Electronic Supplementary Information (ESI)

Cu(0) onto sulfonic acid functionalized silica/carbon composites as bifunctional heterogeneous catalysts for the synthesis of polysubstituted pyridines and nitriles under benign reaction media

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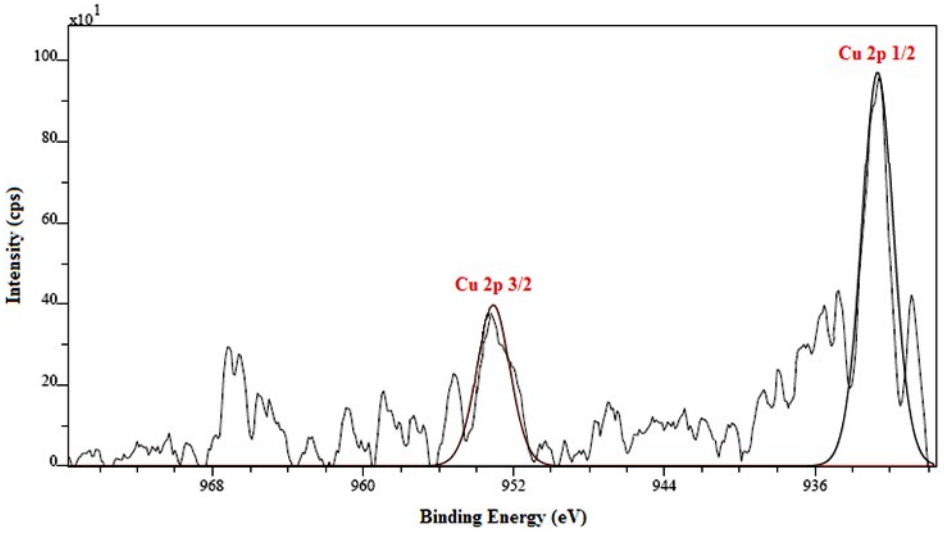


Fig. S1 XPS of the recovered Cu(0)-SilC_{cell}-SO_3H after 6th run.

Table S1 Comparison of the e-factor for the Cu(0)-SilC_{cell}-SO_3H catalyzed synthesis of polysubstituted pyridines and nitriles with reported protocols in the literature

Entry	Catalyst	E-factor (kg waste/kg Product)[c]	Reference
Pyridines[a]	$FeCl_3$ (Homogeneous)	9.81	*J. Org. Chem.*, 2014, 79, 8882
	$SnCl_2.2H_2O$ (Homogeneous)	14.21	*Tetrahedron Lett.*, 2015, 46, 4586
	Cu(0)-SilC_{cell}-SO_3H (Heterogeneous)	**0.19**	*Present work*
Nitriles[b]	$Cu(OTf)_2$/Bipy (Homogeneous)	32.4	*Chem. Commun.*, 2013, 49, 6030
	Polymer-$PhI(OAc)_2$ (Heterogeneous)	26.4	*Synthesis*, 2010, 3121
	Cu(0)-SilC_{cell}-SO_3H (Heterogeneous)	**11**	*Present work*

[a]Reaction using benzaldehyde, malononitrile, ethyl acetoacetate and aniline as substrates.

[b]Reaction using benzaldehyde as substrate.

[c]Amount of recyclable catalysts are excluded from the calculation part as per R. A. Sheldon guidelines.

E-factor calculations

J. Org. Chem.*, 2014, 79, 8882** ***(Homogeneous catalyst)

E = 0.106 g (benzaldehyde) + 0.066 g (malanonitrle) + 0.130 g (ethylacetoacetate) + 0.09 g (aniline) + 0.08 g ($FeCl_3$) + 2.34 g (ethanol) – 0.26 g (product × yield)/0.26 g

= 9.81

Tetrahedron Lett.*, 2015, 46, 4586** ***(Homogeneous catalyst)

E = 0.106 g (benzaldehyde) + 0.066 g (malanonitrle) + 0.130 g (ethylacetoacetate) + 0.09 g (aniline) + 0.02 g ($SnCl_2.2H_2O$) + 4.0 g (water) – 0.29 g (product × yield)/0.29 g

= 14.21

Present work (Heterogeneous catalyst)

E = 0.106 g (benzaldehyde) + 0.066 g (malanonitrle) + 0.130 g (ethylacetoacetate) + 0.09 g (aniline) – 0.328 g (product × yield)/0.328 g

= 0.19

***Chem. Commun.*, 2013, 49, 6030 (Homogeneous catalyst)**

E = 0.318 g (benzaldehyde) + 0.519 g (TEMPO-OH) + 0.91 g (aqueous NH_3) + 0.02 g (NaOH) + 7.8 g (CH_3CN) + 0.11 g [$Cu(OTf)_2$] + 0.046 g (bipypyridine) – 0.29 g (product × yield)/0.29 g

= 32.48

Synthesis*, 2010, 3121 *(Heterogeneous catalyst)

E = 0.106 g (benzaldehyde) + 2.31 g (NH_4OAc) + 0.06 g (SDS) – 0.09 g (product × yield)/0.09 g

= 26.4

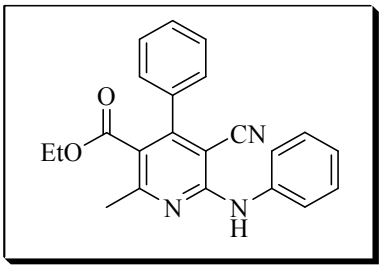
Present work (Heterogeneous catalyst)

E = 0.106 g (benzaldehyde) + 0.91 g (aqueous NH_3) + 0.11 g (H_2O_2) – 0.09 g (product × yield)/0.09 g

= 11

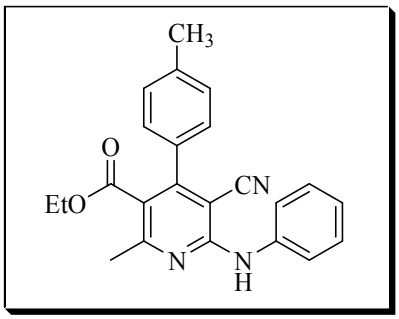
3. Spectral data of synthesized compounds listed in Table 6

Ethyl 5-cyano-2-methyl-4-phenyl-6-(phenylamino)nicotinate (5a)



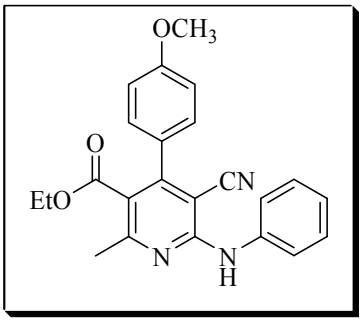
White solid; m.p./lit. m.p. 203-205/205-206 ^{o}C[1]; IR (KBr): 3344 (N-H stretch), 3064 (aromatic C-H stretch), 2222 (CN stretch), 1707 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88-0.91 (t, 3H, J = 8 Hz, CH_3), 2.62 (s, 3H, CH_3), 3.97-4.02 (q, 2H, OCH_2), 7.15-7.19 (t, 1H, J = 8 Hz, H_{arom}), 7.26 (bs, 1H, NH, exchangeable with D_2O), 7.39-7.43 (m, 4H, H_{arom}), 7.49-7.50 (m, 3H, H_{arom}), 7.69-7.71 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.4, 23.8, 61.3, 90.8, 115.9, 120.5, 120.7, 124.0, 127.9, 128.6, 128.9, 129.5, 135.9, 138.3, 154.0, 155.4, 160.3, 167.2; ESI-MS: m/z = 358 $(M)^{+}$.

Ethyl 5-cyano-2-methyl-6-(phenylamino)-4-(p-tolyl)nicotinate (5b)



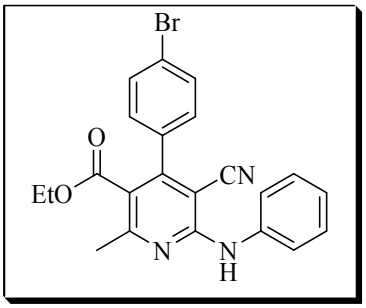
White solid; m.p./lit. m.p. 210-212/211-212 ^{o}C[1]; IR (KBr): 3342 (N-H stretch), 3054 (aromatic C-H stretch), 2222 (CN stretch), 1704 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86-0.89 (t, 3H, J = 8 Hz, CH_3), 2.38 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 3.97-4.02 (q, 2H, OCH_2), 7.18-7.25 (m, 4H, H_{arom}), 7.08-7.13 (m, 1H, H_{arom}), 7.24 (bs, 1H, NH, exchangeable with D_2O), 7.34-7.38 (t, 2H, J = 8 Hz, H_{arom}), 7.65-7.67 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 21.3, 23.8, 90.9, 116.0, 120.7, 127.9, 128.5, 128.9, 129.3, 130.9, 132.9, 138.4, 139.6, 146.3, 159.7, 160.0, 167.4; ESI-MS: m/z = 372 $(M)^{+}$.

Ethyl 5-cyano-4-(4-methoxyphenyl)-2-methyl-6-(phenylamino)nicotinate (5c)



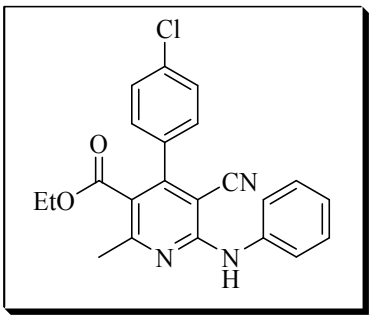
White solid; 178-179/179-180 ^{o}C[1]; IR (KBr): 3317 (N-H stretch), 3068 (aromatic C-H stretch), 2220 (CN stretch), 1712, (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93-0.96 (t, 3H, J = 8 Hz, CH_3), 2.70 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 4.00-4.05 (q, 2H, OCH_2), 6.95-6.97 (d, 3H, J = 8 Hz, H_{arom}), 7.04-7.06 (d, 2H, J = 8 Hz, H_{arom}), 7.16 (bs, 1H, NH, exchangeable with D_2O), 7.23-7.26 (t, 2H, J = 8 Hz, H_{arom}), 7.55-7.56 (d, 2H, J = 4 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 23.8, 55.3, 61.4, 88.0, 110.0, 113.6, 115.0, 120.8, 123.6, 127.6, 129.0, 131.4, 141.1, 144.6, 159.7, 162.6, 165.1; ESI-MS: m/z = 388 $(M)^{+}$.

Ethyl 4-(4-bromophenyl)-5-cyano-2-methyl-6-(phenylamino)nicotinate (5d)



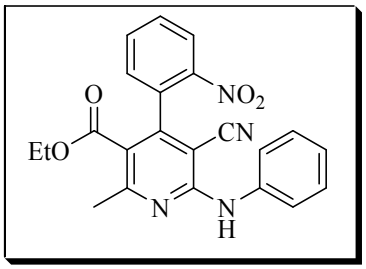
Pale Yellow solid; 175-177/176-178 ^{o}C[1]; IR (KBr): 3329 (N-H stretch), 3068 (aromatic C-H stretch) 2216 (CN stretch), 1714 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01-1.05 (t, 3H, J = 8 Hz, CH_3), 2.34 (s, 3H, CH_3), 4.02-4.07 (q, 2H, OCH_2), 7.06-7.17 (m, 3H, H_{arom}), 7.20 (bs, 1H, NH, exchangeable with D_2O), 7.26-7.30 (t, 2H, J = 8 Hz, H_{arom}), 7.46-7.48 (d, 2H, J = 8 Hz, H_{arom}), 7.65-7.67 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 21.0, 60.0, 88.0, 113.3, 114.6, 122.9, 123.5, 126.6, 129.8, 131.5, 131.7, 132.4, 134.7, 135.2, 136.8, 137.0, 155.3, 168.4; ESI-MS: m/z = 438 $(M)^{+}$, 440 $(M+2)^{+}$.

Ethyl 4-(4-chlorophenyl)-5-cyano-2-methyl-6-(phenylamino)-nicotinate (5e)



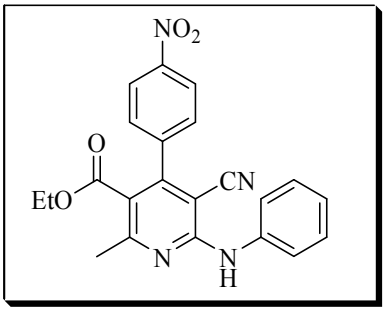
Yellow solid; 190-192/192-194 ^{o}C[1]; IR (KBr): 3331 (N-H stretch), 3069 (aromatic C-H stretch), 2216 (CN stretch), 1714 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96-1.0 (t, 3H, J = 8 Hz, CH_3), 2.31 (s, 3H, CH_3), 4.01-4.06 (q, 2H, OCH_2), 7.04-7.15 (m, 3H, H_{arom}), 7.18-7.22 (t, 2H, J = 8 Hz, H_{arom}), 7.24 (bs, 1H, NH, exchangeable with D_2O), 7.38-7.40 (d, 2H, J = 8 Hz, H_{arom}), 7.62-7.64 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 23.9, 61.4, 90.6, 115.9, 120.8, 124.2, 129.0, 129.4, 134.3, 135.8, 138.2, 152.7, 155.4, 160.6, 167.0; ESI-MS: m/z = 392 $(M)^+$, 394 $(M+2)^+$.

Ethyl 5-cyano-2-methyl-4-(2-nitrophenyl)-6-(phenylamino)nicotinate (5f)



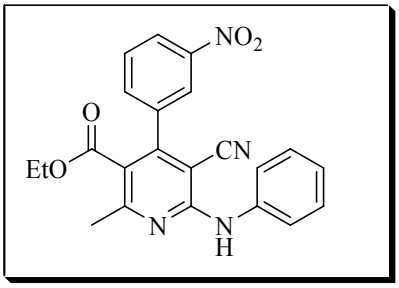
Yellow solid; 186-188/187-189 ^{o}C[1]; IR (KBr): 3361 (N-H stretch), 3058 (aromatic C-H stretch), 2216 (CN stretch), 1708 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94-0.98 (t, 3H, J = 8 Hz, CH_3), 2.73 (s, 3H, CH_3), 4.01-4.07 (q, 2H, OCH_2), 7.19-7.23 (m, 1H, H_{arom}), 7.25 (bs, 1H, NH, exchangeable with D_2O), 7.34-7.38 (t, 1H, J = 8 Hz, H_{arom}), 7.46-7.50 (t, 2H, J = 8 Hz, H_{arom}), 7.73-7.84 (m, 4H, H_{arom}), 8.36-8.38 (m, 1H, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): 13.6, 24.3, 61.6, 90.5, 115.3, 119.8, 121.0, 123.2, 124.3, 124.5, 129.0, 134.1, 137.5, 137.9, 148.1, 151.4, 155.4, 161.6, 166.4; ESI-MS: m/z = 403 $(M)^+$.

