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Supporting Information

Palladium catalyzed cyanation of aryl (pseudo)halides using redox active N-CN reagent

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1. General Comments:

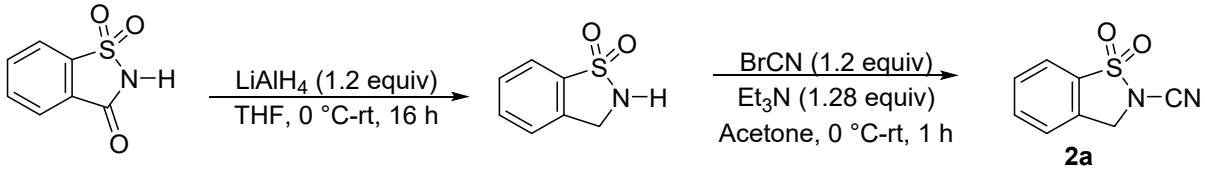
All reactions were carried out under argon atmosphere using oven dried pressure tubes. All electrophilic cyanating reagents (N-CN reagents) were synthesized from corresponding amine/amide[1]. $[Pd(cinnamyl)Cl]_2$ was prepared from known literature[2]. Dry solvents were prepared through standard procedure and stored in an oven using molecular sieves 4Å under argon atmosphere. Column chromatography was performed using Rankem Silica gel (100-200 mesh) and the solvent system used unless otherwise specified was ethyl acetate – hexanes with various percentages of polarity depending on the nature of the substance.

2. Analytical Methods:

NMR data were recorded on 400 and 500 MHz spectrometers. ^{1}H and ^{13}C NMR spectra were referenced to signals of either deuterated solvents or residual protic solvents. Infrared spectra were recorded on a Thermo Nicolet iS10 FT and *J*asco ATR-IR spectrometer. HRMS were recorded by electrospray ionization (ESI) method on a Q-TOF Micro with lock spray source

3. Synthesis of electrophilic cyanating reagents

Synthesis of 2-cyano-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2a)

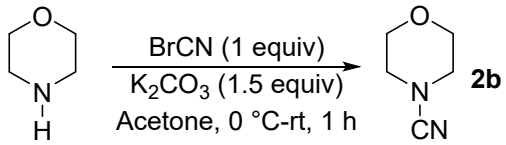


Step 1: To a stirred suspension of $LiAlH_4$ (122 mg, 3.29 mmol, 1.2 equiv) in anhydrous THF (4 mL) in an ice-water bath was added a solution of saccharin (500 mg, 2.74 mmol, 1 equiv) in anhydrous THF (3 mL) dropwise over 30 min under argon. The ice bath was removed and the suspension stirred for 16 h at room temperature. When TLC analysis showed the reaction completed, the reaction mixture was quenched with 10% H_2SO_4 and extracted to ethyl acetate. The combined organic extracts were concentrated to a pale-yellow solid.

Step 2: A dry and argon flashed Schlenk tube was charged with above obtained reduced saccharin (500 mg, 2.95 mmol, 1 equiv), cyanogen bromide (376 mg, 3.54 mmol, 1.2 equiv) and magnetic stir bar and sealed with septum. Acetone (8 mL) was added, and the resultant slurry was cooled to 0 °C. Then, triethylamine (383 mg, 3.78 mmol, 1.28 equiv) was added dropwise over 20 min and stirred at same temperature for 1 h. The reaction mixture was

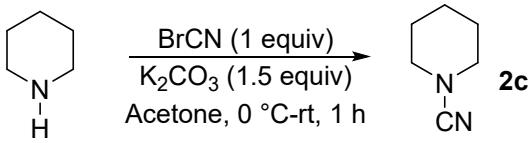
partitioned between ethyl acetate and water. The organic layer was washed to brine and dried over sodium sulphate. Evaporation of solvent and purification by column chromatography using mixture of hexane/ ethyl acetate as an eluent afforded **2a** in 69% of yield (512 mg) as a white solid. R_f = 0.50 in 30:70 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3060, 2360, 2236, 1348, 1184, 734, 668; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.85 (d, J = 7.9 Hz, 1H), 7.77 (t, J = 8.9 Hz, 1H), 7.66 (t, J = 8.3 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 4.98 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, CDCl3, 24 °C): δ 134.8, 131.8, 130.6, 130.5, 125.1, 122.1, 106.0, 51.1; HRMS (ESI/Q-TOF) *m/z*: [M^+] Calcd. for $C_8H_6N_2O_2S$ 194.0150; found 194.0154.

Synthesis of morpholine-4-carbonitrile (2b)



Round bottomed flask was charged with a stir bar, morpholine (535 mg, 6.13 mmol, 1 equiv) and potassium carbonate (1.27 g, 9.20 mmol, 1.5 equiv) followed by acetone (8 mL) was added and cooled to 0 °C. Then, cyanogen bromide (650 mg, 6.13 mmol, 1 equiv) in acetone was added dropwise. The reaction mixture is then allowed to warm to room temperature and water was added followed by extracted with DCM. Evaporation of solvent afford **2b** in 75% (519 mg) yield as a yellow liquid. R_f= 0.50 in 20:80 ethyl acetate/hexane. FTIR (neat, cm^{-1}): 3454, 2862, 2358, 2212, 1449, 1109, 997, 731; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 3.67-3.52 (m, 4H), 3.39-2.96 (m,4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 117.0, 66.2, 65.3, 48.5, 43.9; HRMS (ESI/Q-TOF) *m/z*: [M^+] Calcd. for $C_5H_8N_2O$ 112.0637; found 112.0640.

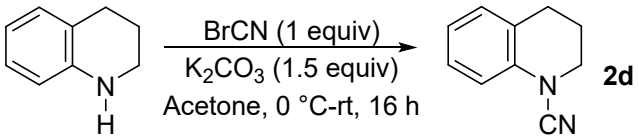
Synthesis of piperidine-1-carbonitrile (2c)



Round bottomed flask was charged with a stir bar, piperidine (500 mg, 5.87 mmol, 1 equiv) and potassium carbonate (1.21 g, 8.80 mmol, 1.5 equiv) followed by acetone (10 mL) was added and cooled it to 0 °C. Then, cyanogen bromide (621 mg, 5.87 mmol, 1 equiv) in acetone was added dropwise. The reaction mixture is then allowed to warm to room temperature and water was added followed by extracted with DCM. Evaporation of solvent afford **2c** in 80%

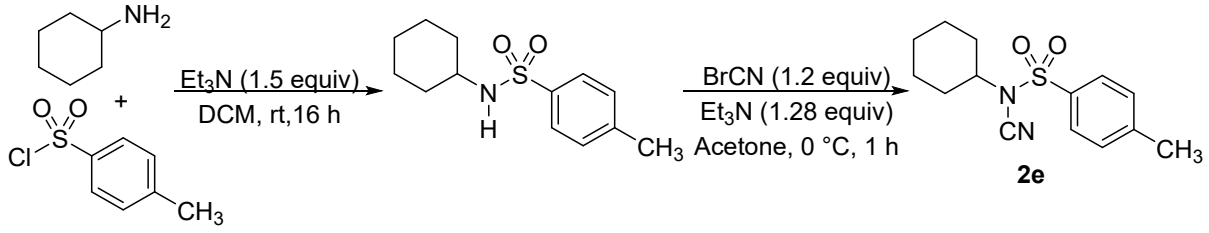
(517 mg) yield as a colourless liquid. R_f = 0.50 in 20:80 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3593, 2941, 2858, 2360, 2207, 1449, 1104, 727; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 3.09 (t, *J*= 6.5 Hz, 4H), 1.59-1.45 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, CDCl3, 24 °C): δ 118.5, 50.0, 24.4, 22.8; HRMS (ESI/Q-TOF) *m/z*: $[M^+]$ Calcd. for $C_8H_{10}N_2$: 110.0844; found: 110.0848.

Preparation of 3,4-dihydroquinoline-1(2H)-carbonitrile (2d)



Round bottomed flask was charged with a stir bar, tetrahydroquinoline (622 mg, 4.67 mmol, 1 equiv) and potassium carbonate (970 mg, 7.00 mmol, 1.5 equiv) followed by acetone (7 mL) was added and cooled it to 0 °C. Then, cyanogen bromide (495 mg, 4.67 mmol, 1 equiv) in acetone was added dropwise. The reaction mixture is then allowed to warm to room temperature and water was added followed by extracted with DCM. Evaporation of solvent and purification by column chromatography using mixture of hexane/ ethyl acetate as an eluent afforded **2d** in 69% (512 mg) yield as a dark brown liquid. R_f = 0.40 in 20:80 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3039, 2945, 2360, 2213, 1496, 1294, 738; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.20-7.12 (m, 2H), 7.05 (d, *J* = 7.78 Hz, 1H), 6.97-6.89 (m, 1H), 3.75-3.68 (m, 2H), 2.77 (t, *J* = 11.0 Hz, 2H), 2.04-1.97 (m, 2H) $^{13}C\{^1H\}$ NMR (100 MHz, CDCl3, 24 °C): δ 135.4, 129.7, 127.4, 123.9, 122.7, 115.4, 113.4, 48.4, 26.1, 20.8; HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for C8H8NO 159.0922; found 159.0922.

Preparation of *N*-cyano-*N*-cyclohexyl-4-methylbenzenesulfonamide (2e)

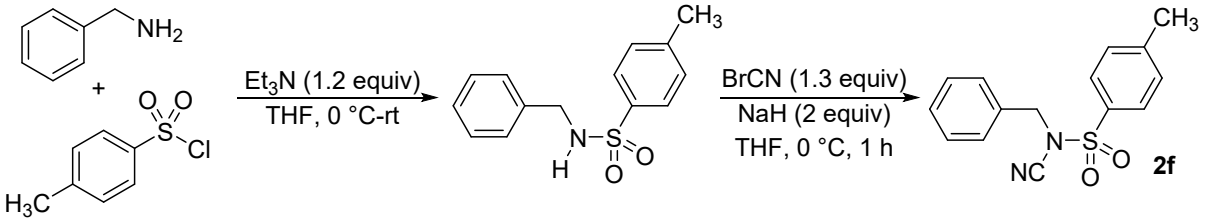


Step 1: Round bottom flask with magnetic stirring bar was charged with cyclohexylamine (600 mg, 6.05 mmol, 1.05 equiv) and THF (10 mL). After the solution had been cooled to 0 °C, a solution of the tosyl chloride (1.1 g, 5.76 mmol, 1 equiv) in THF (10 mL) was added dropwise over a period of 5 min. Subsequently, triethylamine (702 mg, 6.91 mmol, 1.2 equiv) was added

at the same temperature. The reaction was allowed to stir at room temperature for 24 h, before being quenched with water. The reaction mixture was extracted with DCM and dried over sodium sulphate. The solvent was removed under vacuum and the crude product was purified using column chromatography to afford a *N*-tosylamine derivative as a colourless liquid.

Step 2: A dry and argon flashed Schlenk tube was charged with *N*-tosylamine derivative (500 mg, 1.97 mmol, 1 equiv) was dissolved in THF and cooled to 0 °C. To this solution NaH (95 mg, 4.06 mmol, 2 equiv) was added portion wise. Then, the mixture was stirred for half-an-hour at same temperature. To this, cyanogen bromide (271 mg, 2.64 mmol, 1.3 equiv) in THF was added dropwise over 15 minutes and stirred for 2 h at 0 °C then warm to RT, subsequently stirring was continued for 16 h. Aqueous NH_4Cl was added to remove excess NaH then extracted with ethyl acetate. Evaporation of solvent followed by purification of compound through column chromatography using mixture of hexane/ ethyl acetate as an eluent afforded **2e** in 87% (480 mg) yield as a colourless liquid. R_f = 0.6 in 20:80 ethyl acetate/hexane FTIR (neat, cm^{-1}): 3060, 2938, 2359, 2225, 1376, 1171, 979, 735, 665; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.83 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 7.9 Hz, 2H), 3.69-3.57 (m, 1H), 2.47 (s, 3H), 1.82-1.69 (m, 4H), 1.61-1.59 (m, 1H), 1.49-1.38 (m, 2H), 1.33-1.20 (m, 2H), 1.13-1.00 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 146.2, 135.1, 130.5, 127.7, 107.3, 60.0, 31.5, 25.3, 24.6, 21.8; HRMS (ESI/Q-TOF) *m/z*: [M^+] Calcd. for $C_{14}H_{18}N_2O_2S$ 278.1089; found 278.1095.

Synthesis of *N*-benzyl-*N*-cyano-4-methylbenzenesulfonamide (2f)

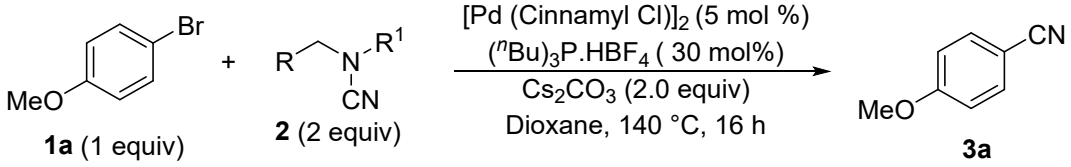


Step 1: To a solution of benzylamine (500 mg, 4.66 mmol, 1 equiv) and triethylamine (708 mg, 6.99 mmol, 1.5 equiv) in DCM (20 mL), tosyl chloride (889 mg, 4.66 mmol, 1 equiv) was added in small portions. The reaction was allowed to stir at room temperature for 1 h, before being quenched by water. The aqueous layer was extracted with DCM. The residue obtained after evaporation was recrystallized from (DCM/hexane) to produce *N*-tosylamine derivative as a colourless crystal.

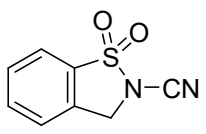
Step 2: A dry and argon flashed Schlenk tube was charged with *N*-tosylamine derivative (500 mg, 1.91 mmol, 1 equiv), cyanogen bromide (242 mg, 2.29 mmol, 1.2 equiv) and magnetic stir bar and sealed with septum. Acetone (5 mL) was added and the resultant slurry was cooled to 0 °C. Then triethylamine (248 mg, 2.45 mmol, 1.28 equiv) was added dropwise over 20 min and stirred at same temperature for 1 h. To the reaction mixture diluted water was added and extracted with ethyl acetate. The organic layer was washed with brine and dried over sodium sulphate. Evaporation of solvent and purification by column chromatography using mixture of hexane/ ethyl acetate as an eluent afforded **2f** in 39% (213 mg) yield as a colourless solid. R_f= 0.50 in 30:80 ethyl acetate/hexane FTIR (neat, cm^{-1}): 3067, 2359, 2229, 1377, 1171, 1009, 896, 706, 658; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.68 (d, J = 8.8 Hz, 2H), 7.29-7.20 (m, 5H), 7.16-7.10 (m, 2H), 4.45 (s, 2H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 146.4, 133.9, 132.2, 130.4, 129.4, 129.1, 128.9, 128.0, 108.7, 54.3, 21.8; HRMS (ESI/Q-TOF) *m/z*: [M^+] Calcd. for $C_{15}H_{14}N_2O_2S$ 286.0776; found 286.0784.

4. Optimization studies

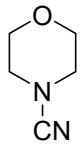
4.1 Screening of cyanating reagent



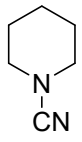
Entry	Cyanating Reagent	Yield (%)
1	**2a**	28
2	**2b**	23
3	**2c**	nr
4	**2d**	15
5	**2e**	14
6	**2f**	11



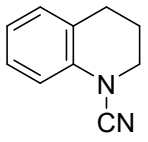
2a



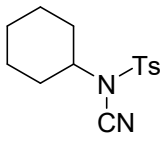
2b



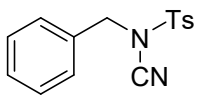
2c



2d

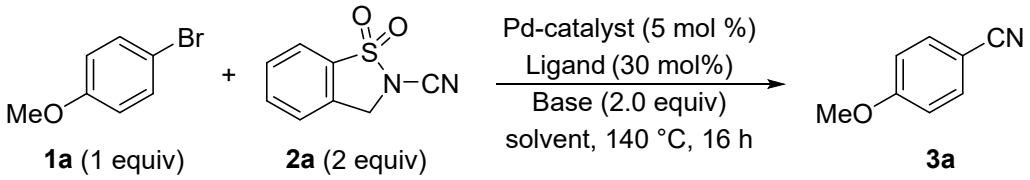


2e



2f

4.2 Screening of catalyst, ligand, base and solvent



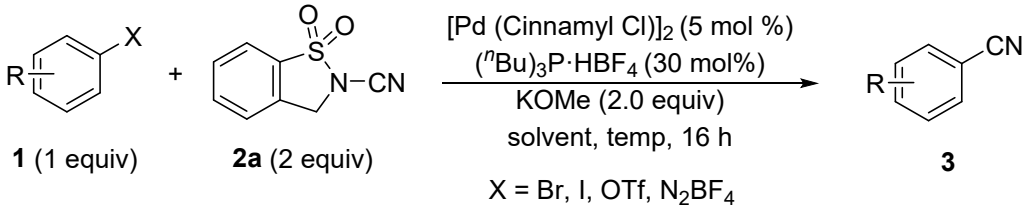
1a (1 equiv) **2a** (2 equiv) **3a**

Entry	Pd-catalyst	Ligand	Base	Solvent	Yield (%)
1	$Pd(OAc)_2$	$(^nBu)_3P{\cdot}HBF_4$	Cs_2CO_3	Dioxane	14
2	$PdCl_2$	$(^nBu)_3P{\cdot}HBF_4$	Cs_2CO_3	Dioxane	18
3	$Pd(PPh_3)_4$	$(^nBu)_3P{\cdot}HBF_4$	Cs_2CO_3	Dioxane	17
4	$Pd(PPh_3)_2Cl_2$	$(^nBu)_3P{\cdot}HBF_4$	Cs_2CO_3	Dioxane	10
5	$[Pd(CH_3CN)_4](BF_4)_2$	$(^nBu)_3P{\cdot}HBF_4$	Cs_2CO_3	Dioxane	15
6	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	Cs_2CO_3	Dioxane	28
7	$Pd(acac)_2$	$(^nBu)_3P{\cdot}HBF_4$	Cs_2CO_3	Dioxane	nr
8	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	KOAc	Dioxane	12
9	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	NaOPiv	Dioxane	10
10	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	NaOMe	Dioxane	25
11	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	K_3PO_4	Dioxane	nr
12	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	Na_2CO_3	Dioxane	10
13	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	KOMe	Dioxane	45
14	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	KOMe	CH_3CN	73
15	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	KOMe	DMSO	20
16	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	KOMe	DCE	37
17	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	KOMe	Diglyme	83
18	$[Pd(cinnamyl)Cl]_2$	PPh_3	KOMe	Diglyme	21
19	$[Pd(cinnamyl)Cl]_2$	Tri(*o*-tolyl)phosphine	KOMe	Diglyme	17
20	$[Pd(cinnamyl)Cl]_2$	Tributylphosphine	KOMe	Diglyme	43
21	$[Pd(cinnamyl)Cl]_2$	X-phos	KOMe	Diglyme	30
22	$[Pd(cinnamyl)Cl]_2$	Bipyridyl	KOMe	Diglyme	nr

23	$[Pd(cinnamyl)Cl]_2$	$(cy)_3P{\cdot}HBF_4$	KOMe	Diglyme	48
24	$[Pd(cinnamyl)Cl]_2$	$(^tBu)_3P{\cdot}HBF_4$	KOMe	Diglyme	<10
25	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	K_2CO_3	Diglyme	46
26	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	KOH	Diglyme	nr
27[(a)]	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	KOMe	Diglyme	50
28[(b)]	$[Pd(cinnamyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	KOMe	Diglyme	13
29	$[Pd(allyl)Cl]_2$	$(^nBu)_3P{\cdot}HBF_4$	KOMe	Diglyme	24

Reaction condition: 1a (50 mg, 0.26 mmol, 1 equiv), **2a** (104 mg, 0.53mmol, 2 equiv), Pd-catalyst (5 mol%), ligand (30 mol%), base (2 equiv), sovlent (2 mL for 0.26 mmol), 140 °C, 16 h; [(a)] 2.5 mol% catalyst and 15 mol% ligand; [(b)] 1.25 mol% catalyst and 7.5 mol% ligand.

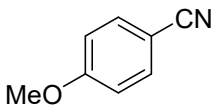
5. General procedure for the synthesis of benzonitrile derivatives:



In an oven dried Schlenk tube, aryl bromide **1** (50 mg, 1 equiv), **2a** (2 equiv), $[Pd(cinnamyl)Cl]_2$ (5 mol%), $P(^nBu)_3{\cdot}HBF_4$ (30 mol%), KOMe (2 equiv) were added under argon atmosphere. Dry diglyme (for aryl bromides) or CH_3CN (for iodides and pseudo halides) (2 mL) was added into the reaction tube using a syringe. The reaction mixture was kept in a pre-heated oil bath at 140 °C/120 °C and stirred at the same temperature for 16 h. The reaction mixture was cooled to room temperature, water was added and extracted with hexane. The solvent was evaporated to get the crude product, which was further purified by column chromatography using ethyl acetate: hexane (5:95) as an eluting solvent to afford the benzonitrile derivatives in good yield.

6. Properties of isolated benzonitriles:

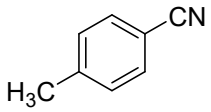
4-methoxybenzonitrile (3a)[3]



Yield: 83% (29 mg); from iodide: 92% (26 mg); from triflate: 45% (13 mg); from diazonium salt: 61% (18 mg); white solid; R_f = 0.5 in 5:95 ethyl

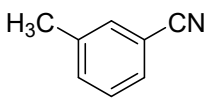
acetate/ hexane; FTIR (neat ,cm^{-1}): 2922, 2364, 2219, 1697, 1600, 1490, 1282, 1023, 827; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.58 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C); δ 162.9, 134.0, 119.3, 114.8, 104.0, 55.6; HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C8H_8NO$ 134.0606; found 134.0592.

4-methylbenzonitrile (3b)[4]



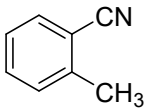
Yield: 70% (24 mg); colourless liquid; R_f=0.3 in 5:95 ethyl acetate/hexane; FTIR (neat,, cm^{-1}): 2838, 2224, 1605, 1509, 1303, 1258, 835, 769, 560; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.53 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 2.42 (s, 3H) $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 143.7, 132.1, 129.9, 119.2, 109.3, 21.9; HRMS (ESI/Q-TOF) *m/z*: $[M^+]$ Calcd for $C8H_7N$ 117.0578; found 117.0562.

3-methylbenzonitrile (3c)[5]



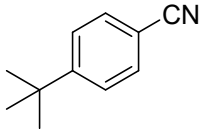
Yield: 68% (23 mg); yellow liquid; R_f = 0.5 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3051, 2931, 2233, 1585, 1390, 1297, 789, 689; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.45-7.44 (m, 2H), 7.40 (d, J = 7.6 Hz, 1H), 7.36- 7.32 (m, 1H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 139.2, 133.7, 132.5, 129.3, 129.0, 119.1, 112.3, 21.2; HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for C_8H_8N 118.0657; found 118.0645.

2-methylbenzonitrile (3d)[3]



Yield: 58% (20 mg); yellow liquid; R_f = 0.5 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3215, 2931, 2239, 1685, 1390, 1129, 789, 689; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.39 (d, J=8.0 Hz, 1H), 7.28 (t, J = 8.6 Hz, 1H), 7.13- 7.05 (m, 2H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 141.9, 132.6, 132.4, 130.2, 126.2, 118.1, 112.7, 20.4.

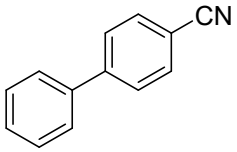
4-(tert-butyl) benzonitrile (3e)[6]



Yield: 65% (24 mg); from iodide: 76% (23 mg); from triflate: 48% (18 mg); colourless liquid; R_f = 0.3 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}):

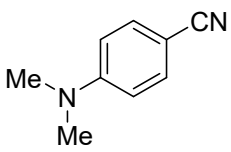
2965, 2227, 1606,1366, 1269, 1107, 838, 750; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.57 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 1.32 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 156.7, 132.0, 126.2, 119.2, 109.3, 35.3, 31.0; HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{14}N$ 160.1126; found 160.1111.

[1,1'-biphenyl]-4-carbonitrile (3f)[4]



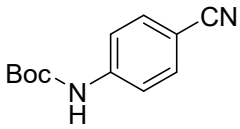
Yield: 78% (30 mg); from iodide: 81% (26 mg); white solid; R_f=0.4 in 5:95 ethyl acetate/hexane FTIR (neat, cm^{-1}): 3058, 2226, 1924, 1687, 1605, 1483, 1266, 842; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.74- 7.67 (m, 4H), 7.59 (d, J = 7.3 Hz, 2H), 7.50- 7.40 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.8, 139.3, 132.7, 129.2, 128.7, 127.8, 127.3, 119.0, 111.0; HRMS (ESI/Q-TOF) *m/z*: $[M^+]$ Calcd for $C_{13}H_9N$ 179.0735; found 179.0727.

4-(dimethylamino)benzonitrile (3g)[7]



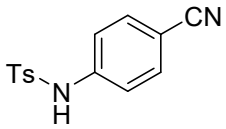
Yield: 76% (28 mg); yellow solid; R_f= 0.5 in 10:90 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 2904, 2361, 2211, 1607, 1528, 1372, 1171, 818, 737; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.45 (d, J = 8.9 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H), 3.03 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 152.5, 133.4, 120.8, 111.5, 97.5, 40.0; HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_9H_{11}N_2$ 147.0922; found 147.0921.

Tert-butyl (4-cyanophenyl) carbamate (3h)[8]



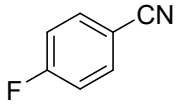
Yield: 63% (25 mg); brown solid; R_f= 0.5 in 20:80 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3445, 2954, 2855, 2316, 1939, 1681, 1607, 1448, 1169, 848; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7,56 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 6.72 (s, 1H), 1.52 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 152.0, 142.7, 133.4, 119.1, 118.2, 106.0, 81.8, 28.3.

N-(4-cyanophenyl)-4-methylbenzenesulfonamide (3i)[9]



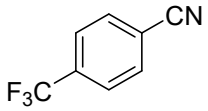
Yield: 74% (31 mg); white solid; R_f = 0.5 in 10:90 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 2924, 2356, 2228, 1926, 1592, 1379, 1169, 1088, 915, 812; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.78 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C); δ 145.7, 138.5, 136.1, 133.1, 132.6, 129.9, 128.6, 117.8, 114.2, 21.8.

4-Fluorobenzonitrile (3j)[4]



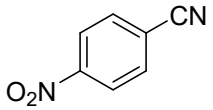
Yield: 42% (15 mg); colourless liquid; R_f = 0.5 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 2957, 2233, 1601, 1504, 1240, 1162, 843, 755; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.69-7.66 (m, 2H), 7.26-7.15 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 165.1 (d, J = 256 Hz), 134.7 (d, J = 9.5 Hz), 118.1, 116.9 (d, J = 22.7 Hz), 108.6 (d, J = 3.7 Hz); HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for C_7H_5FN 122.0406; found 122.0446.

4-(trifluoromethyl)benzonitrile (3k)[4]



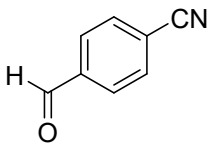
Yield: 56% (21 mg), from iodide: 73% (23 mg), from triflate: 33% (16 mg); colourless solid; R_f = 0.3 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3060, 2239, 2208, 1323, 1176, 1068, 843, 736, 691; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.81 (d, J = 8.5 Hz 2H), 7.75 (d, J = 8.1 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 134.6, (q, J = 32.7 Hz), 132.8, 126.23 (q, J = 3.7 Hz), 123.1 (q, J = 273 Hz), 117.5, 116.1.

4-nitrobenzonitrile (3l)[4]



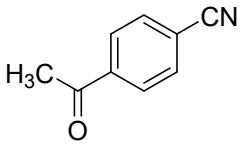
Yield: 87% (32 mg); from iodide: 93% (28 mg); from triflate: 49% (15 mg); from diazonium salt: 69% (21 mg); yellow solid; R_f = 0.4 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3109, 2360, 2232, 1601, 1526, 1347, 1102, 742; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.35 (d, J = 8.8 Hz, 2H), 7.88 (d, J = 8.9 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 150.1, 133.5, 124.4, 118.4, 116.9.

4-formylbenzonitrile (3m)[10]



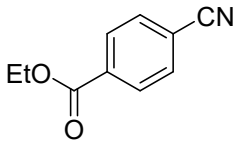
Yield: 76% (27 mg); colourless solid; R_f = 0.6 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3096, 2842, 2221, 1705, 1411, 1297, 1043, 831, 726; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 10.09 (s, 1H), 7.99 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 190.7, 138.8, 133.0, 130.0, 117.8, 117.7; HRMS (ESI/Q-TOF) *m/z*: $[M^+]$ Calcd. for C_8H_5NO 131.0371; found 131.0376.

4-acetylbenzonitrile (3n)[3]



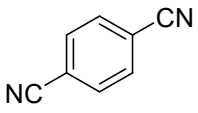
Yield: 81% (30 mg); white solid; R_f = 0.5 in 5:95 ethyl acetate/hexane; FTIR (neat,, cm^{-1}): 3725, 2928, 2360, 2233, 1692, 1402, 1261, 1102, 960, 839, 735; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.04 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 2.64 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C); δ 196.6, 140.0, 132.6, 128.8, 118.0, 116.5, 26.8.

Ethyl 4-cyanobenzoate (3o)[10]



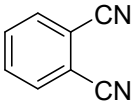
Yield: 84% (32 mg), from iodide: 90% (29 mg); colourless solid; R_f = 0.5 in 10:90 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 2987, 2232, 1937, 1722, 1369, 1176, 1106, 1020, 744; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.13 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 4.43-4.38 (m,2H), 1.40 (t, J = 8.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 165.0, 134.4, 132.2, 130.1, 118.1, 116.3, 61.9, 14.3; HRMS (ESI/Q-TOF) *m/z*: $[M]^+$ Calcd. for $C_{10}H_9NO_2$ 175.0633; found 175.0635.

Terephthalonitrile (3p)[4]



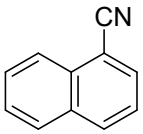
Yield: 62% (14 mg), from diazonium salt: 39% (12 mg); white solid; R_f = 0.6 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3060, 2361, 2229, 1937, 1533, 1265, 1200, 840, 781; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.79 (s, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 132.8, 117.1, 116.8.

Phthalonitrile (3q)[11]



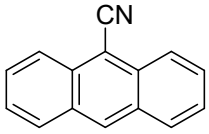
Yield: 53% (19 mg); white solid; R_f= 0.6 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3048, 2355, 2232, 1582, 1481, 1453, 1266, 771, 735; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.83–7.81 (m, 2H), 7.79-7.76 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 133.6, 133.3, 115.9, 115.4; HRMS (ESI/Q-TOF) *m/z*: $[M]^+$ Calcd. for $C_8H_4N_2$ 128.0374; found 128.0366.

1-napthonitrile (3r)[4]



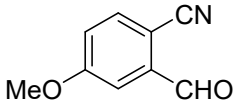
Yield: 74% (28 mg); yellow liquid; R_f = 0.5 in 5:95 ethyl acetate/ hexane; FTIR (neat, cm^{-1}): 3059, 2360, 2222, 1940,1508, 1341, 1216, 801, 768, 689; ^1H NMR(400 MHz, $CDCl_3$, 24 °C): δ 8.23 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.91 (t, J = 7.9 Hz, 2H), 7.69 (t, J = 8.5 Hz, 1H), 7.61 (t, J = 8.4 Hz, 1H), 7.51 (t, J = 8.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 133.3, 133.0, 132.7, 132.4, 128.7, 128.6, 127.6, 125.2, 125.0, 117.9, 110.2; HRMS (ESI/Q-TOF) *m/z*: $[M]^+$ Calcd. for $C_{17}H_7N$ 153.0578; found 153.0559.

Anthracene-9-carbonitrile (3s)[6]



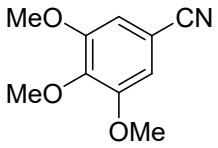
Yield: 69% (27 mg); yellow solid; R_f = 0.5 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3054, 2260, 2219, 1948, 1527, 1265, 1158, 802, 730; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.65 (s, 1H), 8.41 (d, J = 8.7 Hz, 2H), 8.06 (d, J = 8.4 Hz, 2H), 7.71 (t, J = 8.9 Hz, 2H), 7.58 (t, J = 8.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 133.4, 132.8, 130.7, 129.0, 126.5, 125.4, 125.4, 117.4; HRMS (ESI/Q-TOF) *m/z*: $[M]^+$ Calcd. for $C_{15}H_9N$ 203.0735; found 203.0724.

2-formyl-4-methoxybenzonitrile (3t)[12]



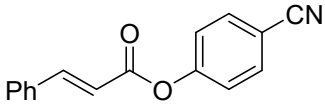
Yield: 71% (26 mg); colourless solid; R_f = 0.5 in 10:90 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3096, 2930, 2364, 2223, 1711, 1692, 1415, 1297, 831, 727; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 10.33 (s, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.50 (d, J = 2.6 Hz, 1H), 7.23-7.20 (m, 1H), 3.93 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 188.6, 163.3, 138.9, 135.5, 121.0, 116.3, 113.1, 106.1, 56.1; HRMS (ESI/Q-TOF) *m/z*: $[M]^+$ Calcd. for $C_9H_8NO_2$ 162.0555; found 162.0555.

