Supporting Information

Pd-Catalyzed One-Pot Dehydroxylative Coupling of Phenols with $K_4[Fe(CN)_6]$ Mediated by SO_2F_2: A Practical Method for Direct Converting Phenols to Aryl nitriles

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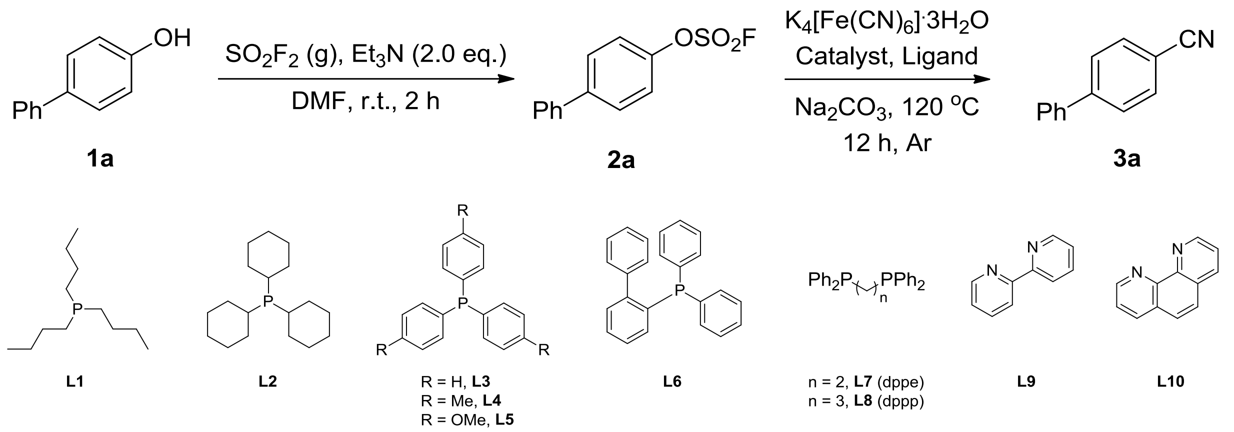
1. General considerations

All reactions were carried out in dried glassware. All reagents were purchased from commercial sources and used without further purification. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 500 MHz (for ^{1}H), 471 MHz (for ^{19}F), 126 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (^{1}H NMR, 0 ppm) as internal standards. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 µm, 4.6 × 150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. MS experiments were performed on a TOF-Q ESI or CI/EI instrument. Melting points were measured and uncorrected.

2. Screening the optimized reaction conditions

Table 1 Screening the Catalyst System[a]

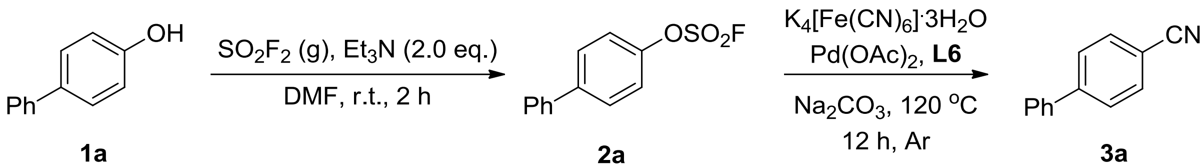


Entry	Cat. (mol%)	Ligand (mol%)	Yield (**3a**, %)[b]
1	$Pd(OAc)_2$ (5)	**L1** (10)	4
2	$Pd(OAc)_2$ (5)	**L2** (10)	12
3	$Pd(OAc)_2$ (5)	**L3** (10)	7
4	$Pd(OAc)_2$ (5)	**L4** (10)	11
5	$Pd(OAc)_2$ (5)	**L5** (10)	43
6	**$Pd(OAc)_2$ (5)**	**L6 (10)**	**85**
7	$Pd(OAc)_2$ (5)	**L7** (10)	29
8	$Pd(OAc)_2$ (5)	**L8** (10)	78
9	$Pd(OAc)_2$ (5)	**L9** (10)	trace
10	$Pd(OAc)_2$ (5)	**L10** (10)	trace
11	$Pd(OAc)_2$ (5)	/	3
12	$NiCl_2$ (5)	**L6** (10)	trace
13	$Pd(OAc)_2$ (1)	**L6** (10)	36
14	$Pd(OAc)_2$ (3)	**L6** (10)	68

15	$Pd(OAc)_2$ (10)	**L6** (10)	86

[a]Reaction conditions: a mixture of 4-phenylphenol (**1a**, 0.2 mmol), Et_3N (0.4 mmol, 2.0 eq.), DMF (2.0 mL) was stirred at room temperature charged with an SO_2F_2 balloon for 2 hours before $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.4 mmol, 2.0 eq.), catalyst, ligand and Na_2CO_3 (0.4 mmol, 2.0 eq.) were added into the mixture to react for an additional 12 h under an argon atmosphere (an Ar balloon) at 120 ^oC. [b]The yield was determined by HPLC using pure **3a** as the external standard (t_R = 4.5 min, λ_{max} = 268.9 nm, water / methanol = 20 : 80 (v / v)).

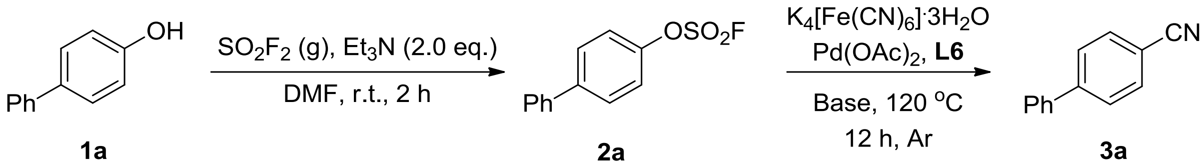
Table 2 Screening $K_4[Fe(CN)_6]\cdot 3H_2O$ Loading[a]



Entry	$K_4[Fe(CN)_6]\cdot 3H_2O$ Loading (X eq.)	Yield (**3a**, %)[b]
1	1	66
2	**2**	**85**
3	4	86
4	6	85
5	8	65
6	10	55

[a]Reaction conditions: a mixture of 4-phenylphenol (**1a**, 0.2 mmol), Et_3N (0.4 mmol, 2.0 eq.), DMF (2.0 mL) was stirred at room temperature charged with an SO_2F_2 balloon for 2 hours before $K_4[Fe(CN)_6]\cdot 3H_2O$ (X eq.), $Pd(OAc)_2$ (5 mol%), **L6** (10 mol%), and Na_2CO_3 (0.4 mmol, 2.0 eq.) were added into the mixture to react for an additional 12 h under an argon atmosphere (an Ar balloon) at 120 ^oC. [b]The yield was determined by HPLC using pure **3a** as the external standard (t_R = 4.5 min, λ_{max} = 268.9 nm, water / methanol = 20 : 80 (v / v)).

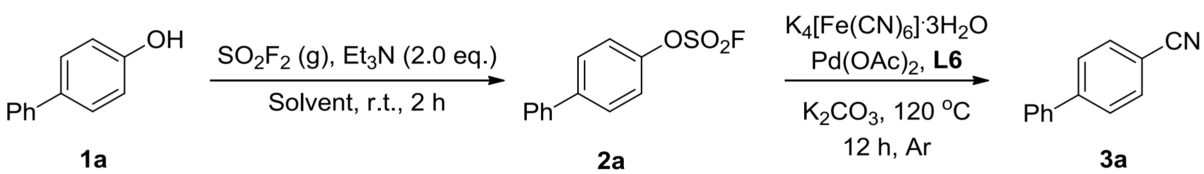
Table 3 Screening the Base[a]



Entry	Base (eq.)	Yield (**3a**, %)[b]
1	Et_3N (2.0)	trace
2	Cs_2CO_3 (2.0)	40
3	KOAc (2.0)	54
4	K_3PO_4 (2.0)	83
5	$NaHCO_3$ (2.0)	trace
6	Na_2CO_3 (2.0)	85
7	**K_2CO_3 (2.0)**	**89**
8	K_2CO_3 (0.2)	trace
9	K_2CO_3 (0.5)	11
10	K_2CO_3 (1.2)	68
11	K_2CO_3 (3.0)	80

[a]Reaction conditions: a mixture of 4-phenylphenol (**1a**, 0.2 mmol), Et_3N (0.4 mmol, 2.0 eq.), DMF (2.0 mL) was stirred at room temperature charged with an SO_2F_2 balloon for 2 hours before $K_4[Fe(CN)_6]·3H_2O$ (0.4 mmol, 2.0 eq.), $Pd(OAc)_2$ (5 mol%), **L6** (10 mol%), and base were added into the mixture to react for an additional 12 h under an argon atmosphere (an Ar balloon) at 120 °C. [b]The yield was determined by HPLC using pure **3a** as the external standard (t_R = 4.5 min, λ_{max} = 268.9 nm, water / methanol = 20 : 80 (v / v)).

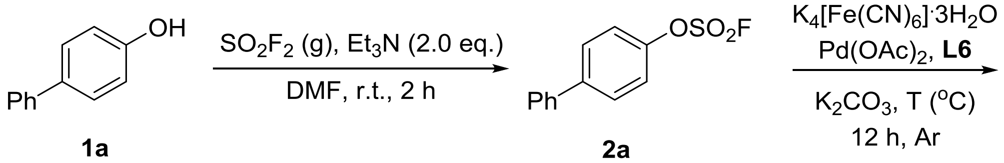
Table 4 Screening the Solvent[a]



Entry	Solvent	Yield (**3a**, %)[b]
1	**DMF**	**89**
2	DMSO	26
3	NMP	67
4	MeCN	trace
5	dioxane	trace

[a]Reaction conditions: a mixture of 4-phenylphenol (**1a**, 0.2 mmol), Et_3N (0.4 mmol, 2.0 eq.), Solvent (2.0 mL) was stirred at room temperature charged with an SO_2F_2 balloon for 2 hours before $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.4 mmol, 2.0 eq.), $Pd(OAc)_2$ (5 mol%), **L6** (10 mol%), and K_2CO_3 (0.4 mmol, 2.0 eq.) were added into the mixture to react for an additional 12 h under an argon atmosphere (an Ar balloon) at 120 ^oC. [b]The yield was determined by HPLC using pure **3a** as the external standard (t_R = 4.5 min, λ_{max} = 268.9 nm, water / methanol = 20 : 80 (v / v)).

Table 5 Screening the Reaction Tempreture[a]

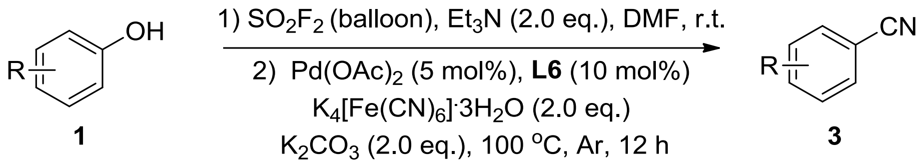


Entry	T (^oC)	Yield (**3a**, %)[b]
1	r.t.	trace
2	60	5
3	80	78
4	**100**	**95**
5	120	89
6	140	87

[a]Reaction conditions: a mixture of 4-phenylphenol (**1a**, 0.2 mmol), Et_3N (0.4 mmol, 2.0 eq.), DMF (2.0 mL) was stirred at room temperature charged with an SO_2F_2 balloon for 2 hours before $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.4 mmol, 2.0 eq.), $Pd(OAc)_2$ (5 mol%), **L6** (10 mol%), and K_2CO_3

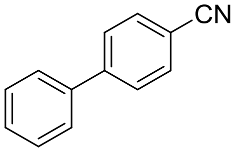
(0.4 mmol, 2.0 eq.) were added into the mixture to react for an additional 12 h under an argon atmosphere (an Ar balloon) at corresponding temperature. [b]The yield was determined by HPLC using pure **3a** as the external standard (t_R = 4.5 min, λ_{max} = 268.9 nm, water / methanol = 20 : 80 (v / v)).

3. General procedure



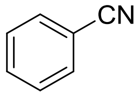
Phenol (**1**, 2.0 mmol, 1.0 eq.), Et_3N (404.8 mg, 4.0 mmol, 2.0 eq.), and DMF (20.0 mL) were added to an oven-dried reaction flask (50 mL) that was equipped with a stirring bar. The flask was fitted with a plastic stopper and SO_2F_2 gas was introduced into the stirring reaction mixture by bubbling from an SO_2F_2 balloon (ca. 5.5 eq.) at room temperature for 2-6 h. After the phenol was completely consumed (confirmed by TLC), $K_4[Fe(CN)_6]\cdot 3H_2O$ (1.69 g, 4.0 mmol, 2.0 eq.), $Pd(OAc)_2$ (22.4 mg, 5 mol%), 2-(diphenylphosphino)-biphenyl (**L6**, 67.7 mg, 10 mol%), K_2CO_3 (552.8 mg, 4 mmol, 2.0 eq.) were added into the reaction mixture. Then the reaction was stirred at 100 °C for an additional 12 h under an argon atmosphere (an Argon balloon). Once the aryl fluorosulfonate had been completely consumed, the mixture was diluted with water and extracted with EtOAc (3×10 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified by column chromatography on silica gel with PE / EA as eluent to afford the desired aryl nitrile (**3**).

4. Product Characterization



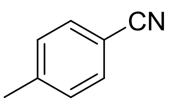
3a

4-Biphenylcarbonitrile (**3a**). White solid (312 mg from **1a**, isolated yield 87%). HPLC yield 95% (using 4-biphenylcarbonitrile (**3a**) (t_R = 4.495 min, λ_{max} = 268.9 nm, water / methanol = 20 : 80 (v / v)) as the external standard). M.p. 79-80 °C. The NMR data is identical to that reported in literature.[1] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.49 (t, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 145.7, 139.2, 132.6, 129.2, 128.7, 127.8, 127.3, 119.0, 110.9.



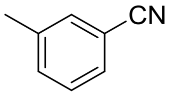
3b

Benzonitrile (**3b**). Colorless oil. HPLC yield 99% (using benzonitrile (**3b**) (t_R = 3.548 min, λ_{max} = 222.8 nm, water / methanol = 30 : 70 (v / v)) as the external standard). The NMR data is identical to that reported in literature.[2] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.62-7.57 (m, 3H), 7.44 (t, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 132.8, 132.0, 129.1, 118.8, 112.3.



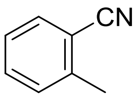
3ca

4-Methylbenzonitrile (**3ca**). Colorless oil. HPLC yield 86% (using 4-methylbenzonitrile (**3ca**) (t_R = 4.354 min, λ_{max} = 232.2 nm, water / methanol = 30 : 70 (v / v)) as the external standard). The NMR data is identical to that reported in literature.[2] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.54 (d, J = 7.9 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 143.8, 132.2, 129.9, 119.3, 109.4, 21.9.



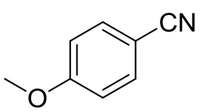
3cb

3-Methylbenzonitrile (**3cb**). Colorless oil. HPLC yield 90% (using 3-methylbenzonitrile (**3cb**) (t_R = 4.623 min, λ_{max} = 228.7 nm, water / methanol = 30 : 70 (v / v)) as the external standard). The NMR data is identical to that reported in literature.[3] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.45-7.44 (m, 2H), 7.40 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 139.3, 133.7, 132.5, 129.3, 129.1, 119.1, 112.3, 21.2.



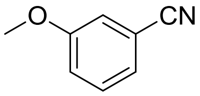
3cc

3-Methylbenzonitrile (**3cc**). Colorless oil. HPLC yield 99% (using 3-methylbenzonitrile (**3cc**) (t_R = 4.493 min, λ_{max} = 227.5 nm, water / methanol = 30 : 70 (v / v)) as the external standard). The NMR data is identical to that reported in literature.[3] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 142.0, 132.7, 132.6, 130.3, 126.3, 118.2, 112.8, 20.5.



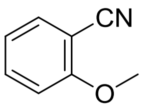
3da

4-Methoxybenzonitrile (**3da**). White solid (162 mg from **1da**, isolated yield 61%). M.p. 53-55 ^{o}C. The NMR data is identical to that reported in literature.[1] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 163.0, 134.1, 119.3, 114.9, 104.1, 55.7.



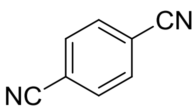
3db

3-Methoxybenzonitrile (**3db**). Colorless oil. HPLC yield 91% (using 3-methoxybenzonitrile (**3db**) (t_R = 4.216 min, λ_{max} = 230.0 nm, water / methanol = 30 : 70 (v / v)) as the external standard). The NMR data is identical to that reported in literature.[2] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37 (t, J = 8.7 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 7.14-7.12 (m, 2H), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 159.7, 130.4, 124.6, 119.4, 118.8, 116.9, 113.3, 55.6.



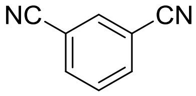
3dc

2-Methoxybenzonitrile (**3dc**). Yellow liquid. HPLC yield 61% (using 2-methoxybenzonitrile (**3dc**) (t_R = 3.662 min, λ_{max} = 231.1 nm, water / methanol = 30 : 70 (v / v)) as the external standard). The NMR data is identical to that reported in literature.[2] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.56-7.52 (m, 2H), 7.02-6.96 (m, 2H), 3.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 161.3, 134.5, 133.8, 120.8, 116.6, 111.4, 101.8, 56.1.



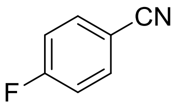
3ea

1,4-Dicyanobenzene (**3ea**). White solid. HPLC yield 92% (using 1,4-dicyanobenzene (**3ea**) (t_R = 3.192 min, λ_{max} = 246.4 nm, water / methanol = 40 : 60 (v / v)) as the external standard). M.p. 220-222 ^{o}C. The NMR data is identical to that reported in literature.[3] ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.07 (s, 4H). ^{13}C NMR (DMSO-d_6, 126 MHz): δ 133.2, 117.5, 115.7.



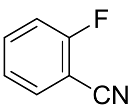
3eb

1,3-Dicyanobenzene (**3eb**). Light yellow solid. HPLC yield 45% (using 1,3-dicyanobenzene (**3eb**) (t_R = 3.307 min, λ_{max} = 230.0 nm, water / methanol = 40 : 60 (v / v)) as the external standard). M.p. 160-162 °C. The NMR data is identical to that reported in literature.[4] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.66 (t, J = 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 136.1, 135.5, 130.5, 116.7, 114.2.



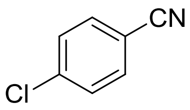
3fa

4-Fluorobenzonitrile (**3fa**). Colorless oil. HPLC yield 50% (using 4-fluorobenzonitrile (**3fa**) (t_R = 3.390 min, λ_{max} = 225.2 nm, water / methanol = 30 : 70 (v / v)) as the external standard). The NMR data is identical to that reported in literature.[3] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69-7.67 (m, 2H), 7.19-7.16 (m, 2H). ^{19}F NMR ($CDCl_3$, 471MHz) δ −102.4 (s, 1F). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 165.2 (d, J = 256.1 Hz), 134.8 (d, J = 9.1 Hz), 118.1, 117.0 (d, J = 22.7 Hz), 108.7 (d, J = 3.6 Hz).



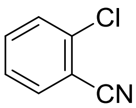
3fb

2-Fluorobenzonitrile (**3fb**). Colorless oil. HPLC yield 44% (using 2-fluorobenzonitrile (**3fb**) (t_R = 3.757 min, λ_{max} = 222.8 nm, water / methanol = 30 : 70 (v / v)) as the external standard). The NMR data is identical to that reported in literature.[3] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.65-7.60 (m, 2H), 7.27 (td, J_1 = 7.7 Hz, J_2 = 0.8 Hz, 1H), 7.22 (t, J = 8.7 Hz, 1H). ^{19}F NMR ($CDCl_3$, 471MHz) δ −106.2 (s, 1F). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 163.3 (d, J = 258.8 Hz), 135.2 (d, J = 8.2 Hz), 133.7, 124.9 (d, J = 3.6 Hz), 116.6 (d, J = 19.1 Hz), 114.0, 101.6 (d, J = 15.4 Hz).



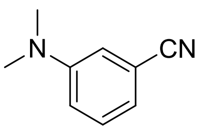
3ga

4-Chlorobenzonitrile (**3ga**). White solid. HPLC yield 77% (using 4-chlorobenzonitrile (**3ga**) (t_R = 3.076 min, λ_{max} = 234.6 nm, water / methanol = 20 : 80 (v / v)) as the external standard). M.p. 90-92 °C. The NMR data is identical to that reported in literature.[4] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.60 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 139.7, 133.5, 129.8, 118.1, 110.9.



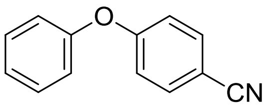
3gb

2-Chlorobenzonitrile (**3gb**). Yellowish solid. HPLC yield 83% (using 2-chlorobenzonitrile (**3gb**) (t_R = 4.460 min, λ_{max} = 229.9 nm, water / methanol = 30 : 70 (v / v)) as the external standard). M.p. 40-41 °C. The NMR data is identical to that reported in literature.[4] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.67 (dd, J = 7.8 Hz, J = 1.5 Hz, 1H), 7.57-7.50 (m, 2H), 7.38 (td, J_1 = 7.4 Hz, J_2 = 1.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 137.0, 134.1, 134.0, 130.2, 127.3, 116.1, 113.5.



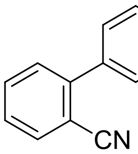
3h

3-(Dimethylamino)benzonitrile (**3h**). Colorless oil (250 mg from **1h**, isolated yield 86%). The NMR data is identical to that reported in literature.[2] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29-7.26 (m, 1H), 6.95 (d, J = 7.3 Hz, 1H), 6.89-6.88 (m, 2H), 2.98 (s, 6H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 150.3, 129.8, 119.9, 119.5, 116.3, 114.9, 112.8, 40.2.



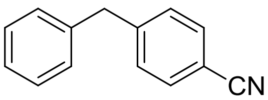
3i

4-Phenoxybenzonitrile (**3i**). White solid (330.4 mg from **1i**, isolated yield 85%). M.p. 31-33 °C. The NMR data is identical to that reported in literature.[5] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60 (d, J = 8.7 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 7.9 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 161.8, 154.9, 134.2, 130.3, 125.2, 120.5, 118.9, 118.0, 105.9.



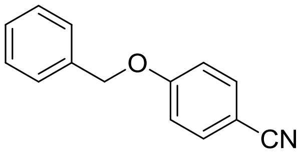
3j

2-Biphenylcarbonitrile (**3j**). White solid (296 mg from **1j**, isolated yield 83%). M.p. 37-38 °C. The NMR data is identical to that reported in literature.[3] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77 (d, J = 7.5 Hz, 2H), 7.67-7.64 (m, 1H), 7.58-7.57 (m, 2H), 7.54-7.49 (m, 3H), 7.47-7.43 (m, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 145.6, 138.2, 133.8, 132.9, 130.2, 128.84, 128.81, 128.8, 127.6, 118.8, 111.3.



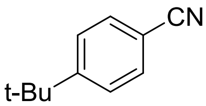
3k

4-(Phenylmethyl)benzonitrile (**3k**). White solid (239 mg from **1k**, isolated yield 62%). The NMR data is identical to that reported in literature.[6] M.p. 41-44 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58 (d, J = 8.2 Hz, 2H), 7.36-7.24 (m, 5H), 7.18 (d, J = 7.2 Hz, 2H), 4.05 (s, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 146.8, 139.4, 132.4, 129.7, 129.1, 128.9, 126.8, 119.1, 110.1, 42.1.



