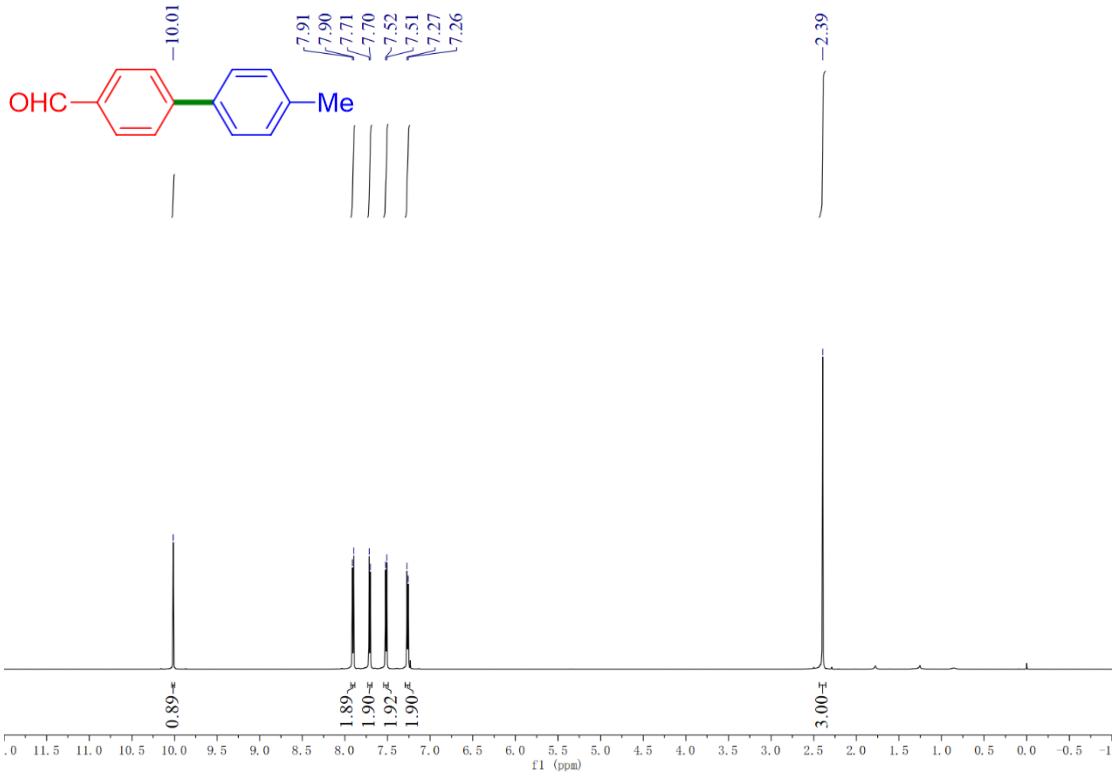


Figure S19. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5g**

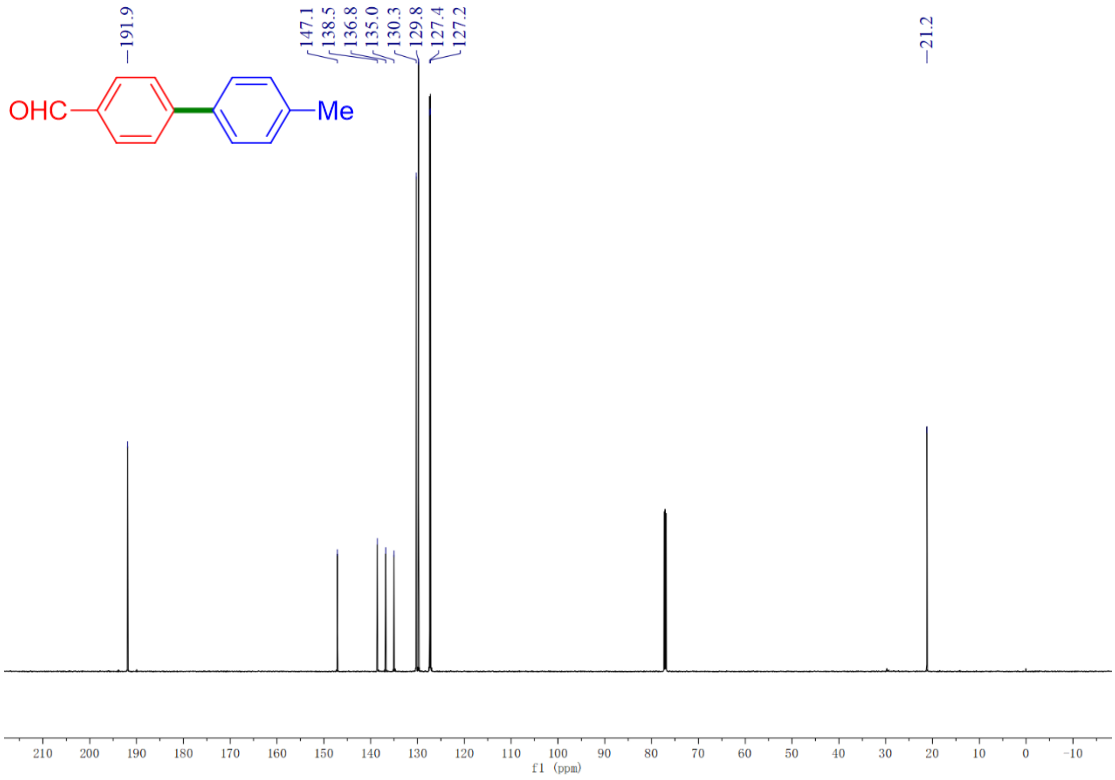


Figure S20. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5g**

4'-Methyl-[1,1'-biphenyl]-3-carbaldehyde (5h).

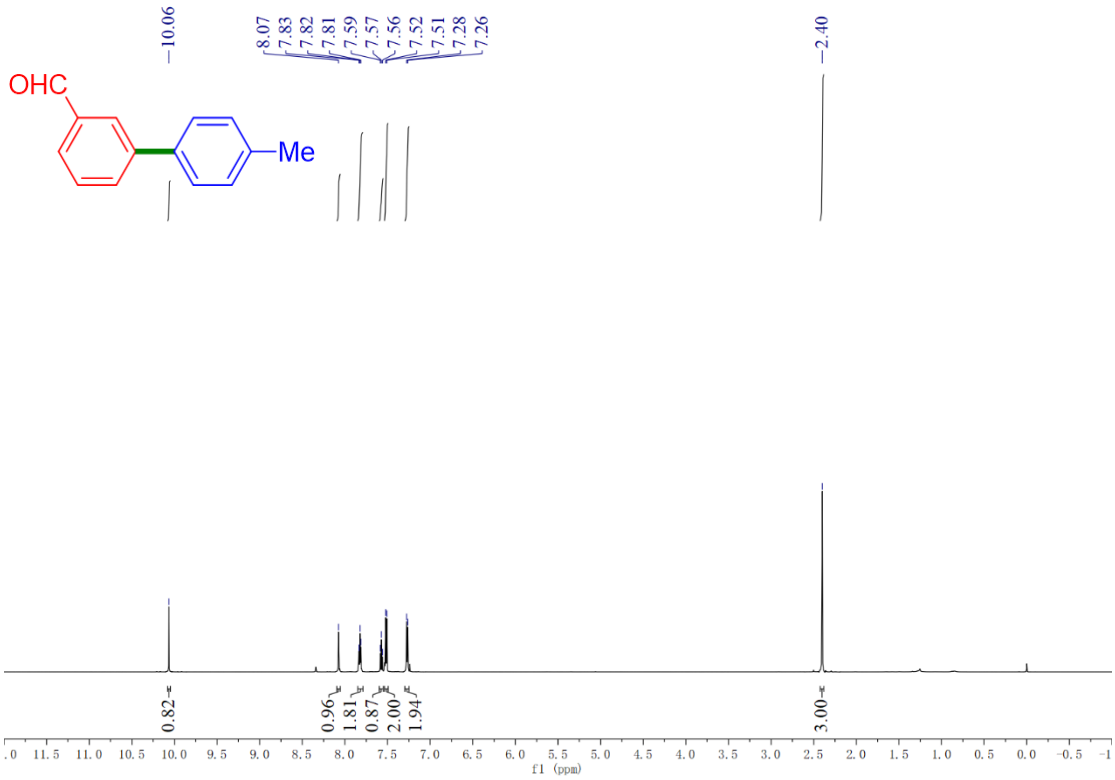


Figure S21. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5h**

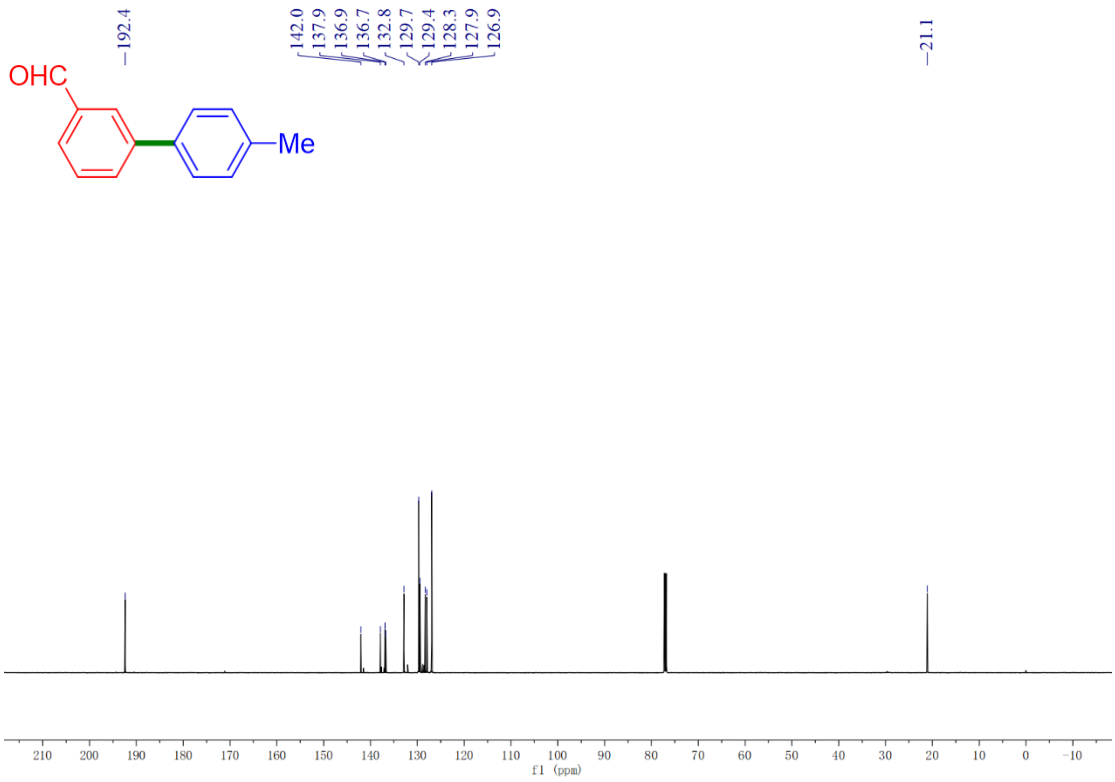


Figure S22. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5h**

1-(4'-Methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (5i).

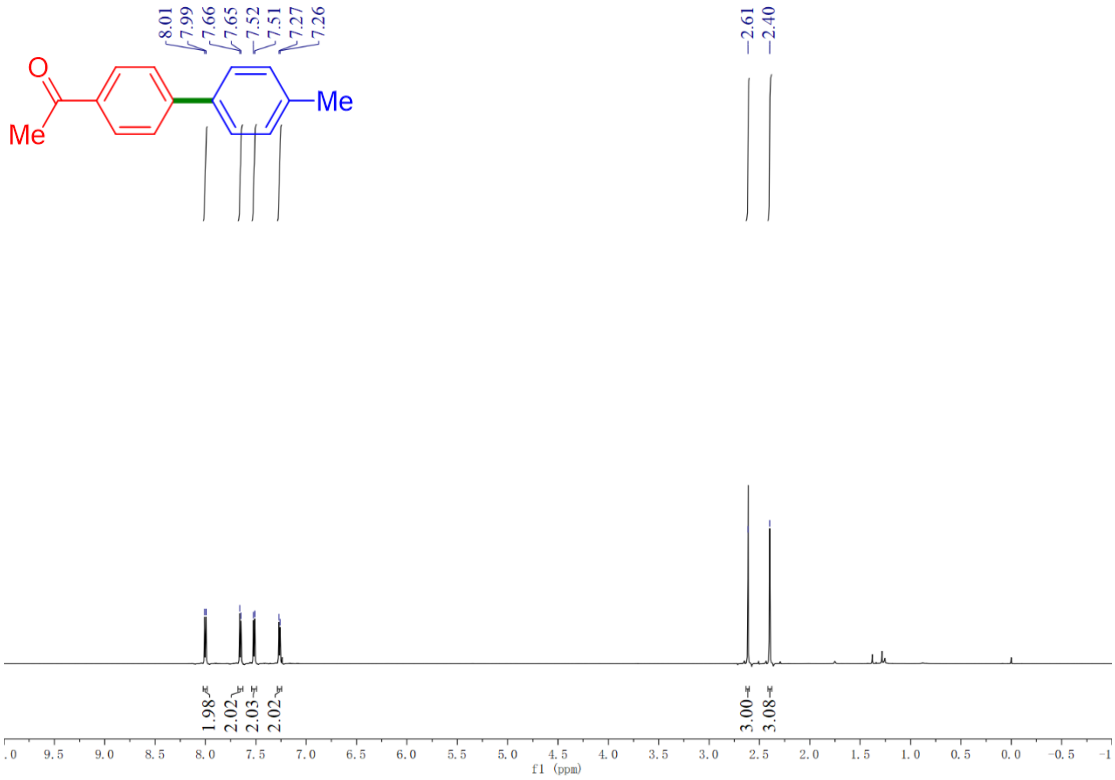


Figure S23. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5i**

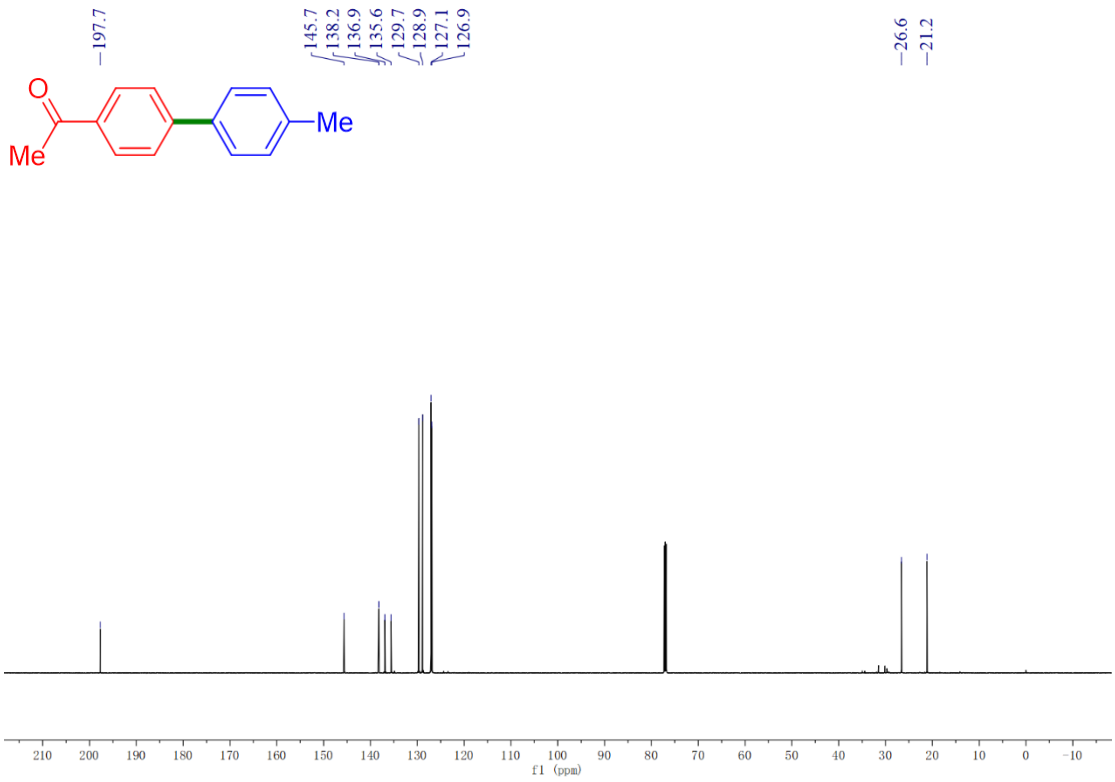


Figure S24. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5i**

4'-Methyl-[1,1'-biphenyl]-2-amine (5j).

