Electronic Supplementary Information for

Metal-Free, Atom and Redox-Economical Construction of C-C Bonds Enabled by Oligofluorenes-Containing Hypercrosslinked Polymers

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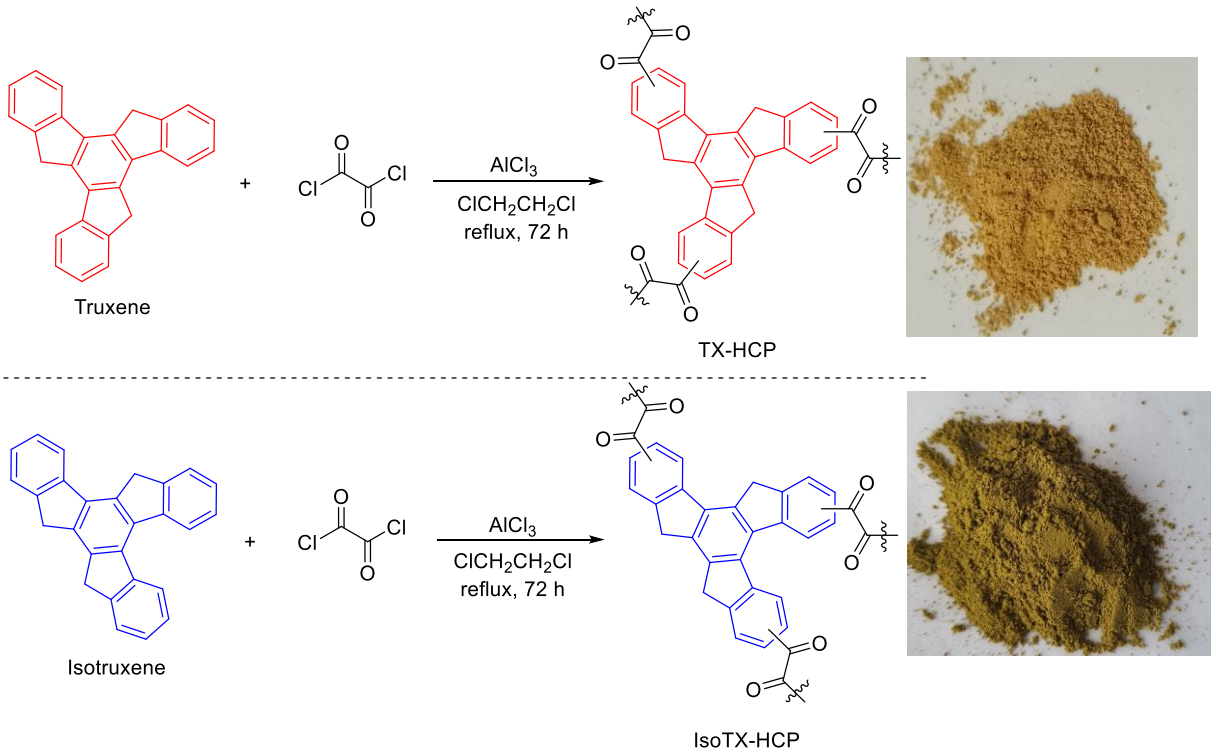
1. General Information

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere. All reagents were commercially purchased and used without any further purification. ^{1}H spectra were recorded on a Bruker instrument (400 MHz) and internally referenced to tetramethylsilane signal or residual protic solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

Powder X-ray diffraction (PXRD) was recorded on a PANalytical X'pert PRO X-ray Diffractometer using Cu-Kα radiation in the 2θ range of 10-90°. The nitrogen adsorption-desorption isotherms at 77 K were measured with a Micromeritics ASAP2460 analyzers, and the BET surface area was estimated by the Brunauer-Emmett-Teller (BET) theory. Fourier Transform Infrared spectra were recorded with a Nicolet iS50 FT-IR spectrophotometer. UV-vis diffuse reflectance spectra (DRS) were performed on a Perkin Elmer Lambda 750 in the 300~800 nm range, with $BaSO_4$ as the reference substance. Electrochemical measurements were performed on an electrochemical workstation (CHI 660E, CH Instruments Inc., Shanghai). Thermogravimetric analysis (TGA) profiles were recorded on a METTLER TGA/SDTA 851 thermal analyzer. Scanning electron microscopy (SEM) images were recorded using a Phenomenon LE electron microscope. Multifunctional imaging electron spectrometer (XPS) measurements were carried out using Thermo ESCALAB 250Xi spectrometer.

2. Synthesis



Synthesis of TX-HCP:

Following a literature reported procedure[1], oxalyl chloride (0.34 mL, 3.90 mmol) was added to a solution of $AlCl_3$ (519 mg, 3.90 mmol, anhydrous) and truxene (1.0 g, 2.92 mmol) in 1,2-dichloroethane (DCE, 15 mL). The resulting mixture was stirred under nitrogen atmosphere at 85 °C for 72 h to complete the cross-linking. Afterwards, the reaction mixture was cooled to room temperature and the obtained precipitate was washed with dilute hydrochloric acid, water, acetone, ethanol, ethyl acetate and dichloromethane, respectively. The product TX-HCP was collected and dried under vacuum as a yellow solid (1.1 g).

Synthesis of IsoTX-HCP:

Following a literature reported procedure,[1] oxalyl chloride (0.34 mL, 3.90 mmol) was added to a solution of $AlCl_3$ (519 mg, 3.90 mmol, anhydrous) and isotruxene (1.0 g, 2.92

mmol) in 1,2-dichloroethane (DCE, 15 mL). The resulting mixture was stirred under nitrogen atmosphere at 85 °C for 72 h to complete the cross-linking. Afterwards, the reaction mixture was cooled to room temperature and the obtained precipitate was washed with dilute hydrochloric acid, water, acetone, ethanol, ethyl acetate and dichloromethane, respectively. The product IsoTX-HCP was collected and dried under vacuum as a green solid (0.63 g).

Synthesis of substrates

Preparation of 1:

Substrates **1t**-**1w** were synthesized according to the reported literature.[2]

Preparation of 2:

To a flask were added the substrate aldehyde (1.0 equiv), malononitrile (1.5 equiv), K_2CO_3 (0.5 equiv), and dichloromethane (20 mL). The mixture was stirred at room temperature for the indicated time (monitored by TLC). Afterwards, the resulting solution was washed with H_2O (20 mL), and extracted with dichloromethane (10 mL × 3), the organic layer was washed with brine (20 mL × 4) and dried over Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure, the residue was purified by silica gel flash column chromatography using ethyl acetate/petroleum ether as the eluent to afford the desired products **2**.

3. Characterization of TX-HCP and IsoTX-HCP

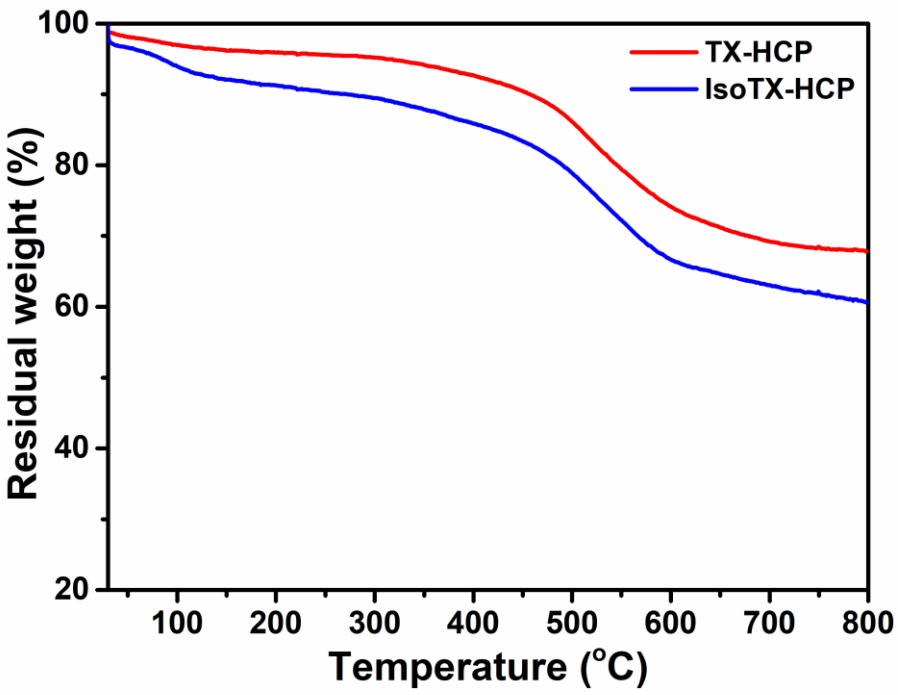


Fig. S1 TGA spectra of TX-HCP and IsoTX-HCP.

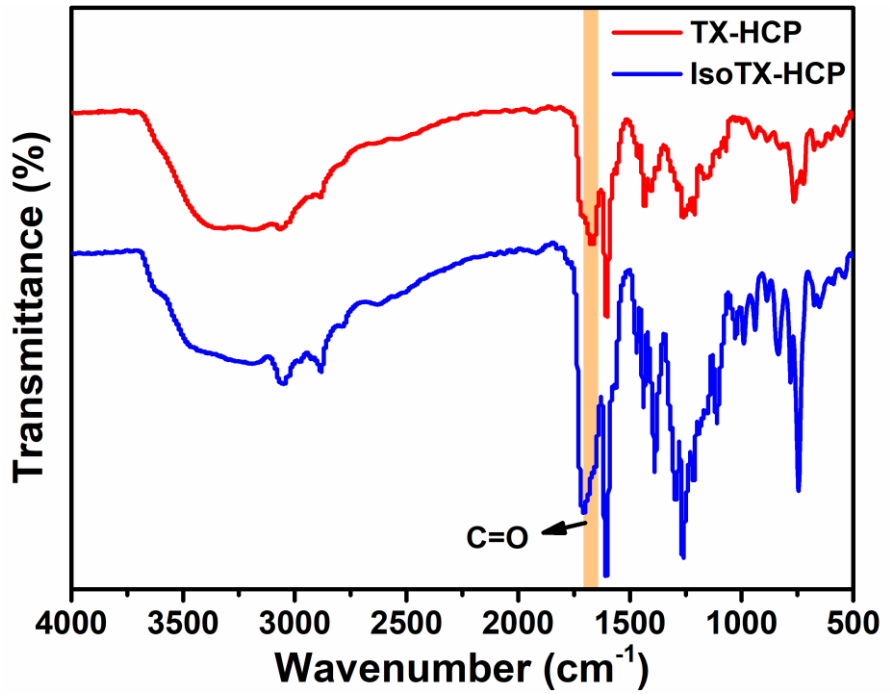


Fig. S2 FTIR spectra of TX-HCP and IsoTX-HCP.

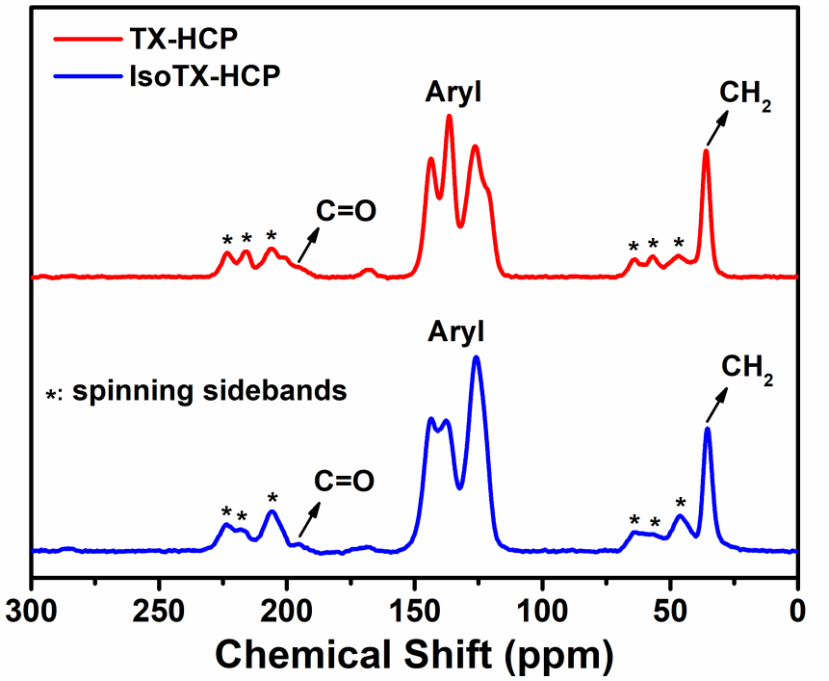


Fig. S3 Solid-state ^{13}C CP/MAS NMR spectra of TX-HCP and IsoTX-HCP.

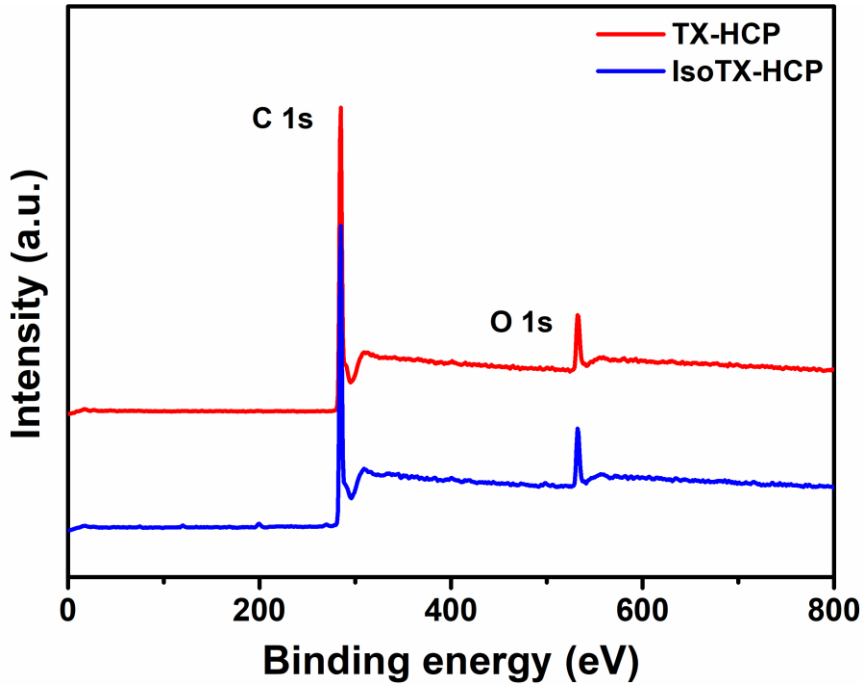


Fig. S4 XPS survey scan spectra of TX-HCP and IsoTX-HCP.

