Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Nitrenium Ions as New Versatile Reagents for Electrophilic Amination

*Idan Avigdori‡, Kuldeep Singh‡, Natalia Fridman, Mark Gandelman**

*Corresponding author: chmark@technion.ac.il

‡These authors contributed equally to this study

Schulich Faculty of Chemistry, Technion - Israel Institute of Technology,
Technion City, Haifa 32000, Israel

Table of Contents

1. General Information

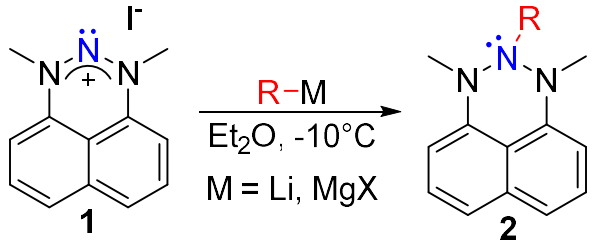
Oxygen- and moisture-sensitive reactions were carried out under an atmosphere of purified nitrogen in a glovebox equipped with an inert gas purifier. However, the electrophilic amination method presented here can also be utilized in a one-pot procedure without the isolation of the triazane intermediate. In this case, the procedure is carried out in a fume hood under inert conditions – using standard Schlenk techniques (as a standard protocol for working with organolithium or Grignard reagents). DCM, THF, Et_2O, hexane and toluene were purified by passing through a column of an activated alumina under inert atmosphere. Anhydrous MeCN, heptane and MeOH packed under inert gas (argon) were used as purchased. All commercially available reagents were used as received, except for 1,8-diaminonaphthalene which was distilled before use. All organomagnesium (Grignard) reagents used were commercially available and were used as received. 1-Adamantyl-lithium was prepared according to a literature procedure.[1] Aryl-lithium reagents were prepared according to a literature procedure.[2] Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F-254 plates (particle size 0.040-0.055 mm, 230-400 mesh). NMR spectra were recorded on either a Bruker Avance300, Bruker AVII400, or on a Bruker AVIII600 spectrometer at 296K, unless mentioned otherwise. All chemical shifts (δ) are reported in parts per million (ppm) and the residual solvent peak was used as an internal standard for $^{1}H/^{13}C$ NMR: CD_2Cl_2: δ=5.32/53.84; $CDCl_3$: δ=7.26/77.16; DMSO-d6: δ=2.50/39.52. ^{19}F, ^{31}P, ^{11}B and ^{15}N NMR signals were referenced to $CFCl_3$, 85% H_3PO_4 in H_2O, $BF_3{\cdot}Et_2O$ and CH_3NO_2, respectively. NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sept = septet, m = multiplet, b = broad), coupling constant(s) (Hz) and integration. High resolution mass spectrometry (HRMS) analyses were conducted on Waters HPLC Acquity - Waters LCT Premier system, using an electrospray ionization (ESI+) technique (conditions: MeCN/H_2O (80/20), flow rate: 0.2 ml/min), or on Bruker Maxis Impact system, using an atmospheric-pressure chemical ionization (APCI+) solid probe.

2. Experimental procedures

Preparation of *1N,3N*-dimethylnaphthotriazinium iodide (NHN **1**):

NHN **1** and the ^{15}N-labelled NHN **1'** were prepared according to a literature procedure.[3]

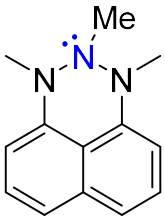
General procedure for the preparation of triazanes:



Scheme S1. Preparation of triazanes from NHN **1**.

Within a glovebox containing nitrogen atmosphere, NHN **1** (0.1 g, 0.308 mmol) was loaded into a 20 ml vial, and then Et_2O was added (4 ml) and the vial was cooled to -10°C. The desired organolithium or Grignard reagent solution (1.1 equiv., 0.338 mmol) was cooled to -10°C as well, and then added dropwise to the vial while stirring. The type of organometallic reagent (RLi or RMgBr) was chosen either for reasons of commercial availability, or for ease of preparation, thus most of the aryl nucleophiles were chosen to be aryl-lithium reagents (prepared using *n*-BuLi and an aryl-iodide derivative).[2] Organolithium and Grignard reagents procured from commercial sources were used directly, while organolithium reagents prepared by us were dissolved in Et_2O (1 ml) before use. The reaction mixture was stirred for 10 minutes while allowing it to reach room temperature, and then the solvent was evaporated. Hexane (2 ml x 5) was then added to the residual solids and the resulting suspension was passed through a pad of Celite. The solvent was evaporated, and the crude triazane product was recrystallized from a hexane or heptane solution.

1*N*,2*N*,3*N*-Trimethylnaphthotriazane **2a**

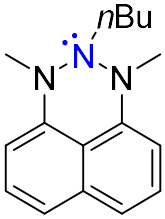


^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.38 (dd, $^3J_{H,H}$=8.3 Hz, $^3J_{H,H}$=7.3 Hz, 2H; Ar-H), 7.33 (dd, $^3J_{H,H}$=8.3 Hz, $^4J_{H,H}$=0.9 Hz, 2H; Ar-H), 6.64 (dd, $^3J_{H,H}$=7.3 Hz, $^4J_{H,H}$=0.9 Hz, 2H; Ar-H), 3.09 (s, 6H; flanking CH_3), 2.40 (s, 3H; central CH_3); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=140.7 (Ar-C),

134.0 (Ar-C), 127.3 (Ar-C), 119.6 (Ar-C), 115.6 (Ar-C), 108.7 (Ar-C), 40.2 (flanking *C*H_3), 36.0 (central *C*H_3).

HRMS (APCI): calc. for $C_{13}H_{16}N_3^+$ [(M+H)$^+$]: 214.1339, found: 214.1326.

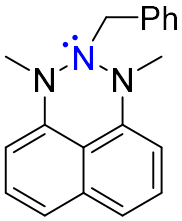
1*N*,3*N*-Dimethyl-2*N*-butylnaphthotriazane **2b**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.38 (dd, $^3J_{H,H}$=8.3 Hz, $^3J_{H,H}$=7.3 Hz, 2H; Ar-H), 7.33 (dd, $^3J_{H,H}$=8.3 Hz, $^4J_{H,H}$=0.9 Hz, 2H; Ar-H), 6.66 (dd, $^3J_{H,H}$=7.3 Hz, $^4J_{H,H}$=0.9 Hz, 2H; Ar-H), 3.15 (s, 6H; flanking C*H*$_3$), 2.58 (t, $^3J_{H,H}$=7.0 Hz, 2H; N-C*H*$_2$), 1.57-1.51 (m, 2H; C*H*$_2$), 1.39-1.32 (m, 2H; C*H*$_2$), 0.92 (t, $^3J_{H,H}$=7.4 Hz, 3H; C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=141.0 (Ar-C), 134.1 (Ar-C), 127.2 (Ar-C), 119.4 (Ar-C), 116.3 (Ar-C), 109.0 (Ar-C), 50.5 (N-*C*H_2), 41.5 (flanking *C*H_3), 29.8 (*C*H_2), 20.8 (*C*H_2), 14.3 (*C*H_3).

HRMS (APCI): calc. for $C_{16}H_{22}N_3^+$ [(M+H)$^+$]: 256.1808, found: 256.1800.

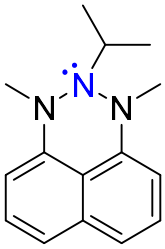
1*N*,3*N*-Dimethyl-2*N*-benzylnaphthotriazane **2c**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.41 (t, $^3J_{H,H}$=7.7 Hz, 2H; Ar-H), 7.38 (d, $^3J_{H,H}$=8.1 Hz, 2H; Ar-H), 7.34-7.30 (m, 2H; Ar-H), 7.30-7.26 (m, 3H; Ar-H), 6.66 (d, $^3J_{H,H}$=7.1 Hz, 2H; Ar-H), 3.72 (s, 2H; C*H*$_2$) 3.07 (s, 6H; flanking C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=140.7 (Ar-C), 138.1 (Ar-C), 134.2 (Ar-C), 129.8 (Ar-C), 128.4 (Ar-C), 127.4 (Ar-C), 127.3 (Ar-C), 119.6 (Ar-C), 116.2 (Ar-C), 109.0 (Ar-C), 54.9 (N-*C*H_2), 41.4 (flanking *C*H_3).

HRMS (APCI): calc. for $C_{19}H_{20}N_3^+$ [(M+H)$^+$]: 290.1652, found: 290.1643.

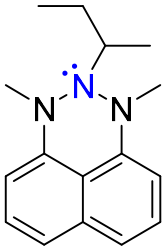
1*N*,3*N*-Dimethyl-2*N*-isopropylnaphthotriazane **2d**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.32 (dd, $^{3}J_{H,H}$=8.3 Hz, $^{3}J_{H,H}$=7.3 Hz, 2H; Ar-H), 7.23 (dd, $^{3}J_{H,H}$=8.3 Hz, $^{4}J_{H,H}$=0.9 Hz, 2H; Ar-H), 6.58 (dd, $^{3}J_{H,H}$=7.3 Hz, $^{4}J_{H,H}$=0.9 Hz, 2H; Ar-H), 3.20 (s, 6H; flanking C*H*$_3$), 2.96 (sept, $^{3}J_{H,H}$=6.2 Hz, 1H; C*H*), 1.02 (d, $^{3}J_{H,H}$=6.2 Hz, 6H; C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=140.7 (Ar-C), 134.5 (Ar-C), 127.3 (Ar-C), 118.7 (Ar-C), 116.6 (Ar-C), 108.3 (Ar-C), 55.4 (N-*C*H), 44.6 (flanking *C*H$_3$), 20.6 (*C*H$_3$).

HRMS (APCI): calc. for $C_{15}H_{20}N_3^+$ [(M+H)$^+$]: 242.1652, found: 242.1666.

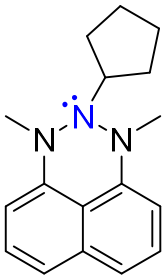
1*N*,3*N*-Dimethyl-2*N*-*sec*-butylnaphthotriazane **2e**



^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm)=7.35 (t, $^{3}J_{H,H}$=7.6 Hz, 2H; Ar-H), 7.29 (d, $^{3}J_{H,H}$=8.1 Hz, 1H; Ar-H), 7.25 (d, $^{3}J_{H,H}$=8.1 Hz, 1H; Ar-H), 6.64 (d, $^{3}J_{H,H}$=7.2 Hz, 1H; Ar-H), 6.55 (d, $^{3}J_{H,H}$=7.3 Hz, 1H; Ar-H), 3.27 (s, 3H; flanking C*H*$_3$), 3.20 (s, 3H; flanking C*H*$_3$), 2.90-2.83 (m, 1H; C*H*), 1.65-1.56 (m, 1H; C*H*$_2$), 1.50-1.41 (m, 1H; C*H*$_2$), 0.99 (d, $^{3}J_{H,H}$=6.4 Hz, 3H; C*H*$_3$) , 0.83 (d, $^{3}J_{H,H}$=7.5 Hz, 3H; C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ(ppm)=140.8 (Ar-C), 140.3 (Ar-C), 134.2 (Ar-C), 127.1 (Ar-C), 127.0 (Ar-C), 119.2 (Ar-C), 118.1 (Ar-C), 116.5 (Ar-C), 109.5 (Ar-C), 106.9 (Ar-C), 60.6 (N-*C*H), 44.8 (flanking *C*H$_3$), 44.3 (flanking *C*H$_3$), 26.5 (*C*H$_2$), 16.6 (*C*H$_3$), 9.7 (*C*H$_3$).

HRMS (APCI): calc. for $C_{16}H_{22}N_3^+$ [(M+H)$^+$]: 256.1808, found: 256.1799.

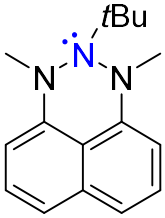
1*N*,3*N*-Dimethyl-2*N*-cyclopentylnaphthotriazane **2f**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.33 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 7.25 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 6.59 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 3.24 (quin, $^{3}J_{H,H}$=7.0 Hz, 1H; N-C*H*), 3.21 (s, 6H; flanking C*H*$_3$), 1.69-1.60 (m, 6H; C*H*$_2$), 1.41-1.32 (m, 2H; C*H*$_2$); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=140.8 (Ar-C), 134.4 (Ar-C), 127.3 (Ar-C), 118.8 (Ar-C), 116.7 (Ar-C), 108.6 (Ar-C), 66.1 (N-*C*H), 44.1 (flanking *C*H$_3$), 30.9 (*C*H$_2$), 23.9 (*C*H$_2$).

HRMS (APCI): calc. for $C_{17}H_{22}N_3^+$ [(M+H)$^+$]: 268.1808, found: 268.1800.

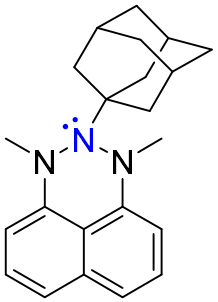
1*N*,3*N*-Dimethyl-2*N*-*tert*-butylnaphthotriazane **2g**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.29 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 7.17 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 6.61 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 3.30 (s, 6H; flanking C*H*$_3$), 0.97 (s, 9H; C(C*H*$_3$)$_3$); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=144.3 (Ar-C), 134.4 (Ar-C), 127.1 (Ar-C), 118.3 (Ar-C), 117.3 (Ar-C), 108.0 (Ar-C), 65.0 (N-*C*(CH$_3$)$_3$), 48.3 (flanking *C*H$_3$), 26.9 (C(*C*H$_3$)$_3$).

HRMS (APCI): calc. for $C_{16}H_{22}N_3^+$ [(M+H)$^+$]: 256.1808, found: 256.1823.

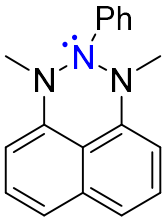
1*N*,3*N*-Dimethyl-2*N*-adamantylnaphthotriazane **2h**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.33-7.28 (m, 2H; Ar-H), 7.21-7.16 (m, 2H; Ar-H), 6.65-6.59 (m, 2H; Ar-H), 3.32 (s, 6H; flanking C*H*$_3$), 1.94-1.88 (m, 1H; adamantyl), 1.66-1.63 (m, 2H; adamantyl), 1.57-1.48 (m, 2H; adamantyl), 1.43-1.38 (m, 4H; adamantyl), 0.99 (s, 6H; adamantyl); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=144.3 (Ar-C), 134.4 (Ar-C), 127.1 (Ar-C), 118.3 (Ar-C), 117.3 (Ar-C), 108.1 (Ar-C), 65.0 (N-*C*), 48.4 (flanking *C*H$_3$), 40.0 (adamantyl), 37.0 (adamantyl), 30.1 (adamantyl), 26.9 (adamantyl).

HRMS (APCI): calc. for $C_{22}H_{27}N_3^+$ [(M+H)$^+$]: 334.2278, found: 334.2245.

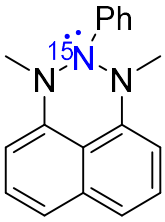
1*N*,3*N*-Dimethyl-2*N*-phenylnaphthotriazane **2i**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.37 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 7.30 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 7.16-7.09 (m, 4H; Ar-H), 6.86-6.80 (m, 3H; Ar-H), 3.44 (s, 6H; flanking C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=151.4 (Ar-C), 141.8 (Ar-C), 134.8 (Ar-C), 129.0 (Ar-C), 127.1 (Ar-C), 122.4 (Ar-C), 120.0 (Ar-C), 117.6 (Ar-C), 116.7 (Ar-C), 109.4 (Ar-C), 43.5 (flanking *C*H$_3$).

HRMS (APCI): calc. for $C_{18}H_{18}N_3^+$ [(M+H)$^+$]: 276.1495, found: 276.1489.

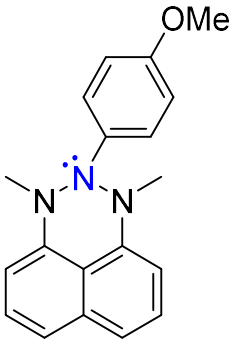
1*N*,3*N*-Dimethyl-2*N*-phenylnaphthotriazane (2-^{15}N) **2i'**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.34 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 7.27 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 7.13-7.06 (m, 4H; Ar-H), 6.83-6.77 (m, 3H; Ar-H), 3.42 (d, $^{3}J_{H,N}$=3.5 Hz, 6H; flanking C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=151.4 (d, $^{1}J_{C,N}$=8.5 Hz; Ar-C), 141.8 (Ar-C), 134.8 (Ar-C), 129.0 (Ar-C), 127.1 (Ar-C), 122.3 (Ar-C), 120.0 (Ar-C), 117.6 (d, $^{2}J_{C,N}$=2.9 Hz; Ar-C), 116.7 (d, $^{2}J_{C,N}$=1.5 Hz; Ar-C), 109.4 (Ar-C), 43.5 (d, $^{2}J_{C,N}$=4.3 Hz; flanking *C*H$_3$); **^{15}N{^{1}H} NMR** (60 MHz, CD_2Cl_2): δ(ppm)=-225.8.

HRMS (APCI): calc. for $C_{18}H_{18}N_2{}^{15}N^+$ [(M+H)$^+$]: 277.1466, found: 277.1452.

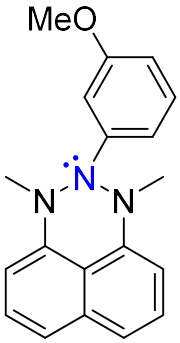
1*N*,3*N*-Dimethyl-2*N*-(4-methoxyphenyl)naphthotriazane **2j**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.34 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 7.30 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 6.98 (d, $^{3}J_{H,H}$=9.2 Hz, 2H; Ar-H), 6.77 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 6.64 (d, $^{3}J_{H,H}$=9.2 Hz, 2H; Ar-H), 3.63 (s, 3H; O-C*H*$_3$), 3.39 (s, 6H; flanking C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=155.4 (Ar-C), 144.6 (Ar-C), 141.7 (Ar-C), 134.7 (Ar-C), 127.1 (Ar-C), 119.9 (Ar-C), 118.9 (Ar-C), 116.7 (Ar-C), 114.2 (Ar-C), 109.3 (Ar-C), 55.7 (O-*C*H$_3$), 43.3 (flanking *C*H$_3$).

HRMS (APCI): calc. for $C_{19}H_{20}N_3O^+$ [(M+H)$^+$]: 306.1601, found: 306.1629.

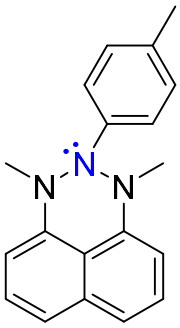
1*N*,3*N*-Dimethyl-2*N*-(3-methoxyphenyl)naphthotriazane **2k**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.33 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 7.27 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 7.00 (t, $^{3}J_{H,H}$=8.2 Hz, 1H; Ar-H), 6.79 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 6.66-6.62 (m, 2H; Ar-H), 6.35 (ddd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=2.4 Hz, $^{4}J_{H,H}$=0.8 Hz, 1H; Ar-H), 3.66 (s, 3H; O-CH_3), 3.40 (s, 6H; flanking CH_3); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=160.6 (Ar-C), 153.0 (Ar-C), 141.9 (Ar-C), 134.9 (Ar-C), 129.7 (Ar-C), 127.1 (Ar-C), 120.0 (Ar-C), 116.7 (Ar-C), 110.0 (Ar-C), 109.4 (Ar-C), 107.3 (Ar-C), 104.1 (Ar-C), 55.4 (O-*C*H_3), 43.5 (flanking *C*H_3).

HRMS (APCI): calc. for $C_{19}H_{20}N_3O^+$ [(M+H)$^+$]: 306.1601, found: 306.1621.

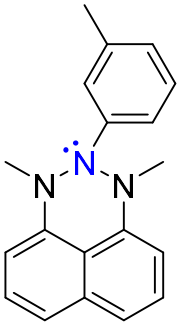
1*N*,3*N*-Dimethyl-2*N*-(4-tolyl)naphthotriazane **2l**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.36 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 7.28 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 6.98 (d, $^{3}J_{H,H}$=8.7 Hz, 2H; Ar-H), 6.93 (d, $^{3}J_{H,H}$=8.7 Hz, 2H; Ar-H), 6.80 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 3.42 (s, 6H; flanking CH_3), 2.17 (s, 3H; C-CH_3); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=149.0 (Ar-C), 141.9 (Ar-C), 134.8 (Ar-C), 131.9 (Ar-C), 129.5 (Ar-C), 127.1 (Ar-C), 119.9 (Ar-C), 117.7 (Ar-C), 116.7 (Ar-C), 109.3 (Ar-C), 43.3 (flanking *C*H_3), 20.5 (C-*C*H_3).

HRMS (APCI): calc. for $C_{19}H_{20}N_3^+$ [(M+H)$^+$]: 290.1652, found: 290.1676.

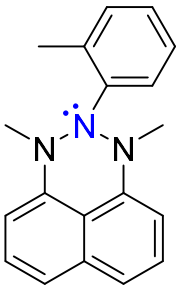
1*N*,3*N*-Dimethyl-2*N*-(3-tolyl)naphthotriazane **2m**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.37 (t, $^{3}J_{H,H}$=7.8 Hz, 2H; Ar-H), 7.30 (d, $^{3}J_{H,H}$=8.2 Hz, 2H; Ar-H), 7.01 (t, $^{3}J_{H,H}$=7.9 Hz, 1H; Ar-H), 6.98-6.95 (m, 1H; Ar-H), 6.86 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=2.0 Hz, 1H; Ar-H), 6.82 (d, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 6.67 (d, $^{3}J_{H,H}$=7.4 Hz, 1H; Ar-H), 3.43 (s, 6H; flanking CH_3), 2.24 (s, 3H; C-CH_3); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=151.4 (Ar-C), 141.9 (Ar-C), 139.0 (Ar-C), 134.9 (Ar-C), 128.8 (Ar-C), 127.1 (Ar-C), 123.2 (Ar-C), 120.0 (Ar-C), 118.4 (Ar-C), 116.7 (Ar-C), 114.5 (Ar-C), 109.4 (Ar-C), 43.5 (flanking *C*H_3), 21.8 (C-*C*H_3).

HRMS (APCI): calc. for $C_{19}H_{20}N_3^+$ [(M+H)$^+$]: 290.1652, found: 290.1663.

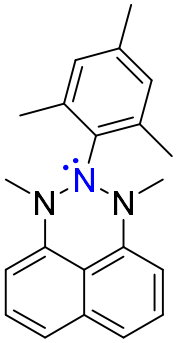
1*N*,3*N*-Dimethyl-2*N*-(2-tolyl)naphthotriazane **2n**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.39 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{3}J_{H,H}$=7.3 Hz, 2H; Ar-H), 7.35 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=1.0 Hz, 2H; Ar-H), 7.17 (d, $^{3}J_{H,H}$=7.3 Hz, 1H; Ar-H), 6.85 (td, $^{3}J_{H,H}$=7.4 Hz, $^{4}J_{H,H}$=1.2 Hz, 1H; Ar-H), 6.79 (d, $^{3}J_{H,H}$=7.7 Hz, 1H; Ar-H), 6.71 (dd, $^{3}J_{H,H}$=7.3 Hz, $^{4}J_{H,H}$=1.0 Hz, 2H; Ar-H), 6.49 (dd, $^{3}J_{H,H}$=8.1 Hz, $^{4}J_{H,H}$=1.0 Hz, 1H; Ar-H), 3.28 (s, 6H; flanking CH_3), 2.55 (s, 3H; C-CH_3); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=146.8 (Ar-C), 142.2 (Ar-C), 134.5 (Ar-C), 133.1 (Ar-C), 132.1 (Ar-C), 127.4 (Ar-C), 125.6 (Ar-C), 123.9 (Ar-C), 119.9 (Ar-C), 117.7 (Ar-C), 116.3 (Ar-C), 108.3 (Ar-C), 42.1 (flanking *C*H_3), 19.9 (C-*C*H_3).

HRMS (APCI): calc. for $C_{19}H_{20}N_3^+$ [(M+H)$^+$]: 290.1652, found: 290.1672.

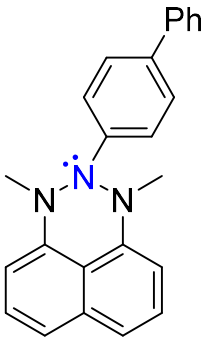
1*N*,3*N*-Dimethyl-2*N*-mesitylnaphthotriazane **2o**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.40-7.35 (m, 4H; Ar-H), 6.74 (s, 2H; Ar-H), 6.66 (dd, $^{3}J_{H,H}$=6.7 Hz, $^{4}J_{H,H}$=1.6 Hz, 2H; Ar-H), 3.23 (s, 6H; flanking CH_3), 2.21 (s, 3H; C-CH_3), 2.05 (s, 6H; C-CH_3); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=143.9 (Ar-C), 143.8 (Ar-C), 135.1 (Ar-C), 133.8 (Ar-C), 132.2 (Ar-C), 131.1 (Ar-C), 127.3 (Ar-C), 119.5 (Ar-C), 116.3 (Ar-C), 108.5 (Ar-C), 44.3 (flanking *C*H_3), 21.8 (C-*C*H_3), 20.5 (C-*C*H_3).

HRMS (APCI): calc. for $C_{21}H_{24}N_3^+$ [(M+H)$^+$]: 318.1965, found: 318.1992.

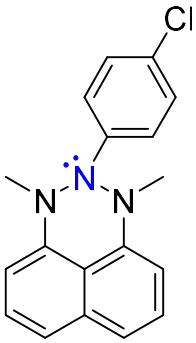
1*N*,3*N*-Dimethyl-2*N*-(4-biphenyl)naphthotriazane **2p**



^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm)=7.42 (d, $^{3}J_{H,H}$=7.8 Hz, 2H; Ar-H), 7.36-7.31 (m, 6H; Ar-H), 7.28 (d, $^{3}J_{H,H}$=8.2 Hz, 2H; Ar-H), 7.23 (t, $^{3}J_{H,H}$=7.4 Hz, 1H; Ar-H), 7.14 (d, $^{3}J_{H,H}$=8.8 Hz, 2H; Ar-H), 6.80 (d, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 3.45 (s, 6H; flanking CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ(ppm)=150.4 (Ar-C), 141.6 (Ar-C), 141.0 (Ar-C), 135.0 (Ar-C), 134.6 (Ar-C), 128.7 (Ar-C), 127.6 (Ar-C), 127.3 (Ar-C), 126.8 (Ar-C), 126.7 (Ar-C), 120.0 (Ar-C), 117.7 (Ar-C), 116.6 (Ar-C), 109.2 (Ar-C), 43.6 (flanking *C*H_3).

HRMS (APCI): calc. for $C_{24}H_{22}N_3^+$ [(M+H)$^+$]: 352.1808, found: 352.1798.

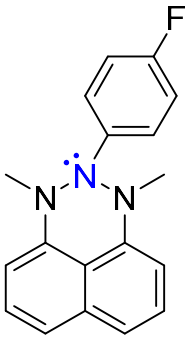
1*N*,3*N*-Dimethyl-2*N*-(4-chlorophenyl)naphthotriazane **2q**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.35 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 7.30 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 7.09-7.01 (m, 4H; Ar-H), 6.81 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{4}J_{H,H}$=0.8 Hz, 2H; Ar-H), 3.41 (s, 6H; flanking C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=150.2 (Ar-C), 141.5 (Ar-C), 134.8 (Ar-C), 128.9 (Ar-C), 127.1 (Ar-C), 127.0 (Ar-C), 120.3 (Ar-C), 119.0 (Ar-C), 116.6 (Ar-C), 109.8 (Ar-C), 43.6 (flanking *C*H$_3$).

HRMS (APCI): calc. for $C_{18}H_{17}ClN_3^+$ [(M+H)$^+$]: 310.1106, found: 310.1144.

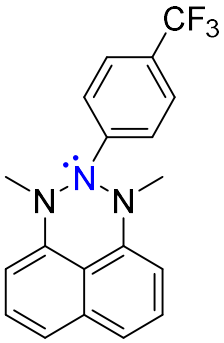
1*N*,3*N*-Dimethyl-2*N*-(4-fluorophenyl)naphthotriazane **2r**



^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm)=7.30 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{3}J_{H,H}$=7.3 Hz, 2H; Ar-H), 7.25 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=0.9 Hz, 2H; Ar-H), 7.02-6.97 (m, 2H; Ar-H), 6.78-6.71 (m, 4H; Ar-H), 3.36 (s, 6H; flanking C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ(ppm)=158.3 (d, $^{1}J_{C,F}$=240.2 Hz; Ar-*C*-F), 147.0 (d, $^{4}J_{C,F}$=2.4 Hz; Ar-C), 141.2 (Ar-C), 134.5 (Ar-C), 126.8 (Ar-C), 120.1 (Ar-C), 118.7 (d, $^{3}J_{C,F}$=7.7 Hz; Ar-C), 116.5 (Ar-C), 115.3 (d, $^{2}J_{C,F}$=22.4 Hz; Ar-C), 109.3 (Ar-C), 43.4 (flanking *C*H$_3$).

HRMS (APCI): calc. for $C_{18}H_{17}FN_3^+$ [(M+H)$^+$]: 294.1401, found: 294.1429.

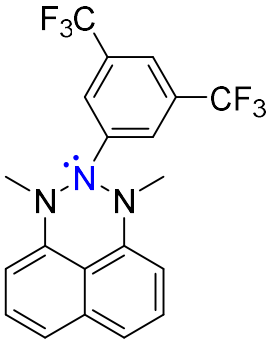
1*N*,3*N*-Dimethyl-2*N*-(4-(trifluoromethyl)phenyl)naphthotriazane **2s**



^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm)=7.33-7.29 (m, 4H; Ar-H), 7.27 (dd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=1 Hz, 2H; Ar-H), 7.14 (d, $^{3}J_{H,H}$=8.5 Hz, 2H; Ar-H), 6.78 (dd, $^{3}J_{H,H}$=7.3 Hz, $^{4}J_{H,H}$=1 Hz, 2H; Ar-H), 3.40 (s, 6H; flanking C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ(ppm)=154.0 (q, $^{4}J_{C,F}$=1.2 Hz; Ar-C), 141.3 (Ar-C), 134.6 (Ar-C), 126.8 (Ar-C), 126.2 (q, $^{3}J_{C,F}$=3.8 Hz; Ar-C), 124.5 (q, $^{1}J_{C,F}$=271.2 Hz; Ar-C), 123.8 (q, $^{2}J_{C,F}$=32.2 Hz; Ar-C), 120.5 (Ar-C), 117.0 (Ar-C), 116.5 (Ar-C), 109.7 (Ar-C), 43.8 (flanking *C*H$_3$).

HRMS (APCI): calc. for $C_{19}H_{17}F_3N_3^+$ [(M+H)$^+$]: 344.1369, found: 344.1398.

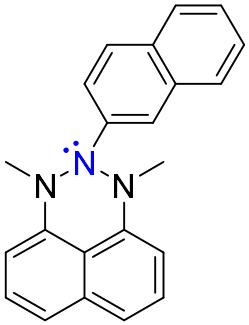
1*N*,3*N*-Dimethyl-2*N*-(3,5-bis(trifluoromethyl)phenyl)naphthotriazane **2t**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.65 (s, 2H; Ar-H), 7.42-7.32 (m, 5H; Ar-H), 7.14 (d, $^{3}J_{H,H}$=8.5 Hz, 2H; Ar-H), 6.95 (dd, $^{3}J_{H,H}$=7.2 Hz, $^{4}J_{H,H}$=1.1 Hz, 2H; Ar-H), 3.49 (s, 6H; flanking C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=153.3 (Ar-C), 141.1 (Ar-C), 135.0 (Ar-C), 132.3 (q, $^{2}J_{C,F}$=32.9 Hz; Ar-C), 127.2 (Ar-C), 124.0 (q, $^{1}J_{C,F}$=272.7 Hz; Ar-C), 121.2 (Ar-C), 117.3 (m, Ar-C), 116.7 (Ar-C), 115.6 (m, Ar-C), 111.1 (Ar-C), 44.6 (flanking *C*H$_3$).

HRMS (APCI): calc. for $C_{20}H_{16}F_6N_3^+$ [(M+H)$^+$]: 412.1243, found: 412.1280.

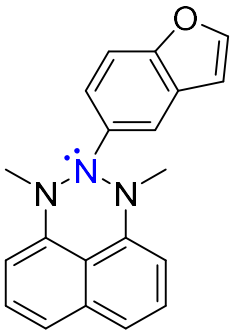
1*N*,3*N*-Dimethyl-2*N*-(2-naphthyl)naphthotriazane **2u**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.70-7.65 (m, 2H; Ar-H), 7.62-7.56 (m, 2H; Ar-H), 7.38 (t, $^{3}J_{H,H}$=7.8 Hz, 2H; Ar-H), 7.34 (t, $^{3}J_{H,H}$=7.5 Hz, 1H; Ar-H), 7.30-7.25 (m, 3H; Ar-H), 7.19 (s, 1H; Ar-H), 6.88 (d, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 3.50 (s, 6H; flanking C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=148.7 (Ar-C), 141.8 (Ar-C), 134.8 (Ar-C), 134.1 (Ar-C), 130.1 (Ar-C), 129.0 (Ar-C), 127.6 (Ar-C), 127.4 (Ar-C), 127.2 (Ar-C), 126.4 (Ar-C), 124.4 (Ar-C), 120.1 (Ar-C), 120.0 (Ar-C), 116.8 (Ar-C), 112.6 (Ar-C), 109.5 (Ar-C), 43.5 (flanking *C*H$_3$).

HRMS (APCI): calc. for $C_{22}H_{20}N_3^+$ [(M+H)$^+$]: 326.1652, found: 326.1620.

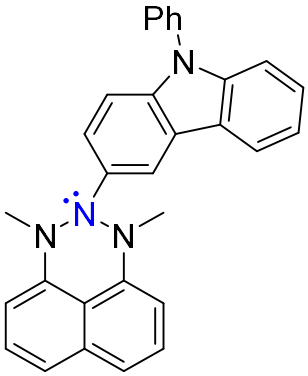
1*N*,3*N*-Dimethyl-2*N*-(5-benzofuranyl)naphthotriazane **2v**



^{1}H NMR (600 MHz, CD_2Cl_2): δ(ppm)=7.51 (d, $^{4}J_{H,H}$=2.1 Hz, 1H; Ar-H), 7.36 (t, $^{3}J_{H,H}$=7.8 Hz, 2H; Ar-H), 7.30-7.27 (m, 3H; Ar-H), 7.23 (dd, $^{3}J_{H,H}$=9.0 Hz, $^{4}J_{H,H}$=2.3 Hz, 1H; Ar-H), 7.17 (d, $^{4}J_{H,H}$=2.3 Hz, 1H; Ar-H), 6.83 (d, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 6.61 (d, $^{4}J_{H,H}$=2.0 Hz, 1H; Ar-H), 3.46 (s, 6H; flanking C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ(ppm)=151.4 (Ar-C), 147.1 (Ar-C), 145.9 (Ar-C), 141.8 (Ar-C), 134.8 (Ar-C), 127.7 (Ar-C), 127.2 (Ar-C), 119.9 (Ar-C), 116.8 (Ar-C), 116.1 (Ar-C), 111.5 (Ar-C), 109.4 (Ar-C), 109.0 (Ar-C), 107.0 (Ar-C), 43.5 (flanking *C*H$_3$).

HRMS (APCI): calc. for $C_{20}H_{18}N_3O^+$ [(M+H)$^+$]: 316.1444, found: 316.1402.

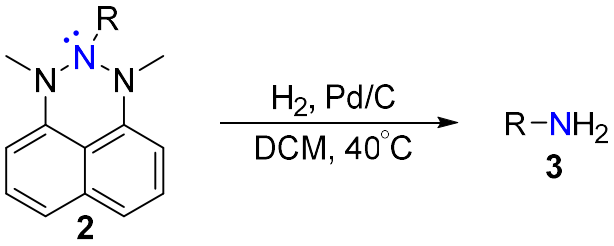
1*N*,3*N*-Dimethyl-2*N*-(3-(9-phenyl)carbazolyl)naphthotriazane **2w**



^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm)=7.95 (d, $^{3}J_{H,H}$=7.8 Hz, 1H; Ar-H), 7.66 (d, $^{4}J_{H,H}$=2.1 Hz, 1H; Ar-H), 7.47 (t, $^{3}J_{H,H}$=7.7 Hz, 2H; Ar-H), 7.39 (d, $^{3}J_{H,H}$=7.8 Hz, 2H; Ar-H), 7.33 (t, $^{3}J_{H,H}$=7.4 Hz, 1H; Ar-H), 7.30-7.25 (m, 4H; Ar-H), 7.21-7.18 (m, 3H; Ar-H), 7.16-7.11 (m, 2H; Ar-H), 6.77 (d, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 3.45 (s, 6H; flanking C*H*$_3$); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ(ppm)=144.5 (Ar-C), 141.7 (Ar-C), 141.3 (Ar-C), 138.0 (Ar-C), 137.1 (Ar-C), 134.5 (Ar-C), 129.8 (Ar-C), 127.2 (Ar-C), 127.0 (Ar-C), 126.9 (Ar-C), 125.8 (Ar-C), 123.5 (Ar-C), 123.4 (Ar-C), 120.3 (Ar-C), 119.8 (Ar-C), 119.5 (Ar-C), 117.6 (Ar-C), 116.7 (Ar-C), 110.0 (Ar-C), 109.8 (Ar-C), 109.0 (Ar-C), 108.9 (Ar-C), 43.5 (flanking *C*H$_3$).

HRMS (APCI): calc. for $C_{30}H_{27}N_4^+$ [(M+3H)$^+$]: 443.2219, found: 443.2195.

General procedure for the hydrogenolysis of triazanes to generate primary amines:



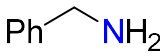
Scheme S2. Hydrogenolysis of triazanes.

Within a glovebox containing nitrogen atmosphere, in a vial, each triazane (0.2 mmol) was dissolved in 0.7 ml of DCM and Pd/C (0.002 g, 10 mol%) was added to the solution. Toluene (0.0212 ml, 0.2 mmol) was then added as an internal standard for measurement of the yield by ^{1}H NMR. This solution was then transferred into a Schlenk tube containing a stirring magnet. The Schlenk tube was then sealed, removed from the glovebox, cooled to -78°C, and then the N_2 atmosphere was quickly evacuated by vacuum and replaced with H_2 gas (1 bar). The reaction

mixture was then stirred at 40°C for 2 hours. For volatile amines (**3a-b**, **3d-g**), CD_2Cl_2 was used instead of non-deuterated DCM, and the yield was measured directly by ^{1}HNMR. For all the other amines which were separated, the reaction mixture was then passed through a small column of Celite using DCM as the eluent. The solvent was evaporated, and the product was isolated by preparative TLC (silica), using Hexane/EtOAc (7:3).

The following are the NMR spectra of the amines we isolated:

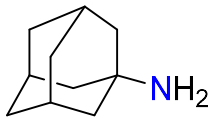
Benzylamine **3c**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=7.37-7.29 (m, 4H; Ar-H), 7.28-7.22 (m, 1H; Ar-H), 3.87 (s, 2H; CH_2), 1.42 (bs, 2H; NH_2); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=143.4 (Ar-C), 128.6 (Ar-C), 127.1 (Ar-C), 126.8 (Ar-C), 46.6 (*C*H_2).

HRMS (ESI+): calc. for $C_7H_{10}N^+$ [(M+H)$^+$]: 108.0808, found: 108.0813.

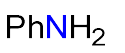
1-Adamantylamine (Amantadine) **3h**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=2.04 (s, 3H; adamantyl), 1.68-1.52 (m, 12H; adamantyl), 0.90-1.25 (bs, 2H; NH_2); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=47.4 (adamantyl *C*-N), 46.4 (adamantyl), 36.4 (adamantyl), 29.9 (adamantyl).

HRMS (ESI+): calc. for $C_{10}H_{18}N^+$ [(M+H)$^+$]: 152.1434, found: 152.1439.

Aniline **3i**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=7.22 (dd, $^3J_{H,H}$=8.4 Hz, $^3J_{H,H}$=7.4 Hz, 2H; Ar-H), 6.82 (tt, $^3J_{H,H}$=7.4 Hz, $^4J_{H,H}$=1.0 Hz, 1H; Ar-H), 6.72 (dd, $^3J_{H,H}$=8.4 Hz, $^4J_{H,H}$=1.0 Hz, 2H; Ar-H), 3.62 (bs, 2H; NH_2); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=146.4 (Ar-*C*-N), 129.3 (Ar-C), 118.5 (Ar-C), 115.1 (Ar-C).

HRMS (ESI+): calc. for $C_6H_8N^+$ [(M+H)$^+$]: 94.0651, found: 94.0657.

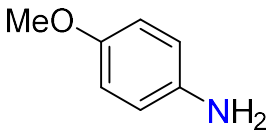
Aniline-^{15}N **3i'**

$Ph^{15}NH_2$

^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm)=7.19 (dd, $^3J_{H,H}$=8.4 Hz, $^3J_{H,H}$=7.4 Hz, 2H; Ar-H), 6.79 (tt, $^3J_{H,H}$=7.4 Hz, $^4J_{H,H}$=1.0 Hz, 1H; Ar-H), 6.71 (d, $^3J_{H,H}$=7.8 Hz, 2H; Ar-H), 3.56 (bs, 2H; $^{15}NH_2$); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=146.5 (d, $^1J_{C,N}$=10.8 Hz, Ar-*C*-^{15}N), 129.4 (d, $^3J_{C,N}$=1.1 Hz, Ar-C), 118.6 (Ar-C), 115.2 (d, $^2J_{C,N}$=2.7 Hz, Ar-C); **^{15}N{^{1}H} NMR** (60 MHz, $CDCl_3$): δ(ppm)=-325.4.

HRMS (ESI+): calc. for $C_6H_8{}^{15}N^+$ [(M+H)$^+$]: 95.0622, found: 95.0628.

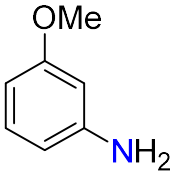
4-Methoxyaniline (p-anisidine) **3j**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=6.75 (d, $^3J_{H,H}$=8.8 Hz, 2H; Ar-H), 6.65 (d, $^3J_{H,H}$=8.8 Hz, 2H; Ar-H), 3.75 (s, 3H; OCH_3), 3.32 (bs, 2H; NH_2); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=152.9 (Ar-C), 140.0 (Ar-C), 116.5 (Ar-C), 114.9 (Ar-C), 55.8 (O*C*H$_3$).

HRMS (ESI+): calc. for $C_7H_{10}NO^+$ [(M+H)$^+$]: 124.0757, found: 124.0762.

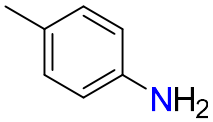
3-Methoxyaniline (m-anisidine) **3k**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=7.08 (t, $^3J_{H,H}$=8.1 Hz, 1H; Ar-H), 6.35 (ddd, $^3J_{H,H}$=8.1 Hz, $^4J_{H,H}$=2.3 Hz, $^4J_{H,H}$=0.8 Hz, 1H; Ar-H), 6.31 (ddd, $^3J_{H,H}$=7.9 Hz, $^4J_{H,H}$=2.1 Hz, $^4J_{H,H}$=0.8 Hz, 1H; Ar-H), 6.26 (t, $^4J_{H,H}$=2.2 Hz, 1H; Ar-H), 3.78 (s, 3H; OCH_3), 3.69 (bs, 2H; NH_2); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=160.8 (Ar-C), 147.9 (Ar-C), 130.1 (Ar-C), 107.9 (Ar-C), 103.9 (Ar-C), 101.1 (Ar-C), 55.1 (O*C*H$_3$).

HRMS (ESI+): calc. for $C_7H_{10}NO^+$ [(M+H)$^+$]: 124.0757, found: 124.0763.

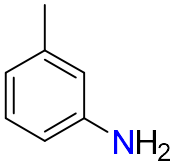
4-Methylaniline (p-toluidine) **3l**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=7.00 (d, $^{3}J_{H,H}$=8.2 Hz, 2H; Ar-H), 6.63 (d, $^{3}J_{H,H}$=8.2 Hz, 2H; Ar-H), 3.46 (bs, 2H; NH_2), 2.27 (s, 3H; CH_3); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=143.9 (Ar-C), 129.8 (Ar-C), 127.8 (Ar-C), 115.3 (Ar-C), 20.5 (*C*H_3).

HRMS (ESI+): calc. for $C_7H_{10}N^+$ [(M+H)$^+$]: 108.0808, found: 108.0812.

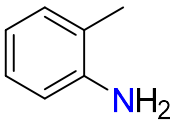
3-Methylaniline (m-toluidine) **3m**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=7.13 (t, $^{3}J_{H,H}$=7.6 Hz, 1H; Ar-H), 6.67 (d, $^{3}J_{H,H}$=7.6 Hz, 1H; Ar-H), 6.59-6.53 (m, 2H; Ar-H), 3.61 (bs, 2H; NH_2), 2.35 (s, 3H; CH_3); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=146.4 (Ar-C), 139.1 (Ar-C), 129.2 (Ar-C), 119.4 (Ar-C), 115.9 (Ar-C), 112.2 (Ar-C), 21.4 (*C*H_3).

HRMS (ESI+): calc. for $C_7H_{10}N^+$ [(M+H)$^+$]: 108.0808, found: 108.0813.

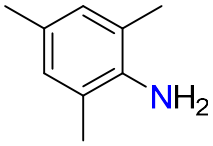
2-Methylaniline (o-toluidine) **3n**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=7.17-7.11 (m, 2H; Ar-H), 6.82 (t, $^{3}J_{H,H}$=7.4 Hz, 1H; Ar-H), 6.75 (d, $^{3}J_{H,H}$=7.4 Hz, 1H; Ar-H), 3.61 (bs, 2H; NH_2), 2.25 (s, 3H; CH_3); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=144.6 (Ar-C), 130.4 (Ar-C), 127.0 (Ar-C), 122.3 (Ar-C), 118.6 (Ar-C), 114.9 (Ar-C), 17.3 (*C*H_3).

HRMS (ESI+): calc. for $C_7H_{10}N^+$ [(M+H)$^+$]: 108.0808, found: 108.0813.

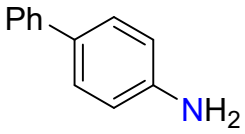
2,4,6-Trimethylaniline (mesitylamine) **3o**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=6.84 (s, 2H; Ar-H), 3.50 (bs, 2H; N*H*$_2$), 2.28 (s, 3H; C*H*$_3$), 2.22 (s, 6H; C*H*$_3$); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=140.2 (Ar-C), 128.9 (Ar-C), 127.2 (Ar-C), 121.9 (Ar-C), 20.4 (*C*H$_3$), 17.6 (*C*H$_3$).

HRMS (ESI+): calc. for $C_9H_{14}N^+$ [(M+H)$^+$]: 136.1121, found: 136.1125.

