Supporting information

Palladium Catalyzed Suzuki Crossing-coupling of Benzyltrimethylammonium Salts via C-N Bond Cleavage

Tao Wang, [a,b] Shuwu Yang,[b] Silin Xu,[b] Chunyu Han,[b] Ge Guo,[b] Junfeng Zhao*,[a,b]

[a]National Research Center for Carbohydrate Synthesis and Key Laboratory of Chemical Biology, Jiangxi Province, Nanchang 330022, Jiangxi, P. R. China

[b]College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, 330022, Jiangxi, P. R. China

E-mail: zhaojf@jxnu.edu.cn

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General Information

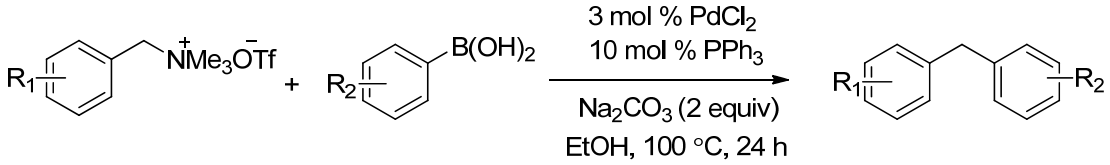
Reactions were performed in a N_2-atmosphere in oven-dried glassware unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. All the reactions were monitored by thin-layer chromatography (TLC); products purification was done using silica gel column chromatography. $^1H/^{13}C$ NMR spectra were recorded on Bruker avance 400 MHz and Bruker AMX 400 MHz spectrometer at 400/100 MHz, respectively, in $CDCl_3$ unless otherwise stated, using either TMS or the undeuterated solvent residual signal as the reference. Chemical shifts are given in ppm and are measured relative to $CDCl_3$ or DMSO-d_6 as an internal standard. Mass spectra were obtained by the electrospray ionization time-of-flight (ESI-TOF) mass spectrometry. GC yields were obtained using naphthalene as an internal standard. Flash column chromatography purification of compounds was carried out by gradient elution using ethyl acetate (EA) in light petroleum ether (PE).

Synthesis of Benzyl Ammonium Salts:

Dimethyl benzyl amines were prepared via reductive amination of the corresponding benzaldehydes. Benzylic ammonium triflates were synthesized according to the procedures reported in the literature.[1] N,N-Dimethylbenzylamine (2.0 mmol, 1.0 equiv) was dissolved in Et_2O (6 mL). MeOTf (2.6 mmol, 1.3 equiv) was added dropwise at 0 °C. White precipitate formed immediately. After complete addition, the reaction mixture was stirred for 2 h at room temperature. The precipitate was isolated by filtration and washed with Et_2O. The resulting solid was dried under vacuum to give the product as a white solid.

Cross-Coupling of Benzyl Ammonium Triflates to Give Diarylmethanes

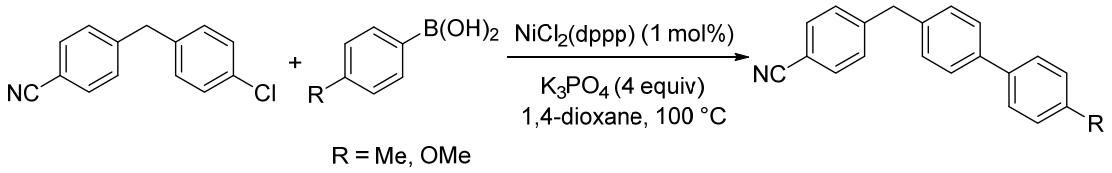
General Procedure:



Ammonium triflate (0.2 mmol, 1equiv), $PdCl_2$ (1.1 mg, 0.006 mmol), PPh_3 (5.3 mg, 0.02 mmol), boronic acid (2 equiv) and Na_2CO_3 (2 equiv) were combined in a sealed tube equipped with a magnetic stirrer bar under a nitrogen atmosphere. Then, EtOH (3 mL) were added to the tube through a syringe. The mixture was stirred for 18-24 h at 100 °C. The reaction mixture was then diluted with Et_2O (1.5 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (10 mL). The filtrate was

concentrated and then purified by silica gel chromatography to give the diarylmethane product.

Applications of Suzuki crossing coupling[2]



To a 25-mL Schlenk tube equipped with a magnetic bar was added $NiCl_2$(dppp) (0.01 mmol, 0.5 mg), aryl halides (0.1 mmol), aryboronic acids (0.2 mmol), and anhydrous K_3PO_4 (0.4 mmol).The tube was then evacuated (3 × 10 min) under vacuum and backfilled with N_2. Dried dioxane (1.0 mL) was injected *via* syringe, and the reaction mixture was stirred at 100−110 °C until the aryl halides had disappeared as monitored by TLC. The reaction mixture was poured into water (5 mL) and then extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to dryness. The crude material was purified by flash chromatography on silica gel using a mixture of hexane and CH_2Cl_2 (or hexane and ethyl acetate) as eluents to give the desired cross-coupled products.

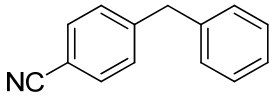
Reference

(1) Maity, P.; Shacklady-McAtee, D. M.; Yap, G. P.; Sirianni, E. R.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 280.

(2) Zhao, Y.-L.; Li, Y.; Li, S.-M.; Zhou, Y.-G.; Sun, F.-Y.; Gao, L.-X.; Han, F.-S. *Adv. Syn. & Cat.* **2011**, *353*, 1543.

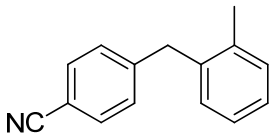
Characterization of products:

4-benzylbenzonitrile(3a)



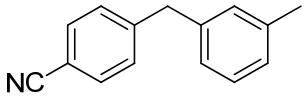
Colorless liquid; yield 98% (37.7 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.10 (m, 5H), 7.07 (d, *J* = 7.0 Hz, 2H), 3.94 (s, 2H).**^{13}C NMR (100 MHz, CDCl3)** δ 146.3, 138.9, 131.8, 129.2, 128.5, 128.3, 126.2, 118.5, 109.6, 41.5. **HRMS (ESI^+)** calculated for $C_{14}H_{11}N$ $[M+H]^+$: 194.0970; found: 194.0969.

4-(2-methylbenzyl)benzonitrile (3b)



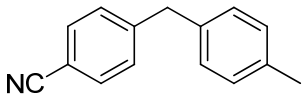
Yellow liquid; yield 98% (40.6 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.15 (m, 5H), 7.10 – 7.06 (m, 1H), 4.03 (s, 2H), 2.19 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.2, 137.2, 136.6, 132.3, 130.6, 130.1, 129.4, 127.1, 126.3, 119.1, 109.9, 39.6, 19.7.**HRMS (ESI^+)** calculated for $C_{15}H_{13}N$ $[M+H]^+$: 208.1126; found: 208.1122.

4-(3-methylbenzyl)benzonitrile (3c)



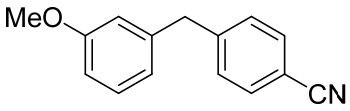
Yellow liquid; yield 99% (41.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 2H), 3.97 (s, 2H), 2.31 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.9, 139.3, 138.5, 132.3, 129.8, 129.7, 128.7, 127.5, 126.0, 119.1, 110.0, 42.0, 21.4. **HRMS (ESI^+)** calculated for $C_{15}H_{13}N$ $[M+H]^+$: 208.1126; found: 208.1122.

4-(4-methylbenzyl)benzonitrile (3d)



Yellow liquid; yield 99% (41.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 3.89 (s, 2H), 2.23 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.1, 136.3, 136.3, 132.3, 129.6, 129.5, 128.9, 119.1, 110.0, 41.6,21.1. **HRMS (ESI^+)** calculated for $C_{15}H_{13}N$ $[M+H]^+$: 208.1126; found: 208.1121.

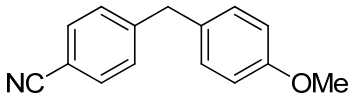
4-(3-methoxybenzyl)benzonitrile (3e)



Yellow liquid; yield 99% (44.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.82 – 6.71 (m, 2H), 6.69 (s, 1H), 3.99 (s, 2H), 3.76 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.9, 146.6, 140.9, 132.3, 129.8, 129.7, 121.4, 119.0, 115.0,

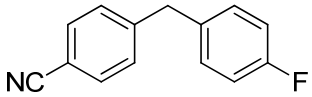
111.8, 110.1, 55.2, 42.0. **HRMS (ESI$^+$)** calculated for $C_{15}H_{13}NO$ $[M+Na]^+$: 246.0895; found: 246.0891.

4-(4-methoxybenzyl)benzonitrile（3f）



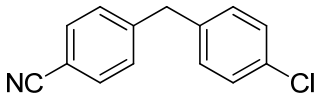
Yellow liquid; yield 98% (43.7 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 8.1 Hz, 2H), 3.88 (s, 2H), 3.70 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.4, 147.3, 132.3, 131.4, 123.0, 129.5, 119.1, 114.2, 109.9, 55.3, 41.1.**HRMS (ESI$^+$)** calculated for $C_{15}H_{13}NO$ $[M+H]^+$: 224.1075; found: 224.1078.

4-(4-fluorobenzyl)benzonitrile (3g)



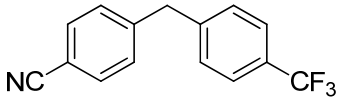
Light yellow liquid; yield 95% (40.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.15 – 7.07 (m, 2H), 6.99 (t, *J* = 8.3 Hz, 2H), 4.00 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.7 (d, $J_{C\text{-}F}$=244.5Hz), 146.5, 135.0 (d, $J_{C\text{-}F}$=3.3Hz), 132.4, 130.4(d, $J_{C\text{-}F}$=7.9Hz), 129.6, 118.9, 115.6(d, $J_{C\text{-}F}$=21.4Hz), 110.2, 41.1.**HRMS (ESI$^+$)** calculated for $C_{14}H_{10}FN$ $[M+H]^+$: 212.0876; found: 212.0880.

4-(4-chlorobenzyl)benzonitrile (3h)



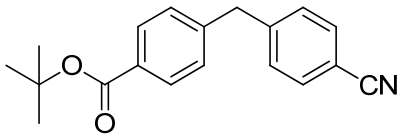
White solid;yield 89% (40.4 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.22-7.29 (m, 4H), 7.08 (d, *J* = 7.4 Hz, 2H), 4.00 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.1, 137.8, 132.6, 132.4, 130.3, 129.6, 128.9, 118.9, 110.3, 41.3. **HRMS (ESI$^+$)** calculated for $C_{14}H_{10}ClN$ $[M+H]^+$: 228.0580; found: 228.0575.

4-(4-(trifluoromethyl)benzyl)benzonitrile (3i)



Yellow solid;yield 83% (43.3 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (t, *J* = 8.3 Hz, 4H), 7.28 (d, *J* = 7.9 Hz, 4H), 4.09 (s, 2H). **^{13}C NMR (100 MHz,$CDCl_3$)** δ 145.5,143.4,132.5,129.7,129.3,128.9,125.7(q, $J_{C\text{-}F}$=3.78 Hz), 124.1(q, $J_{C\text{-}F}$ =272.4 Hz), 118.8, 110.5, 41.7.**HRMS (ESI$^+$)** calculated for $C_{15}H_{10}F_3N$ $[M+H]^+$: 262.0844; found: 262.0846.

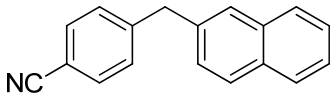
tert-butyl 4-(4-cyanobenzyl)benzoate (3j)



White solid; yield 91% (53.3 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.06 (s, 2H), 1.57 (s, 9H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.5, 146.0, 144.0, 132.4, 130.6,

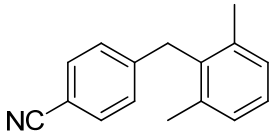
130.0, 129.7, 128.9, 118.9, 110.3, 81.0, 41.9, 28.2. **HRMS (ESI$^+$)** calculated for $C_{19}H_{19}NO_2$ $[M+Na]^+$: 316.1313; found: 316.1317.

4-(naphthalen-2-ylmethyl)benzonitrile (3k)



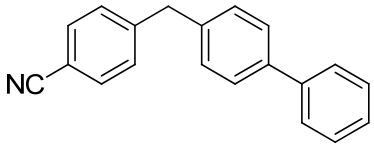
White solid; yield 86% (41.8 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 – 7.74 (m, 3H), 7.60 (s, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.50 – 7.40 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 6.9 Hz, 1H), 4.18 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.6, 136.8, 133.6, 132.4, 132.3, 129.8, 128.5, 127.7, 127.6, 127.4, 127.3, 126.3, 125.8, 119.0, 110.2, 42.1. **HRMS (ESI$^+$)** calculated for $C_{18}H_{13}N$ $[M+Na]^+$ 266.0946; found: 266.0944.

4-(2,6-dimethylbenzyl)benzonitrile (3aa)



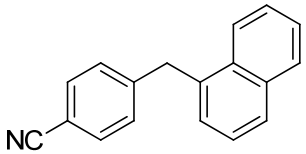
Yellow liquid;yield 57% (25.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.15 – 7.04 (m, 5H), 4.10 (s, 2H), 2.20 (s, 6H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.8, 137.0, 135.2, 132.3, 128.6, 128.4, 126.9, 119.0, 109.8, 35.2, 20.2. **HRMS (ESI$^+$)** calculated for $C_{16}H_{15}N$ $[M+H]^+$: 222.1283; found: 222.1280.

4-([1,1'-biphenyl]-4-ylmethyl)benzonitrile (3ab)



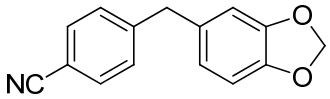
White solid; yield 92% (49.4 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 7.50 (m, 6H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.32 (dd, *J* = 12.1, 7.7 Hz, 3H), 7.22 (d, *J* = 7.7 Hz, 2H), 4.06 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.7, 140.7, 139.7, 138.4, 132.4, 129.7, 129.4, 128.8, 127.5, 127.3, 127.0, 119.0, 110.2, 41.6. **HRMS (ESI$^+$)** calculated for $C_{20}H_{15}N$ $[M+H]^+$: 270.1283; found: 270.1277.

4-(naphthalen-1-ylmethyl)benzonitrile (3ac)



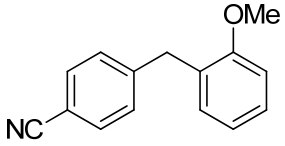
White solid; yield 95% (48.6 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (ddd, *J* = 14.5, 11.2, 5.1 Hz, 3H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.26 (dd, *J* = 13.5, 7.6 Hz, 3H), 4.46 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.4, 134.9, 134.1, 132.3, 131.9, 129.4, 128.9, 127.9, 127.7, 126.4, 125.9, 125.6, 123.9, 119.0, 110.1, 39.2. **HRMS (ESI$^+$)** calculated for $C_{18}H_{13}N$ $[M+H]^+$: 244.1126; found: 244.1122.

4-((benzo[d][1,3]dioxol-5-yl)methyl)benzonitrile (3ad)



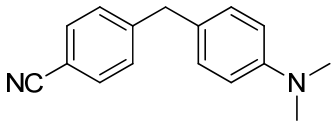
White solid; yield 93% (44.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.62 (d, *J* = 10.6 Hz, 2H), 5.92 (s, 2H), 3.93 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.0, 146.9, 146.4, 133.1, 132.3, 129.5, 122.0, 119.0, 110.1, 109.4, 108.4, 101.1, 41.7. **HRMS (ESI^+)** calculated for $C_{15}H_{11}NO_2$ $[M+H]^+$: 238.0868; found: 238.0871.

4-(2-methoxybenzyl)benzonitrile (3ae)



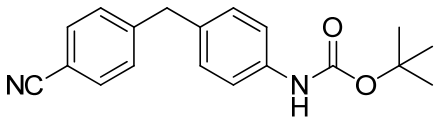
White solid; yield 95% (42.5 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 7.0 Hz, 1H), 6.89 (dd, *J* = 15.4, 7.8 Hz, 2H), 4.00 (s, 2H), 3.78 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.3, 145.0, 132.1, 130.5, 129.6, 128.2, 127.9, 120.7, 119.3, 110.6, 109.6, 55.3, 36.4. **HRMS (ESI^+)** calculated for $C_{15}H_{13}NO$ $[M+H]^+$: 224.1075; found: 224.1077.

4-(4-(dimethylamino)benzyl)benzonitrile (3af)



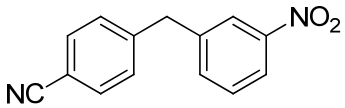
White solid; yield 78% (36.8 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 2H), 2.91 (s, 6H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.4, 147.9, 132.2, 129.7, 129.5, 127.2, 119.2, 112.9, 109.7, 41.1, 40.7. **HRMS (ESI^+)** calculated for $C_{16}H_{16}N_2$ $[M+H]^+$: 237.1392; found: 237.1386.

tert-butyl (4-(4-cyanobenzyl)phenyl)carbamate (3ag)



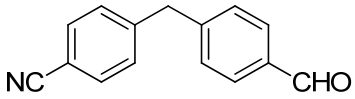
White solid; yield 76% (46.8 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.56 (s, 1H), 3.96 (s, 2H), 1.51 (s, 9H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.8, 147.0, 137.0, 133.9, 132.3, 129.6, 129.5, 119.1, 119.0, 109.9, 80.6, 41.3, 28.4. **HRMS (ESI^+)** calculated for $C_{19}H_{20}N_2O_2$ $[M+H]^+$: 309.1603; found: 309.1598.

4-(3-nitrobenzyl)benzonitrile (3ah)



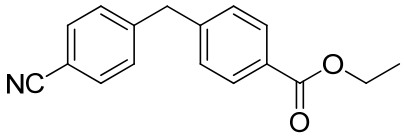
White solid; yield 53% (25.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 – 8.07 (m, 1H), 8.05 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 4.3, 1.2 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.15 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.6, 144.8, 141.4, 135.1, 132.7, 129.8, 129.7, 123.8, 121.9, 118.7, 110.8, 41.4. **HRMS (ESI^+)** calculated for $C_{14}H_{10}N_2O_2$ $[M+H]^+$: 239.0821; found: 239.0827.

4-(4-formylbenzyl)benzonitrile (3ai)



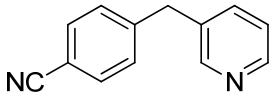
Yellow solid; yield 89% (37.7 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.99 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 4.12 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 191.8, 146.4, 145.3, 135.1, 132.5, 130.2, 129.7, 129.6, 118.8, 110.6, 42.0. **HRMS (ESI^+)** calculated for $C_{15}H_{11}NO$ $[M+H]^+$: 222.0919; found: 222.0920.

ethyl 4-(4-cyanobenzyl)benzoate (3aj)



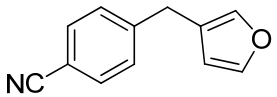
White solid; yield 91% (48.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.08 (s, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.3, 145.8, 144.5, 132.4, 130.1, 129.7, 129.0, 129.0, 118.9, 110.4, 61.0, 41.9, 14.4. **HRMS (ESI^+)** calculated for $C_{17}H_{15}NO_2$ $[M+H]^+$: 266.1181; found: 266.1176.

4-(pyridin-3-ylmethyl)benzonitrile (3ak)



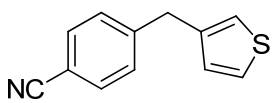
Yellow liquid; yield 89% (34.4 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.50 (s, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.20 (m, 3H), 4.05 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.1, 148.2, 145.3, 136.4, 134.9, 132.5, 129.6, 123.7, 118.7, 110.6, 39.1. **HRMS (ESI^+)** calculated for $C_{13}H_{10}N_2$ $[M+H]^+$: 195.0922; found: 195.0919.

4-(furan-3-ylmethyl)benzonitrile (3al)



Yellow liquid; yield 60% (22 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.38 (t, *J* = 1.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.22 (m, 1H), 6.21 (d, *J* = 0.8 Hz, 1H), 3.83 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.0, 143.5, 139.9, 132.3, 129.4, 122.6, 119.0, 111.0, 110.2, 31.3. **HRMS (ESI^+)** calculated for $C_{12}H_9NO$ $[M+H]^+$: 184.0762; found: 184.0768.

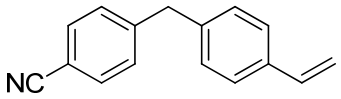
4-(thiophen-3-ylmethyl)benzonitrile (3am)



Yellow liquid; yield 83% (33 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.28 (dd, *J* = 7.8, 4.6 Hz, 3H), 6.94 (d, *J* = 1.7 Hz, 1H), 6.87 (dd, *J* = 4.9, 1.1 Hz, 1H), 4.03 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.2, 139.5, 132.4, 129.5, 128.2,

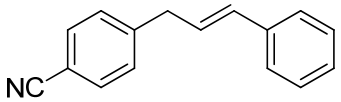
126.3, 122.0, 119.0, 112.0, 36.6. **HRMS (ESI$^+$)** calculated for $C_{13}H_{10}N_2$ $[M+H]^+$: 200.0534; found: 200.0531.

