SUPPORTING INFORMATION

TXPhos: a highly stable and efficient ligand designed for ppm level Pd-catalyzed Suzuki-Miyaura coupling in water

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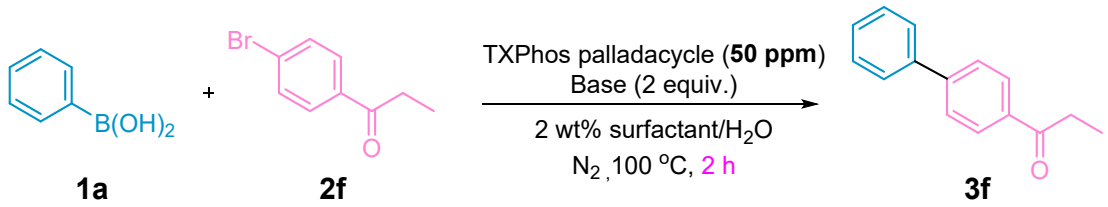
1. General information

All starting materials were purchased from commercial sources. TPGS-750-M was synthesized accroding to Lipshutz's work[1]. ^{1}H NMR and ^{13}C NMR were recorded on a 400 MHz Bruker spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). The high resolution mass spectra (HRMS) data were measured on a UHPLC Q-TOF HR-MS by means of the ESI technique. The low resolution mass spectra (LRMS) data were measured on the SHIMADZU GCMS-QP 2010 SE mass spectrometer (Kyoto, Japan) by means of EI technique. The melting points of these compounds were determined by an X-4A micro-melting point apparatus (Shanghai, China).

Table S1. Surfactant screening.[a]

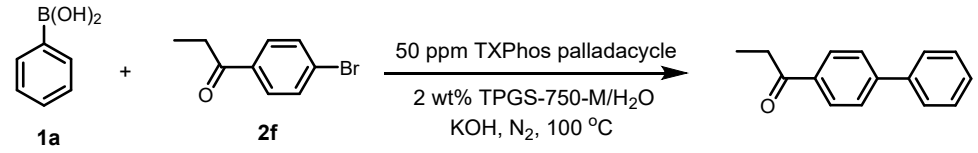


1a 2f 3f

Entry	Variations from the standard condition	Yield/[%][b]
1	Tween-80	26
2	TritonX-100	84
3	mPEG-750	trace
4	DDAB	61
5	Tween-60	59

[a] **1a** (0.36 mmol), **2f** (0.3 mmol), TXPhos palladacycle (50 ppm), KOH (2.0 equiv.), N_2, 2 wt% surfactant/H_2O (2 mL), 100 °C, 2 h. [b] Isolated yields.

Table S2. Control experiments to study the effects of surfactant fragments.[a]



entry	Variations from the standard condition	yield/%[b]
1	-	99
2	tocopherol (10 mol%) + mPEG-750 (10 mol%)	75
3	tocopherol (10 mol%) + mPEG-750 (10 mol%) + potassiuns succinate (10 mol%)	55
4	tocopherol (10 mol%)	19

[a] **1a** (0.36 mmol), **2f** (0.3 mmol), TXPhos palladacycle (50 ppm), KOH (2.0 equiv.), 2 wt% TPGS-750-M/H_2O (2 mL), N_2, 100 °C, 30 min. [b] Isolated yields.

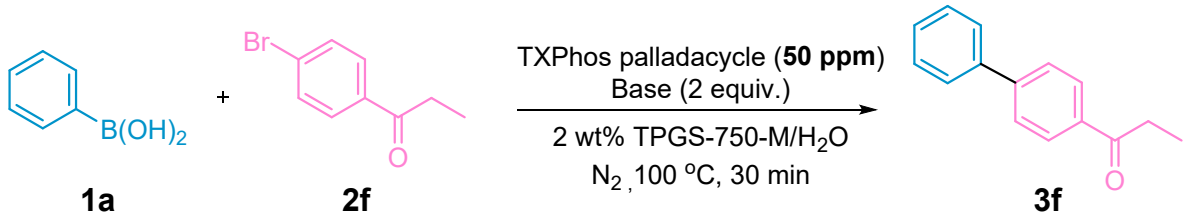
2. Preparation of a stock solution

The catalyst solution was prepared by dissolving the TXPhos paladacycle 5.3 mg (5×10^{-3} mmol) in 10 mL dry THF. This stock solution was used to carry out the reactions (stock solution can either be used fresh or can be stored up to at least a month under air in a fridge). For 50 ppm catalyst loading, 30 μL of this stock solution was used.

3. General procedure for Suzuki-Miyaura couplings

From the stock solution above, the desired amount (30 μL for 50 ppm Pd) of catalyst solution was added to an oven-dried 25 mL schlenk tube containing a Teflon coated magnet and covered with a rubber septum. The THF from this solution was evacuated under low pressure (~20 min). Aryl halides **2** (0.3 mmol; if solid or added after an evacuation/backfill sequence if liquid), 0.36 mmol boronic acid **1** and 0.6 mmol KOH were added to this vial. Then Aqueous 2 wt % TPGS-750-M solution (2 mL) were added . The vial was evacuated and backfilled with N_2 (this procedure was repeated three times). Then the reaction was placed into an oil bath and stirred (1000-1500 rpm) at 100 °C for 30 min. The schlenk tube was removed from oil bath and allowed to cool to room temperature. The products were then separated by either filtration, decantation of the aqueous layer, or use of ethyl acetate (400 μL) added to the schlenk tube and stirred briefly. Stirring was halted and after separation, the organic layer was removed via pipette. An additional extraction was performed with ethyl acetate (200 μL). The organic layers were combined, and dried with Na_2SO_4. Organic solvents were removed under vacuum, and the crude residue was purified by silica gel column chromatography to give the product **3a-4j**.

4.Catalyst solution life test

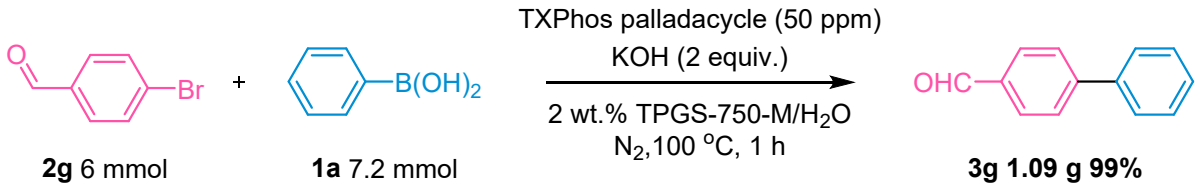


1a **2f** **3f**

entry	Storage time of catalyst stock solution	Yield/[%][a]
1	3 day (r.t.)	>99
2	7 day (r.t.)	>99
3	1 month (in fridge)	>99

[a] Reaction conditions: **1a** (0.36 mmol), **2g** (0.3 mmol), TXPhos palladacycle (50 ppm), KOH (2.0 equiv.), N_2, 2 wt% TPGS-750-M/H_2O (2 mL), 100 °C, 30 min.

5. Gram-Scale synthesis of 3h



2g 6 mmol **1a** 7.2 mmol **3g 1.09 g 99%**

To an oven-dried 100 mL schlenk tube with a magnetic stir bar was added 600 μL stock solution (50 ppm TXPhos palladacycle for 6.0 mmol scale reaction), the THF from this solution was evacuated under low pressure (~20 min). Then 1.1 g 4-bromobenzaldehyde **2g** (6.0 mmol, 1.0 equiv.), 0.88 g phenylboronic acid **1a** (7.2 mmol, 1.2 equiv.), and 672 mg KOH (2.0 equiv.) were added in a vial. Then add 40 ml of TPGS-750-M/H_2O . The tube was sealed with rubber septum, evacuated, and

backfilled with nitrogen three times. Then the reaction was placed into an oil bath and stirred (1000-1500 rpm) at 100 °C for 30 min. The schlenk tube was removed from oil bath and allowed to cool to room temperature. Ethyl acetate (1 mL) was added to the schlenk tube and stirred briefly. Stirring was halted and after separation, the organic layer was removed via pipette. An additional extraction was performed with ethyl acetate (0.5 mL). The organic layes were combined, and dried with Na_2SO_4. Volatiles were removed under vacuum, and the crude residue was purified by silica gel column chromatography to give the product **3g** (1.09 g)**.**

6. DLS results:

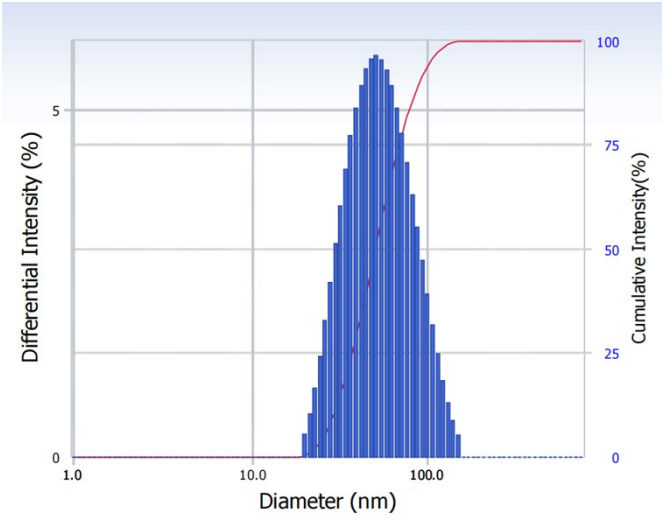


Figure S1. Intensity Distribution. Conditions: 2 wt% TPGS-750-M/H_2O(2 mL) and KOH(0.6 mmol).

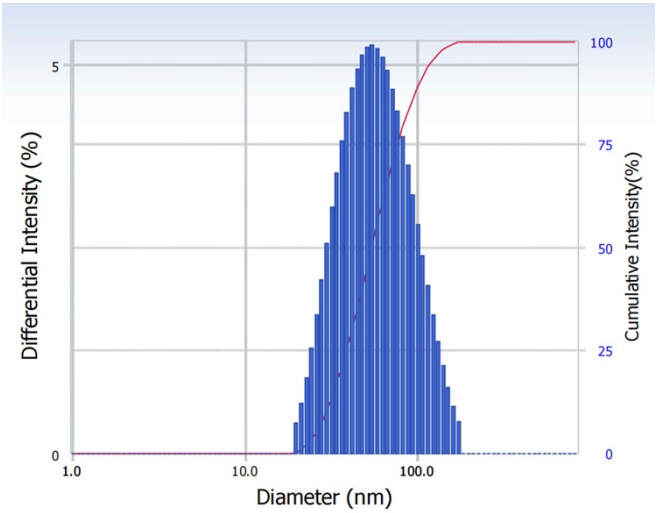


Figure S2. Intensity Distribution. Conditions: TXPhos paladacycle stock solution(30 μL), 2 wt% TPGS-750-M/H_2O(2 mL) and KOH(0.6 mmol).

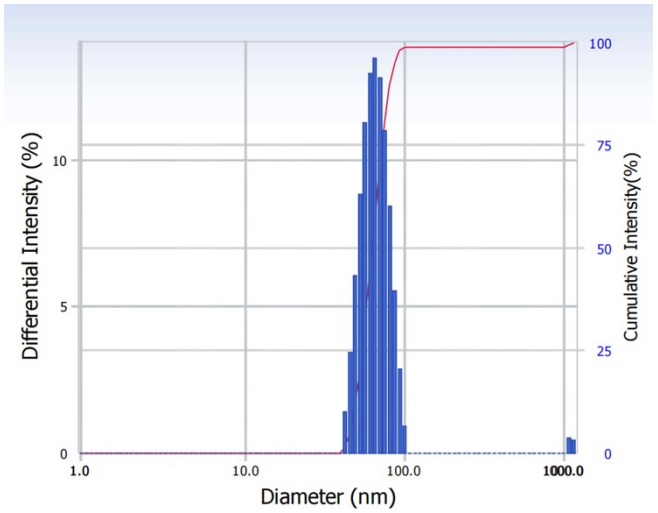


Figure S3. Intensity Distribution. Conditions: **1a**(0.36 mmol), **2f**(0.3 mmol), TXPhos paladacycle stock solution(30 μL), 2 wt% TPGS-750-M/H_2O(2 mL) and KOH(0.6 mmol).

7. The NMR of crude product

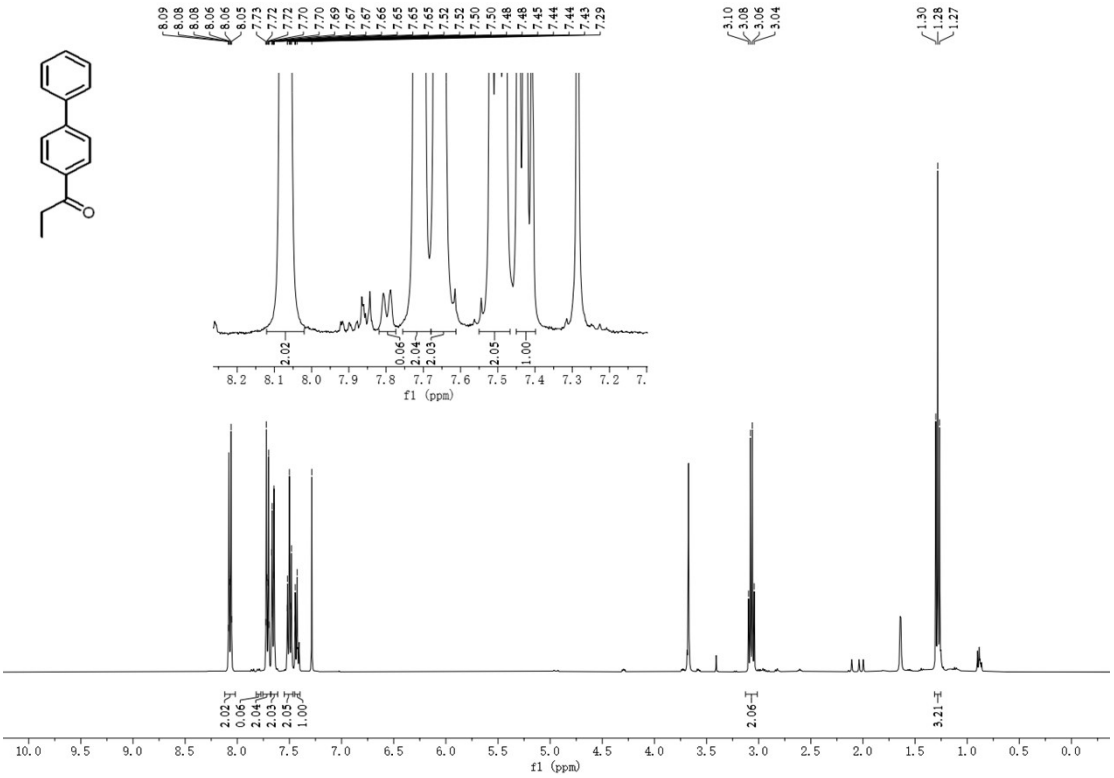


Figure S4. ^{1}H NMR for the crude product

8. E Factor calulations[2]:

Note: Using the density of each liquid at 25 °C, water = 1.00 g/mL, ethyl acetate = 0.897 g/mL. Additionally, the using solvents of silica gel column chromatography is NOT included as we are only considering solvents from the experimental procedure.

