Protective group-free synthesis of new chiral diamines via direct azidation of 1,1-diaryl-2-aminoethanols†

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Supporting Information

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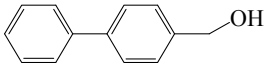
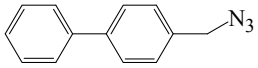
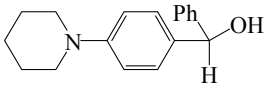
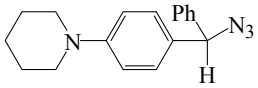
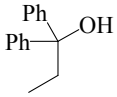
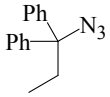
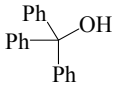
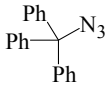
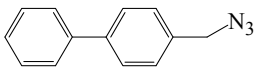
General

All the chemicals used in this work were purchased from Aldrich and used without further purification. Melting points were determined on a Clarkson IA9200 Electro thermal melting point apparatus and temperatures were uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Rudolph Autopoly-IV digital polarimeter; $[\alpha]_D$ values are given in unit of 10 deg^{-1} cm^2 g^{-1}. ^1H NMR &^{13}C NMR spectra were recorded at 300 MHz and 75 MHz respectively on a Jeol Eclipse FT 300 MHz spectrometer in $CDCl_3$ as a solvent using TMS as internal standard and chemical shifts were expressed as δ in ppm; coupling constants *J* are given in Hz. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Flash column chromatography was performed using Merck Kiegel 60 silica gel (particles size 0.040-0.063 mm). For thin-layer chromatography (TLC), Merck silica gel 60 F_{254} plates were used. Mass spectra were recorded by electronic impact (EI) and obtained on an Agilent 1100 series VLL or JEOL the MStation JMS700 mass spectrometer.

Preliminary studies for azidation of benzyl alcohols

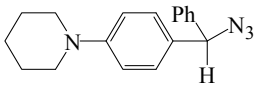
Entry	Substrate	Equiv of NaN_3	Solvent	Product	Yield (%)
1		3	toluene		47
2	 **1a**	5	toluene	 **2a**	67
3		7	toluene		79
4	 **1b**	3	toluene	 **2b**	30
5		7	toluene		81
6		7	$CHCl_3$		55
7		7	THF		38
8		7	toluene		87

4-Azidomethylbiphenyl (entry 1)



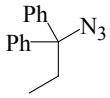
Yellow oil (37 mg, 47%); IR (neat); 2104 cm^{-1}; ^1H NMR ($CDCl_3$): δ_H 7.62-7.57 (m, 4H), 7.47-7.33 (m, 5H), 4.39 (s, 2H); ^{13}C NMR ($CDCl_3$, 300Hz): δ_C 141.2, 140.4, 134.3, 128.8, 128.6, 127.5, 127.4, 127.0, 54.5; EI-MS: *m/z* (%) 209 (M^+, 17), 180 (29), 167 (100), 151 (62).

1-[4-(Azidophenylmethyl)]phenylpiperidine (2a, entry 3)



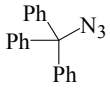
Colorless oil (107 mg, 79%); IR (neat) 2103 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.37-7.20 (m, 7H), 6.88 (d, 2H, J = 8.7 Hz), 5.78 (s, 1H), 3.15-3.11 (m, 4H), 1.70-1.65 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 128.3, 127.5, 127.2, 126.4, 116.2, 75.9, 50.4, 25.7, 24.2; EI-MS: *m/z* (%) 292 (M^+, 6), 264 (7), 250 (100), 207 (9).

1,1-Diphenyl-1-azidopropane (2b, entry 5)



Colorless oil (61 mg, 81%); IR (neat); 2101 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz): δ_H 7.35-7.22 (m, 10H), 2.43 (q, 2H, J = 6.0 Hz), 0.83 (t, 3H, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 75MHz): δ_C 142.9, 128.2, 127.3, 127.1, 73.0, 31.5, 8.56; EI-MS: *m/z* (%) 237 (M^+, 3), 208 (12), 195 (36), 180 (100).

Triphenylazidomethane (entry 8)

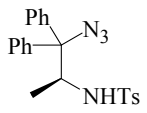


Colorless oil (143 mg, 87%); IR (neat); 2103 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ_H 7.37-7.25 (m, 15H); ^{13}C NMR ($CDCl_3$, 75MHz): δ_C 142.8, 128.7, 128.6, 128.4, 128.3, 128.1, 128.0, 127.7, 127.6, 127.3, 126.8, 77.1; EI-MS: *m/z* (%) 285 (3), 243 (100), 180 (43), 165 (77), 77 (59).

General procedure for the azidation of 1/4.

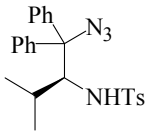
To a suspension of NaN_3 (228 mg, 3.5 mmol) in toluene (7 mL) was added concentrated sulfuric acid (0.19 mL, 3.5 mmol) drop-wise for 10 min using syringe pump and the mixture was stirred for 15 min at room temperature. To this mixture, a solution of **1/4** (0.5 mmol) in toluene (15 mL) was added via syringe at ice-cold temperature and the resulting mixture was stirred vigorously for 5-10 min at room temperature. The reaction mixture was quenched with a saturated $NaHCO_3$ solution (15 mL, until pH 10), then organic layer was extracted with EtOAc (3 x 10 mL). The combined organic extracts were washed with brine (10 mL) and dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure to give a residue. The crude residue was purified by flash silica gel chromatography (15-20% EtOAc/hexane) to afford **2/5**.

(*S*)-*N*-(1-azido-1,1-diphenylpropan-2-yl)-4-methylbenzenesulfonamide (2c)



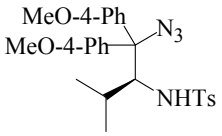
Obtained as a white solid (168 mg, 83%); mp: 137 ^oC; $[\alpha]_D^{25}$= -12.6 (*c* 0.56, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ_H 7.67 (dd, 2H, *J* = 6.7, 1.6 Hz, ArH), 7.39-7.24 (m, 12H, ArH), 4.53 (dd, 1H, *J* = 9.3, 6.5 Hz, CH), 4.25 (d, 1H, *J* = 9.2 Hz, NH), 2.43 (s, 3H, $ArCH_3$), 1.12 (d, 3H, *J* = 6.5 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 143.3, 139.2, 138.6, 138.1, 129.5, 128.41, 128.40, 128.2, 128.1, 128.0, 127.8, 127.0, 75.6, 54.9, 21.5, 18.7; FT-IR: 2106 cm^{-1}; EI-MS: *m/z* (%) 364 $[M-N_3]^+$, 299, 241, 223, 198 (100); ESI-LC/MS: *m/z* 407 $[M+H]^+$.

(*S*)-*N*-(1-azido-3-methyl-1,1-diphenylbutan-2-yl)-4-methylbenzenesulfonamide (2d)



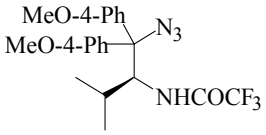
Obtained as a white solid (171 mg, 79%); mp: 139 °C; $[\alpha]_D^{25}$= -8.68 (*c* 0.54, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ_H 7.58 (d, 2H, *J* =1.8 Hz, ArH), 7.35-7.25 (m, 10H, ArH), 7.18 (d, 2H, *J* = 7.8, ArH), 4.48 (d, 1H, *J* =10.0 Hz, CHN), 4.30 (d, 1H, *J* = 10.2 Hz, NHTs), 2.38 (s, 3H, Ar CH_3), 2.08-2.03 (m, 1H, $CHCH_3$), 1.06 (d, 3H, *J* = 6.2 Hz, CH_3CH), 0.42 (d, 3H, *J* = 6.1 Hz, CH_3CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 143.0, 139.9, 139.2, 139.0, 129.4, 128.6, 128.6, 128.3, 128.2, 127.8, 126.9, 63.4, 31.0, 28.7, 23.0, 21.6, 16.9; FT-IR: 2103 cm^{-1}; EI-MS: *m/z* (%) 392 $[M-N_3]^+$ (0.1), 260, 226 (100); ESI-LC/MS: *m/z* 435 $[M+H]^+$; 433, 405, 224.

(*S*)-*N*-(1-azido-1,1-bis(4-methoxyphenyl)-3-methylbutan-2-yl)-4-methylbenzenesulfonamide (2e)



White solid (173 mg, 70%); mp: 169 °C; $[\alpha]_D^{25}$= -8.22 (*c* 0.52, $CHCl_3$);^1H NMR (300 MHz, $CDCl_3$): δ_H 7.61 (d, 2H, *J* = 8.4 Hz, ArH), 7.26-7.14 (m, 6H, ArH), 6.84-6.78 (m, 4H, ArH), 4.29 (m, 2H, CHNH, NHTs), 3.80 (s, 6H, OMe), 2.39 (s, 3H, $ArCH_3$), 2.06-2.01 (m, 1H, $CHCH_3$), 1.05 (d, 3H, *J* = 6.9 Hz, CH_3CH), 0.39 (d, 3H, *J* = 6.9 Hz, CH_3CH); ^{13}C NMR (75 MHz, $CDCl_3$,): δ_C 159.2, 159.0, 142.7, 138.9, 131.8, 130.9, 129.4, 129.2, 128.9, 126.7, 113.6, 75.9, 63.4, 55.2, 55.1, 28.5, 22.9, 21.4, 16.9; FT-IR (neat): 3307, 2961, 2103 cm^{-1}; EI-MS: *m/z* (%) 452 $[M-N_3]^+$, 408 (6), 296 (100); ESI-LC/MS: *m/z* 495 $[M+H]^+$; 468, 450.

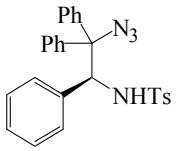
(*S*)-*N*-(1-azido-1,1-bis(4-methoxyphenyl)-3-methylbutan-2-yl)-2,2,2-trifluoroacetamide (2f)



Colorless oil (124 mg, 57%); $[\alpha]_D^{25}$= - 17.7 (*c* 0.65, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ_H 7.28-7.22 (m,

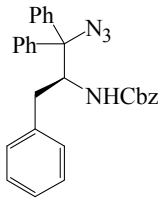
4H, ArH), 6.93-6.86 (m, 4H, ArH), 6.34 (d, 1H, *J* = 10.5 Hz, NHCO), 4.92 (d, 1H, *J* = 10.5 Hz, CHN), 3.79 (s, 3H, OMe), 3.75 (s, 3H, ArOMe), 2.07 (m, 1H, $CHCH_3$), 1.00 (d, 3H, *J* = 6.7 Hz, CH_3CH), 0.61 (d, 3H, *J* = 6.7 Hz, CH_3CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 159, 157.6 (q, *J* = 36.6 Hz, $-CF_3$), 132.3, 131.9, 128.7, 128.6, 121.7, 117.9, 114.4, 114.1, 114.0, 113.9, 75.4, 58.4, 28.7, 23.0, 16.6; FT-IR: 2107 cm^{-1}; EI-MS: *m/z* (%) 394 $[M-N_3]^+$, 351, 321, 268, 239 (100); ESI-LC/MS: *m/z* = 437 $[M+H]^+$ 435, 405, 379, 141.

(*S*)-*N*-(2-azido-1,2,2-triphenylethyl)-4-methylbenzenesulfonamide (2g)



White solid (147 mg, 63%); mp: 193 °C; $[\alpha]_D^{25}$= -25.7 (*c* 0.55, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.38-7.31 (m, 5H, ArH), 7.22-7.13 (m, 8H, ArH), 6.95 (t, 1H, *J* = 7.5 Hz, ArH), 6.86-6.76 (m, 3H, ArH), 6.46 (d, 2H, *J* = 7.5 Hz, ArH), 5.44 (d, 1H, *J* = 9.6 Hz, CHN), 5.08 (dd, 1H, *J* = 2.6, 9.6 Hz, NHTs), 2.23 (s, 3H, $ArCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 142.9, 140.0, 138.9, 137.2, 135.2, 129.0, 128.5, 128.5, 128.2, 128.1, 127.3, 127.2, 127.1, 75.6, 62.5, 21.4; FT-IR (Neat): 3287, 2107 cm^{-1}; EI-MS: *m/z* (%) 426 $[M-N_3]^+$ (0.99), 260 (100); ESI-LC/MS: *m/z* 469 $[M+H]^+$, 467, 439.

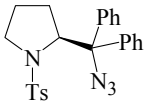
(*S*)-benzyl (1-azido-1,1,3-triphenylpropan-2-yl)carbamate (2h)



Colorless oil (152 mg, 66%); $[\alpha]_D^{25}$= -21.8 (*c* 0.55, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.47-7.10 (m,

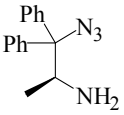
20H, ArH), 5.13-5.05 (m, 1H, CHN), 4.95-4.78 (m, 2H, CbzCH$_2$), 3.31 (dd, 1H, J = 14.1, 2.4 Hz, CH$_2$CH), 2.20-2.16 (m, 1H, CH$_2$CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 155.8, 140.0, 139.7, 137.7, 136.5, 129.3, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 126.6, 76.2, 66.7, 57.5, 38.6; FT-IR: 2103 cm^{-1}; ESI-LC/MS: *m/z* 463 $[M+H]^+$, 462, 461, 252, 171.

(S)-2-(azidodiphenylmethyl)-1-tosylpyrrolidine (2i)



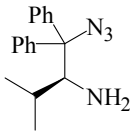
White solid (149 mg, 69%); mp 231 °C, $[\alpha]_D^{25}$= -38.2 (*c* 0.54, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.68 (dd, 2H, J = 1.6, 6.5 Hz, ArH), 7.39-7.24 (m, 12H, ArH), 5.21 (dd, 1H, J = 3.3, 9.0 Hz, CHNTs), 3.45-3.36 (m, 1H, CH$_2$NTs), 2.44 (s, 3H, ArCH$_3$), 2.43-2.34 (m, 1H, CH$_2$NTs), 2.06-1.85 (m, 2H, CH$_2$CH$_2$), 1.38-1.35 (m, 1H, CH$_2$CH$_2$), 1.34-1.29 (m, 1H, CH$_2$CH$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 143.4, 140.3, 139.5, 137.1, 129.6, 129.3, 128.8, 128.4, 128.3, 128.1, 128.0, 127.5, 76.2, 65.7, 49.4, 29.0, 24.2, 21.7; FT-IR (neat): 3336, 2990, 2106 cm^{-1}; FAB-MS: *m/z* 433 $[M+H]^+$, 390, 224.

(*S*)-2-Azido-2,2-diphenyl-1-methyl-1-aminoethane (5a)



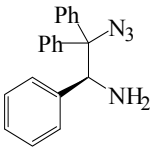
Colorless oil (94.5 mg, 75%); $[\alpha]_D^{23}$= -25.7 (*c* 0.56, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.43-7.23 (m, 10H, ArH), 4.04 (q, 1H, J = 6.5 Hz, CHNH), 1.25 (brs, 2H, NH$_2$), 1.03 (d, 3H, J = 6.5 Hz, CH$_3$CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 140.2, 140.1, 128.4, 128.2, 128.0, 127.9, 127.8, 127.6, 77.2, 52.9, 18.6; FT-IR: 3159, 2927, 2103 cm^{-1}; FAB-MS *m/z* 253 $[M+H]^+$, 210, 194, 182, 132, 105.

(*S*)-1-azido-3-methyl-1,1-diphenylbutan-2-amine (5b)



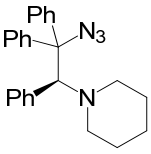
Semi-solid (103 mg, 74%); $[\alpha]_D^{20}$= -90.2 (*c* 0.49, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.47-7.24 (m, 10H, ArH), 3.78 (s, 1H, CHNH), 1.84-1.77 (m, 1H, CHCH$_3$), 1.20 (brs, 2H, NH$_2$), 1.01 (d, 3H, *J* = 6.9 Hz, CH$_3$CH), 0.58 (d, 3H, *J* = 6.9 Hz, CH$_3$CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 141.6, 141.2, 128.6, 128.5, 128.0, 127.7, 127.5, 127.4, 76.9, 61.6, 27.9, 23.5, 15.7; FT-IR: 3167, 2104 cm^{-1}; EI-HRMS calc. for $C_{17}H_{20}N_4$ $[M]^+$ 280.1688, found 280.1695.

(*S*)-2-azido-1,2,2-triphenylethanamine (5c)



Colorless oil (122 mg, 78%); ^{1}H NMR (300 MHz, $CDCl_3$): $[\alpha]_D^{25}$= -86^0 (c, 0.545, $CHCl_3$); δ_H 7.44-7.32 (m, 5H, ArH), 7.18-7.06 (m, 8H, ArH), 6.95-6.91 (m, 2H, ArH), 5.04 (s, 1H, CHNH), 1.71 (brs, 2H, NH$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 141.2, 140.4, 139.7, 128.8, 128.7, 128.3, 127.9, 127.6, 127.5, 127.4, 127.3, 76.5, 62.8; FT-IR: 2104 cm^{-1}; FAB-MS *m/z* 315 $[M+H]^+$, 298, 272, 210, 180, 167, 106.

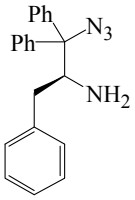
(*S*)-1-(2-azido-1,2,2-triphenylethyl)piperidine (5d)



White solid (138.8 mg, 72.6%); mp:128.5-129.5; $[\alpha]_D^{25}$= -13.8 (*c* 1.33, $CHCl_3$); ^{1}H NMR (300 MHz,

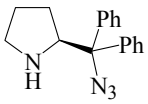
$CDCl_3$): δ_H 7.64 (d, *J* = 6.9 Hz, 2H, ArH), 7.41-7.24 (m, 7H, ArH), 7.19-7.03 (m, 6H, ArH), 4.63 (s, 1H, CHN), 2.85 (pent, *J* = 5.8 Hz, 2H, CH_2N), 2.28 (brs, 2H, CH_2N), 1.64-1.58 (m, 4H, CH_2CH_2), 1.33 (pent, 2H, *J* = 5.5 Hz, CH_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 143.2, 134.9, 130.8, 128.7, 127.9, 127.6, 127.5, 127.3, 127.1, 126.5, 76.2, 75.7, 54.0, 26.6, 24.0; FT-IR: 3167, 2104 cm^{-1}; FABMS: *m/z* 382 $[M+H]^+$.

(*S*)-1-azido-1,1,3-triphenylpropan-2-amine (5e)



White solid (123 mg, 75%); mp: 123 °C; $[\alpha]_D^{25}$= -50.8 (*c* 0.51, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$): δ_H 7.38-7.02 (m, 15H, ArH), 3.98-3.94 (m, 1H, CHNH), 2.79 (d, 1H, *J* = 15.5 Hz, CH_2CH), 2.04-1.96 (m, 1H, CH_2CH), 1.05 (brs, 2H, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 140.9, 140.3, 139.7, 129.3, 128.6, 128.6, 128.6, 128.1, 127.8, 127.7, 127.6, 126.6, 76.4. FT-IR: 2104 cm^{-1}; EI-HRMS calc. for $C_{21}H_{20}N_4$ $[M]^+$ 328.1688, found 328.1682.

(*S*)-2-(azidodiphenylmethyl)pyrrolidine[1] (5f)



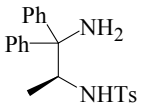
For azidation of **4f**, $CHCl_3$ was used as a solvent because of the solubility problem, and **5f** (106 mg, 76%) was obtained as light yellow liquid; $[\alpha]_D^{25}$ = - 92.90 (*c* 2.0, $CHCl_3$.); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.49-7.45 (m, 2H, ArH), 7.38-7.20 (m, 8H, ArH), 4.31 (t, *J* = 7.2 Hz, 1H, CHNH), 2.96-2.92 (m, 2H, CH_2N), 1.88 (s, 1H, NH), 1.72-1.58 (m, 4H, CH_2CH_2, CH_2CH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 142.6, 142.2, 128.5, 128.1, 127.9, 127.5, 127.1, 127.0, 75.2, 65.3, 47.2, 28.0, 26.0 ppm; FT-IR: 2109 cm^{-1} FABMS: *m/z* 279

$[M+H]^+$; EI-HRMS calc. for $C_{17}H_{18}N_4$ $[M]^+$ 278.1531, found 278.1527

General Procedure for the reduction of 2/5.

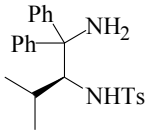
To a solution of **2/5** (~150 mg) in a mixture of EtOH/EtOAc (2:1, 9 mL) was added 10% Pd/C (15 mg) under argon atmosphere. Then the flask was fit tightly over with a balloon filled with hydrogen gas. The mixture stirred at room temperature for 2h. The reaction mixture was filtered through a pad of Celite and the solvents were evaporated under reduced pressure to give a residue. The crude residue was purified by flash silica gel chromatography (15-30% EtOAc/hexane for **3** or 5-15% MeOH/$CHCl_3$ for **6**) to afford the desired product.

(*S*)-*N*-(1-amino-1,1-diphenylpropan-2-yl)-4-methylbenzenesulfonamide (3c)



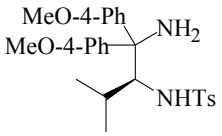
White solid (143 mg, 75%); mp 145 ^oC; $[\alpha]_D^{25}$= - 43.0 (*c* 0.54, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ_H 7.52 (d, 2H, *J* = 8.4 Hz, ArH), 7.33-7.12 (m, 12H, ArH), 4.89 (d, 1H, *J* = 7.5 Hz, NHTs), 4.29-4.25 (m, 1H, CHCH$_3$), 2.39 (s, 3H, Ar CH$_3$), 1.78 (brs, 2H, NH$_2$), 1.09 (d, 3H, *J* = 6.6 Hz, CH$_3$CH); ^{13}C NMR (75 MHz, $CDCl_3$,): δ_C 145.2, 145.1, 143.0, 138.1, 129.6, 128.4, 128.3, 127.06, 127.02, 126.8, 126.6, 64.3, 55.7, 21.8, 18.1; FT-IR: 3321, 3129 cm^{-1}; ESI-LCMS: *m/z* 381 $[M+H]^+$, 380, 365, 364.

(*S*)-*N*-(1-amino-3-methyl-1,1-diphenylbutan-2-yl)-4-methylbenzenesulfonamide (3d)



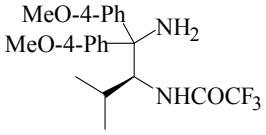
White solid (167 mg, 82%); mp 106 °C; $[\alpha]_D^{25}$= +72.4 (*c* 0.63, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ_H 7.44 (d, 2H, *J* = 8.1 Hz, ArH), 7.39-7.27 (m, 8H, ArH), 7.26-7.10 (m, 4H, ArH), 5.03 (d, 1H, *J* = 8 Hz, NHTs), 4.10 (d, 1H, *J* = 8 Hz, CHCH), 2.37 (s, 3H, $ArCH_3$), 1.95-1.93 (m, 3H, $CHCH_3$, NH_2), 0.94 (d, 3H, *J* = 6 Hz, CH_3CH), 0.64 (d, 3H, *J* = 6 Hz, CH_3CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 146.2, 145.5, 142.5, 138.9, 129.4, 128.2, 128.0, 126.8, 126.8, 126.7, 126.5, 126.5, 115.7, 66.4, 64.5, 29.1, 23.5, 21.5, 18.2; FT-IR (neat): 3323, 3129 cm^{-1}; EI-HRMS calc. for $C_{24}H_{28}N_2O_2S$ $[M]^+$ 408.1871, found 408.1865.

(*S*)-*N*-(1-amino-1,1-bis(4-methoxyphenyl)-3-methylbutan-2-yl)-4-methylbenzenesulfonamide (3e)



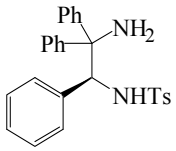
White solid (173 mg, 74%); mp 173 °C; $[\alpha]_D^{25}$= +93.1 (*c* 0.51, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ_H 7.45 (d, 2H, *J* = 8.4 Hz, ArH), 7.27 (d, 2H, *J* = 6.3 Hz, ArH), 7.13-7.09 (m, 4H, ArH), 6.85 (d, 2H, *J* = 8.4 Hz, ArH), 6.59 (d, 2H, *J* = 8.4 Hz, ArH), 4.98 (d, 1H, *J* = 9.0 Hz, NHTs), 4.07 (d, 1H, *J* = 9.0 Hz, CHCH), 3.79 (s, 3H, OMe), 3.73 (s, 3H, OMe), 2.37 (s, 3H, $ArCH_3$), 1.99-1.88 (m, 3H, $CHCH_3$, NH_2), 0.97 (d, 3H, *J* = 6.0 Hz, CH_3CH), 0.67 (d, 3H, *J* = 6.1 Hz, CH_3CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 158.2, 142.2, 138.8, 138, 137.6, 129.8, 129.1, 128.6, 128.1, 128.0, 127.8, 127.6, 127.5, 127.0, 126.9, 126.6, 113.4, 113.1, 69.0, 65.5, 64.6, 55.1, 49.7, 29.0, 23.3, 21.5; FT-IR: 3331, 2941 cm^{-1}; EI-HRMS calc. for $C_{26}H_{32}N_2O_4S$ $[M]^+$ 468.2083, found 468.2081.

(*S*)-*N*-(1-amino-1,1-bis(4-methoxyphenyl)-3-methylbutan-2-yl)-2,2,2-trifluoroacetamide (3f)



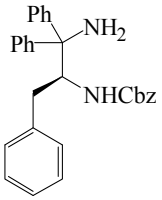
To a solution of **2d** (150 mg, 0.34 mmol) in a mixture of EtOH/EtOAc (2:1, 9 mL) was added Pt_2O (15 mg), and then the mixture was hydrogenated for 2h under 50 psi using Parr hydrogenation apparatus. The reaction mixture was filtered through a pad of Celite and the solvents were evaporated under reduced pressure to give a residue. The crude residue was purified by flash silica gel chromatography (30% EtOAc/hexane) to afford **3d** (126 mg, 90%) as a colorless oil; $[\alpha]_D^{25}$= -38.2 (*c* 0.55, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.31 (dd, 2H, *J* = 3.0, 5.2 Hz, ArH), 7.18 (dd, 2H *J* = 2.1, 6.8 Hz, ArH), 6.89 (dd, 2H, *J* = 3.1, 5.1 Hz, ArH), 6.77 (dd, 2H, *J* =2.3, 6.8 Hz, ArH), 4.71 (dd, 1H, *J* = 1.9, 9.6 Hz, CHNH), 3.80 (s, 3H, OMe), 3.73 (s, 3H, OMe), 2.02-1.94 (m, 3H, $CHCH_3$, NH_2), 0.96 (d, 3H, *J* = 6.9 Hz, CH_3CH), 0.81(d, 3H, *J* = 6.9 Hz, CH_3CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 158.5, 158.4, 157.1 (q, *J* = 36.6, $-CF_3$), 138.4, 137.7, 127.9, 113.9, 113.8, 64.7, 58.8, 55.4, 55.3, 29.2, 23.6, 17.8; FT-IR: 3336, 3234 cm^{-1}; EI-HRMS calc. for $C_{21}H_{25}F_3N_2O_3$ $[M]^+$ 410.1837, found 410.1838.

(*S*)- N^2-Tosyl-1,1,2-triphenylethane-1,2-diamine (3g)



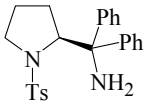
White solid (179 mg, 81%); mp: 212 °C; $[\alpha]_D^{25}$= -13.9 (*c* 0.51, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.52 (d, 2H, *J* = 6.6 Hz, ArH), 7.36-7.23 (m, 7H, ArH), 7.11-7.05 (m, 2H, ArH), 6.98-6.87 (m, 4H, ArH), 6.83-6.74 (m, 2H, ArH), 6.54 (d, 2H, *J* = 7.5 Hz, ArH), 5.77 (d, 1H, *J* = 7.5 Hz, NHTs), 5.40 (d, 1H, *J* = 7.5 Hz, CHNH), 2.27 (s, 3H, $ArCH_3$), 1.94 (brs, 2H, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 145.6, 144.5, 142.5, 137.8, 135.7, 128.9, 128.8, 128.6, 127.9, 127.6, 127.2, 127.1, 127, 126.8, 126.7, 64.9, 62.8, 21.3; FT-IR (neat): 3103, 2931 cm^{-1}; EI-HRMS calc. for $C_{27}H_{26}N_2O_2S$ $[M]^+$ 442.1715, found 442.1738.

(*S*)- N^2-Benzyloxycarbonyl-1,1,3-triphenylpropane-1,2-diamine (3h)



A solution of **2h** (158 mg, 0.34 mmol) in THF (8 mL) was added to a well stirred suspension of LAH (16 mg, 0.42 mmol) in THF (2 mL), and then the mixture was stirred for 30 min at room temperature. Ethyl acetate (2 mL) was carefully introduced to consume the excess reagent and the reaction was quenched with ice-cold water (5 mL). The solution was extracted with EtOAc (3 x 10 mL) and the combined organic layer was washed with brine, dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give a residue. The crude residue was purified by flash silica gel chromatography (15% EtOAc/hexane) to afford **3h** (101 mg, 68%) as a white solid; mp: 129 ^oC; $[\alpha]_D^{21}$= -10.8 (*c* 0.25, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$): δ_H 7.50-7.09 (m, 20H, ArH), 5.19 (d, 1H, *J* = 10.1 Hz, NHCO), 4.97-4.79 (m, 3H, CHNH, $ArCH_2O$), 2.93 (dd, 1H, *J* = 1.9, 13.8 Hz, CH_2CH), 2.39-2.32 (m, 1H, CH_2CH), 1.84 (brs, 2H, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 156, 146.5, 145.8, 138.6, 136.9, 129.3, 128.5, 128.4, 128.3, 128.3, 127.9, 126.9, 126.8, 126.7, 126.4, 66.3, 65.1, 58.2, 37.9; FT-IR: 2104 cm^{-1}; EI-HRMS calc. for $C_{29}H_{28}N_2O_2[M]^+$ 436.2151, found 436.2155.