4-(4-vinylbenzyl)benzonitrile (3an)



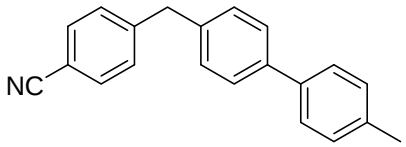
Yellow solid; yield 92% (40.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 4.00 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.7, 139.0, 136.4, 136.1, 132.3, 129.6, 129.2, 126.6, 119.0, 113.8, 110.1, 41.7.**HRMS (ESI$^+$)** calculated for $C_{16}H_{13}N$ $[M+H]^+$: 220.1126; found: 220.1121.

4-cinnamylbenzonitrile (3ao)



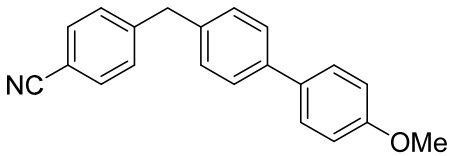
Yellow solid; yield 95% (41.6 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.33 (ddd, *J* = 9.7, 5.4, 0.9 Hz, 5H), 7.26 – 7.20 (m, 2H), 6.47 (d, *J* = 14.9 Hz, 1H), 6.29 (dt, *J* = 15.7, 6.9 Hz, 1H), 3.59 (d, *J* = 7.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.9, 137.0, 132.5, 132.4, 129.5, 128.6, 127.6, 127.2, 126.2, 119.1, 110.2, 39.3.

4-((4'-methyl-[1,1'-biphenyl]-4-yl)methyl)benzonitrile (3ap)



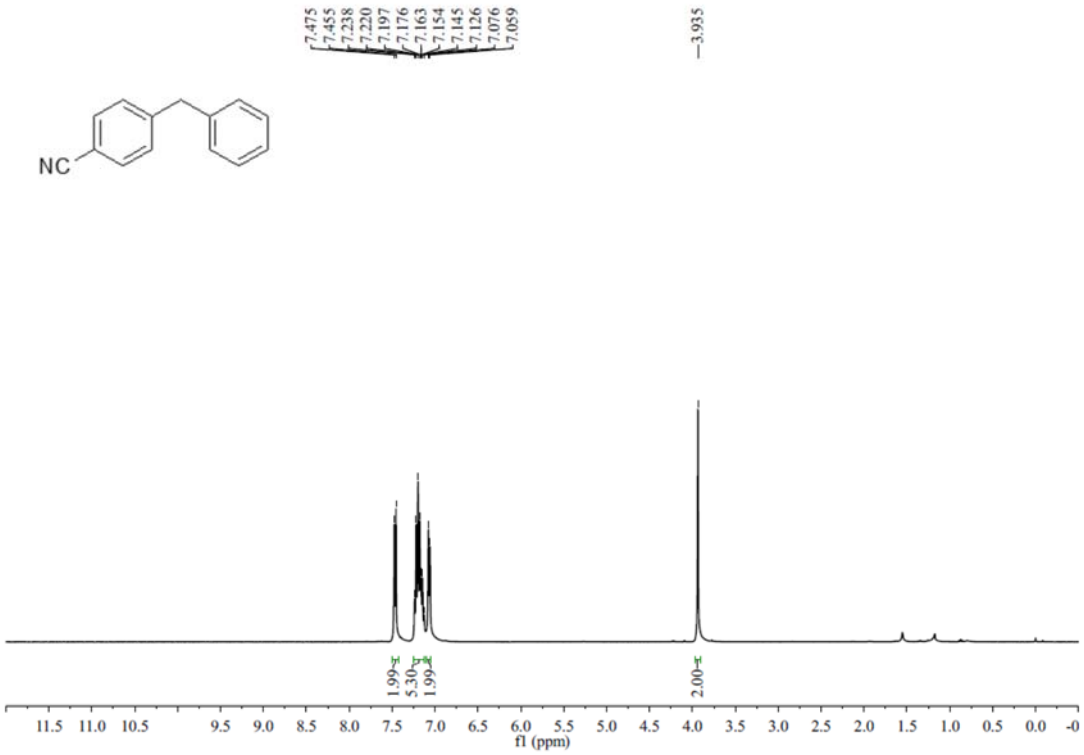
White solid; yield 83% (23.5 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 4.05 (s, 2H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 146.7, 139.6, 138.1, 137.8, 137.1, 132.4, 129.7, 129.5, 129.3, 127.3, 126.9, 119.0, 110.1, 41.6, 21.1.

4-((4'-methoxy-[1,1'-biphenyl]-4-yl)methyl)benzonitrile (3aq)

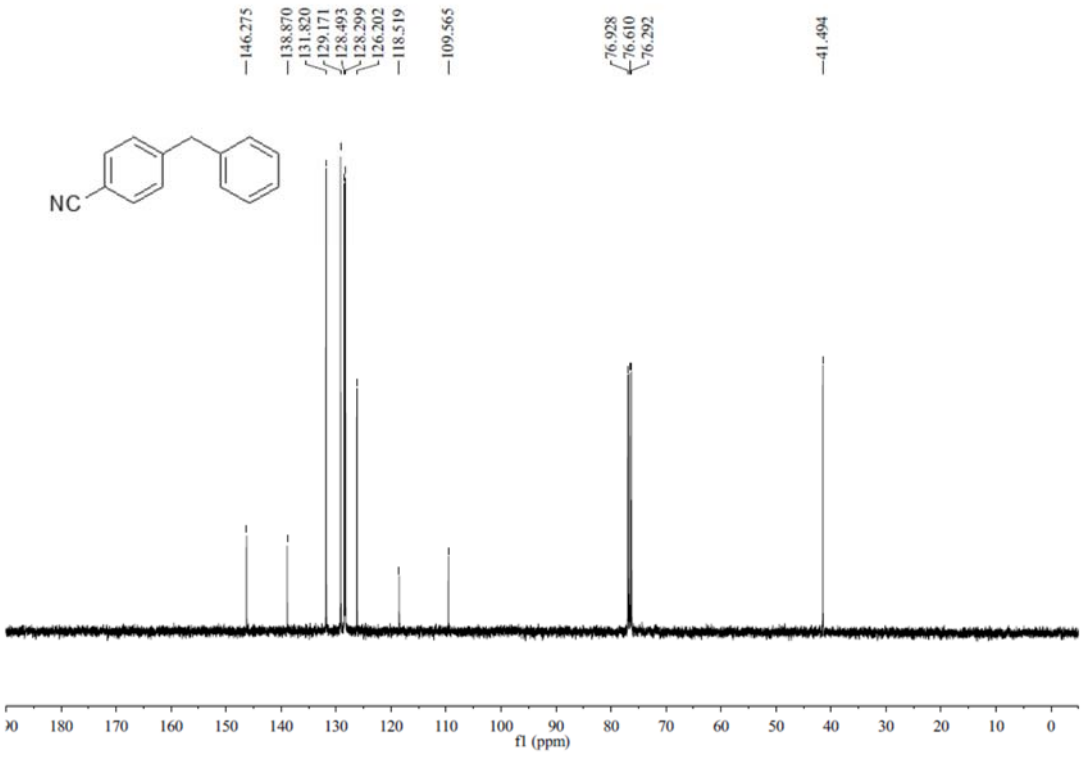


White solid; yield 56% (16.8 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.47 (m, 4H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 4.05 (s, 2H), 3.84 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.2, 146.8, 139.3, 137.8, 133.2, 132.4, 129.7, 129.4, 128.0, 127.1, 119.0, 114.3, 110.1, 55.4, 41.6.