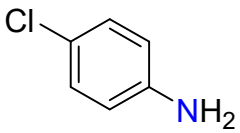
4-Aminobiphenyl (4-phenylaniline) **3p**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=7.55 (d, $^{3}J_{H,H}$=7.8 Hz, 2H; Ar-H), 7.46-7.38 (m, 4H; Ar-H), 7.28 (t, $^{3}J_{H,H}$=7.4 Hz, 1H; Ar-H), 6.77 (d, $^{3}J_{H,H}$=8.4 Hz, 2H; Ar-H), 3.73 (bs, 2H; N*H*$_2$); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=146.0 (Ar-C), 141.3 (Ar-C), 131.7 (Ar-C), 128.8 (Ar-C), 128.1 (Ar-C), 126.5 (Ar-C), 126.4 (Ar-C), 115.5 (Ar-C).

HRMS (ESI+): calc. for $C_{12}H_{12}N^+$ [(M+H)$^+$]: 170.0964, found: 170.0970.

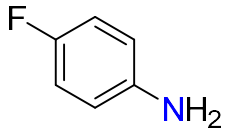
4-Chloroaniline **3q**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=7.10 (d, $^{3}J_{H,H}$=8.7 Hz, 2H; Ar-H), 6.60 (d, $^{3}J_{H,H}$=8.7 Hz, 2H; Ar-H), 3.61 (bs, 2H; N*H*$_2$); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=145.1 (Ar-C), 129.2 (Ar-C), 123.2 (Ar-C), 116.3 (Ar-C).

HRMS (ESI+): calc. for $C_6H_7ClN^+$ [(M+H)$^+$]: 128.0262, found: 128.0269.

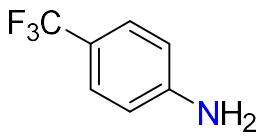
4-Fluoroaniline **3r**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=6.86 (t, $^{3}J_{H,H}$=$^{3}J_{H,F}$=8.7 Hz, 2H; Ar-H), 6.61 (dd, $^{3}J_{H,H}$=8.7 Hz, $^{4}J_{H,F}$=4.5 Hz, 2H; Ar-H), 3.51 (bs, 2H; N*H*$_2$); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=156.5 (d, $^{1}J_{C,F}$=235.4 Hz, Ar-*C*-F), 142.5 (d, $^{4}J_{C,F}$=2.1 Hz, Ar-C), 116.1 (d, $^{3}J_{C,F}$=7.6 Hz, Ar-C), 115.7 (d, $^{2}J_{C,F}$=22.4 Hz, Ar-C); **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ(ppm)=-126.87.

HRMS (ESI+): calc. for $C_6H_7FN^+$ [(M+H)$^+$]: 112.0557, found: 112.0563.

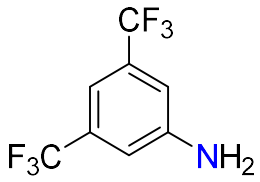
4-Trifluoromethylaniline **3s**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=7.40 (d, $^{3}J_{H,H}$=8.4 Hz, 2H; Ar-H), 6.69 (d, $^{3}J_{H,H}$=8.4 Hz, 2H; Ar-H), 3.94 (bs, 2H; N*H*$_2$); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=149.5 (Ar-C), 126.8 (q, $^{3}J_{C,F}$=3.8 Hz, Ar-C), 125.0 (q, $^{1}J_{C,F}$=270.5 Hz, Ar-C), 120.2 (q, $^{2}J_{C,F}$=32.5 Hz, Ar-C), 114.3 (Ar-C); **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ(ppm)=-61.20.

HRMS (ESI+): calc. for $C_7H_7F_3N^+$ [(M+H)$^+$]: 162.0525, found: 162.0531.

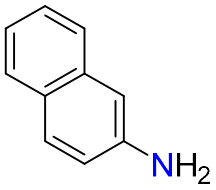
3,5-Bis(trifluoromethyl)aniline **3t**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=7.21 (s, 1H; Ar-H), 7.03 (s, 2H; Ar-H), 4.07 (bs, 2H; N*H*$_2$); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=147.5 (Ar-C), 132.7 (q, $^{2}J_{C,F}$=32.9 Hz, Ar-C), 123.6 (q, $^{1}J_{C,F}$=272.3 Hz, Ar-C), 114.3 (m, Ar-C), 111.7 (sept, $^{3}J_{C,F}$=4.0 Hz, Ar-C); **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ(ppm)=-63.35.

HRMS (ESI+): calc. for $C_8H_6F_6N^+$ [(M+H)$^+$]: 230.0399, found: 162.0402.

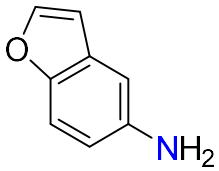
2-Naphthylamine **3u**



^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm)=7.29 (d, $^{3}J_{H,H}$=8.2 Hz, 1H; Ar-H), 7.26 (d, $^{3}J_{H,H}$=8.6 Hz, 1H; Ar-H), 7.19 (d, $^{3}J_{H,H}$=8.2 Hz, 1H; Ar-H), 6.97 (t, $^{3}J_{H,H}$=7.5 Hz, 1H; Ar-H), 6.85-6.80 (m, 1H; Ar-H), 6.59-6.56 (m, 1H; Ar-H), 6.54 (dd, $^{3}J_{H,H}$=8.6 Hz, $^{4}J_{H,H}$=2.3 Hz, 1H; Ar-H), 3.41 (bs, 2H; NH_2); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ(ppm)=144.2 (Ar-C), 135.0 (Ar-C), 129.3 (Ar-C), 128.1 (Ar-C), 127.8 (Ar-C), 126.5 (Ar-C), 125.9 (Ar-C), 122.6 (Ar-C), 118.3 (Ar-C), 108.7 (Ar-C).

HRMS (ESI+): calc. for $C_{10}H_{10}N^+$ [$(M+H)^+$]: 144.0808, found: 144.0812.

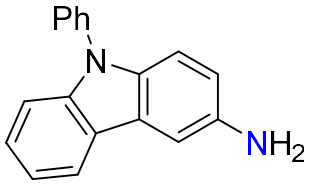
5-Benzofurylamine **3v**



^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm)=7.48 (d, $^{4}J_{H,H}$=2.1 Hz, 1H; Ar-H), 7.23 (d, $^{3}J_{H,H}$=8.6 Hz, 1H; Ar-H), 6.81 (d, $^{4}J_{H,H}$=2.3 Hz, 1H; Ar-H), 6.63 (dd, $^{3}J_{H,H}$=8.6 Hz, $^{4}J_{H,H}$=2.3 Hz, 1H; Ar-H), 6.57-6.54 (m, 1H; Ar-H), 3.56 (bs, 2H; NH_2); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ(ppm)=145.6 (Ar-C), 142.1 (Ar-C), 132.6 (Ar-C), 128.4 (Ar-C), 113.7 (Ar-C), 111.7 (Ar-C), 106.2 (Ar-C), 106.1 (Ar-C).

HRMS (ESI+): calc. for $C_8H_8NO^+$ [$(M+H)^+$]: 134.0600, found: 134.0607.

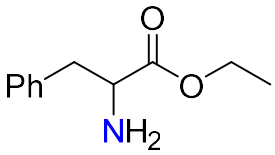
3-Amino-9-phenylcarbazole **3w**



^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm)=8.04 (d, $^{3}J_{H,H}$=7.7 Hz, 1H; Ar-H), 7.60-7.54 (m, 4H; Ar-H), 7.46 (d, $^{4}J_{H,H}$=2.1 Hz, 1H; Ar-H), 7.43 (t, $^{3}J_{H,H}$=7.1 Hz, 1H; Ar-H), 7.41-7.35 (m, 2H; Ar-H), 7.25 (d, $^{3}J_{H,H}$=8.0 Hz, 1H; Ar-H), 7.22 (t, $^{3}J_{H,H}$=7.3 Hz, 1H; Ar-H), 6.85 (dd, $^{3}J_{H,H}$=8.6 Hz, $^{4}J_{H,H}$=2.3 Hz, 1H; Ar-H), 3.67 (bs, 2H; NH_2); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ(ppm)=141.3 (Ar-C), 140.0 (Ar-C), 138.3 (Ar-C), 135.5 (Ar-C), 129.9 (Ar-C), 127.1 (Ar-C), 127.0 (Ar-C), 125.9 (Ar-C), 124.4 (Ar-C), 123.2 (Ar-C), 120.4 (Ar-C), 119.4 (Ar-C), 115.8 (Ar-C), 110.6 (Ar-C), 109.8 (Ar-C), 106.0 (Ar-C).

HRMS (ESI+): calc. for $C_{18}H_{15}N_2^+$ [(M+H)$^+$]: 259.1230, found: 259.1236.

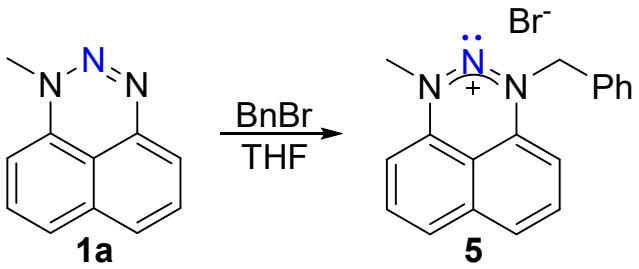
Phenylalanine ethyl ester **3x**



^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm)=7.30 (t, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 7.23 (t, $^{3}J_{H,H}$=7.4 Hz, 1H; Ar-H), 7.19 (d, $^{3}J_{H,H}$=7.4 Hz, 2H; Ar-H), 4.16 (q, $^{3}J_{H,H}$=7.1 Hz, 2H; O-CH_2), 3.71 (dd, $^{3}J_{H,H}$=7.3 Hz, $^{3}J_{H,H}$=5.8 Hz, 1H; N-C*H*), 3.08 (dd, $^{3}J_{H,H}$=13.5 Hz, $^{3}J_{H,H}$=5.3 Hz, 1H; Ph-CH_2), 2.86 (dd, $^{3}J_{H,H}$=13.5 Hz, $^{3}J_{H,H}$=7.9 Hz, 1H; Ph-CH_2), 1.44 (bs, 2H; NH_2), 1.24 (t, $^{3}J_{H,H}$=7.1 Hz, 3H; CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ(ppm)=175.2 (C=O), 137.4 (Ar-C), 129.4 (Ar-C), 128.6 (Ar-C), 126.9 (Ar-C), 61.0 (O-*C*H_2), 56.0 (N-*C*H), 41.3 (Ph-*C*H_2), 14.3 (*C*H_3).

HRMS (ESI+): calc. for $C_{11}H_{16}NO_2^+$ [(M+H)$^+$]: 194.1176, found: 194.1181.

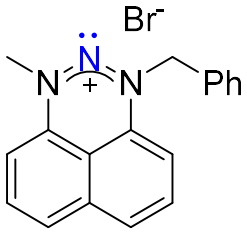
Preparation of recyclable NHN **5**:



Scheme S3. Preparation of NHN **5**.

In a round-bottom flask, triazine **1a** (0.9161 g, 5 mmol) was dissolved in THF (10 ml) and then benzyl bromide (2.97 ml, 25 mmol) was added. A reflux condenser was installed and then the mixture was stirred at 60°C for 16 hours. The solvent was evaporated, and the product was isolated using column chromatography (DCM:MeOH – 9:1, 1.4878g, 4.2mmol, 84% yield).

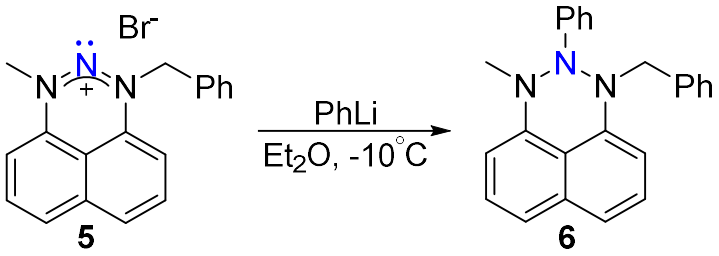
1*N*-Methyl-3*N*-benzyl-naphthotriazinium bromide **5**



^{1}H NMR (600 MHz, CD_3OD): δ(ppm)=7.69-7.64 (m, 3H, Ar-H), 7.62 (d, $^{3}J_{H,H}$=8.5 Hz, 1H; Ar-H), 7.55 (t, $^{3}J_{H,H}$=8.1 Hz, 1H; Ar-H), 7.49-7.45 (m, 2H; Ar-H), 7.44-7.39 (m, 2H; Ar-H), 7.16 (d, $^{3}J_{H,H}$=7.7 Hz, 1H; Ar-H), 7.04 (d, $^{3}J_{H,H}$=7.7 Hz, 1H; Ar-H), 5.56 (s, 2H; CH_2), 4.02 (s, 3H; CH_3); **^{13}C{^{1}H} NMR** (151 MHz, CD_3OD): δ(ppm)=135.4 (Ar-C), 132.5 (Ar-C), 132.2 (Ar-C), 131.5 (Ar-C), 130.5 (Ar-C), 130.4 (Ar-C), 130.1 (Ar-C), 129.9 (Ar-C), 129.3 (Ar-C), 127.8 (Ar-C), 127.3 (Ar-C), 124.1 (Ar-C), 109.8 (Ar-C), 109.6 (Ar-C), 61.4 (*C*H_2), 45.1 (*C*H_3).

HRMS (APCI): calc. for $C_{18}H_{16}N_3^+$ [M^+]: 274.1339, found: 274.1317.

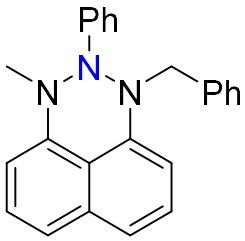
Preparation of triazane **6**:



Scheme S4. Preparation of triazane **6**.

Triazane **6** was prepared using the general procedure for the preparation of triazanes, using NHN **5** as the starting material instead of NHN **1**.

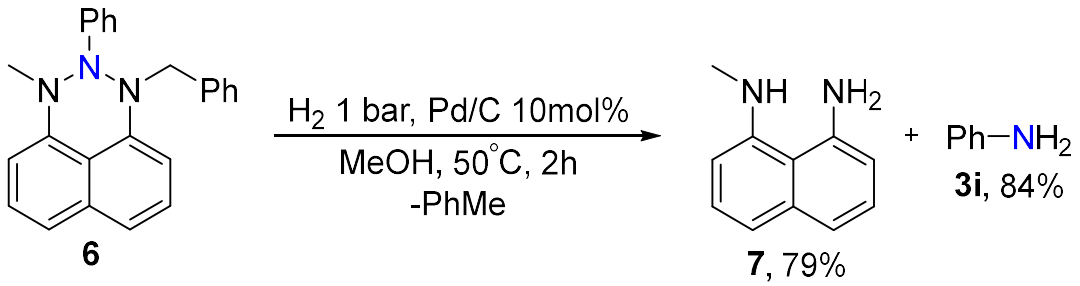
1*N*-Methyl-2*N*-phenyl-3*N*-benzyl-naphthotriazane **6**



^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm)=7.52 (d, $^{3}J_{H,H}$=7.3 Hz, 2H; Ar-H), 7.37-7.32 (m, 4H; Ar-H), 7.30-7.27 (m, 2H; Ar-H), 7.20 (d, $^{3}J_{H,H}$=8.3 Hz, 1H; Ar-H), 7.05-7.02 (m, 2H; Ar-H), 6.98 (d, $^{3}J_{H,H}$=8.2 Hz, 2H; Ar-H), 6.88 (dd, $^{3}J_{H,H}$=7.3 Hz, $^{4}J_{H,H}$=0.8 Hz, 1H; Ar-H), 6.74 (t, $^{3}J_{H,H}$=7.2 Hz, 1H; Ar-H), 6.65 (d, $^{3}J_{H,H}$=7.4 Hz, 1H; Ar-H), 4.65 (d, $^{3}J_{H,H}$=14.1 Hz, 1H; CH_2), 4.36 (d, $^{3}J_{H,H}$=14.1 Hz, 1H; CH_2), 3.40 (s, 3H; CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ(ppm)=150.9 (Ar-C), 141.5 (Ar-C), 140.8 (Ar-C), 138.5 (Ar-C), 134.6 (Ar-C), 129.2 (Ar-C), 128.7 (Ar-C), 128.5 (Ar-C), 127.5 (Ar-C), 126.9 (Ar-C), 126.7 (Ar-C), 122.0 (Ar-C), 121.9 (Ar-C), 118.1 (Ar-C), 117.4 (Ar-C), 116.9 (Ar-C), 113.0 (Ar-C), 105.3 (Ar-C), 60.8 (*C*H_2), 41.3 (*C*H_3).

HRMS (APCI): calc. for $C_{24}H_{22}N_3^+$ [(M+H)$^+$]: 352.1808, found: 352.1789.

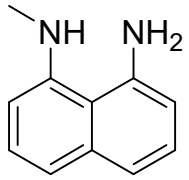
Hydrogenolysis of triazane **6** to generate aniline **3i** and *N*-methyl-1,8-diaminonaphthalene **7**:



Scheme S5. Hydrogenolysis of triazane **6**.

This reaction was performed according to the general procedure for the hydrogenolysis of triazanes, with a few differences: MeOH was used as the solvent (instead of DCM), and the reaction was stirred at 50°C (instead of 40°C) for 2h.

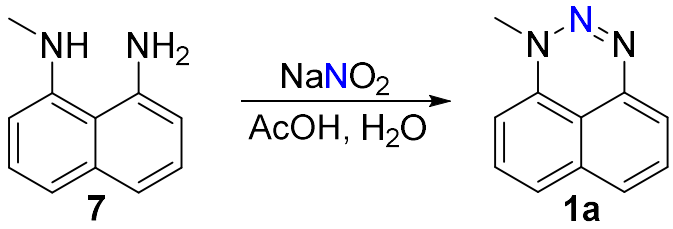
N-methyl-1,8-diaminonaphthalene **7**



^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm)=7.29-7.24 (m, 2H, Ar-H), 7.19-7.13 (m, 2H; Ar-H), 6.62 (d, $^{3}J_{H,H}$=7.3 Hz, 1H; Ar-H), 6.51 (d, $^{3}J_{H,H}$=7.6 Hz, 1H; Ar-H), 4.96 (m, 3H; NH+NH_2), 2.88 (s, 3H; CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ(ppm)=147.8 (Ar-C), 143.8 (Ar-C), 136.9 (Ar-C), 126.8 (Ar-C), 126.0 (Ar-C), 120.7 (Ar-C), 118.2 (Ar-C), 117.2 (Ar-C), 112.9 (Ar-C), 105.2 (Ar-C), 31.7 (*C*H_3).

HRMS (APCI): calc. for $C_{11}H_{13}N_2^+$ [(M+H)$^+$]: 173.1073, found: 173.1089.

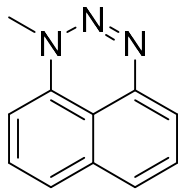
Preparation (recycling) of triazine **1a** from *N*-methyl-1,8-diaminonaphthalene **7**:



Scheme S6. Preparation of triazine **1a**.

A round bottom flask was loaded with compound **7** (0.02 g, 0.116 mmol) and then water (3 ml) and acetic acid (3 ml) were added. The mixture was cooled to 0°C while stirring, and then a solution of $NaNO_2$ (0.01 g, 0.145 mmol) in water (1 ml) was added dropwise. The solution was stirred for 3h while allowing it to reach room temperature. The solution was carefully quenched with saturated aqueous $NaHCO_3$ solution (10 ml) and the product was extracted with DCM (20 ml x 3). The solvent was evaporated and the product was purified by column chromatography (Hexane:EtOAc=4:1; 0.0196 g, 0.107 mmol, 92% yield).

1*N*-methylnaphthotriazine **1a**

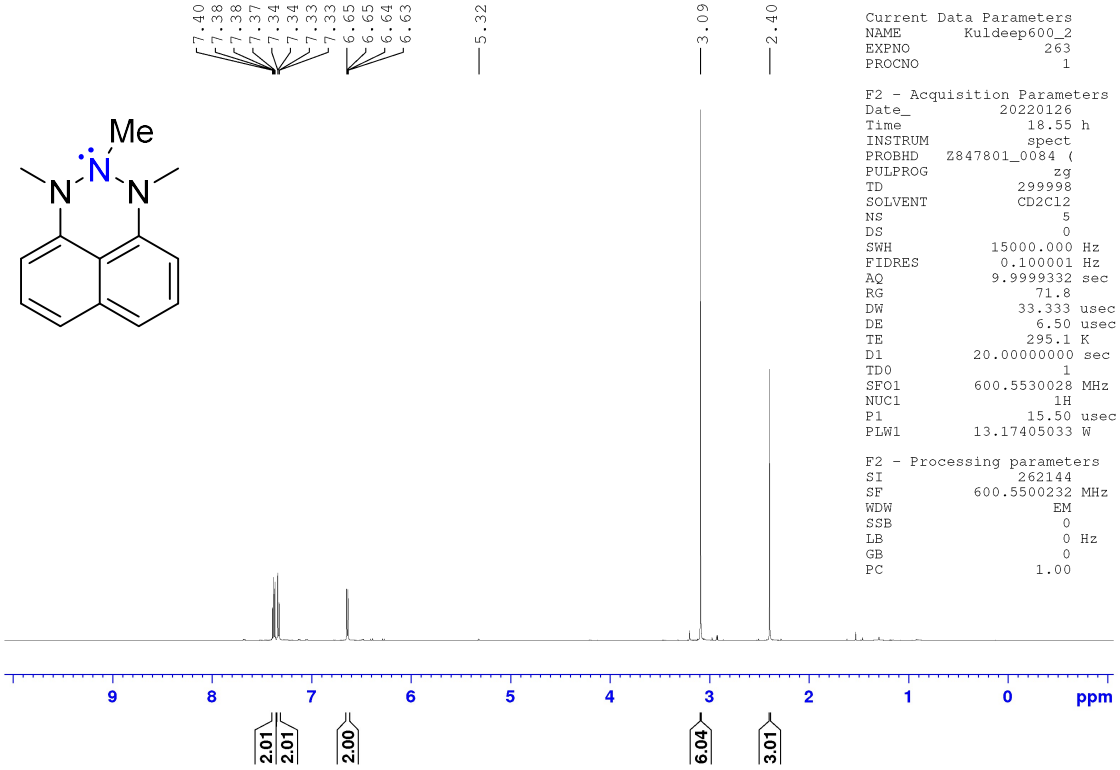


^{1}H NMR (600 MHz, $CDCl_3$): δ(ppm)=7.35-7.29 (m, 2H, Ar-H), 7.17 (dd, $^3J_{H,H}$=8.5 Hz, $^3J_{H,H}$=7.5 Hz, 1H; Ar-H), 7.12 (dd, $^3J_{H,H}$=6.8 Hz, $^4J_{H,H}$=1.4 Hz, 1H; Ar-H), 7.10 (d, $^3J_{H,H}$=8.5 Hz, 1H; Ar-H), 5.99 (d, $^3J_{H,H}$=7.5 Hz, 1H; Ar-H), 3.56 (s, 3H; CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ(ppm)=138.8 (Ar-C), 134.3 (Ar-C), 133.9 (Ar-C), 129.2 (Ar-C), 128.6 (Ar-C), 124.1 (Ar-C), 119.6 (Ar-C), 118.9 (Ar-C), 115.9 (Ar-C), 98.0 (Ar-C), 39.4 (*C*H_3).

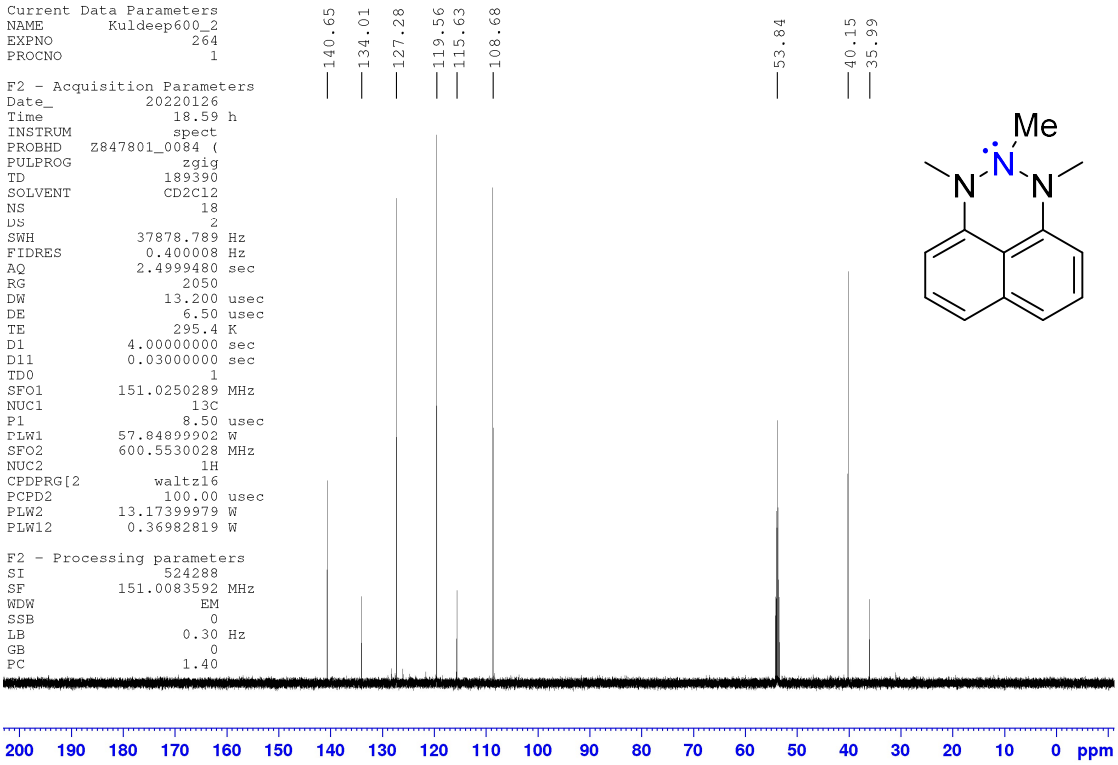
HRMS (APCI): calc. for $C_{11}H_{10}N_3^+$ [$(M+H)^+$]: 184.0869, found: 184.0846.

3. NMR spectra

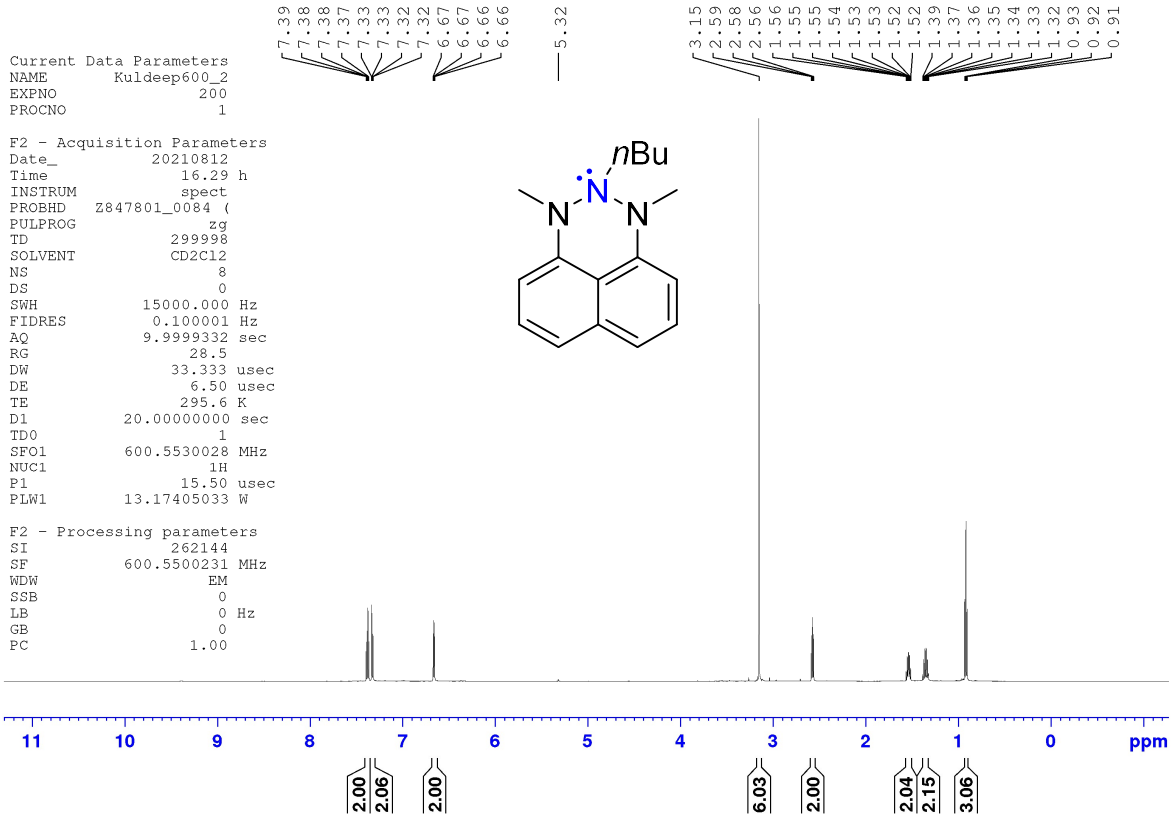
1*N*,2*N*,3*N*-Trimethylnaphthotriazane **2a** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



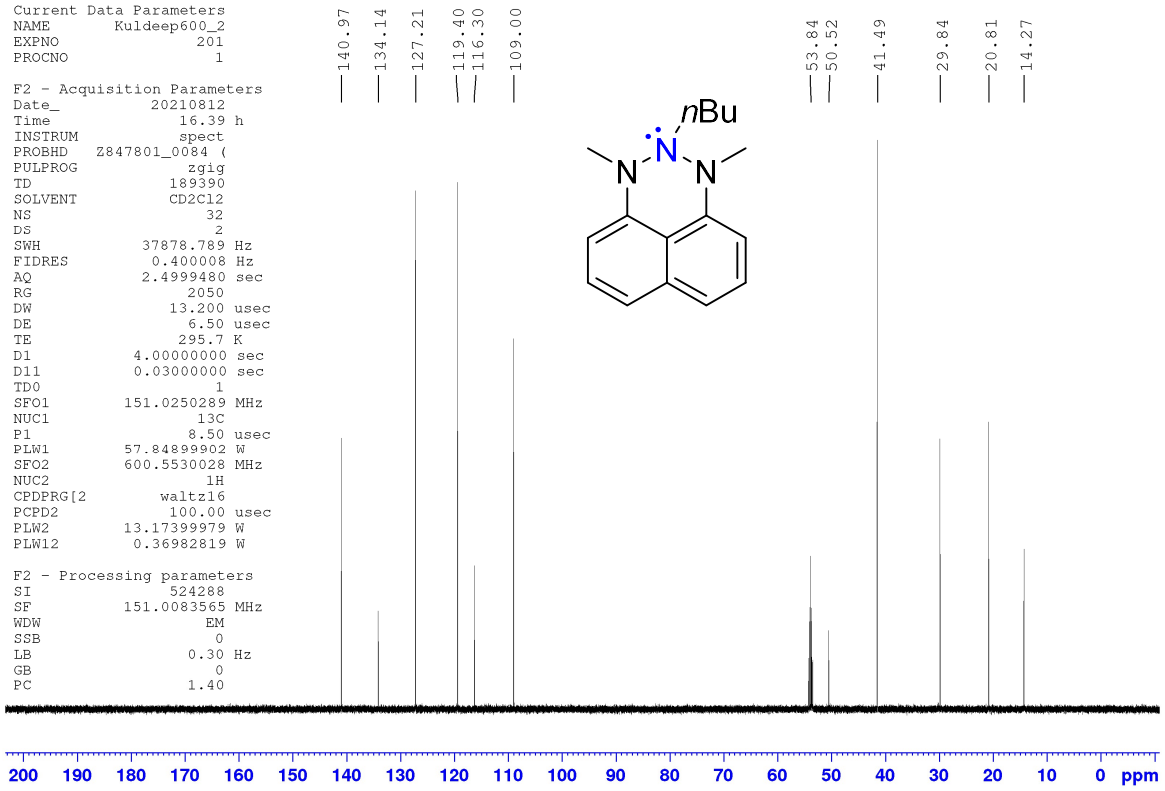
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



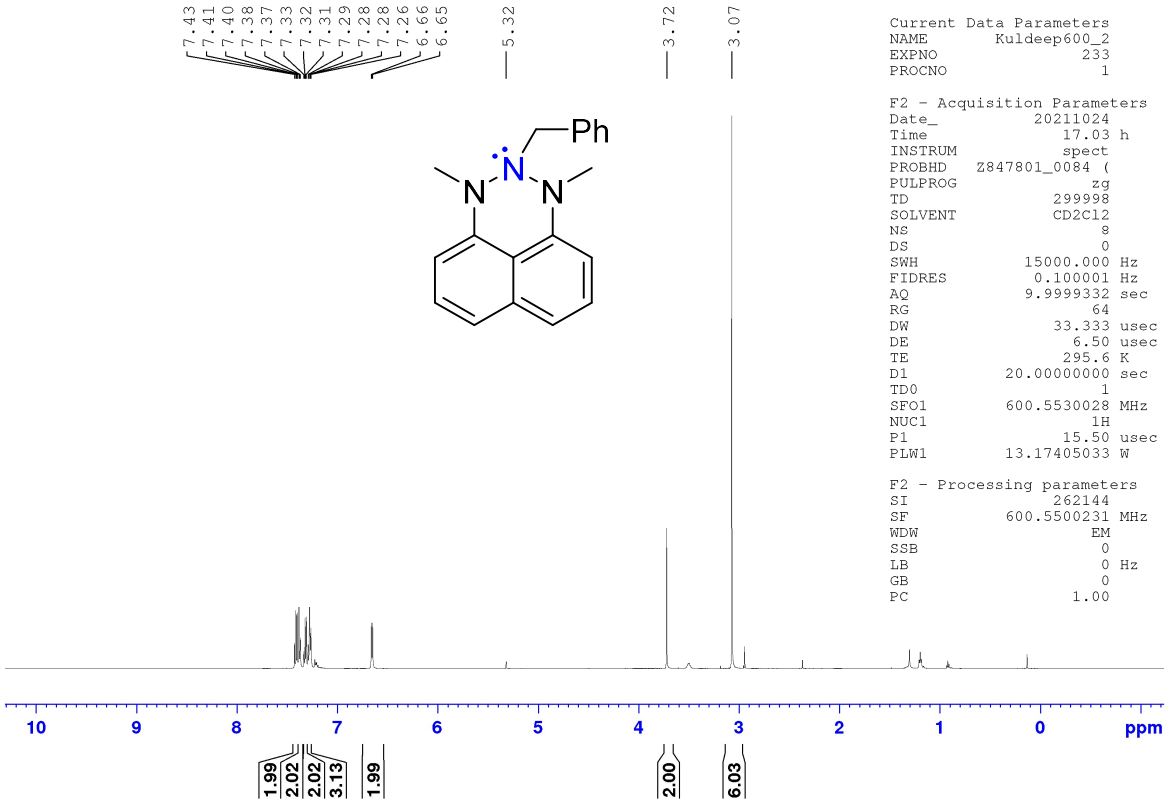
1*N*,3*N*-Dimethyl-2*N*-butylnaphthotriazane **2b** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



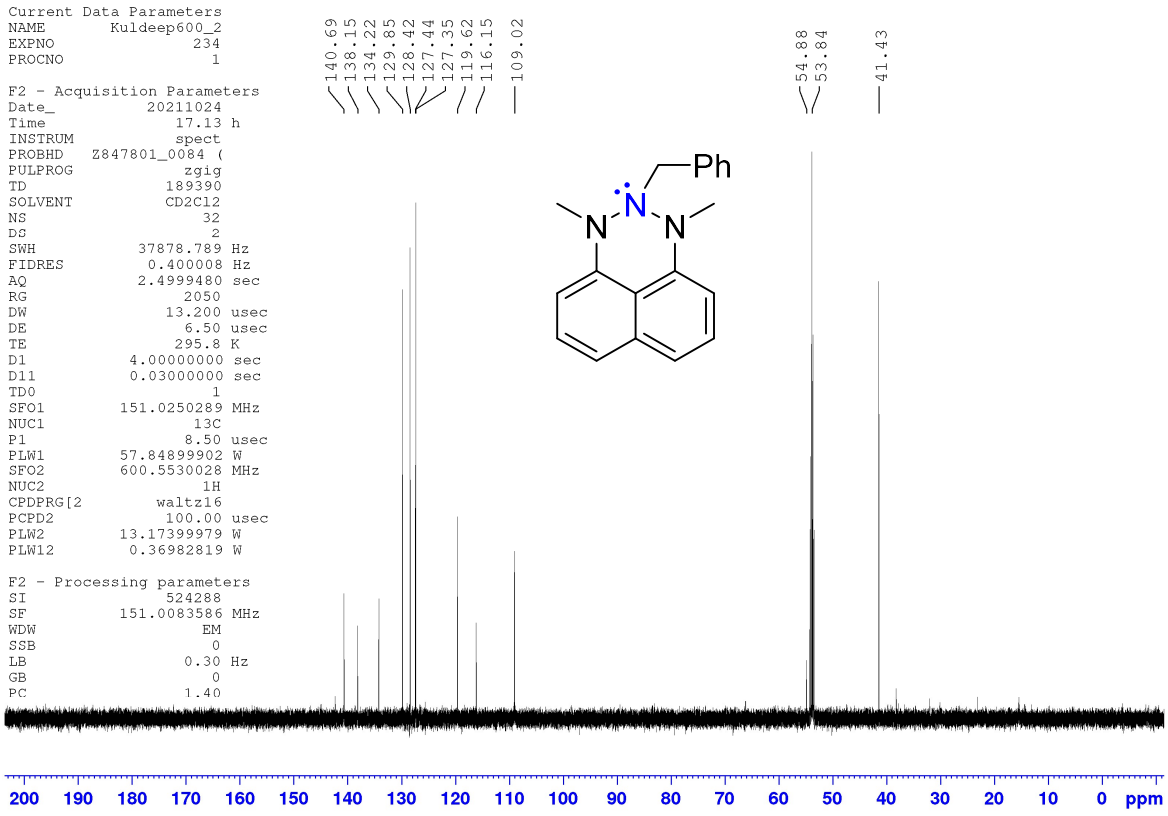
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



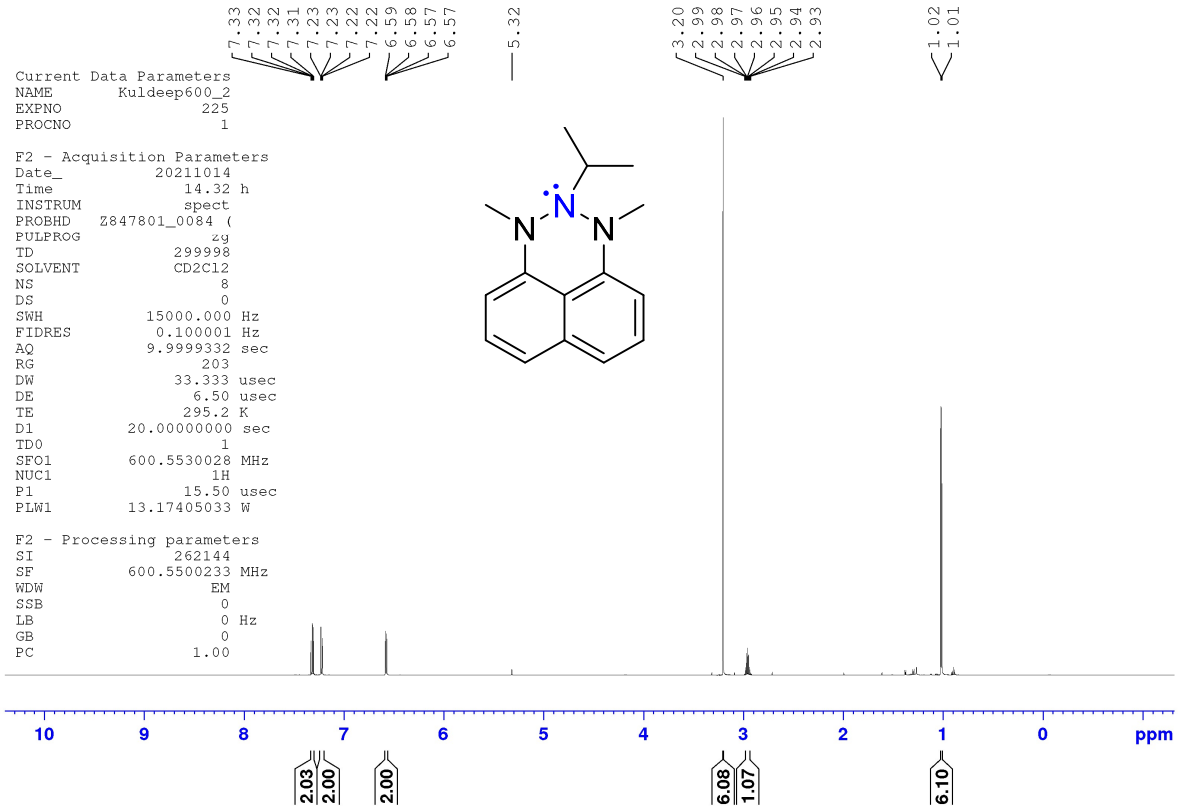
1*N*,3*N*-Dimethyl-2*N*-benzylnaphthotriazane **2c** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



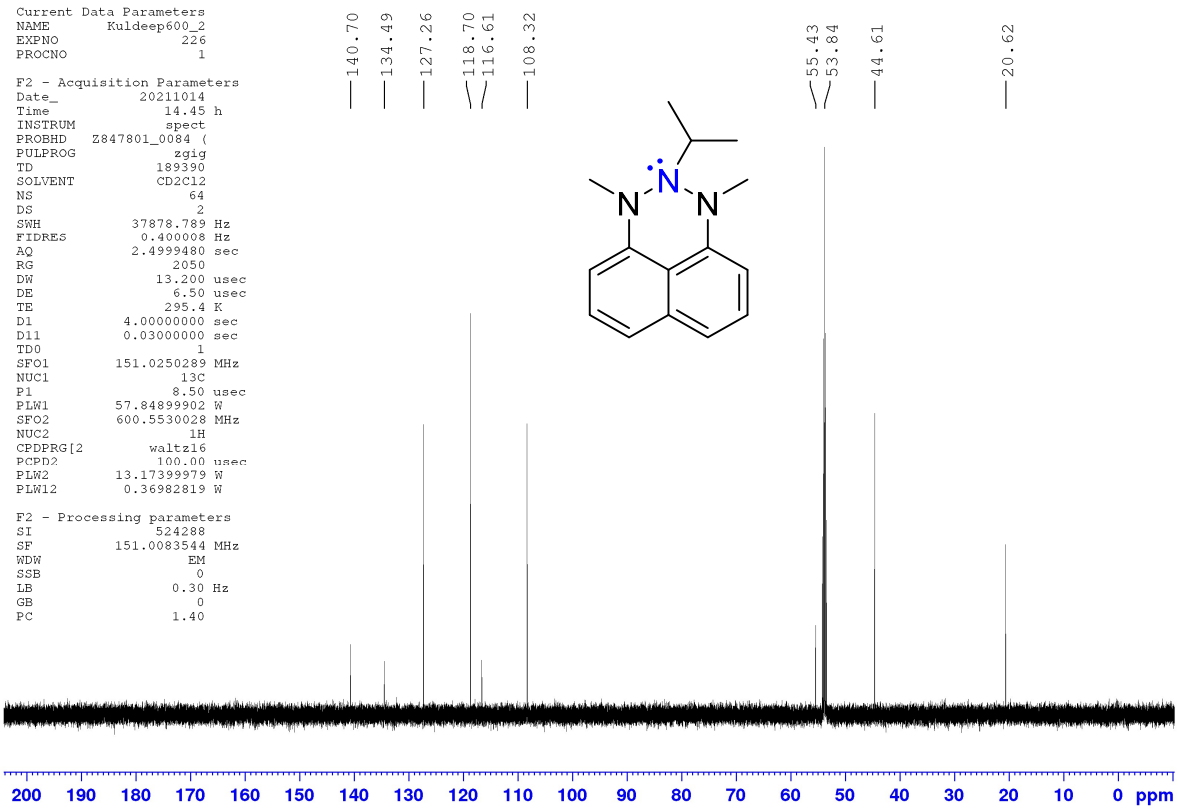
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



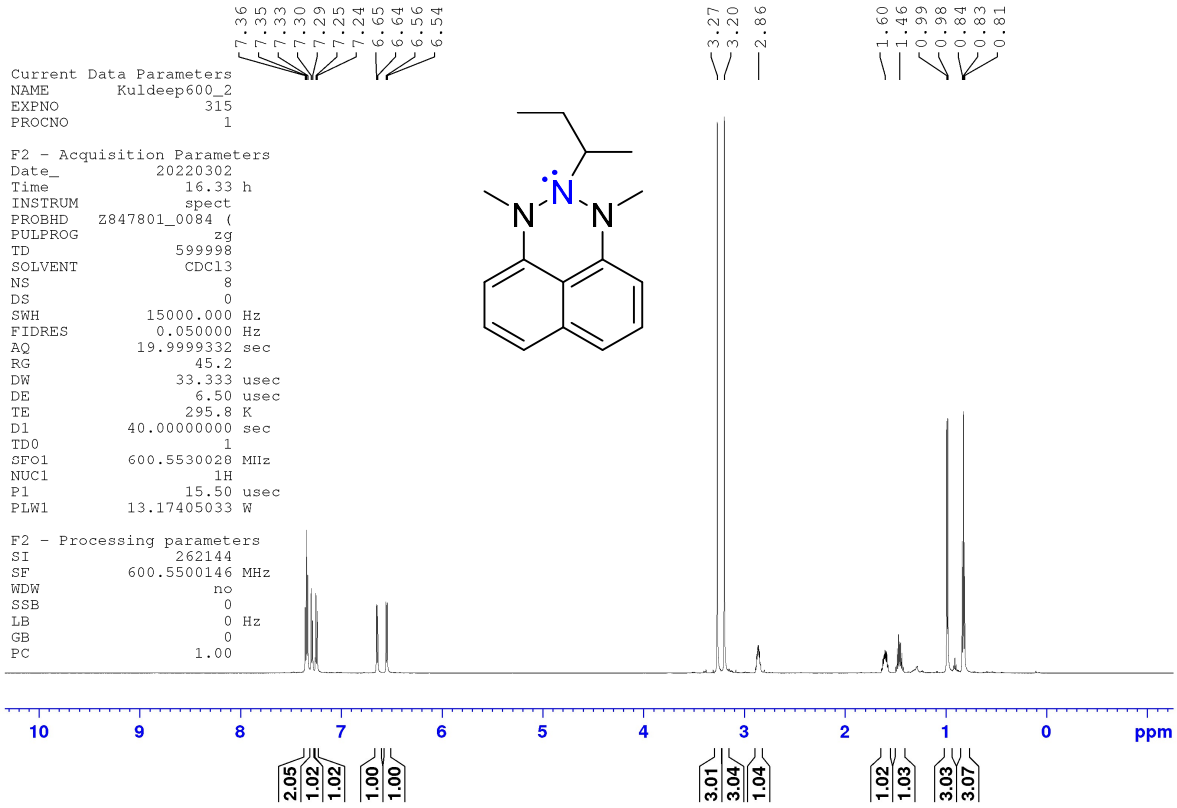
1*N*,3*N*-Dimethyl-2*N*-isopropylnaphthotriazane **2d** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