Ethyl 5-cyano-2-methyl-4-(4-nitrophenyl)-6-(phenylamino)nicotinate (5g)



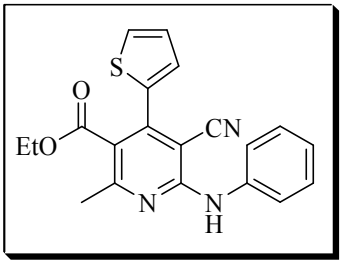
Yellow solid; 219-221/220-221 ^{o}C[1]; IR (KBr): 3327 (N-H stretch), 3055 (aromatic C-H stretch), 2221 (CN stretch), 1712 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94-0.98 (t, 3H, J = 8 Hz, CH_3), 2.65 (s, 3H, CH_3), 4.0-4.05 (q, 2H, OCH_2), 7.18-7.22 (t, 1H, J = 8 Hz, H_{arom}), 7.29 (bs, 1H, NH, exchangeable with D_2O), 7.40-7.44 (t, 2H, J = 8 Hz, H_{arom}), 7.57-7.59 (d, 2H, J = 8 Hz, H_{arom}), 7.68-7.70 (d, 2H, J = 8 Hz, H_{arom}), 8.37-8.39 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 24.3, 61.6, 90.2, 115.2, 119.5, 123.8, 124.5, 129.0, 129.2, 137.8, 142.4, 148.3, 151.8, 155.3, 161.5, 166.4; ESI-MS: m/z = 403 $(M)^{+}$.

Ethyl 5-cyano-2-methyl-4-(3-nitrophenyl)-6-(phenylamino)-nicotinate (5h)



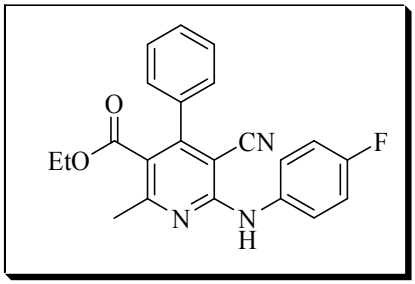
Yellow solid; 196-198/198-200 ^{o}C[1]; IR (KBr): 3361 (N-H stretch), 3058 (aromatic C-H stretch), 2218 (CN stretch), 1714, (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96-1.0 (t, 3H, J = 8 Hz, CH_3), 2.65 (s, 3H, CH_3), 4.02-4.07 (q, 2H, OCH_2), 7.18-7.23 (m, 1H, H_{arom}), 7.18-7.22 (t, 1H, J = 8 Hz, H_{arom}), 7.32 (bs, 1H, NH, exchangeable with D_2O), 7.40-7.44 (t, 2H, J = 8 Hz, H_{arom}), 7.68-7.74 (m, 4H, H_{arom}), 8.29-8.39 (m, 1H, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): 13.6, 24.3, 61.6, 90.5, 115.3, 119.8, 121.0, 123.2, 124.3, 124.5, 129.0, 129.9, 134.1, 137.5, 137.9, 148.1, 151.4, 155.4, 161.4, 166.4; ESI-MS: m/z = 403 $(M)^{+}$.

Ethyl 5-cyano-2-methyl-6-(phenylamino)-4-(thiophen-2-yl)nicotinate (5i)



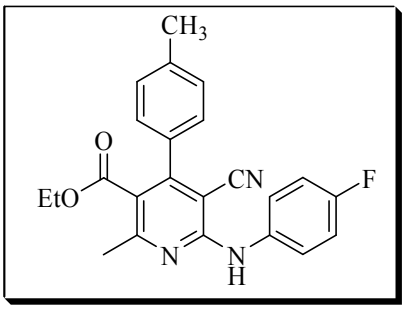
White solid; 188-190/191-192 ^{o}C[2]; IR (KBr): 3421 (N-H stretch), 3085 (aromatic C-H stretch), 2215 (CN stretch), 1719 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26-1.29 (t, 3H, J = 8 Hz, CH_3), 2.19 (s, 3H, CH_3), 4.11-4.16 (q, 2H, OCH_2), 7.24-7.26 (t, 1H, J = 4 Hz, H_{arom}), 7.30 (bs, 1H, NH, exchangeable with D_2O), 7.81-7.91 (m, 5H, H_{arom}), 8.37-7.38 (d, 2H, J = 4 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 21.0, 60.4, 62.5, 109.2, 116.0, 128.6, 129.0, 135.1, 136.0, 136.8, 137.1, 141.1, 146.7, 151.0, 162.7, 171.1; ESI-MS: m/z = 364 $(M)^{+}$.

Ethyl 6-(4-fluorophenylamino)-5-cyano-2-methyl-4-phenyl-nicotinate (5j)



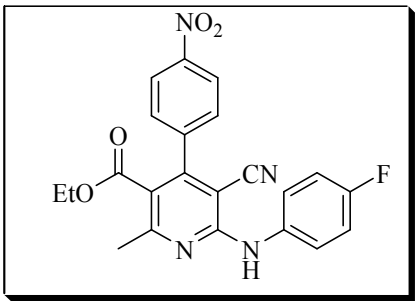
White solid; 192-194 ^{o}C; IR (KBr): 3408 (N-H stretch), 3085 (aromatic C-H stretch), 2218 (CN stretch), 1691 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94-0.98 (t, 3H, J = 8 Hz, CH_3), 2.59 (s, 3H, CH_3), 3.94-3.99 (q, 2H, OCH_2), 7.18-7.20 (d, 2H, J = 8 Hz, H_{arom}), 7.23 (bs, 1H, NH, exchangeable with D_2O), 7.39-7.41 (d, 2H, J = 8 Hz, H_{arom}), 7.47-7.50 (m, 3H, H_{arom}), 7.56-7.58 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.4, 20.9, 61.3, 90.4, 116.0, 120.3, 121.0, 125.1, 126.9, 128.4, 129.5, 129.9, 133.8, 135.4, 153.7, 154.5, 161.4, 167.7; ESI-MS: m/z = 376 $(M)^{+}$.

Ethyl 6-(4-fluorophenylamino)-5-cyano-2-methyl-4-(4-methylphenyl)nicotinate (5k)



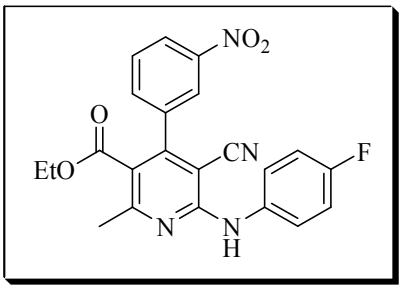
White solid; 175-176 ^{o}C; IR (KBr): 3420 (N-H stretch), 3072 (aromatic C-H stretch), 2221 (CN stretch), 1694 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91-0.93 (t, 3H, J = 8 Hz, CH_3), 2.40 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 4.02-4.08 (q, 2H, OCH_2), 7.15-7.17 (d, 2H, J = 8 Hz, H_{arom}), 7.18-7.20 (d, 2H, J = 8 Hz, H_{arom}), 7.22 (bs, 1H, NH, exchangeable with D_2O), 7.25-7.27 (d, 2H, J = 8 Hz, H_{arom}), 7.53-7.55 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 20.8, 21.3, 61.2, 90.5, 116.1, 119.7, 121.0, 126.0, 127.8, 129.2, 129.4, 133.0, 133.7, 135.7, 139.5, 155.6, 160.1, 167.4; ESI-MS: m/z = 390 $(M)^{+}$.

Ethyl 6-(4-fluorophenylamino)-5-cyano-2-methyl-4-(4-nitrophenyl)nicotinate (5l)



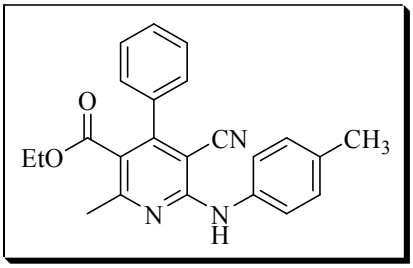
Pale Yellow solid; 213-215 ^{o}C; IR (KBr): 3273 (N-H stretch), 3054 (aromatic C-H stretch), 2181 (CN stretch), 1654 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42-1.46 (t, 3H, J = 8 Hz, CH_3), 2.19 (s, 3H, CH_3), 4.41-4.47 (q, 2H, OCH_2), 7.22-7.24 (d, 2H, J = 8 Hz, H_{arom}), 7.26 (bs, 1H, NH, exchangeable with D_2O), 7.34-7.36 (d, 2H, J = 8 Hz, H_{arom}), 7.64-7.66 (d, 2H, J = 8 Hz, H_{arom}), 8.14-8.16 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 29.7, 30.9, 41.6, 61.5, 63.3, 107.3, 114.5, 123.4, 124.3, 127.8, 129.8, 131.5, 136.9, 149.7, 151.7, 161.4, 166.6; ESI-MS: m/z = 421 $(M)^{+}$.

Ethyl 6-(4-fluorophenylamino)-5-cyano-2-methyl-4-(3-nitrophenyl)nicotinate (5m)



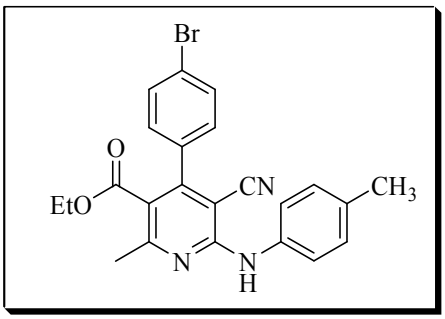
Yellow solid; 196-198 ^{o}C; IR (KBr): 3332 (N-H stretch), 3057 (aromatic C-H stretch), 2214 (CN stretch), 1714 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97-1.0 (t, 3H, J = 8 Hz, CH_3), 2.63 (s, 3H, CH_3), 4.02-4.08 (q, 2H, OCH_2), 7.09-7.13 (t, 2H, J = 8 Hz, H_{arom}), 7.25 (bs, 1H, NH, exchangeable with D_2O), 7.60-7.63 (m, 2H, H_{arom}), 7.70-7.76 (m, 2H, H_{arom}), 8.37-8.39 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 24.2, 30.9, 61.6, 90.3, 115.2, 115.6, 115.8, 120.0, 123.2, 123.3, 124.3, 129.9, 133.7, 133.8, 134.0, 137.4, 148.1, 151.4, 155.4, 158.4, 160.8, 161.4, 166.3; ESI-MS: m/z = 421 $(M)^{+}$.

Ethyl 5-cyano-2-methyl-4-phenyl-6-(4-methylphenylamino)nicotinate (5n)



White solid; 139-141/141-142 ^{o}C[1]; IR (KBr): 3331 (N-H stretch), 3061 (aromatic C-H stretch), 2220 (CN stretch), 1712 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84-0.88 (t, 3H, J = 8 Hz, CH_3), 2.36 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 3.96-4.01 (q, 2H, OCH_2), 7.14-7.16 (d, 2H, J = 8 Hz, H_{arom}), 7.22 (bs, 1H, NH, exchangeable with D_2O), 7.34-7.36 (d, 2H, J = 8 Hz, H_{arom}), 7.45-7.48 (m, 3H, H_{arom}), 7.55-7.57 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.4, 20.9, 23.9, 61.3, 90.4, 116.0, 120.1, 121.0, 127.9, 128.6, 129.4, 126.1, 129.9, 133.8, 135.6, 153.9, 155.5, 160.4, 167.3; ESI-MS: m/z = 372 $(M)^{+}$.

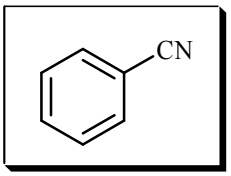
Ethyl 4-(4-bromophenyl)-5-cyano-2-methyl-6-(4-methylphenylamino)nicotinate (5o)



Pale Yellow solid; 164-166/166-168 ^{o}C[1]; IR (KBr): 3323 (N-H stretch), 3064 (aromatic C-H stretch), 2222 (CN stretch), 1708 (C=O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94-0.98 (t, 3H, J = 8 Hz, CH_3), 2.36 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 4.02-4.08 (q, 2H, OCH_2), 7.16-7.25 (m, 4H, H_{arom}), 7.25 (bs, 1H, NH, exchangeable with D_2O), 7.53-7.55 (d, 2H, J = 8 Hz, H_{arom}), 7.62-7.64 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 20.9, 24.0, 61.4, 90.1, 115.8, 119.8, 121.1, 123.9, 129.5, 129.6, 131.3, 134.0, 134.8, 135.4, 152.7, 155.5, 160.7, 167.0; ESI-MS: m/z = 451 $(M)^+$, 453 $(M+2)^+$.

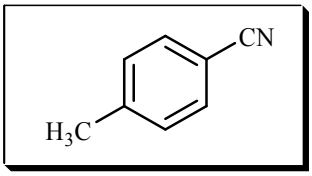
Spectral data of synthesized compounds listed in Table 8

Benzonitrile (2a)



Liquid[3], IR (KBr): 2228 (CN stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.46. (t, 2H, J = 8 Hz, H_{arom}), 7.50-7.53 (t, 1H, J = 8 Hz, H_{arom}), 7.58-7.59 (d, 2H, J = 4 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 113.1, 119.1, 129.0, 132.0, 133.1; ESI-MS: m/z = 104 $(M)^+$.

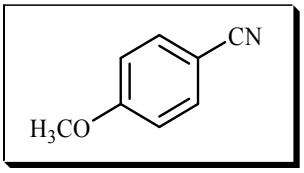
4-Methylbenzonitrile (2b)



Pale Yellow solid; 19-21/21-22 ^{o}C[4]; IR (KBr): 2226 (CN stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.36 (s, 3H, CH_3), 7.23-7.25 (d, 2H, J = 8 Hz, H_{arom}), 7.46-7.48 (d, 2H, J = 8 Hz,

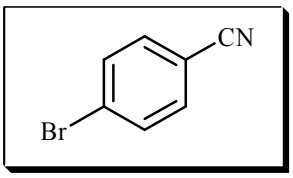
H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.6, 108.1, 119.4, 128.9, 132.8, 144.5; ESI-MS: m/z = 118 $(M)^+$.