3,4,5-trimethoxybenzonitrile (3u)[13]



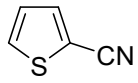
Yield: 53% (21 mg); colourless solid; R_f = 0.5 in 10:90 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 2928, 2849, 2220, 1729, 1502, 1245, 1137, 1038, 855, 516; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 6.85 (s, 2H), 3.89 (s, 3H), 3.87 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 153.7, 142.4, 119.0, 109.7, 106.8, 61.1, 56.5.

4-cyanophenyl cinnamate (3v)[14]



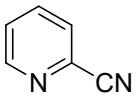
Yield: 56% (24 mg); colourless solid; R_f = 0.5 in 10:90 ethy lacetate/hexane; FTIR (neat, cm^{-1}): 2923, 2362, 2232, 1766, 1600,, 1308, 1221, 1136, 855, 762; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.89 (d, J = 15.9 Hz, 1H), 7.72 (d, J = 8.5 Hz, 2H), 7.59 (t, J = 4.3 Hz, 2H), 7.44-7.43 (m, 3H), 7.32 (d, J = 8.5 Hz, 2H), 6.61 (d, J = 15.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 164.6, 154.2, 148.0, 133.9, 133.8, 131.2, 129.2, 128.5, 122.9, 118.4, 116.4, 109.7.

Thiophene-2-carbonitrile (3w)[4]



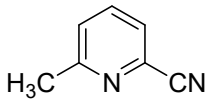
Yield: 59% (20 mg); yellow liquid; R_f = 0.5 in 10:90 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3627, 3103, 2220, 1674, 1234, 1043, 721; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.63- 7.60 (m, 2H), 7.14- 7.12 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 137.5, 132.6, 127.7, 114.3, 109.9; HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for C_5H_4NS 110.0064; found 110.0065.

Picolinonitrile (3x)[15]



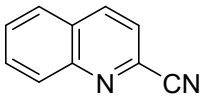
Yield: 66% (22 mg); white solid; R_f = 0.4 in 20:80 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3060, 2359, 2238, 1579, 1433, 1092, 993, 781; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.71 (d, J = 4.5 Hz, 1H), 7.86- 7.82 (m, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.54-7.51 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 151.2, 137.1, 134.0, 128.6, 127.0, 117.2; HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_6H_5N_2$ 105.0453; found 105.0445.

6-methylpicolinonitrile (3y)[15]



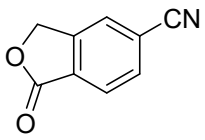
Yield: 62% (21 mg); brown liquid; R_f = 0.4 in 20:80 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3058, 2980, 2238, 1912, 1588, 1267, 796, 736; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.70 (t, J = 8.5 Hz, 1H), 7.50 (d, J = 7.4 Hz, 1H), 7.37 (d, J = 7.9 Hz, 1H), 2.59 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C); δ 160.7, 137.1, 133.2, 126.9, 125.7, 117.4, 24.8; HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_7H_7N_2$ 119.0609; found 119.0602.

Quinoline-2-carbonitrile (3z)[15]



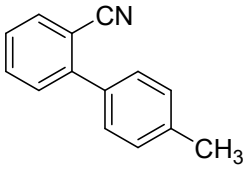
Yield: 75% (28 mg); yellow liquid; R_f = 0.5 in 10:90 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3060, 2211, 1608, 1400, 1375, 1266, 953, 825, 736; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.30 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 7.90-7.81 (m, 2H), 7.71-7.68 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 148.2, 137.6, 133.6, 131.3, 130.0, 129.5, 128.7, 127.8, 123.4, 117.6; HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{10}H_7N_2$ 155.0609; found 155. 0603.

1-oxo-1,3-dihydroisobenzofuran-5-carbonitrile (3aa)[10]



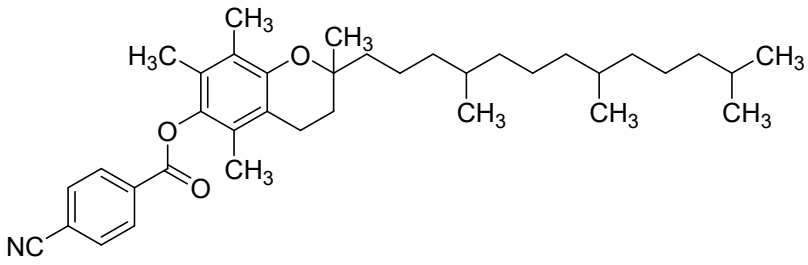
Yield: 76% (28 mg); yellow solid; R_f = 0.5 in 20:80 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3495, 3057, 2235, 1754, 1459, 1121, 1050, 997, 738, 678; ^1H NMR (400 MHz, DMSO, 24 °C): δ 8.19 (s, 1H), 8.01 (s, 2H), 5.46 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO, 24 °C): δ 169.3, 147.7, 132.8, 128.9, 127.5, 126.0, 118.0, 116.1, 69.9.

4'-methyl-[1,1'-biphenyl]-2-carbonitrile (3ab)[16]



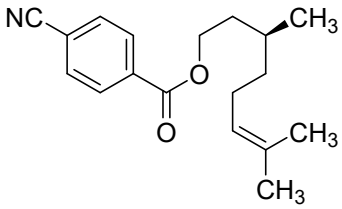
Yield: 70% (27 mg); brown liquid; R_f = 0.5 in 10:90 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3069, 2360, 2226, 1630, 1478, 1267, 1078, 755; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.75 (d, J = 7.7 Hz, 1H), 7.62 (t, J = 8.4 Hz, 1H), 7.51-7.39 (m, 4H), 7.30 (d, J = 7.8 Hz, 2H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.6, 138.8, 135.3, 133.8, 132.8, 130.0, 129.5, 128.7, 127.3, 118.9, 111.2, 21.3.

2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-cyanobenzoate (3ac)[11]



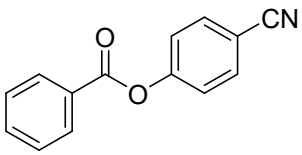
Yield: 21% (10 mg); yellow solid; R_f = 0.5 in 10:90 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 2928, 2232, 1738, 1458, 1240, 1094, 1016, 918, 860, 756, 688; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.34 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.5 Hz, 2H), 2.62 (t, J = 7.8 Hz, 2H), 2.12 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.87-1.76 (m, 2H), 1.55-150 (m, 2H), 1.42-1.38 (m, 5H), 1.26 (s, 13H), 1.64-1.06 (m, 7H), 0.87 (s, 3H), 0.86 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 163.7, 149.9, 140.5, 133.6, 132.5, 130.7, 126.7, 125.0, 123.5, 118.0, 117.8, 117.0, 75.3, 39.5, 37.6, 37.5, 37.5, 37.4, 32.9, 32.8, 31.2, 28.1, 24.9, 24.6, 22.8, 22.7, 21.1, 20.7, 19.9, 19.8, 19.7, 19.7, 13.1, 12.3, 11.9.

(*S*)-3,7-dimethyloct-6-en-1-yl 4-cyanobenzoate (3ad)



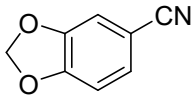
Yield: 80% (34 mg); colourless liquid; R_f = 0.5 in 10:90 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3428, 2921, 2232, 1760, 1605, 1458, 1274, 1110, 860, 691; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.12 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 5.08 (t, J = 9.3 Hz, 1H), 4.43-4.35 (m, 2H), 2.04-1.96 (m, 2H), 1.84-1.78 (m, 2H), 1.66 (s, 3H), 1.59 (s, 3H), 1.38-1.25 (m, 3H), 0.96 (d, J = 6.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 165.1, 132.3, 130.1, 124.5, 118.1, 116.3, 68.2, 64.4, 37.0, 35.4, 29.6, 25.8, 25.4, 19.5, 17.7, 14.1.

4-cyanophenyl benzoate (3ae)[17]



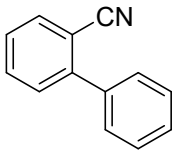
Yield: 81% (28 mg); colourless solid; R_f = 0.5 in 10:90 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3067, 2360, 2230, 1744, 1594, 1260, 1057, 736; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.19 (d, J = 7.7 Hz, 2H), 7.75 (d, J = 8.59 Hz, 2H), 7.69- 7.63 (m, 1H), 7.53 (t, J = 8.1 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 164.4, 154.4, 134.3, 133.8, 130.4, 128.9, 128.3, 123.0, 118.4, 109.9.

Benzo[d][1,3]dioxole-5-carbonitrile (3af)[16]



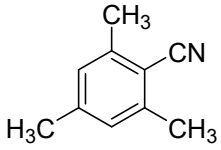
Yield: 71% (21 mg); colourless solid; R_f = 0.5 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 2923, 2866, 2223, 1724, 1486, 1441, 1258, 1035, 919, 811, 736, 613; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.22- 7.19 (m, 1H), 7.03 (s, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.06 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 151.6, 148.1, 128.3, 119.0, 111.5, 109.2, 105.1, 102.3.

[1,1'-biphenyl]-2-carbonitrile (3ag)[7]



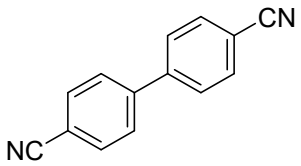
Yield: 76% (24 mg); white solid; R_f = 0.4 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3063, 2360, 2226, 1630, 1475, 1267, 1078, 758; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.77 (d, J = 7.7 Hz, 1H), 7.66- 7.62 (m, 1H), 7.57- 7.42 (m, 7H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.6, 138.2, 133.8, 132.9, 130.1, 128.8, 128.8, 127.6, 118.8, 111.3; HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{10}N$ 180.0813; found 180.0806.

2,4,6-trimethylbenzonitrile (3ah)[3]



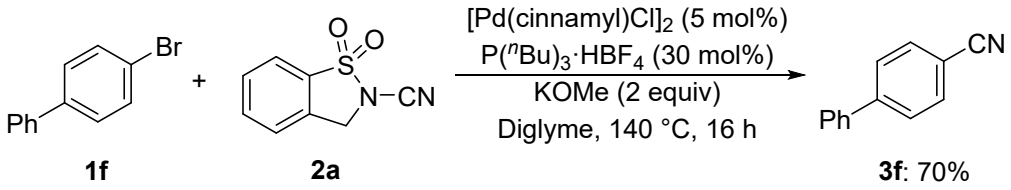
Yield: 59% (17 mg); white solid; R_f = 0.5 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 2927, 2855, 2226, 1628, 1591, 1265, 1031, 828, 748; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.26 (s, 1H), 7.12 (s, 1H), 2.73 (s, 3H), 2.55 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 146.6, 146.3, 129.6, 115.9, 112.6, 21.3, 20.1.

[1,1'-biphenyl]-4,4'-dicarbonitrile (3ai)[18]



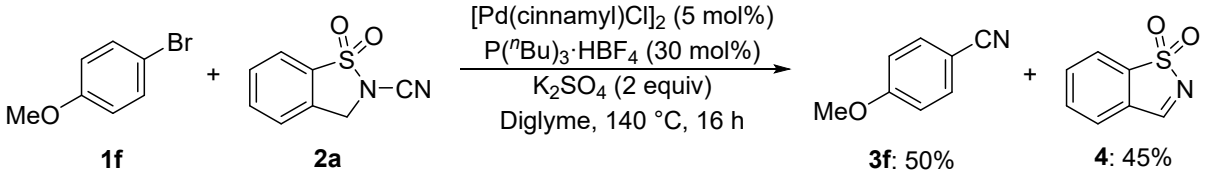
Yield: 61% (15 mg); colourless solid; R_f = 0.6 in 5:95 ethyl acetate/hexane; FTIR (neat, cm^{-1}): 3048, 2360, 2223, 1489, 1266, 818, 741; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.78 (d, J = 7.69 Hz, 4H), 7.69 (d, J = 7.69 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 143.6, 133.0, 128.0, 118.5 ,112.5.

7. Procedure for the synthesis of benzonitrile derivative in 1 mmol scale:

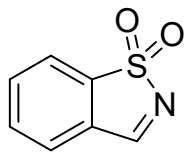


In an oven dried Schlenk tube, 4-bromo-1,1'-biphenyl (233 mg, 1 mmol, 1 equiv), **2a** (388 mg, 2 mmol, 2 equiv), $[Pd(cinnamyl)Cl]_2$ (26 mg, 0.05 mmol, 5 mol%), $P(^nBu)_3 \cdot HBF_4$ (87 mg, 0.3 mmol, 30 mol%), KOMe (204 mg, 2 mmol, 2 equiv) were added under argon atmosphere. Dry diglyme (10 mL) was added into the reaction tube using a syringe. The reaction mixture was kept in a pre-heated oil bath at 140 °C and stirred at the same temperature for 16 h. The reaction mixture was cooled to room temperature, water was added and extracted with hexane. The solvent was evaporated to get the crude product, which was further purified by column chromatography using ethyl acetate: hexane (5:95) as an eluting solvent to afford the [1,1'-biphenyl]-4-carbonitrile in 70% yield.

8. Isolation of benzo[d]isothiazole 1,1-dioxide (4):



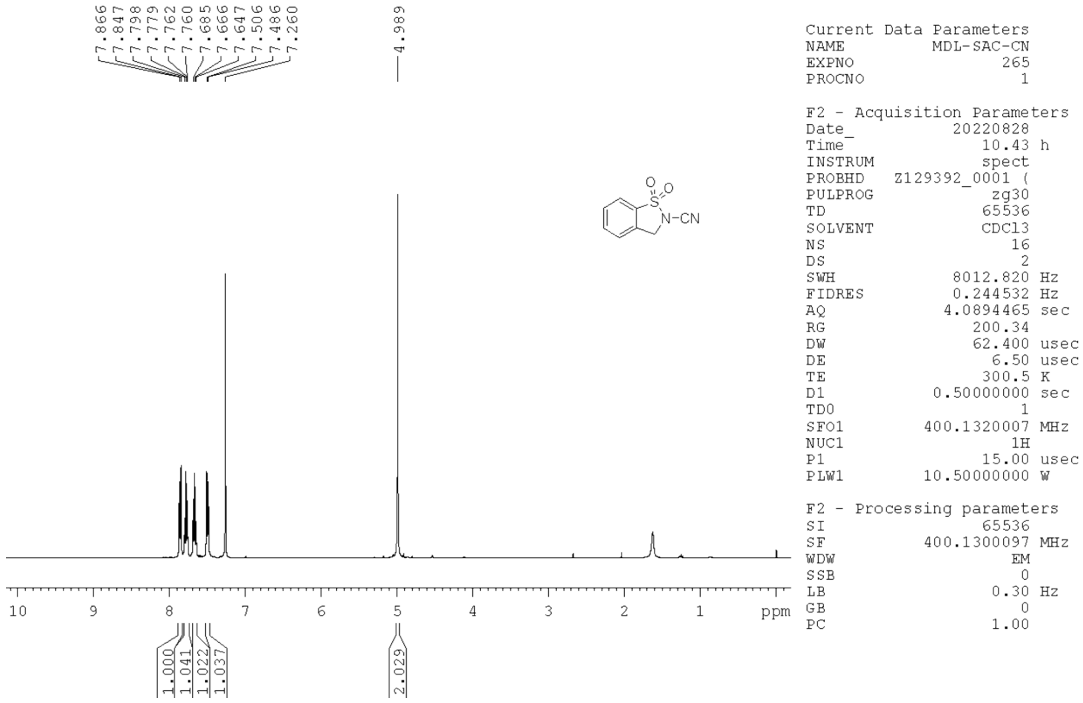
In an oven dried Schlenk tube, 4-bromoanisole (50 mg, 0.26 mmol, 1 equiv), **2a** (104 mg, 0.53 mmol, 2 equiv), $[Pd(cinnamyl)Cl]_2$ (6.9 mg, 0.01 mmol, 5 mol%), $P(^nBu)_3 \cdot HBF_4$ (23 mg, 0.08 mmol, 30 mol%), K_2SO_4 (92 mg, 0.53 mmol, 2 equiv) were added under argon atmosphere. Dry diglyme (10 mL) was added into the reaction tube using a syringe. The reaction mixture was kept in a pre-heated oil bath at 140 °C and stirred at the same temperature for 16 h. The reaction mixture was cooled to room temperature, water was added and extracted with hexane. The solvent was evaporated to get the crude product, which was further purified by column chromatography using ethyl acetate: hexane (5:95) as an eluting solvent to afford the 4-methoxybenzonitrile and imine **4** in 50% and 45% yield, respectively.



Yield: 45% (20 mg); white solid; R_f= 0.5 in 30:70 ethyl acetate/hexane; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 9.0 (s, 1H), 7.86 (d, J = 8.08 Hz, 1H), 7.73 (t, J = 8.54 Hz, 1H), 7.62 (t, J = 8.21 Hz, 1H), 7.52 (d, J = 8.15 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 157.3, 134.4, 134.2, 131.5, 130.0, 125.4, 121.7.

9. NMR spectra of isolated compounds:

2-Cyano-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2a)

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PROCNO                 1

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TD                 65536
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DS                     2
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FIDRES          0.244532 Hz
AQ              4.0894465 sec
RG                200.34
DW                62.400 usec
DE                 6.50 usec
TE                300.5 K
D1             0.50000000 sec
TD0                    1
SFO1          400.1320007 MHz
NUC1                  1H
P1                15.00 usec
PLW1          10.50000000 W

F2 - Processing parameters
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WDW                   EM
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LB                0.30 Hz
GB                     0
PC                1.00
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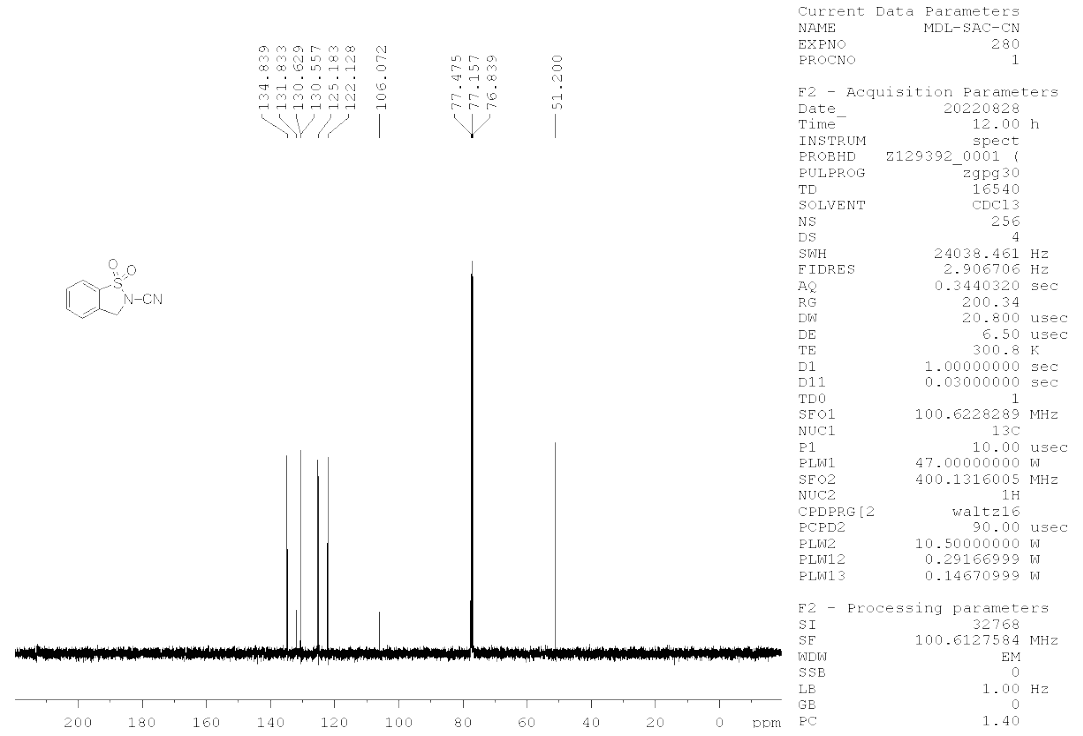
^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 2a

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RG                200.34
DW                20.800 usec
DE                 6.50 usec
TE                300.8 K
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D11            0.03000000 sec
TD0                    1
SFO1          100.6228289 MHz
NUC1                  13C
P1                10.00 usec
PLW1          47.00000000 W
SFO2          400.1316005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2          10.50000000 W
PLW12          0.29166999 W
PLW13          0.14670999 W

F2 - Processing parameters
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WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
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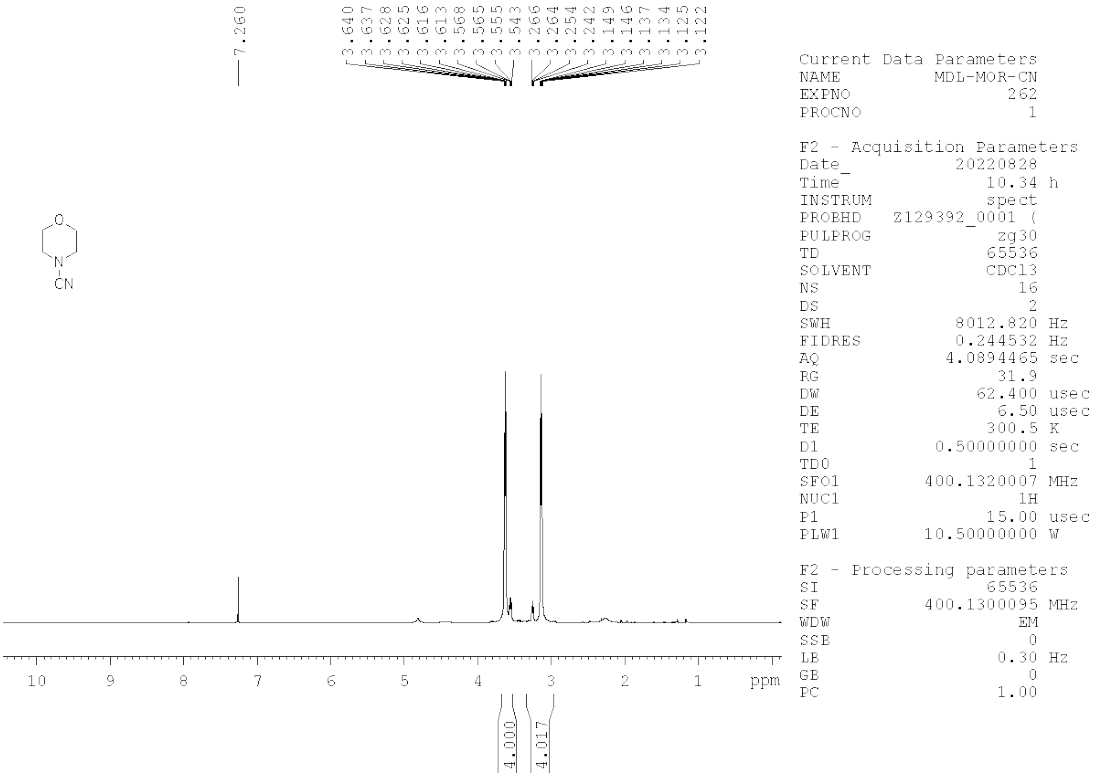
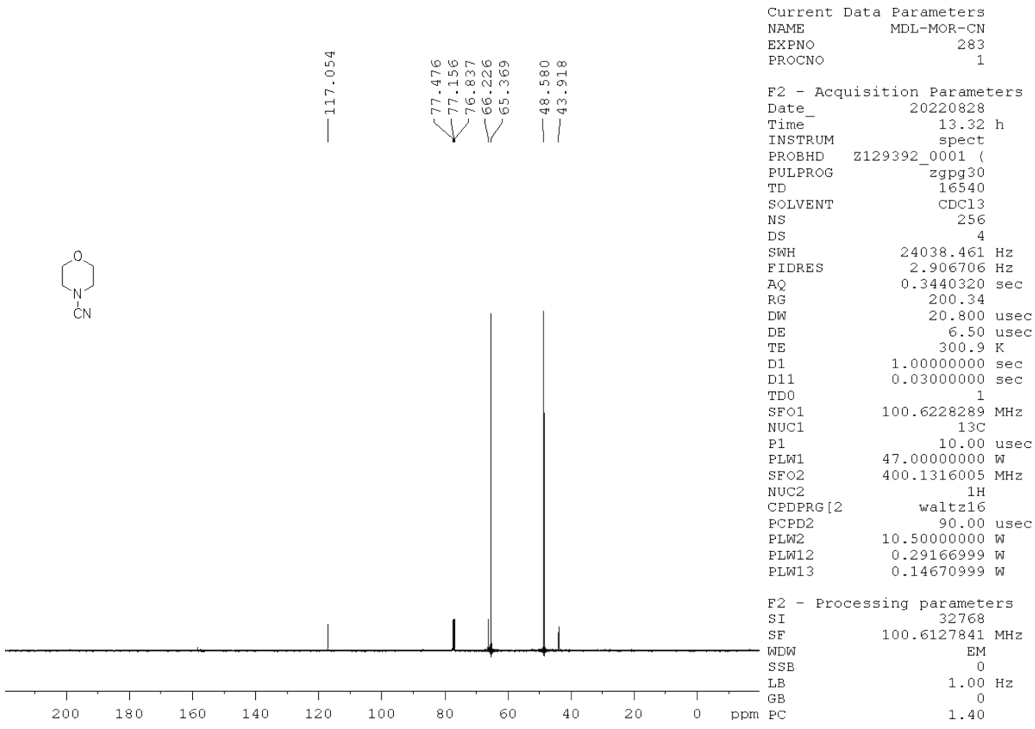
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 2a

Morpholine-4-carbonitrile (2b)

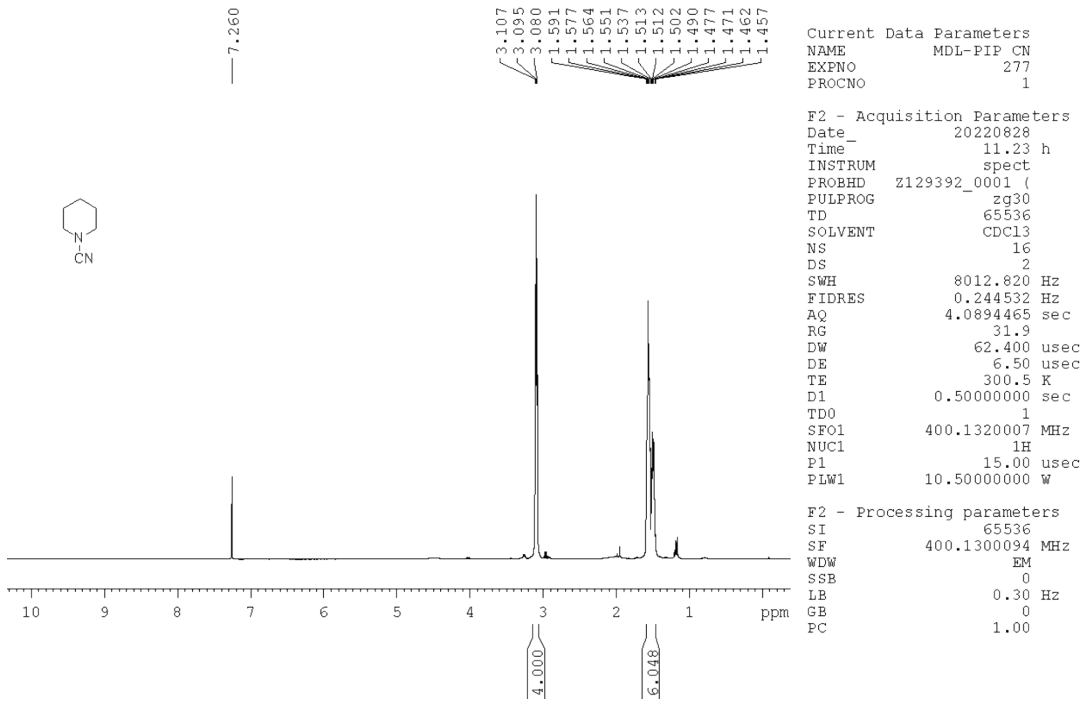


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 2b

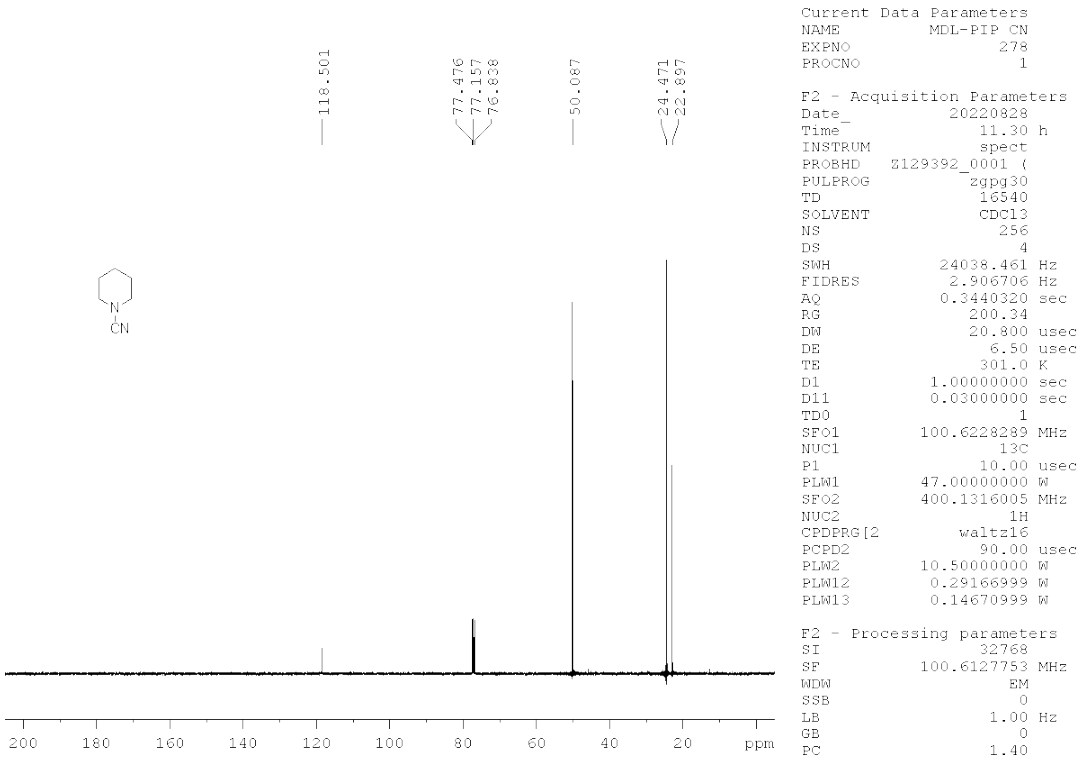


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 2b

Piperidine-1-carbonitrile (2c)