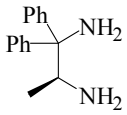
(*S*)-diphenyl (1-tosylpyrrolidin-2-yl)methanamine (3i)



White solid (169 mg, 83%); mp 150 ^oC; $[\alpha]_D^{25}$= -90.1 (*c* 0.49, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.75 (d, 2H, *J* = 8.4 Hz, ArH), 7.38-7.21 (m, 12H, ArH), 4.82 (dd, 1H, *J* = 2.6, 8.9 Hz, CHNH), 3.31-3.22 (m, 1H, CH_2NTs), 2.52-2.04 (m, 1H, CH_2NTs), 2.44 (s, 3H, $ArCH_3$), 1.86 (brs, 2H, NH_2), 1.81-1.65 (m, 2H, CH_2CH_2), 1.25-1.05 (m, 1H, CH_2CH_2), 0.63-0.54 (m, 1H, CH_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 146.7, 144.3, 143.6, 135.4, 129.7, 128.6, 128, 127.6, 127.4, 126.9, 126.8, 69.2, 64.4, 49.7, 28.9, 23.4, 21.5; FT-IR:

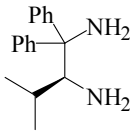
3345, 2957 cm^{-1}; EI-HRMS calc. for $C_{24}H_{26}N_2O_2S$ $[M]^+$ 406.1715, found 406.1711;

(*S*)-1,1-diphenylpropane-1,2-diamine[2] (6a)



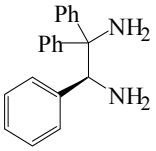
obtained as white solid (93.8 mg, 83%); $[\alpha]_D^{27}$ = +12.21 (*c* 1.05, $CHCl_3$); lit.[2] $[\alpha]_D^{27}$ +12.8 (*c* 1.05, $CHCl_3$); mp: 126.5-127.5 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.73 (dd, *J* = 1.3, 8.5 Hz, 2H, ArH), 7.48 (dd, *J* = 1.3, 8.6 Hz, 2H, ArH), 7.32-7.26 (m, 4H, ArH), 7.20-7.15 (m, 2H, ArH), 4.05 (q, *J* = 6.3 Hz, 1H, CHNH), 1.52 (brs, 4H, NH_2), 1.00 (d, *J* = 6.3 Hz, 3H, CH_3CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 147.3, 146.6, 128.5, 128.2, 126.8, 126.7, 126.5,126.4 64.5, 52.3, 18.0 ppm; IR (KBr): 3465, 3336, 3270, 3057, 2975, 2935, 1966, 1594, 1490, 1443 cm^{-1}; FABMS: *m/z* 227 $[M+H]^+$; EI-HRMS calc. for $C_{15}H_{18}N_2$ $[M]^+$ 226.1470, found 227.1474; Anal.Calc. for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found C, 75.64; H, 7.65; N, 11.51.

(*S*)-3-methyl-1,1-diphenylbutane-1,2-diamine (6b)



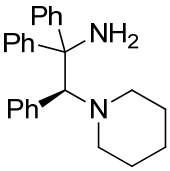
White solid (105 mg, 83%); mp 87 ^{o}C; $[\alpha]_D^{25}$= +13.3 (*c* 0.47, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.50-7.43 (m, 4H, ArH), 7.29-7.23 (m, 4H, ArH), 7.20-7.13 (m, 2H, ArH), 3.67 (d, 1H, *J* = 0.5 Hz, CHNH), 1.92-1.81 (m, 1H, $CHCH_3$), 1.57 (brs, 4H, NH_2), 0.98 (d, 3H, *J* = 6.9 Hz, CH_3CH), 0.74 (d, 3H, *J* = 6.9 Hz, CH_3CH); ^{13}C NMR (75 MHZ, $CDCl_3$): δ_C 147.9, 147.2, 128.4, 128.3, 128.2, 127.5, 127.5, 126.7, 126.3, 65.8, 60.8, 28.0, 24.1, 17.1; FT-IR: 3334, 2932 cm^{-1} ESI-LC/MS *m/z* 255 $[M+H]^+$, 239, 238, 237.

(*S*)-1,1,2-triphenylethane-1,2-diamine (6c)



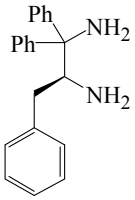
obtained as colourles oil (102.6 mg, 71.3%); $[\alpha]_D^{25} = -120.6$ (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ_H 7.73 (dd, *J* = 1.2, 7.7 Hz, 2H, ArH), 7.43-7.38 (m, 2H, ArH), 7.31-7.11 (m, 9H, ArH), 7.06-7.03 (dd, *J* = 1.4, 7.6 Hz, 2H, ArH), 5.11(s, 1H, CHN), 1.87(brs, 4H, NH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 146.1, 145.8, 140.8, 128.8, 128.3 127.7, 127.4, 127.2, 126.8, 126.2, 65.1, 62.0 ppm; FT-IR: 3341, 3251 cm^{-1}; FABMS: *m/z* 289 $[M+H]^+$; EI-HRMS calc. for $C_{20}H_{20}N_2$ $[M]^+$ 288.1626, found 288.1635

(*S*)-1,1,2-triphenyl-2-(piperidin-1-yl)ethanamine (6d)



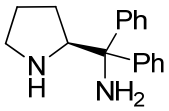
obtained as white solid (110.2 mg, 61.8%); $[\alpha]_D^{25} = +46.6$ (*c* 1.0, $CHCl_3$); mp: 141.5-142.5 ^0C; ^1H NMR (300 MHz, $CDCl_3$): δ_H 7.59 (d, *J* = 7.9 Hz, 1H, ArH), 7.56 (d, *J* = 7.9 Hz, 1H, ArH), 7.28-7.23 (m, 7H, ArH), 7.17-7.00 (m, 6H, ArH), 4.43 (s, 1H, CHAr), 2.53 (q, *J* = 7.9 Hz, 2H, CH_2N), 2.26 (brs, 2H, NH_2), 2.03-1.93 (m, 2H, CH_2N), 1.47-1.39 (m. 4H, CH_2CH_2, CH_2CH_2), 1.30-1.21 (m, 2H, CH_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 149.9, 147.0, 138.3, 131.1, 127.8, 127.6, 127.5, 127.4, 126.5, 126.1, 125.9, 77.3, 65.3, 54.9, 27.1, 24.6 ppm; IR (KBr, cm^{-1}): 3367, 3303, 3082, 3058, 2931, 2849, 2788, 1952, 1492, 1467; FABMS: *m/z* 357 $[M+H]^+$; EI-HRMS calc. for $C_{25}H_{28}N_2$ $[M]^+$ 356.2252, found 356.2242; Anal.Calcd for $C_{25}H_{28}N_2$: C, 84.23; H, 7.92; N, 7.86. Found C, 83.51; H, 7.59; N, 7.52.

(*S*)-1,1,3-triphenylpropane-1,2-diamine[3] (6e)



White solid (127 mg, 84%); mp: 139 ^{o}C; ; $[\alpha]_D^{22}$= -10.8 (*c* 0.25, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.63-7.57 (m, 5H, ArH), 7.37-7.15 (m, 10H, ArH), 4.16-4.09 (m, 1H, CHN), 2.85 (dd, 1H, *J* = 1.5, 12 Hz, CH_2CH), 2.34-2.26 (m, 1H, CH_2CH), 1.65 (brs, 4H, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 147.1, 146.3, 140.4, 129.2, 128.7, 128.5, 128.5, 126.5, 126.4, 64.2, 59.1, 38.2; FT-IR: 3449, 3344, 3296, 1598, 1492 cm^{-1}; ESI-LC/MS *m/z* 303 $[M+H]^+$, 287, 286, 285.

(*S*)-diphenyl(pyrrolidin-2-yl)methanamine[4] (6f)



To a solution of **5f** (100 mg, 0.35 mmol) in toluene (5 mL) was added triphenylphosphine (364 mg, 1.38 mmol). The reaction mixture was stirred at 60 ^{o}C for 2 h. Then H_2O (2 mL) was added and the mixture was stirred at room temperature for 30 min. The reaction mixture was extracted with EtOAc (3 x 5 mL) and the combined organic layer was washed with brine, dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give a residue. The crude residue was purified by flash silica gel chromatography (10% MeOH/$CHCl_3$) to afford **6f** (65 mg, 73%) as light brown liquid; $[\alpha]_D^{25}$ = -35.43 (*C* = 1.5, $CHCl_3$.); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.58 (d, 2H, *J* = 7.4 Hz, NH_2), 7.37-7.21 (m, 10H, ArH), 4.68 (dd, *J* = 3.7, 7.4 Hz, 1H, CHN), 3.11 (m, 1H, CH_2N), 2.91 (m, 1H, CH_2N), 1.87-1.77 (m, 4H, $CH_2CH_2CH_2CH$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ_C 145.4, 144.7, 128.9, 128.5, 127.2, 127.1, 126.7, 125.9, 65.0, 62.4, 47.0, 27.3, 24.6 ppm; IR (KBr): 3441, 3250, 2961, 2924, 2806, 1960, 1647, 1491, 1448, 1389 cm^{-1}; FABMS: *m/z* 253 $[M+H]^+$; EI-HRMS calc. for $C_{17}H_{20}N_2$ $[M]^+$ 252.1626, found 252.1625.

References

1. Shi, Z.; Tan, B.; Leong, W. W. Y.; Zeng, X.; Lu, M.; Zhong, G. *Org. Lett.* **2010**, *12*, 5401.

2. Kohmura, Y.; Mase, T. *J. Org. Chem*. **2004**, *69*, 6329.

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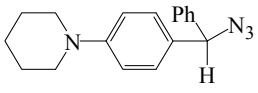
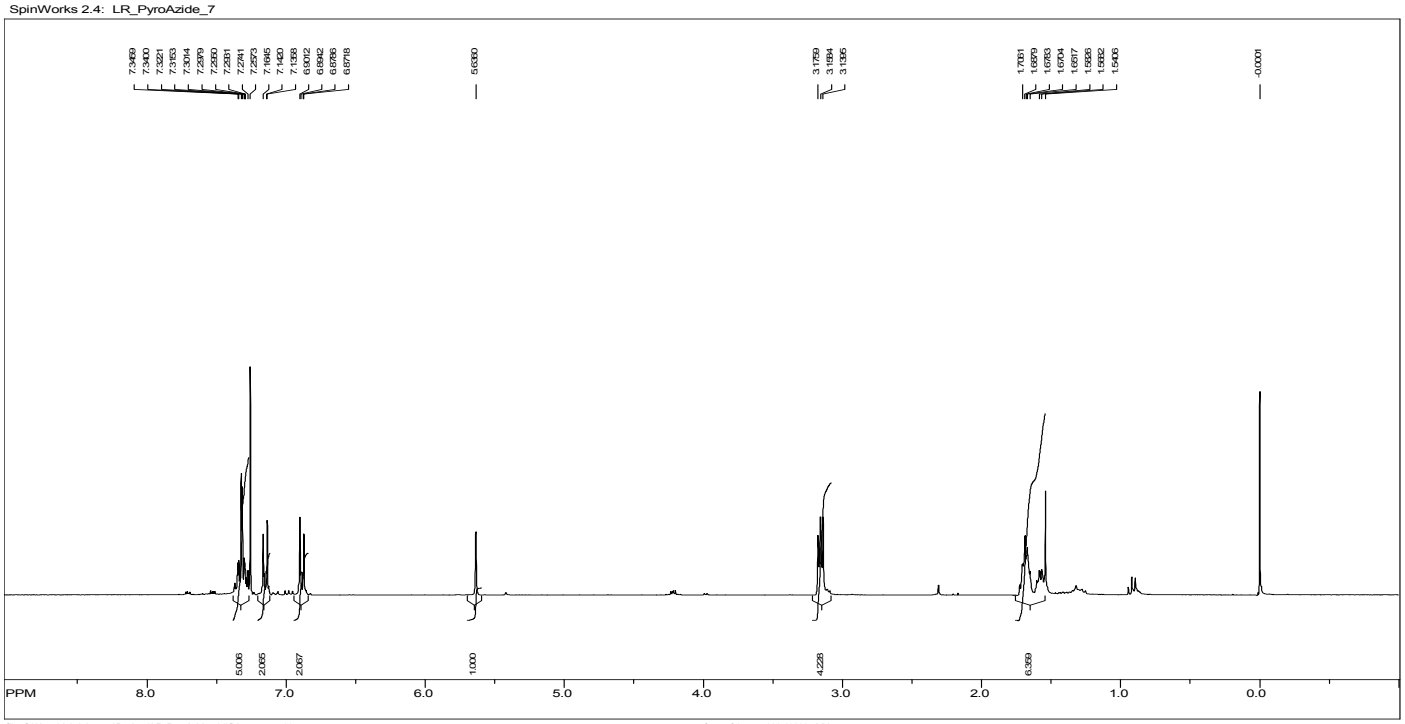
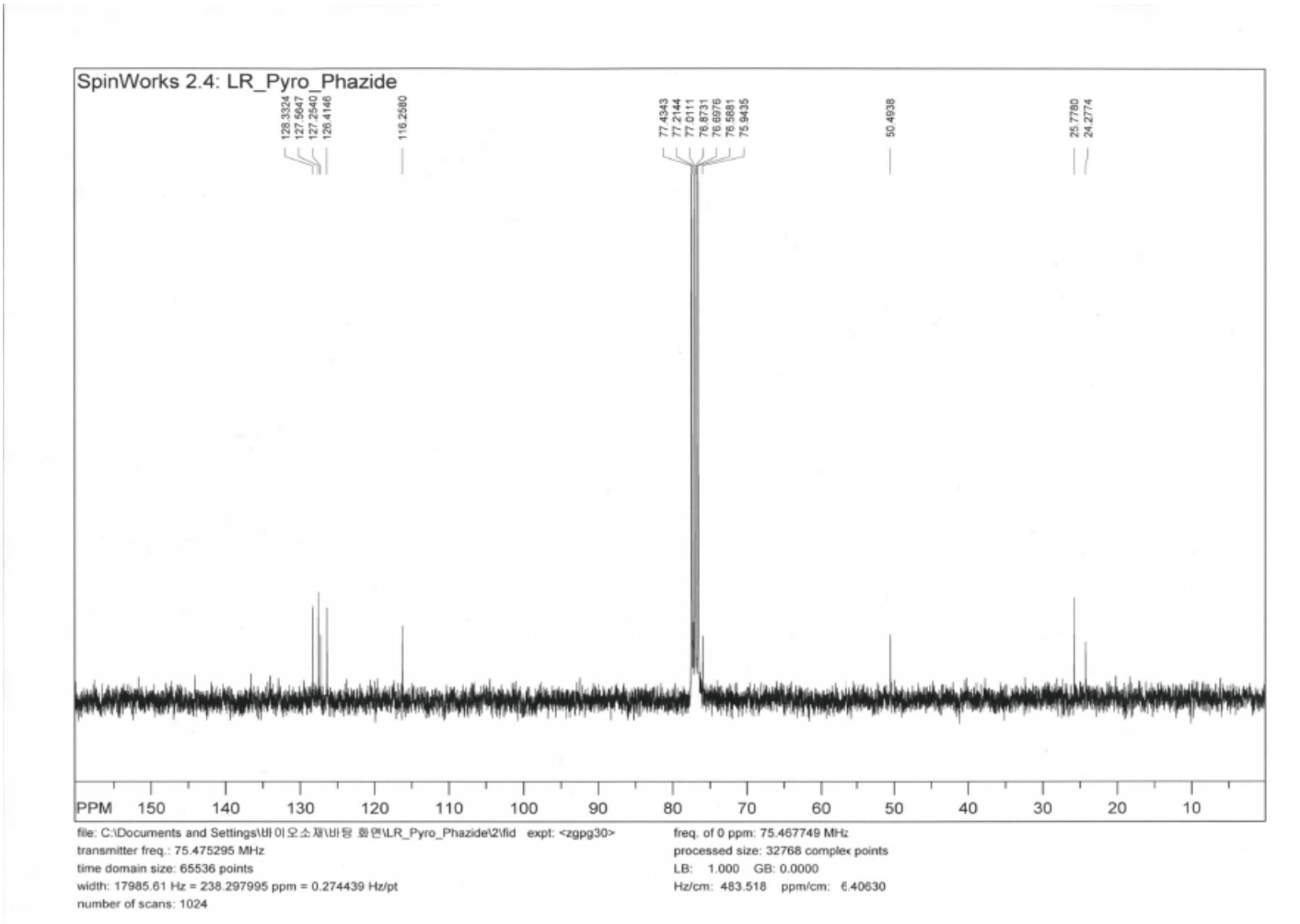
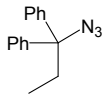
4. Olivares-Romero, J. L.; Juaristi, E. *Tetrahedron* **2008**, *64*, 9992.


Ph
N3
N
H

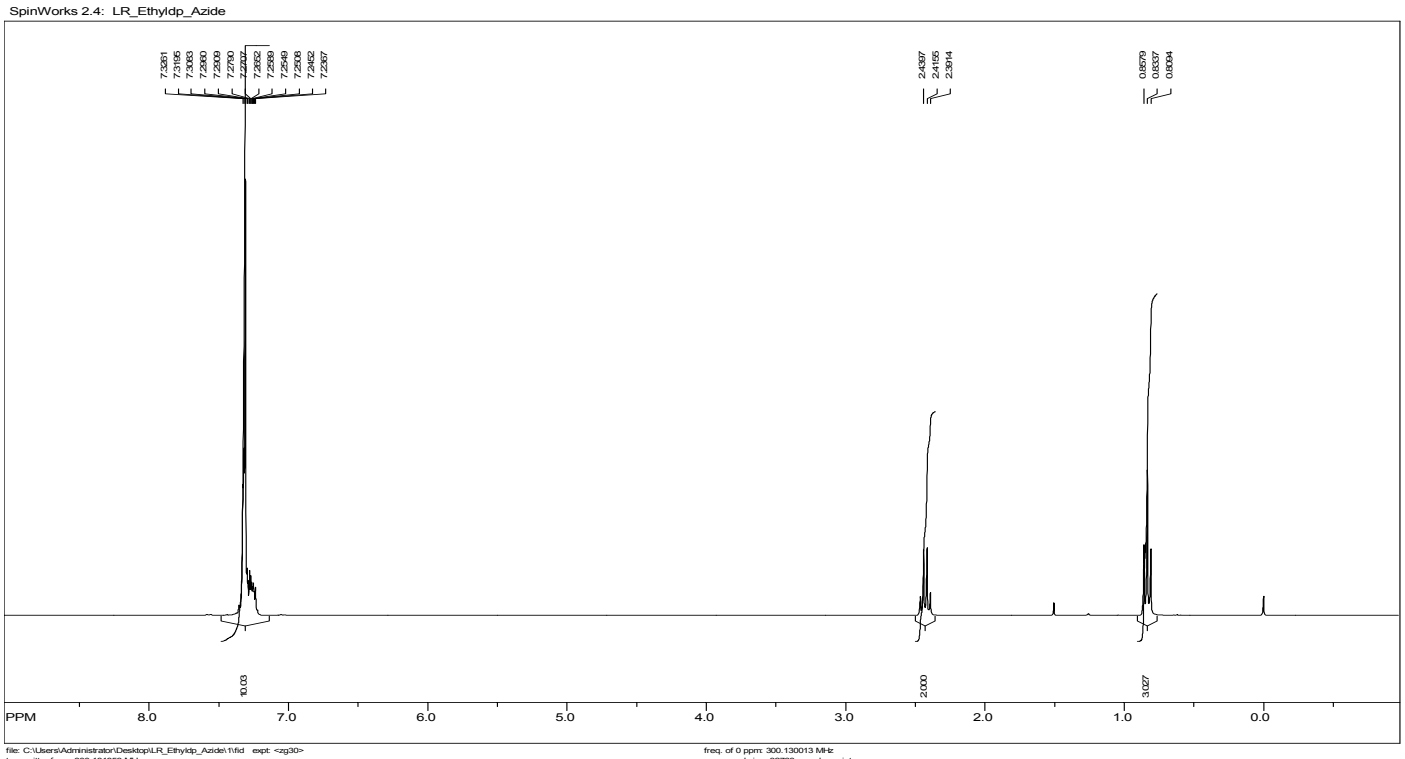
(2a)


SpinWorks 2.4: LR_PyroAzide_7
7.3469
7.3400
7.3221
7.3153
7.3014
7.2899
7.2830
7.2351
7.2241
7.2073
7.1945
7.1400
7.1338
6.9012
6.8942
6.8796
6.8718
5.6300
3.1759
3.1694
3.1535
1.7061
1.6979
1.6783
1.6704
1.6617
1.5926
1.5932
1.5406
-0.0001
5.006
2.095
2.007
1.000
4.228
6.359
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
file: C:\Users\Administrator\Desktop\LR_PyroAzide_7\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16
freq. of 0 ppm: 300.130007 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000


SpinWorks 2.4: LR_Pyro_Phazide
128.3324
127.5647
127.2540
126.4146
116.2580
77.4343
77.2144
77.0111
76.8731
76.6976
76.5681
75.9435
50.4938
25.7780
24.2774
PPM
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
file: C:\Documents and Settings\바이오소재\바탕 화면\LR_Pyro_Phazide\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 483.518 ppm/cm: 6.40630


Ph
N3
Ph

(2b)


SpinWorks 2.4: LR_Ethyldp_Azide
7.3261
7.3195
7.3083
7.2980
7.2909
7.2790
7.2707
7.2652
7.2589
7.2549
7.2508
7.2462
7.2397
2.4387
2.4155
2.3914
0.8579
0.8337
0.8094
10.03
2.000
3.027
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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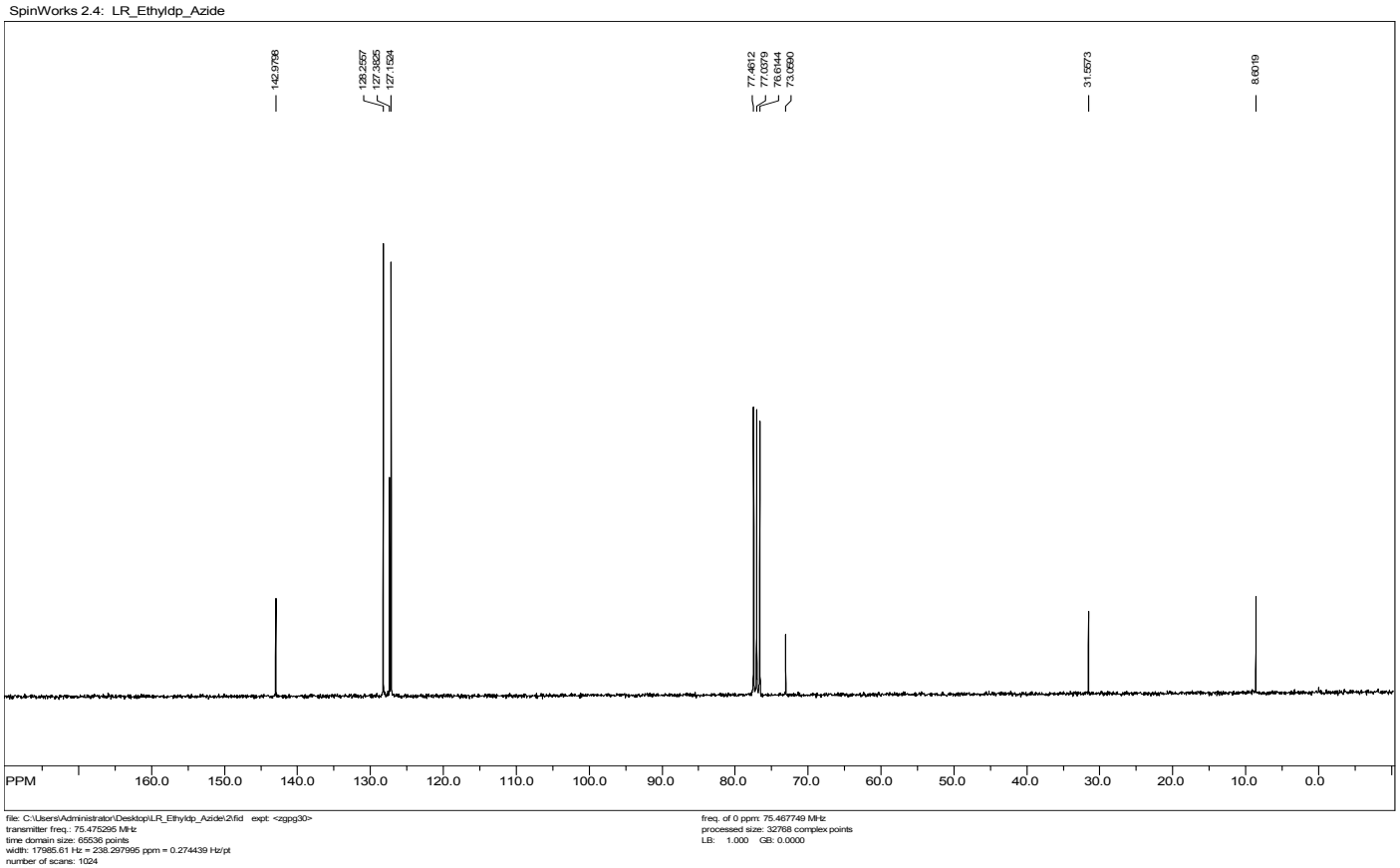
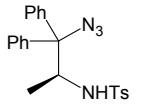
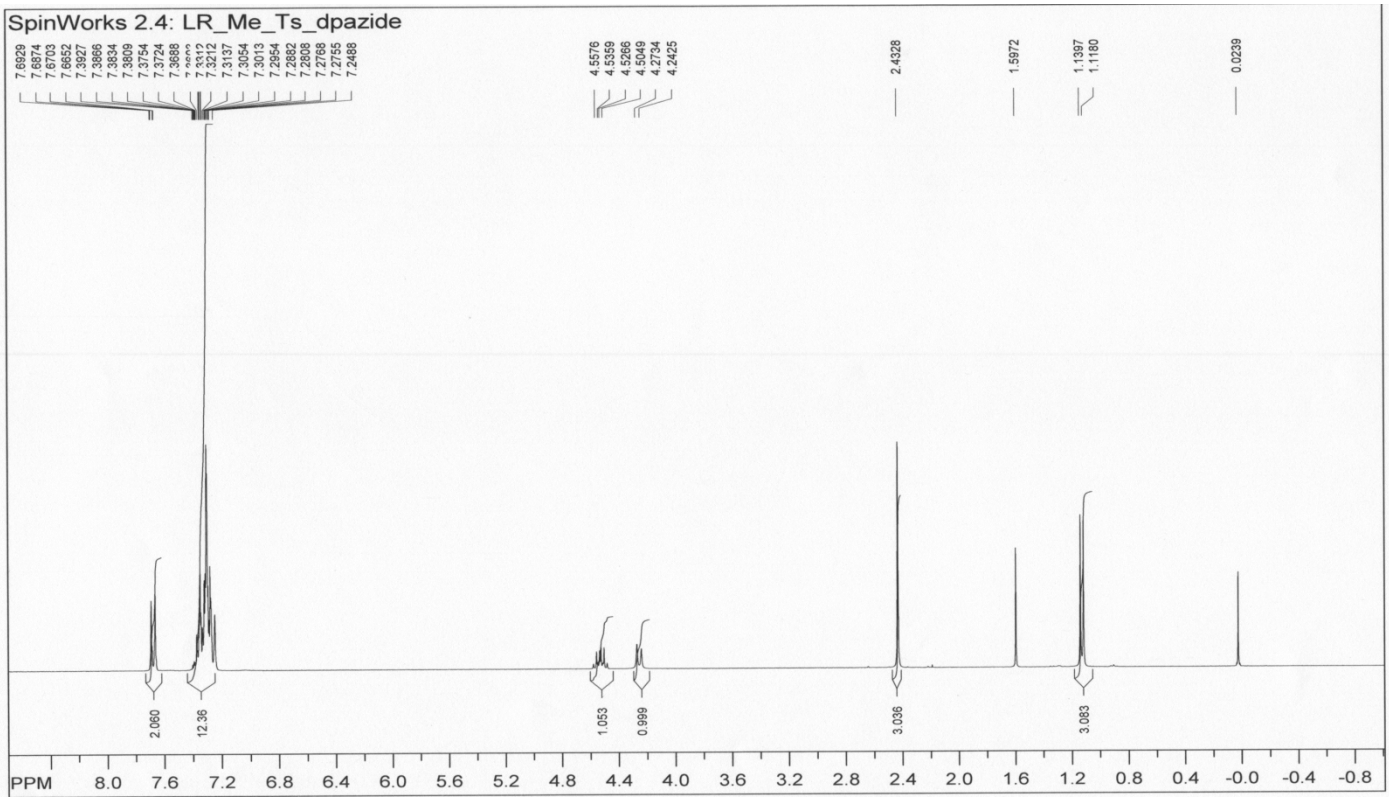
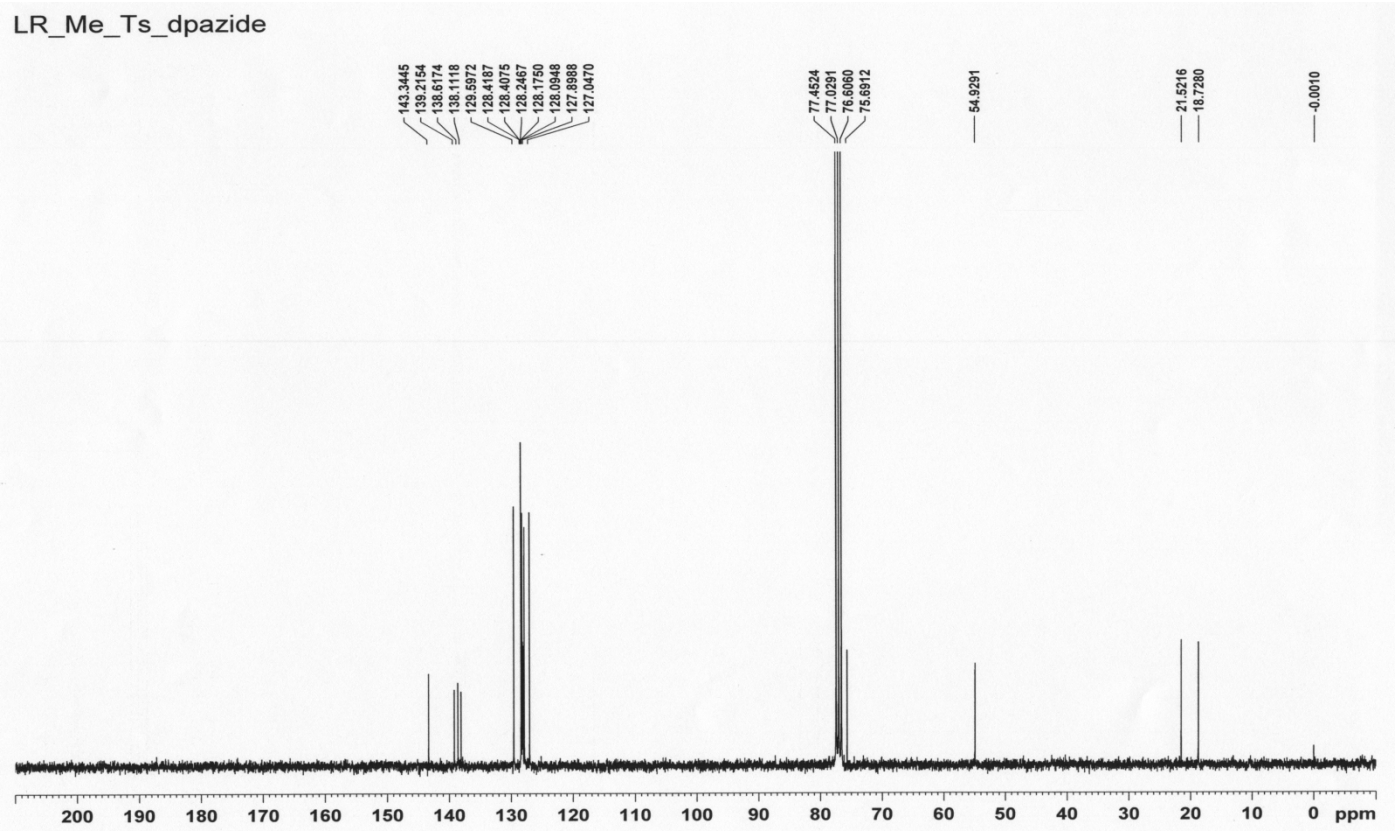
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16
freq. of 0 ppm: 300.130013 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

