A highly efficient and recyclable ligand-free protocol for Suzuki coupling reaction of potassium trifluoroborates in water

Leifang Liu*, Yan Dong & Nana Tang

(Key Laboratory of Coordination Chemistry and Functional Materials in Universities of Shandong, Dezhou University, Dezhou 253023, People's Republic of China)

*Corresponding author. Tel.: +086-0534-8987866; Fax: +086-0534-8985835.

Supporting Information

Content

General

All reactions were carried out in air without any protection of inert gases. Potassium aryltrifluoroborates used were prepared by corresponding arylboronic acids following the method reported in literature. [1] Other starting materials were purchased from common commercial sources and used without further purification. All products were isolated by chromatography on a silica gel (300-400 mesh) using petroleum ether (60 ^{o}C-90 ^{o}C) and ethyl acetate.

^{1}H NMR spectra were recorded on a Bruker Advance 300MHz or 400 MHz spectrometer using TMS as internal standard ($CDCl_3$: δ 7.26 ppm, *d*-DMSO: δ 2.50 ppm). Datas were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. Mass spectroscopy data were collected on Shimadzu GCMS-QP 2010 instrument.

Typical Procedure for the Product

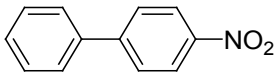
General procedure for the Suzuki coupling of aryl and heteroaryl halides with potassium aryltrifluoroborates

A 25 mL round-bottom flask was charged with aryl or heteroaryl halides (0.5 mmol), $ArBF_3K$ (0.60 mmol), base (1 mmol), $Pd(OAc)_2$ (1 mol%), and H_2O/PEG (3: 3 g) and the mixture was stirred at 80 ^{o}C for indicated time in air. Then the mixture was cooled to room temperature, and extracted by diethyl ether (4×10 mL). The combined organic layer was concentrated under reduced pressure. And the residue was isolated by chromatography on a silica gel (300-400 mesh) column using petroleum and ethyl acetate to afford corresponding biaryl product.

General Procedure for the Reusability of $Pd(OAc)_2/H_2O/PEG$ in the Suzuki Coupling Reaction of 1-bromo-4-nitrobenzene with $PhBF_3K$

A 25 mL round-bottom flask was charged with 1-bromo-4-nitrobenzene (0.5 mmol), $PhBF_3K$ (0.60 mmol), Na_2CO_3 (1 mmol), $Pd(OAc)_2$ (1 mol%), and H_2O/PEG (3: 3 g) and the mixture was stirred at 80 ^oC for 1 h. Then the mixture was cooled to room temperature, and extracted by diethyl ether (4×10 mL). The residue ($Pd(OAc)_2$-H_2O-PEG) was subjected to the next run of the Suzuki reaction by charging with the same substrates (1-bromo-4-nitrobenzene (0.5 mmol), $PhBF_3K$ (0.60 mmol), Na_2CO_3 (1 mmol)) under the same reaction conditions. Water (0.5 mL) was added to the catalytic system in the third, fifth and seventh run. The combined organic layer was concentrated under reduced pressure, and the residue was isolated by chromatography on a silica gel (300-400 mesh) column using petroleum and ethyl acetate to afford the product.

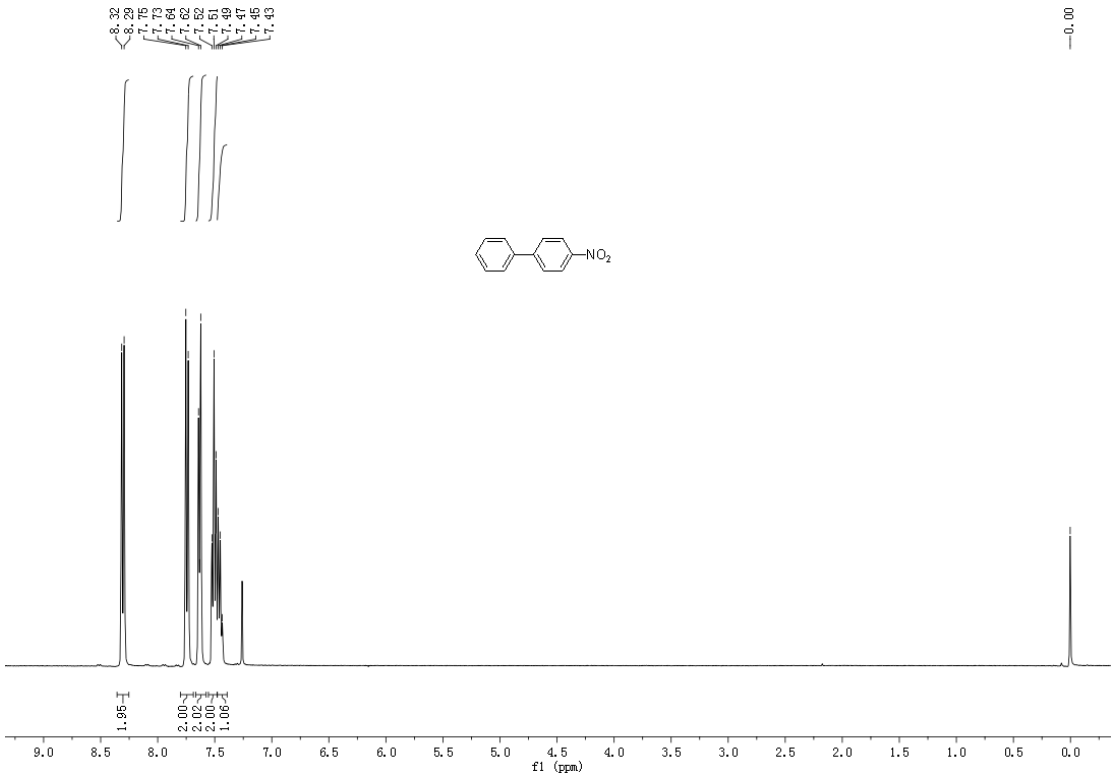
Characterization Data of the Products

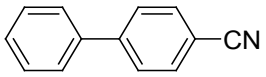


[ref 2]

(4-Nitro-1, 1'-biphenyl, CAS: 92-93-3, T1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.48-7.39 (m, 1H). MS (EI): m/e (%) 200 (10), 199 (71), 169 (28), 153 (29), 152 (100), 151 (29), 150 (9), 141 (19), 127 (10), 126 (9), 115 (12), 77 (9), 76 (14), 75 (7), 63 (7), 51 (7).

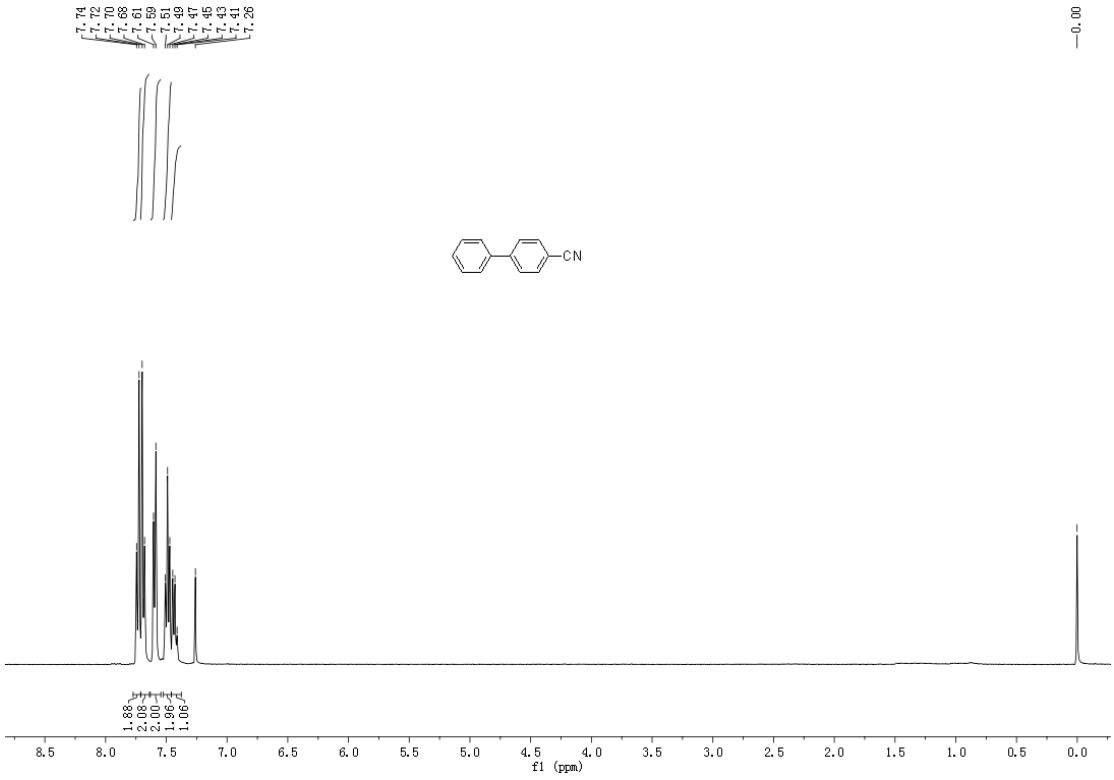


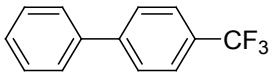


[ref 2]

(1, 1'-Biphenyl-4-carbonitrile, CAS: 2920-38-9, T2-2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.46-7.39 (m, 1H). MS (EI): m/e (%) 180 (15), 179 (100), 178 (24), 152 (9), 151 (20), 150 (5), 89 (10), 76 (38).

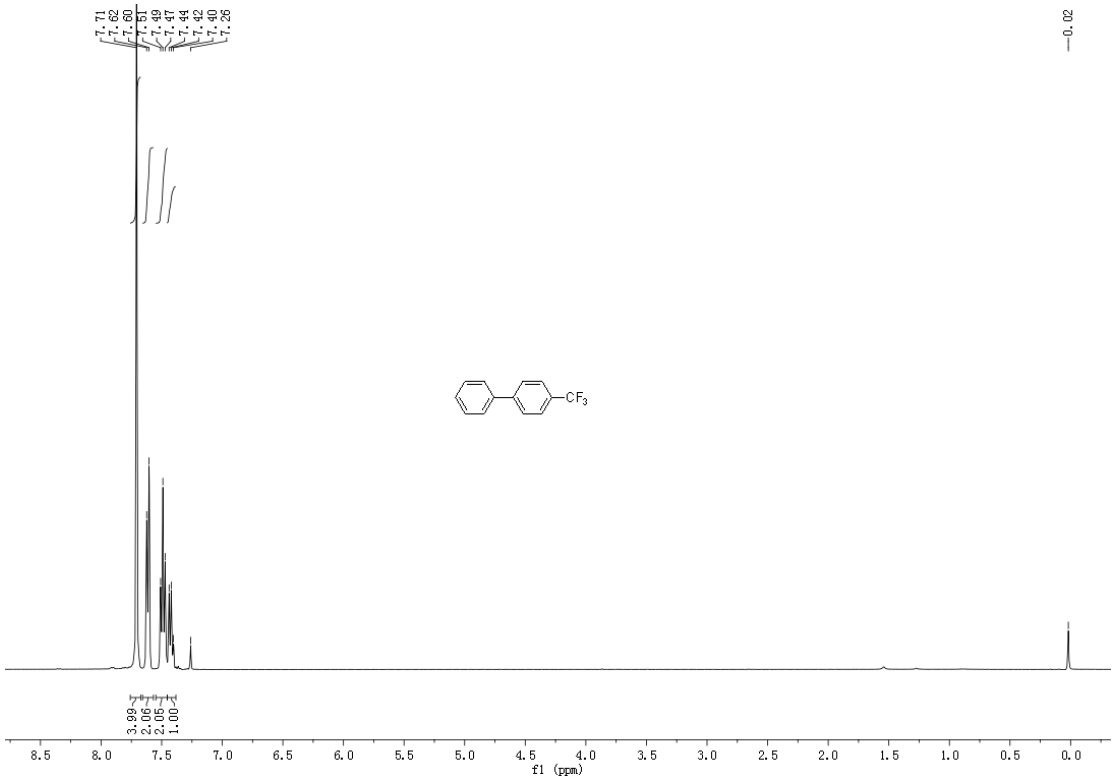


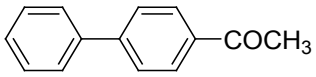


[ref 2]

(4-Trifluoromethyl-1, 1'-biphenyl, CAS: 398-36-7, T2-3)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 4H), 7.61 (d, J = 7.8 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H). MS (EI): m/e (%) 223 (15), 222 (100), 201 (7), 153 (24), 152 (29), 151 (10), 86 (7).