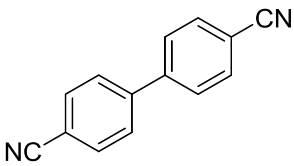
3l

4-Benzyloxybenzonitrile (**3l**). White solid (301 mg from **1l**, isolated yield 72%). M.p. 90-92 °C. The NMR data is identical to that reported in literature.[7] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58 (d, J = 8.3 Hz, 2H), 7.42-7.38 (m, 5H), 7.03 (d, J = 8.3 Hz, 2H), 5.12 (s, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 162.1, 135.8, 134.1, 128.9, 128.5, 127.6, 119.3, 115.7, 104.3, 70.4.



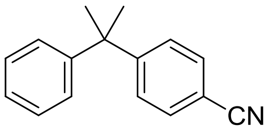
3m

4-*tert*-Butylbenzonitrile (**3m**). Colorless oil. HPLC yield 45% (using 4-*tert*-butylbenzonitrile (**3m**) (t_R = 8.418 min, λ_{max} = 233.4 nm, water / methanol = 30 : 70 (v / v)) as the external standard). The NMR data is identical to that reported in literature.[1] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 156.8, 132.1, 126.3, 119.3, 109.4, 35.4, 31.0.



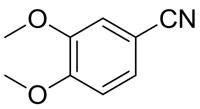
3n

[1,1'-Biphenyl]-4,4'-dicarbonitrile (**3n**). White solid (294 mg from **1n**, isolated yield 72%). M.p. 232-234 °C. HPLC yield 82% (using [1,1'-biphenyl]-4,4'-dicarbonitrile (**3n**) (t_R = 4.227 min, λ_{max} = 274.9 nm, water / methanol = 30 : 70 (v / v)) as the external standard). The NMR data is identical to that reported in literature.[8] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78 (d, J = 7.3 Hz, 4H), 7.70 (d, J = 7.3 Hz, 4H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 143.7, 133.0, 128.1, 118.5, 112.6.



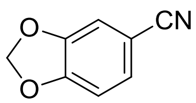
3o

4-(1-Methyl-1-phenylethyl)benzonitrile (**3o**). Colorless liquid (272 mg from **1o**, isolated yield 62%). The NMR data is identical to that reported in literature.[9] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.56 (d, J = 7.6 Hz, 2H), 7.34-7.28 (m, 4H), 7.23-7.18 (m, 3H), 1.69 (s, 6H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 156.4, 149.2, 132.0, 128.4, 127.8, 126.8, 126.3, 119.2, 109.7, 43.6, 30.5.



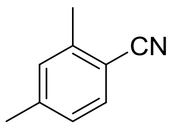
3p

3,4-Dimethoxybenzonitrile (**3p**). White solid (218 mg from **1p**, isolated yield 67%). HPLC yield 82% (using 3,4-dimethoxybenzonitrile (**3p**) (t_R = 3.065 min, λ_{max} = 254.7 nm, water / methanol = 30 : 70 (v / v)) as the external standard). M.p. 61-63 °C. The NMR data is identical to that reported in literature.[9] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27 (d, J = 8.3 Hz, 1H), 7.06 (s, 1H), 6.89 (d, J = 8.3 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 152.9, 149.2, 126.5, 119.3, 114.0, 111.3, 103.9, 56.2, 56.1.



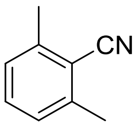
3q

Benzo[d][1,3]dioxole-5-carbonitrile (**3q**). White solid (232 mg from **1q**, isolated yield 79%). M.p. 87-89 °C. The NMR data is identical to that reported in literature.[1] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.21 (d, J = 8.1 Hz, 1H), 7.03 (s, 1H), 6.86 (d, J = 7.9 Hz, 1H), 6.07 (s, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 151.7, 148.2, 128.4, 119.0, 111.6, 109.3, 105.1, 102.3.



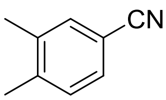
3r

2,4-Dimethylbenzonitrile (**3r**). White solid. HPLC yield 75% (using 2,4-dimethylbenzonitrile (**3r**) (t_R = 5.746 min, λ_{max} = 235.8 nm, water / methanol = 30 : 70 (v / v)) as the external standard). M.p. 20-22 °C. The NMR data is identical to that reported in literature.[1] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.47 (d, J = 7.9 Hz, 1H), 7.12 (s, 1H), 7.06 (d, J = 7.8 Hz, 1H), 2.49 (s, 3H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 143.6, 141.9, 132.5, 131.1, 127.1, 118.6, 109.8, 21.8, 20.4.



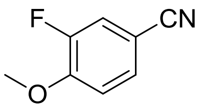
3s

2,6-Dimethylbenzonitrile (**3s**). White solid. HPLC yield 52% (using 2,6-dimethylbenzonitrile (**3s**) (t_R = 5.762 min, λ_{max} = 232.3 nm, water / methanol = 30 : 70 (v / v)) as the external standard). M.p. 86-88 °C. The NMR data is identical to that reported in literature.[10] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34 (t, J = 7.8 Hz, 1H), 7.12 (d, J = 7.8 Hz, 2H), 2.53 (s, 6H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 142.2, 132.2, 127.4, 117.4, 113.5, 20.9.



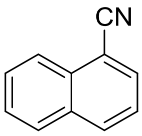
3t

3,4-Dimethylbenzonitrile (**3t**). White solid (191 mg from **1t**, isolated yield 73%). M.p. 62-64 °C. HPLC yield 89% (using 3,4-dimethylbenzonitrile (**3t**) (t_R = 5.663 min, λ_{max} = 235.8 nm, water / methanol = 30 : 70 (v / v)) as the external standard). The NMR data is identical to that reported in literature.[1] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.37 (m, 2H), 7.21 (d, J = 7.6 Hz, 1H), 2.32 (s, 3H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 142.6, 138.0, 132.9, 130.4, 129.7, 119.4, 109.6, 20.2, 19.6.



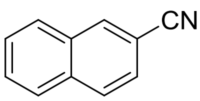
3u

3-Fluoro-4-methoxybenzonitrile (**3u**). White solid (173 mg from **1u**, isolated yield 57%). M.p. 94-96 °C. HPLC yield 77% (using 3-fluoro-4-methoxybenzonitrile (**3u**) (t_R = 3.818 min, λ_{max} = 246.4 nm, water / methanol = 30 : 70 (v / v)) as the external standard). The NMR data is identical to that reported in literature.[2] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.43 (d, J = 8.5 Hz, 1H), 7.35 (d, J = 10.7 Hz, 1H), 7.02 (t, J = 8.4 Hz, 1H), 3.95 (s, 3H). ^{19}F NMR ($CDCl_3$, 471MHz) δ −131.9-−132.0 (m, 1F). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 151.9 (d, J = 10.9 Hz), 151.8 (d, J = 249.8 Hz), 129.8 (d, J = 3.6 Hz), 119.6 (d, J = 21.8 Hz), 118.1 (d, J = 2.8 Hz), 113.7 (d, J = 1.9 Hz), 104.0 (d, J = 8.1 Hz), 56.5.



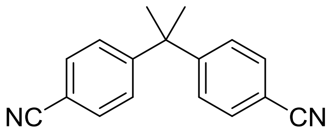
3v

1-Cyanonaphthalene (**3v**). Yellowish oil (277 mg from **1v**, isolated yield 91%). The NMR data is identical to that reported in literature.[1] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.23 (d, J = 8.3 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.93-7.90 (m, 2H), 7.71-7.67 (m, 1H), 7.63-7.60 (m, 1H), 7.53-7.50 (m, 1H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 133.4, 133.0, 132.7, 132.4, 128.8, 128.7, 127.7, 125.2, 125.0, 117.9, 110.3.



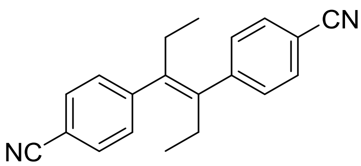
3w

2-Naphthonitrile (**3w**). Yellowish solid (265 mg from **1w**, isolated yield 87%). M.p. 59-61 °C. The NMR data is identical to that reported in literature.[1] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.23 (s, 1H), 7.92-7.89 (m, 3H), 7.65-7.60 (m, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 134.8, 134.3, 132.4, 129.3, 129.2, 128.5, 128.2, 127.8, 126.5, 119.4, 109.5.



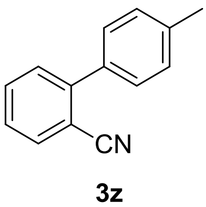
3x

4,4'-(1-Methylethylidene)bis-benzonitrile (**3x**). White solid (294 mg from **1x**, isolated yield 60%). M.p. 138-140 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58 (d, J = 8.2 Hz, 4H), 7.29 (d, J = 8.2 Hz, 4H), 1.70 (s, 6H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 154.7, 132.3, 127.7, 118.8, 110.3, 44.1, 30.2. ESI-MS HRMS calculated for $C_{17}H_{15}N_2$ $[M+H]^+$ 247.1230, found 247.1232.



3y

4,4'-(Hex-3-ene-3,4-diyl)dibenzonitrile (**3y**). White solid (360 mg from **1y**, isolated yield 63%). M.p. 206-208 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (d, J = 7.5 Hz, 4H), 7.32 (d, J = 7.4 Hz, 4H), 2.11 (q, J = 7.2 Hz, 4H), 0.76 (t, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 146.9, 139.2, 132.2, 129.5, 119.0, 110.8, 28.3, 13.1. ESI-MS HRMS calculated for $C_{20}H_{19}N_2$ $[M+H]^+$ 287.1543, found 287.1542.



3z

4'-Methyl[1,1'-biphenyl]-2-carbonitrile (**3z**). Light grey solid (296 mg from **1z**, isolated yield 77%). M.p. 45-47 °C. The NMR data is identical to that reported in literature.[11] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76 (dd, J = 7.8 Hz, J = 0.9 Hz, 1H), 7.63 (td, J = 7.8 Hz, J = 1.2 Hz, 1H), 7.51 (dd, J = 7.9 Hz, J = 0.6 Hz, 1H), 7.47 (d, J = 8.1 Hz, 2H), 7.42 (td, J = 7.6 Hz, J = 1.2 Hz, 1H), 7.31 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz) δ 145.6, 138.8, 135.4, 133.8, 132.9, 130.1, 129.6, 128.7, 127.4, 119.0, 111.3, 21.4.

5. Reference

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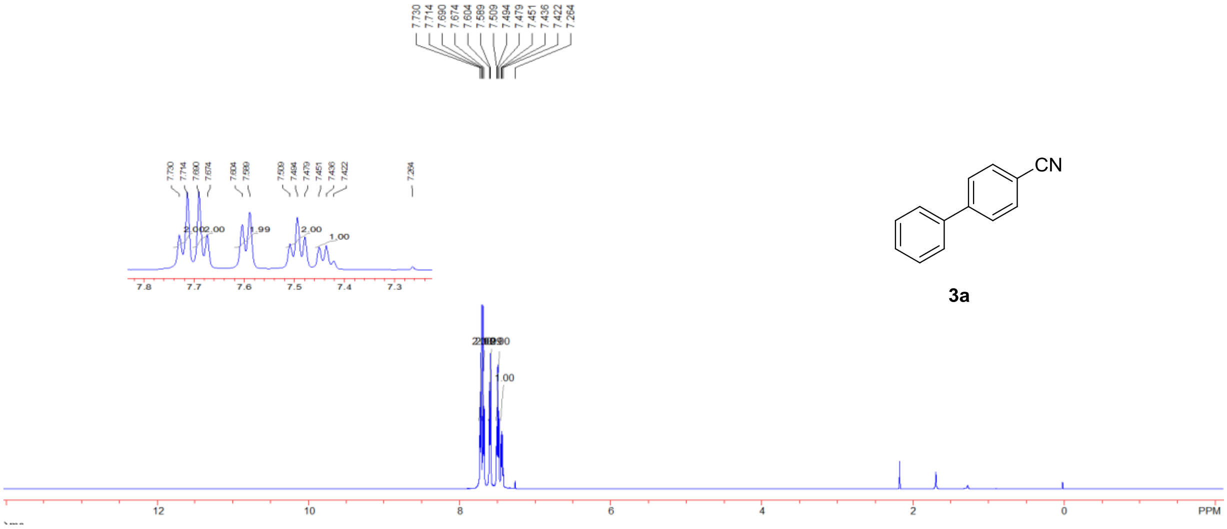
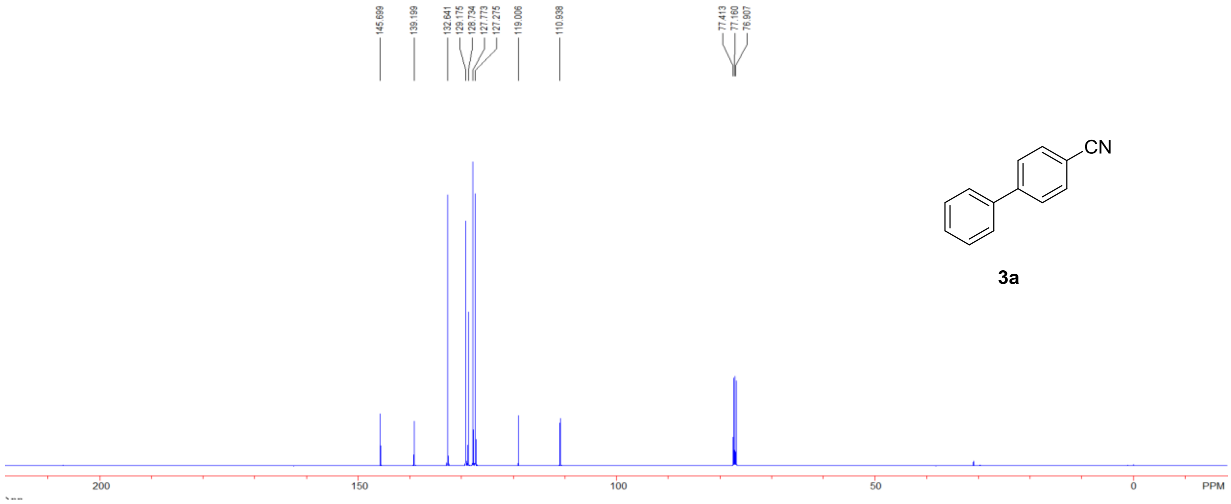
6. NMR Spectra

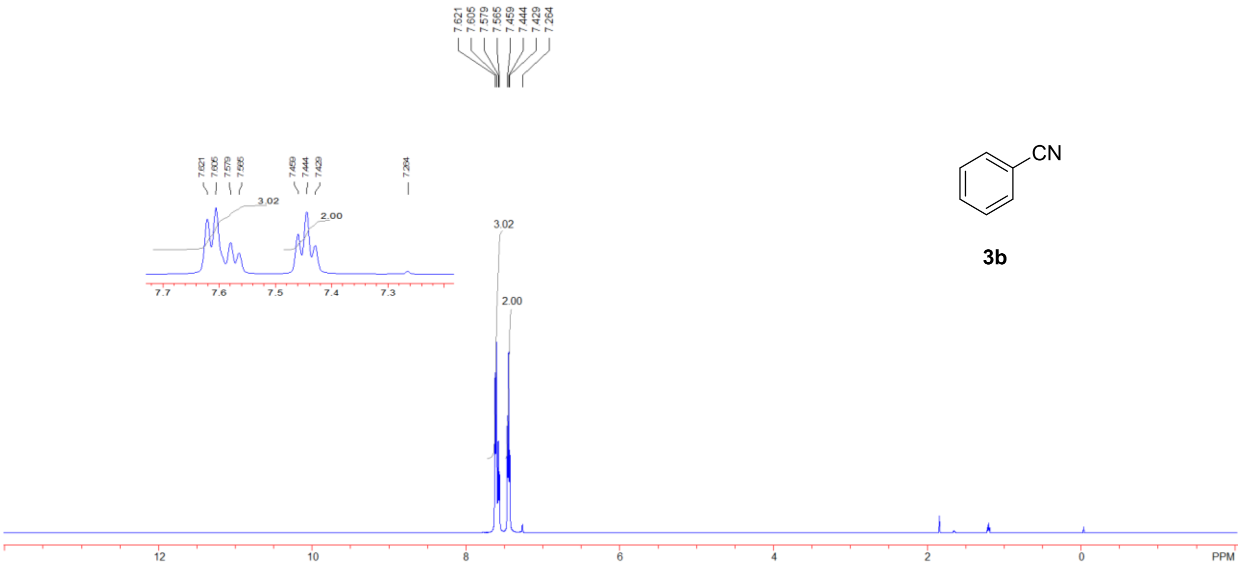
3a, ^{1}H NMR, 500 MHz, $CDCl_3$



3a, ^{13}C NMR, 126 MHz, $CDCl_3$



3b, ^{1}H NMR, 500 MHz, $CDCl_3$



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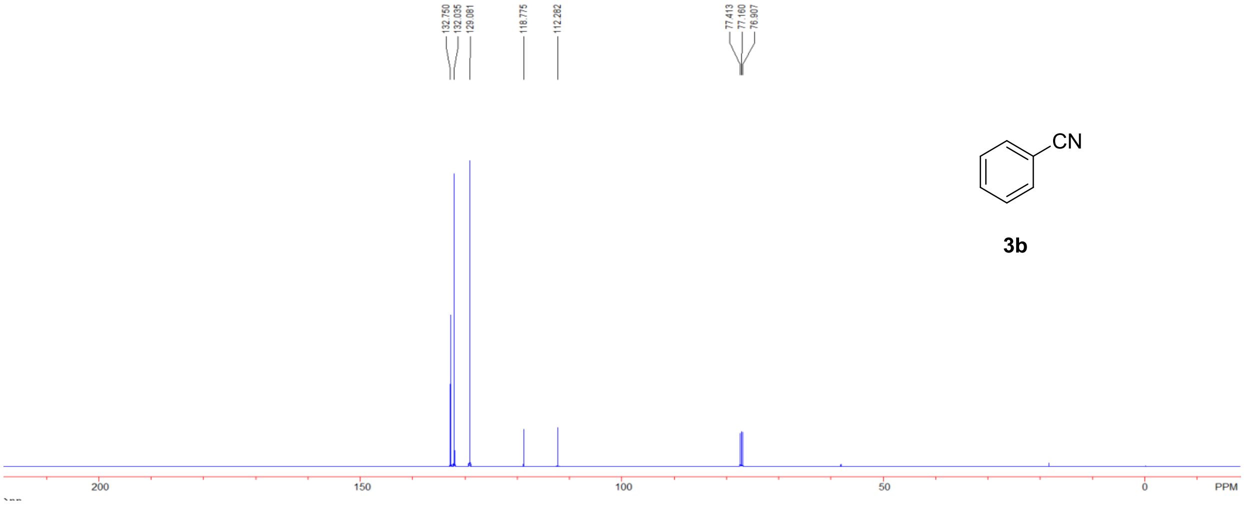
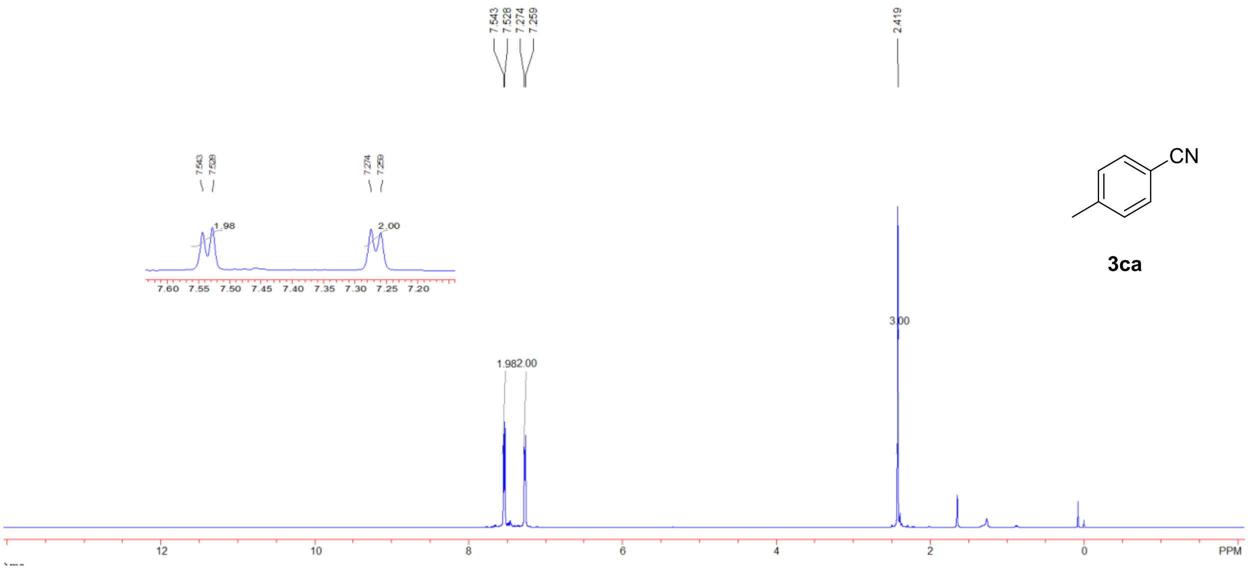
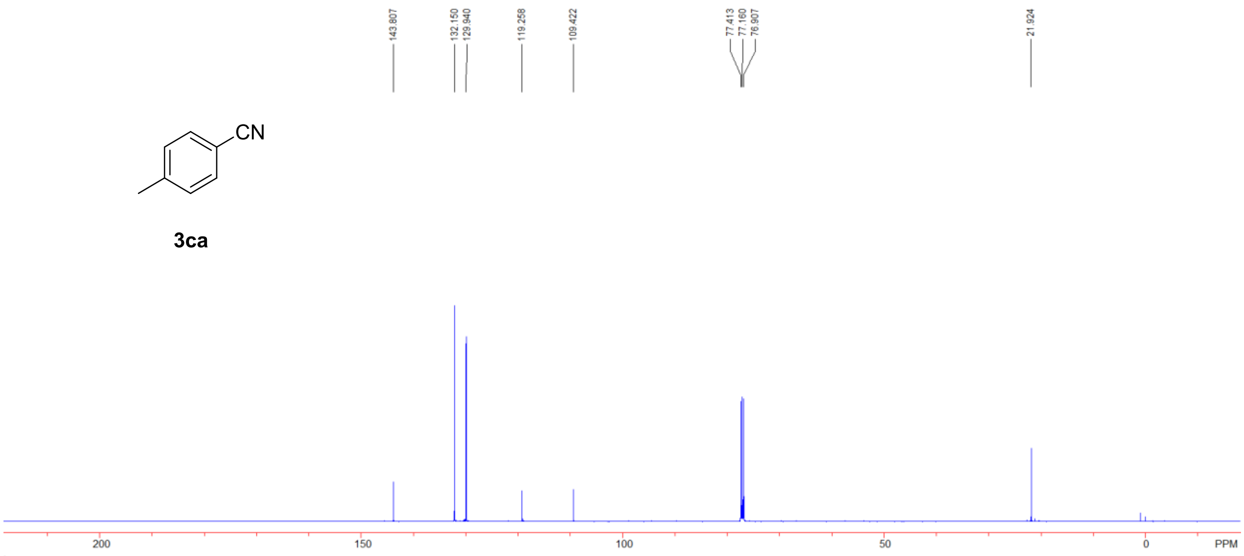