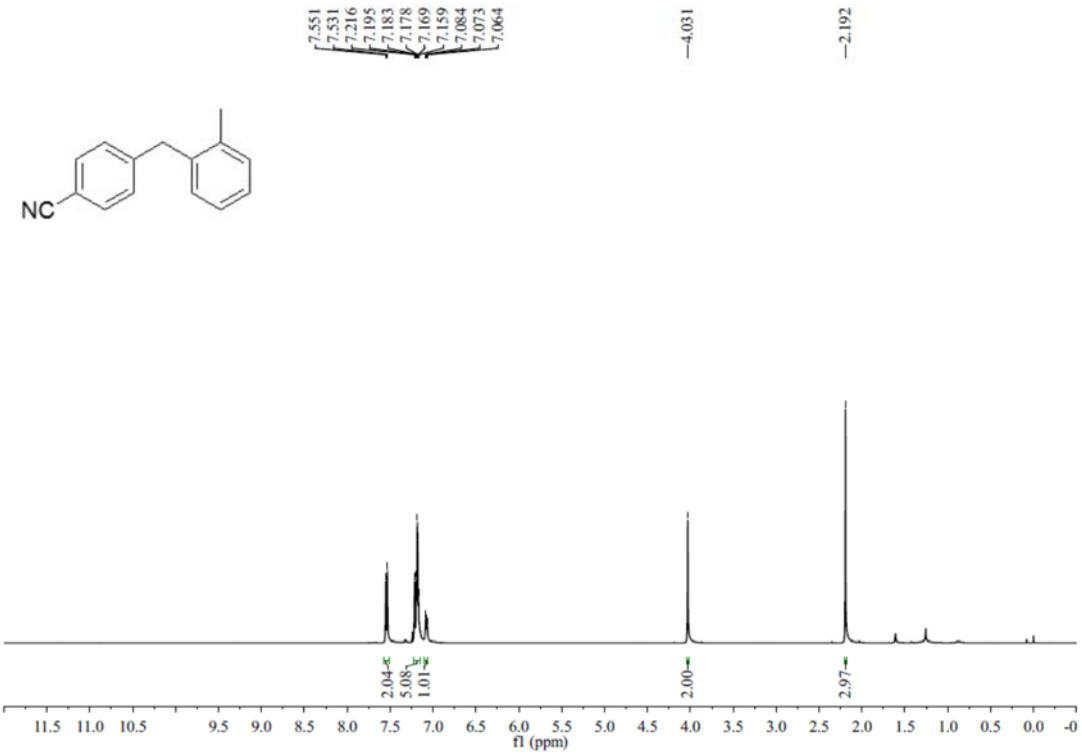
NMR Spectra



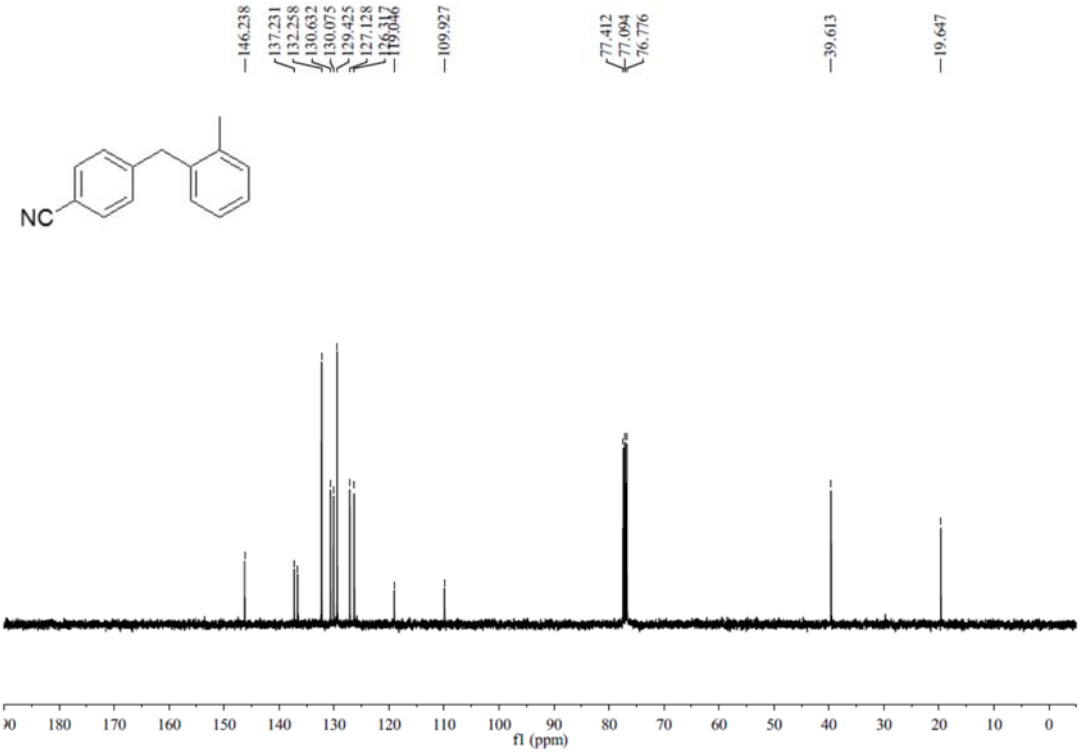
^{1}H NMR Spectrum of Compound 3a



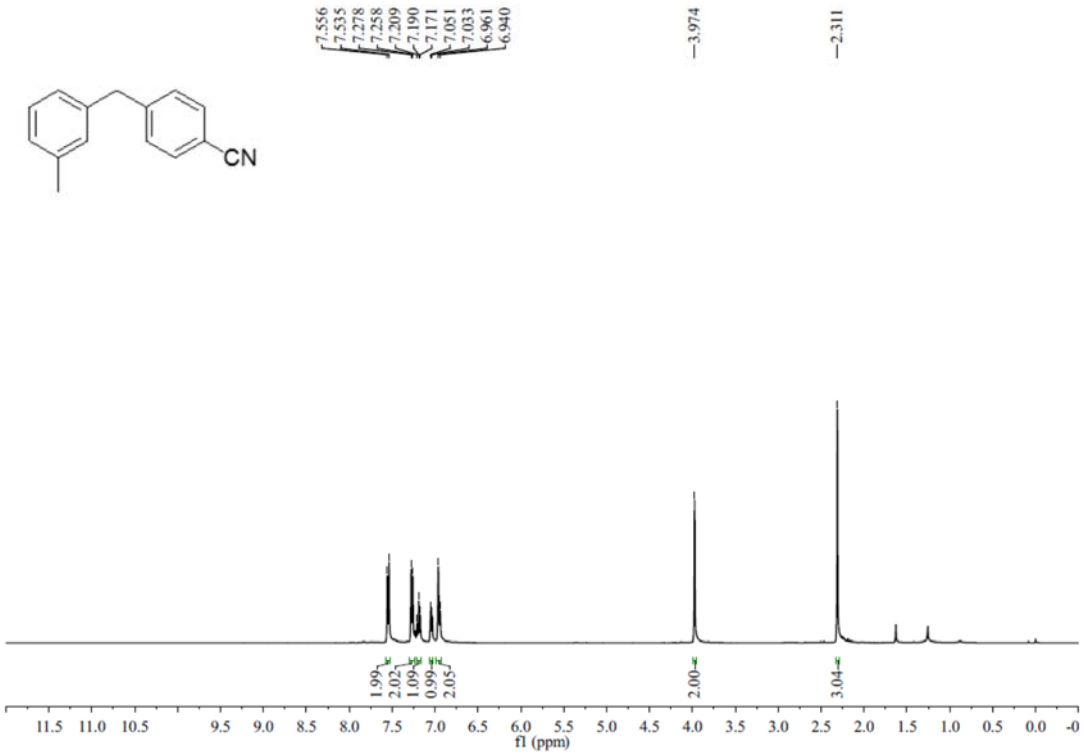
^{13}C NMR Spectrum of Compound 3a



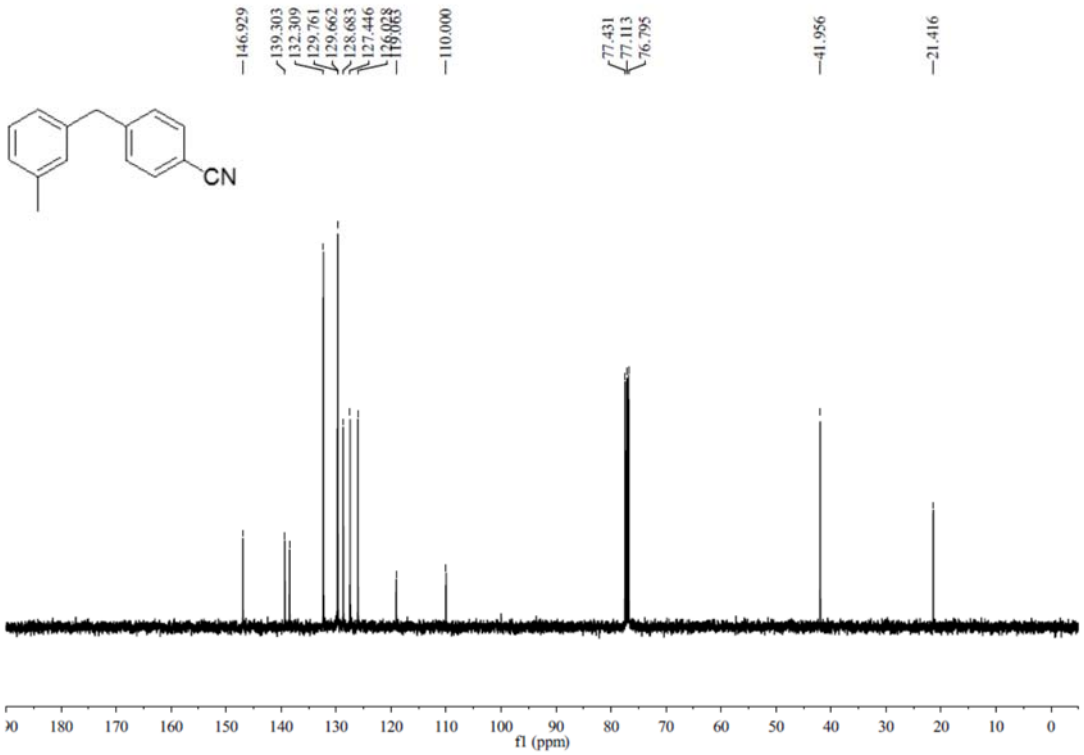
^{1}H NMR Spectrum of Compound 3b



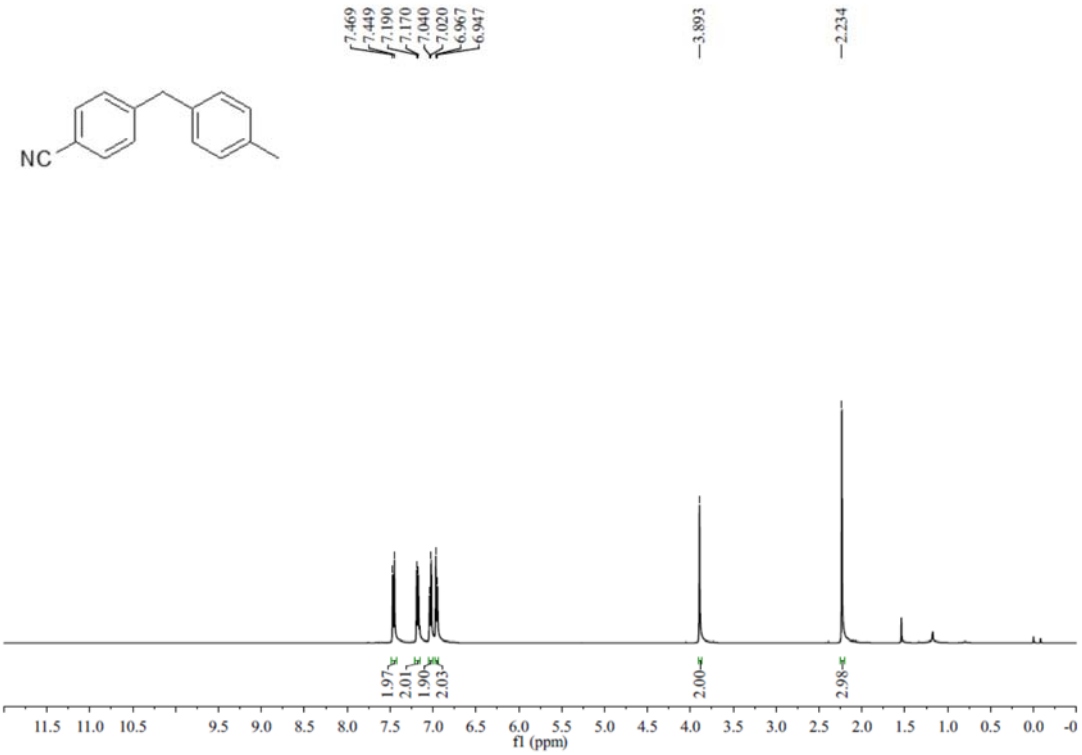
^{13}C NMR Spectrum of Compound 3b



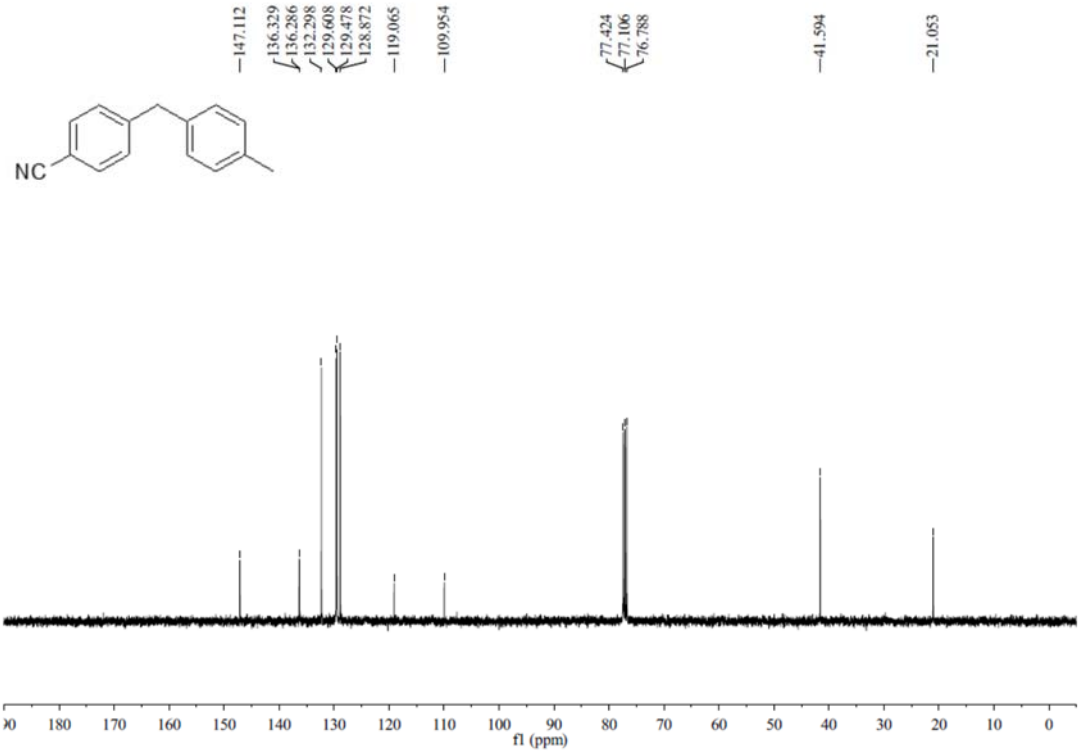
[1]H NMR Spectrum of Compound 3c



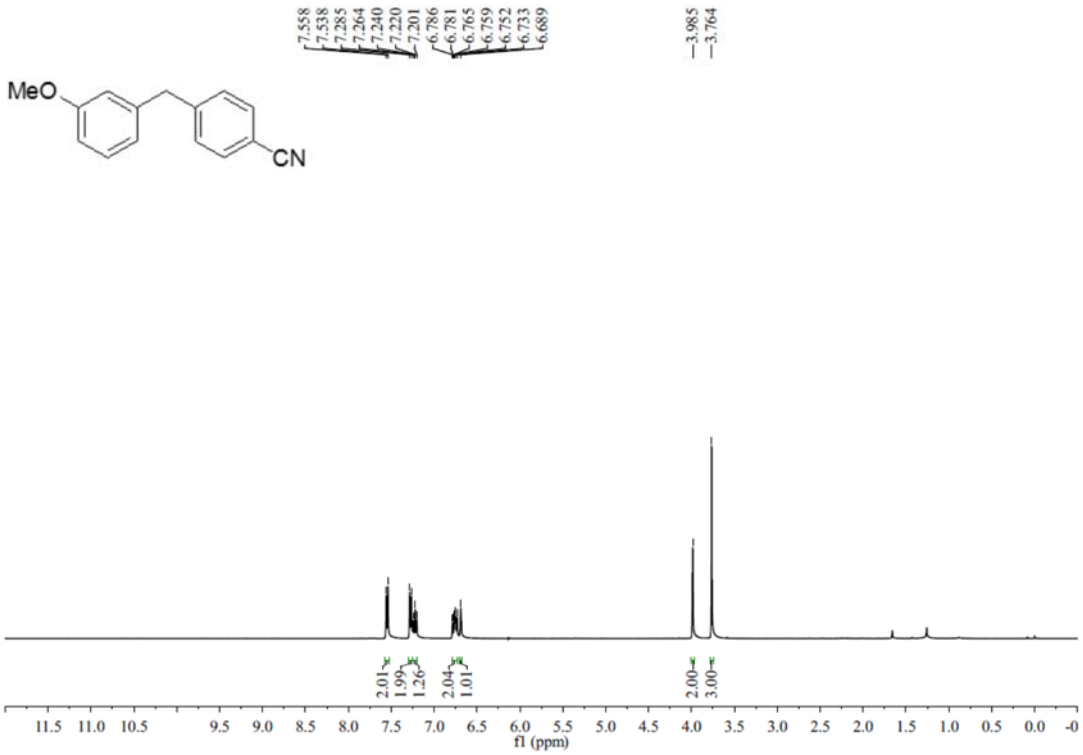
[13]C NMR Spectrum of Compound 3c



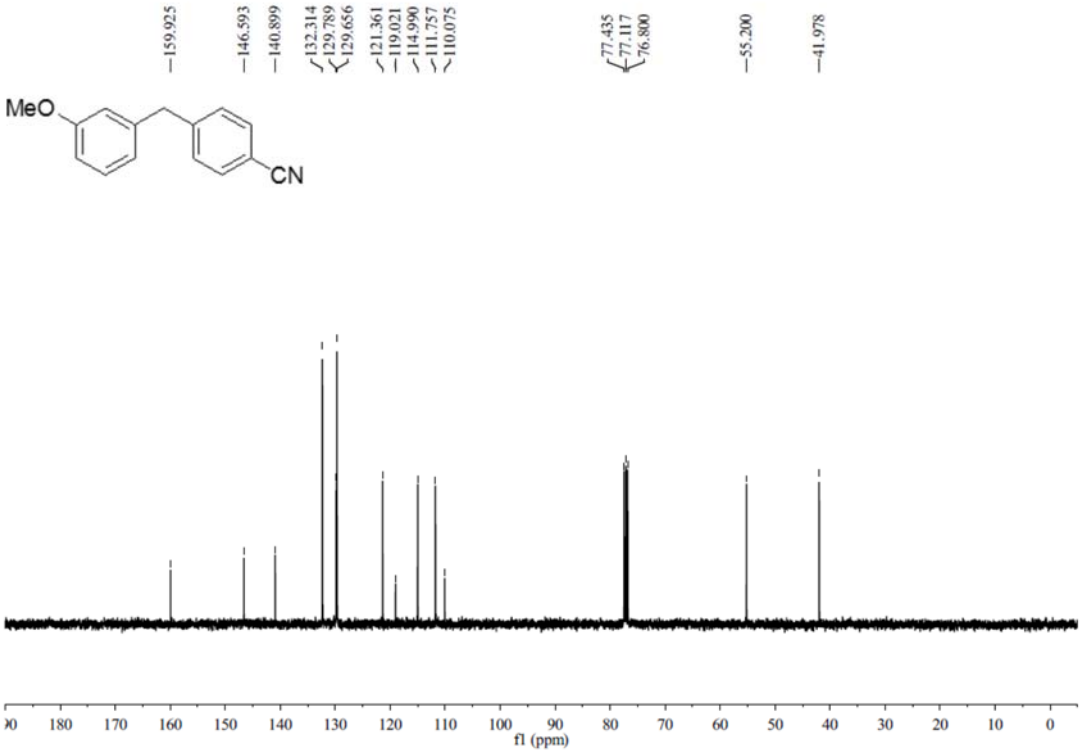
[1]H NMR Spectrum of Compound 3d



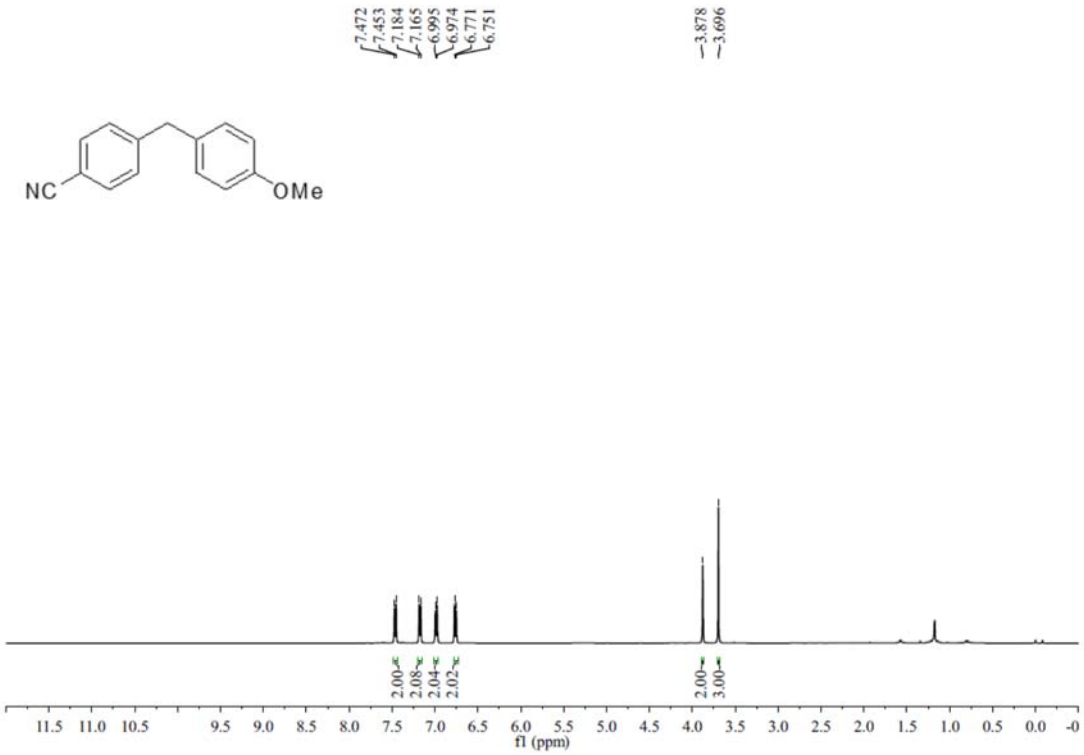
[13]C NMR Spectrum of Compound 3d



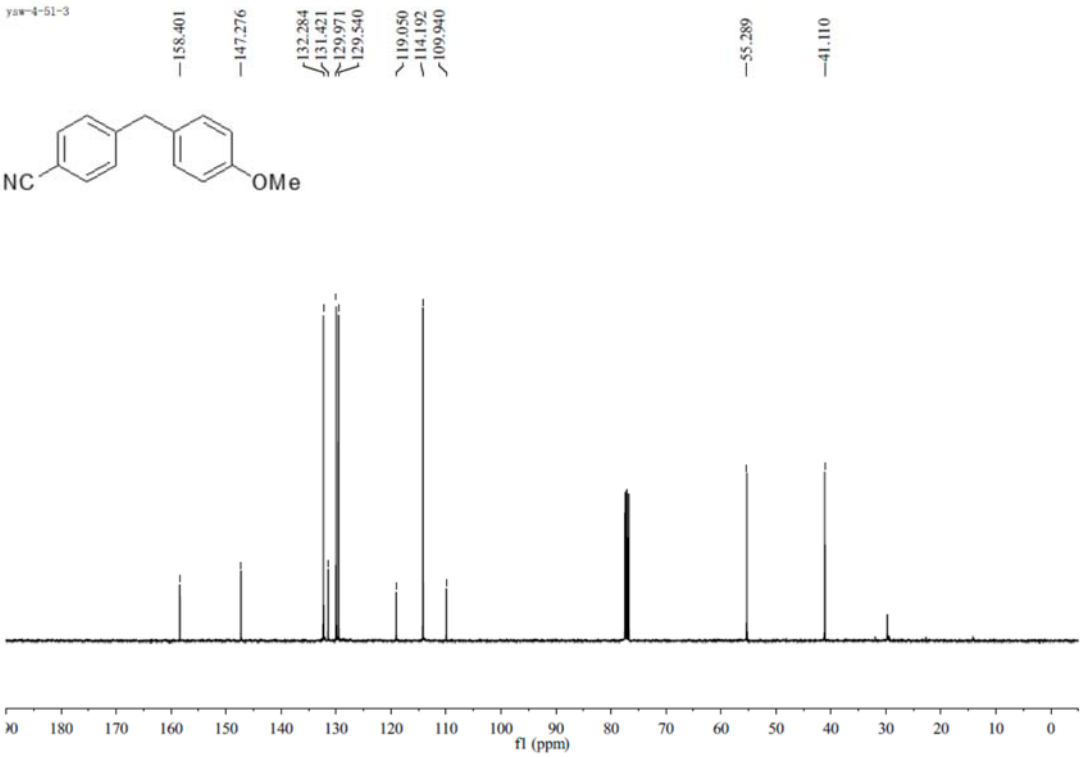