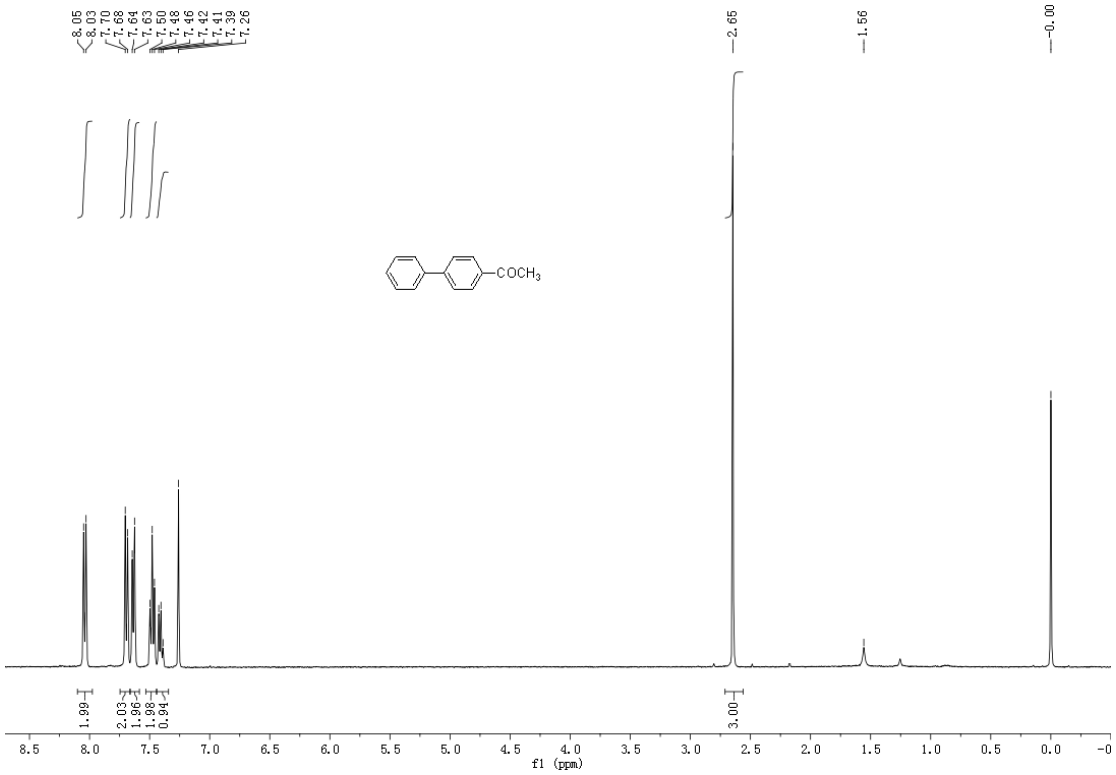


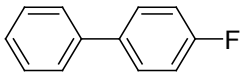


[ref 2]

(1-[1, 1'-biphenyl]-4-yl-ethanone, CAS: 92-91-1, T2-4)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.1 Hz, 1H), 2.65 (s, 3H). MS (EI): m/e (%) 197 (6), 196 (54), 182 (20), 181 (100), 154 (5), 153 (54), 152 (78), 151 (21), 128 (5), 127 (5), 91 (5), 84 (5), 77 (7), 76 (24), 75 (5), 63 (5), 39 (6).

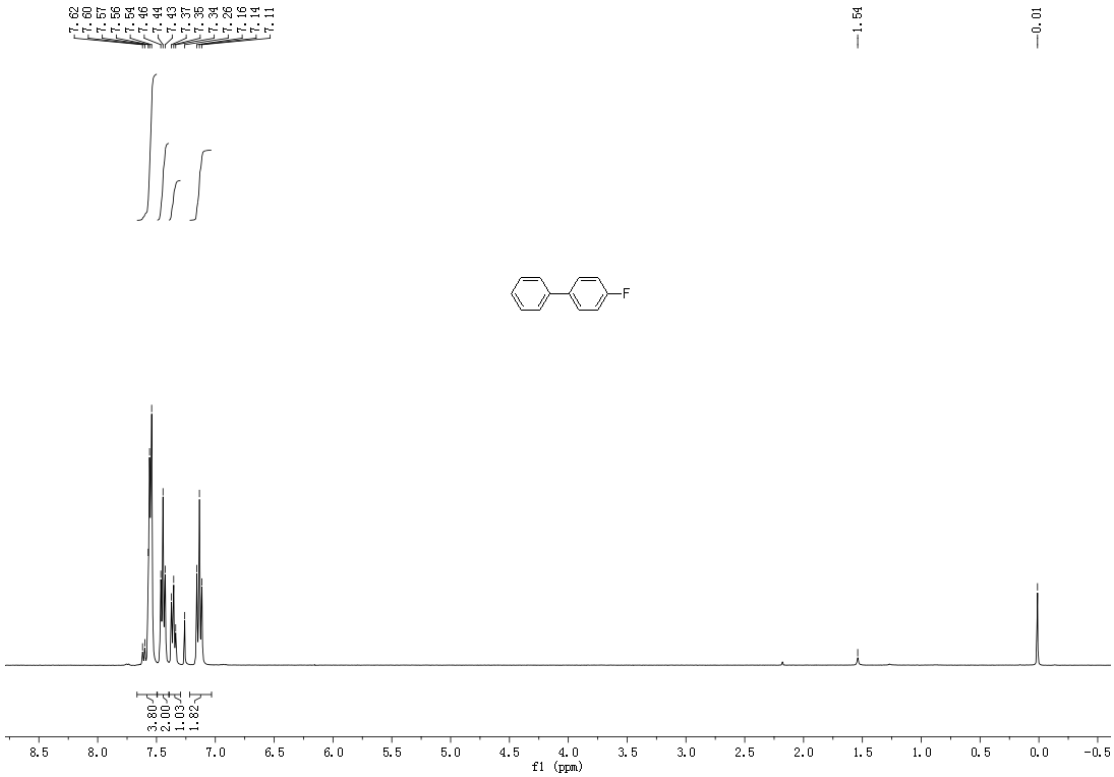


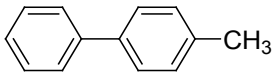


[ref 3]

(4-Fluoro-1, 1'-biphenyl, CAS: 324-74-3, T2-5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.50 (m, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 8.6 Hz, 2H). MS (EI): m/e (%) 173 (12), 172 (100), 171 (37), 170 (24), 154 (5), 152 (5), 146 (5), 87 (7), 86 (12), 76 (5).

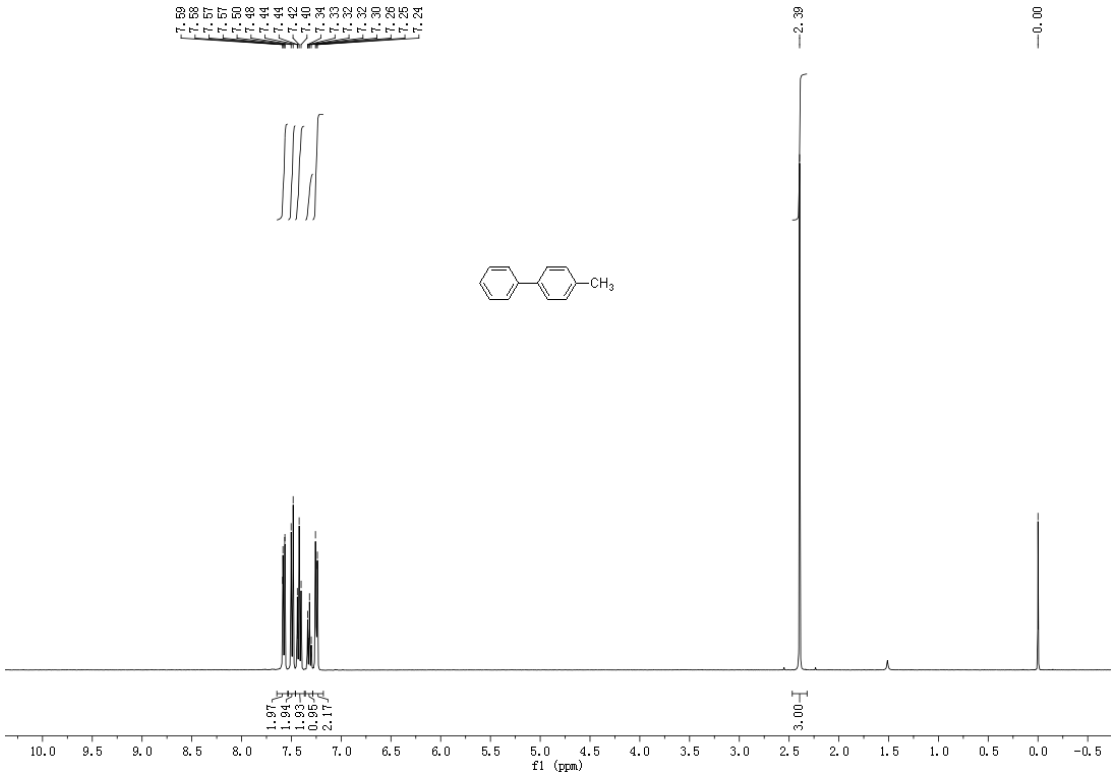


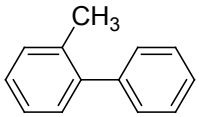


[ref 2]

(4-Methyl-1, 1'-biphenyl, CAS: 644-08-6, T2-6)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.42 (m, 2H), 7.36 -7.28 (m, 1H), 7.28-7.18 (m, 2H), 2.39 (s, 3H). MS (EI): m/e (%) 169 (12), 168 (100), 167 (51), 165 (15), 154 (7), 153 (24), 152 (24), 115 (7), 84 (7), 83 (10).

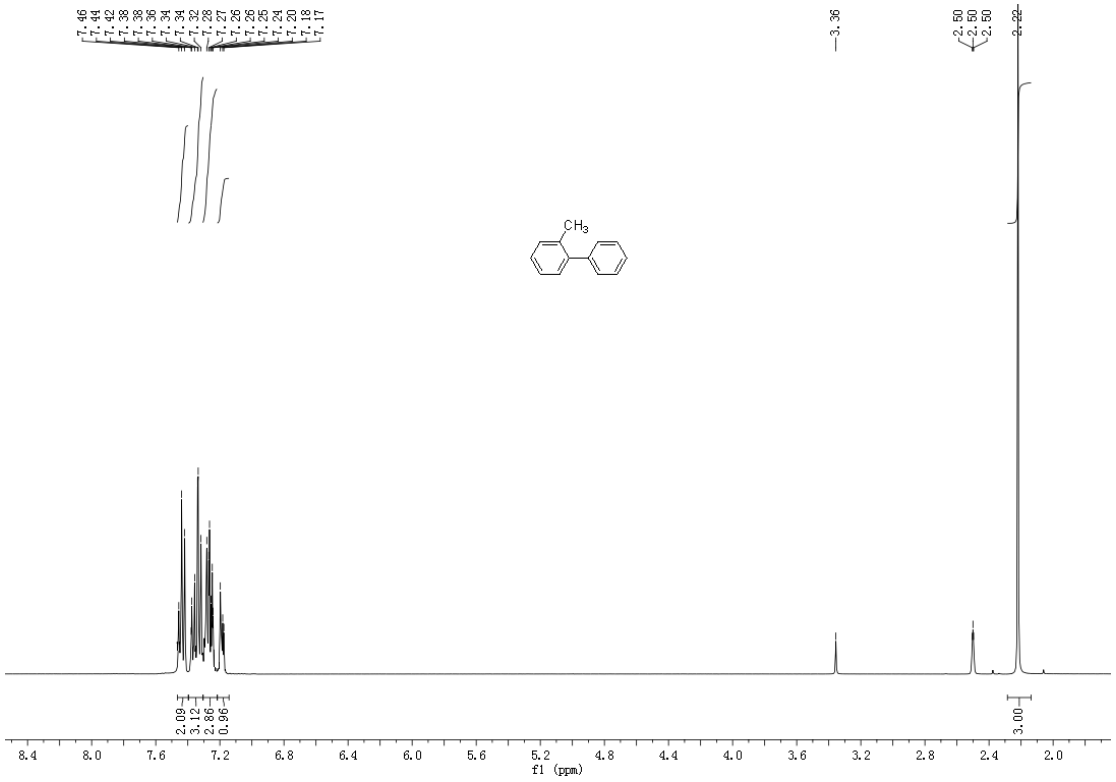


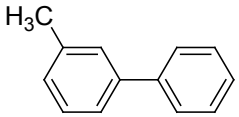


[ref 2]

(2-Methyl-1, 1'-biphenyl, CAS: 643-58-3, T2-7)

^{1}H NMR (400 MHz, DMSO) δ 7.44 (m, 2H), 7.35 (m, 3H), 7.31-7.22 (m, 3H), 7.22-7.14 (m, 1H), 2.22 (s, 3H). MS (EI): m/e (%) 168 (100), 153 (48), 128 (5), 115 (9), 83 (17), 76 (6).

