

Supporting Information

for

Palladacycles Derived from Arylphosphinamides for Mild Suzuki-Miyaura Cross-Couplings

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Contents

General information.....	S2
Experimental procedures.....	S2
Product characterization.....	S2
References.....	S15
Spectra of coupling products.....	S16

General Information

Unless otherwise stated, all starting materials were obtained from commercial supplies and used as received. Palladacyclic complex **3** were synthesized following the reported procedure.^[1] The ¹H NMR spectra were recorded at 300, 400 MHz in CDCl₃ and the ¹³C NMR spectra were recorded at 101 MHz in CDCl₃ or DMSO-d₆ with TMS as internal standard. All shifts are given in ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel with 100–200 mesh.

Experimental procedures

General procedure for cross-coupling under nitrogen atmosphere:

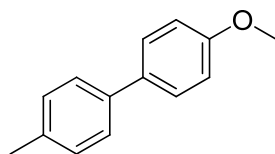
To a Schlenk tube equipped with a magnetic bar was charged solid aryl bromide or triflate (0.5 mmol), boronic acid (0.75 mmol), **3a** (1.0 mol%), anhydrous K₃PO₄ (1.5 mmol). The tube was then evacuated under vacuum and backfilled with N₂. EtOH (3.0 mL) was injected *via* syringe (the aryl bromide or triflate (0.5 mmol) was also added at this stage if it is liquid). The reaction mixture was stirred at rt or 50 °C until the arylbromide or triflate had disappeared as monitored by TLC. The reaction mixture was poured into water (30 mL) and then extracted with CH₂Cl₂ (20 mL × 3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated to dryness. The crude material was purified by flash chromatography on silica gel using a mixture of hexane and CH₂Cl₂ as eluents to give the desired cross-coupled products.

General procedure for cross-coupling under air atmosphere:

To a Schlenk tube equipped with a magnetic bar was charged solid aryl bromide or triflate (0.5 mmol), boronic acid (0.75 mmol), **3a** (1.0 mol%), anhydrous K₃PO₄ (1.5 mmol). EtOH (3.0 mL) was injected *via* syringe and the tube was sealed with a screw cap. The reaction mixture was stirred at rt until the arylbromide or triflate had disappeared as monitored by TLC. The reaction mixture was poured into water (30 mL) and then extracted with CH₂Cl₂ (20 mL × 3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated to dryness. The crude material was purified by flash chromatography on silica gel using a mixture of hexane and CH₂Cl₂ as eluents to give the desired cross-coupled products.

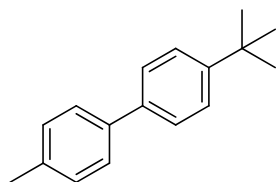
Product characterization

4-methoxy-4'-methyl-1,1'-biphenyl (**7a**)^[2]



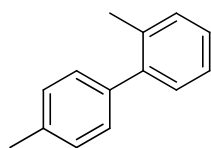
¹H NMR (300 MHz, CDCl₃) δ 7.53 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.25 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 2.40 (s, 3H).

4-(*tert*-butyl)-4'-methyl-1,1'-biphenyl (7b)^[3,4]



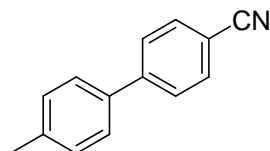
¹H NMR (300 MHz, CDCl₃) δ 7.57–7.44 (m, 6H), 7.27–7.23 (m, 2H), 2.41 (s, 3H), 1.38 (s, 9H).

2,4'-dimethyl-1,1'-biphenyl (7c)^[5]



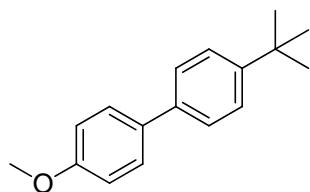
¹H NMR (300 MHz, CDCl₃) δ 7.30–7.22 (m, 8H), 2.43 (s, 3H), 2.30 (s, 3H).

4'-methyl-[1,1'-biphenyl]-4-carbonitrile (7d)^[4]



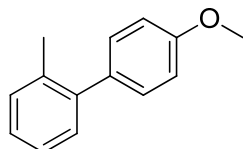
¹H NMR (300 MHz, CDCl₃) δ 7.75–7.66 (m, 4H), 7.52 (d, *J* = 9.0 Hz, 2H), 7.31 (d, *J* = 9.0 Hz, 2H), 2.43 (s, 3H).

4-(*tert*-butyl)-4'-methoxy-1,1'-biphenyl (7e)^[3]



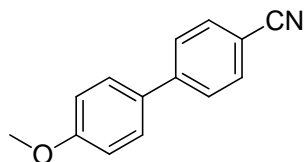
¹H NMR (300 MHz, CDCl₃) δ 7.57–7.44 (m, 6H), 7.01–6.96 (m, 2H), 3.87 (s, 3H), 1.38 (s, 9H).

4'-methoxy-2-methyl-1,1'-biphenyl (7f)^[6,7]



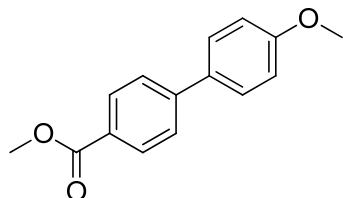
¹H NMR (300 MHz, CDCl₃) δ 7.33–7.25 (m, 6H), 7.03–6.96 (m, 2H), 3.89 (s, 3H), 2.32 (s, 3H).

4'-methoxy-[1,1'-biphenyl]-4-carbonitrile (7g)^[8]



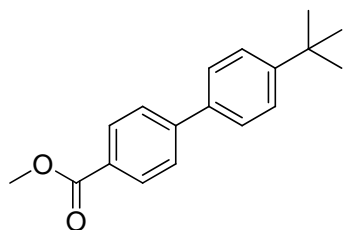
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.74–7.63 (m, 4H), 7.58–7.53 (m, 2H), 7.06–6.99 (m, 2H), 3.89 (s, 3H).

methyl 4'-methoxy-[1,1'-biphenyl]-4-carboxylate (7h)^[2,8,9]



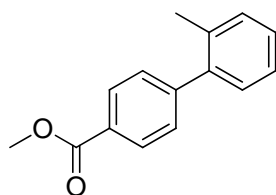
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.10 (d, $J = 9.0$ Hz, 2H), 7.65–7.59 (m, 4H), 7.02 (d, $J = 9.0$ Hz, 2H), 3.95 (s, 3H), 3.88 (s, 3H).

methyl 4'-(tert-butyl)-[1,1'-biphenyl]-4-carboxylate (7i)^[10]



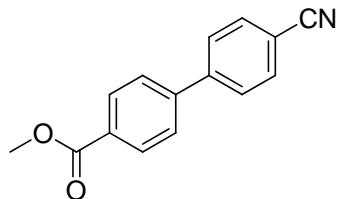
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.12 (d, $J = 9.0$ Hz, 2H), 7.68 (d, $J = 9.0$ Hz, 2H), 7.60 (d, $J = 9.0$ Hz, 2H), 7.52 (d, $J = 9.0$ Hz, 2H), 3.96 (s, 3H), 1.39 (s, 9H).

methyl 2'-methyl-[1,1'-biphenyl]-4-carboxylate (7j)^[8]



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.06 (d, $J = 9.0$ Hz, 2H), 7.37 (d, $J = 9.0$ Hz, 2H), 7.27–7.18 (m, 4H), 3.92 (s, 3H), 2.24 (s, 3H).

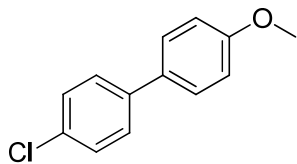
methyl 4'-cyano-[1,1'-biphenyl]-4-carboxylate (7k)^[8,9]



$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.19 (d, $J = 9.0$ Hz, 2H), 7.81–7.71 (m, 4H), 7.68 (d, J

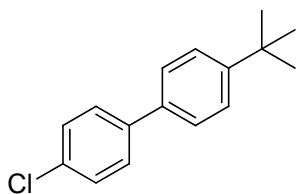
= 9.0 Hz, 2H), 3.97 (s, 3H).

4-chloro-4'-methoxy-1,1'-biphenyl (7l)^[11]



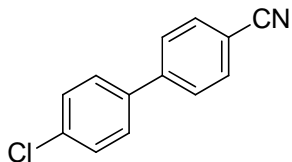
¹H NMR (300 MHz, CDCl₃) δ 7.54–7.46 (m, 4H), 7.43–7.36 (m, 2H), 7.02–6.96 (m, 2H), 3.87 (s, 3H).

4-(tert-butyl)-4'-chloro-1,1'-biphenyl (7m)



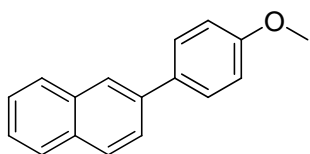
¹H NMR (300 MHz, CDCl₃) δ 7.56–7.45 (m, 6H), 7.43–7.37 (m, 2H), 1.38 (s, 9H).
¹H NMR (300 MHz, CDCl₃) δ 7.56–7.45 (m, 6H), 7.43–7.37 (m, 2H), 1.38 (s, 9H).
¹³C NMR (101 MHz, CDCl₃) δ 150.6, 139.4, 136.9, 132.9, 128.7, 128.1, 126.5, 125.7, 34.5, 31.2.

4'-chloro-[1,1'-biphenyl]-4-carbonitrile (7n)^[9]



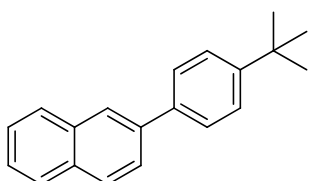
¹H NMR (300 MHz, CDCl₃) δ 7.78–7.64 (m, 4H), 7.57–7.45 (m, 4H).

2-(4-methoxyphenyl)naphthalene (7o)^[2,4,6,7]



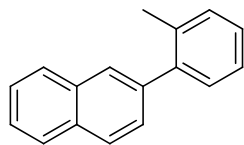
¹H NMR (300 MHz, CDCl₃) δ 8.01 (s, 1H), 7.94–7.84 (m, 3H), 7.78–7.65 (m, 3H), 7.55–7.45 (m, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H).

2-(4-(tert-butyl)phenyl)naphthalene (7p)^[3]



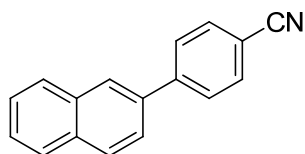
^1H NMR (300 MHz, CDCl_3) δ 8.06 (s, 1H), 7.95–7.85 (m, 3H), 7.80–7.75 (m, 1H), 7.70 (d, $J = 9.0$ Hz, 2H), 7.57–7.46 (m, 4H), 1.41 (s, 9H).

2-(*o*-tolyl)naphthalene (7q)^[2,6]



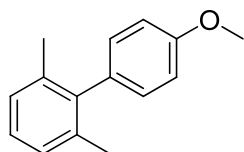
^1H NMR (400 MHz, CDCl_3) δ 7.91–7.84 (m, 3H), 7.77 (s, 1H), 7.53–7.45 (m, 3H), 7.35–7.25 (m, 4H), 2.31 (s, 3H).

4-(naphthalen-2-yl)benzotrile (7r)^[12]



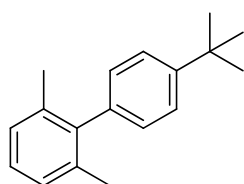
^1H NMR (300 MHz, CDCl_3) δ 8.08 (s, 1H), 8.00–7.70 (m, 8H), 7.60–7.54 (m, 2H).

4'-methoxy-2,6-dimethyl-1,1'-biphenyl (7s)^[7]



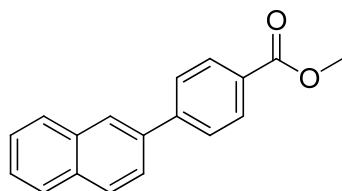
^1H NMR (300 MHz, CDCl_3) δ 7.18–7.05 (m, 5H), 6.98 (d, $J = 6$ Hz, 2H), 3.88 (s, 3H), 2.06 (s, 6H).

4'-(*tert*-butyl)-2,6-dimethyl-1,1'-biphenyl (7t)^[13]



^1H NMR (300 MHz, CDCl_3) δ 7.46–7.41 (m, 2H), 7.21–7.05 (m, 5H), 2.06 (s, 6H), 1.39 (s, 9H).

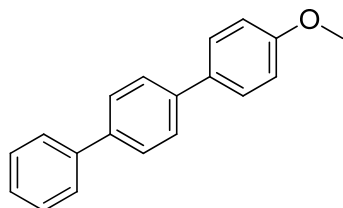
methyl 4-(naphthalen-2-yl)benzoate (7u)^[6]



^1H NMR (300 MHz, CDCl_3) δ 8.20–8.09 (m, 3H), 7.99–7.87 (m, 3H), 7.85–7.76 (m,

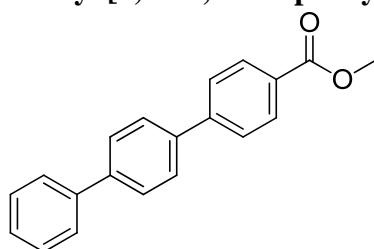
3H), 7.59–7.50 (m, 2H), 3.98 (s, 3H).

4-methoxy-1,1':4',1''-terphenyl (7v) ^[2,7]



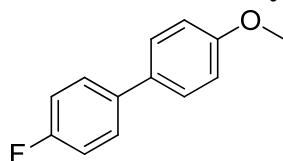
¹H NMR (300 MHz, CDCl₃) δ 7.70–7.57 (m, 8H), 7.52–7.44 (m, 2H), 7.41–7.34 (m, 1H), 7.02 (d, *J* = 6.0 Hz, 2H), 3.89 (s, 3H).

methyl [1,1':4',1''-terphenyl]-4-carboxylate (7w) ^[14]



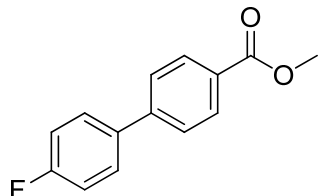
¹H NMR (300 MHz, CDCl₃) δ 8.15 (d, *J* = 9.0 Hz, 2H), 7.77–7.64 (m, 8H), 7.54–7.45 (m, 2H), 7.45–7.36 (m, 1H), 3.97 (s, 3H).

4-fluoro-4'-methoxy-1,1'-biphenyl (7x) ^[2,6,11]



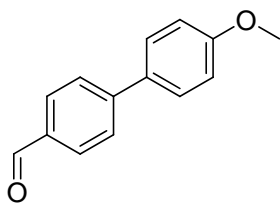
¹H NMR (300 MHz, CDCl₃) δ 7.55–7.46 (m, 4H), 7.16–7.06 (m, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H).

methyl 4'-fluoro-[1,1'-biphenyl]-4-carboxylate (7y) ^[2]



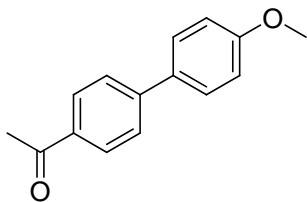
¹H NMR (300 MHz, CDCl₃) δ 8.14–8.10 (m, 2H), 7.65–7.58 (m, 4H), 7.21–7.13 (m, 2H), 3.96 (s, 3H).

4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (7z) ^[15]



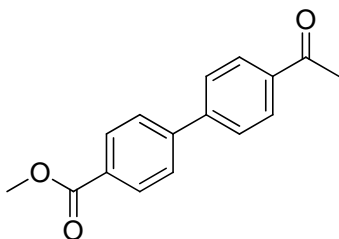
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 10.06 (s, 1H), 7.95 (d, $J = 9.0$ Hz, 2H), 7.74 (d, $J = 9.0$ Hz, 2H), 7.62 (d, $J = 9.0$ Hz, 2H), 7.04 (d, $J = 9.0$ Hz, 2H), 3.89 (s, 3H).

1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethanone (7aa)^[2]



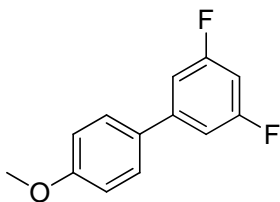
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.03 (d, $J = 9.0$ Hz, 2H), 7.67 (d, $J = 9.0$ Hz, 2H), 7.61 (d, $J = 9.0$ Hz, 2H), 7.03 (d, $J = 9.0$ Hz, 2H), 3.89 (s, 3H), 2.65 (s, 3H).

methyl 4'-acetyl-[1,1'-biphenyl]-4-carboxylate (7ab)^[9]



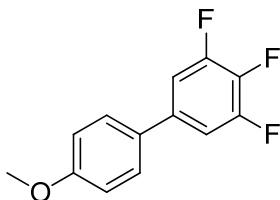
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.14 (d, $J = 6.0$ Hz, 2H), 8.06 (d, $J = 6.0$ Hz, 2H), 7.71 (t, $J = 6.0$ Hz, 4H), 3.95 (s, 3H), 2.65 (s, 3H).

3,5-difluoro-4'-methoxy-1,1'-biphenyl (10a)^[16]



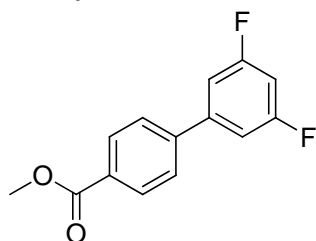
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.51 (d, $J = 9.0$ Hz, 2H), 7.13–6.96 (m, 4H), 6.80–6.69 (m, 1H), 3.87 (s, 3H).

3,4,5-trifluoro-4'-methoxy-1,1'-biphenyl (10b)^[17]



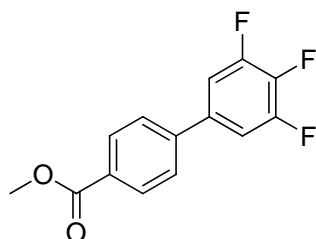
^1H NMR (300 MHz, CDCl_3) δ 7.45 (d, $J = 9.0$ Hz, 2H), 7.20–7.09 (m, 2H), 7.00 (d, $J = 9.0$ Hz, 2H), 3.87 (s, 3H).

methyl 3',5'-difluoro-[1,1'-biphenyl]-4-carboxylate (10c)



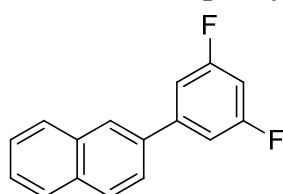
^1H NMR (300 MHz, CDCl_3) δ 8.14 (d, $J = 9.0$ Hz, 2H), 7.64 (d, $J = 9.0$ Hz, 2H), 7.20–7.10 (m, 2H), 6.90–6.80 (m, 1H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.6, 163.4 (dd, $J = 13.1, 249.5$ Hz), 143.3 (t, $J = 10.1$ Hz), 143.1, 130.3, 130.1, 127.0, 110.2 (dd, $J = 7.1, 19.2$ Hz), 103.35 (t, $J = 25.3$ Hz), 52.2.

methyl 3',4',5'-trifluoro-[1,1'-biphenyl]-4-carboxylate (10d)



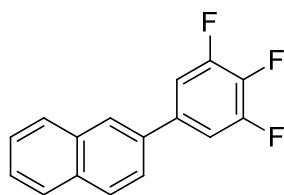
^1H NMR (300 MHz, CDCl_3) δ 8.14 (d, $J = 9.0$ Hz, 2H), 7.59 (d, $J = 9.0$ Hz, 2H), 7.29–7.20 (m, 2H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.5, 151.5 (dd, $J = 4.0, 9.1, 252.5$ Hz), 142.4, 139.8 (td, $J = 15.2, 254.5$ Hz), 136.1, 130.3, 130.1, 126.8, 111.3 (dd, $J = 6.1, 16.2$ Hz), 52.2.

2-(3,5-difluorophenyl)naphthalene (10e)



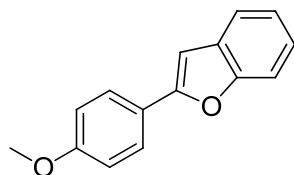
^1H NMR (300 MHz, CDCl_3) δ 8.07–7.86 (m, 4H), 7.74–7.65 (m, 1H), 7.60–7.50 (m, 2H), 7.29–7.20 (m, 2H), 6.88–6.77 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.9 (dd, $J = 14.1, 249.5$ Hz), 144.0 (t, $J = 10.1$ Hz), 135.7, 133.0, 132.7, 128.4, 127.9, 127.2, 126.2, 126.1, 125.7, 124.4, 109.7 (dd, $J = 7.1, 18.2$ Hz), 102.1 (t, $J = 25.3$ Hz).

2-(3,4,5-trifluorophenyl)naphthalene (10f)



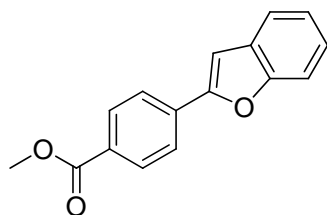
^1H NMR (300 MHz, CDCl_3) δ 8.00–7.86 (m, 4H), 7.67–7.51 (m, 3H), 7.39–7.30 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.0 (ddd, $J = 4.0, 10.1, 251.5$ Hz), 138.8 (td, $J = 15.2, 253.5$ Hz), 136.8, 135.0, 133.0, 132.5, 128.5, 127.8, 127.2, 126.3, 126.2, 125.5, 124.1, 110.8 (dd, $J = 6.1, 17.2$ Hz).