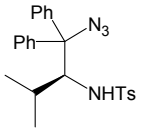

SpinWorks 2.4: LR_Ethyldp_Azide
142.9796
128.2557
127.3925
127.1524
77.4612
77.0379
76.6144
73.0590
31.5573
8.6019
PPM
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
file: C:\Users\Administrator\Desktop\LR_Ethyldp_Azide\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000


Ph
N3
Ph
NHTs

(2c)

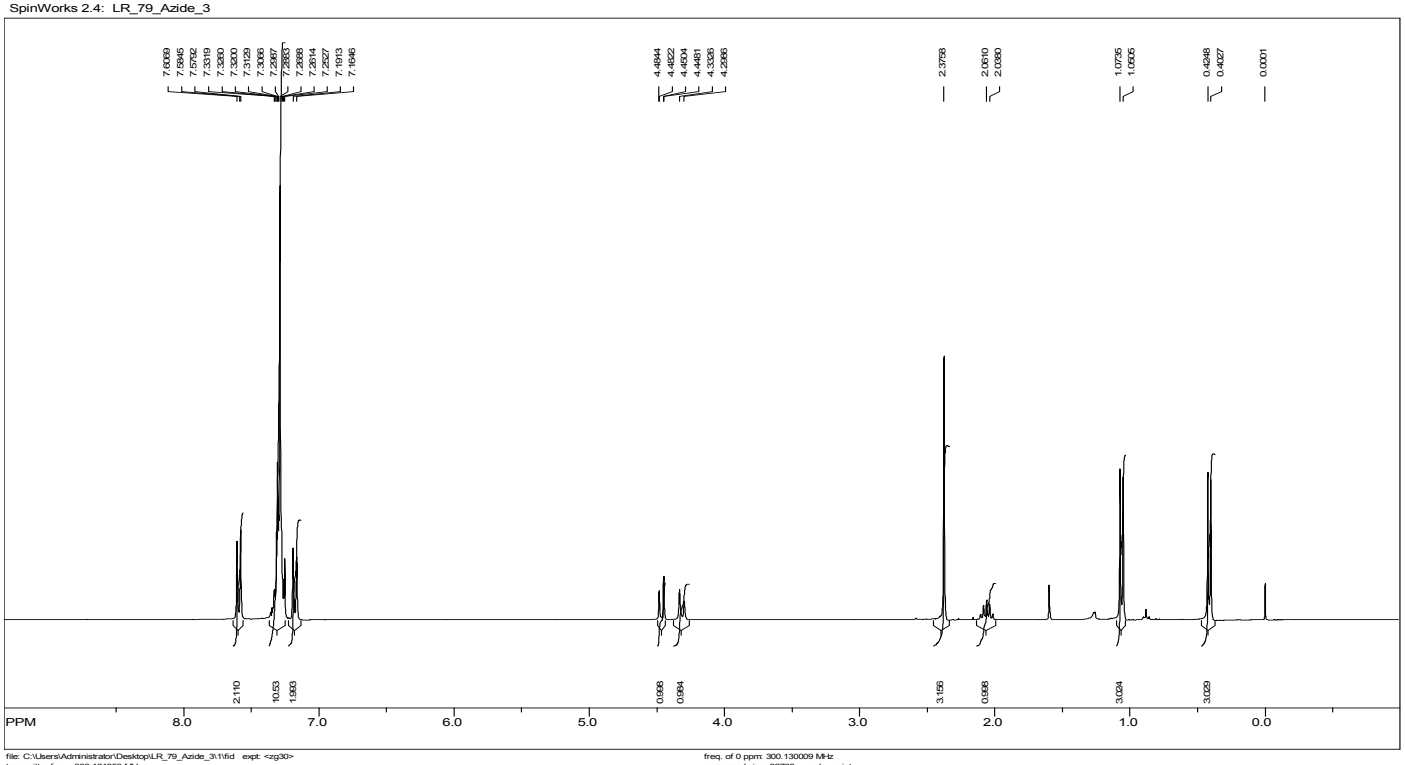

SpinWorks 2.4: LR_Me_Ts_dpazide
7.6929
7.6874
7.6703
7.6652
7.3927
7.3866
7.3834
7.3809
7.3754
7.3724
7.3688
7.3312
7.3212
7.3137
7.3054
7.3013
7.2954
7.2882
7.2808
7.2768
7.2755
7.2488
4.5576
4.5359
4.5266
4.5049
4.2734
4.2425
2.4328
1.5972
1.1397
1.1180
0.0239
2.060
12.36
1.053
0.999
3.036
3.083
PPM
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
-0.0
-0.4
-0.8


LR_Me_Ts_dpazide
143.3445
139.2154
138.6174
138.1118
129.5972
128.4187
128.4075
128.2467
128.1750
128.0948
127.8988
127.0470
77.4524
77.0291
76.6060
75.6912
54.9291
21.5216
18.7280
-0.0010
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



(2d)

SpinWorks 2.4: LR_79_Azide_3



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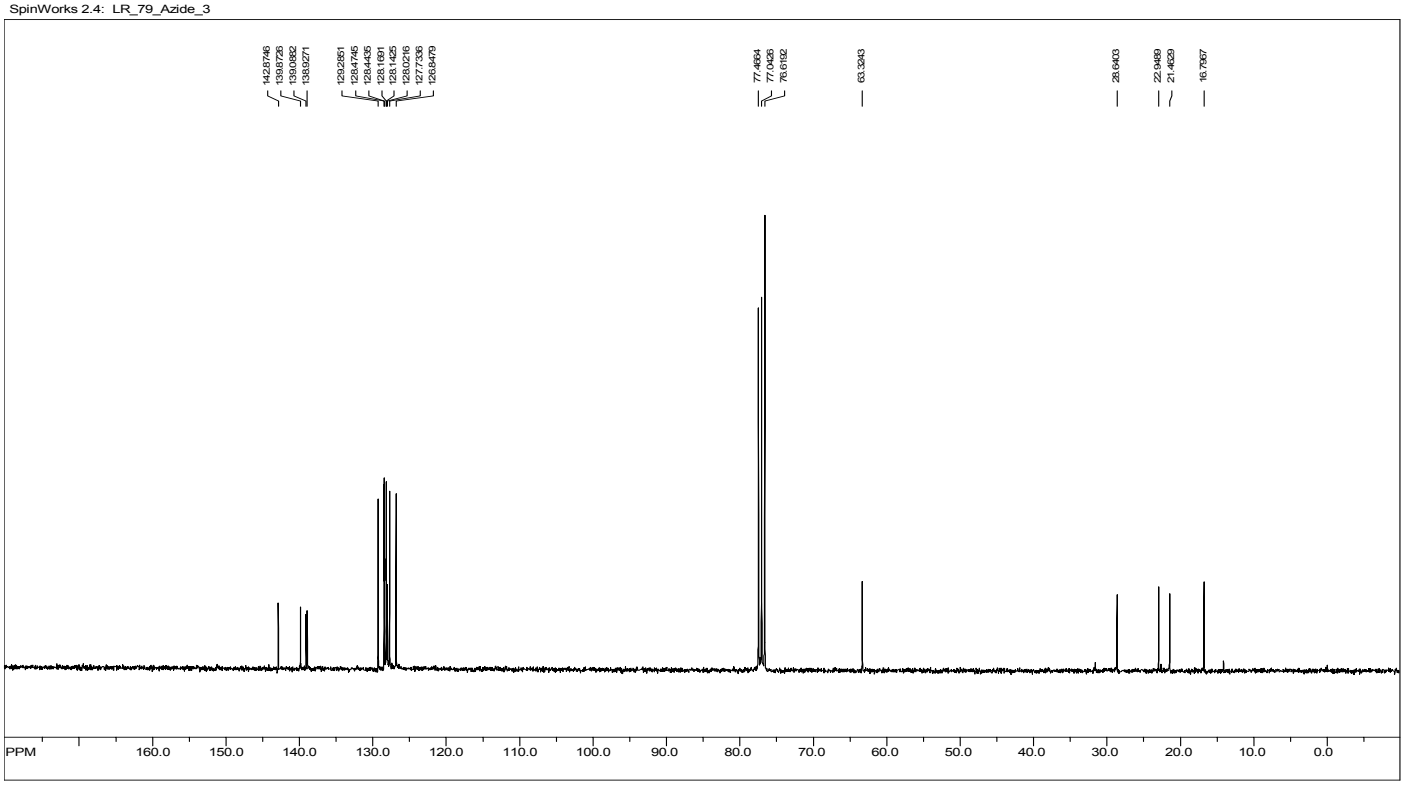
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130009 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: LR_79_Azide_3



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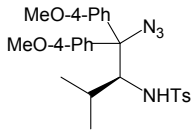
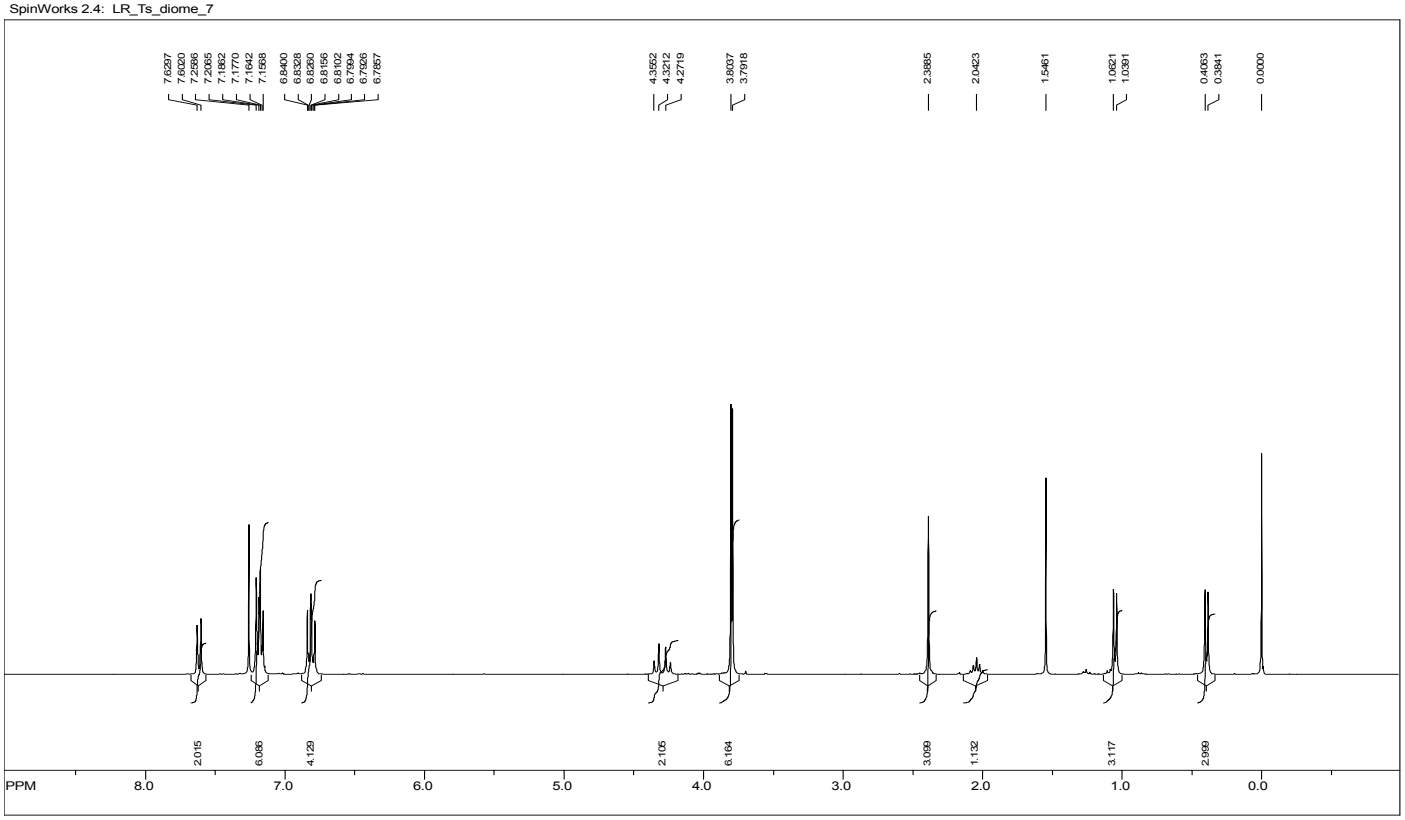
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000



(2e)

SpinWorks 2.4: LR_Ts_diome_7



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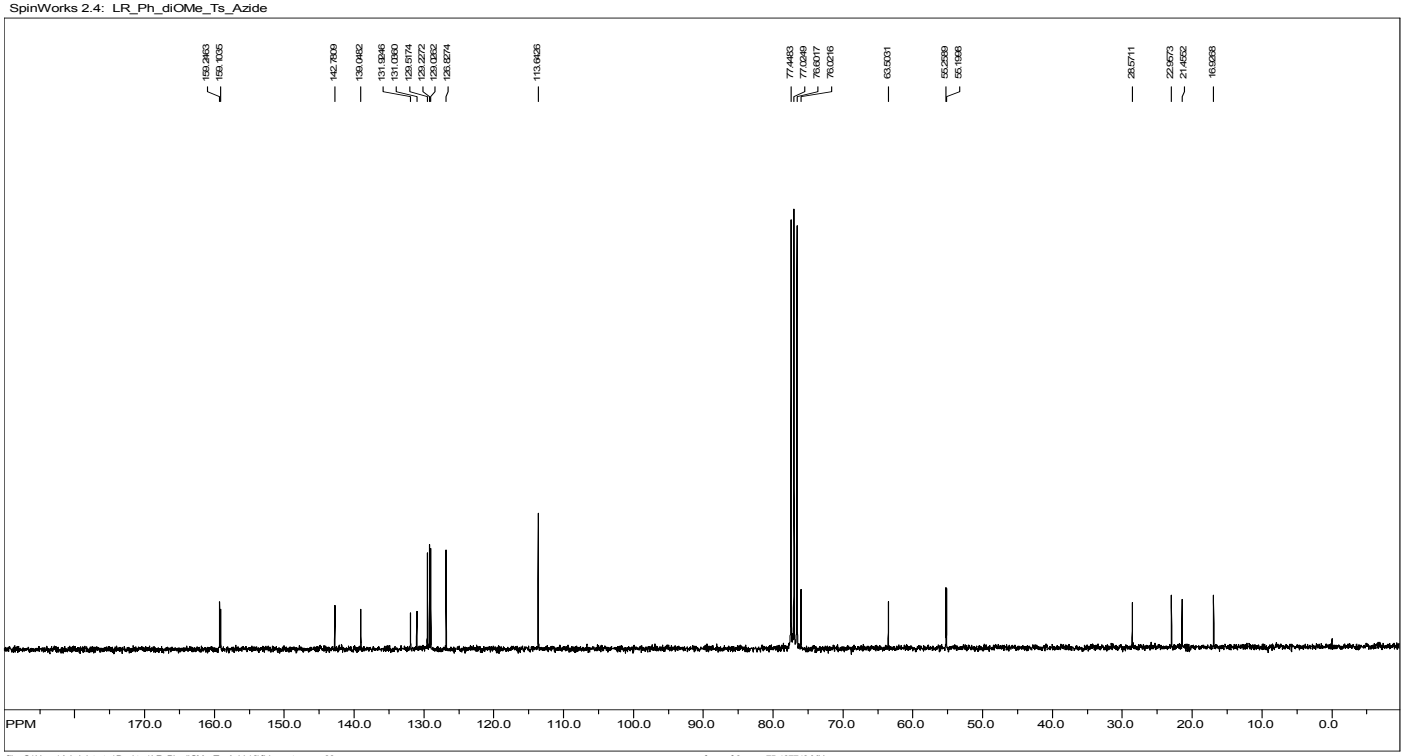
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: LR_Ph_diOMe_Ts_Azide



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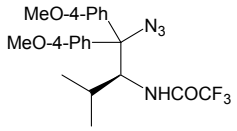
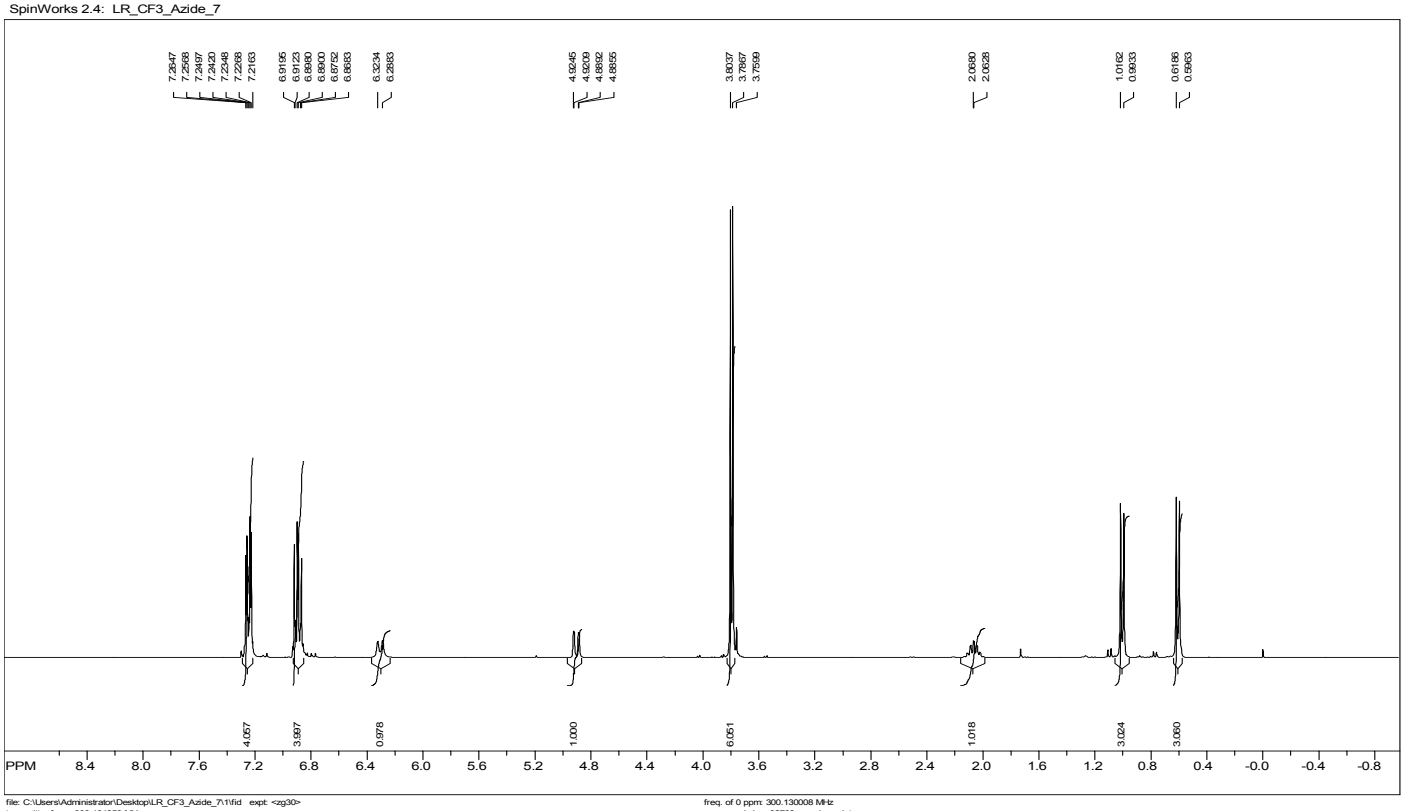
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000



(2f)

SpinWorks 2.4: LR_CF3_Azide_7



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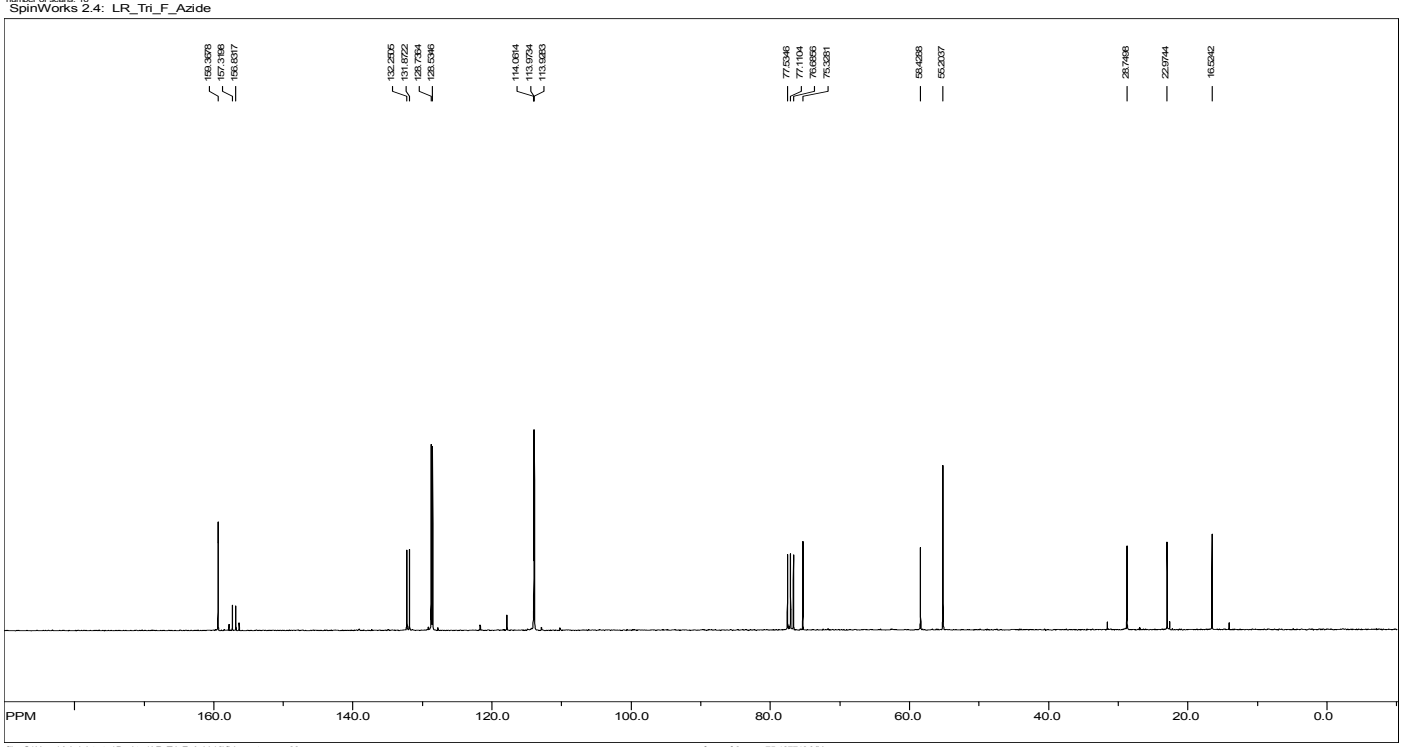
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130008 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: LR_Tri_F_Azide



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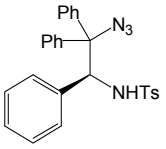
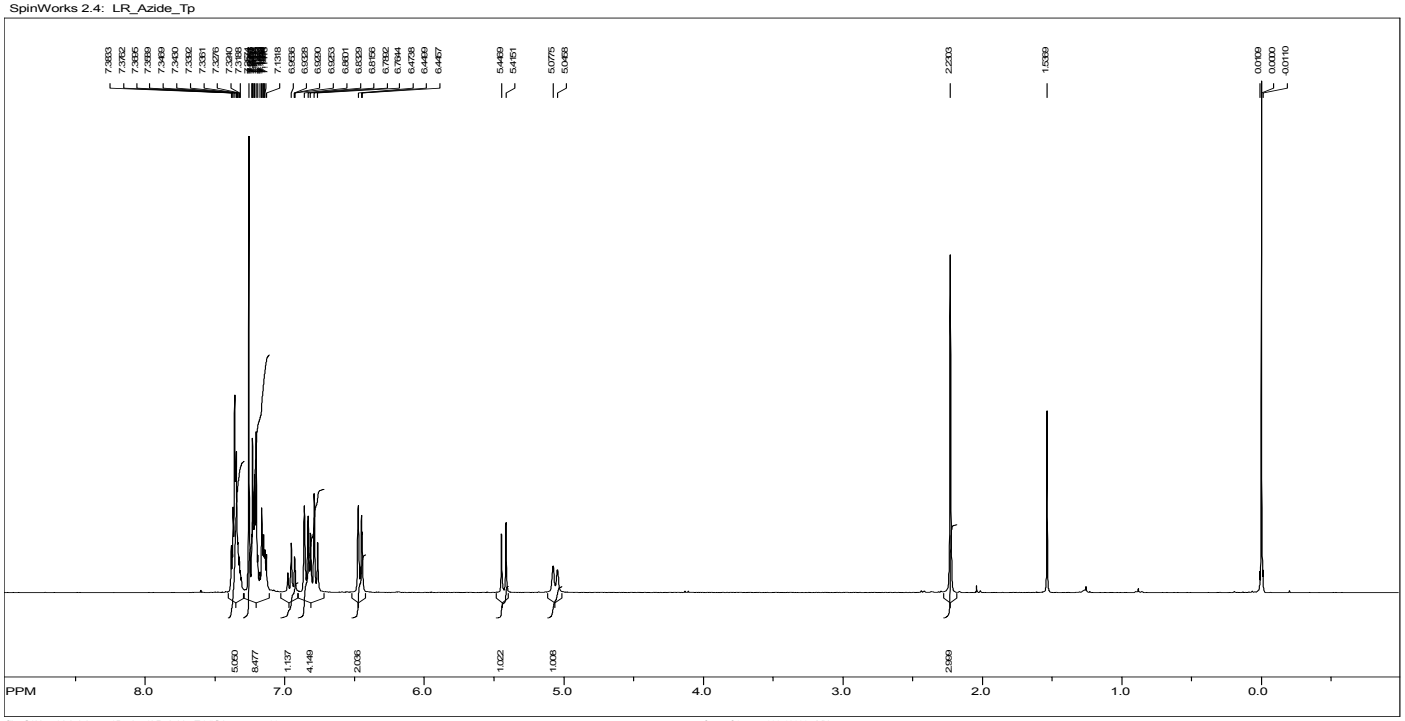
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000



(2g)

SpinWorks 2.4: LR_Azide_Tp



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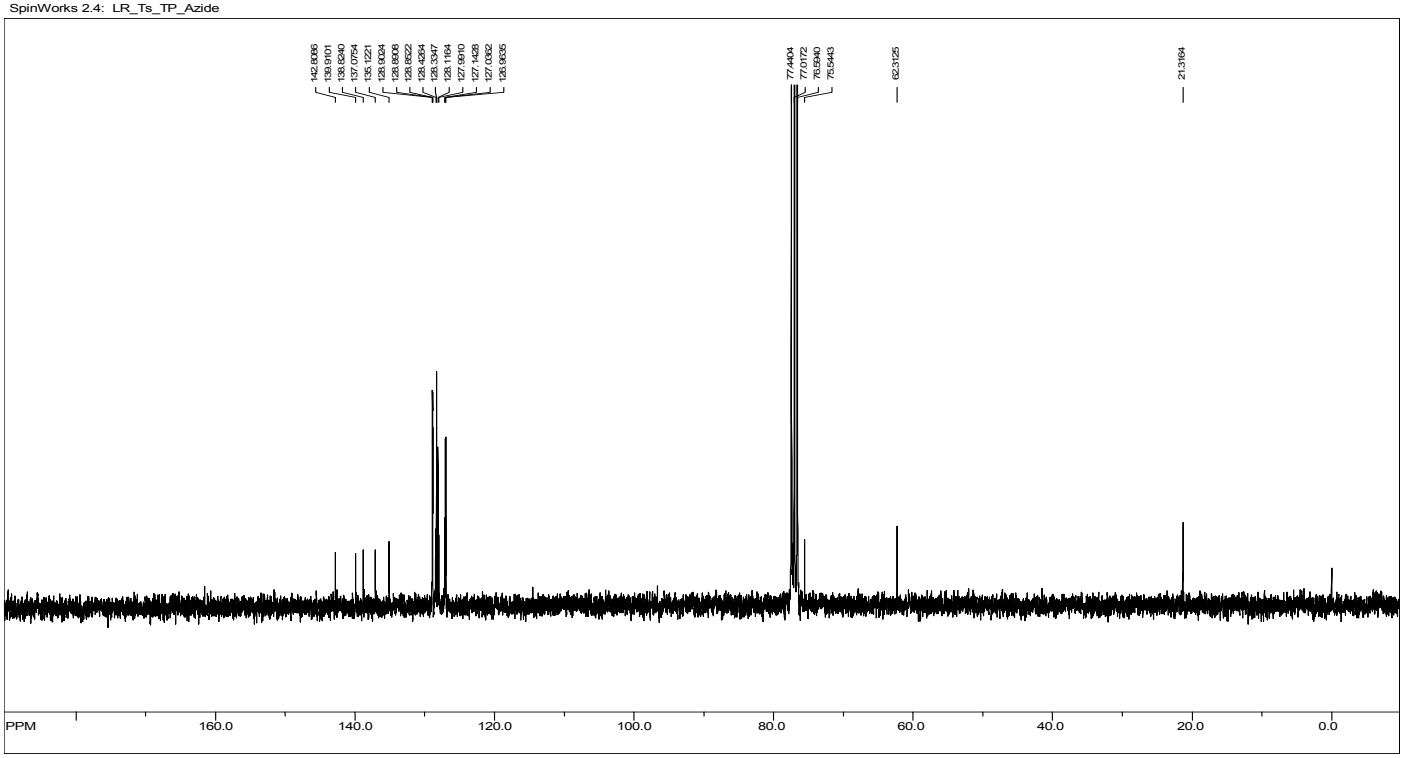
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

