

Supporting Information

Room-temperature borylation and one-pot two-step borylation/Suzuki-Miyaura cross-coupling reaction of aryl chlorides

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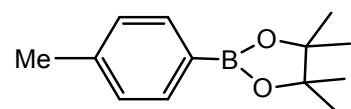
General Information

All the reactions were carried out under N₂ atmosphere. Melting points were determined by the open capillary tube method and are uncorrected. ¹H and ¹³C NMR spectra were recorded on Bruker AV III (300 MHz) and JOEL ECA-400 spectrometers by using CDCl₃ or DMSO-*d*₆ as the solvent and tetramethylsilane (TMS) as the internal standard. Silica gel (200-300 mesh) was used for column chromatography.

General procedure for screening

A glass vessel was charged with Palladium Catalyst (0.02 mmol), ligand (0.04 mmol), boron reagent (3.00 mmol), and KOAc (294 mg, 3.00 mmol) in dioxane (2 ml). The mixture under nitrogen was stirred for 10 min, followed by the addition of **1a** (127 mg, 1.00 mmol). The reaction mixture was stirred at the indicated temperature for the indicated time in Table 1. The reaction solution was diluted with ethyl acetate (4 ml) and filtered through a thin pad of celite (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via column chromatography on silica gel (petroleum ether/ethyl acetate).

2-(4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2a**)¹



White solid, m. p. 53-55 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 2.37 (s, 3H), 1.34 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 141.39, 134.73, 128.49, 83.57, 24.79, 21.72.

General procedure for optimization of reaction parameters

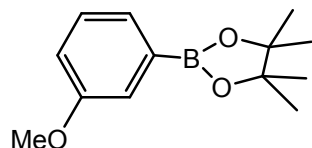
A glass vessel was charged with XPhos-Pd-G2 (15.7 mg, 0.02 mmol), XPhos (19 mg, 0.04 mmol), B₂pin₂ (508 mg, 2.00 mmol), and base (3.00 mmol) in the solvent (2 ml) indicated in the table 2. The mixture under nitrogen was stirred for 10 min, followed by the addition of **1a** (127 mg, 1.00 mmol). The reaction mixture was stirred at room

temperature for 30 minutes. The reaction solution was diluted with ethyl acetate (4 ml) and filtered through a thin pad of celite (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via column chromatography on silica gel (petroleum ether/ethyl acetate).

General procedure for borylation of aryl chlorides

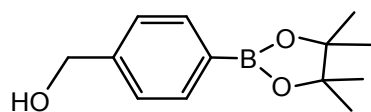
A glass vessel was charged with XPhos-Pd-G2 (4 mg, 0.005 mmol), XPhos (1.2 mg, 0.0025 mmol), B₂pin₂ (305 mg, 1.20 mmol), and K₃PO₄·7H₂O (1.01 g, 3.00 mmol) in EtOH (2 ml). The mixture under nitrogen was stirred for 10 min, followed by the addition of **1** (1.00 mmol). The reaction mixture was stirred at room temperature until the reaction was complete as monitored by TLC. The reaction solution was diluted with ethyl acetate (4 ml) and filtered through a thin pad of celite (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via column chromatography on silica gel (petroleum ether/ethyl acetate).

2-(3-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b**)¹ (Table 3, entry 1)



White solid, m. p. 106-107°C. ¹H NMR (300 MHz, CDCl₃) δ 7.43 – 7.37 (m, 1H), 7.33 (d, *J* = 3.5 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.01 (ddd, *J* = 8.2, 2.8, 1.2 Hz, 1H), 3.83 (s, 3H), 1.34 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 158.98, 128.88, 127.12, 118.66, 117.82, 83.75, 55.14, 24.80.

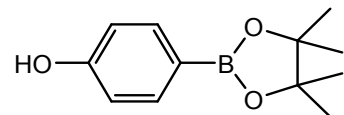
2-(4-Hydroxymethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2c**)² (Table 3, entry 2)



White solid, m. p. 122-124°C. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 2H), 1.35 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ

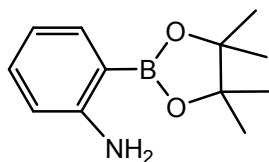
143.94, 134.95, 126.02, 83.78, 65.12, 24.79.

2-(4-Hydroxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d) ¹ (Table 3, entry 3)



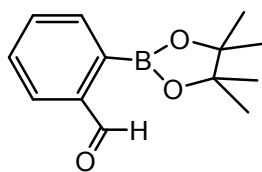
White solid, m. p. 109-110°C. ¹H NMR (300 MHz, CDCl₃) δ 7.70 (d, *J* = 8.5 Hz, 2H), 6.87 – 6.77 (m, 2H), 1.33 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 158.78, 136.71, 114.96, 83.79, 24.72.

2-(2-Aminophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e) ³ (Table 3, entry 4)



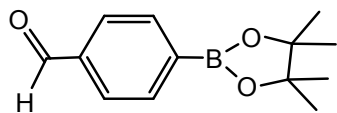
White solid, m. p. 89-90°C. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.21 (ddd, *J* = 8.1, 7.2, 1.7 Hz, 1H), 6.67 (td, *J* = 7.3, 1.0 Hz, 1H), 6.61 – 6.57 (m, 1H), 4.73 (s, 2H), 1.34 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 153.58, 136.73, 132.67, 116.80, 114.70, 83.43, 24.85.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-benzaldehyde (2f) ¹ (Table 3, entry 5)



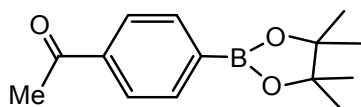
White solid, m. p. 71-73°C. ¹H NMR (400 MHz, CDCl₃) δ 10.55 (s, 1H), 7.98 – 7.93 (m, 1H), 7.88 – 7.84 (m, 1H), 7.61 – 7.52 (m, 2H), 1.39 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 194.46, 141.11, 135.34, 132.86, 130.60, 127.75, 84.26, 24.72.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-benzaldehyde (2g) ³ (Table 3, entry 6)



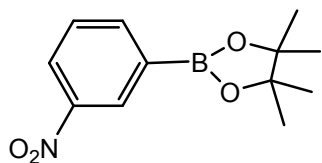
White solid, m. p. 55-57°C. ^1H NMR (400 MHz, CDCl_3) δ 10.05 (s, 1H), 7.97 (d, J = 7.9 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 1.37 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.79, 137.95, 135.16, 128.70, 84.30, 24.82.

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethanone (2h) ¹ (Table 3, entry 7)



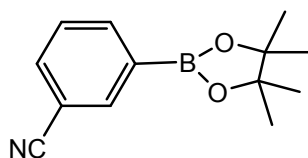
White solid, m. p. 63-65°C. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (td, J = 8.2, 6.5 Hz, 4H), 2.63 (s, 3H), 1.36 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.56, 138.82, 134.85, 127.25, 84.17, 26.82, 24.82.

2-(3-Nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i) ¹ (Table 3, entry 8)



White solid, m. p. 108-109°C. ^1H NMR (300 MHz, CDCl_3): δ 8.64 (d, J = 1.7 Hz, 1H), 8.30 (ddd, J = 8.2, 2.4, 1.1 Hz, 1H), 8.10 (d, J = 7.3 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 1.37 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.65, 140.62, 129.31, 128.70, 125.80, 84.52, 24.78.

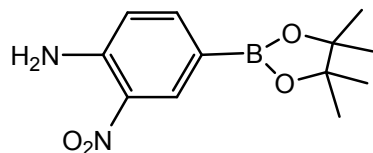
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (2j) ³ (Table 3, entry 9)



White solid, m. p. 93-94°C. ^1H NMR (300 MHz, CDCl_3) δ 8.09 (s, 1H), 8.04 – 7.96 (m, 1H), 7.72 (dt, J = 7.8, 1.5 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 1.35 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.65, 138.28, 134.27, 128.30, 118.71, 111.95, 84.38,

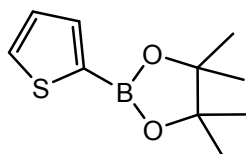
24.76.

2-Nitro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (2k) ⁴ (Table 3, entry 10)



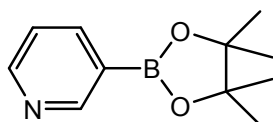
White solid, m. p. 176-177°C. ¹H NMR (300 MHz, CDCl₃) δ 8.59 (d, J = 1.1 Hz, 1H), 7.72 (dd, J = 8.3, 1.3 Hz, 1H), 6.77 (d, J = 8.3 Hz, 1H), 6.21 (s, 2H), 1.33 (s, 13H). ¹³C NMR (101 MHz, CDCl₃) δ 146.43 (s), 141.04 (s), 133.70 (s), 131.99 (s), 117.93 (s), 83.95 (s), 24.80 (s).

4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolan (2l) ¹ (Table 3, entry 11)



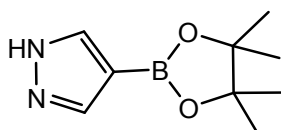
White solid, m. p. 76-78°C. ¹H NMR (300 MHz, CDCl₃) δ 7.65 (dd, J = 5.9, 4.1 Hz, 2H), 7.19 (dd, J = 4.6, 3.5 Hz, 1H), 1.35 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 137.12, 132.33, 128.18, 84.03, 24.73.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (2m) ⁵ (Table 3, entry 12)



White solid, m. p. 102-104°C. ¹H NMR (400 MHz, CDCl₃) δ 8.95 (s, 1H), 8.67 (dd, J = 4.9, 1.9 Hz, 1H), 8.06 (d, J = 7.5 Hz, 1H), 7.32 – 7.27 (m, 1H), 1.36 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 155.32, 151.87, 142.19, 123.05, 84.14, 24.78.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole (2m) ⁶ (Table 3, entry 13)



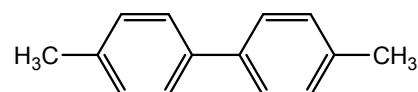
White solid, m. p. 143-145°C. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 2H), 1.34 (s,

12H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.27 (s), 83.37 (s), 24.75 (s).

General procedure for synthesis of symmetrical biaryl compounds

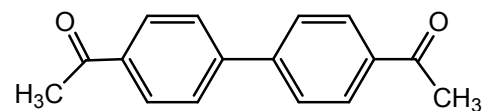
A glass vessel was charged with XPhos-Pd-G2 (4 mg, 0.005 mmol), XPhos (2.4 mg, 0.005 mmol), B_2pin_2 (127 mg, 0.50 mmol), and $\text{K}_3\text{PO}_4 \cdot 7\text{H}_2\text{O}$ (1.01 g, 3.00 mmol) in EtOH (5 ml). The mixture under nitrogen was stirred for 10 min, followed by the addition of aryl chlorides (1.00 mmol). The reaction mixture was stirred at room temperature for 8 h. The reaction solution was diluted with ethyl acetate (6 ml) and filtered through a thin pad of celite (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via column chromatography on silica gel (petroleum ether/ethyl acetate).

4,4'-Dimethylbiphenyl (3a) ⁷



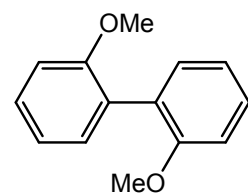
White solid, m. p. 118-119 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, J = 7.8 Hz, 4H), 7.24 (d, J = 7.9 Hz, 4H), 2.39 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.18, 136.67, 129.40, 126.76, 21.08.

4,4'-Diacetylbiphenyl (3b) ⁸



White solid, m. p. 193-195 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 8.3 Hz, 4H), 7.73 (d, J = 8.3 Hz, 4H), 2.66 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.68, 144.21, 136.35, 128.95, 127.37, 26.73.

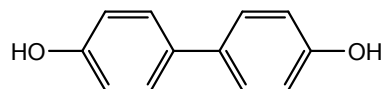
2,2'-Dimethoxybiphenyl (3c) ⁹



White solid, m. p. 152-154 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.33 (ddd, J = 8.1, 7.5, 1.8 Hz, 2H), 7.26 (d, J = 1.8 Hz, 1H), 7.23 (d, J = 1.8 Hz, 1H), 7.00 (ddd, J = 8.2, 6.5,

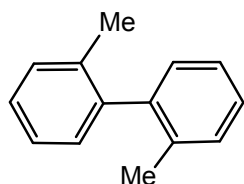
2.8 Hz, 4H), 3.77 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.97, 131.40, 128.55, 127.75, 120.28, 111.03, 55.62.

2,2'-Biphenol (3d)¹⁰



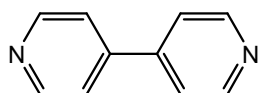
Grey solid, m. p. 281-282°C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.64 – 9.30 (m, 2H), 7.63 – 7.26 (m, 4H), 6.88 (d, J = 8.4 Hz, 4H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 156.35, 131.31, 127.12, 115.73.

2,2'-Dimethylbiphenyl (3e)¹¹



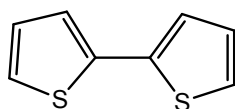
White solid, m. p. 90-92°C. ^1H NMR (300 MHz, CDCl_3) δ 7.28 – 7.18 (m, 6H), 7.14 – 7.07 (m, 2H), 2.08 – 2.02 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.56, 135.78, 129.77, 129.25, 127.12, 125.50, 19.80.

4,4'-Bipyridine (3f)¹²



White solid, m. p. 109-111°C. ^1H NMR (400 MHz, CDCl_3) δ 8.75 (d, J = 5.9 Hz, 4H), 7.55 (d, J = 6.0 Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.52, 145.35, 121.27.

2,2'-Bithiophene (3g)⁵

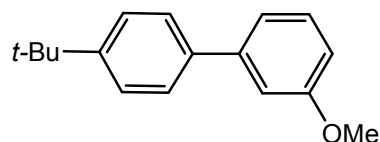


White solid, m. p. 32-33°C. ^1H NMR (400 MHz, CDCl_3) δ 7.21 (dd, J = 5.1, 0.8 Hz, 2H), 7.18 (dd, J = 3.6, 0.7 Hz, 2H), 7.02 (dd, J = 5.0, 3.7 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.30, 127.74, 124.31, 123.69.

General procedure for synthesis of asymmetrical biaryl compounds

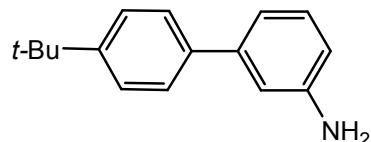
A glass vessel was charged with XPhos-Pd-G2 (8 mg, 0.01 mmol), XPhos (4.8 mg, 0.01 mmol), B₂pin₂ (305 mg, 1.20 mmol), and K₃PO₄·7H₂O (1.01 g, 3.00 mmol) in EtOH (4 ml). The mixture under nitrogen was stirred for 10 min, followed by the addition of the first chloride (1.10 mmol). The reaction mixture was stirred at room temperature for 2 h. At this point the second aryl chloride (1.0 mmol) and K₃PO₄·7H₂O (3.0 M aqueous solution, 1.0 ml) were added to the reaction mixture under nitrogen. The reaction mixture was stirred at room temperature for the time indicated in Table 5 and 6. The reaction solution was diluted with ethyl acetate (5 ml) and filtered through a thin pad of celite (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via column chromatography on silica gel (petroleum ether/ethyl acetate).

3-Methoxy-4'-(*tert*-butyl)-1,1'-biphenyl (4a) ¹³



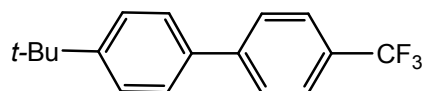
White solid, m. p. 107-109°C. ¹H NMR (300 MHz, CDCl₃) δ 7.58 – 7.41 (m, 4H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.21 – 7.14 (m, 1H), 7.14 – 7.09 (m, 1H), 6.88 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 3.86 (s, 3H), 1.36 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 159.86, 150.40, 142.59, 138.16, 129.65, 126.80, 125.66, 119.54, 112.72, 112.37, 55.23, 34.52, 31.34.

4'-(*tert*-Butyl)-[1,1'-biphenyl]-3-amine (4b) ¹⁴



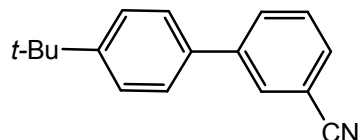
White solid, m. p. 146-148°C. ¹H NMR (300 MHz, CDCl₃) δ 7.54 – 7.40 (m, 4H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.03 – 6.96 (m, 1H), 6.91 (t, *J* = 1.9 Hz, 1H), 6.71 – 6.61 (m, 1H), 1.35 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 150.09, 146.60, 142.16, 138.37, 129.53, 126.64, 125.51, 117.47, 113.81, 113.70, 34.43, 31.31.

4-(*tert*-Butyl)-4'-(trifluoromethyl)-1,1'-biphenyl (4c) ¹⁵



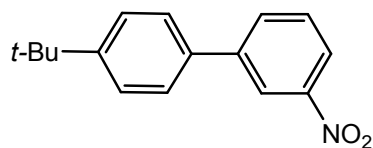
White solid, m. p. 133-134°C. ^1H NMR (300 MHz, CDCl_3) δ 7.68 (s, 4H), 7.58 – 7.46 (m, 4H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.35, 144.53, 136.81, 127.19, 126.91, 125.95, 125.66, 125.62, 34.62, 31.30.

4'-(*tert*-Butyl)-[1,1'-biphenyl]-3-carbonitrile (4d) ¹⁴



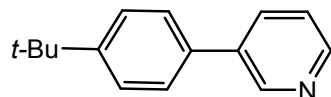
White solid, m. p. 103-105°C. ^1H NMR (300 MHz, CDCl_3) δ 7.85 (dd, J = 2.3, 1.1 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.60 (dt, J = 7.7, 1.4 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.50 (s, 4H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.45, 142.09, 135.75, 131.14, 130.32, 130.28, 129.42, 126.59, 125.97, 118.81, 112.74, 34.50, 31.17.

4'-(*tert*-Butyl)-3-nitro-1,1'-biphenyl (4e) ¹⁶



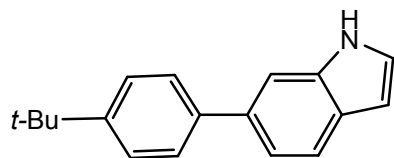
White solid, m. p. 111-112°C. ^1H NMR (300 MHz, CDCl_3) δ 8.45 (t, J = 1.9 Hz, 1H), 8.18 (ddd, J = 8.2, 2.3, 1.0 Hz, 1H), 7.91 (ddd, J = 7.8, 1.7, 1.0 Hz, 1H), 7.65 – 7.48 (m, 5H), 1.38 (s, 9H). ^{13}C NMR (101 MHz,) δ 151.69, 148.64, 142.62, 135.63, 132.74, 129.56, 126.73, 126.06, 121.65, 121.63, 34.59, 31.22.

3-[4-(*tert*-Butyl)phenyl]pyridine (4f) ¹⁷



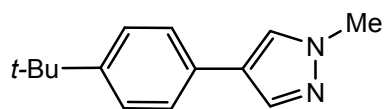
White solid, m. p. 87-88°C. ^1H NMR (300 MHz, CDCl_3) δ 8.85 (d, J = 1.7 Hz, 1H), 8.57 (dd, J = 4.8, 1.6 Hz, 1H), 7.88 (ddd, J = 7.9, 2.3, 1.7 Hz, 1H), 7.52 (d, J = 1.9 Hz, 4H), 7.36 (ddd, J = 7.9, 4.8, 0.8 Hz, 1H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.20, 148.12, 148.07, 136.43, 134.81, 134.14, 126.74, 126.00, 123.47, 34.56, 31.20.

6-[4-(*tert*-Butyl)phenyl]-1*H*-indole (4g) ¹⁸



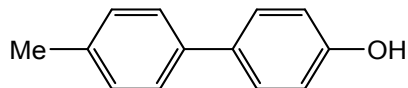
White solid, m. p. 74-76°C. ^1H NMR (300 MHz, CDCl_3) δ 8.15 (brs, 1H), 7.68 (d, J = 8.3 Hz, 1H), 7.65 – 7.54 (m, 3H), 7.51 – 7.43 (m, 2H), 7.39 (dd, J = 8.2, 1.6 Hz, 1H), 7.21 (dd, J = 3.2, 2.5 Hz, 1H), 6.56 (ddd, J = 3.1, 2.0, 0.9 Hz, 1H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.52, 139.32, 136.33, 135.34, 126.95, 125.63, 124.66, 120.78, 119.70, 109.32, 102.41, 34.46, 31.39.

4-[4-(*tert*-Butyl)phenyl]-1-methyl-1*H*-pyrazole (4h) ¹⁹



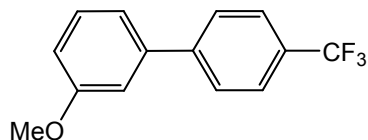
White solid, m. p. 68-69°C. ^1H NMR (300 MHz, CDCl_3) δ 7.74 (s, 1H), 7.57 (s, 1H), 7.40 (d, J = 1.1 Hz, 4H), 3.94 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.20, 136.59, 129.69, 126.62, 125.64, 125.16, 123.02, 38.92, 34.38, 31.25.

4'-Methyl-[1,1'-biphenyl]-4-ol (6a) ²⁰ (Table 6, entry 1)



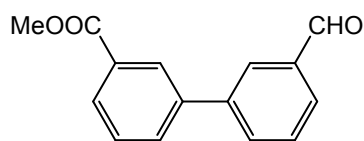
White solid, m. p. 153-154°C. ^1H NMR (400 MHz, CDCl_3) δ 7.45 (t, J = 8.7 Hz, 4H), 7.23 (d, J = 7.9 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 4.96 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.77, 137.80, 136.39, 133.86, 129.41, 128.15, 126.52, 115.52, 21.06.

3-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (6b) ²¹ (Table 6, entry 2)



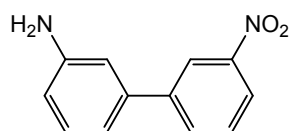
White solid, m. p. 156-158°C. ^1H NMR (300 MHz, CDCl_3) δ 7.68 (s, 4H), 7.39 (t, J = 7.9 Hz, 1H), 7.18 (ddd, J = 7.6, 1.6, 1.0 Hz, 1H), 7.14 – 7.10 (m, 1H), 6.95 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.06, 144.56, 141.20, 129.99, 127.42, 125.62, 125.68, 125.59, 119.69, 113.41, 113.10, 55.25.

Methyl 3'-formyl-[1,1'-biphenyl]-3-carboxylate (6c) ²² (Table 6, entry 3)



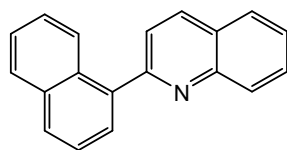
White solid, m. p. 101-103°C. ¹H NMR (400 MHz, CDCl₃) δ 10.03 (s, 1H), 8.07 (dd, *J* = 5.8, 4.0 Hz, 3H), 7.83 (ddd, *J* = 7.9, 4.8, 1.4 Hz, 2H), 7.65 – 7.61 (m, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 3.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 192.05, 166.75, 143.98, 140.93, 136.95, 133.08, 130.27, 129.66, 129.58, 129.49, 128.14, 127.08, 52.22.

3'-Nitro-[1,1'-biphenyl]-3-amine (6d) ²³ (Table 6, entry 4)



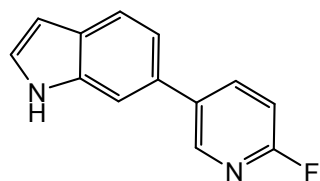
White solid, m. p. 224-225°C. ¹H NMR (300 MHz, CDCl₃) δ 8.42 (t, *J* = 2.0 Hz, 1H), 8.18 (ddd, *J* = 8.2, 2.3, 1.0 Hz, 1H), 7.88 (ddd, *J* = 7.7, 1.7, 1.1 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 3.9 Hz, 1H), 7.03 – 6.97 (m, 1H), 6.92 (t, *J* = 2.0 Hz, 1H), 6.75 (ddd, *J* = 8.0, 2.3, 0.8 Hz, 1H), 3.82 (brs, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 148.57, 147.08, 143.02, 139.77, 132.96, 130.07, 129.52, 121.91, 121.84, 117.36, 115.13, 113.53.

2-(Naphthalen-1-yl)quinoline (6e) ²⁴ (Table 6, entry 5)



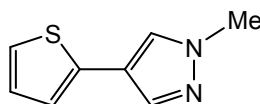
White solid, m. p. 95-97°C. ¹H NMR (400 MHz, CDCl₃) δ 8.21 (t, *J* = 8.9 Hz, 2H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.91 (t, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.71 – 7.68 (m, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.55 (dd, *J* = 14.8, 7.4 Hz, 2H), 7.50 – 7.41 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 159.29, 147.99, 138.60, 136.15, 133.88, 131.13, 129.63, 129.59, 129.01, 128.30, 127.65, 127.48, 126.86, 126.48, 125.86, 125.58, 125.28, 123.14.

6-(6-Fluoropyridin-3-yl)-1*H*-indole (6f) ²⁵ (Table 6, entry 6)



White solid, m. p. 69-71 °C. ^1H NMR (300 MHz, CDCl_3) δ 8.47 (dd, $J = 1.6, 0.7$ Hz, 1H), 8.40 (brs, 1H), 8.02 (ddd, $J = 8.4, 7.7, 2.6$ Hz, 1H), 7.73 (d, $J = 8.2$ Hz, 1H), 7.56 (d, $J = 0.7$ Hz, 1H), 7.33 – 7.27 (m, 2H), 7.00 (ddd, $J = 8.5, 3.0, 0.6$ Hz, 1H), 6.60 (ddd, $J = 3.0, 2.0, 0.9$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.93, 145.75, 139.88, 136.26, 135.97, 130.70, 127.79, 125.39, 121.41, 119.33, 109.51, 109.09, 102.65.

1-Methyl-4-(thiophen-2-yl)-1H-pyrazole (6g) ²⁴ (Table 6, entry 7)



White solid, m. p. 64-65 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.66 (s, 1H), 7.54 (s, 1H), 7.16 (dd, $J = 5.0, 1.2$ Hz, 1H), 7.03 (ddd, $J = 8.5, 4.2, 2.4$ Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.93, 135.00, 127.56, 126.99, 122.90, 122.37, 117.08, 39.03.