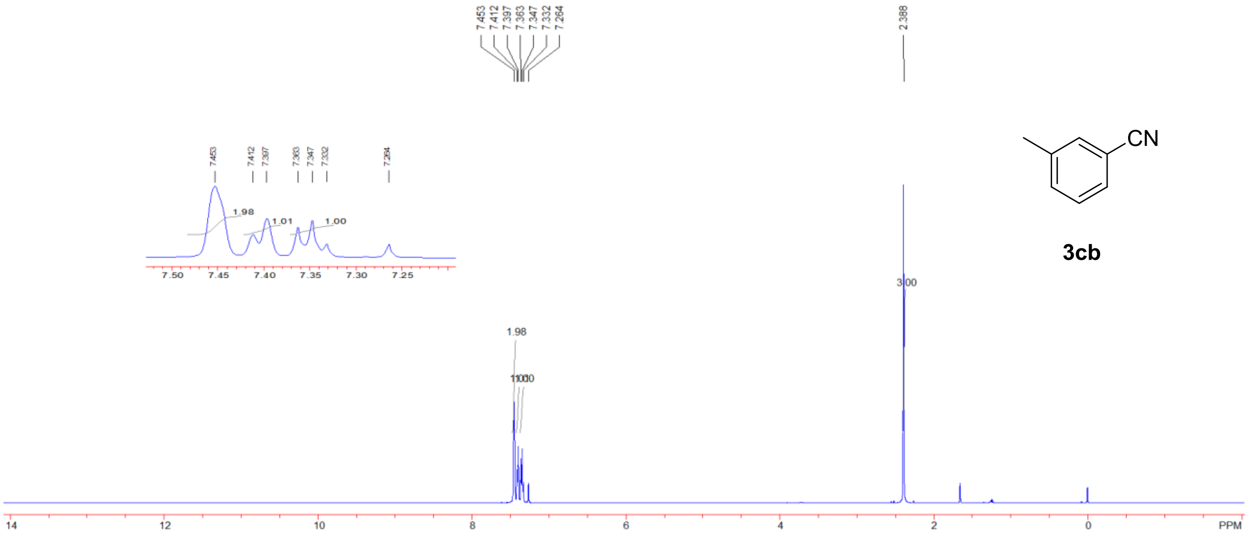
3ca, ^{1}H NMR, 500 MHz, $CDCl_3$



3ca, ^{13}C NMR, 126 MHz, $CDCl_3$



3cb, ^{1}H NMR, 500 MHz, $CDCl_3$



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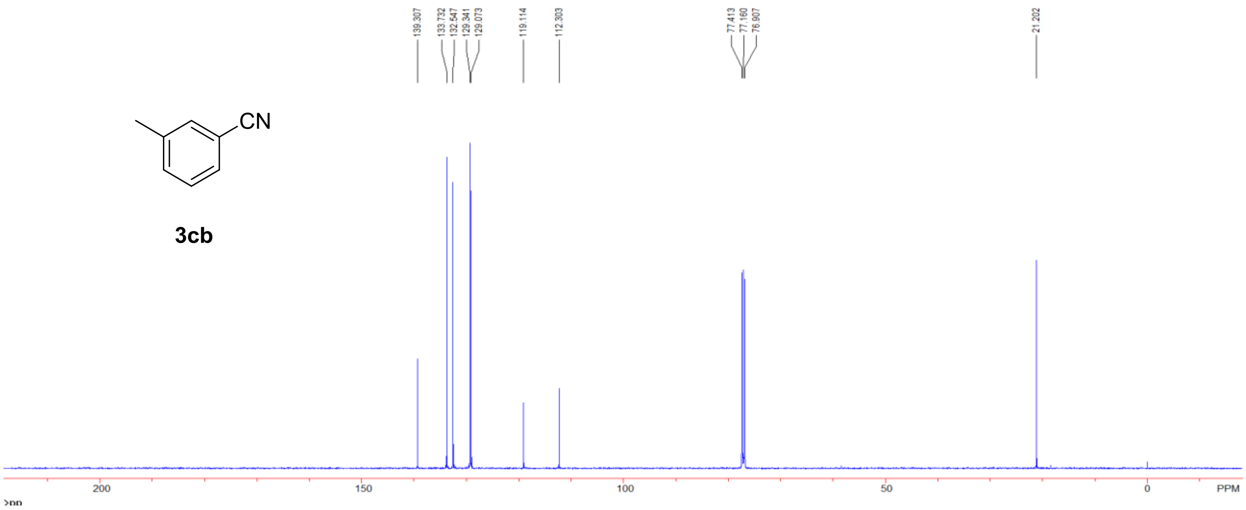
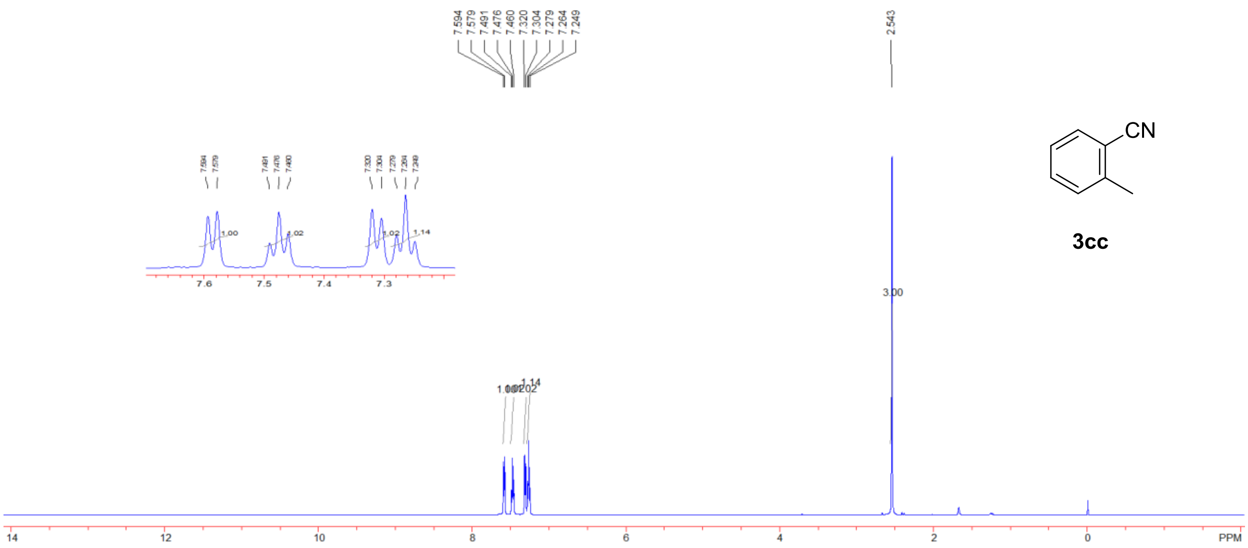
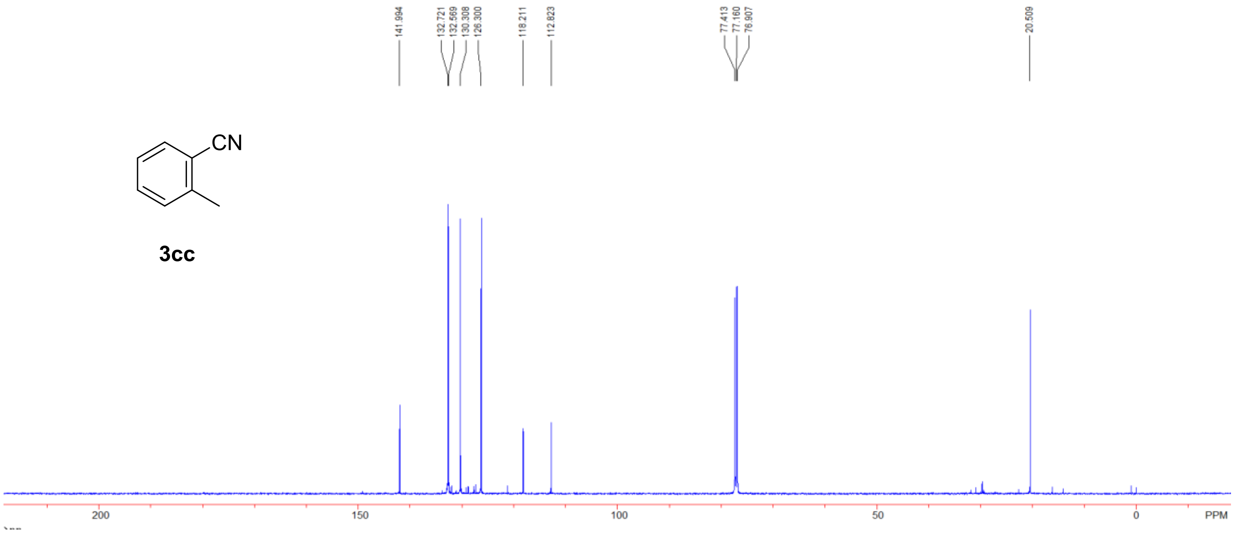