This work (Water NOT included as waste):

Solvents:

1.5 mL Ethyl acetate (1.35 g)

$$\frac{\text{1.35 g waste}}{\text{1.09 g Product}} = \text{1.24 E Factor}$$

9. Recycling study:

The initial reaction was set up according to the general procedure. Typically, 150 uL TXPhos palladacycle solution (Pd content: 7.50×10^{-5} mmol) was added in to disperse the substrates, drain the organic solvent. Then 4'-bromopropiophenone (319.5 mg, 1.5 mmol), phenylboronic acid (219.6 mg, 1.8 mmol) and KOH (162 mg, 3.0 mmol) were added in a vial of 25 mL. Add 10 ml of TPGS-750-M/H_2O. The reaction vial was put into a reaction block which had already been heated at 100 °C, then the reaction mixture was simultaneously stirred vigorously by a magnetic stirrer under ambient atmosphere. After 30 minutes, the aqueous catalytic solution was filtrated on a sand core funnel with teflon filter paper. The crude product was isolated on the filter paper which may be purified by washing with water several times. The filtrate of the aqueous catalytic solution containing Pd species, base and TPGS-750-M/H_2O was collected to be reused. A fresh batch of substrates and base was added to the recovered aqueous phase for the next run. The isolated product yields are as following: 1st run (94%), 2nd run (90%), 3rd run (85%). In the forth run, a fresh batch of precatalyst (50 ppm) was added along with starting materials, resulting in 93% yield.

10. Stability of the surfactant:

TPGS-750-M (102 mg, 0.08 mmol) was dissolved in 5 mL of water. Subsequently, 1.5 mmol of KOH was added, and the mixture was subjected to evacuation and N_2 backfilling, with this process repeated three times to ensure an inert atmosphere. The reaction mixture was stirred at 100 °C for 30 minutes and then cooled to room temperature. The aqueous phase was extracted with dichloromethane (DCM) using 3 × 10 mL portions. The combined organic layers were dried over anhydrous sodium sulfate (Na_2SO_4) and concentrated in vacuo to afford the crude residue. For internal

standardization, 0.1 mmol of benzoic acid (12.2 mg) was added. The nuclear magnetic resonance (NMR) spectrum of TPGS-750-M was acquired, and characteristic peaks originating from succinate ester fragments were identified at 2.85 (t) and 2.71 (t). Integration of these peaks allowed the quantification of TPGS-750-M, resulting in a determination of 0.005 mmol, corresponding to 6.25% of the initial amount (Figure S5). The observed decomposition suggests the influence of the model reaction conditions on TPGS-750-M stability. In conclusion, the NMR analysis reveals decomposition of TPGS-750-M during the model reaction, indicating its sensitivity to alkaline environments.

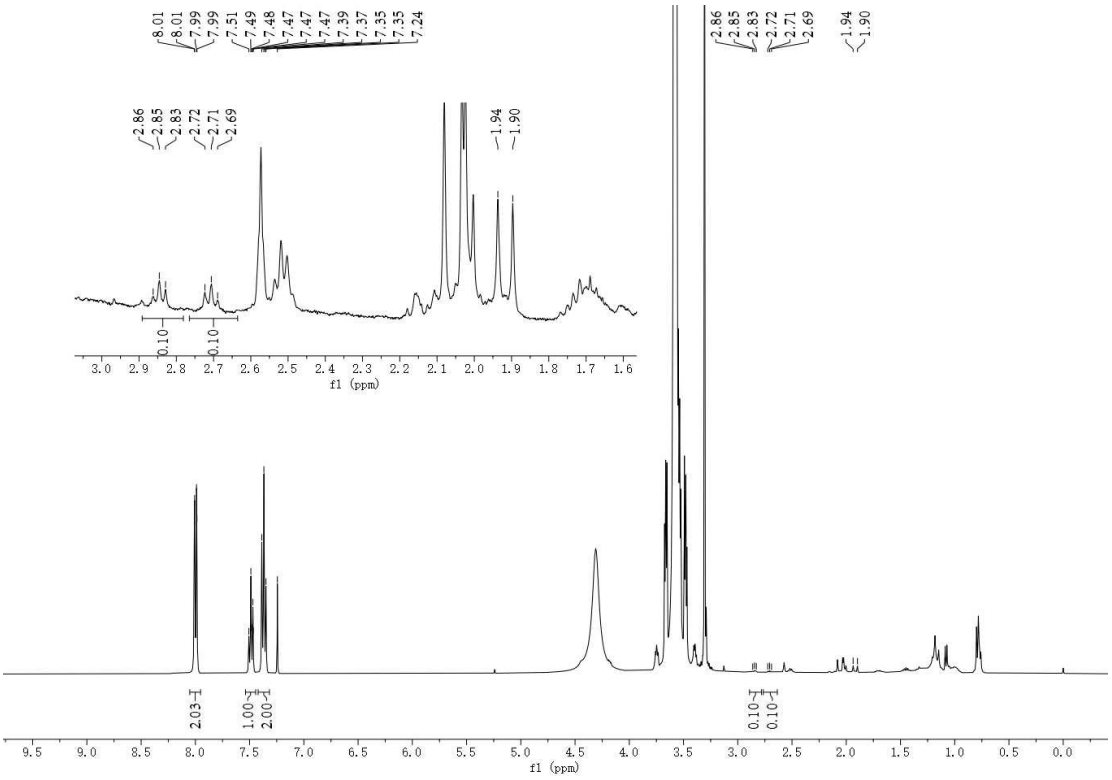
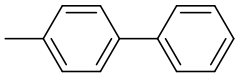
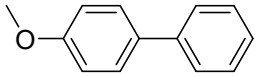


Figure S5. NMR study on the stability of TPGS-750-M under alkaline condition.

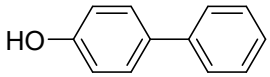
11. Characterization data of all products



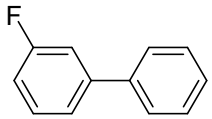
4-**methyl-1,1'-biphenyl (3a)**[3] Light white powder (42.3 mg,85% yield) (PE/DCM = 20:1 as eluent). mp 44 – 47 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.47 (m, 2H), 7.44 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 7.27 – 7.21 (m, 1H), 7.16 (dd, *J* = 7.7, 5.7 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.3, 138.5, 137.2, 129.6, 128.9, 127.1, 127.1, 21.2. LRMS (EI): m/z calcd for $C_{13}H_{12}[M]^{+}$, 168.09; found, 168.15.



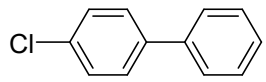
4-methoxy-1,1'-biphenyl (3b)[4] white powder (51.8 mg, 94% yield) (PE/DCM = 10:1 as eluent). mp 86 – 90 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.52 (m, 4H), 7.46 –7.40 (m, 2H), 7.35 – 7.29 (m, 1H), 7.02 – 6.97 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.3, 141.0, 133.9, 128.9, 128.3, 126.9, 126.8, 114.3, 55.5. LRMS (EI): m/z calcd for $C_{13}H_{12}O[M]^{+}$, 184.09; found, 184.00.



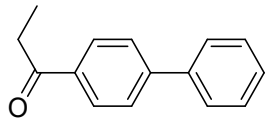
[1,1'-biphenyl]-4-ol (3c)[3] Pale white solid (49.5 mg, 97% yield) (PE/DCM = 10:1 as eluent). mp 164 – 166 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 2H), 7.51 – 7.46 (m, 2H), 7.45 – 7.38 (m, 2H), 7.34 – 7.28 (m, 1H), 6.95 – 6.87 (m, 2H), 4.81 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.1, 140.8, 134.1, 128.7, 128.4, 126.7, 115.6. LRMS(EI): m/z calcd for $C_{12}H_{10}O[M]^{+}$, 170.07; found, 170.10.



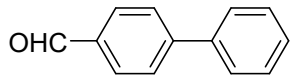
3-**fluoro-1,1'-biphenyl (3d)**[5] colourless liquid (42.3 mg, 82% yield) (PE/DCM = 20:1 as eluent). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.55 (m, 2H), 7.49 – 7.43 (m, 2H), 7.42–7.34 (m, 3H), 7.32 – 7.27 (m, 1H), 7.08 – 7.01 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.4, 162.0, 143.6, 143.5, 139.9 (d, J = 2.2 Hz), 130.3, 130.2, 128.9, 127.9, 127.1, 122.8(d, J=2.7 Hz), 114.2, 113.9, 113.9. LRMS(EI): m/z calcd for $C_{12}H_{9}F[M]^{+}$, 172.07; found, 172.05.



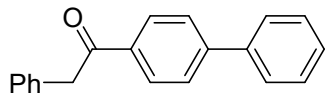
4-chloro-1,1'-biphenyl (3e)[3] white powder (50.8 mg,90% yield) (PE/DCM = 20:1 as eluent). mp 32 – 34 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.50 (m, 4H), 7.50 –7.35 (m, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.1, 139.8, 133.5, 129.0, 129.0, 128.5, 127.7, 127.1. LRMS(EI): m/z calcd for $C_{12}H_9Cl$ $[M]^+$, 188.04; found, 188.05.



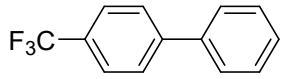
1-**([1,1'-biphenyl]-4-yl)propan-1-one (3f)[6]** white powder (62.9 mg, 99% yield) (PE/DCM = 5:1 as eluent). mp: 90 – 93 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.00 (m, 2H), 7.70 – 7.65 (m, 2H), 7.65 – 7.59 (m, 2H), 7.49 – 7.43 (m, 2H), 7.43 – 7.36 (m, 1H), 3.03 (q, J = 7.2 Hz, 2H), 1.25 (t, J = 7.3 Hz. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.6, 145.7, 140.1, 135.8, 129.1, 128.7, 128.3, 127.4, 127.3, 32.0, 8.4. LRMS(EI): m/z calcd for $C_{15}H_{14}O$ $[M]^+$, 210.10; found, 210.10.



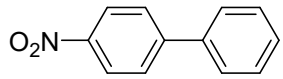
[1,1'-biphenyl]-4-carbaldehyde (3g)[3] White acicular crystal (54 mg,100% yield) (PE/DCM = 5:1 as eluent). mp 55-58 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.06 (s, 1H), 8.01 – 7.90 (m, 2H), 7.80 – 7.72 (m, 2H), 7.68 – 7.61 (m, 2H), 7.53 – 7.45 (m, 2H), 7.45 – 7.39 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.0, 147.3, 139.8, 135.3, 130.4, 129.1, 128.6, 127.8, 127.5. LRMS(EI): m/z calcd for $C_{13}H_{10}O$ $[M]^+$, 182.07; found, 182.10.



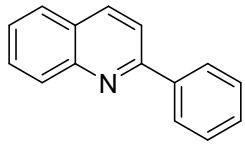
1-([1,1'-biphenyl]-4-yl)-2-phenylethan-1-one (3h)[7] white solid (63.6 mg, 78% yield) (PE/DCM = 4 :1 as eluent). mp 142 – 146 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.06 (m, 2H), 7.70 – 7.65 (m, 2H), 7.64 – 7.59 (m, 2H), 7.49 – 7.44 (m, 2H), 7.43 – 7.37 (m, 1H), 7.37 – 7.34 (m, 1H), 7.33 – 7.24 (m, 4H), 4.32 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.2, 145.9, 139.8, 135.3, 134.6, 129.5, 129.3, 129.0, 128.7, 128.3, 127.3, 127.3, 126.9, 45.6. LRMS(EI): m/z calcd for $C_{20}H_{16}O$ $[M]^+$, 272.12; found, 272.05.



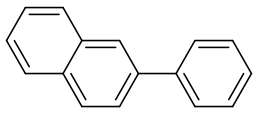
4-(trifluoromethyl)-1,1'-biphenyl(3i)[8] white powder (63.3 mg, 95% yield) (PE/DCM = 20:1 as eluent). mp 68-69 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 4H), 7.64 – 7.59 (m, 2H), 7.49 (ddd, *J* = 7.7, 6.4, 1.4 Hz, 2H), 7.44 – 7.39 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144. 9, 139.9, 129.1, 128.33, 127.6, 127.4, 125.8 (q, J = 3.7 Hz),122.3 (q, J = 268 Hz). LRMS(EI): m/z calcd for $C_{13}H_9F_3$ $[M]^+$, 222.07; found, 222.05.



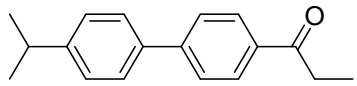
4-nitro-1,1'-biphenyl (3g)[4] white powder (50.0 mg,78%) (PE/DCM = 5:1 as eluent). mp 113-116 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 – 8.27 (m, 2H), 7.77 – 7.72 (m, 2H), 7.66 – 7.61 (m, 2H), 7.51 (ddt, *J* = 8.1, 6.4, 1.2 Hz, 2H), 7.48 – 7.42 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.8, 147.2, 138.9, 129.3, 129.1, 127.9, 127.5, 124.3. LRMS(EI): m/z calcd for $C_{12}H_9NO_2$ $[M]^+$, 199.06; found, 199.10.



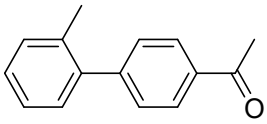
2-phenylquinoline (3k)[9] white powder (57.2 mg, 93%) (PE/EA = 10:1 as eluent). mp 73-75 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.13 (m, 4H), 7.91 – 7.81 (m, 2H), 7.74 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.58 – 7.44 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.4, 148.3, 139.7, 136.8, 129.8, 129.7, 129.3, 128.9, 127.6, 127.5, 127.2, 126.3, 119.0. LRMS(EI): m/z calcd for $C_{15}H_{11}N$ $[M]^+$, 205.09; found, 205.15.



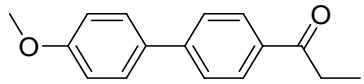
2-phenylnaphthalene (3l)[3] white powder (51.5 mg, 84%) (PE/DCM = 50:1 as eluent). mp 103-106 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, J = 1.8 Hz, 1H), 7.96 – 7.86 (m, 3H), 7.80–7.72 (m, 3H), 7.56 – 7.46 (m, 4H), 7.44 – 7.36 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.3, 138.7, 133.8, 132.8, 129.0, 128.6, 128.3, 127.8, 127.6, 127.5, 126.4, 126.1, 126.0, 125.7. LRMS(EI): m/z calcd for $C_{16}H_{12}$ $[M]^+$, 204.09; found, 204.15.



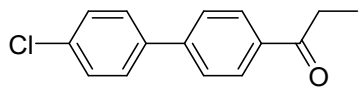
1-(4'-isopropyl-[1,1'-biphenyl]-4-yl)propan-1-one (4a) white powder (68 mg, 90%) (PE/DCM = 5 :1 as eluent). mp 101 - 103 ℃ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.00 (m, 2H), 7.71 – 7.65 (m, 2H), 7.60 – 7.55 (m, 2H), 7.36 – 7.31 (m, 2H), 3.01 (dq, *J* = 21.3, 7.1 Hz, 3H), 1.30 (d, *J* = 6.9 Hz, 6H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.4, 146.0, 140.0, 135.4, 134.8, 129.6, 129.4, 129.1, 128.9, 128.4, 127.4, 127.4, 127.1, 45.7. HRMS (ESI): calcd for $C_{18}H_{20}O$ $[M+H]^+$, 253.1587; found, 253.1591.



1-(2'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one(4b)[10] White solid (51.7 mg, 82%) (PE/DCM = 10:1 as eluent). mp 42-45 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.38 (m, 2H), 7.31 – 7.21 (m, 4H), 3.05 (q, *J* = 7.2 Hz, 2H), 2.28 (s, 3H), 1.27 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.7, 146.9, 141.0, 135.5, 135.3, 130.7, 129.7, 129.6, 128.0, 127.99, 126.1, 32.0, 20.5, 8.5. LRMS(EI): m/z calcd for $C_{15}H_{14}O$ $[M]^+$, 210.10; found, 210.09.