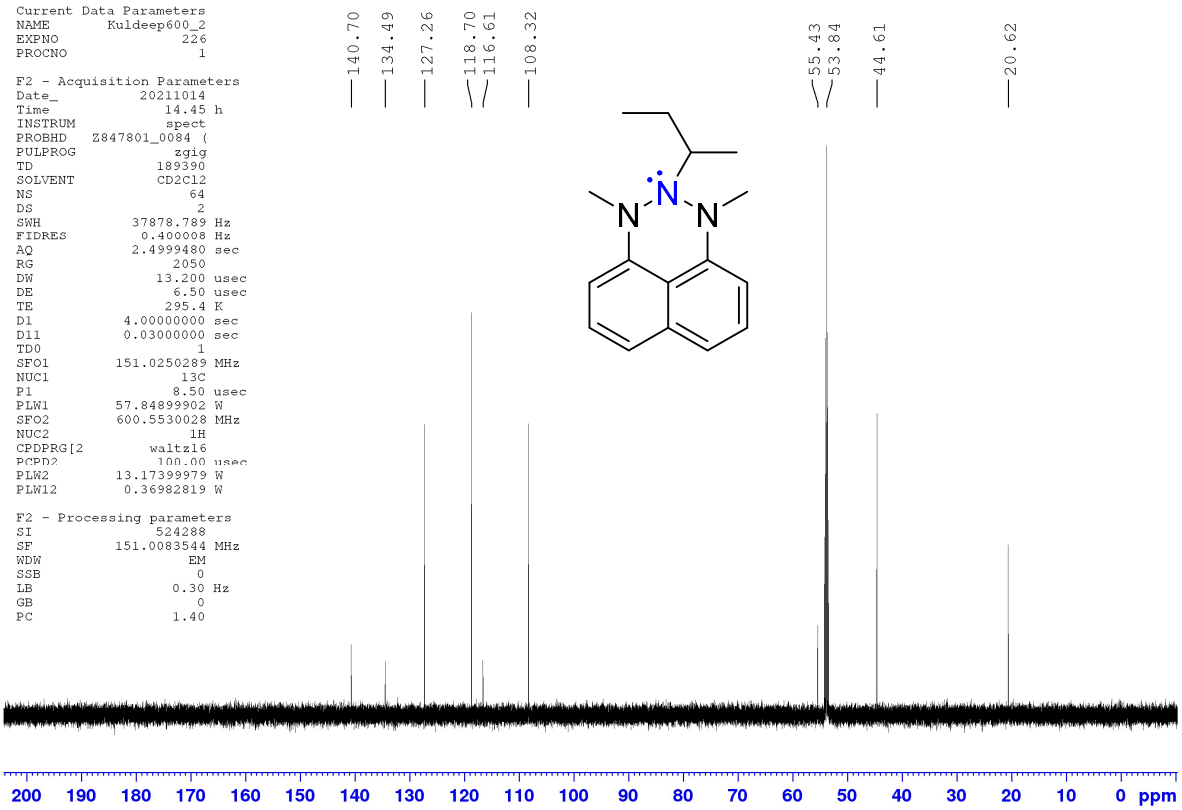
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



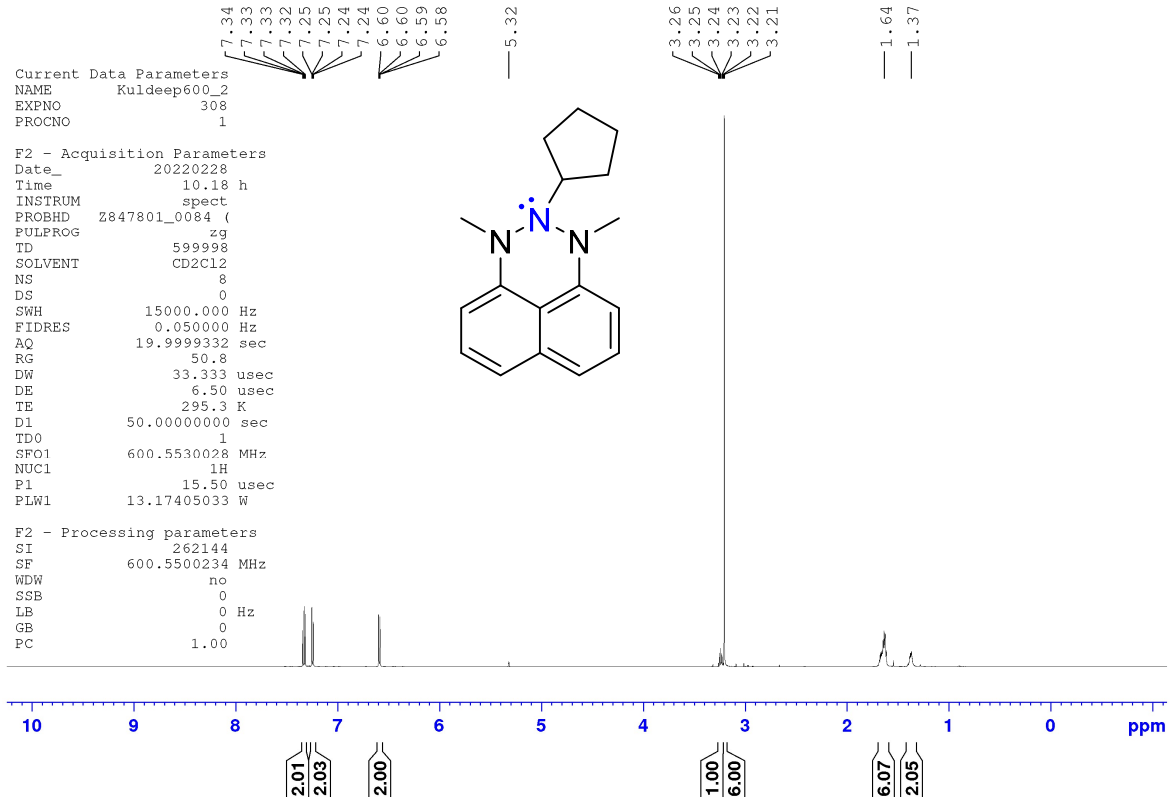
1*N*,3*N*-Dimethyl-2*N*-*sec*-butylnaphthotriazane **2e** – **^{1}H NMR** (600 MHz, $CDCl_3$):



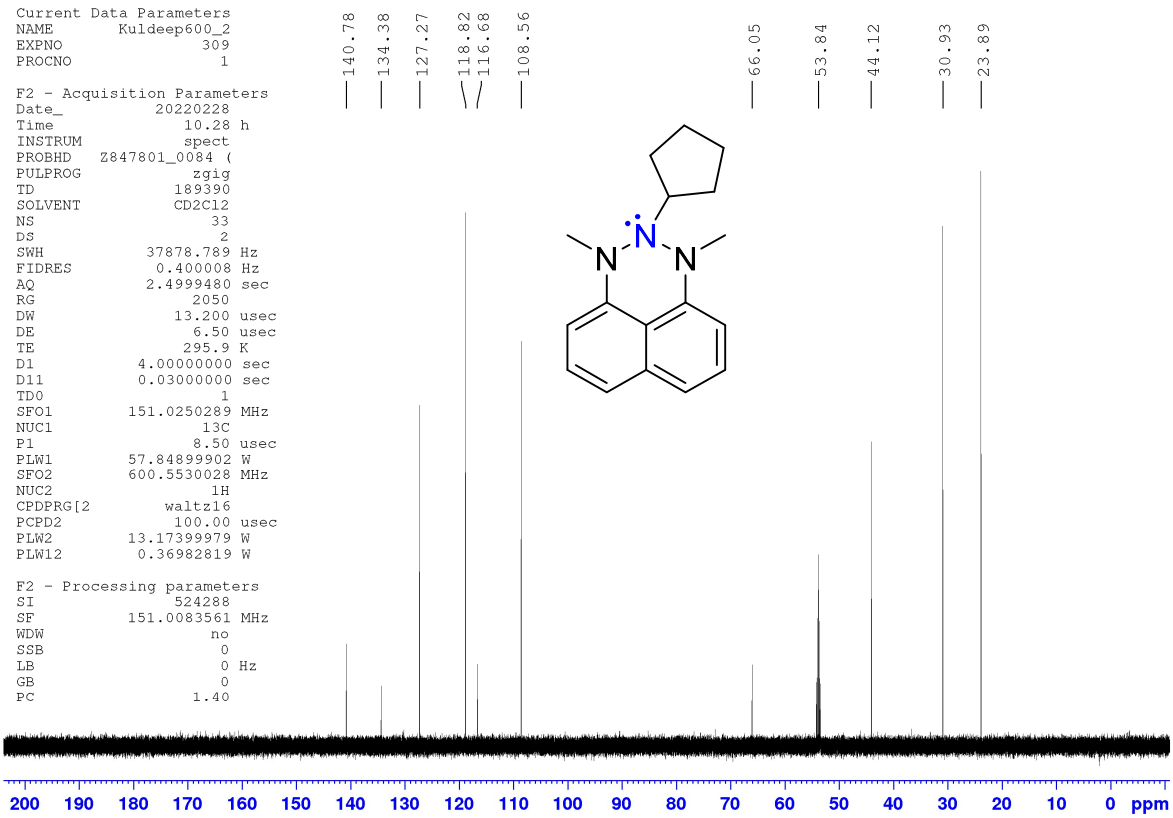
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):



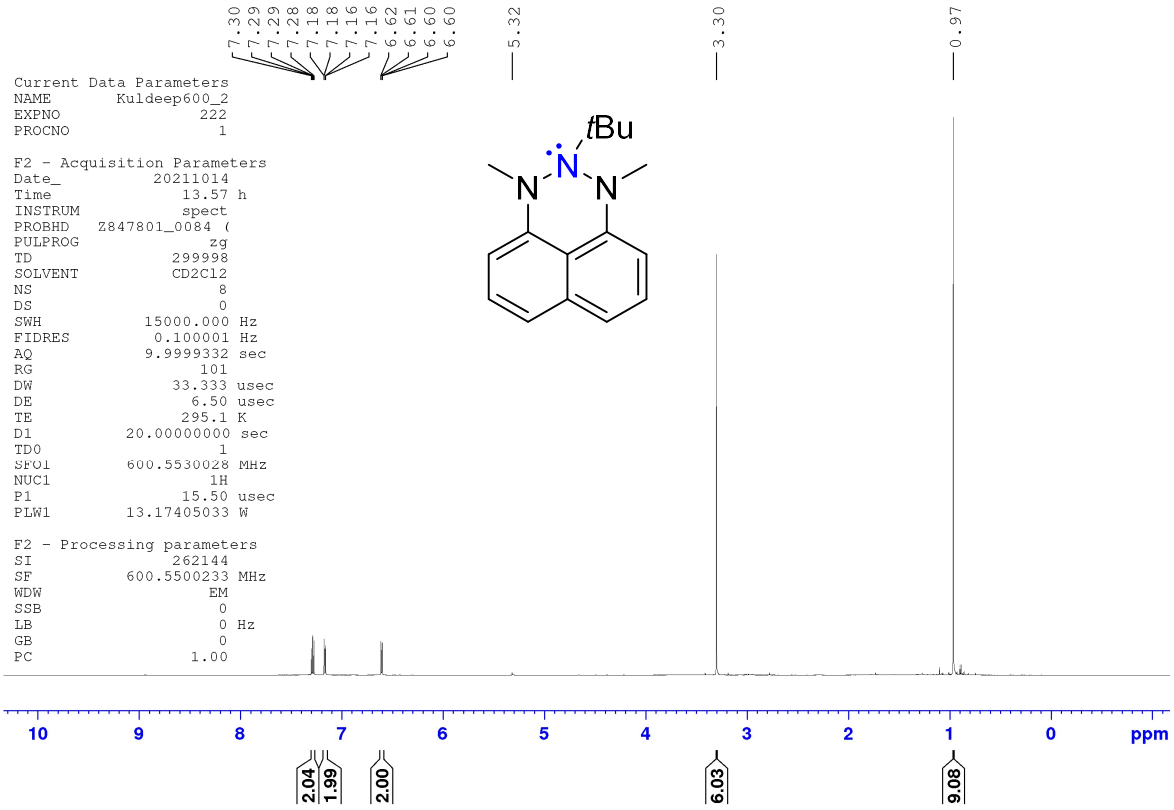
1*N*,3*N*-Dimethyl-2*N*-cyclopentylnaphthotriazane **2f** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



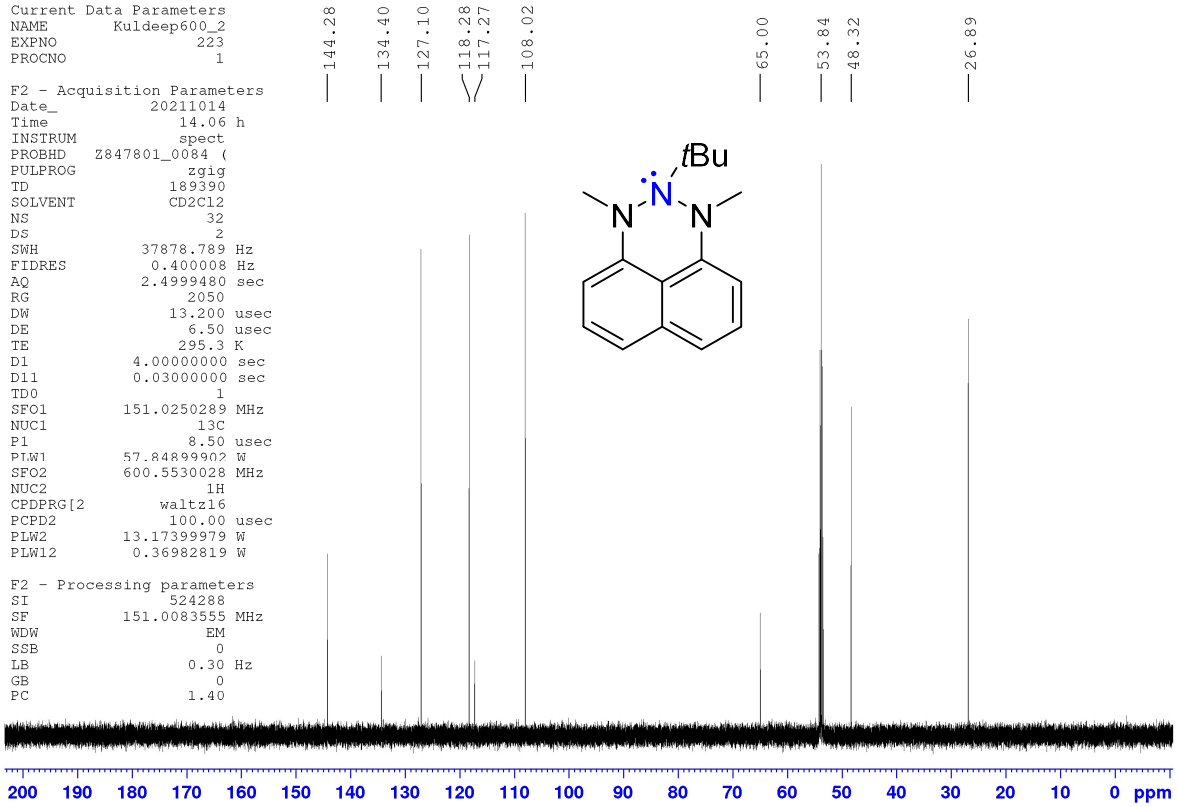
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



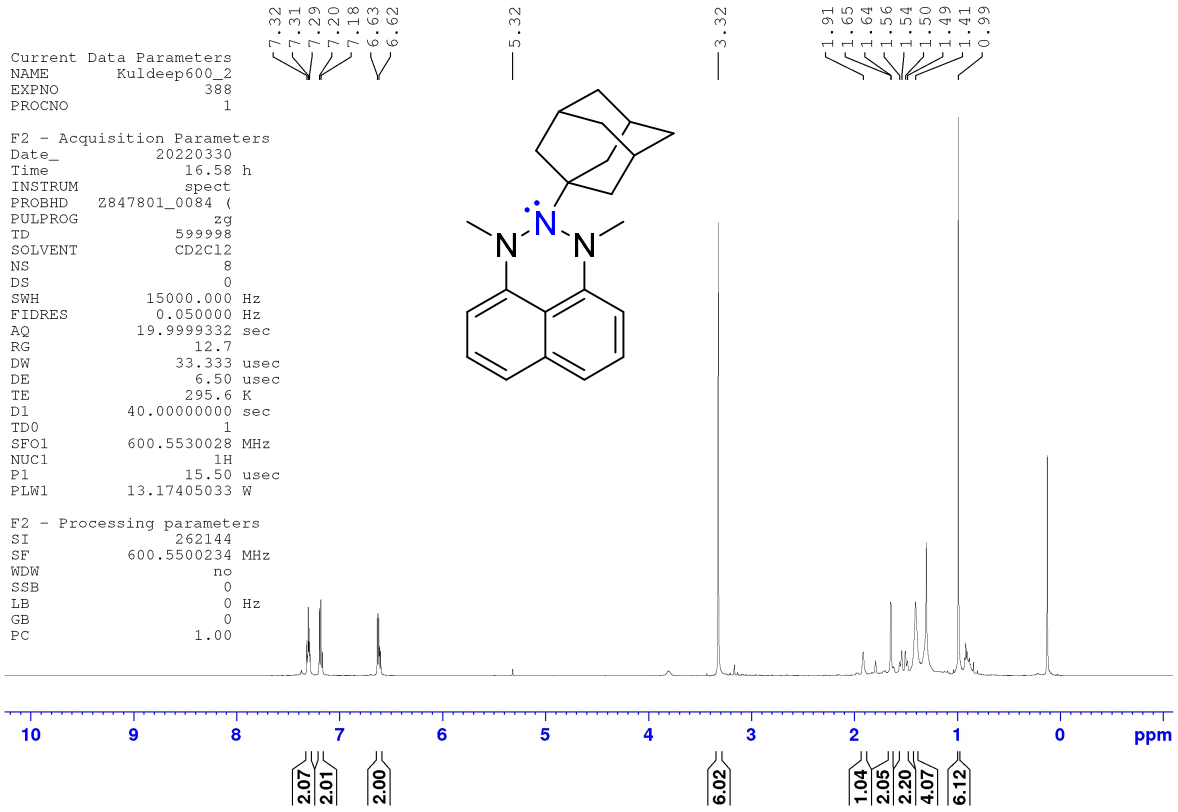
1*N*,3*N*-Dimethyl-2*N*-*tert*-butylnaphthotriazane **2g** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



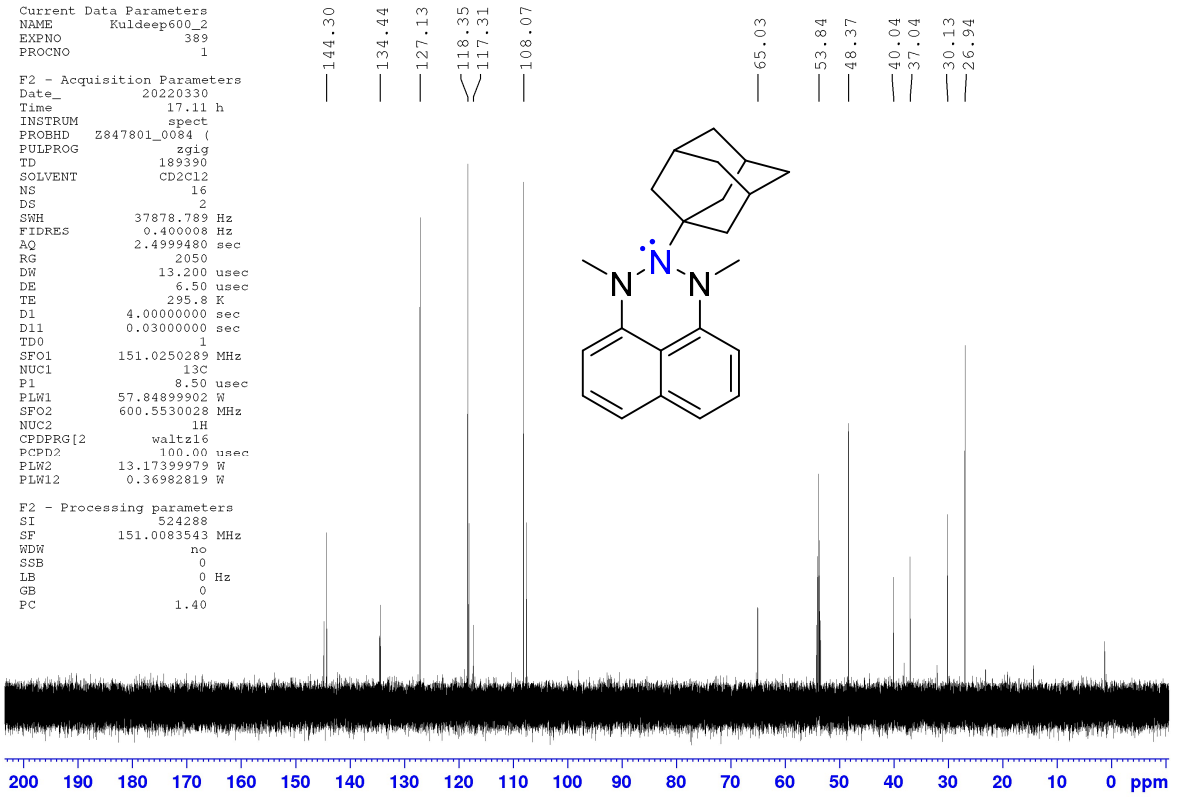
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



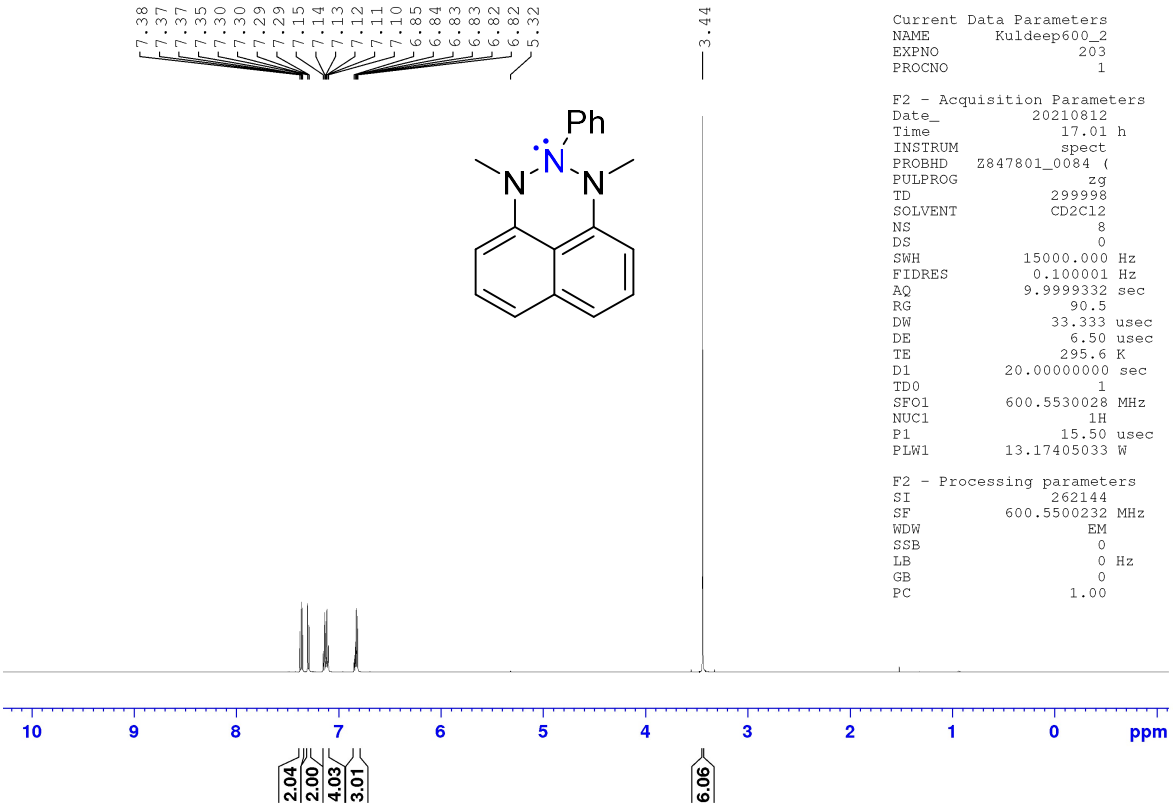
1*N*,3*N*-Dimethyl-2*N*-adamantylnaphthotriazane **2h** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



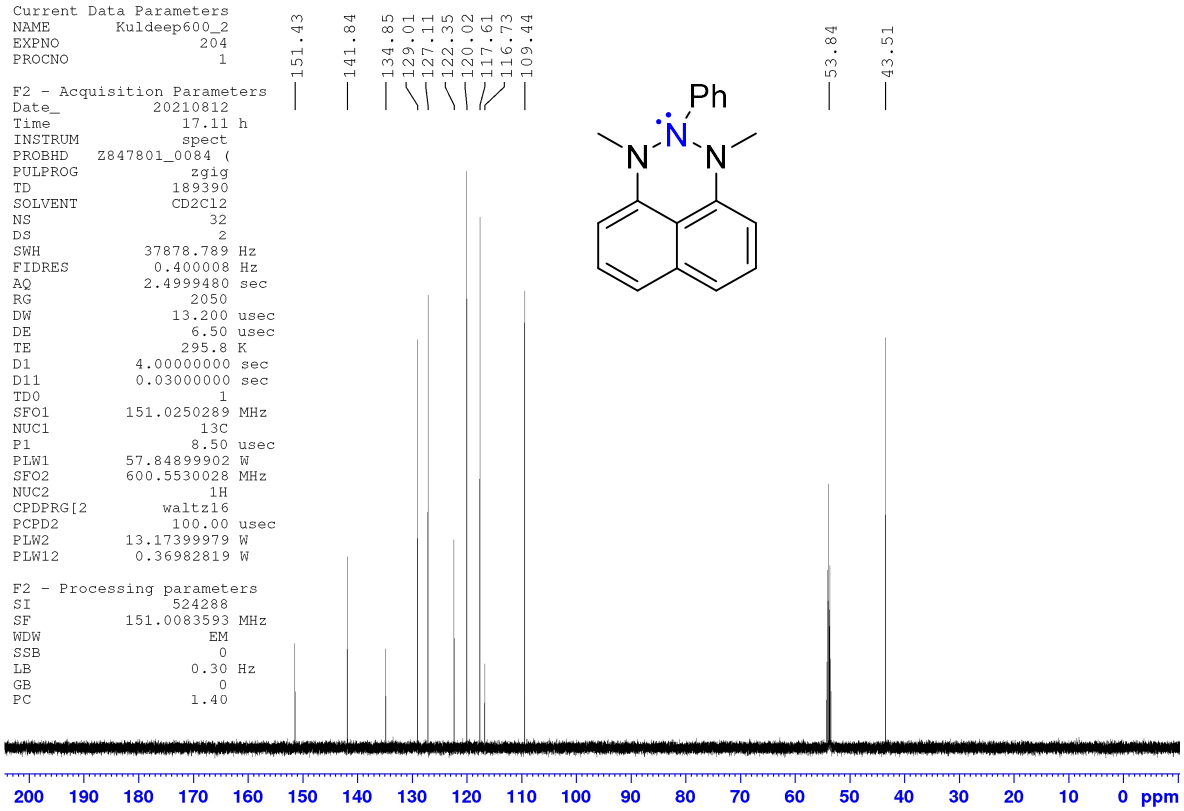
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



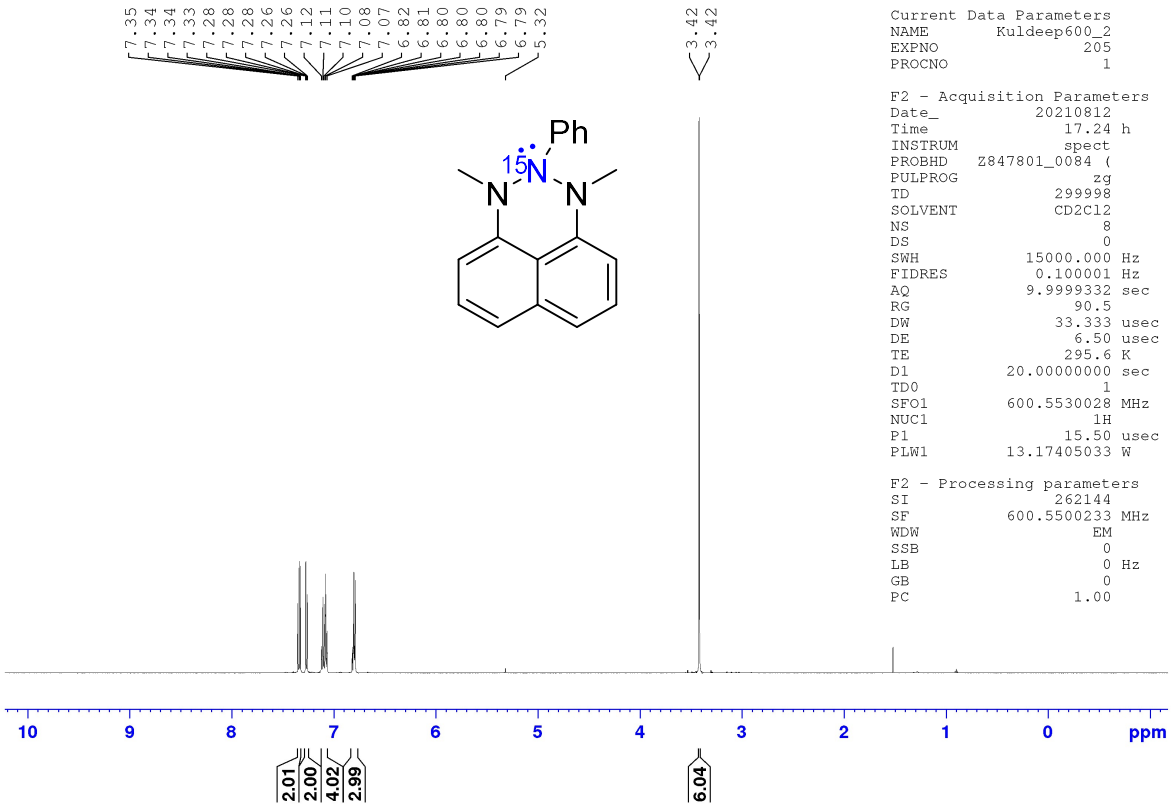
1*N*,3*N*-Dimethyl-2*N*-phenylnaphthotriazane **2i** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



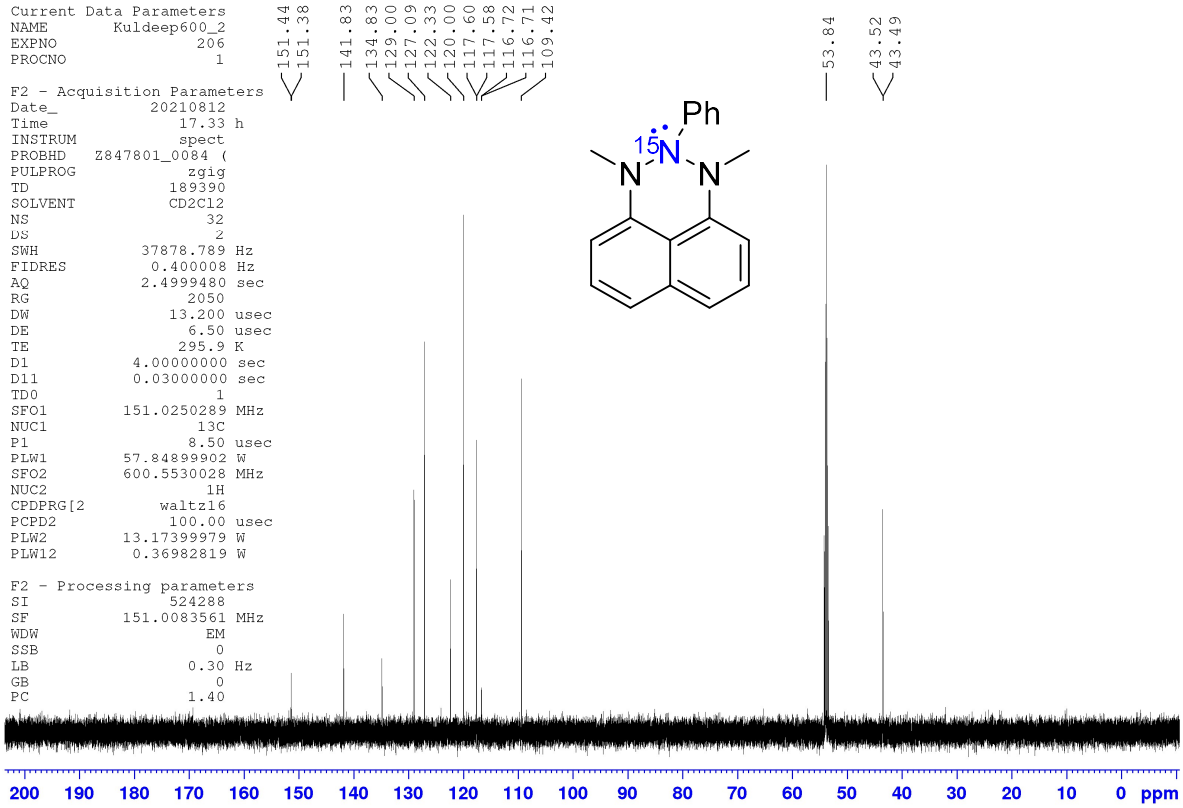
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



1*N*,3*N*-Dimethyl-2*N*-phenylnaphthotriazane (2-^{15}N) **2i'** – **^{1}H NMR** (600 MHz, CD_2Cl_2):

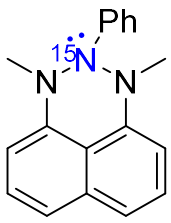


^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):

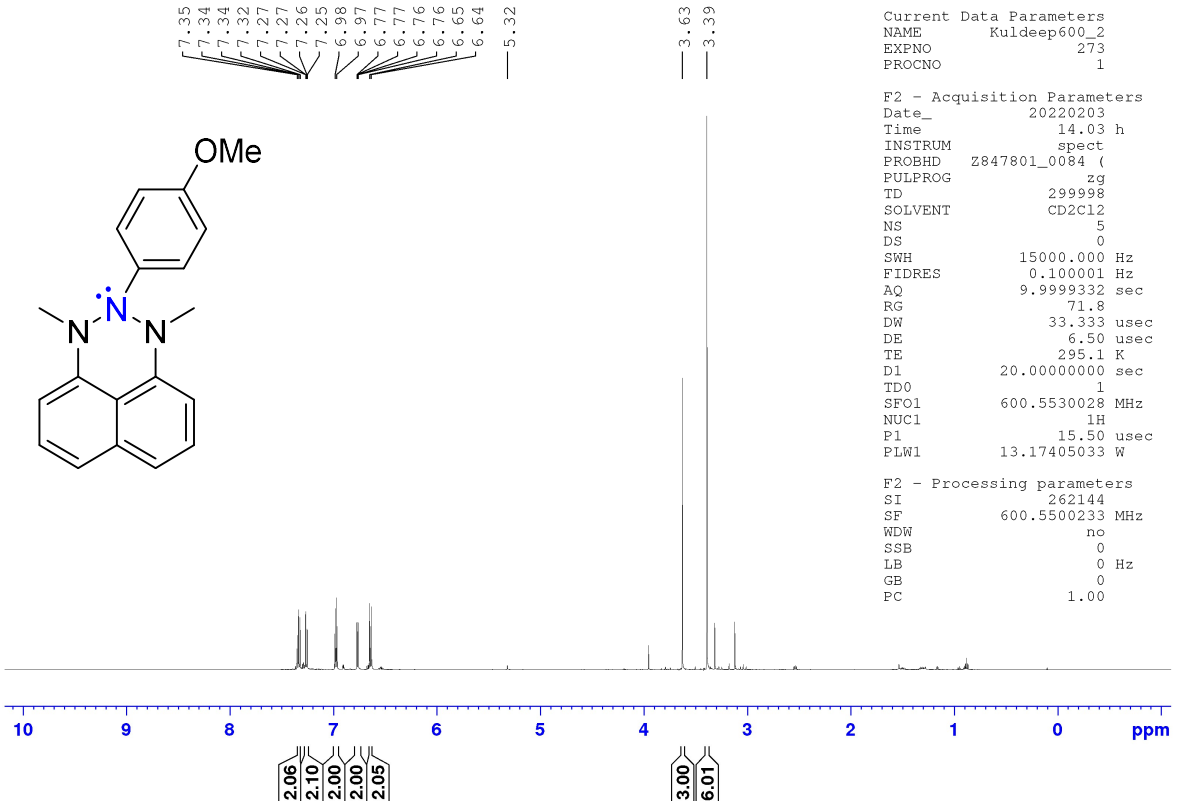


$^{15}N\{^{1}H\}$ NMR (60 MHz, CD_2Cl_2):

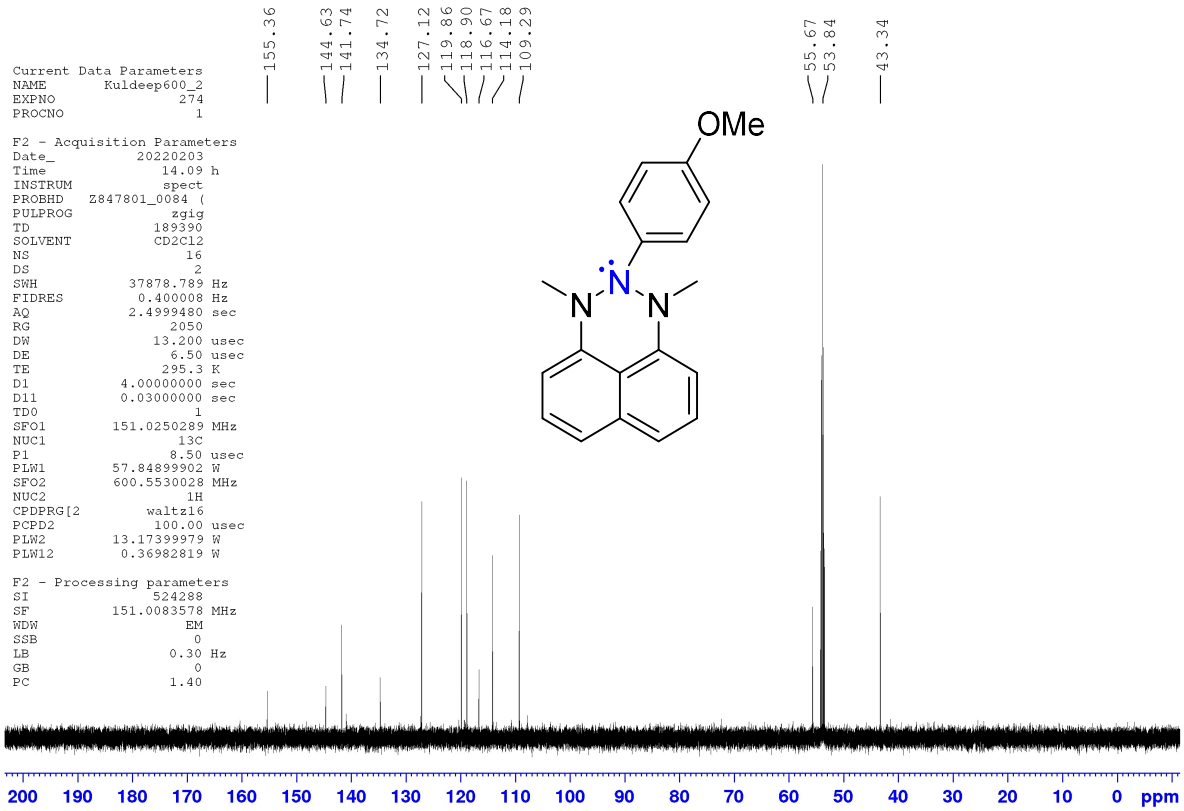
```
Current Data Parameters
NAME          Idan600_2
EXPNO                82
PROCNO                1

F2 - Acquisition Parameters
Date_          20210207
Time              18.48 h
INSTRUM           spect
PROBHD   Z847801_0084 (
PULPROG           zgig
TD               65536
SOLVENT          CD2Cl2
NS                 257
DS                   0
SWH           24350.648 Hz
FIDRES         0.743123 Hz
AQ            1.3456725 sec
RG                  16
DW               20.533 usec
DE                6.50 usec
TE                295.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                  1
SFO1         60.8684163 MHz
NUC1                15N
P1                12.70 usec
PLW1       123.96130371 W
SFO2        600.5543840 MHz
NUC2                1H
CPDPRG[2         waltz64
PCPD2             100.00 usec
PLW2        13.17405033 W
PLW12        0.29493019 W

F2 - Processing parameters
SI                262144
SF           60.8763617 MHz
WDW                  EM
SSB                   0
LB                    0 Hz
GB                    0
PC                 1.00
```



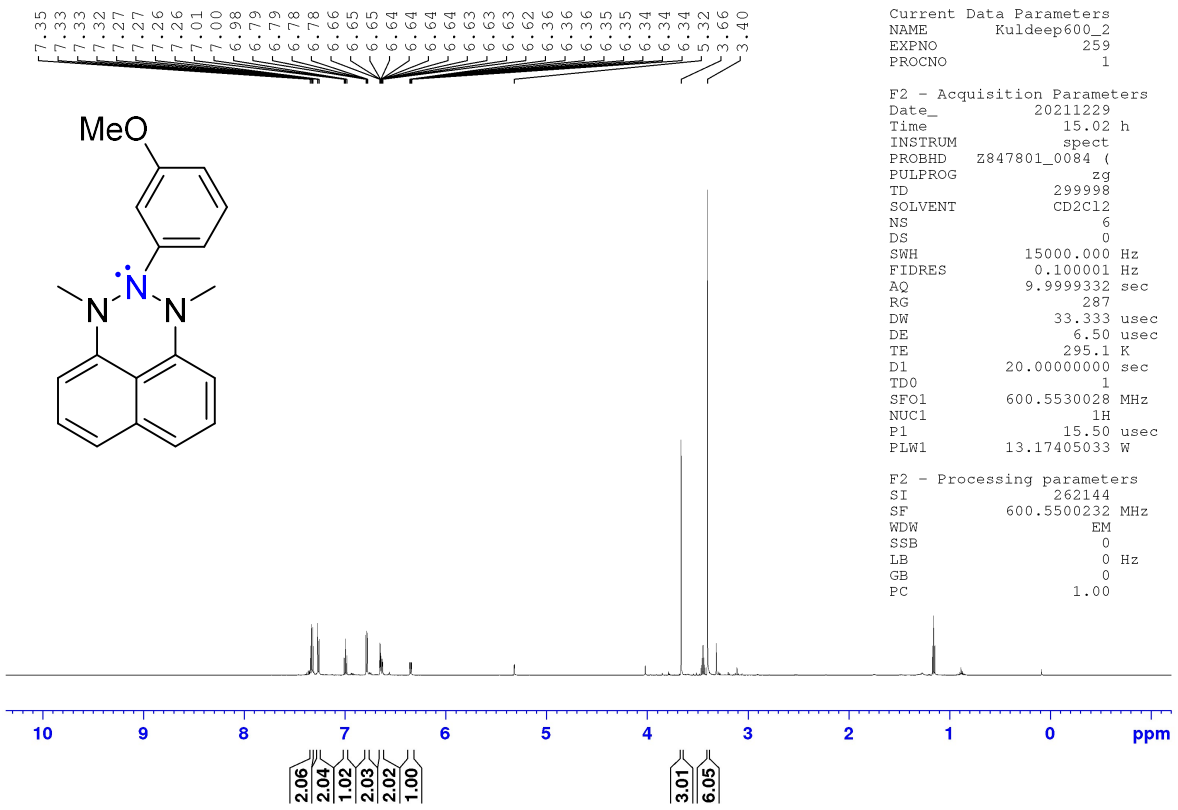
1*N*,3*N*-Dimethyl-2*N*-(4-methoxyphenyl)naphthotriazane **2j** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



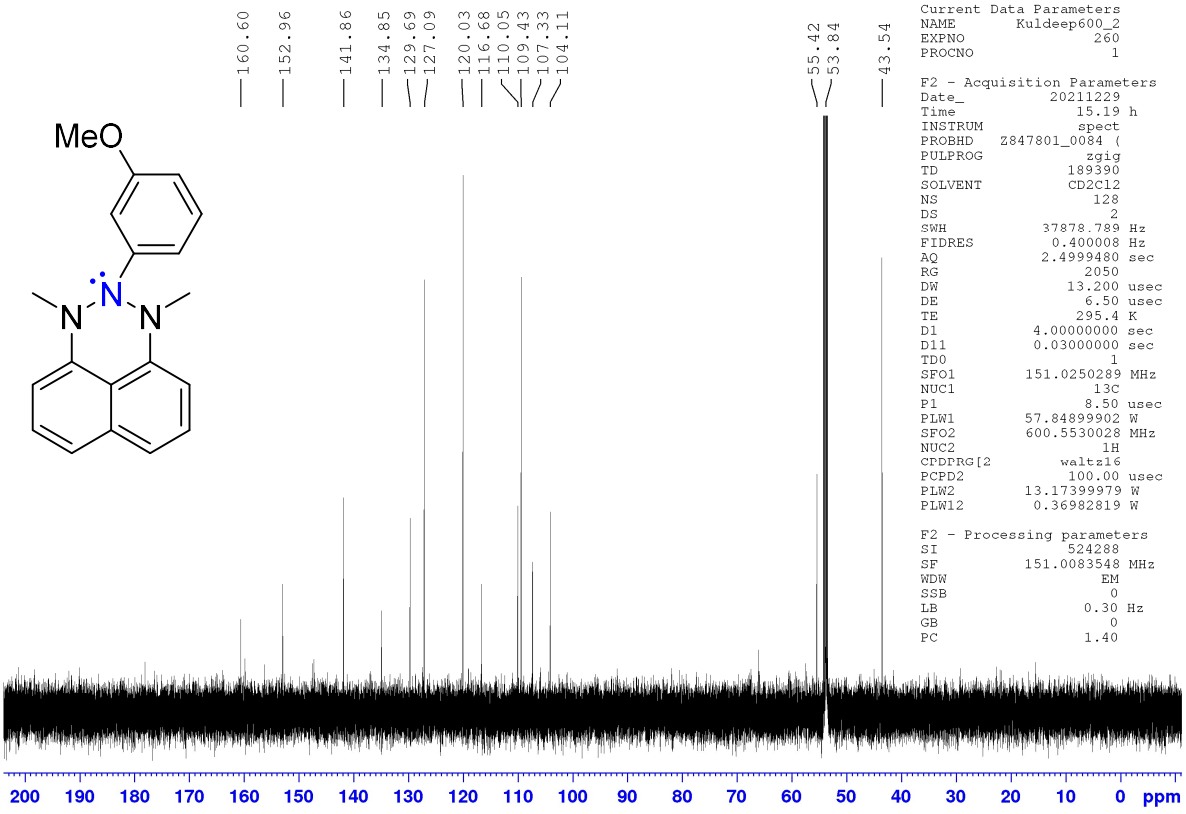
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



