SUPPORTING INFORMATION

Half-Sandwich (η^5-Cp*)Rh(III) Complex of Pyrazolated Organo-sulfur/selenium/tellurium Ligands: Efficient Catalysts for Base/ Solvent Free C−N Coupling of Chloroarenes under Aerobic Conditions

Charu Sharma, [a] Avinash Kumar Srivastava, [a] Kamal Nayan Sharma*[b] Raj Kumar Joshi*[a]

[a] Department of Chemistry, Malaviya National Institute of Technology Jaipur, J.L.N. Marg, Jaipur 302017, Rajasthan, India

[b] Department of Chemistry, Amity School of Applied Sciences, Amity University Haryana, Manesar, Gurugram 122413, Haryana, India

Chemicals and reagents: Reactants, reagents, chemicals and solvents available commercially within the country were used.

Experimental

Chemicals and instrumentation. The common chemicals and reagents which were available commercially within the country were used as received. $RhCl_3.xH_2O$, Ph_2Se_2, $NaBH_4$, and 4-bromopyrazole were procured from Sigma-Aldrich (USA). Pyrazolated organoselenium ligand (**L**) and Rh(III)-dimer; $[Rh(\eta^5\text{-Cp*})Cl(\mu\text{-Cl})]_2$, were prepared by previously reported methods. Standard methods were used for drying and distillation of the solvents. Silica gel (100-200 and 60-120 mesh) and sheets for TLC (silica gel $60F_{254}$) used in column chromatography, were procured from Fisher Scientific and Merck, respectively. The melting point of solid compounds were determined in an open capillary and reported as such. All the reaction products were vacuum dried for several hours prior to being analyzed and weighted as well. JEOL ECS-400 spectrometer operating at 400 MHz and 101 MHz for ^1H and ^{13}C nuclei, respectively were used to record the NMR spectra of all the compounds synthesized. FT-IR spectra were recorded on a Perkin-Elmer 10.4.00 FT-IR spectrometer within the range 4000-400 cm^{-1} using KBr pellets of the sample. High-Resolution Electron Impact Mass Spectra (HR-EIMS) were obtained with Xevo G2-S Q-Tof (Waters, USA). The diffraction data on a single crystal of **1** was collected on a Bruker AXS SMART Apex CCD Diffractometer using Mo-Ka (0.71073 Å) radiation at 298(2) K. The SADABS program was used for absorption correction and SHELXTL for space group, structure determination, and refinements. Olex2 was employed for the final data presentation and structure plots. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were

included in idealized position with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they are attached. The structure was refined (weighted least squares refinement on F^2) to convergence.

Synthesis of half-sandwich (η5-Cp*)Rh(III) complex (1 - 3). Pyrazolated selenoether ligand (L) was prepared by using a reported method.20-23 Ligand (L1) (0.056 g, 0.2 mmol), (L2) (0.066 g, 0.2 mmol), or (L3) (0.076 g, 0.2 mmol) solid [Rh(η5-Cp*)Cl2]2 (0.062 g, 0.1 mmol) and methanol (25 mL) were taken in a round bottom flask and stirred overnight under ambient reaction conditions. The resulting reaction mixture was filtered, and the volume of the filtrate was reduced to 5mL at rotary evaporator. It was mixed with solid NH4PF6 (0.032 g, 0.2 mmol) and further stirred at rt for 5 h. The resulting orange coloured precipitated solid was filtered, washed with 5 mL of chilled methanol, and dried in vacuo. The complex 1 was isolated as orange solid (82%, mp: 127 ± 2 °C). Complex 2 was isolated as orange solid (89%, mp: 121 ± 2 °C) and Complex 3 was isolated as orange solid with an excellent yield of (80%, mp: 180 ± 2 °C). Single crystals of the complex were grown by slow evaporation of a solution of 1 and 2 made in acetonitrile: methanol (3:1).

Complex 1: NMR (CD_3CN, *δ*/ppm): **^{1}H** (400 MHz) 7.98 (s, 1H), 7.77 (s, 1H), 7.29 – 7.39 (m, 5H), 4.85 – 4.81 (d, 1H), 3.95 – 3.88 (t, 1H), 3.81 – 3.79 (d, 1H), 3.00 – 2.94 (t, 1H), 2.13 (s, 15H). **^{13}C{^{1}H}** (100 MHz): 145.28, 136.86, 131.75, 130.42, 129.75, 129.08, 117.44, 100.28, 97.99, 96.37, 49.54, 35.49. **IR** (cm^{-1}, powder film): 458, 553, 831, 1021, 1372, 1468, 1738; **Mass** (CH_3CN) $[(M - PF_6]^+$ (*m/z*) Found: 554.9711, Calc. Value for $[C_{21}H_{27}BrClN_2RhS]^+$: 554.9714

Complex 2: NMR (CD_3CN, *δ*/ppm): **^{1}H** (400 MHz) 8.03 (s, 1H, H_9), 7.80 (s, 1H, H_7), 7.55 (s, 1H, H_8), 7.32 – 7.30 (m, 1H, H_1), 7.24 – 7.21 (m, 2H, H_2), 6.90 – 6.89 (m, 2H, H_3), 4.99 – 4.95 (m, 1H, H_6), 3.95 – 3.94 (m, 2H, H_6, H_5), 2.87 – 2.81 (m, 1H, H_5), 1.59 (s, 15H, CH_3 of Cp*); **^{13}C{^{1}H}** (100 MHz) 145.3 (C_9), 136.9 (C_7), 132.3 (C_3), 129.9 (C_1), 129.2 (C_2), 125.15 (C_4), 117.5 (CH_3 of Cp*), 99.6 (C of Cp*), 96.4 (C_8), 50.7 (C_6), 30.9 (C_5). **IR** (cm^{-1}, powder film): 457, 556, 831, 1018, 1369, 1469, and 1743; **Mass** (CH_3CN) $[(M - PF_6]^+$ (*m/z*) Found: 602.9187; Calc. Value for $[C_{21}H_{27}BrClN_2RhSe]^+$: 602.9188.

Complex 3: NMR ($CDCl_3$, *δ*/ppm): **^{1}H** (400 MHz) 7.93 – 7.91 (d, 2H), 7.31 (s, 1H), 7.16 – 7.13 (t, 2H), 6.74 – 6.72 (d, 2H), 5.30 – 5.27 (d, 1H), 4.15 – 4.11 (m, 2H), 2.52 – 2.44 (m, 1H), 1.75 (s, 15H); **^{13}C{^{1}H}** (100 MHz) 145.51, 136.54, 136.30, 134.94, 131.29, 130.77, 129.80, 99.89, 99.61, 52.45, 9.69, 9.17. **IR** (cm^{-1}, powder film): 456, 556, 831, 1018, 1299,

1433, 1627, **Mass** (CH_3CN) [(M – PF_6]$^+$ (*m/z*) Found: 652.2506; Calc. Value for [$C_{21}H_{27}BrClN_2RhTe$]$^+$: 652.9085.

General Procedure for the Catalyst synthesis: Take primary or secondary amine and aryl halide, 1 mmol of each in a reaction tube. Then add a mixture of prepared Rh catalyst and $Cu(OAc)_2$, 10 mol% of each as catalyst. Heat the reaction mixture at 110 °C with continuous stirring for 6 h. After completion allow the reaction mixture to cool at room temperature and separate the organic layer through solvent extraction using ethyl acetate and water. The collected organic layer was dried over Anhydrous Na_2SO_4, and concentrated on a rotatory evaporator. The desired products were separated through column chromatography.

Table s1. Summary of crystallographic data and structural refinement parameters for complex **1**.

Empirical formula	$C_{21}H_{26}BrClN_2RhSe \cdot PF_6$	$C_{21}H_{26}BrClN_2RhS \cdot PF_6$
Formula weight	748.64	701.73
Crystal size [mm]	0.29×0.25×0.23	0.25×0.23×0.21
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*C* 1 *c* 1
Unit cell dimension	*a* = 9.3467(19)Å *b* = 11.887(2)Å *c* = 11.887(2)Å α = 97.25° β = 97.072(2)° γ = 97.072(2)°	*a* = 12.562(3)Å *b* = 11.151(2)Å *c* = 19.041(4) α = 90° β = 91.874(3)° γ = 90°
Cell volume [$Å^3$]	1287.3(4)	2666.1(9)
Z	2	4
Density (Calc.) [$Mg \cdot m^{-3}$]	1.931	1.748
Absorption coeff. [mm^{-1}]	3.852	2.433
F(000)	732	1392
θ Range [°]	1.744–24.999	2.140−24.998
Index ranges	$-11 \leq h \leq 11$ $-14 \leq k \leq 14$ $-14 \leq l \leq 14$	$-14 \leq h \leq 14$ $-13 \leq k \leq 13$ $-22 \leq l \leq 22$
Reflections collected	12218	11514
Independent reflections ($R_{int.}$)	4496 (0.0474)	4650 (0.0364)
Max./Min. transmission	0.415/0.337	0.600/0.550
Data/Restraints/Parameters	4496/0/312	4650/2/312
Goodness-of-Fit on F^2	0.971	1.068
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0373$, $wR_2 = 0.0782$	$R_1 = 0.0477$, $wR_2 = 0.1033$
R Indices (All Data)	$R_1 = 0.0566$, $wR_2 = 0.0835$	$R_1 = 0.0544$ $wR_2 = 0.1057$
Largest diff. peak/Hole [$e.Å^{-3}$]	0.692/–0.472	0.758/–1.101

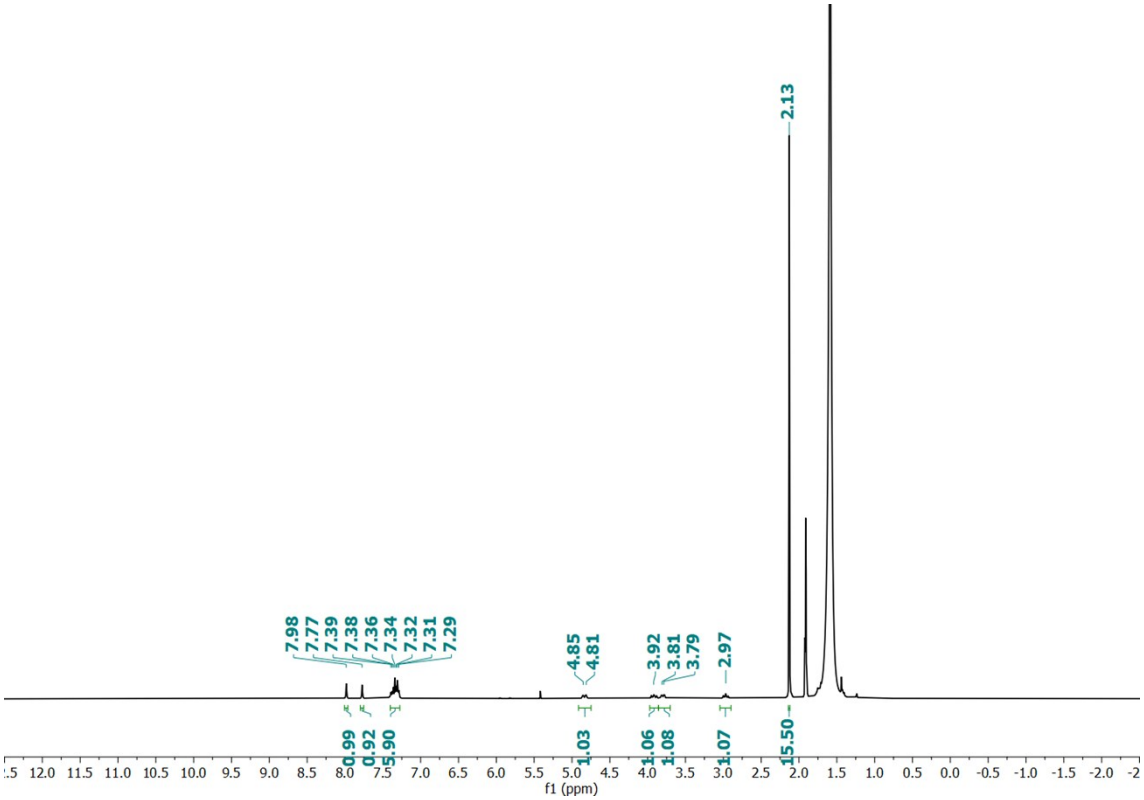


Figure s1. ^{1}H NMR of half-sandwich complex of (η^5-Cp*)Rh(III) with L1 (in CD_3CN).

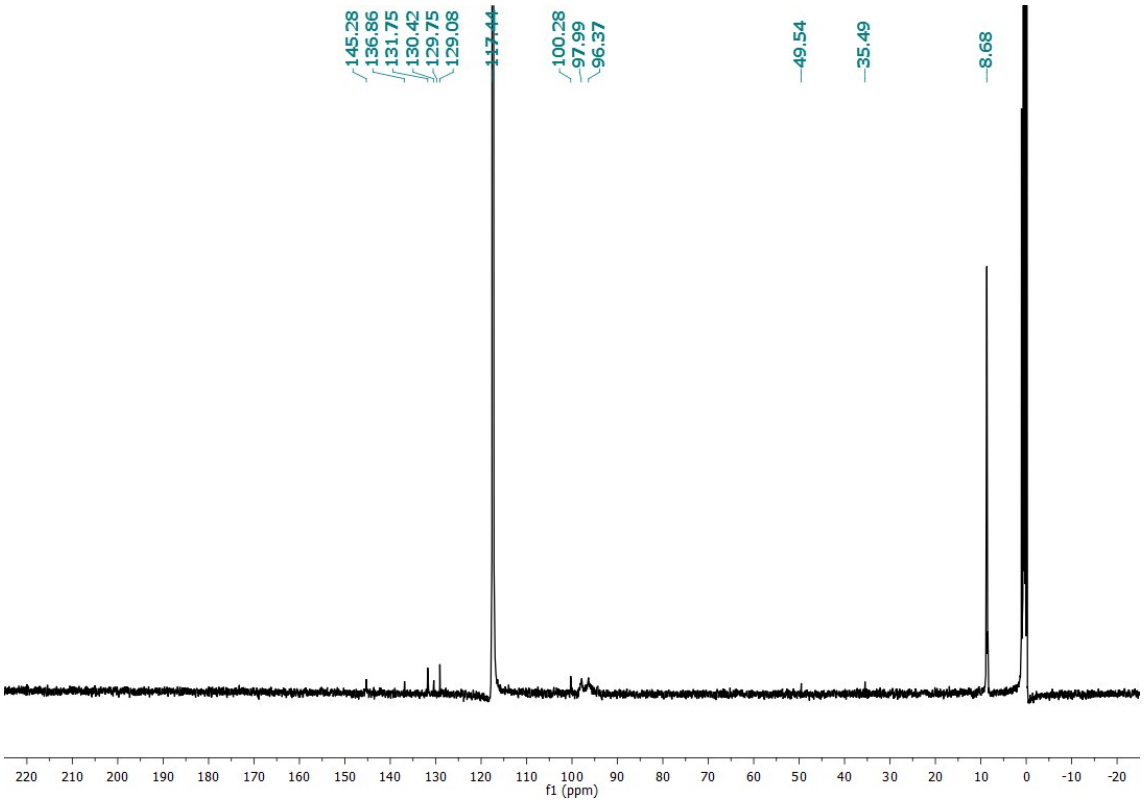


Figure s2.. $^{13}C\{^{1}H\}$ NMR of half-sandwich complex of (η^5-Cp*)Rh(III) with L1 (in CD_3CN).

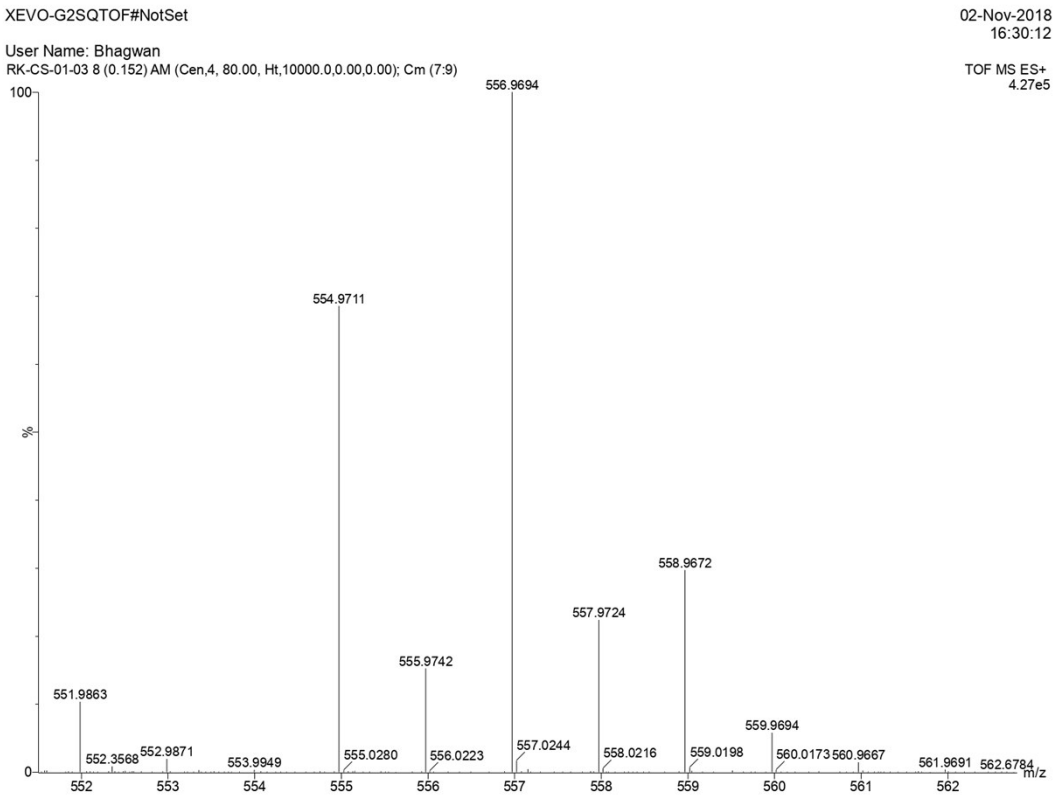


Figure s3. Mass spectrum of half-sandwich complex of (η^5-Cp*)Rh(III) with L1

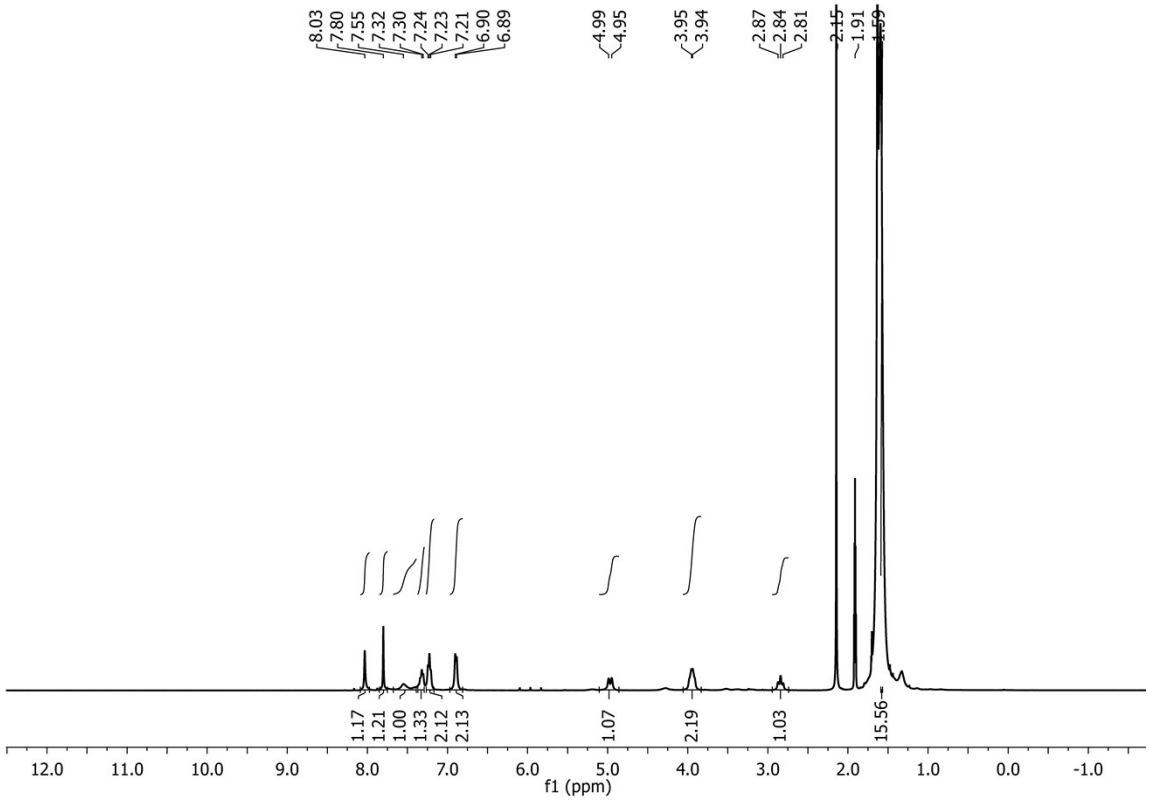


Figure s4. ^{1}H NMR of half-sandwich complex of (η^5-Cp*)Rh(III) with L2 (in CD_3CN).