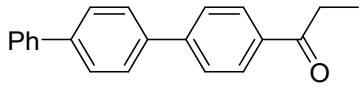


1-(4'-methoxy-[1,1'-biphenyl]-4-yl)propan-1-one (4c)[11] white powder (67.1 mg, 93%) (PE/DCM = 5 :1 as eluent). mp 133-137 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.94 (m, 2H), 7.68 – 7.60 (m, 2H), 7.60 – 7.52 (m, 2H), 7.06 – 6.92 (m, 2H), 3.86 (s, 3H), 3.02 (q, J = 7.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.5, 160.0, 145.3, 135.2, 132.5, 128.7, 128.5, 126.7, 114.5, 55.5, 31.9, 8.5. LRMS(EI): m/z calcd for $C_{16}H_{16}O_2$[M]$^+$, 240.11; found, 240.05.

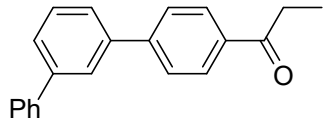


1-(4'-chloro-[1,1'-biphenyl]-4-yl)propan-1-one (4d)[12] white powder (66.5 mg, 93%) (PE/DCM = 5 :1 as eluent). mp 98-102 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06

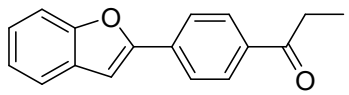
– 7.99 (m, 2H), 7.66 – 7.60 (m, 2H), 7.57 – 7.51 (m, 2H), 7.47 – 7.38 (m, 2H), 3.03 (q, J = 7.3 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.4, 144.3, 138.5, 136.0, 134.5, 129.3, 128.8, 128.6, 127.2, 32.0, 8.4. LRMS(EI): m/z calcd for $C_{15}H_{13}ClO$ $[M]^+$, 244.07; found, 244.05.



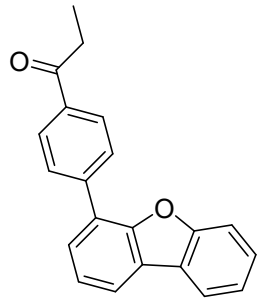
1-([1,1':4',1''-terphenyl]-4-yl)propan-1-one (4e) white powder (72.9 mg, 93%) (PE/DCM = 3:1 as eluent). mp 243-245 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.05 (m, 2H), 7.85 (t, J = 1.8 Hz, ^{1}H), 7.77 – 7.72 (m, 2H), 7.68 – 7.60 (m, 4H), 7.55 (t, J = 7.6 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.43 – 7.37 (m, 1H), 3.06 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.5, 145.6, 142.1, 141.0, 140.6, 135.9, 129.5, 129.0, 128.7, 127.7, 127.4, 127.4, 127.1, 126.3, 32.0, 8.4. HRMS (ESI): calcd for $C_{21}H_{18}O$ $[M+H]^+$, 287.1430; found, 287.1433.



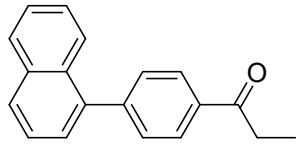
1-([1,1':3',1''-terphenyl]-4-yl)propan-1-one (4f) White acicular crystal (72.9 mg, 85%) (PE/DCM = 3:1 as eluent). mp 99-101 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.05 (m, 2H), 7.85 (t, J = 1.8 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.68 – 7.60 (m, 4H), 7.55 (t, J = 7.6 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.43 – 7.37 (m, 1H), 3.06 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.5, 145.6, 142.1, 141.0, 140.6, 135.9, 129.5, 129.0, 128.7, 127.7, 127.4, 127.3, 127.1, 126.3, 32.0, 8.4. HRMS (ESI): calcd for $C_{21}H_{18}O$ $[M+H]^+$, 287.1430; found, 287.1429.



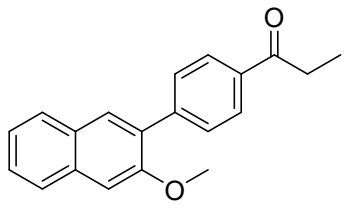
1-(4-(benzofuran-2-yl)phenyl)propan-1-one (4g) white powder (64.5 mg, 86%) (PE/DCM = 1:1 as eluent). mp 182-185 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.98 (m, 2H), 7.96 – 7.88 (m, 2H), 7.64 – 7.57 (m, 1H), 7.53 (dq, J = 8.2, 0.9 Hz, 1H), 7.32 (ddd, J = 8.3, 7.2, 1.4 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.14 (d, J = 1.0 Hz, 1H), 3.01 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.1, 155.3, 154.7, 136.4, 134.5, 129.0, 128.7, 125.2, 124.9, 123.4, 121.4, 111.5, 103.6, 32.0, 8.4. HRMS (ESI): calcd for $C_{17}H_{14}O_2$ $[M+H]^+$, 251.1067; found, 251.1065.



1-(4-(dibenzo[b,d]furan-4-yl)phenyl)propan-1-one (4h) white powder (76.5 mg, 85%) (PE/DCM = 1:3 as eluent). mp 112-114 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 – 8.10 (m, 2H), 8.07 – 7.94 (m, 4H), 7.69 – 7.58 (m, 2H), 7.52 – 7.43 (m, 2H), 7.38 (td, J = 7.4, 1.0 Hz, 1H), 3.09 (q, J = 7.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.5, 156.2, 153.4, 141.0, 135.9, 128.9, 128.4, 127.5, 126.8, 125.2, 124.7, 124.0, 123.3, 123.0, 120.8, 120.6, 111.9, 31.9, 8.4. HRMS (ESI): calcd for $C_{21}H_{16}O_2$ $[M+H]^+$, 301.1223; found, 301.1227.



1-(4-(naphthalen-1-yl)phenyl)propan-1-one (4i)[6] white powder (63.2 mg, 81%) (PE/DCM = 1 :1 as eluent). mp 102-104 ℃. 1H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.08 (m, 2H), 7.98 – 7.81 (m, 3H), 7.66 – 7.58 (m, 2H), 7.57 – 7.40 (m, 4H), 3.09 (q, J = 7.3 Hz, 2H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.7, 145. 7, 139.2, 135.9, 133.9, 131.4, 130.4, 128.6, 128.4, 128.2, 127.1, 126.5, 126.1, 125.7, 125.5, 32.0, 8.5. LRMS(EI): m/z calcd for $C_{19}H_{16}O$ $[M]^+$, 260.12; found, 260.05.



1-**(4-(3-methoxynaphthalen-2-yl)phenyl)propan-1-one (4j)** white powder (72.5 mg, 83%) (PE/DCM = 1:3 as eluent). mp 93-96 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.00 (m, 2H), 7.84 – 7.75 (m, 3H), 7.74 – 7.67 (m, 2H), 7.48 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.38 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.25 (s, 1H), 3.94 (s, 3H), 3.06 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.7,

155.1, 143.3, 135.7, 134.4, 131.4, 130.3, 130.1, 128.9, 128.0, 127.9, 126.9, 126.6, 124.3, 106.1, 55.7, 32.0, 8.5. HRMS (ESI): calcd for $C_{20}H_{18}O_2$ $[M+H]^+$, 291.1380; found, 291.1388

12. References

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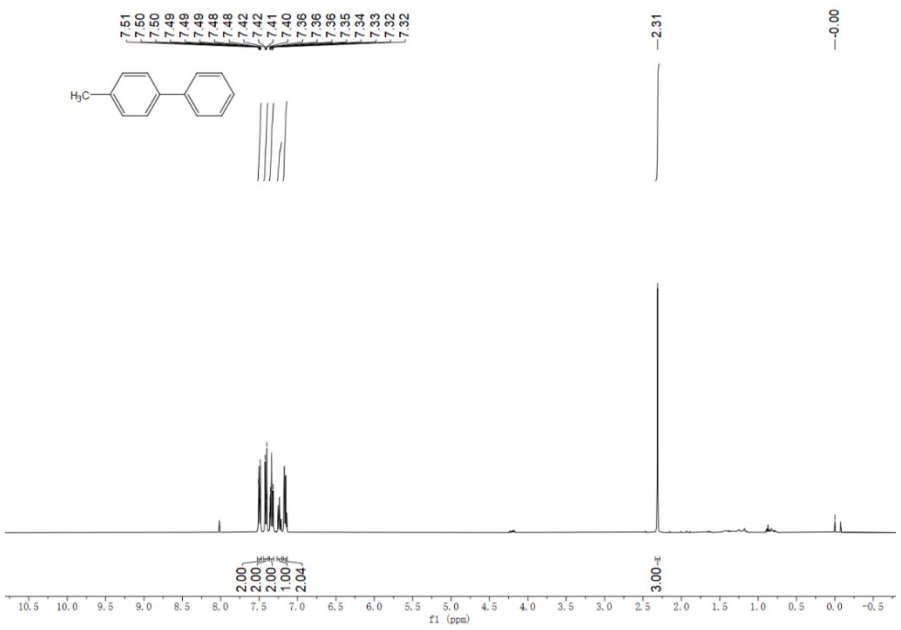
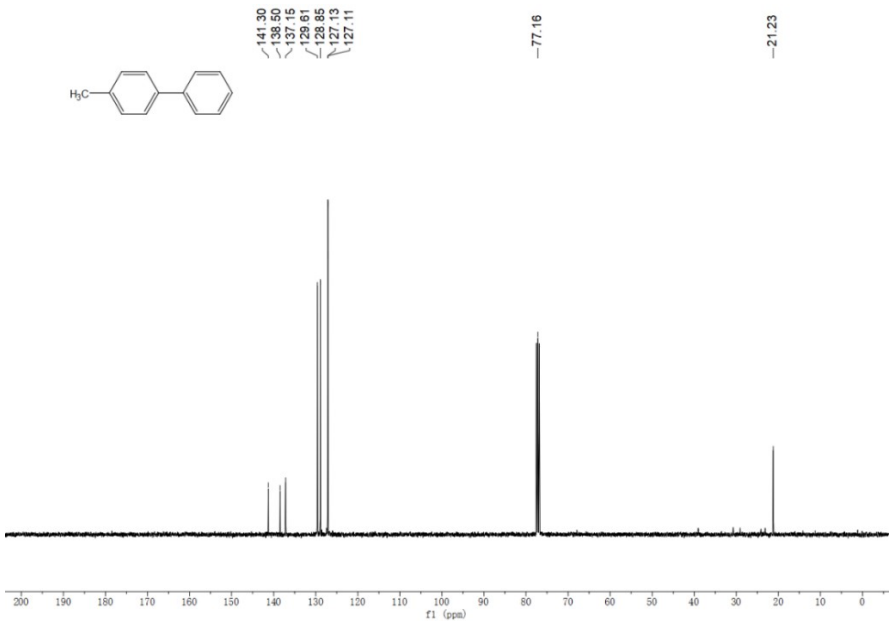
13. The NMR spectra of all products

4-methyl-1,1'-biphenyl (3a)