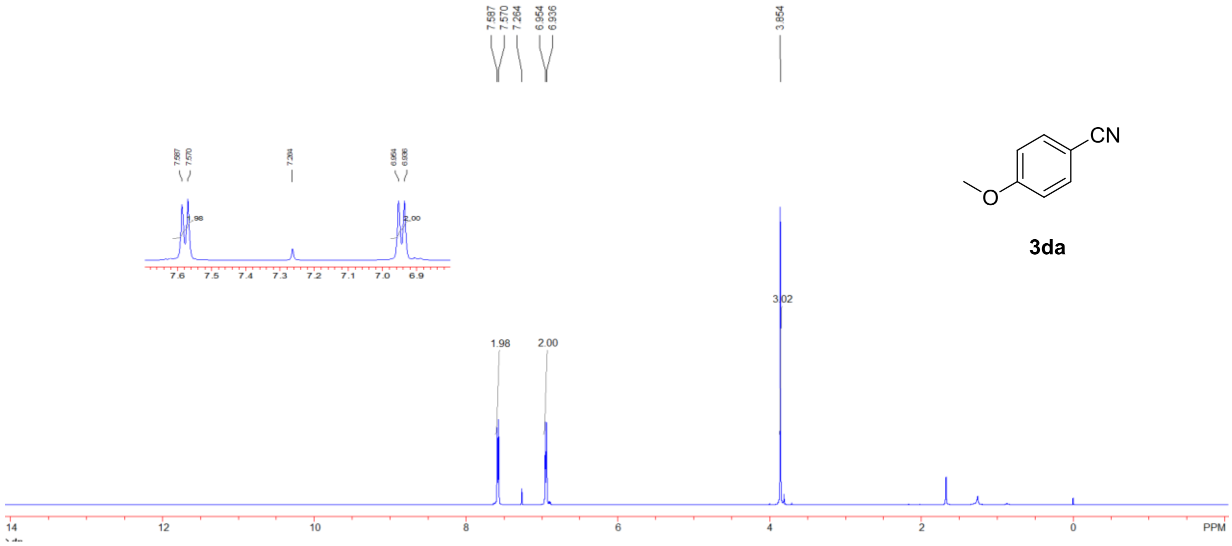
3cc, ^{1}H NMR, 500 MHz, $CDCl_3$



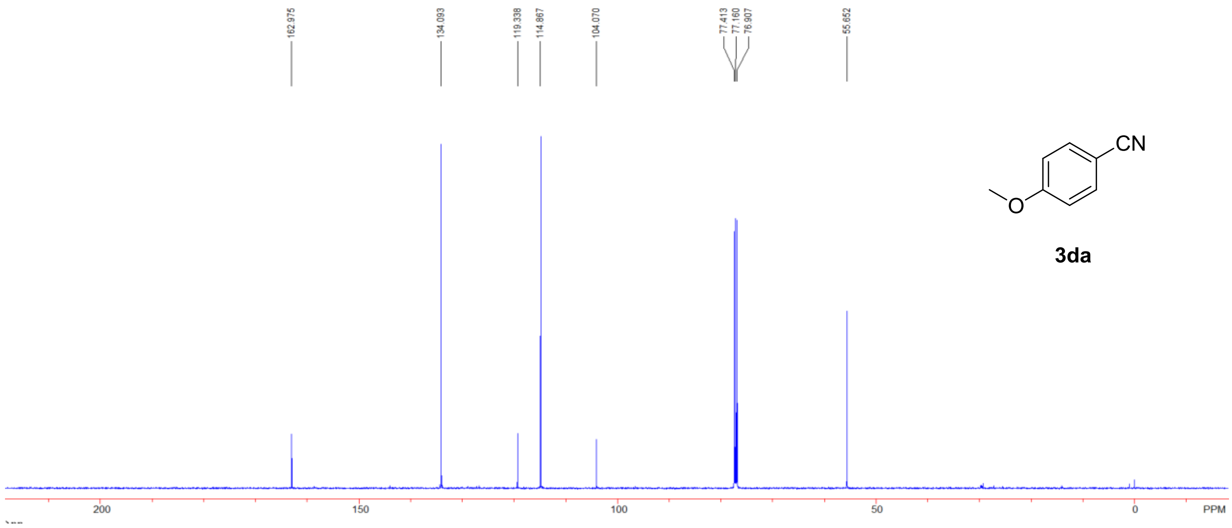
3cc, ^{13}C NMR, 126 MHz, $CDCl_3$



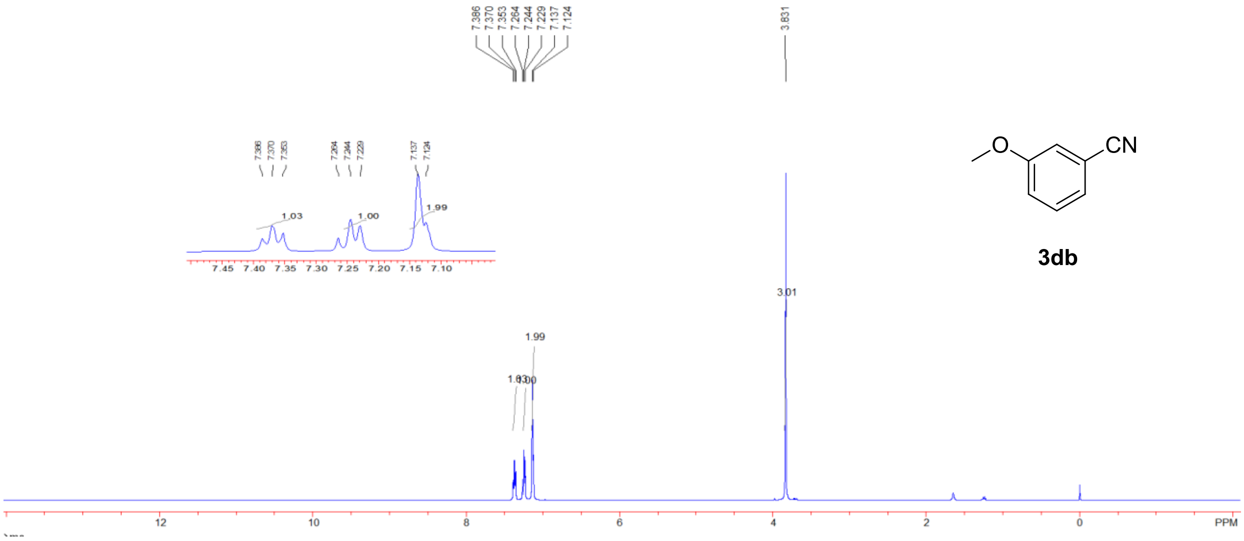
3da, ^{1}H NMR, 500 MHz, $CDCl_3$



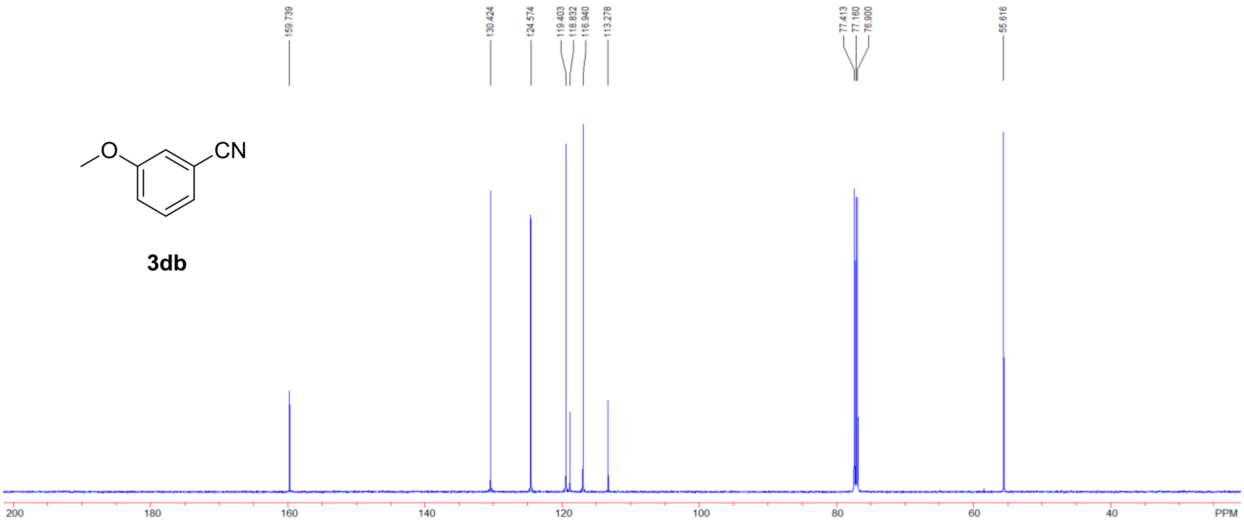
3da, ^{13}C NMR, 126 MHz, $CDCl_3$



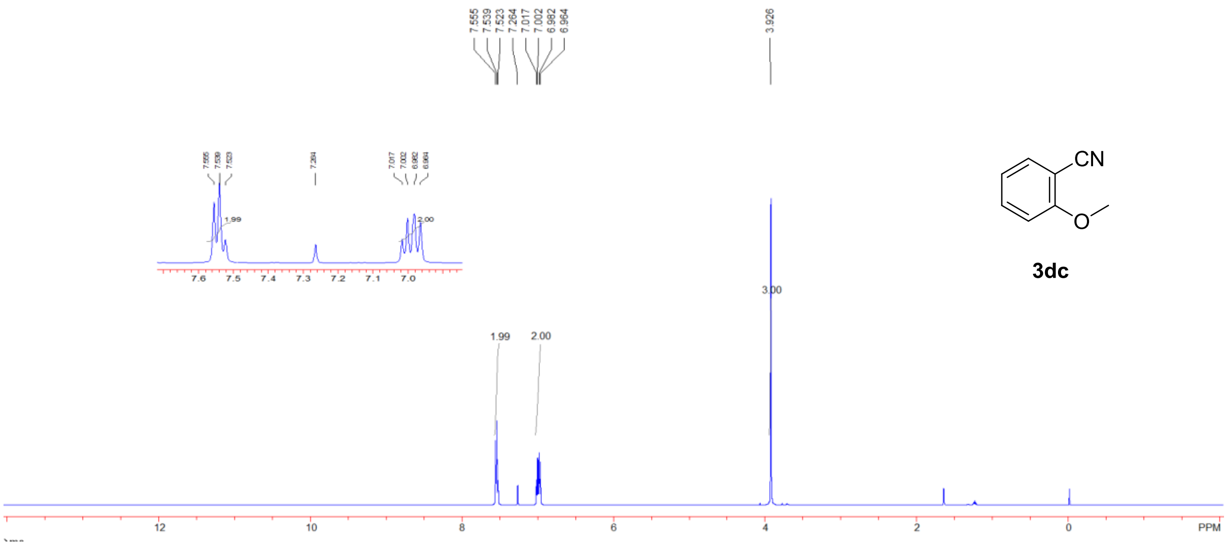
3db, ^{1}H NMR, 500 MHz, $CDCl_3$



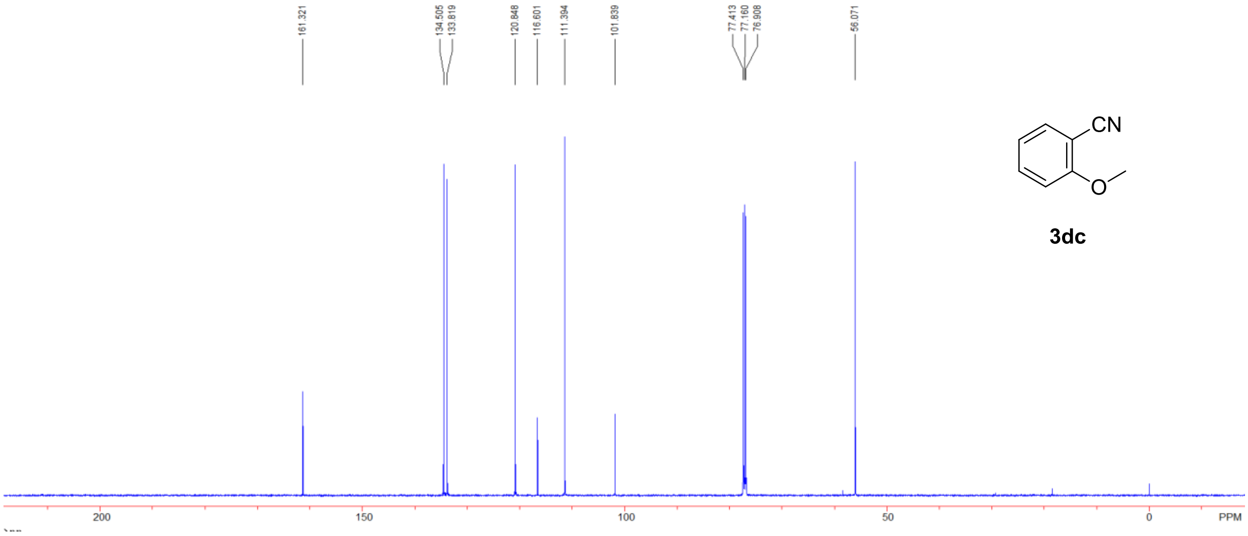
3db, ^{13}C NMR, 126 MHz, $CDCl_3$



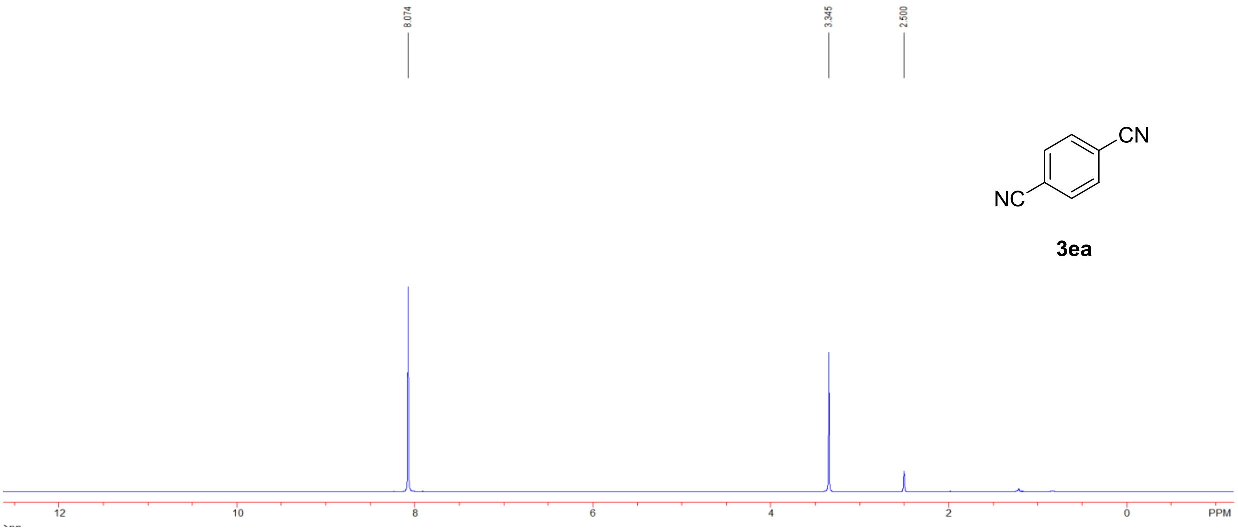
3dc, ^{1}H NMR, 500 MHz, $CDCl_3$



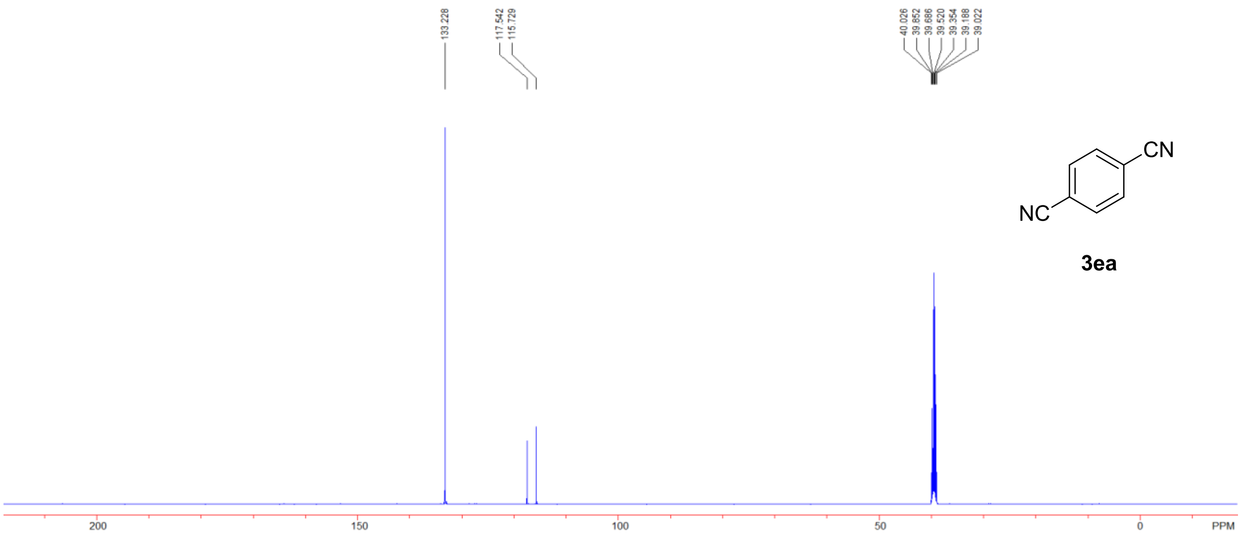
3dc, ^{13}C NMR, 126 MHz, $CDCl_3$



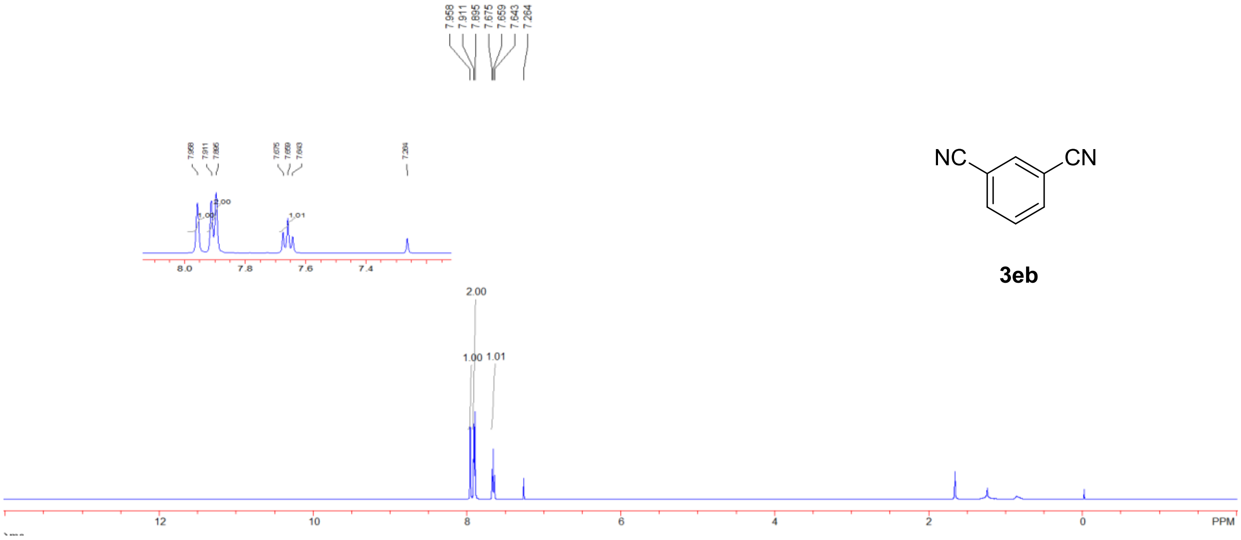
3ea, ^{1}H NMR, 500 MHz, DMSO-d_6



3ea, ^{13}C NMR, 126 MHz, DMSO-d_6

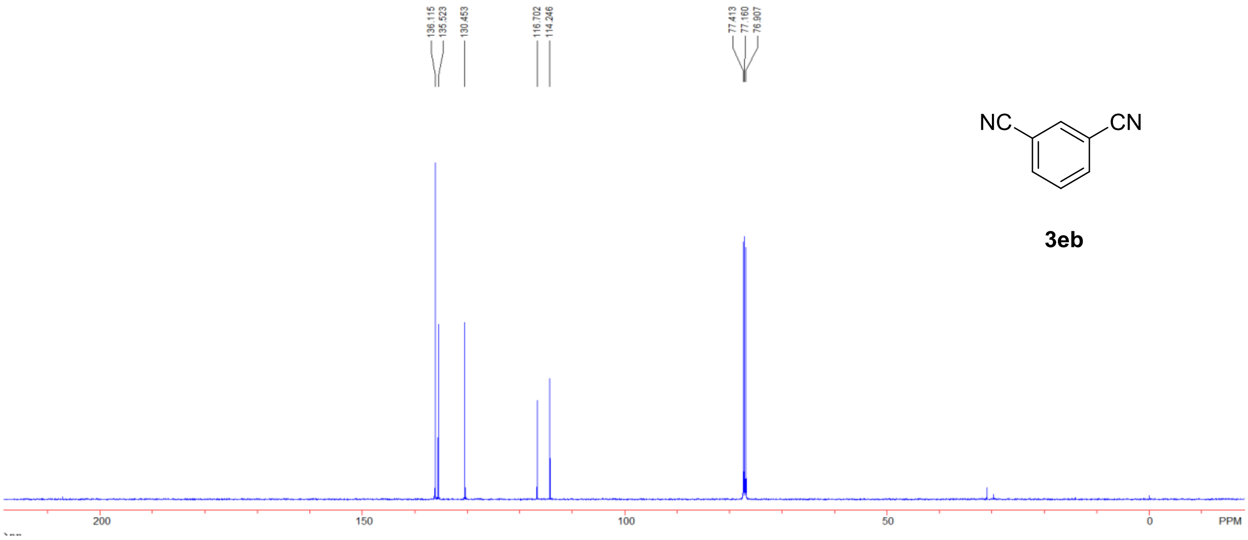


3eb, ^{1}H NMR, 500 MHz, $CDCl_3$



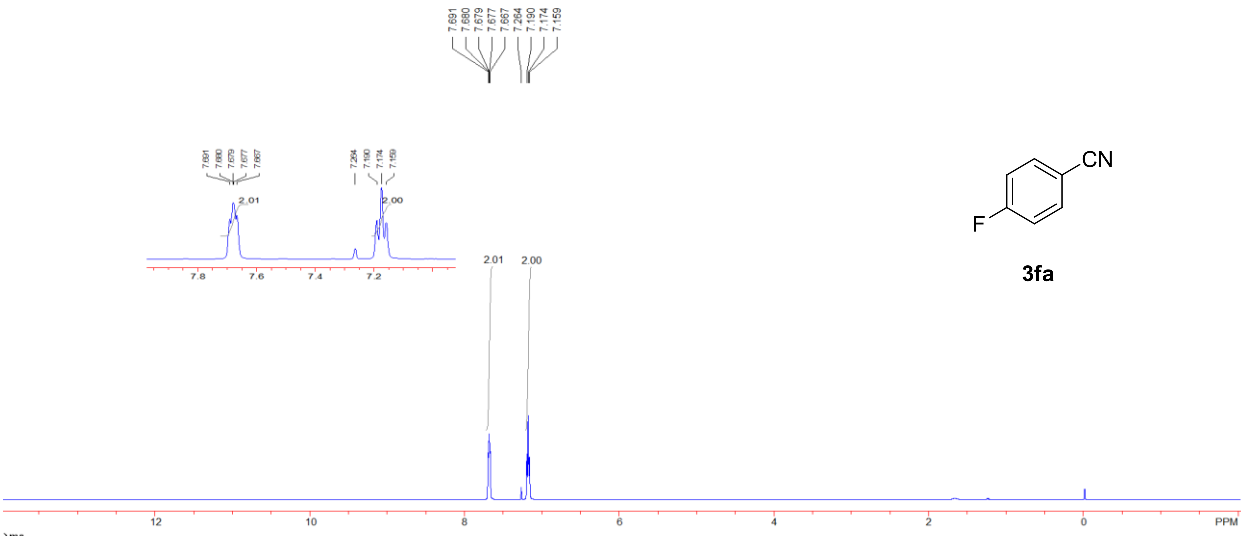
3eb

3eb, ^{13}C NMR, 126 MHz, $CDCl_3$



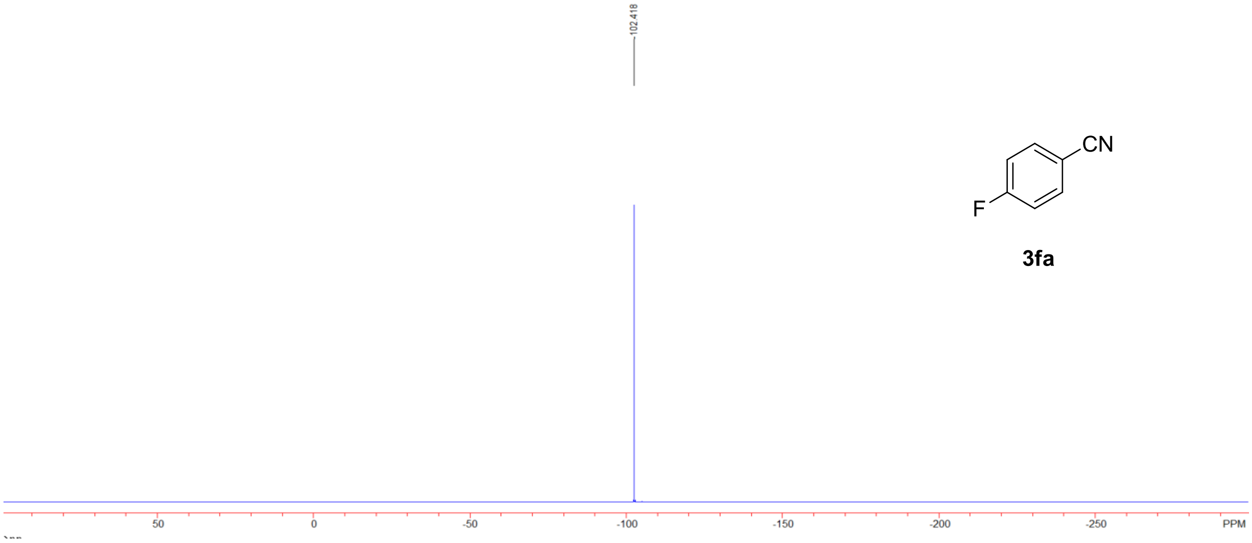