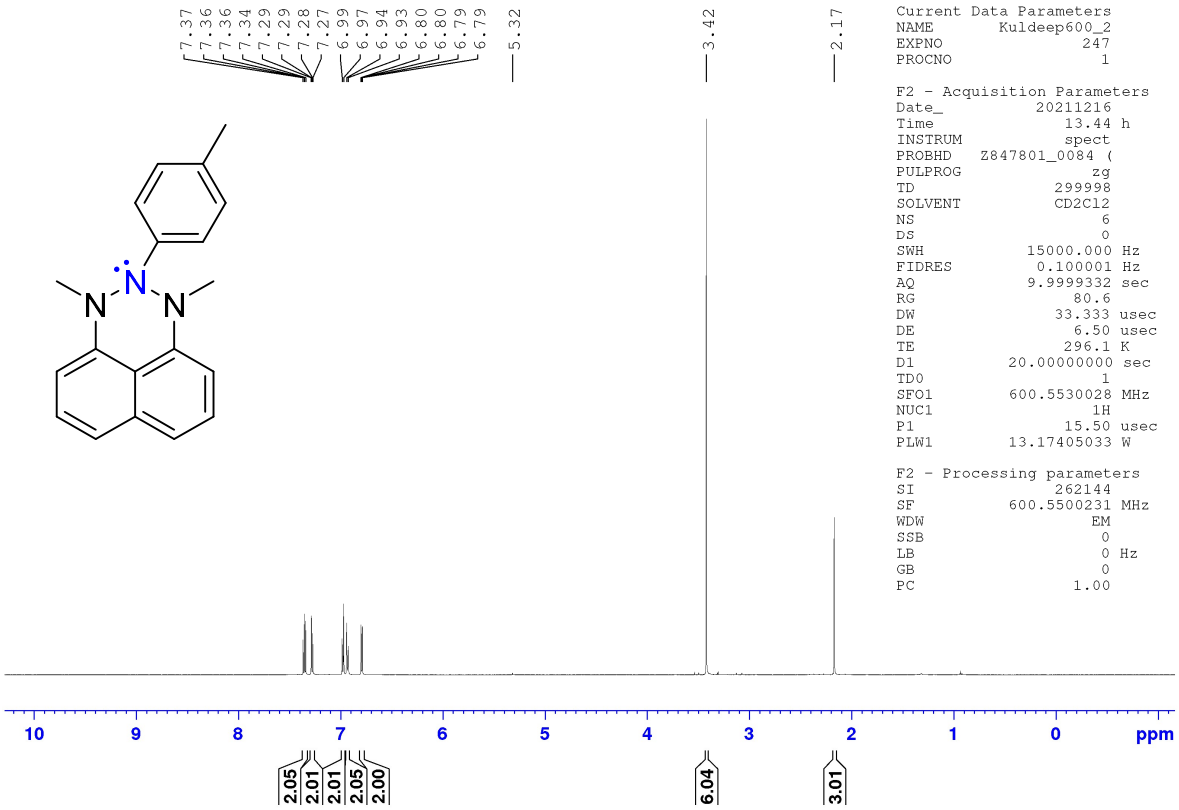
1*N*,3*N*-Dimethyl-2*N*-(3-methoxyphenyl)naphthotriazane **2k** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



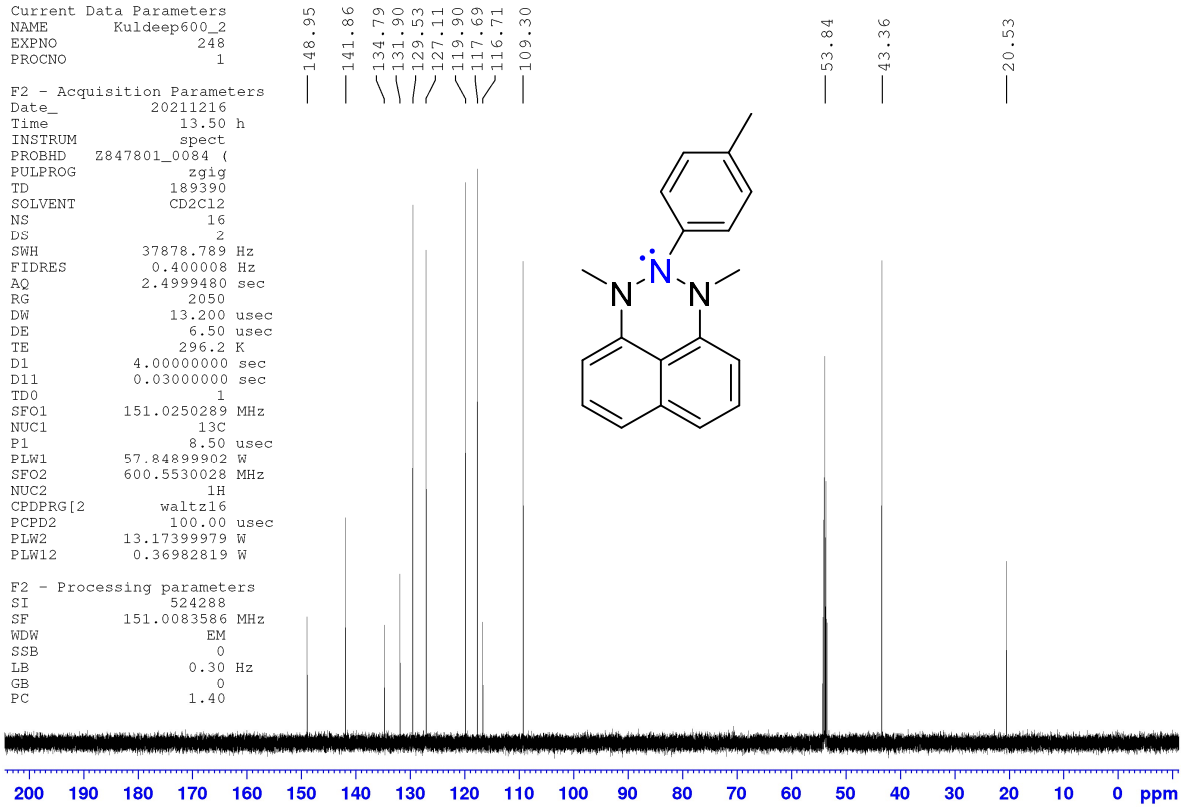
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



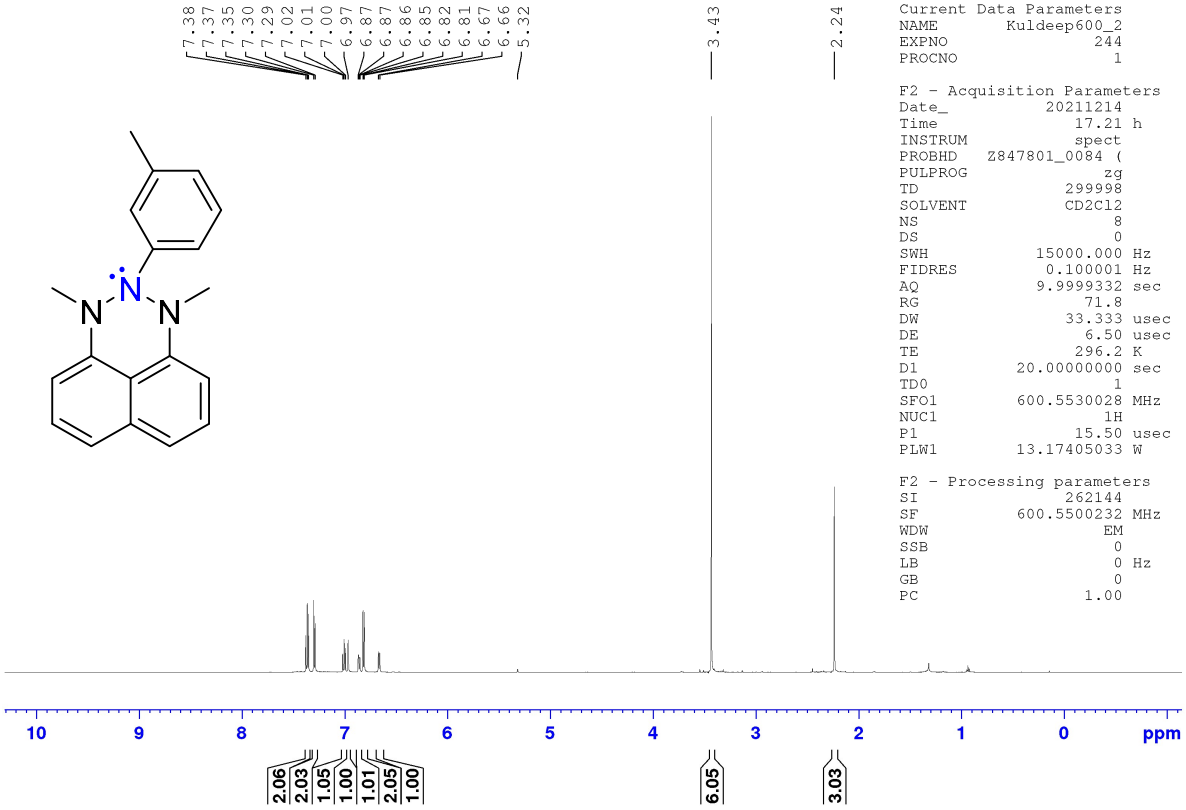
1*N*,3*N*-Dimethyl-2*N*-(4-tolyl)naphthotriazane **2l** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



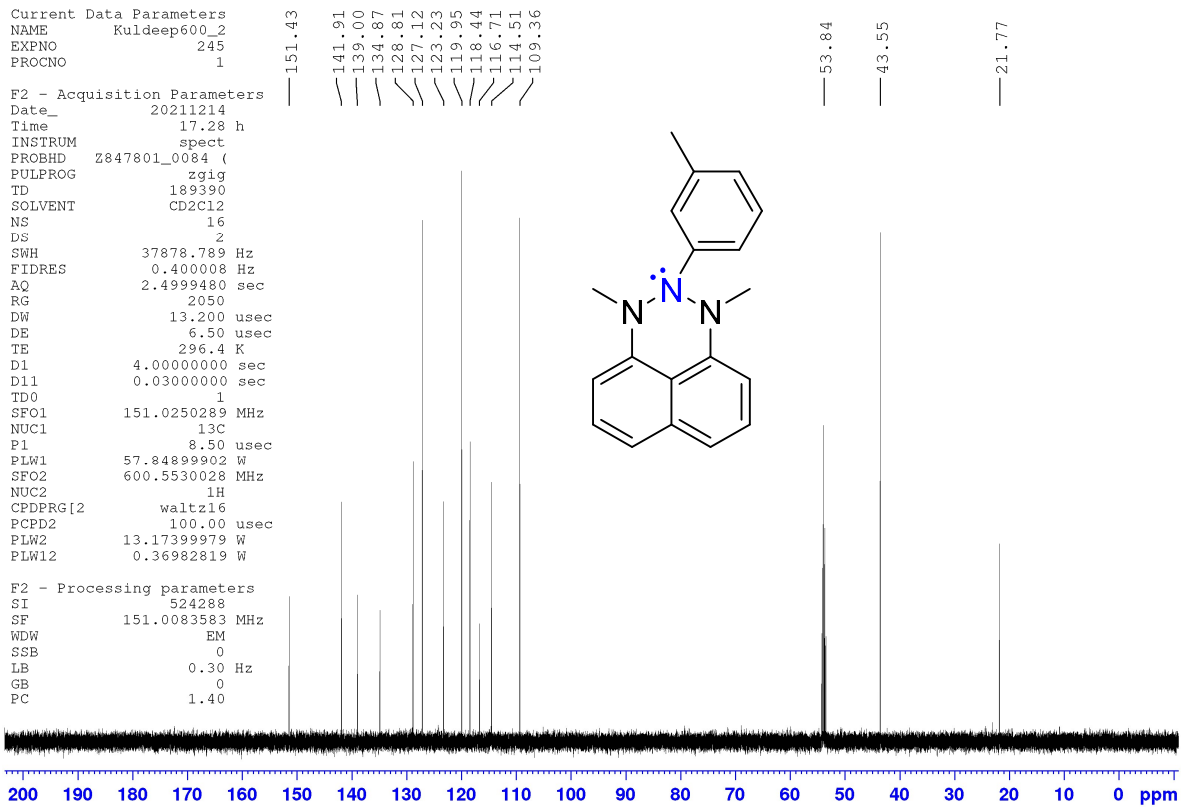
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



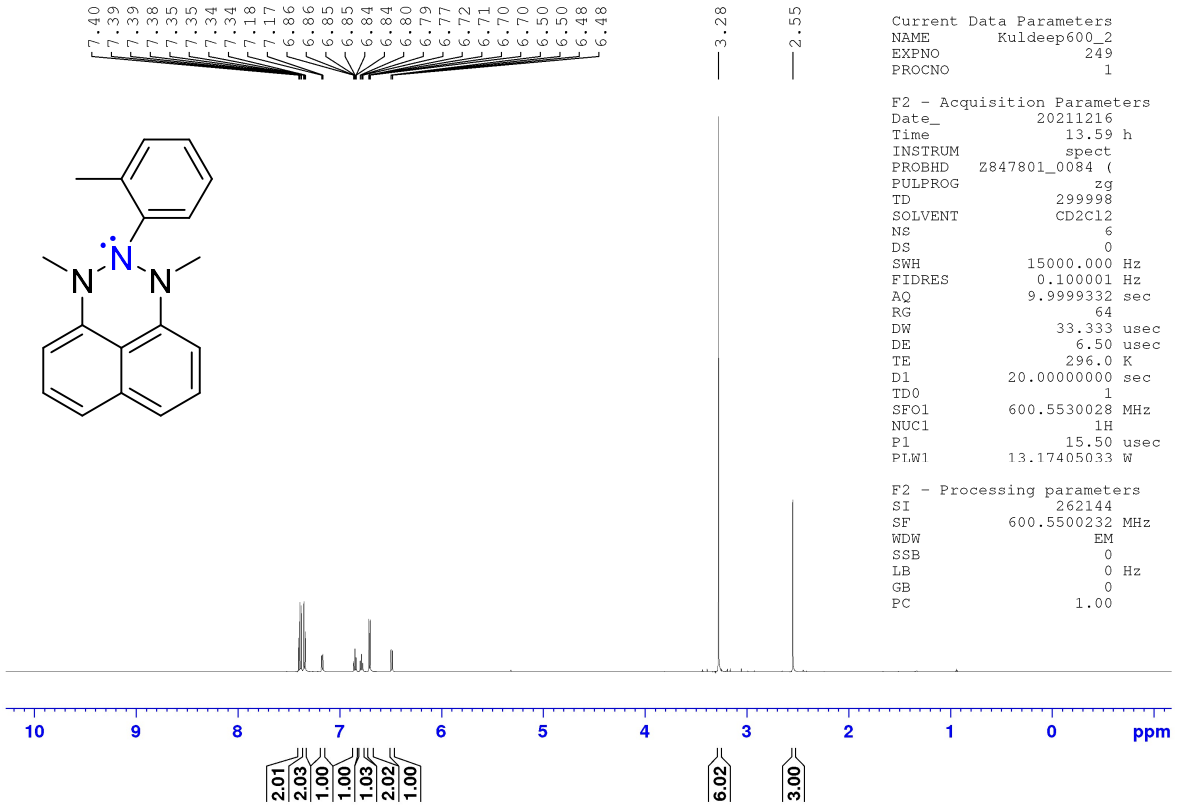
1*N*,3*N*-Dimethyl-2*N*-(3-tolyl)naphthotriazane **2m** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



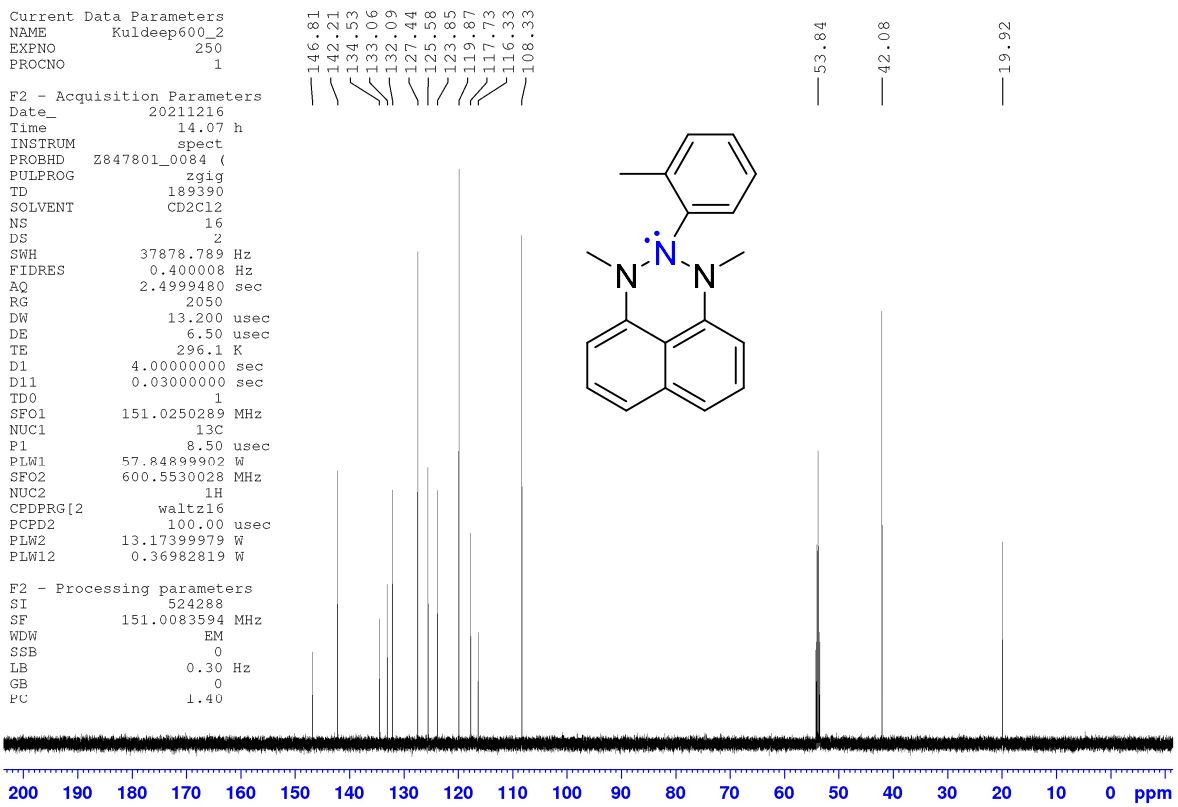
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



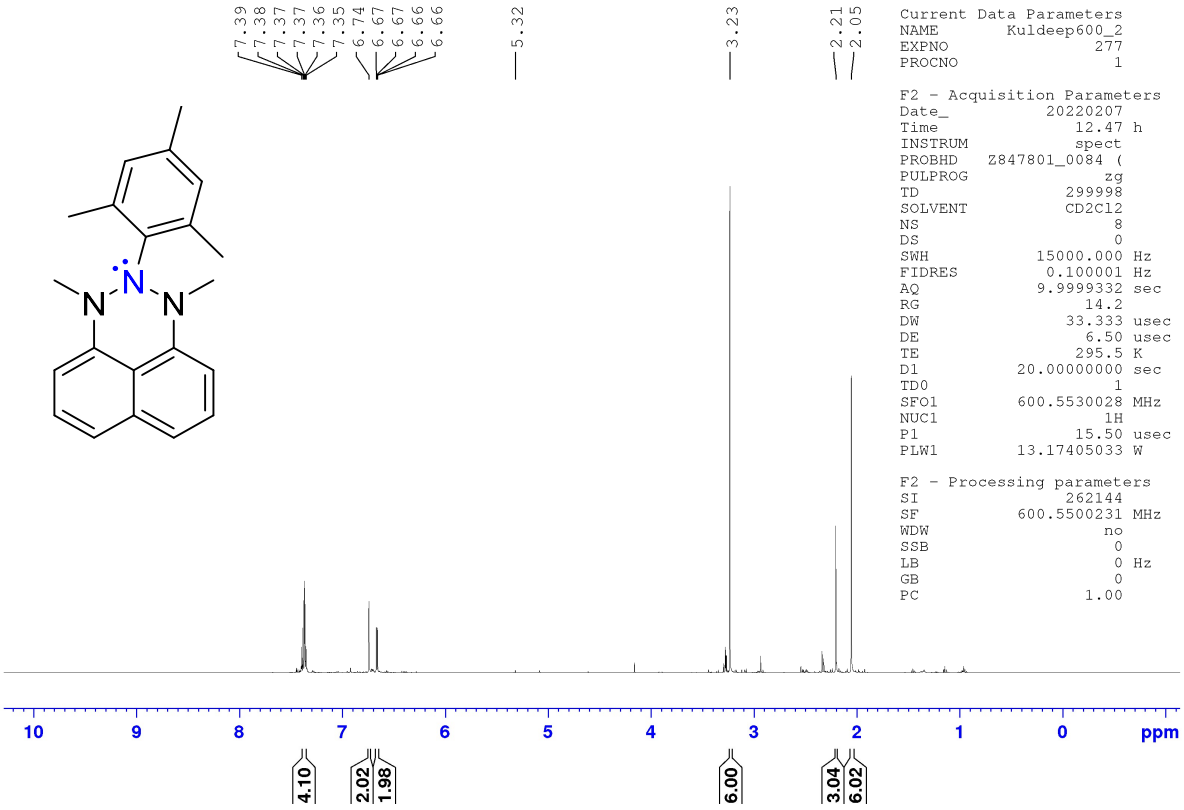
1*N*,3*N*-Dimethyl-2*N*-(2-tolyl)naphthotriazane **2n** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



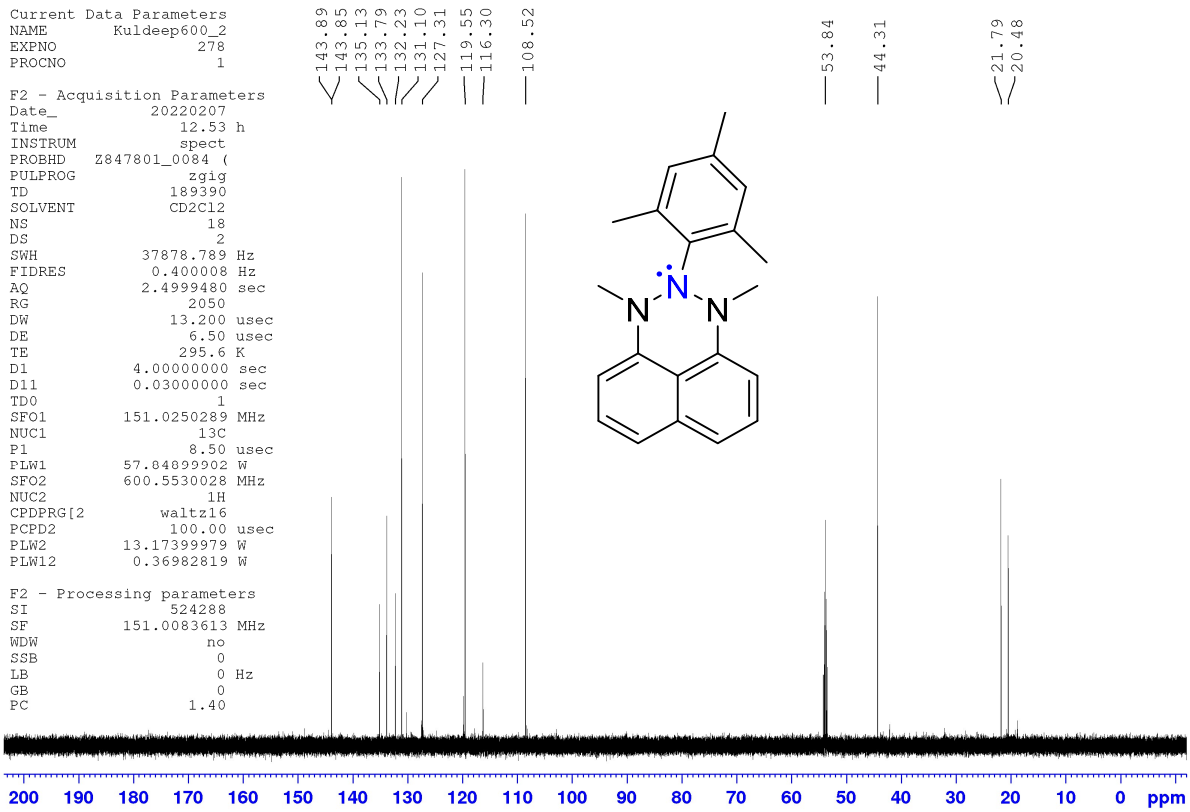
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



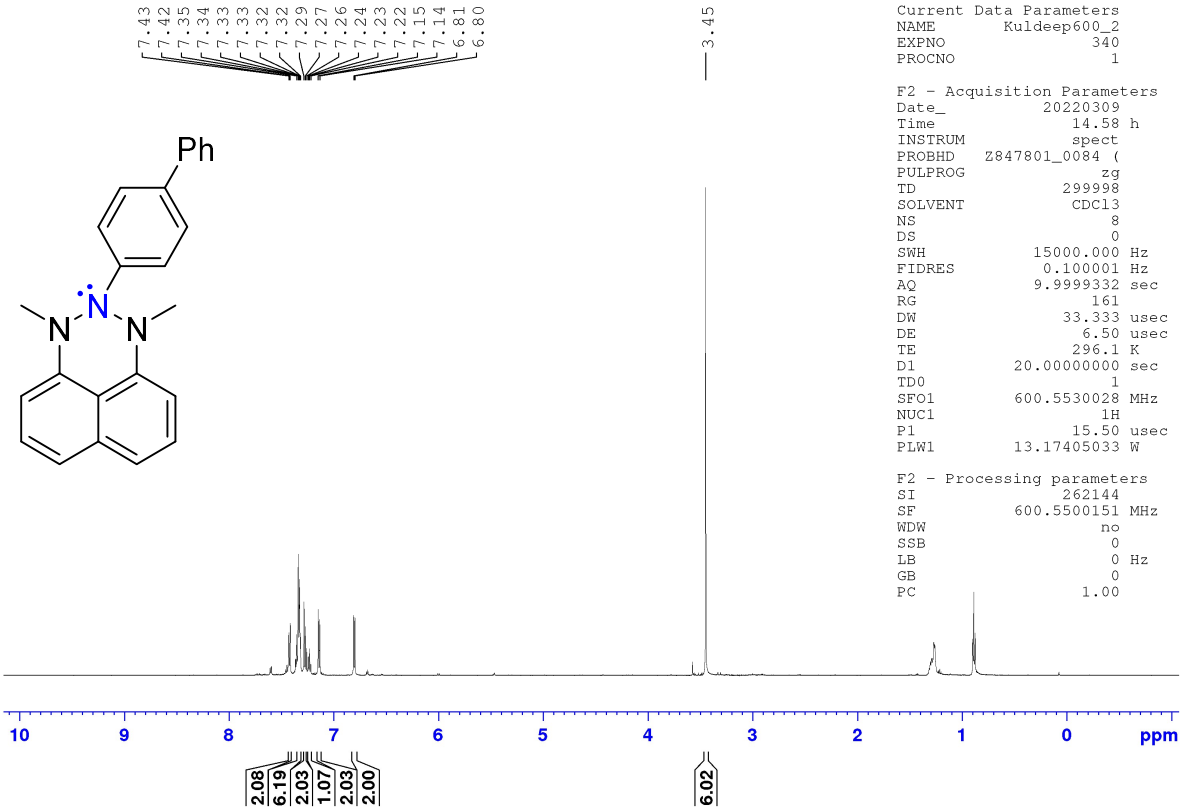
1*N*,3*N*-Dimethyl-2*N*-mesitylnaphthotriazane **2o** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



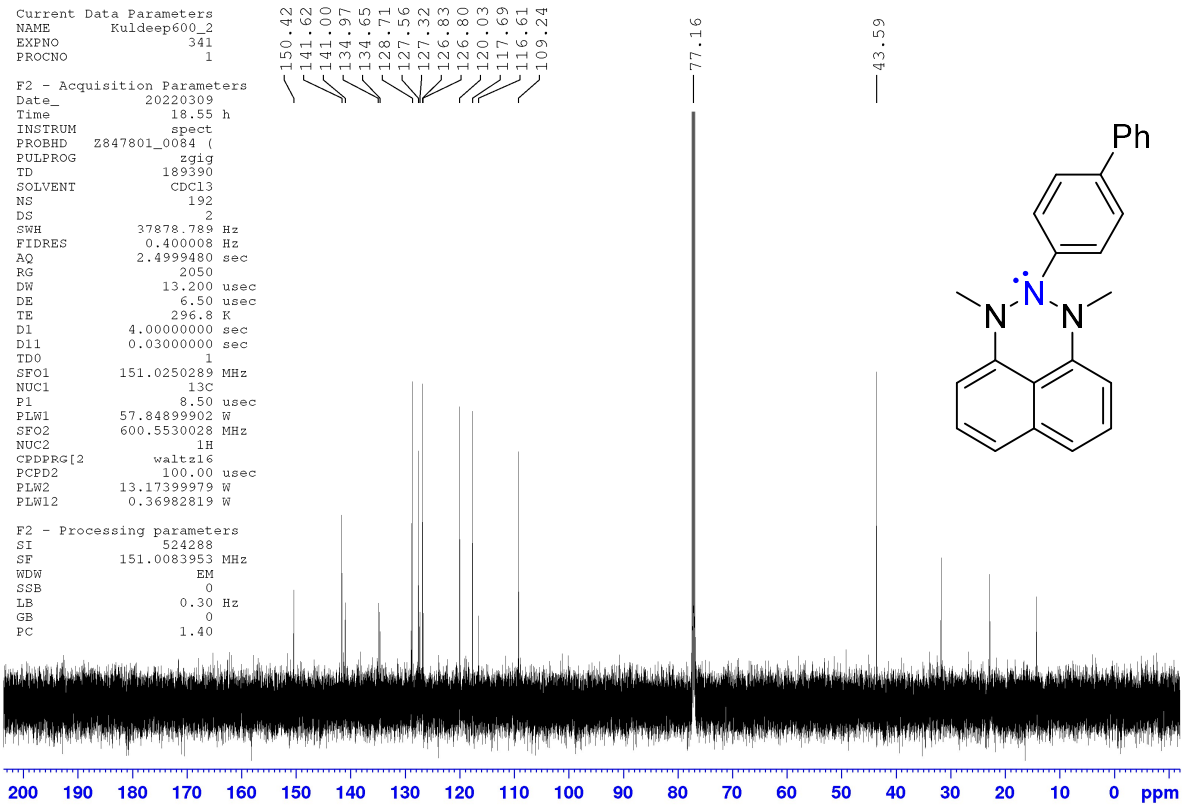
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



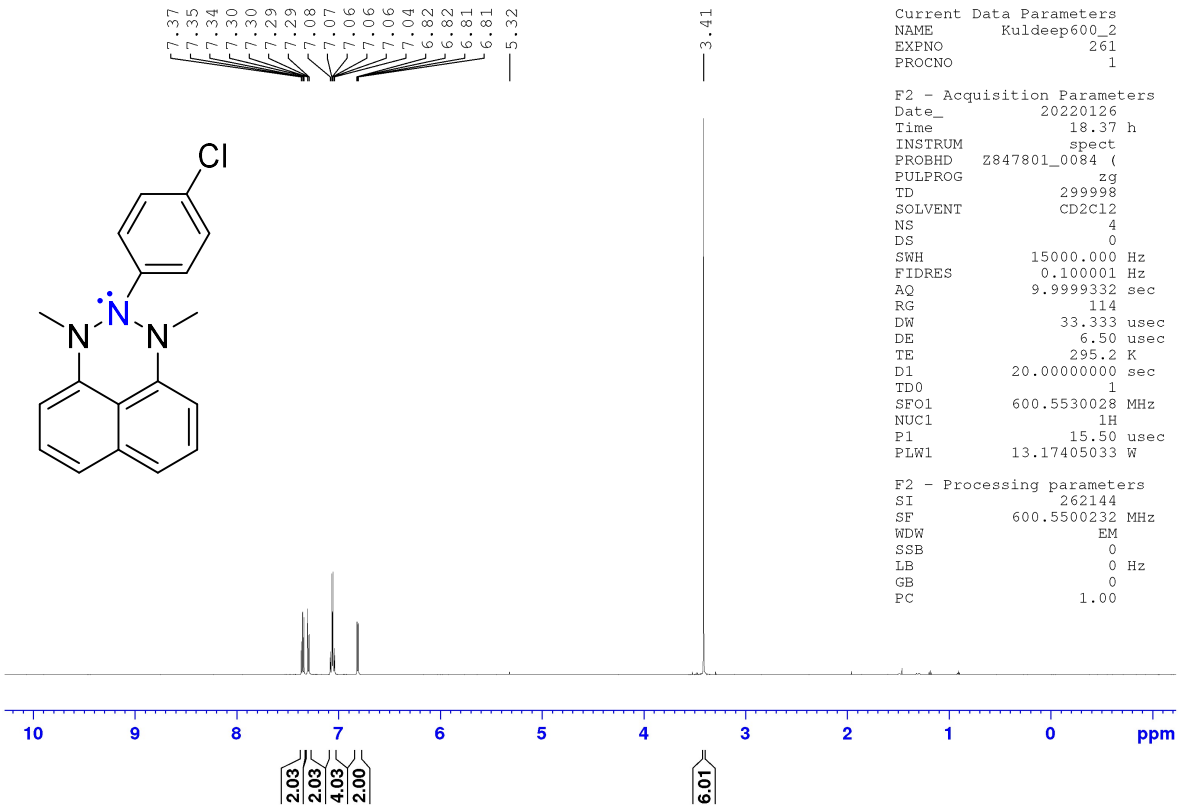
1*N*,3*N*-Dimethyl-2*N*-(4-biphenyl)naphthotriazane **2p** – ^{1}H **NMR** (600 MHz, $CDCl_3$):



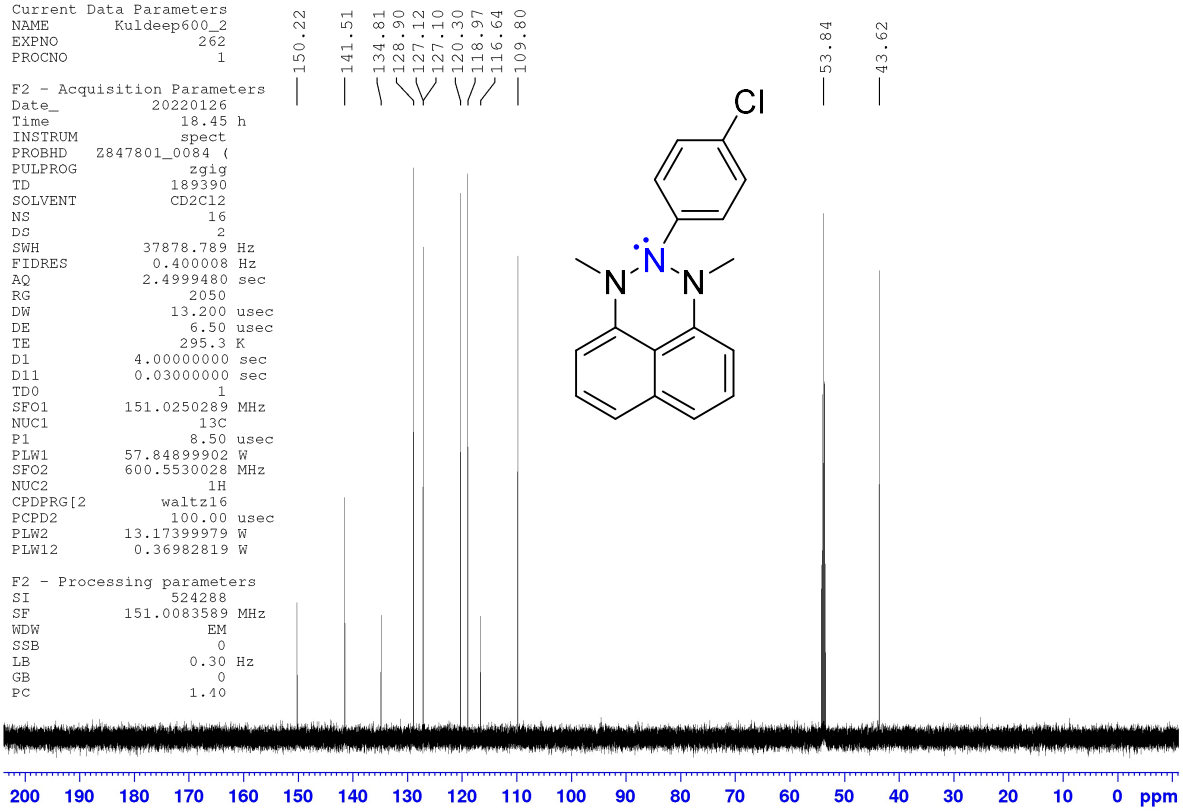
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):



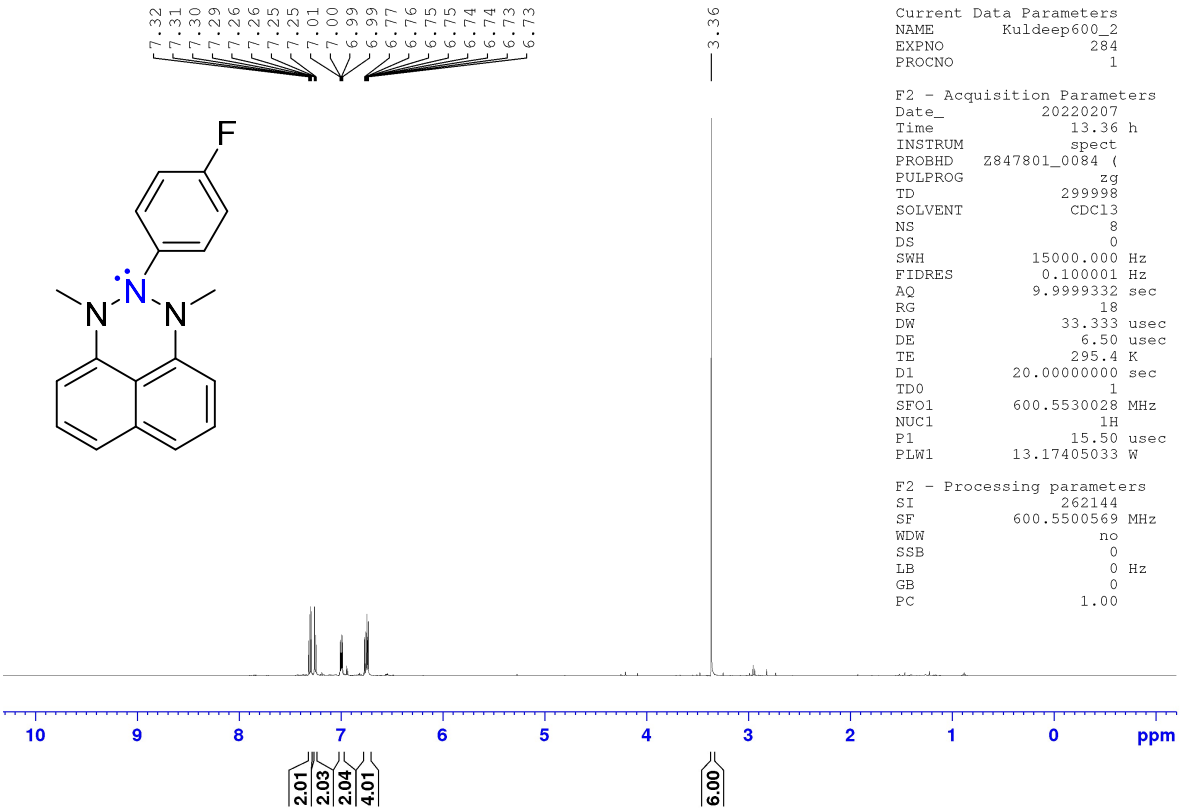
1*N*,3*N*-Dimethyl-2*N*-(4-chlorophenyl)naphthotriazane **2q** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



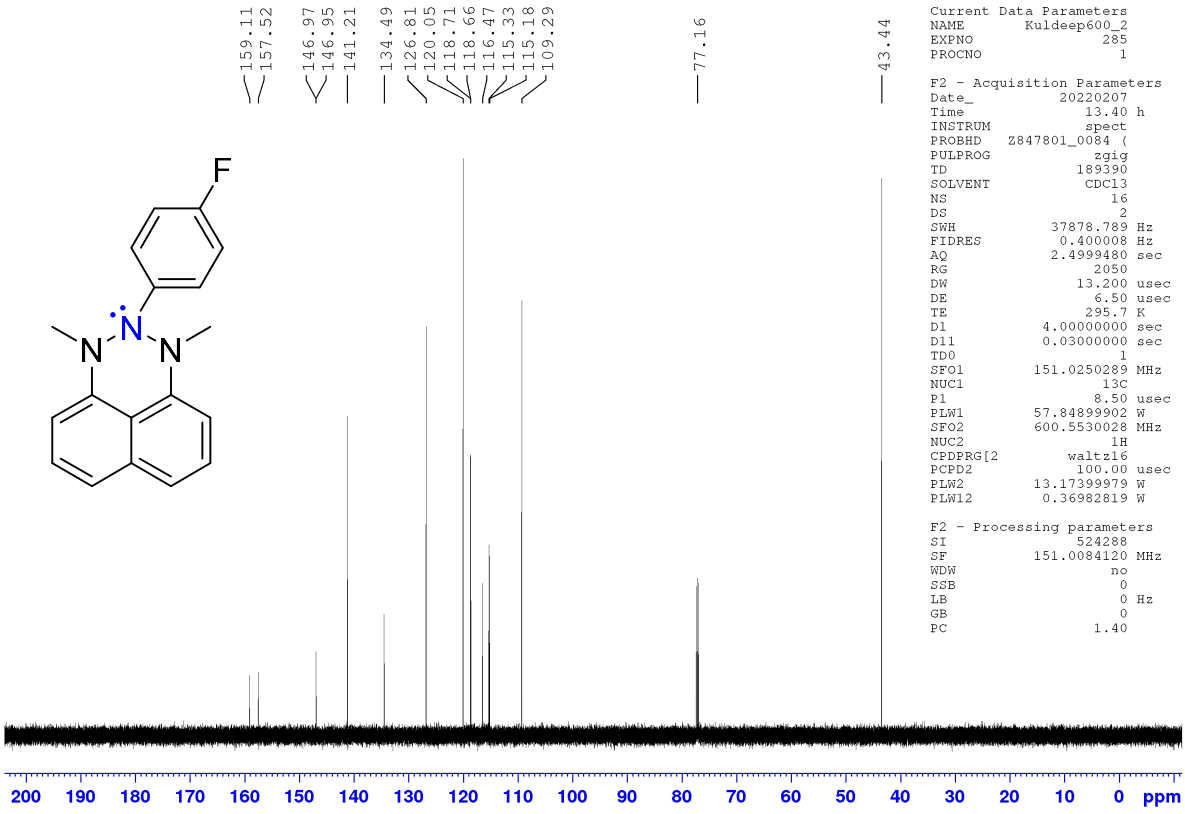
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



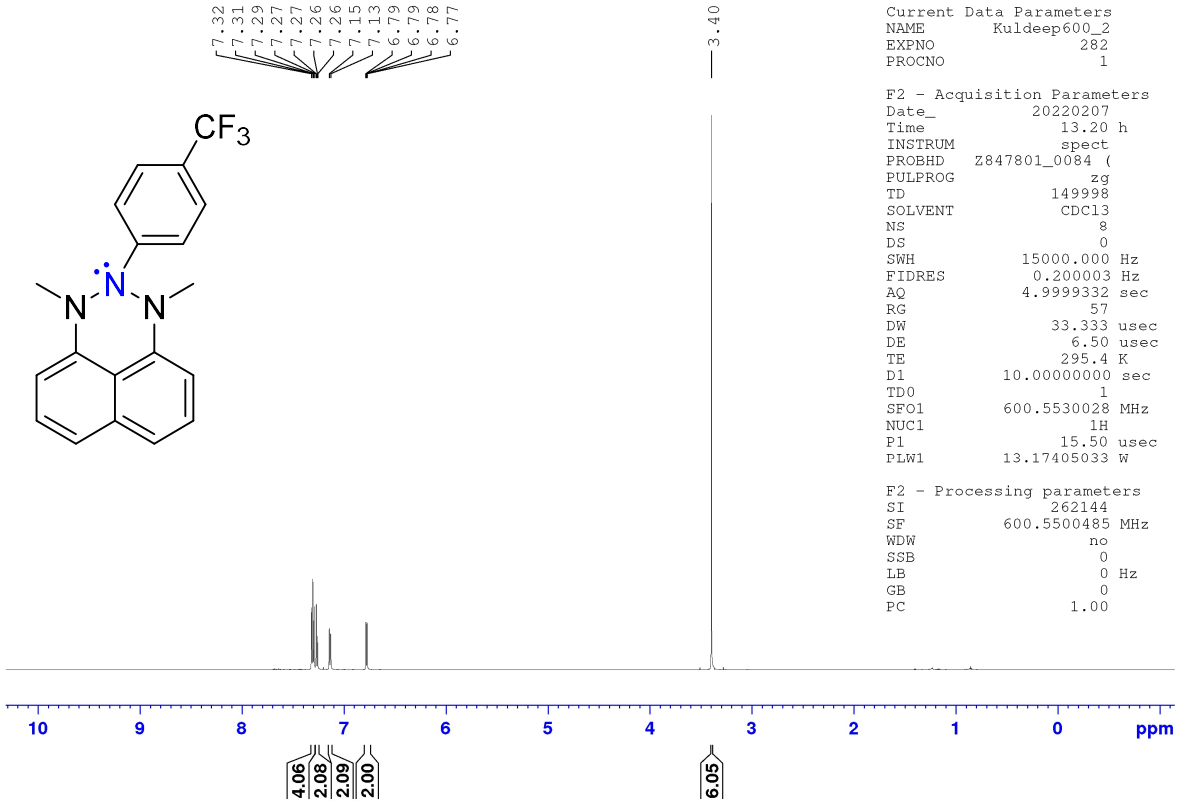
1*N*,3*N*-Dimethyl-2*N*-(4-fluorophenyl)naphthotriazane **2r** – **^{1}H NMR** (600 MHz, $CDCl_3$):