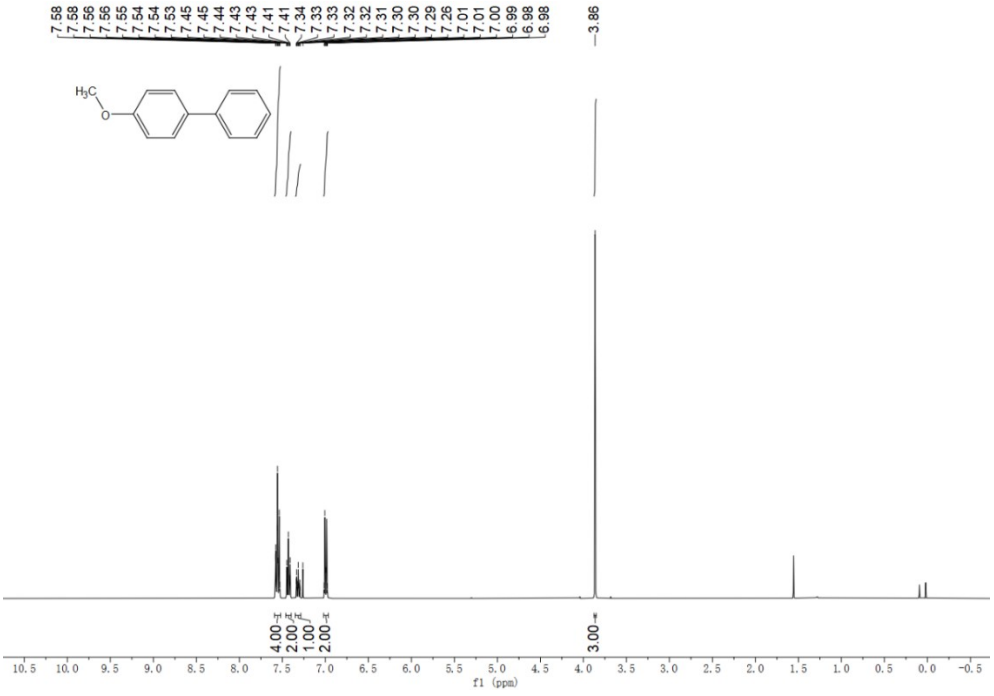


^{1}H NMR ($CDCl_3$, 400 MHz) of **3a**

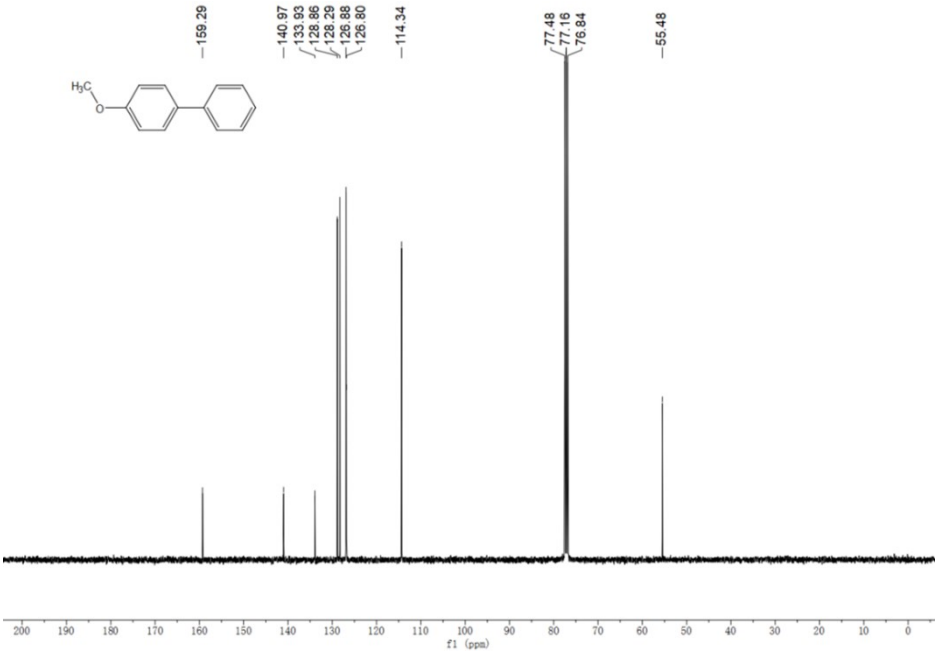


^{13}C NMR ($CDCl_3$, 100 MHz) of **3a**

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

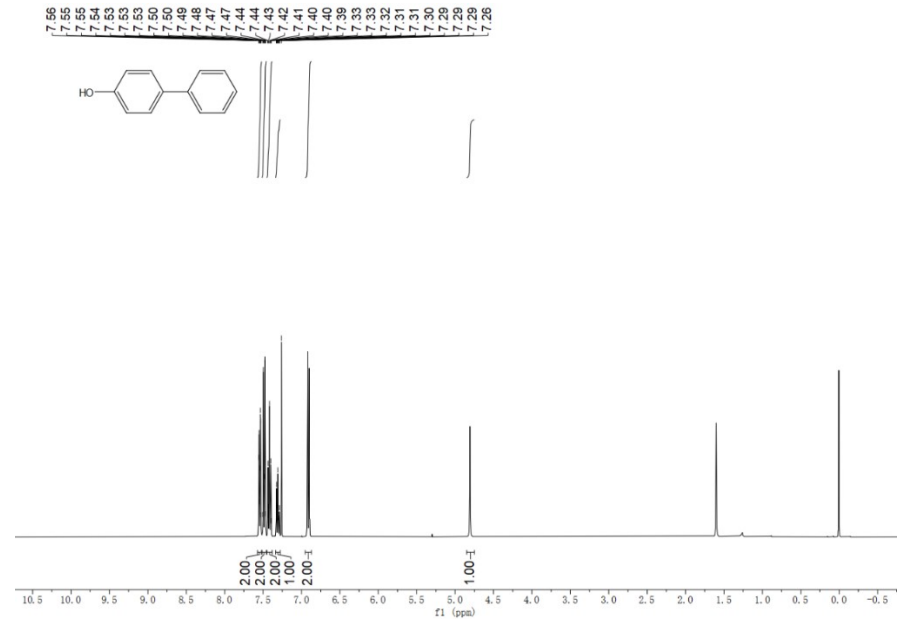


^{1}H NMR ($CDCl_3$, 400 MHz) of **3b**

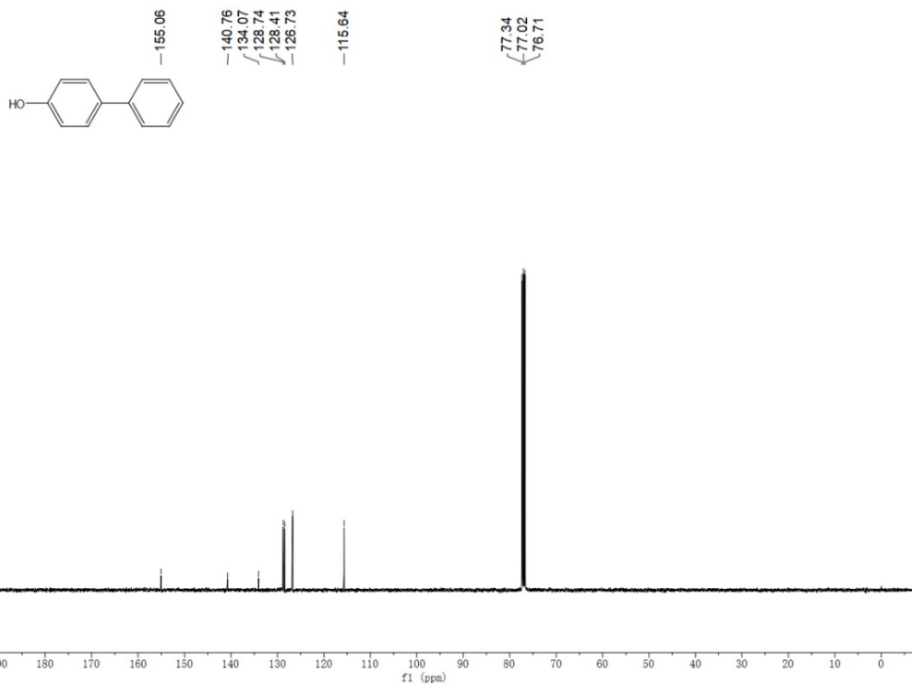


^{13}C NMR ($CDCl_3$, 100 MHz) of **3b**

[1,1'-biphenyl]-4-ol (3c)

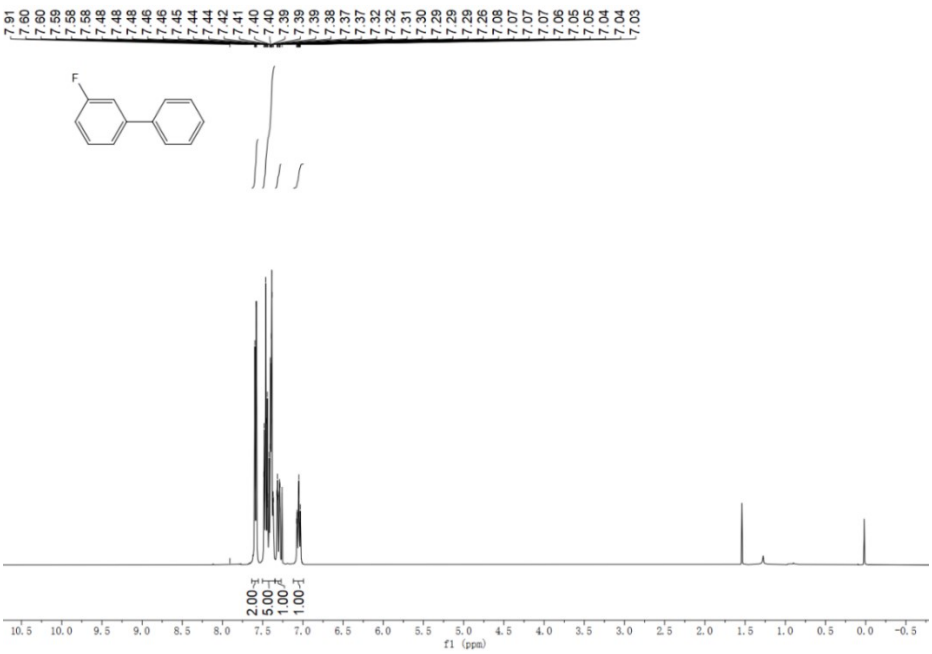


^{1}H NMR ($CDCl_3$, 400 MHz) of **3c**

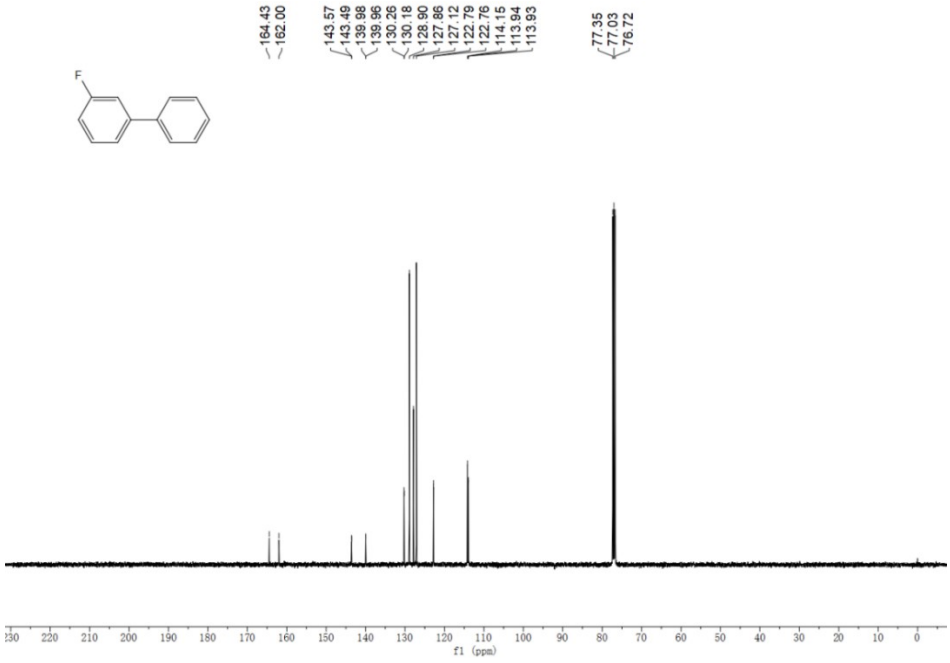


^{13}C NMR ($CDCl_3$, 100 MHz) of **3c**

3-fluoro-1,1'-biphenyl (3d)

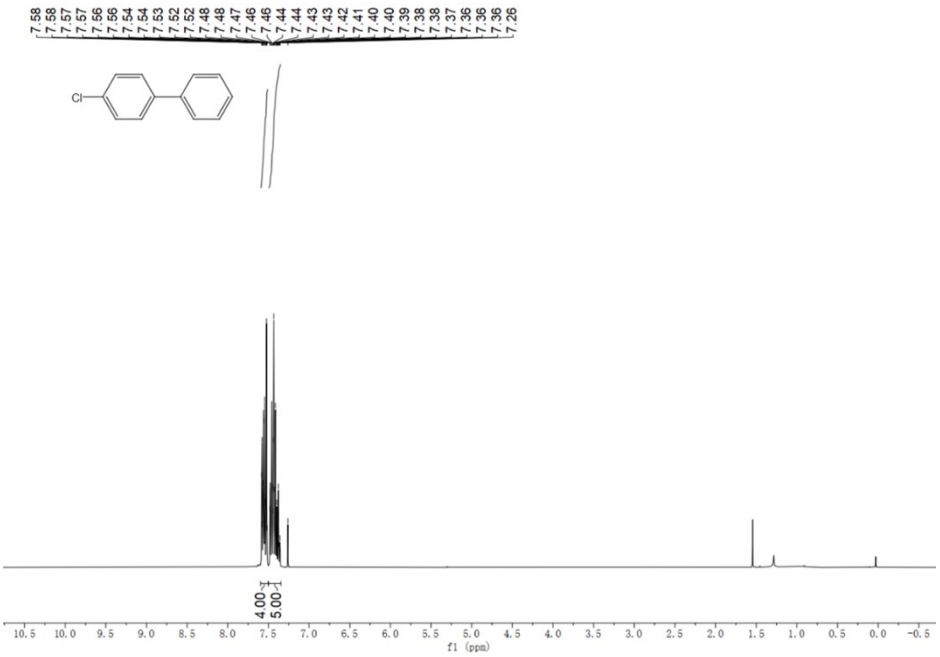


^{1}H NMR ($CDCl_3$, 400 MHz) of **3d**

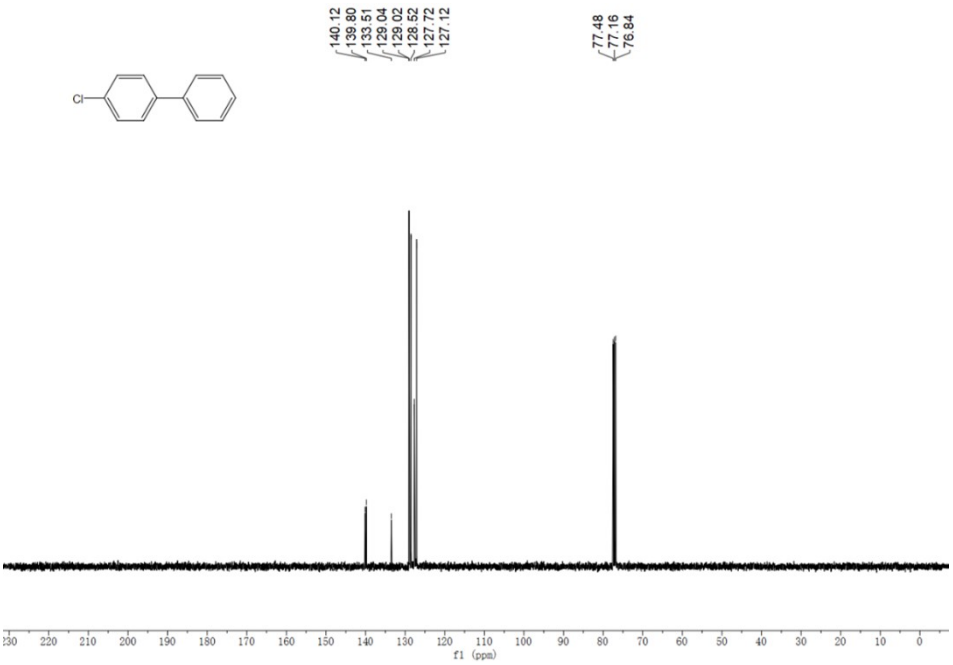


^{13}C NMR ($CDCl_3$, 100 MHz) of **3d**

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

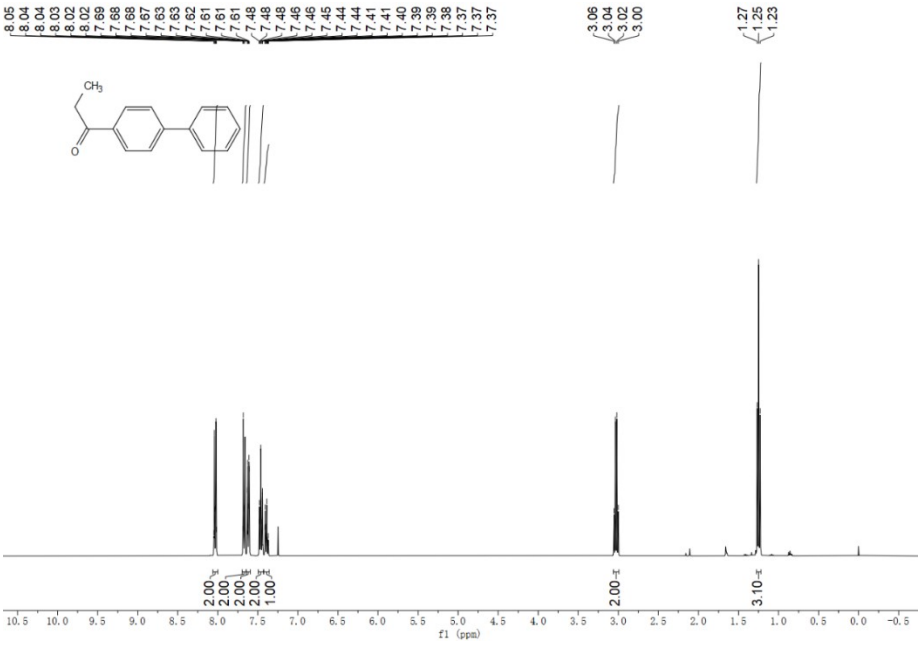


^{1}H NMR ($CDCl_3$, 400 MHz) of **3e**

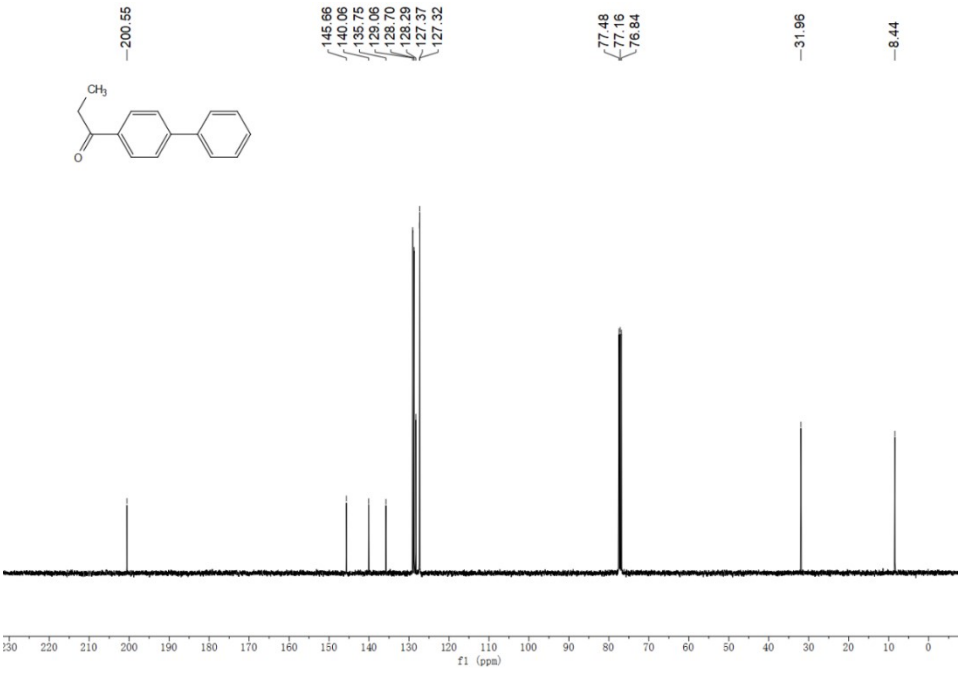


^{13}C NMR ($CDCl_3$, 100 MHz) of **3e**

1-([1,1'-biphenyl]-4-yl)propan-1-one (3f)