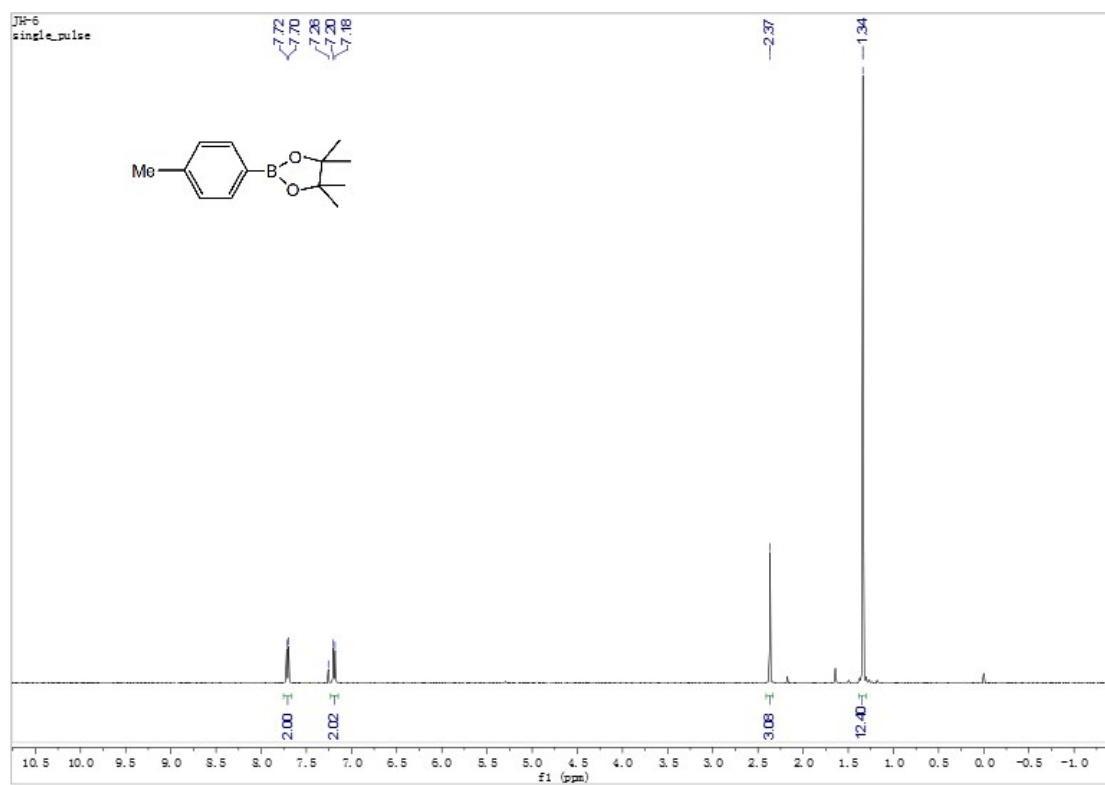
Reference

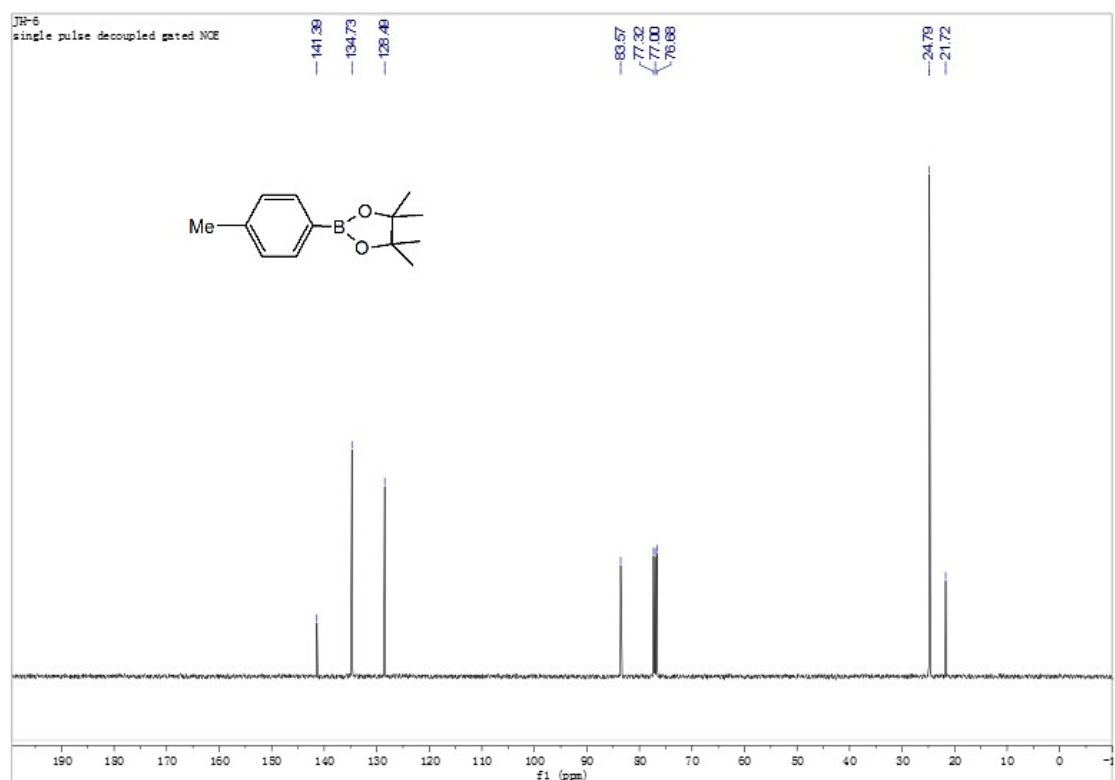
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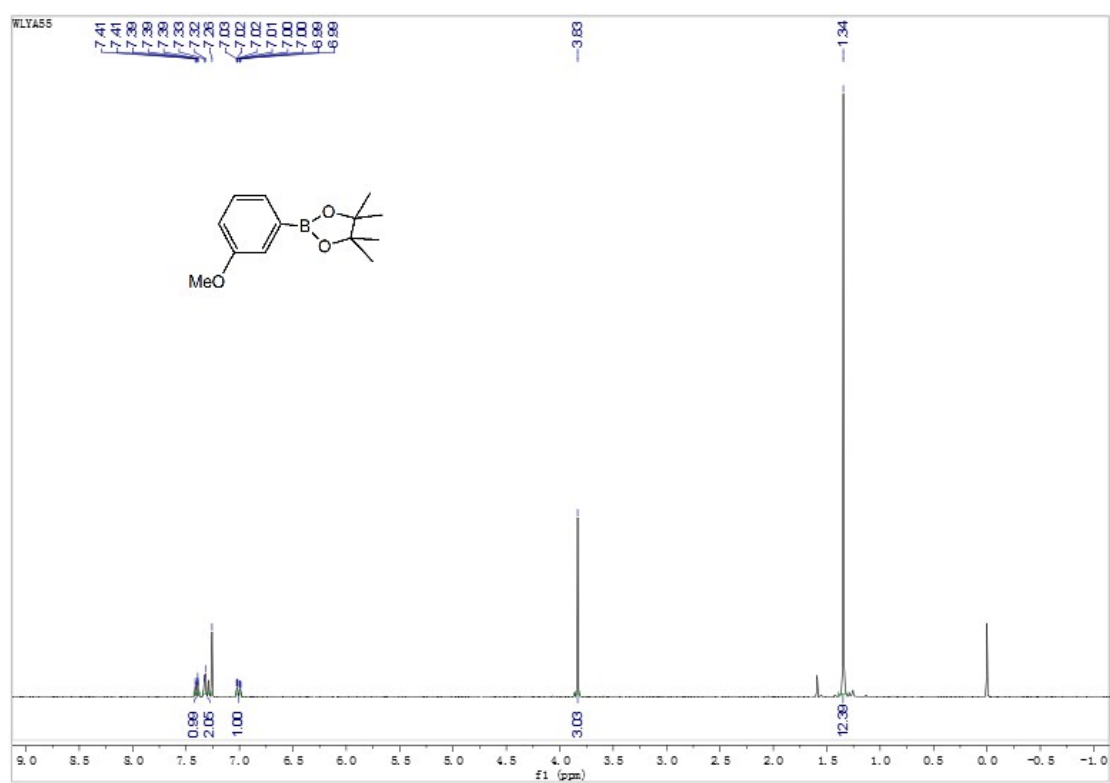
Copies of the ^1H and ^{13}C NMR spectra of the products

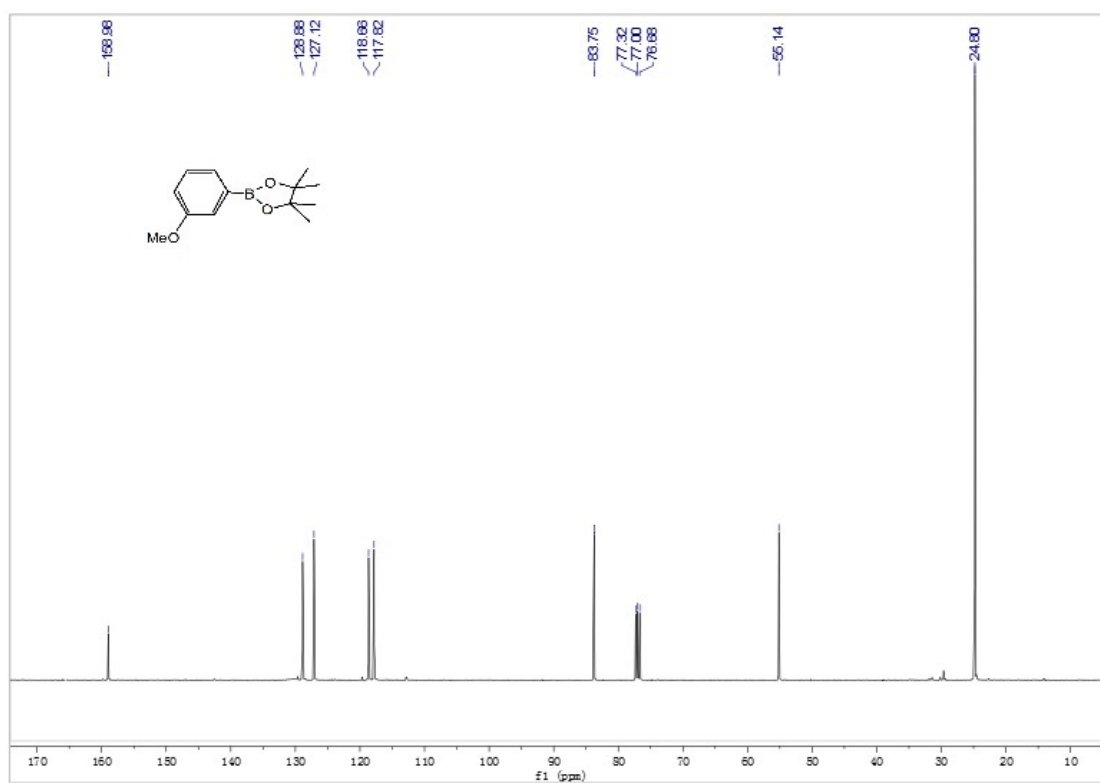
^1H and ^{13}C NMR spectra of compound 2a



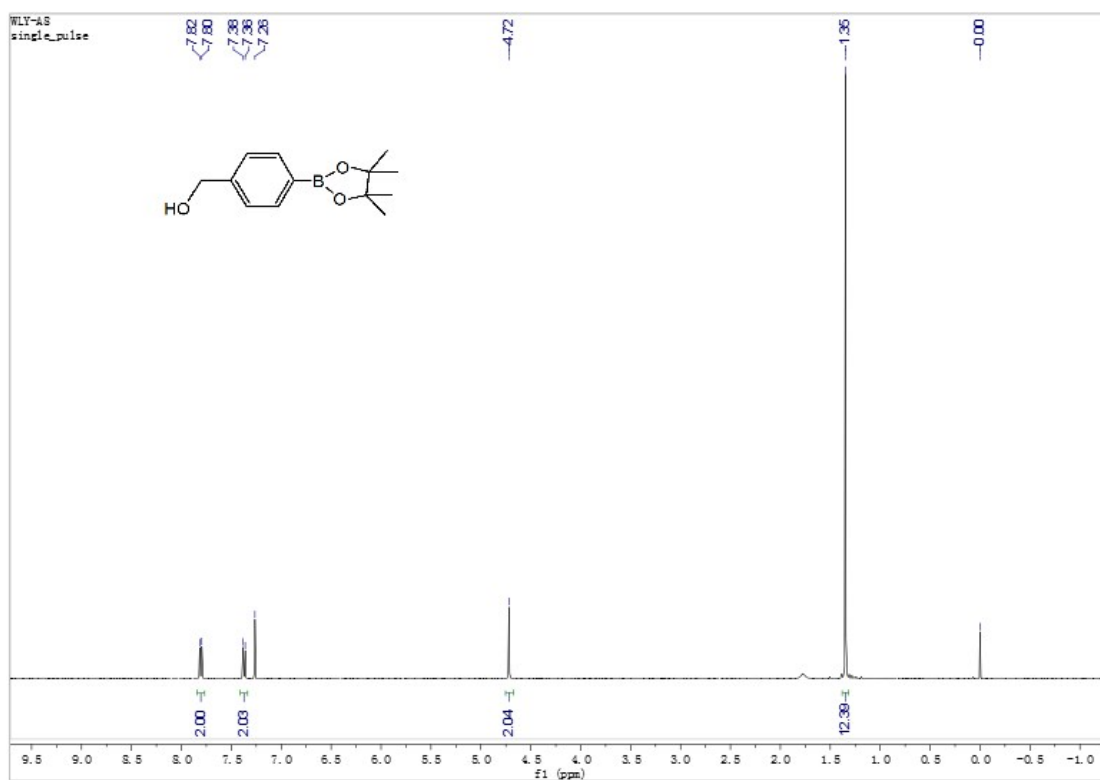


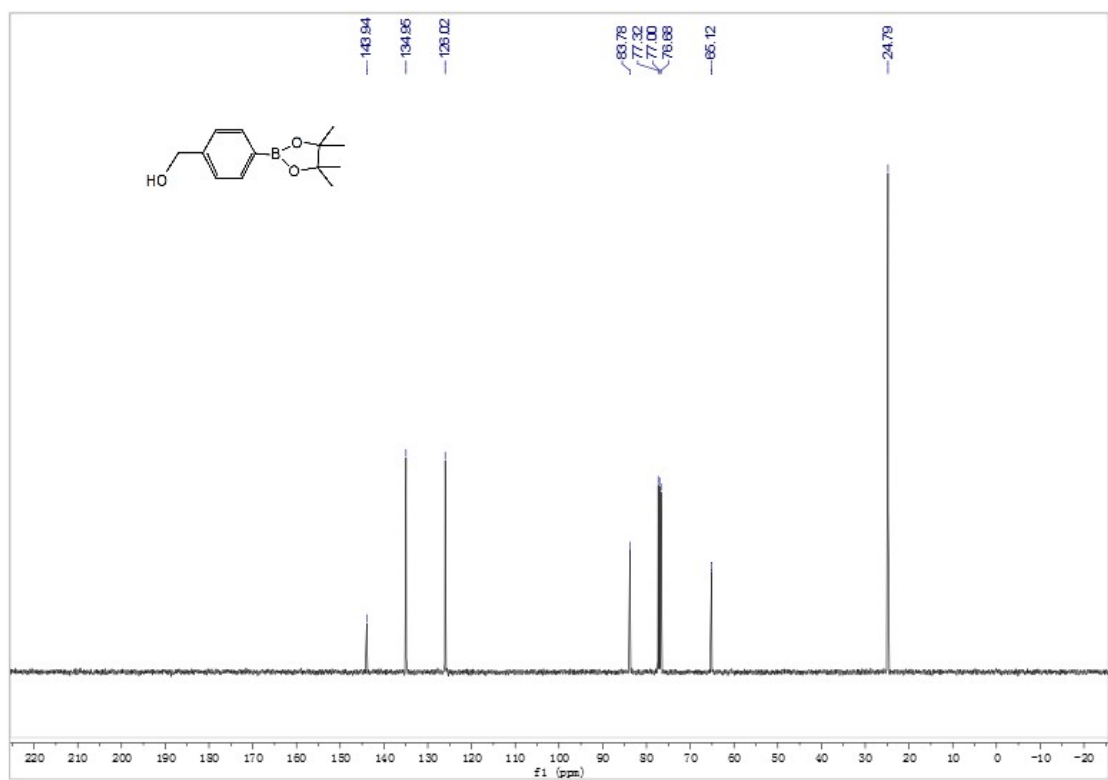
^1H and ^{13}C NMR spectra of compound 2b



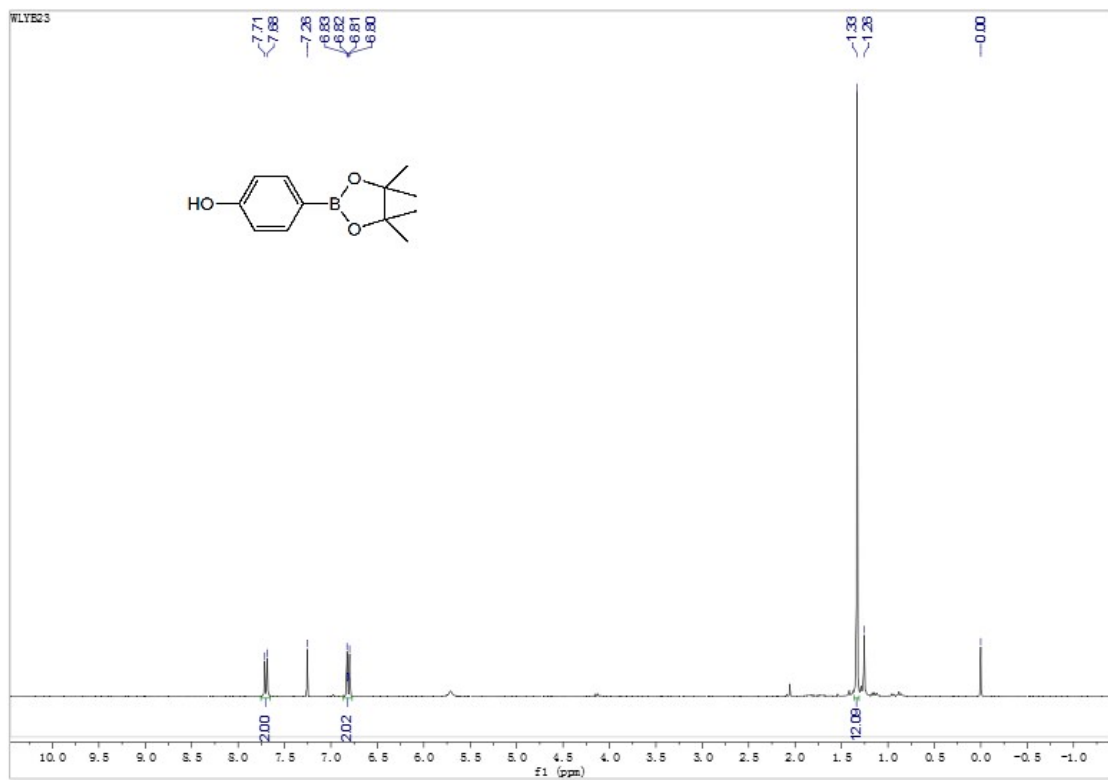


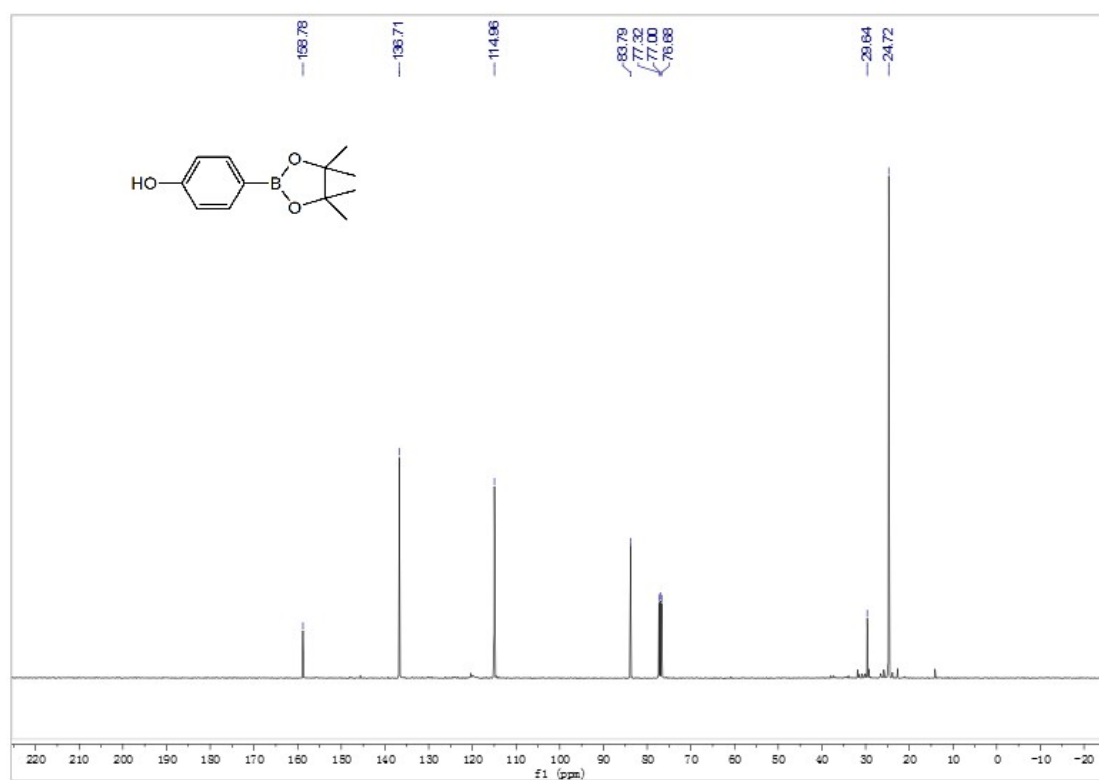
¹H and ¹³C NMR spectra of compound 2c



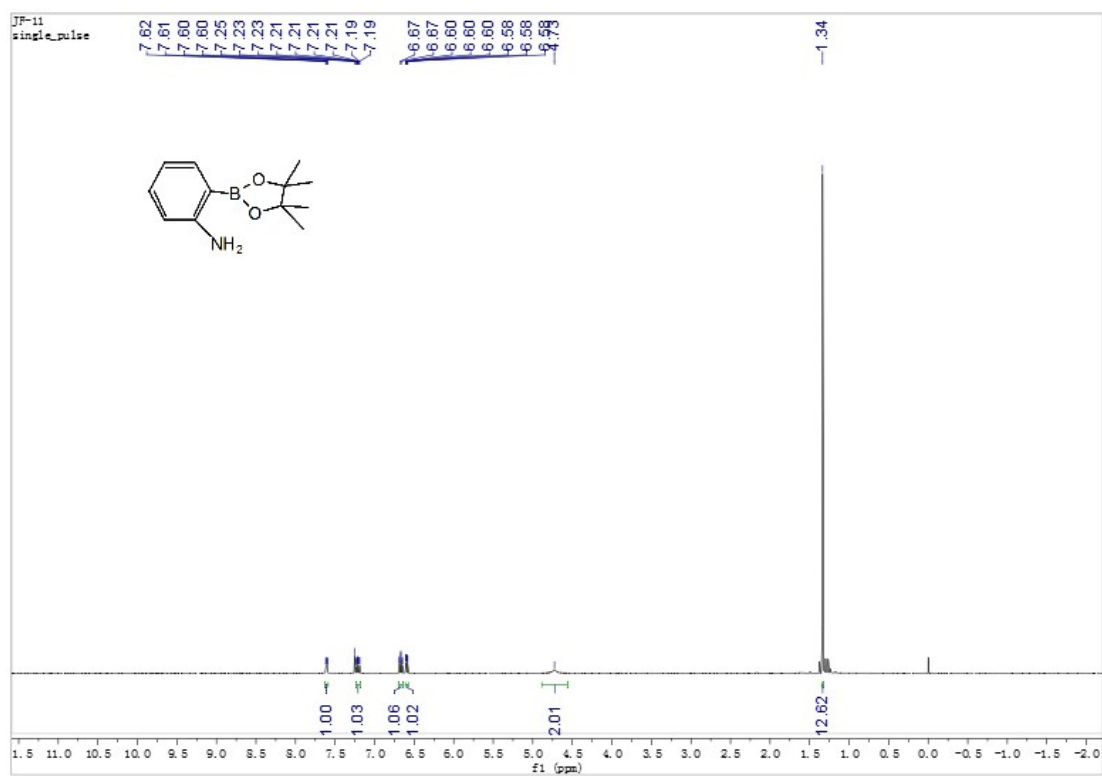


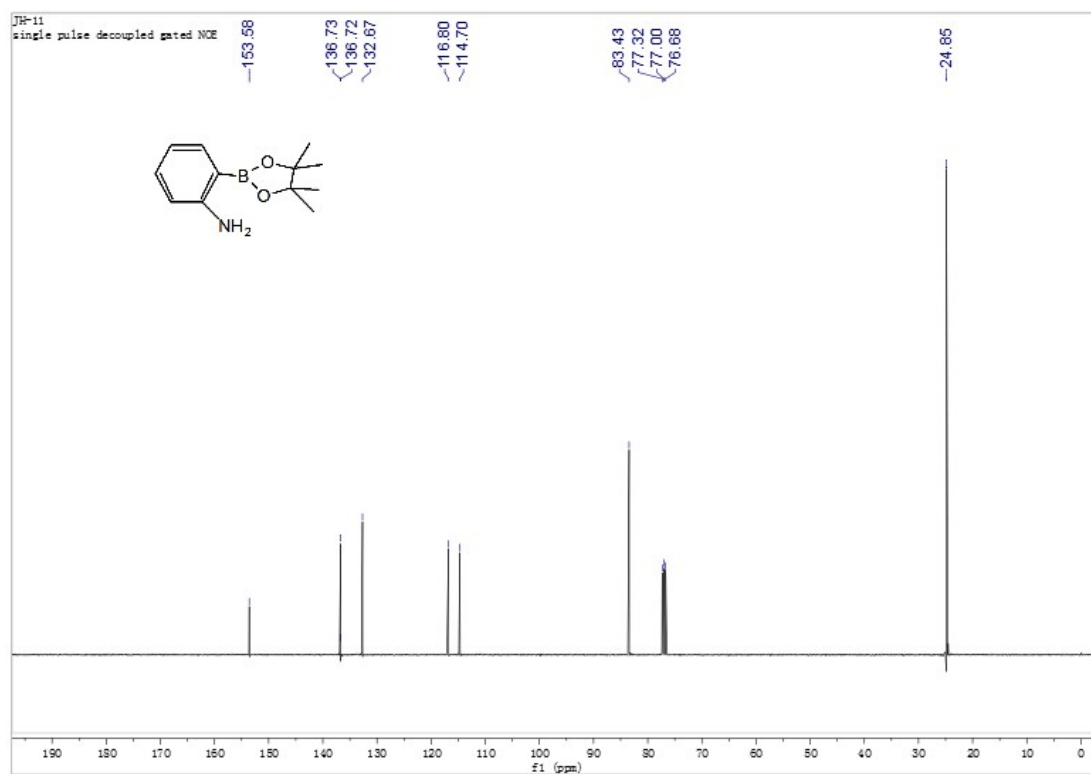
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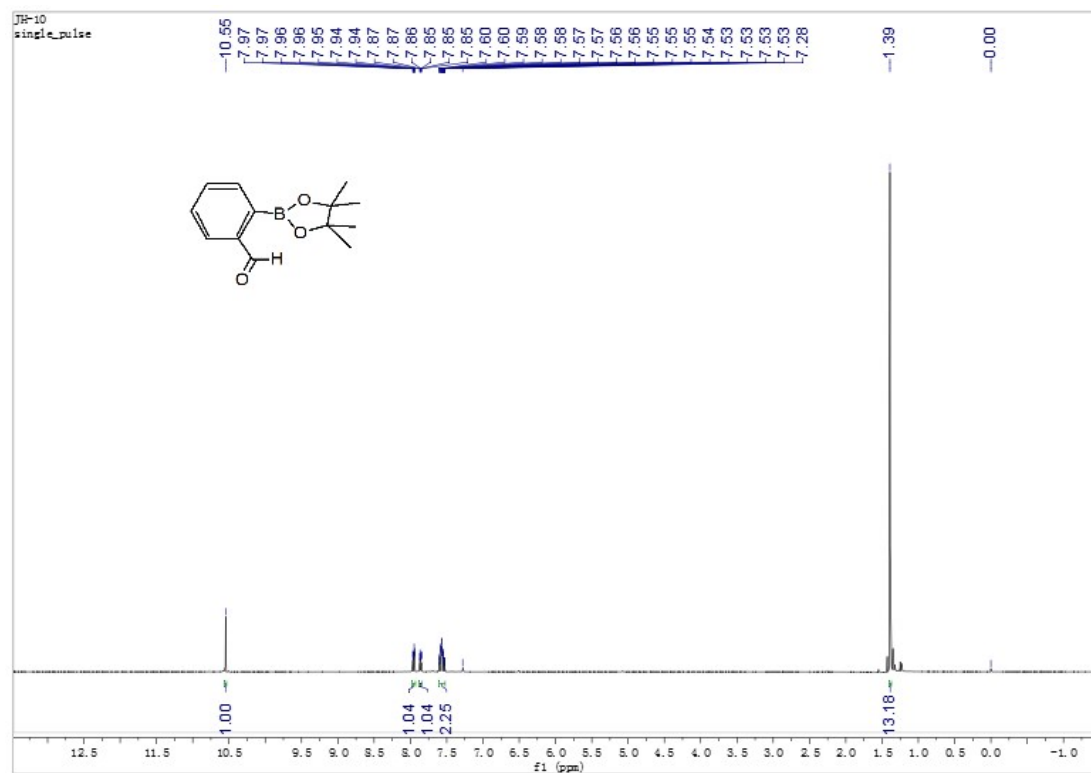