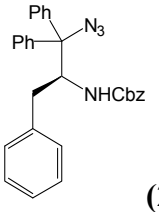
freq. of 0 ppm: 300.130007 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: LR_Ts_TP_Azide



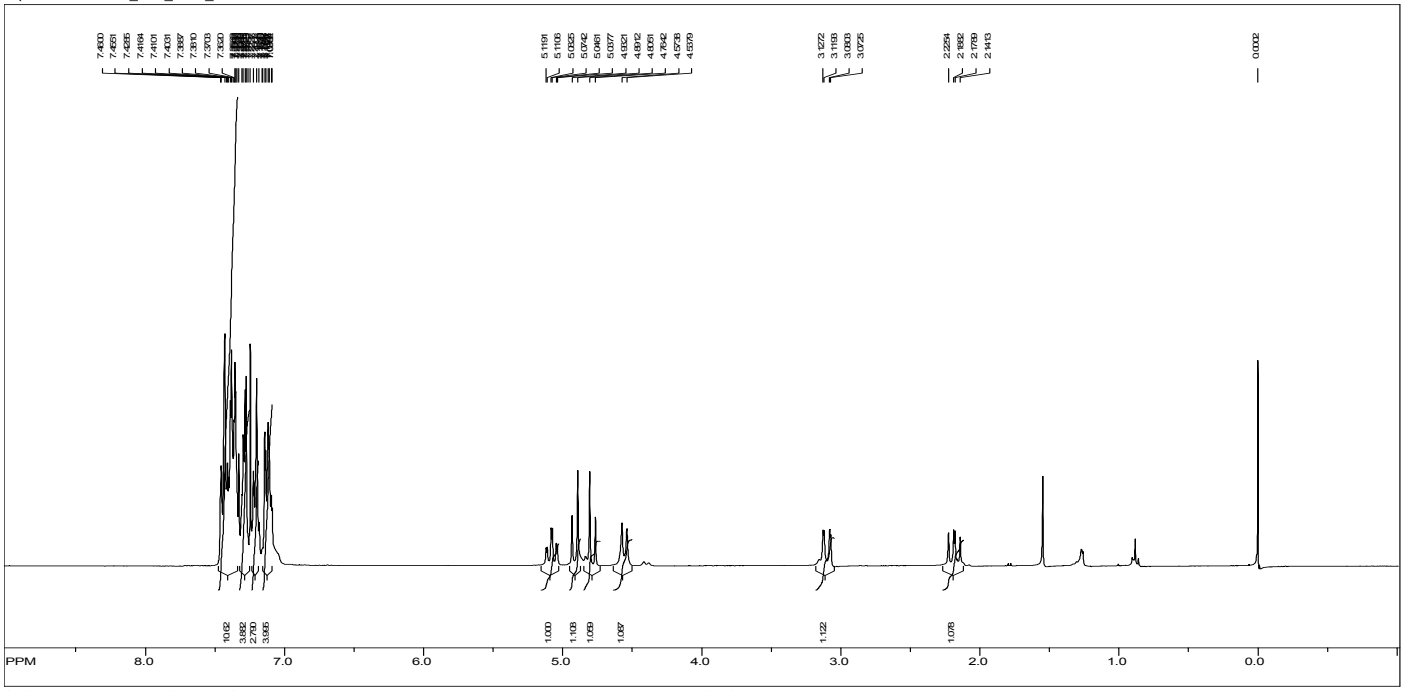
file: C:\Users\Administrator\Desktop\LR_Ts_TP_Azide\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000



(2h)

SpinWorks 2.4: LR_CBZ_azide_7



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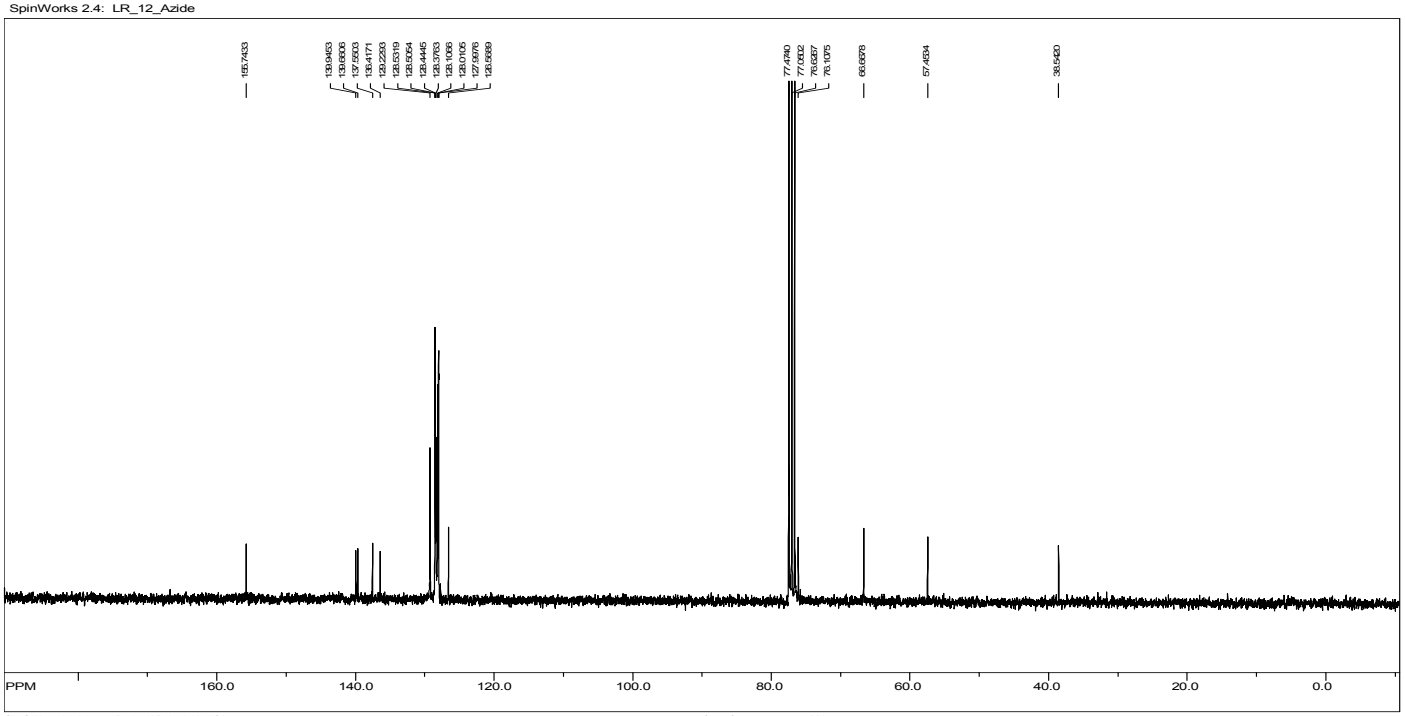
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130011 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: LR_12_Azide



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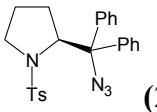
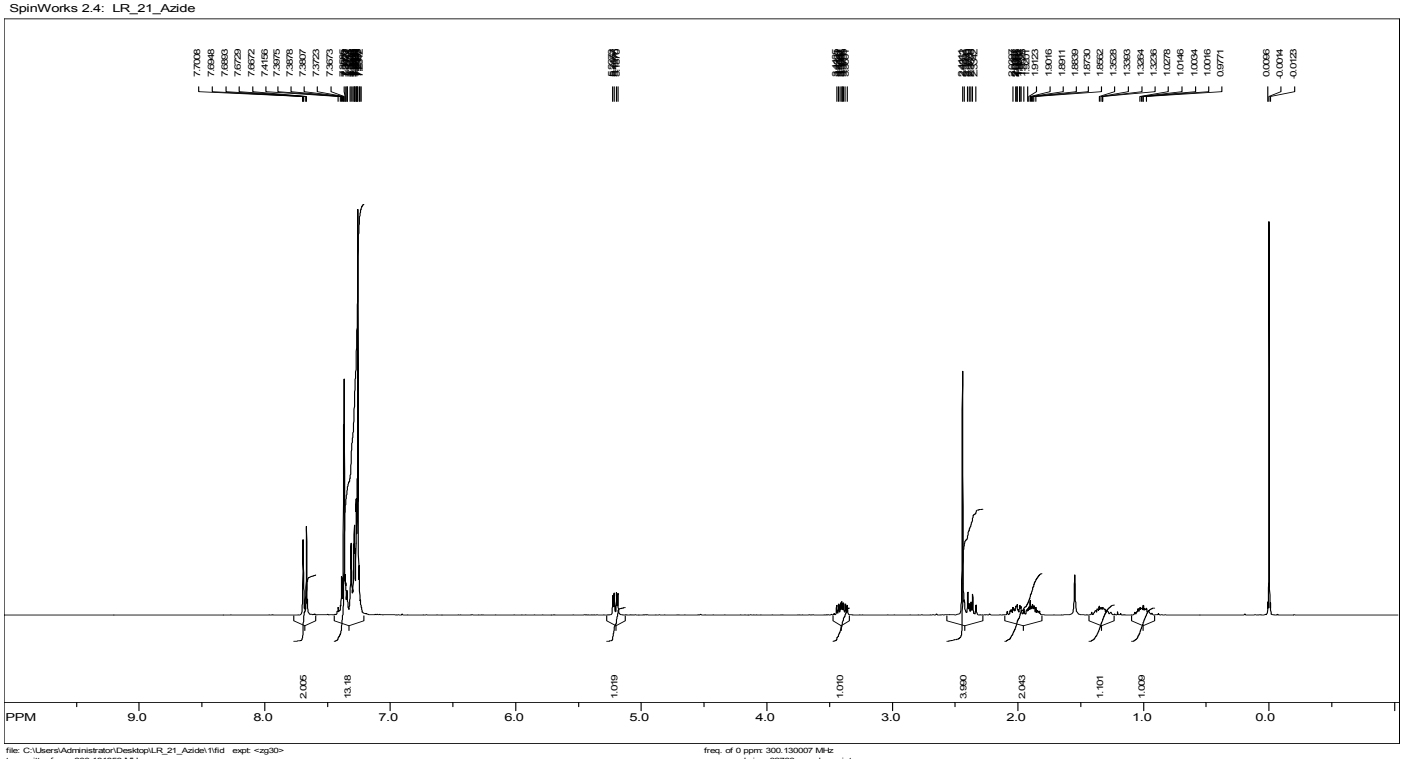
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000



(2i)

SpinWorks 2.4: LR_21_Azide



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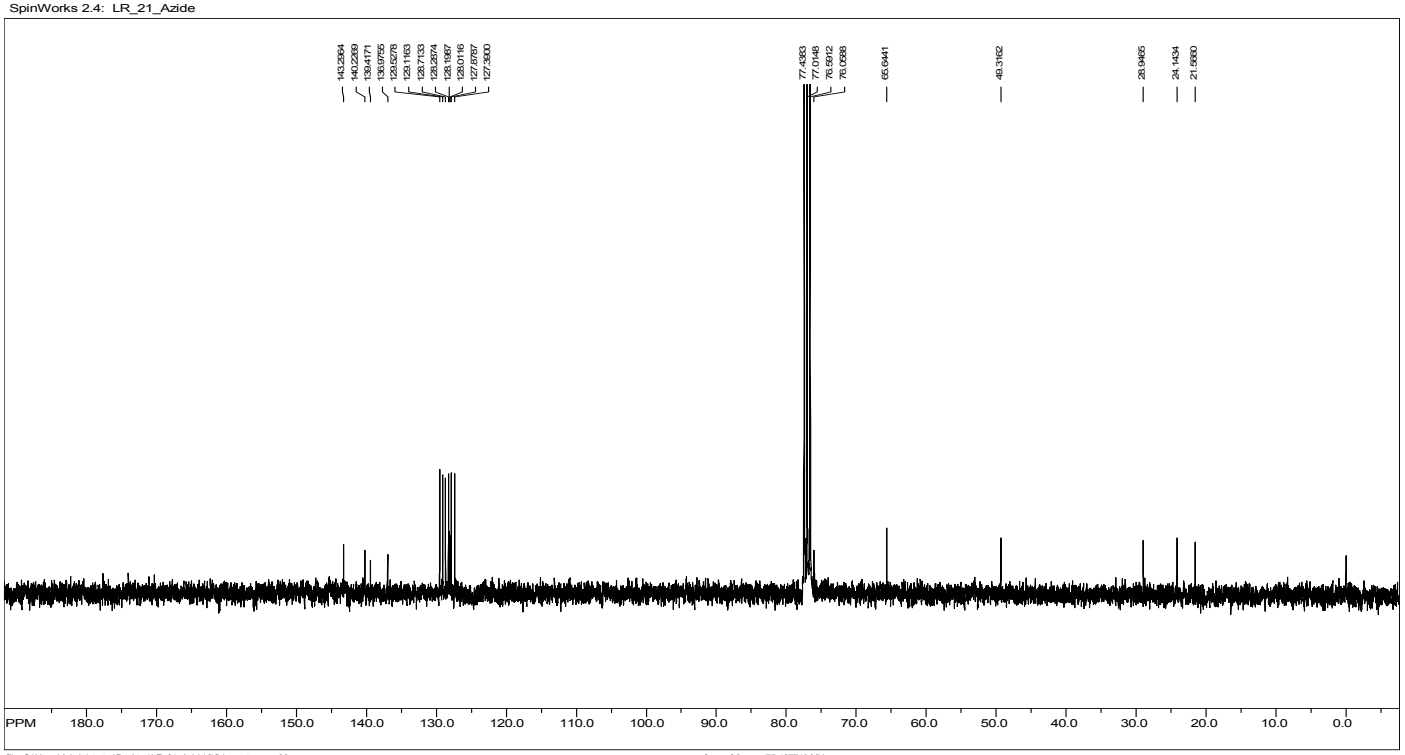
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

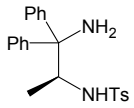
freq. of 0 ppm: 300.130007 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000

SpinWorks 2.4: LR_21_Azide



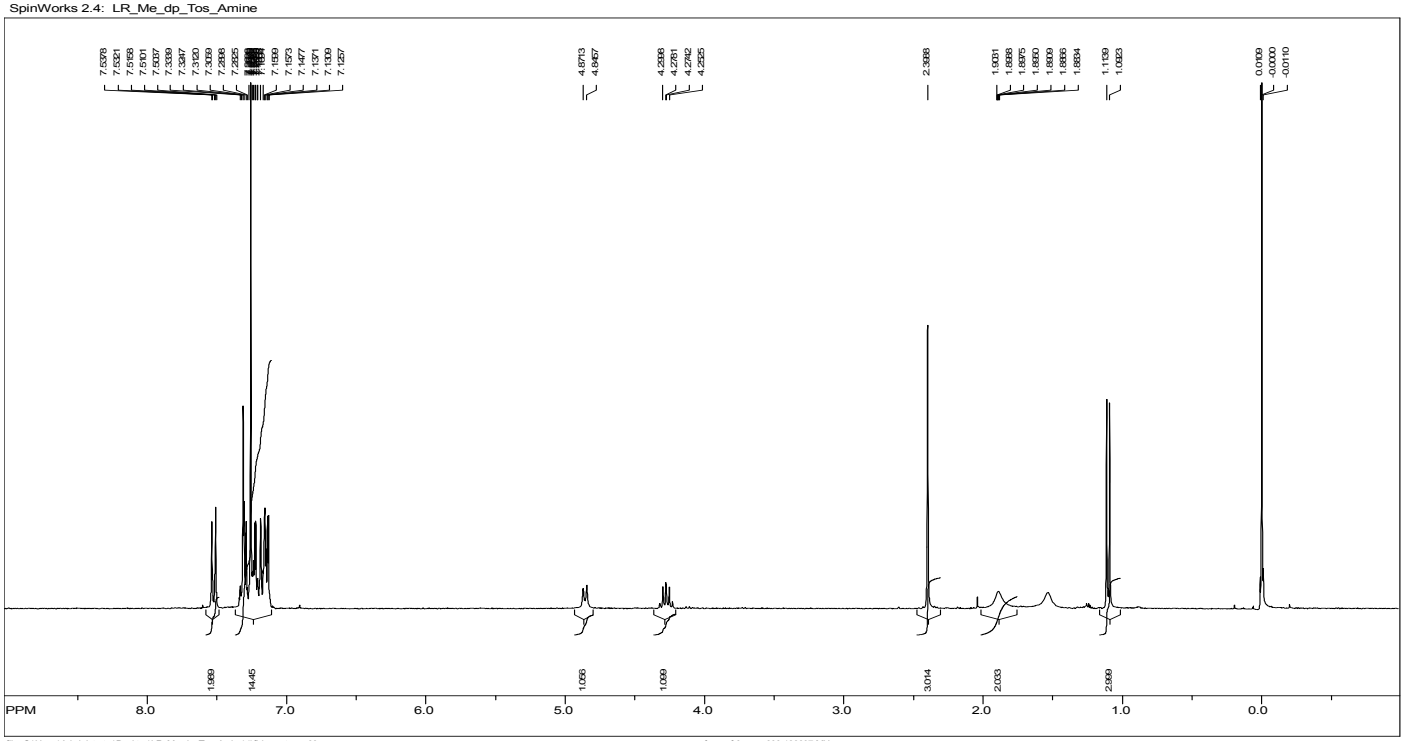
file: C:\Users\Administrator\Desktop\LR_21_Azide\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000



(3c)

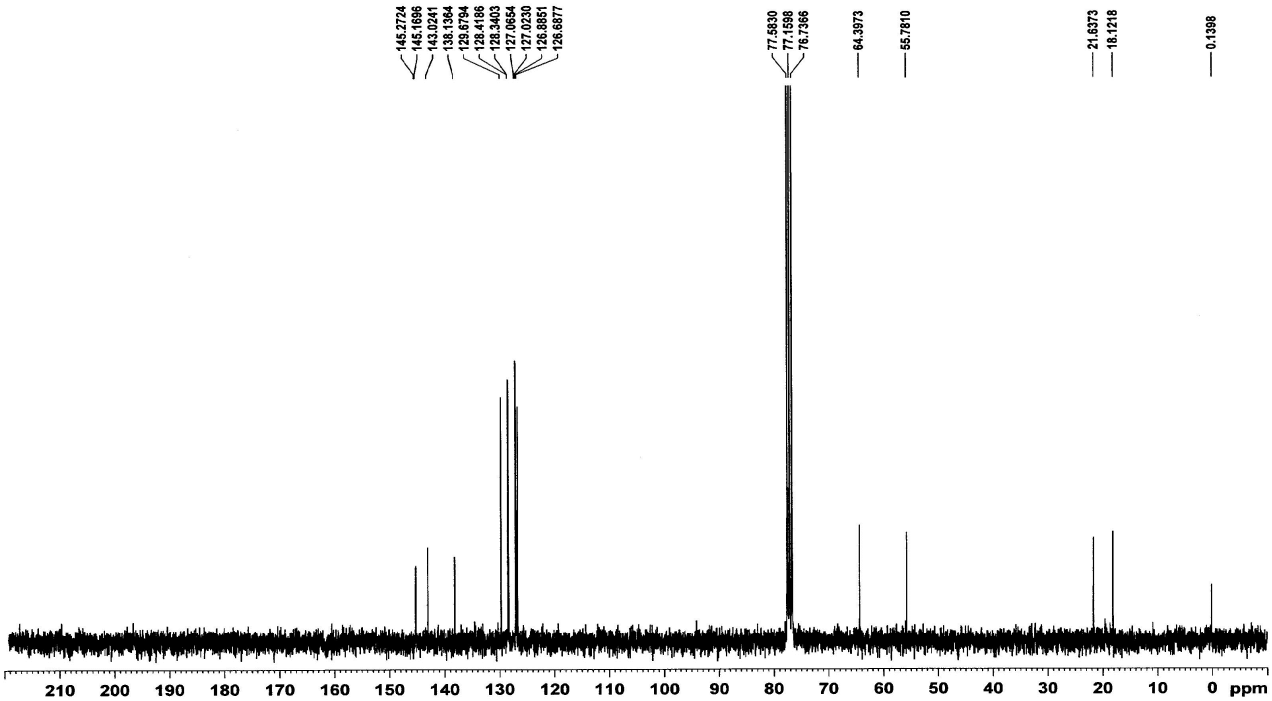
SpinWorks 2.4: LR_Me_dp_Tos_Amine

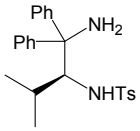


file: C:\Users\Administrator\Desktop\LR_Me_dp_Tos_Amine\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130007 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

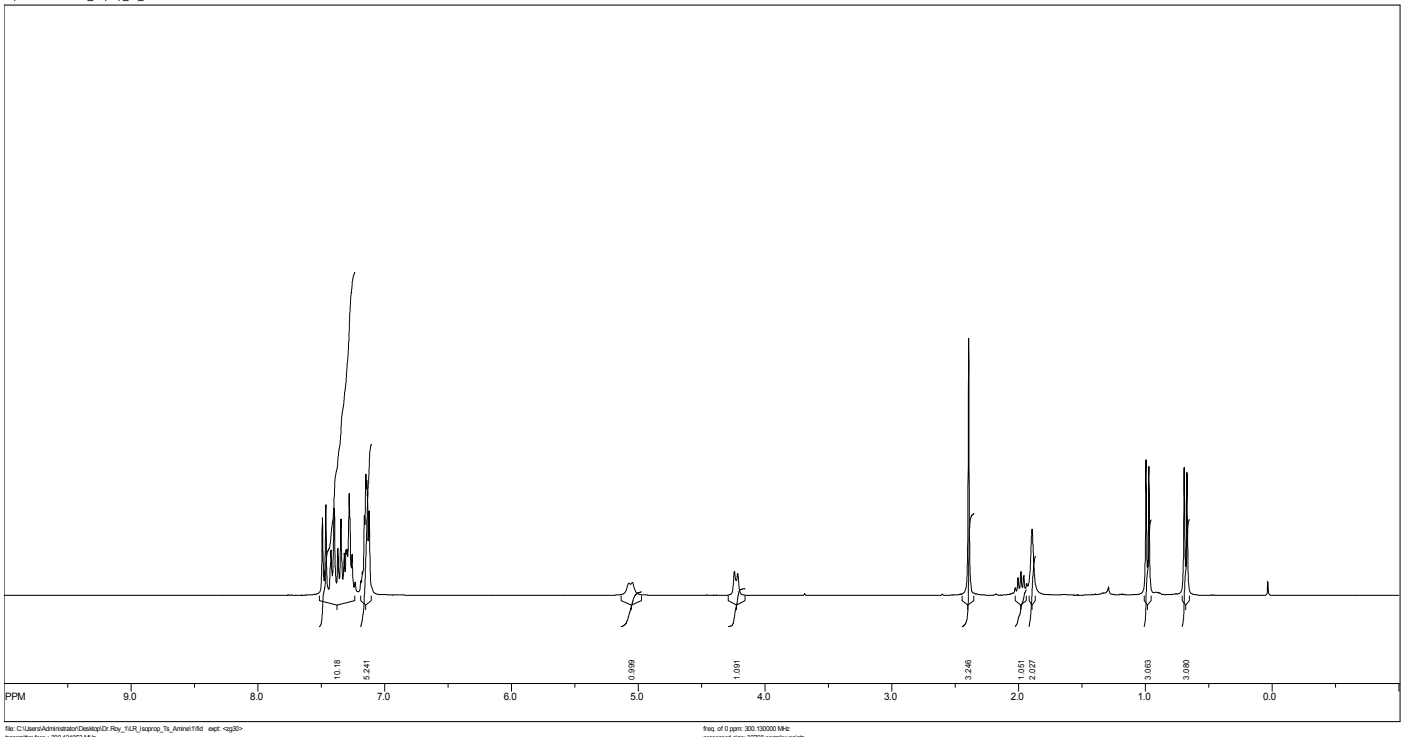
LR_Me_dp_Ts_Amine





(3d)

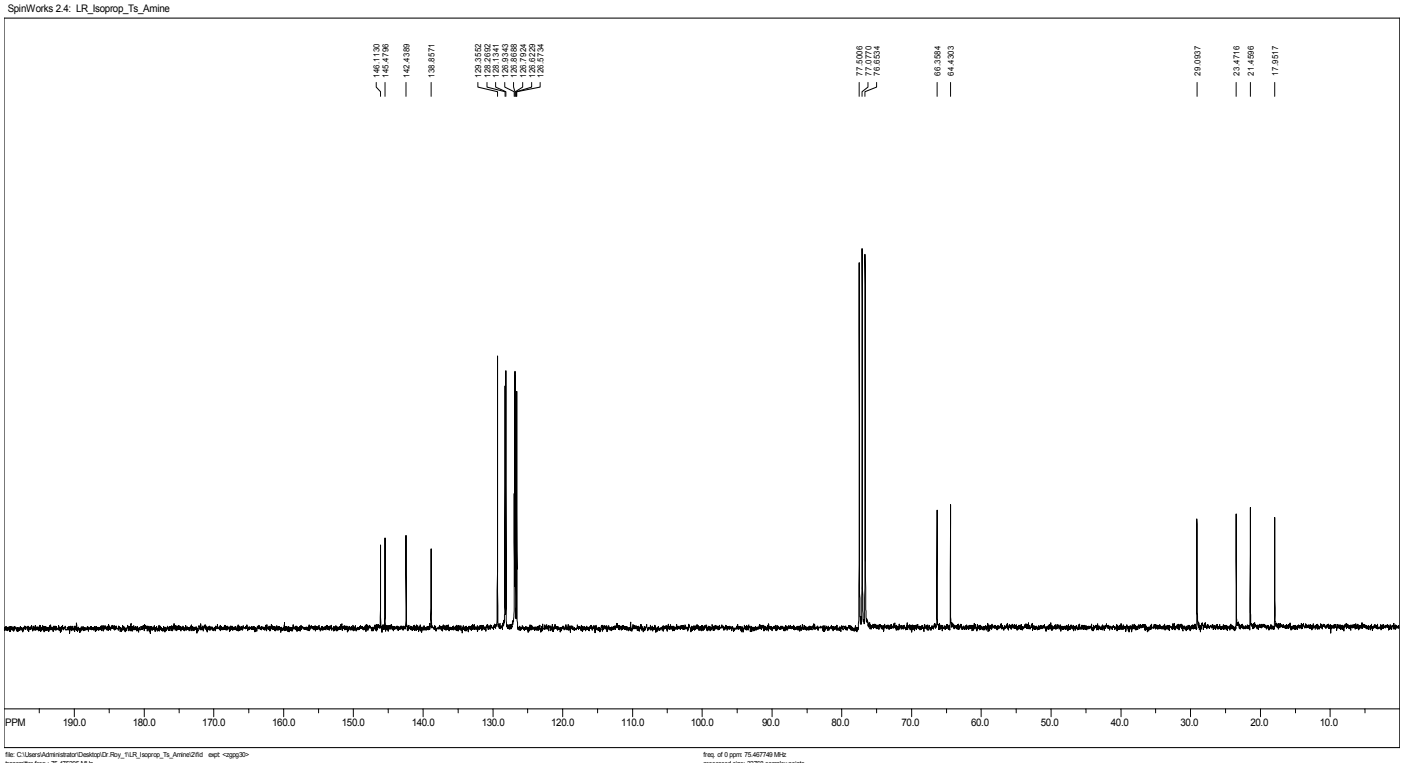
SpinWorks 2.4: LR_Isoprop_Ts_Amine



file: C:\Users\Administrator\Desktop\Dr.Roy_1\LR_Isoprop_Ts_Amine\1\fid expt: <cg30>
transmitter freq.: 300.131683 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

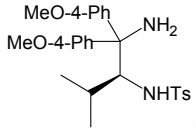
freq. of 0 ppm: 300.130000 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: LR_Isoprop_Ts_Amine



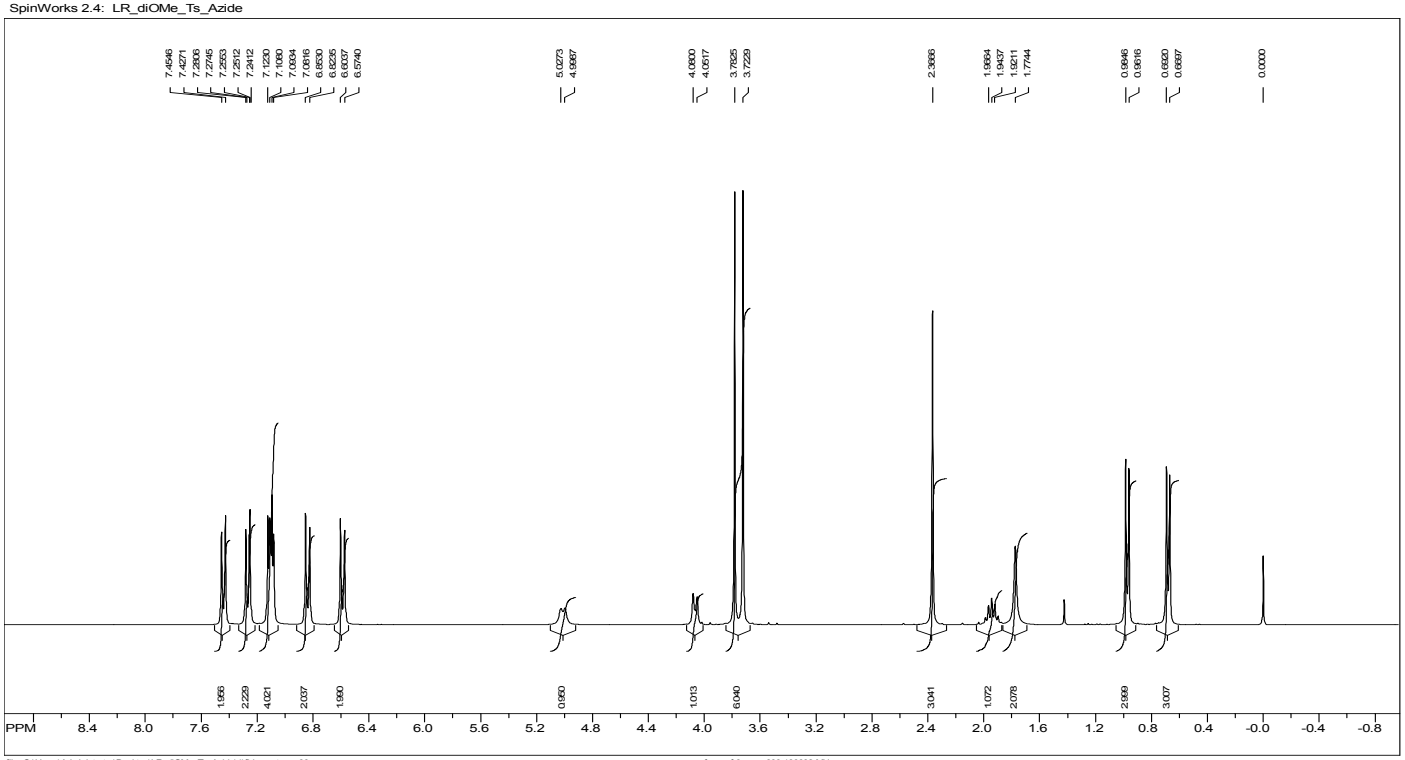
file: C:\Users\Administrator\Desktop\Dr.Roy_1\LR_Isoprop_Ts_Amine\2\fid expt: <cgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000