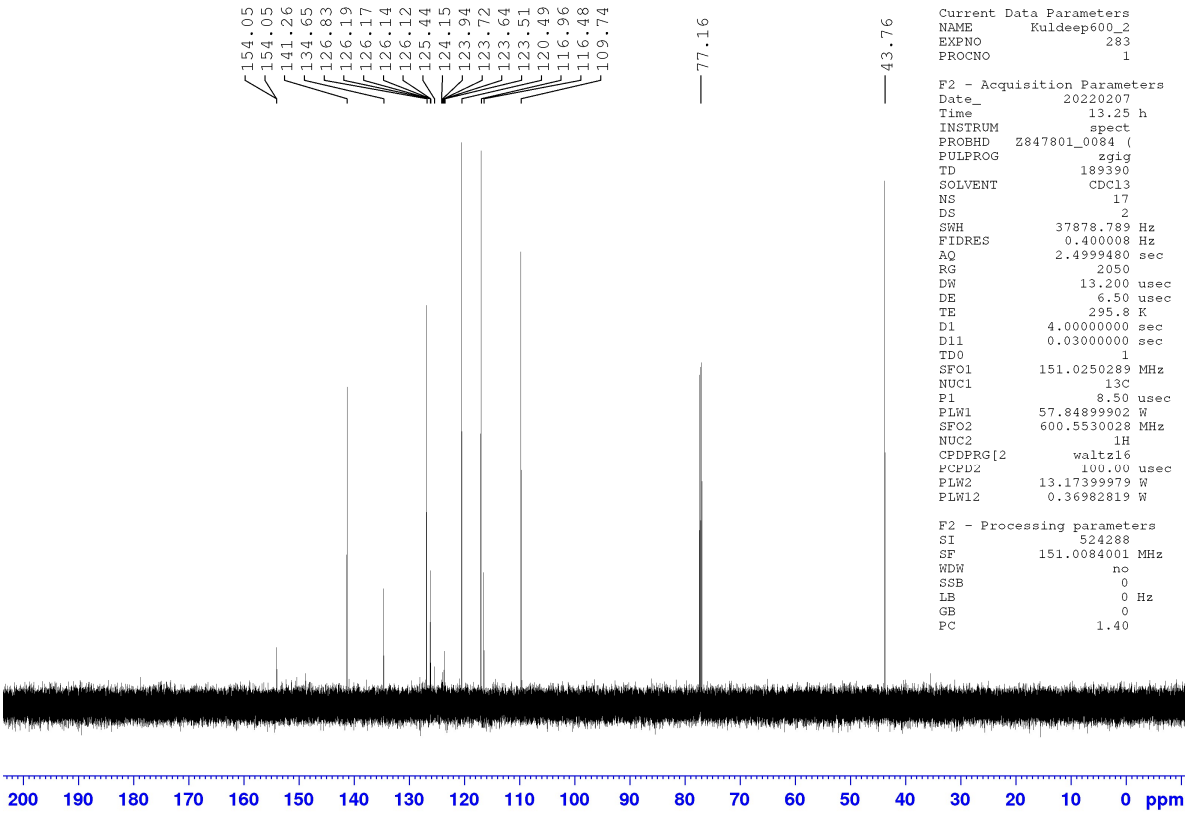
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):



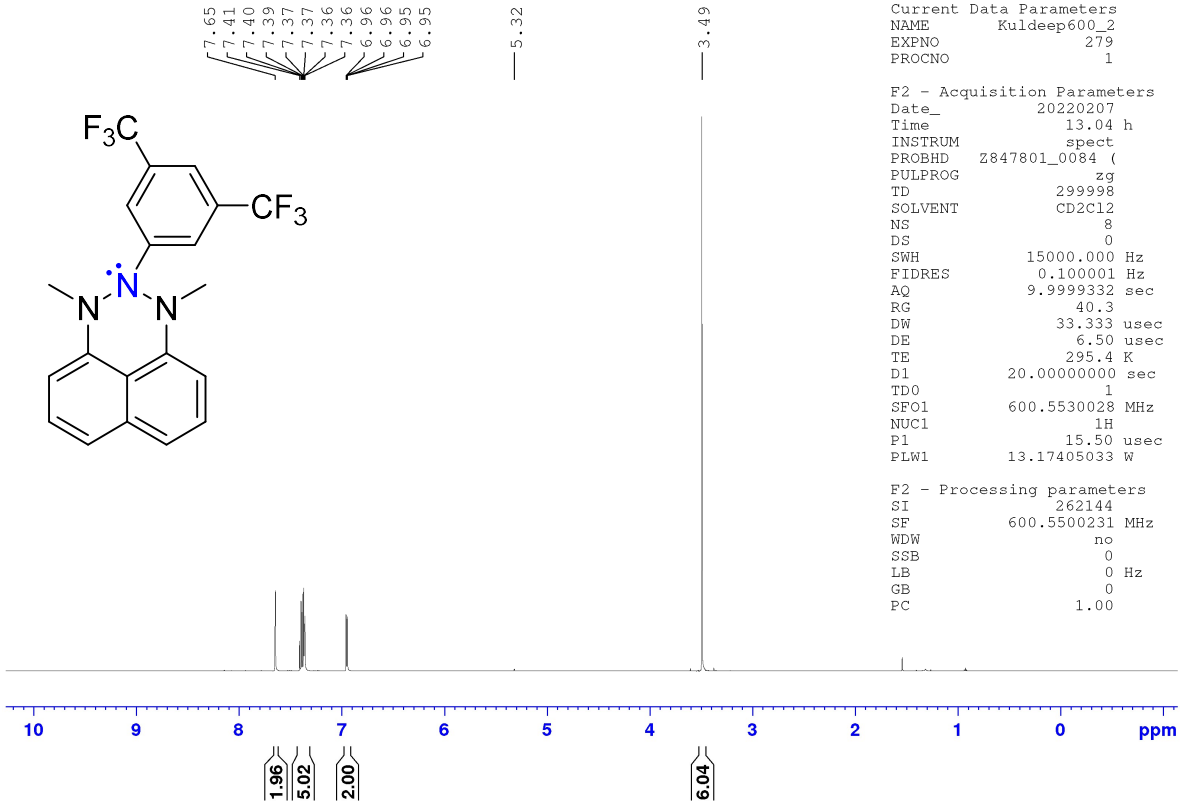
1*N*,3*N*-Dimethyl-2*N*-(4-(trifluoromethyl)phenyl)naphthotriazane **2s** – **^{1}H NMR** (600 MHz, $CDCl_3$):



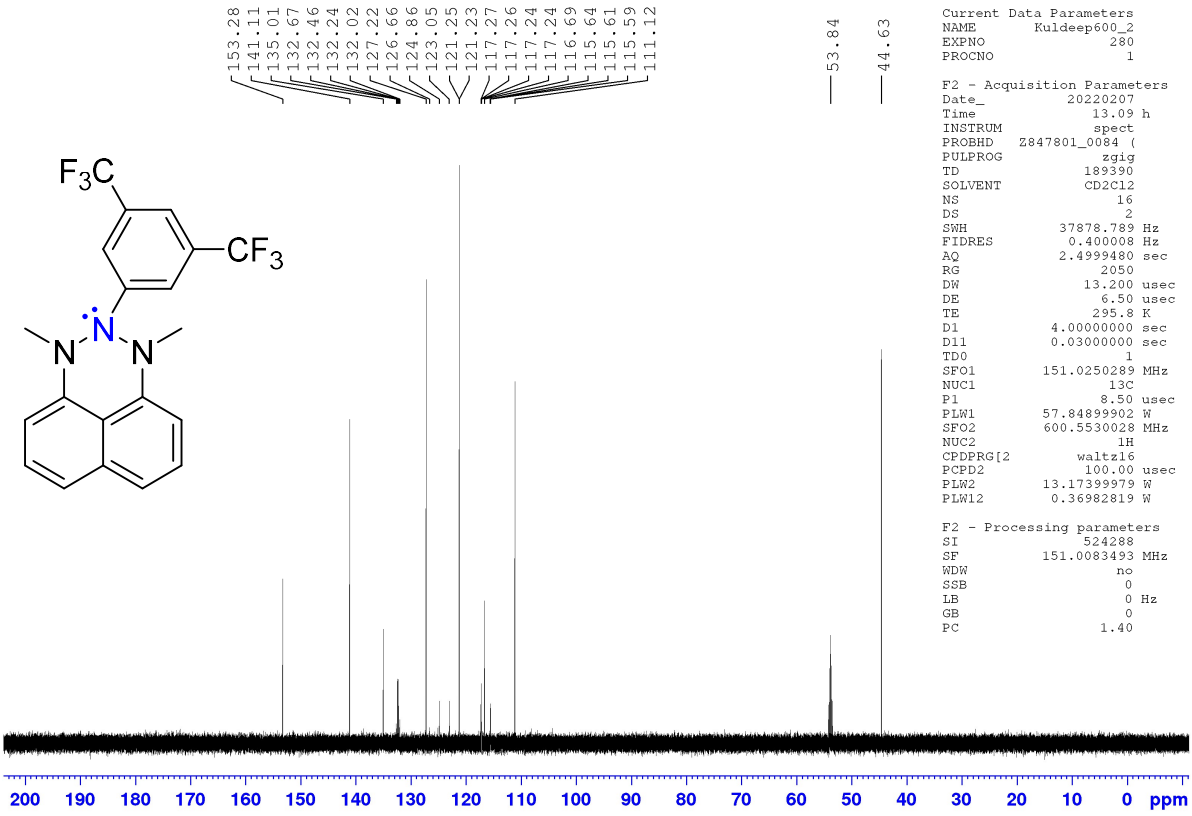
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):



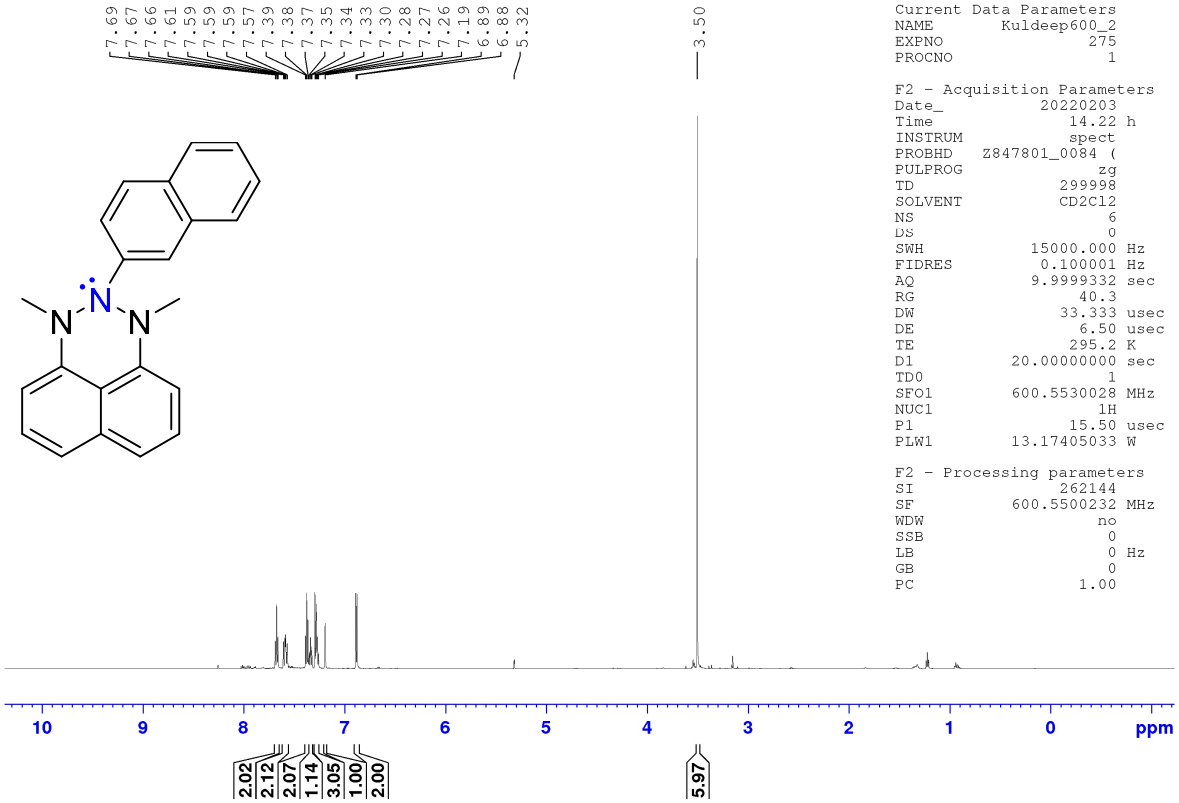
1*N*,3*N*-Dimethyl-2*N*-(3,5-bis(trifluoromethyl)phenyl)naphthotriazane **2t** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



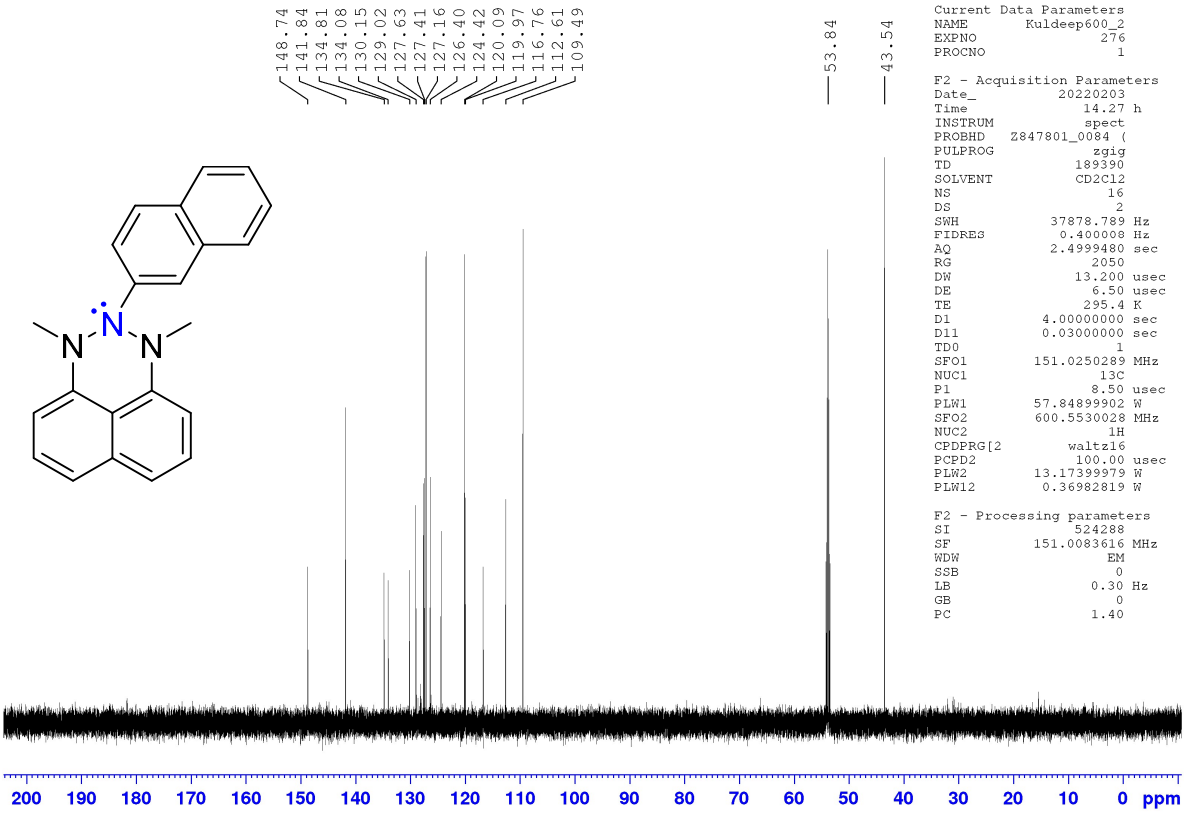
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



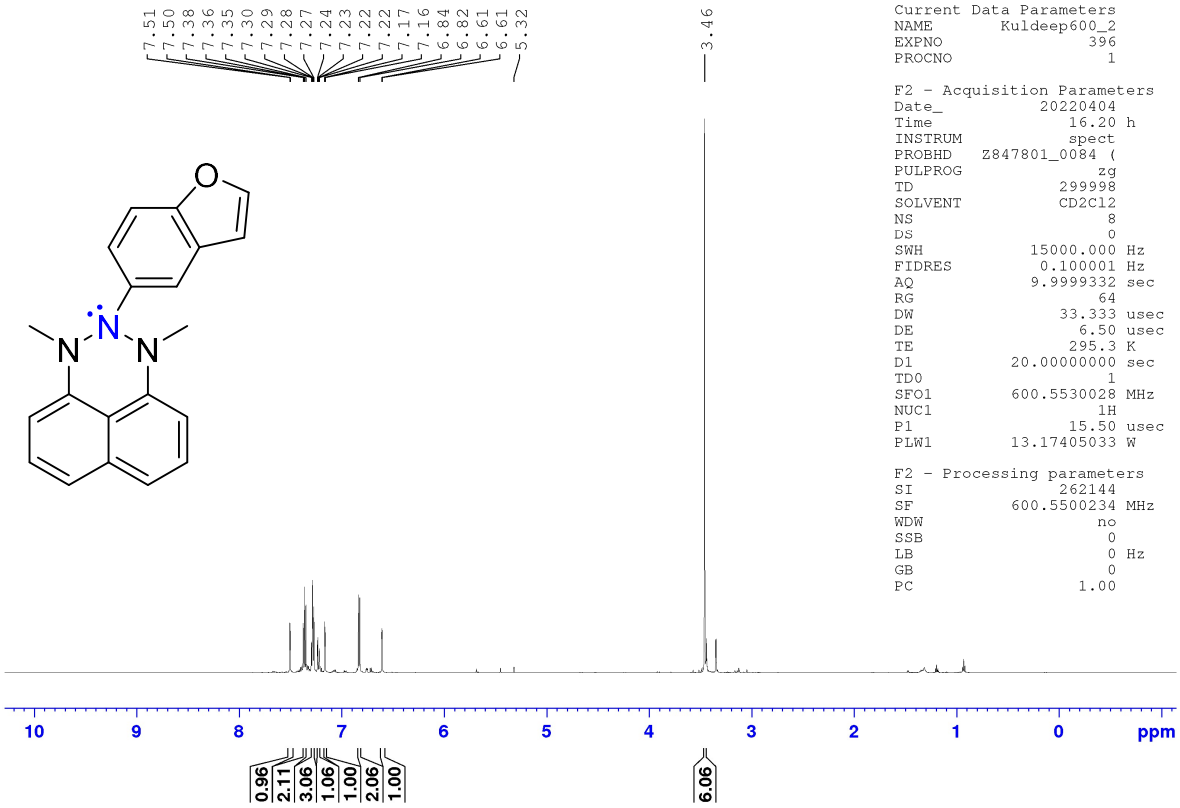
1*N*,3*N*-Dimethyl-2*N*-(2-naphthyl)naphthotriazane **2u** – **^{1}H NMR** (600 MHz, CD_2Cl_2):



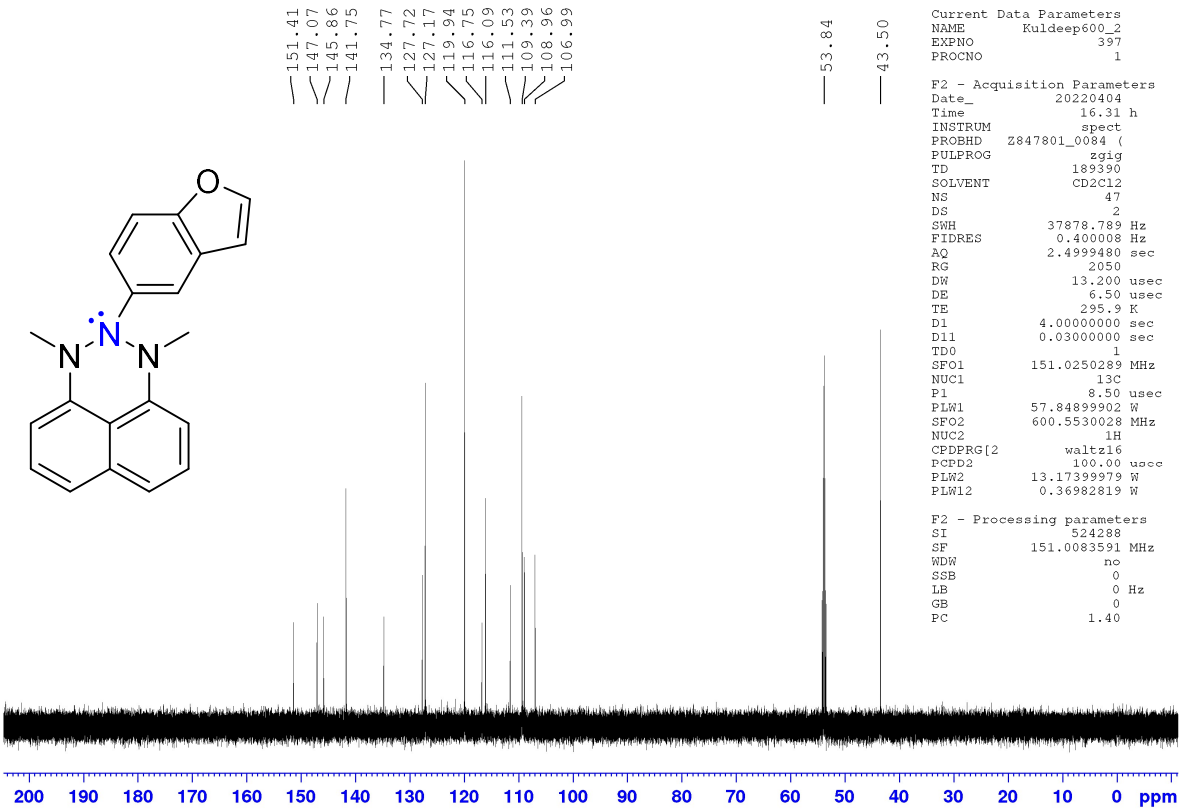
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



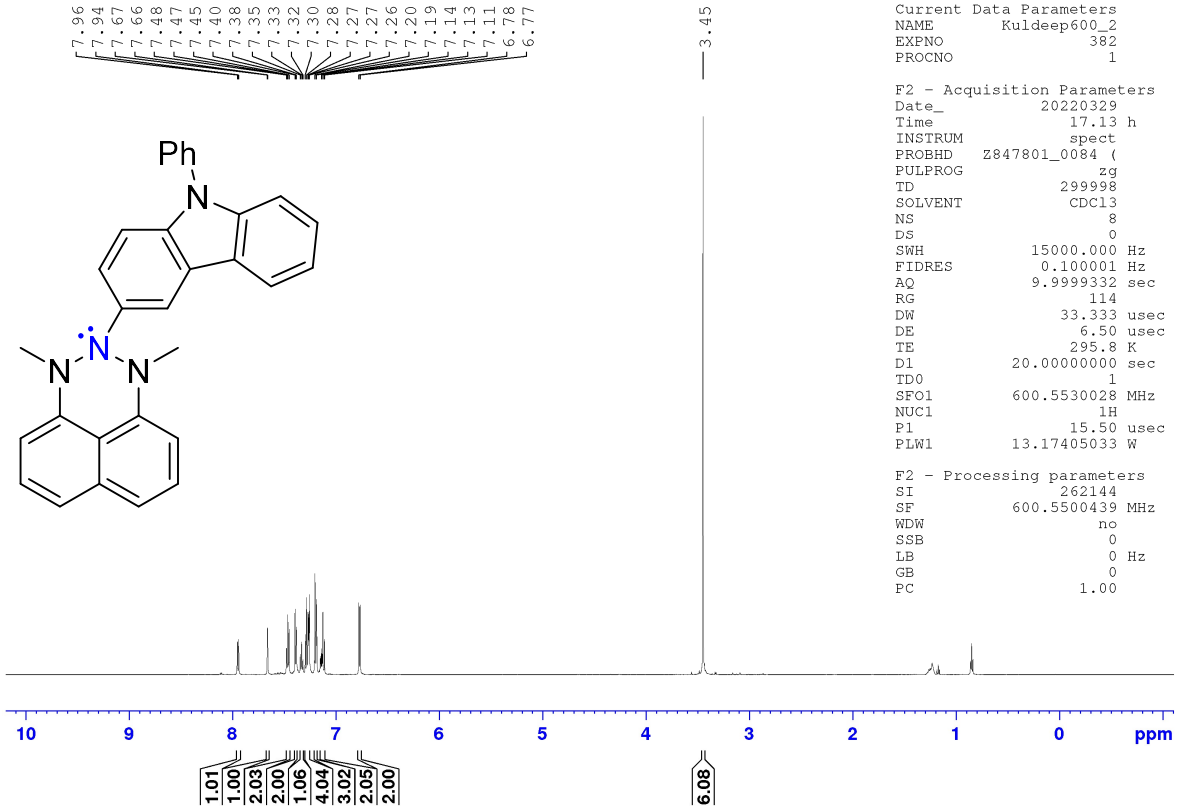
1*N*,3*N*-Dimethyl-2*N*-(5-benzofuranyl)naphthotriazane **2v** - **^{1}H NMR** (600 MHz, CD_2Cl_2):



^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2):



1*N*,3*N*-Dimethyl-2*N*-(3-(9-phenyl)carbazolyl)naphthotriazane **2w** – **^{1}H NMR** (600 MHz, $CDCl_3$):

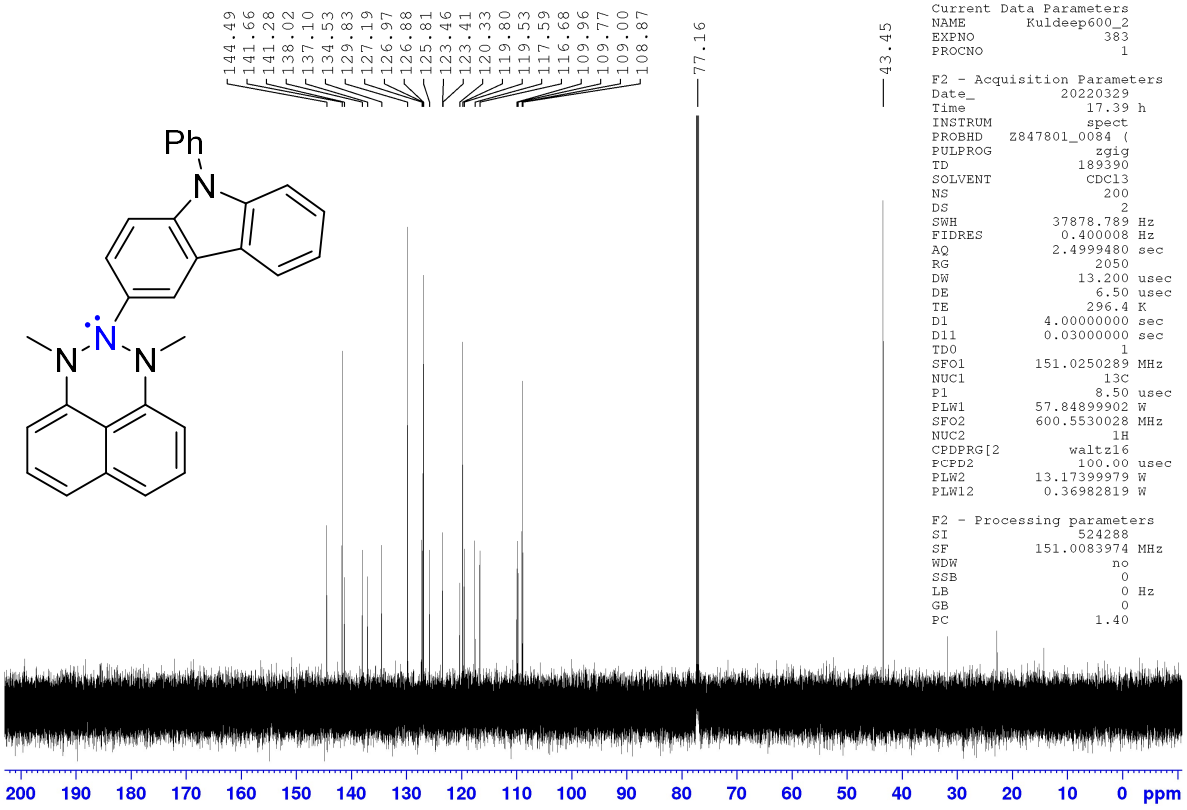


Current Data Parameters
NAME Kuldeep600_2
EXPNO 382
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220329
Time 17.13 h
INSTRUM spect
PROBHD Z847801_0084 (
PULPROG zg
TD 299998
SOLVENT CDCl3
NS 8
DS 0
SWH 15000.000 Hz
FIDRES 0.100001 Hz
AQ 9.9999332 sec
RG 114
DW 33.333 usec
DE 6.50 usec
TE 295.8 K
D1 20.00000000 sec
TD0 1
SFO1 600.5530028 MHz
NUC1 1H
P1 15.50 usec
PLW1 13.17405033 W

F2 - Processing parameters
SI 262144
SF 600.5500439 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):

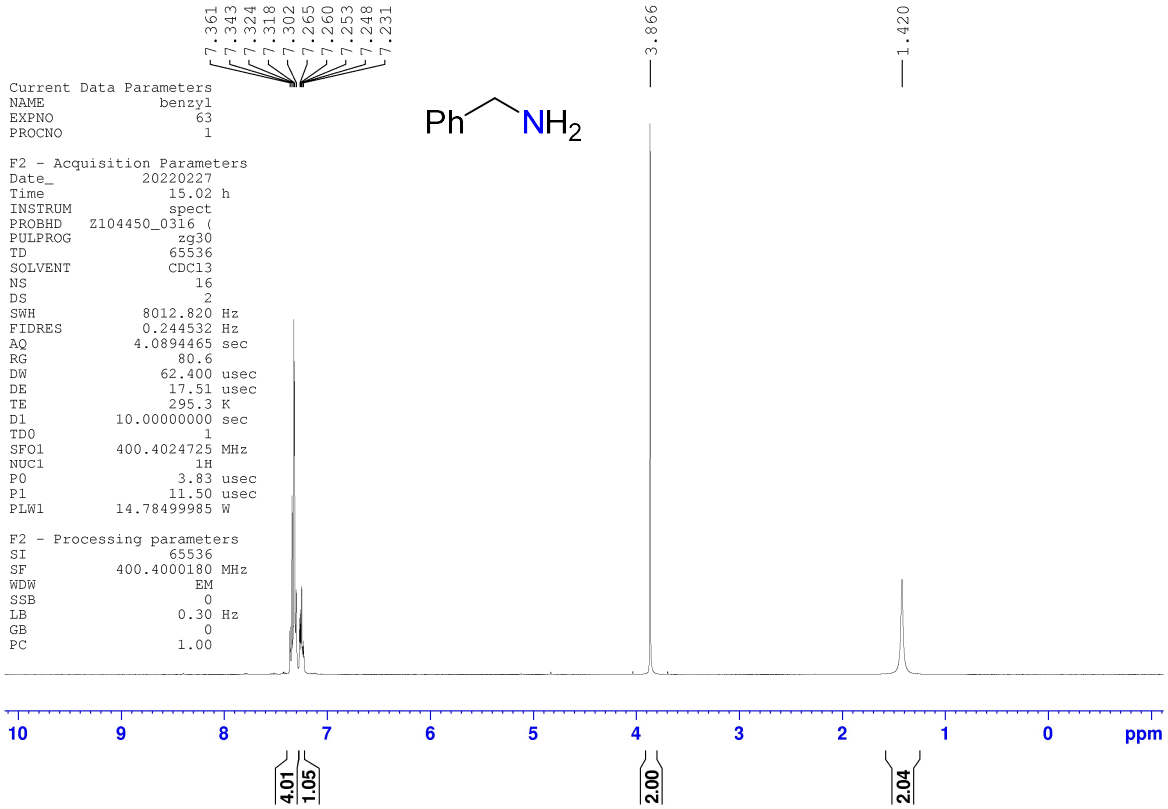


Current Data Parameters
NAME Kuldeep600_2
EXPNO 383
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220329
Time 17.39 h
INSTRUM spect
PROBHD Z847801_0084 (
PULPROG zgig
TD 189390
SOLVENT CDCl3
NS 200
DS 2
SWH 37878.789 Hz
FIDRES 0.400008 Hz
AQ 2.4999480 sec
RG 2050
DW 13.200 usec
DE 6.50 usec
TE 296.4 K
D1 4.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 151.0250289 MHz
NUC1 13C
P1 8.50 usec
PLW1 57.84899902 W
SFO2 600.5530028 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 100.00 usec
PLW2 13.17399979 W
PLW12 0.36982819 W

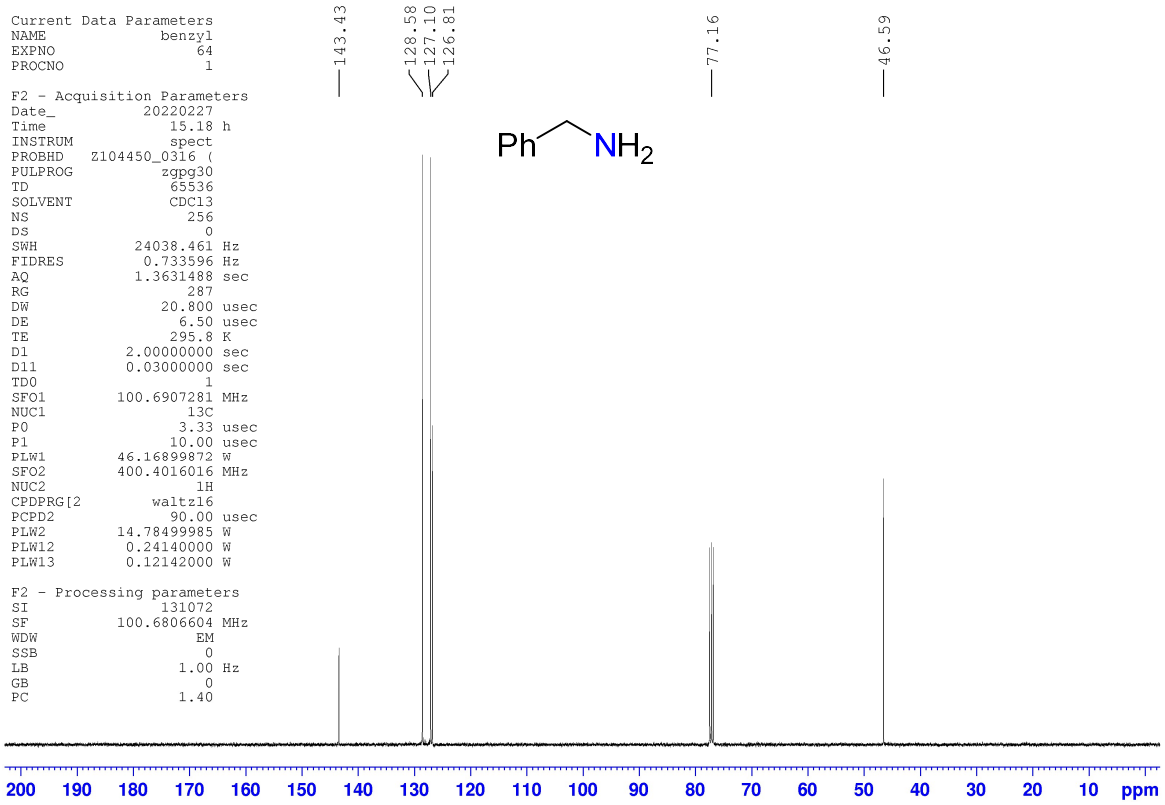
F2 - Processing parameters
SI 524288
SF 151.0083974 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40

Benzylamine **3c** – **^{1}H NMR** (400 MHz, $CDCl_3$):



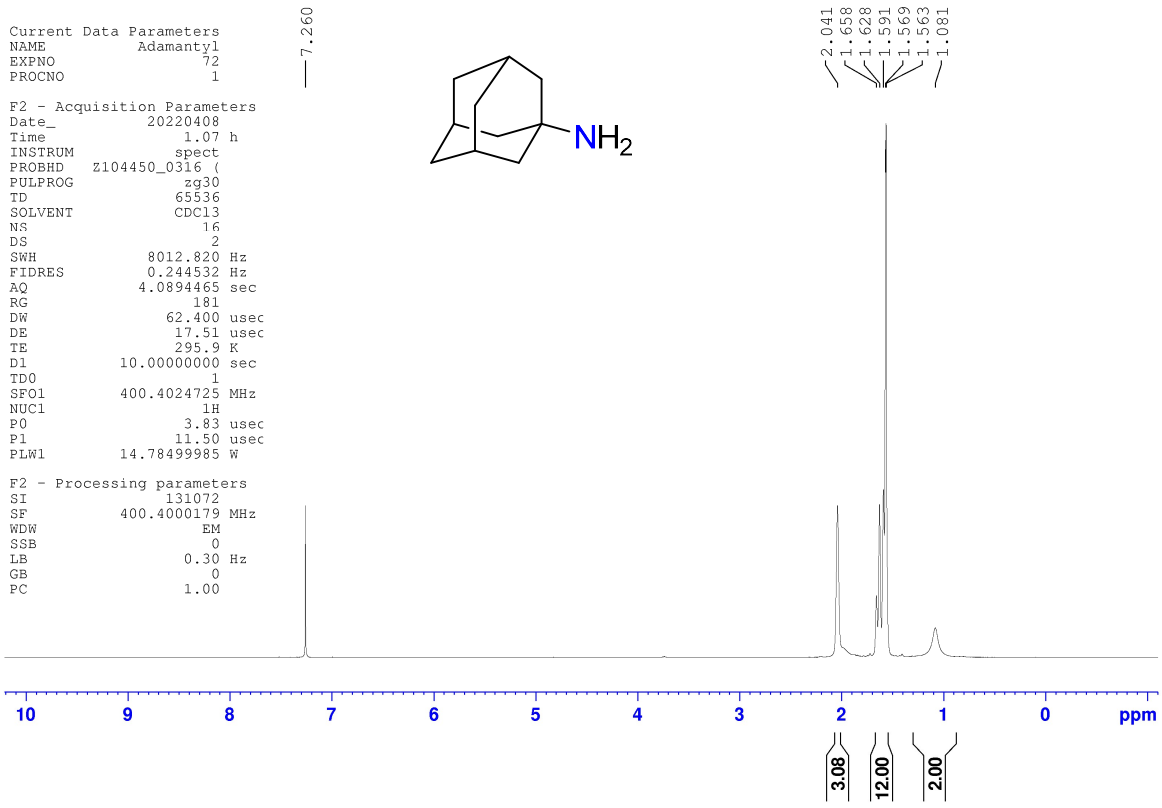

```
Current Data Parameters
NAME              benzyl
EXPNO                 63
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220227
Time              15.02 h
INSTRUM            spect
PROBHD   Z104450_0316 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.244532 Hz
AQ              4.0894465 sec
RG                  80.6
DW                 62.400 usec
DE                 17.51 usec
TE                 295.3 K
D1           10.00000000 sec
TD0                    1
SFO1          400.4024725 MHz
NUC1                  1H
P0                  3.83 usec
P1                 11.50 usec
PLW1         14.78499985 W

F2 - Processing parameters
SI                 65536
SF            400.4000180 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):

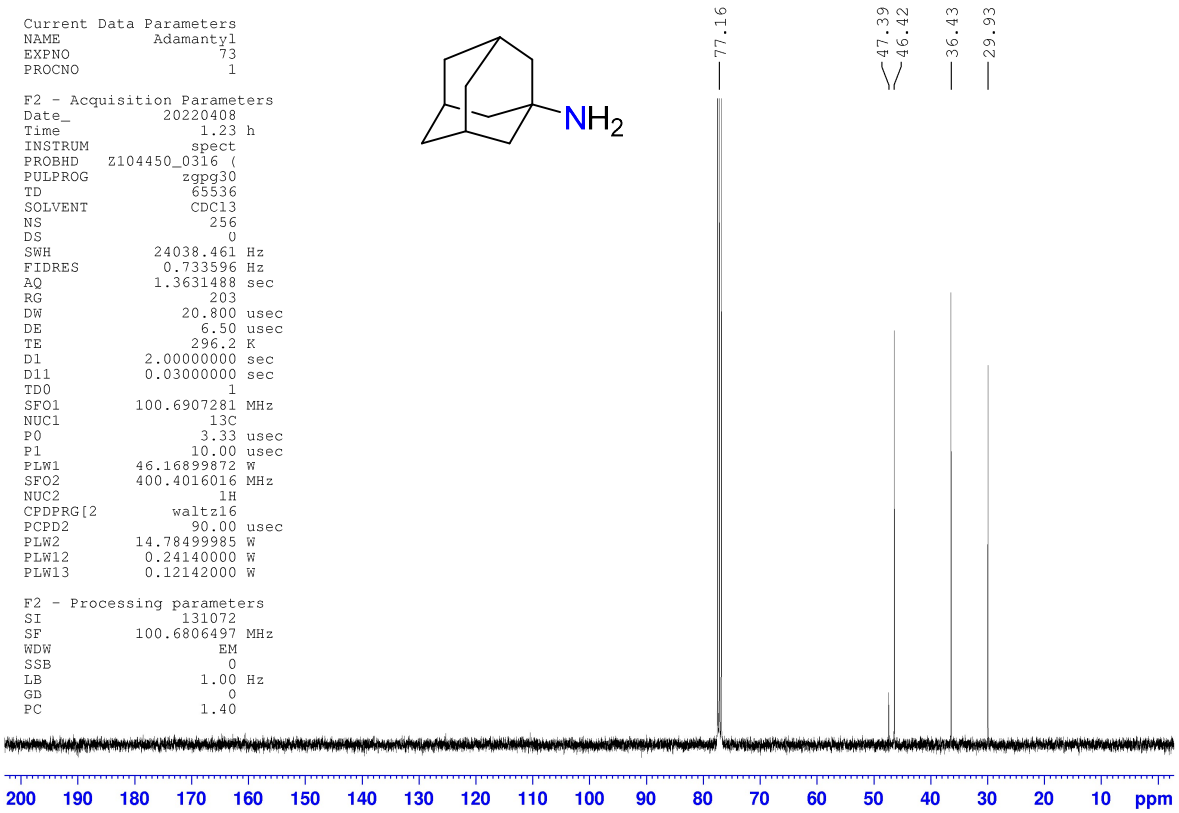



```
Current Data Parameters
NAME              benzyl
EXPNO                 64
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220227
Time              15.18 h
INSTRUM            spect
PROBHD   Z104450_0316 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     0
SWH            24038.461 Hz
FIDRES             0.733596 Hz
AQ              1.3631488 sec
RG                   287
DW                 20.800 usec
DE                  6.50 usec
TE                 295.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1          100.6907281 MHz
NUC1                  13C
P0                  3.33 usec
P1                 10.00 usec
PLW1         46.16899872 W
SFO2          400.4016016 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         14.78499985 W
PLW12         0.24140000 W
PLW13         0.12142000 W

F2 - Processing parameters
SI                131072
SF            100.6806604 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

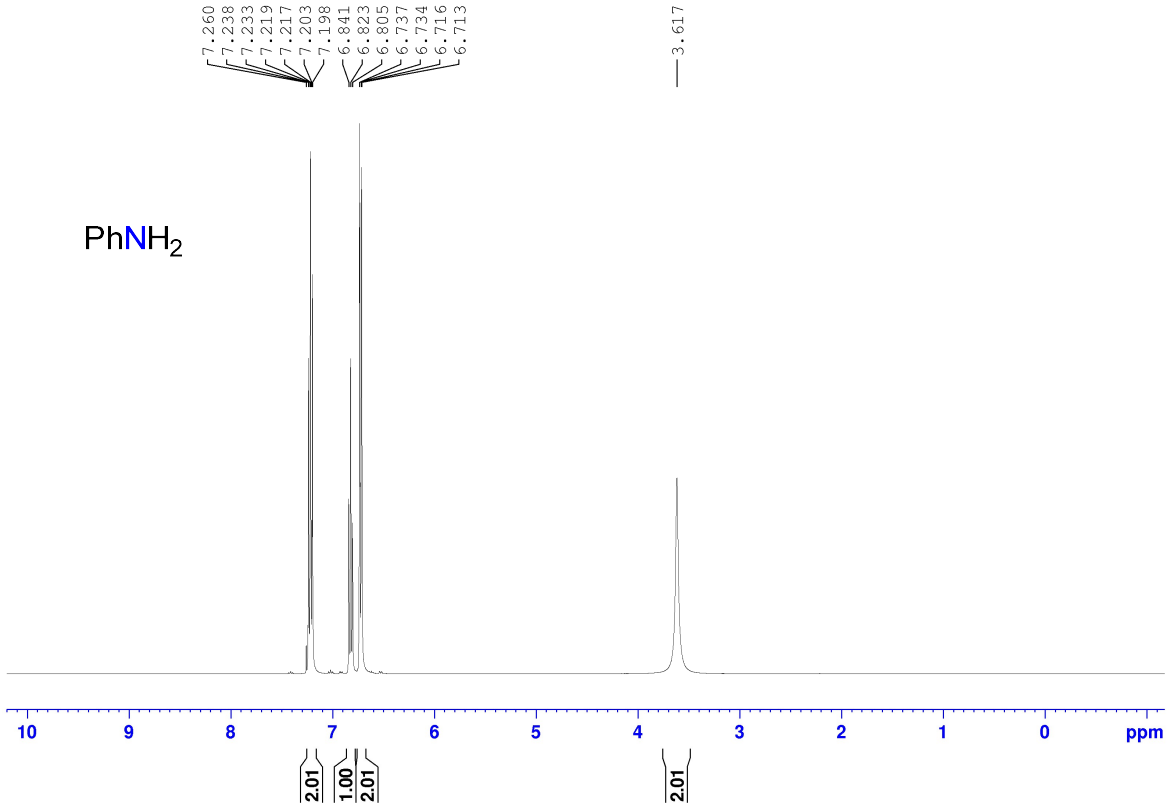
1-Adamantylamine (Amantadine) **3h** – **^{1}H NMR** (400 MHz, $CDCl_3$):