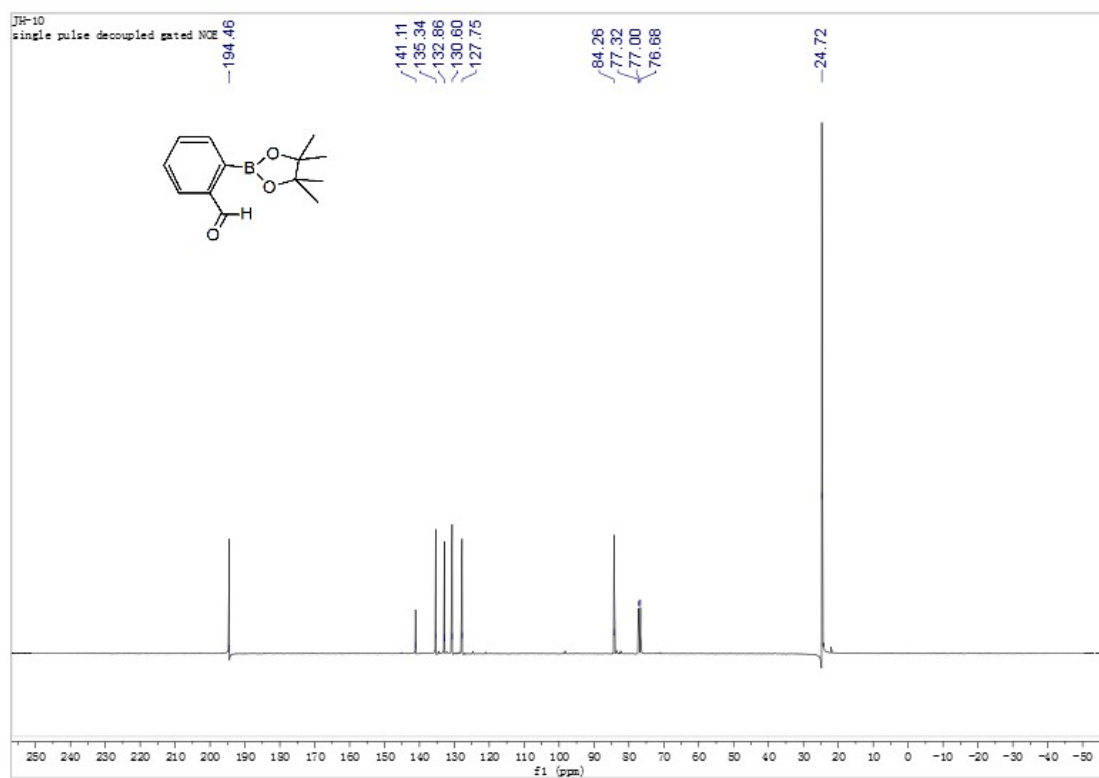
¹H and ¹³C NMR spectra of compound 2e



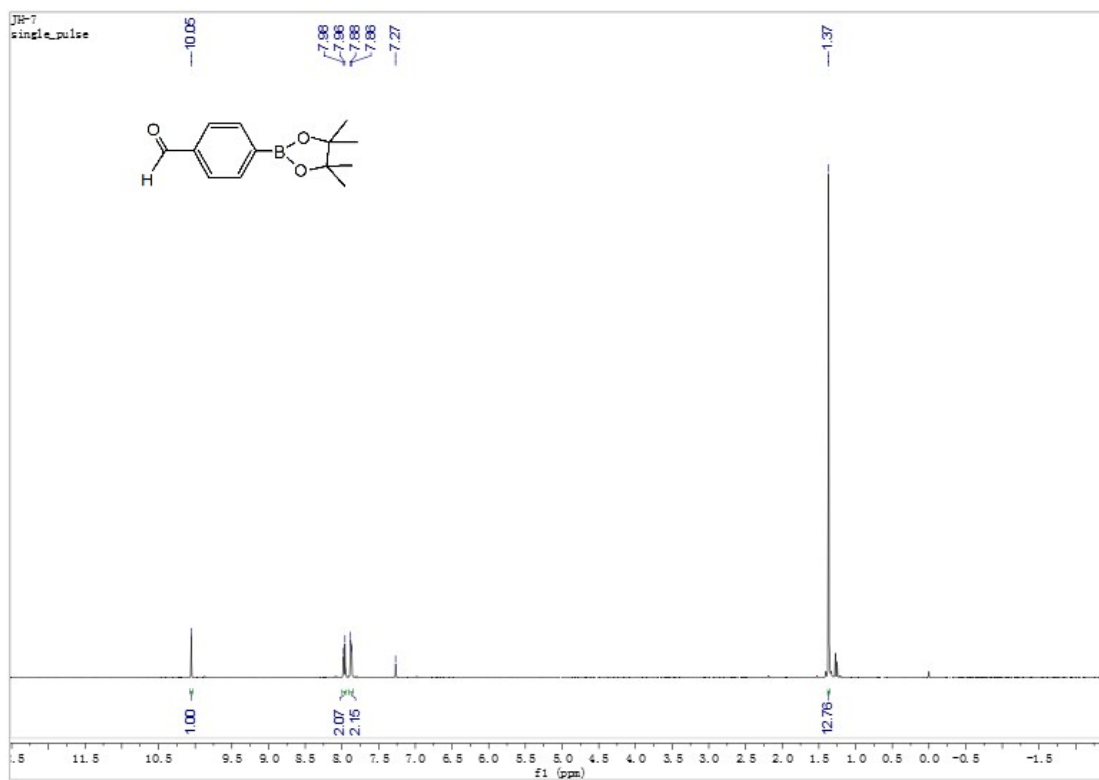


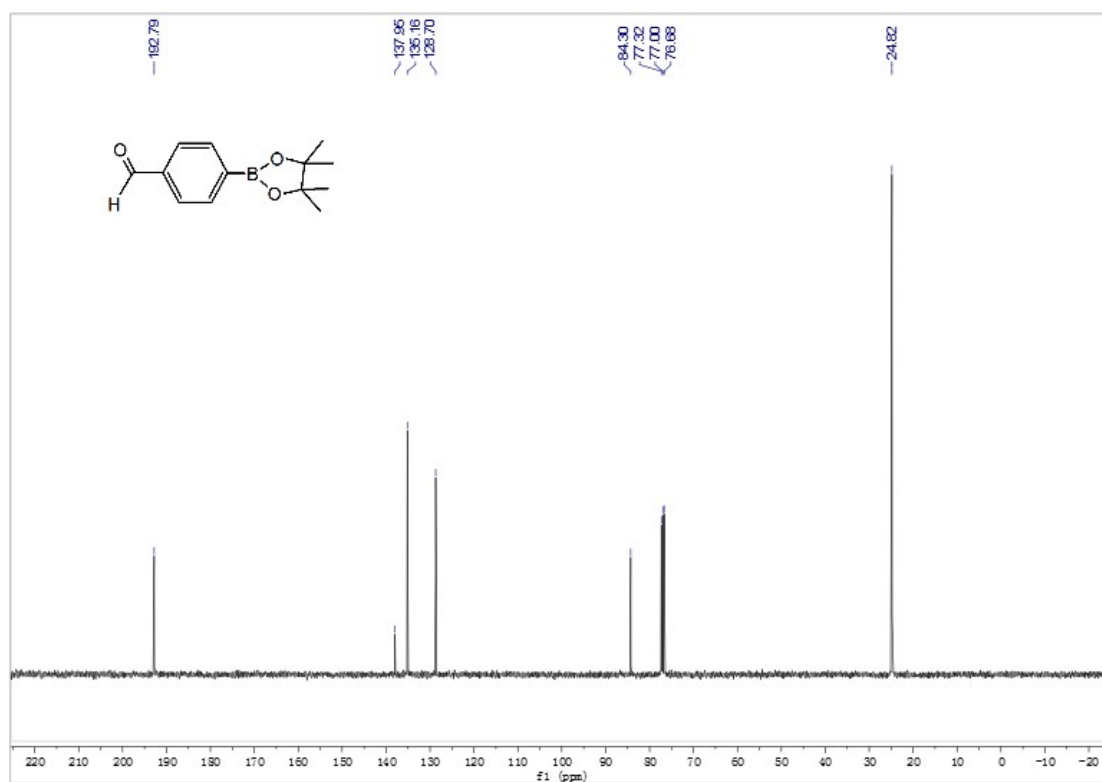
¹H and ¹³C NMR spectra of compound 2f



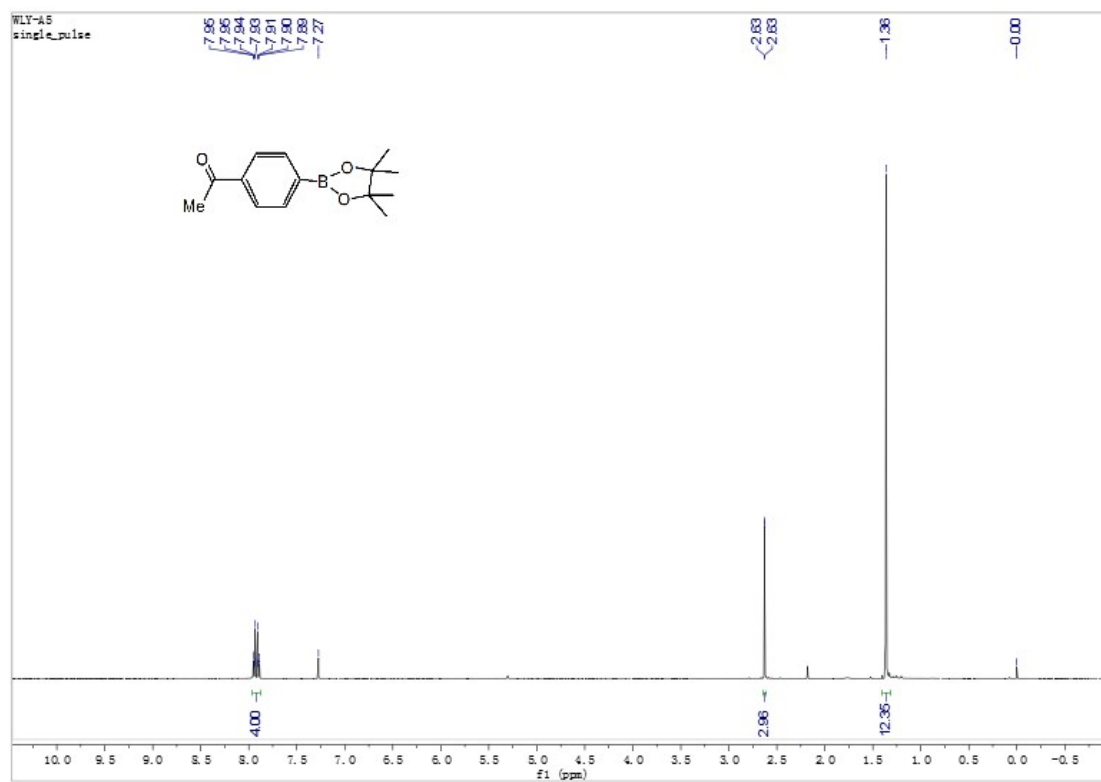


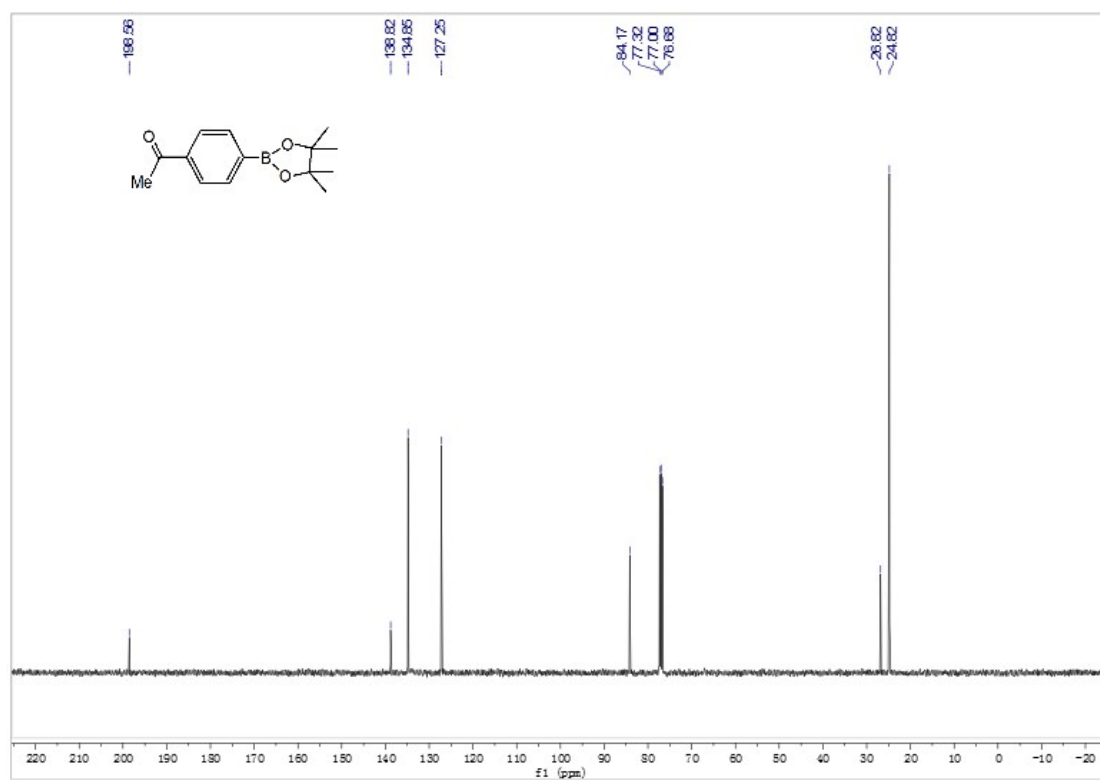
¹H and ¹³C NMR spectra of compound 2g



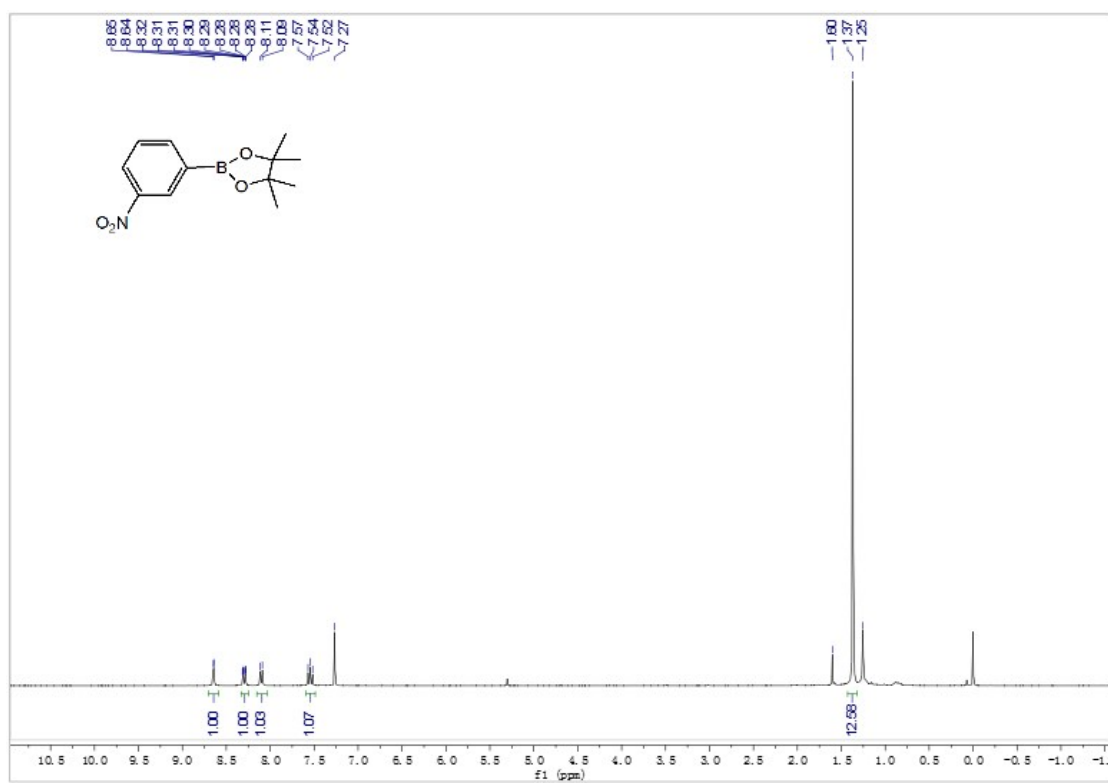


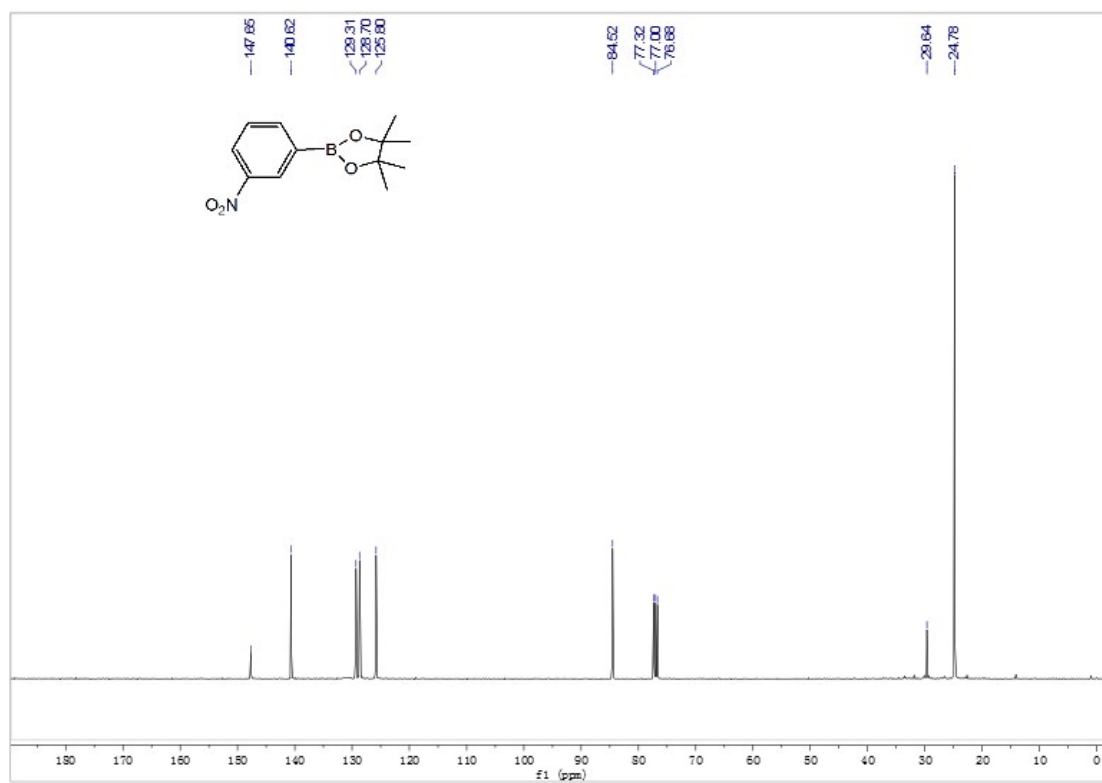
¹H and ¹³C NMR spectra of compound 2h



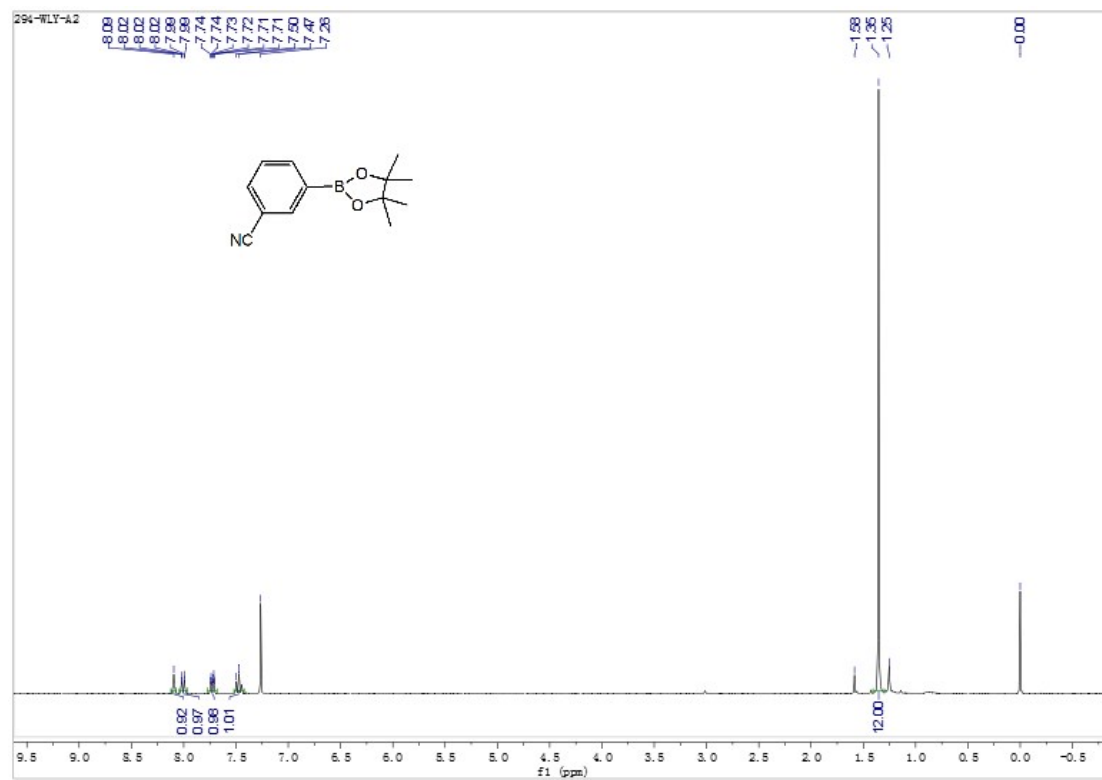


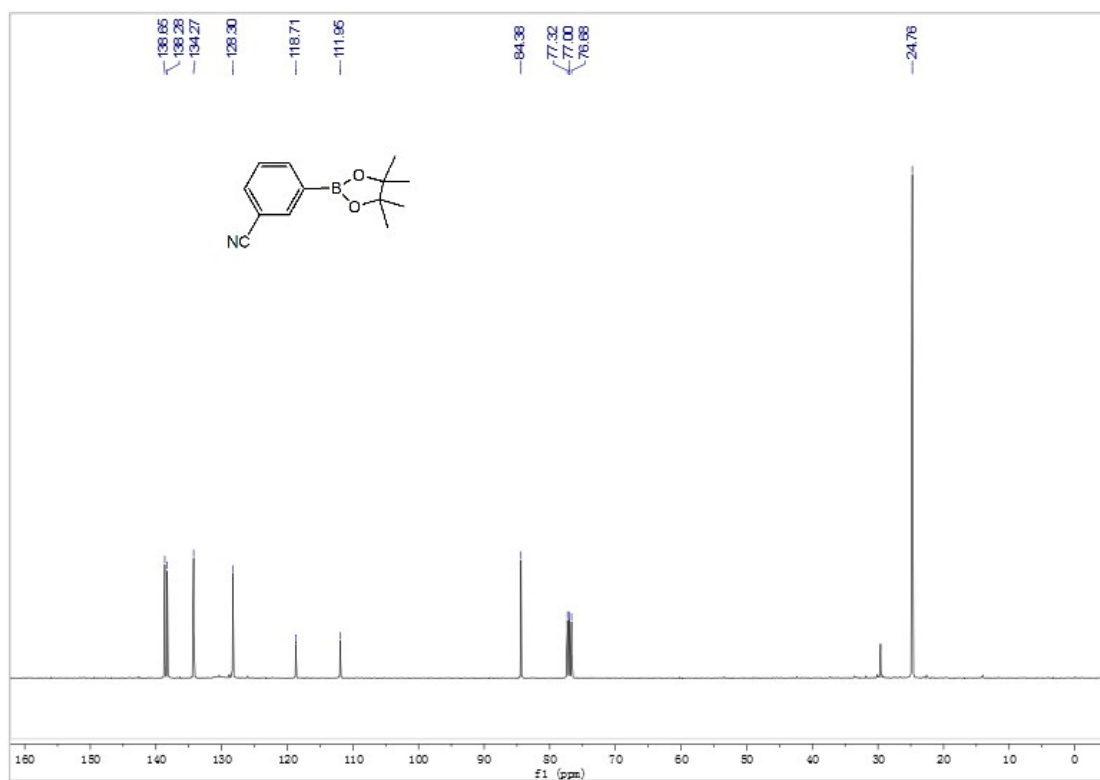
¹H and ¹³C NMR spectra of compound 2i



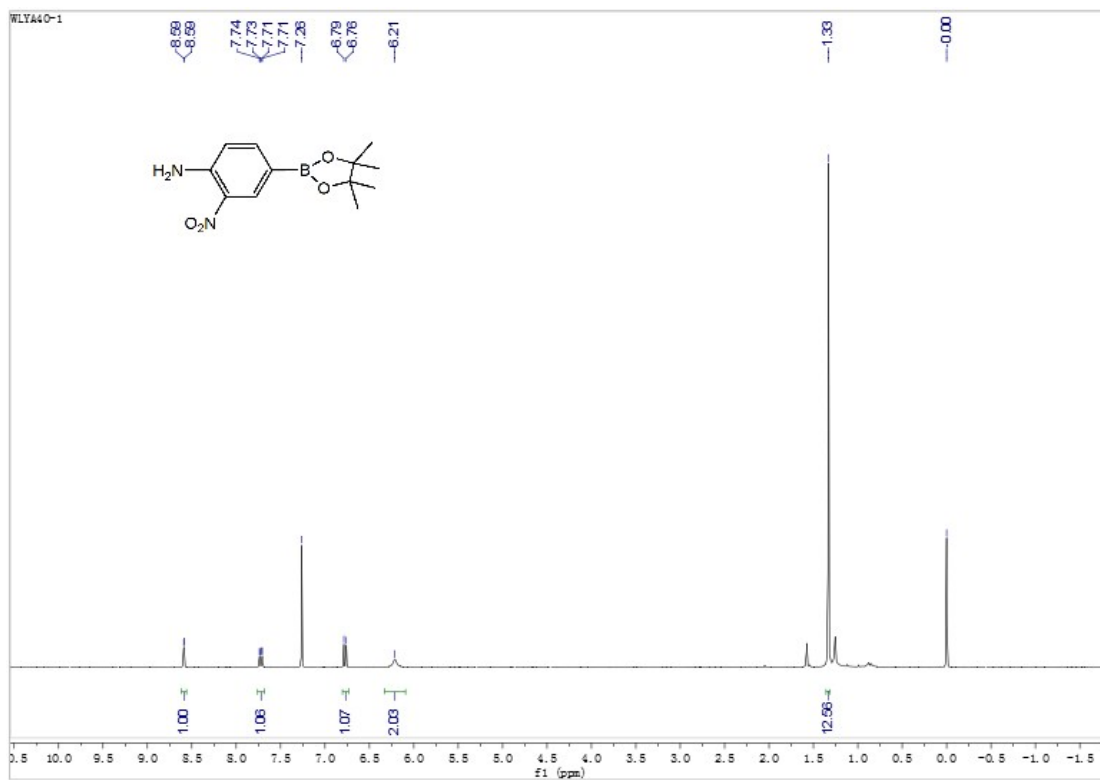