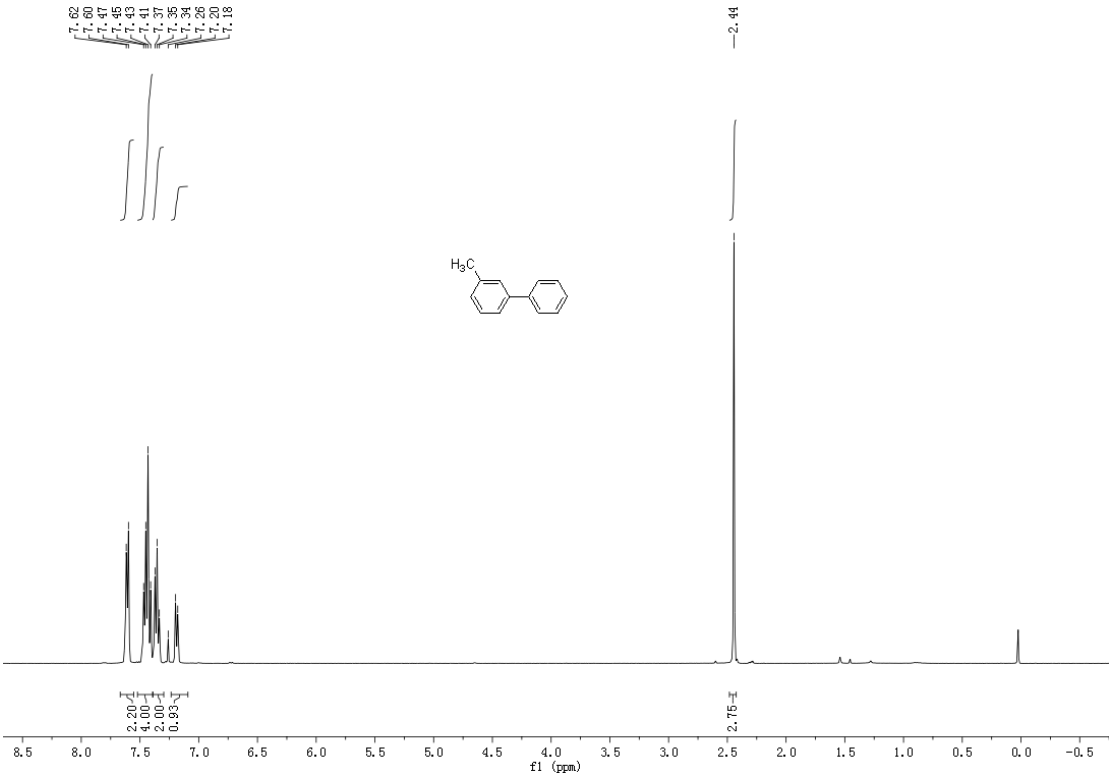


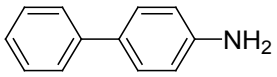


[ref 4]

(3-Methyl-1, 1'-biphenyl, CAS: 643-93-6, T2-8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 2H), 7.44 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.19 (d, *J* = 7.4 Hz, 1H), 2.44 (s, 3H). MS (EI): m/e (%) 168 (100), 152 (25), 115 (5), 83 (10), 63 (7), 51 (5).

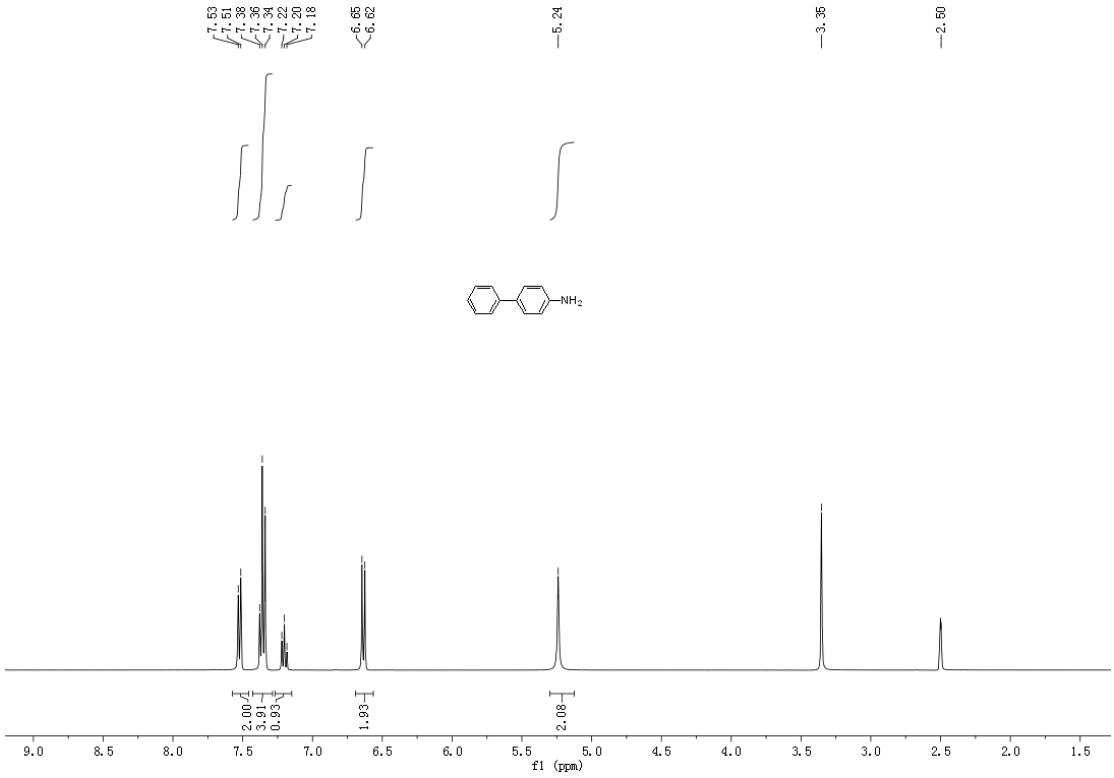


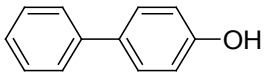


[ref 2]

(1, 1'-Biphenyl-4-amine, CAS: 92-67-1, T2-9)

^{1}H NMR (400 MHz, DMSO) δ 7.52 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 4H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 2H), 5.24 (s, 2H). MS (EI): m/e 169 (100), 139 (10),115 (9), 83 (10). MS (ESI): m/e 169 (100), 139 (10), 115 (9), 83 (10).

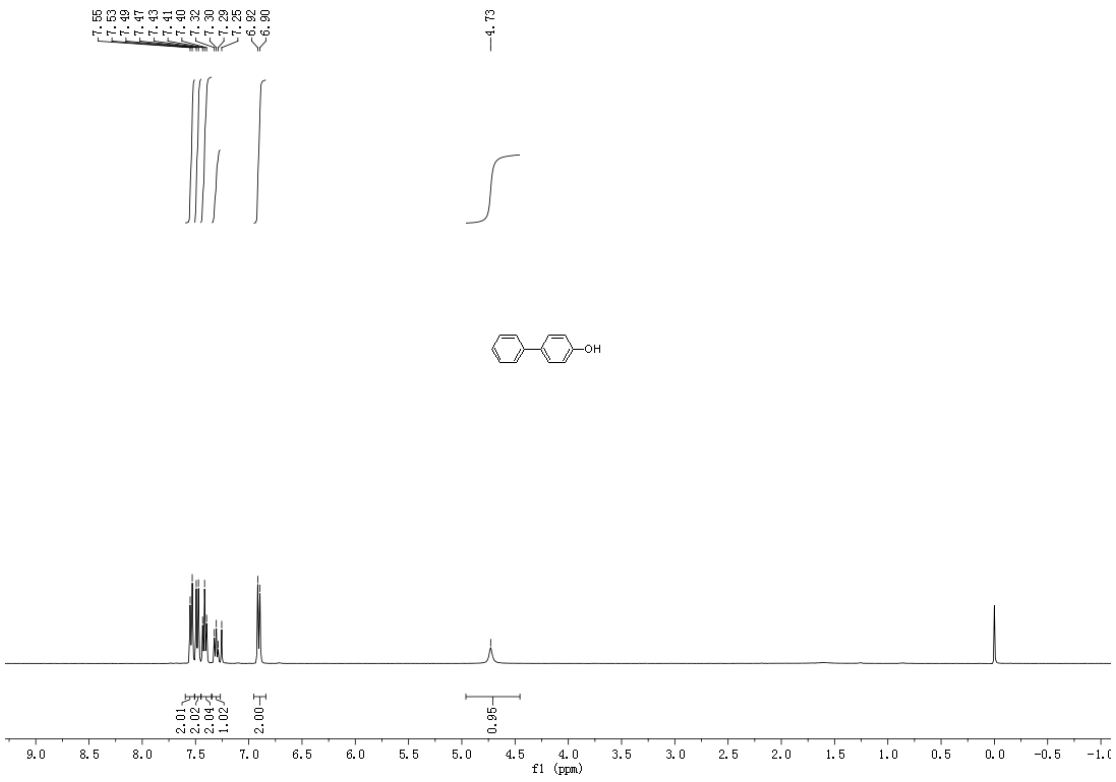


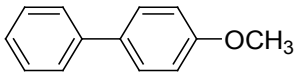


[ref 4]

(1, 1'-Biphenyl-4-ol, CAS: 92-69-3, T2-10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 2H), 4.73 (s, 1H). MS (EI): m/e 170 (100), 169 (90), 141 (33), 115 (24), 83 (9.8), 51 (5), 39 (5).

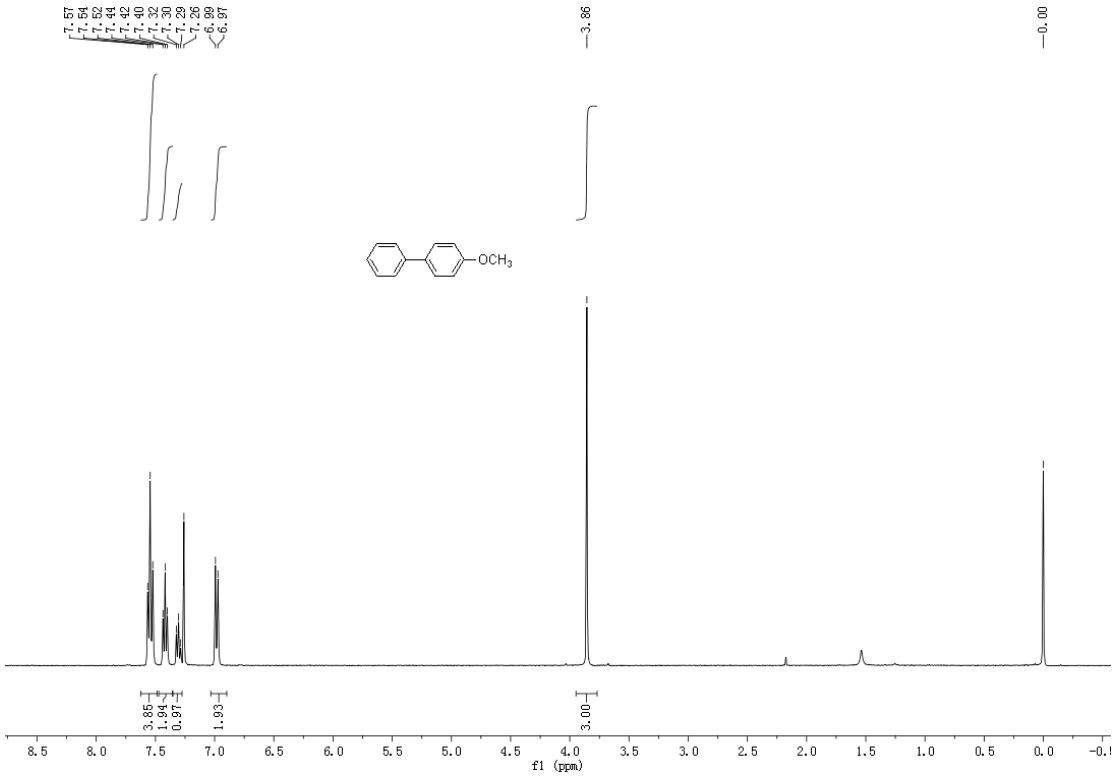


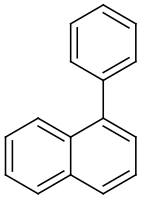


[ref 2]