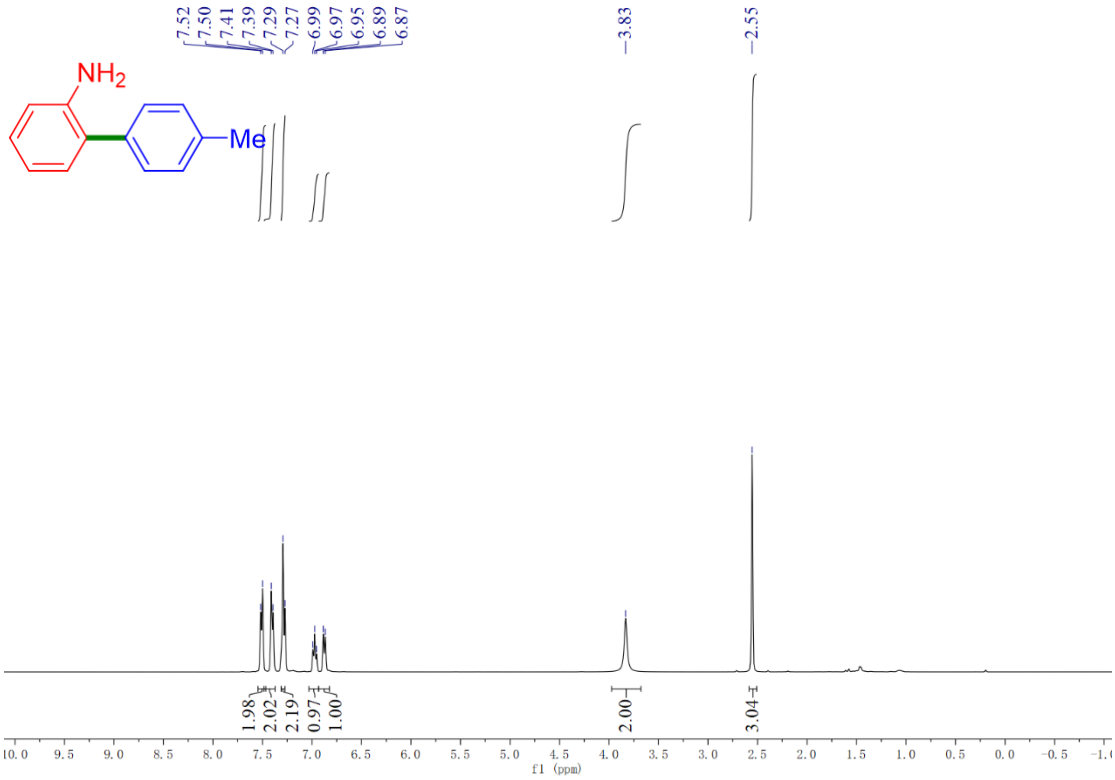


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5j**

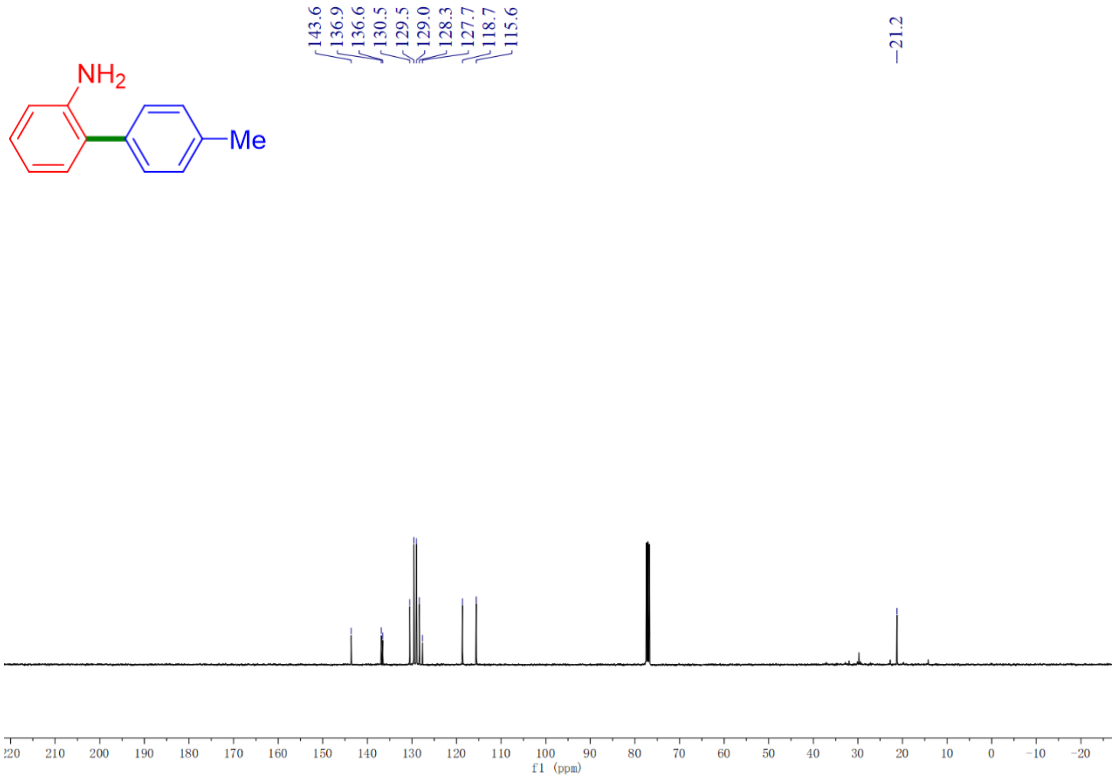


Figure S26. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5j**

4'-Methyl-[1,1'-biphenyl]-3-amine (5k).

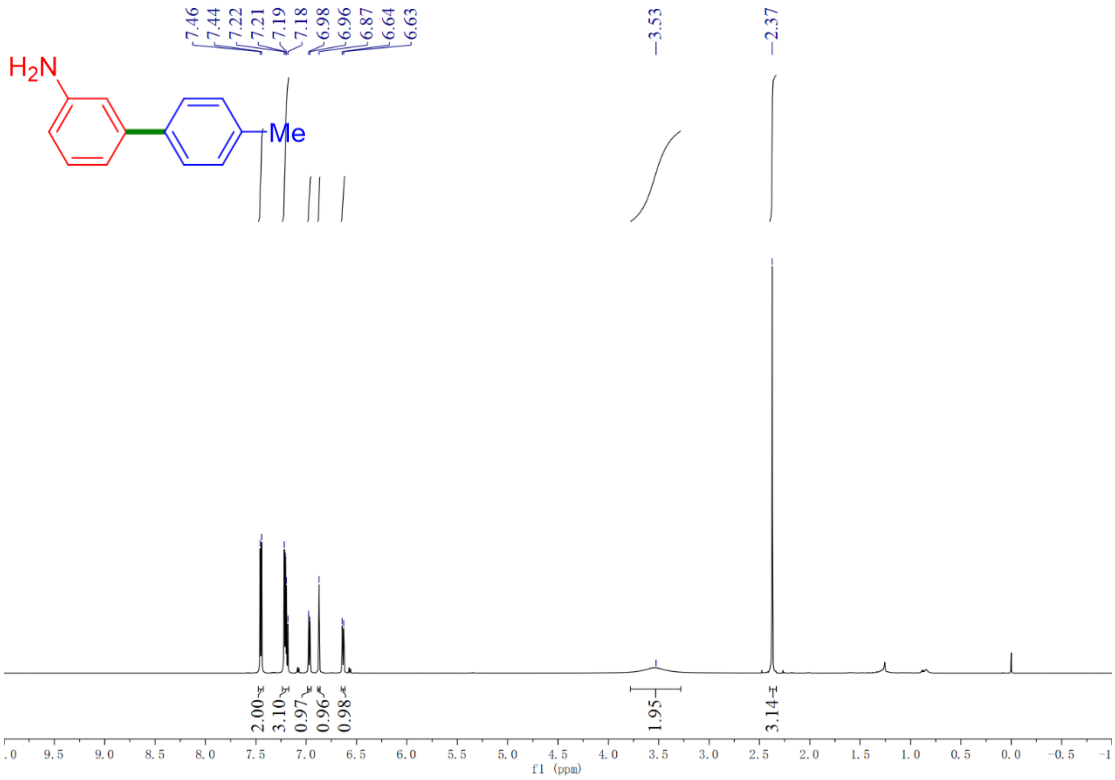


Figure S27. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5k**

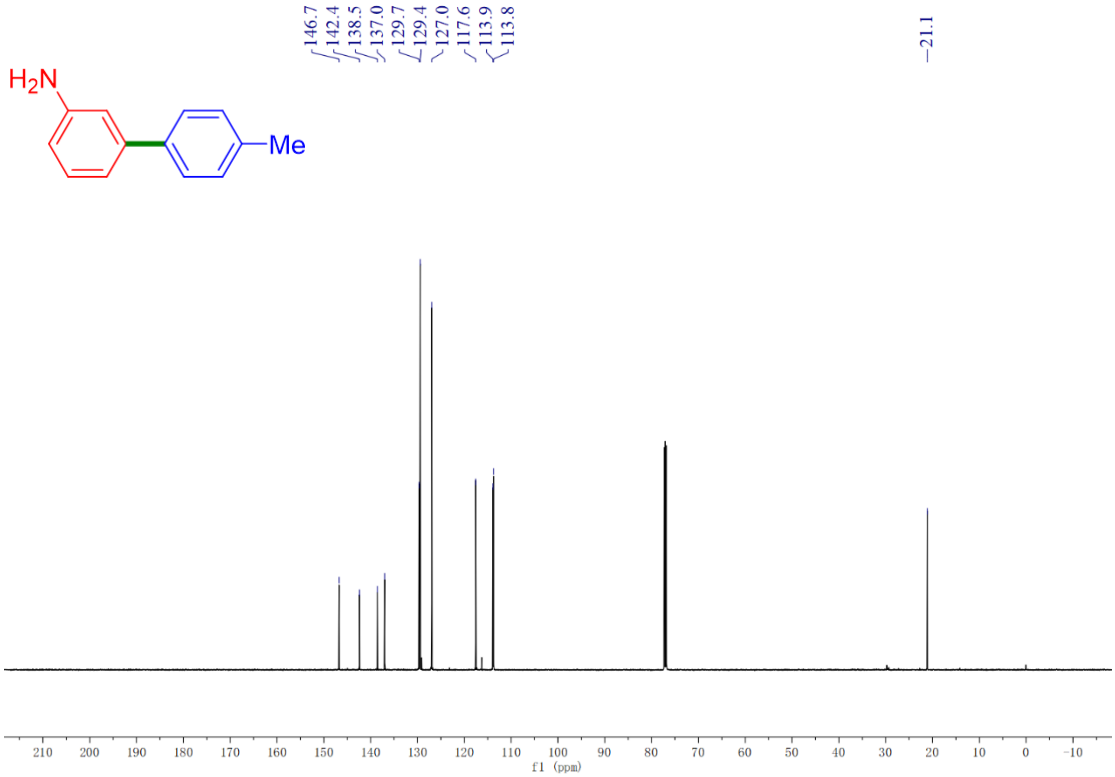


Figure S28. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5k**

4'-Methyl-[1,1'-biphenyl]-4-amine (5l).

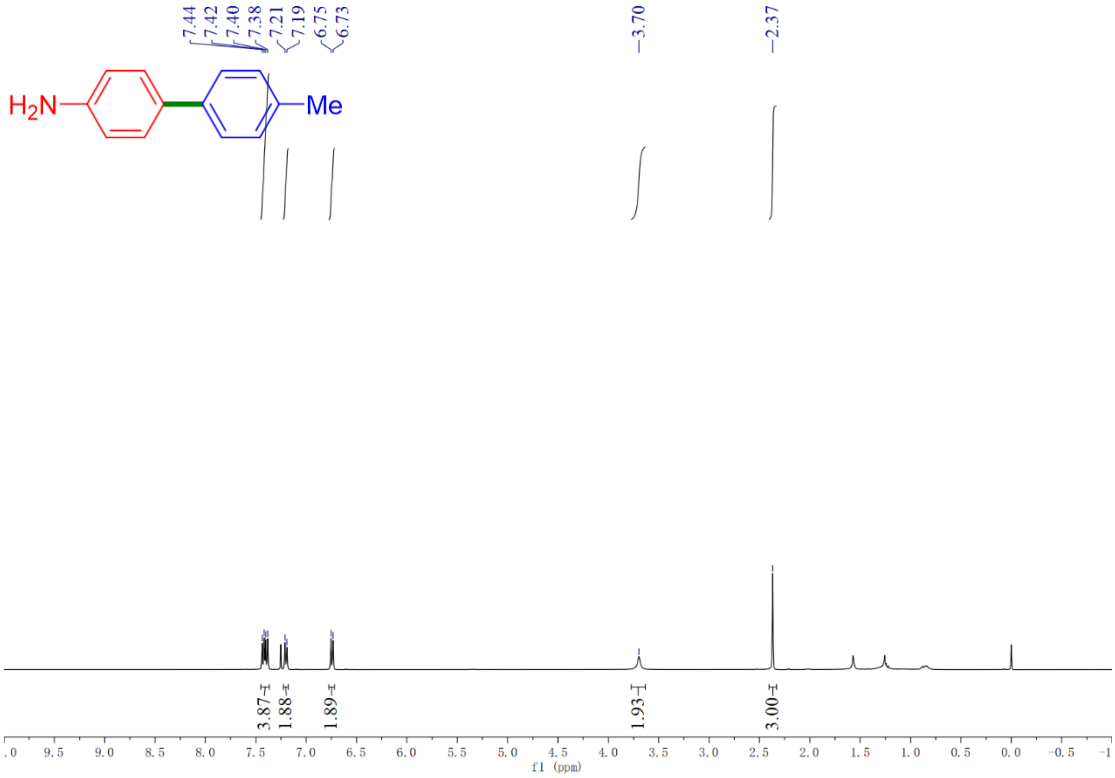


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5l**

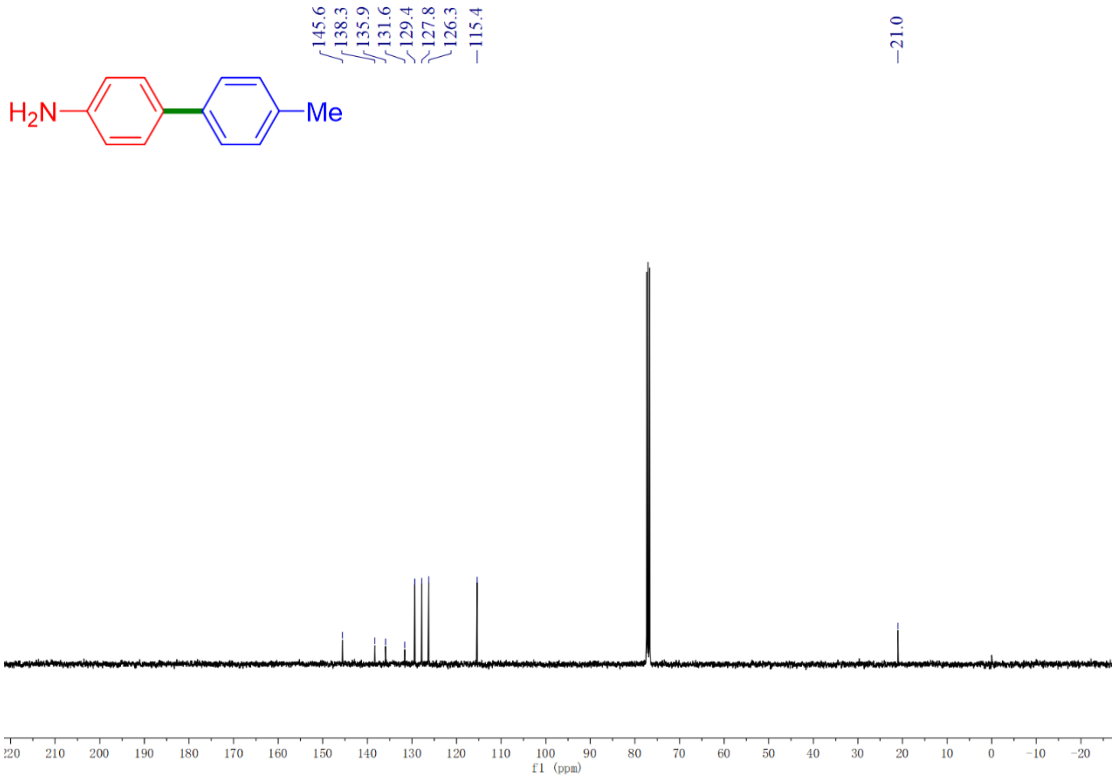


Figure S30. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5l**

3-(*p*-Tolyl)pyridine (5m).

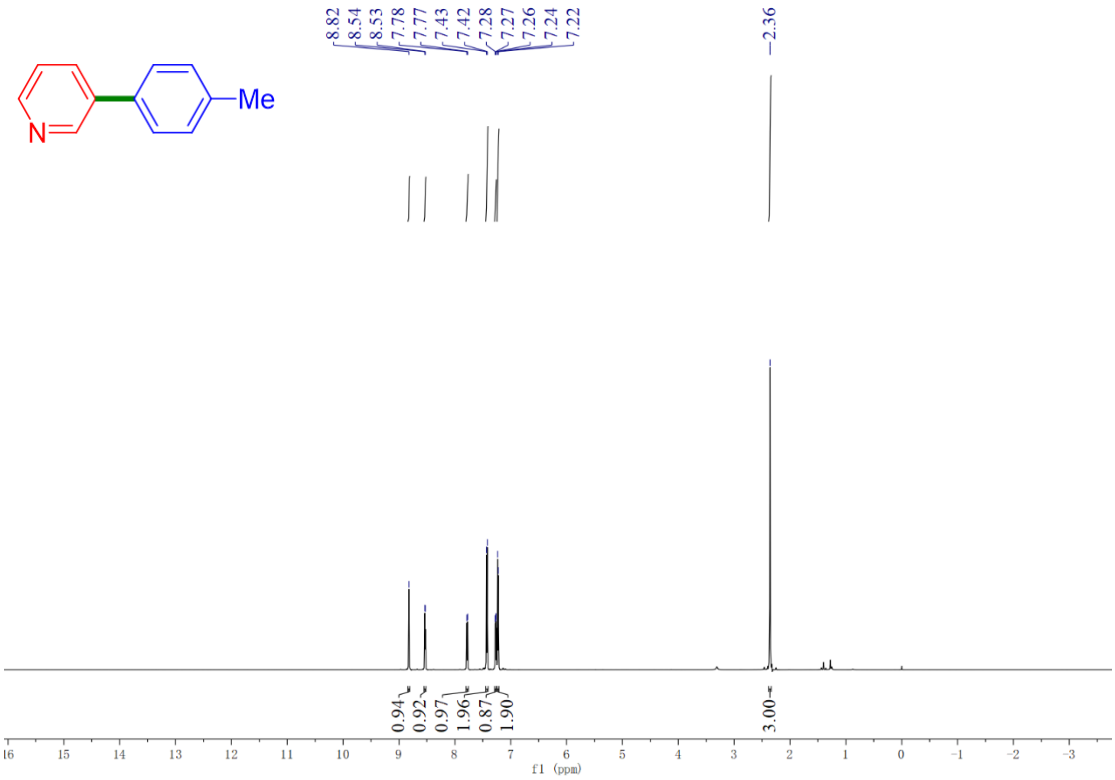


Figure S31. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5m**

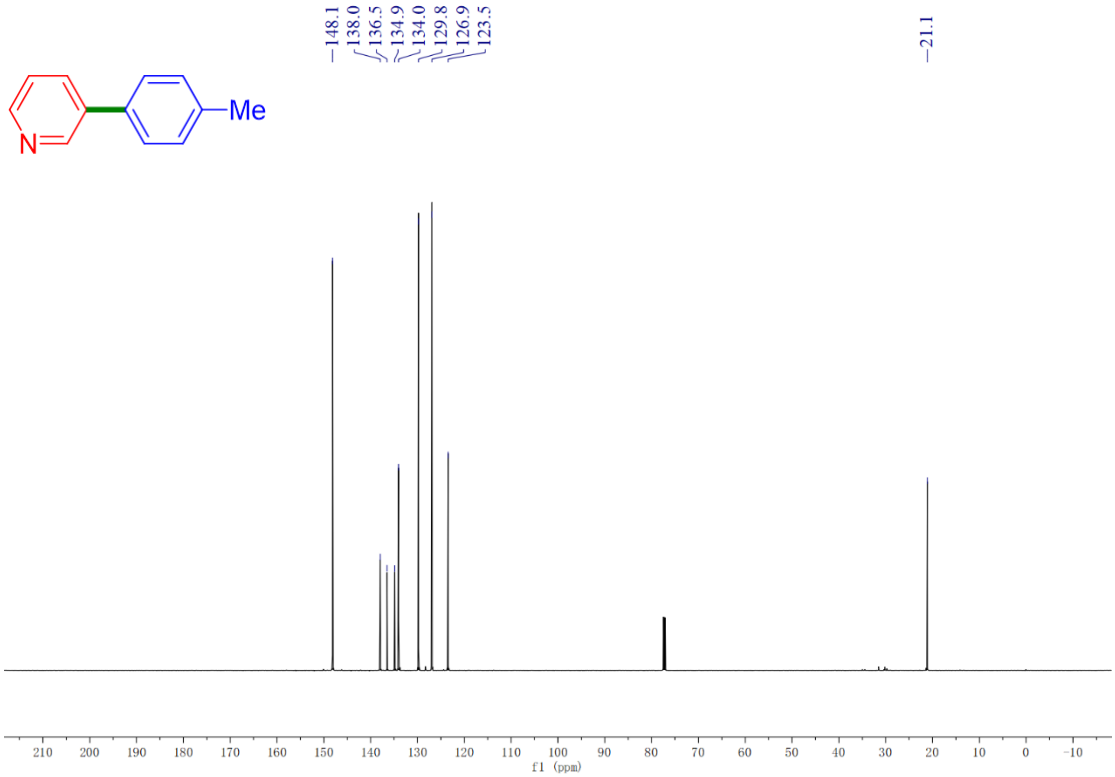


Figure S32. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5m**

4-Methyl-1,1'-biphenyl (5n).