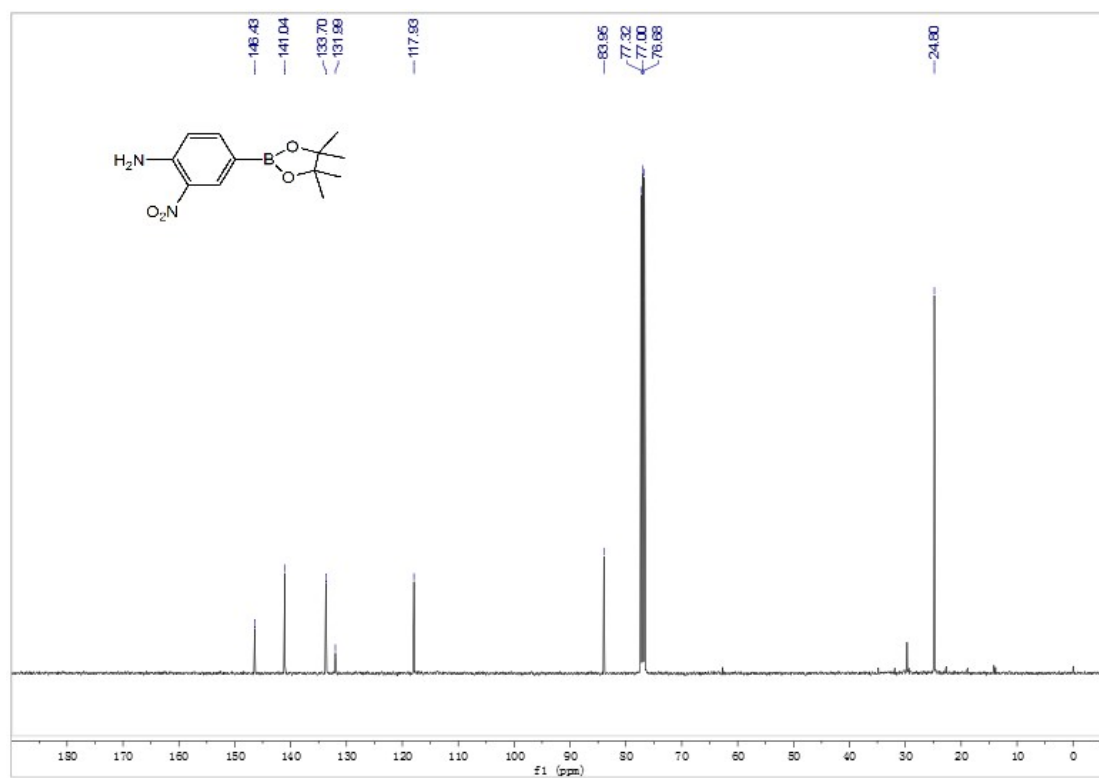
¹H and ¹³C NMR spectra of compound 2j



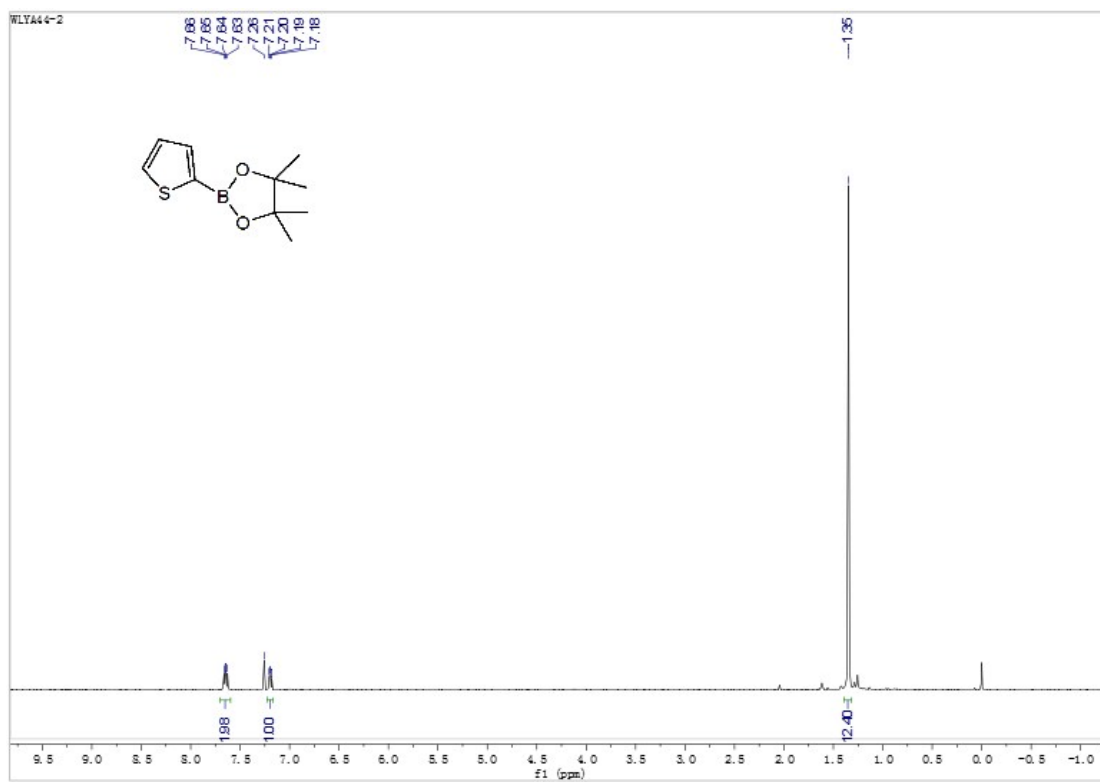


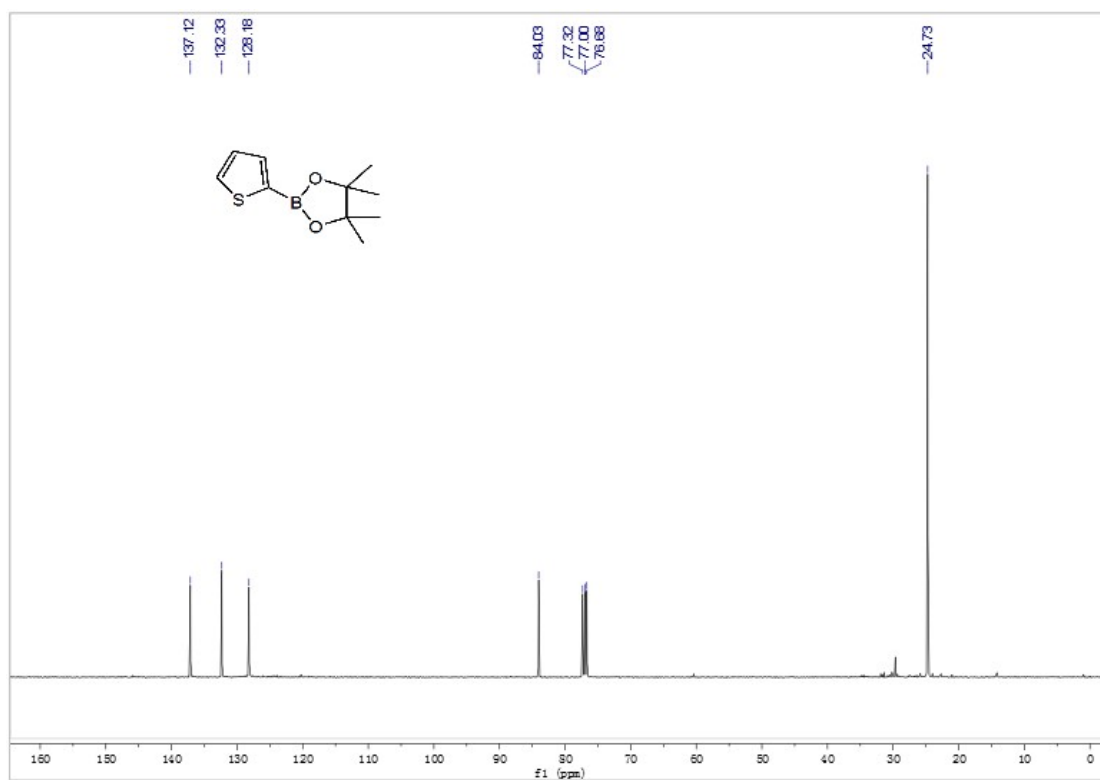
¹H and ¹³C NMR spectra of compound 2k



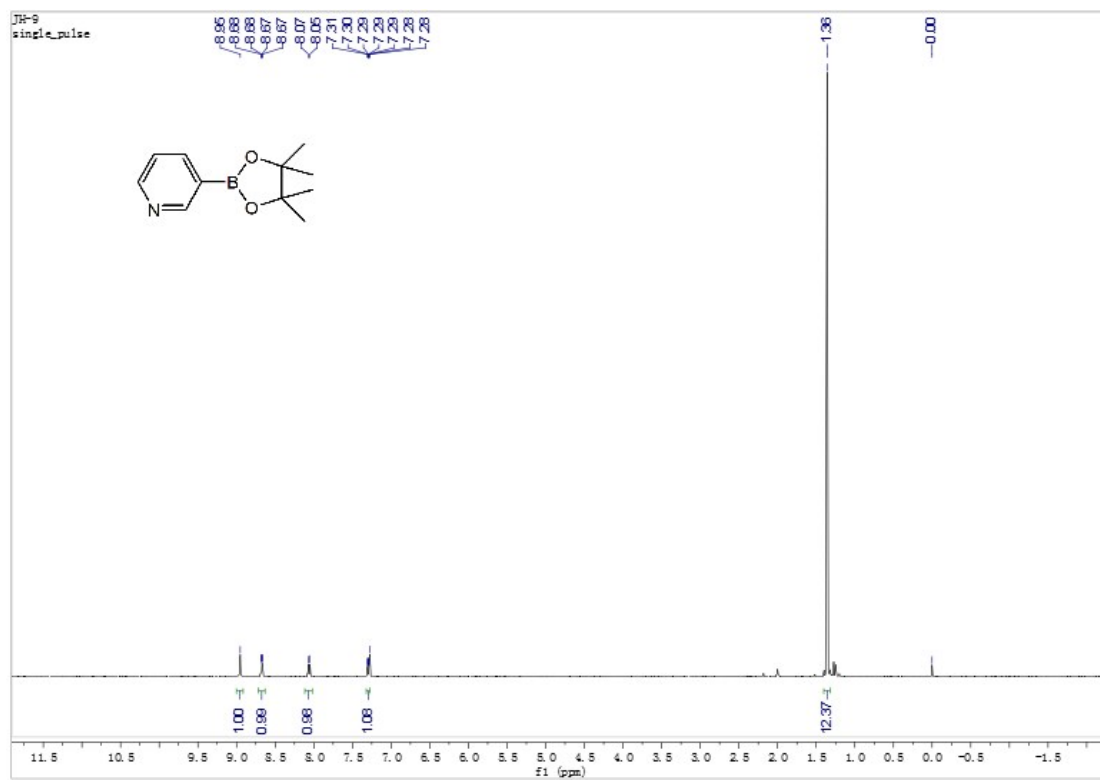


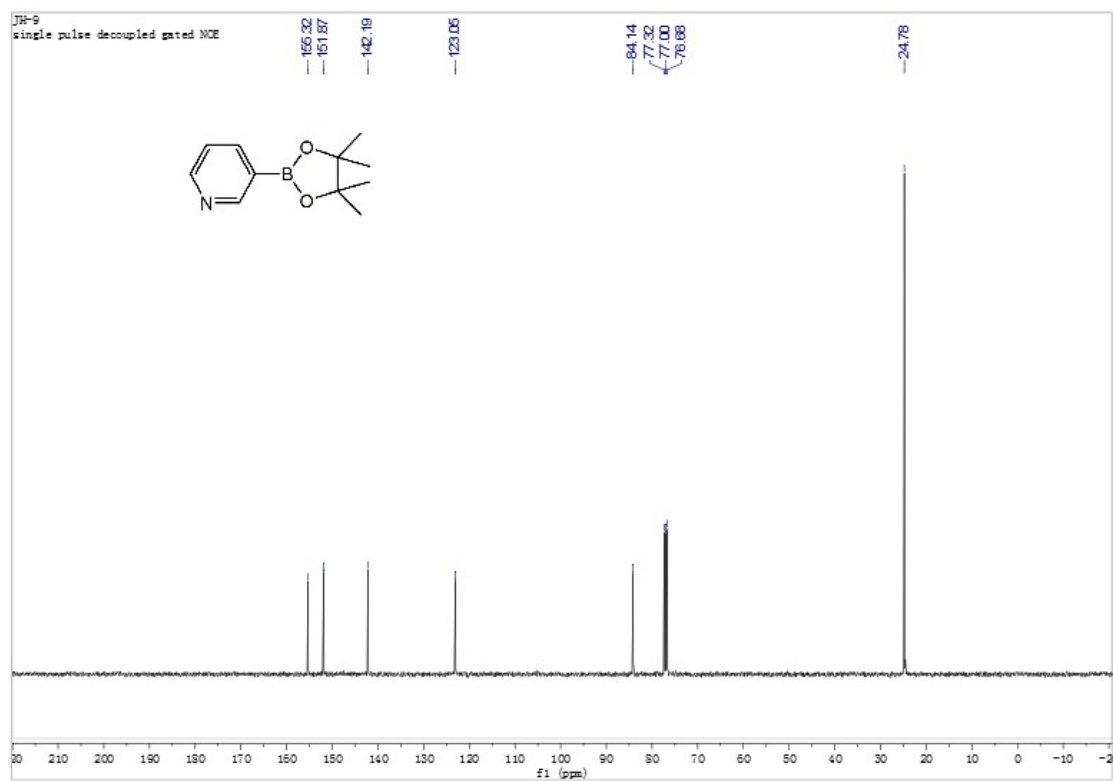
¹H and ¹³C NMR spectra of compound 21



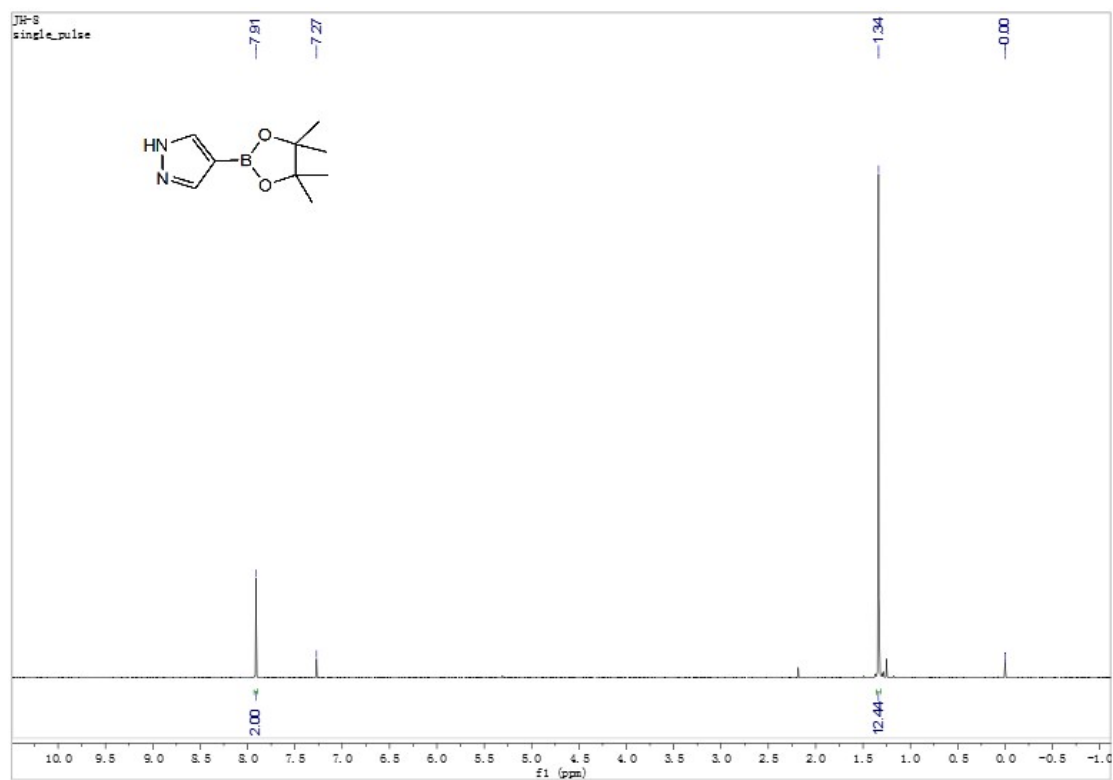


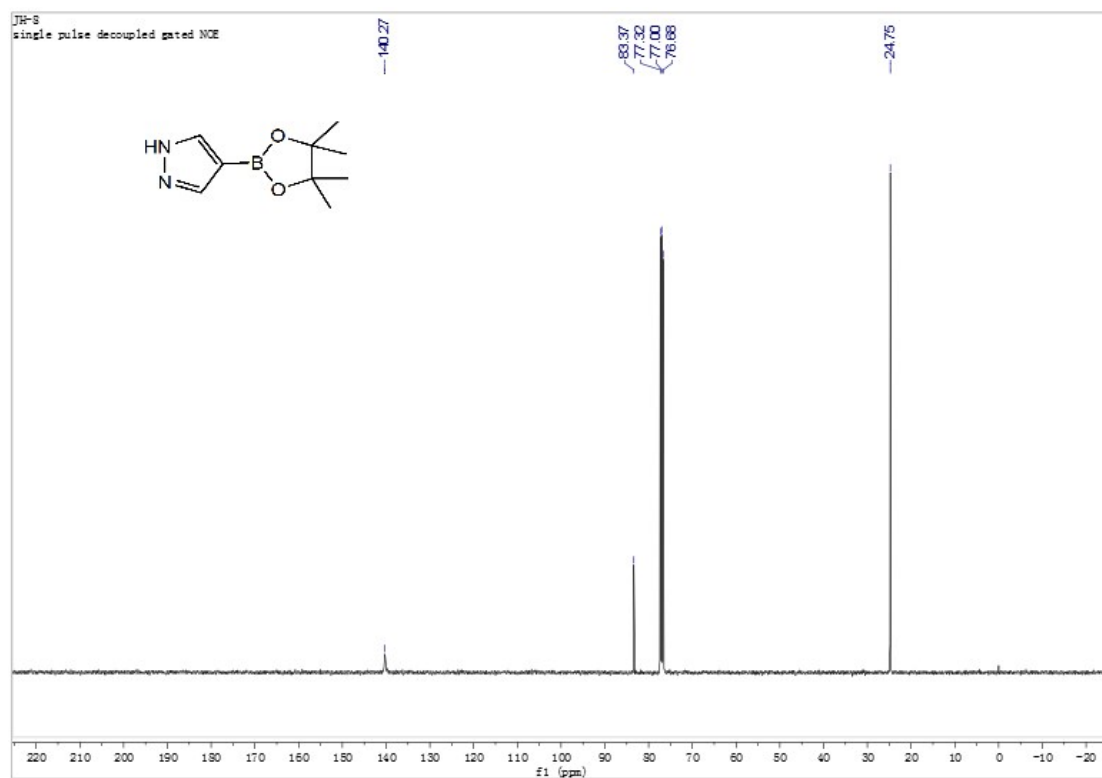
¹H and ¹³C NMR spectra of compound 2m



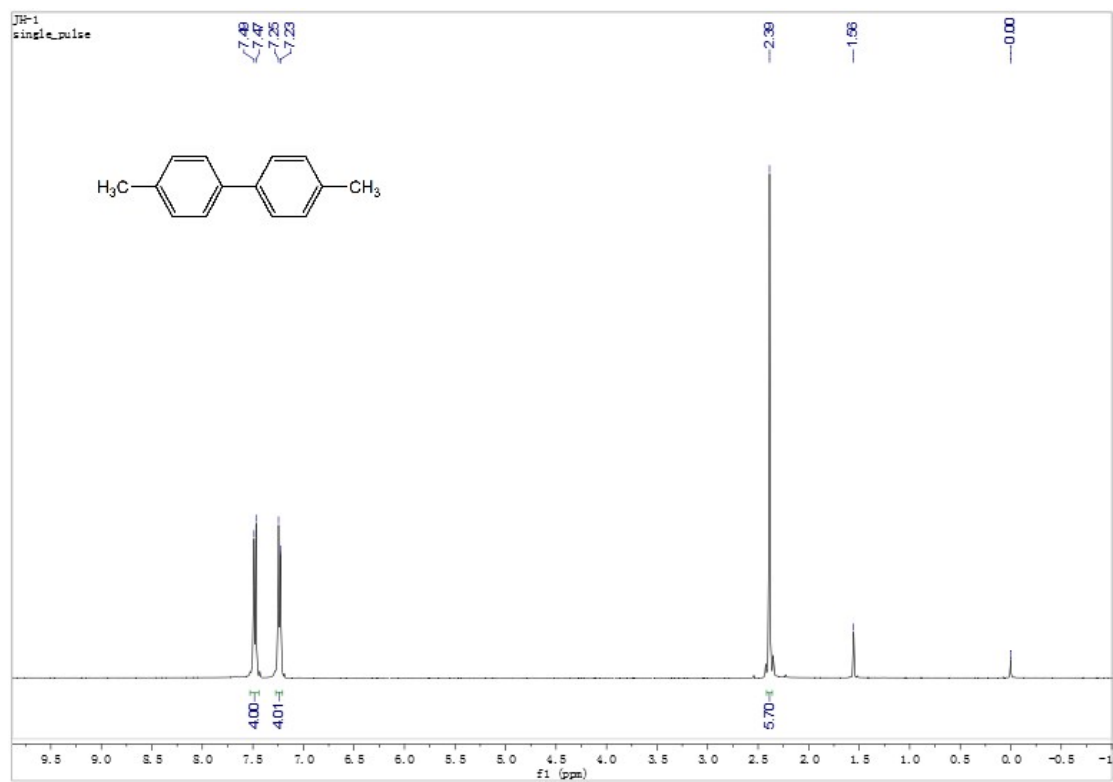


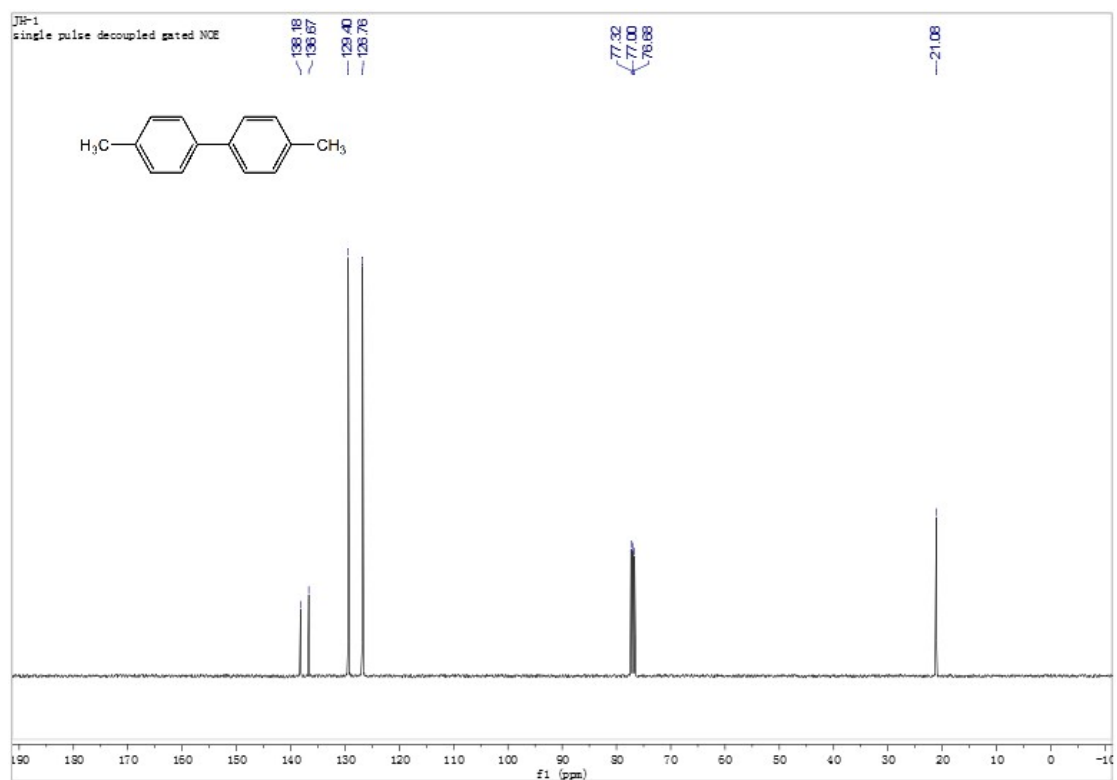
^1H and ^{13}C NMR spectra of compound 2n