4-Methoxybenzonitrile (2c)



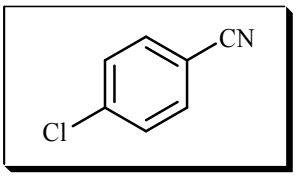
White solid; 60-62/63-64 ^oC[4]; IR (KBr): 2227 (CN stretch) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 3H, OCH_3), 6.96-6.98 (d, 2H, J = 8 Hz, H_{arom}), 7.60-7.62 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 103.9, 114.7, 119.2, 134.0, 162.8; ESI-MS: m/z = 134 $(M)^+$.

4-Bromobenzonitrile (2d)



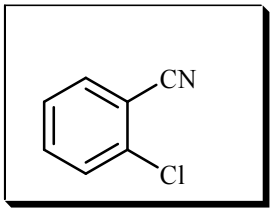
White solid; 110-112/110-115 ^oC[5]; IR (KBr): 2227 (CN stretch) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54-7.56 (d, 2H, J = 8 Hz, H_{arom}), 7.64-7.66 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.2, 118.1, 128.1, 132.6, 133.4; ESI-MS: m/z = 182 $(M)^+$, 184 $(M+2)^+$.

4-Chlorobenzonitrile (2e)



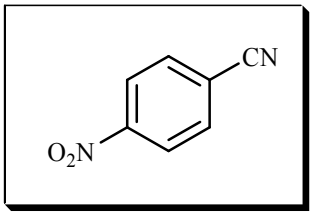
White solid; 90-92/90-91 ^oC[4]; IR (KBr): 2229 (CN stretch) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.50 (d, 2H, J = 8 Hz, H_{arom}), 7.62-7.64 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.9, 118.1, 129.9, 133.7, 139.7; ESI-MS: m/z = 139 $(M)^+$, 141 $(M+2)^+$.

2-Chlorobenzonitrile (2f)



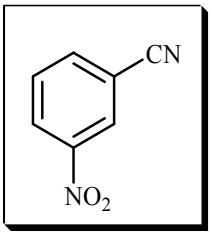
Pale yellow solid; 40-42/42-43 ^{o}C[6]; IR (KBr): 2231 (CN stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.43 (d, 1H, J = 8 Hz, H_{arom}), 7.48-7.61 (m, 2H, J = 8 Hz, H_{arom}), 7.67-7.69 (d, 1H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 113.4, 116.2, 127.1, 130.4, 133.8, 134.2, 136.8; ESI-MS: m/z = 139 $(M)^+$, 141 $(M+2)^+$.

4-Nitrobenzonitrile (2g)



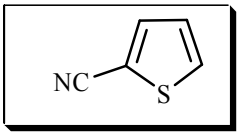
Pale yellow solid; 115-117/116-117 ^{o}C[4]; IR (KBr): 2233 (CN stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.93 (d, 2H, J = 8 Hz, H_{arom}), 8.38-8.40 (d, 2H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.8, 118.3, 123.6, 124.3, 133.4; ESI-MS: m/z = 152 $(M)^+$.

3-Nitrobenzonitrile (2h)



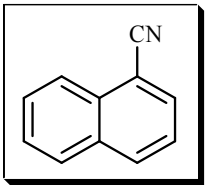
Pale yellow solid; 116-118/118 ^{o}C[7]; IR (KBr): 2235 (CN stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H, H_{arom}), 8.01-8.03 (d, 2H, J = 8 Hz, H_{arom}), 8.07-8.11 (t, 1H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.2, 116.2, 127.3, 130.6, 133.3, 137.5, 148.2; ESI-MS: m/z = 152 $(M)^+$.

2-Thiophenecarbonitrile (2i)



Liquid[4], IR (KBr): 2221 (CN stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09-7.12 (t, 1H, J = 8 Hz, H_{arom}), 7.49-7.50 (d, 1H, J = 4 Hz, H_{arom}), 7.54-7.56 (d, 1H, J = 8 Hz, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 109.5, 114.5, 127.8, 129.5, 138.2; ESI-MS: m/z = 110 $(M)^+$.

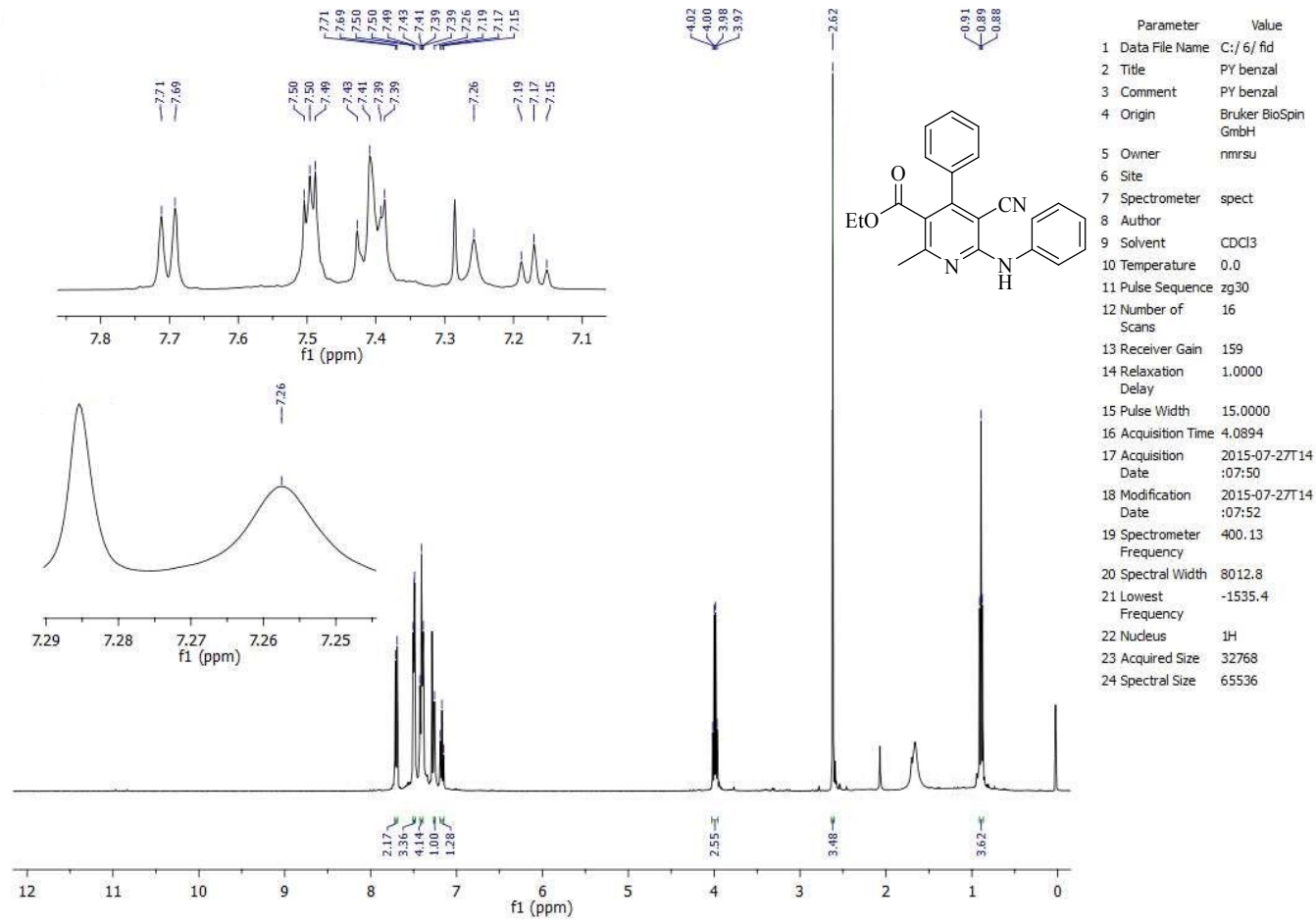
1-Naphthalenecarbonitrile (2j)



Pale yellow solid; 116-118/118 ^{o}C[3]; IR (KBr): 2219 (CN stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.55 (d, 1H, J = 8 Hz, H_{arom}), 7.64-7.66 (d, 1H, J = 8 Hz, H_{arom}), 7.75-7.92 (m, 5H, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ110.3, 117.7, 124.6, 125.1, 127.4, 128.5, 128.6; ESI-MS: m/z = 154 $(M)^+$.

4. Spectral data of some selected compounds

^{1}H spectrum of 5a



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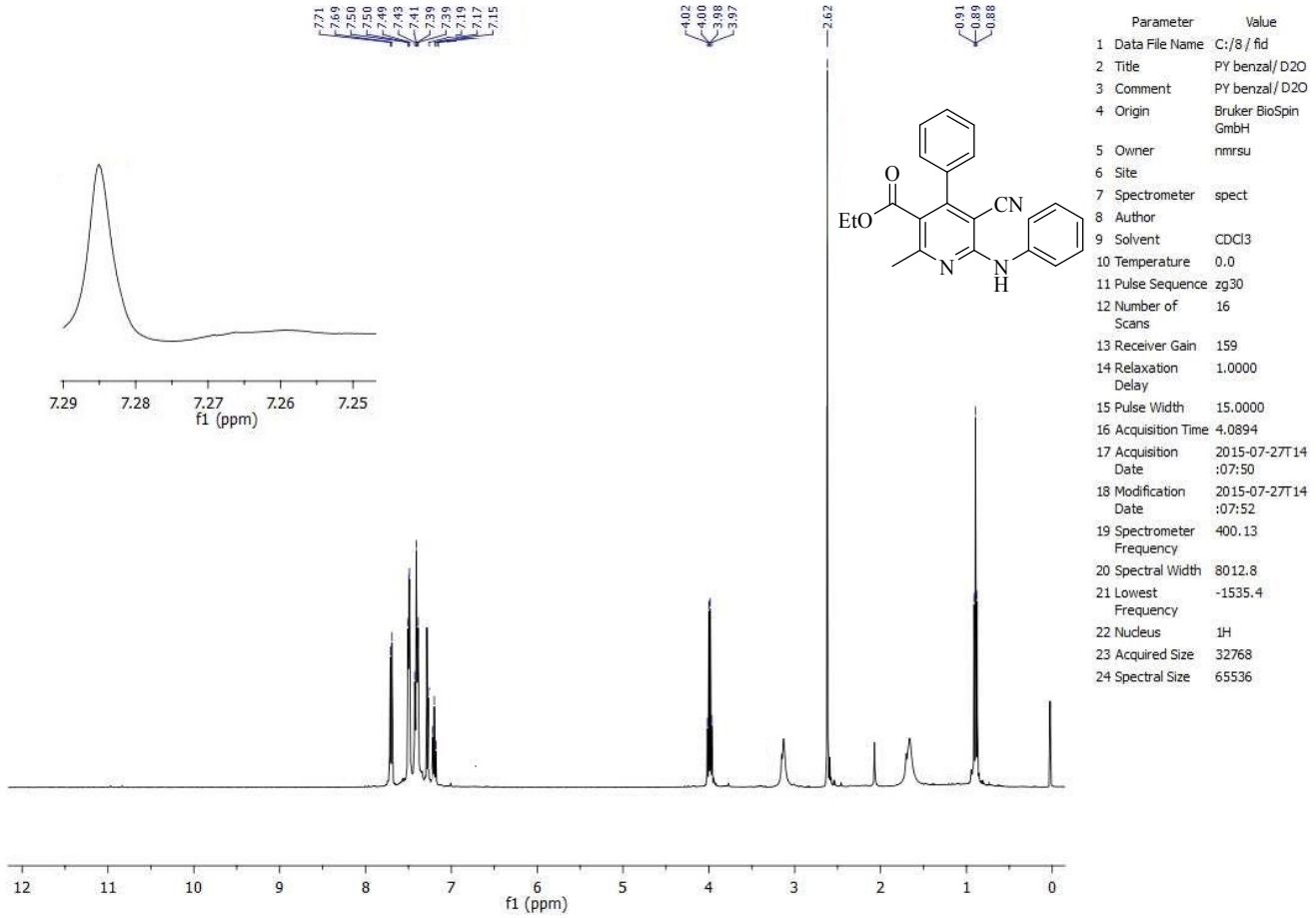
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	0.0
11	Pulse Sequence	zg30
12	Number of Scans	16
13	Receiver Gain	159
14	Relaxation Delay	1.0000
15	Pulse Width	15.0000
16	Acquisition Time	4.0894
17	Acquisition Date	2015-07-27T14 :07:50
18	Modification Date	2015-07-27T14 :07:52
19	Spectrometer Frequency	400.13
20	Spectral Width	8012.8
21	Lowest Frequency	-1535.4
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