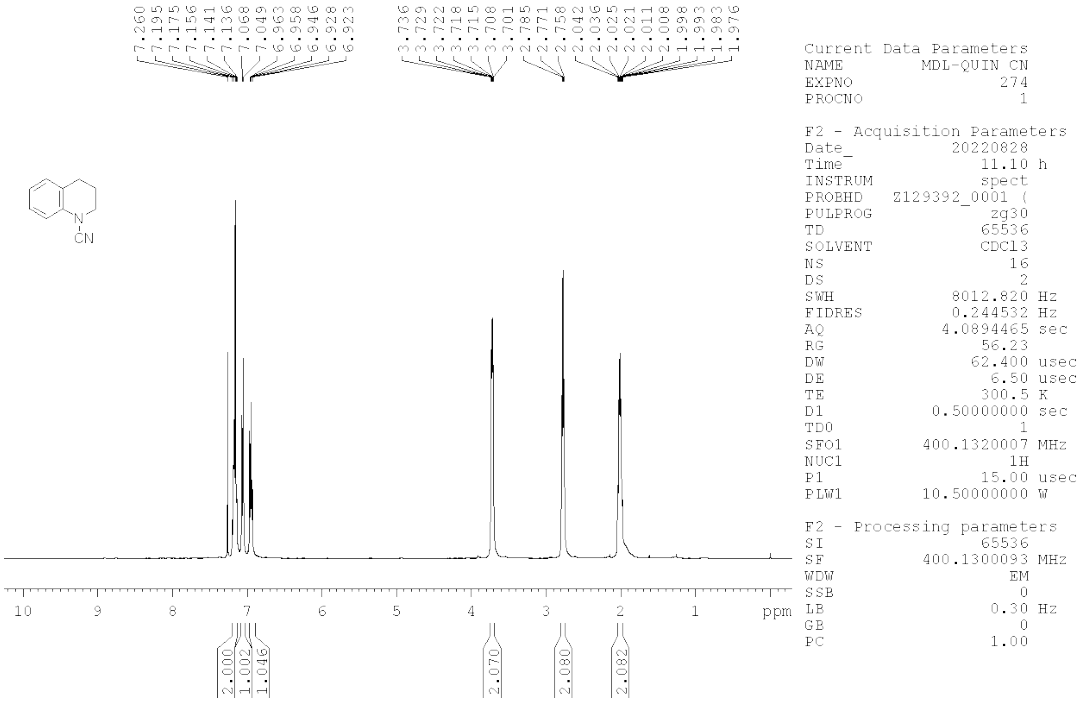


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 2c

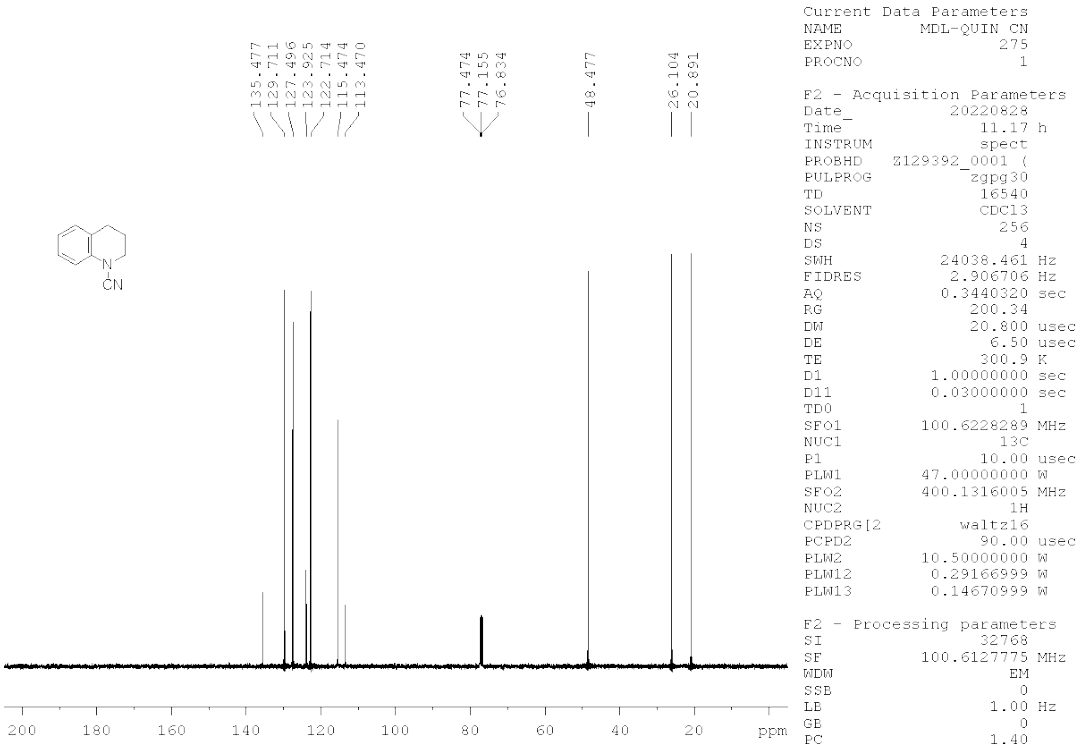


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 2c

3,4-Dihydroquinoline-1(2H)-carbonitrile (2d)

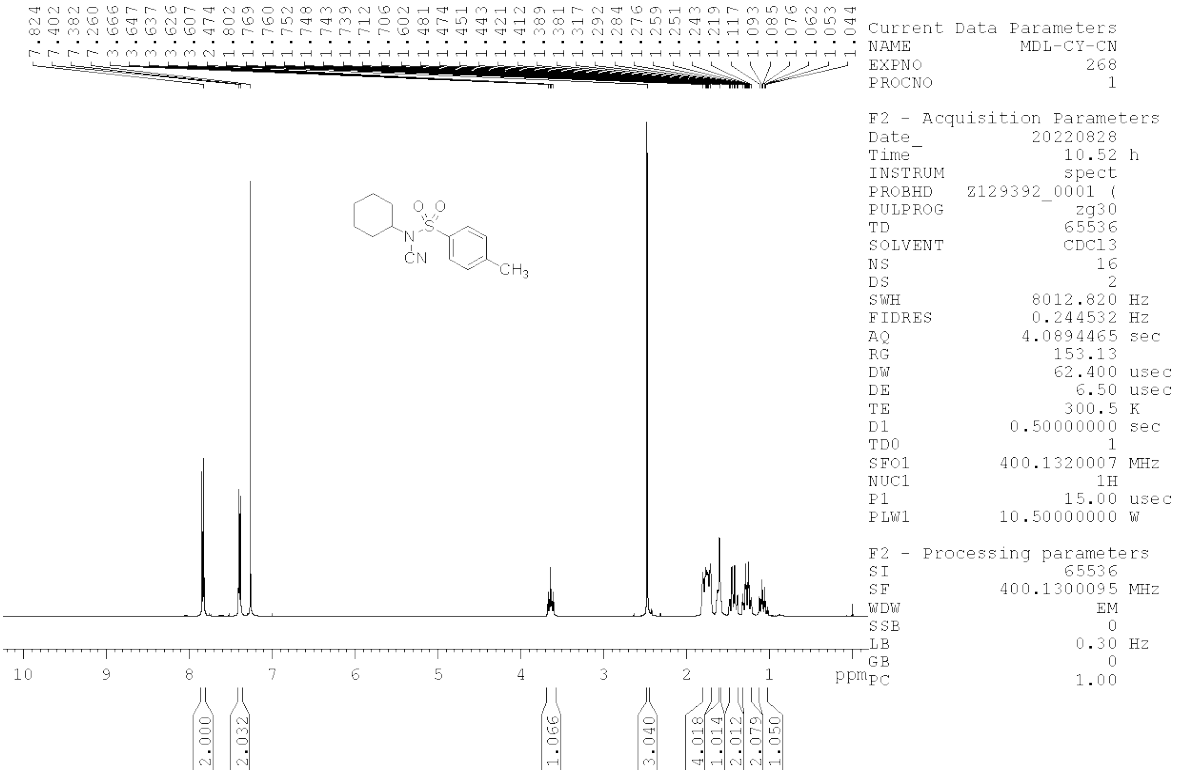


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 2d

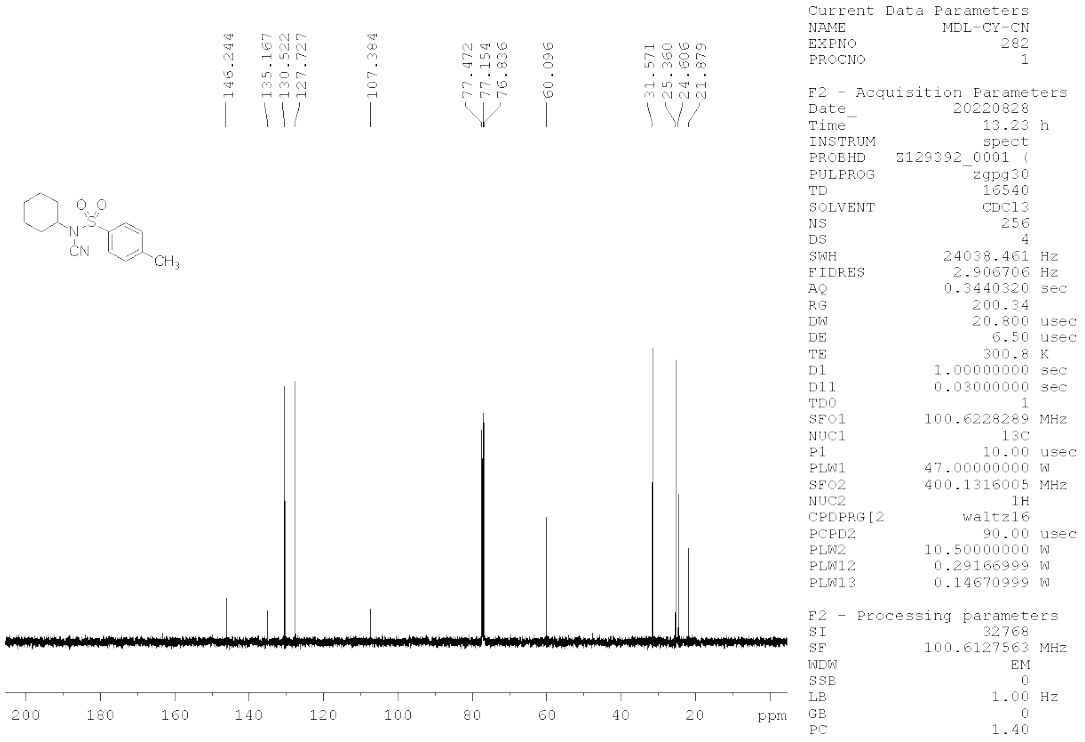


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 2d

N-Cyano-*N*-cyclohexyl-4-methylbenzenesulfonamide (2e)

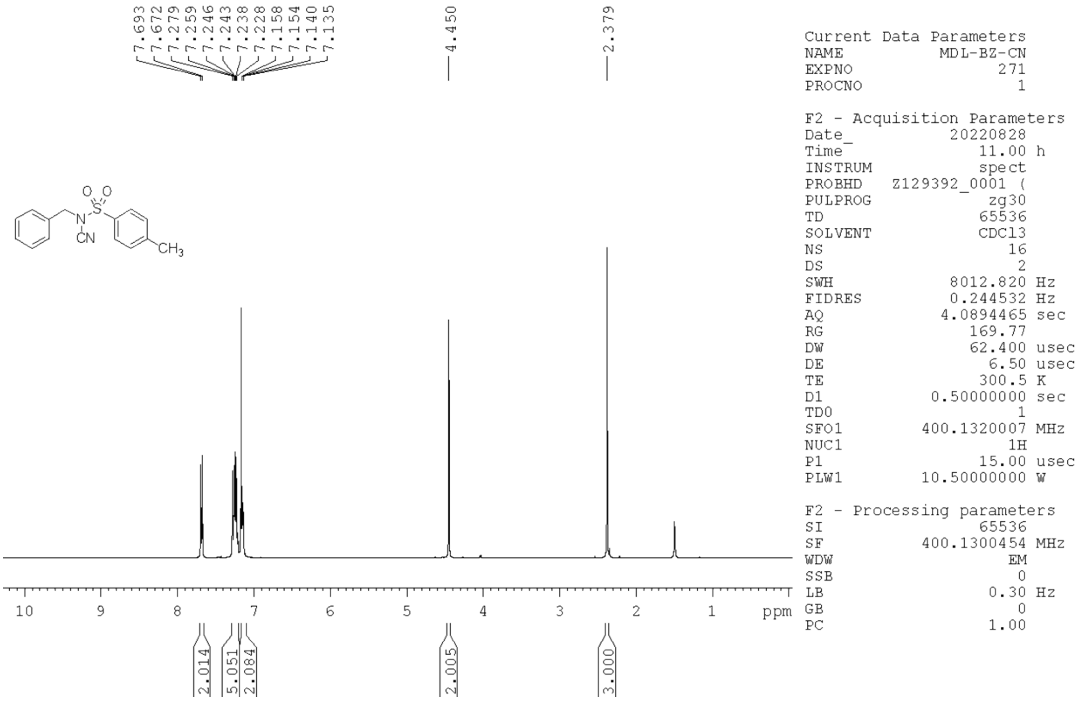


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 2e

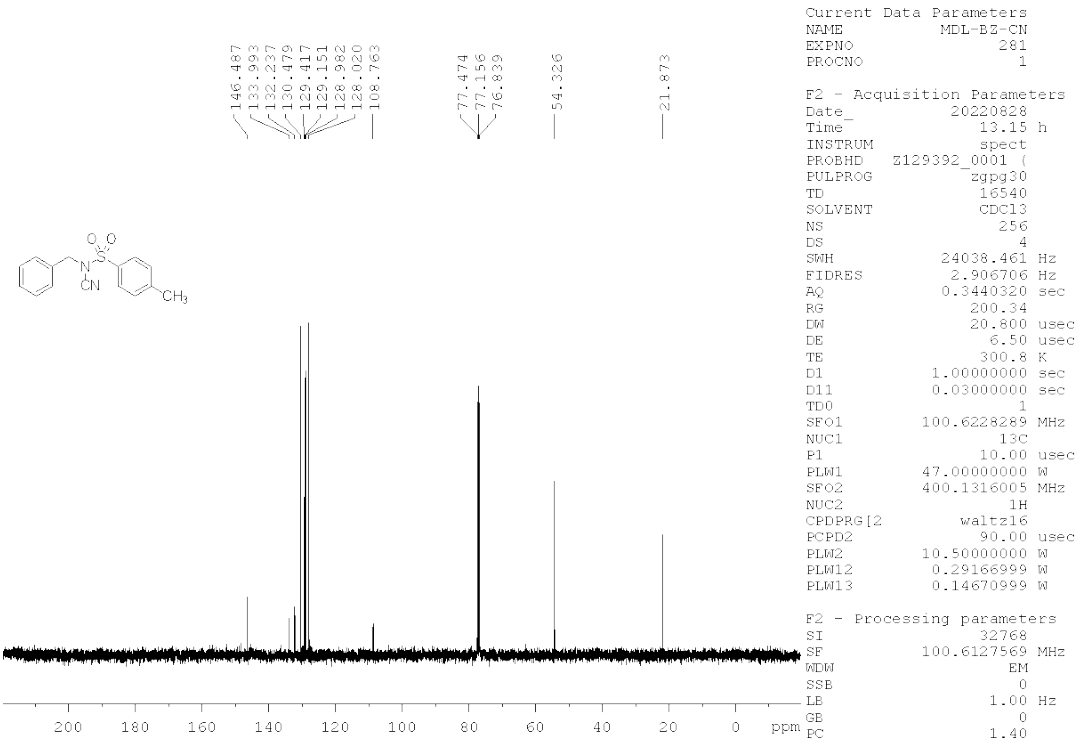


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 2e

***N*-benzyl-*N*-cyano-4-methylbenzenesulfonamide (2f)**

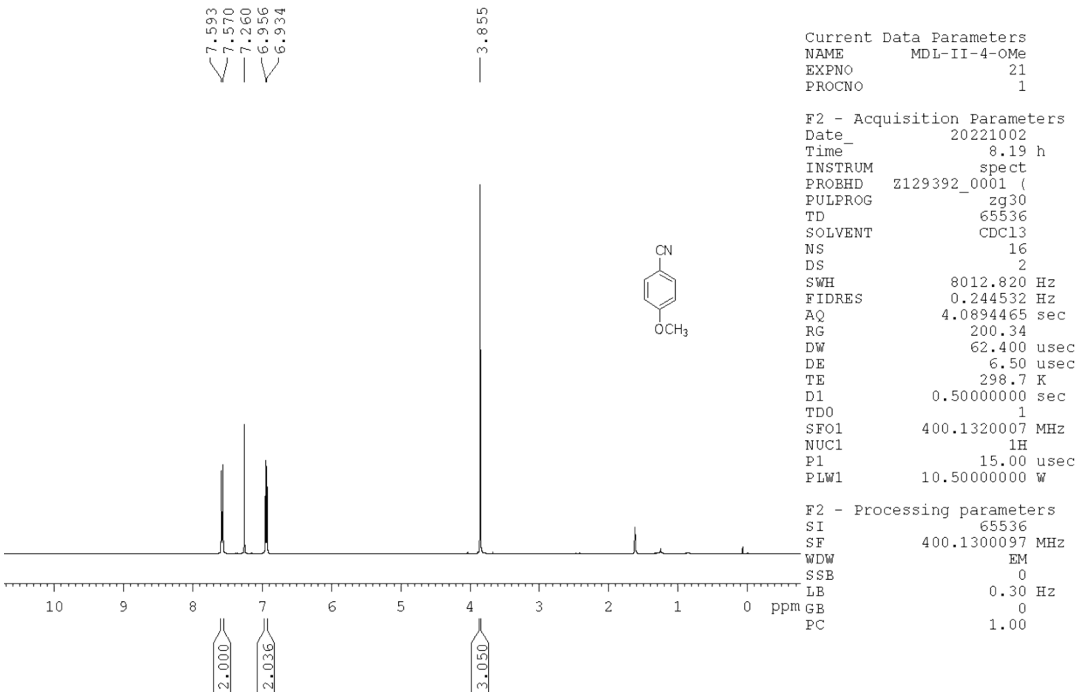


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 2f

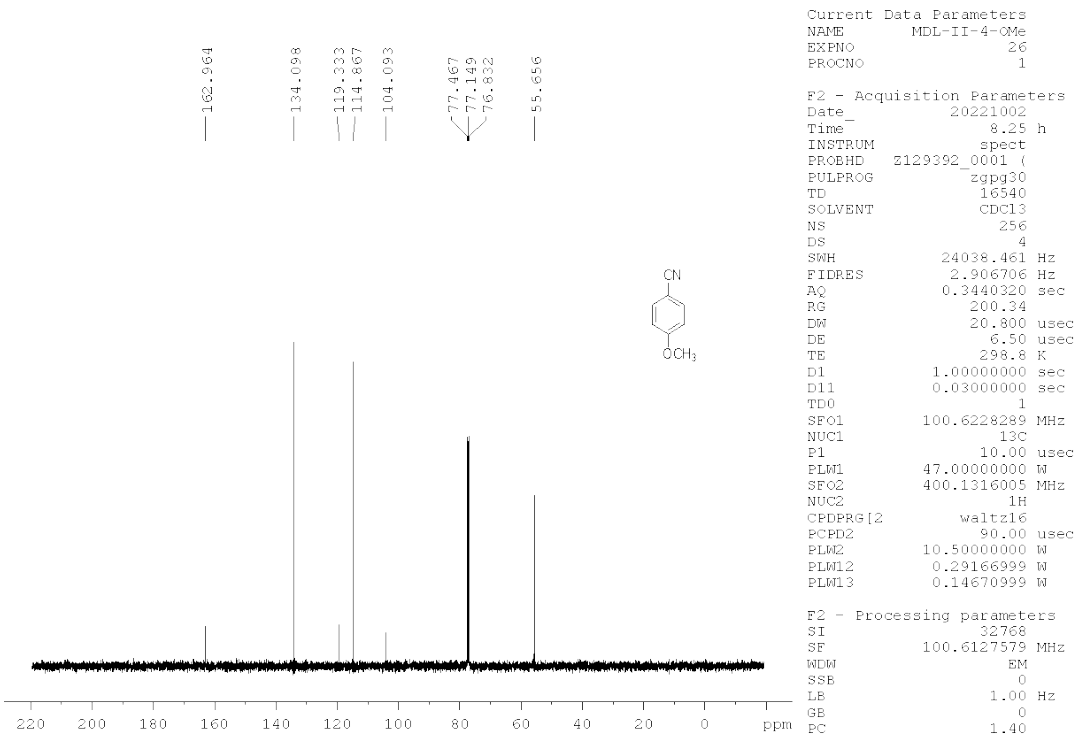


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 2f

4-methoxybenzonitrile (3a)

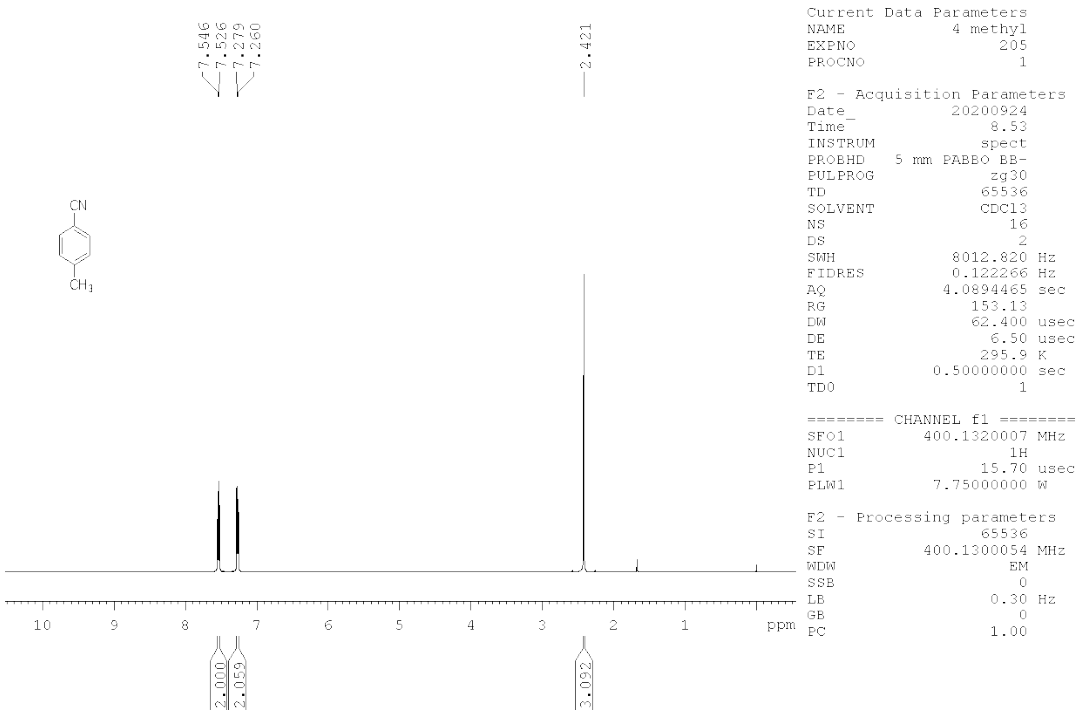


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3a

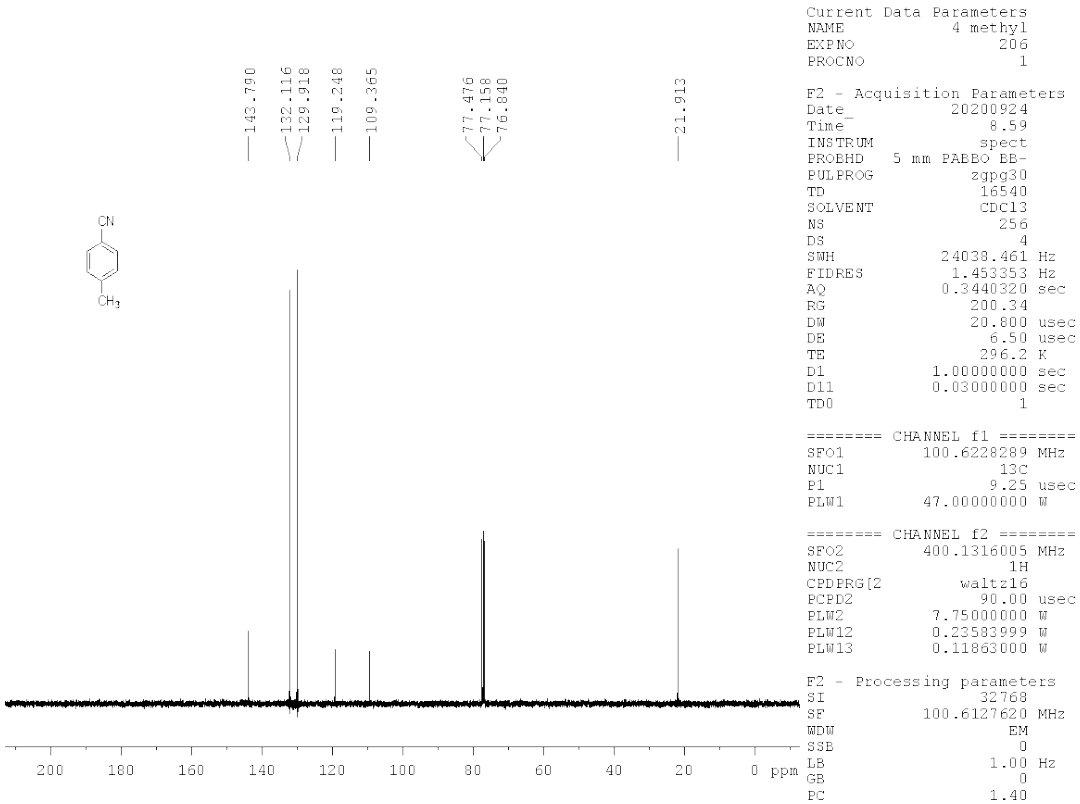


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3a

4-methylbenzonitrile (3b)

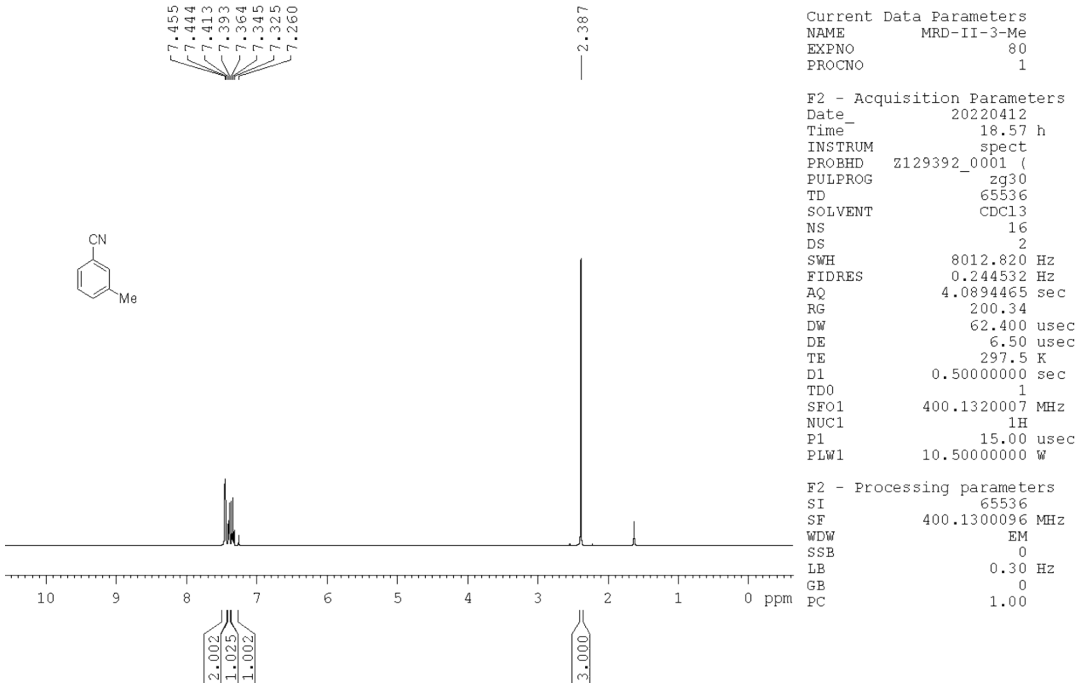


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3b

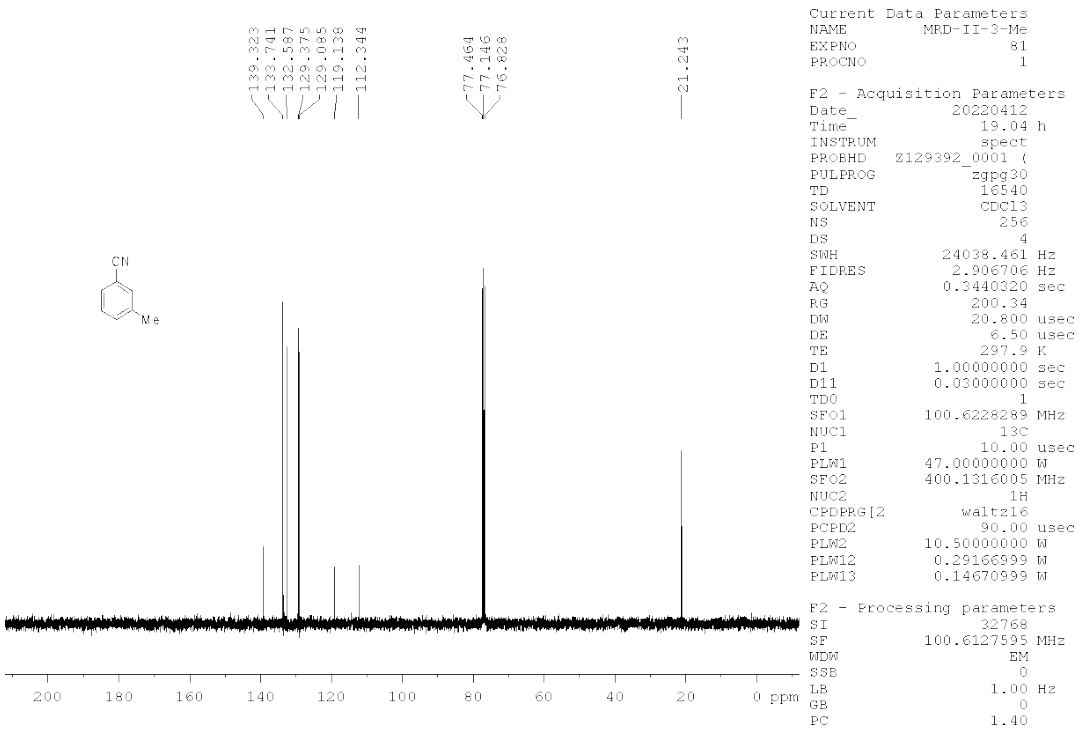


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3b

3-methylbenzonitrile (3c)

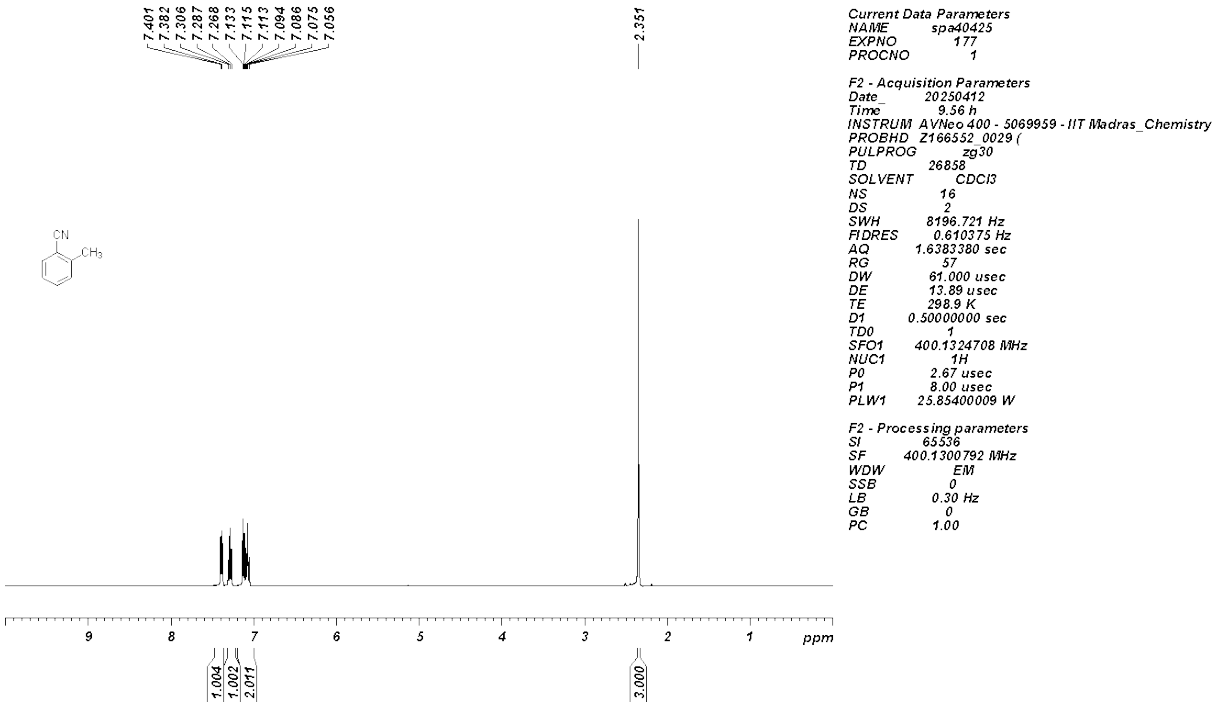


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3c

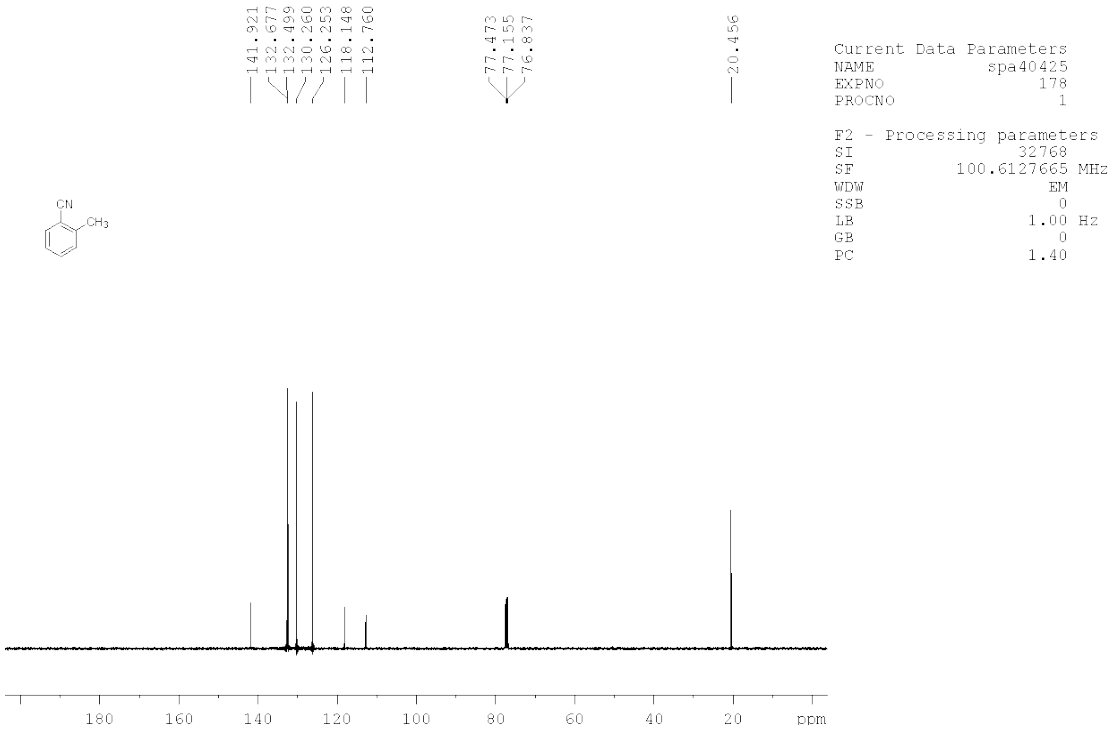


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3c

2-methylbenzonitrile (3d)

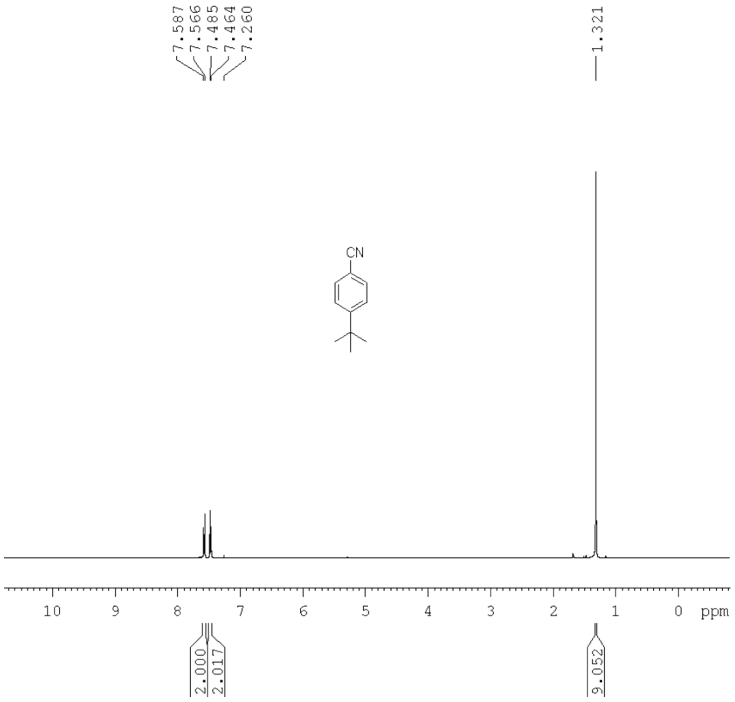


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3d



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3d

4-(tert-butyl)benzonitrile (3e)

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Current Data Parameters
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EXPNO                291
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220228
Time                12.00 h
INSTRUM             spect
PROBHD   Z129392_0001 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH              8012.820 Hz
FIDRES           0.244532 Hz
AQ               4.0894465 sec
RG                  79.8
DW                 62.400 usec
DE                  6.50 usec
TE                 297.3 K
D1              0.50000000 sec
TD0                    1
SFO1          400.1320007 MHz
NUC1                  1H
P1                 15.00 usec
PLW1          10.50000000 W

F2 - Processing parameters
SI                 65536
SF            400.1300096 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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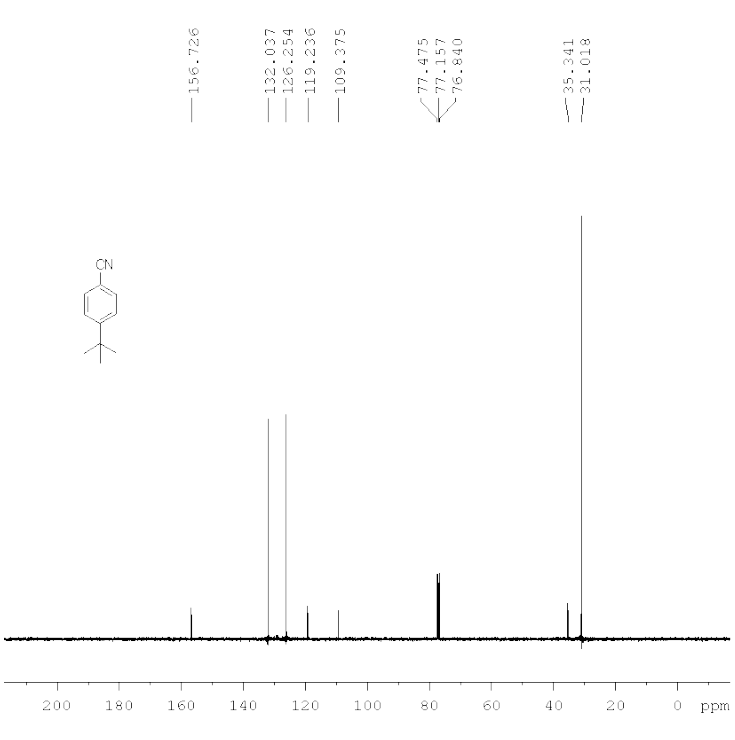
^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3e

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Current Data Parameters
NAME      4 tert butylbenozonitrile
EXPNO                292
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220228
Time                12.07 h
INSTRUM             spect
PROBHD   Z129392_0001 (
PULPROG           zgpg30
TD                 16540
SOLVENT            CDCl3
NS                   256
DS                     4
SWH             24038.461 Hz
FIDRES           2.906706 Hz
AQ               0.3440320 sec
RG                 200.34
DW                 20.800 usec
DE                  6.50 usec
TE                 297.8 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                    1
SFO1          100.6228289 MHz
NUC1                  13C
P1                 10.00 usec
PLW1          47.00000000 W
SFO2          400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2          10.50000000 W
PLW12          0.29166999 W
PLW13          0.14670999 W

F2 - Processing parameters
SI                 32768
SF            100.6127616 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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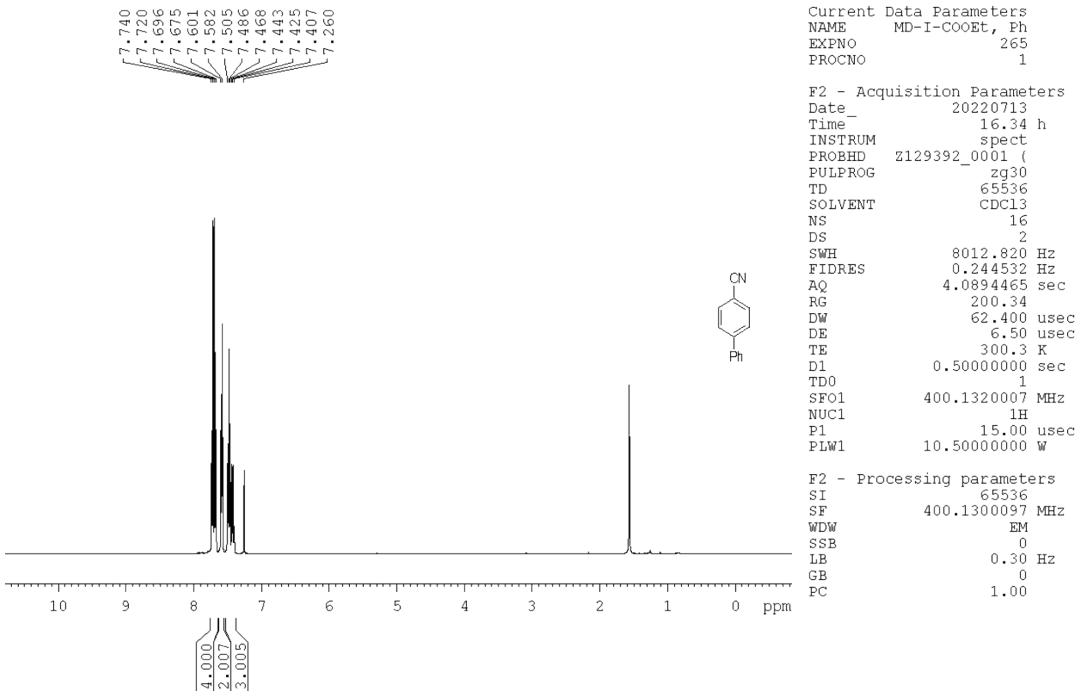
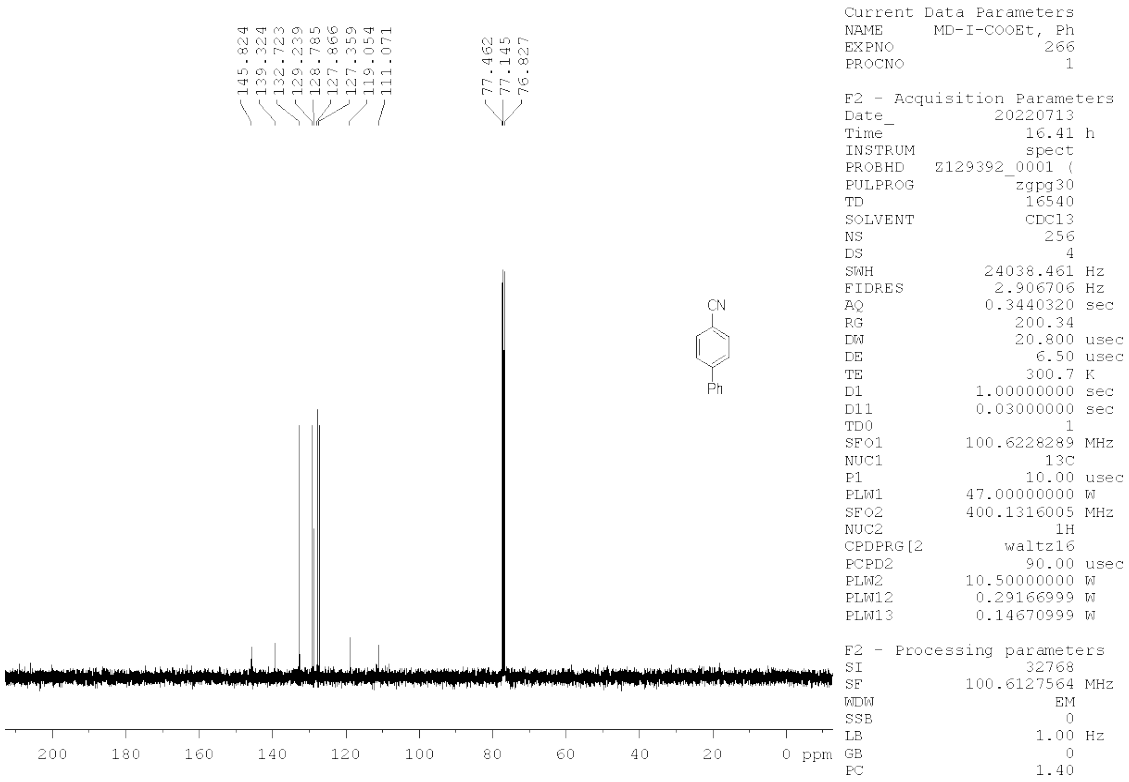
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3e

[1,1'-biphenyl]-4-carbonitrile: (3f)

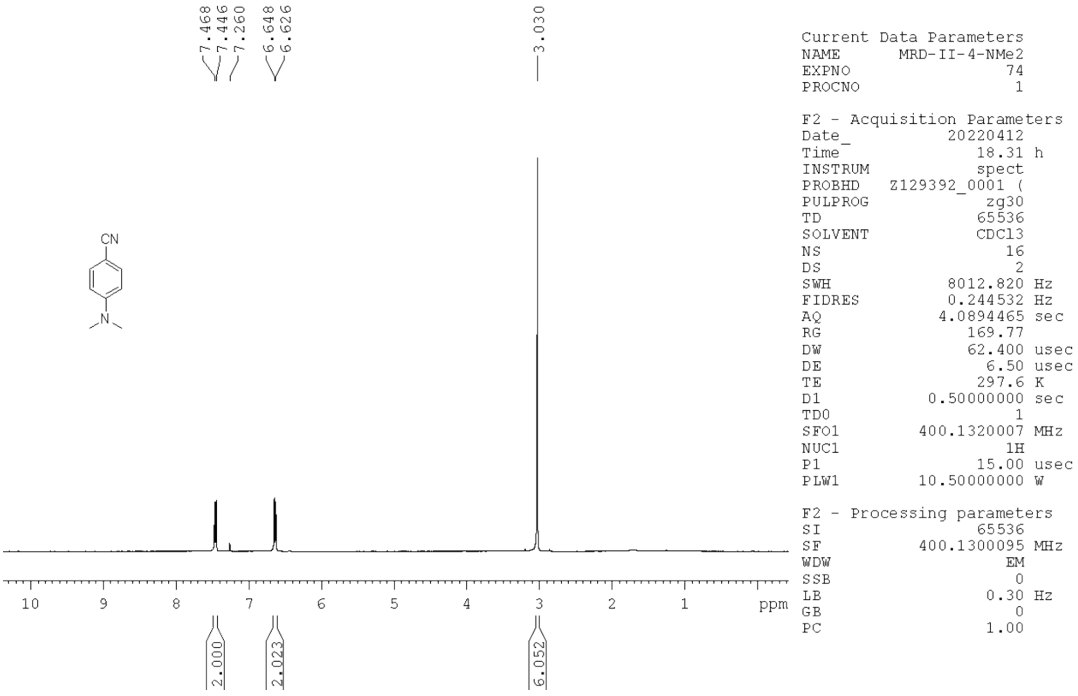


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3f

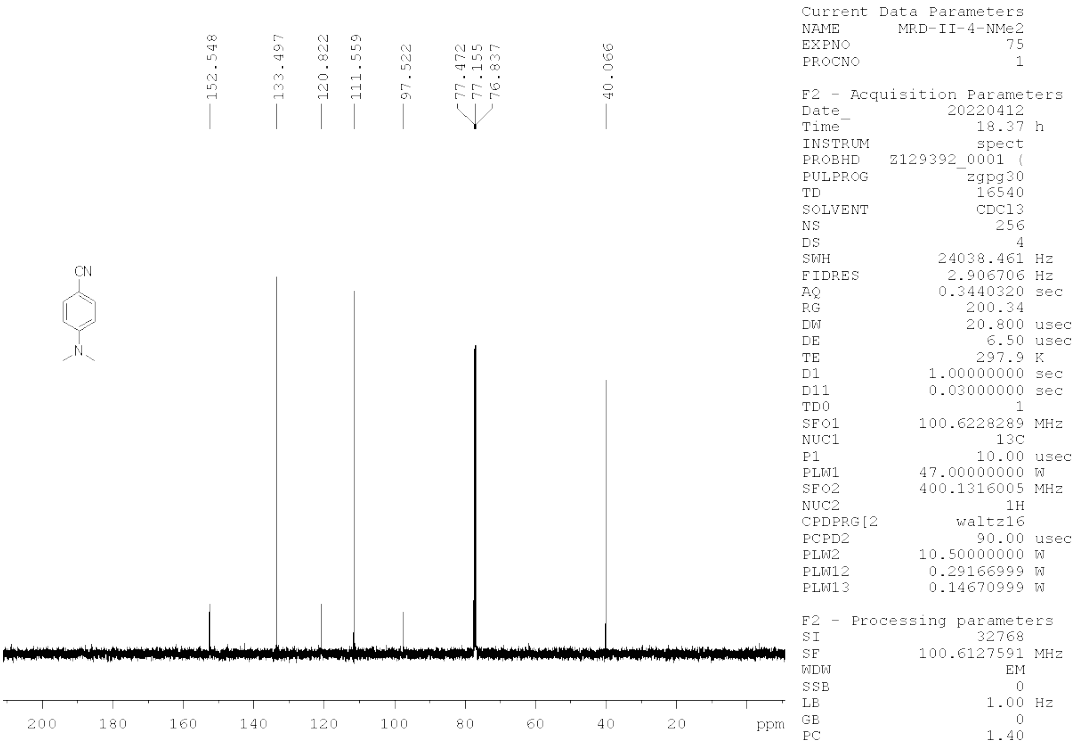


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3f

4-(dimethylamino)benzonitrile (3g)

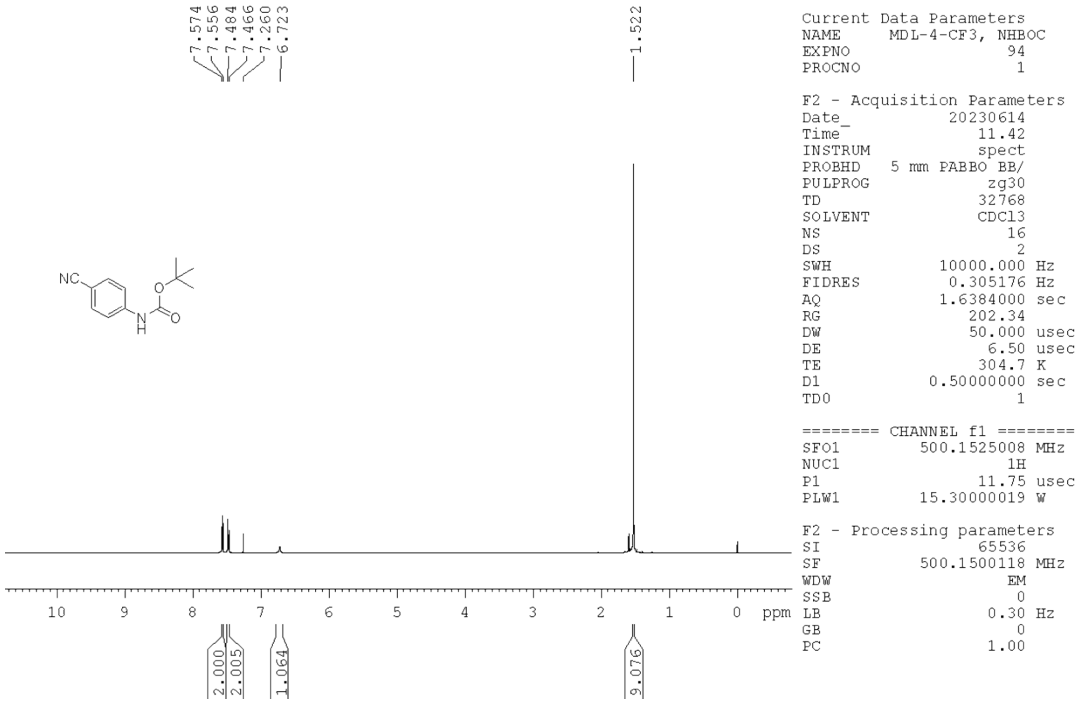


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3g

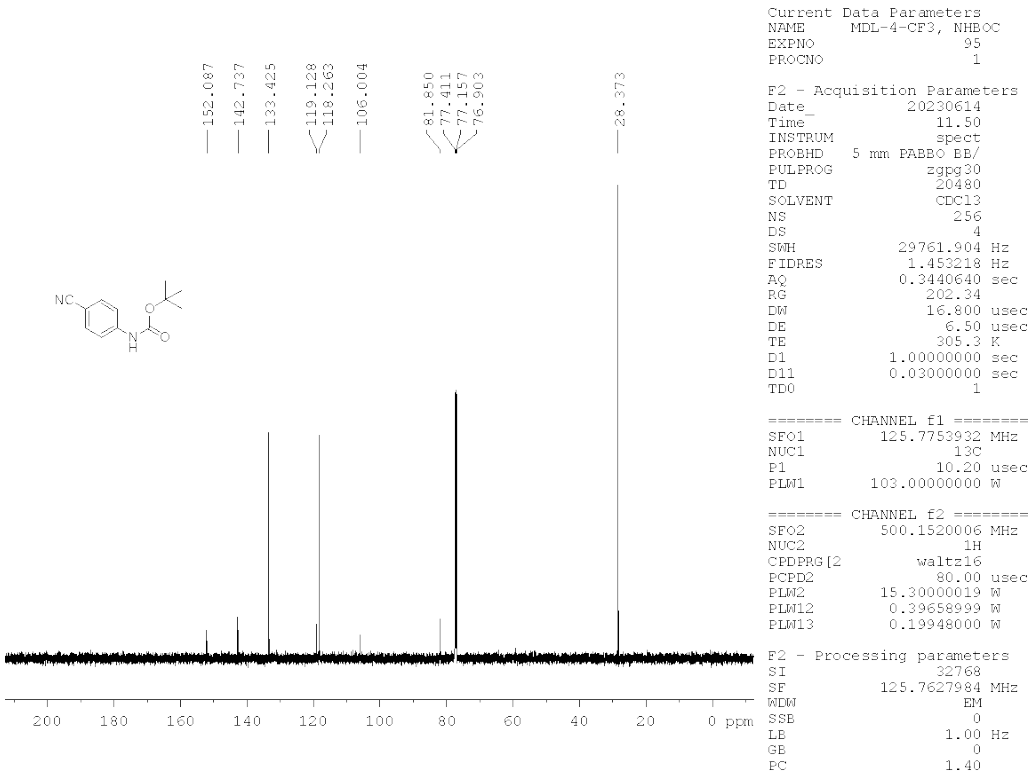


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3g

Tert-butyl (4-cyanophenyl)carbamate (3h)

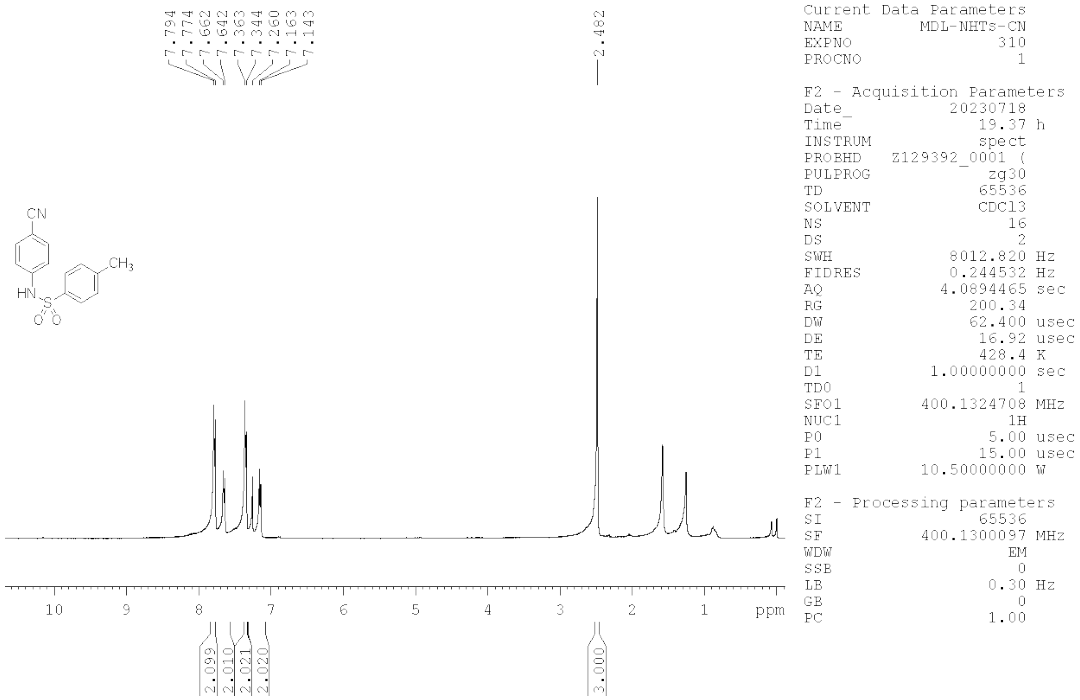


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3h

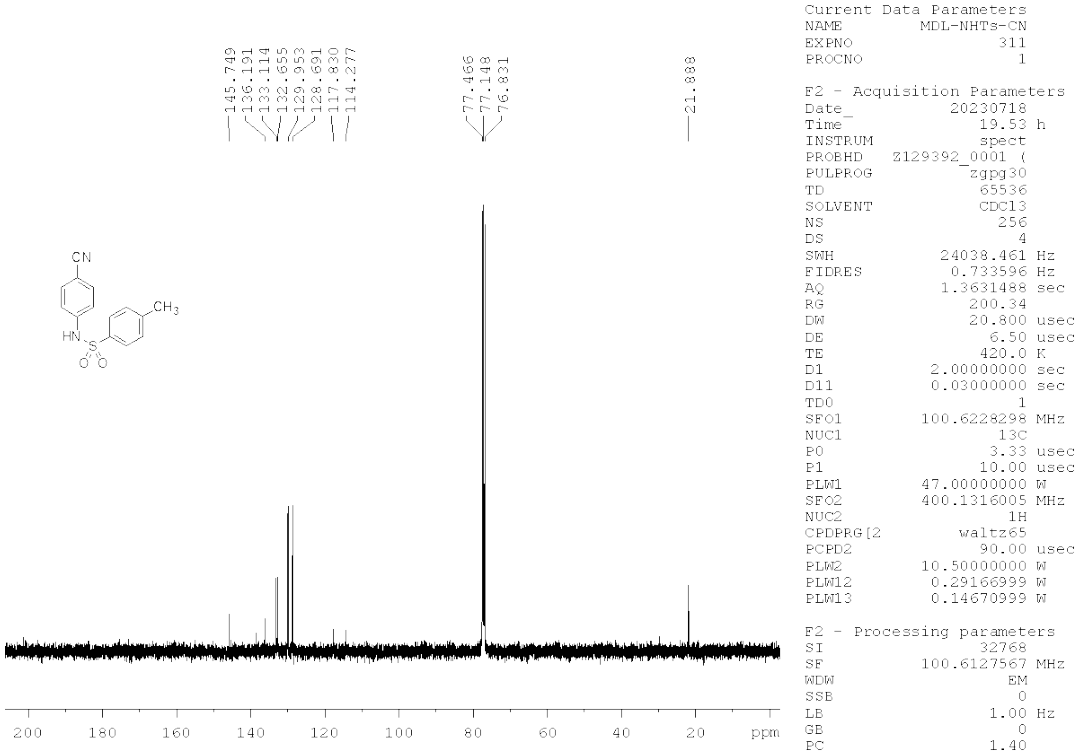


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3h

N-(4-cyanophenyl)-4-methylbenzenesulfonamide (3i)

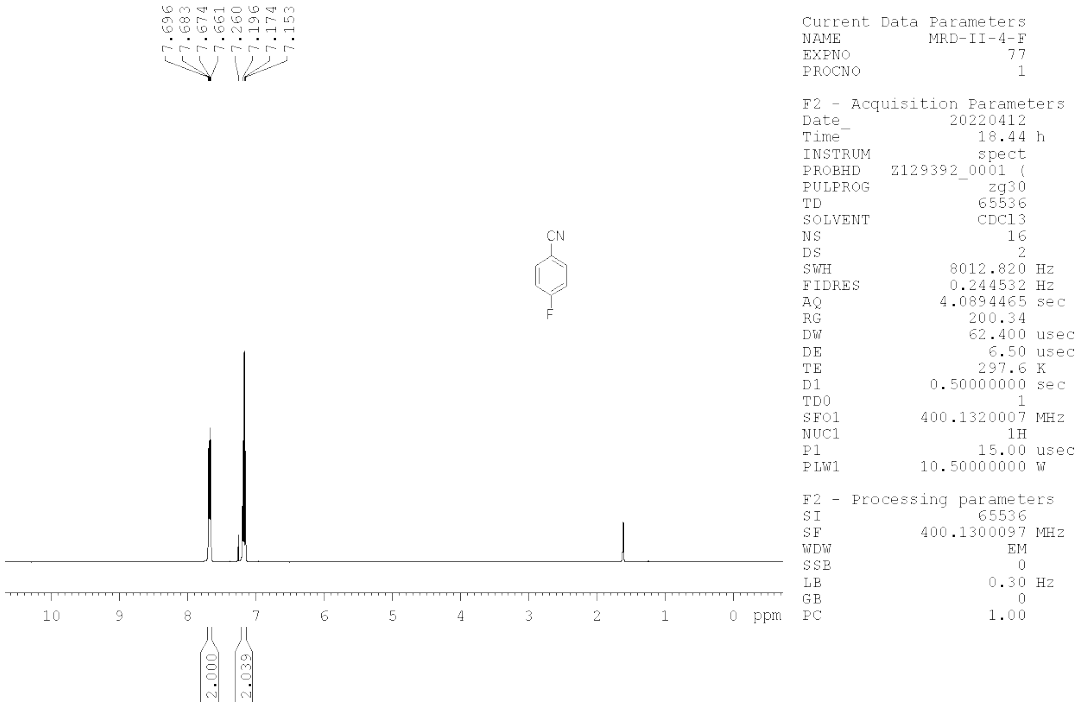


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3i

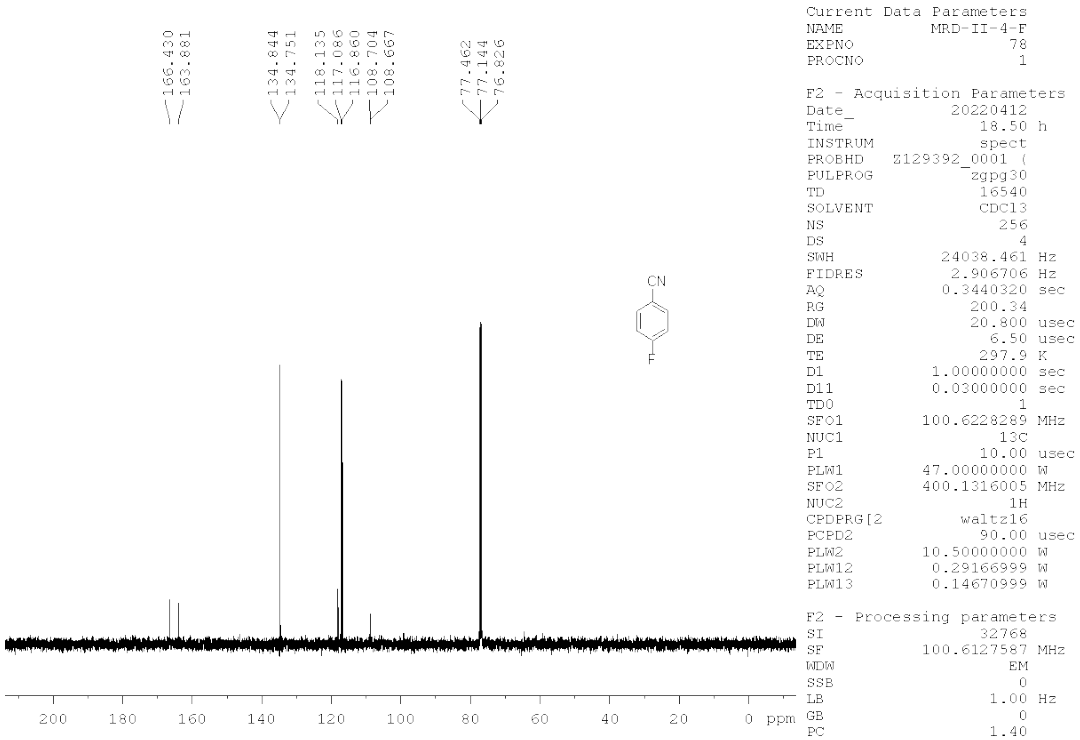


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3i

4-fluorobenzonitrile (3j)

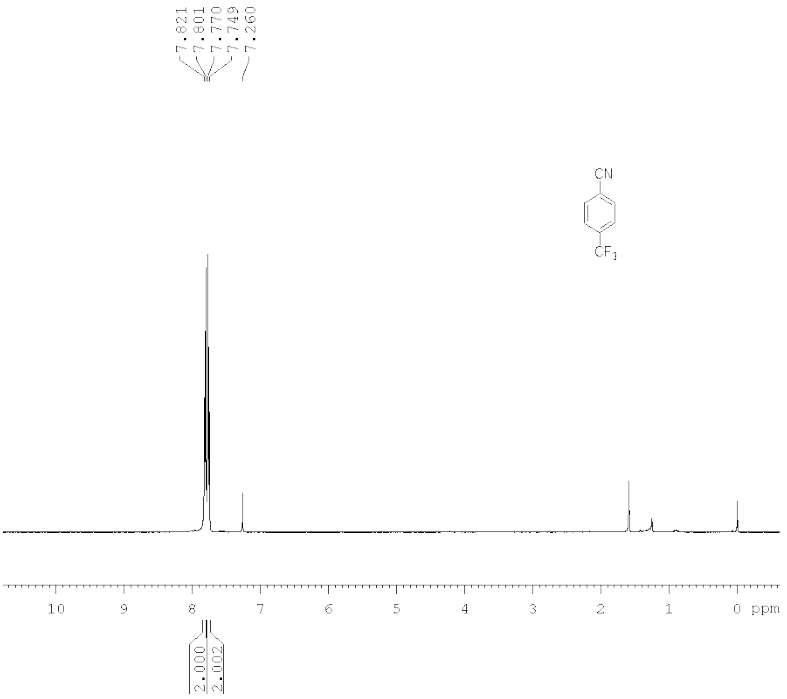


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3j



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3j

4-(trifluoromethyl)benzonitrile (3k)

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Current Data Parameters
NAME                  MDL-CF3-P
EXPNO                       607
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20230629
Time                      18.11 h
INSTRUM                   spect
PROBHD    Z129392_0001 (
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8012.820 Hz
FIDRES                 0.244532 Hz
AQ                     4.0894465 sec
RG                       200.34
DW                       62.400 usec
DE                       16.92 usec
TE                       430.6 K
D1                    1.00000000 sec
TD0                           1
SFO1                400.1324708 MHz
NUC1                         1H
P0                        5.00 usec
P1                       15.00 usec
PLW1                10.50000000 W

F2 - Processing parameters
SI                        65536
SF                  400.1300094 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
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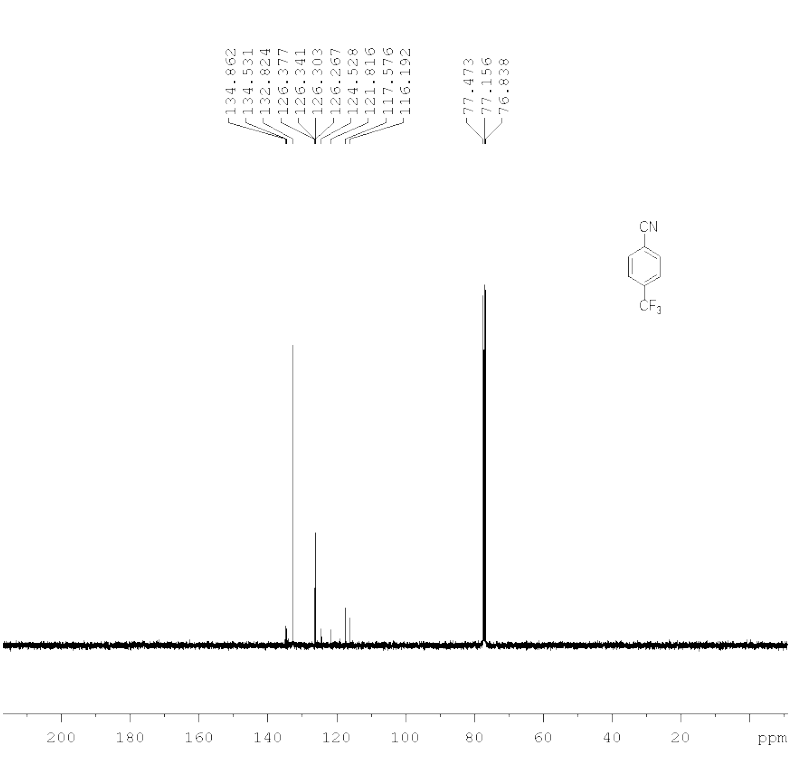
^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3k

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Current Data Parameters
NAME                  MDL-CF3-P
EXPNO                       628
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20230630
Time                       8.52 h
INSTRUM                   spect
PROBHD    Z129392_0001 (
PULPROG                 zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                          256
DS                            4
SWH                   24038.461 Hz
FIDRES                 0.733596 Hz
AQ                     1.3631488 sec
RG                       200.34
DW                       20.800 usec
DE                        6.50 usec
TE                       404.0 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                           1
SFO1                100.6228298 MHz
NUC1                         13C
P0                        3.33 usec
P1                       10.00 usec
PLW1                47.00000000 W
SFO2                400.1316005 MHz
NUC2                         1H
CPDPRG[2                waltz65
PCPD2                    90.00 usec
PLW2                10.50000000 W
PLW12                0.29166999 W
PLW13                0.14670999 W

F2 - Processing parameters
SI                        32768
SF                  100.6127563 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
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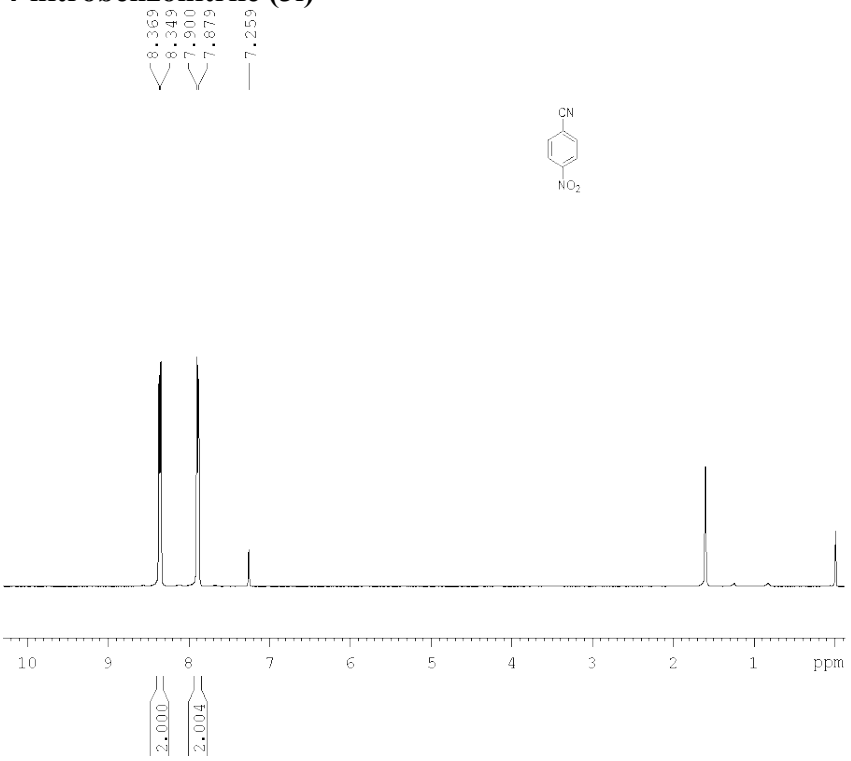
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3k

4-nitrobenzonitrile (3l)

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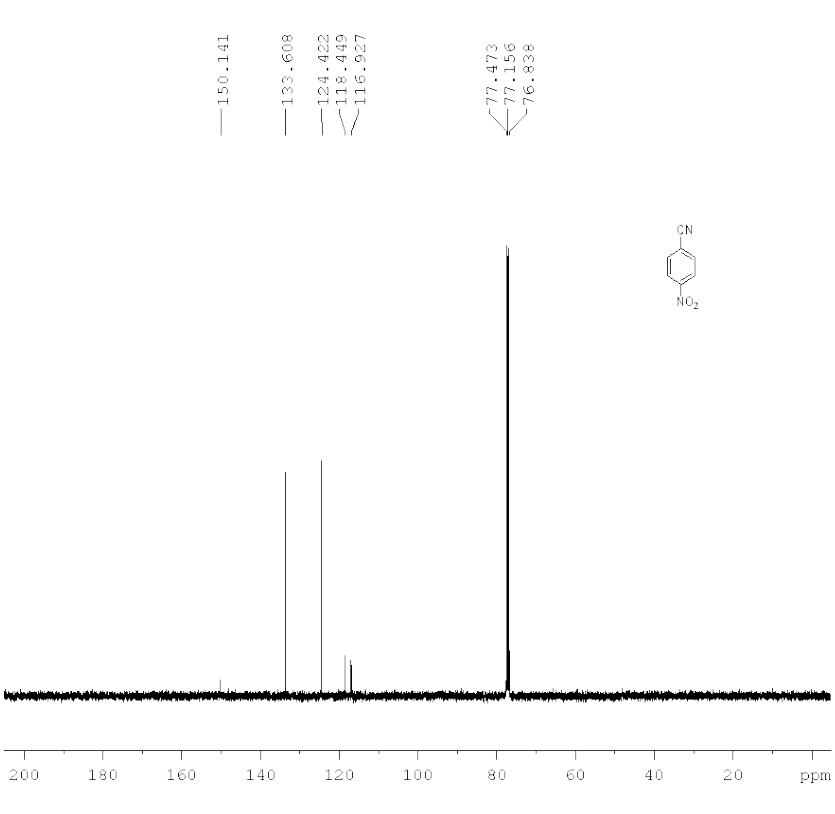
Current Data Parameters
NAME      MDL-III-I-4-NO2 CN
EXPNO                  142
PROCNO                   1

F2 - Acquisition Parameters
Date_             20240115
Time                 9.17 h
INSTRUM             spect
PROBHD   Z129392_0001 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.244532 Hz
AQ               4.0894465 sec
RG                  200.34
DW                  62.400 usec
DE                  16.92 usec
TE                  293.3 K
D1              1.00000000 sec
TD0                     1
SFO1           400.1324708 MHz
NUC1                   1H
P0                  5.00 usec
P1                 15.00 usec
PLW1           10.50000000 W

F2 - Processing parameters
SI                  65536
SF             400.1300098 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3l

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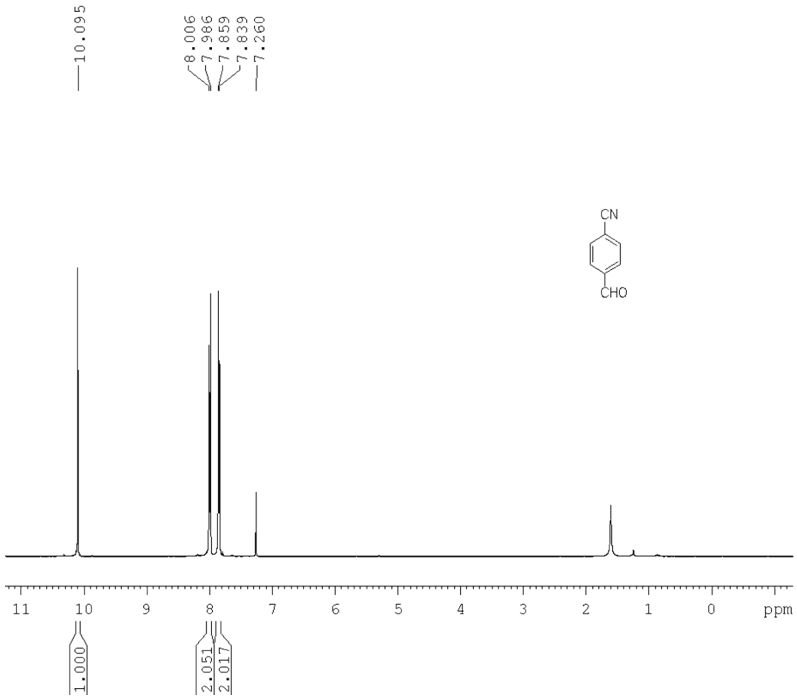
Current Data Parameters
NAME      MDL-III-I-4-NO2 CN
EXPNO                  143
PROCNO                   1

F2 - Acquisition Parameters
Date_             20240115
Time                 9.32 h
INSTRUM             spect
PROBHD   Z129392_0001 (
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ               1.3631488 sec
RG                  200.34
DW                  20.800 usec
DE                   6.50 usec
TE                  293.7 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1
SFO1           100.6228298 MHz
NUC1                   13C
P0                   3.33 usec
P1                  10.00 usec
PLW1           47.00000000 W
SFO2           400.1316005 MHz
NUC2                   1H
CPDPRG[2         waltz65
PCPD2               90.00 usec
PLW2           10.50000000 W
PLW12           0.29166999 W
PLW13           0.14670999 W

F2 - Processing parameters
SI                  32768
SF             100.6127583 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3l

4-formylbenzonitrile (3m)

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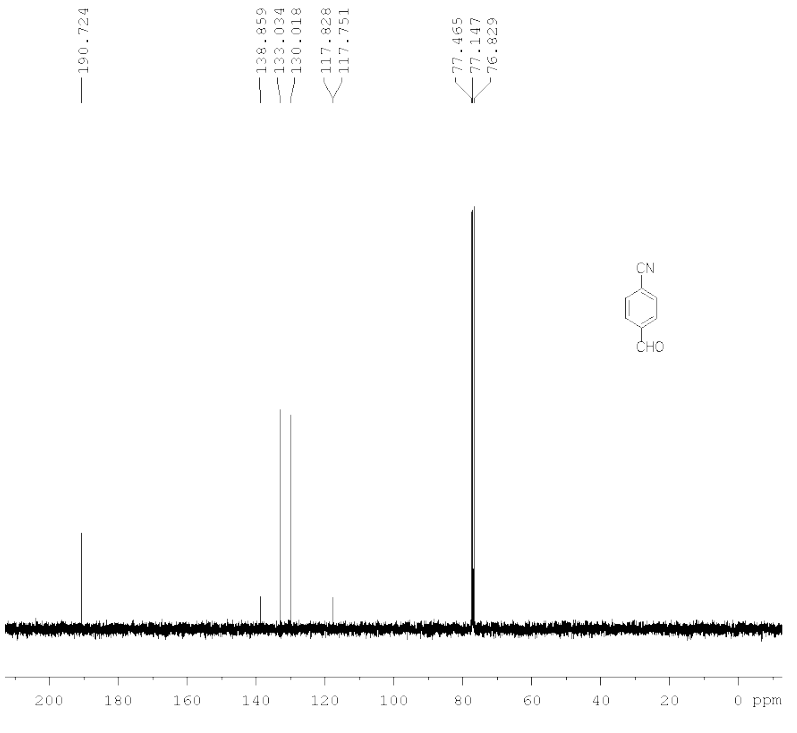
Current Data Parameters
NAME       MDL-II-4-CHO
EXPNO                90
PROCNO                1

F2 - Acquisition Parameters
Date_          20220606
Time              19.53 h
INSTRUM           spect
PROBHD   Z129392_0001 (
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES        0.244532 Hz
AQ            4.0894465 sec
RG               200.34
DW               62.400 usec
DE                6.50 usec
TE               296.6 K
D1            0.50000000 sec
TD0                   1
SFO1        400.1320007 MHz
NUC1                 1H
P1               15.00 usec
PLW1        10.50000000 W

F2 - Processing parameters
SI                65536
SF          400.1300096 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3m

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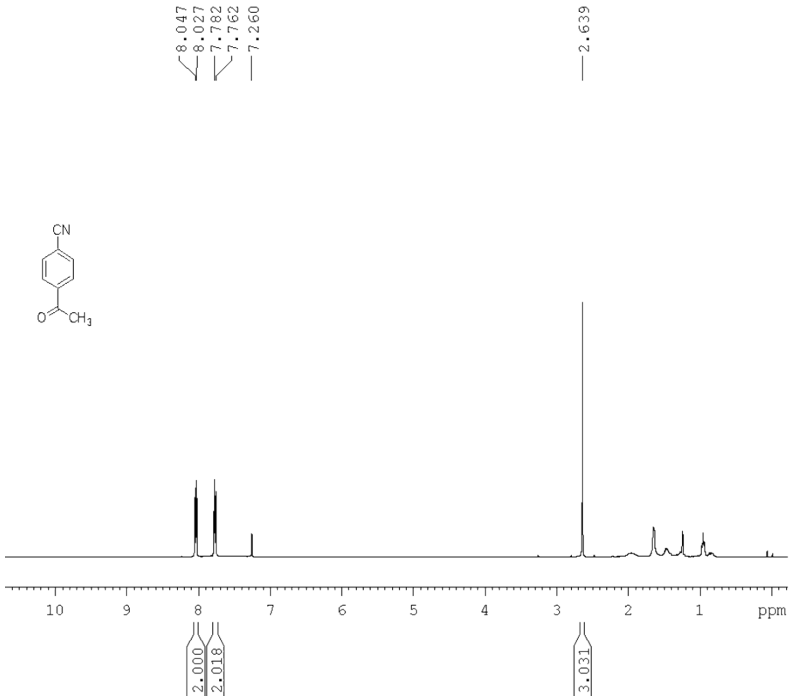
Current Data Parameters
NAME       MDL-II-4-CHO
EXPNO                91
PROCNO                1

F2 - Acquisition Parameters
Date_          20220606
Time              19.59 h
INSTRUM           spect
PROBHD   Z129392_0001 (
PULPROG          zgpg30
TD                16540
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           24038.461 Hz
FIDRES         2.906706 Hz
AQ            0.3440320 sec
RG               200.34
DW               20.800 usec
DE                6.50 usec
TE               297.1 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1        100.6228289 MHz
NUC1                13C
P1               10.00 usec
PLW1        47.00000000 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        10.50000000 W
PLW12        0.29166999 W
PLW13        0.14670999 W

F2 - Processing parameters
SI                32768
SF          100.6127574 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3m

4-acetylbenzonitrile (3n)

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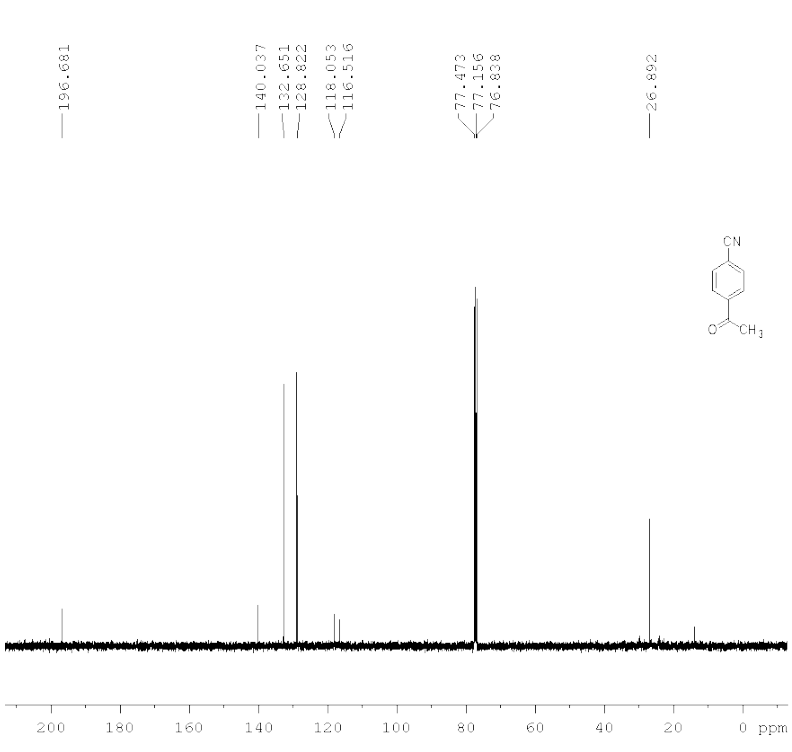
Current Data Parameters
NAME      MDL-COCH3-CN(SIP)
EXPNO                  148
PROCNO                   1

F2 - Acquisition Parameters
Date_           20230711
Time                8.09 h
INSTRUM            spect
PROBHD   Z129392_0001 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ              4.0894465 sec
RG                200.34
DW                62.400 usec
DE                16.92 usec
TE                468.4 K
D1             1.00000000 sec
TD0                    1
SFO1         400.1324708 MHz
NUC1                  1H
P0                 5.00 usec
P1                15.00 usec
PLW1         10.50000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300094 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3n

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Current Data Parameters
NAME      MDL-COCH3-CN(SIP)
EXPNO                  149
PROCNO                   1

F2 - Acquisition Parameters
Date_           20230711
Time                8.24 h
INSTRUM            spect
PROBHD   Z129392_0001 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ              1.3631488 sec
RG                200.34
DW                20.800 usec
DE                 6.50 usec
TE                453.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1         100.6228298 MHz
NUC1                  13C
P0                 3.33 usec
P1                10.00 usec
PLW1         47.00000000 W
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz65
PCPD2             90.00 usec
PLW2         10.50000000 W
PLW12         0.29166999 W
PLW13         0.14670999 W

F2 - Processing parameters
SI                 32768
SF           100.6127578 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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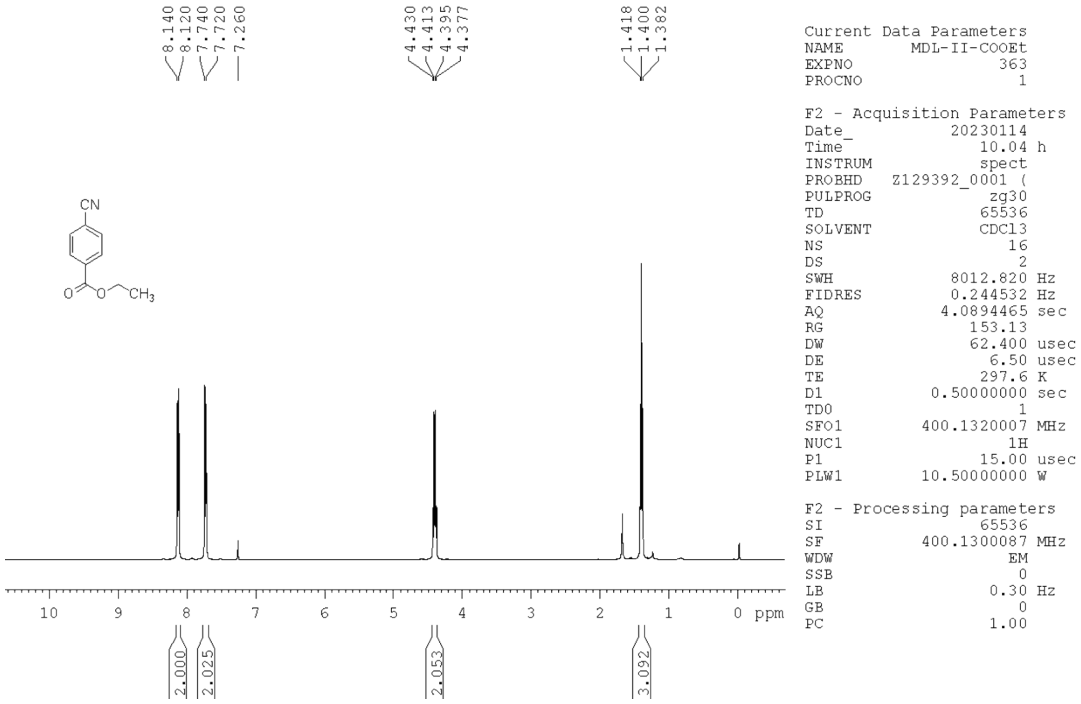
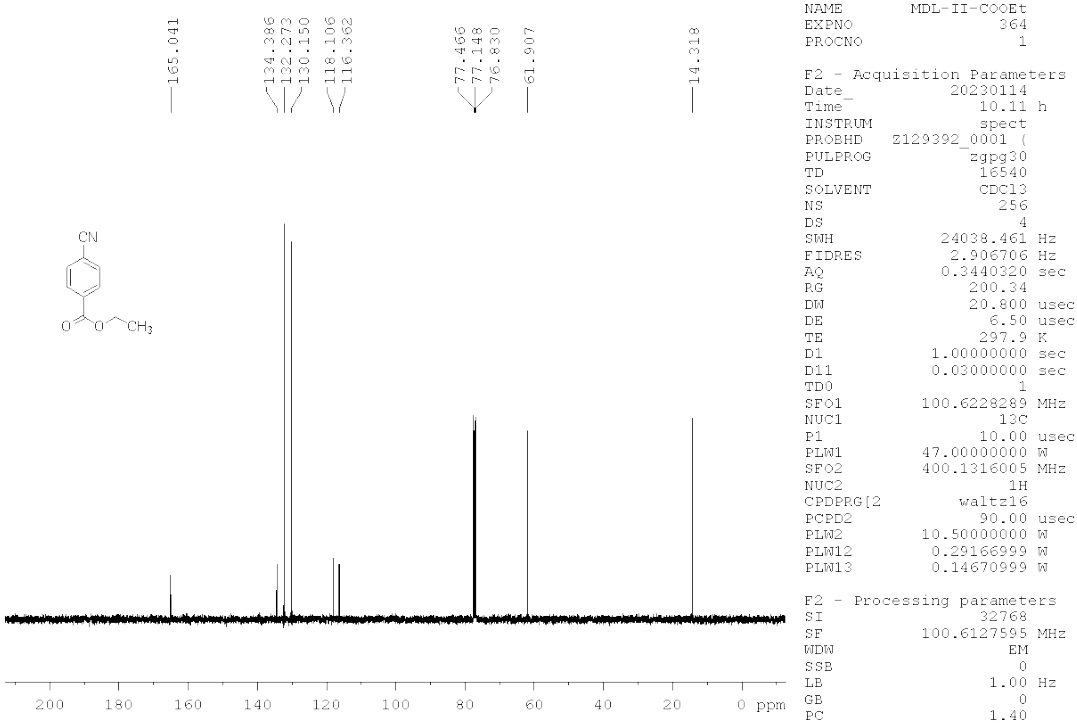
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3n

Ethyl 4-cyanobenzoate (3o)

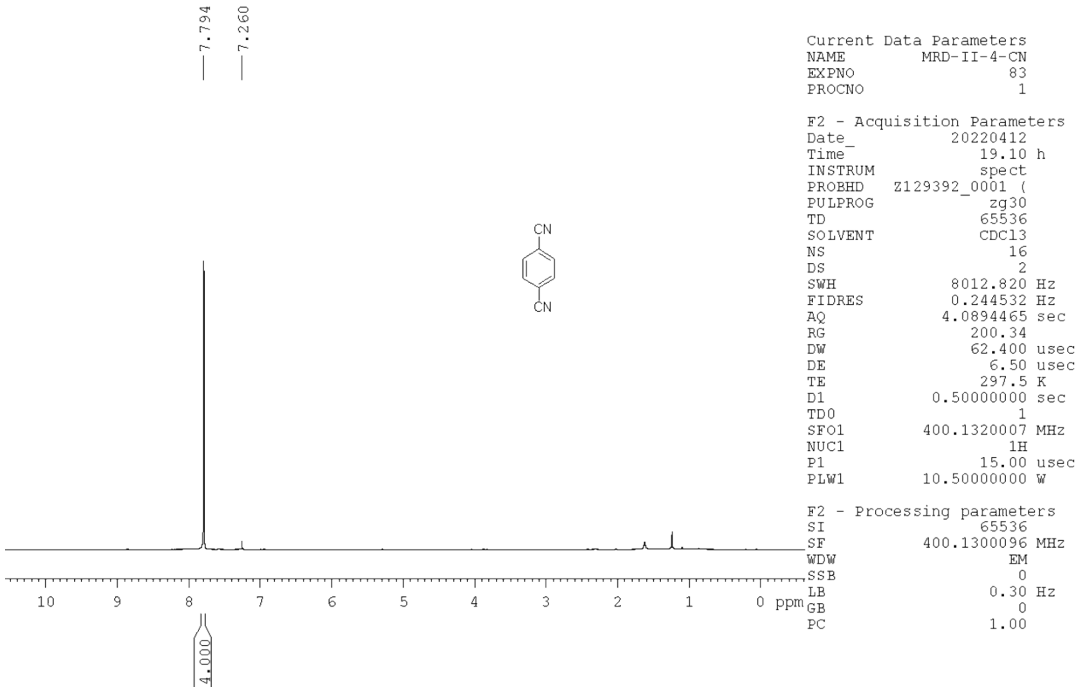


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3o

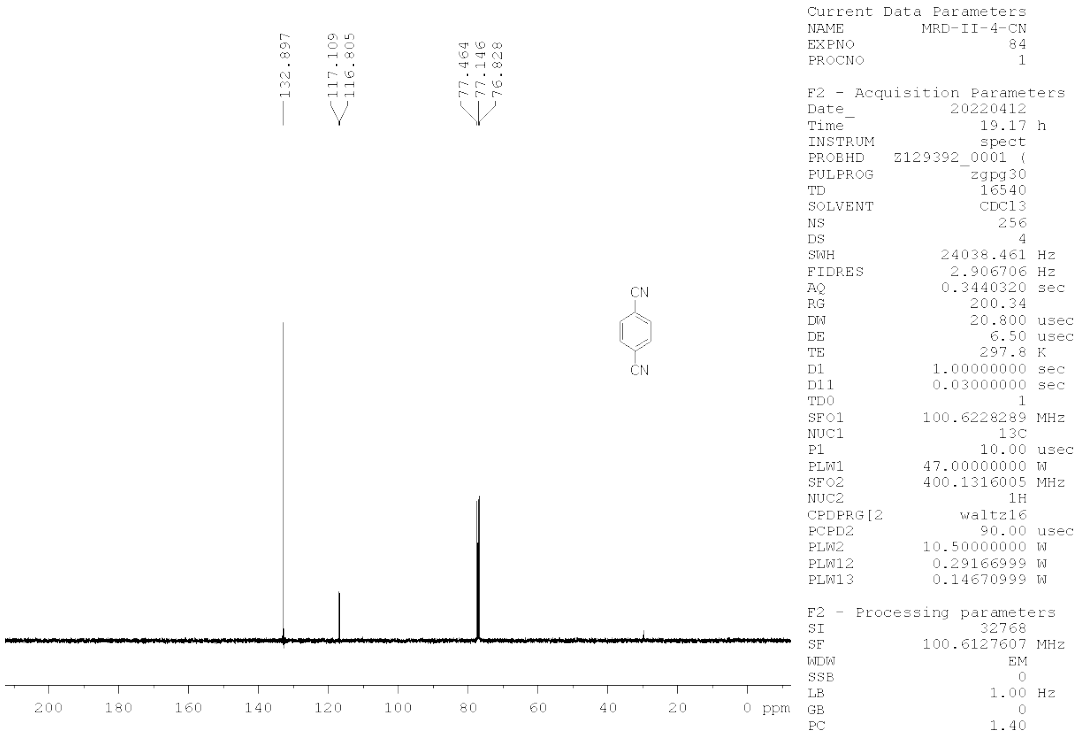


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3o

Terephthalonitrile (3p)

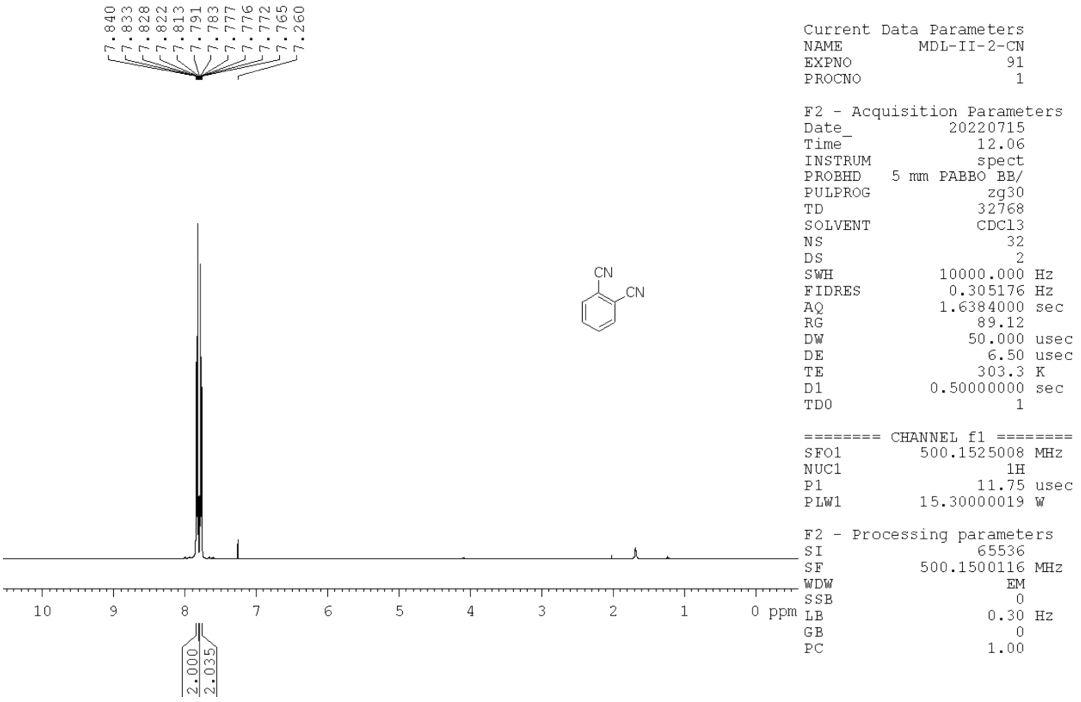


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3p

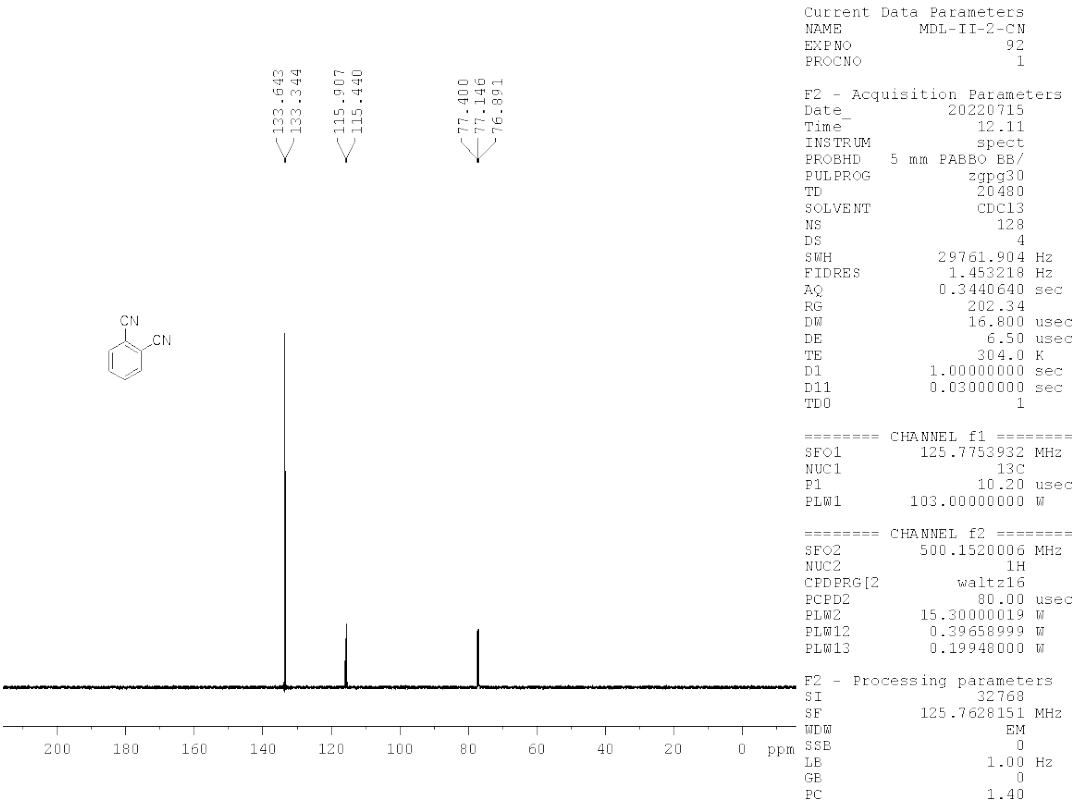


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3p

Phthalonitrile (3q)

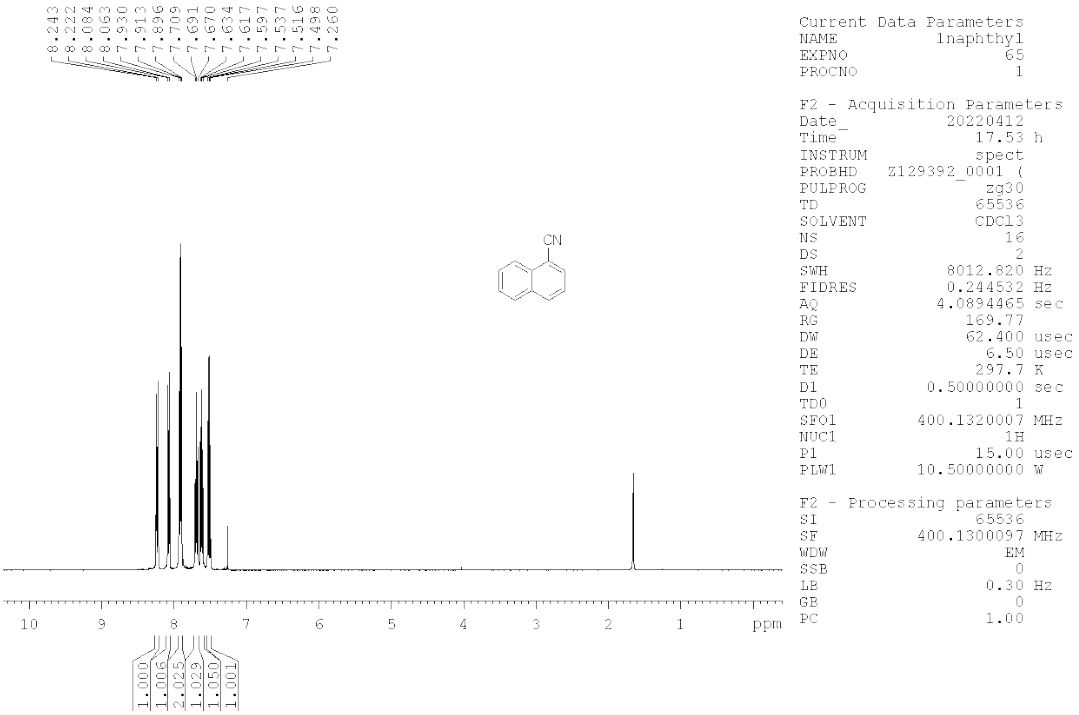


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3q

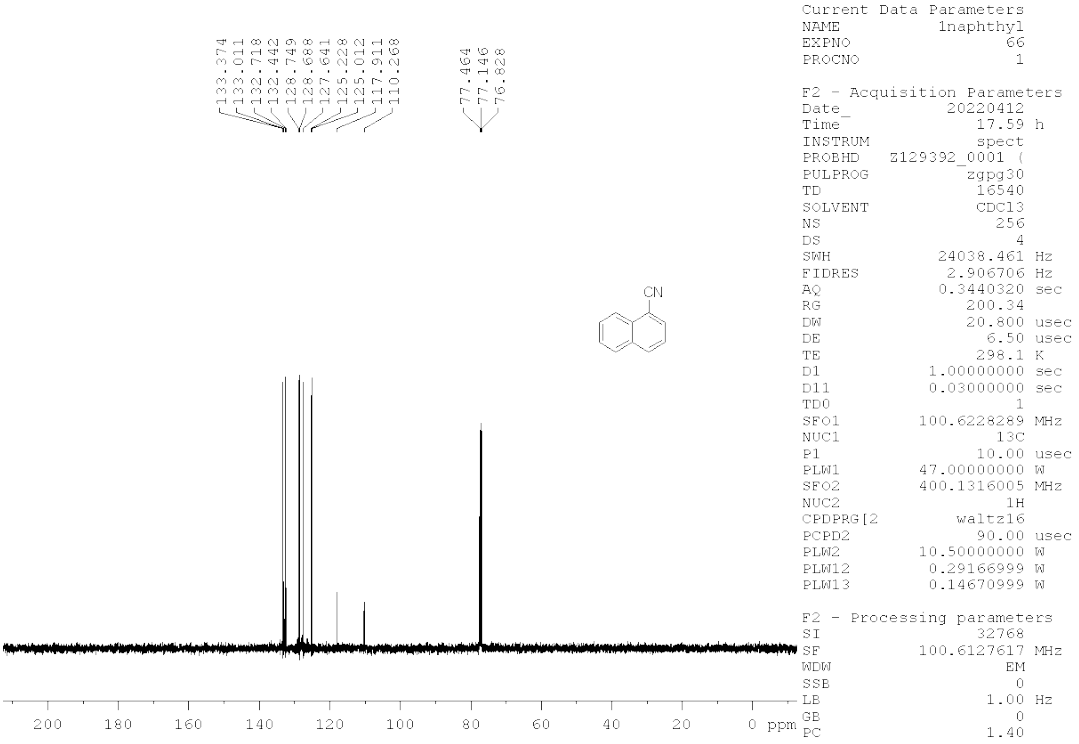


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3q

1-naphthonitrile (3r)

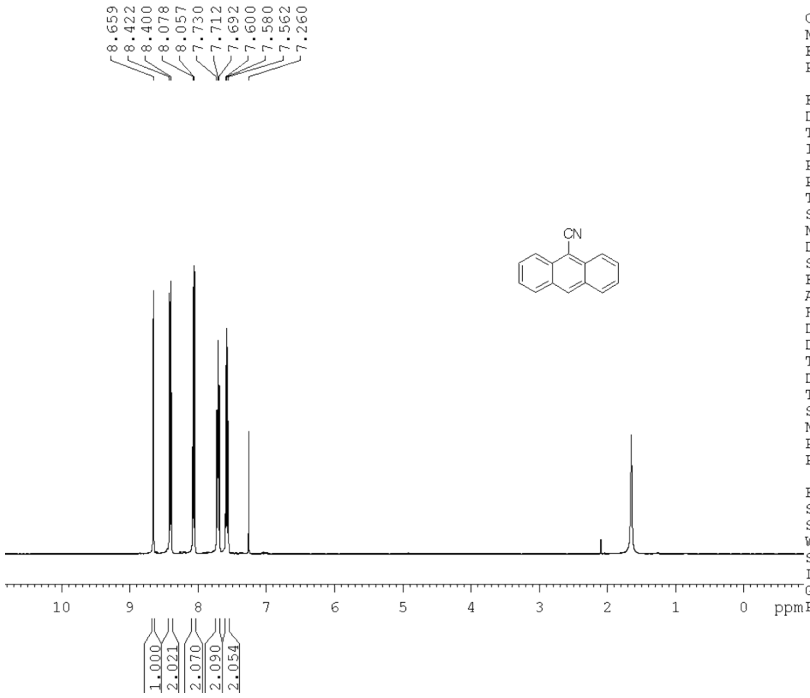


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3r



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3r

Anthracene-9-carbonitrile (3s)

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Current Data Parameters
NAME      MRD-II-9-anthracene
EXPNO                      71
PROCNO                      1

F2 - Acquisition Parameters
Date_              20220412
Time                  18.18 h
INSTRUM               spect
PROBHD    Z129392_0001 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                4.0894465 sec
RG                   200.34
DW                   62.400 usec
DE                    6.50 usec
TE                   297.6 K
D1              0.50000000 sec
TD0                       1
SFO1           400.1320007 MHz
NUC1                    1H
P1                   15.00 usec
PLW1           10.50000000 W

F2 - Processing parameters
SI                    65536
SF             400.1300095 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
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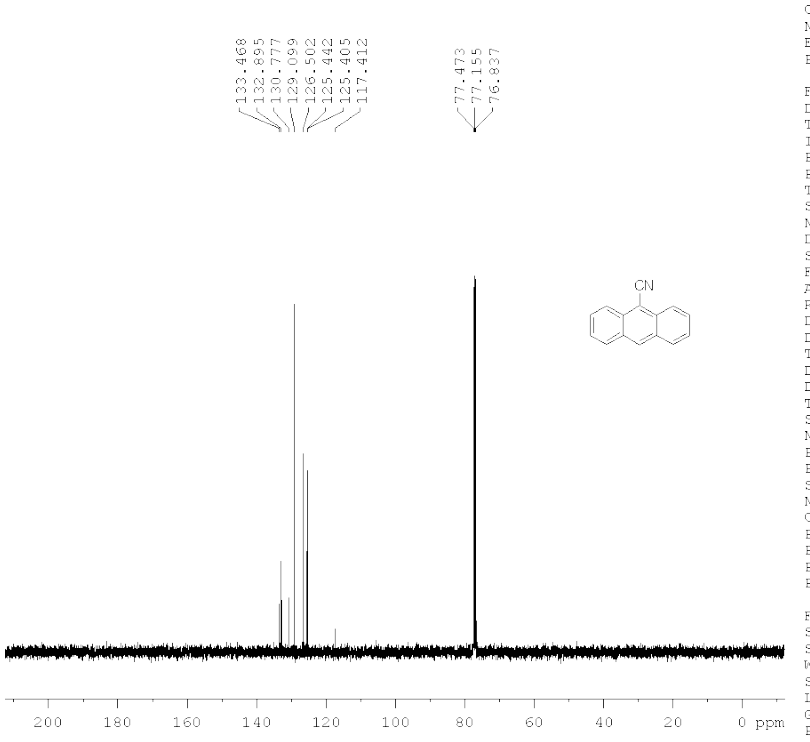
^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3s

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Current Data Parameters
NAME      MRD-II-9-anthracene
EXPNO                      72
PROCNO                      1

F2 - Acquisition Parameters
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Time                  18.24 h
INSTRUM               spect
PROBHD    Z129392_0001 (
PULPROG             zgpg30
TD                    16540
SOLVENT               CDCl3
NS                      256
DS                        4
SWH               24038.461 Hz
FIDRES             2.906706 Hz
AQ                0.3440320 sec
RG                   200.34
DW                   20.800 usec
DE                    6.50 usec
TE                   298.0 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                       1
SFO1           100.6228289 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           47.00000000 W
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2                90.00 usec
PLW2           10.50000000 W
PLW12           0.29166999 W
PLW13           0.14670999 W

F2 - Processing parameters
SI                    32768
SF             100.6127562 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
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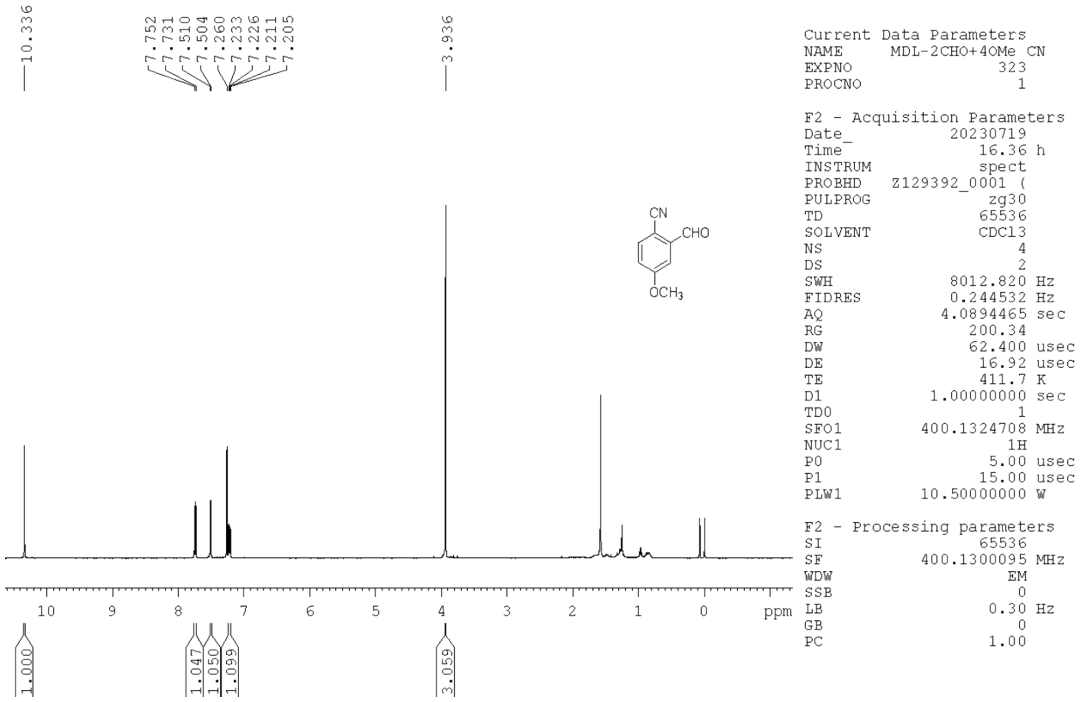
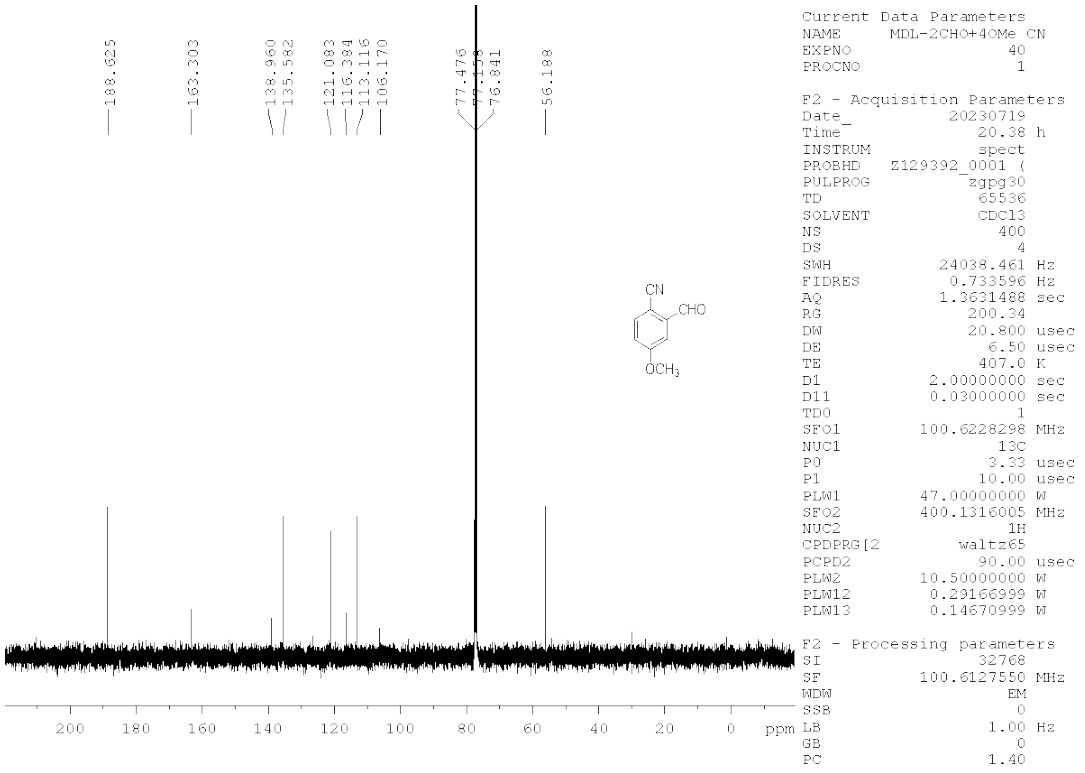
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3s

2-formyl-4-methoxybenzonitrile (3t)

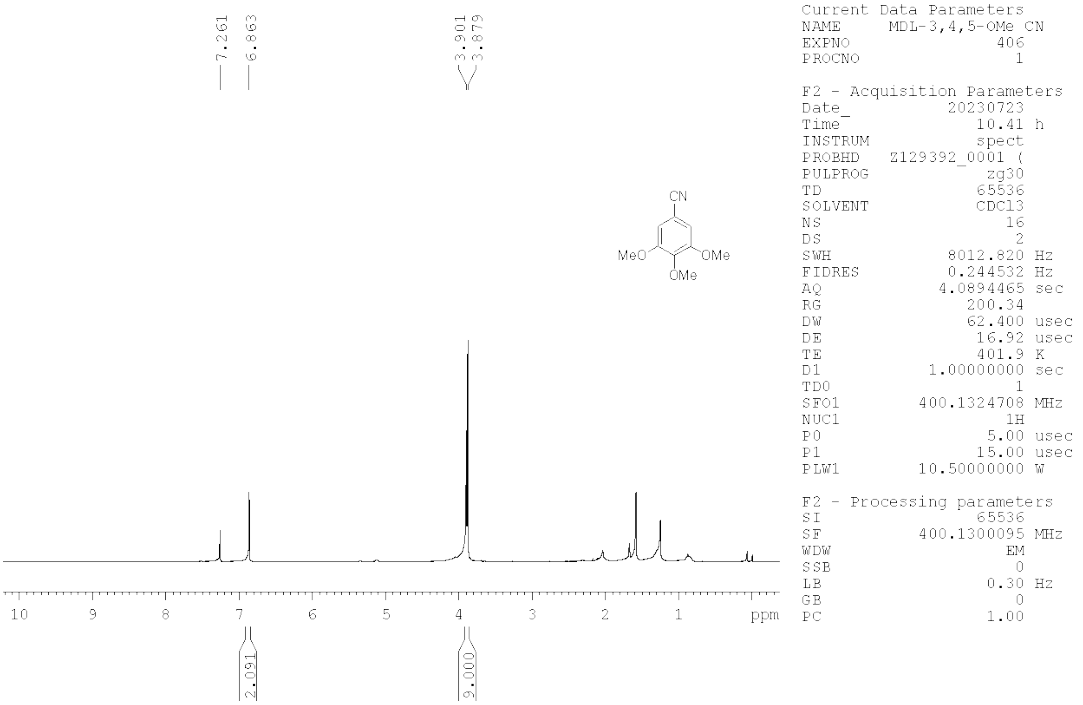


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3t

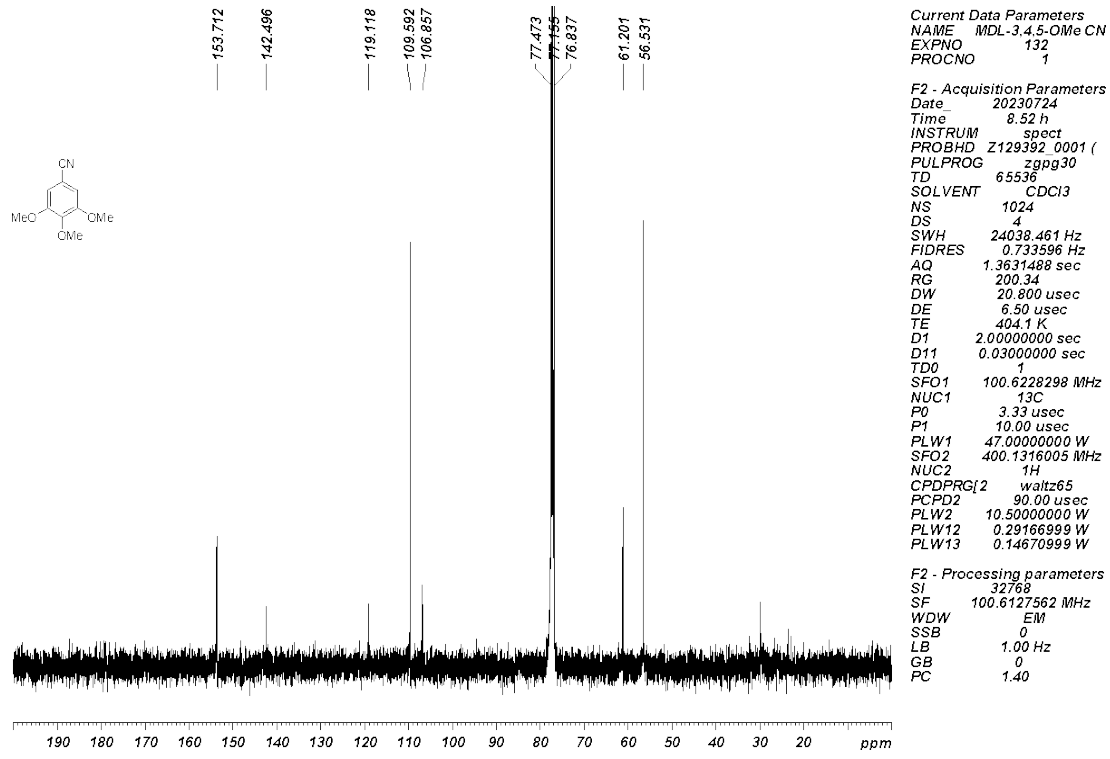


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3t

3,4,5-trimethoxybenzonitrile (3u)

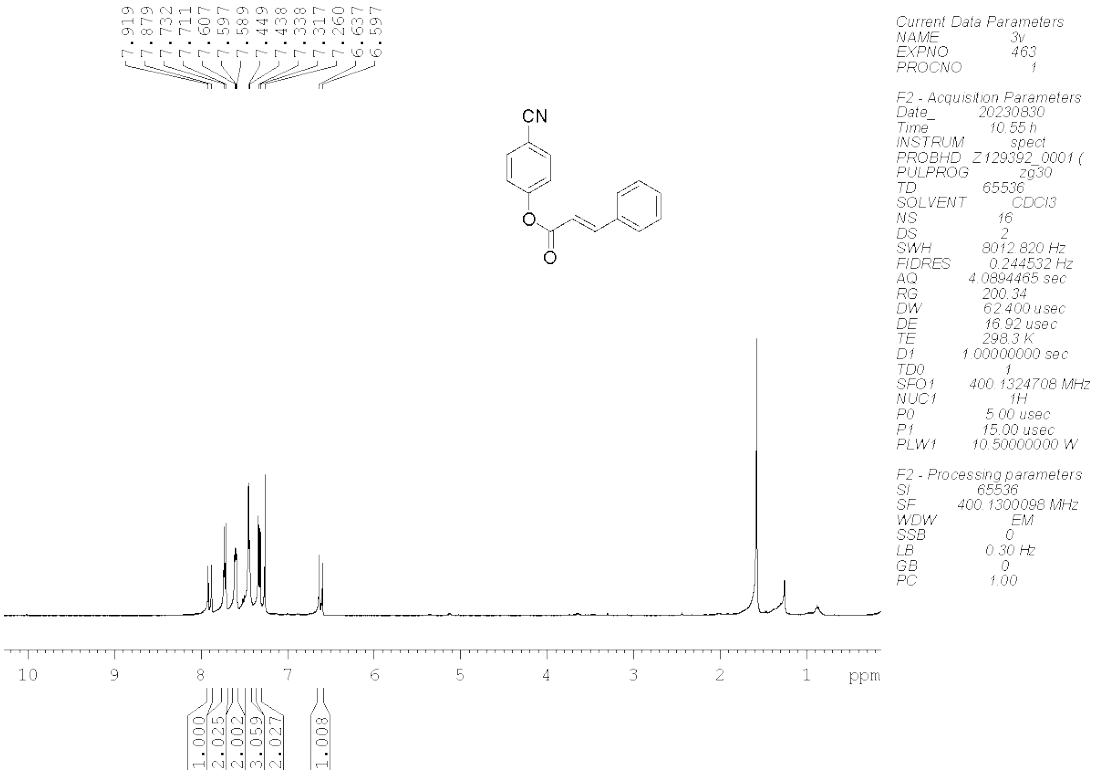


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3u

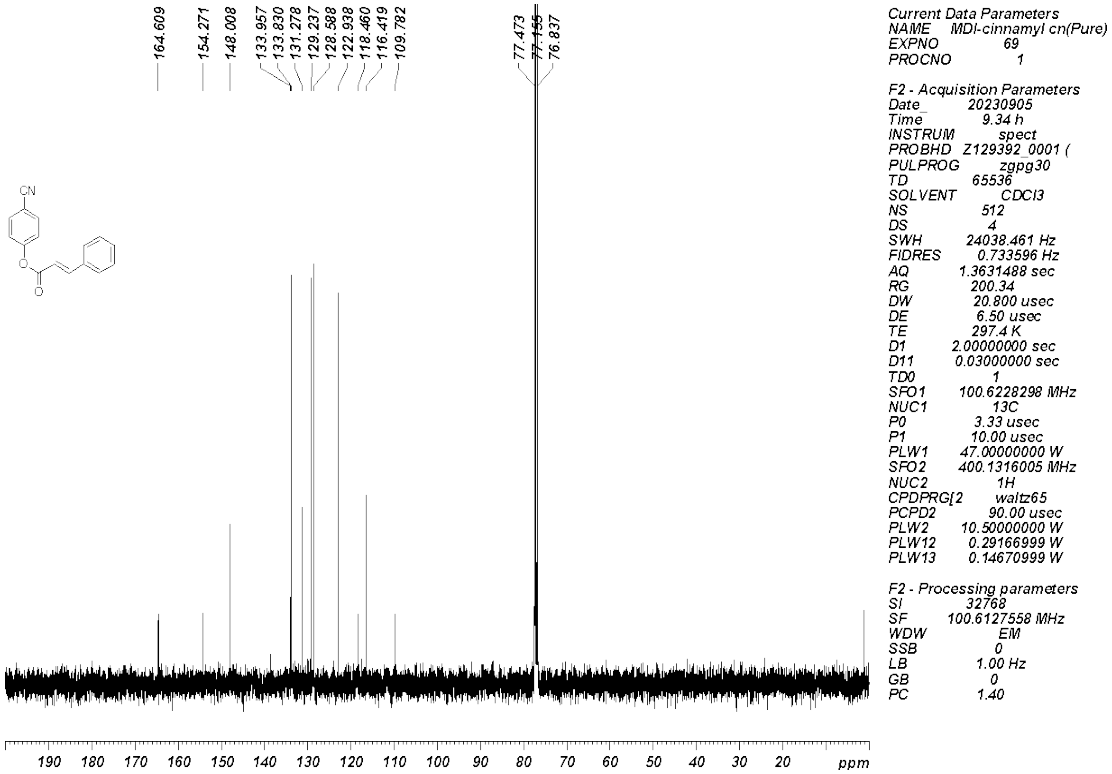


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3u

4-cyanophenyl cinnamate (3v)

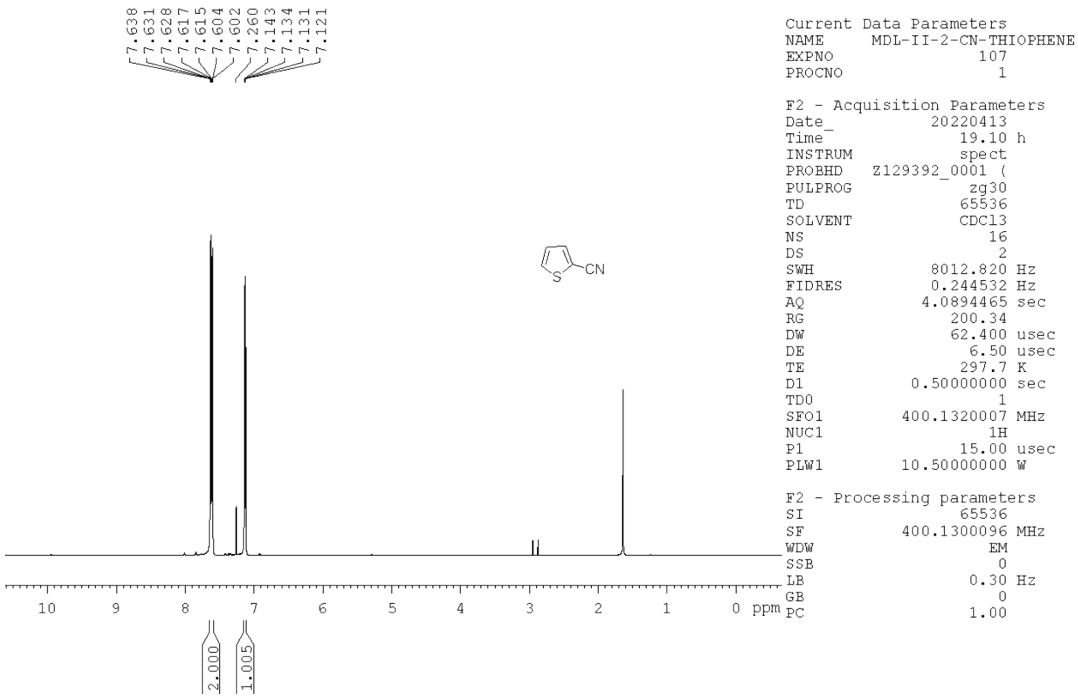


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3v

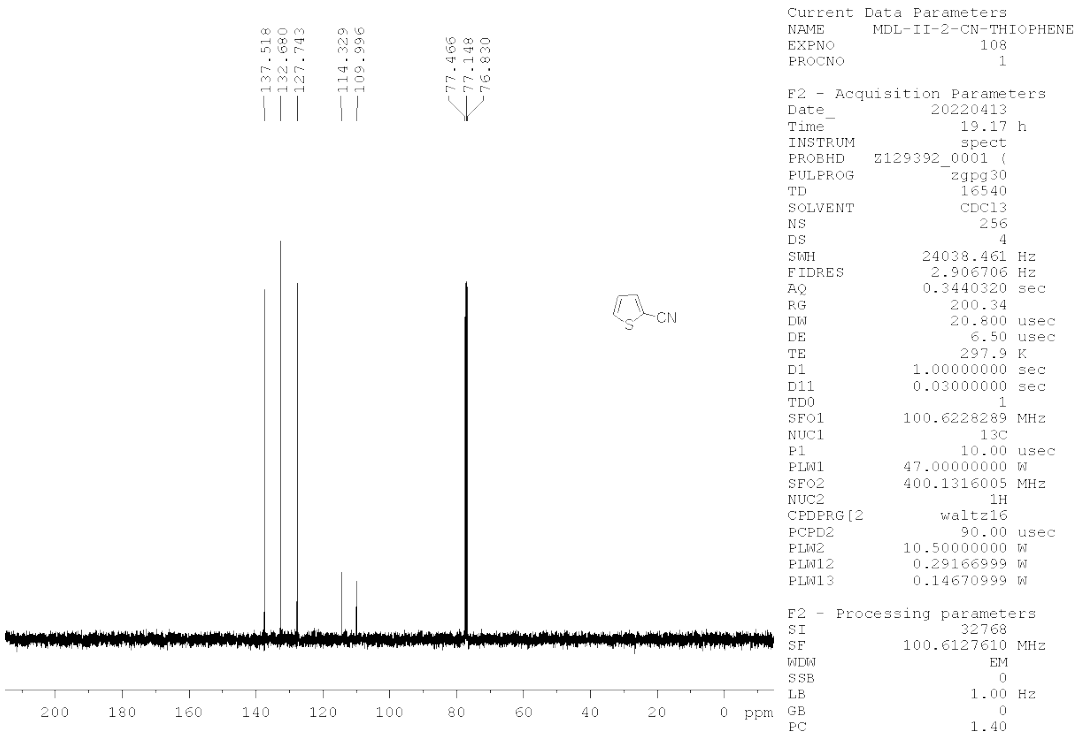


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3v

Thiophene-2-carbonitrile (3w)

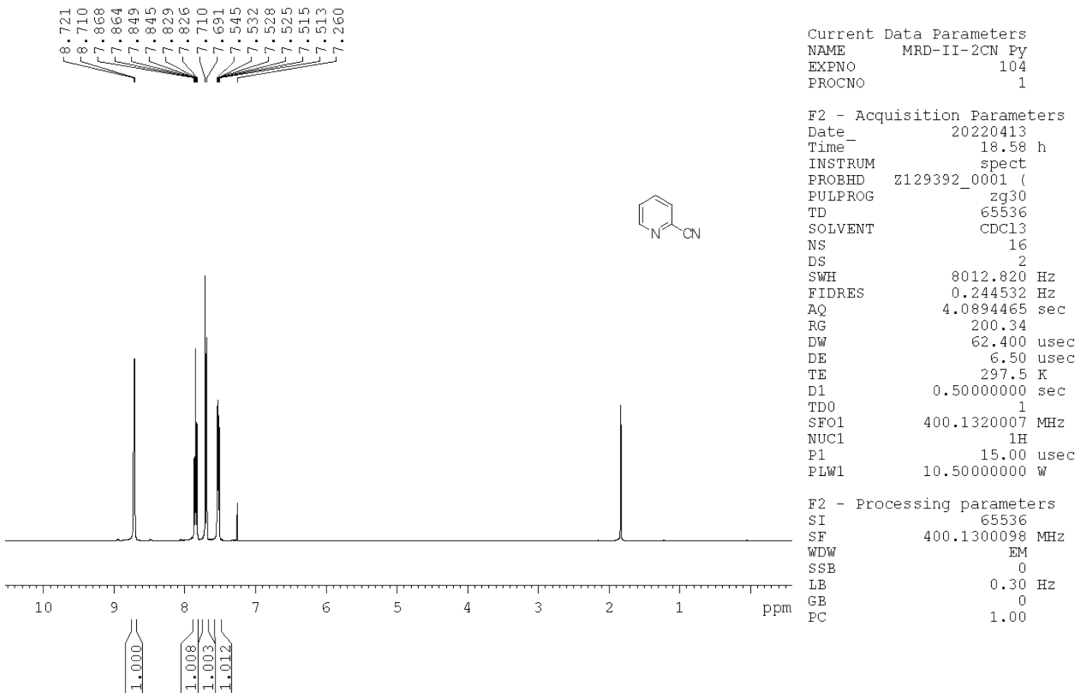


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3w

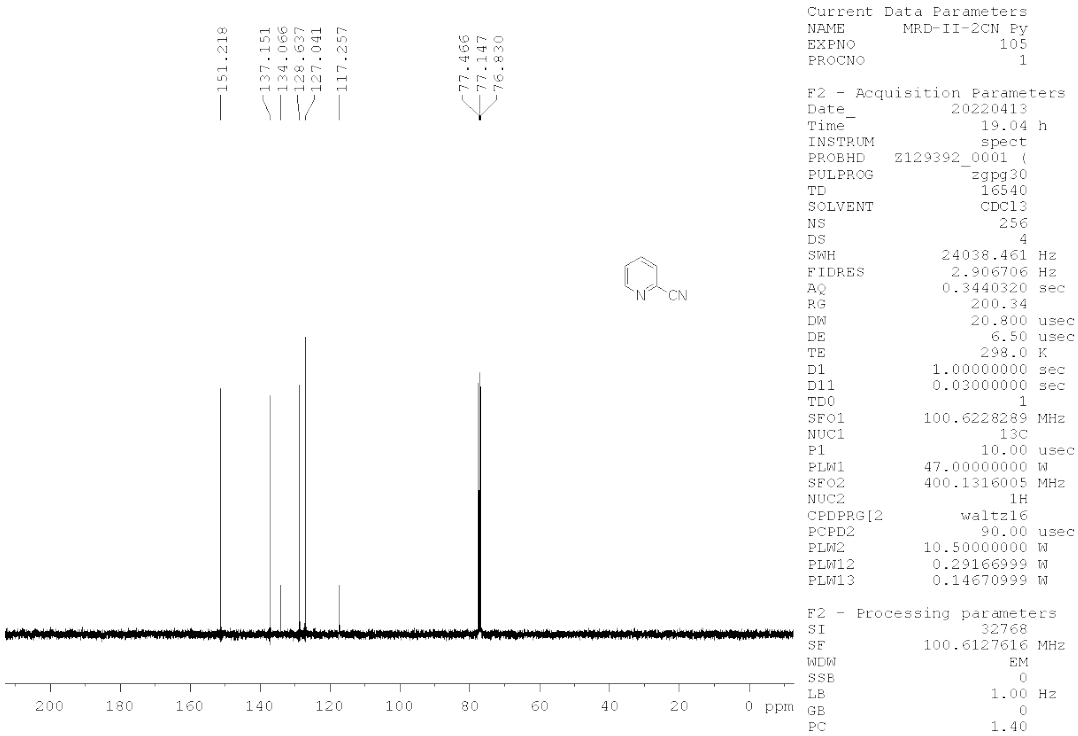


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3w

Picolinonitrile (3x)

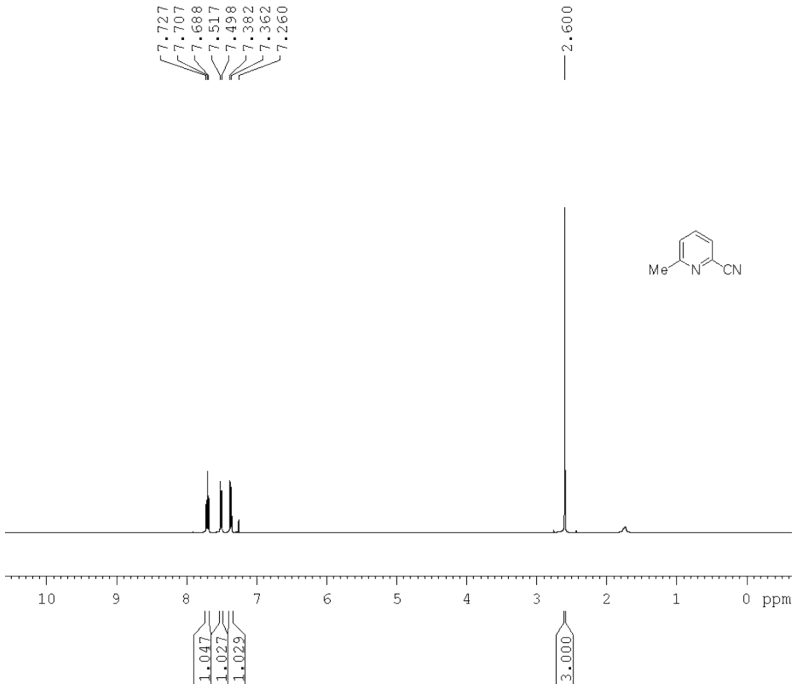


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3x



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3x

6-methylpicolinonitrile (3y)

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Current Data Parameters
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EXPNO                   95
PROCNO                   1

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Time              18.19 h
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PROBHD   Z129392_0001 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ              4.0894465 sec
RG                200.34
DW                62.400 usec
DE                 6.50 usec
TE                297.4 K
D1             0.50000000 sec
TD0                    1
SFO1         400.1320007 MHz
NUC1                  1H
P1                15.00 usec
PLW1         10.50000000 W

F2 - Processing parameters
SI                 65536
SF          400.1300095 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
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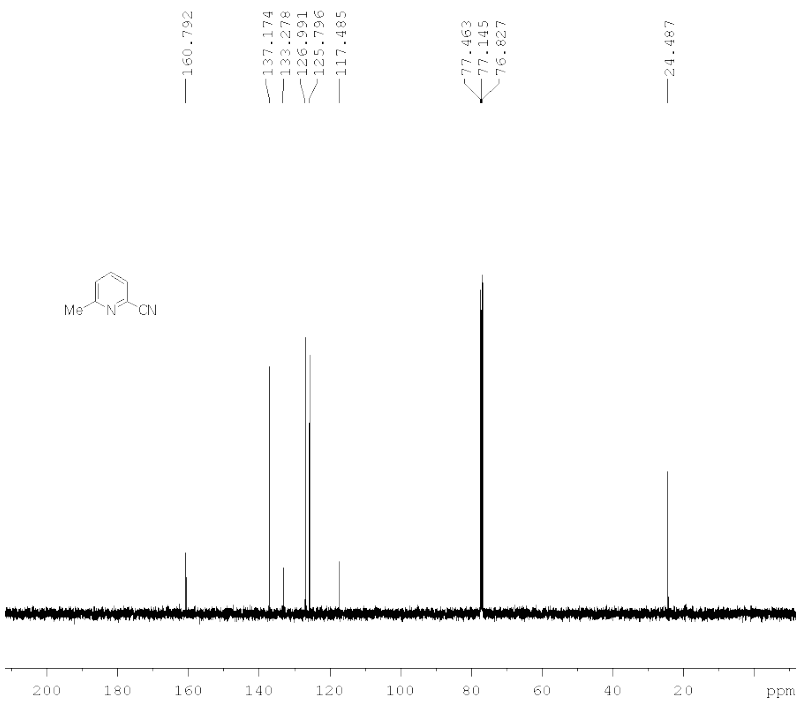
^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3y

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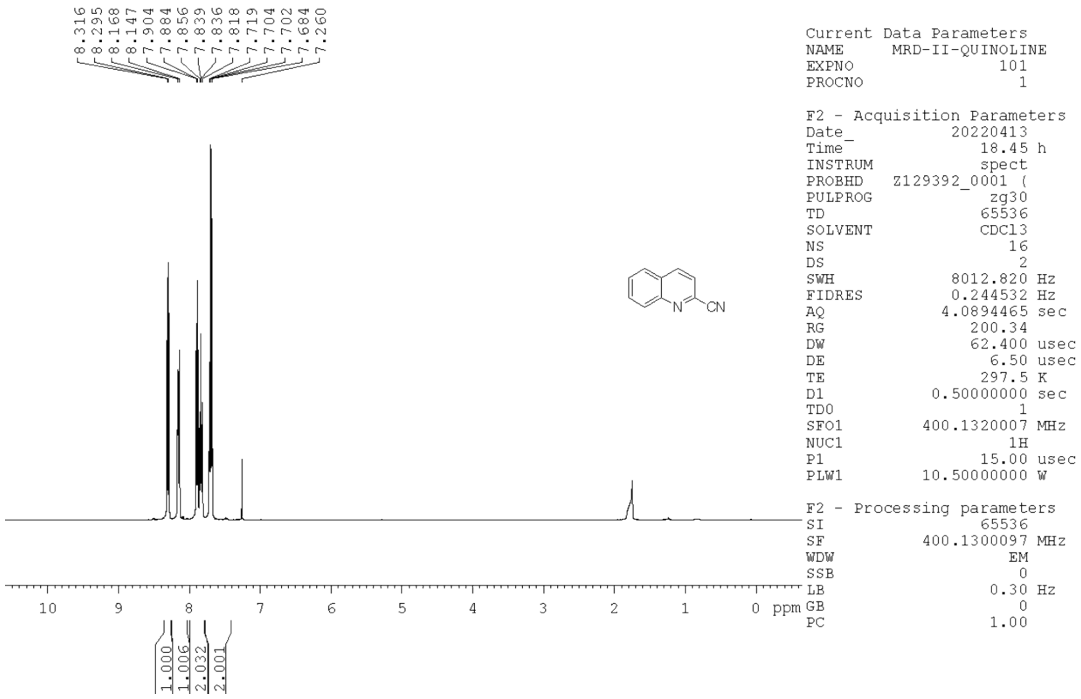
Current Data Parameters
NAME      MRD-II-6-Me 2-CN Py
EXPNO                   96
PROCNO                   1

F2 - Acquisition Parameters
Date_           20220413
Time              18.26 h
INSTRUM             spect
PROBHD   Z129392_0001 (
PULPROG           zgpg30
TD                 16540
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            24038.461 Hz
FIDRES          2.906706 Hz
AQ              0.3440320 sec
RG                200.34
DW                20.800 usec
DE                 6.50 usec
TE                297.9 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1         100.6228289 MHz
NUC1                 13C
P1                10.00 usec
PLW1         47.00000000 W
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2         10.50000000 W
PLW12         0.29166999 W
PLW13         0.14670999 W

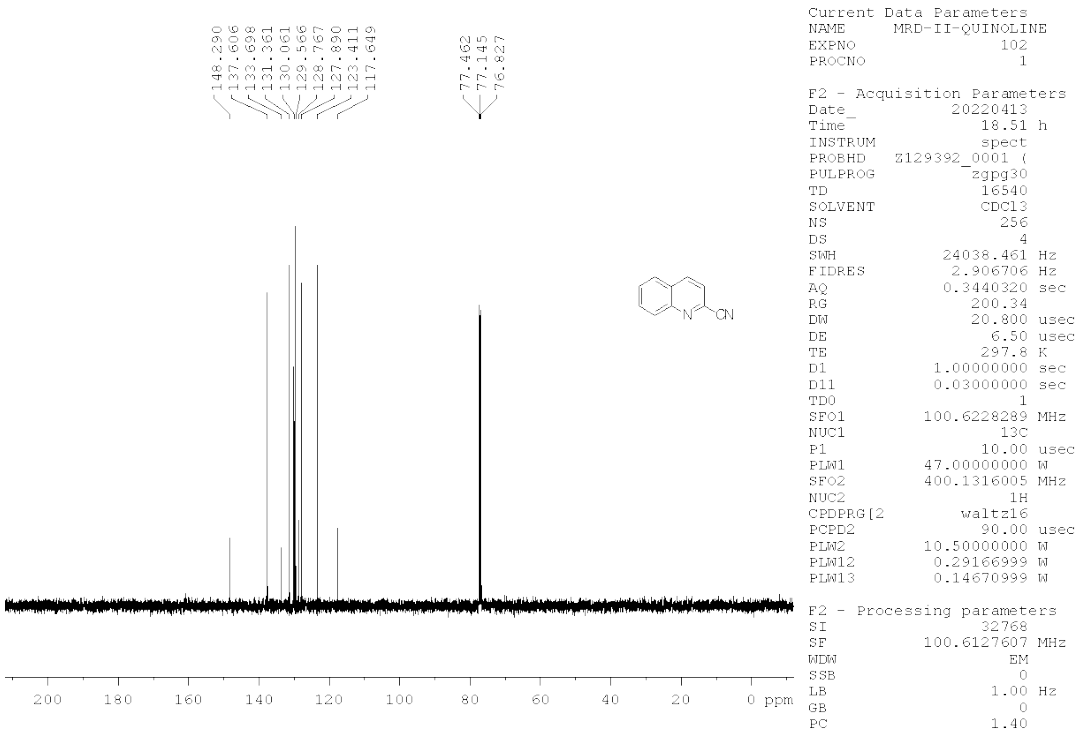
F2 - Processing parameters
SI                 32768
SF          100.6127594 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3y

Quinoline-2-carbonitrile (3z)

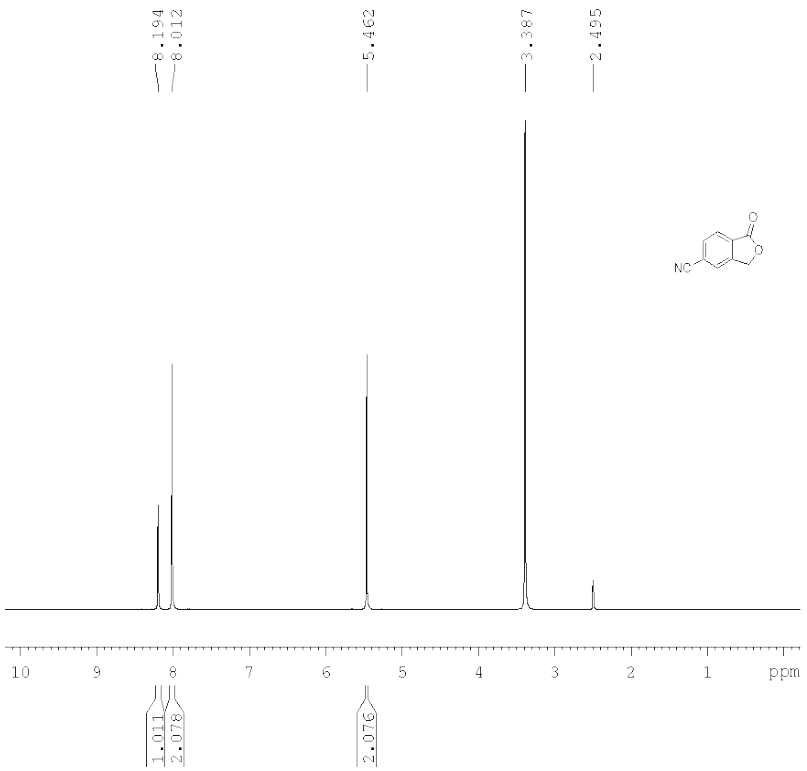


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3z



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3z

1-oxo-1,3-dihydroisobenzofuran-5-carbonitrile (3aa)

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Current Data Parameters
NAME      MDL-II-PHTHALIDE
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
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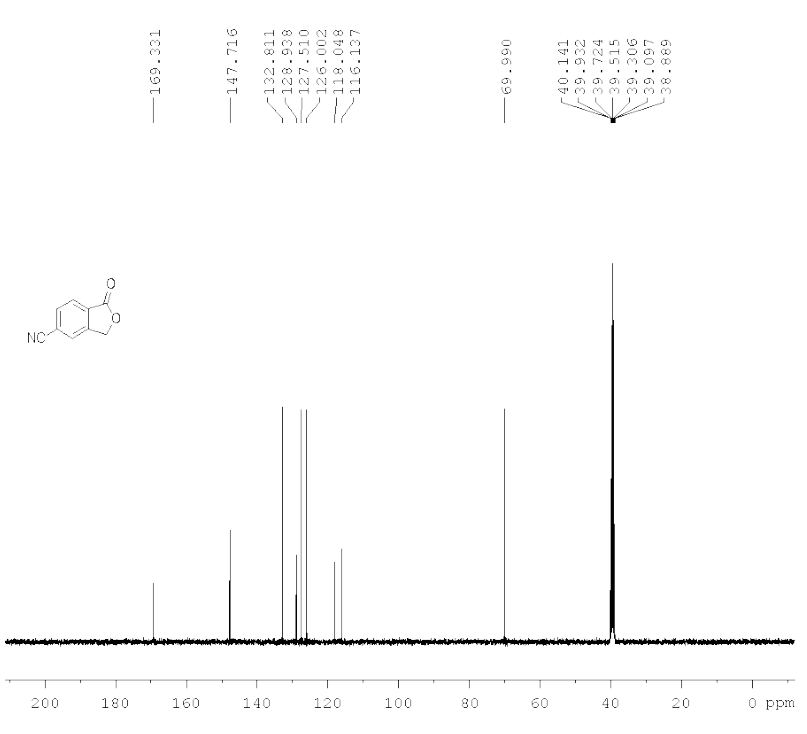
Time                17.30 h
INSTRUM              spect
PROBHD   Z129392_0001 (
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH               8012.820 Hz
FIDRES               0.244532 Hz
AQ                4.0894465 sec
RG                   124.58
DW                   62.400 usec
DE                    6.50 usec
TE                   297.1 K
D1              0.50000000 sec
TD0                     1
SFO1           400.1320007 MHz
NUC1                   1H
P1                   15.00 usec
PLW1           10.50000000 W

F2 - Processing parameters
SI                  65536
SF             400.1300049 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR (400 MHz, DMSO, 24 °C) of compound 3aa

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Current Data Parameters
NAME      MDL-II-PHTHALIDE
EXPNO                   12
PROCNO                   1

F2 - Acquisition Parameters
Date_            20230101
Time                17.42 h
INSTRUM              spect
PROBHD   Z129392_0001 (
PULPROG            zgpg30
TD                  16540
SOLVENT              DMSO
NS                    512
DS                      4
SWH              24038.461 Hz
FIDRES               2.906706 Hz
AQ                0.3440320 sec
RG                   200.34
DW                   20.800 usec
DE                    6.50 usec
TE                   297.5 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                     1
SFO1           100.6228289 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           47.00000000 W
SFO2           400.1316005 MHz
NUC2                   1H
CPDPRG[2            waltz16
PCPD2                90.00 usec
PLW2           10.50000000 W
PLW12           0.29166999 W
PLW13           0.14670999 W

F2 - Processing parameters
SI                  32768
SF             100.6128100 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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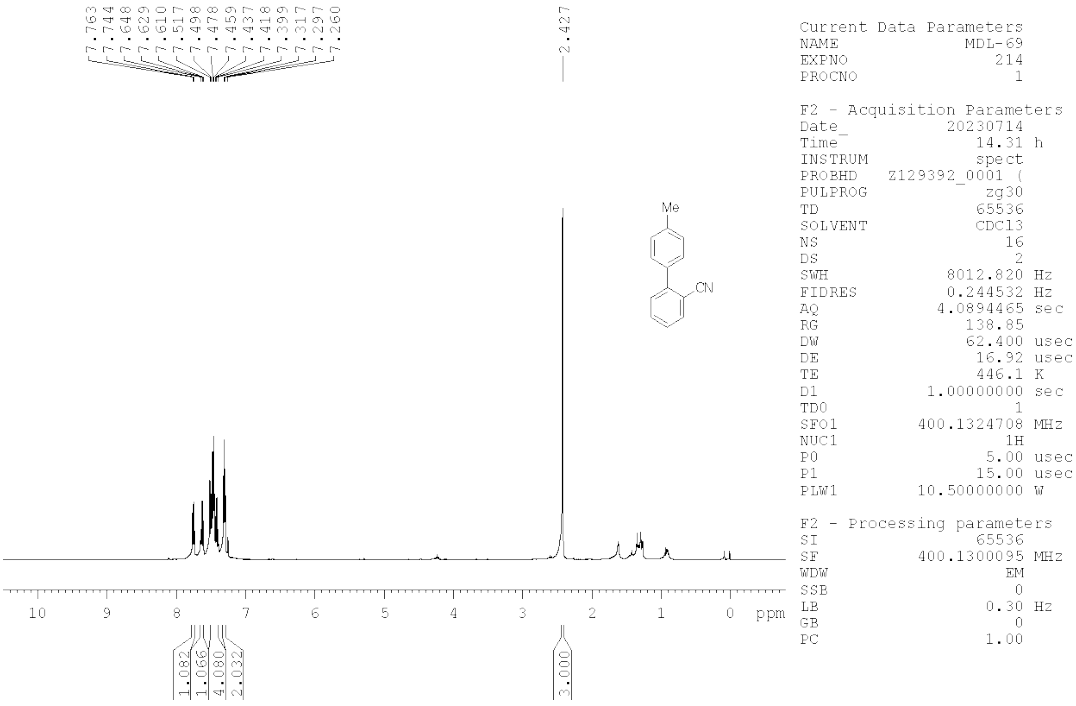
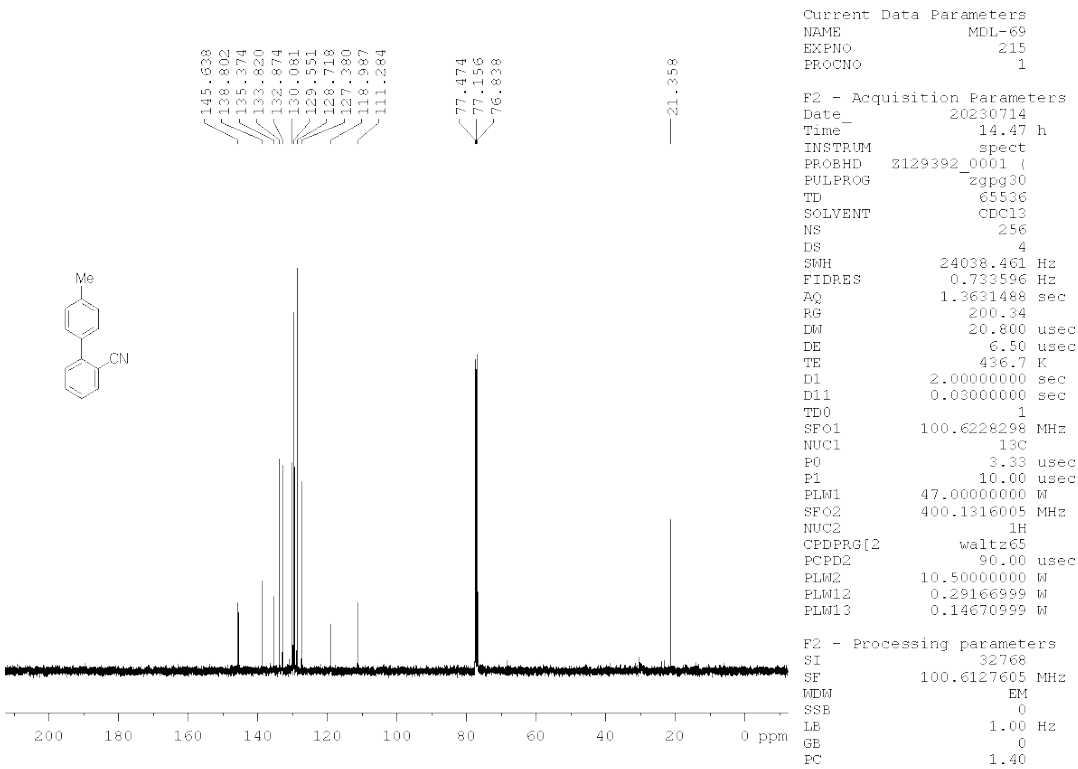
^{13}C{^{1}H} NMR (100 MHz, DMSO, 24 °C) of compound 3aa

4'-methyl-[1,1'-biphenyl]-2-carbonitrile(3ab)

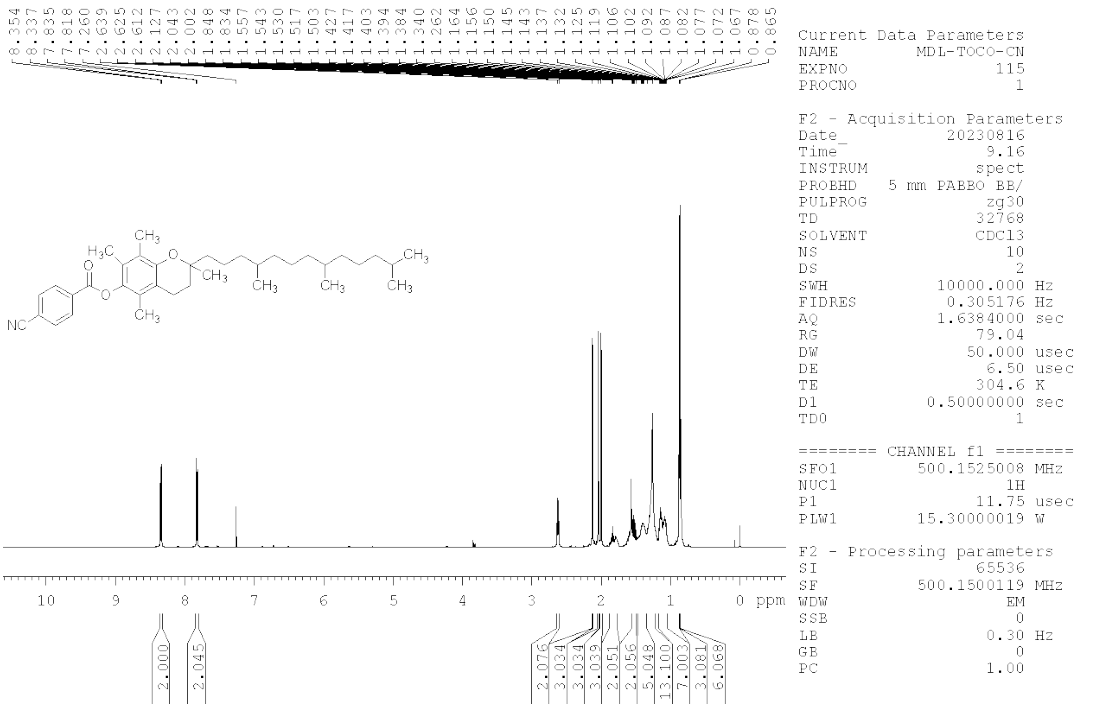


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3ab

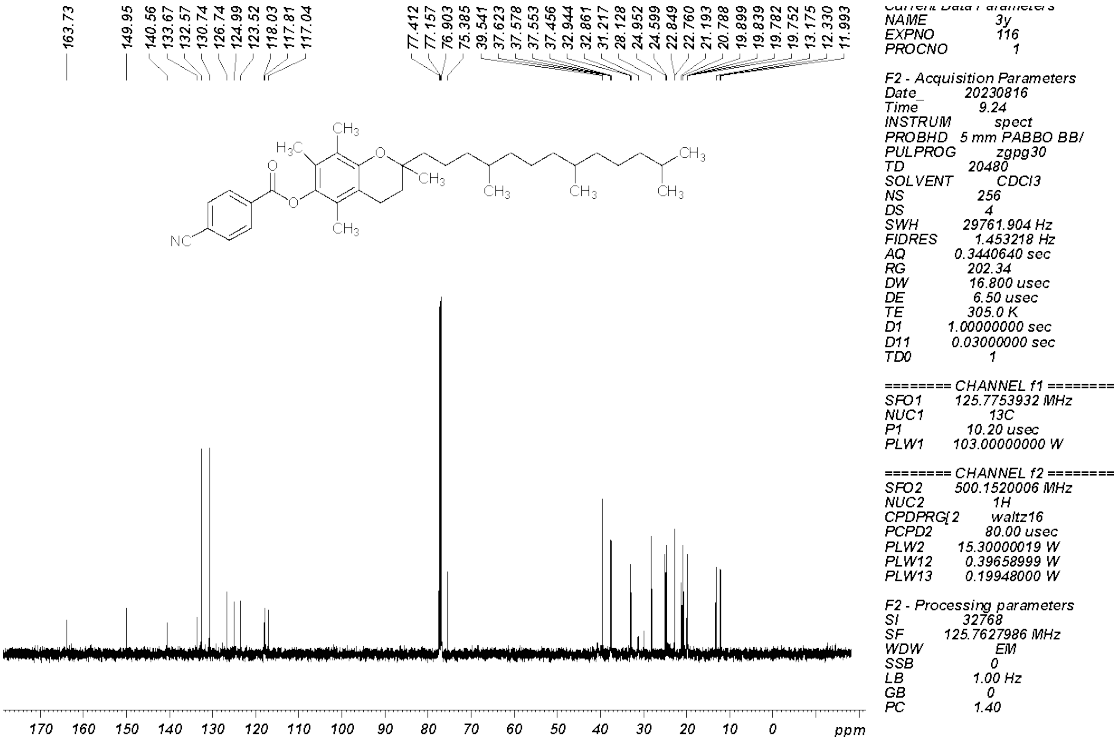


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3ab

2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-cyanobenzoate (3ac)

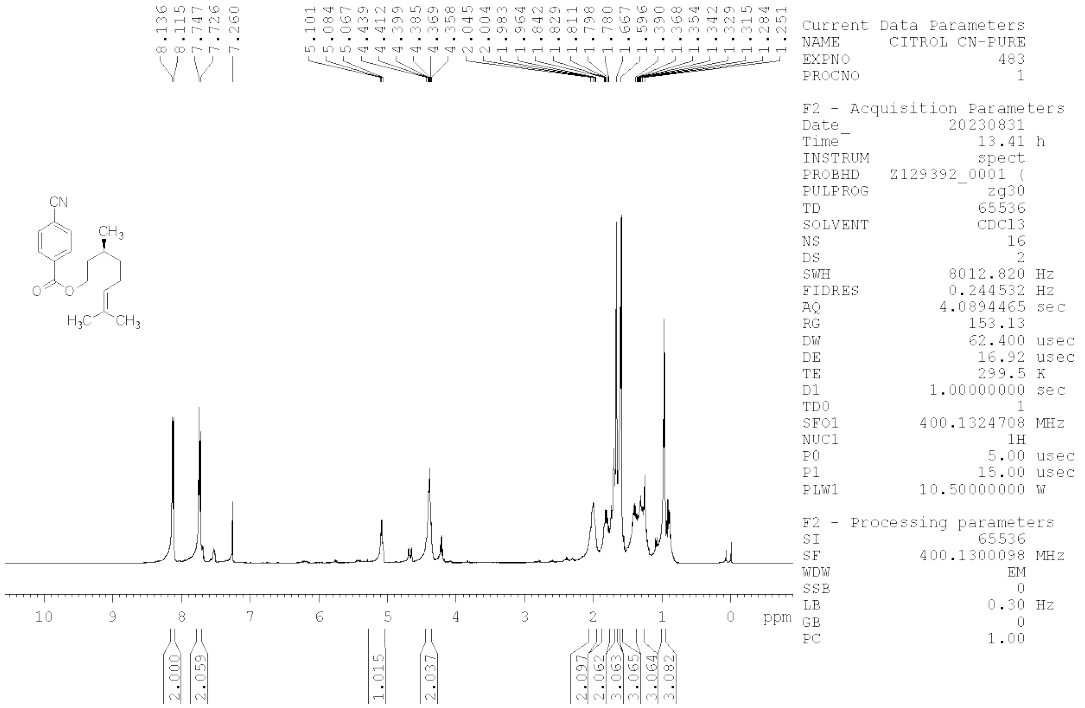


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3ac

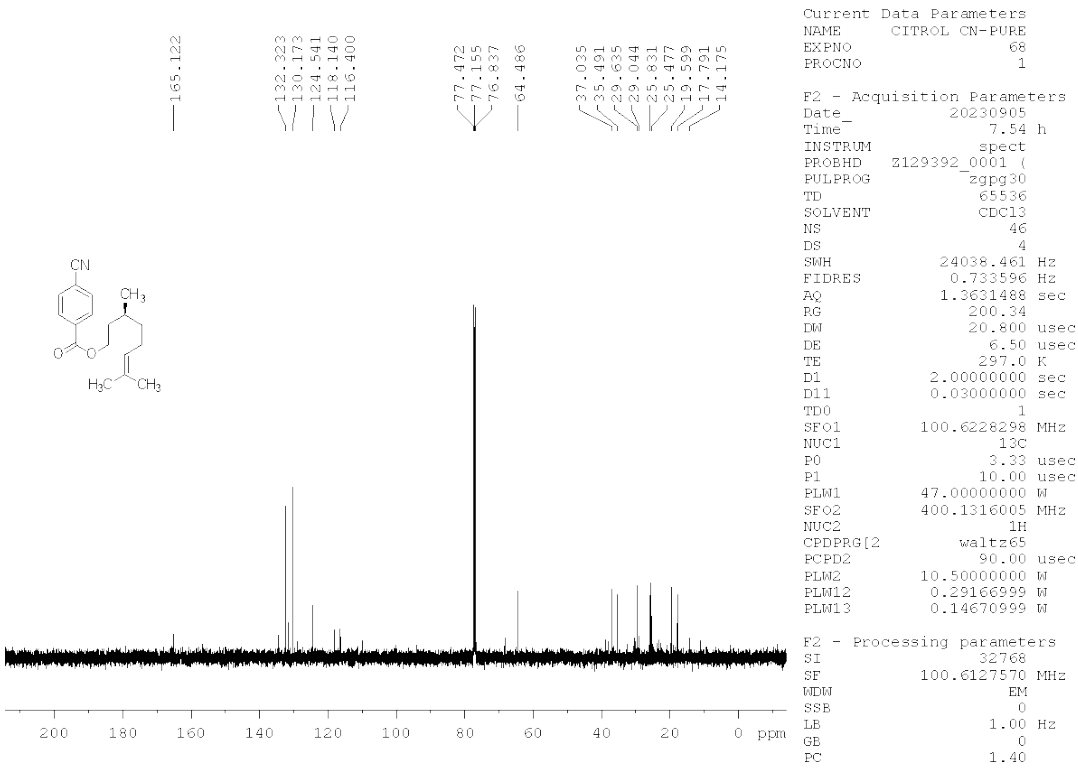


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3ac

(S)-3,7-dimethyloct-6-en-1-yl 4-cyanobenzoate (3ad)

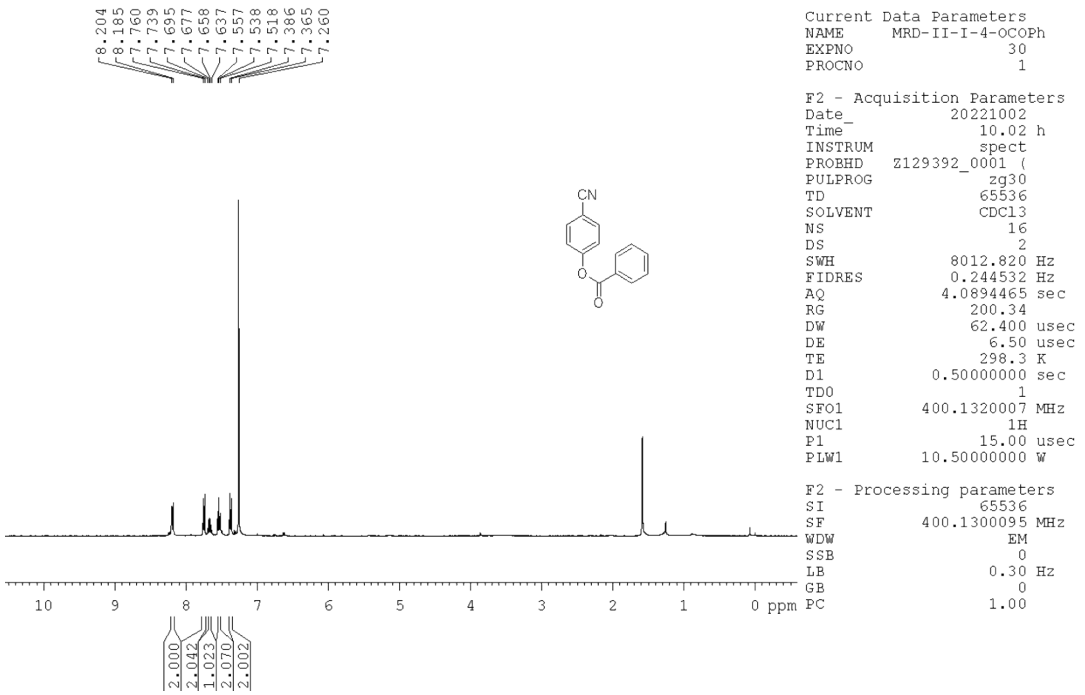


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3ad

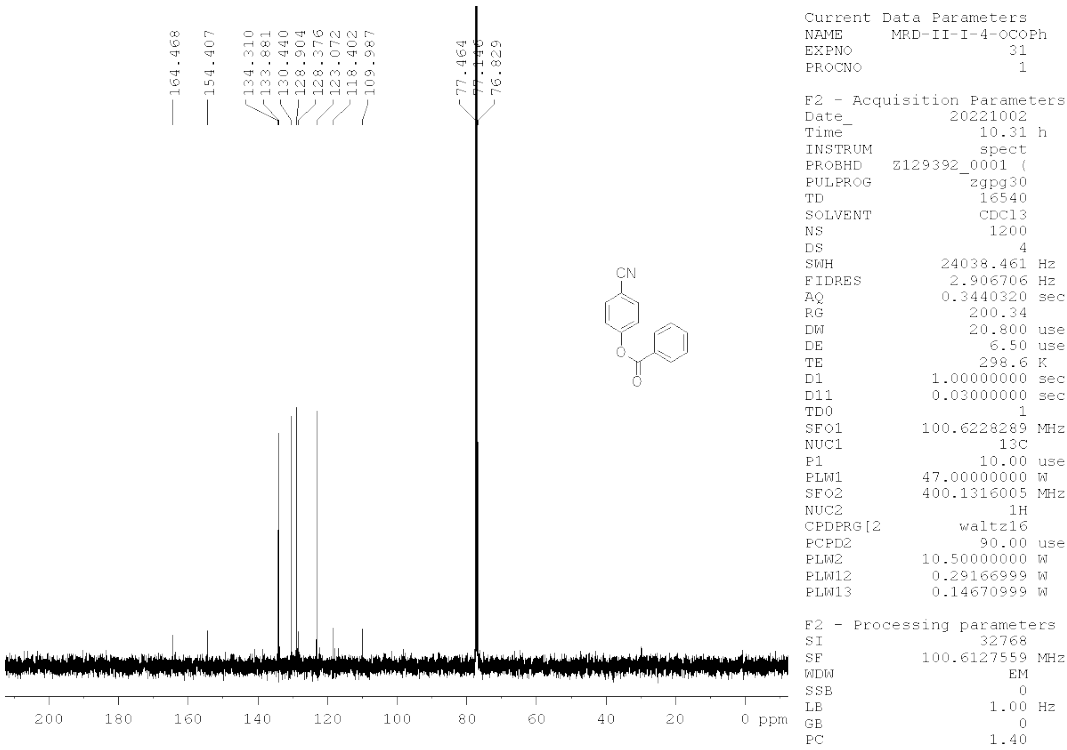


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3ad

4-cyanophenyl benzoate (3ae)

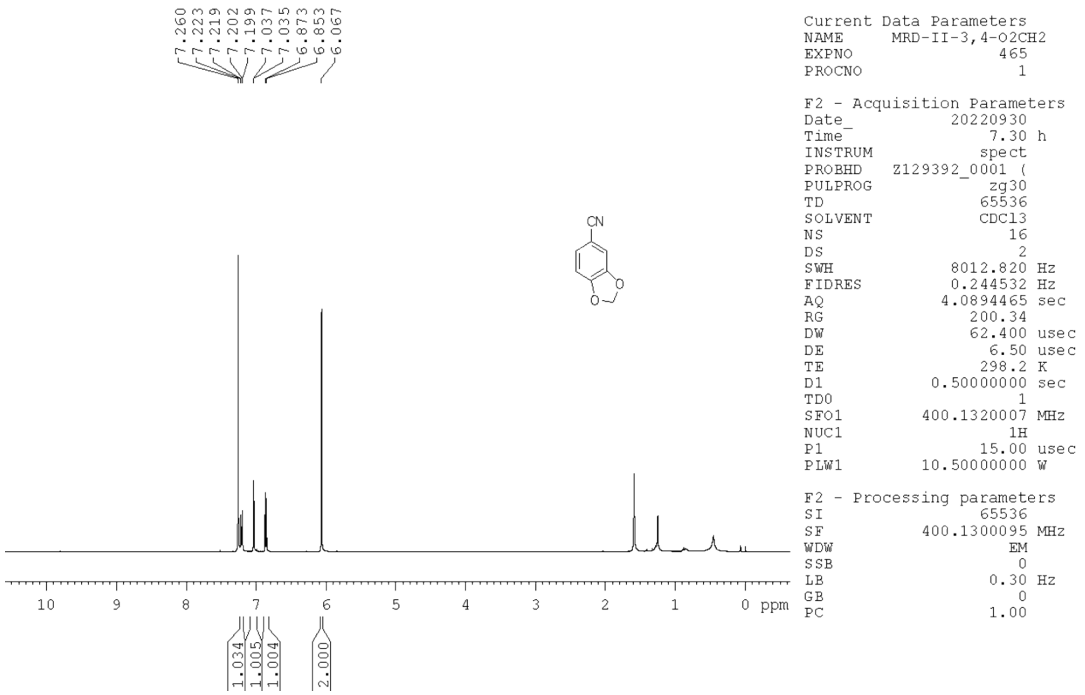


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3ae

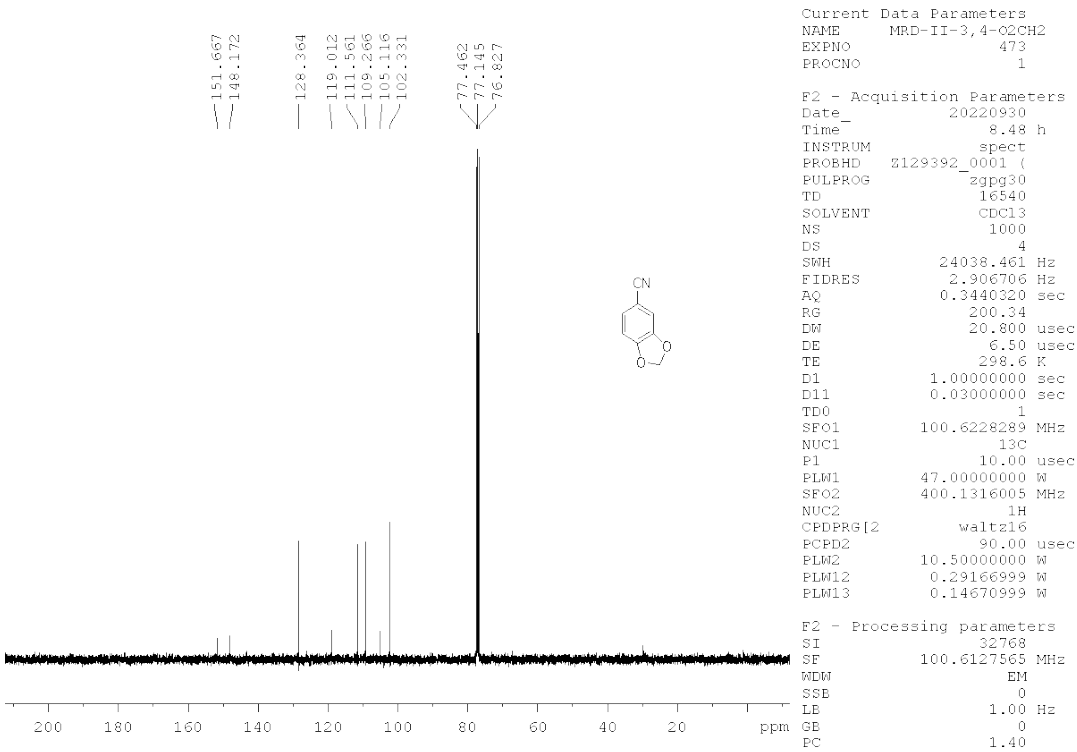


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3ae

Benzo[d][1,3]dioxole-5-carbonitrile (3af)

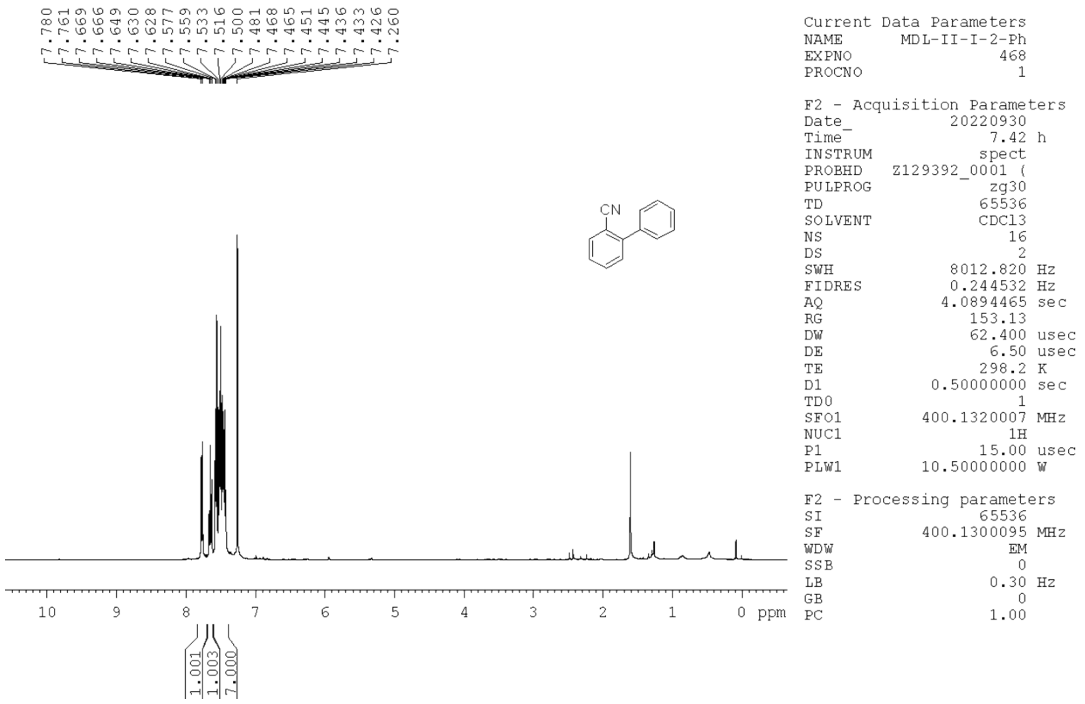


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3af

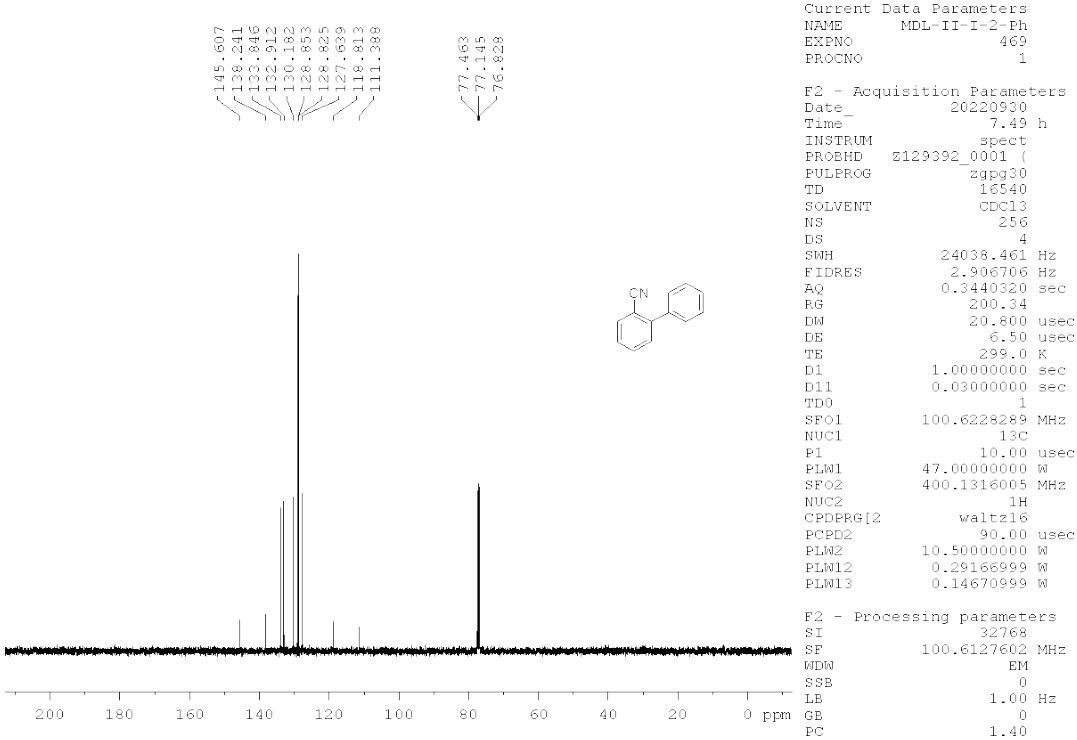


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3af

[1,1'-biphenyl]-2-carbonitrile (3ag)

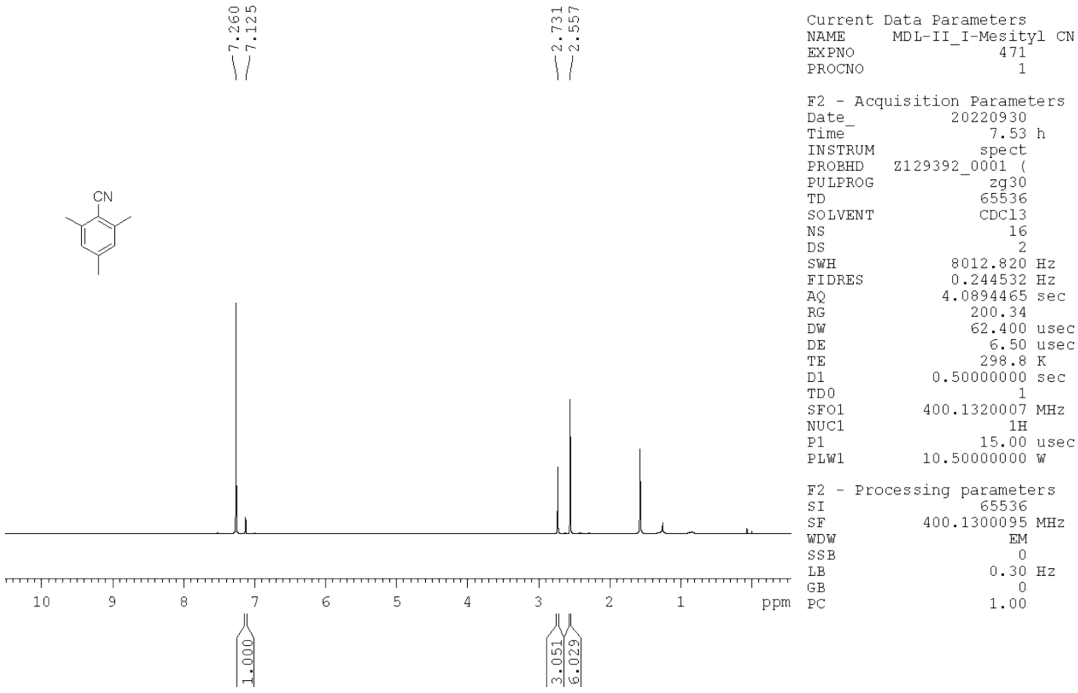


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3ag

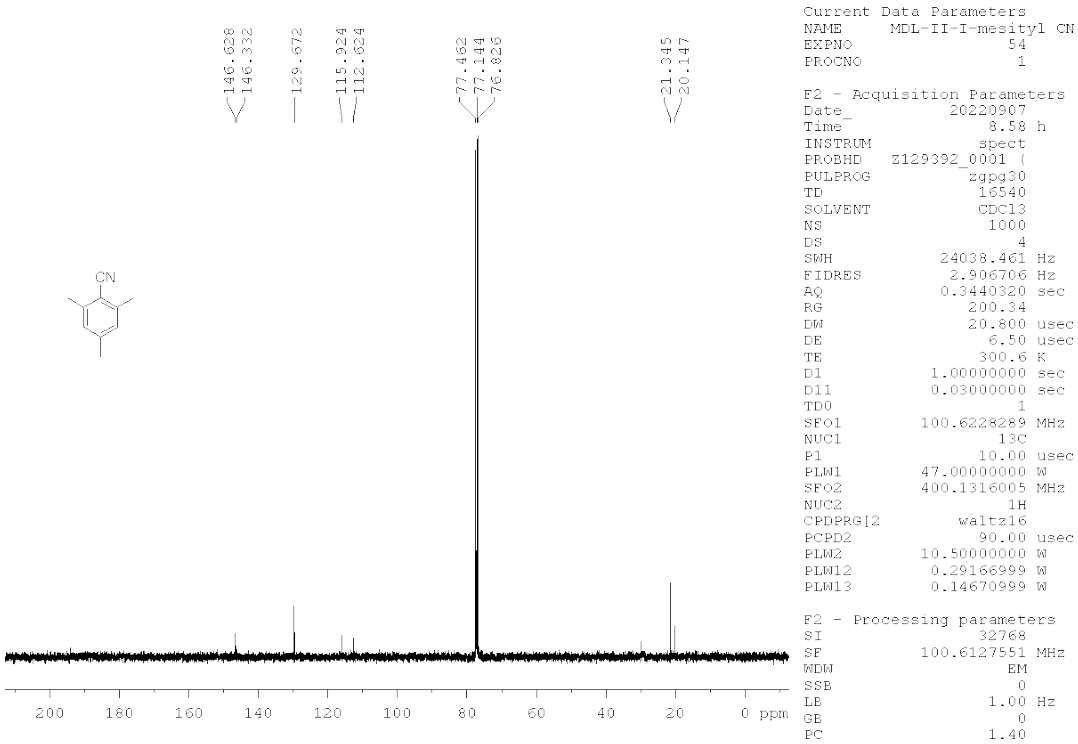


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3ag

2,4,6-trimethylbenzonitrile (3ah)

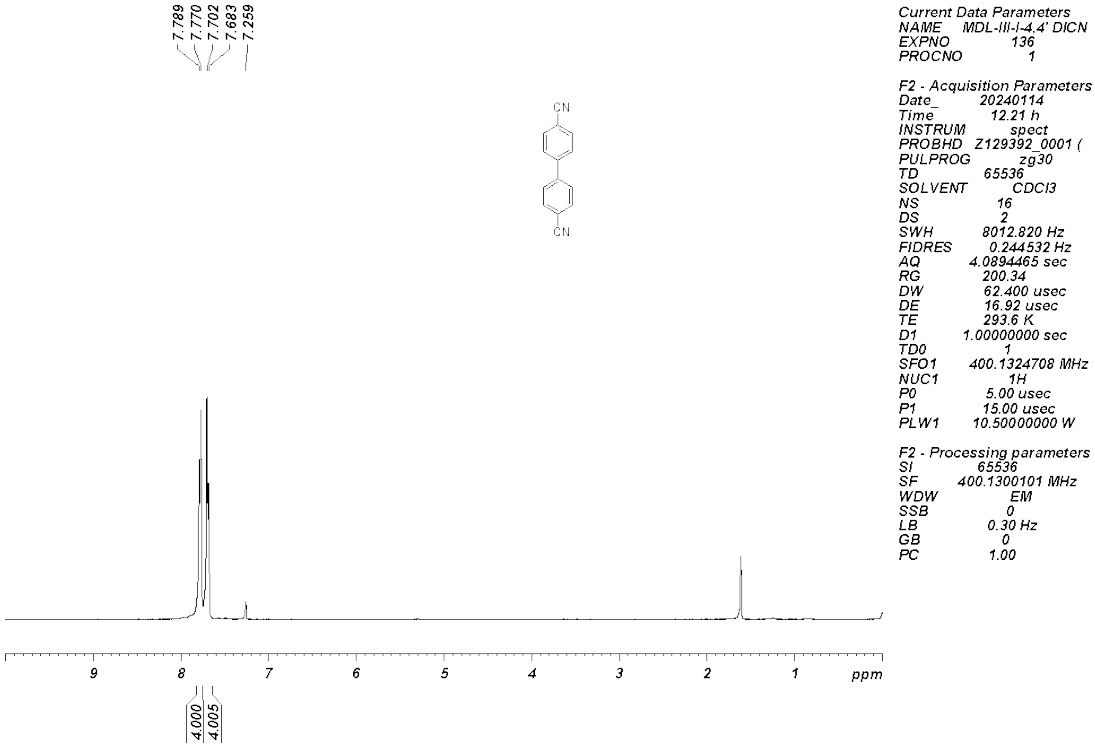


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3ah

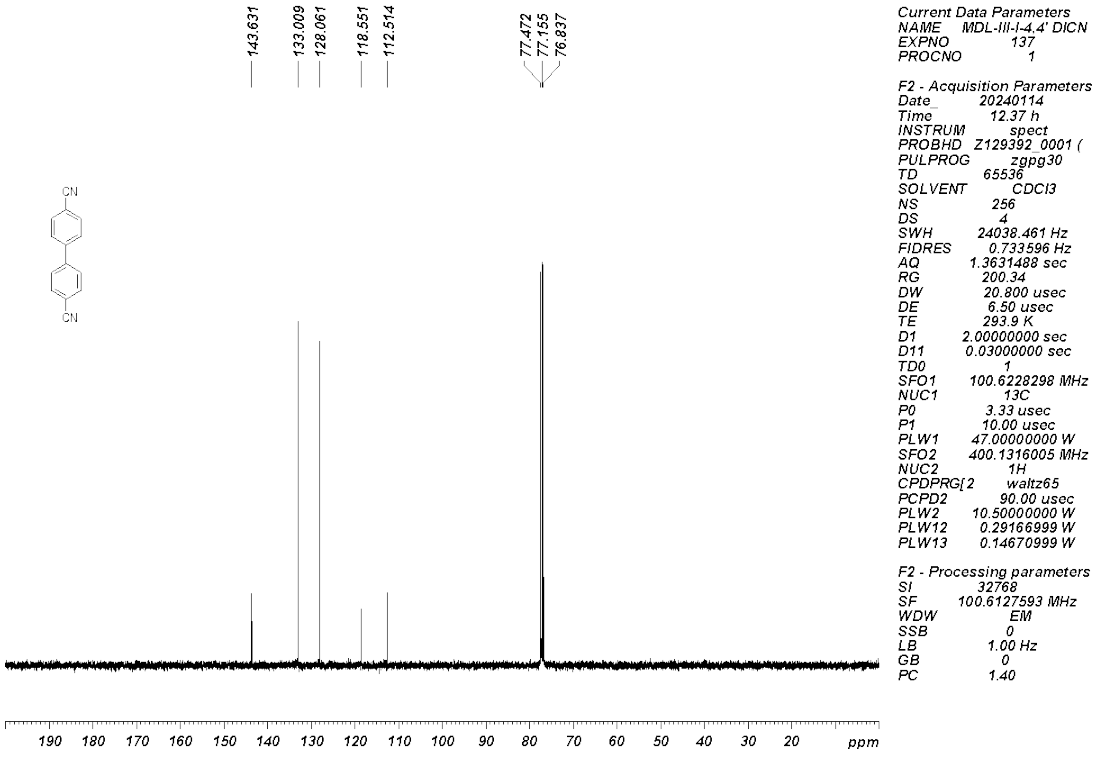


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3ah

[1,1'-biphenyl]-4,4'-dicarbonitrile(3ai)

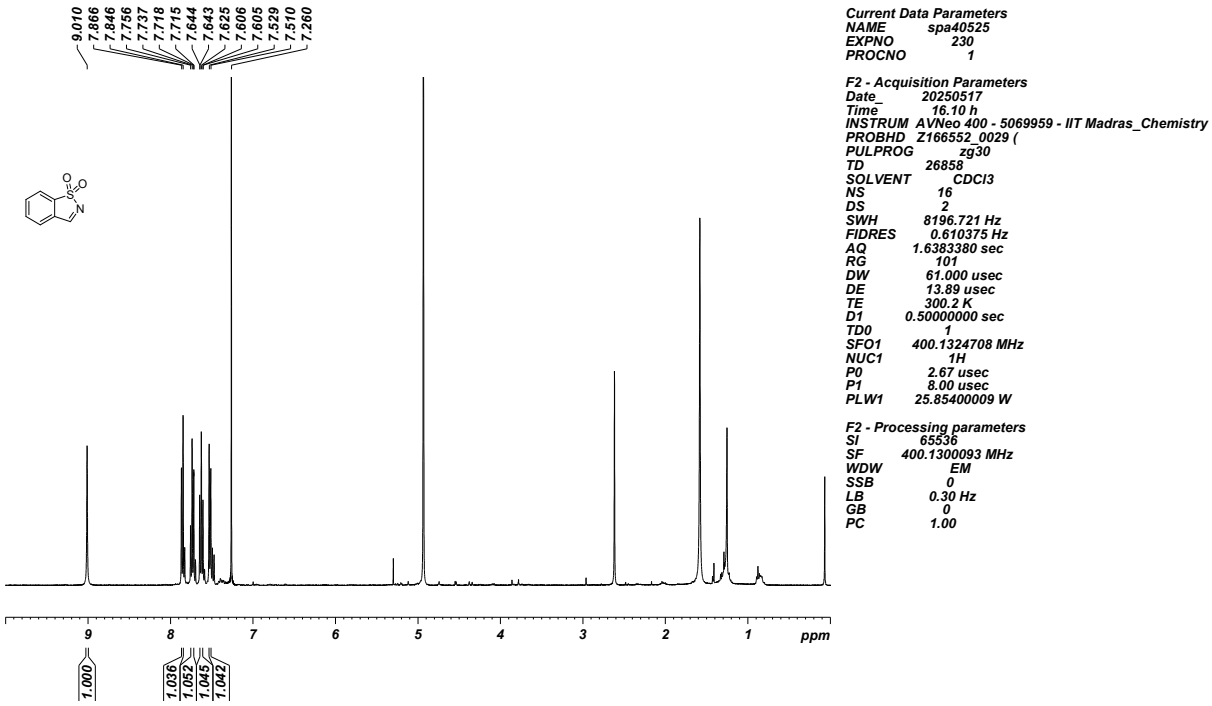


^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 3ai

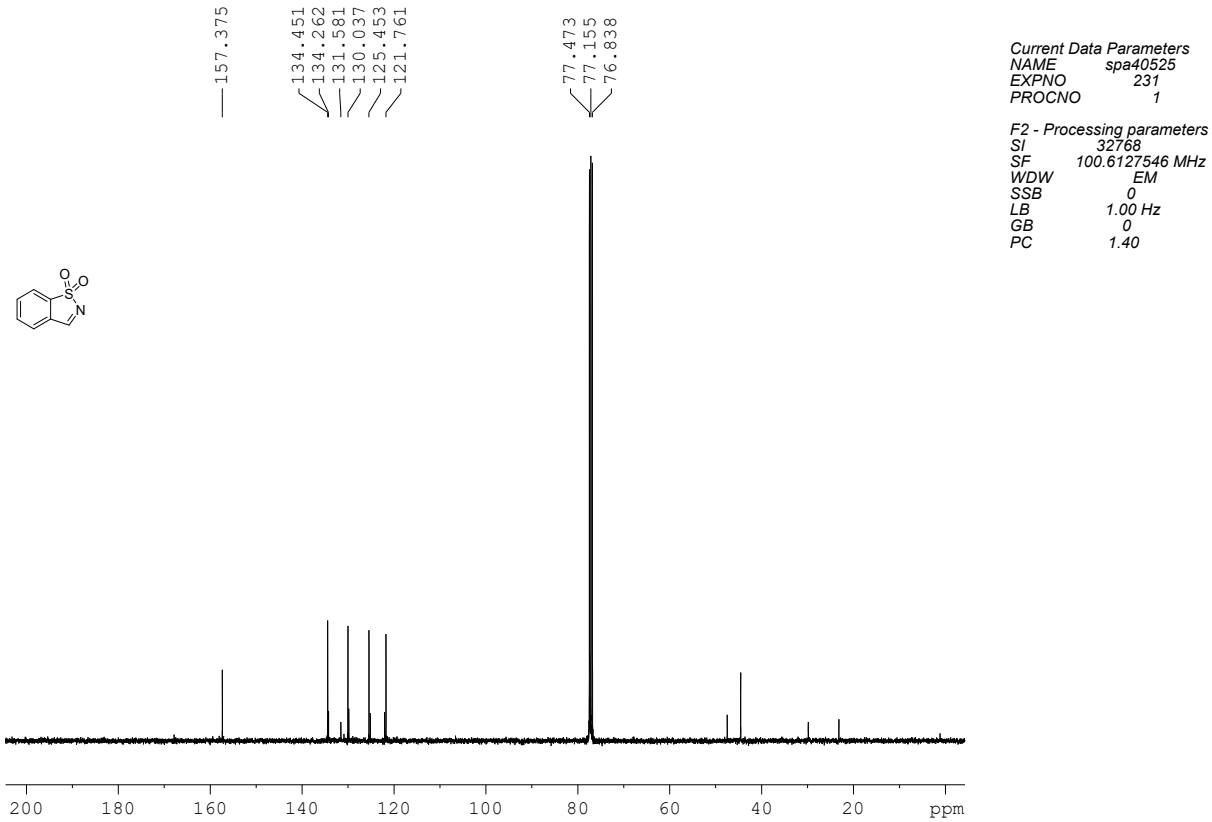


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 3ai

Benzo[d]isothiazole 1,1-dioxide (4):



^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) of compound 4



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C) of compound 4

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