2-(4-methoxyphenyl)benzofuran (11a)^[18]



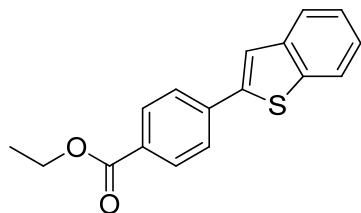
^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 6.0$ Hz, 2H), 7.54–7.45 (m, 2H), 7.26–7.15 (m, 2H), 6.95 (d, $J = 6.0$ Hz, 2H), 6.86 (s, 1H), 3.83 (s, 3H).

methyl 4-(benzofuran-2-yl)benzoate (11b)^[19]



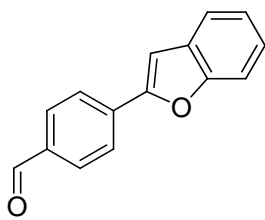
^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 9.0$ Hz, 2H), 7.95 (d, $J = 9.0$ Hz, 2H), 7.66–7.53 (m, 2H), 7.38–7.25 (m, 2H), 7.18 (s, 1H), 3.96 (s, 3H).

ethyl 4-(benzo[b]thiophen-2-yl)benzoate (11c)^[20]



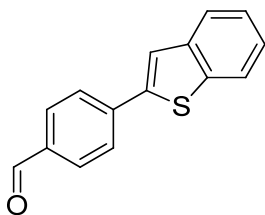
^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, $J = 9.0$ Hz, 2H), 7.89–7.76 (m, 4H), 7.68 (s, 1H), 7.43–7.33 (m, 2H), 4.43 (q, $J = 6.0$ Hz, 2H), 1.44 (t, $J = 6.0$ Hz, 3H).

4-(benzofuran-2-yl)benzaldehyde (11d)^[21]



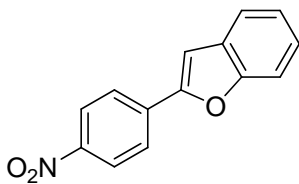
^1H NMR (300 MHz, CDCl_3) δ 10.06 (s, 1H), 8.05 (d, $J = 9.0$ Hz, 2H), 7.98 (d, $J = 9.0$ Hz, 2H), 7.68–7.55 (m, 2H), 7.40–7.25 (m, 2H), 7.23 (s, 1H).

4-(benzo[b]thiophen-2-yl)benzaldehyde (11e)^[22]



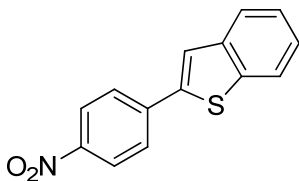
^1H NMR (300 MHz, CDCl_3) δ 10.06 (s, 1H), 7.98–7.82 (m, 6H), 7.73 (s, 1H), 7.44–7.35 (m, 2H).

2-(4-nitrophenyl)benzofuran (11f)^[18]



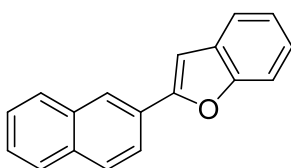
^1H NMR (300 MHz, CDCl_3) δ 8.34 (d, $J = 9.0$ Hz, 2H), 8.03 (d, $J = 9.0$ Hz, 2H), 7.70–7.55 (m, 2H), 7.43–7.25 (m, 3H).

2-(4-nitrophenyl)benzo[b]thiophene (11g)^[23]



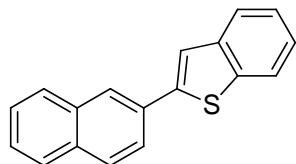
^1H NMR (300 MHz, CDCl_3) δ 8.32 (d, $J = 9.0$ Hz, 2H), 7.91–7.83 (m, 4H), 7.74 (s, 1H), 7.46–7.37 (m, 2H).

2-(naphthalen-2-yl)benzofuran (11h)^[6,24]



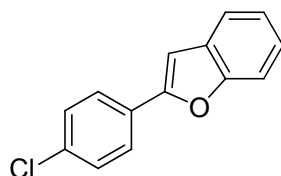
^1H NMR (300 MHz, CDCl_3) δ 8.40 (s, 1H), 7.98–7.85 (m, 4H), 7.66–7.48 (m, 4H), 7.37–7.24 (m, 2H), 7.17 (s, 1H).

2-(naphthalen-2-yl)benzo[b]thiophene (11i)^[20]



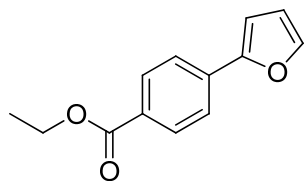
^1H NMR (300 MHz, CDCl_3) δ 8.17 (s, 1H), 7.94–7.81 (m, 6H), 7.70 (s, 1H), 7.58–7.48 (m, 2H), 7.43–7.33 (m, 2H).

2-(4-chlorophenyl)benzofuran (11j)^[24]



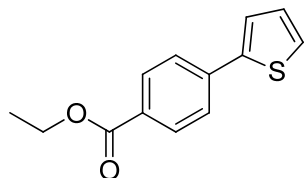
^1H NMR (300 MHz, CDCl_3) δ 7.82 (d, $J = 9.0$ Hz, 2H), 7.64–7.51 (m, 2H), 7.44 (d, $J = 9.0$ Hz, 2H), 7.35–7.22 (m, 2H), 7.04 (s, 1H).

ethyl 4-(furan-2-yl)benzoate (11k)^[5,25,26]



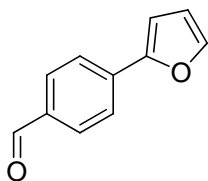
^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.55–7.53 (m, 1H), 6.81–6.78 (m, 1H), 6.55–6.50 (m, 1H), 4.40 (q, $J = 8.0$ Hz, 2H), 1.42 (t, $J = 8.0$ Hz, 3H).

ethyl 4-(thiophen-2-yl)benzoate (11l)^[5,26]



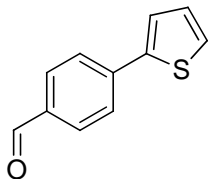
^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 9.0$ Hz, 2H), 7.69 (d, $J = 9.0$ Hz, 2H), 7.45–7.36 (m, 2H), 7.16–7.11 (m, 1H), 4.40 (q, $J = 6.0$ Hz, 2H), 1.43 (t, $J = 6.0$ Hz, 3H).

4-(furan-2-yl)benzaldehyde (11m)^[25]



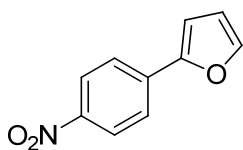
^1H NMR (300 MHz, CDCl_3) δ 10.01 (s, 1H), 7.92 (d, $J = 9.0$ Hz, 2H), 7.84 (d, $J = 9.0$ Hz, 2H), 7.58–7.56 (m, 1H), 6.88–6.86 (m, 1H), 6.57–6.53 (m, 1H).

4-(thiophen-2-yl)benzaldehyde (11n)^[23]



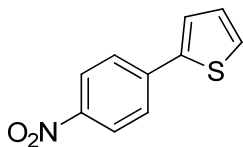
^1H NMR (300 MHz, CDCl_3) δ 10.02 (s, 1H), 7.91 (d, $J = 6.0$ Hz, 2H), 7.79 (d, $J = 6.0$ Hz, 2H), 7.50–7.47 (m, 1H), 7.44–7.40 (m, 1H), 7.18–7.13 (m, 1H).

2-(4-nitrophenyl)furan (11o)^[25]



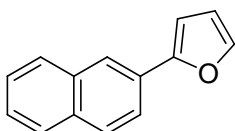
^1H NMR (300 MHz, CDCl_3) δ 8.27 (d, $J = 9.0$ Hz, 2H), 7.82 (d, $J = 9.0$ Hz, 2H), 7.61–7.58 (m, 1H), 6.92–6.88 (m, 1H), 6.59–6.56 (m, 1H).

2-(4-nitrophenyl)thiophene (11p)^[26]



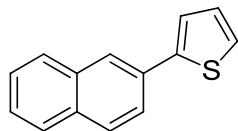
^1H NMR (300 MHz, CDCl_3) δ 8.26 (d, $J = 9.0$ Hz, 2H), 7.77 (d, $J = 9.0$ Hz, 2H), 7.51–7.44 (m, 2H), 7.20–7.15 (m, 1H).

2-(naphthalen-2-yl)furan (11q)^[6]



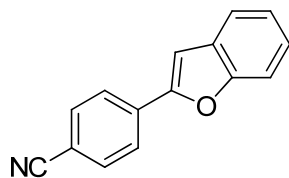
^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 7.88–7.75 (m, 4H), 7.54–7.42 (m, 3H), 6.79–6.76 (m, 1H), 6.54–6.51 (m, 1H).

2-(naphthalen-2-yl)thiophene (11r)^[27]



^1H NMR (300 MHz, CDCl_3) δ 8.15 (s, 1H), 7.88–7.75 (m, 4H), 7.54–7.42 (m, 3H), 6.79–6.76 (m, 1H), 6.54–6.51 (m, 1H).

4-(benzofuran-2-yl)benzonitrile (11s)^[18,25]



^1H NMR (300 MHz, CDCl_3) δ 7.98 (d, $J = 9.0$ Hz, 2H), 7.75 (d, $J = 9.0$ Hz, 2H), 7.68–7.53 (m, 2H), 7.41–7.28 (m, 2H), 7.20 (s, 1H).

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Spectra of coupling products

