Electronic supplementary materials *Mendeleev Commun.*, 2027, **37**, just accepted

Preparation of *N*-bornylindoles through Au-catalyzed cyclization of *N*-bornyl-2-ethynylanilines

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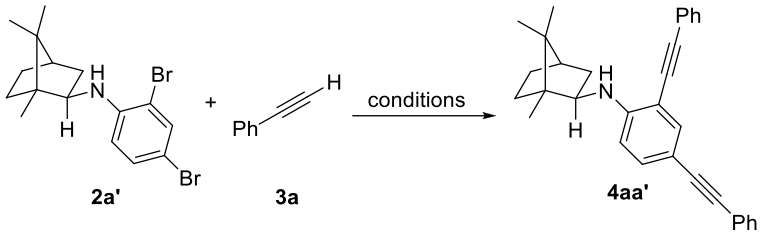
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General information.

Silica gel chromatography purifications were performed by flash chromatography using EM Science silica gel 60 (230-400 mesh). All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and High Resolution Mass Spectrometry (HRMS). Chemicals and solvents were obtained from commercial sources and used without further purification. NMR spectra were obtained on a Bruker Avance III HD (400 MHz ^{1}H, 101 MHz ^{13}C, 376 MHz ^{19}F). NOESY NMR spectrum was acquired at 298 K (mixing time value D8 = 900 ms, relaxation time D1 = 1.82 s). Chemical shifts are reported relative to residual undeuterated solvent signals. Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as ''s", ''d", "t" or ''m" for singlet, doublet, triplet or multiplet, respectively. The abbreviation ''br" is given for broadened signals. APPI HRMS spectra in positive ion mode were acquired for toluene solutions using AB Sciex TripleTOF 5600+ instrument equipped with a PhotoSpray ion source. FT-IR spectra were obtained in a Bruker "Alpha-T" FTIR (KBr).

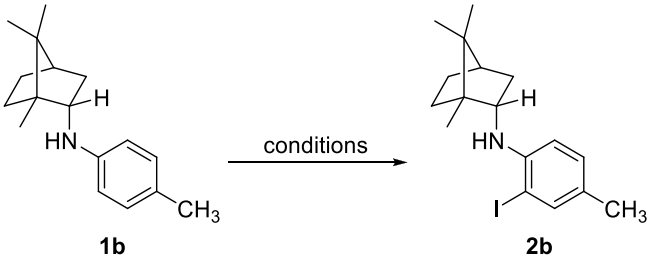
Reactions optimization

Table S1. Cross-coupling reaction optimization



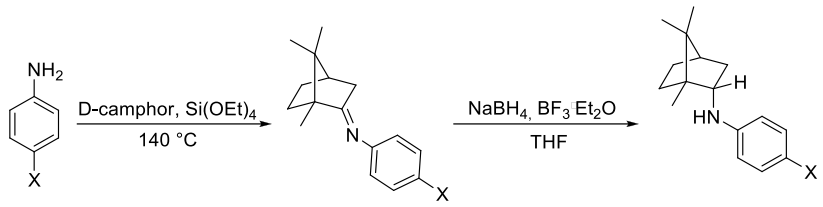
Entry	Conditions	Yield
1	$Pd(PPh_3)_2Cl_2$ (4 mol%), CuI (4 mol%) Et_3N (1 ml/mmol)	20%
2	$Pd(dppf)Cl_2$ (5 mol%), CuI (10 mol%) $PhCH_3/Et_3N$ (4/1 ml/mmol)	51%

Table S2. Iodination reaction optimization



Entry	Conditions	Yield
1	NIS (1 eq.), CH_3CN (4 ml/mmol)	0%
2	NIS (1 eq.), HFIP (4 ml/mmol)	19%
3	ICl (1 eq.), CH_2Cl_2 (6 ml/mmol)	28%
4	ICl(1.1 eq.), $BnNEt_3^+Cl^-$(1.1 eq.), $CaCO_3$ (1.3 eq.), $MeOH/CH_2Cl_2$ (3/6 ml/mmol)	62%
5	ICl (1.1 eq.), $BnNEt_3^+Cl^-$ (1.1 eq.), $CaCO_3$ (3 eq.), $MeOH/CH_2Cl_2$ (3/6 ml/mmol)	67%
6	ICl (1.1 eq.), $BnNEt_3^+Cl^-$ (1.1 eq.), K_2CO_3 (3 eq.), $MeOH/CH_2Cl_2$ (3/6 ml/mmol)	51%
7	**ICl (1.1 eq.), $BnNEt_3^+Cl^-$ (1.1 eq.), $CaCO_3$ (4 eq.), $MeOH/CH_2Cl_2$ (3/6 ml/mmol)**	**70%**

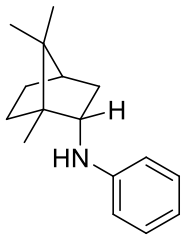
General procedure for N-bornylaniline synthesis (GP-1)



A mixtrure of aniline (1.1 eq), D-camphor (1 eq), $Si(OEt)_4$ (1.1 eq) and two drops of sulfuric acid were stirred with continuously removing ethanol by distillation under an inert atmosphere at 140 °C overnight. Reaction mixture was evaporated and the residue was passed through a pad of silica gel (ca. h = 2 cm, Φ = 4 cm). Purity of the resulting product was determined by ^{1}H NMR spectroscopy with internal standard (1,3,5-trimethoxybenzene) and was typically 60-70%. The products were use in next stage without further purification.

To a solution of $NaBH_4$ (2.5 eq) in THF (1 ml/mmol based on imine) was added solution of imine (1 eq) in THF (1M) at room temperature. The reaction mixture was cooled to 10 °C and BF_3•Et_2O (1.1 eq) was added dropwise. Reaction mixture was stirred at 15 °C for 0.5h and then refluxed overnight. Resulting solution was quenched with MeOH and concentrated, The residue was treated with H_2O (20 ml) and extracted with CH_2Cl_2 (3×20 ml). Organic layer was evaporated and resulting yellow oil was purified with column chromatography (PE/DCM) to afford the *endo*-isomer.

*(1S,2S,4R)-1,7,7-trimethyl-N-phenylbicyclo[2.2.1]heptan-2-amine (**1a**)*

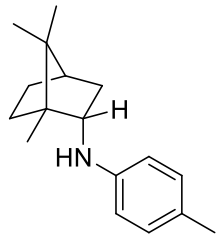


Following GP-1 (1S,2S,4R)-1,7,7-trimethyl-N-phenylbicyclo[2.2.1]heptan-2-amine was obtained as colorless oil (1.8 g, 62%). Rf = 0.21 (PE/CH_2Cl_2 = 10:1; for *exo*-isomer Rf = 0.32). NMR are in agreement with lit. data. [S1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3H), 0.92 (s, 3H), 0.99 (s, 3H), 1.20 – 1.28 (m, 1H), 1.35 – 1.47 (m, 1H), 1.68 – 1.82 (m, 3H), 2.35 – 2.49 (m, 1H), 3.45 (br. s, 1H), 3.60 (ddd, J = 10.1, 4.2, 1.9 Hz, 1H), 6.61 (d, J = 7.7 Hz, 2H), 6.67 (t, J = 7.3 Hz, 1H), 7.16 (dd, J = 8.5, 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 129.3, 117.0, 113.3, 58.5, 49.5, 48.3, 45.2, 38.9, 28.4, 28.0, 20.0, 18.9, 14.5.

*(1S,2S,4R)-1,7,7-trimethyl-N-p-tolylbicyclo[2.2.1]heptan-2-amine (**1b**)*



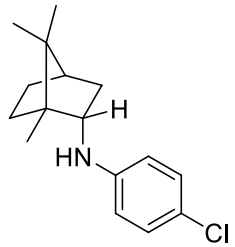
Following GP-1 (1S,2S,4R)-1,7,7-trimethyl-N-p-tolylbicyclo[2.2.1]heptan-2-amine was obtained as yellow oil (1.2 g, 60%). Rf = 0.15 (PE/CH_2Cl_2 = 10:1; for *exo*-isomer Rf = 0.23).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (s, 3H), 0.92 (s, 3H), 0.99 (s, 3H), 1.18 – 1.29 (m, 1H), 1.34 – 1.46 (m, 1H), 1.67 – 1.84 (m, 3H), 2.24 (s, 3H), 2.40 (dddd, J = 13.0, 10.1, 4.7, 3.0 Hz, 1H), 3.50 (br. s, 1H), 3.57 (ddd, J = 10.1, 4.1, 1.9 Hz, 1H), 6.54 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 129.8, 126.2, 113.4, 58.9, 49.5, 48.3, 45.2, 38.9, 28.4, 27.9, 20.5, 20.0, 18.9, 14.5.

IR (υ/cm^{-1}): 3413 (VW), 2982 (W), 2948 (M), 2872 (M), 1618 (M), 1518 (VS), 1472 (M), 1453 (M), 1388 (W), 1371 (W), 1313 (M), 1302 (M), 1253 (M), 1181 (W), 1140 (W), 1109 (W), 1071 (W), 1036 (W), 937 (W), 804 (S).

*(1S,2S,4R)-N-(4-chlorophenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (**1c**)*



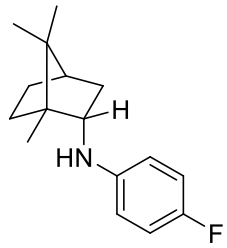
Following GP-1 (1S,2S,4R)-N-(4-chlorophenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine was obtained as yellow oil (1.53 g, 62%). Rf = 0.36 (PE/CH_2Cl_2 = 10:1; for *exo*-isomer Rf = 0.44).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 3H), 0.91 (s, 3H), 0.98 (s, 3H), 1.16 – 1.26 (m, 1H), 1.34 – 1.47 (m, 1H), 1.65 – 1.85 (m, 3H), 2.32 – 2.43 (m, 1H), 3.48 – 3.61 (m, 1H), 3.78 (br. s, 1H), 6.50 (d, J = 8.9 Hz, 2H), 7.08 (d, J = 8.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 129.1, 121.3, 114.2, 58.6, 49.6, 48.3, 45.1, 38.7, 28.4, 27.9, 20.0, 18.9, 14.5.

IR (υ/cm^{-1}): 3421 (VW), 2982 (W), 2950 (M), 2875 (W), 2362 (VW), 2337 (VW), 1857 (VW), 1597 (M), 1495 (VS), 1453 (M), 1397 (W), 1389 (M), 1371 (W), 1314 (S), 1293 (M), 1253 (M), 1175 (M), 1141 (W), 1089 (M), 1070 (M), 1035 (W), 1026 (W), 1002 (W), 937 (W), 920 (W), 811 (VS), 745 (W), 696 (W), 676 (M), 643 (M).

*(1S,2S,4R)-N-(4-fluorophenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (**1d**)*



Following GP-1 (1S,2S,4R)-N-(4-fluorophenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine was obtained as pale yellow oil (3.13 g, 61%). Rf = 0.18 (PE/CH_2Cl_2 = 10:1; for *exo*-isomer Rf = 0.30).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (s, 3H), 0.92 (s, 3H), 0.98 (s, 3H), 1.22 (ddd, J = 12.8, 9.6, 4.6 Hz, 1H), 1.34 – 1.47 (m, 1H), 1.68 – 1.83 (m, 3H), 2.34 – 2.43 (m, 1H), 3.52 (ddd, J = 10.0, 4.1, 1.9 Hz, 1H), 3.64 (br. s, 1H), 6.52 (dd, J = 9.0, 4.4 Hz, 2H), 6.86 (t, J = 8.8 Hz, 2H).

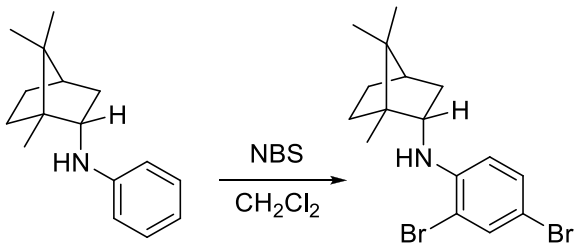
^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5, 18.9, 20.0, 27.9, 28.4, 38.8, 45.2, 48.3, 49.6, 59.2, 113.9 (d, J = 7.3 Hz), 115.7 (d, J = 22.2 Hz), 145.4 (d, J = 1.7 Hz), 155.6 (d, J = 234.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -128.9.

IR (υ/cm–1): 3417 (VW), 2982 (W), 2950 (M), 2875 (W), 1842 (VW), 1611 (W), 1507 (VS), 1475 (M), 1454 (M), 1389 (W), 1371 (W), 1313 (M), 1305 (M), 1281 (W), 1254 (W), 1219 (S), 1173 (W), 1155 (W), 1140 (W), 1113 (W), 1101 (W), 1070 (W), 1035 (W), 1026 (W), 994 (W), 979 (VW), 936 (W), 912 (W), 862 (W), 815 (S), 792 (M), 771 (M), 742 (W), 697 (W), 651 (W).

Bromination of 1a and 1a'

*(1S,2S,4R)-N-(2,4-dibromophenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (**2a**)*



The starting *endo-N*-bornylaniline was prepared according to GP-1. To a solution of *endo*-N-bornylaniline (459 mg, 2 mmol, 1 eq) in CH_2Cl_2 (6 ml) was added NBS (730 mg, 4.1 mmol, 2.05 eq) in one portion. Mixture was stirred for 30 min and purified by column chromatography (petroleum ether/CH_2Cl_2). Product was obtained as white solid (750 mg, 97%), m.p. (PE) 74-75 °C.

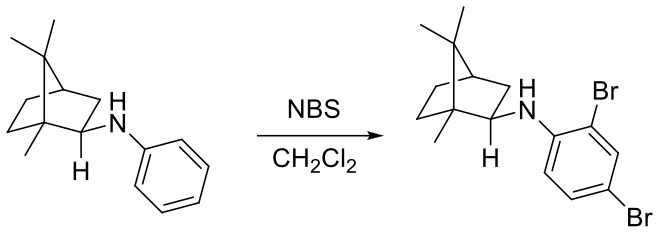
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3H), 0.93 (s, 3H), 0.98 (s, 3H), 1.20 – 1.31 (m, 1H), 1.40 – 1.51 (m, 1H), 1.70 – 1.86 (m, 3H), 2.40 (dddd, J = 12.9, 10.0, 4.6, 2.9 Hz, 1H), 3.51 – 3.60

(m, 1H), 4.55 (d, J = 6.1 Hz, 1H), 6.45 (d, J = 8.8 Hz, 1H), 7.21 (dd, J = 8.7, 2.3 Hz, 1H), 7.51 (d, J = 2.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 134.3, 131.3, 112.8, 110.2, 107.3, 58.5, 49.8, 48.3, 45.2, 38.5, 28.3, 28.2, 20.0, 18.9, 14.5.

IR (υ/cm–1): 3403 (W), 2987 (W), 2952 (S), 2941 (S), 2879 (M), 1589 (S), 1492 (VS), 1480 (VS), 1469 (S), 1453 (S), 1389 (S), 1364 (M), 1318 (S), 1264 (M), 1234 (M), 1225 (M), 1207 (W), 1173 (M), 1148 (M), 1113 (M), 1092 (M), 1074 (M), 1029 (M), 939 (W), 867 (S), 801 (VS), 707 (S), 634 (M).

(1S,2R,4R)-N-(2,4-dibromophenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine ***(2a')***



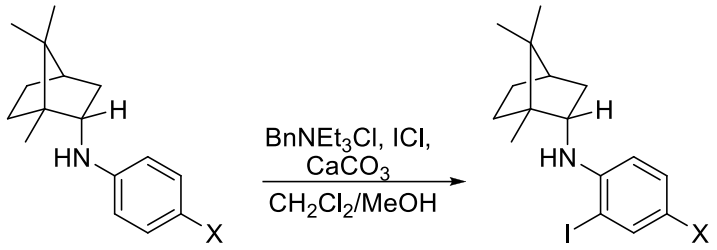
The starting *exo-N*-bornylaniline was prepared according to the reported procedure [S2]. To a solution of *exo*-N-isobornylaniline (459 mg, 2 mmol, 1 eq) in CH_2Cl_2 (6 ml) was added NBS (730 mg, 4.1 mmol, 2.05 eq) in one portion. Mixture was stirred for 30 min and purified by column chromatography (petroleum ether/CH_2Cl_2). Product was obtained as white solid (757 mg, 98%), m.p. (PE) 60-61 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 3H), 0.94 (s, 3H), 1.05 (s, 3H), 1.17 – 1.31 (m, 2H), 1.64 – 1.83 (m, 4H), 1.88 (dd, J = 12.9, 8.2 Hz, 1H), 3.20 – 3.33 (m, 1H), 4.54 (d, J = 5.9 Hz, 1H), 6.48 (d, J = 8.8 Hz, 1H), 7.21 (dd, J = 8.7, 2.2 Hz, 1H), 7.50 (d, J = 2.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 134.3, 131.2, 112.3, 109.9, 107.0, 61.4, 49.1, 47.4, 45.3, 40.4, 36.8, 27.5, 20.6, 20.5, 12.5.

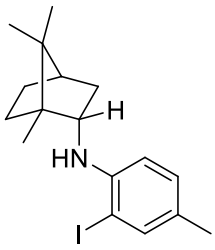
IR (υ/cm–1): 3440 (W), 2986 (W), 2948 (S), 2873 (M), 1586 (S), 1495 (S), 1460 (S), 1438 (M), 1388 (S), 1377 (M), 1330 (M), 1312 (M), 1306 (M), 1264 (M), 1234 (M), 1192 (M), 1164 (M), 1140 (W), 1114 (M), 1092 (M), 1079 (M), 1028 (M), 1021 (M), 942 (W), 868 (S), 802 (VS), 709 (S), 697 (M).

General procedure for 2-iodo-N-bornylaniline synthesis (GP-2)



To a solution of $BnEt_3NCl$ (1.1 eq) in CH_2Cl_2 (1.5 ml/mmol based on aniline) was added ICl (1.1 eq) solution in CH_2Cl_2 (1.5 ml/mmol based on aniline) at 15 °C in a dark. Resulting yellow solution was added dropwise to a suspension of aniline (1 eq) and $CaCO_3$ (4 eq) in CH_2Cl_2/MeOH (1/1, 6 ml/mmol). After stirring the resulting mixture in the dark for 24 h, mixture was diluted with CH_2Cl_2 and washed with saturated sodium hydrocarbonate solution. Organic layer was evaporated and the residue was purified by column chromatography (petroleum ether). S3

*(1S,2S,4R)-N-(2-iodo-4-methylphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (**2b**)*



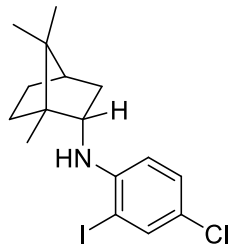
Following GP-2 (1S,2S,4R)-N-(2-iodo-4-methylphenyl)-1,7,7-trimethylbicyclo[2.2.1] heptan-2-amine was obtained as white solid (1.6 g, 70%), m.p. (PE) 70-71 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 3H), 0.93 (s, 3H), 0.98 (s, 3H), 1.27 (ddd, J = 12.2, 9.3, 4.6 Hz, 1H), 1.41 – 1.51 (m, 1H), 1.69 – 1.92 (m, 3H), 2.20 (s, 3H), 2.40 (tdd, J = 10.0, 4.7, 2.3 Hz, 1H), 3.50 – 3.63 (m, 1H), 4.26 (br. s, 1H), 6.42 (d, J = 8.3 Hz, 1H), 6.96 – 7.01 (m, 1H), 7.49 (d, J = 1.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 139.3, 130.1, 127.6, 111.2, 86.1, 59.2, 49.8, 48.2, 45.2, 38.7, 28.3, 28.3, 20.0, 19.9, 19.0, 14.5.

IR (υ/cm–1): 3380 (VW), 3027 (VW), 2982 (W), 2947 (S), 2928 (M), 2876 (M), 2165 (VW), 1854 (VW), 1605 (M), 1510 (VS), 1480 (M), 1452 (M), 1390 (M), 1375 (M), 1361 (M), 1314 (S), 1295 (M), 1274 (M), 1255 (M), 1233 (W), 1207 (W), 1172 (M), 1151 (W), 1138 (W), 1111 (M), 1094 (W), 1073 (M), 1028 (M), 993 (W), 938 (W), 869 (M), 795 (VS), 780 (M), 744 (W), 702 (M), 665 (M).

*(1S,2S,4R)-N-(4-chloro-2-iodophenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (**2c**)*



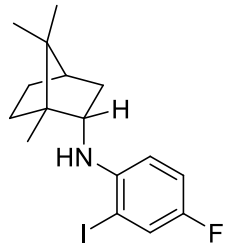
Following GP-2 (1S,2S,4R)-N-(4-chloro-2-iodophenyl)-1,7,7-trimethylbicyclo[2.2.1] heptan-2-amine was obtained as white solid (1.2 g, 83%), m.p. (PE) 117-118 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 3H), 0.93 (s, 3H), 0.98 (s, 3H), 1.26 (ddd, J = 12.1, 9.9, 4.6 Hz, 1H), 1.40 – 1.53 (m, 1H), 1.70 – 1.88 (m, 3H), 2.33 – 2.49 (m, 1H), 3.47 – 3.62 (m, 1H), 4.42 (d, J = 6.0 Hz, 1H), 6.40 (d, J = 8.8 Hz, 1H), 7.13 (dd, J = 8.7, 2.4 Hz, 1H), 7.60 (d, J = 2.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 137.8, 129.3, 121.2, 111.3, 85.2, 59.1, 49.8, 48.2, 45.1, 38.4, 28.3, 28.3, 20.0, 18.9, 14.5.

IR (υ/cm–1): 3400 (W), 2982 (M), 2952 (S), 2923 (M), 2881 (M), 2160 (W), 1853 (VW), 1719 (VW), 1583 (M), 1493 (VS), 1479 (S), 1453 (S), 1385 (S), 1358 (M), 1314 (S), 1299 (M), 1278 (M), 1263 (M), 1232 (W), 1222 (M), 1205 (M), 1173 (M), 1144 (M), 1114 (W), 1101 (M), 1077 (M), 1030 (M), 1019 (M), 937 (W), 862 (S), 794 (VS), 746 (W), 710 (S), 695 (M), 655 (M), 646 (M).

*(1S,2S,4R)-N-(4-fluoro-2-iodophenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (**2d**)*



Following GP-2 (1S,2S,4R)-N-(4-fluoro-2-iodophenyl)-1,7,7-trimethylbicyclo[2.2.1] heptan-2-amine was obtained as white solid (1.54 g, 51%), m.p. (PE) 82-83 ℃.

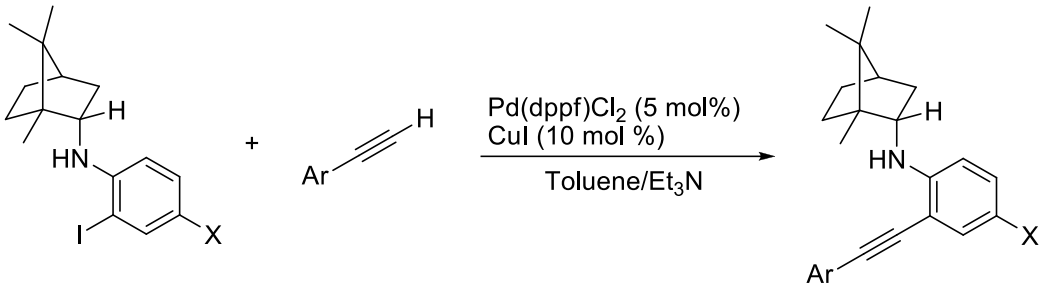
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 3H), 0.93 (s, 3H), 0.98 (s, 3H), 1.23 – 1.33 (m, 1H), 1.40 – 1.52 (m, 1H), 1.69 – 1.94 (m, 3H), 2.39 (dddd, J = 13.0, 9.9, 4.7, 3.2 Hz, 1H), 3.52 (d, J = 1.7 Hz, 1H), 4.22 (d, J = 5.5 Hz, 1H), 6.42 (dd, J = 9.0, 4.9 Hz, 1H), 6.89 – 6.96 (m, 1H), 7.40 (dd, J = 7.9, 2.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5, 19.0, 20.0, 28.3, 28.3, 38.5, 45.2, 48.2, 49.8, 59.6, 84.3 (d, J = 8.7 Hz), 110.8 (d, J = 7.3 Hz), 116.0 (d, J = 21.7 Hz), 125.4 (d, J = 24.6 Hz), 144.8 (d, J = 1.8 Hz), 154.4 (d, J = 238.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -128.0.

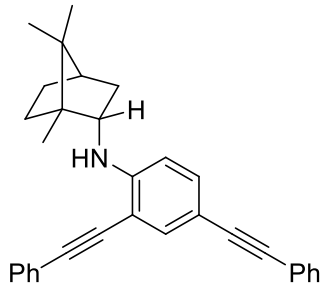
IR (υ/cm–1): 3390 (W), 2979 (W), 2952 (M), 2928 (M), 2876 (W), 1827 (VW), 1593 (W), 1579 (VW), 1502 (VS), 1476 (S), 1458 (M), 1414 (W), 1390 (M), 1360 (W), 1316 (M), 1301 (M), 1283 (W), 1267 (M), 1226 (M), 1209 (W), 1185 (S), 1140 (M), 1112 (W), 1095 (W), 1077 (W), 1037 (W), 1022 (W), 993 (W), 980 (W), 958 (W), 936 (W), 887 (W), 863 (VS), 832 (M), 796 (VS), 782 (S), 741 (W), 717 (W), 696 (W), 683 (W), 663 (M), 653 (W).

General procedure for Sonogashira coupling (GP-3)



To a Schlenk tube were added corresponding iodoaniline (0.6 mmol, 1 eq), $Pd(dppf)Cl_2$ (22 mg, 0.03 mmol, 5 mol%) and CuI (12 mg, 0.06 mmol, 10 mol%) and the mixture was evacuated and refilled with Ar for 3 times. To the mixture was added toluene (2.4 ml), corresponding alkyne (0.72 mmol, 1.2 eq) and Et_3N (0.6 ml). The mixture was immediately placed in an oil bath, previously heated to 100 °C. After stirring for 16h the mixture was evaporated and purified with column chromatography (PE/CH_2Cl_2).

(1S,2S,4R)-N-(2,4-bis(phenylethynyl)phenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine ***(4aa)***



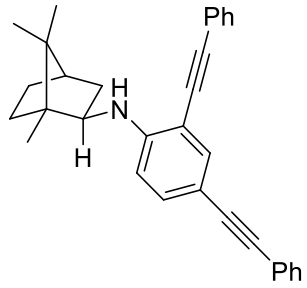
Following GP-3 (from dibromoaniline 2a with 2.4 eq of phenylacetylene) (1S,2S,4R)-N-(2,4-bis(phenylethynyl)phenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine was obtained as yellow oil (194 mg, 76%).

^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (s, 6H), 1.02 (s, 3H), 1.25 – 1.33 (m, 1H), 1.44 – 1.55 (m, 1H), 1.65 – 1.99 (m, 3H), 2.34 – 2.59 (m, 1H), 3.59 – 3.88 (m, 1H), 5.22 (d, J = 6.8 Hz, 1H), 6.55 (d, J = 8.6 Hz, 1H), 7.27 – 7.41 (m, 7H), 7.45 – 7.55 (m, 4H), 7.57 (d, J = 2.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 135.2, 133.6, 131.4, 131.4, 128.7, 128.4, 128.4, 127.7, 124.1, 123.3, 110.0, 110.0, 107.6, 95.7, 90.1, 87.3, 85.5, 57.9, 50.0, 48.3, 45.2, 38.7, 28.4, 28.2, 20.0, 18.9, 14.5.

IR (υ/cm^{-1}): 3404 (VW), 2949 (M), 2875 (W), 1950 (VW), 1877 (VW), 1606 (M), 1593 (S), 1564 (W), 1515 (S), 1489 (M), 1442 (M), 1414 (W), 1389 (W), 1374 (W), 1338 (M), 1319 (M), 1296 (W), 1262 (M), 1224 (W), 1173 (W), 1155 (M), 1136 (W), 1112 (W), 1069 (M), 1026 (W), 910 (W), 893 (W), 809 (M), 751 (VS), 687 (VS).

(1S,2R,4R)-N-(2,4-bis(phenylethynyl)phenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine ***(4aa')***



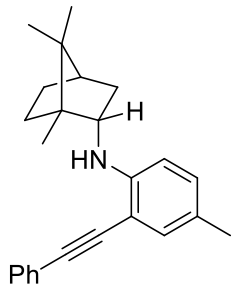
Following GP-3 (from dibromoaniline 2a' with 2.4 eq of phenylacetylene) (1S,2R,4R)-N-(2,4-bis(phenylethynyl)phenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine was obtained as yellow oil (131 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 2.0 Hz, 1H), 7.52 – 7.45 (m, 4H), 7.42 – 7.27 (m, 7H), 6.57 (d, J = 8.7 Hz, 1H), 5.18 (d, J = 7.3 Hz, 1H), 3.50 – 3.34 (m, 1H), 1.94 (dd, J = 12.6, 8.3 Hz, 1H), 1.85 – 1.72 (m, 3H), 1.67 (td, J = 12.0, 4.0 Hz, 1H), 1.36 – 1.17 (m, 3H), 1.10 (s, 3H), 0.98 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 135.4, 133.6, 131.4, 131.4, 128.6, 128.4, 127.7, 124.2, 123.3, 109.8, 109.5, 107.4, 95.4, 90.1, 87.3, 85.5, 60.8, 49.1, 47.4, 45.3, 40.6, 36.8, 27.5, 20.7, 20.6, 12.5.

IR (υ/cm^{-1}): 3420 (W), 3057 (VW), 2951 (M), 2929 (W), 2874 (W), 1953 (VW), 1877 (VW), 1741 (VW), 1673 (VW), 1605 (M), 1592 (S), 1565 (W), 1515 (S), 1489 (M), 1442 (M), 1413 (W), 1388 (M), 1376 (W), 1337 (M), 1306 (M), 1291 (W), 1262 (M), 1212 (W), 1193 (M), 1154 (M), 1116 (W), 1078 (W), 1069 (W), 1026 (M), 909 (M), 893 (M), 809 (M), 752 (VS), 733 (M), 688 (VS).

(1S,2S,4R)-1,7,7-trimethyl-N-(4-methyl-2-(phenylethynyl)phenyl)bicyclo[2.2.1]heptan-2-amine ***(4ba)***



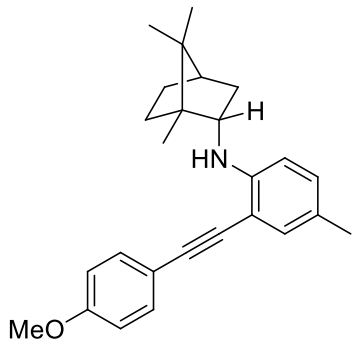
Following GP-3 (1S,2S,4R)-1,7,7-trimethyl-N-(4-methyl-2-(phenylethynyl) phenyl)bicyclo[2.2.1]heptan-2-amine was obtained as orange oil (196 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 – 0.97 (m, 6H), 1.01 (s, 3H), 1.29 (ddd, J = 12.2, 9.3, 4.6 Hz, 1H), 1.43 – 1.54 (m, 1H), 1.71 – 1.86 (m, 2H), 1.91 (ddd, J = 13.3, 9.3, 4.1 Hz, 1H), 2.24 (s, 3H), 2.39 – 2.49 (m, 1H), 3.60 – 3.74 (m, 1H), 4.86 (d, J = 6.6 Hz, 1H), 6.52 (d, J = 8.4 Hz, 1H), 7.01 (dd, J = 8.4, 1.8 Hz, 1H), 7.28 – 7.43 (m, 3H), 7.44 – 7.60 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 132.2, 131.3, 130.9, 128.6, 128.1, 125.0, 123.7, 110.5, 107.5, 95.1, 86.7, 58.4, 49.8, 48.2, 45.3, 38.9, 28.4, 28.1, 20.3, 20.0, 19.0, 14.5.

IR (υ/cm^{-1}): 3407 (W), 3021 (W), 2981 (W), 2949 (M), 2874 (M), 2197 (W), 1613 (W), 1598 (W), 1576 (W), 1511 (S), 1490 (M), 1455 (M), 1442 (M), 1413 (W), 1389 (W), 1373 (W), 1361 (W), 1319 (M), 1271 (M), 1224 (W), 1205 (W), 1173 (W), 1153 (M), 1139 (W), 1111 (W), 1069 (M), 1025 (M), 935 (W), 909 (W), 879 (W), 801 (S), 753 (VS), 688 (VS).

*(1S,2S,4R)-N-(2-((4-methoxyphenyl)ethynyl)-4-methylphenyl)-1,7,7-trimethylbicyclo [2.2.1]heptan-2-amine (**4bb**)*



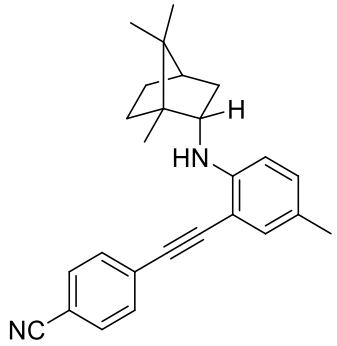
Following GP-3 (1S,2S,4R)-N-(2-((4-methoxyphenyl)ethynyl)-4-methylphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine was obtained as yellow oil (170 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 – 0.95 (m, 6H), 1.00 (s, 3H), 1.22 – 1.31 (m, 1H), 1.46 (td, J = 11.8, 3.8 Hz, 1H), 1.70 – 1.83 (m, 2H), 1.89 (ddd, J = 13.2, 9.4, 4.0 Hz, 1H), 2.22 (s, 3H), 2.37 – 2.47 (m, 1H), 3.64 (d, J = 7.4 Hz, 1H), 3.84 (s, 3H), 4.82 (br. s, 1H), 6.51 (d, J = 8.3 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.3 Hz, 1H), 7.14 – 7.19 (m, 1H), 7.44 (d, J = 8.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 147.5, 134.2, 132.8, 132.0, 130.5, 125.1, 115.9, 114.2, 110.5, 95.0, 85.2, 58.5, 55.5, 49.8, 48.2, 45.3, 38.9, 28.4, 28.1, 20.3, 20.0, 19.0, 14.5.

IR (υ/cm^{-1}): 3406 (VW), 2981 (W), 2949 (M), 2874 (W), 2835 (W), 1604 (M), 1576 (W), 1567 (W), 1507 (VS), 1462 (M), 1440 (M), 1415 (W), 1389 (W), 1373 (W), 1319 (M), 1303 (M), 1286 (M), 1277 (M), 1246 (VS), 1207 (W), 1171 (S), 1153 (W), 1105 (W), 1071 (W), 1031 (S), 935 (W), 879 (W), 829 (S), 802 (S), 739 (W), 667 (W), 643 (W).

*4-((5-methyl-2-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylamino)phenyl) ethynyl)benzonitrile (**4bc**)*



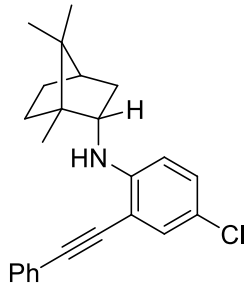
Following GP-3 4-((5-methyl-2-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylamino)phenyl)ethynyl)benzonitrile was obtained as pale yellow solid (219 mg, 99%), m.p. (PE) 192-193 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 3H), 0.94 (s, 3H), 1.00 (s, 3H), 1.22 – 1.31 (m, 1H), 1.49 (td, J = 12.6, 11.2, 3.9 Hz, 1H), 1.75 (t, J = 4.4 Hz, 1H), 1.82 (tq, J = 10.8, 6.7, 5.4 Hz, 2H), 2.23 (s, 3H), 2.43 (ddd, J = 13.1, 8.1, 5.0 Hz, 1H), 3.65 (d, J = 10.8 Hz, 1H), 4.77 (br. s, 1H), 6.52 (d, J = 8.4 Hz, 1H), 7.03 (dd, J = 8.4, 1.7 Hz, 1H), 7.18 (d, J = 1.8 Hz, 1H), 7.54 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 132.4, 132.3, 132.0, 131.6, 128.7, 125.3, 118.7, 111.1, 110.8, 106.2, 93.7, 91.7, 58.3, 49.8, 48.3, 45.2, 38.9, 28.4, 28.2, 20.3, 20.0, 18.9, 14.5.

IR (υ/cm^{-1}): 3384 (VW), 2948 (M), 2928 (M), 2875 (W), 2224 (M), 2196 (S), 1614 (W), 1600 (S), 1578 (M), 1513 (S), 1504 (S), 1483 (M), 1456 (M), 1405 (M), 1388 (W), 1373 (M), 1317 (M), 1302 (M), 1278 (M), 1170 (M), 1156 (M), 1139 (M), 1114 (M), 1101 (M), 1069 (M), 1037 (W), 1024 (W), 997 (W), 977 (W), 908 (W), 875 (M), 842 (S), 821 (S), 798 (S), 728 (M).

*(1S,2S,4R)-N-(4-chloro-2-(phenylethynyl)phenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (**4ca**)*



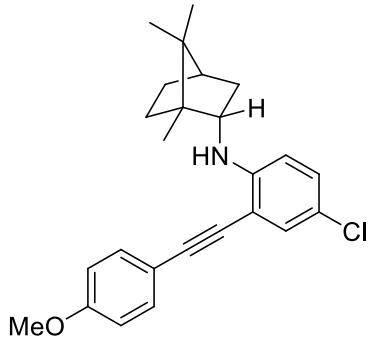
Following GP-3 (1S,2S,4R)-N-(4-chloro-2-(phenylethynyl)phenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine was obtained as yellow oil (214 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 3H), 0.93 (s, 3H), 1.00 (s, 3H), 1.27 (ddd, J = 12.0, 10.0, 4.7 Hz, 1H), 1.42 – 1.53 (m, 1H), 1.70 – 1.92 (m, 3H), 2.37 – 2.50 (m, 1H), 3.56 – 3.71 (m, 1H), 4.97 (d, J = 6.6 Hz, 1H), 6.49 (d, J = 8.9 Hz, 1H), 7.11 (dd, J = 8.8, 2.5 Hz, 1H), 7.31 (d, J = 2.5 Hz, 1H), 7.34 – 7.44 (m, 3H), 7.44 – 7.56 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 131.4, 131.1, 129.9, 128.7, 128.6, 123.1, 120.1, 111.3, 108.8, 96.3, 85.2, 58.2, 49.9, 48.3, 45.2, 38.7, 28.4, 28.1, 20.0, 18.9, 14.5.

IR (υ/cm^{-1}): 3413 (W), 3065 (VW), 2984 (W), 2943 (M), 2875 (W), 1592 (M), 1566 (M), 1504 (S), 1480 (M), 1440 (M), 1413 (M), 1390 (M), 1375 (W), 1360 (W), 1329 (M), 1321 (M), 1298 (M), 1260 (S), 1223 (W), 1205 (W), 1173 (M), 1156 (M), 1139 (M), 1112 (M), 1069 (M), 1025 (W), 936 (W), 909 (W), 899 (M), 874 (M), 838 (W), 806 (M), 799 (S), 752 (VS), 725 (M), 687 (VS), 661 (M), 649 (M), 623 (M).

*(1S,2S,4R)-N-(4-chloro-2-((4-methoxyphenyl)ethynyl)phenyl)-1,7,7-trimethylbicyclo [2.2.1]heptan-2-amine (**4cb**)*



Following GP-3 (1S,2S,4R)-N-(4-chloro-2-((4-methoxyphenyl)ethynyl)phenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine was obtained as pale yellow oil (234 mg, 99%).

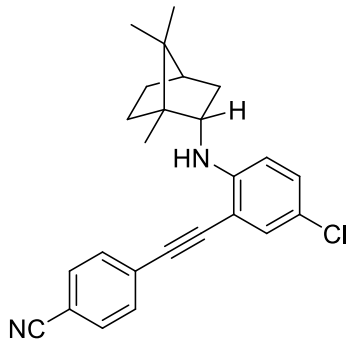
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 3H), 0.93 (s, 3H), 1.00 (s, 3H), 1.22 – 1.30 (m, 1H), 1.42 – 1.52 (m, 1H), 1.69 – 1.89 (m, 3H), 2.36 – 2.49 (m, 1H), 3.56 – 3.67 (m, 1H), 3.84 (s, 3H),

4.95 (d, J = 6.2 Hz, 1H), 6.48 (d, J = 8.8 Hz, 1H), 6.90 (d, J = 8.9 Hz, 2H), 7.09 (dd, J = 8.8, 2.5 Hz, 1H), 7.29 (d, J = 2.5 Hz, 1H), 7.44 (d, J = 8.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 148.1, 132.9, 130.9, 129.5, 120.1, 115.2, 114.3, 109.3, 96.3, 83.8, 58.2, 55.5, 49.9, 48.3, 45.2, 38.7, 28.4, 28.1, 20.0, 18.9, 14.5.

IR (υ/cm^{-1}): 3406 (W), 2981 (W), 2950 (M), 2876 (W), 2836 (W), 1605 (M), 1595 (M), 1569 (M), 1510 (VS), 1482 (M), 1463 (M), 1441 (M), 1410 (M), 1389 (W), 1374 (W), 1362 (W), 1320 (M), 1302 (M), 1286 (S), 1247 (VS), 1172 (S), 1152 (W), 1106 (M), 1070 (W), 1031 (M), 901 (M), 877 (M), 829 (S), 802 (S), 732 (M), 691 (W), 648 (M), 642 (M).

*4-((5-chloro-2-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylamino)phenyl) ethynyl)benzonitrile (**4cc**)*



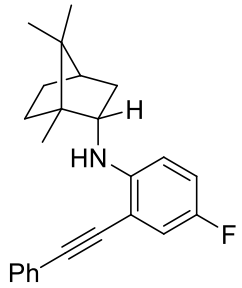
Following GP-3 4-((5-chloro-2-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylamino)phenyl)ethynyl)benzonitrile was obtained as pale yellow solid (228 mg, 98%), m.p. (PE) 235-236 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 3H), 0.94 (s, 3H), 1.00 (s, 3H), 1.25 (ddd, J = 14.7, 9.8, 4.7 Hz, 1H), 1.45 – 1.54 (m, 1H), 1.70 – 1.90 (m, 3H), 2.43 (dddd, J = 13.1, 10.1, 6.2, 3.3 Hz, 1H), 3.53 – 3.71 (m, 1H), 4.89 (d, J = 6.2 Hz, 1H), 6.51 (d, J = 8.9 Hz, 1H), 7.14 (dd, J = 8.9, 2.5 Hz, 1H), 7.31 (d, J = 2.5 Hz, 1H), 7.55 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 132.4, 131.8, 131.4, 131.0, 128.0, 120.3, 118.6, 111.7, 111.6, 107.5, 94.6, 89.9, 58.2, 49.9, 48.3, 45.2, 38.6, 28.4, 28.2, 19.9, 18.9, 14.5.

IR (υ/cm^{-1}): 3400 (W), 2978 (W), 2952 (M), 2869 (W), 2223 (M), 2193 (M), 1598 (M), 1570 (M), 1507 (S), 1479 (M), 1446 (W), 1415 (M), 1405 (M), 1389 (M), 1372 (M), 1330 (M), 1303 (M), 1273 (M), 1261 (M), 1225 (W), 1173 (W), 1153 (M), 1143 (M), 1112 (M), 1102 (M), 1070 (M), 1012 (W), 950 (W), 938 (W), 899 (M), 872 (M), 842 (S), 825 (S), 795 (S), 733 (M), 675 (M), 651 (W), 639 (W).

*(1S,2S,4R)-N-(4-fluoro-2-(phenylethynyl)phenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (**4da**)*



Following GP-3 (1S,2S,4R)-N-(4-fluoro-2-(phenylethynyl)phenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine was obtained as yellow oil (206 mg, 99%).

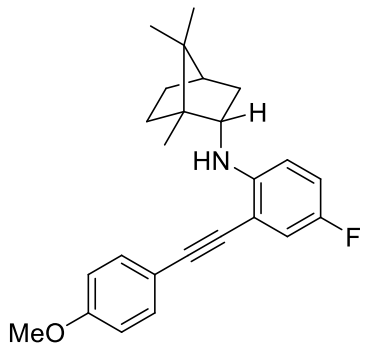
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 – 0.94 (m, 6H), 1.00 (s, 3H), 1.23 – 1.33 (m, 1H), 1.42 – 1.53 (m, 1H), 1.64 – 1.99 (m, 3H), 2.42 (dddd, J = 13.1, 10.0, 4.7, 3.2 Hz, 1H), 3.48 – 3.75 (m, 1H), 4.82 (d, J = 4.4 Hz, 1H), 6.50 (dd, J = 9.1, 4.6 Hz, 1H), 6.91 (td, J = 8.7, 3.0 Hz, 1H), 7.08 (dd, J = 8.9, 3.0 Hz, 1H), 7.37 (dq, J = 8.4, 2.8, 2.2 Hz, 3H), 7.46 – 7.57 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5, 18.9, 20.0, 28.1, 28.4, 38.8, 45.3, 48.3, 49.8, 58.7, 85.5 (d, J = 3.1 Hz), 96.0, 108.0 (d, J = 9.1 Hz), 111.0 (d, J = 7.8 Hz), 117.0 (d, J = 22.2 Hz), 117.8 (d, J = 23.6 Hz), 123.2, 128.5, 128.7, 131.4, 146.5 (d, J = 1.2 Hz), 154.2 (d, J = 233.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -129.6

IR (υ/cm^{-1}): 3408 (VW), 2982 (W), 2950 (M), 2875 (W), 1611 (VW), 1597 (VW), 1585 (W), 1510 (S), 1490 (M), 1482 (M), 1458 (M), 1443 (M), 1422 (M), 1389 (W), 1374 (W), 1362 (W), 1328 (W), 1303 (M), 1260 (M), 1224 (W), 1190 (M), 1140 (M), 1111 (W), 1069 (M), 1026 (W), 998 (VW), 954 (M), 911 (W), 866 (M), 846 (W), 801 (M), 776 (M), 753 (VS), 687 (VS), 655 (W).

*(1S,2S,4R)-N-(4-fluoro-2-((4-methoxyphenyl)ethynyl)phenyl)-1,7,7-trimethylbicyclo [2.2.1]heptan-2-amine (**4db**)*



Following GP-3 (1S,2S,4R)-N-(4-fluoro-2-((4-methoxyphenyl)ethynyl)phenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine was obtained as yellow oil (222 mg, 98%).

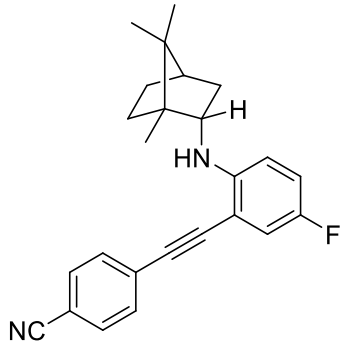
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 3H), 0.93 (s, 3H), 0.99 (s, 3H), 1.23 – 1.31 (m, 1H), 1.42 – 1.52 (m, 1H), 1.70 – 1.95 (m, 3H), 2.34 – 2.52 (m, 1H), 3.53 – 3.65 (m, 1H), 3.84 (s, 3H), 4.80 (br. s, 1H), 6.48 (dd, J = 9.0, 4.7 Hz, 1H), 6.82 – 6.95 (m, 3H), 7.05 (dd, J = 9.0, 3.0 Hz, 1H), 7.45 (d, J = 8.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5, 18.9, 20.0, 28.1, 28.4, 38.8, 45.3, 48.2, 49.8, 55.5, 58.7, 84.2 (d, J = 3.1 Hz), 96.0, 108.5 (d, J = 9.1 Hz), 110.9 (d, J = 7.8 Hz), 114.3, 115.2, 116.6 (d, J = 22.3 Hz), 117.6 (d, J = 23.6 Hz), 132.9, 146.3 (d, J = 1.2 Hz), 154.2 (d, J = 233.8 Hz), 159.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -129.7.

IR (υ/cm^{-1}): 3406 (W), 2981 (W), 2950 (M), 2875 (W), 2836 (W), 1603 (M), 1568 (W), 1509 (VS), 1481 (M), 1462 (M), 1441 (M), 1423 (M), 1389 (W), 1373 (W), 1362 (W), 1329 (W), 1303 (M), 1287 (M), 1247 (VS), 1204 (M), 1186 (M), 1171 (S), 1140 (M), 1106 (M), 1081 (W), 1069 (W), 1031 (M), 953 (M), 866 (M), 829 (S), 801 (S), 757 (W), 741 (M), 662 (W), 643 (W).

*4-((5-fluoro-2-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylamino)phenyl) ethynyl)benzonitrile (**4dc**)*



Following GP-3 4-((5-fluoro-2-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylamino)phenyl)ethynyl)benzonitrile was obtained as yellow solid (214 mg, 96%), m.p. (PE) 181-182 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 3H), 0.94 (s, 3H), 1.00 (s, 3H), 1.21 – 1.30 (m, 1H), 1.44 – 1.55 (m, 1H), 1.71 – 1.89 (m, 3H), 2.37 – 2.48 (m, 1H), 3.53 – 3.71 (m, 1H), 4.74 (d, J = 6.5 Hz, 1H), 6.51 (dd, J = 9.1, 4.6 Hz, 1H),6.95 (td, J = 8.7, 3.0 Hz, 1H), 7.06 (dd, J = 8.7, 3.0 Hz, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H).

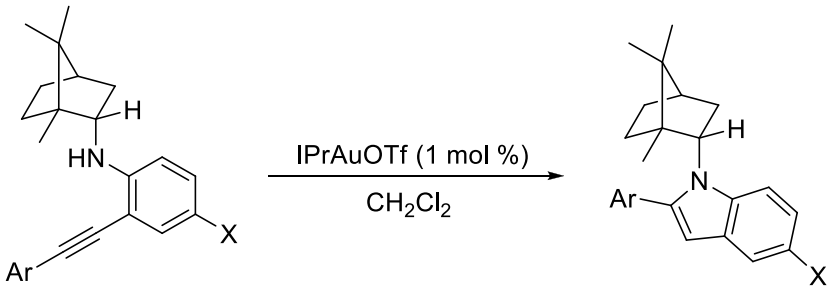
^{13}C NMR (101 MHz, $CDCl_3$) δ 14.5, 18.9, 19.9, 28.2, 28.4, 38.8, 45.2, 48.3, 49.9, 58.6, 90.18 (d, J = 3.1 Hz), 94.3, 106.6 (d, J = 9.0 Hz), 111.4 (d, J = 7.7 Hz), 111.7, 118.0 (d, J = 13.1 Hz), 118.2 (d, J = 11.9 Hz), 118.6, 128.0, 131.8, 132.4, 146.8 (d, J = 1.1 Hz), 154.1 (d, J = 234.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -129.2.

IR (υ/cm^{-1}): 3399 (VW), 2979 (W), 2953 (M), 2879 (W), 2224 (M), 2195 (M), 1599 (M), 1582 (W), 1517 (S), 1483 (S), 1441 (M), 1427 (M), 1405 (M), 1387 (M), 1374 (M), 1331 (W),

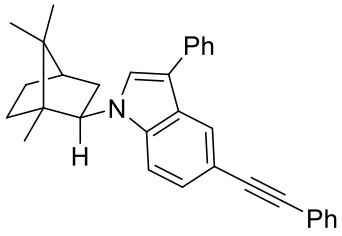
1304 (M), 1295 (M), 1271 (M), 1259 (S), 1227 (M), 1204 (M), 1188 (M), 1170 (S), 1145 (M), 1129 (M), 1113 (M), 1102 (M), 1068 (M), 1037 (W), 1018 (W), 979 (W), 951 (M), 861 (S), 843 (VS), 825 (S), 795 (VS), 759 (M), 728 (M), 717 (M).

General procedure for Au-catalyzed cyclization (GP-4)



To a screw-capped vial were added 2-ethynyl-N-bornylaniline (0.25 mmol, 1 eq), IPrAuOTf (1.8 mg, 2.5 μmol, 1 mol%) and CH_2Cl_2 (1 ml). The resulting solution was stirred for 16h and passed through a thin pad of silica gel (ca. h = 2 cm, Φ = 4 cm). Evaporation of the solvent afforded the corresponding indoles.

*3-phenyl-5-(phenylethynyl)-1-((1S,2R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole (**5aa'**)*



Following GP-4 2-phenyl-5-(phenylethynyl)-1-((1S,2R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole was obtained as white solid (106 mg, 99%), m.p. ($CHCl_3$) 148-149 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.37 (s, 3H), 0.76 (s, 3H), 0.83 (s, 3H), 0.85 – 0.93 (m, 2H), 1.20 – 1.35 (m, 2H), 1.37 – 1.47 (m, 1H), 1.69 – 1.82 (m, 2H), 1.90 (dd, J = 12.3, 9.5 Hz, 1H), 2.76 – 3.09 (m, 1H), 5.02 (t, J = 9.1 Hz, 1H), 6.45 (s, 1H), 7.28 – 7.50 (m, 9H), 7.57 (dd, J = 8.1, 1.5 Hz, 2H), 7.63 (d, J = 8.7 Hz, 1H), 7.81 (d, J = 1.5 Hz, 1H).

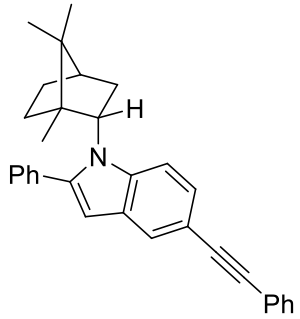
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 138.9, 135.4, 131.6, 130.6, 128.7, 128.4, 127.9, 127.9, 127.8, 124.6, 124.3, 124.2, 113.9, 113.9, 106.7, 91.1, 87.4, 66.2, 52.9, 46.3, 45.1, 37.5, 34.7, 26.7, 21.5, 21.4, 12.0.

IR (υ/cm^{-1}): 3067 (VW), 3024 (VW), 2985 (W), 2955 (M), 2939 (W), 2879 (W), 2208 (W), 2160 (W), 1597 (W), 1494 (W), 1486 (W), 1460 (S), 1443 (M), 1390 (W), 1377 (W), 1337

(M), 1322 (M), 1296 (M), 1273 (M), 1264 (M), 1236 (W), 1193 (W), 1172 (W), 1159 (W), 1125 (W), 1112 (W), 1083 (W), 1072 (W), 1020 (W), 886 (M), 837 (W), 805 (S), 784 (M), 759 (VS), 749 (S), 707 (S), 692 (S), 668 (M), 623 (M), 611 (M).

APPI-HRMS (m/z): calc. for $(C_{32}H_{31}N)^+$ $[M]^+$ 429.2451; found: 429.2449.

*2-phenyl-5-(phenylethynyl)-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole (**5aa**)*



Following GP-4 2-phenyl-5-(phenylethynyl)-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole was obtained as white solid (107 mg, 99%), m.p. ($CHCl_3$) 85-86 °C.

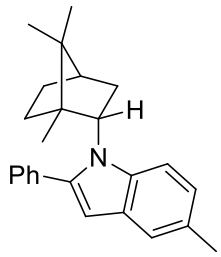
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.33 (s, 3H), 0.73 (s, 3H), 0.81 (s, 3H), 1.29 – 1.35 (m, 1H), 1.74 – 1.84 (m, 1H), 1.86 – 2.03 (m, 3H), 2.24 – 2.37 (m, 1H), 2.51 (dd, J = 13.7, 6.5 Hz, 1H), 5.04 (ddd, J = 12.3, 6.5, 2.5 Hz, 1H), 6.50 (s, 1H), 7.28 – 7.49 (m, 9H), 7.57 (dd, J = 8.1, 1.5 Hz, 2H), 7.83 (d, J = 1.5 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 137.3, 134.5, 131.6, 130.4, 129.0, 128.4, 128.3, 128.1, 127.8, 124.6, 124.5, 124.2, 113.9, 112.7, 103.9, 91.2, 87.3, 61.4, 53.0, 48.0, 45.5, 30.0, 29.5, 28.6, 19.9, 18.4, 13.9.

IR (υ/cm^{-1}): 2951 (M), 2887 (W), 1596 (W), 1487 (M), 1460 (M), 1447 (M), 1389 (W), 1368 (W), 1339 (M), 1318 (M), 1295 (M), 1266 (M), 1219 (W), 1195 (W), 1170 (M), 1120 (W), 1106 (M), 1071 (W), 1027 (W), 951 (W), 925 (W), 909 (W), 876 (M), 795 (S), 754 (VS), 701 (S), 689 (VS), 666 (M).

APPI-HRMS (m/z): calc. for $(C_{32}H_{31}N)^+$ $[M]^+$ 429.2451; found: 429.2453.

*5-methyl-2-phenyl-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole (**5ba**)*



Following GP-4 5-methyl-2-phenyl-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole was obtained as white solid (85 mg, 99%), m.p. ($CHCl_3$) 132-133 °C.

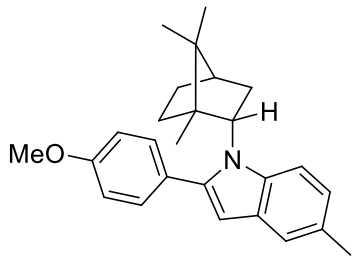
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.32 (s, 3H), 0.73 (s, 3H), 0.80 (s, 3H), 1.26 – 1.33 (m, 2H), 1.85 – 1.95 (m, 2H), 1.97 – 2.10 (m, 1H), 2.22 – 2.34 (m, 1H), 2.47 (s, 3H), 2.53 (dd, J = 13.6, 6.5 Hz, 1H), 5.01 (ddd, J = 12.2, 6.5, 2.5 Hz, 1H), 6.43 (s, 1H), 7.01 (dd, J = 8.6, 1.6 Hz, 1H), 7.29 – 7.59 (m, 6H), 7.81 (d, J = 8.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 135.9, 135.1, 130.5, 129.3, 128.6, 128.2, 127.8, 122.6, 120.3, 112.4, 103.1, 61.1, 52.9, 47.9, 45.5, 30.1, 29.5, 28.6, 21.3, 19.9, 18.4, 13.9.

IR (υ/cm^{-1}): 3116 (VW), 3018 (W), 2988 (W), 2953 (M), 2933 (M), 2890 (W), 2869 (W), 2855 (W), 1550 (VW), 1484 (W), 1463 (M), 1448 (M), 1390 (W), 1352 (M), 1336 (M), 1312 (S), 1300 (M), 1216 (W), 1199 (W), 1169 (M), 1117 (M), 1104 (W), 1074 (W), 1034 (W), 1001 (W), 970 (W), 941 (W), 924 (W), 908 (W), 865 (M), 784 (VS), 761 (S), 736 (M), 702 (VS), 674 (M), 629 (M), 594 (M).

APPI-HRMS (m/z): calc. for $(C_{25}H_{29}N)^+$ $[M]^+$ 343.2295; found: 343.2295.

*2-(4-methoxyphenyl)-5-methyl-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole (**5bb**)*



Following GP-4 2-(4-methoxyphenyl)-5-methyl-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole was obtained as white solid (93 mg, 99%), m.p. ($CHCl_3$) 159-160 °C.

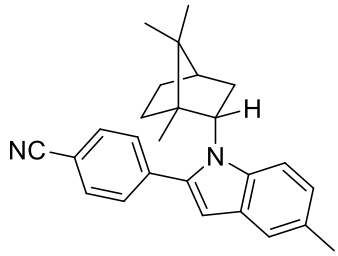
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.35 (s, 3H), 0.77 (s, 3H), 0.82 (s, 3H), 1.23 – 1.41 (m, 2H), 1.74 – 1.94 (m, 3H), 1.97 – 2.10 (m, 1H), 2.21 – 2.32 (m, 1H), 2.47 (s, 3H), 2.52 (dd, J = 13.6, 6.5 Hz, 1H), 3.88 (s, 3H), 5.00 (ddd, J = 12.2, 6.4, 2.3 Hz, 1H), 6.38 (s, 1H), 6.89 – 7.07 (m, 3H), 7.30 (d, J = 8.6 Hz, 2H), 7.40 (s, 1H), 7.80 (d, J = 8.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 144.0, 135.8, 131.6, 129.3, 128.5, 127.4, 122.4, 120.2, 113.6, 112.3, 102.9, 61.0, 55.4, 52.9, 47.9, 45.5, 30.1, 29.4, 28.6, 21.3, 20.0, 18.5, 14.0.

IR (υ/cm^{-1}): 2997 (W), 2954 (W), 2948 (M), 2883 (W), 2838 (W), 1613 (W), 1578 (VW), 1555 (W), 1503 (M), 1490 (W), 1473 (M), 1460 (M), 1442 (M), 1389 (W), 1371 (W), 1350 (M), 1339 (W), 1298 (M), 1286 (M), 1243 (S), 1200 (W), 1168 (M), 1116 (W), 1106 (M), 1080 (W), 1054 (W), 1036 (M), 1004 (W), 933 (W), 929 (W), 907 (W), 864 (M), 830 (S), 785 (VS), 743 (M), 730 (M), 702 (W), 684 (M), 649 (W), 605 (M), 591 (M).

APPI-HRMS (m/z): calc. for $(C_{26}H_{31}NO)^+$ $[M]^+$ 373.2400; found: 373.2404.

*4-(5-methyl-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indol-2-yl)benzonitrile (**5bc**)*



Following GP-4 4-(5-methyl-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indol-2-yl)benzonitrile was obtained as yellow solid (91 mg, 99%), m.p. ($CHCl_3$) 213-214 °C.

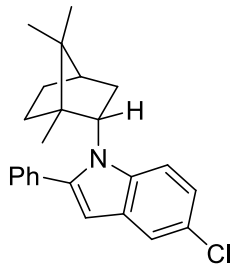
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, 3H), 0.75 (s, 3H), 0.81 (s, 3H), 1.22 – 1.32 (m, 1H), 1.71 – 2.02 (m, 4H), 2.26 – 2.38 (m, 1H), 2.45 (s, 3H), 2.55 (dd, J = 13.7, 6.5 Hz, 1H), 4.88 (ddd, J = 12.2, 6.4, 2.4 Hz, 1H), 6.46 (s, 1H), 7.04 (dd, J = 8.7, 1.6 Hz, 1H), 7.41 (s, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 139.9, 136.6, 132.1, 130.7, 129.2, 129.2, 123.6, 120.7, 118.9, 112.6, 111.3, 104.6, 61.7, 53.2, 48.0, 45.4, 29.9, 29.5, 28.5, 21.3, 19.8, 18.4, 13.9.

IR (υ/cm^{-1}): 3037 (VW), 3018 (VW), 2984 (W), 2947 (M), 2919 (W), 2885 (W), 2869 (W), 2855 (W), 1597 (W), 1489 (W), 1472 (W), 1447 (M), 1404 (M), 1389 (W), 1369 (W), 1354 (M), 1340 (M), 1310 (M), 1303 (M), 1268 (W), 1197 (M), 1168 (M), 1142 (W), 1117 (M), 1104 (W), 1079 (W), 1053 (W), 1017 (W), 941 (W), 906 (W), 875 (W), 848 (S), 806 (VS), 788 (VS), 747 (W), 732 (W), 702 (M), 680 (W), 647 (W).

APPI-HRMS (m/z): calc. for $(C_{26}H_{28}N_2)^+$ $[M]^+$ 368.2247; found: 368.2251.

*5-chloro-2-phenyl-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole (**5ca**)*



Following GP-4 5-chloro-2-phenyl-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole was obtained as white solid (90 mg, 99%), m.p. ($CHCl_3$) 162-163 °C.

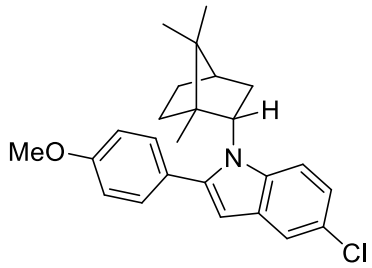
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.31 (s, 3H), 0.72 (s, 3H), 0.80 (s, 3H), 1.26 – 1.36 (m, 1H), 1.61 – 2.05 (m, 4H), 2.29 (t, J = 13.0 Hz, 1H), 2.45 (dd, J = 13.7, 6.5 Hz, 1H), 5.02 (ddd, J = 12.0, 6.4, 2.1 Hz, 1H), 6.44 (s, 1H), 7.12 (dd, J = 8.9, 1.9 Hz, 1H), 7.29 – 7.53 (m, 5H), 7.57 (d, J = 1.9 Hz, 1H), 7.81 (d, J = 9.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 136.0, 134.4, 130.4, 130.2, 128.3, 128.1, 125.1, 121.1, 119.9, 113.7, 103.2, 61.3, 53.0, 48.0, 45.5, 30.1, 29.5, 28.6, 19.9, 18.3, 13.9.

IR (υ/cm^{-1}): 2989 (W), 2954 (M), 2934 (M), 2889 (W), 2869 (W), 1603 (W), 1566 (W), 1485 (W), 1473 (W), 1456 (M), 1443 (M), 1424 (M), 1389 (W), 1351 (M), 1337 (M), 1309 (M), 1299 (M), 1279 (W), 1173 (W), 1164 (M), 1155 (W), 1116 (M), 1073 (M), 1034 (W), 969 (W), 927 (W), 912 (M), 907 (M), 858 (S), 835 (W), 787 (VS), 762 (VS), 735 (M), 701 (VS), 663 (M), 645 (W), 627 (M), 614 (M), 592 (M).

APPI-HRMS (m/z): calc. for $(C_{24}H_{26}ClN)^+$ $[M]^+$ 363.1748; found: 363.1747.

*5-chloro-2-(4-methoxyphenyl)-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole (**5cb**)*



Following GP-4 5-chloro-2-(4-methoxyphenyl)-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole was obtained as white solid (99 mg, 99%), m.p. ($CHCl_3$) 156-157 °C.

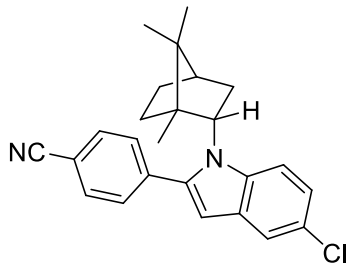
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.33 (s, 3H), 0.75 (s, 3H), 0.80 (s, 3H), 1.24 – 1.33 (m, 1H), 1.68 – 1.81 (m, 1H), 1.83 – 2.05 (m, 3H), 2.21 – 2.34 (m, 1H), 2.43 (dd, J = 13.7, 6.5 Hz, 1H), 3.87 (s, 3H), 5.00 (ddd, J = 12.2, 6.5, 2.4 Hz, 1H), 6.39 (s, 1H), 6.96 (d, J = 8.7 Hz, 2H), 7.09 (dd, J = 9.0, 2.2 Hz, 1H), 7.25 – 7.30 (m, 2H), 7.54 (d, J = 2.1 Hz, 1H), 7.79 (d, J = 9.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 145.3, 135.8, 131.6, 130.2, 126.7, 125.0, 120.9, 119.7, 113.7, 113.6, 103.0, 61.2, 55.5, 52.9, 48.0, 45.5, 30.1, 29.5, 28.6, 19.9, 18.4, 13.9.

IR (υ/cm^{-1}): 2990 (W), 2952 (W), 2943 (W), 2890 (W), 2865 (VW), 1613 (W), 1574 (W), 1552 (W), 1491 (M), 1444 (M), 1390 (W), 1346 (W), 1336 (M), 1309 (M), 1300 (M), 1246 (M), 1196 (W), 1176 (M), 1166 (M), 1150 (W), 1115 (M), 1068 (W), 1027 (M), 916 (M), 870 (W), 831 (S), 786 (VS), 735 (M).

APPI-HRMS (m/z): calc. for $(C_{25}H_{28}ClNO)^+$ $[M]^+$ 393.1854; found: 393.1856.

*4-(5-chloro-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indol-2-yl)benzonitrile (**5cc**)*



Following GP-4 4-(5-chloro-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indol-2-yl)benzonitrile was obtained as white solid (97 mg, 99%), m.p. ($CHCl_3$) 198-199 °C.

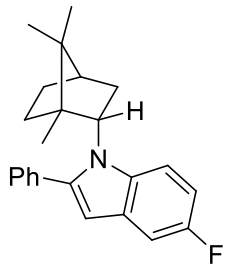
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.27 (s, 3H), 0.74 (s, 3H), 0.81 (s, 3H), 1.19 – 1.35 (m, 1H), 1.64 – 1.79 (m, 1H), 1.80 – 2.05 (m, 3H), 2.24 – 2.40 (m, 1H), 2.47 (dd, J = 13.8, 6.5 Hz, 1H), 4.88 (ddd, J = 12.1, 6.4, 2.4 Hz, 1H), 6.47 (s, 1H), 7.15 (dd, J = 9.0, 2.2 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 2.2 Hz, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 9.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 139.2, 136.5, 132.2, 130.8, 129.9, 125.6, 122.1, 120.3, 118.7, 113.9, 111.8, 104.5, 61.9, 53.2, 48.1, 45.4, 29.8, 29.6, 28.5, 19.8, 18.3, 13.9.

IR (υ/cm^{-1}): 2985 (W), 2964 (W), 2947 (M), 2920 (W), 2886 (W), 2227 (M), 1608 (M), 1489 (W), 1473 (W), 1455 (M), 1443 (S), 1428 (W), 1403 (W), 1371 (W), 1351 (M), 1340 (M), 1307 (M), 1284 (W), 1216 (VW), 1200 (W), 1171 (M), 1152 (W), 1116 (W), 1078 (W), 1017 (W), 918 (M), 906 (W), 869 (W), 844 (S), 801 (VS), 790 (VS), 735 (M), 687 (W), 669 (M), 643 (W), 631 (W).

APPI-HRMS (m/z): calc. for $(C_{25}H_{25}ClN_2)^+$ $[M]^+$ 388.1701; found: 388.1702.

*5-fluoro-2-phenyl-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole (**5da**)*



Following GP-4 5-fluoro-2-phenyl-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole was obtained as yellow solid (86 mg, 99%), m.p. ($CHCl_3$) 92-93 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.32 (s, 3H), 0.73 (s, 3H), 0.81 (s, 3H), 1.26 – 1.37 (m, 1H), 1.74 (d, J = 11.7 Hz, 1H), 1.83 – 2.04 (m, 3H), 2.30 (ddd, J = 13.2, 8.7, 3.7 Hz, 1H), 2.47 (dd, J = 13.7, 6.5 Hz, 1H), 5.03 (ddd, J = 12.1, 6.5, 2.3 Hz, 1H), 6.46 (s, 1H), 6.92 (td, J = 9.1, 2.6 Hz, 1H), 7.25 (dd, J = 9.4, 1.3 Hz, 1H), 7.31 – 7.52 (m, 5H), 7.82 (dd, J = 9.1, 4.3 Hz, 1H).

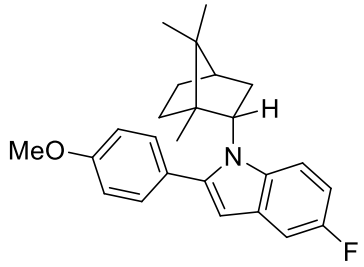
^{13}C NMR (101 MHz, $CDCl_3$) δ 13.9, 18.3, 19.9, 28.6, 29.6, 30.1, 45.5, 48.0, 52.9, 61.3, 103.5 (d, J = 4.4 Hz), 105.1 (d, J = 22.6 Hz), 109.2 (d, J = 25.6 Hz), 113.3 (d, J = 9.3 Hz), 128.1, 128.3, 129.5 (d, J = 9.8 Hz), 130.4, 134.2, 134.6, 145.7, 157.6 (d, J = 235.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -125.6.

IR (υ/cm^{-1}): 3058 (VW), 3040 (VW), 3025 (VW), 3000 (VW), 2981 (W), 2962 (W), 2948 (M), 2925 (W), 2889 (W), 1616 (W), 1580 (W), 1543 (VW), 1490 (W), 1474 (M), 1462 (M), 1446 (M), 1426 (M), 1391 (W), 1375 (W), 1355 (M), 1342 (M), 1312 (M), 1287 (W), 1275 (W), 1260 (W), 1223 (VW), 1194 (M), 1152 (M), 1123 (M), 1102 (M), 1073 (W), 1029 (M), 956 (M), 918 (W), 867 (S), 840 (W), 800 (M), 784 (S), 762 (VS), 736 (M), 701 (VS), 674 (M), 633 (S), 602 (M).

APPI-HRMS (m/z): calc. for $(C_{24}H_{26}FN)^+$ $[M]^+$ 347.2044; found: 347.2048.

*5-fluoro-2-(4-methoxyphenyl)-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole (**5db**)*



Following GP-4 5-fluoro-2-(4-methoxyphenyl)-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indole was obtained as white solid (95 mg, 99%), m.p. ($CHCl_3$) 142-143 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.34 (s, 3H), 0.75 (s, 3H), 0.81 (s, 3H), 1.20 – 1.38 (m, 1H), 1.65 – 1.82 (m, 1H), 1.83 – 2.06 (m, 3H), 2.20 – 2.35 (m, 1H), 2.45 (dd, J = 13.7, 6.5 Hz, 1H), 3.87 (s, 3H), 5.00 (ddd, J = 12.2, 6.4, 2.3 Hz, 1H), 6.40 (s, 1H), 6.90 (td, J = 9.1, 2.6 Hz, 1H), 6.96 (d, J = 8.6 Hz, 2H), 7.22 (dd, J = 9.3, 2.6 Hz, 1H), 7.26 – 7.32 (m, 2H), 7.79 (dd, J = 9.1, 4.3 Hz, 1H).

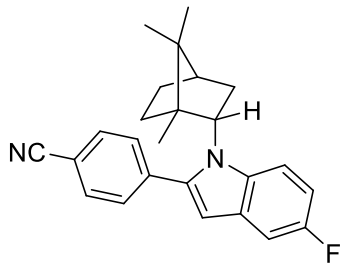
^{13}C NMR (101 MHz, $CDCl_3$) δ 14.0, 18.4, 19.9, 28.6, 29.5, 30.1, 45.5, 48.0, 52.9, 55.5, 61.2, 103.3 (d, J = 4.5 Hz), 104.9 (d, J = 22.6 Hz), 109.0 (d, J = 25.7 Hz), 113.2 (d, J = 9.2 Hz), 113.7, 126.9, 129.4 (d, J = 9.9 Hz), 131.6, 134.0, 145.6, 157.6 (d, J = 234.8 Hz), 159.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -125.8.

IR (υ/cm^{-1}): 2994 (W), 2976 (W), 2952 (M), 2887 (W), 2838 (W), 1614 (M), 1585 (W), 1574 (W), 1553 (W), 1505 (W), 1488 (M), 1461 (M), 1445 (S), 1390 (W), 1369 (W), 1358 (M), 1345 (M), 1315 (W), 1302 (M), 1290 (M), 1253 (S), 1202 (M), 1195 (M), 1173 (S), 1152 (M), 1138 (M), 1120 (M), 1105 (M), 1078 (W), 1036 (S), 1009 (W), 956 (M), 937 (W), 907 (W), 874 (W), 861 (M), 856 (M), 829 (S), 789 (S), 779 (VS), 738 (M), 728 (M), 700 (W), 684 (M), 653 (M).

APPI-HRMS (m/z): calc. for $(C_{25}H_{28}FNO)^+$ $[M]^+$ 377.2149; found: 377.2140.

*4-(5-fluoro-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indol-2-yl)benzonitrile (**5dc**)*



Following GP-4 with using equimolar mixture of IPrAuCl (1.6 mg, 1 mol%) and $AgNTf_2$ (1 mg, 1 mol%) instead of IPrAuOTf 4-(5-fluoro-1-((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-1H-indol-2-yl)benzonitrile was obtained as white solid (92 mg, 99%), m.p. ($CHCl_3$) 270-271 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, 3H), 0.74 (s, 3H), 0.81 (s, 3H), 1.24 – 1.31 (m, 1H), 1.68 – 1.79 (m, 1H), 1.81 – 2.02 (m, 3H), 2.22 – 2.40 (m, 1H), 2.49 (dd, J = 13.8, 6.5 Hz, 1H), 4.88 (ddd, J = 12.1, 6.4, 2.4 Hz, 1H), 6.49 (s, 1H), 6.95 (td, J = 9.1, 2.7 Hz, 1H), 7.21 – 7.28 (m, 1H), 7.48 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.84 (dd, J = 9.2, 4.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 104.9 (d, J = 4.6 Hz), 105.5 (d, J = 22.7 Hz), 110.3 (d, J = 25.7 Hz), 111.7, 113.6 (d, J = 9.2 Hz), 118.7, 129.3 (d, J = 10.0 Hz), 130.8, 132.1, 134.8, 139.4, 143.3, 157.7 (d, J = 236.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -124.7.

IR (υ/cm^{-1}): 2978 (W), 2957 (W), 2939 (W), 2887 (W), 2229 (M), 1610 (W), 1579 (W), 1488 (W), 1468 (M), 1458 (W), 1446 (S), 1404 (W), 1389 (W), 1358 (M), 1347 (M), 1311 (W), 1273 (W), 1205 (M), 1196 (M), 1181 (M), 1152 (M), 1123 (W), 1102 (M), 1077 (W), 1016 (W), 957 (M), 866 (M), 852 (S), 786 (VS), 762 (M), 736 (W), 705 (W), 684 (M), 648 (M).

APPI-HRMS (m/z): calc. for $(C_{25}H_{25}FN_2)^+$ $[M]^+$ 372.1996; found: 372.1999.

References

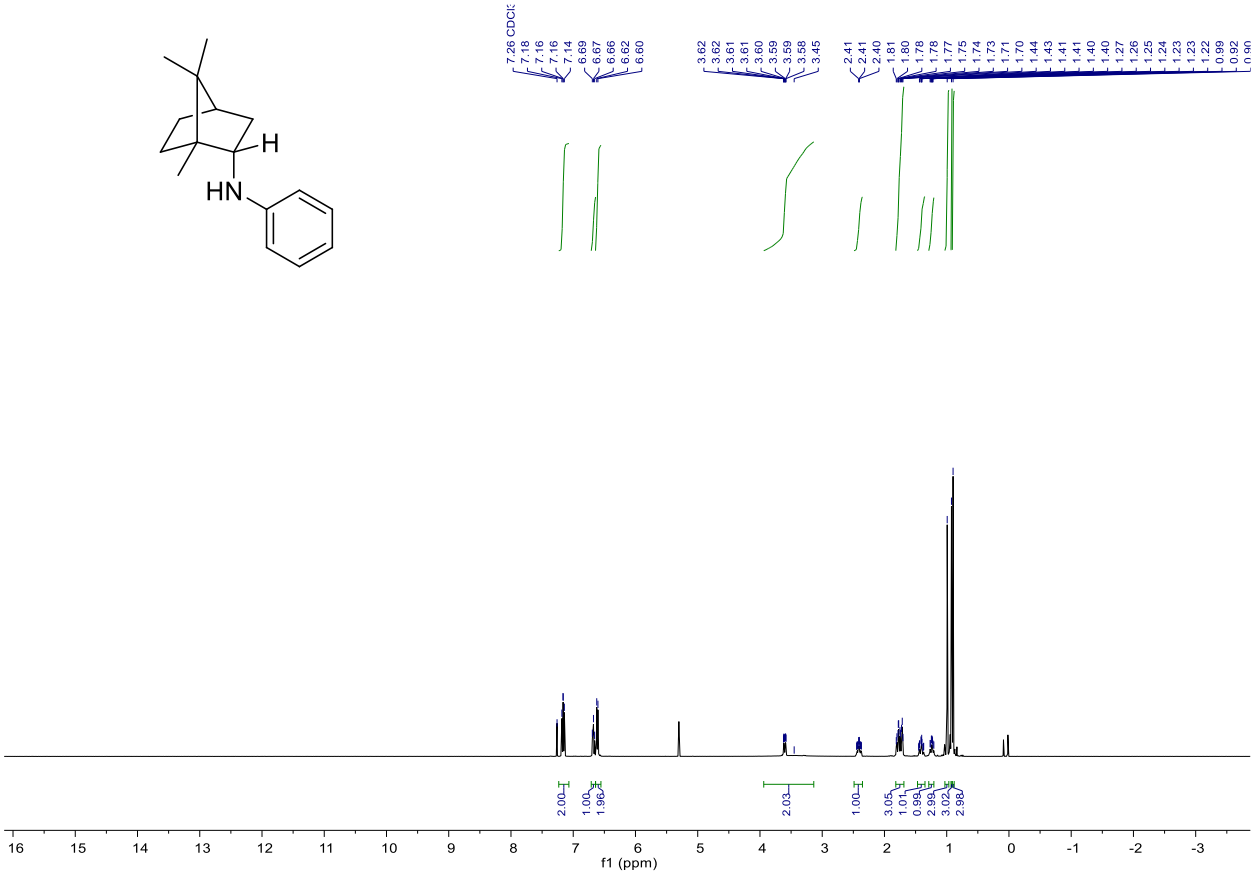
S1. A. H. Vetter and A. Berkessel, *Synthesis*, 1995, **1995**, 419-422.

S2. I. Y. Chukicheva, O. A. Shumova, O. G. Shevchenko and A. V. Kutchin, *Russian Chemical Bulletin*, 2024, **73**, 580-587.

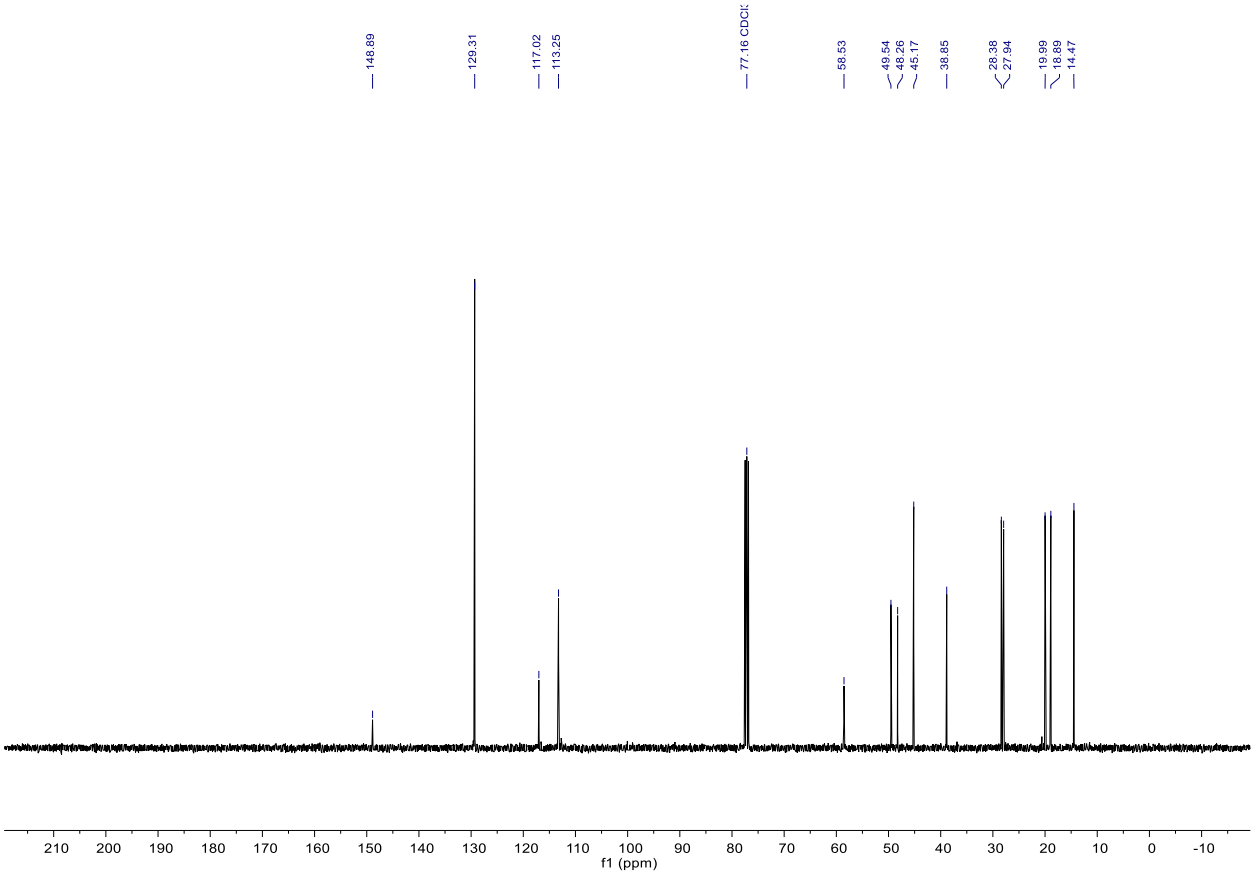
S3. M. Petit, A. J. B. Lapierre and D. P. Curran, *Journal of the American Chemical Society*, 2005, **127**, 14994-14995.