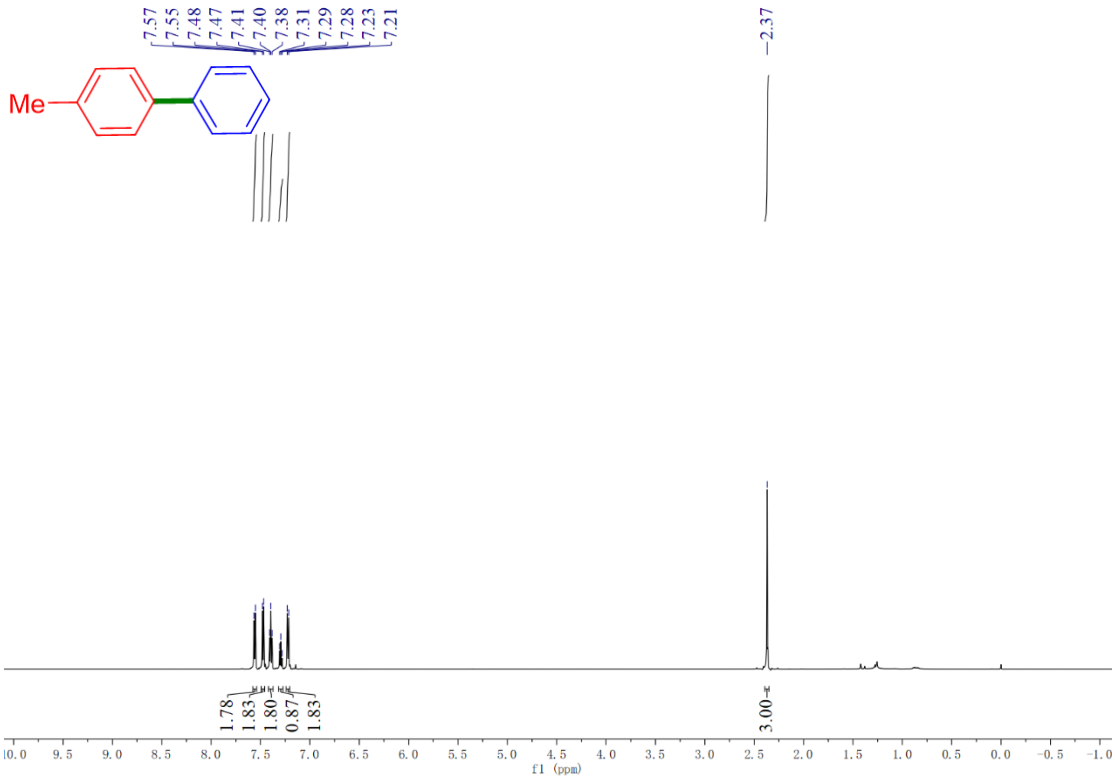


Figure S33. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5n**

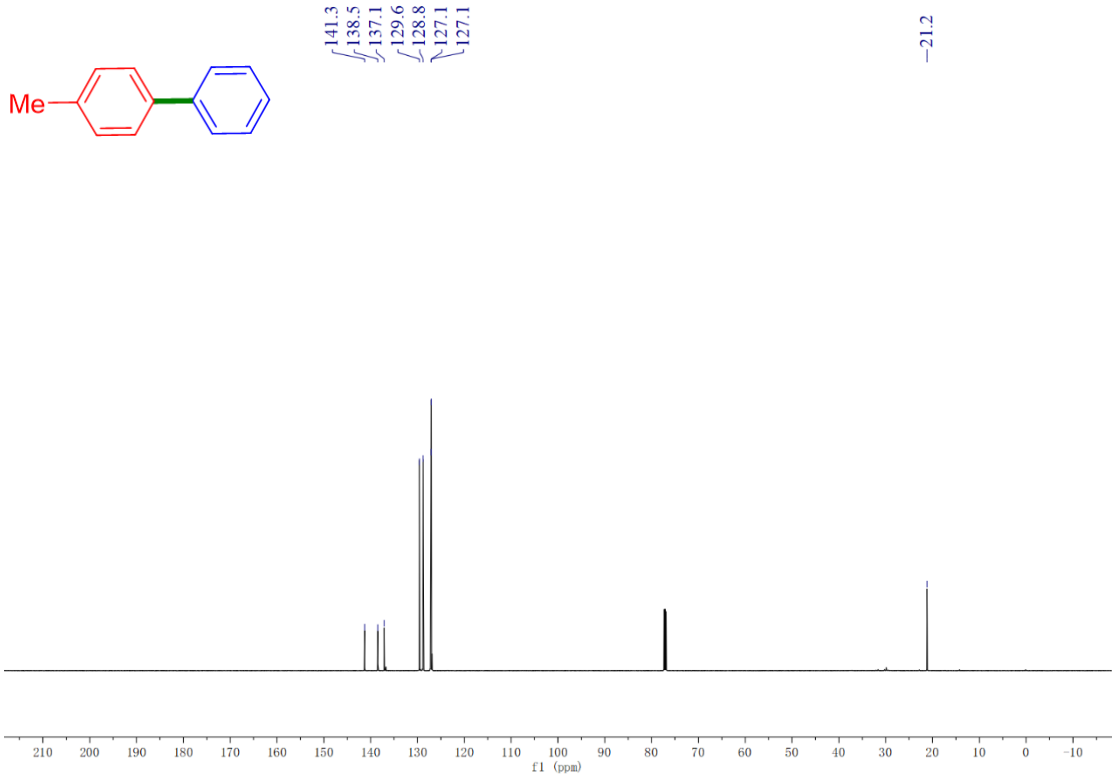


Figure S34. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5n**

4-Methoxy-4'-methyl-1,1'-biphenyl (5o).

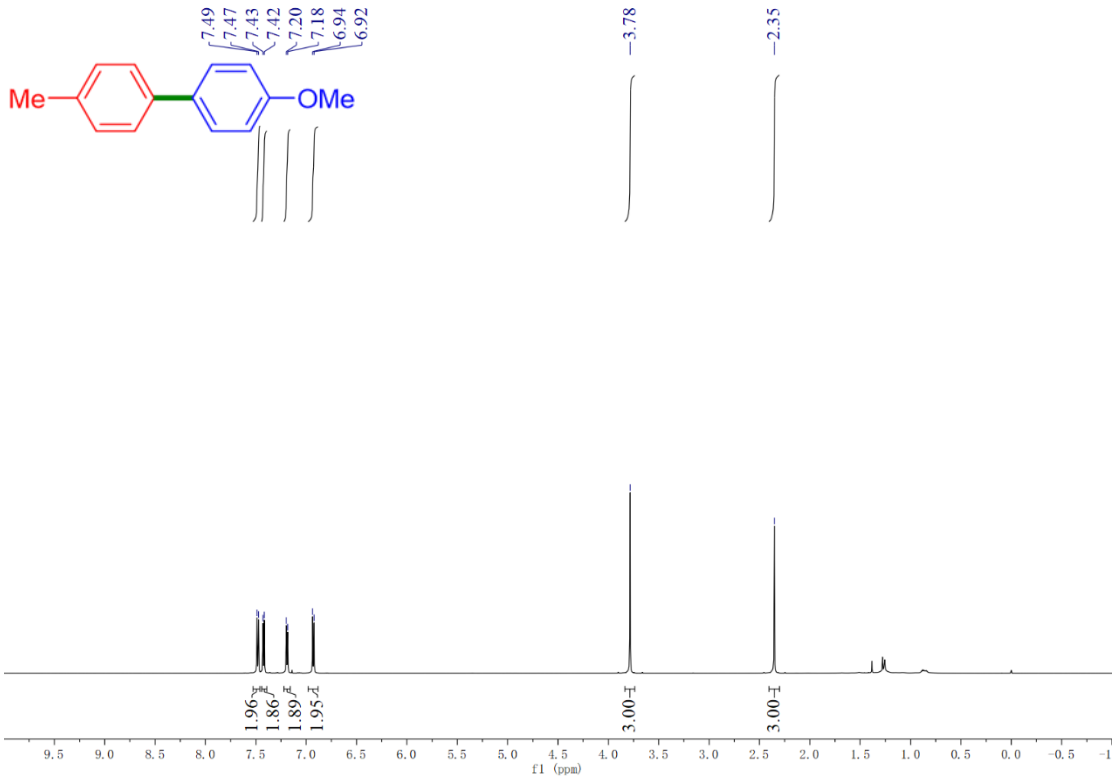


Figure S35. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5o**

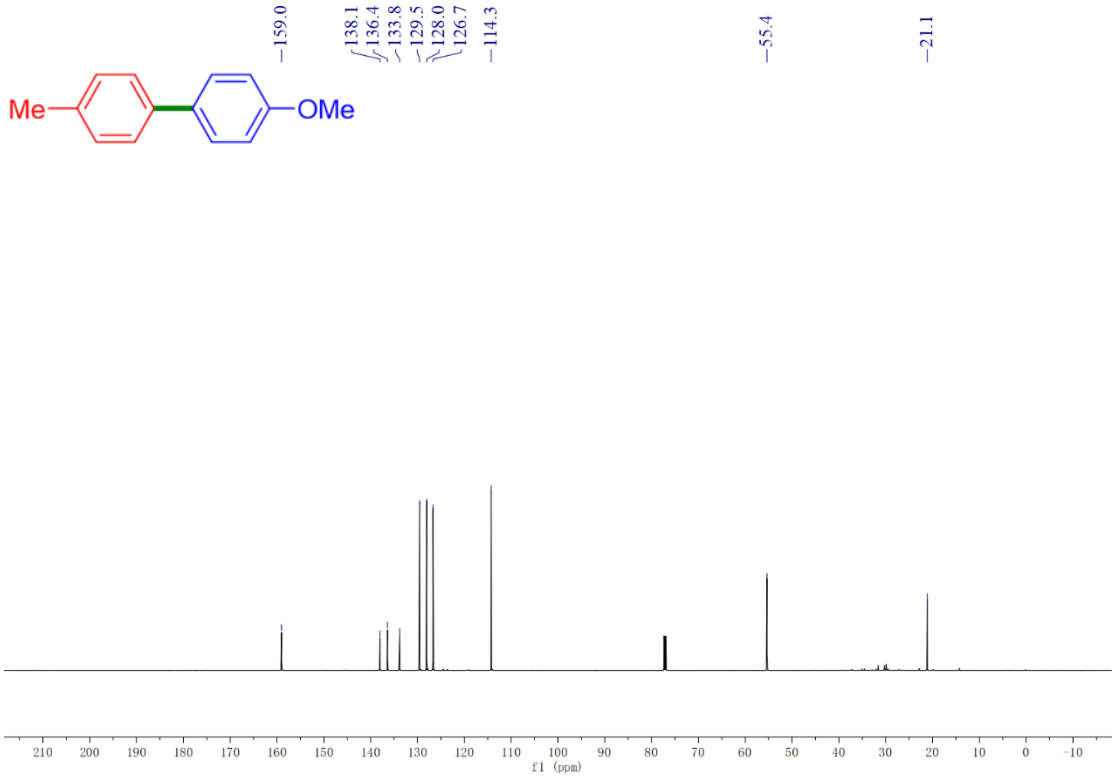


Figure S36. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5o**

2-Dethoxy-4'-methyl-1,1'-biphenyl (5p).

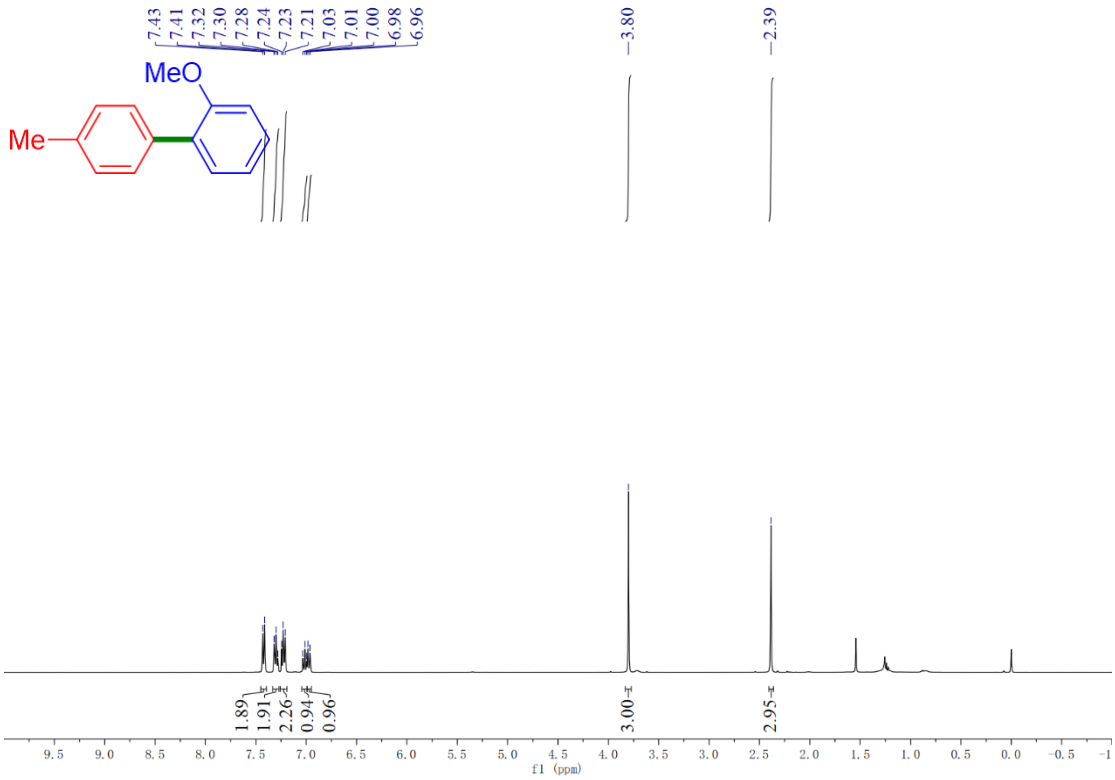


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5p**

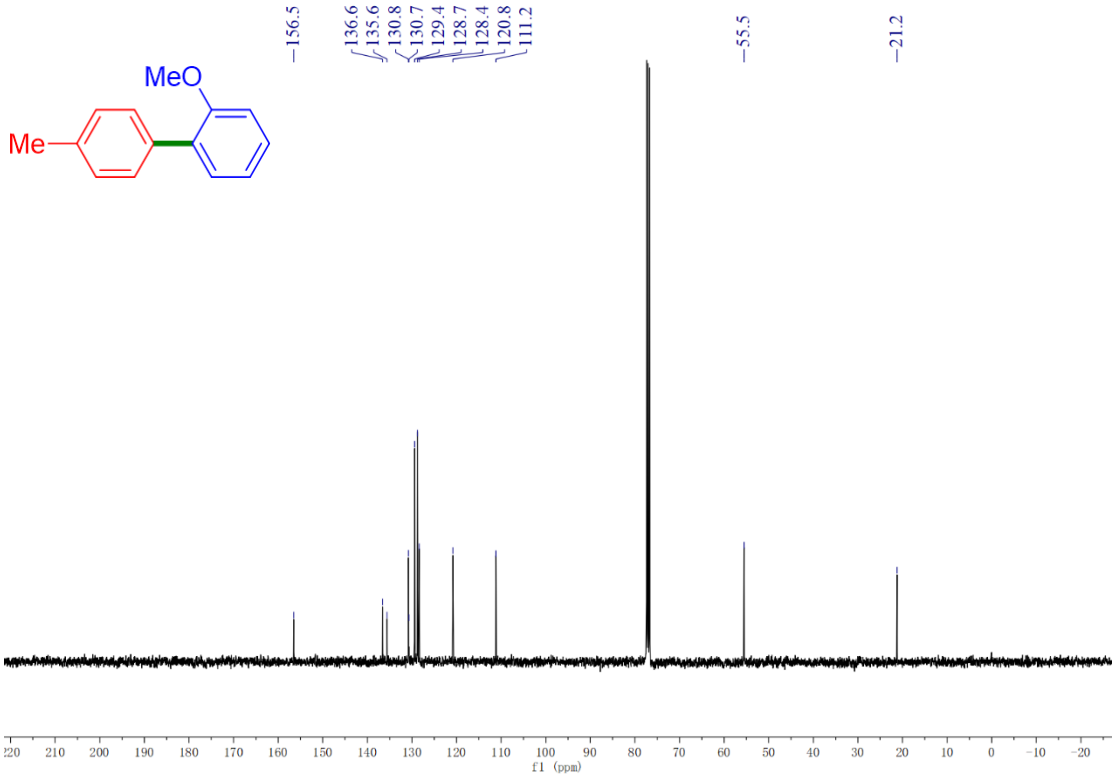


Figure S38. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5p**

4-Methoxy-2,4'-dimethyl-1,1'-biphenyl (5q).