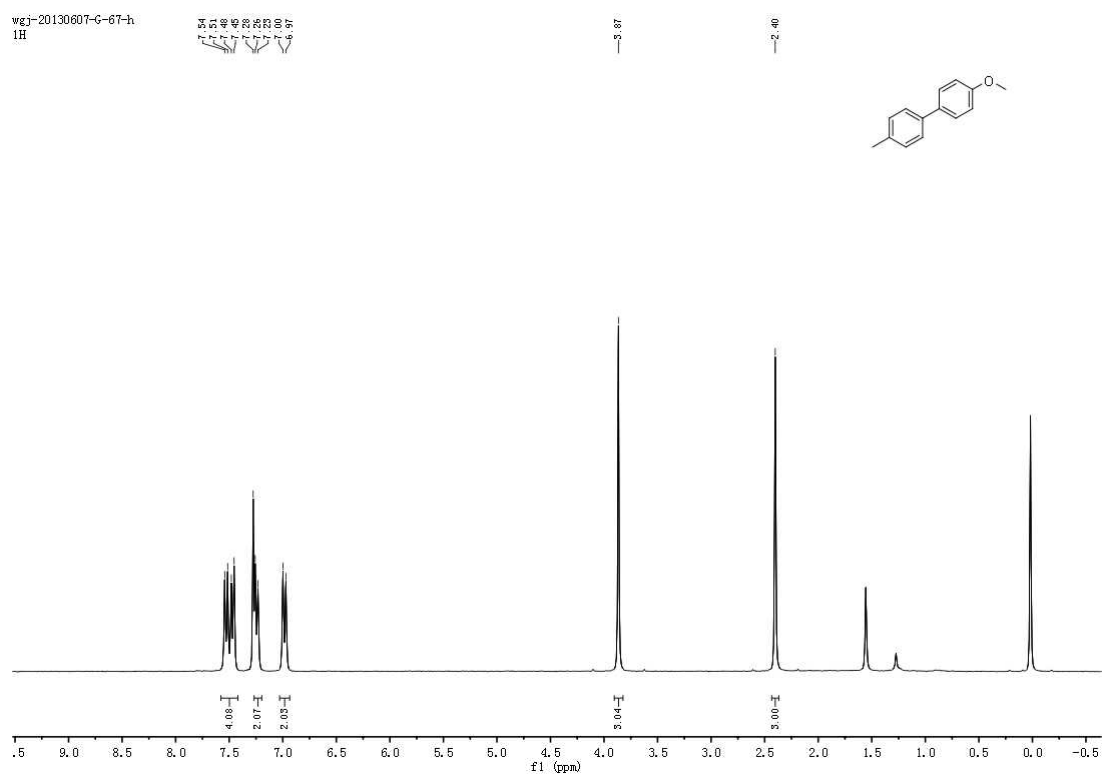


Figure S1. ^1H -NMR spectra of **7a**

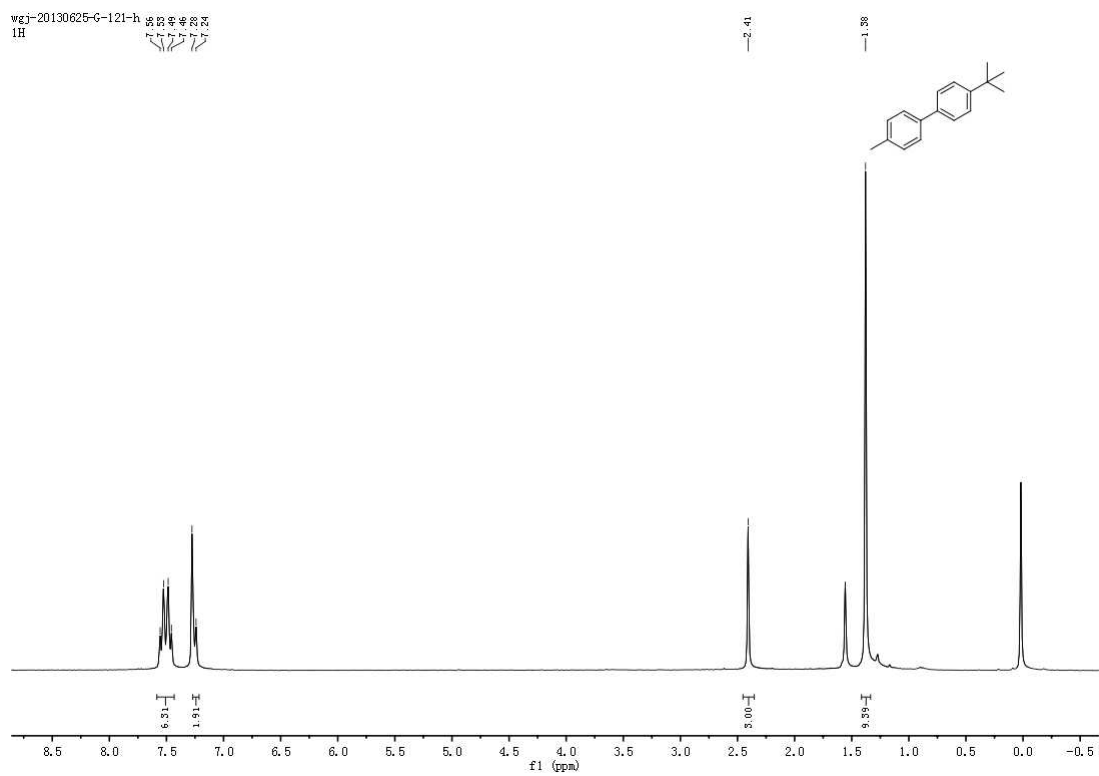


Figure S2. ^1H -NMR spectra of **7b**

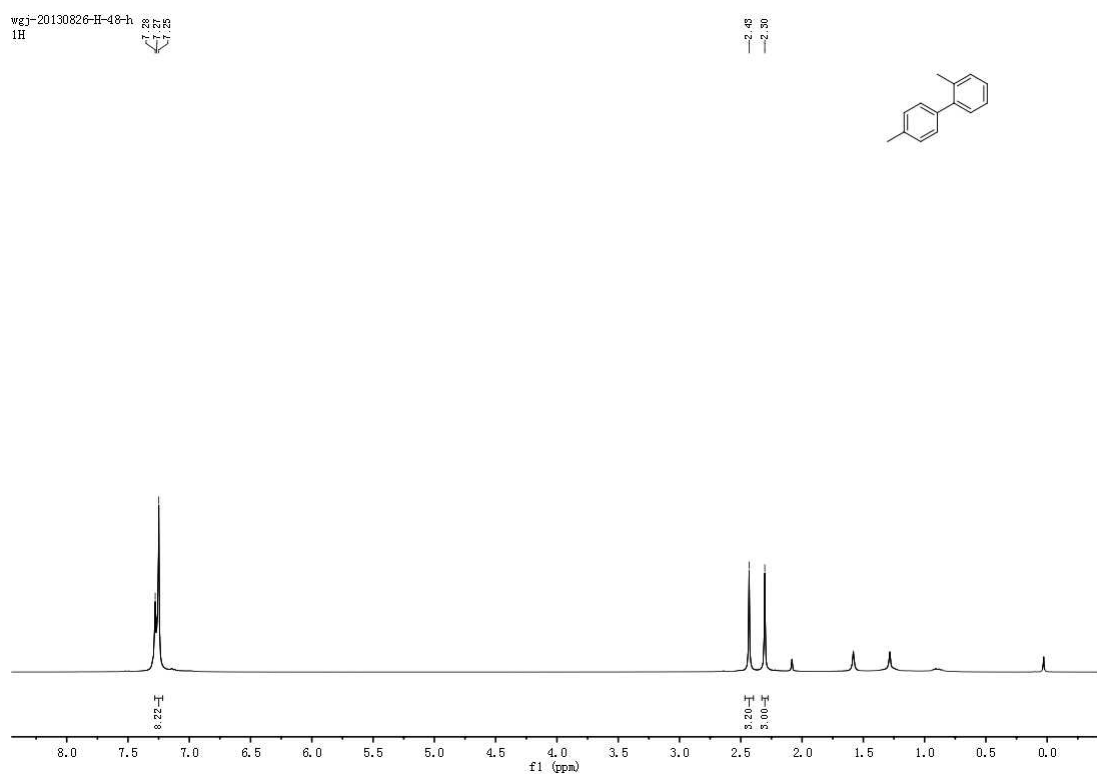


Figure S3. ^1H -NMR spectra of **7c**

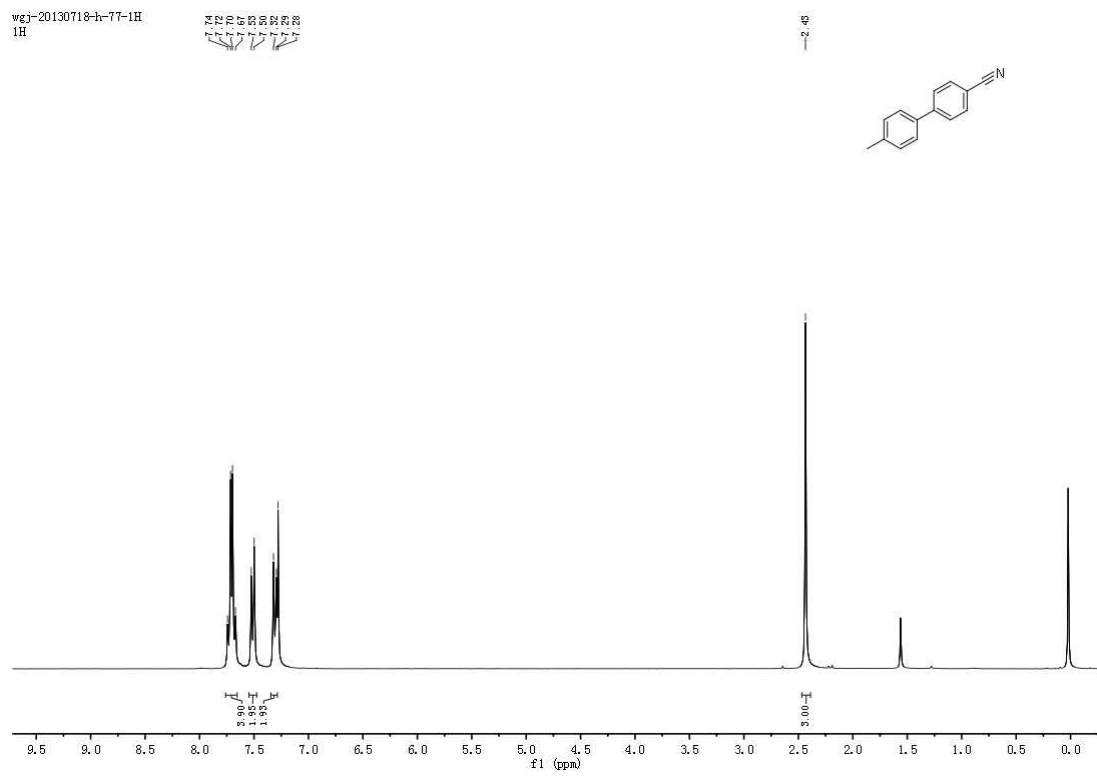


Figure S4. ^1H -NMR spectra of **7d**

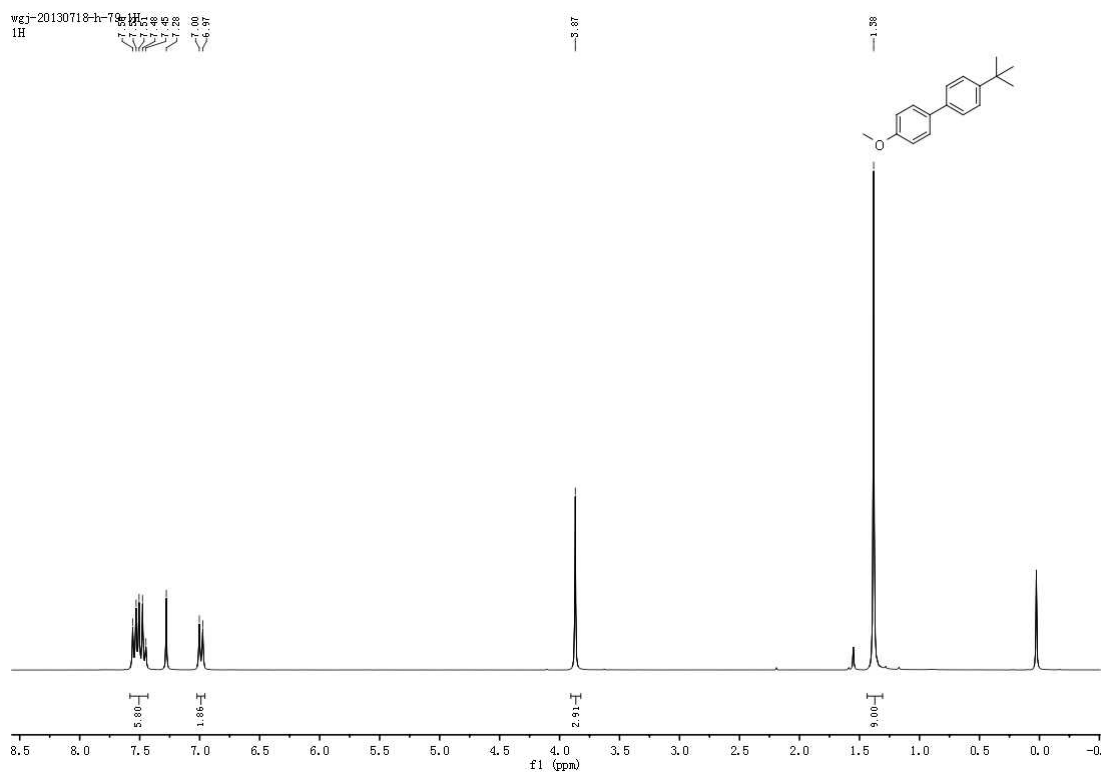


Figure S5. ^1H -NMR spectra of **7e**

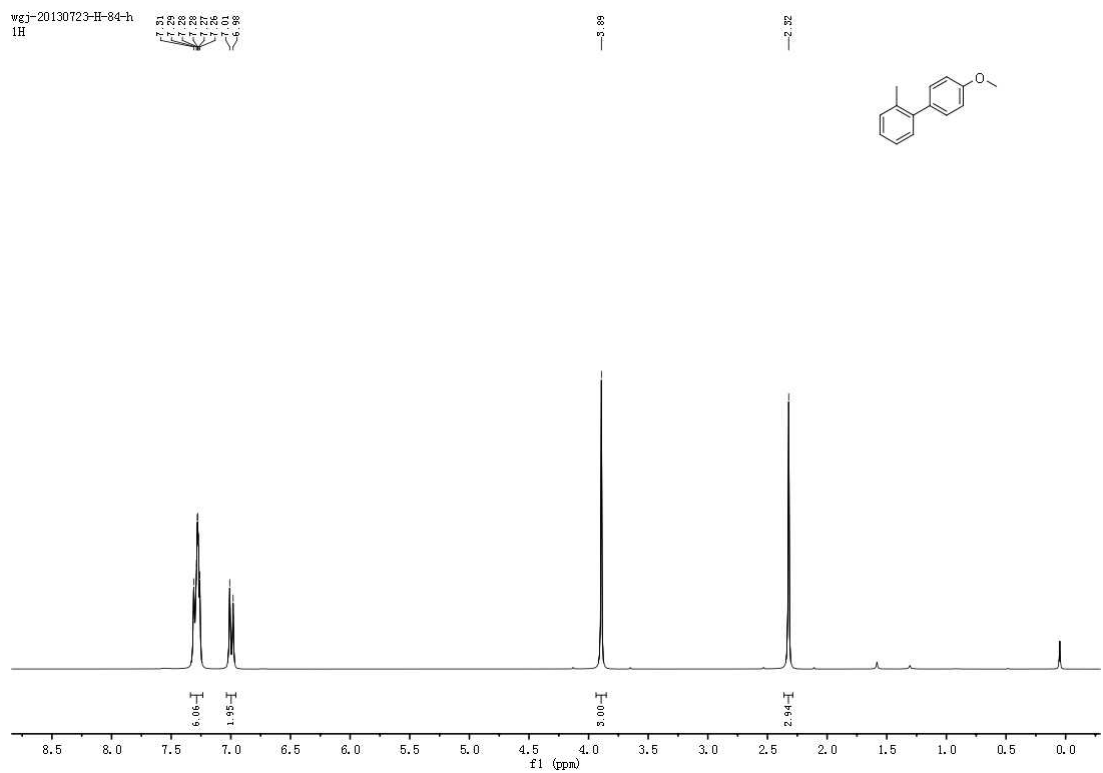


Figure S6. ^1H -NMR spectra of **7f**

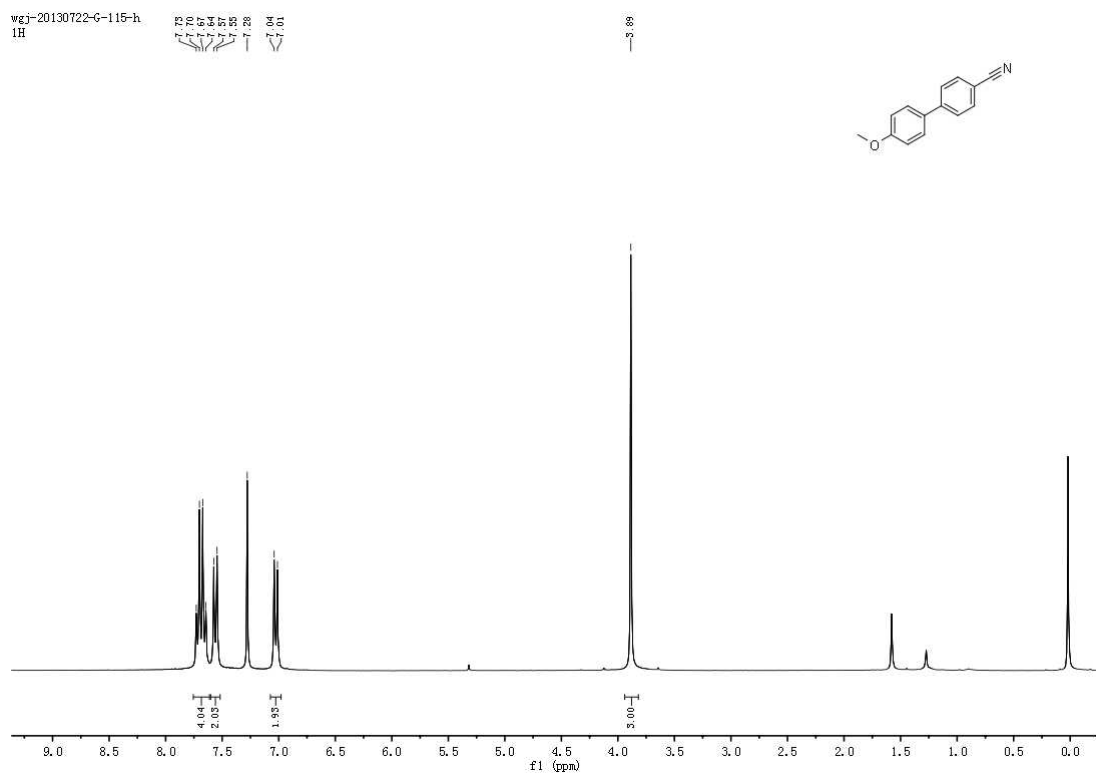


Figure S7. ^1H -NMR spectra of **7g**

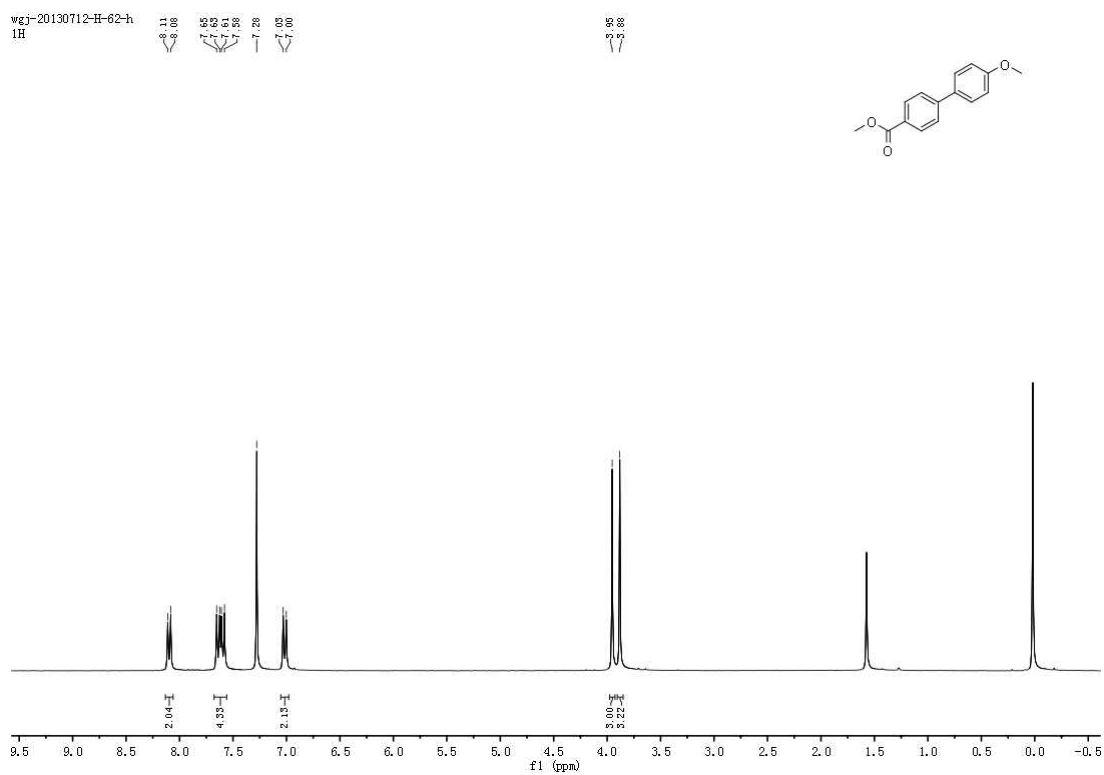
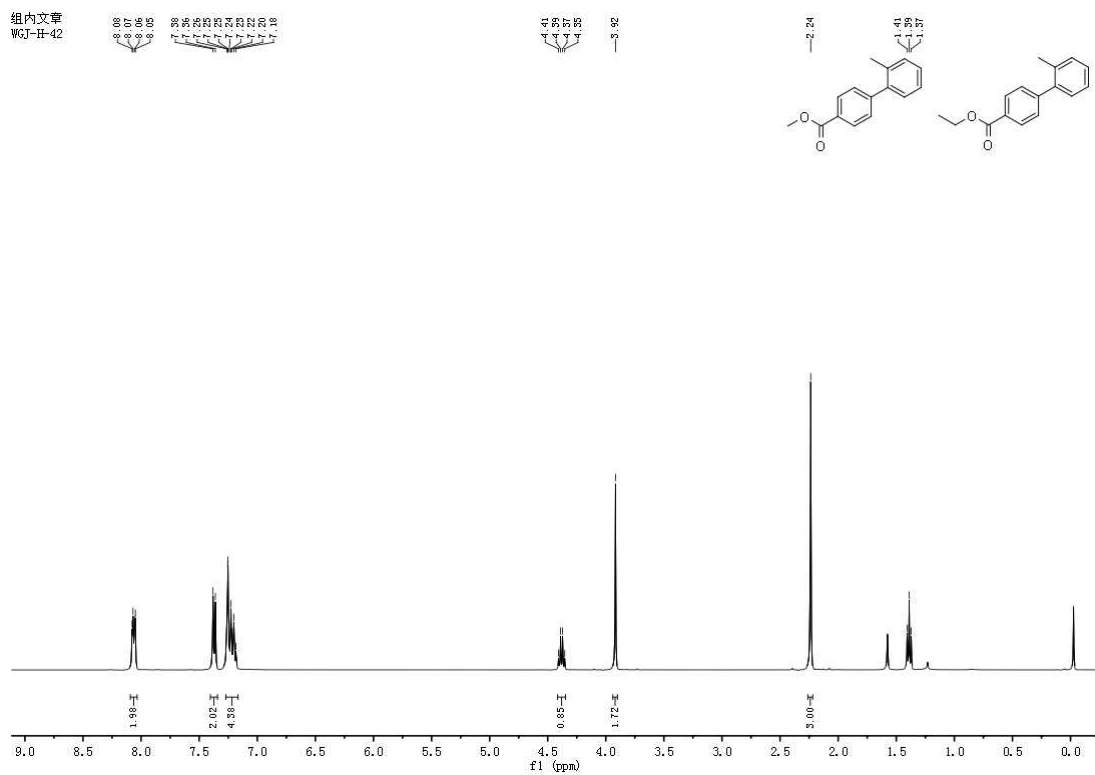
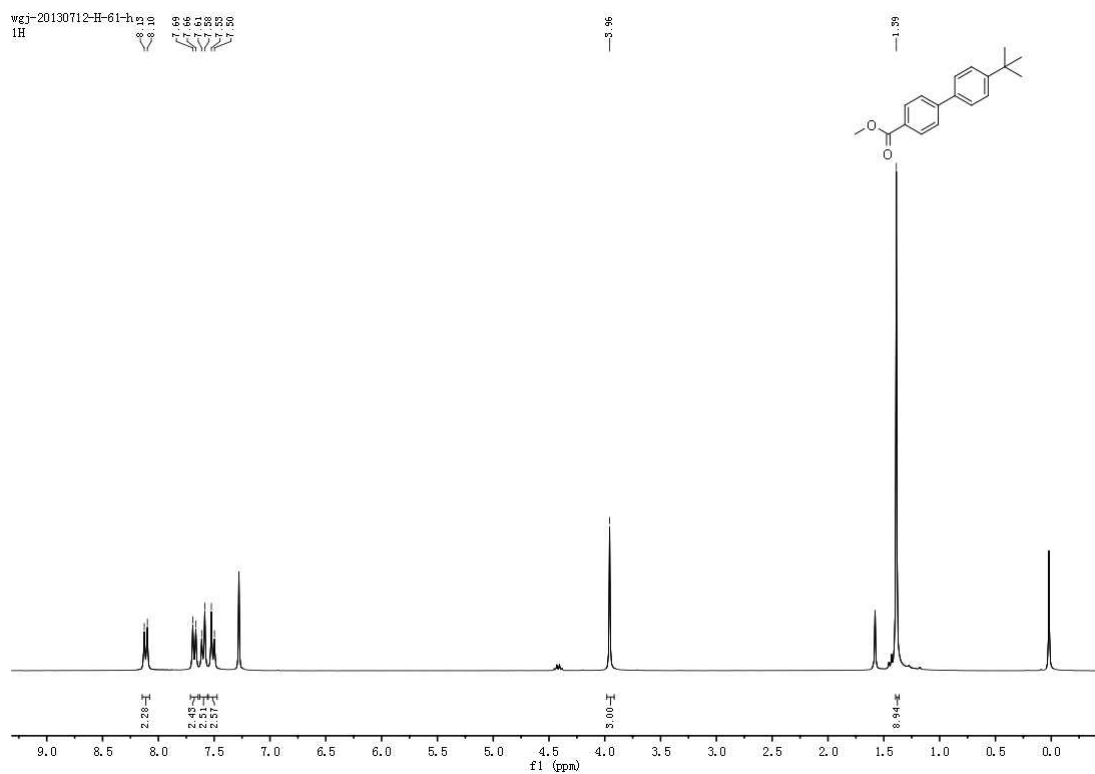