NMR spectra pictures

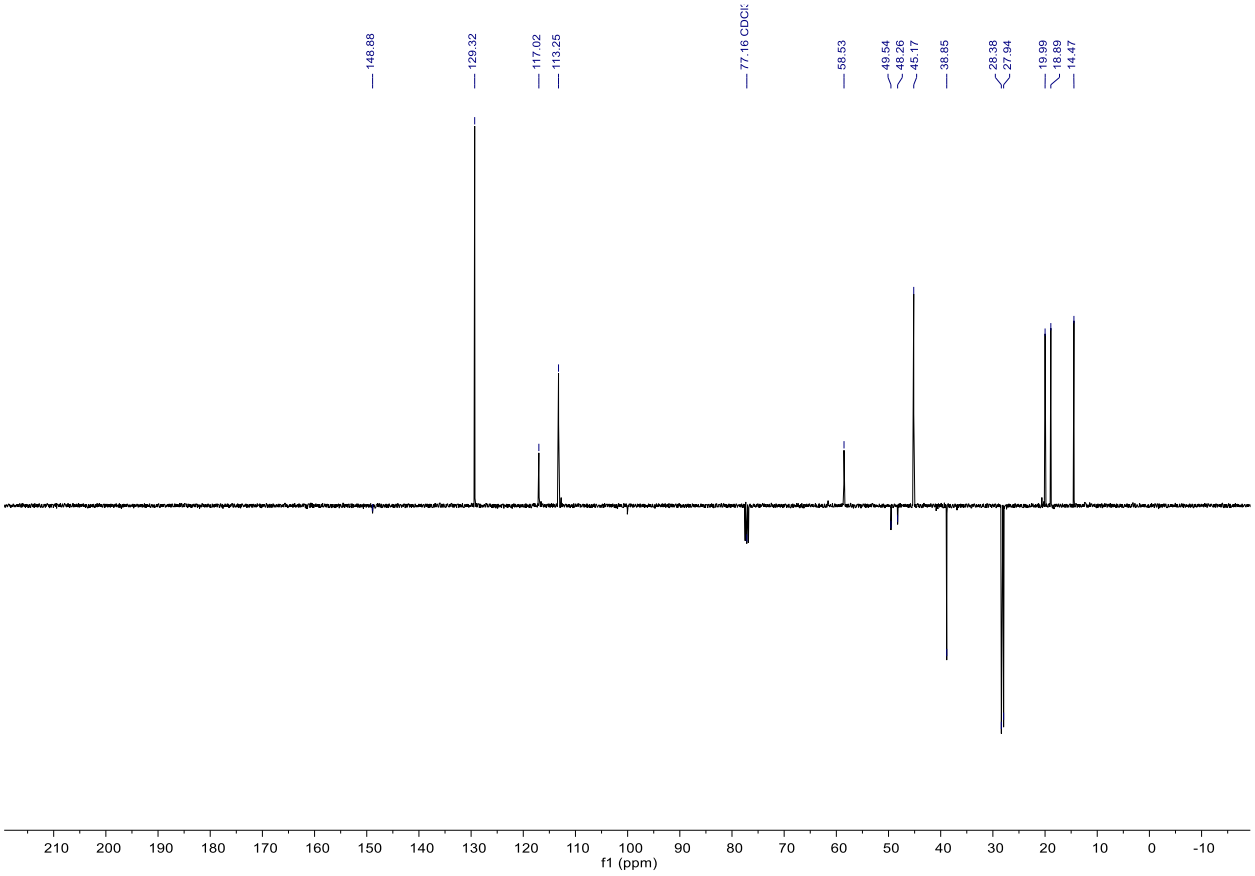
^{1}H NMR Spectrum of Compound 1a (400 MHz, CDCl3)



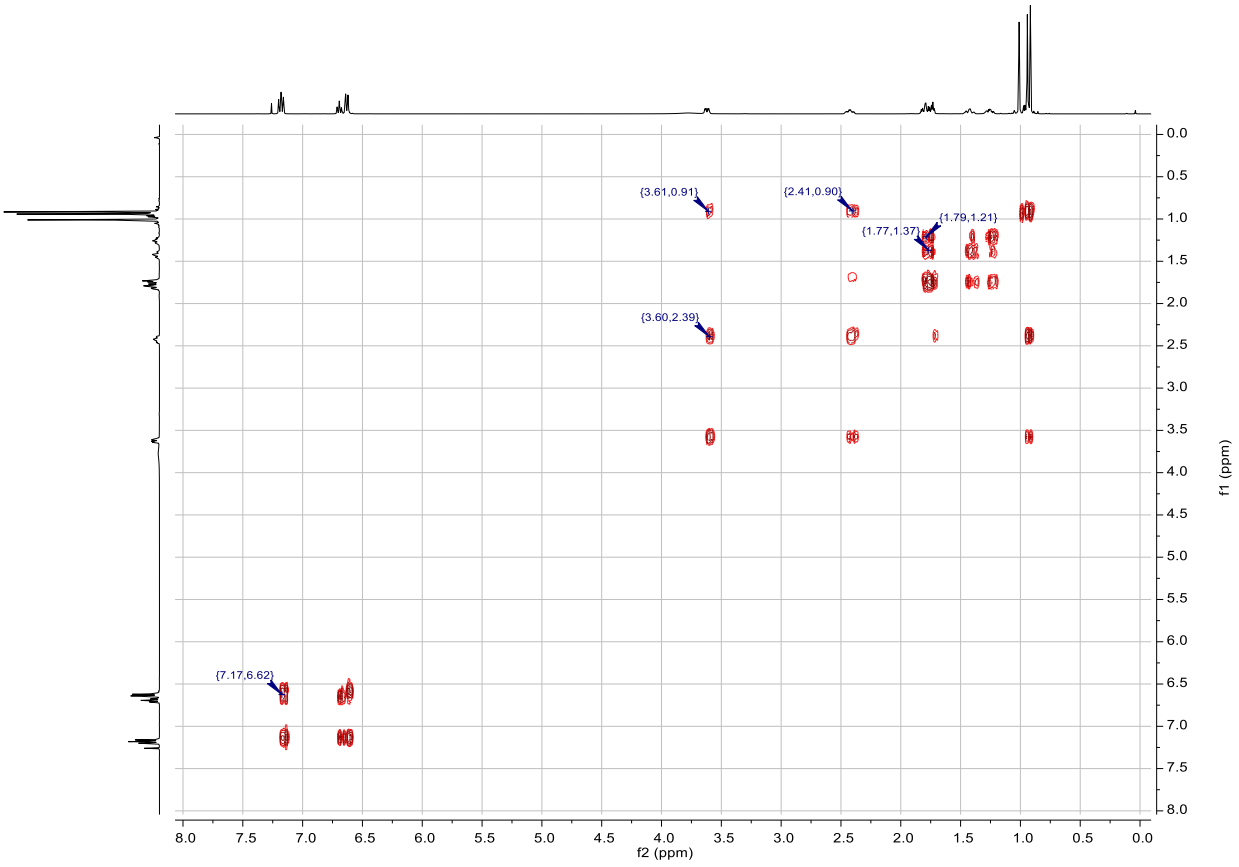
^{13}C NMR Spectrum of Compound 1a (101 MHz, $CDCl_3$)



^{13}C DEPTQ-135 NMR Spectrum of Compound 1a



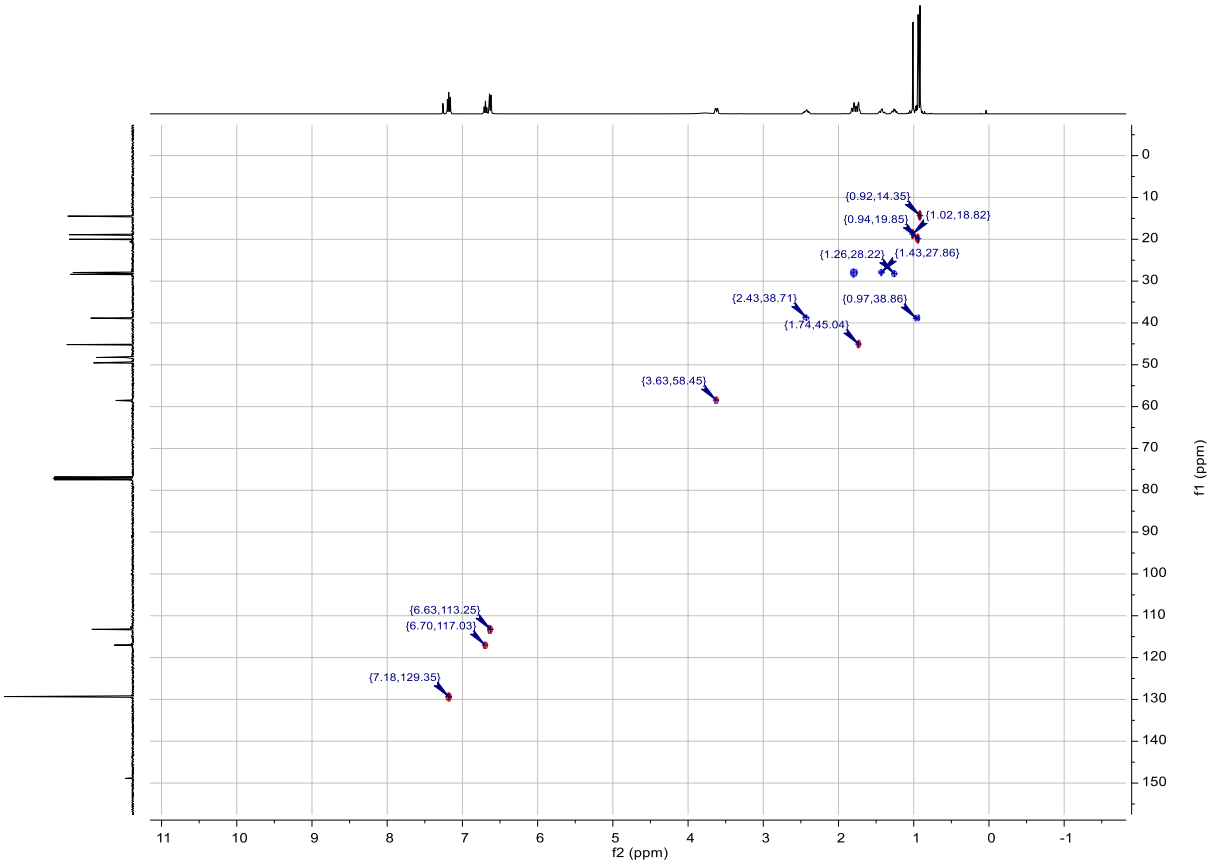
1H-1H COSY NMR Spectrum of Compound 1a



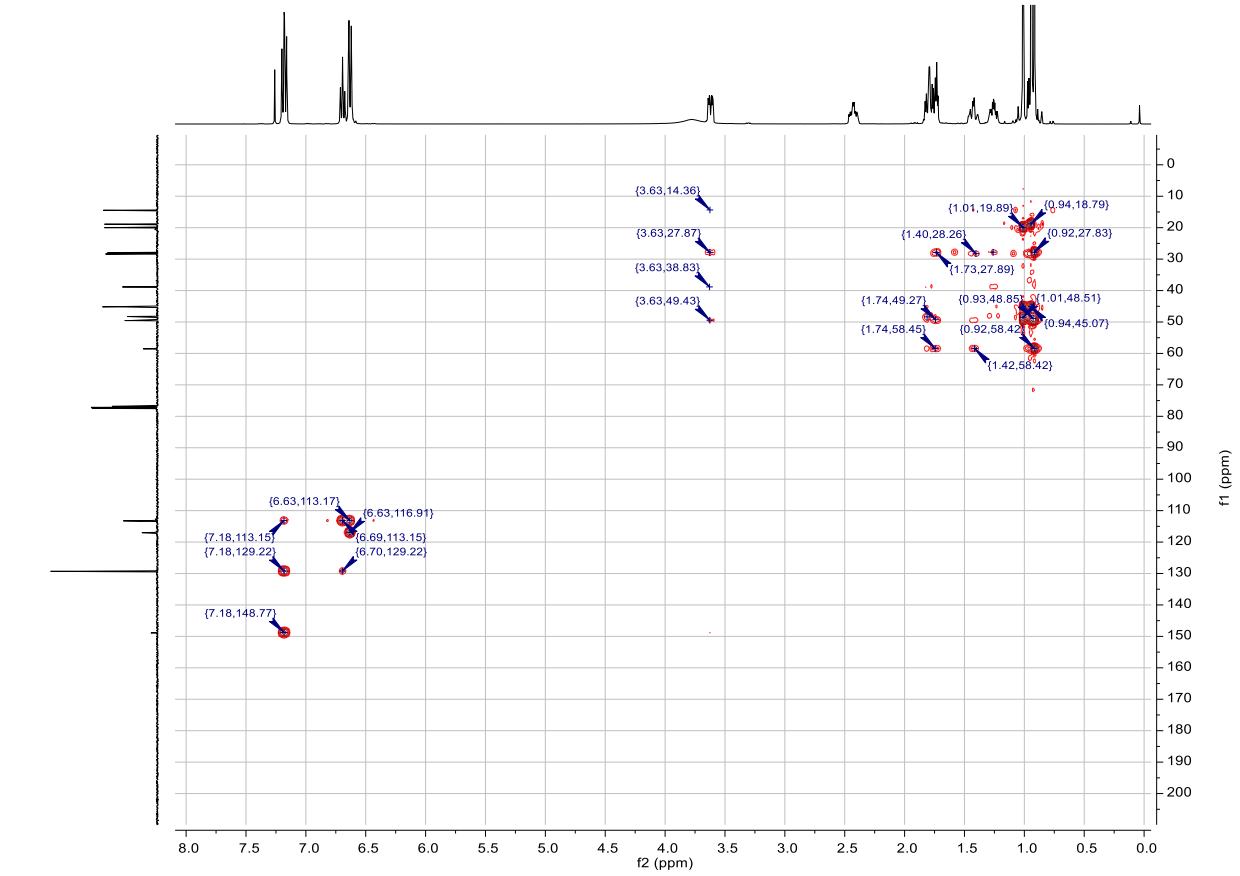
1H-1H NOESY NMR Spectrum of Compound 1a



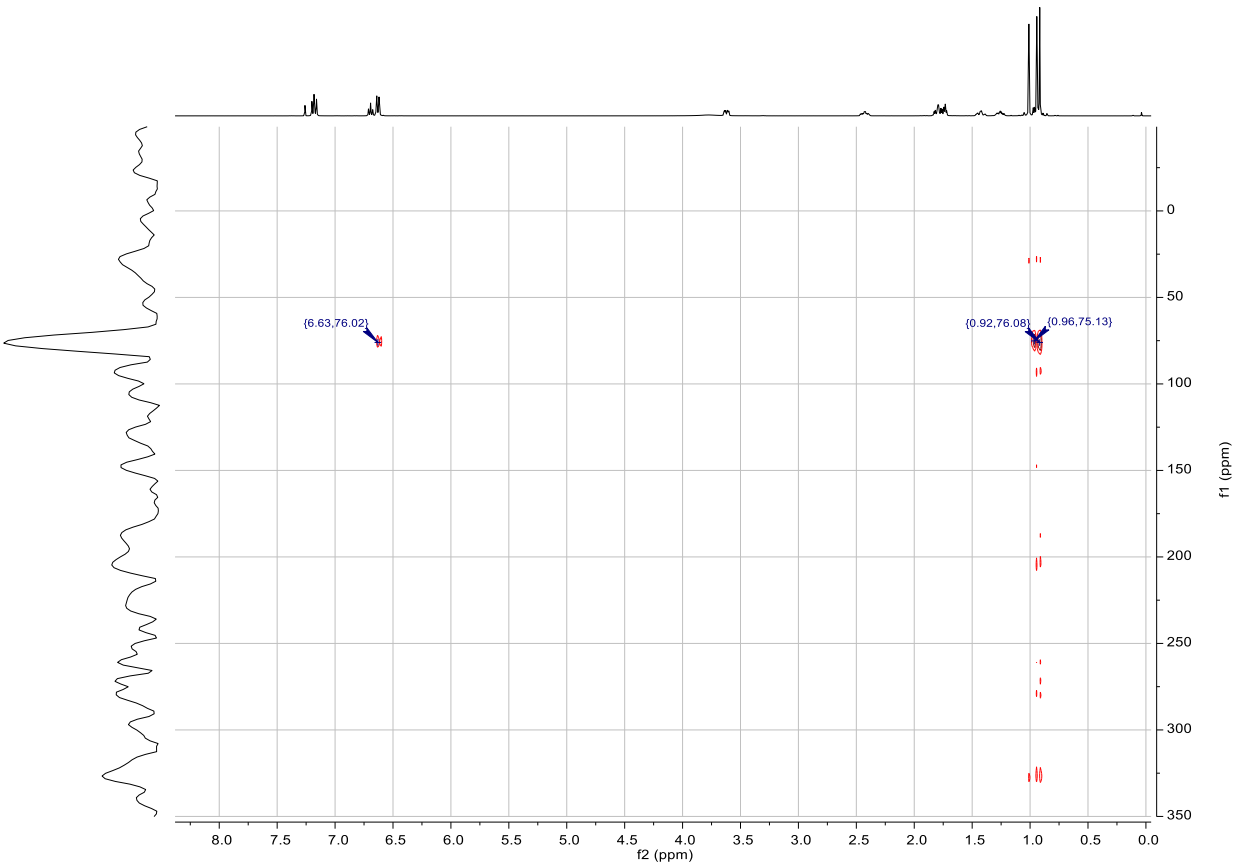
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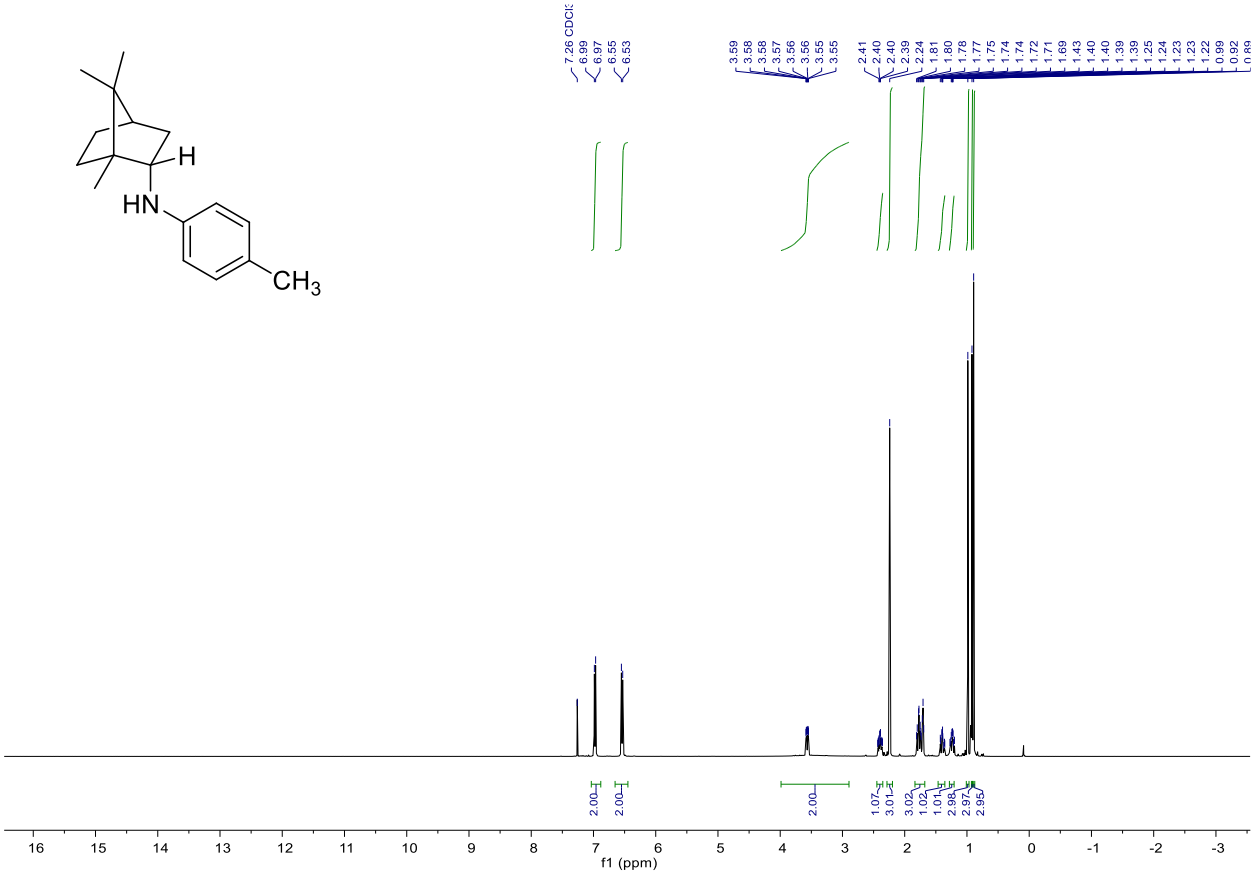
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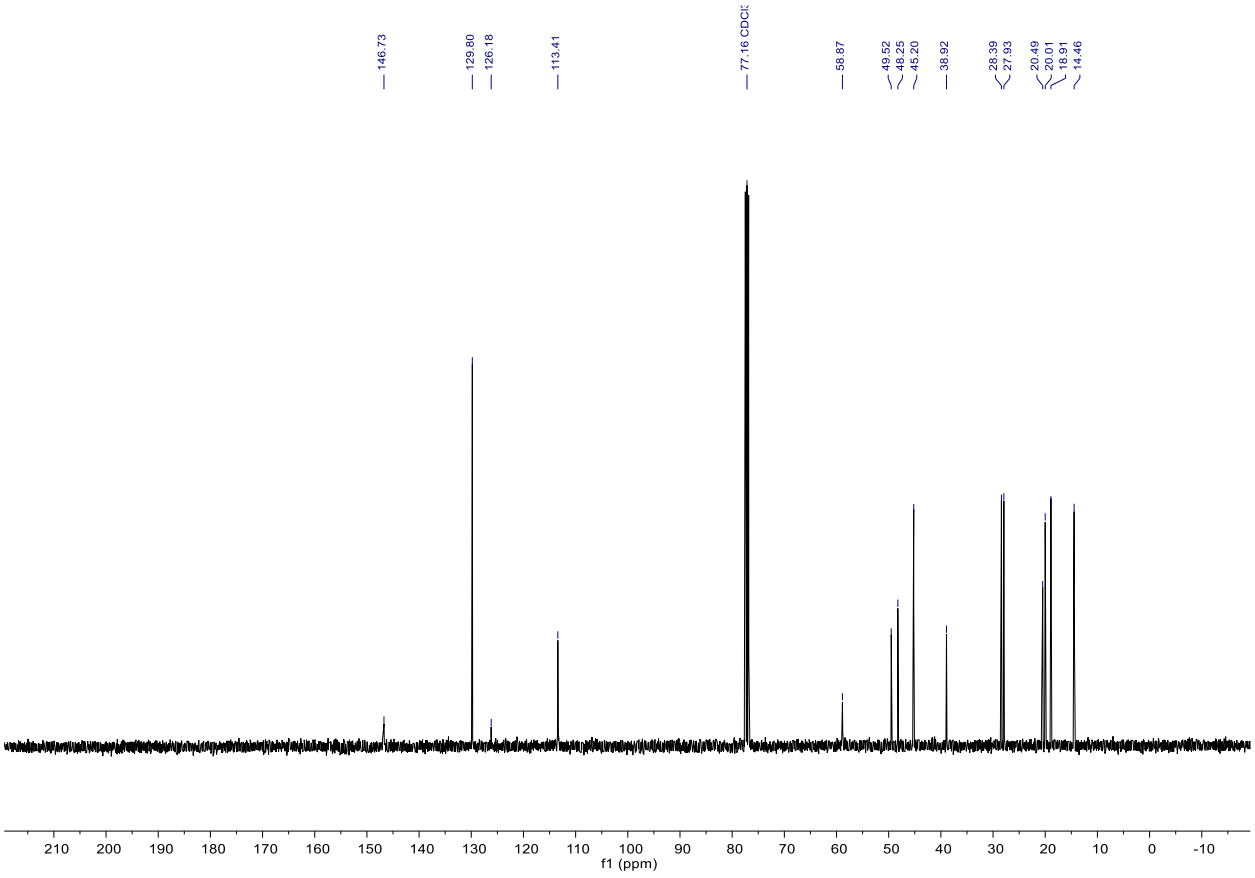
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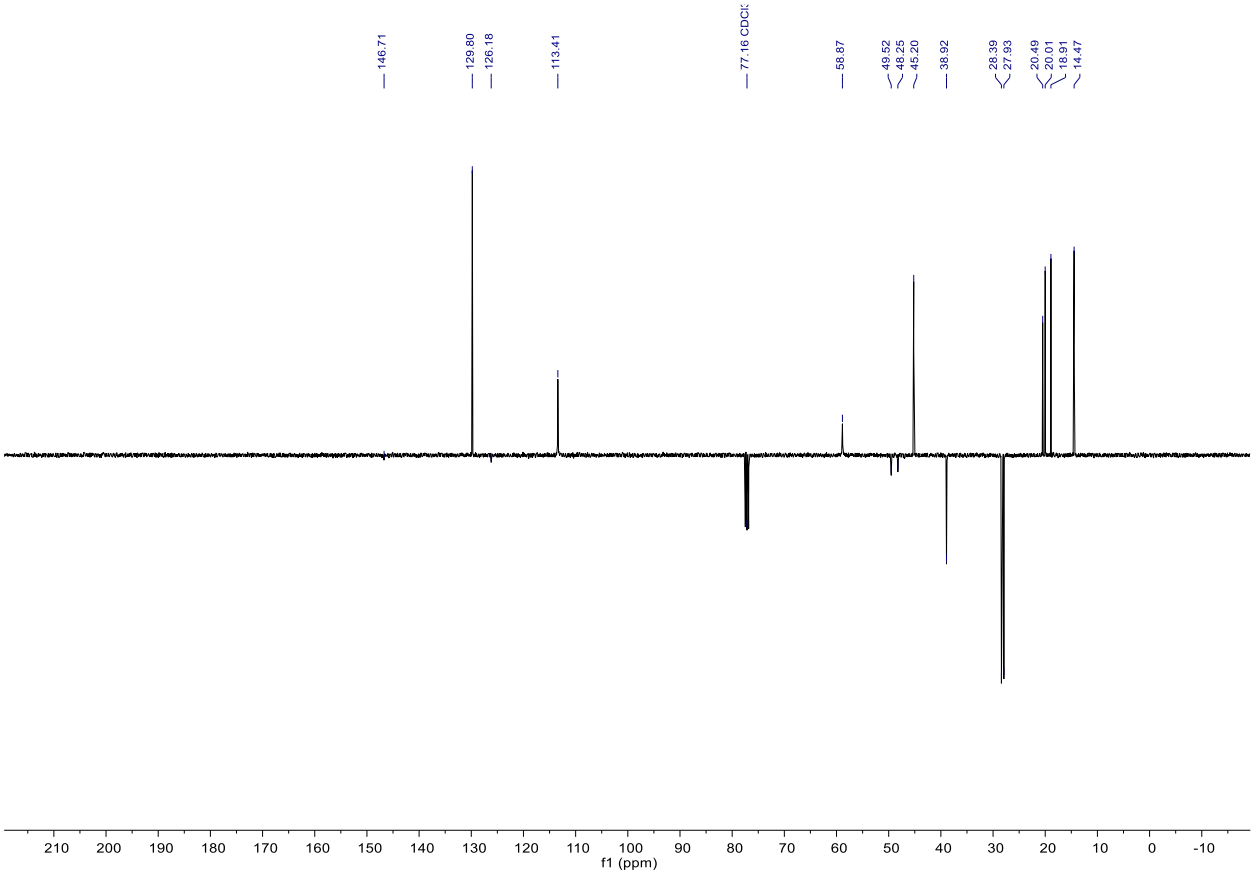
^{1}H NMR Spectrum of Compound 1b (400 MHz, $CDCl_3$)



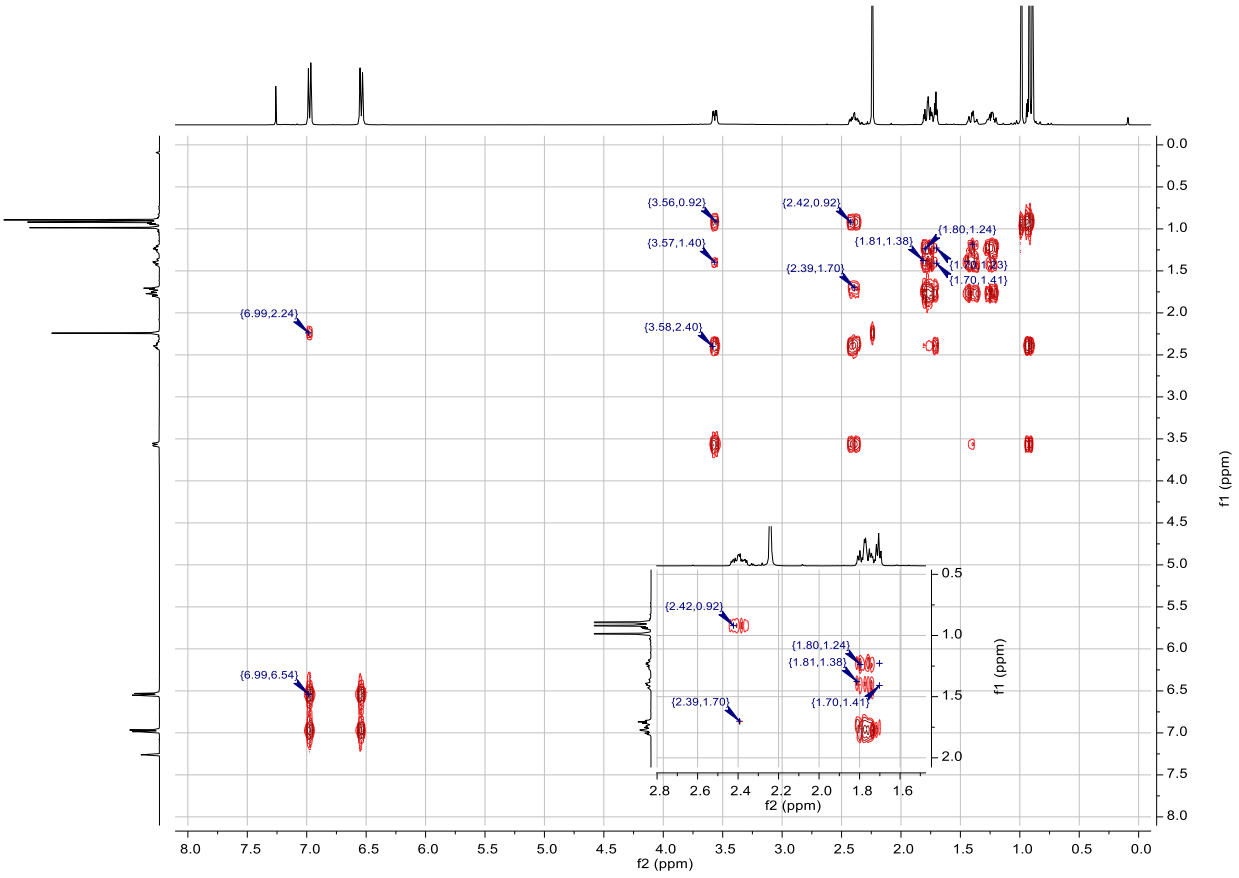
^{13}C NMR Spectrum of Compound 1b (101 MHz, $CDCl_3$)



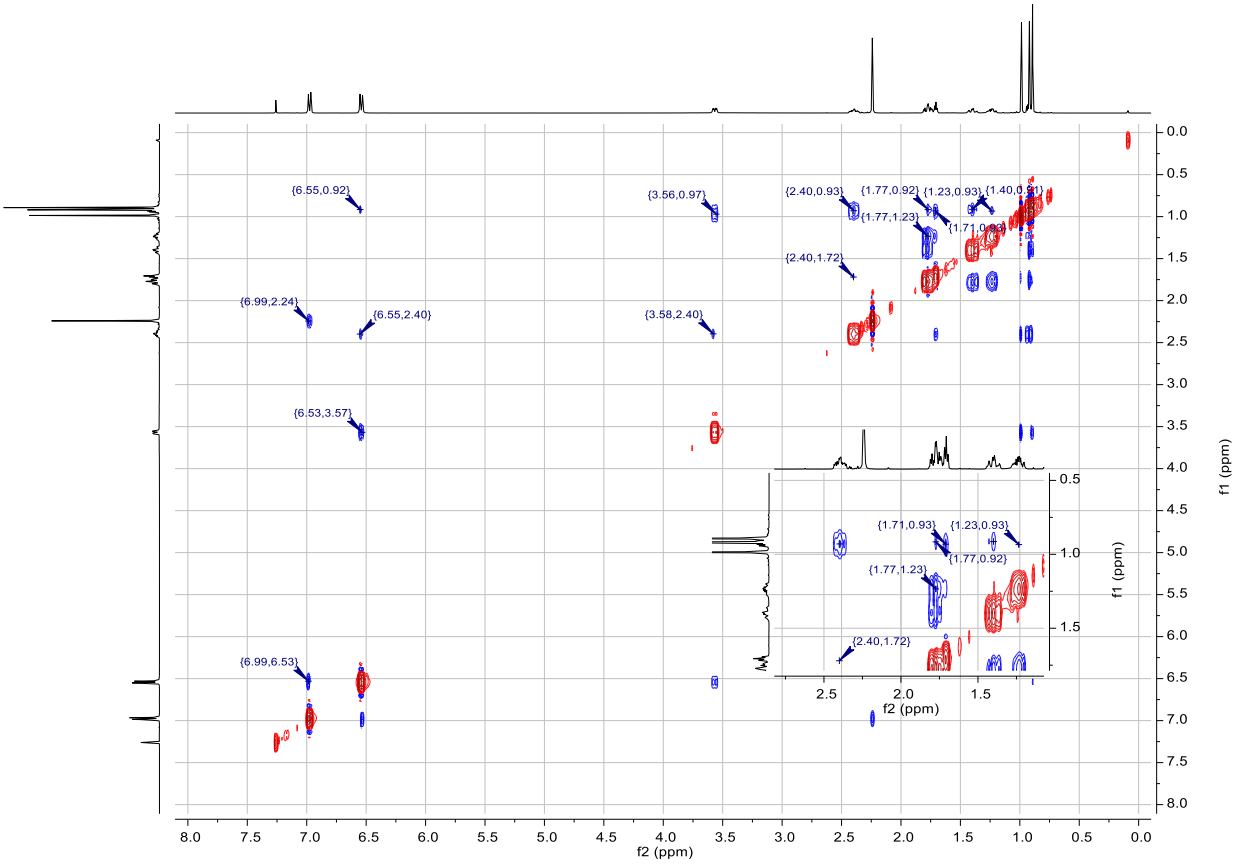
^{13}C DEPTQ-135 NMR Spectrum of Compound 1b



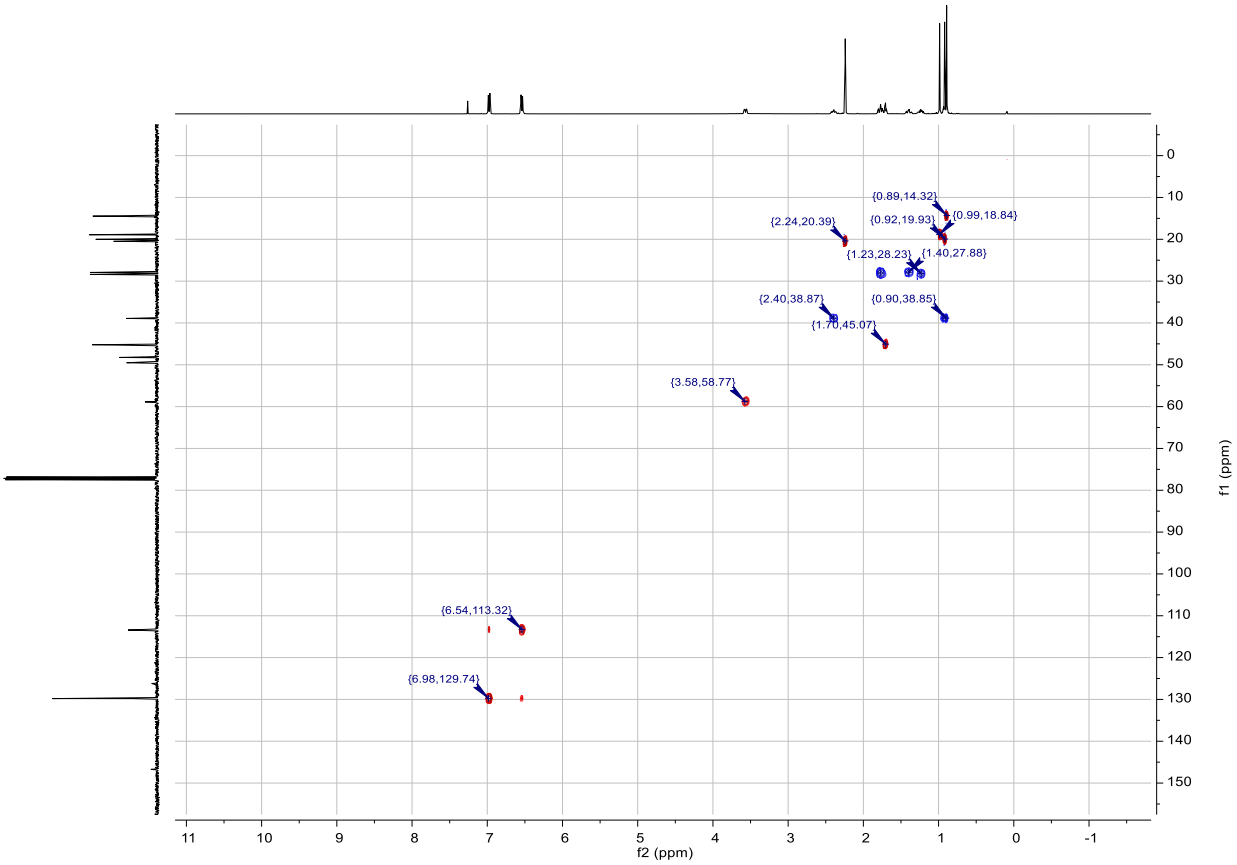
1H-1H COSY NMR Spectrum of Compound 1b



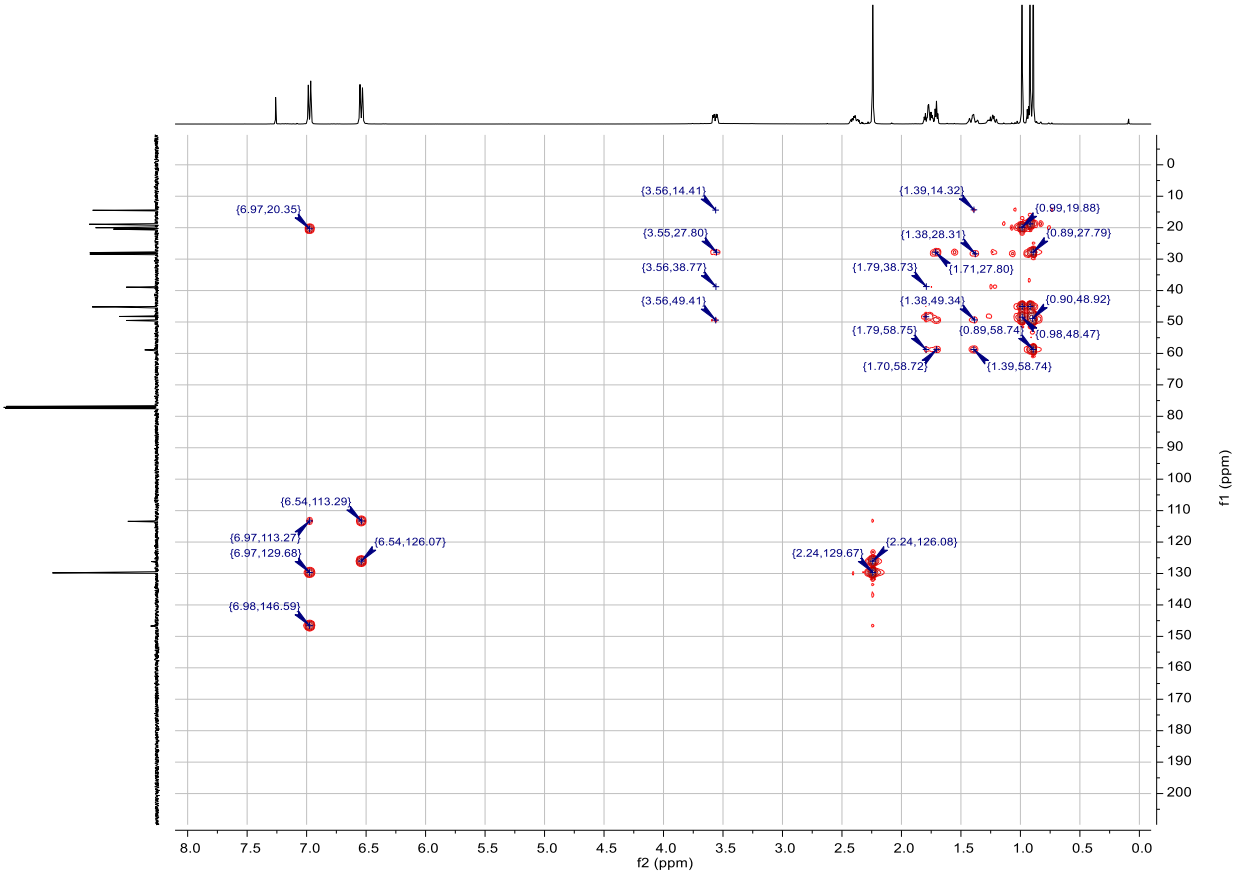
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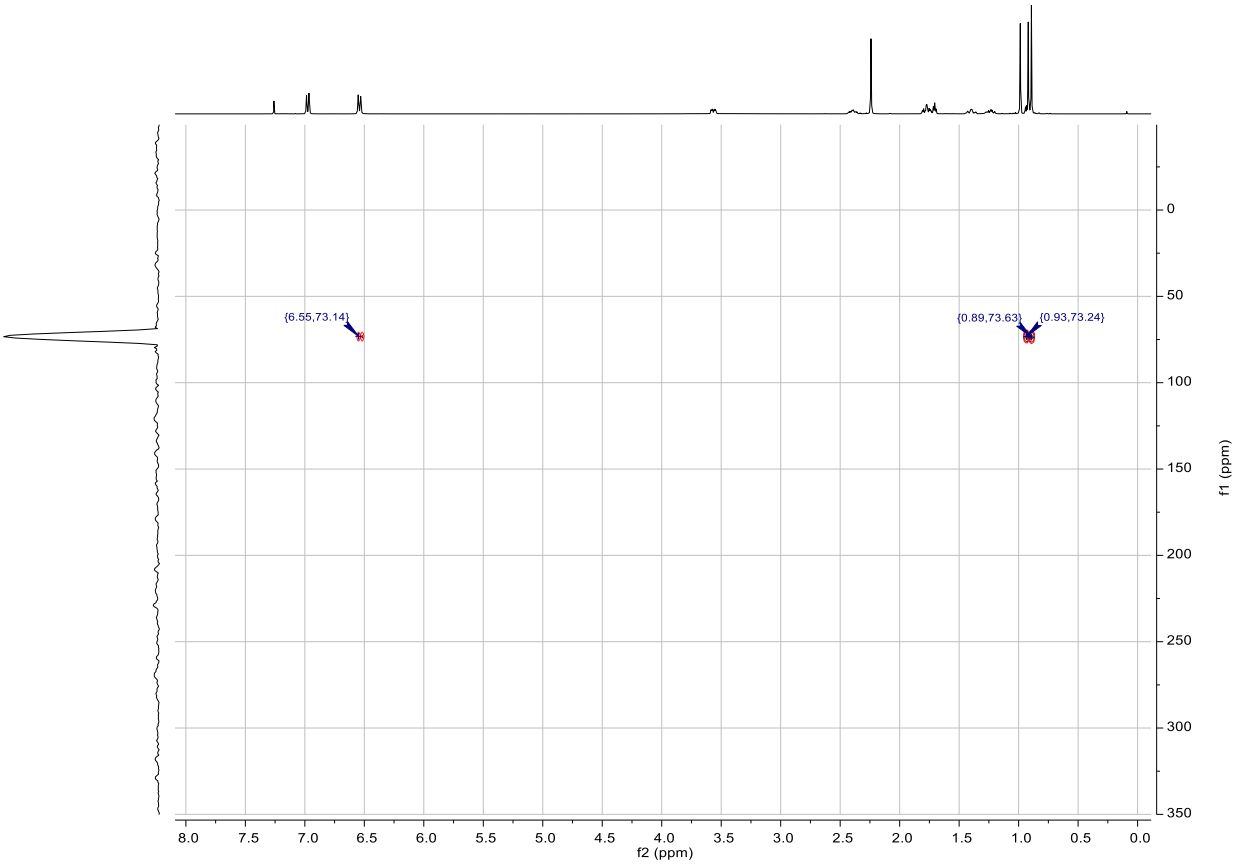
1H-13C HSQC NMR Spectrum of Compound 1b



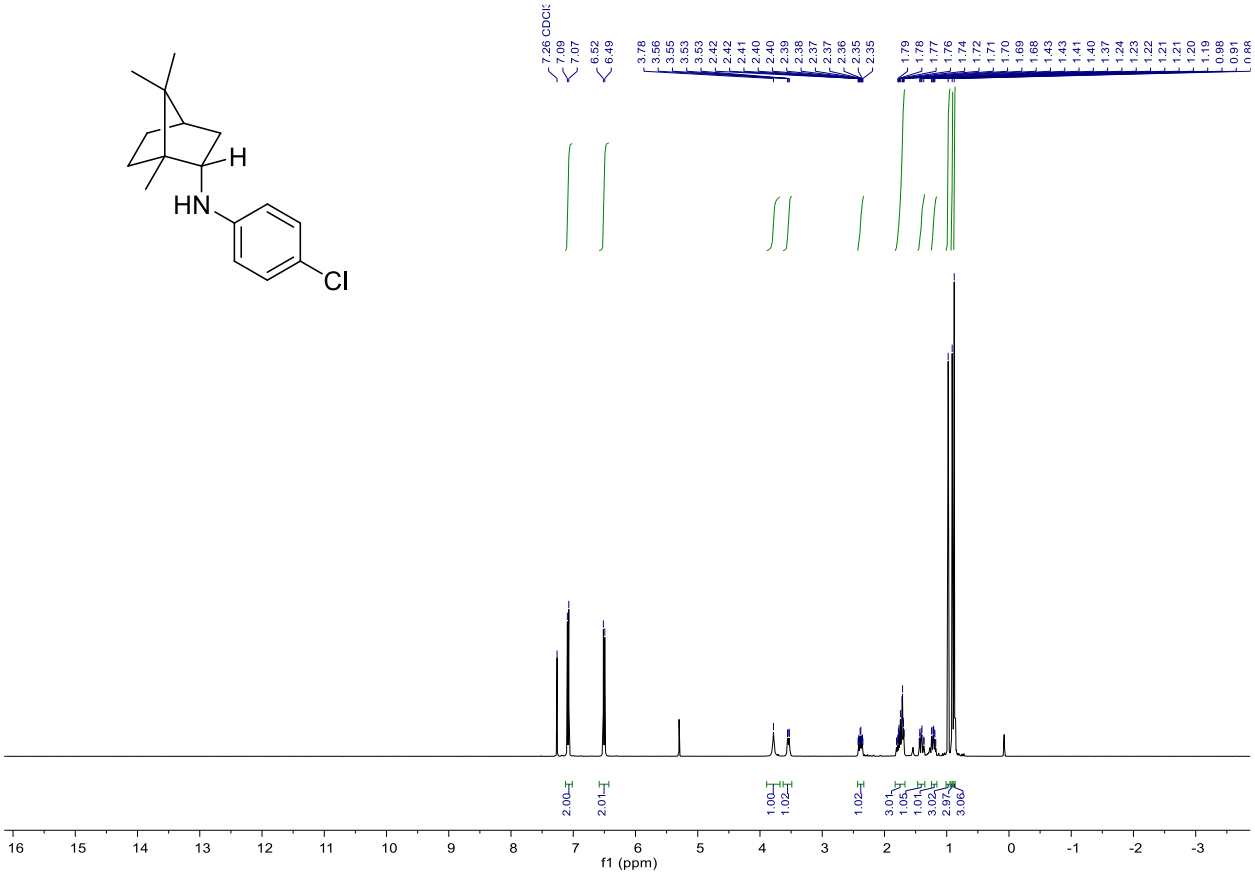
1H-13C HMBC NMR Spectrum of Compound 1b



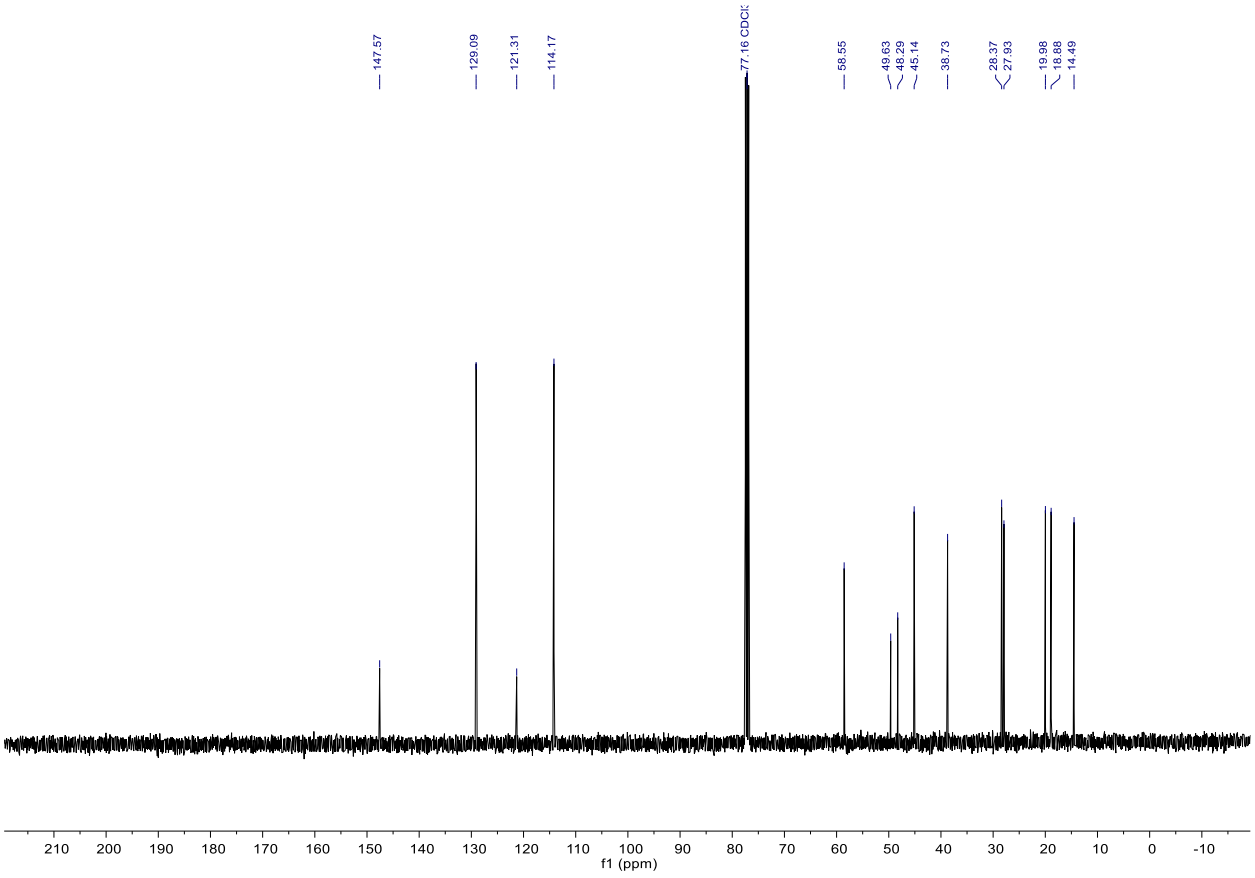
1H-15N HMBC NMR Spectrum of Compound 1b



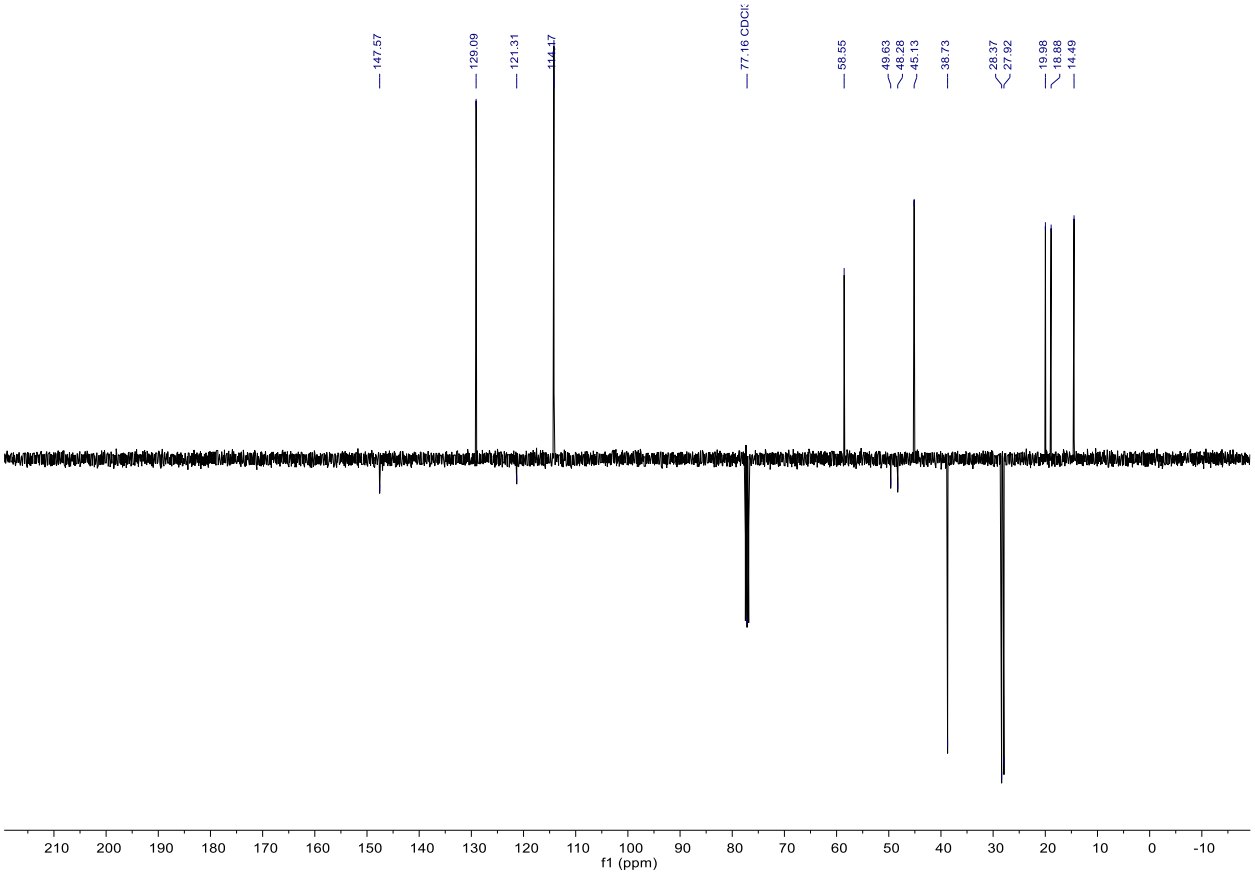
^{1}H NMR Spectrum of Compound 1c (400 MHz, CDCl3)



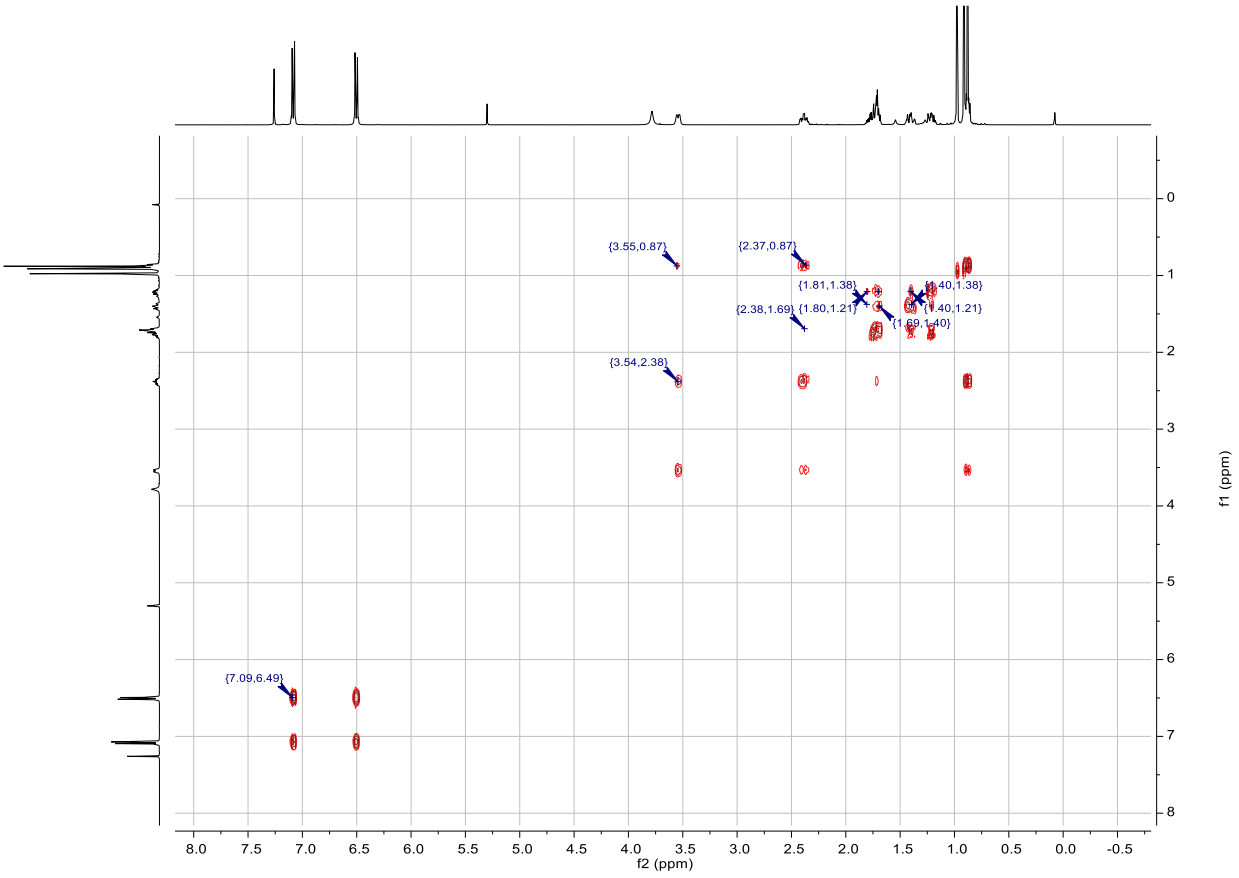
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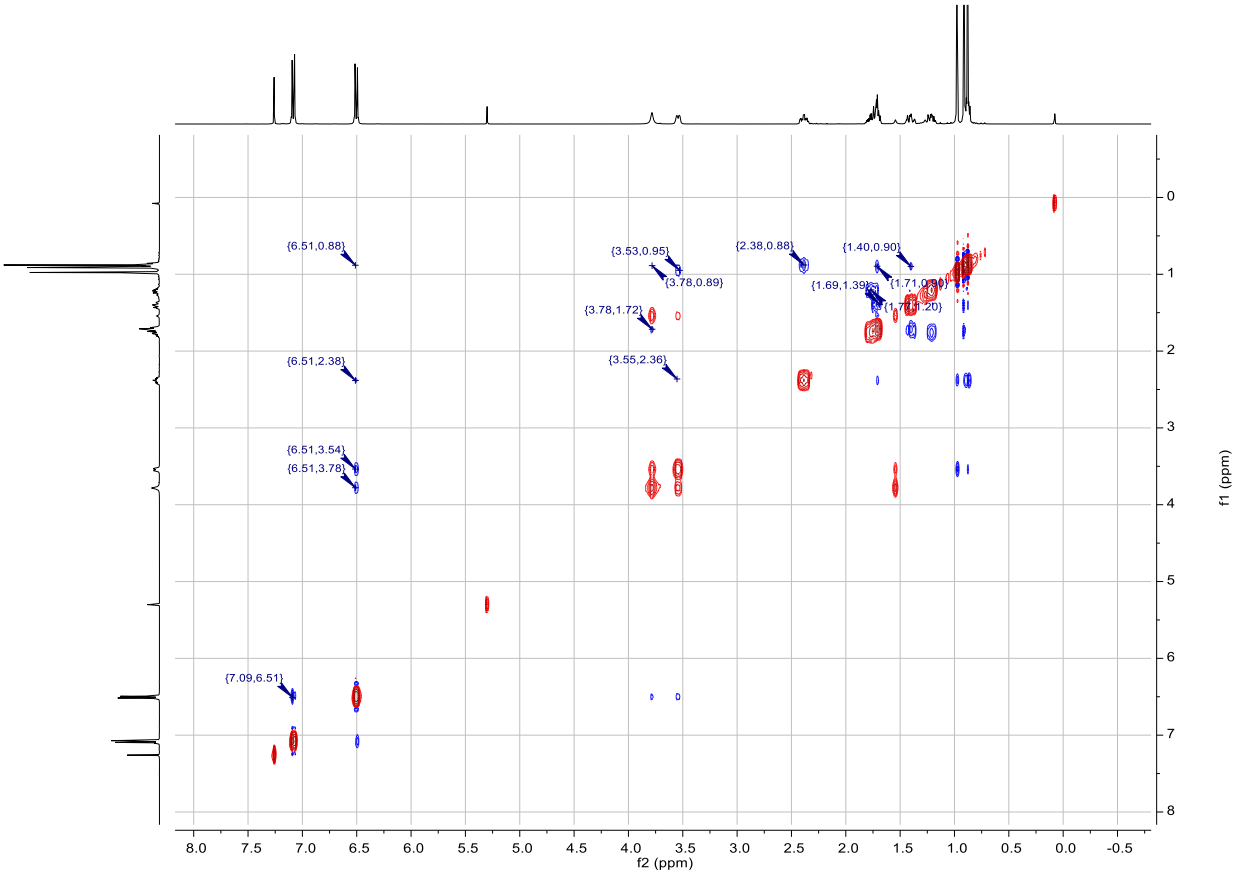
^{13}C DEPTQ-135 NMR Spectrum of Compound 1c



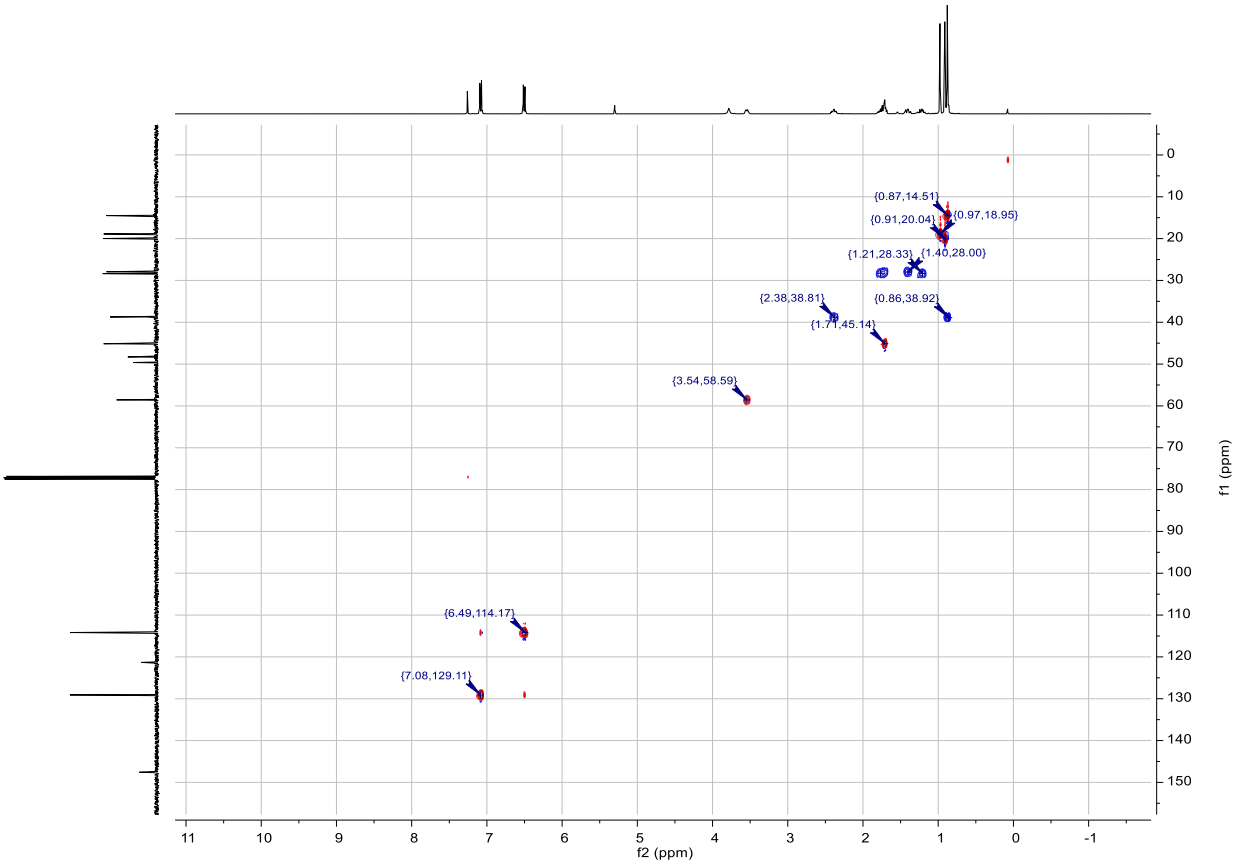
1H-1H COSY NMR Spectrum of Compound 1c



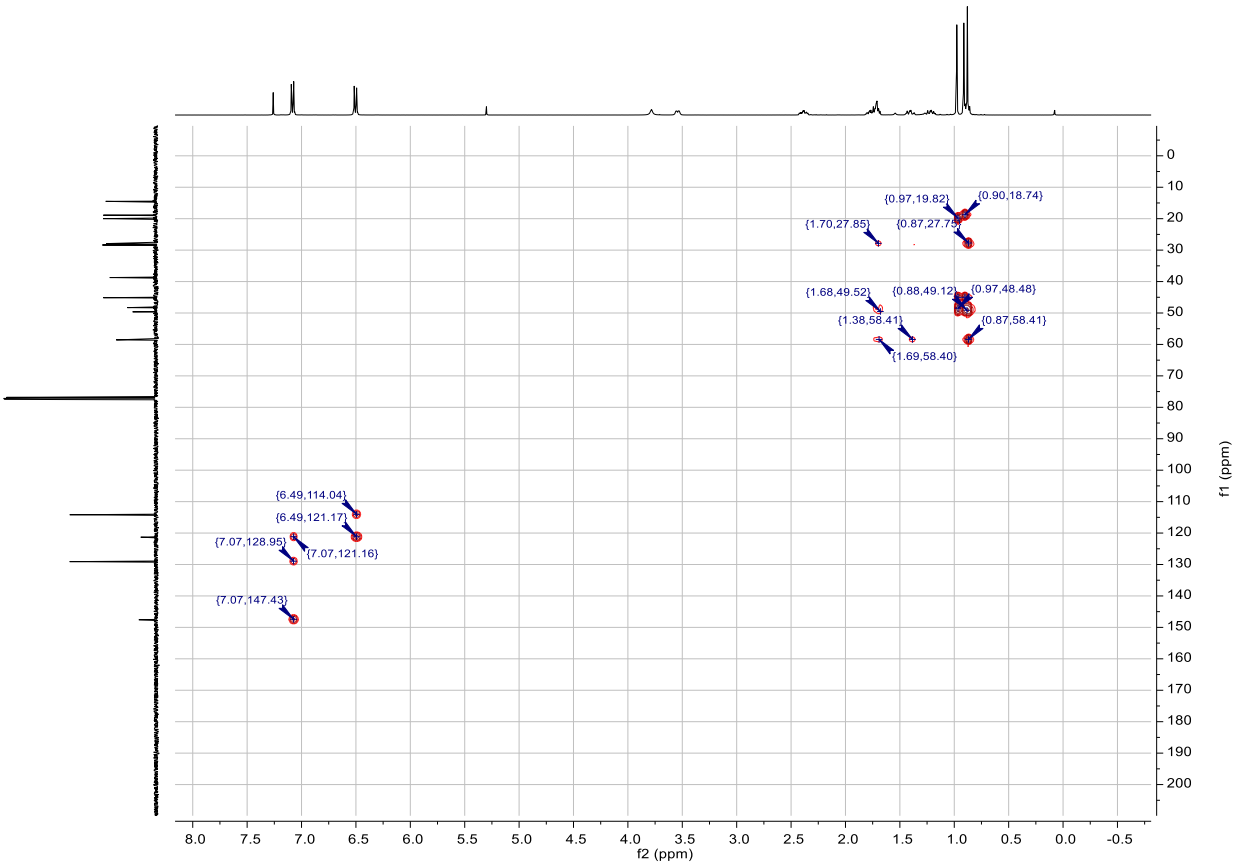
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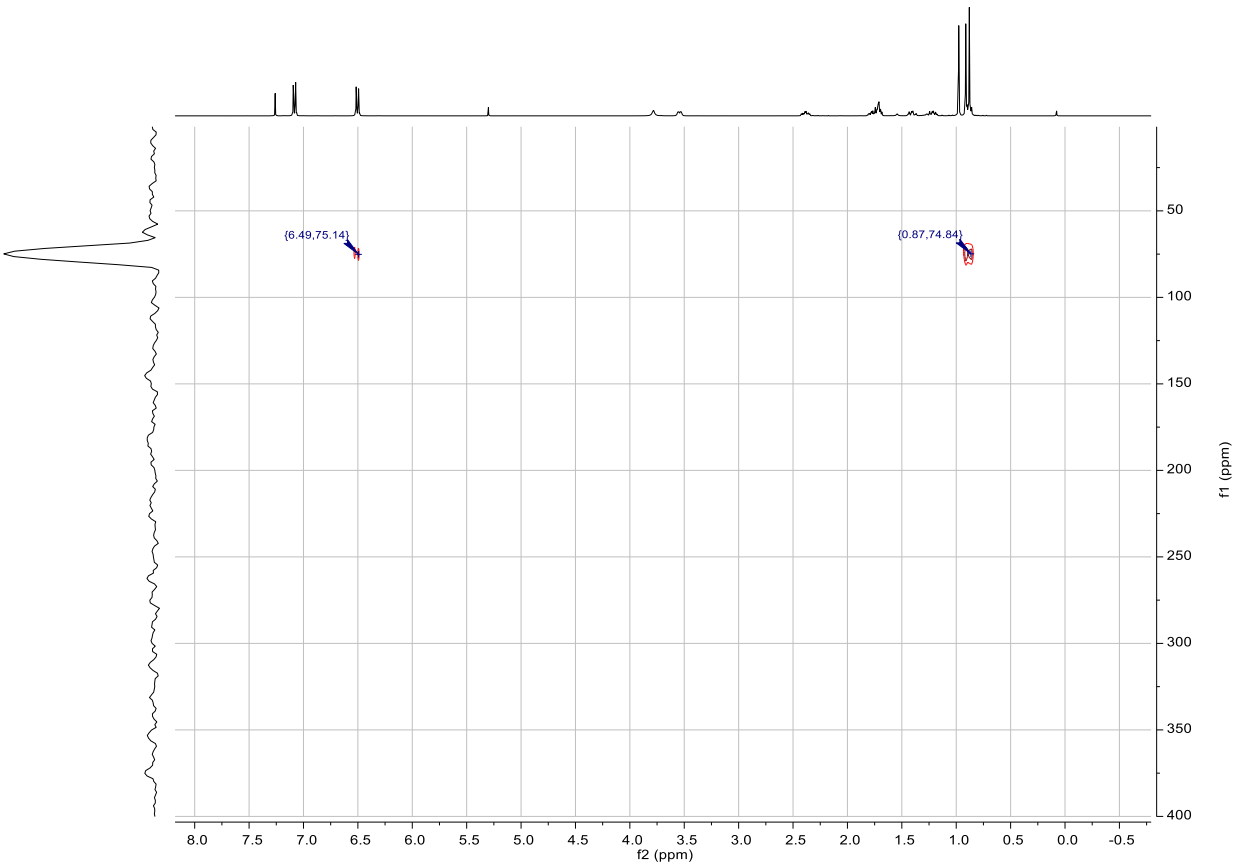
1H-13C HSQC NMR Spectrum of Compound 1c



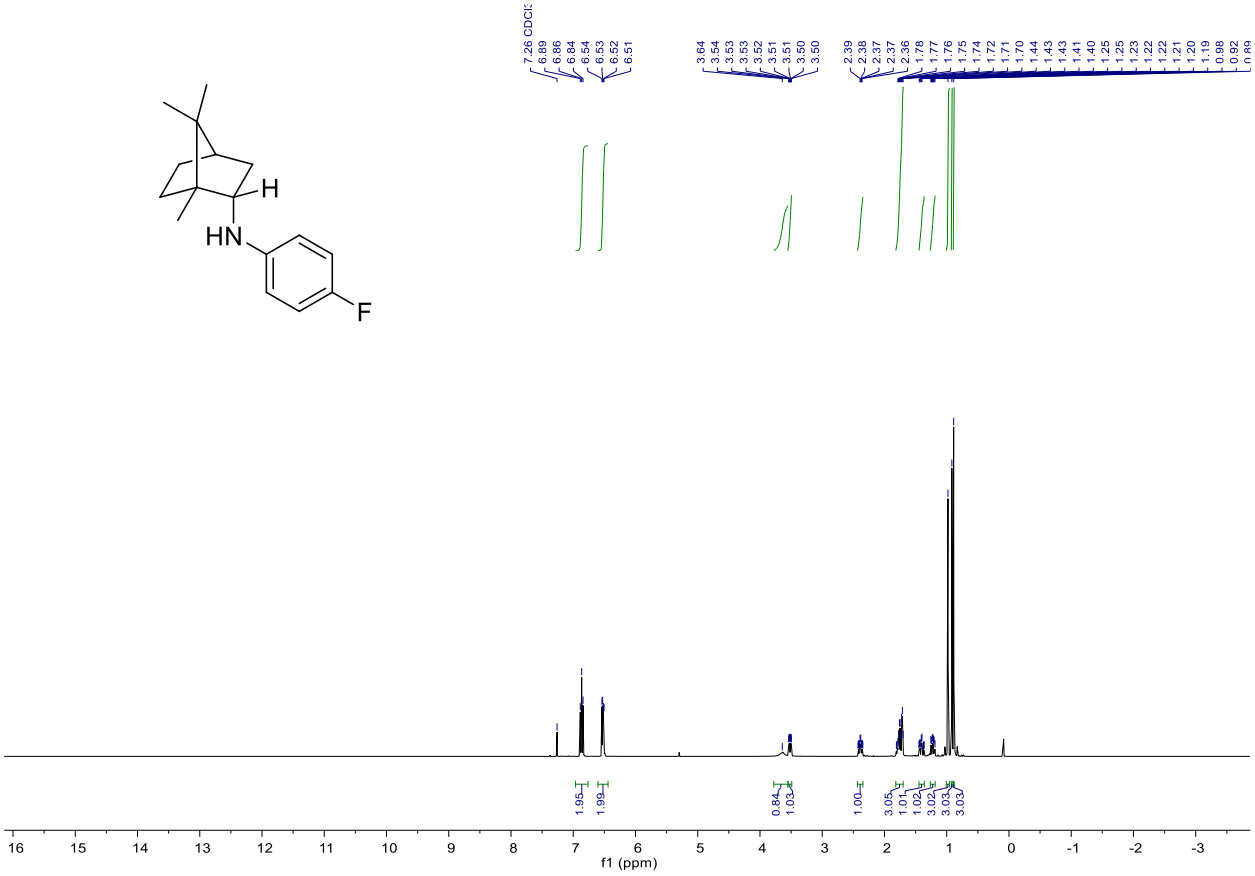
1H-13C HMBC NMR Spectrum of Compound 1c



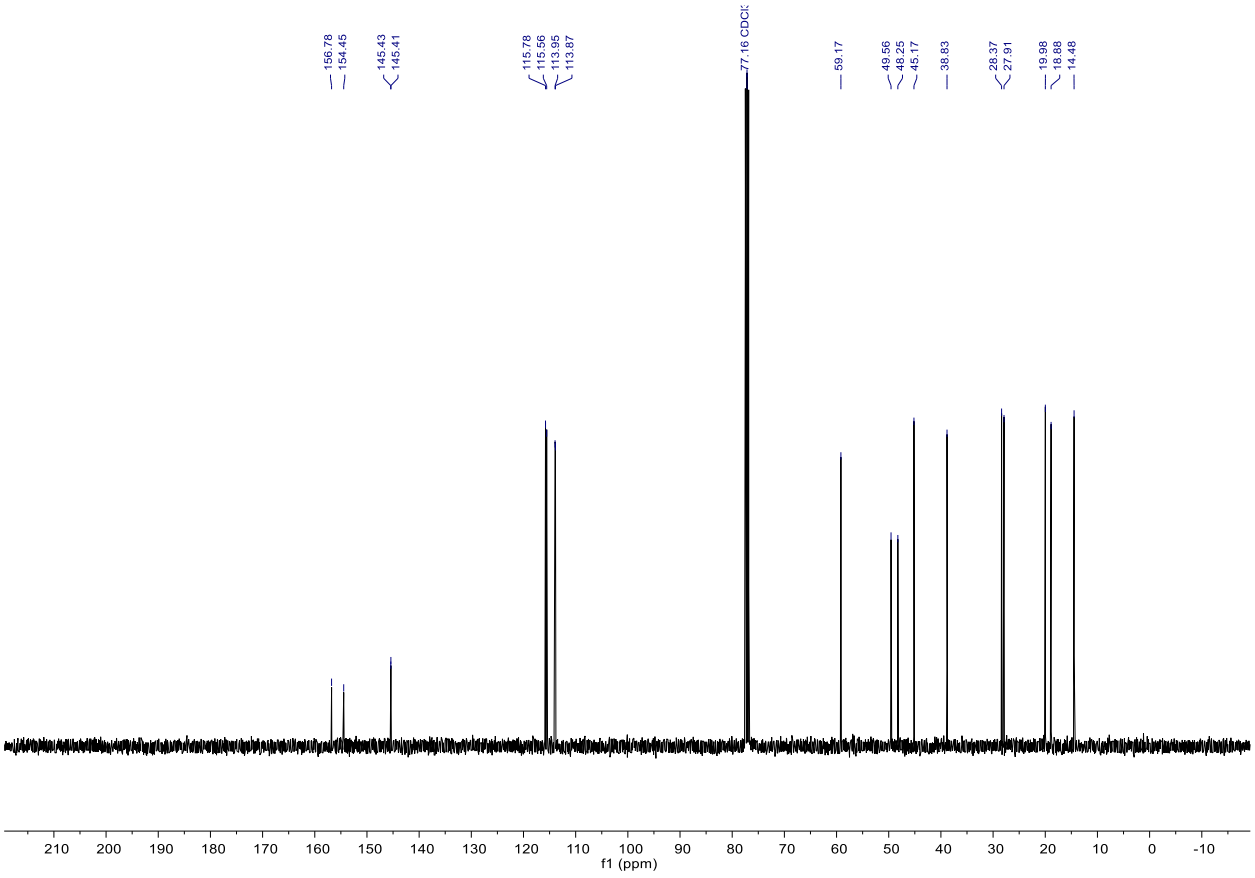
1H-15N HMBC NMR Spectrum of Compound 1c



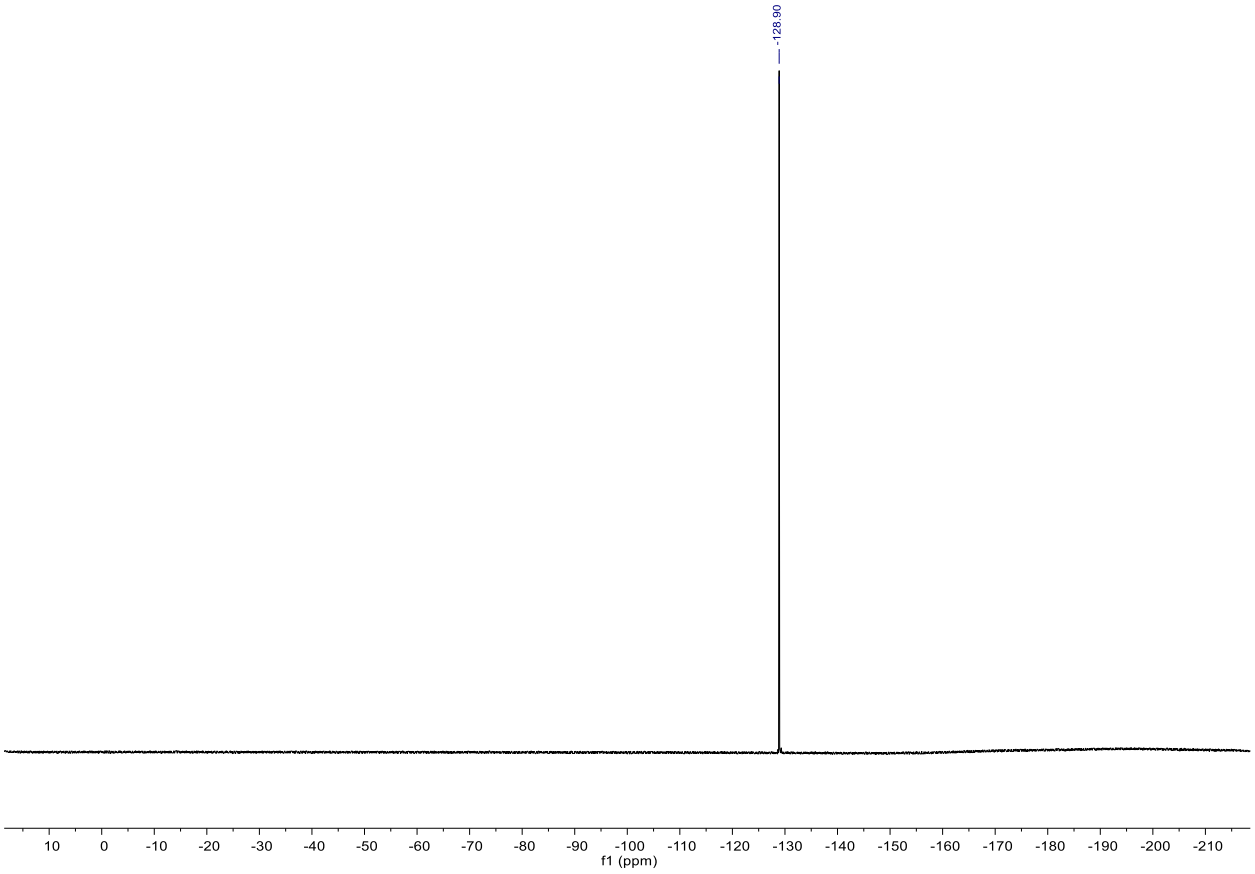
^{1}H NMR Spectrum of Compound 1d (400 MHz, CDCl3)



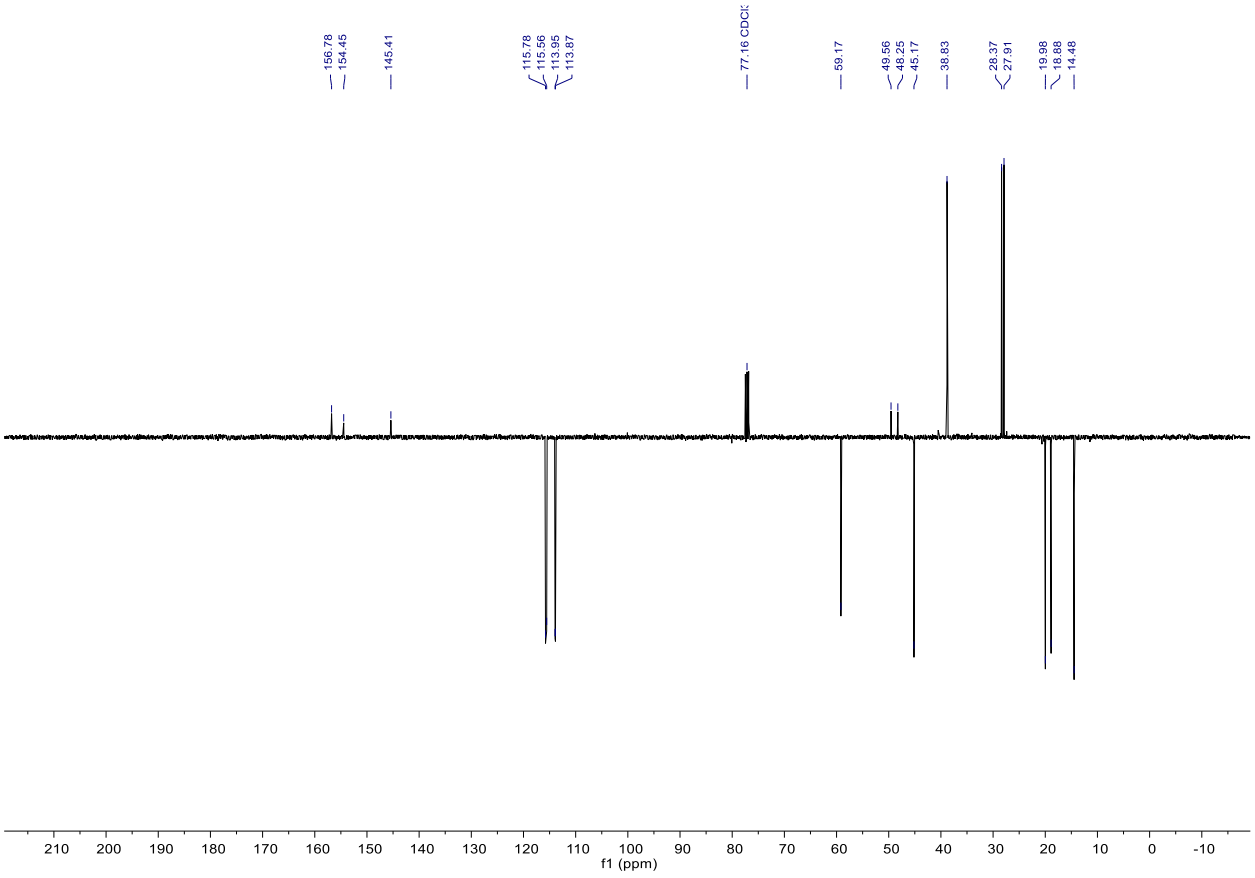
^{13}C NMR Spectrum of Compound 1d (101 MHz, CDCl3)



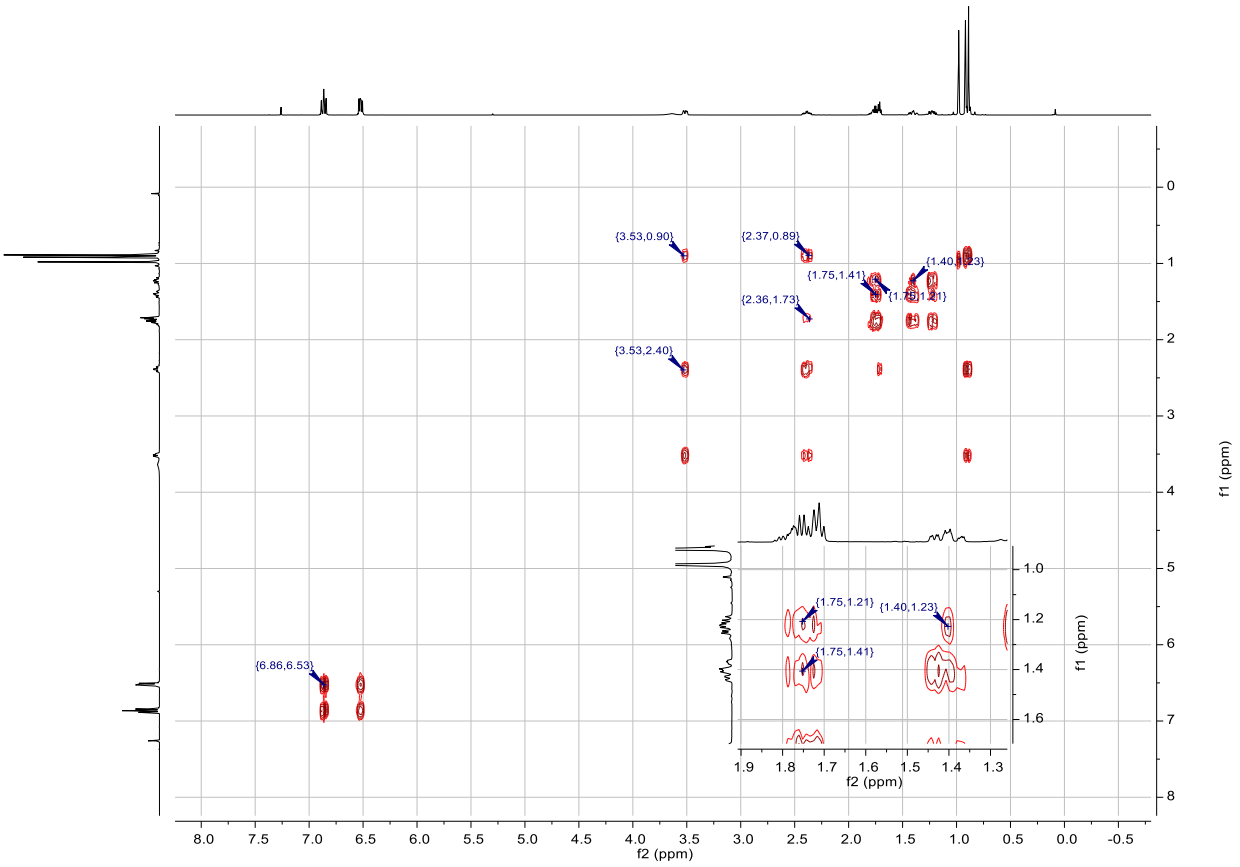
^{19}F NMR Spectrum of Compound 1d (376 MHz, CDCl3)