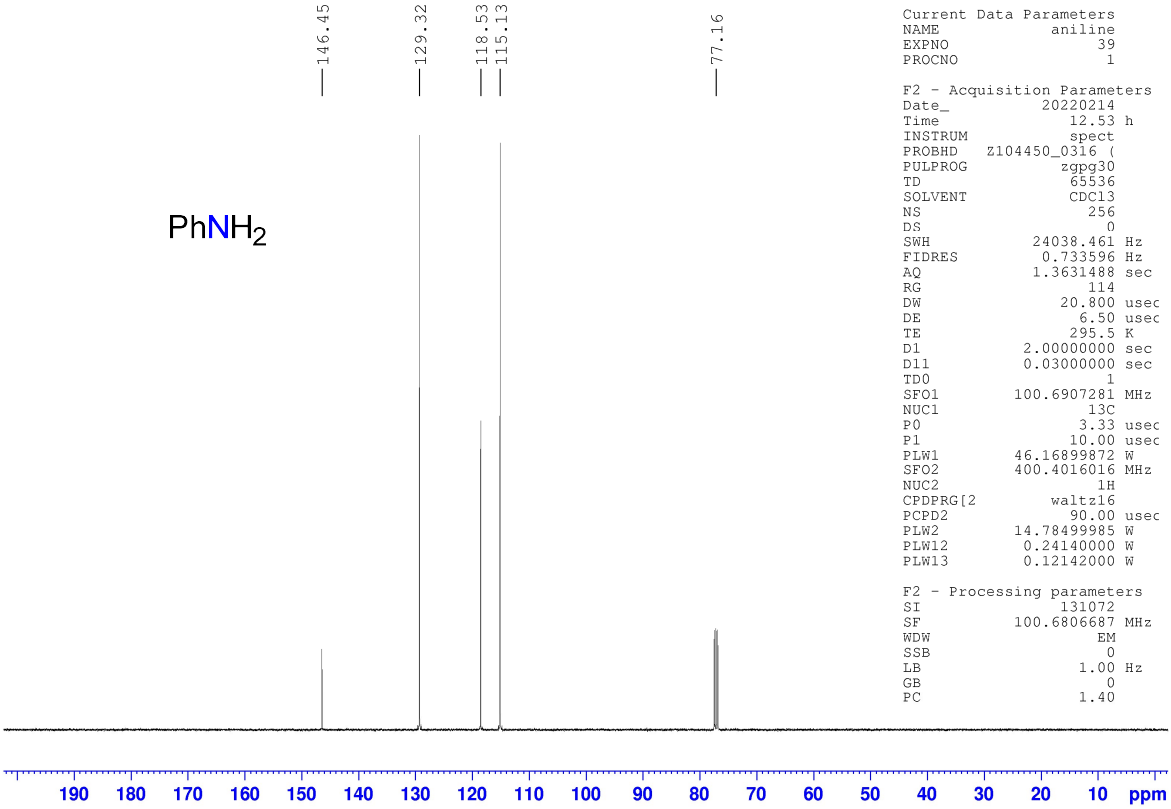
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):



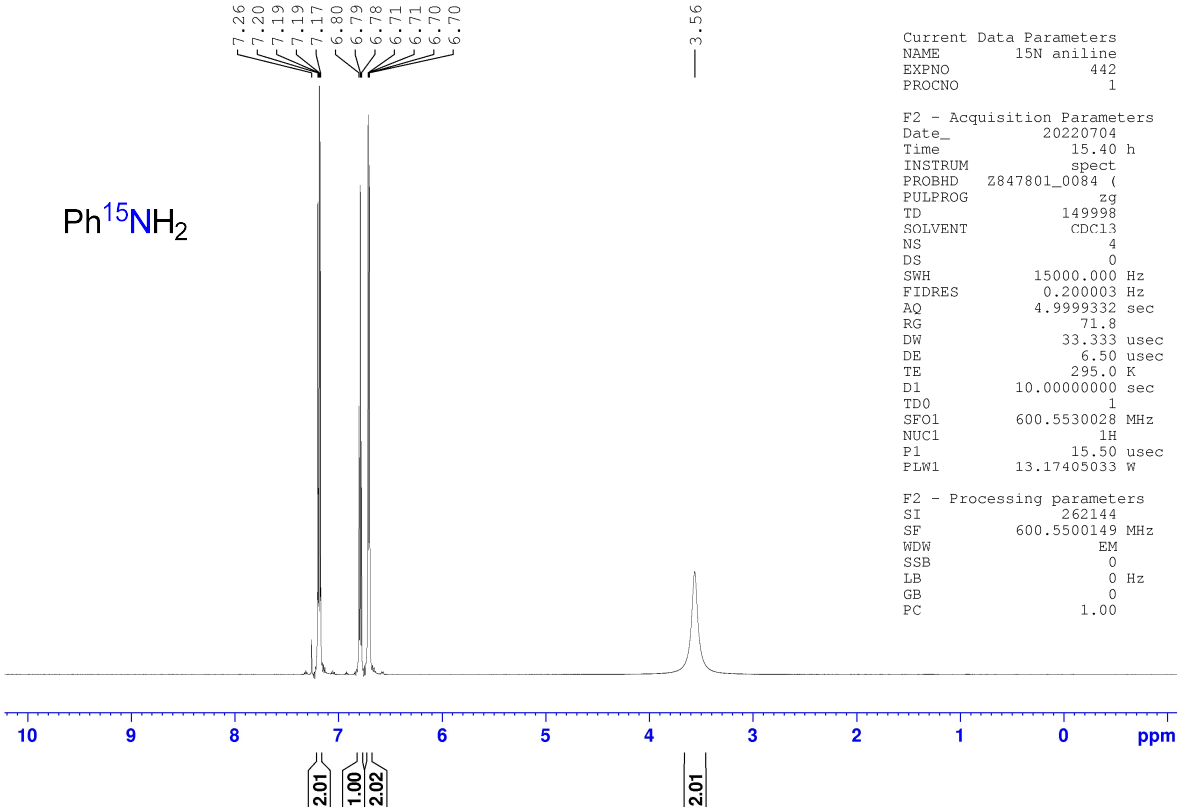
Aniline **3i** – **^{1}H NMR** (400 MHz, $CDCl_3$):



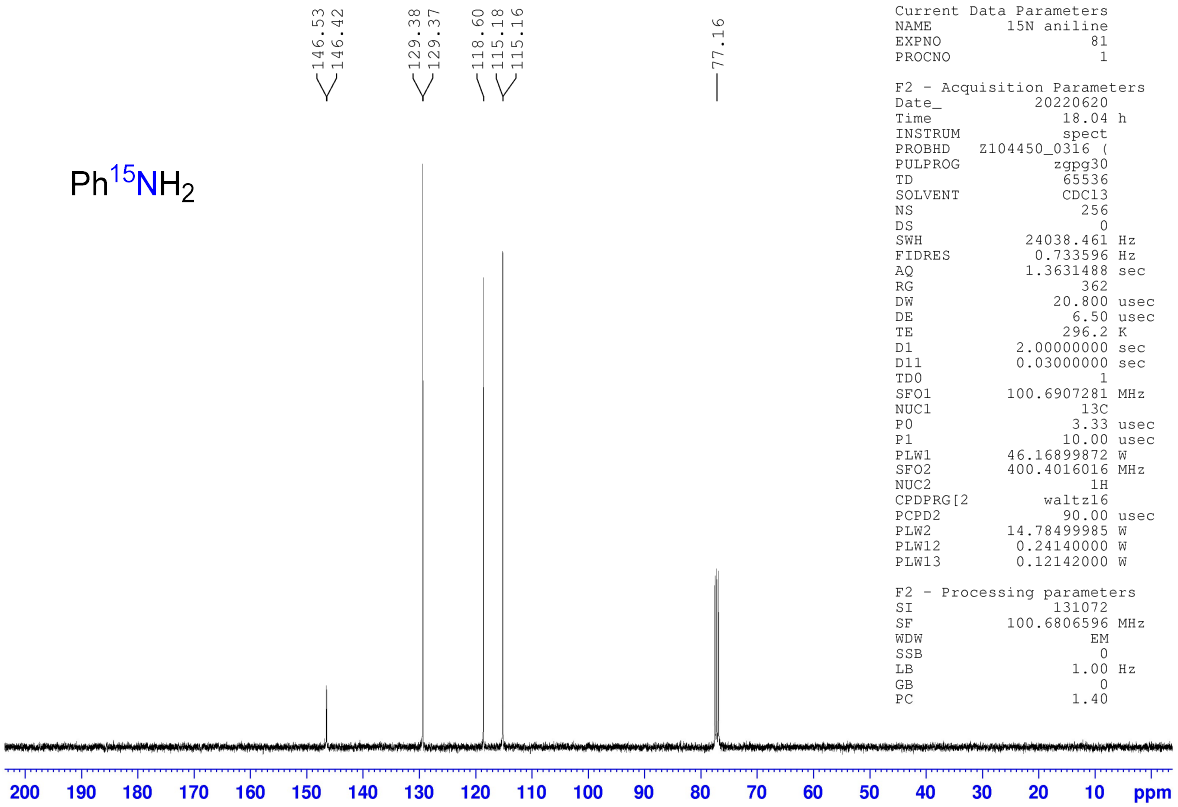
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):



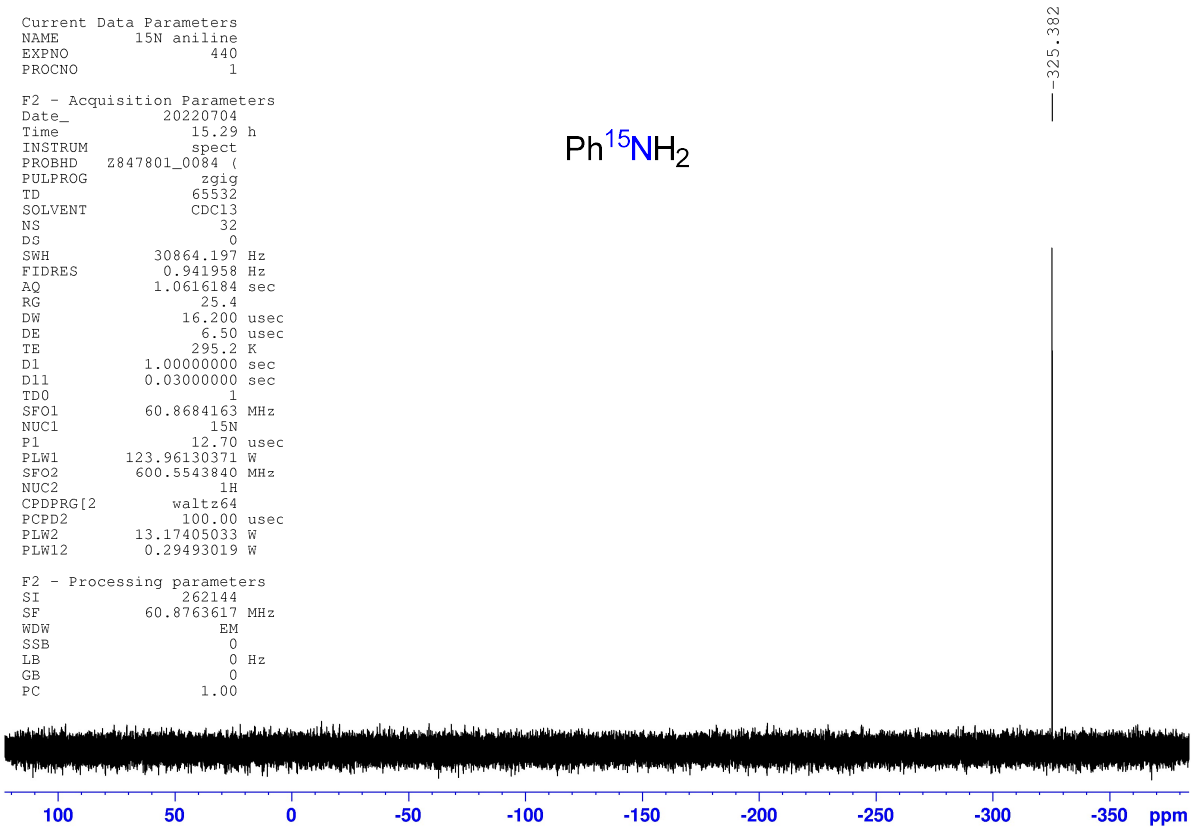
Aniline-^{15}N **3i'** – **^{1}H NMR** (600 MHz, $CDCl_3$):



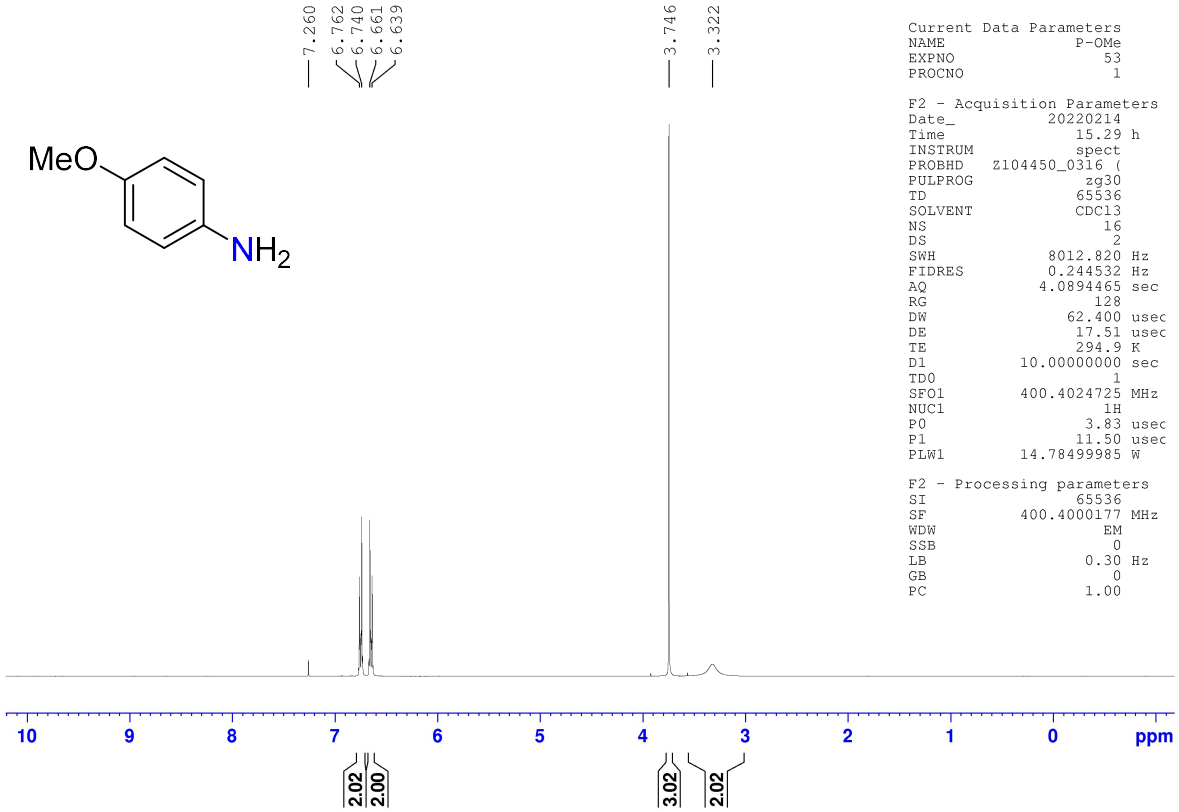
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):



$^{15}N\{^{1}H\}$ NMR (60 MHz, $CDCl_3$):

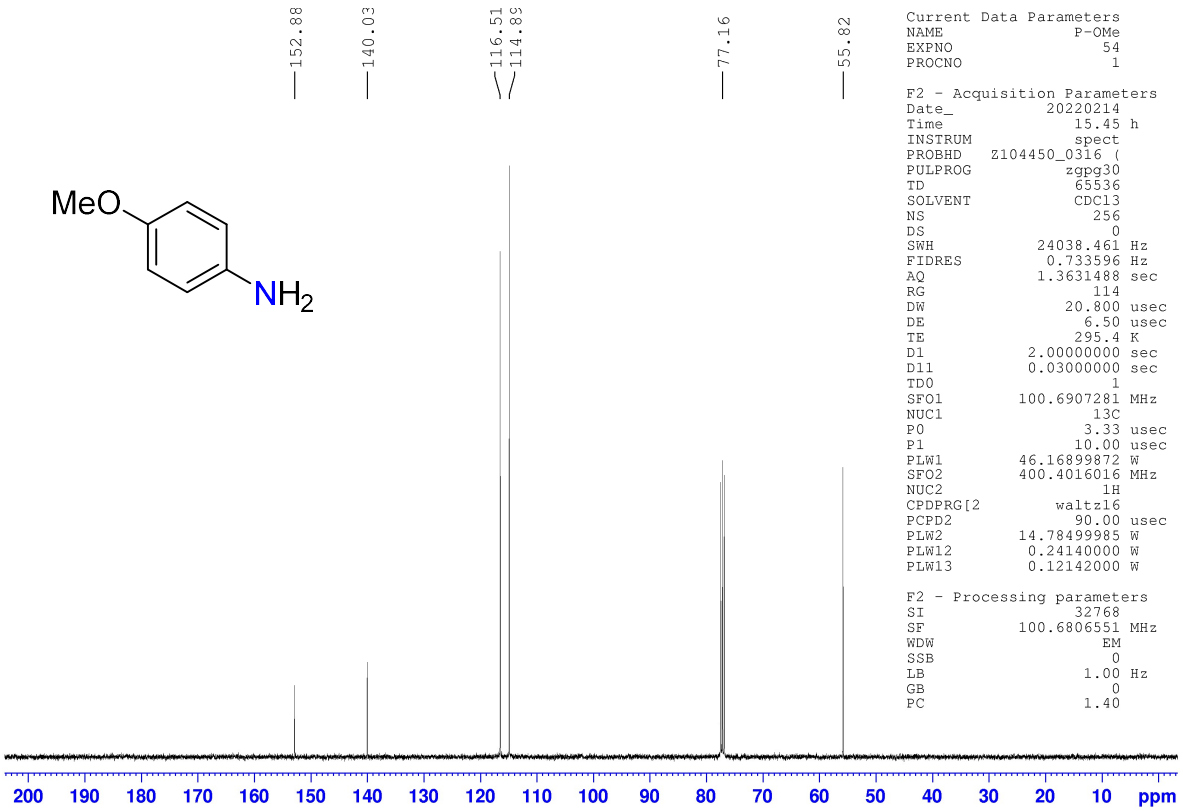


4-Methoxyaniline (p-anisidine) **3j** – **^{1}H NMR** (400 MHz, $CDCl_3$):



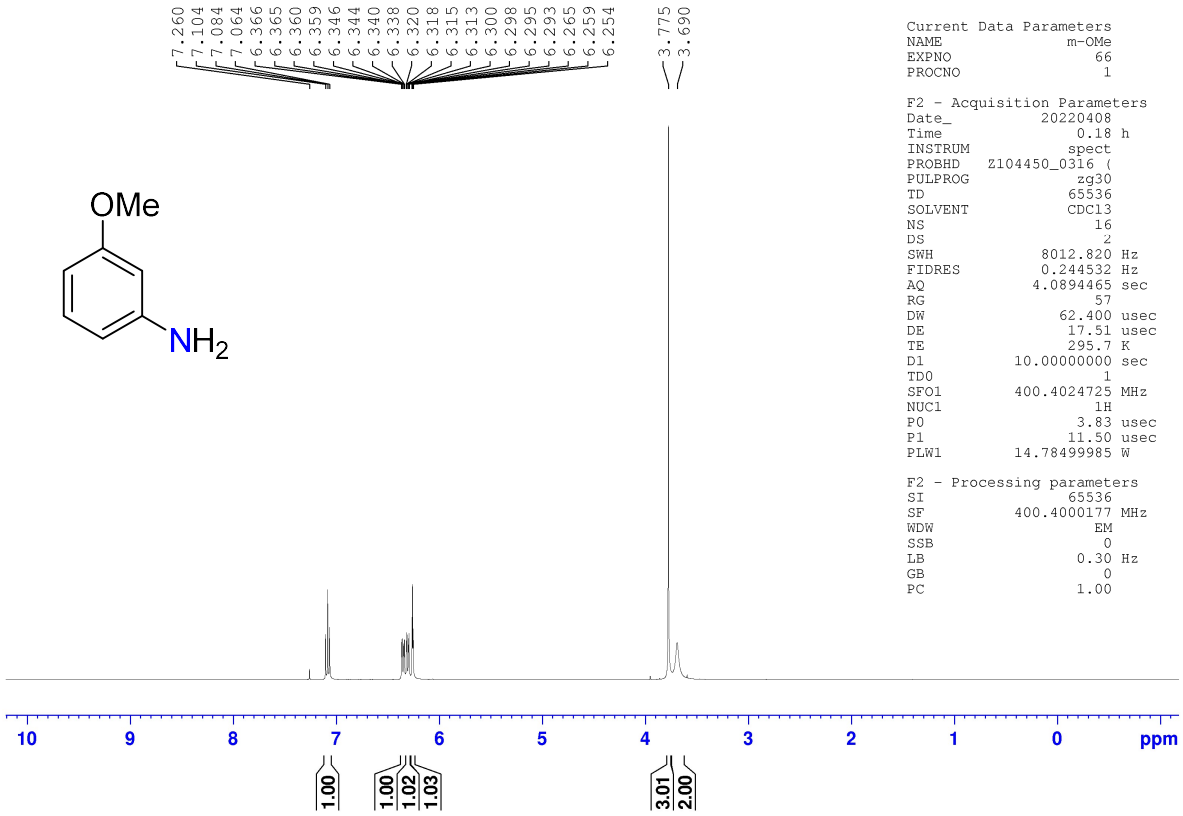

```
Current Data Parameters
NAME                  P-OMe
EXPNO                    53
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220214
Time                 15.29 h
INSTRUM              spect
PROBHD    Z104450_0316 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES                0.244532 Hz
AQ                 4.0894465 sec
RG                      128
DW                    62.400 usec
DE                    17.51 usec
TE                    294.9 K
D1                10.00000000 sec
TD0                       1
SFO1              400.4024725 MHz
NUC1                      1H
P0                     3.83 usec
P1                    11.50 usec
PLW1              14.78499985 W

F2 - Processing parameters
SI                        65536
SF                400.4000177 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):



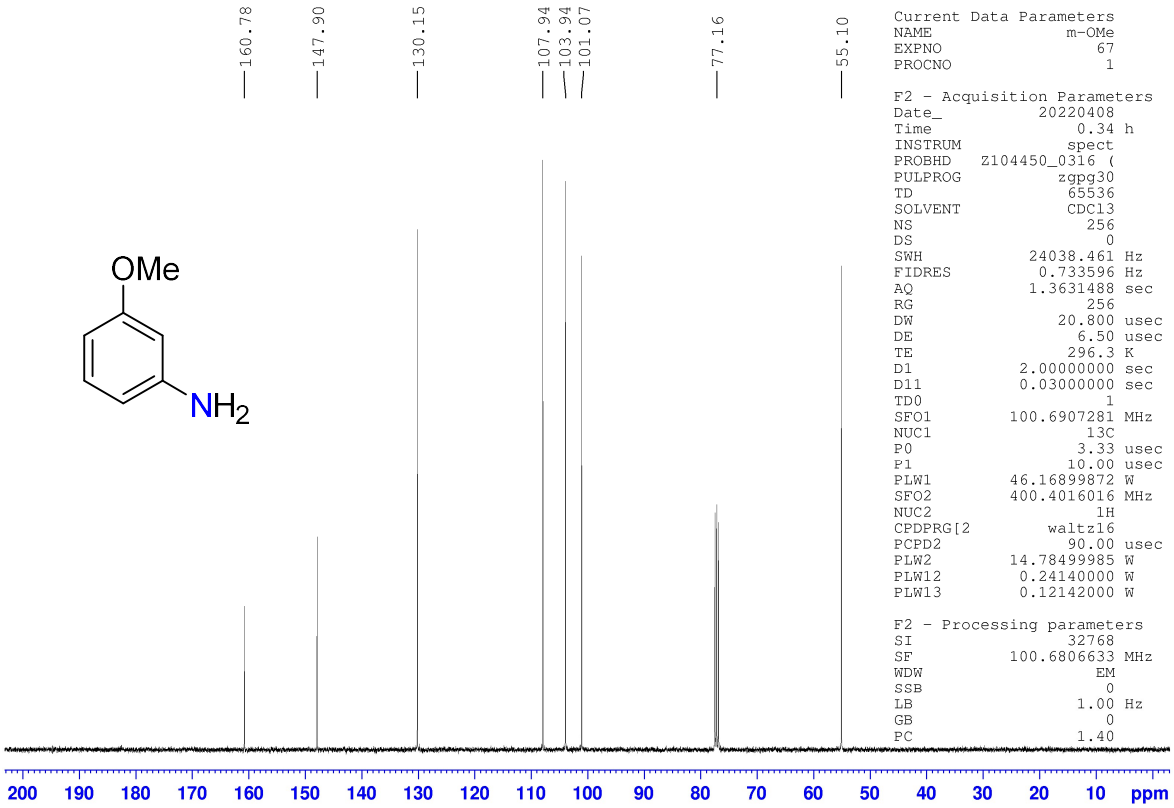

```
Current Data Parameters
NAME                  P-OMe
EXPNO                    54
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220214
Time                 15.45 h
INSTRUM              spect
PROBHD    Z104450_0316 (
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      256
DS                        0
SWH               24038.461 Hz
FIDRES                0.733596 Hz
AQ                 1.3631488 sec
RG                      114
DW                    20.800 usec
DE                     6.50 usec
TE                    295.4 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1
SFO1              100.6907281 MHz
NUC1                     13C
P0                     3.33 usec
P1                    10.00 usec
PLW1              46.16899872 W
SFO2              400.4016016 MHz
NUC2                      1H
CPDPRG[2              waltz16
PCPD2                 90.00 usec
PLW2              14.78499985 W
PLW12              0.24140000 W
PLW13              0.12142000 W

F2 - Processing parameters
SI                        32768
SF                100.6806551 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

3-Methoxyaniline (m-anisidine) **3k** – **^{1}H NMR** (400 MHz, $CDCl_3$):



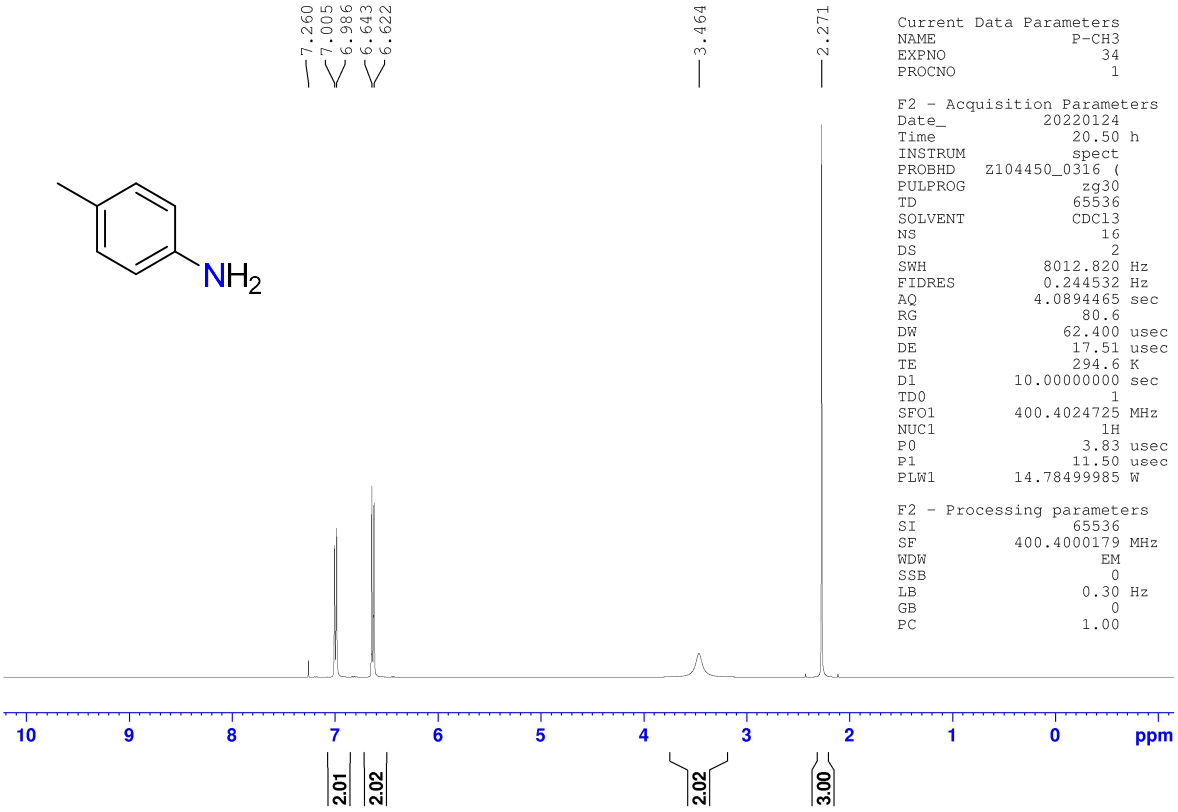

```
Current Data Parameters
NAME                  m-OMe
EXPNO                    66
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220408
Time                   0.18 h
INSTRUM               spect
PROBHD    Z104450_0316 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES                0.244532 Hz
AQ                 4.0894465 sec
RG                       57
DW                    62.400 usec
DE                    17.51 usec
TE                    295.7 K
D1              10.00000000 sec
TD0                       1
SFO1           400.4024725 MHz
NUC1                     1H
P0                    3.83 usec
P1                   11.50 usec
PLW1           14.78499985 W

F2 - Processing parameters
SI                    65536
SF             400.4000177 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):

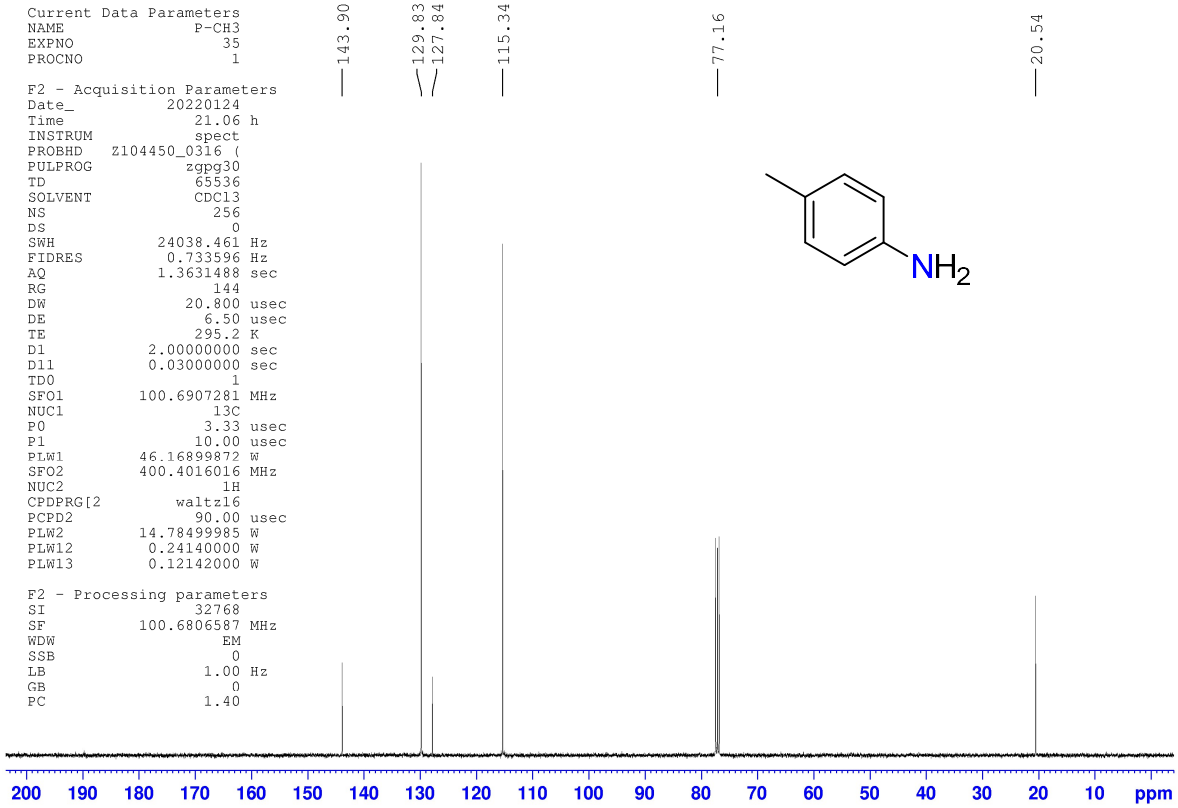



```
Current Data Parameters
NAME                  m-OMe
EXPNO                    67
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220408
Time                   0.34 h
INSTRUM               spect
PROBHD    Z104450_0316 (
PULPROG            zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      256
DS                        0
SWH               24038.461 Hz
FIDRES                0.733596 Hz
AQ                 1.3631488 sec
RG                      256
DW                    20.800 usec
DE                     6.50 usec
TE                    296.3 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1
SFO1           100.6907281 MHz
NUC1                    13C
P0                    3.33 usec
P1                   10.00 usec
PLW1           46.16899872 W
SFO2           400.4016016 MHz
NUC2                     1H
CPDPRG[2             waltz16
PCPD2                90.00 usec
PLW2           14.78499985 W
PLW12           0.24140000 W
PLW13           0.12142000 W

F2 - Processing parameters
SI                    32768
SF             100.6806633 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.40
```

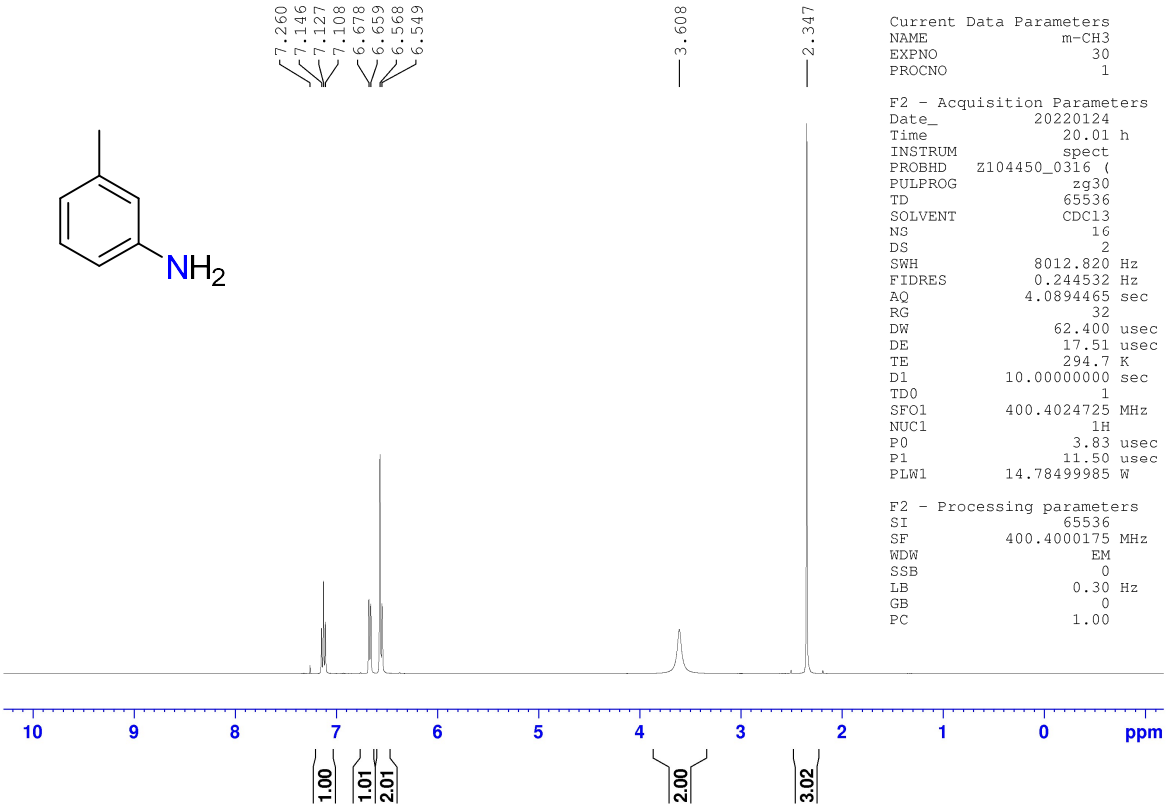
4-Methylaniline (p-toluidine) **3l** – **^{1}H NMR** (400 MHz, $CDCl_3$):



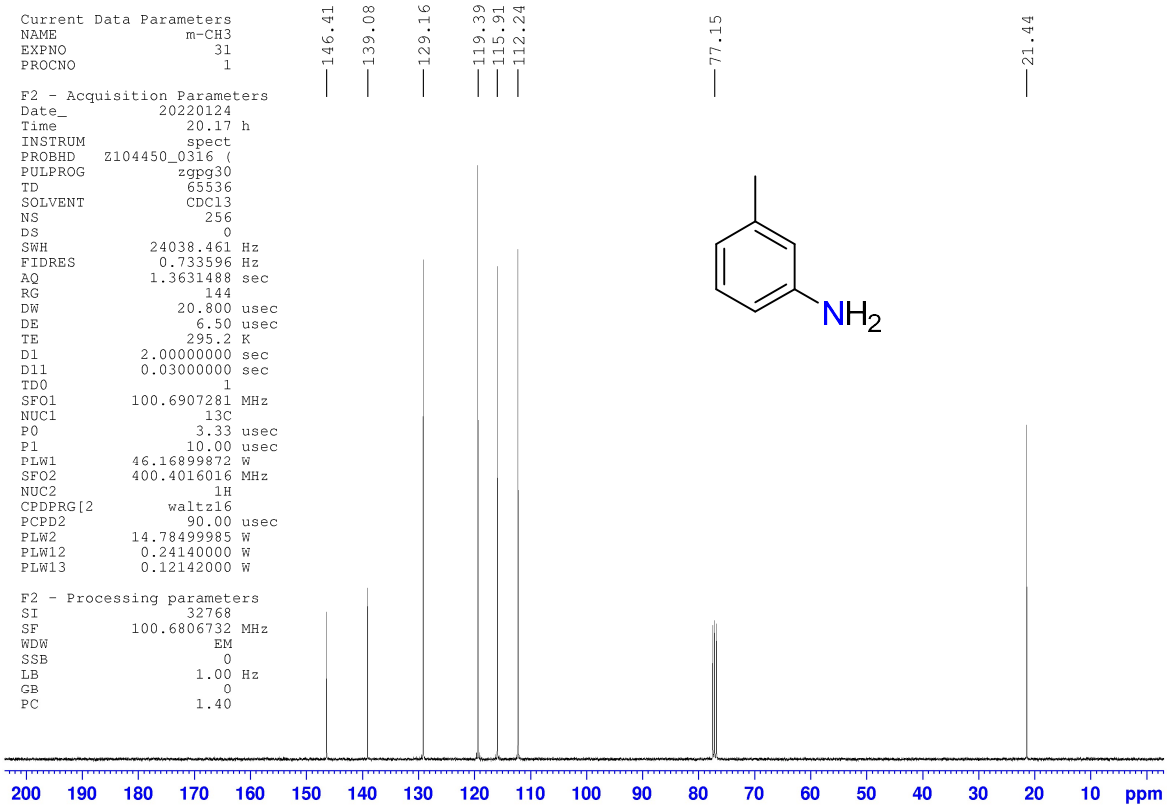
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):



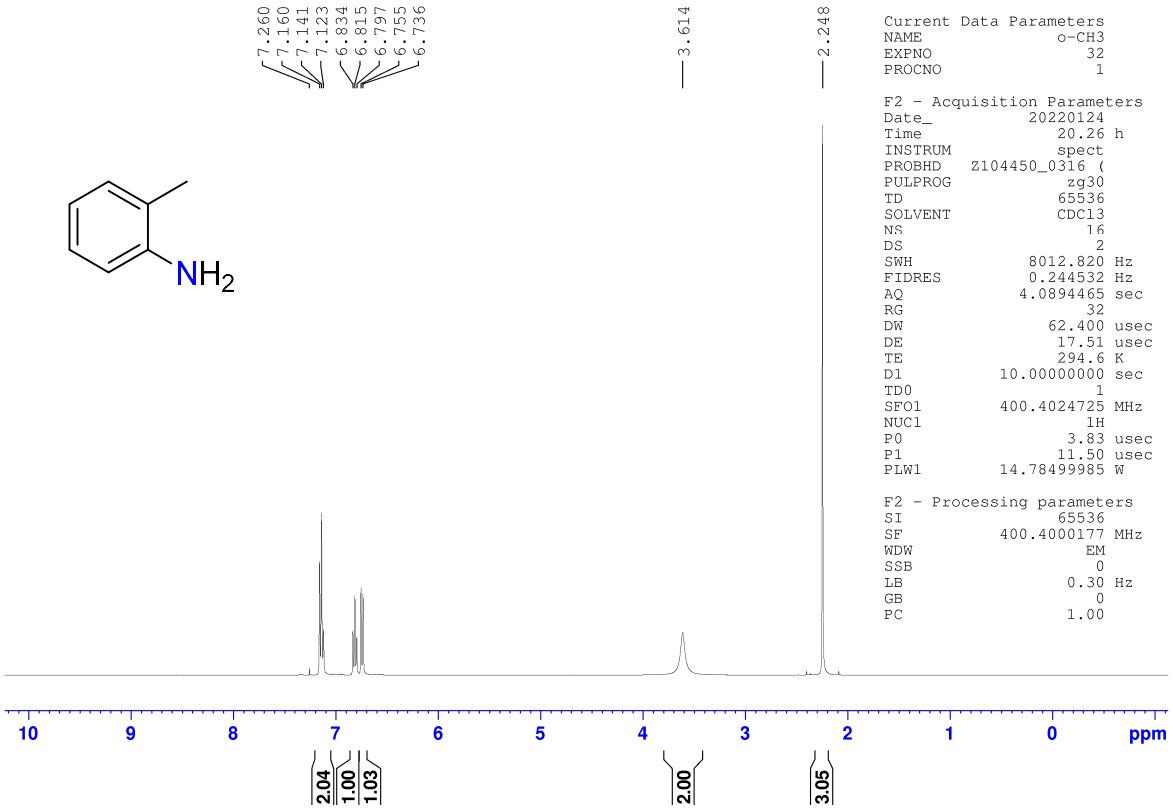
3-Methylaniline (m-toluidine) **3m** – **^{1}H NMR** (400 MHz, $CDCl_3$):



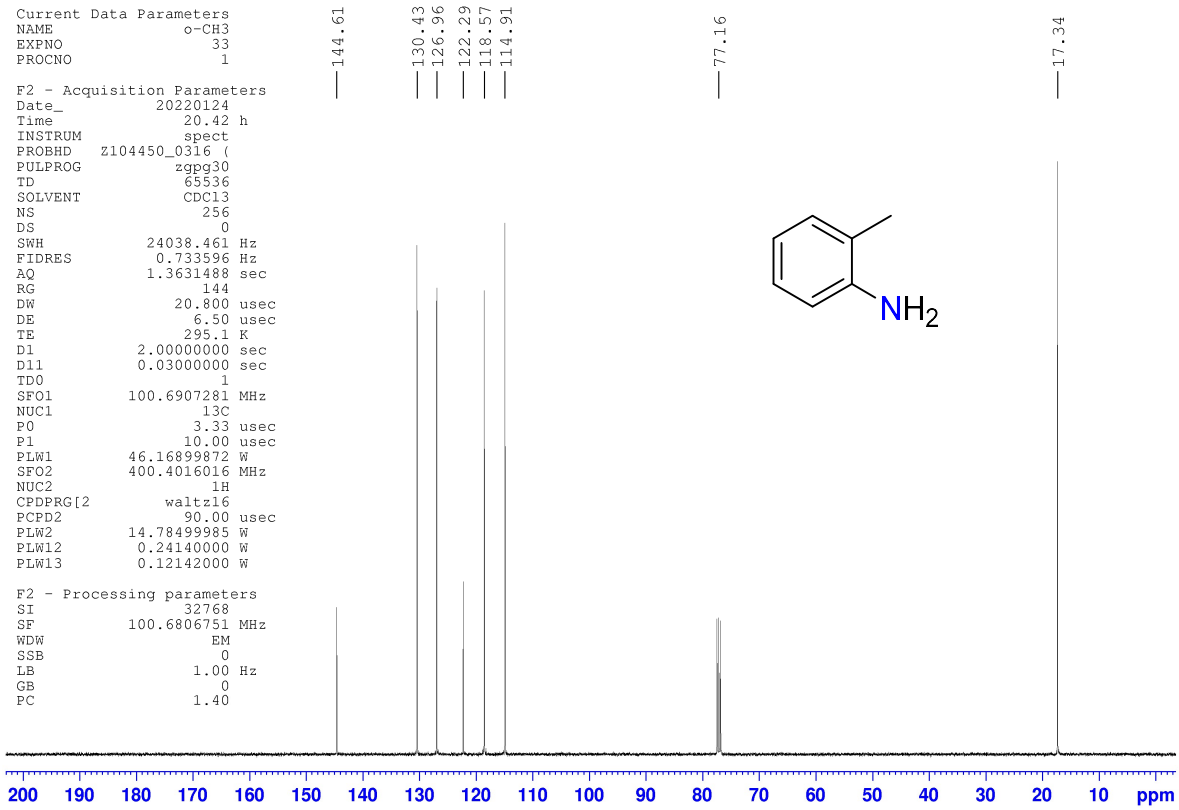
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):



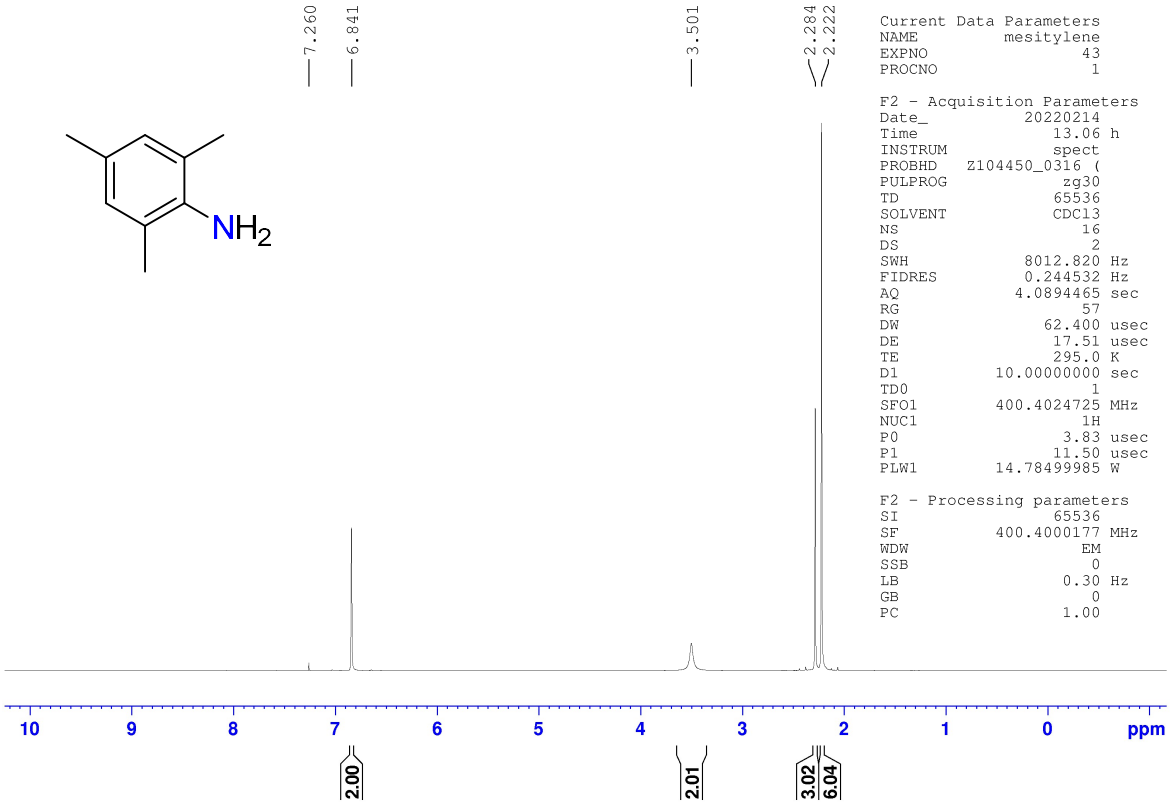
2-Methylaniline (o-toluidine) **3n** – **^{1}H NMR** (400 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):

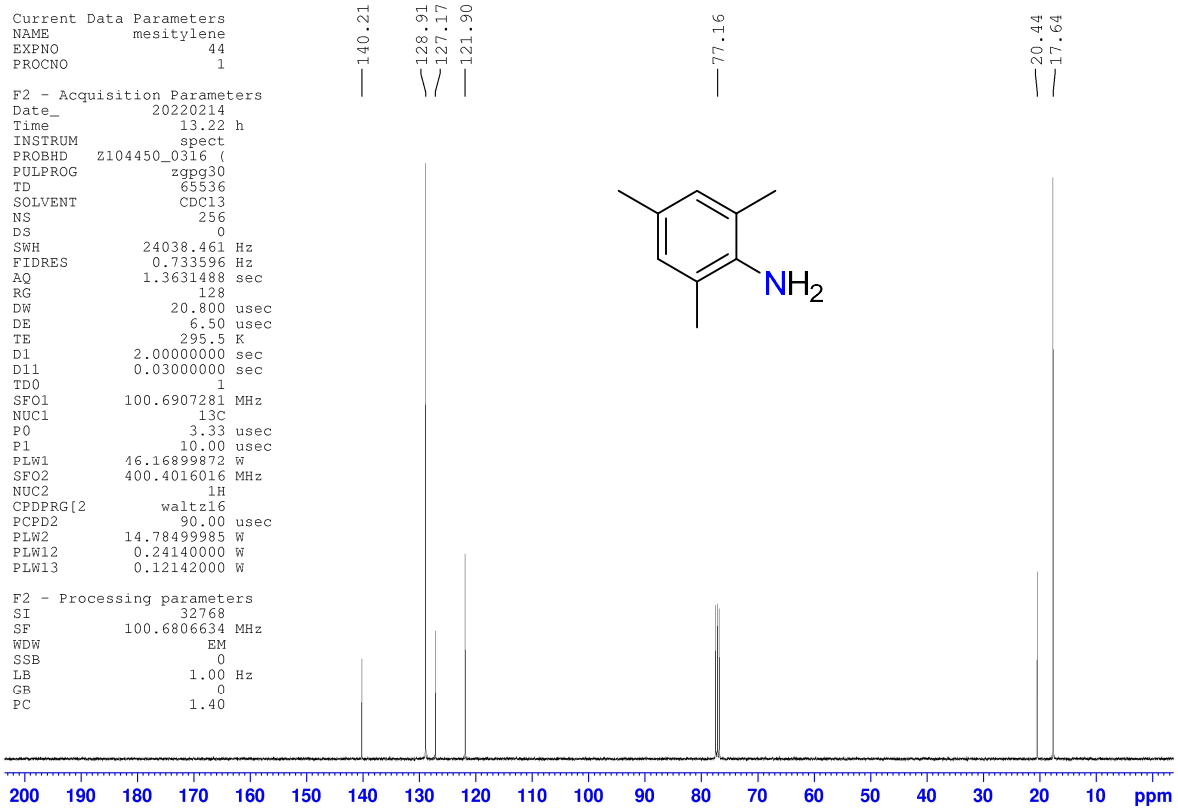


2,4,6-Trimethylaniline (mesitylamine) **3o** – **^{1}H NMR** (400 MHz, $CDCl_3$):



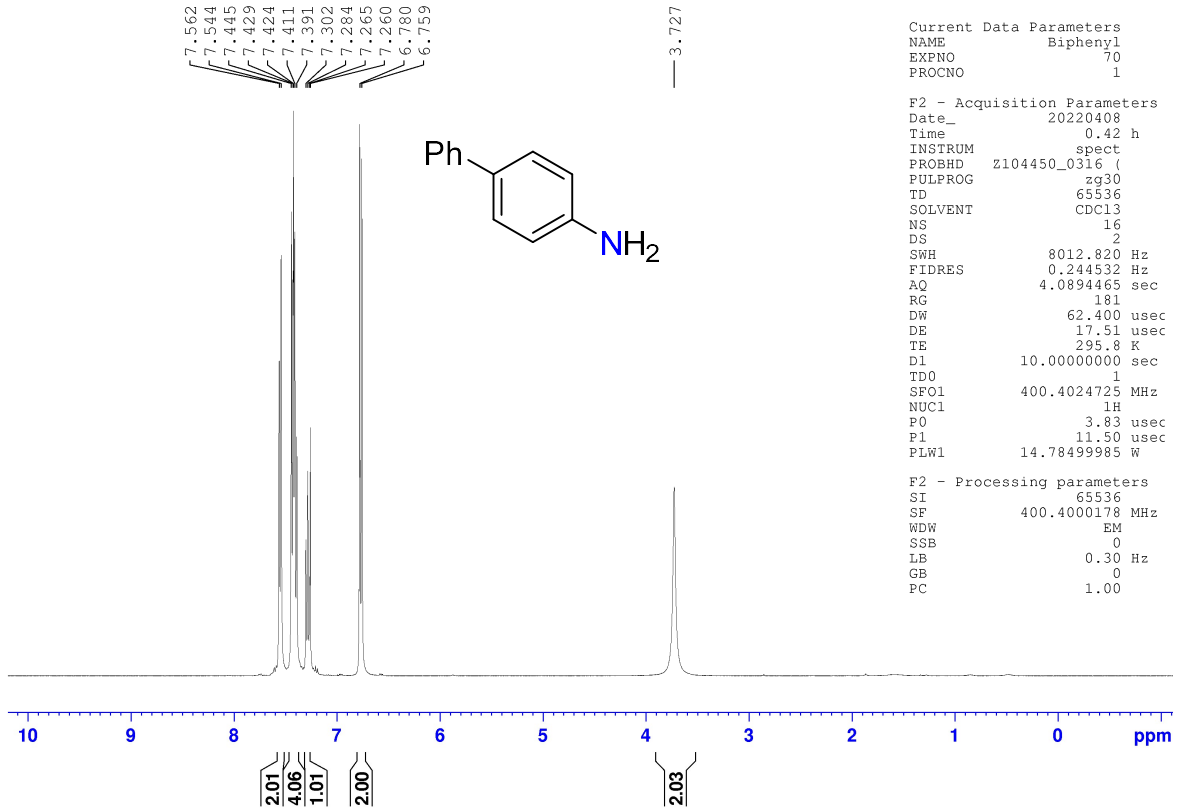

```
Current Data Parameters
NAME          mesitylene
EXPNO                 43
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220214
Time               13.06 h
INSTRUM            spect
PROBHD    Z104450_0316 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ              4.0894465 sec
RG                    57
DW                62.400 usec
DE                17.51 usec
TE                295.0 K
D1           10.00000000 sec
TD0                    1
SFO1          400.4024725 MHz
NUC1                  1H
P0                 3.83 usec
P1                11.50 usec
PLW1         14.78499985 W

F2 - Processing parameters
SI                 65536
SF           400.4000177 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):



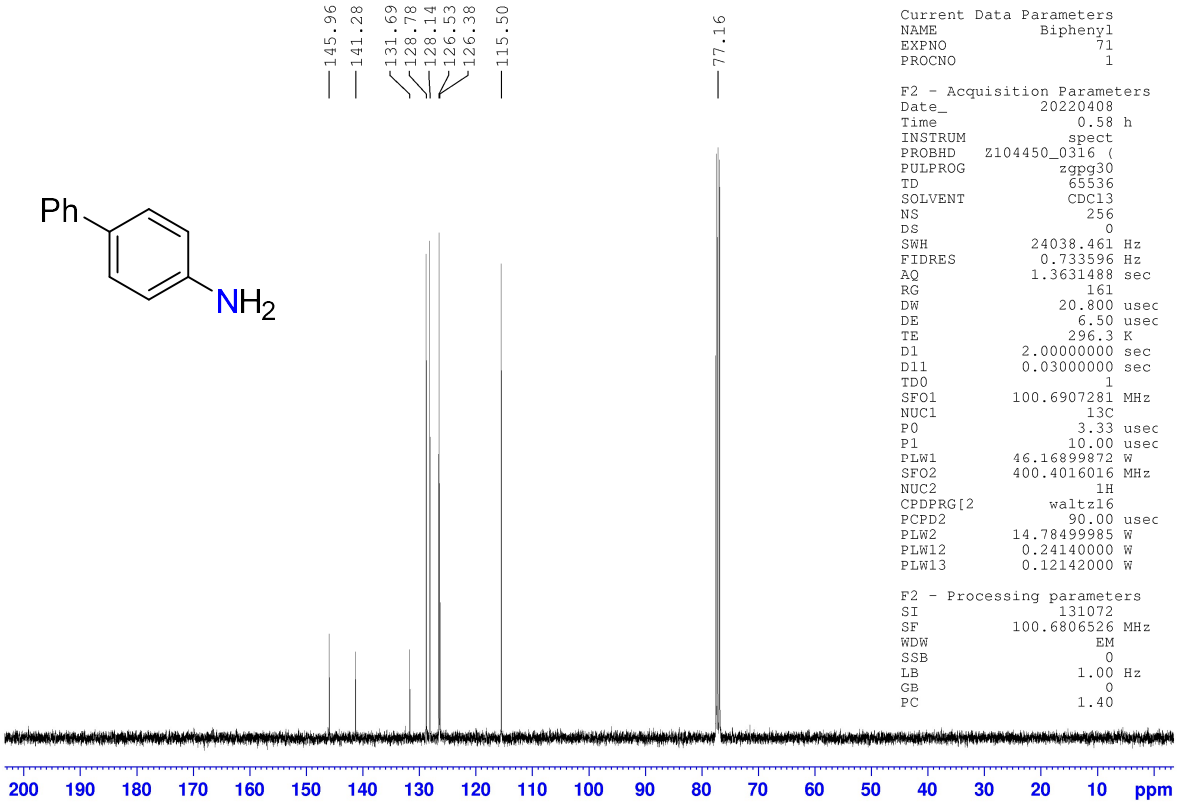

```
Current Data Parameters
NAME          mesitylene
EXPNO                 44
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220214
Time               13.22 h
INSTRUM            spect
PROBHD    Z104450_0316 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     0
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ              1.3631488 sec
RG                   128
DW                20.800 usec
DE                 6.50 usec
TE                295.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1        100.6907281 MHz
NUC1                  13C
P0                 3.33 usec
P1                10.00 usec
PLW1        46.16899872 W
SFO2        400.4016016 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        14.78499985 W
PLW12        0.24140000 W
PLW13        0.12142000 W

F2 - Processing parameters
SI                 32768
SF          100.6806634 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

4-Aminobiphenyl (4-phenylaniline) **3p** – **^{1}H NMR** (400 MHz, $CDCl_3$):



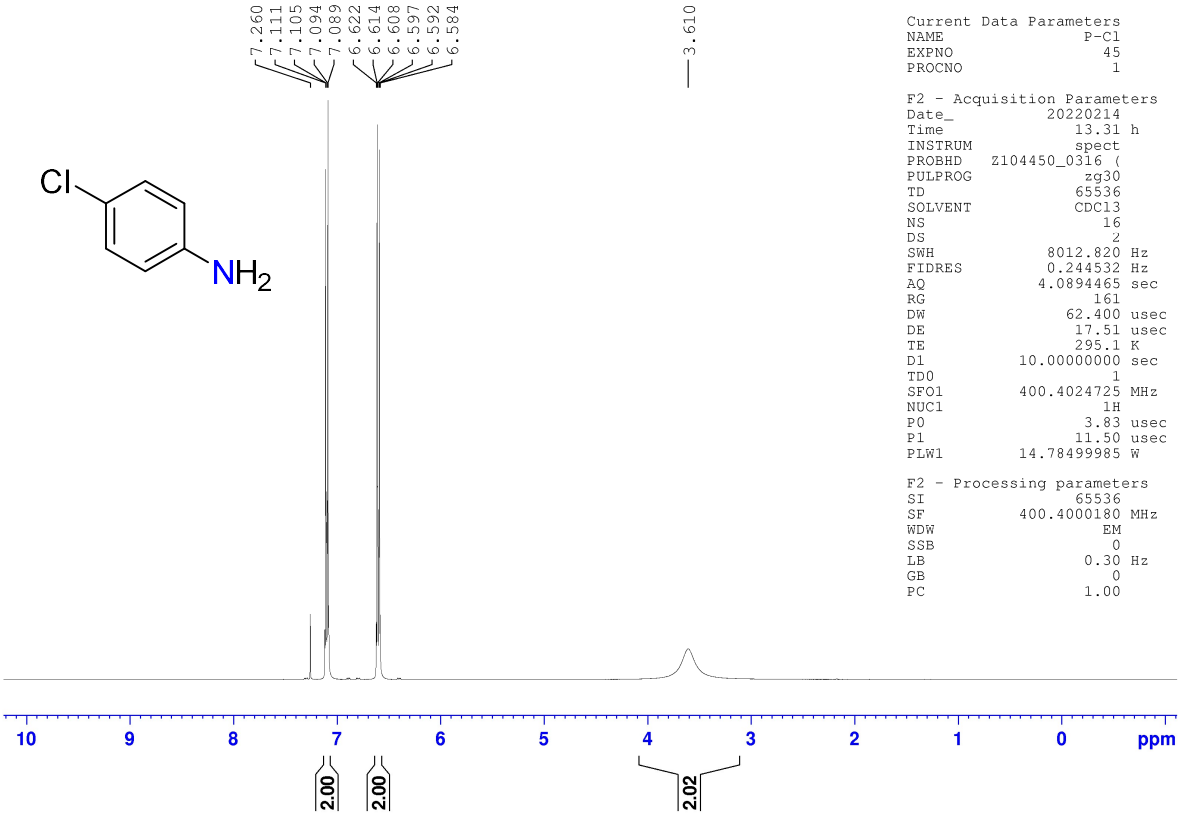

```
Current Data Parameters
NAME            Biphenyl
EXPNO                 70
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220408
Time                0.42 h
INSTRUM            spect
PROBHD    Z104450_0316 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH              8012.820 Hz
FIDRES           0.244532 Hz
AQ               4.0894465 sec
RG                   181
DW                62.400 usec
DE                17.51 usec
TE                295.8 K
D1           10.00000000 sec
TD0                    1
SFO1         400.4024725 MHz
NUC1                  1H
P0                 3.83 usec
P1                11.50 usec
PLW1         14.78499985 W

F2 - Processing parameters
SI                 65536
SF           400.4000178 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):



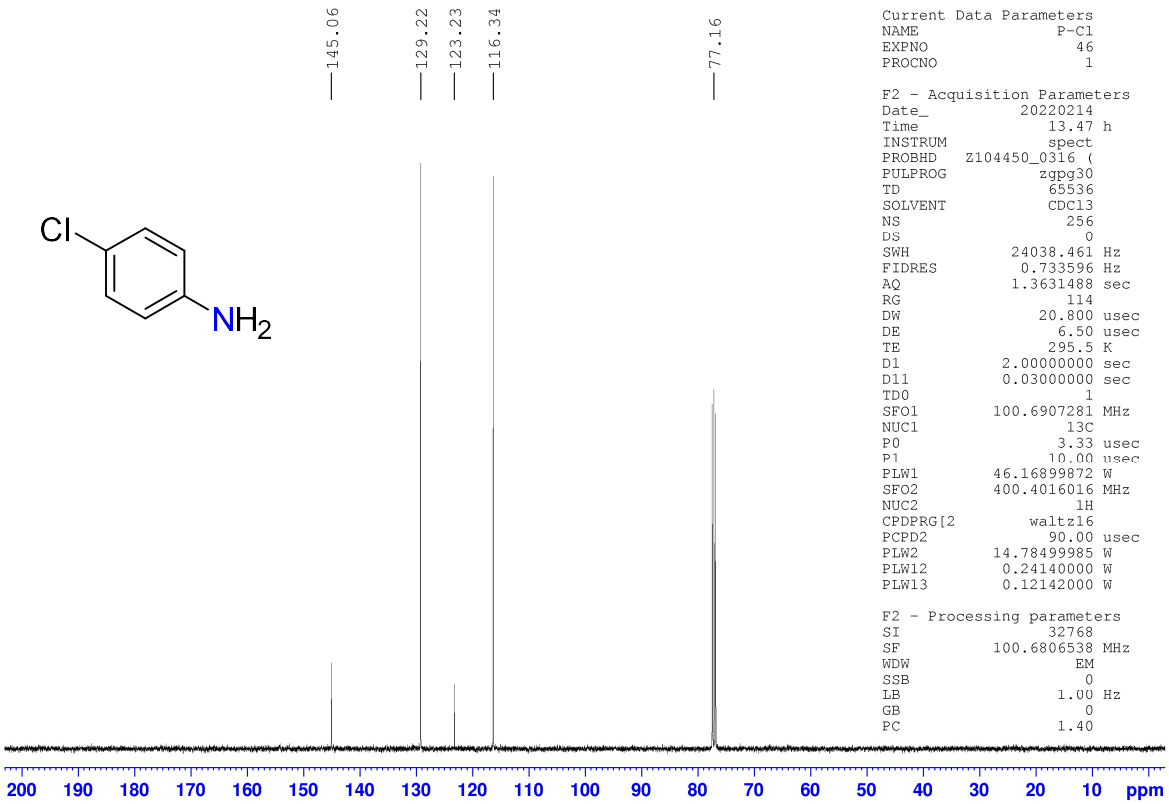

```
Current Data Parameters
NAME            Biphenyl
EXPNO                 71
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220408
Time                0.58 h
INSTRUM            spect
PROBHD    Z104450_0316 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     0
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ               1.3631488 sec
RG                   161
DW                20.800 usec
DE                 6.50 usec
TE                296.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1         100.6907281 MHz
NUC1                  13C
P0                 3.33 usec
P1                10.00 usec
PLW1         46.16899872 W
SFO2         400.4016016 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2         14.78499985 W
PLW12         0.24140000 W
PLW13         0.12142000 W

F2 - Processing parameters
SI                131072
SF           100.6806526 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

4-Chloroaniline **3q** – **^{1}H NMR** (400 MHz, $CDCl_3$):



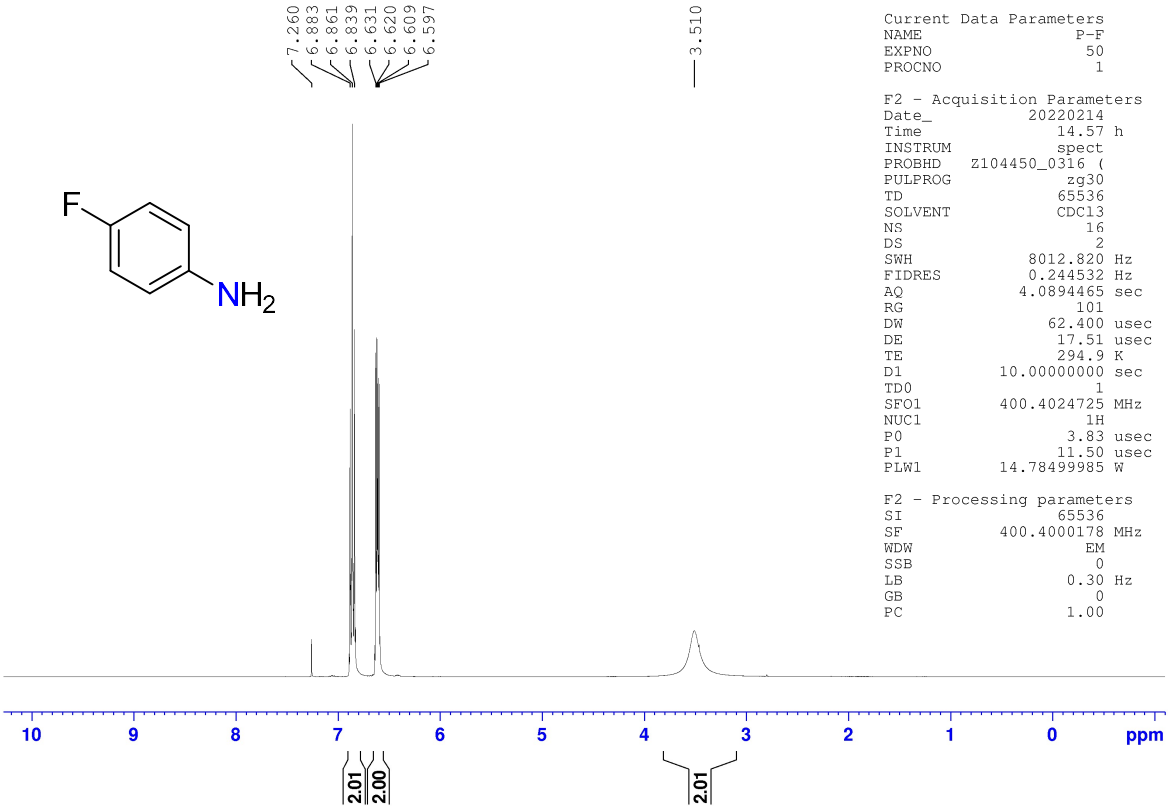

```
Current Data Parameters
NAME                  P-Cl
EXPNO                   45
PROCNO                   1

F2 - Acquisition Parameters
Date_           20220214
Time                13.31 h
INSTRUM             spect
PROBHD    Z104450_0316 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES              0.244532 Hz
AQ               4.0894465 sec
RG                    161
DW                 62.400 usec
DE                 17.51 usec
TE                 295.1 K
D1           10.00000000 sec
TD0                     1
SFO1          400.4024725 MHz
NUC1                   1H
P0                  3.83 usec
P1                 11.50 usec
PLW1         14.78499985 W

F2 - Processing parameters
SI                  65536
SF           400.4000180 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):



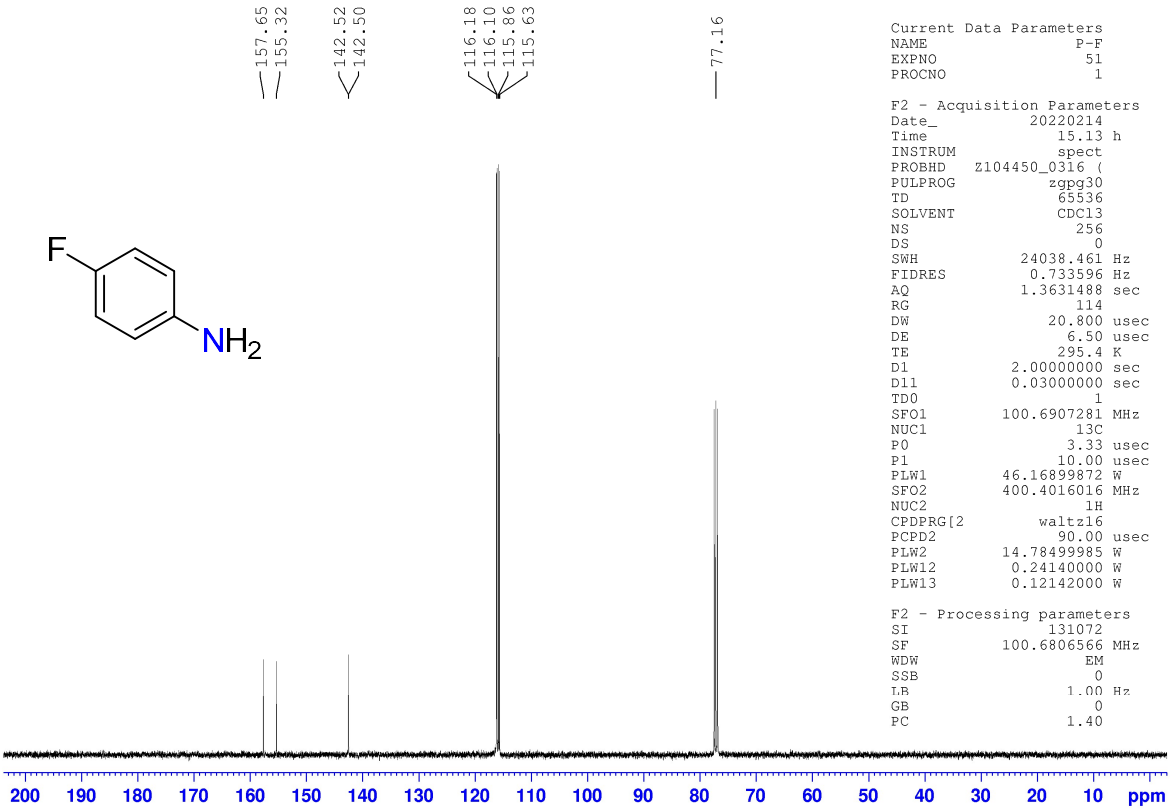

```
Current Data Parameters
NAME                  P-Cl
EXPNO                   46
PROCNO                   1

F2 - Acquisition Parameters
Date_           20220214
Time                13.47 h
INSTRUM             spect
PROBHD    Z104450_0316 (
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      0
SWH             24038.461 Hz
FIDRES              0.733596 Hz
AQ               1.3631488 sec
RG                    114
DW                 20.800 usec
DE                  6.50 usec
TE                 295.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                     1
SFO1         100.6907281 MHz
NUC1                   13C
P0                  3.33 usec
P1                 10.00 usec
PLW1         46.16899872 W
SFO2         400.4016016 MHz
NUC2                   1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         14.78499985 W
PLW12         0.24140000 W
PLW13         0.12142000 W

F2 - Processing parameters
SI                  32768
SF           100.6806538 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

4-Fluoroaniline **3r** – **^{1}H NMR** (400 MHz, $CDCl_3$):




```
Current Data Parameters
NAME                  P-F
EXPNO                  50
PROCNO                  1

F2 - Acquisition Parameters
Date_           20220214
Time               14.57 h
INSTRUM            spect
PROBHD   Z104450_0316 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.244532 Hz
AQ              4.0894465 sec
RG                   101
DW                62.400 usec
DE                17.51 usec
TE                294.9 K
D1           10.00000000 sec
TD0                    1
SFO1          400.4024725 MHz
NUC1                  1H
P0                 3.83 usec
P1                11.50 usec
PLW1          14.78499985 W

F2 - Processing parameters
SI                 65536
SF            400.4000178 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
```

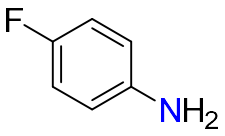
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):



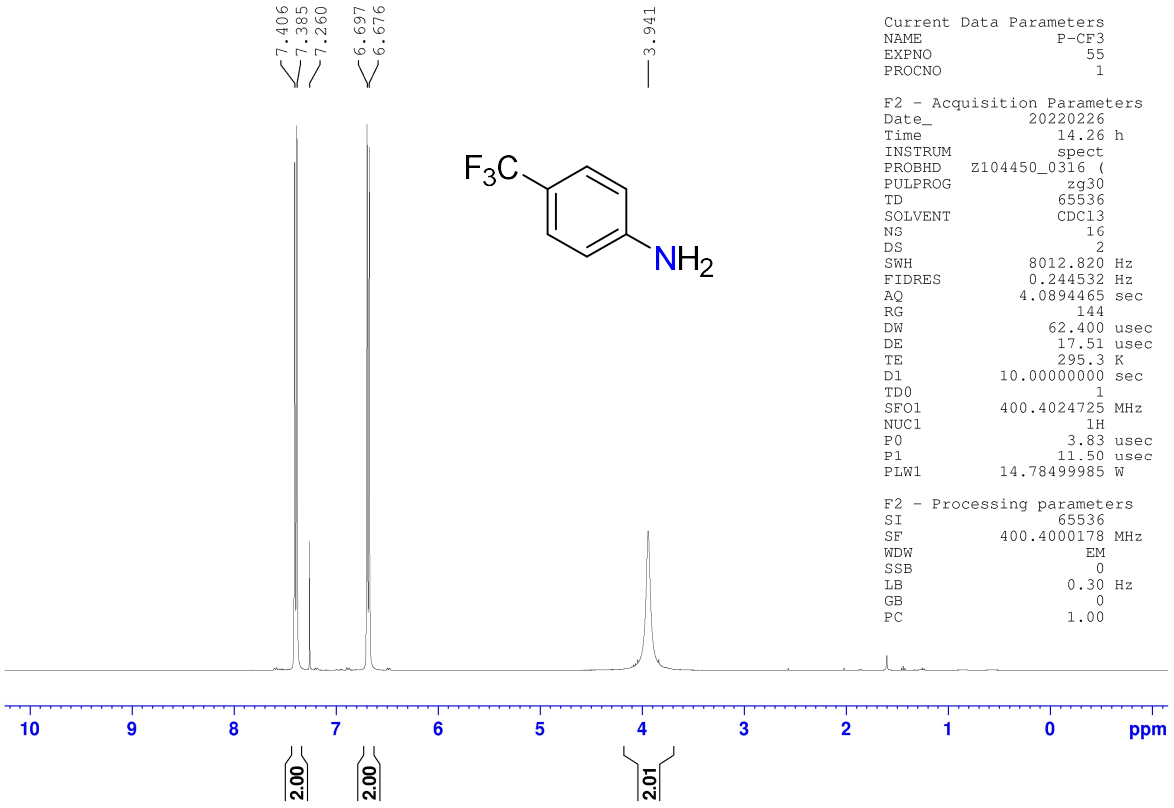

```
Current Data Parameters
NAME                  P-F
EXPNO                  51
PROCNO                  1

F2 - Acquisition Parameters
Date_           20220214
Time               15.13 h
INSTRUM            spect
PROBHD   Z104450_0316 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     0
SWH            24038.461 Hz
FIDRES             0.733596 Hz
AQ              1.3631488 sec
RG                   114
DW                20.800 usec
DE                 6.50 usec
TE                295.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1          100.6907281 MHz
NUC1                  13C
P0                 3.33 usec
P1                10.00 usec
PLW1          46.16899872 W
SFO2          400.4016016 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2          14.78499985 W
PLW12          0.24140000 W
PLW13          0.12142000 W

F2 - Processing parameters
SI                131072
SF            100.6806566 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                  1.40
```

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$):

```
Current Data Parameters
NAME                 P-F
EXPNO                 52
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220214
Time               15.21 h
INSTRUM            spect
PROBHD   Z104450_0316 (
PULPROG          zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                   128
DS                     2
SWH            89285.711 Hz
FIDRES          1.362392 Hz
AQ             0.7340032 sec
RG                  2050
DW                 5.600 usec
DE                 6.50 usec
TE                 295.1 K
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1
SFO1         376.7147448 MHz
NUC1                  19F
P1                12.50 usec
PLW1         21.29999924 W
SFO2         400.4016016 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         14.78499985 W
PLW12         0.24140000 W

F2 - Processing parameters
SI                262144
SF           376.7524368 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

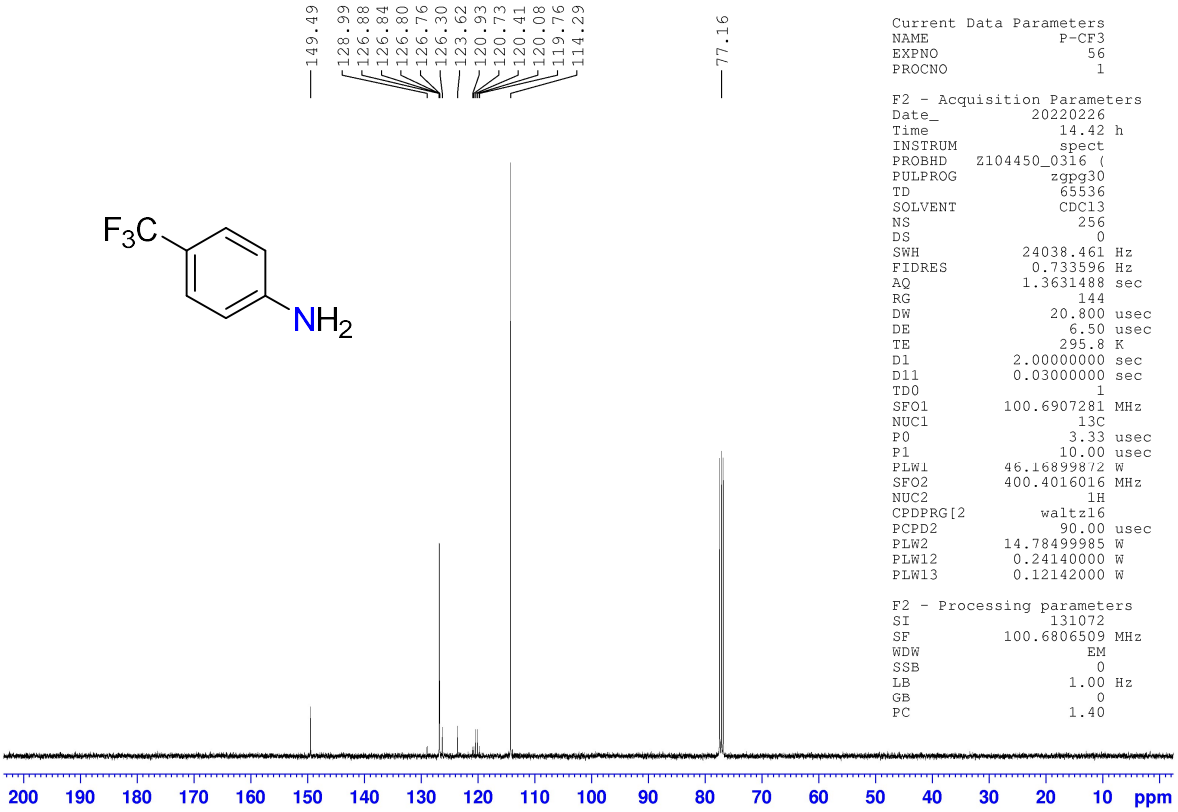


4-Trifluoromethylaniline **3s** – **^{1}H NMR** (400 MHz, $CDCl_3$):



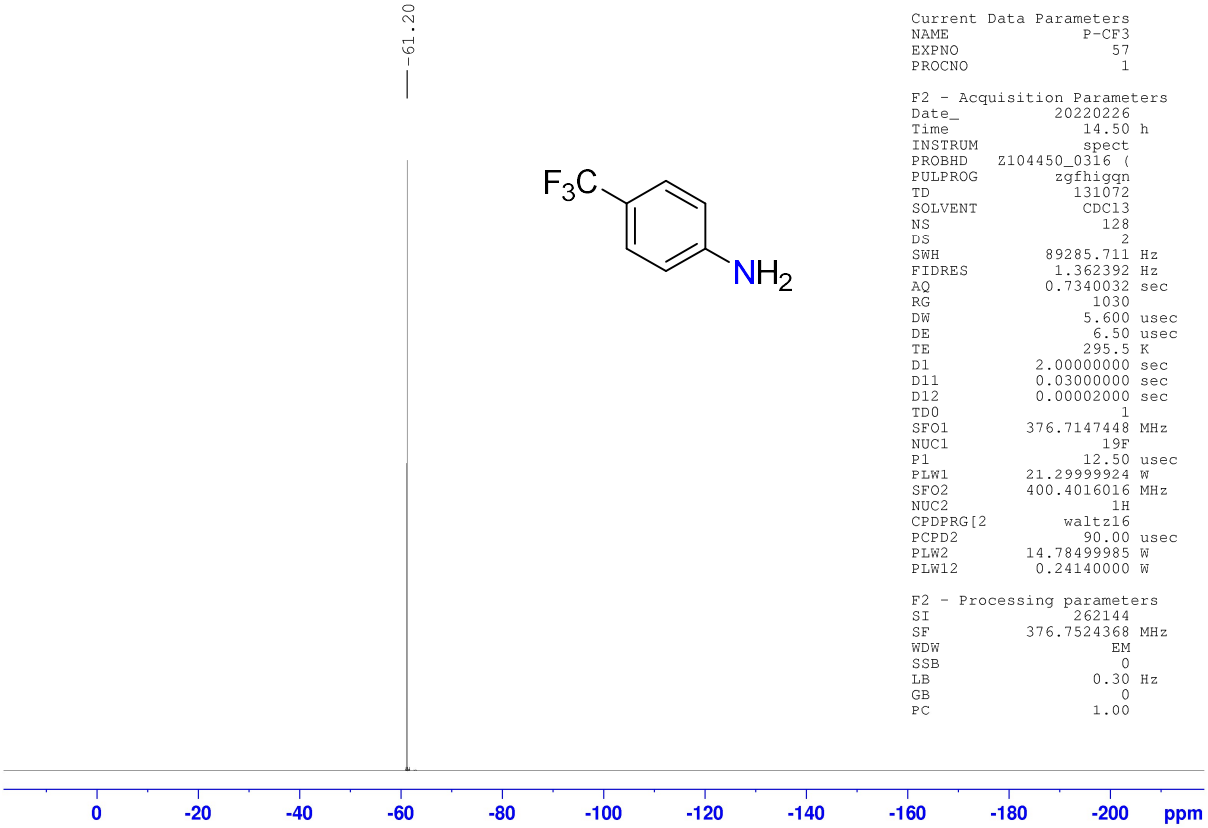

```
Current Data Parameters
NAME                  P-CF3
EXPNO                    55
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220226
Time                 14.26 h
INSTRUM              spect
PROBHD    Z104450_0316 (
PULPROG              zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES               0.244532 Hz
AQ                4.0894465 sec
RG                     144
DW                  62.400 usec
DE                  17.51 usec
TE                  295.3 K
D1             10.00000000 sec
TD0                      1
SFO1           400.4024725 MHz
NUC1                    1H
P0                   3.83 usec
P1                  11.50 usec
PLW1           14.78499985 W

F2 - Processing parameters
SI                   65536
SF             400.4000178 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):



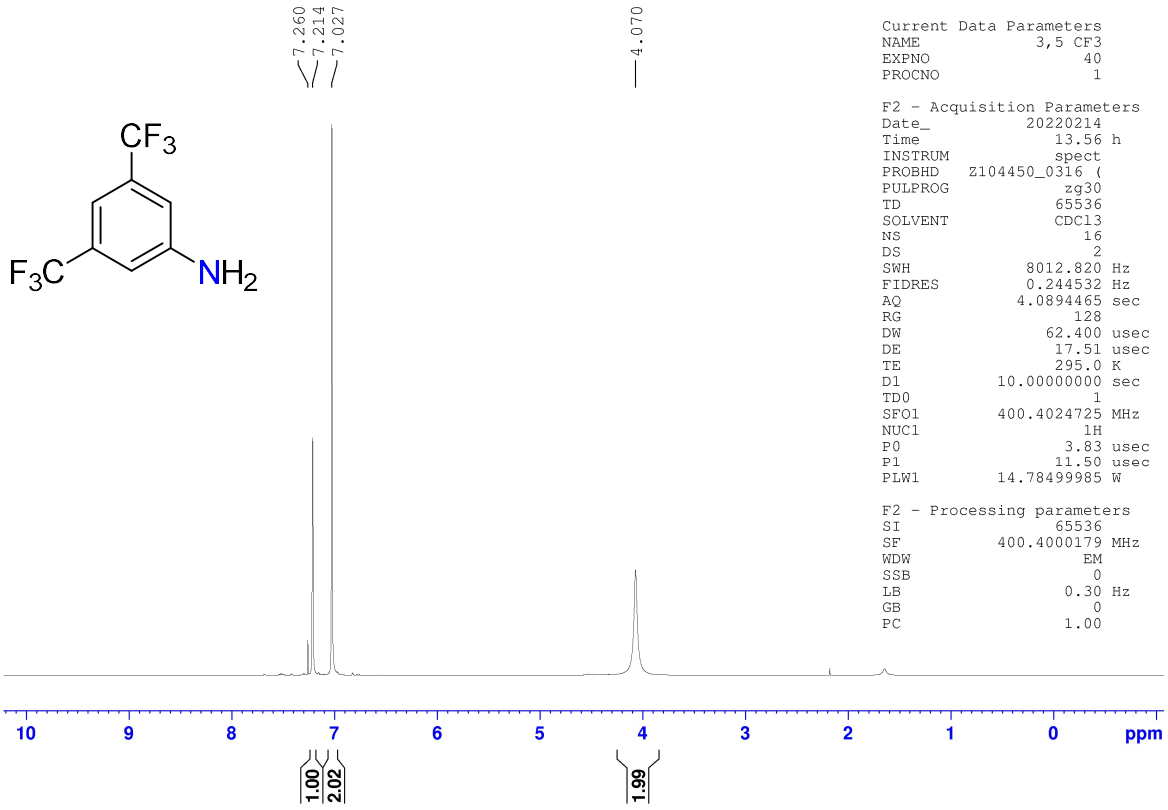

```
Current Data Parameters
NAME                  P-CF3
EXPNO                    56
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220226
Time                 14.42 h
INSTRUM              spect
PROBHD    Z104450_0316 (
PULPROG           zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     256
DS                       0
SWH              24038.461 Hz
FIDRES               0.733596 Hz
AQ                1.3631488 sec
RG                     144
DW                  20.800 usec
DE                   6.50 usec
TE                  295.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1
SFO1           100.6907281 MHz
NUC1                   13C
P0                   3.33 usec
P1                  10.00 usec
PLW1           46.16899872 W
SFO2           400.4016016 MHz
NUC2                    1H
CPDPRG[2          waltz16
PCPD2                90.00 usec
PLW2           14.78499985 W
PLW12           0.24140000 W
PLW13           0.12142000 W

F2 - Processing parameters
SI                  131072
SF             100.6806509 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$):

