Palladium-Catalyzed C-3 Desulfitative Arylation of Indolizines with Sodium Arylsulfinates and Arylsulfonyl Hydrazides

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Supporting Materials

Content

General Unless stated otherwise, all reactions were performed under a purified N_2 atmosphere. All solvents were purified and dried according to standard methods prior

to use. ^{1}H NMR spectra were recorded at 400 MHz using TMS as internal standard. ^{13}C NMR spectra were recorded at 100 MHz using TMS as internal standard. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), and broad resonances (br). Mass spectroscopy data were collected on an HRMS-EI and HRMS-ESI instrument. Indolizines were prepared according to related literature. [1] Arylsulfinate salts and arylsulfonyl hydrazides were obtained from the corresponding arylsulfonyl chlorides. Other substrates and catalysts were commercially available and used without additional purification.

Typical procedure for the products:

Preparation of C-3 arylation indolizines with arylsulfonyl hydrazides:

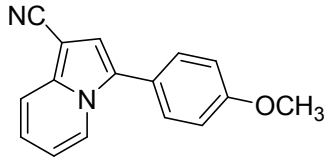
A mixture of indolizines (0.5 mmol), arylsulfonyl hydrazides (0.6 mmol), $Pd(TFA)_2$ (3 mol%), $CuCl_2$ (1.0 mmol) in MTBE/CH_3CN (1.0 ml, v/v = 1:1) solution was stirred at 70 ^{o}C for 6 h. Afterward, the mixture was cooled to room temperature, filtered through a pad of celite. The solvent was evaporated under reduced pressure, and the residue was subjected to flash column chromatography to obtain the desired product.

Preparation of C-3 arylation indolizines with arylsulfinate salts:

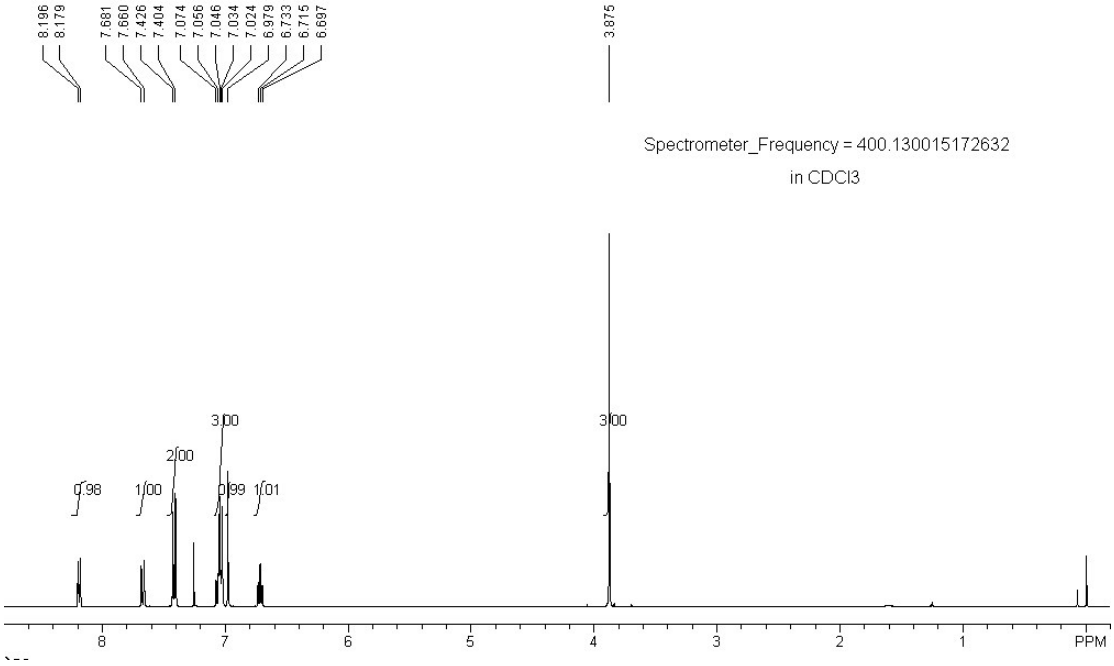
A mixture of indolizines (0.5 mmol), sodium benzenesulfinate (0.6 mmol), $Pd(OAc)_2$ (3 mol%), bipyridine (10 mol%), and TBPA (0.6 mmol) in CH_3CN (1.0 ml) solution was stirred at 100 ^{o}C for 6 h. Afterward, the mixture was cooled to room temperature, filtered through a pad of celite. The solvent was evaporated under reduced pressure, and the residue was subjected to flash column chromatography to obtain the desired product.

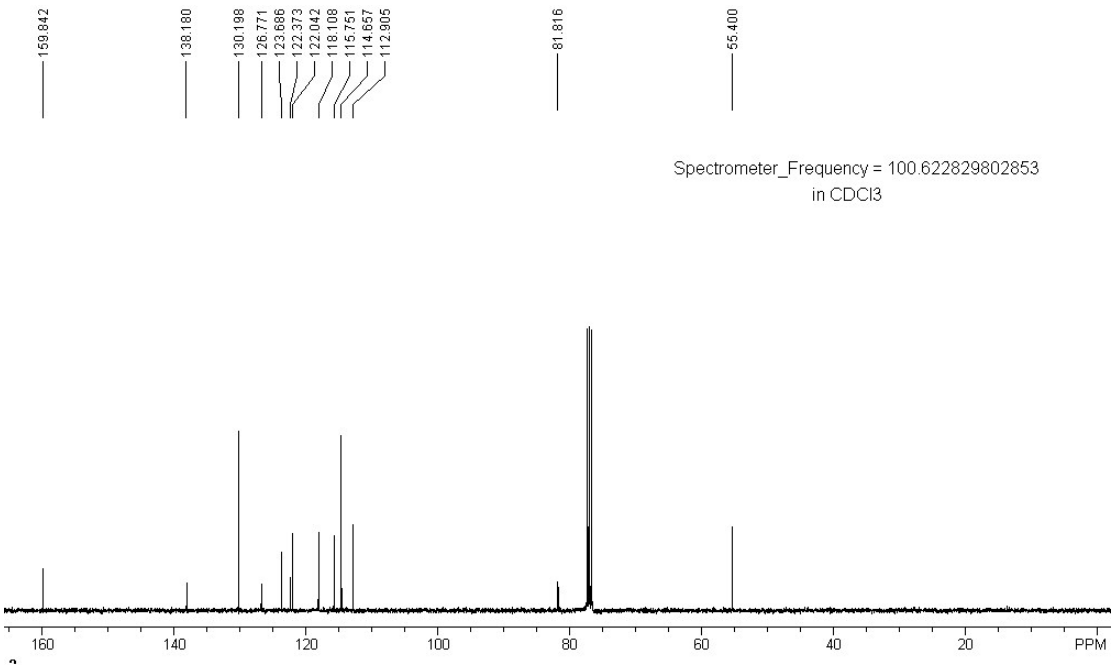
Characterization data of the product

(1) 3-(4-methoxyphenyl)indolizine-1-carbonitrile (T 5-1)

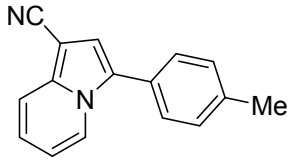


White solid. m.p. 239-241 °C (lit.[1] mp 241-242°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.18 (d, *J* = 7.2 Hz, 1 H), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 7.03-7.09 (m, 3 H), 6.99 (s, 1 H), 6.71 (t, *J* = 7.2 Hz, 1 H), 3.87 (s, 3 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 159.7, 138.1, 130.3, 126.8, 123.6, 122.5, 122.0, 118.2, 115.6, 114.8, 112.8, 81.7, 55.3. HRMS (EI) Calcd for $C_{16}H_{12}N_2O$ (M^+) 248.0950, Found 248.0951.

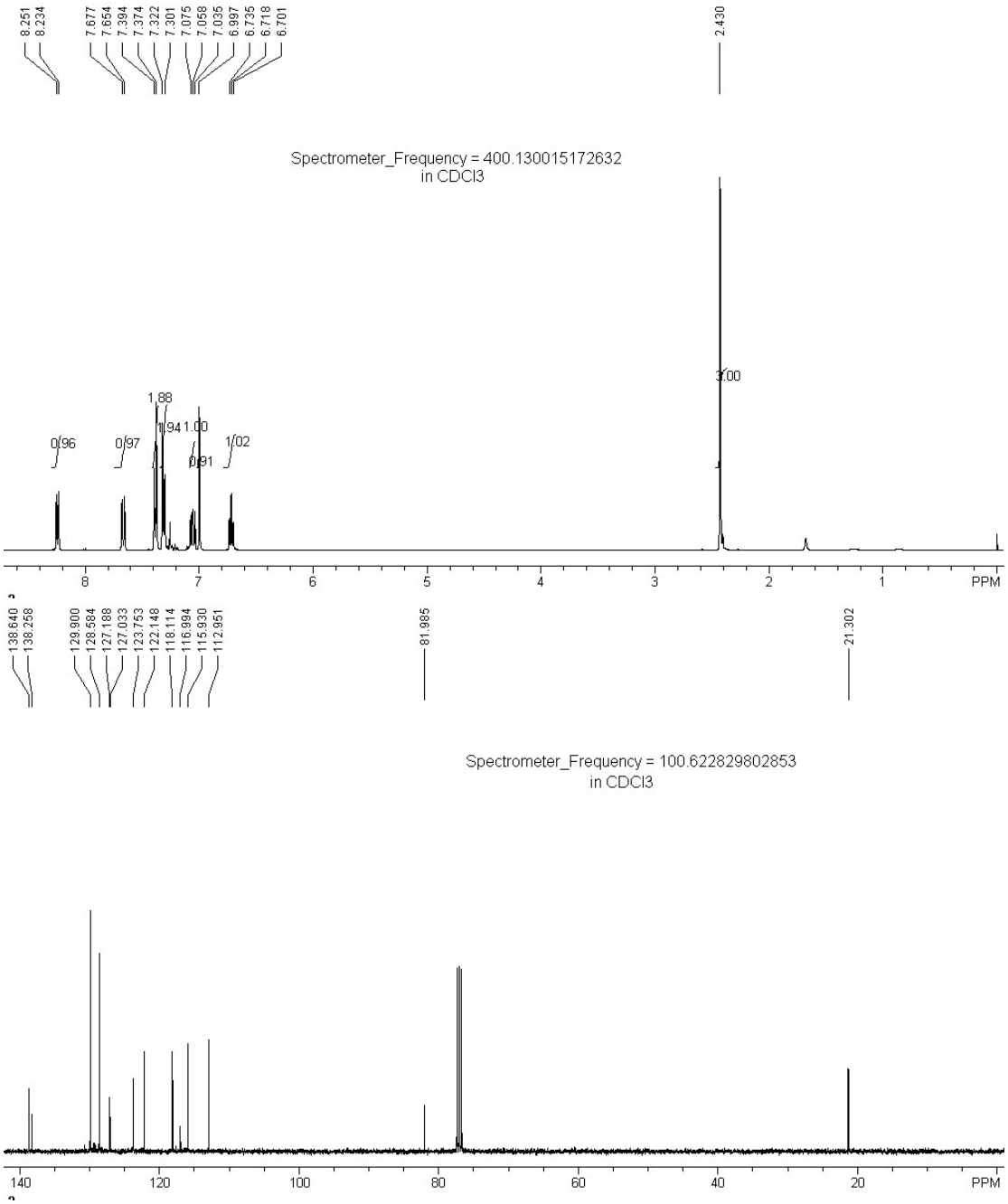




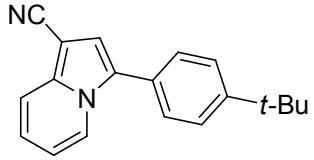
(2) 3-p-tolylindolizine-1-carbonitrile (T 5-2)



White solid. m.p. 233-235 ^{o}C (lit.[1] mp 232-233°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.25 (d, *J* = 7.2 Hz, 1 H), 7.66 (d, *J* = 9.2 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.07 (t, *J* = 8.0 Hz, 1 H), 6.99 (s, 1 H), 6.71 (t, *J* = 7.2 Hz, 1 H), 2.42 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.3, 129.8, 128.5, 127.2, 126.9, 123.7, 122.1, 118.2, 117.0, 115.8, 113.1, 82.2, 21.4. HRMS (EI) Calcd for $C_{16}H_{12}N_2$ (M^+) 232.1000, Found 232.0997.

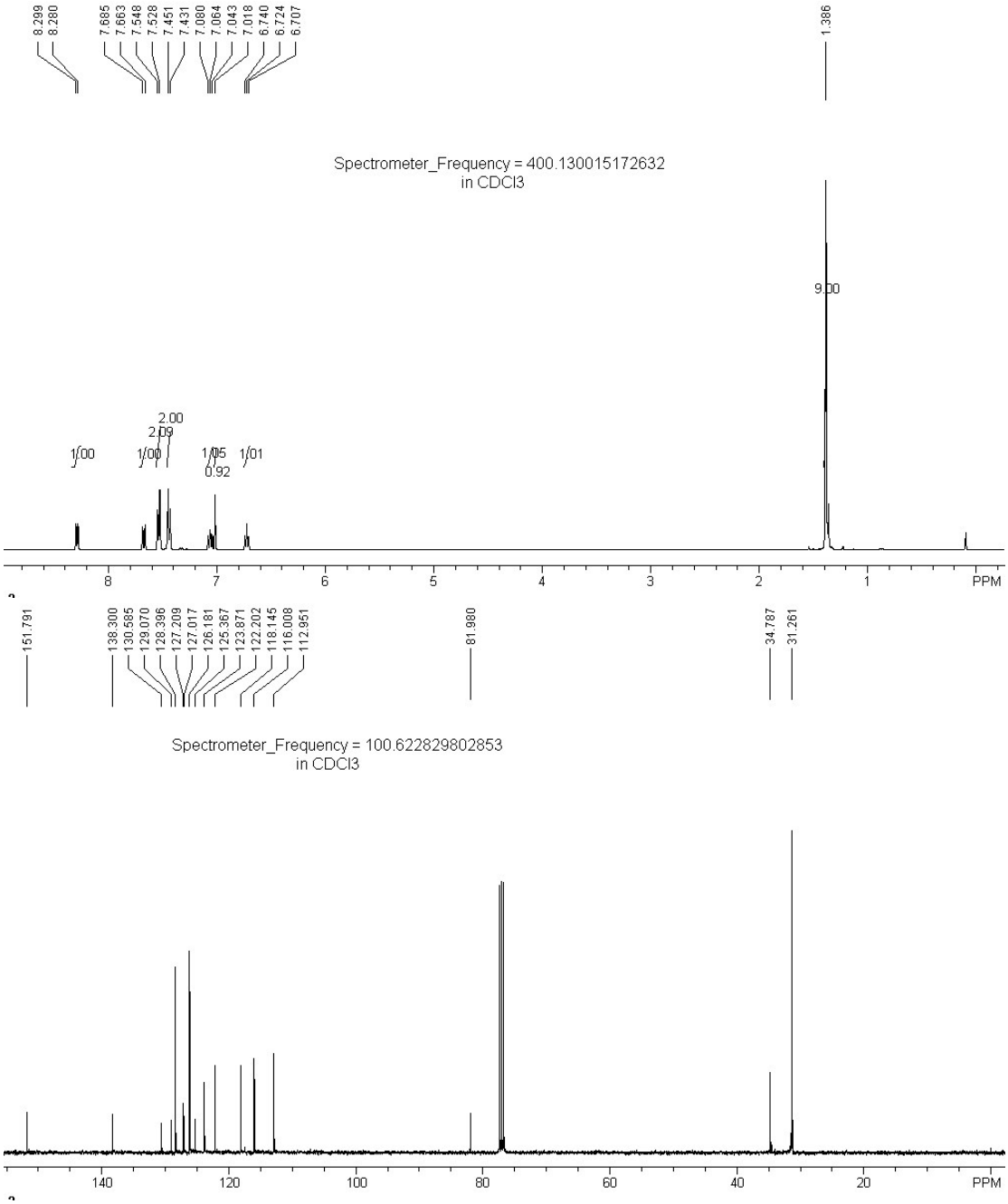


(3) 3-(4-tert-butylphenyl)indolizine-1-carbonitrile (T 5-3)

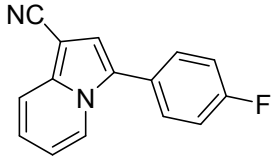


White solid. m.p. 235-237 ^{o}C (lit.[1] mp 236-238°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.28 (d, *J* = 7.2 Hz, 1 H), 7.67 (d, *J* = 8.4 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 7.06 (t, *J* = 7.6 Hz, 1 H), 7.01 (s, 1 H), 6.71 (t, *J* = 6.8 Hz, 1 H), 1.38 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 138.4, 130.5, 129.2, 128.5, 127.3, 127.0, 126.1, 125.3, 123.8, 122.2, 118.0, 116.1, 113.1, 82.0, 34.7,