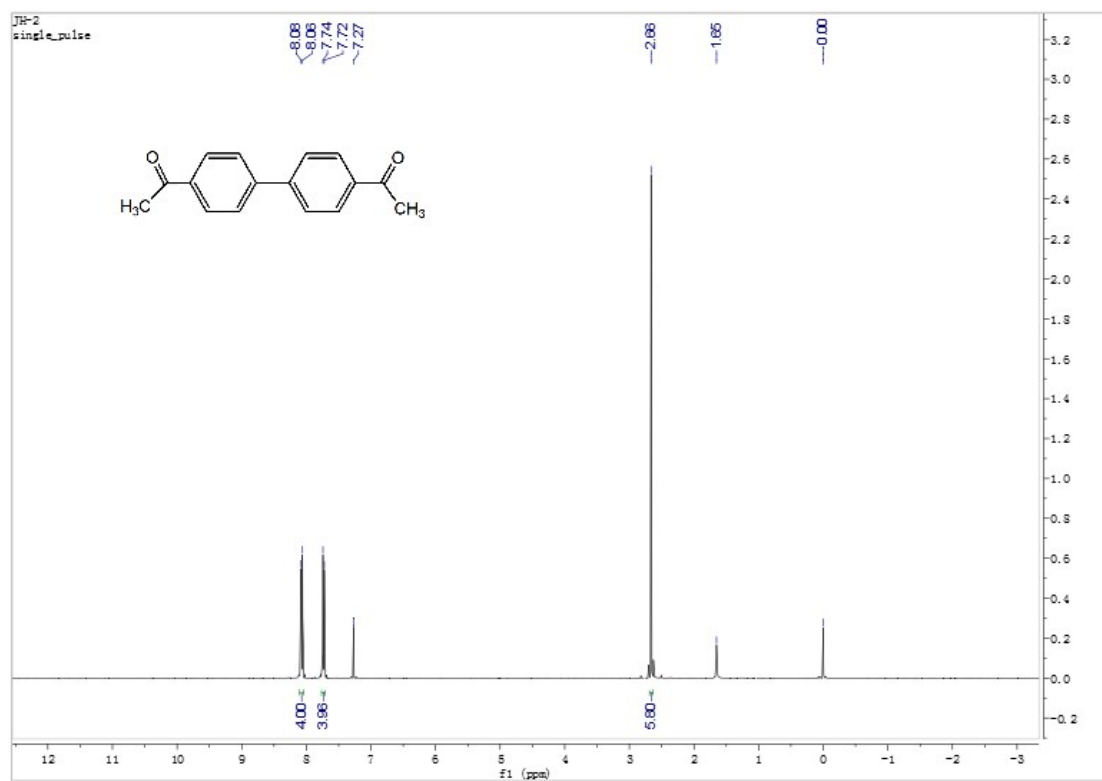


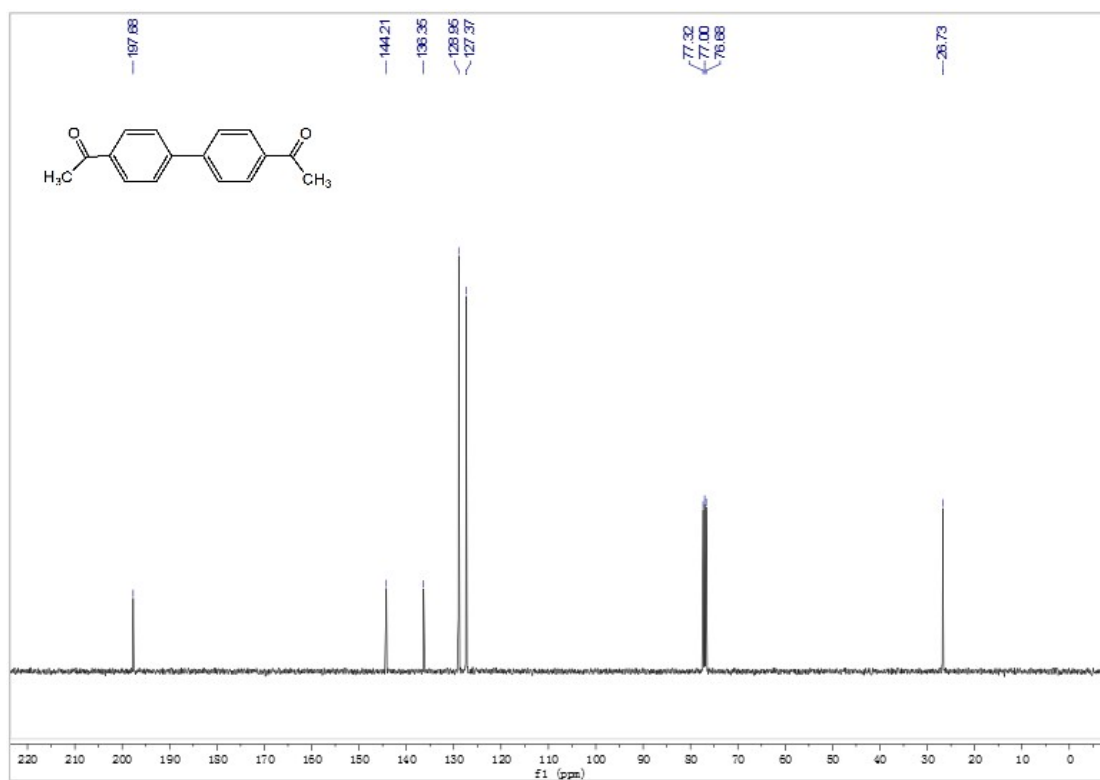
^1H and ^{13}C NMR spectra of compound 3a



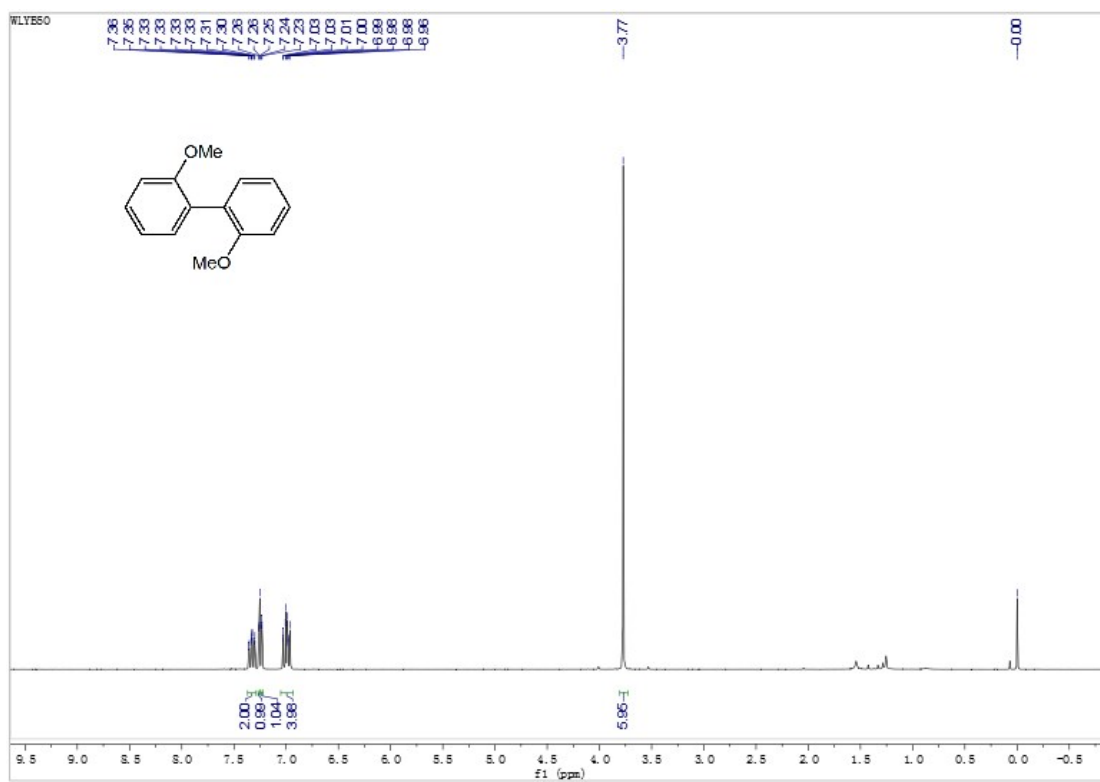


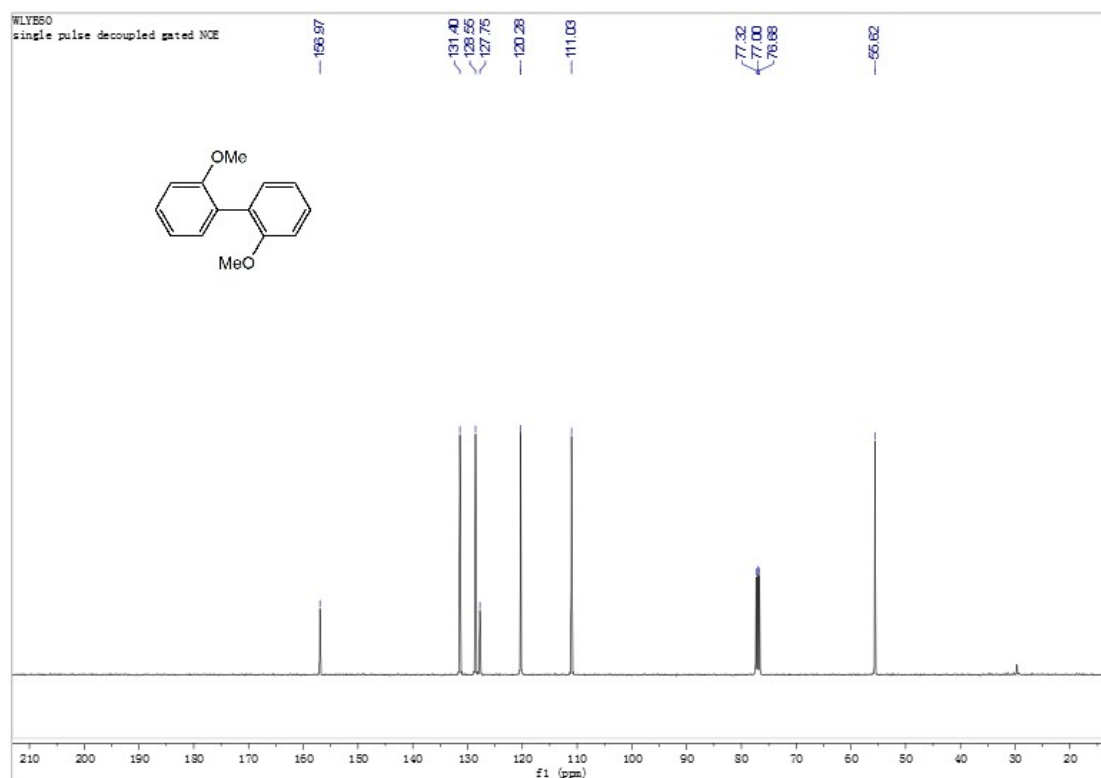
¹H and ¹³C NMR spectra of compound 3b



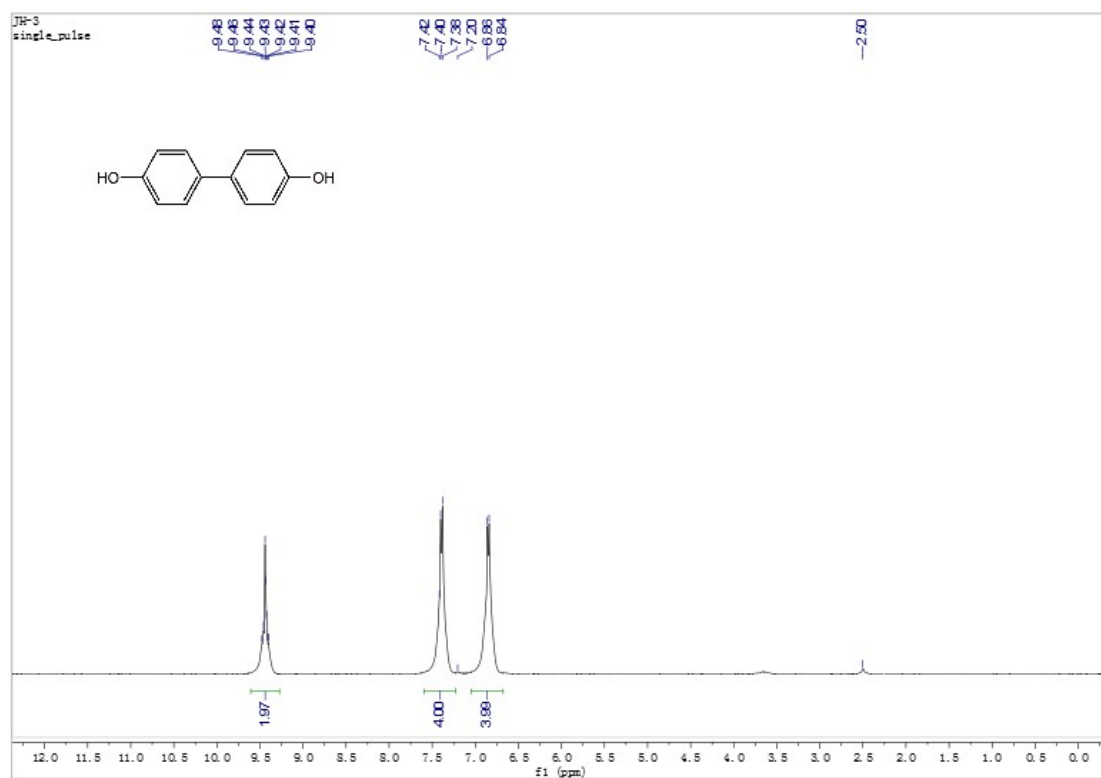


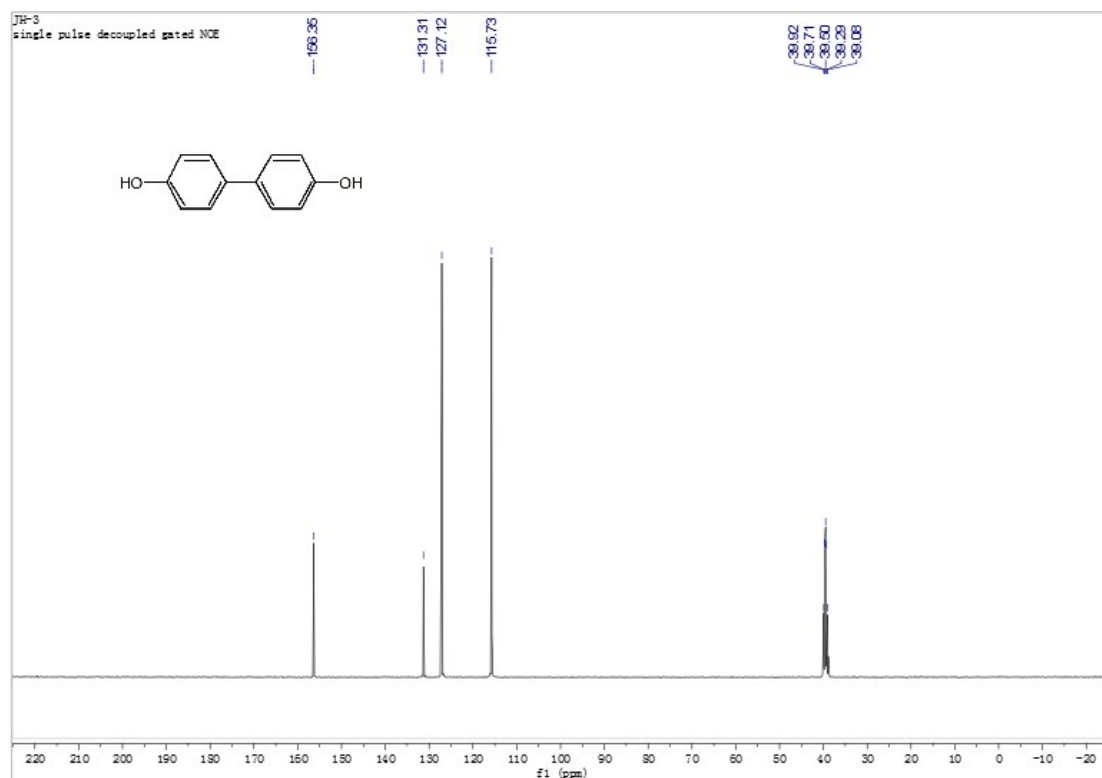
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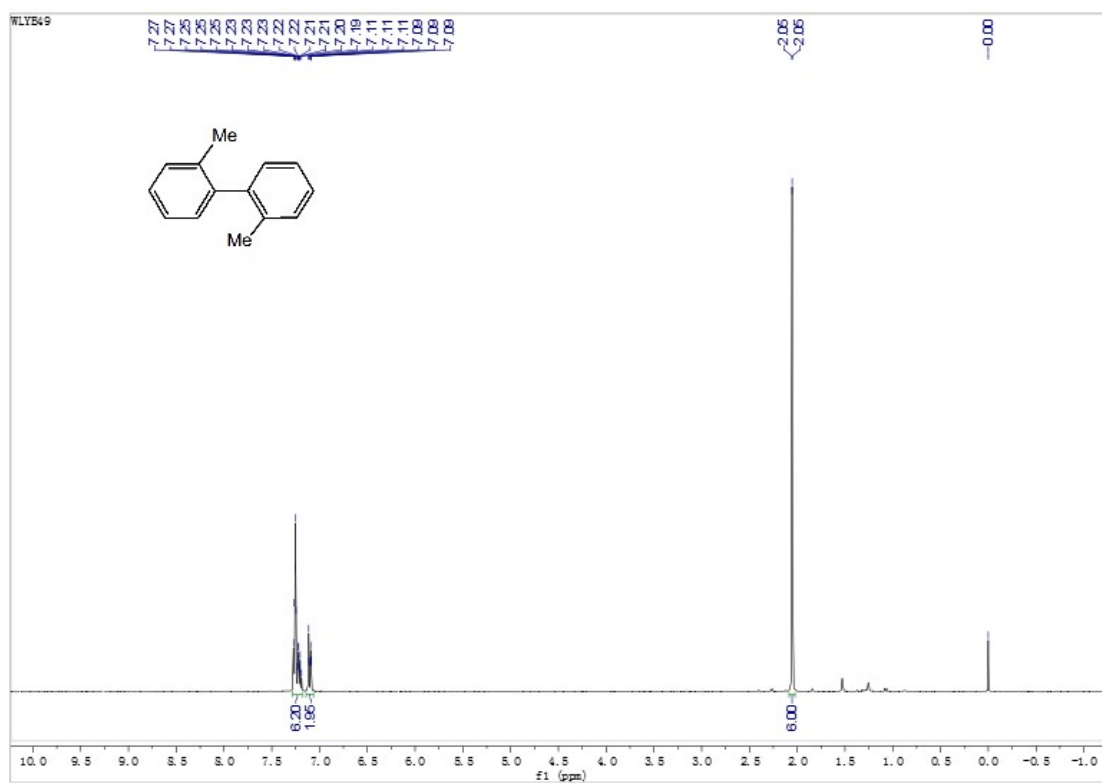


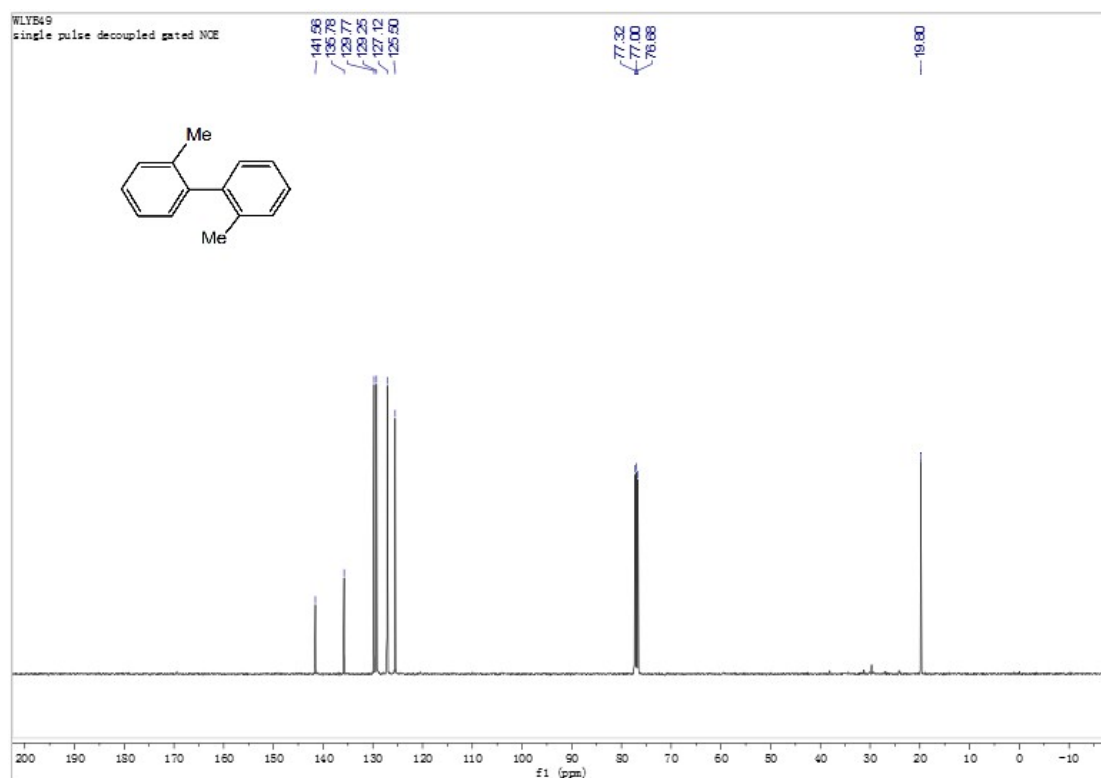
^1H and ^{13}C NMR spectra of compound 3d