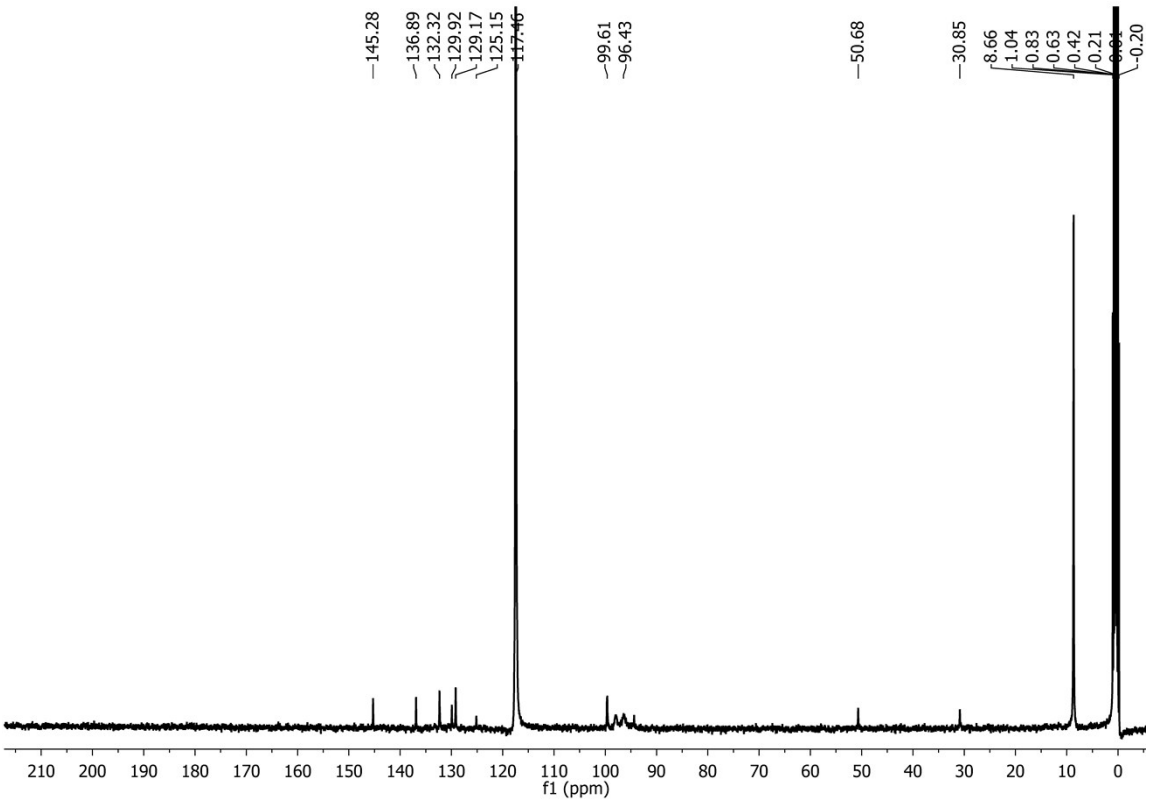


Figure s5. $^{13}C\{^{1}H\}$ NMR of half-sandwich complex of (η^5-Cp*)Rh(III) with L2 (in CD_3CN)

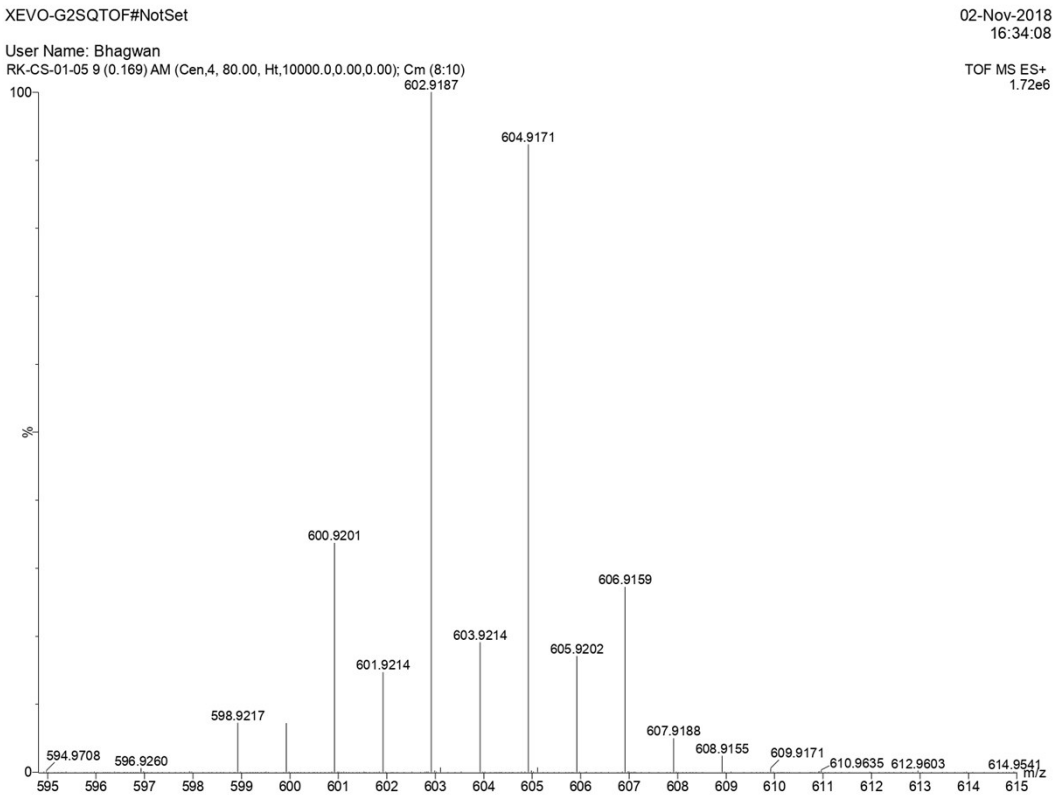


Figure s6. Mass spectrum of half-sandwich complex of (η^5-Cp*)Rh(III) with L2

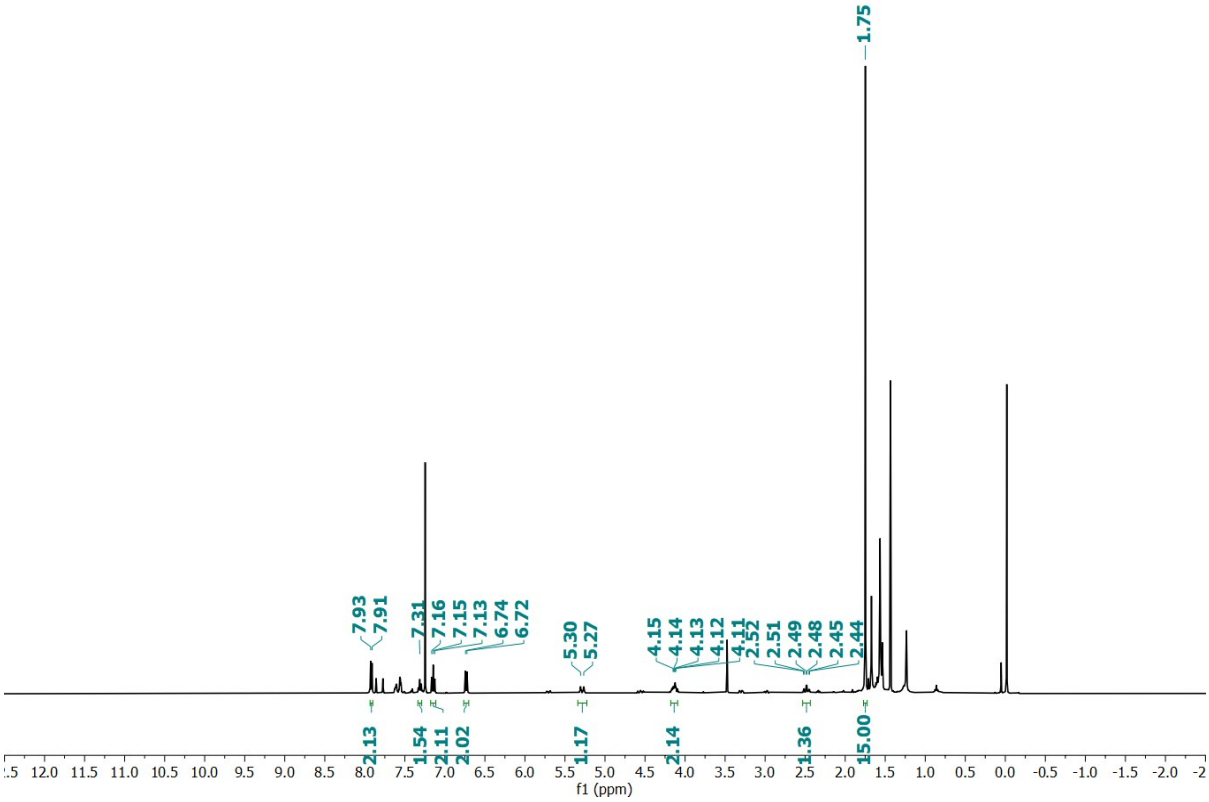


Figure s7. ^{1}H NMR of half-sandwich complex of (η^5-Cp*)Rh(III) with L3 (in CDCl3).

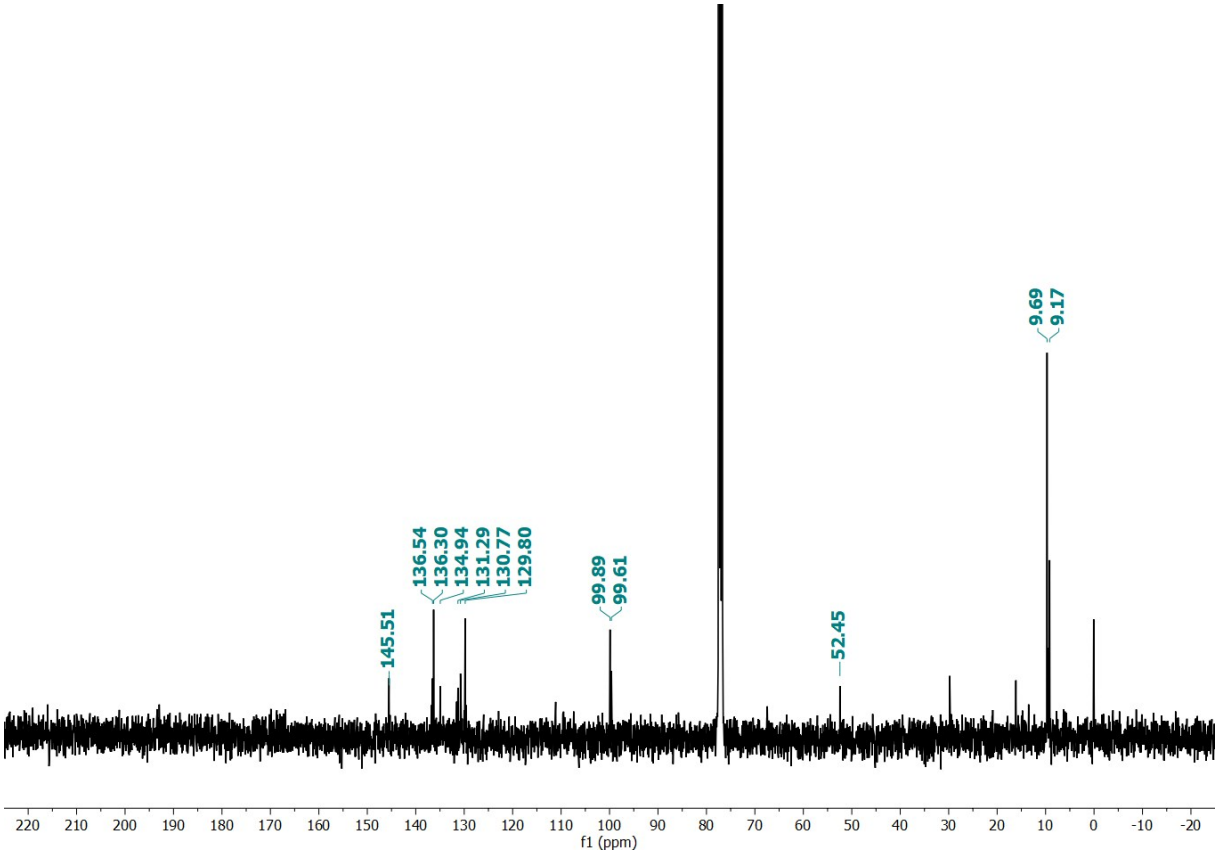


Figure s8. $^{13}C\{^{1}H\}$ NMR of half-sandwich complex of (η^5-Cp*)Rh(III) with L3 (in CDCl3)

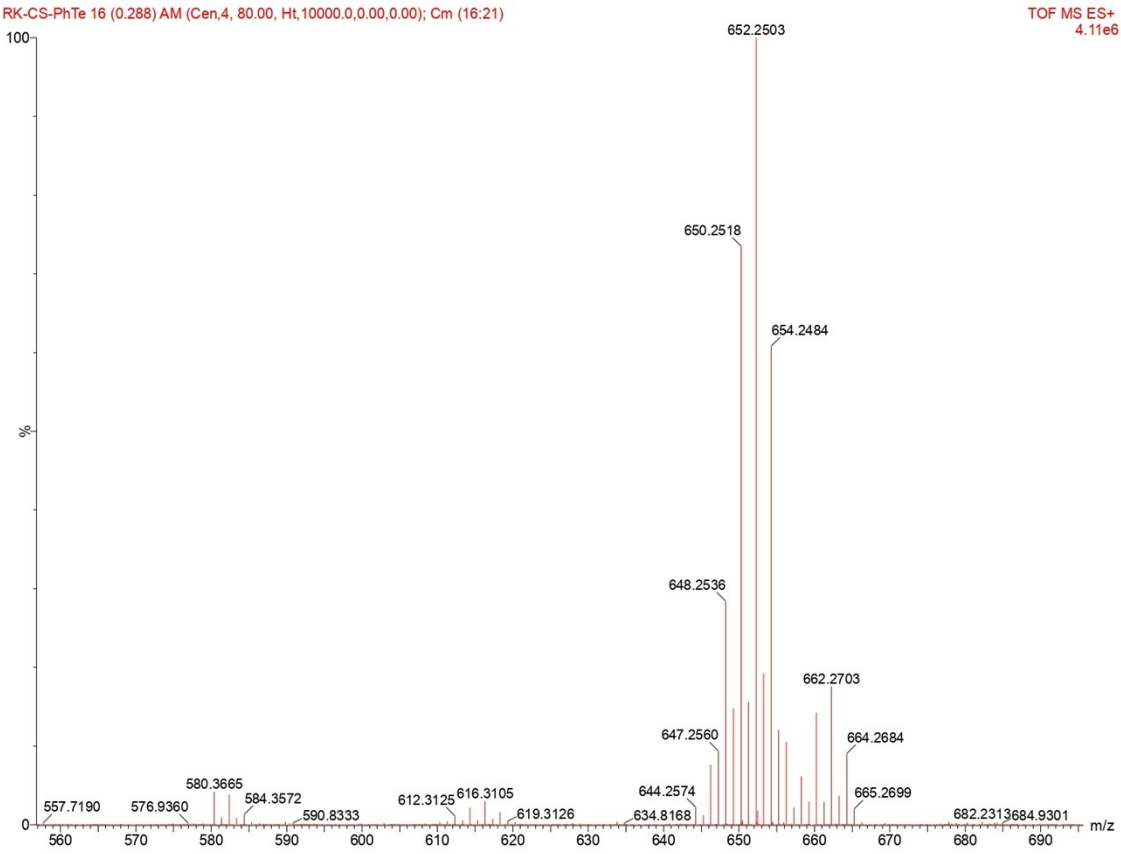
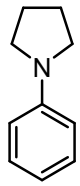
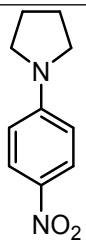
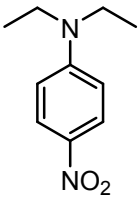
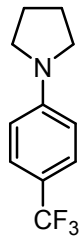
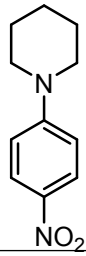
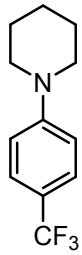
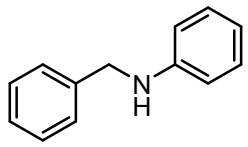
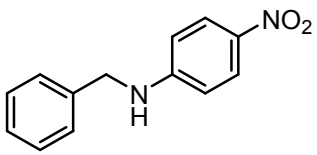
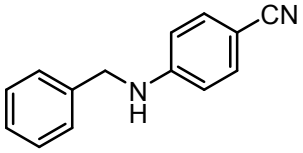
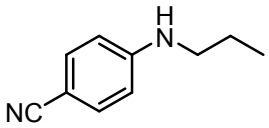
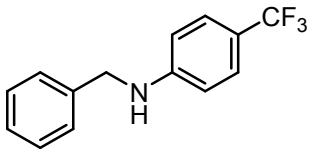
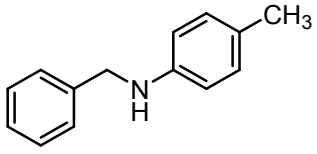
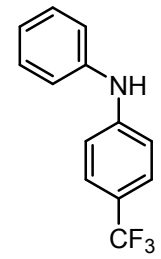
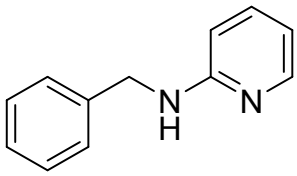
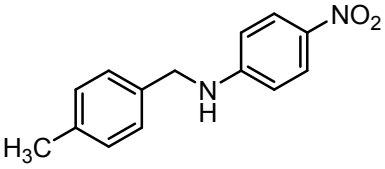
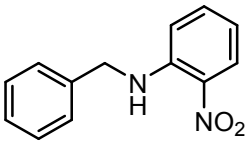
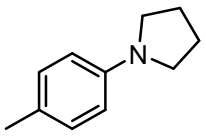
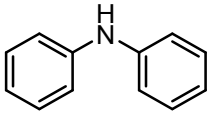


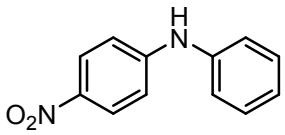
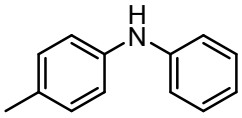
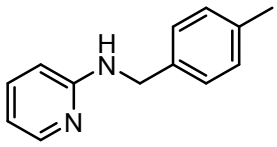
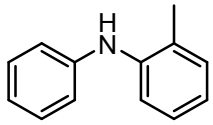
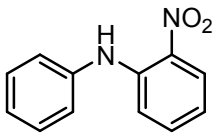
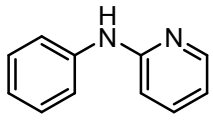
Figure s9. Mass spectrum of half-sandwich complex of (η^5-Cp*)Rh(III) with L3

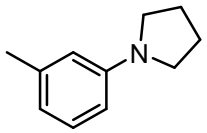
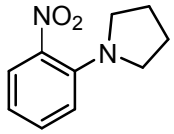
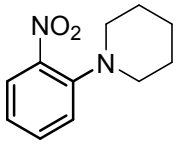
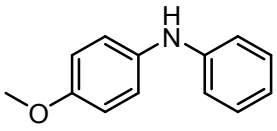
Characterisation Data

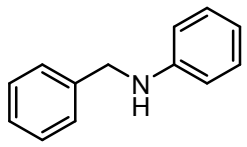
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.30 – 7.25 (m, 2H), 6.72 – 6.72 (m, 1H), 6.70 – 6.60 (m, 2H), 3.34 – 3.30 (m, 4H), 2.07 – 2.00 (m, 4H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 148.07, 129.25, 115.44, 111.73, 47.67, 25.59.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 8.12 – 8.08 (m, 2H), 6.47 – 6.43 (m, 2H), 3.41 – 3.37 (m, 4H), 2.09 – 2.03 (m, 4H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 151.91, 136.61, 126.45, 110.49, 47.99, 25.52.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 8.10 – 8.08 (m, 2H), 6.58 – 6.55 (m, 2H), 3.47 – 3.41 (q, 4H), 1.23 – 1.20 (t, 6H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 152.28, 136.34, 126.60, 109.88, 45.04, 12.48.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.45 – 7.43 (d, 2H), 6.55 – 6.53 (d, 2H), 3.33 – 3.27 (t, 4H), 2.06 – 1.99 (m, 4H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 149.83, 132.16, 127.00, 126.96, 126.50, 126.46, 126.43, 126.39, 116.81, 116.49, 110.89, 47.57, 25.53.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 8.10 – 8.06 (m, 2H), 6.79 – 6.75 (m, 2H), 3.44 – 3.41 (d, 4H), 1.67 (s, 6H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 154.96, 137.49, 126.24, 112.38, 48.46, 25.36, 24.32.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.45 – 7.43 (d, 2H), 6.91 – 6.89 (d, 2H), 3.27 – 3.24 (m, 4H), 1.71 – 1.58 (m, 6H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 153.87, 126.42, 126.38, 123.61, 119.77, 119.44, 114.66, 49.39, 25.49, 24.35.

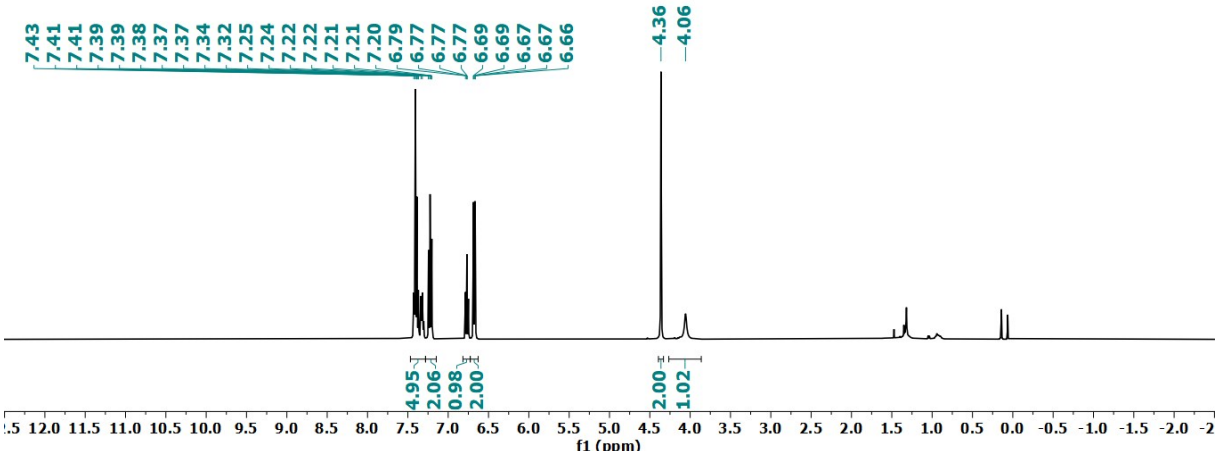
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.43 – 7.32 (m, 5H), 7.25 – 7.20 (m, 2H), 6.79 – 6.77 (m, 1H), 6.69 – 6.66 (m, 2H), 4.36 (s, 2H), 4.06 (s, 1H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 148.26, 139.54, 129.39, 128.76, 127.63, 127.35, 117.66, 112.94, 48.41.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 8.08 – 8.04 (m, 2H), 7.35 – 7.32 (m, 5H), 6.67 – 6.55 (m, 2H), 4.92 (s, 1H), 4.43 - 441 (d, 2H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 153.15, 137.44, 129.05, 127.96, 127.44, 126.51, 111.42, 100.00, 47.72.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.73 – 7.70 (m, 2H), 7.40 – 7.27 (m, 7H), 6.39 (s, 1H), 4.63 – 4.61 (d, 2H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 166.35, 137.98, 137.90, 132.78, 128.94, 128.48, 128.05, 127.85, 44.33.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.70 – 7.66 (m, 2H), 7.37 – 7.33 (m, 2H), 6.37 (s, 1H), 3.39 – 3.34 (m, 2H), 1.65 – 1.55 (h, 2H), 0.96 – 0.92 (d, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 166.65, 137.56, 133.25, 128.82, 128.41, 41.93, 22.94, 11.52.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.42 – 7.30 (m, 7H), 6.64 – 6.62 (d, 2H), 4.38 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 150.56, 138.55, 128.90, 127.63, 127.46, 126.78, 126.75, 126.71, 126.68, 119.24, 118.91, 112.06, 47.86.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.40 – 7.27 (m, 5H), 7.02 - 7.00 (d, 2H), 6.59 – 6.57 (d, 2H), 4.33 (s, 2H), 3.87 (s, 1H), 2.27 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 129.81, 128.67, 127.58, 127.23, 113.10, 48.75, 20.46.