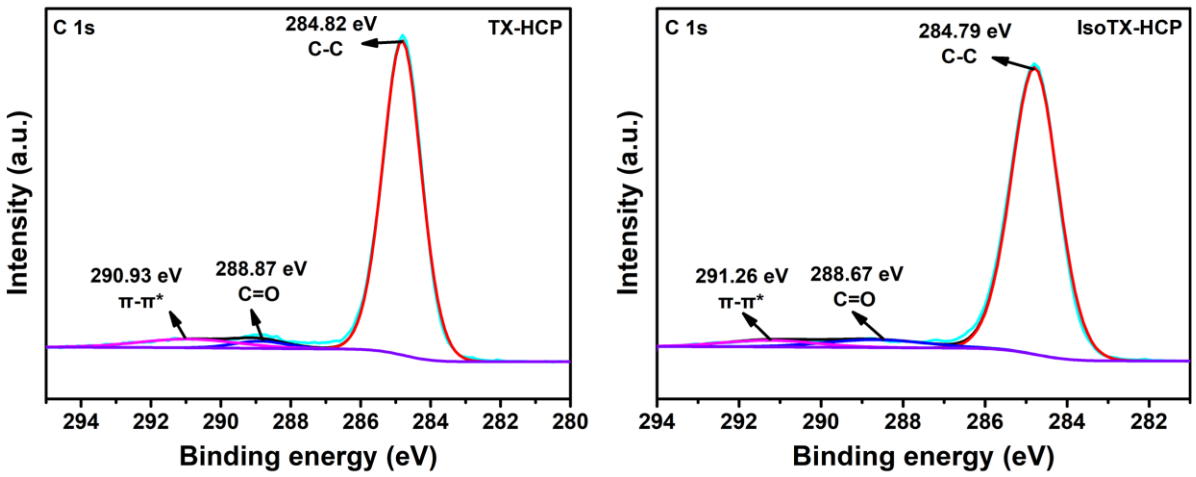


Fig. S5 C1s XPS spectra of TX-HCP and IsoTX-HCP.

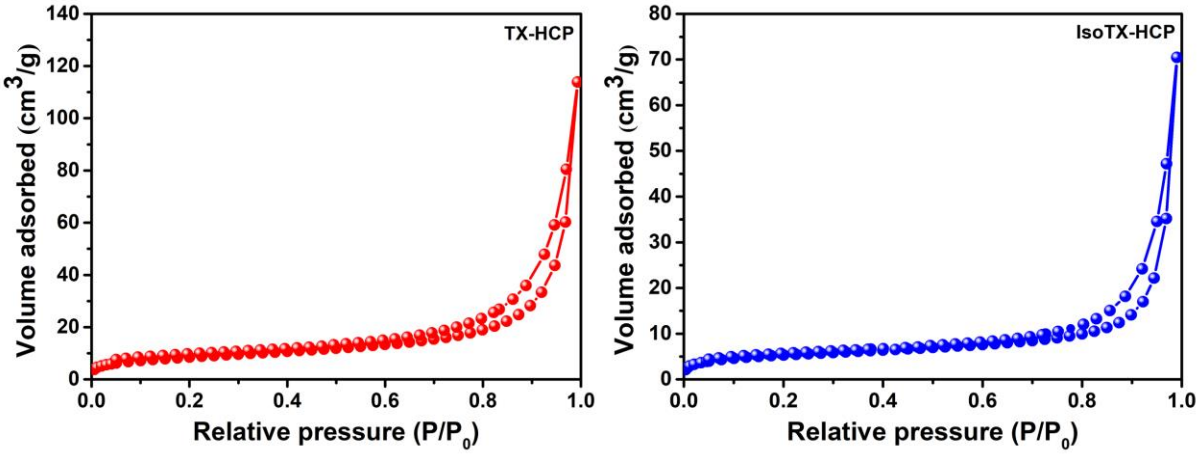


Fig. S6 N_2-physisorption isotherms of TX-HCP and IsoTX-HCP.

Surface Area	
Single point surface area at P/Po = 0.275377484:	29.5149 m²/g
BET Surface Area:	30.4645 m²/g
t-Plot Micropore Area:	2.0644 m²/g
t-Plot external surface area:	28.4001 m²/g
BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm width:	26.3864 m²/g
BJH Desorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm width:	27.9582 m²/g
Pore Volume	
Single point adsorption total pore volume of pores less than 40.3122 nm width at P/Po = 0.950000000:	0.069185 cm³/g
Single point desorption total pore volume of pores less than 40.3122 nm width at P/Po = 0.950000000:	0.095121 cm³/g
t-Plot micropore volume:	0.000738 cm³/g
BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm width:	0.174019 cm³/g
BJH Desorption cumulative volume of pores between 1.7000 nm and 300.0000 nm width:	0.172807 cm³/g
Pore Size	
Adsorption average pore diameter (4V/A by BET):	9.0840 nm
Desorption average pore diameter (4V/A by BET):	12.4894 nm
BJH Adsorption average pore width (4V/A):	26.3801 nm
BJH Desorption average pore width (4V/A):	24.7236 nm

Surface Area	
Single point surface area at P/Po = 0.275318302:	18.2551 m²/g
BET Surface Area:	18.9440 m²/g
t-Plot Micropore Area:	1.0108 m²/g
t-Plot external surface area:	17.9332 m²/g
BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm width:	15.3302 m²/g
BJH Desorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm width:	16.5308 m²/g
Pore Volume	
Single point adsorption total pore volume of pores less than 40.3122 nm width at P/Po = 0.950000000:	0.034660 cm³/g
Single point desorption total pore volume of pores less than 40.3122 nm width at P/Po = 0.950000000:	0.050281 cm³/g
t-Plot micropore volume:	0.000297 cm³/g
BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm width:	0.096323 cm³/g
BJH Desorption cumulative volume of pores between 1.7000 nm and 300.0000 nm width:	0.096639 cm³/g
Pore Size	
Adsorption average pore diameter (4V/A by BET):	7.3183 nm
Desorption average pore diameter (4V/A by BET):	10.6168 nm
BJH Adsorption average pore width (4V/A):	25.1329 nm
BJH Desorption average pore width (4V/A):	23.3840 nm

Fig. S7 Pore properties of TX-HCP (left) and IsoTX-HCP (right).

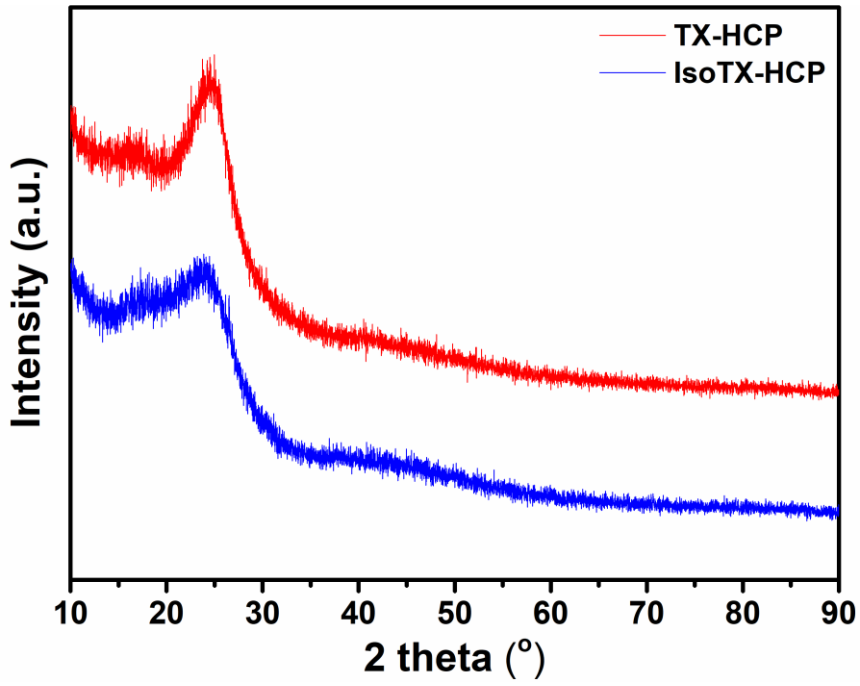


Fig. S8 PXRD patterns of TX-HCP and IsoTX-HCP.

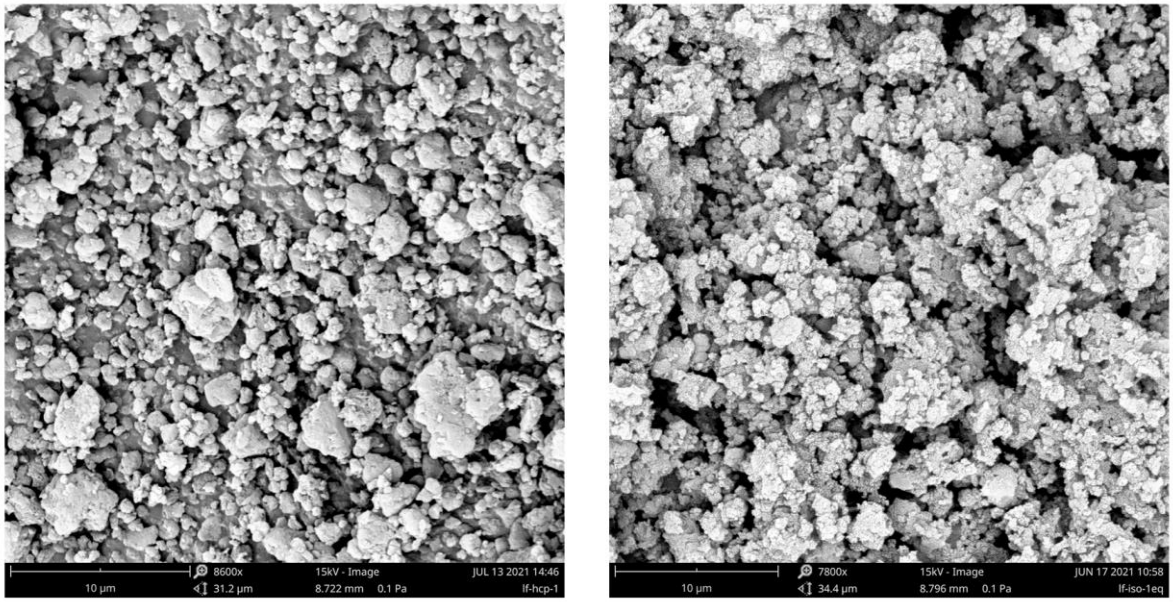
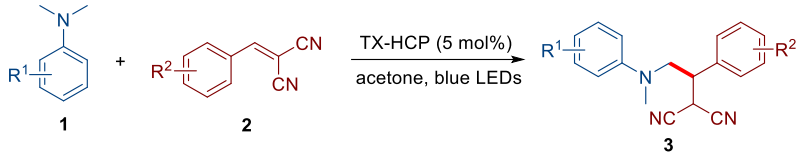
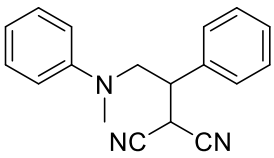


Fig. S9 SEM images of TX-HCP and IsoTX-HCP.

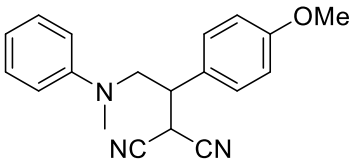
4. General Procedure for Visible-Light-Induced C-C Bond Formations



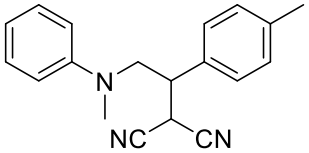
To a Schlenk tube were added the substrates **1** (0.3 mmol, 1.5 equiv), **2** (0.2 mmol, 1.0 equiv), TX-HCP (5 mol%), and acetone (1 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from a 30 W blue LEDs lamp. The mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the catalyst was separated by filtration and washed with dichloromethane. Then the filtrate was concentrated by rotary evaporation and the residue was purified by silica gel flash column chromatography using ethyl acetate/petroleum ether as the eluent to afford the desired products **3**. The analytical data of the products are summarized below.



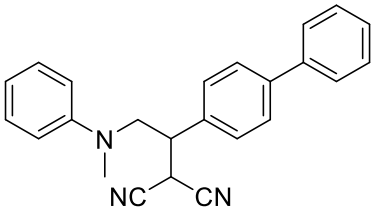
3a,[3] yellow oil, 50.3 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.39 (m, 5H), 7.32-7.28 (m, 2H), 6.88-6.80 (m, 3H), 4.23 (d, *J* = 4.4 Hz, 1H), 3.93-3.87 (m, 1H), 3.73-3.68 (m, 1H), 3.65-3.60 (m, 1H), 2.97 (s, 3H).



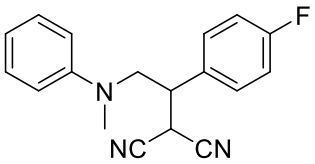
3b,[4] yellow oil, 51.4 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 4H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 2H), 4.19 (d, *J* = 4.4 Hz, 1H), 3.90-3.85 (m, 1H), 3.82 (s, 3H), 3.68-3.63(m, 1H), 3.60-3.55 (m, 1H), 2.96 (s, 3H).



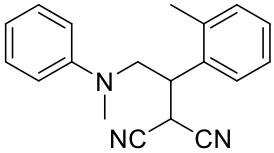
3c,[4] yellow oil, 49.5 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 6H), 6.86-6.79 (m, 3H), 4.19 (d, *J* = 4.4 Hz, 1H), 3.90-3.84 (m, 1H), 3.69-3.64 (m, 1H), 3.61-3.56 (m, 1H), 2.96 (s, 3H), 2.38 (s, 3H).



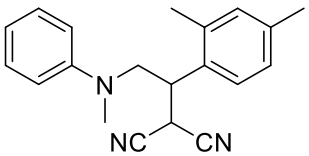
3d, white oil, 92.0 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.46-7.42 (m, 4H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.31-7.27 (m, 2H), 6.86-6.79 (m, 3H), 4.20 (d, *J* = 4.4 Hz, 1H), 3.92-3.86 (m, 1H), 3.72-3.63 (m, 2H), 2.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 142.1, 139.9, 133.7, 129.5, 128.8, 128.5, 127.9, 127.7, 127.0, 118.6, 113.7, 112.2, 111.8, 55.2, 44.3, 40.7, 26.9. IR (thin film): νmax (cm^{-1}) = 3662, 2988, 2901, 1599, 1505, 1450, 1412, 1343, 1242, 1066, 1008, 993, 908, 839, 752, 733, 695, 669. HRMS (ESI) calcd for $C_{24}H_{20}N_3$ $[M-H]^-$: 350.1663. Found: 350.1660.



3e,[4] white oil, 53.0 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.32-7.28 (m, 2H), 7.16 (t, *J* = 8.4 Hz, 2H), 6.88 (t, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 2H), 4.22 (d, *J* = 4.4 Hz, 1H), 3.88-3.82 (m, 1H), 3.69-3.59 (m, 2H), 2.96 (s, 3H).

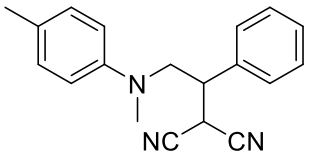


3f, white oil, 82.6 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 1H), 7.30-7.22 (m, 5H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 4.07 (d, *J* = 6.0 Hz, 1H), 4.02-3.97 (m, 1H), 3.94-3.88 (m, 1H), 3.64-3.59 (m, 1H), 2.88 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 137.0, 133.8, 131.4, 129.5, 128.7, 127.0, 126.0, 118.3, 113.3, 112.1, 111.9, 55.7, 40.7, 38.9, 26.4, 19.6. IR (thin film): νmax (cm^{-1}) = 1598, 1505, 1463, 1342, 1286, 1244, 1194, 1121, 1034, 993, 942, 910, 753, 728, 695. HRMS (ESI) calcd for $C_{19}H_{18}N_3$ $[M-H]^-$: 288.1506. Found: 288.1501.