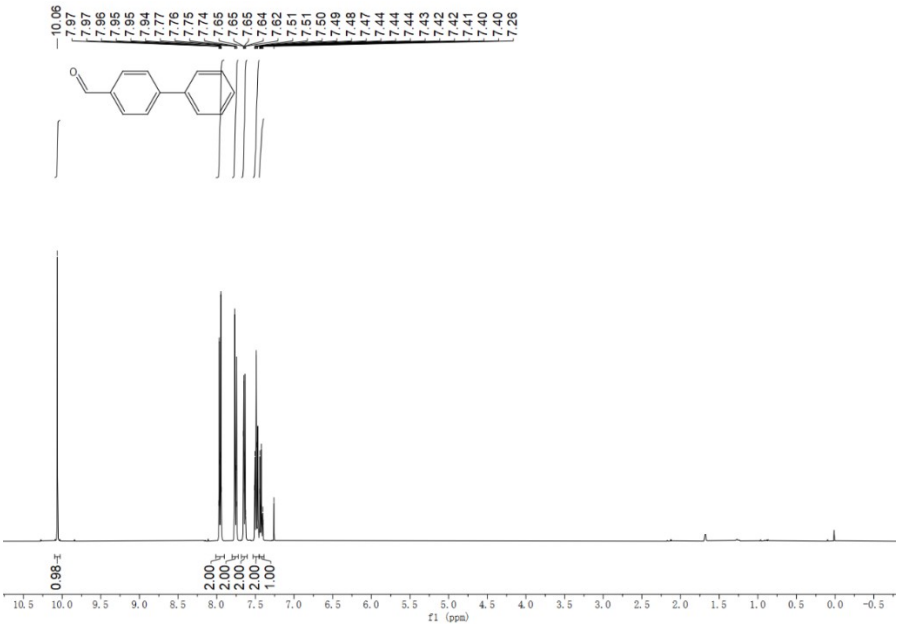


^{1}H NMR ($CDCl_3$, 400 MHz) of **3f**

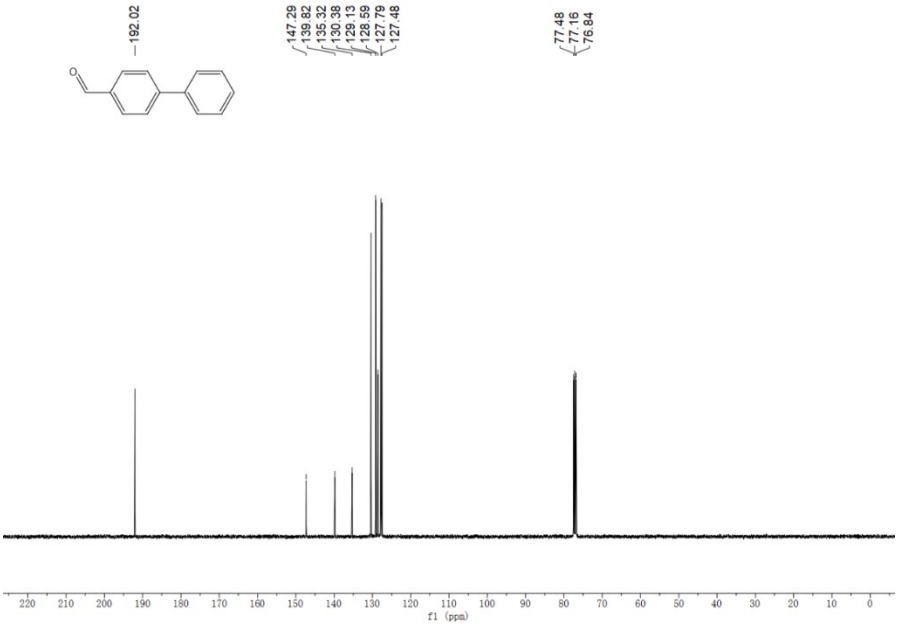


^{13}C NMR ($CDCl_3$, 100 MHz) of **3f**

[1,1'-biphenyl]-4-carbaldehyde (3g)

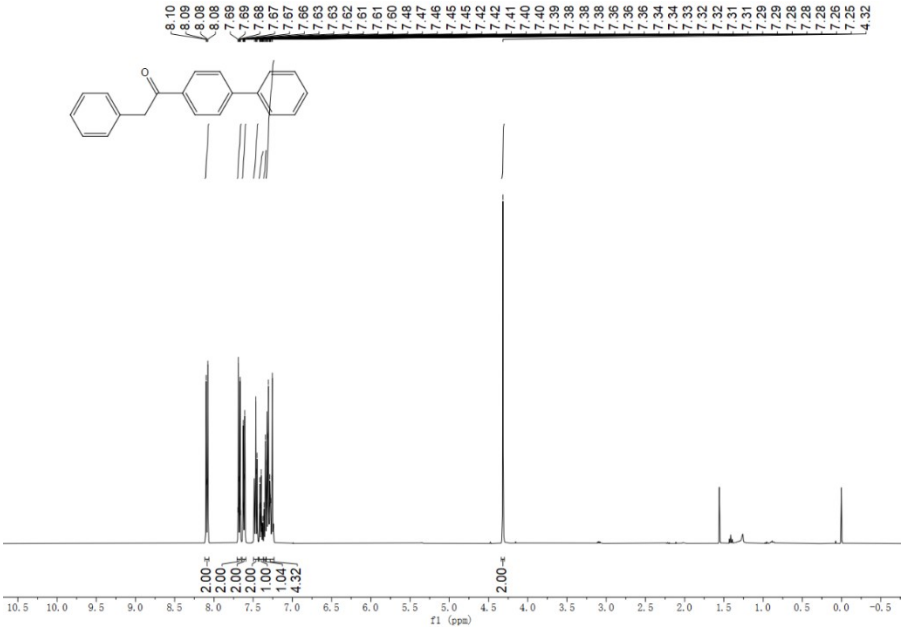


^{1}H NMR ($CDCl_3$, 400 MHz) of **3g**

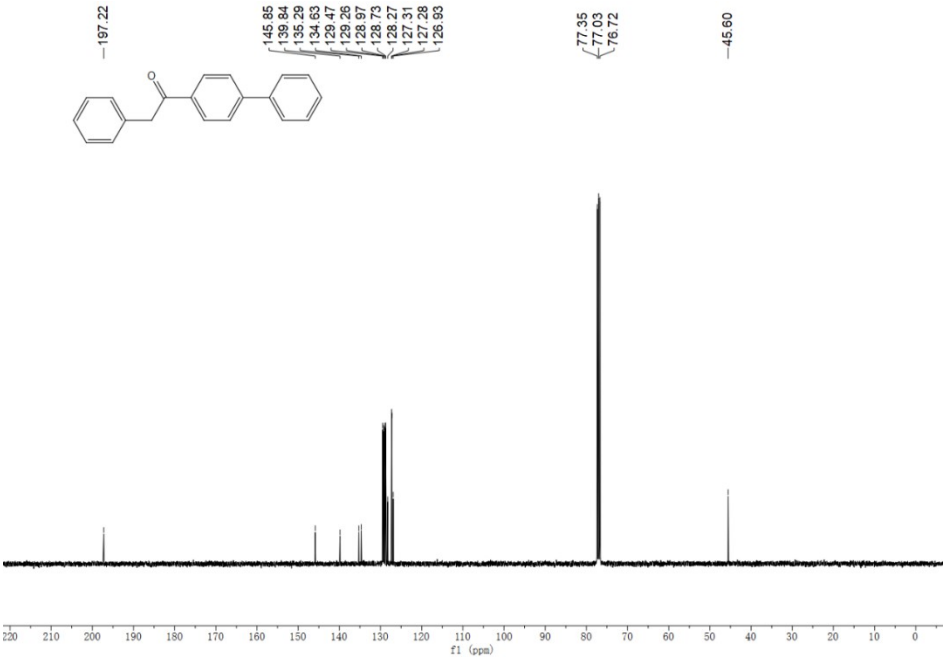


^{13}C NMR ($CDCl_3$, 100 MHz) of **3g**

1-([1,1'-biphenyl]-4-yl)-2-phenylethan-1-one (3h)

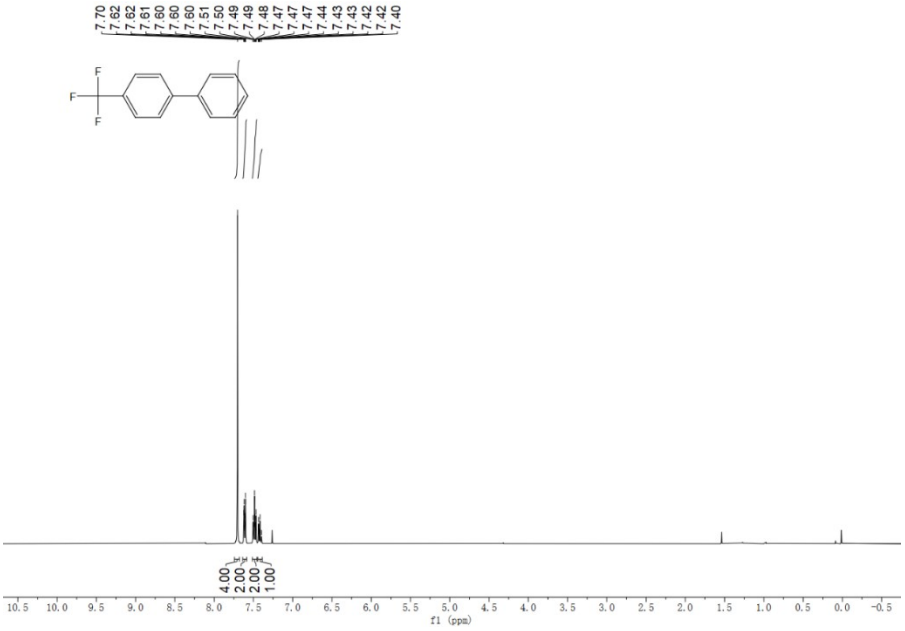


^{1}H NMR ($CDCl_3$, 400 MHz) of **3h**

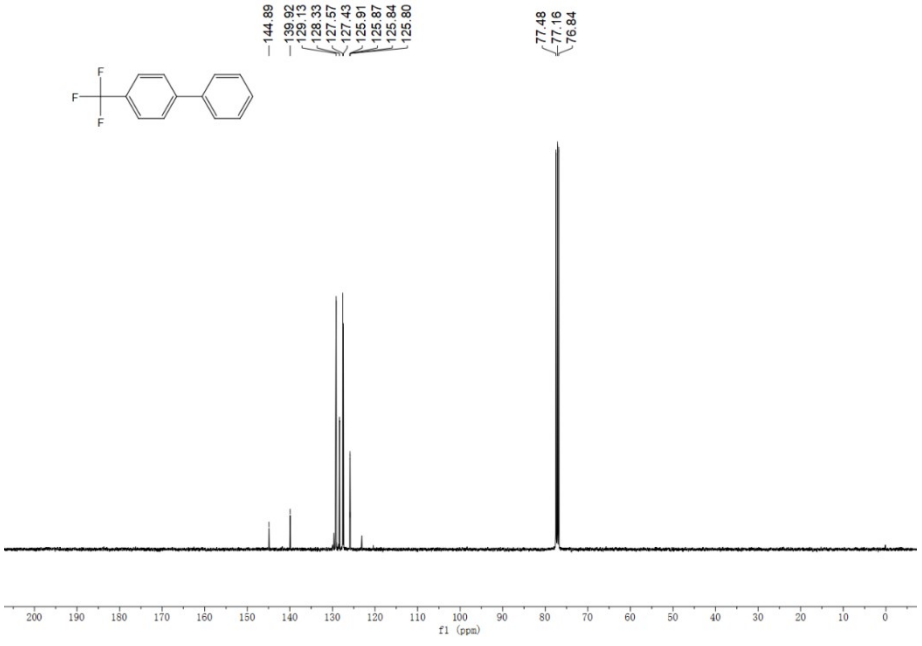


^{13}C NMR ($CDCl_3$, 100 MHz) of **3h**

4-(trifluoromethyl)-1,1'-biphenyl(3i)

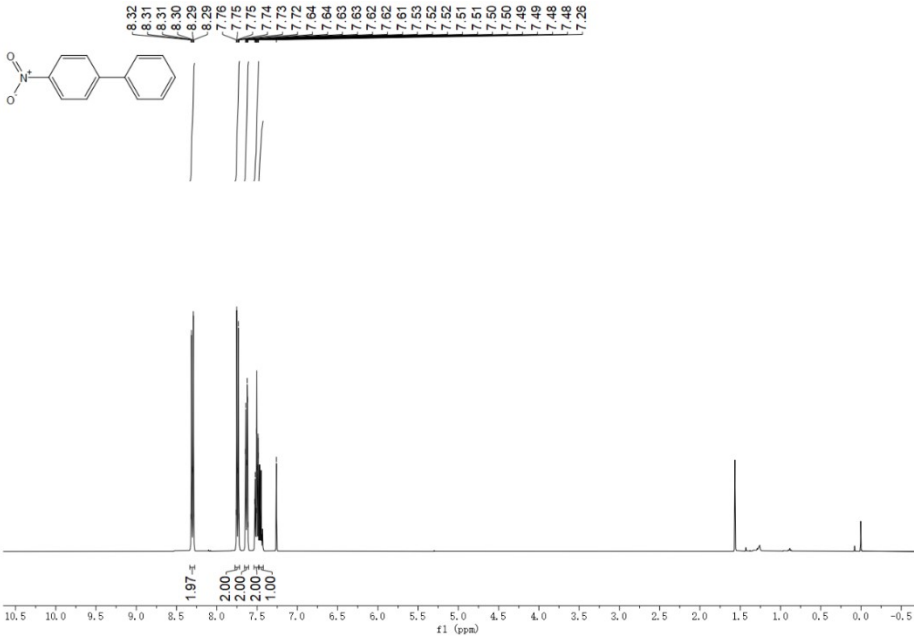


^{1}H NMR ($CDCl_3$, 400 MHz) of **3i**

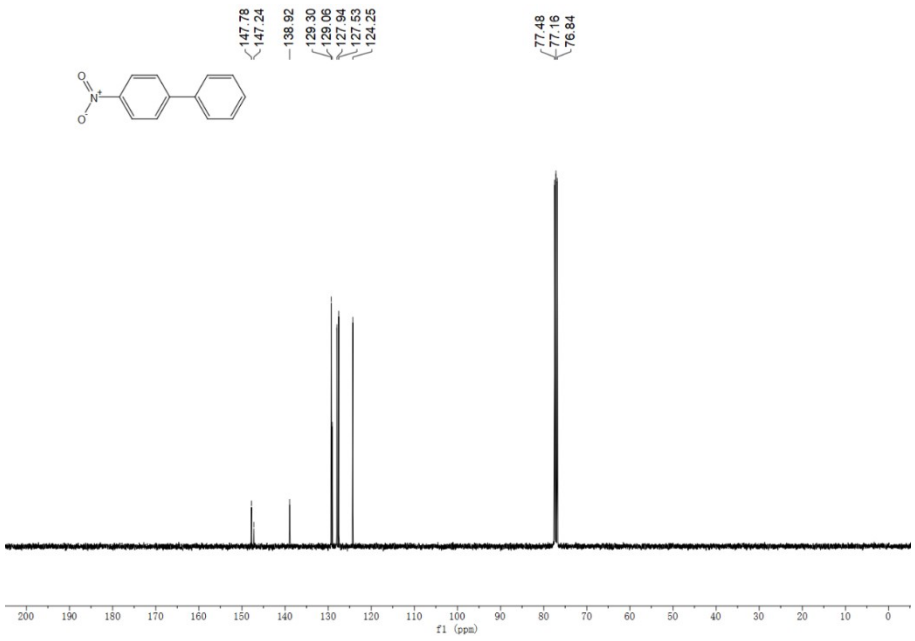


^{13}C NMR ($CDCl_3$, 100 MHz) of **3i**

4-nitro-1,1'-biphenyl (3j)

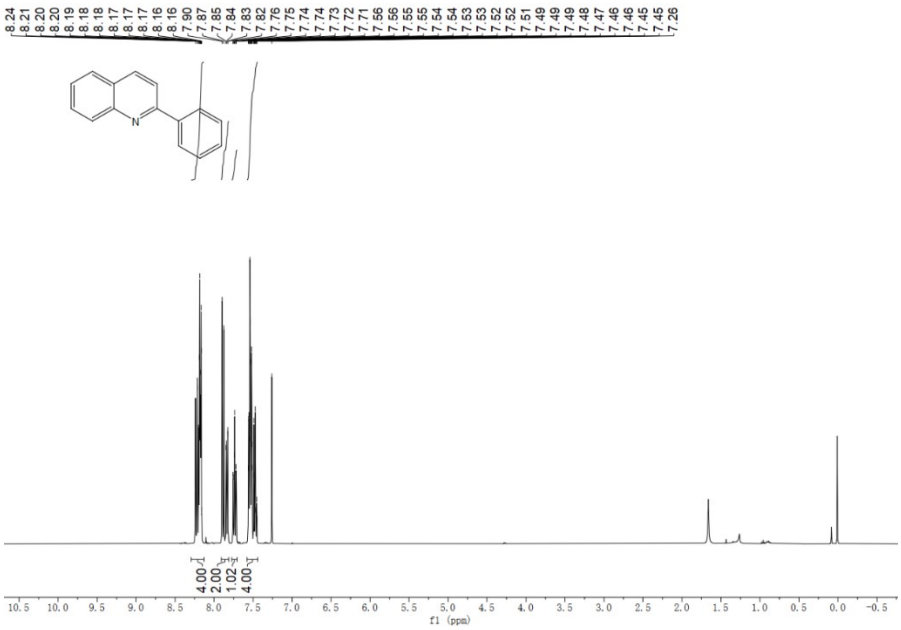


^{1}H NMR ($CDCl_3$, 400 MHz) of **3j**

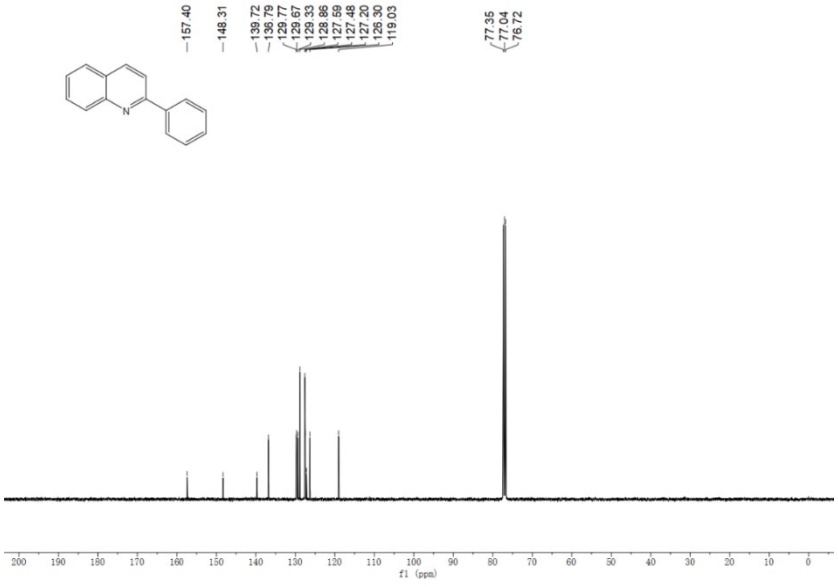


^{13}C NMR ($CDCl_3$, 100 MHz) of **3j**

2-phenylquinoline (3k)

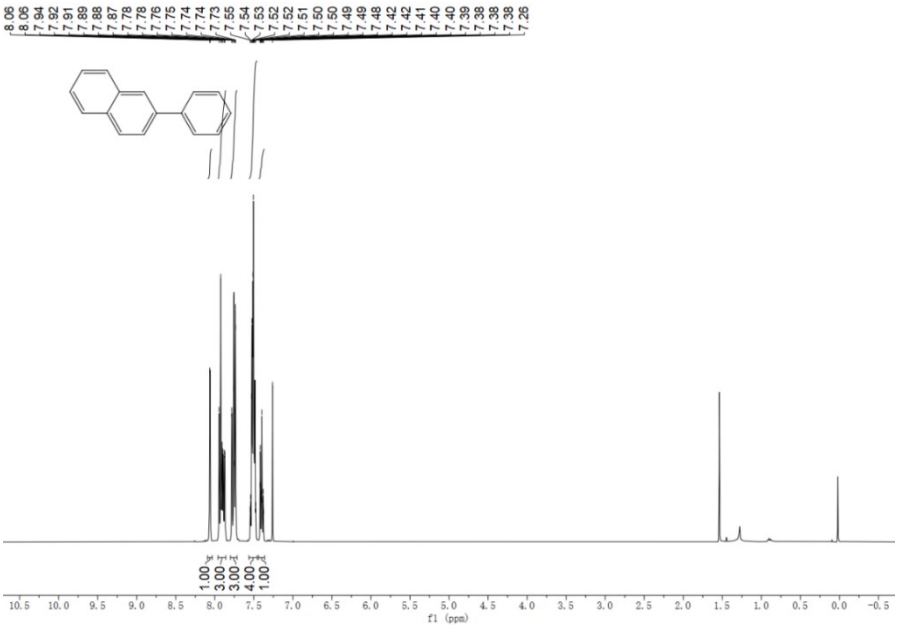


^{1}H NMR ($CDCl_3$, 400 MHz) of **3k**

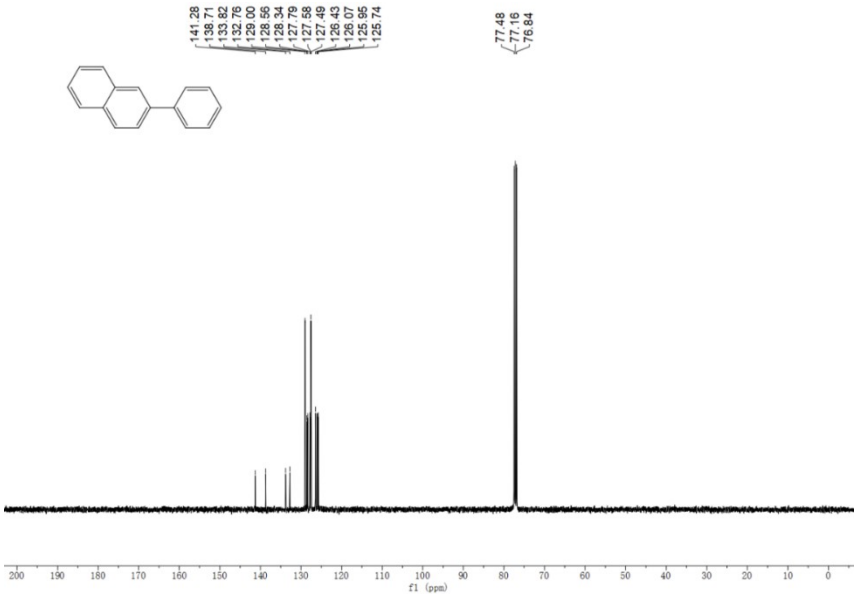


^{13}C NMR ($CDCl_3$, 100 MHz) of **3k**

2-phenylnaphthalene (3l)

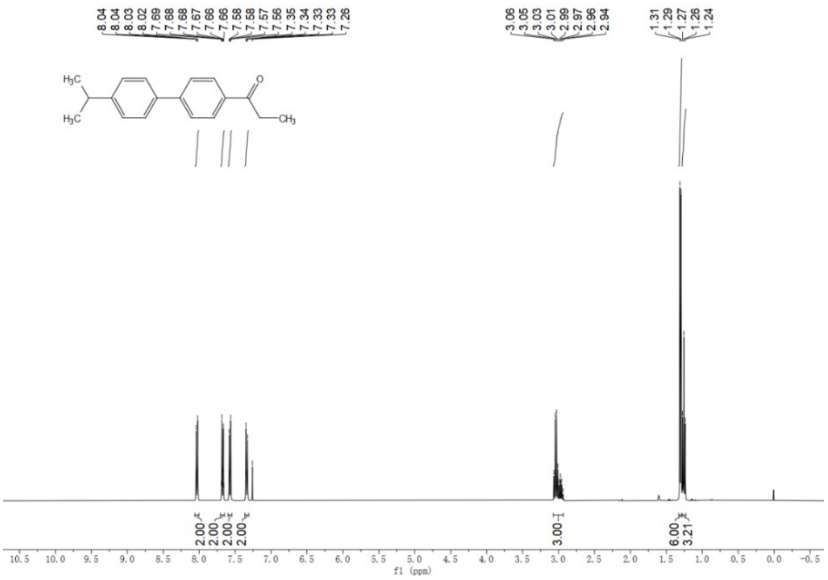


^{1}H NMR ($CDCl_3$, 400 MHz) of **3l**

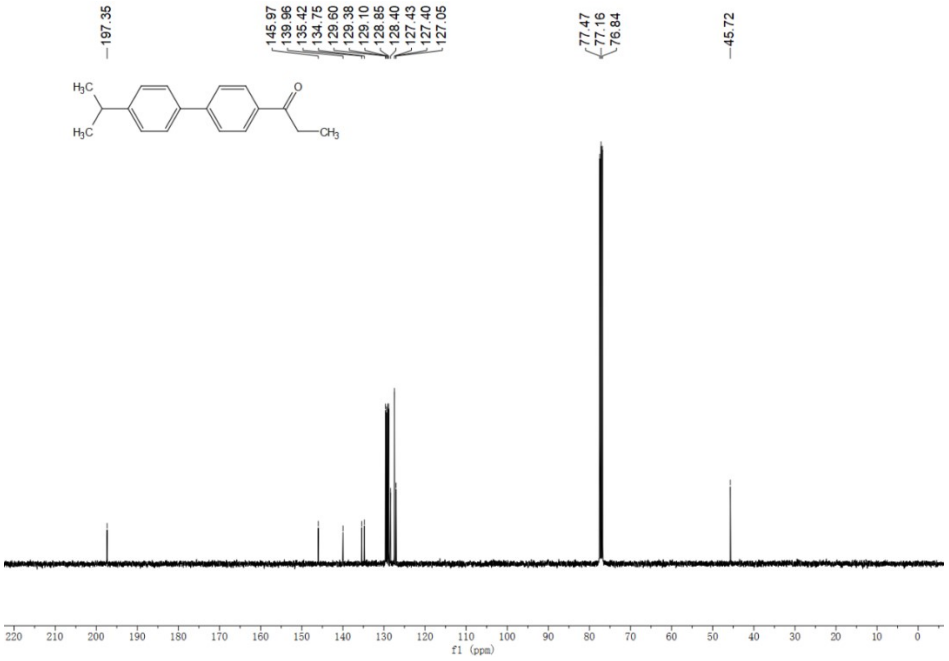


^{13}C NMR ($CDCl_3$, 100 MHz) of **3l**

1-(4'-isopropyl-[1,1'-biphenyl]-4-yl)propan-1-one (4a)

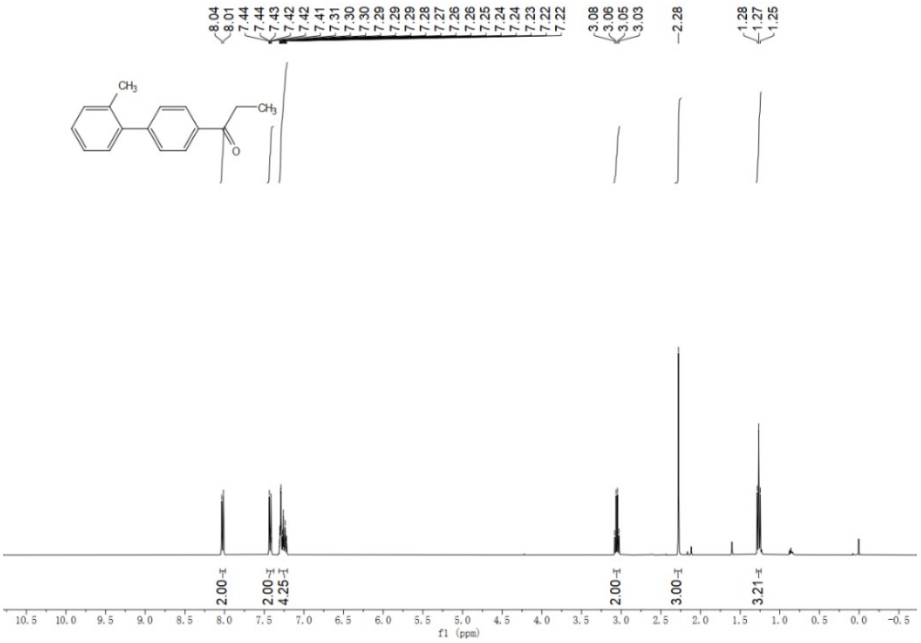


^{1}H NMR ($CDCl_3$, 400 MHz) of **4a**

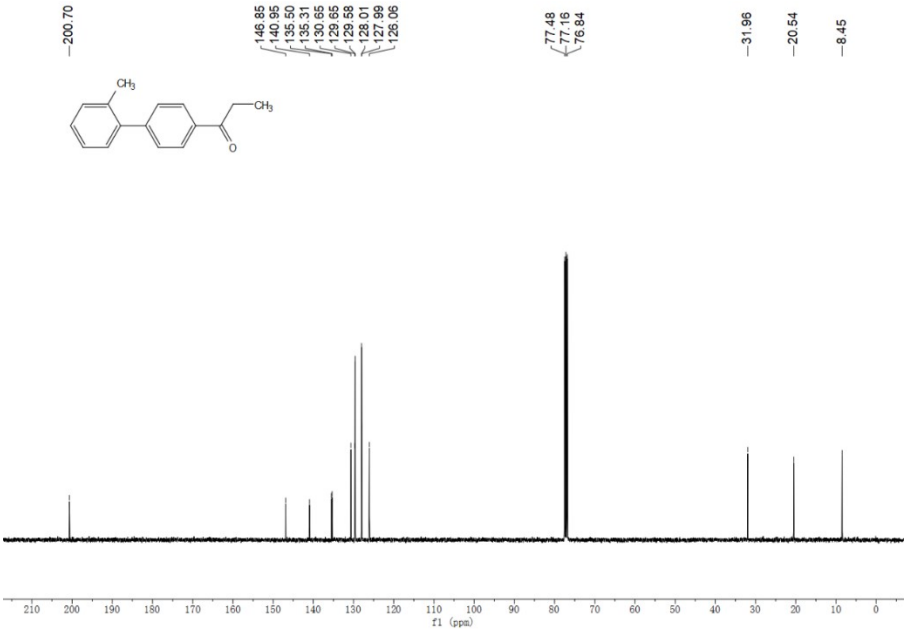


^{13}C NMR ($CDCl_3$, 100 MHz) of **4a**

1-(2'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one(4b)

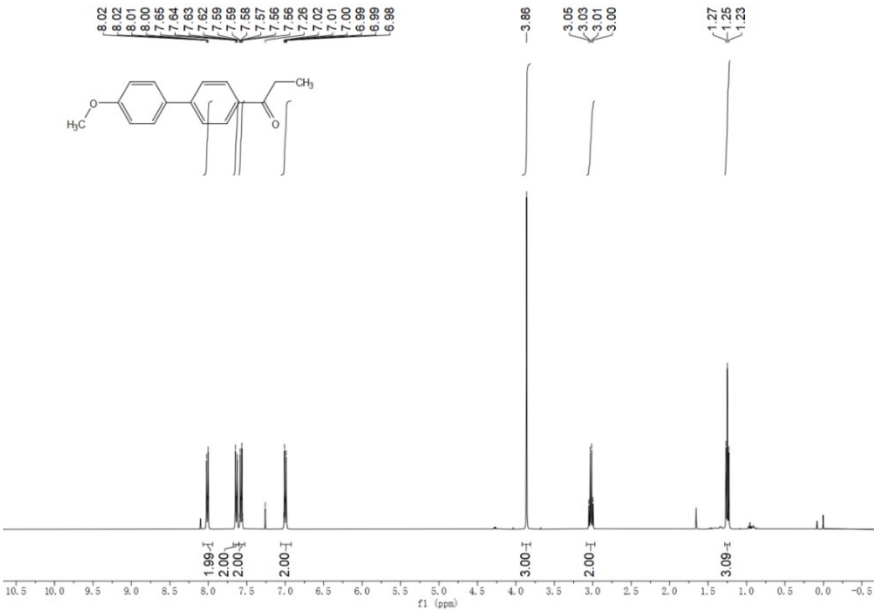


^{1}H NMR ($CDCl_3$, 400 MHz) of **4b**

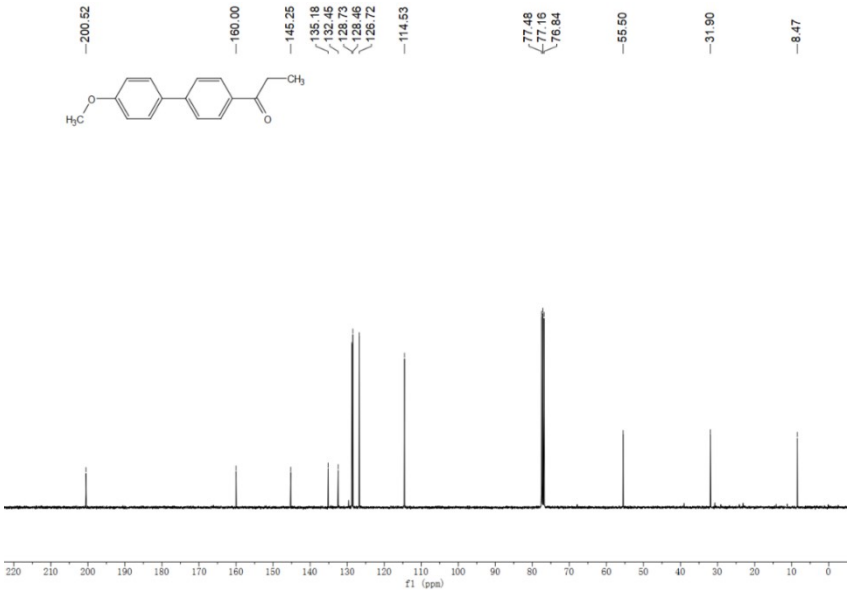


^{13}C NMR ($CDCl_3$, 100 MHz) of **4b**

1-(4'-methoxy-[1,1'-biphenyl]-4-yl)propan-1-one (4c)

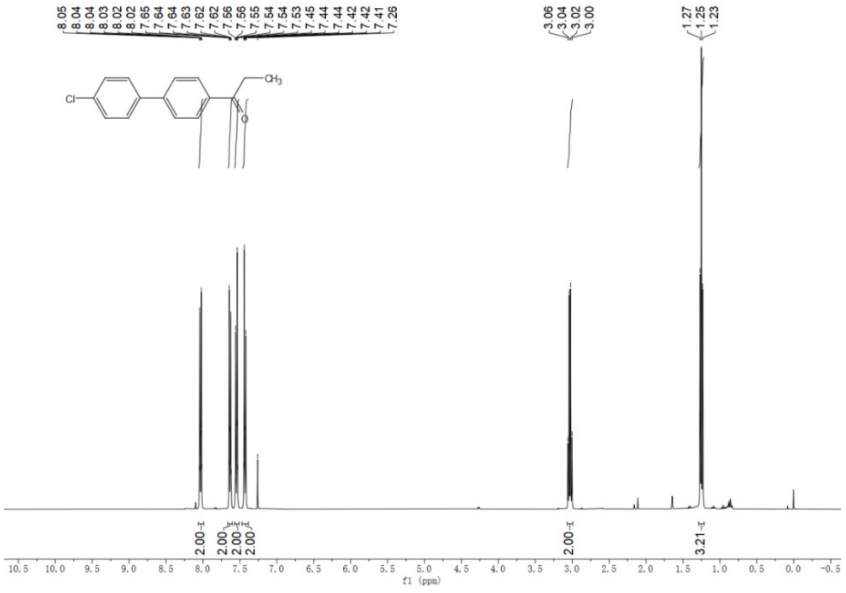


^{1}H NMR ($CDCl_3$, 400 MHz) of **4c**

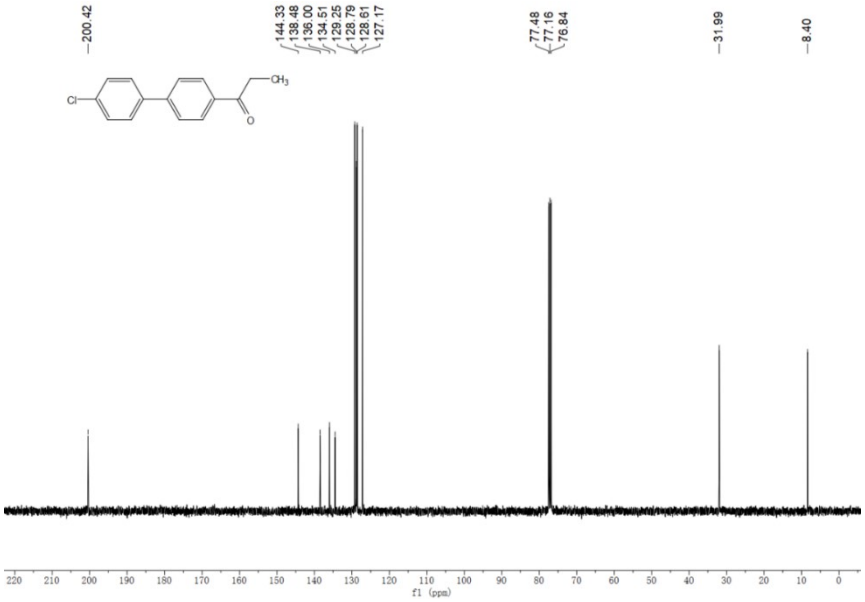


^{13}C NMR ($CDCl_3$, 100 MHz) of **4c**

1-(4'-chloro-[1,1'-biphenyl]-4-yl)propan-1-one (4d)

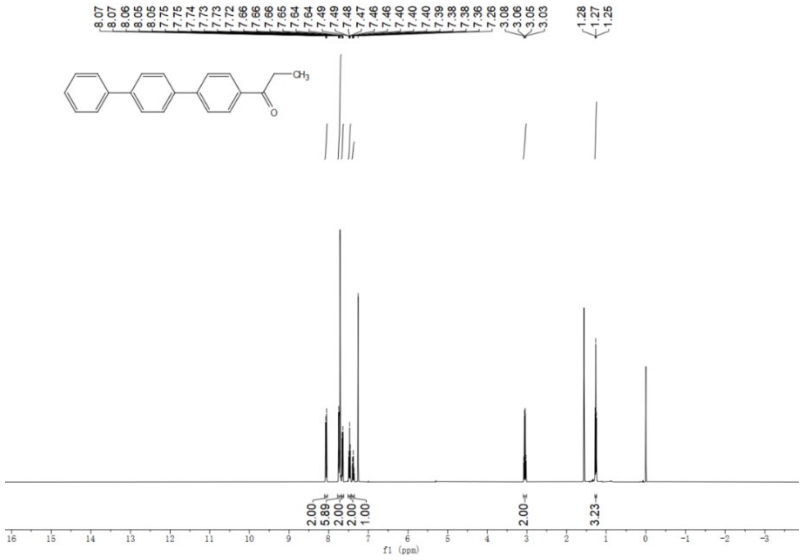


^{1}H NMR ($CDCl_3$, 400 MHz) of **4d**

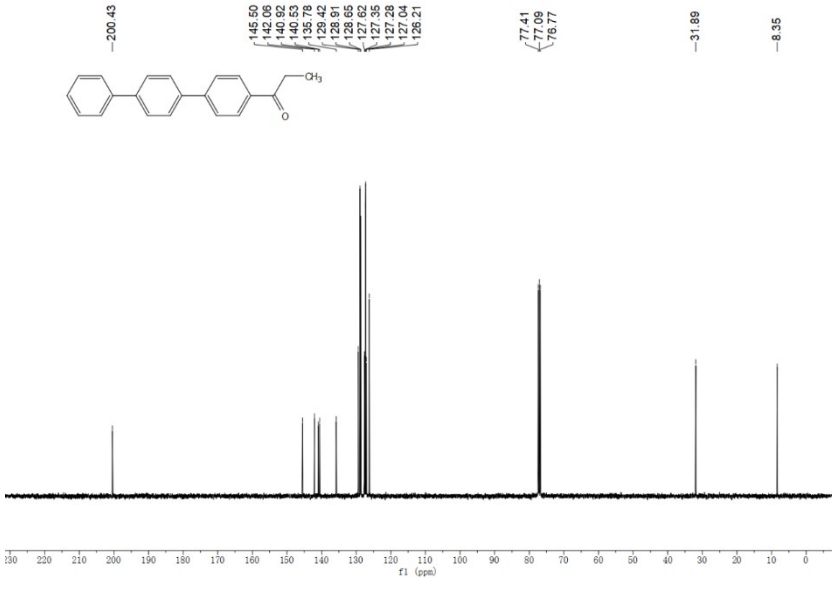


^{13}C NMR ($CDCl_3$, 100 MHz) of **4d**

1-([1,1':4',1''-terphenyl]-4-yl)propan-1-one (4e)

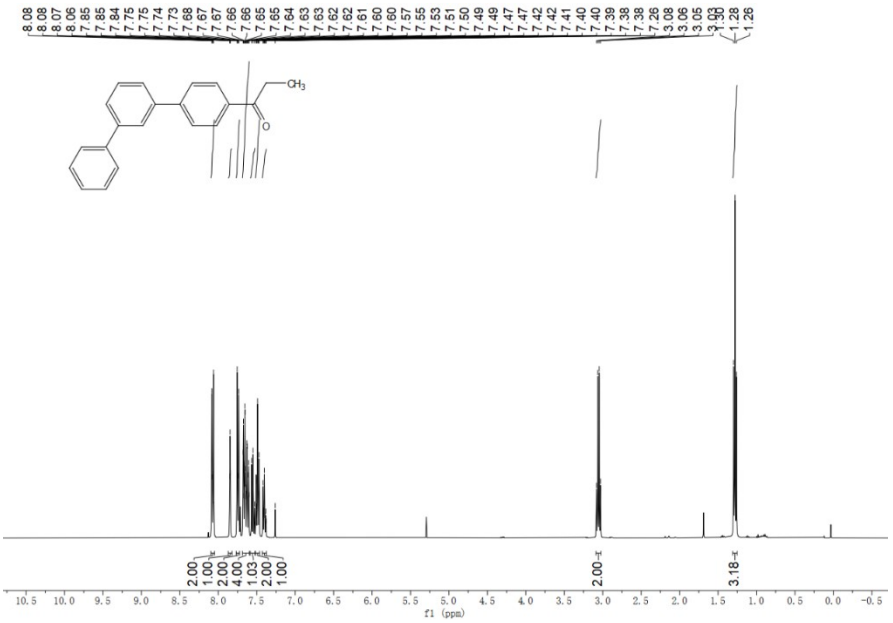


^{1}H NMR ($CDCl_3$, 400 MHz) of **4e**

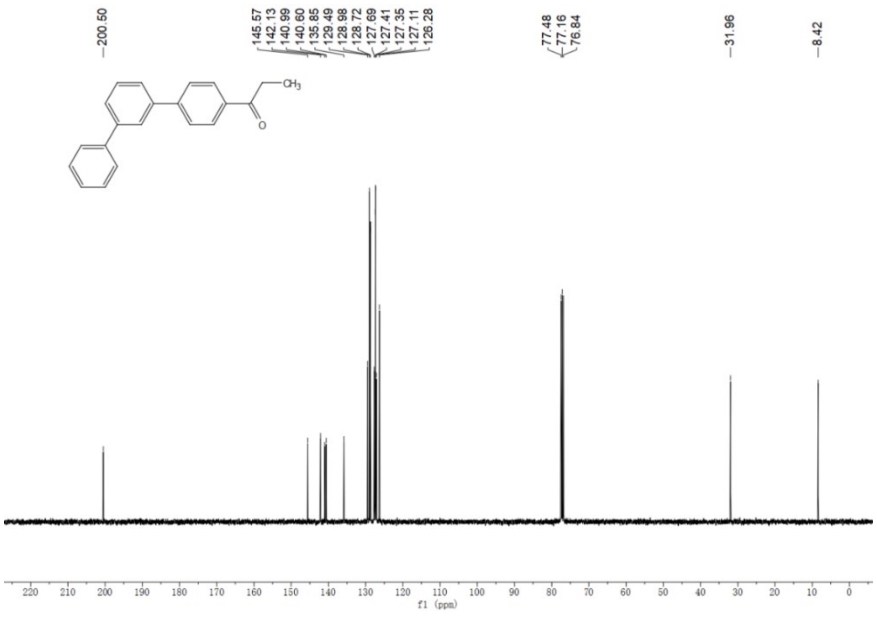


^{13}C NMR ($CDCl_3$, 100 MHz) of **4e**

1-([1,1':3',1''-terphenyl]-4-yl)propan-1-one(4f)

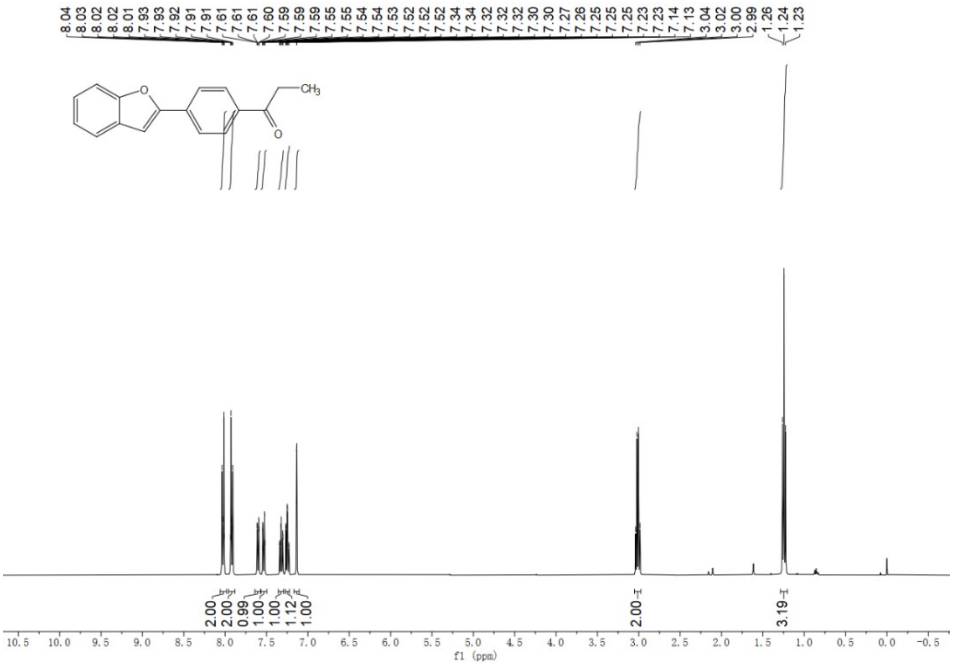


^{1}H NMR ($CDCl_3$, 400 MHz) of **4f**

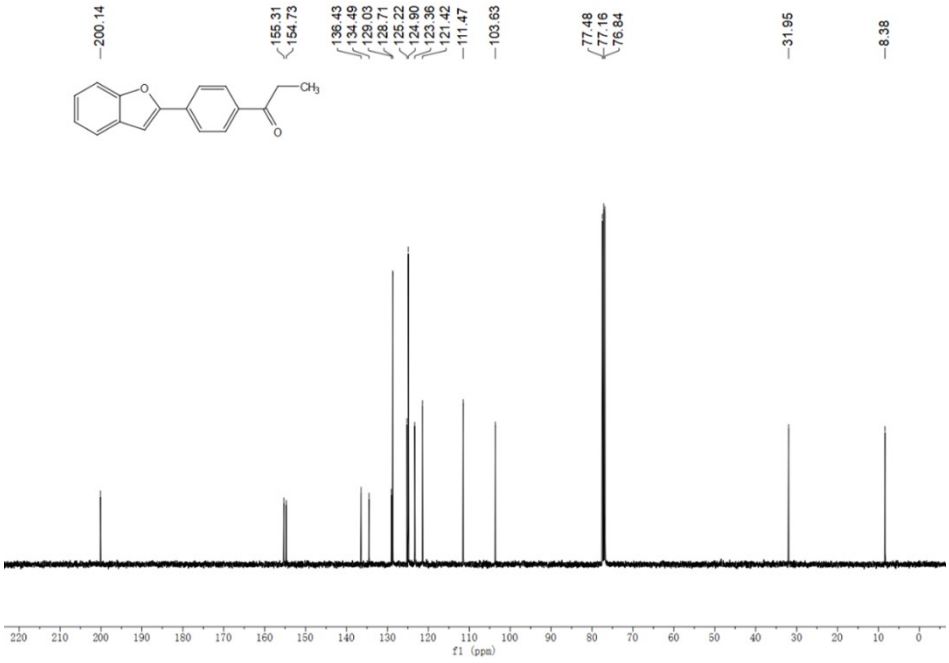


^{13}C NMR ($CDCl_3$, 100 MHz) of **4f**

1-(4-(benzofuran-2-yl)phenyl)propan-1-one (4g)

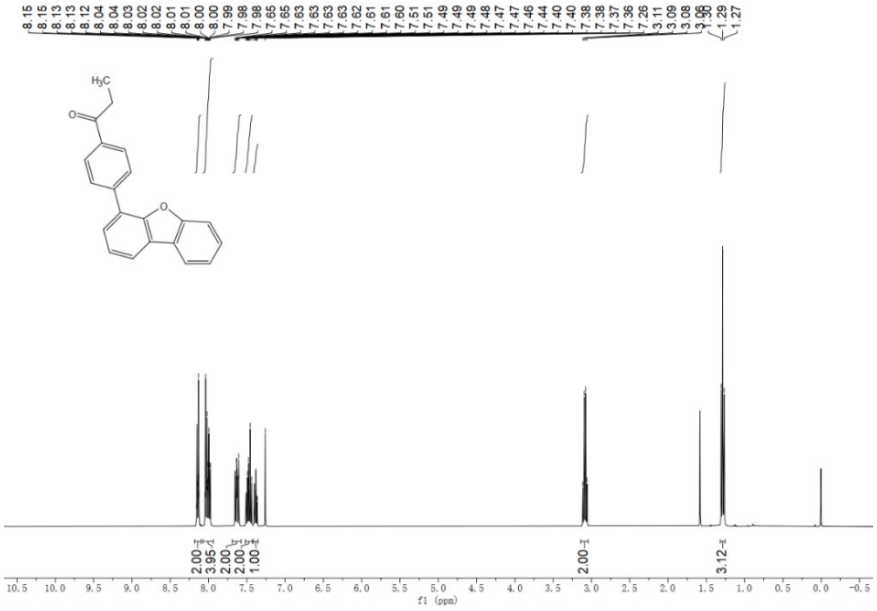


^{1}H NMR ($CDCl_3$, 400 MHz) of **4g**

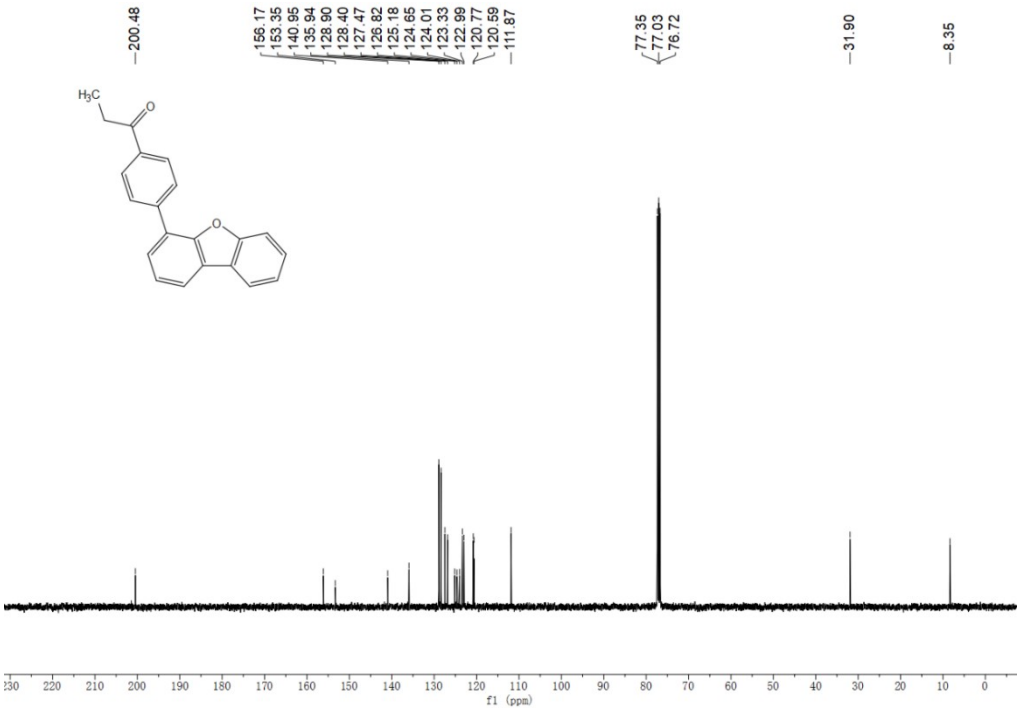


^{13}C NMR ($CDCl_3$, 100 MHz) of **4g**

1-(4-(dibenzo[b,d]furan-4-yl)phenyl)propan-1-one (4h)

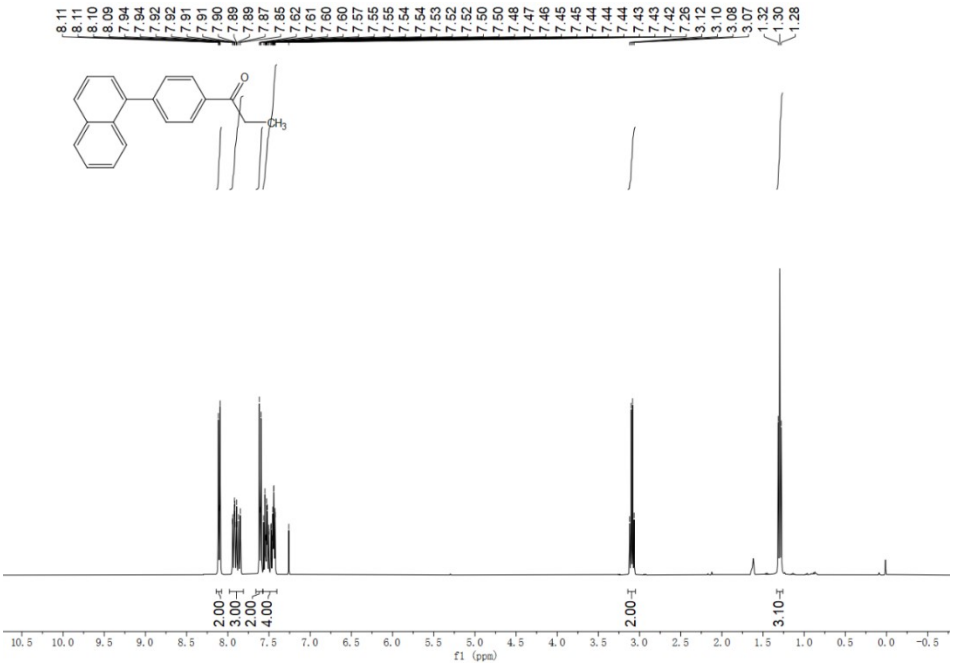


^{1}H NMR ($CDCl_3$, 400 MHz) of **4h**

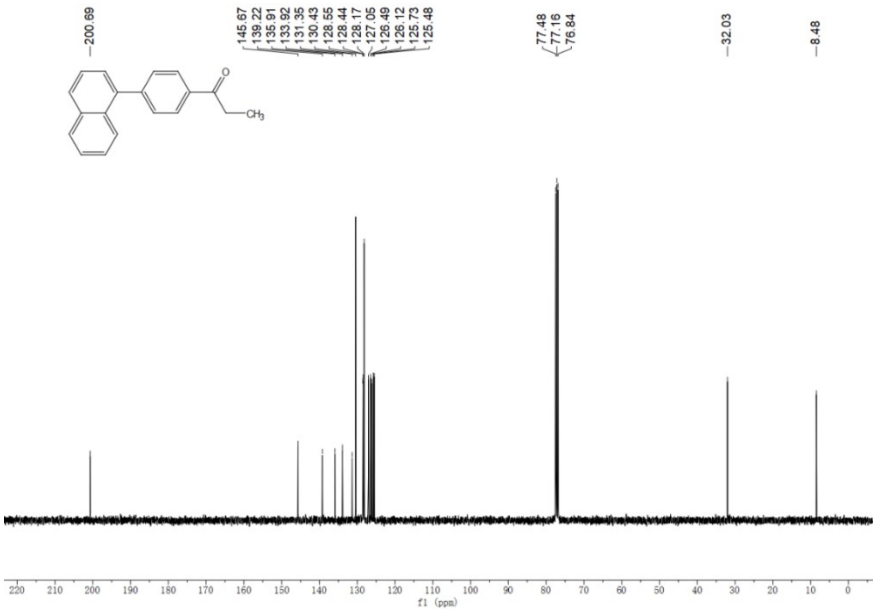


^{13}C NMR ($CDCl_3$, 100 MHz) of **4h**

1-(4-(naphthalen-1-yl)phenyl)propan-1-one(4i)

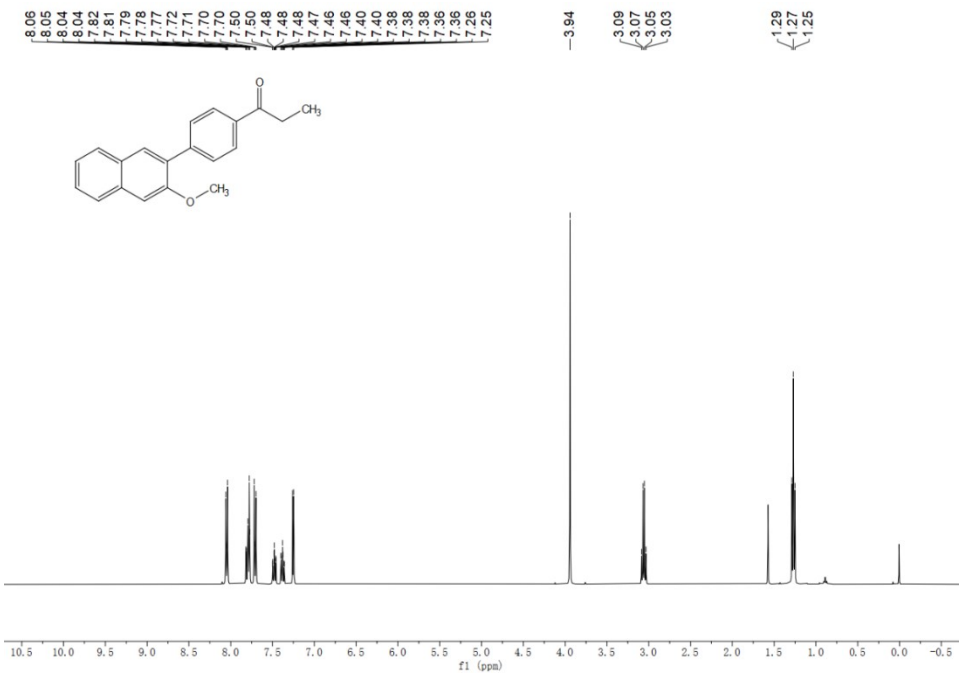


^{1}H NMR ($CDCl_3$, 400 MHz) of **4i**

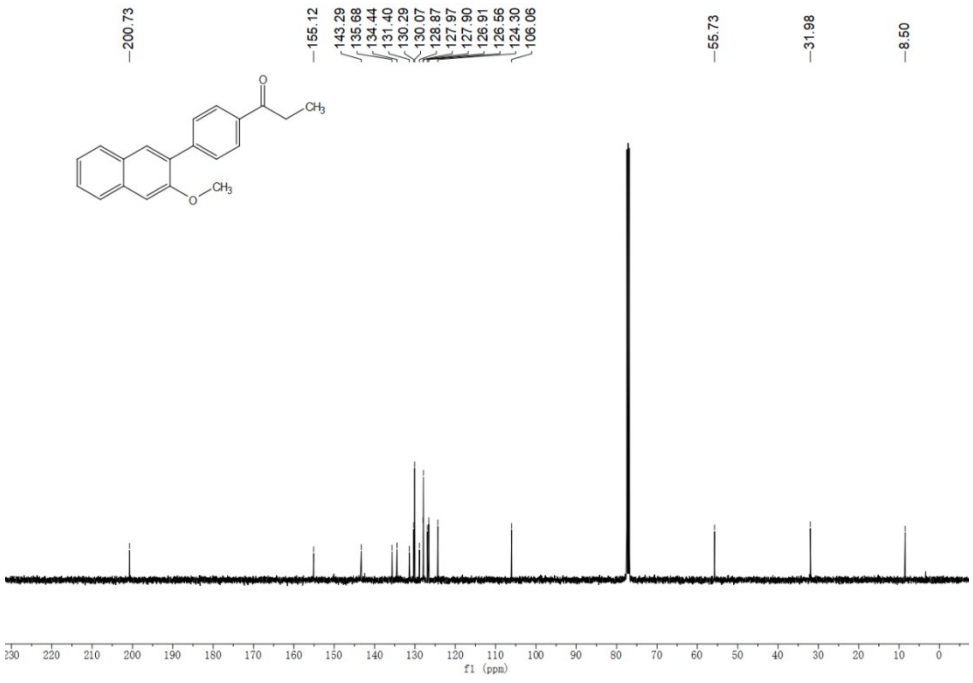


^{13}C NMR ($CDCl_3$, 100 MHz) of **4i**

1-(4-(3-methoxynaphthalen-2-yl)phenyl)propan-1-one (4j)



^{1}H NMR ($CDCl_3$, 400 MHz) of **4j**



^{13}C NMR ($CDCl_3$, 100 MHz) of **4j**