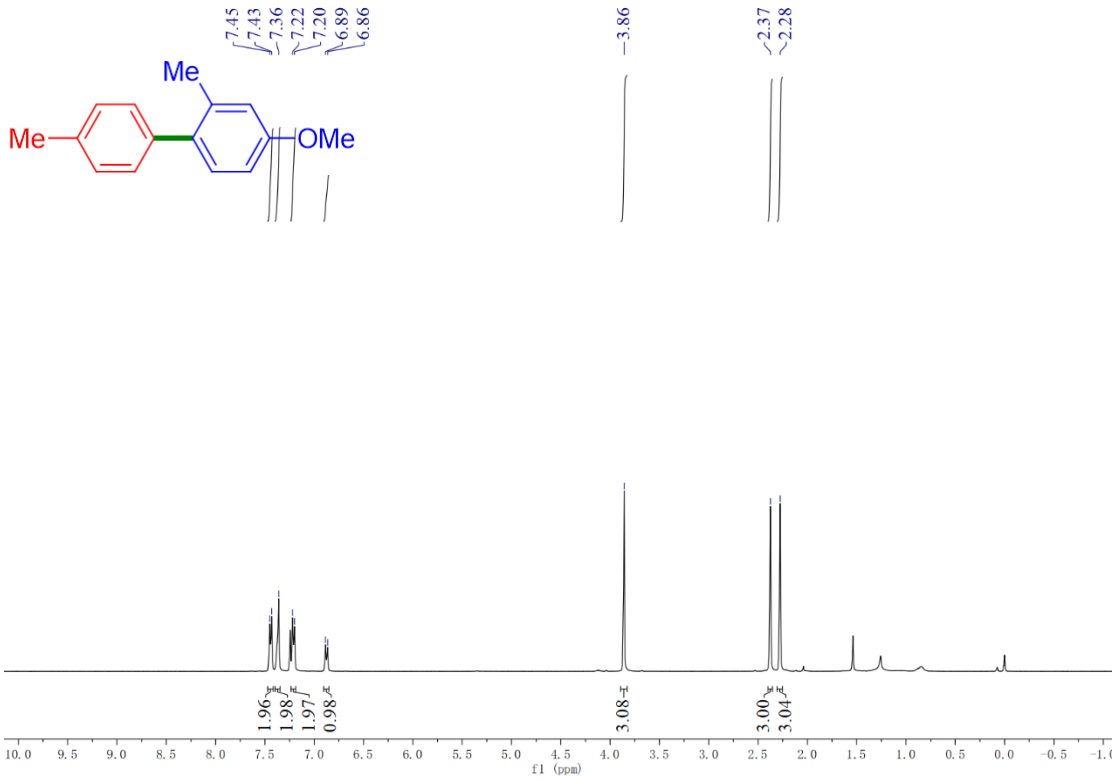


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5q**

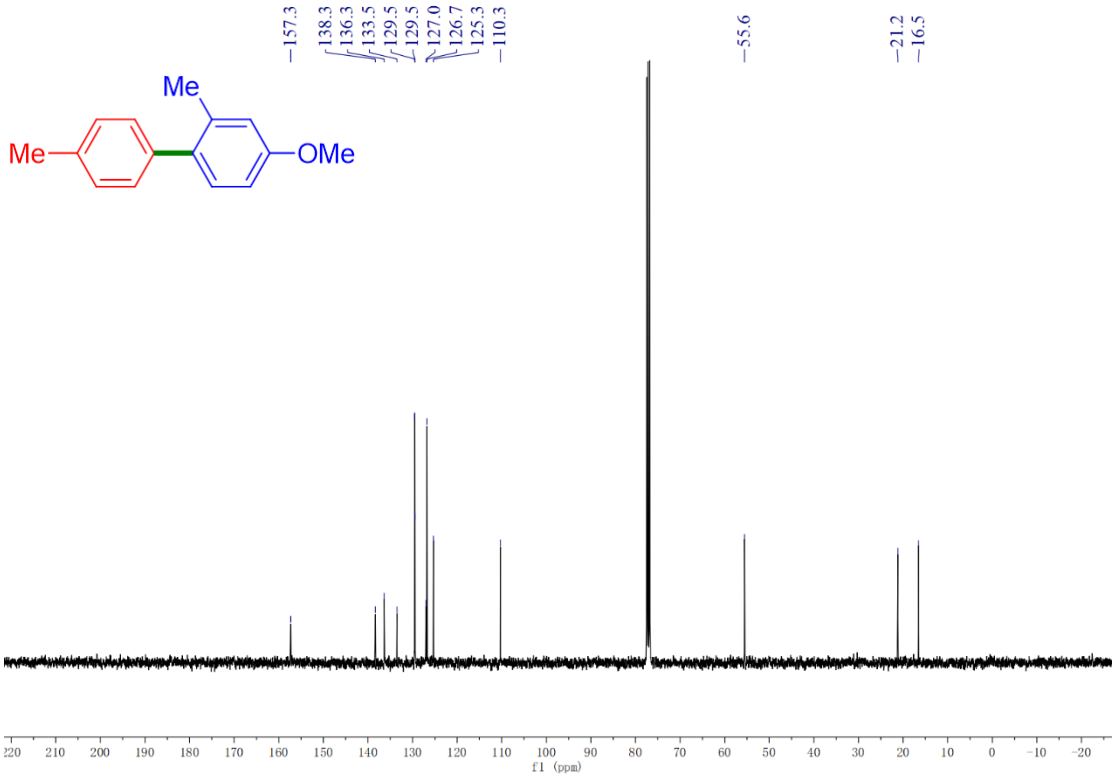


Figure S40. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5q**

4'-Methyl-[1,1'-biphenyl]-3-carbonitrile (5r).

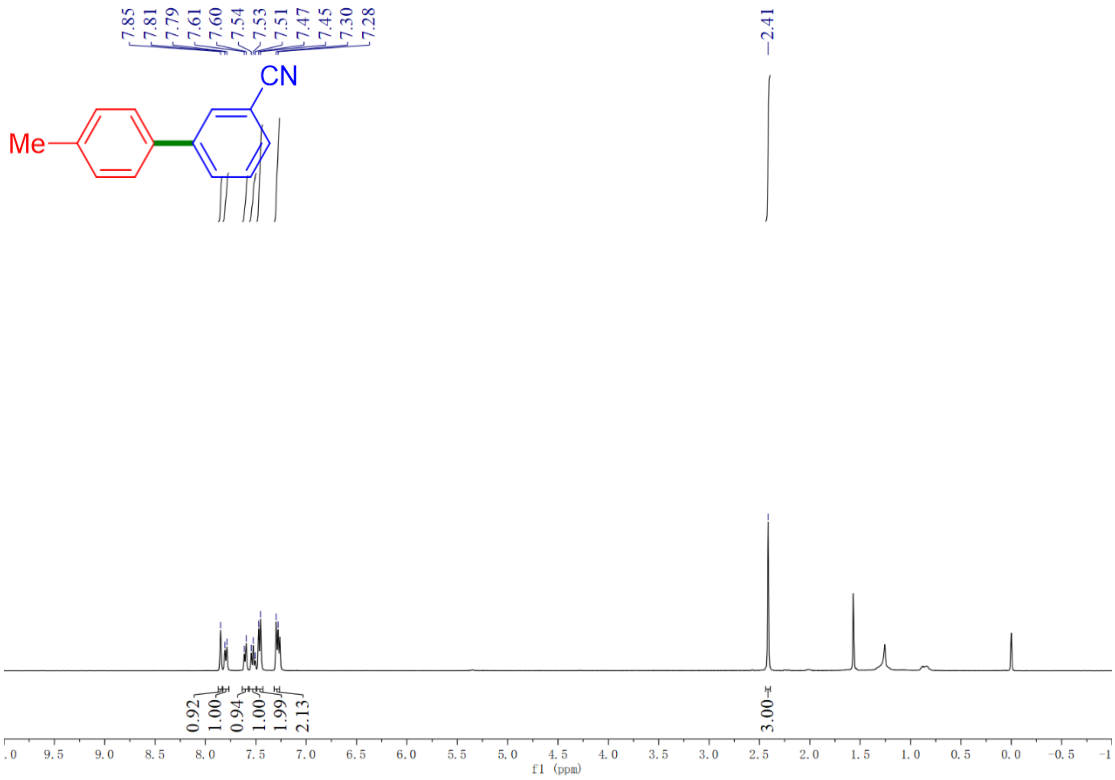


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5r**

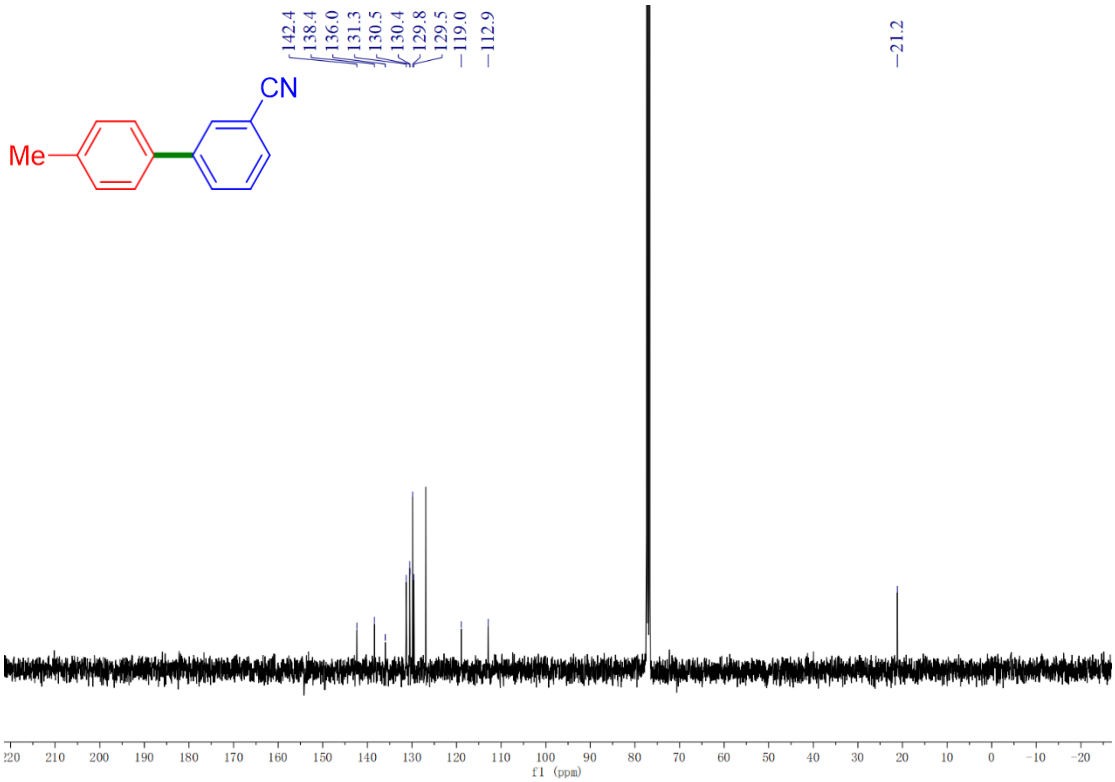


Figure S42. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5r**

1-(4'-Methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (5s).

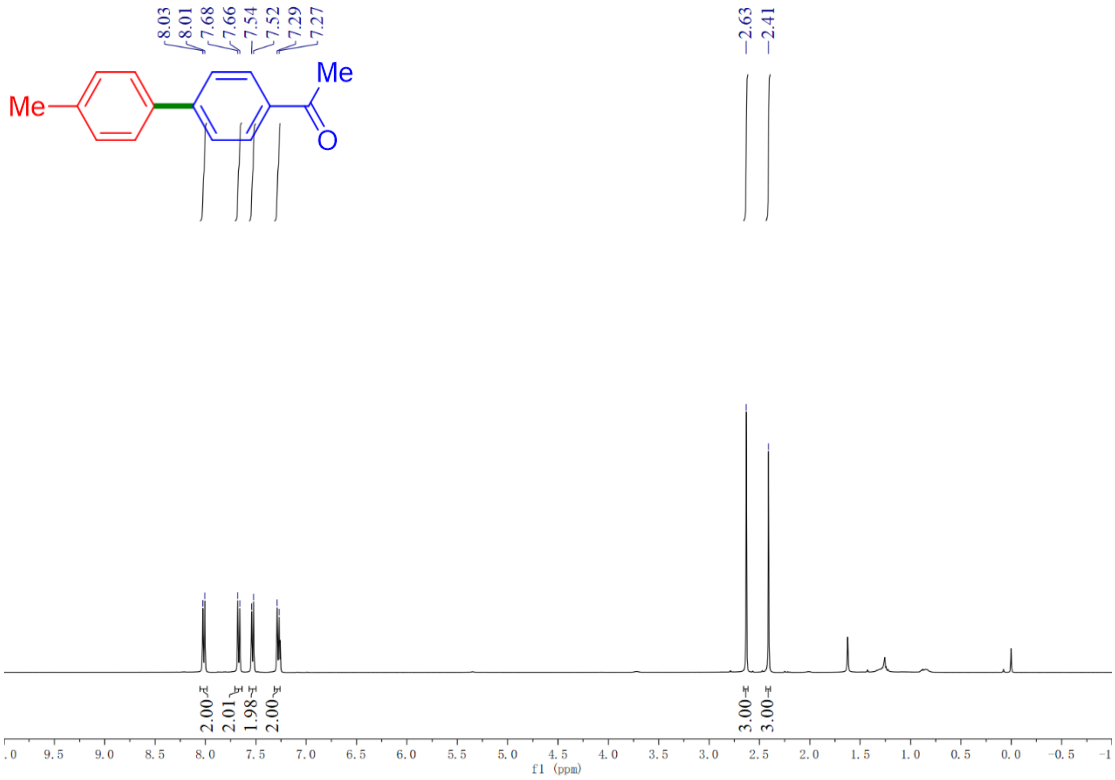


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5s**

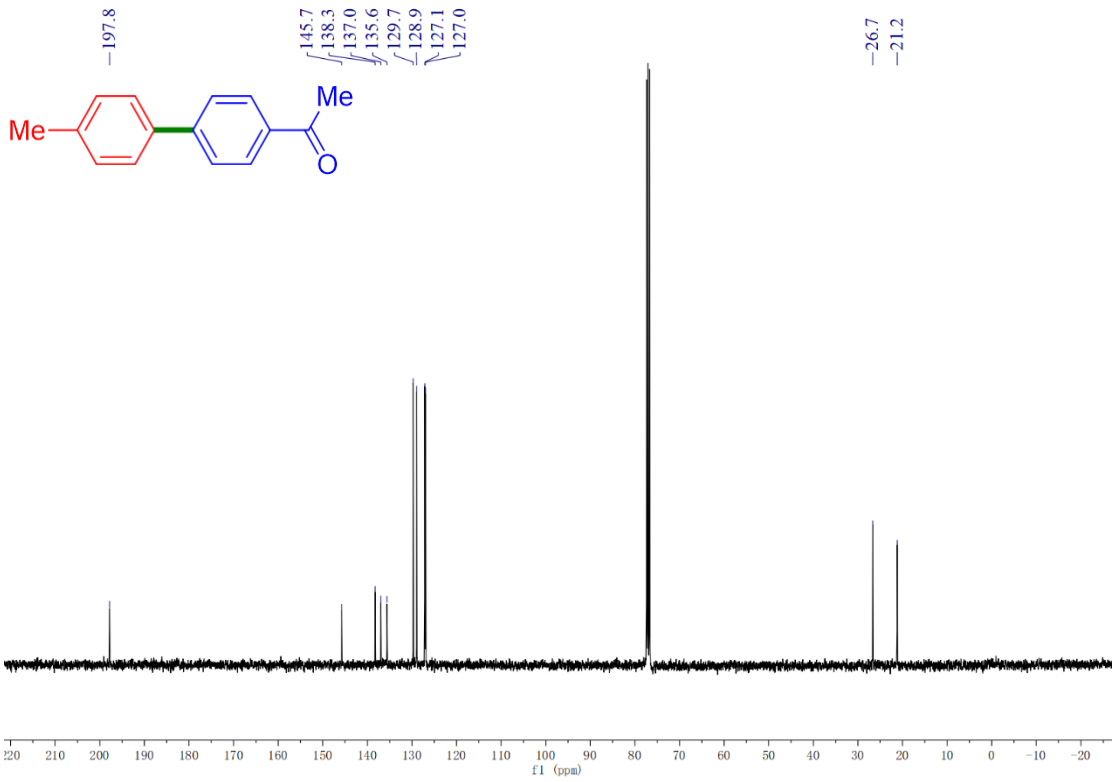


Figure S44. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5s**

4-Methyl-4'-vinyl-1,1'-biphenyl (5t).