(3e)

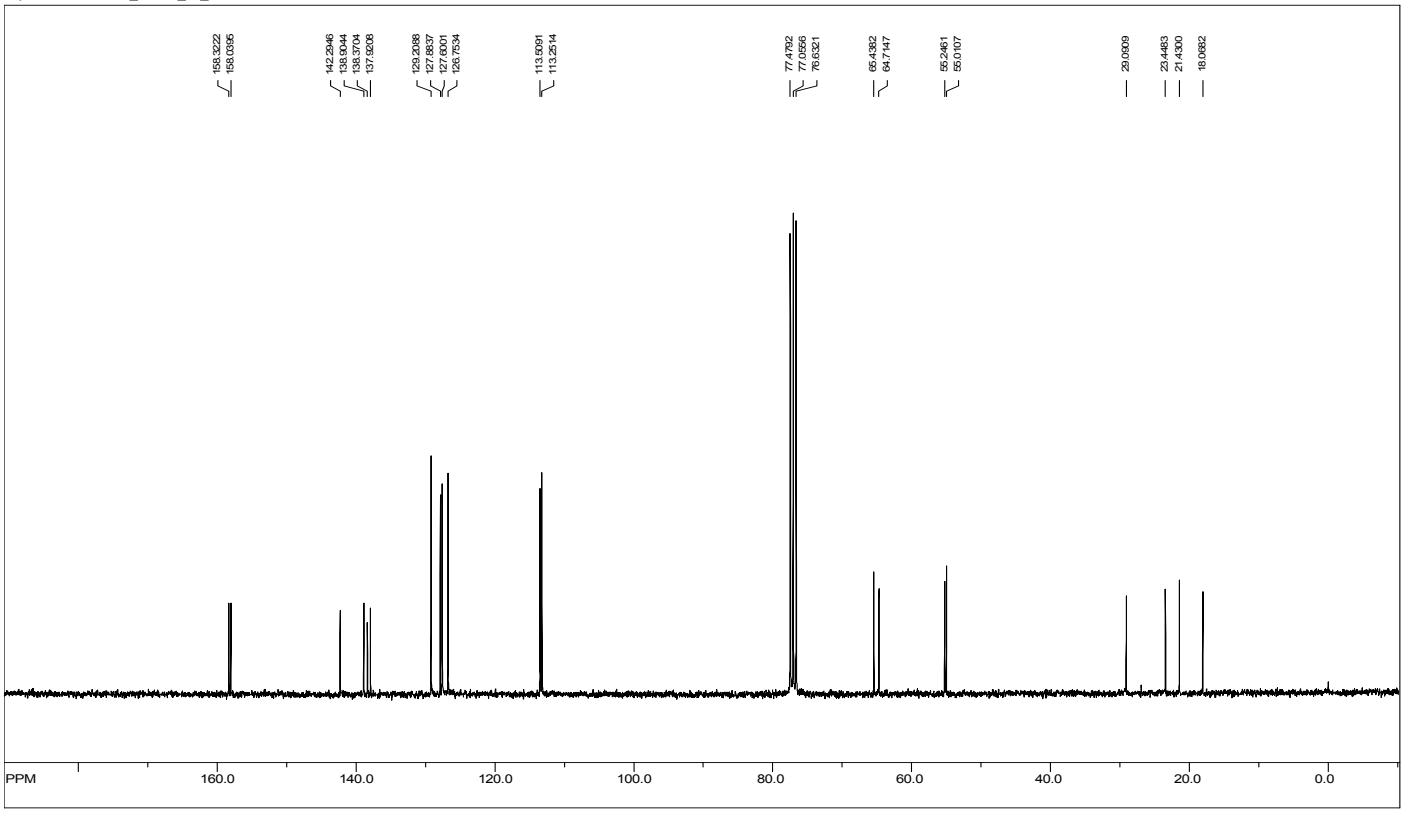
SpinWorks 2.4: LR_diOMe_Ts_Azide



file: C:\Users\Administrator\Desktop\LR_diOMe_Ts_Azide\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

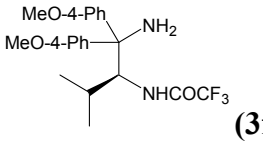
freq. of 0 ppm: 300.130008 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: LR_diOMe_Ts_Azide

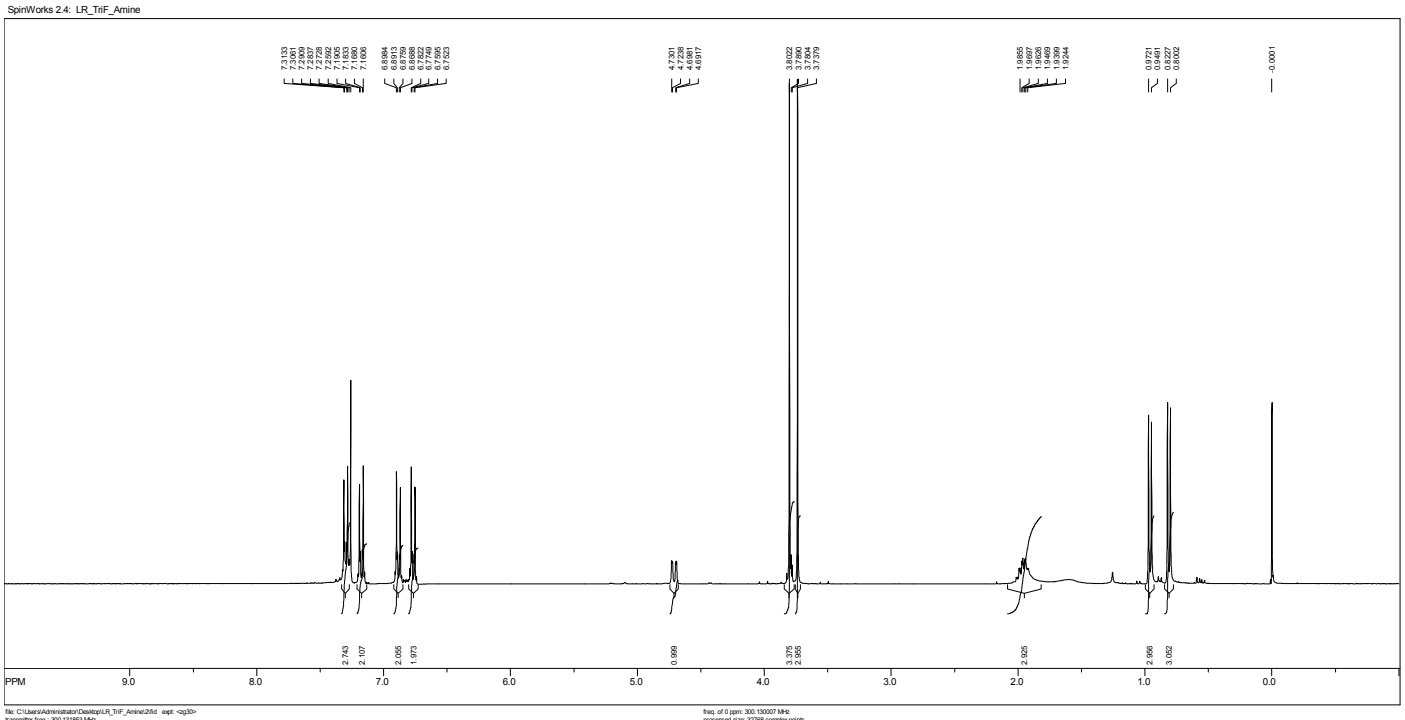


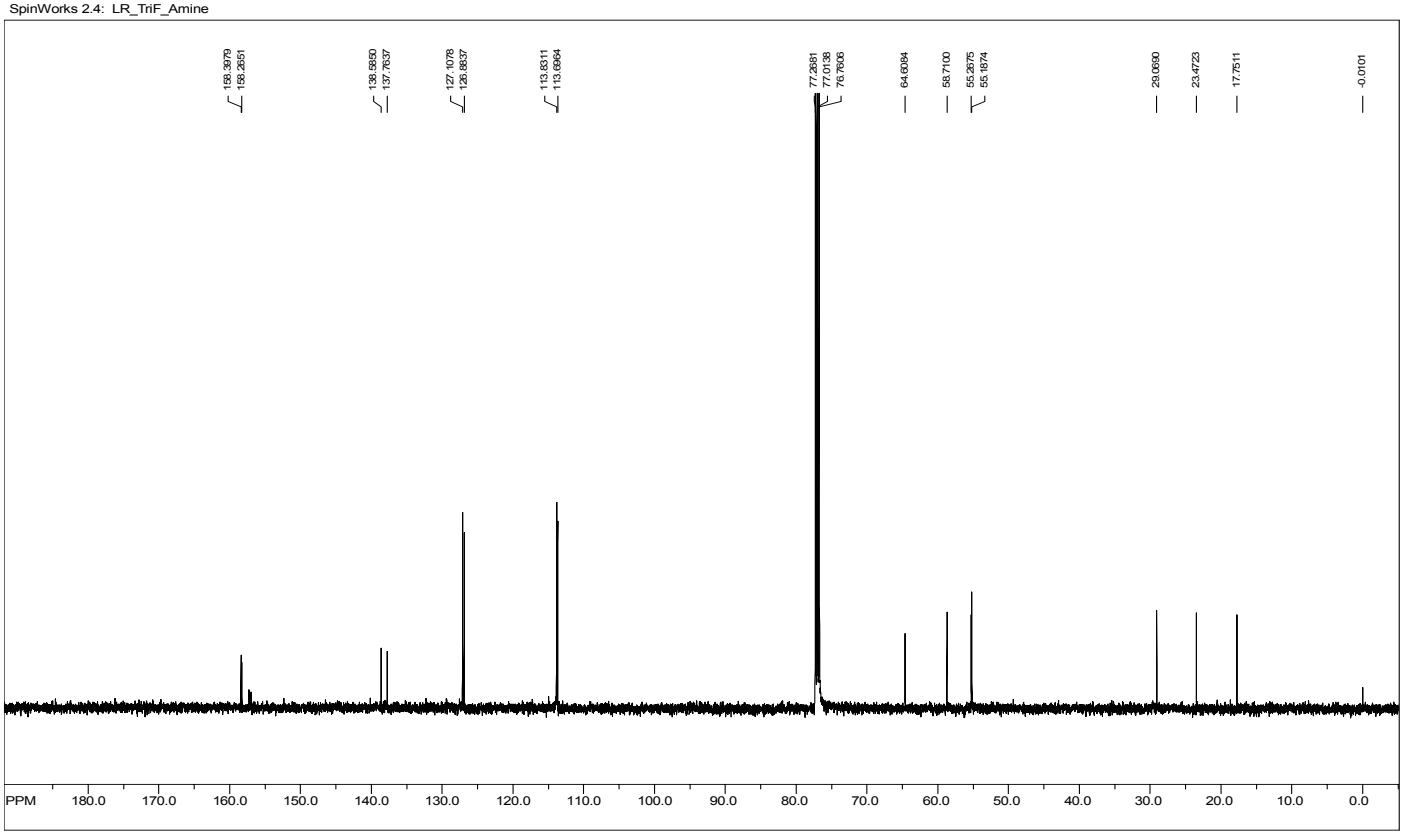
file: C:\Users\Administrator\Desktop\LR_diOMe_Ts_Azide\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

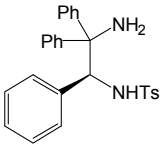
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000


MeO-4-Ph
NH2
MeO-4-Ph
NHCOCF3

(3f)

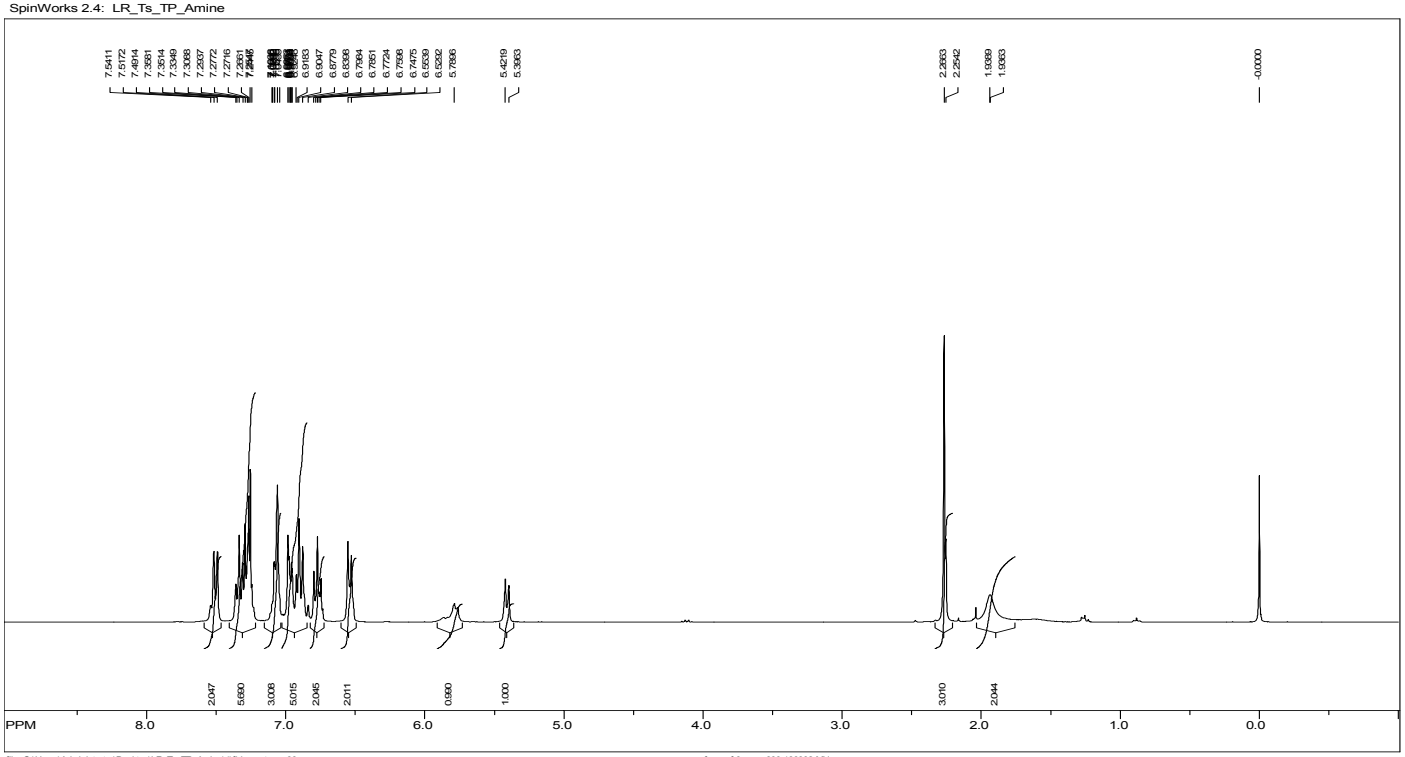

SpinWorks 2.4: LR_TriF_Amine
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


SpinWorks 2.4: LR_TriF_Amine
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0



(3g)

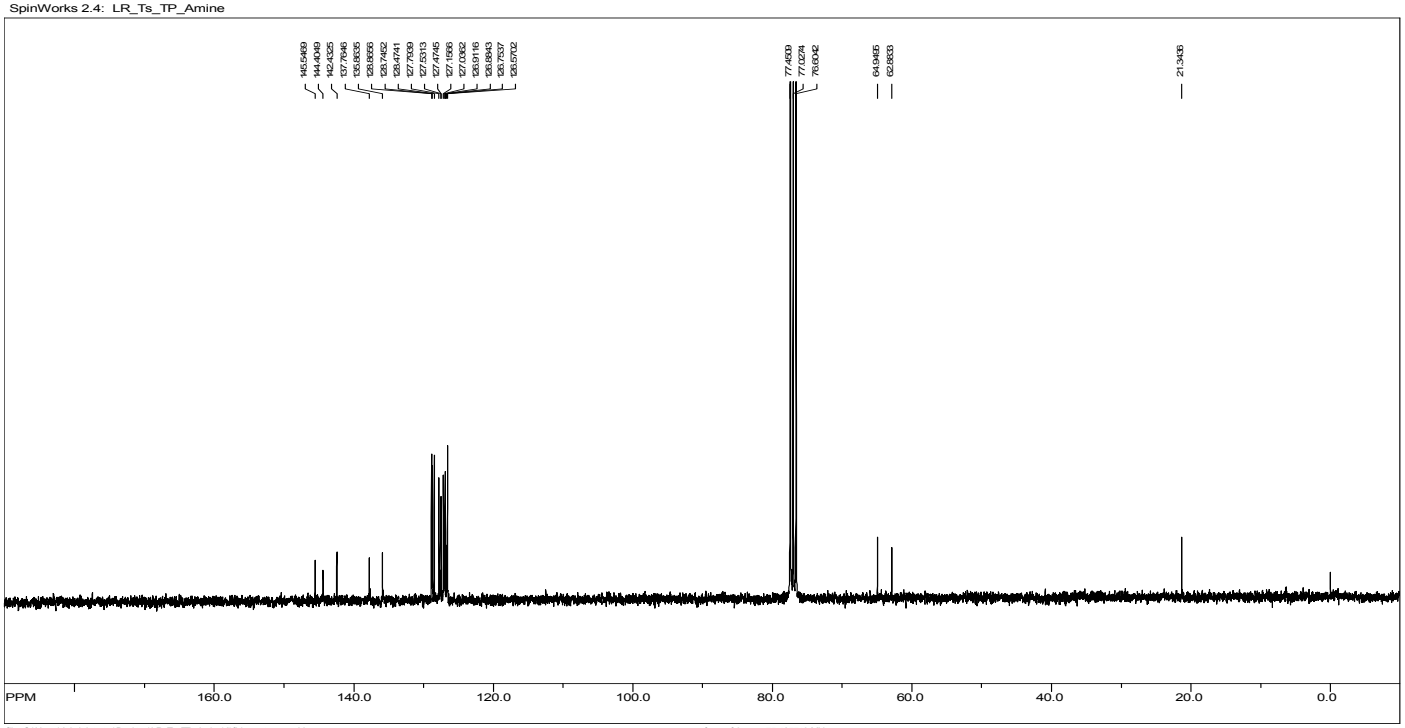
SpinWorks 2.4: LR_Ts_TP_Amine



file: C:\Users\Administrator\Desktop\LR_Ts_TP_Amine\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

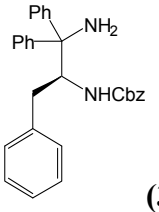
freq. of 0 ppm: 300.130008 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: LR_Ts_TP_Amine

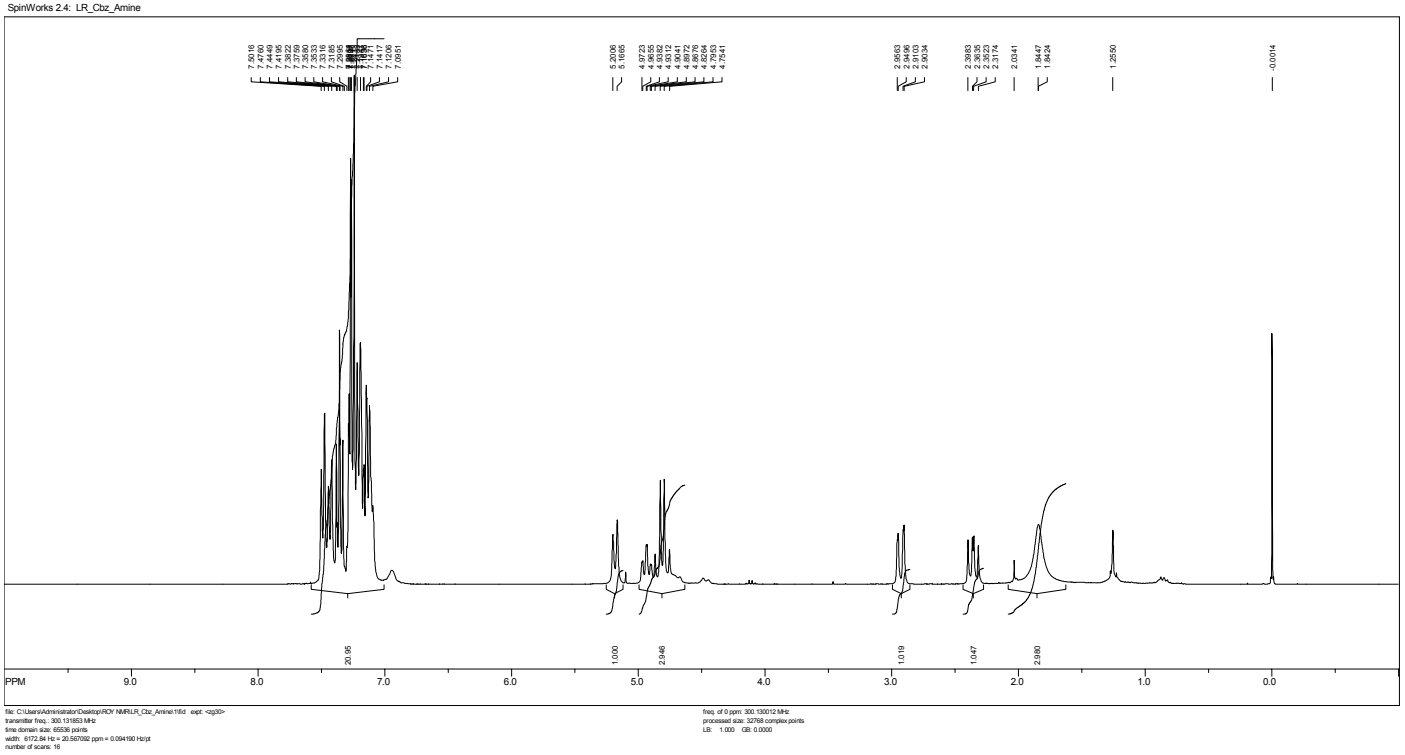


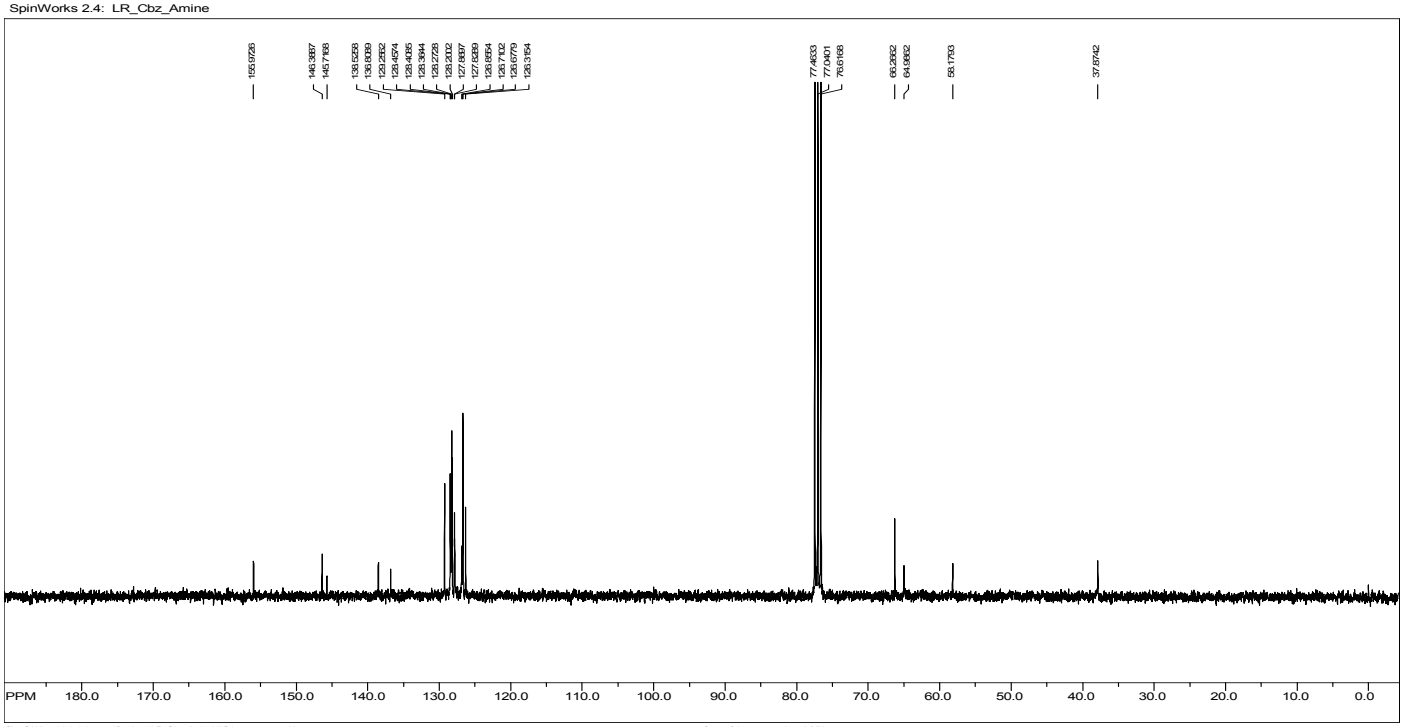
file: C:\Users\Administrator\Desktop\LR_Ts_TP_Amine\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

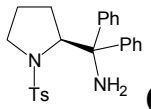
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000


Ph
NH2
Ph
NHCbz

(3h)

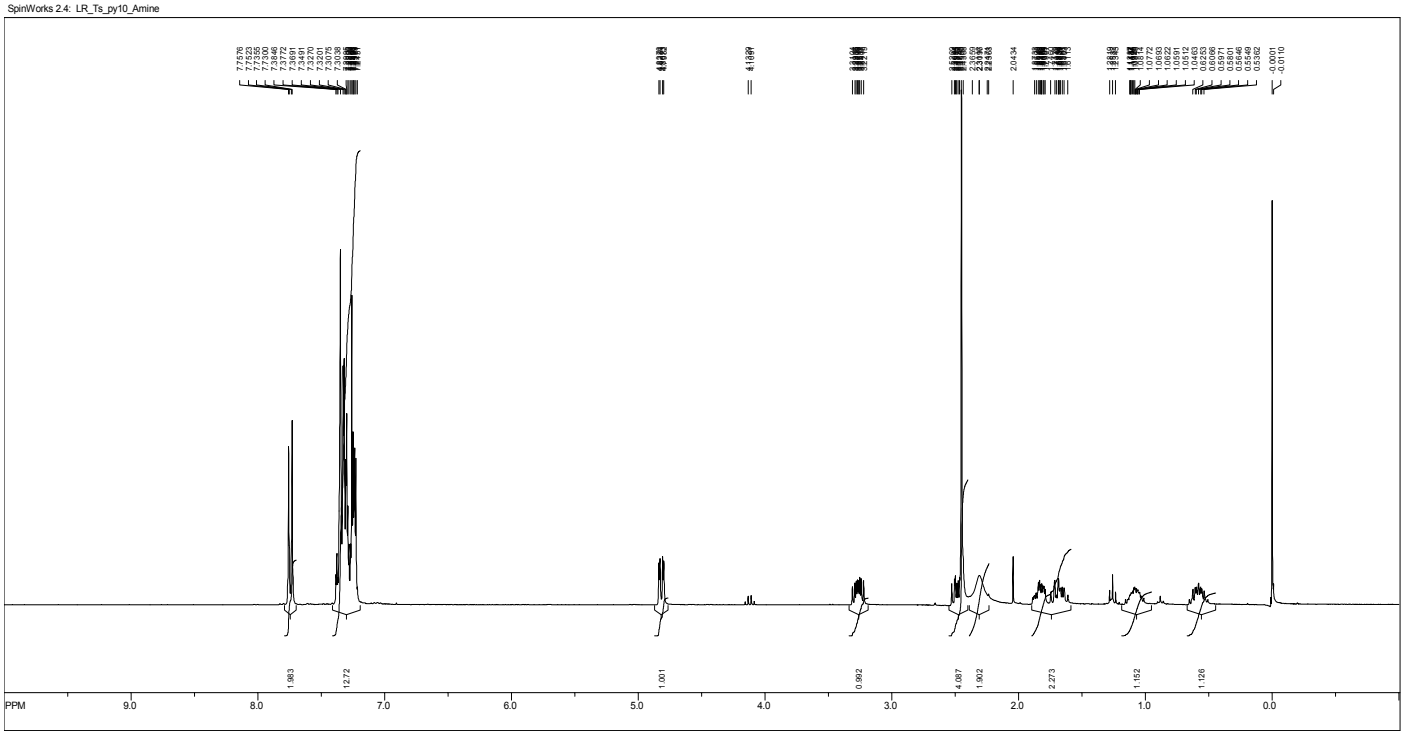

SpinWorks 2.4: LR_Cbz_Amine
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