3eb

3fa, ^{1}H NMR, 500 MHz, $CDCl_3$

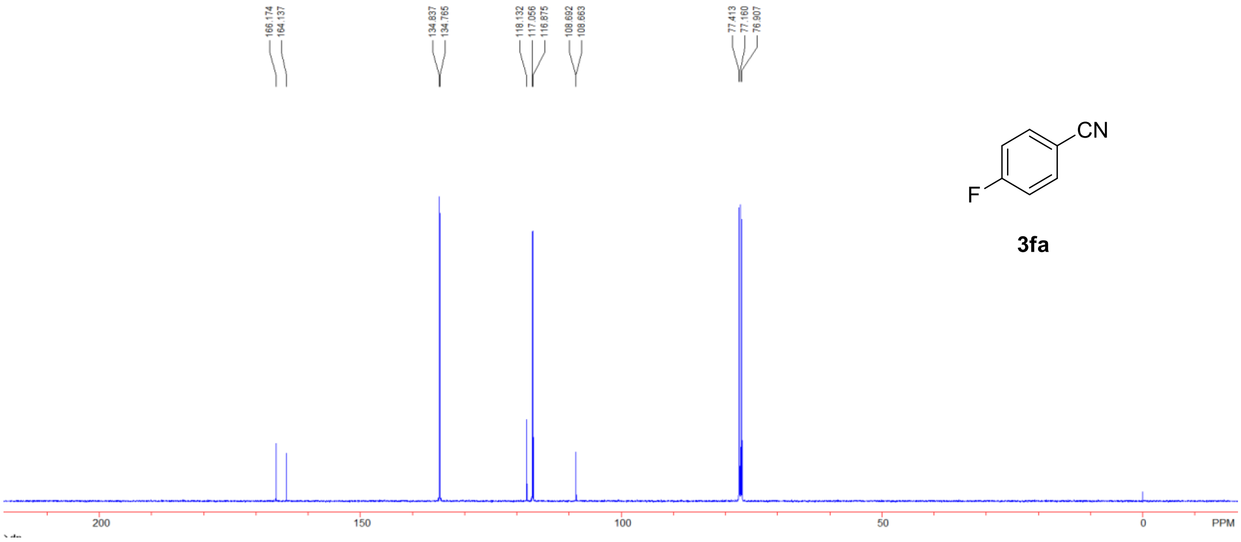


3fa

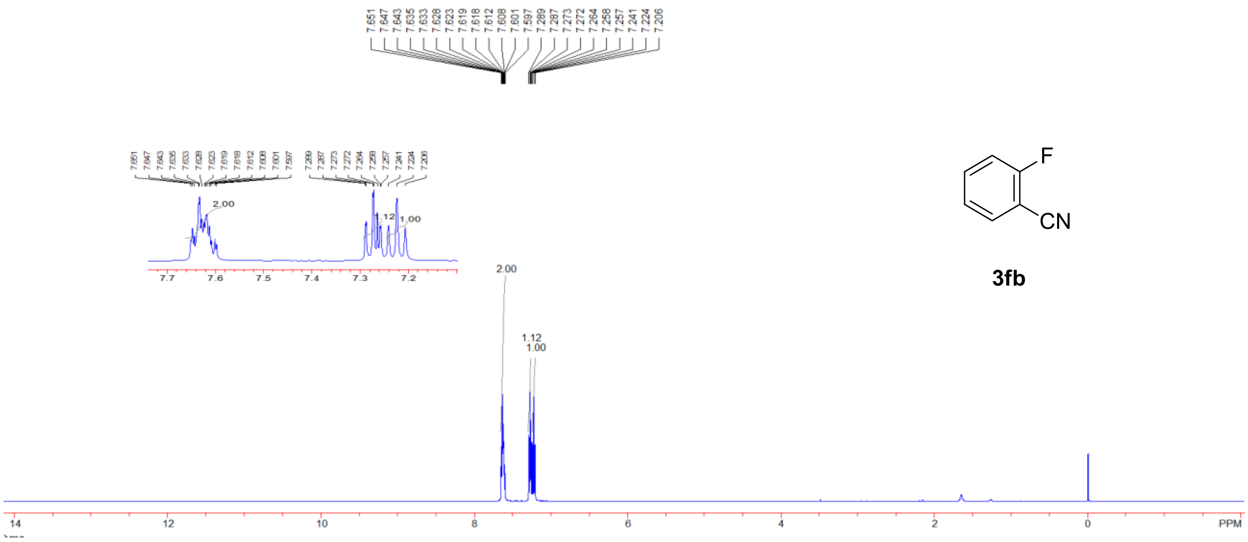
3fa, ^{19}F NMR, 471 MHz, $CDCl_3$



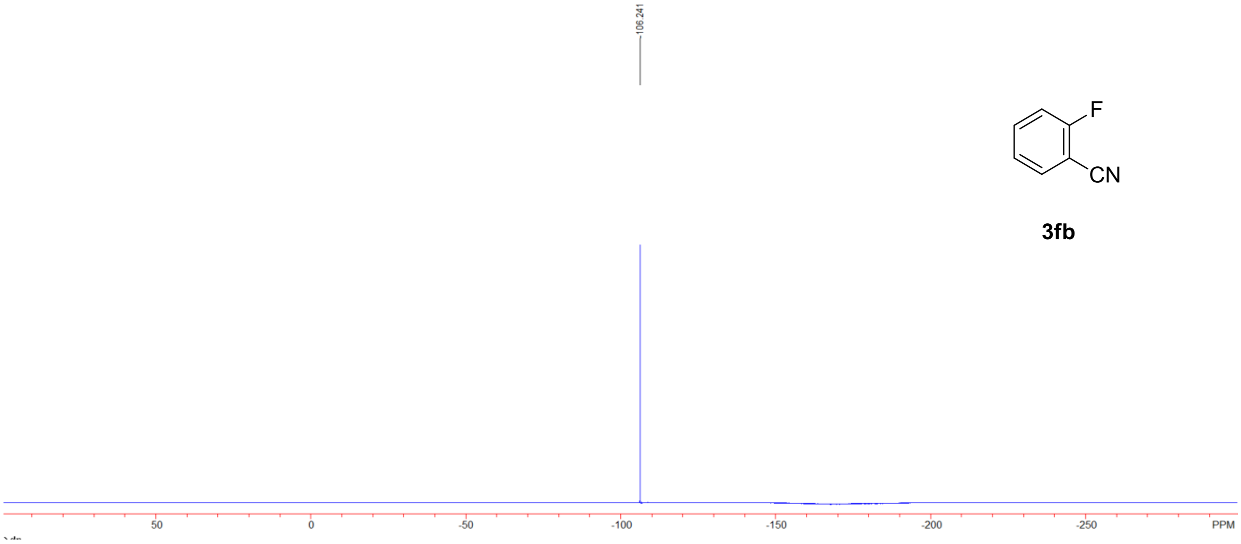
3fa, ^{13}C NMR, 126 MHz, $CDCl_3$



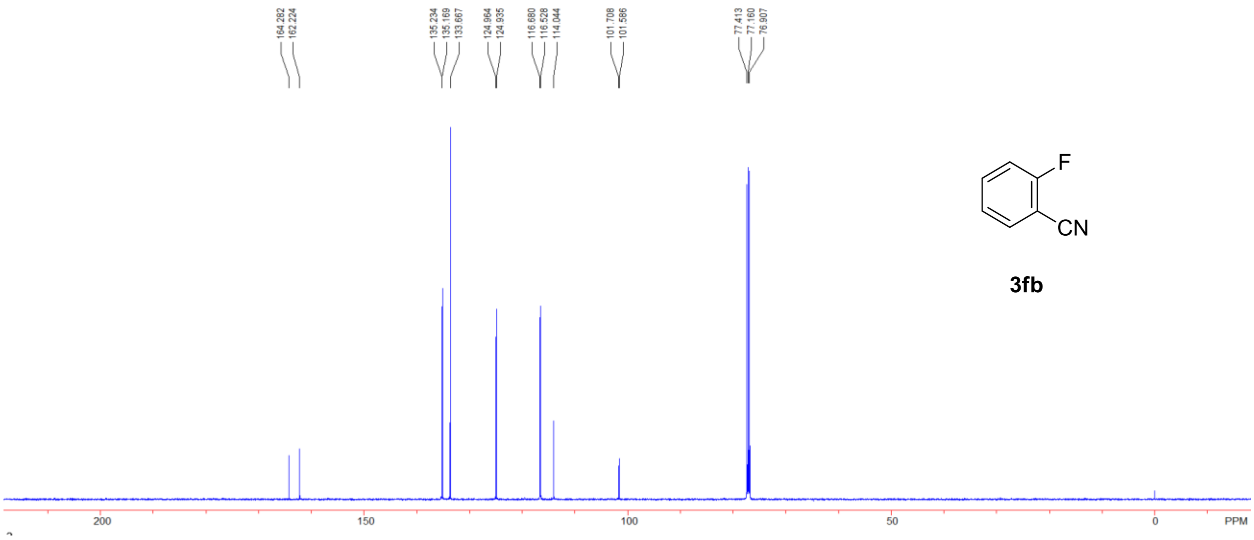
3fb, ^{1}H NMR, 500 MHz, $CDCl_3$



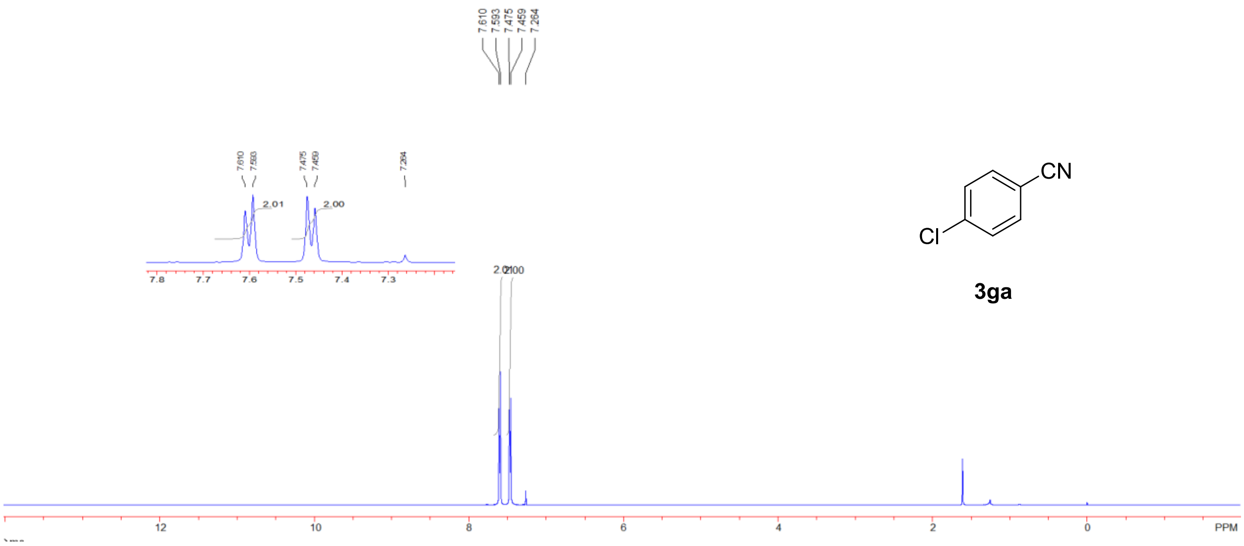
3fb, ^{19}F NMR, 471 MHz, $CDCl_3$



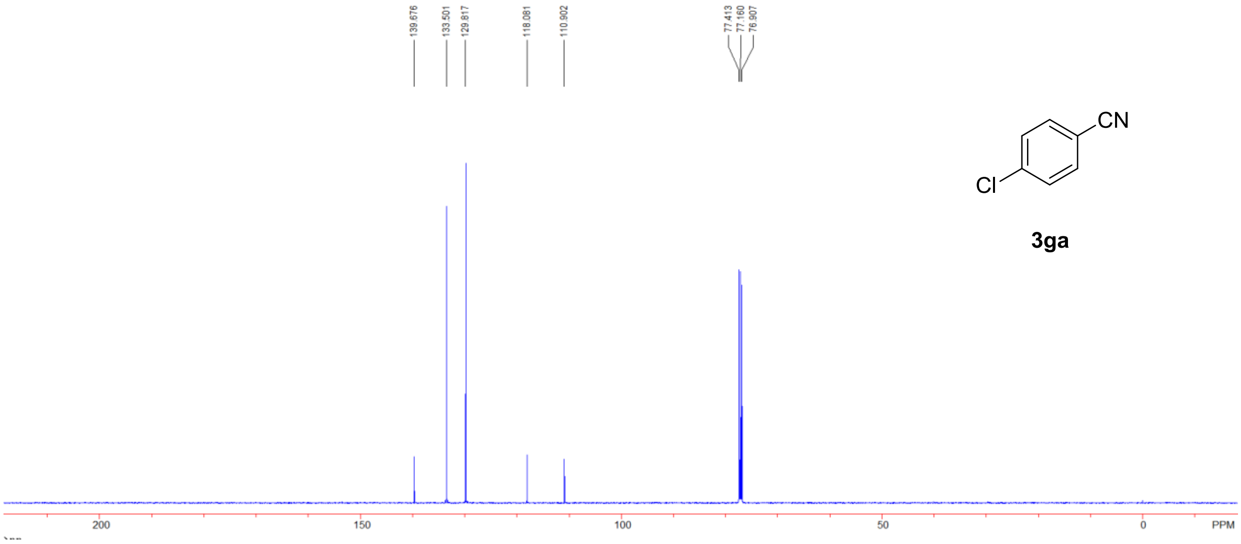
3fb, ^{13}C NMR, 126 MHz, $CDCl_3$



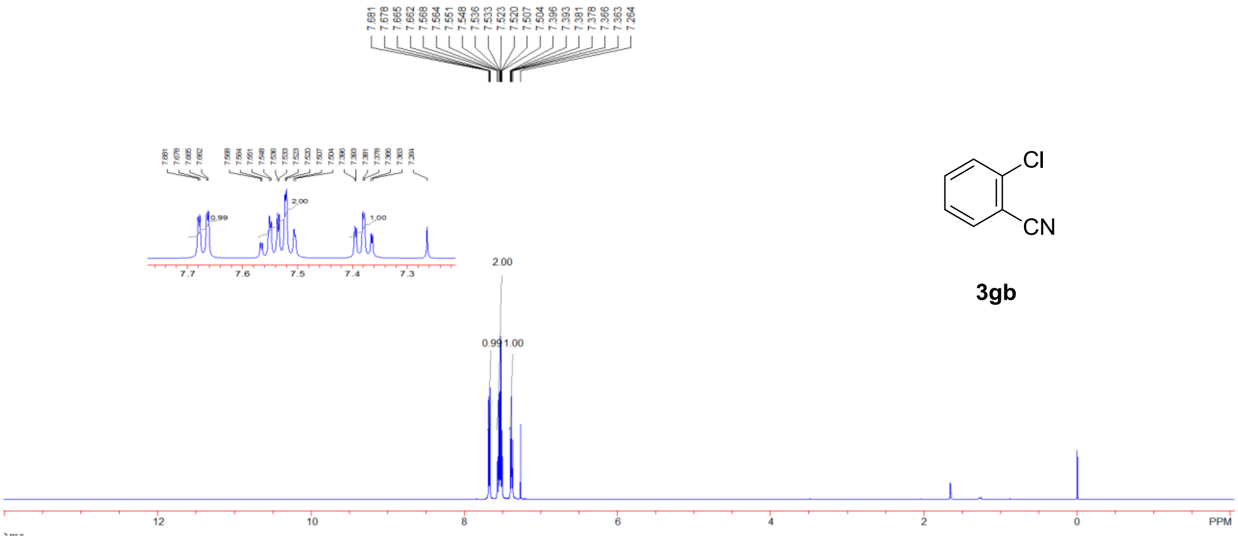
3ga, ^{1}H NMR, 500 MHz, $CDCl_3$



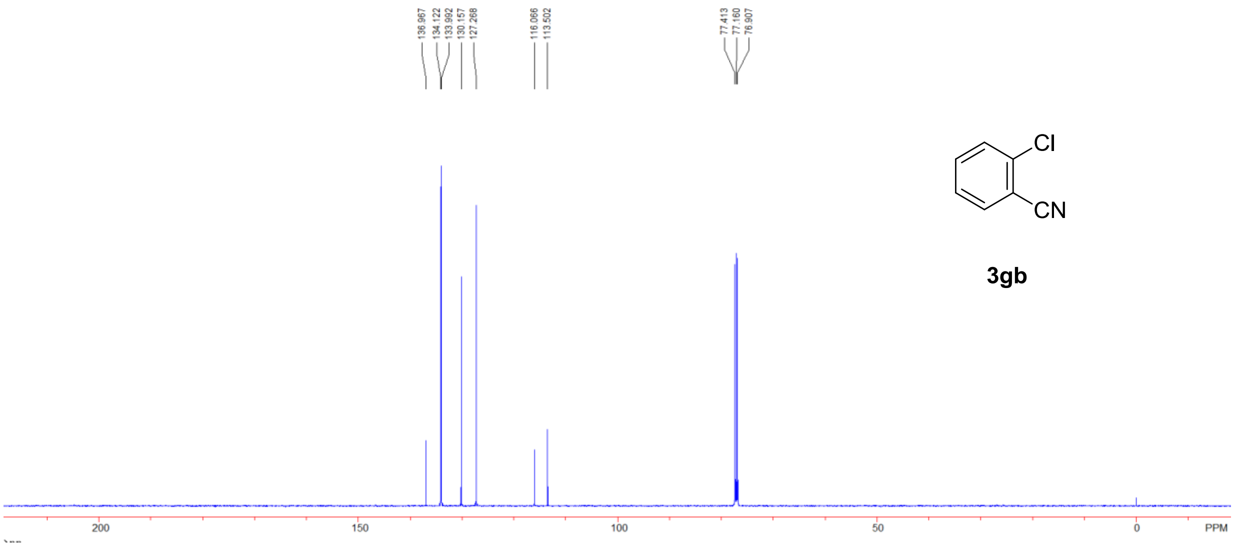
3ga, ^{13}C NMR, 126 MHz, $CDCl_3$



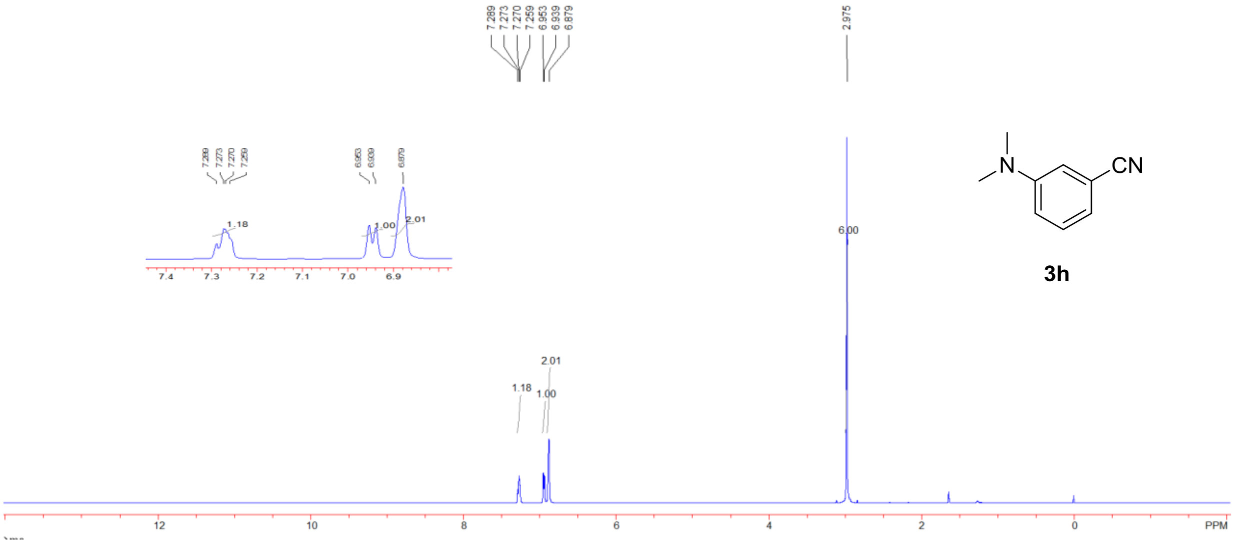
3gb, ^{1}H NMR, 500 MHz, $CDCl_3$



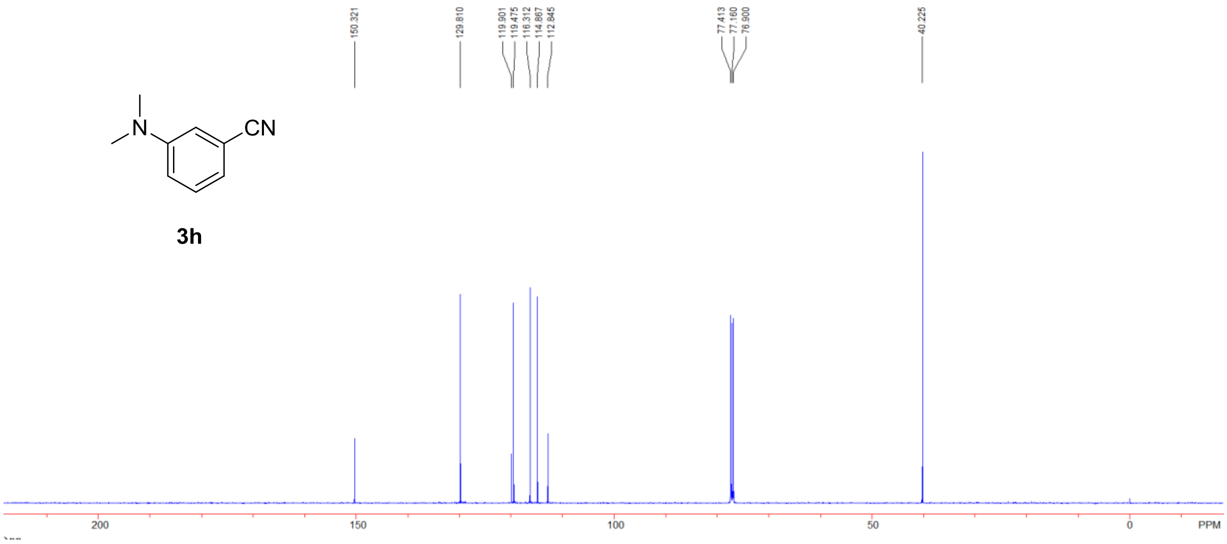
3gb, ^{13}C NMR, 126 MHz, $CDCl_3$



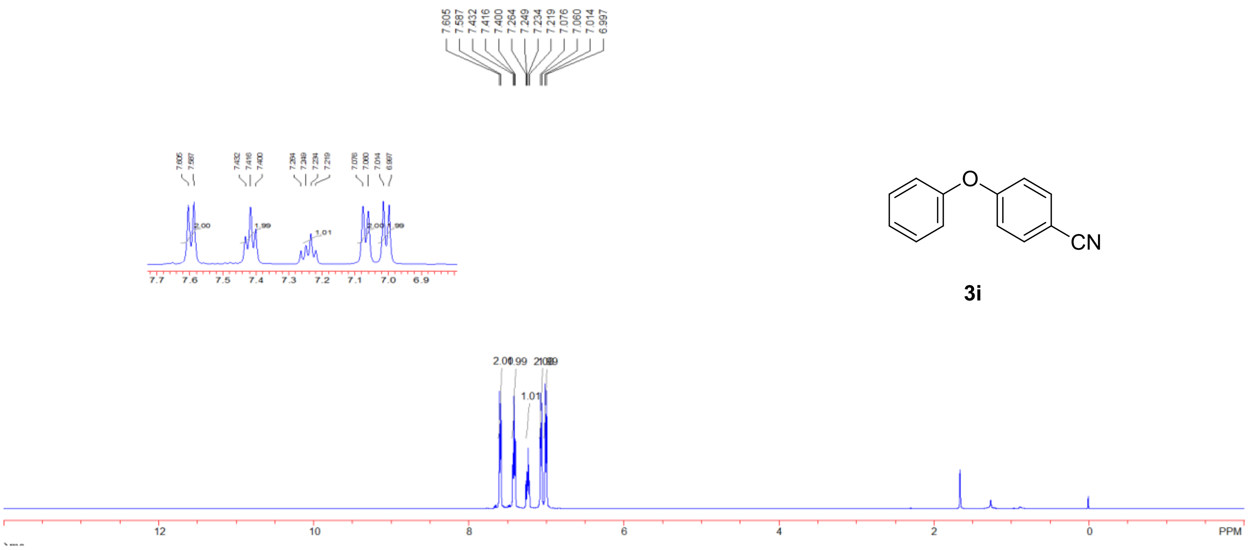
3h, ^{1}H NMR, 500 MHz, $CDCl_3$



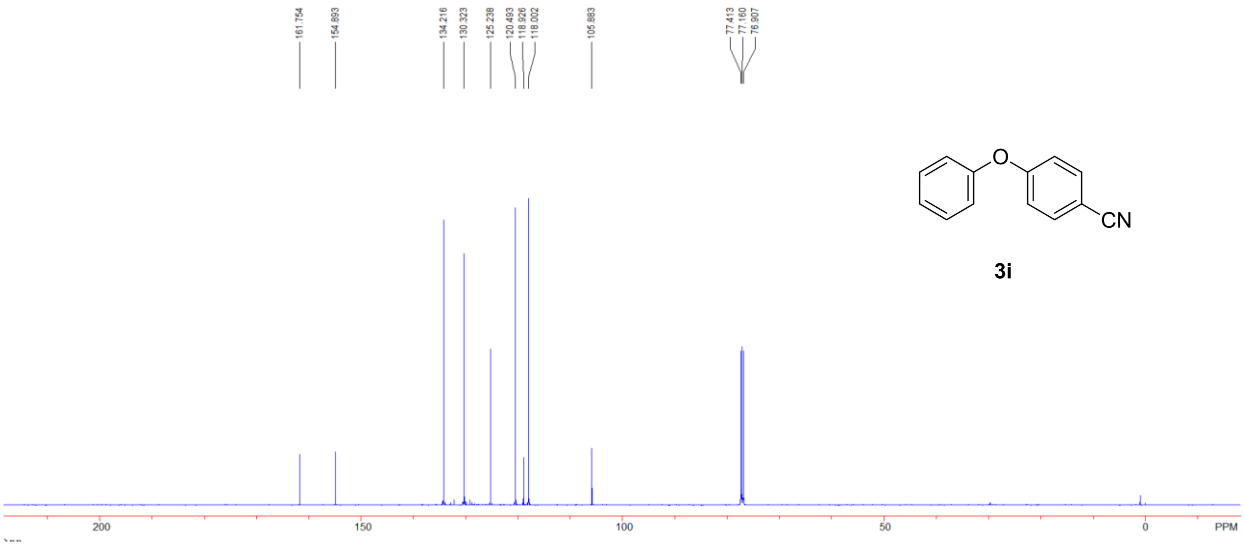