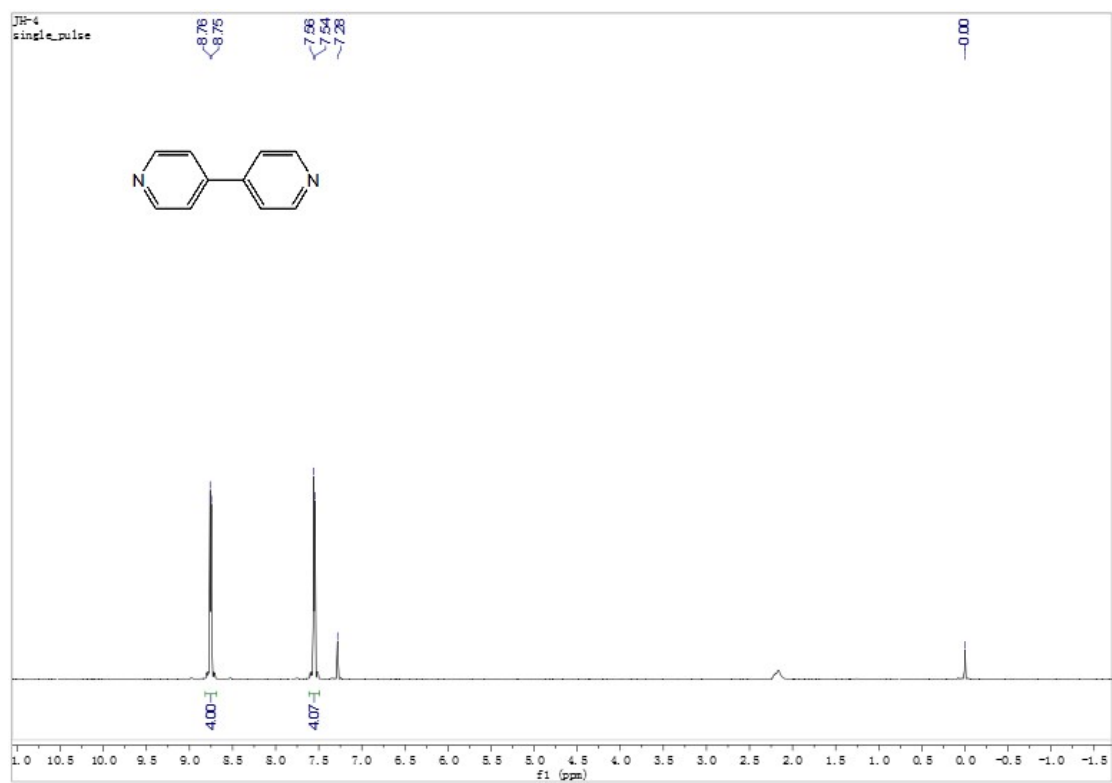


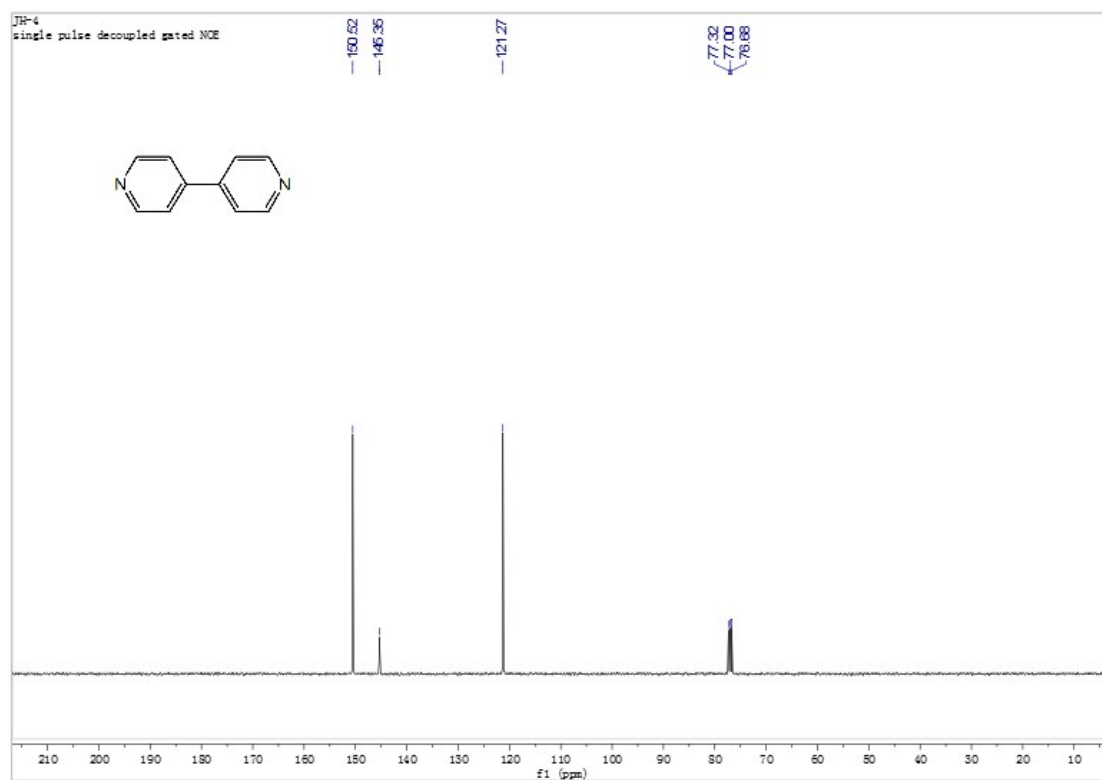
¹H and ¹³C NMR spectra of compound 3e



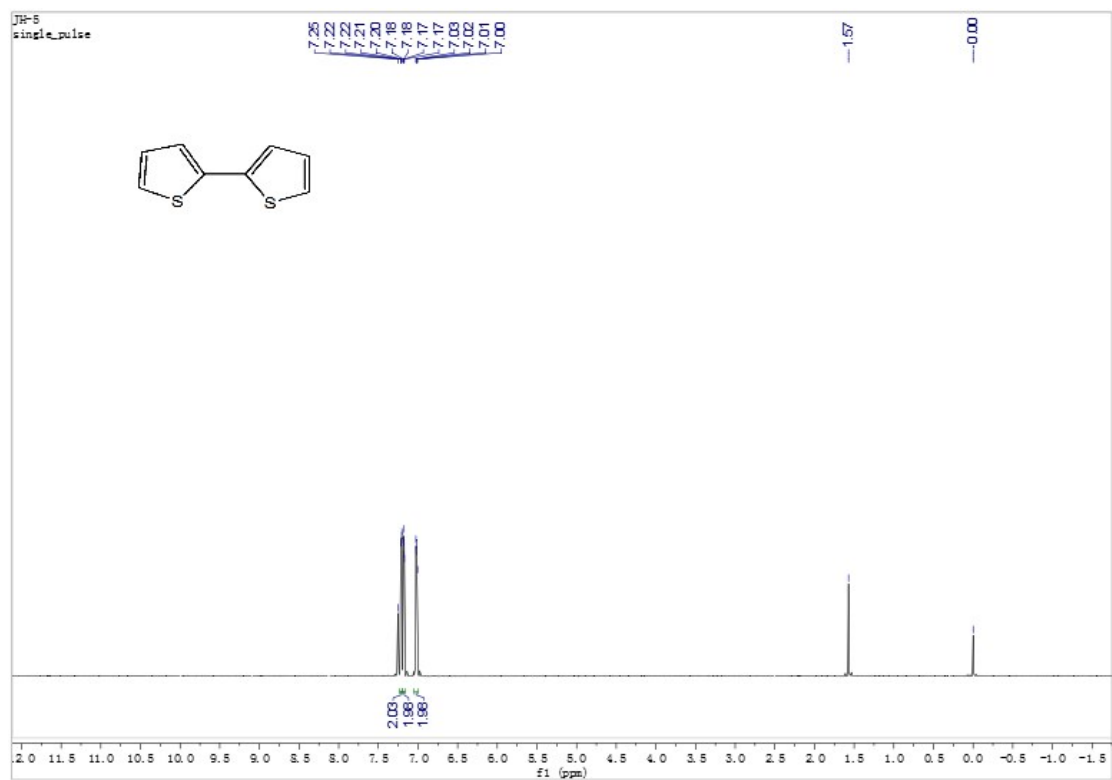


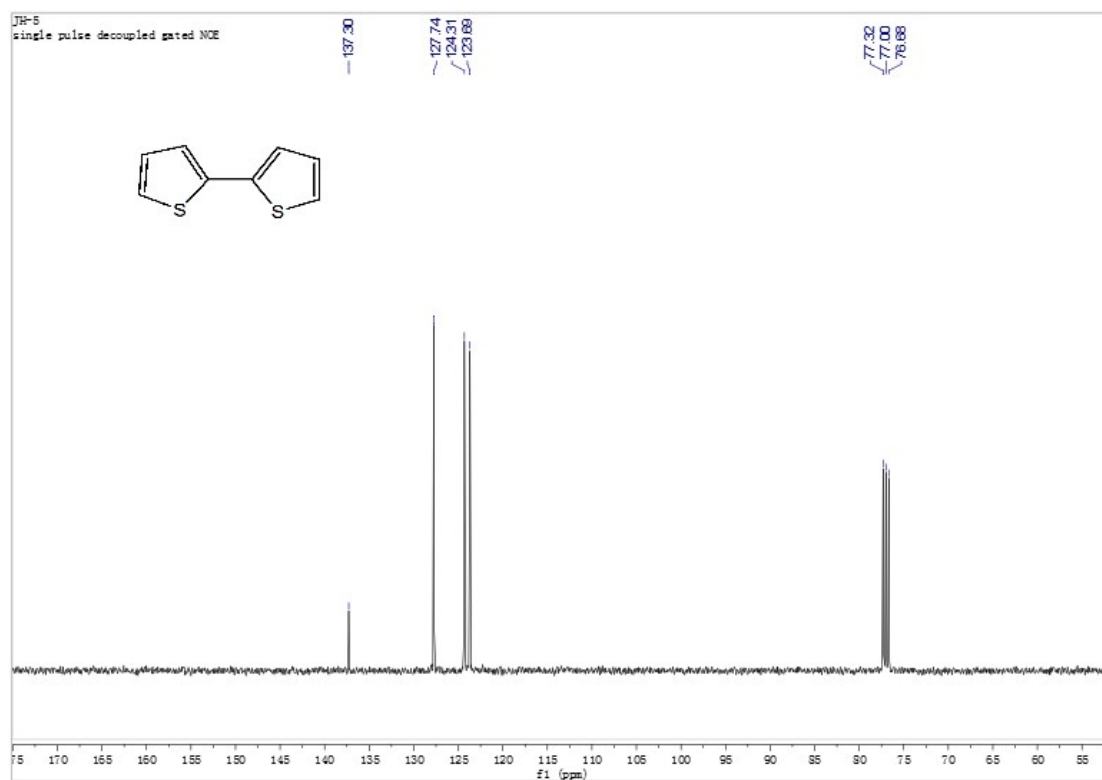
¹H and ¹³C NMR spectra of compound 3f



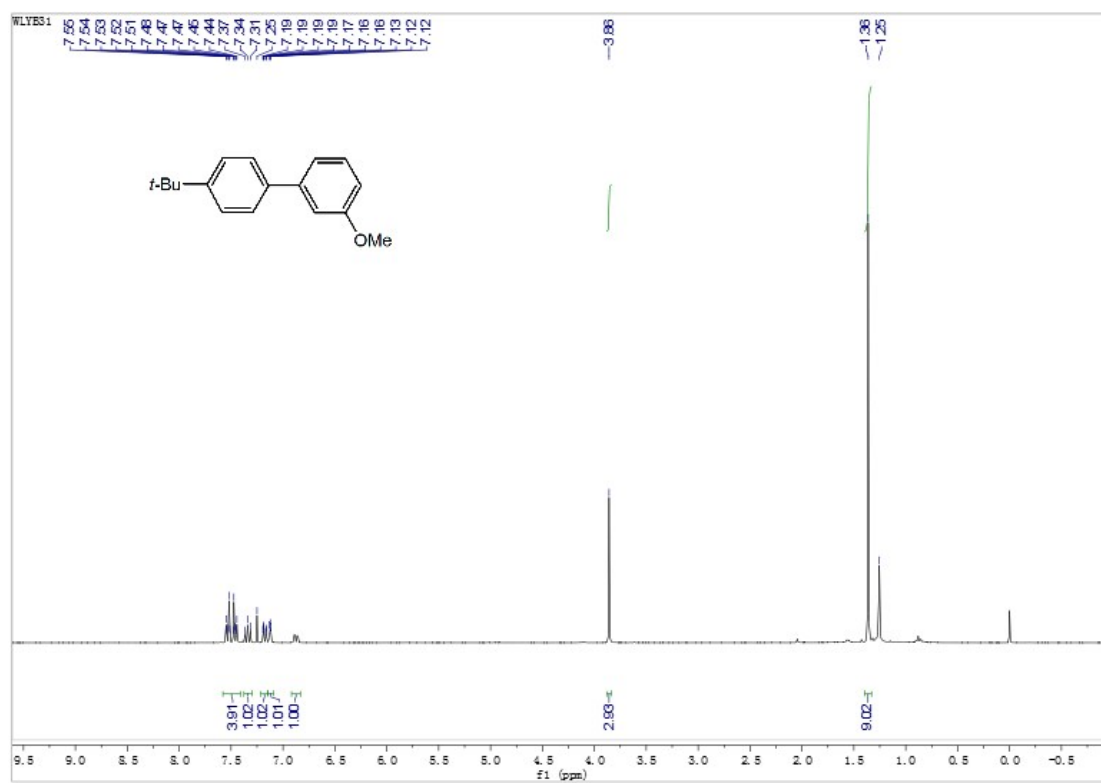


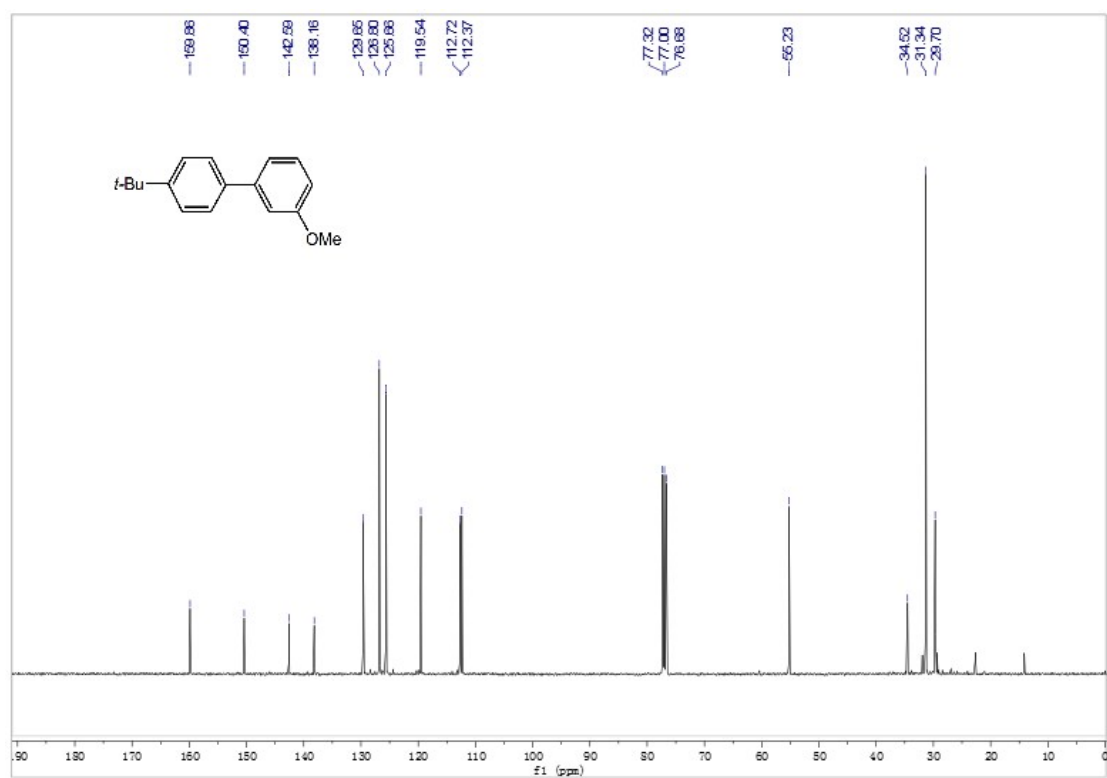
^1H and ^{13}C NMR spectra of compound 3g



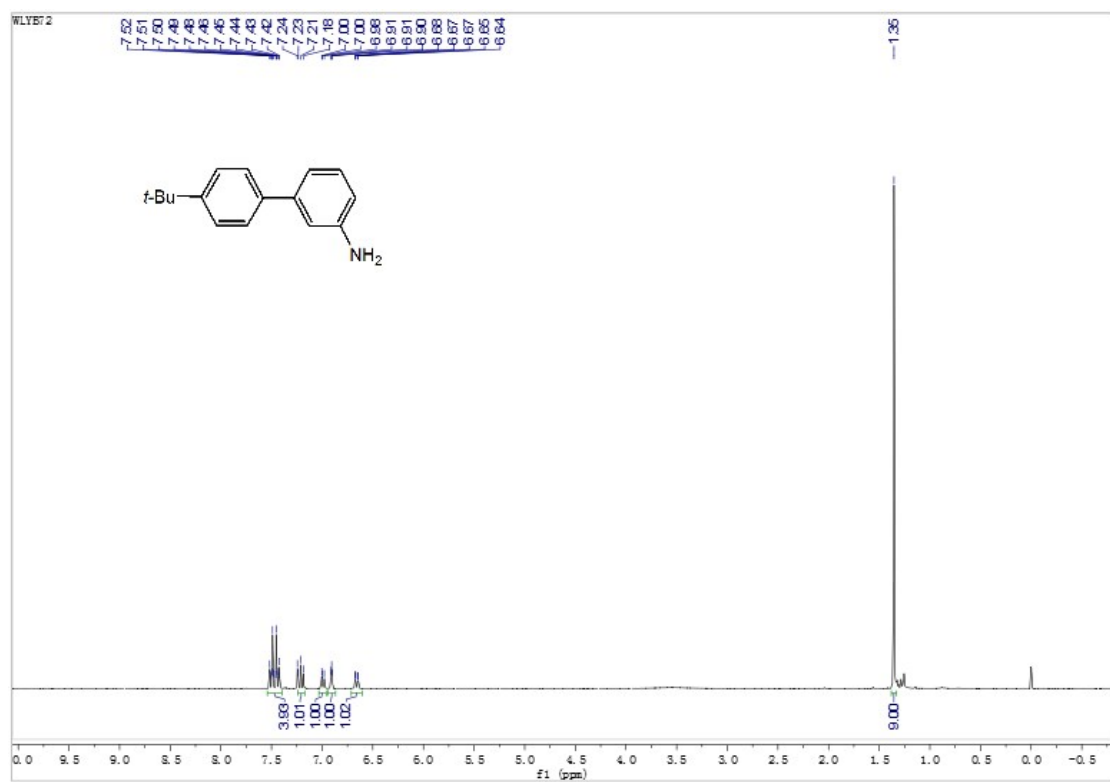


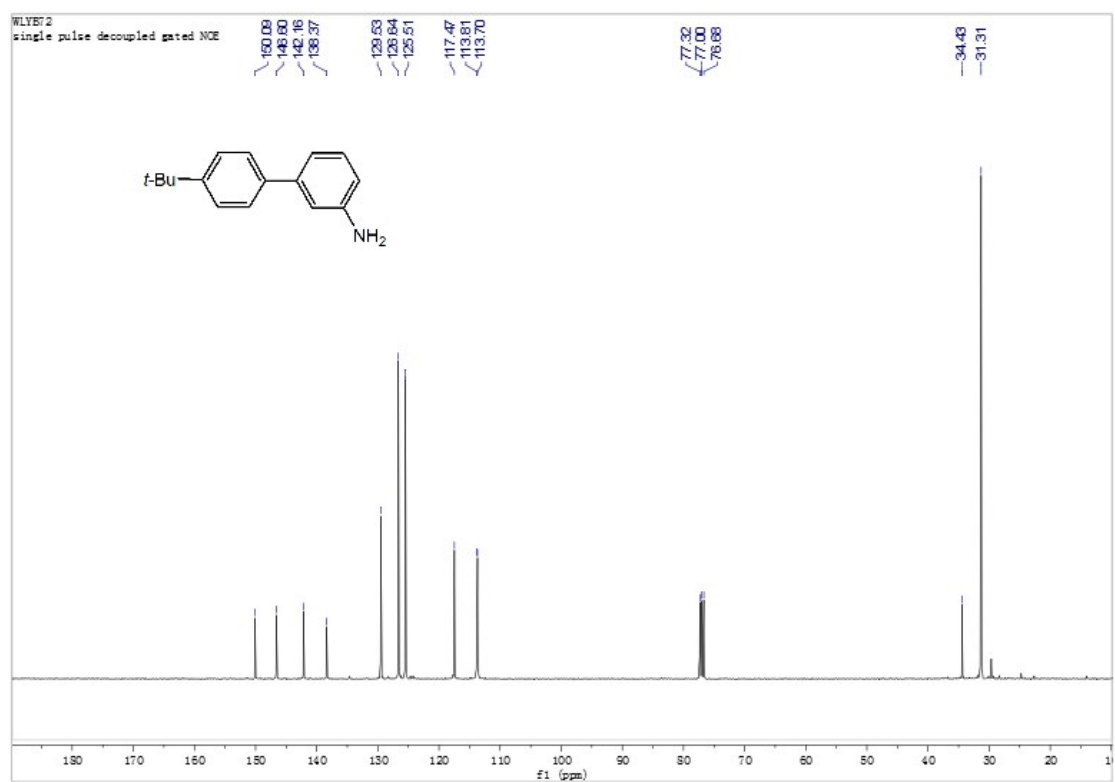
^1H and ^{13}C NMR spectra of compound 4a



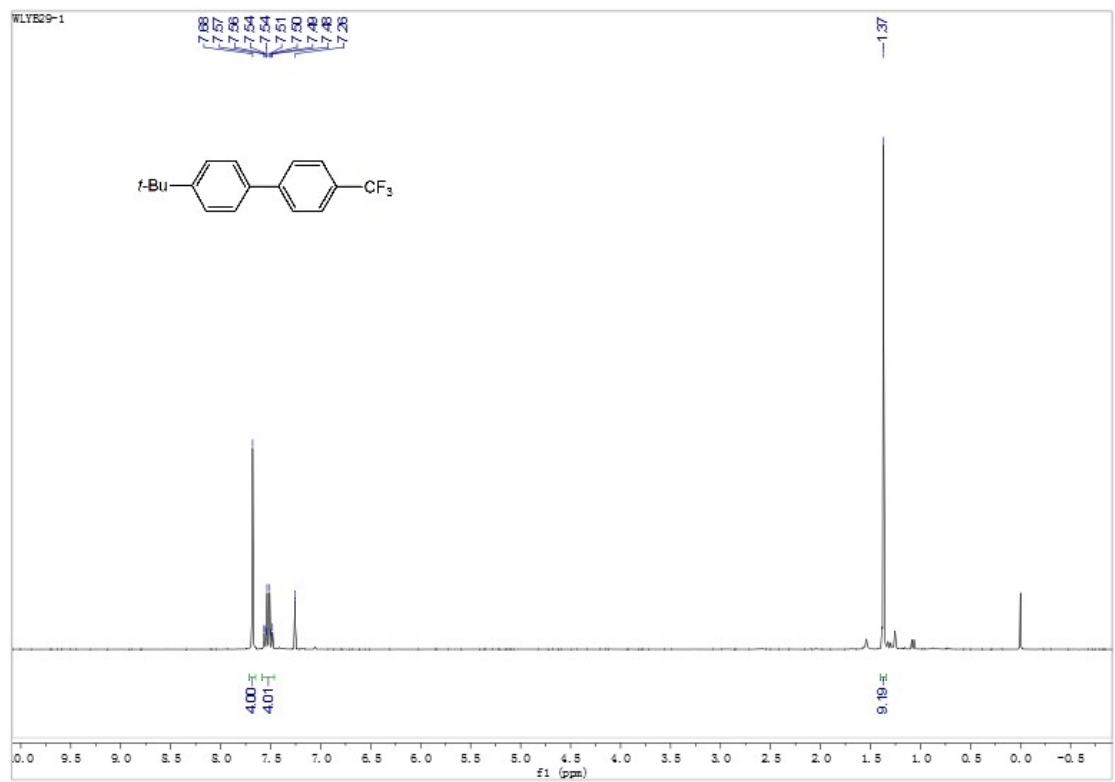


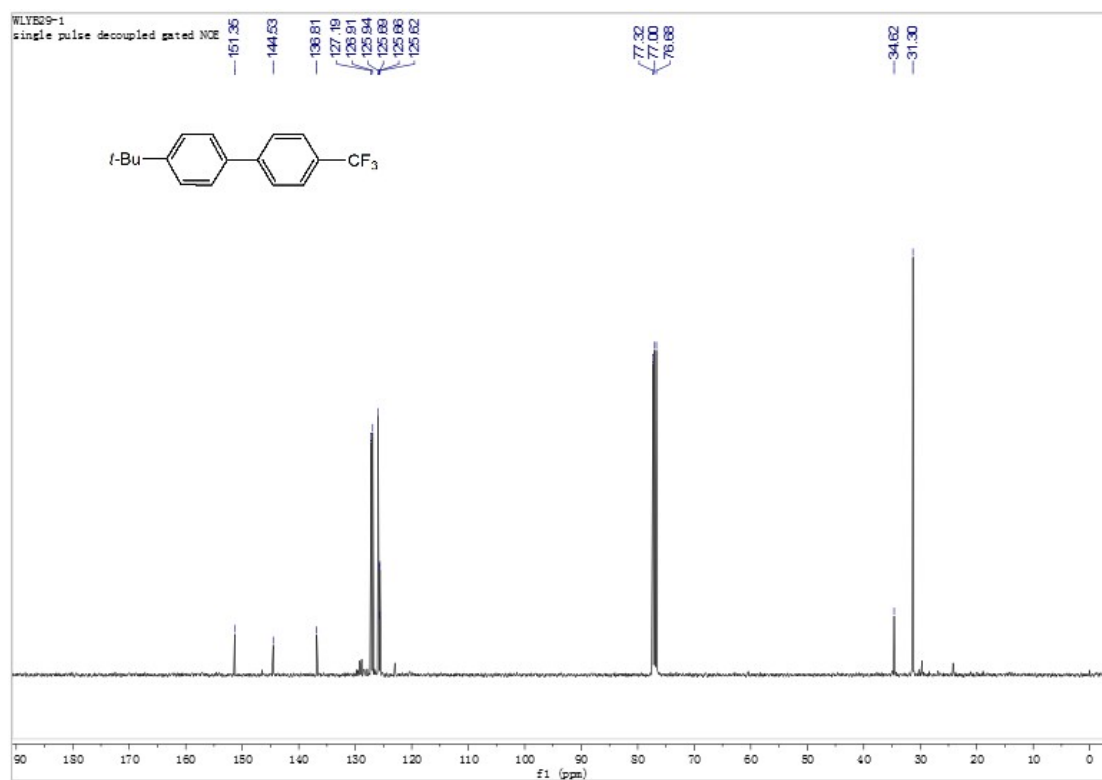
¹H and ¹³C NMR spectra of compound 4b



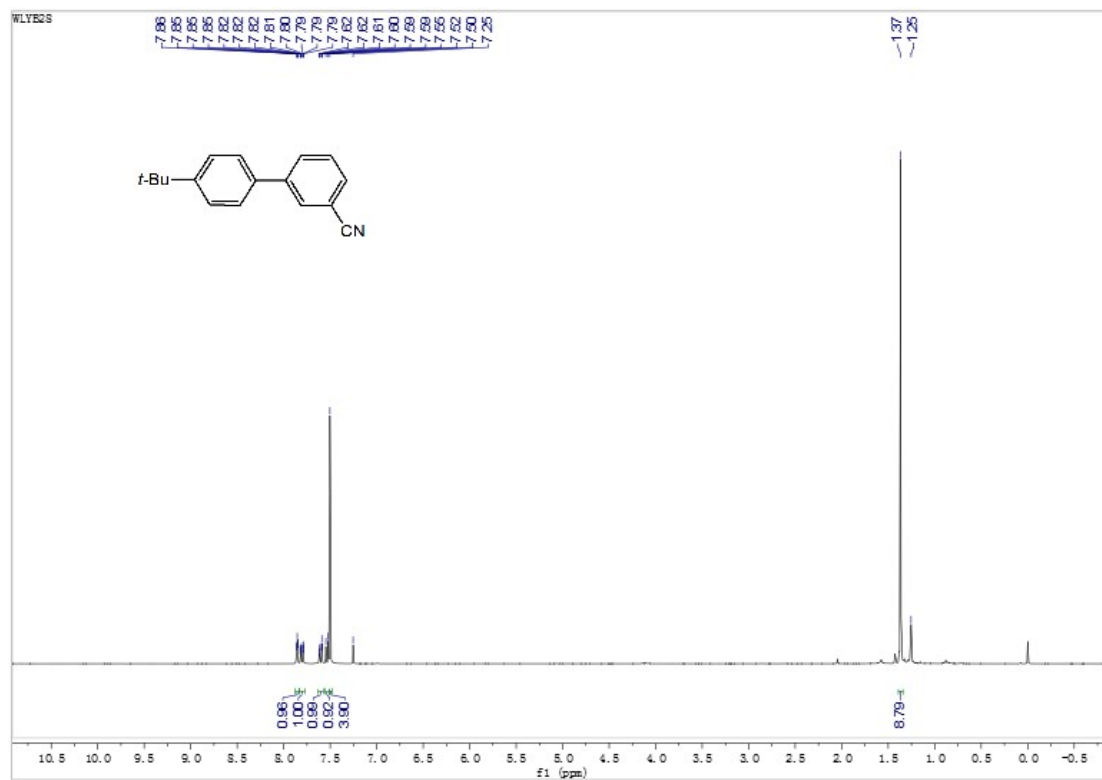


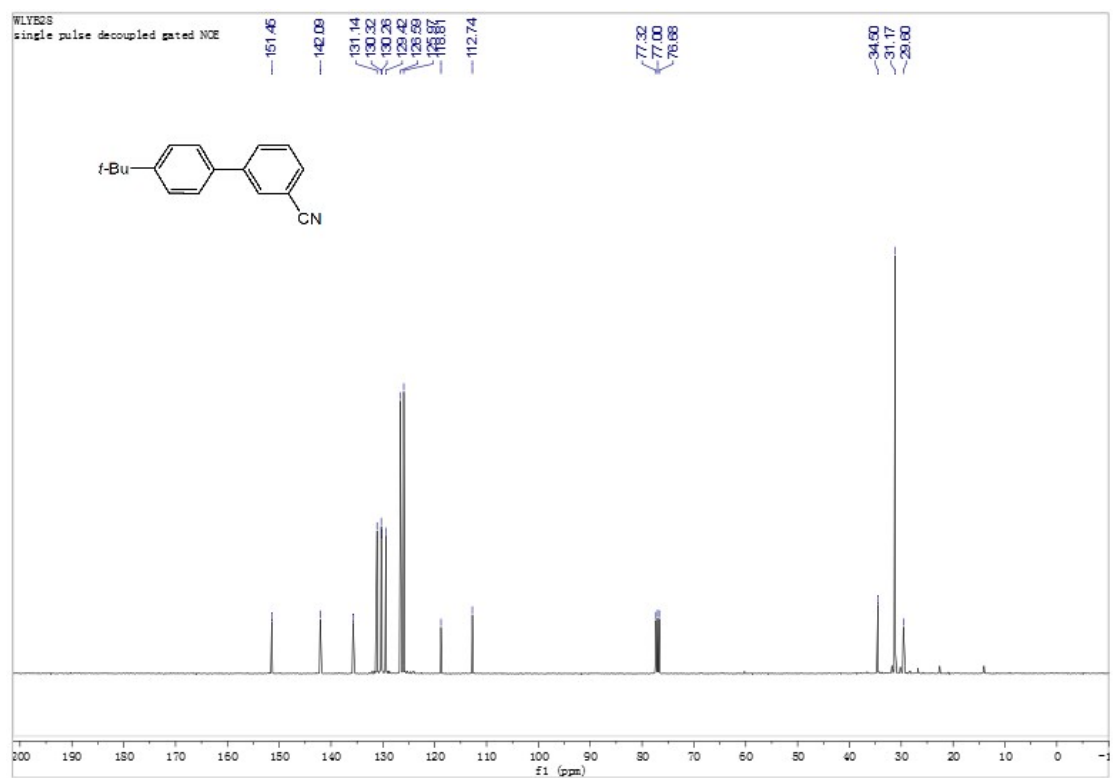
^1H and ^{13}C NMR spectra of compound 4c