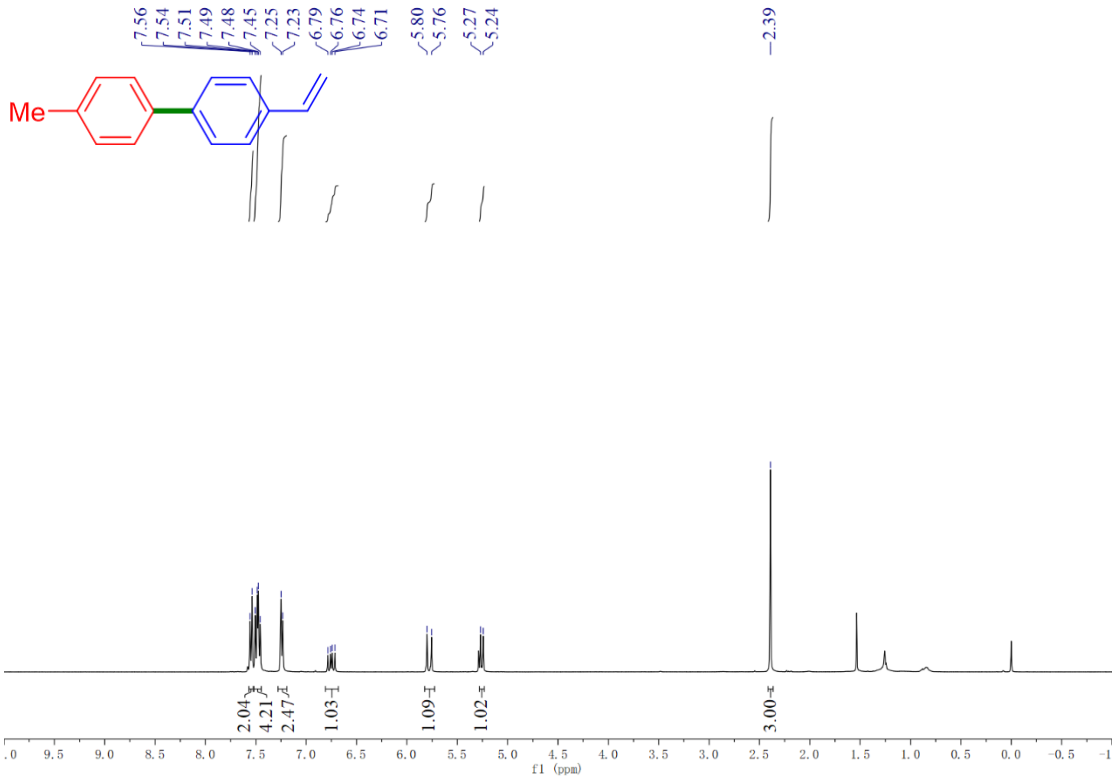


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5t**

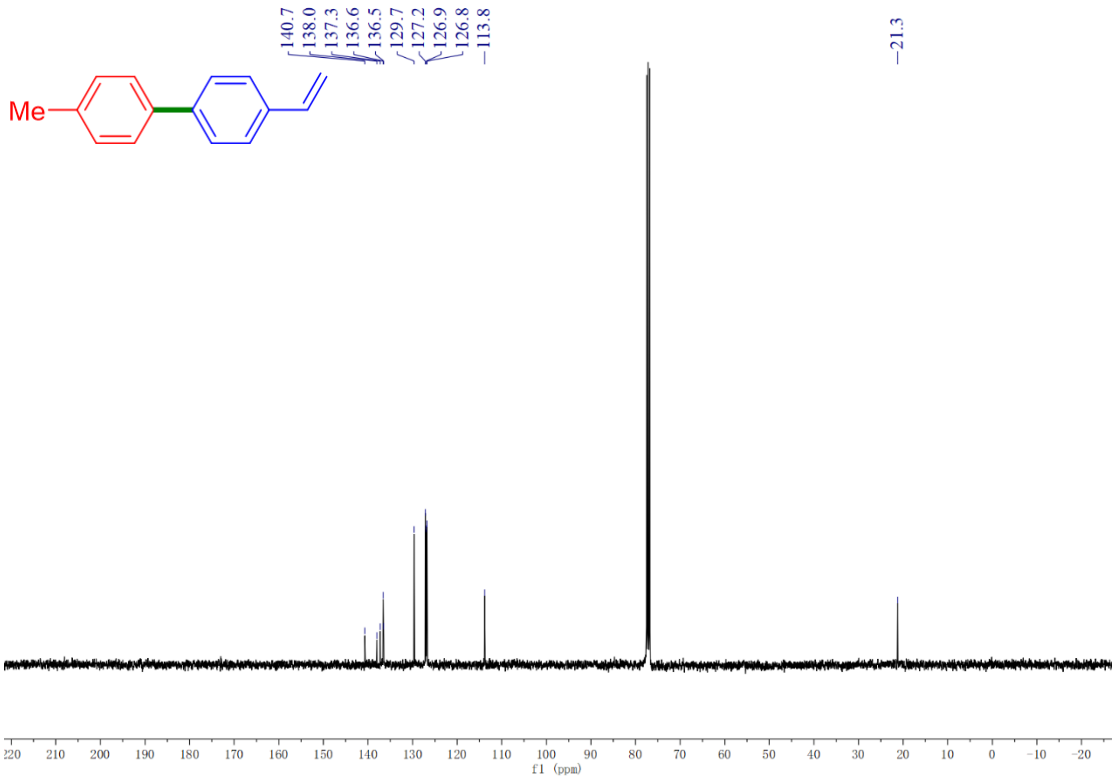


Figure S46. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5t**

1-(4'-Methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one (5u).

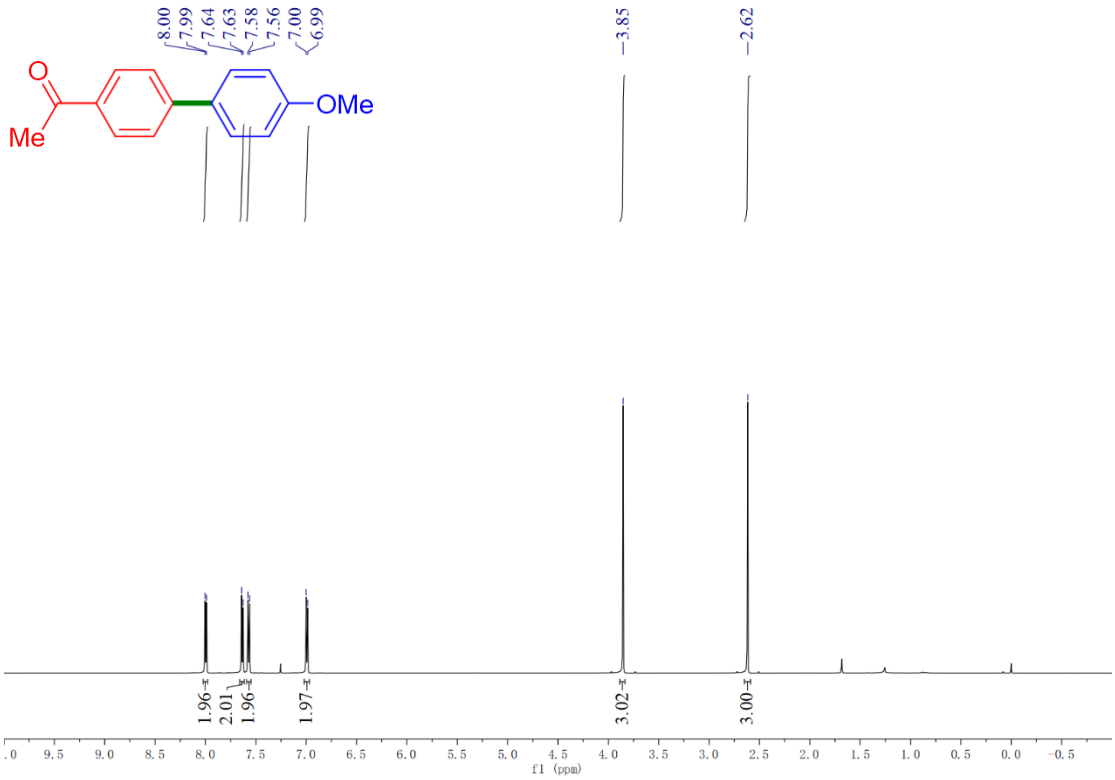


Figure S47. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5u**

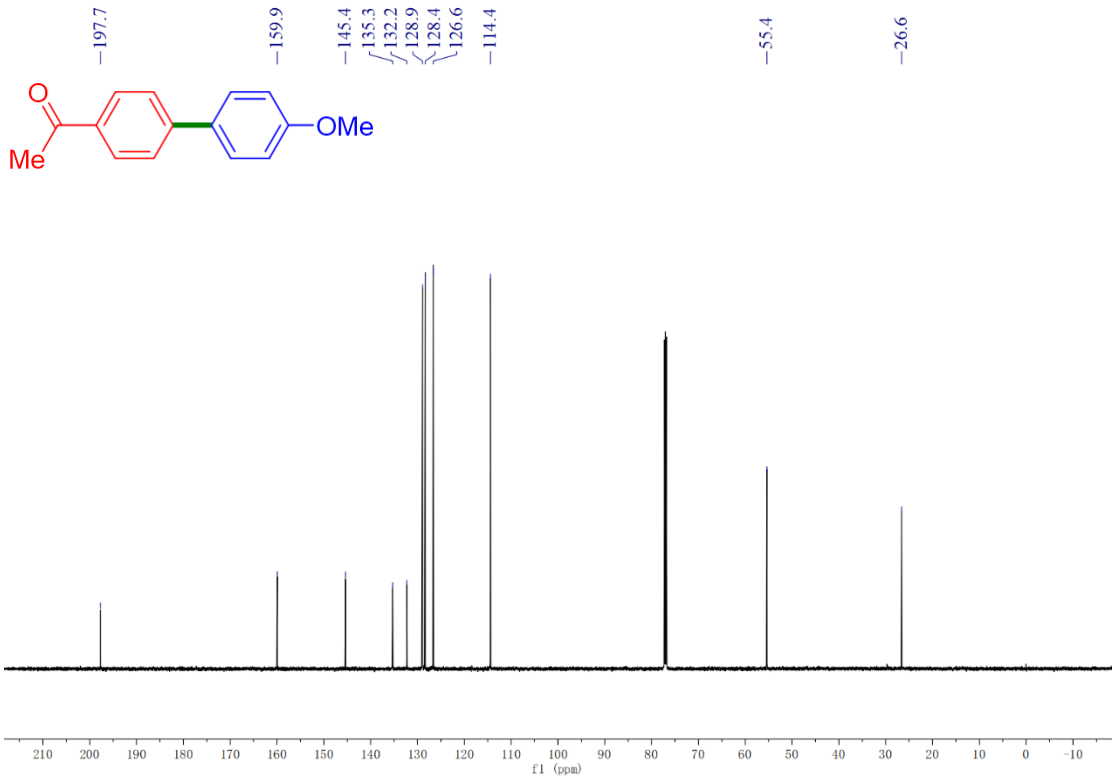


Figure S48. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5u**

1-(4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (5v).

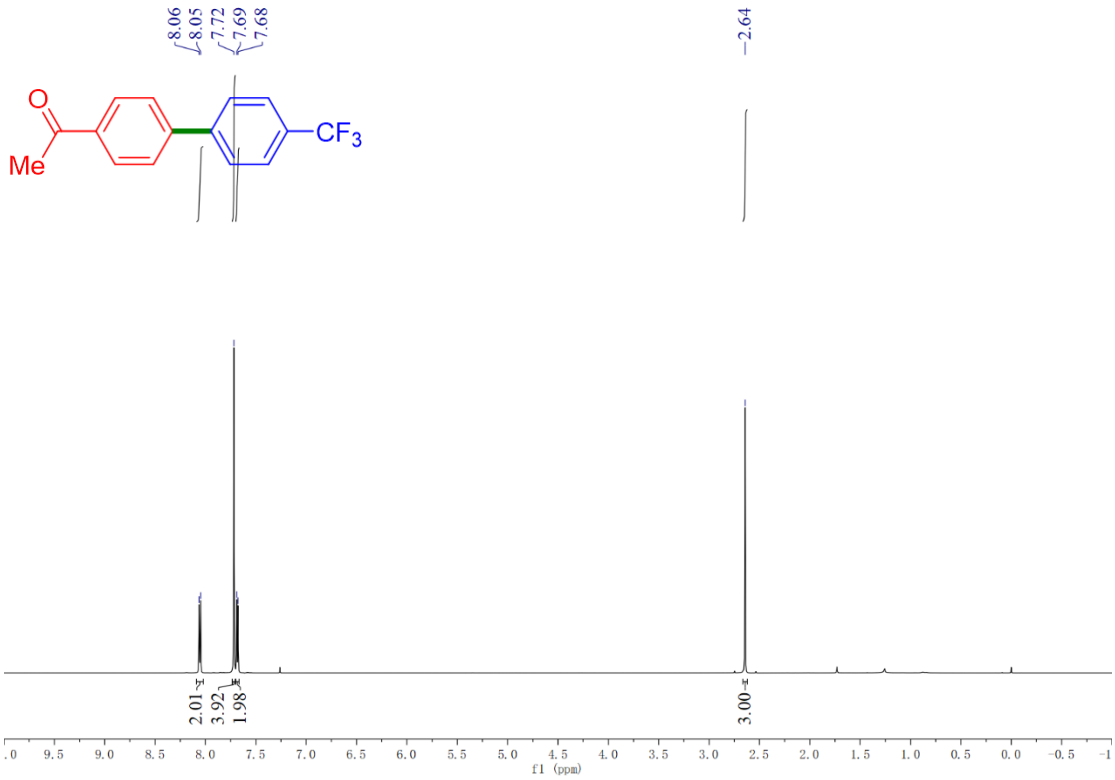


Figure S49. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5v**

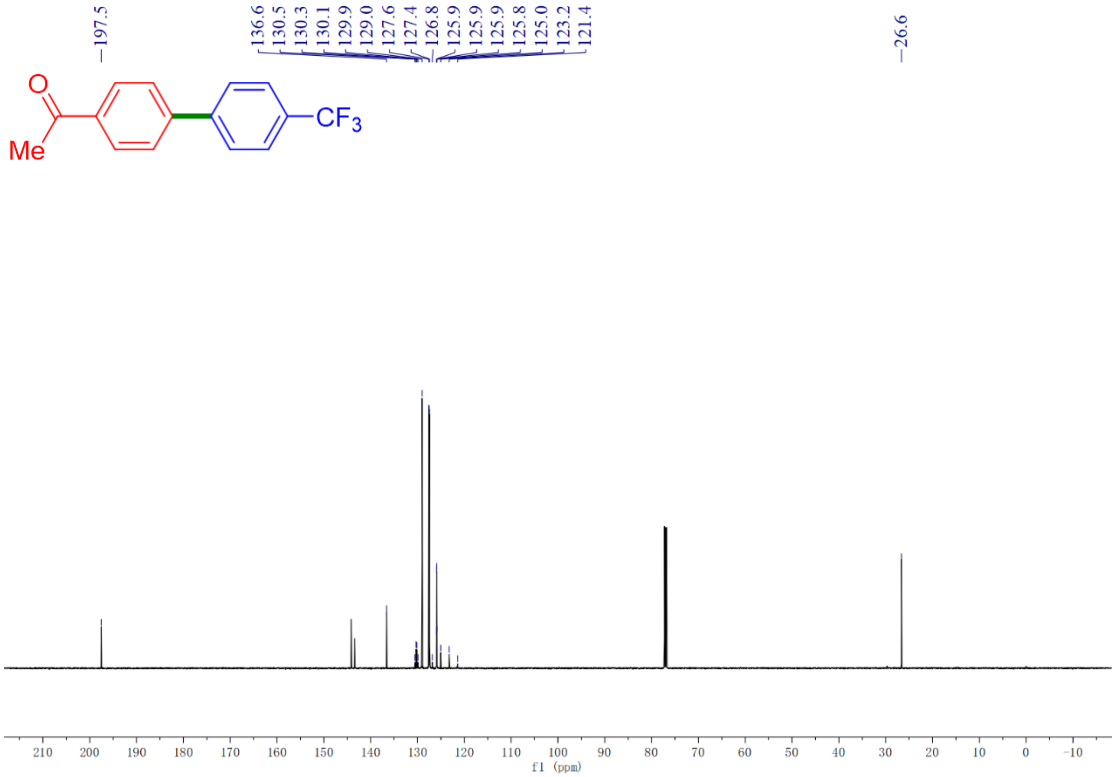


Figure S50. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5v**

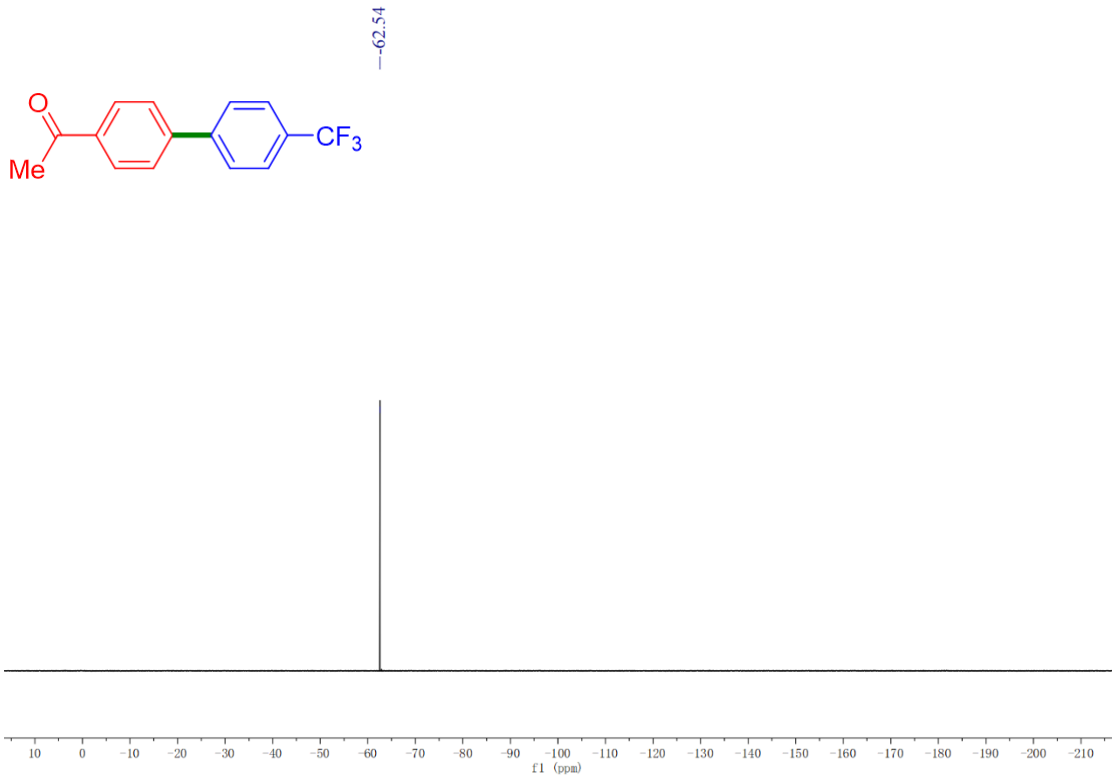


Figure S51. ^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **5v**

1-(4-(Furan-2-yl)phenyl)ethan-1-one (5w).