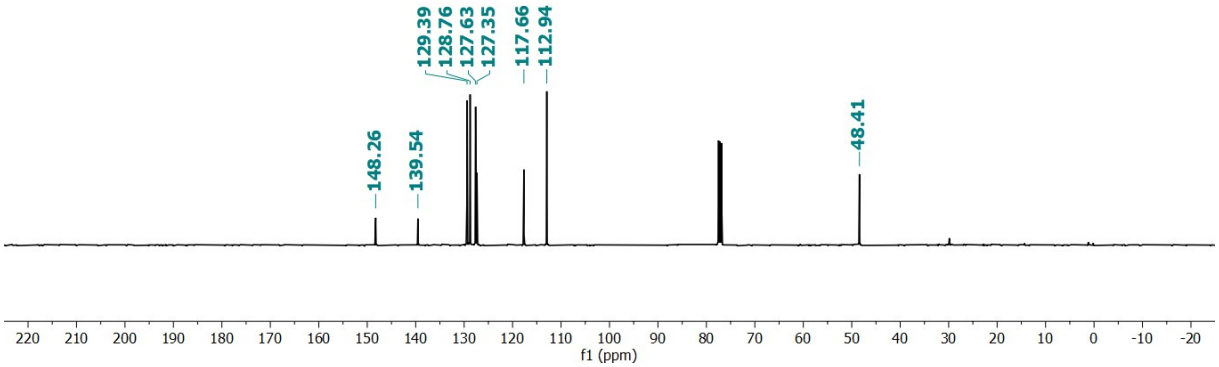
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.47 - 7.45 (d, 2H), 7.35 – 7.31 (m, 2H), 7.15 – 7.13 (m, 2H), 7.07 – 7.03 (m, 3H), 5.91 (s, 1H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 146.82, 141.20, 129.64, 126.80, 126.77, 123.01, 121.87, 121.54, 120.09, 115.40.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 8.09 – 8.07 (m, 1H), 7.41 – 7.24 (m, 6H), 6.59 – 6.56 (m, 1H), 6.37 – 6.35 (d, 1H), 5.04 (s, 1H), 4.50 – 4.59 (d, 2H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 158.73, 148.24, 139.26, 137.60, 128.73, 127.49, 127.32, 113.22, 106.88, 46.40.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 8.08 – 8.06 (d, 2H), 7.22 – 7.16 (m, 4H), 6.56 – 6.54 (d, 2H), 4.80 (s, 1H), 4.37 – 4.36 (d, 2H), 2.34 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 153.09, 137.77, 134.22, 129.70, 127.46, 126.49, 122.27, 111.36, 47.53, 21.20.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 8.43 (s, 1H), 8.20 - 8.18 (m, 1H), 7.39 – 7.26 (m, 6H), 6.81 – 6.79 (d, 1H), 6.68 – 6.65 (m, 1H), 4.56 – 4.54 (d, 2H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 145.33, 137.42, 136.33, 129.02, 127.78, 127.12, 126.96, 115.81, 114.28, 47.17.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.07 – 7.05 (d, 2H), 6.54 – 6.52 (m, 2H), 3.29 – 3.26 (q, 4H), 2.28 (s, 3H), 2.02 – 1.99 (m, 4H). **^{13}C NMR (100MHz, $CDCl_3$)**: δ 146.22, 129.75, 124.58, 111.93, 47.97, 25.52, 20.41.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.29 - 7.25 (m, 4H), 7.09 – 7.07 (m, 4H), 6.94 – 6.92 (m, 2H), 5.70 (s, 1H) **^{13}C NMR (100MHz, $CDCl_3$)**: δ 143.21, 129.46, 121.10, 117.90

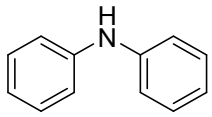
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 8.12 – 8.10 (d, 2H), 7.40 – 7.36 (m, 2H), 7.21 – 6.94 (m, 3H), 6.92 – 6.91 (d, 2H), 6.21 (s, 1H) **^{13}C NMR (100MHz, $CDCl_3$)**: δ 150.21, 139.89, 139.55, 129.84, 129.33, 124.77, 122.01, 113.76
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.27 – 7.23 (m, 2H), 7.11 – 7.09 (d, 2H), 7.03 – 7.00 (m, 4H), 6.91 – 6.88 (m, 1H), 5.61 (s, 1H) **^{13}C NMR (100MHz, $CDCl_3$)**: δ 144.06, 140.39, 131.04, 129.98, 129.42, 120.40, 119.01, 116.97, 20.80
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 8.10 – 8.08 (m, 1H), 7.40 – 7.36 (m, 1H), 7.25 – 7.20 (m, 2H), 7.15 – 7.13 (m, 2H), 6.57 – 6.57 (d, 1H), 6.36 – 6.34 (d, 1H), 4.88 (s, 1H), 4.45 – 4.43 (d, 2H) **^{13}C NMR (100MHz, $CDCl_3$)**: δ 158.75, 148.30, 137.54,
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.28 – 7.24 (t, 3H), 7.22 – 7.20 (d, 1H), 7.17 – 7.13 (t, 1H), 6.98 – 6.94 (m, 3H), 6.93 – 6.89 (t, 1H), 5.39 (s, 1H), 2.27 (s, 3H) **^{13}C NMR (100MHz, $CDCl_3$)**: δ 144.07, 141.32, 131.06, 129.43, 128.38, 126.88, 122.08, 120.58, 118.85, 117.56
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 9.48 (s, 1H), 8.20 – 8.18 (dd, 1H), 7.43 – 7.39 (m, 2H), 7.37 – 7.33 (m, 1H), 7.28 – 7.26 (d, 2H), 7.22 – 7.20 (d, 2H), 6.78 – 6.74 (m, 1H) **^{13}C NMR (100MHz, $CDCl_3$)**: δ 143.19, 138.79, 135.79, 129.83, 126.77, 125.76, 124.49, 117.60, 116.13
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 8.19- 8.18 (d, 1H), 7.50 – 7.46 (m, 1H), 7.32 – 7.30 (m, 4H), 7.06 – 7.02 (m, 1H), 6.88 – 6.86 (d, 1H), 6.74 – 6.71 (m, 1H), 6.60 (s, 1H) **^{13}C NMR (100MHz, $CDCl_3$)**: δ 156.05, 148.51, 140.51, 137.80, 129.39, 122.93, 120.43, 115.16, 108.30

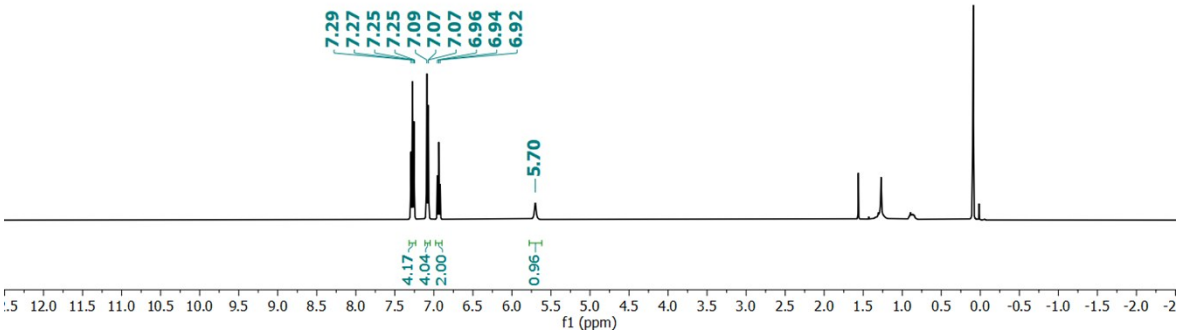
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.14 – 7.10 (t, 1H), 6.50 – 6.48 (d, 1H), 6.40 (s, 2H), 3.29 – 3.26 (m, 4H), 2.32 (s, 3H), 2.02 – 1.95 (m, 4H) **^{13}C NMR (100MHz, $CDCl_3$)**: δ 148. 16, 138.89, 129.10, 116.45, 112.47, 108.99, 47.69, 25.55, 21.96
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.73 – 7.70 (m, 1H), 7.36 – 7.32 (m, 1H), 6.89 – 6.87 (d, 1H), 6.70 – 6.66 (t, 1H), 3.20 – 3.17 (m, 4H), 1.97 – 1.94 (m, 4H) **^{13}C NMR (100MHz, $CDCl_3$)**: δ 142.85, 137.13, 133.07, 126.82, 115.98, 115.53, 50.45, 25.82.
	**^{1}H NMR (400MHz, $CDCl_3$)**: δ 7.71 – 7.68 (m, 1H), 7.42 – 7.37 (m, 1H), 7.08 – 7.06 (d, 1H), 6.93 – 6.89 (m, 1H), 2.98 – 2.95 (t, 4H), 1.69 – 1.64 (m, 1H), 1.57 – 1.53 (m, 2H) **^{13}C NMR (100MHz, $CDCl_3$)**: δ 147.10, 142.66, 126.05, 120.94, 120.66, 53.00, 26.03, 24.10
	**^{1}H NMR (400MHz, $CDCl_3$)**: 7.23 – 7.19 (t, 2H), 7.09 – 7.07 (d, 2H), 6.90 – 6.81 (m, 5H), 3.80 (s, 3H). **^{13}C NMR (100MHz, $CDCl_3$)**: 155.35, 145.24, 135.78, 129.39, 122.28, 119.64, 116.50, 115.70, 114.74, 55.67.

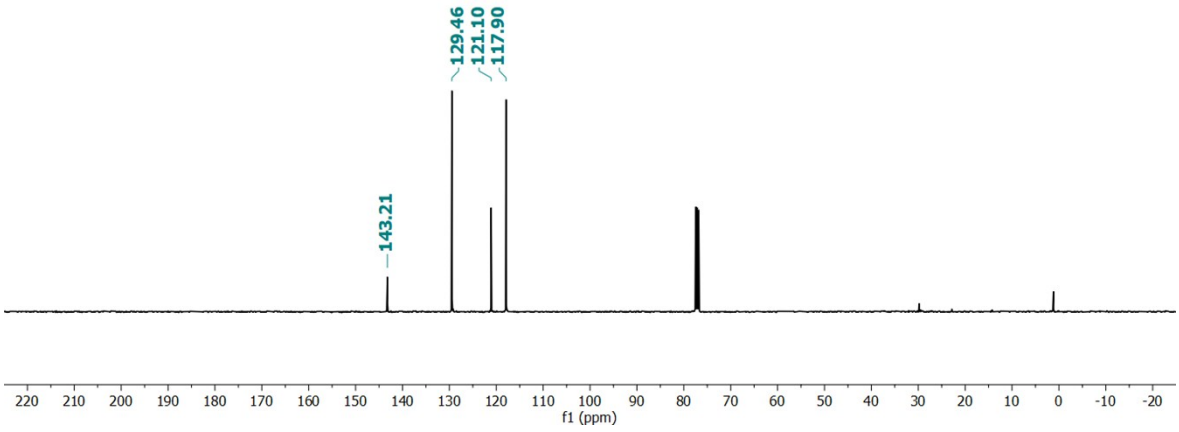


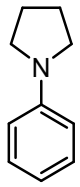

7.43
7.41
7.41
7.39
7.39
7.38
7.37
7.37
7.34
7.32
7.25
7.24
7.22
7.22
7.21
7.21
7.20
6.79
6.77
6.77
6.77
6.69
6.69
6.67
6.67
6.66
4.36
4.06
4.95
2.06
0.98
2.00
2.00
1.02
f1 (ppm)

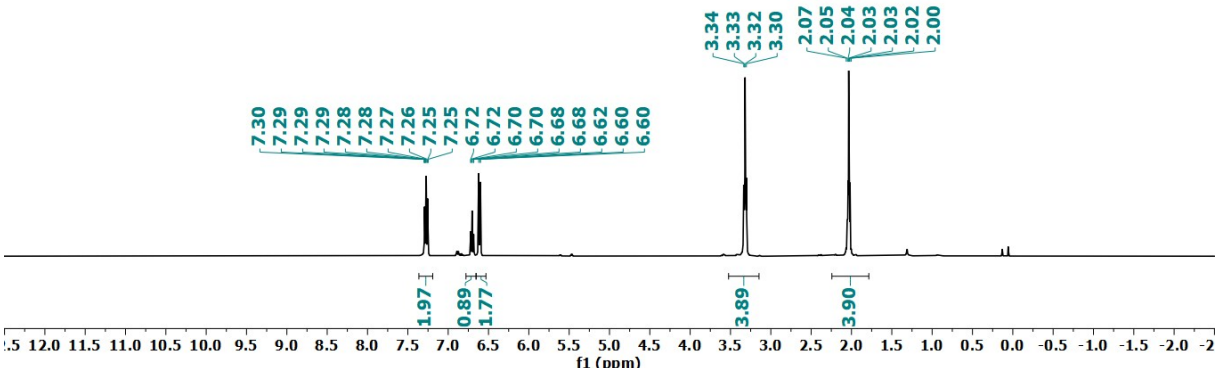

129.39
128.76
127.63
127.35
117.66
112.94
148.26
139.54
48.41
f1 (ppm)

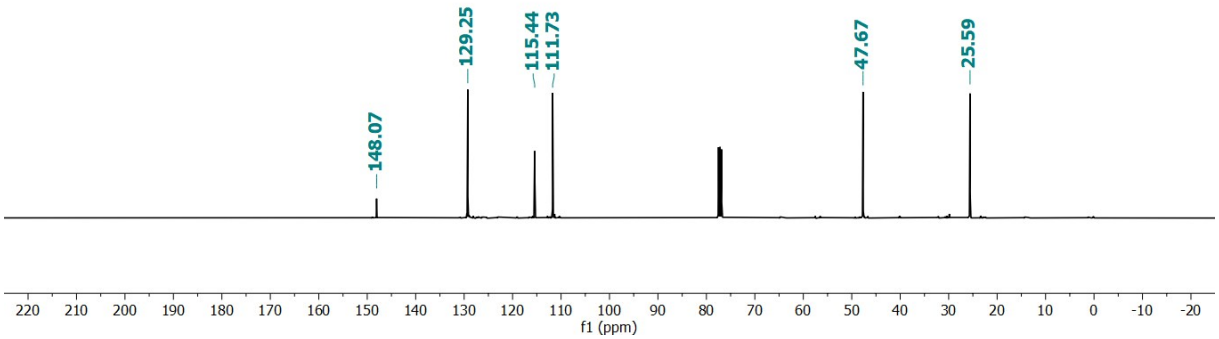


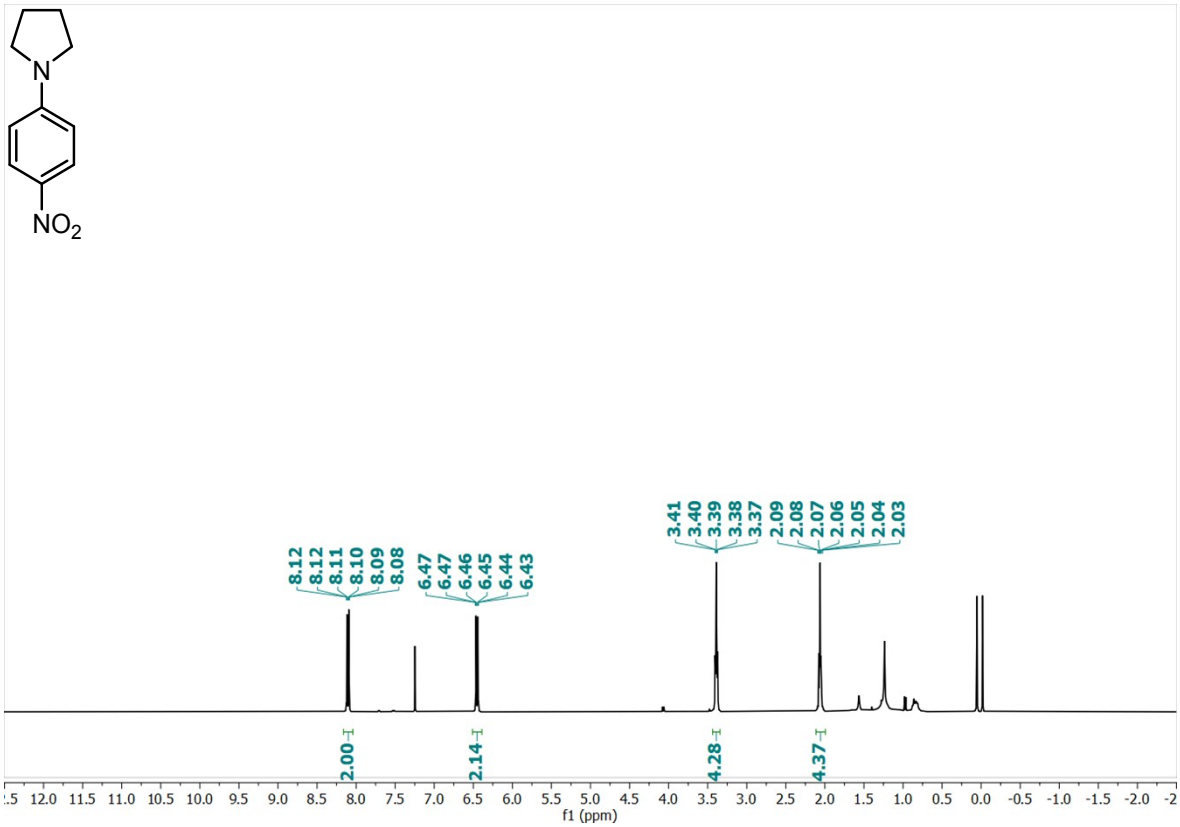

7.29
7.27
7.25
7.25
7.09
7.07
7.07
6.96
6.94
6.92
5.70
4.17
4.04
2.00
0.96
f1 (ppm)

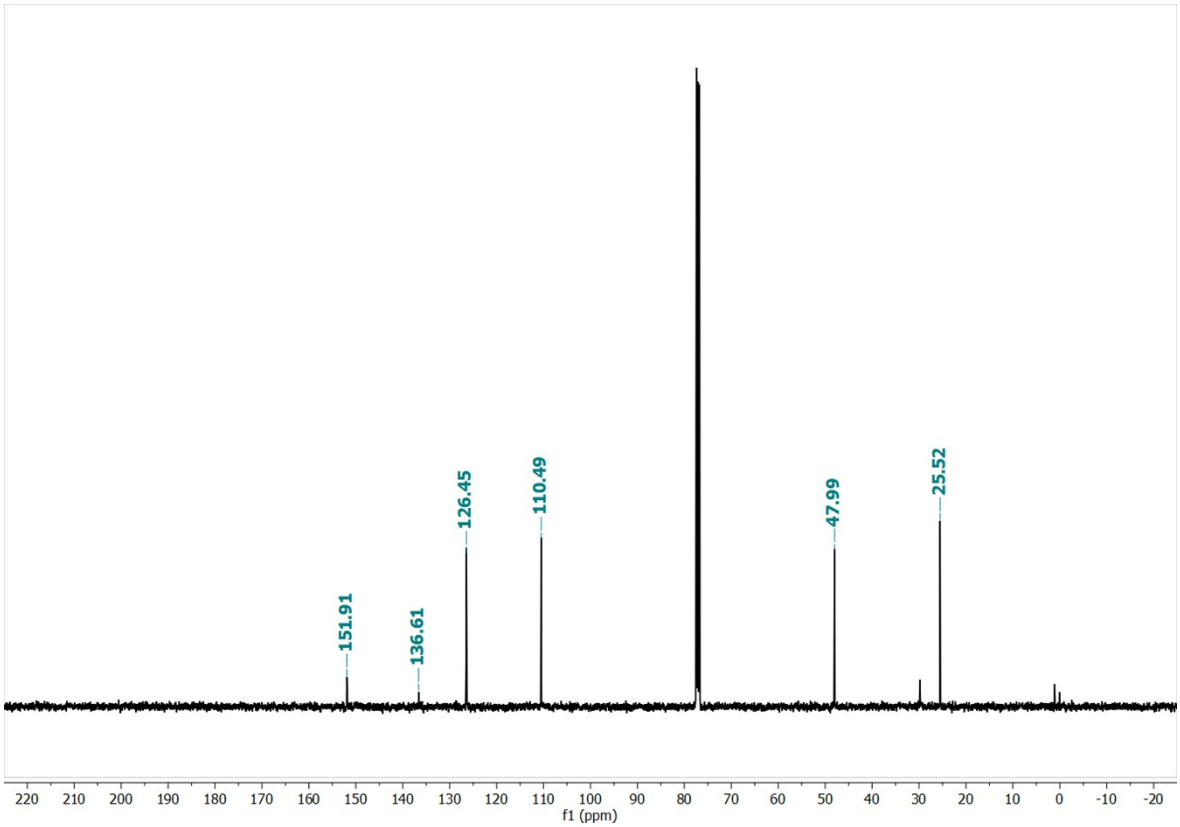

129.46
121.10
117.90
143.21
f1 (ppm)

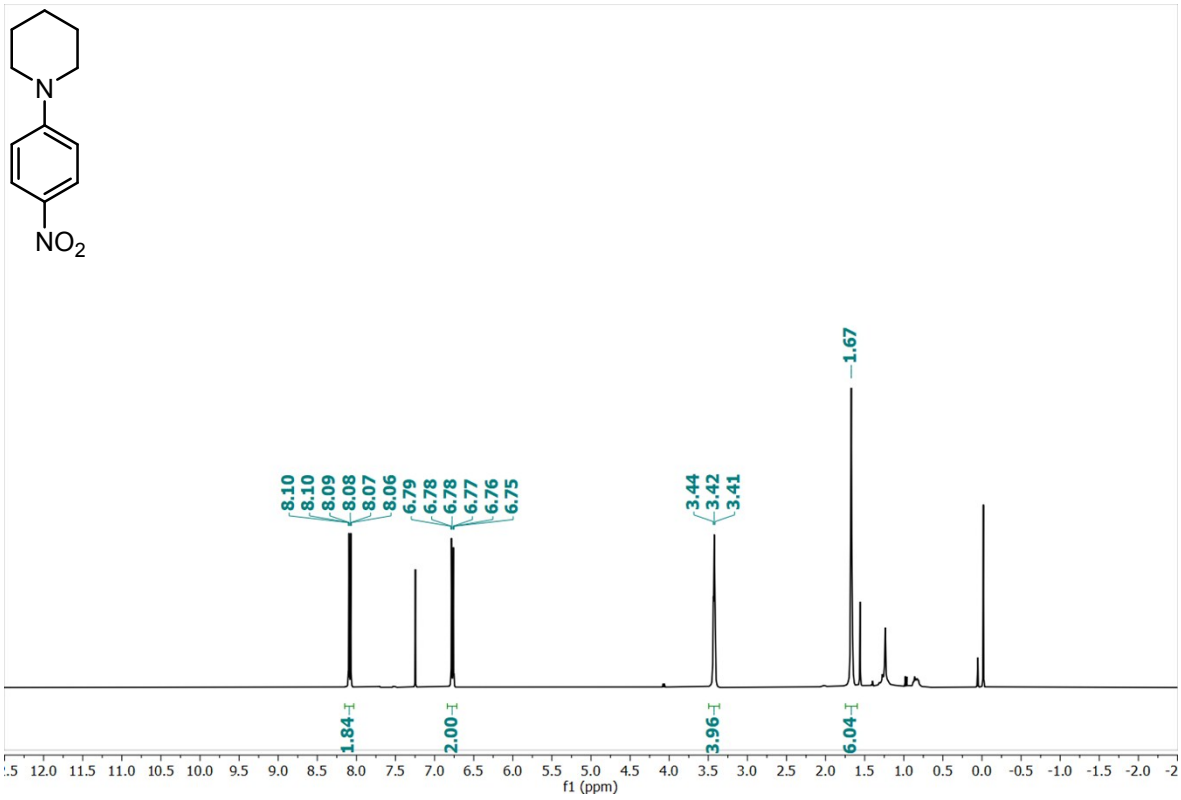


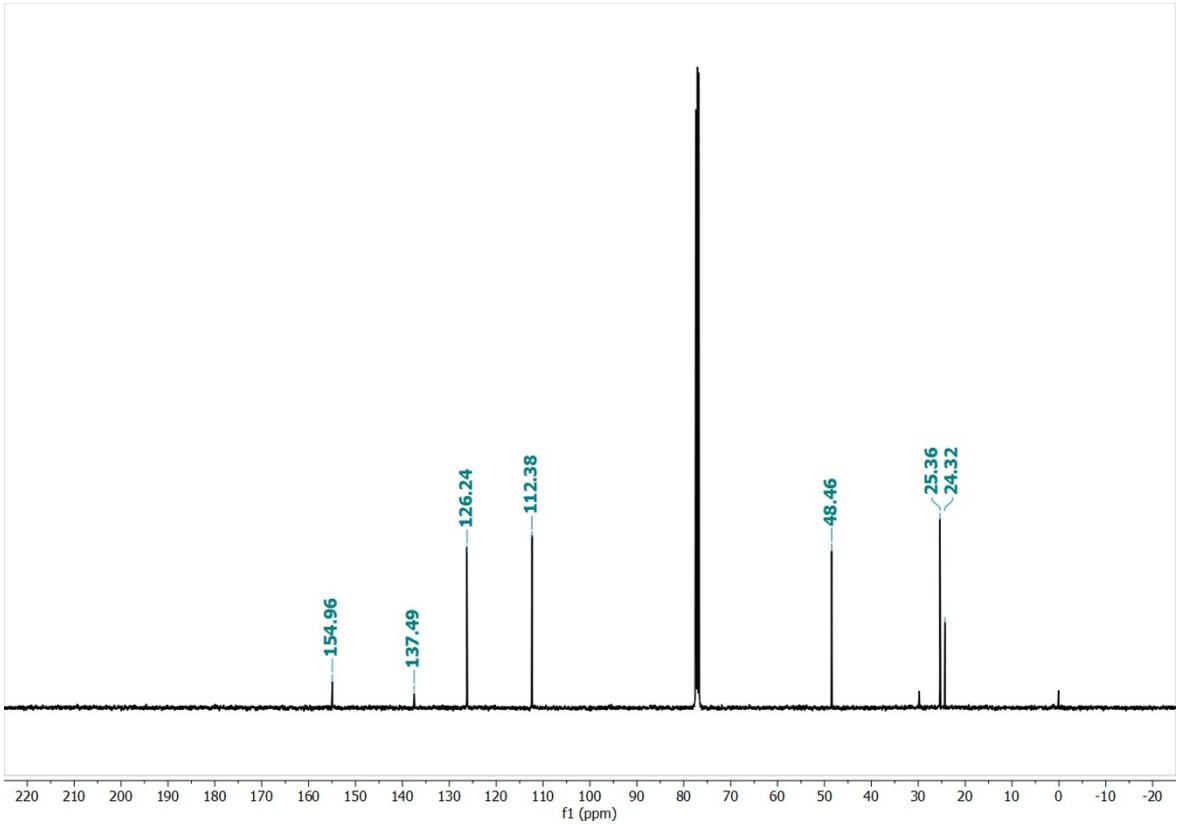

7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.26
7.25
7.25
6.72
6.72
6.70
6.70
6.68
6.68
6.62
6.60
6.60
3.34
3.33
3.32
3.30
2.07
2.05
2.04
2.03
2.03
2.02
2.00
1.97
0.89
1.77
3.89
3.90
f1 (ppm)

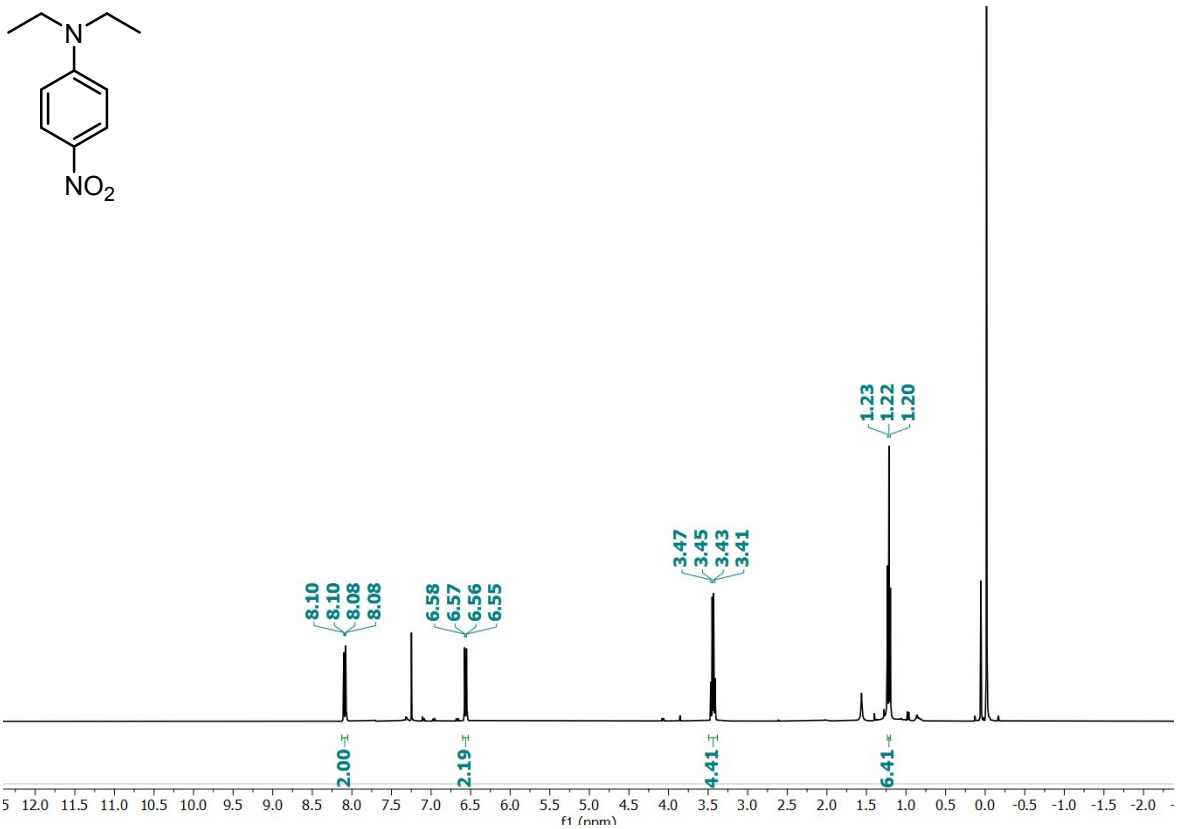

148.07
129.25
115.44
111.73
47.67
25.59
f1 (ppm)

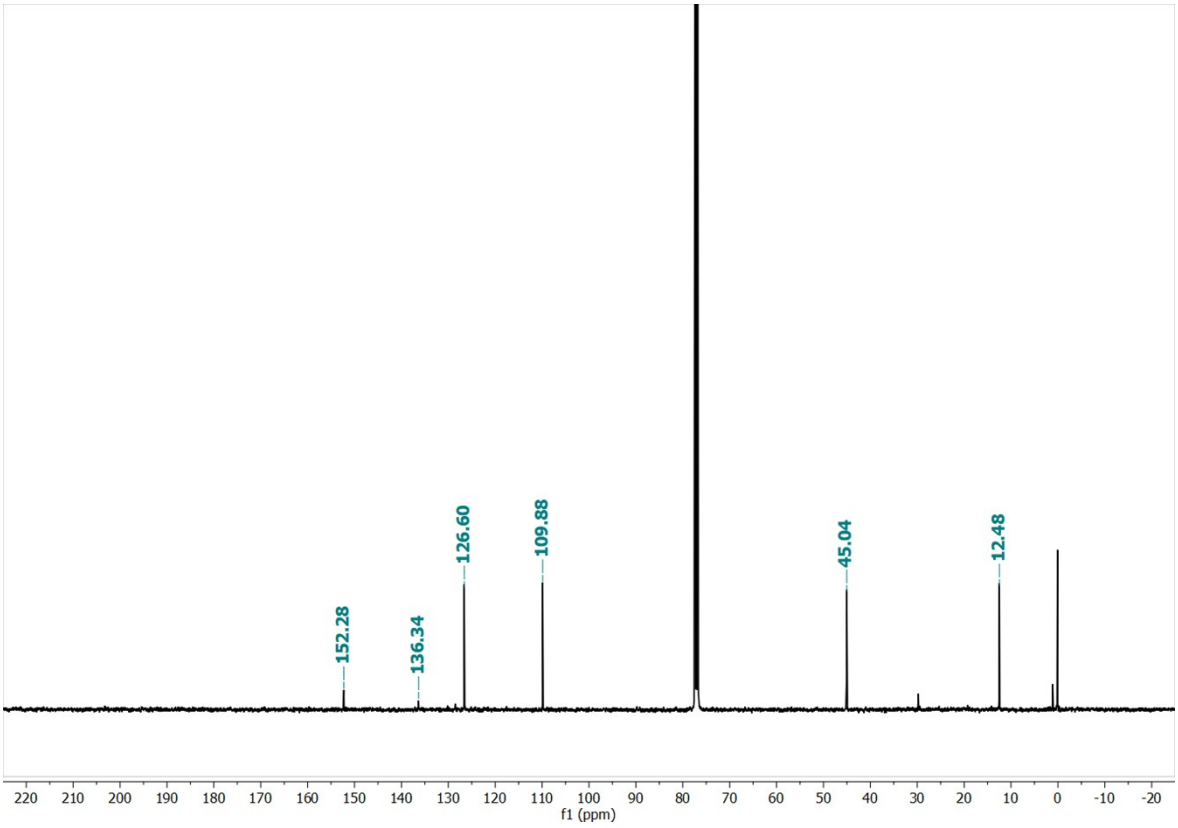

N
NO2
8.12
8.12
8.11
8.10
8.09
8.08
6.47
6.47
6.46
6.45
6.44
6.43
3.41
3.40
3.39
3.38
3.37
2.09
2.08
2.07
2.06
2.05
2.04
2.03
2.00
2.14
4.28
4.37
f1 (ppm)

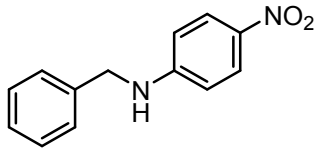

151.91
136.61
126.45
110.49
47.99
25.52
f1 (ppm)

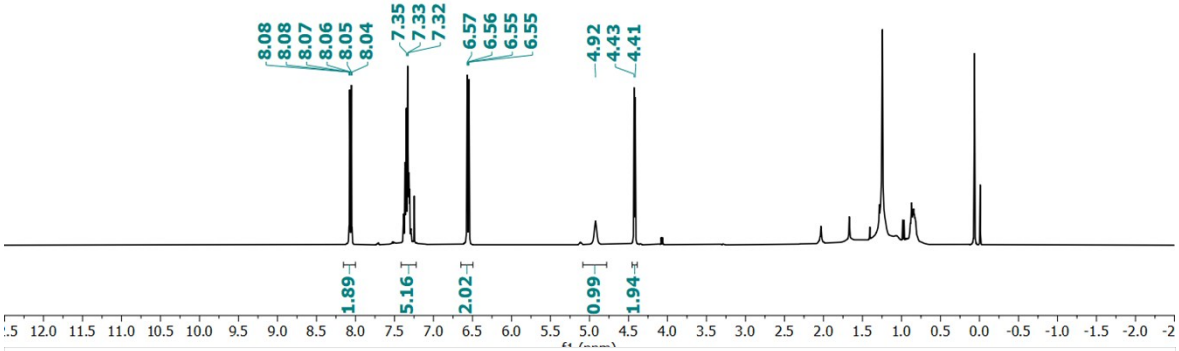

N
NO2
8.10
8.10
8.09
8.08
8.07
8.06
6.79
6.78
6.78
6.77
6.76
6.75
3.44
3.42
3.41
1.67
1.84
2.00
3.96
6.04
f1 (ppm)

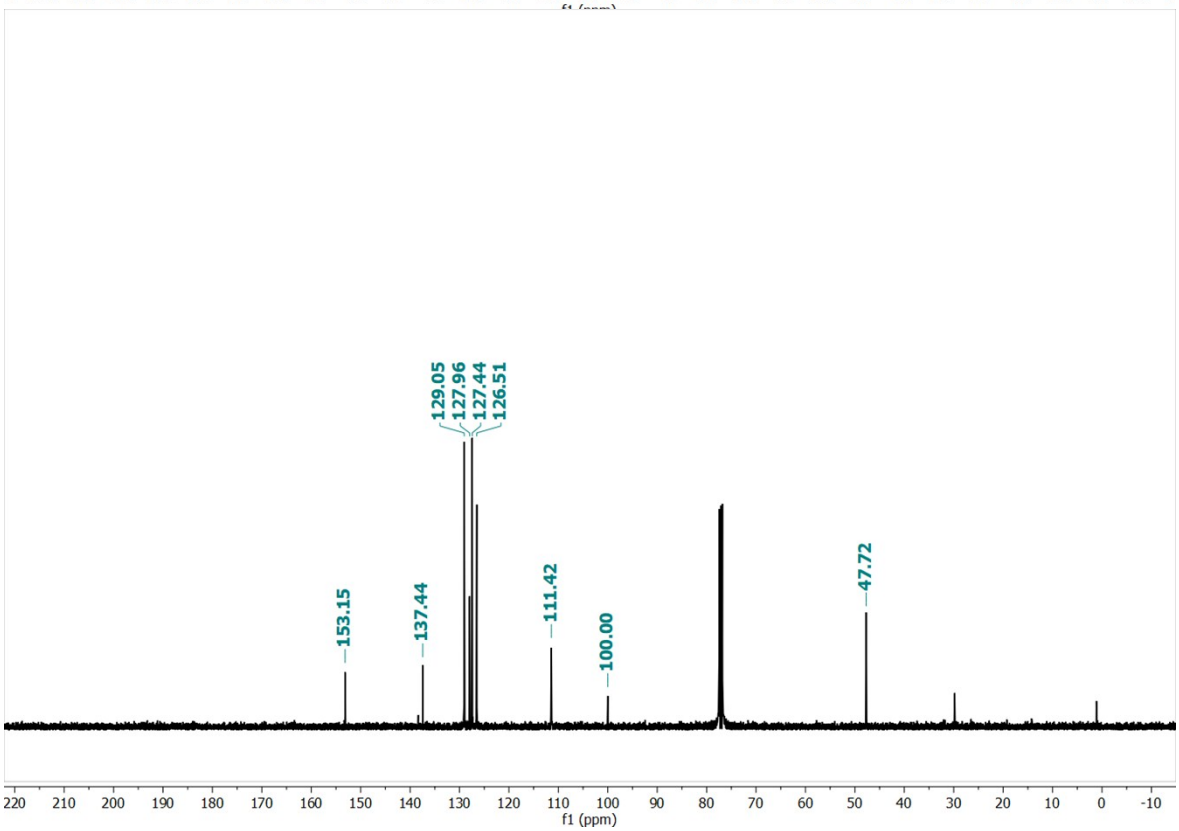

154.96
137.49
126.24
112.38
48.46
25.36
24.32
f1 (ppm)

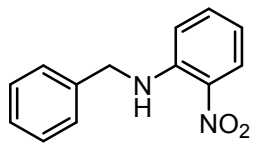

N
NO2
8.10
8.10
8.08
8.08
6.58
6.57
6.56
6.55
3.47
3.45
3.43
3.41
1.23
1.22
1.20
2.00
2.19
4.41
6.41
f1 (ppm)

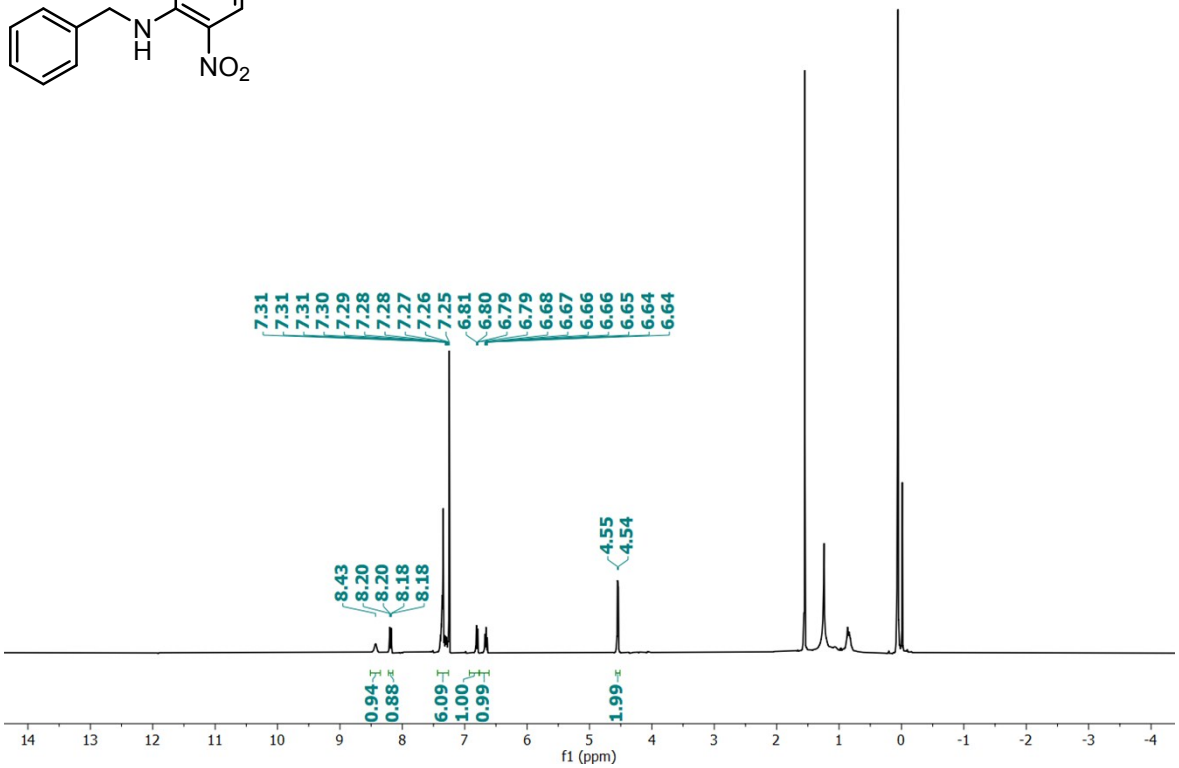

152.28
136.34
126.60
109.88
45.04
12.48
f1 (ppm)

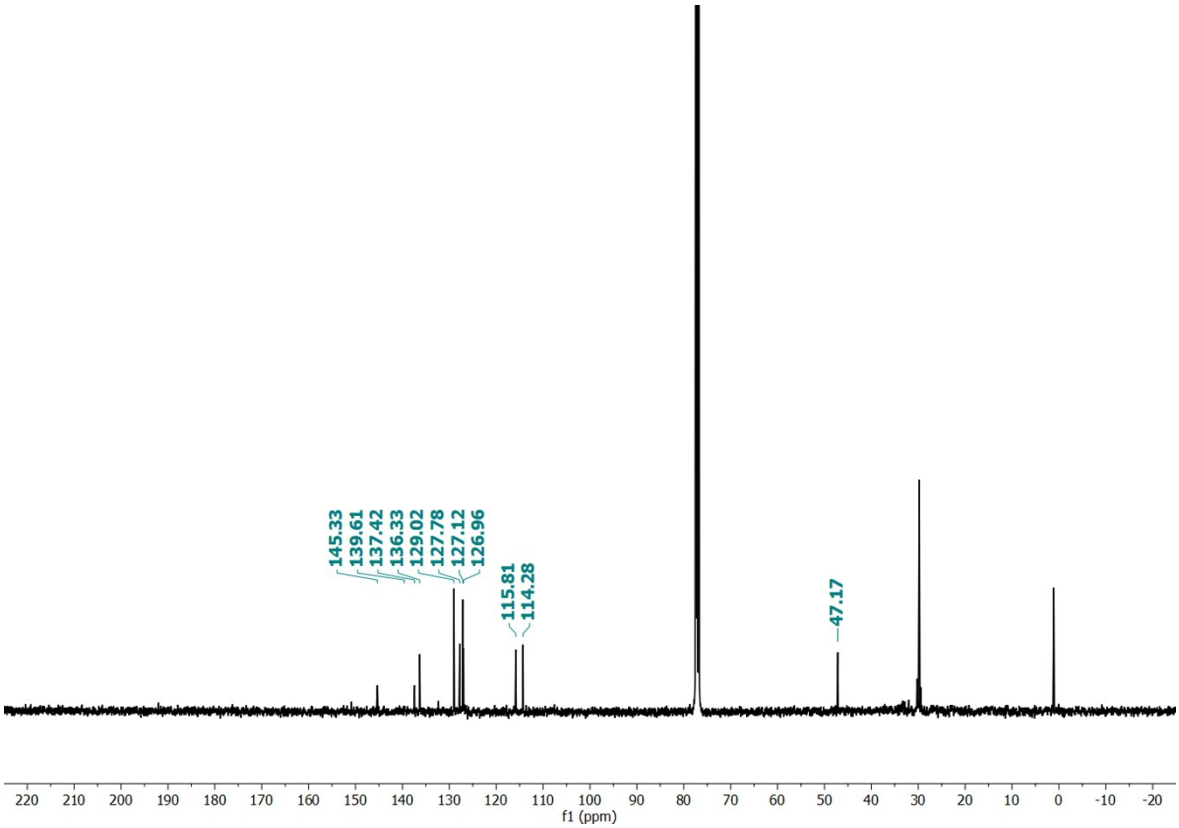

NO2
N
H

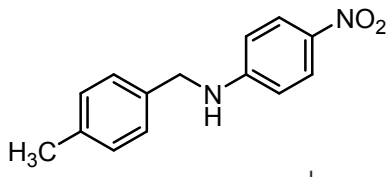

8.08
8.08
8.07
8.06
8.05
8.04
7.35
7.33
7.32
6.57
6.56
6.55
6.55
4.92
4.43
4.41
1.89
5.16
2.02
0.99
1.94

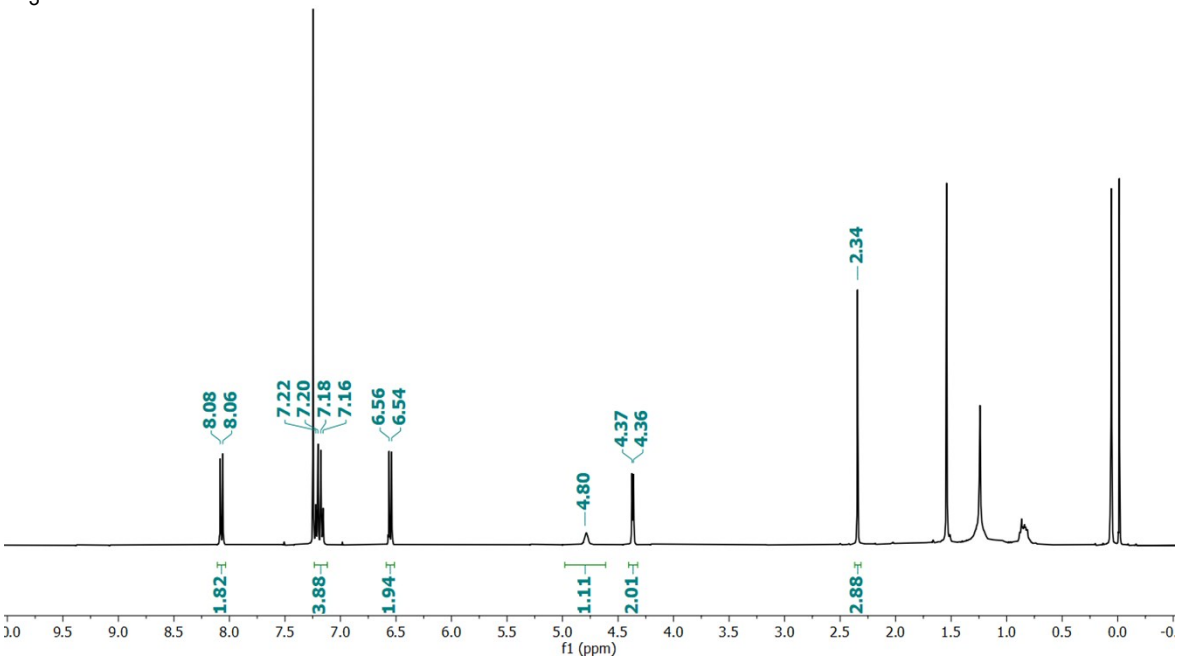

129.05
127.96
127.44
126.51
153.15
137.44
111.42
100.00
47.72
f1 (ppm)

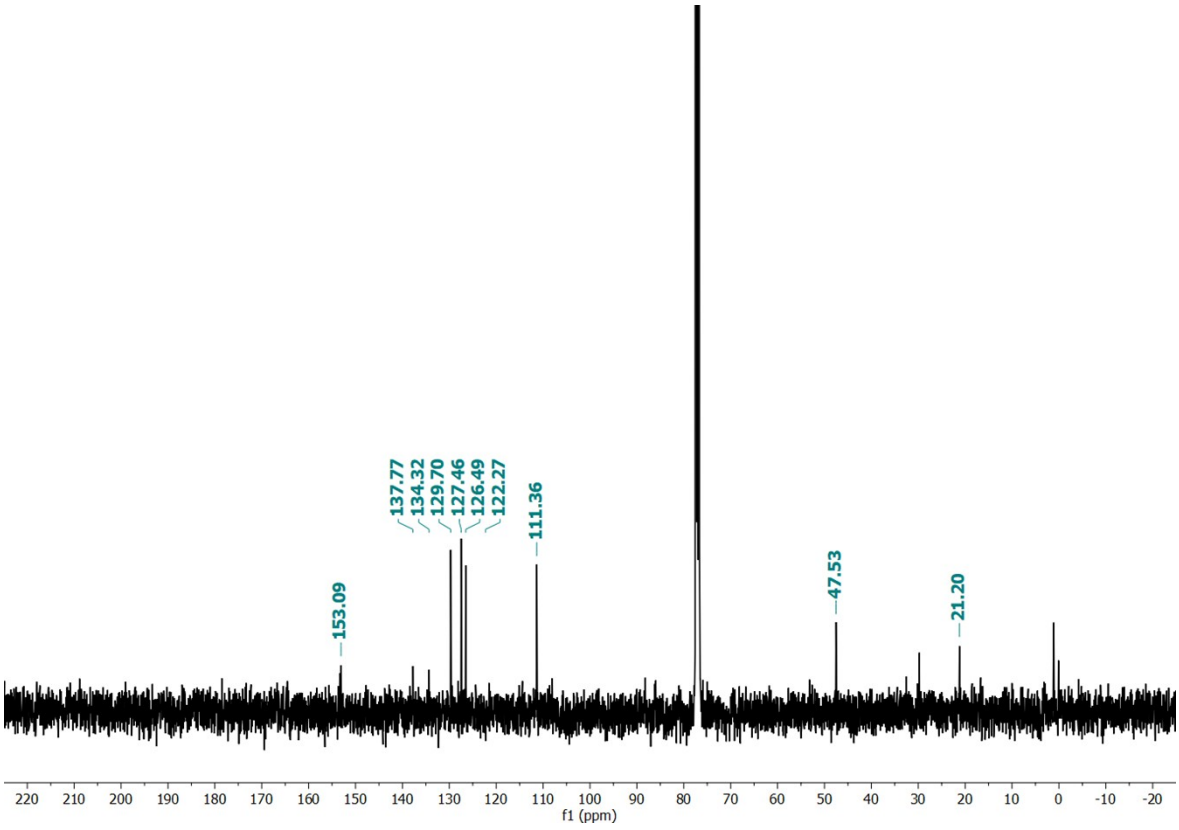

N
H
NO2

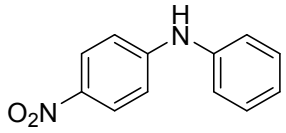

7.31
7.31
7.31
7.30
7.29
7.28
7.28
7.27
7.26
7.25
6.81
6.80
6.79
6.79
6.68
6.67
6.66
6.66
6.65
6.64
6.64
8.43
8.20
8.20
8.18
8.18
4.55
4.54
0.94
0.88
6.09
1.00
0.99
1.99
f1 (ppm)

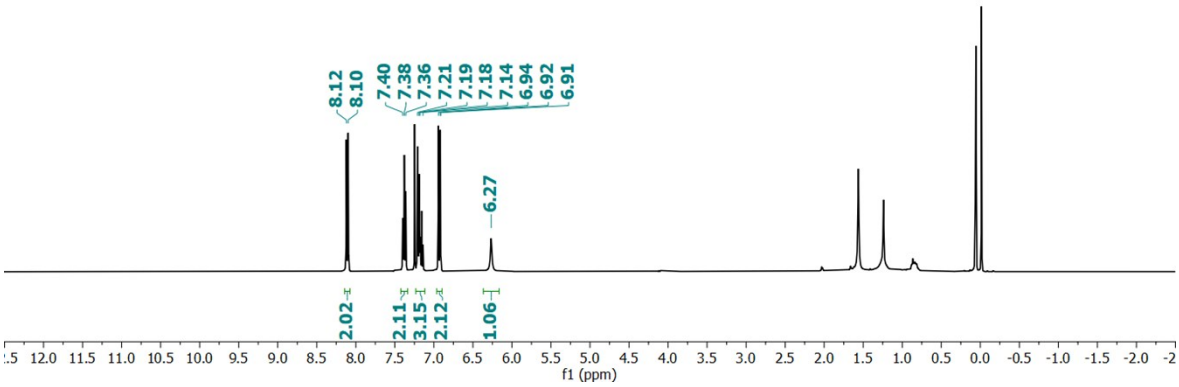

145.33
139.61
137.42
136.33
129.02
127.78
127.12
126.96
115.81
114.28
47.17
f1 (ppm)

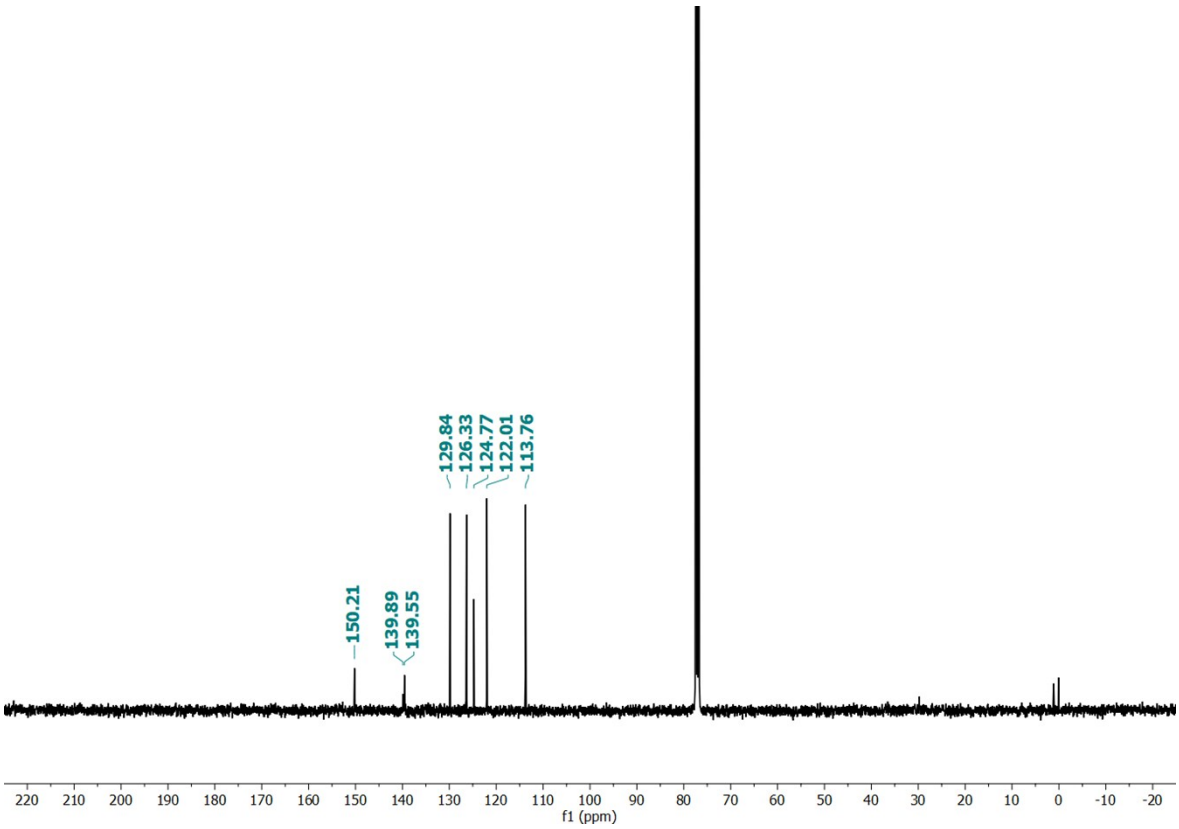

NO2
N
H
H3C

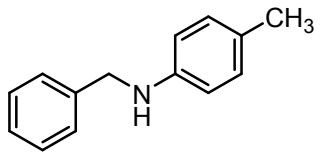

8.08
8.06
7.22
7.20
7.18
7.16
6.56
6.54
4.80
4.37
4.36
2.34
1.82
3.88
1.94
1.11
2.01
2.88
f1 (ppm)

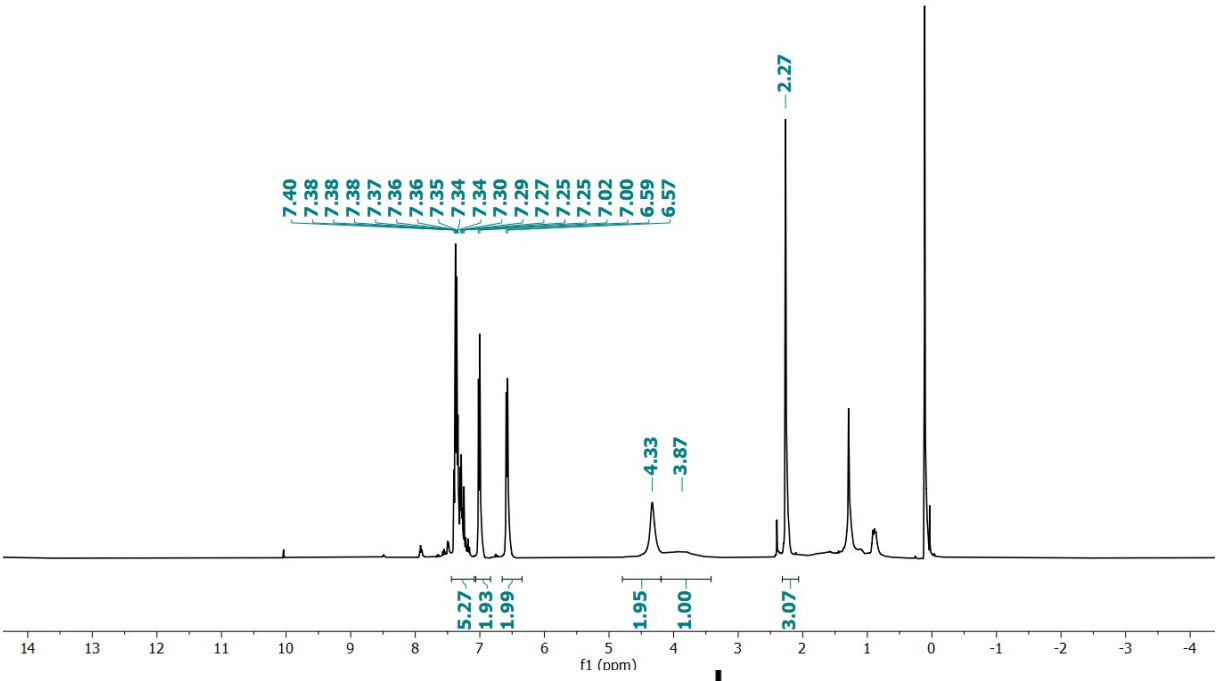

137.77
134.32
129.70
127.46
126.49
122.27
111.36
153.09
47.53
21.20
f1 (ppm)

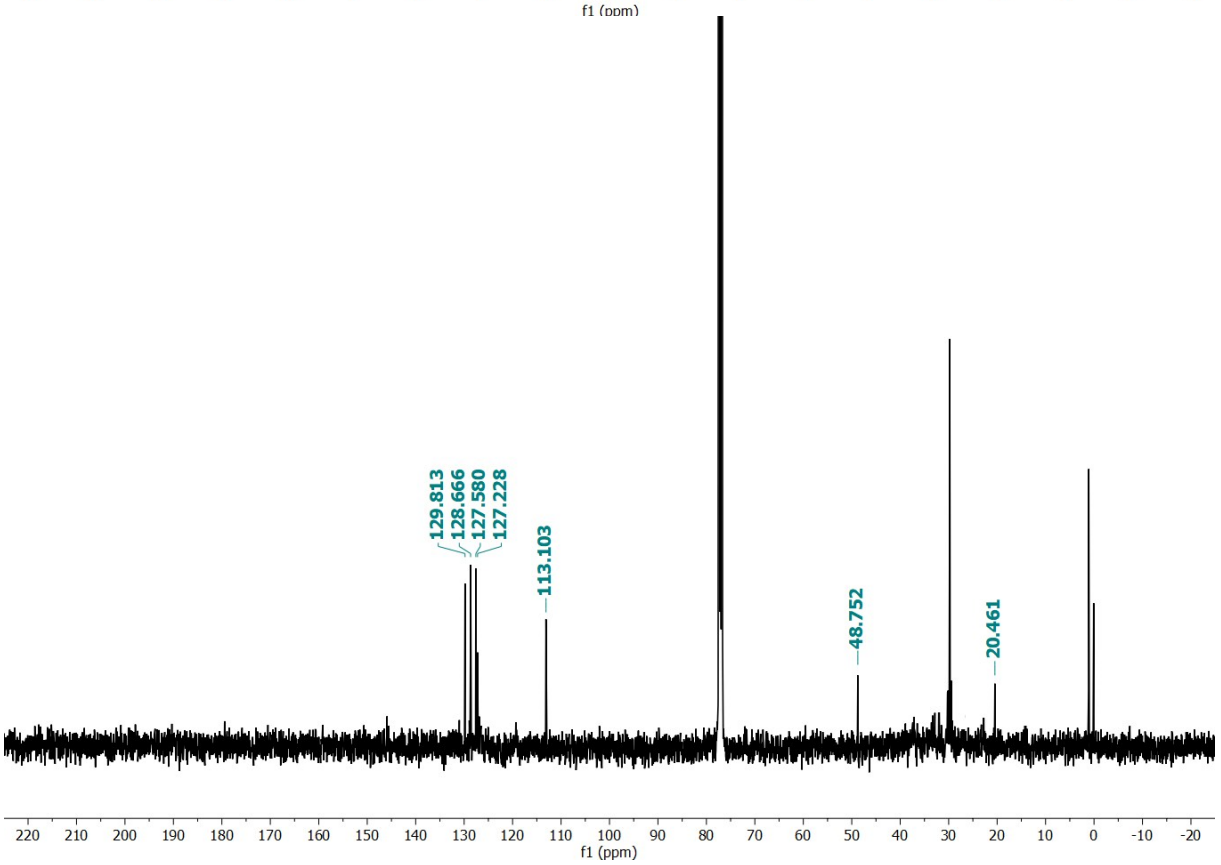

H
N
O2N

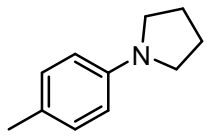

8.12
8.10
7.40
7.38
7.36
7.21
7.19
7.18
7.14
6.94
6.92
6.91
6.27
2.02
2.11
3.15
2.12
1.06
f1 (ppm)

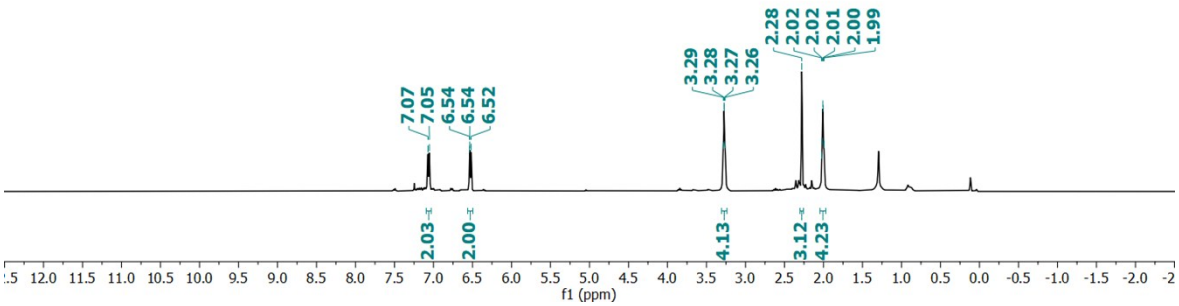

129.84
126.33
124.77
122.01
113.76
150.21
139.89
139.55
f1 (ppm)

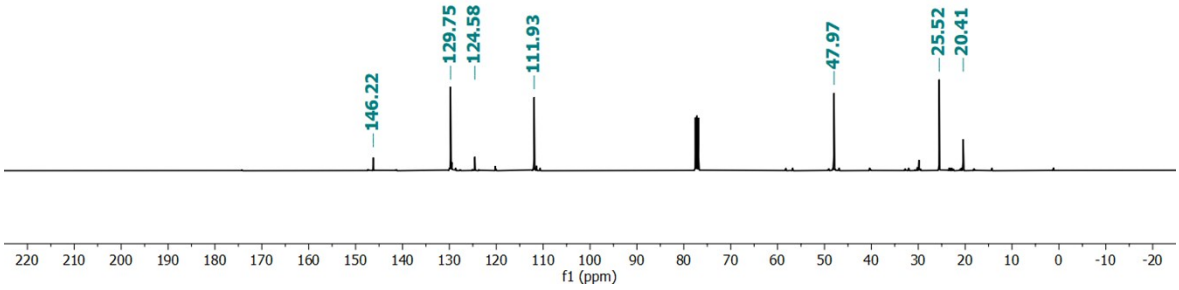

CH3
N
H

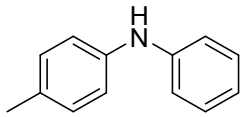

7.40
7.38
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.30
7.29
7.27
7.25
7.25
7.02
7.00
6.59
6.57
2.27
4.33
3.87
5.27
1.93
1.99
1.95
1.00
3.07
f1 (ppm)

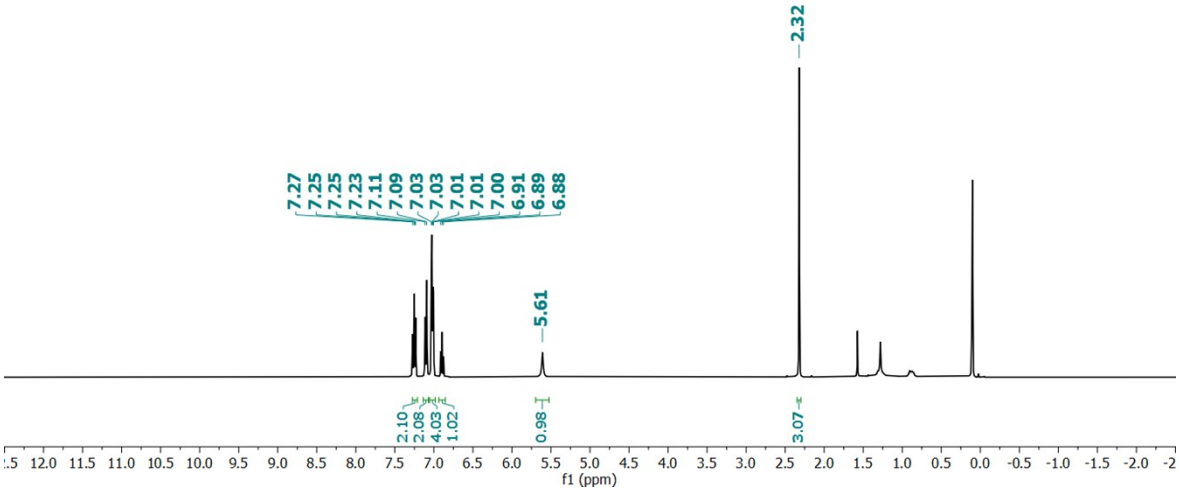

129.813
128.666
127.580
127.228
113.103
48.752
20.461
f1 (ppm)

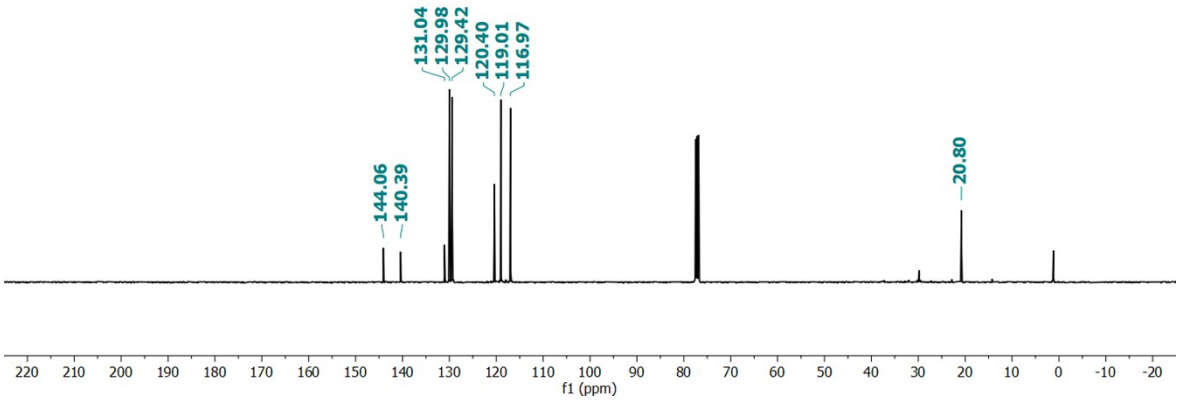


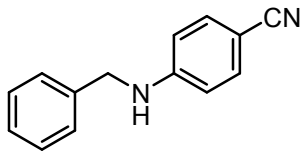

7.07
7.05
6.54
6.54
6.52
3.29
3.28
3.27
3.26
2.28
2.02
2.02
2.01
2.00
1.99
2.03
2.00
4.13
3.12
4.23
f1 (ppm)

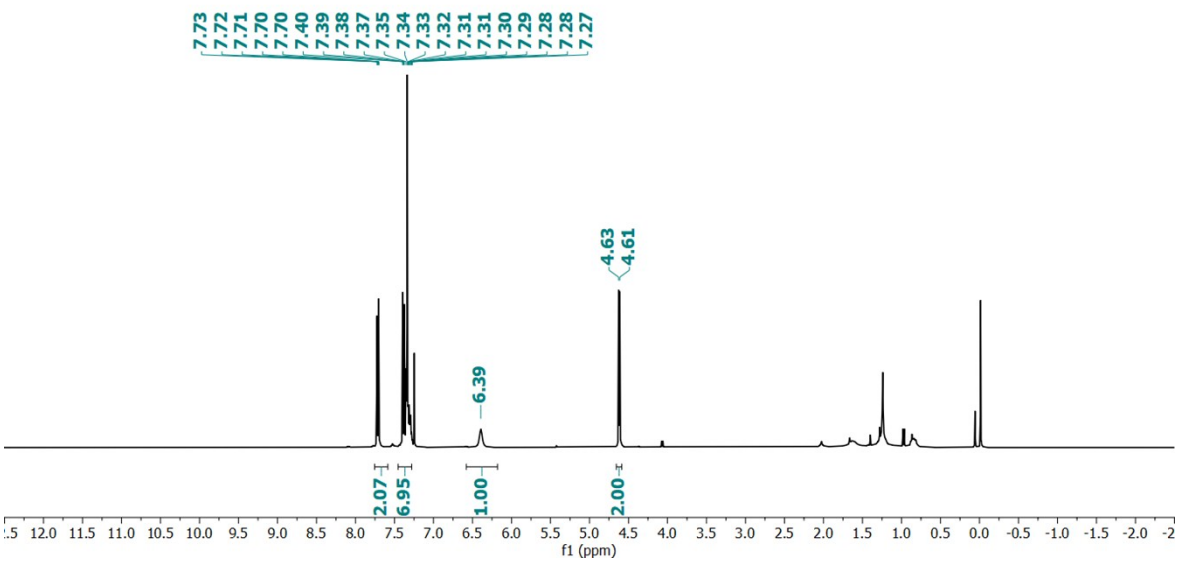

146.22
129.75
124.58
111.93
47.97
25.52
20.41
f1 (ppm)

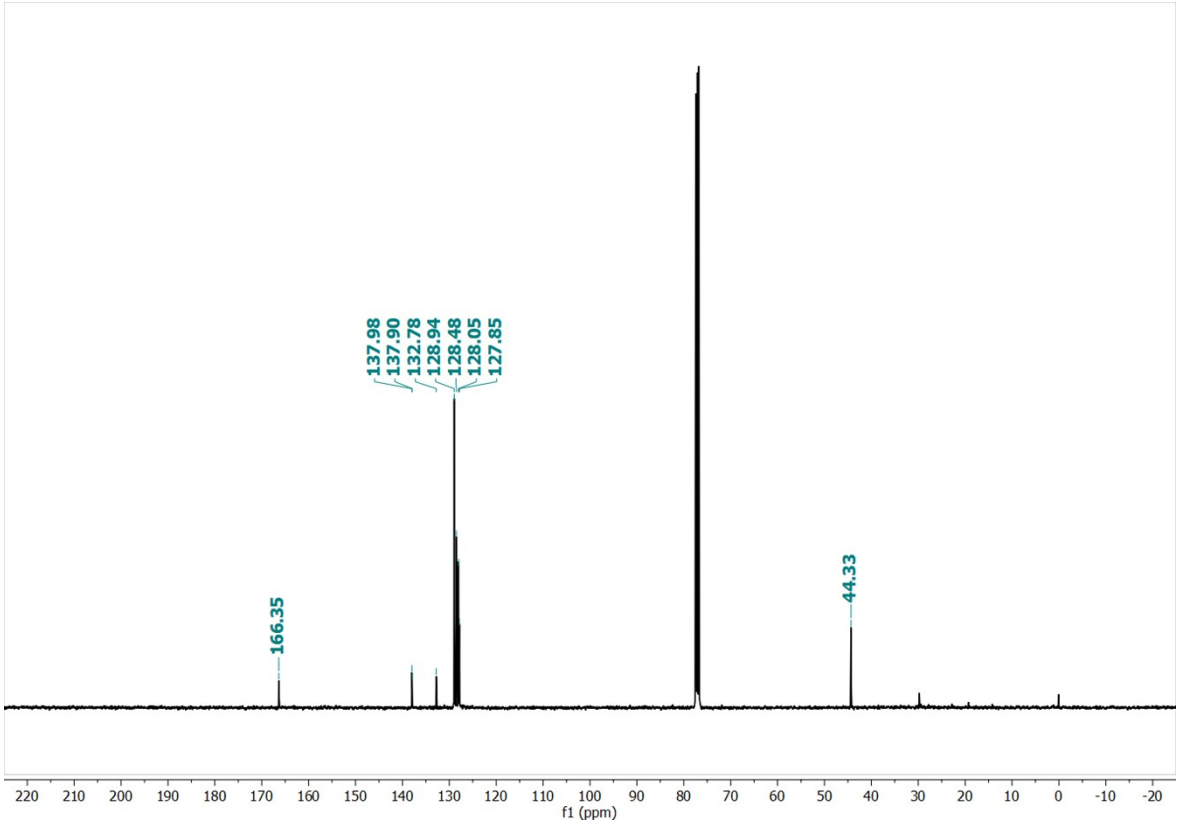


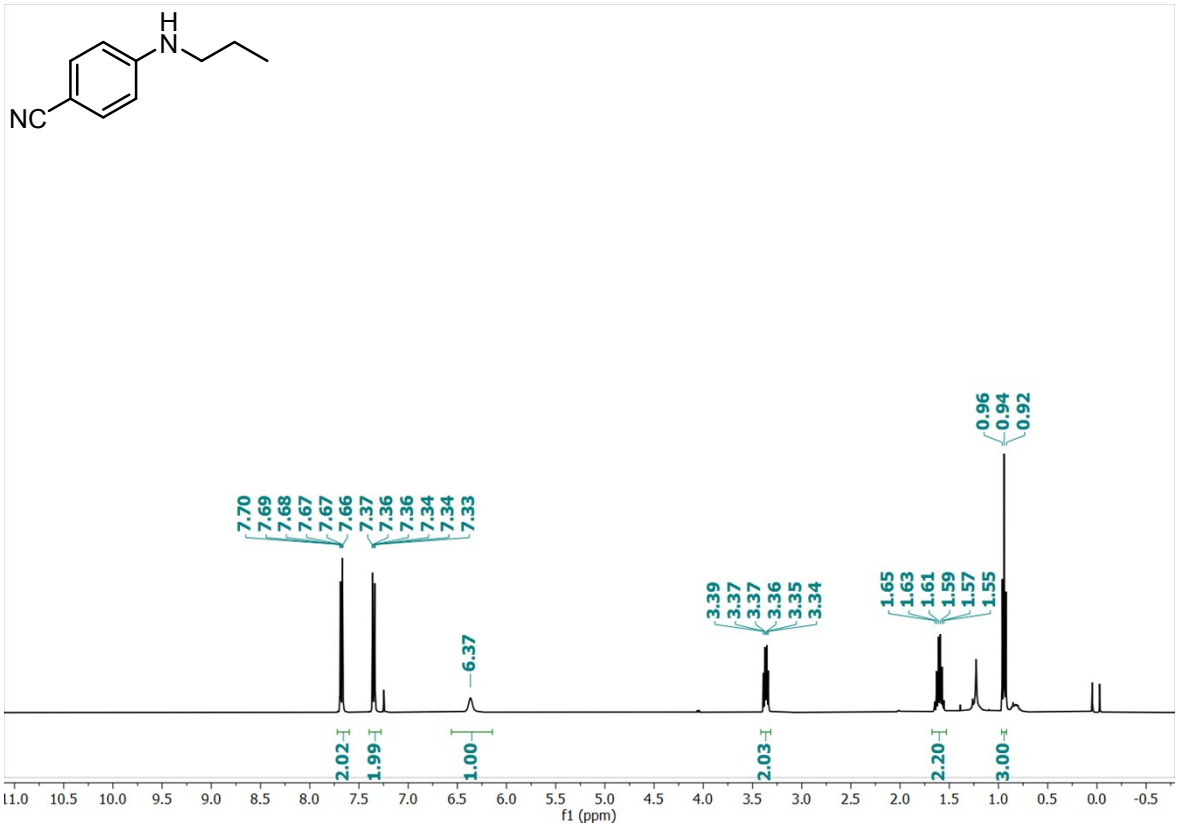

2.32
7.27
7.25
7.25
7.23
7.11
7.09
7.03
7.03
7.01
7.01
7.00
6.91
6.89
6.88
5.61
2.10
2.08
4.03
1.02
0.98
3.07
f1 (ppm)

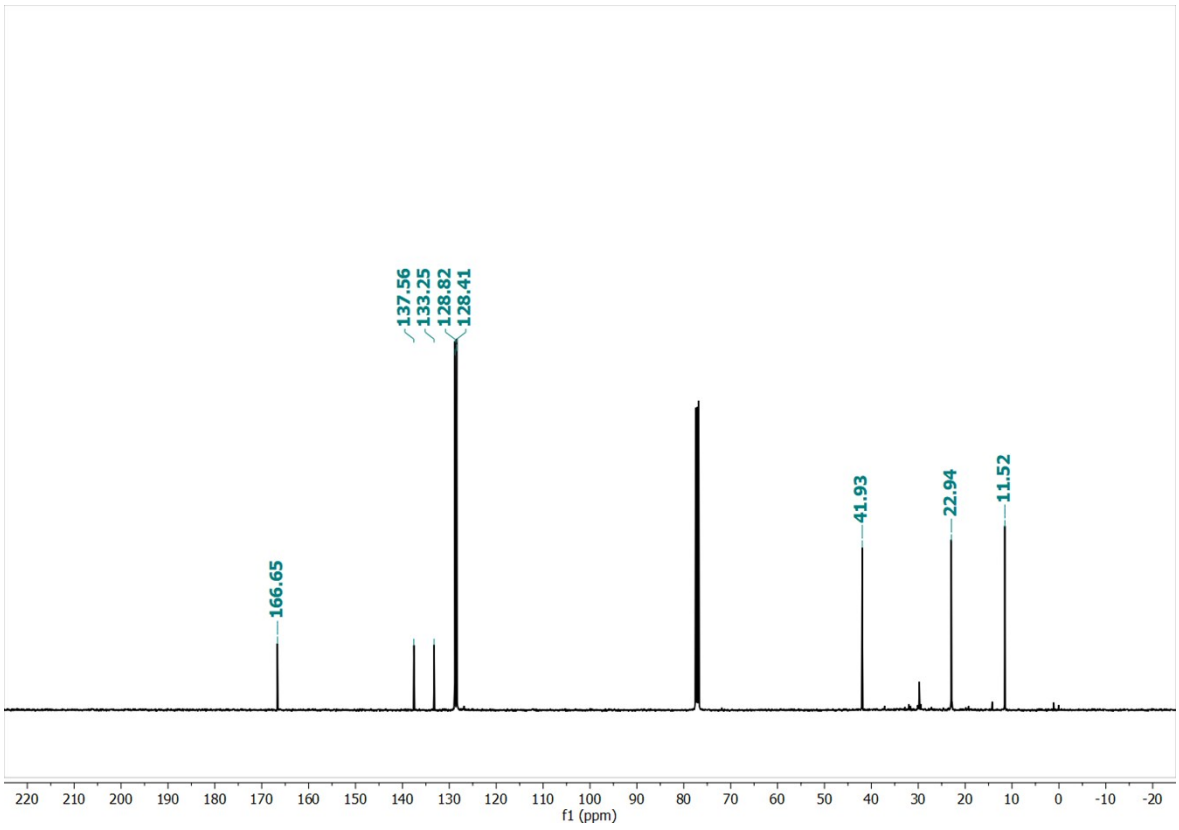

131.04
129.98
129.42
120.40
119.01
116.97
144.06
140.39
20.80
f1 (ppm)

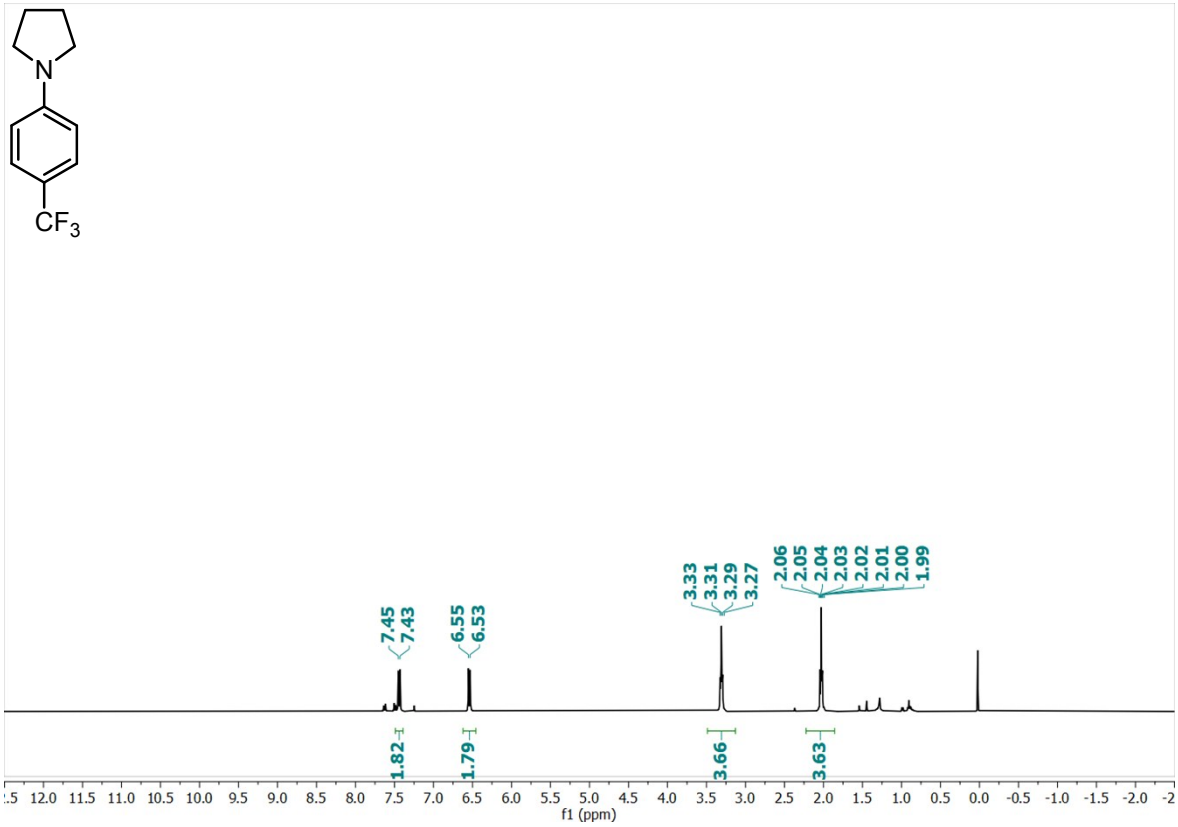

CN
N
H

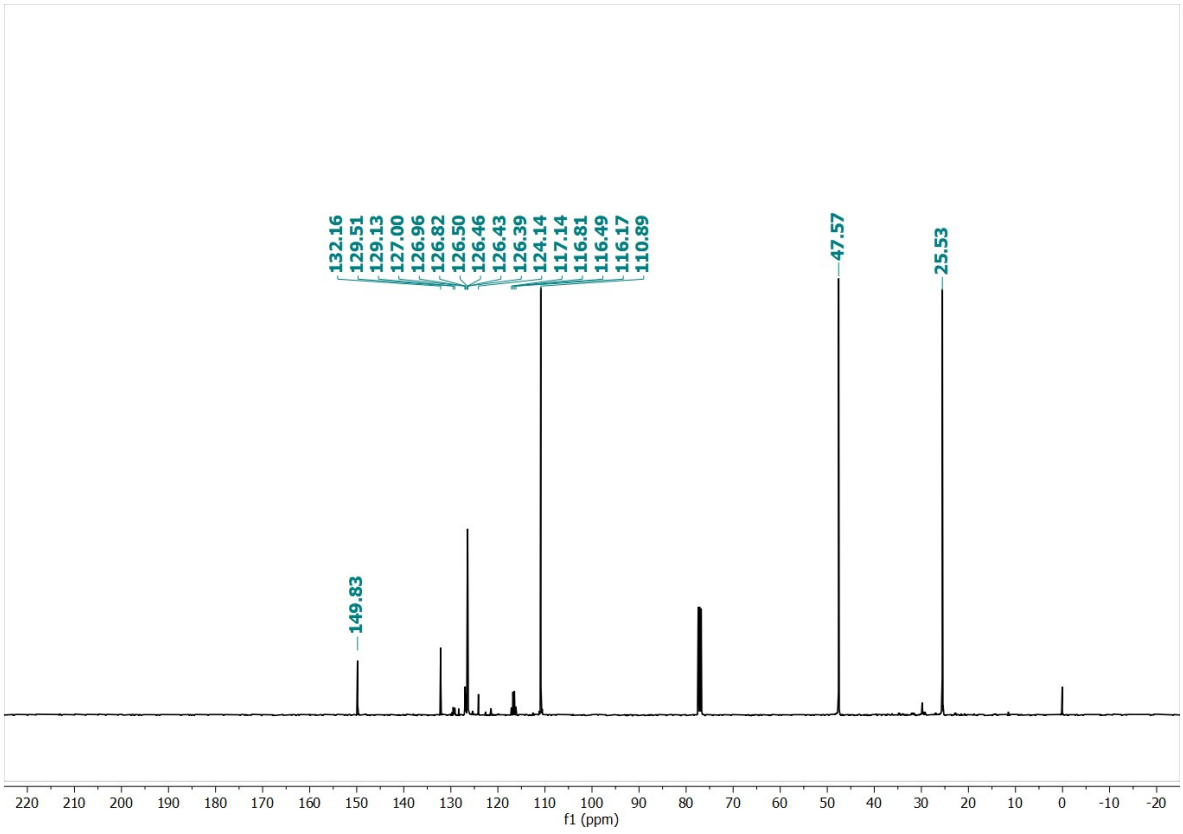

7.73
7.72
7.71
7.70
7.70
7.40
7.39
7.38
7.37
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.28
7.27
4.63
4.61
6.39
2.07
6.95
1.00
2.00
f1 (ppm)

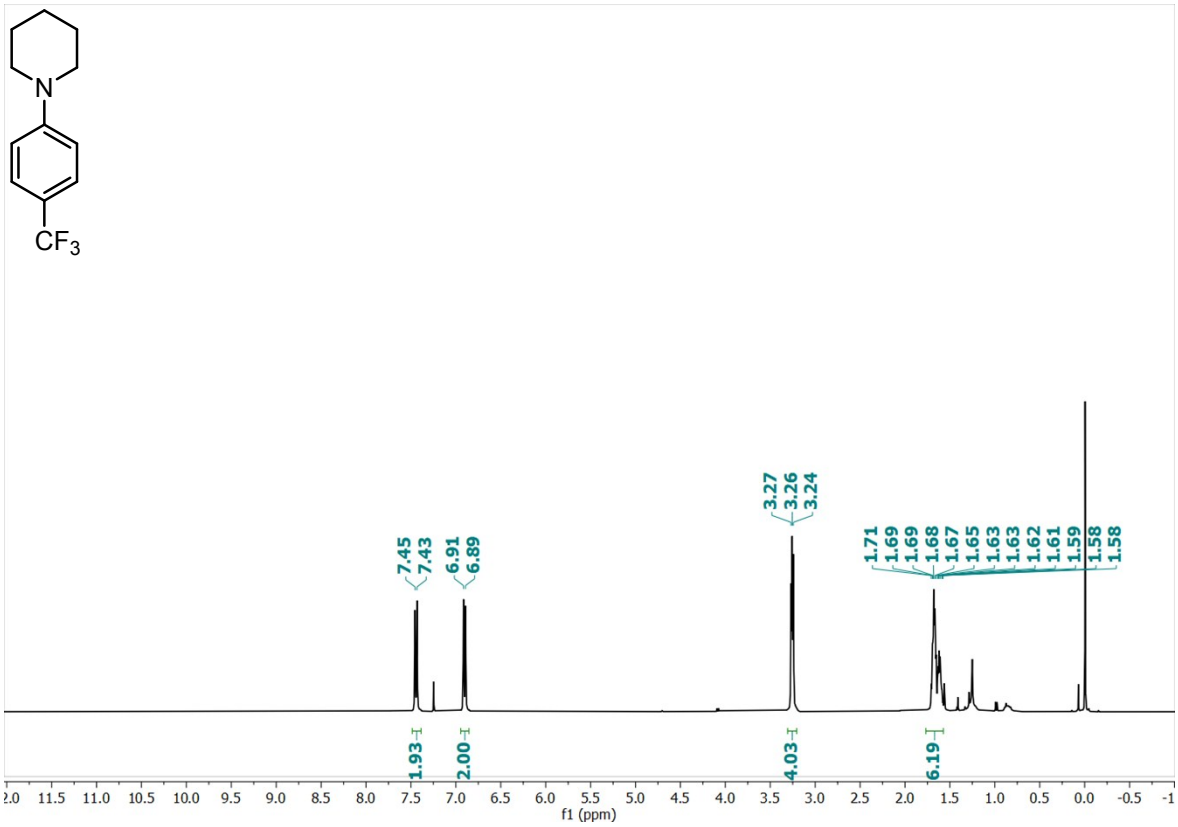

137.98
137.90
132.78
128.94
128.48
128.05
127.85
166.35
44.33
f1 (ppm)

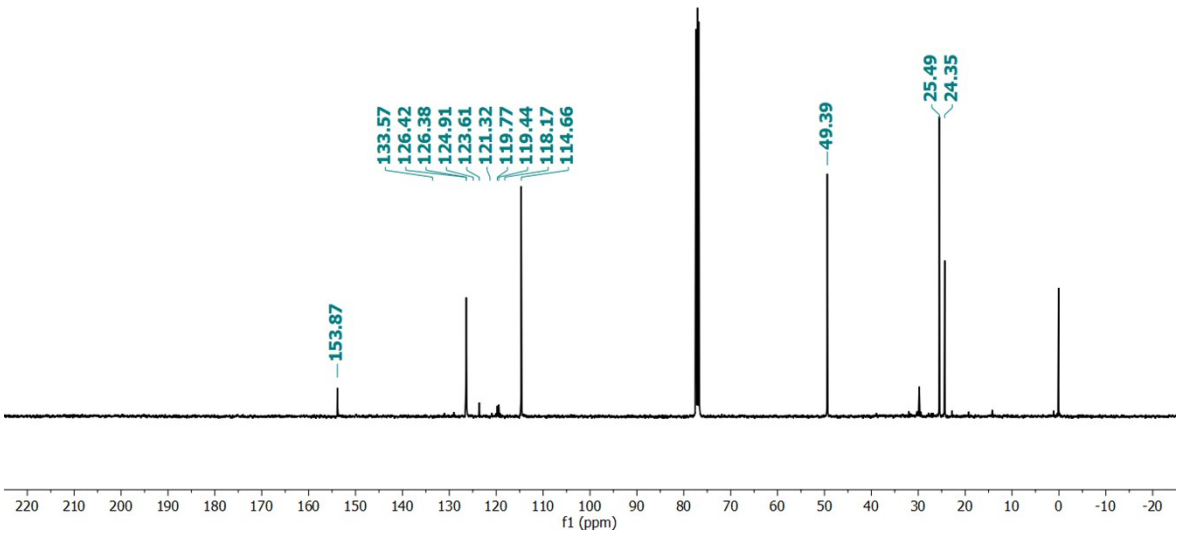

NC
H
N
7.70
7.69
7.68
7.67
7.67
7.66
7.37
7.36
7.36
7.34
7.34
7.33
6.37
3.39
3.37
3.37
3.36
3.35
3.34
1.65
1.63
1.61
1.59
1.57
1.55
0.96
0.94
0.92
2.02
1.99
1.00
2.03
2.20
3.00
f1 (ppm)

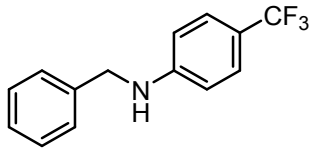

137.56
133.25
128.82
128.41
166.65
41.93
22.94
11.52
f1 (ppm)

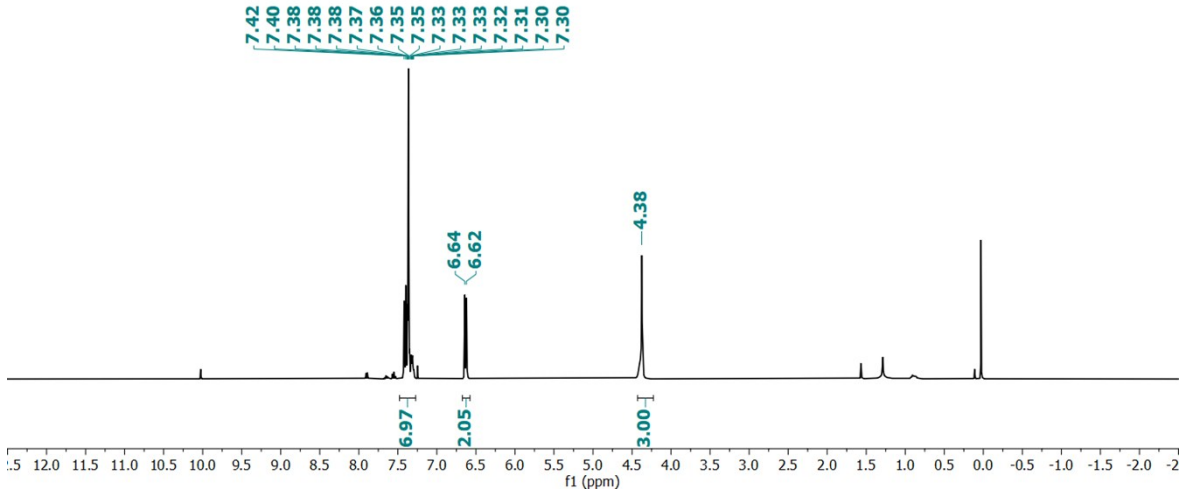

N
CF3
7.45
7.43
6.55
6.53
3.33
3.31
3.29
3.27
2.06
2.05
2.04
2.03
2.02
2.01
2.00
1.99
1.82
1.79
3.66
3.63
f1 (ppm)

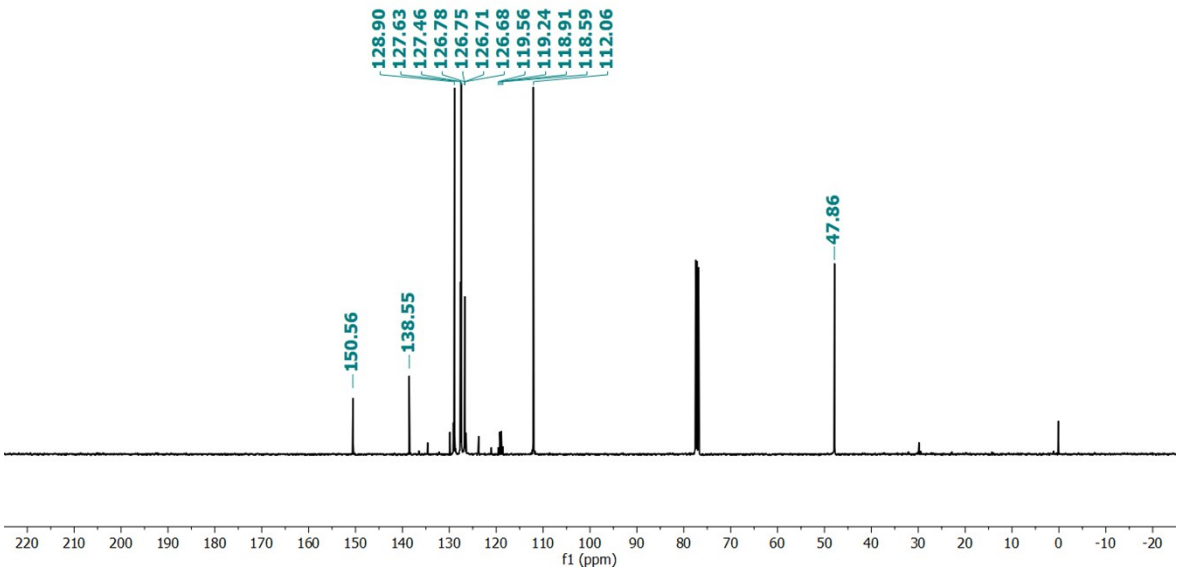

132.16
129.51
129.13
127.00
126.96
126.82
126.50
126.46
126.43
126.39
124.14
117.14
116.81
116.49
116.17
110.89
149.83
47.57
25.53
f1 (ppm)

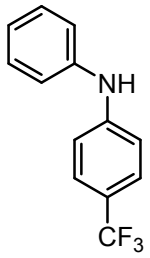

N
CF3
7.45
7.43
6.91
6.89
3.27
3.26
3.24
1.71
1.69
1.69
1.68
1.67
1.65
1.63
1.63
1.62
1.61
1.59
1.58
1.58
1.93
2.00
4.03
6.19
f1 (ppm)

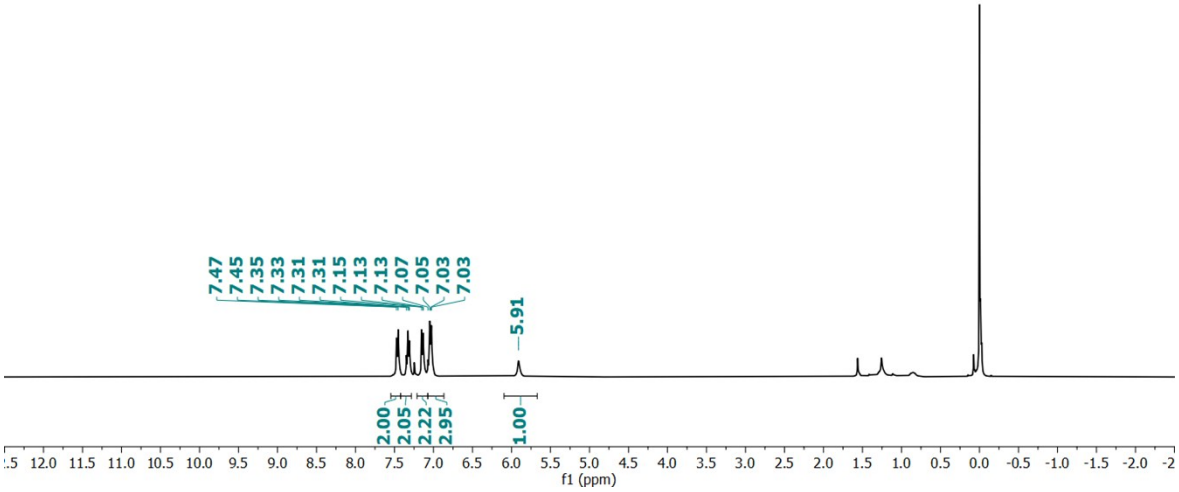

133.57
126.42
126.38
124.91
123.61
121.32
119.77
119.44
118.17
114.66
153.87
49.39
25.49
24.35
f1 (ppm)

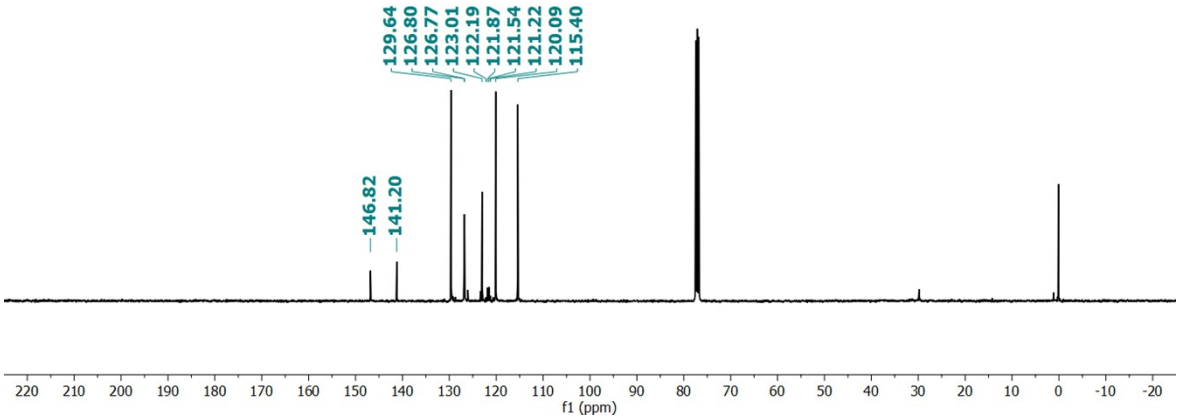

CF3
N
H

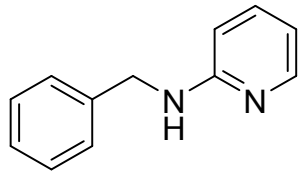

7.42
7.40
7.38
7.38
7.38
7.37
7.36
7.35
7.35
7.33
7.33
7.33
7.32
7.31
7.30
7.30
6.64
6.62
4.38
6.97
2.05
3.00
f1 (ppm)

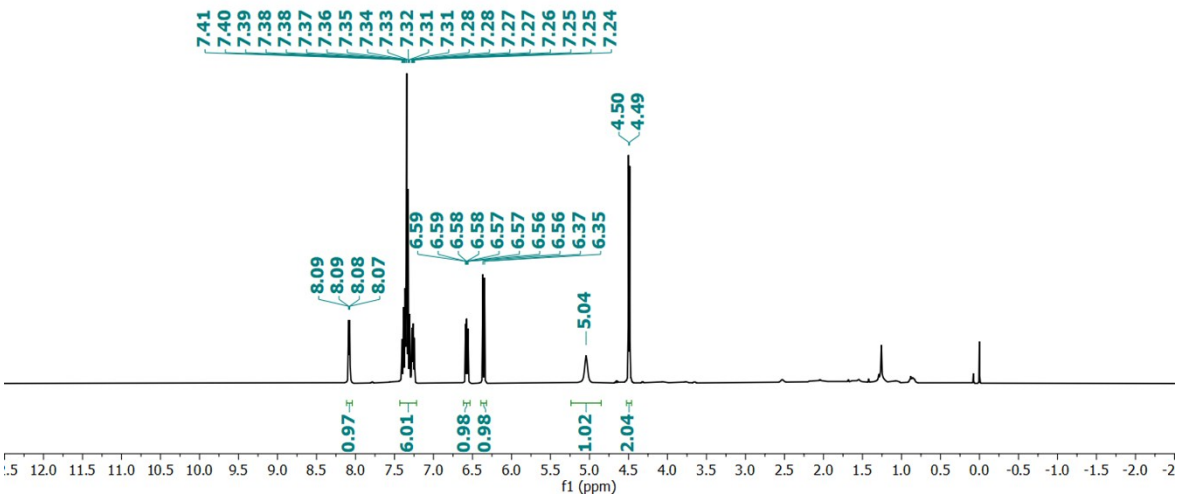

128.90
127.63
127.46
126.78
126.75
126.71
126.68
119.56
119.24
118.91
118.59
112.06
150.56
138.55
47.86
f1 (ppm)

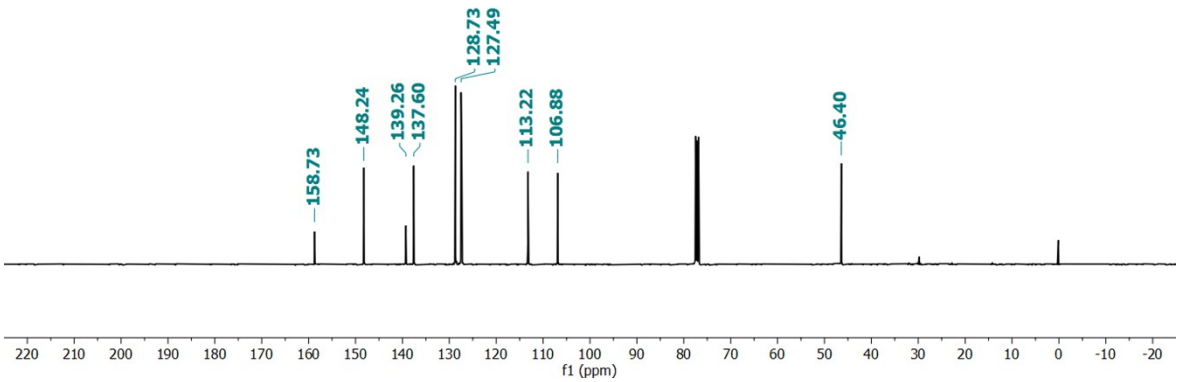

NH
CF3

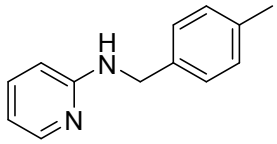

7.47
7.45
7.35
7.33
7.31
7.31
7.15
7.13
7.13
7.07
7.05
7.03
7.03
5.91
2.00
2.05
2.22
2.95
1.00
f1 (ppm)

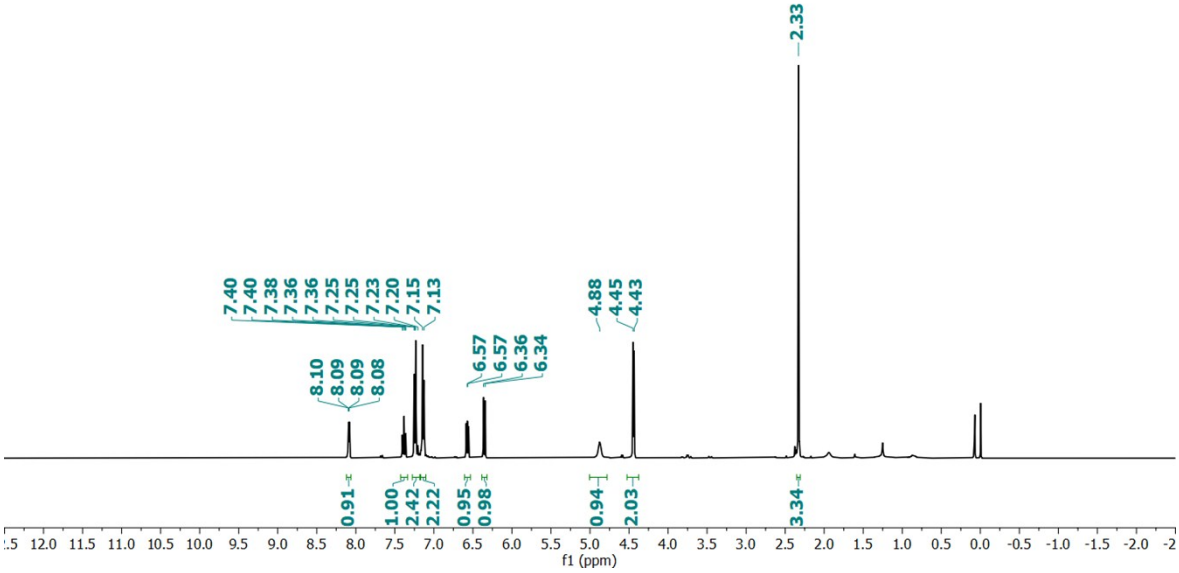

129.64
126.80
126.77
123.01
122.19
121.87
121.54
121.22
120.09
115.40
146.82
141.20
f1 (ppm)

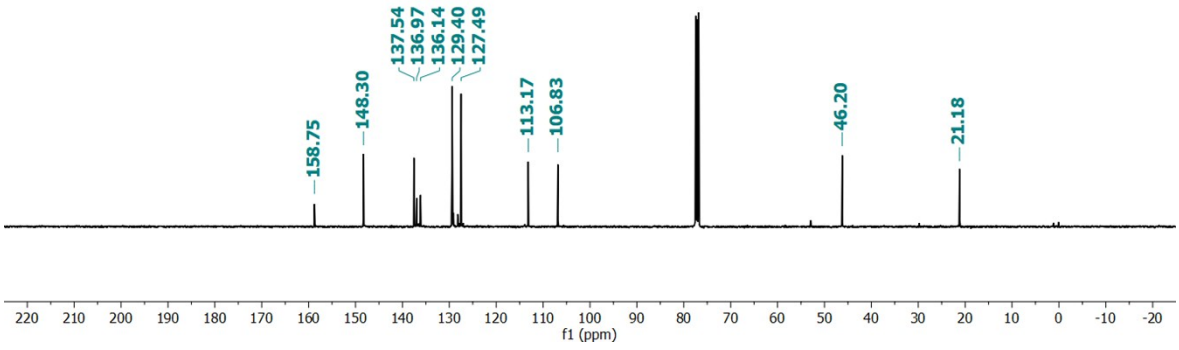

N
H
N

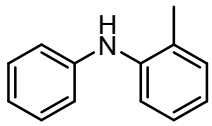

7.41
7.40
7.39
7.38
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.31
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.24
4.50
4.49
6.59
6.59
6.58
6.58
6.57
6.57
6.56
6.56
6.37
6.35
8.09
8.09
8.08
8.07
5.04
0.97
6.01
0.98
0.98
1.02
2.04
f1 (ppm)

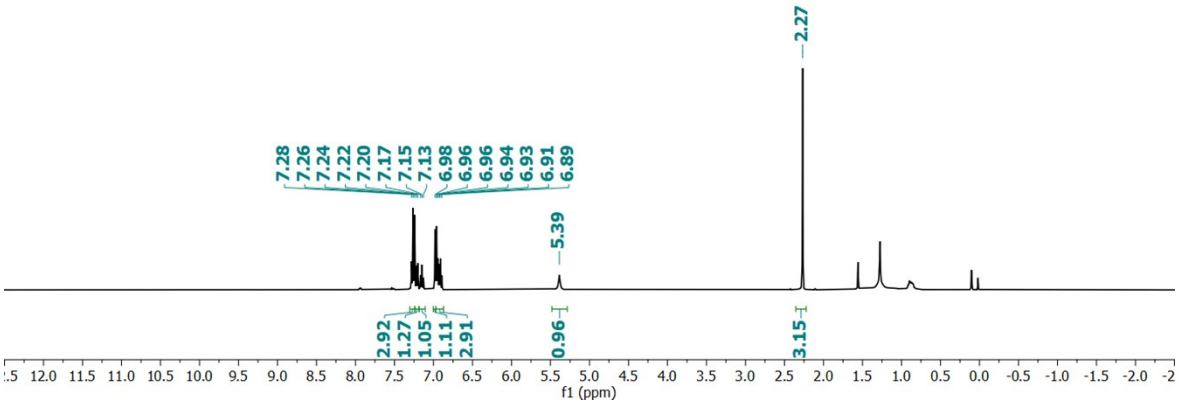

158.73
148.24
139.26
137.60
128.73
127.49
113.22
106.88
46.40
f1 (ppm)

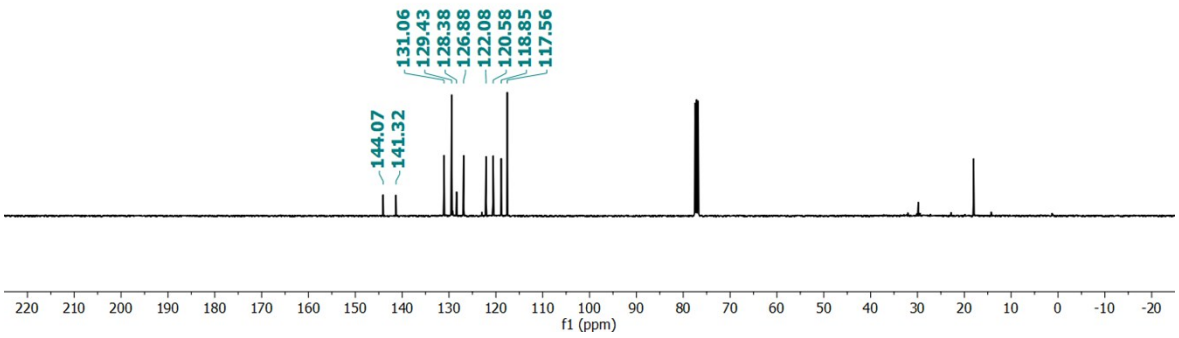

H
N
N

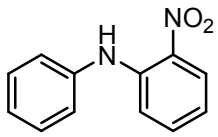

2.33
7.40
7.40
7.38
7.36
7.36
7.25
7.25
7.23
7.20
7.15
7.13
4.88
4.45
4.43
8.10
8.09
8.09
8.08
6.57
6.57
6.36
6.34
0.91
1.00
2.42
2.22
0.95
0.98
0.94
2.03
3.34
f1 (ppm)

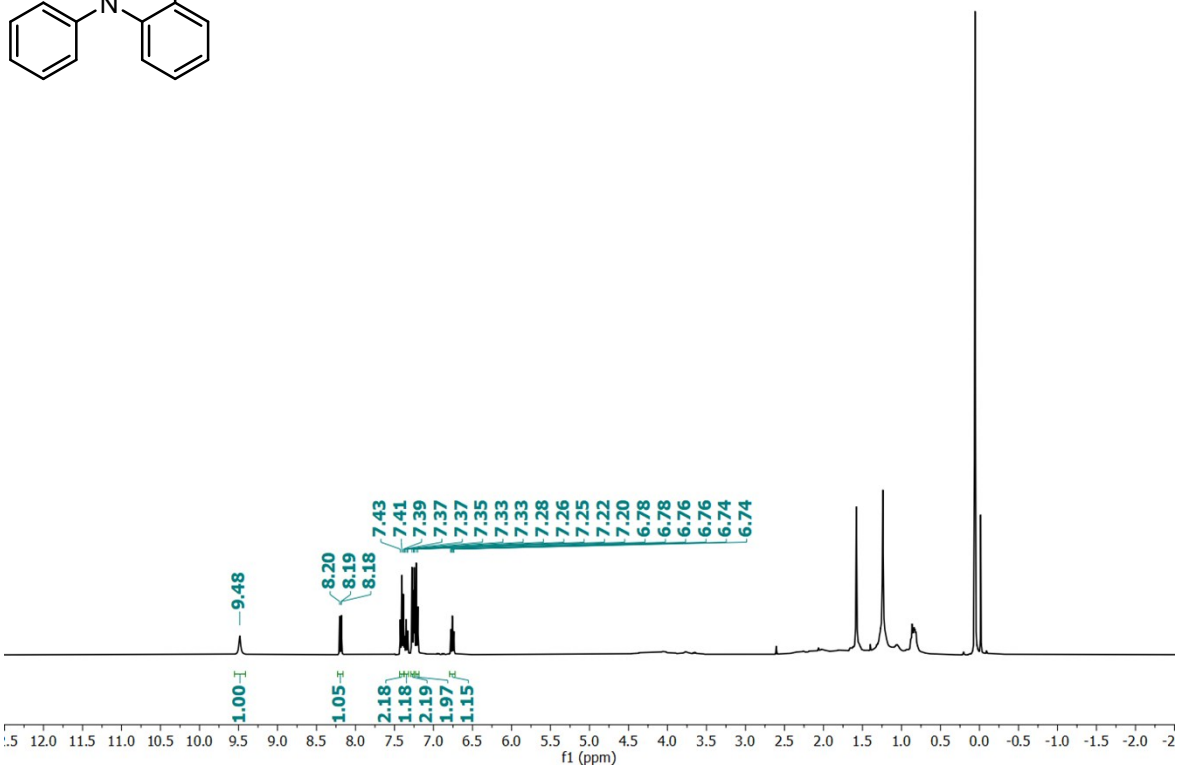

158.75
148.30
137.54
136.97
136.14
129.40
127.49
113.17
106.83
46.20
21.18
f1 (ppm)

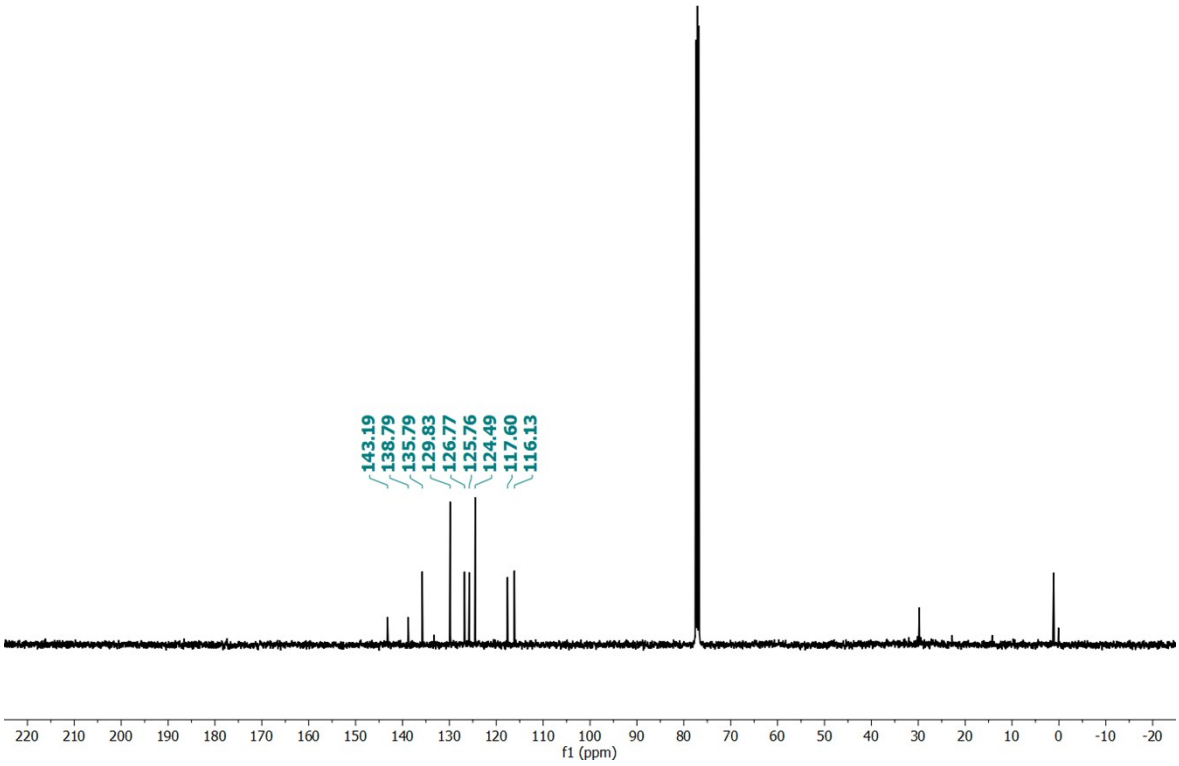


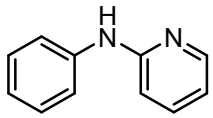

7.28
7.26
7.24
7.22
7.20
7.17
7.15
7.13
6.98
6.96
6.96
6.94
6.93
6.91
6.89
5.39
2.27
2.92
1.27
1.05
1.11
2.91
0.96
3.15
f1 (ppm)

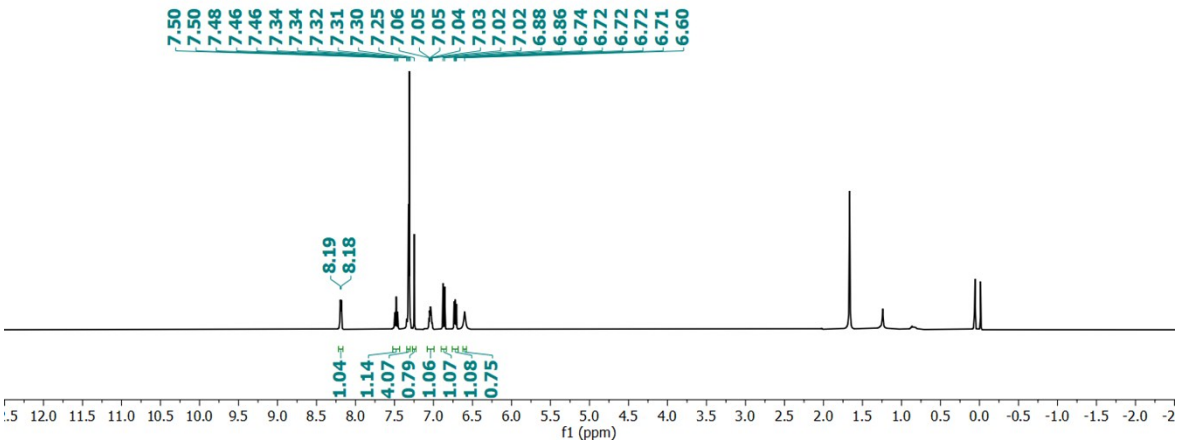

131.06
129.43
128.38
126.88
122.08
120.58
118.85
117.56
144.07
141.32
f1 (ppm)

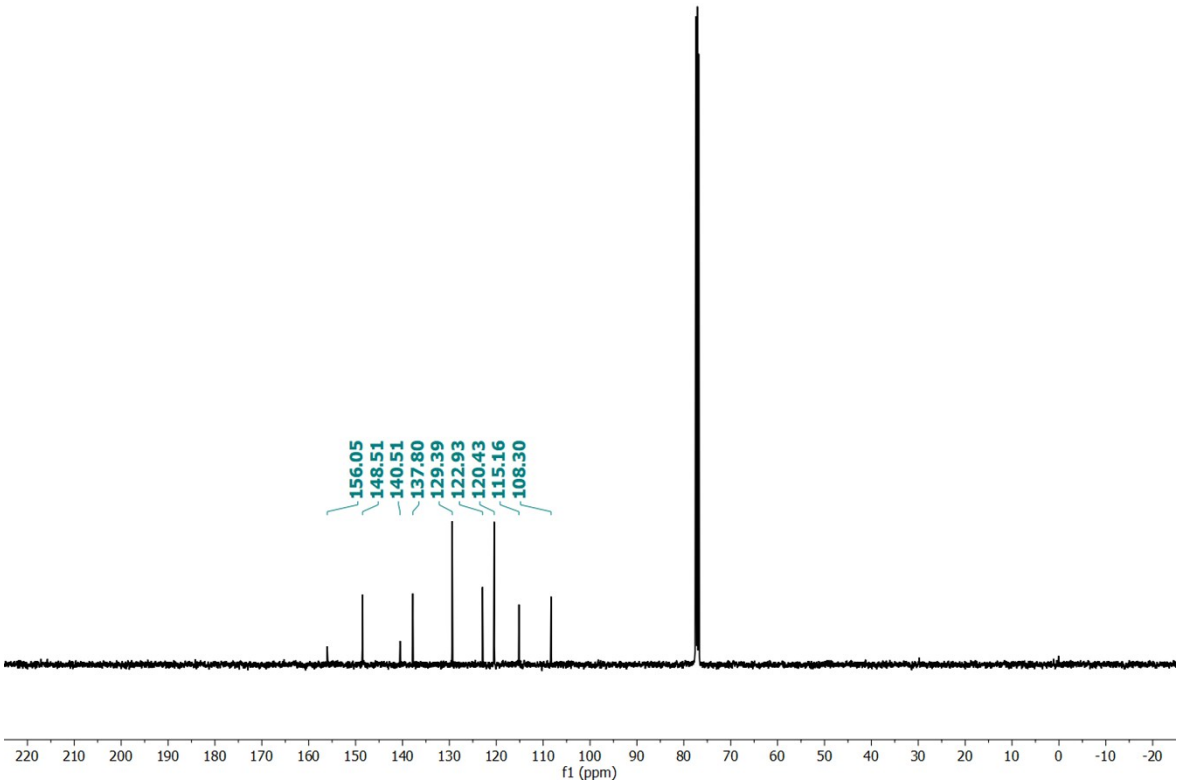

NO2
H
N

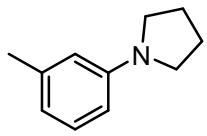

9.48
8.20
8.19
8.18
7.43
7.41
7.39
7.37
7.37
7.35
7.33
7.33
7.28
7.26
7.25
7.22
7.20
6.78
6.78
6.76
6.76
6.74
6.74
1.00
1.05
2.18
1.18
2.19
1.97
1.15
f1 (ppm)

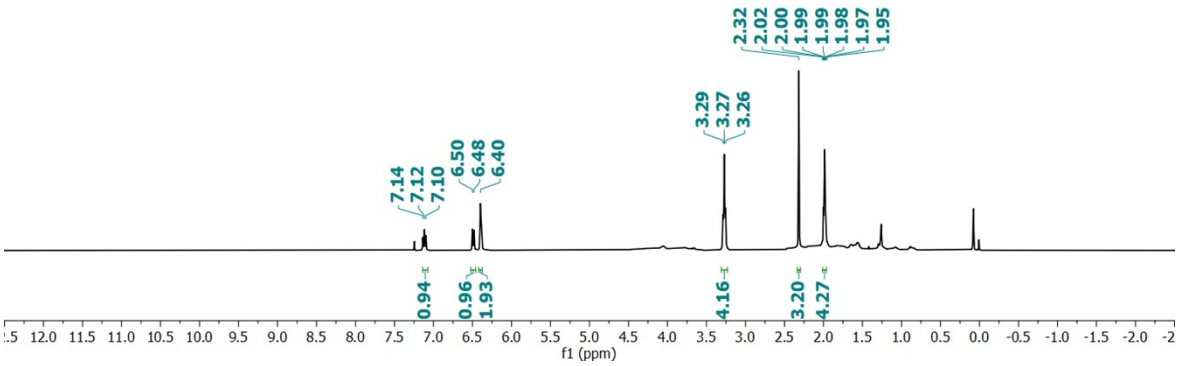

143.19
138.79
135.79
129.83
126.77
125.76
124.49
117.60
116.13
f1 (ppm)

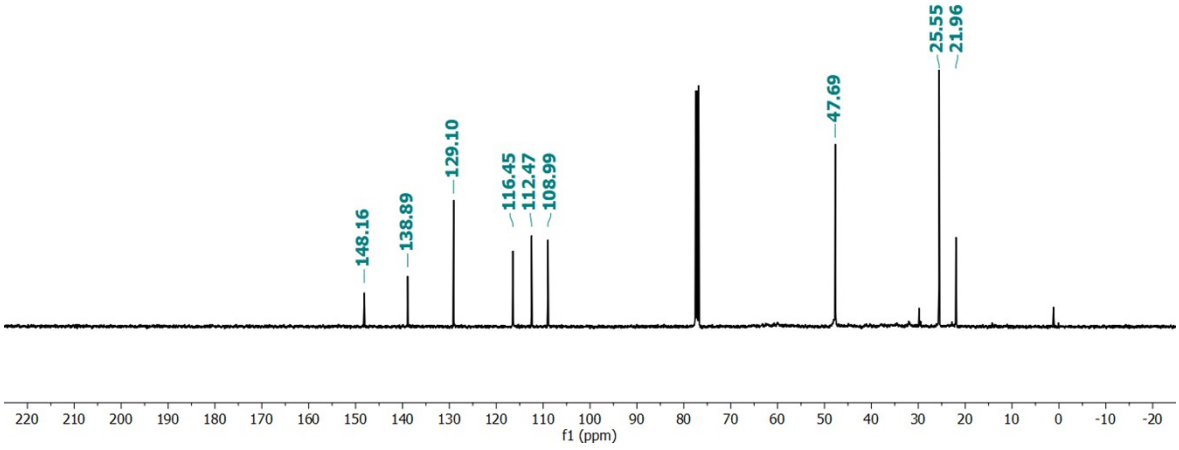

H
N
N

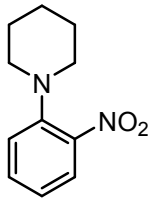

7.50
7.50
7.48
7.46
7.46
7.34
7.34
7.32
7.31
7.30
7.25
7.06
7.05
7.05
7.04
7.03
7.02
7.02
6.88
6.86
6.74
6.72
6.72
6.71
6.60
8.19
8.18
1.04
1.14
4.07
0.79
1.06
1.07
1.08
0.75
f1 (ppm)

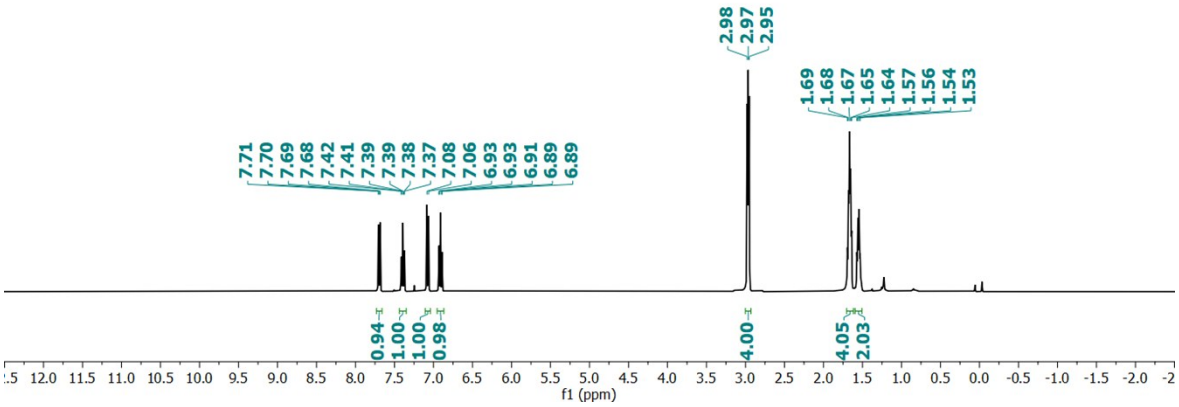

156.05
148.51
140.51
137.80
129.39
122.93
120.43
115.16
108.30
f1 (ppm)

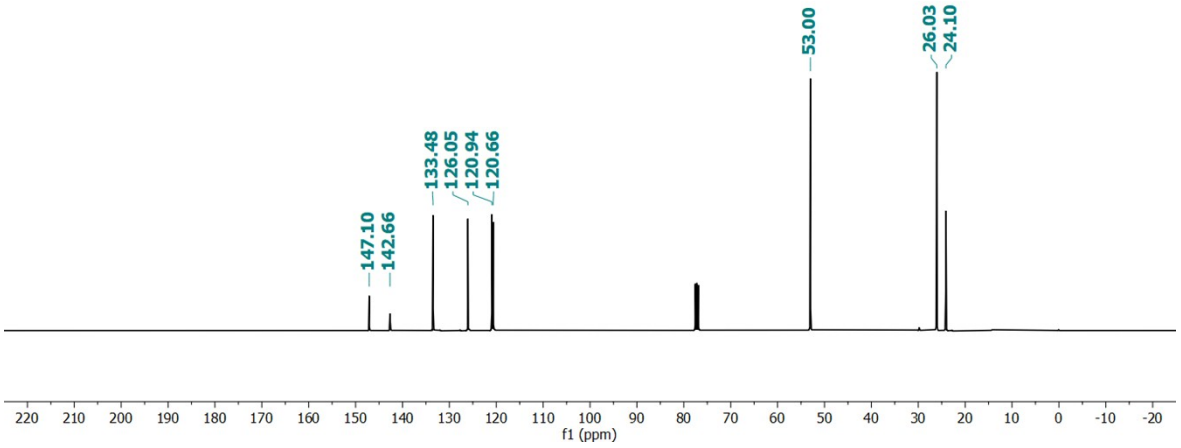


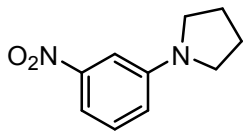

2.32
2.02
2.00
1.99
1.99
1.98
1.97
1.95
3.29
3.27
3.26
7.14
7.12
7.10
6.50
6.48
6.40
0.94
0.96
1.93
4.16
3.20
4.27
f1 (ppm)

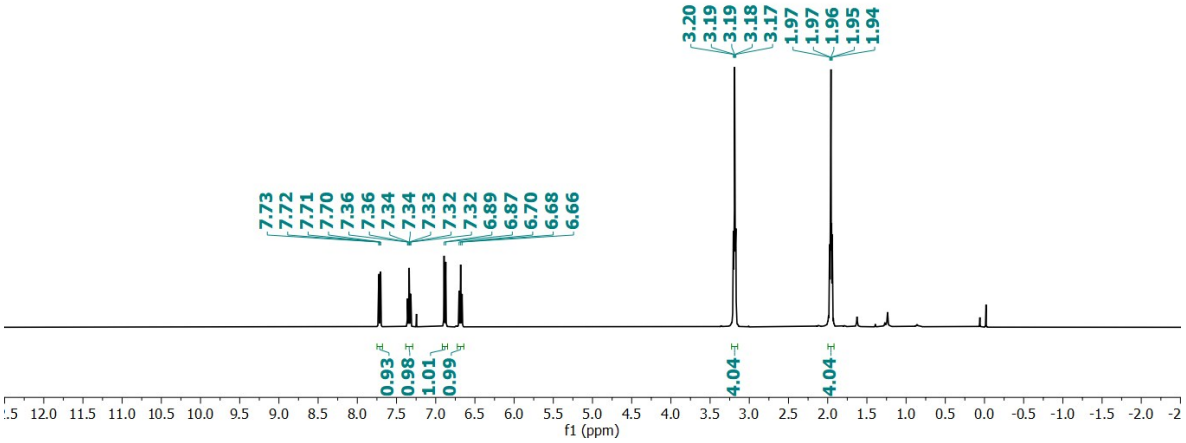

25.55
21.96
47.69
148.16
138.89
129.10
116.45
112.47
108.99
f1 (ppm)

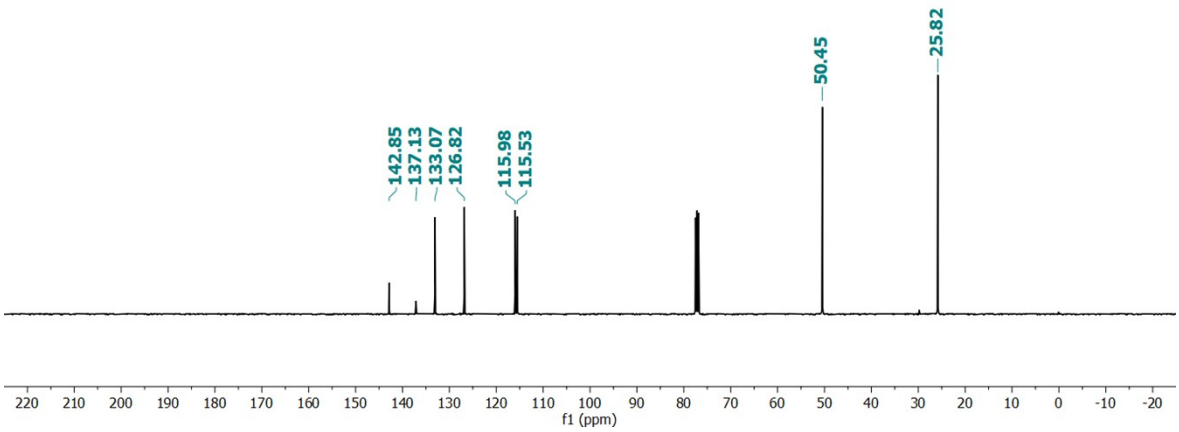

N
NO2

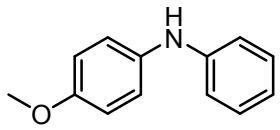

7.71
7.70
7.69
7.68
7.42
7.41
7.39
7.39
7.38
7.37
7.08
7.06
6.93
6.93
6.91
6.89
6.89
2.98
2.97
2.95
1.69
1.68
1.67
1.65
1.64
1.57
1.56
1.54
1.53
0.94
1.00
1.00
0.98
4.00
4.05
2.03
f1 (ppm)

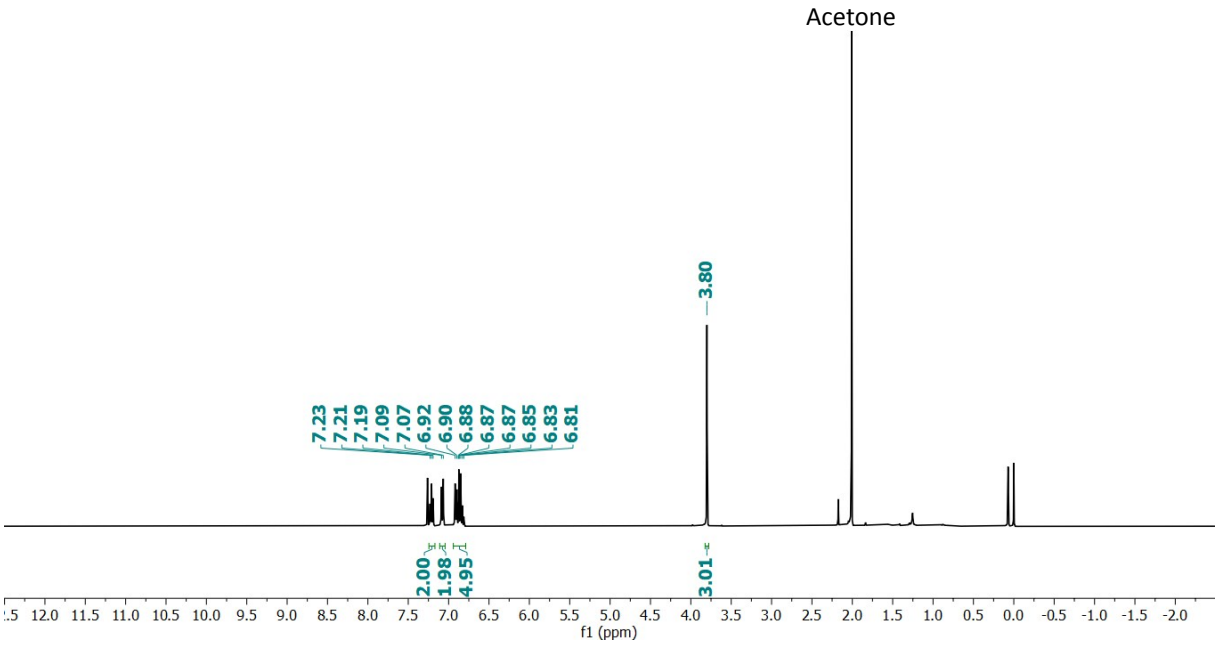

147.10
142.66
133.48
126.05
120.94
120.66
53.00
26.03
24.10
f1 (ppm)

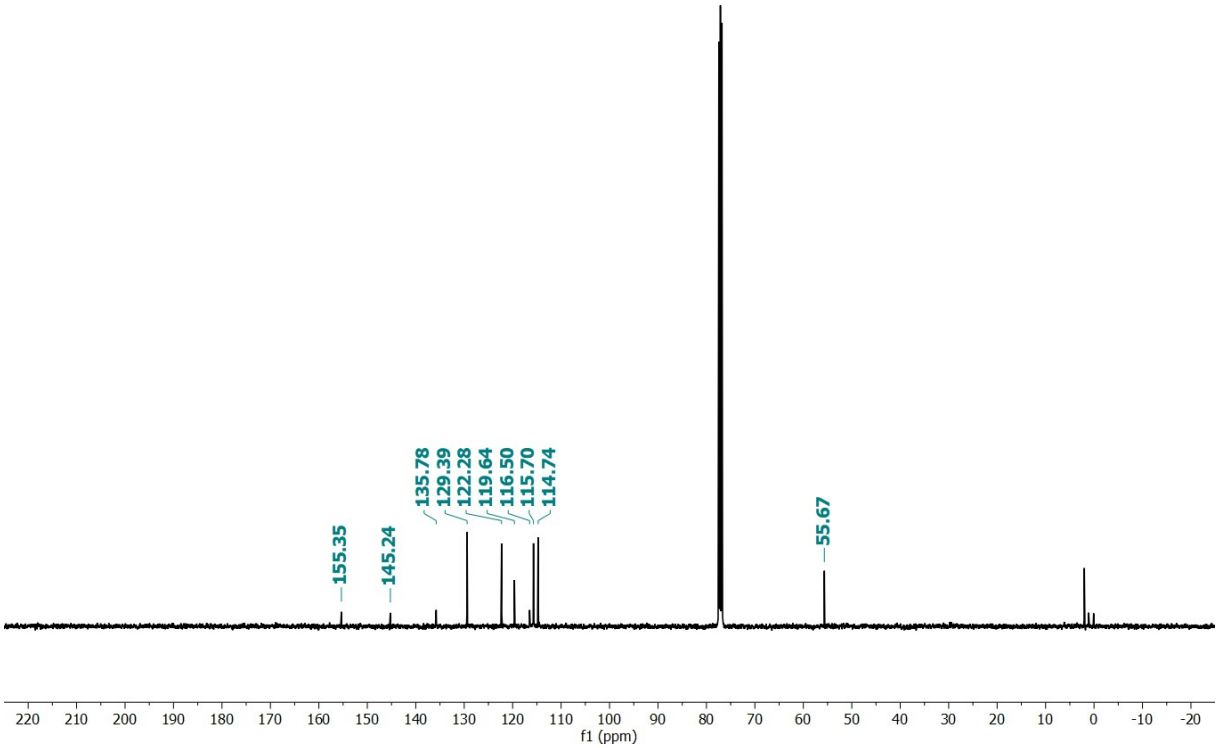

O2N
N


3.20
3.19
3.19
3.18
3.17
1.97
1.97
1.96
1.95
1.94
7.73
7.72
7.71
7.70
7.36
7.34
7.34
7.33
7.32
7.32
6.89
6.87
6.70
6.68
6.66
0.93
0.98
1.01
0.99
4.04
4.04
f1 (ppm)


142.85
137.13
133.07
126.82
115.98
115.53
50.45
25.82
f1 (ppm)


H
N
O


Acetone
3.80
7.23
7.21
7.19
7.09
7.07
6.92
6.90
6.88
6.87
6.87
6.85
6.83
6.81
2.00
1.98
4.95
3.01
f1 (ppm)


155.35
145.24
135.78
129.39
122.28
119.64
116.50
115.70
114.74
55.67
f1 (ppm)

References

1. B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell, Vogel's Textbook of Practical Organic Chemistry. 5th ed.; ELBS, Longman Group U K Ltd.: **1989**
2. G. Sheldrick, SADABS v. 2.10. Bruker AXS Inc., Madison, Wisconsin, USA **2003**
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, 42, 339-341.
4. (a) G. Sheldrick, A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, 64, 112-122; (b) G. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallography. Sect. A: Found. Crystallogr.* **2015**, 71, 3-8; (c) G. Sheldrick, Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C* **2015**, 71, 3-8.
5. K. N. Sharma, H. Joshi, V. V. Singh, P. Singh, A. K. Singh, *Dalton Trans.* **2013**, 42, 3908-3918