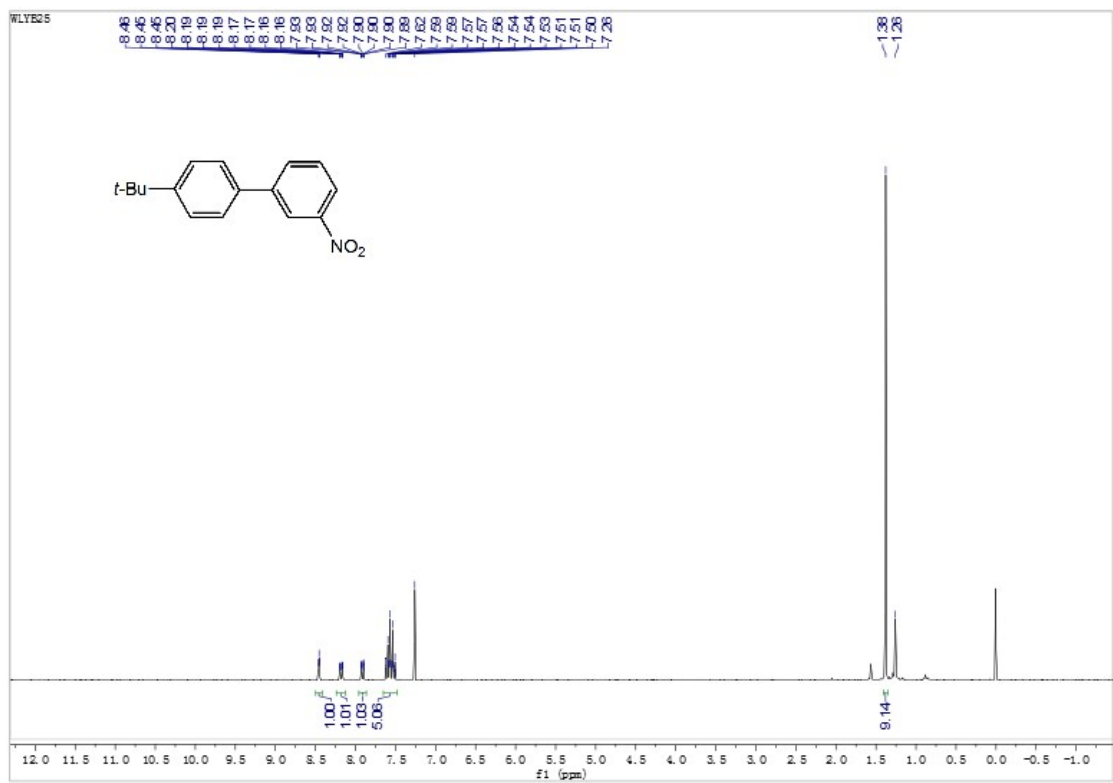


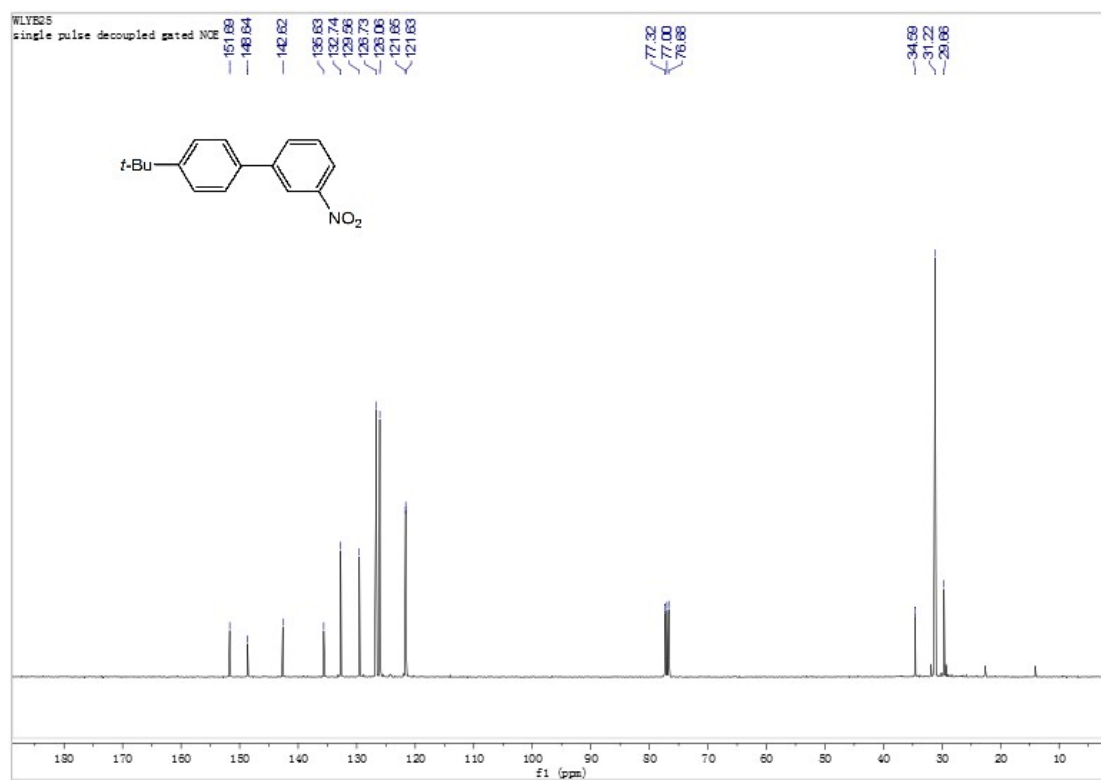
¹H and ¹³C NMR spectra of compound 4d



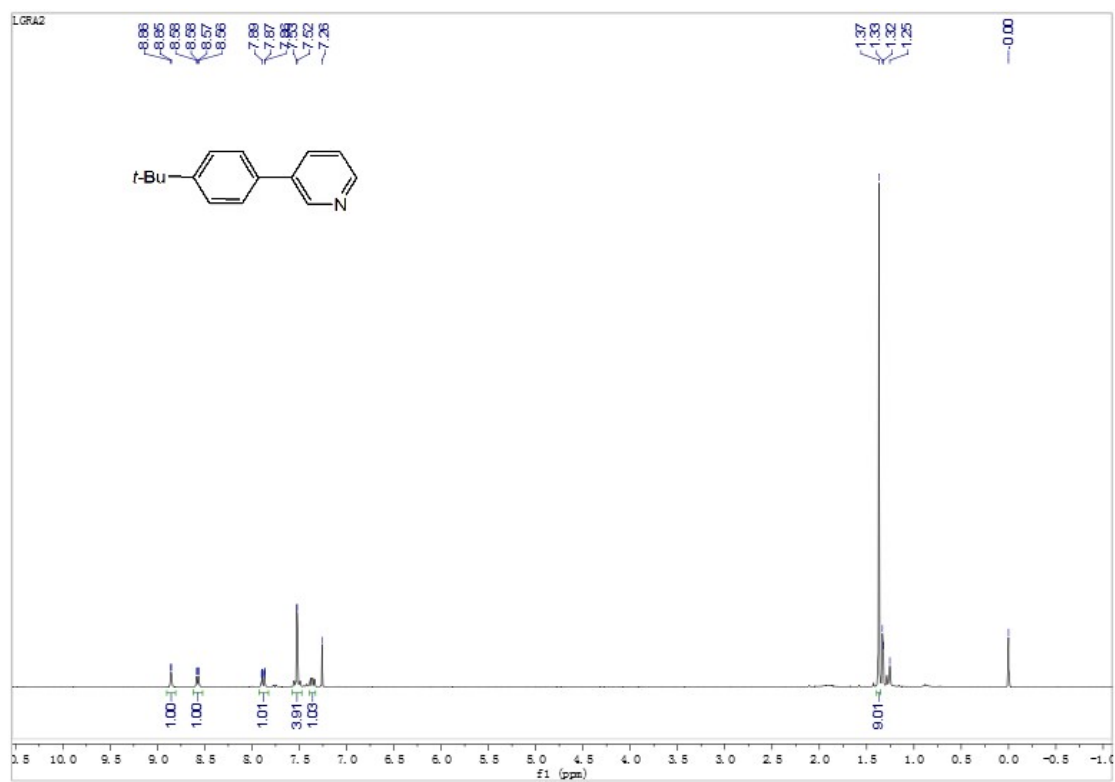


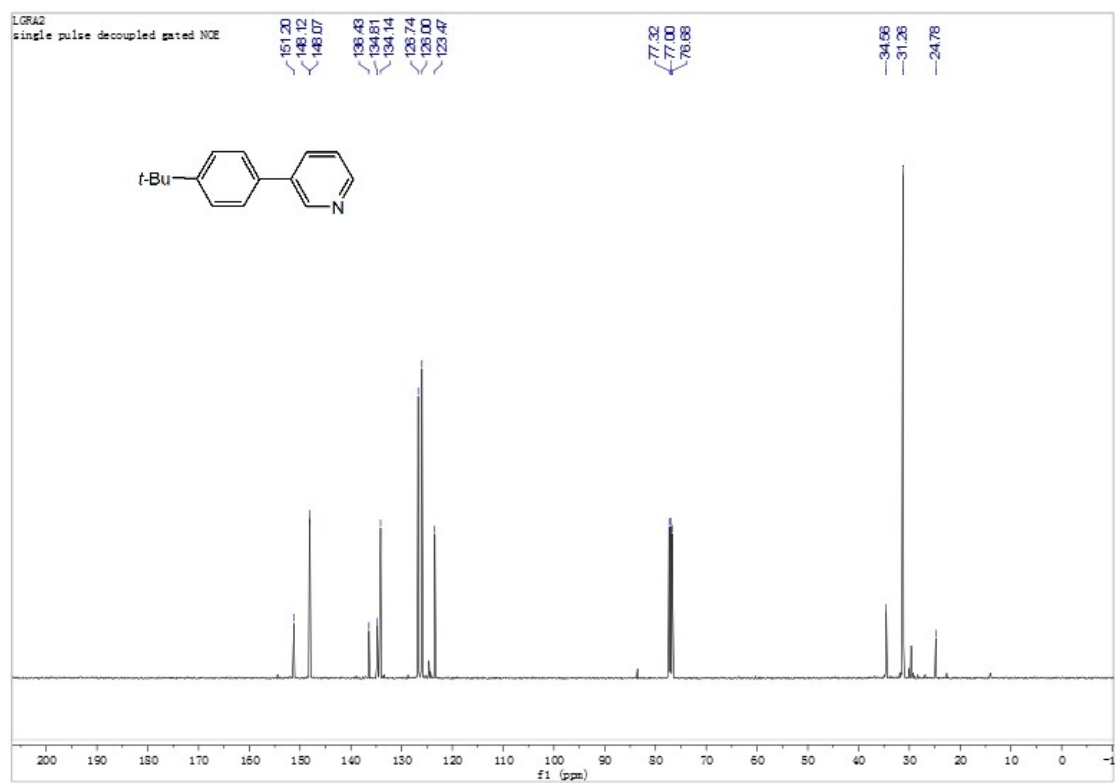
¹H and ¹³C NMR spectra of compound 4e



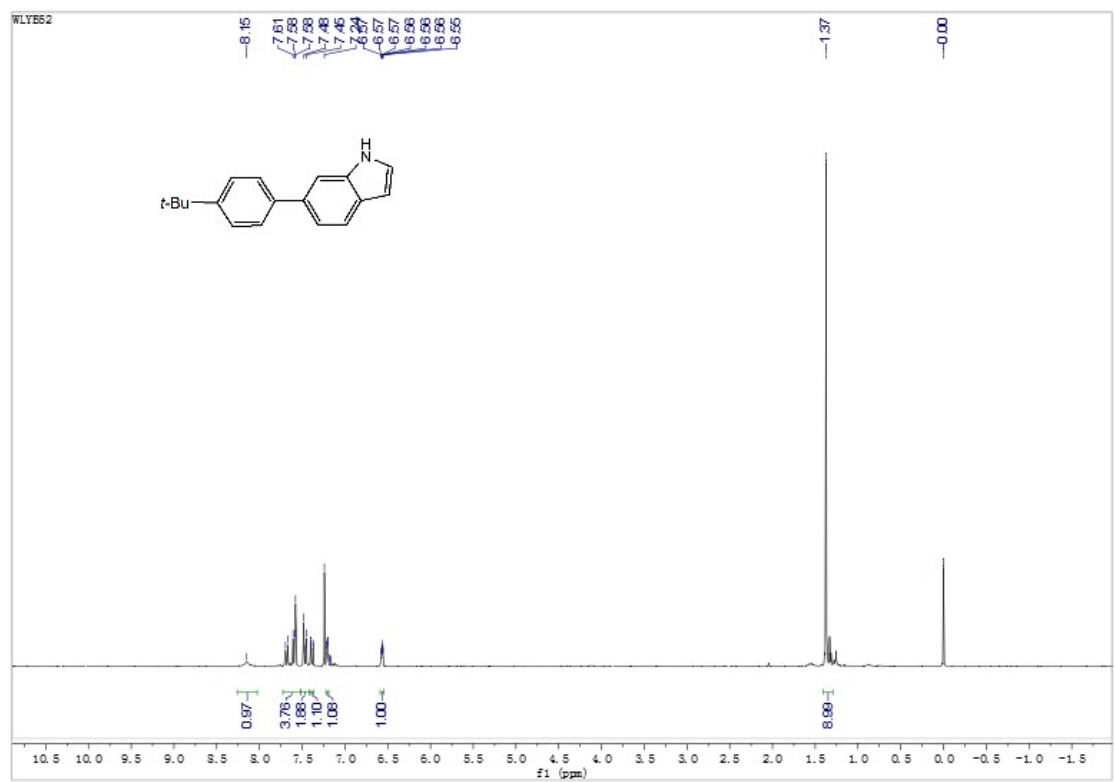


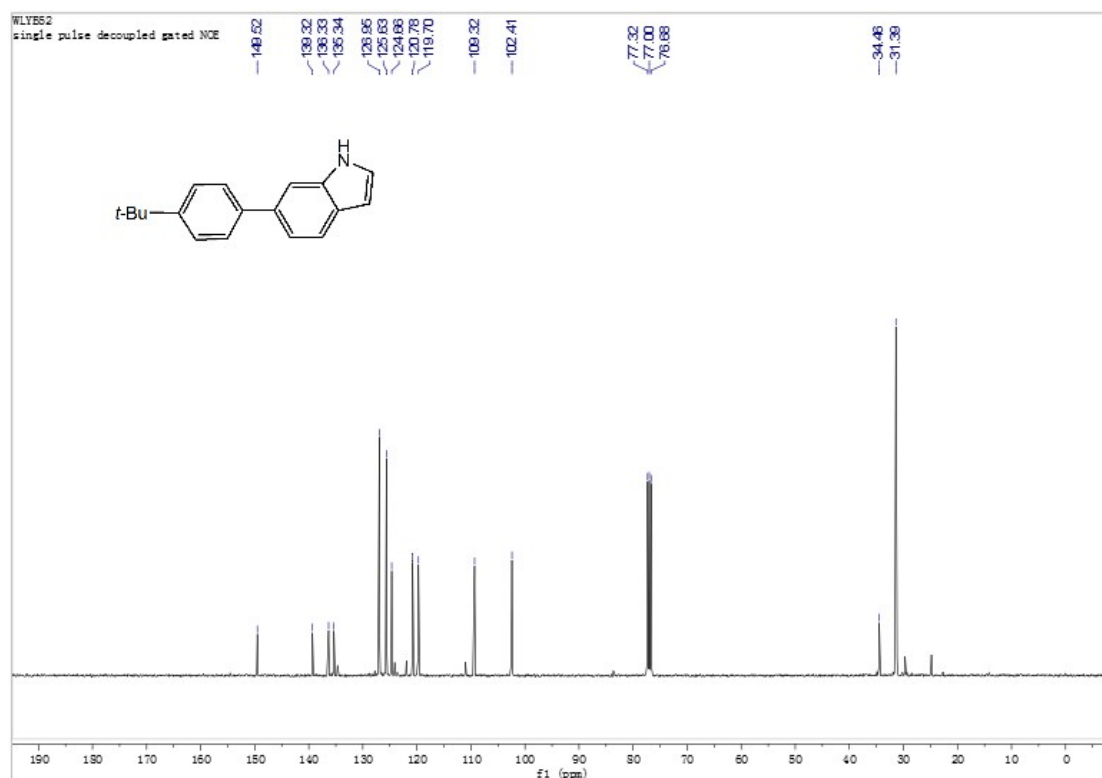
¹H and ¹³C NMR spectra of compound 4f



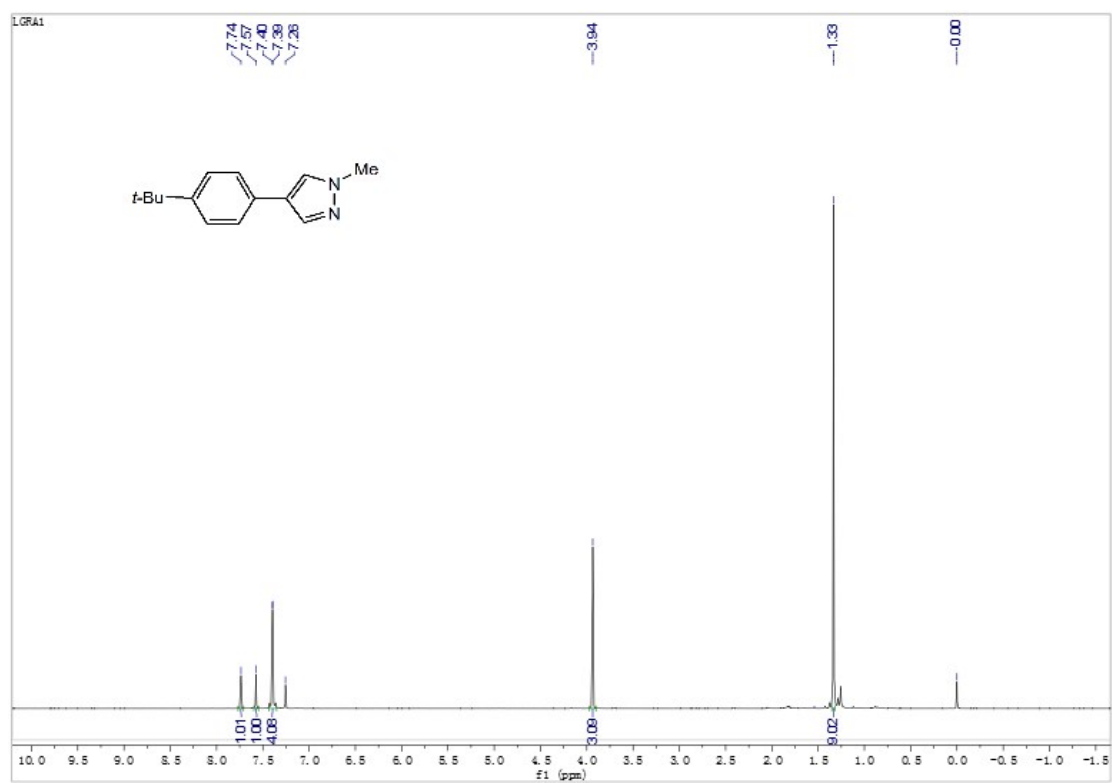


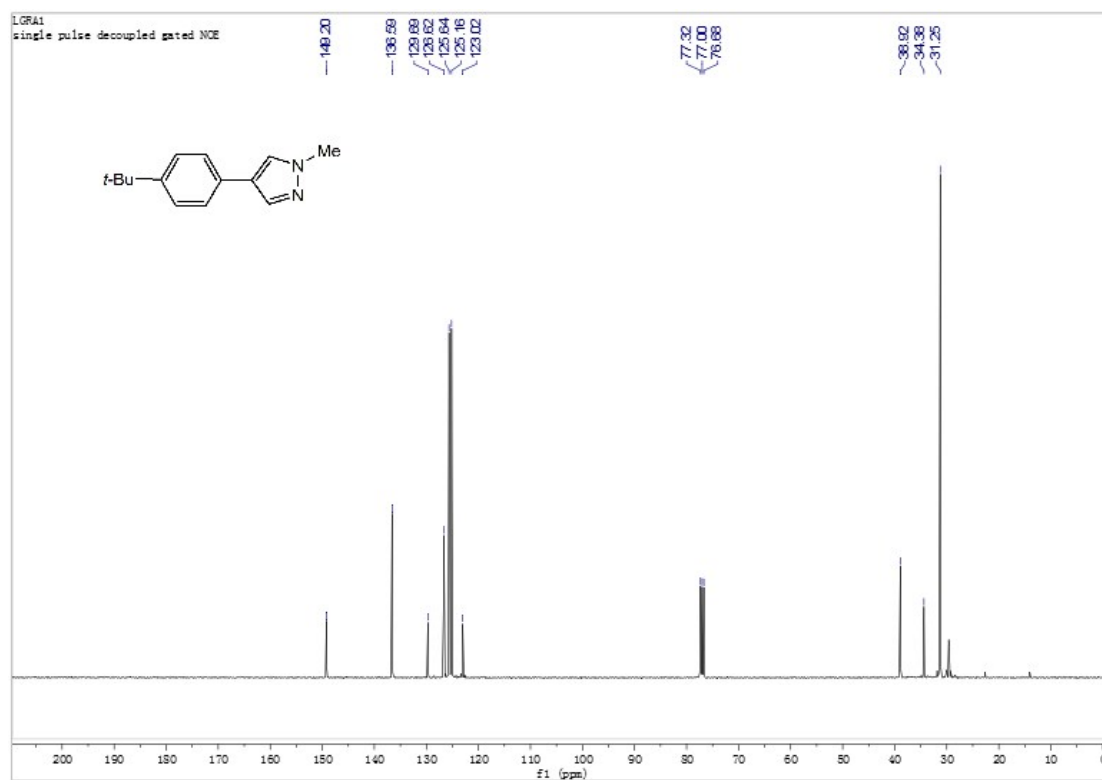
¹H and ¹³C NMR spectra of compound 4g



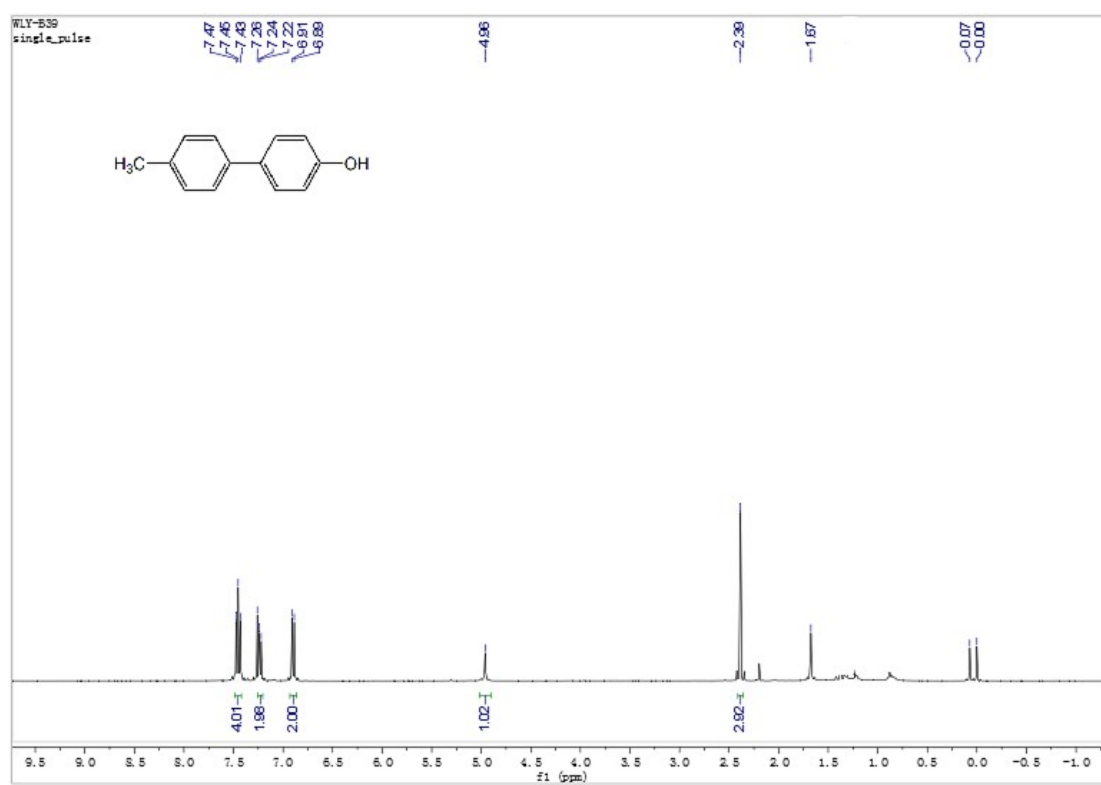


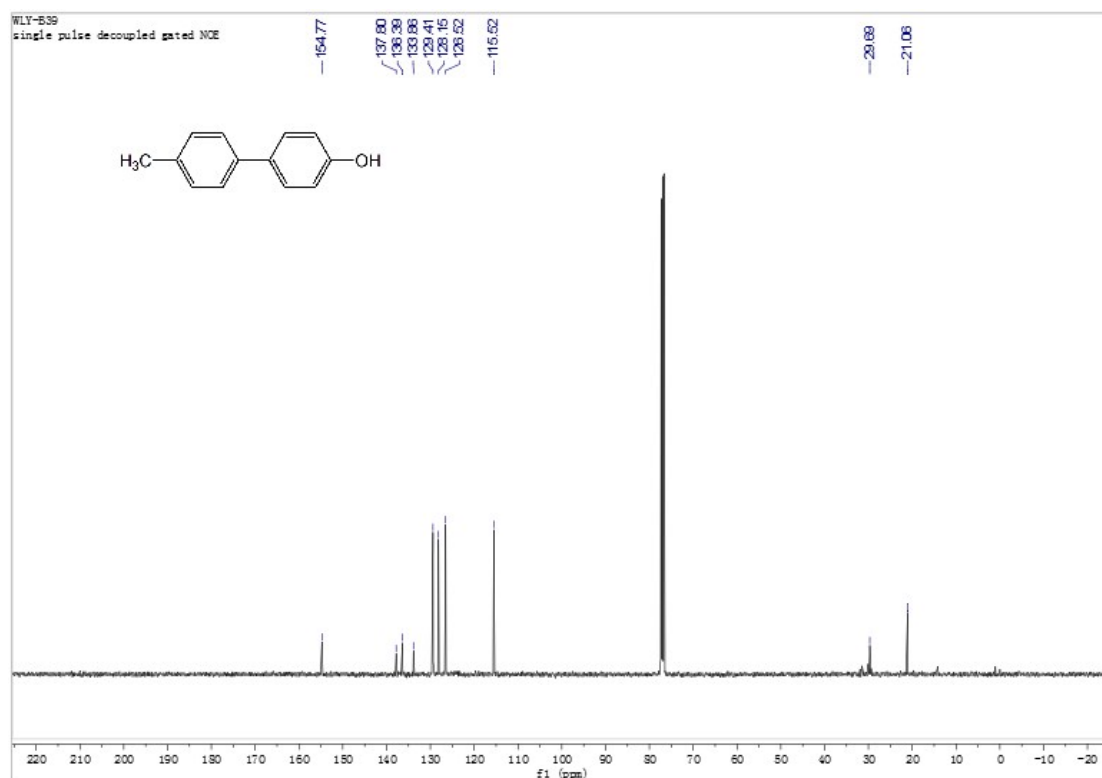
¹H and ¹³C NMR spectra of compound 4h



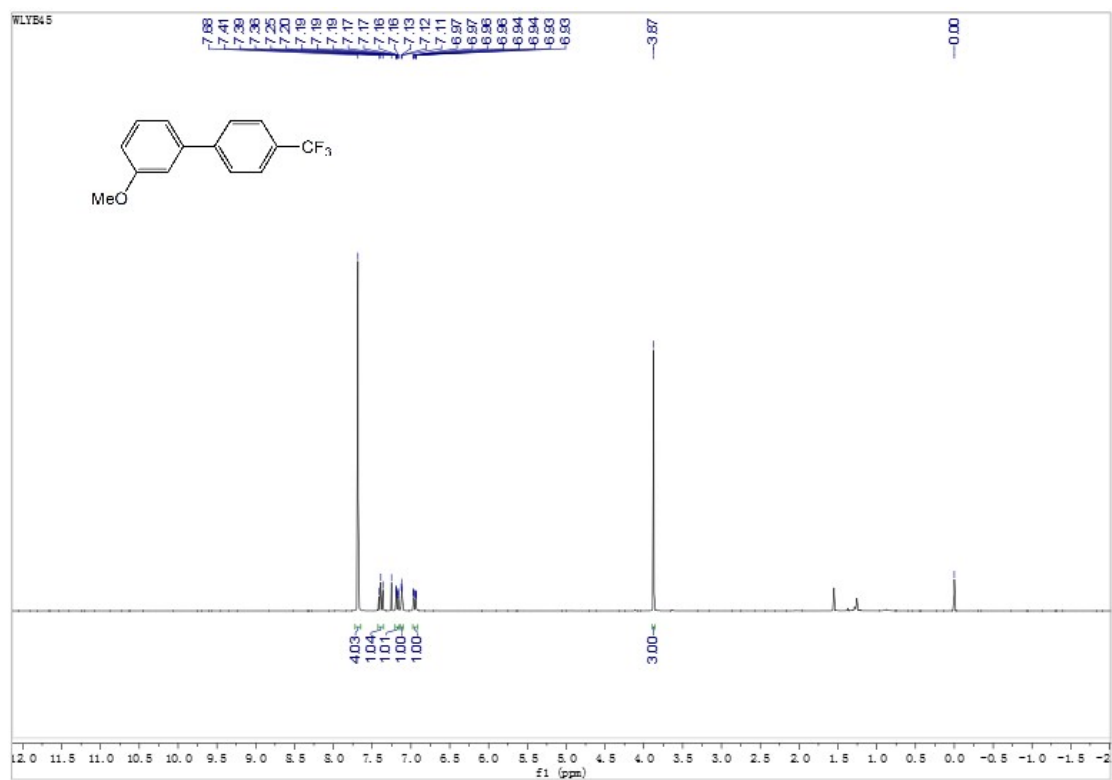


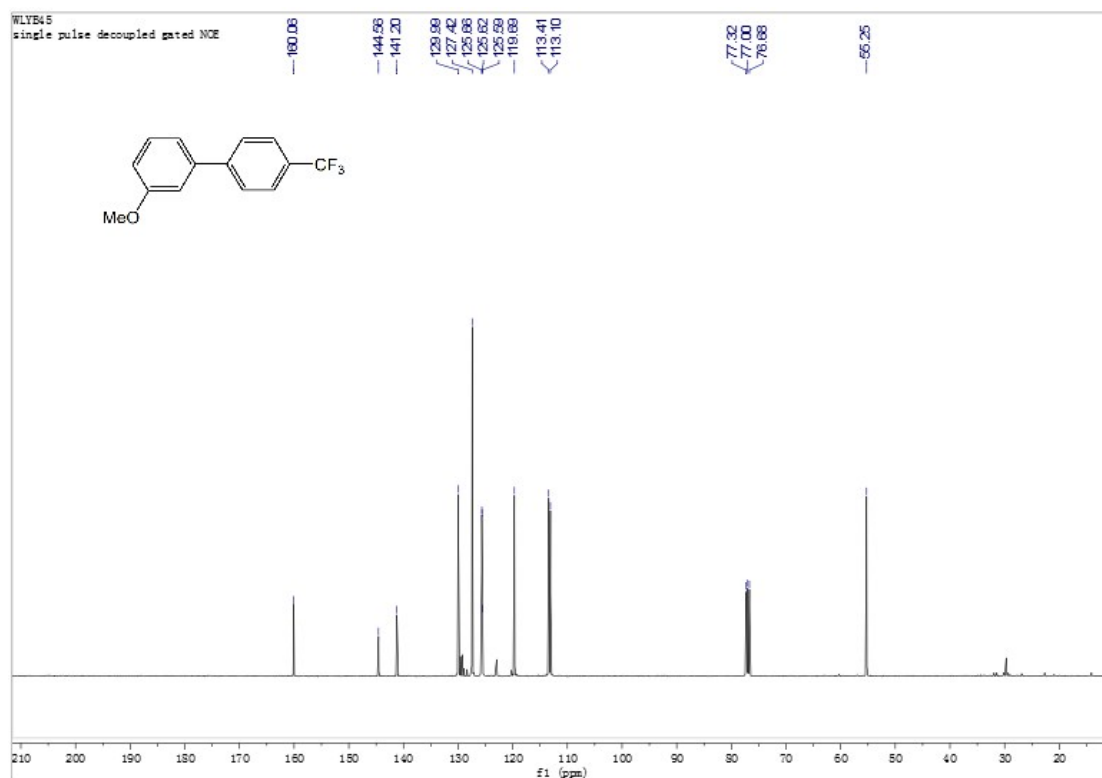
^1H and ^{13}C NMR spectra of compound 6a



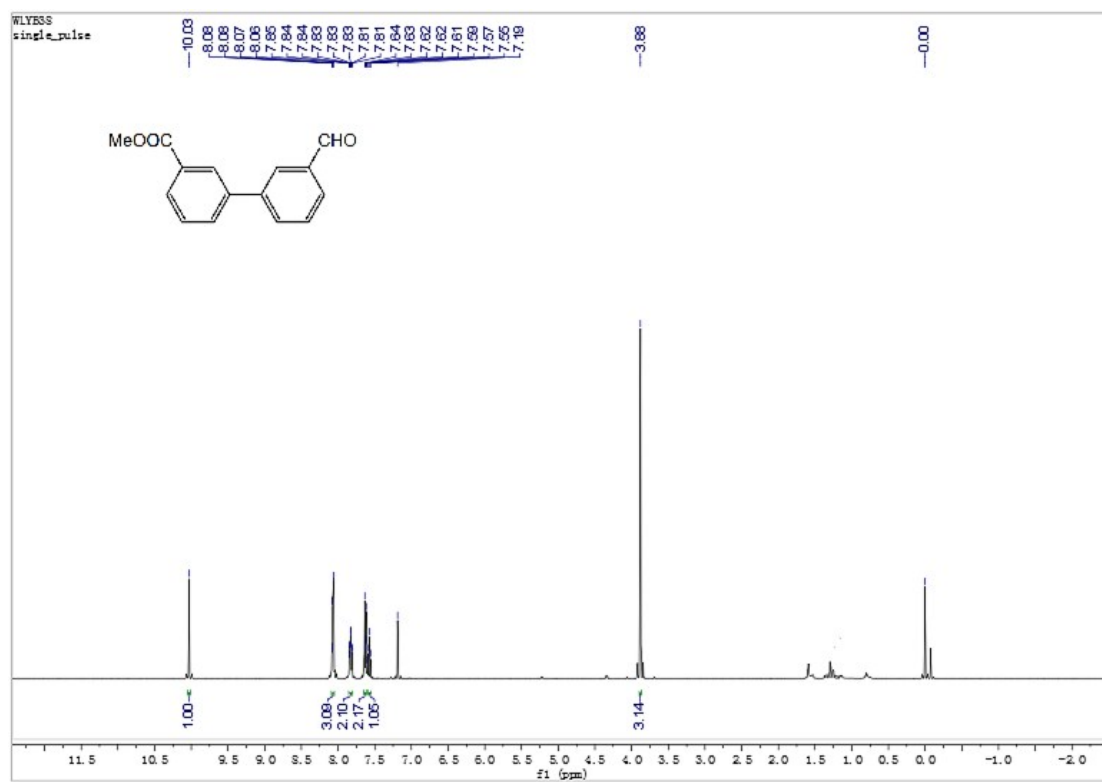


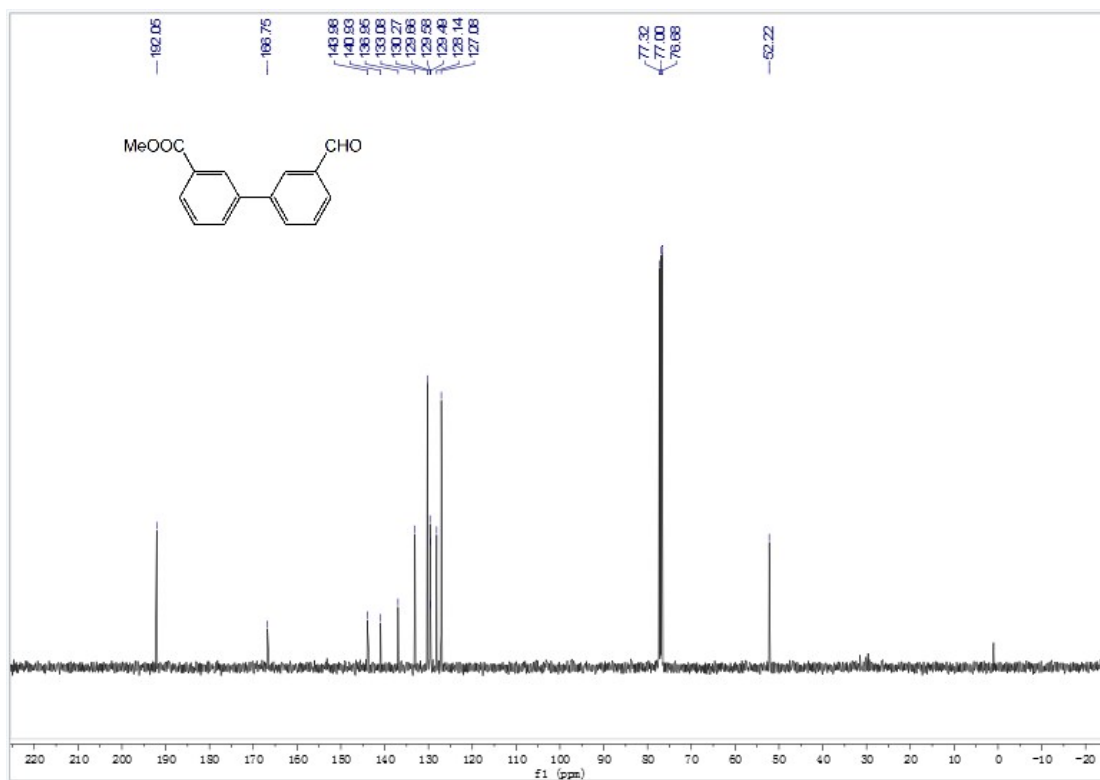
¹H and ¹³C NMR spectra of compound 6b



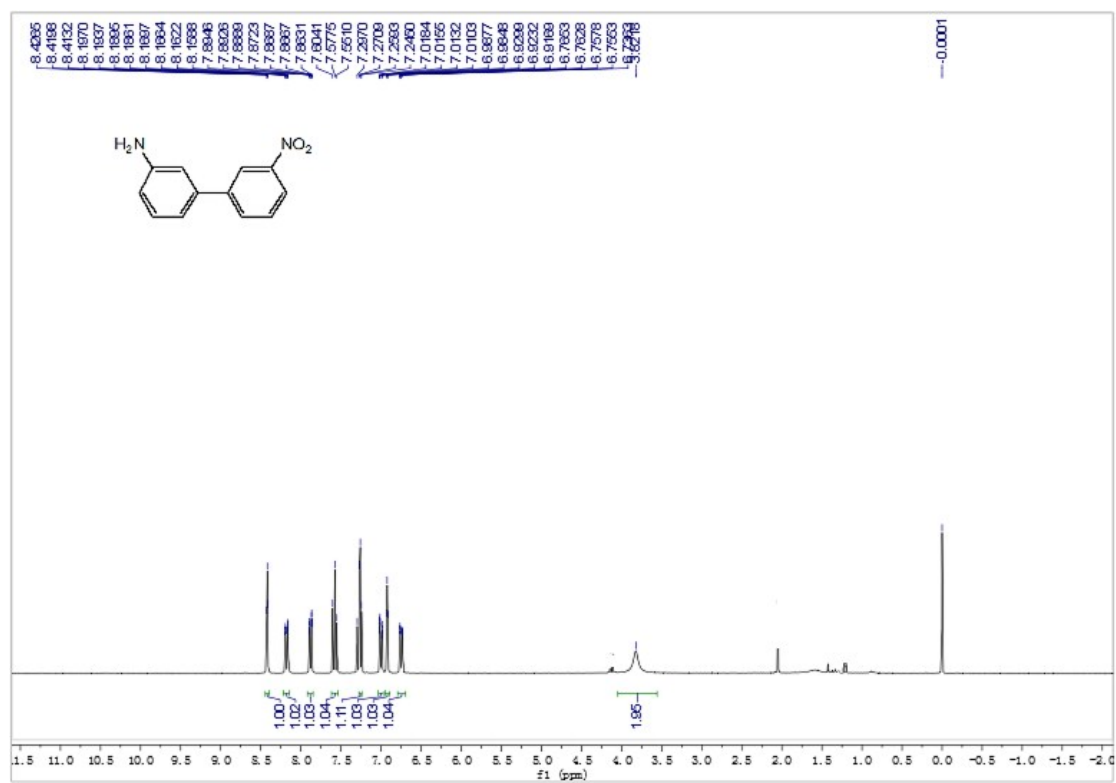


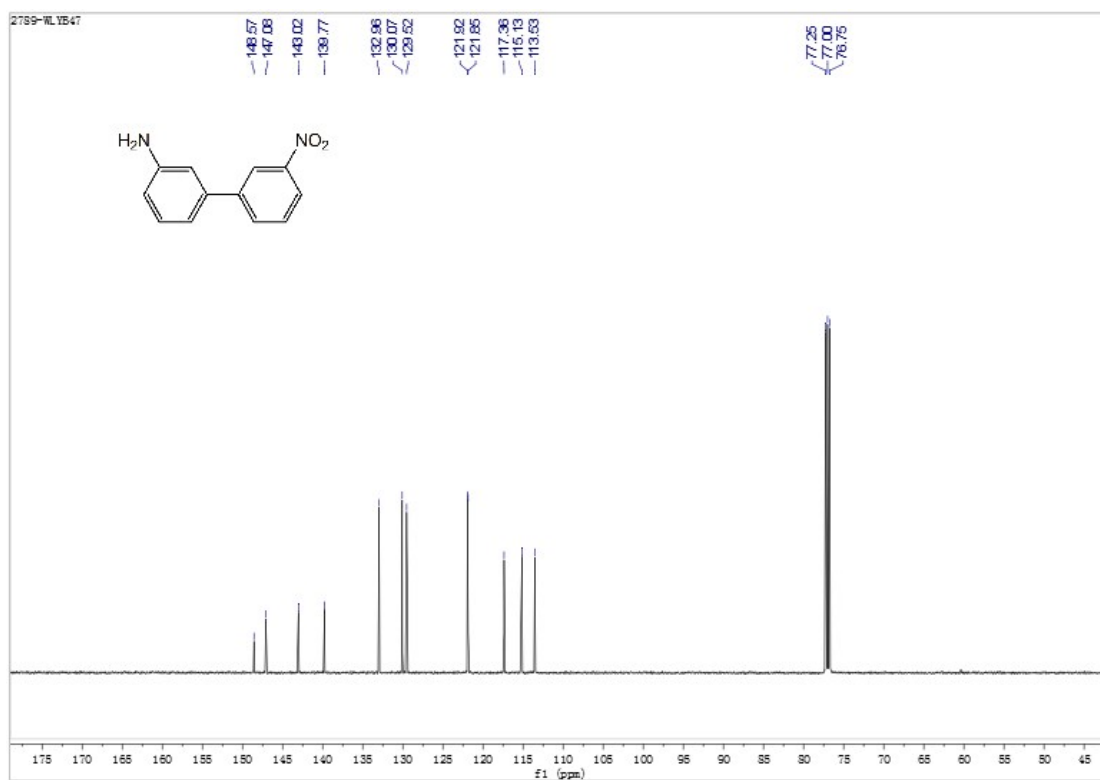
¹H and ¹³C NMR spectra of compound 6c



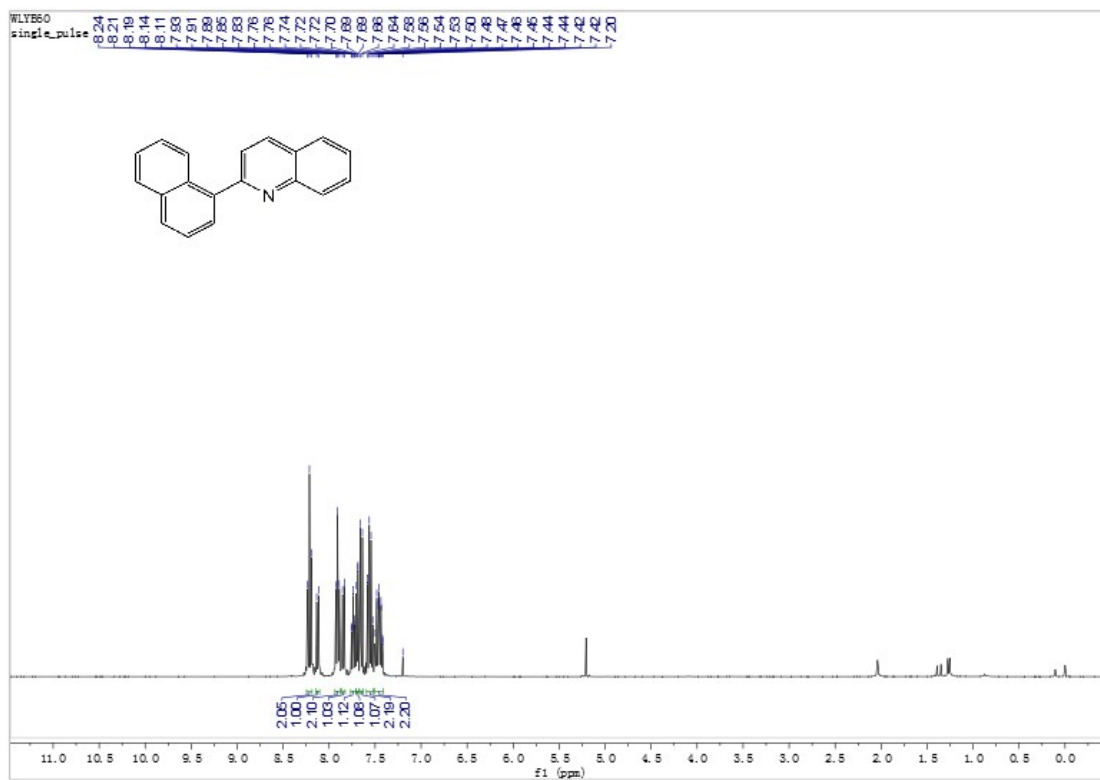


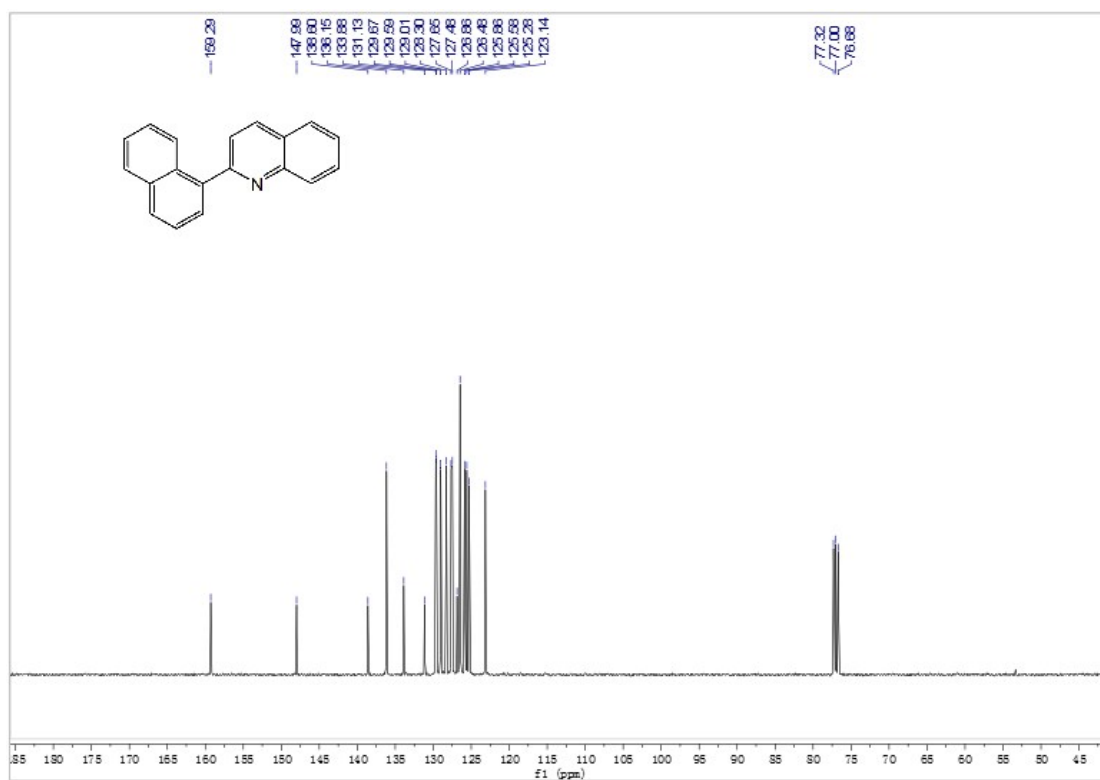
¹H and ¹³C NMR spectra of compound 6d



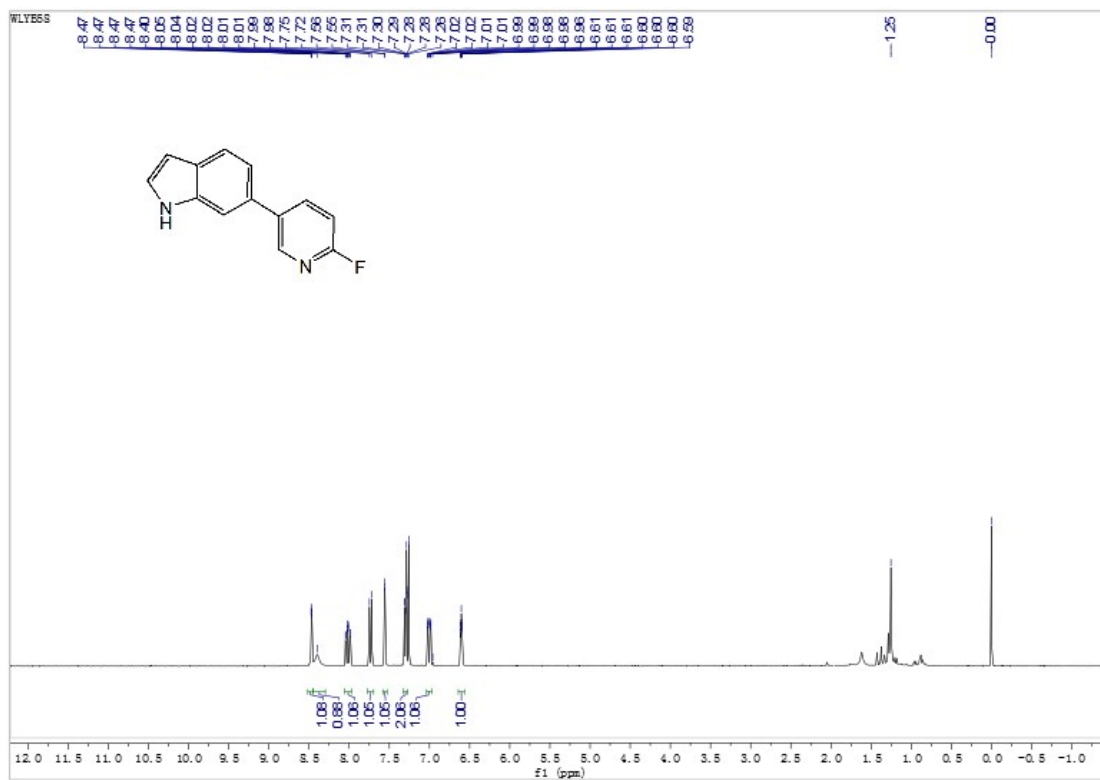


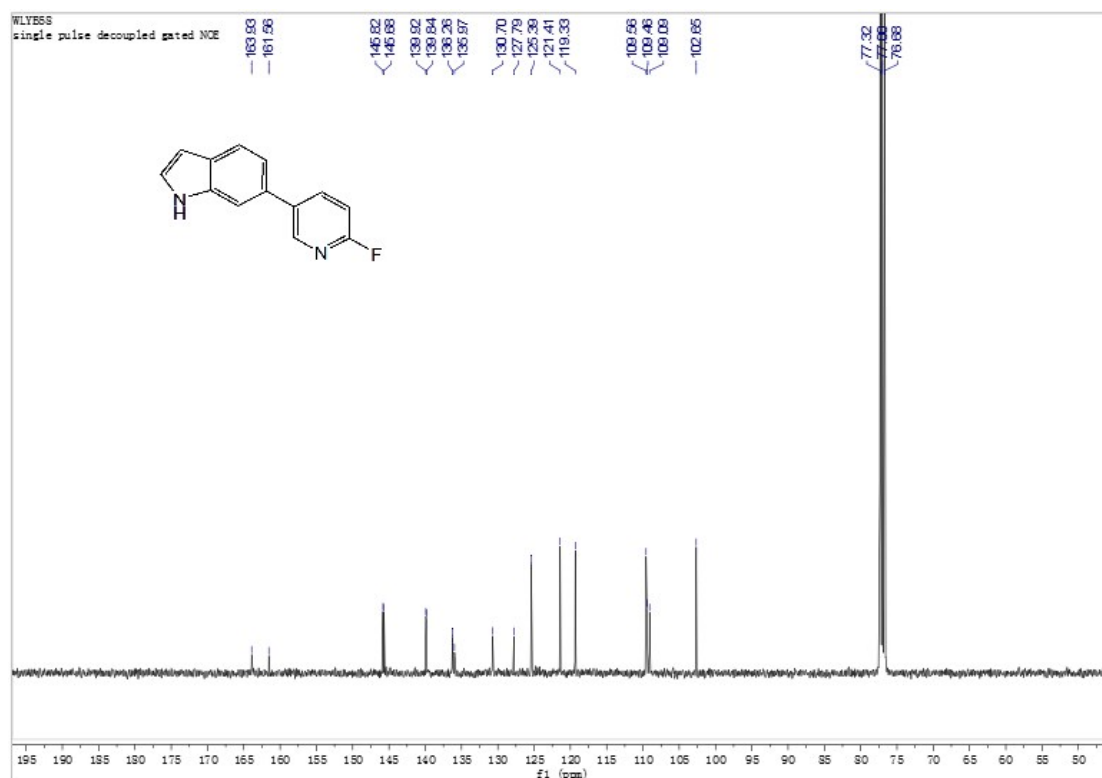
^1H and ^{13}C NMR spectra of compound 6e





¹H and ¹³C NMR spectra of compound 6f





^1H and ^{13}C NMR spectra of compound 6g