^{1}H NMR Spectrum of Compound 3e



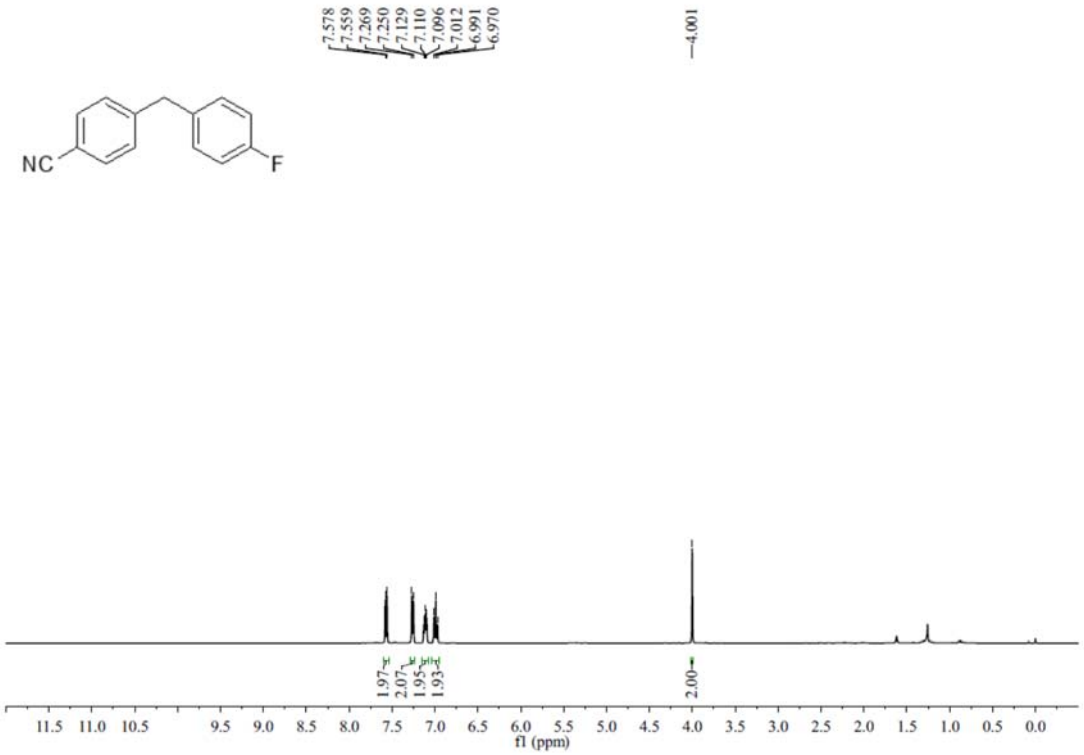
^{13}C NMR Spectrum of Compound 3e



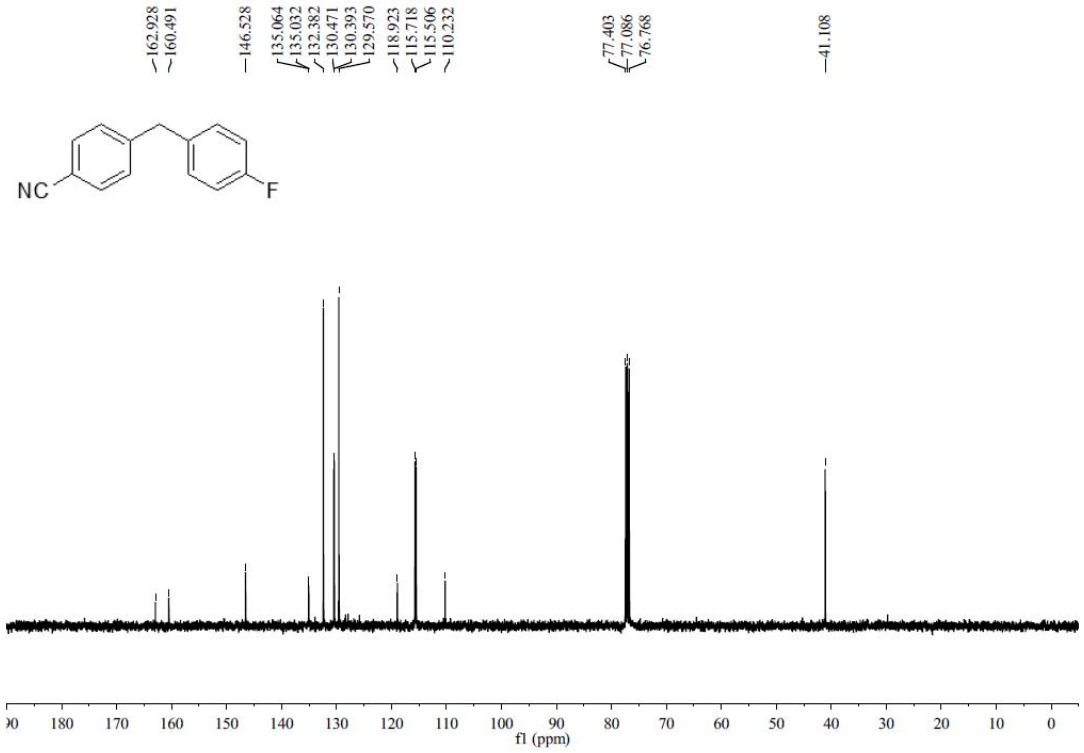
[1]H NMR Spectrum of Compound 3f



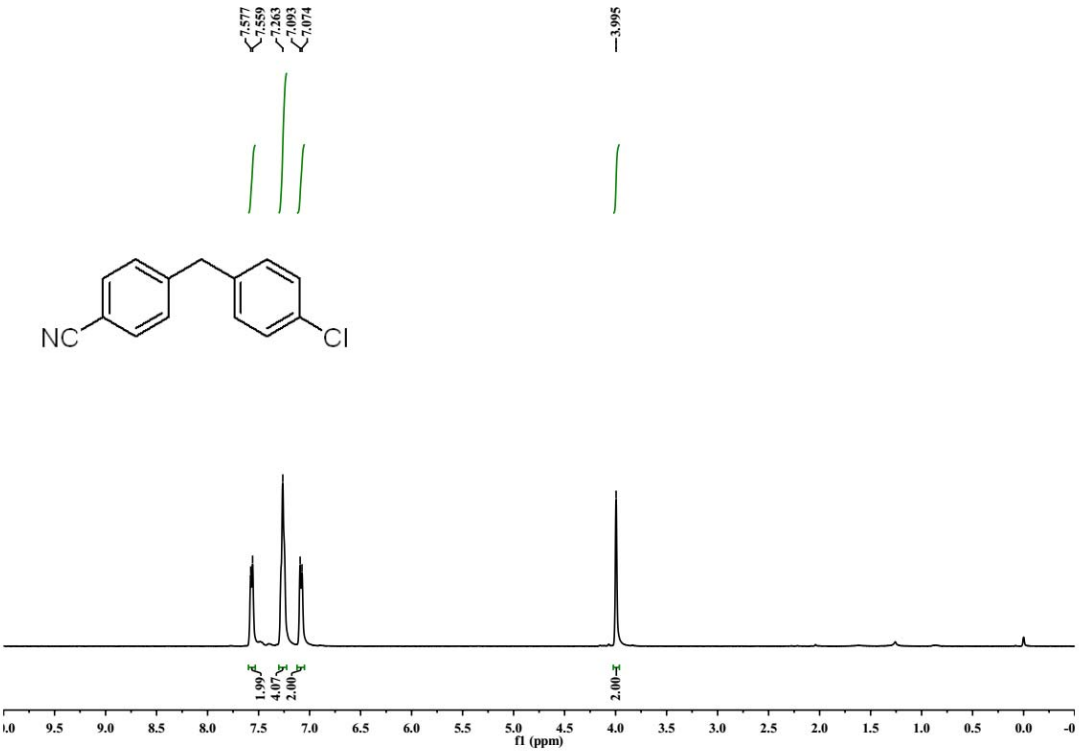
[13]C NMR Spectrum of Compound 3f



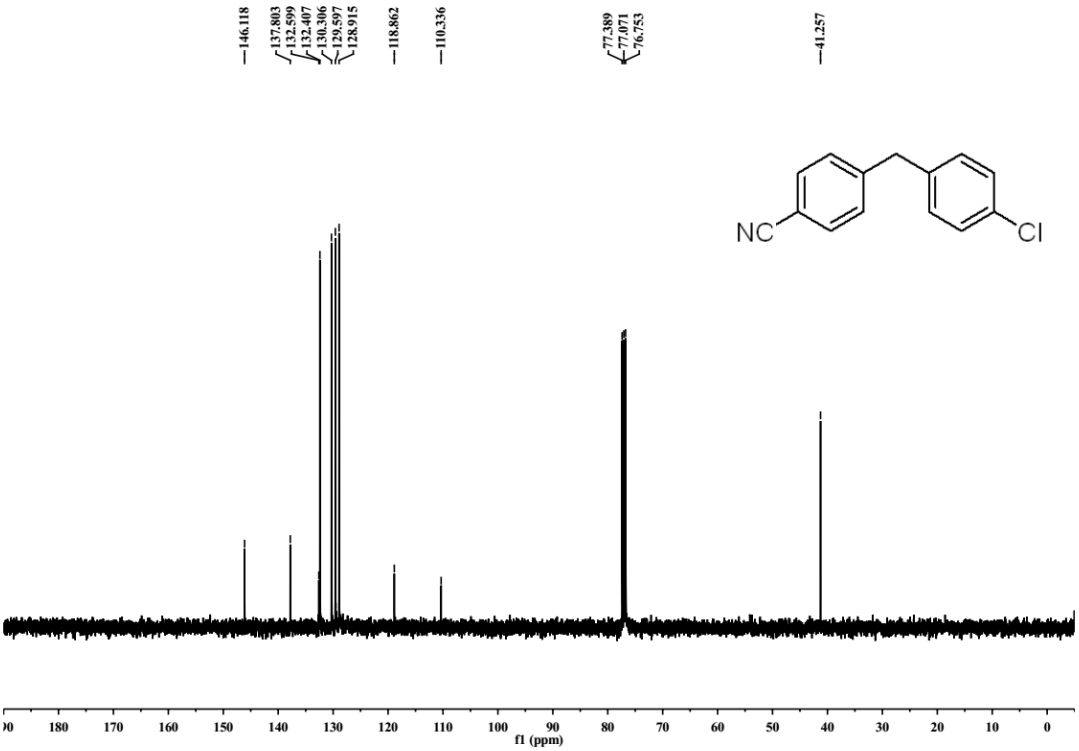
^{1}H NMR Spectrum of Compound 3g



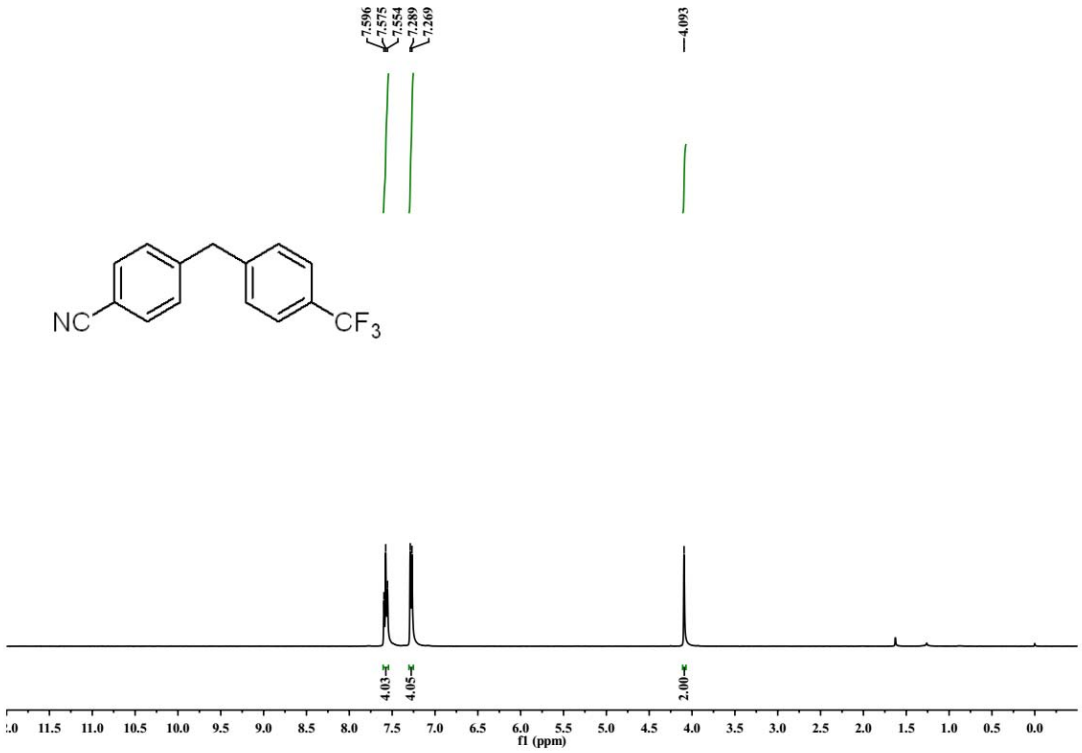
^{13}C NMR Spectrum of Compound 3g



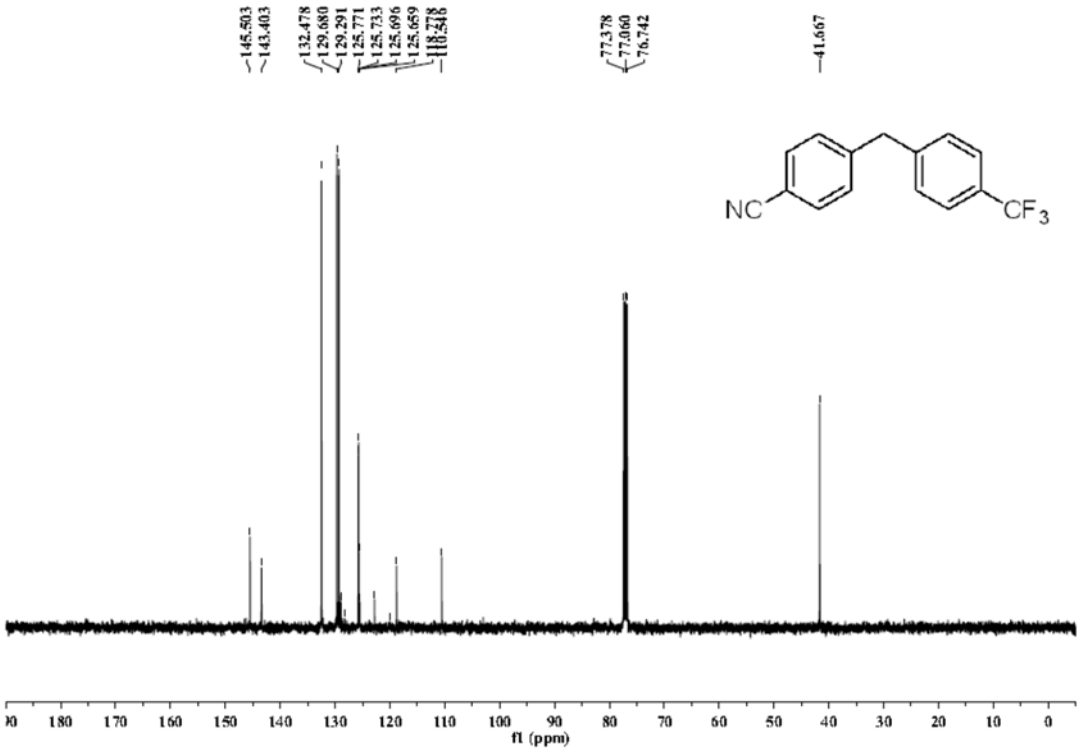
^{1}H NMR Spectrum of Compound 3h



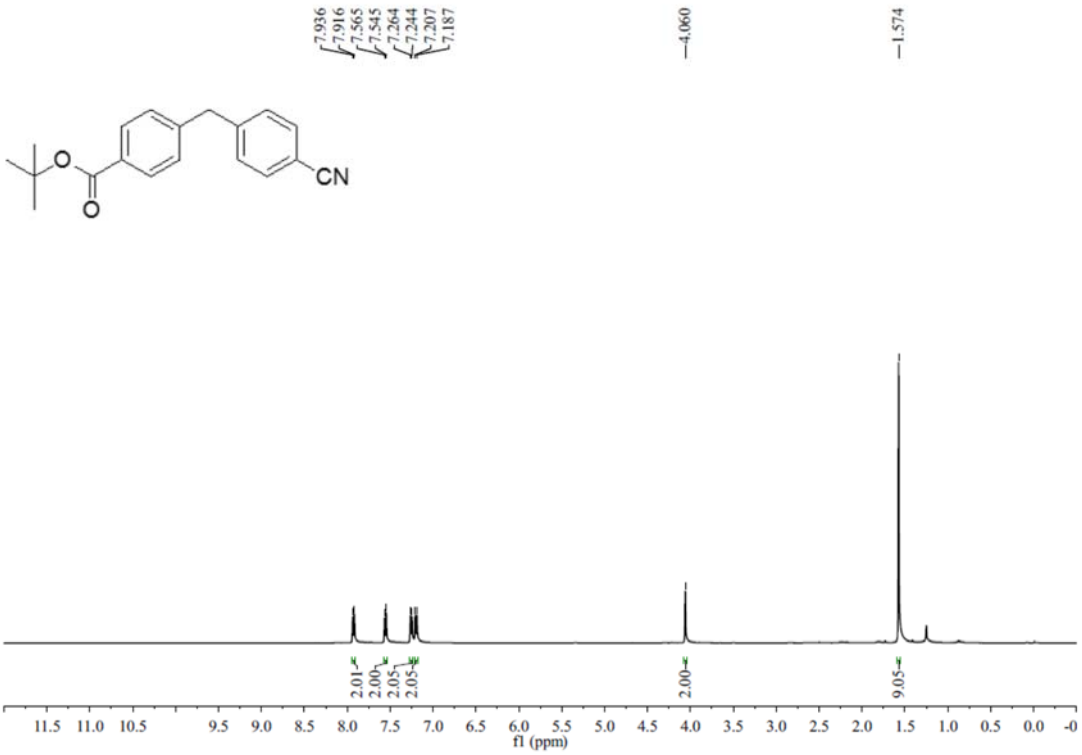
^{13}C NMR Spectrum of Compound 3h



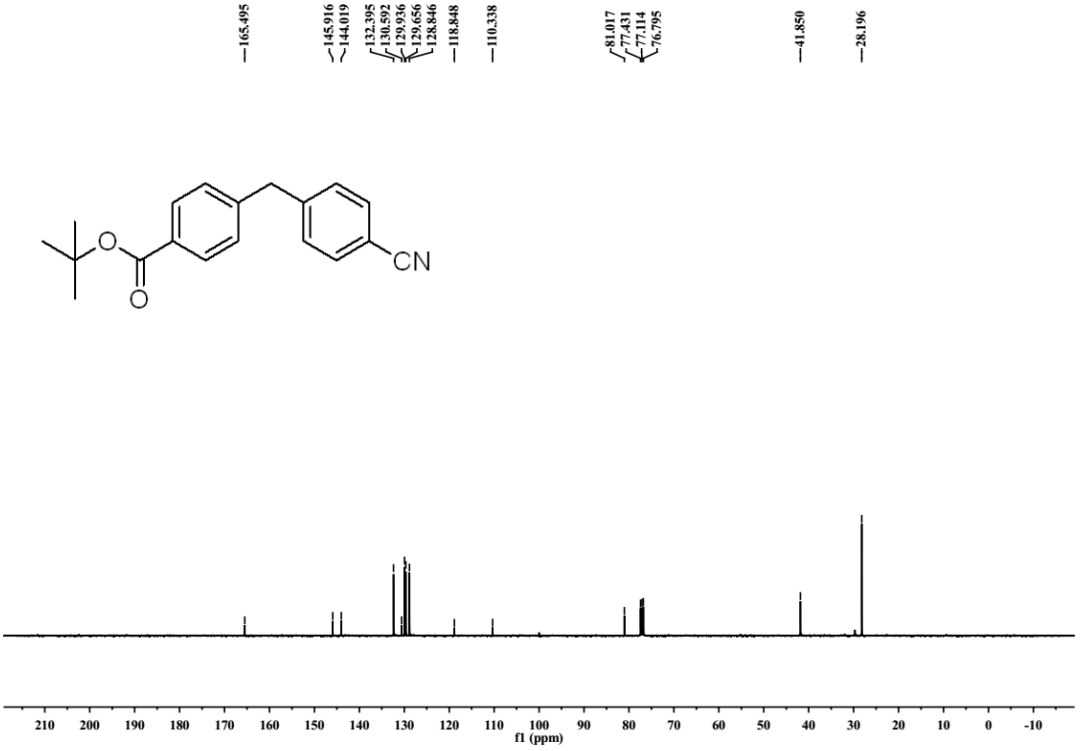
^{1}H NMR Spectrum of Compound 3i



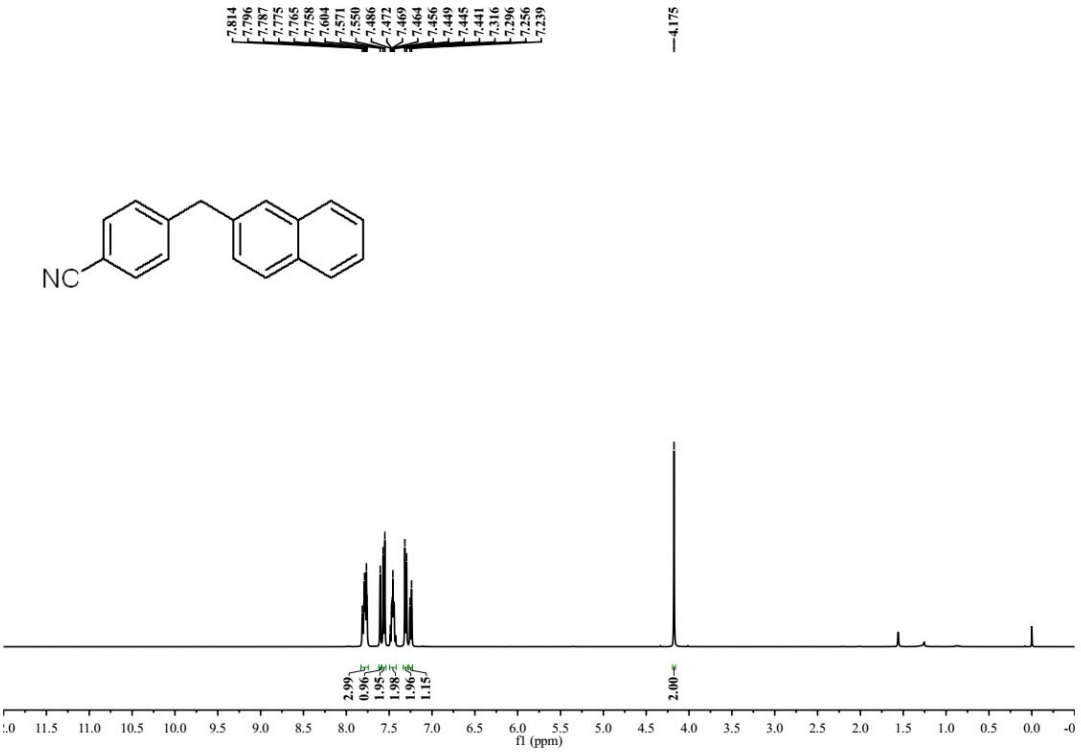