3h, ^{13}C NMR, 126 MHz, $CDCl_3$



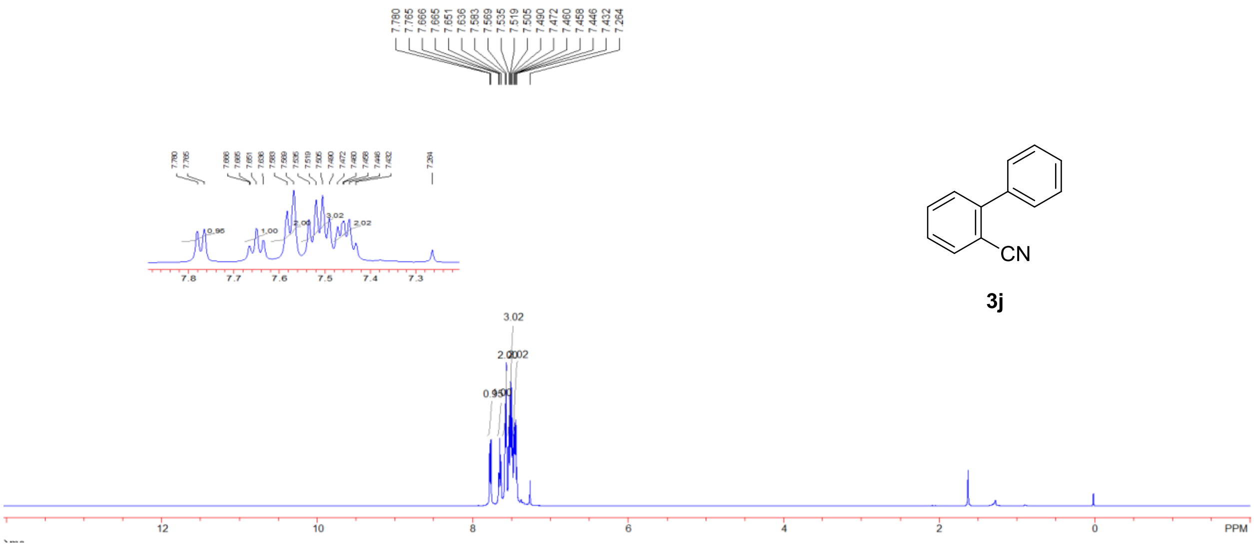
3i, ^{1}H NMR, 500 MHz, $CDCl_3$



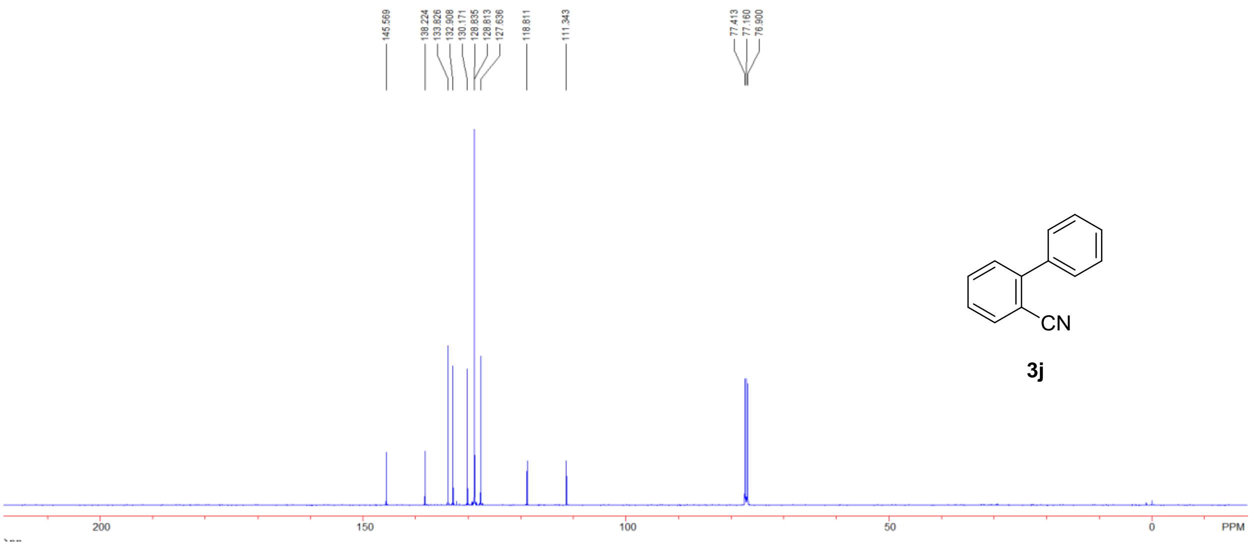
3i, ^{13}C NMR, 126 MHz, $CDCl_3$



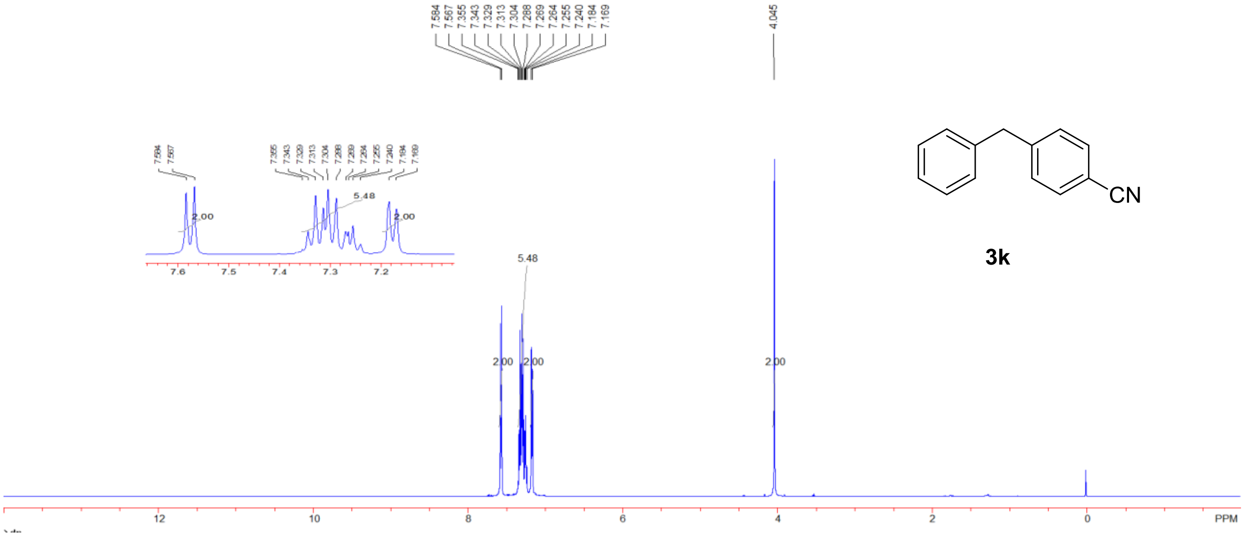
3j, ^{1}H NMR, 500 MHz, $CDCl_3$



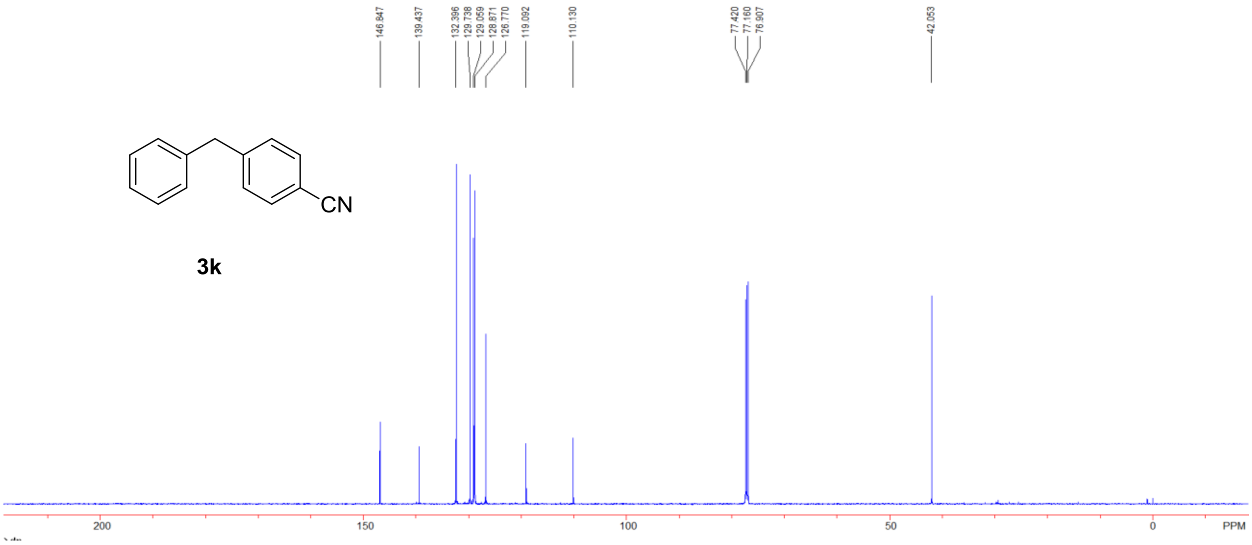
3j, ^{13}C NMR, 126 MHz, $CDCl_3$



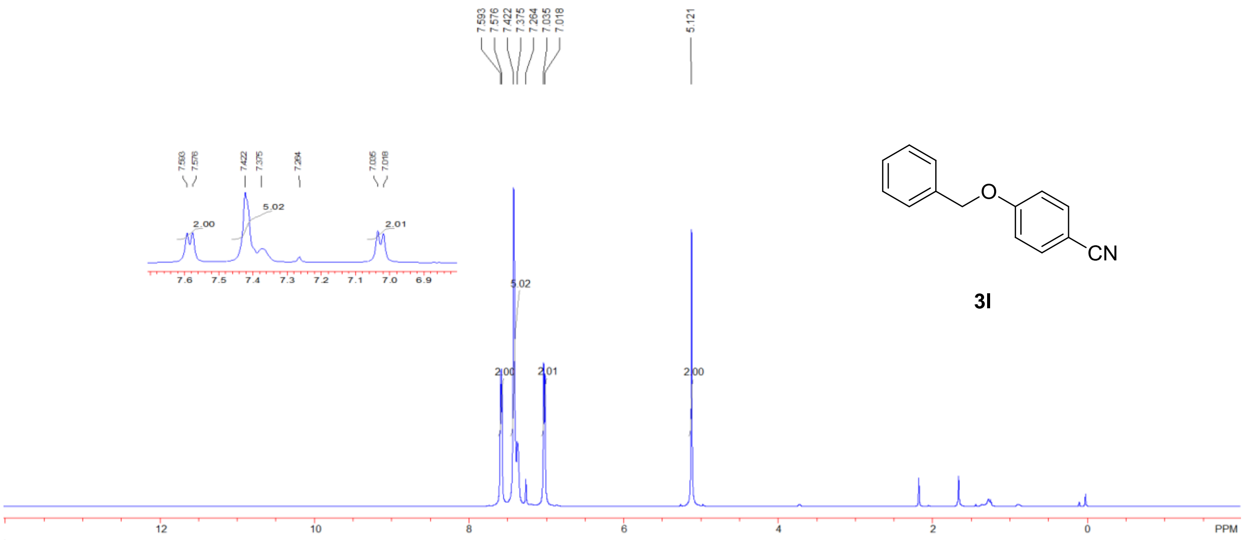
3k, ^{1}H NMR, 500 MHz, $CDCl_3$



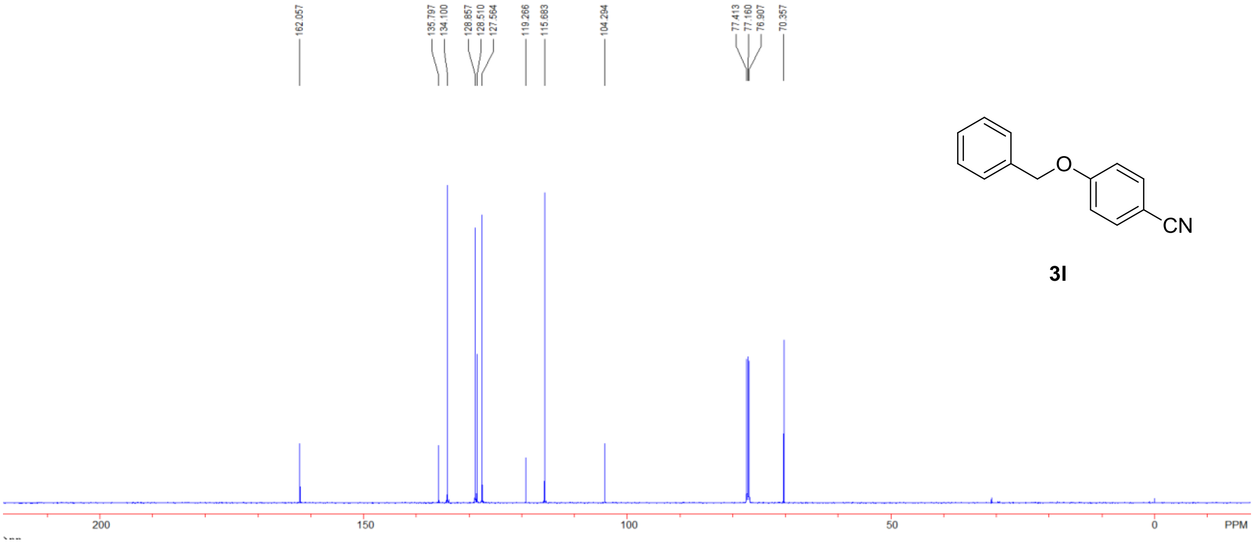
3k, ^{13}C NMR, 126 MHz, $CDCl_3$



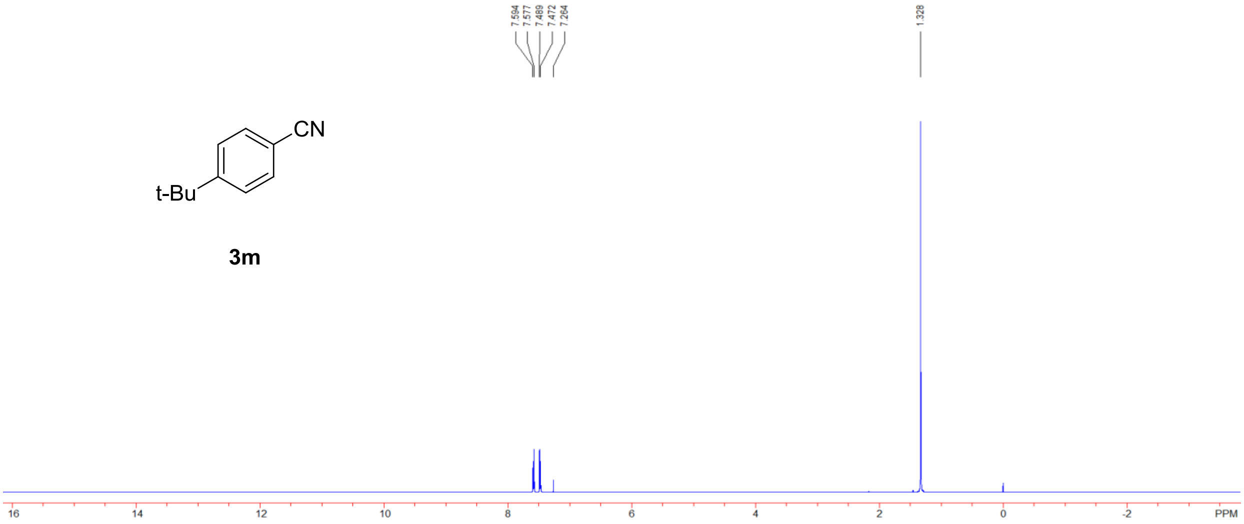
3l, ^{1}H NMR, 500 MHz, $CDCl_3$



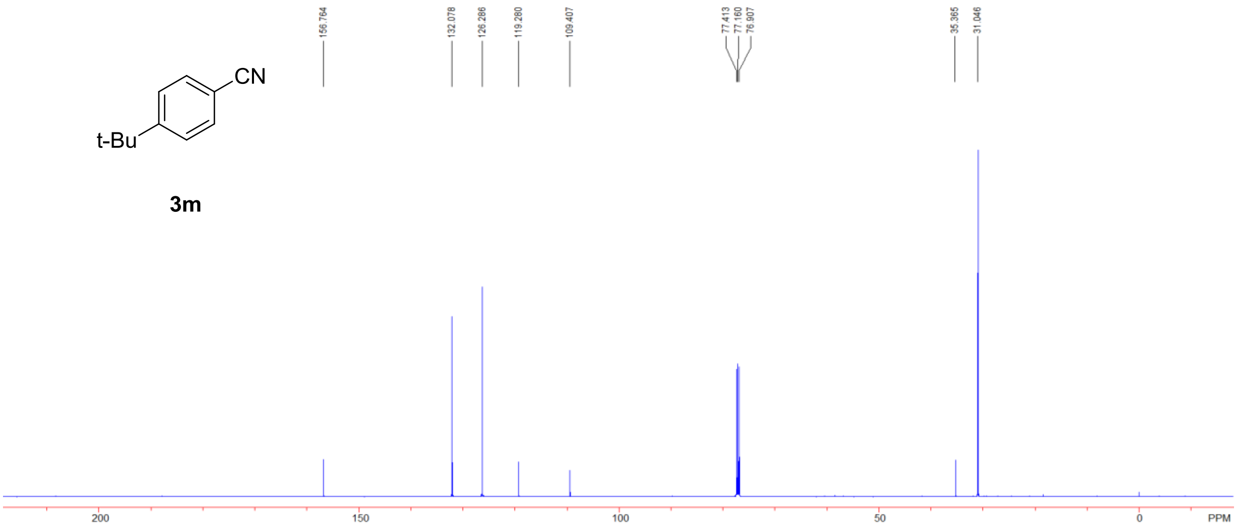
3l, ^{13}C NMR, 126 MHz, $CDCl_3$



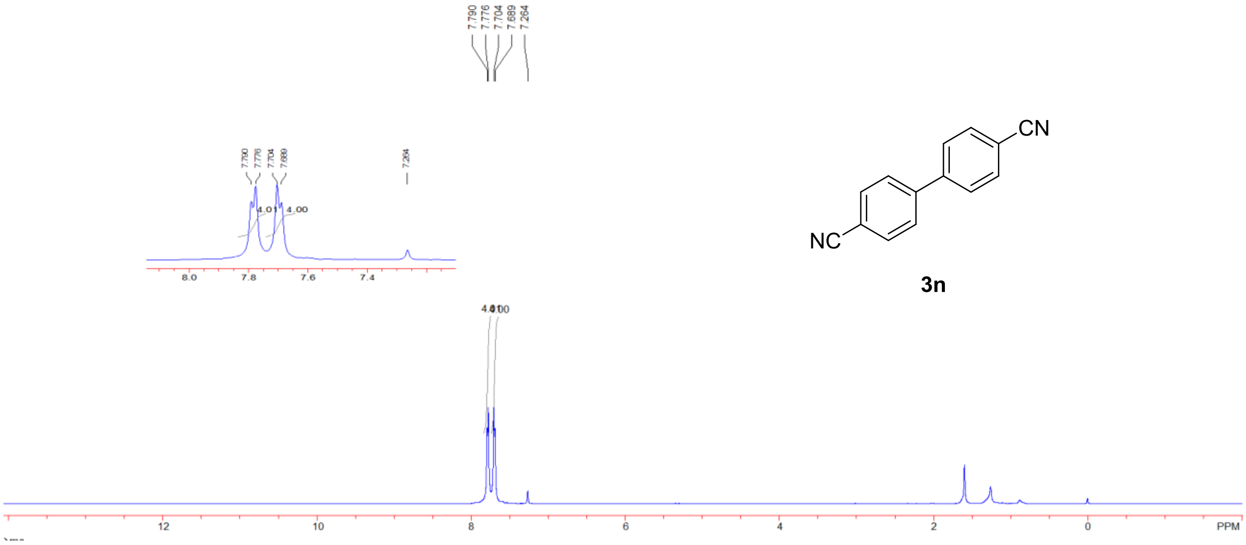
3m, ^{1}H NMR, 500 MHz, $CDCl_3$



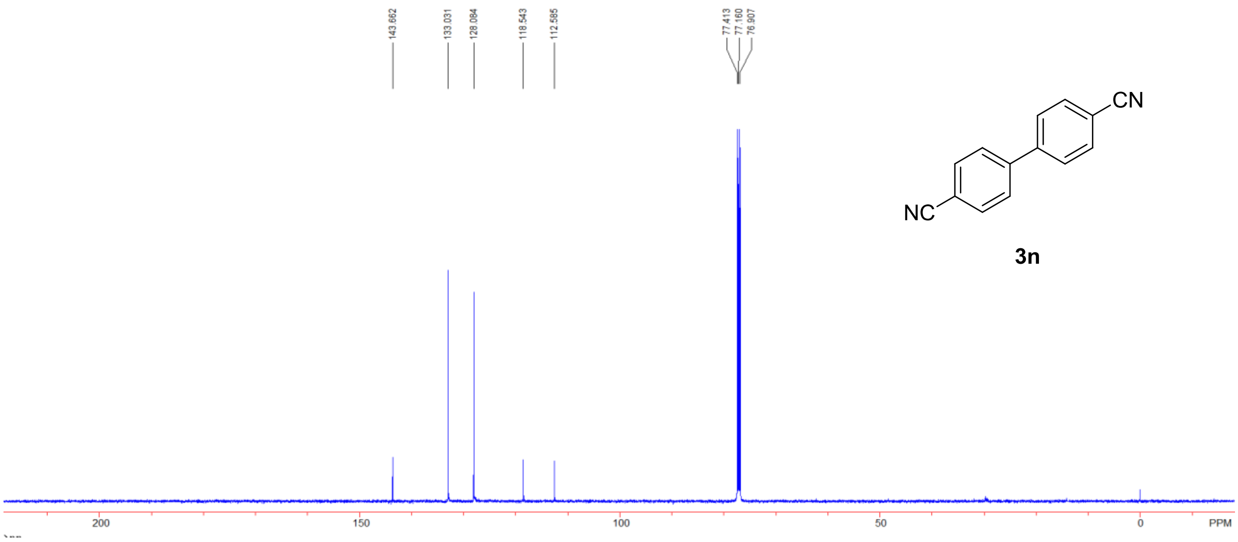
3m, ^{13}C NMR, 126 MHz, $CDCl_3$



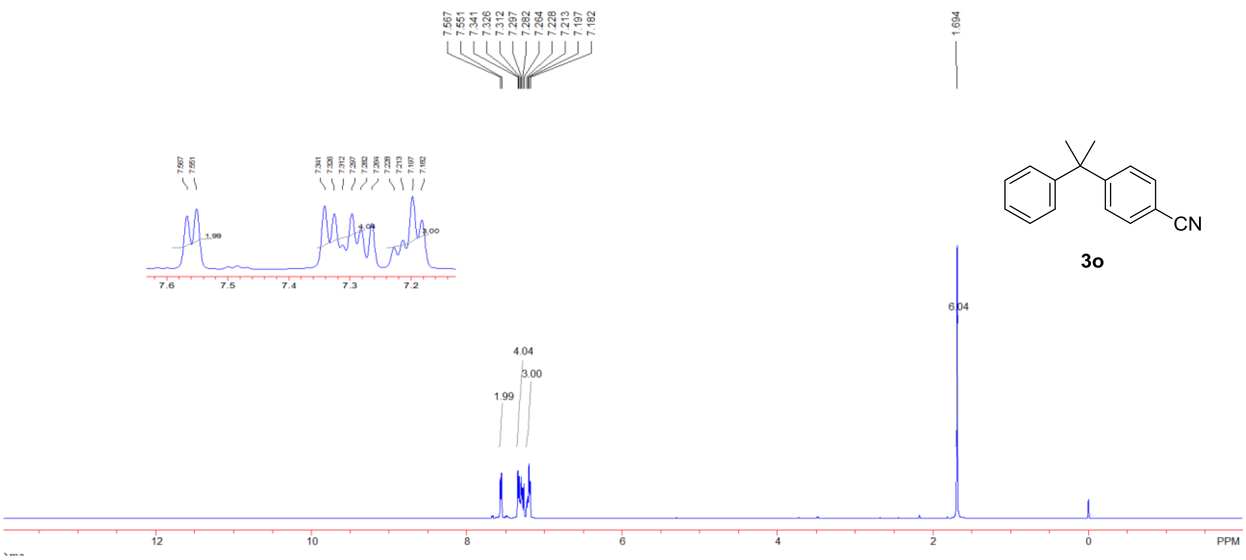
3n, ^{1}H NMR, 500 MHz, $CDCl_3$



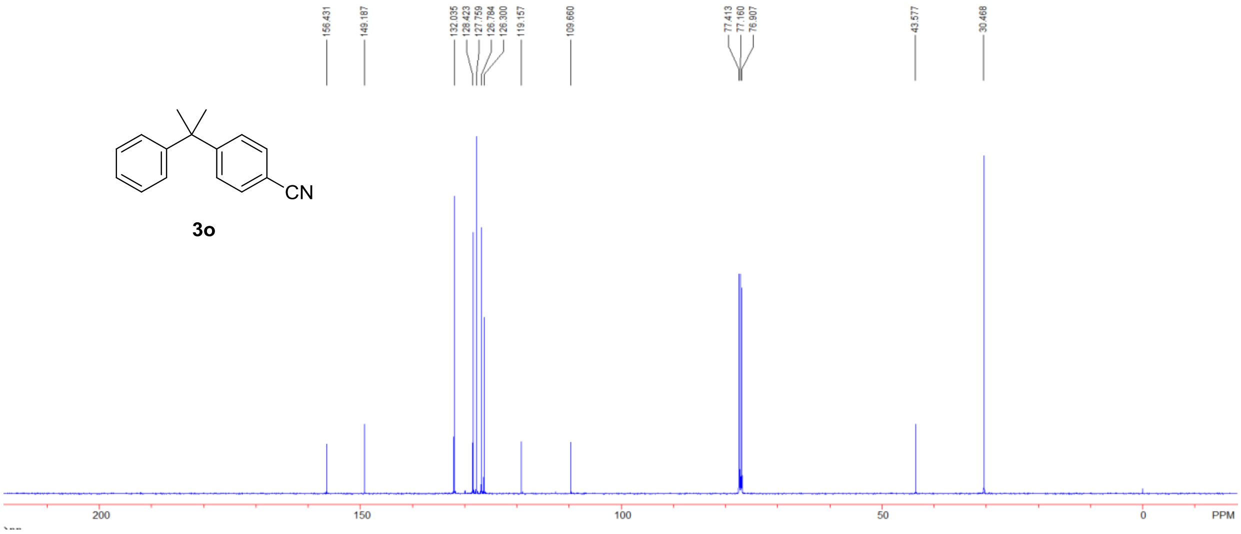