31.2. HRMS (ESI) Calcd for $C_{19}H_{18}N_2$ (M^+) 274.1470, Found 274.1468.

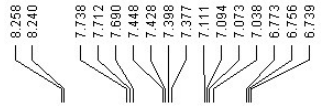


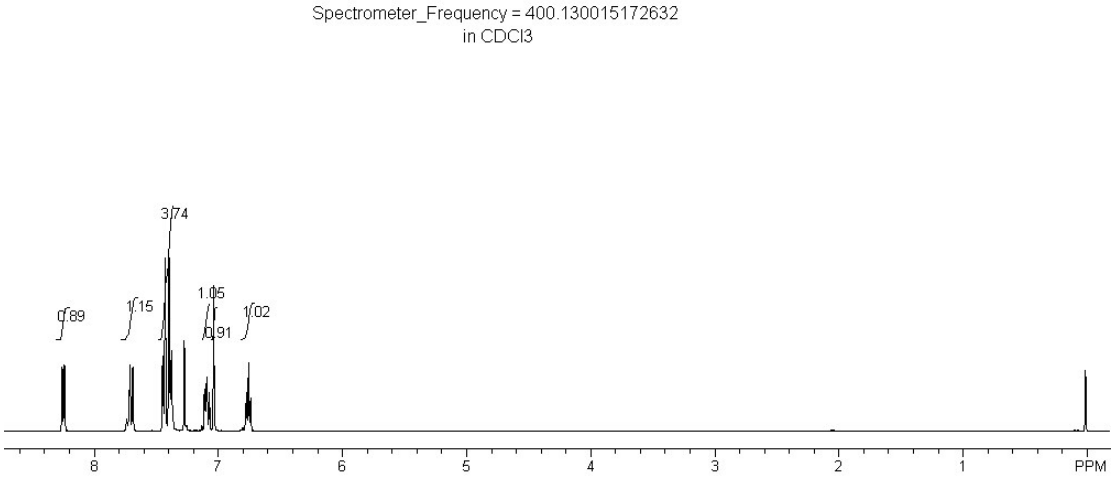
(4) 3-(4-fluorophenyl)indolizine-1-carbonitrile (T 5-4)

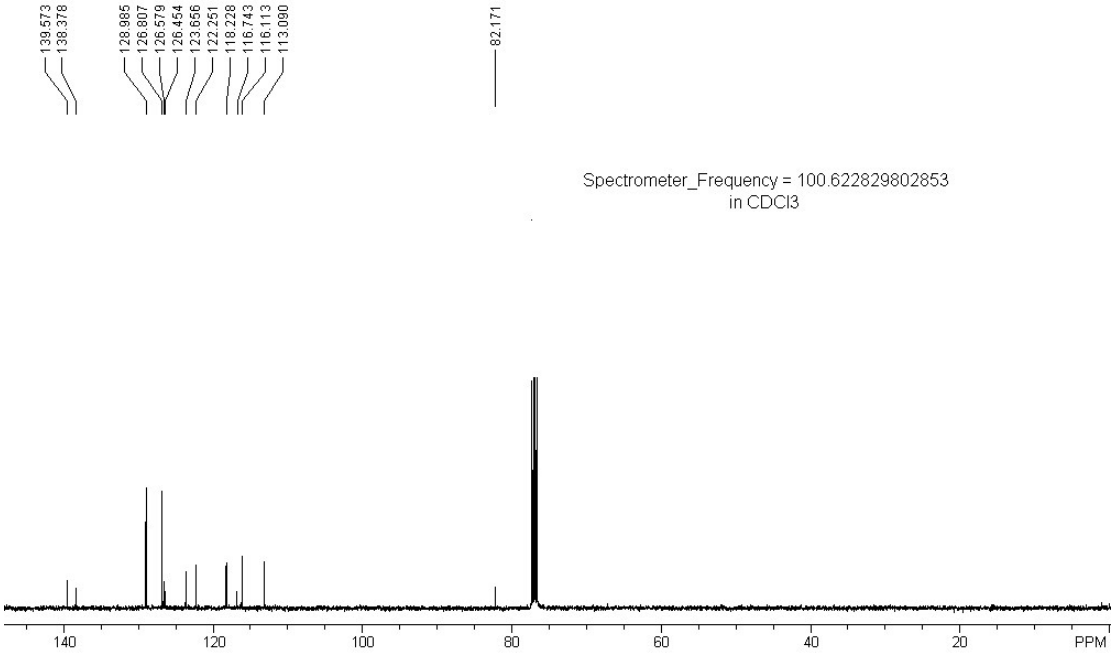


White solid. m.p. 183-185 ^oC. ^1H NMR (400 MHz, $CDCl_3$, TMS) 8.24 (d, J = 7.6 Hz, 1 H), 7.72 (t, J = 9.2 Hz, 1 H), 7.37-7.45 (m, 4 H), 7.08 (t, J = 7.2 Hz, 1 H), 7.03 (s, 1 H), 6.75 (t, J = 7.2 Hz, 1 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 139.7, 138.3, 129.4, 126.7, 126.6, 126.4, 123.6, 122.3, 118.3, 116.7, 116.0, 113.2, 82.2. HRMS (EI)

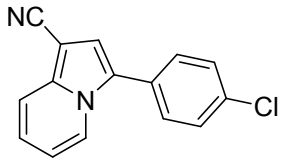
Calcd for $C_{15}H_9FN_2$ (M^+) 236.0750, Found 236.0753.





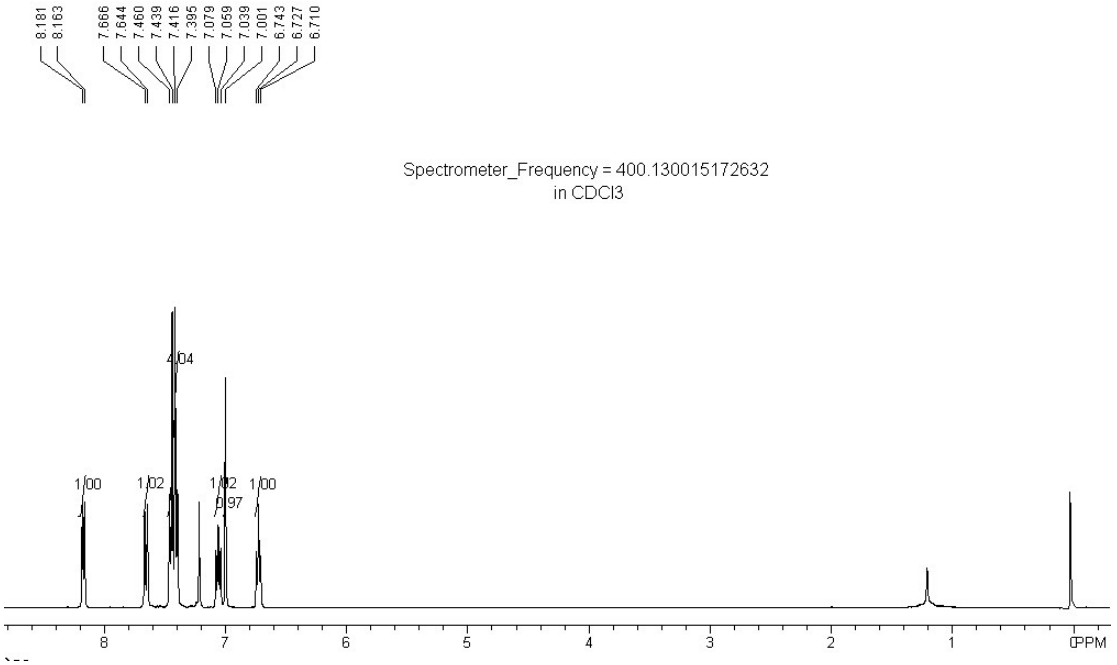


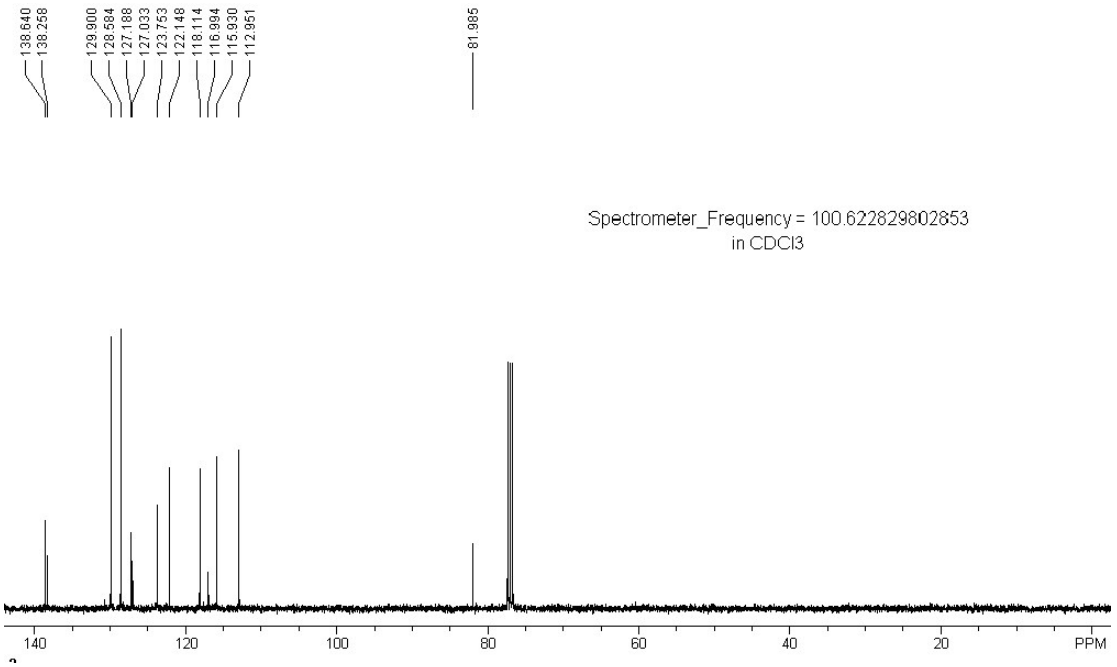
(5) 3-(4-chlorophenyl)indolizine-1-carbonitrile (T 5-5)



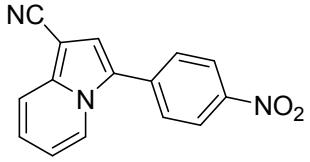
Yellow solid. m.p. 244-245 °C (lit.[1] mp 244-246°C). ^{1}H NMR (400 MHz, $CDCl_3$,

TMS) δ 8.18 (d, *J* = 7.6 Hz, 1 H), 7.64 (d, *J* = 8.4 Hz, 1 H), 7.40-7.47 (m, 4 H), 7.07 (t, *J* = 8.4 Hz, 1 H), 7.00 (s, 1 H), 6.72 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.3, 129.8, 128.5, 127.2, 127.1, 123.7, 122.2, 118.1, 117.1, 115.8, 113.2, 82.1. HRMS (EI) Calcd for $C_{15}H_9N_2Cl$ (M^+) 252.0454, Found 252.0452.

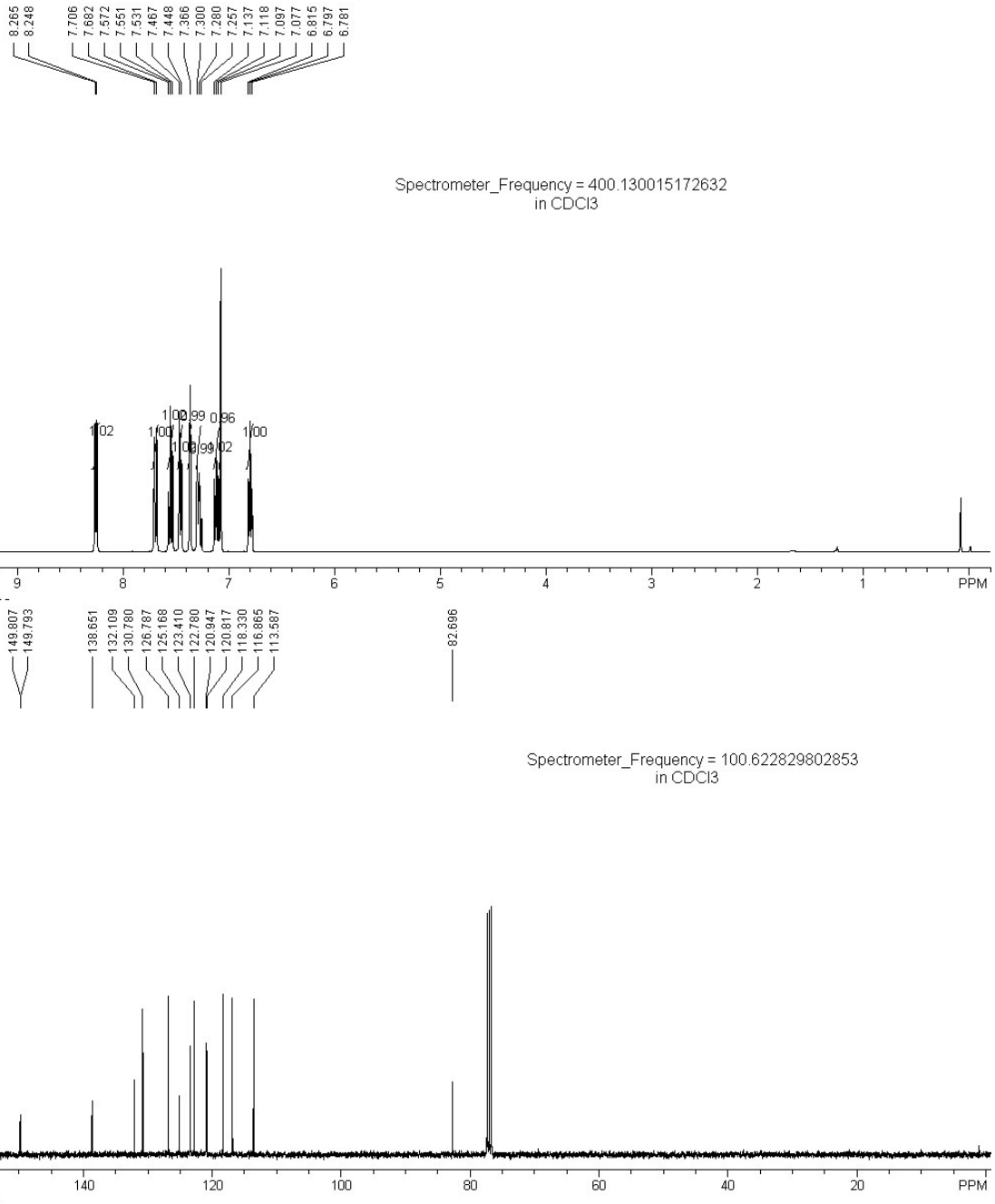




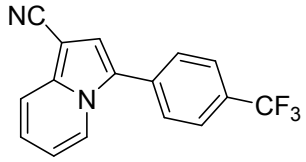
(6) 3-(4-nitrophenyl)indolizine-1-carbonitrile (T 5-6)



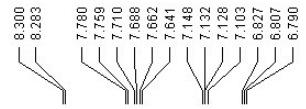
Yellow solid. m.p. 222-224 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.27 (d, J = 6.8 Hz, 1 H), 7.68 (d, J = 9.2 Hz, 1 H), 7.54 (t, J = 8.8 Hz, 1 H), 7.45 (d, J = 7.6 Hz, 1 H), 7.36 (s, 1 H), 7.27 (t, J = 8.4 Hz, 1 H), 7.11 (t, J = 8.4 Hz, 1 H), 7.07 (s, 1 H), 7.80 (t, J = 7.2 Hz, 1 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 149.8, 149.7, 138.6, 132.1, 131.7, 126.8, 125.3, 123.3, 122.9, 120.8, 120.7, 118.4, 116.9, 113.5, 82.8. HRMS (EI) Calcd for $C_{15}H_9N_3O_2$ (M^+) 263.0695, Found 263.0692.