(4-Methoxy-1, 1'-biphenyl, CAS: 613-37-6, T2-11)

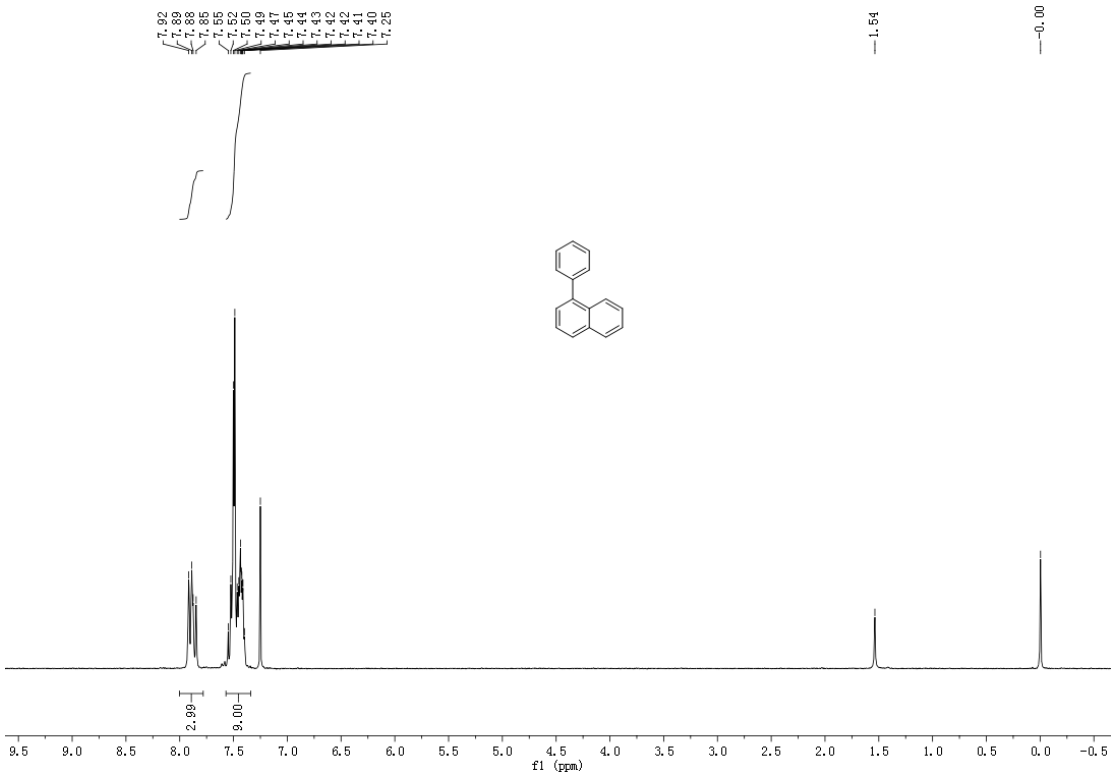
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (t, *J* = 8.6 Hz, 4H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 3H). MS (EI): m/e (%) 185 (14), 184 (100), 169 (57), 152 (7), 141 (71), 139 (15), 115 (45), 92 (7), 89 (5), 76 (9), 71 (5), 62 (7), 57 (7), 39 (5).

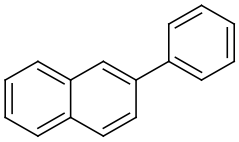



[ref 5]

(1-Phenyl-naphthalene, CAS: 605-02-7, T2-12)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (m, 3H), 7.57-7.34 (m, 9H). MS (EI): m/e (%) 204 (100), 101 (55), 88 (17), 76 (8).

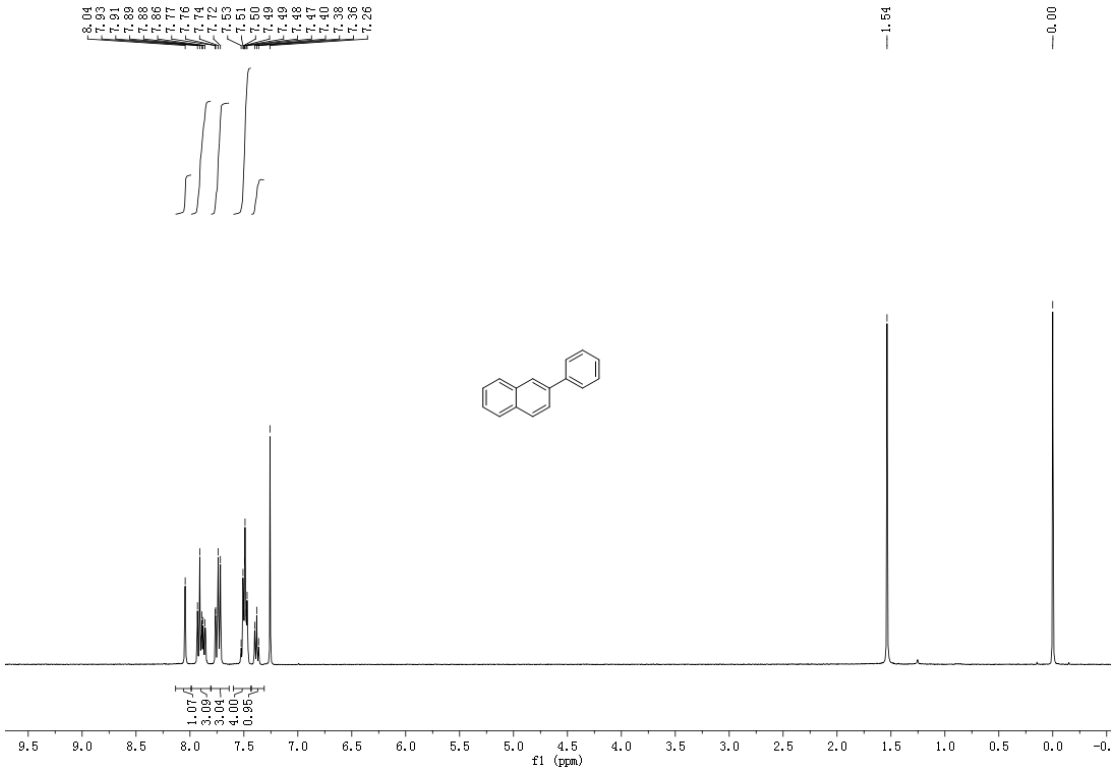


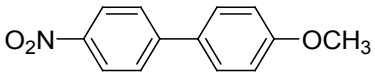


[ref 5]

(2-Phenyl-naphthalene, CAS: 612-94-2, T2-13)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.99-7.81 (m, 3H), 7.75 (m, 3H), 7.60-7.43 (m, 4H), 7.38 (t, J = 7.4 Hz, 1H). MS (EI): m/e (%) 204 (100), 101 (30), 89 (11), 76 (8).

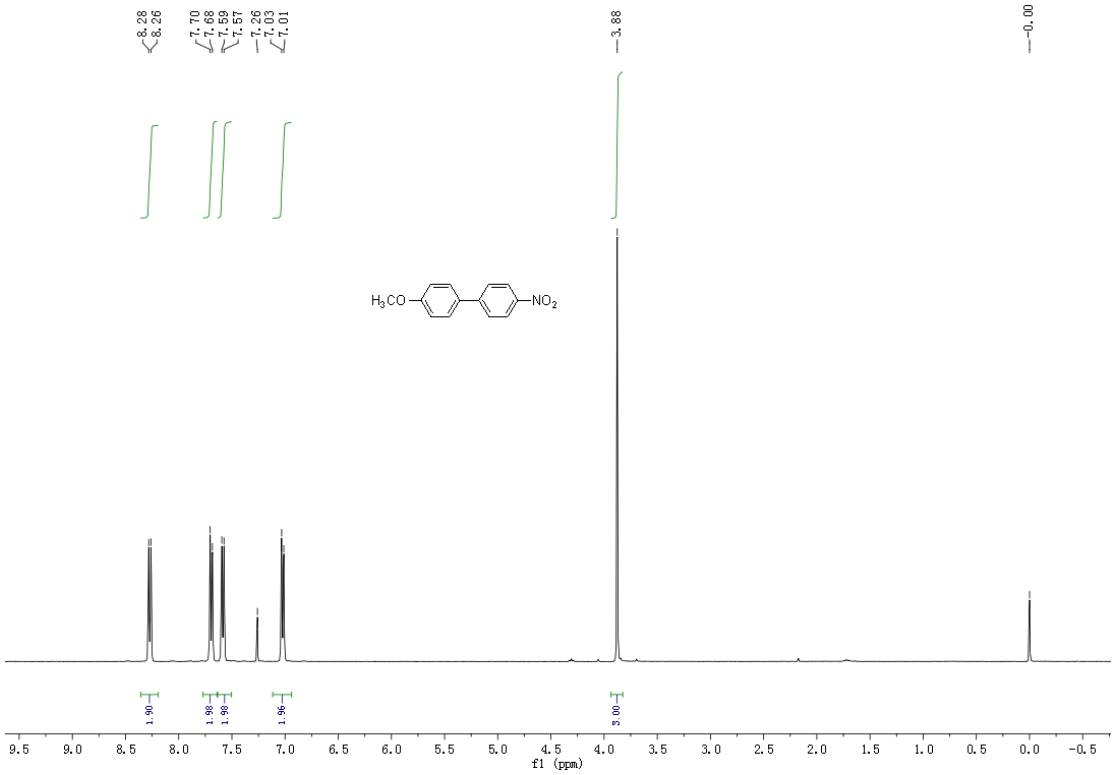


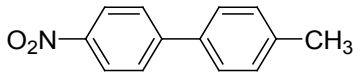


[ref 4]

(4'-Methoxy-4-nitro-biphenyl, CAS: 2143-90-0, T2-14)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 3.88 (s, 3H). MS (EI): m/e (%) 229 (100), 199 (20), 183 (12), 171 (10), 168 (24), 156 (7), 153 (20), 139 (49), 128 (10), 63 (7).

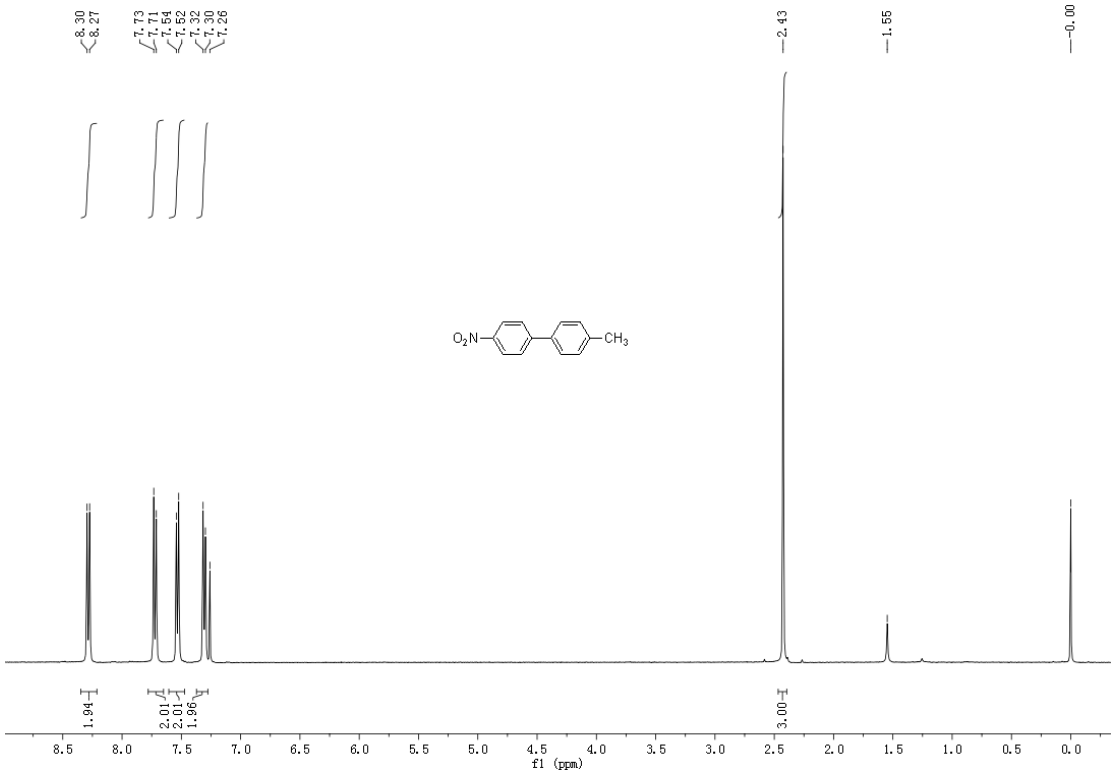


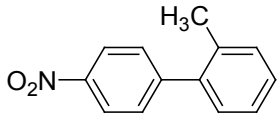


[ref 6]

(4'-Methyl-4-nitro-biphenyl, CAS: 2143-88-6, T2-15)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H). MS (EI): m/e (%) 214 (15), 213 (100), 183 (27), 165 (46), 155 (27), 153 (15), 152 (83), 151 (13), 139 (10), 128 (7), 115 (15), 82 (7), 63 (5).