D_2O spectrum of 5a



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8	Author	
9	Solvent	CDCl3
10	Temperature	0.0
11	Pulse Sequence	zg30
12	Number of Scans	16
13	Receiver Gain	159
14	Relaxation Delay	1.0000
15	Pulse Width	15.0000
16	Acquisition Time	4.0894
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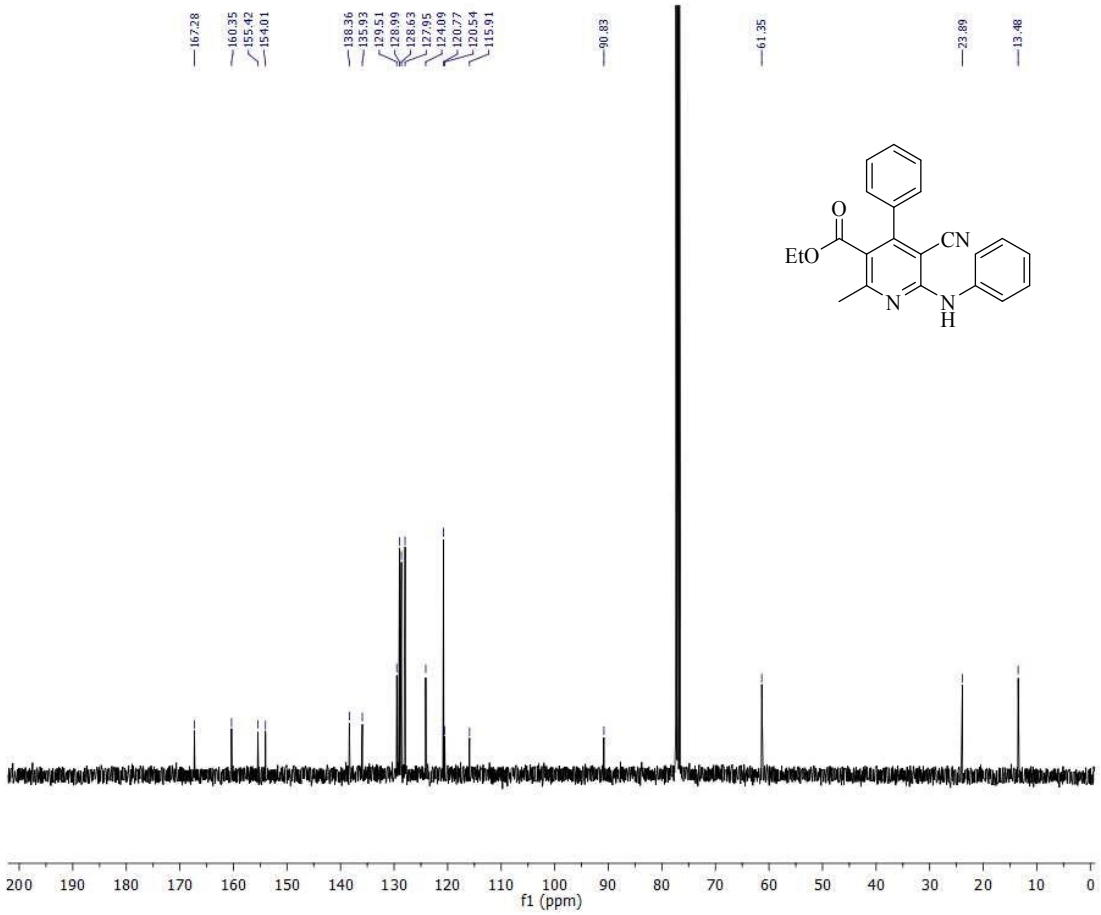
18	Modification Date	2015-07-27T14 :07:52
19	Spectrometer Frequency	400.13
20	Spectral Width	8012.8
21	Lowest Frequency	-1535.4
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

^{13}C spectrum of 5a



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9	Solvent	CDCl3
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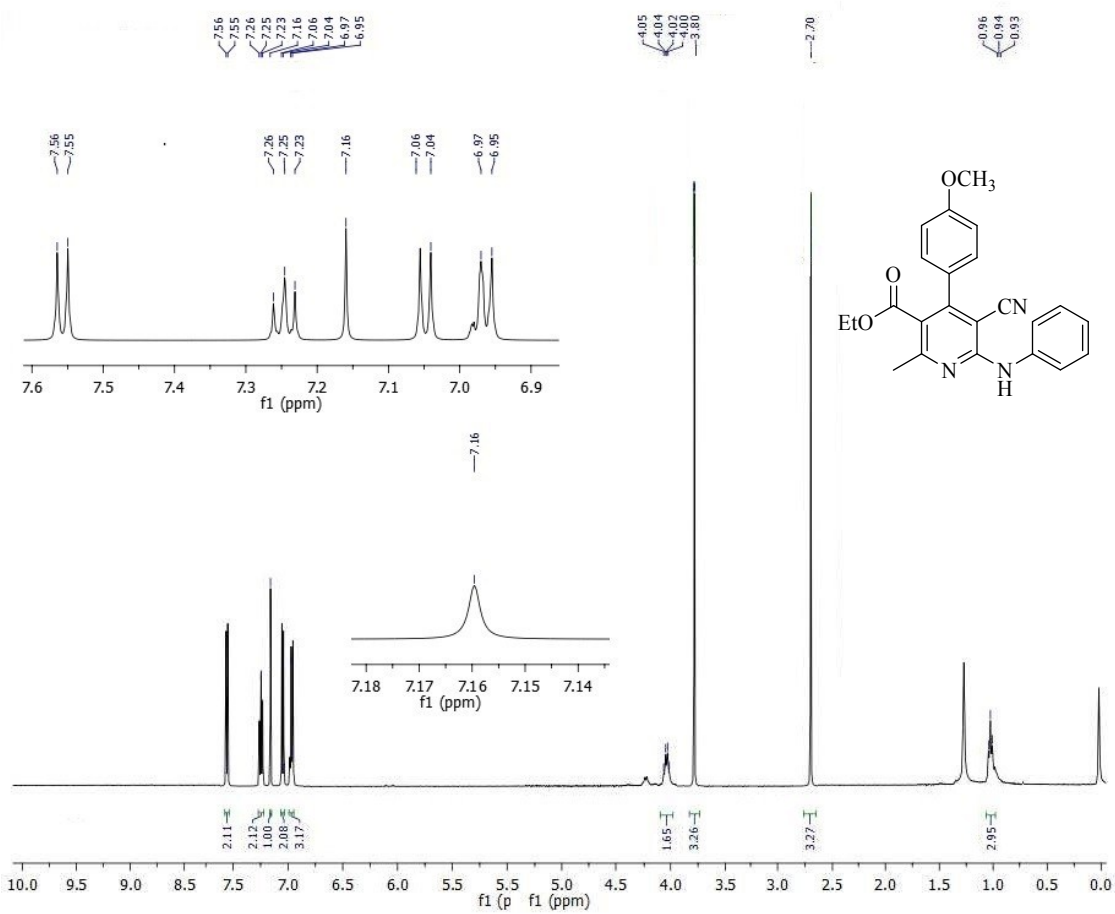
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

^{1}H spectrum of 5c



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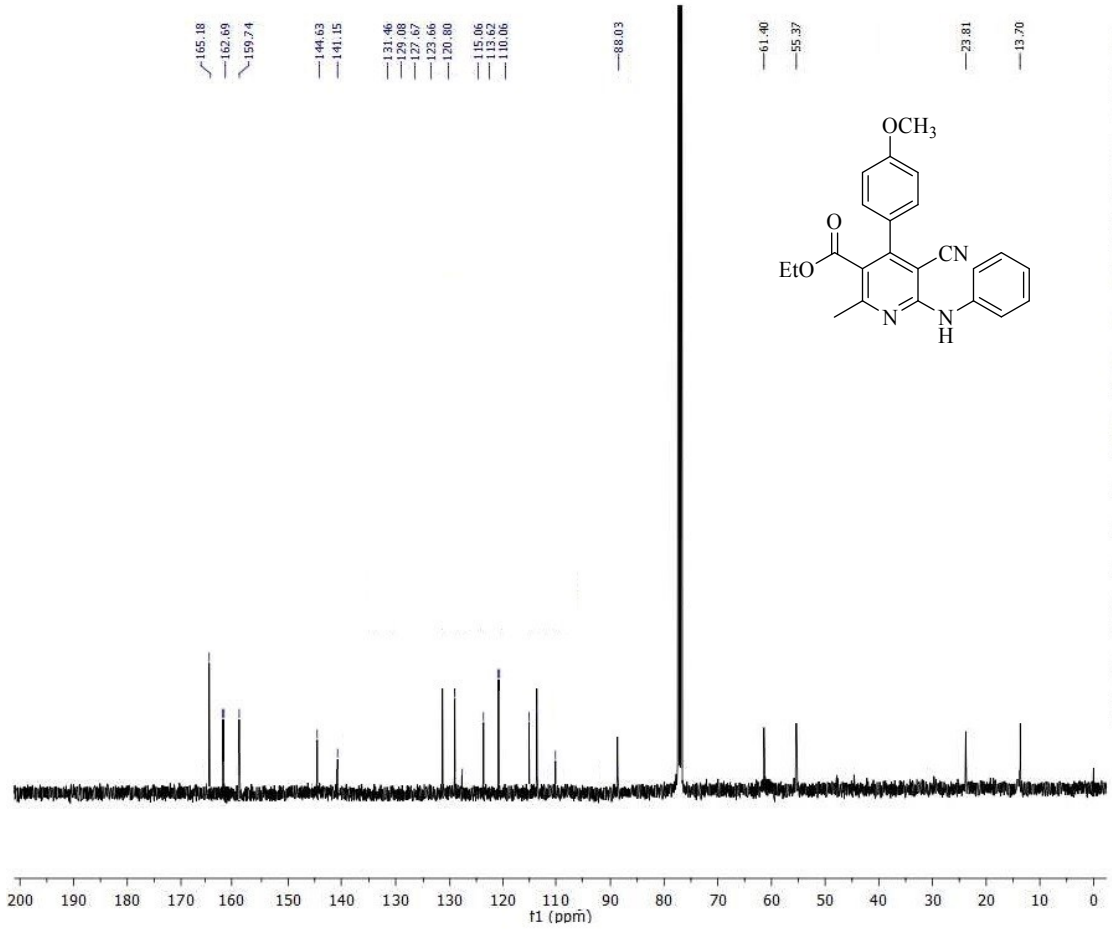
20	Spectral Width	8012.8
21	Lowest Frequency	-1535.4
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

^{13}C spectrum of 5c



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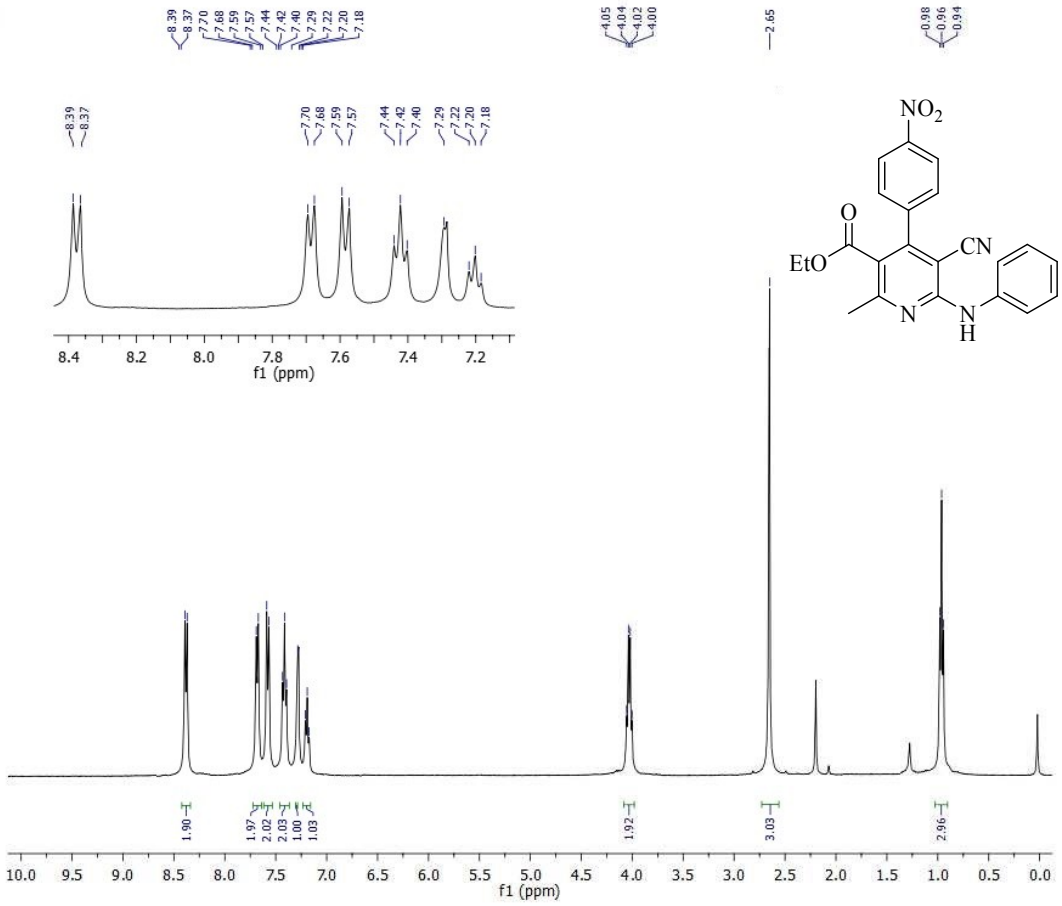
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

^{1}H spectrum of 5g



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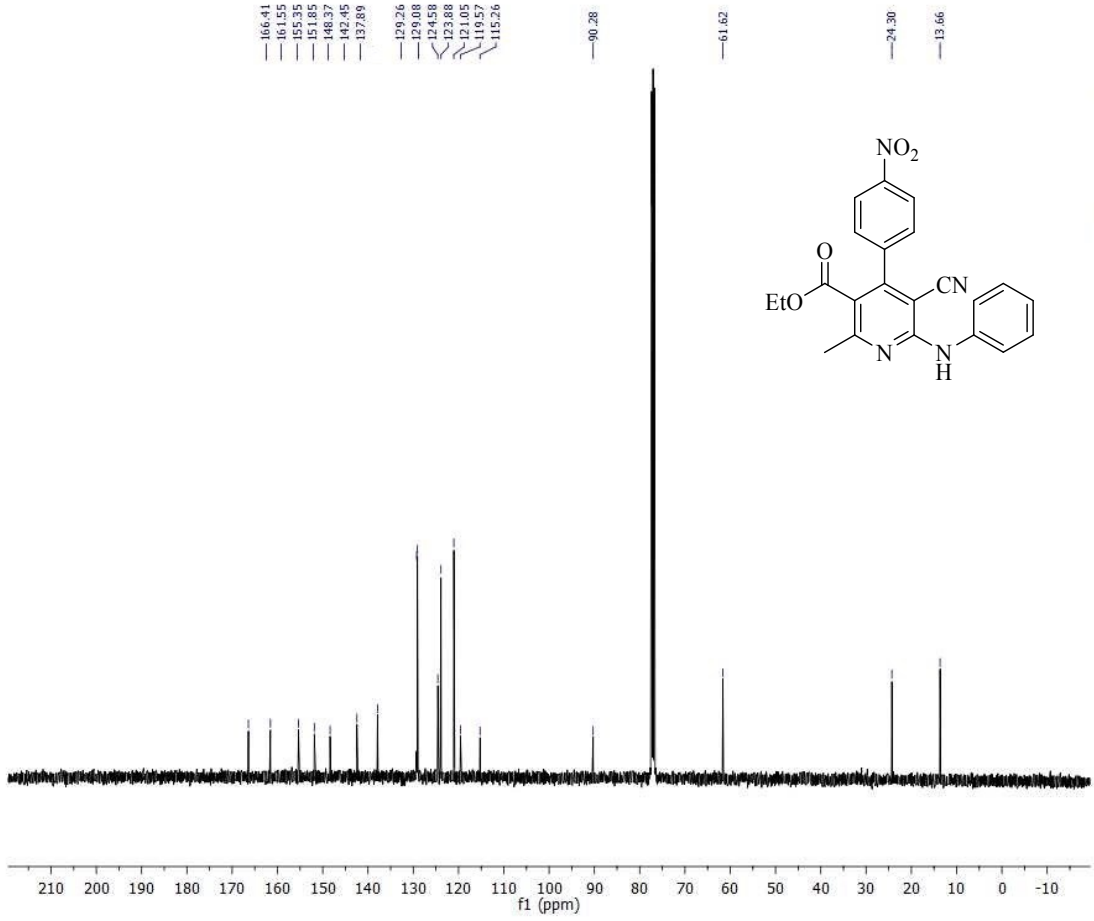
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