SpinWorks 2.4: LR_Cbz_Amine
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0



(3i)

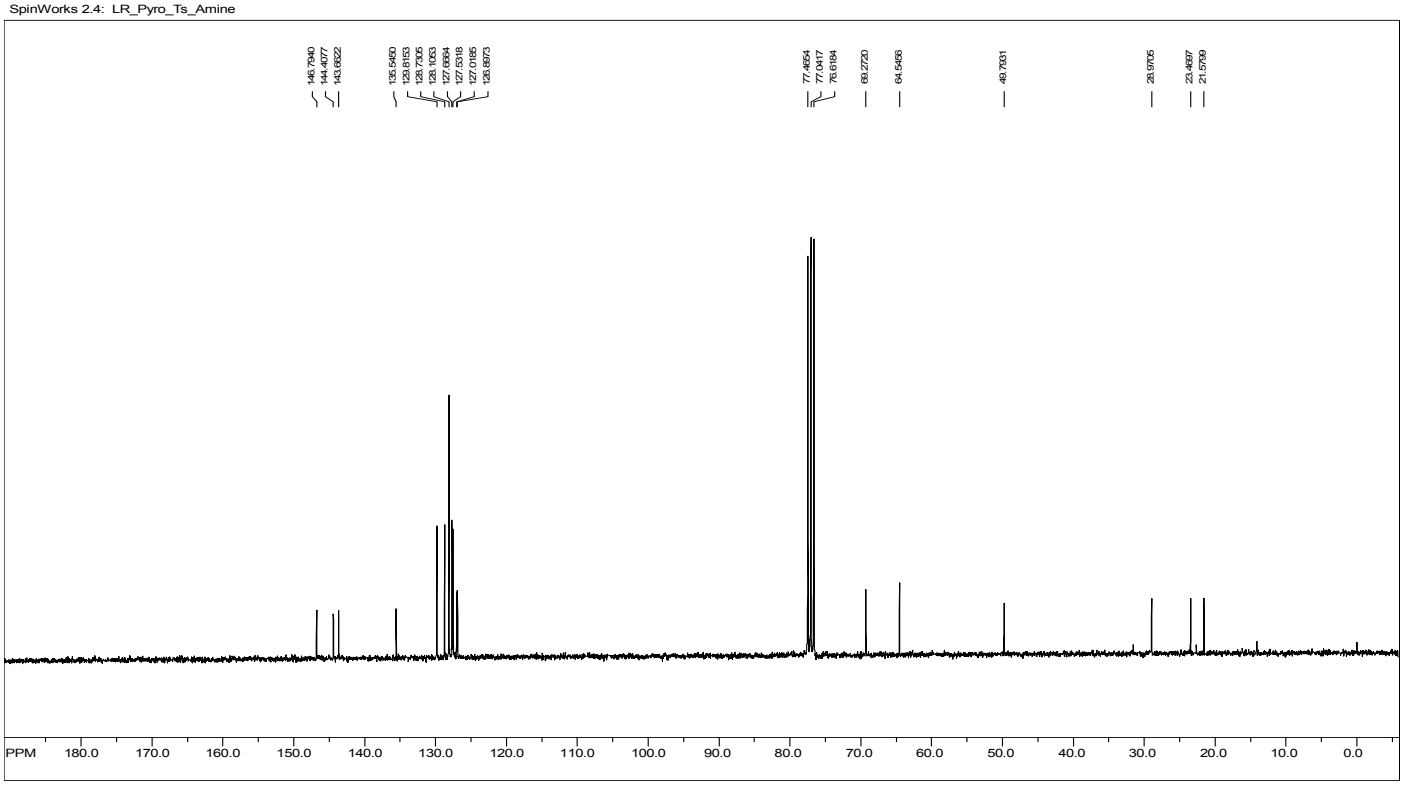
SpinWorks 2.4: LR_Ts_py10_Amine



file: C:\Users\Administrator\Desktop\LR_Ts_py10_Amine\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130009 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

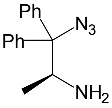
SpinWorks 2.4: LR_Pyro_Ts_Amine



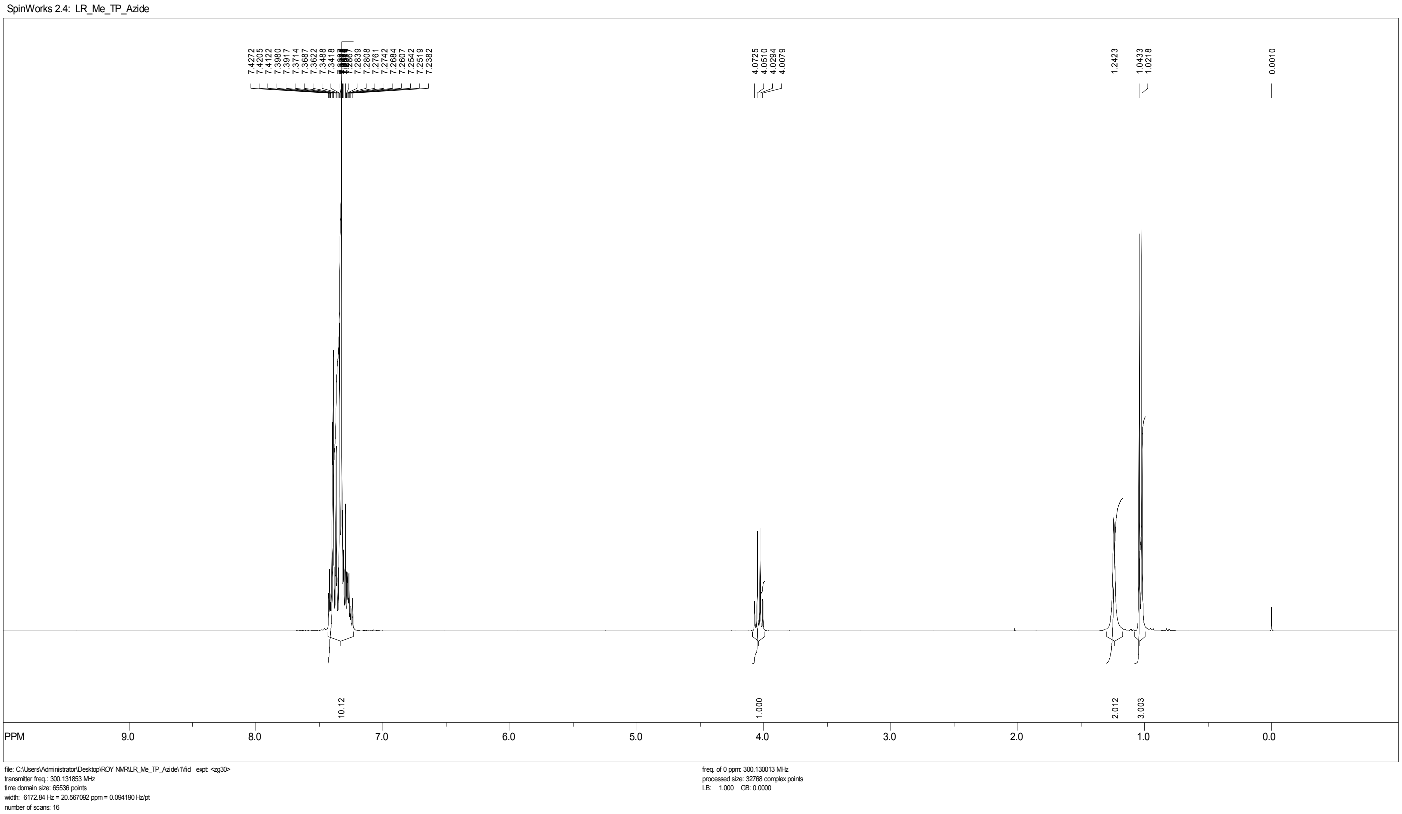
file: C:\Users\Administrator\Desktop\LR_Pyro_Ts_Amine\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

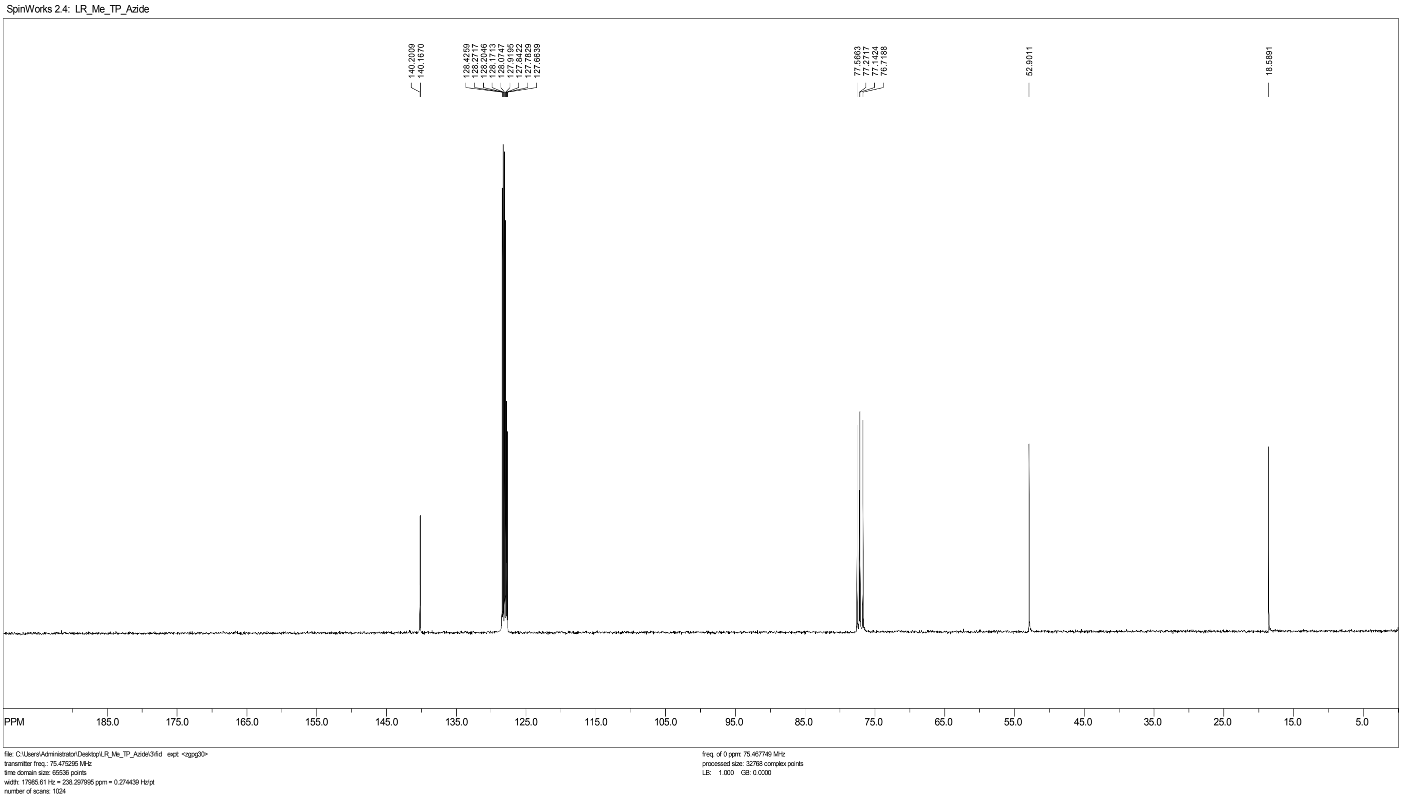
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000

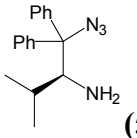
Electronic Supplementary Material (ESI) for RSC Advances



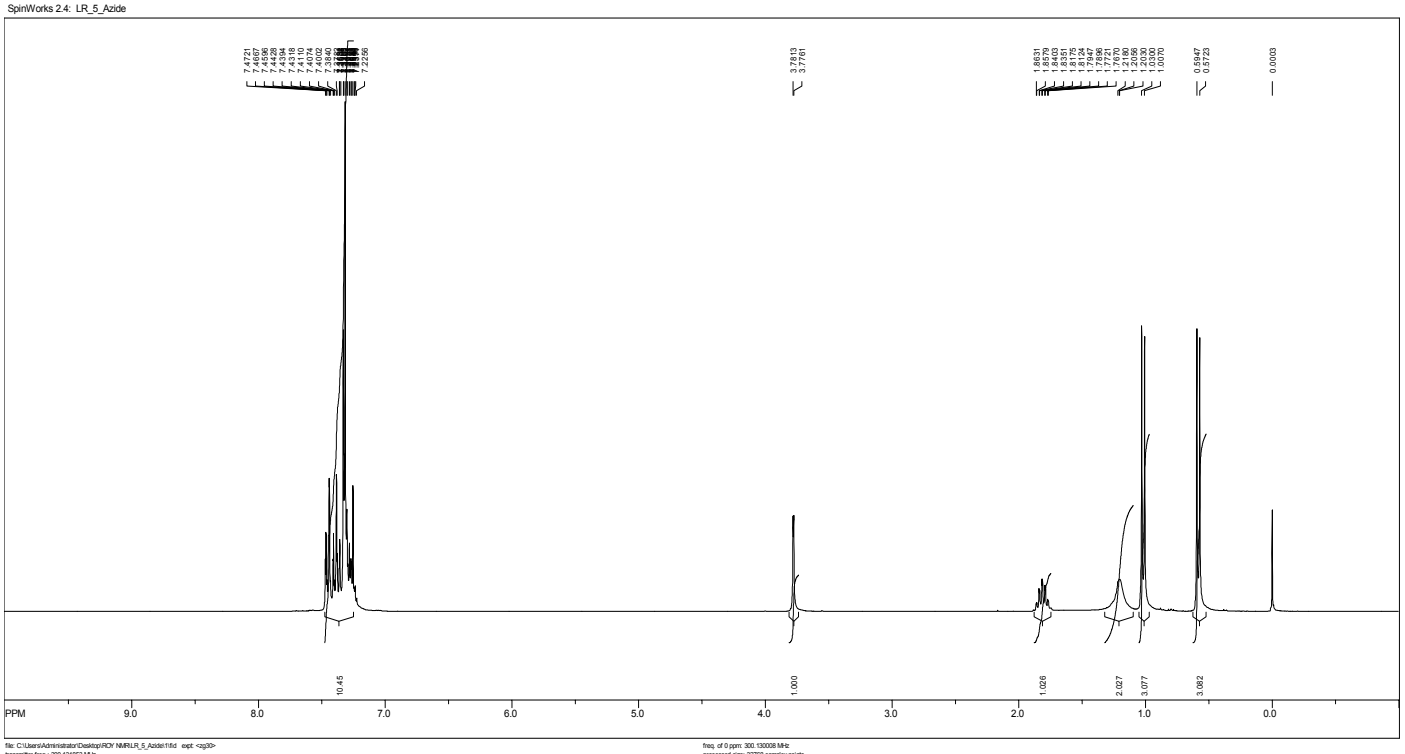
(5a)

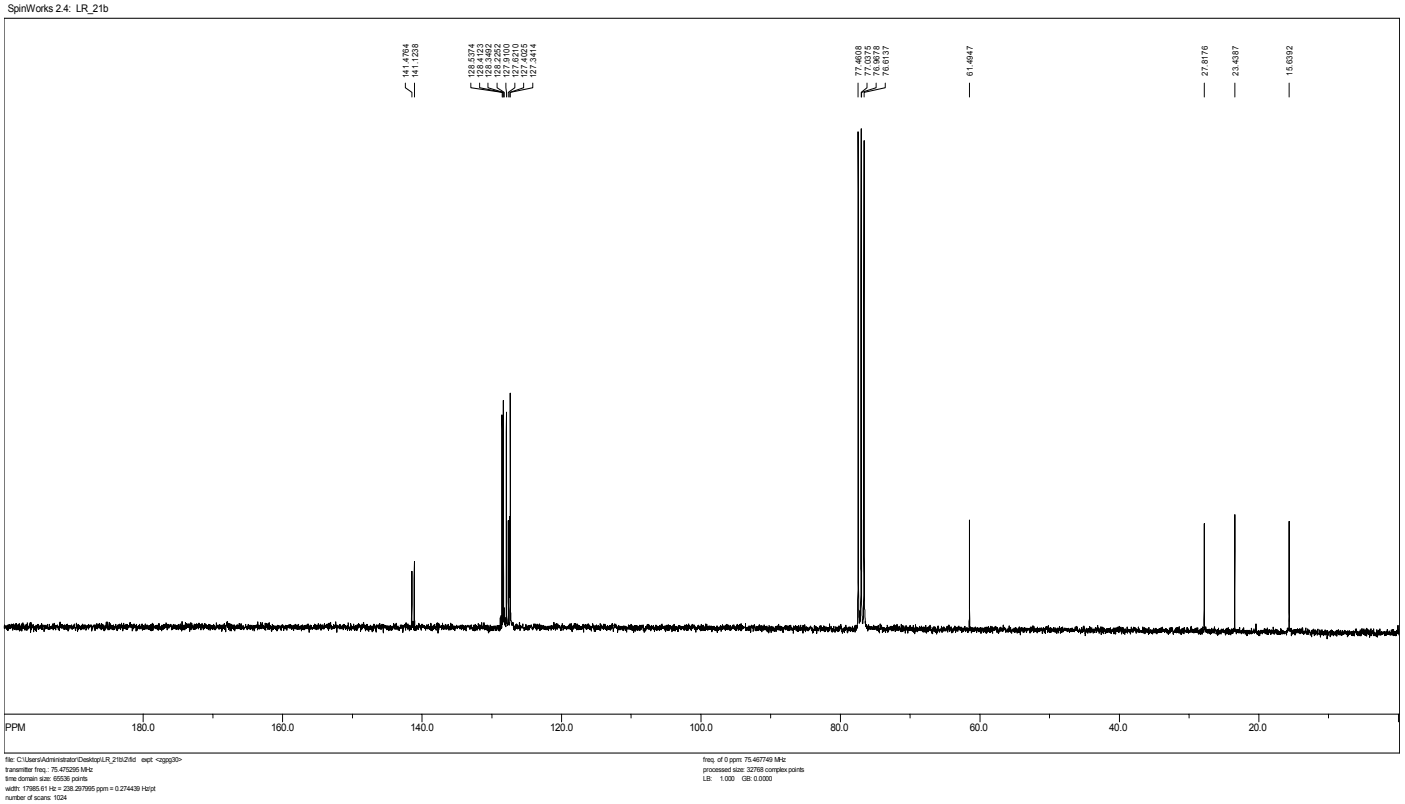


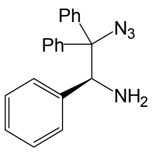



Ph
N3
Ph
NH2

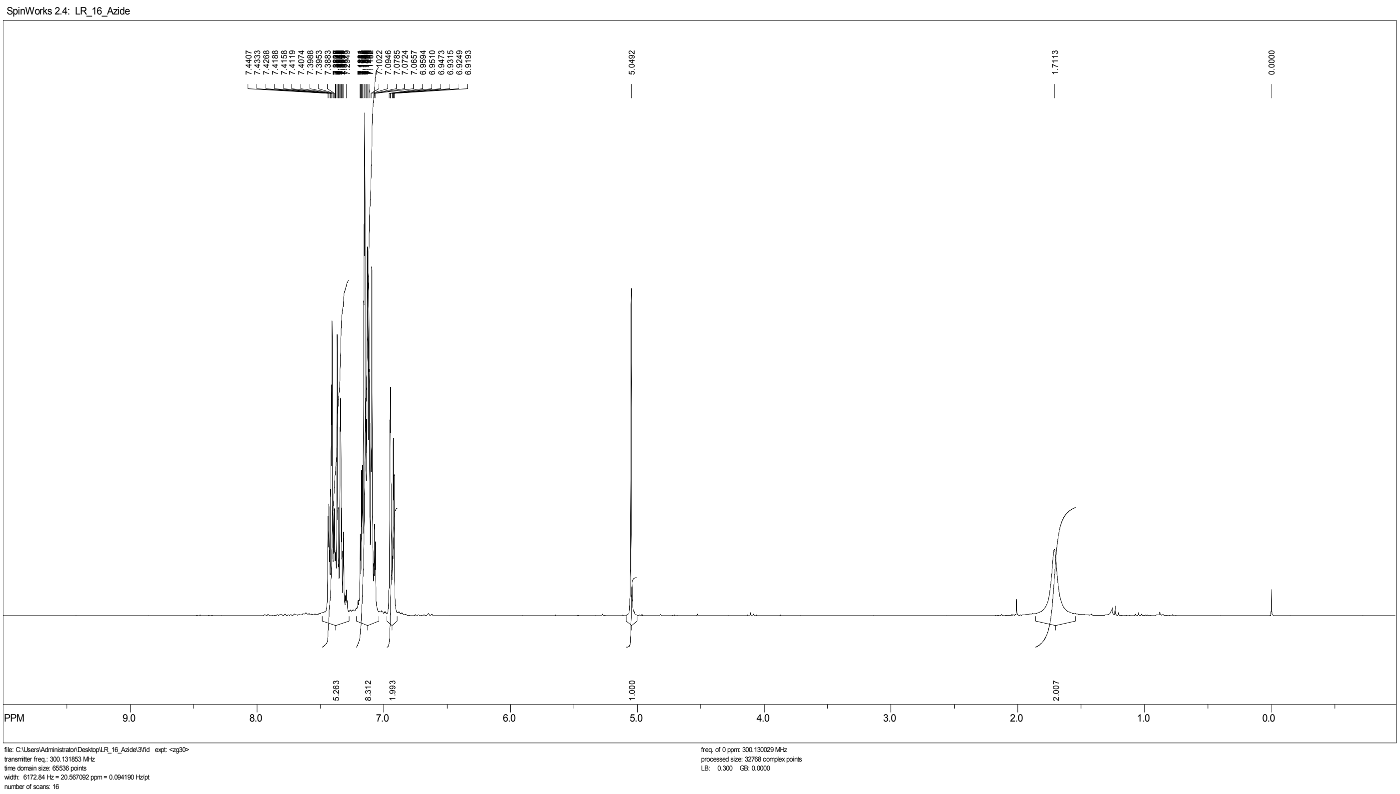
(5b)

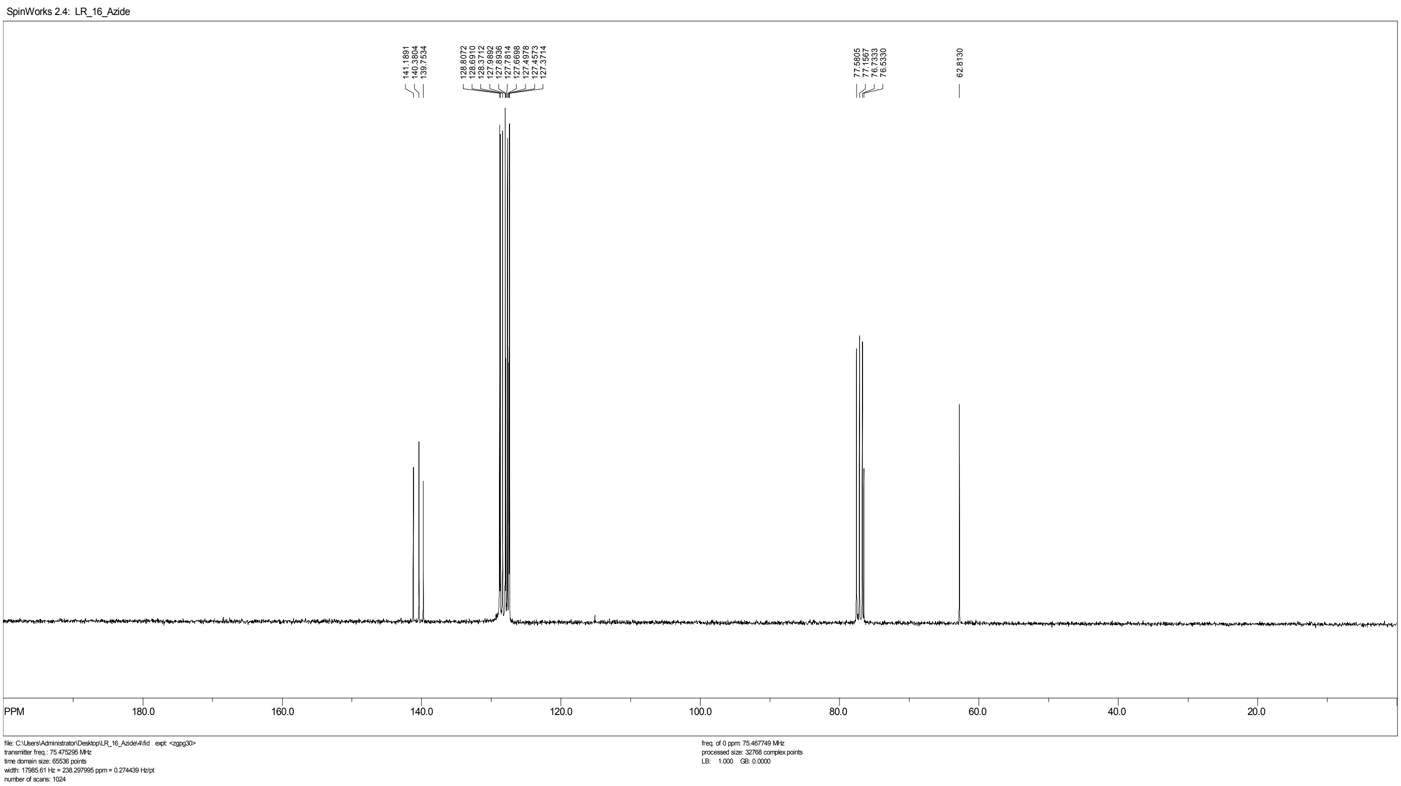

SpinWorks 2.4: LR_5_Azide
7.4721
7.4697
7.4586
7.4428
7.4318
7.4110
7.4004
7.4002
7.3840
7.2285
3.7813
3.7761
1.8631
1.8579
1.8403
1.8351
1.8175
1.7947
1.7896
1.7721
1.7670
1.2190
1.2038
1.2030
1.0030
1.0000
0.5947
0.5723
0.0003
10.45
1.000
1.026
2.027
3.077
3.082
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
file: C:\Users\Administrator\Desktop\ROY NMR\LR_5_Azide\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16
freq. of 0 ppm: 300.130008 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000

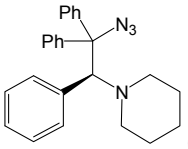

SpinWorks 2.4: LR_21b
141.4764
141.1238
128.5374
128.4123
128.3492
128.2252
128.2000
127.6210
127.4025
127.3414
77.4698
77.0572
76.9678
76.6137
61.4847
27.8176
23.4387
15.6892
PPM
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
file: C:\Users\Administrator\Desktop\LR_21b\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297895 ppm = 0.274439 Hz/pt
number of scans: 1024
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000



(5c)

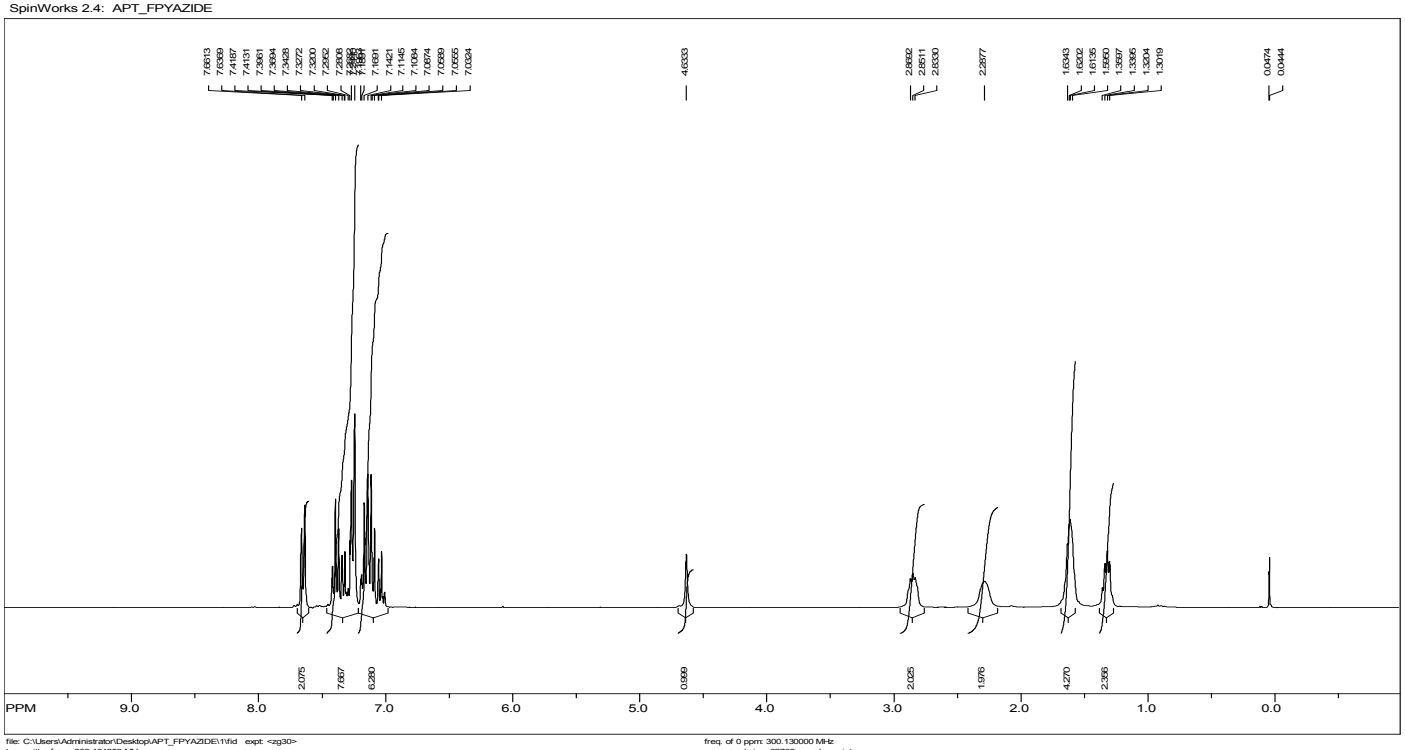

SpinWorks 2.4: LR_16_Azide
7.4407
7.4333
7.4268
7.4188
7.4158
7.4119
7.4074
7.3988
7.3953
7.1022
7.0946
7.0785
7.0724
7.0657
6.9594
6.9510
6.9473
6.9315
6.9249
6.9193
5.0492
1.7113
0.0000
5.263
8.312
1.993
1.000
2.007
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