Figure S8. ^1H -NMR spectra of **7h**



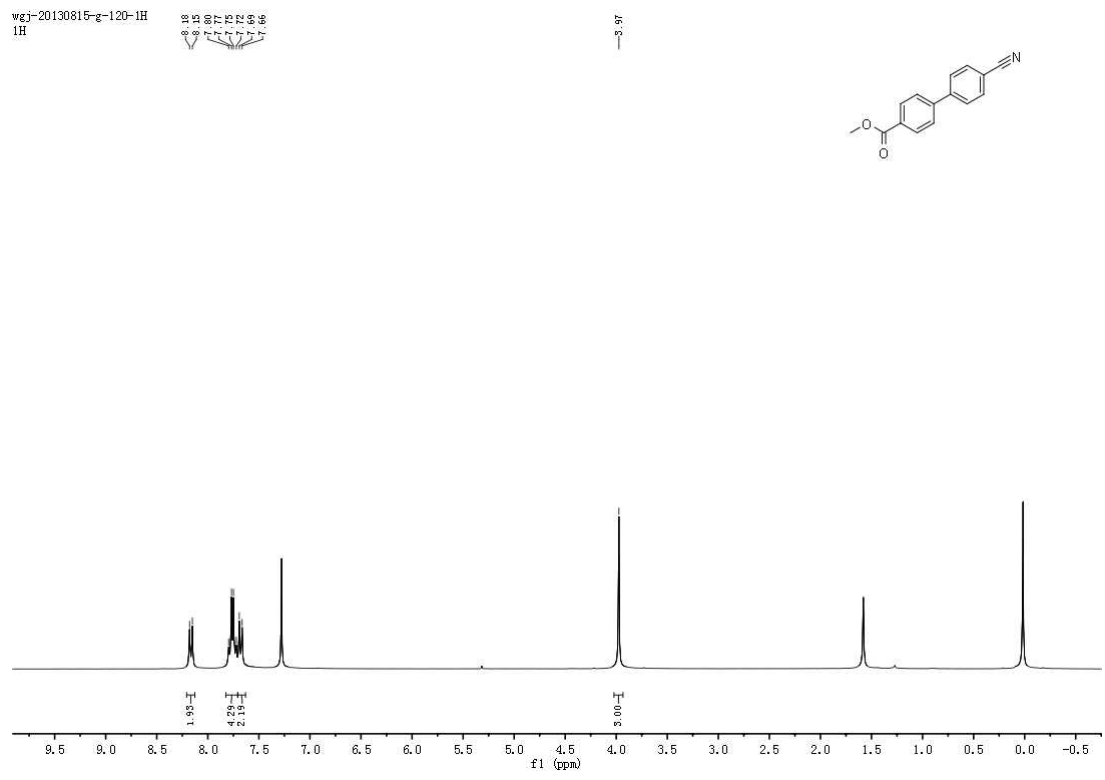


Figure S11. ¹H -NMR spectra of **7k**

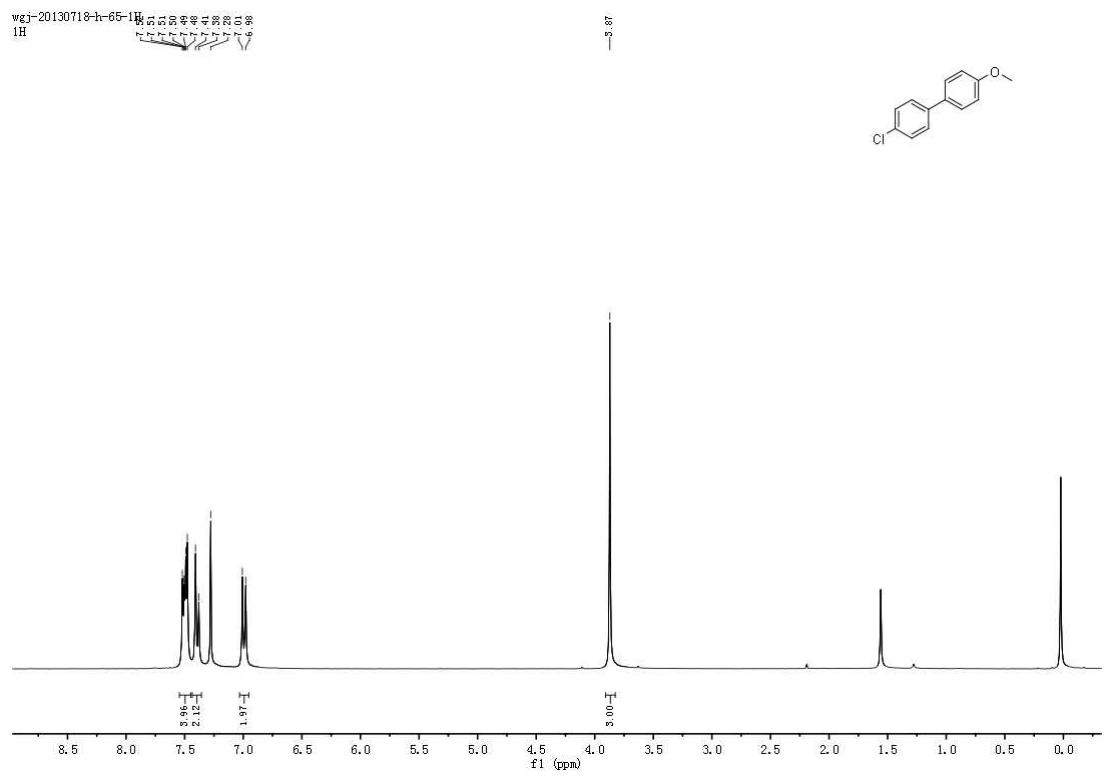
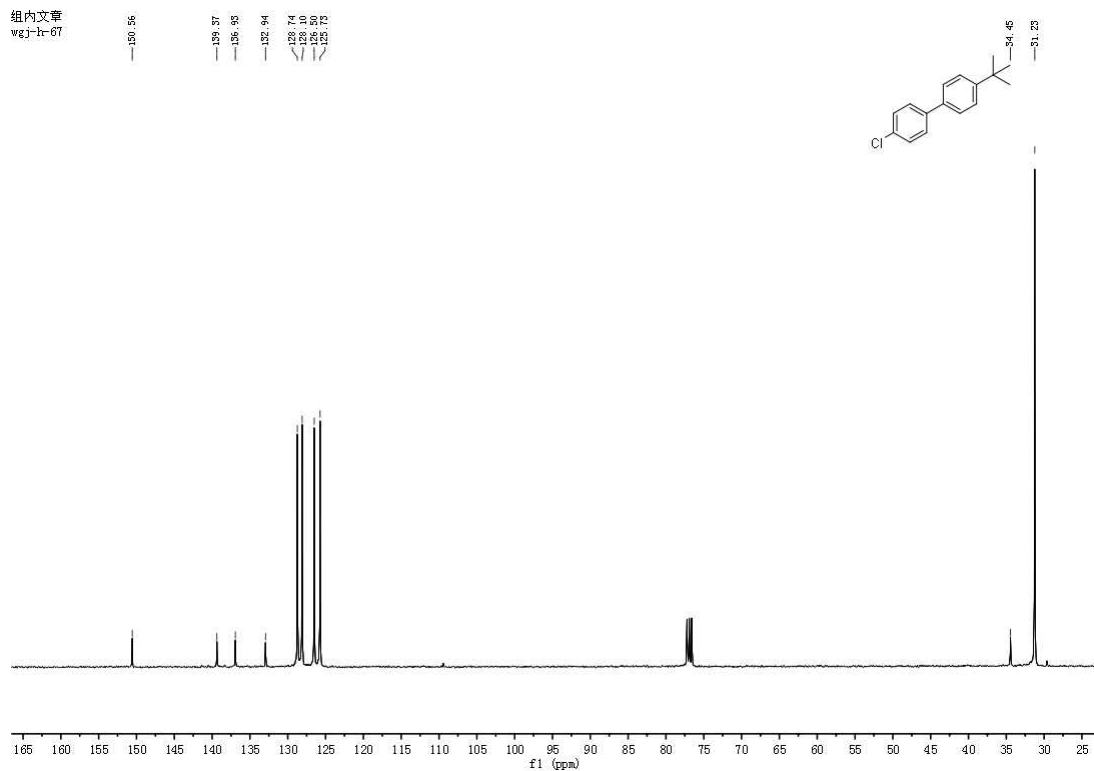
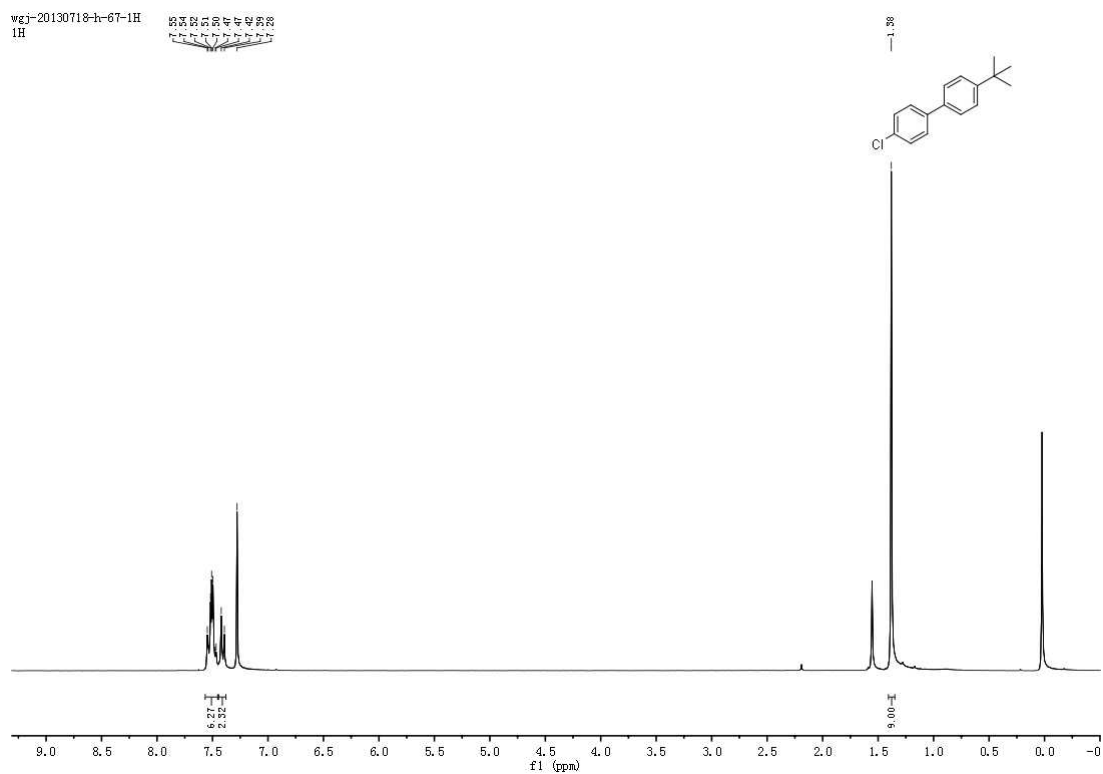


Figure S12. ¹H -NMR spectra of **7l**



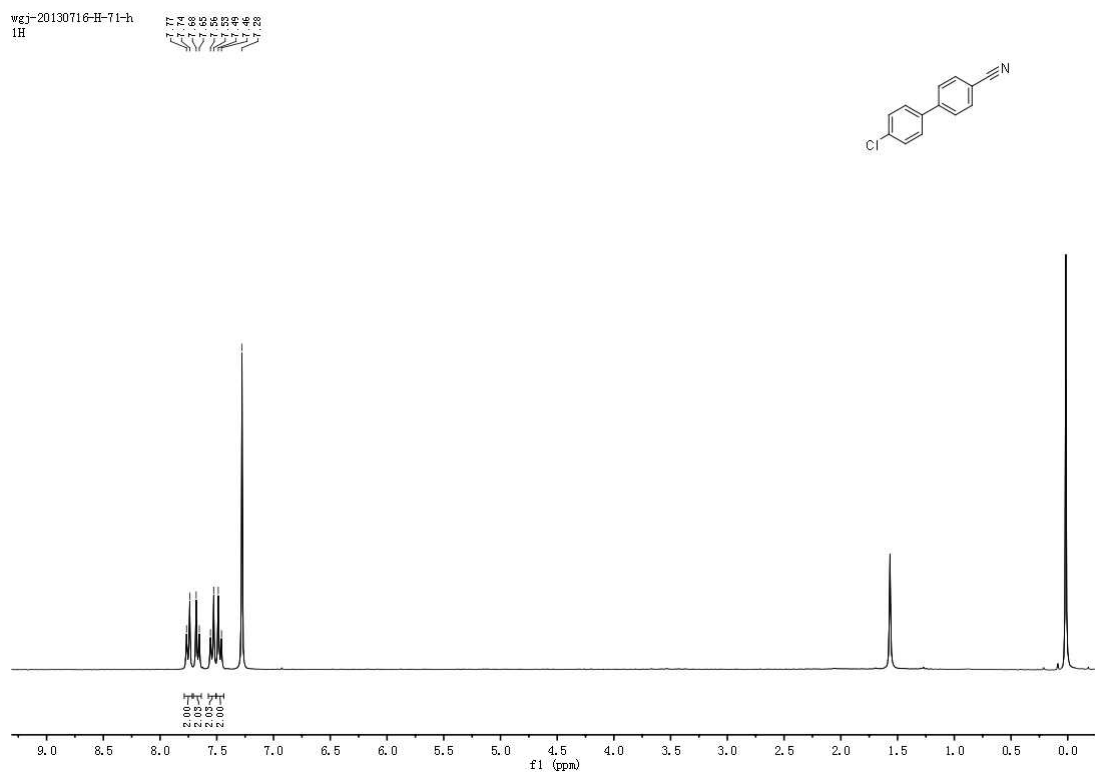


Figure S15. ¹H-NMR spectra of **7n**

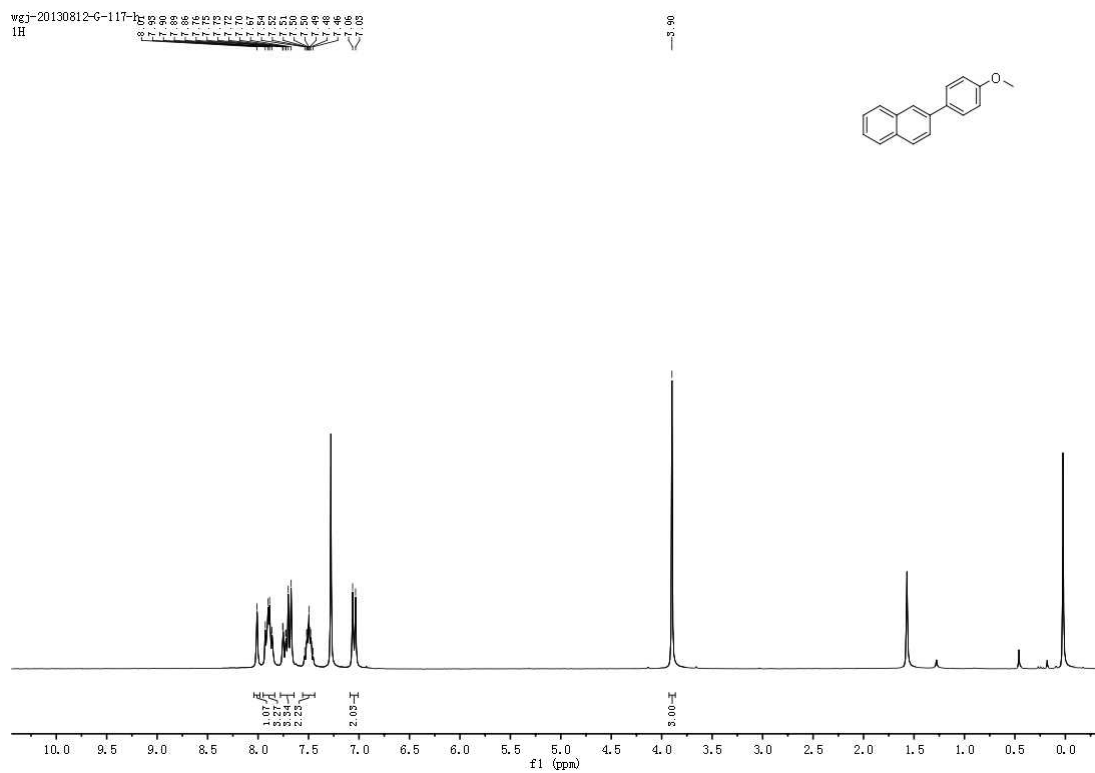


Figure S16. ¹H-NMR spectra of **7o**

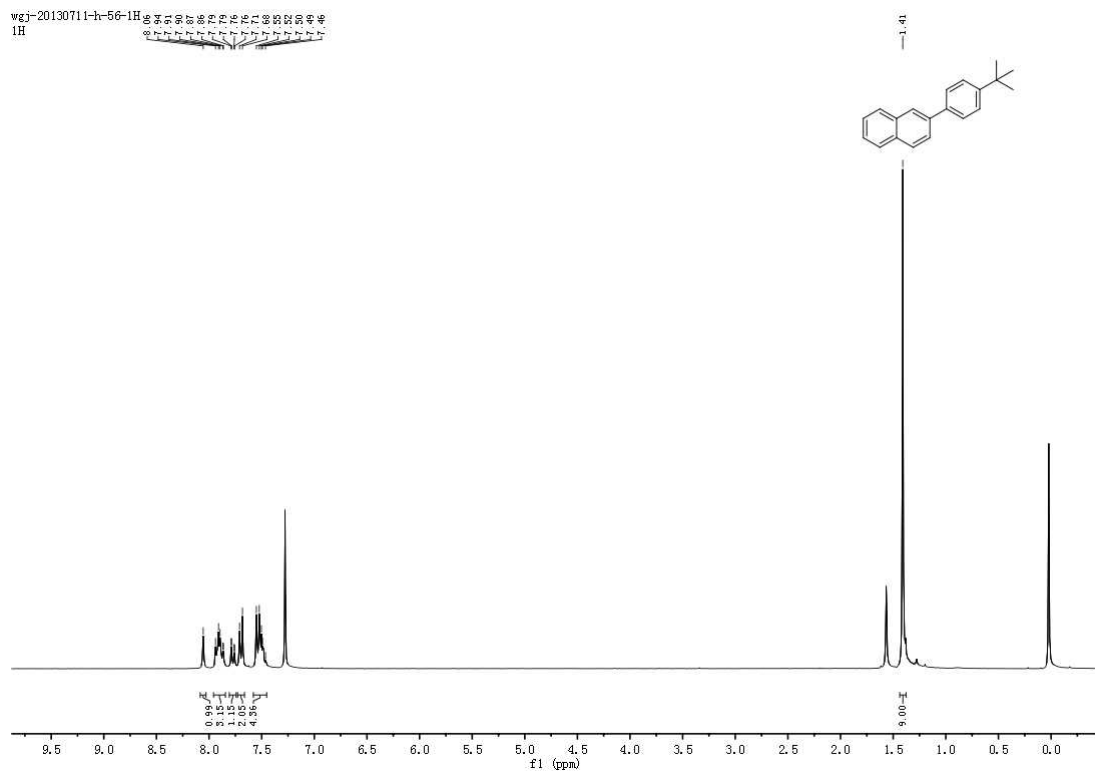


Figure S17. ^1H -NMR spectra of **7p**

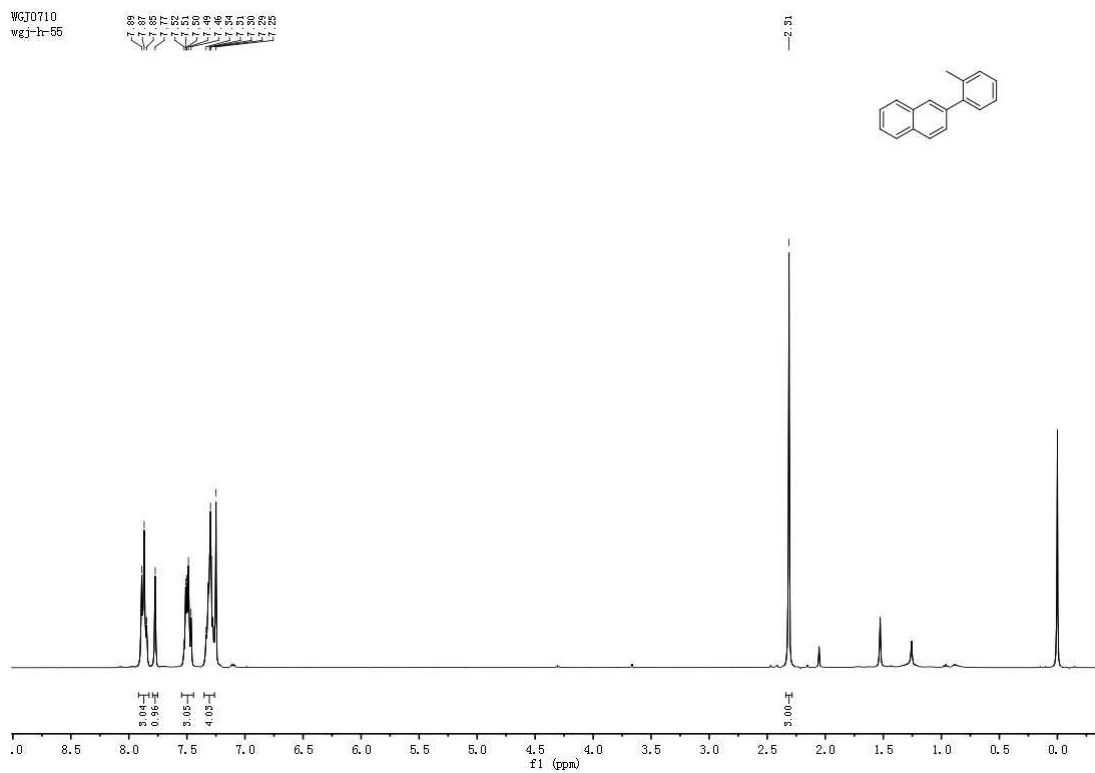


Figure S18. ^1H -NMR spectra of **7q**

wj-20130711-h-57-1h
1H

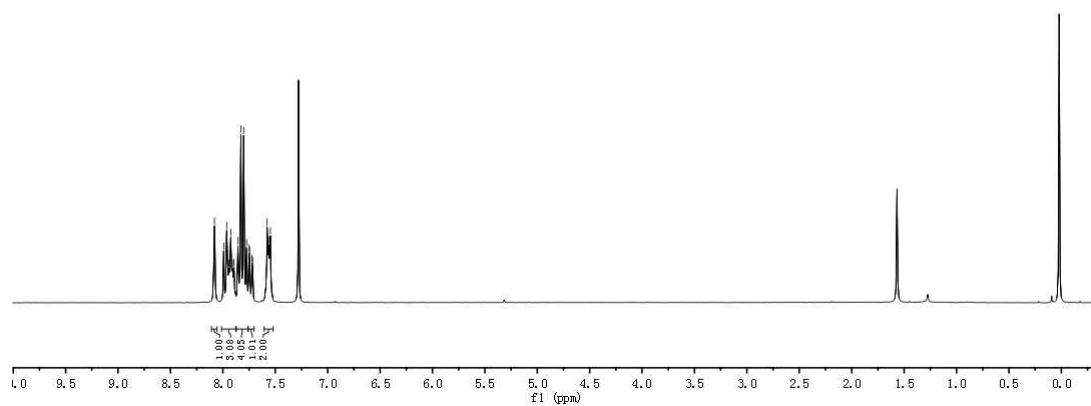
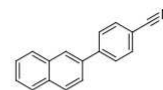