^{13}C spectrum of 5g



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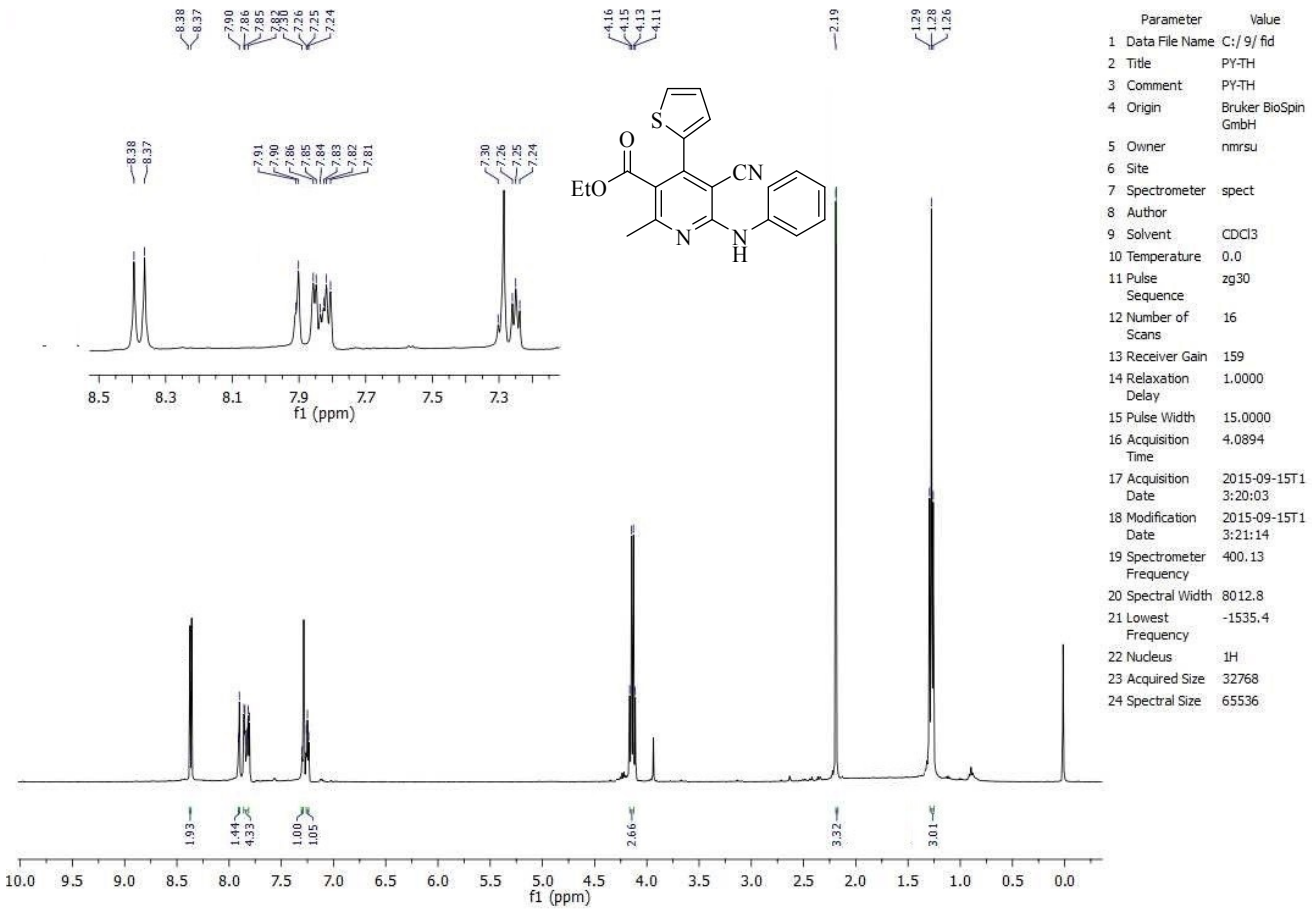
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

^{1}H spectrum of 5i



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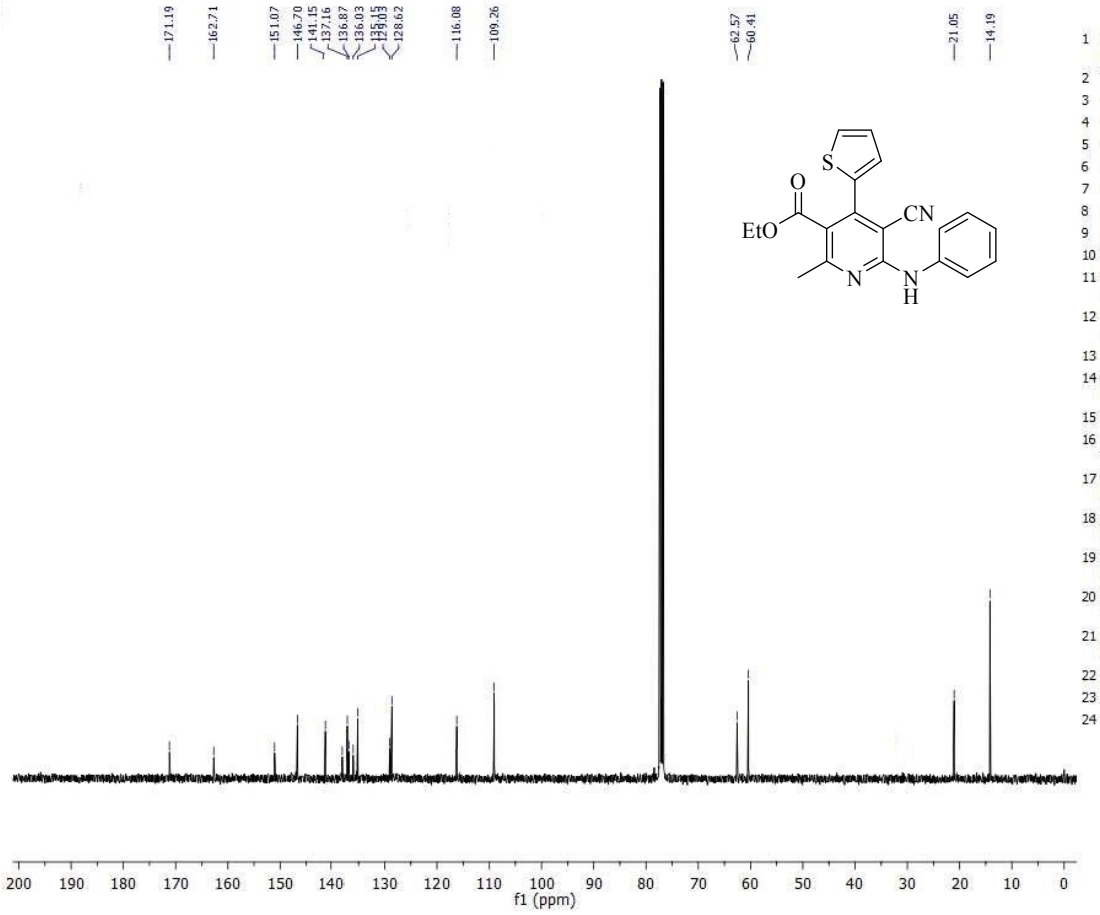
23	Acquired Size	32768
24	Spectral Size	65536

^{13}C spectrum of 5i



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8	Author	
9	Solvent	CDCl3
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15	Pulse Width	9.8000
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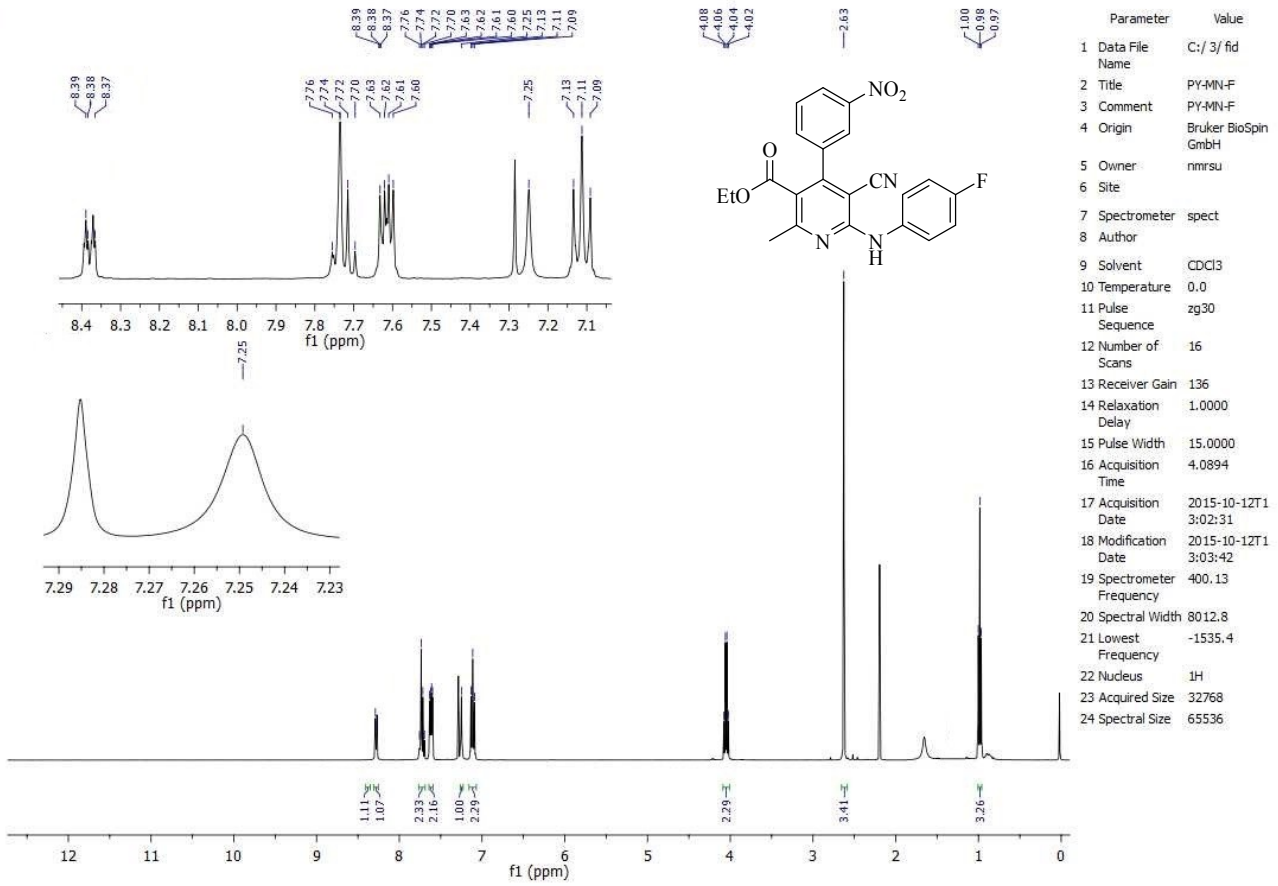
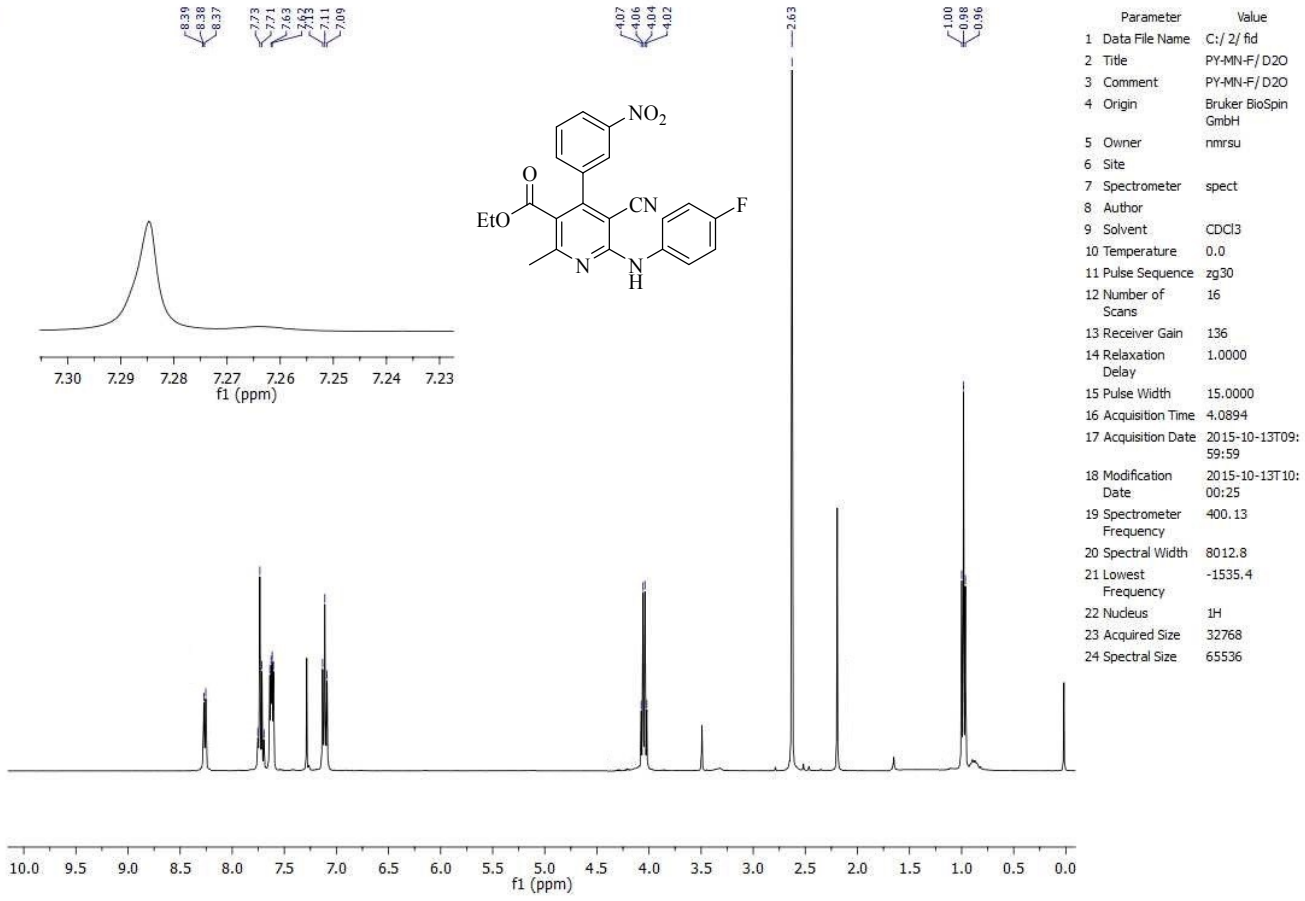
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

^{1}H spectrum of 5m



D_2O spectrum of 5m



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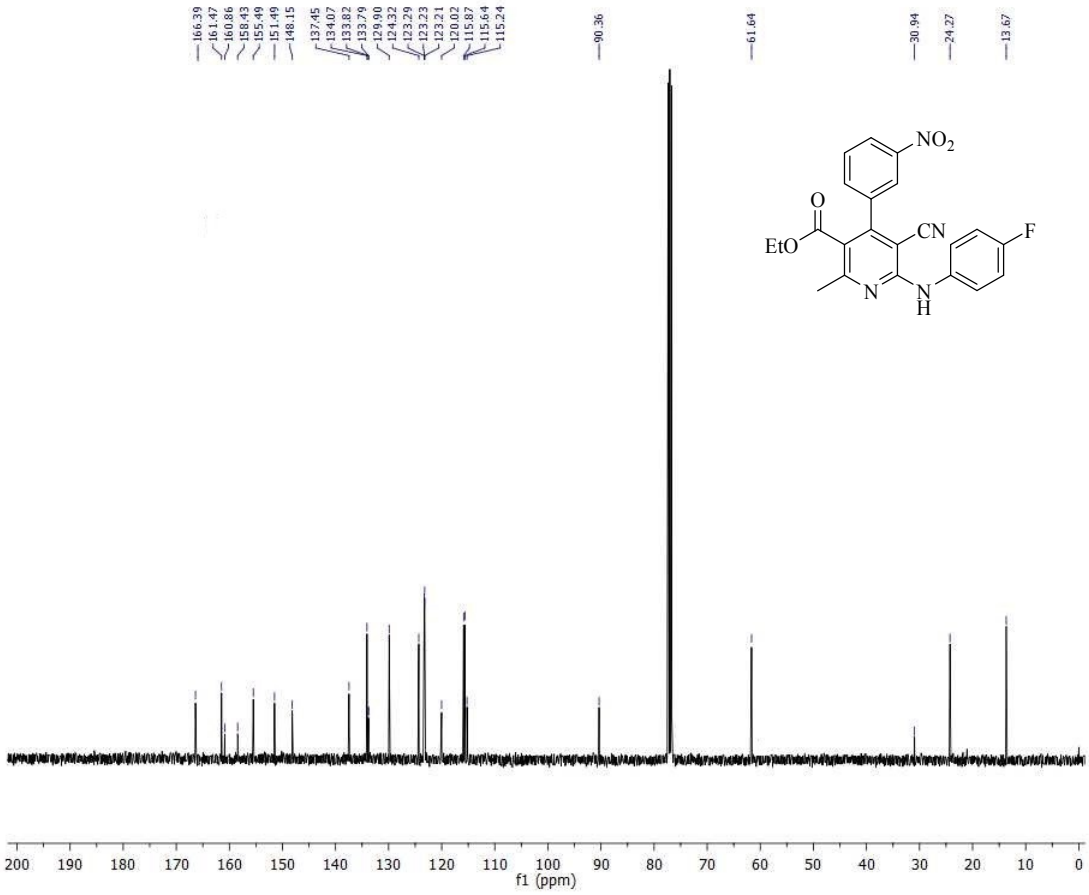
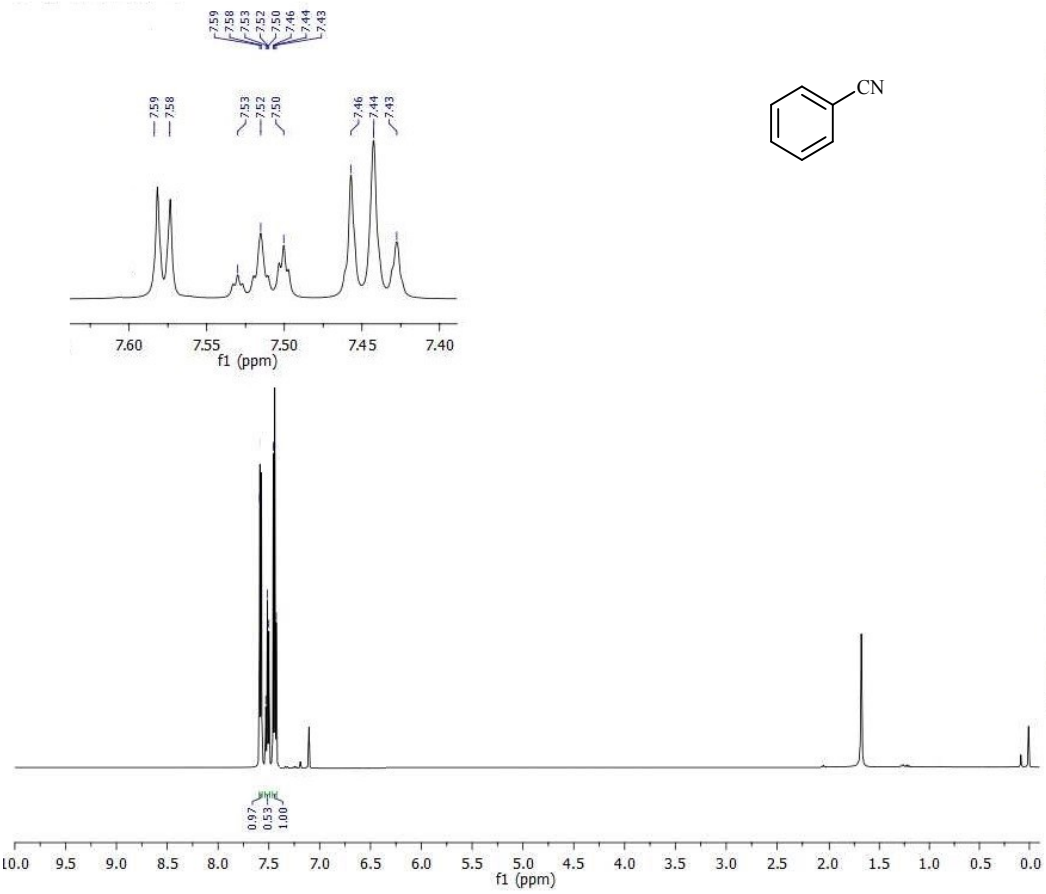
2	Title	PY-MN-F/ D2O
3	Comment	PY-MN-F/ D2O
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	0.0
11	Pulse Sequence	zg30
12	Number of Scans	16
13	Receiver Gain	136
14	Relaxation Delay	1.0000
15	Pulse Width	15.0000
16	Acquisition Time	4.0894
17	Acquisition Date	2015-10-13T09:59:59
18	Modification Date	2015-10-13T10:00:25
19	Spectrometer Frequency	400.13
20	Spectral Width	8012.8
21	Lowest Frequency	-1535.4
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

^{13}C spectrum of 5m



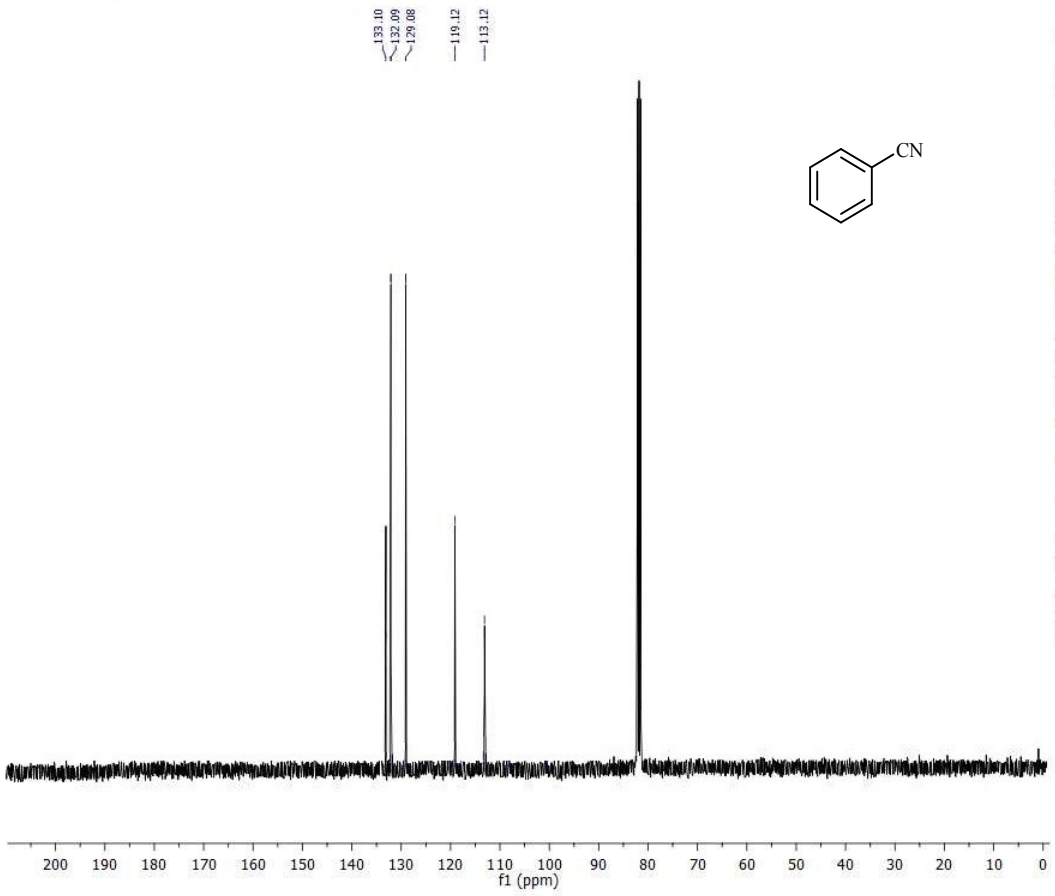
	Parameter	Value
1	Data File Name	C:/ 4/ fid
2	Title	PY-MN-F
3	Comment	PY-MN-F
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	0.0
11	Pulse Sequence	zgpg30
12	Number of Scans	405
13	Receiver Gain	199
14	Relaxation Delay	2.0000
15	Pulse Width	9.8000
16	Acquisition Time	1.3631
17	Acquisition Date	2015-10-12T13:05:47
18	Modification Date	2015-10-12T13:28:00
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

^{1}H spectrum of 2a



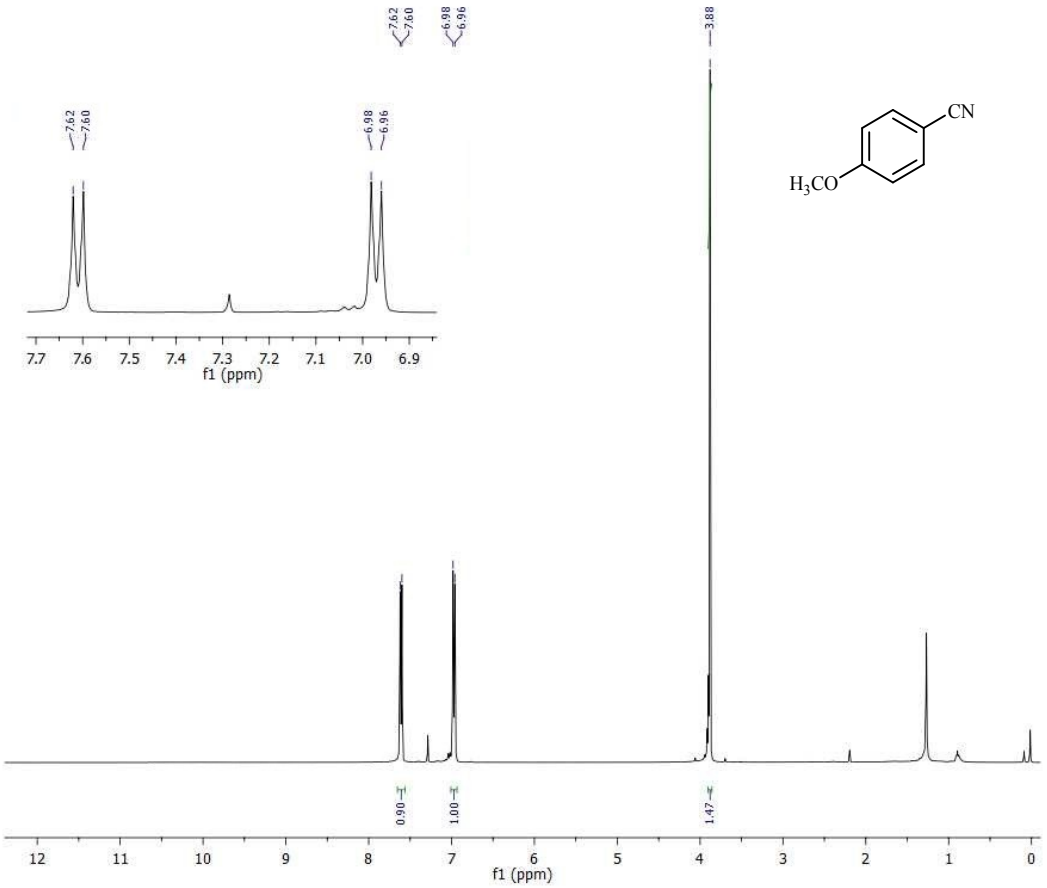
	Parameter	Value
1	Data File Name	C:/Users/MADHAVI/benzal/10/fid
2	Title	Dec22-2015
3	Comment	BA-BZ
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	293.9
11	Pulse Sequence	zg30
12	Number of Scans	16
13	Receiver Gain	136
14	Relaxation Delay	1.0000
15	Pulse Width	15.0000
16	Acquisition Time	4.0894
17	Acquisition Date	2015-12-22T15:41:00
18	Modification Date	2015-12-22T11:12:52
19	Spectrometer Frequency	400.13
20	Spectral Width	8012.8
21	Lowest Frequency	-1535.4
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

^{13}C spectrum of 2a



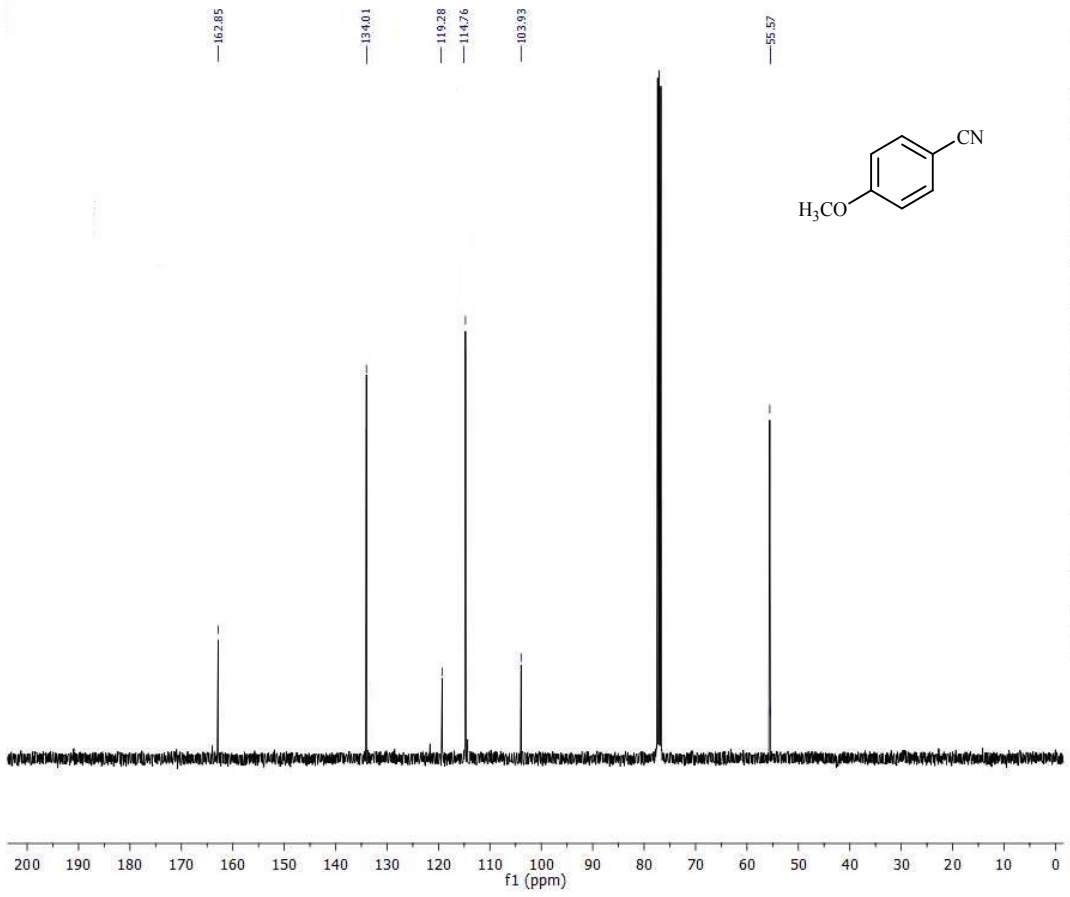
	Parameter	Value
1	Data File Name	C:/Users/MADHAVI/benzal/11/fid
2	Title	Dec22-2015
3	Comment	BA-BZ
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.6
11	Pulse Sequence	zgpg30
12	Number of Scans	214
13	Receiver Gain	199
14	Relaxation Delay	2.0000
15	Pulse Width	9.8000
16	Acquisition Time	1.3631
17	Acquisition Date	2015-12-22T14:59:00
18	Modification Date	2015-12-22T10:38:12
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

^{1}H spectrum of 2c



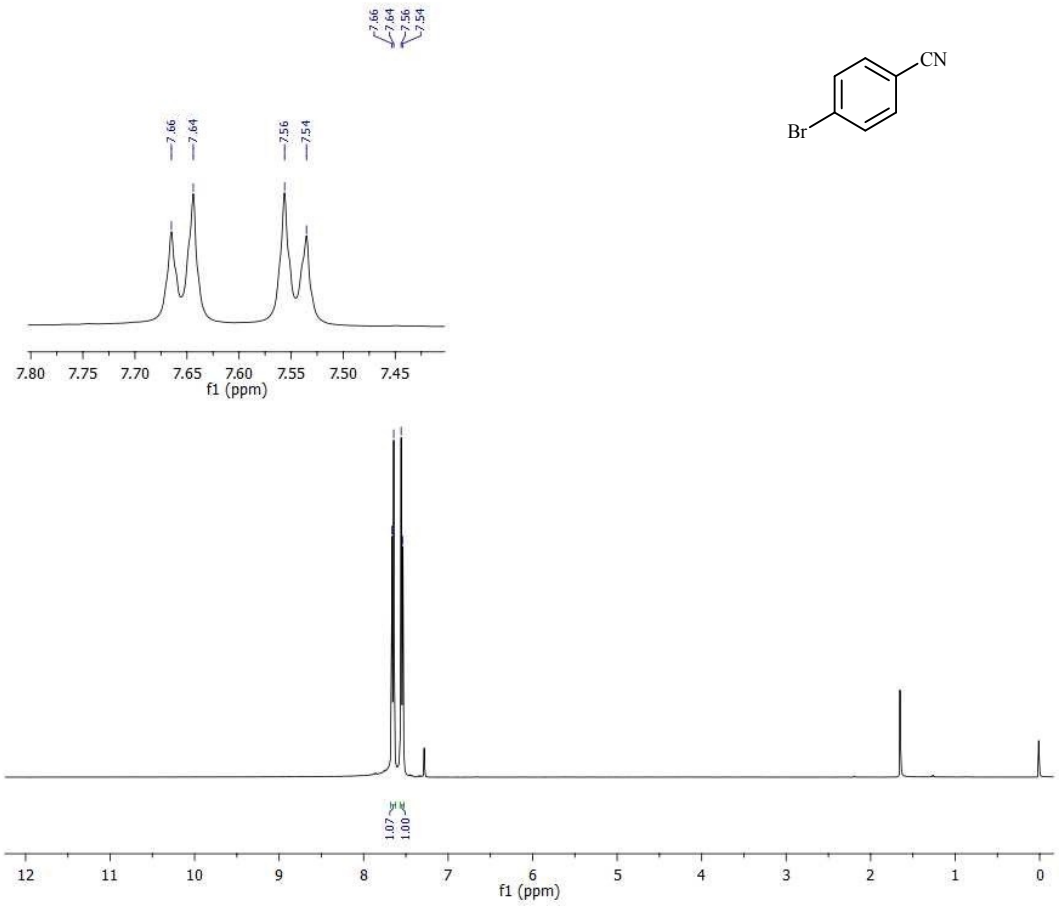
	Parameter	Value
1	Data File Name	C:/Users/MADHAVI/20/fid
2	Title	Mar24-2015
3	Comment	1H
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	291.2
11	Pulse Sequence	zg30
12	Number of Scans	16
13	Receiver Gain	114
14	Relaxation Delay	1.0000
15	Pulse Width	15.0000
16	Acquisition Time	4.0894
17	Acquisition Date	2015-03-24T16:06:00
18	Modification Date	2015-03-24T11:36:40
19	Spectrometer Frequency	400.13
20	Spectral Width	8012.8
21	Lowest Frequency	-1535.4
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

^{13}C spectrum of 2c



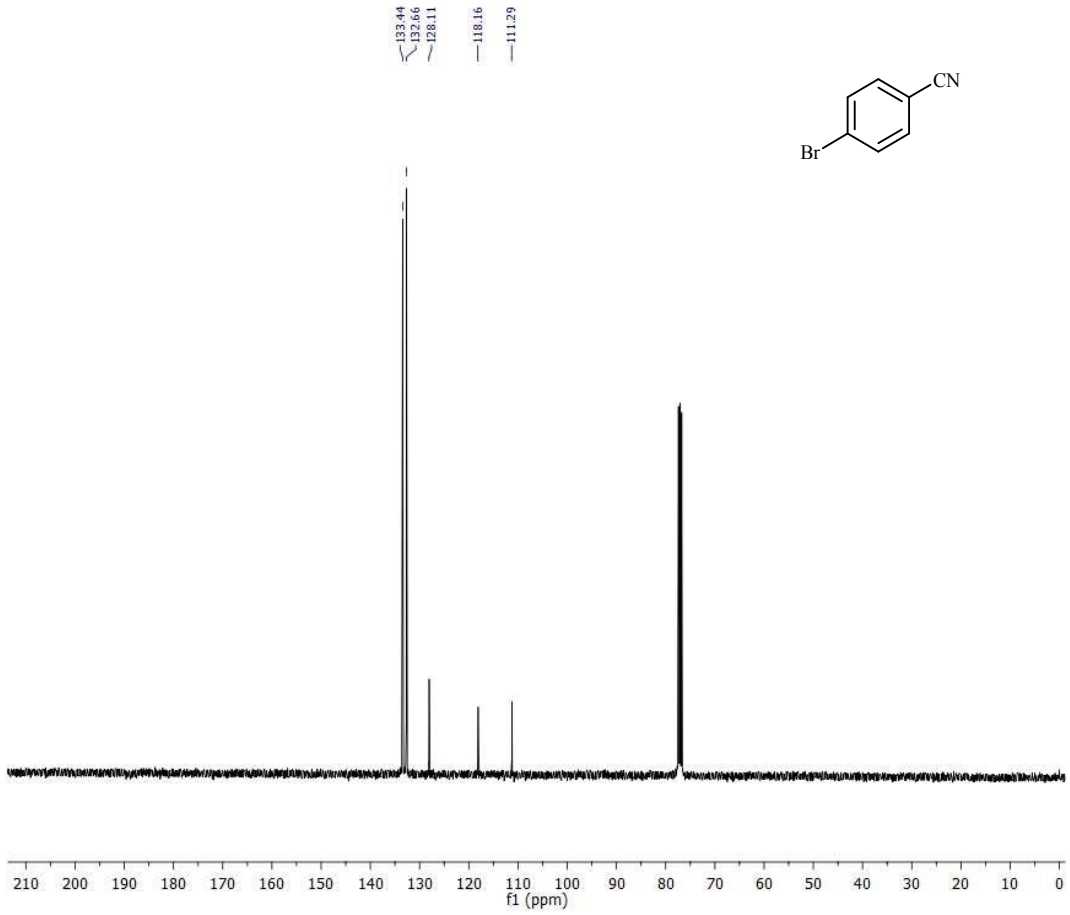
	Parameter	Value
1	Data File Name	C:/Users/MADHAVI/21/fid
2	Title	Mar24-2015
3	Comment	13C
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	291.9
11	Pulse Sequence	zgpg30
12	Number of Scans	353
13	Receiver Gain	199
14	Relaxation Delay	2.0000
15	Pulse Width	9.8000
16	Acquisition Time	1.3631
17	Acquisition Date	2015-03-24T16:12:00
18	Modification Date	2015-03-24T11:57:36
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

^{1}H spectrum of 2d



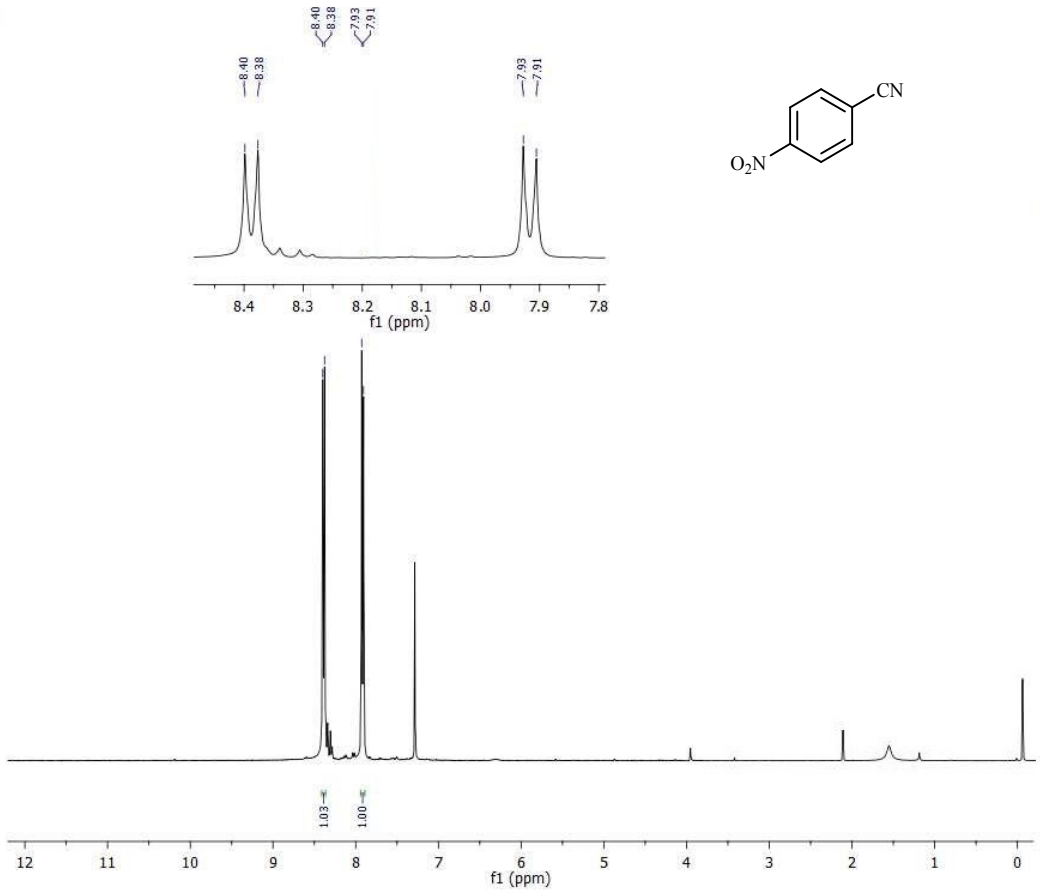
	Parameter	Value
1	Data File Name	C:/Users/MADHAVI/1/fid
2	Title	Nitile series-P-bromo benzal
3	Comment	P-BR-CN
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	0.0
11	Pulse Sequence	zg30
12	Number of Scans	16
13	Receiver Gain	178
14	Relaxation Delay	1.0000
15	Pulse Width	15.0000
16	Acquisition Time	4.0894
17	Acquisition Date	2015-07-03T11:16:35
18	Modification Date	2015-07-03T11:16:36
19	Spectrometer Frequency	400.13
20	Spectral Width	8012.8
21	Lowest Frequency	-1535.4
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