3n, ^{13}C NMR, 126 MHz, $CDCl_3$



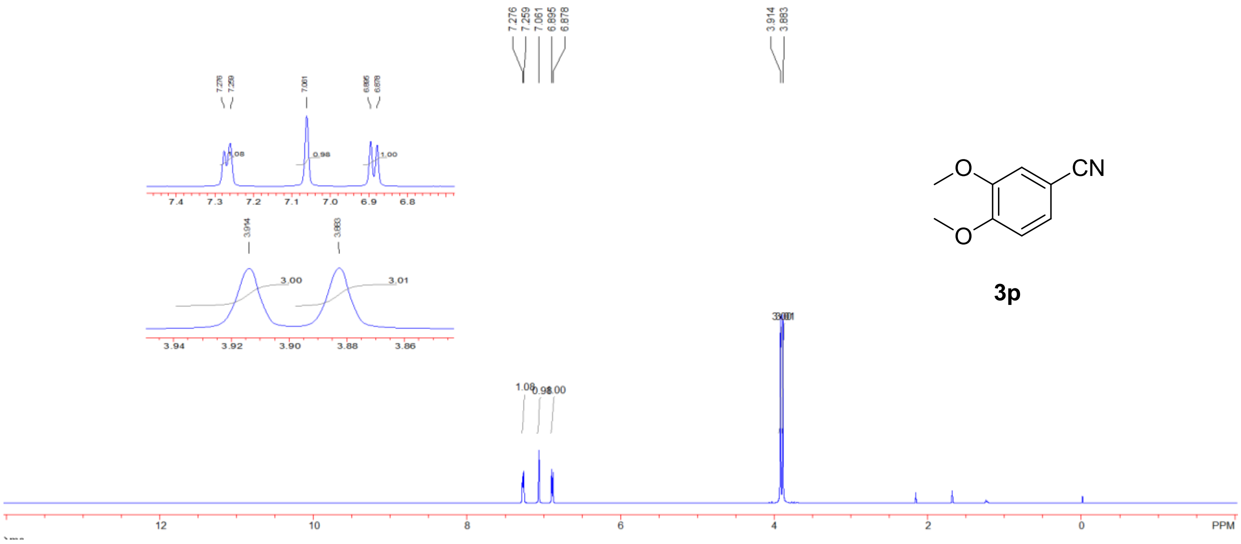
3o, ^{1}H NMR, 500 MHz, $CDCl_3$



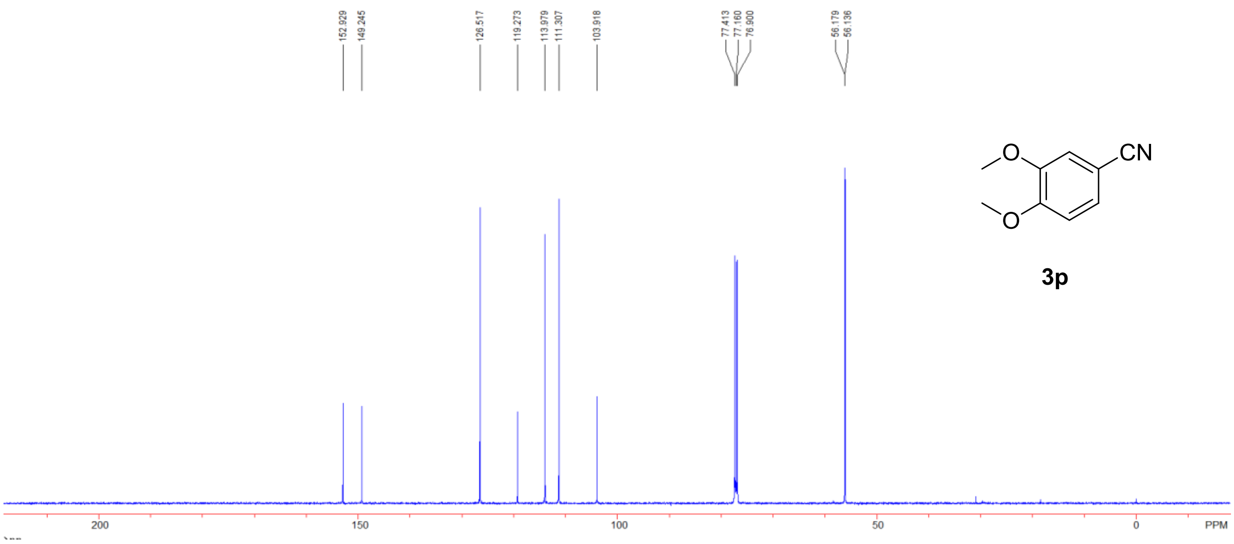
3o, ^{13}C NMR, 126 MHz, $CDCl_3$



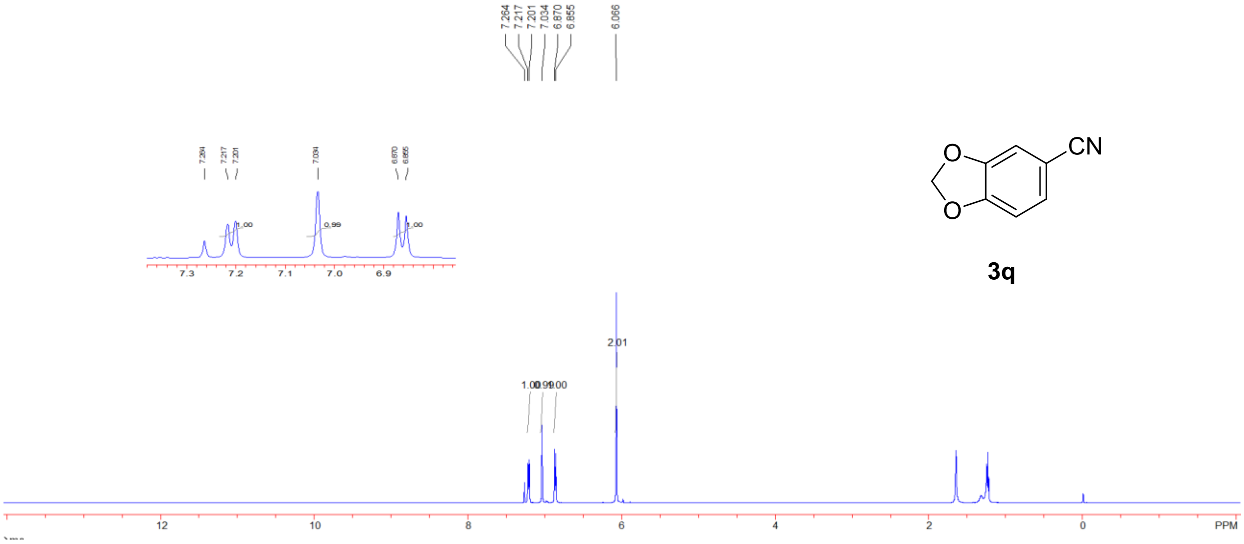
3p, ^{1}H NMR, 500 MHz, $CDCl_3$



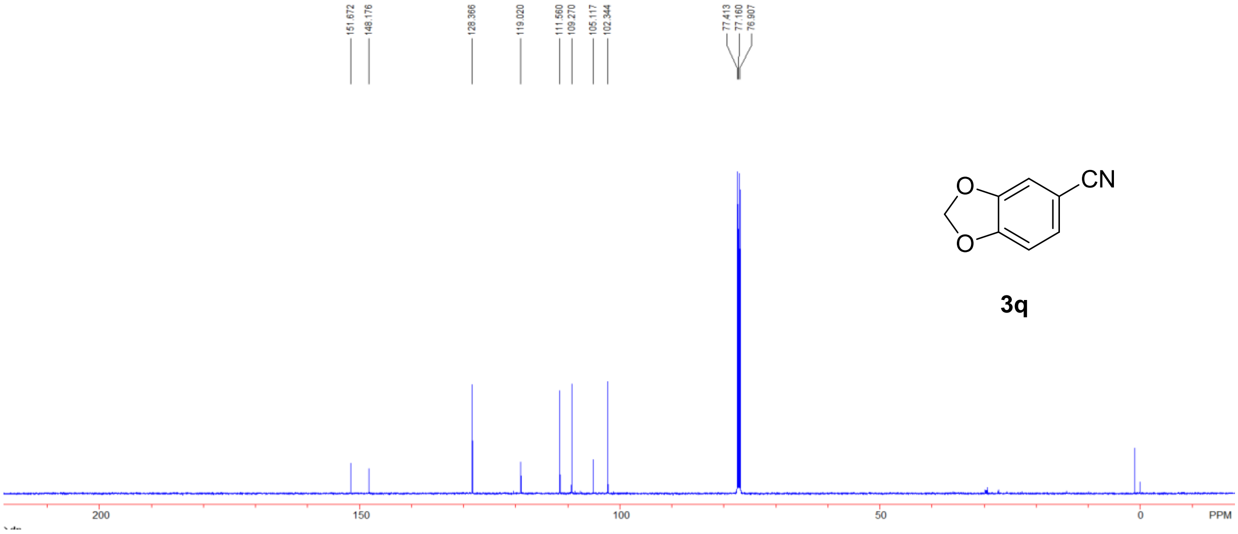
3p, ^{13}C NMR, 126 MHz, $CDCl_3$



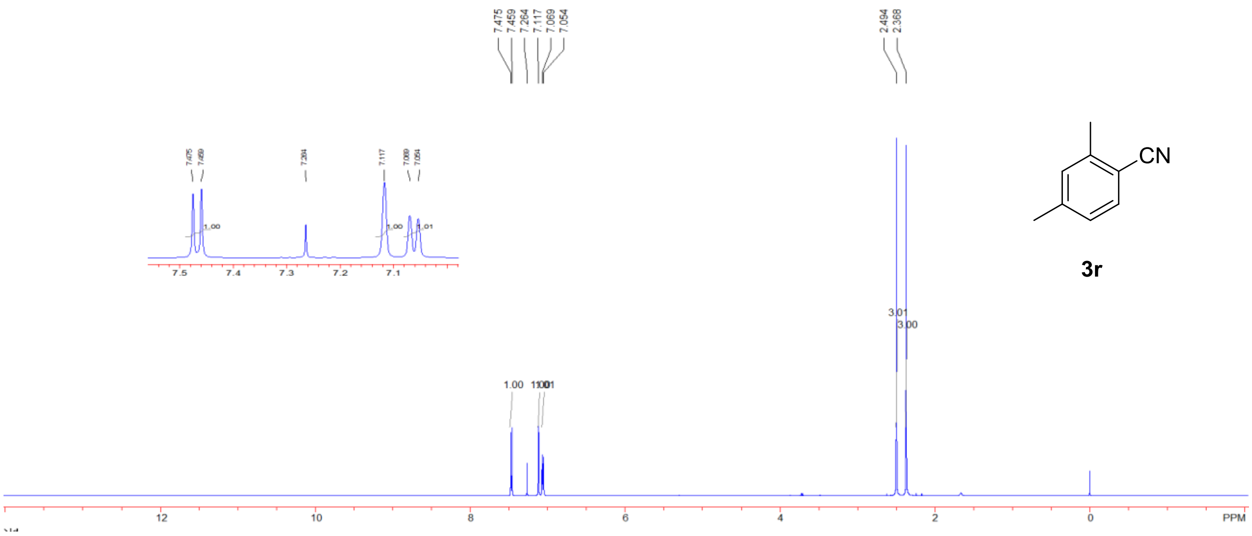
3q, ^{1}H NMR, 500 MHz, $CDCl_3$



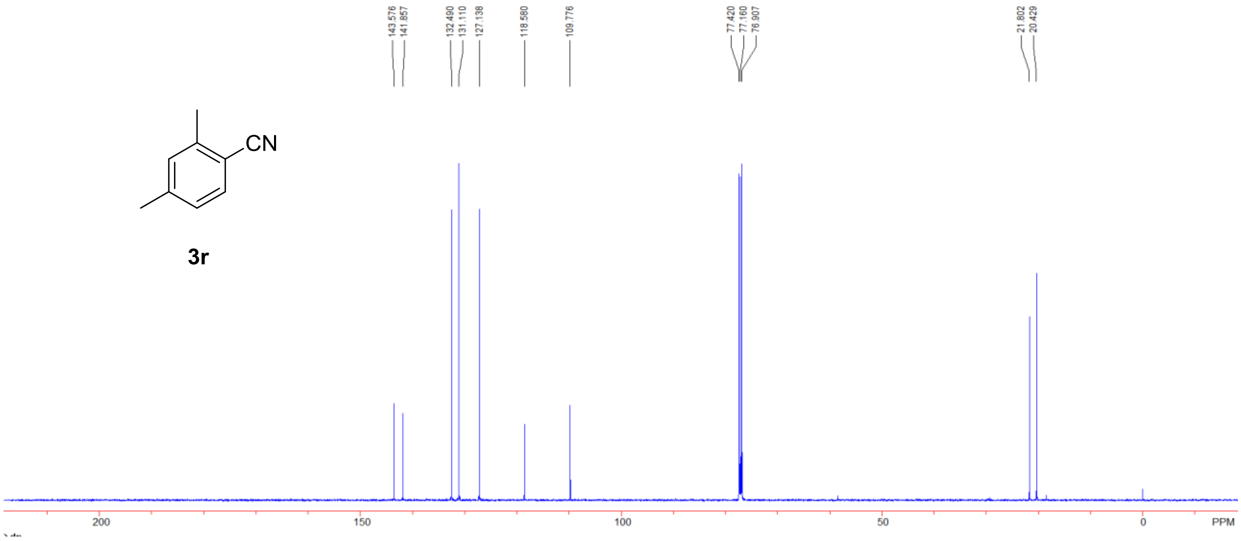
3q, ^{13}C NMR, 126 MHz, $CDCl_3$



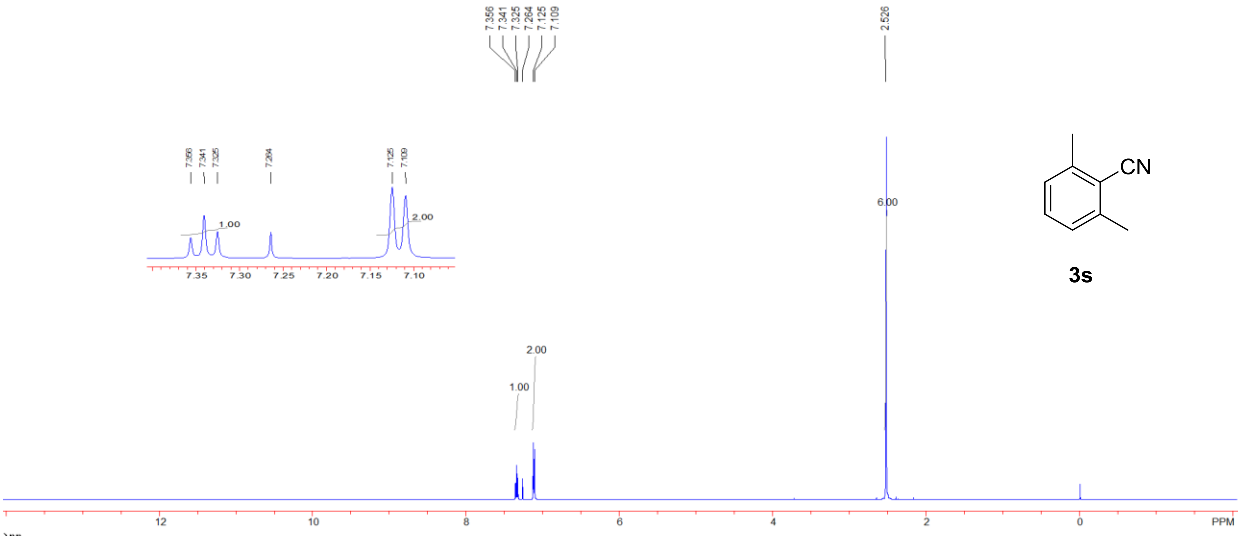
3r, ^{1}H NMR, 500 MHz, $CDCl_3$



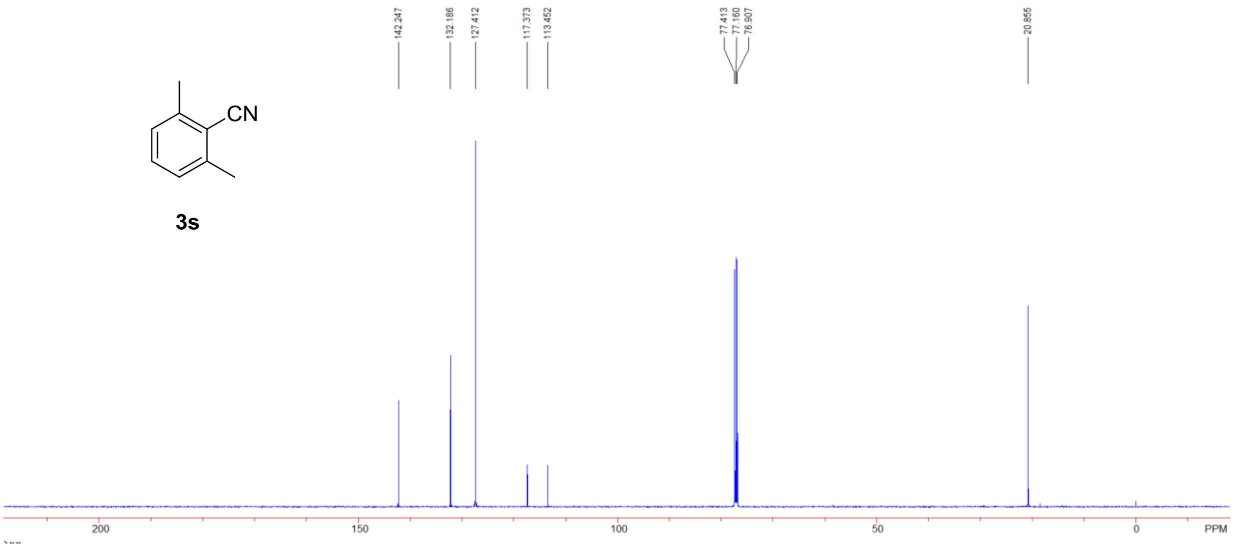
3r, ^{13}C NMR, 126 MHz, $CDCl_3$



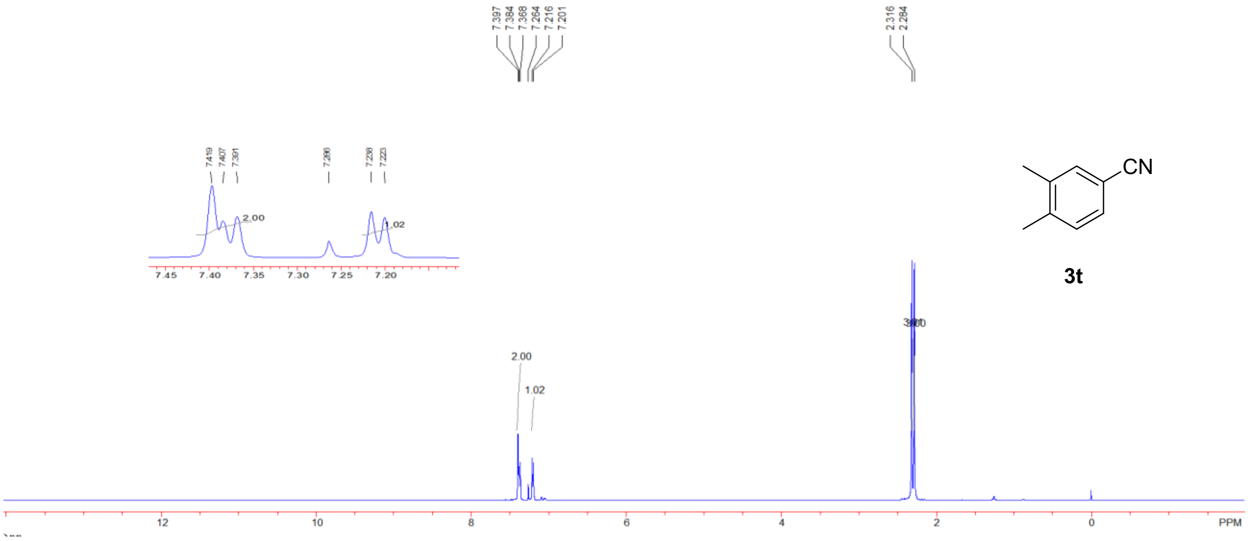
3s, ^{1}H NMR, 500 MHz, $CDCl_3$



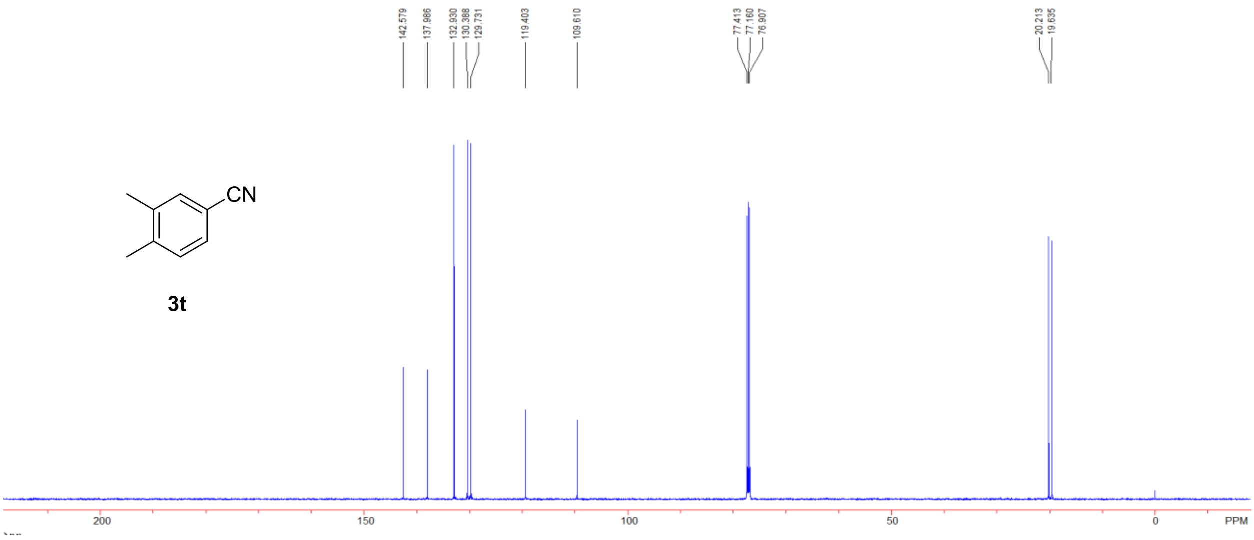
3s, ^{13}C NMR, 126 MHz, $CDCl_3$



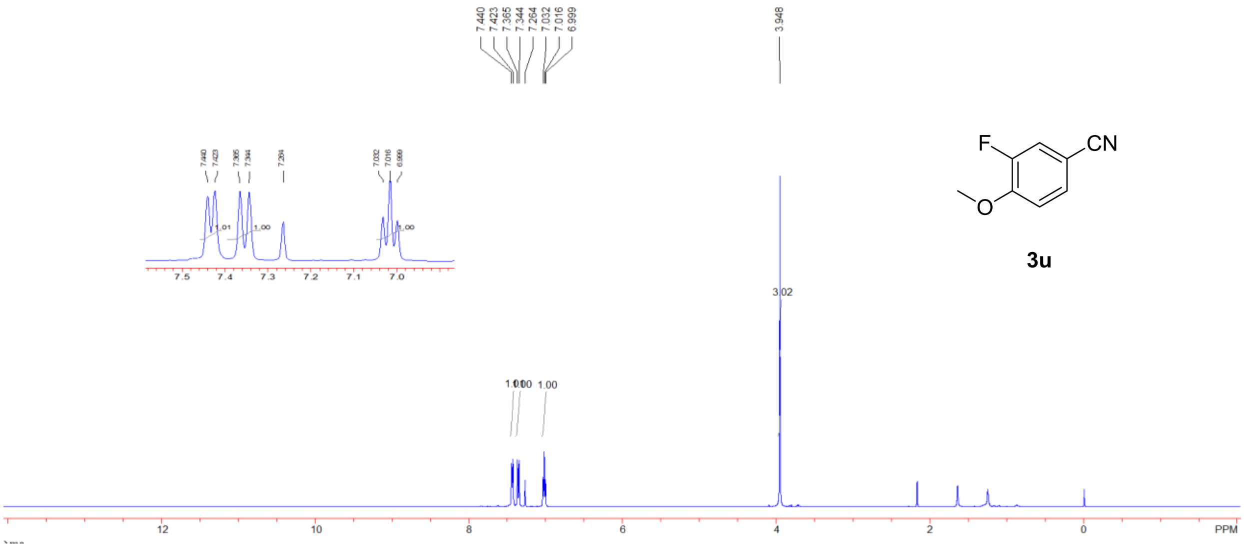
3t, ^{1}H NMR, 500 MHz, $CDCl_3$



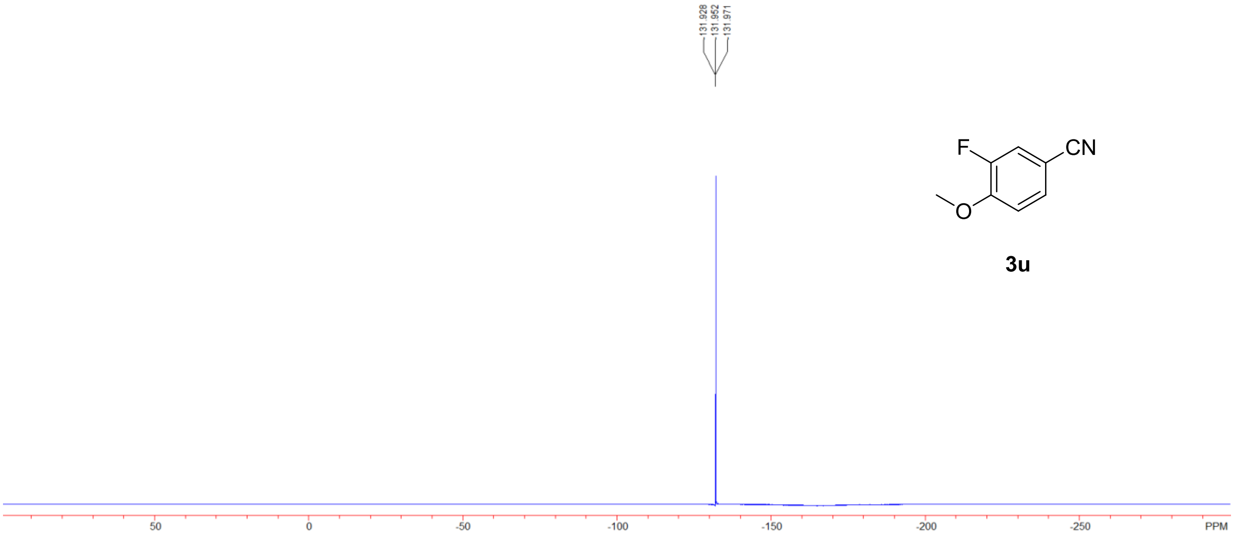