Figure S19. ¹H-NMR spectra of 7r

wj-20130627-h-15-1h
1H

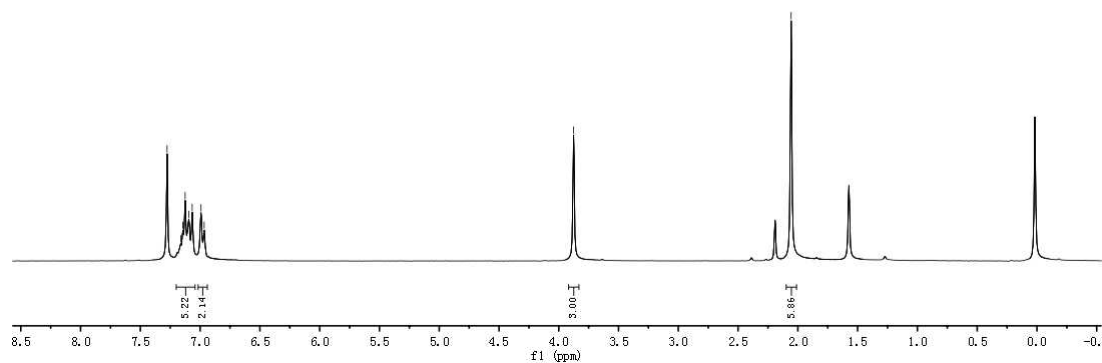
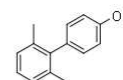
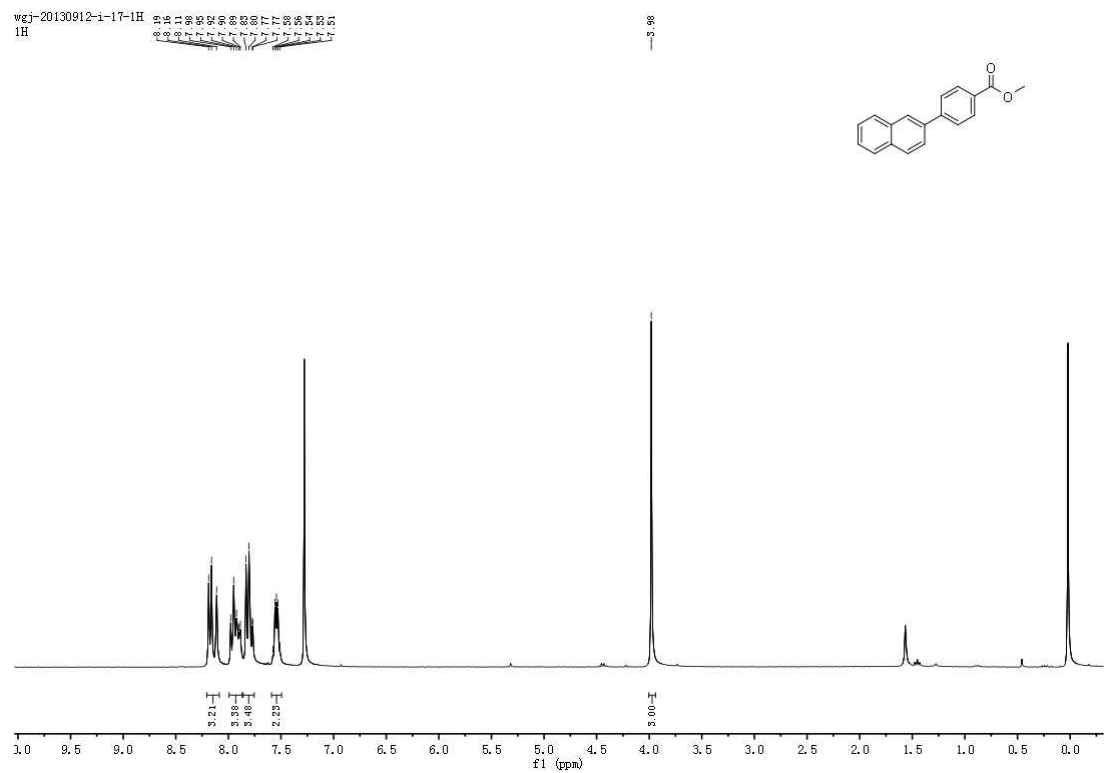
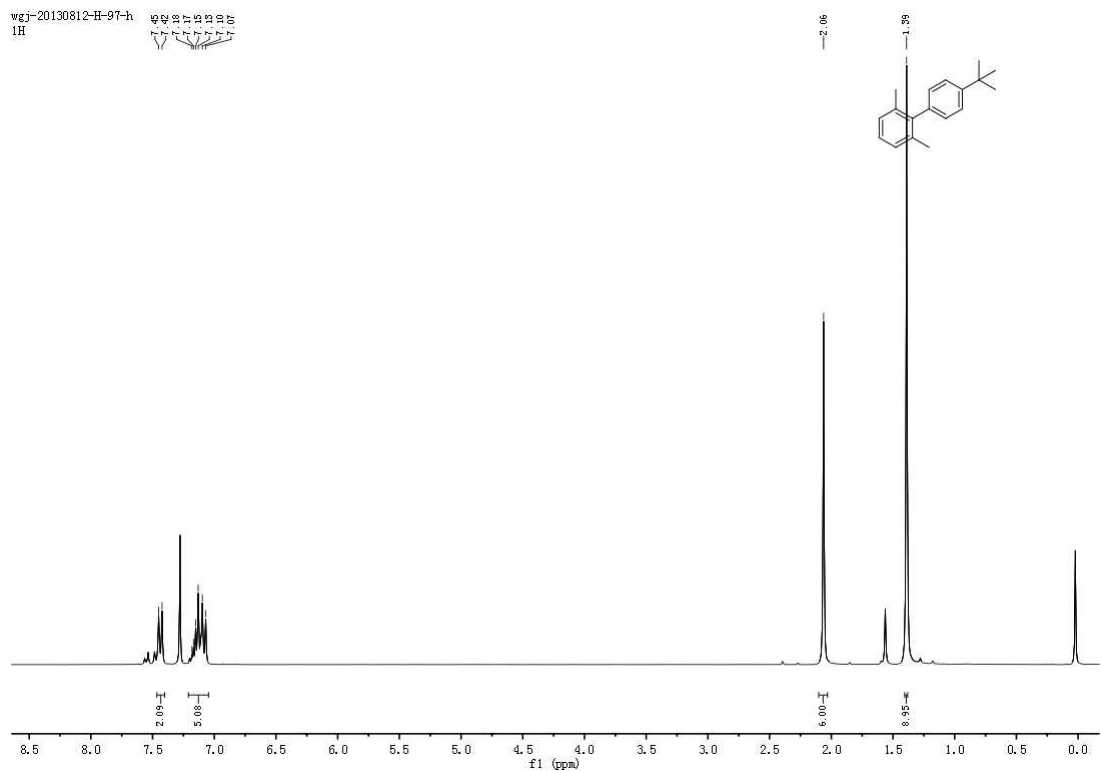


Figure S20. ¹H-NMR spectra of 7s



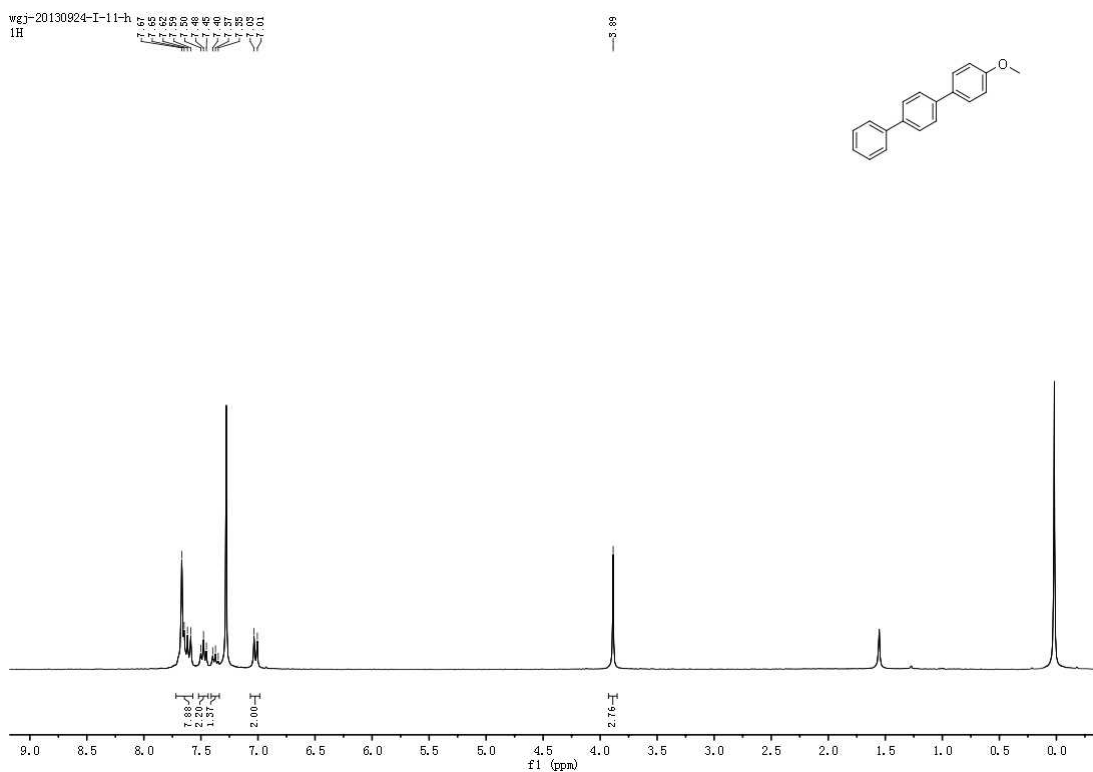


Figure S23. ^1H -NMR spectra of **7v**

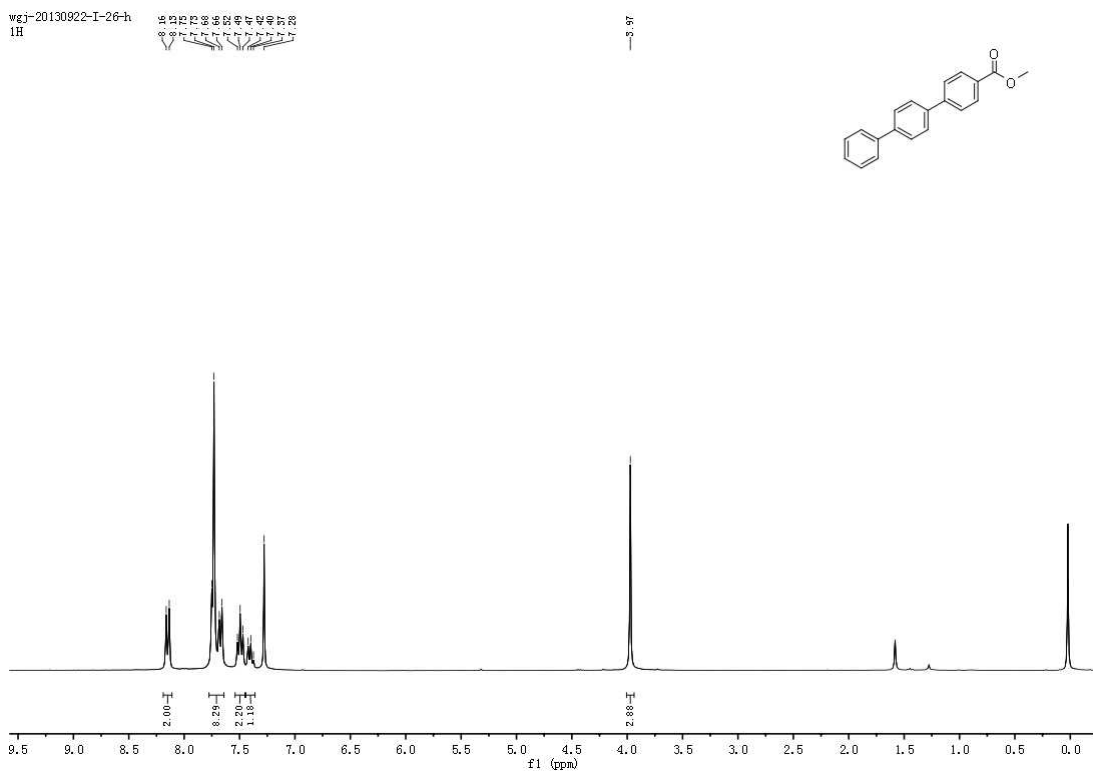


Figure S24. ^1H -NMR spectra of **7w**

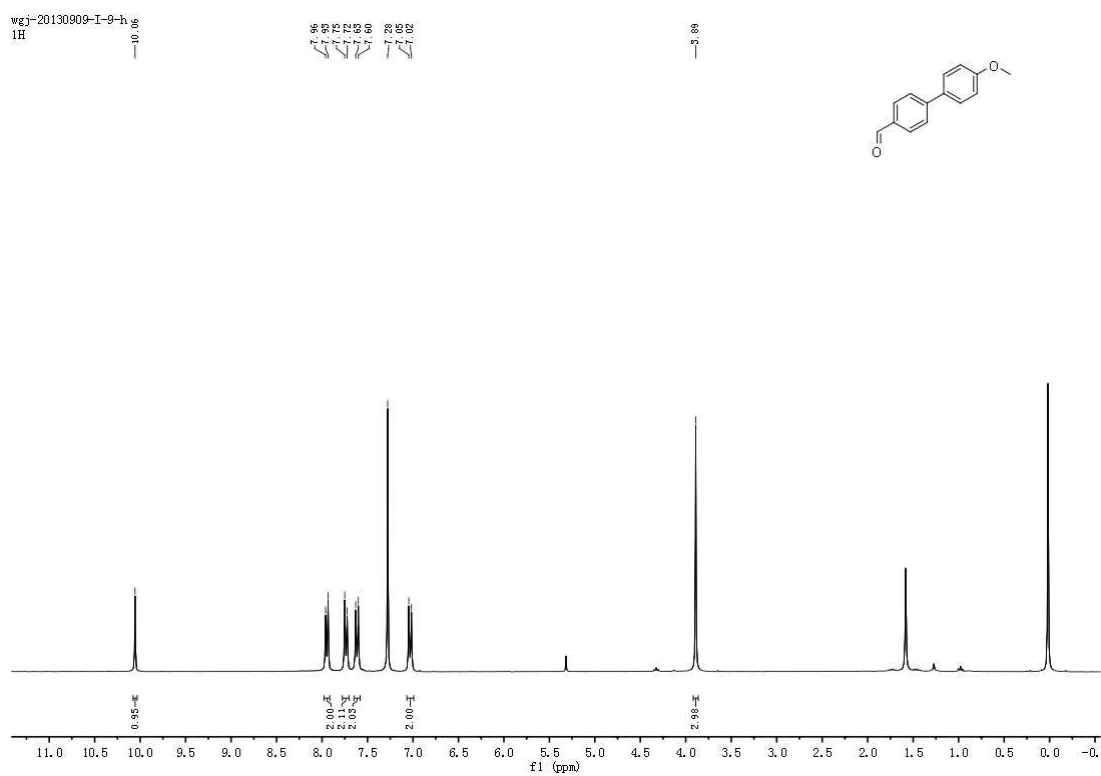


Figure S27. ^1H -NMR spectra of **7z**

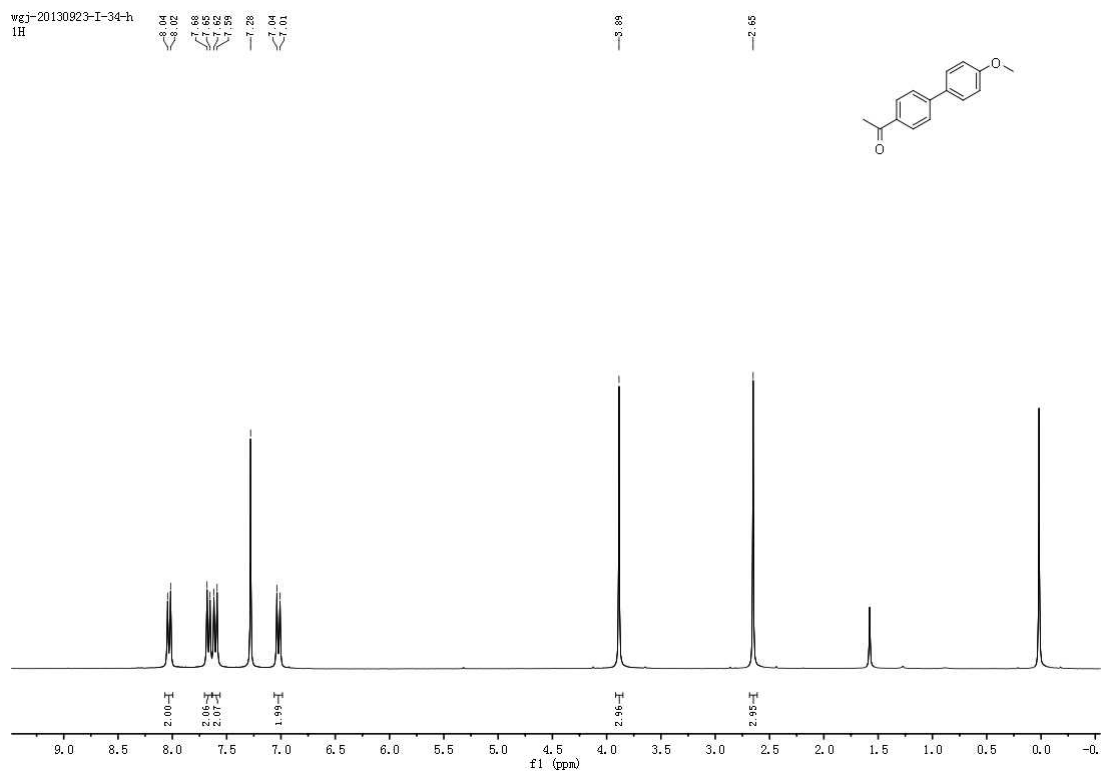


Figure S28. ^1H -NMR spectra of **7aa**

组内文章
WGJ-J-77-2

8.15
8.07
7.86
7.72
7.69

3.95

2.65

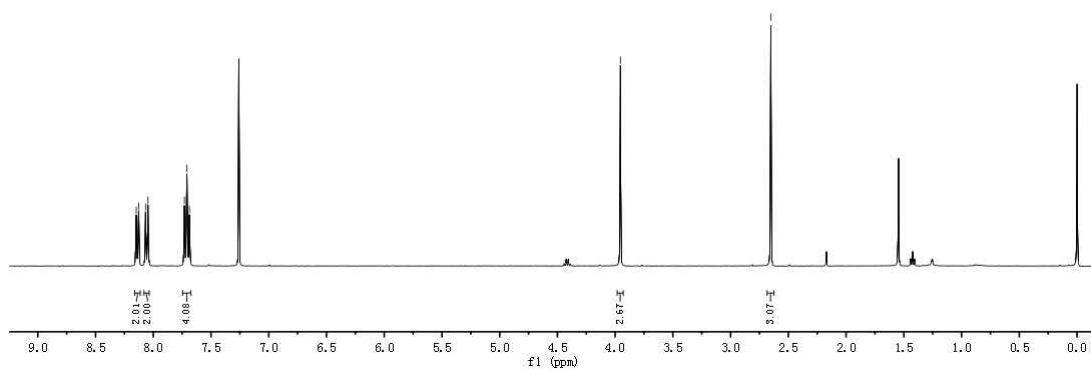
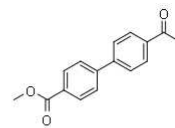


Figure S29. ¹H -NMR spectra of 7ab

wgj-20131125-I-83-h
1H

8.08
7.27
7.01
6.92
6.82
6.72

3.87

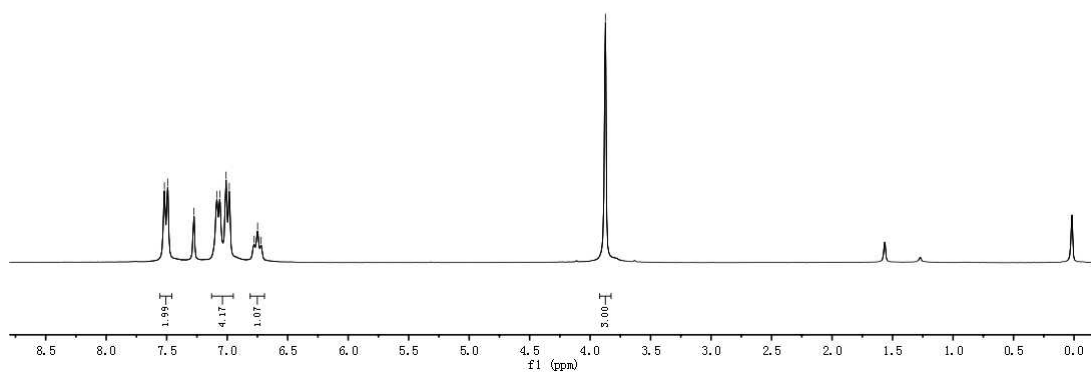
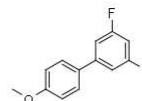
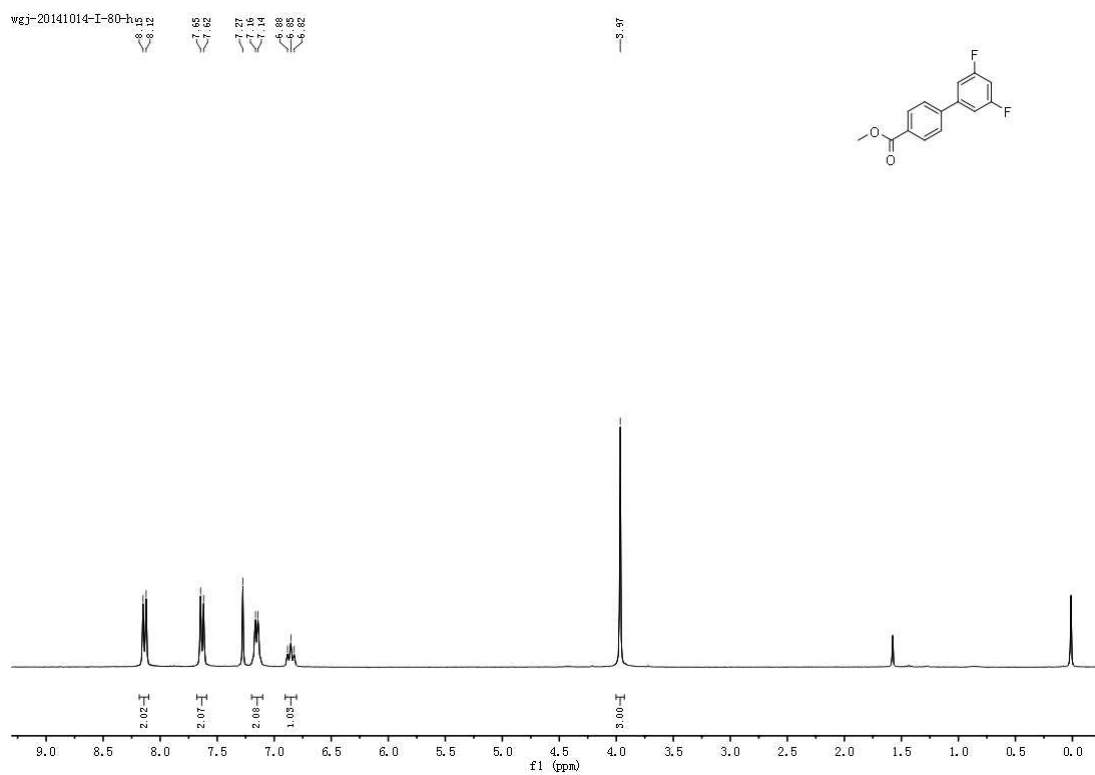
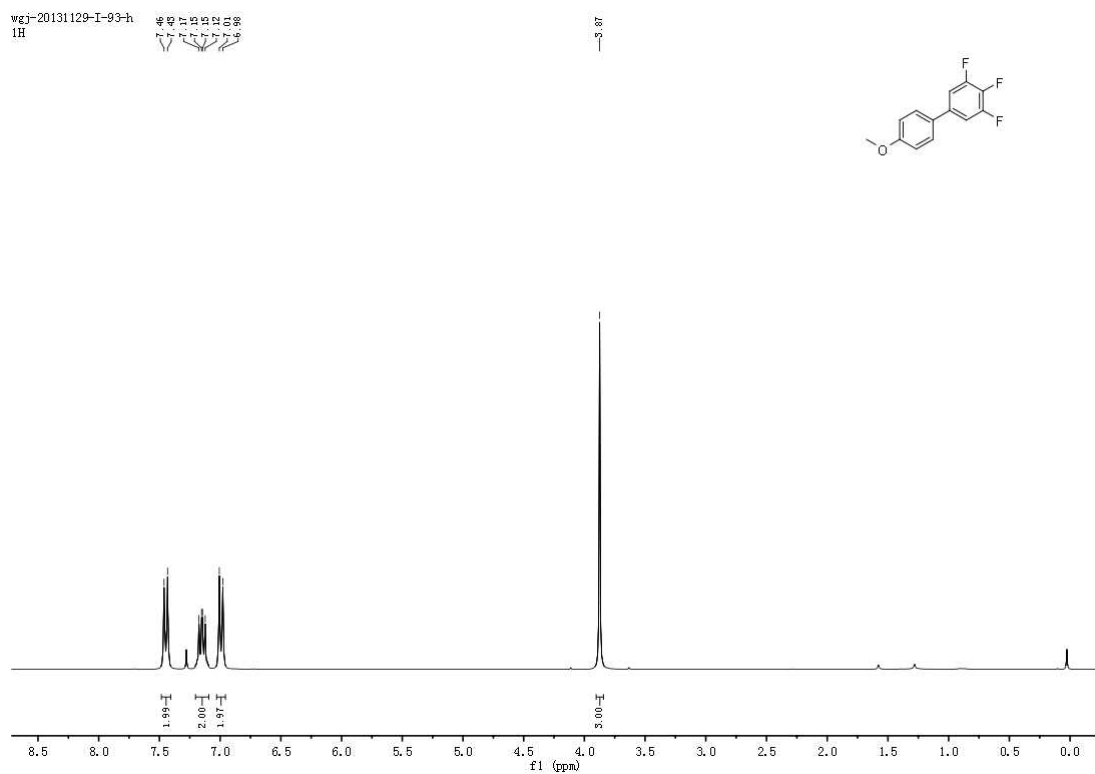


Figure S30. ¹H -NMR spectra of 10a



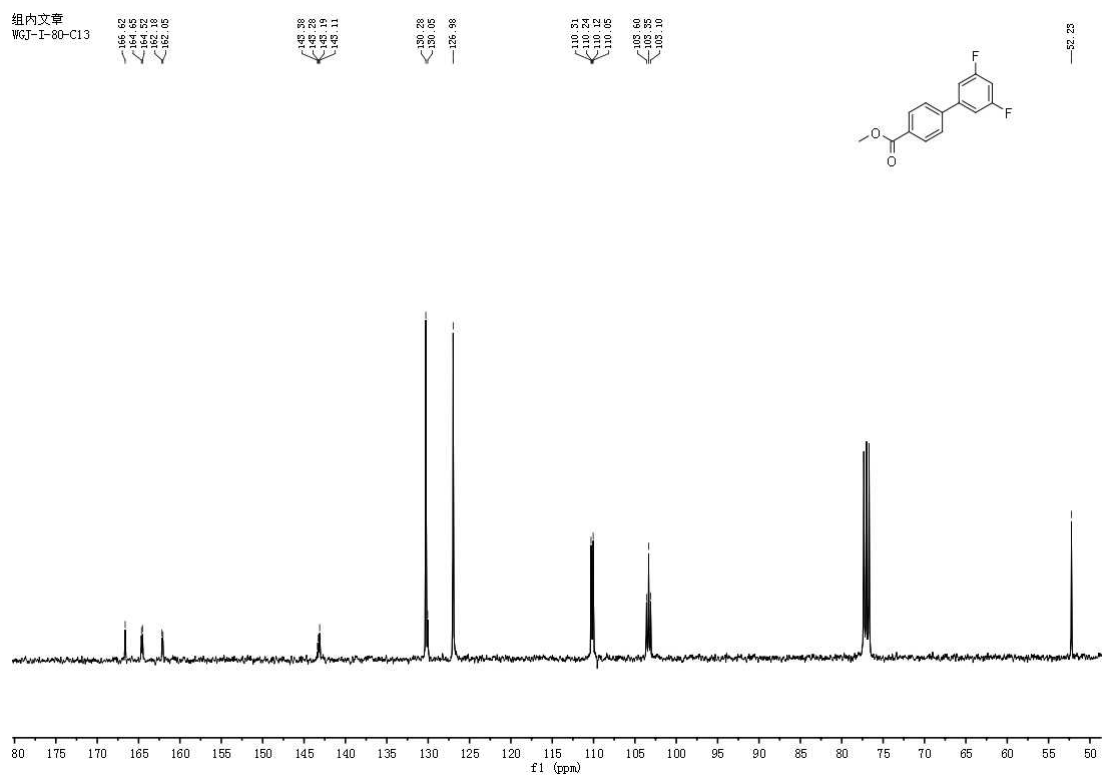


Figure S33. ^{13}C -NMR spectra of **10c**

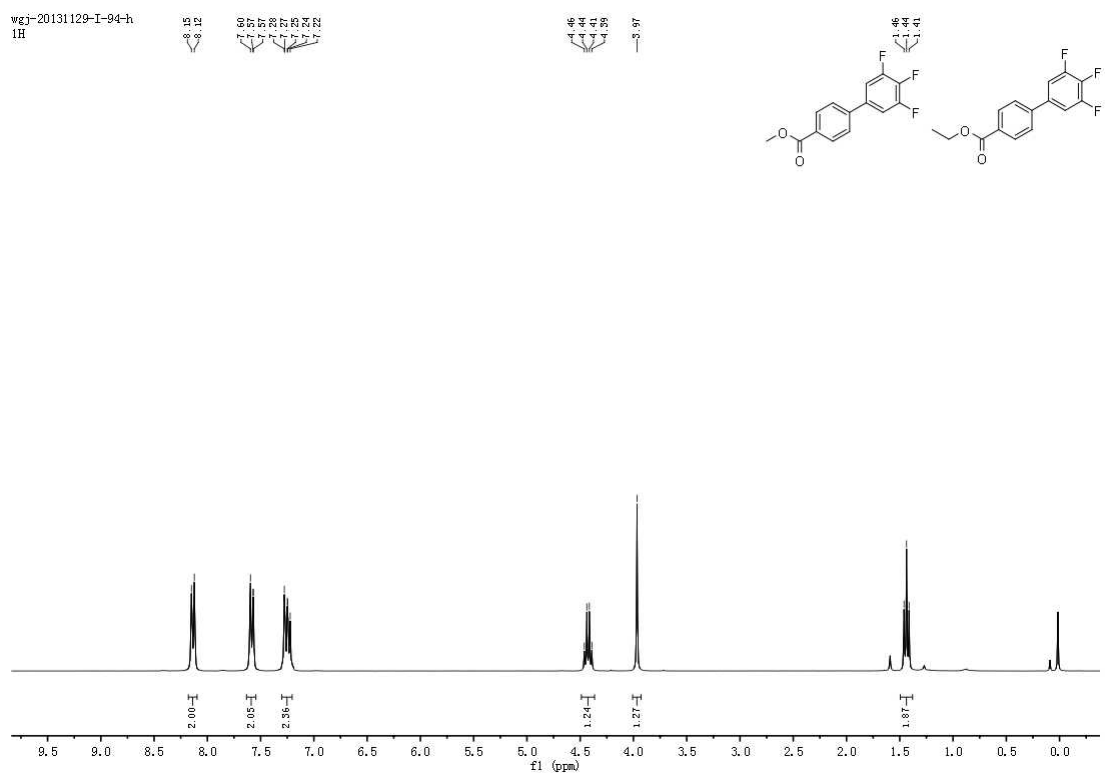
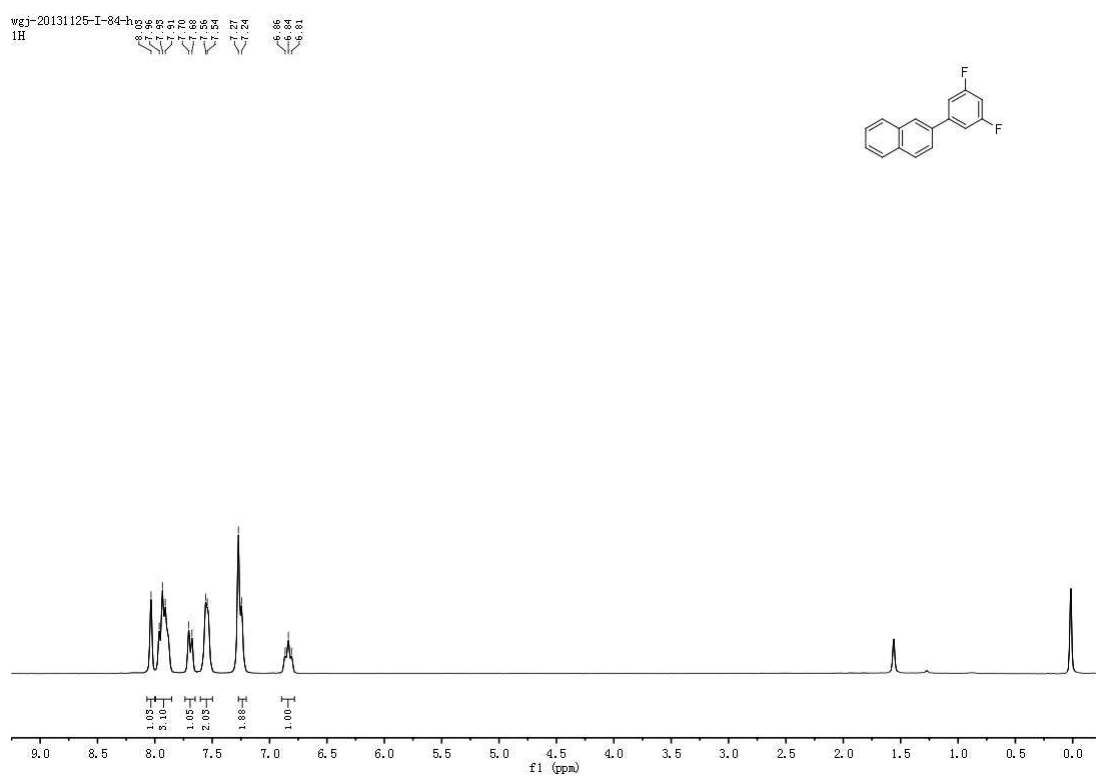
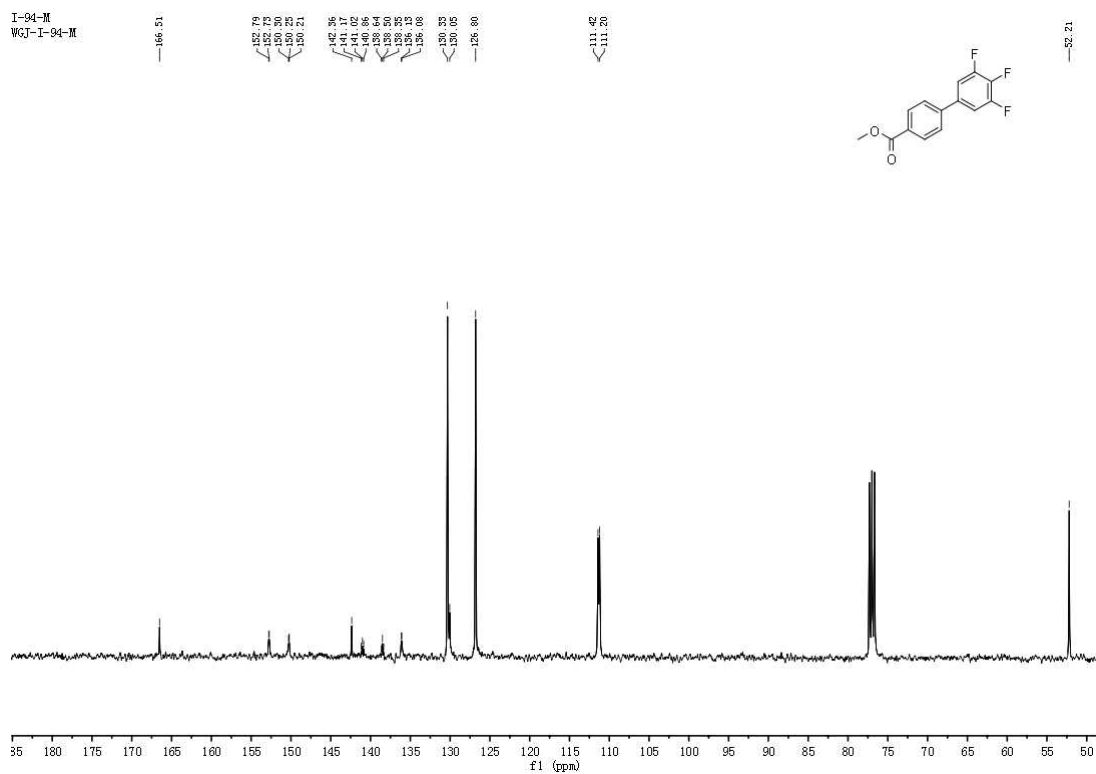


Figure S34. ^1H -NMR spectra of **10d**



组内文章
WGJ-I-84

164.25
164.11
161.79
151.65

144.02
143.95

137.70

133.05
132.65

130.35
130.24
129.89
129.65
127.85
127.35

109.85
109.75
109.64
109.55

103.35
103.24
101.84

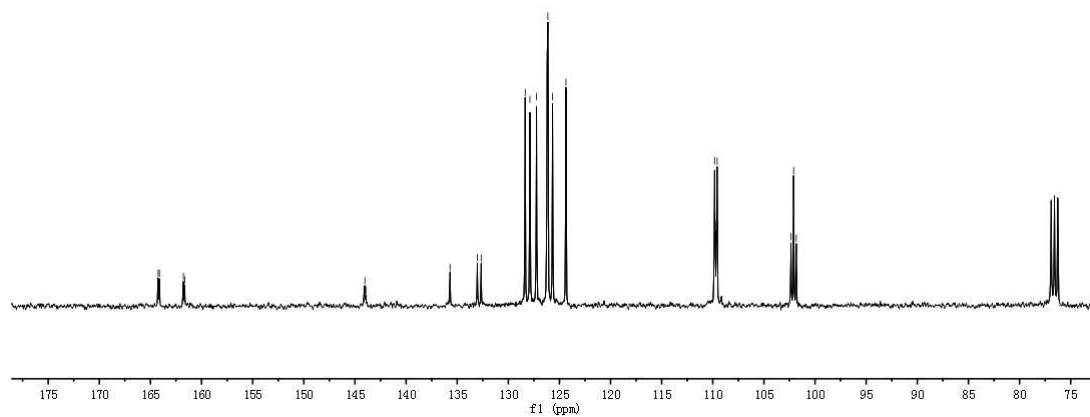
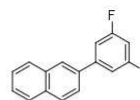


Figure S37. ¹³C -NMR spectra of 10e

wgj-20131129-I-95-1
1H

8.02, 8.01, 7.99, 7.98, 7.97, 7.96, 7.95, 7.94, 7.93, 7.92, 7.91, 7.90, 7.89, 7.88, 7.87, 7.86, 7.85, 7.84, 7.83, 7.82, 7.81, 7.80, 7.79, 7.78, 7.77, 7.76, 7.75, 7.74, 7.73, 7.72, 7.71, 7.70, 7.69, 7.68, 7.67, 7.66, 7.65, 7.64, 7.63, 7.62, 7.61, 7.60, 7.59, 7.58, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.58, 1.57, 1.56, 1.55, 1.54, 1.53, 1.52, 1.51, 1.50, 1.49, 1.48, 1.47, 1.46, 1.45, 1.44, 1.43, 1.42, 1.41, 1.40, 1.39, 1.38, 1.37, 1.36, 1.35, 1.34, 1.33, 1.32, 1.31, 1.30, 1.29, 1.28, 1.27, 1.26, 1.25, 1.24, 1.23, 1.22, 1.21, 1.20, 1.19, 1.18, 1.17, 1.16, 1.15, 1.14, 1.13, 1.12, 1.11, 1.10, 1.09, 1.08, 1.07, 1.06, 1.05, 1.04, 1.03, 1.02, 1.01, 1.00, 0.99, 0.98, 0.97, 0.96, 0.95, 0.94, 0.93, 0.92, 0.91, 0.90, 0.89, 0.88, 0.87, 0.86, 0.85, 0.84, 0.83, 0.82, 0.81, 0.80, 0.79, 0.78, 0.77, 0.76, 0.75, 0.74, 0.73, 0.72, 0.71, 0.70, 0.69, 0.68, 0.67, 0.66, 0.65, 0.64, 0.63, 0.62, 0.61, 0.60, 0.59, 0.58, 0.57, 0.56, 0.55, 0.54, 0.53, 0.52, 0.51, 0.50, 0.49, 0.48, 0.47, 0.46, 0.45, 0.44, 0.43, 0.42, 0.41, 0.40, 0.39, 0.38, 0.37, 0.36, 0.35, 0.34, 0.33, 0.32, 0.31, 0.30, 0.29, 0.28, 0.27, 0.26, 0.25, 0.24, 0.23, 0.22, 0.21, 0.20, 0.19, 0.18, 0.17, 0.16, 0.15, 0.14, 0.13, 0.12, 0.11, 0.10, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, 0.01, 0.00

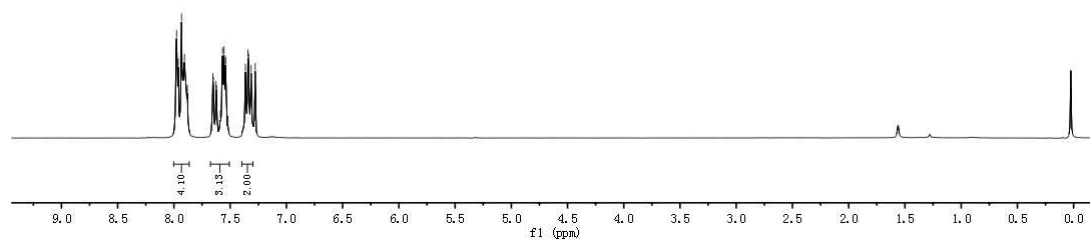
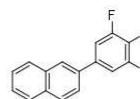


Figure S38. ¹H -NMR spectra of 10f

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WGJ-I-95

152.25
152.11
152.03
151.88
151.77
151.64

140.24
139.05
138.94

137.85
137.83
137.79
137.74
137.62
137.52

127.45
127.23
127.03
126.83
126.63
126.43

110.89
110.85
110.75
110.67

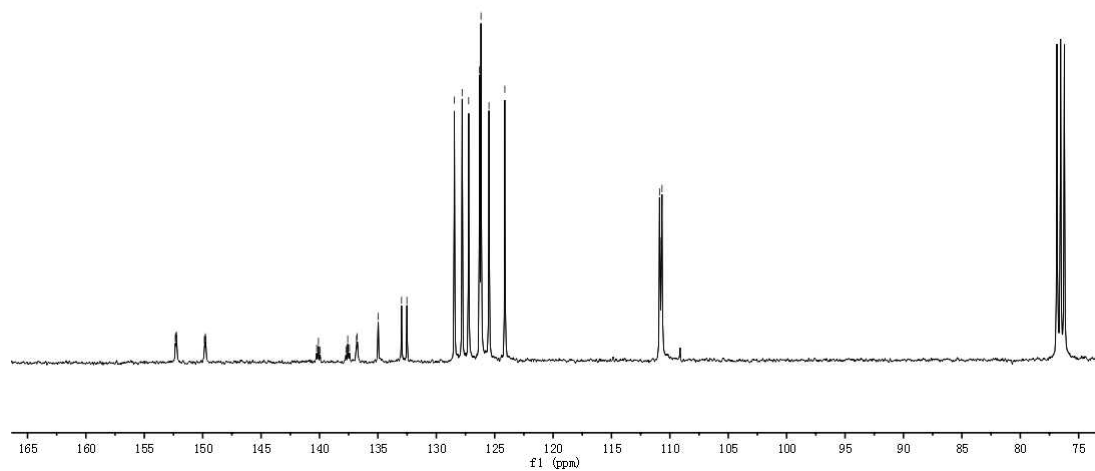
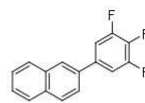