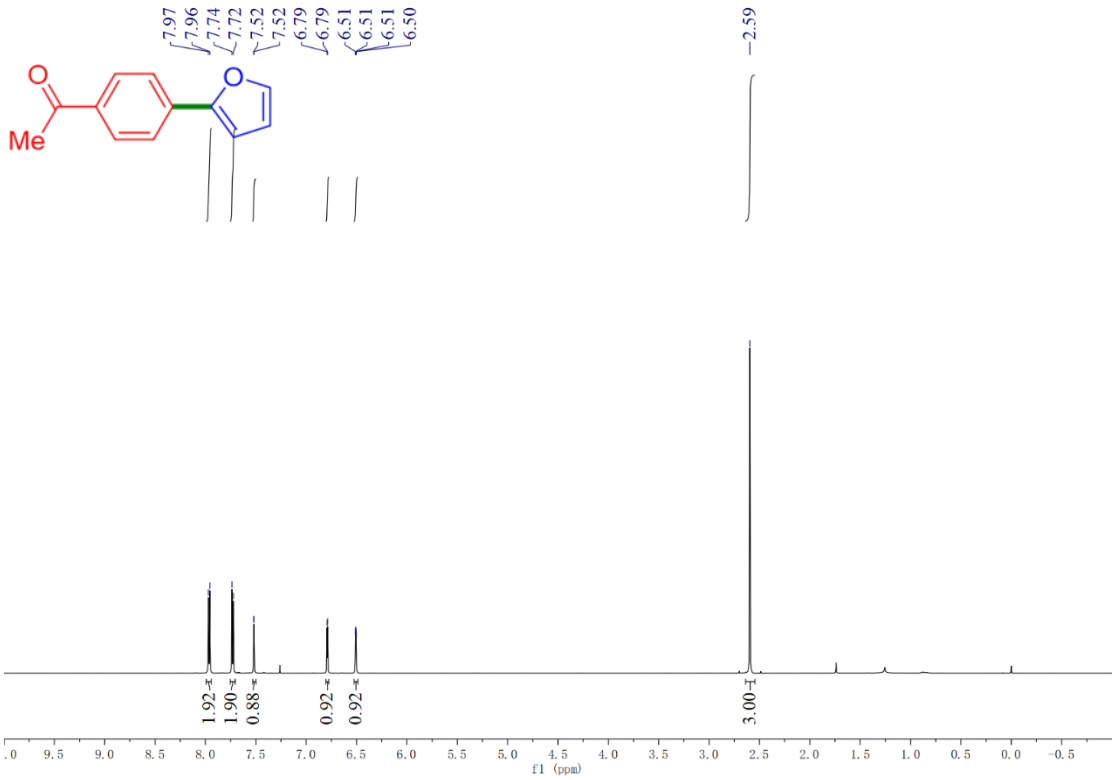


Figure S52. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5w**

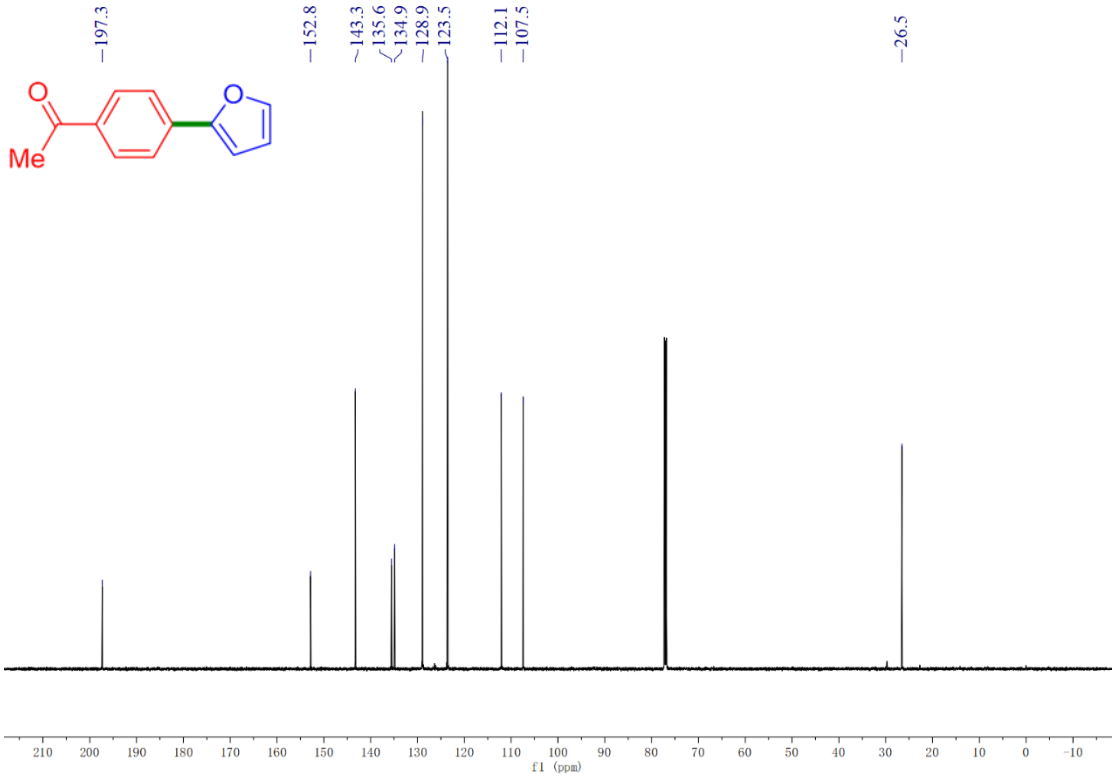


Figure S53. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5w**

1-(4-(Thiophen-2-yl)phenyl)ethan-1-one (5x).

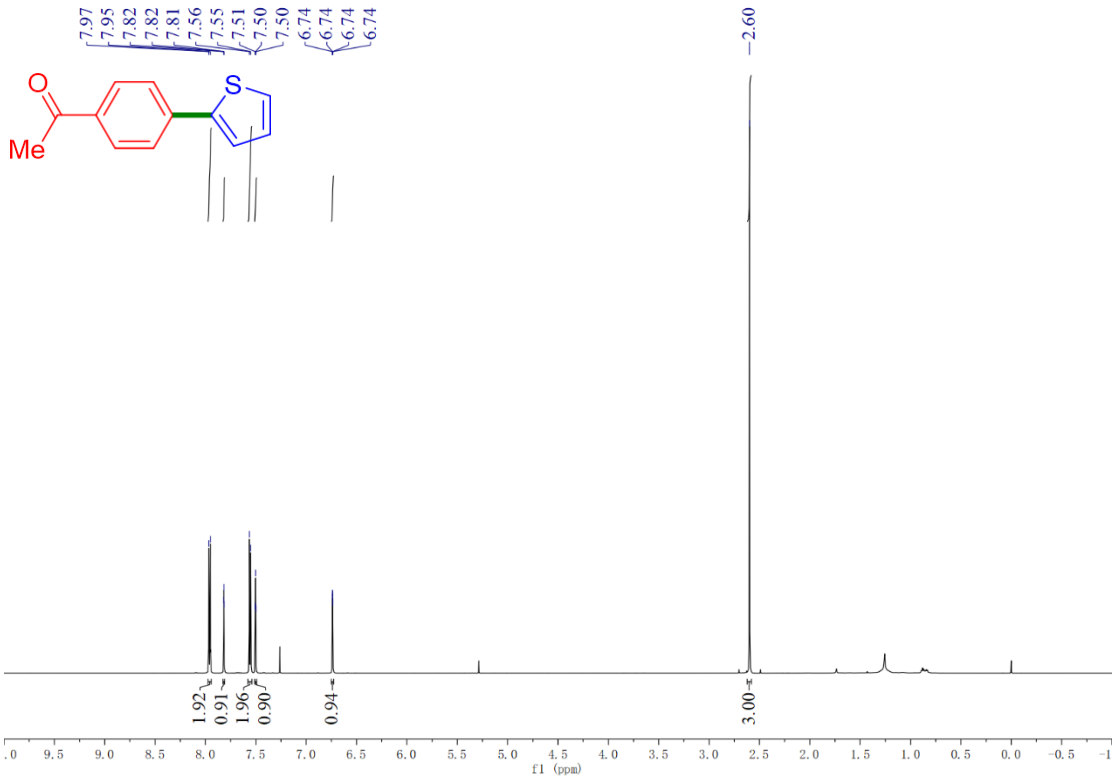


Figure S54. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5x**

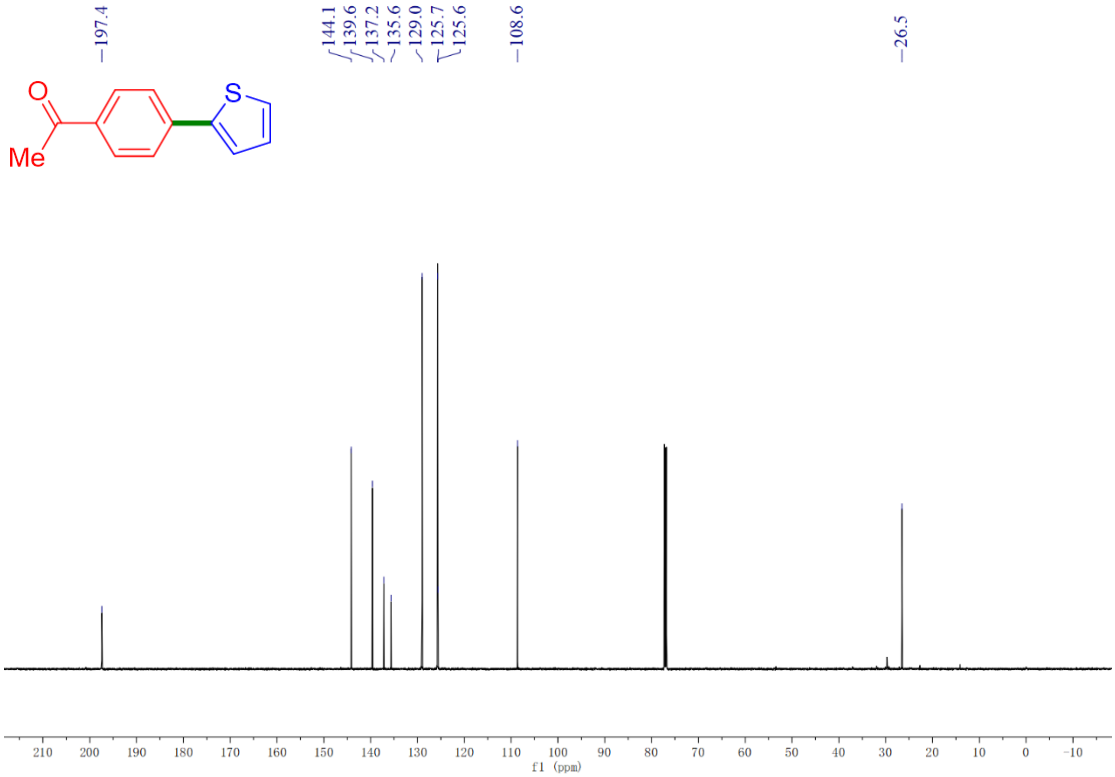


Figure S55. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5x**

1-(4-(Furan-3-yl)phenyl)ethan-1-one (5y).

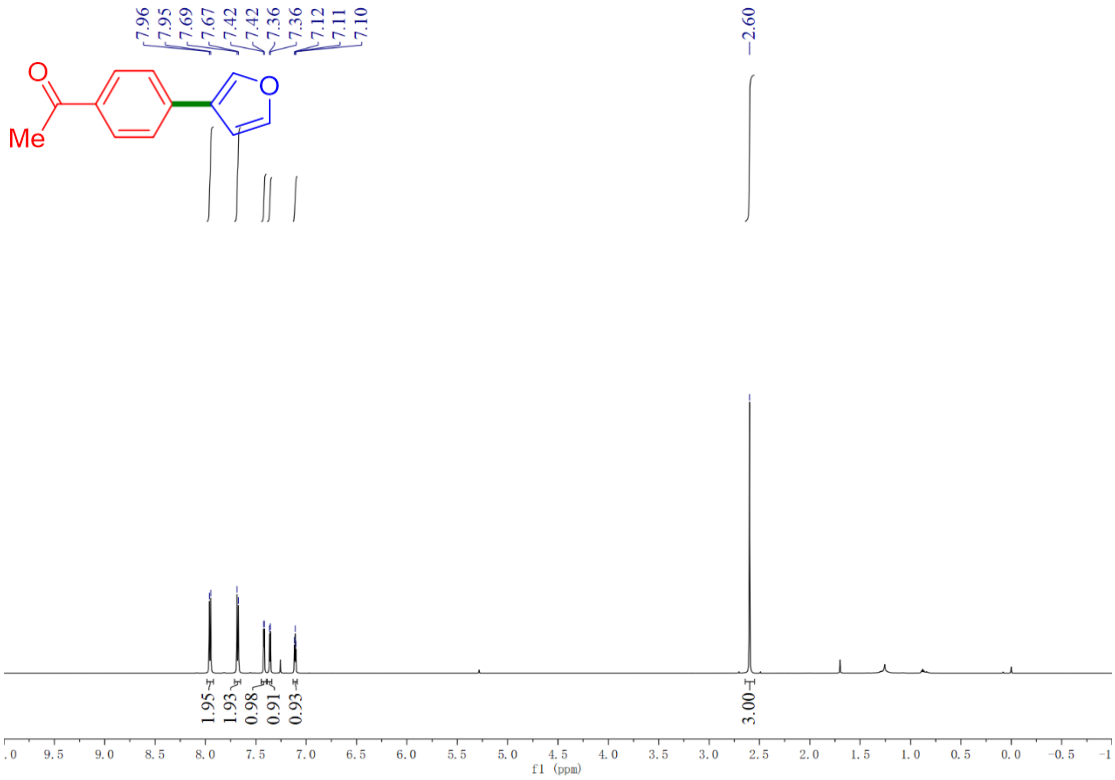


Figure S56. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5y**

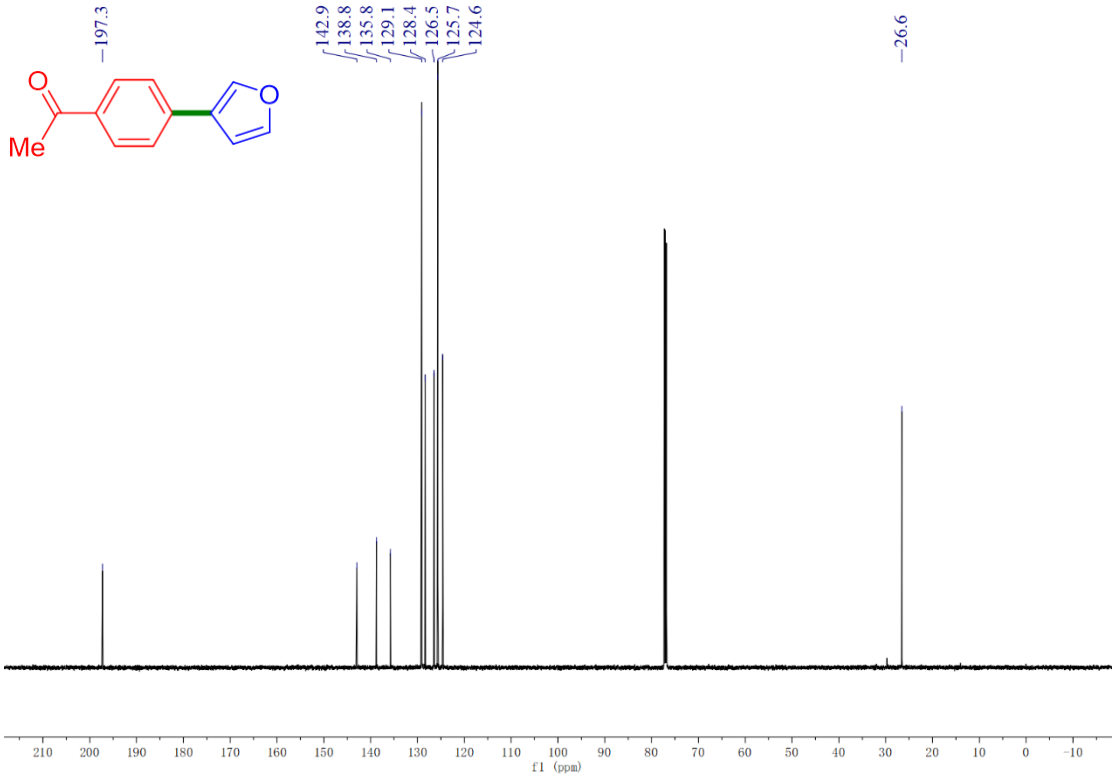


Figure S57. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5y**

1-(4-(Thiophen-3-yl)phenyl)ethan-1-one (5z).

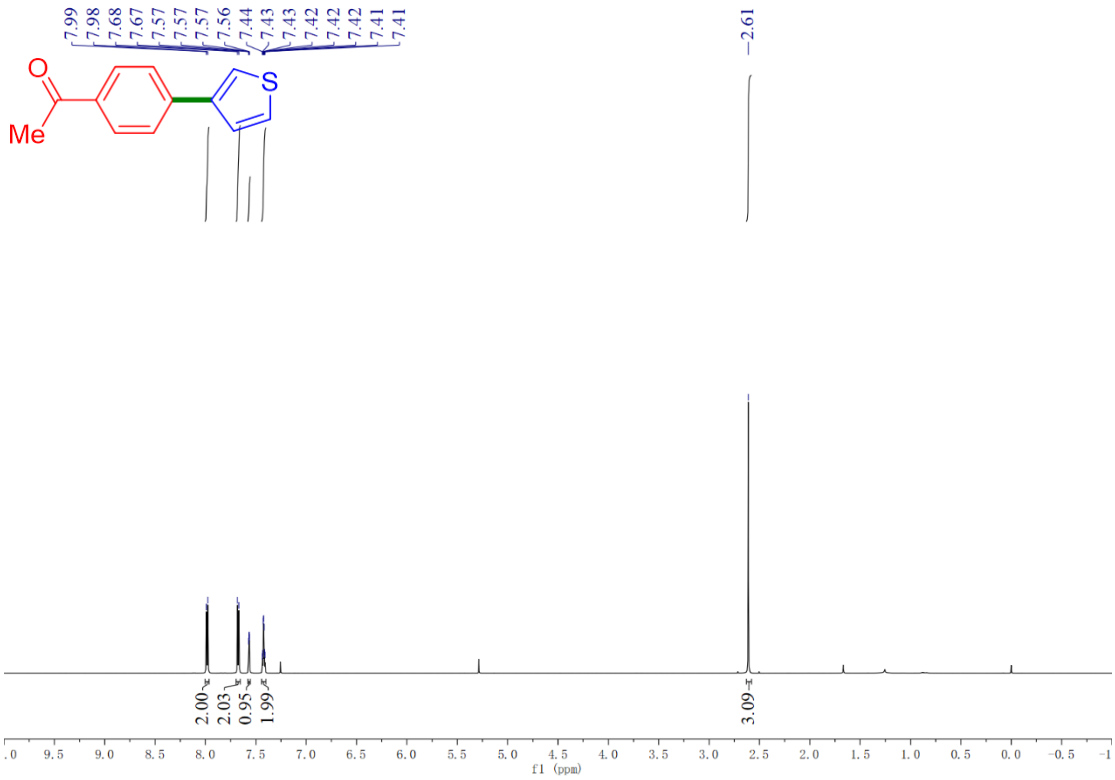


Figure S58. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5z**

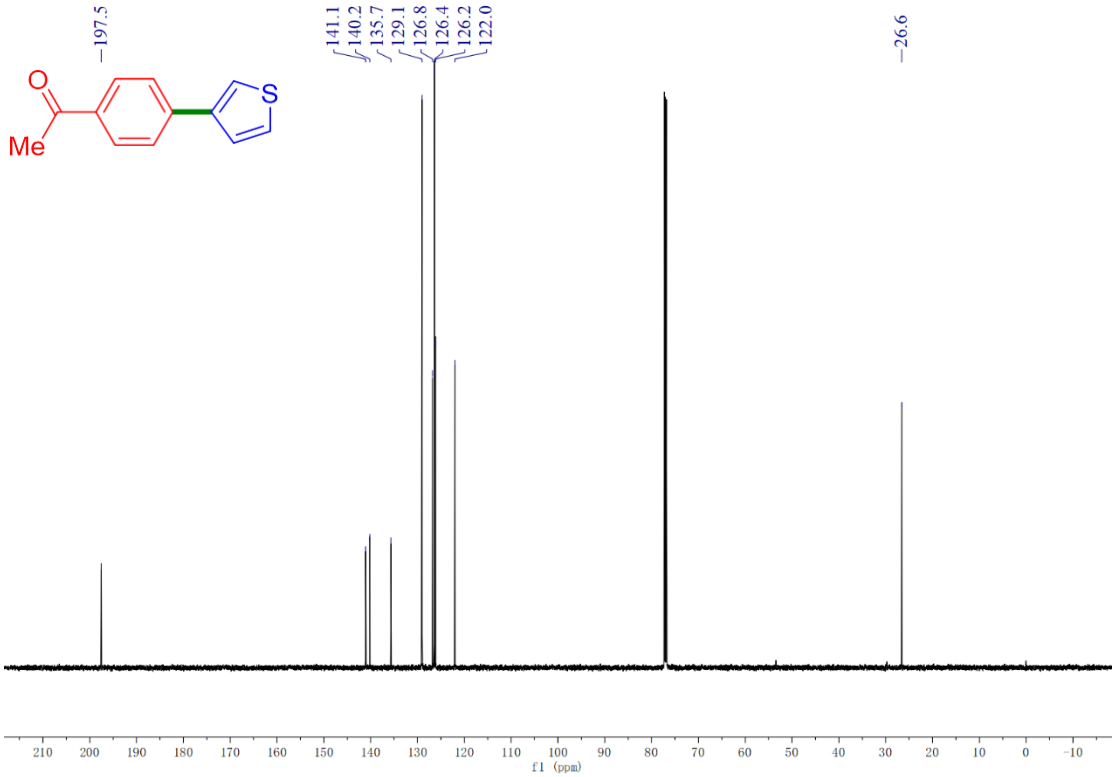


Figure S59. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5z**

4,4''-Dimethyl-1,1':4',1''-terphenyl (5aa).

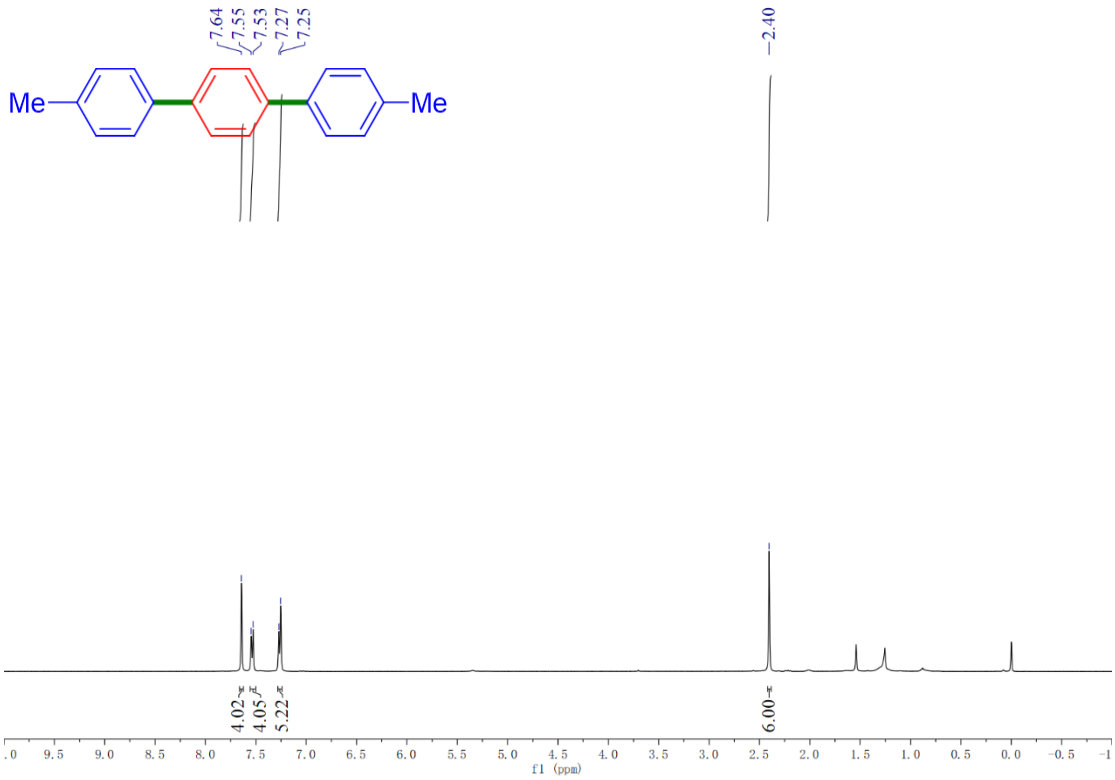


Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5aa**

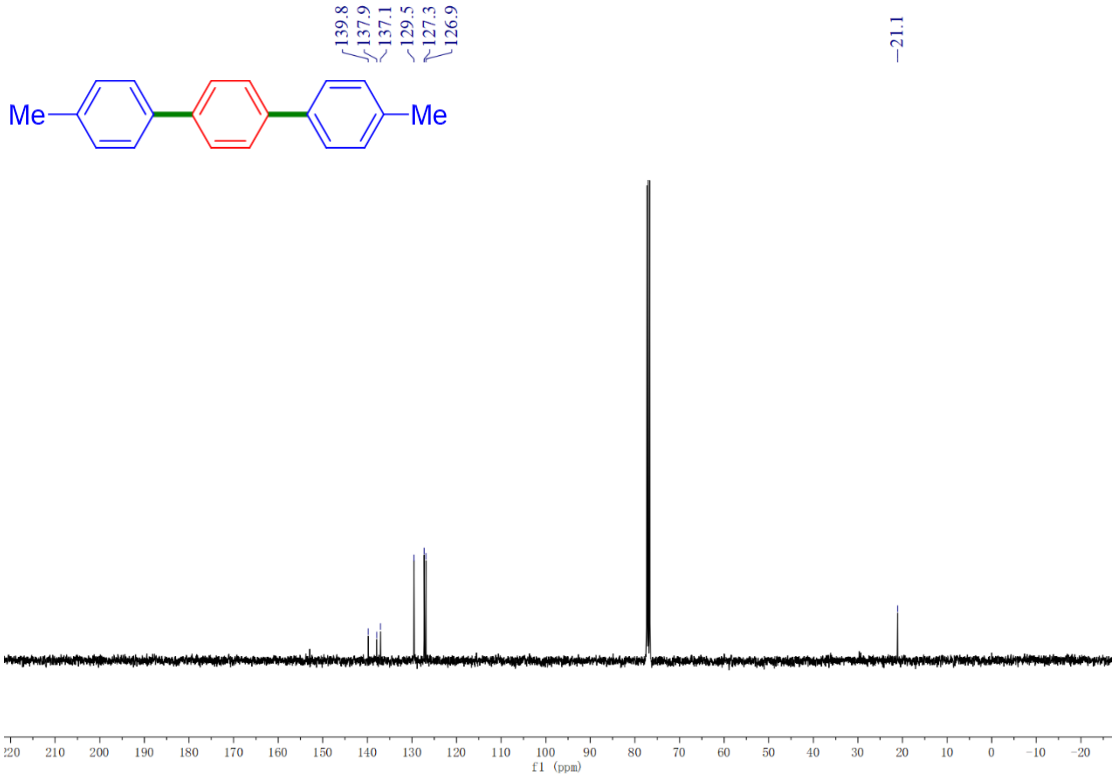


Figure S61. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5aa**

4,4''-Dimethyl-1,1':3',1''-terphenyl (5ab).

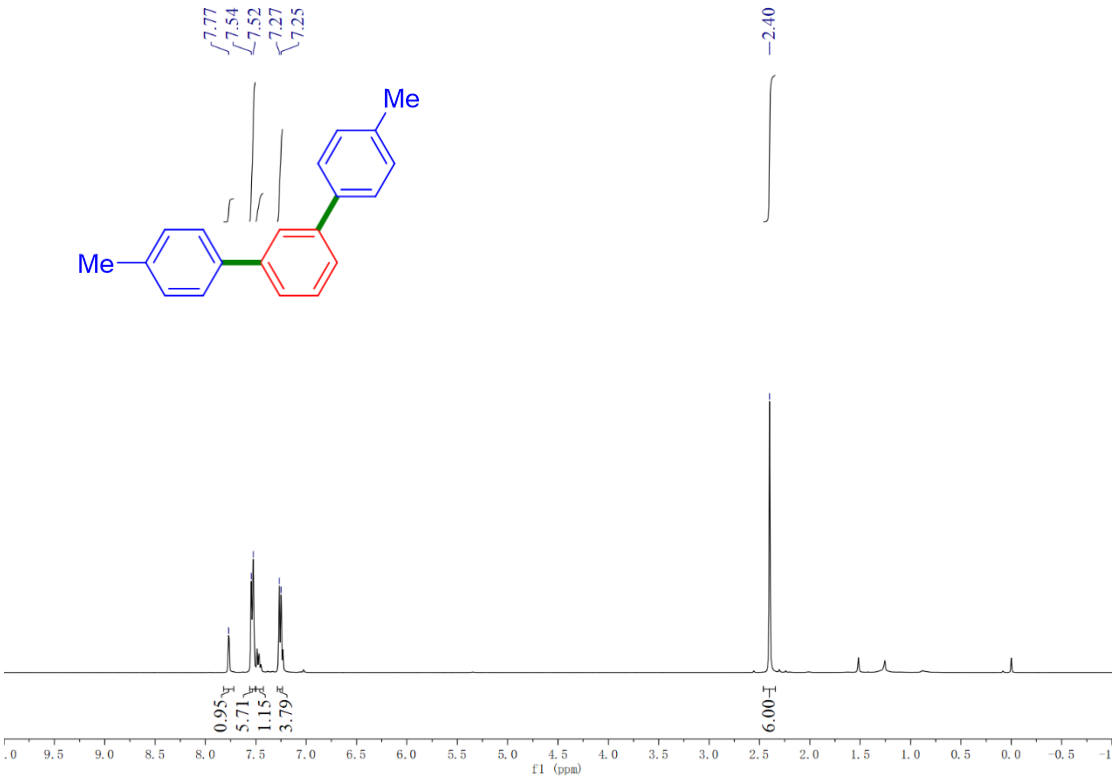


Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5ab**

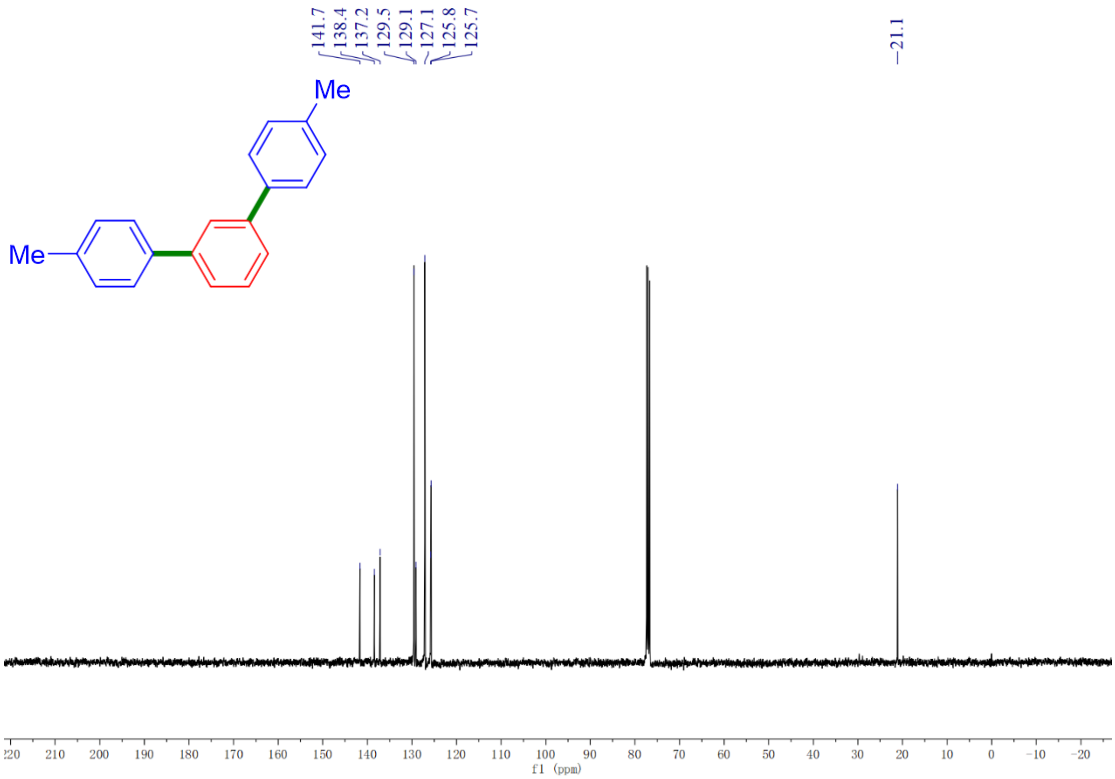


Figure S63. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5ab**

4,4''-Dimethyl-1,1':2',1''-terphenyl (5ac).

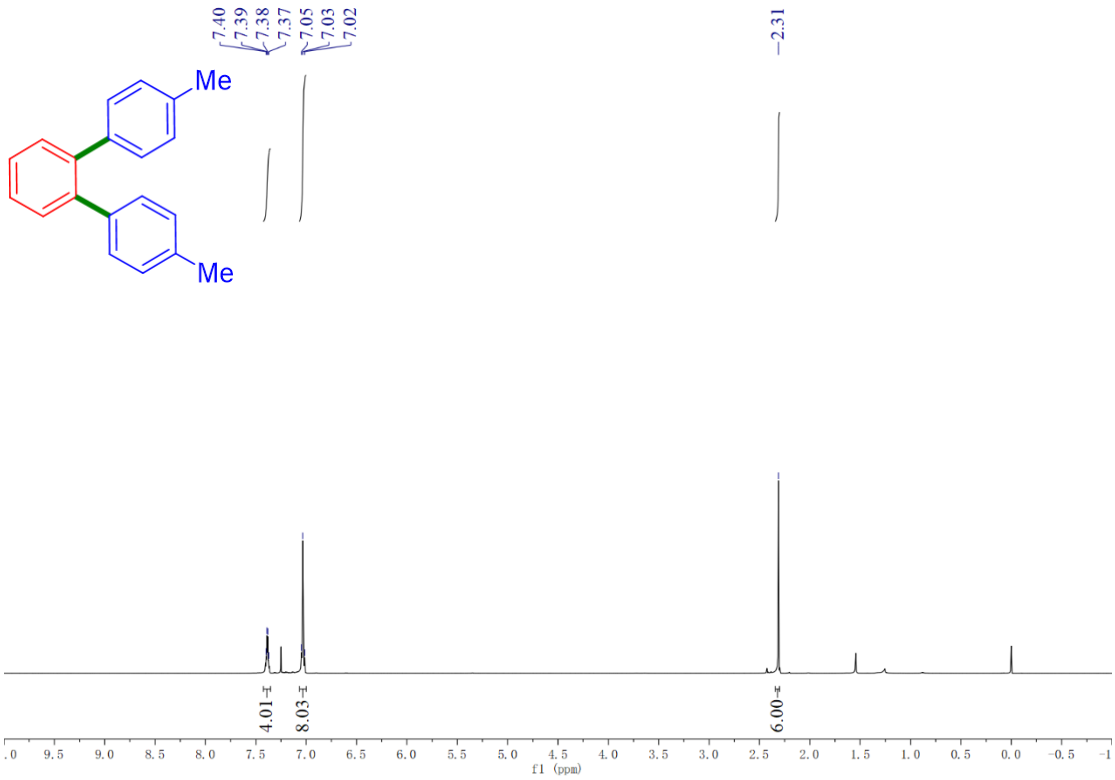


Figure S64. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5ac**

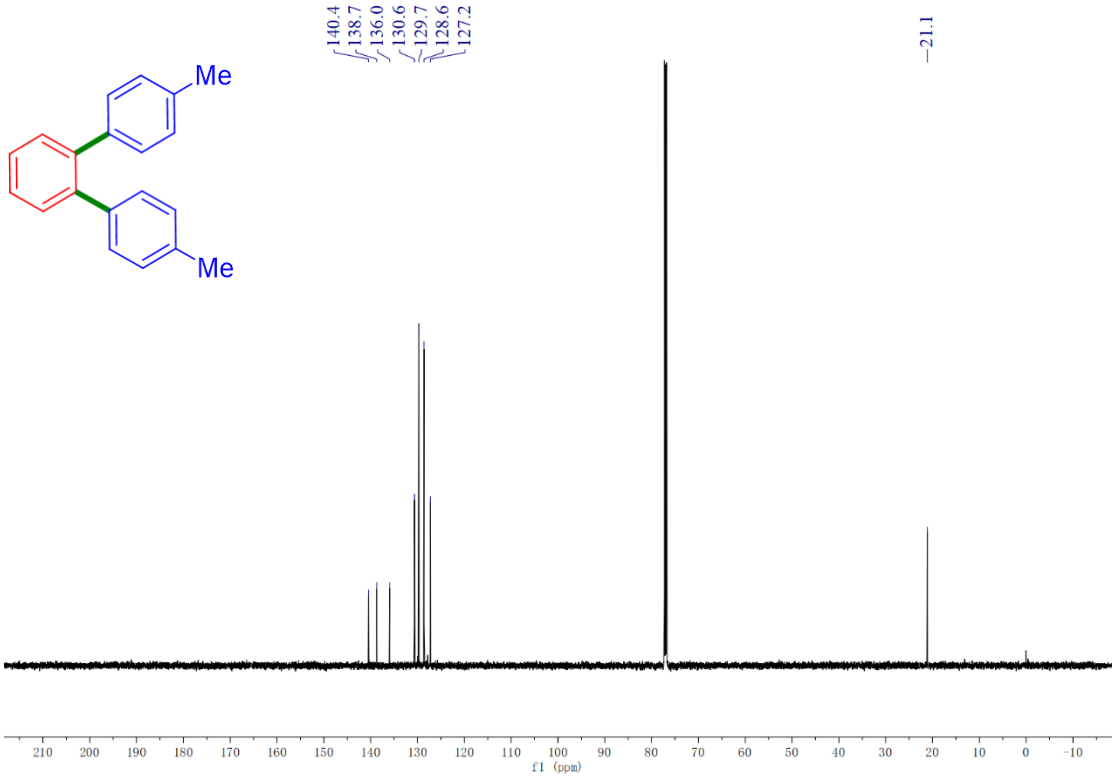


Figure S65. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5ac**

4,4''-Dimethyl-5'-(*p*-tolyl)-[1,1':3',1''-terphenyl]-2'-amine (5ad).