3t, ^{13}C NMR, 126 MHz, $CDCl_3$



3u, ^{1}H NMR, 500 MHz, $CDCl_3$

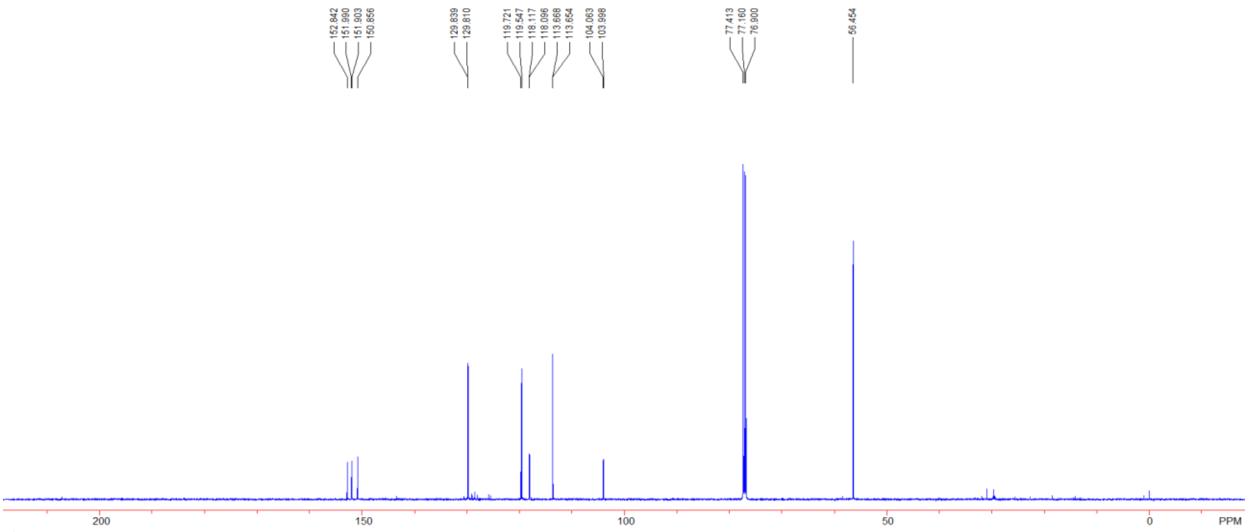


3u, ^{1}H NMR, 500 MHz, $CDCl_3$

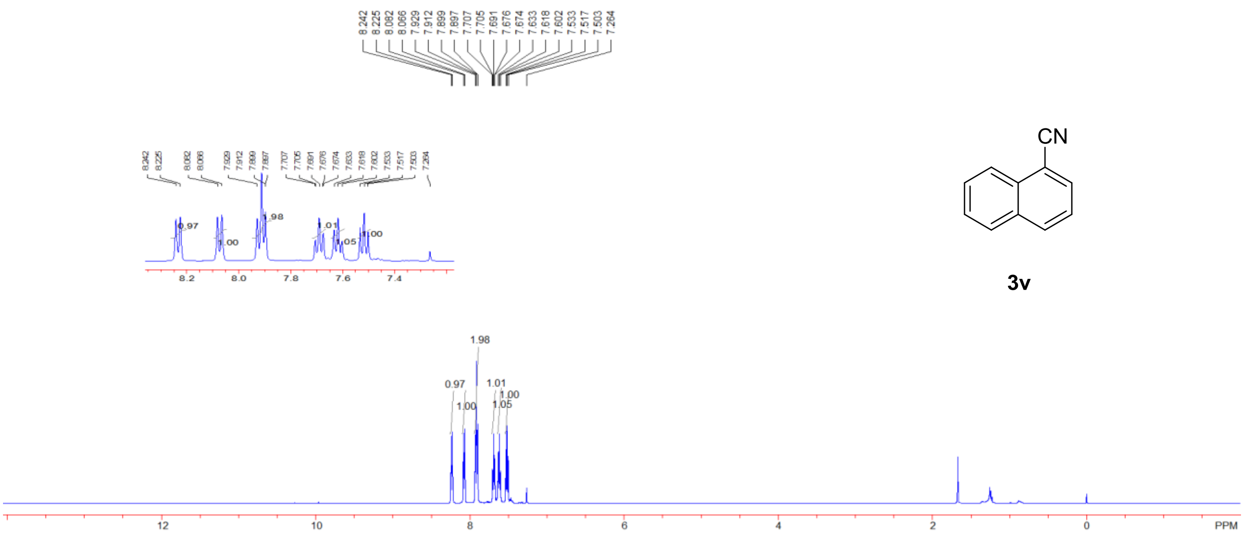


3u

3u, ^{13}C NMR, 126 MHz, $CDCl_3$

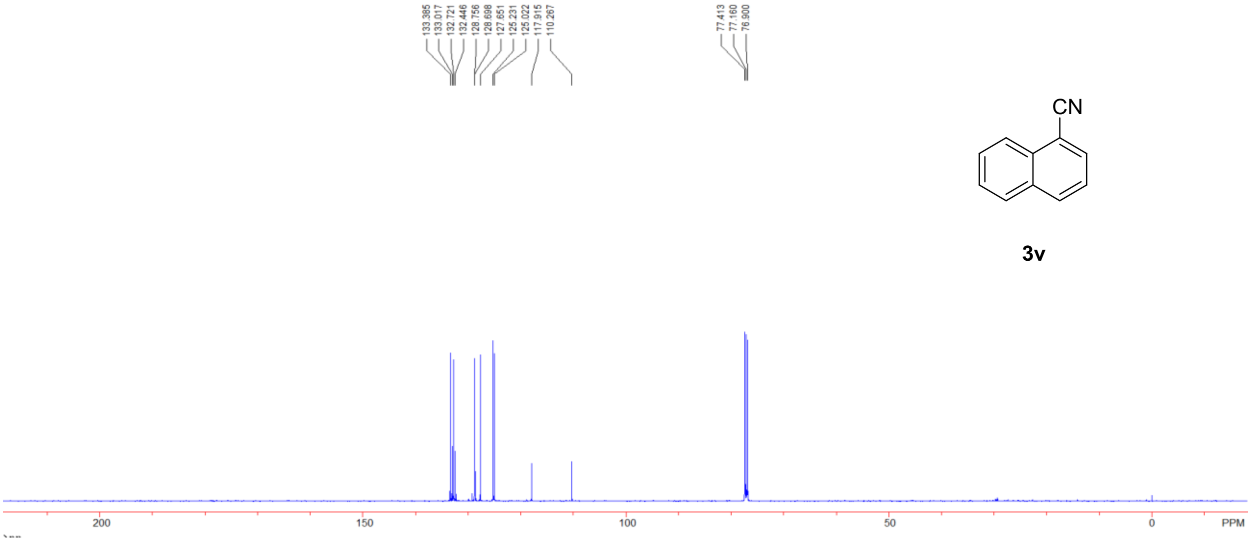


3v, ^{1}H NMR, 500 MHz, $CDCl_3$

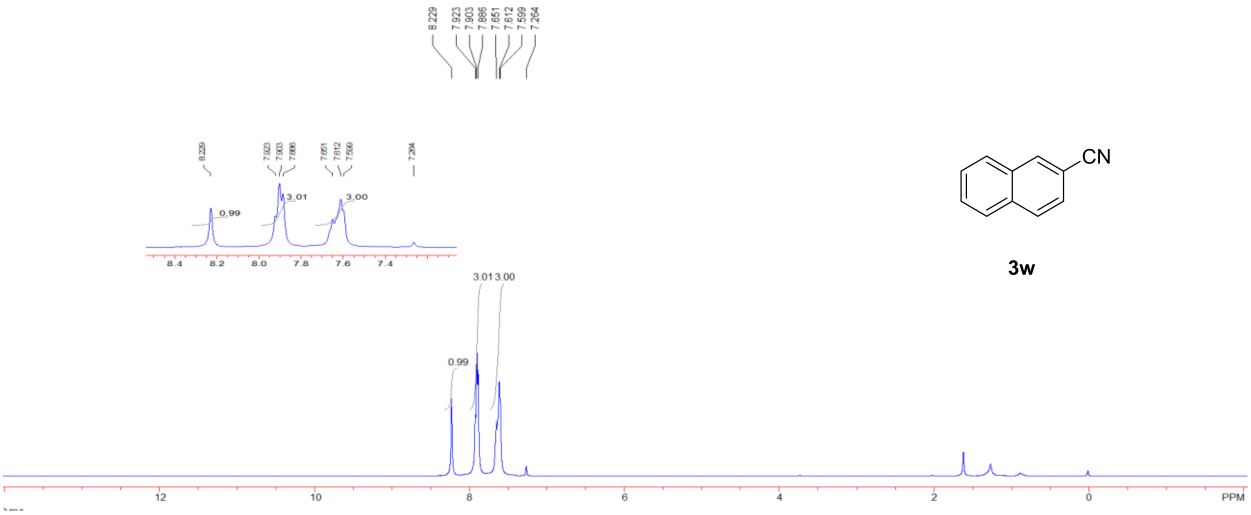


3v

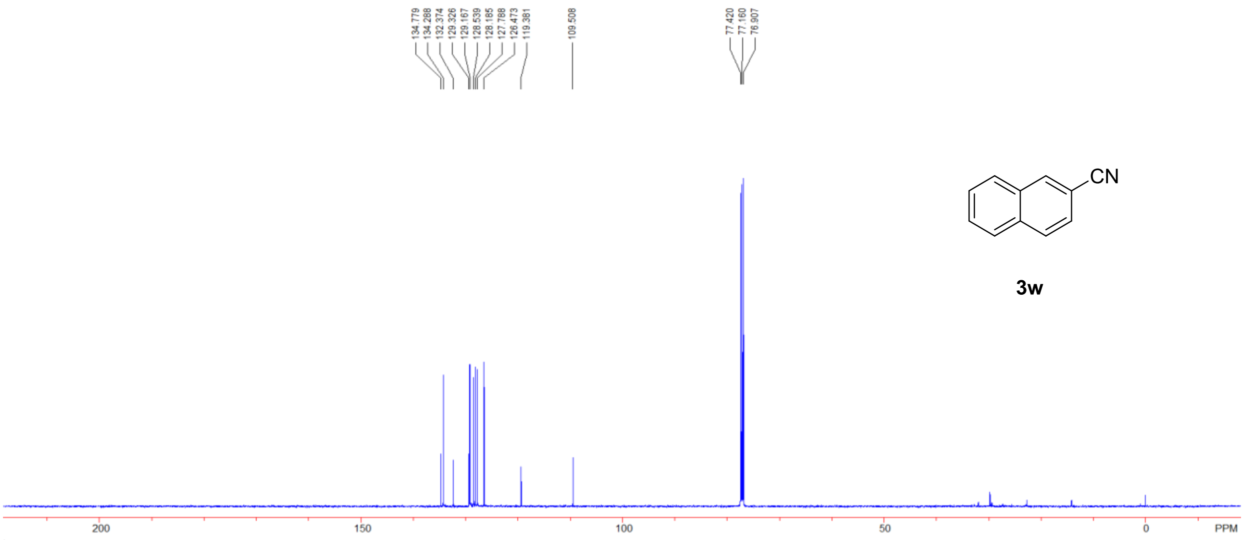
3v, ^{13}C NMR, 126 MHz, $CDCl_3$



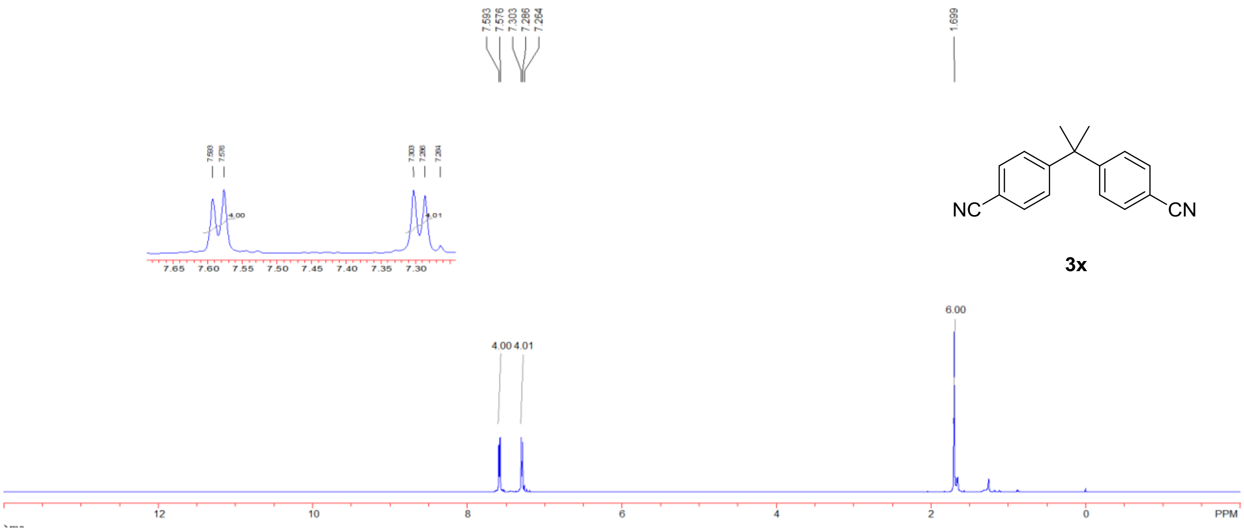
3w, ^{1}H NMR, 500 MHz, $CDCl_3$



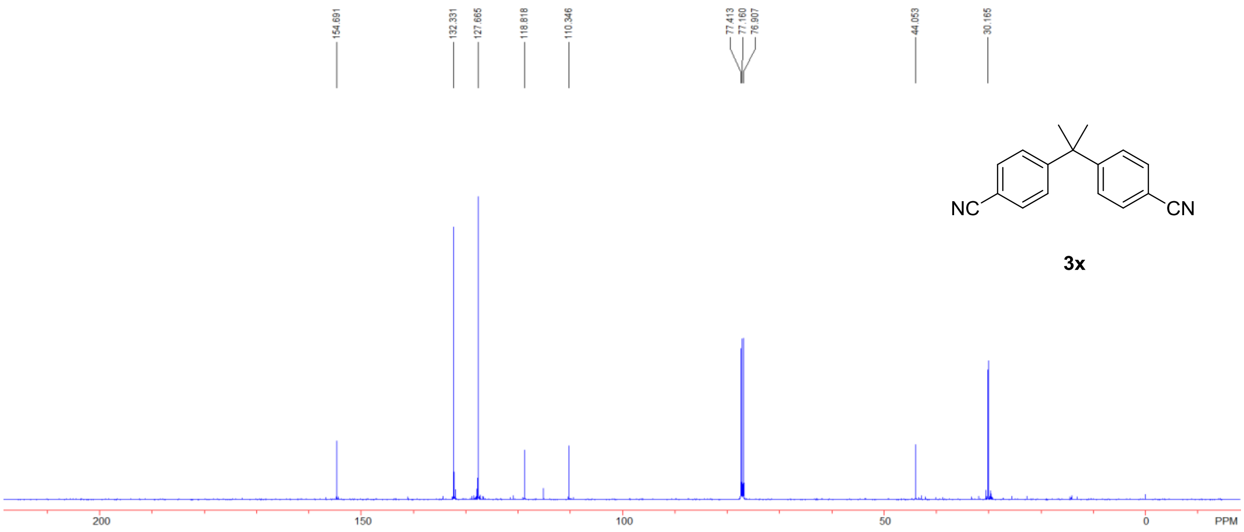
3w, ^{13}C NMR, 126 MHz, $CDCl_3$



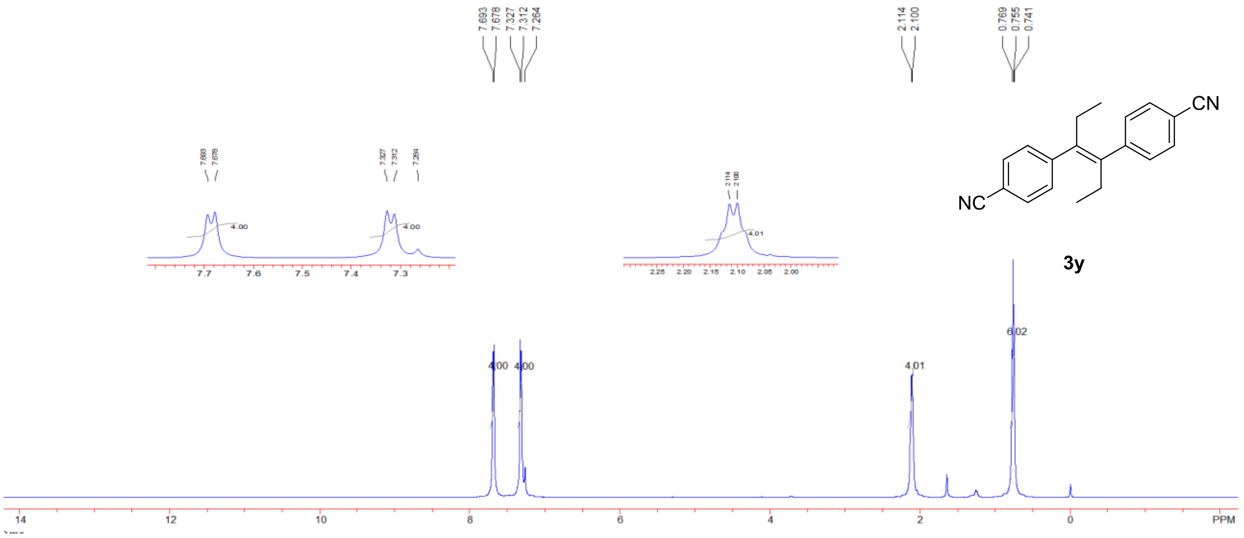
3x, ^{1}H NMR, 500 MHz, $CDCl_3$



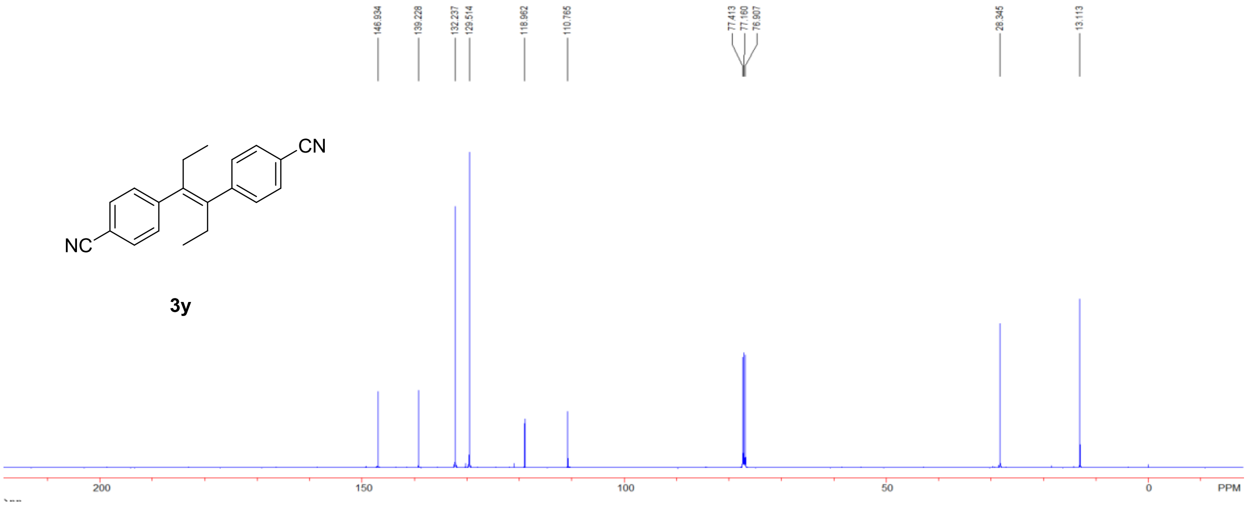
3x, ^{13}C NMR, 126 MHz, $CDCl_3$



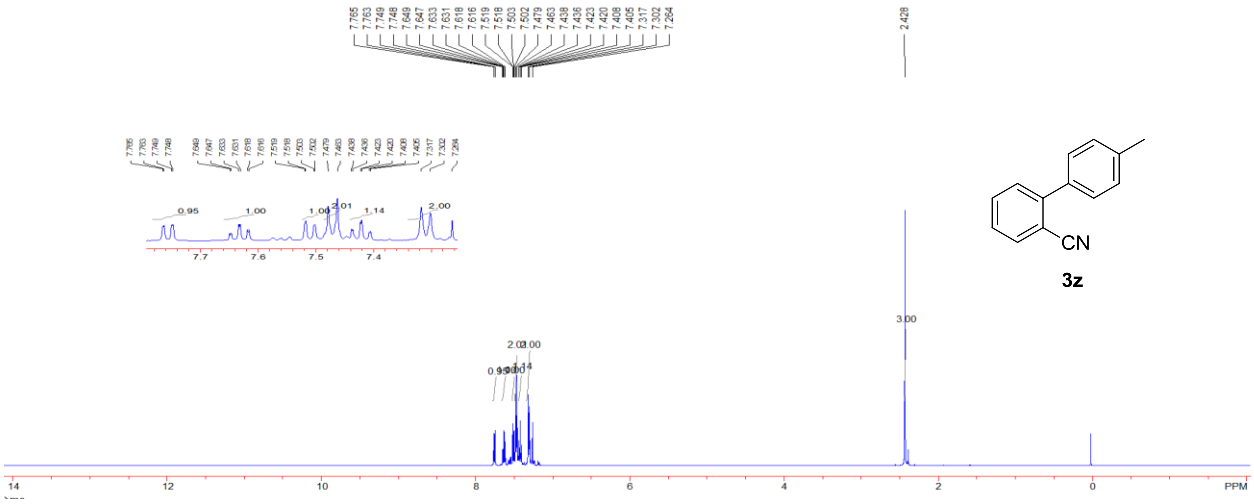
3y, ^{1}H NMR, 500 MHz, $CDCl_3$



3y, ^{13}C NMR, 126 MHz, $CDCl_3$



3z, ^{1}H NMR, 500 MHz, $CDCl_3$



3z, ^{13}C NMR, 126 MHz, $CDCl_3$