^{13}C DEPTQ-135 NMR Spectrum of Compound 1d



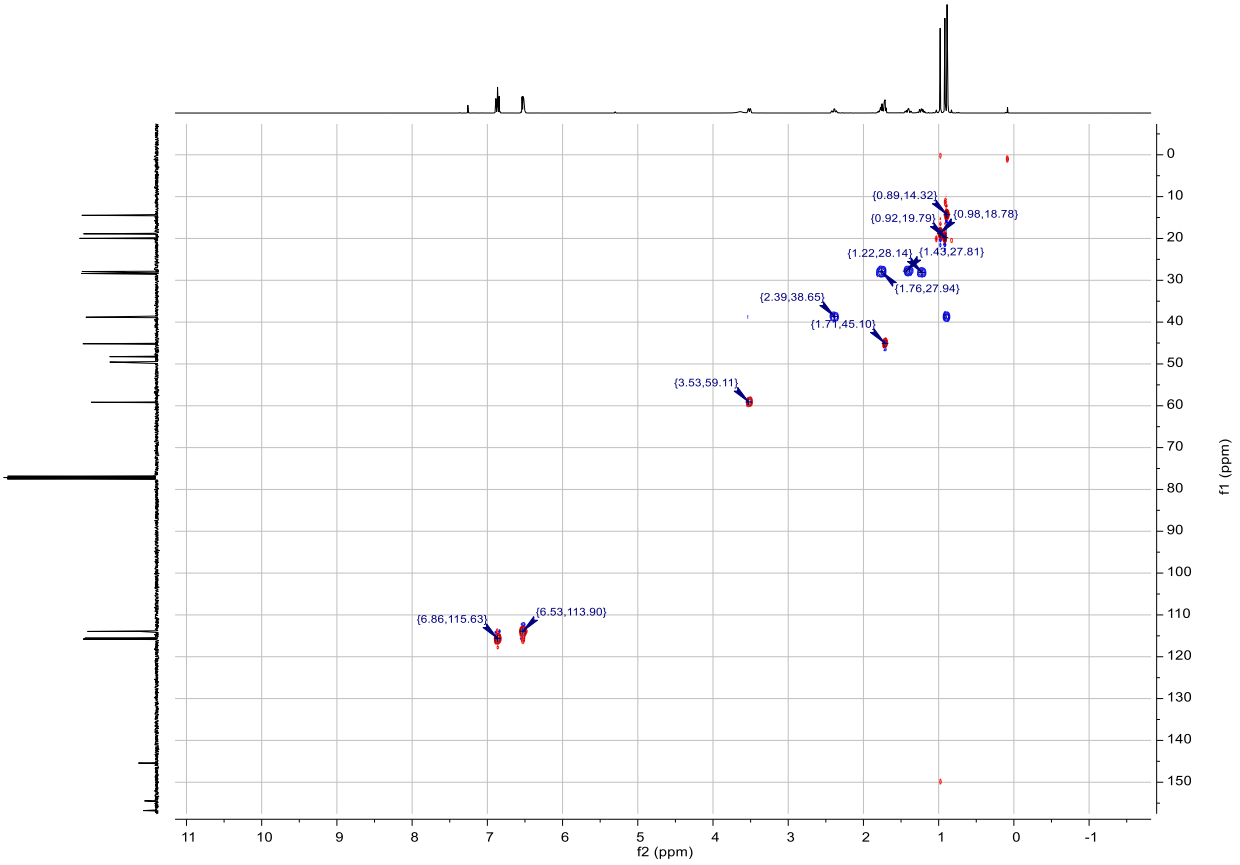
1H-1H COSY NMR Spectrum of Compound 1d



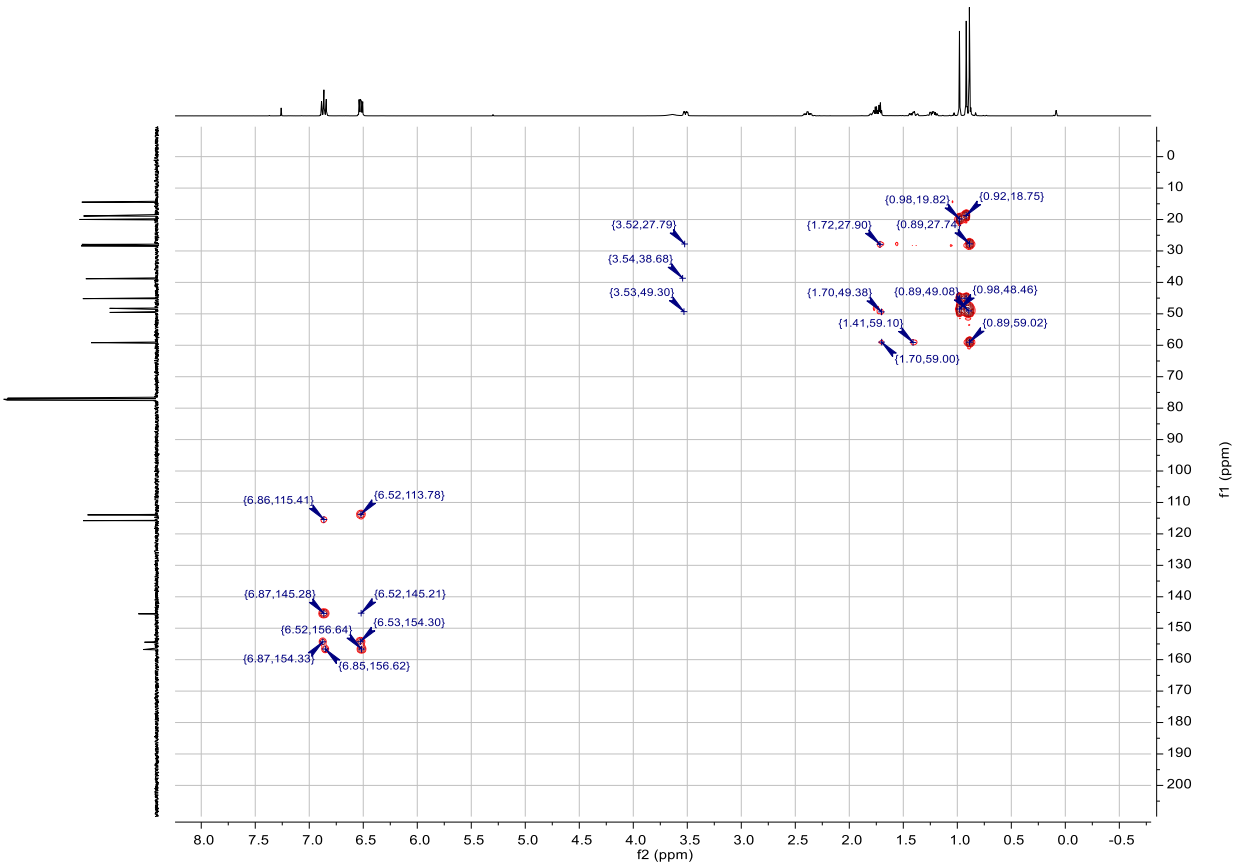
1H-1H NOESY NMR Spectrum of Compound 1d



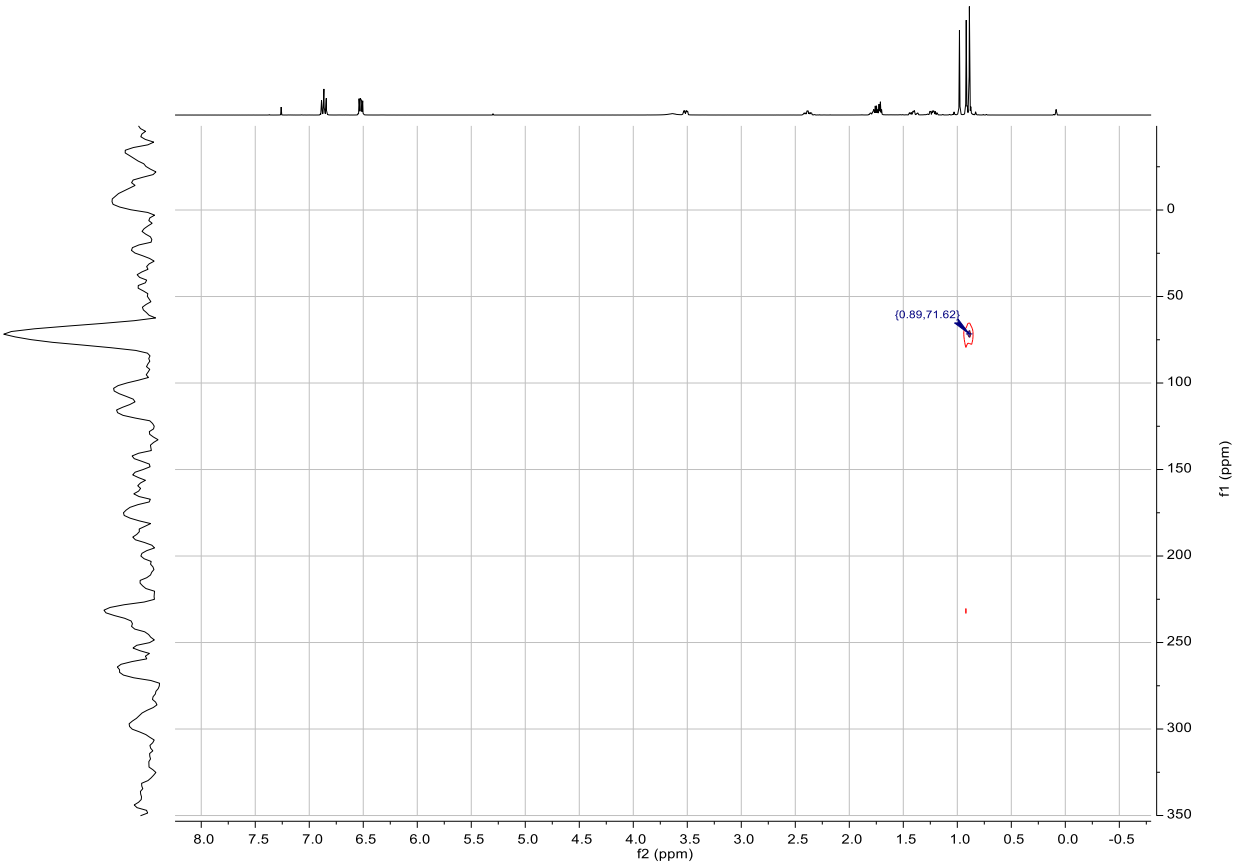
1H-13C HSQC NMR Spectrum of Compound 1d



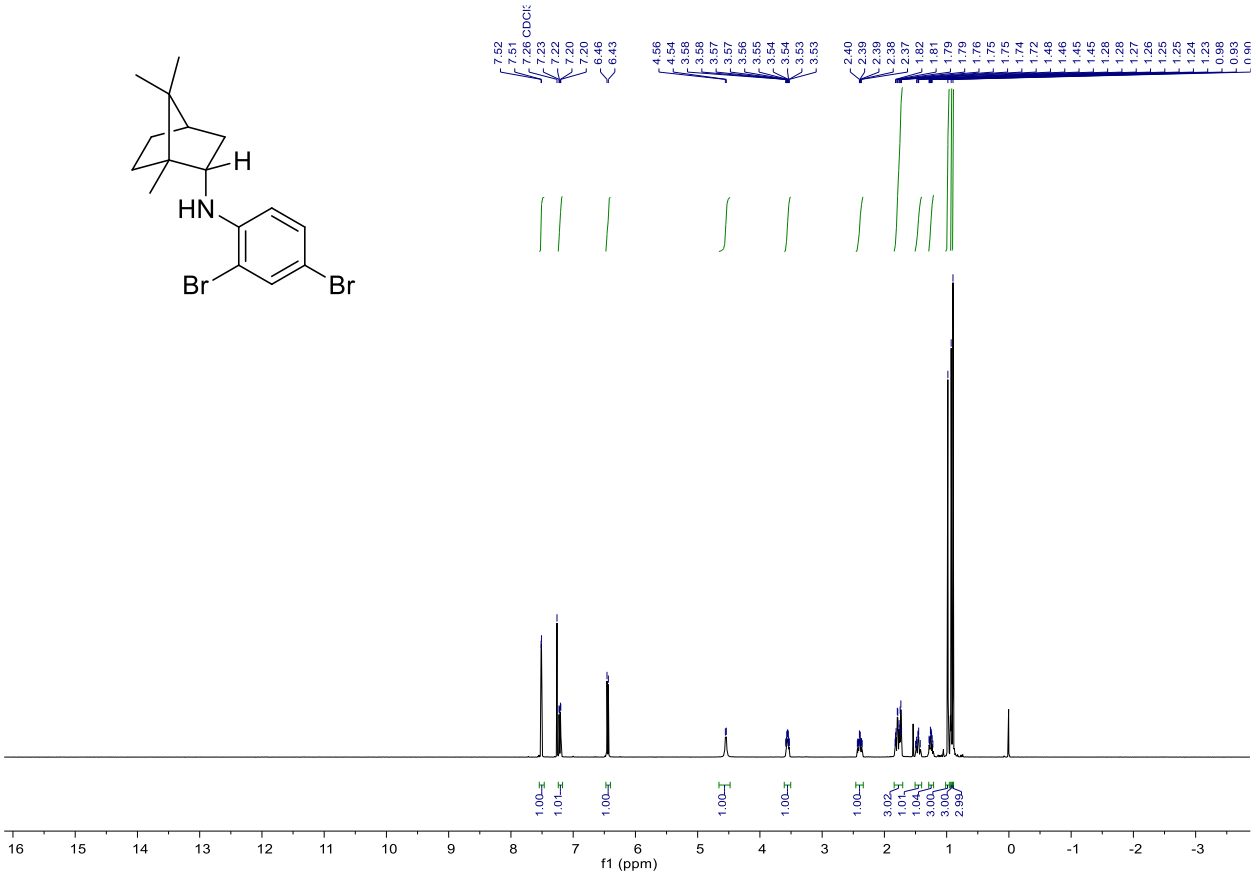
1H-13C HMBC NMR Spectrum of Compound 1d



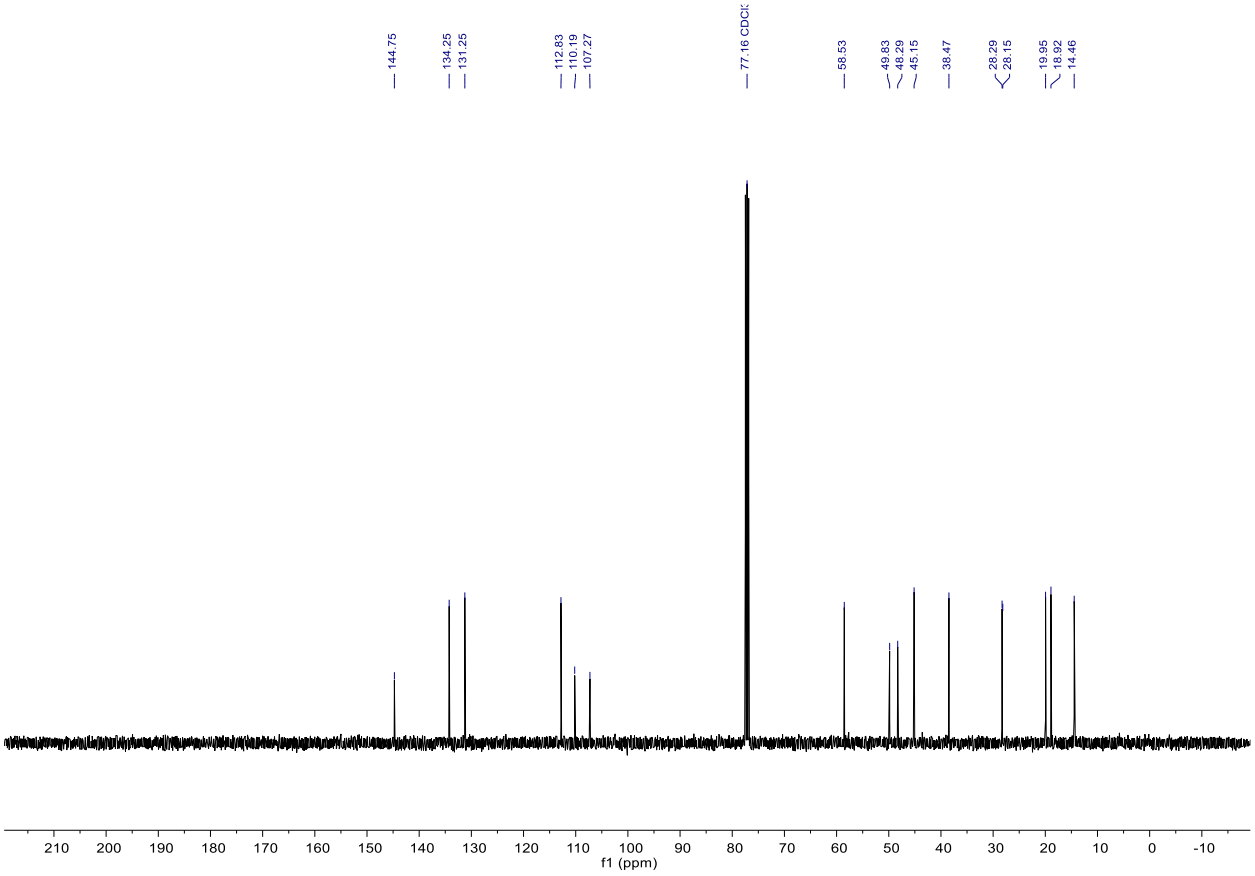
1H-15N HMBC NMR Spectrum of Compound 1d



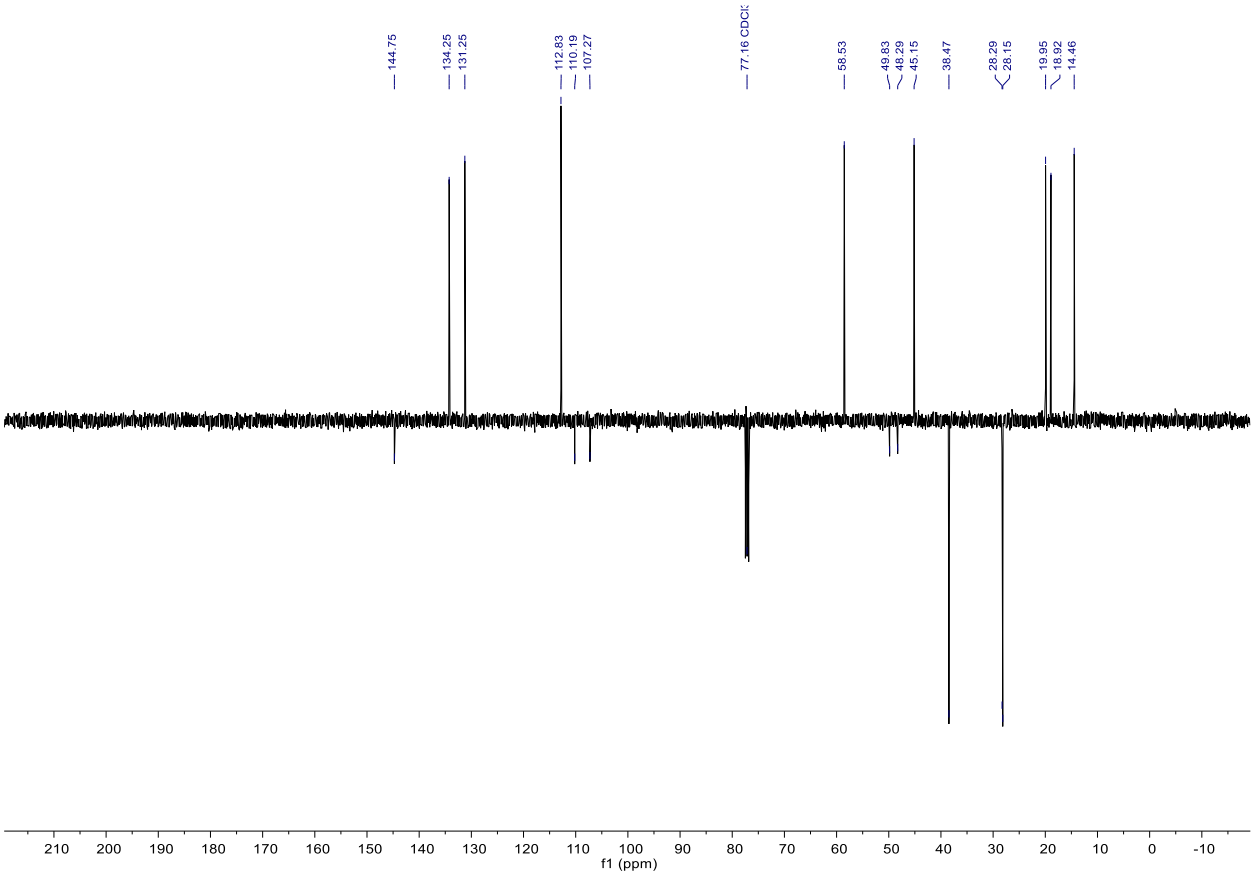
^{1}H NMR Spectrum of Compound 2a (400 MHz, CDCl3)



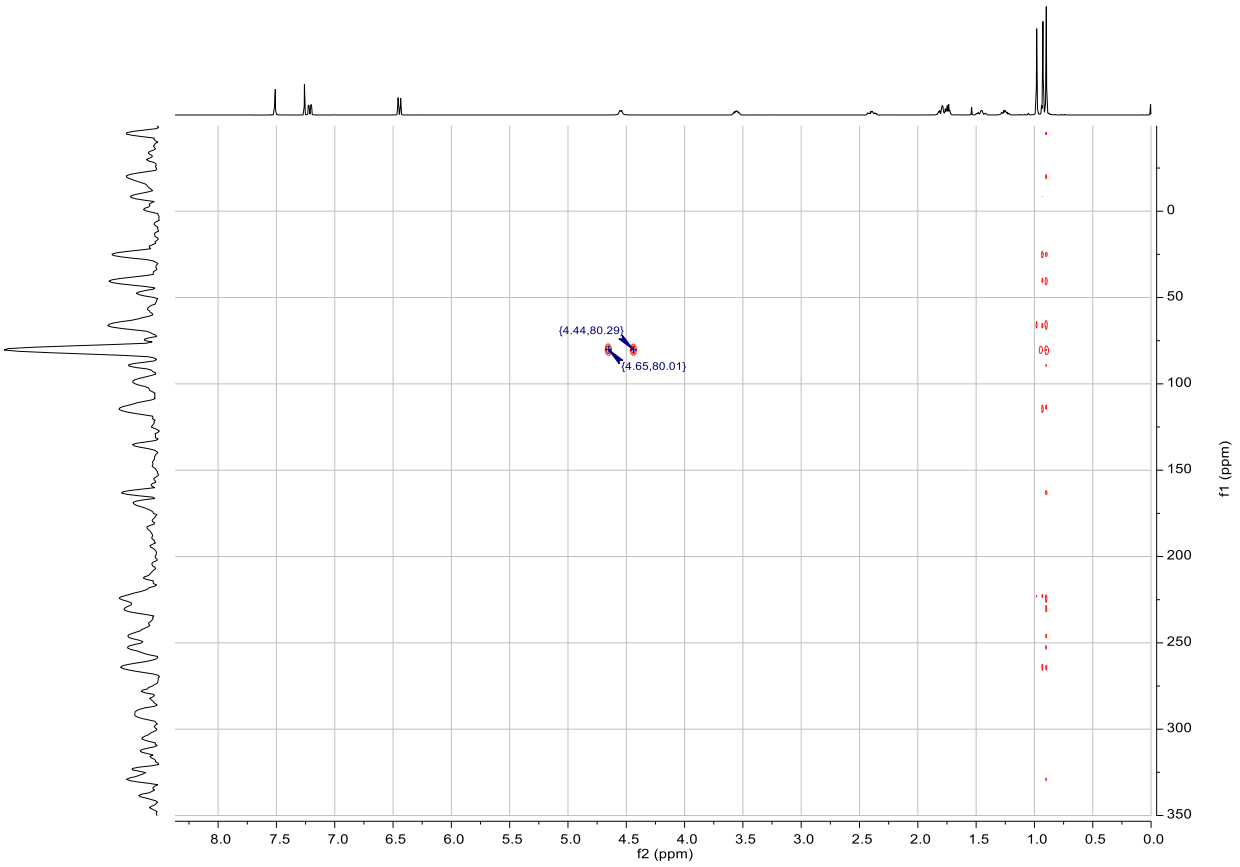
^{13}C NMR Spectrum of Compound 2a (101 MHz, CDCl3)



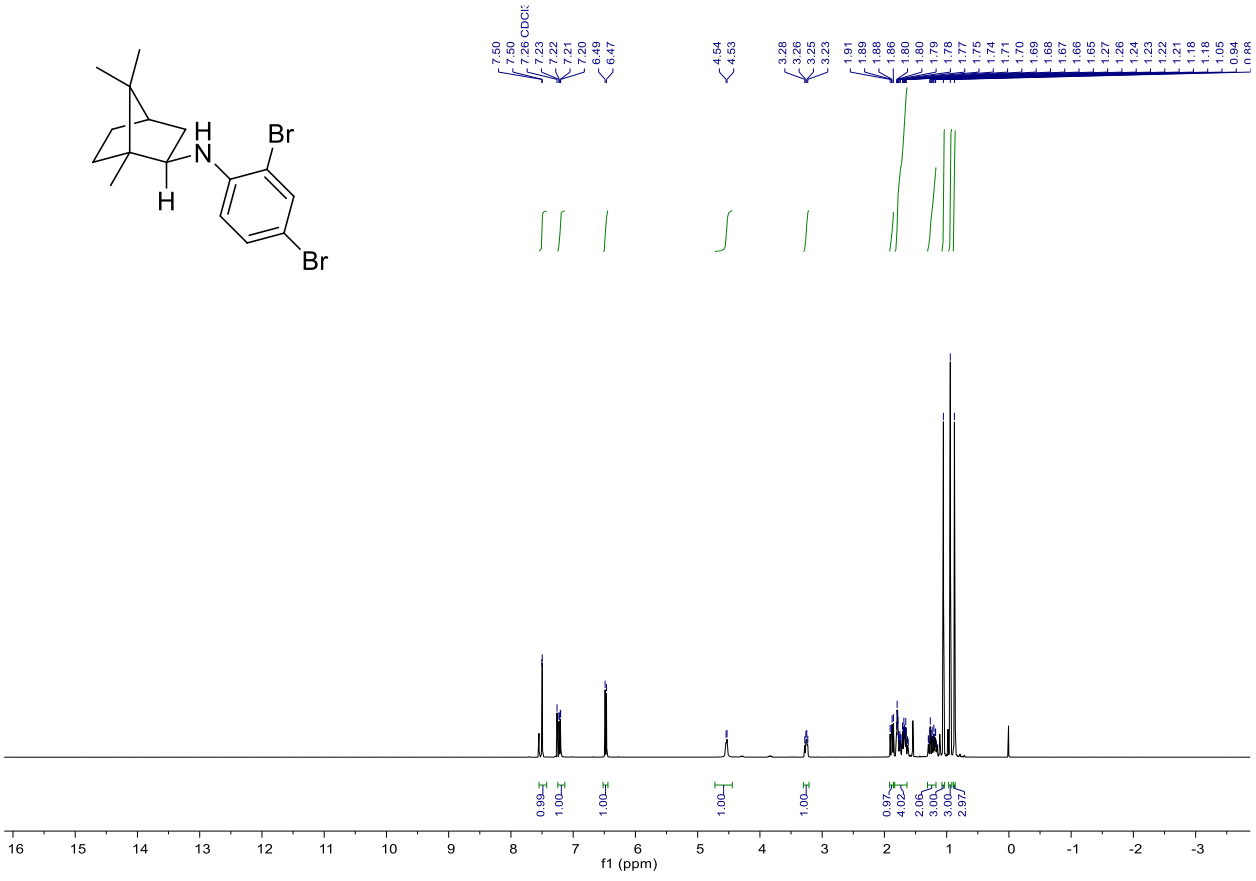
^{13}C DEPTQ-135 NMR Spectrum of Compound 2a



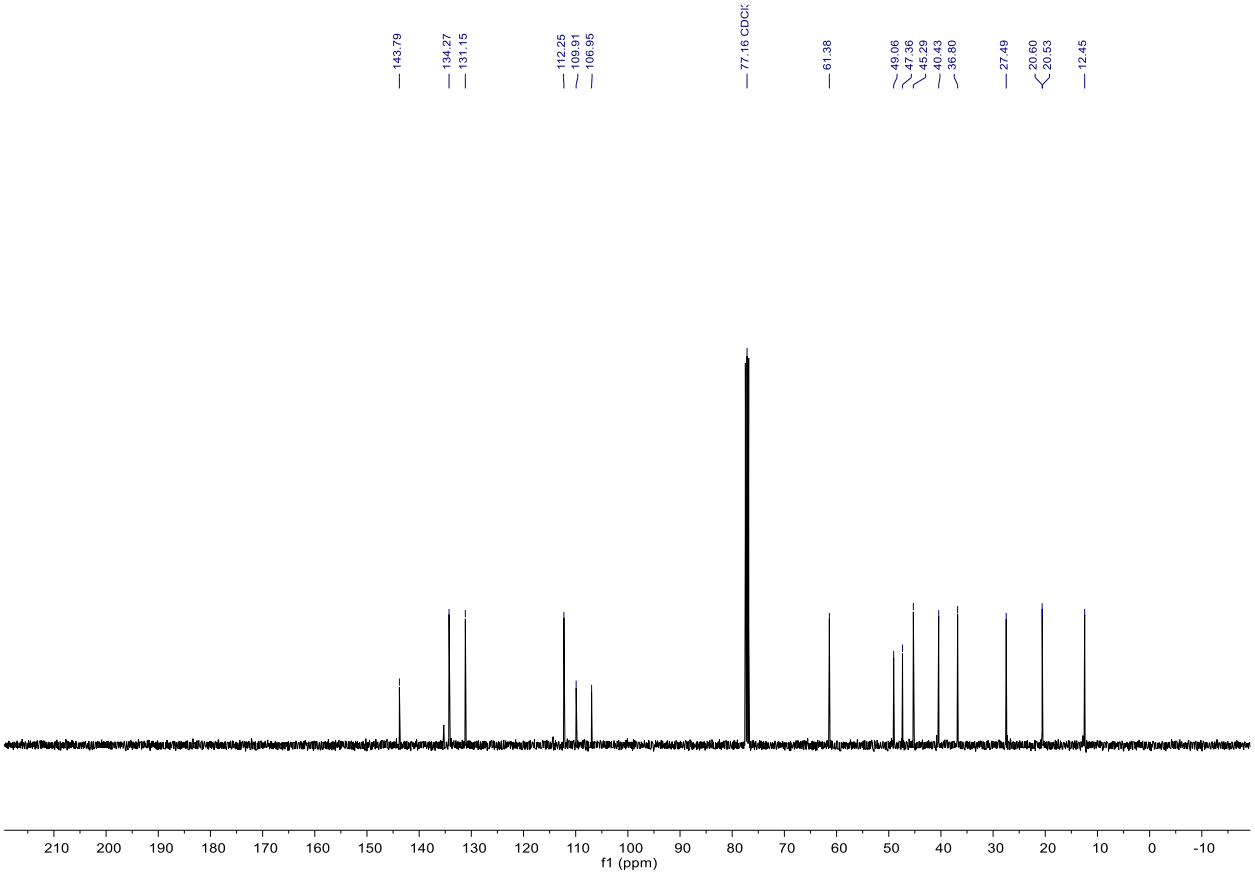
1H-15N HMBC NMR Spectrum of Compound 2a



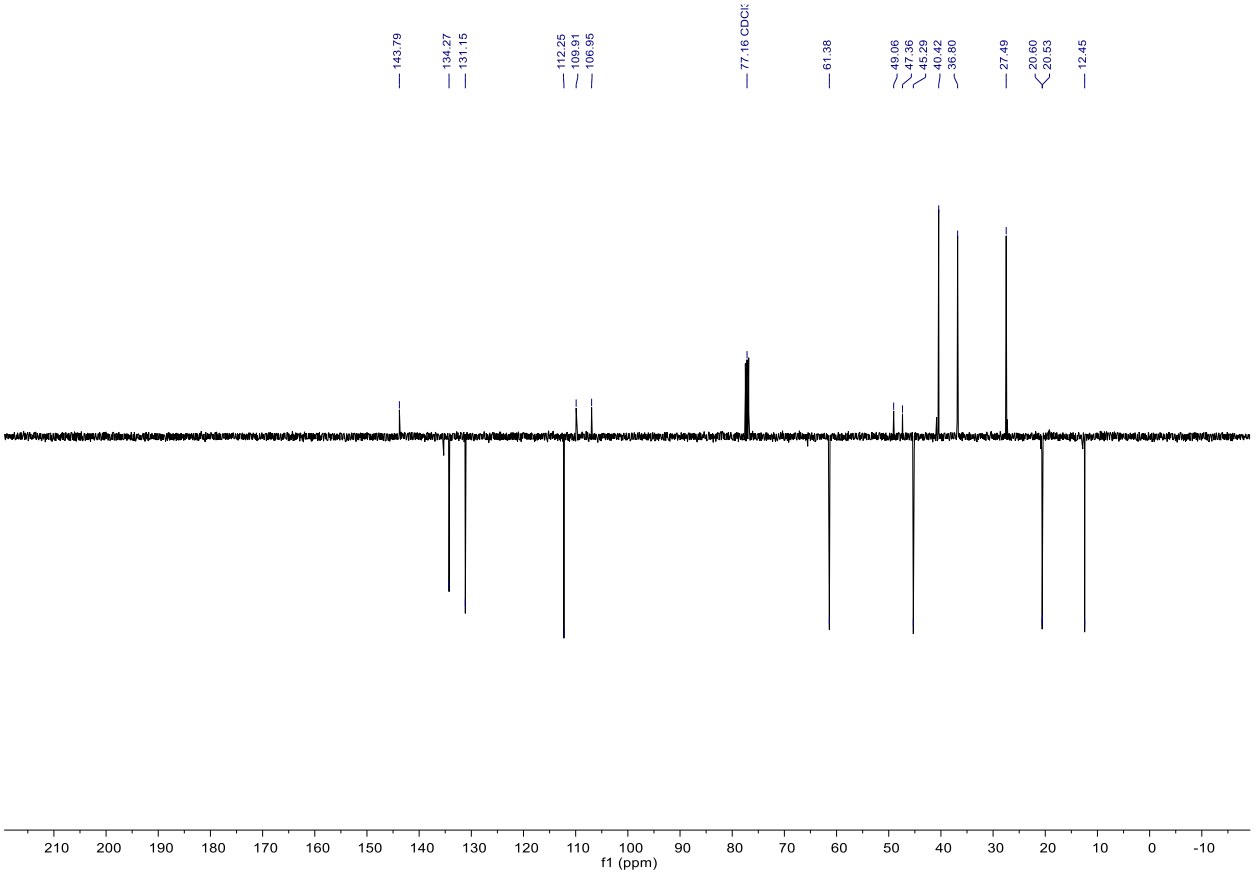
^{1}H NMR Spectrum of Compound 2a' (400 MHz, CDCl3)



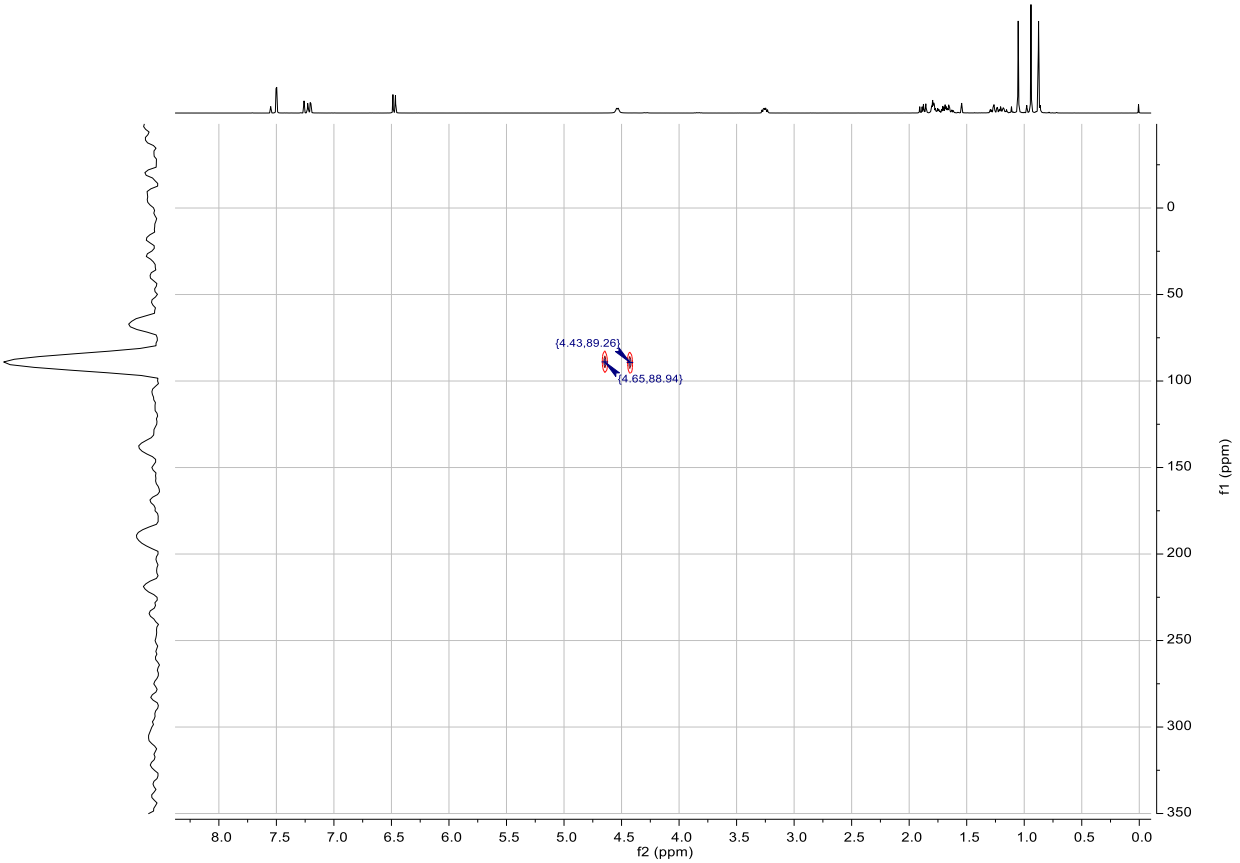
^{13}C NMR Spectrum of Compound 2a' (101 MHz, CDCl3)



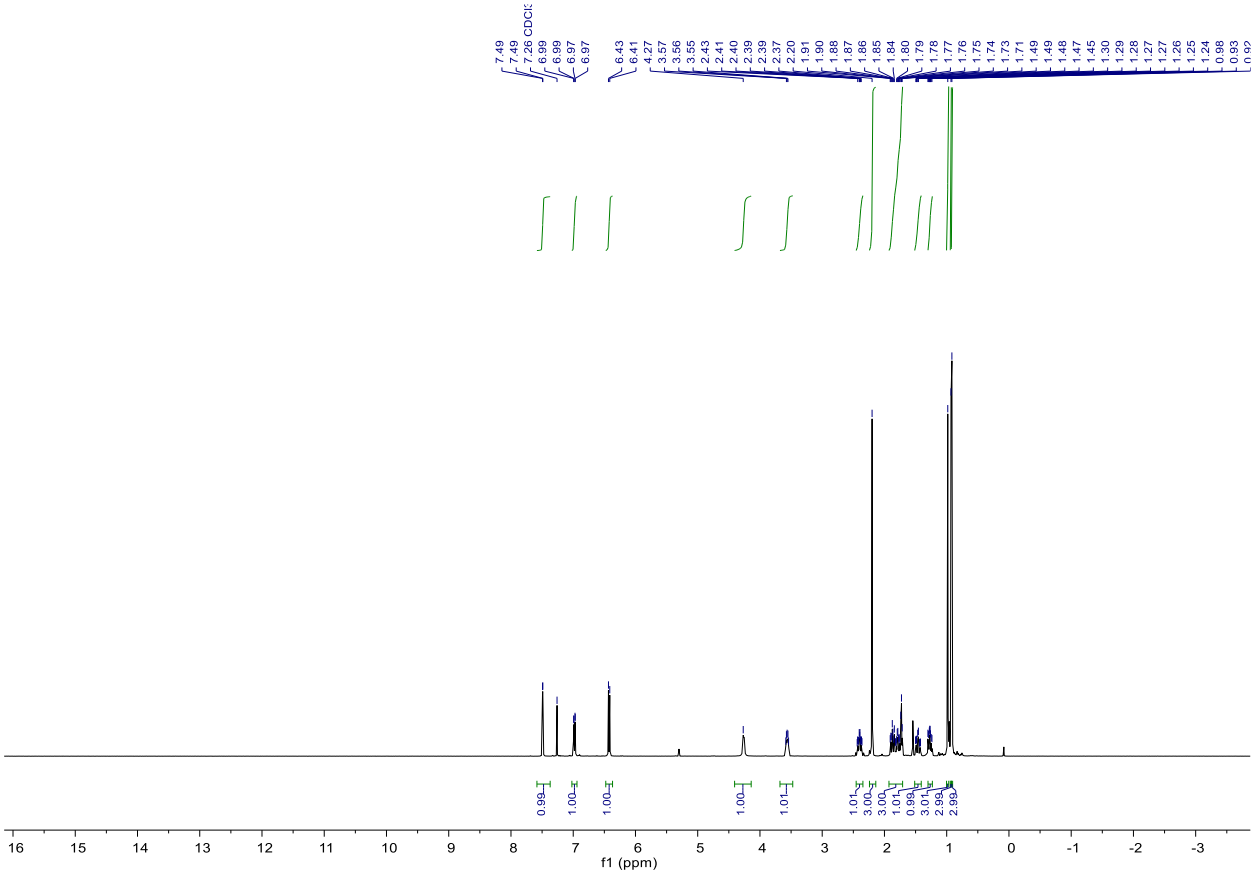
^{13}C DEPTQ-135 NMR Spectrum of Compound 2a'



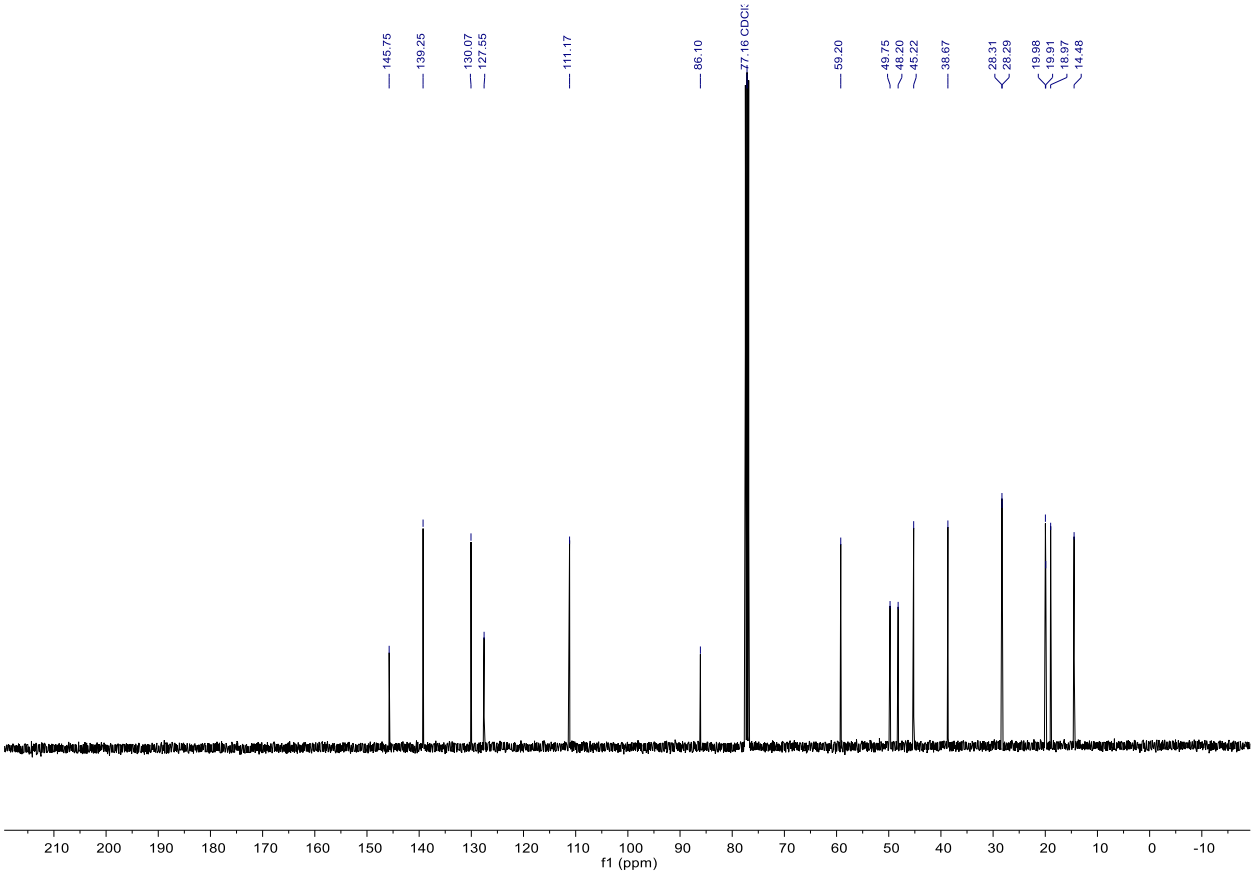
1H-15N HMBC NMR Spectrum of Compound 2a’



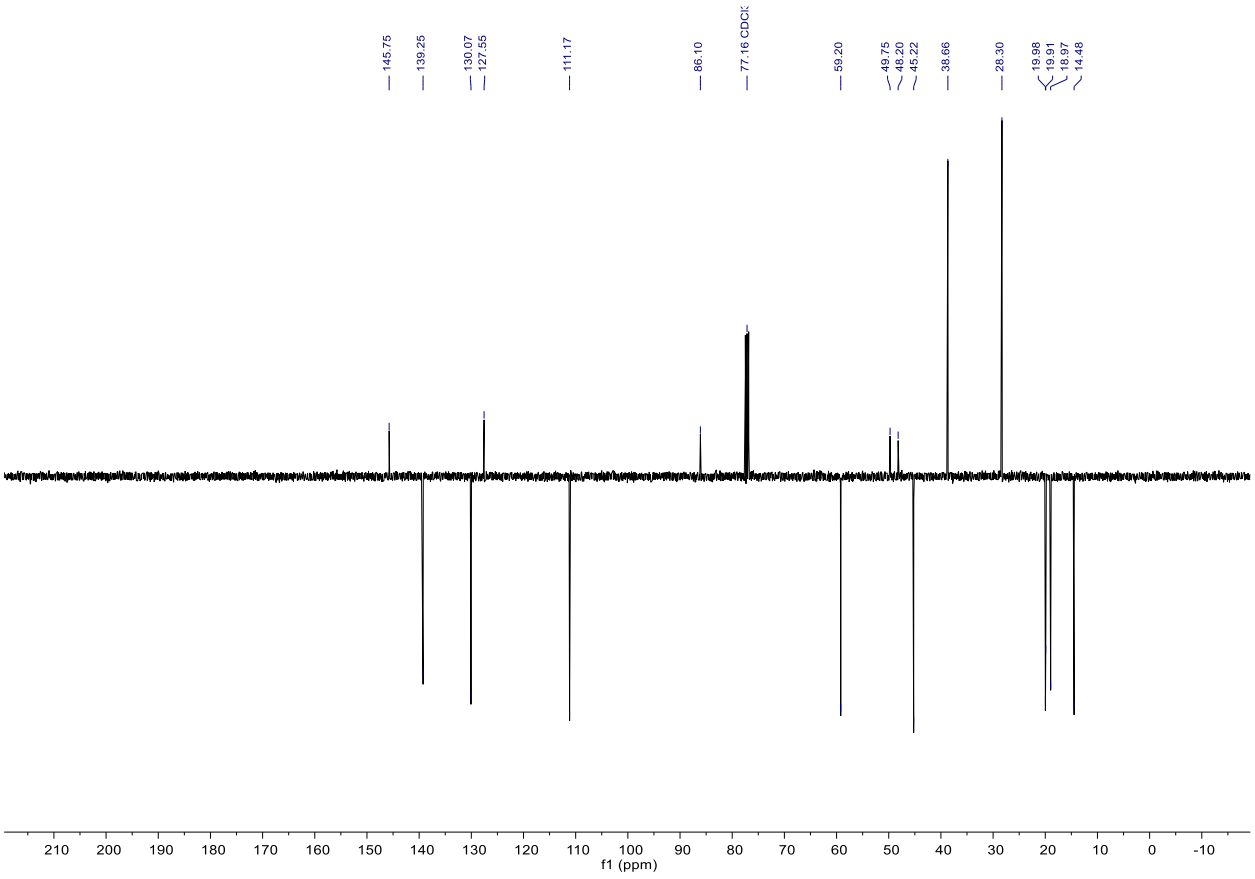
^{1}H NMR Spectrum of Compound 2b (400 MHz, CDCl3)



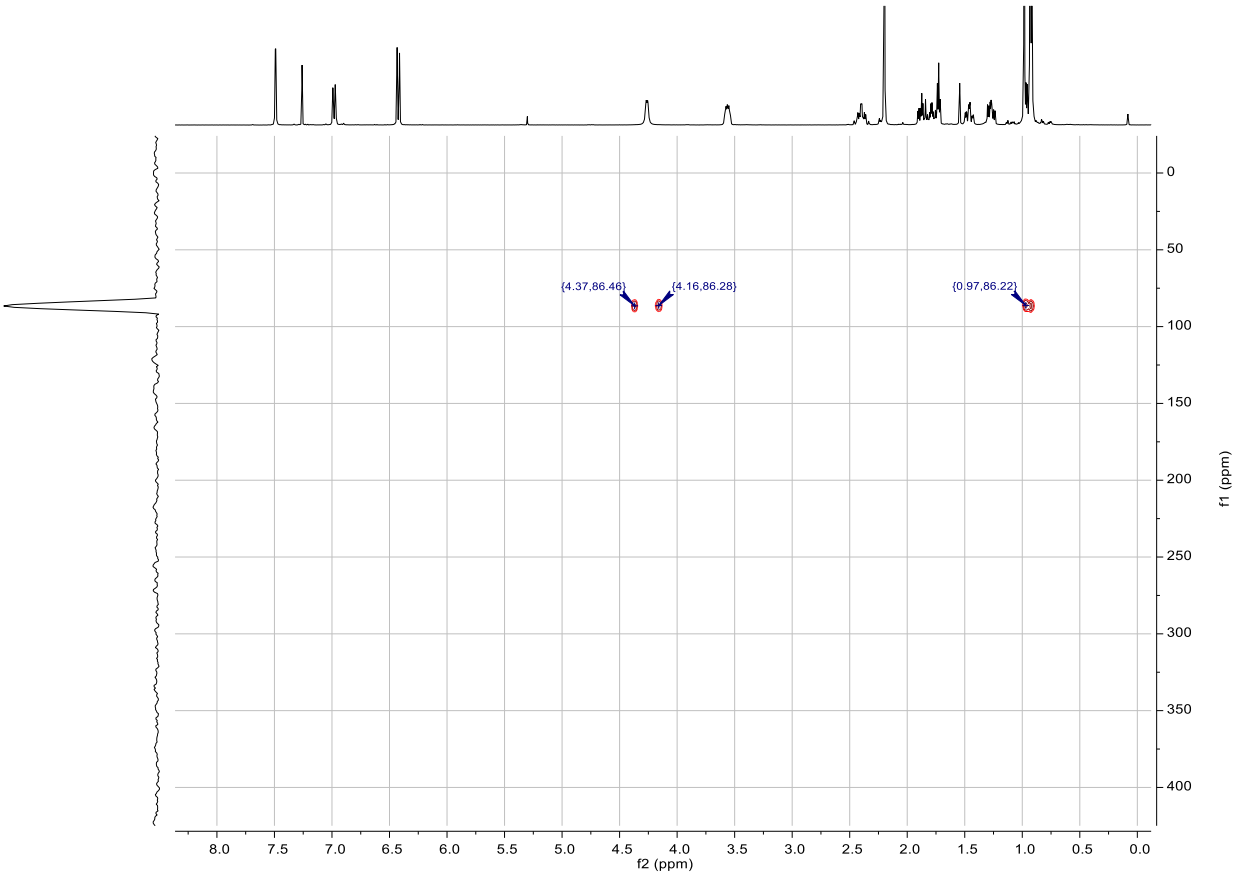
^{13}C NMR Spectrum of Compound 2b (101 MHz, CDCl3)



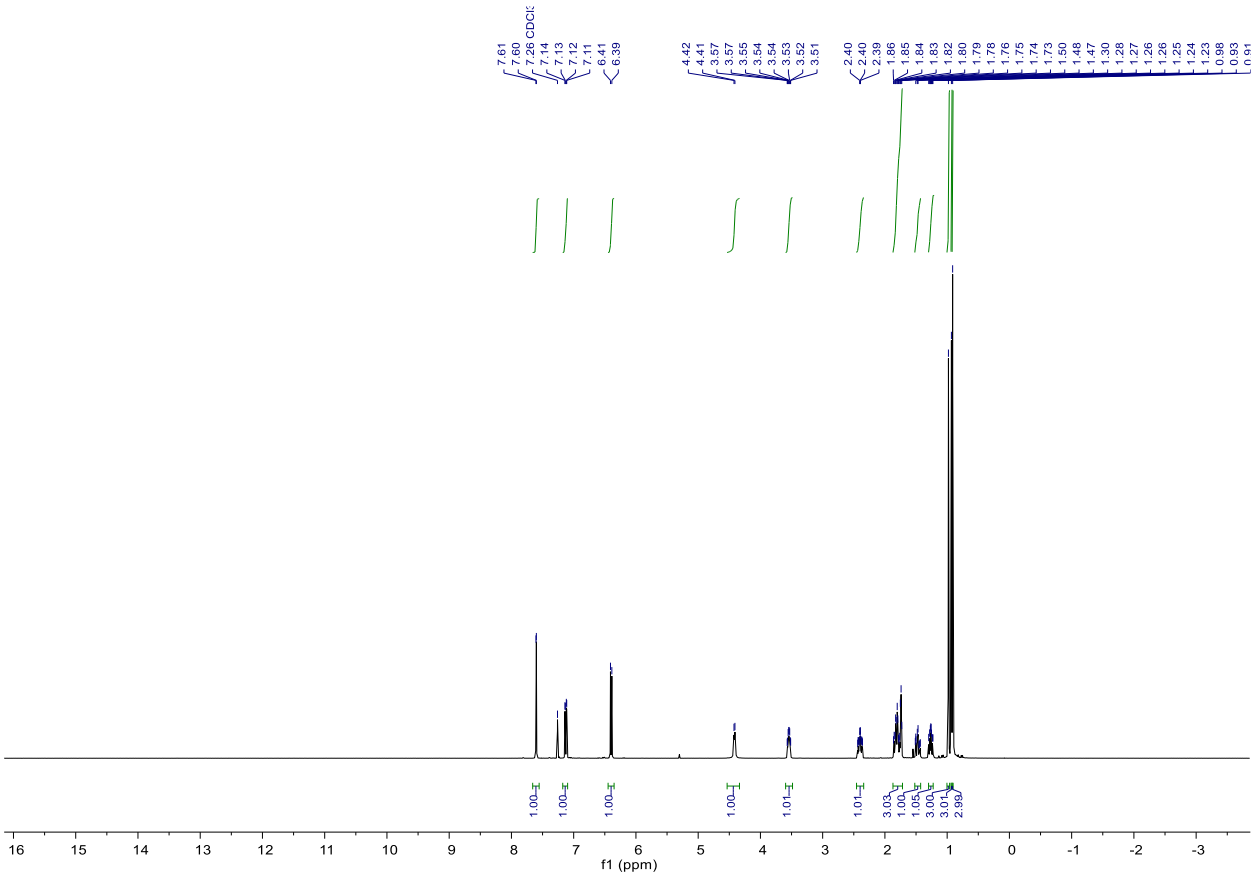
^{13}C DEPTQ-135 NMR Spectrum of Compound 2b



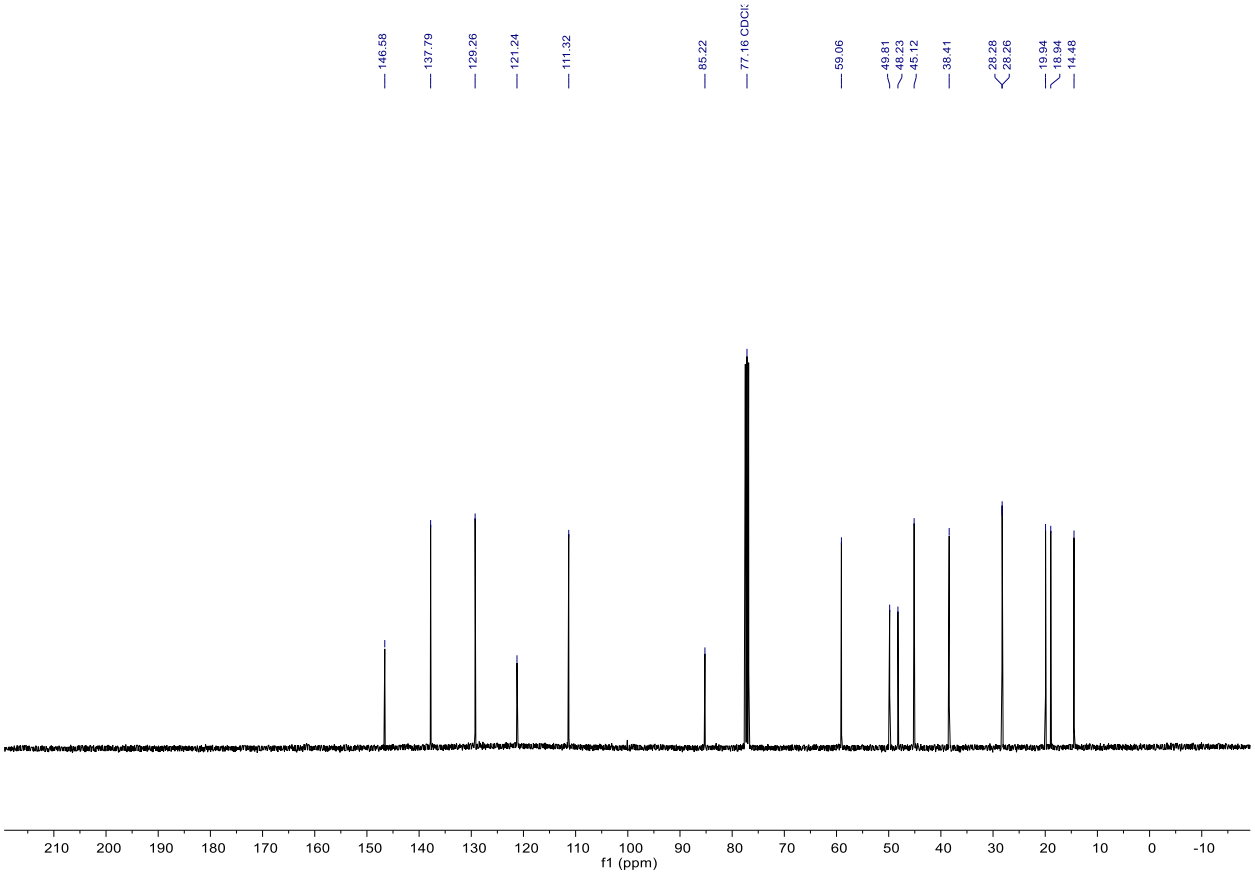
1H-15N HMBC NMR Spectrum of Compound 2b



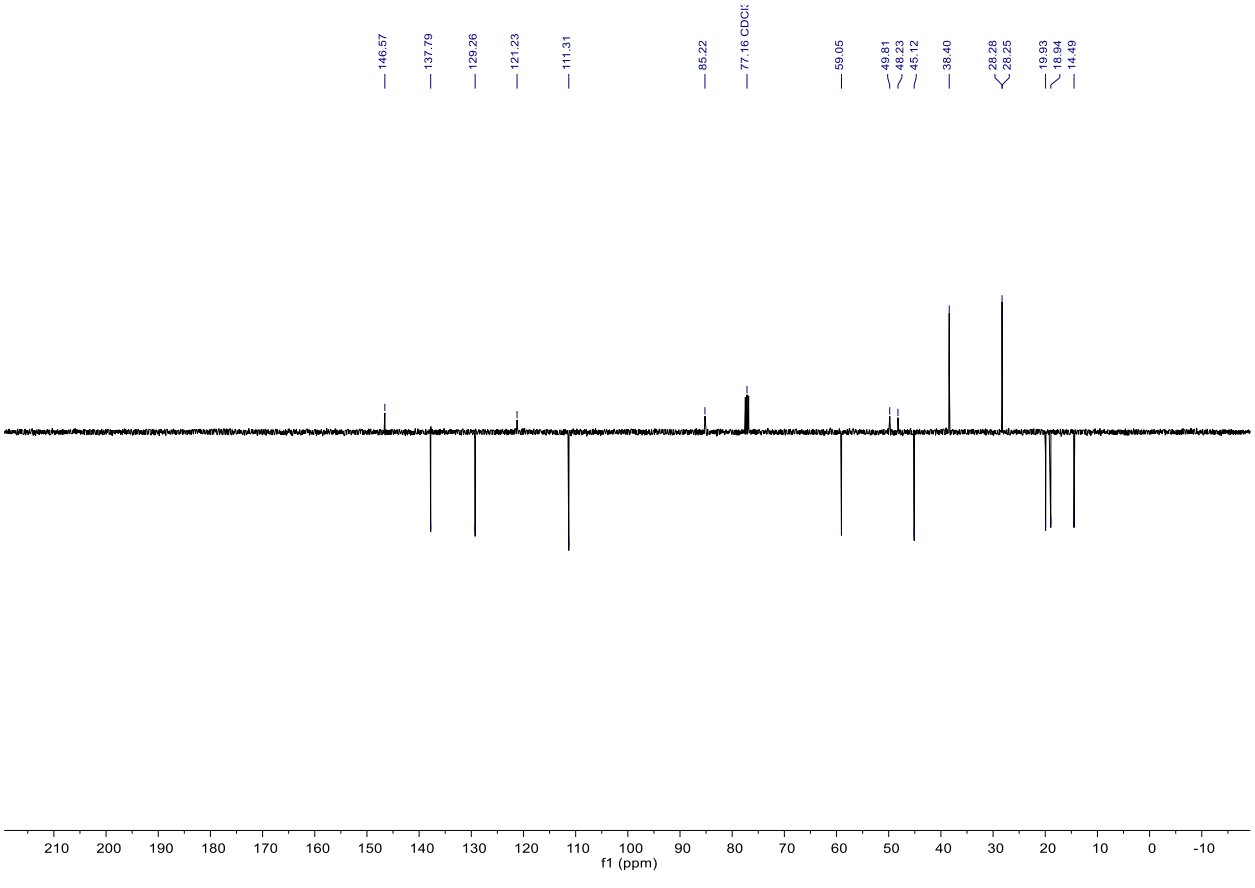
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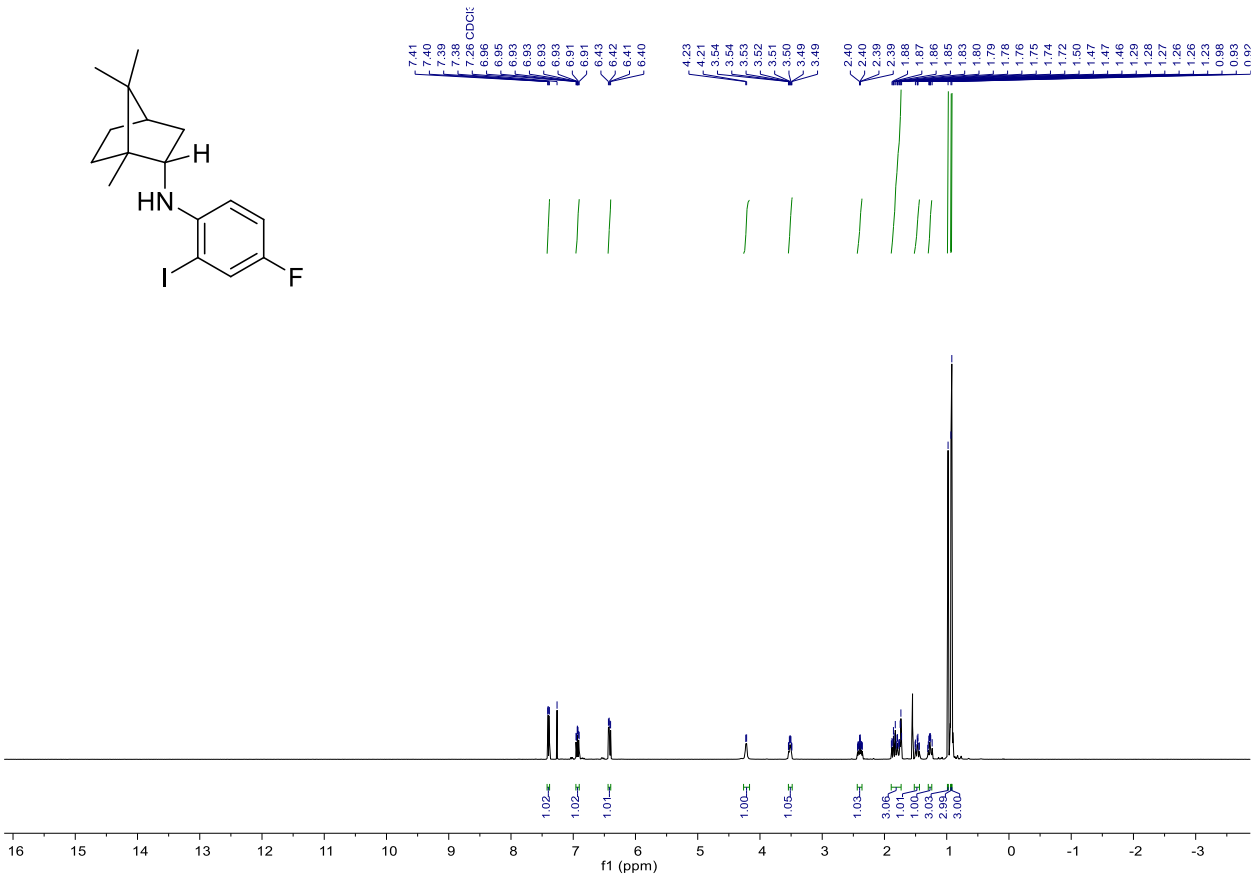
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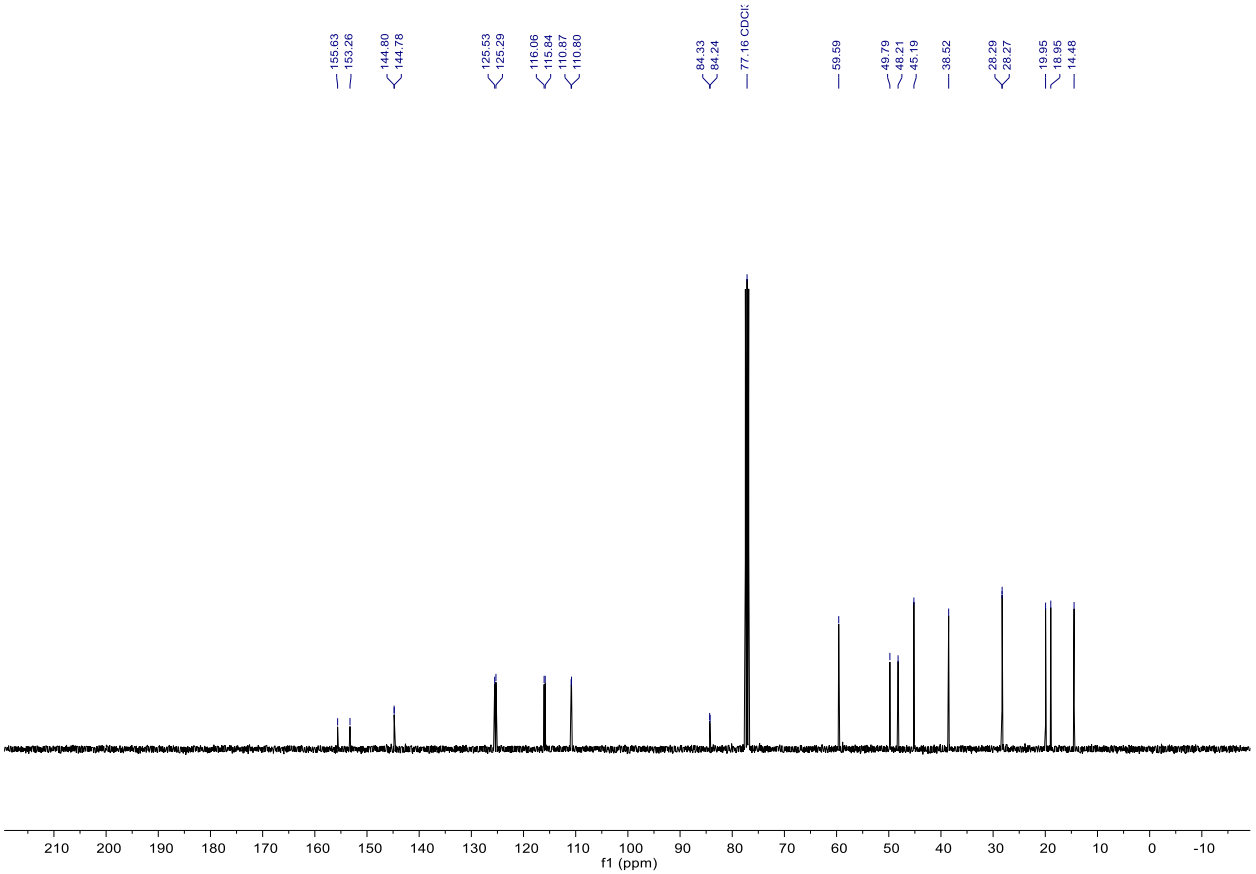
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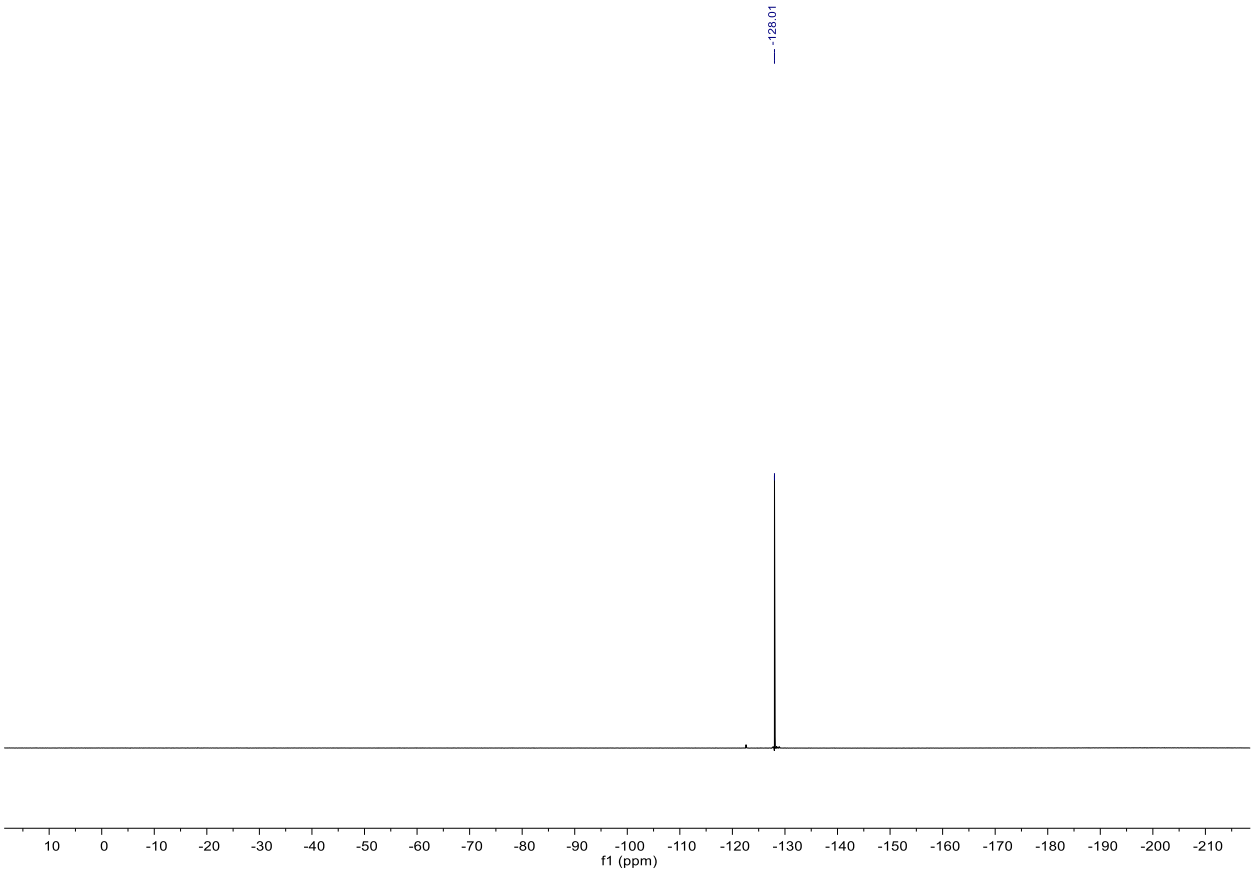
^{1}H NMR Spectrum of Compound 2d (400 MHz, CDCl3)



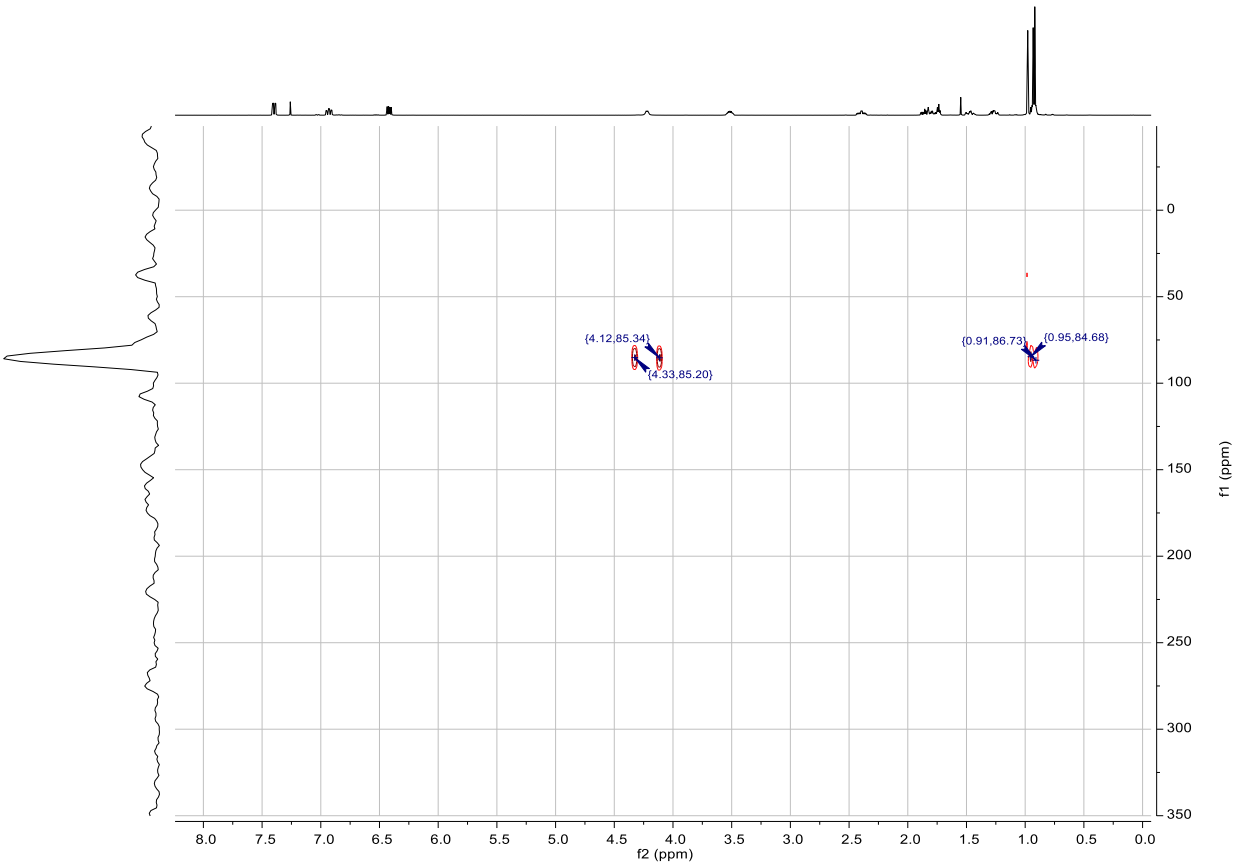
^{13}C NMR Spectrum of Compound 2d (101 MHz, CDCl3)



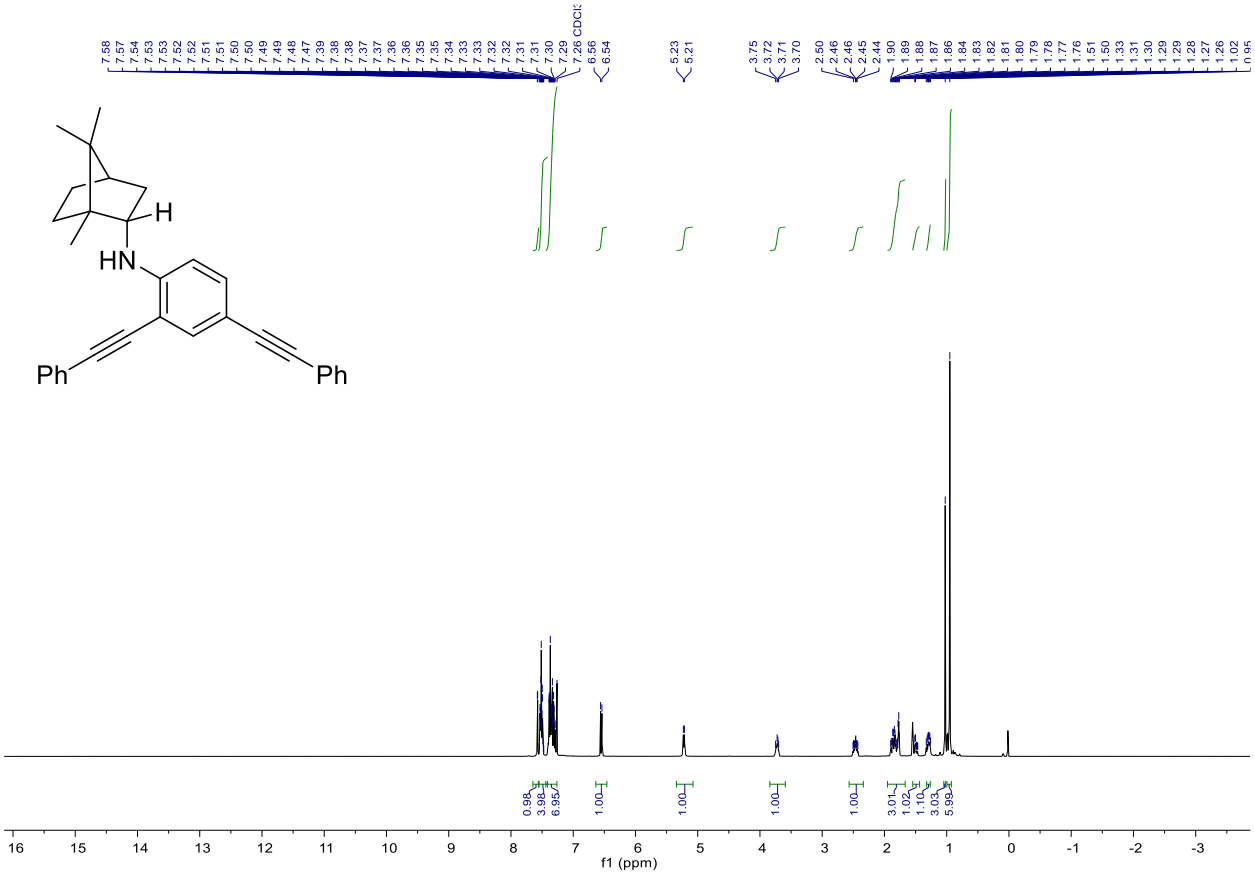
^{19}F NMR Spectrum of Compound 2d(376 MHz, CDCl3)



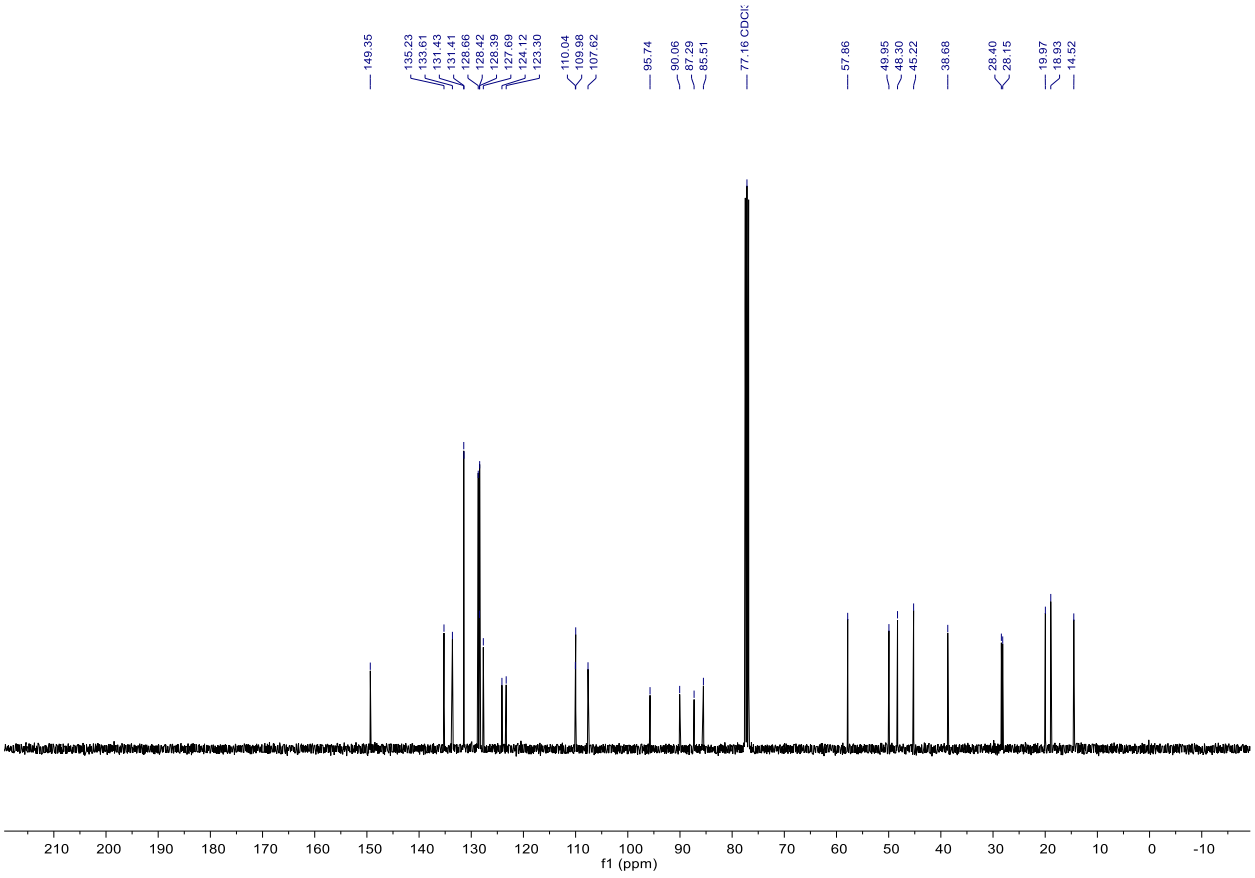
1H-15N HMBC NMR Spectrum of Compound 2d



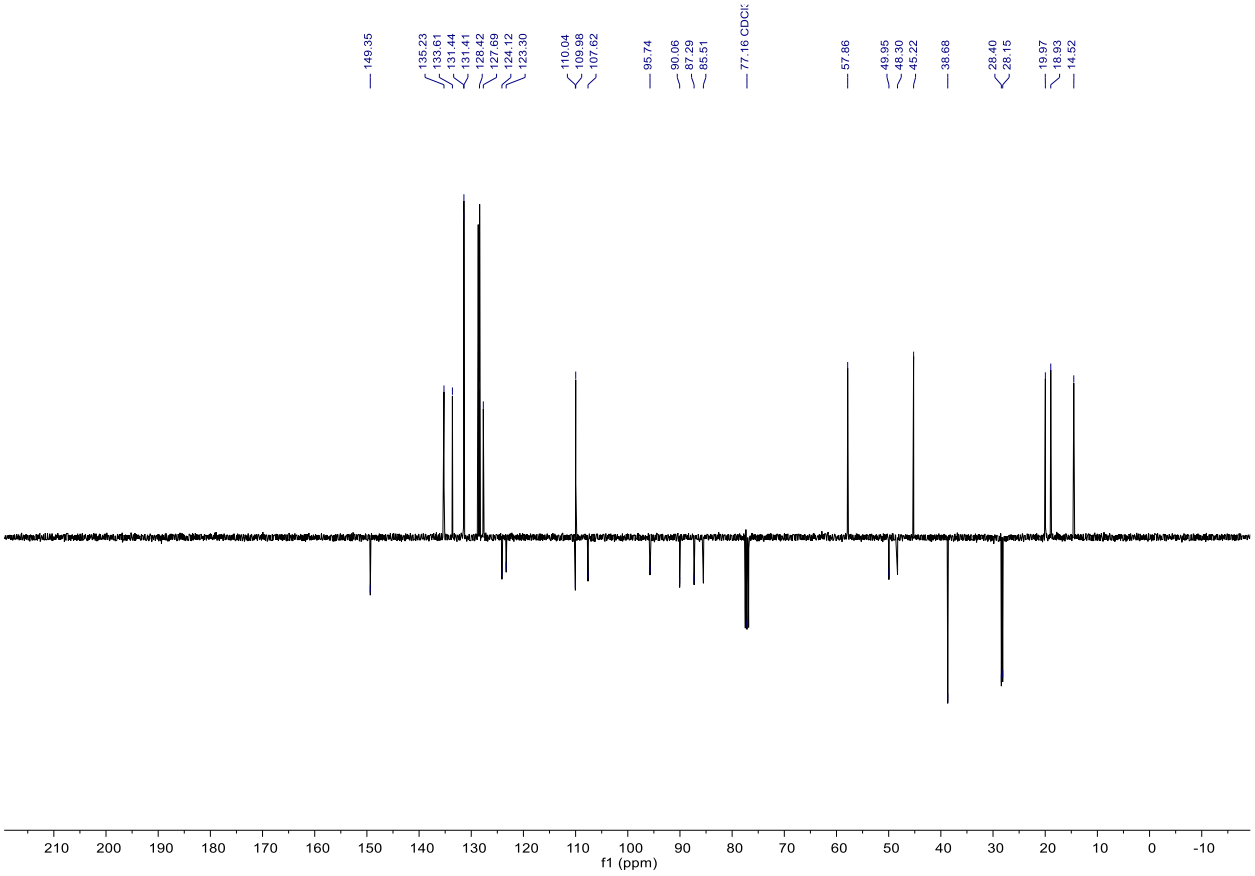
^{1}H NMR Spectrum of Compound 4aa (400 MHz, CDCl3)



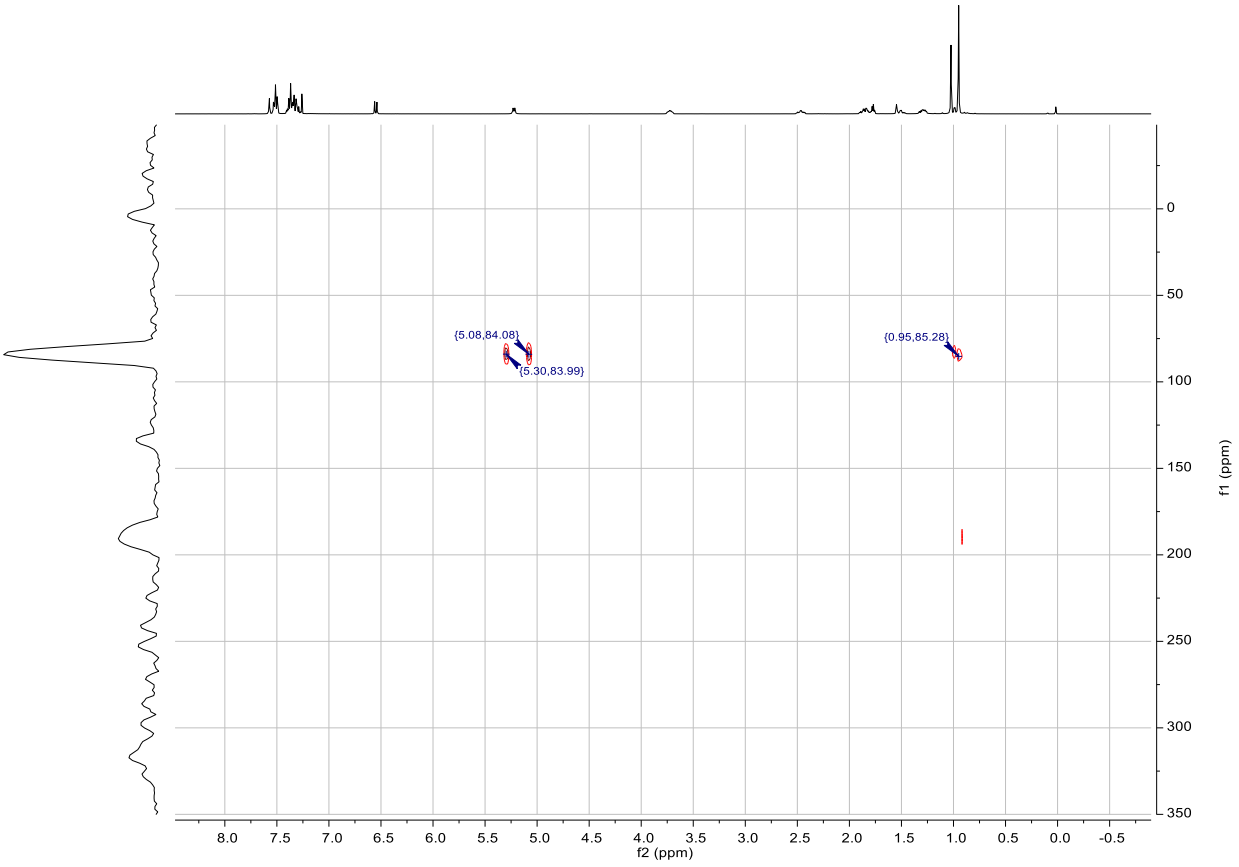
^{13}C NMR Spectrum of Compound 4aa (101 MHz, CDCl3)



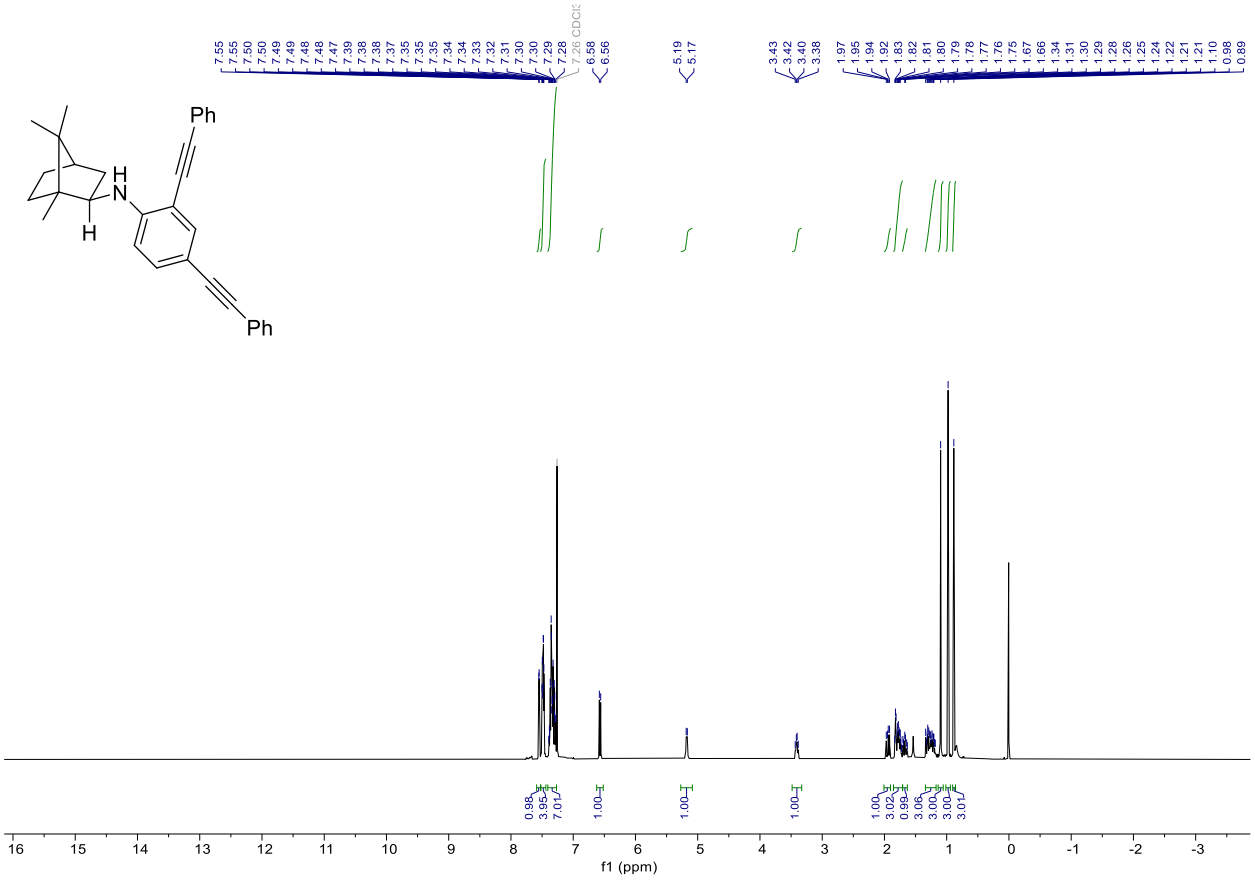
^{13}C DEPTQ-135 NMR Spectrum of Compound 4aa



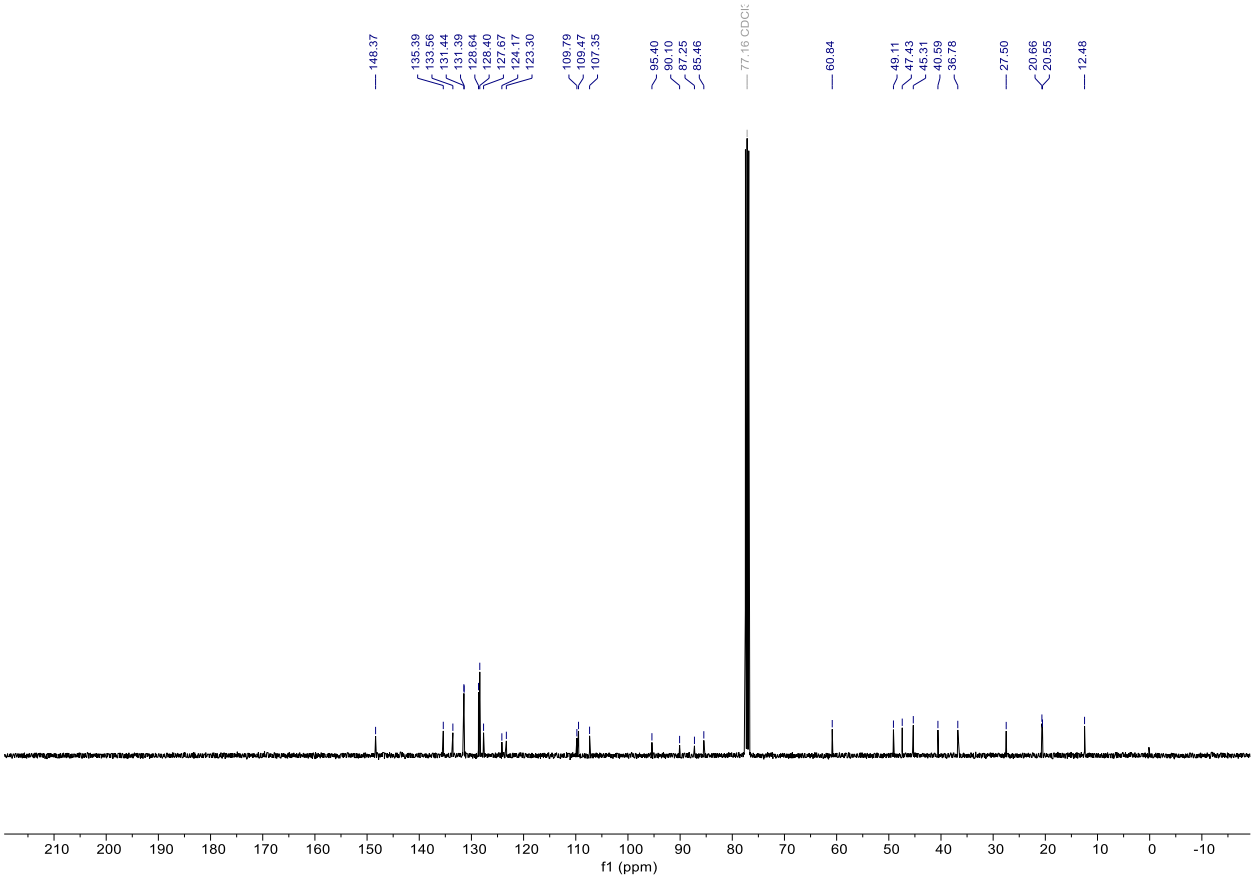
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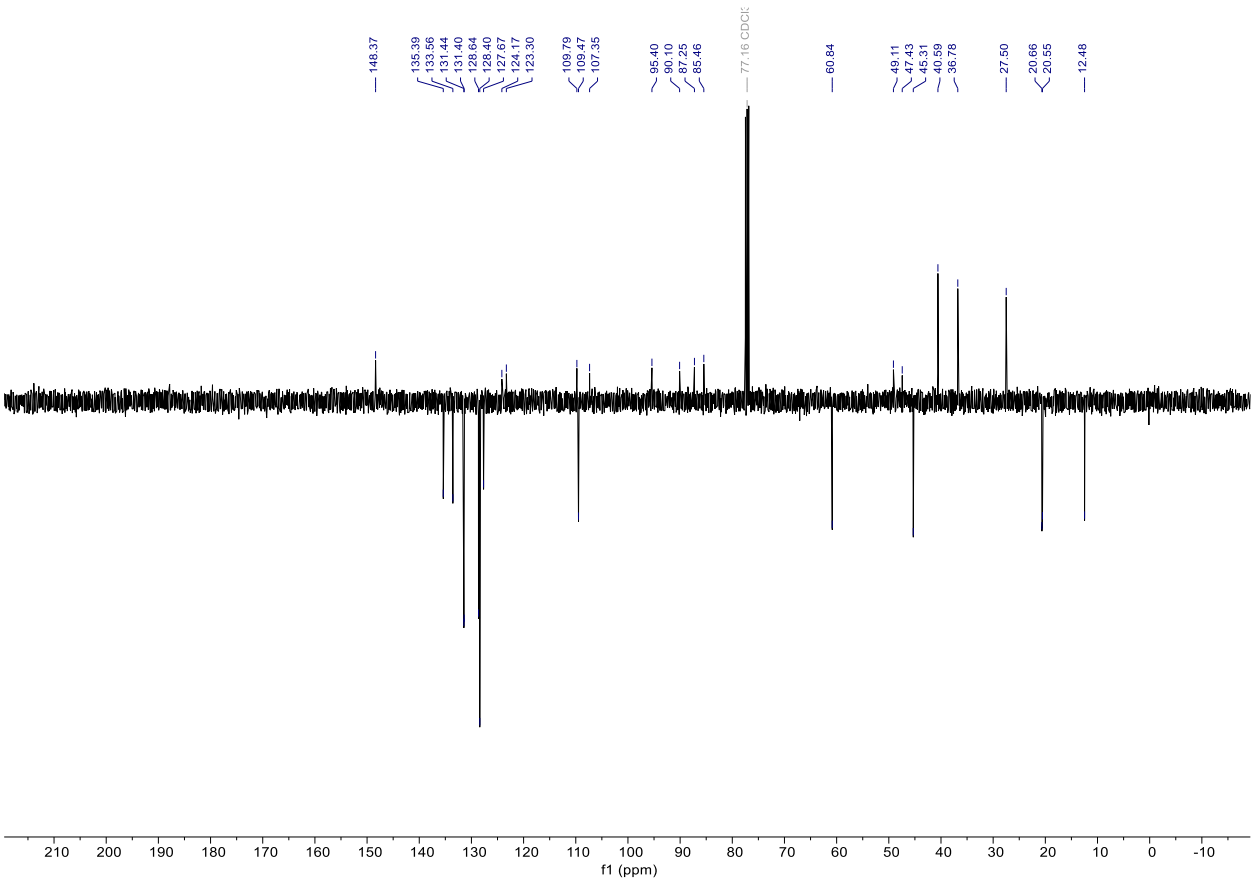
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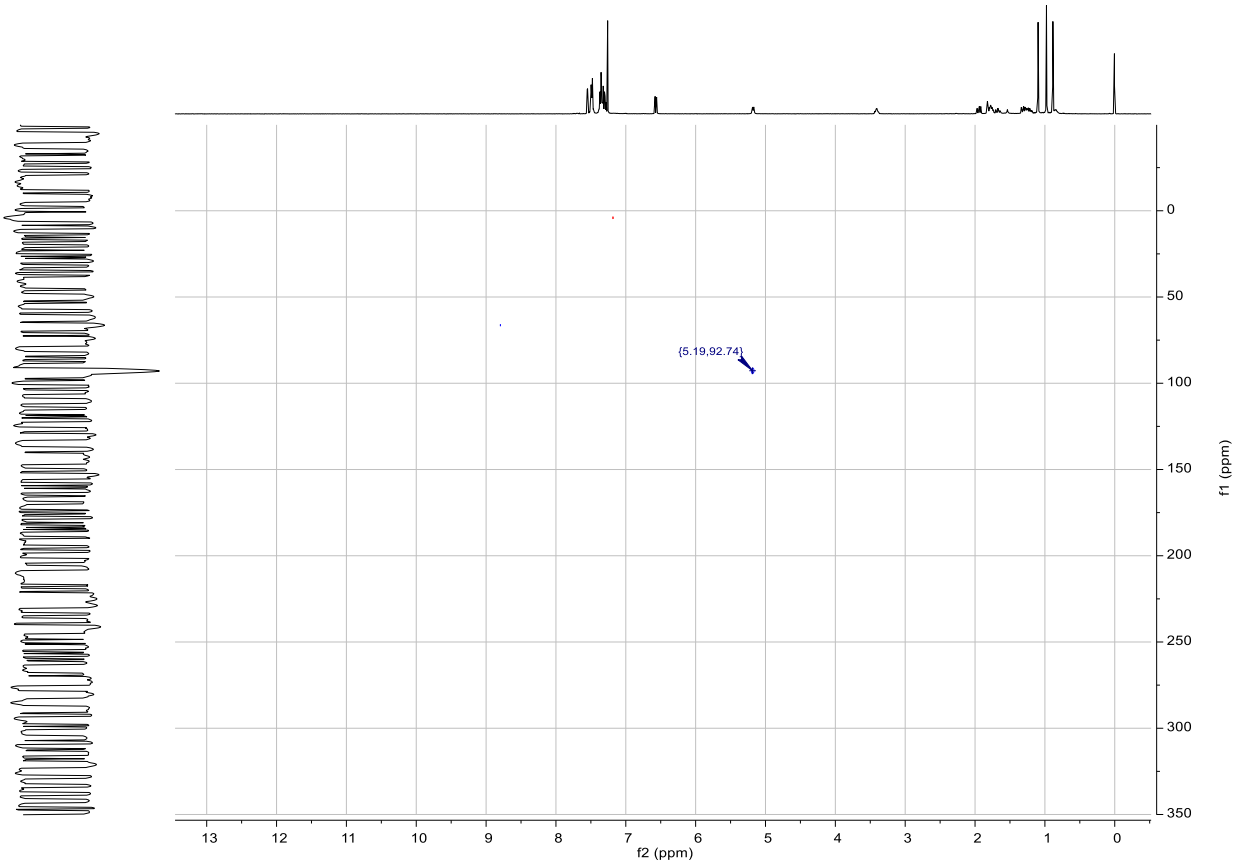
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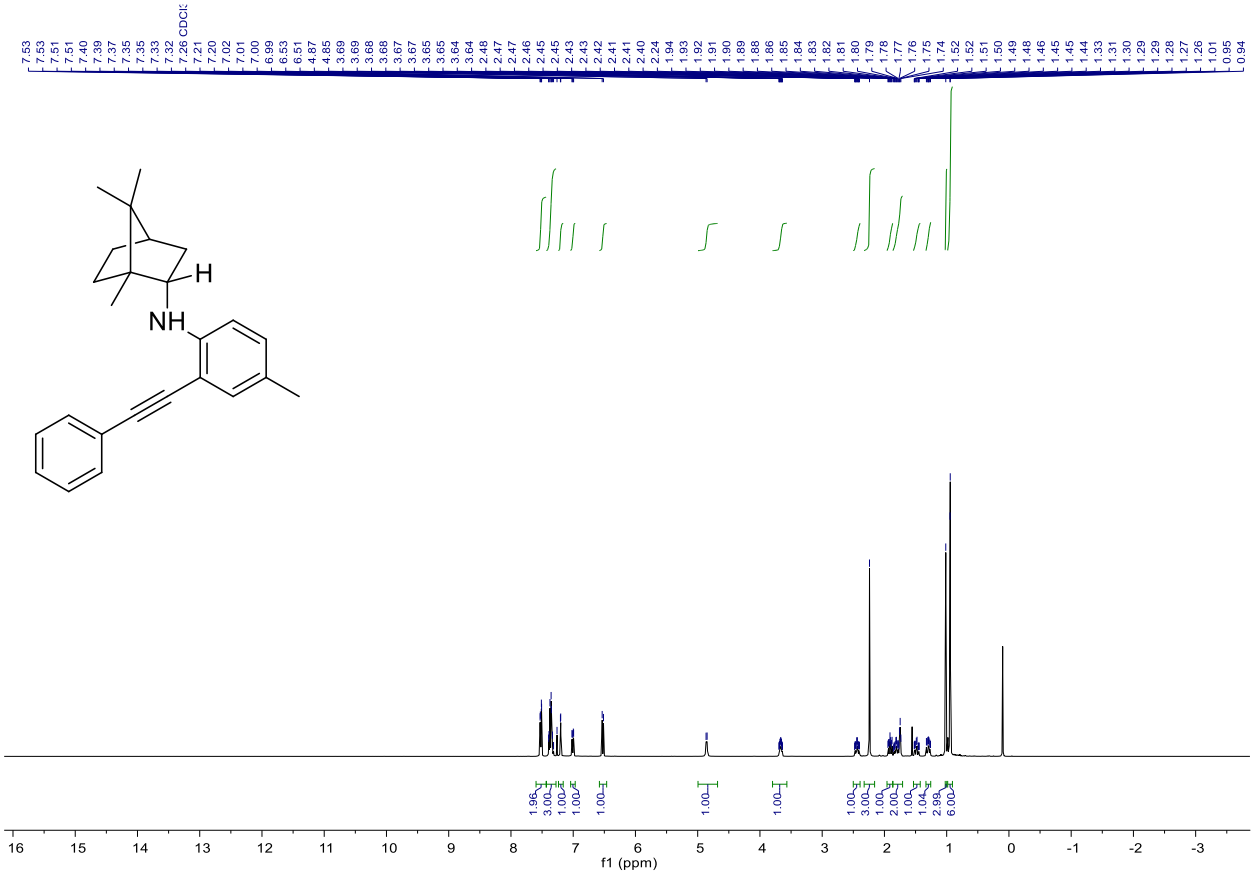
^{13}C DEPTQ-135 NMR Spectrum of Compound 4aa’



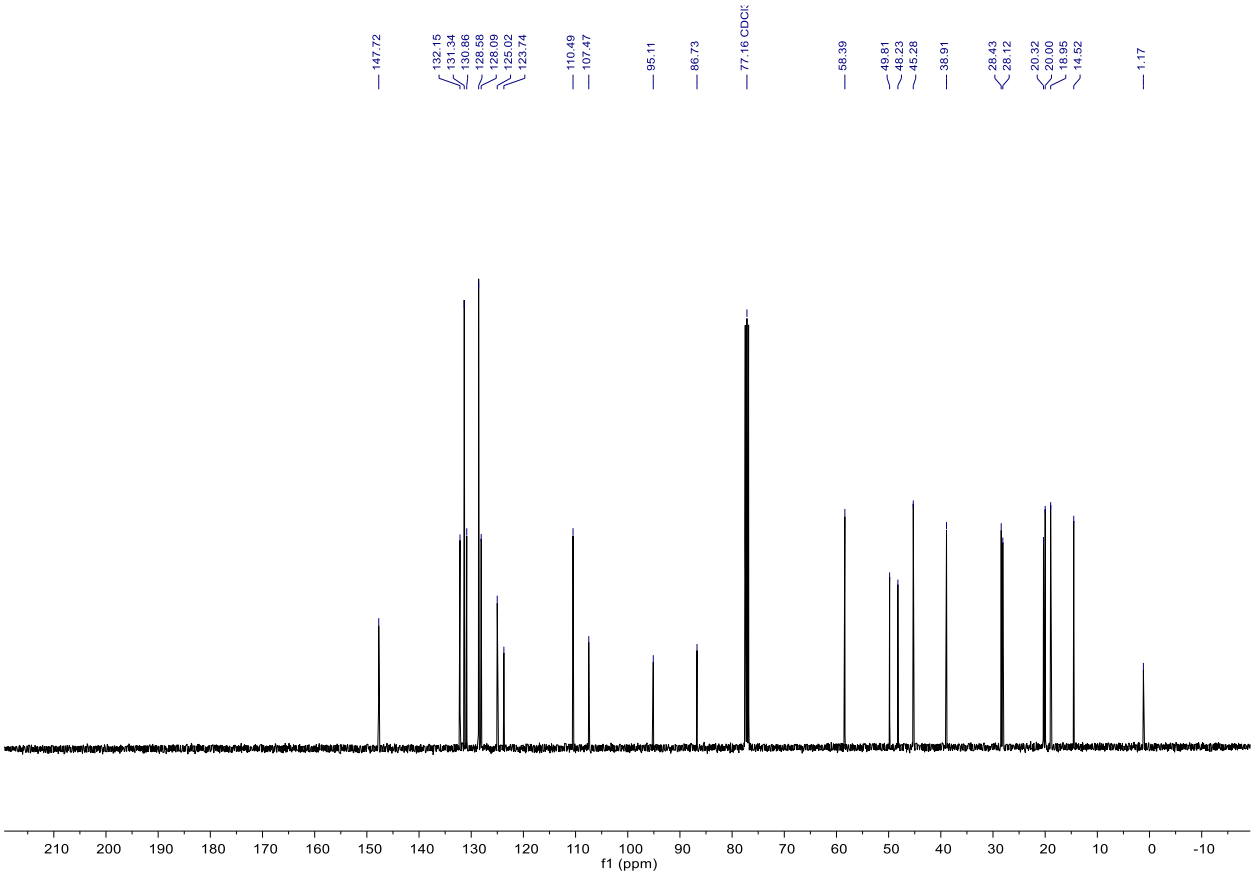
1H-15N HSQC NMR Spectrum of Compound 4aa’



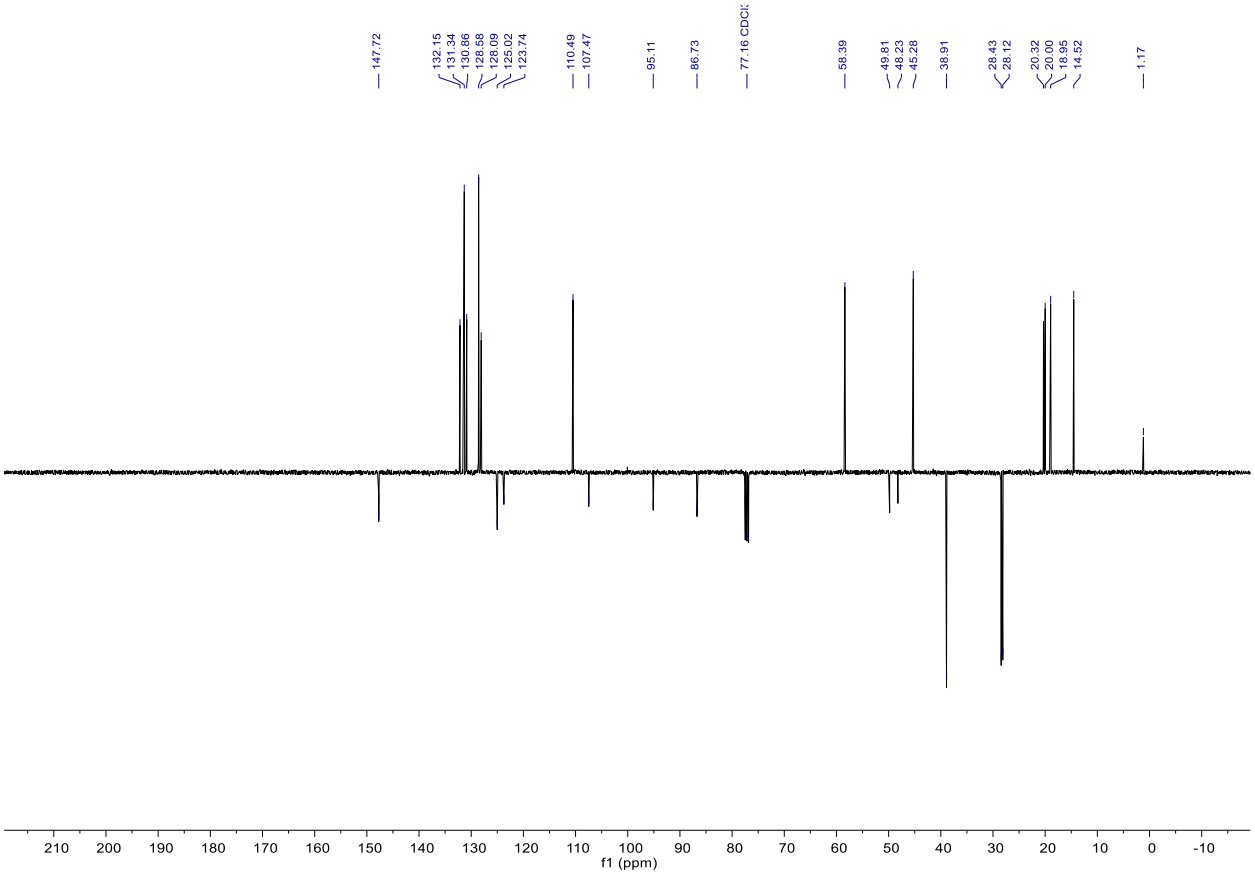
^{1}H NMR Spectrum of Compound 4ba (400 MHz, CDCl3)



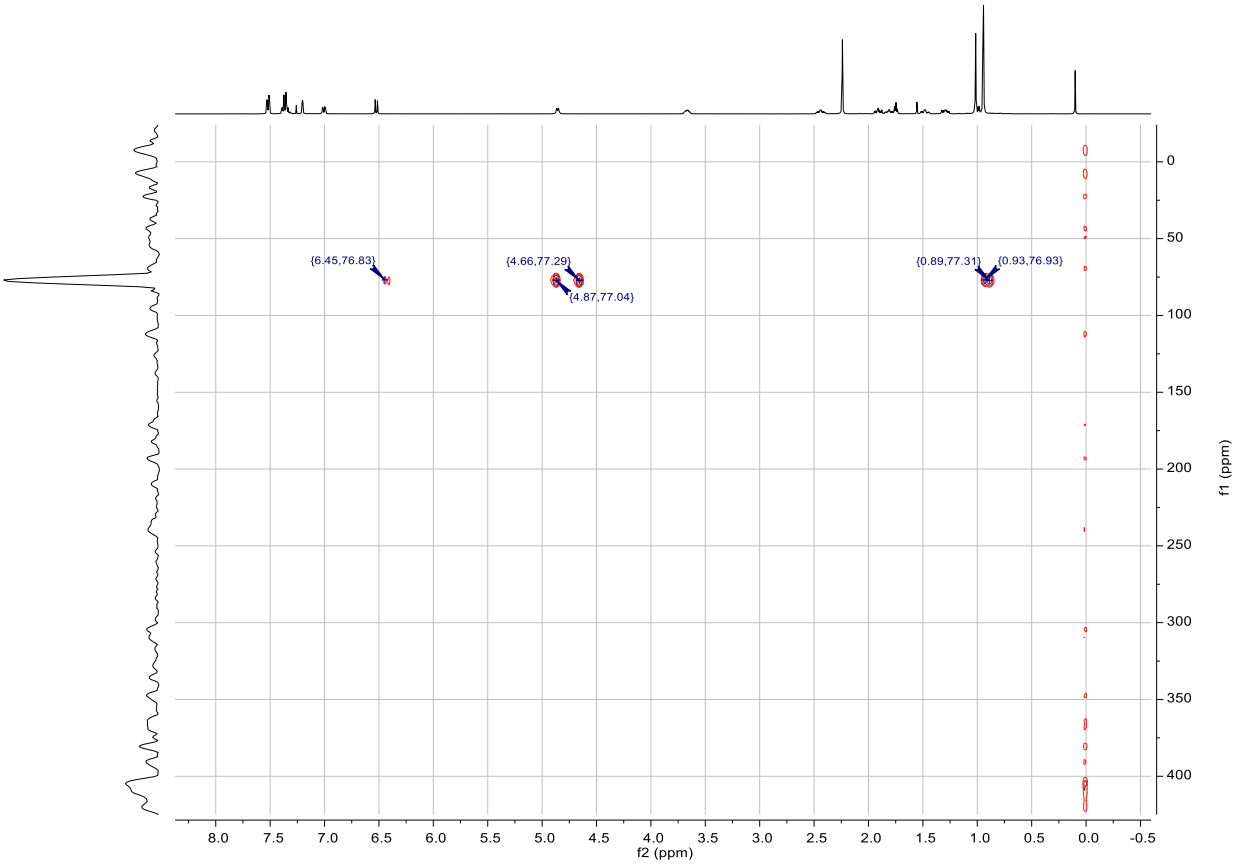
^{13}C NMR Spectrum of Compound 4ba (101 MHz, CDCl3)



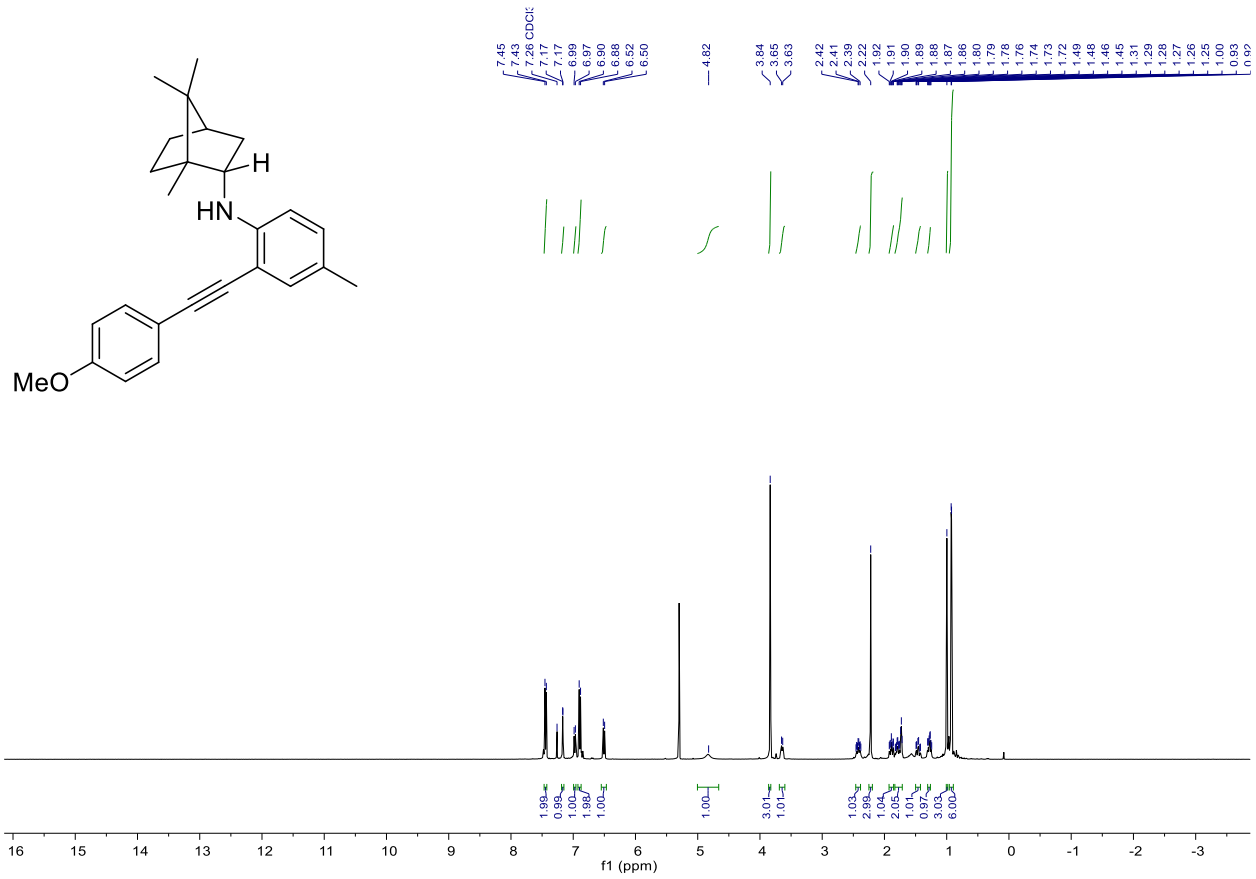
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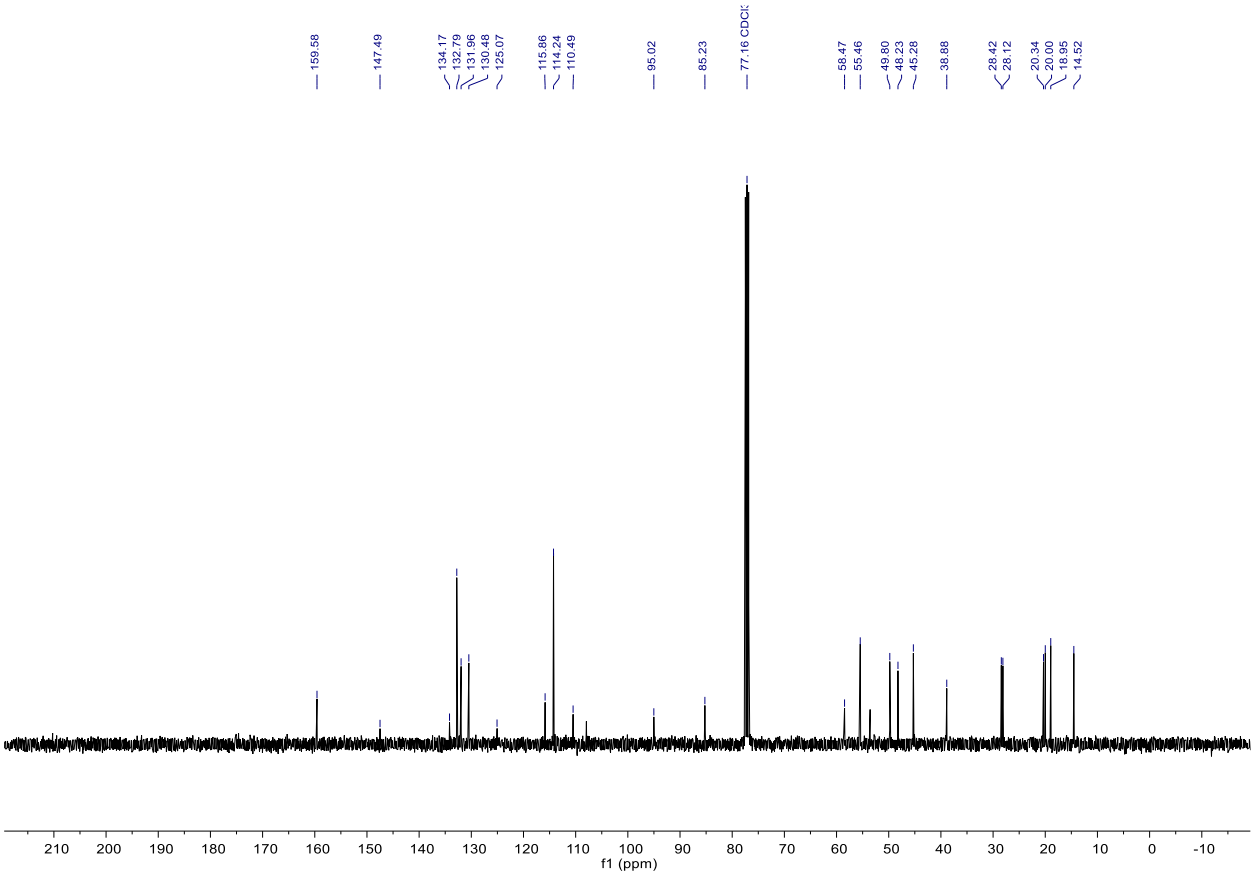
1H-15N HMBC NMR Spectrum of Compound 4ba



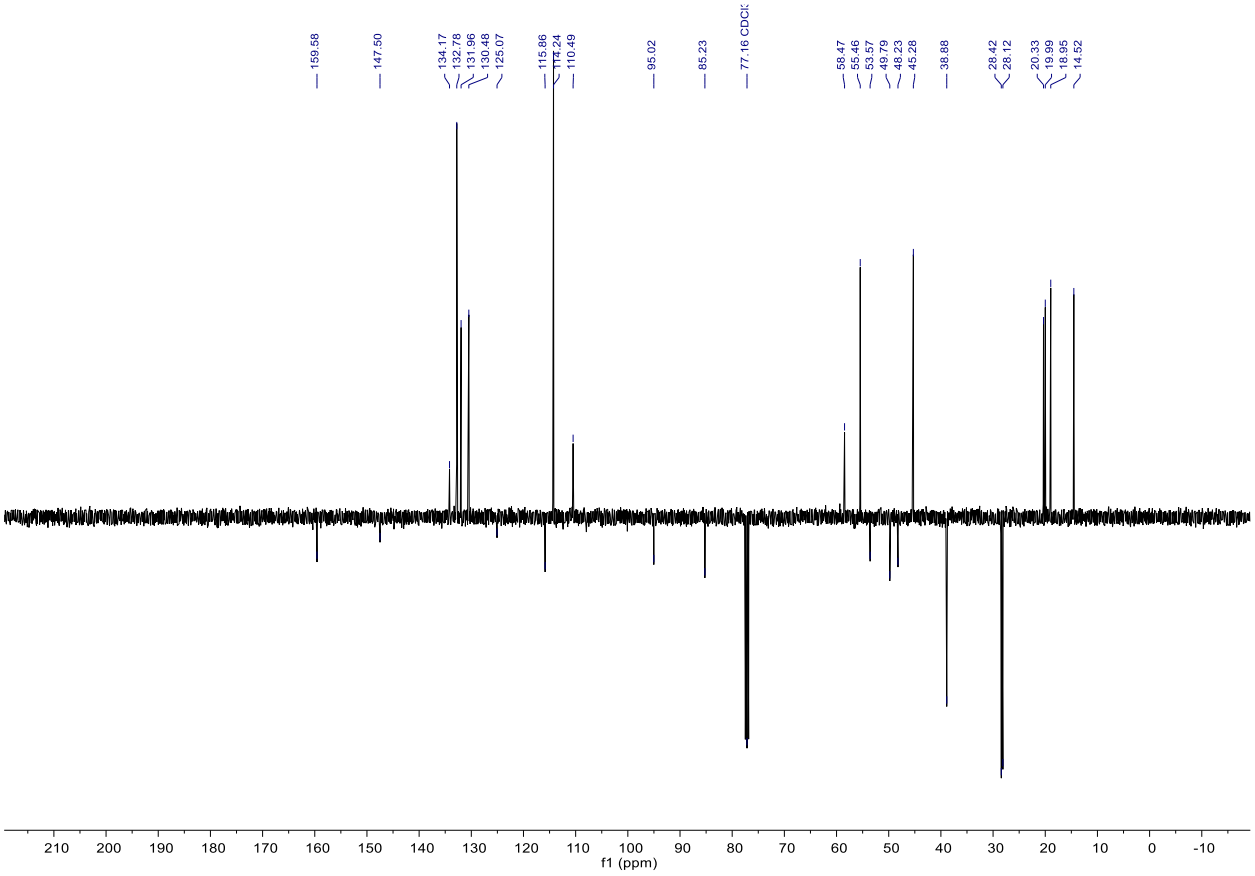
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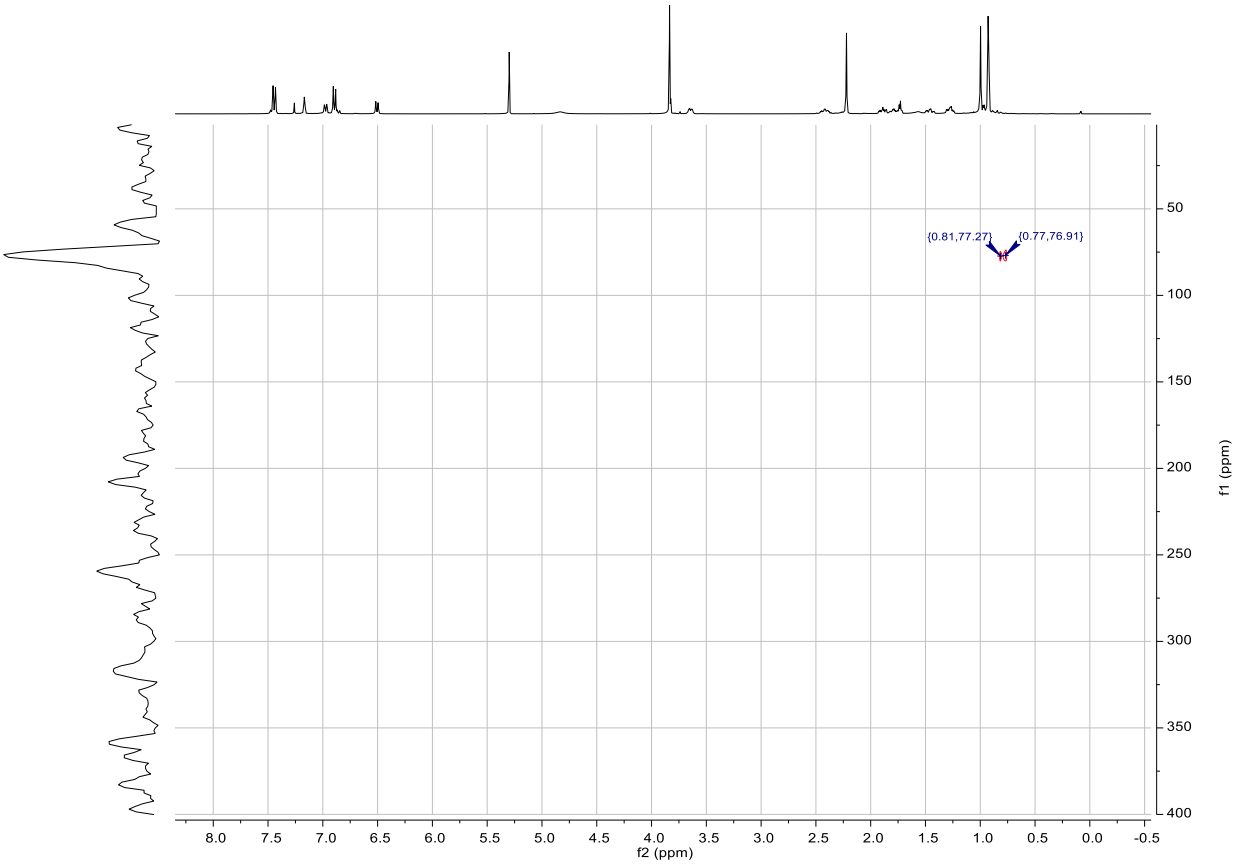
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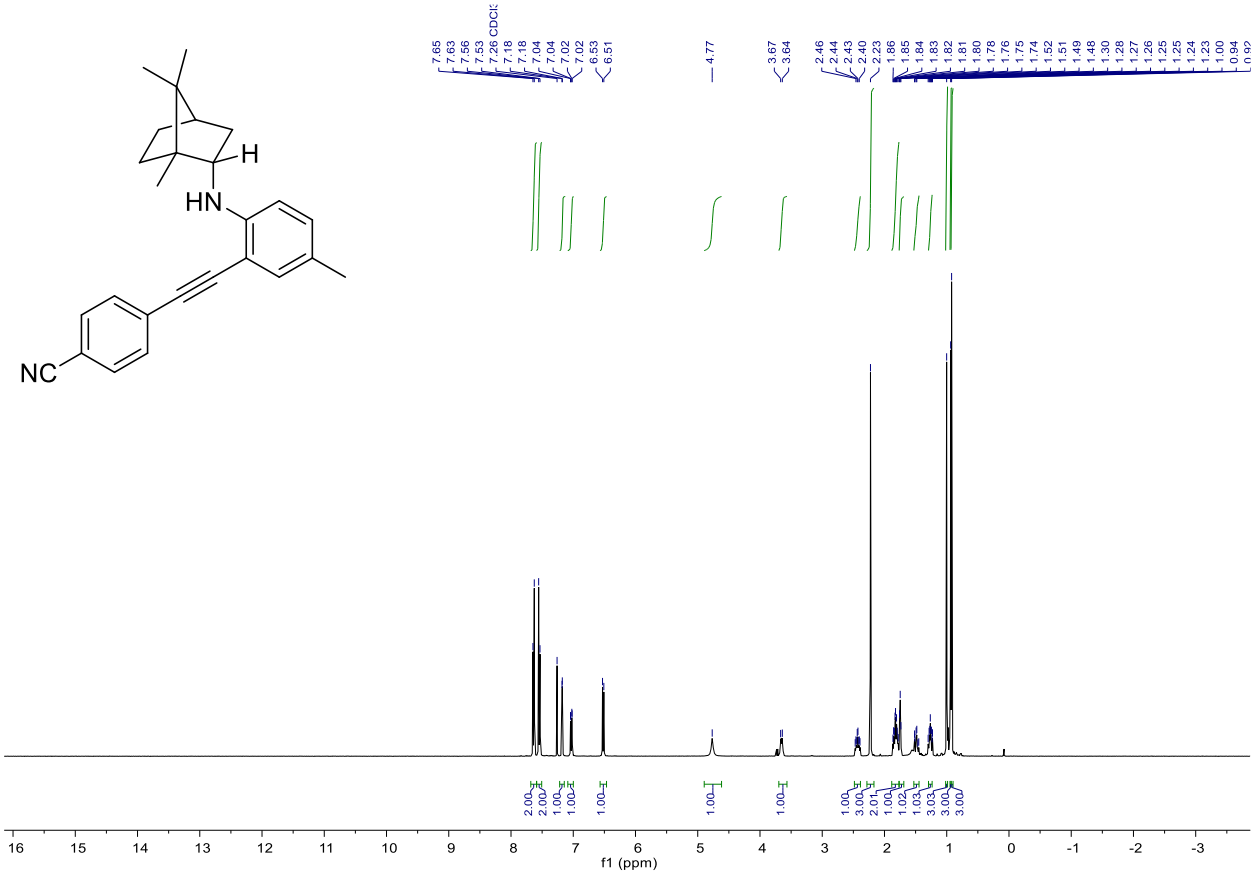
^{13}C DEPTQ-135 NMR Spectrum of Compound 4bb



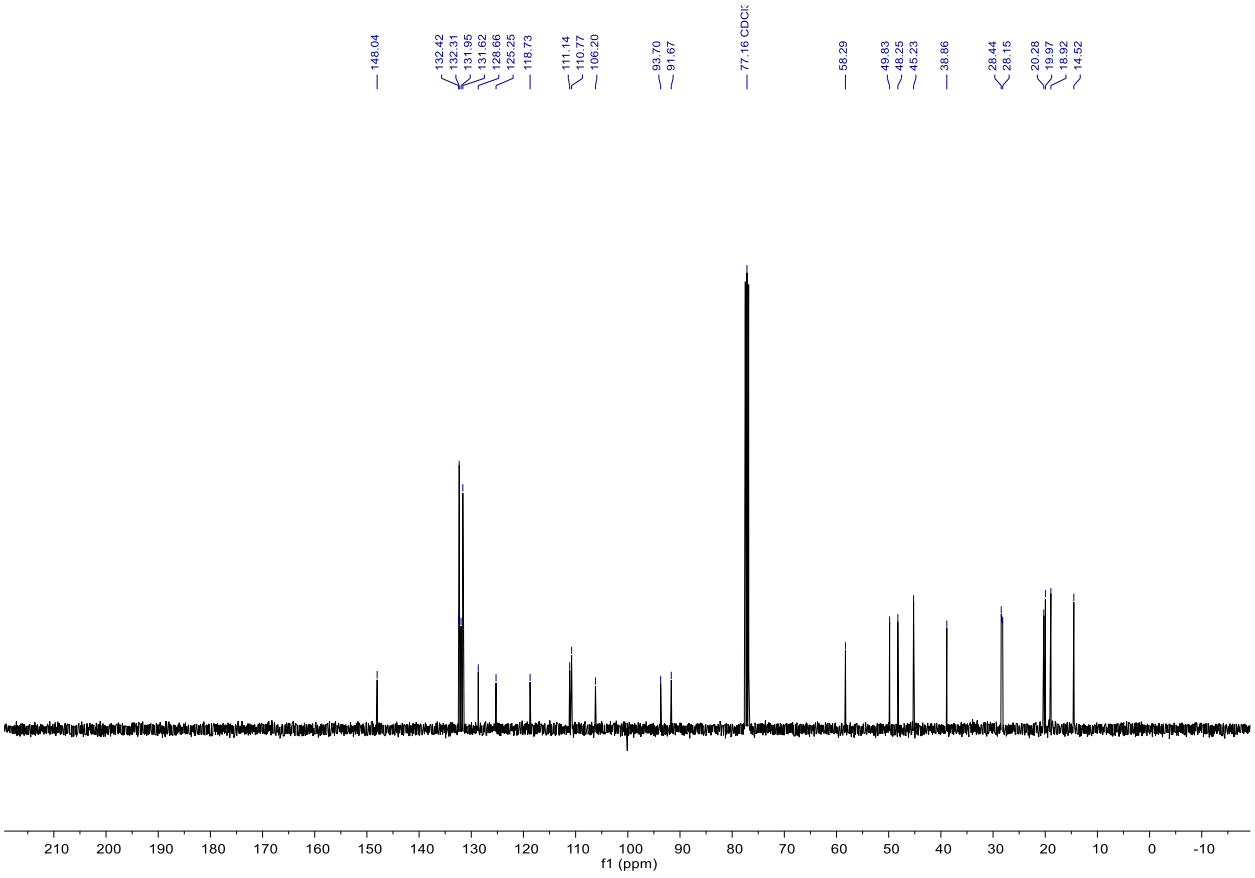
1H-15N HMBC NMR Spectrum of Compound 4bb



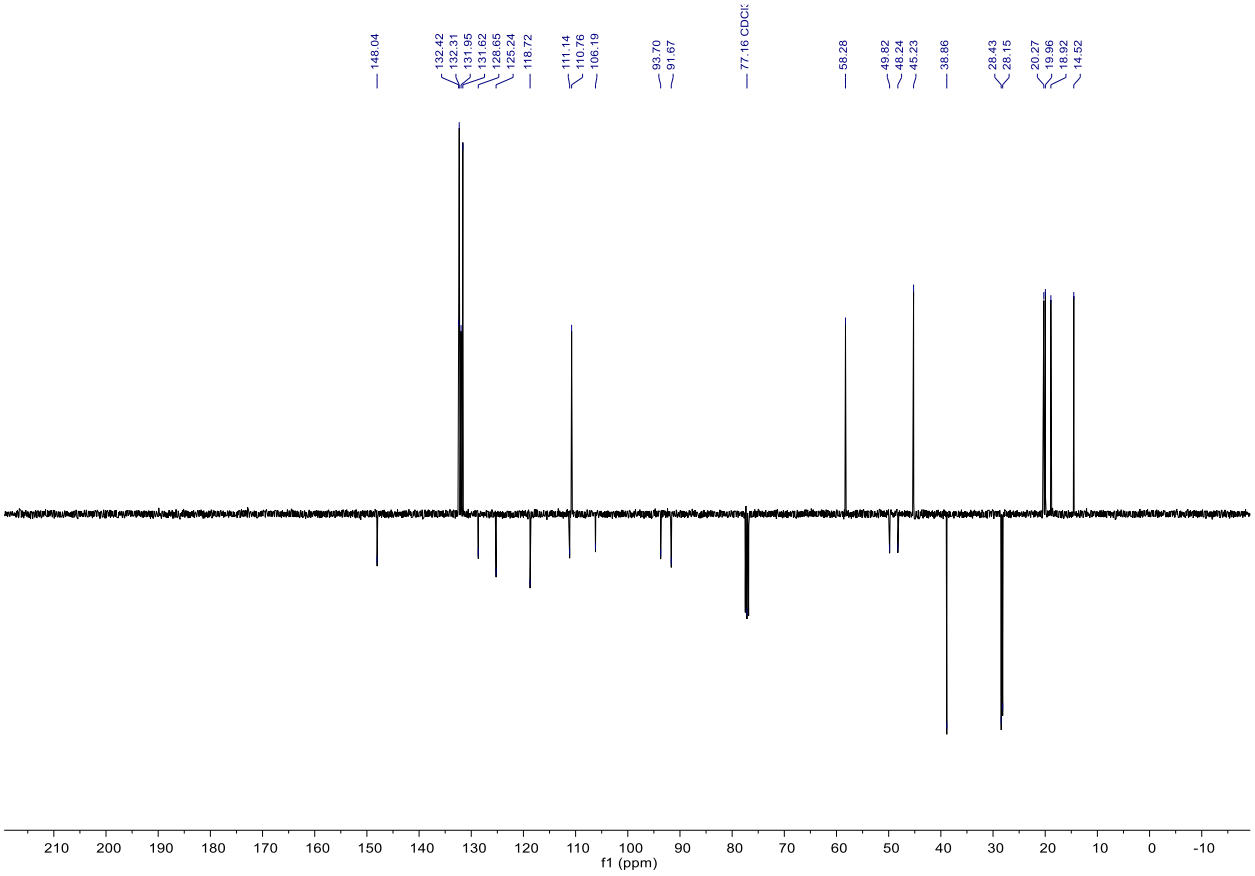
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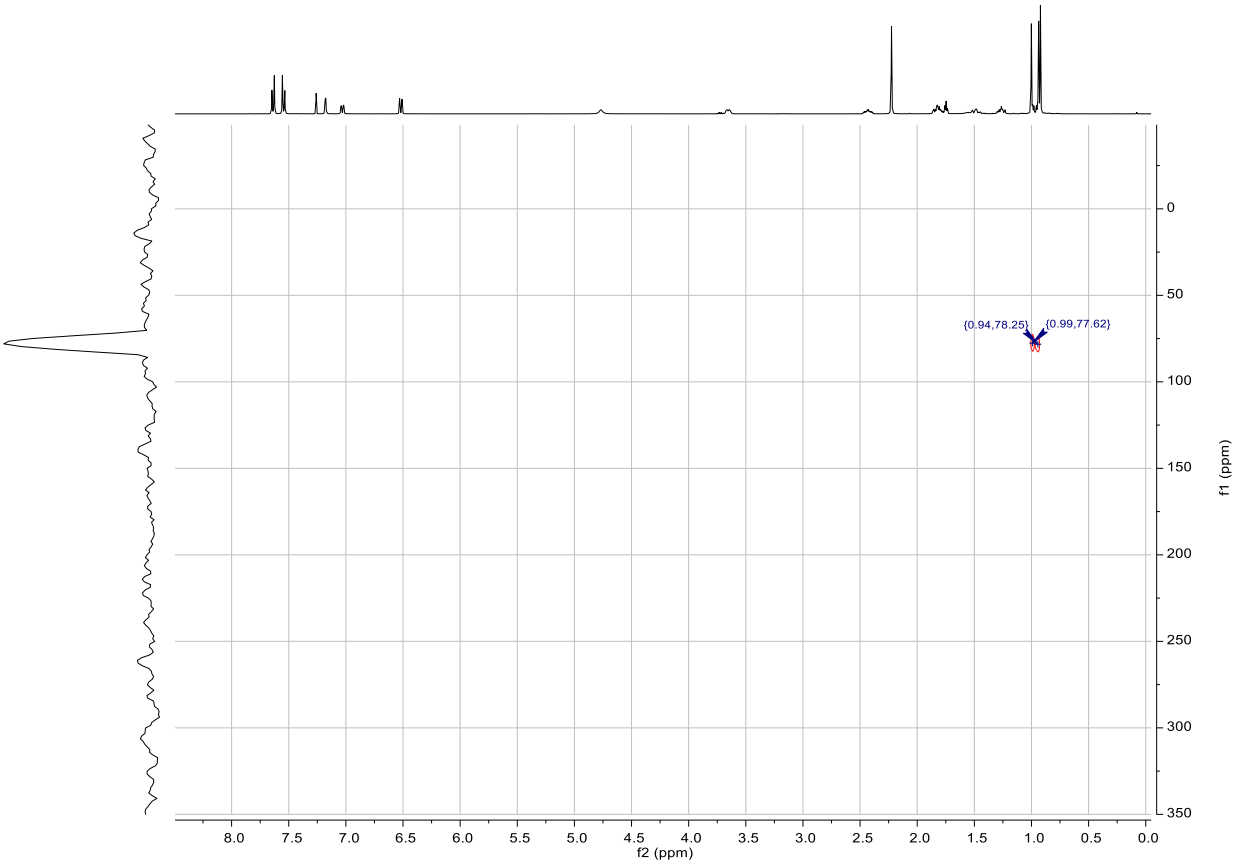
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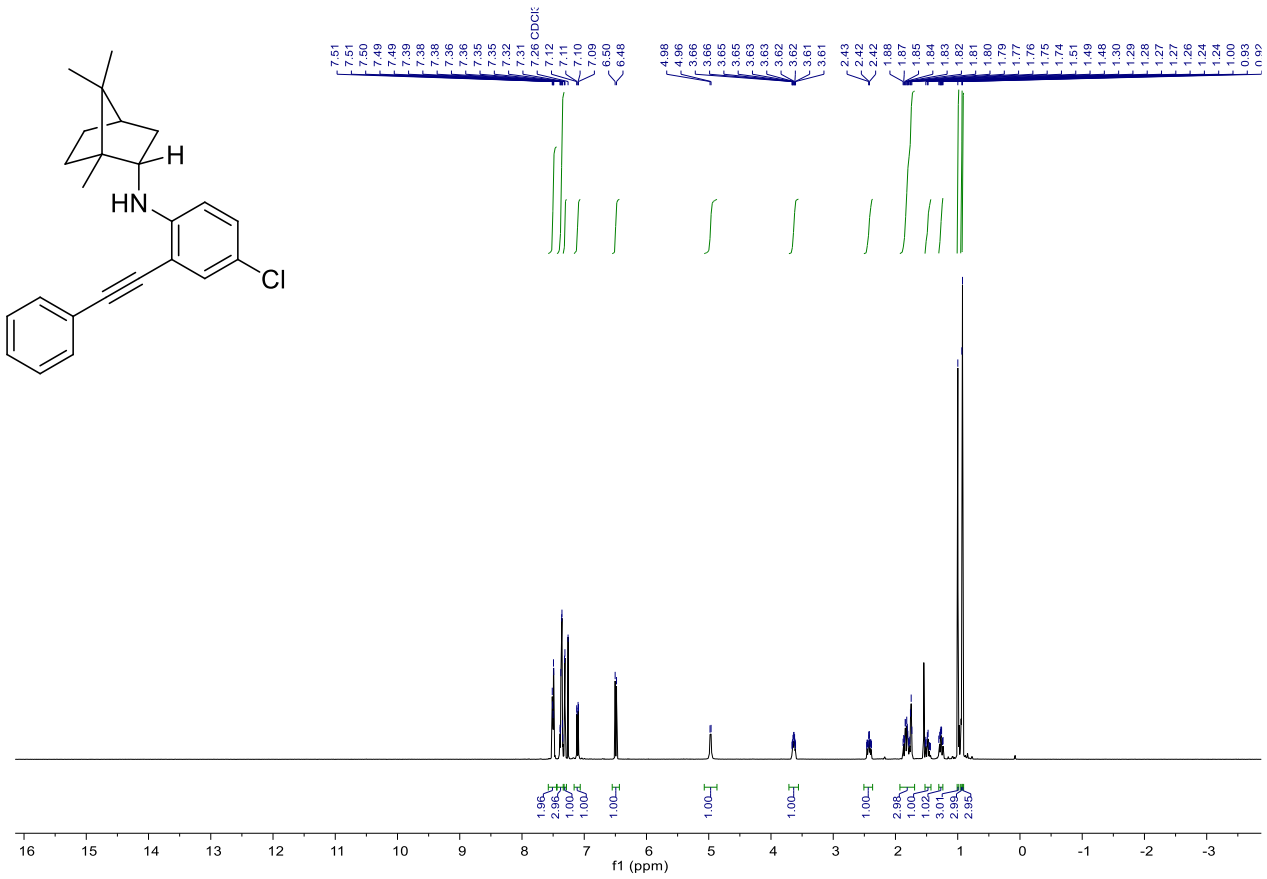
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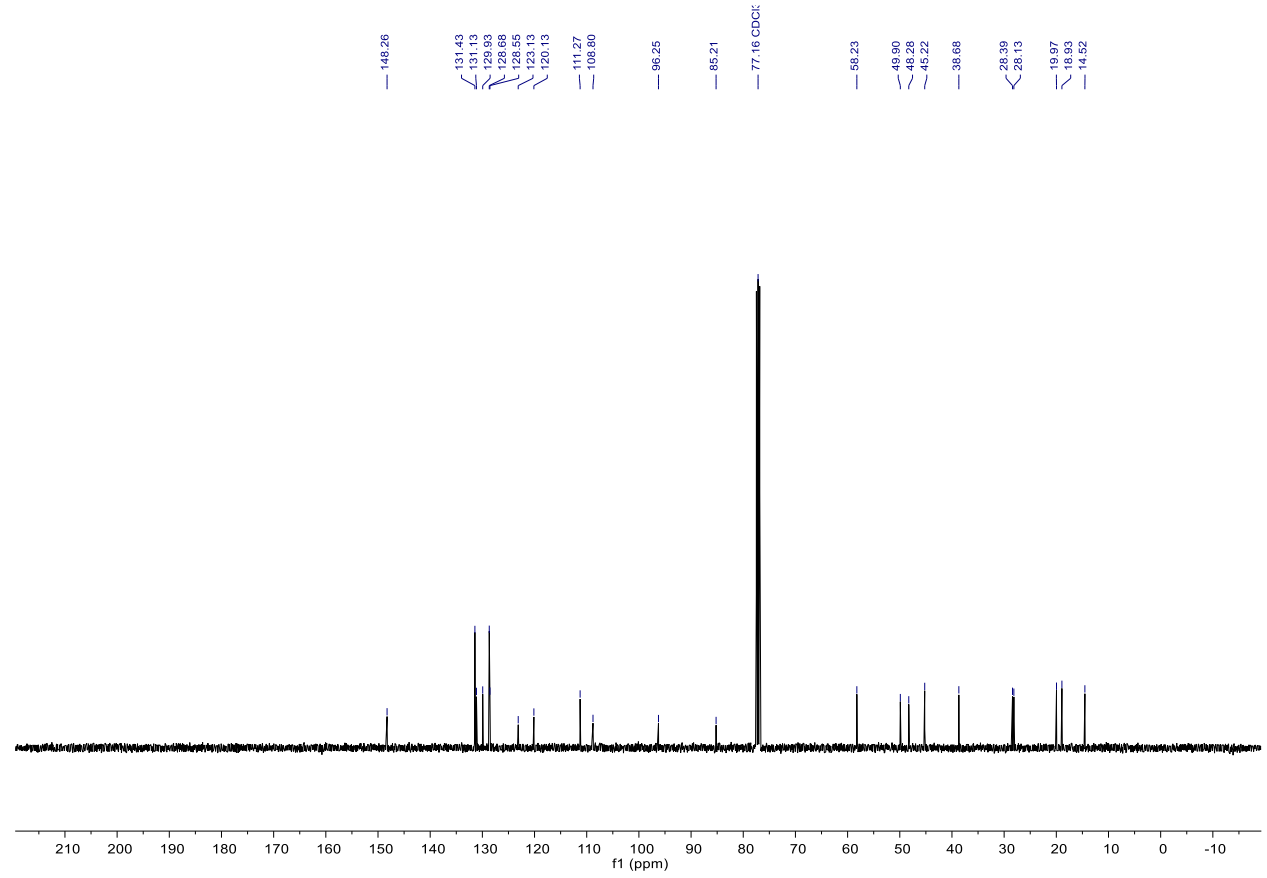
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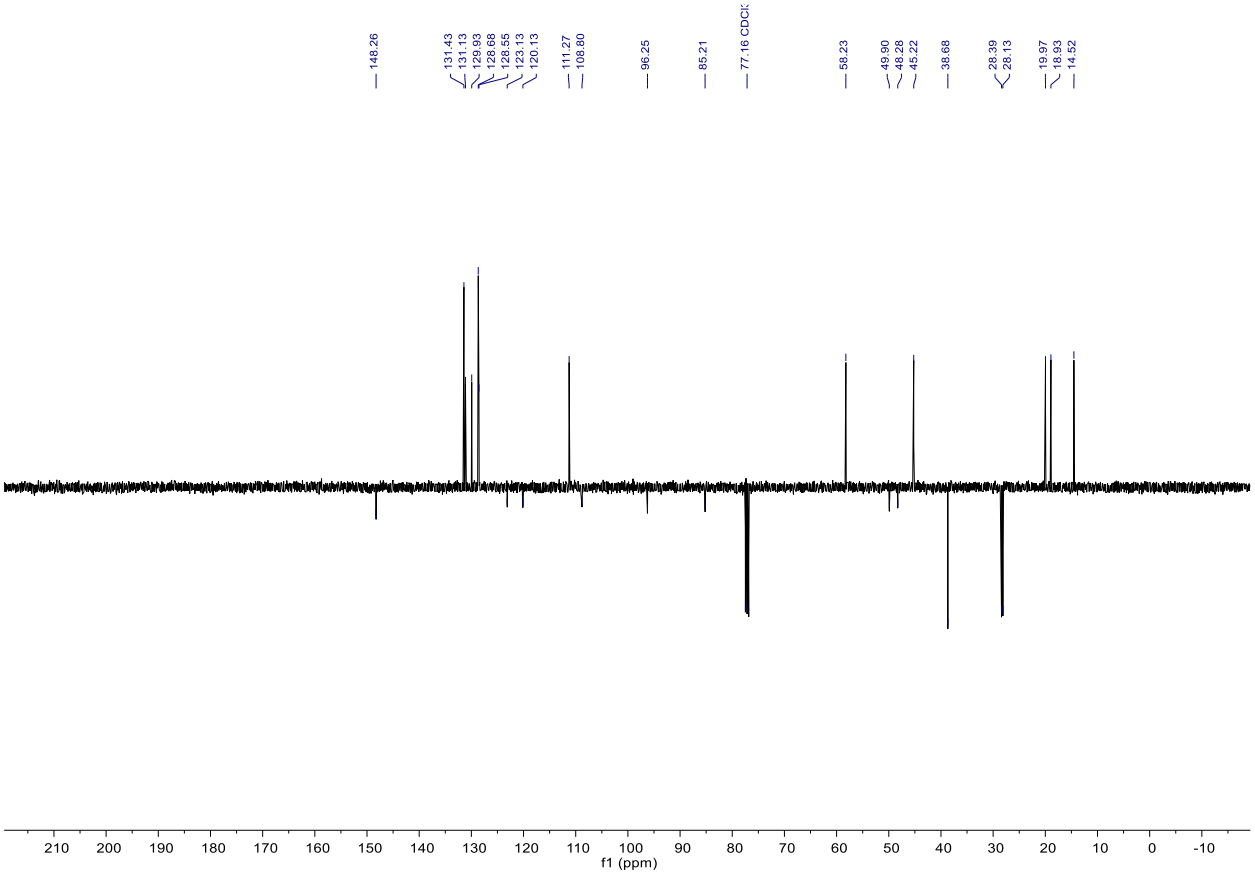
^{1}H NMR Spectrum of Compound 4ca (400 MHz, CDCl3)



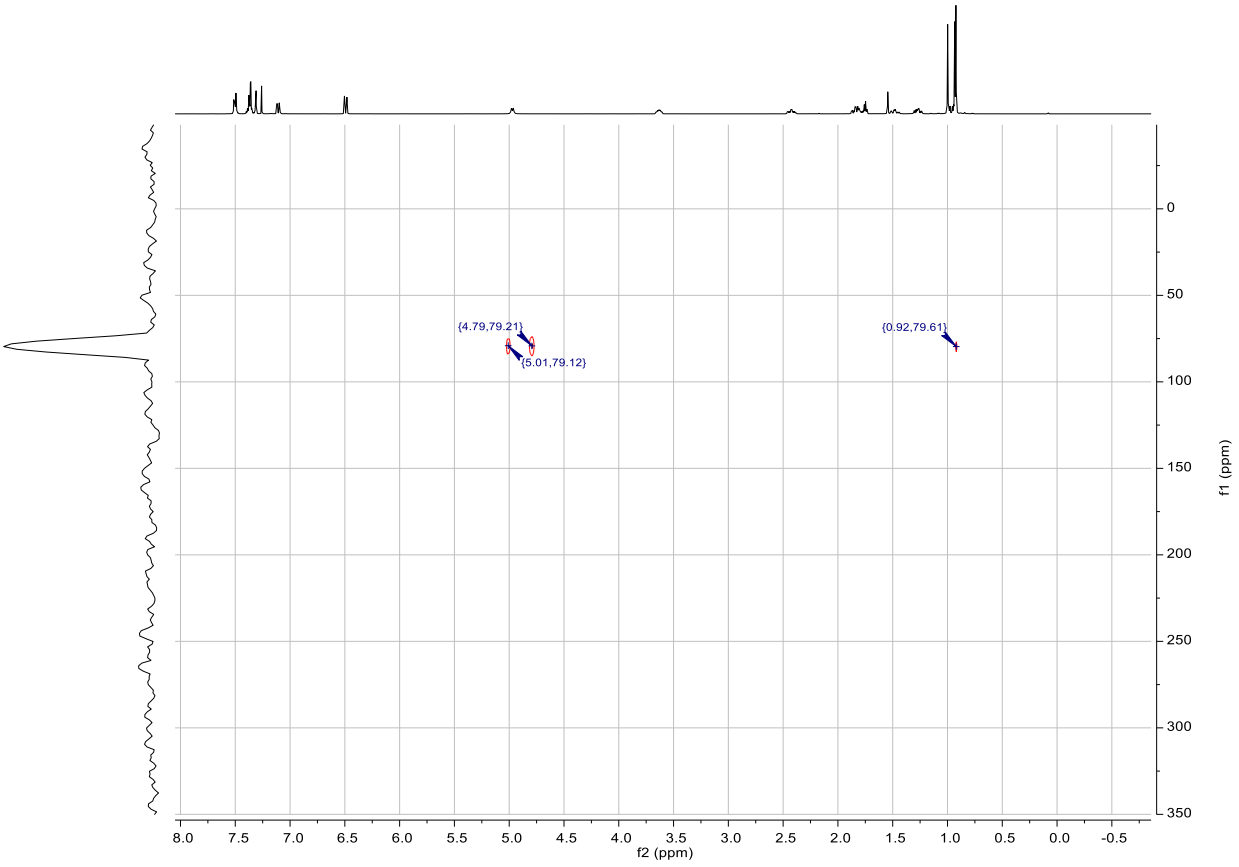
^{13}C NMR Spectrum of Compound 4ca (101 MHz, CDCl3)



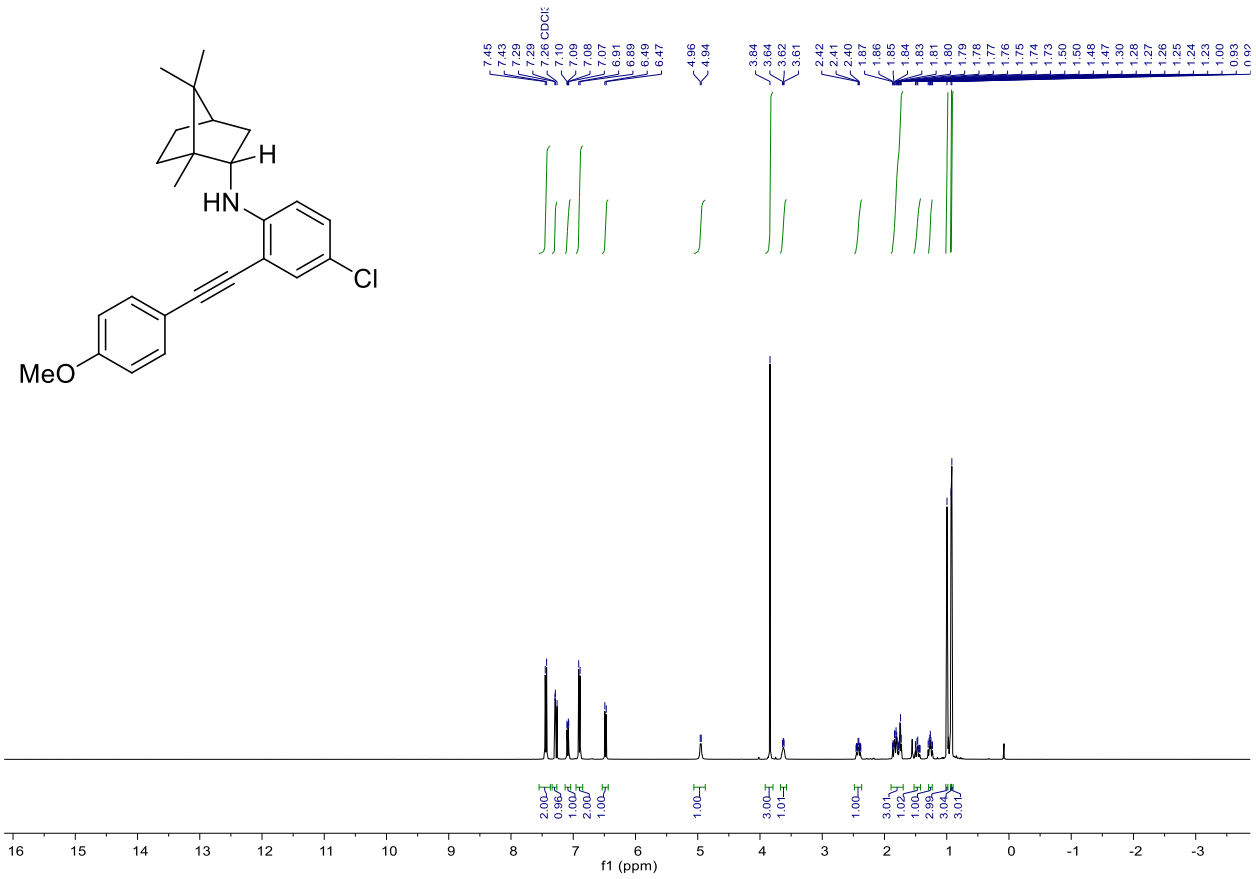
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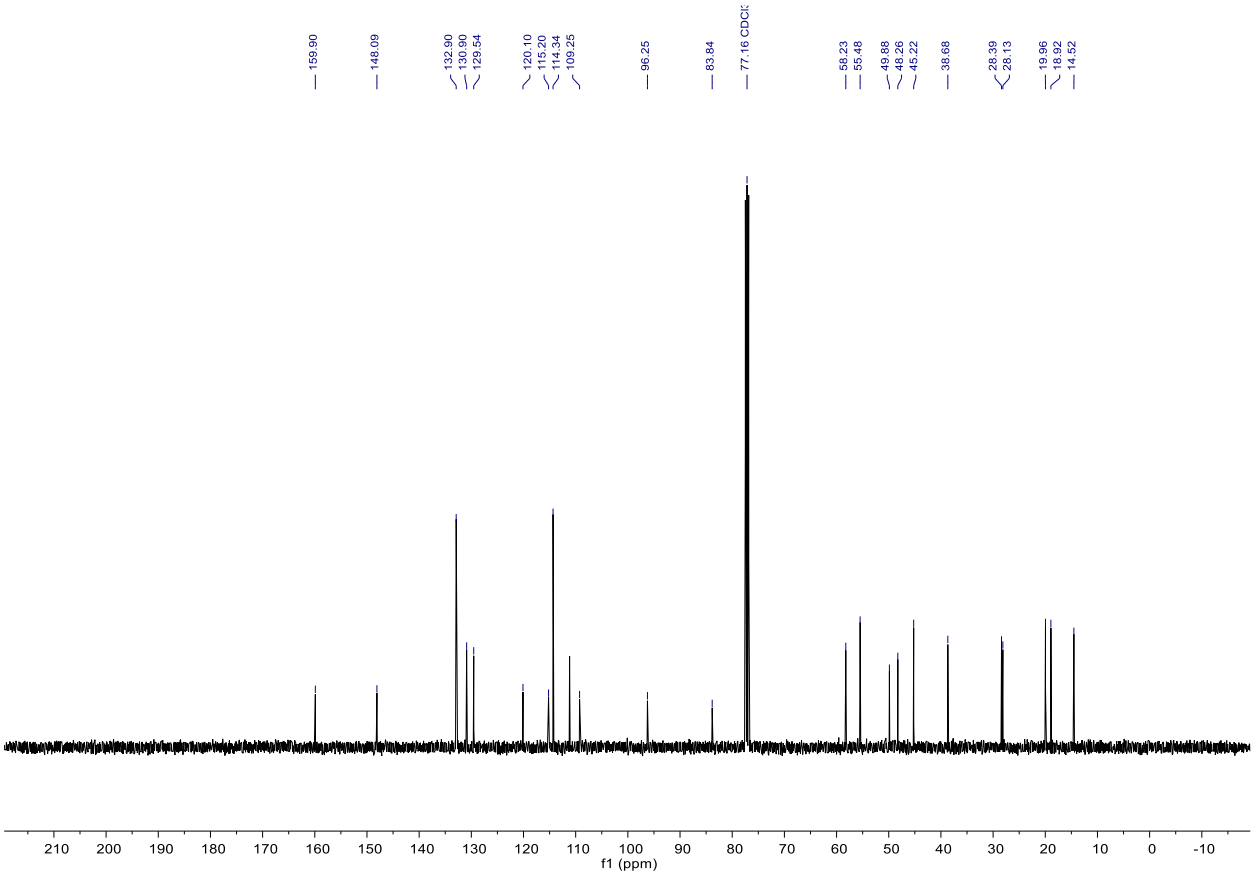
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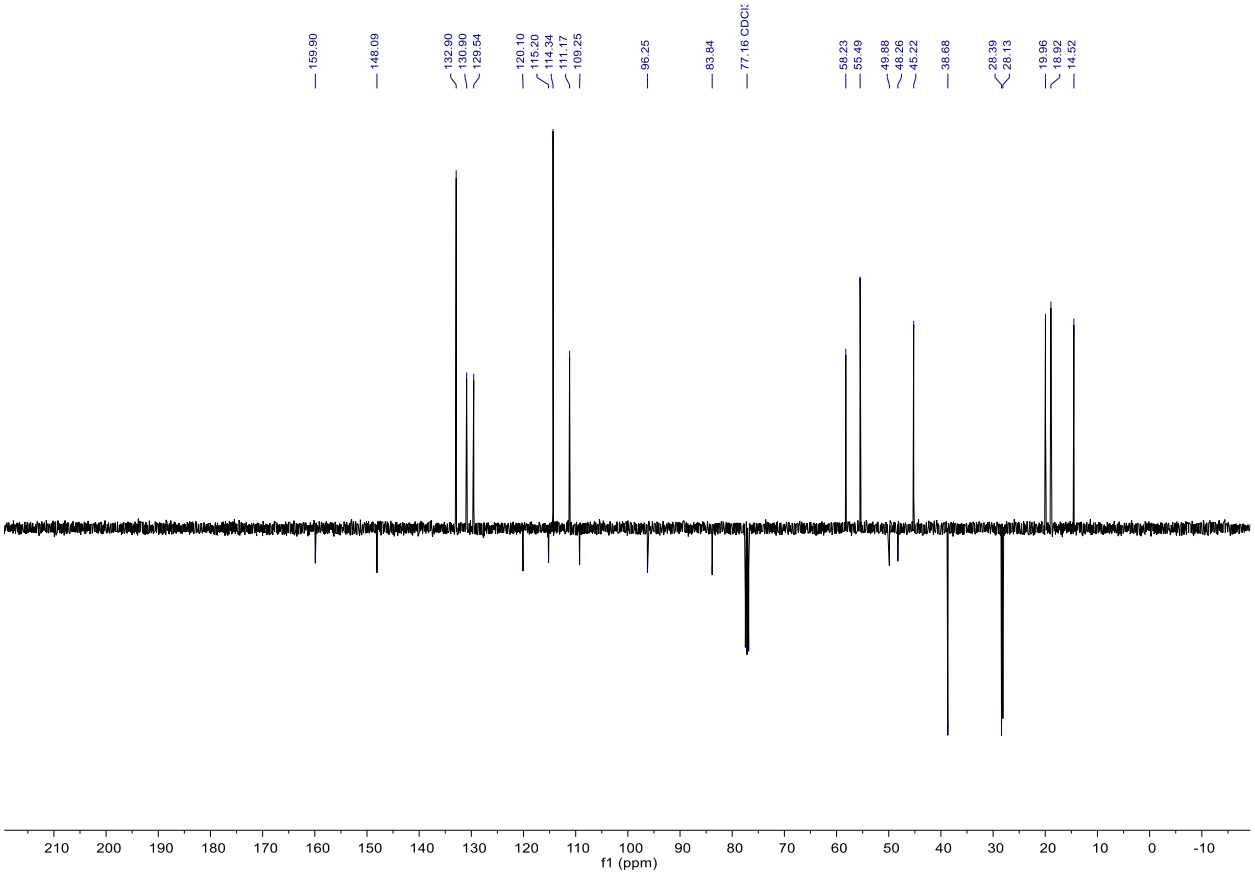
^{1}H NMR Spectrum of Compound 4cb (400 MHz, CDCl3)



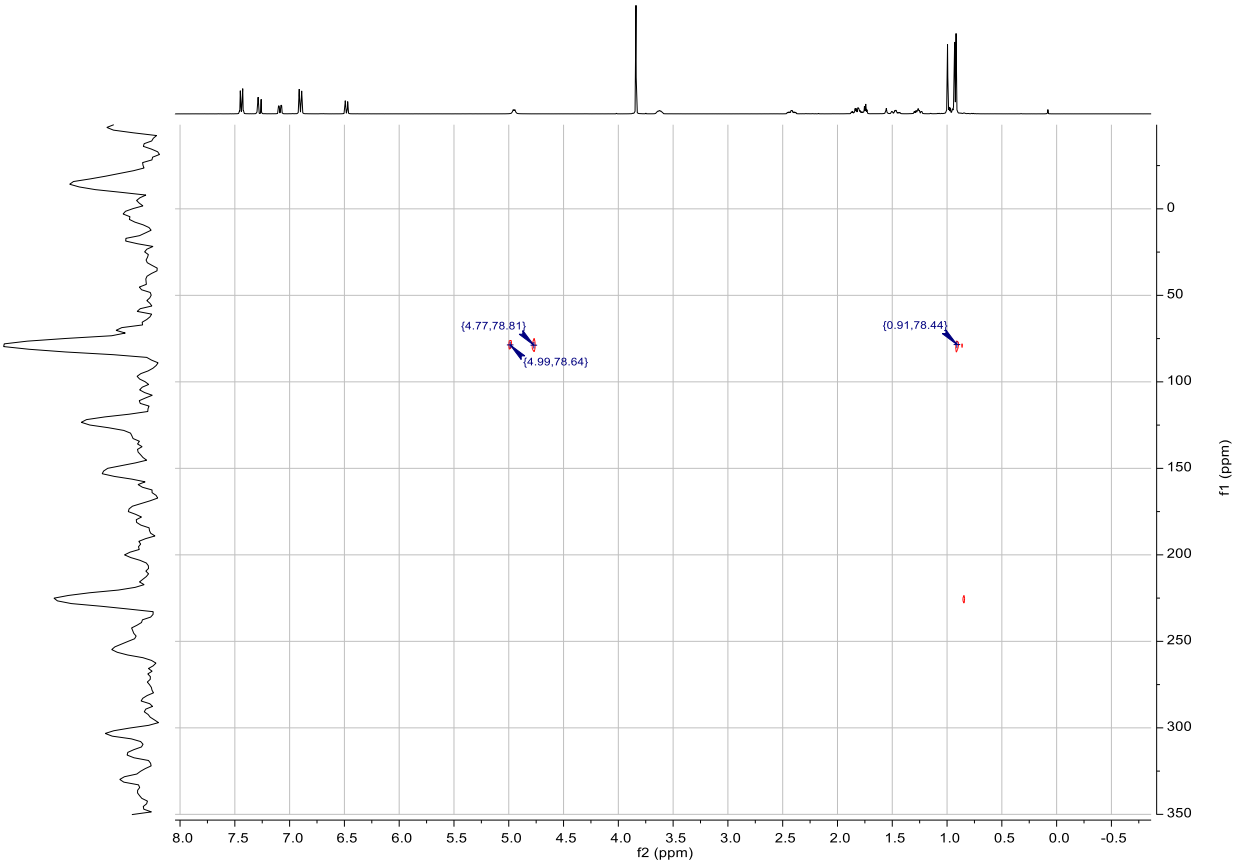
^{13}C NMR Spectrum of Compound 4cb (101 MHz, CDCl3)



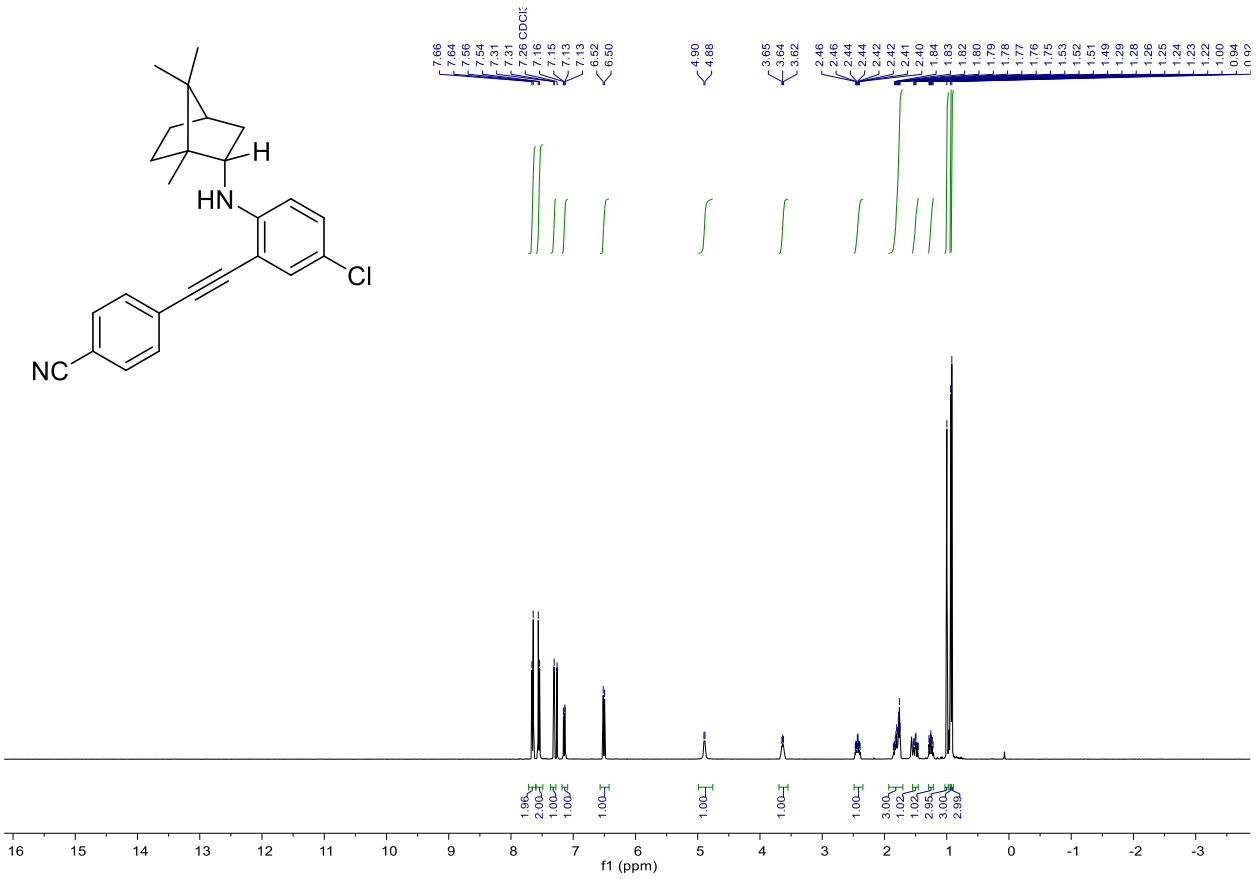
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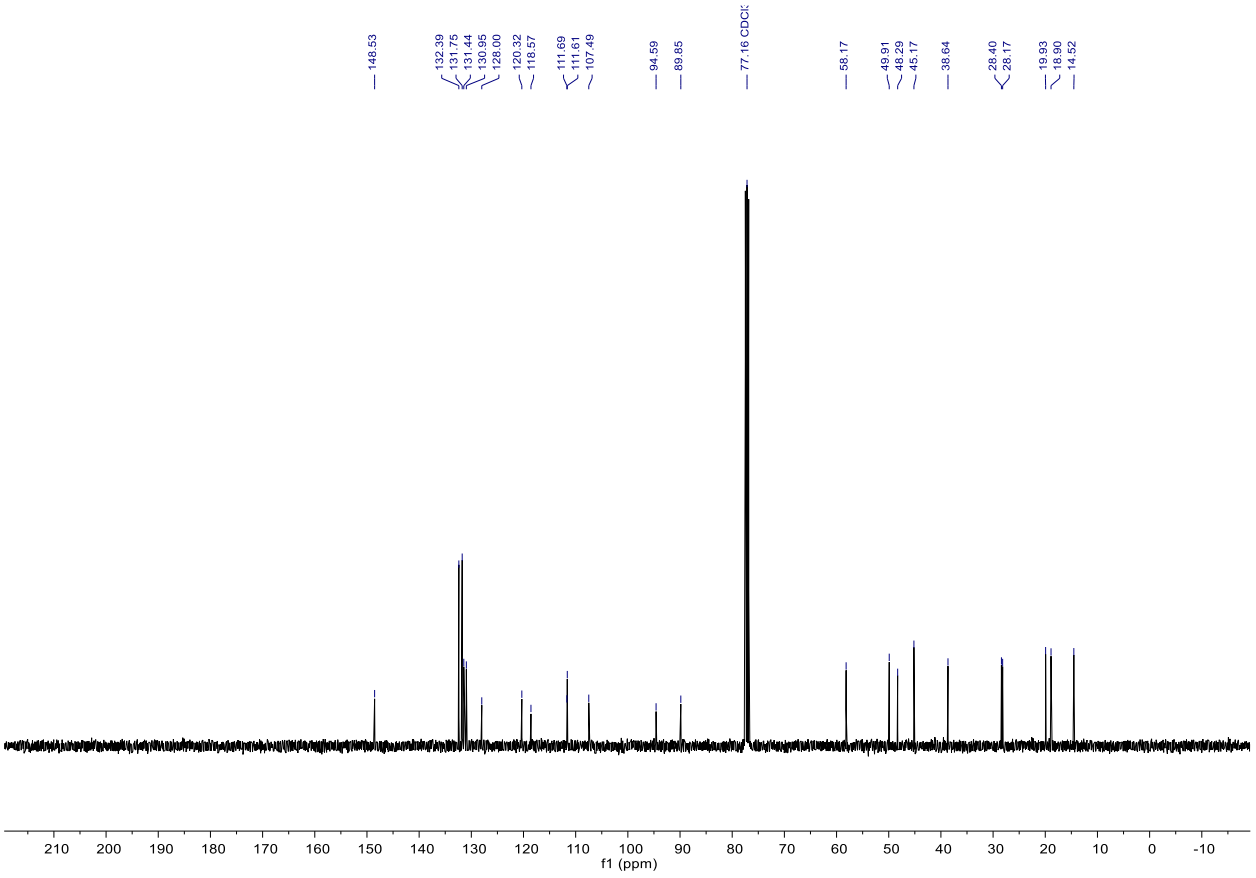
1H-15N HMBC NMR Spectrum of Compound 4cb



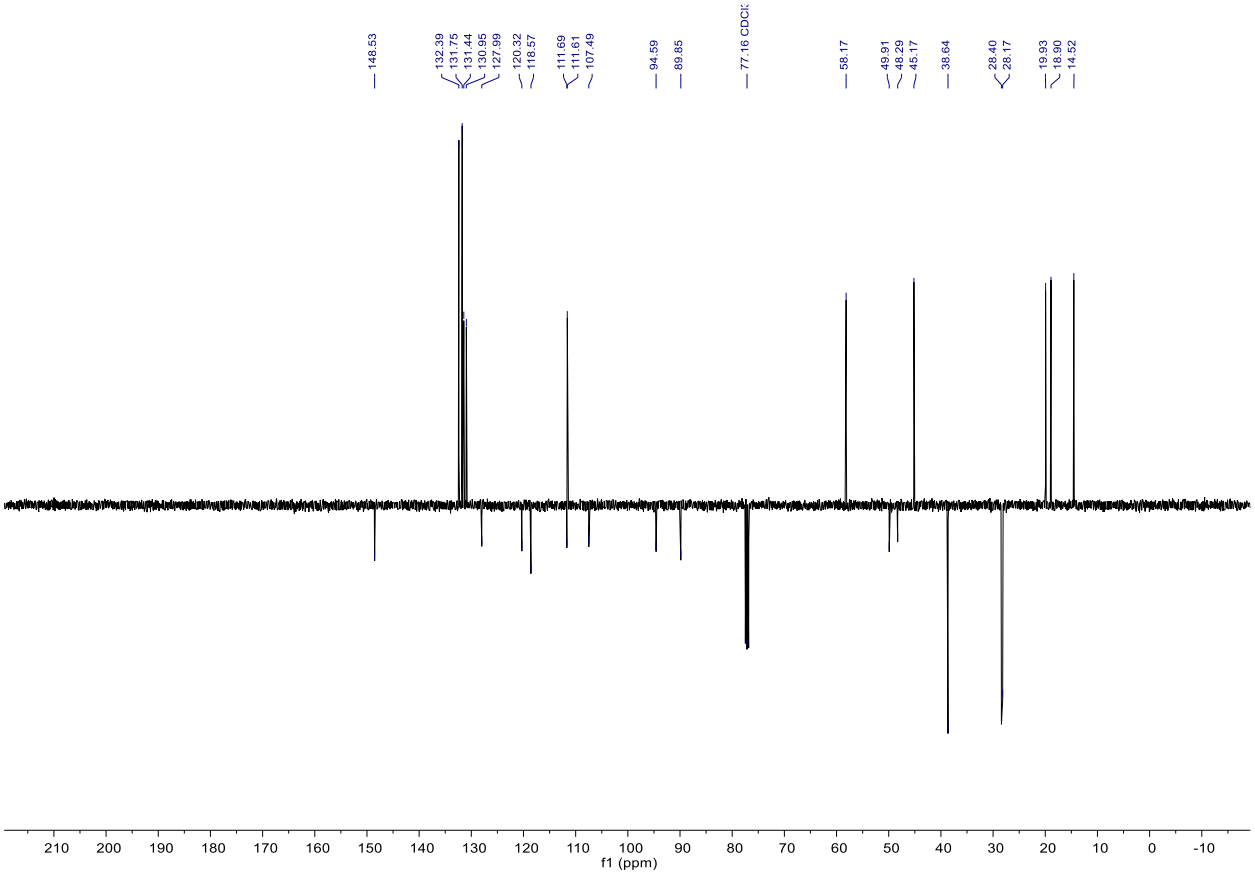
^{1}H NMR Spectrum of Compound 4cc (400 MHz, CDCl3)



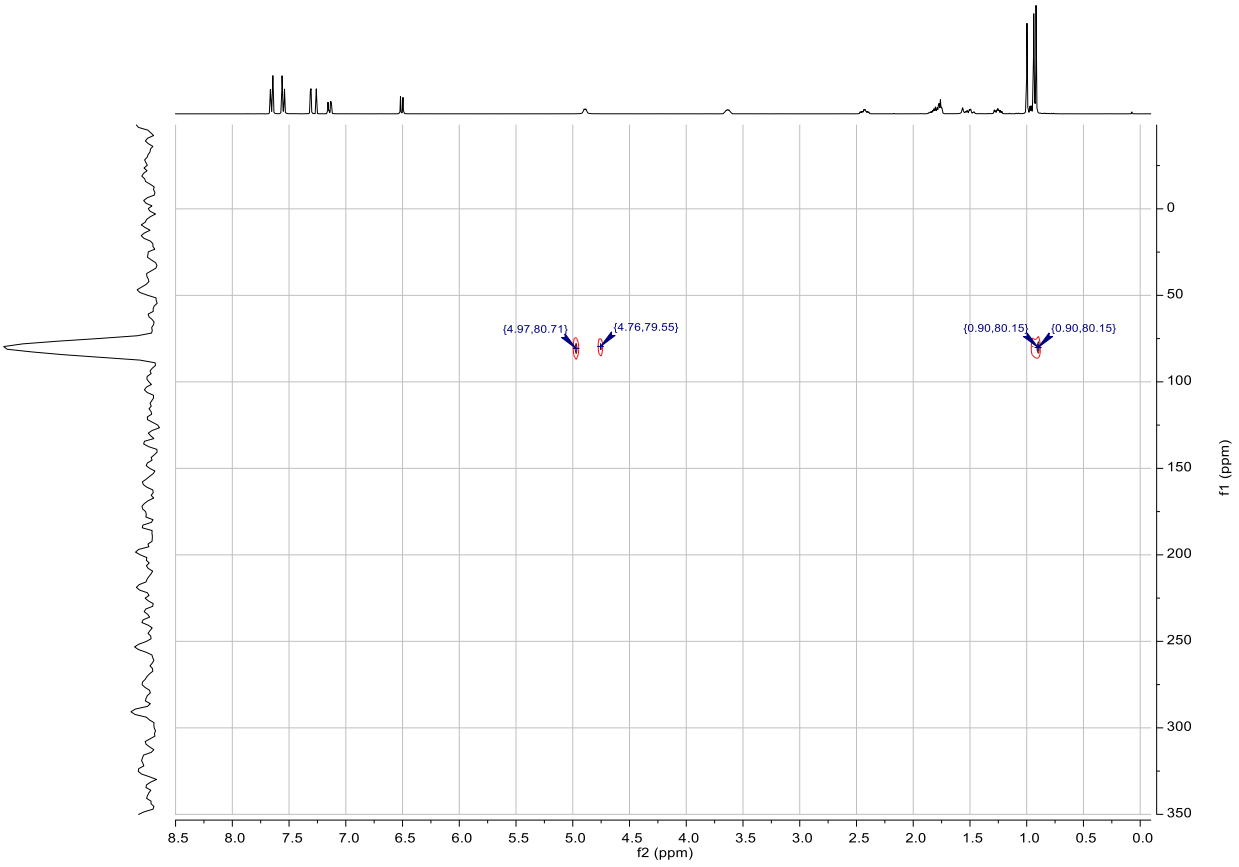
^{13}C NMR Spectrum of Compound 4cc (101 MHz, CDCl3)



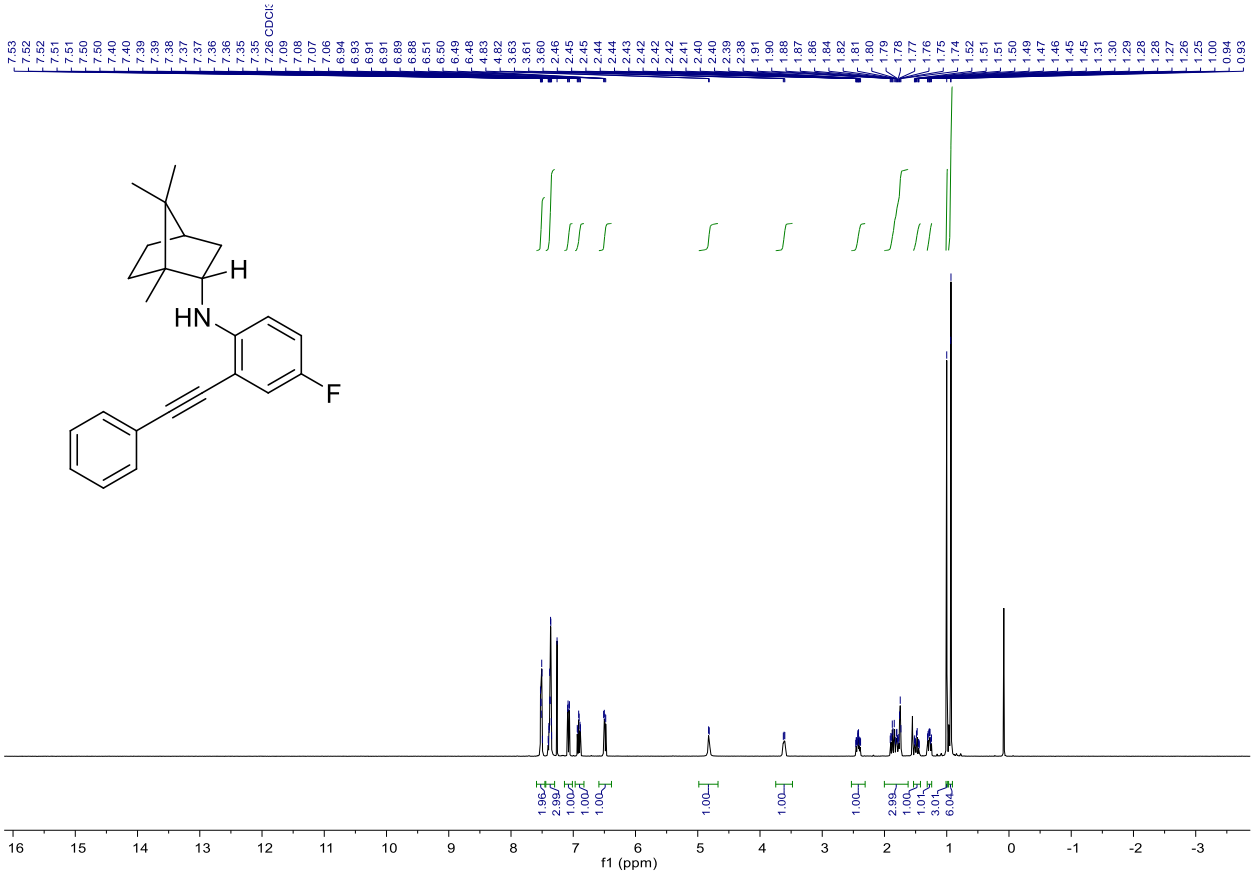
^{13}C DEPTQ-135 NMR Spectrum of Compound 4cc



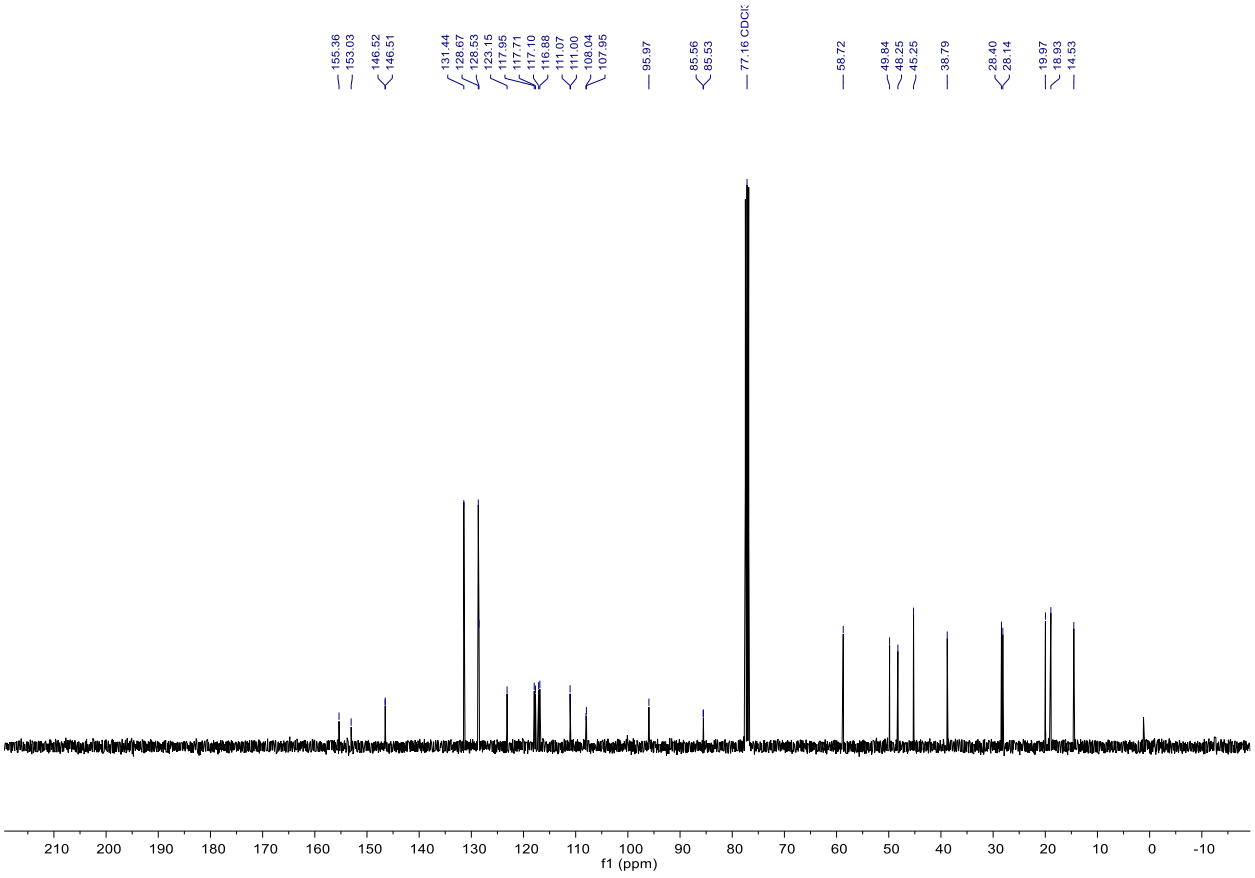
1H-15N HMBC NMR Spectrum of Compound 4cc



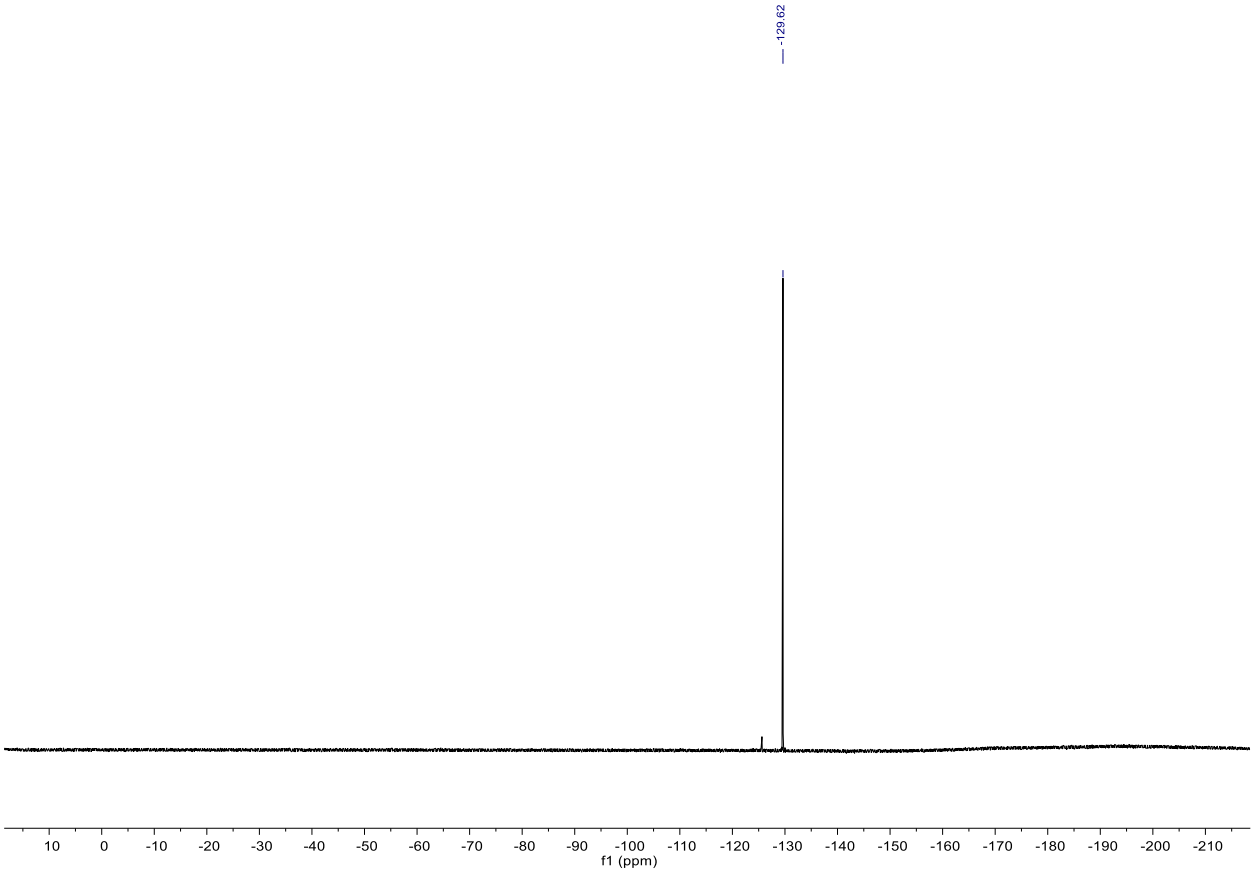
^{1}H NMR Spectrum of Compound 4da (400 MHz, CDCl3)



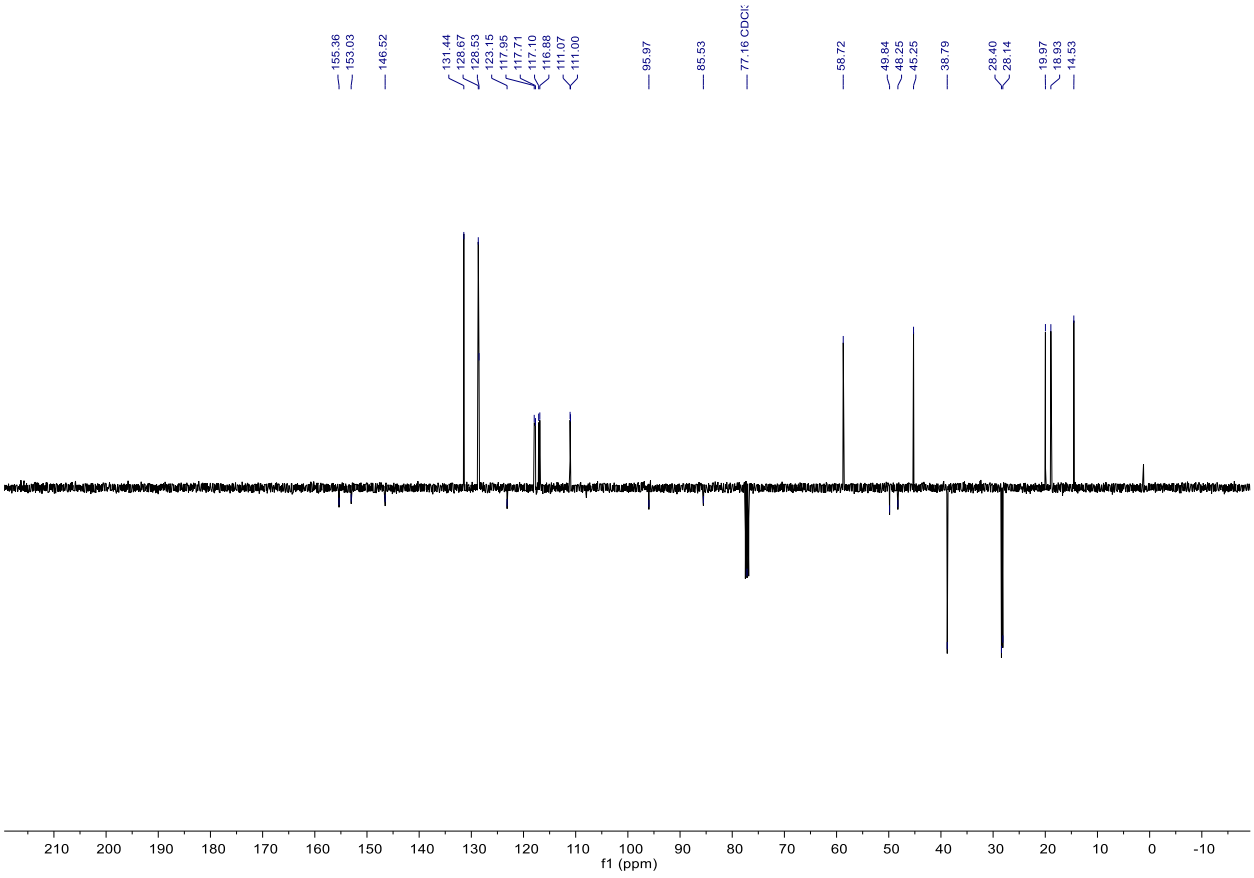
^{13}C NMR Spectrum of Compound 4da (101 MHz, CDCl3)



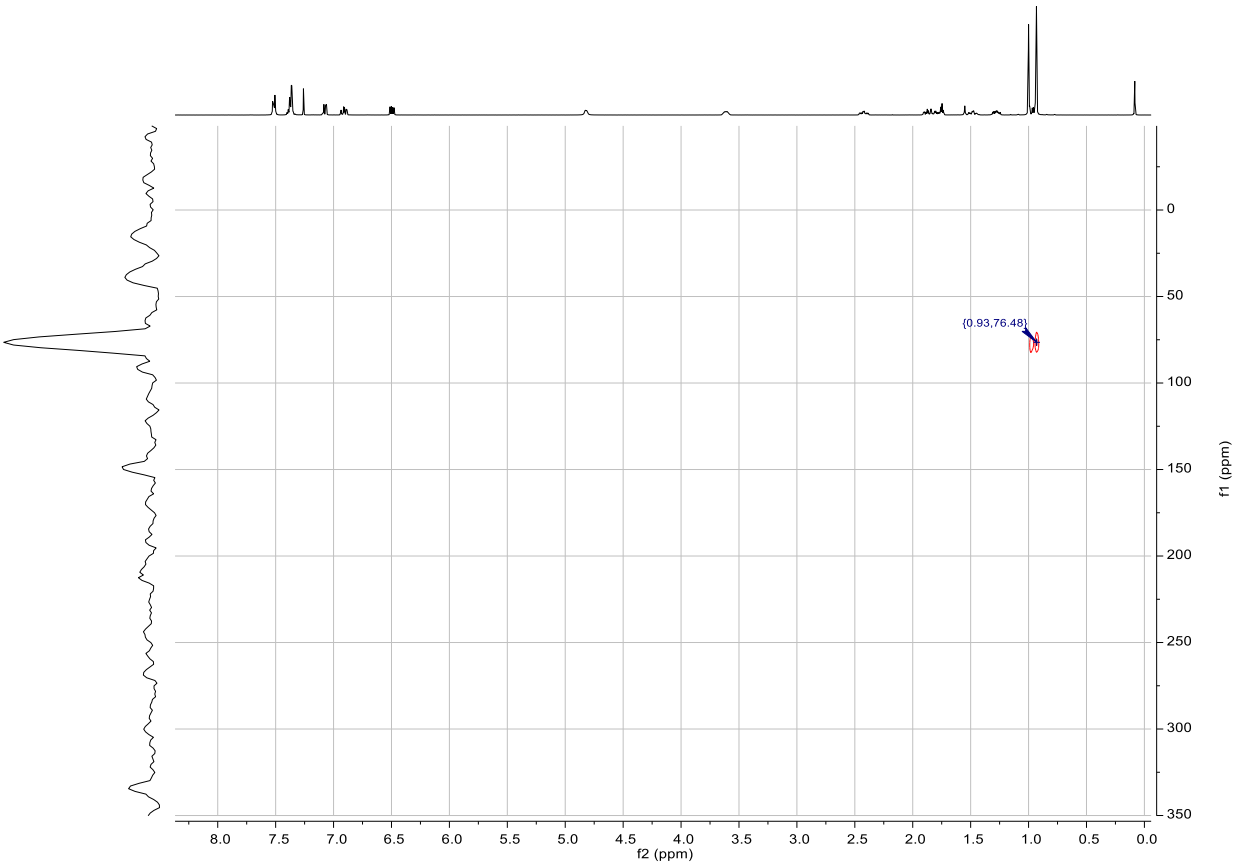
^{19}F NMR Spectrum of Compound 4da(376 MHz, CDCl3)



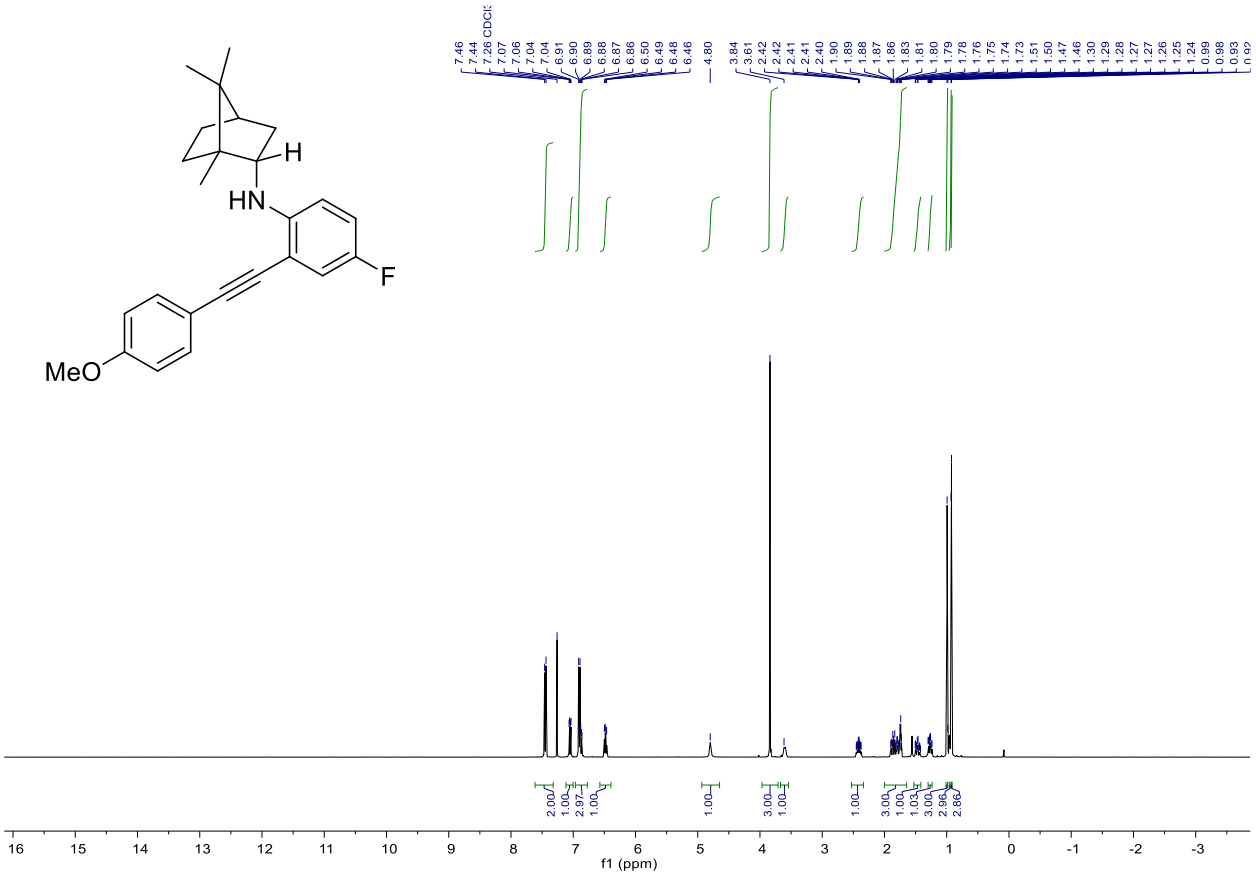
^{13}C DEPTQ-135 NMR Spectrum of Compound 4da



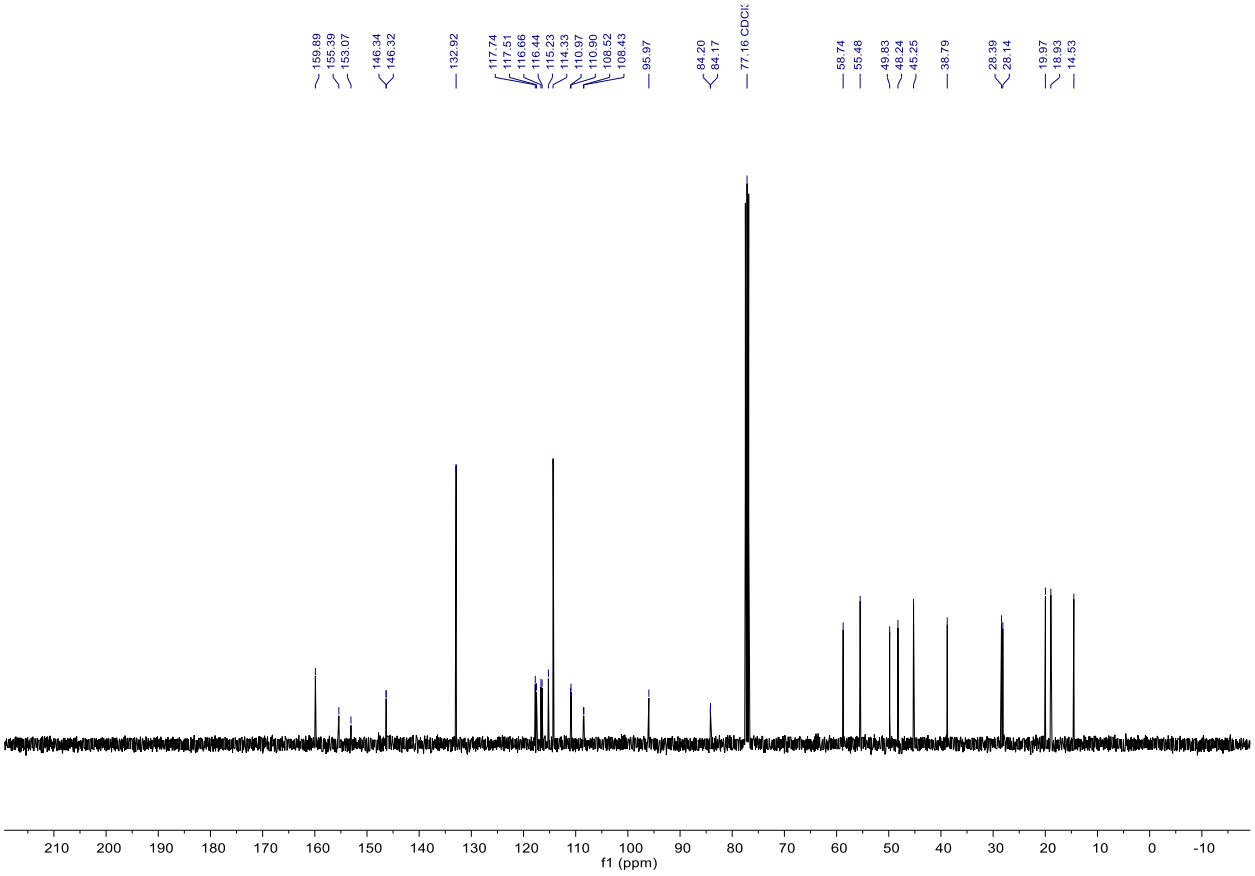
1H-15N HMBC NMR Spectrum of Compound 4da



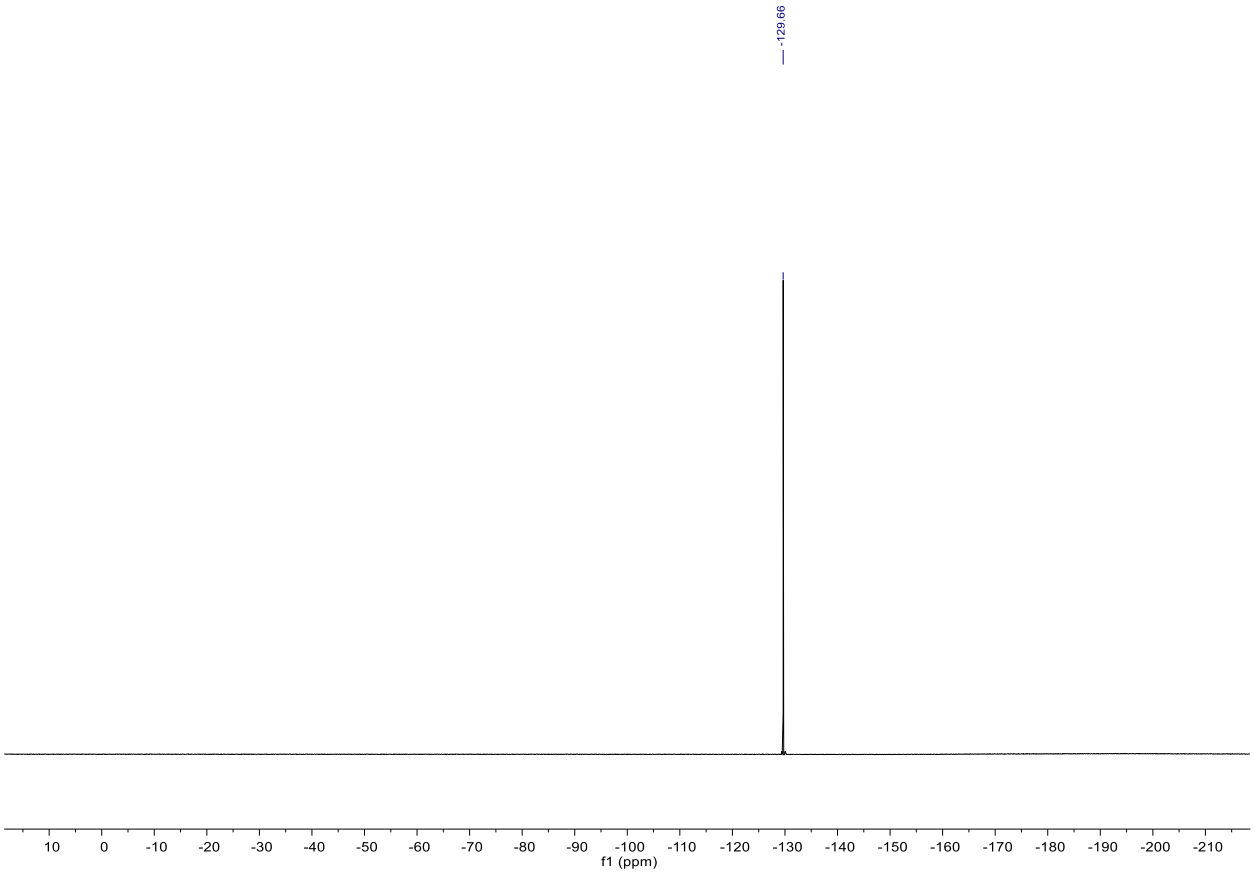
^{1}H NMR Spectrum of Compound 4db (400 MHz, CDCl3)



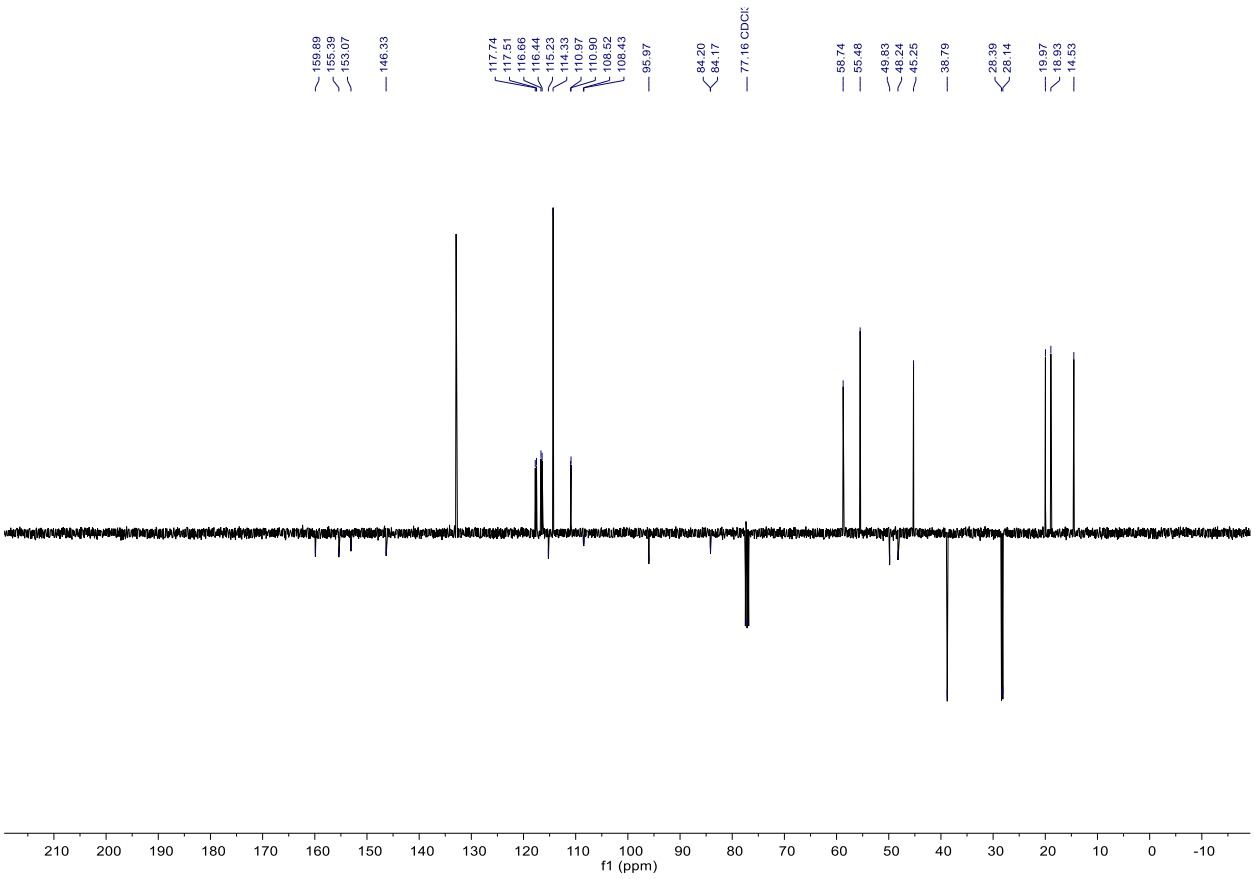
^{13}C NMR Spectrum of Compound 4db (101 MHz, CDCl3)



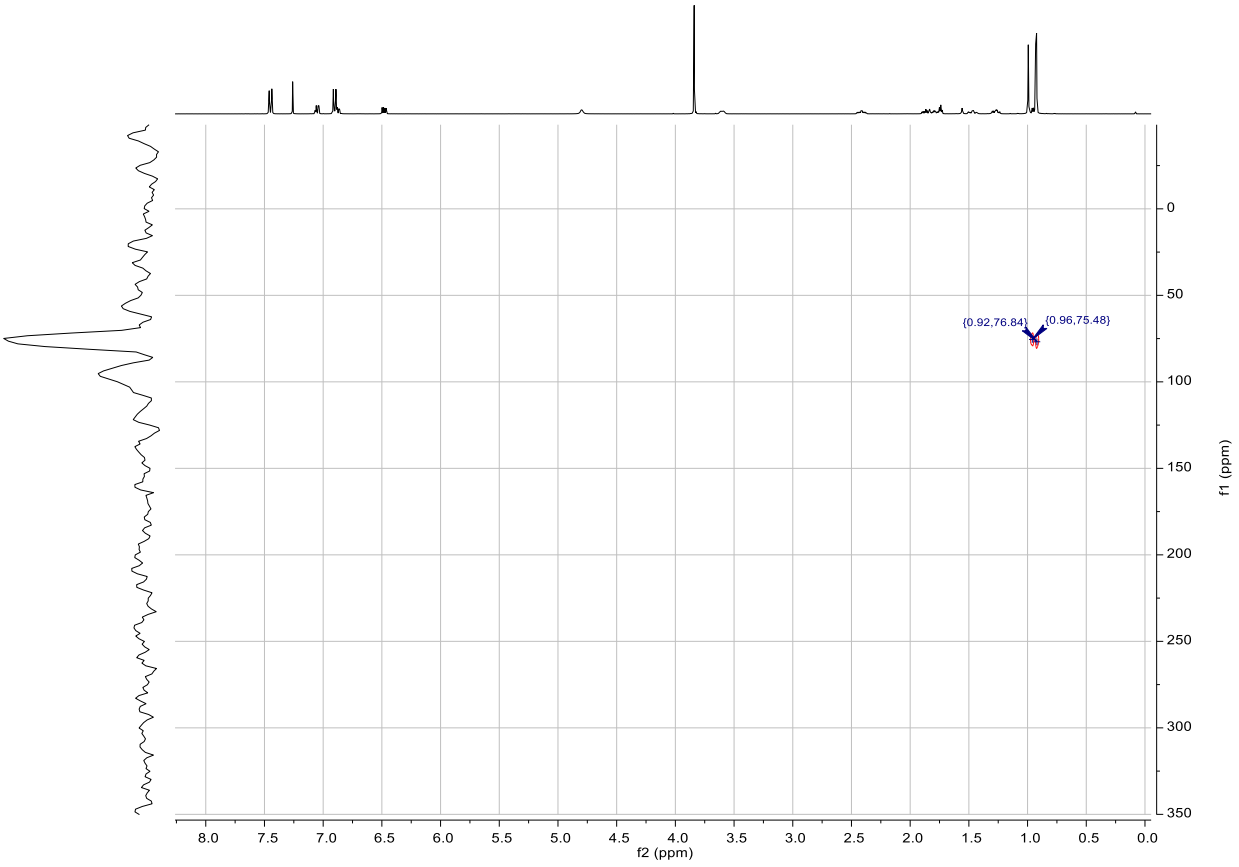
^{19}F NMR Spectrum of Compound 4db (376 MHz, CDCl3)



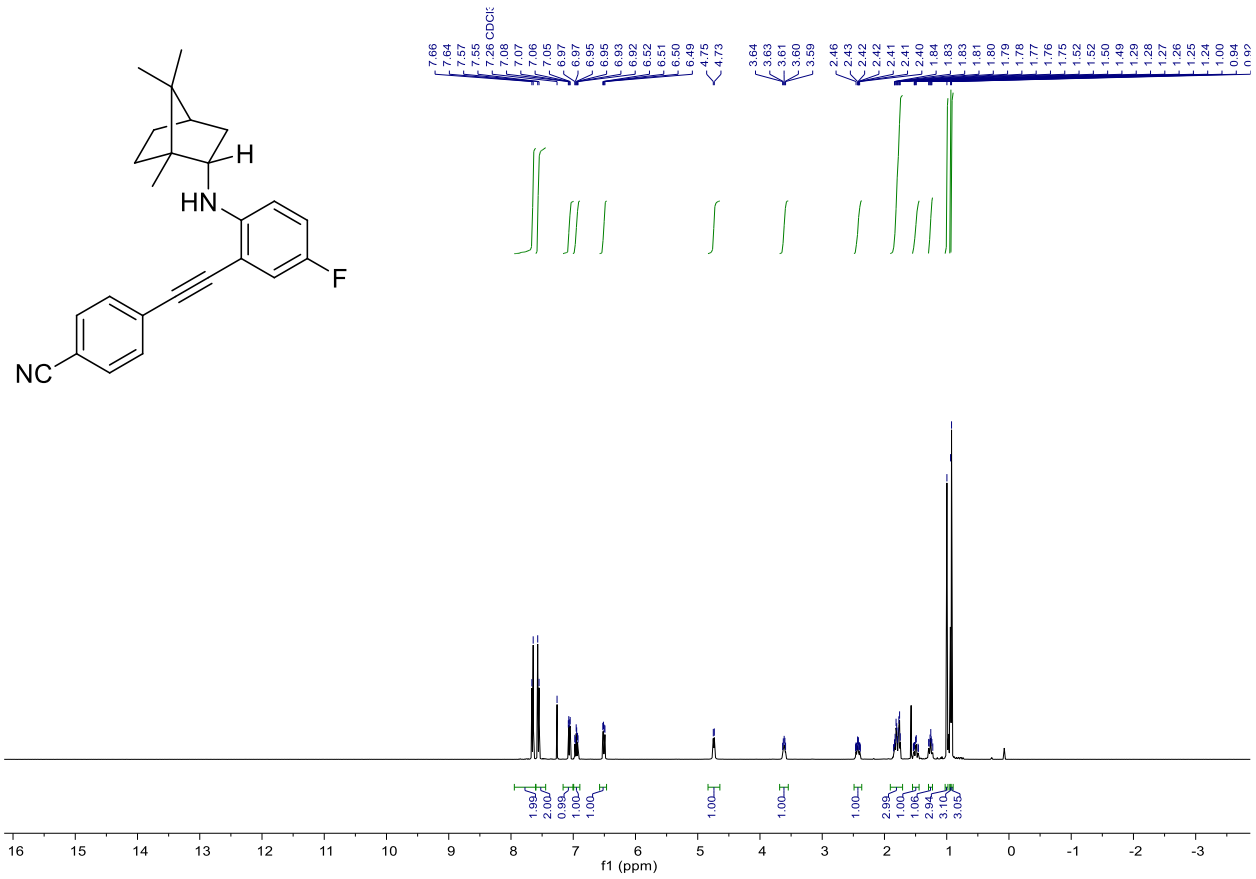
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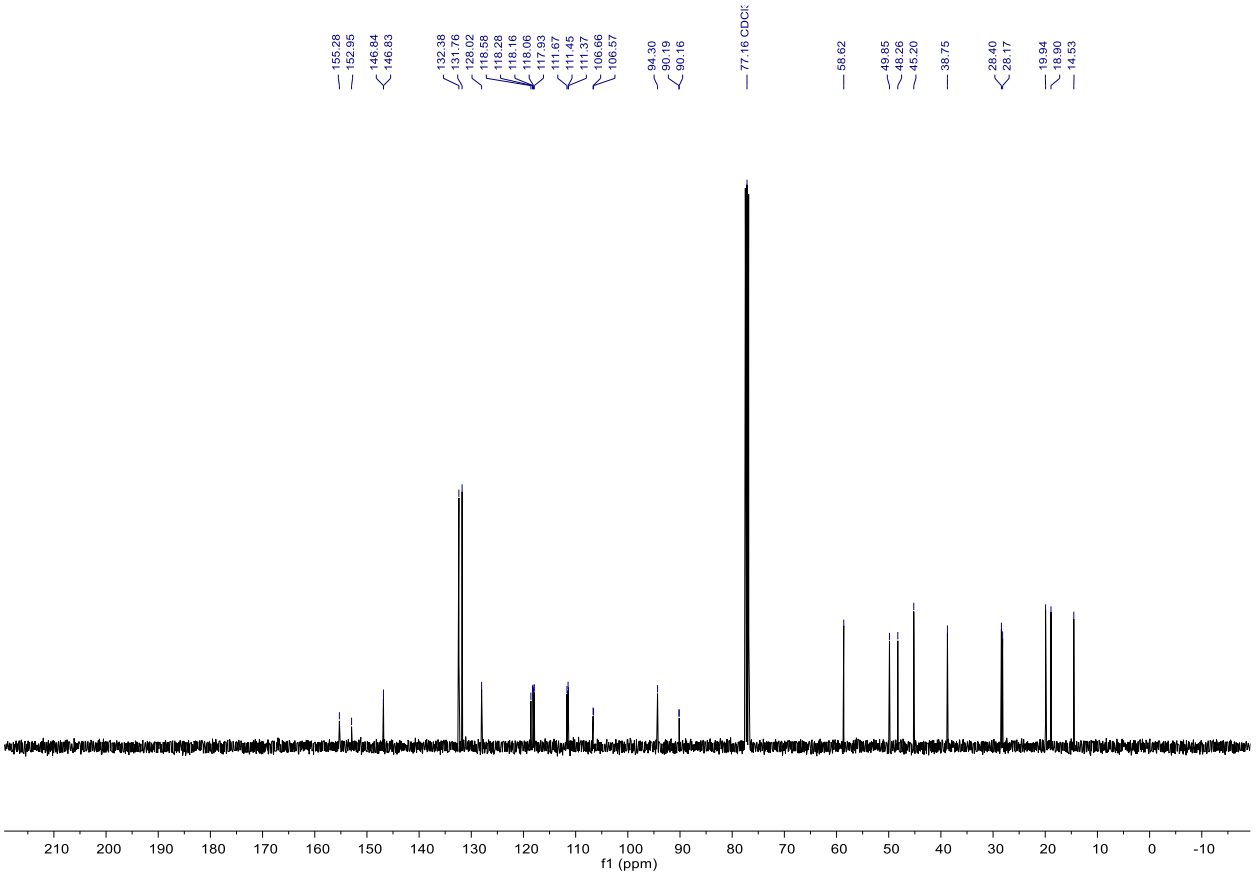
1H-15N HMBC NMR Spectrum of Compound 4db



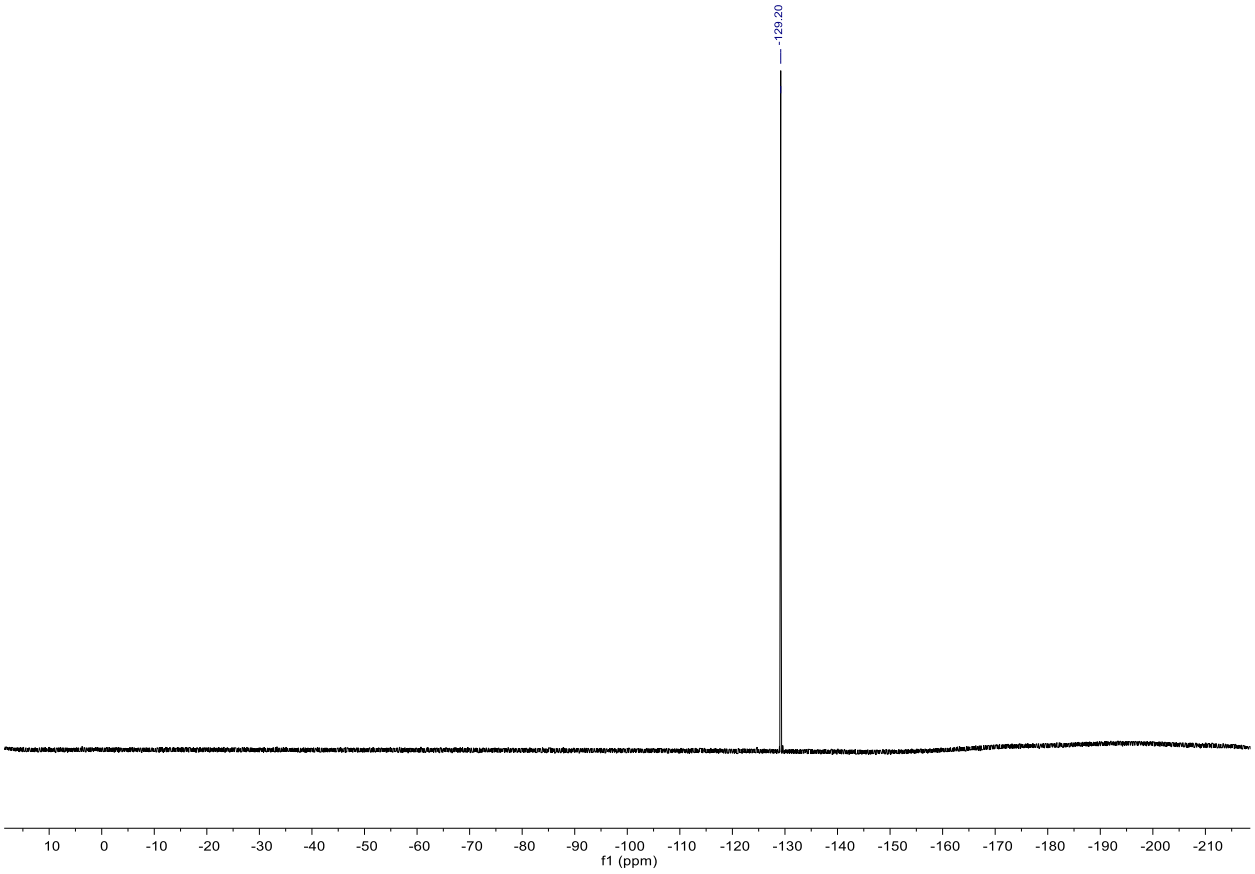
^{1}H NMR Spectrum of Compound 4dc (400 MHz, CDCl3)



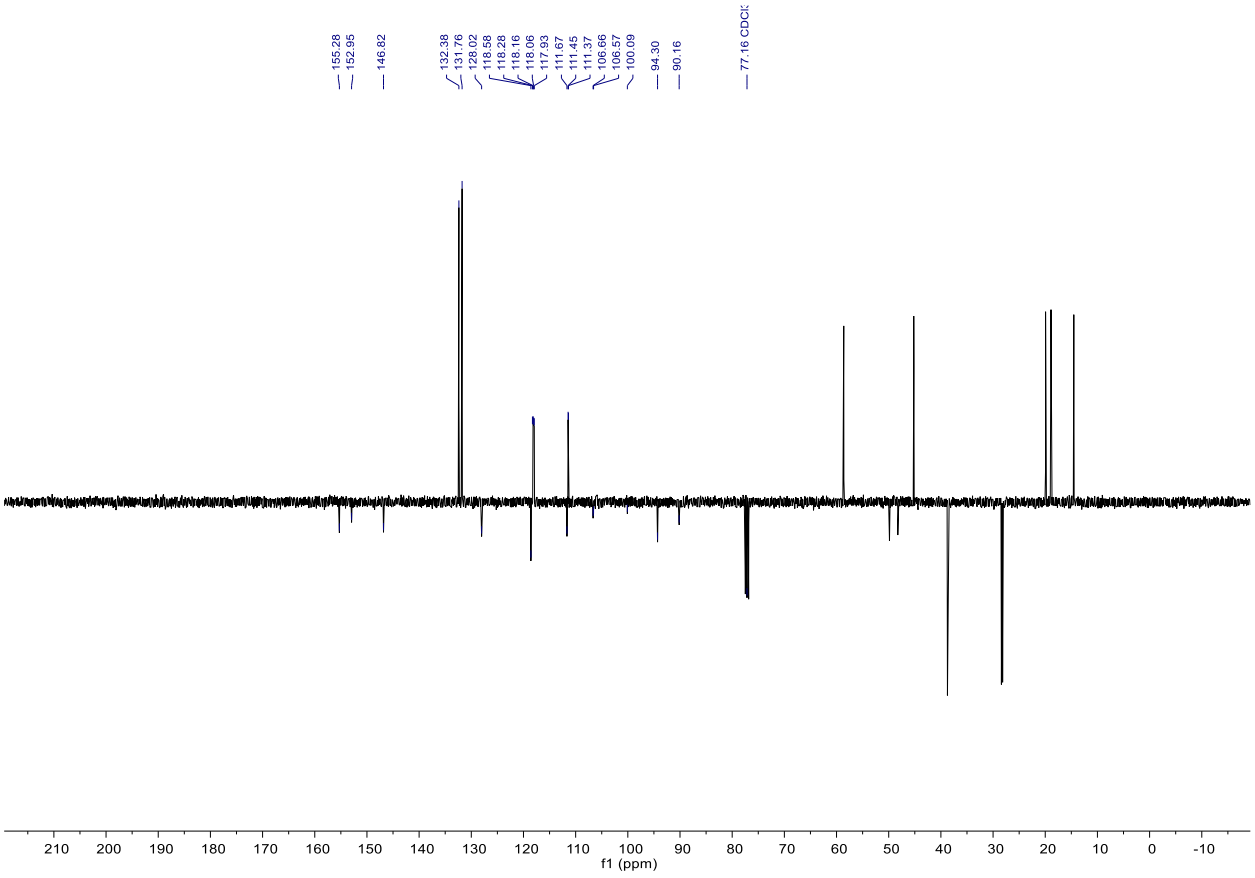
^{13}C NMR Spectrum of Compound 4dc (101 MHz, CDCl3)



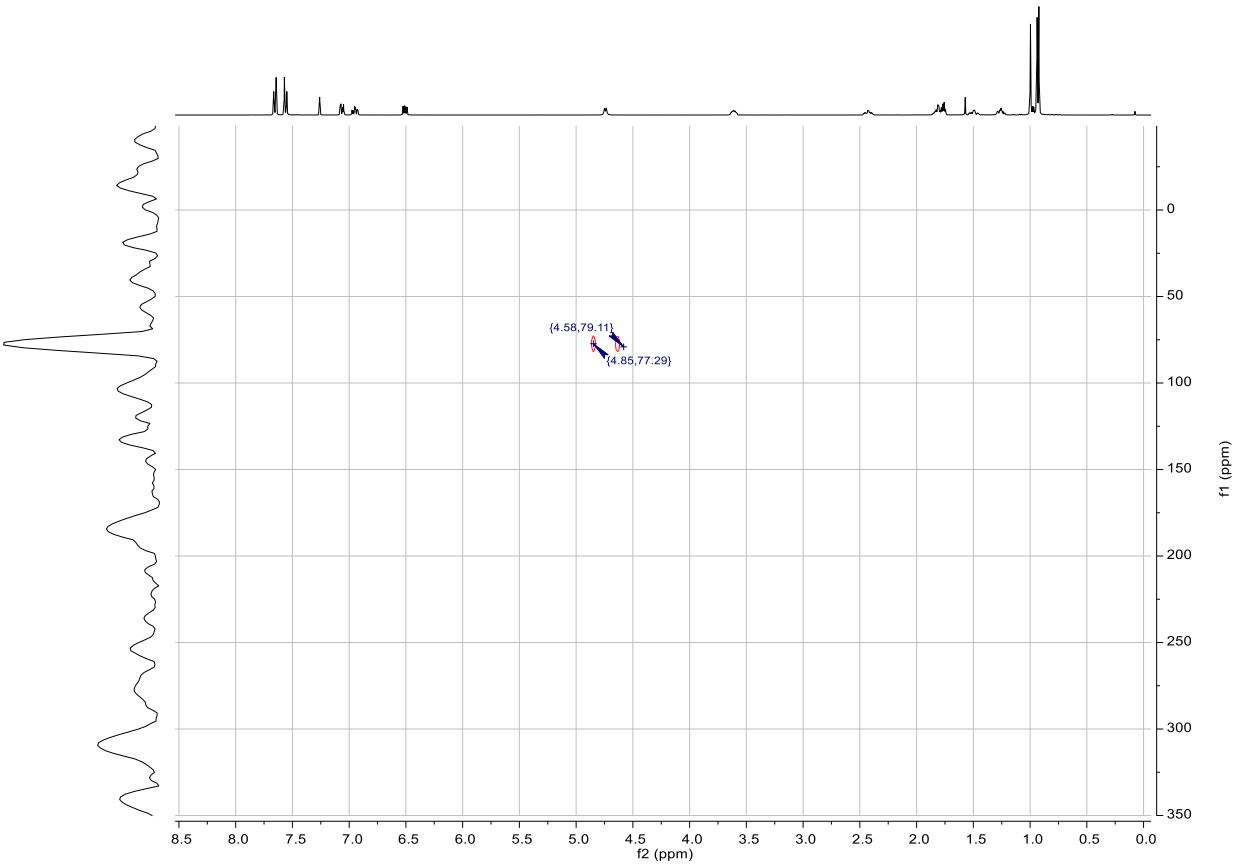
^{19}F NMR Spectrum of Compound 4dc (376 MHz, CDCl3)



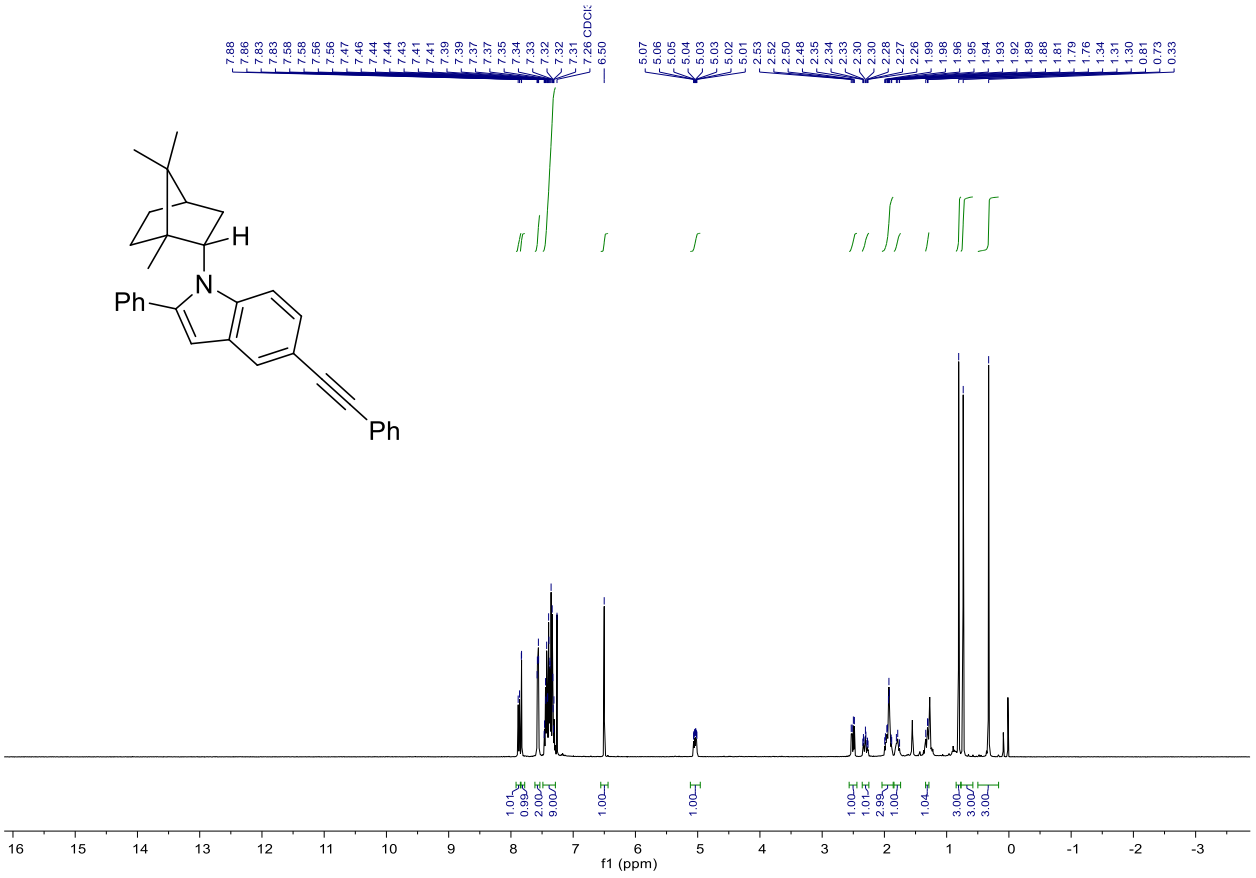
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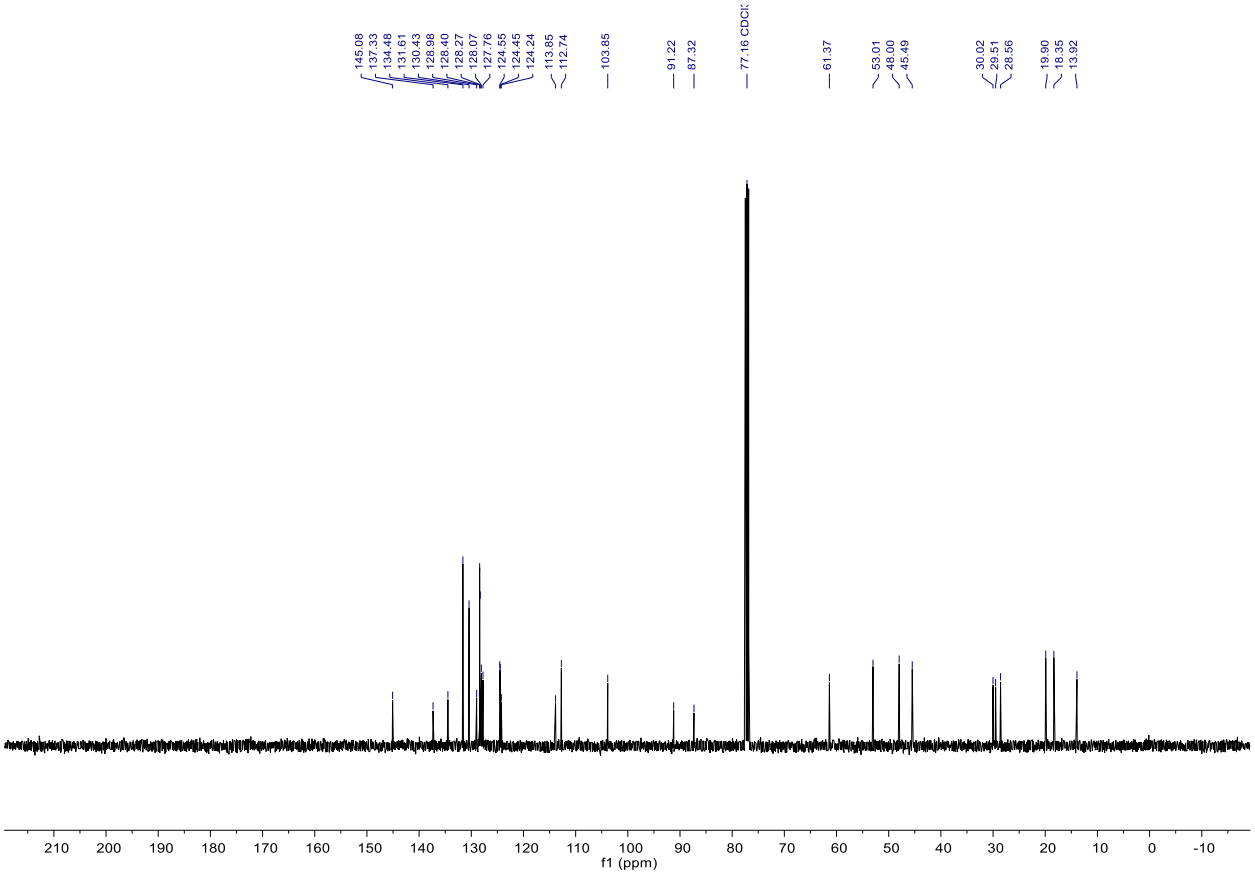
1H-15N HMBC NMR Spectrum of Compound 4dc



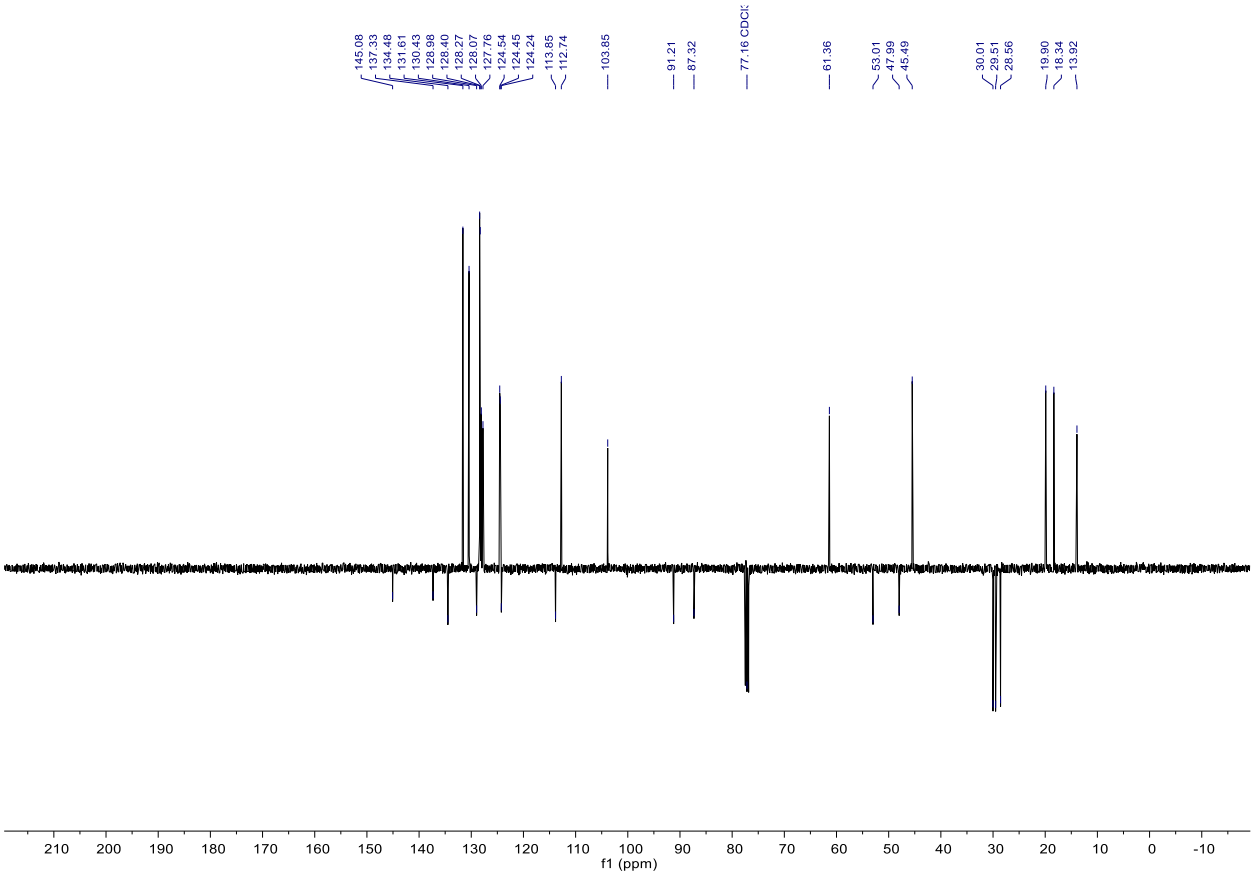
^{1}H NMR Spectrum of Compound 5aa (400 MHz, CDCl3)



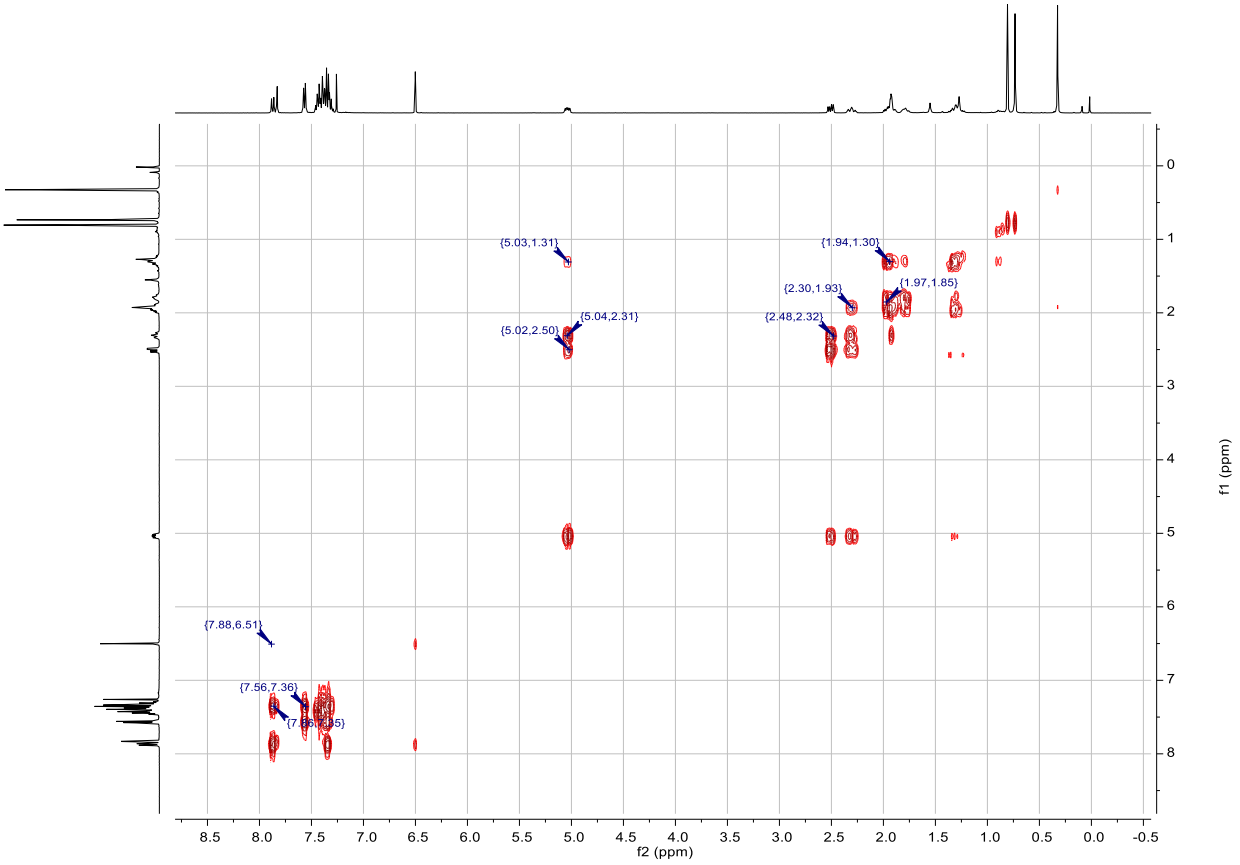
^{13}C NMR Spectrum of Compound 5aa (101 MHz, CDCl3)



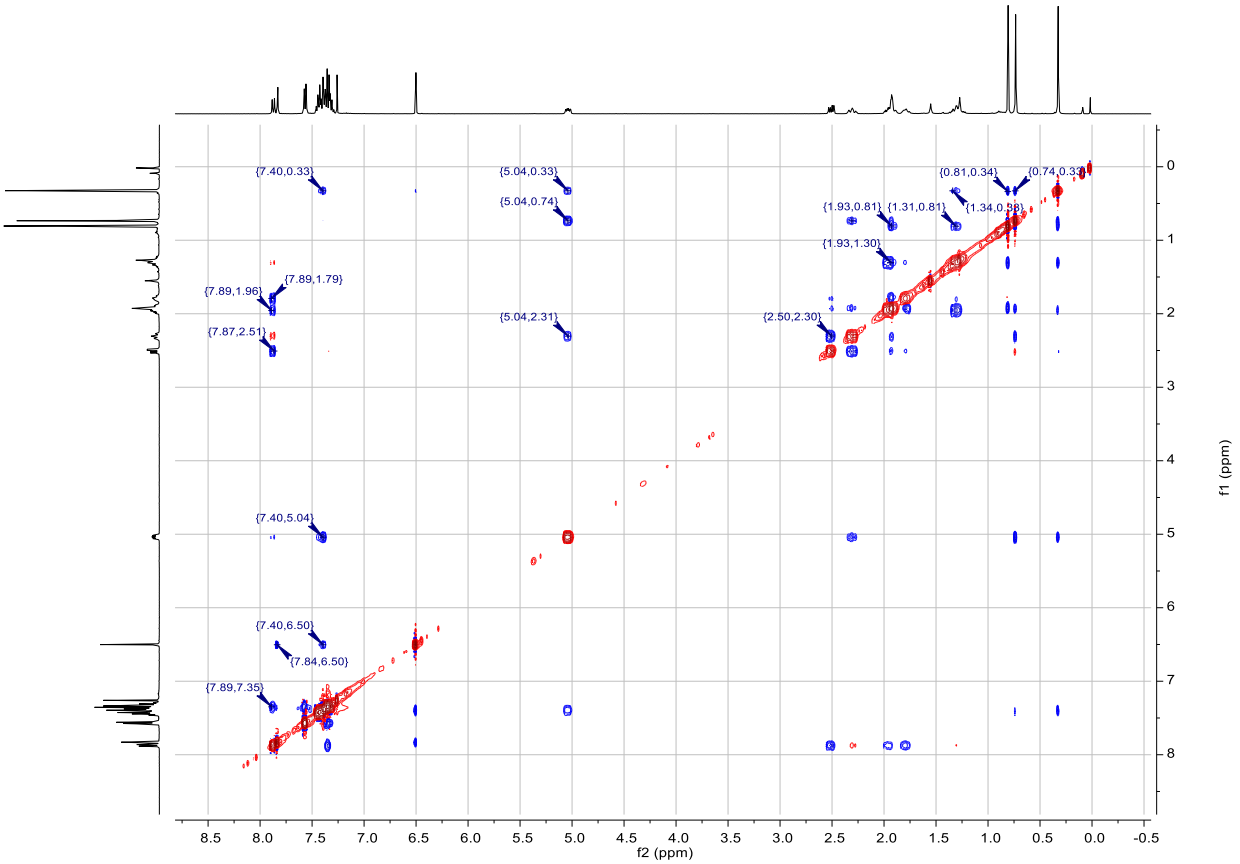
^{13}C DEPTQ-135 NMR Spectrum of Compound 5aa



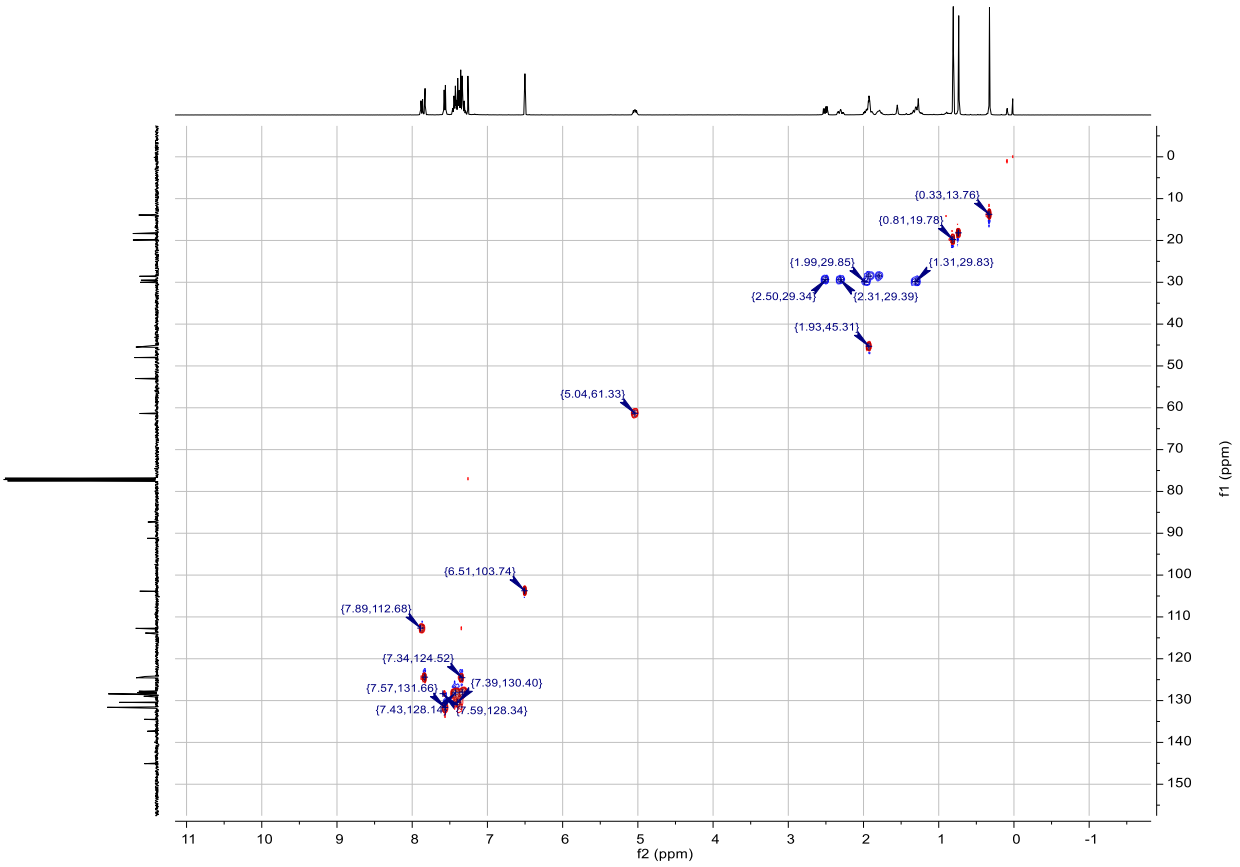
1H-1H COSY NMR Spectrum of Compound 5aa



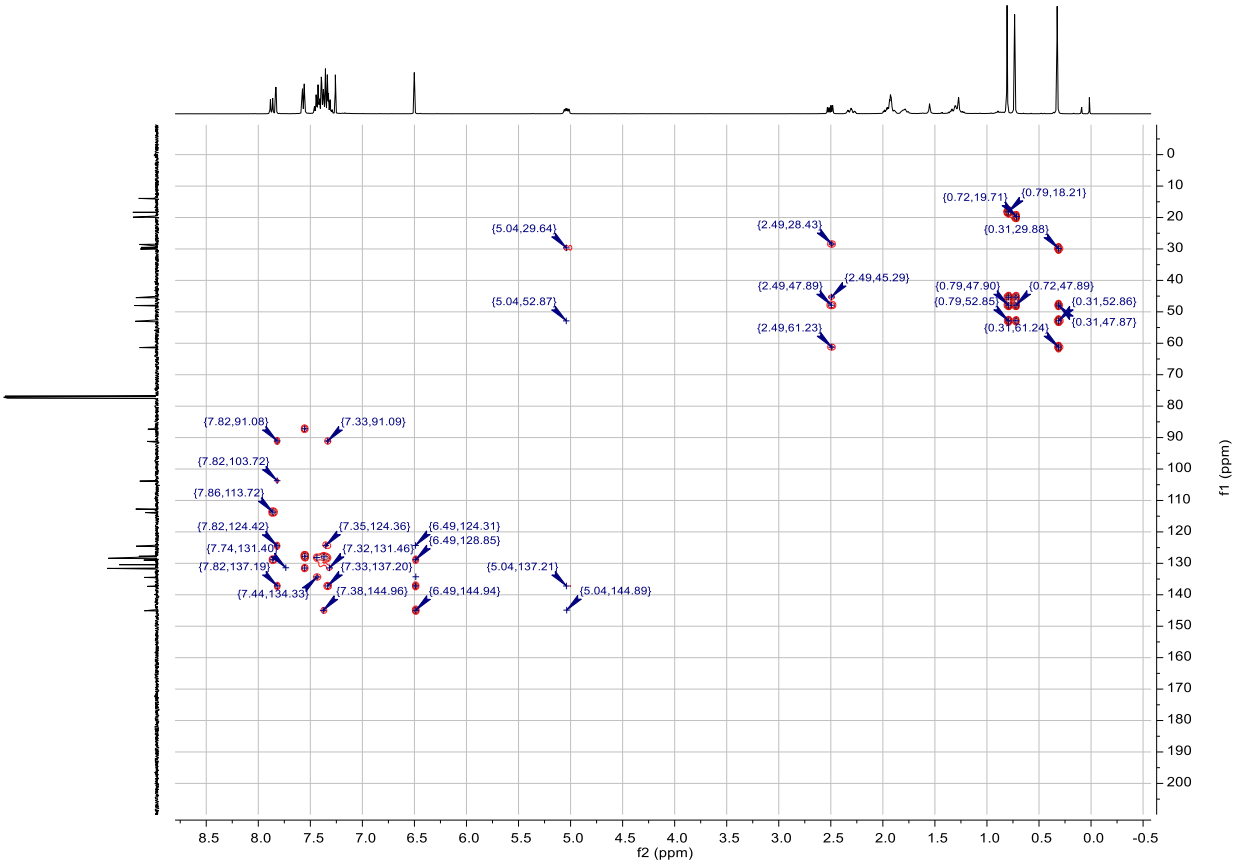
1H-1H NOESY NMR Spectrum of Compound 5aa



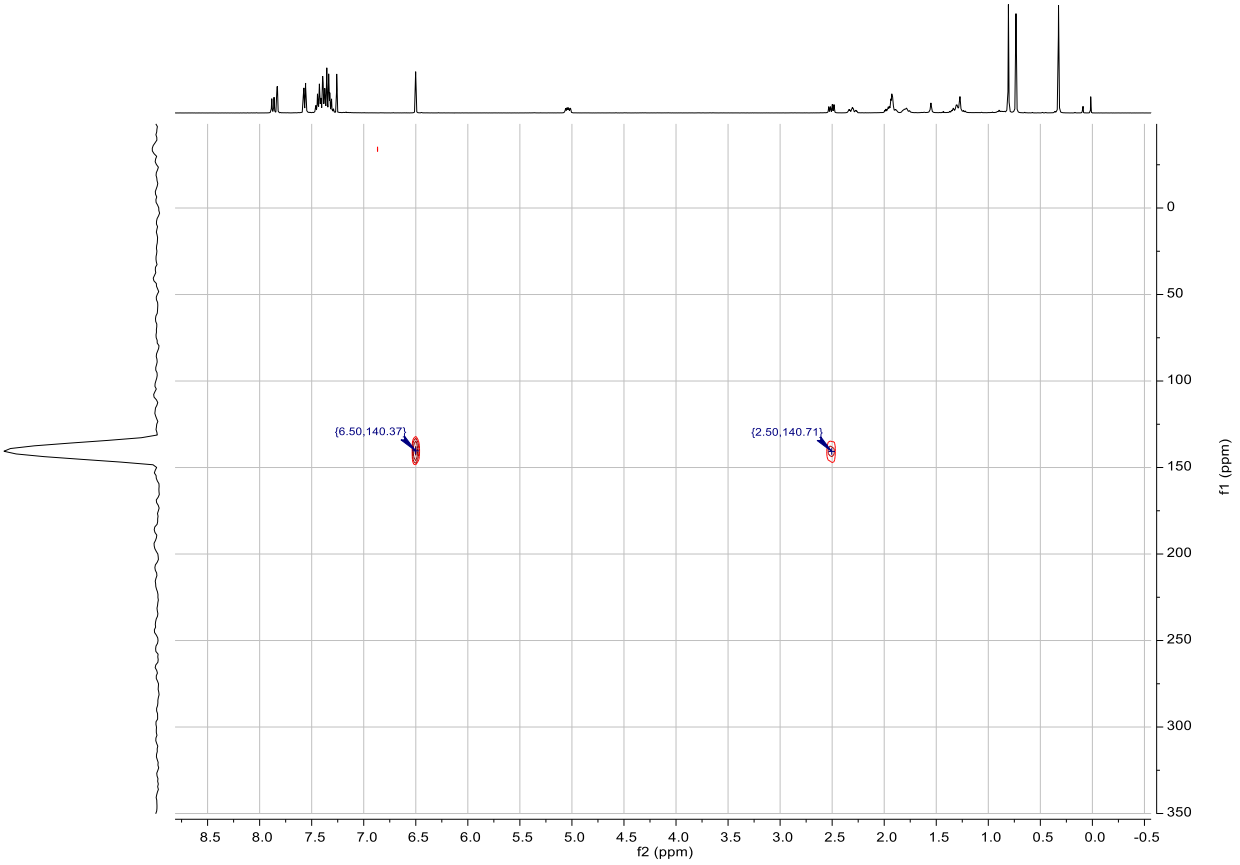
1H-13C HSQC NMR Spectrum of Compound 5aa



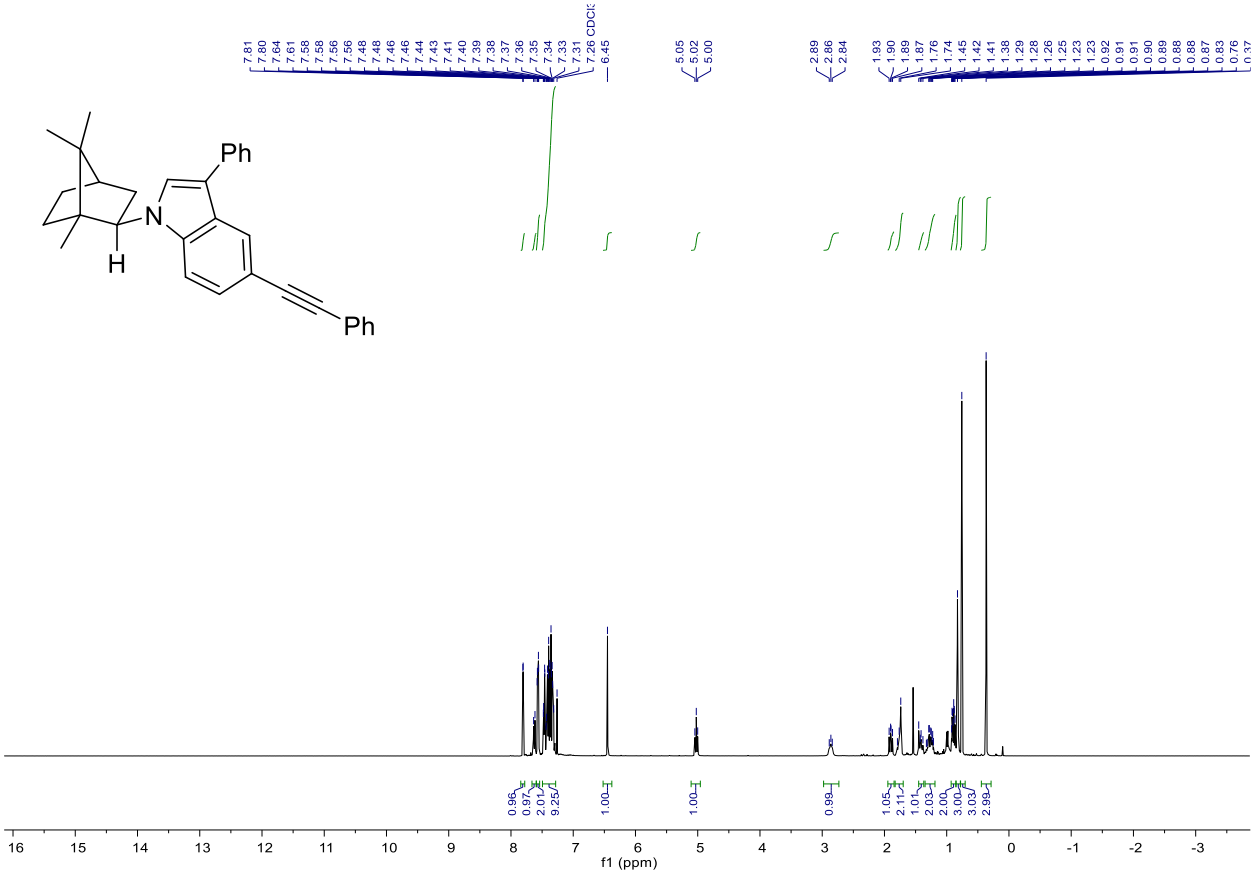
1H-13C HMBC NMR Spectrum of Compound 5aa



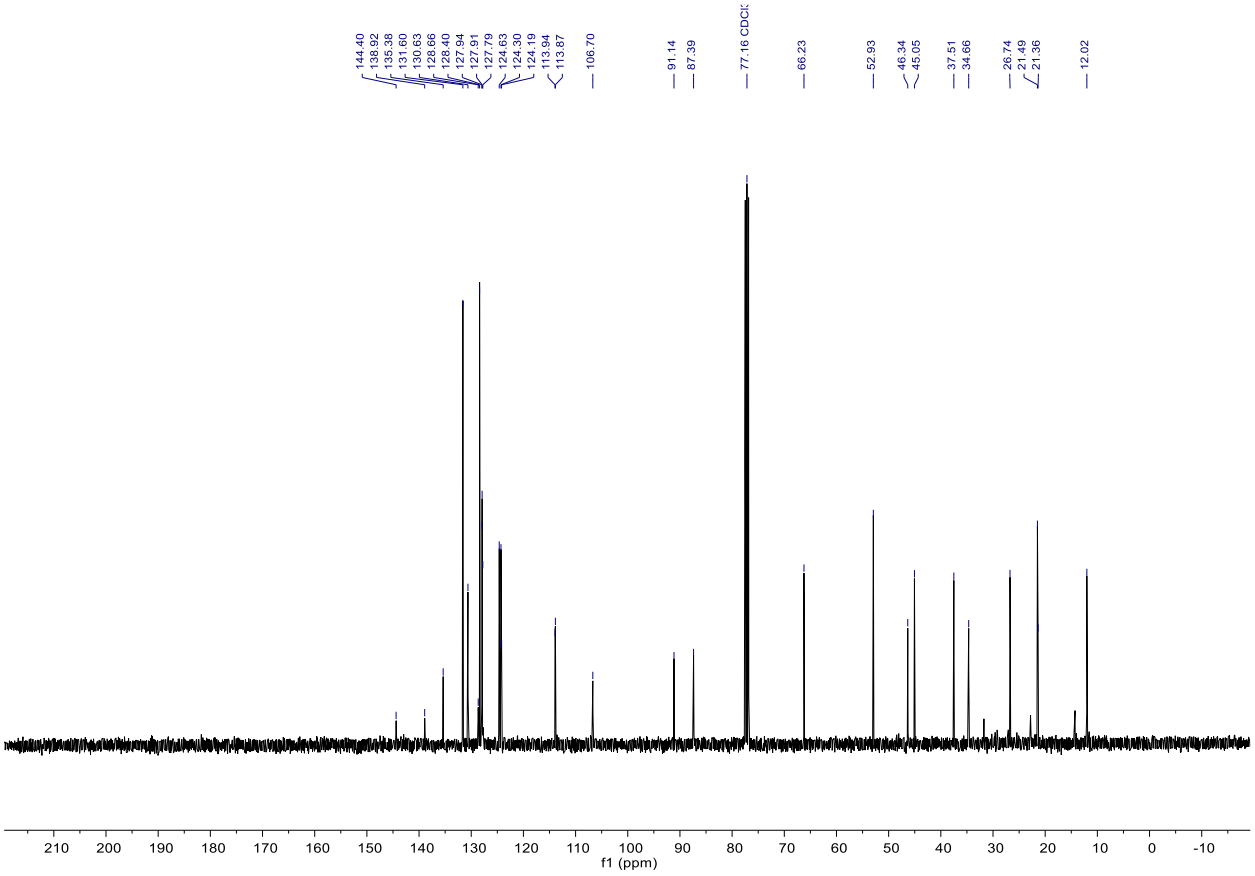
1H-15N HMBC NMR Spectrum of Compound 5aa



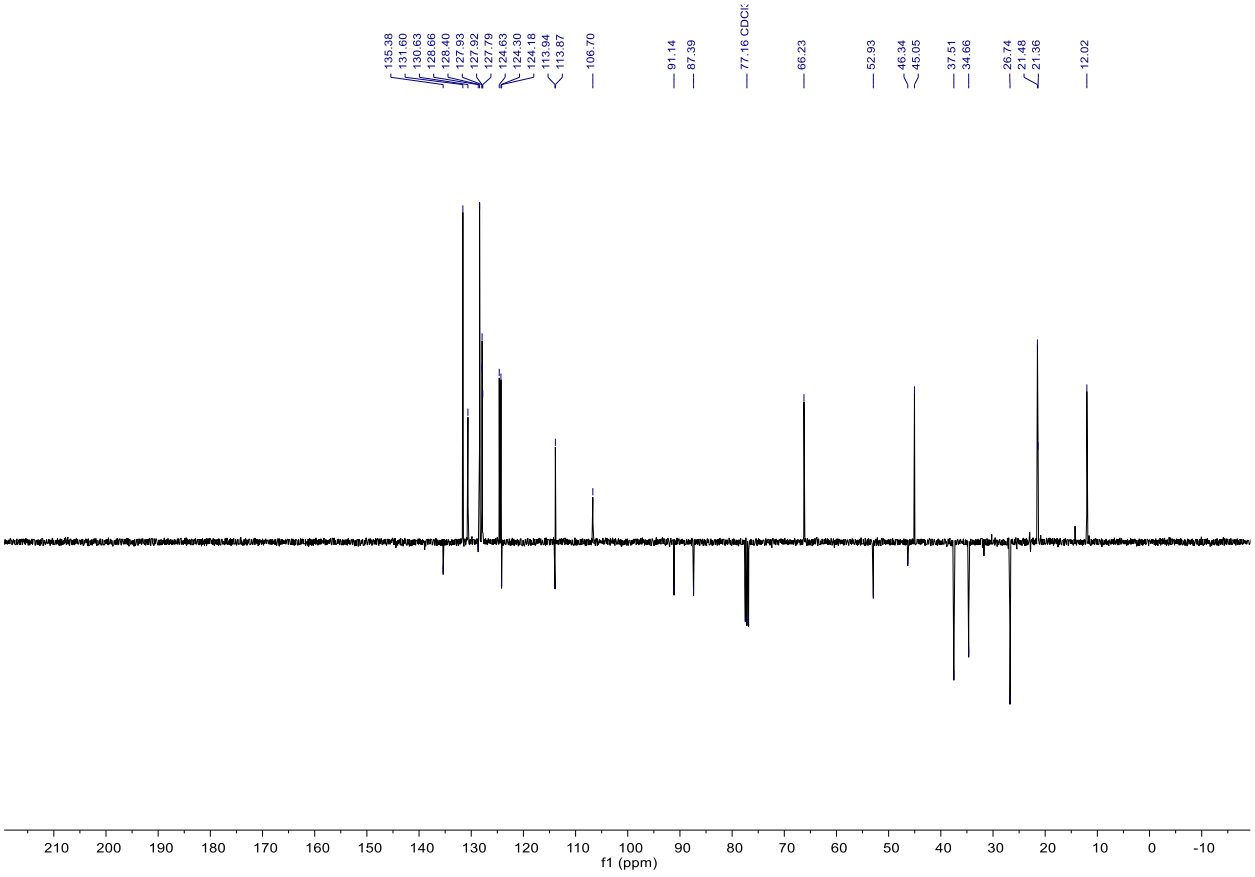
^{1}H NMR Spectrum of Compound 5aa' (400 MHz, CDCl3)



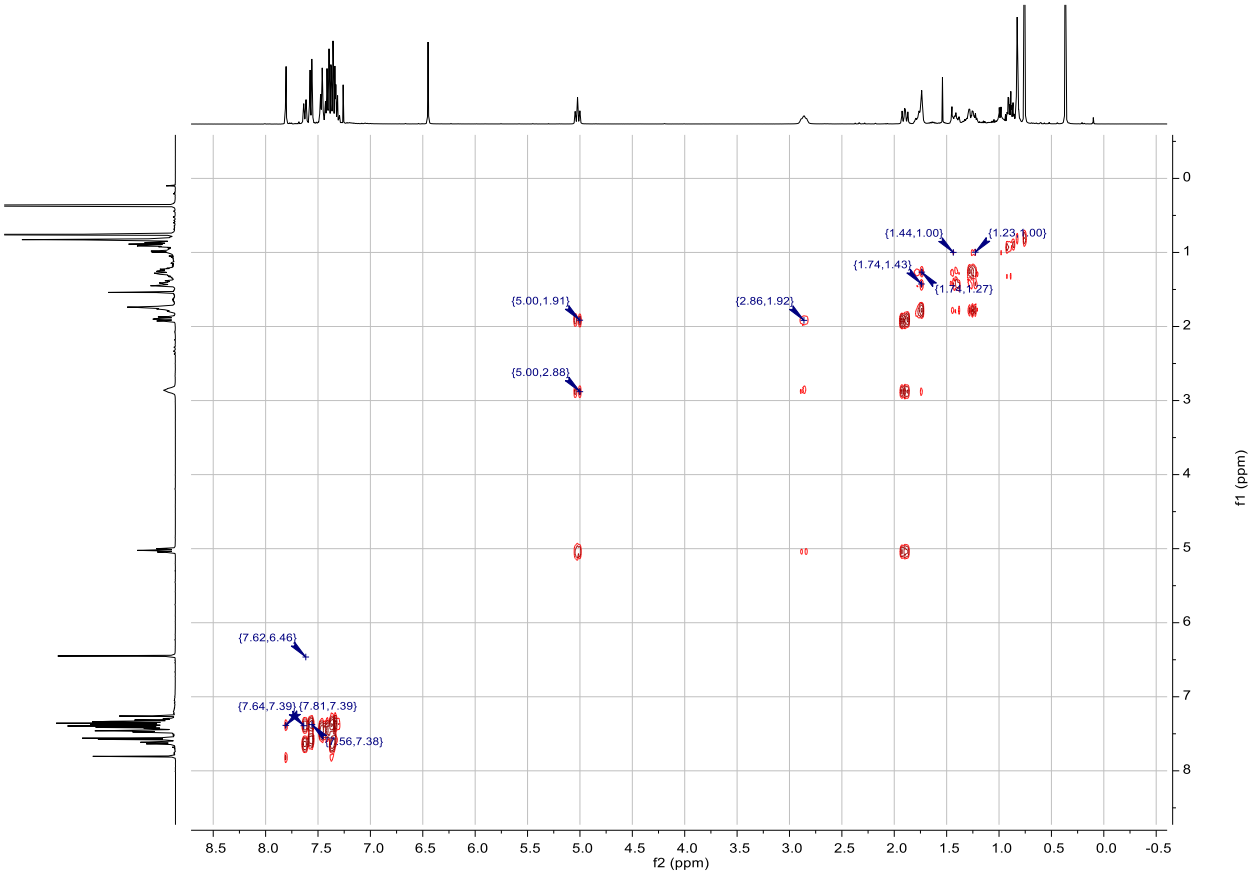
^{13}C NMR Spectrum of Compound 5aa' (101 MHz, CDCl3)



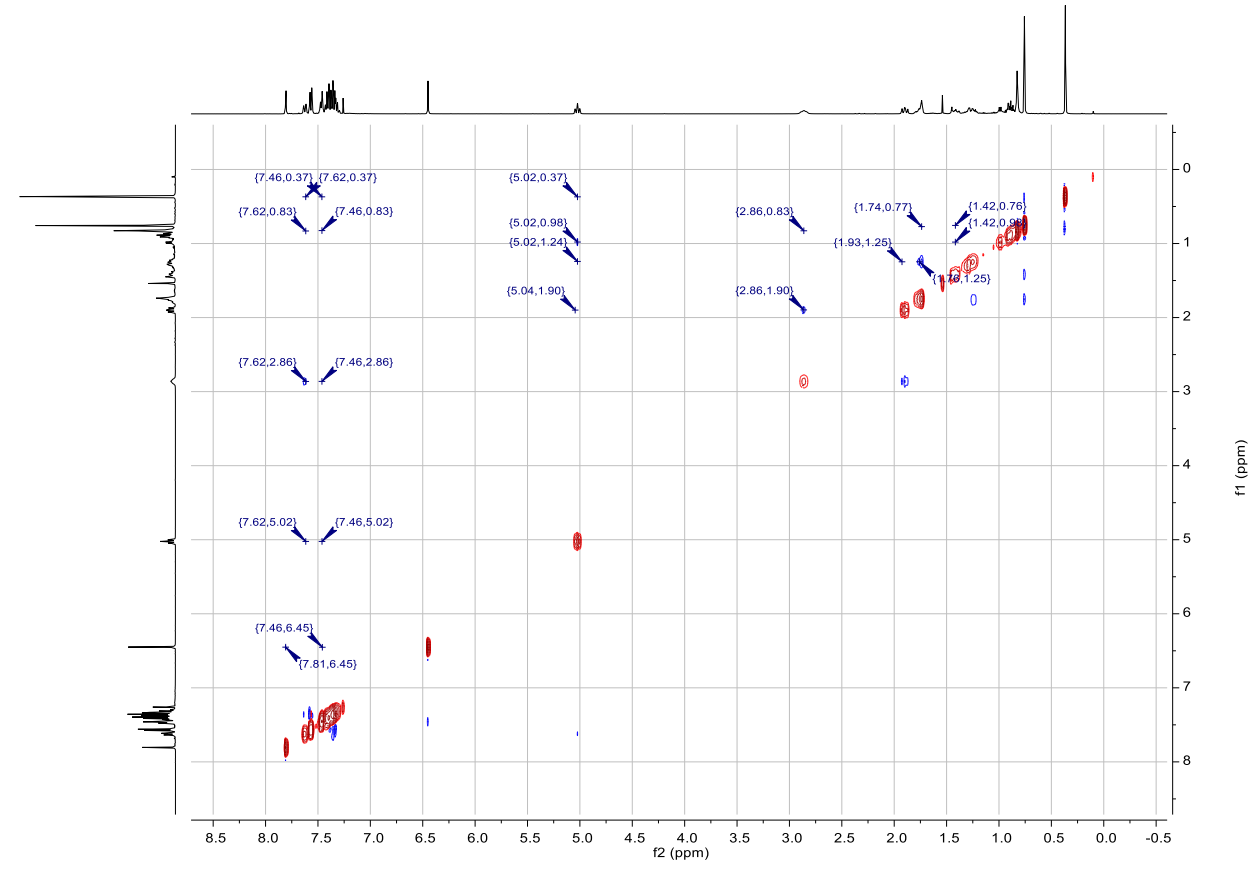
^{13}C DEPTQ-135 NMR Spectrum of Compound 5aa'



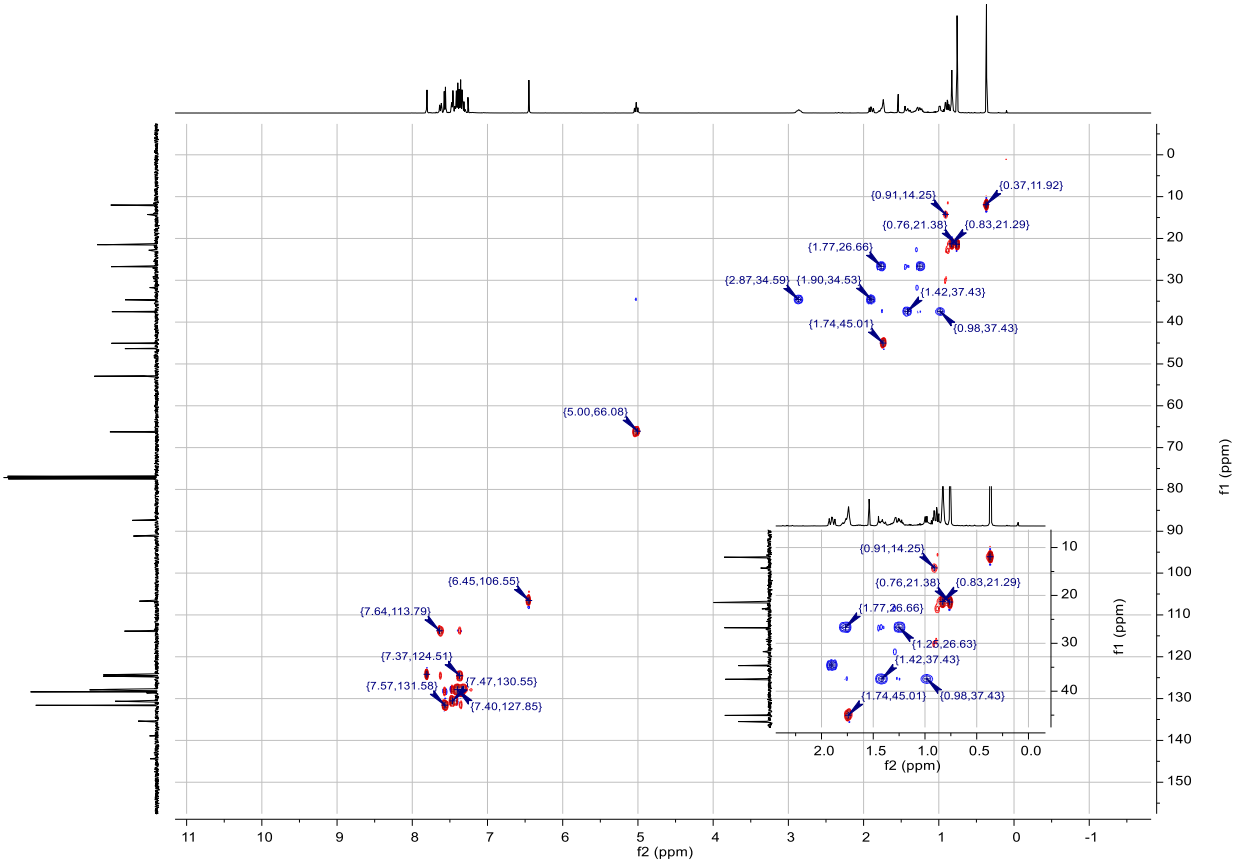
1H-1H COSY NMR Spectrum of Compound 5aa’



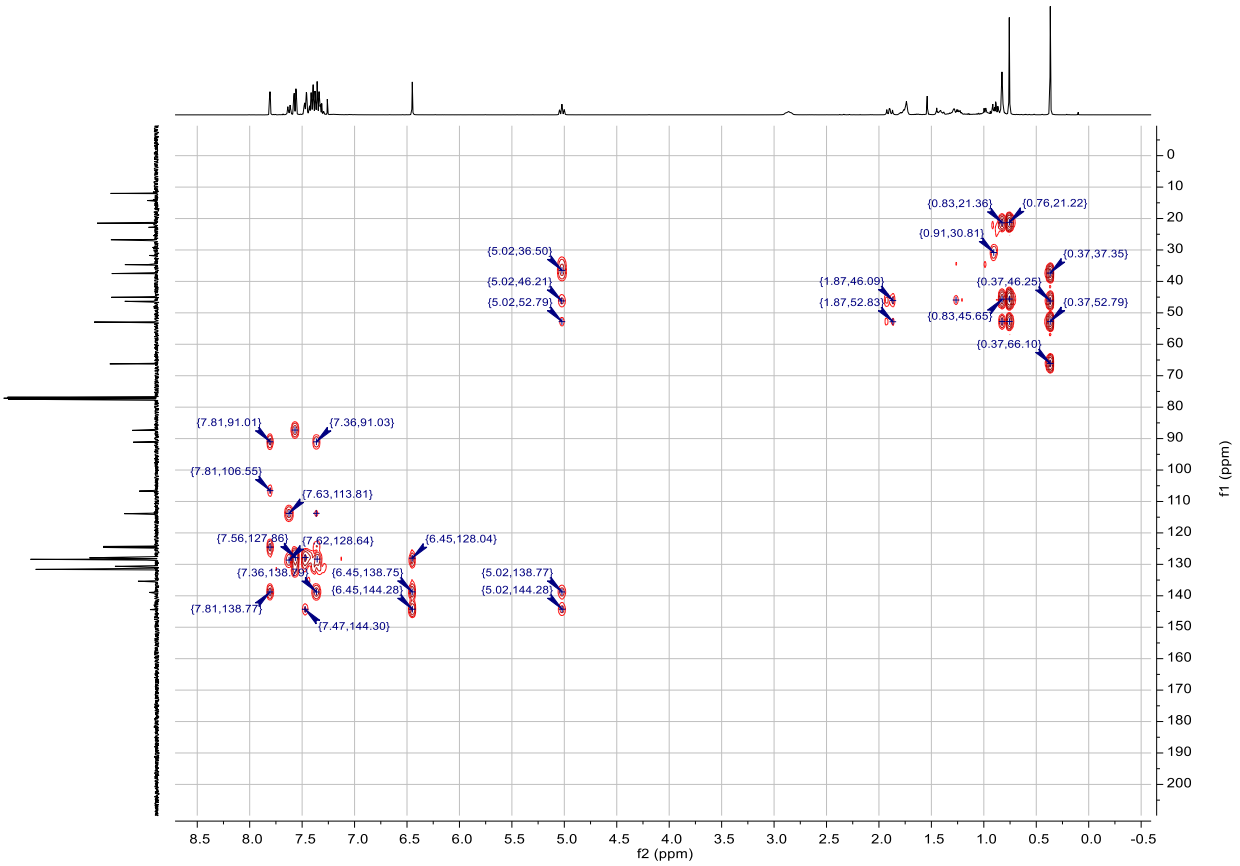
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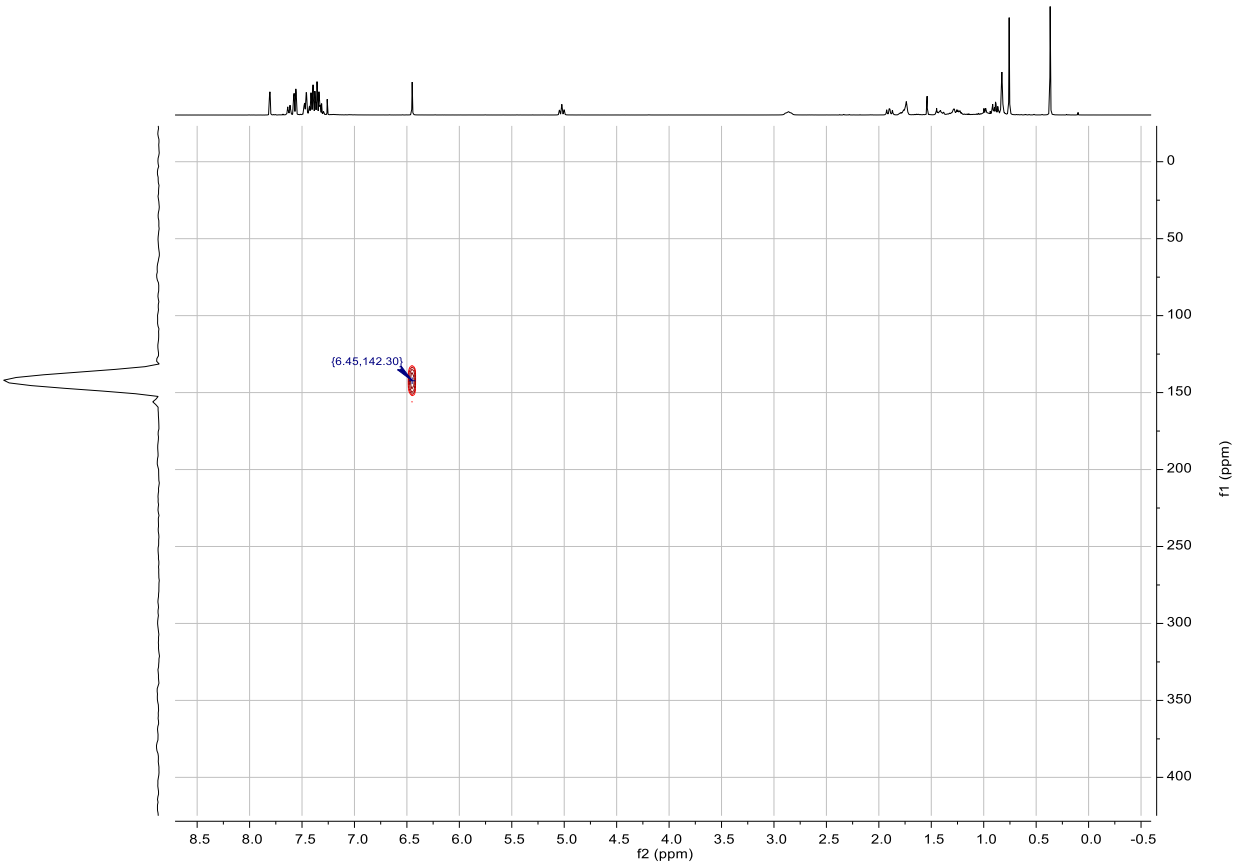
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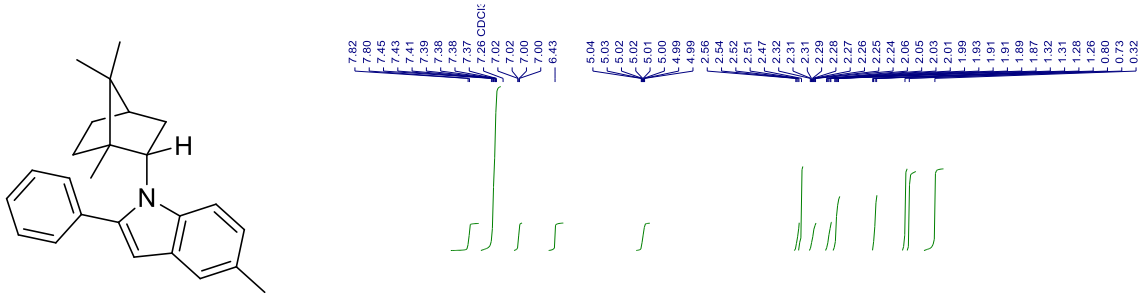
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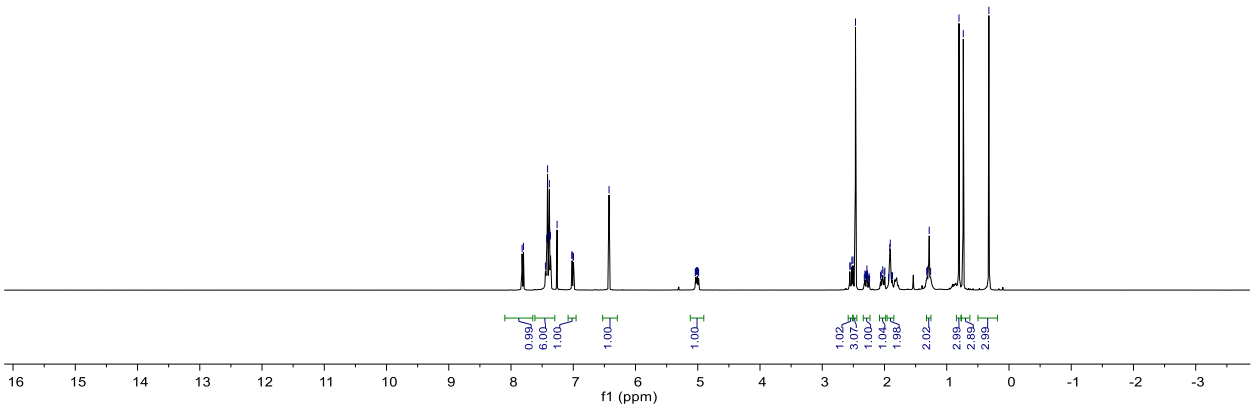


1H-15N HMBC NMR Spectrum of Compound 5aa’

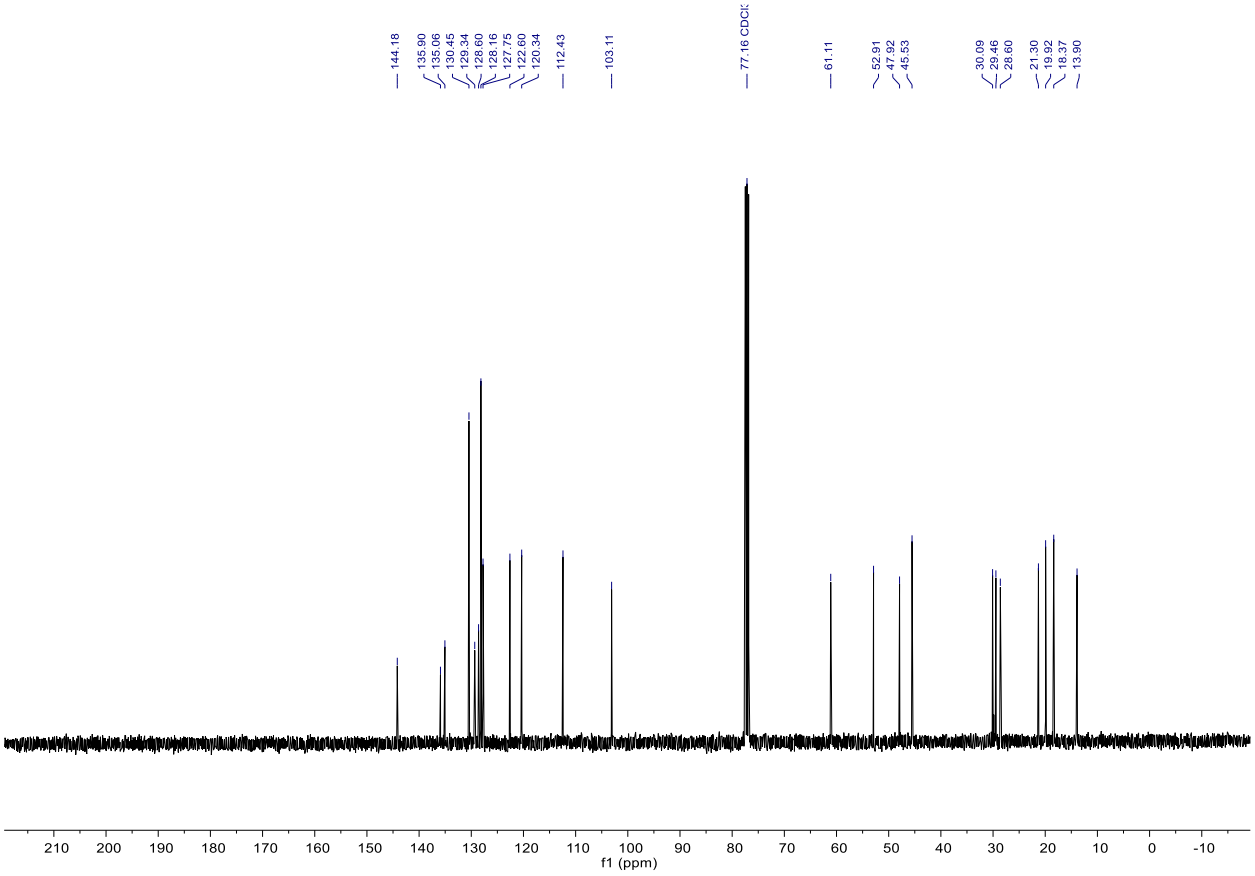


^{1}H NMR Spectrum of Compound 5ba (400 MHz, CDCl3)

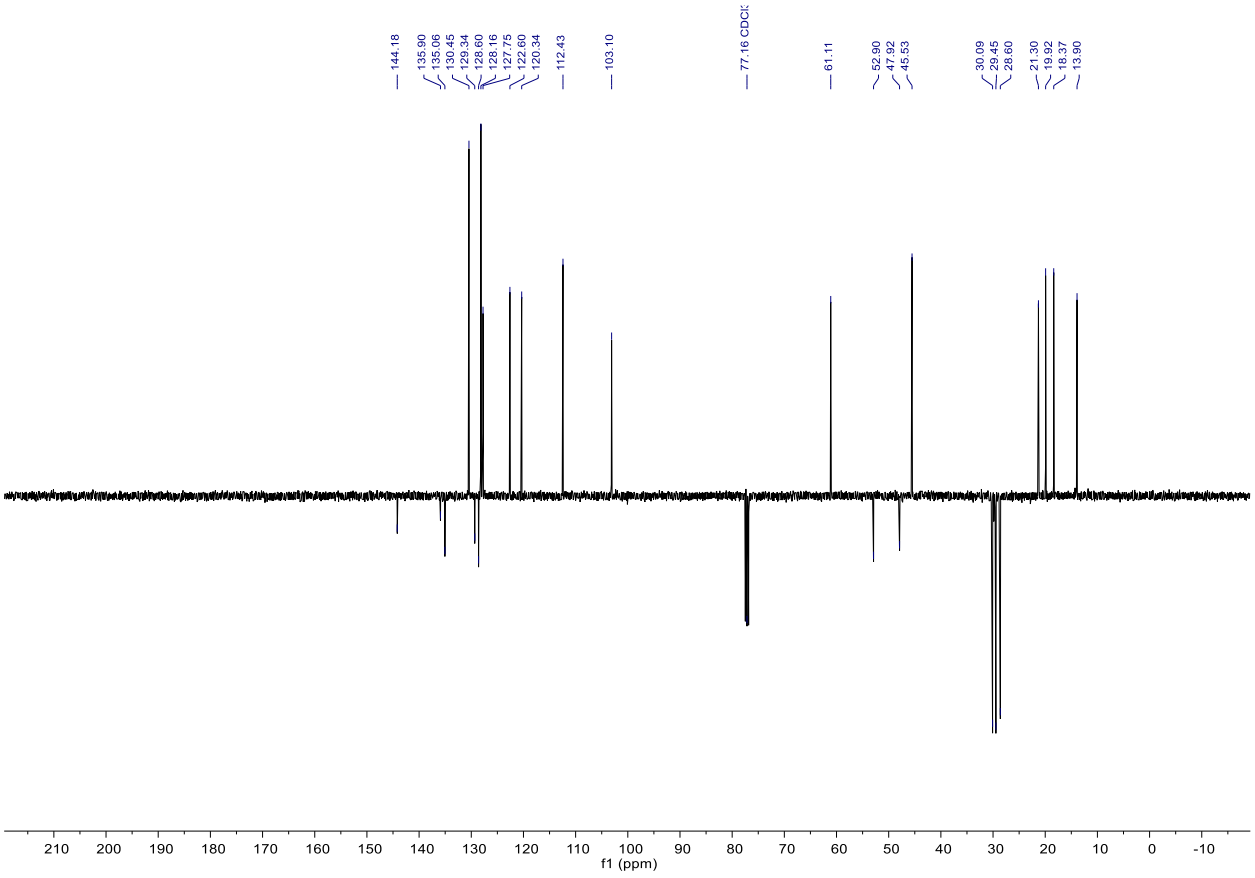




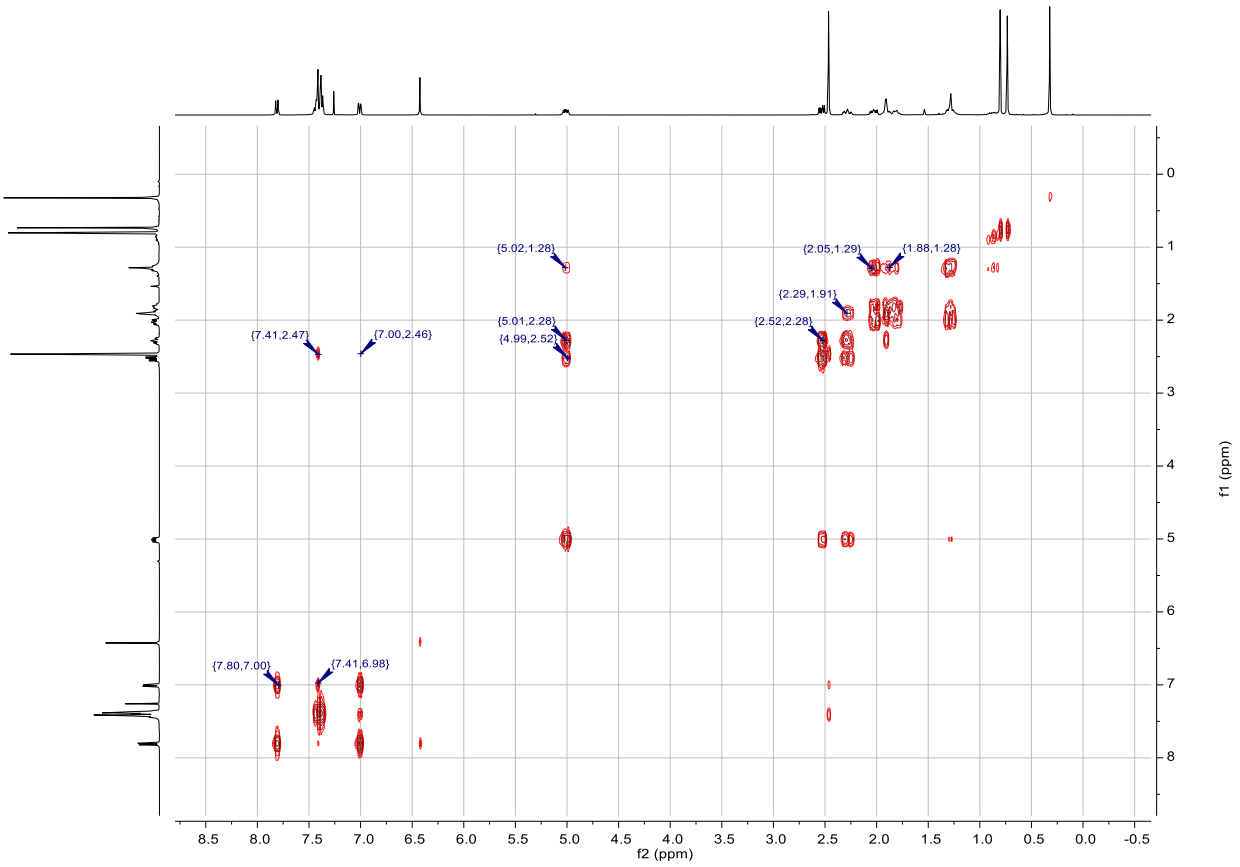
^{13}C NMR Spectrum of Compound 5ba (101 MHz, CDCl3)



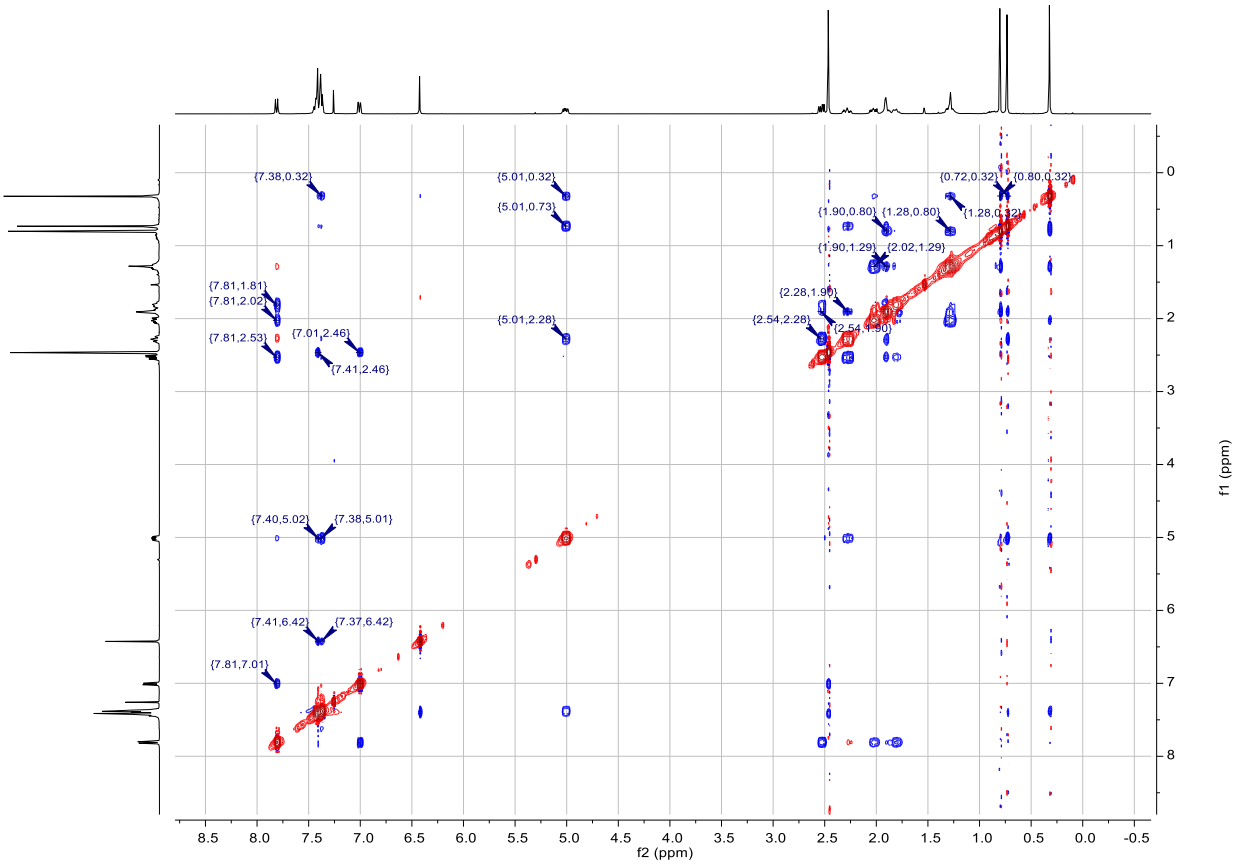
^{13}C DEPTQ-135 NMR Spectrum of Compound 5ba



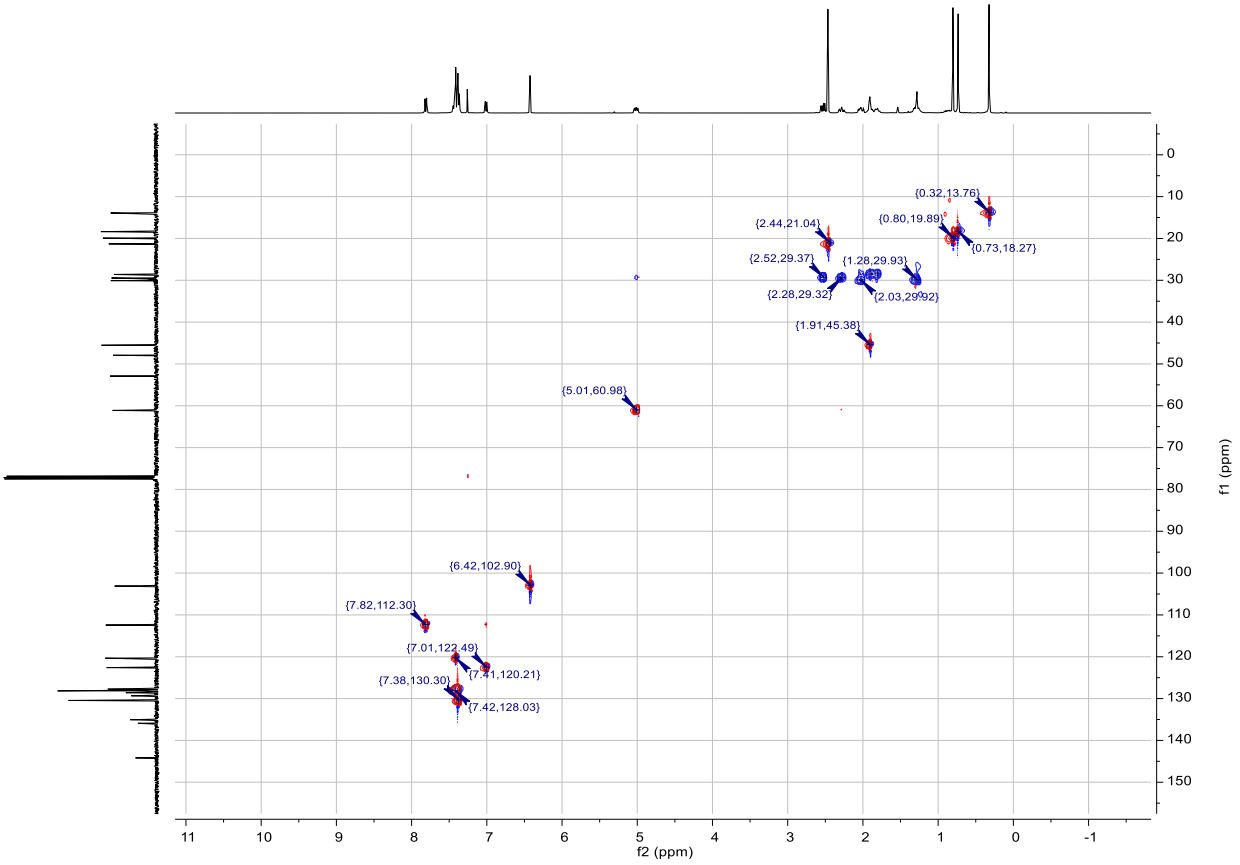
1H-1H COSY NMR Spectrum of Compound 5ba



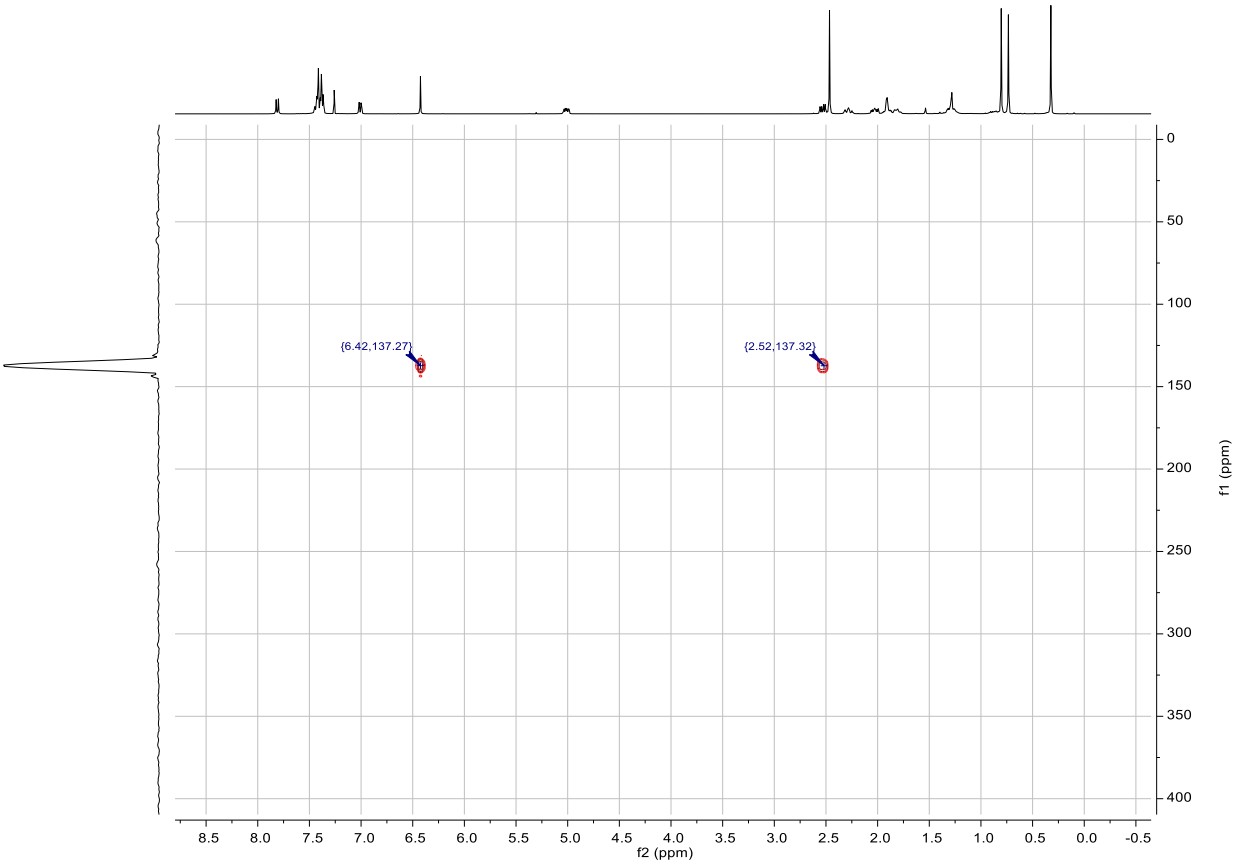
1H-1H NOESY NMR Spectrum of Compound 5ba



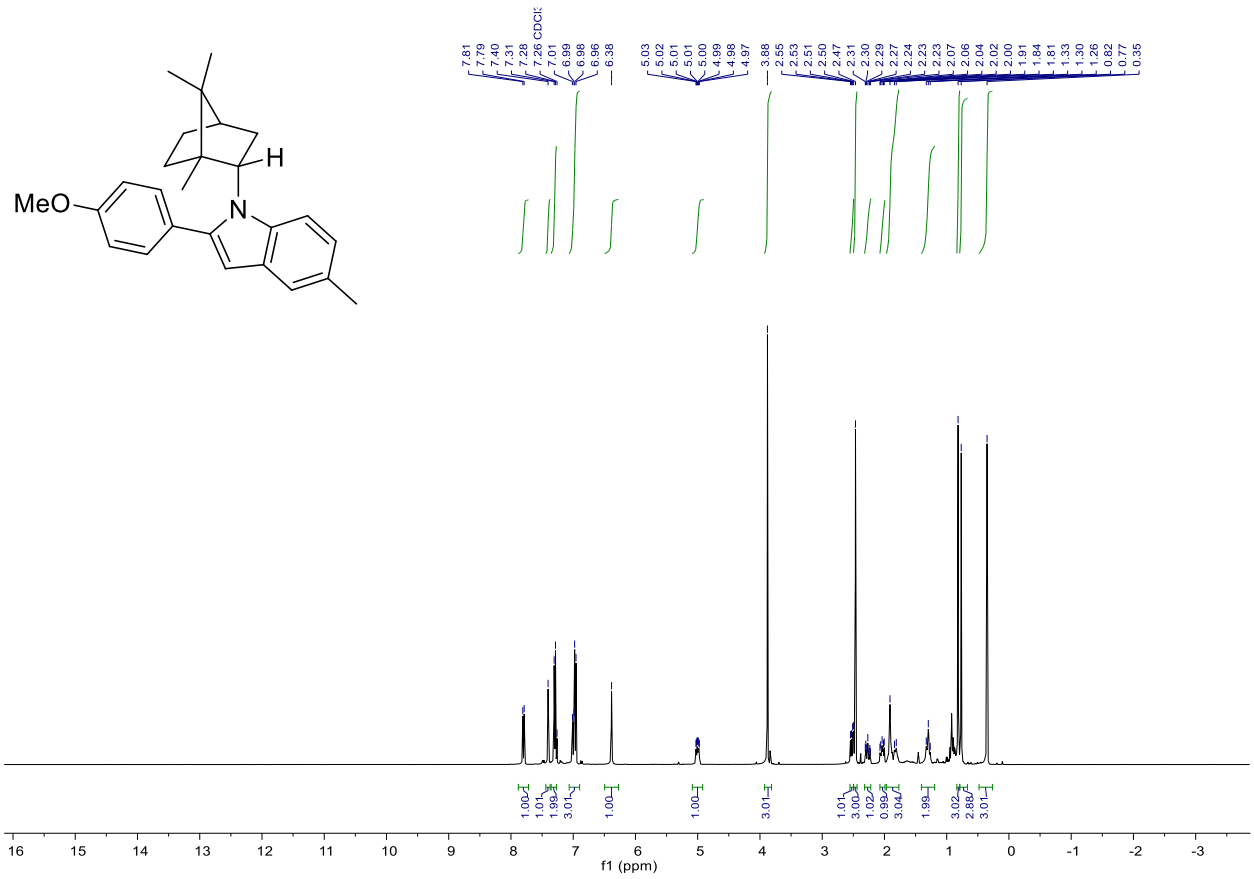
1H-13C HSQC NMR Spectrum of Compound 5ba



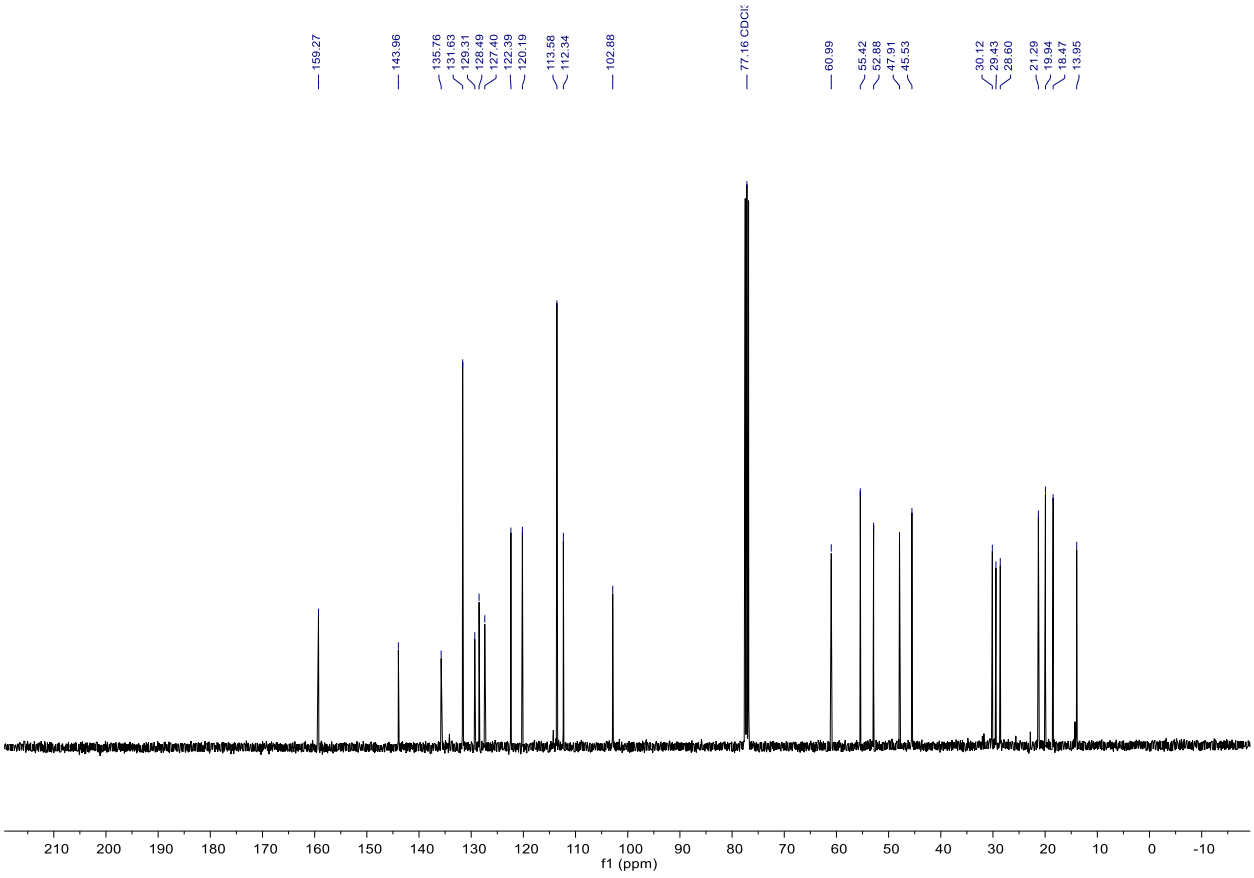
1H-15N HMBC NMR Spectrum of Compound 5ba



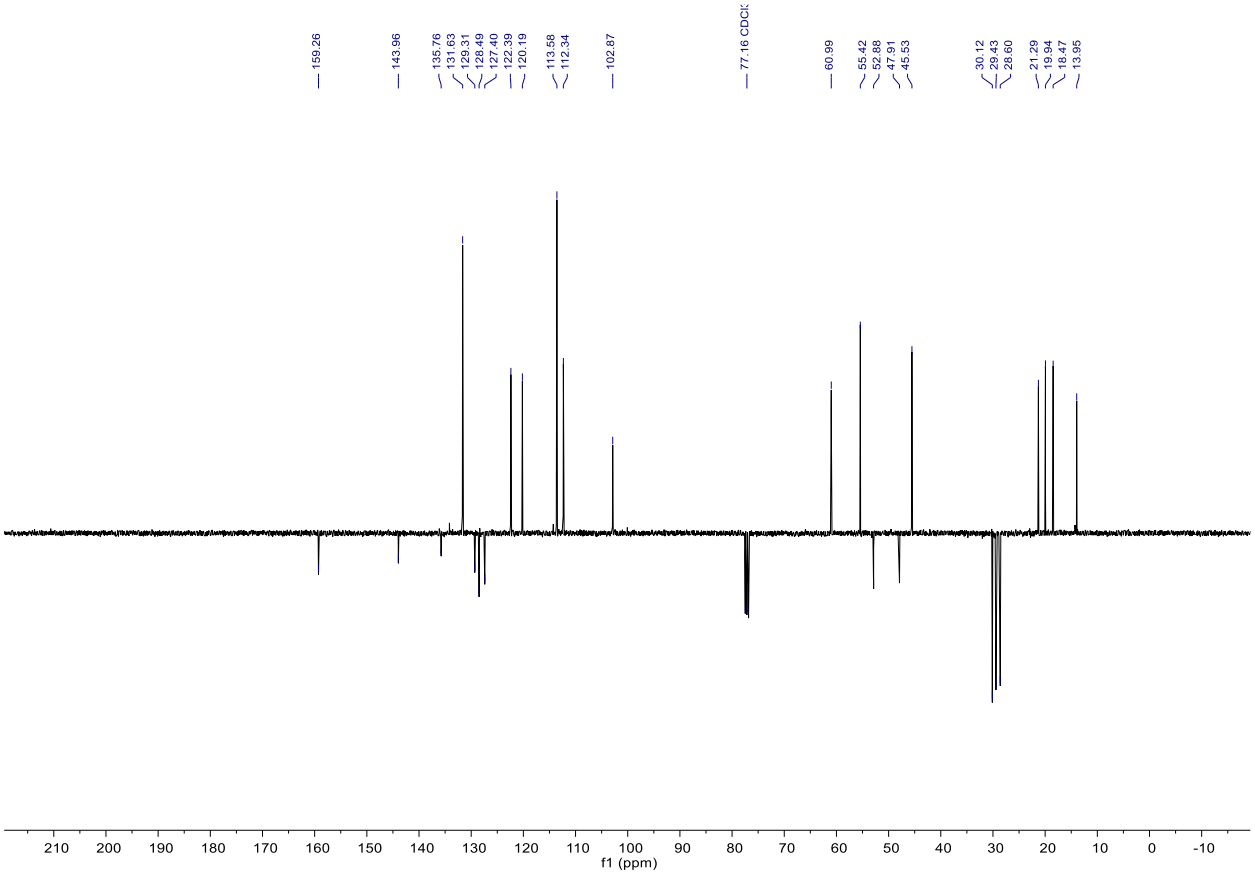
^{1}H NMR Spectrum of Compound 5bb (400 MHz, CDCl3)



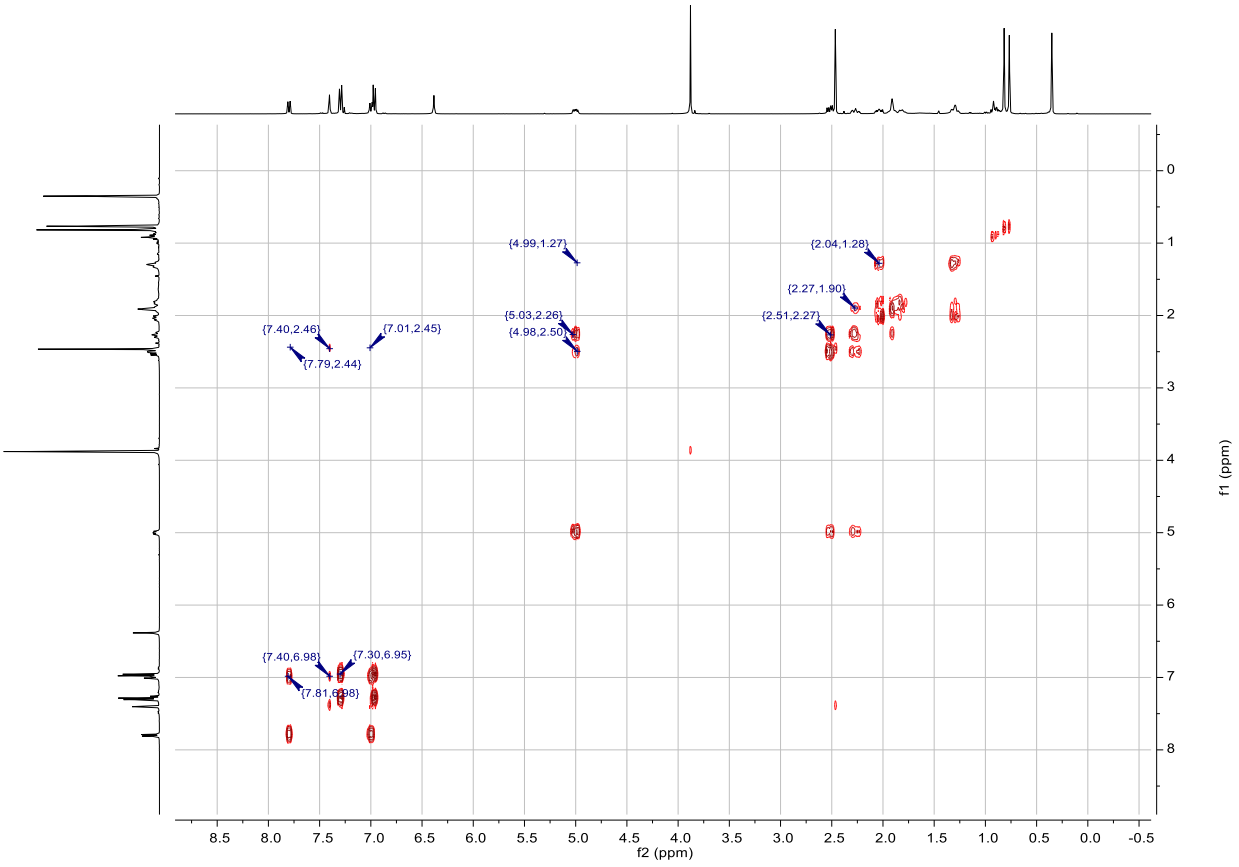
^{13}C NMR Spectrum of Compound 5bb (101 MHz, CDCl3)



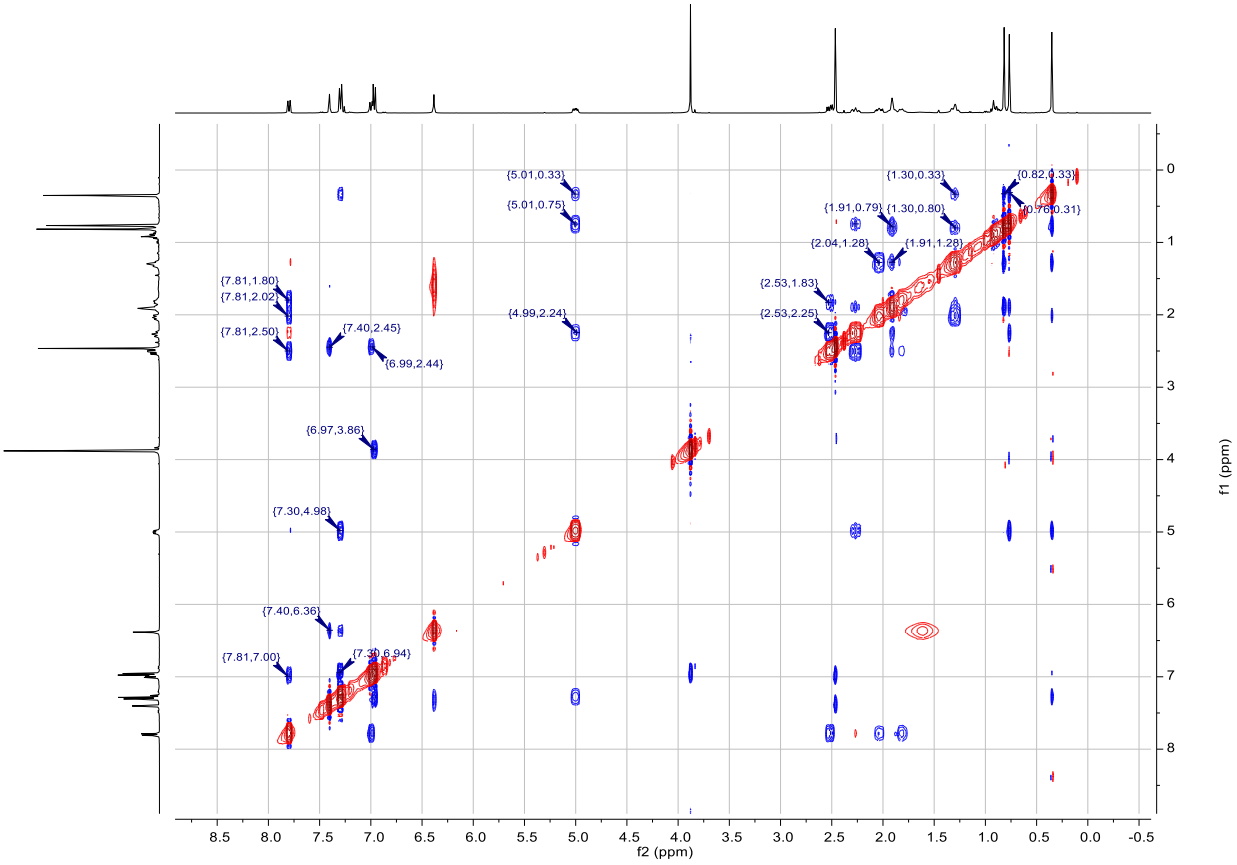
^{13}C DEPTQ-135 NMR Spectrum of Compound 5bb



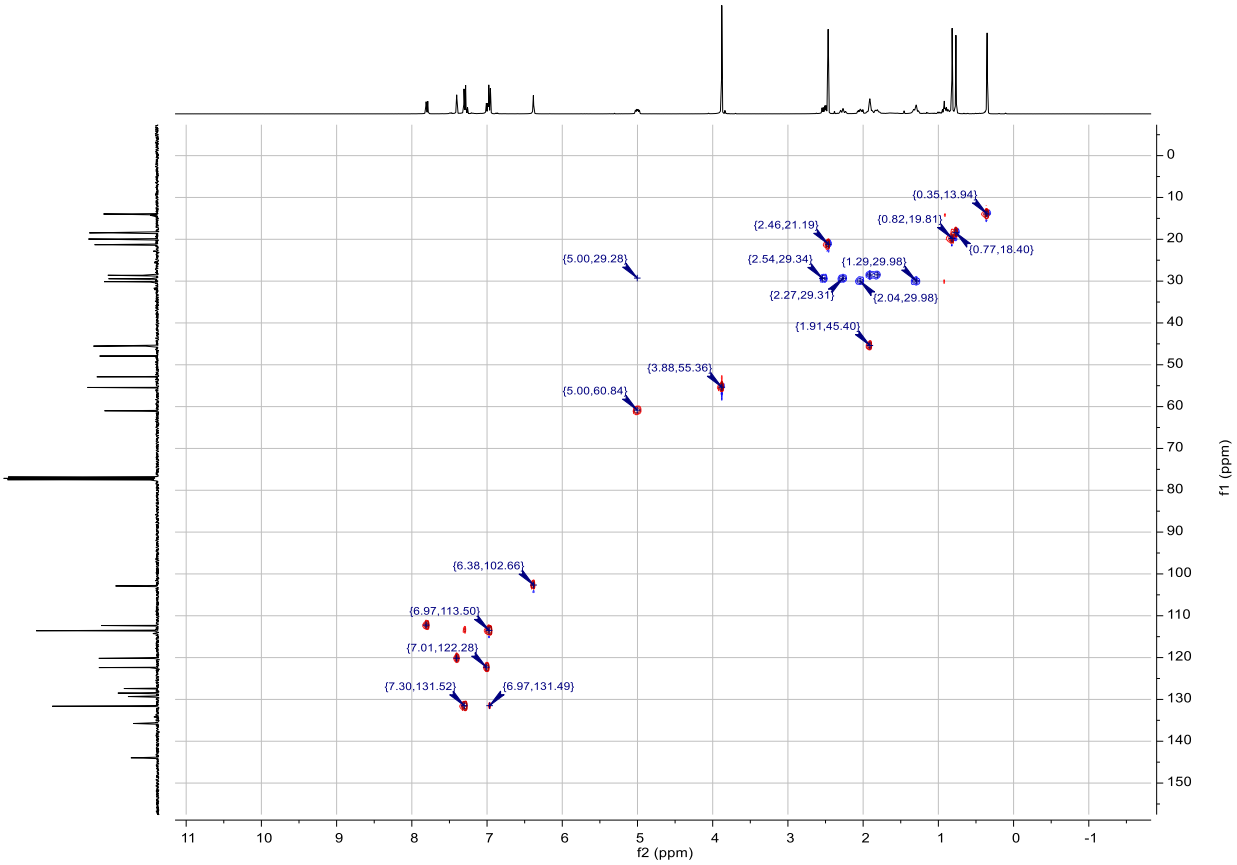
1H-1H COSY NMR Spectrum of Compound 5bb



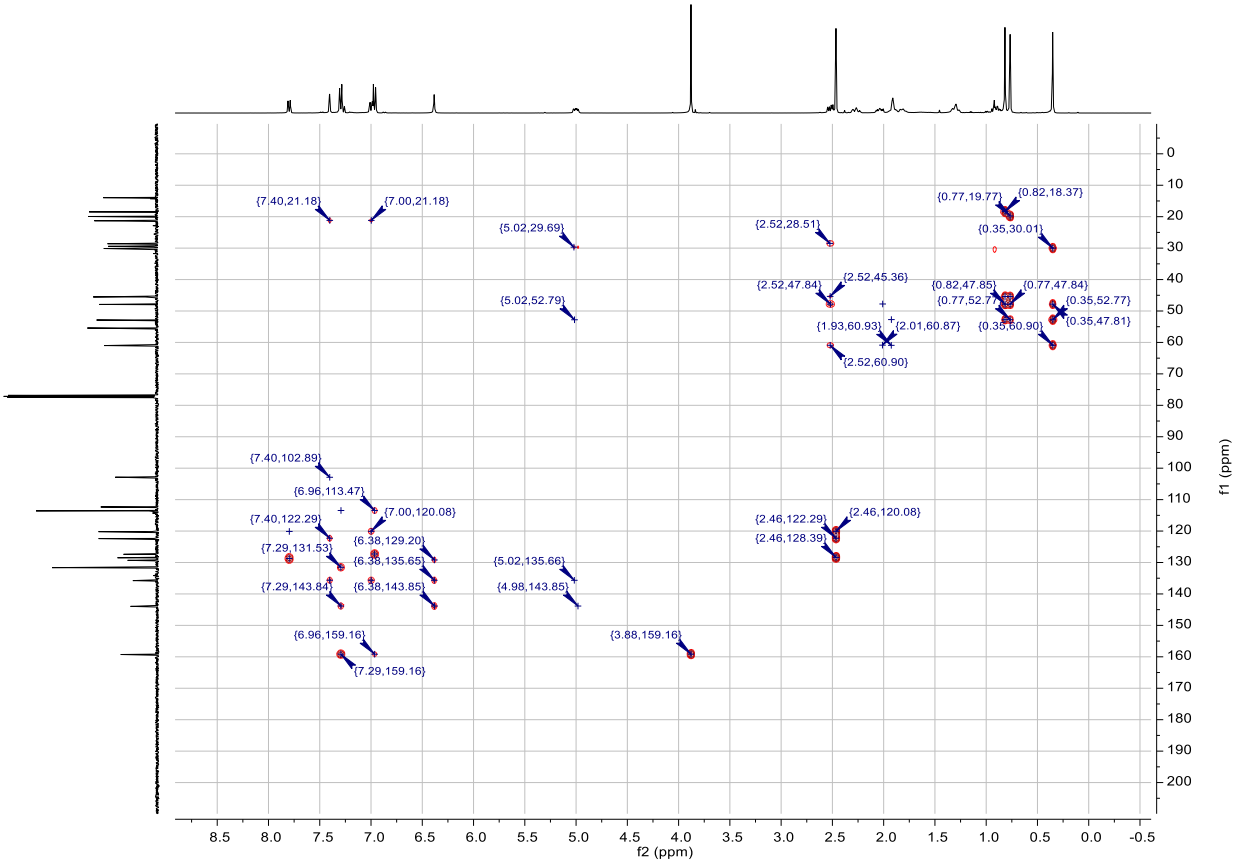
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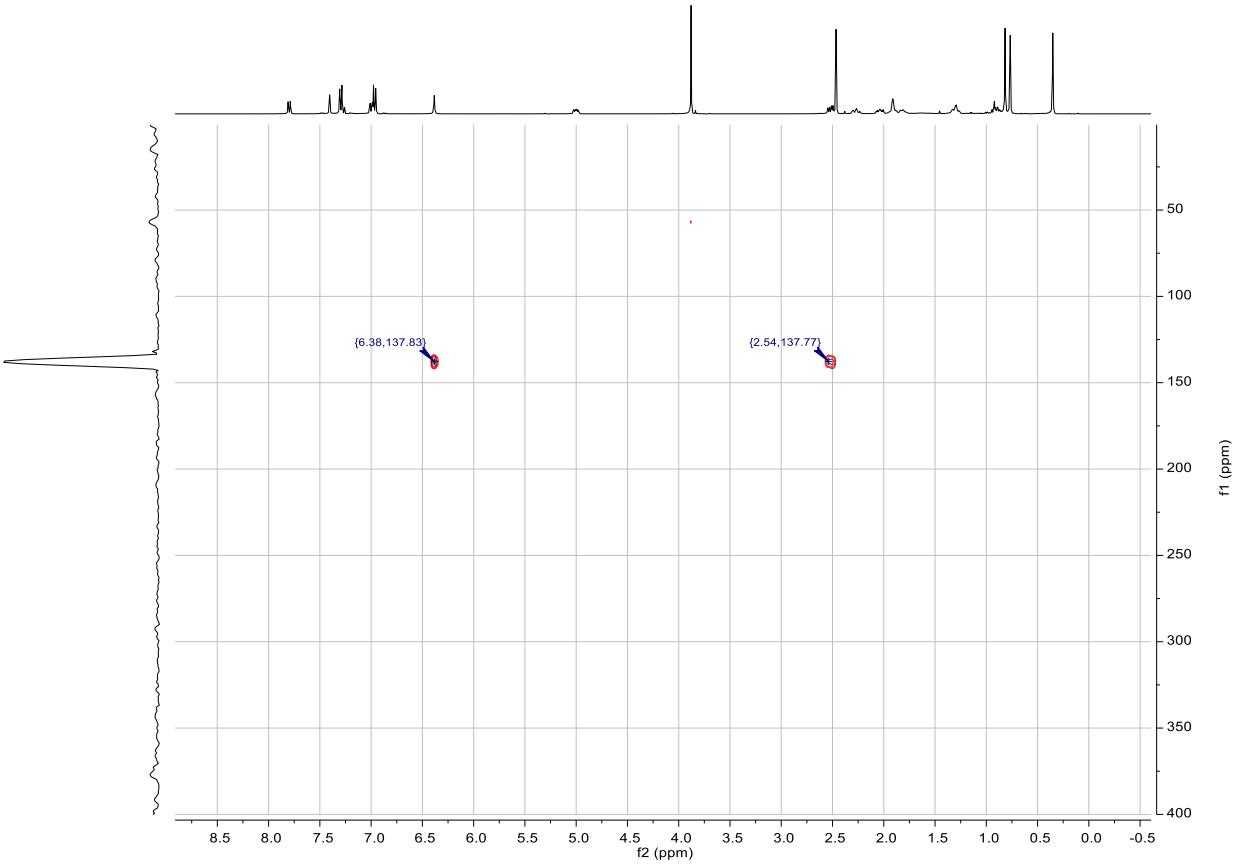
1H-13C HSQC NMR Spectrum of Compound 5bb



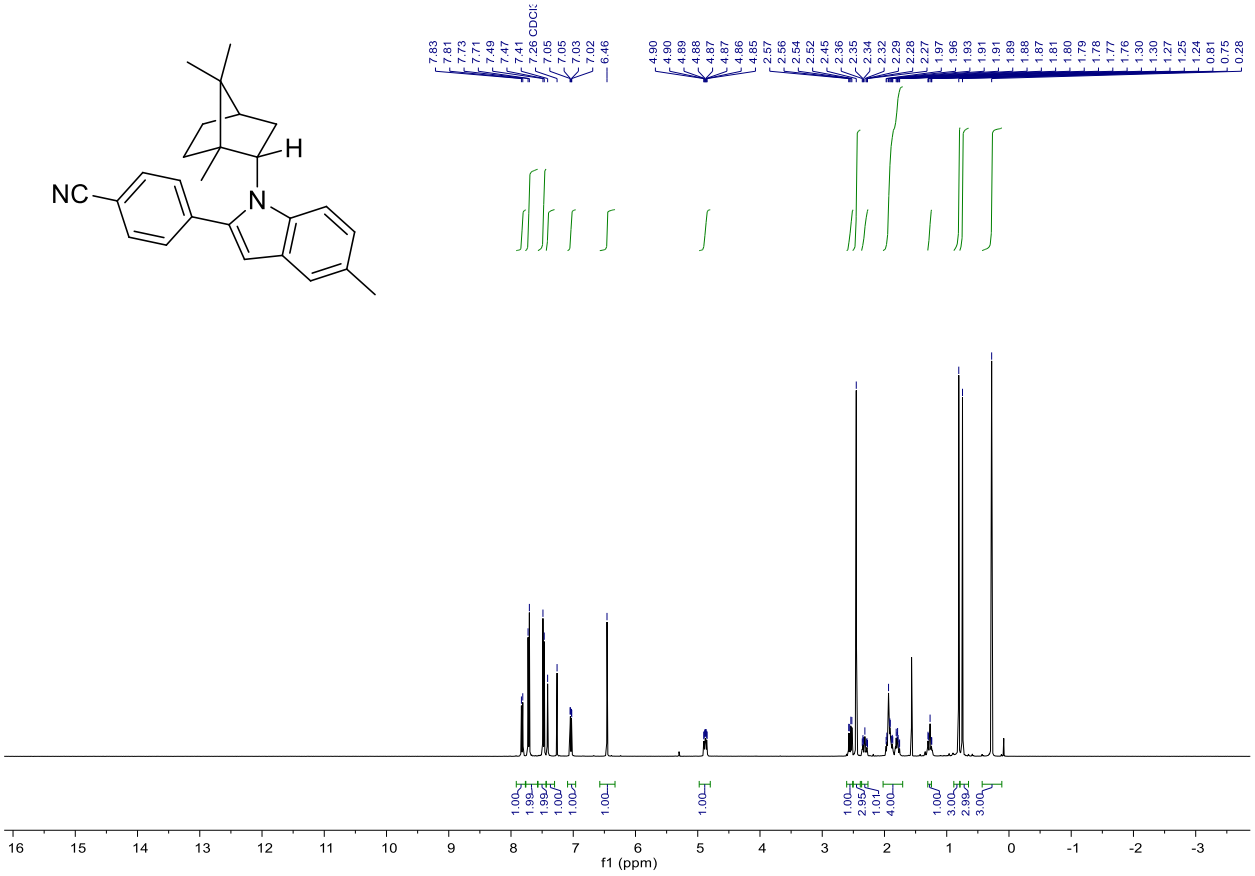
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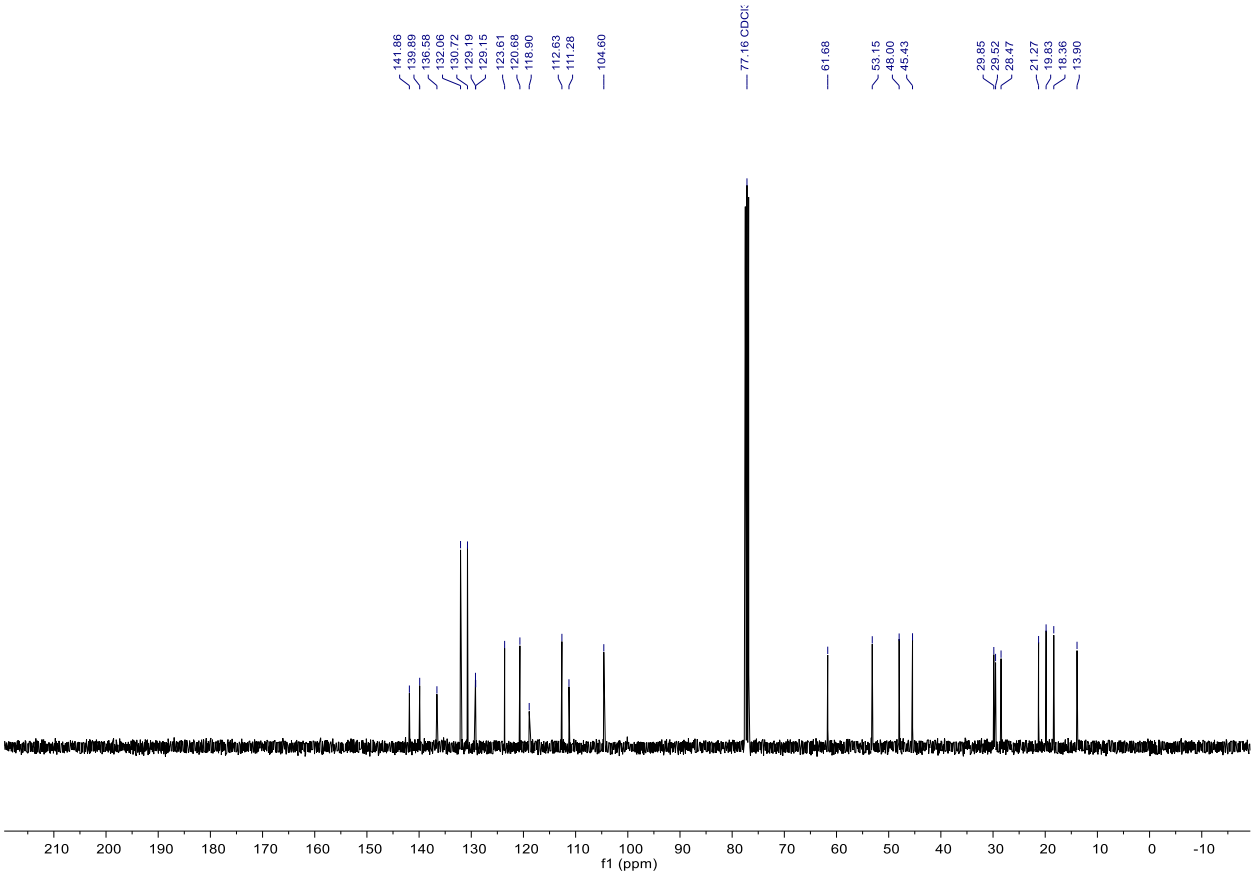
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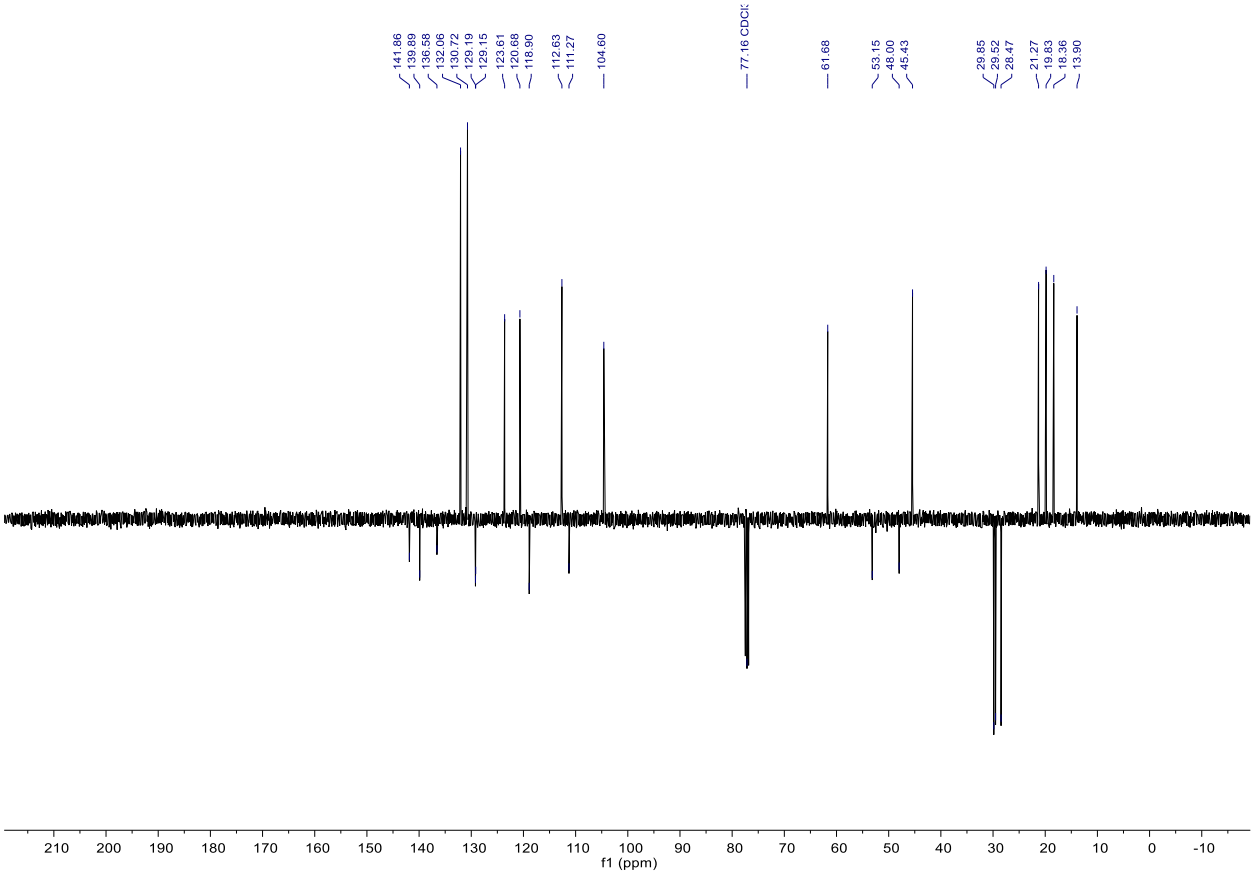
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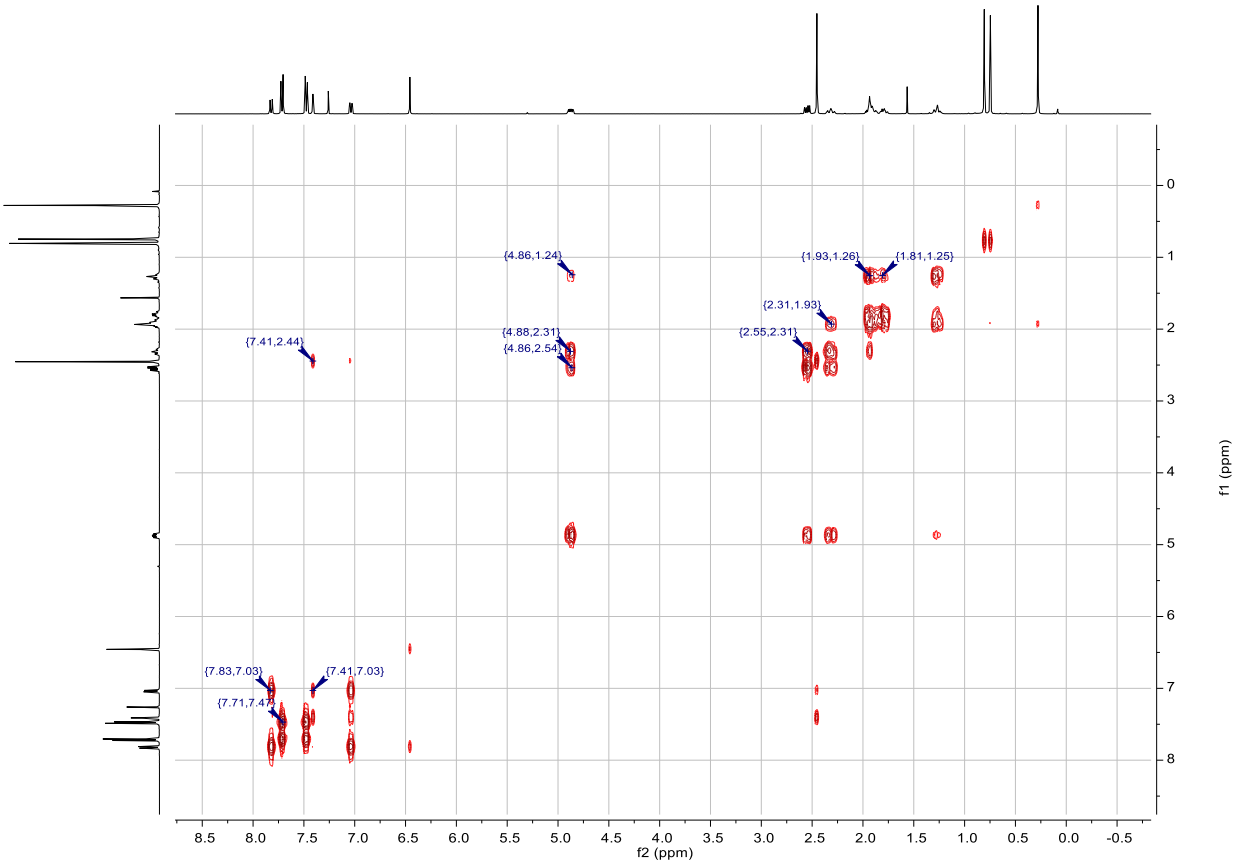
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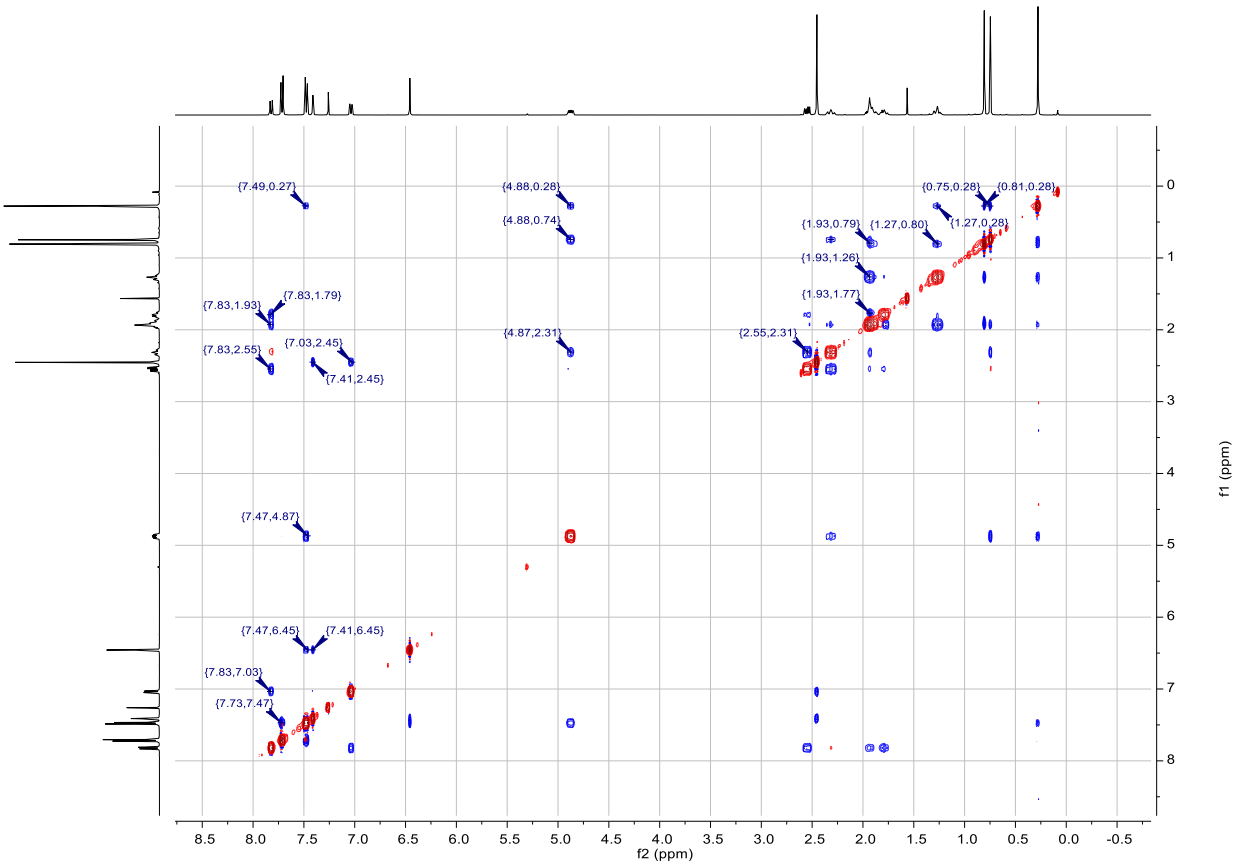
^{13}C DEPTQ-135 NMR Spectrum of Compound 5bc



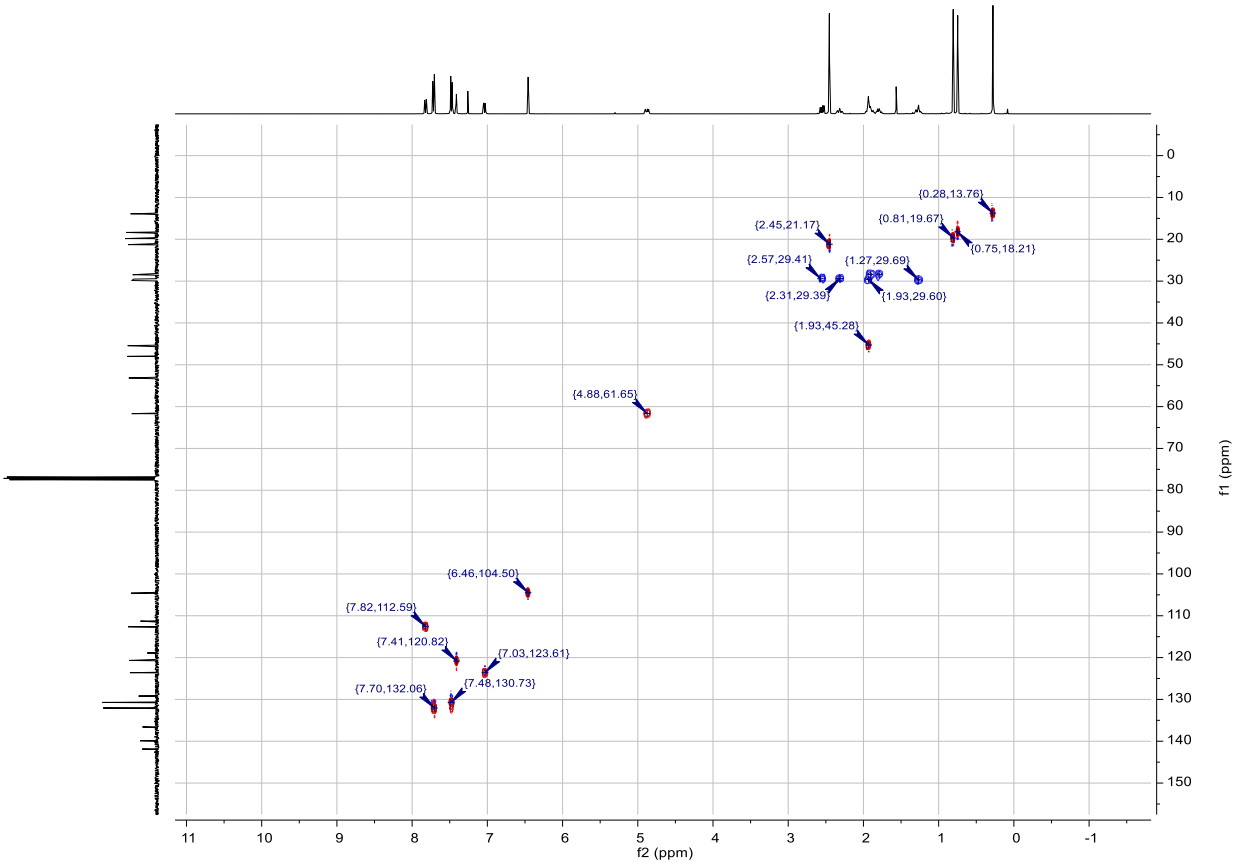
1H-1H COSY NMR Spectrum of Compound 5bc



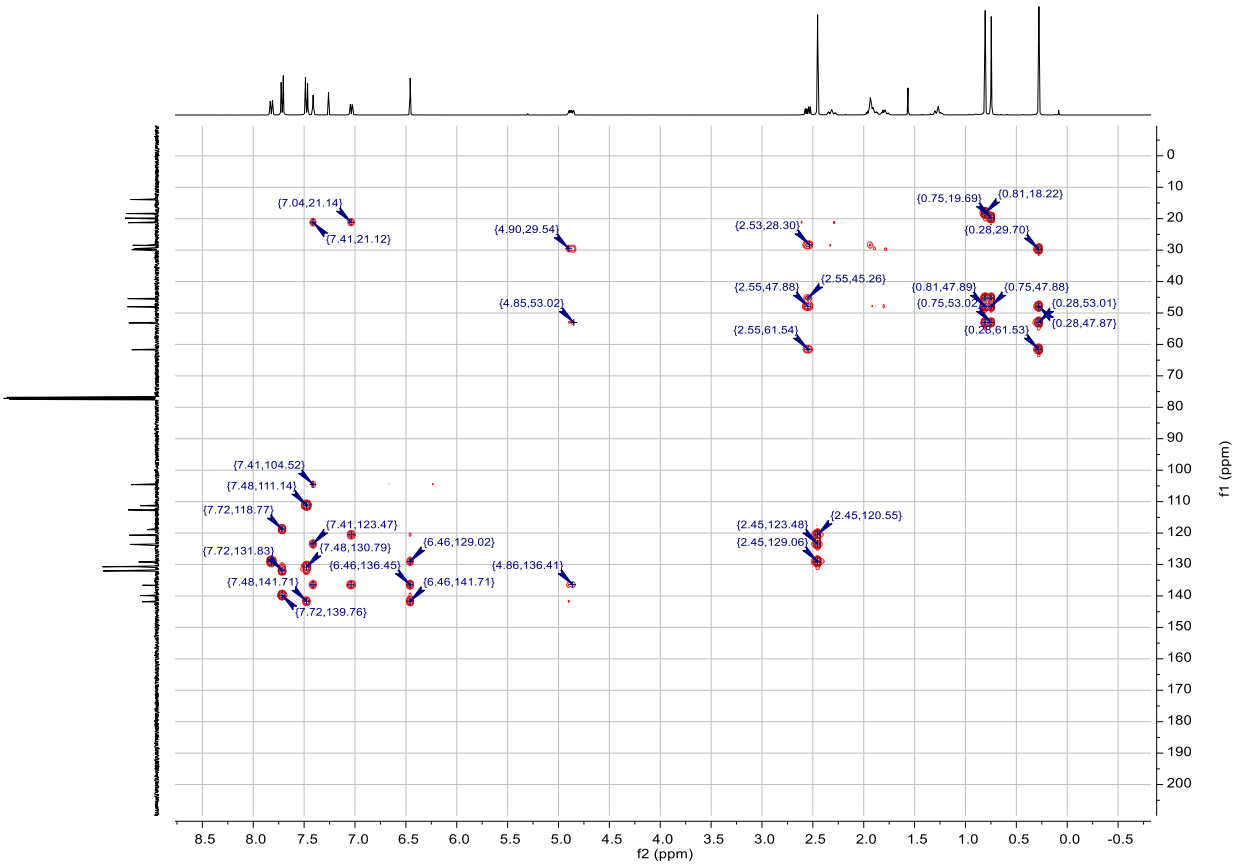
1H-1H NOESY NMR Spectrum of Compound 5bc



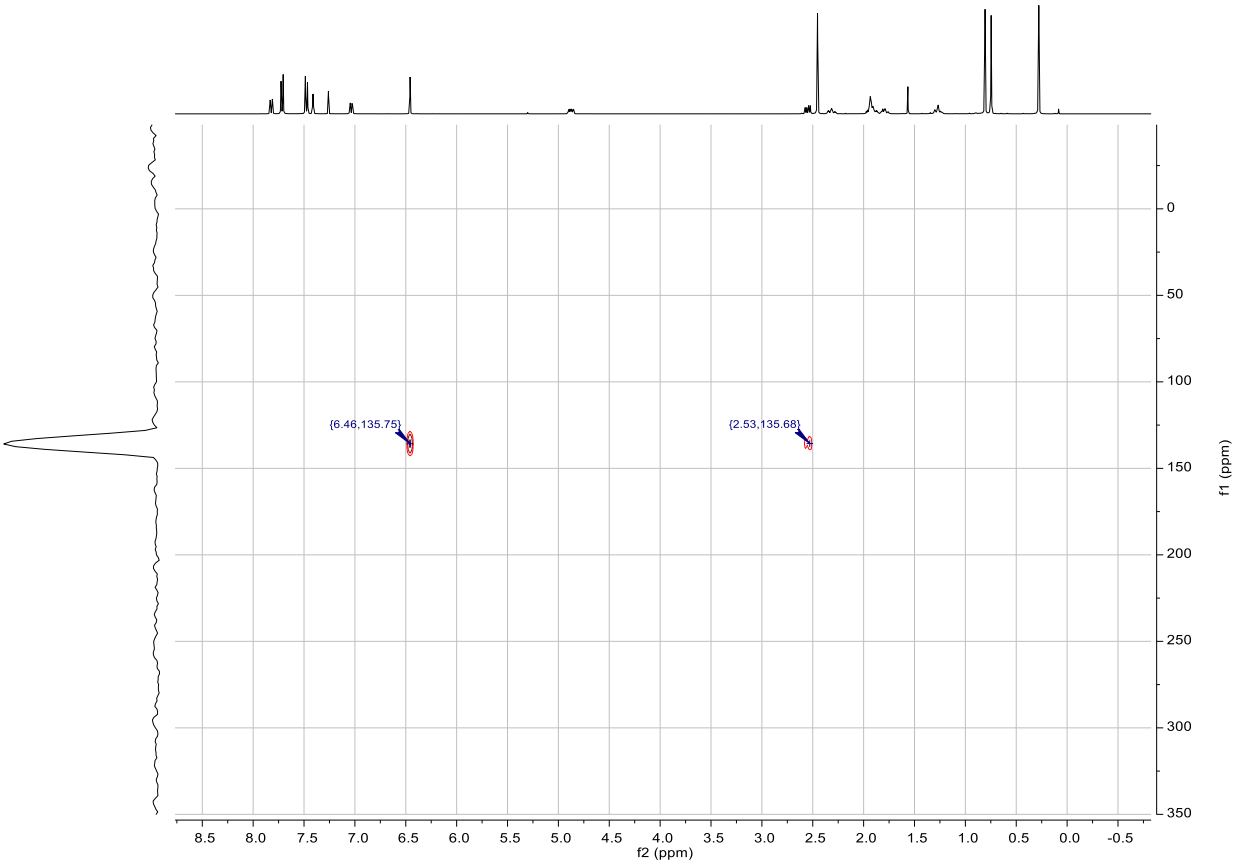
1H-13C HSQC NMR Spectrum of Compound 5bc



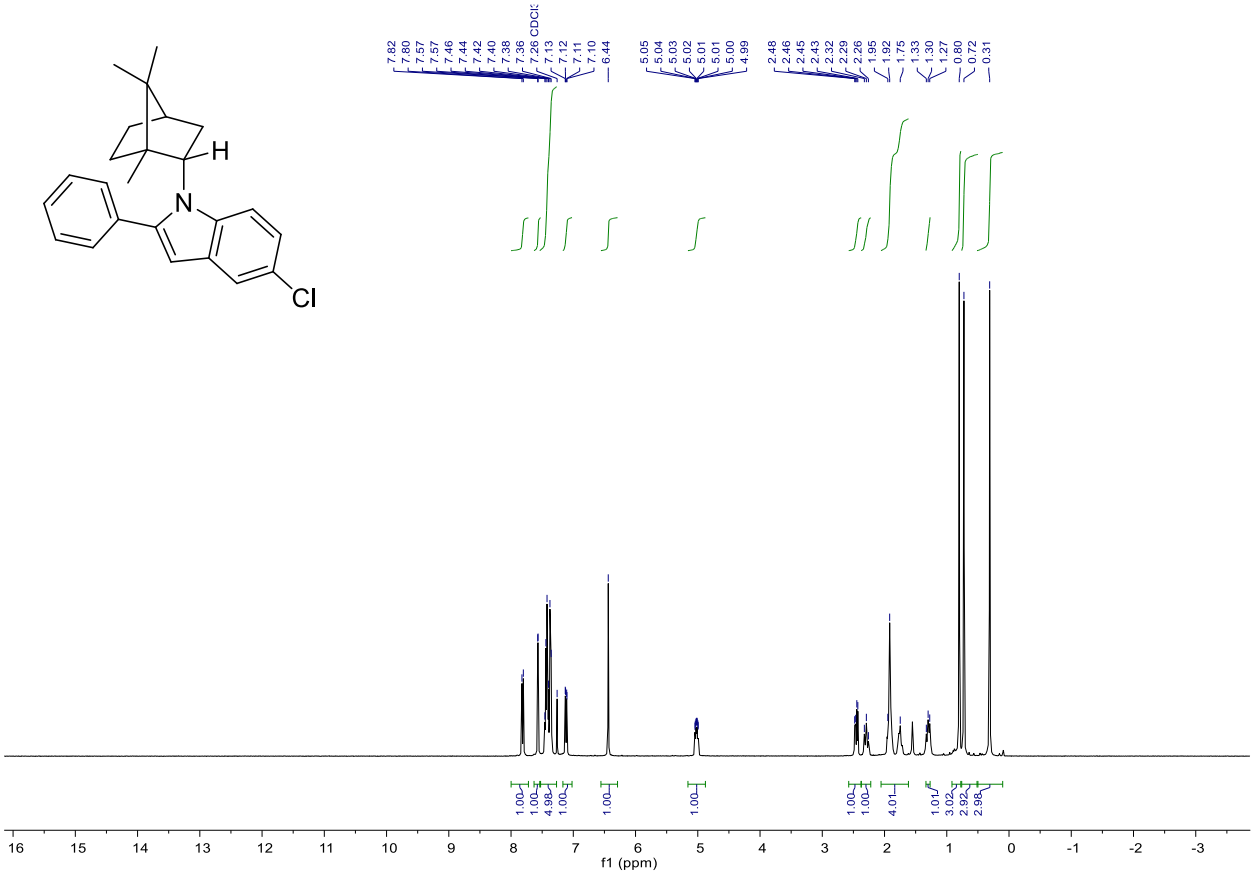
1H-13C HMBC NMR Spectrum of Compound 5bc



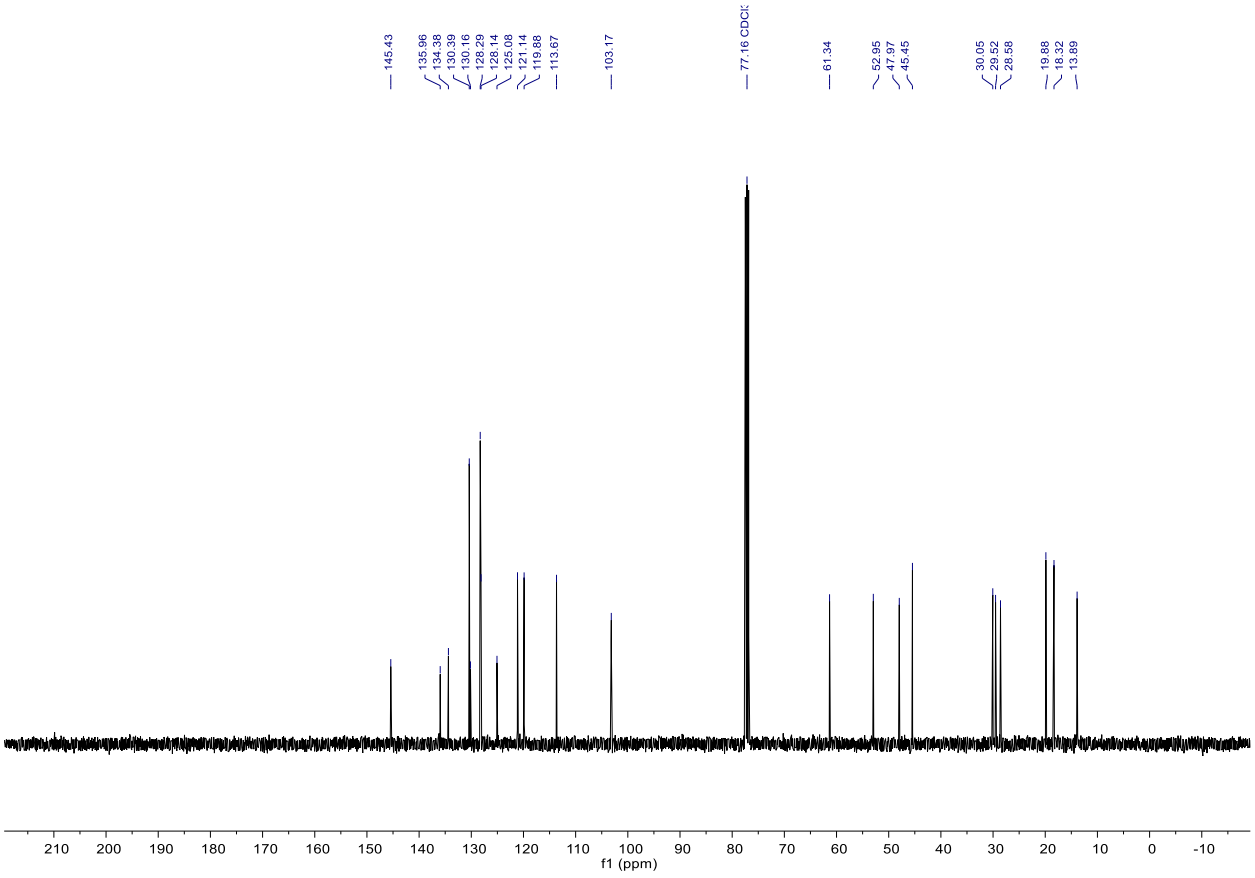
1H-15N HMBC NMR Spectrum of Compound 5bc



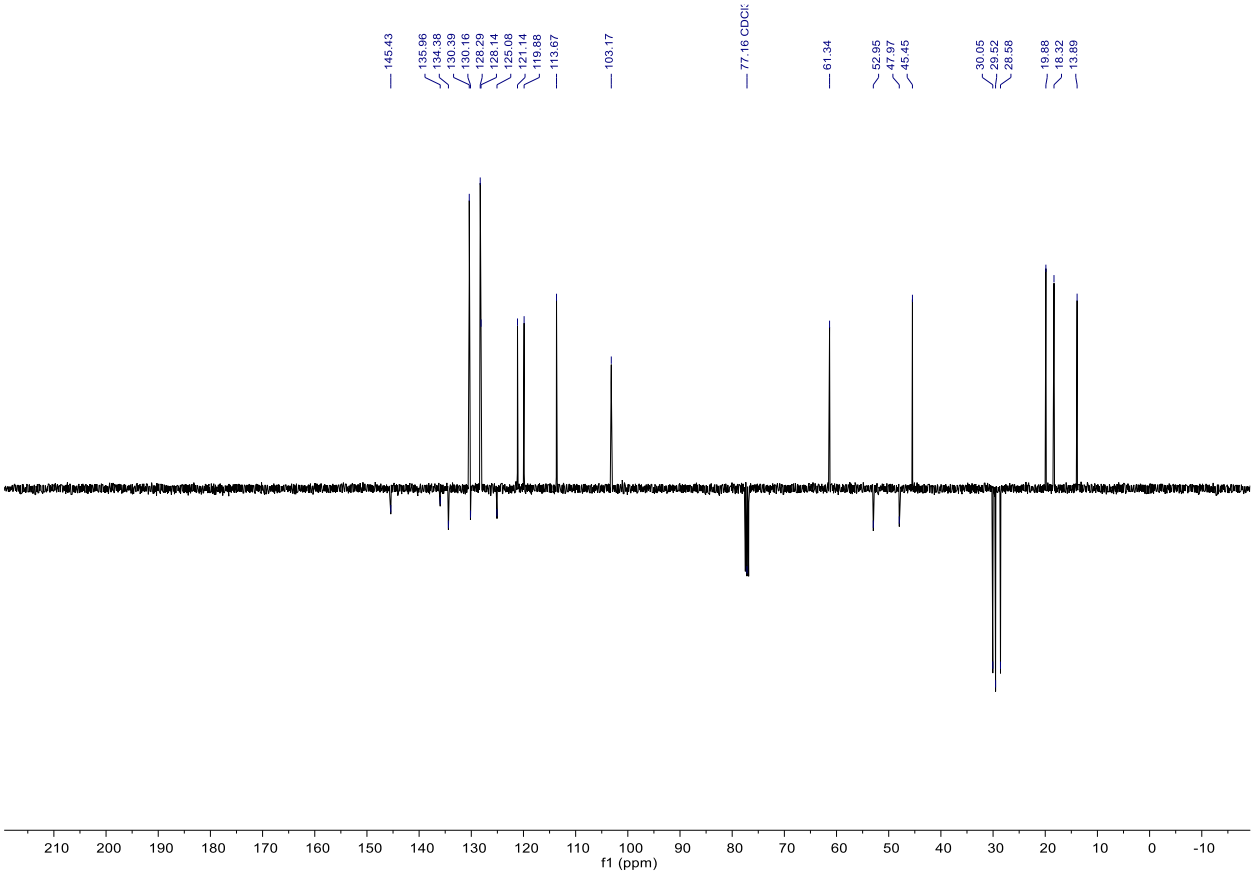
^{1}H NMR Spectrum of Compound 5ca (400 MHz, CDCl3)



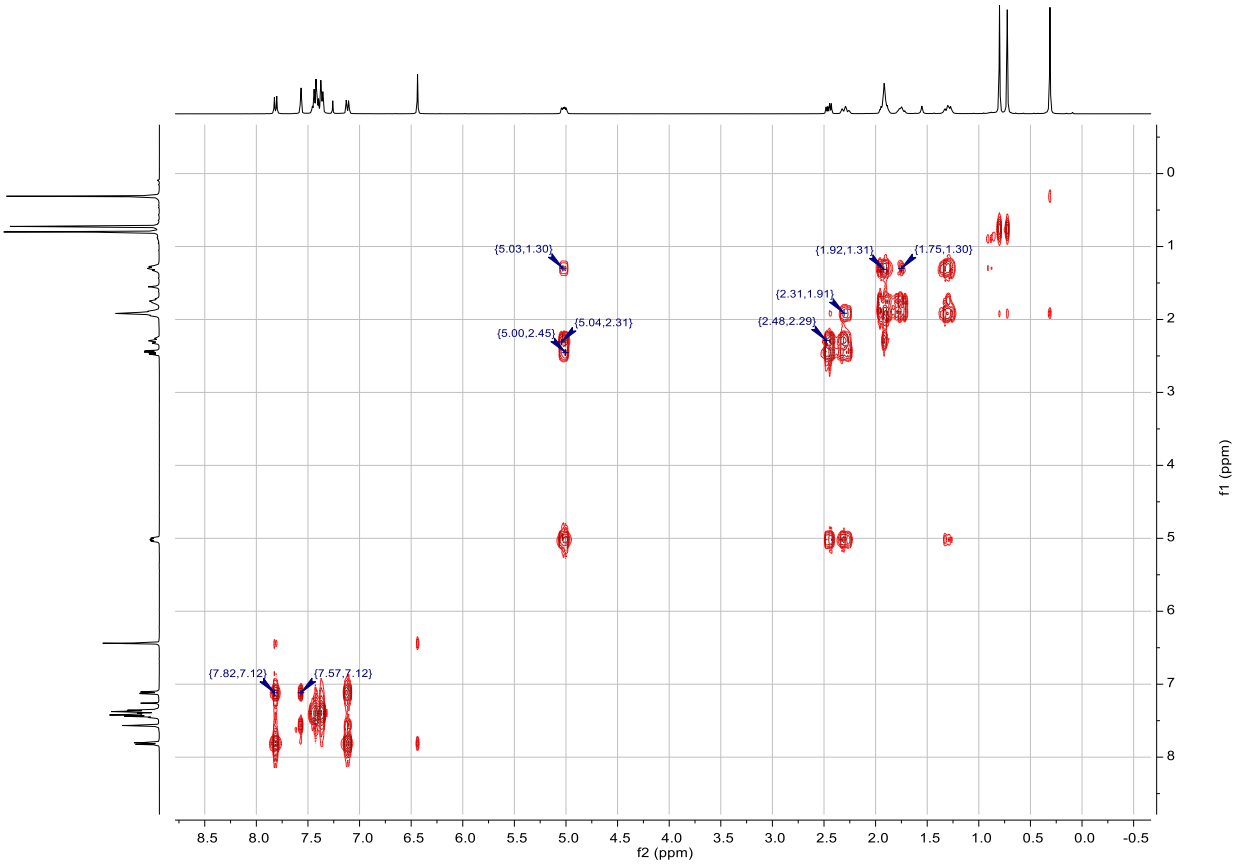
^{13}C NMR Spectrum of Compound 5ca (101 MHz, CDCl3)



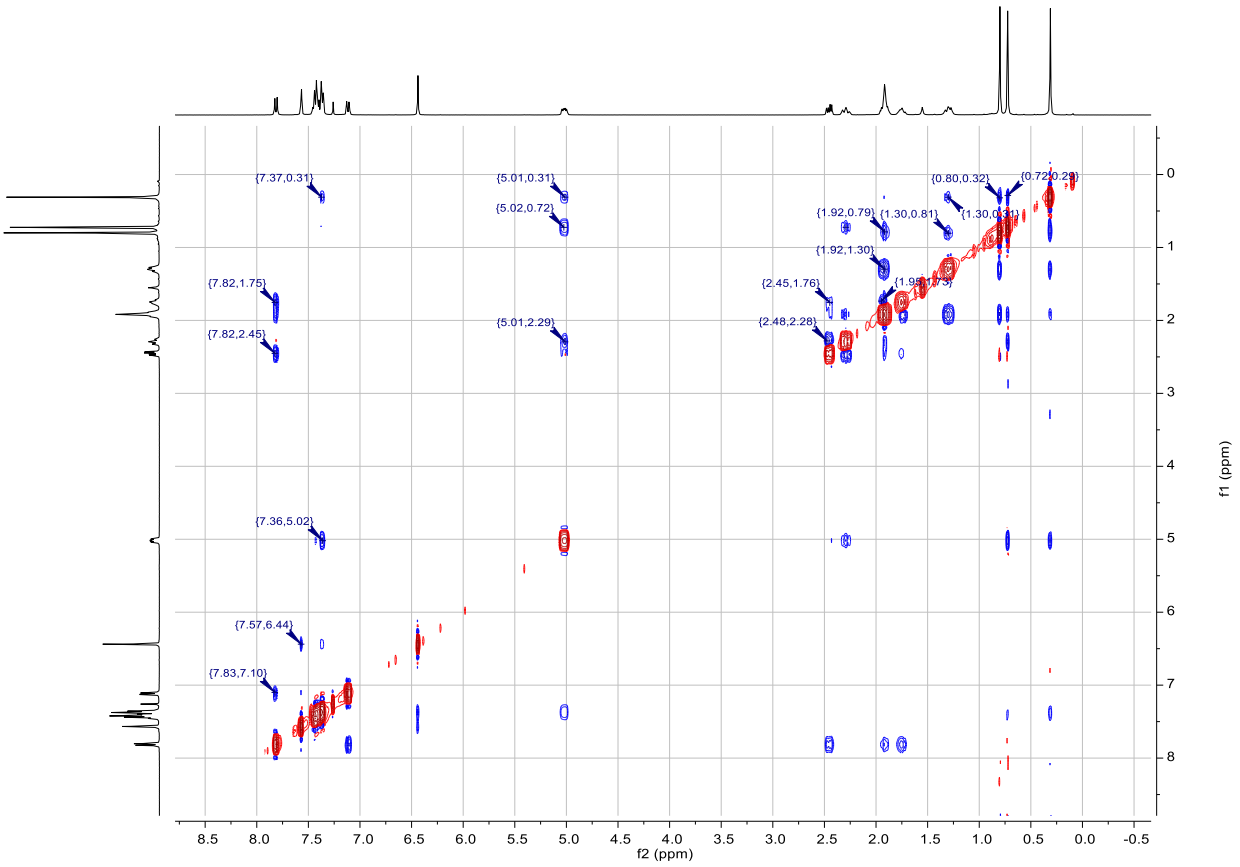
^{13}C DEPTQ-135 NMR Spectrum of Compound 5ca



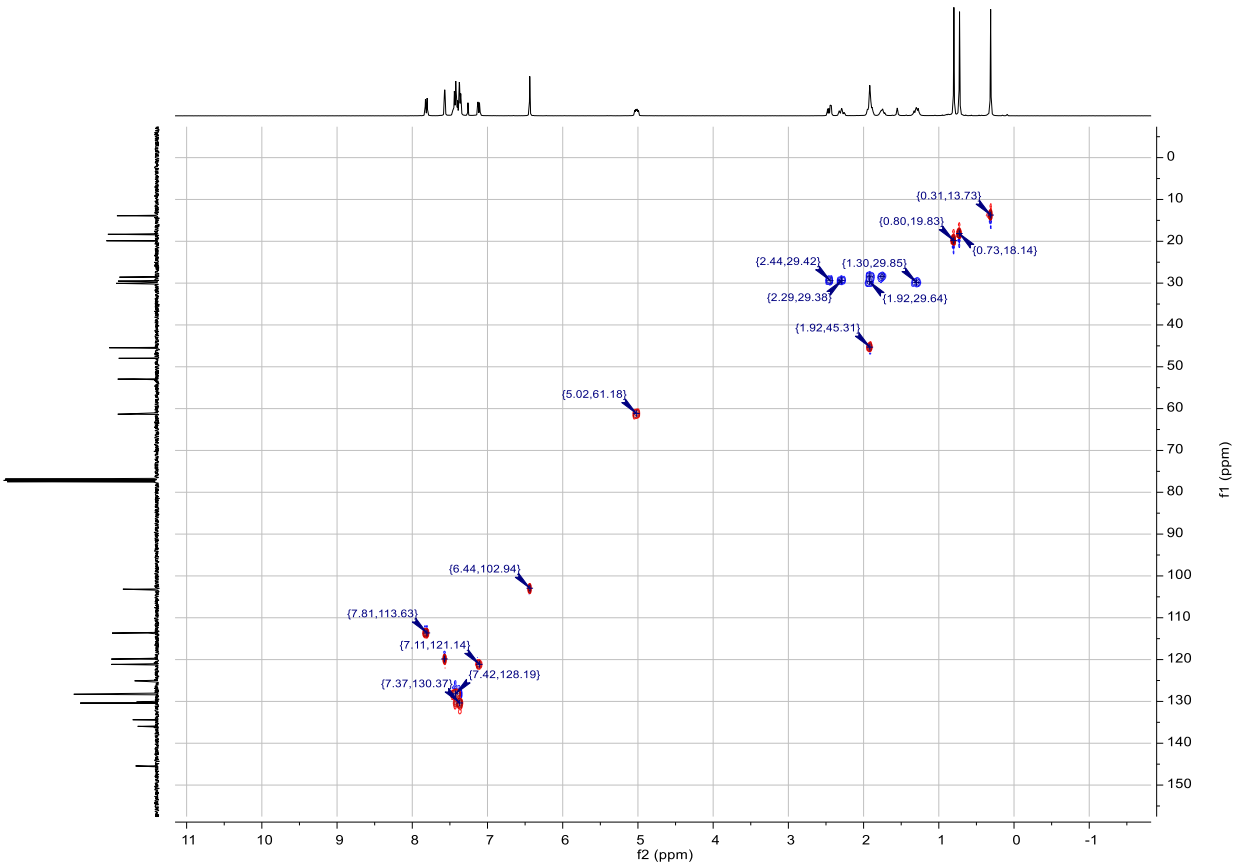
1H-1H COSY NMR Spectrum of Compound 5ca



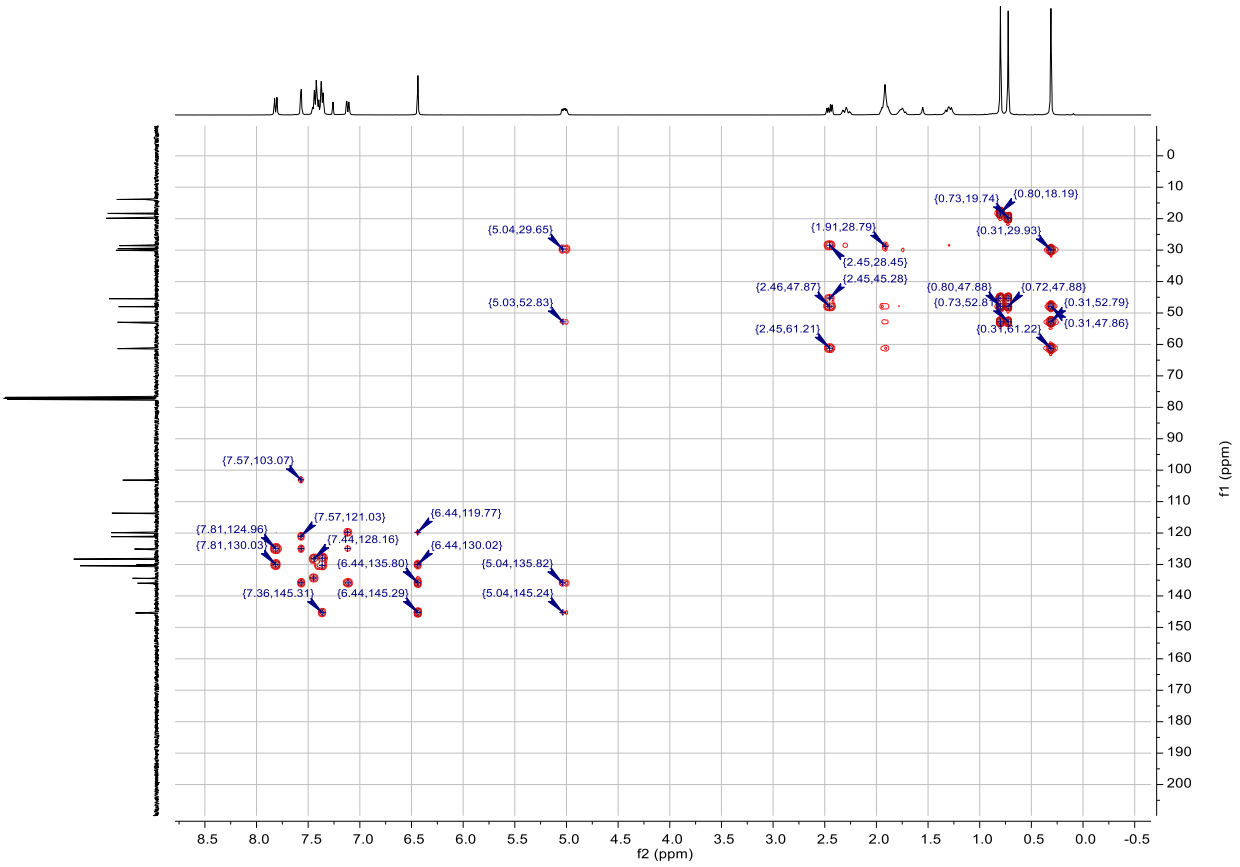
1H-1H NOESY NMR Spectrum of Compound 5ca



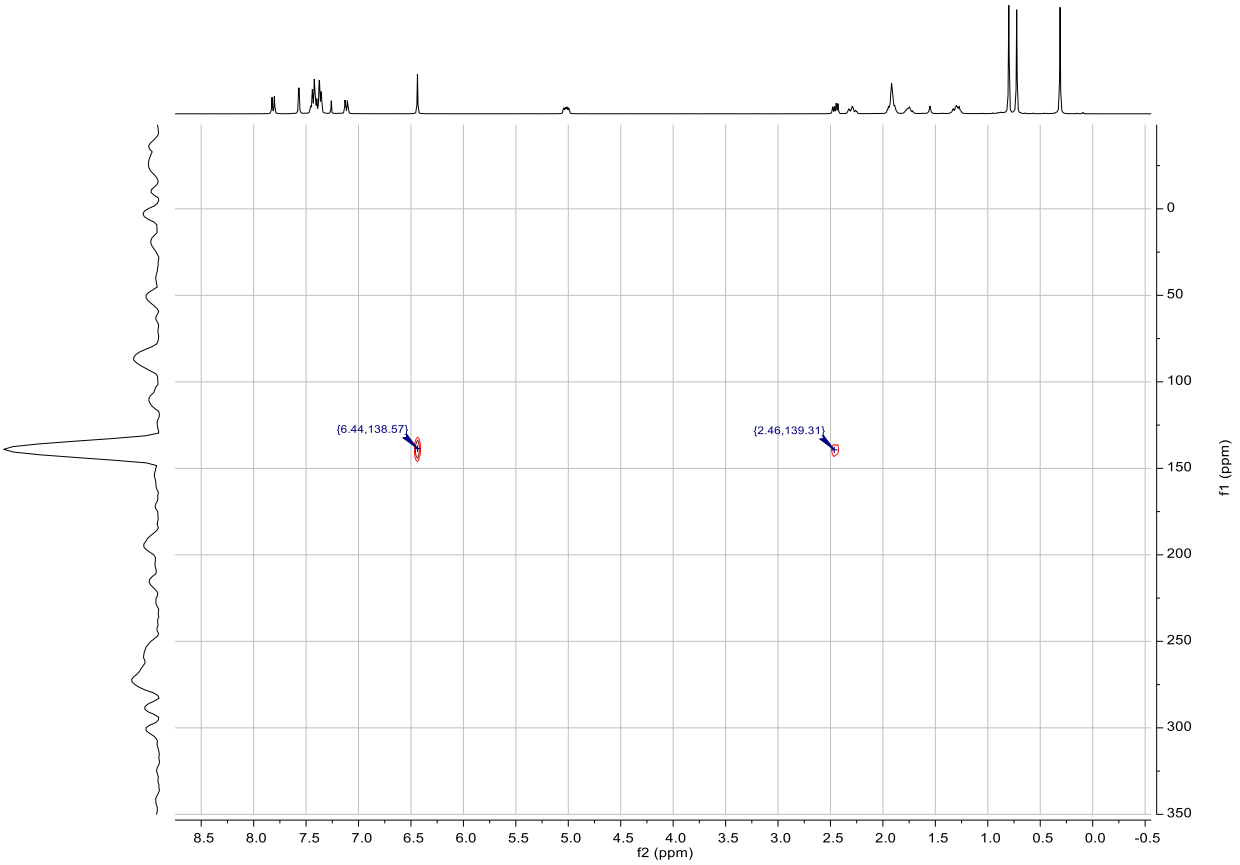
1H-13C HSQC NMR Spectrum of Compound 5ca



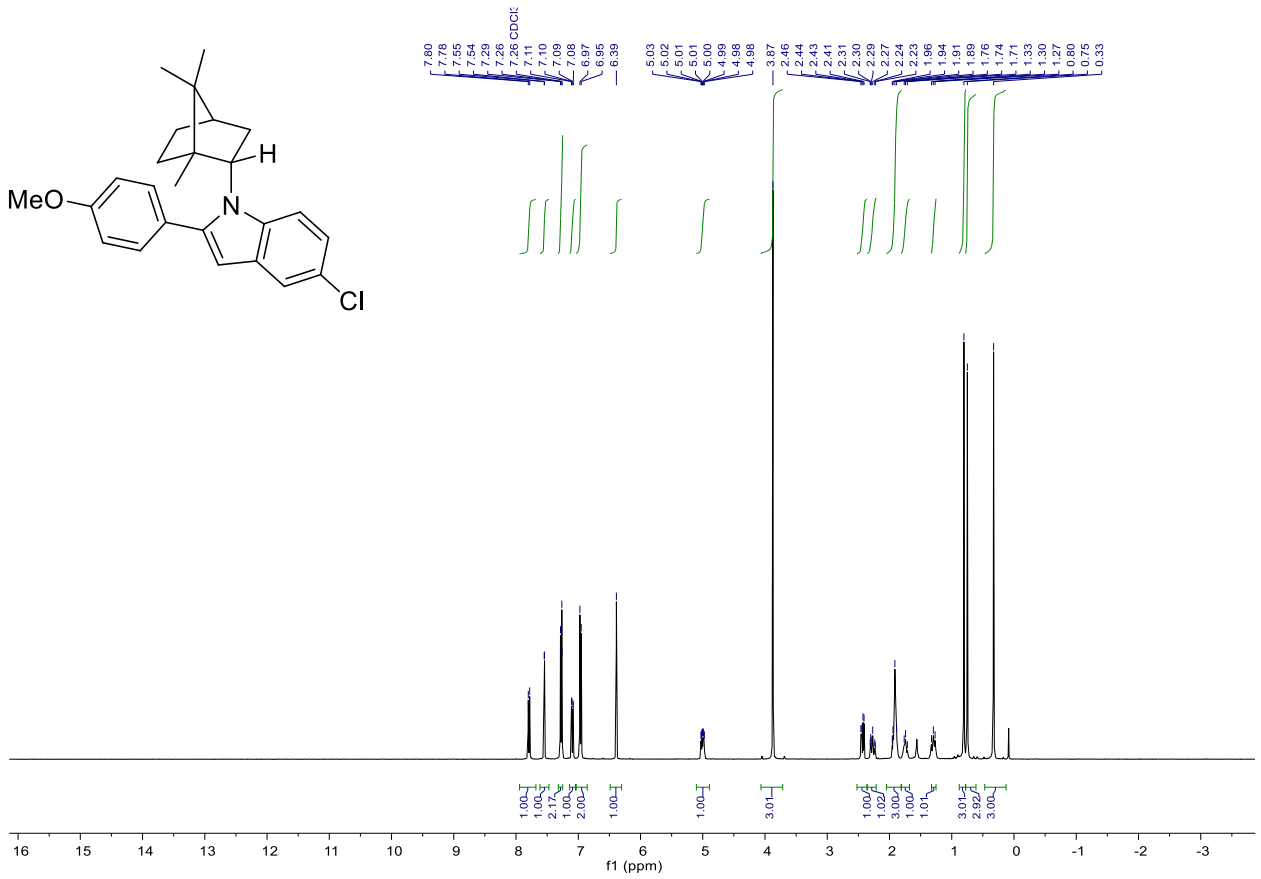
1H-13C HMBC NMR Spectrum of Compound 5ca



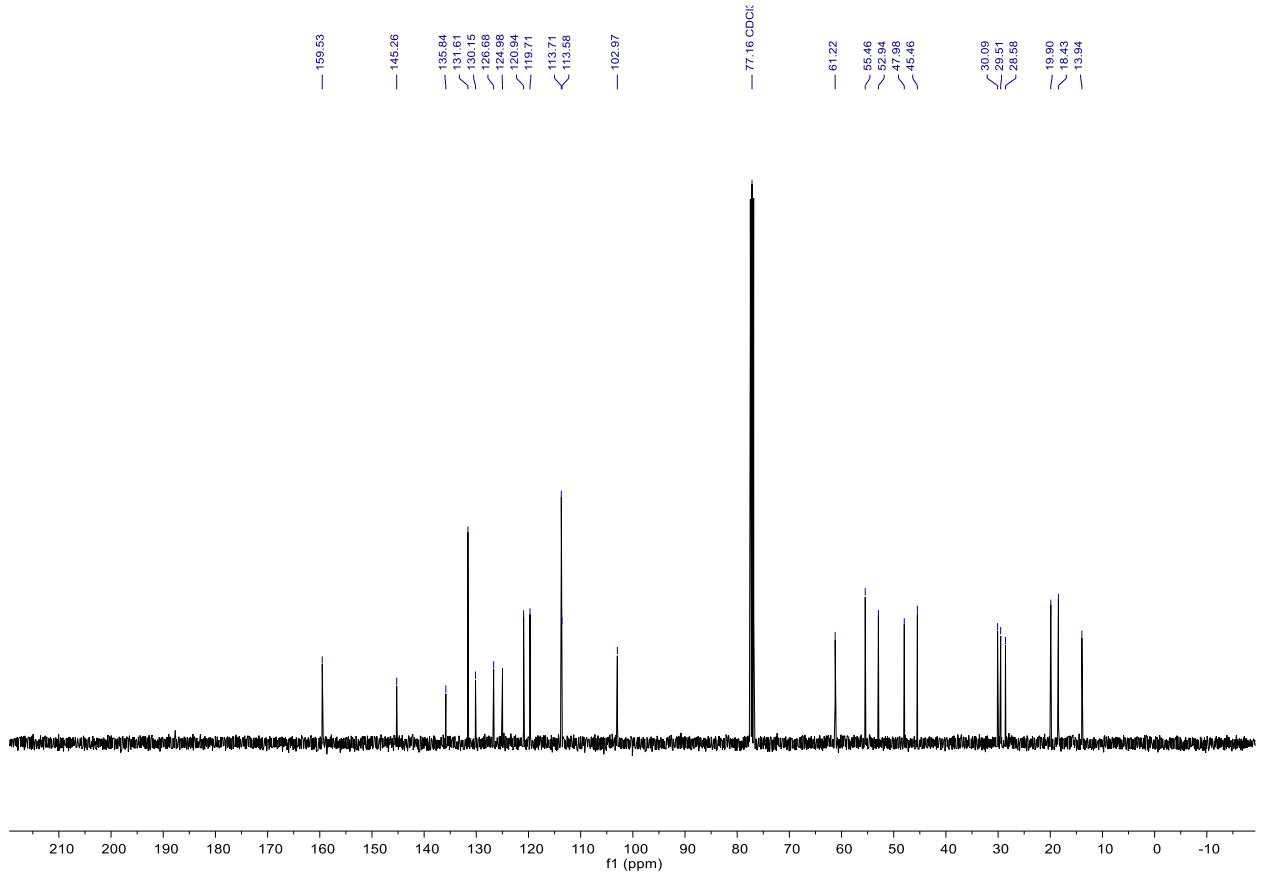
1H-15N HMBC NMR Spectrum of Compound 5ca



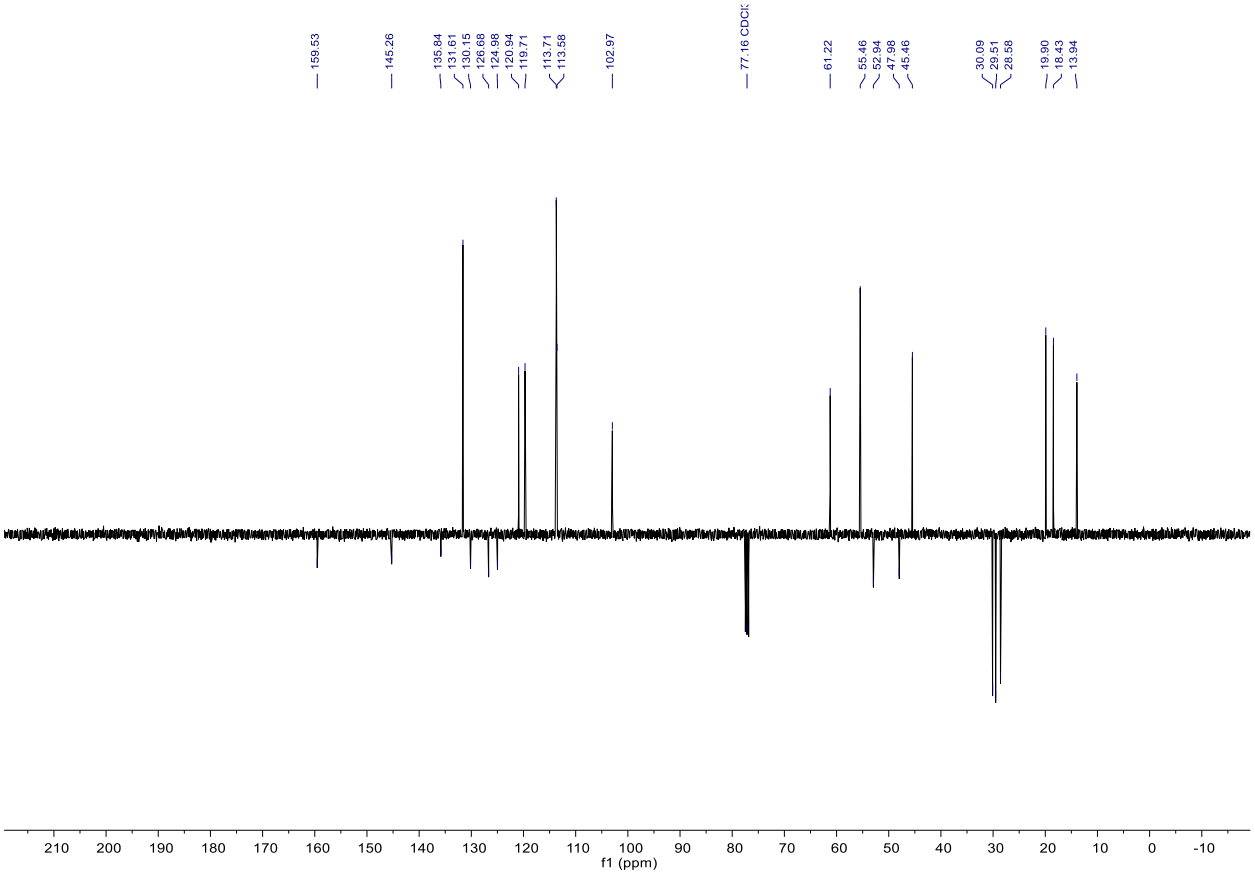
^{1}H NMR Spectrum of Compound 5cb (400 MHz, CDCl3)



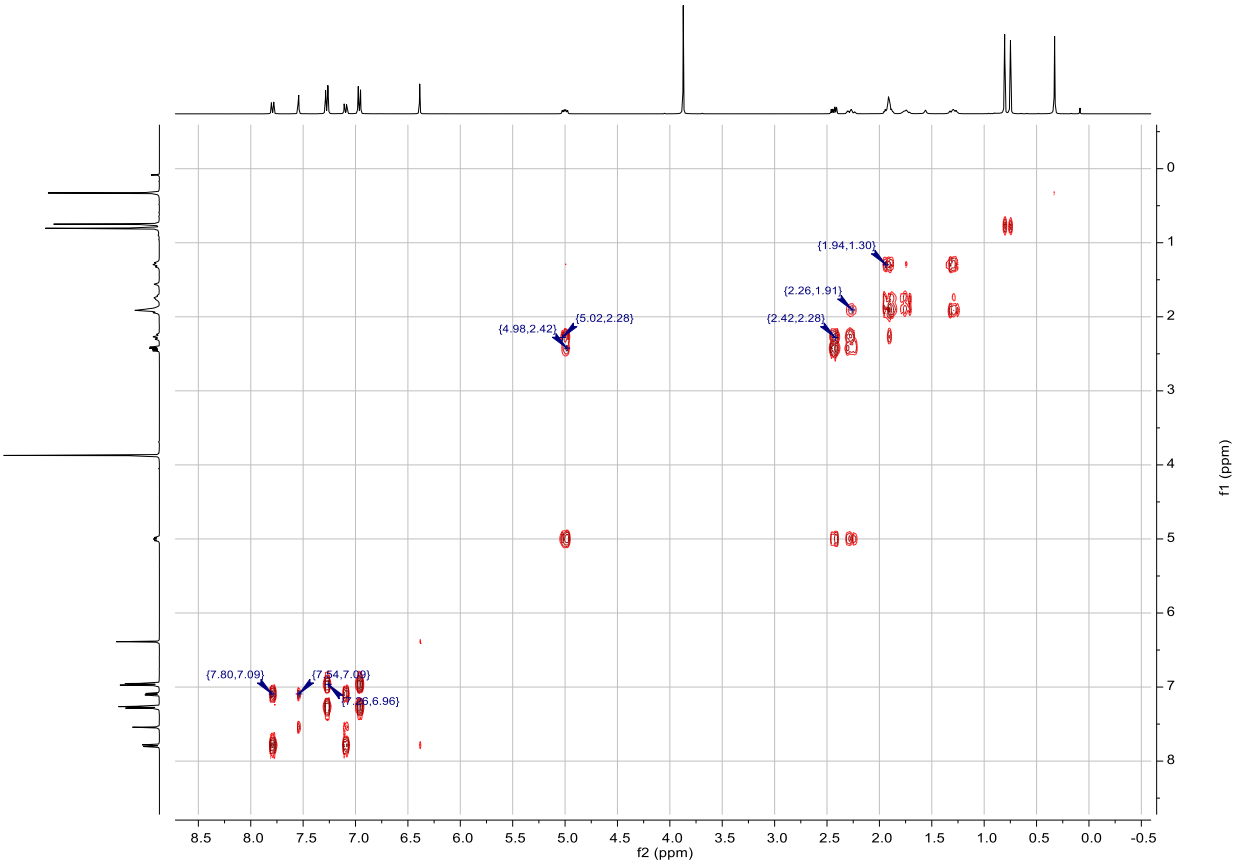
^{13}C NMR Spectrum of Compound 5cb (101 MHz, CDCl3)



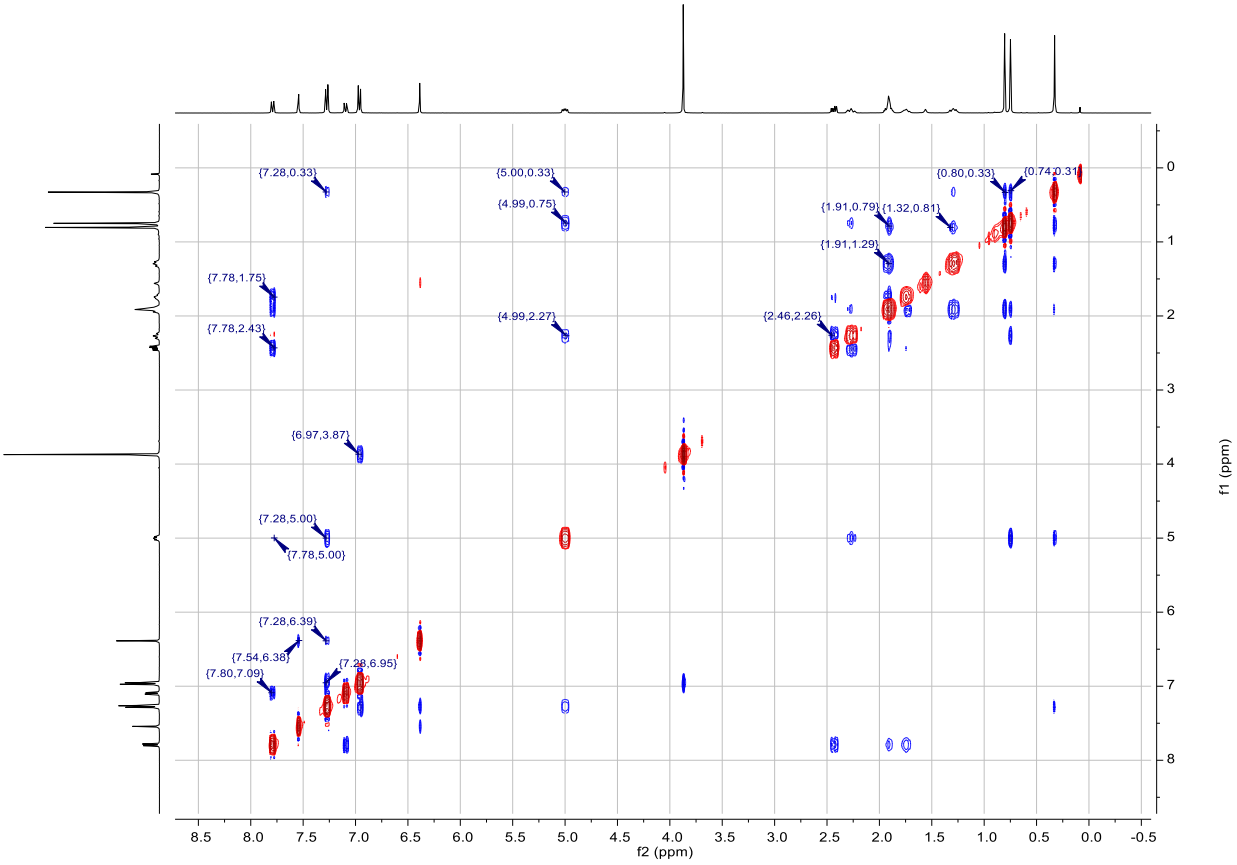
^{13}C DEPTQ-135 NMR Spectrum of Compound 5cb



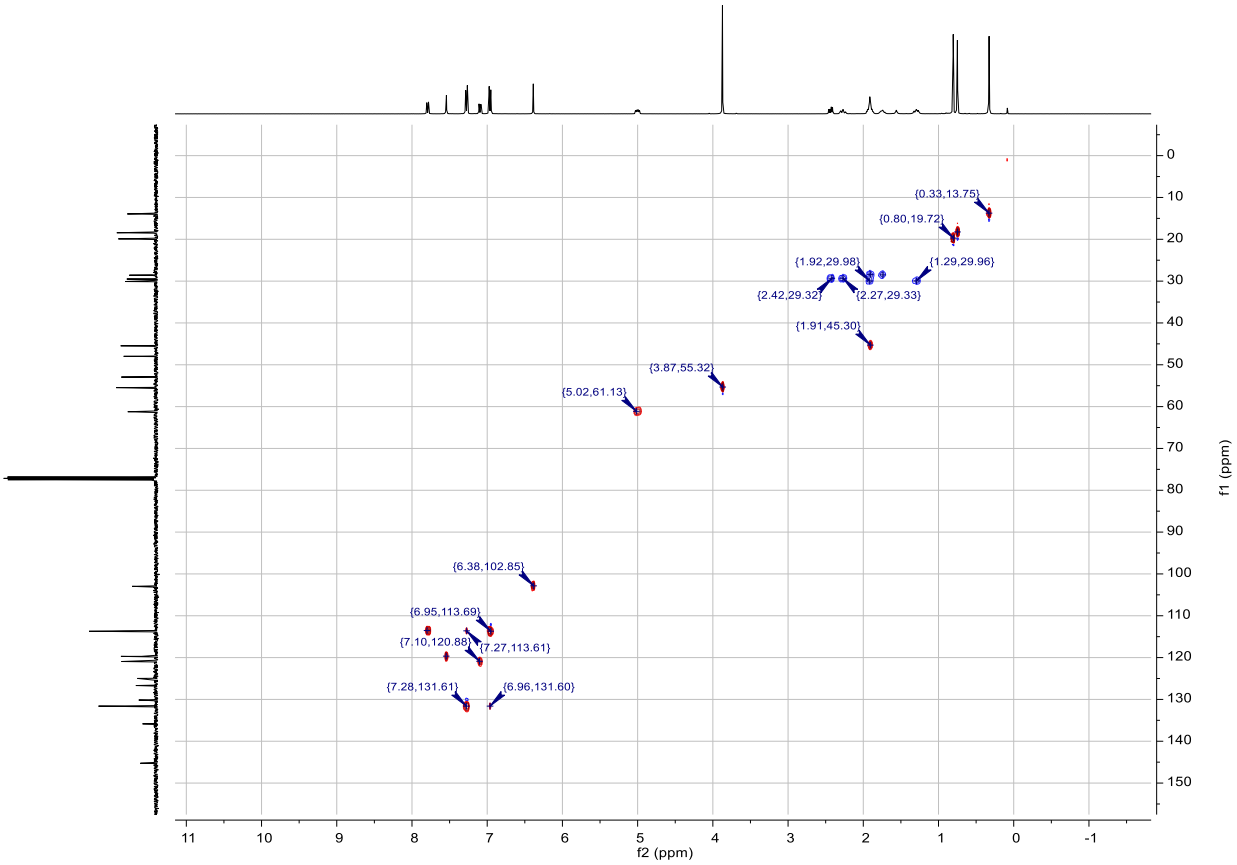
1H-1H COSY NMR Spectrum of Compound 5cb



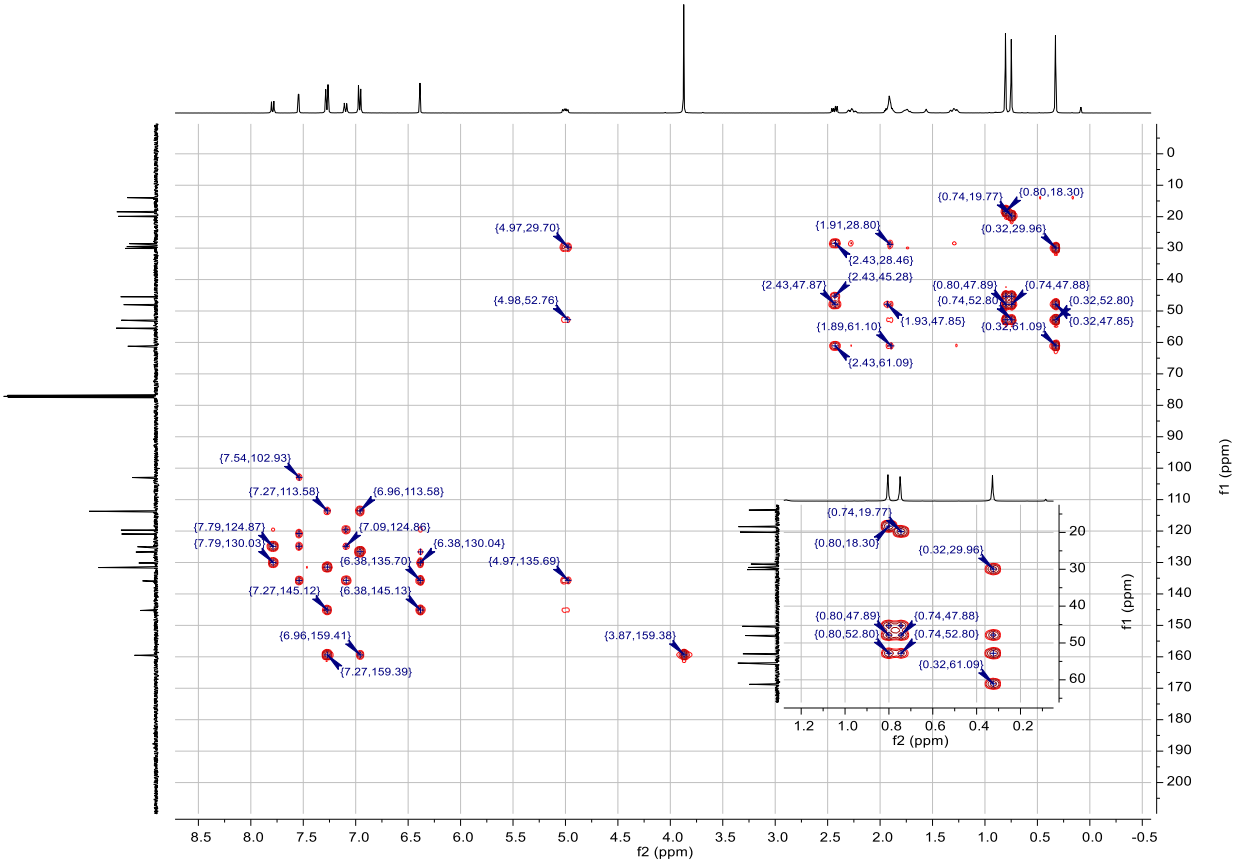
1H-1H NOESY NMR Spectrum of Compound 5cb



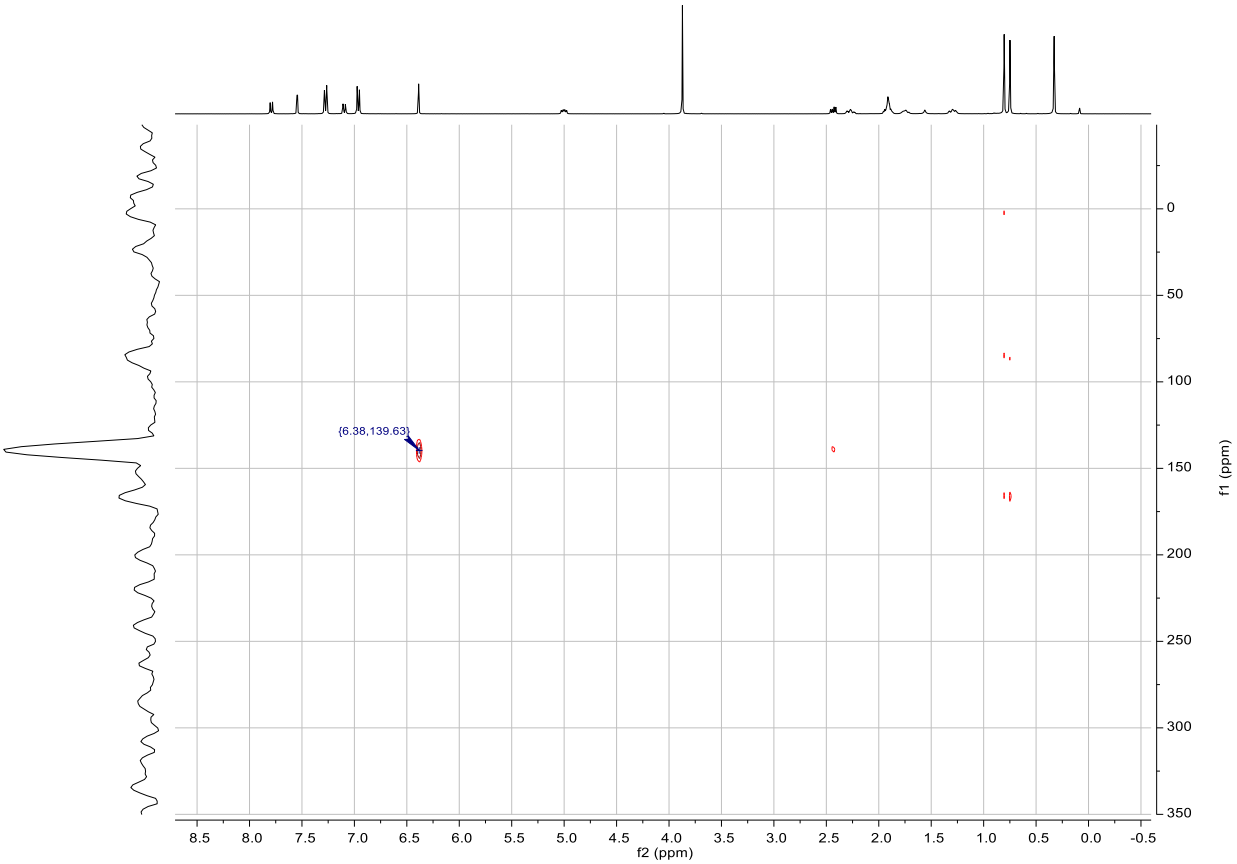
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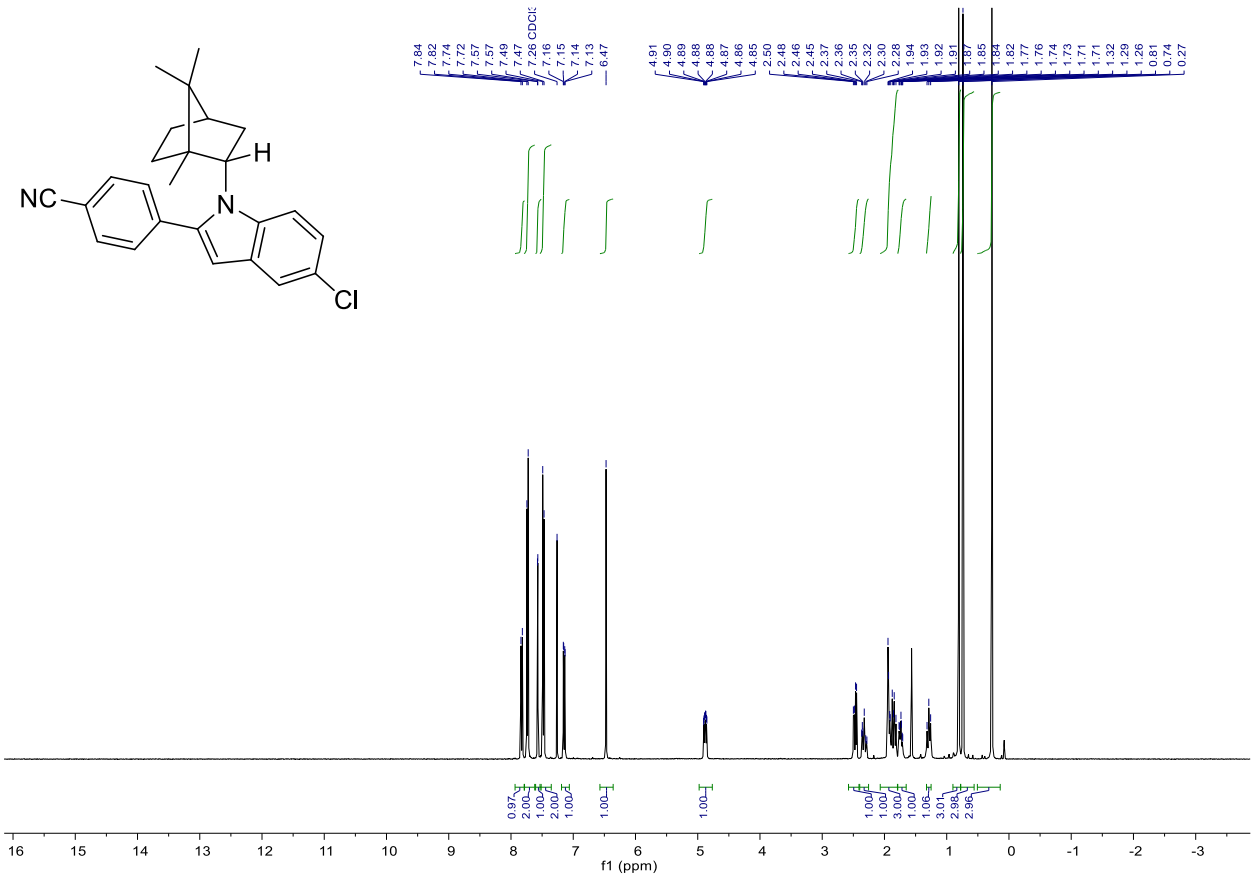
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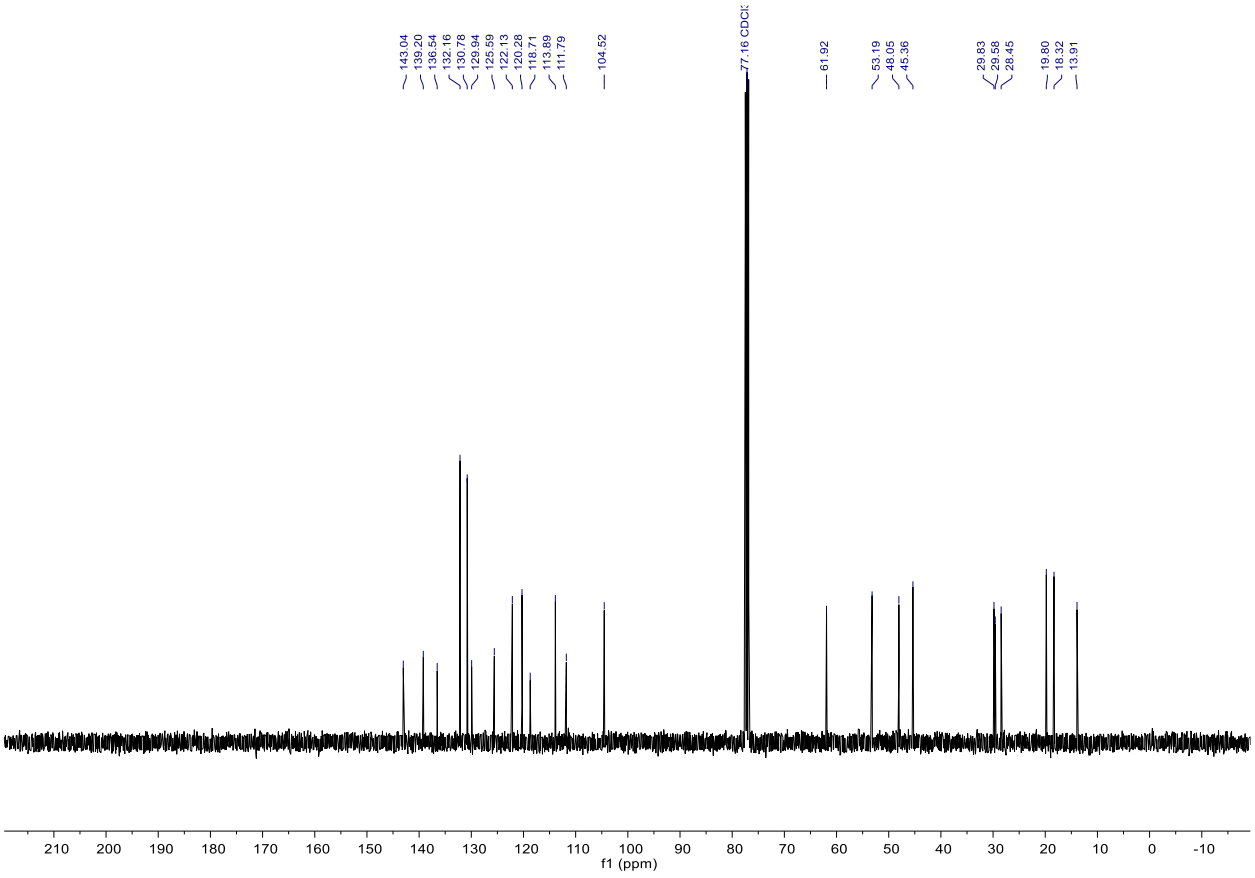
1H-15N HMBC NMR Spectrum of Compound 5cb



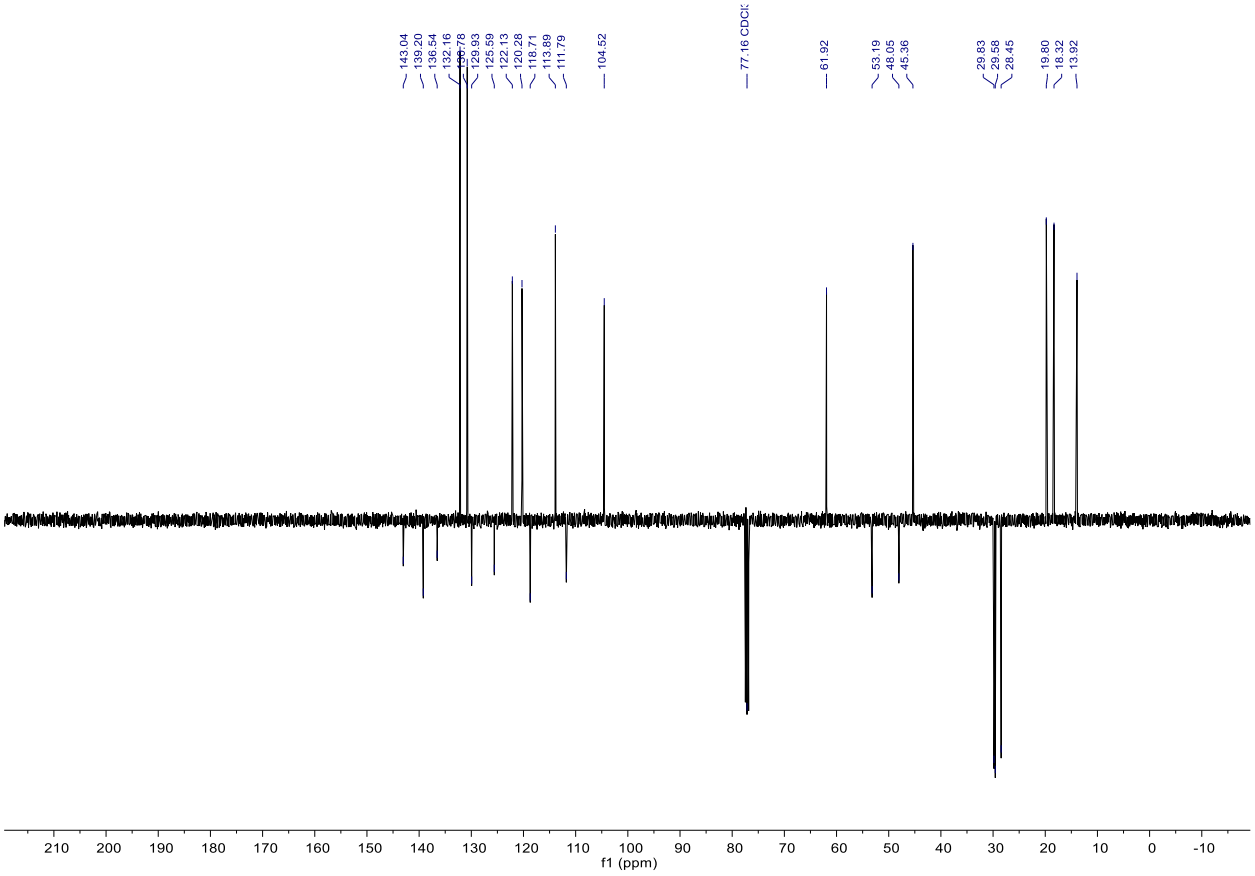
^{1}H NMR Spectrum of Compound 5cc (400 MHz, CDCl3)



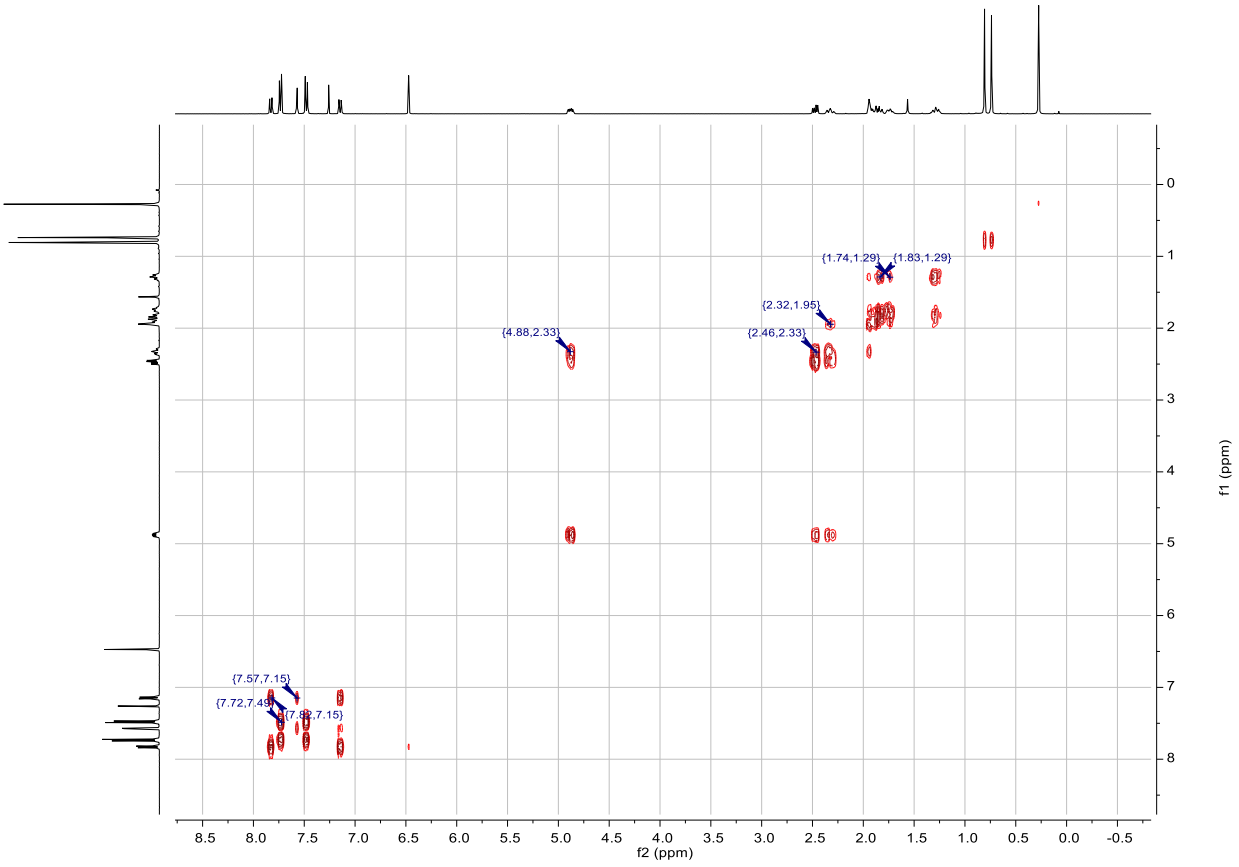
^{13}C NMR Spectrum of Compound 5cc (101 MHz, CDCl3)



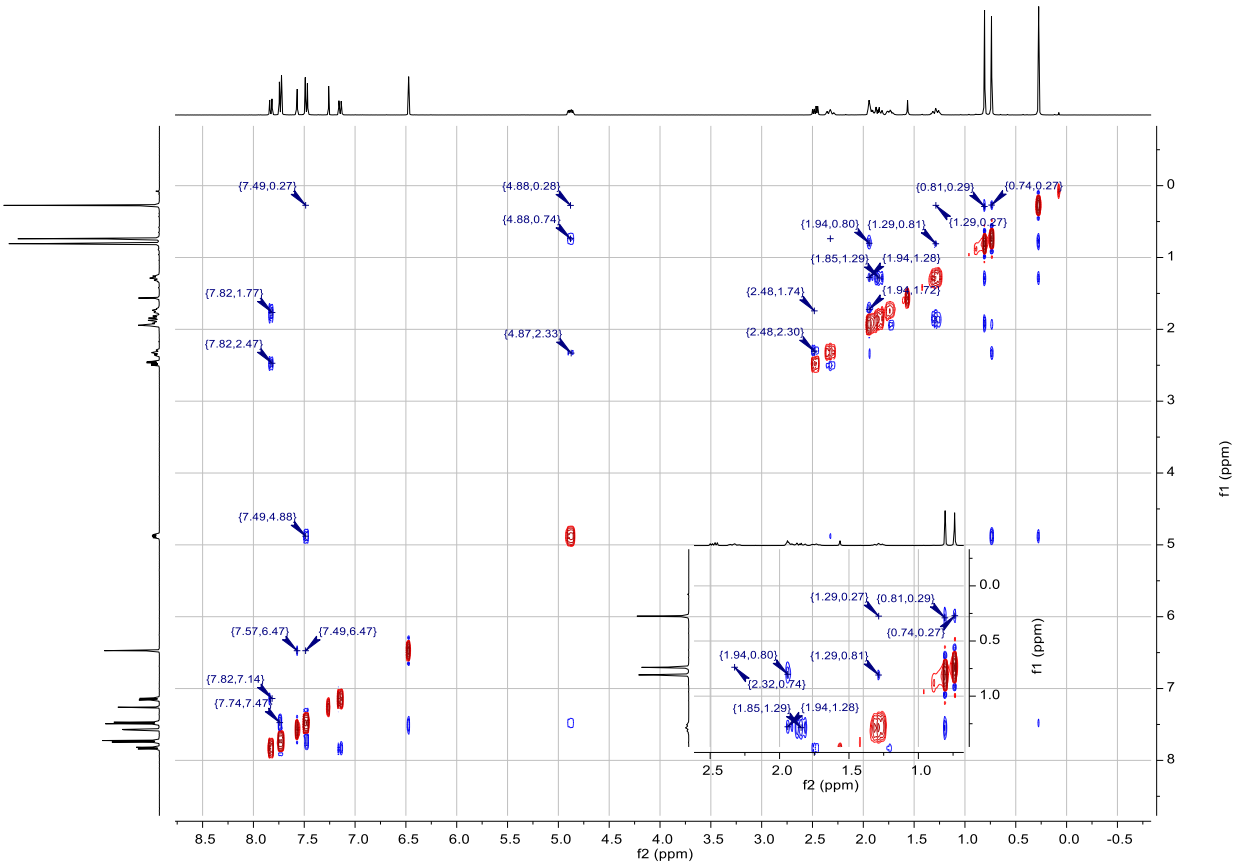
^{13}C DEPTQ-135 NMR Spectrum of Compound 5cc



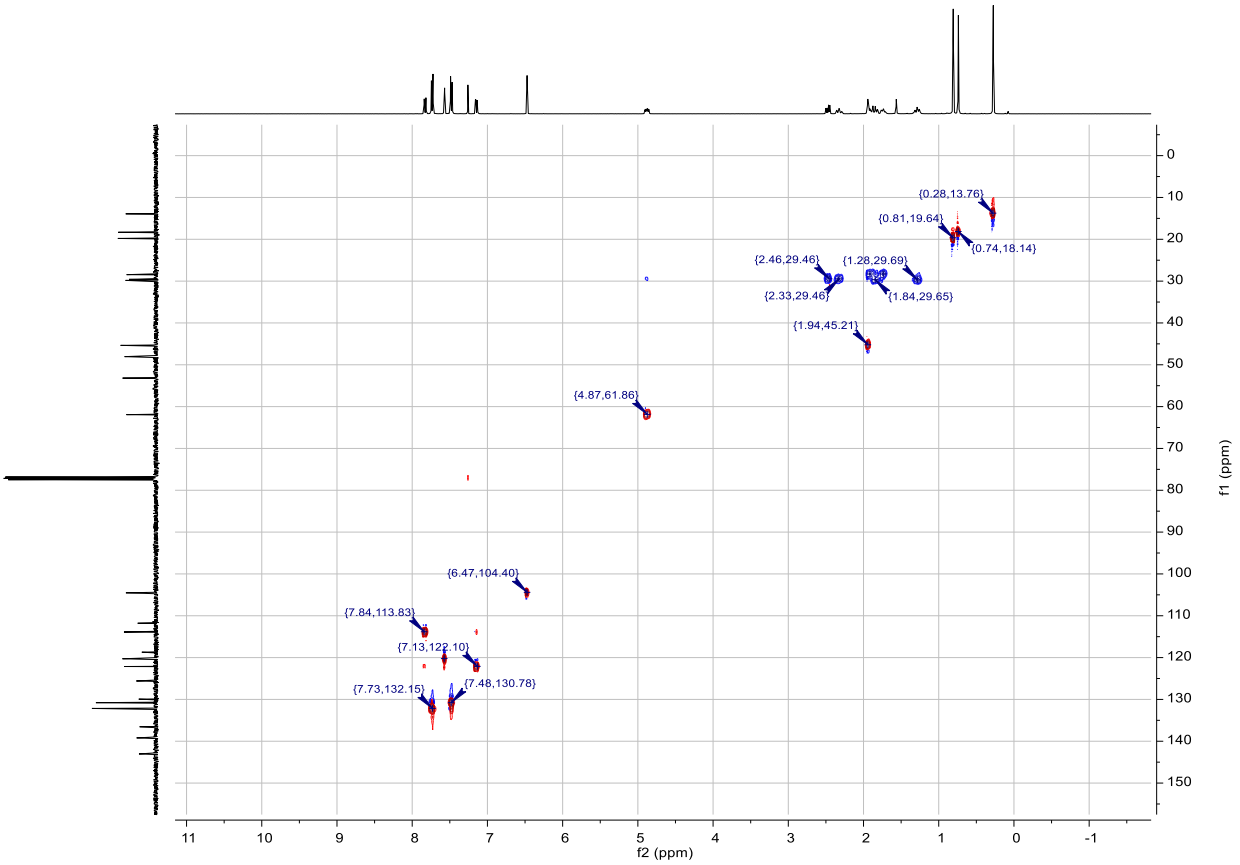
1H-1H COSY NMR Spectrum of Compound 5cc



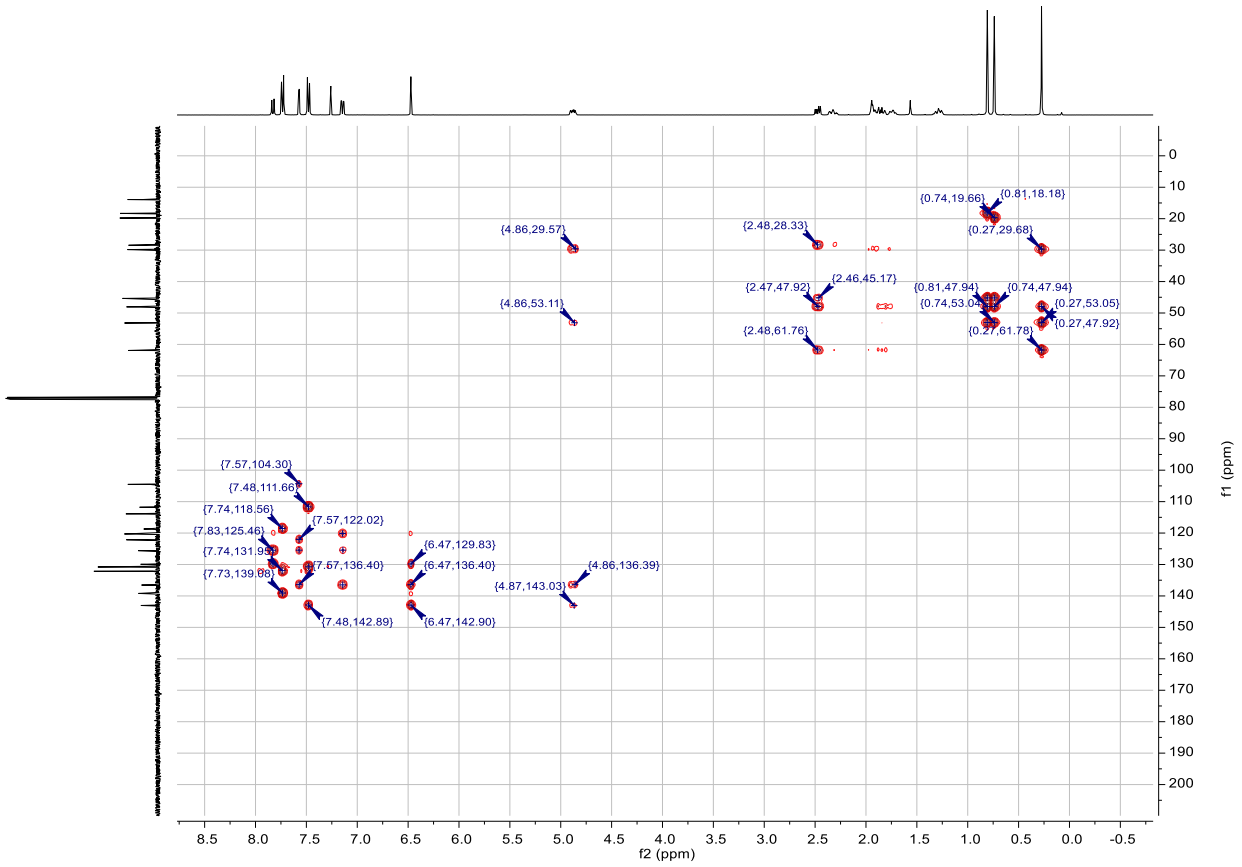
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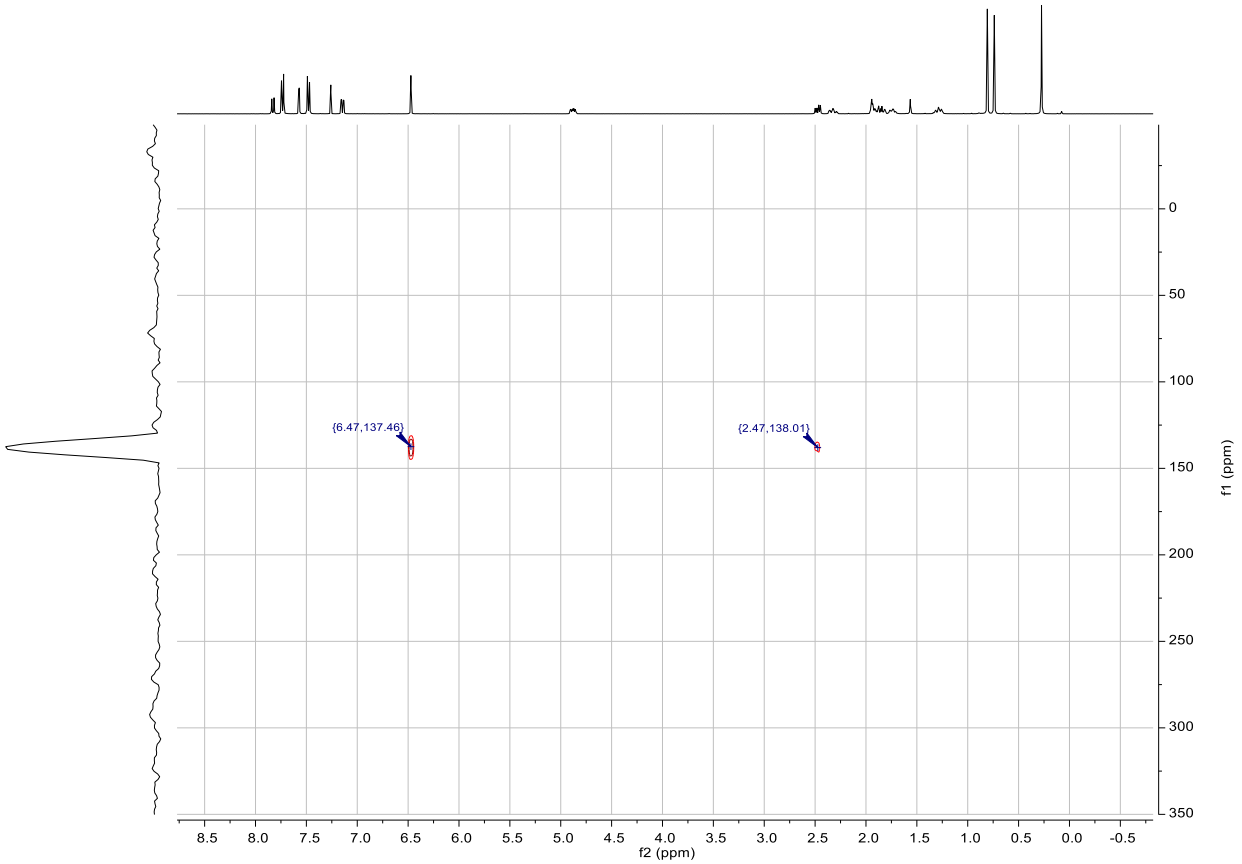
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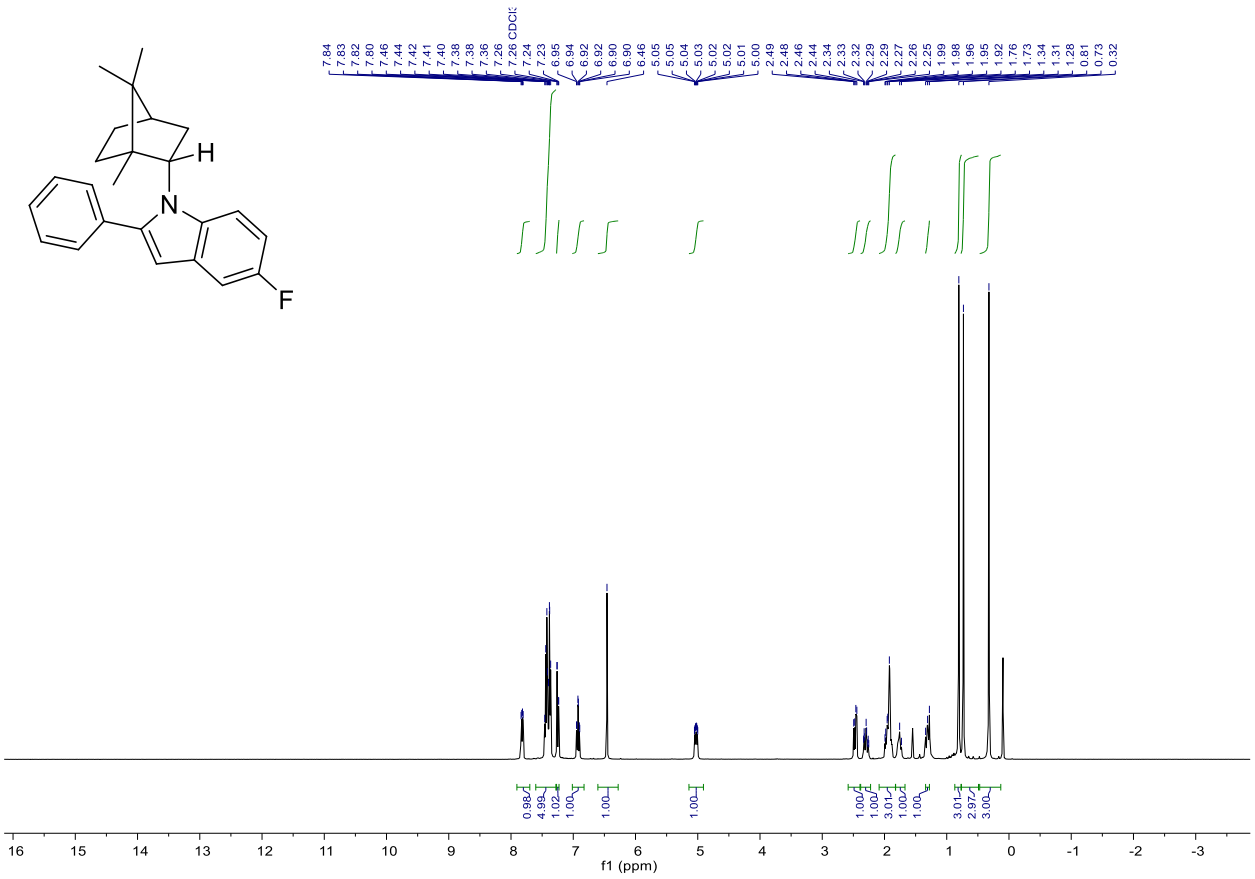
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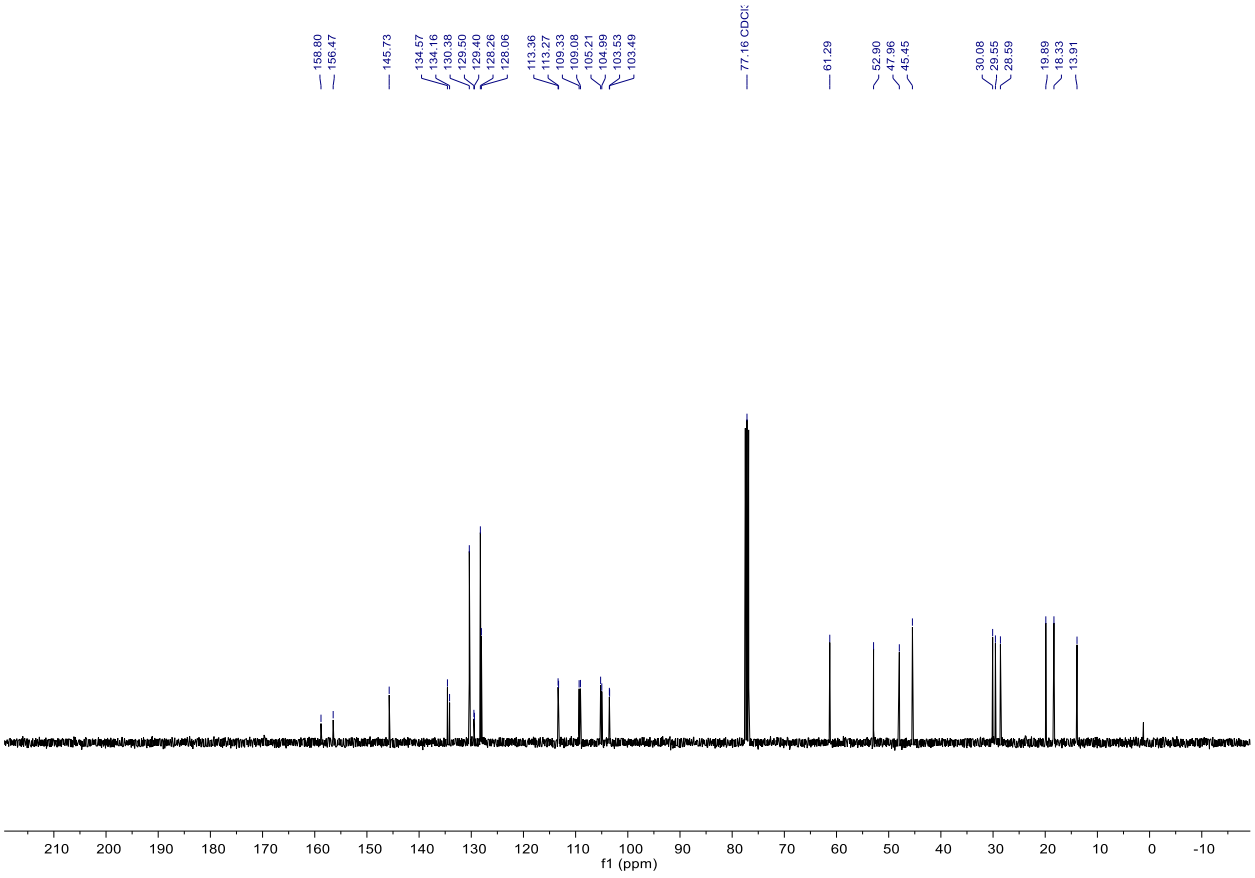
1H-15N HMBC NMR Spectrum of Compound 5cc