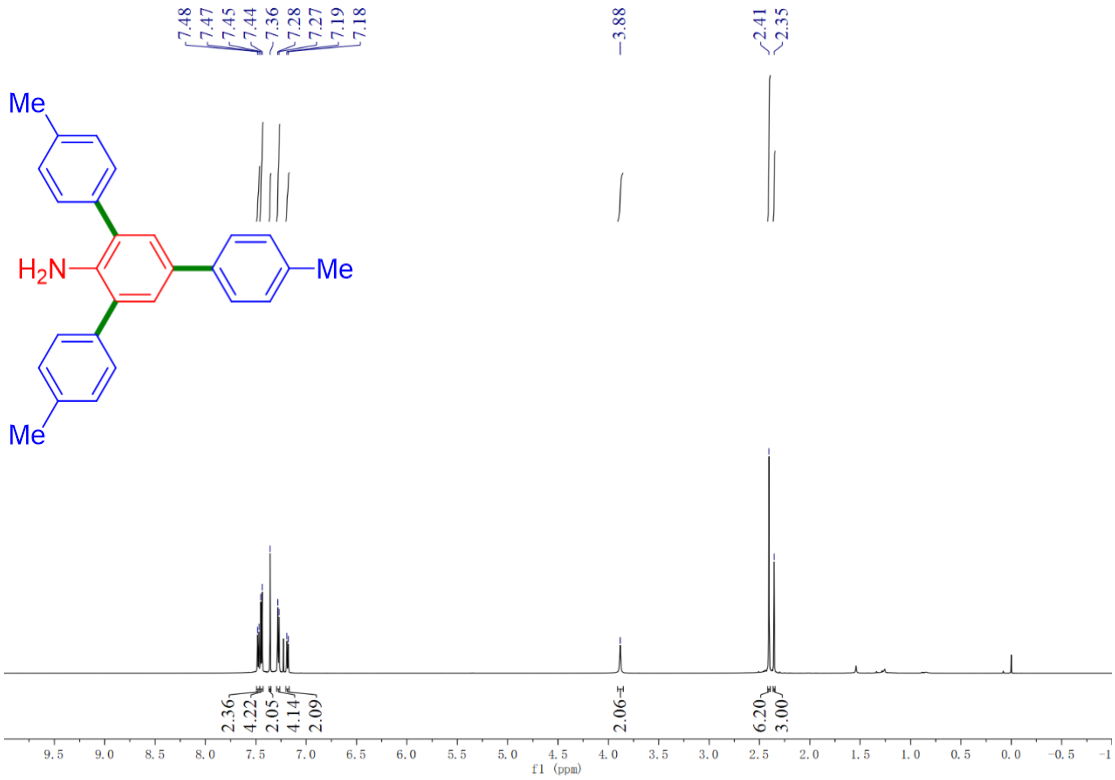


Figure S66. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of Compound **5ad**

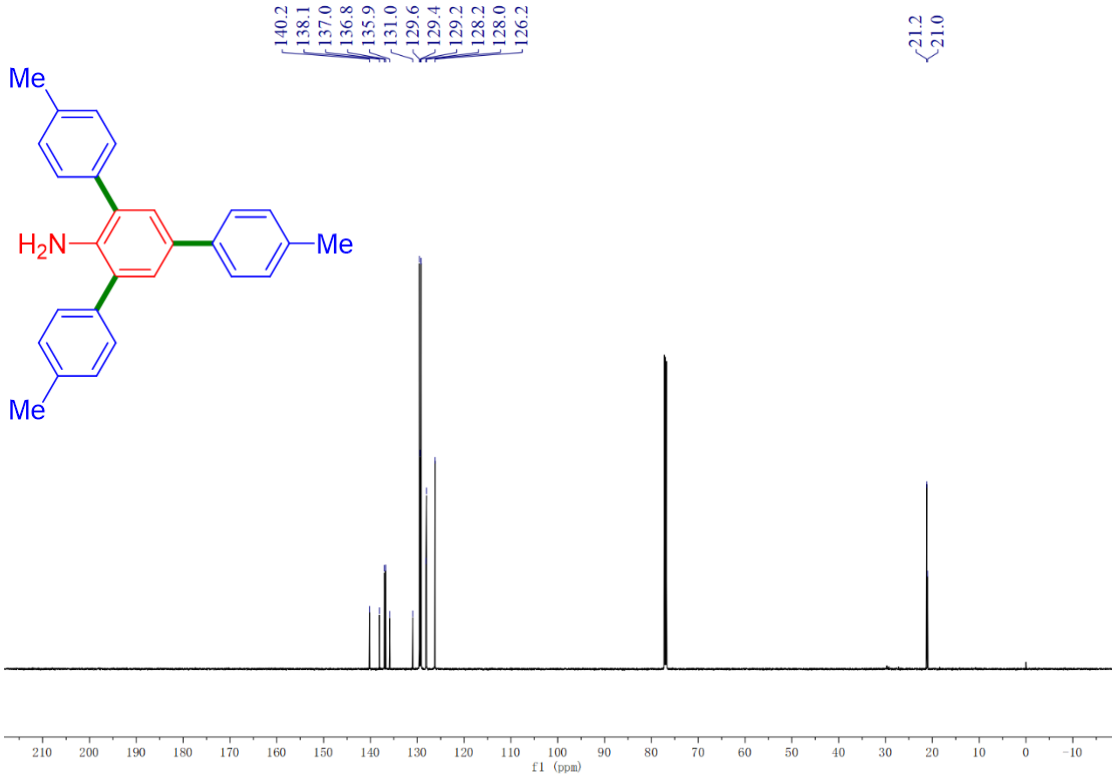


Figure S67. ^{13}C NMR (150 MHz, $CDCl_3$) Spectrum of Compound **5ad**

4,4''-Dimethyl-5'-(*p*-tolyl)-1,1':3',1''-terphenyl (5ae).

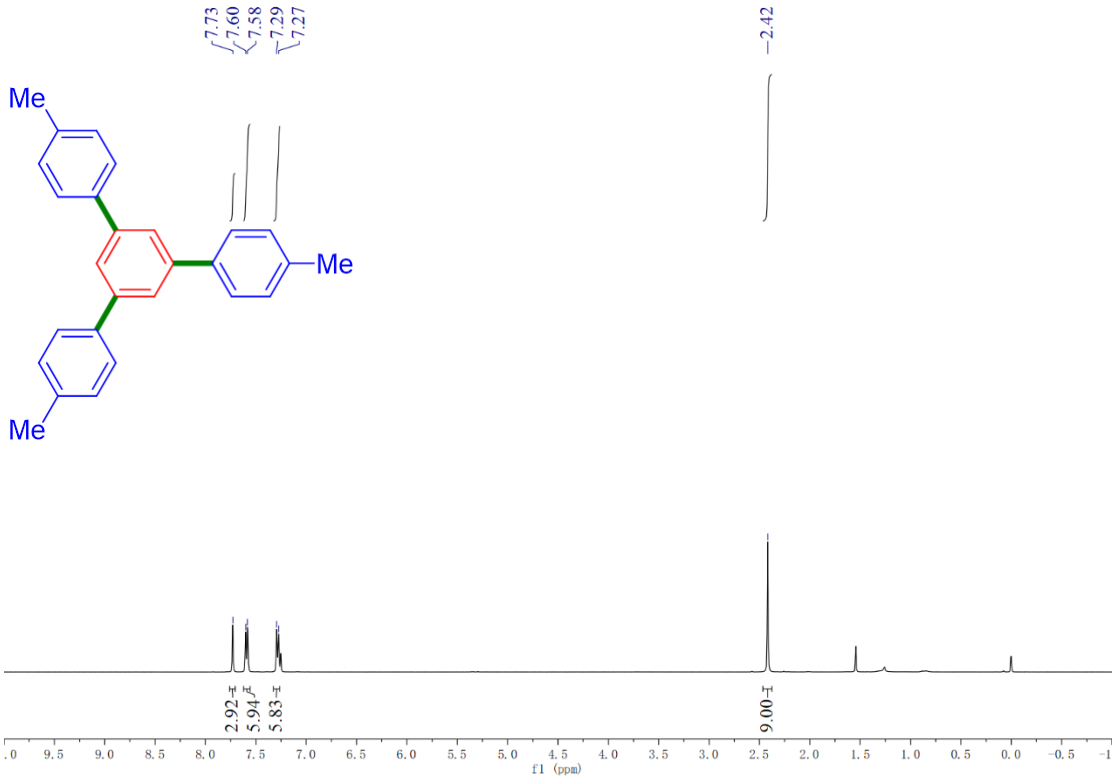


Figure S68. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5ae**

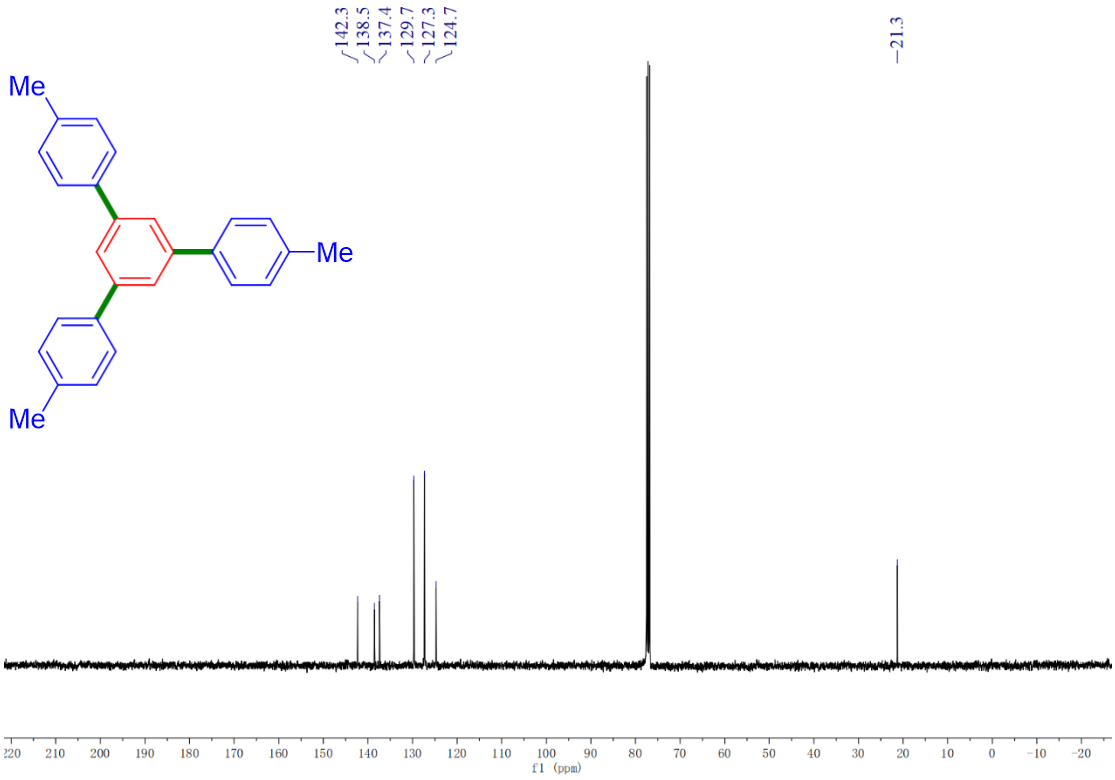


Figure S69. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5ae**

4,4''-Dimethyl-4',5'-di-*p*-tolyl-1,1':2',1''-terphenyl (5af).

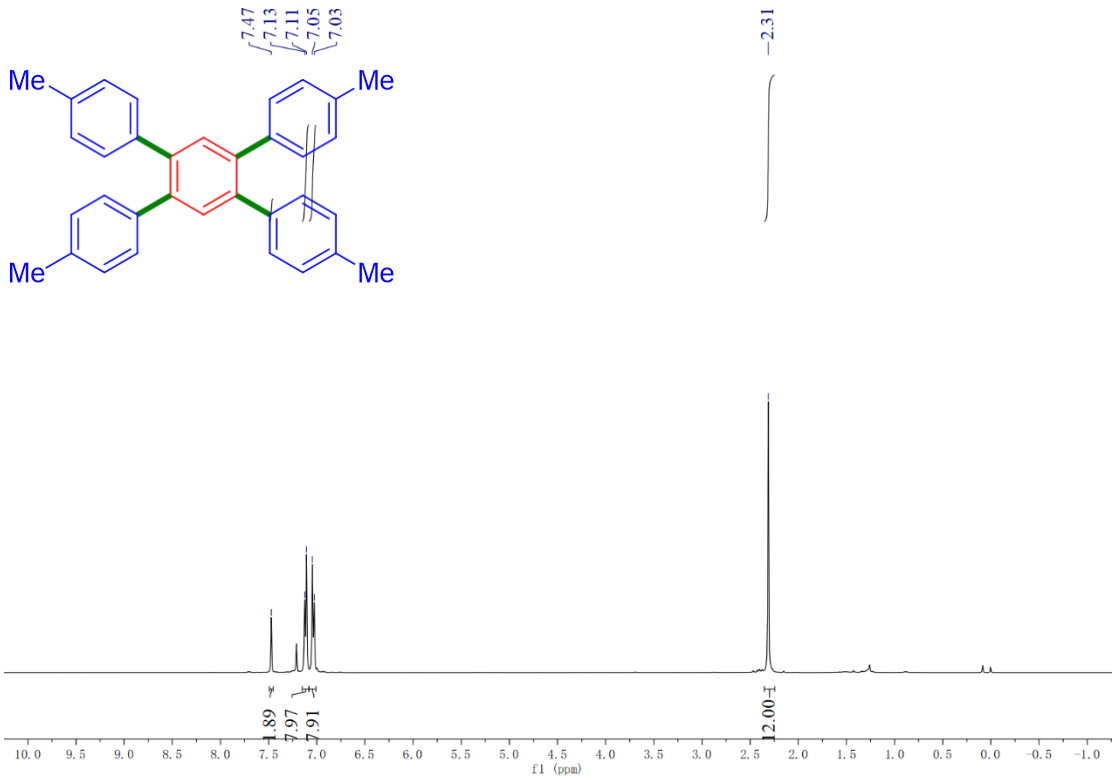


Figure S70. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5af**

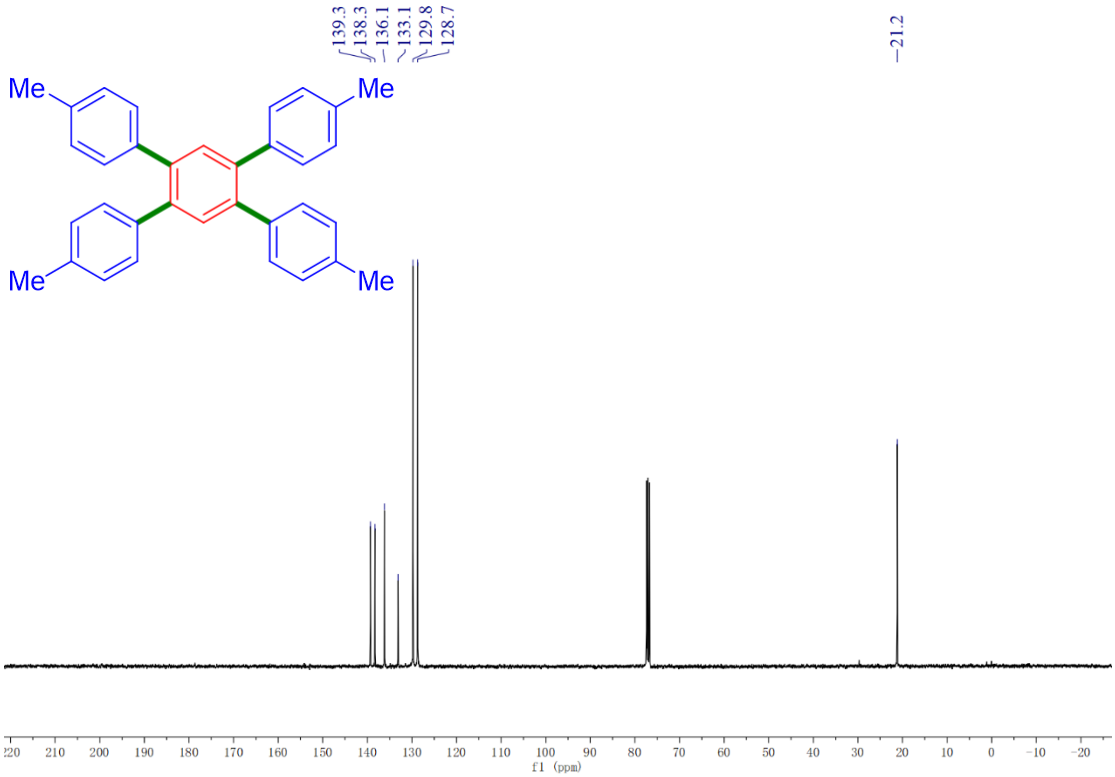


Figure S71. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5af**

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