SpinWorks 2.4: LR_16_Azide
141.1891
140.3804
139.7534
128.8072
128.6910
128.3712
127.9892
127.8936
127.7814
127.6698
127.4978
127.4573
127.3714
77.5805
77.1567
76.7333
76.5330
62.8130
PPM
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0



(5d)

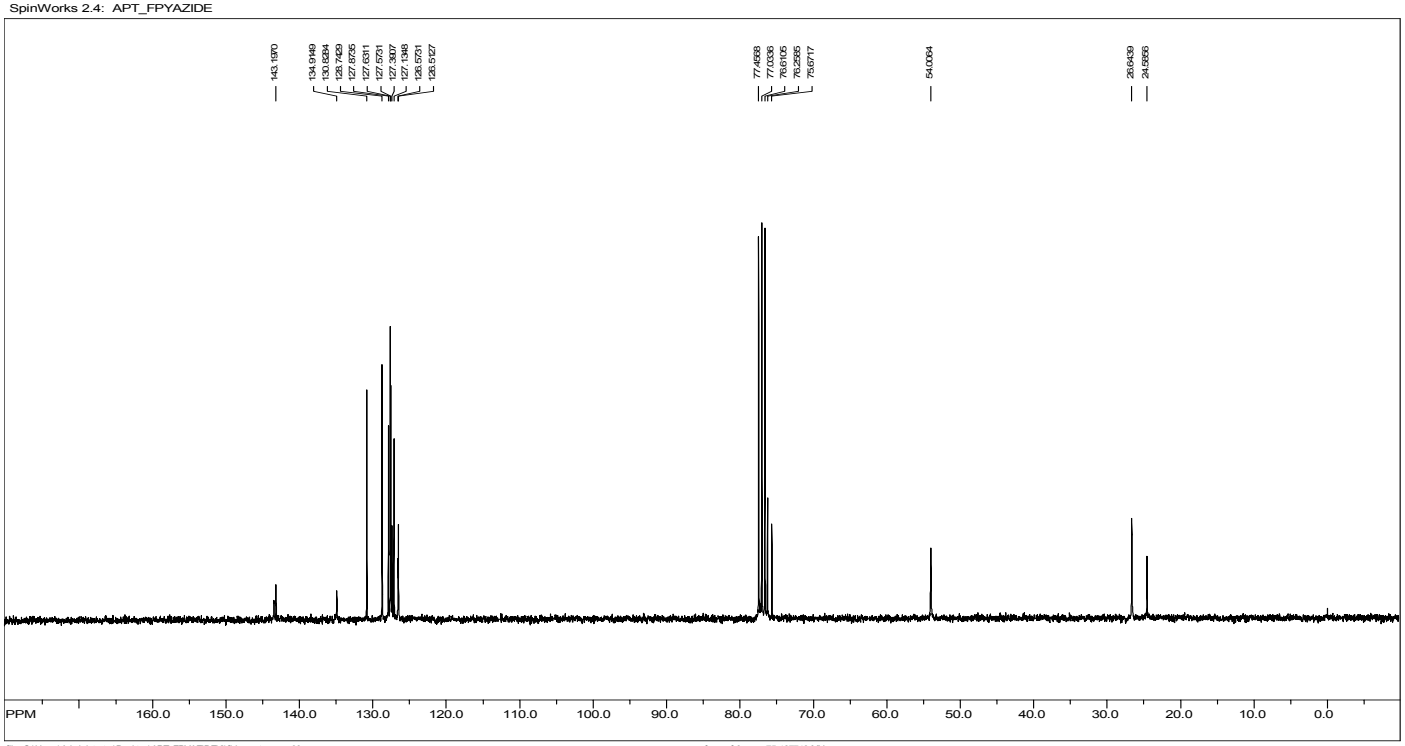
SpinWorks 2.4: APT_FPYAZIDE



file: C:\Users\Administrator\Desktop\APT_FPYAZIDE\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

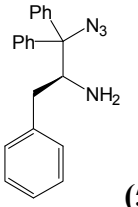
freq. of 0 ppm: 300.130000 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: APT_FPYAZIDE



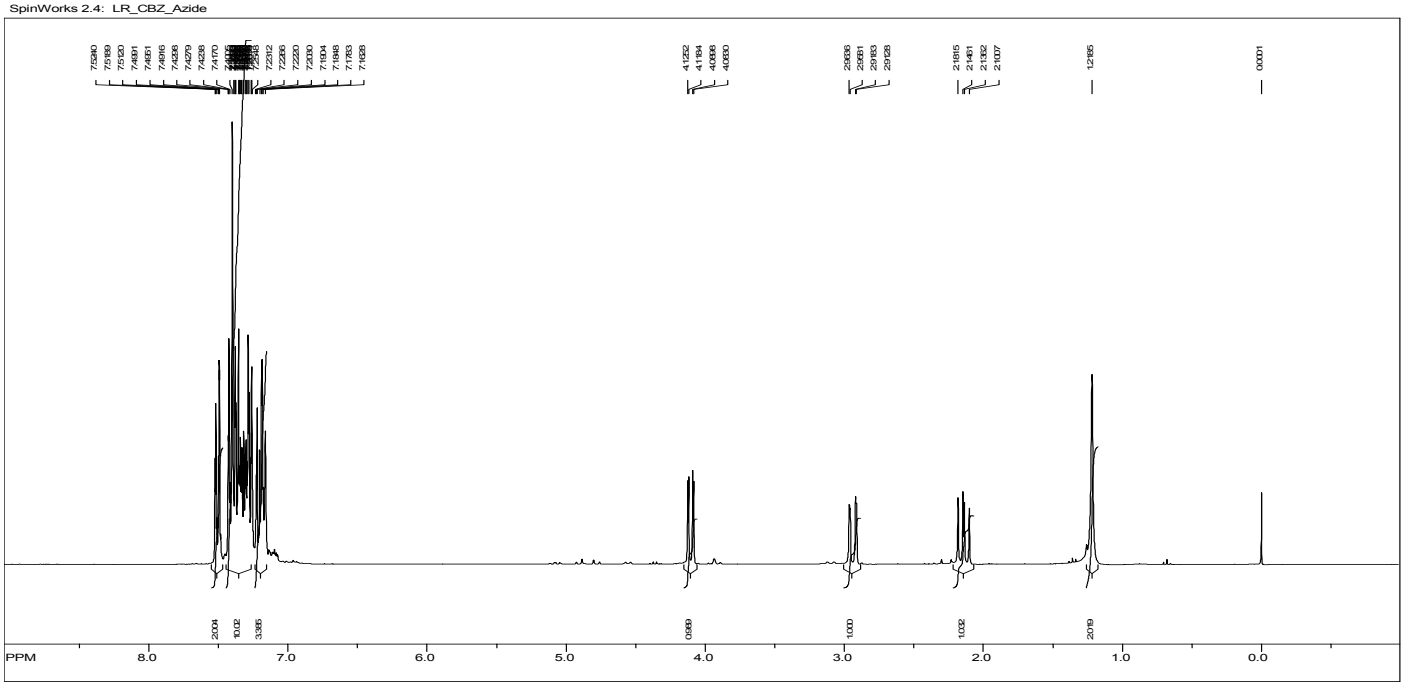
file: C:\Users\Administrator\Desktop\APT_FPYAZIDE\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000



(5e)

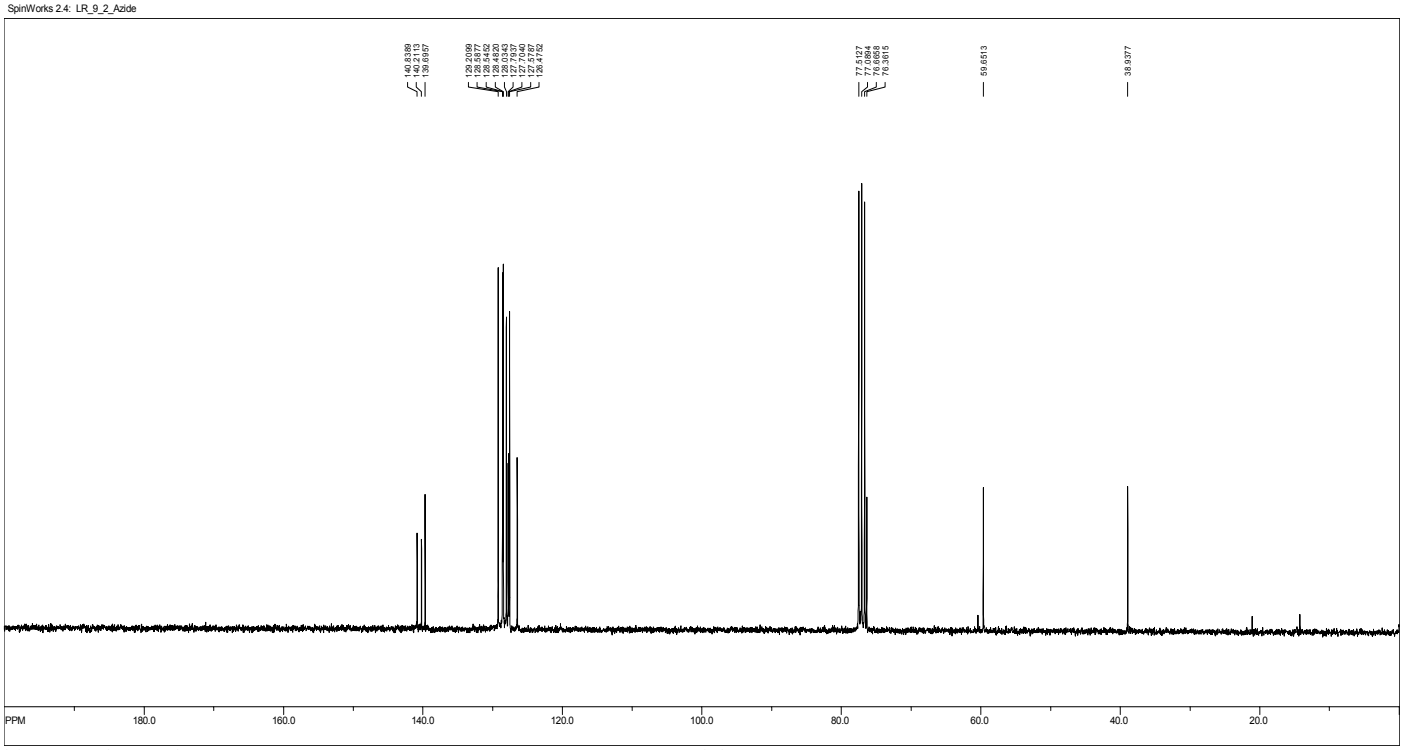
SpinWorks 2.4: LR_CBZ_Azide



file: C:\Users\Administrator\Desktop\LR_CBZ_Azide\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

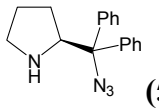
freq. of 0 ppm: 300.130018 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: LR_9_2_Azide



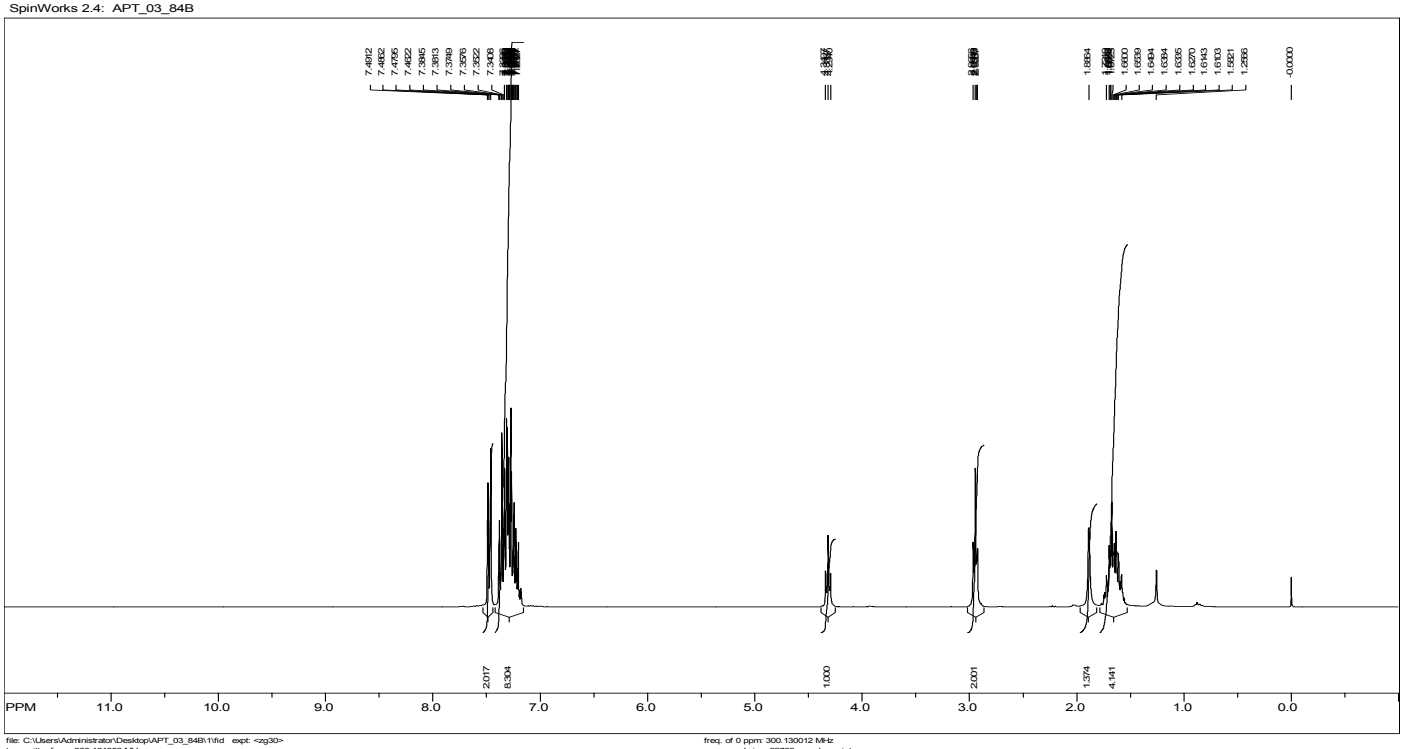
file: C:\Users\Administrator\Desktop\ROY NMR\LR_9_2_Azide\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297695 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000



(5f)

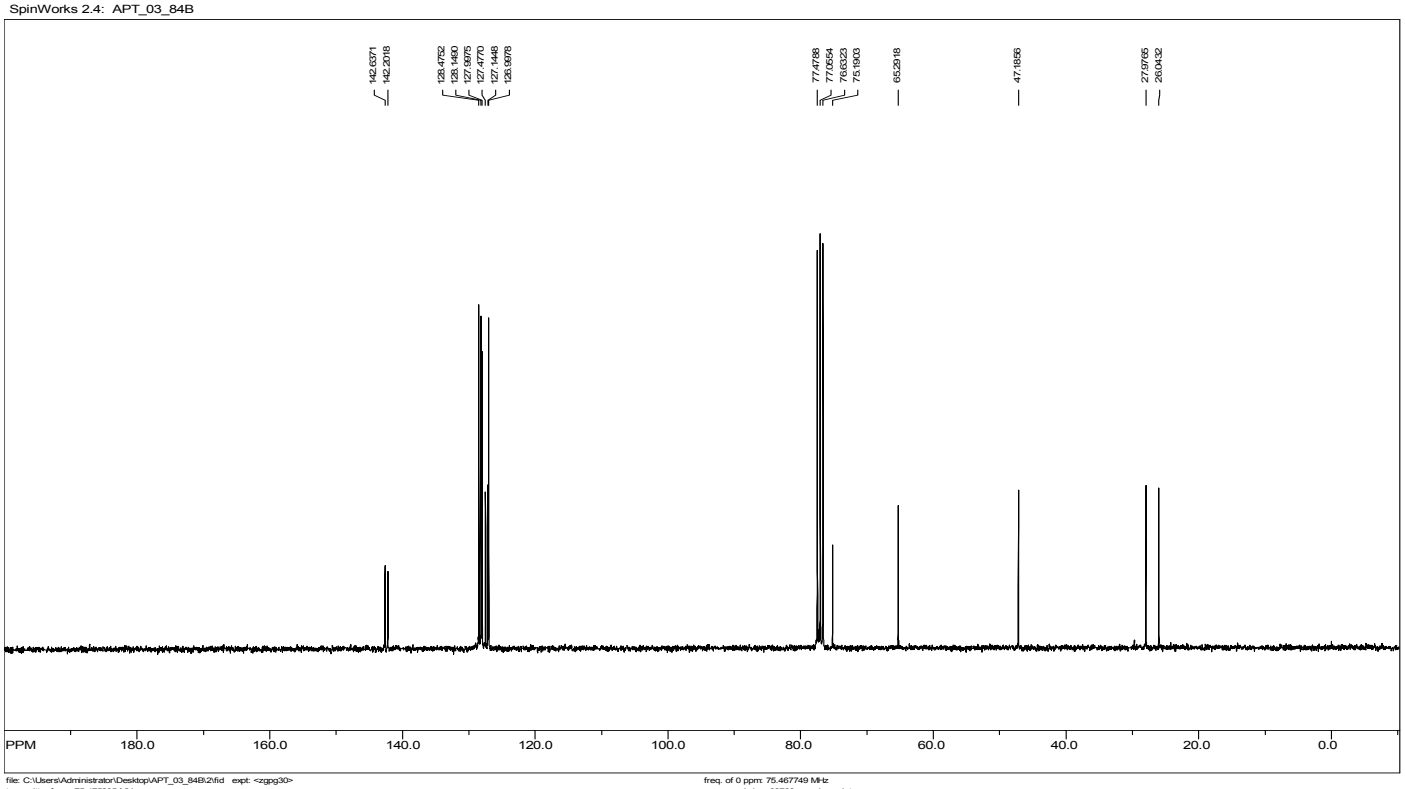
SpinWorks 2.4: APT_03_84B



file: C:\Users\Administrator\Desktop\APT_03_84B\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

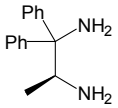
freq. of 0 ppm: 300.130012 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: APT_03_84B



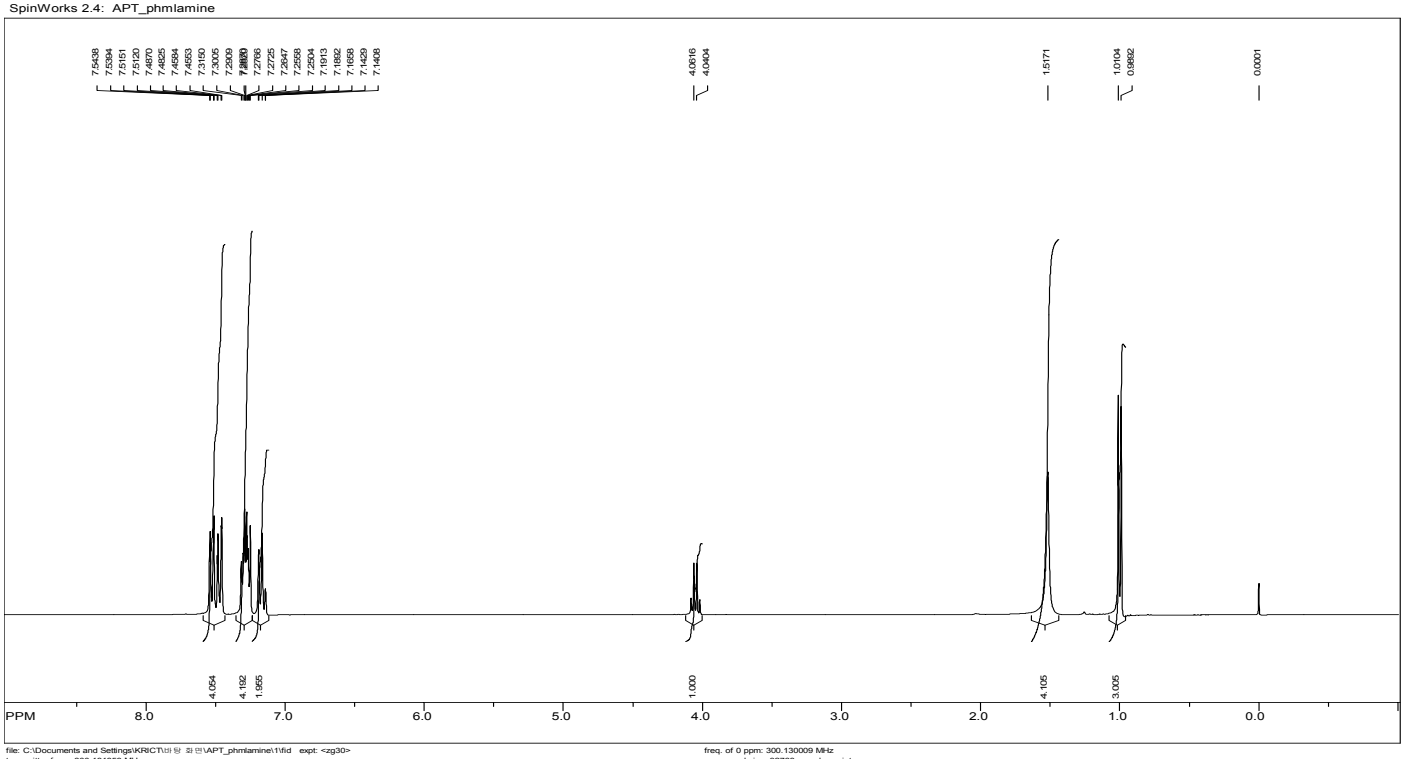
file: C:\Users\Administrator\Desktop\APT_03_84B\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000



(6a)

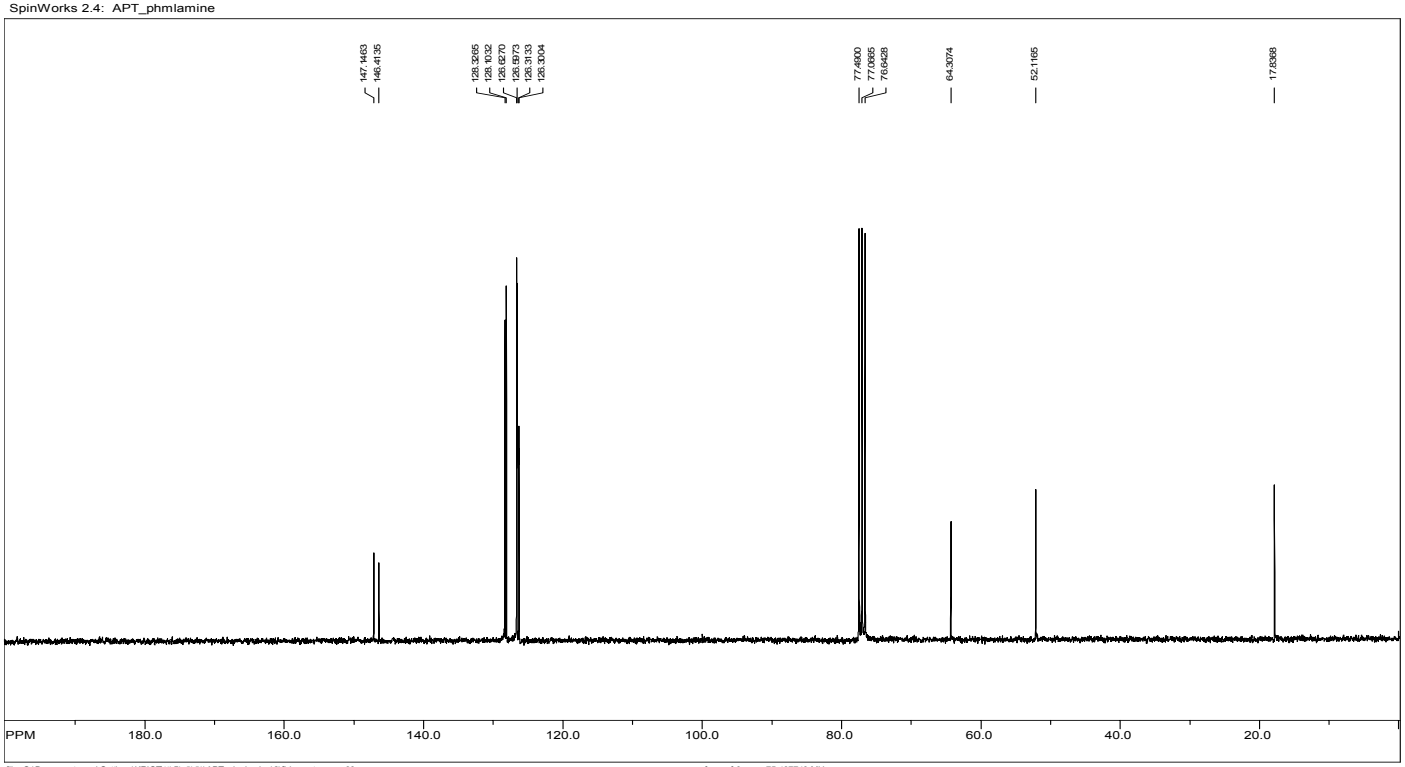
SpinWorks 2.4: APT_phmlamine



file: C:\Documents and Settings\KRICT\바탕 화면\APT_phmlamine\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

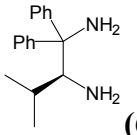
freq. of 0 ppm: 300.130009 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: APT_phmlamine



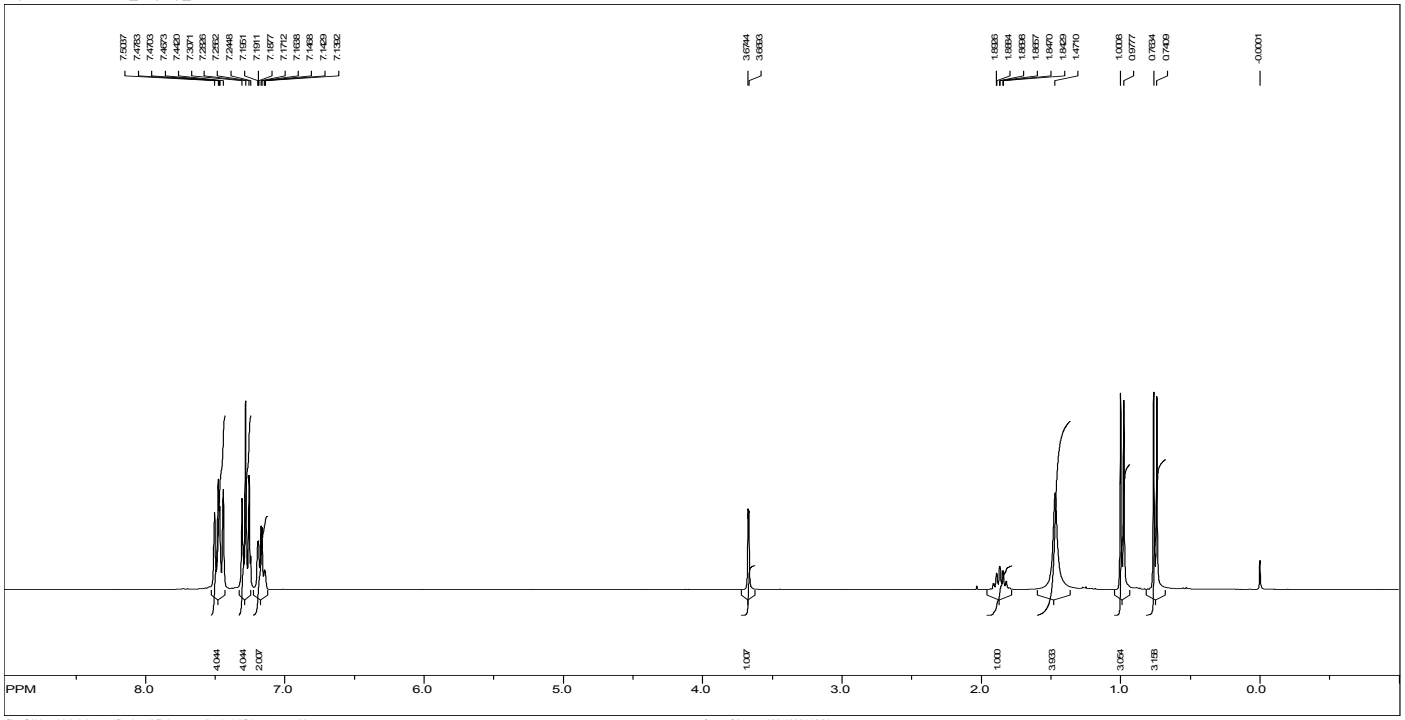
file: C:\Documents and Settings\KRICT\바탕 화면\APT_phmlamine\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000



(6b)