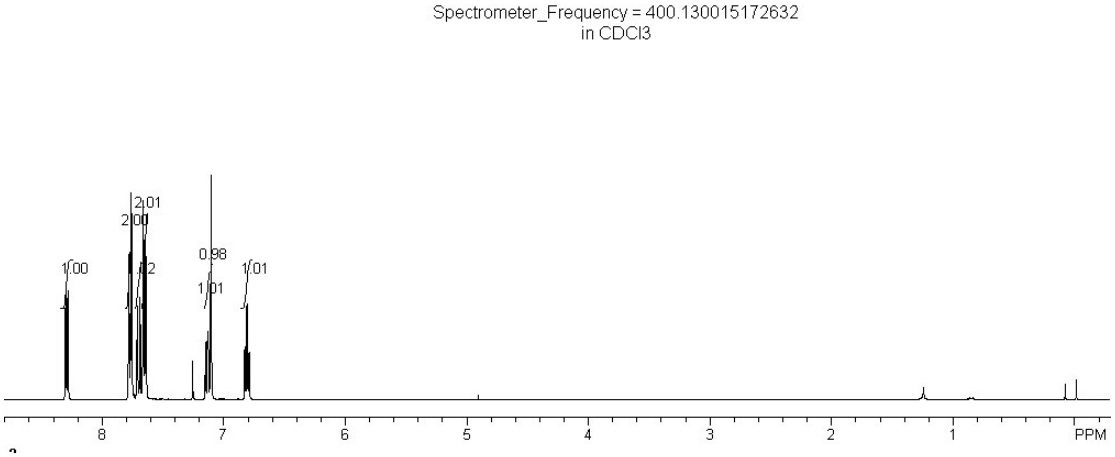


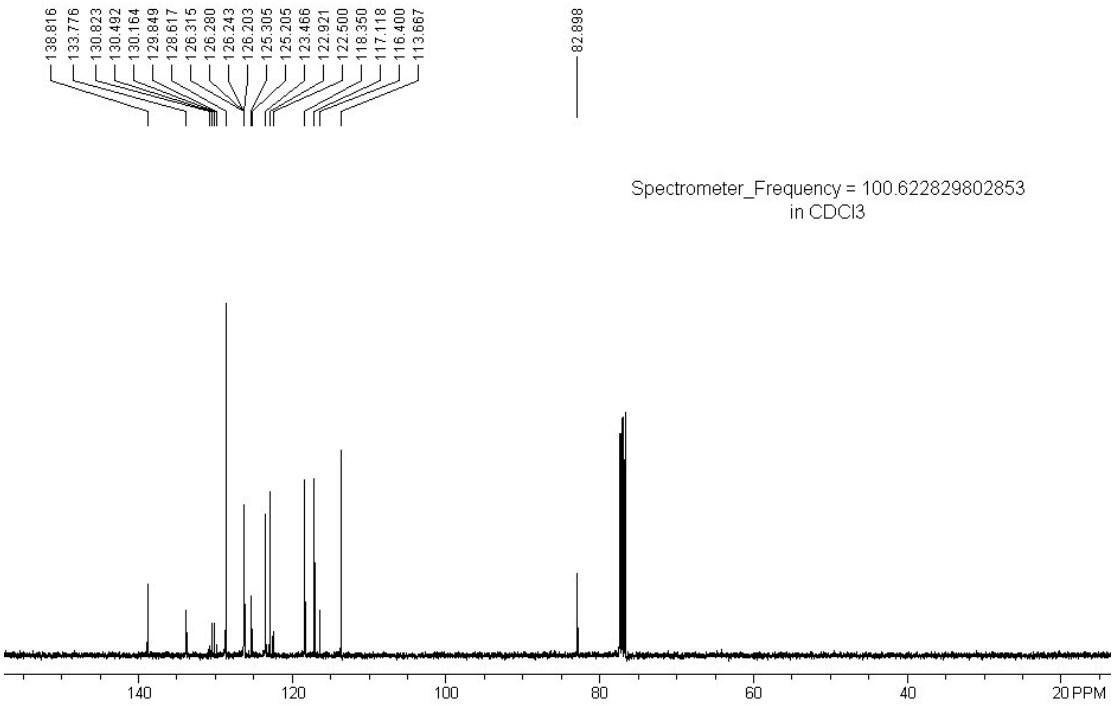
(7) 3-(4-(trifluoromethyl)phenyl)indolizine-1-carbonitrile (T 5-7)



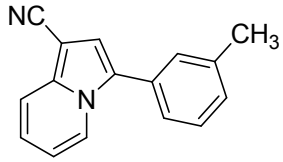
White solid. m.p. 271-272 °C (lit.[1] mp 269-270°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.28 (d, *J* = 7.2 Hz, 1 H), 7.76 (d, *J* = 8.8 Hz, 2 H), 7.67 (d, *J* = 8.8 Hz, 1 H), 7.64 (d, *J* = 8.8 Hz, 2 H), 7.14 (t, *J* = 6.8 Hz, 1 H), 7.10 (s, 1 H), 6.82 (t, *J* = 6.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 133.8, 130.4 (q, *J* = 31 Hz), 128.6, 126.4(q, *J* = 4.0 Hz), 125.4, 125.2, 123.4, 122.9, 122.6, 118.3, 117.0, 116.3, 113.7, 82.8. HRMS (EI) Calcd for $C_{16}H_9N_2F_3$ (M^+) 286.0718, Found 286.0722.



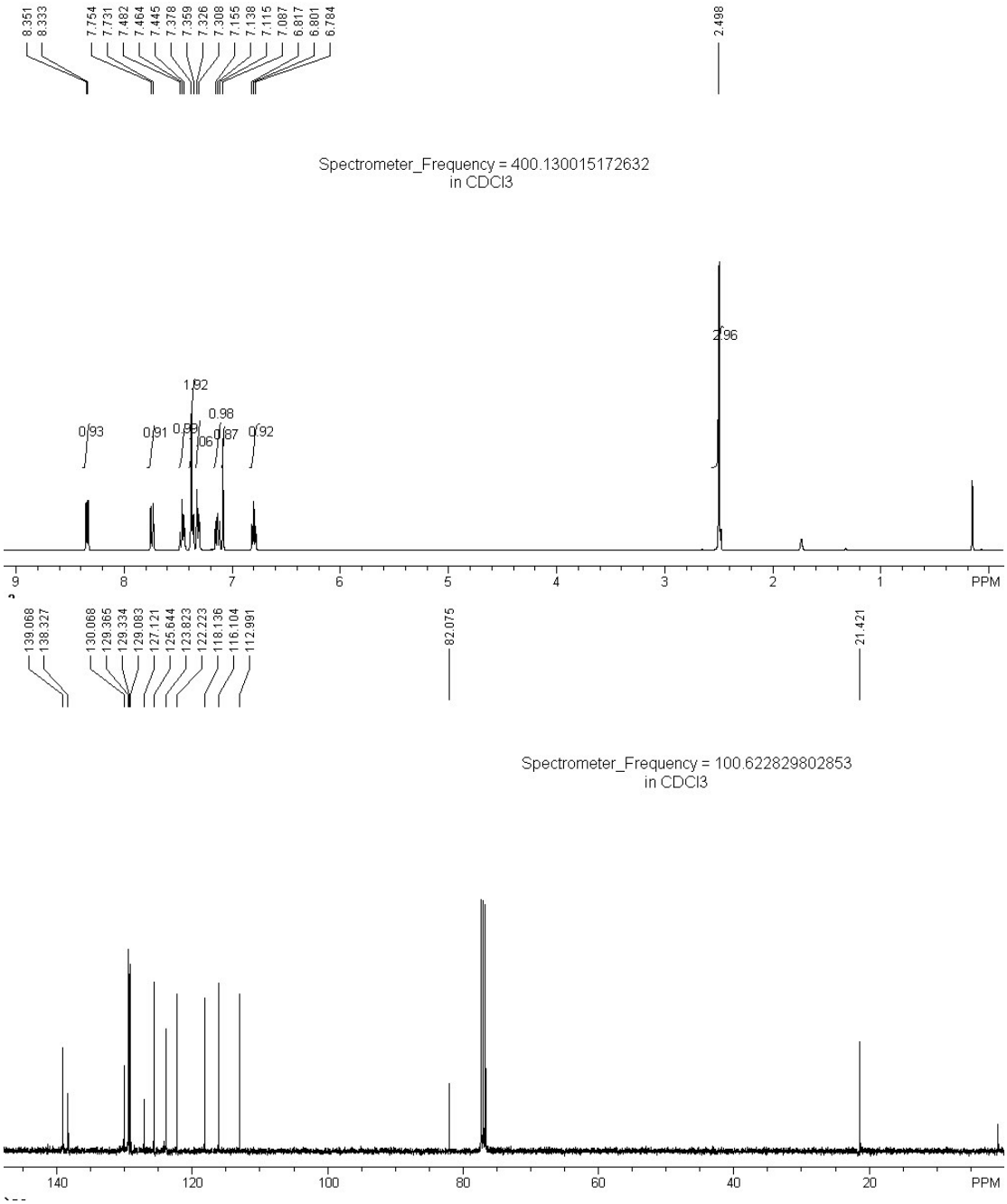




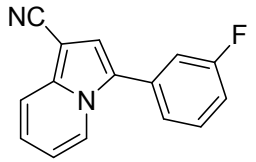
(8) 3-m-tolylindolizine-1-carbonitrile (T 5-8)



White solid. m.p. 239-242 °C (lit.[1] mp 239-241°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.33 (d, *J* = 7.2 Hz, 1 H), 7.75 (d, *J* = 8.8 Hz, 1 H), 7.45 (d, *J* = 7.6 Hz, 1 H), 7.31-7.39 (m, 3 H), 7.14 (t, *J* = 8.0 Hz, 1 H), 7.08 (s, 1 H), 6.81 (d, *J* = 7.2 Hz, 1 H), 2.51 (s, 3 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 139.2, 138.2, 130.1, 129.5, 129.3, 129.0, 127.2, 125.6, 123.7, 118.2, 116.1, 113.1, 82.0, 21.5. HRMS (EI) Calcd for $C_{16}H_{12}N_2$ (M^+) 232.1000, Found 232.0995.

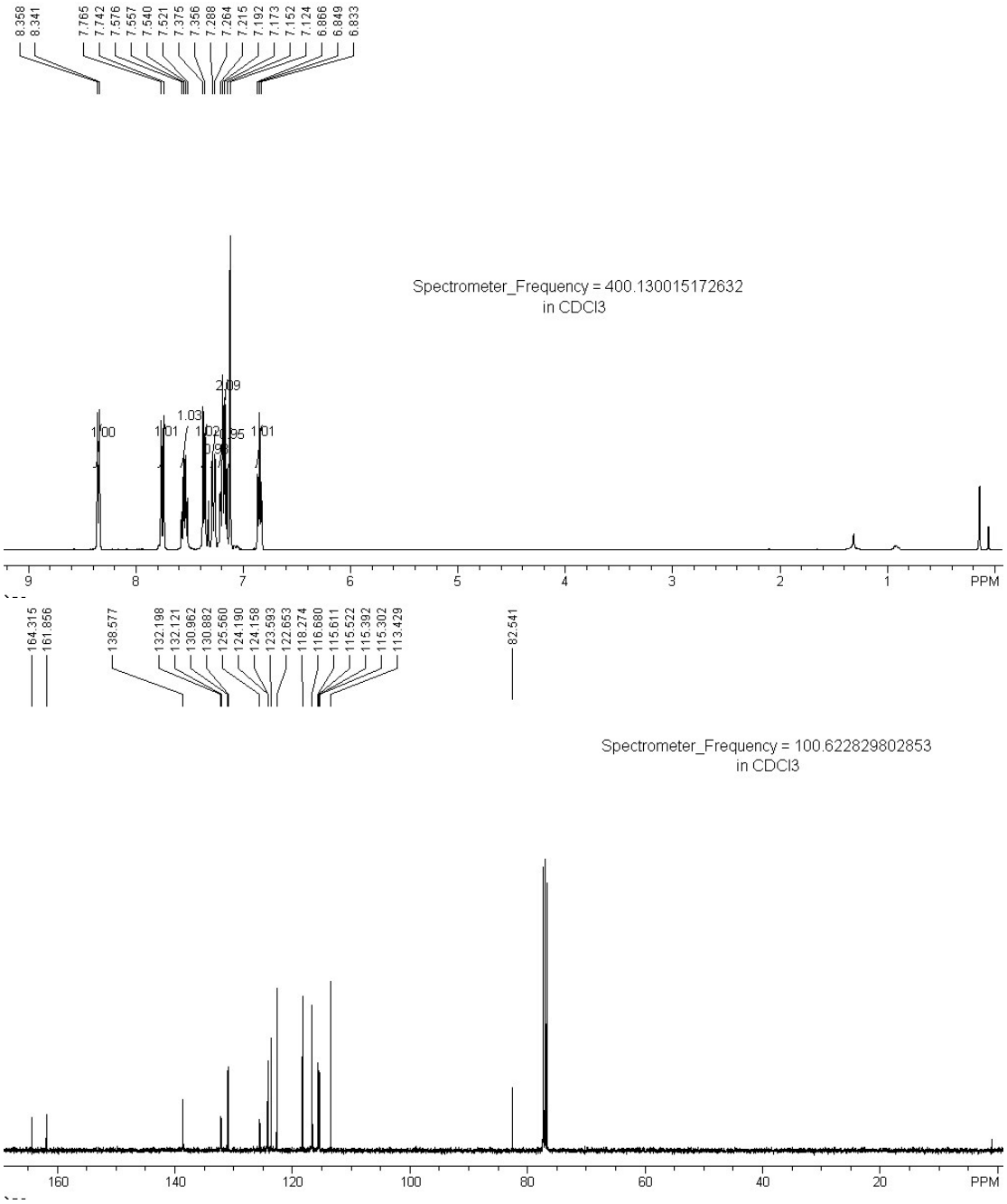


(9) 3-(3-fluorophenyl)indolizine-1-carbonitrile (T 5-9)

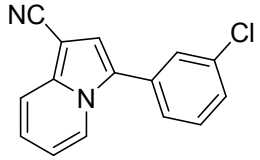


White solid. m.p. 262-264 ^{o}C (lit.[1] mp 261-262°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.36 (d, *J* = 7.2 Hz, 1 H), 7.76 (d, *J* = 8.8 Hz, 1 H), 7.52-7.59 (m, 1 H), 7.38 (d, *J* = 7.2 Hz, 1 H), 7.27 (d, *J* = 9.2 Hz, 1 H), 7.15-7.21 (m, 2 H), 7.13 (s, 1 H), 6.84 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 164.4, 161.8, 138.5, 132.1 (d, *J* = 7.6 Hz), 130.8(d, *J* = 8.0 Hz), 125.6, 124.1(d, *J* = 3.4 Hz), 123.5,

122.6, 118.4, 116.8, 115.5(d, *J* = 8.8 Hz), 115.2(d, *J* = 8.8 Hz), 113.5, 82.4. HRMS (EI) Calcd for $C_{15}H_9N_2F$ (M^+) 236.0750, Found 236.0749.

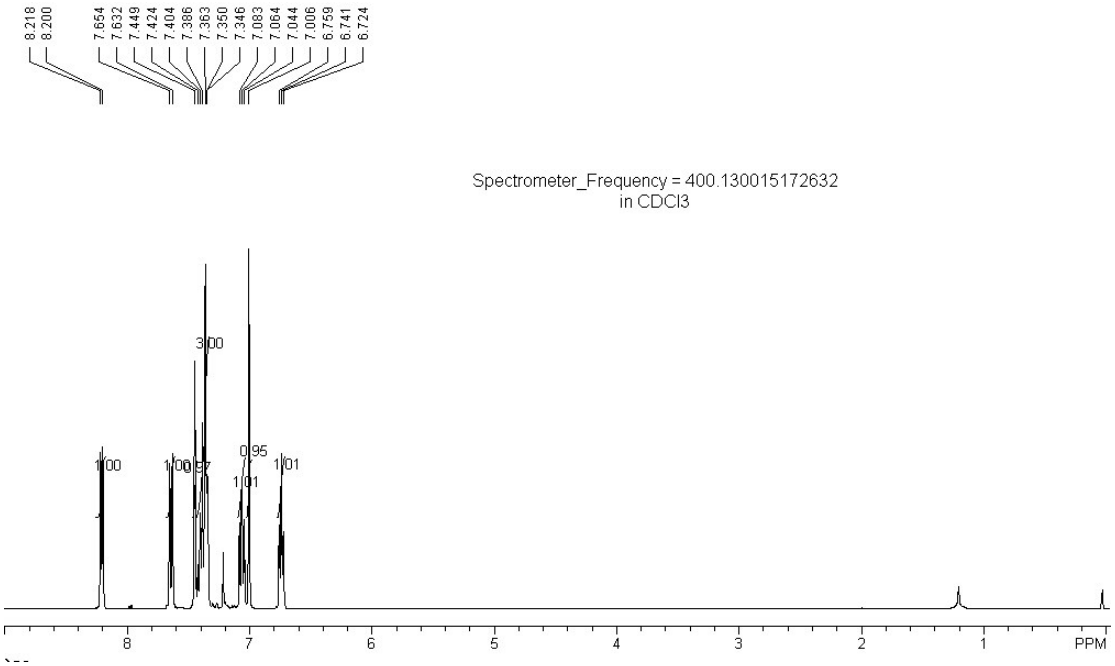


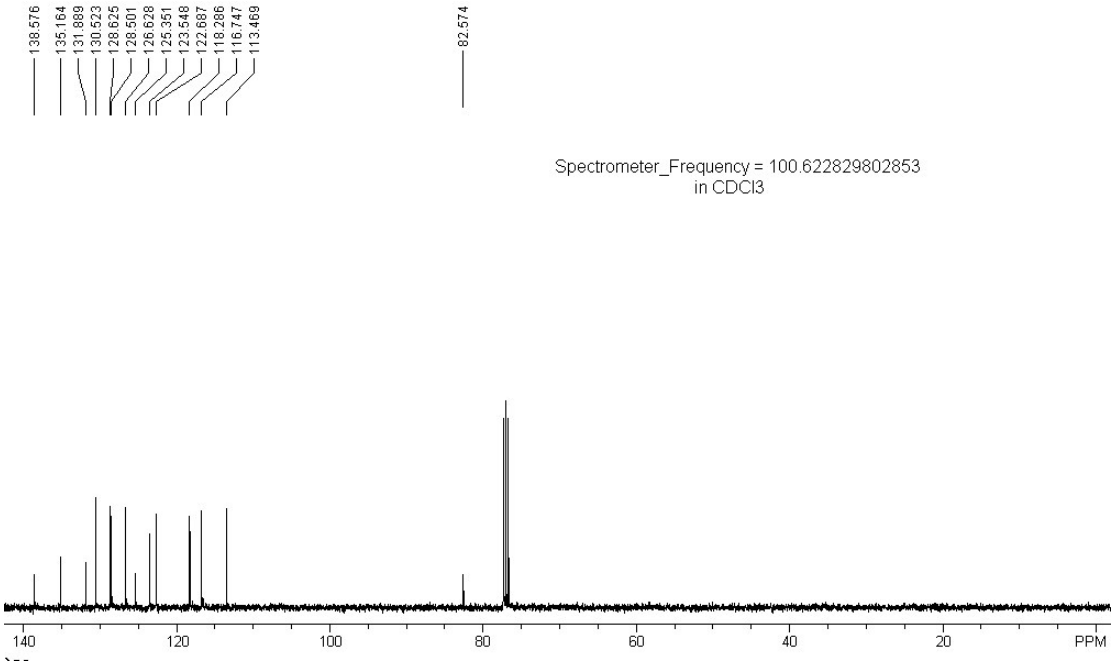
(10) 3-(3-chlorophenyl)indolizine-1-carbonitrile (T 5-10)



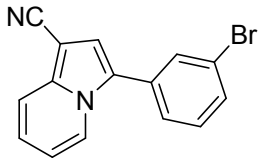
Yellow solid. m.p. 246-247 ^oC (lit.[1] mp 245-246°C). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.22 (d, *J* = 7.2 Hz, 1 H), 7.63 (d, *J* = 8.4 Hz, 1 H), 7.14 (s, 1 H), 7.07 (t, *J* = 8.4 Hz, 1 H), 7.02 (s, 1 H), 6.75 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100MHz,

$CDCl_3$) δ 138.7, 135.2, 131.8, 130.4, 128.7, 128.5, 126.5, 125.3, 123.5, 122.6, 118.4, 116.6, 113.4, 82.7. HRMS (EI) Calcd for $C_{15}H_9N_2Cl$ (M^+) 252.0454, Found 252.0457.



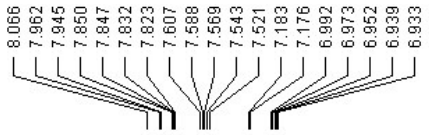


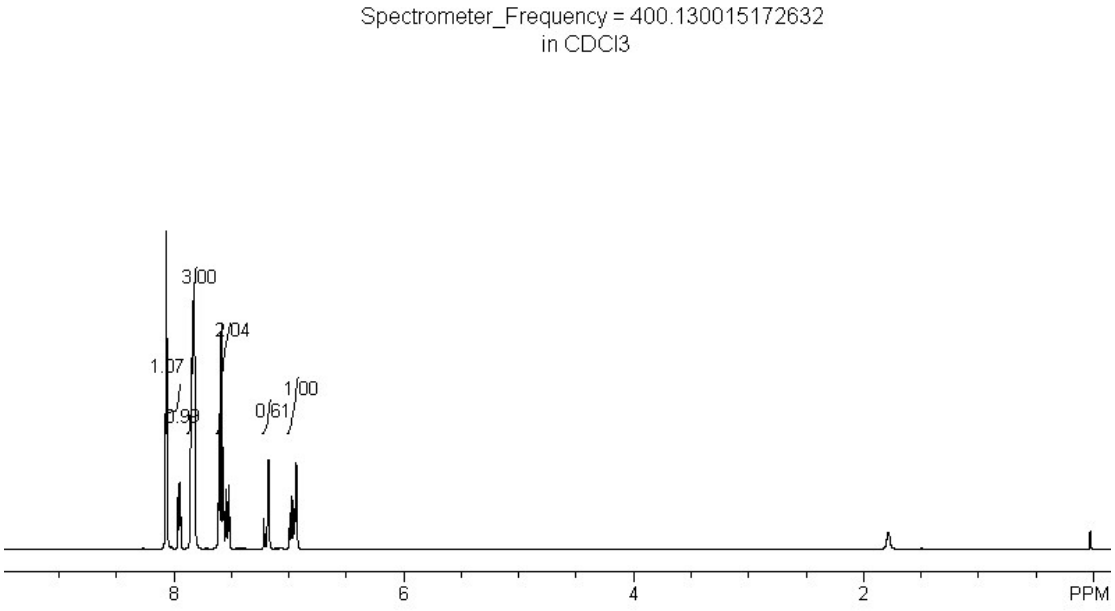
(11) 3-(3-bromophenyl)indolizine-1-carbonitrile (T 5-11)

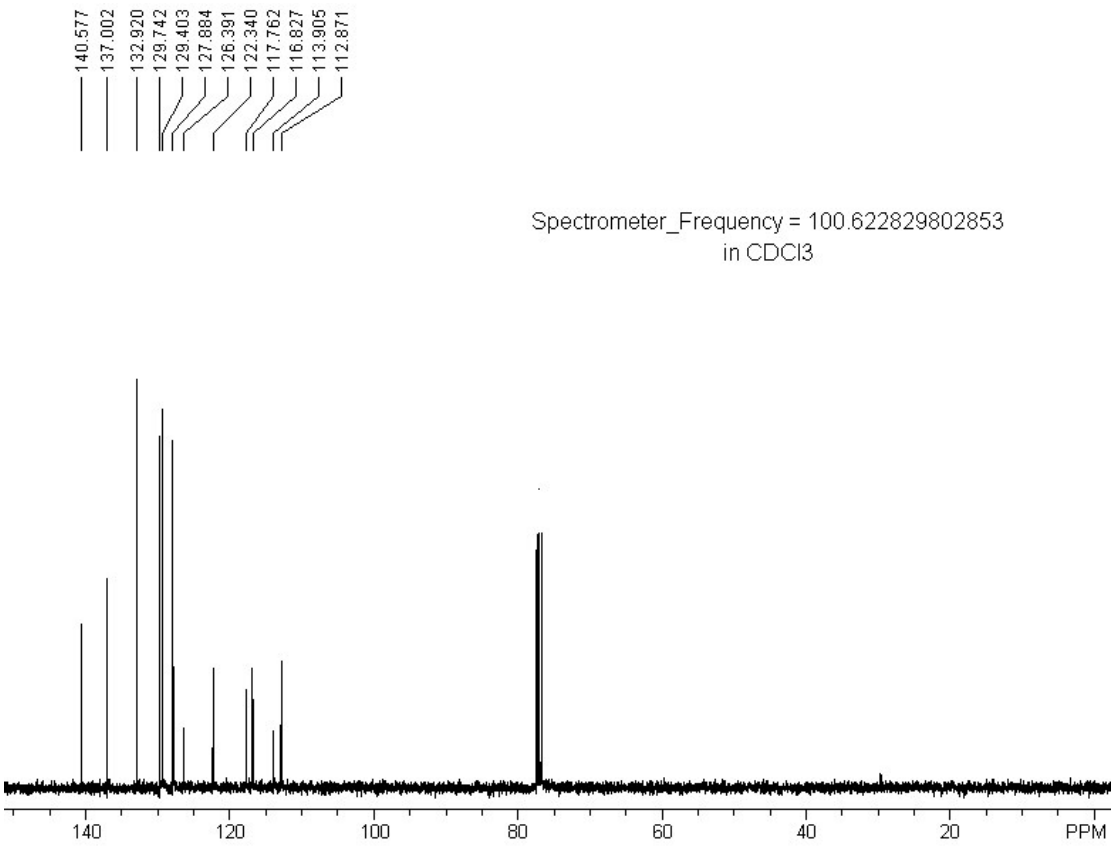


White solid. m.p. 208-209 ^oC. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02 (s, 1 H), 7.95 (d, *J* = 7.2 Hz, 1 H), 7.81-7.85 (m, 3 H), 7.51-7.61 (m, 2 H), 7.26-7.30 (m, 2

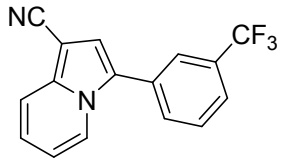
H), 7.17 (d, *J* = 7.2 Hz, 1 H), 6.92-6.99 (m, 1 H). ^{13}C NMR (100MHz, $CDCl_3$) δ140.7, 137.1, 132.8, 129.7, 129.3, 127.8, 126.3, 122.2, 117.9, 116.7, 113.8, 112.9, 82.7. HRMS (EI) Calcd for $C_{15}H_9BrN_2$ (M^+) 295.9949, Found 295.9951.



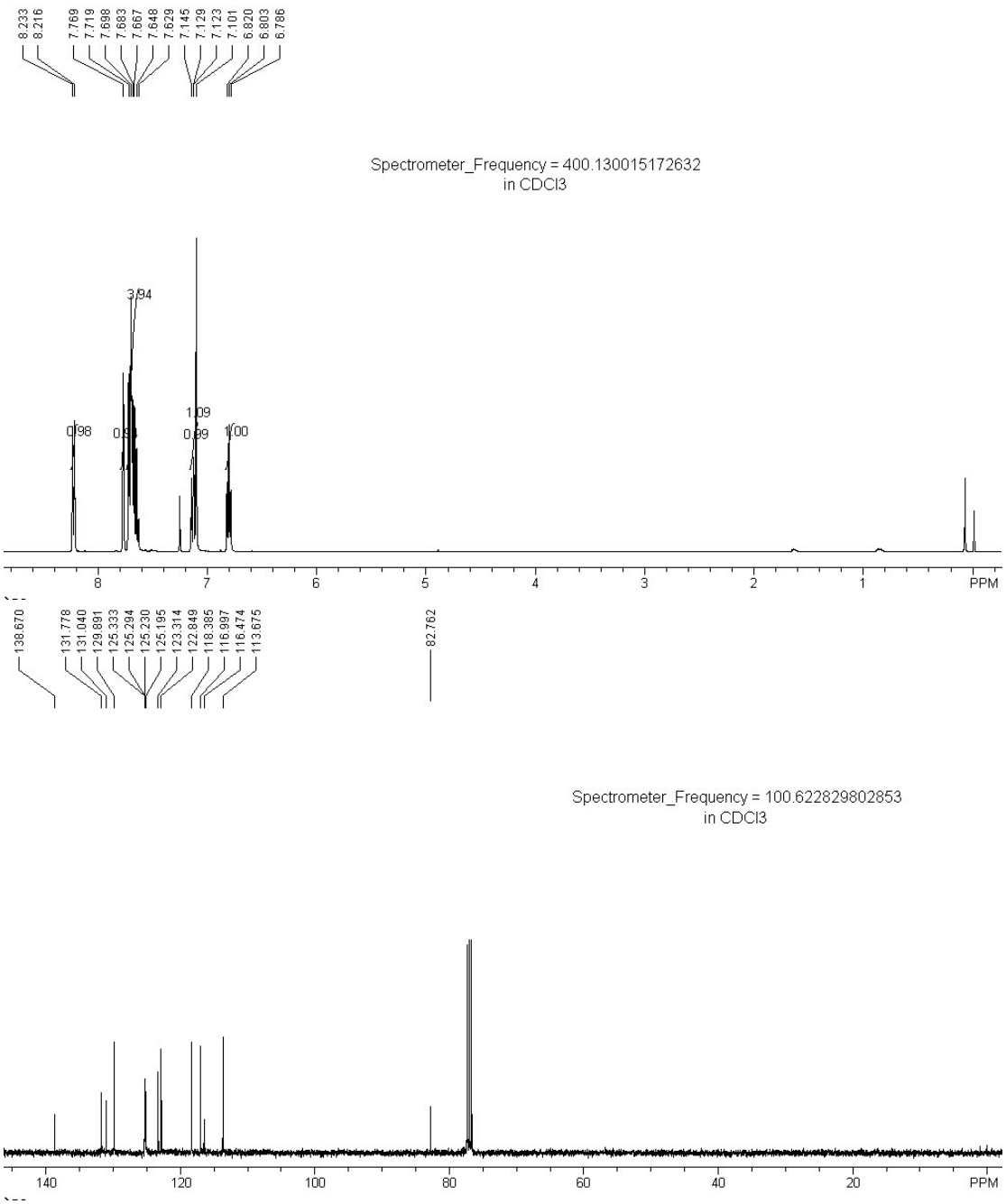




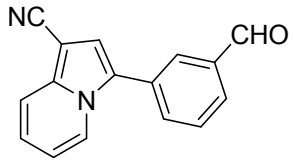
(12) 3-(3-(trifluoromethyl)phenyl)indolizine-1-carbonitrile (T 5-12)



White solid. m.p. 263-264 ^{o}C (lit.[1] mp 262-264°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.21 (d, *J* = 6.8 Hz, 1 H), 7.73 (s, 1 H), 7.63-7.71 (m, 4 H), 7.14 (t, *J* = 6.8 Hz, 1 H), 7.09 (s, 1 H), 6.81 (t, *J* = 6.8 Hz, 1 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 138.8, 131.7, 131.1, 129.8, 125.4(q, *J* = 4.8 Hz), 123.4, 122.8, 118.5, 117.1, 116.4, 113.7, 82.7. HRMS (EI) Calcd for $C_{16}H_9N_2F_3$ (M^+) 286.0718, Found 286.0722.

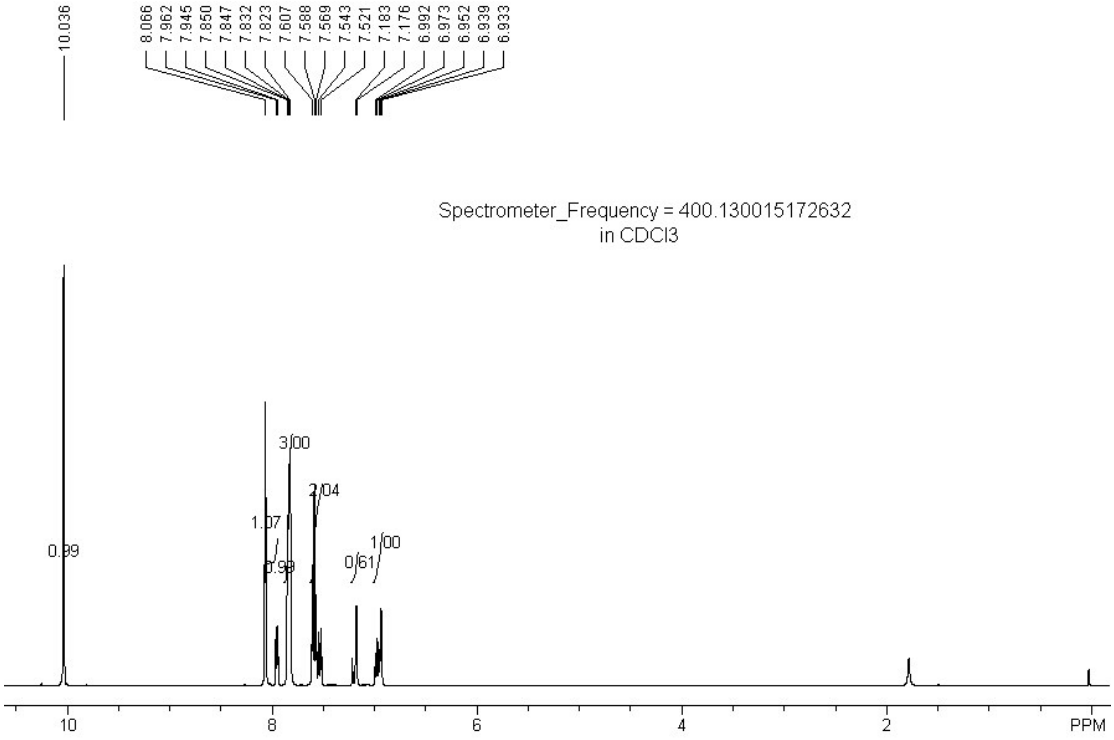


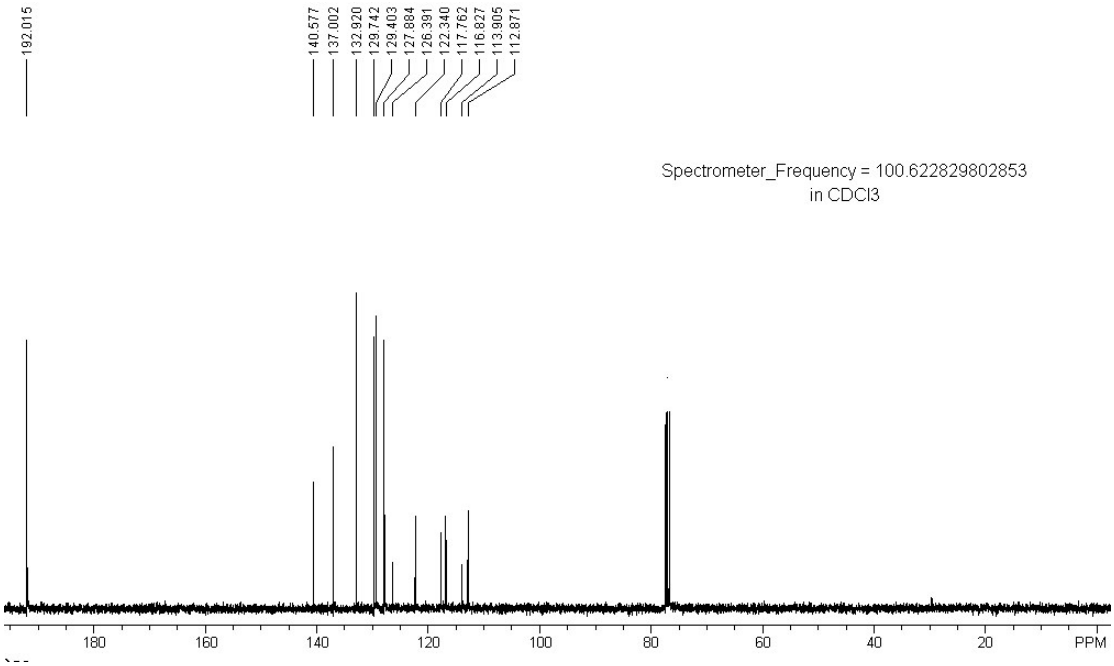
(13) 3-(3-formylphenyl)indolizine-1-carbonitrile (T 5-13)



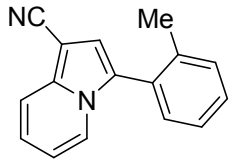
White solid. m.p. 185-186 ^{o}C (lit.[1] mp 183-186°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ10.05 (s, 1 H), 8.02 (s, 1 H), 7.95 (d, J = 7.2 Hz, 1 H), 7.81-7.85 (m, 3 H), 7.51-7.61 (m, 2 H), 7.26-7.30 (m, 2 H), 7.17 (d, J = 7.2 Hz, 1 H), 6.92-6.99 (m, 1 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 192.1, 140.7, 137.1, 132.8, 129.7, 129.3, 127.8,

126.3, 122.2, 117.9, 116.7, 113.8, 112.9, 82.7. HRMS (EI) Calcd for $C_{16}H_{10}N_2O$ (M^+) 246.0793, Found 246.0790.

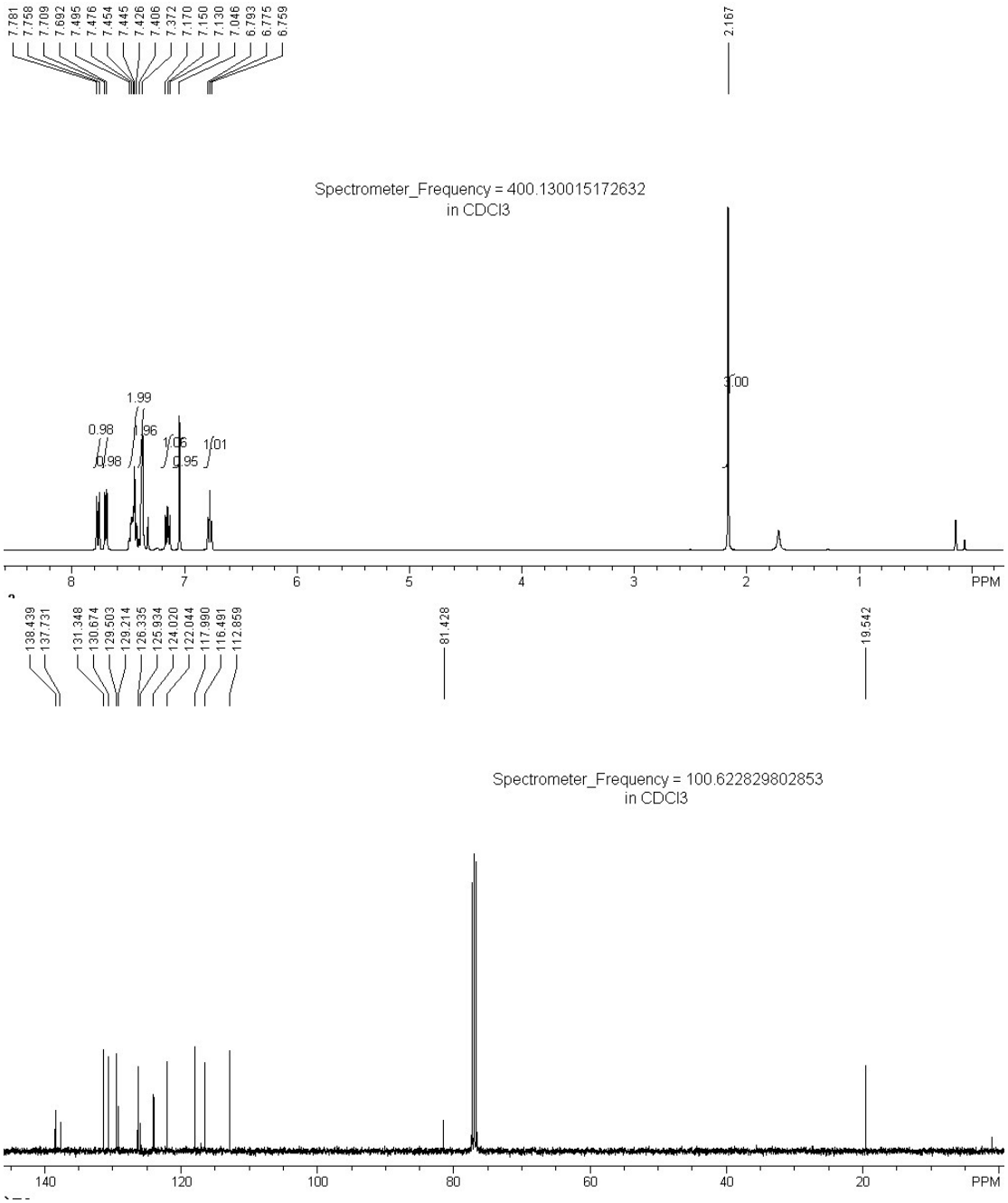




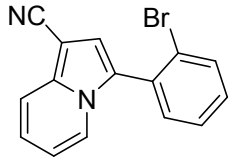
(14) 3-o-tolylindolizine-1-carbonitrile (T 5-14)



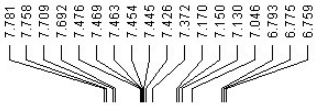
White solid. m.p. 211-213 °C (lit.[1] mp 209-210°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.76 (d, *J* = 8.8 Hz, 1 H), 7.71 (d, *J* = 6.8 Hz, 1 H), 7.37-7.51 (m, 4 H), 7.16 (t, *J* = 8.0 Hz, 1 H), 7.06 (s, 1 H), 6.79 (t, *J* = 6.8 Hz, 1 H), 2.16 (s, 3 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 138.5, 137.4, 131.4, 130.7, 129.6, 129.3, 126.3, 125.8, 124.1, 122.0, 118.1, 116.4, 112.8, 81.3, 19.6. HRMS (EI) Calcd for $C_{16}H_{12}N_2$ (M^+) 232.1000, Found 232.1004.

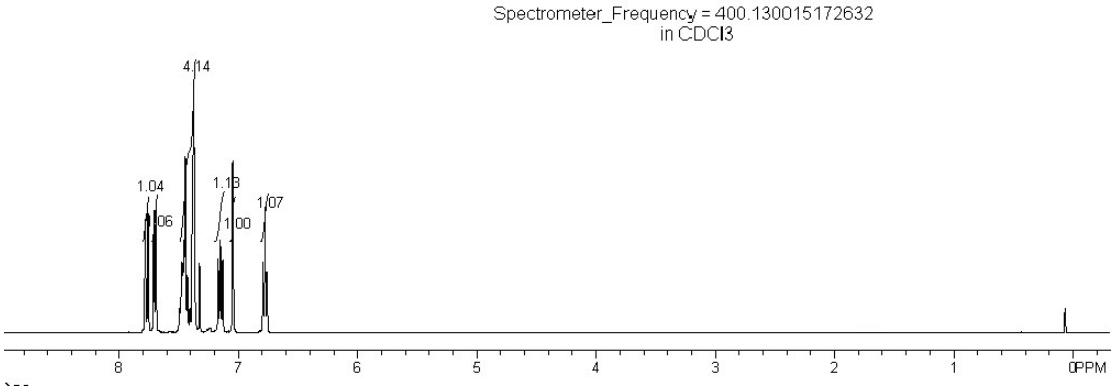


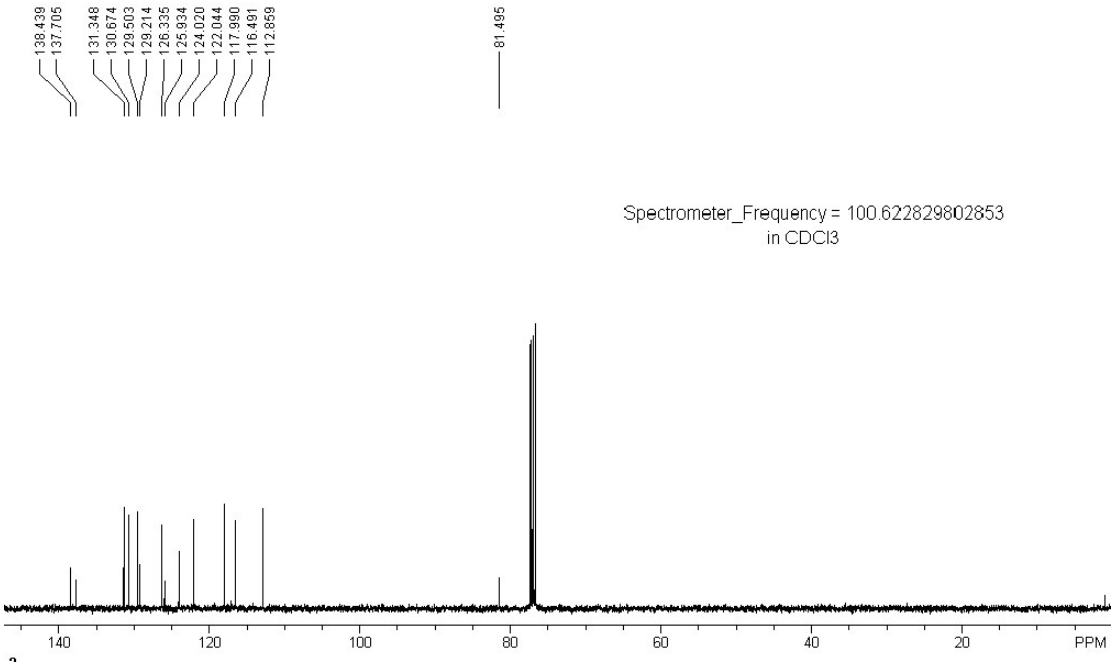
(15) 3-(2-bromophenyl)indolizine-1-carbonitrile (T 5-15)



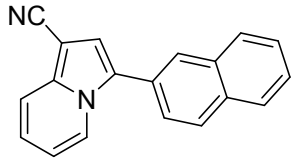
Yellow solid. m.p. 279-281 °C (lit.[1] mp 278-279°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.78 (d, *J* = 9.2 Hz, 1 H), 7.71 (d, *J* = 7.2 Hz, 1 H), 7.36-7.50 (m, 4 H), 7.14 (t, *J* = 8.0 Hz, 1 H), 7.04 (s, 1 H), 6.79 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 138.5, 137.4, 131.4, 130.8, 129.5, 129.1, 126.2, 125.8, 124.1, 122.0, 118.1, 116.6, 112.8, 120.0, 81.5. HRMS (EI) Calcd for $C_{15}H_9N_2Br$ (M^+) 295.9949, Found 295.9952.



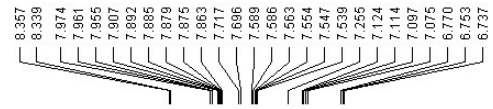


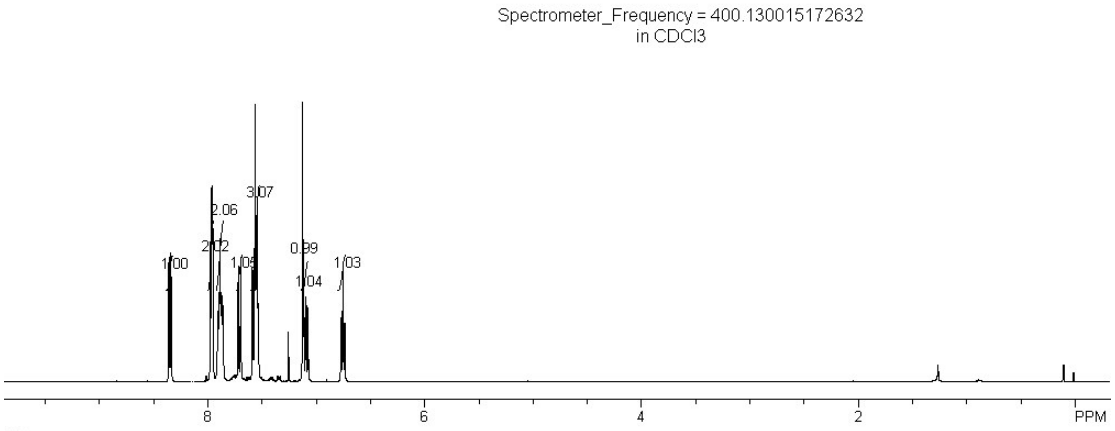


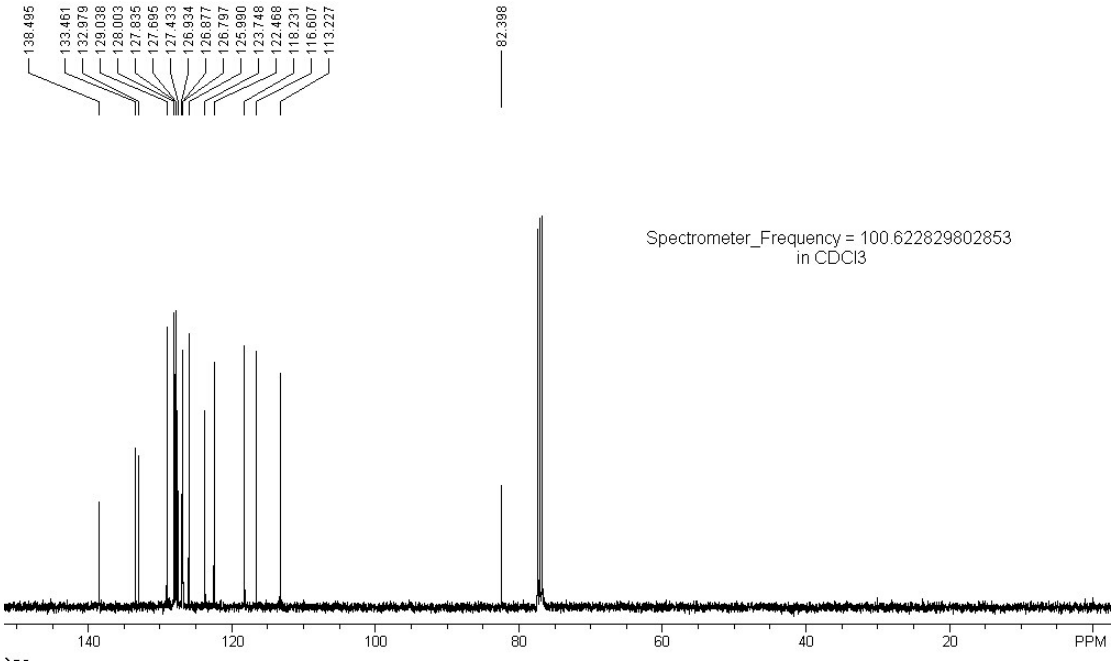
(16) 3-(naphthalen-2-yl)indolizine-1-carbonitrile (T 5-16)



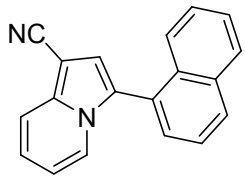
White solid. m.p. 311-313 ^{o}C (lit.[1] mp 311-312°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.36 (d, *J* = 6.8 Hz, 1 H), 7.95-7.99 (m, 2 H), 7.85-7.91 (m, 2 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.54-7.58 (m, 3 H), 7.13 (s, 1 H), 7.11 (t, *J* = 8.0 Hz, 1 H), 6.76 (t, *J* = 6.8 Hz, 1 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 138.4, 133.4, 133.0, 129.1, 128.0, 127.9, 127.7, 126.9, 126.8, 126.1, 123.6, 122.5, 118.1, 116.6, 113.3, 82.3. HRMS (ESI) Calcd for $C_{19}H_{12}N_2$ (M^+) 268.1000, Found 268.1004.





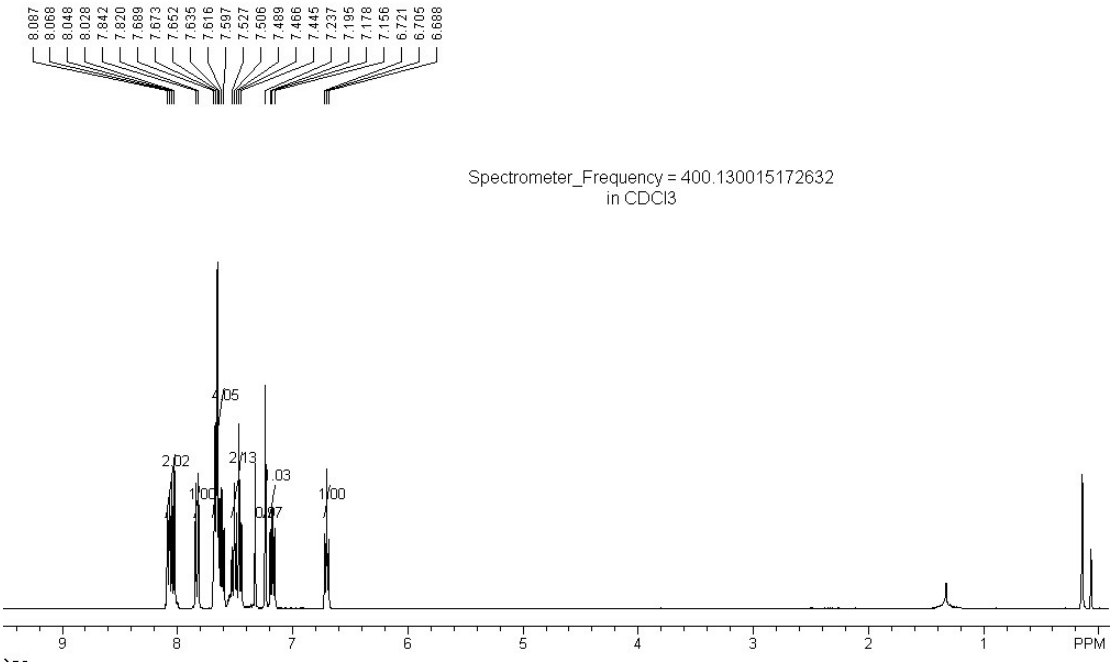


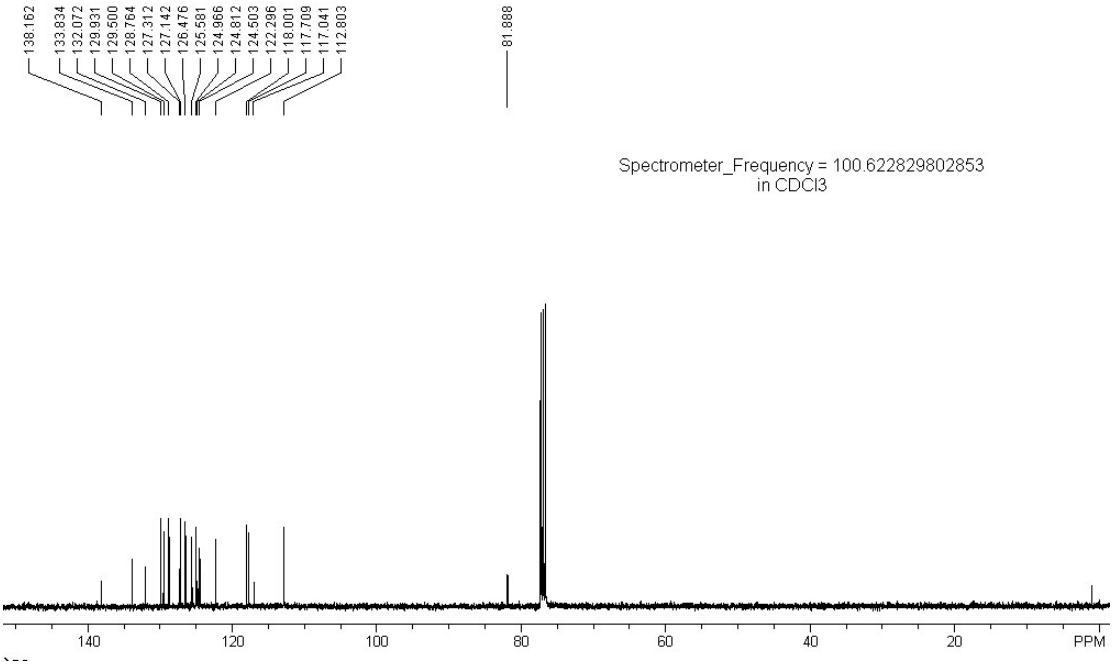
(17) 3-(naphthalen-1-yl)indolizine-1-carbonitrile (T 5-17)



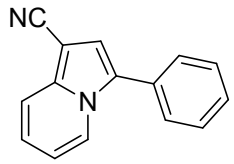
White solid. m.p. 304-307 ^{o}C (lit.[1] mp 303-305°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02-8.09 (m, 2 H), 7.84 (d, *J* = 8.4 Hz, 1 H), 7.60-7.68 (m, 4 H), 7.44-7.53 (m, 2 H), 7.25 (s, 1 H), 7.19 (t, *J* = 8.0 Hz, 1 H), 6.72 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 138.1, 133.7, 132.2, 129.9, 129.4, 128.7, 127.4, 127.1,

126.4, 125.6, 125.1, 124.7, 124.5, 122.4, 118.0, 117.6, 112.7, 81.8. HRMS (ESI) Calcd for $C_{19}H_{12}N_2$ (M^+) 268.1000, Found 268.0999.



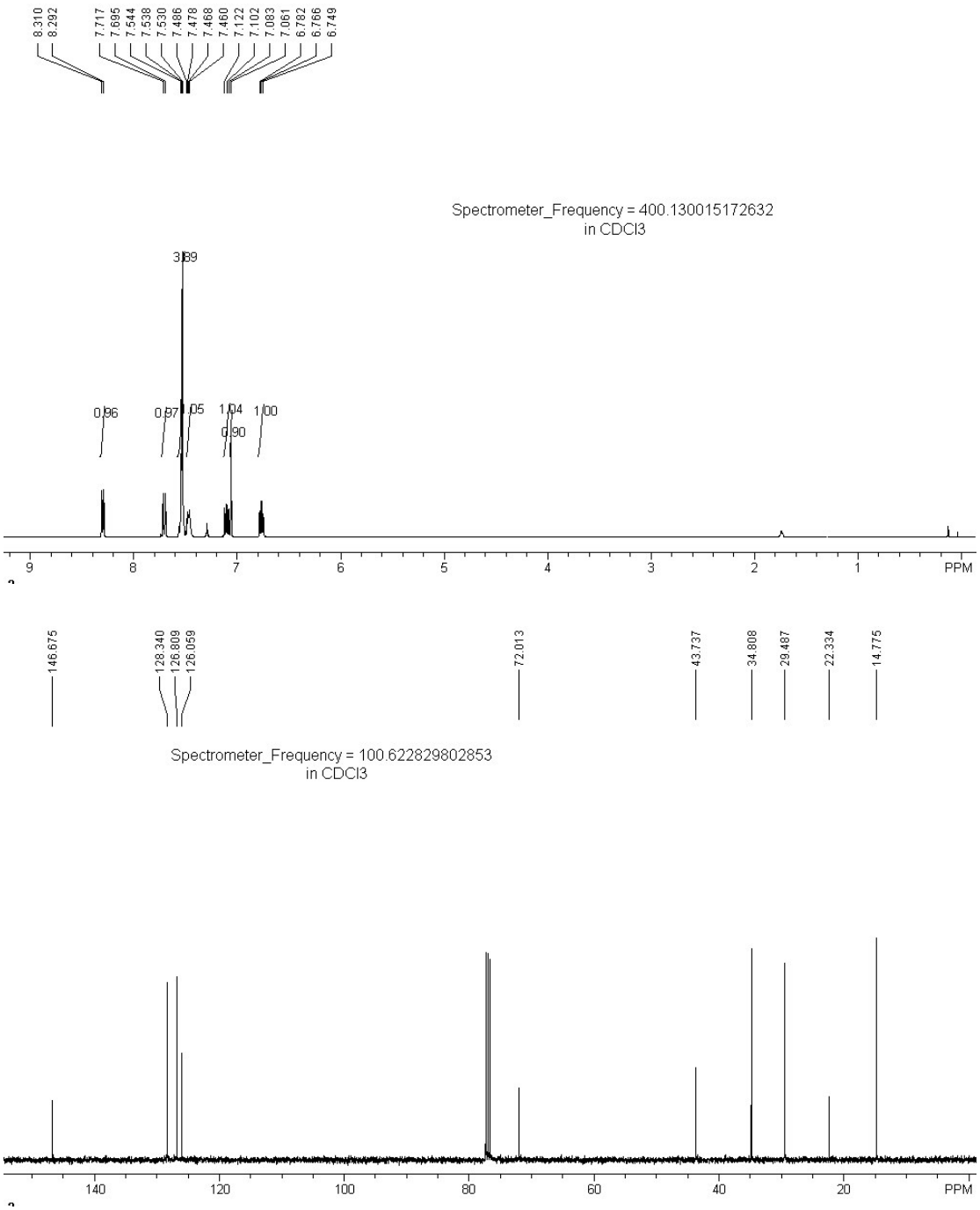


(18) 3-phenylindolizine-1-carbonitrile (T 6-1)

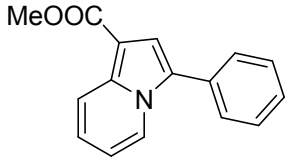


White solid. m.p. 94-95 °C (lit.[2] mp 93-95°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.31 (d, *J* = 7.2 Hz, 1 H), 7.72 (d, *J* = 8.4 Hz, 1 H), 7.51-7.55 (m, 4 H), 7.45-7.49 (

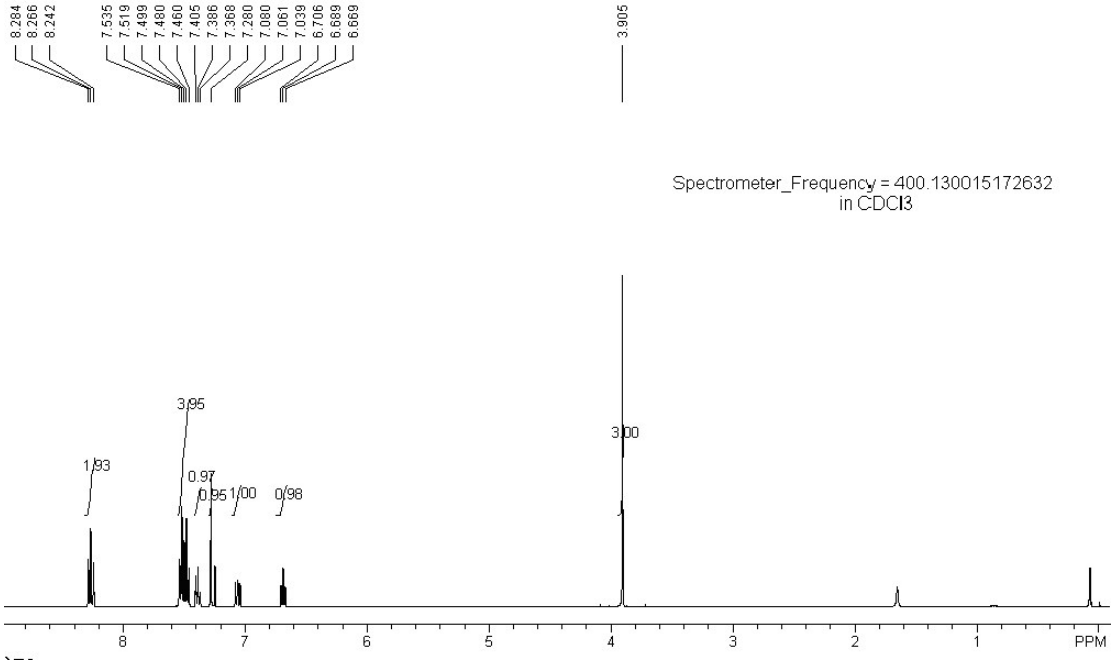
m, 1 H), 7.11 (t, *J* = 8.0 Hz, 1 H), 7.06 (s, 1 H), 6.76 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 138.4, 137.6, 131.3, 130.6, 129.5, 129.1, 126.4, 125.9, 124.1, 122.0, 117.8, 116.4, 112.8, 81.3. HRMS (EI) Calcd for $C_{15}H_{10}N_2$ (M^+) 218.0844, Found 218.0846.

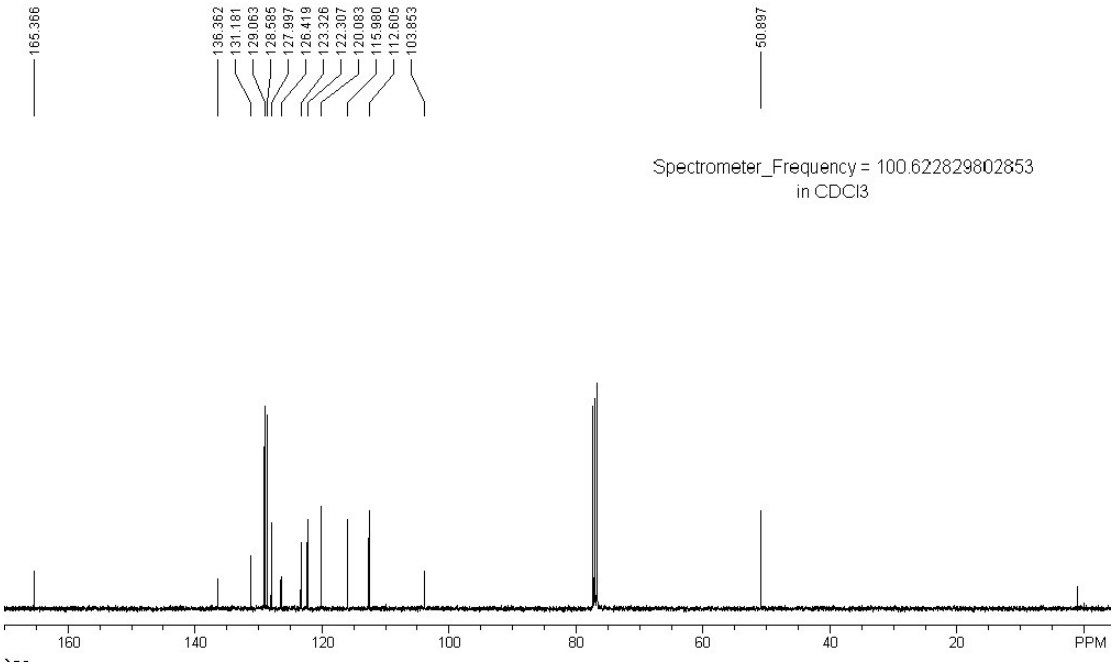


(19) methyl 3-phenylindolizine-1-carboxylate (T 6-2)

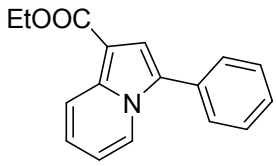


Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.28 (t, *J* = 8.4 Hz, 2 H), 7.51 (m, 4 H), 7.38 (t, *J* = 7.2 Hz, 1 H), 7.28 (s, 1 H), 7.05 (t, *J* = 8.0 Hz, 1 H), 6.68 (t, *J* = 8.0 Hz, 1 H), 3.92 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 136.5, 131.1, 129.2, 128.7, 128.1, 126.5, 123.4, 122.3, 120.6, 112.6, 103.8, 50.8. HRMS (EI) Calcd for $C_{16}H_{13}NO_2$ (M^+) 251.0946, Found 251.0950.

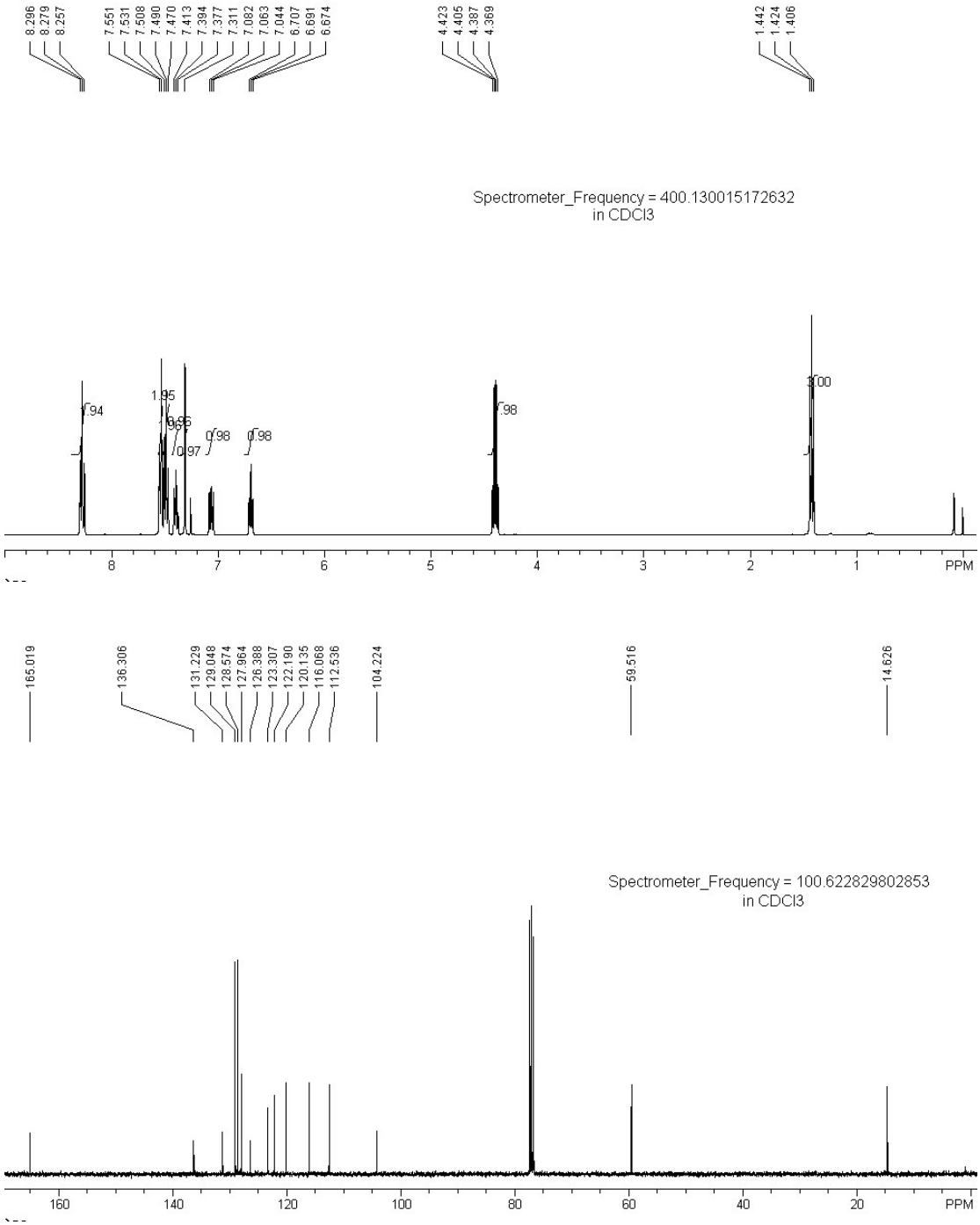




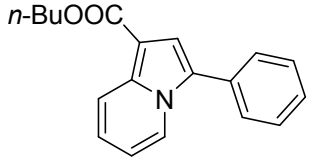
(20) ethyl 3-(1-p-tolylvinyl)indolizine-1-carboxylate(T 6-3)



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.29 (t, *J* = 7.6 Hz, 2 H), 7.55 (d, *J* = 7.6 Hz, 2 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.39 (t, *J* = 7.6 Hz, 1 H), 7.30 (s, 1 H), 7.07 (d, *J* = 7.6 Hz, 1 H), 6.68 (t, *J* = 6.8 Hz, 1 H), 4.41 (m, 2 H), 1.43 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 165.1, 136.2, 131.1, 129.0, 128.7, 128.1, 126.4, 123.2, 122.3, 120.1, 116.1, 112.4, 104.2, 59.6, 14.5. HRMS (EI) Calcd for $C_{17}H_{15}NO_2$ (M^+) 265.1103, Found 265.1100.

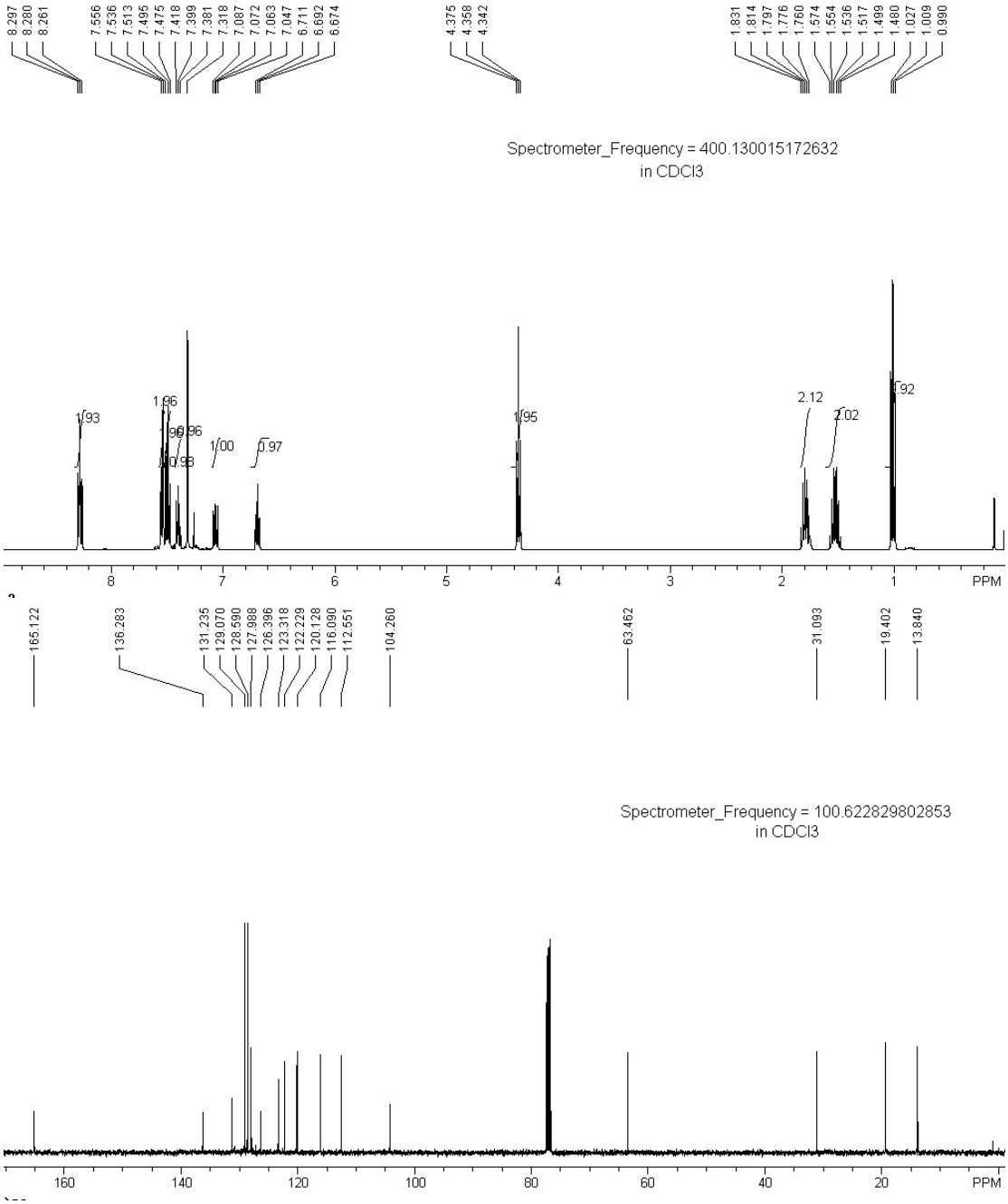


(21) butyl 3-phenylindolizine-1-carboxylate (T 6-4)



Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.27 (t, *J* = 7.2 Hz, 2 H), 7.54 (d, *J* = 8.0 Hz, 2 H), 7.51 (t, *J* = 7.2 Hz, 2 H), 7.40 (t, *J* = 7.2 Hz, 1 H), 7.33 (s, 1 H), 7.06 (m,1 H), 6.71 (t, *J* = 7.2 Hz, 1 H), 4.37 (t, *J* = 6.8 Hz, 2 H), 1.81 (m,2 H), 1.52 (m,2 H), 1.01 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2,

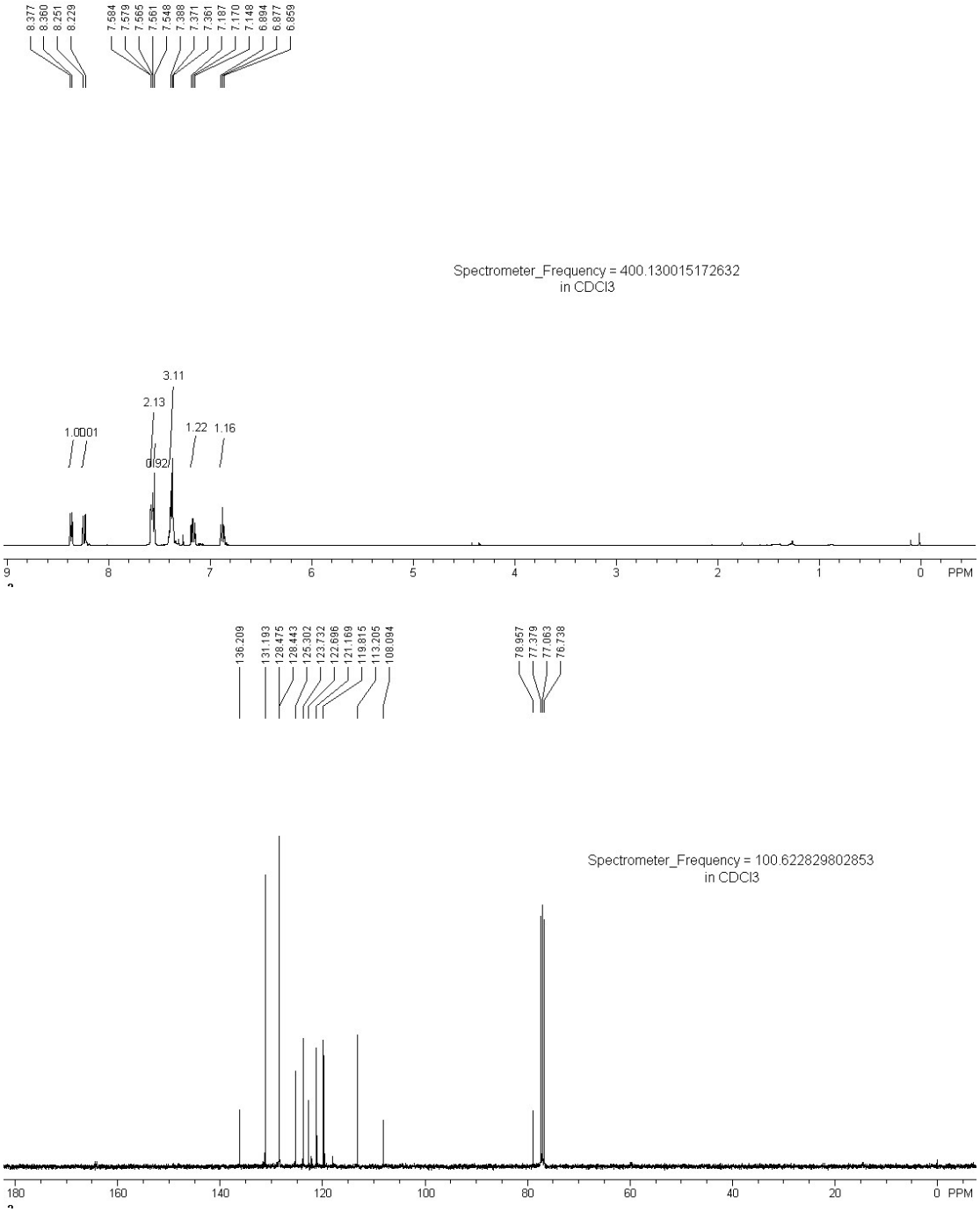
136.2, 131.3, 129.2, 128.5, 128.0, 126.3, 123.2, 122.1, 120.2, 116.1, 114.8, 112.5, 104.3, 63.4, 31.1, 19.3, 13.7. HRMS (EI) Calcd for $C_{19}H_{19}NO_2$ (M^+) 293.1416, Found 293.1411.



(22) 1-nitro-3-phenylindolizine (T 6-5, new compound)

Yellow solid. m.p. 185-187 ^oC. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.36 (d, J = 7.2 Hz, 1 H), 8.23 (d, J = 8.8 Hz, 1 H), 7.56-7.59 (m, 2 H), 7.55 (s, 1 H), 7.35-7.39 (m, 3 H), 7.17 (t, J = 8.0 Hz, 1 H), 6.87 (t, J = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 131.2, 128.6, 128.4, 125.4, 123.8, 122.6, 121.1, 119.8, 113.4, 108.1,

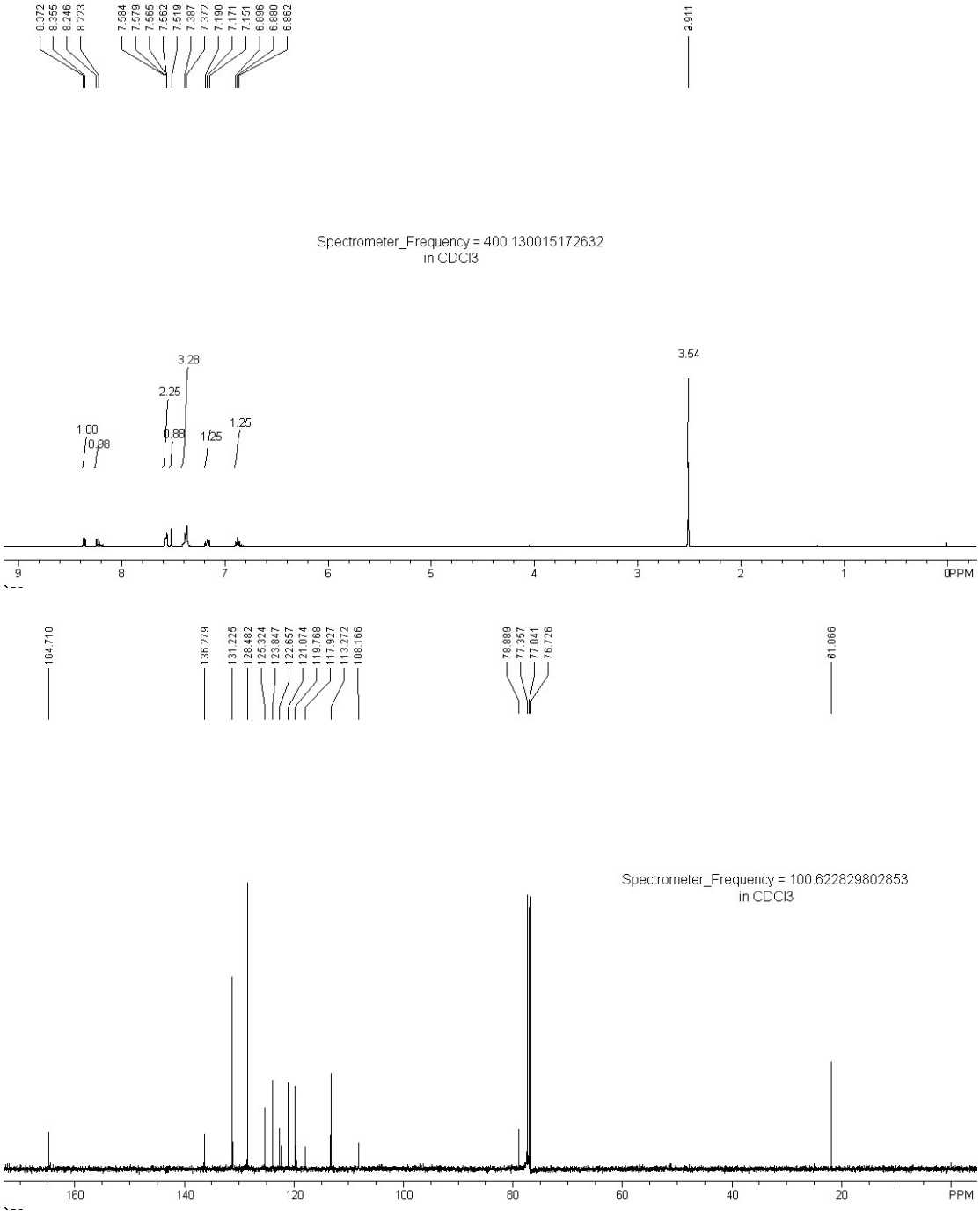
79.1, 59.6. HRMS (EI) Calcd for $C_{14}H_{10}N_2O_2$ (M^+) 238.0742, Found 238.0745.



(23) 1-(3-phenylindolizin-1-yl)ethan-1-one (T 6-6, new compound)

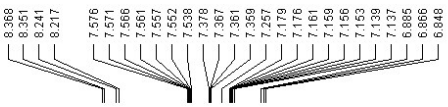
White solid. m.p. 125-126 ^oC. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.35 (d, J = 6.8 Hz, 1 H), 8.23 (d, J = 8.8 Hz, 1 H), 7.56-7.59 (m, 2 H), 7.52 (s, 1 H), 7.37-7.39 (m, 3 H), 7.16 (t, J = 8.0 Hz, 1 H), 6.87 (t, J = 6.8 Hz, 1 H), 2.51 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 136.3, 131.3, 128.5, 125.5, 123.8, 122.6, 121.2, 119.8, 117.8, 113.3, 108.3, 78.9, 21.1. HRMS (EI) Calcd for $C_{16}H_{13}NO$ (M^+)

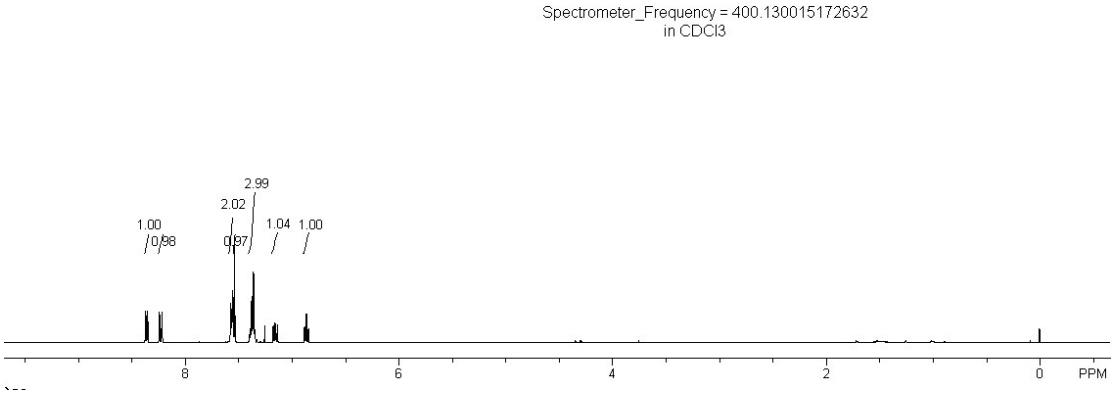
235.0997, Found 235.0994.

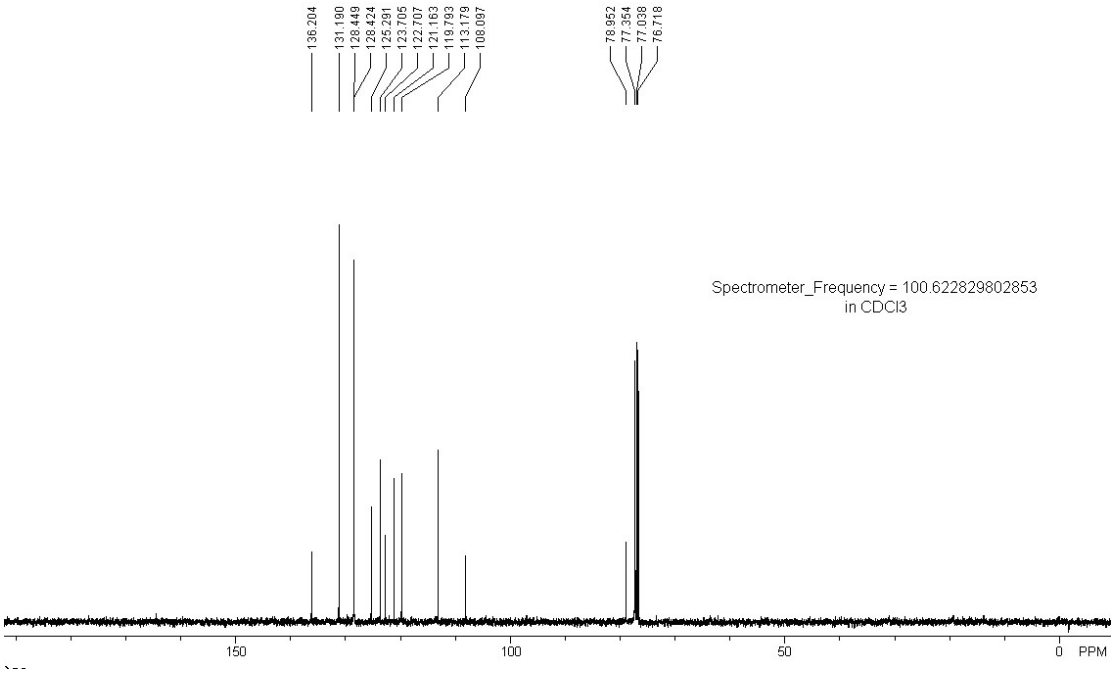


(24) 1-chloro-3-phenylindolizine (T 6-7, new compound)

Yellow solid. m.p. 202-204 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.36 (d, J = 6.8 Hz, 1 H), 8.23 (d, J = 9.6 Hz, 1 H), 7.55-7.58 (m, 2 H), 7.54 (s, 1 H), 7.36-7.38 (m, 3 H), 7.14-7.18 (m, 1 H), 6.87 (t, J = 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 131.3, 128.5, 128.3, 125.3, 123.7, 122.6, 121.2, 119.7, 113.2, 108.2, 78.8. HRMS (EI) Calcd for $C_{14}H_{10}ClN$ (M^+) 227.0502, Found 227.0507.

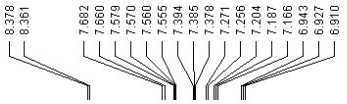


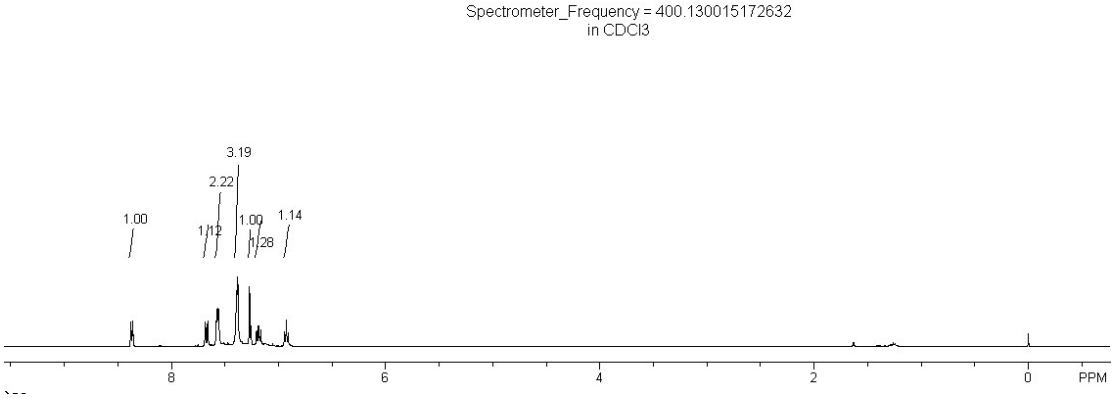


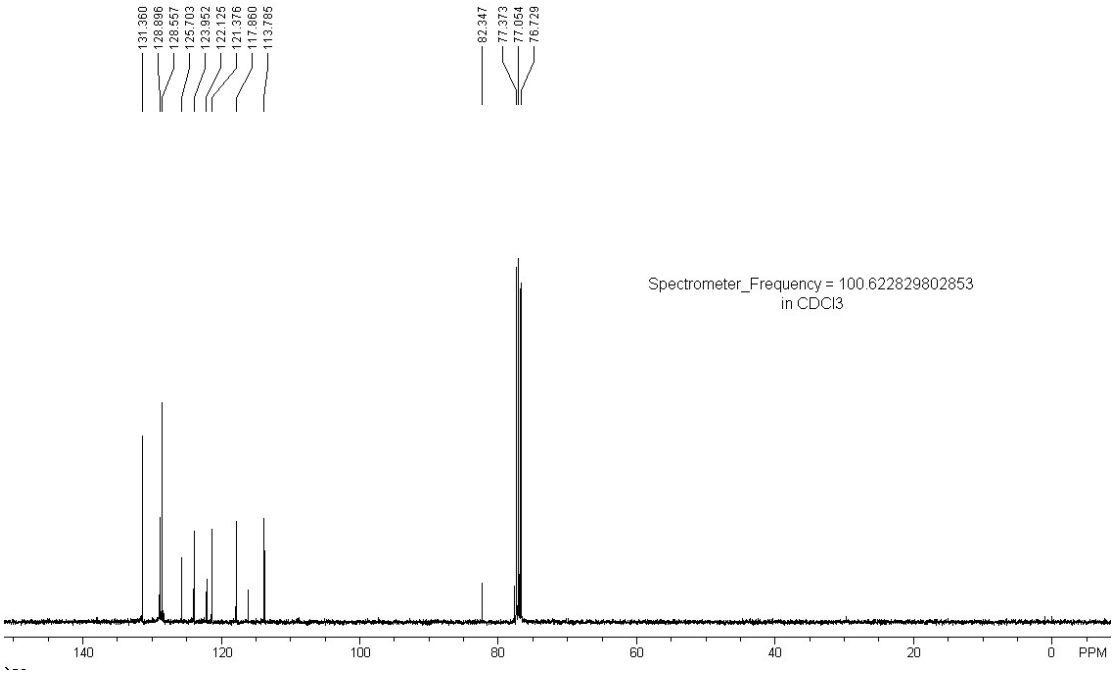


(25) 1-bromo-3-phenylindolizine (T 6-8, new compound)

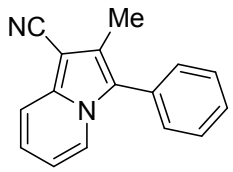
Brown solid. m.p. 254-255 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.36 (d, J = 6.8 Hz, 1 H), 7.68 (d, J = 8.8 Hz, 1 H), 7.56-7.59 (m, 2 H), 7.37-7.39 (m, 3 H), 7.28 (s, 1 H),7.18 (t, J = 7.6 Hz, 1 H), 6.92 (t, J = 6.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 131.4, 128.9, 128.5, 125.7, 124.0, 122.1, 121.4, 117.9, 113.8, 82.3. HRMS (EI) Calcd for $C_{14}H_{10}BrN$ (M^+) 270.9997, Found 270.9993.





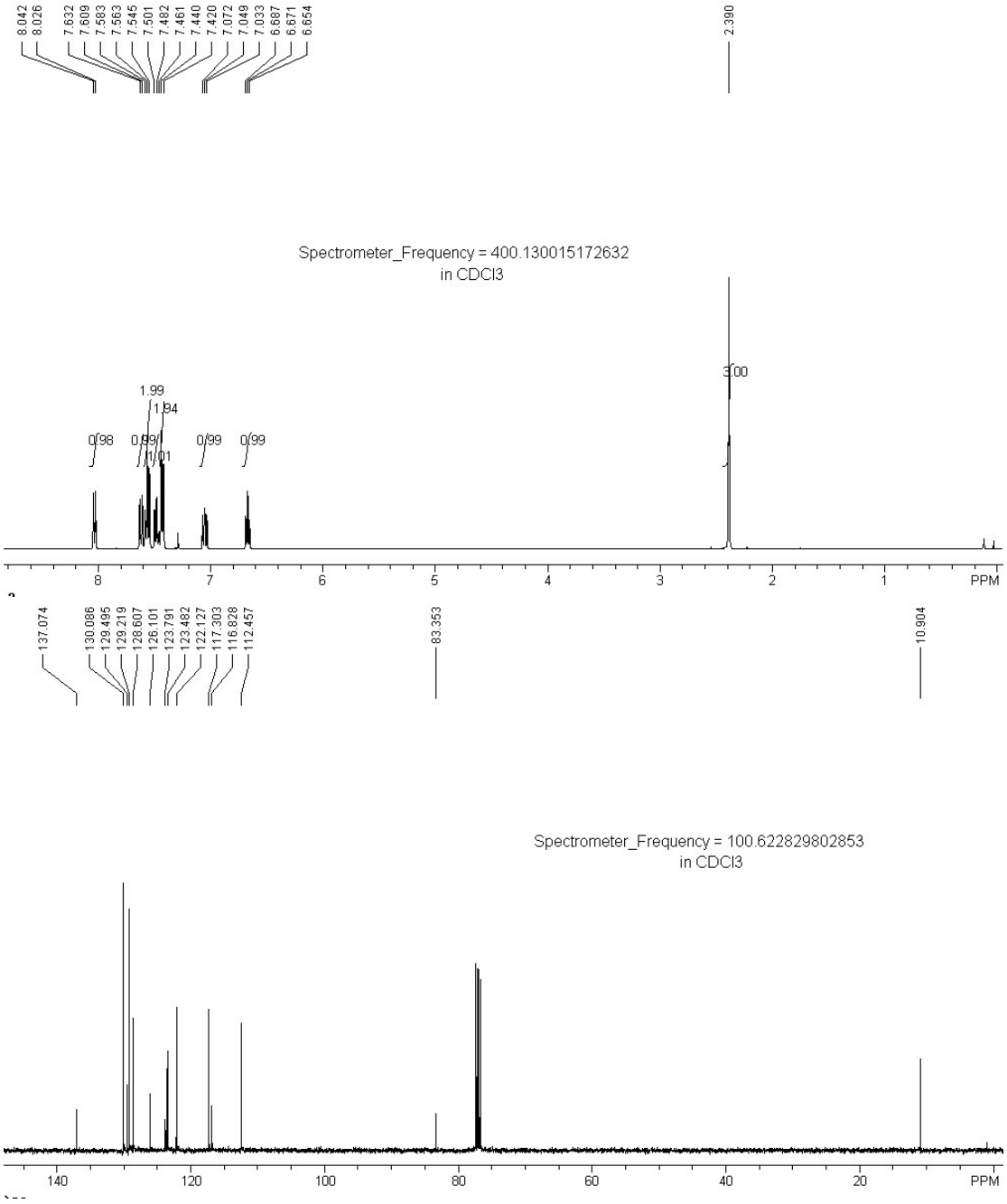


(26) 2-methyl-3-phenylindolizine-1-carbonitrile (T 6-9)

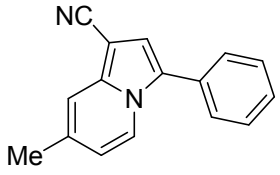


White solid. m.p. 251-253 ^{o}C(lit.[1] mp 253-254°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.04 (d, *J* = 7.2 Hz, 1 H), 7.63 (d, *J* = 9.2 Hz, 1 H), 7.55 (t, *J* = 8.0 Hz, 2 H),

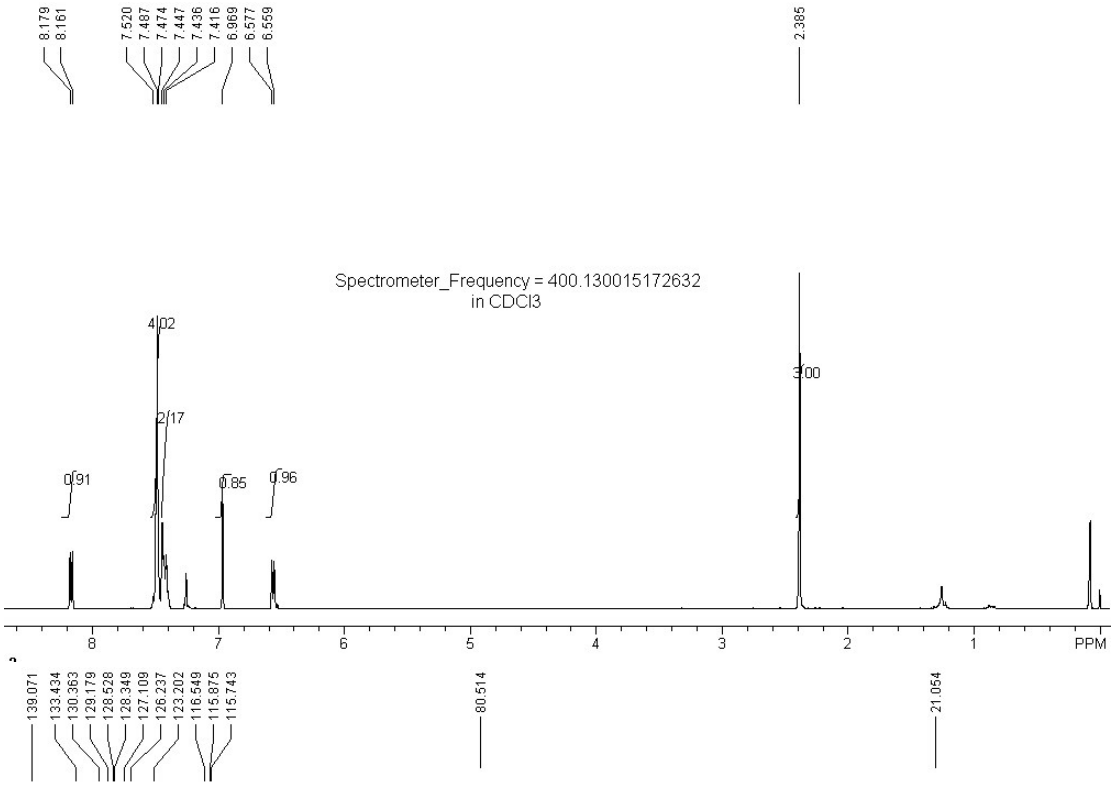
7.47 (t, *J* = 8.0 Hz, 1 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.04 (t, *J* = 8.0 Hz, 1 H), 6.66 (t, *J* = 6.8 Hz, 1 H), 2.38 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 130.2, 129.5, 129.1, 128.5, 126.2, 123.8, 122.2, 117.3, 116.7, 112.5, 83.3, 10.8. HRMS (EI) Calcd for $C_{16}H_{12}N_2$ (M^+) 232.1000, Found 232.0996.

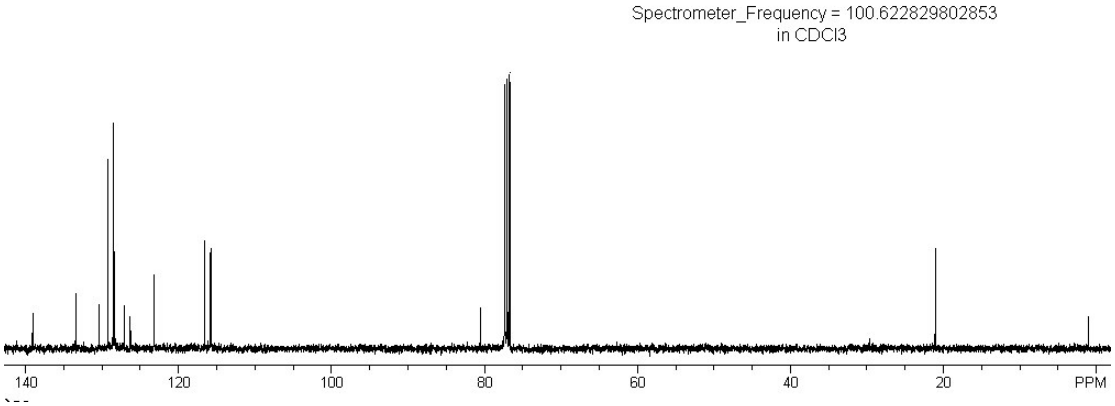


(27) 7-methyl-3-phenylindolizine-1-carbonitrile (T 6-10)



White solid. m.p. 235-236 °C(lit.[1] mp 237-238°C). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.16 (d, *J* = 7.2 Hz, 1 H), 7.84 (d, *J* = 7.2 Hz, 1 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.47-7.53 (m, 4 H), 7.40-7.45 (m, 2 H), 6.98 (s, 1 H), 6.56 (d, *J* = 7.2 Hz, 1 H), 2.38 (s, 3 H),. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 133.3, 130.5, 129.2, 128.6, 128.3, 127.0, 126.2, 123.3, 116.5, 115.8, 115.7, 80.4, 21.2. HRMS (EI) Calcd for $C_{16}H_{12}N_2$ (M^+) 232.1000, Found 232.0999.





References

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2. Xia, J.-B.; You, S.-L. *Org. Lett*. **2009**, *11*, 1187.