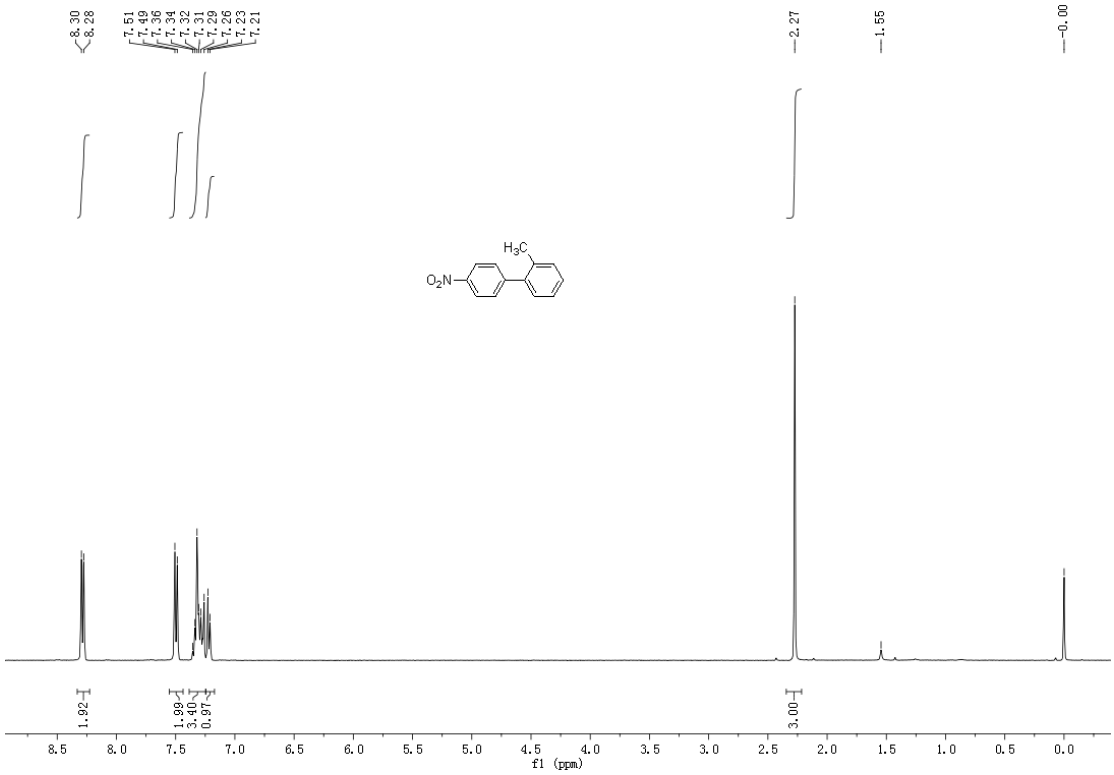


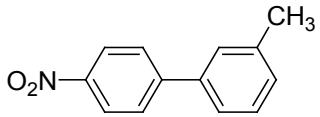


[ref 7]

(2'-Methyl-4-nitro-1, 1'-biphenyl, CAS: 33350-73-1, T2-16)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.39-7.25 (m, 3H), 7.22 (d, *J* = 7.3 Hz, 1H), 2.27 (s, 3H). MS (EI): m/e (%) 213 (100), 165 (88), 152 (78), 151 (12), 115 (27), 82 (15), 77 (5), 63 (11), 51 (7), 39 (7).

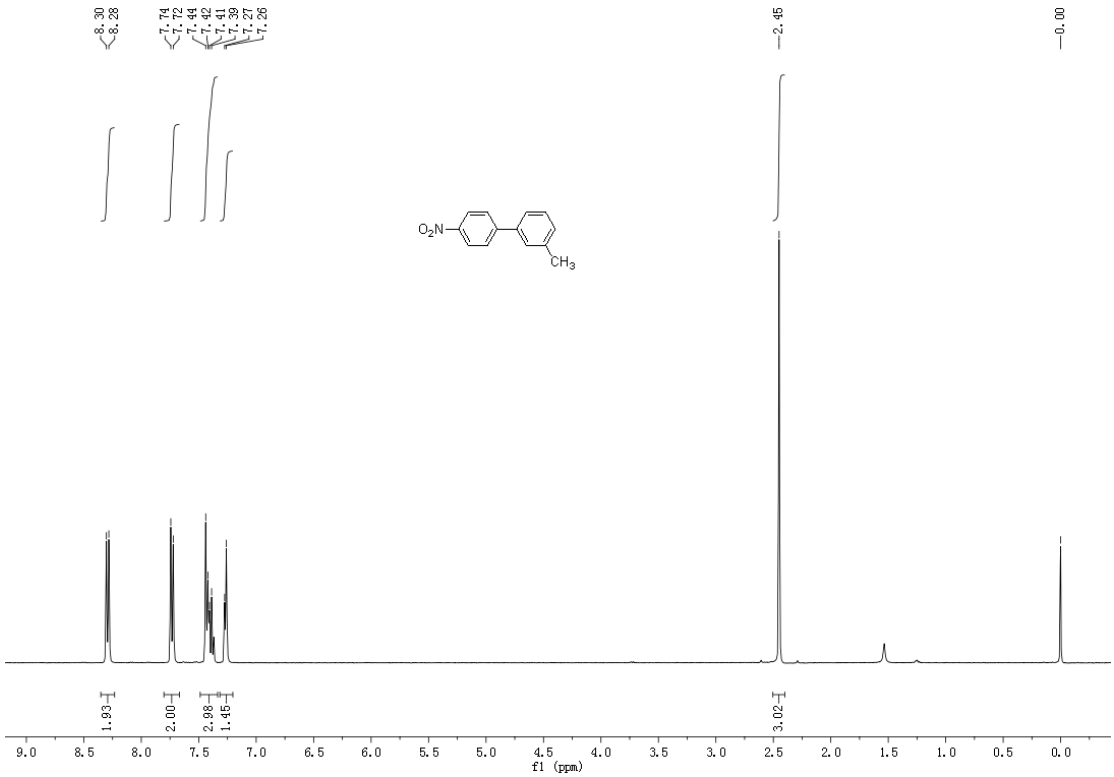


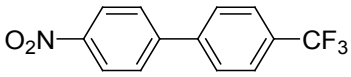


[ref 7]

(3'-Methyl-4-nitro-1, 1'-biphenyl, CAS: 952-21-6, T2-17)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.41 (m, 3H), 7.27 (d, *J* = 5.9 Hz, 1H), 2.45 (s, 3H). MS (EI): m/e (%) 213 (88), 183 (29), 165 (53), 152 (100), 115 (20), 82 (12), 63 (10), 51 (7), 39 (7).

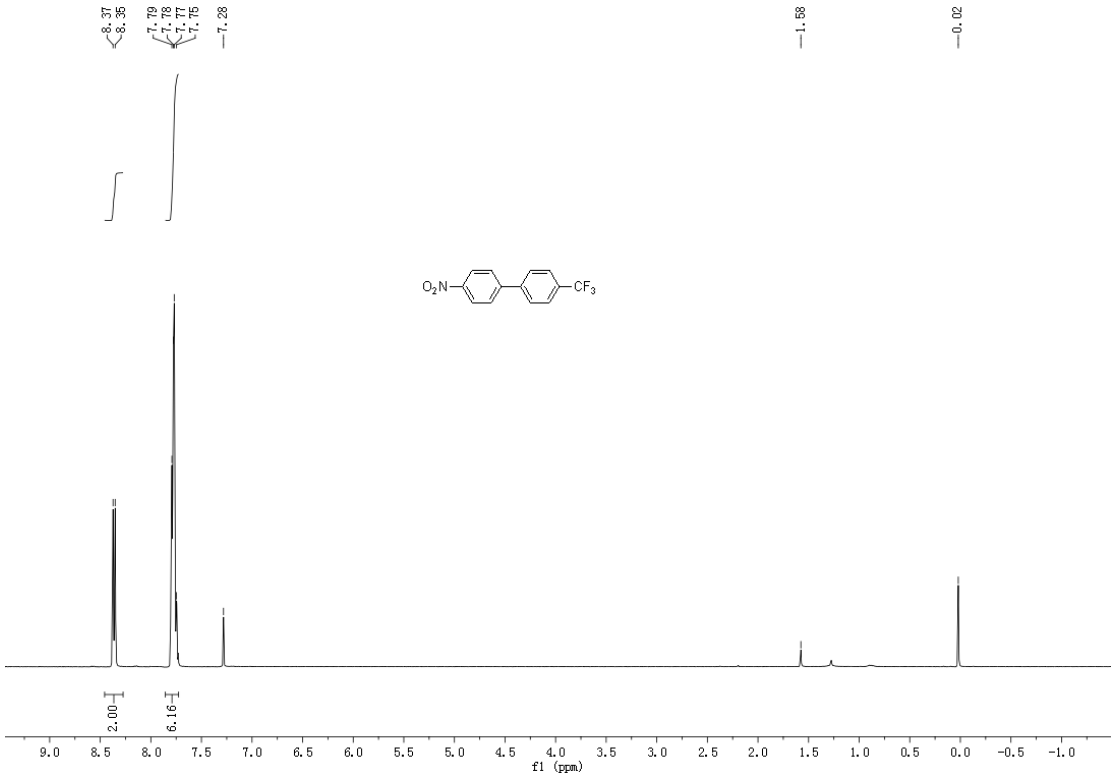


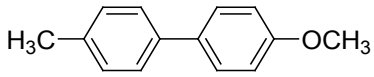


[ref 4]

(4-Nitro-4`-trifluoromethyl-1, 1'-biphenyl, CAS: 80245-34-7, T2-18)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.4 Hz, 2H), 7.86-7.73 (m, 6H). MS (EI): m/e (%) 268 (15), 267 (100), 266 (7), 248 (7), 237 (33), 221 (7), 209 (27), 201 (34), 170 (7), 153 (7), 152 (59), 151 (17), 75 (7).

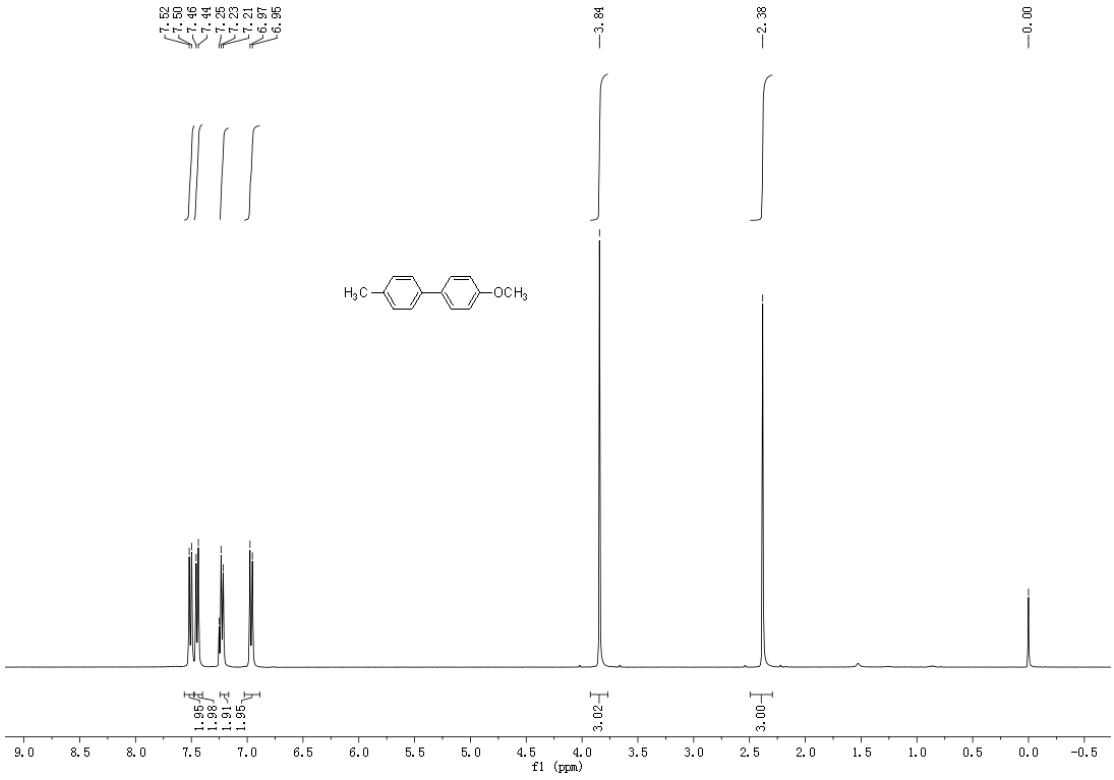


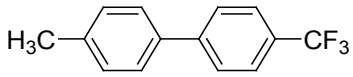


[ref 2]

(4-Methoxy-4'-methyl-1, 1'-biphenyl, CAS: 53040-92-9, T2-19)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 3H), 2.38 (s, 3H). MS (EI): m/e (%) 198 (100), 183 (52), 155 (39), 127 (5), 115 (7), 99 (7).

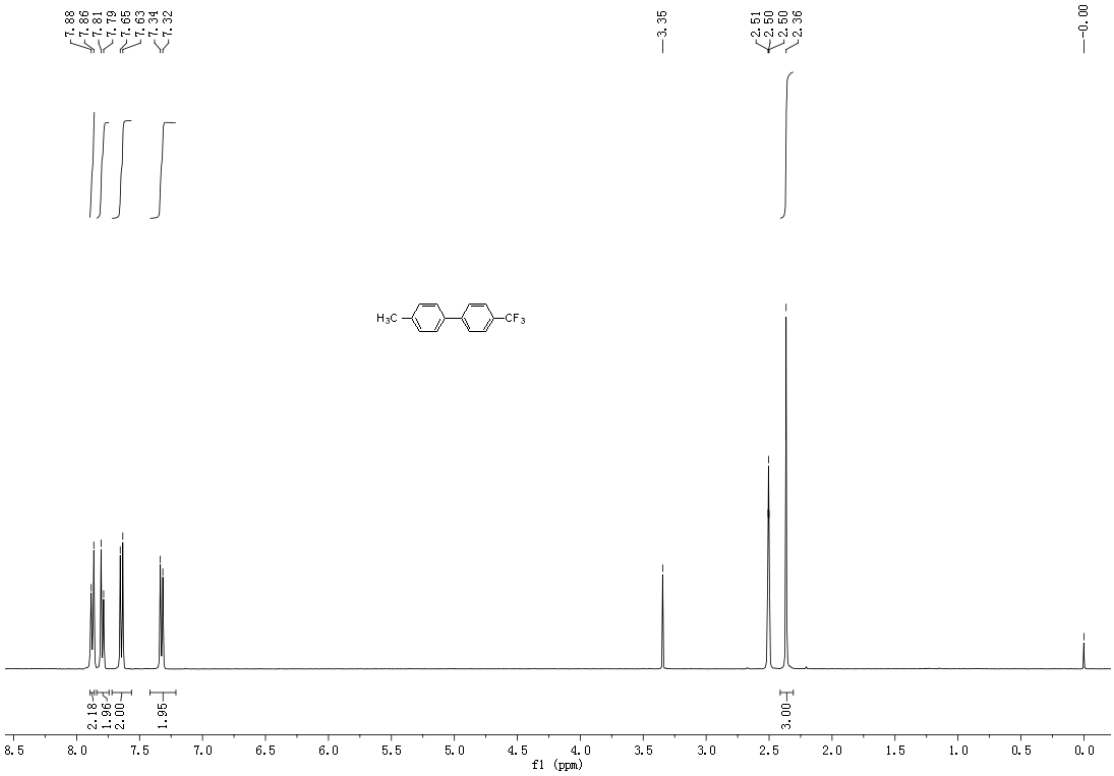


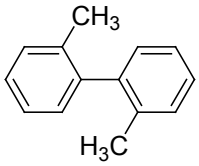


[ref 2]

(4-Methyl-4'-(trifluoromethyl)-1, 1'-biphenyl, CAS: 97067-18-0, T2-20)

^{1}H NMR (400 MHz, DMSO) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H). MS (EI): m/e (%) 236 (100), 167 (42), 152 (9), 91 (8).



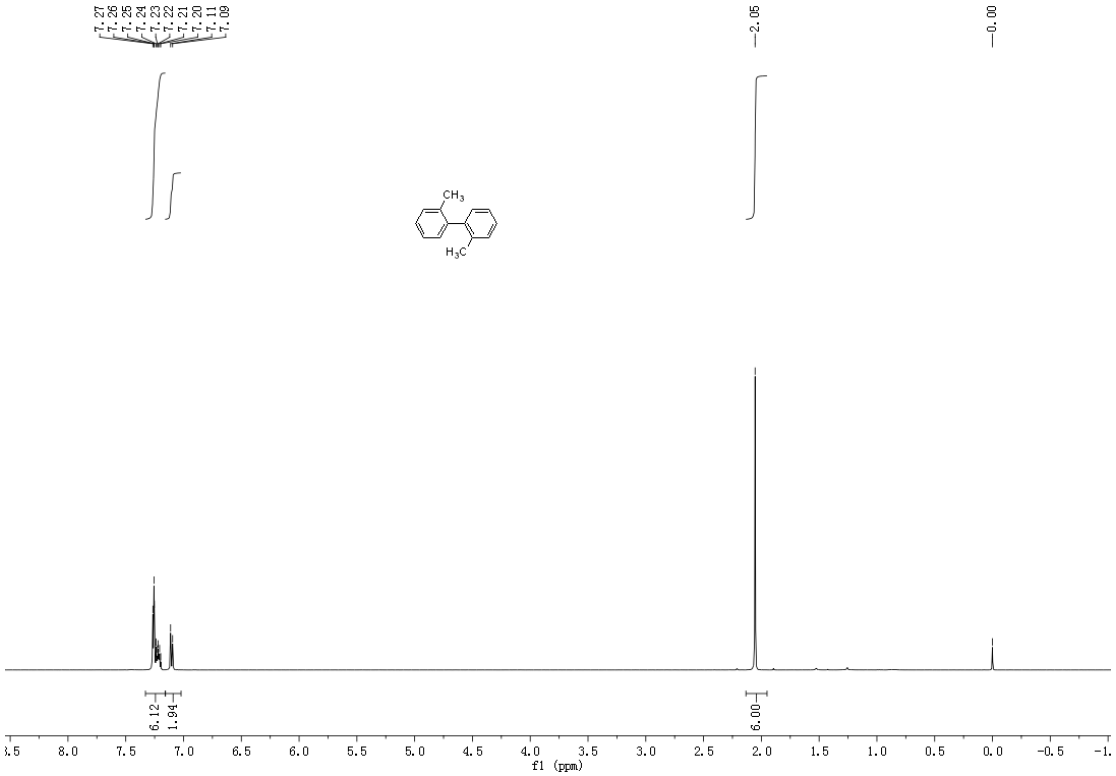


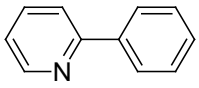
[ref 8]

(2, 2'-dimethyl-1, 1'-biphenyl, CAS: 605-39-0, T2-21)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (m, 6H), 7.10 (d, *J* = 7.0 Hz, 2H), 2.05 (s, 6H).

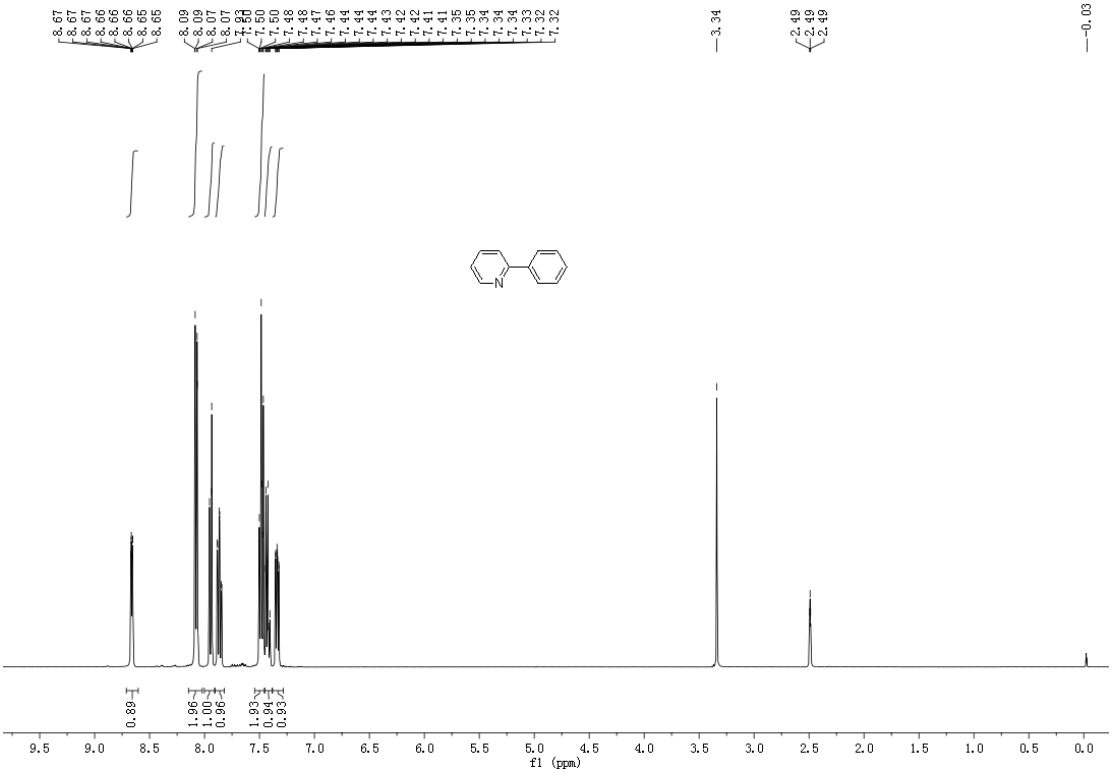
MS (EI): m/e (%) 182 (65), 167 (100), 152 (22), 115 (10), 89 (20), 76 (10), 51 (5), 39 (8).

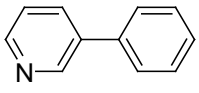



[ref 5]

(2-Phenyl-pyridine, CAS: 1008-89-5, T3-1)

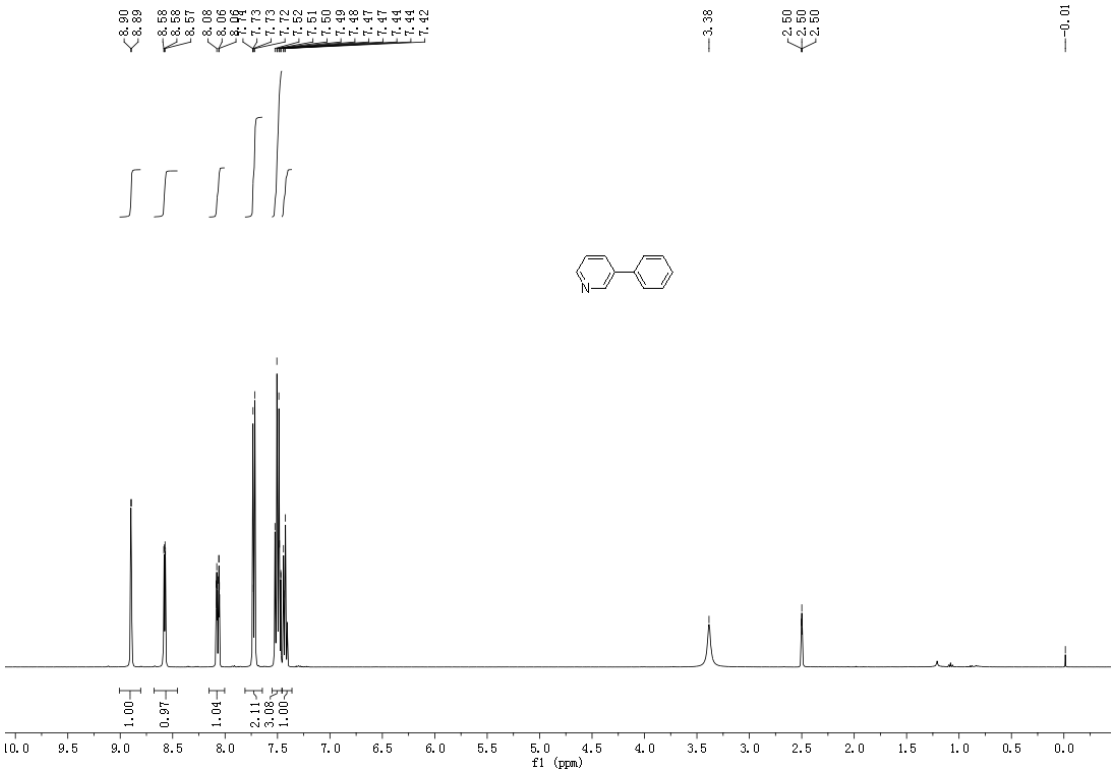
^{1}H NMR (400 MHz, DMSO) δ 8.66 (m, 1H), 8.15-8.02 (m, 2H), 8.00-7.91 (m, 1H), 7.86 (m, 1H), 7.54-7.46 (m, 2H), 7.43 (m, 1H), 7.34 (m, 1H). MS (EI): m/e (%) 155 (100), 127 (19), 77 (22), 63 (5), 51 (14).

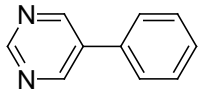



[ref 5]

(3-Phenylpyridine, CAS: 1008-88-4, T3-2)

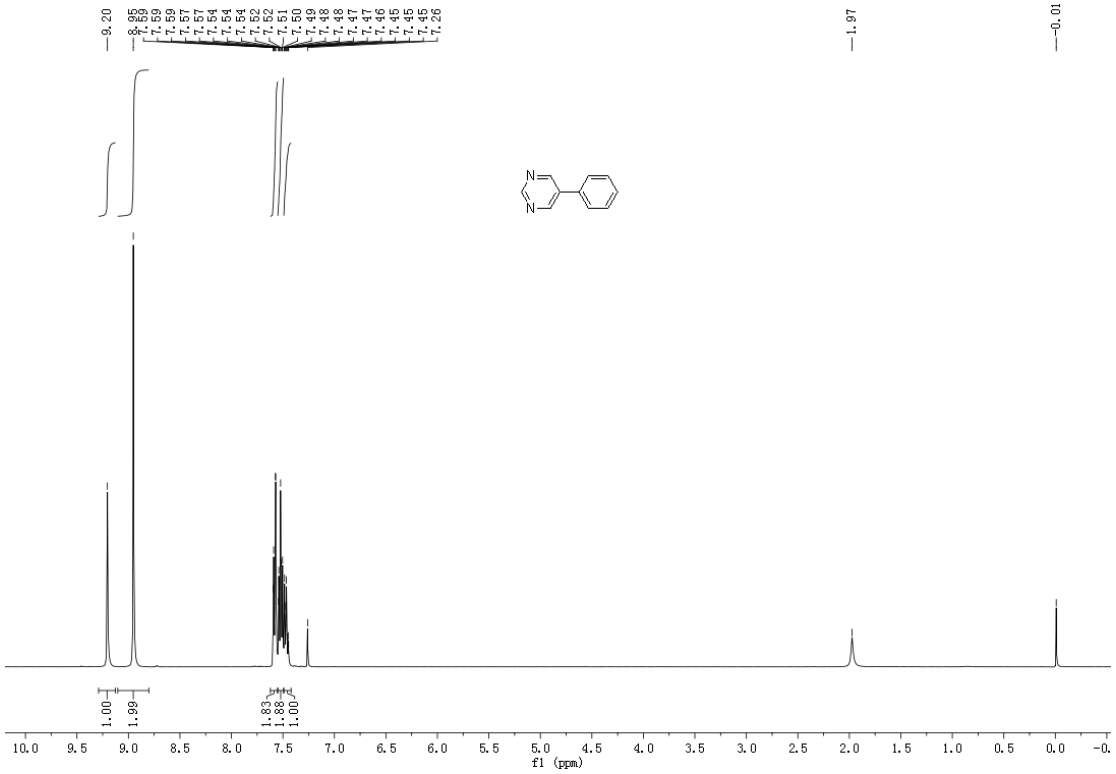
^{1}H NMR (400 MHz, DMSO) δ 8.90 (d, *J* = 2.0 Hz, 1H), 8.58 (m 1H), 8.15-8.00 (m, 1H), 7.73 (m, 2H), 7.55-7.46 (m, 3H), 7.46-7.36 (m, 1H). MS (EI): m/e (%) 155 (100), 127 (15), 102 (11), 76 (10).

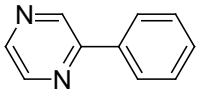



[ref 5]

(5-Phenylpyrimidine, CAS: 34771-45-4, T3-3)

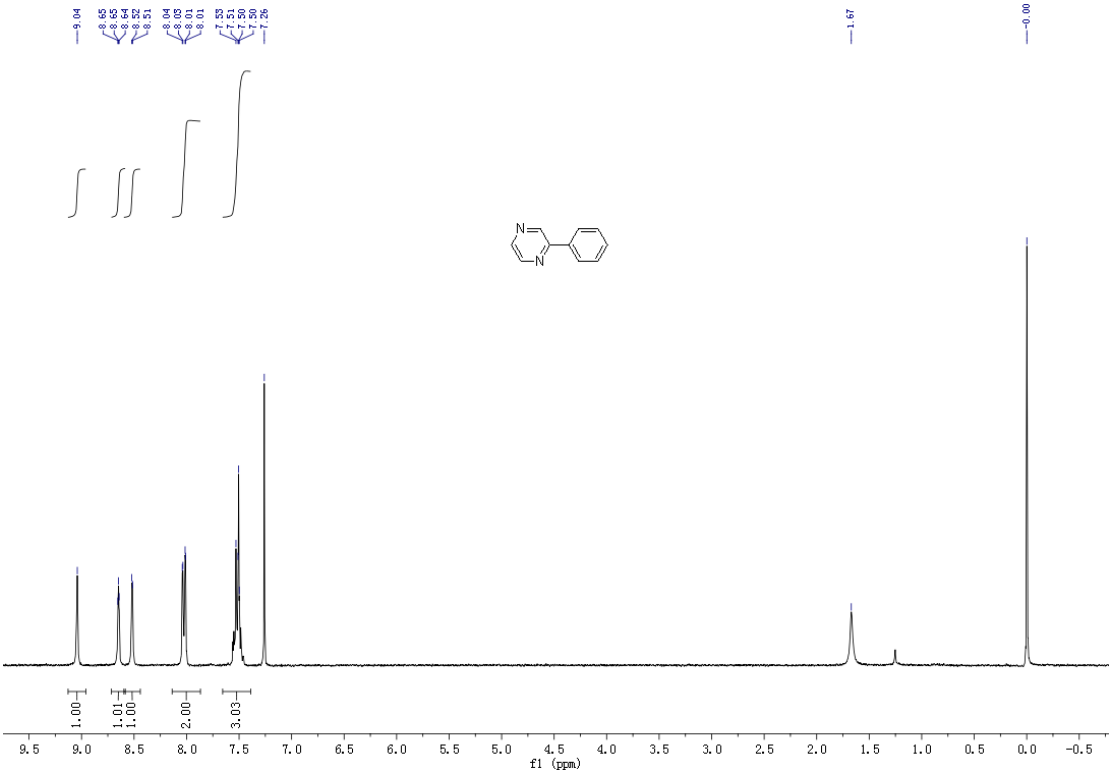
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.95 (s, 2H), 7.62-7.55 (m, 2H), 7.55-7.49 (m, 2H), 7.49-7.41 (m, 1H). MS (EI): m/e (%) 156 (100), 102 (73), 76 (15), 51(22).

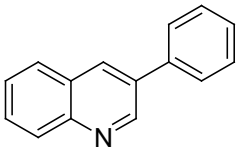



[ref 9]

(2-Phenyl-pyrazine, CAS: 29460-97-7, T3-4)

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.72-8.58 (m, 1H), 8.52 (d, *J* = 2.4 Hz, 1H), 8.02 (m, 2H), 7.51 (m, 3H). MS (EI): m/e (%) 156 (100), 129 (22), 103 (91), 76 (25), 51 (18), 39 (5).

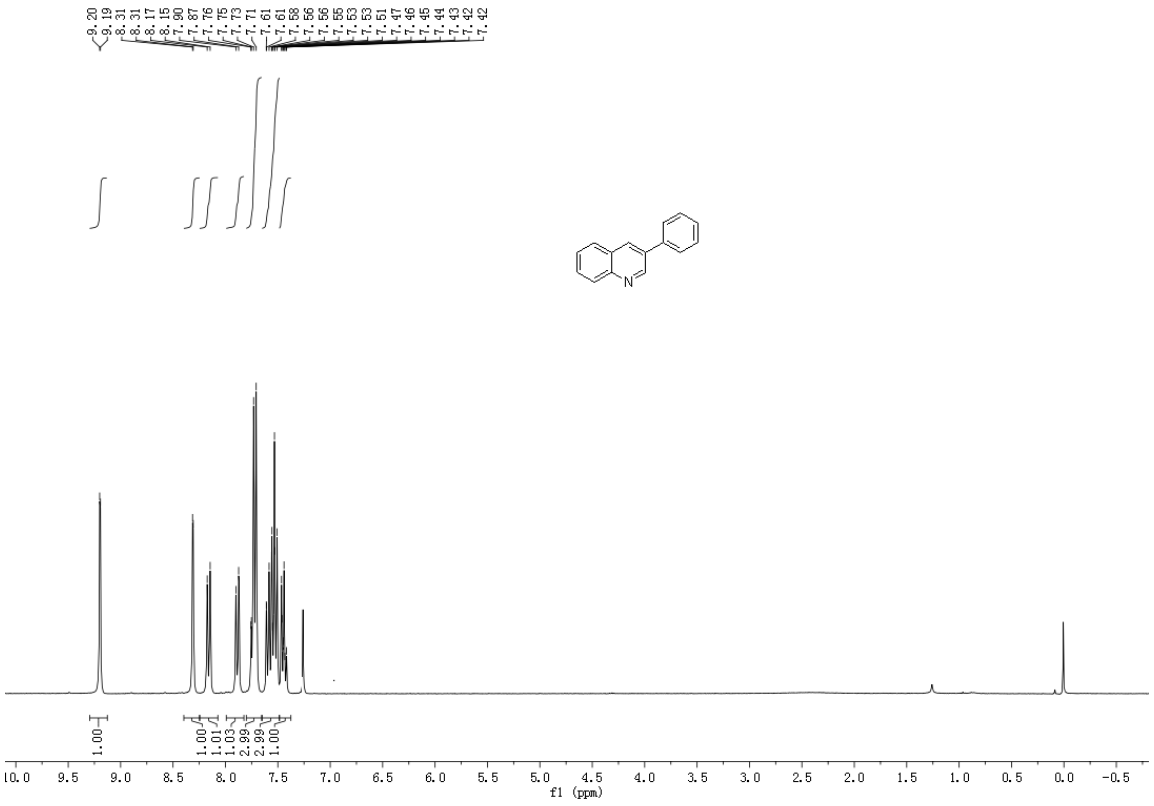


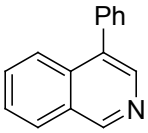


[ref 5]

(3-Phenyl-quinoline, CAS: 1666-92-2, T3-6)

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.20 (d, *J* = 3.0 Hz, 1H), 8.31 (d, *J* = 1.9 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.74 (m, 3H), 7.65-7.48 (m, 3H), 7.48-7.38 (m, 1H). MS (EI): m/e (%) 205 (100), 176 (12), 151 (8), 102 (15), 88 (13), 76 (28), 51 (5).

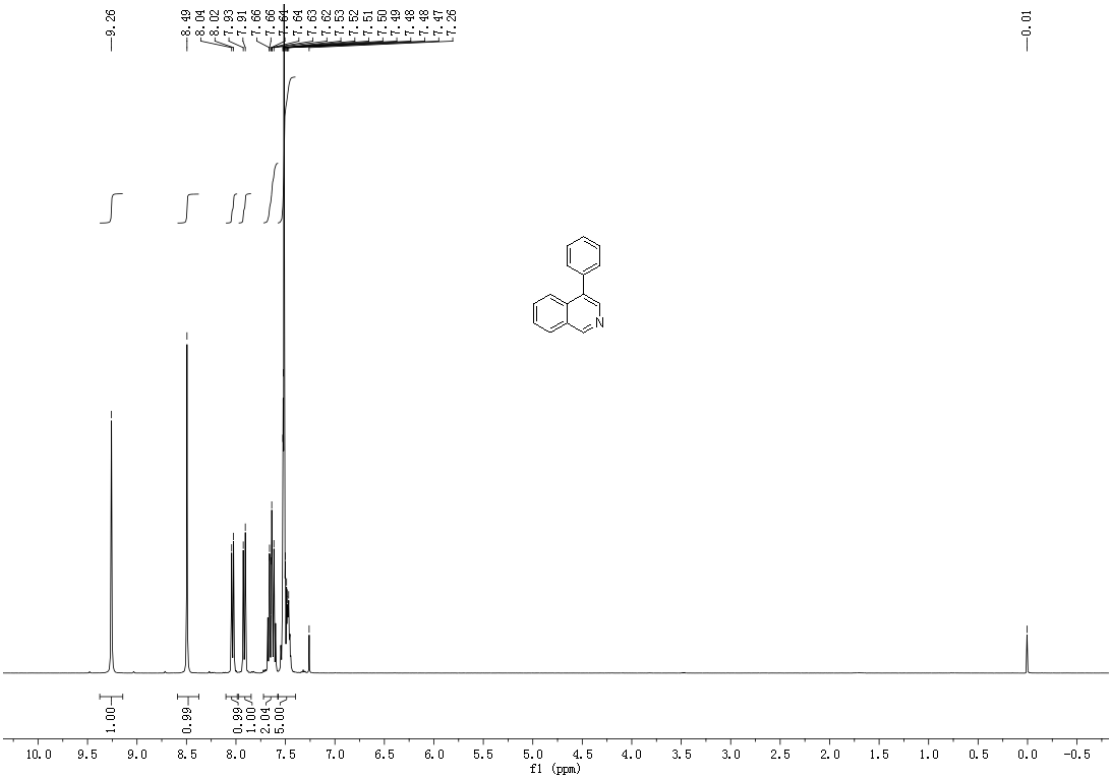


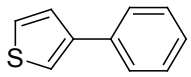


[ref 5]

(4-Phenylisoquinoline, CAS: 19571-30-3, T3-7)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.49 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.72-7.57 (m, 2H), 7.58-7.40 (m, 5H). MS (EI): m/e (%) 205 (100), 176 (20), 151 (9), 102 (23), 88 (21), 76 (15).

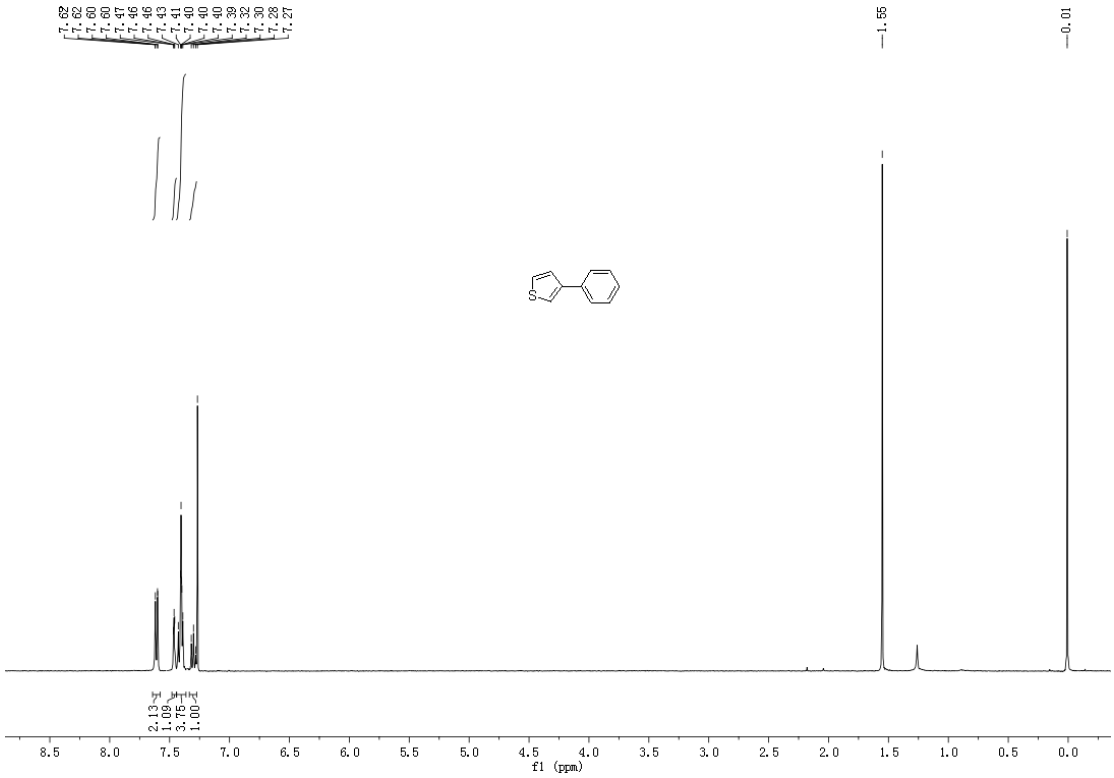


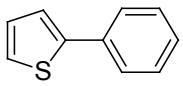


[ref 5]

(3-Phenyl-thiophene, CAS: 2404-87-7, T3-8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (m, 2H), 7.48-7.44 (m, 1H), 7.44-7.36 (m, 4H), 7.30 (m, 1H). MS (EI): m/e (%) 160 (100), 115 (33).

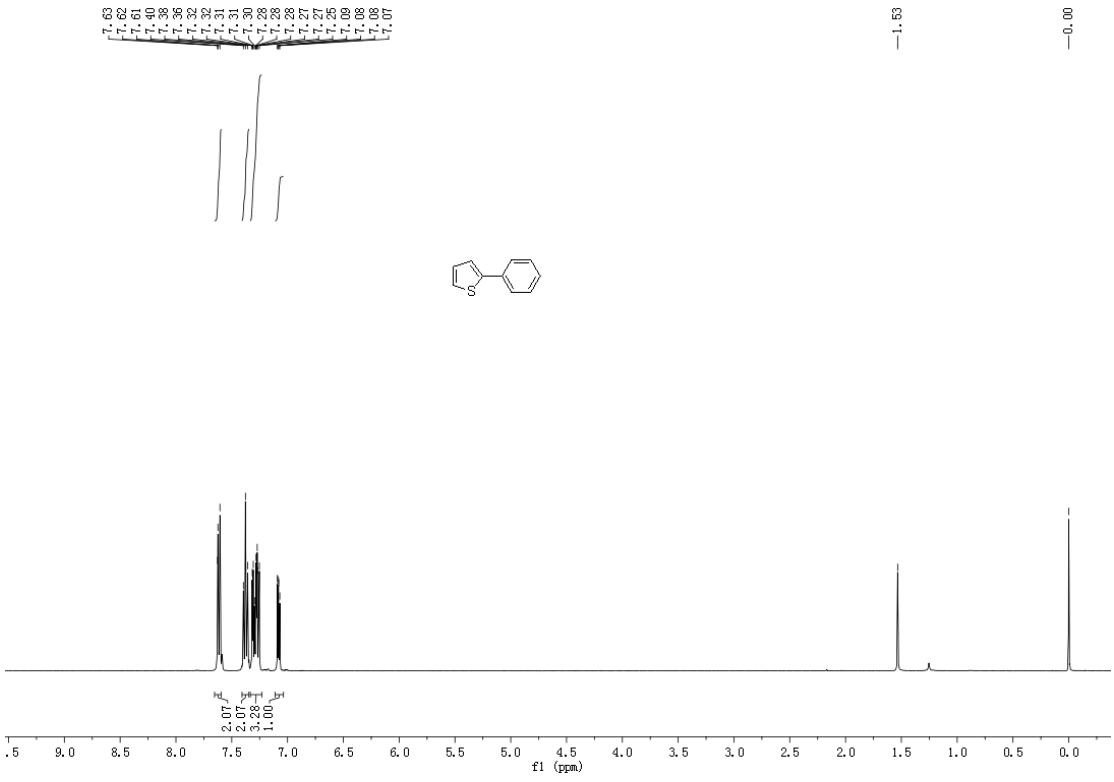


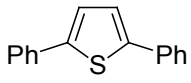


[ref 5]

(2-Phenyl-thiophene, CAS: 825-55-8, T3-9)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.61 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33-7.23 (m, 3H), 7.08 (m, 1H). MS (EI): m/e (%) 160 (100), 128 (14), 115 (42), 63 (6), 39 (6).

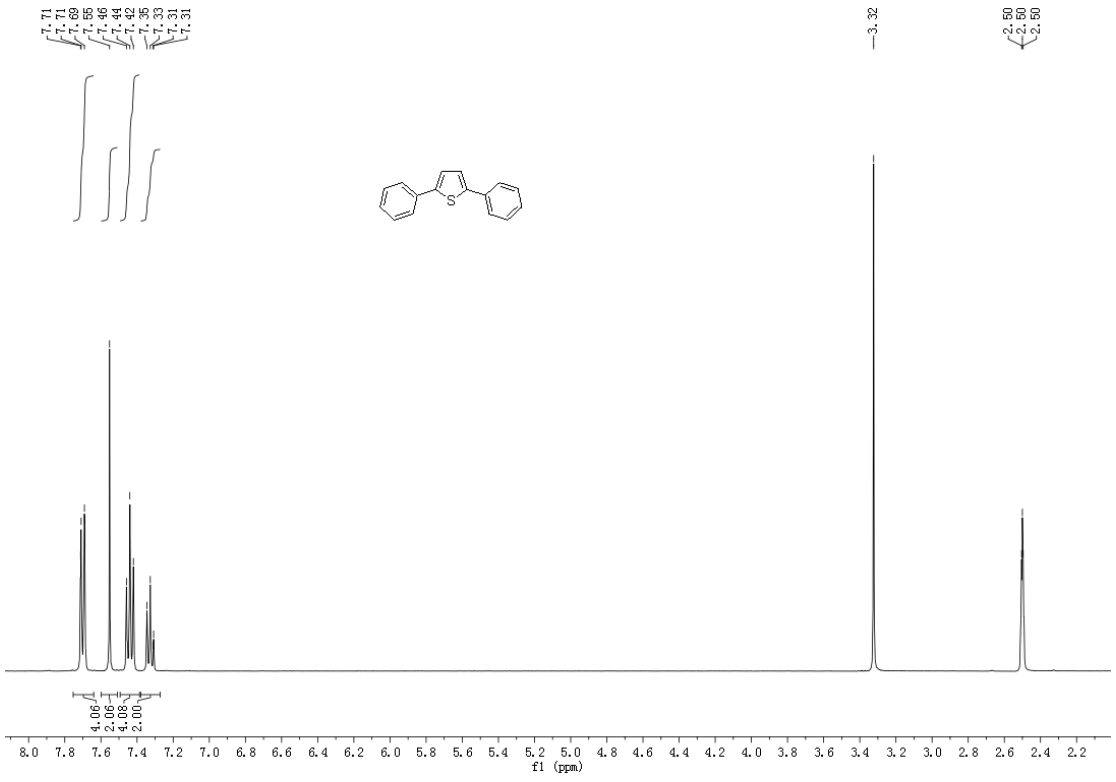




[ref 10]

(2, 5-diphenylthiophene, CAS: 1445-78-9, T3-10)

^{1}H NMR (400 MHz, DMSO) δ 7.75-7.64 (m, 4H), 7.55 (s, 2H), 7.44 (t, *J* = 7.7 Hz, 4H), 7.32 (m, 2H). MS (EI): m/e (%) 236 (100), 202 (8), 121 (22), 77 (9).



References:

[1] E. Vedejs, R. W. Chapman, S. C. Fields, S. Lin and M. R. Schrimpf, *J. Org. Chem.*, 1995, **60**, 3020.

[2] L. Liu, Y. Zhang and B. Xin, *J. Org. Chem.*, 2006, **71**, 3994.

[3] W. -J. Zhou, K. -H. Wang and J.-X. Wang, *J. Org. Chem.*, 2009, **74**, 5599.

[4] L. Liu, Y. Zhang and Y. Wang, *J. Org. Chem.*, 2005, **70**, 6122.

[5] S. Y. Shi and Y. H. Zhang, *Green Chem.*, 2008, **10**, 868.

[6] Q. Luo, J. Tan, Z. Li and D. Xiao, *J. Org. Chem.*, 2012, **77**, 8332.

[7] C. Zhou, J. Wang, L. Li, R. Wang and M. Hong, *Green Chem.*, 2011, **13**, 2100.

[8] D. W. Lee and M. J. Jin, *Org. Lett.*, 2011, **13**, 252.

[9] J. Yang, S. Liu, J. Zheng and J. Zhou, *Eur. J. Org. Chem.*, 2012, **31**, 6248.

[10] K. Funaki, T. Sato and S. Qi, *Org. Lett.*, 2012, **14**, 6186.