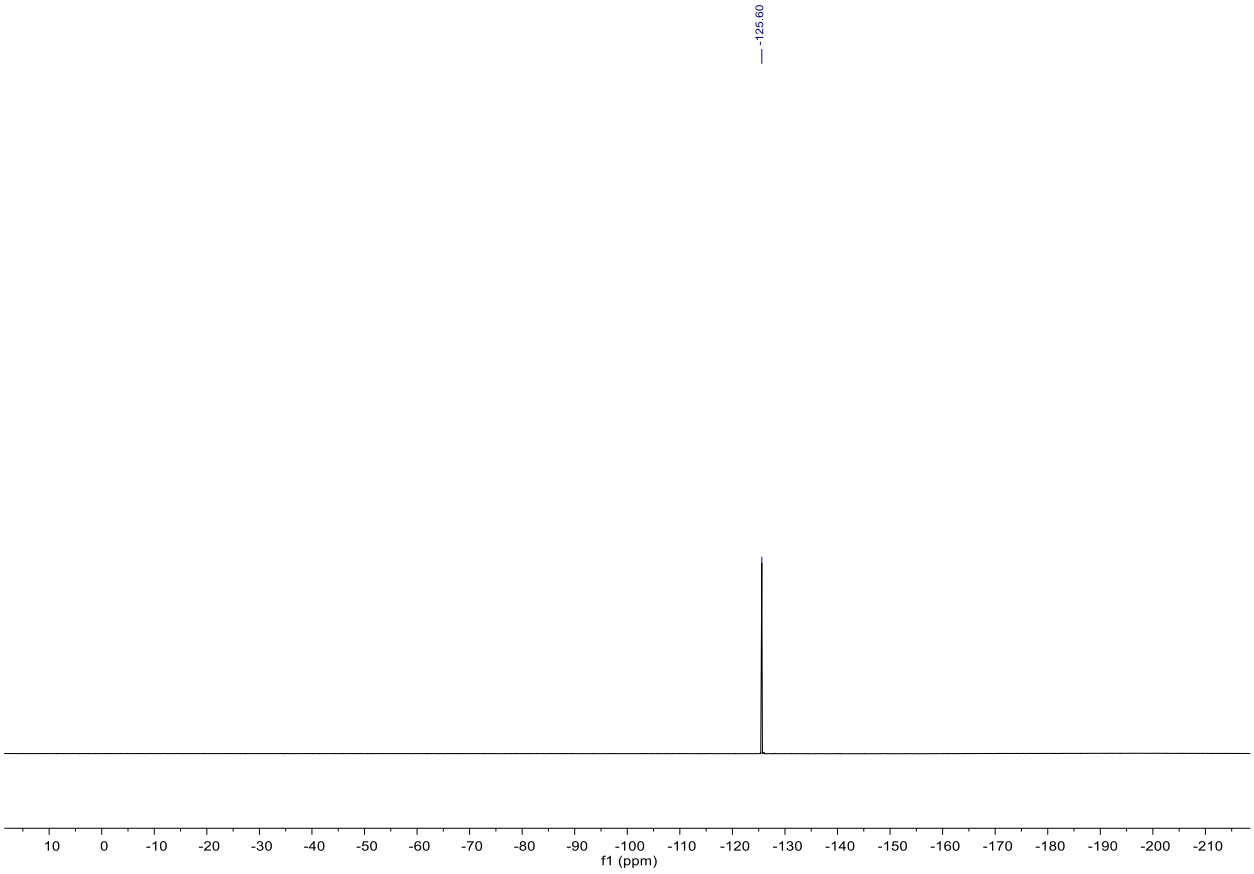
^{1}H NMR Spectrum of Compound 5da (400 MHz, CDCl3)



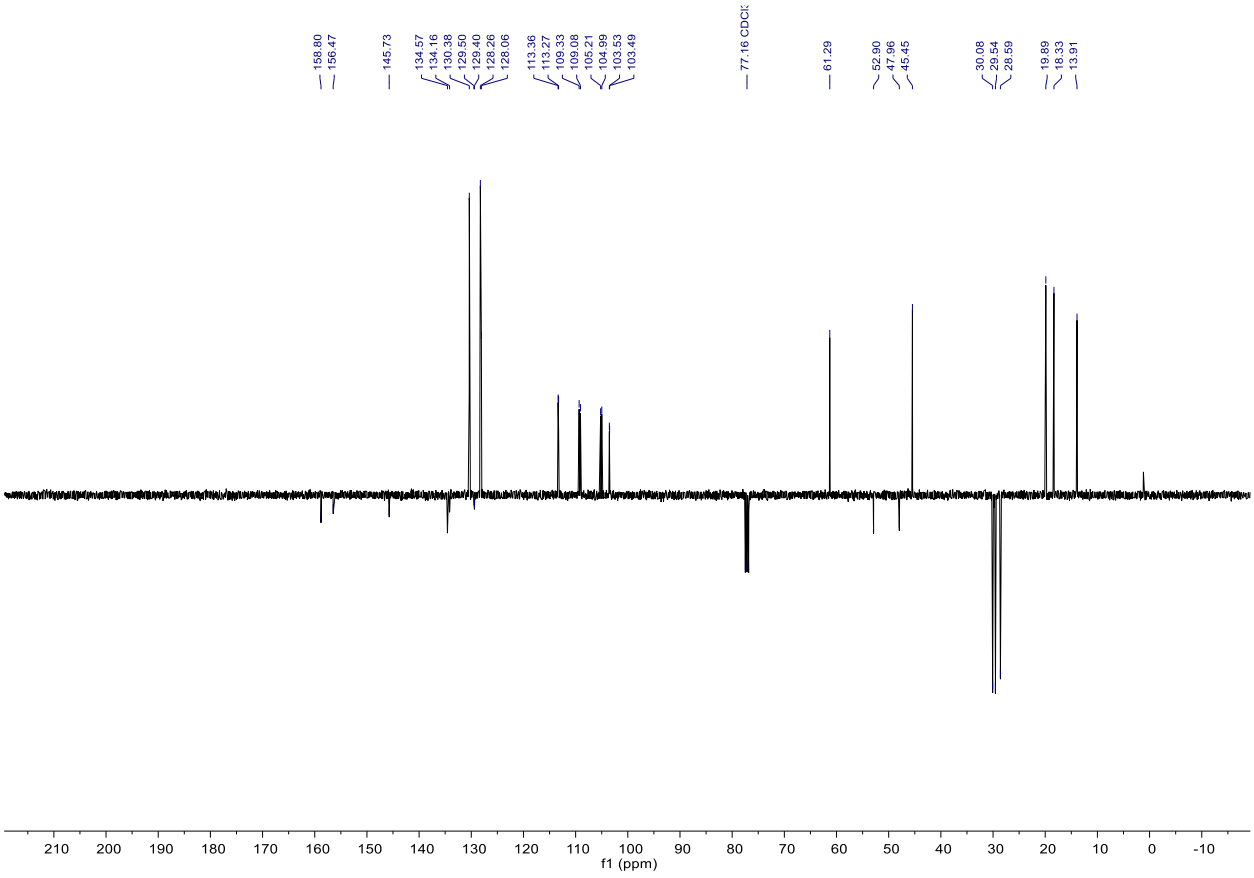
^{13}C NMR Spectrum of Compound 5da (101 MHz, CDCl3)



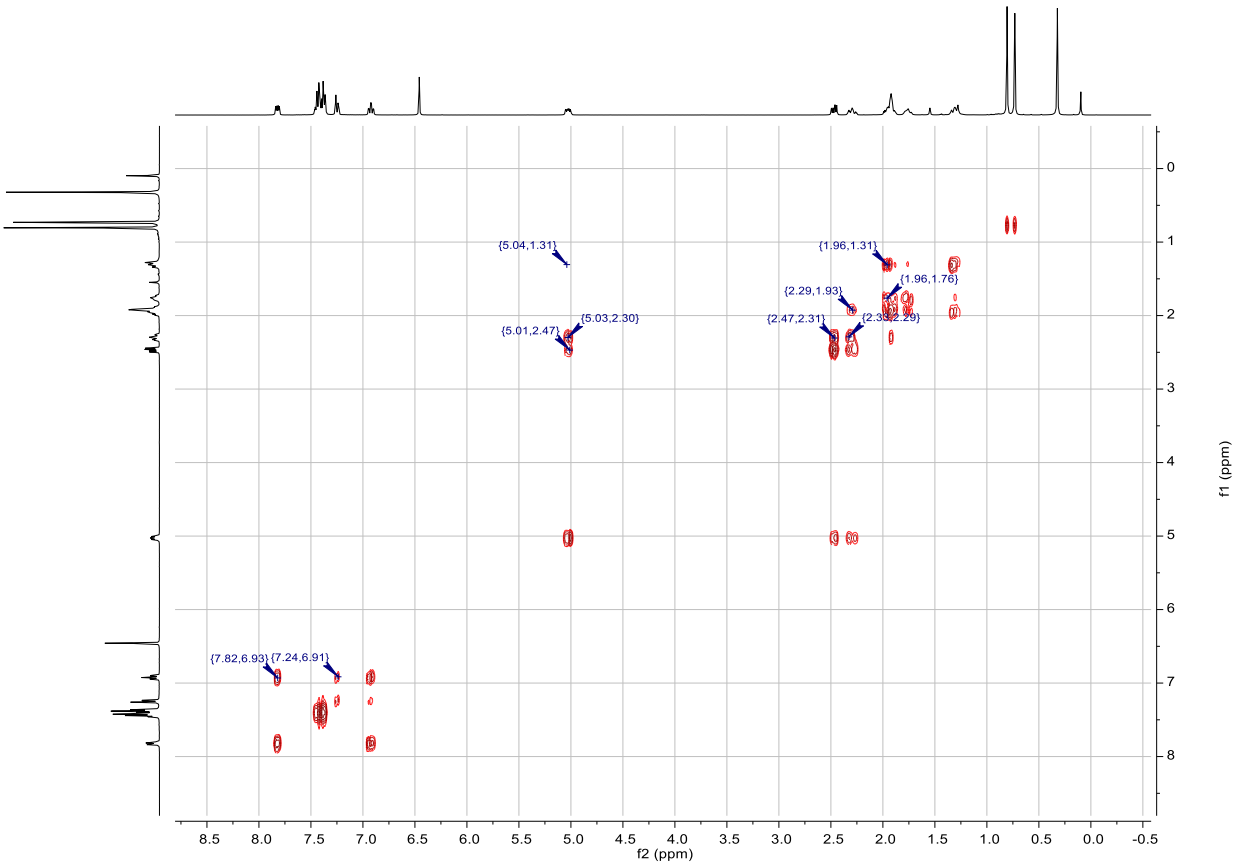
^{19}F NMR Spectrum of Compound 1a(376 MHz, CDCl3)



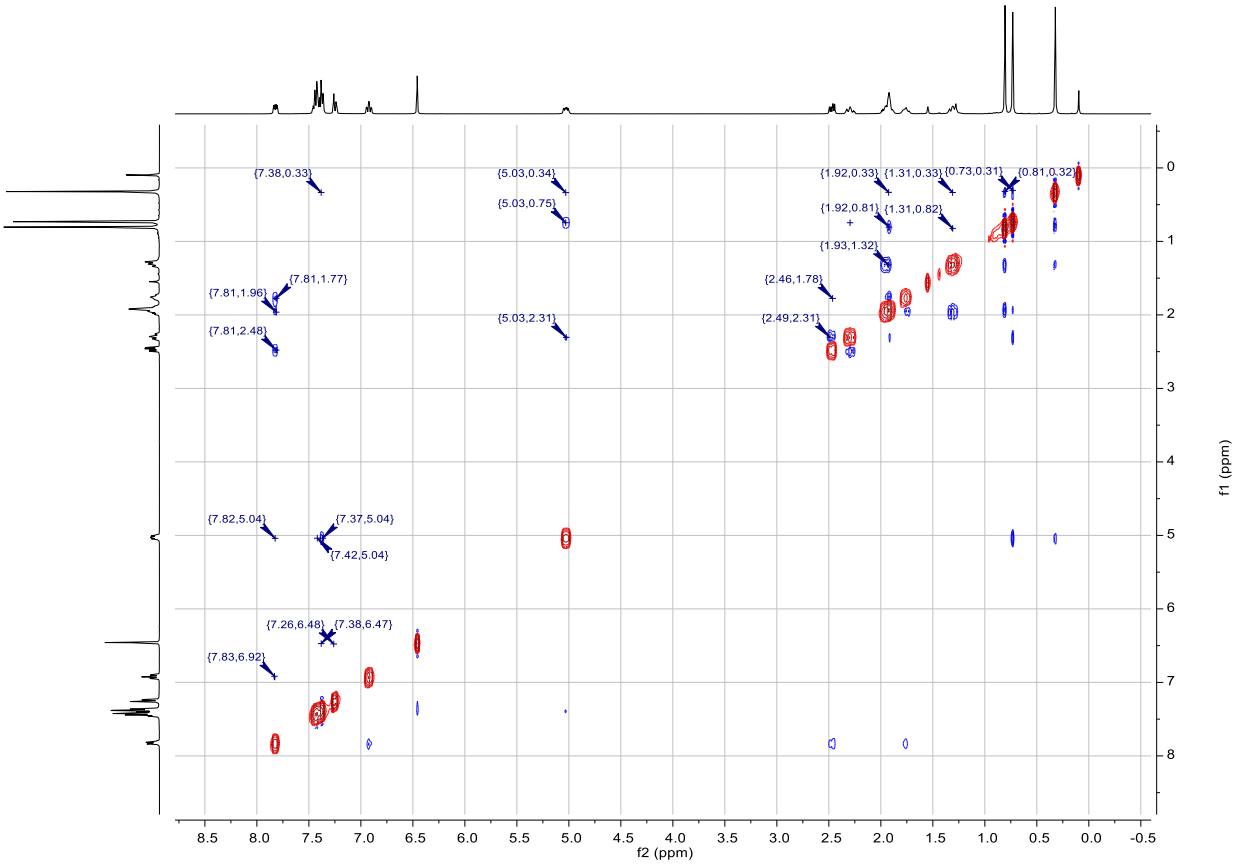
^{13}C DEPTQ-135 NMR Spectrum of Compound 5da



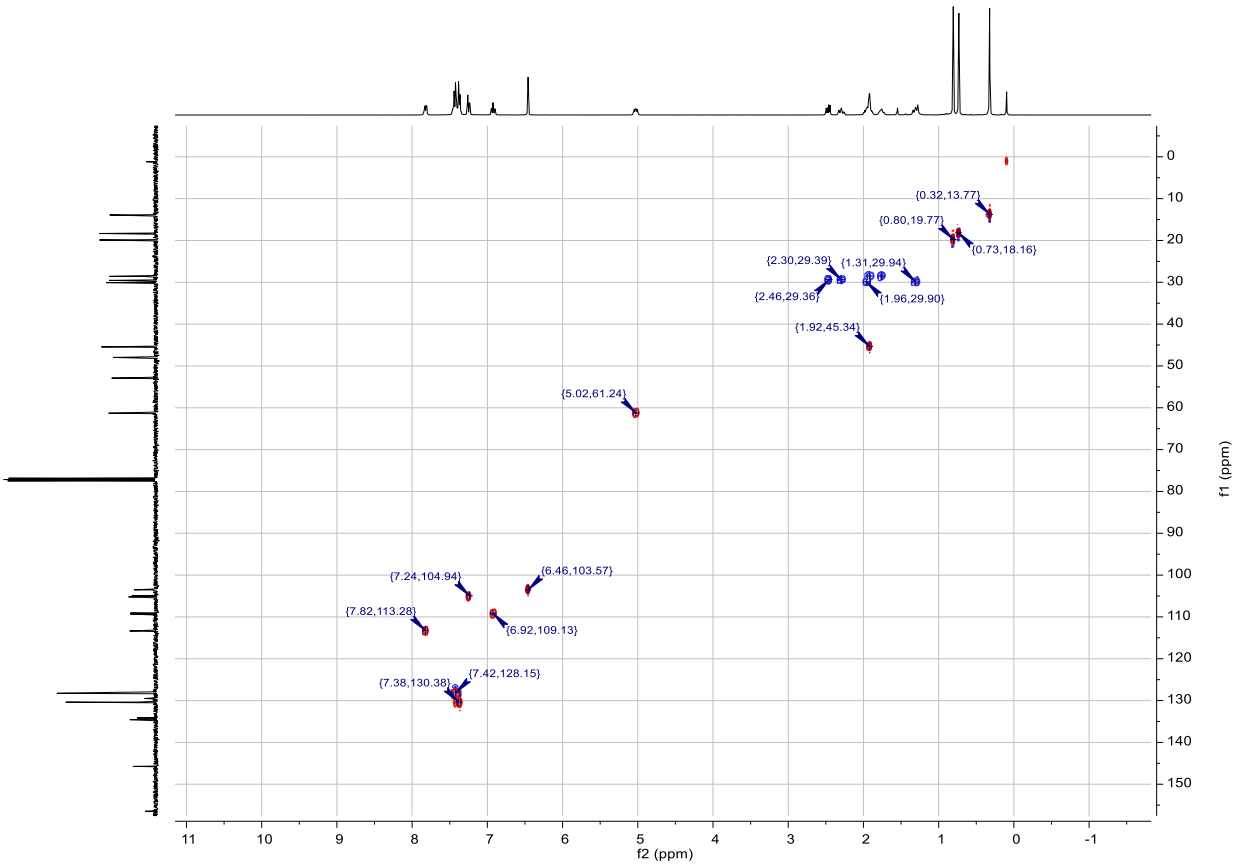
1H-1H COSY NMR Spectrum of Compound 5da



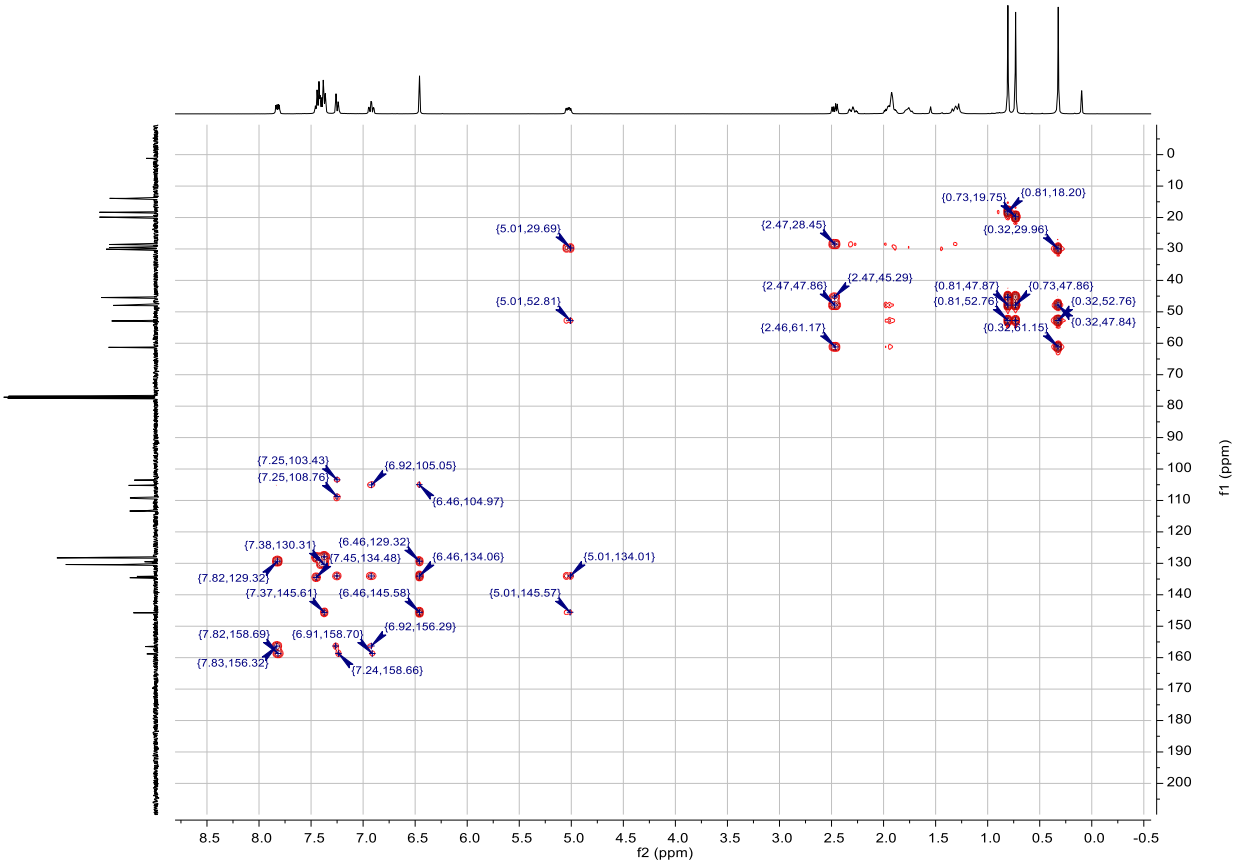
1H-1H NOESY NMR Spectrum of Compound 5da



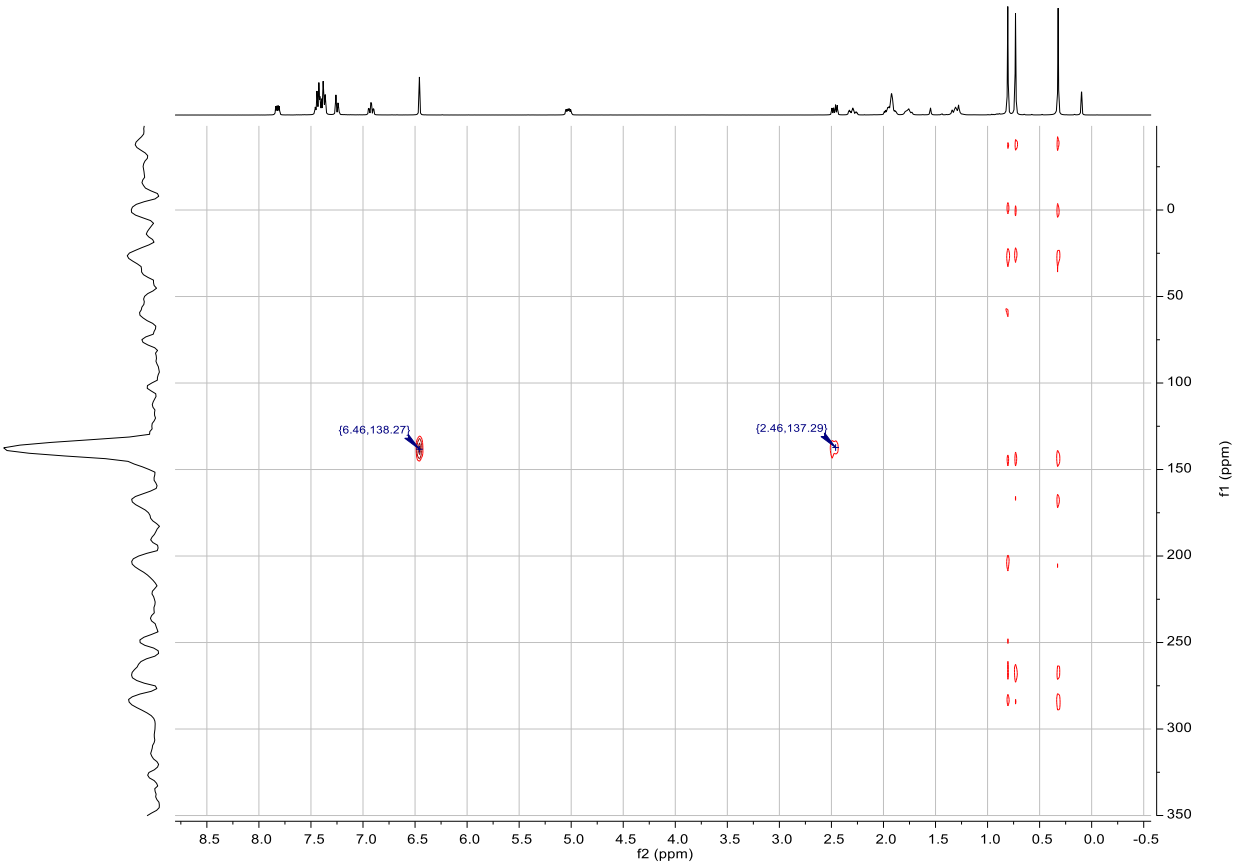
1H-13C HSQC NMR Spectrum of Compound 5da



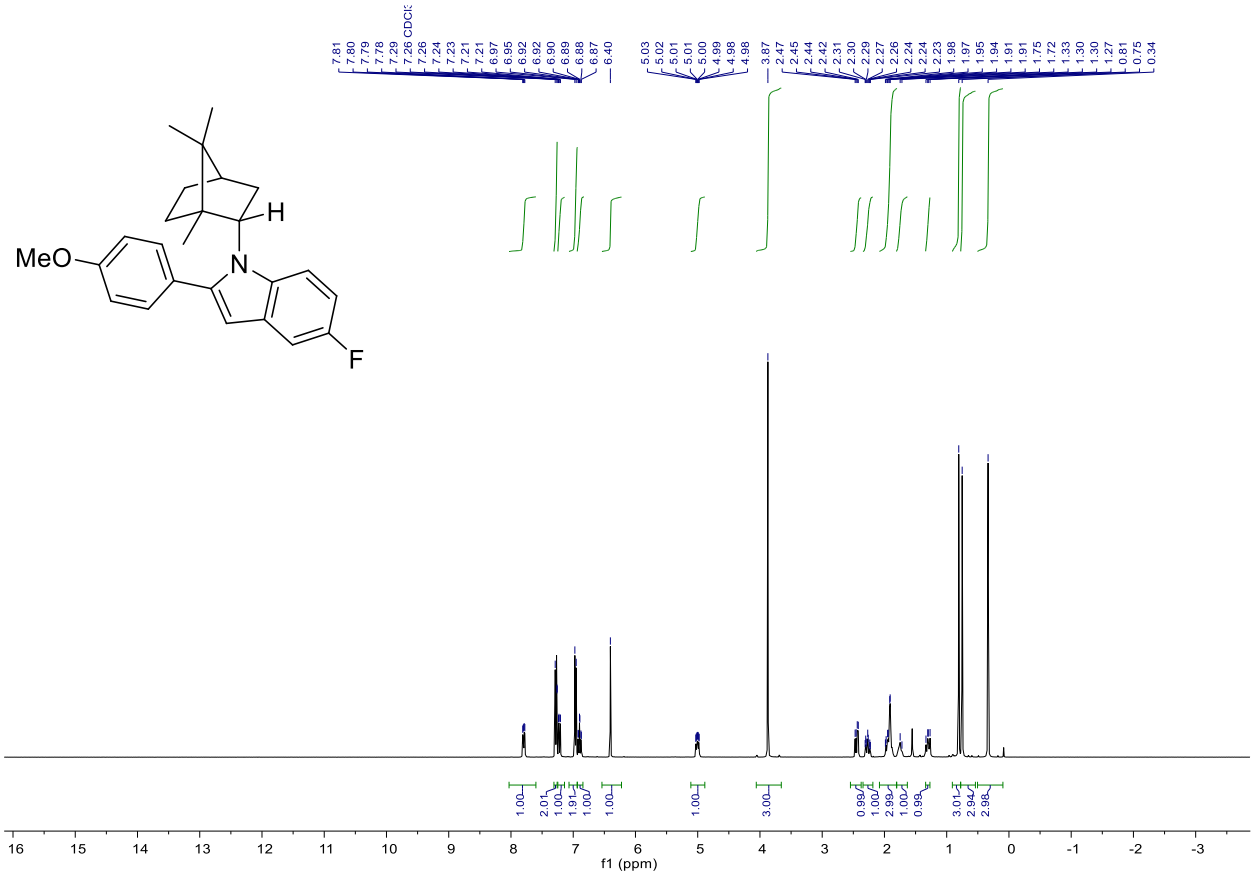
1H-13C HMBC NMR Spectrum of Compound 5da



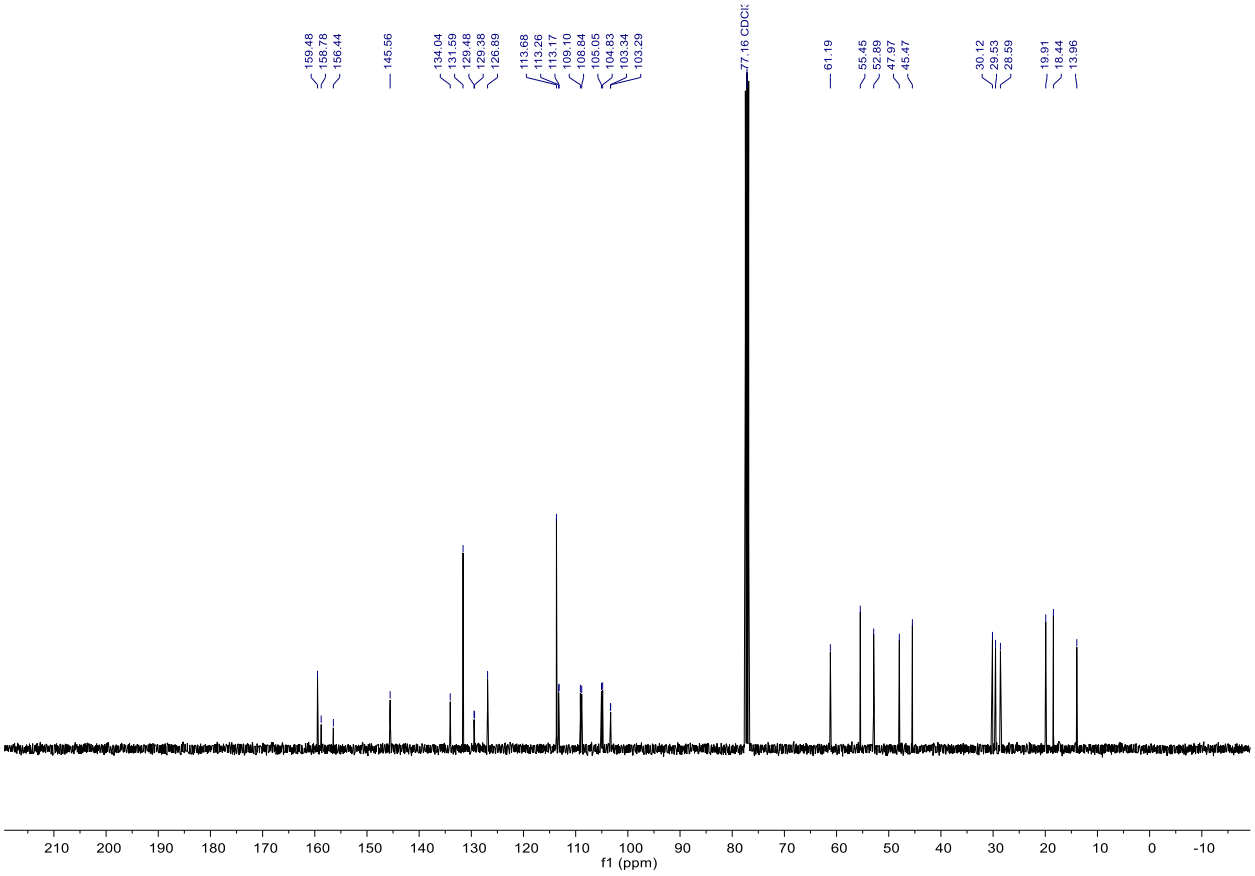
1H-15N HMBC NMR Spectrum of Compound 5da



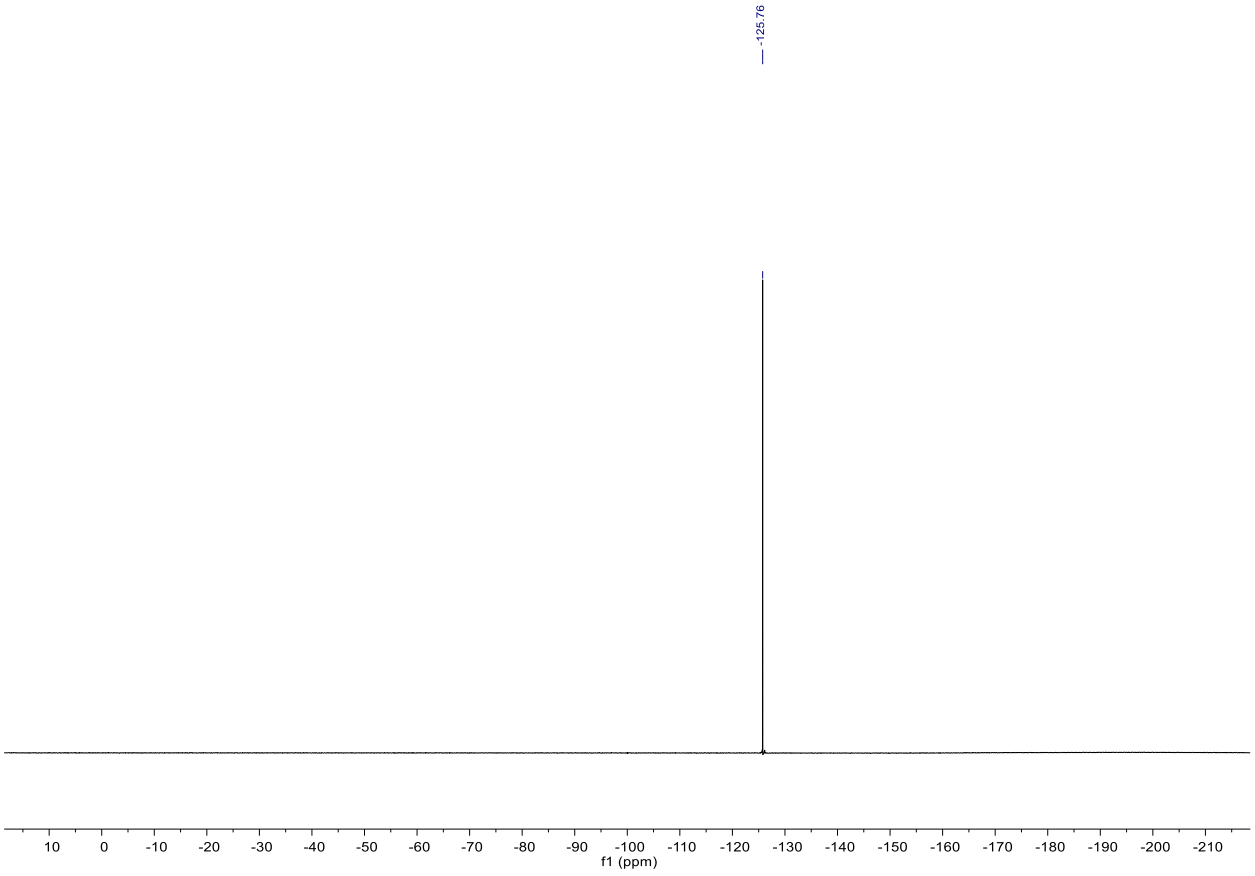
^{1}H NMR Spectrum of Compound 5db (400 MHz, CDCl3)



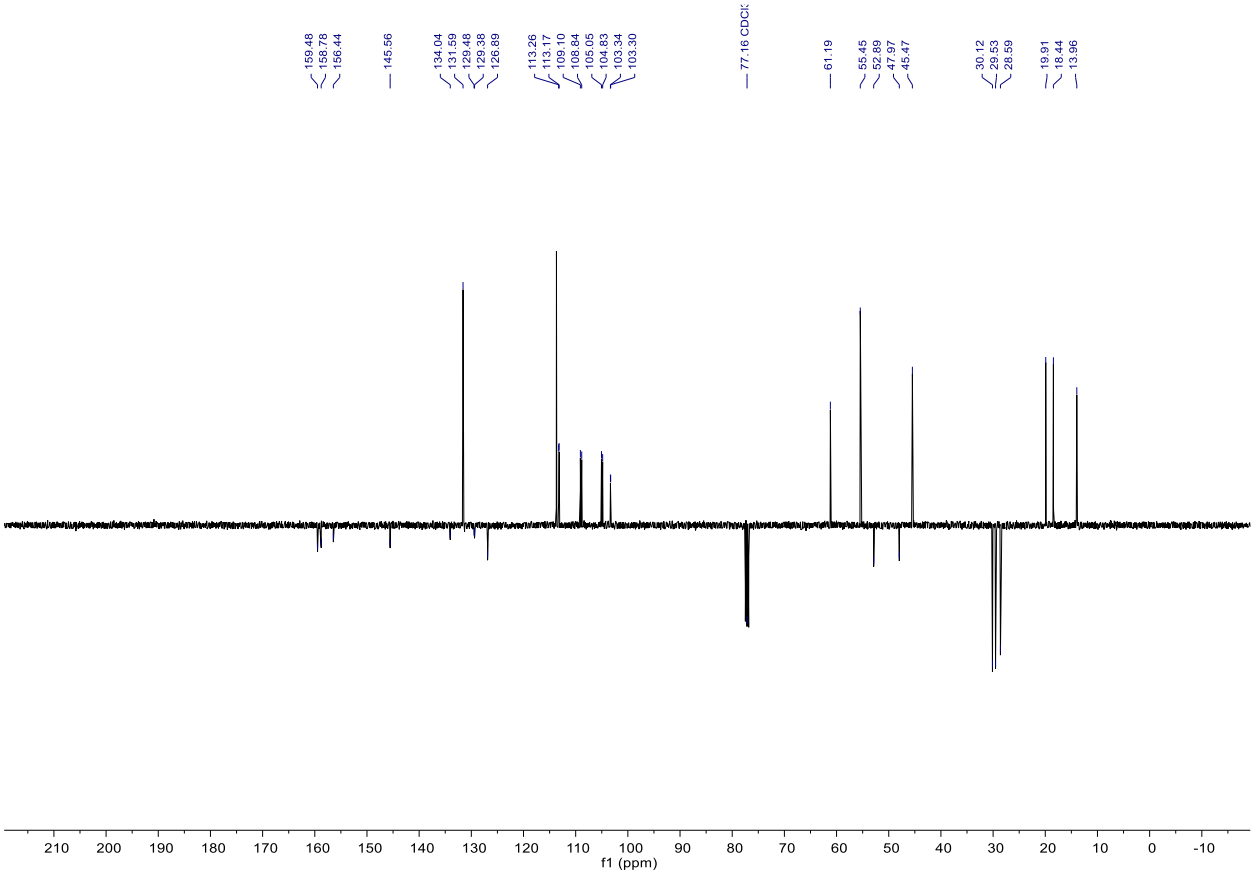
^{13}C NMR Spectrum of Compound 5db (101 MHz, CDCl3)



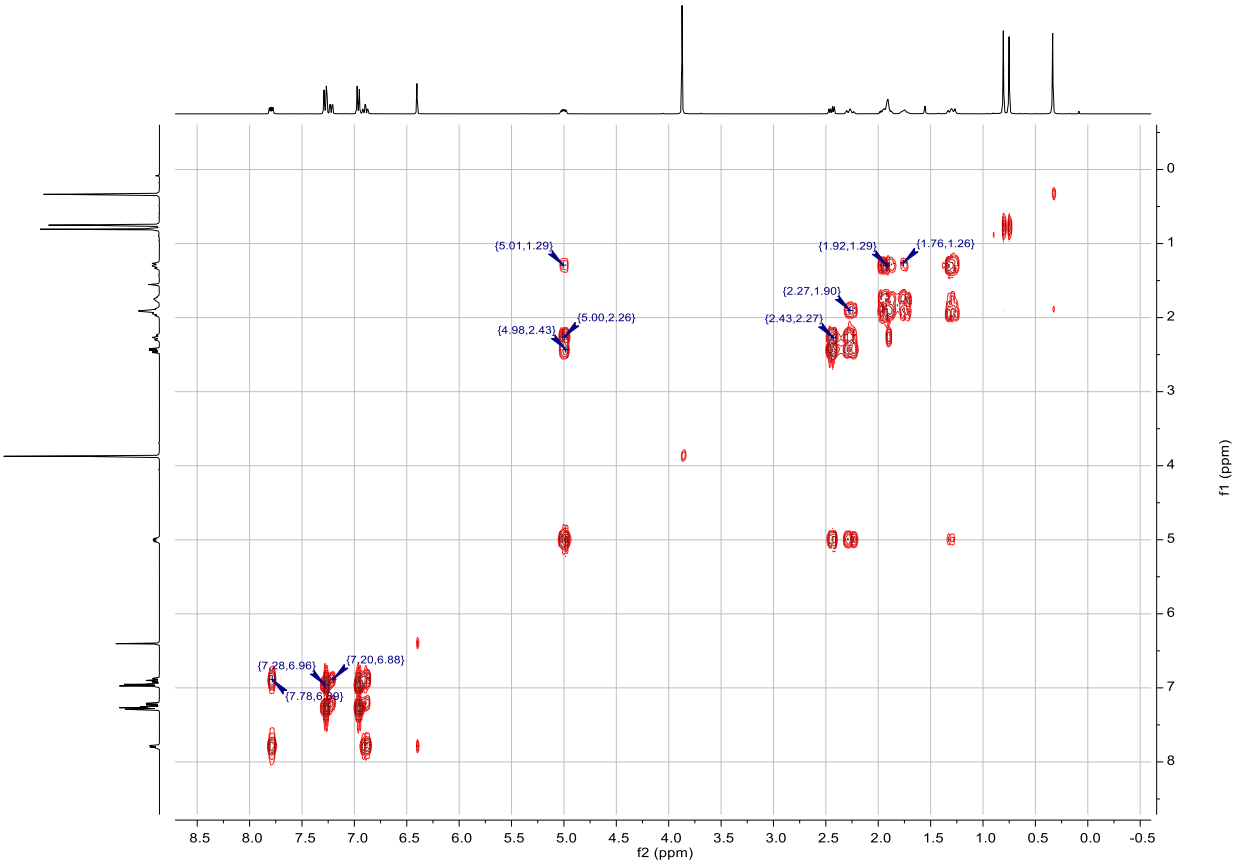
^{19}F NMR Spectrum of Compound 1a(376 MHz, CDCl3)



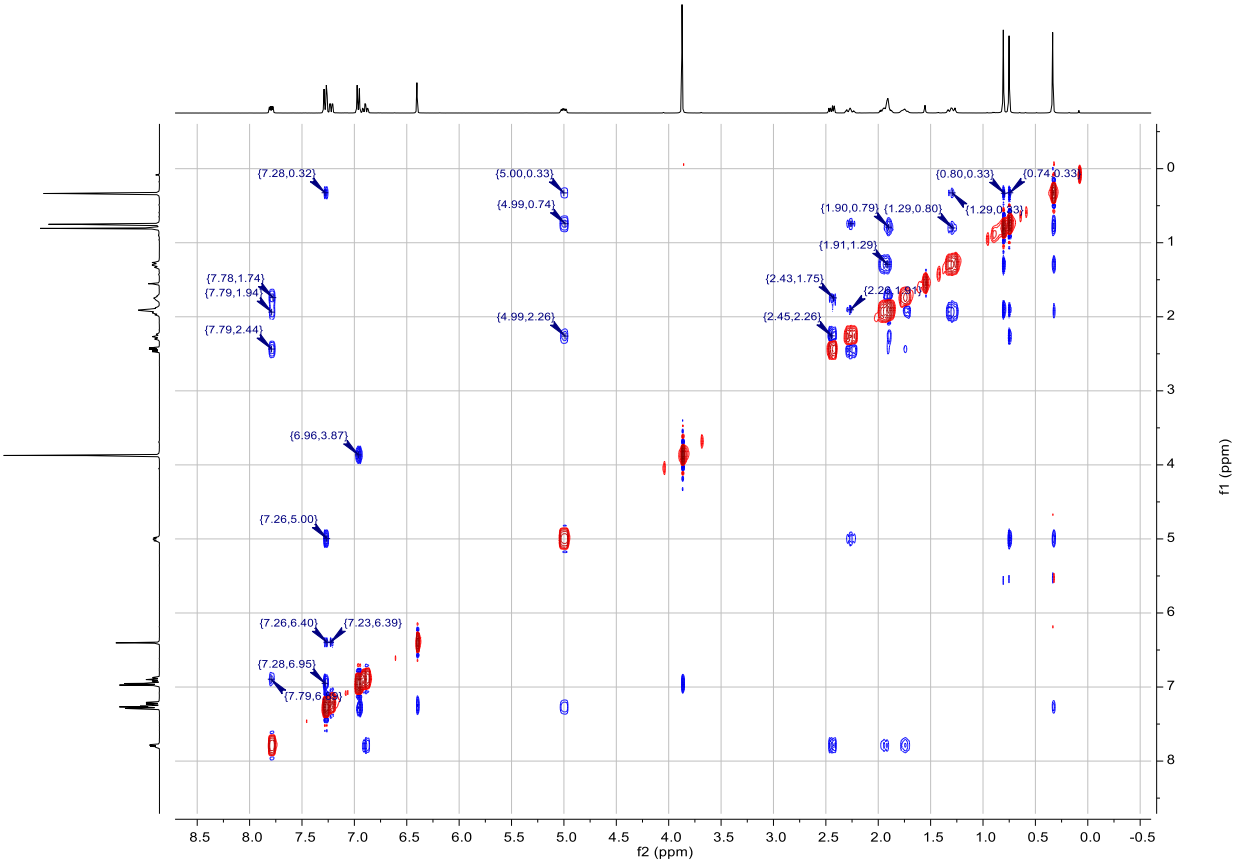
^{13}C DEPTQ-135 NMR Spectrum of Compound 5db



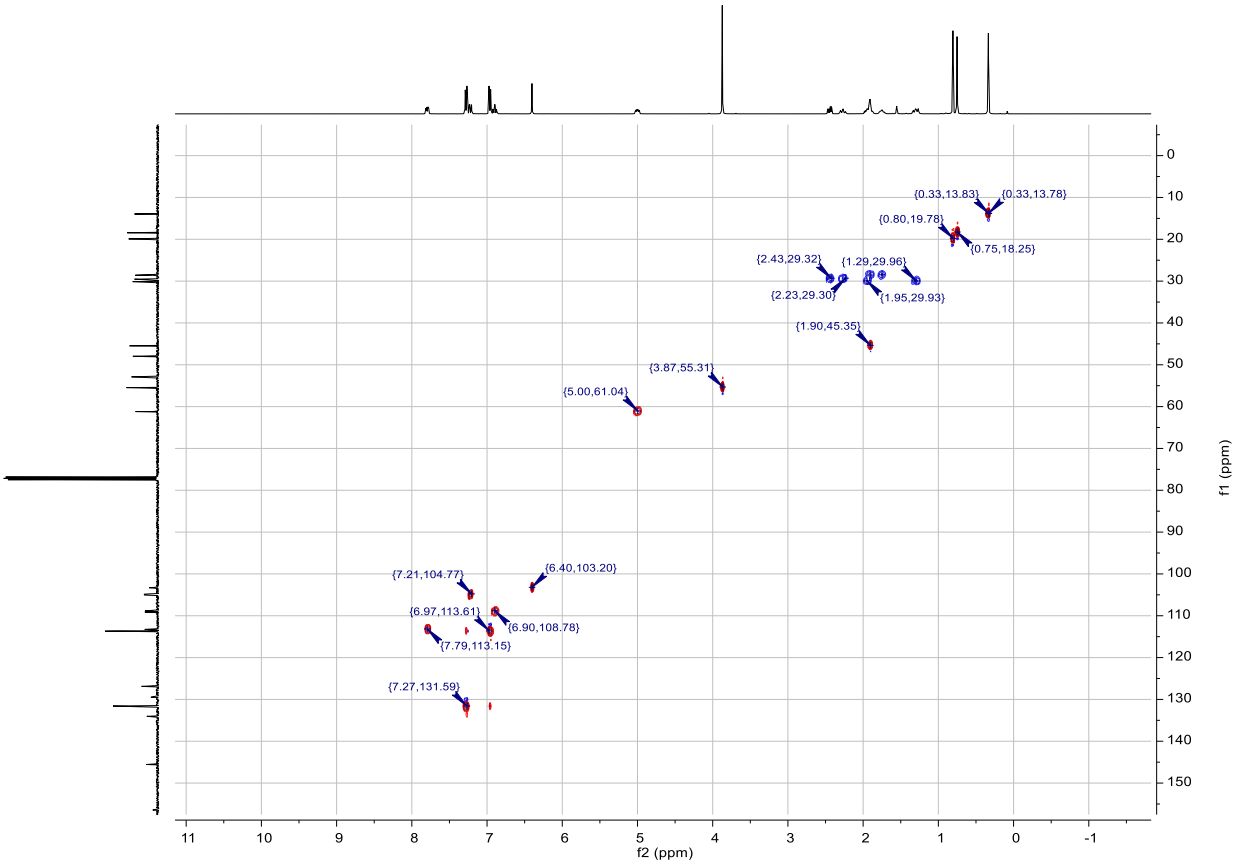
1H-1H COSY NMR Spectrum of Compound 5db



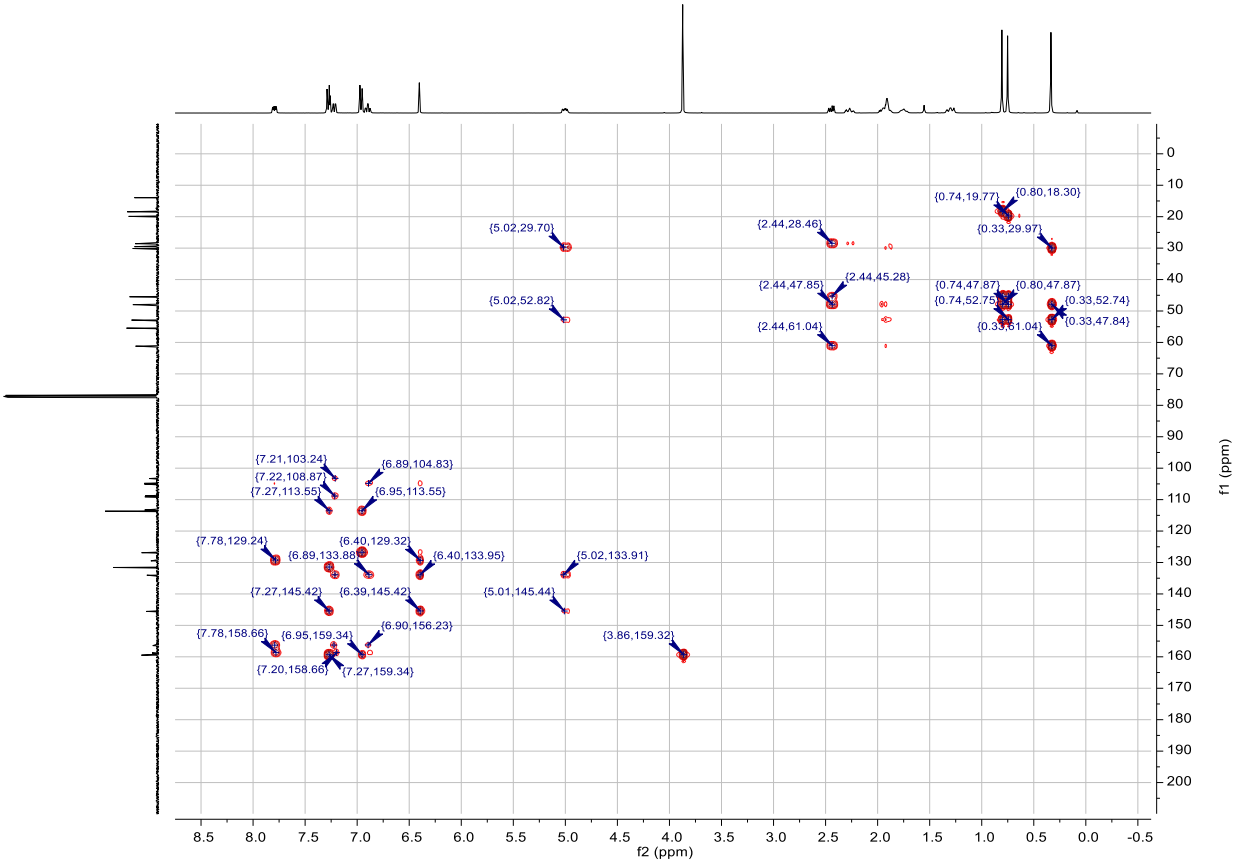
1H-1H NOESY NMR Spectrum of Compound 5db



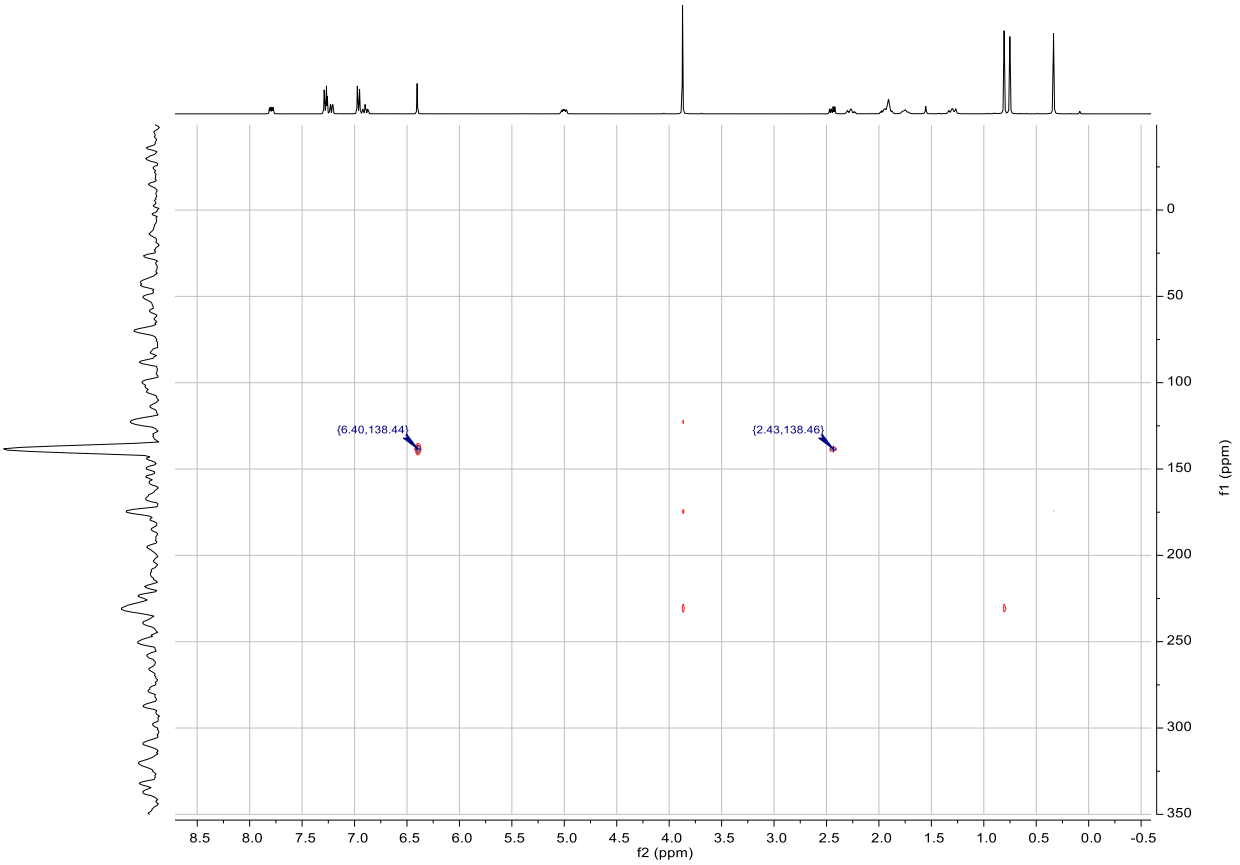
1H-13C HSQC NMR Spectrum of Compound 5db



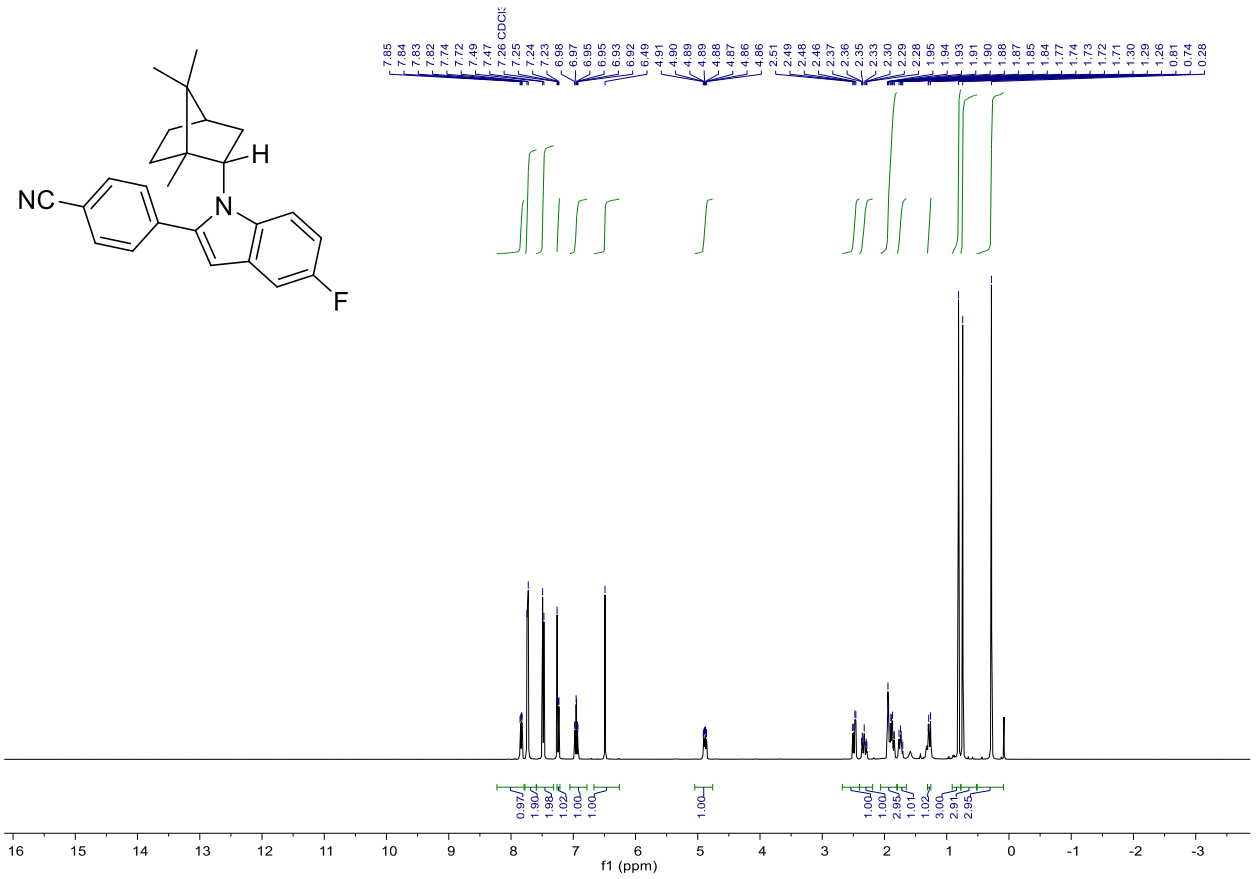
1H-13C HMBC NMR Spectrum of Compound 5db



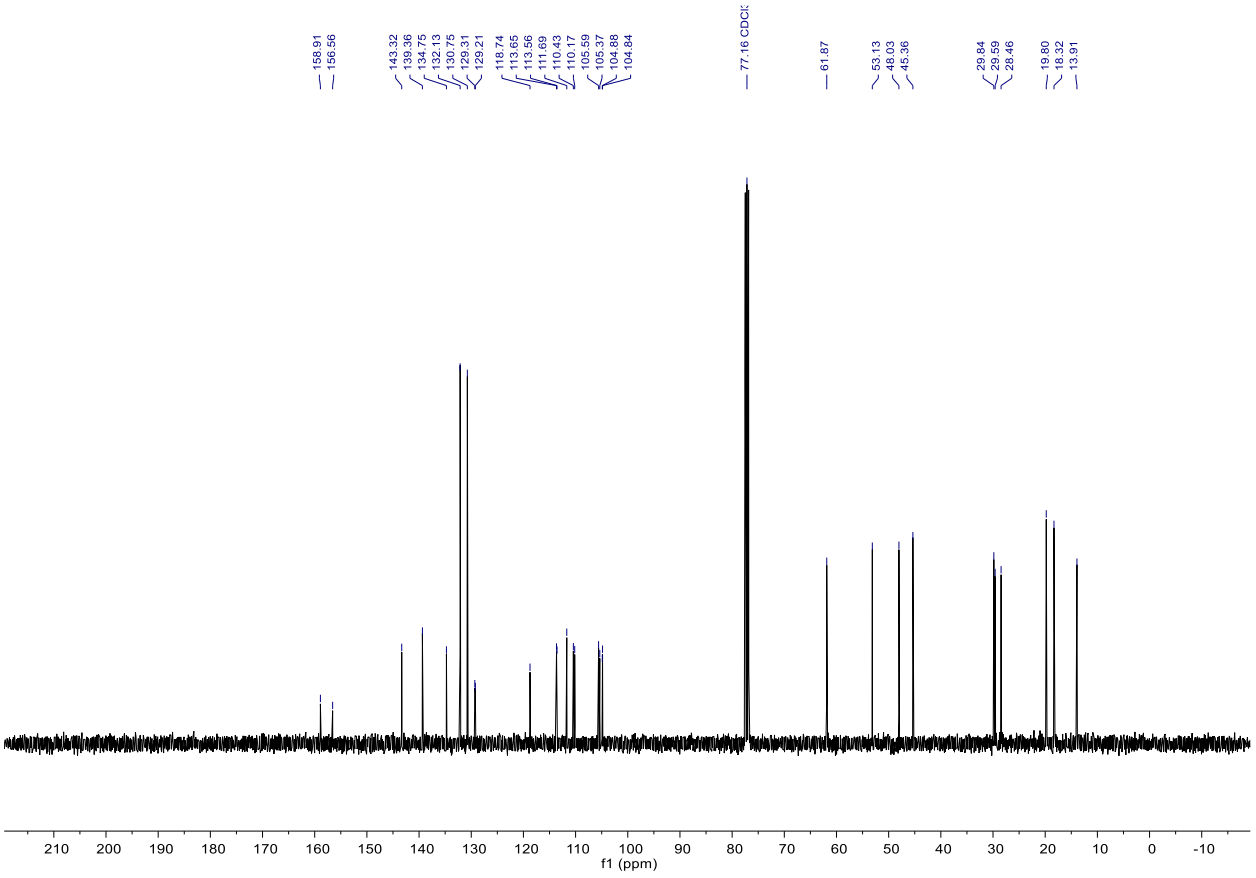
1H-15N HMBC NMR Spectrum of Compound 5db



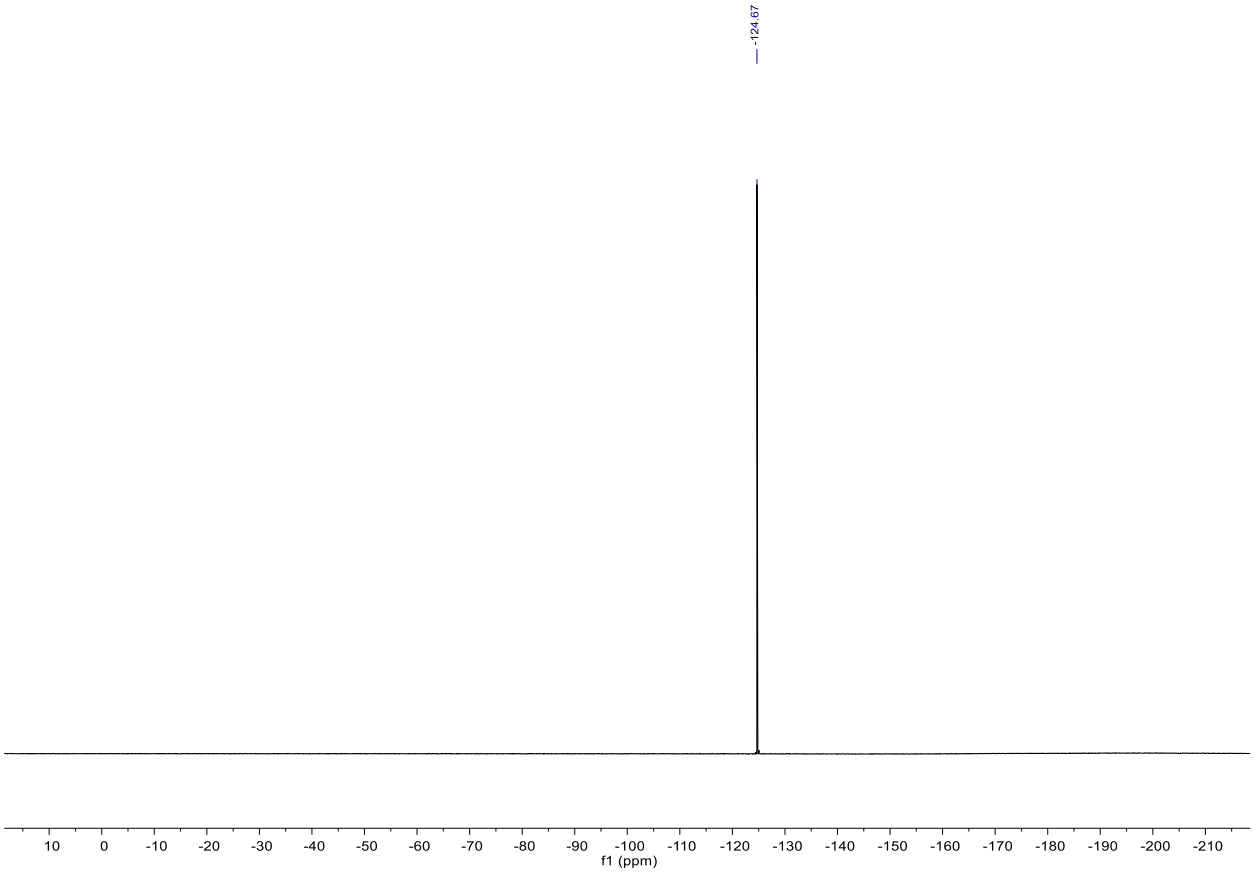
^{1}H NMR Spectrum of Compound 5dc (400 MHz, CDCl3)



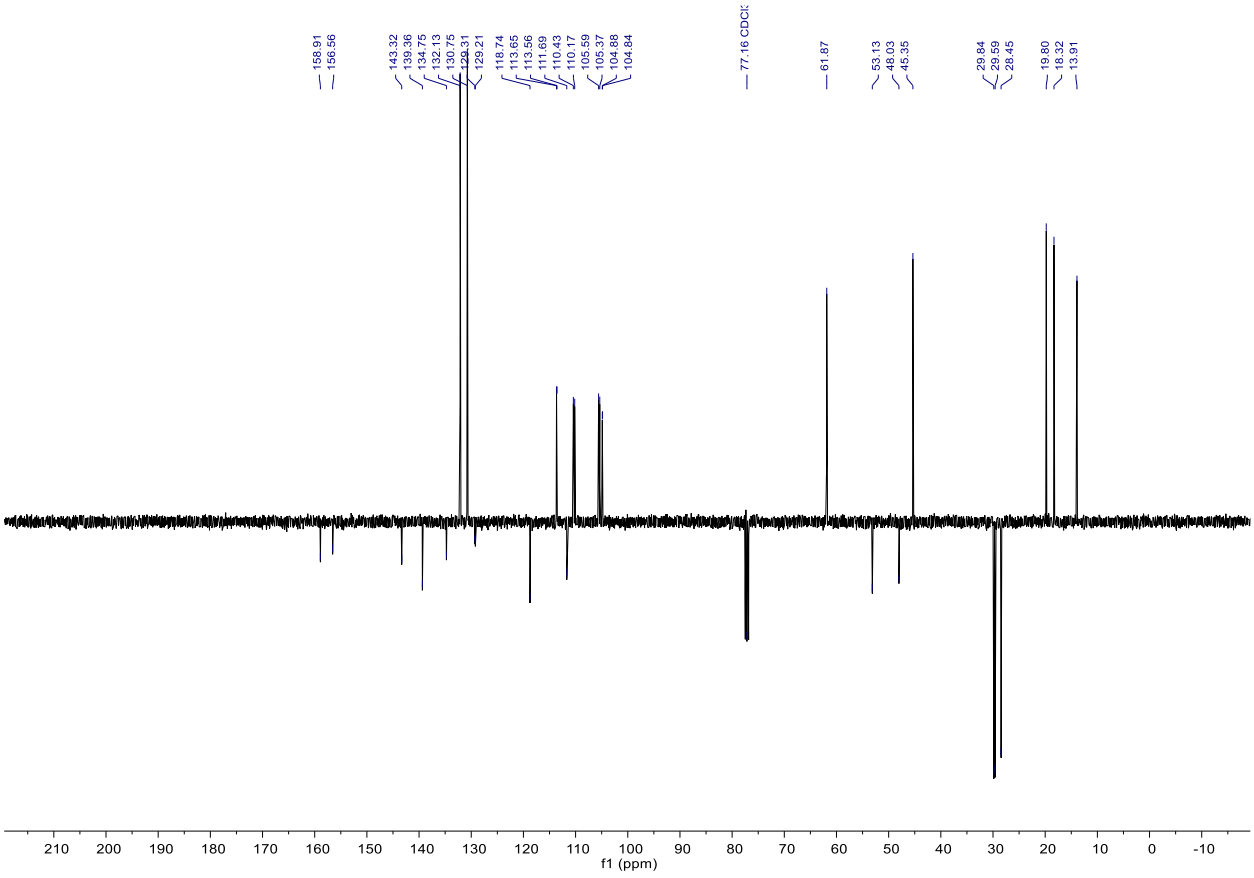
^{13}C NMR Spectrum of Compound 5dc (101 MHz, CDCl3)



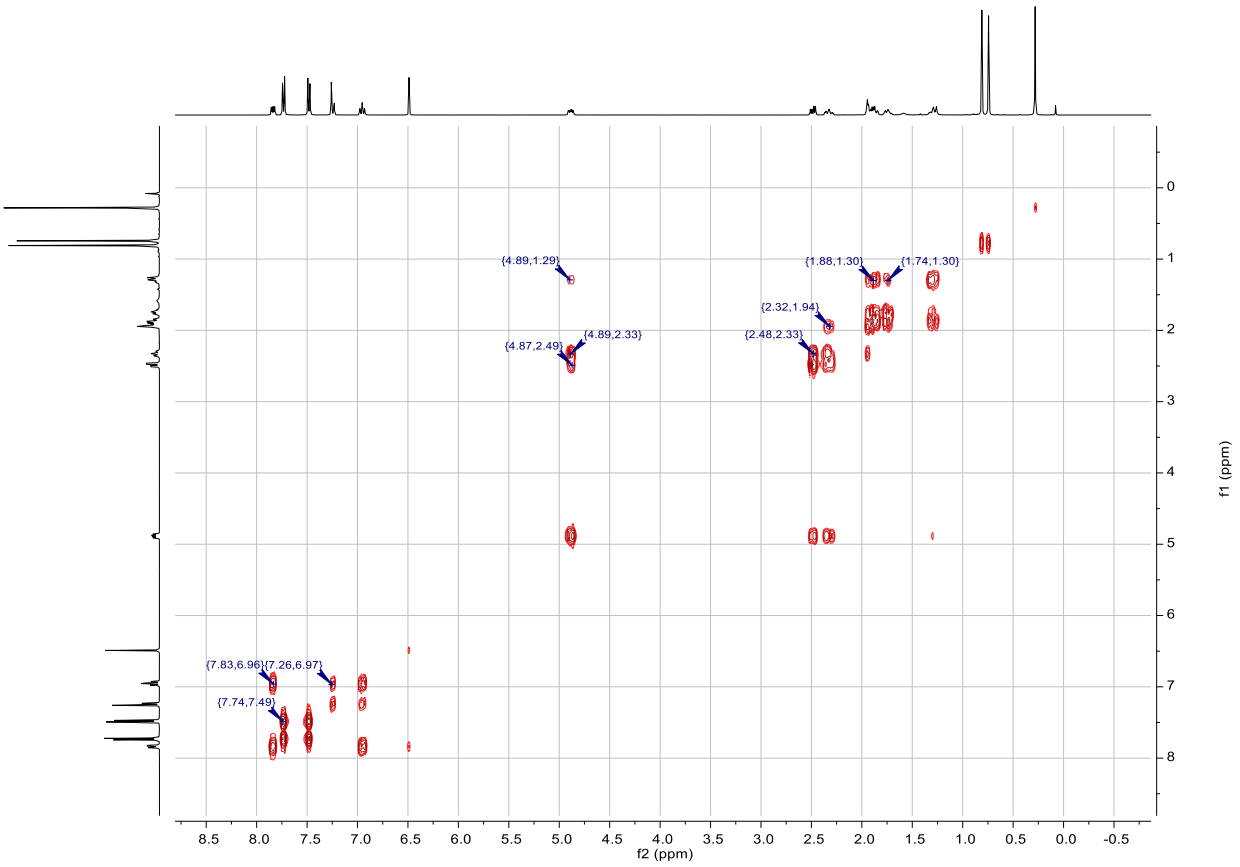
^{19}F NMR Spectrum of Compound 1a(376 MHz, CDCl3)



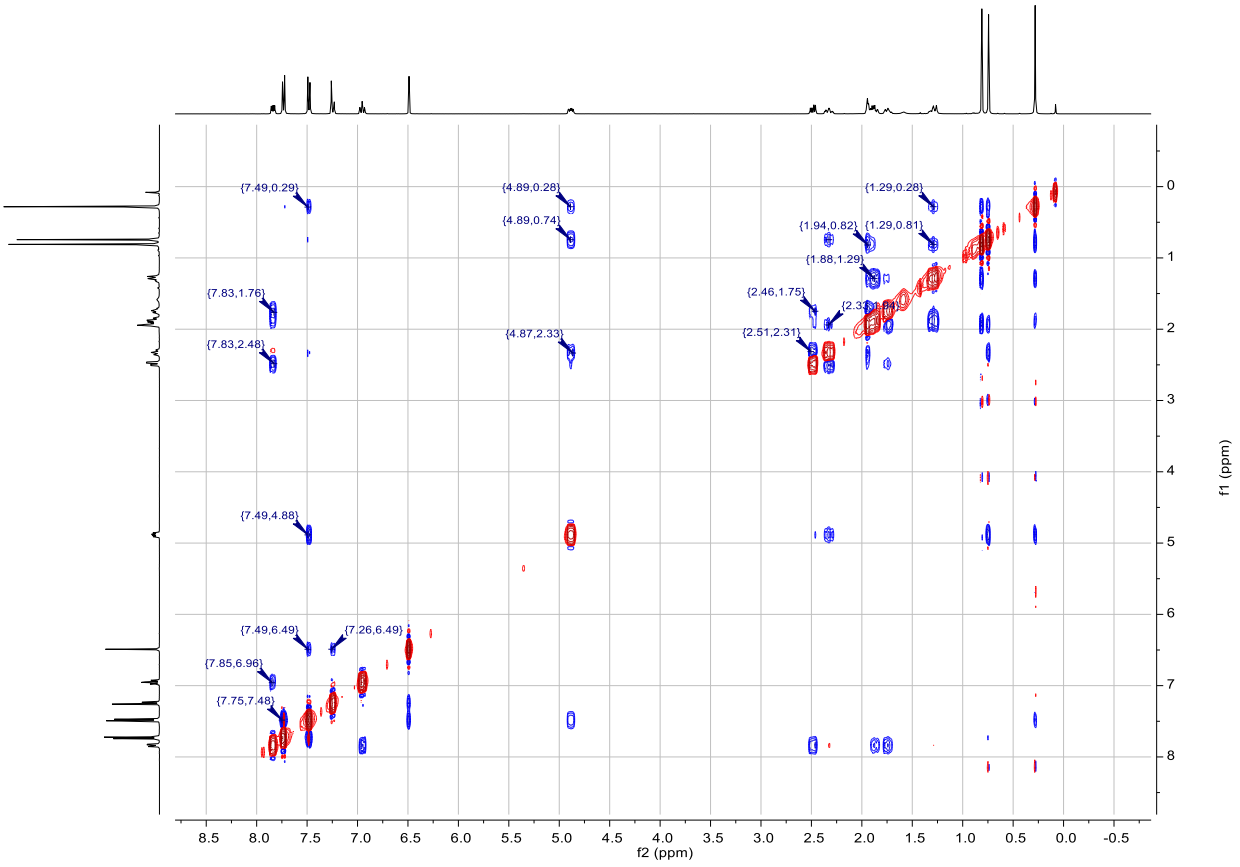
^{13}C DEPTQ-135 NMR Spectrum of Compound 5dc



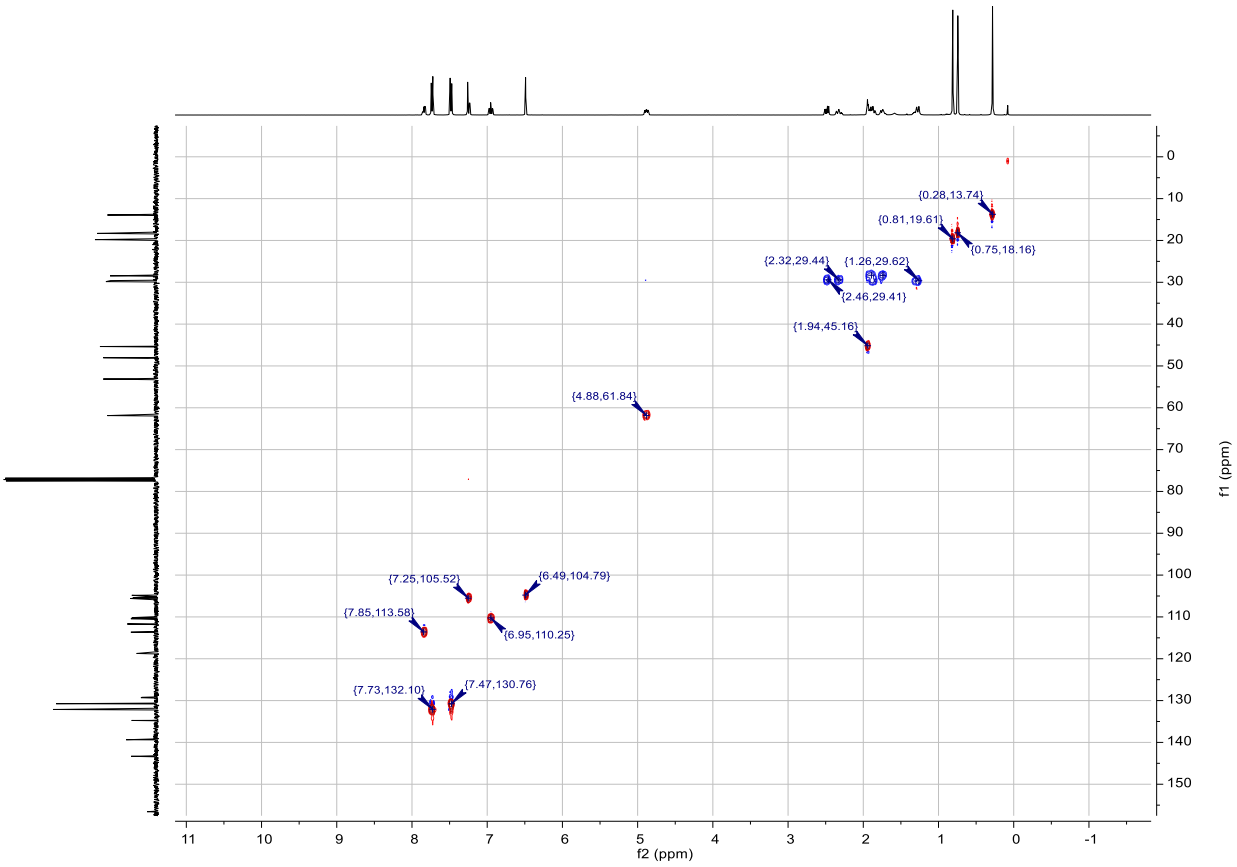
1H-1H COSY NMR Spectrum of Compound 5dc



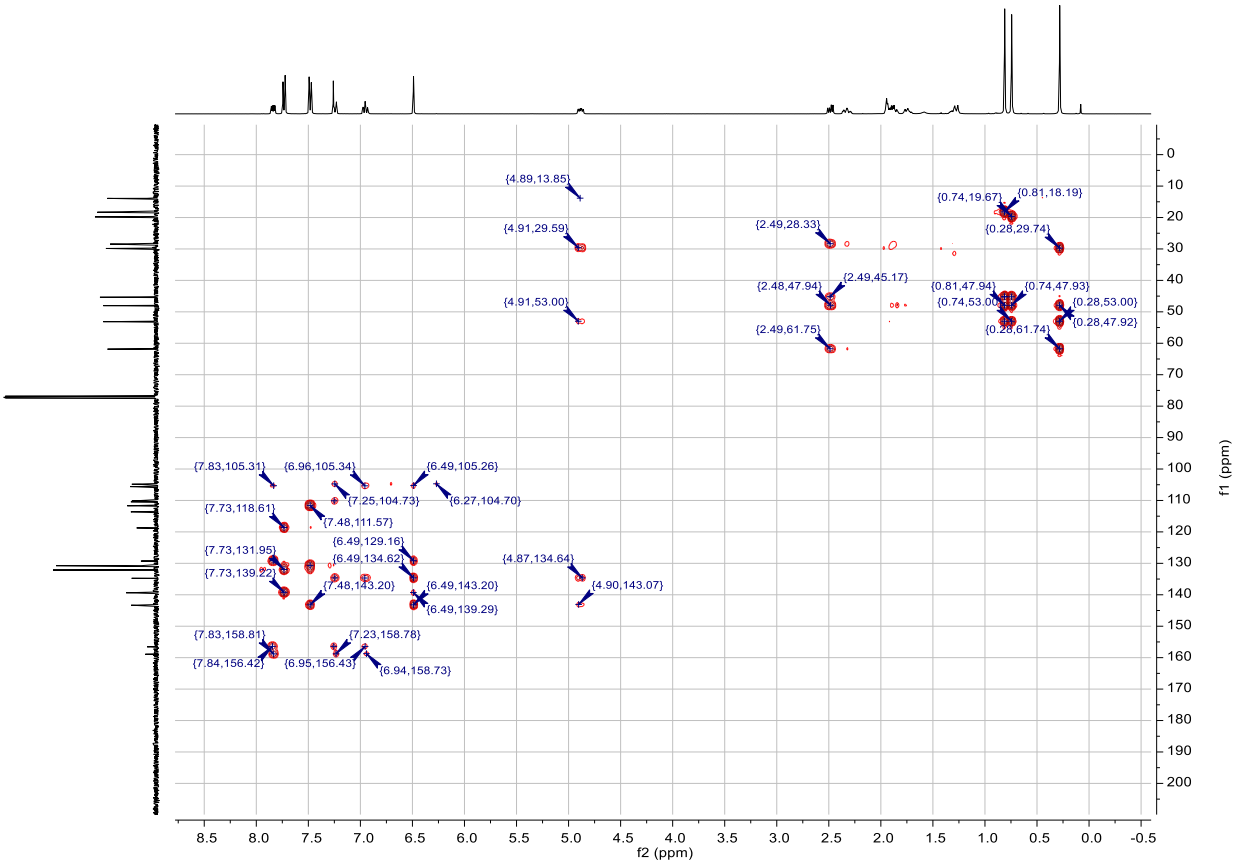
1H-1H NOESY NMR Spectrum of Compound 5dc



1H-13C HSQC NMR Spectrum of Compound 5dc



1H-13C HMBC NMR Spectrum of Compound 5dc



1H-15N HMBC NMR Spectrum of Compound 5dc