Figure S39. ^{13}C -NMR spectra of **10f**

组内文章
WGJ-H-26

82.12
82.02
81.92
81.82
81.72
81.62

3.83

3.83

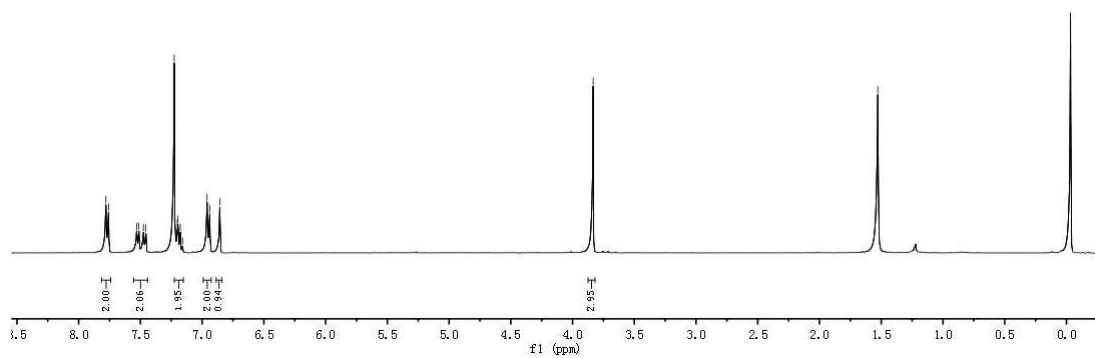
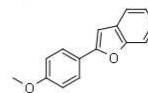
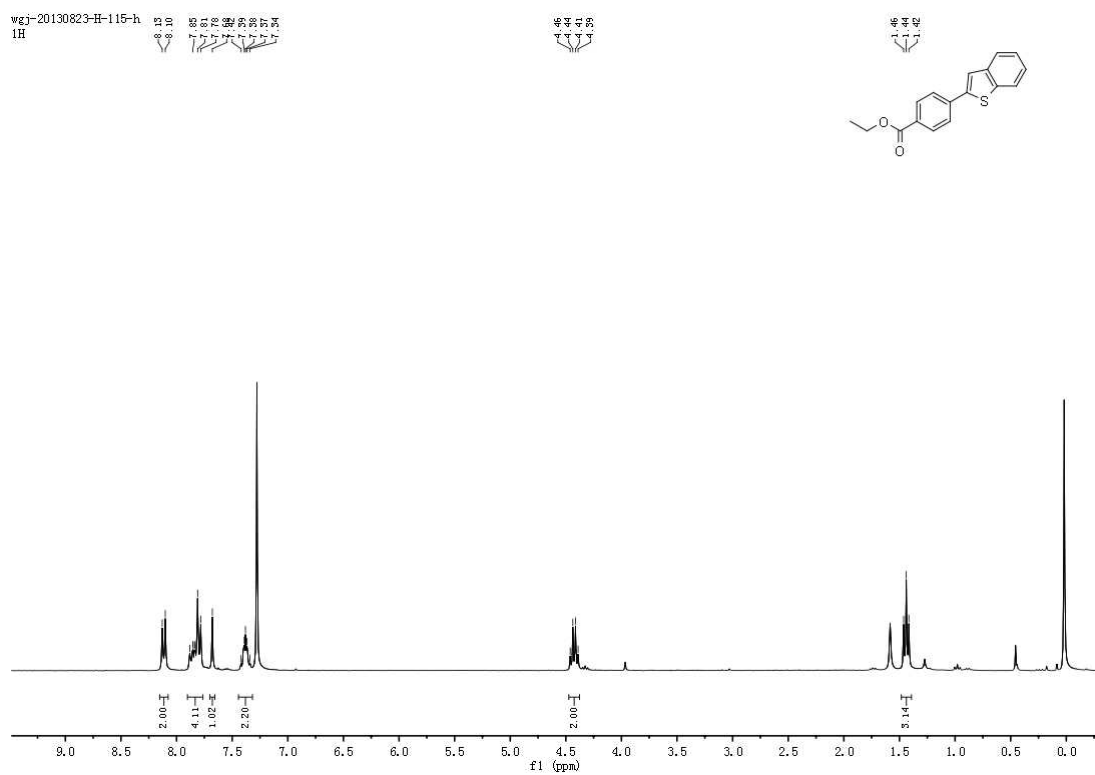
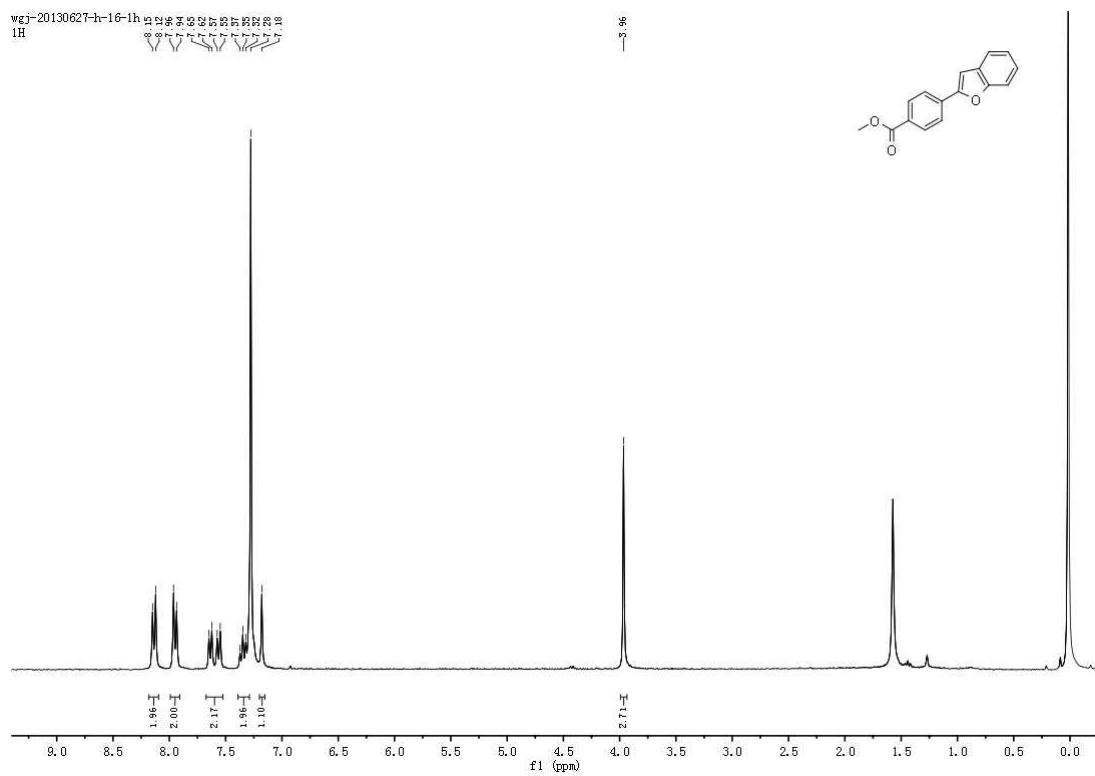


Figure S40. ^1H -NMR spectra of **11a**



wzj-20130827-Hg119-h
1H

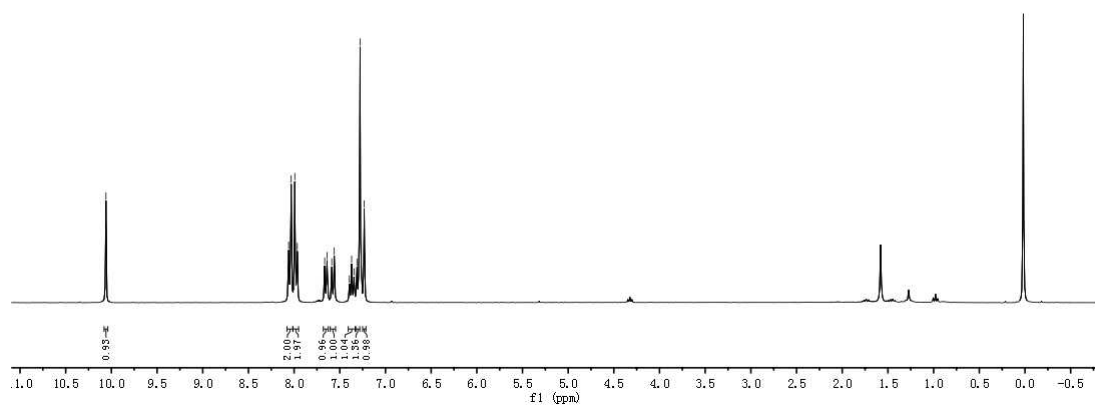
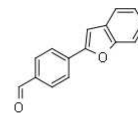
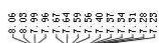


Figure S43. ^1H -NMR spectra of 11d

wzj-20130823-H-116gh
1H

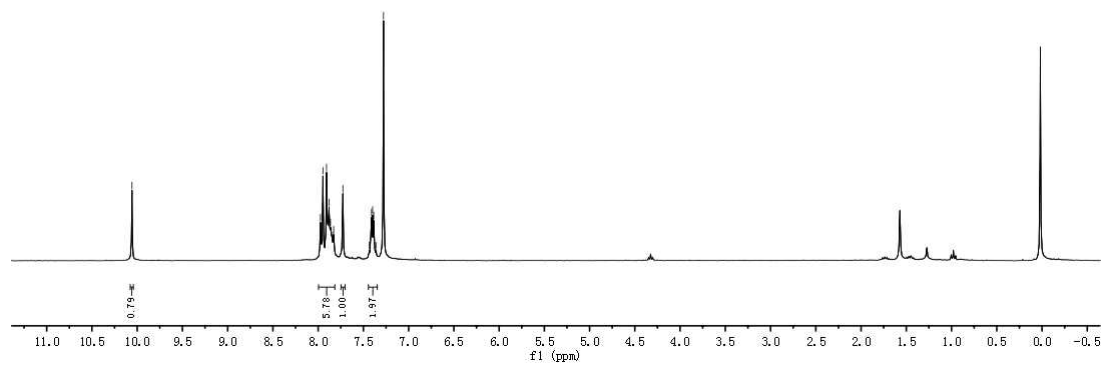
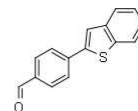
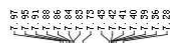


Figure S44. ^1H -NMR spectra of 11e

wgj-20130829-h-122-1H
1H

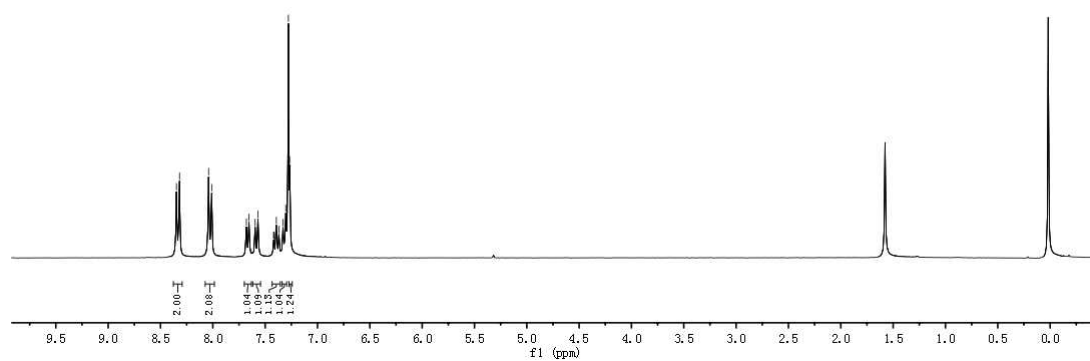
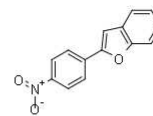
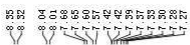


Figure S45. ¹H -NMR spectra of **11f**

wgj-20130829-h-120-1H
1H

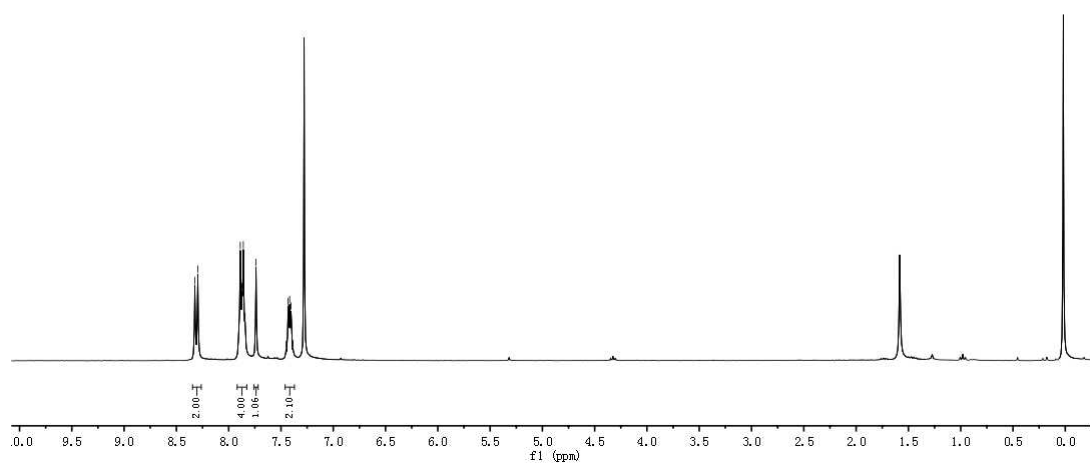
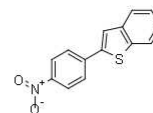
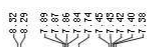
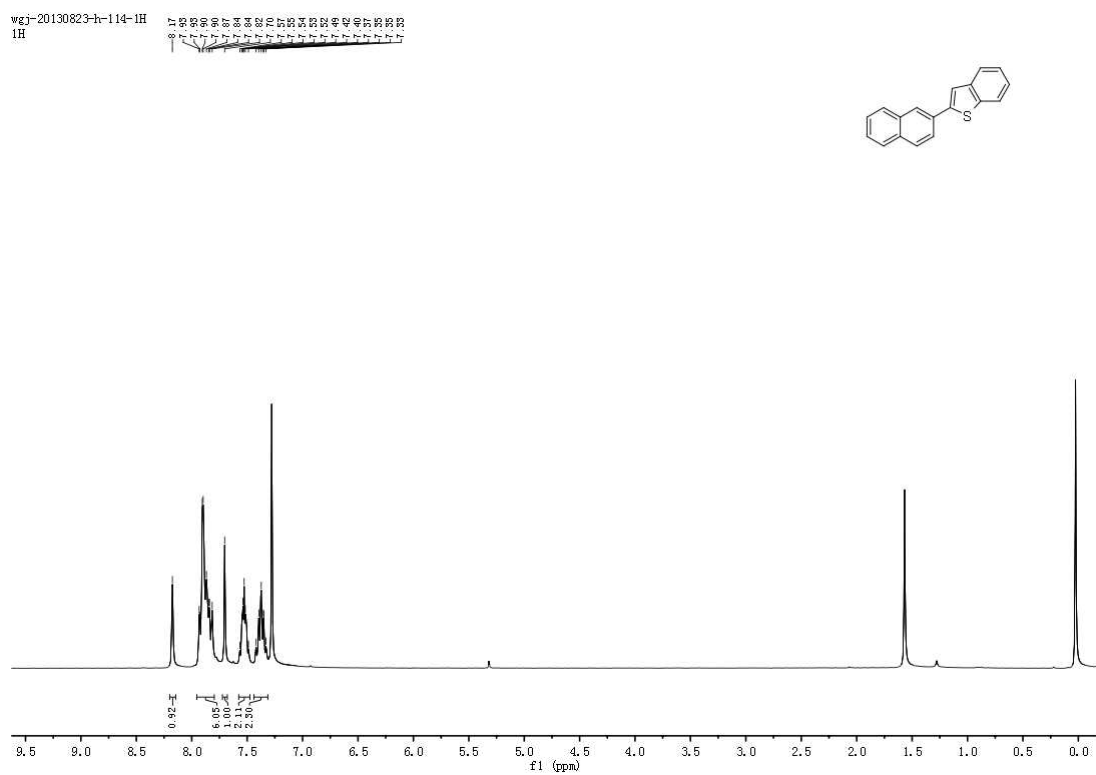
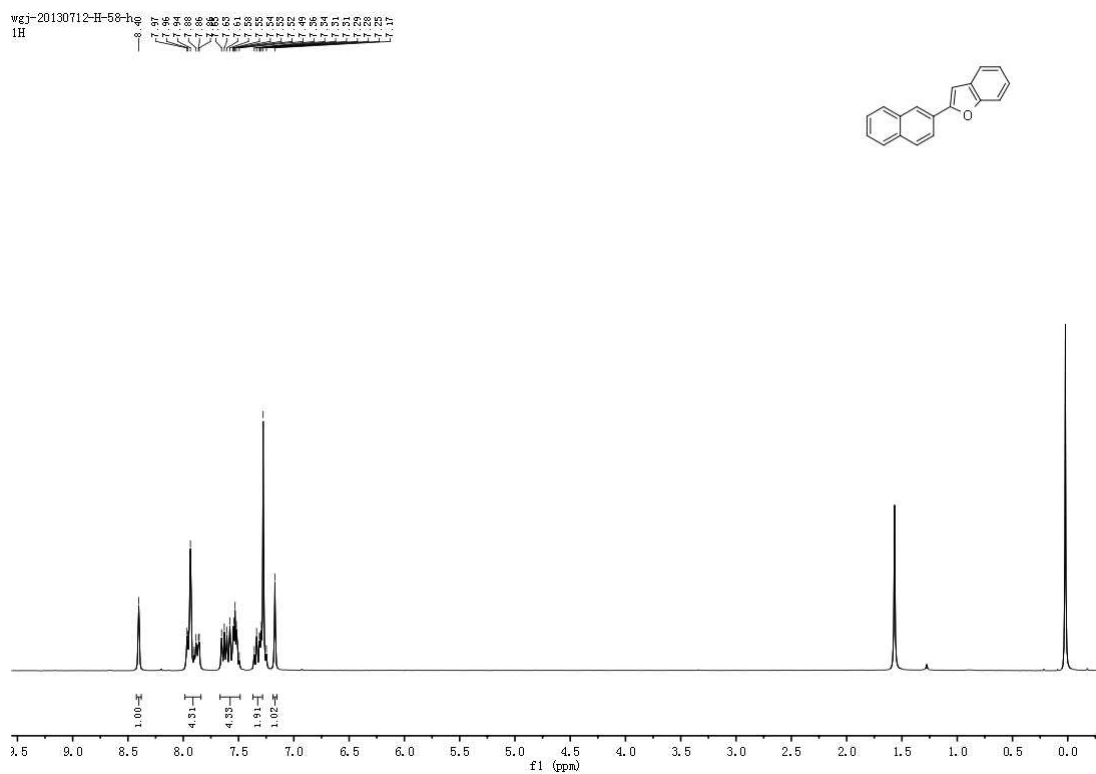