^{13}C NMR Spectrum of Compound 3i



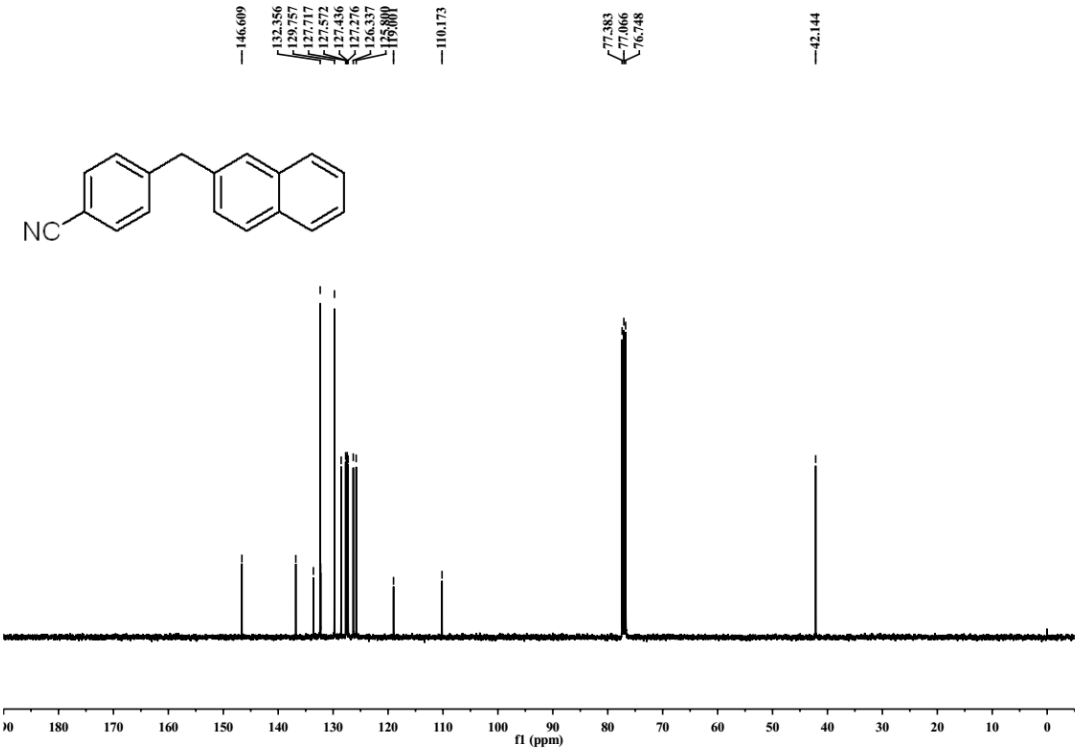
^{1}H NMR Spectrum of Compound 3j



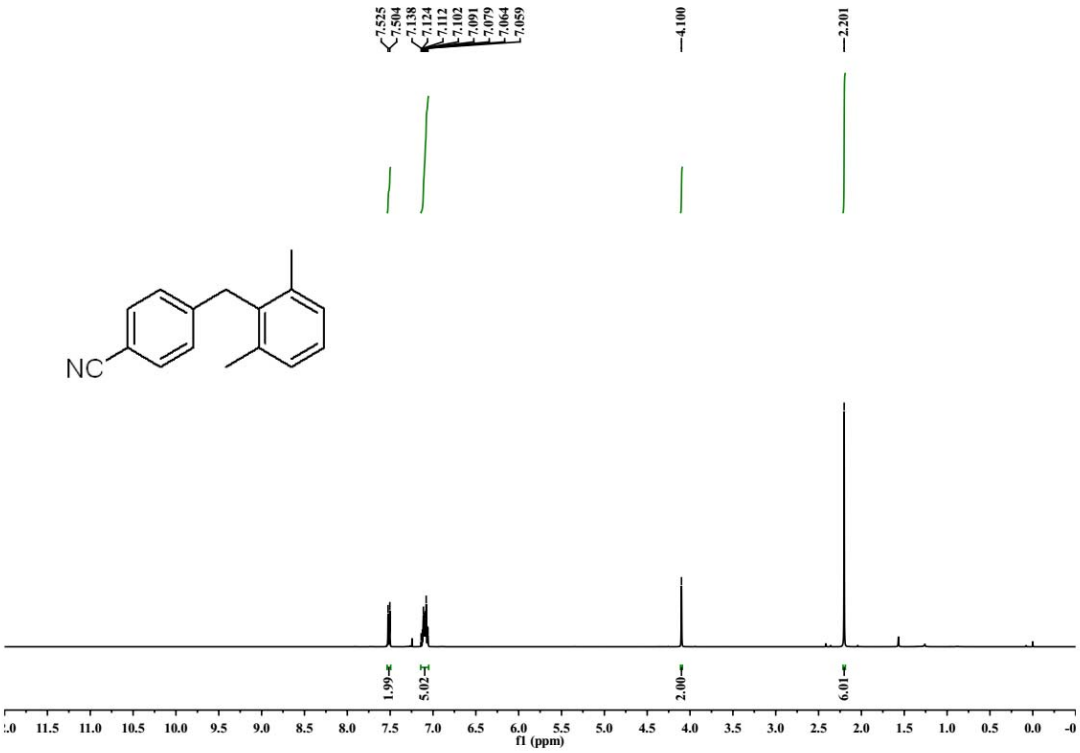
^{13}C NMR Spectrum of Compound 3j



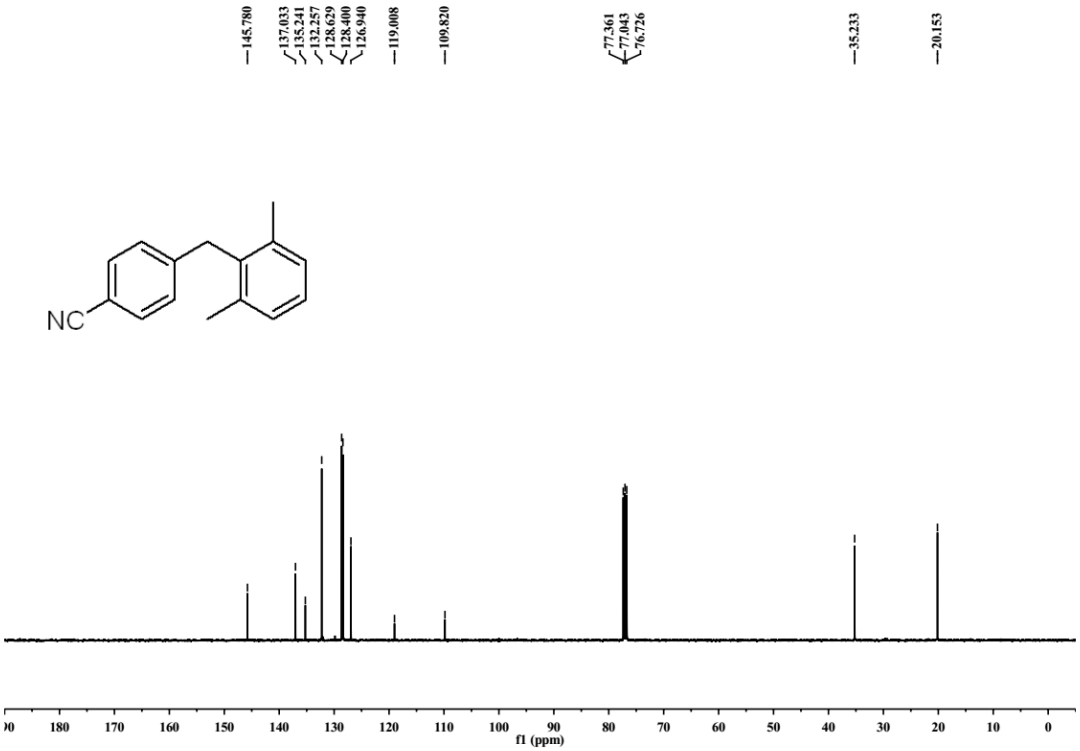
^{1}H NMR Spectrum of Compound 3k



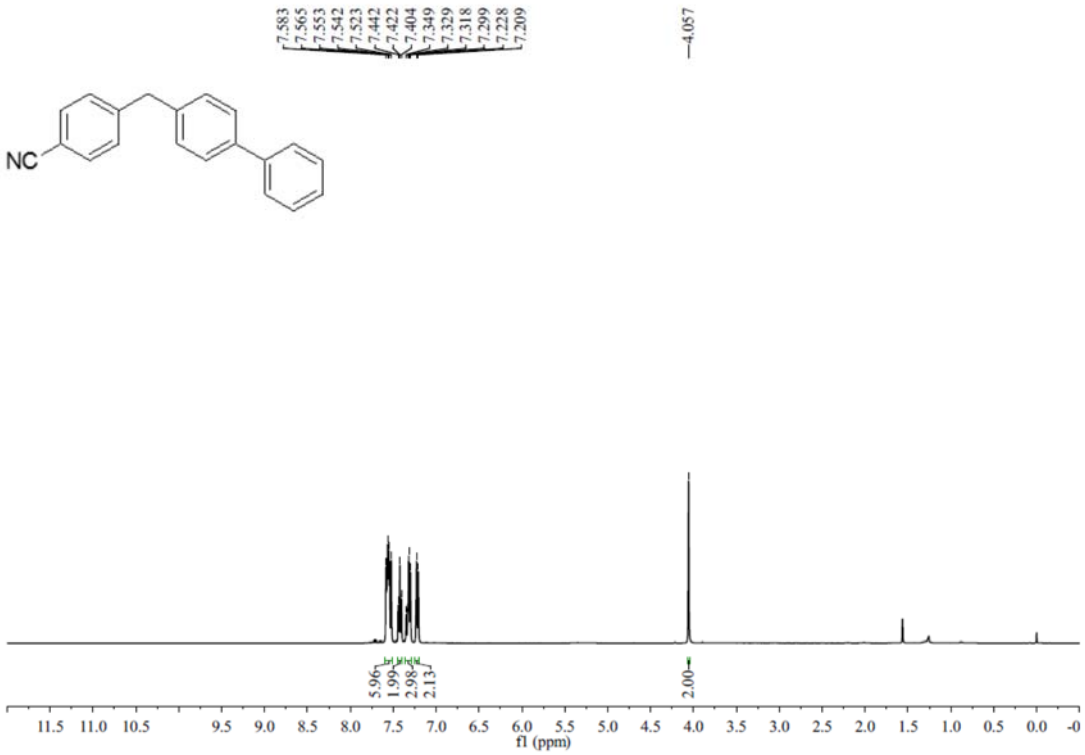
^{13}C NMR Spectrum of Compound 3k



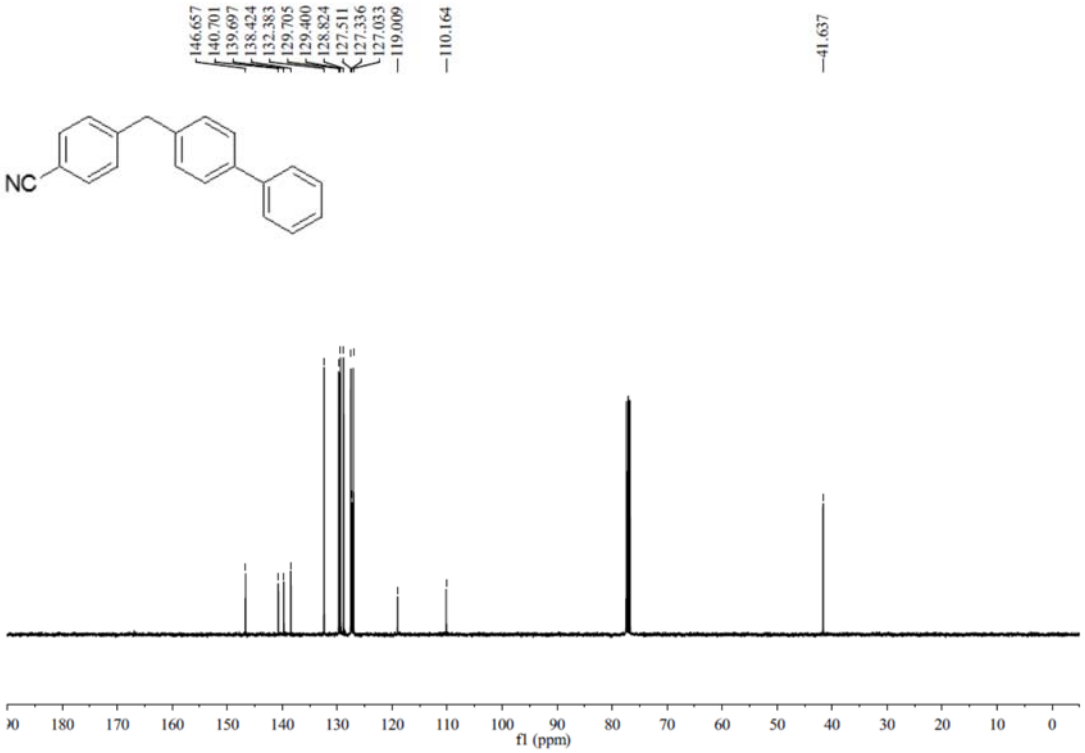
^{1}H NMR Spectrum of Compound 3aa



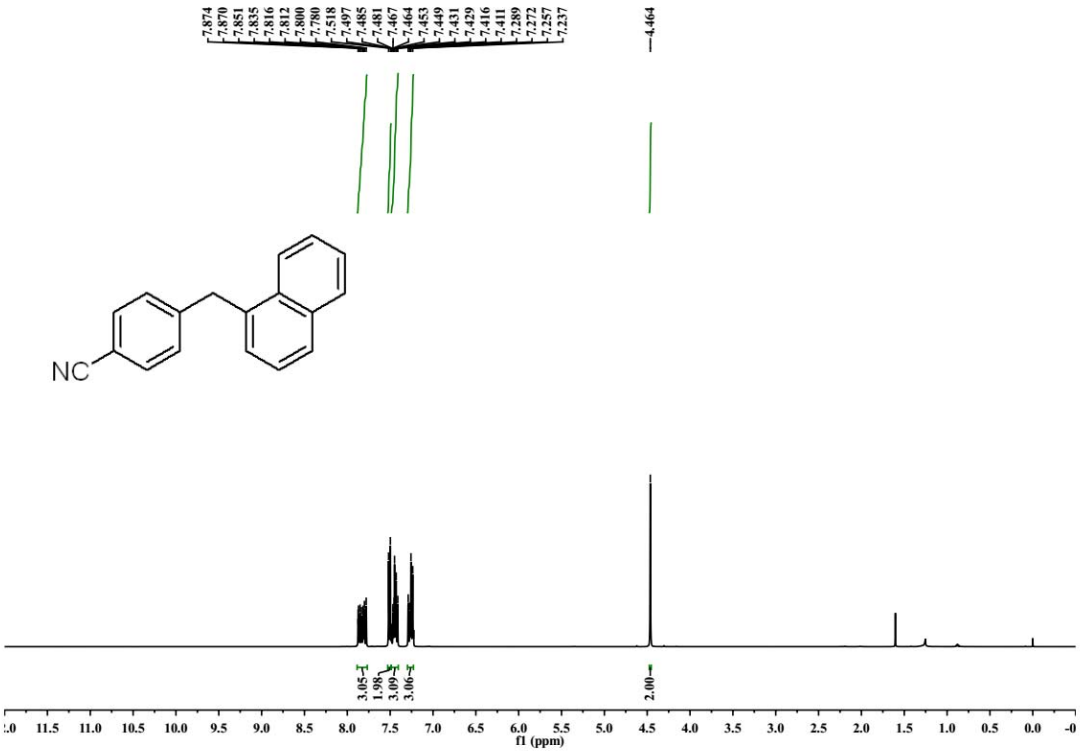
^{13}C NMR Spectrum of Compound 3aa



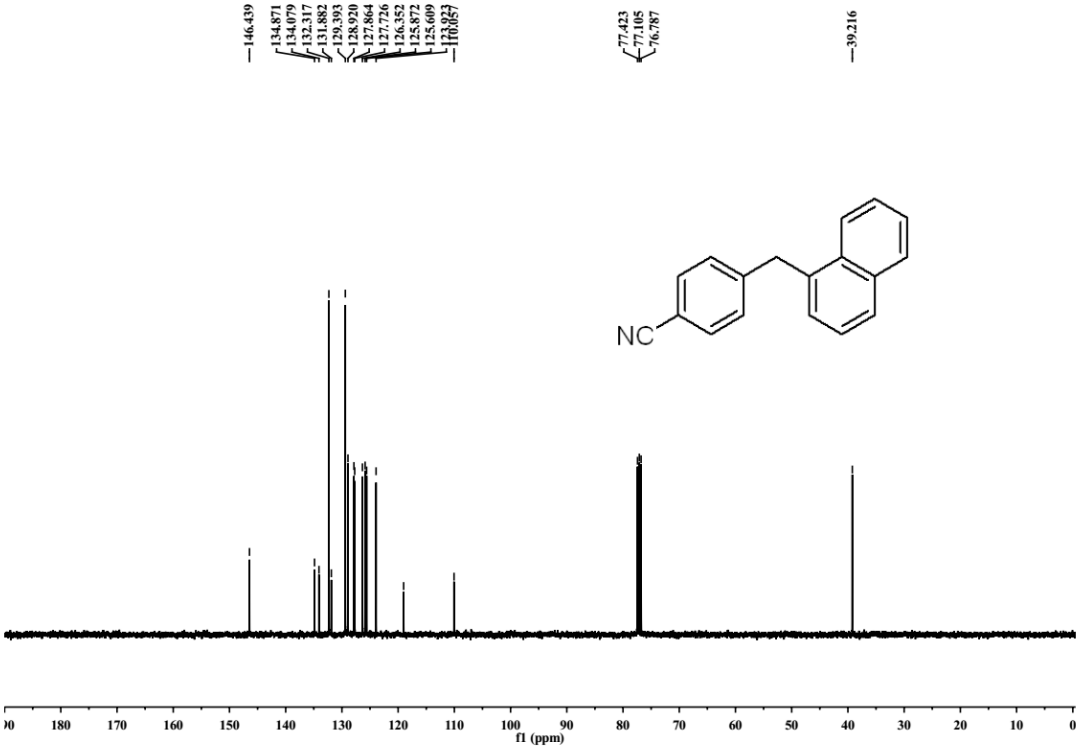
^{1}H NMR Spectrum of Compound 3ab



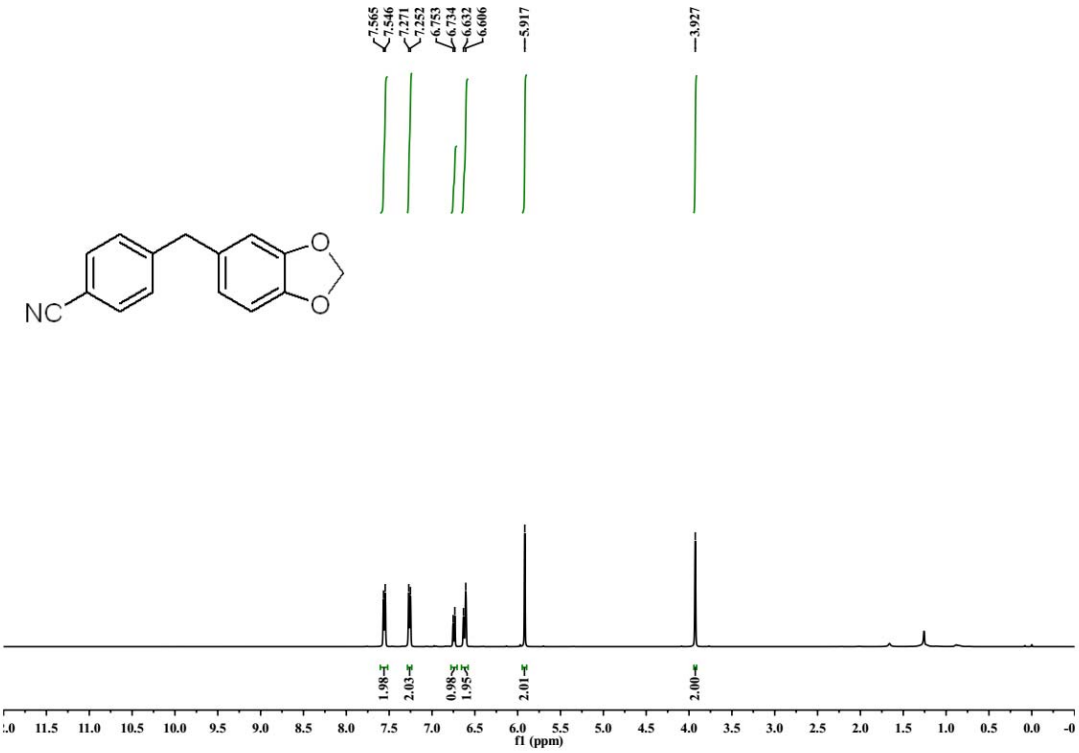
^{13}C NMR Spectrum of Compound 3ab



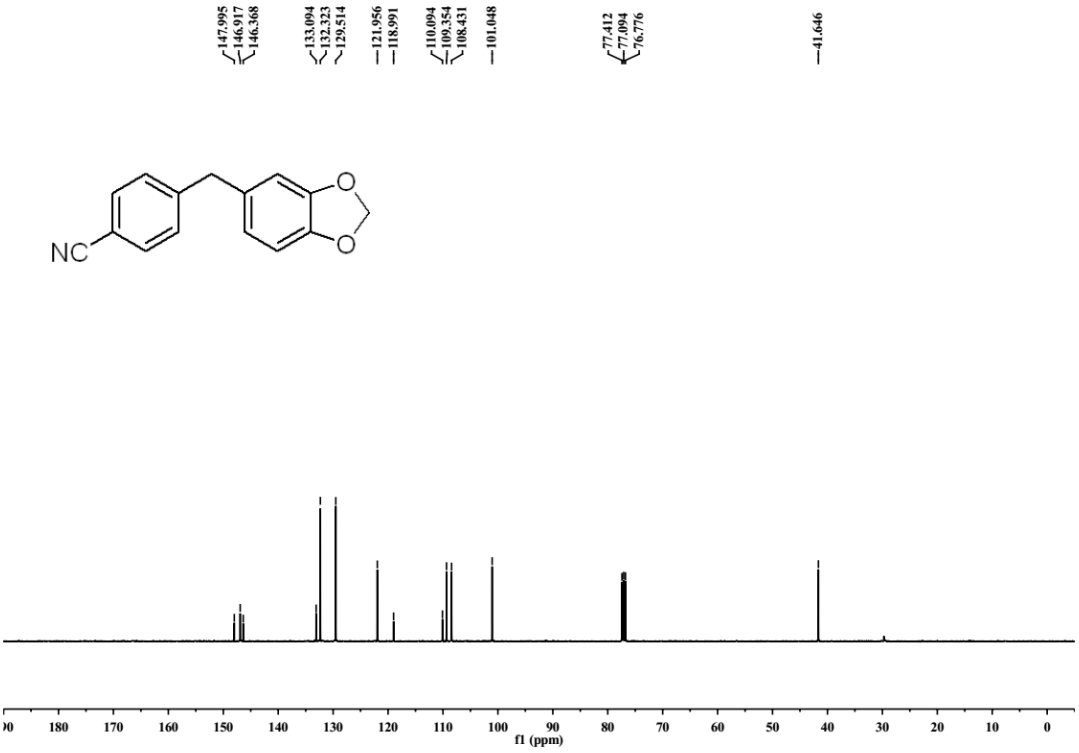
^{1}H NMR Spectrum of Compound 3ac



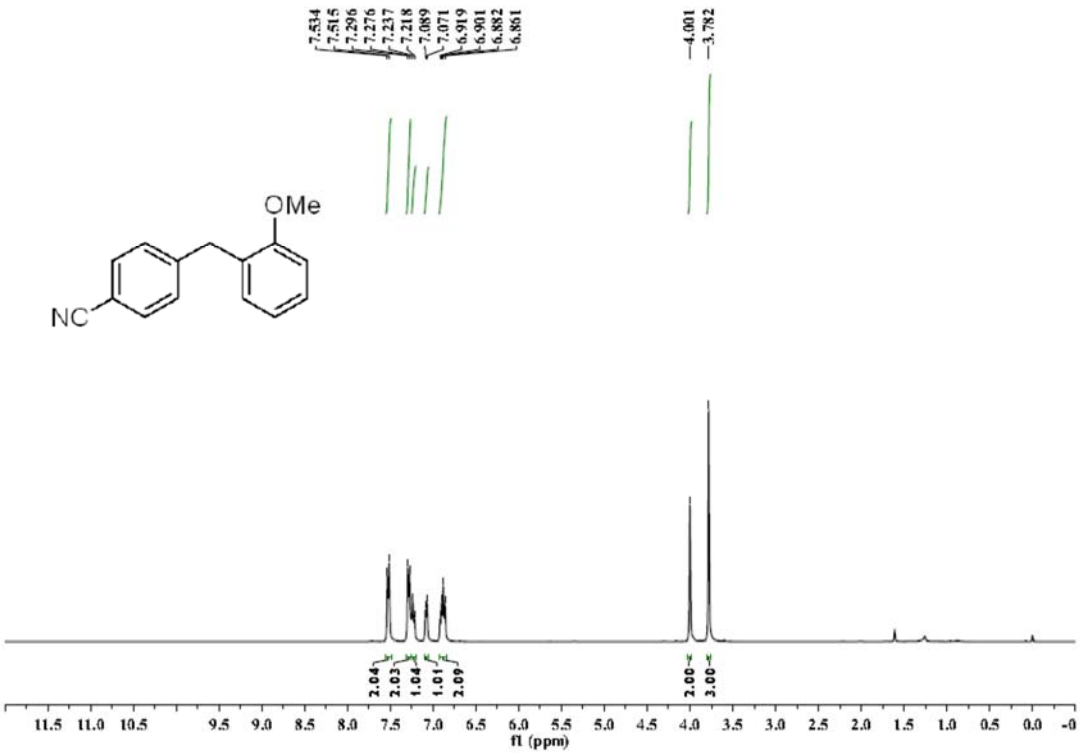
^{13}C NMR Spectrum of Compound 3ac



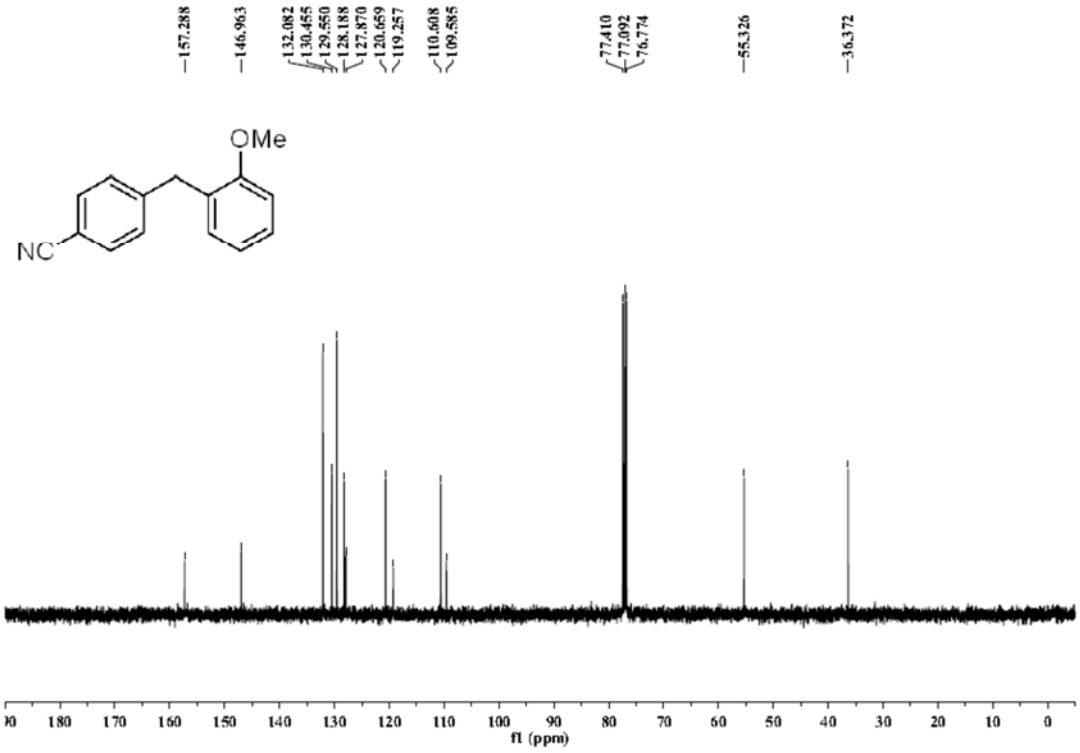
^{1}H NMR Spectrum of Compound 3ad



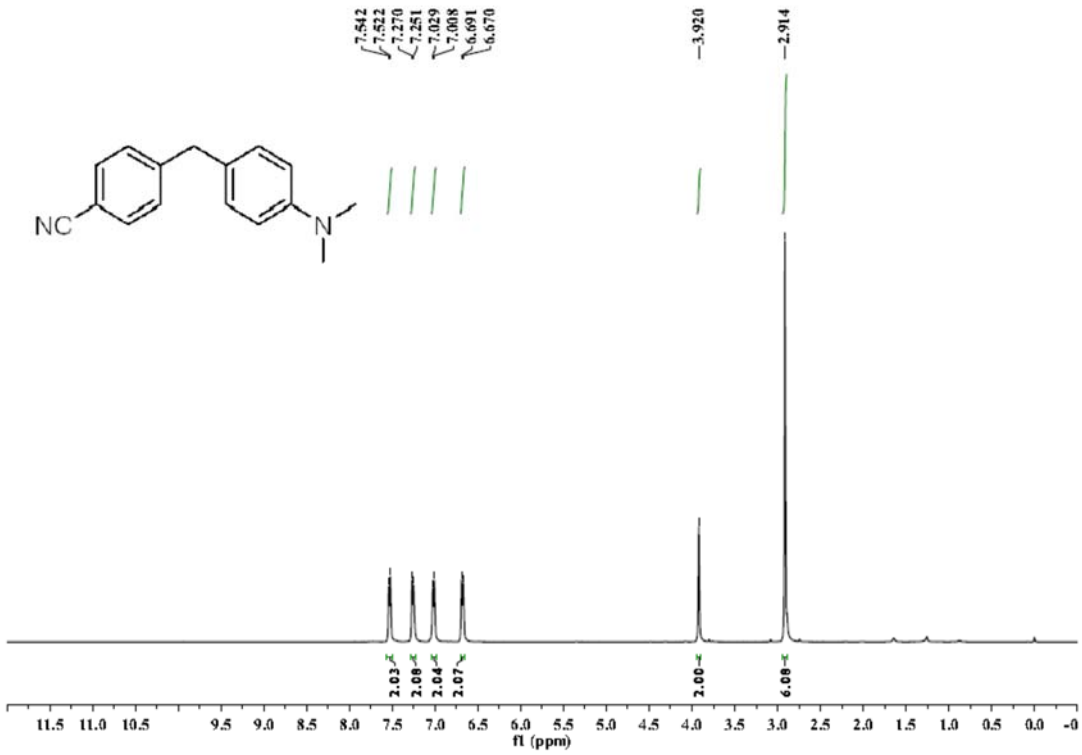
^{13}C NMR Spectrum of Compound 3ad



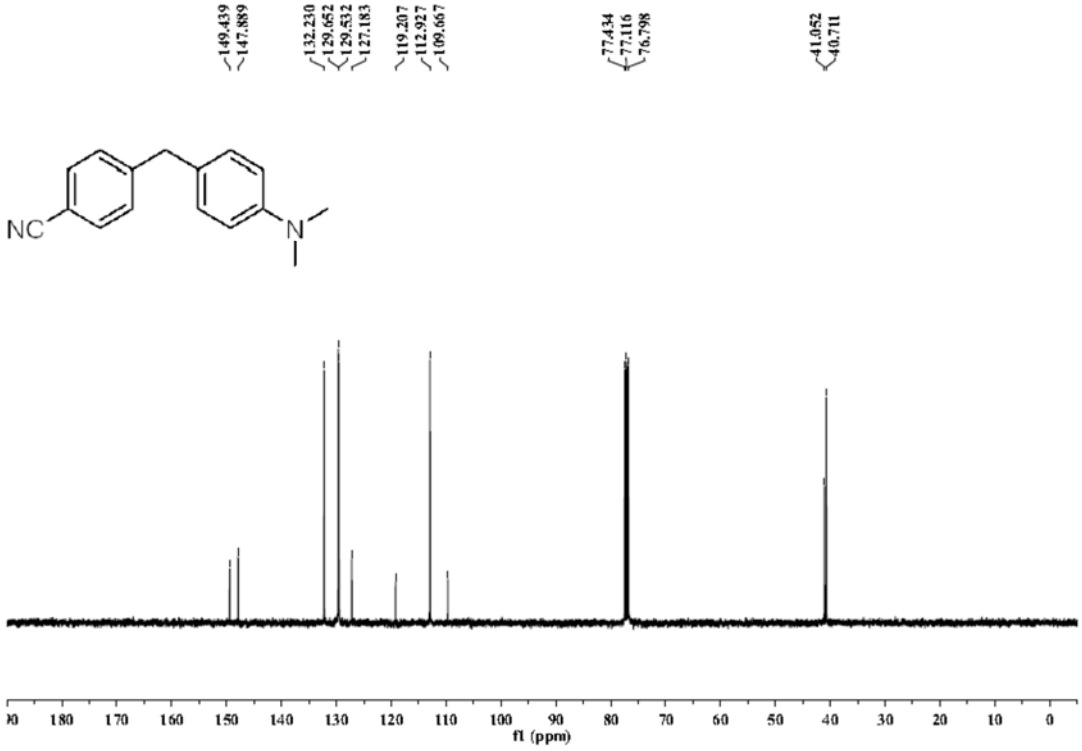
[1]H NMR Spectrum of Compound 3ae



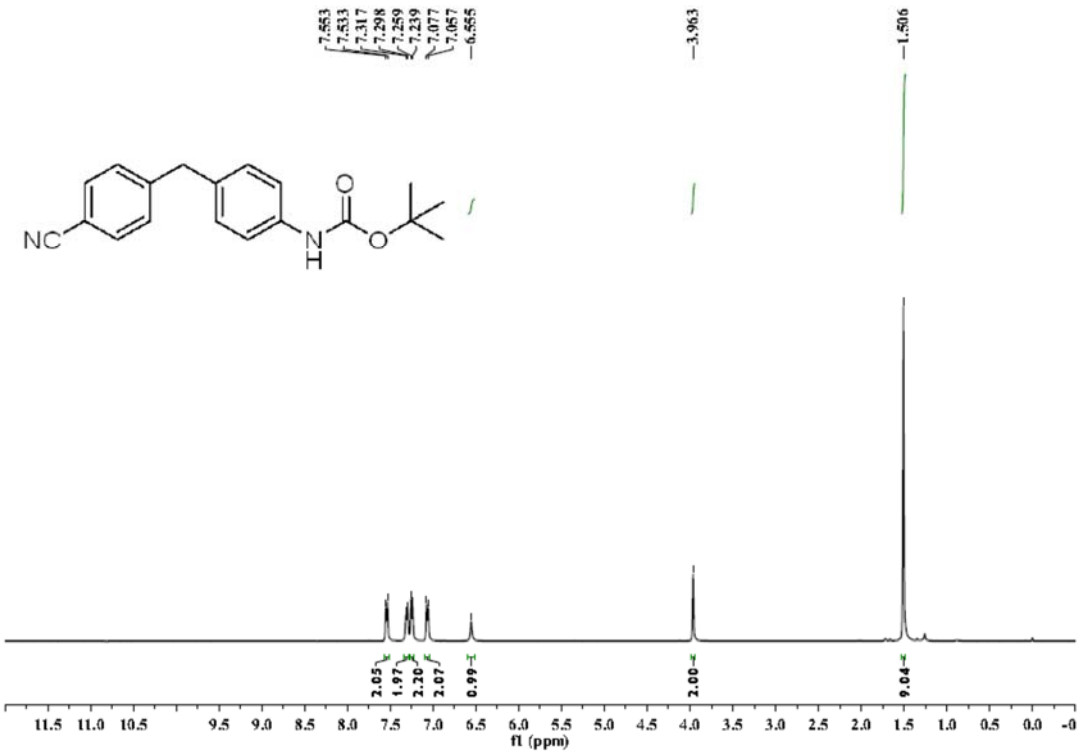
[13]C NMR Spectrum of Compound 3ae



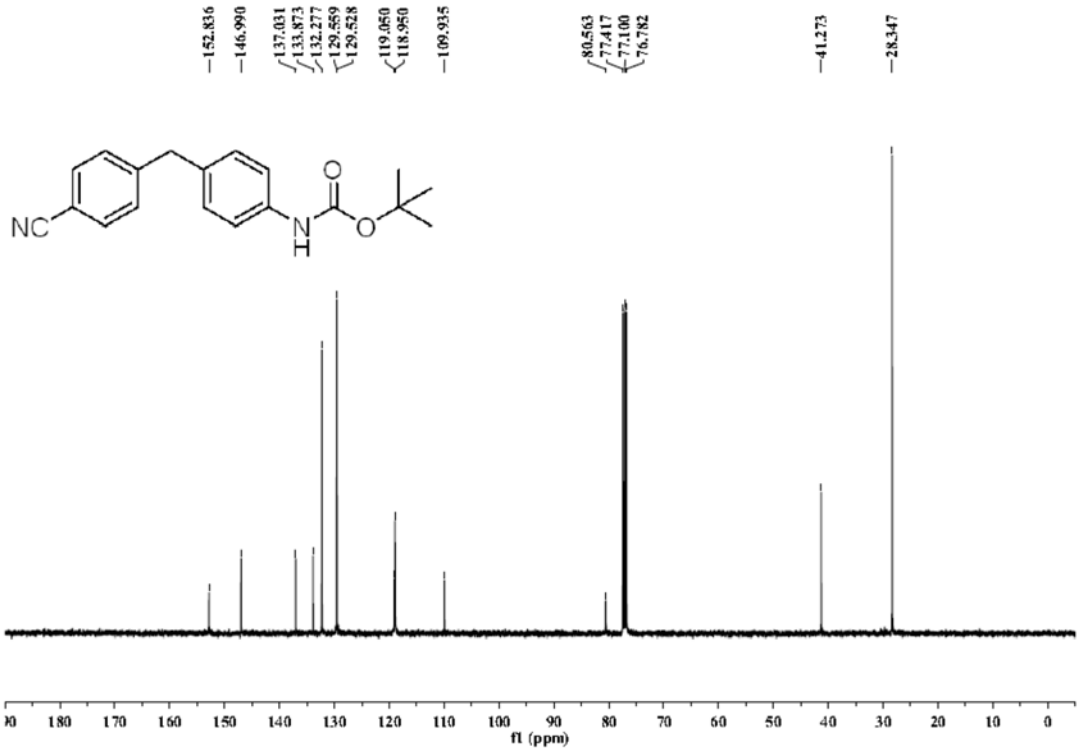
^{1}H NMR Spectrum of Compound 3af



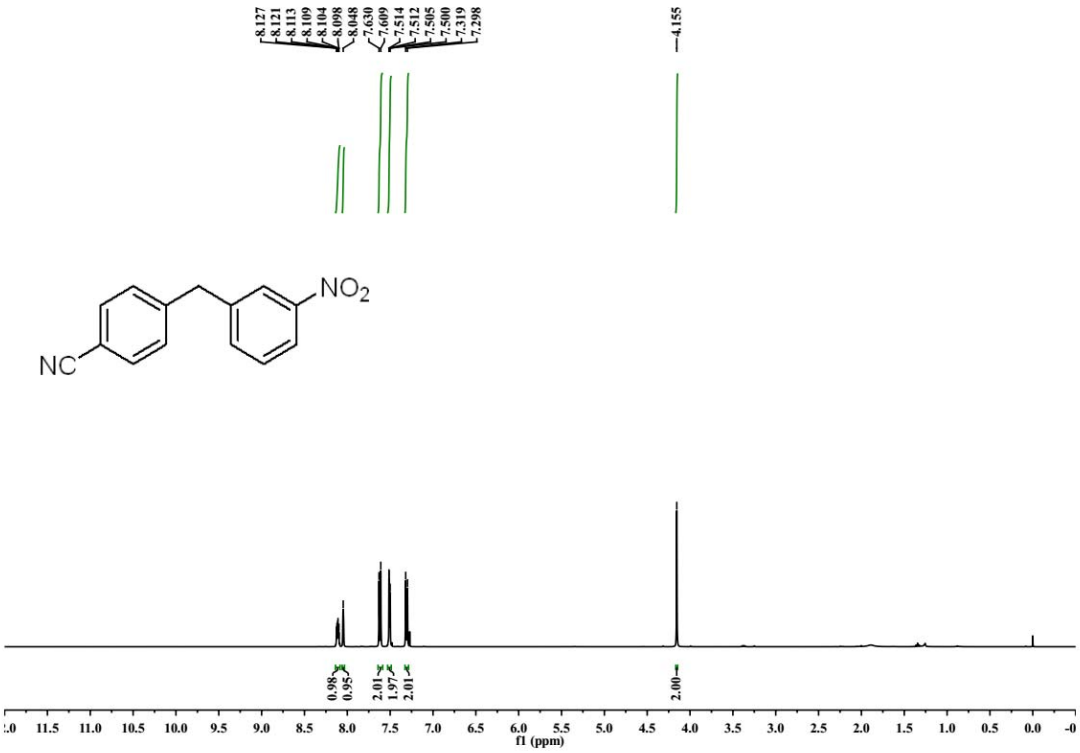
^{13}C NMR Spectrum of Compound 3af



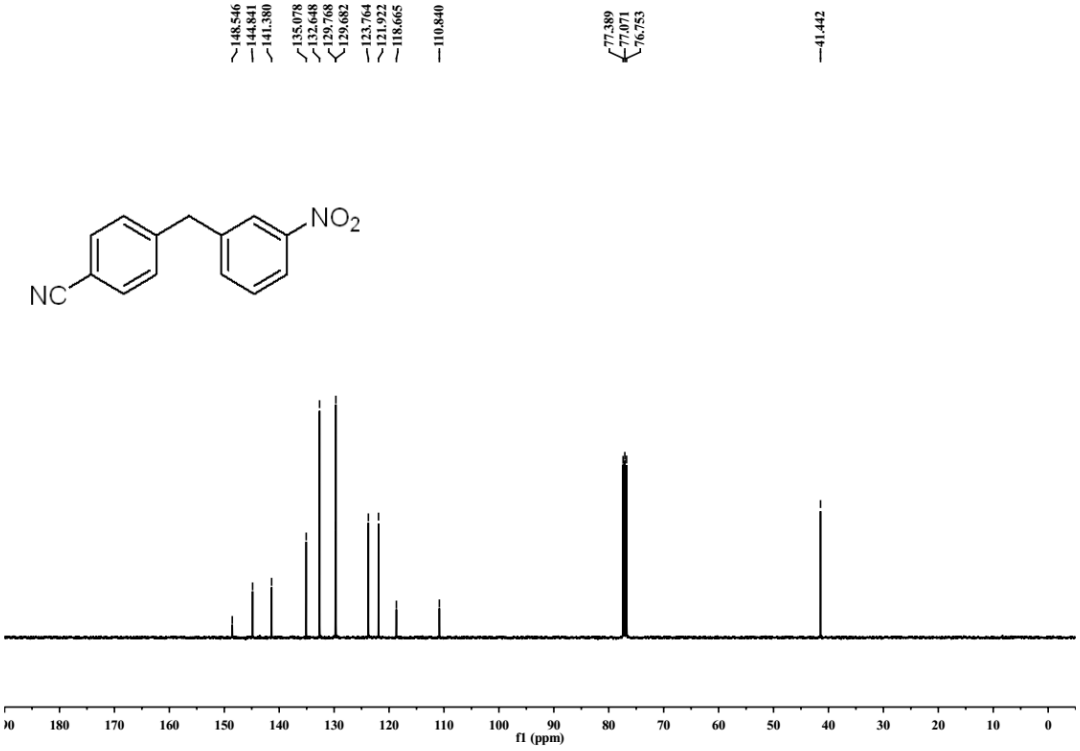
[1]H NMR Spectrum of Compound 3ag



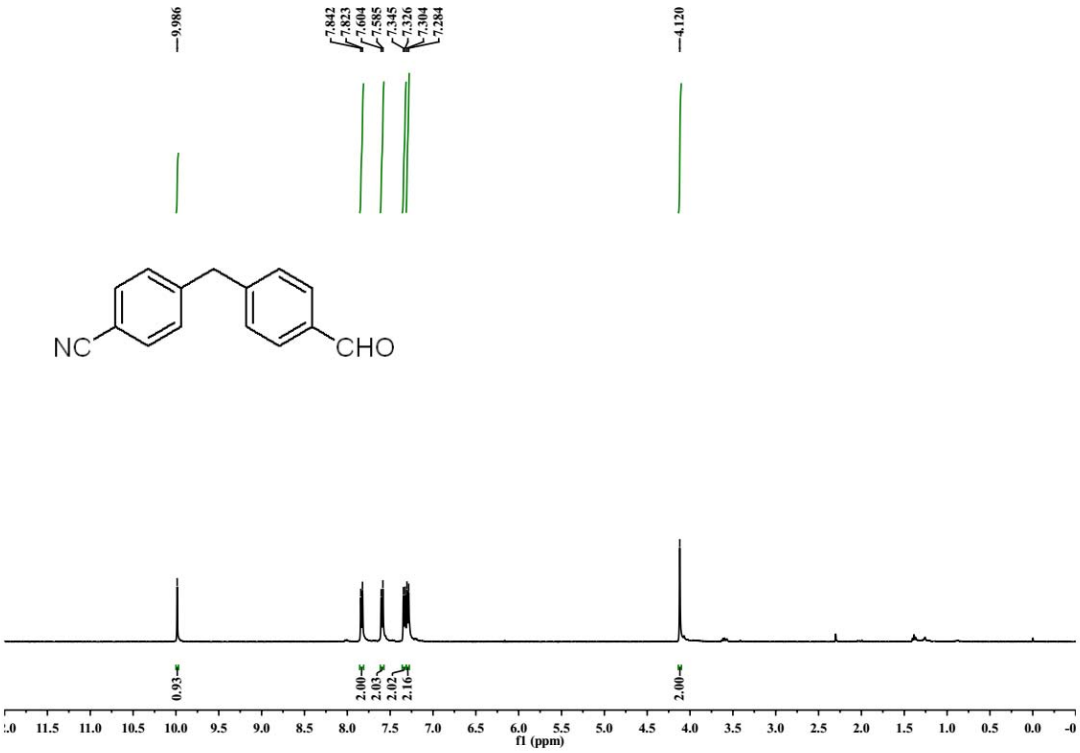
[13]C NMR Spectrum of Compound 3ag



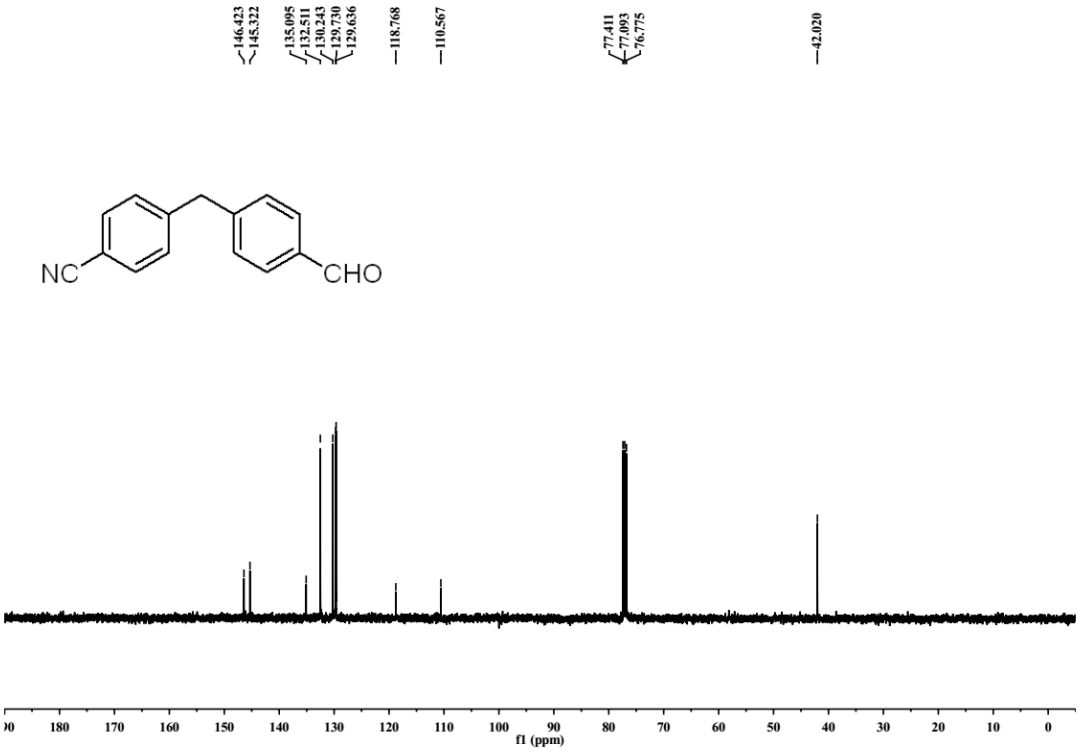
^{1}H NMR Spectrum of Compound 3ah



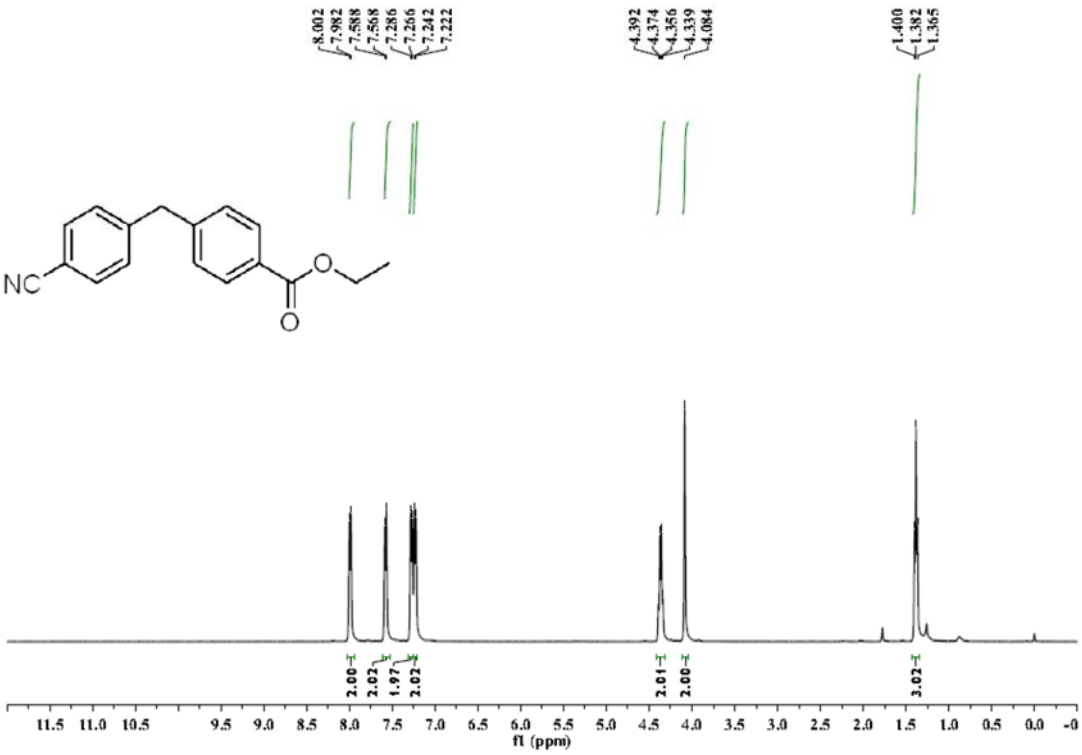
^{13}C NMR Spectrum of Compound 3ah



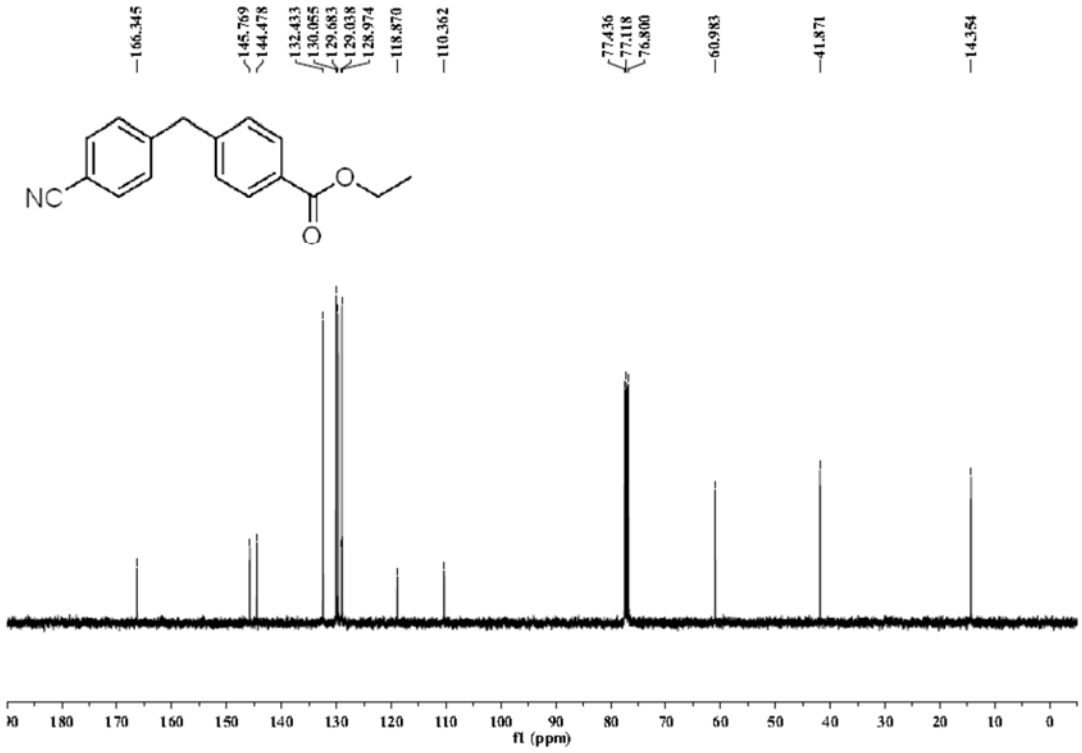
^{1}H NMR Spectrum of Compound 3ai



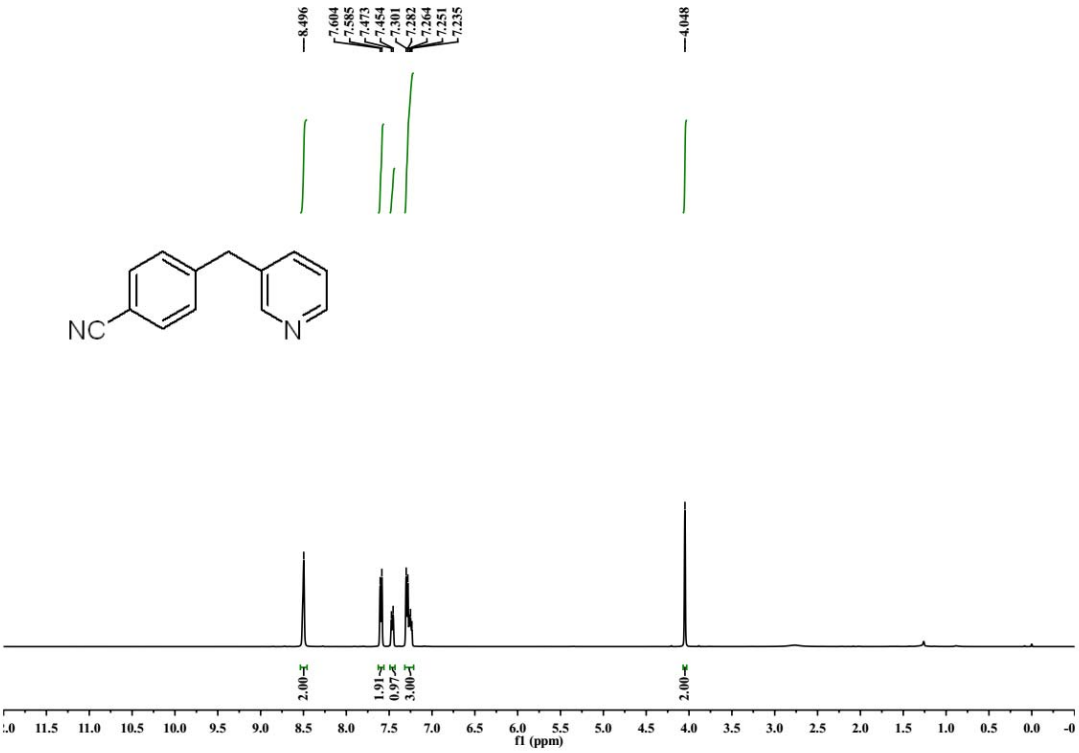
^{13}C NMR Spectrum of Compound 3ai



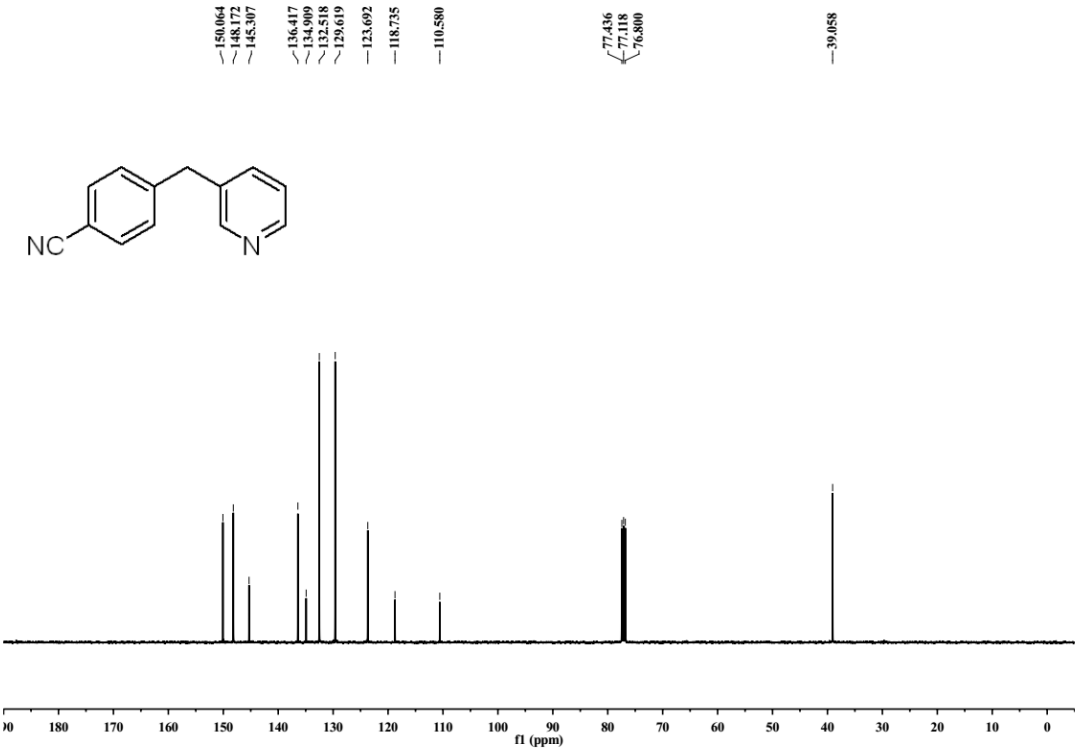
^{1}H NMR Spectrum of Compound 3aj



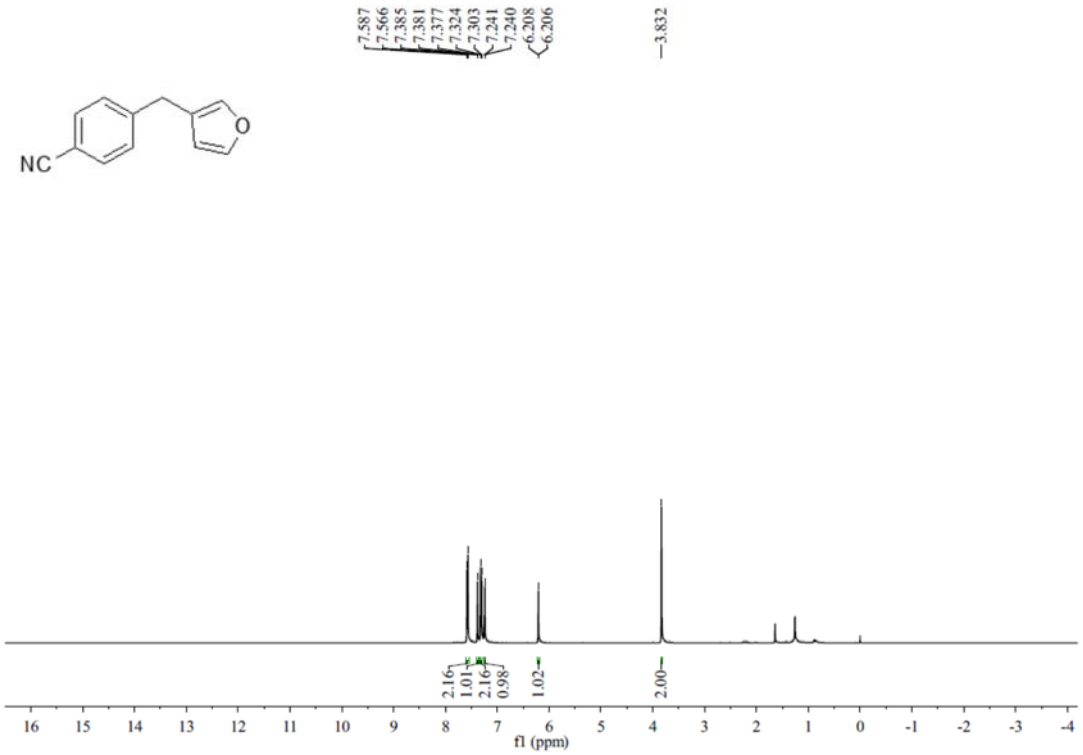
^{13}C NMR Spectrum of Compound 3aj



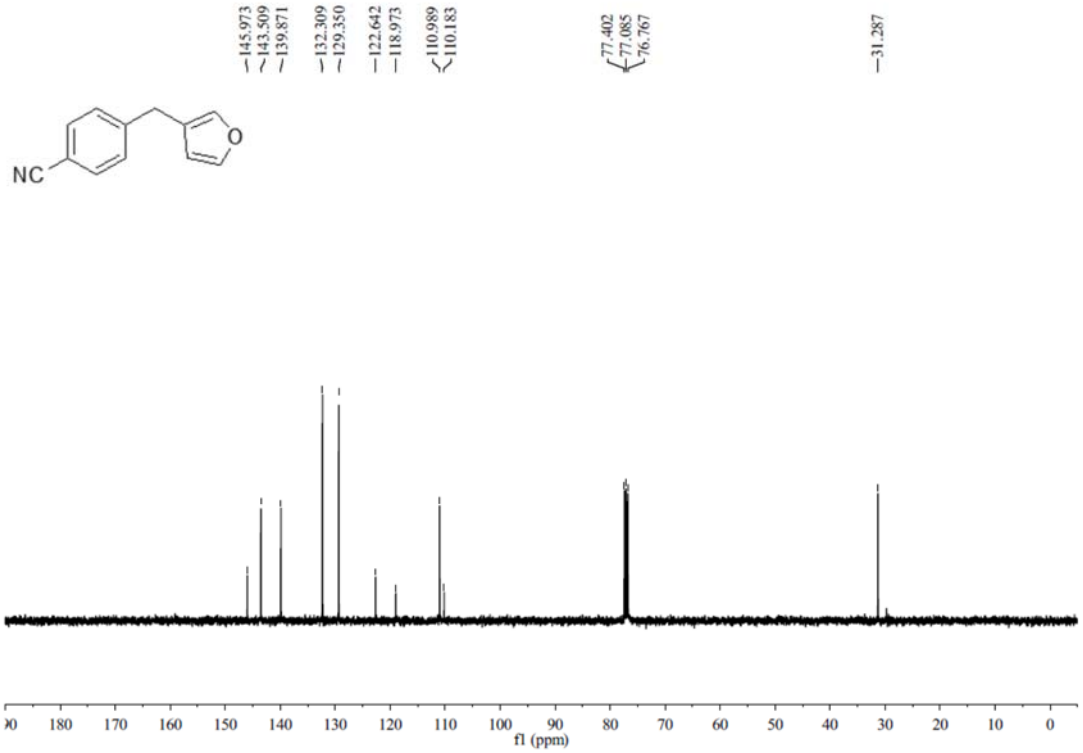
^{1}H NMR Spectrum of Compound 3ak



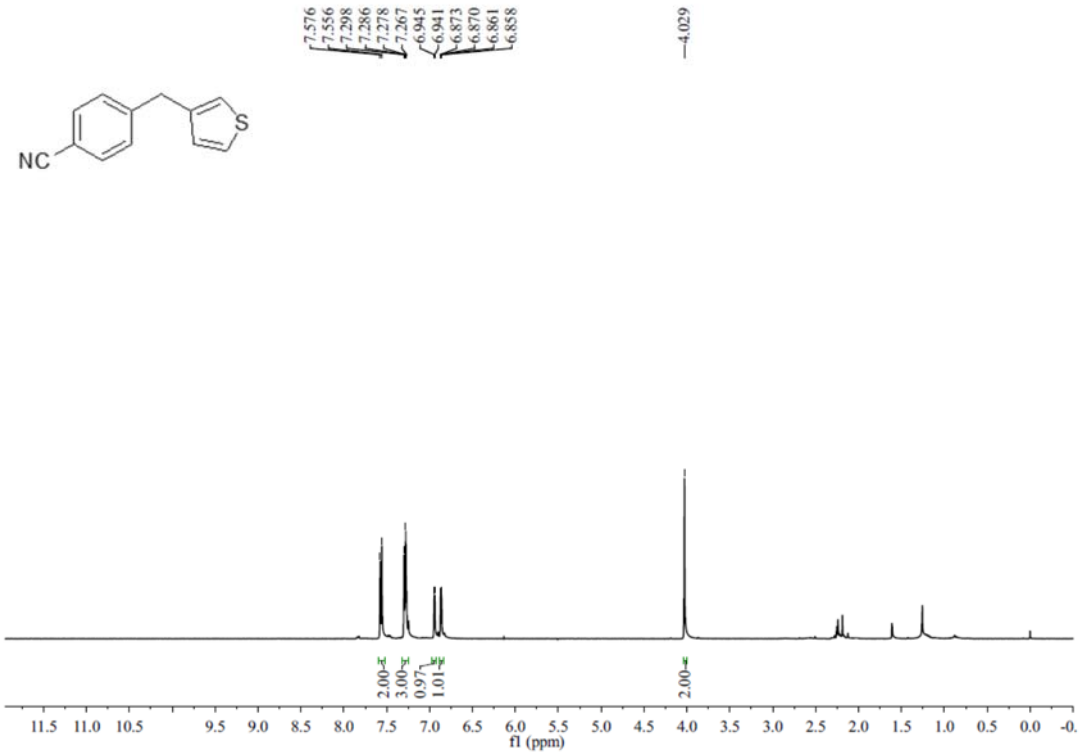
^{13}C NMR Spectrum of Compound 3ak



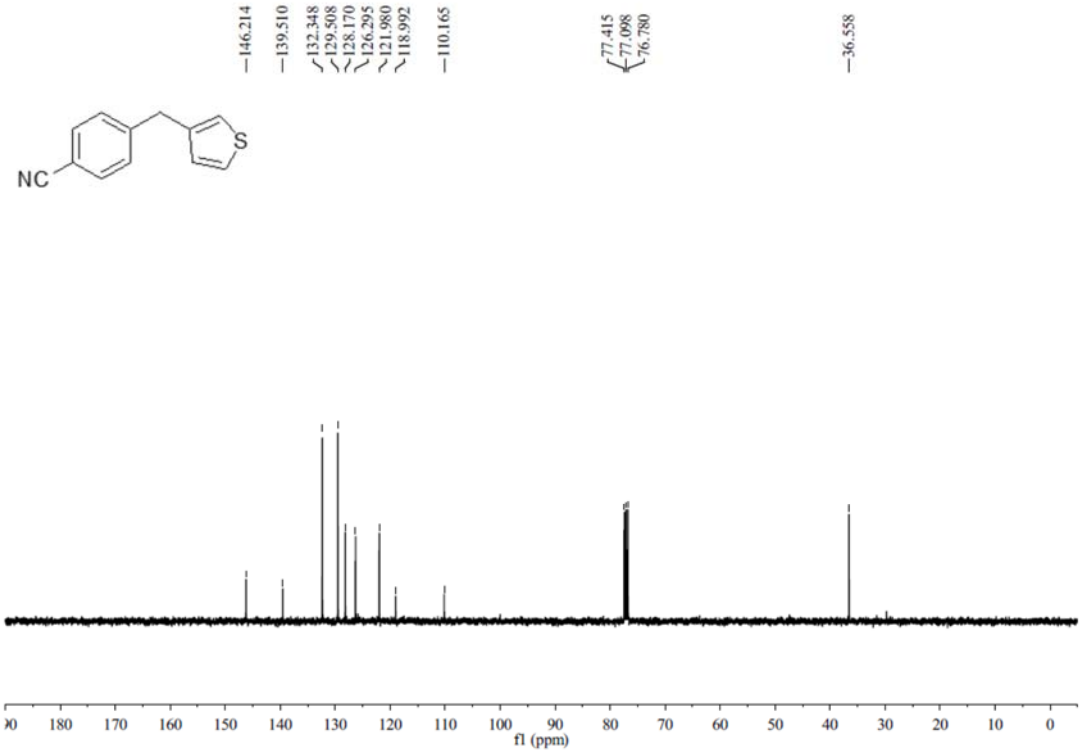
^{1}H NMR Spectrum of Compound 3al



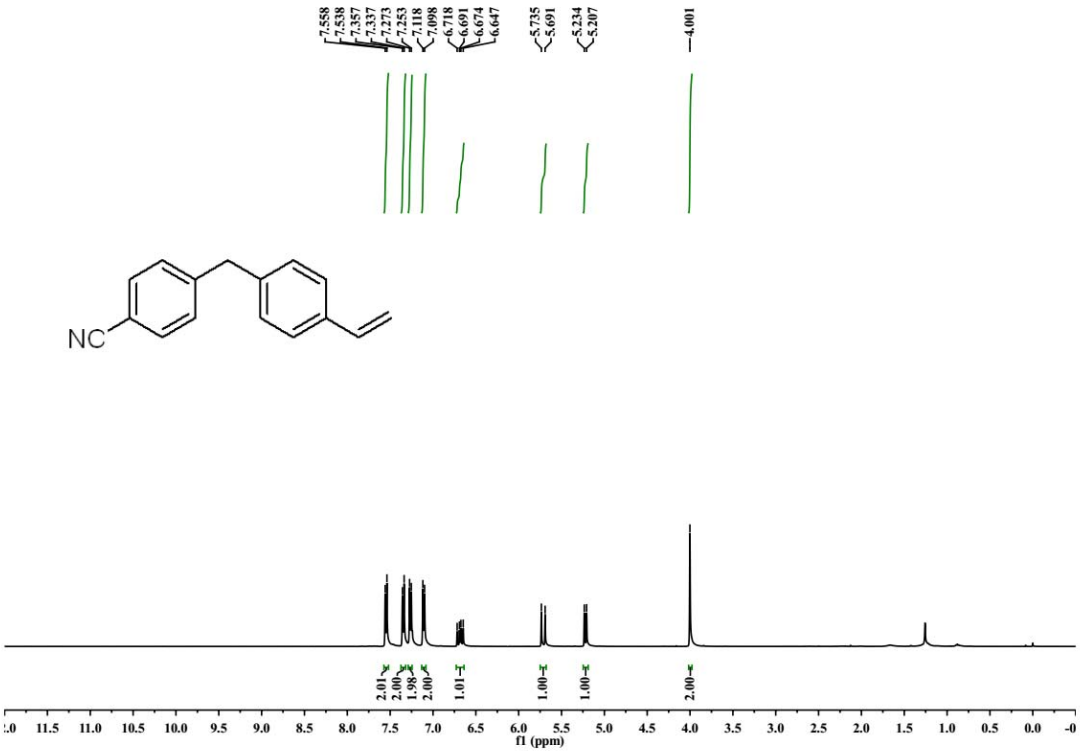
^{13}C NMR Spectrum of Compound 3al



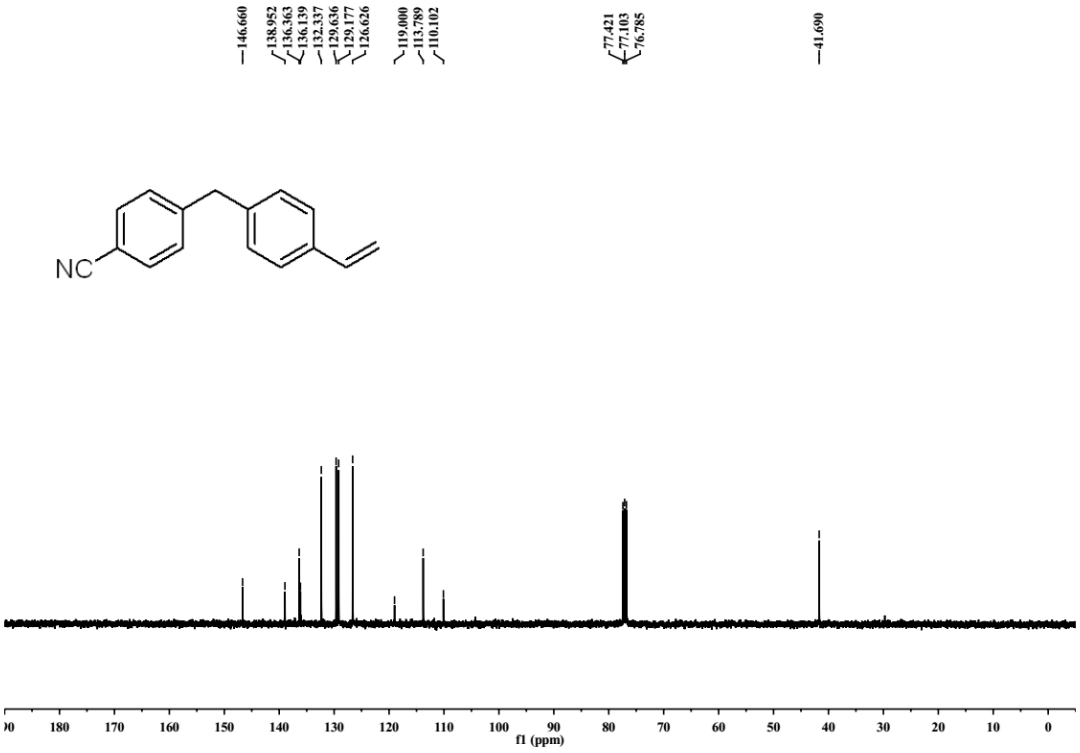
^{1}H NMR Spectrum of Compound 3am



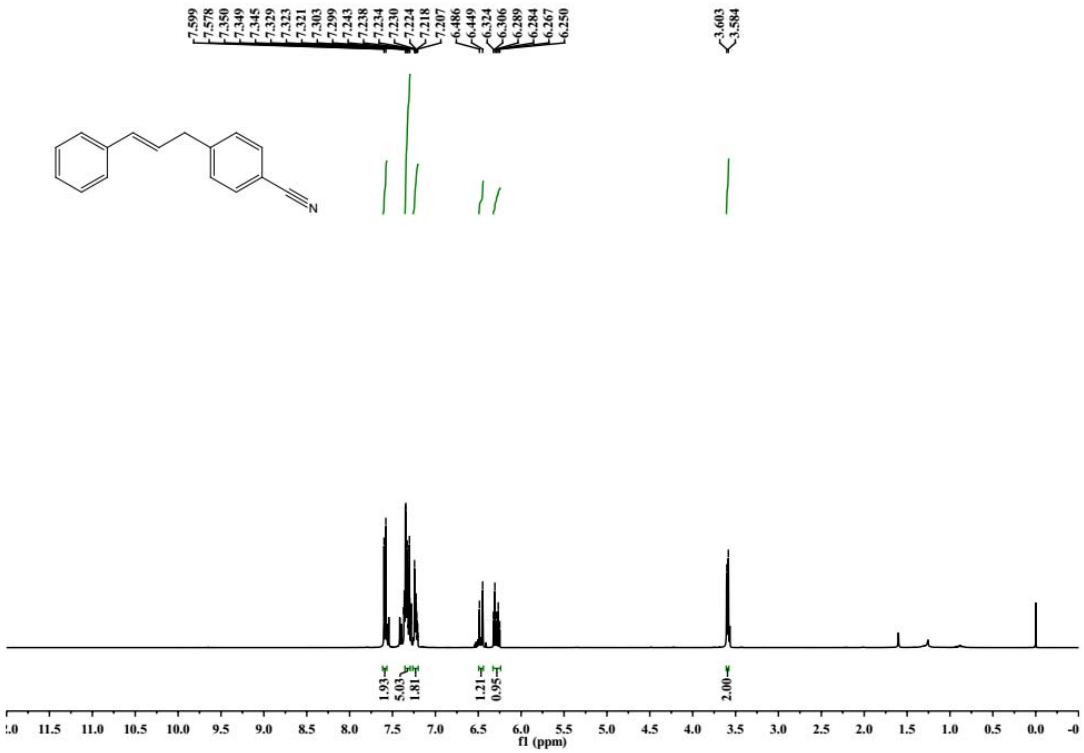
^{13}C NMR Spectrum of Compound 3am



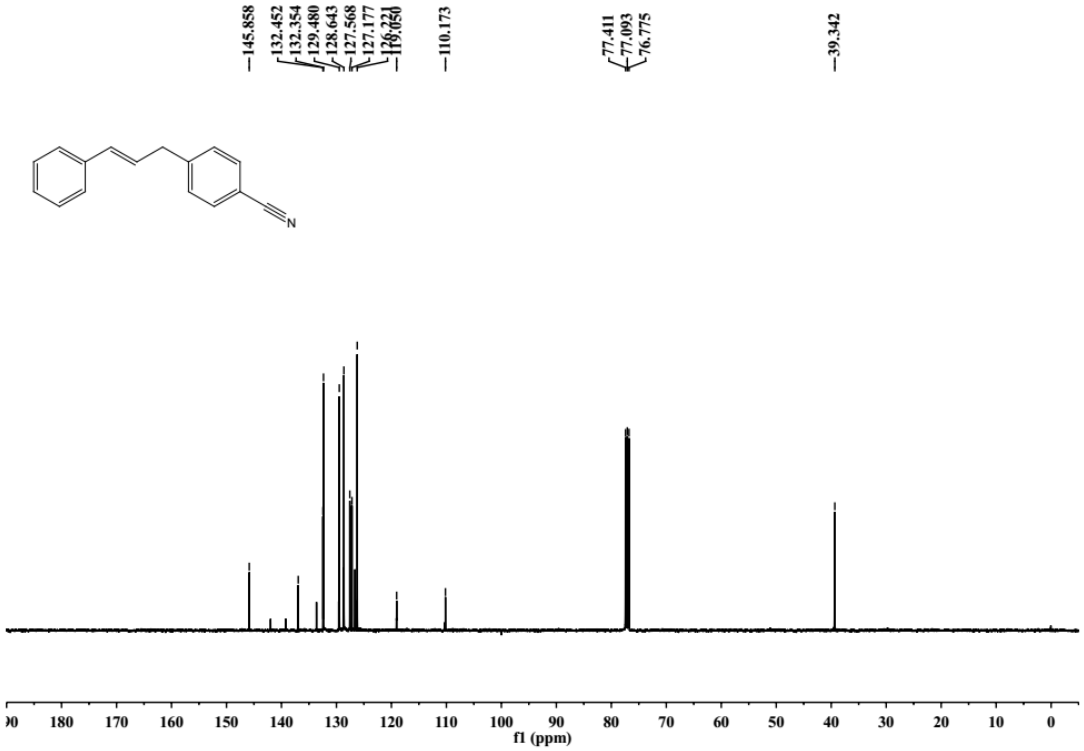
^{1}H NMR Spectrum of Compound 3an



^{13}C NMR Spectrum of Compound 3an

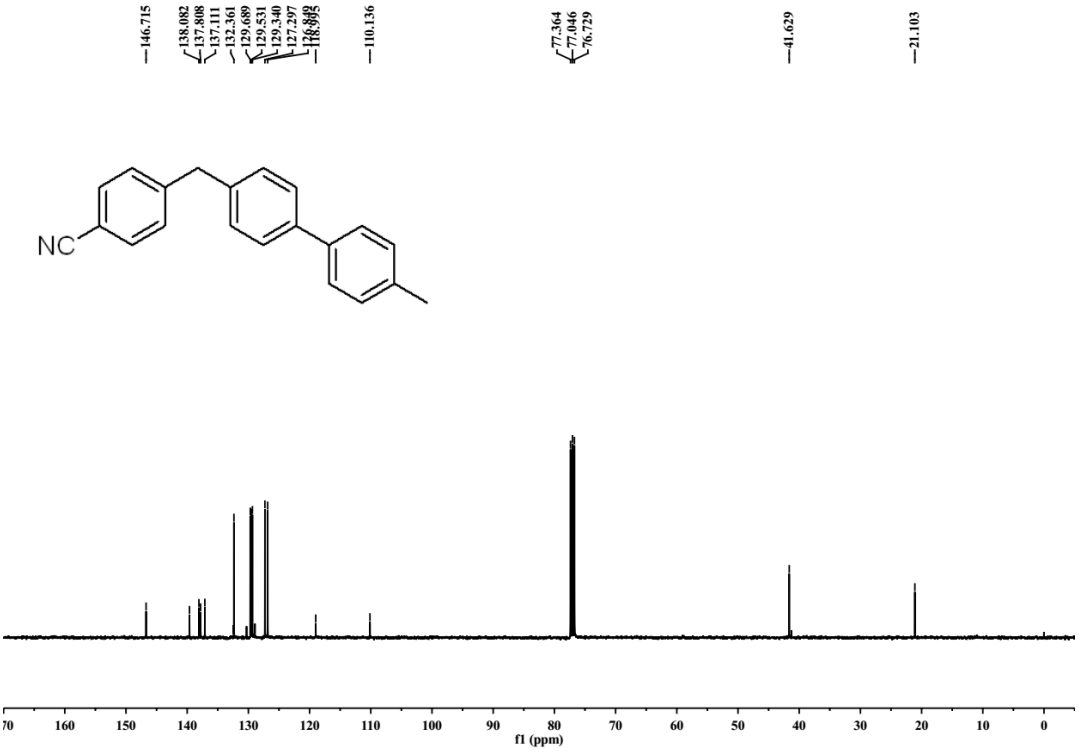


^{1}H NMR Spectrum of Compound 3ao

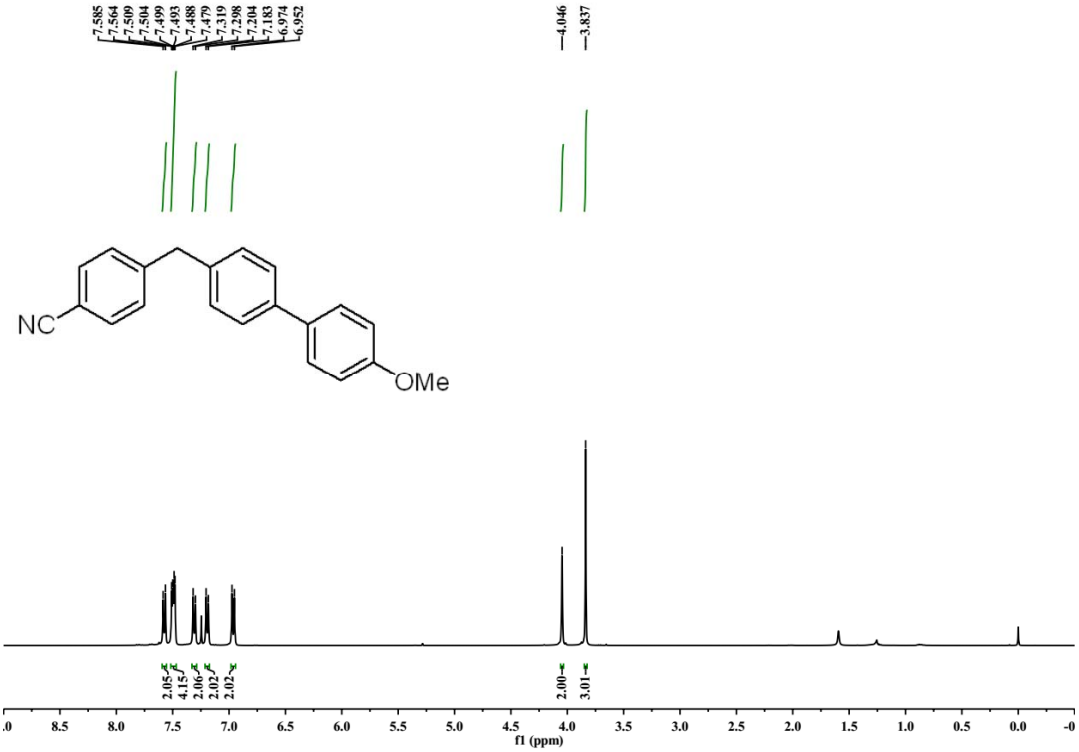


^{13}C NMR Spectrum of Compound 3ao

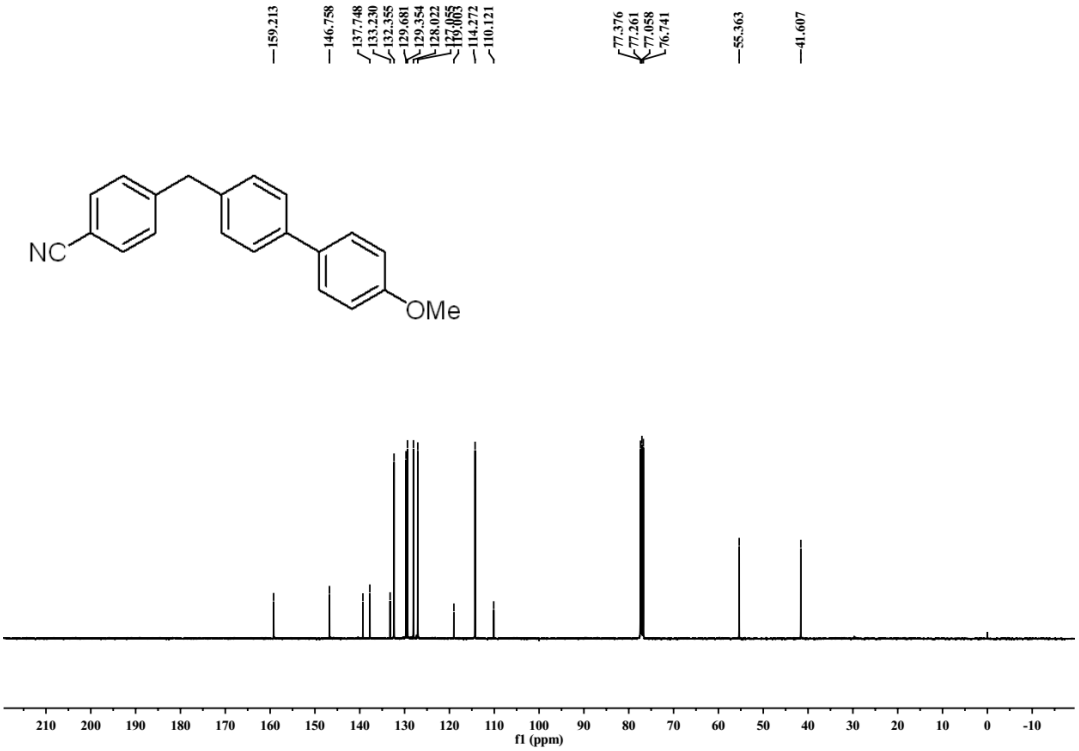
^{1}H NMR Spectrum of Compound 3ap



^{13}C NMR Spectrum of Compound 3ap



^{1}H NMR Spectrum of Compound 3aq



^{13}C NMR Spectrum of Compound 3ap