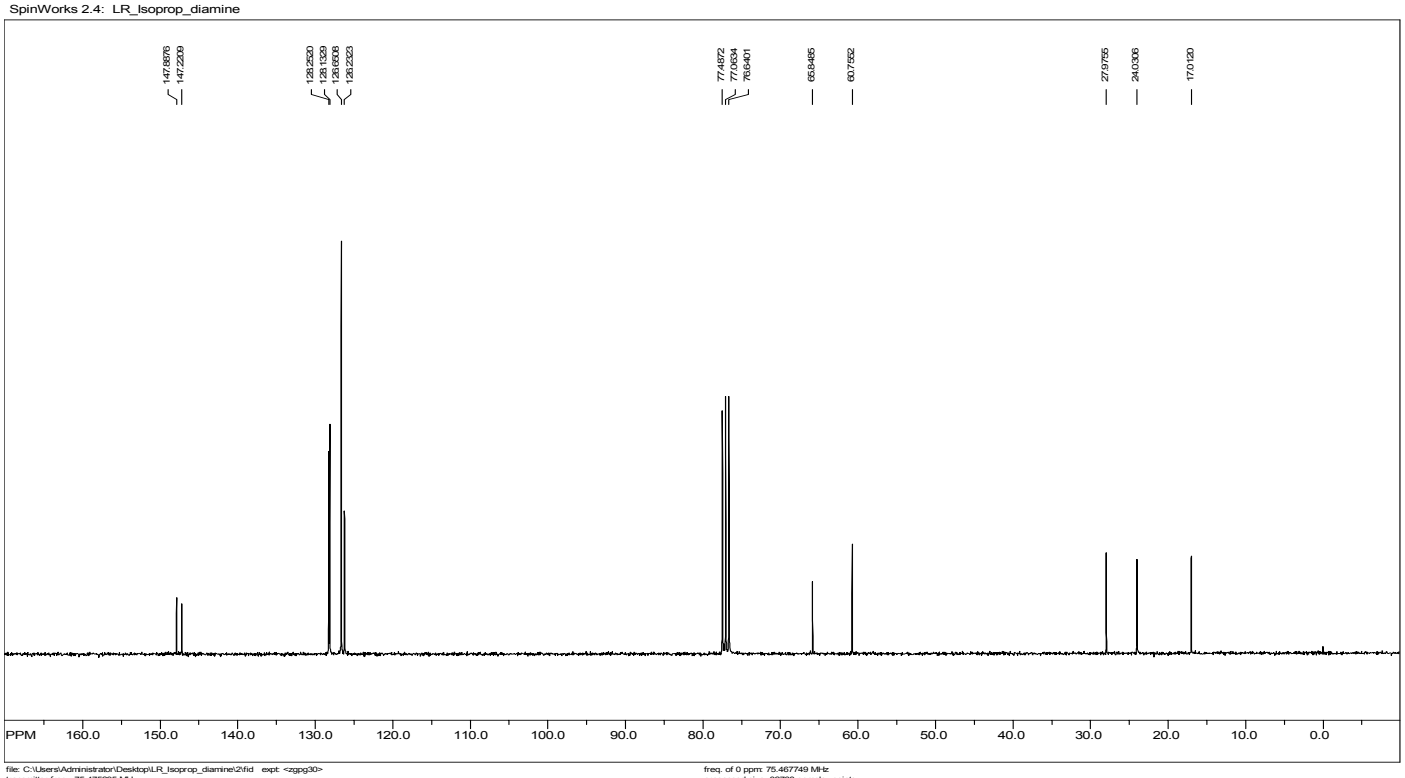
SpinWorks 2.4: LR_Isoprop_diamine



file: C:\Users\Administrator\Desktop\LR_Isoprop_diamine\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

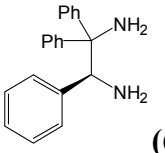
freq. of 0 ppm: 300.130011 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

SpinWorks 2.4: LR_Isoprop_diamine



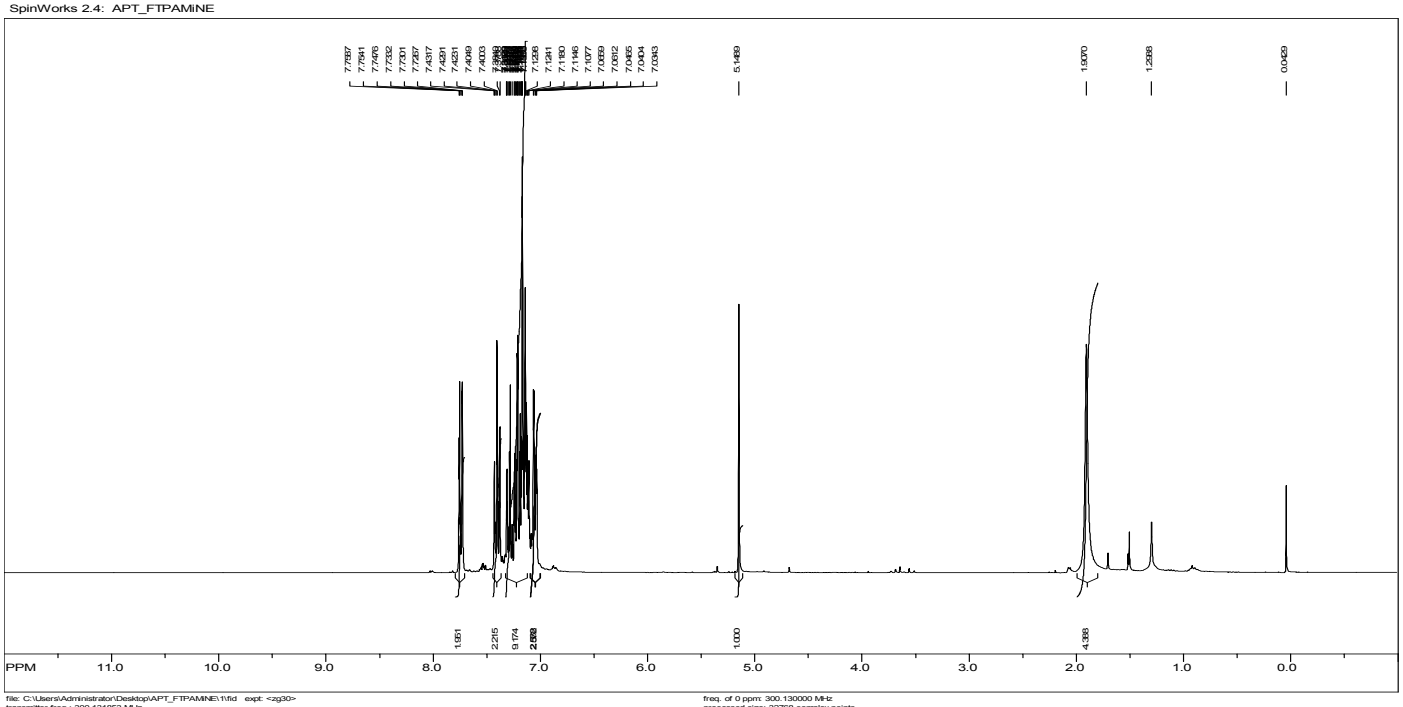
file: C:\Users\Administrator\Desktop\LR_Isoprop_diamine\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000



(6c)

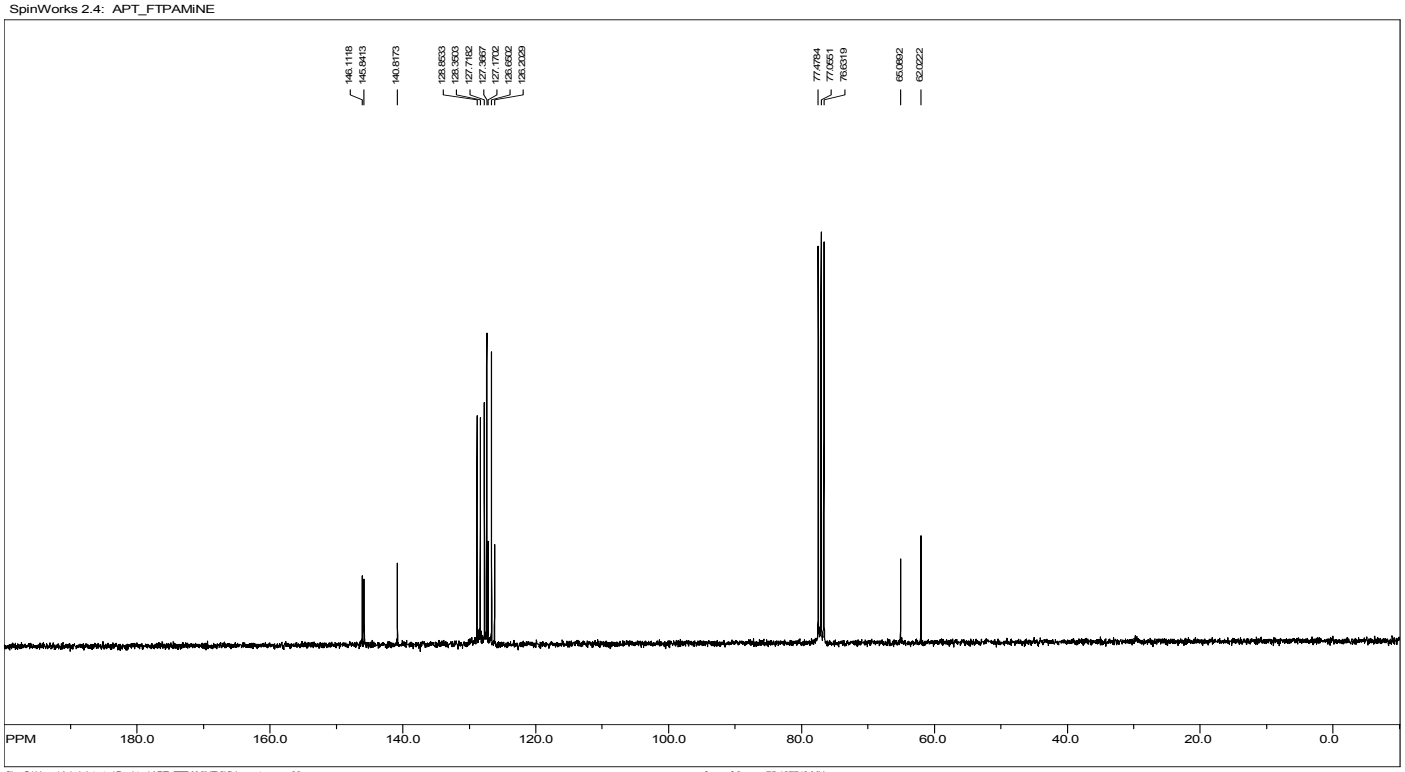
SpinWorks 2.4: APT_FTPAMiNE



file: C:\Users\Administrator\Desktop\APT_FTPAMiNE\1\fid expt: <zg30>
transmitter freq.: 300.131953 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16

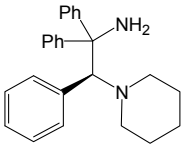
freq. of 0 ppm: 300.130000 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000

SpinWorks 2.4: APT_FTPAMiNE

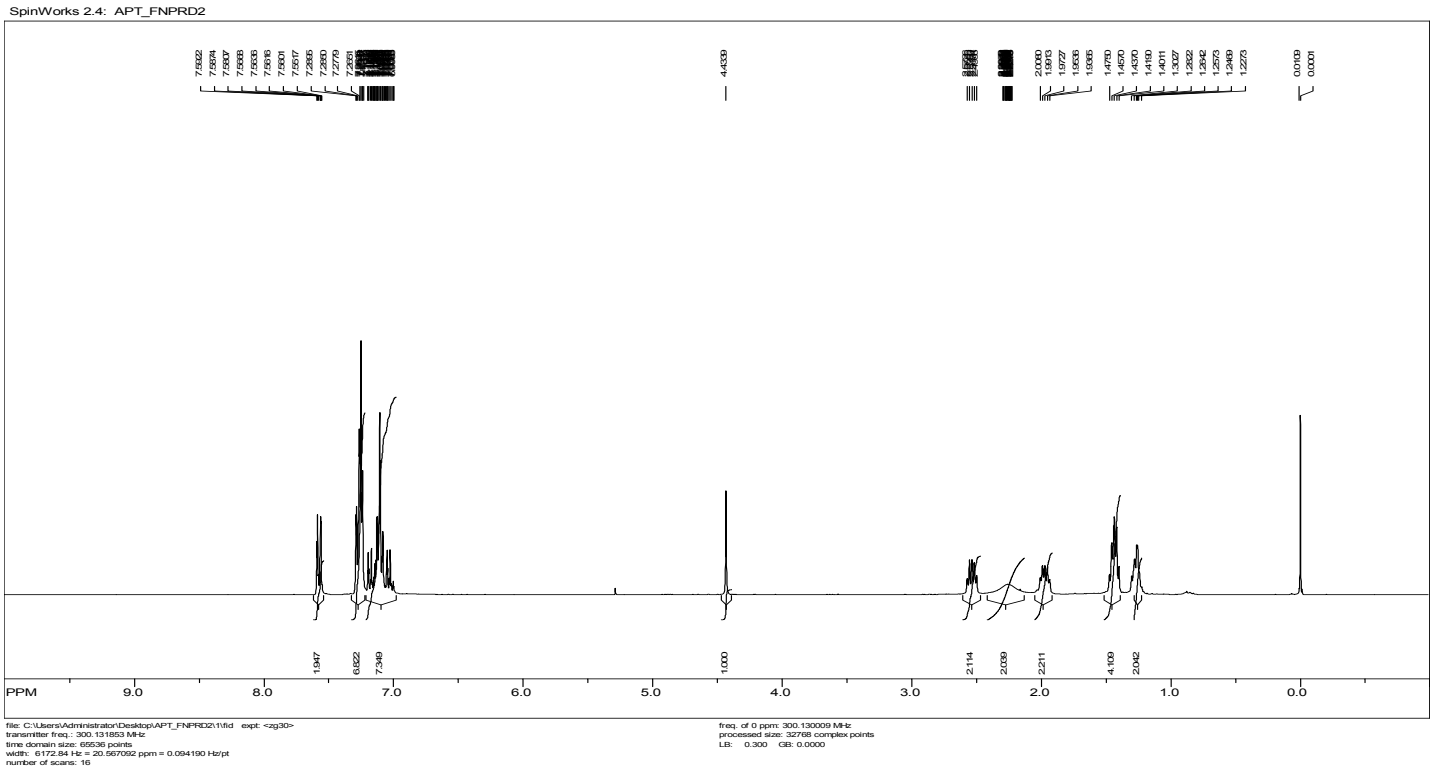


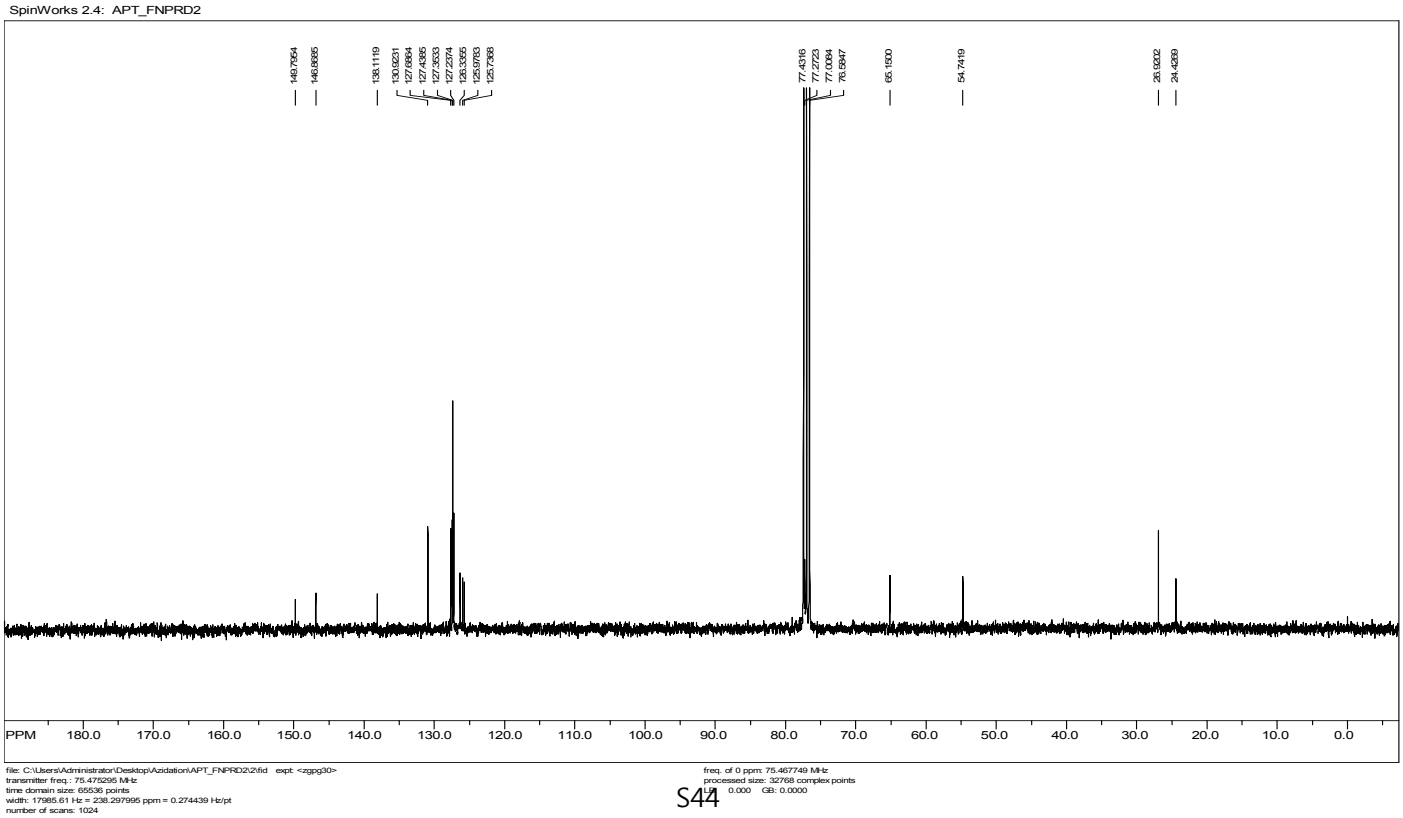
file: C:\Users\Administrator\Desktop\APT_FTPAMiNE\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024

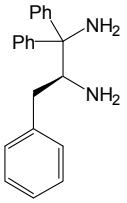
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000


Ph
NH2
Ph
N

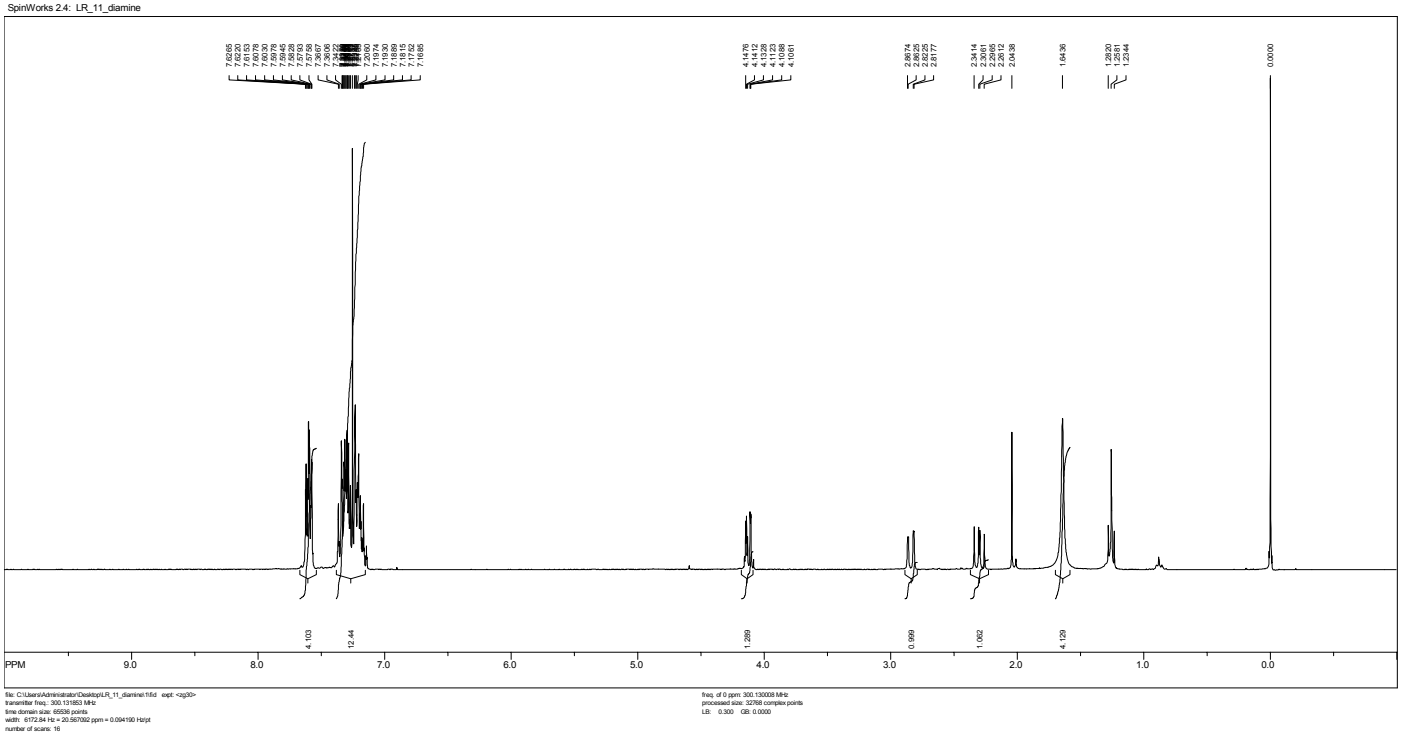
(6d)

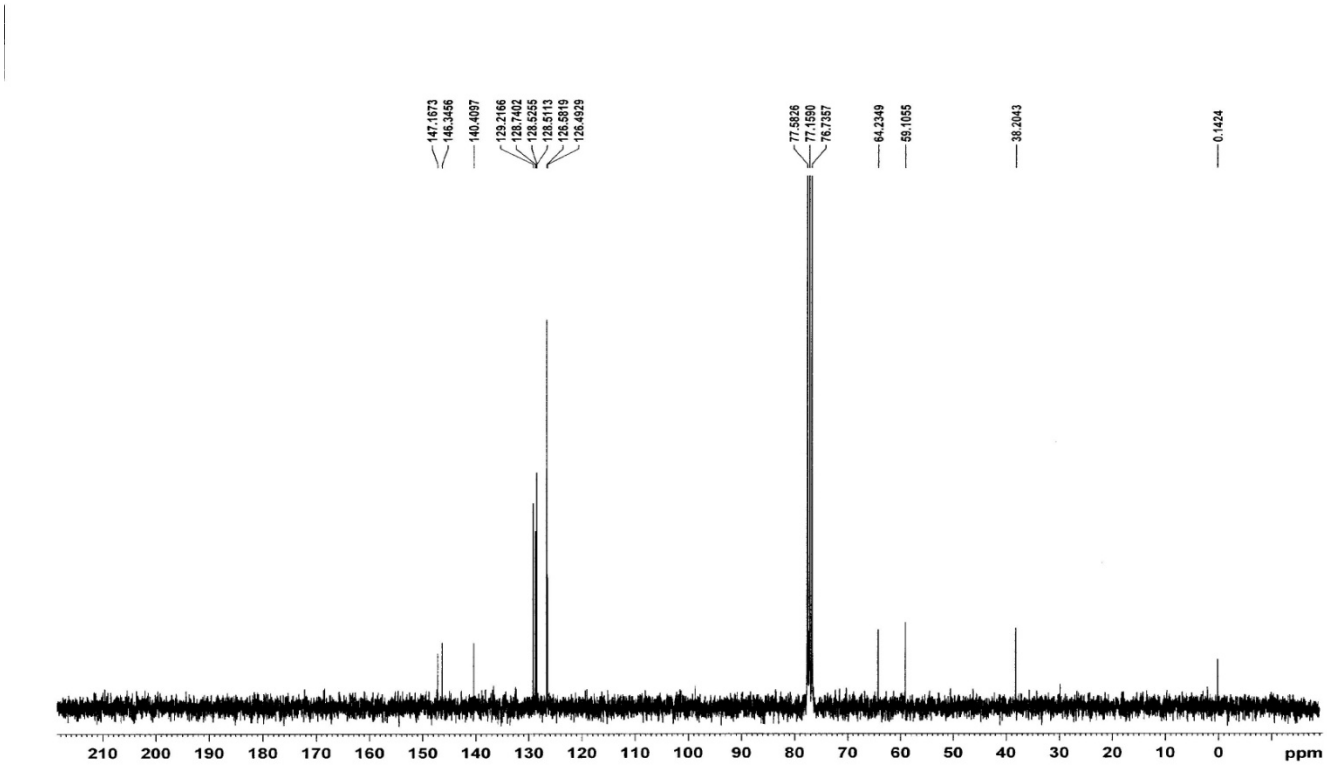

SpinWorks 2.4: APT_FNPRD2
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1.947
6.822
7.349
1.000
2.114
2.039
2.211
4.109
2.042
file: C:\Users\Administrator\Desktop\APT_FNPRD2\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.567092 ppm = 0.094190 Hz/pt
number of scans: 16
freq. of 0 ppm: 300.130009 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

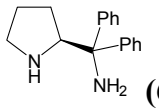

SpinWorks 2.4: APT_FNPRD2
149.7954
146.8885
138.1119
130.0231
127.8864
127.4385
127.2353
127.2274
126.5365
125.9763
125.7368
77.4316
77.2723
77.0084
76.5847
65.1900
54.7419
26.9202
24.4269
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
file: C:\Users\Administrator\Desktop\Azidation\APT_FNPRD2\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1024
freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000


Ph
NH2
Ph
NH2

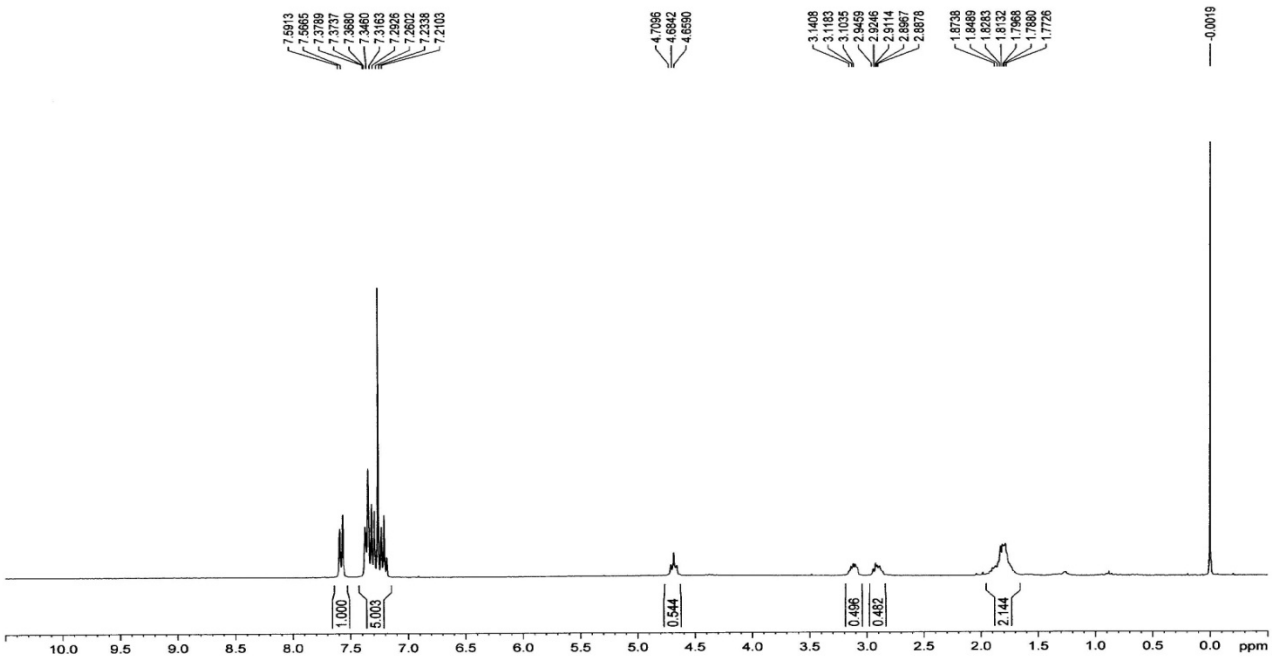
(6e)

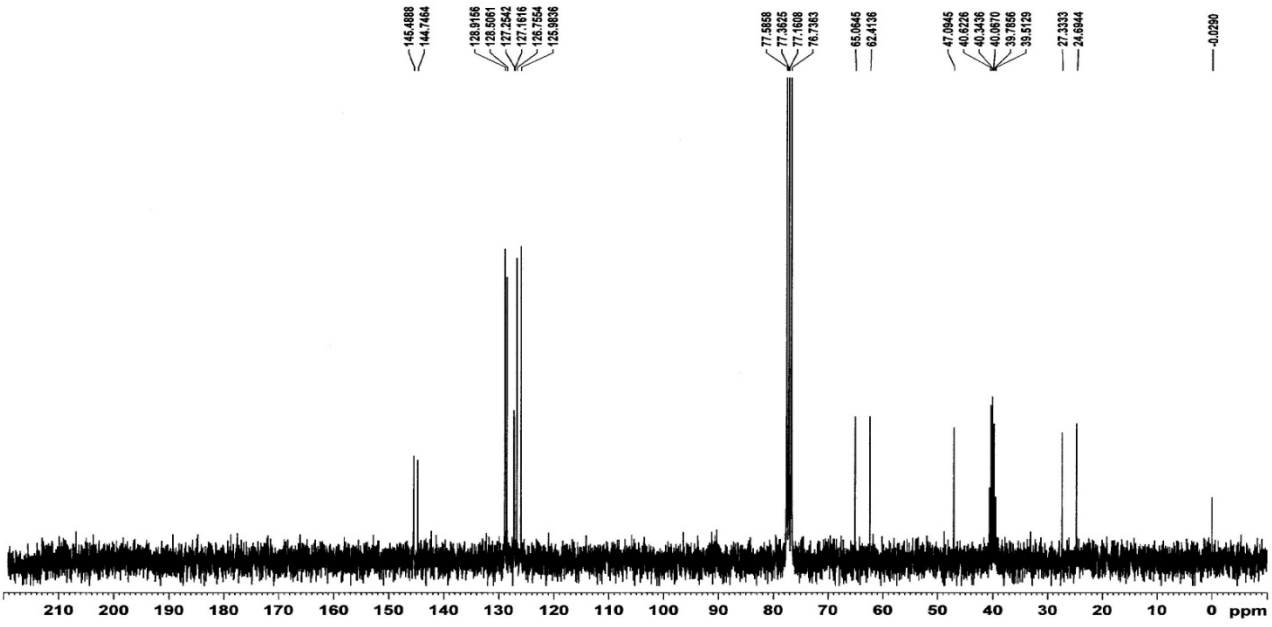

SpinWorks 2.4: LR_11_diamine
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


147.1673
146.3456
140.4097
129.2166
128.7402
128.5255
128.5113
126.5819
126.4929
77.5826
77.1590
76.7357
64.2349
59.1055
38.2043
0.1424
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Ph
Ph
N
H
NH2

(6f)


7.5913
7.5865
7.3789
7.3737
7.3680
7.3460
7.3163
7.2926
7.2802
7.2338
7.2103
4.7096
4.6842
4.6590
3.1408
3.1183
3.1035
2.9459
2.9246
2.9114
2.8897
2.8878
1.8738
1.8489
1.8283
1.8132
1.7968
1.7880
1.7726
-0.0019
1.000
5.003
0.544
0.496
0.462
2.144
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


145.4888
144.7464
128.9166
128.5061
127.2542
127.1616
126.7554
125.9636
77.5858
77.3625
77.1608
76.7363
65.0645
62.4136
47.0945
40.8226
40.3436
40.0670
39.7856
39.5129
27.3333
24.6944
-0.0290
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm