K_2CO_3-Catalyzed Synthesis of 2,5-Dialkyl-4,6,7-tricyano-Decorated Indoles via Carbon-Carbon Bond Cleavage

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Table of contents

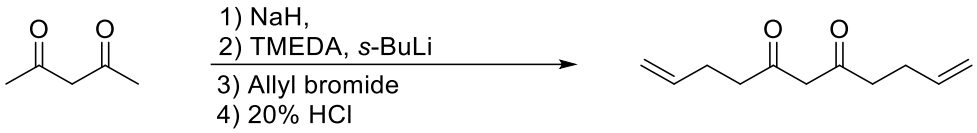
1. General Information

All the glassware including the 4-dram borosilicate scintillation (Wheaton), 1-dram borosilicate (Kimble-Chase) vials, and 15 mL pressure tubes were properly cleaned and dried in an oven before use. All glassware was cleaned with soap before being rinsed with acetone and dried in the oven at 150 ^{o}C. All chemicals (solvents, starting materials, and reagents) used for both diketone and indole synthesis were obtained from commercial sources and used as received. Fumaronitrile (TCI), K_2CO_3 (Fisher Scientific), and dioxane (TCI and Sigma Aldrich) were used as reagents to synthesize indoles. The following diketones were ordered and used as received from their respective vendor to synthesize indoles: 2, 4-pentanedione (99%) (Alfa Aesar), 3, 5-heptanedione (95%) (OxChem), 2, 2-dimethyl-3, 5-hexanedione (97%) (Sigma Aldrich), 6-methyl-2, 4-heptanedione (98%) (Alfa Aesar), 2, 4-octandione (98%) (Alfa Aesar), 2, 2, 6, 6-tetramethyl-3, 5-heptanedione (98%) (Sigma Aldrich). The following diketones were synthesized for indole synthesis: undeca-1, 10-diene-5,7-dione, 2, 8-dimethylnonane-4, 6-dione, 2, 2, 8-trimethylnonane-4, 6-dione, 2, 2, 6-trimethylheptane-3, 5-dione, 2, 2, 8-trimethyloctane-4, 6-dione, and 2, 8-dimethyloctane-4, 6-dione. The following reagents were purchased and used as received from their respective vendor in order to synthesize diketones: 3-Methyl-2-Butanone (Beantown Chemical), 2-Methyl-4-pentanone (TCI), ethyl isovalerate (TCI), Ethyl 3,3-dimethylbutanoate (TCI), ethyl trimethylacetate (Sigma Aldrich), 2, 4- pentanedione 99% (Alfa Aesar), sodium hydride (Alfa Aesar), tetramethylethylenediamine (Sigma Aldrich), *sec*-butyllitium (Sigma Aldrich), and allyl bromide (Sigma Aldrich). High resolution mass and NMR spectra for new compounds were recorded at the Mass Spectrometry and NMR Facilities in the Department of Chemistry and Chemical Biology at the University of New Mexico. NMR spectra were recorded on a Bruker instrument spectrometer (300MHz for ^{1}H, 75MHz for ^{13}C) at room temperature. Chemical shifts are recorded in parts per million. ^{1}H NMR shifts are referenced to chloroform-d (d = 7.26) or acetone-d_6 (d =2.05). ^{13}C shifts are referenced to acetone-d_6 (d =29.84 and 206.26) or DMSO-d_6 (39.52). NMR splitting patterns were represented by the following: s for singlet; d for doublet; t for triplet; q for quartet, and m for multiplet. Mass spectroscopy samples were ran using Atmospheric Pressure Photoionization (APPI) in Positive Mode and Electrospray Ionization (ESI) in Positive Mode. 2, 5-Di-*tert*-butyl-4, 6, 7-tricyano-1*H*-indole was the only sample analyzed by ESI method for mass spectroscopy. Infrared (IR) spectra were

recorded on a Bruker Alpha-P ATR-IR and ν_{max} is reported in cm^{-1}. The GC-MS was recorded in Agilent 7820 GC-system with Agilent J&W advanced capillary GC column with 20 mL/min of the helium flow. X-ray diffraction was performed on Bruker Kappa APEX II CCD diffractometer at the Department of Chemistry and Chemical Biology, UNM.

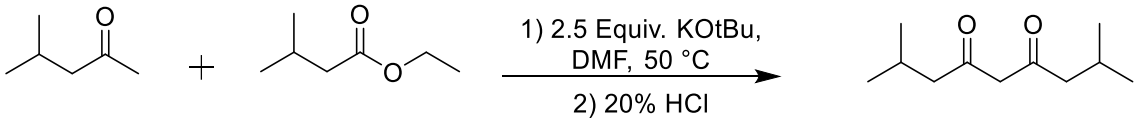
2. Procedures for the preparation of diketones substrates

a. Synthesis of undeca-1, 10-diene-5, 7-dione



The synthesis procedure of undeca-1, 10-diene-5, 7-dione was utilized from the described procedure by Hubbard and Harris.[1] For the synthesis procedure of undeca-1, 10-diene-5, 7-dione, 1.1 g of 2,4-pentanedione (10 mmol) and 240 mg (1 equiv) of NaH was added to 100 mL of cyclohexane. The mixture was stirred for 30 minutes at room temperature (20 ^{o}C). 2.324 g (2 equiv) of TMEDA was added to the mixture followed with a slow addition of 14.3 mL (2 equiv) of *sec*-butyllithium at 0 ^{o}C on an ice bath. The mixture was stirred for 24 hours at 20 ^{o}C. The reaction was then cooled to -78 ^{o}C for 30 minutes. Once cooled, 2.418 g (2 equiv) of allyl bromide was slowly added dropwise to the solution while stirring. This solution was mixed over night at room temperature. After mixing the reaction overnight, the reaction mixture was slowly neutralized dropwise with 20% HCl solution. The product 1, 10-undecene-5, 7-dione was obtained as a yellow oil (631.0 mg, 31% isolated yield) after purification by silica gel column chromatography with EtOAc as the solvent system. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 15.41 (s, 1H), 5.77 (m, 2H), 5.49 (s, 1H), 5.01 (t, *J* = 14.85 Hz, 4H), 2.38 (s, 8H).

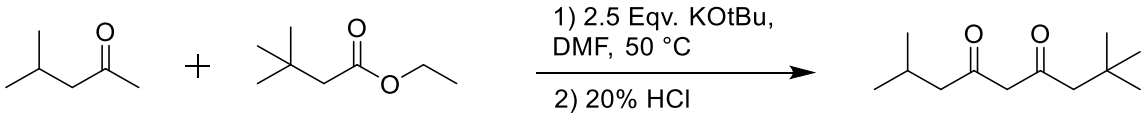
b. Synthesis of 2, 8-dimethylnonane-4, 6-dione



The synthesis procedure of 2, 8-dimethylnonane-4, 6-dione was utilized from the described procedure by Nandurkar et al.[2] For the synthesis of 2, 8-dimethylnonane-4,6-dione, a mixture of 25 mL of DMF and 5.6 g of KO*t*Bu (2.5 equiv) was heated in an oil bath to 50 ^{o}C under nitrogen conditions. 3.485 g of ethyl isovalerate (30 mmol) was added dropwise to the DMF and KO*t*Bu

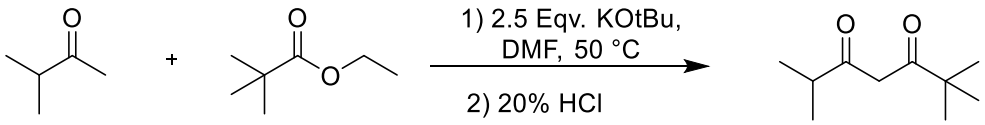
solution, followed by a solution of 2.036 g of 2-methyl-4-pentanone (20 mmol) in 2.5 mL DMF. After the completion of the reaction, the reaction mixture was allowed to cool and slowly neutralized with 20% HCl solution. 25 mL of water was added to separate two layers. The product 2, 8-dimethylnonane-4, 6-dione was obtained as a yellow oil (2.524 g, 70% isolated yield) after purification by silica gel column chromatography with EtOAc as the solvent system. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 15.65 (s, 1H), 5.45 (s, 1H), 2.14 (m, 6H), 0.95 (m. 12H).

c. Synthesis of 2, 2, 8-trimethylnonane-4, 6-dione



The synthesis procedure of 2, 2, 8-trimethylnonane-4, 6-dione was utilized from the described procedure by Nandurkar et al.[2] For the synthesis of 2, 2, 8-trimethylnonane-4, 6-dione, a mixture of 25 mL of DMF and 5.6 g of KO*t*Bu (50 mmol) was heated in an oil bath to 50 °C under nitrogen conditions. 4.320 g of ethyl-3,3-dimethylbutanoate (30 mmol) was added dropwise to the DMF KO*t*Bu solution, followed by a solution of 2.036 g of 2-methyl-4-pentanone (20 mmol) in 2.5 mL DMF. After the completion of the reaction, the reaction mixture was allowed to cool and slowly neutralized with 20% HCl solution. 25 mL of water was further added to separate two layers. The product 2, 2, 8-trimethylnonane-4, 6-dione was obtained as an orange oil (1.135 g, 30% isolated yield) after purification by silica gel column chromatography with EtOAc as the solvent system. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 15.73 (s, 1H), 5.40 (s, 1H), 2.08 (m, 5H), 0.99 (s, 9H), 0.93 (d, *J* = 6.6 Hz, 6H).

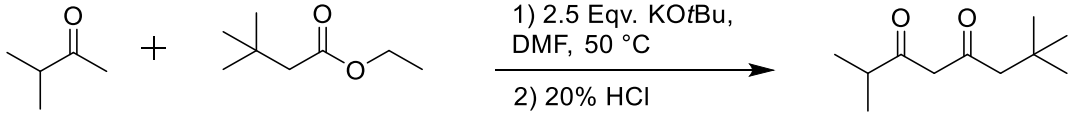
d. Synthesis of 2, 2, 6-trimethylheptane-3, 5-dione



The synthesis procedure of 2, 2, 6-trimethylheptane-3, 5-dione was utilized from the described procedure by Nandurkar et al.[2] For the synthesis of 2, 2, 6-trimethylheptane-3, 5-dione, a mixture of 25 mL of DMF and 5.6 g of KO*t*Bu (50 mmol) was heated in an oil bath to 50 °C under nitrogen conditions. 4.320 g of ethyl trimethylacetate (30 mmol) was added dropwise to the DMF KO*t*BU solution, followed by a solution of 1.722 g of 2-methyl-3-butanone (20 mmol) in 2.5 mL DMF. After the completion of the reaction, the reaction mixture was allowed to cool and slowly neutralized with 20% HCl solution. 25 mL of water was further added to separate two layers. The

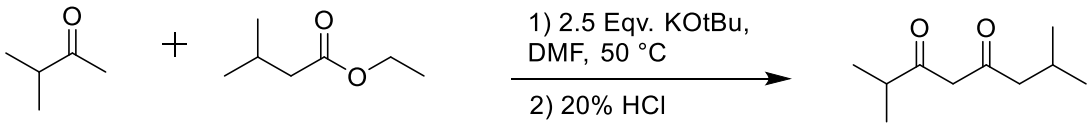
product 2, 2, 6-trimethylheptane-3, 5-dione was obtained as a red oil (2.109 g, 62% isolated yield) after purification by silica gel column chromatography with EtOAc as the solvent system. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 15.90 (s, 1H), 5.96 (s, 1H), 2.48 (m, 1H), 1.14 (m, 15H).

e. Synthesis of 2, 2, 7-trimethyloctane-3, 5-dione



The synthesis of 2, 2, 7-trimethyloctane-3, 5-dione was utilized from the described procedure by Nandurkar et al.[2] For the synthesis of 2, 7, 7-trimethyloctane-3, 5-dione, a mixture of 25 mL of DMF and 5.6 g of KO*t*Bu (50 mmol) was heated in an oil bath to 50 ^oC under nitrogen conditions. 4.320 g of Ethyl 3, 3-dimethylbutanoate (30 mmol) was added dropwise to the DMF KO*t*Bu solution, followed by a solution of 1.722 g of 2-methyl-3-butanone (20 mmol) in 2.5 mL DMF. After the completion of the reaction, the reaction mixture was allowed to cool and slowly neutralized with 20% HCl solution. 25 mL of water was further added to separate two layers. The product 2, 2, 7-trimethyloctane-3, 5-dione was obtained as an orange colored oil (577.2 mg, 15% isolated yield) after purification by silica gel column chromatography with EtOAc as the solvent system. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 15.67 (s, 1H), 7.25 (s, 1H), 2.45 (m, 1H), 2.12 (s, 2H), 1.13 (d, *J* = 6.9 Hz, 6H), 0.99 (s, 9H).

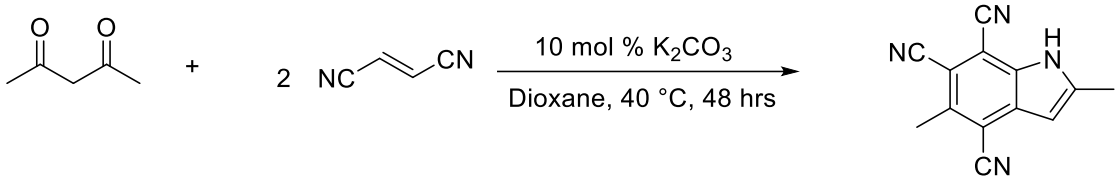
f. Synthesis of 2, 7-Dimethyloctane-3, 5-dione



The synthesis of 2, 7-Dimethyloctane-3, 5-dione was utilized from the described procedure by Nandurkar et al.[2] For the synthesis of 22, 7-dimethyloctane-3, 5-dione, a mixture of 25 mL of DMF and 5.6 g of KO*t*Bu (50 mmol) was heated in an oil bath to 50 ^oC under nitrogen conditions. 3.485 g of ethyl isovalerate (30 mmol) was added dropwise to the DMF KO*t*Bu solution, followed by a solution of 1.722 g of 2-methyl-3-butanone (20 mmol) in 2.5 mL DMF. After the completion of the reaction, the reaction mixture was allowed to cool and slowly neutralized with 20% HCl solution. 25 mL of water was further added to separate two layers. The product 2, 7-dimethyloctane-4, 5-dione was obtained as a yellow oil (594.2 g, 16% isolated yield) after purification by silica gel column chromatography with EtOAc as the solvent system. **^{1}H NMR**

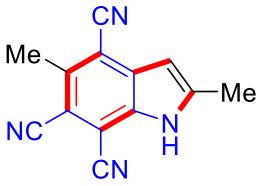
(300 MHz, $CDCl_3$): δ 15.61 (s, 1H), 5.47 (s, 1H), 2.44 (m, 1H), 2.12 (m, 3H), 1.13 (d, *J* = 6.0 Hz, 6H), 0.94 (d, *J* = 6.0 Hz, 6H).

3. General procedure for the synthesis of Indole

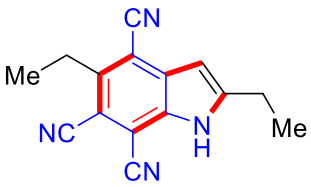


For a 1 mmol scale reaction, mix 100.1 mg of 2, 4-pentanedione, 156.1 mg fumaronitrile (2 equivalents), and 13.8 mg K_2CO_3 (10 mol %) into 5 mL of dioxane in a 15mL sealed tube under normal atmospheric conditions. Cap the 15 mL sealed tube and heat in an oil bath at 40 ^oC for 48 hours while rapidly stirring the mixture. The reaction mixture was filtered through a pad of Celite, the solvent was removed by rotary evaporator and the product was purified by silica gel column chromatography.

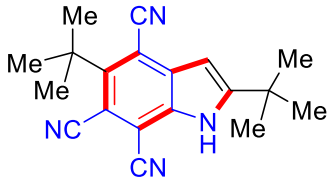
4. Characterization data for new compounds



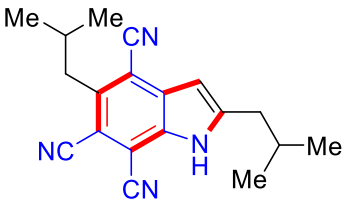
2, 5-Dimethyl-1H-indole-4, 6, 7-tricarbonitrile **1***:* The title compound **1** was obtained as a yellow solid (183 mg, 83% isolated yield) after purification by silica gel column chromatography with a solvent system of 20% EtOAc in hexane. Rf; 0.3 (EtOAc:Hexanes; 1:4); **^{1}H NMR (300 MHz, Acetone- d_6)**: δ 11.76 (s, 1H) 6.60 (s, 1H), 2.77 (s, 3H), 2.64 (s, 3H); **^{13}C NMR (75 MHz, DMSO)**: δ 14.1, 19.5, 100.3, 100.7, 105.9, 116.2, 134.5, 134.7, 137.0, 149.1; **IR (Neat):** 3298, 2925, 2466, 2227, 1548, 1309, 1263, 797; **HRMS (APPI)** m/z: $[M + H]^+$ Calcd $C_{13}H_9N_4$ 221.0827; found 221.0833.



2, 5-Diethyl-1H-indole-4, 6, 7-tricarbonitrile **2**: The title compound **2** was isolated by silica gel column chromatography with a solvent system of 20% EtOAc in hexane. The title compound was obtained as a yellow solid (183 mg, 74% isolated yield) after purification by silica gel column chromatography with a solvent system of 20% EtOAc in hexane. Rf; 0.3 (EtOAc:Hexanes; 1:4); **^{1}H NMR (300 MHz, Acetone- d$_6$)** δ 11.73 (s, 1H), 6.54 (s, 1H), 3.02 (q, *J* = 8.0 Hz, 2H), 2.90 (q, *J* = 8.0 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H), 1.24 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR (75 MHz, Acetone-d$_6$)**: δ 13.0, 15.5, 22.1, 27.9, 100.1, 101.8, 106.3, 107.2, 114.1, 115.7, 116.0, 135.4, 135.7, 143.7, 154.7; **IR (neat):** 3297, 2917, 2228, 1544, 1304, 827, 711, 691; **HRMS (APPI)** m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}N_4$ 249.1140; found 249.1140.

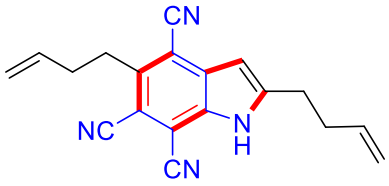


2, 5-Di-tert-butyl-1H-indole-4, 6, 7-tricarbonitrile **3:** The title compound was obtained as an orange solid (103 mg, 34% isolated yield) after purification by silica gel column chromatography with a solvent system of 25% EtOAc in hexane. Rf; 0.4 (EtOAc:Hexanes; 1:4); **^{1}H NMR (300 MHz, Acetone- d$_6$):** δ 11.75 (s, 1H), 6.62 (s, 1H), 1.78 (s, 9 H), 1.50 (s 9H); **^{13}C NMR (75 MHz, Acetone-d$_6$):** δ 31.9, 33.6, 38.6, 99.5, 105.2, 105.9, 107.4, 114.5, 117.9, 118.7, 135.1, 137.1, 148.2, 161.1; **IR (neat):** 3284, 3236, 2968, 2229, 1532, 1466, 1370, 1269, 1029, 828, 717; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}N_4$ 305.1766; found 305.1768.

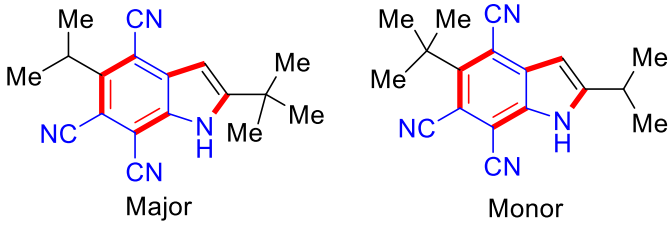


2, 5-Diisobutyl-1H-indole-4, 6, 7-tricarbonitrile **4:** The title compound was obtained as a yellow solid (159 mg, 52% isolated yield) after purification by silica gel column chromatography with a solvent system of 30% EtOAc in hexane. Rf; 0.4 (EtOAc:Hexanes; 1:4); **^{1}H NMR (300 MHz, Acetone- d$_6$):** 11.84 (s, 1H), 6.67 (s, 1H), 2.975 (d, *J* = 9.0 Hz, 2H), 2.85 (d, *J* = 6.0 Hz, 2H), 2.24-2.06 (m, 2H), 0.99 (q, *J* = 4.0 Hz, 12H); **^{13}C NMR (75 MHz, Acetone- d$_6$):** δ 22.3, 22.6, 31.5, 37.8, 42.8, 101.6, 101.9, 107.2, 108.0, 114.2, 116.1, 116.4, 135.3, 135.6, 141.2, 152.1; IR (neat):

3275, 2960, 2225, 1545, 1472, 1304, 991, 830, 694; **HRMS (APPI)** m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}N_4$ 305.1766; found 305.1773.

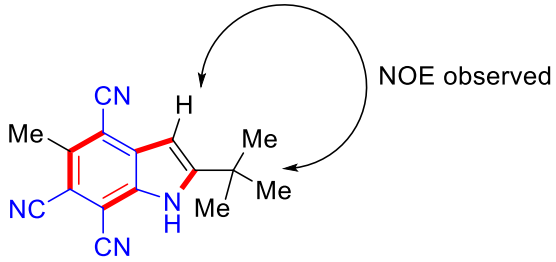


2, 5-Di(but-3-en-1-yl)-1H-indole-4, 6, 7-tricarbonitrile **5:** The title compound was obtained as a yellow solid (183 mg, 61% isolated yield) after purification by silica gel column chromatography with a solvent system of 25% EtOAc in hexane. Rf; 0.4 (EtOAc:Hexanes; 1:4); **^{1}H NMR (300 MHz, Acetone- d$_6$):** δ 11.82, (s, 1H), 6.67 (s, 1H), 5.84-6.00 (m, 2H), 5.05-5.14 (m, 2H), 4.98-5.02 (m, 2H), 3.205 (t, *J* = 7.2 Hz, 2H), 3.093 (t, *J* = 7.5 Hz, 2H), 2.60 (q, *J* = 10.8 Hz, 2H), 2.50 (q, *J* = 11.1 Hz, 2H); **^{13}C NMR (75 MHz, Acetone- d$_6$):** δ 27.3, 32.3, 32.9, 34.5, 100.9, 100.1, 106.1, 106.9, 113.2, 114.9, 115.2, 115.9, 134.3, 134.7, 136.1, 136.8, 140.4, 151.4; **IR (neat):** 3239, 2919, 2409, 2227, 1643, 1543, 1307, 995, 921, 819, 705; **HRMS (APPI)** m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}N_4$ 301.1453; found 301.1452.

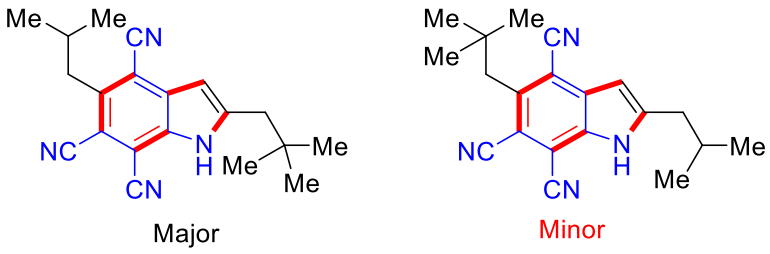


2-Isopropyl-5-(tert-butyl)-1H-indole-4, 6, 7-tricarbonitrile and 5-(tert-butyl)-2-Isopropyl-1H-indole-4, 6, 7-tricarbonitrile **6:** The title compound was obtained as a yellow solid (145 mg, 50% yield) after purification by silica gel column chromatography with a solvent system of 25% EtOAc in hexane. The regiomeric ratio (9:1) was determined by integrating the peaks at 6.68 and 6.66 ppm in ^{1}H NMR in crude reaction mixture. Rf; 0.4 (EtOAc:Hexanes; 1:4); Only the single regioisomer was able to isolate from column chromatography and the minor isomer was only observed in crude NMR. **^{1}H NMR (400 MHz, Acetone- d$_6$):** δ 11.77 (s, 1H), 6.67 (s, 1H), 3.79-3.70 (m, 1H), 1.59 (d, *J* = 8 Hz, 6H), 1.52 (s, 9H); **^{13}C (100 MHz, Acetone-d$_6$):** δ 20.7,, 29.0,, 32.8,, 33.6,, 98.0, , 102.1, 105.1, , 106.4,, 113.5, 115.5, 115.8, 135.0, 135.2, 146.4, 160.7; **IR**

(neat): 3282, 3234, 2970, 2229, 1536, 1371, 1297, 1271, 1072, 824, 717; **HRMS (APPI)** m/z: [M + H]$^+$ Calcd for $C_{18}H_{19}N_4$ 291.1610; found 291.1609.

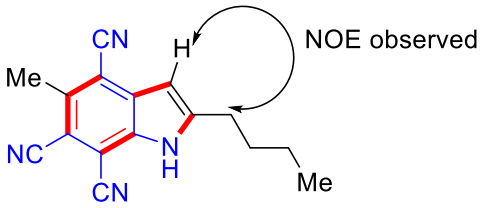


2-(tert-butyl)-5-methyl-1H-indole-4, 6, 7-tricarbonitrile and 5-(tert-butyl)-2-methyl-1H-indole-4, 6, 7-tricarbonitrile **7:** The title compound was obtained as a yellow solid (178 mg, 68% isolated yield rr 9:1) after purification by silica gel column chromatography with a solvent system of 20% EtOAc in hexane. The regiomeric ratio (5:1) was determined by integrating the peaks at 6.54 and 6.84 ppm in ^{1}H NMR in crude reaction mixture. Rf; 0.4 (EtOAc:Hexanes; 1:4); **^{1}H NMR (300 MHz, Acetone-d$_6$):** δ 11.67 (s, 1H),6.84(s, 0.17x1,1H), 6.54 (s, 0.83x1, 1H), 2.94 (s,0.13x3,3H), 2.80 (s, 0.83x3, 3H), 1.96(s,0.17x9,9H) 1.52 (s, 0.83x9, 9H); **^{13}C NMR (75 MHz, Acetone- d$_6$):** δ 19.5, 31.9, 33.7, 98.5, 101.7, 107.5, 108.6, 114.2, 115.9, 116.2, 134.9, 135.7, 137.7, 161.4; **IR (neat):** 3256, 2966, 2927, 2414, 2228, 1531, 1308, 1273, 821, 720; **HRMS (APPI)** m/z: [M + H]$^+$ Calcd $C_{16}H_{15}N_4$ 263.1297; found 263.1294. The major compound in the mixture of this reaction product had t-butyl group. Therefore, we performed the NOE experiment and was observed correlation between the proton at 1.40 ppm and 6.54 which suggest that major product had t-butyl group in the second position. There was no-correlation between the methyl proton and aromatic proton. It suggests that the bulkier the substituent in the 1,3-diketone, preferentially it takes the position two of the substituted indole.

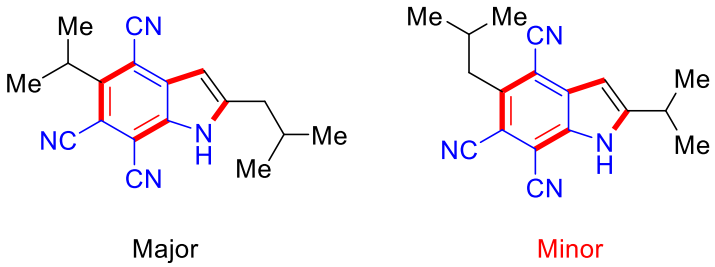


2-Isopropyl-5-neopentyl-1H-indole-4, 6, 7-tricarbonitrile and 5-Isopropyl-2-neopentyl-1H-indole-4, 6, 7-tricarbonitrile **8:** The title compound was obtained as a yellow solid (94 mg, 31% yield) after purification by silica gel column chromatography with a solvent system of 25% EtOAc in hexane. The regiomeric ratio (3:2) was determined by integrating the peaks at 6.65 and 6.61

ppm in ^{1}H NMR in crude reaction mixture. Rf; 0.4 (EtOAc:Hexanes; 1:4); **^{1}H NMR (300 MHz, Acetone-d$_6$):** δ 11.84 (s,1H), 6.67 (s, 0.60x1, 1H), 6.65 (s, 0.40x1, 1H), 3.79-3.70 (m, 0.6x1,1H), 3.38-3.28(m, 0.4x1,1H), 2.90 (s, 0.60x4, 4H), 2.88 (s, 0.0x4, 4H), 2.26-2.11 (m, 0.6x1, 1H), 2.10-2.05(m,0.4x1, 1H)1.60 (d, J = 6 Hz, 0.6x6, 6H), 1.44(d, J = 6 Hz, 0.4x6, 6H) 1.04 (s, 0.6x9, 9H), 1.00 (s, J =0.40x9, 9H),**^{13}C NMR (75 MHz, Acetone-d$_6$):** δ 14.5, 20.7, 21.4, 21.5, 21.7, 28.9, 32.0, 33.6, 35.8, 37.0, 37.9, 46.5, 60.5,101.0, 102.1, 113.5, 115.5, 115.8, 120.4, 126.5, 127.0, 134.4,134.7, 146.4, 205.0,205.3; **IR (neat):** 3241, 2957, 2236, 1538, 1463, 1368, 1304, 1075, 993, 797, 766, 693; **HRMS (APP)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_4$ 305.1766: found 305.1774.



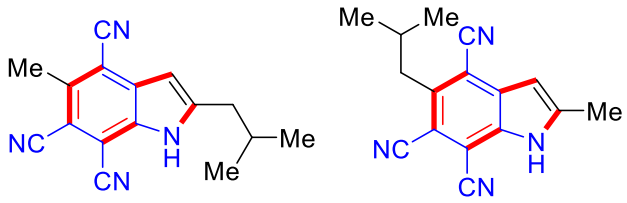
5-Butyl-2-methyl-1H-indole-4, 6, 7-tricarbonitrile and 2-Butyl-5-methyl-1H-indole-4, 6, 7-tricarbonitrile **9:** The title compound was obtained as an orange solid (141 mg, 61% isolated yield) after purification by silica gel column chromatography with a solvent system of 20% EtOAc in hexane. The regiomeric ratio (2:1) was determined by integrating the peaks at 6.65 and 6.63 ppm in ^{1}H NMR in crude reaction mixture. Rf; 0.4 (EtOAc:Hexanes; 1:4); **^{1}H NMR (300 MHz, Acetone-d$_6$):** δ 11.80 (s,1H), 6.65 (s, 0.66x1, 1H), 6.63 (s, 0.33x1, 1H), 3.13 (t, J = 7.5 Hz, 0.33x2, 2H), 3.00 (t, J = 7.5Hz, 0.66x2, 2H), 2.84 (s, 0.33x3, 3H), 2.79(s, 0.66x3, 3H), 2.66 (s, 0.33x3, 3H), 2.65(s,0.66x3, 3H), 1.88-1.68(m, 0.33x2,2H), 1.54-1.38(m, 0.66x2, 2H), (m, 0.5x2H), 1.01-0.93 (m, 3H); **^{13}C NMR (75 MHz, Acetone):** δ 13.9, 19.4, 19.5, 23.0, 31.4, 91.5, 100.6, 101.4, 107.0, 107.9, 114.1, 115.9, 116.1,128.5, 129.5, 135.1, 135.5, 137.6,148.7, 149.7, 153.3; **IR (neat):** 3249, 2931, 2871, 2418, 2230, 1541, 1307, 821; **HRMS (APPI)** m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_4$ 263.1297: found 263.1302. The major component in the mixture of this reaction product had n-butyl group. Therefore, we performed the NOE experiment and was observed correlation between the proton at 2.85 ppm and 6.5 which suggest that major product had n-butyl group in the second position. There was no-correlation between the methyl proton and aromatic proton. It suggests that the bulkier the substituent in the 1,3-diketone, preferentially it takes the position 2 of the substituted indole.



Major Minor

5-Isobutyl-2-isopropyl-1H-indole-4, 6, 7-tricarbonitrile and 2-Isobutyl-5-isopropyl-1H-indole-4, 6, 7-tricarbonitrile **10:** The title compound was obtained as a yellow solid (102 mg, 35% isolated yield) after purification by silica gel column chromatography with a solvent system of 25% EtOAc in hexane. The regiomeric ratio (6:1) was determined by integrating the peaks at 6.67 and 6.85 ppm in ^{1}H NMR in crude reaction mixture. Rf; 0.4 (EtOAc:Hexanes; 1:4); **^{1}H NMR (300 MHz, Acetone-d_6):** δ 11.81 (s, 1H), 6.85(s,0.14x1, 1H), 6.67 (s, 0.86x1, 1H)), 3.78-3.69 (m, 0.86x1, 1H), 3.38-3.29 (m, 0.14x1, 1H),

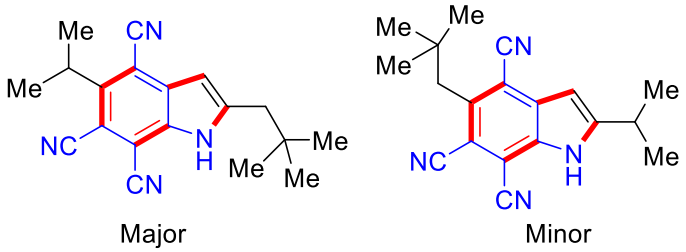
2.98 (d, *J* = 7.5 Hz, 0.14x2, 2H), 2.86 (d, J = 7.5 Hz, 0.86x2, 2H), 2.22-2.09 (m, 1H), 1.58 (d, *J* = 7.2 Hz, 0.86x6, 6H), 1.45 (d, *J* = 6.9 Hz, 0.14x6, 6H), 1.00 (app. t, *J* = 6.2 Hz, 6H); **^{13}C NMR (75 MHz, Acetone-d_6):** δ 21.5, 22.2, 22.3, 22.5, 31.5, 34.4, 37.8, 42.5, 42.8, 98.1, 98.8, 101.8, 102.8, 105.4, 106.6, 114.3, 116.3, 116.6, 135.3, 135.6. 136.3, 136.6, 141.2, 147.2, 152.2; **IR (neat):** 3248, 2959, 2871, 2228, 1756, 1538, 1464, 1305, 1079, 798, 719; **HRMS (APPI)** m/z: [M + H]$^{+}$ Calcd for $C_{18}H_{19}N_4$ 291.1610: found 291.1610.



Major Minor

2-Isobutyl-5-methyl-1H-indole-4, 6, 7-tricarbonitrile and 5-Isobutyl-2-methyl-1H-indole-4, 6, 7-tricarbonitrile **11:** The title compound was obtained as a yellow solid (176 mg, 67% isolated yield) after purification by silica gel column chromatography with a solvent system of 20% EtOAc in hexane. The regiomeric ratio (4:1) was determined by integrating the peaks at 6.67 and 6.65 ppm in ^{1}H NMR in crude reaction mixture. Rf; 0.4 (EtOAc:Hexanes; 1:4); **^{1}H NMR (300 MHz, Acetone-d_6):** δ 11.83 (s, 1H), 6.67(s, 0.8x1, 1H), 6.65 (s, 0.2x1, 1H), 3.02 (d, *J* = 6 Hz, 0.2x2, 2H), 2.87 (d, *J* = 6 Hz, 0.8x2, 2H),2.83 (s, 0.2x3, 3H), 2.80 (s, 0.8x3, 3H), 2.26-2.13 (m, 1H), 1.02 (d, *J* = 6.0 Hz, 0.2x6, 6H), 0.99

(d, *J* = 6.0 Hz, 0.8x6, 6H); **^{13}C NMR (75 MHz, Acetone-d$_6$)**: δ 19.4, 22.6, 37.9, 101.5, 107.1, 108.0, 114.2, 116.0, 116.2, 135.2, 135.5, 137.7, 152.2; **IR (neat):** 3259, 2955, 2425, 2228, 1542, 1306, 830, 692; **HRMS (APPI)** m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_4$ 263.1297; found 263.1299.



5-Isobutyl-2-neopentyl-1H-indole-4, 6, 7-tricarbonitrile and 2-Isobutyl-5-neopentyl-1H-indole-4, 6, 7-tricarbonitrile **12:** The title compound was obtained as a yellow solid (114 mg, 36% isolated yield) after purification by silica gel column chromatography with a solvent system of 30% EtOAc in hexane. The regiomeric ratio (3:2) was determined by integrating the peaks at 6.67 and 6.76 ppm in ^{1}H NMR in crude reaction mixture. Rf; 0.4 (EtOAc:Hexanes; 1:4); **^{1}H NMR (300 MHz, Acetone-d$_6$):** δ 11.85 (s, 1H), 6.68 (s 0.4x1, 1H), 6.66 (s, 0.6x1,1H), 3.12 (s, 0.4x1, 1H), 3.02 (d, *J* = 9.0 Hz, 0.6x2, 2H), 2.90 (s, 0.6x2, 2H), 2.85 (d, *J* = 9.0 Hz, 0.4x2, 2H), 2.18-2.07 (m, 1H), 1.06(d, *J* = 9 Hz, 0.6x6, 6H) 1.03(s, 9H), 1.00(d, *J* = 9.0 Hz, 0.4x6, 6H); **^{13}CNMR (75 MHz, Acetone-d$_6$):** δ 22.4, 29.7, 31.5, 32.8, 42.6, 42.9, 102.0, 107.3, 108.2, 114.3, 116.2, 116.5, 135.2, 135.4, 141.3, 149.4, 150.5, 151.6 ; **IR (neat):** 3246, 2958, 2872, 2227, 1539, 1466, 1307, 1228, 990, 804, 751, 681; **HRMS (APPI)** m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}N_4$ 319.1923, found 319.1930.

5. X-ray of the compound 1

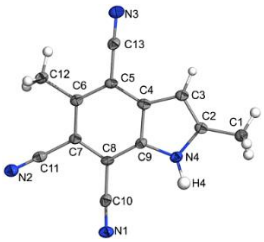


Table 1. Sample and crystal data for rgrp1_28a.

Identification code	rgrp1_28a

Chemical formula	$C_{13}H_8N_4$	
Formula weight	220.23 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.066 x 0.138 x 0.601 mm	
Crystal habit	colorless needle	
Crystal system	monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 10.4869(14) Å	α = 90°
	b = 5.4668(7) Å	β = 100.989(5)°
	c = 18.984(3) Å	γ = 90°
Volume	1068.4(2) $Å^3$	
Z	4	
Density (calculated)	1.369 g/cm^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	456	

Table 2. Data collection and structure refinement for rgrp1_28a.

Diffractometer	Bruker APEXII CCD
Radiation source	fine-focus sealed tube (Mo K_α, λ = 0.71073 Å)
Theta range for data collection	2.07 to 25.75°
Index ranges	-11<=h<=12, -6<=k<=6, -23<=l<=23
Reflections collected	18501
Independent reflections	2047 [R(int) = 0.0989]
Coverage of independent reflections	99.7%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9940 and 0.9490
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2047 / 0 / 160
Goodness-of-fit on F^2	1.023

Final R indices	1293 data; I>2σ(I)	R1 = 0.0517, wR2 = 0.1201
	all data	R1 = 0.0971, wR2 = 0.1444
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0767P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.236 and -0.247 eÅ^{-3}	
R.M.S. deviation from mean	0.064 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for rgrp1_28a.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
N1	0.9296(2)	0.8580(4)	0.41623(11)	0.0259(5)
N2	0.6338(2)	0.8342(4)	0.24154(12)	0.0261(5)
N3	0.3606(2)	0.8472(4)	0.37038(11)	0.0278(5)
N4	0.8246(2)	0.3910(4)	0.51325(11)	0.0205(5)
C1	0.8528(2)	0.6747(5)	0.61711(13)	0.0247(6)
C2	0.7807(2)	0.5912(4)	0.54660(13)	0.0193(6)
C3	0.6683(2)	0.6758(4)	0.50518(13)	0.0196(6)
C4	0.6398(2)	0.5246(4)	0.44377(13)	0.0187(6)
C5	0.5407(2)	0.5176(4)	0.38249(12)	0.0182(6)
C6	0.5390(2)	0.3420(4)	0.32910(12)	0.0187(6)
C7	0.6393(2)	0.1684(4)	0.33817(12)	0.0178(6)
C8	0.7407(2)	0.1696(4)	0.39838(12)	0.0173(5)
C9	0.7394(2)	0.3460(4)	0.45033(12)	0.0169(5)
C10	0.8442(2)	0.9933(4)	0.40685(13)	0.0202(6)
C11	0.6381(2)	0.9827(5)	0.28417(14)	0.0208(6)
C12	0.4337(2)	0.3359(4)	0.26355(13)	0.0234(6)
C13	0.4398(2)	0.6996(4)	0.37538(13)	0.0198(6)

Table 4. Bond lengths (Å) for rgrp1_28a.

N1-C10	1.149(3)	N2-C11	1.141(3)
N3-C13	1.149(3)	N4-C9	1.371(3)

N4-C2	1.386(3)	N4-H4	0.98(3)
C1-C2	1.479(3)	C1-H1A	0.98
C1-H1B	0.98	C1-H1C	0.98
C2-C3	1.366(3)	C3-C4	1.414(3)
C3-H3	0.95	C4-C5	1.405(3)
C4-C9	1.417(3)	C5-C6	1.394(3)
C5-C13	1.440(3)	C6-C7	1.402(3)
C6-C12	1.499(3)	C7-C8	1.405(3)
C7-C11	1.441(3)	C8-C9	1.381(3)
C8-C10	1.437(3)	C12-H12A	0.98
C12-H12B	0.98	C12-H12C	0.98

Table 5. Bond angles (°) for rgrp1_28a.

C9-N4-C2	108.8(2)	C9-N4-H4	127.7(18)
C2-N4-H4	123.5(18)	C2-C1-H1A	109.5
C2-C1-H1B	109.5	H1A-C1-H1B	109.5
C2-C1-H1C	109.5	H1A-C1-H1C	109.5
H1B-C1-H1C	109.5	C3-C2-N4	109.2(2)
C3-C2-C1	130.8(2)	N4-C2-C1	120.0(2)
C2-C3-C4	107.5(2)	C2-C3-H3	126.3
C4-C3-H3	126.3	C5-C4-C3	134.9(2)
C5-C4-C9	118.0(2)	C3-C4-C9	107.1(2)
C6-C5-C4	121.7(2)	C6-C5-C13	120.0(2)
C4-C5-C13	118.2(2)	C5-C6-C7	118.1(2)
C5-C6-C12	121.6(2)	C7-C6-C12	120.2(2)
C6-C7-C8	122.0(2)	C6-C7-C11	119.0(2)
C8-C7-C11	119.0(2)	C9-C8-C7	118.3(2)
C9-C8-C10	119.9(2)	C7-C8-C10	121.8(2)
N4-C9-C8	130.8(2)	N4-C9-C4	107.4(2)
C8-C9-C4	121.7(2)	N1-C10-C8	177.0(3)
N2-C11-C7	178.1(2)	C6-C12-H12A	109.5
C6-C12-H12B	109.5	H12A-C12-H12B	109.5
C6-C12-H12C	109.5	H12A-C12-H12C	109.5
H12B-C12-H12C	109.5	N3-C13-C5	178.9(3)

Table 6. Torsion angles (°) for rgrp1_28a.

C9-N4-C2-C3	-0.4(3)	C9-N4-C2-C1	178.0(2)

N4-C2-C3-C4	0.1(3)	C1-C2-C3-C4	-178.1(2)
C2-C3-C4-C5	-179.6(3)	C2-C3-C4-C9	0.2(2)
C3-C4-C5-C6	179.6(2)	C9-C4-C5-C6	-0.2(3)
C3-C4-C5-C13	0.1(4)	C9-C4-C5-C13	-179.6(2)
C4-C5-C6-C7	0.5(3)	C13-C5-C6-C7	179.9(2)
C4-C5-C6-C12	-179.6(2)	C13-C5-C6-C12	-0.1(3)
C5-C6-C7-C8	-0.9(3)	C12-C6-C7-C8	179.2(2)
C5-C6-C7-C11	179.0(2)	C12-C6-C7-C11	-0.9(3)
C6-C7-C8-C9	1.0(3)	C11-C7-C8-C9	-178.9(2)
C6-C7-C8-C10	-179.1(2)	C11-C7-C8-C10	1.0(3)
C2-N4-C9-C8	179.5(2)	C2-N4-C9-C4	0.5(2)
C7-C8-C9-N4	-179.5(2)	C10-C8-C9-N4	0.6(4)
C7-C8-C9-C4	-0.7(3)	C10-C8-C9-C4	179.4(2)
C5-C4-C9-N4	179.4(2)	C3-C4-C9-N4	-0.5(2)
C5-C4-C9-C8	0.3(3)	C3-C4-C9-C8	-179.5(2)

Table 8. Anisotropic atomic displacement parameters (Å^2) for rgrp1_28a.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	0.0180(12)	0.0302(12)	0.0305(13)	0.0009(10)	0.0075(10)	0.0048(10)
N2	0.0179(12)	0.0301(12)	0.0307(13)	-0.0020(11)	0.0056(10)	0.0013(10)
N3	0.0195(12)	0.0307(13)	0.0334(13)	0.0030(10)	0.0057(10)	0.0026(11)
N4	0.0160(11)	0.0244(12)	0.0212(11)	0.0014(9)	0.0033(9)	0.0026(10)
C1	0.0197(14)	0.0284(14)	0.0253(14)	-0.0022(11)	0.0029(11)	0.0025(11)
C2	0.0167(13)	0.0207(13)	0.0225(13)	0.0005(11)	0.0086(11)	0.0000(10)
C3	0.0143(13)	0.0218(13)	0.0240(13)	0.0005(11)	0.0072(11)	0.0012(10)
C4	0.0149(13)	0.0196(13)	0.0236(13)	0.0021(10)	0.0087(10)	0.0008(10)
C5	0.0142(13)	0.0197(13)	0.0217(13)	0.0026(10)	0.0058(10)	0.0016(10)
C6	0.0139(13)	0.0210(13)	0.0221(13)	0.0028(10)	0.0057(10)	-0.0024(10)
C7	0.0133(12)	0.0196(13)	0.0215(13)	0.0005(10)	0.0057(10)	0.0003(10)
C8	0.0129(12)	0.0183(13)	0.0216(13)	0.0032(10)	0.0058(10)	0.0026(10)
C9	0.0122(12)	0.0204(13)	0.0186(13)	0.0022(10)	0.0042(10)	-0.0010(10)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	0.0150(14)	0.0250(14)	0.0208(13)	-0.0007(11)	0.0036(10)	-0.0045(12)
C11	0.0136(13)	0.0251(14)	0.0249(14)	0.0055(12)	0.0070(10)	0.0010(11)
C12	0.0179(13)	0.0266(14)	0.0248(14)	0.0014(11)	0.0020(11)	0.0026(11)
C13	0.0126(13)	0.0246(13)	0.0228(13)	0.0006(11)	0.0047(10)	-0.0025(11)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for rgrp1_28a.

	x/a	y/b	z/c	U(eq)
H4	0.903(3)	0.299(5)	0.5337(17)	0.056(9)
H1A	0.8350	0.5642	0.6547	0.037
H1B	0.8251	0.8408	0.6266	0.037
H1C	0.9461	0.6745	0.6168	0.037
H3	0.6185	0.8113	0.5157	0.024
H12A	0.4726	0.3248	0.2207	0.035
H12B	0.3816	0.4856	0.2614	0.035
H12C	0.3779	0.1934	0.2658	0.035

Table 9. Hydrogen bond distances (Å) and angles (°) for rgrp1_28a.

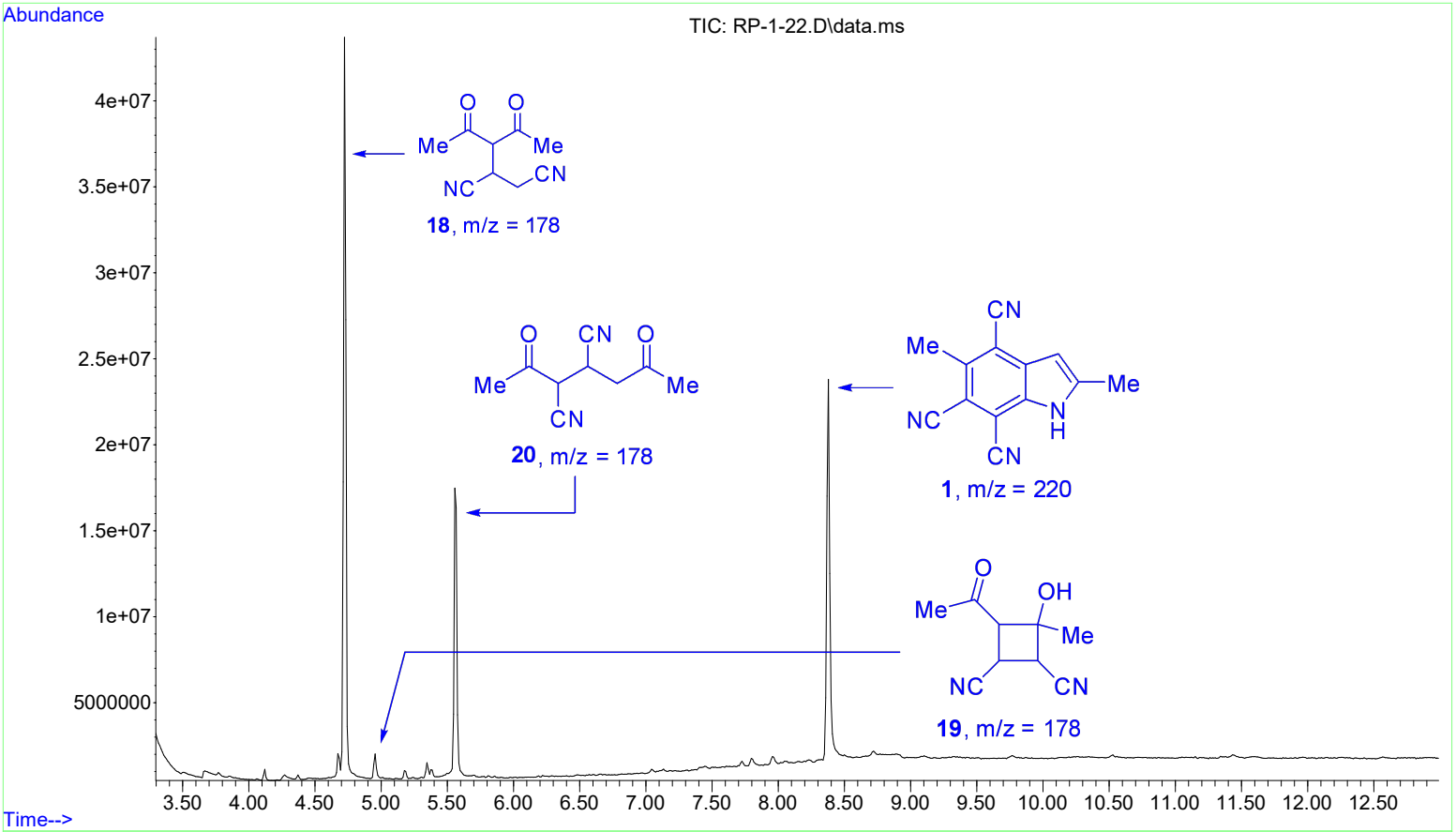
	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N4-H4···N1	0.98(3)	2.02(3)	2.996(3)	173.(3)

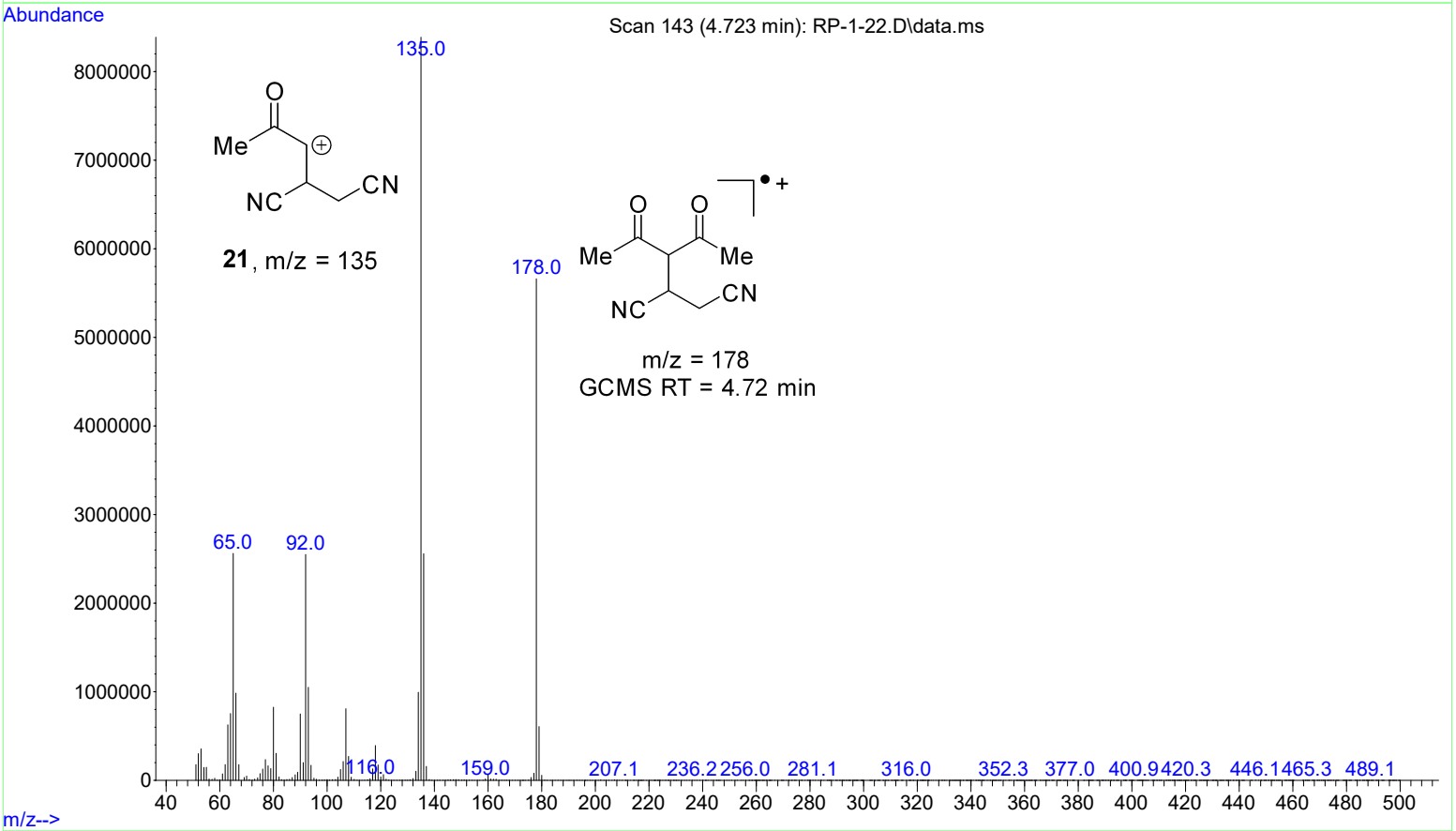
6. References:

1. Hubbard, J. S., and T. M. Harris. "α, α' Dianions of Aliphatic Ketones and the1,3,5 Trianion of 2,4-Pentanedione: Strongly Nucleophilic Carbonyl Synthons." *Journal of the American Chemical Society* **1980**, 2110-112
2. Nandurkar, Nitin S., Mayur J. Bhanushali, Dinkar S. Patil, and Bhalchandra M. Bhanage. "Synthesis of Sterically Hindered 1,3-Diketones." *Synthetic Communications* 39.17 (2008): 4111-115.

7. GC-MS analysis and fragmentation

File :F:\GCMS data backup 02-12-19\RP-1-22.D
Operator :
Acquired : 13 Apr 2015 18:14 using AcqMethod Biaryl-300.M
Instrument : GCMS
Sample Name: RP-1-22
Misc Info :
Vial Number: 31





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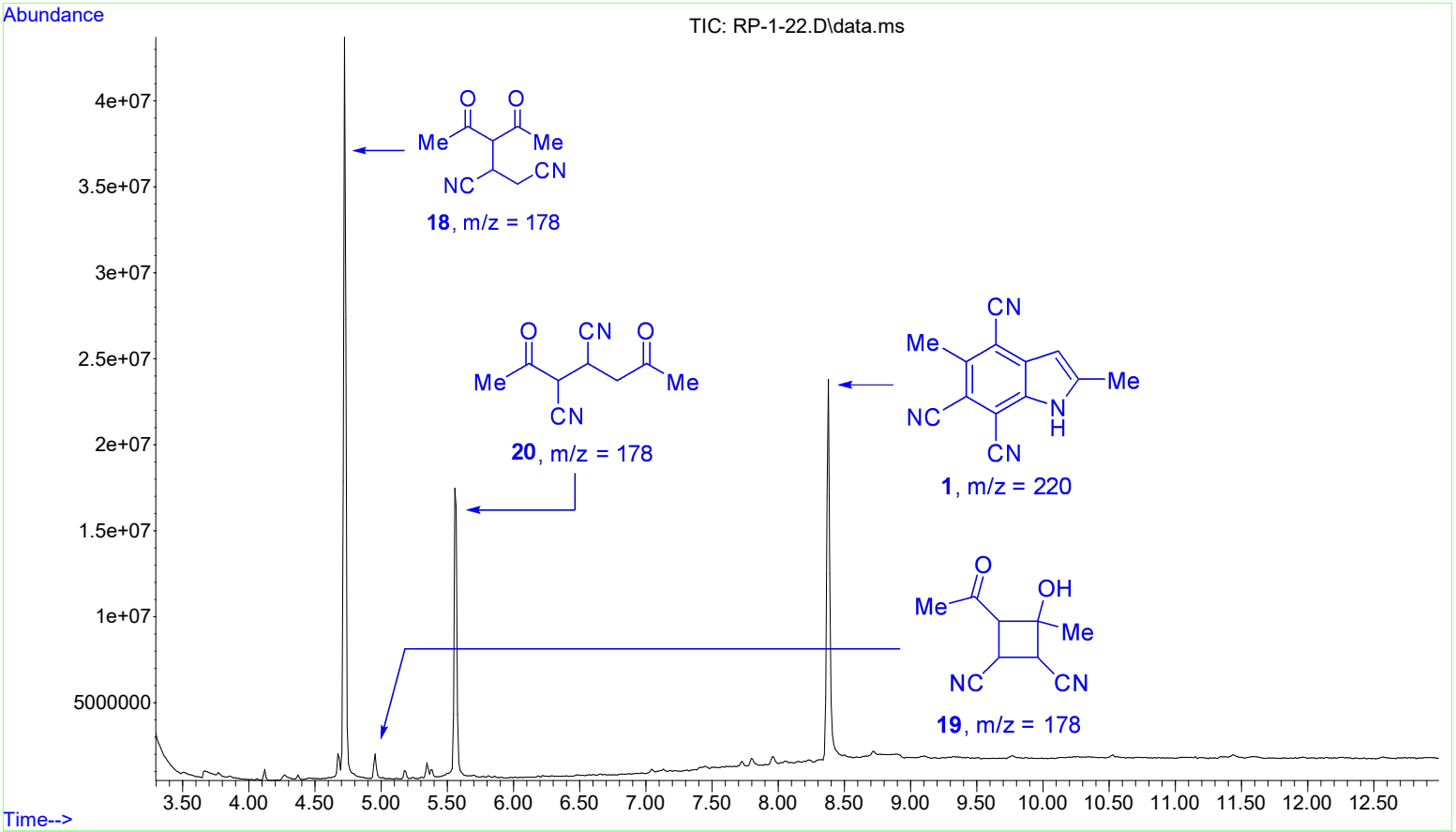
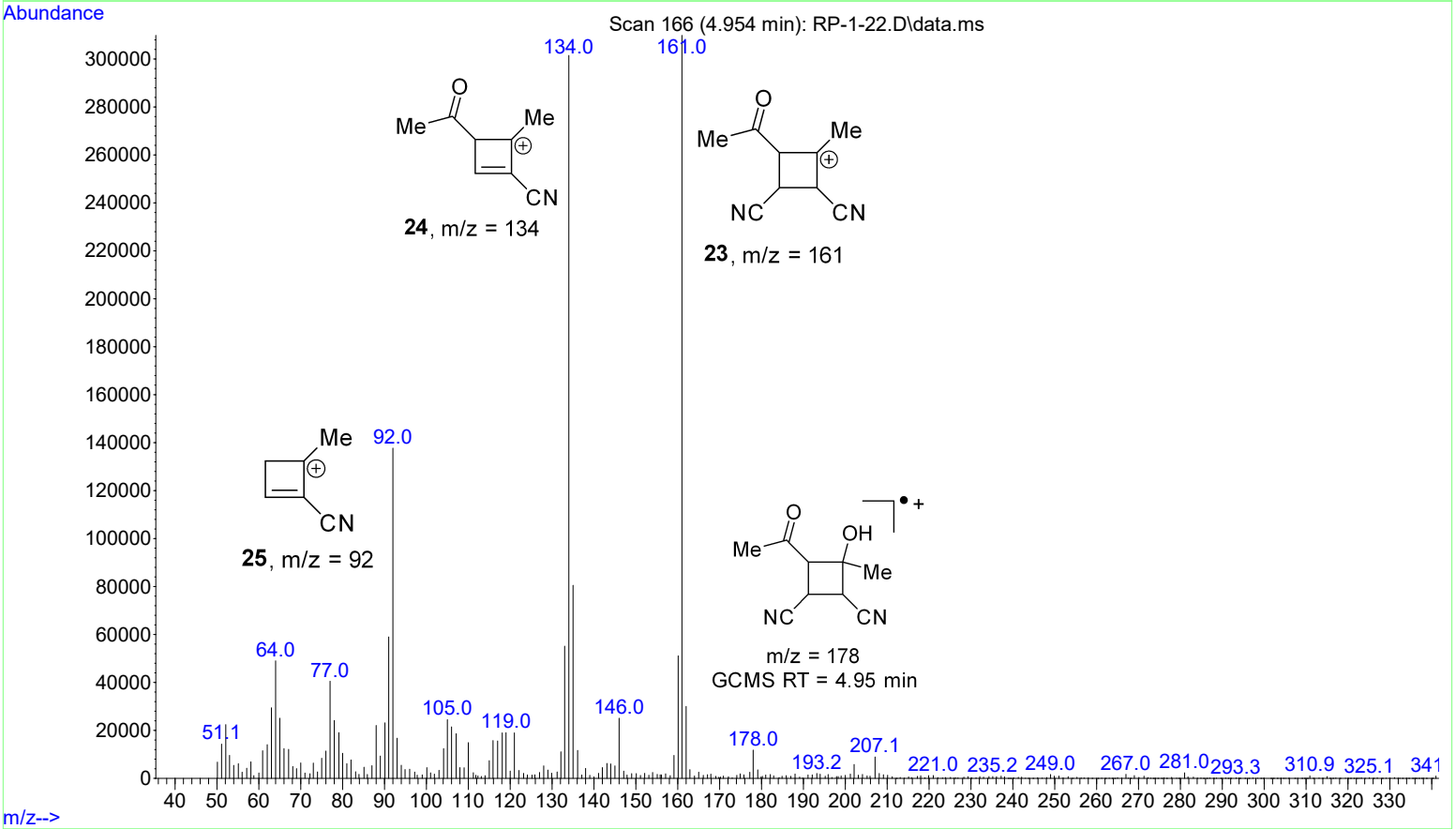
Operator :
Acquired : 13 Apr 2015 18:14 using AcqMethod Biaryl-300.M
Instrument : GCMS
Sample Name: RP-1-22
Misc Info :
Vial Number: 31





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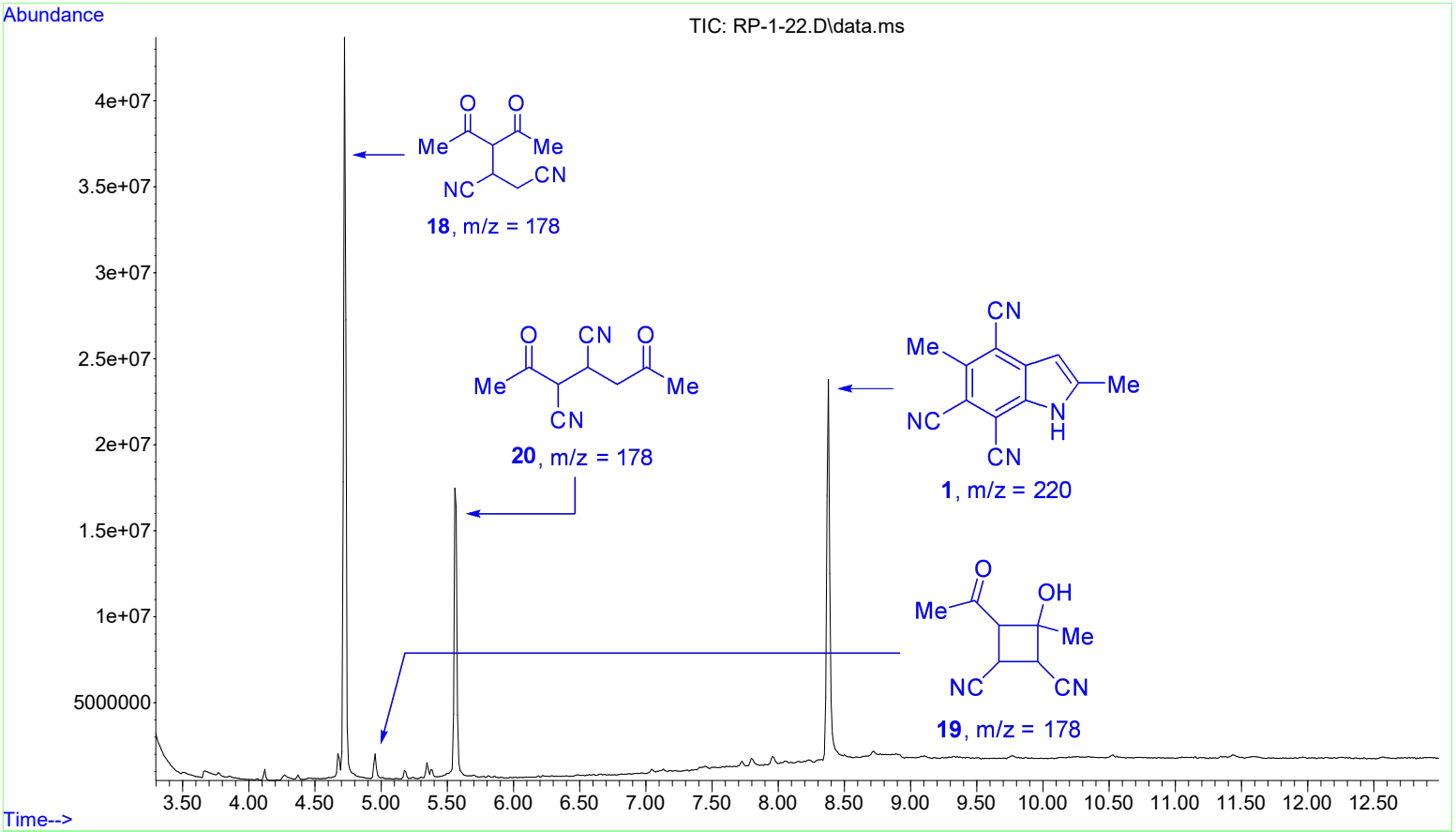
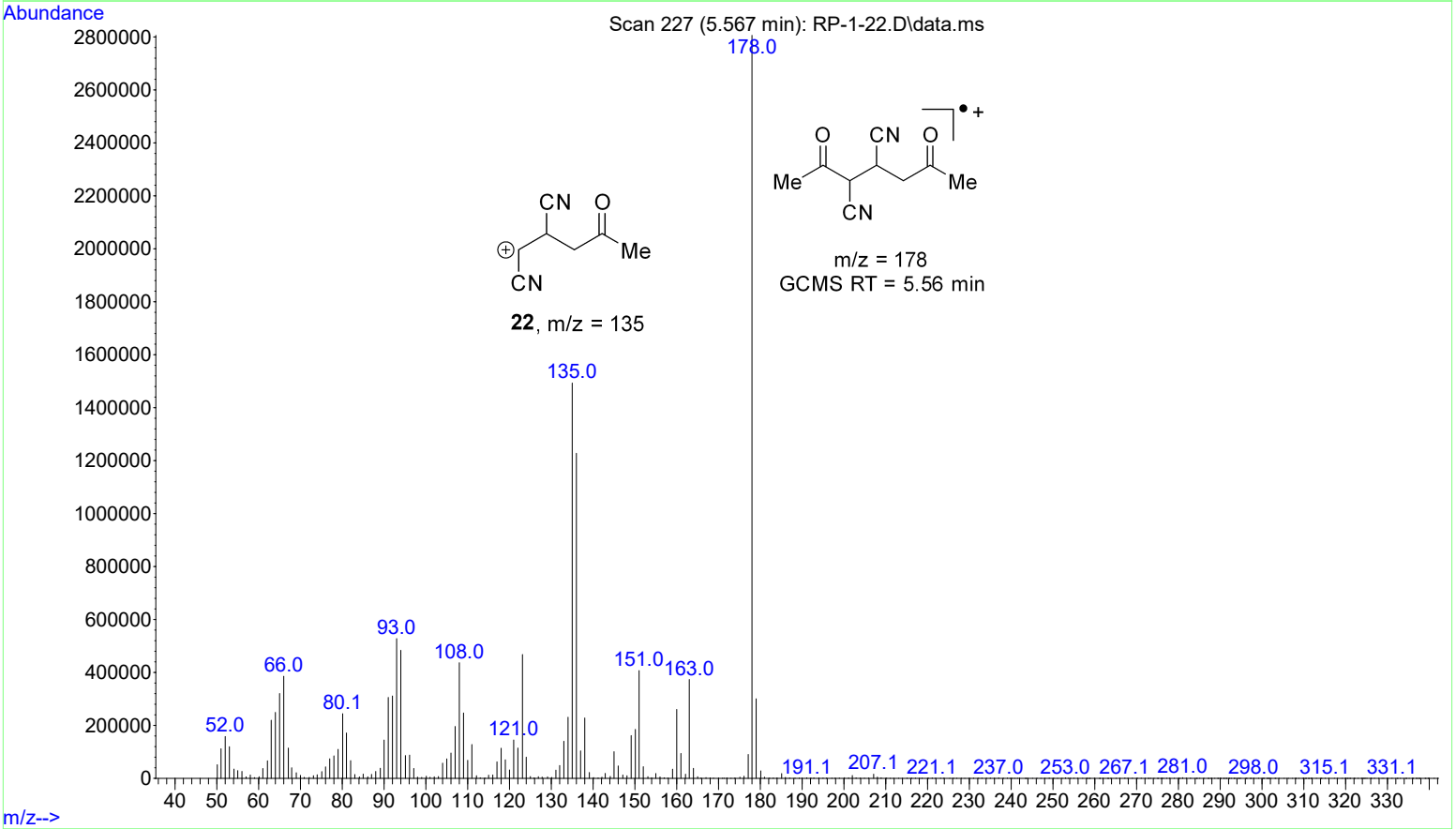
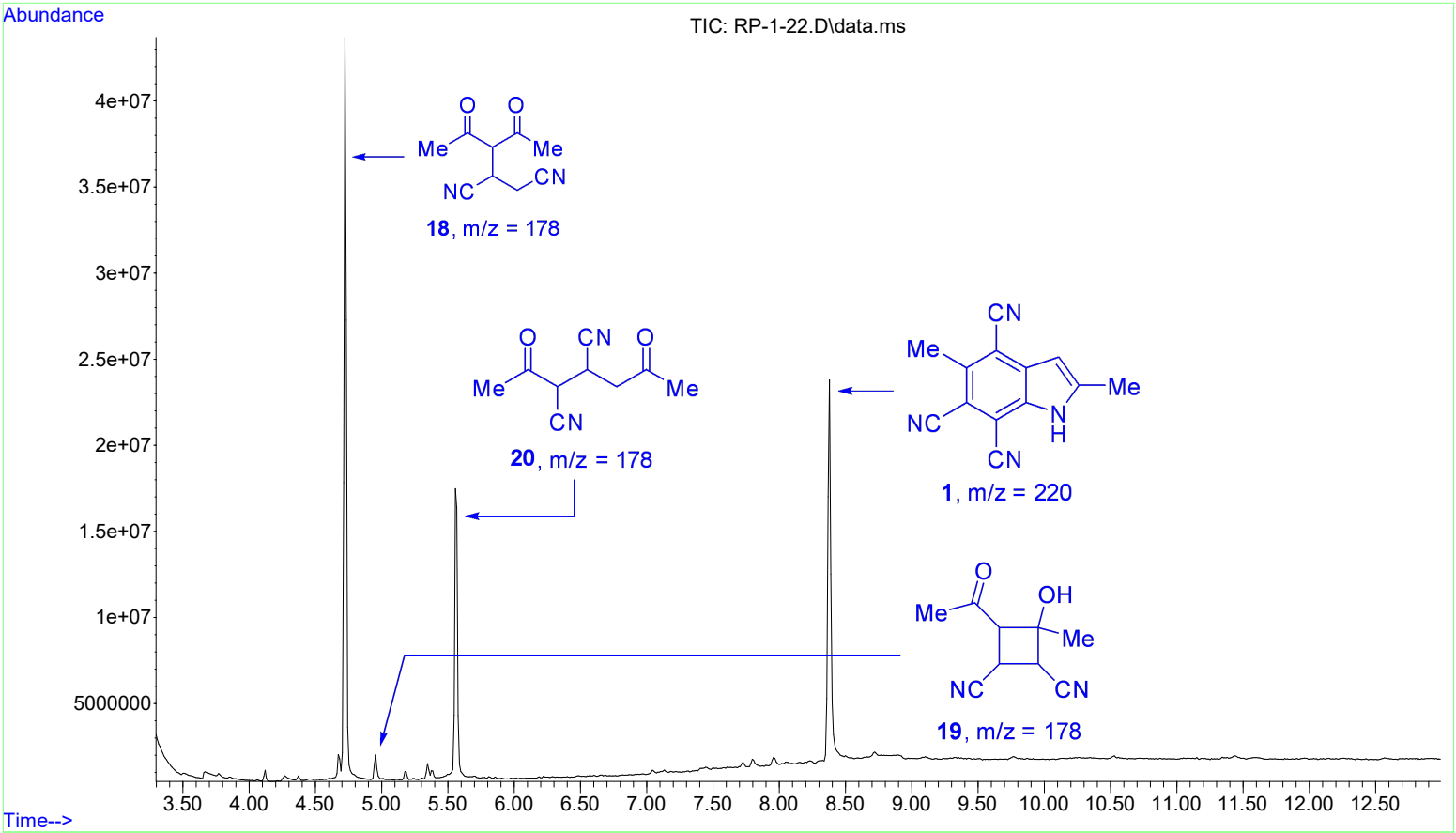
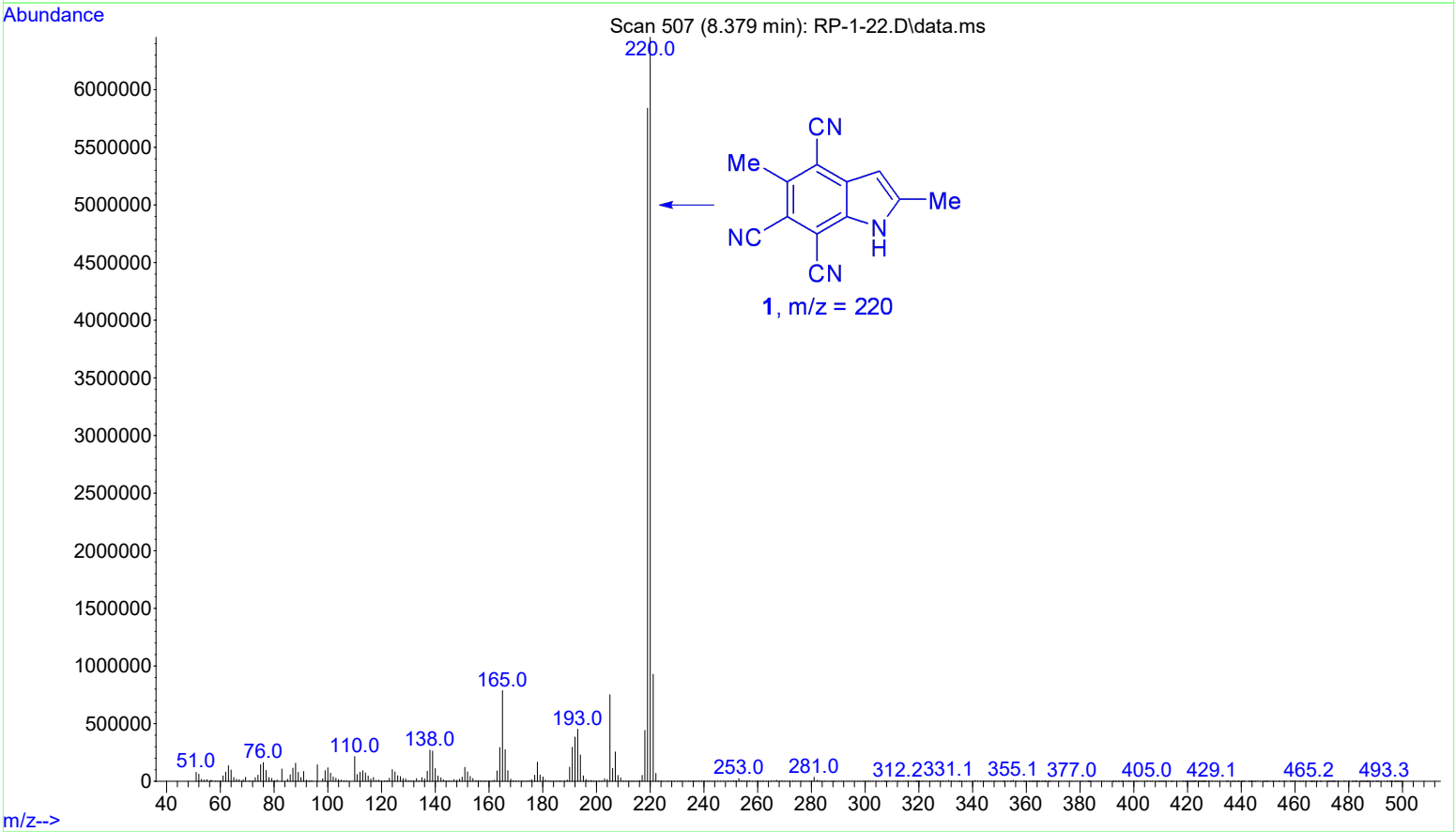
Operator :
Acquired : 13 Apr 2015 18:14 using AcqMethod Biaryl-300.M
Instrument : GCMS
Sample Name: RP-1-22
Misc Info :
Vial Number: 31



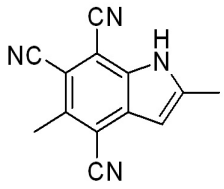


File :F:\GCMS data backup 02-12-19\RP-1-22.D
Operator :
Acquired : 13 Apr 2015 18:14 using AcqMethod Biaryl-300.M
Instrument : GCMS
Sample Name: RP-1-22
Misc Info :
Vial Number: 31





RP-1-32-1H.3.fid
RP-1-32-1H



1

1H NMR: 300 MHz

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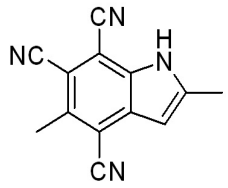
2	Solvent	Acetone
3	Acquisition Time	2.0972
4	Acquisition Date	300.13
5	Modification Date	2015-11-17T19:44:00
6	Spectrometer Frequency	3906.2
7	Spectral Width	2015-11-17T19:44:52
8	Lowest Frequency	-303.9
9	Nucleus	1H
10	Acquired Size	8192
11	Spectral Size	65536
12	Digital Resolution	0.06

RP-1-90A-13C.1.fid
RP-1-90A-13C

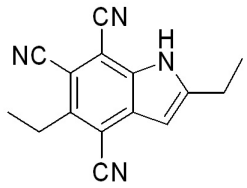


1

13C NMR: 75 MHz

	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-90A-13C/ 1/ fid
2	Solvent	DMSO
3	Acquisition Time	0.9437
4	Acquisition Date	2015-12-05T14:14:00
5	Modification Date	2015-12-05T13:14:20
6	Spectrometer Frequency	75.48
7	Spectral Width	17361.1
8	Lowest Frequency	-877.2
9	Nucleus	13C
10	Acquired Size	16384
11	Spectral Size	32768
12	Digital Resolution	0.53

RP-1-90B-1H.4.fid
RP-1-90B-1H



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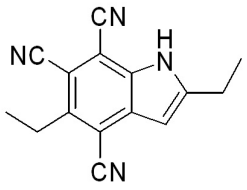
1H NMR: 300 MHz

	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-90B-1H/ 4/ fid
2	Solvent	Acetone
3	Acquisition Time	2.0972
4	Acquisition Date	2015-12-05T15:17:00
5	Modification Date	2015-12-05T14:17:38
6	Spectrometer Frequency	300.13
7	Spectral Width	3906.2
8	Lowest Frequency	-336.8
9	Nucleus	1H
10	Acquired Size	8192
11	Spectral Size	65536
12	Digital Resolution	0.06

RP-1-90B-13C.1.fid
RP-1-90B-13C

13C NMR: 75 MHz



2

	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-90B-13C/ 1/ fid
2	Solvent	Acetone
3	Acquisition Time	0.9437
4	Acquisition Date	2015-12-07T12:22:00
5	Modification Date	2015-12-07T11:22:10
6	Spectrometer Frequency	75.48
7	Spectral Width	17361.1
8	Lowest Frequency	-815.1
9	Nucleus	13C
10	Acquired Size	16384
11	Spectral Size	32768
12	Digital Resolution	0.53

206.19
154.65
143.75
135.67
135.39
116.00
115.70
114.10
107.22
106.33
101.77
100.06
30.57 Acetone
30.31 Acetone
30.05 Acetone
29.80 Acetone
29.54 Acetone
29.28 Acetone
29.03 Acetone
27.85
22.13
15.49
13.01

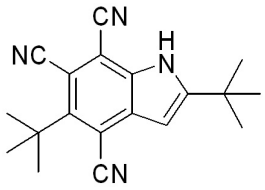
16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

RP-1-155-F1-1H.1.fid
RP-1-155-F1-1H

1H NMR: 300 MHz



3

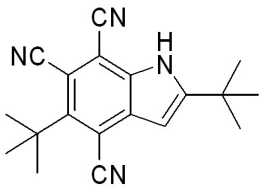
	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-155-F1-1H/ 1/ fid
2	Solvent	Acetone
3	Acquisition Time	2.0972
4	Acquisition Date	2016-06-02T17:44:00
5	Modification Date	2016-06-02T16:44:08
6	Spectrometer Frequency	300.13
7	Spectral Width	3906.2
8	Lowest Frequency	-302.8
9	Nucleus	1H
10	Acquired Size	8192
11	Spectral Size	65536
12	Digital Resolution	0.06

RP-1-155-F1-13C.1.fid
RP-1-155-F1-13C

206.12 161.14 148.18 137.13 135.14 118.66 117.90 114.54 107.43 105.93 105.18 99.54

38.57 33.63 31.85 30.57 Acetone 30.31 Acetone 30.06 Acetone 29.79 Acetone 29.54 Acetone 29.29 Acetone 29.03 Acetone

13C NMR: 75 MHz



3

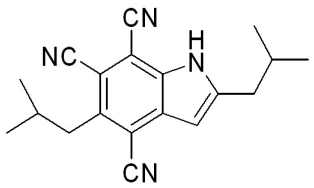
	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-155-F1-13C/ 1/ fid
2	Solvent	Acetone
3	Acquisition Time	0.9437
4	Acquisition Date	2016-06-02T19:28:00
5	Modification Date	2016-06-02T18:28:30
6	Spectrometer Frequency	75.48
7	Spectral Width	17361.1
8	Lowest Frequency	-816.3
9	Nucleus	13C
10	Acquired Size	16384
11	Spectral Size	32768
12	Digital Resolution	0.53

170000 160000 150000 140000 130000 120000 110000 100000 90000 80000 70000 60000 50000 40000 30000 20000 10000 0 -10000

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

RP-1-165-fraction2.1.fid
RP-1-165-fraction2



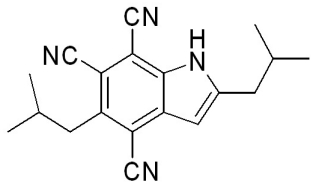
4

1H NMR: 300 MHz

	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-165-fraction2/ 1/ fid
2	Solvent	Acetone
3	Acquisition Time	2.0972
4	Acquisition Date	2016-06-23T10:22:00
5	Modification Date	2016-06-23T09:22:46
6	Spectrometer Frequency	300.13
7	Spectral Width	3906.2
8	Lowest Frequency	-304.0
9	Nucleus	1H
10	Acquired Size	8192
11	Spectral Size	65536
12	Digital Resolution	0.06

RP-1-165-13C.1.fid
RP-1-165-13C

206.15 152.14 141.20 135.64 135.27 116.39 116.14 114.21 108.02 107.24 101.88 101.63 42.81 37.83 31.49 30.55 Acetone 30.29 Acetone 30.04 Acetone 29.78 Acetone 29.52 Acetone 29.27 Acetone 29.01 Acetone 22.56 22.33



4

13C NMR: 75 MHz

	Parameter	Value
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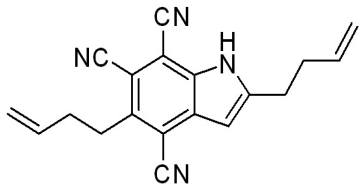
2	Solvent	Acetone
3	Acquisition Time	0.9437
4	Acquisition Date	2016-06-23T10:56:00
5	Modification Date	2016-06-23T09:56:02
6	Spectrometer Frequency	75.48
7	Spectral Width	17361.1
8	Lowest Frequency	-818.4
9	Nucleus	13C
10	Acquired Size	16384
11	Spectral Size	32768
12	Digital Resolution	0.53

RP-1-128-1H.2.fid
RP-1-128-1H

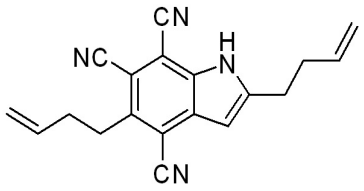


5

1H NMR: 300 MHz

	Parameter	Value
1	Data File Name	G:/ Thesis Data/ NMR/ Indoles/ RP-1-128-1H/ 2/ fid
2	Solvent	Acetone
3	Acquisition Time	2.0972
4	Acquisition Date	2016-02-24T18:33:00
5	Modification Date	2016-02-24T17:33:02
6	Spectrometer Frequency	300.13
7	Spectral Width	3906.2
8	Lowest Frequency	-303.8
9	Nucleus	1H
10	Acquired Size	8192
11	Spectral Size	65536
12	Digital Resolution	0.06

RP-1-128-13C.2.fid
RP-1-128-13C

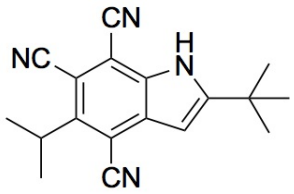


5

13C NMR: 75 MHz

	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-128-13C/ 2/ fid
2	Solvent	Acetone
3	Acquisition Time	0.9437
4	Acquisition Date	2016-02-24T20:05:00
5	Modification Date	2016-02-19T19:57:50
6	Spectrometer Frequency	75.48
7	Spectral Width	17361.1
8	Lowest Frequency	-889.4
9	Nucleus	13C
10	Acquired Size	16384
11	Spectral Size	32768
12	Digital Resolution	0.53

RD-organic-letter-P.2.fid
RD-organic-letter-P



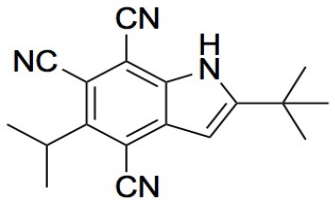
6

1H NMR: 400 MHz

	Parameter	Value
1	Data File Name	C:/ Users/ girigroup/ Documents/ Rishi/ RD-organic-letter-P/ 2/ fid
2	Solvent	Acetone
3	Acquisition Time	3.9977
4	Acquisition Date	2020-03-21T20:25:56
5	Modification Date	2020-03-21T20:25:31
6	Spectrometer Frequency	400.13
7	Spectral Width	8196.7
8	Lowest Frequency	-1632.2
9	Nucleus	1H
10	Acquired Size	32768
11	Spectral Size	65536
12	Digital Resolution	0.13

RD-organic-letter-C.3.fid
RD-organic-letter-C

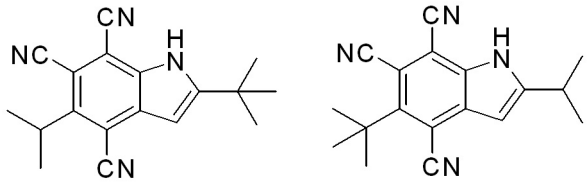
13C NMR: 100 MHz



6

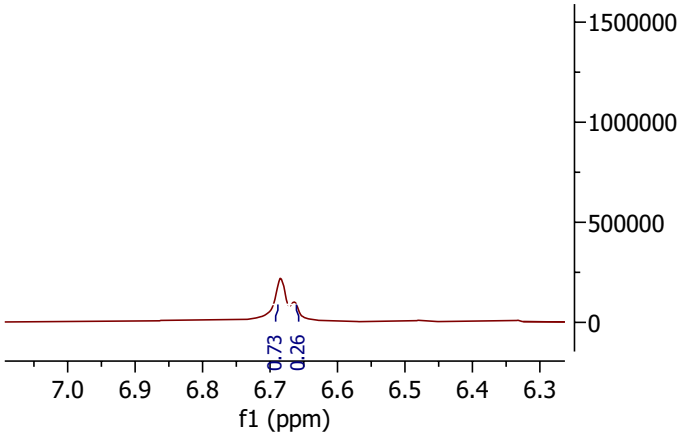
	Parameter	Value
1	Data File Name	C:/ Users/ girigroup/ Documents/ Rishi/ RD-organic-letter-C/ 3/ fid
2	Solvent	Acetone
3	Acquisition Time	1.3763
4	Acquisition Date	2020-03-21T20:45:06
5	Modification Date	2020-03-21T20:44:41
6	Spectrometer Frequency	100.62
7	Spectral Width	23809.5
8	Lowest Frequency	-1843.5
9	Nucleus	13C
10	Acquired Size	32768
11	Spectral Size	65536
12	Digital Resolution	0.36

RD-organic-letter-regioisomers-P.1.fid
RD-organic-letter-regioisomers-P

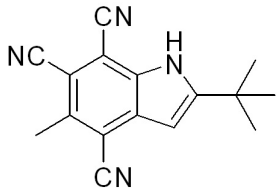


6
regioisomeric protons peak zoomed

1H NMR: 400 MHz



RP-1-90C-1H.4.fid
RP-1-90C-1H



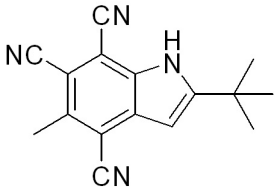
7

1H NMR: 300 MHz

	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-90C-1H/ 4/ fid
2	Solvent	Acetone
3	Acquisition Time	2.0972
4	Acquisition Date	2015-12-05T15:26:00
5	Modification Date	2015-12-05T14:26:44
6	Spectrometer Frequency	300.13
7	Spectral Width	3906.2
8	Lowest Frequency	-300.8
9	Nucleus	1H
10	Acquired Size	8192
11	Spectral Size	65536
12	Digital Resolution	0.06

RP-1-90C-13C.1.fid
RP-1-90C-13C

206.2 161.5 137.7 135.8 134.9 116.2 115.9 114.3 108.6 107.5 101.7 98.5 33.7 31.9 30.6 Acetone 30.4 Acetone 30.1 Acetone 29.8 Acetone 29.6 Acetone 29.3 Acetone 29.1 Acetone 19.5



7

13C NMR: 75 MHz

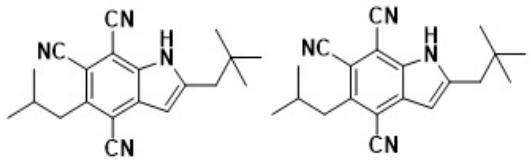
	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-90C-13C/ 1/ fid
2	Solvent	Acetone
3	Acquisition Time	0.9438
4	Acquisition Date	2015-12-07T14:03:00
5	Modification Date	2015-12-07T13:03:06
6	Spectrometer Frequency	75.48
7	Spectral Width	17361.1
8	Lowest Frequency	-811.5
9	Nucleus	13C
10	Acquired Size	16384
11	Spectral Size	32768
12	Digital Resolution	0.53

35000 30000 25000 20000 15000 10000 5000 0

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

RP-1-166-1H.1.fid
RP-1-166-1H



8

1H NMR: 300 MHz

	Parameter	Value
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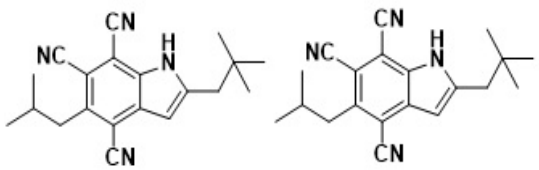
2	Solvent	Acetone
3	Acquisition Time	2.0972
4	Acquisition Date	2016-06-25T15:33:00
5	Modification Date	2016-06-25T14:33:12
6	Spectrometer Frequency	300.13
7	Spectral Width	3906.2
8	Lowest Frequency	-303.7
9	Nucleus	1H
10	Acquired Size	8192
11	Spectral Size	65536
12	Digital Resolution	0.06

RP-1-166-13C.2.fid
RP-1-166-13C

206.10
150.53
141.30
135.39
135.17
127.01
126.52
120.41
116.47
116.23
114.32
108.20
107.33
102.83
102.05
60.47
46.51
42.87
42.65
37.87
35.83
32.80
31.55
30.57 Acetone
30.31 Acetone
30.05 Acetone
29.80 Acetone
29.70
29.54 Acetone
29.28 Acetone
29.03 Acetone
22.37
14.45

13C NMR: 75 MHz



8

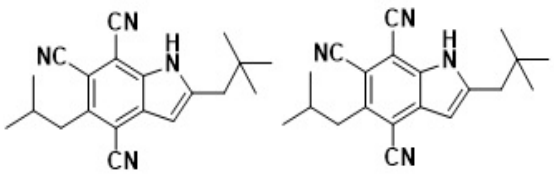
	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-166-13C/ 2/ fid
2	Solvent	Acetone
3	Acquisition Time	0.9437
4	Acquisition Date	2016-06-25T18:12:00
5	Modification Date	2016-06-25T17:12:38
6	Spectrometer Frequency	75.48
7	Spectral Width	17361.1
8	Lowest Frequency	-814.8
9	Nucleus	13C
10	Acquired Size	16384
11	Spectral Size	32768
12	Digital Resolution	0.53

5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

RP-1-192 TT 1-15.1.fid
RP-188-C



9

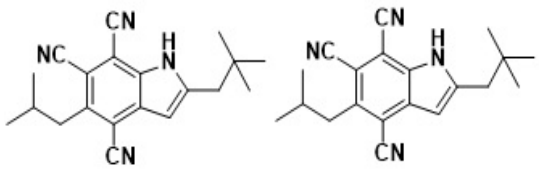
1H NMR: 300 MHz

	Parameter	Value
1	Data File Name	G:/ Thesis Data/ NMR/ Indoles/ RP-1-192 TT 1-15/ 1/ fid
2	Solvent	Acetone
3	Acquisition Time	2.0972
4	Acquisition Date	2017-04-12T19:05:32
5	Modification Date	2017-04-12T17:05:32
6	Spectrometer Frequency	300.13
7	Spectral Width	3906.2
8	Lowest Frequency	-300.6
9	Nucleus	1H
10	Acquired Size	8192
11	Spectral Size	65536
12	Digital Resolution	0.06

f1 (ppm)

RP-1-119-13C.2.fid
RP-1-119-13C

13C NMR: 75 MHz



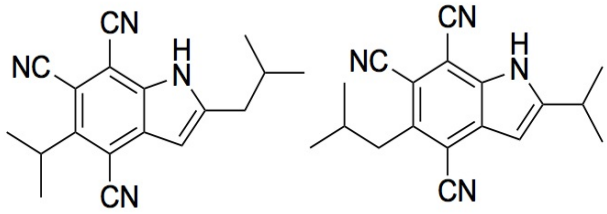
9

	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-119-13C/ 2/ fid
2	Solvent	Acetone
3	Acquisition Time	0.9437
4	Acquisition Date	2016-02-11T20:11:00
5	Modification Date	2016-02-11T19:11:38
6	Spectrometer Frequency	75.48
7	Spectral Width	17361.1
8	Lowest Frequency	-810.7
9	Nucleus	13C
10	Acquired Size	16384
11	Spectral Size	32768
12	Digital Resolution	0.53

206.2 206.2 170.6 166.6 153.3 150.1 148.8 137.7 135.5 135.2 116.2 115.9 114.2 107.9 107.1 101.4 100.7 91.5 31.5 30.6 Acetone 30.4 Acetone 30.1 Acetone 29.8 Acetone 29.6 Acetone 29.3 Acetone 29.1 Acetone 28.6 23.0 19.5 14.0

f1 (ppm)

RP-1-174-F1-1H.1.fid
RP-1-174-F1-1H



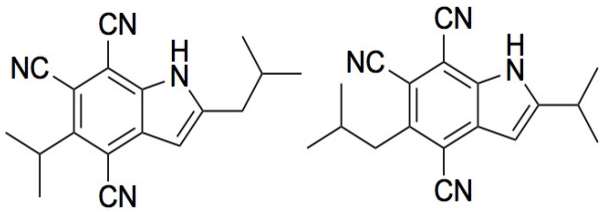
10

1H NMR: 300 MHz

	Parameter	Value
1	Data File Name	G:/ Thesis Data/ NMR/ Indoles/ RP-1-174-F1-1H/ 1/ fid
2	Solvent	Acetone
3	Acquisition Time	2.0972
4	Acquisition Date	2016-07-20T10:54:00
5	Modification Date	2016-07-20T09:54:40
6	Spectrometer Frequency	300.13
7	Spectral Width	3906.2
8	Lowest Frequency	-300.0
9	Nucleus	1H
10	Acquired Size	8192
11	Spectral Size	65536
12	Digital Resolution	0.06

RP-1-174-tt15-13C.1.fid
RP-1-174-tt15-13C

206.17
152.29
147.28
136.33
135.64
116.69
116.40
114.34
106.63
105.51
102.91
101.88
98.67
98.12
97.78
42.90
37.89
34.50
31.58
30.61 Acetone
30.35 Acetone
30.10 Acetone
29.84 Acetone
29.58 Acetone
29.33 Acetone
29.07 Acetone
22.61
22.39
22.24
21.60



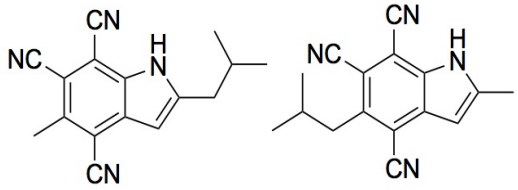
10

13C NMR: 75 MHz

	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-174-tt15-13C/ 1/ fid
2	Solvent	Acetone
3	Acquisition Time	0.9437
4	Acquisition Date	2016-08-13T10:58:00
5	Modification Date	2016-08-13T09:58:52
6	Spectrometer Frequency	75.48
7	Spectral Width	17361.1
8	Lowest Frequency	-811.6
9	Nucleus	13C
10	Acquired Size	16384
11	Spectral Size	32768
12	Digital Resolution	0.53

f1 (ppm)

RP-1-194 TT 20-36.1.fid
RP-188-C



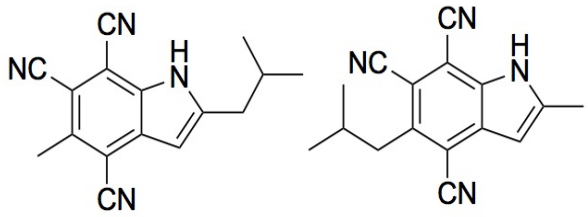
11

1H NMR: 300 MHz

	Parameter	Value
1	Data File Name	G:/ Thesis Data/ NMR/ Indoles/ RP-1-194 TT 20-36/ 1/ fid
2	Solvent	Acetone
3	Acquisition Time	2.0972
4	Acquisition Date	2017-04-12T19:12:11
5	Modification Date	2017-04-12T17:12:10
6	Spectrometer Frequency	300.13
7	Spectral Width	3906.2
8	Lowest Frequency	-300.6
9	Nucleus	1H
10	Acquired Size	8192
11	Spectral Size	65536
12	Digital Resolution	0.06

RP-1-120-13C.1.fid
RP-1-120-13C

206.2
152.2
137.8
135.6
135.2
116.2
116.0
114.2
108.0
107.2
101.6
101.5
37.9
30.6 Acetone
30.4 Acetone
30.1 Acetone
29.8 Acetone
29.6 Acetone
29.3 Acetone
29.1 Acetone
22.6
19.5

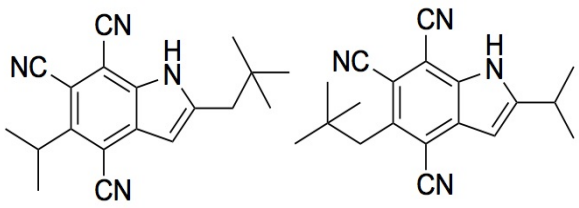


11

13C NMR: 75 MHz

	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-120-13C/ 1/ fid
2	Solvent	Acetone
3	Acquisition Time	0.9437
4	Acquisition Date	2016-02-11T21:18:00
5	Modification Date	2016-02-11T20:18:28
6	Spectrometer Frequency	75.48
7	Spectral Width	17361.1
8	Lowest Frequency	-810.1
9	Nucleus	13C
10	Acquired Size	16384
11	Spectral Size	32768
12	Digital Resolution	0.53

RP-1-175-tt17.1.fid
RP-1-175-tt17



12

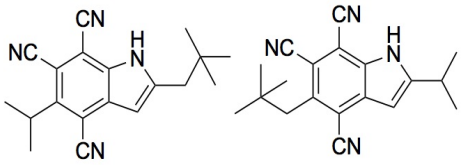
1H NMR: 300 MHz

	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-175-tt17/ 1/ fid
2	Solvent	Acetone
3	Acquisition Time	2.0972
4	Acquisition Date	2016-08-13T12:54:00
5	Modification Date	2016-08-13T11:54:30
6	Spectrometer Frequency	300.13
7	Spectral Width	3906.2
8	Lowest Frequency	-303.8
9	Nucleus	1H
10	Acquired Size	8192
11	Spectral Size	65536
12	Digital Resolution	0.06

RP-1-175 re 13c 083117.1.fid
RP-1-175 re

205.31
205.03
146.41
134.77
134.43
115.83
115.55
113.50
102.14
101.01

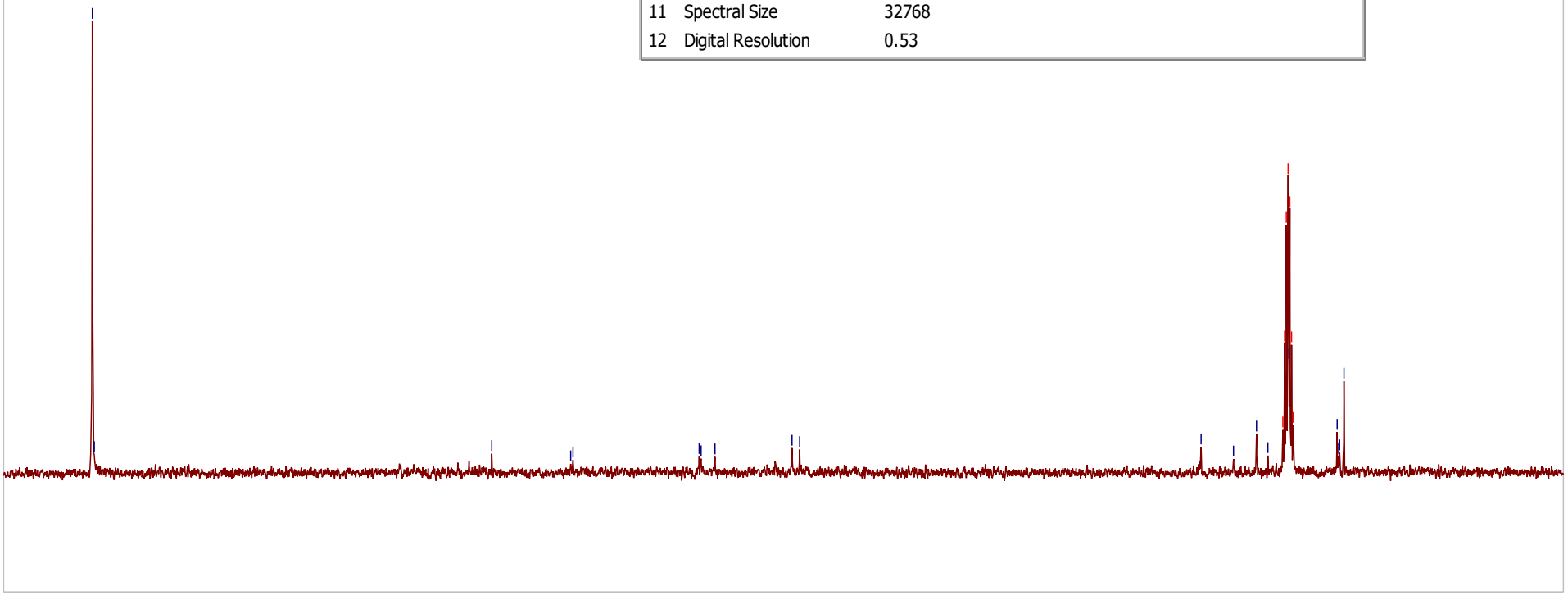
41.81
37.03
33.64
31.96
29.75 Acetone
29.49 Acetone
29.24 Acetone
28.98 Acetone
28.86
28.72 Acetone
28.47 Acetone
28.21 Acetone
21.74
21.53
21.38
20.74



12

13C NMR: 75 MHz

	Parameter	Value
1	Data File Name	E:/ Thesis Data/ NMR/ Indoles/ RP-1-175 re 13c 083117/ 1/ fid
2	Solvent	Acetone
3	Acquisition Time	0.9437
4	Acquisition Date	2017-08-31T19:33:53
5	Modification Date	2017-08-31T17:33:54
6	Spectrometer Frequency	75.48
7	Spectral Width	17361.1
8	Lowest Frequency	-877.2
9	Nucleus	13C
10	Acquired Size	16384
11	Spectral Size	32768
12	Digital Resolution	0.53



1100 1000 900 800 700 600 500 400 300 200 100 0 -100

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)