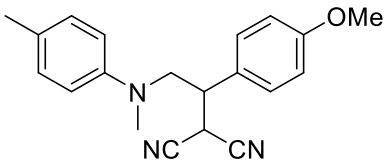


3g, yellow oil, 80.6 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.06 (s, 1H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 4.07 (d, *J* = 5.6 Hz, 1H), 3.96-3.87 (m, 2H), 3.63-3.58 (m, 1H), 2.90 (s, 3H), 2.32 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 138.5, 136.7, 132.2, 130.7, 129.5, 127.7, 125.9, 118.3, 113.3, 112.2, 112.0, 55.8, 40.8, 38.7, 26.6, 21.0, 19.6. IR

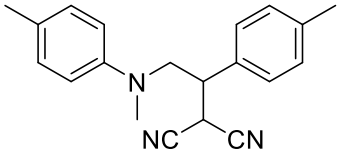
(thin film): νmax (cm^{-1}) = 2971, 2901, 1599, 1505, 1076, 1066, 1048, 1037, 993, 750, 734, 693, 669, 514, 452, 412. HRMS (ESI) calcd for $C_{20}H_{20}N_3$ $[M-H]^-$: 302.1663. Found: 302.1661.



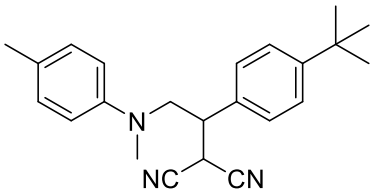
3h,[3] yellow oil, 40.4 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.39 (m, 5H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 4.30 (d, *J* = 4.4 Hz, 1H), 3.85-3.79 (m, 1H), 3.66-3.58 (m, 2H), 2.94 (s, 3H), 2.29 (s, 3H).



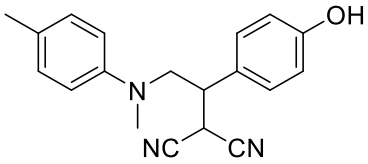
3i,[3] yellow oil, 49.9 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 4.25 (d, *J* = 4.0 Hz, 1H), 3.82 (s, 3H), 3.77-3.75 (m, 1H), 3.61-3.57 (m, 2H), 2.93 (s, 3H), 2.28 (s, 3H).



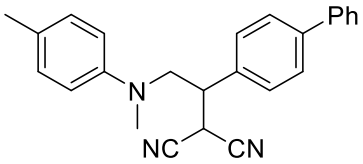
3j,[3] yellow oil, 53.3 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 5.2 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 4.25 (d, *J* = 4.4 Hz, 1H), 3.82-3.76 (m, 1H), 3.62-3.54 (m, 2H), 2.93 (s, 3H), 2.37 (s, 3H), 2.28 (s, 3H).



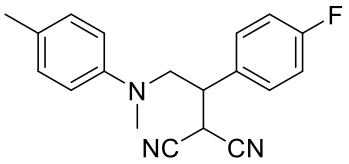
3k,[3] yellow oil, 52.6 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 4.27 (d, *J* = 4.4 Hz, 1H), 3.82-3.76 (m, 1H), 3.64-3.55 (m, 2H), 2.94 (s, 3H), 2.28 (s, 3H), 1.33 (s, 9H).



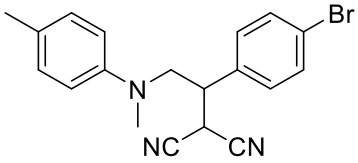
3l, yellow oil, 55.6 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 5.65 (s, 1H), 4.27 (d, *J* = 4.4 Hz, 1H), 3.79-3.73 (m, 1H), 3.61-3.53 (m, 2H), 2.93 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 146.6, 130.1, 129.5, 128.6, 126.6, 116.2, 114.7, 112.4, 111.8, 55.6, 44.2, 41.3, 27.2, 20.3. IR (thin film): νmax (cm^{-1}) = 1614, 1515, 1446, 1351,1266, 1212, 1191, 1177, 1121, 909, 832, 804, 730, 538, 518. HRMS (ESI) calcd for $C_{19}H_{18}N_3O$ $[M-H]^-$: 304.1455. Found: 304.1448.



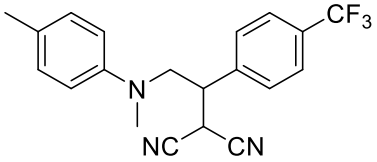
3m,[3] yellow oil, 54.7 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.48-7.44 (m, 4H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.33 (d, *J* = 4.4 Hz, 1H), 3.87-3.81 (m, 1H), 3.70-3.63 (m, 2H), 2.97 (s, 3H), 2.29 (s, 3H).



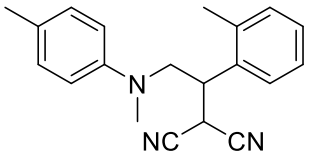
3n,[3] yellow oil, 44.7 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.16-7.10 (m, 4H), 6.75 (d, *J* = 8.8 Hz, 2H), 4.28 (d, *J* = 4.0 Hz, 1H), 3.80-3.74 (m, 1H), 3.62-3.55 (m, 2H), 2.94 (s, 3H), 2.29 (s, 3H).



3o,[3] yellow oil, 52.5 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 4.29 (d, *J* = 4.4 Hz, 1H), 3.80-3.73 (m, 1H), 3.62-3.54 (m, 2H), 2.93 (s, 3H), 2.29 (s, 3H).

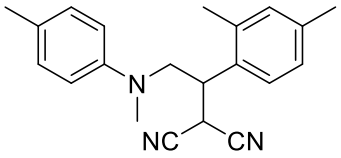


3p,[3] yellow oil, 45.5 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 4.35 (d, *J* = 4.4 Hz, 1H), 3.84-3.78 (m, 1H), 3.66-3.63 (m, 2H), 2.95 (s, 3H), 2.29 (s, 3H).

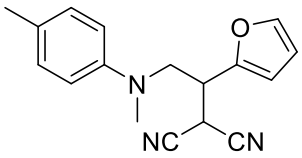


3q,[3] yellow oil, 53.2 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 6.8 Hz, 1H), 7.32-7.24 (m, 3H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 4.16 (d, *J* = 5.6 Hz, 1H),

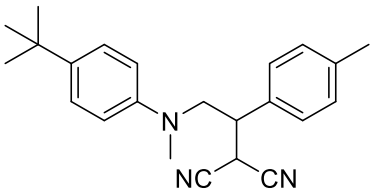
4.01-3.96 (m, 1H), 3.86-3.80 (m, 1H), 3.60-3.55 (m, 1H), 2.90 (s, 3H), 2.32 (s, 3H), 2.28 (s, 3H).



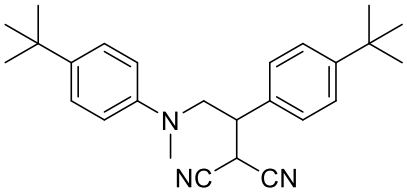
3r, yellow oil, 72.5 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 3H), 7.06 (s, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 4.12 (d, *J* = 5.6 Hz, 1H), 3.95-3.92 (m, 1H), 3.84-3.77(m, 1H), 3.57-3.52 (m, 1H), 2.89 (s, 3H), 2.32 (s, 3H), 2.28 (d, *J* = 2.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 138.5, 136.7, 132.1, 130.8, 130.0, 128.0, 127.7, 126.0, 114.1, 112.3, 112.1, 56.0, 41.3, 38.8, 26.5, 21.0, 20.2, 19.6. IR (thin film): νmax (cm^{-1}) = 2971, 2901, 1519, 1450, 1407, 1394, 1379, 1343, 1241, 1191, 1066, 1057, 909, 805, 733. HRMS (ESI) calcd for $C_{21}H_{22}N_3$ [M-H]$^-$: 316.1819. Found: 316.1810.



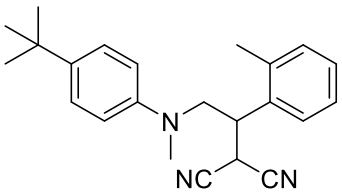
3s, yellow oil, 46.3 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.43-6.41 (m, 2H), 4.21 (d, *J* = 4.4 Hz, 1H), 3.79-3.69 (m, 3H), 2.90 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 146.2, 143.4, 130.1, 128.4, 114.3, 111.9, 111.3, 110.8, 109.6, 53.9, 40.8, 39.0, 25.2, 20.2. IR (thin film): νmax (cm^{-1}) = 2878, 1615, 1519, 1328, 1190, 1148, 1118, 1074, 1014, 910, 885, 806, 743, 598. HRMS (ESI) calcd for $C_{17}H_{16}N_3O$ [M-H]$^-$: 278.1299. Found: 278.1291.



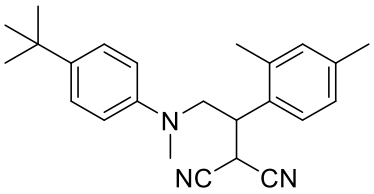
3t,[3] yellow oil, 58.0 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 4H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.27 (d, *J* = 4.0 Hz, 1H), 3.84-3.77 (m, 1H), 3.65-3.56 (m, 2H), 2.96 (s, 3H), 2.38 (s, 3H), 1.30 (s, 9H).



3u,[3] yellow oil, 58.7 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.35-7.32 (m, 4H), 6.79 (d, *J* = 9.2 Hz, 2H), 4.30 (d, *J* = 4.0 Hz, 1H), 3.84-3.77 (m, 1H), 3.67-3.58 (m, 2H), 2.98 (s, 3H), 1.34 (s, 9H), 1.31 (s, 9H).

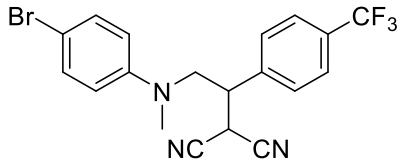


3v,[3] yellow oil, 51.4 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.2 Hz, 1H), 7.33-7.22 (m, 5H), 6.76 (d, *J* = 9.2 Hz, 2H), 4.19 (d, *J* = 5.6 Hz, 1H), 4.04-3.99 (m, 1H), 3.86-3.80 (m, 1H), 3.62-3.57 (m, 1H), 2.92 (s, 3H), 2.35 (s, 3H), 1.30 (s, 9H).



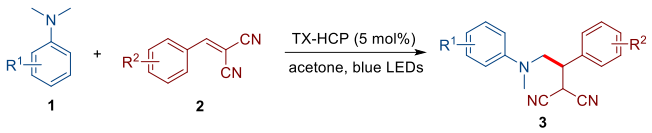
3w,[3] yellow oil, 54.7 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 1H),

7.33 (d, *J* = 9.2 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.08 (s, 1H), 6.76 (d, *J* = 9.2 Hz, 2H), 4.18 (d, *J* = 5.6 Hz, 1H), 4.00-3.95 (m, 1H), 3.84-3.78 (m, 1H), 3.60-3.55 (m, 1H), 2.94 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H), 1.30 (s, 9H).



3x,[3] white oil, 59.3 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 9.2 Hz, 2H), 6.66 (d, *J* = 9.2 Hz, 2H), 4.21 (d, *J* = 4.8 Hz, 1H), 3.94-3.87 (m, 1H), 3.71-3.64 (m, 2H), 2.93 (s, 3H).

5. Recyclability tests of TX-HCP



cycle	results
1	**3q**, 86% yield, 48 h
2	**3q**, 86% yield, 48 h
3	**3q**, 83% yield, 48 h
4	**3q**, 84% yield, 64 h
5	**3q**, 84% yield, 72 h

cycle	results
1	**3q**, 86% yield, 48 h
2	**3j**, 90% yield, 48 h
3	**3i**, 78% yield, 48 h
4	**3g**, 87% yield, 64 h
5	**3d**, 85% yield, 72 h

6. References

1. L. Wang, Y. Zhang, H. Jiang and H. Wang, *Ind. Eng. Chem. Res.*, 2020, **59**, 15955-15966.

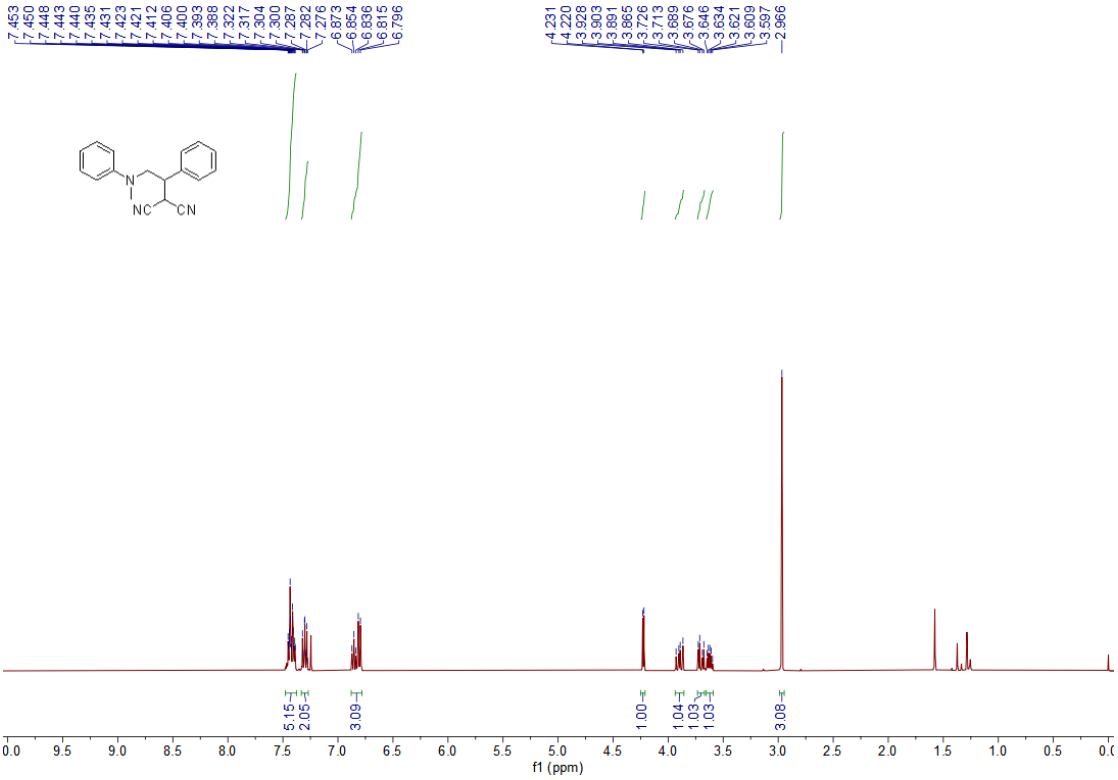
2. M. Tajbakhsh, R. Hosseinzadeh, H. Alinezhad, S. Ghahari, A. Heydari and S. Khaksarc, *Synthesis*, 2011, **3**, 490-496.

3. S. Zhu, A. Das, L. Bui, H. Zhou, D. P. Curran and M. Rueping, *J. Am. Chem. Soc.*, 2013, **135**, 1823-1829.

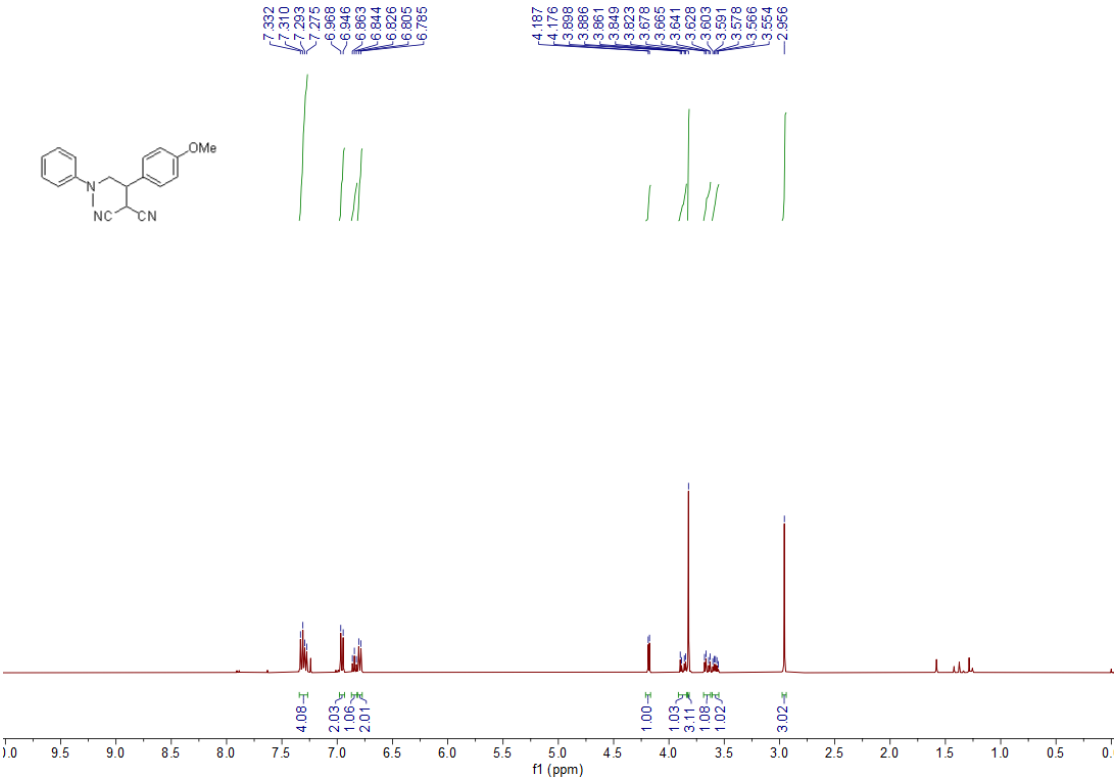
4. Y. Cai, Y. Tang, L. Fan, Q. Lefebvre, H. Hou and M. Rueping, *ACS Catal.*, 2018, **8**, 9471-9476.

7. Copies of NMR spectra

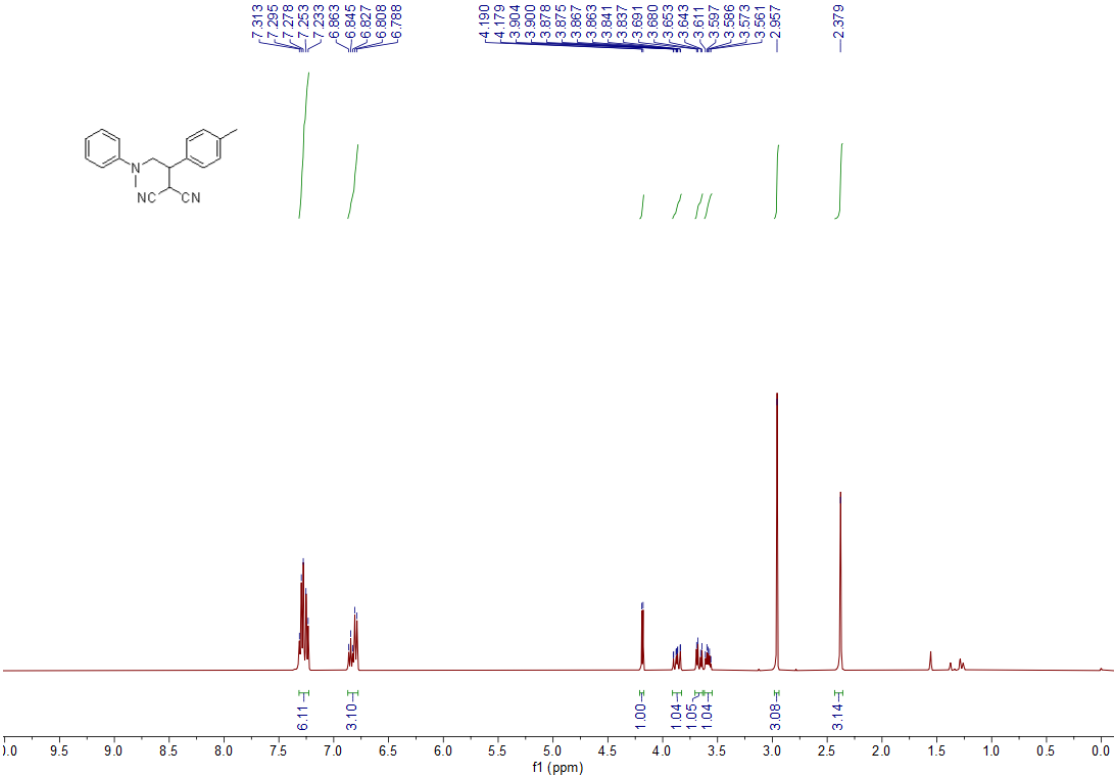
^{1}H NMR Spectrum of **3a**



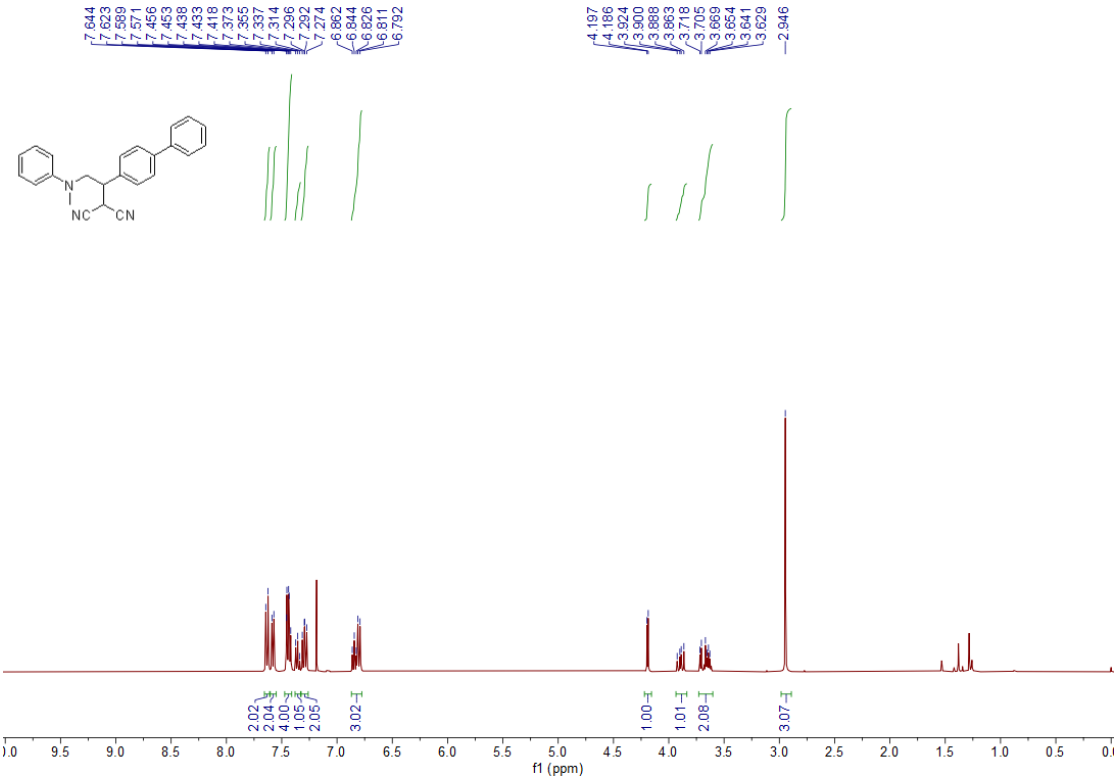
^{1}H NMR Spectrum of **3b**



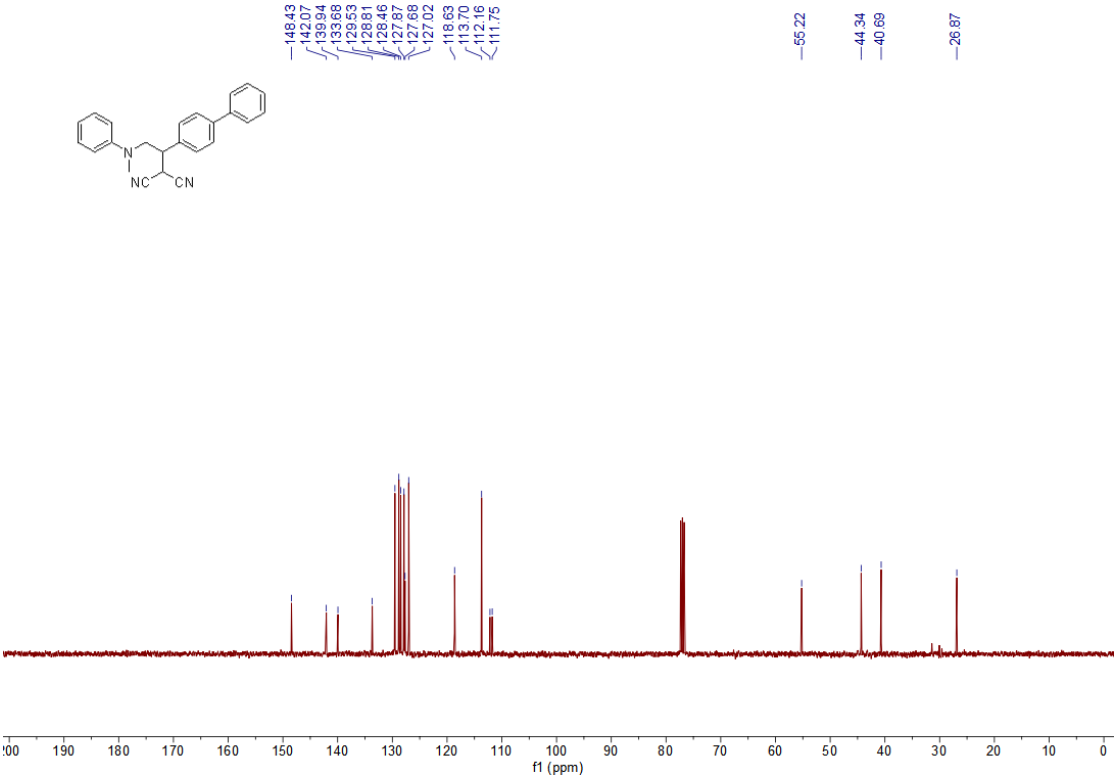
^{1}H NMR Spectrum of **3c**



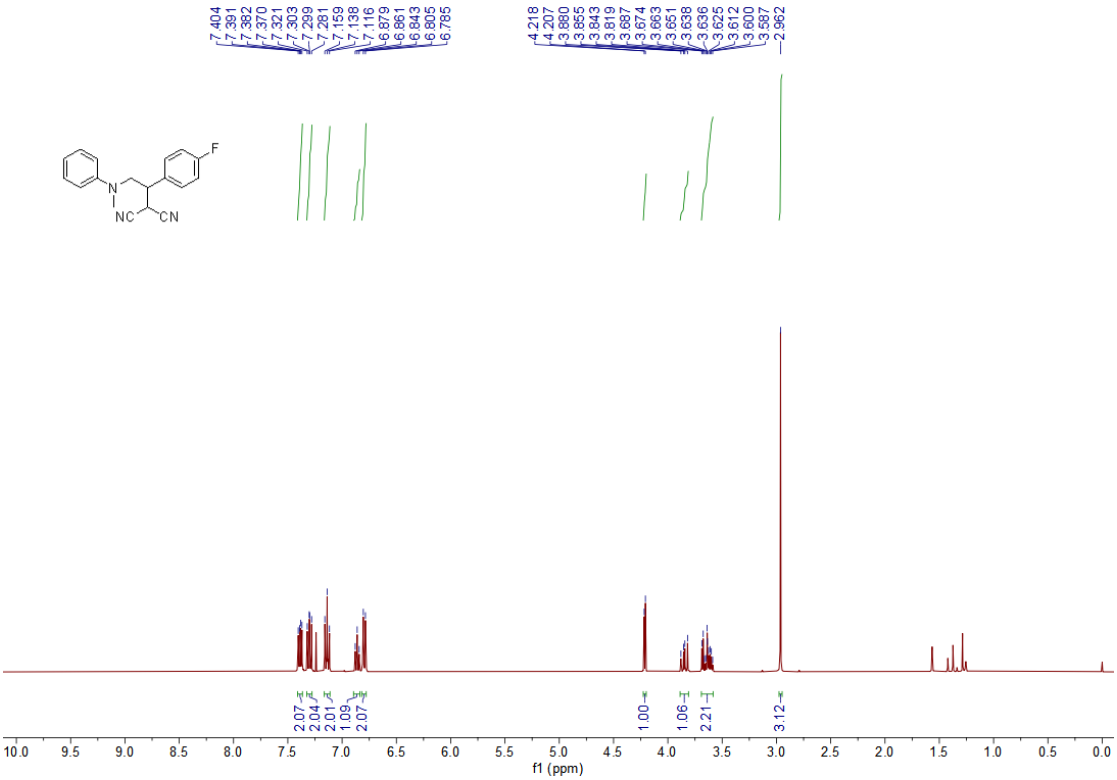
^{1}H NMR Spectrum of **3d**



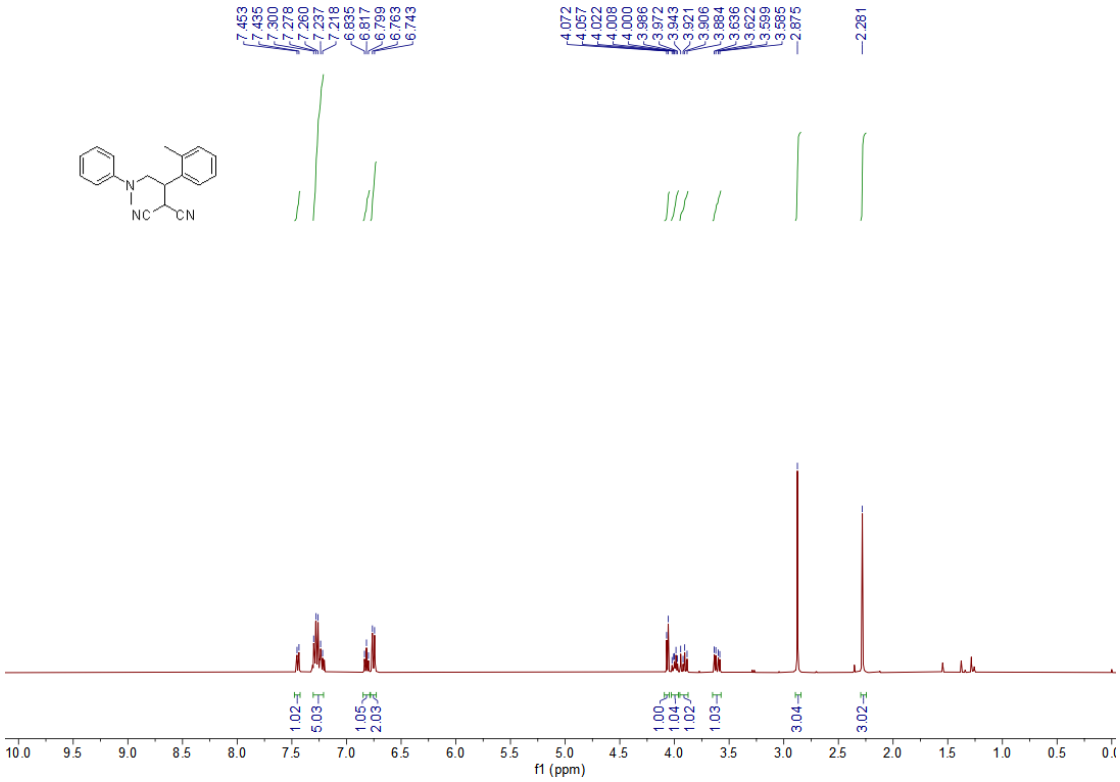
^{13}C NMR Spectrum of **3d**



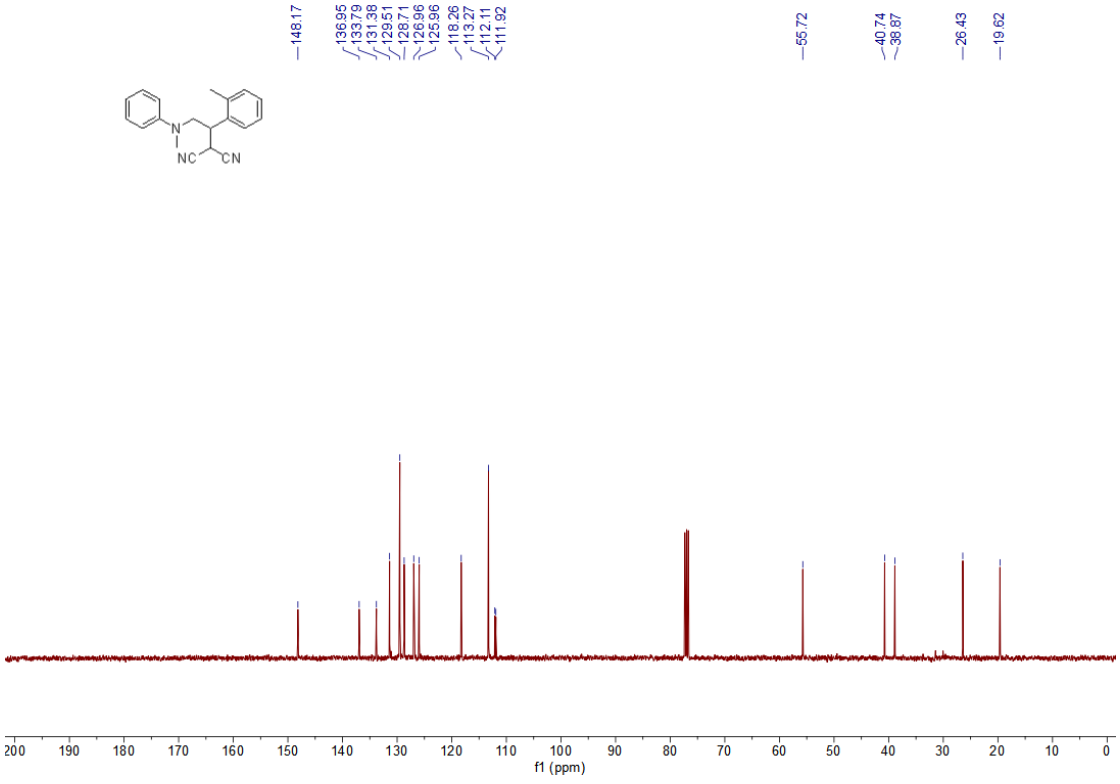
^{1}H NMR Spectrum of **3e**



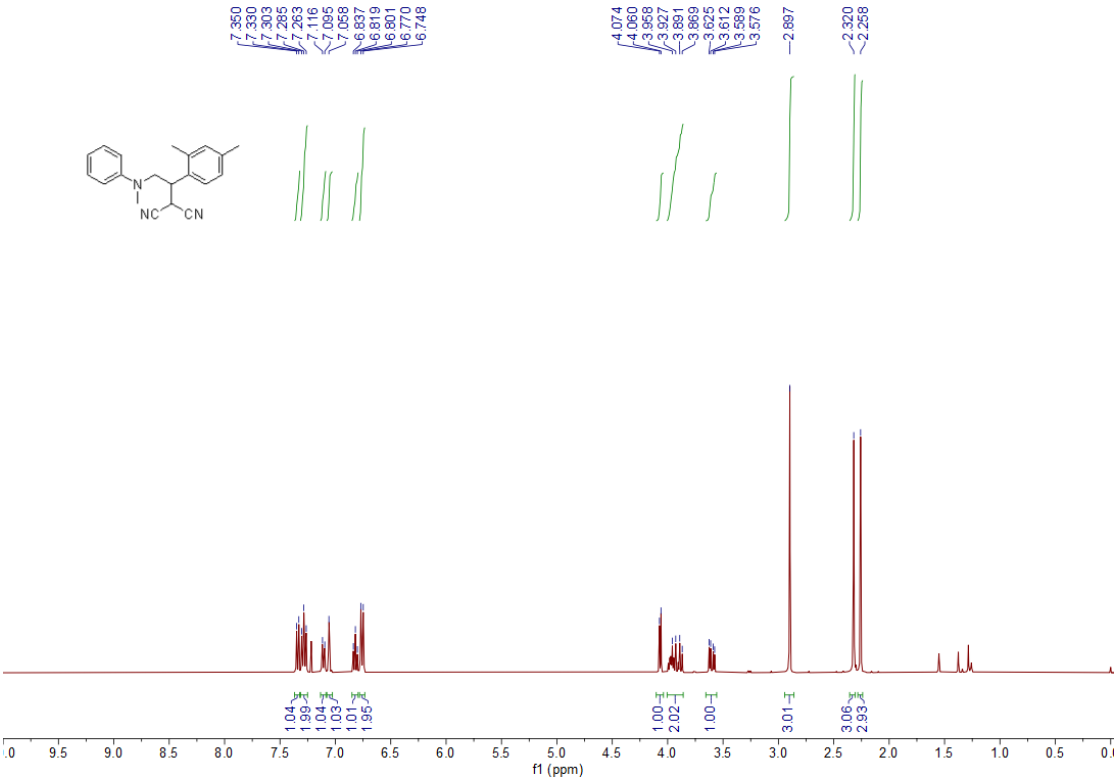
^{1}H NMR Spectrum of **3f**



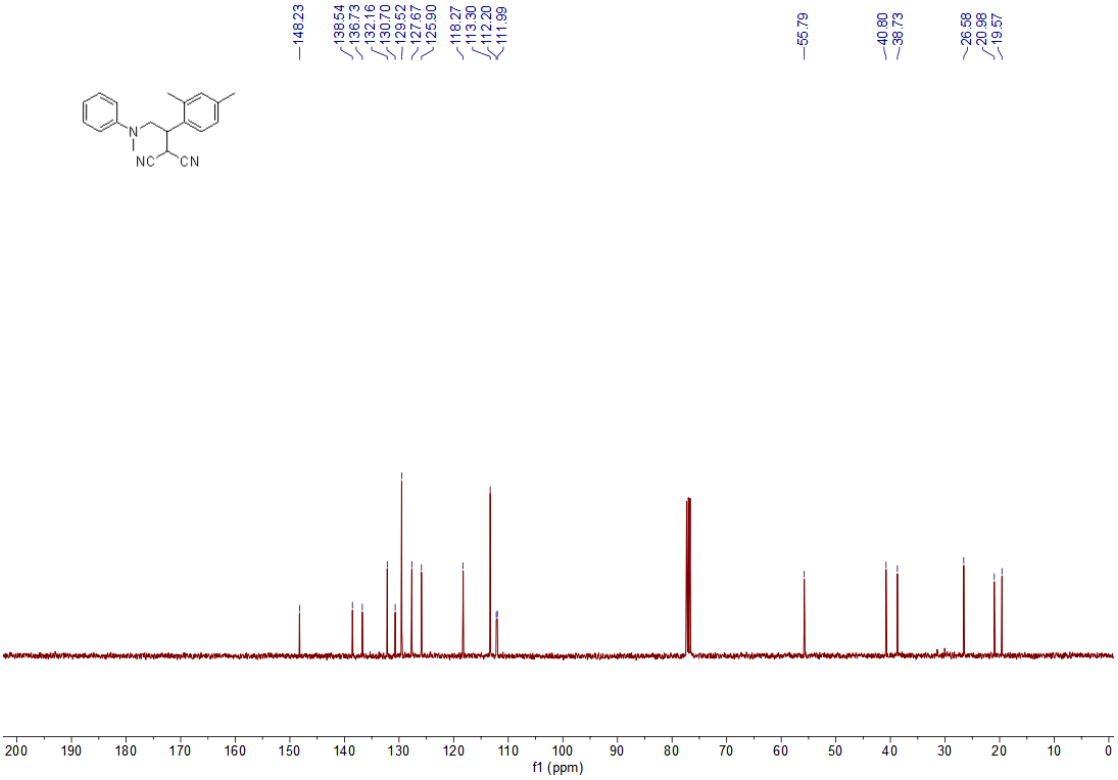
^{13}C NMR Spectrum of **3f**



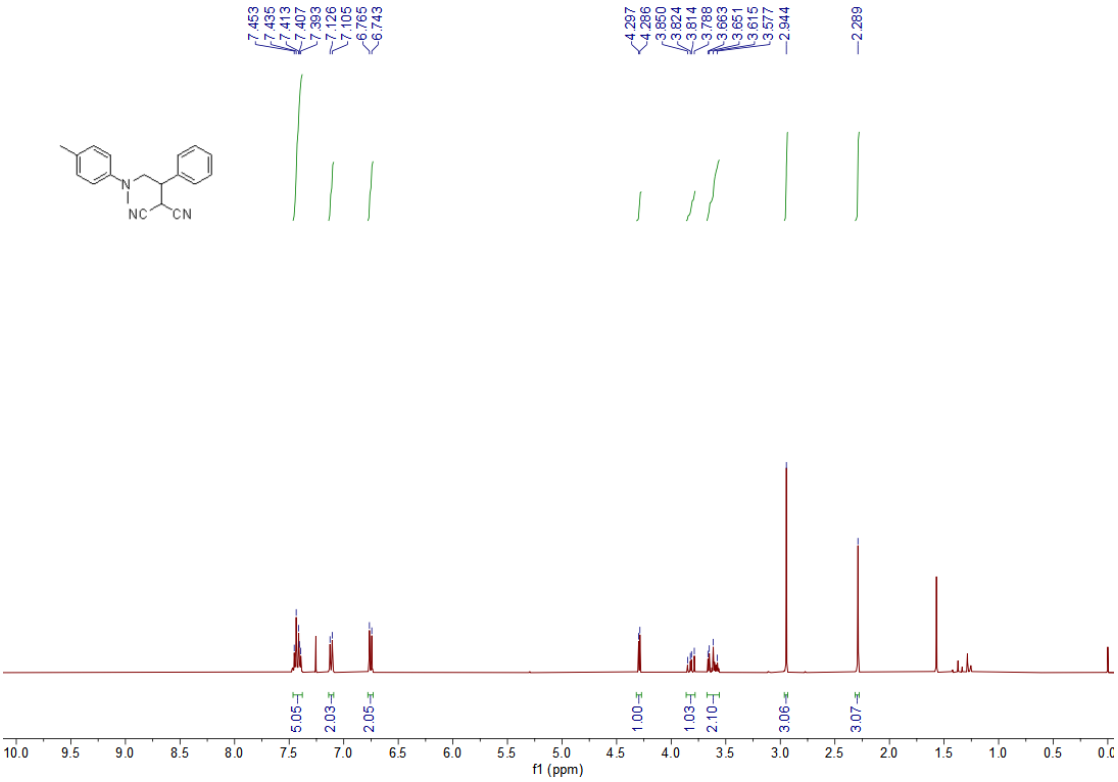
^{1}H NMR Spectrum of **3g**



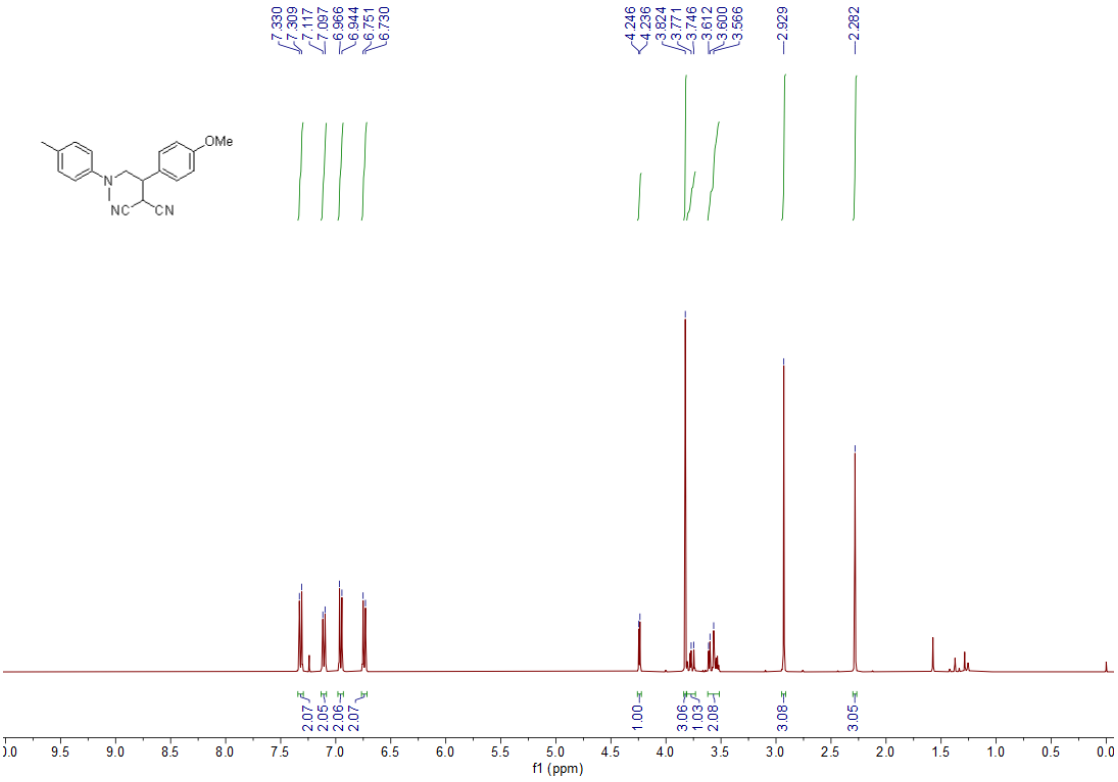
^{13}C NMR Spectrum of **3g**



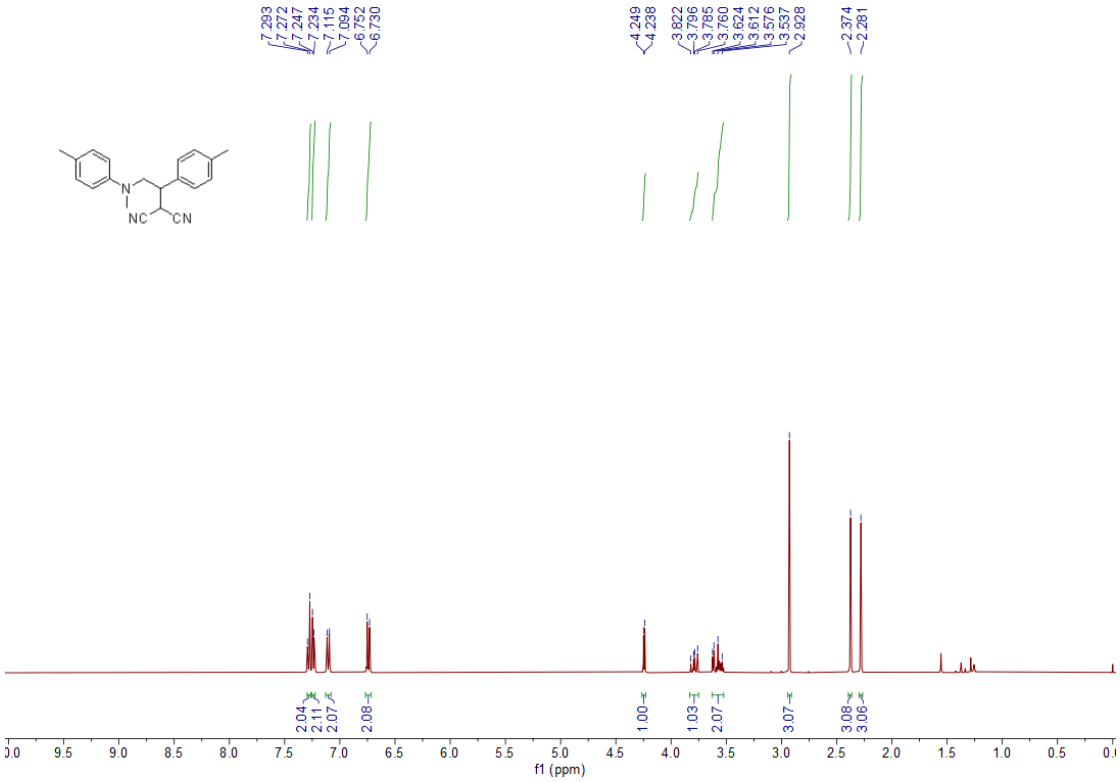
^{1}H NMR Spectrum of **3h**



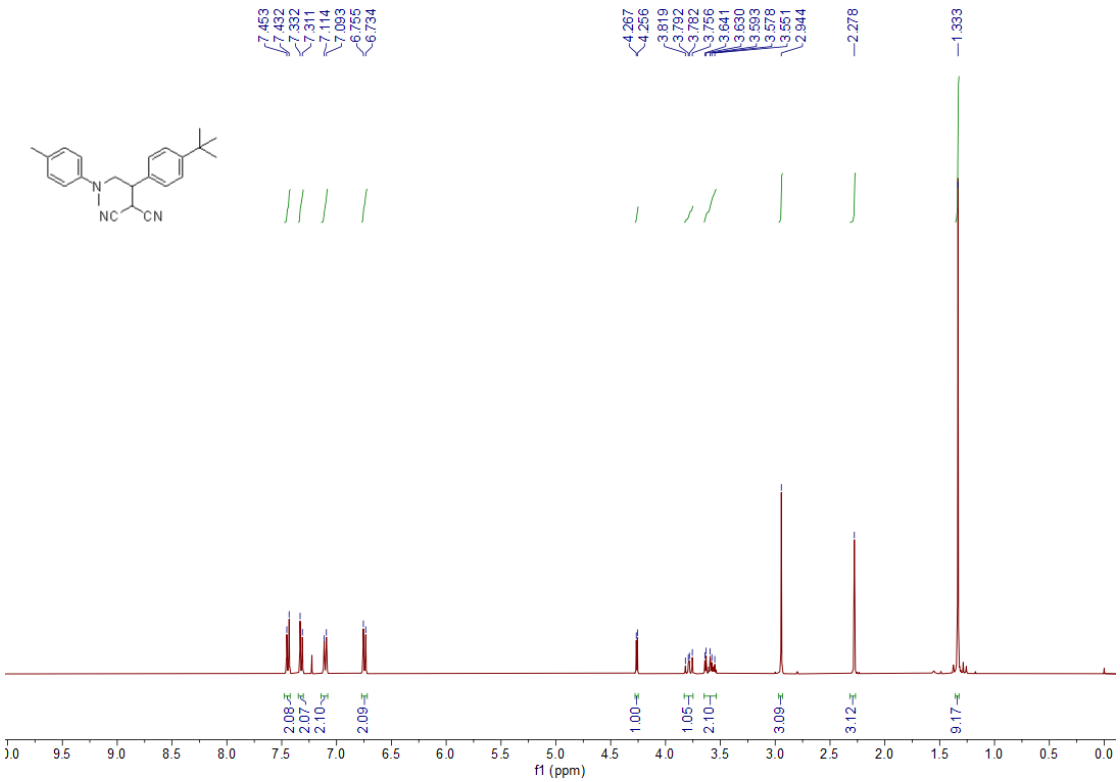
^{1}H NMR Spectrum of **3i**



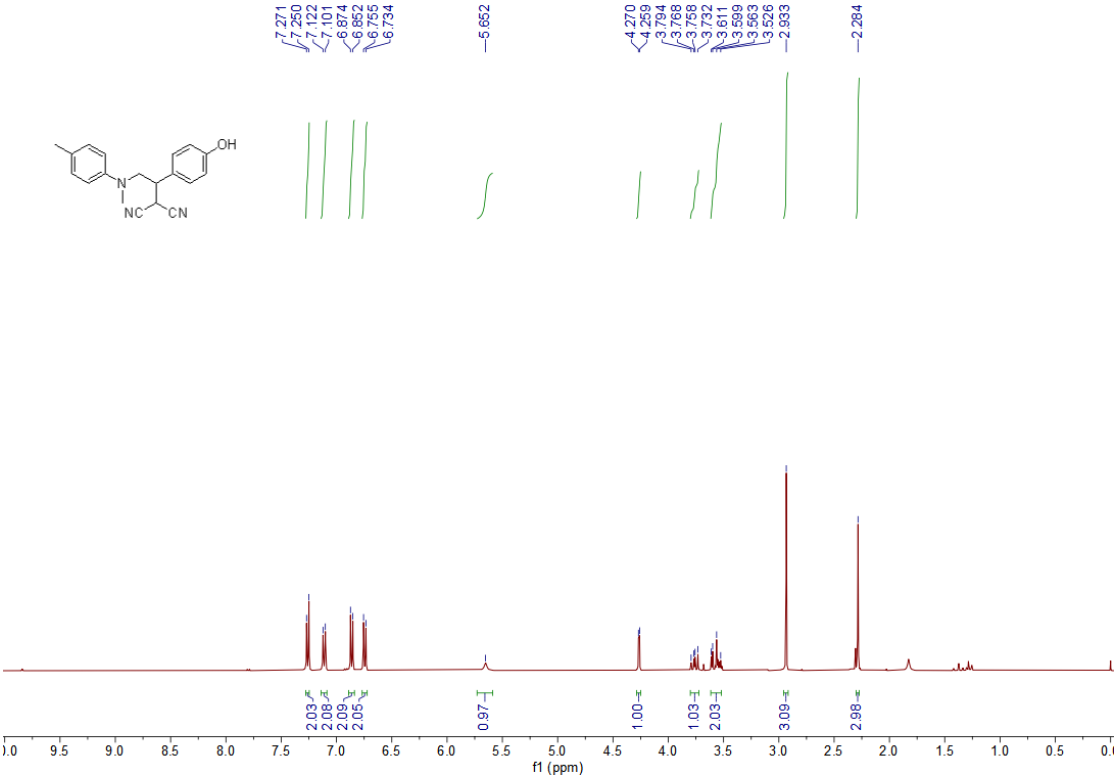
^{1}H NMR Spectrum of **3j**



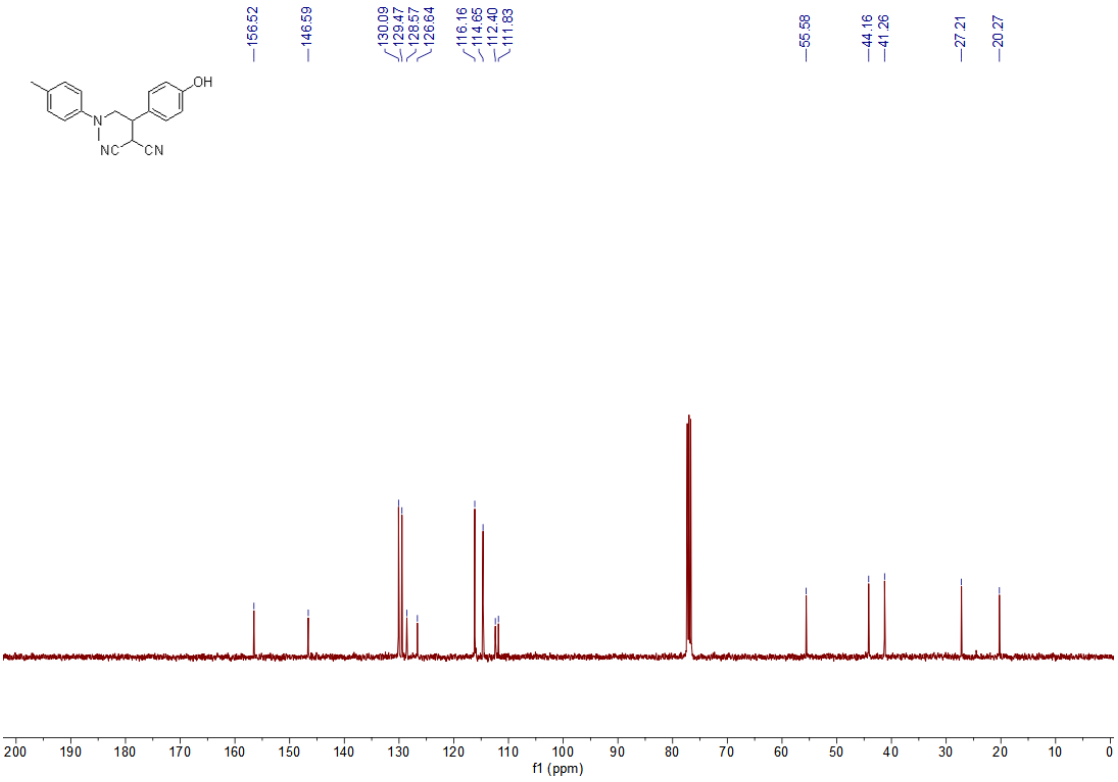
^{1}H NMR Spectrum of **3k**



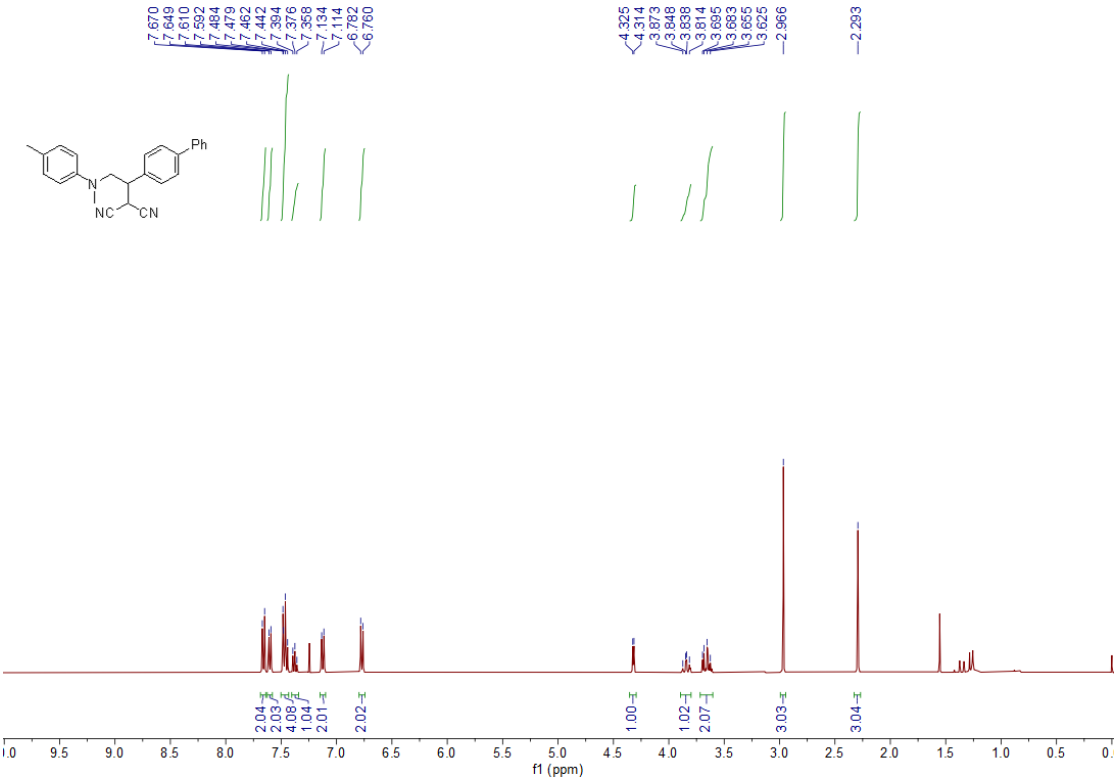
^{1}H NMR Spectrum of **3l**



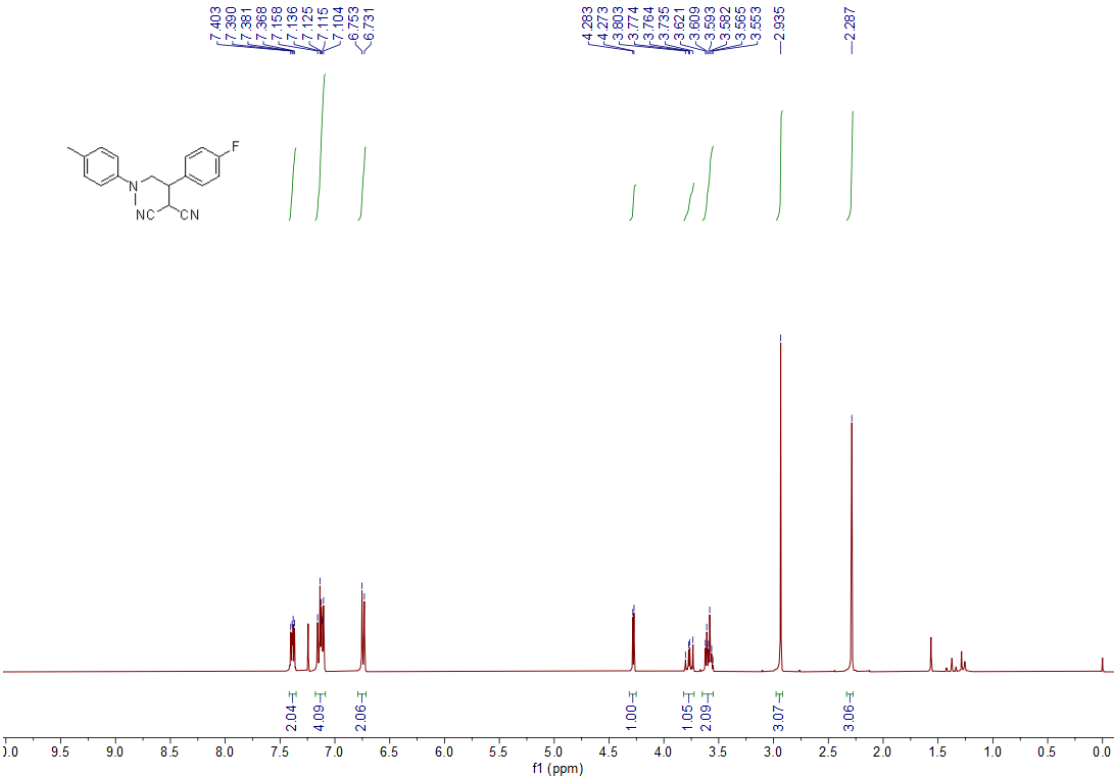
^{13}C NMR Spectrum of **3l**



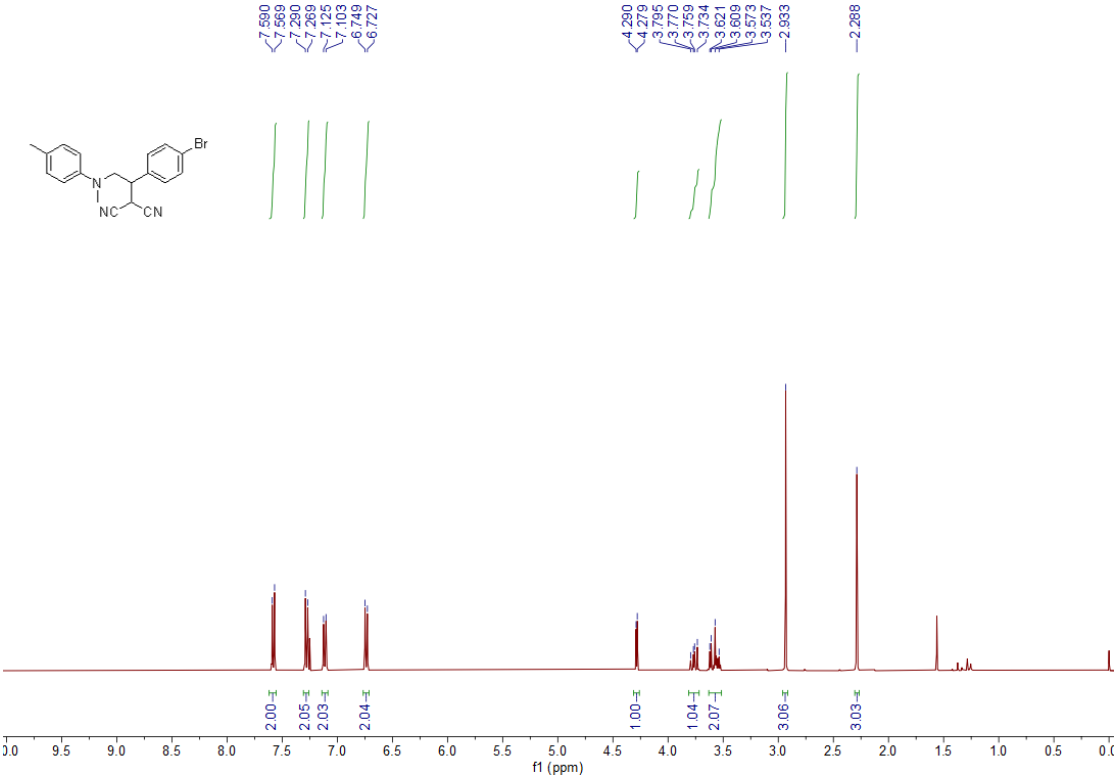
^{1}H NMR Spectrum of **3m**



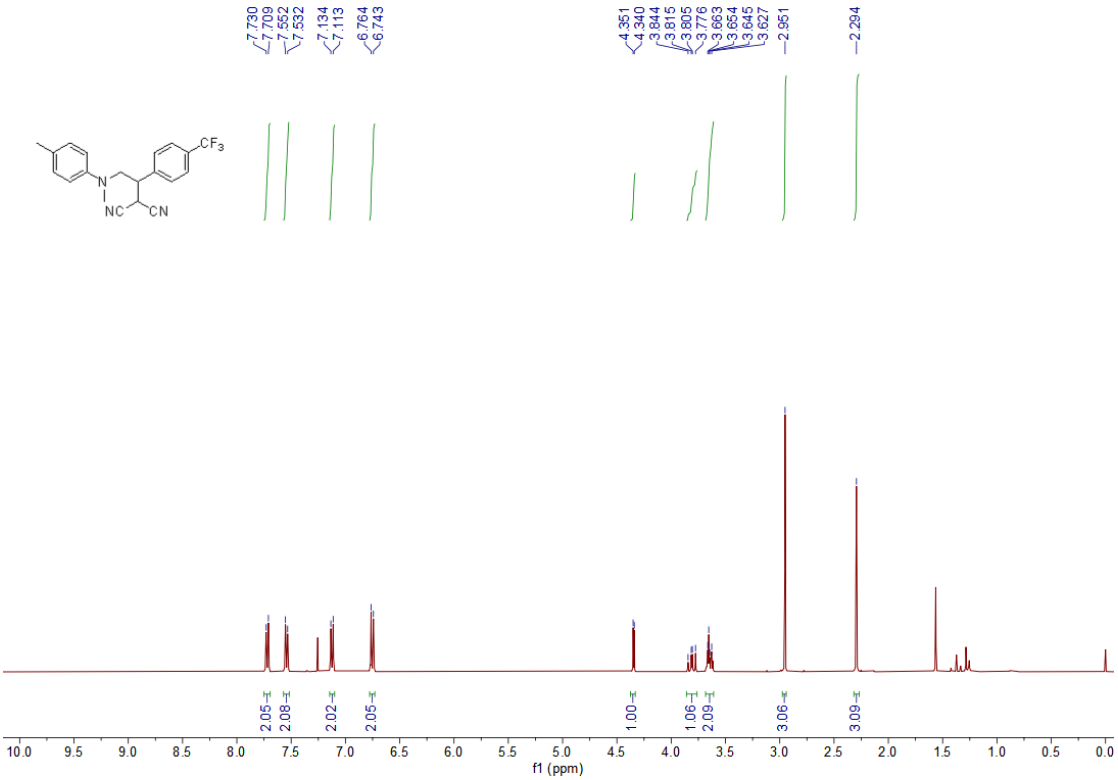
^{1}H NMR Spectrum of **3n**



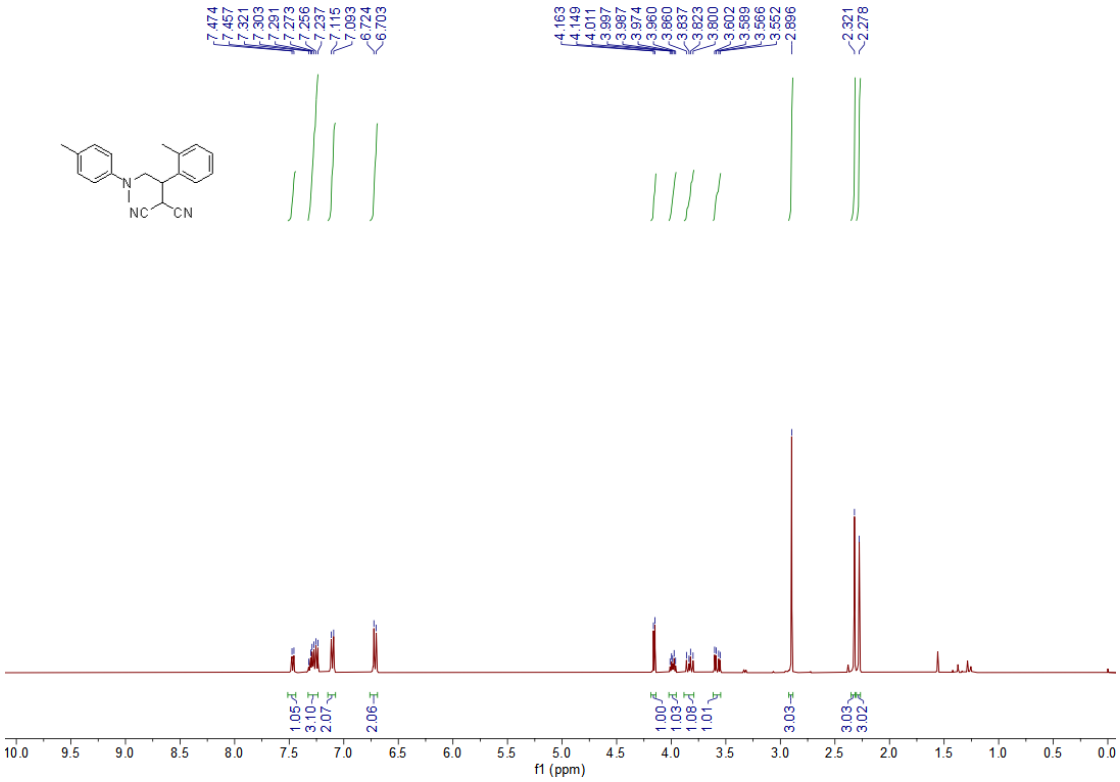
^{1}H NMR Spectrum of **3o**



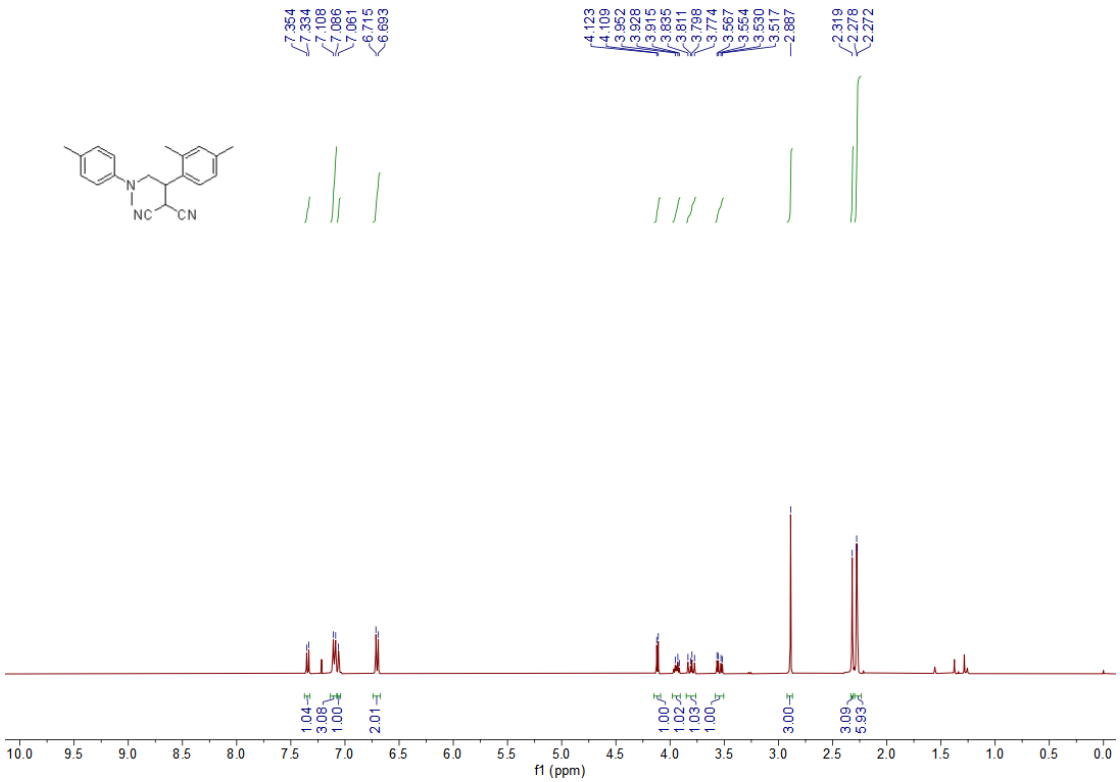
^{1}H NMR Spectrum of **3p**



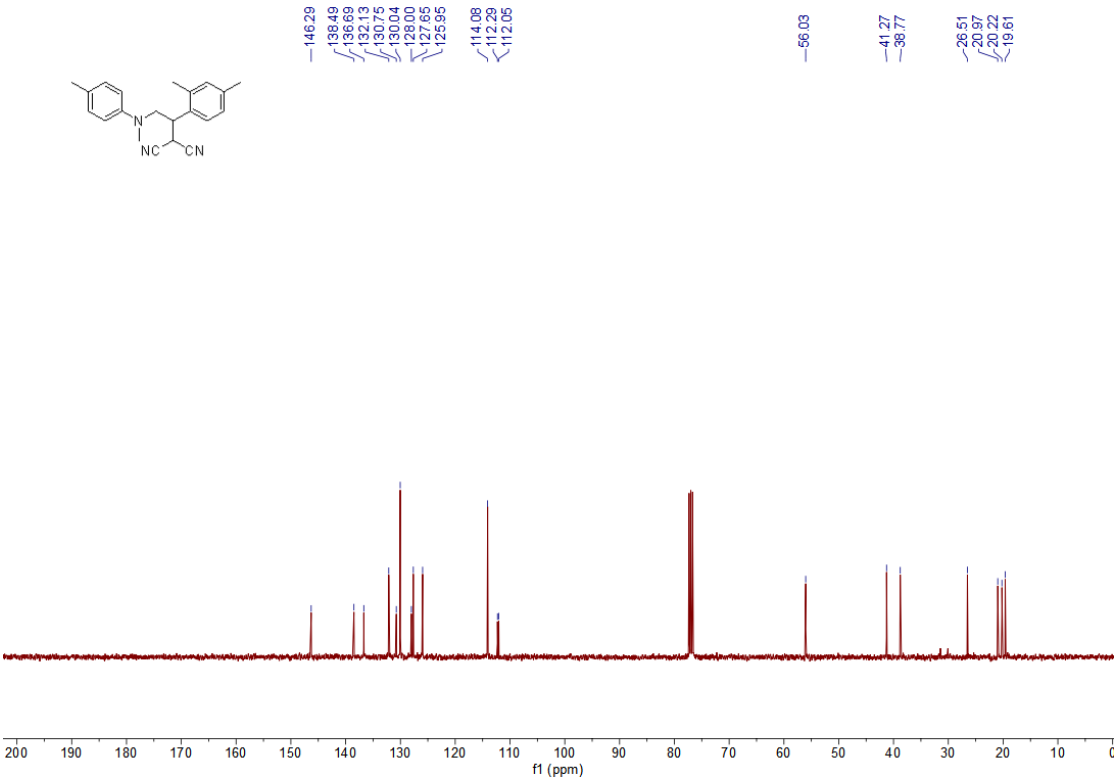
^{1}H NMR Spectrum of **3q**



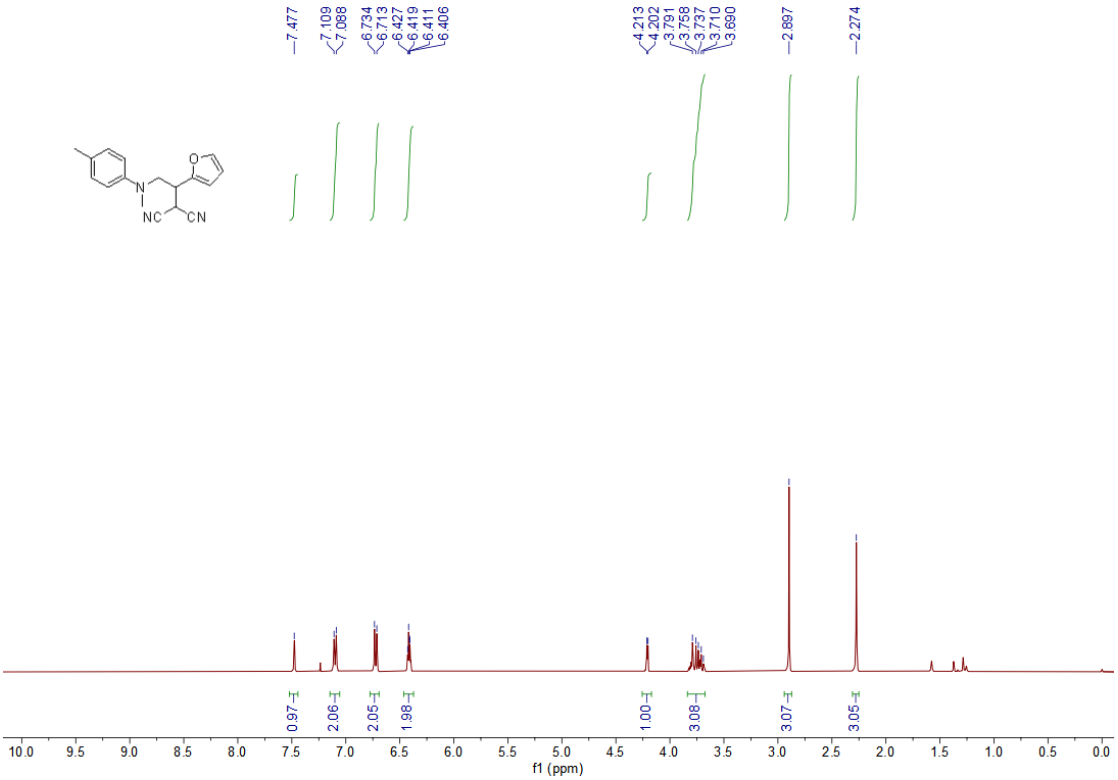
^{1}H NMR Spectrum of **3r**



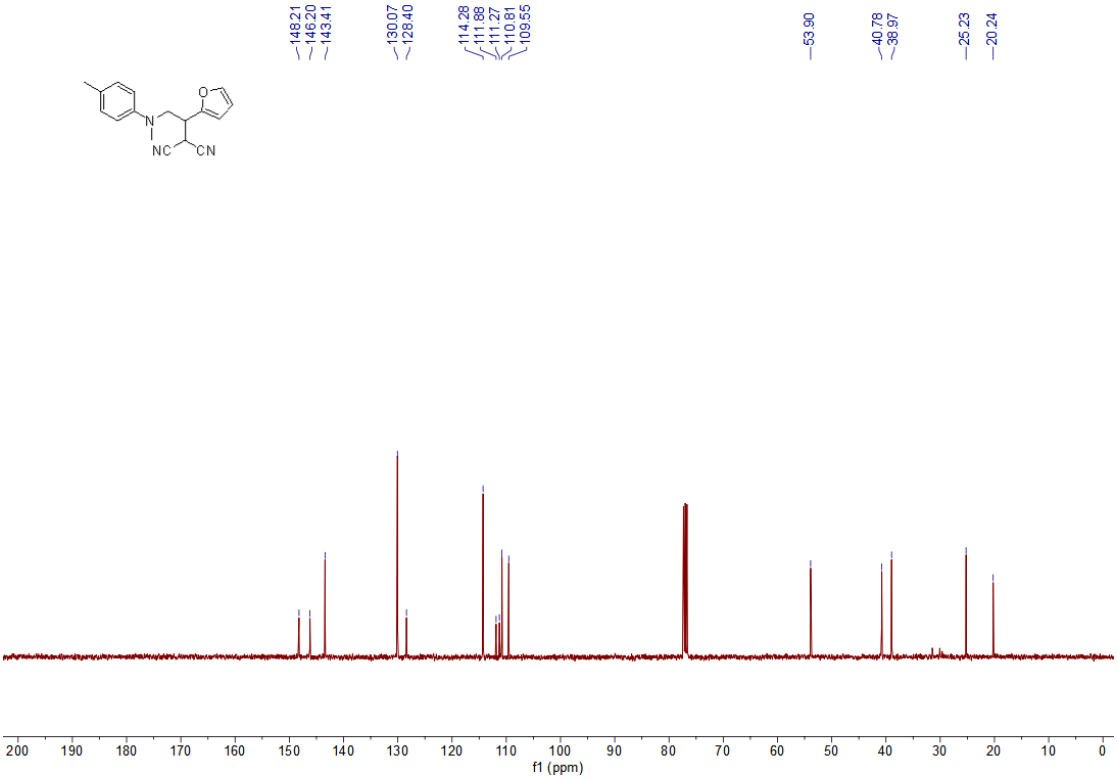
^{13}C NMR Spectrum of **3r**



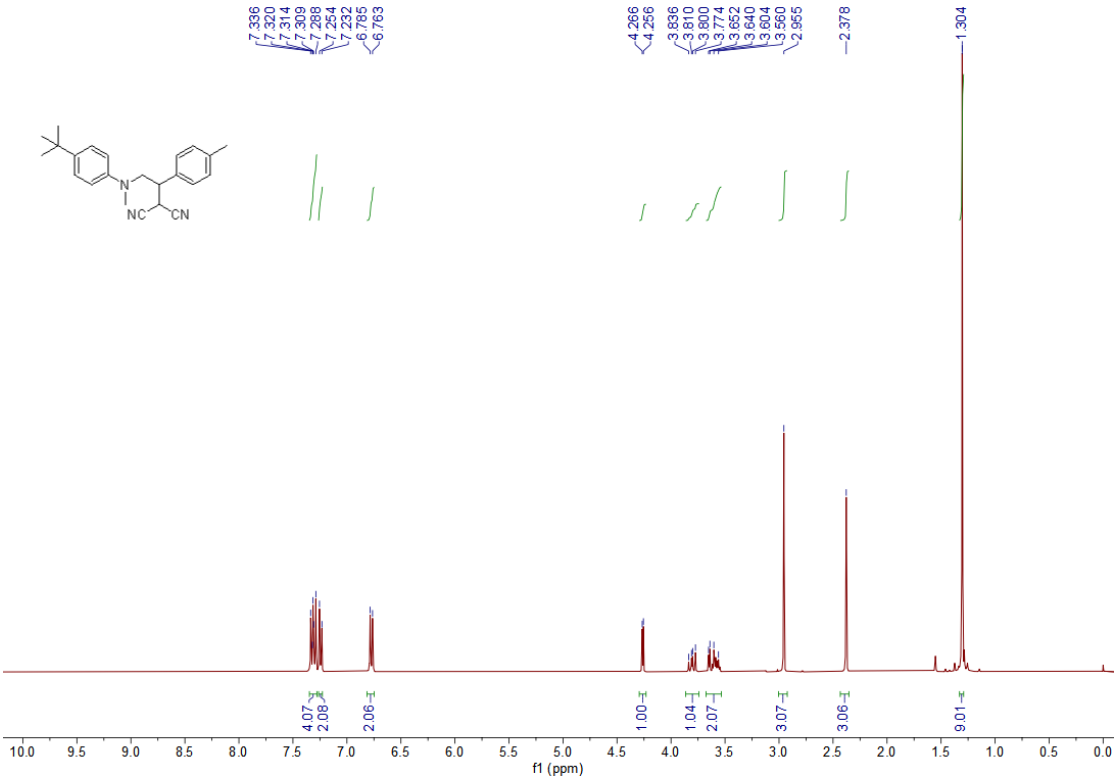
^{1}H NMR Spectrum of **3s**



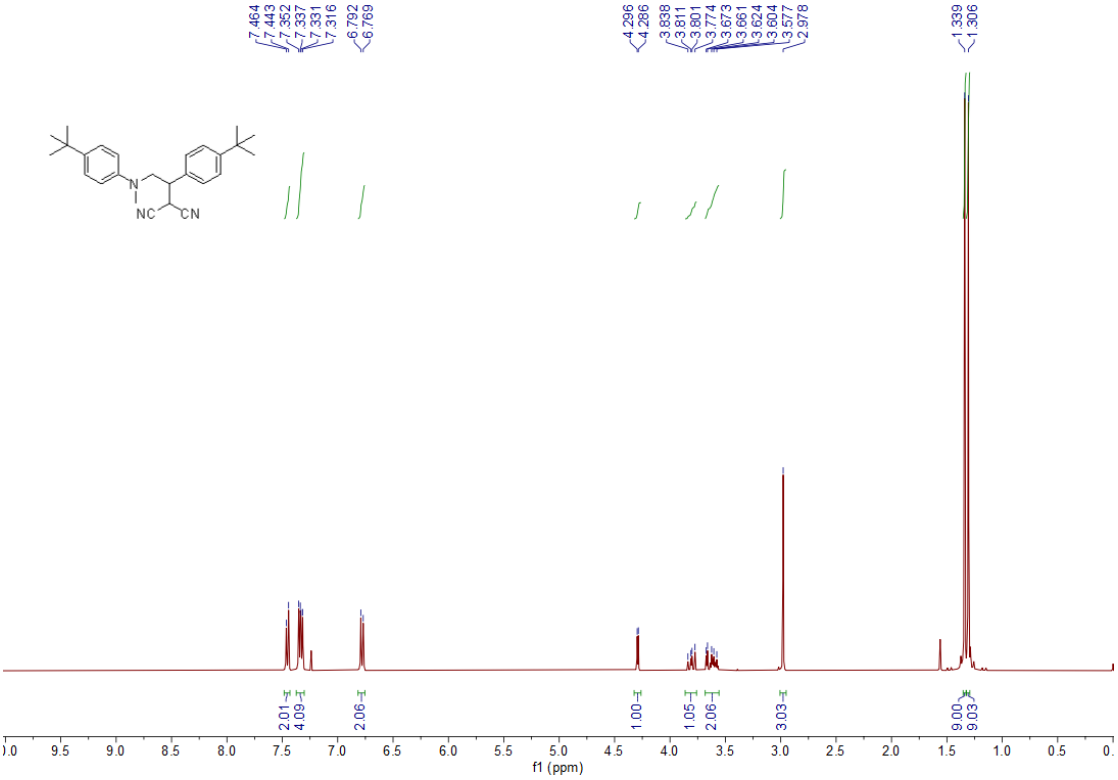
^{13}C NMR Spectrum of **3s**



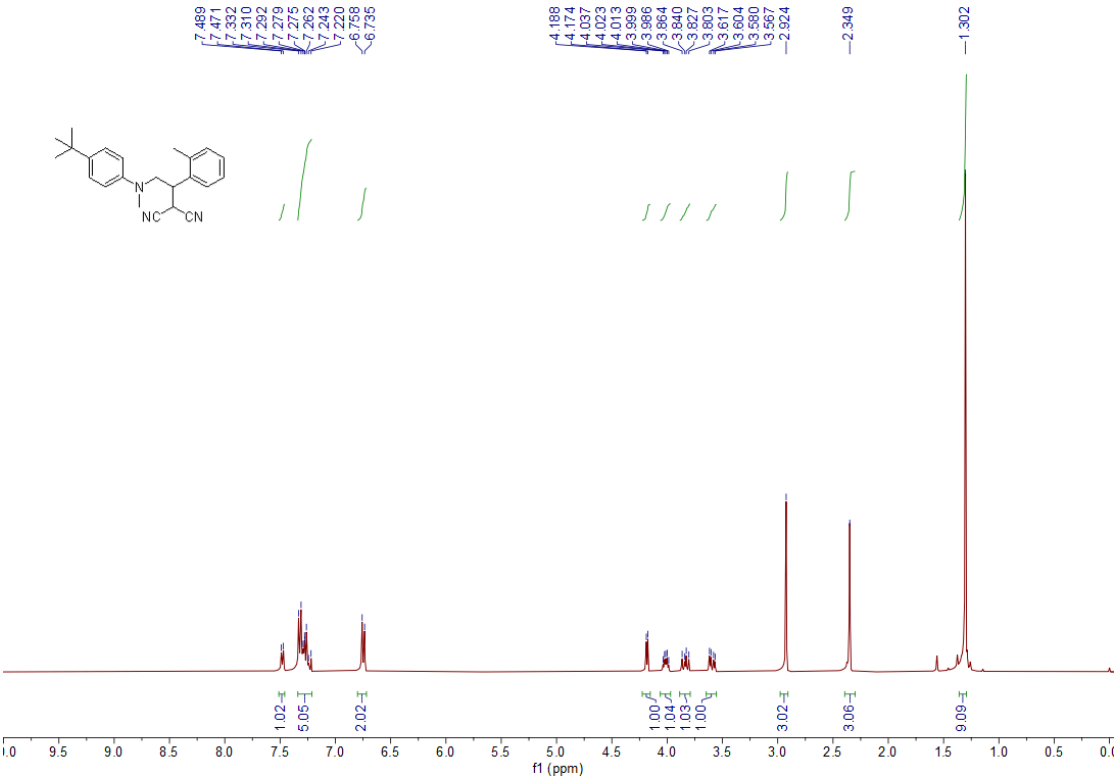
^{1}H NMR Spectrum of **3t**



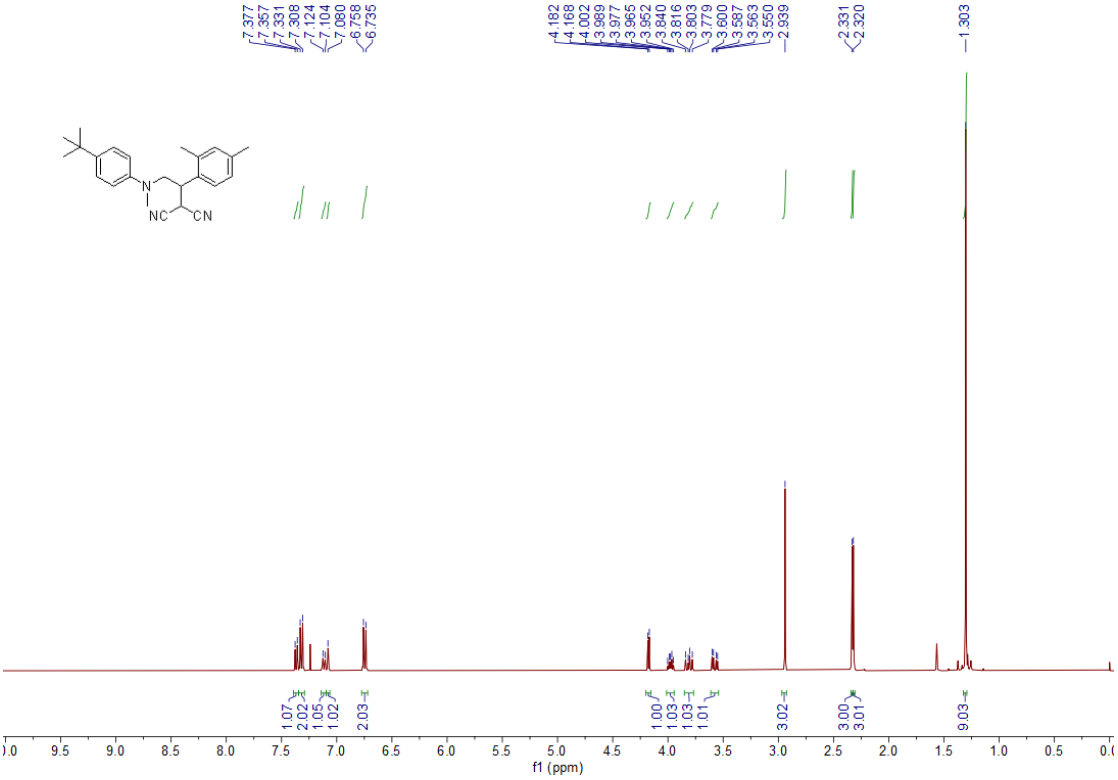
^{1}H NMR Spectrum of **3u**



^{1}H NMR Spectrum of **3v**



^{1}H NMR Spectrum of **3w**



^{1}H NMR Spectrum of **3x**