Figure S46. ¹H -NMR spectra of **11g**



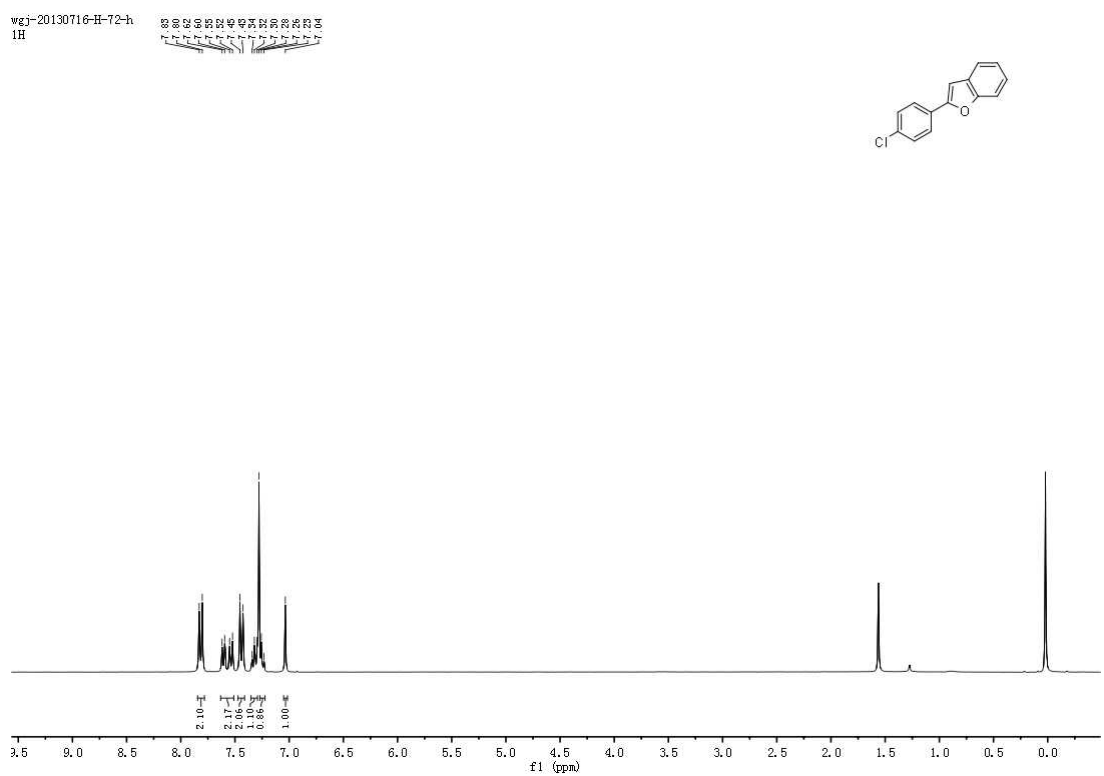


Figure S49. ^1H -NMR spectra of **11j**

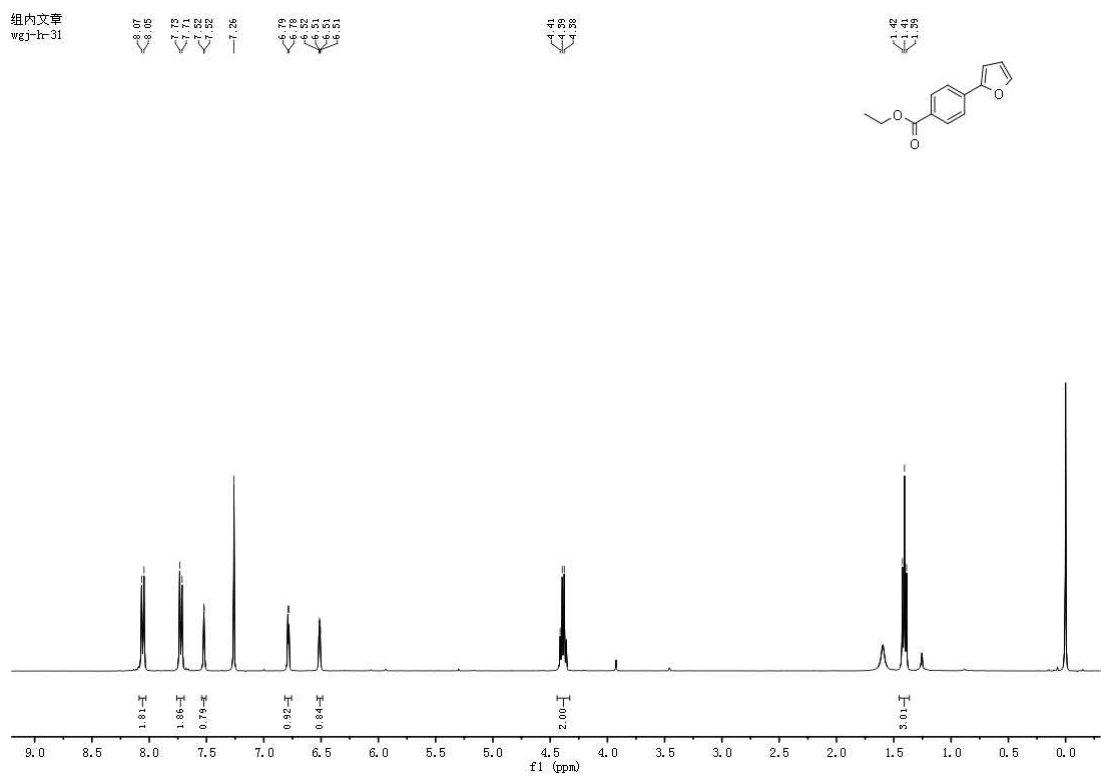


Figure S50. ^1H -NMR spectra of **11k**

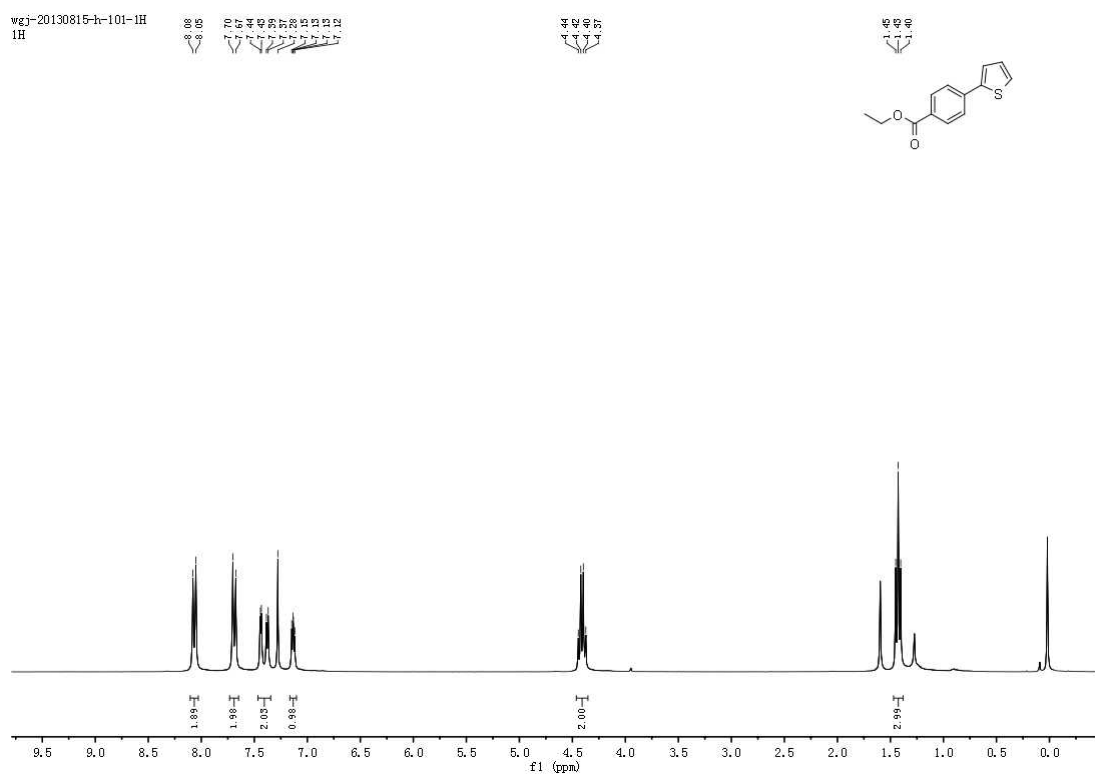


Figure S51. ^1H -NMR spectra of **11l**

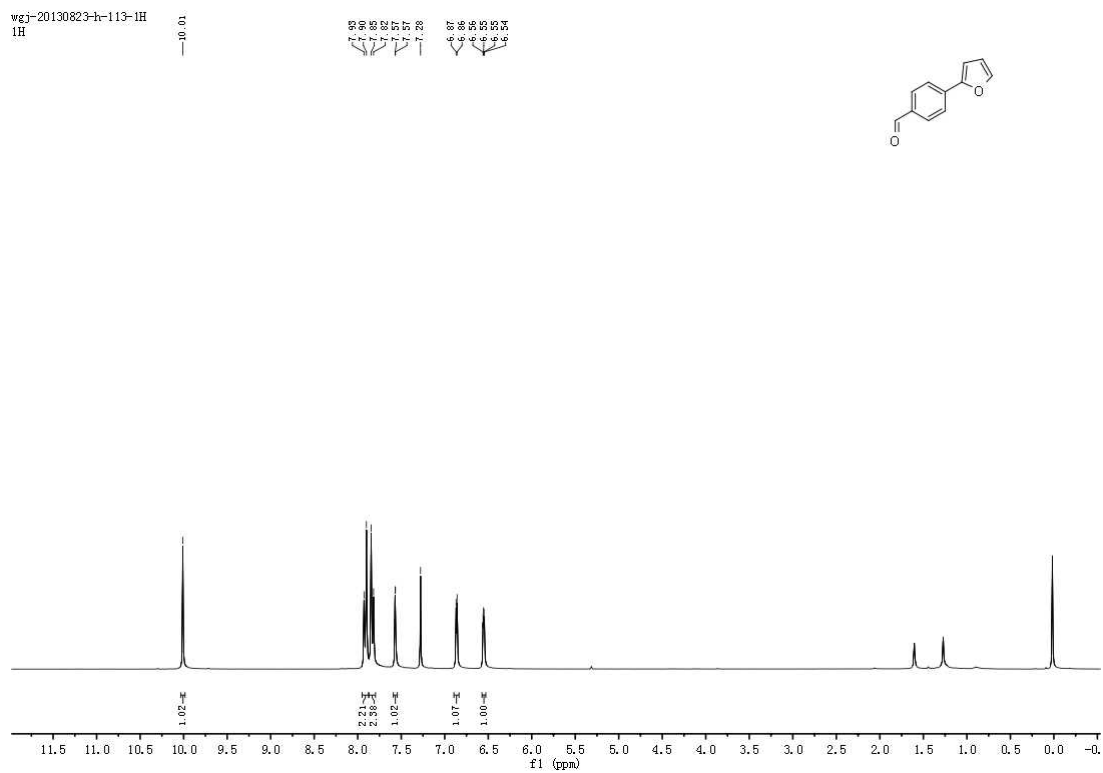


Figure S52. ^1H -NMR spectra of **11m**

wgj-20130823-H-112-h
1H

8.00
7.98
7.96
7.94
7.92
7.90
7.88
7.86
7.84
7.82
7.80
7.78
7.76
7.74
7.72
7.70
7.68
7.66
7.64
7.62
7.60
7.58
7.56
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7.52
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7.12
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7.08
7.06
7.04
7.02
7.00
6.98
6.96
6.94
6.92
6.90
6.88
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6.72
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6.18
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6.12
6.10
6.08
6.06
6.04
6.02
6.00
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5.96
5.94
5.92
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5.86
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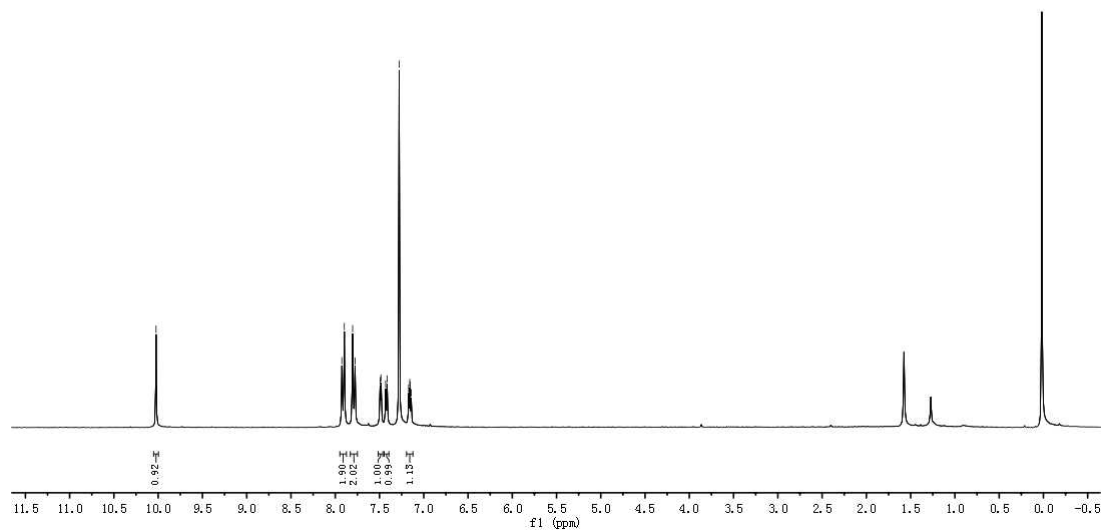
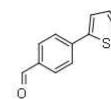


Figure S53. ¹H -NMR spectra of **11n**

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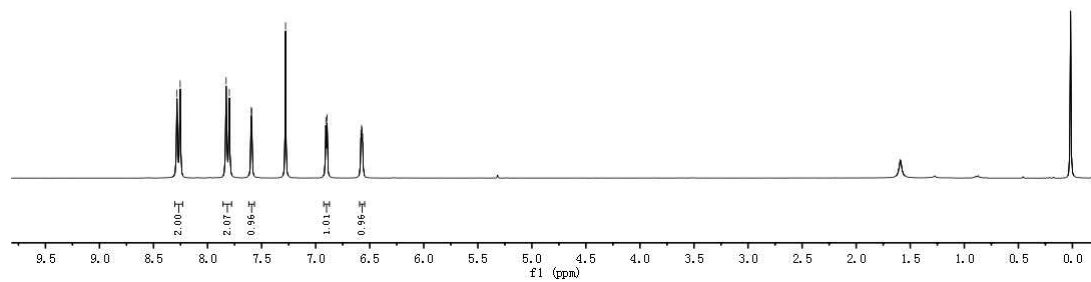
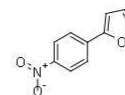


Figure S54. ¹H -NMR spectra of **11o**

wj-20130830-H-125-h
1H

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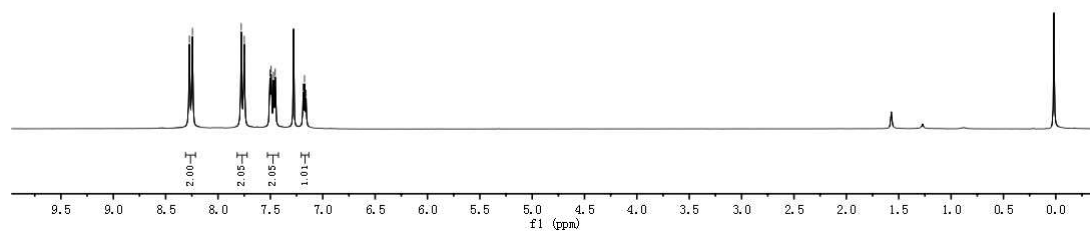
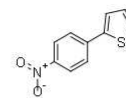


Figure S55. ¹H -NMR spectra of **11p**

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WJ-H-52

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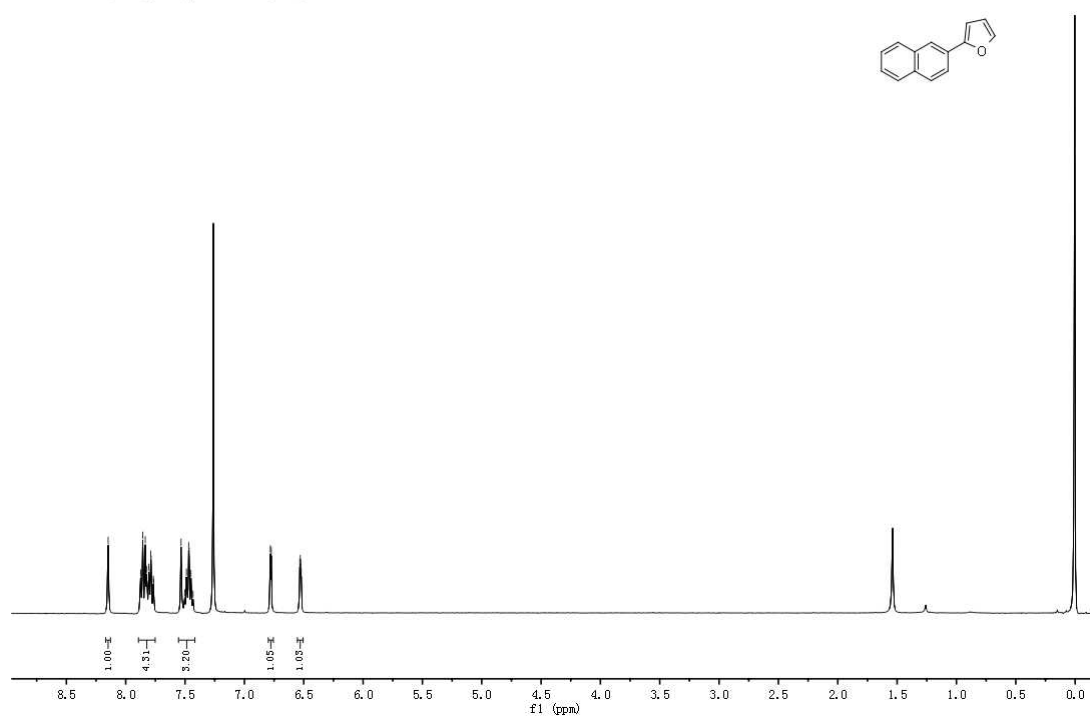
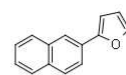


Figure S56. ¹H -NMR spectra of **11q**

wgj-20130726-H-92-h
1H

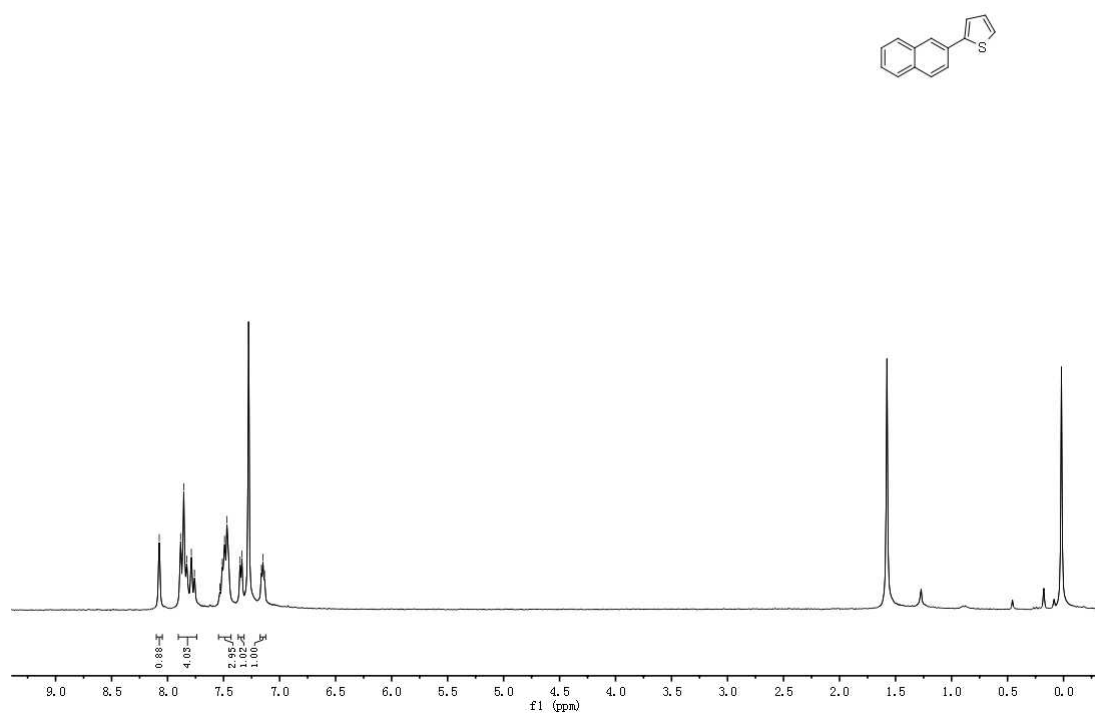


Figure S57. ¹H -NMR spectra of 11r

wgj-20130829-I-41-h
1H

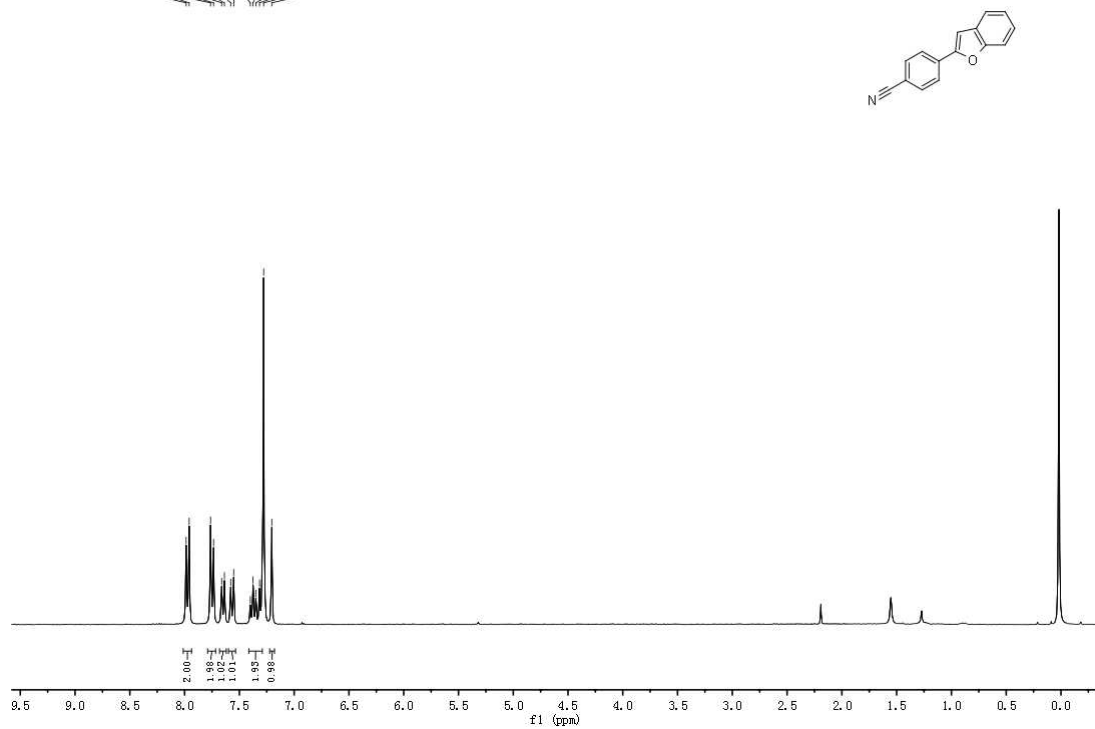


Figure S58. ¹H -NMR spectra of 11s