^{13}C spectrum of 2d



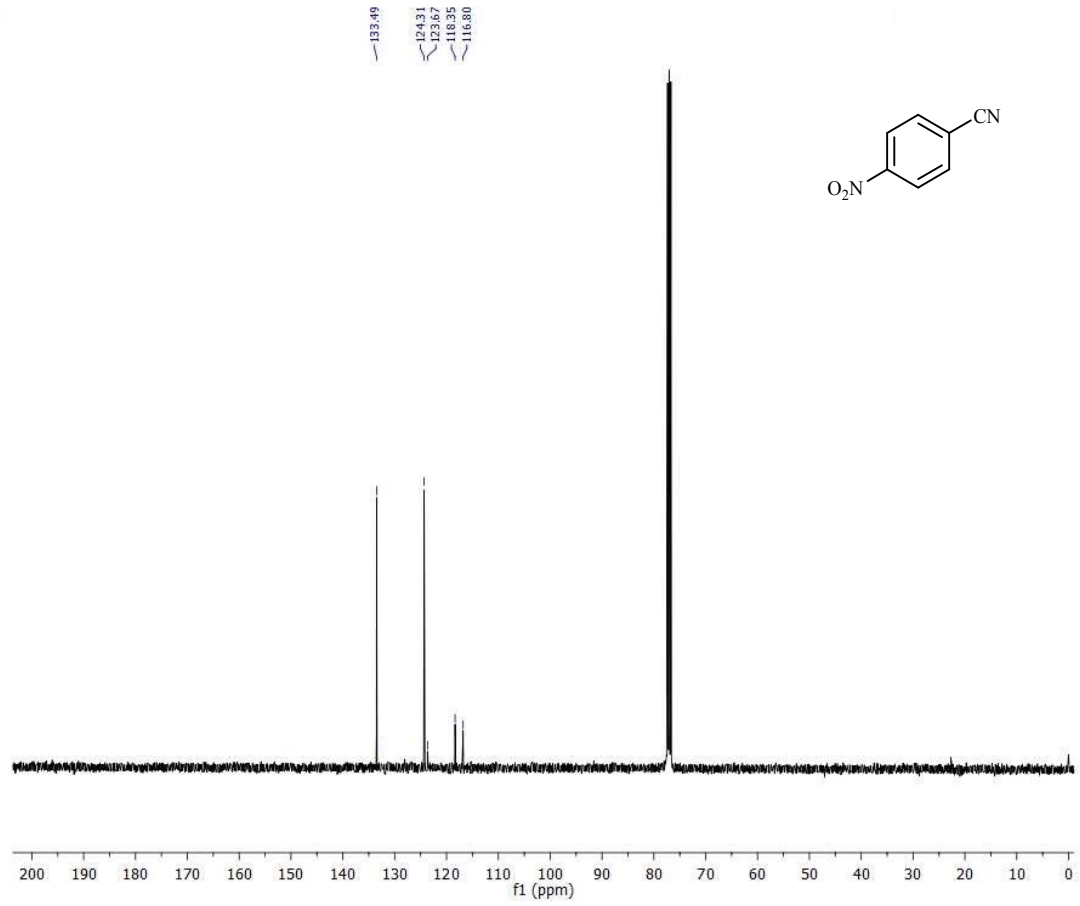
	Parameter	Value
1	Data File Name	C:/Users/MADHAVI/2/fid
2	Title	Nitile series-P-bromo benzal
3	Comment	P-BR-CN
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	0.0
11	Pulse Sequence	zgpg30
12	Number of Scans	1002
13	Receiver Gain	199
14	Relaxation Delay	2.0000
15	Pulse Width	9.8000
16	Acquisition Time	1.3631
17	Acquisition Date	2015-07-03T12:15:16
18	Modification Date	2015-07-03T12:15:18
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

^{1}H spectrum of 2g



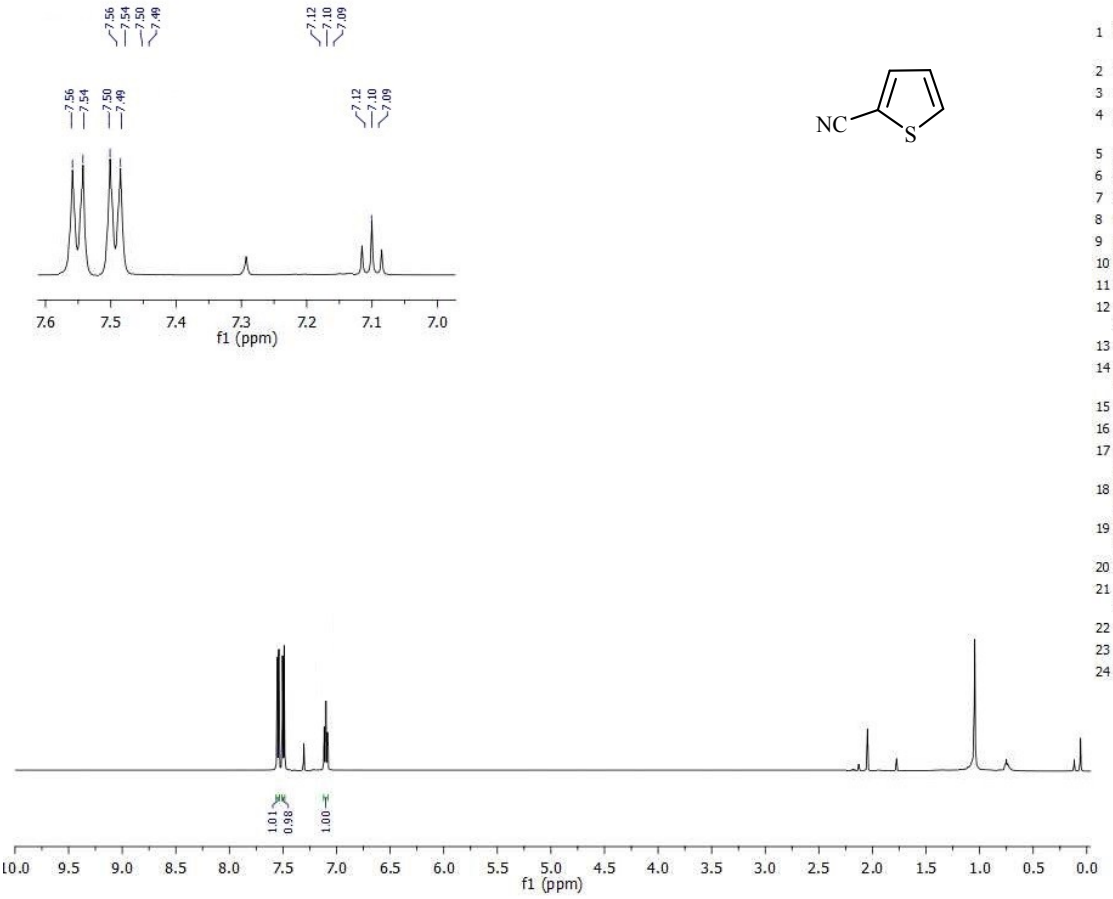
	Parameter	Value
1	Data File Name	C:/Users/MADHAVI/4/fid
2	Title	Dec17-2014
3	Comment	PNO2
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.9
11	Pulse Sequence	zg30
12	Number of Scans	16
13	Receiver Gain	199
14	Relaxation Delay	1.0000
15	Pulse Width	15.0000
16	Acquisition Time	4.0894
17	Acquisition Date	2014-12-17T12:55:00
18	Modification Date	2014-12-17T08:26:38
19	Spectrometer Frequency	400.13
20	Spectral Width	8012.8
21	Lowest Frequency	-1535.4
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

^{13}C spectrum of 2g



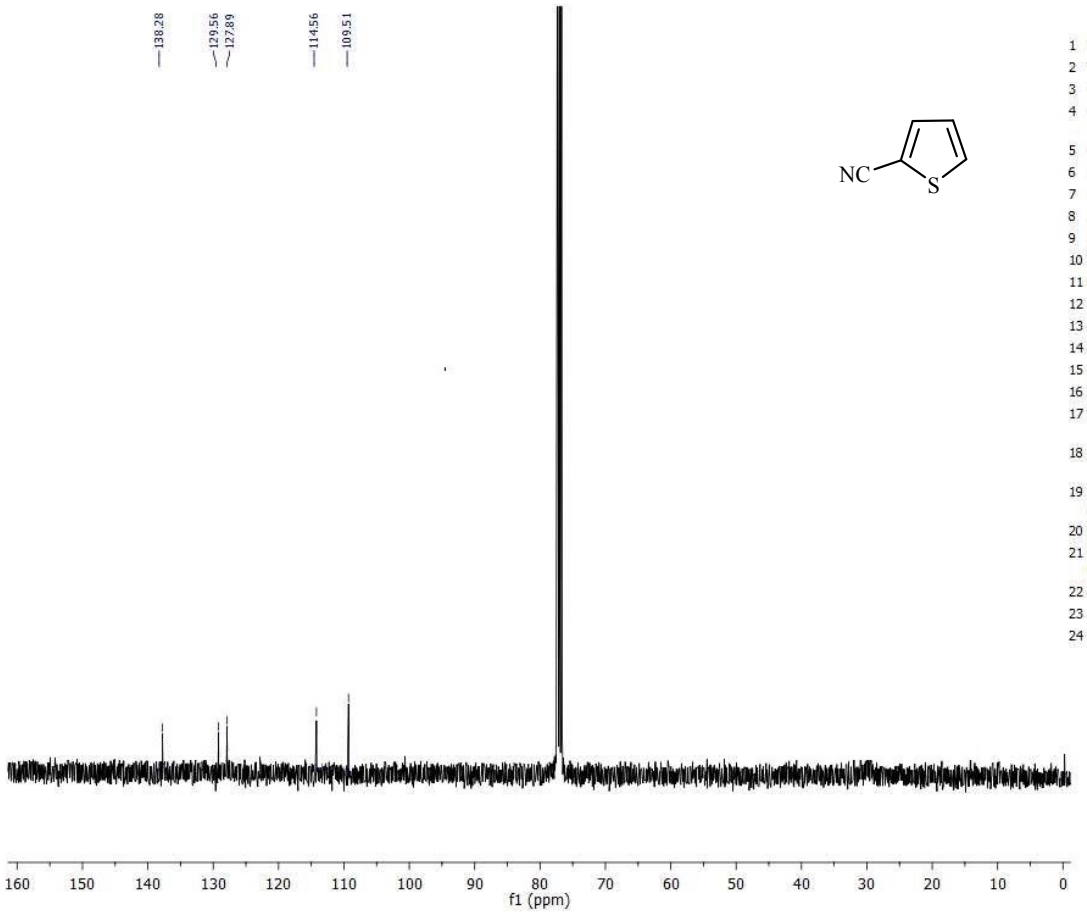
	Parameter	Value
1	Data File Name	C:/ Users/ MADHAVI/ Desktop/ 5/ fid
2	Title	Dec17-2014
3	Comment	13C
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.4
11	Pulse Sequence	zgpg30
12	Number of Scans	802
13	Receiver Gain	199
14	Relaxation Delay	2.0000
15	Pulse Width	9.8000
16	Acquisition Time	1.3631
17	Acquisition Date	2014-12-17T13: 42:00
18	Modification Date	2014-12-17T09: 13:14
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

^{1}H spectrum of 2i



	Parameter	Value
1	Data File Name	C:/ Users/ 3/ fid
2	Title	CN-Thiphene
3	Comment	CN-THIO
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	0.0
11	Pulse Sequence	zgpg30
12	Number of Scans	734
13	Receiver Gain	199
14	Relaxation Delay	2.0000
15	Pulse Width	9.8000
16	Acquisition Time	1.3631
17	Acquisition Date	2015-08-12T12 :12:21
18	Modification Date	2015-08-12T12 :47:11
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

^{13}C spectrum of 2i



	Parameter	Value
1	Data File Name	C:/ Users/ 2/ fid
2	Title	CN-Thiphene
3	Comment	CN-THIO
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	0.0
11	Pulse Sequence	zgpg30
12	Number of Scans	734
13	Receiver Gain	199
14	Relaxation Delay	2.0000
15	Pulse Width	9.8000
16	Acquisition Time	1.3631
17	Acquisition Date	2015-08-12T12:12:21
18	Modification Date	2015-08-12T12:47:11
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

5. References

1. X. He, Y. Shang, Zhiyu Yu, M. Fang, Y. Zhou, G. Han and F. Wu, *J. Org. Chem.*, 2014, **79**, 8882.
2. D. N. K. Reddy, K. B. Chandrasekhar, Y. S. S. Ganesh, B. S. Kumar, R. Adepu and M. Pal, *Tetrahedron Lett.*, 2015, **56**, 4586.
3. C. Tao, F. Liu, Y. Zhu, W. Liu and Z. Cao, *Org. Biomol. Chem.*, 2013, **11**, 3349.
4. S. Enthaler, *Eur. J. Org. Chem.*, 2011, 4760.
5. *Aldrich Advancing Science Handbook of Fine Chemicals,* 2015.
6. F. Drouet, P. Fontaine, G. Masson and J. Zhu, *Synthesis*, 2009, 1370.
7. C. S. Rao, M. Rambabu and P. S. Srinivasan, *Synth. Commun*., 1989, **19**, 1431.