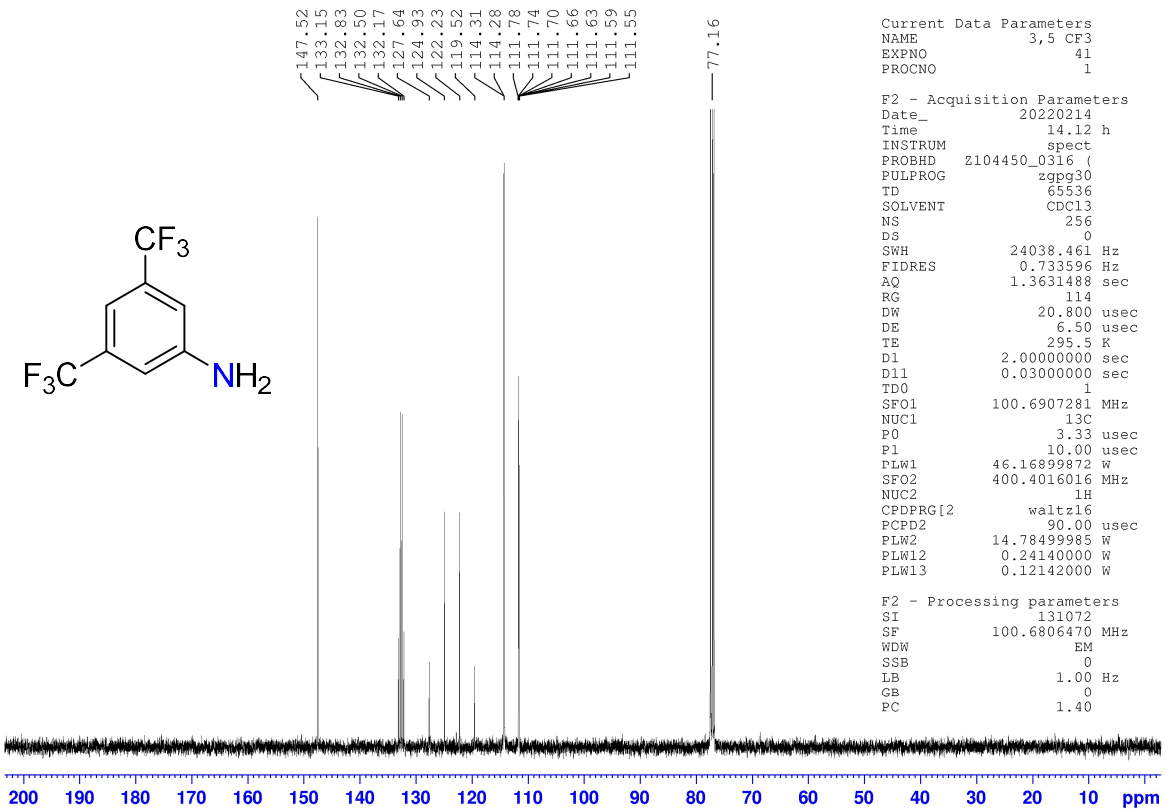



```
Current Data Parameters
NAME                 P-CF3
EXPNO                   57
PROCNO                   1

F2 - Acquisition Parameters
Date_             20220226
Time                 14.50 h
INSTRUM              spect
PROBHD   Z104450_0316 (
PULPROG           zgfhigqn
TD                 131072
SOLVENT              CDCl3
NS                     128
DS                       2
SWH              89285.711 Hz
FIDRES           1.362392 Hz
AQ               0.7340032 sec
RG                    1030
DW                 5.600 usec
DE                 6.50 usec
TE                 295.5 K
D1              2.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
TD0                      1
SFO1           376.7147448 MHz
NUC1                   19F
P1                  12.50 usec
PLW1           21.29999924 W
SFO2           400.4016016 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2           14.78499985 W
PLW12           0.24140000 W

F2 - Processing parameters
SI                  262144
SF             376.7524368 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

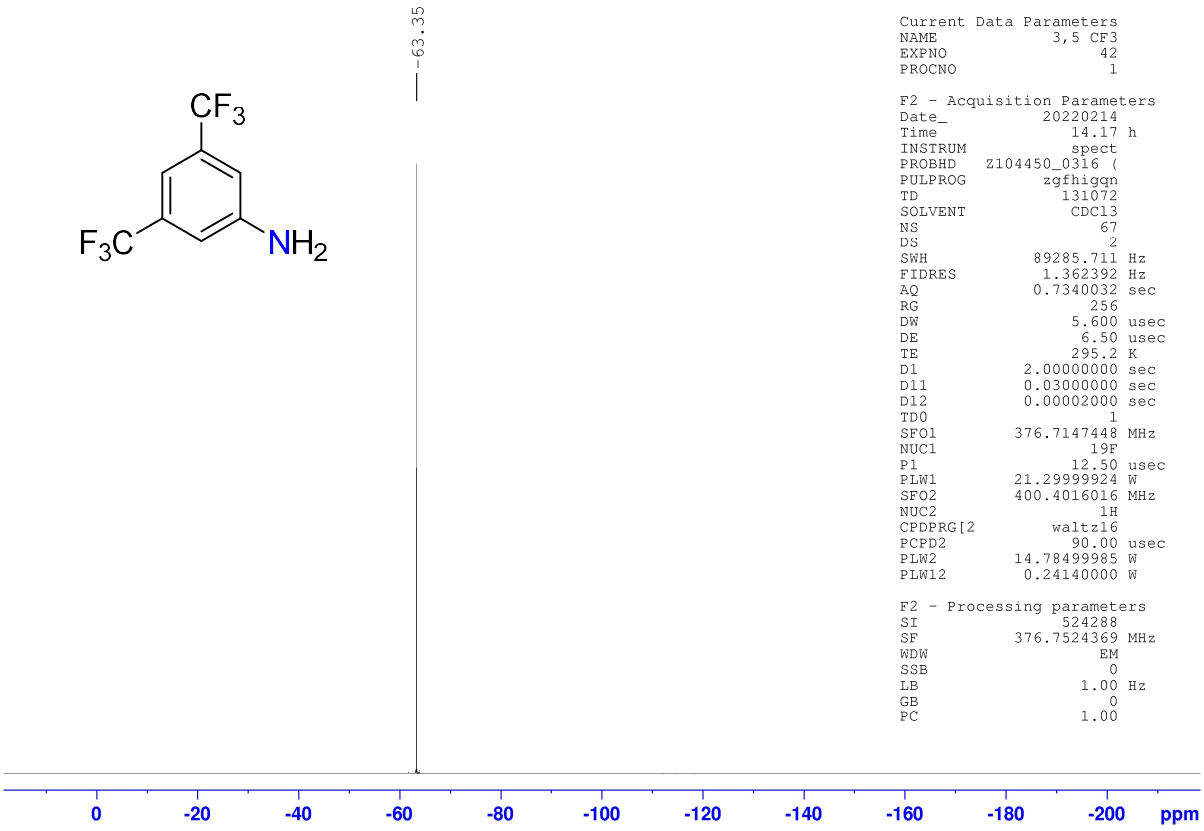
3,5-Bis(trifluoromethyl)aniline **3t** – **^{1}H NMR** (400 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):

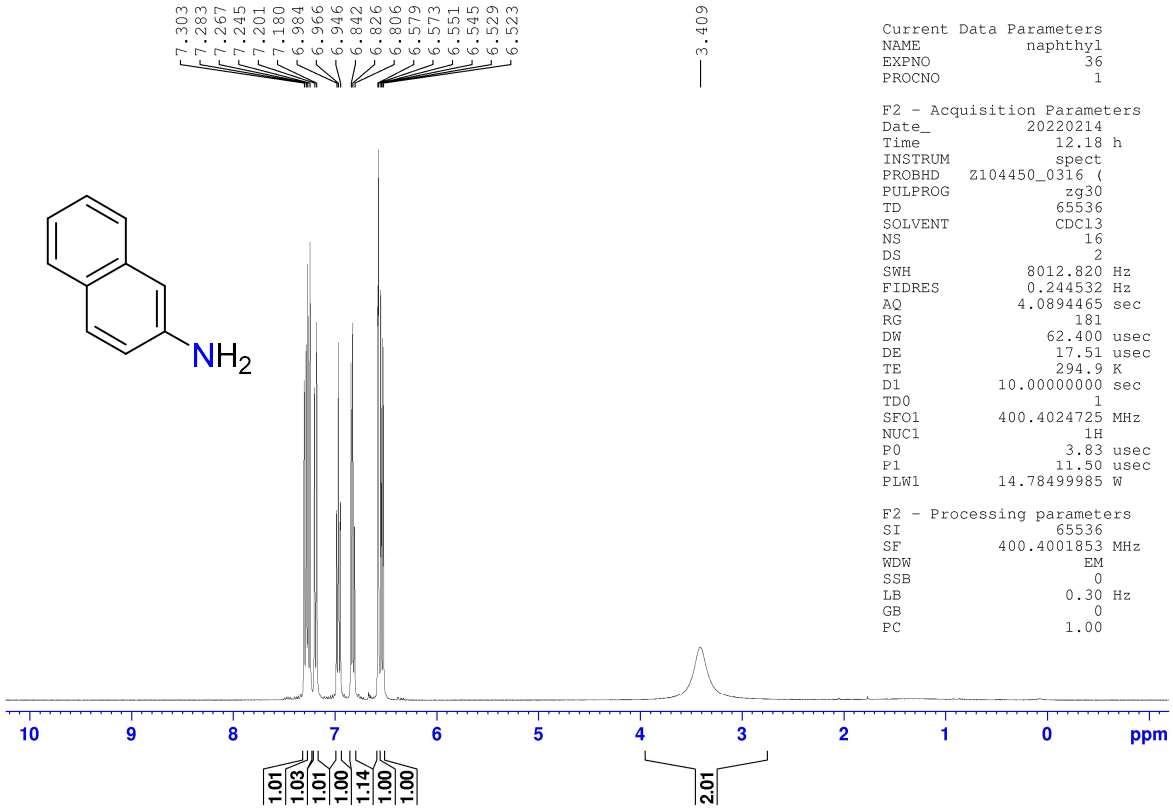


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$):



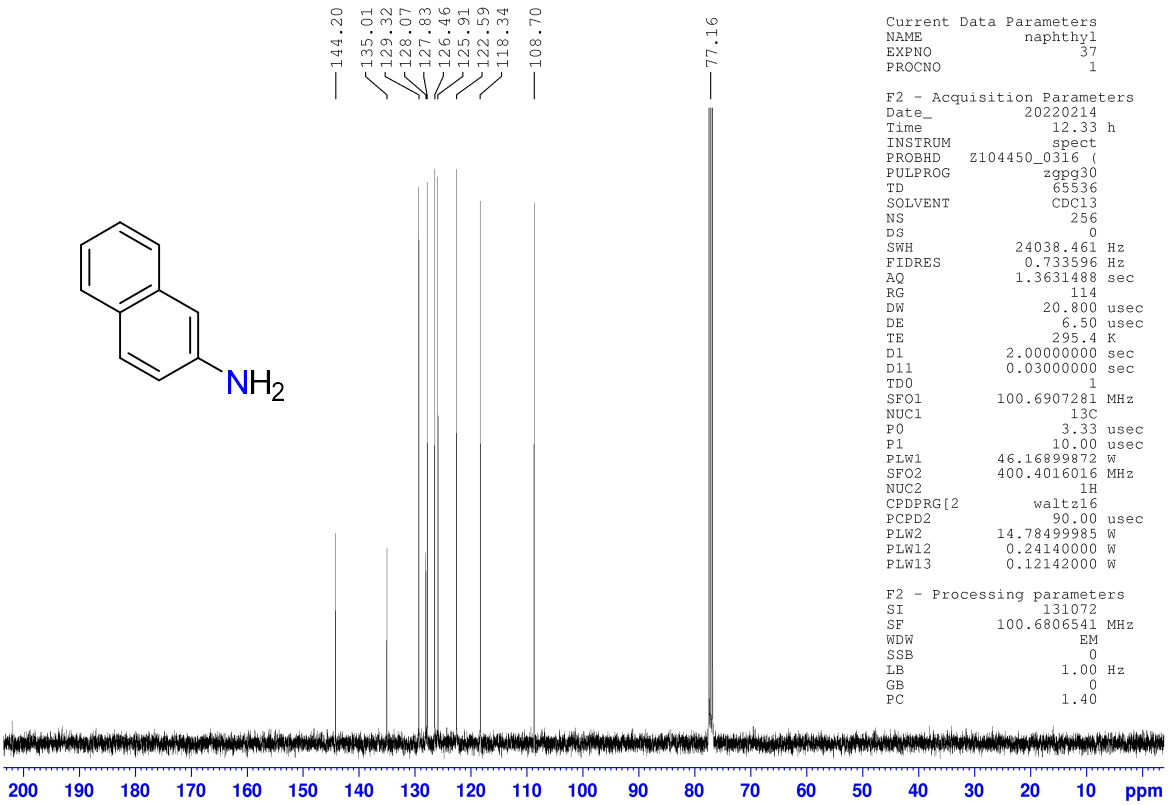

```
Current Data Parameters
NAME             3,5 CF3
EXPNO                 42
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220214
Time               14.17 h
INSTRUM             spect
PROBHD   Z104450_0316 (
PULPROG          zgfhigqn
TD                131072
SOLVENT             CDCl3
NS                     67
DS                      2
SWH            89285.711 Hz
FIDRES          1.362392 Hz
AQ              0.7340032 sec
RG                    256
DW                5.600 usec
DE                 6.50 usec
TE                295.2 K
D1           2.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                    1
SFO1         376.7147448 MHz
NUC1                 19F
P1                12.50 usec
PLW1         21.29999924 W
SFO2         400.4016016 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         14.78499985 W
PLW12         0.24140000 W

F2 - Processing parameters
SI                524288
SF           376.7524369 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.00
```

2-Naphthylamine **3u** – **^{1}H NMR** (400 MHz, $CDCl_3$):



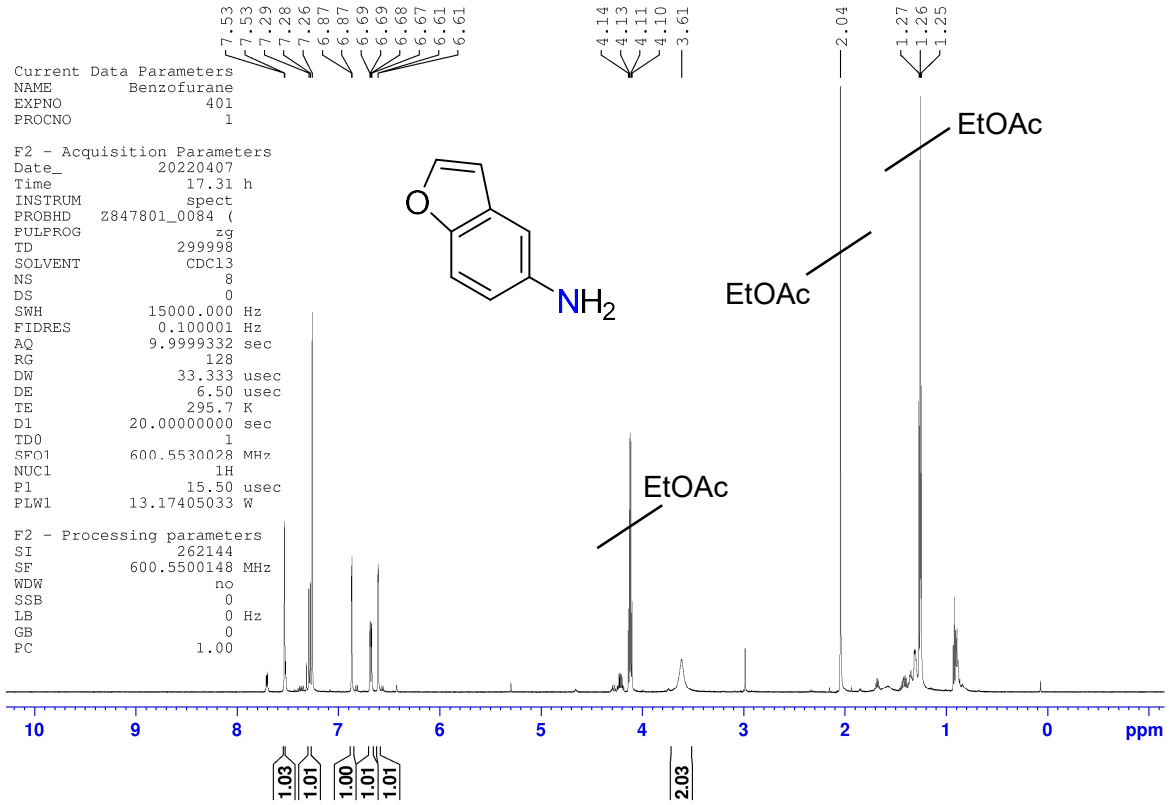

```
Current Data Parameters
NAME            naphthyl
EXPNO                 36
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220214
Time               12.18 h
INSTRUM            spect
PROBHD   Z104450_0316 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ              4.0894465 sec
RG                   181
DW                62.400 usec
DE                17.51 usec
TE                294.9 K
D1           10.00000000 sec
TD0                    1
SFO1         400.4024725 MHz
NUC1                  1H
P0                 3.83 usec
P1                11.50 usec
PLW1         14.78499985 W

F2 - Processing parameters
SI                 65536
SF           400.4001853 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):

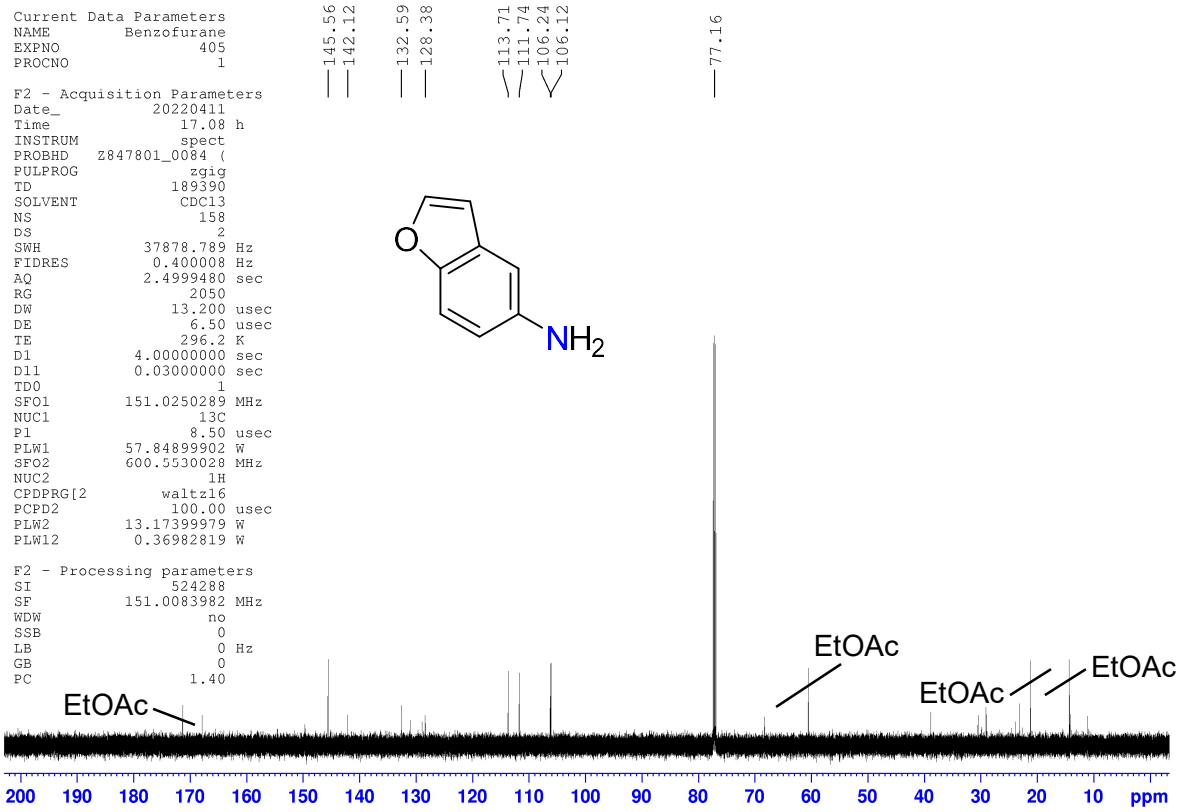



```
Current Data Parameters
NAME            naphthyl
EXPNO                 37
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220214
Time               12.33 h
INSTRUM            spect
PROBHD   Z104450_0316 (
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     0
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ              1.3631488 sec
RG                   114
DW                20.800 usec
DE                 6.50 usec
TE                295.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1         100.6907281 MHz
NUC1                 13C
P0                 3.33 usec
P1                10.00 usec
PLW1         46.16899872 W
SFO2         400.4016016 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2         14.78499985 W
PLW12         0.24140000 W
PLW13         0.12142000 W

F2 - Processing parameters
SI                131072
SF           100.6806541 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

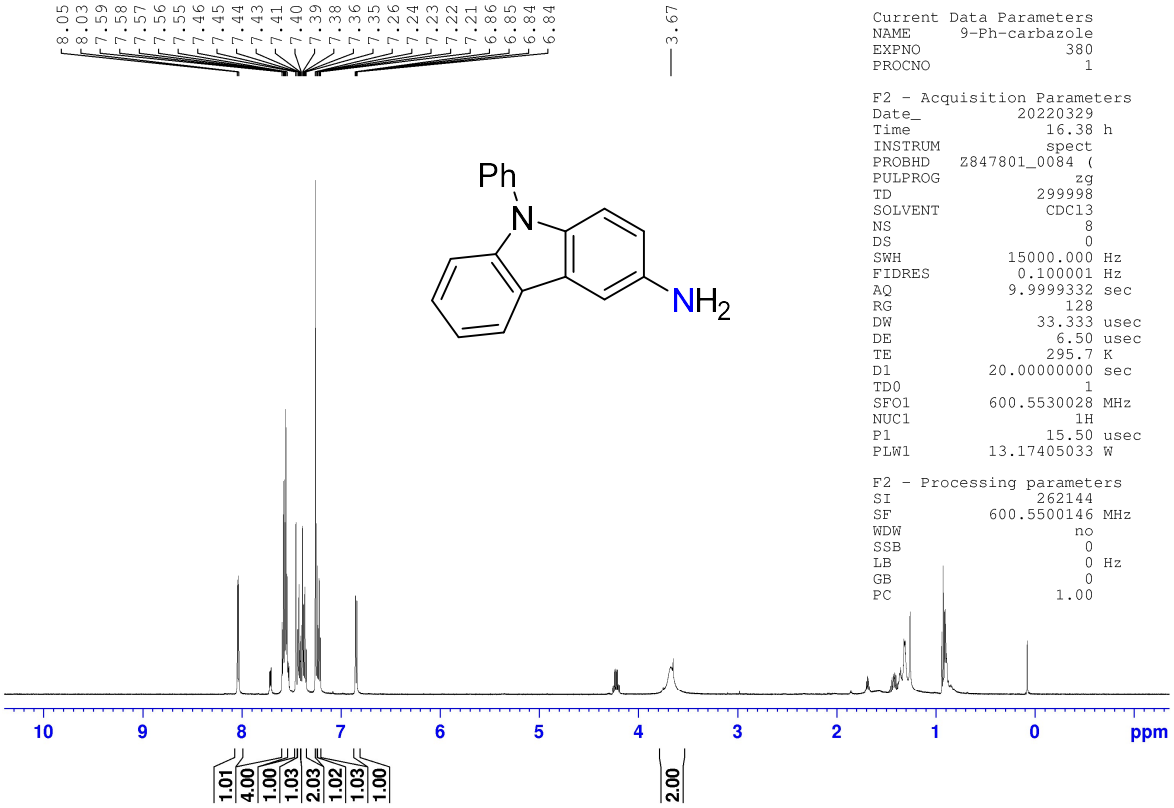
5-Benzofurylamine **3v** – **^{1}H NMR** (600 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$):



3-Amino-9-phenylcarbazole **3w** – **^{1}H NMR** (600 MHz, $CDCl_3$):

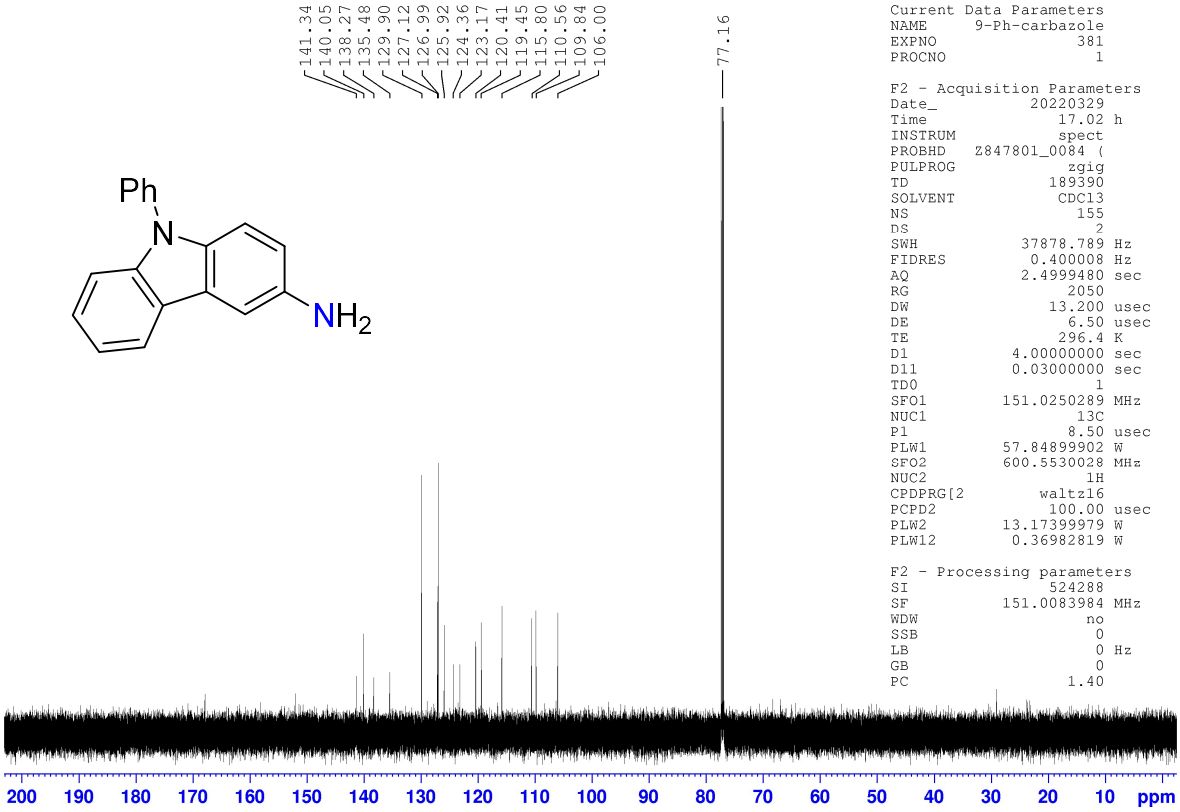


Current Data Parameters
NAME 9-Ph-carbazole
EXPNO 380
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220329
Time 16.38 h
INSTRUM spect
PROBHD Z847801_0084 (
PULPROG zg
TD 299998
SOLVENT CDCl3
NS 8
DS 0
SWH 15000.000 Hz
FIDRES 0.100001 Hz
AQ 9.9999332 sec
RG 128
DW 33.333 usec
DE 6.50 usec
TE 295.7 K
D1 20.00000000 sec
TD0 1
SFO1 600.5530028 MHz
NUC1 1H
P1 15.50 usec
PLW1 13.17405033 W

F2 - Processing parameters
SI 262144
SF 600.5500146 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$):

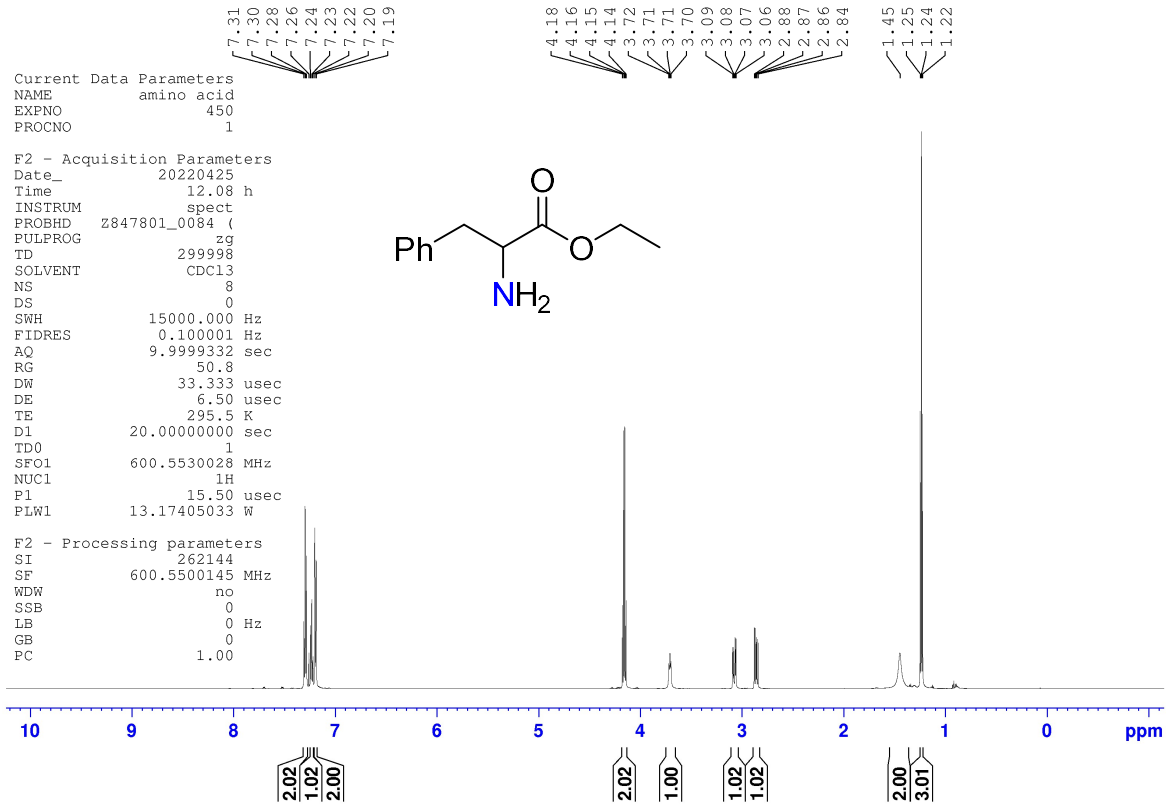


Current Data Parameters
NAME 9-Ph-carbazole
EXPNO 381
PROCNO 1

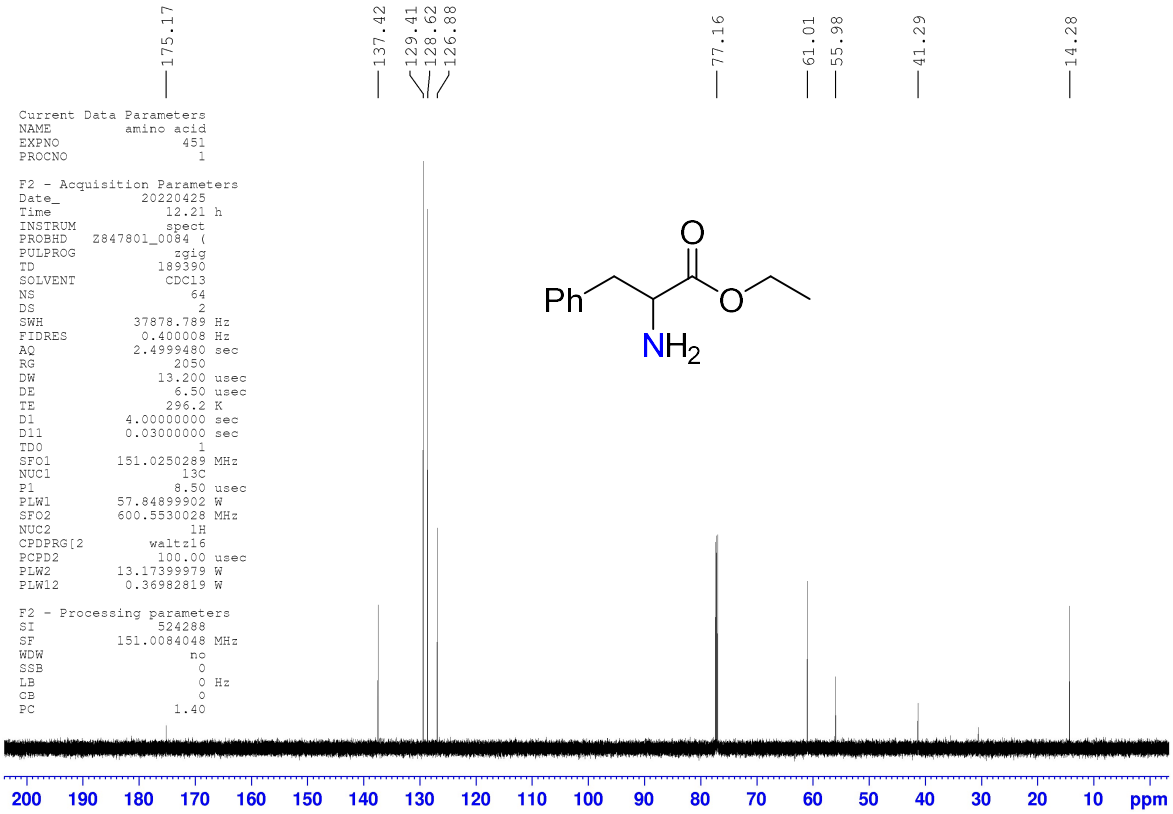
F2 - Acquisition Parameters
Date_ 20220329
Time 17.02 h
INSTRUM spect
PROBHD Z847801_0084 (
PULPROG zgig
TD 189390
SOLVENT CDCl3
NS 155
DS 2
SWH 37878.789 Hz
FIDRES 0.400008 Hz
AQ 2.4999480 sec
RG 2050
DW 13.200 usec
DE 6.50 usec
TE 296.4 K
D1 4.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 151.0250289 MHz
NUC1 13C
P1 8.50 usec
PLW1 57.84899902 W
SFO2 600.5530028 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 100.00 usec
PLW2 13.17399979 W
PLW12 0.36982819 W

F2 - Processing parameters
SI 524288
SF 151.0083984 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40

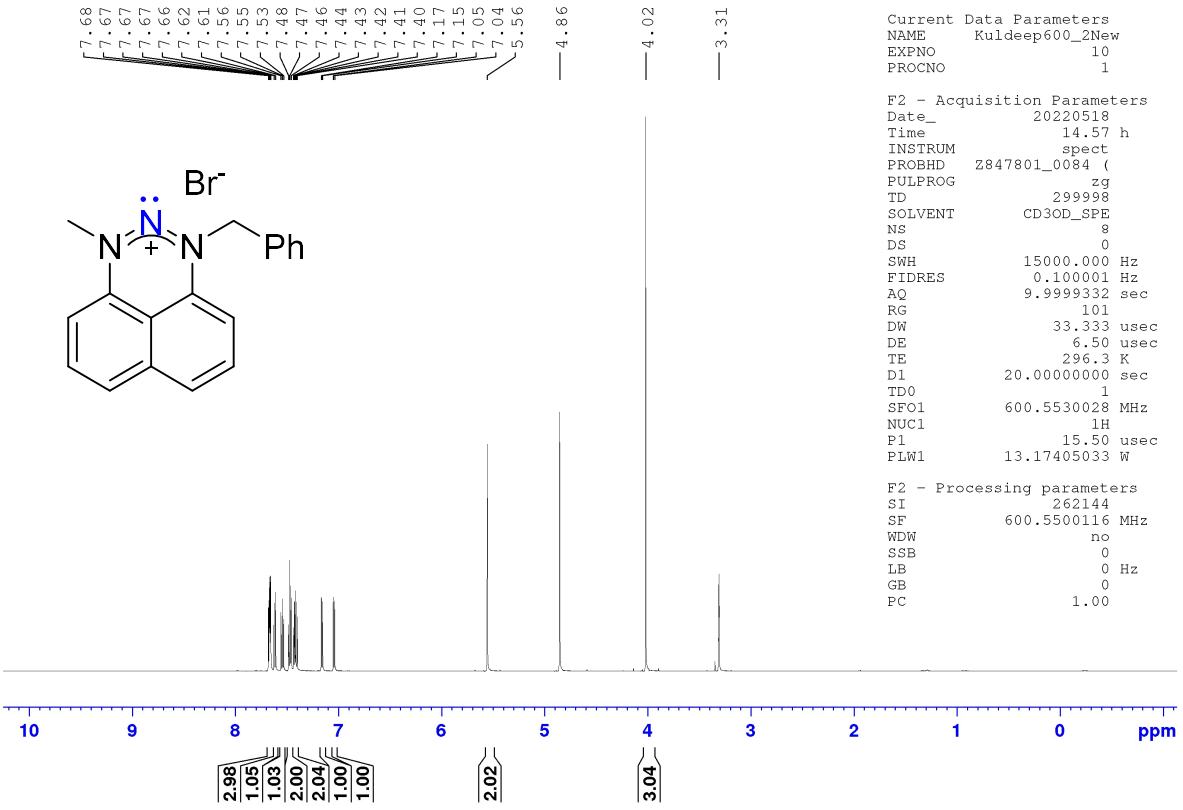
Phenylalanine ethyl ester **3x** – **^{1}H NMR** (600 MHz, $CDCl_3$):



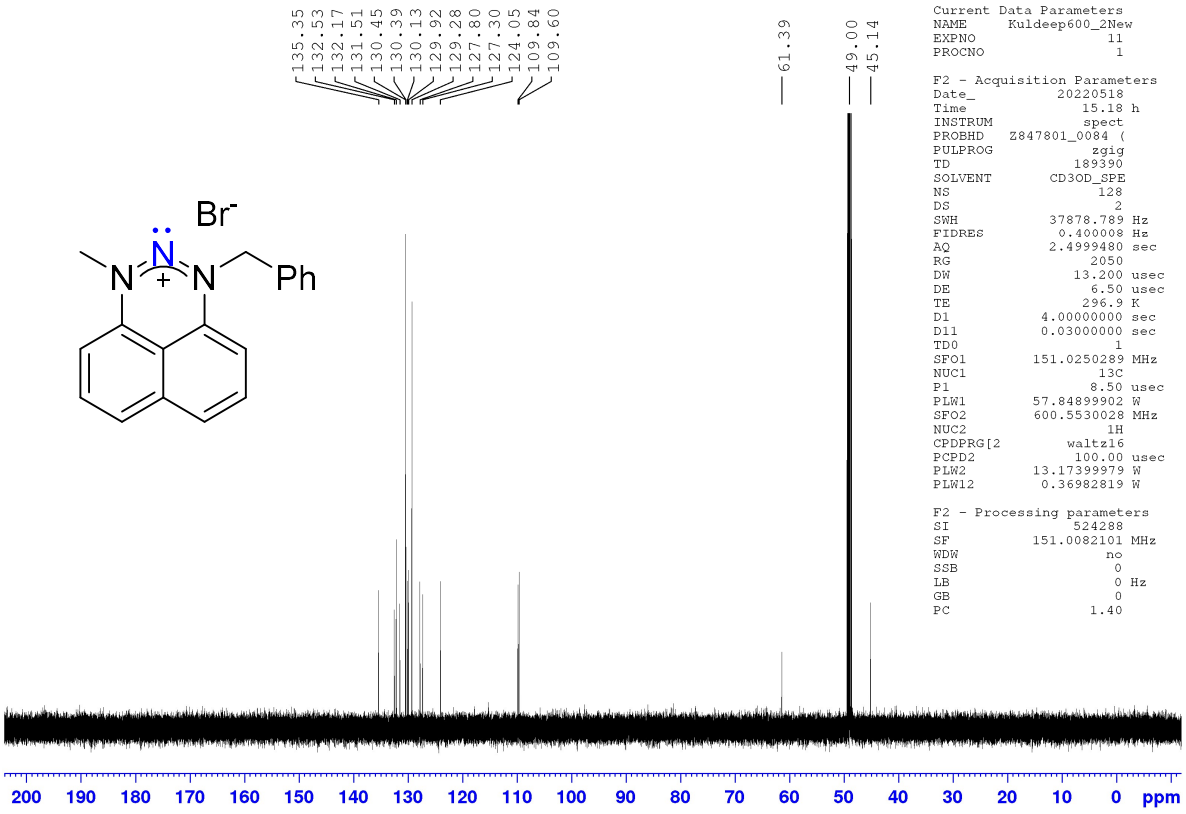
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$):



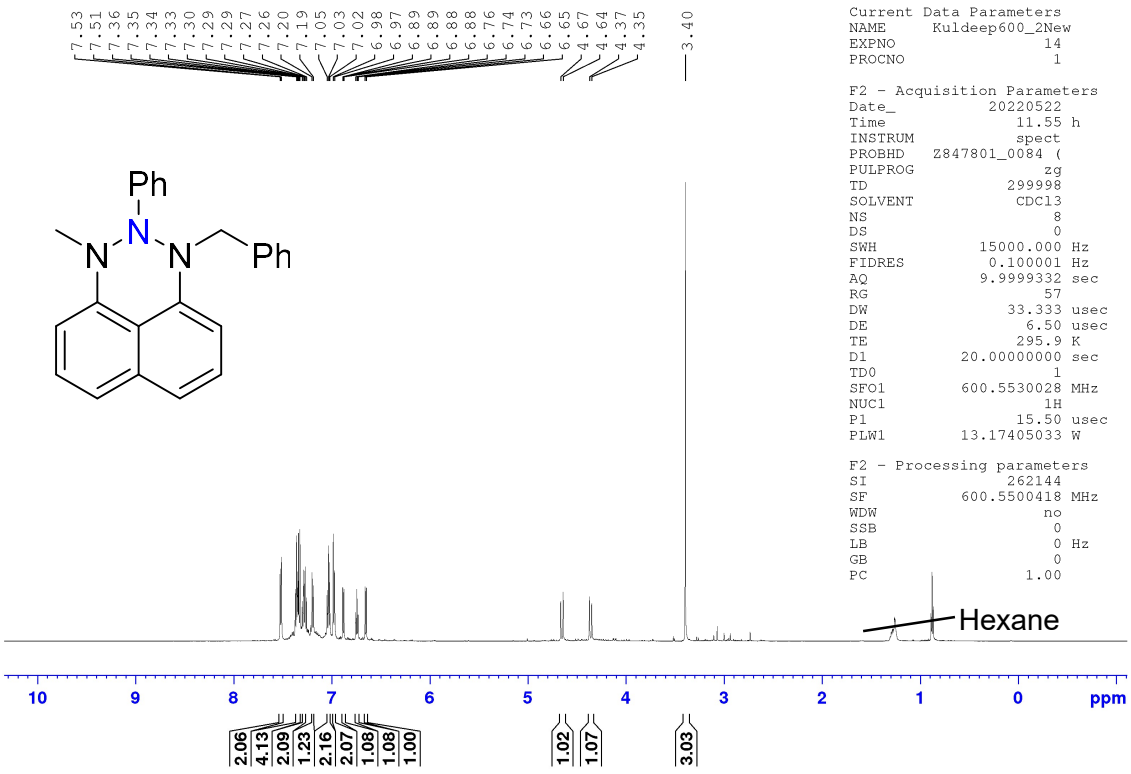
1*N*-Methyl-3*N*-benzyl-naphthotriazinium bromide **5** – **^{1}H NMR** (600 MHz, CD_3OD):



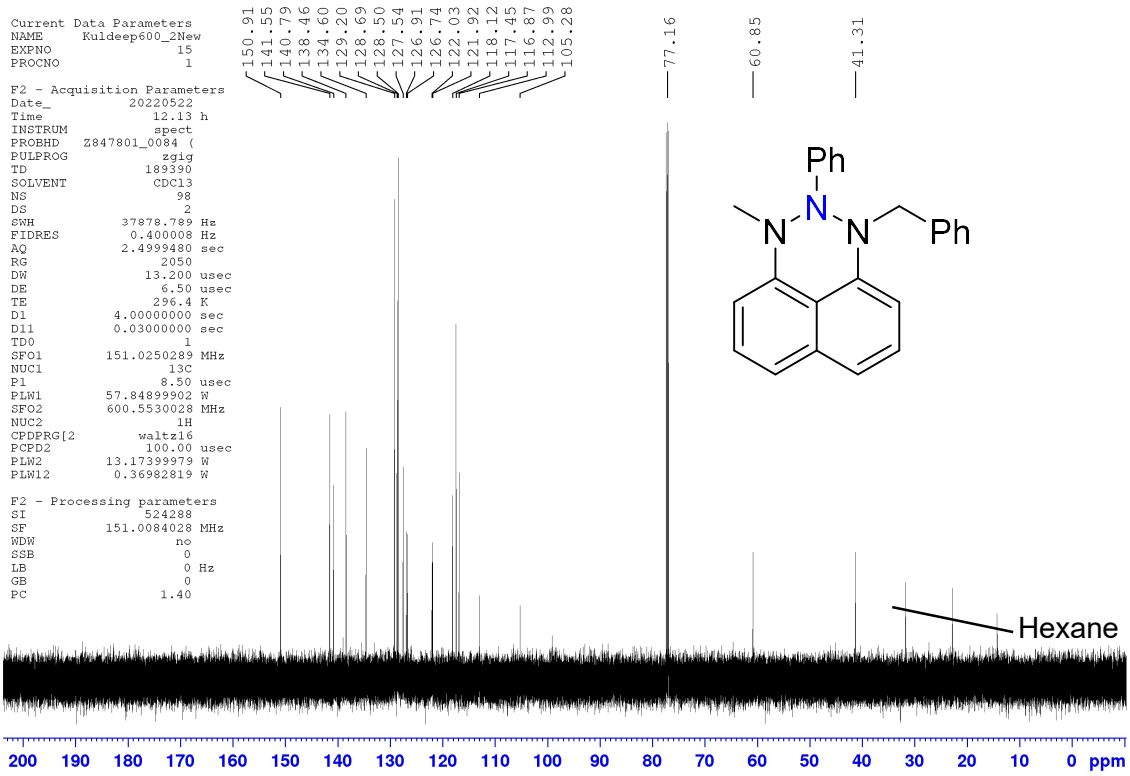
^{13}C{^{1}H} NMR (151 MHz, CD_3OD):



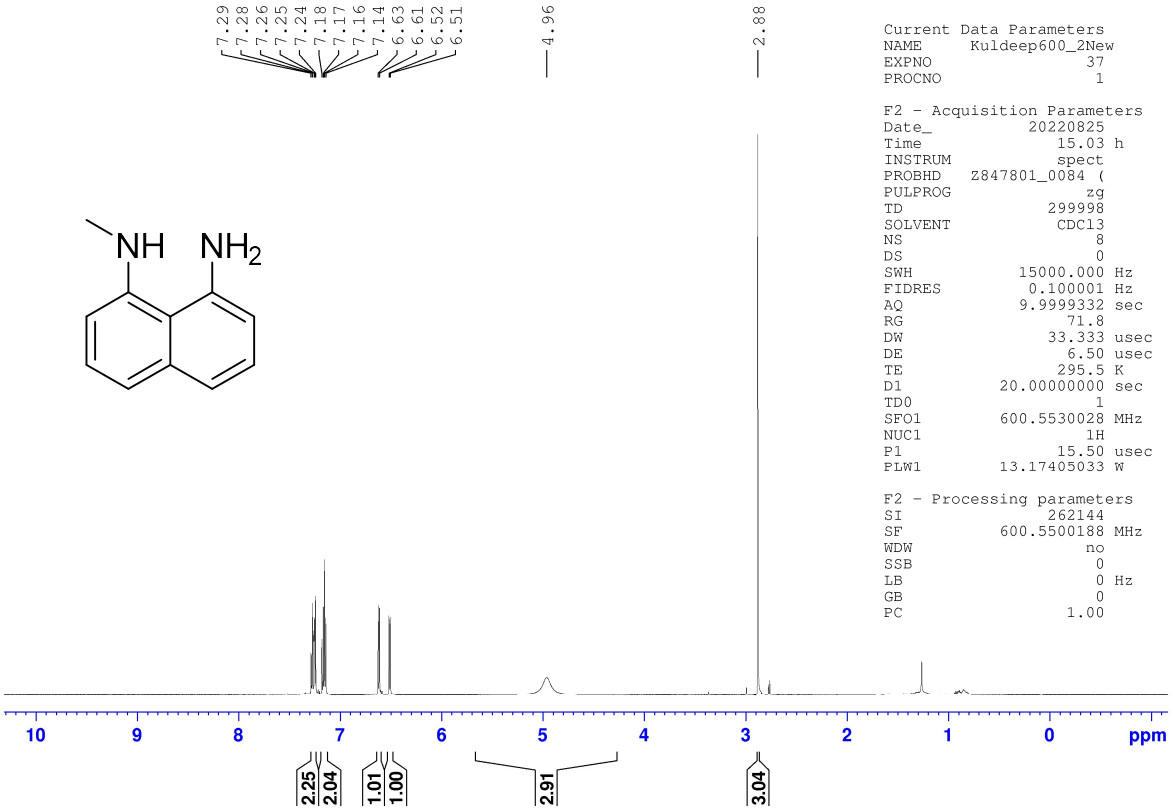
1*N*-Methyl-2*N*-phenyl-3*N*-benzyl-naphthotriazane **6** – **^{1}H NMR** (600 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):

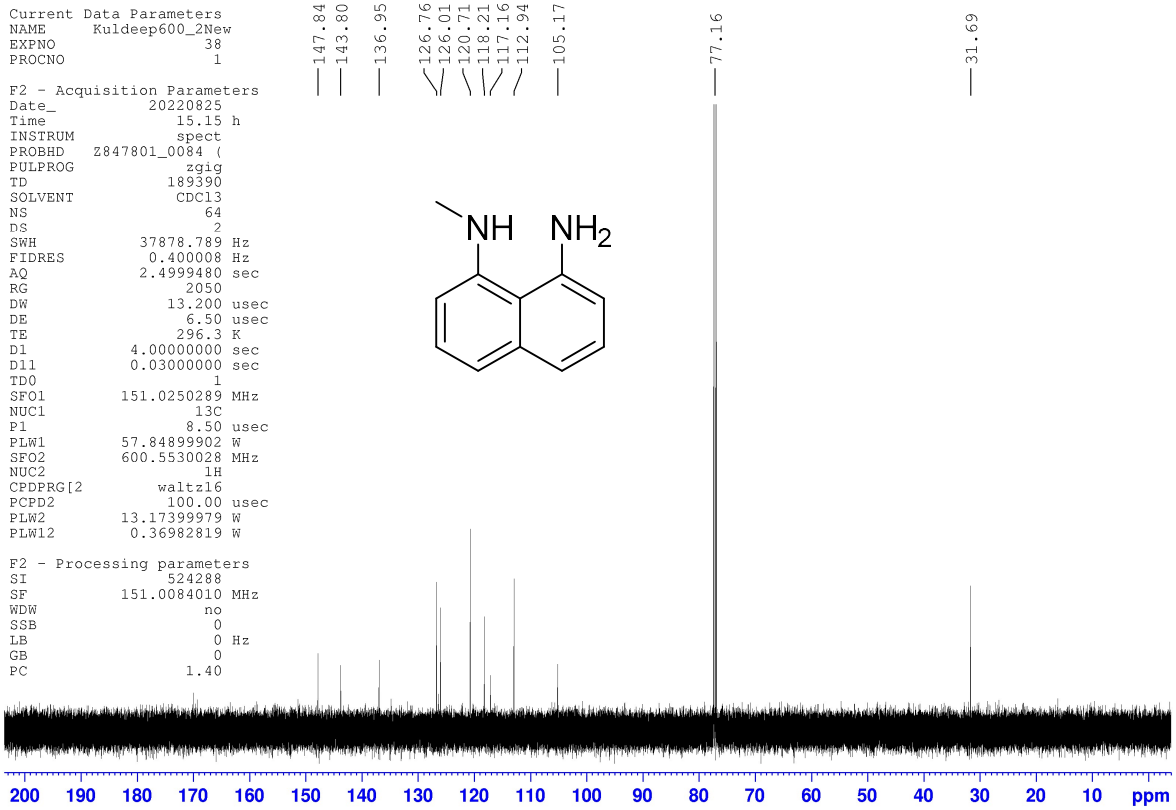


N-methyl-1,8-diaminonaphthalene **7** – **^{1}H NMR** (600 MHz, $CDCl_3$):



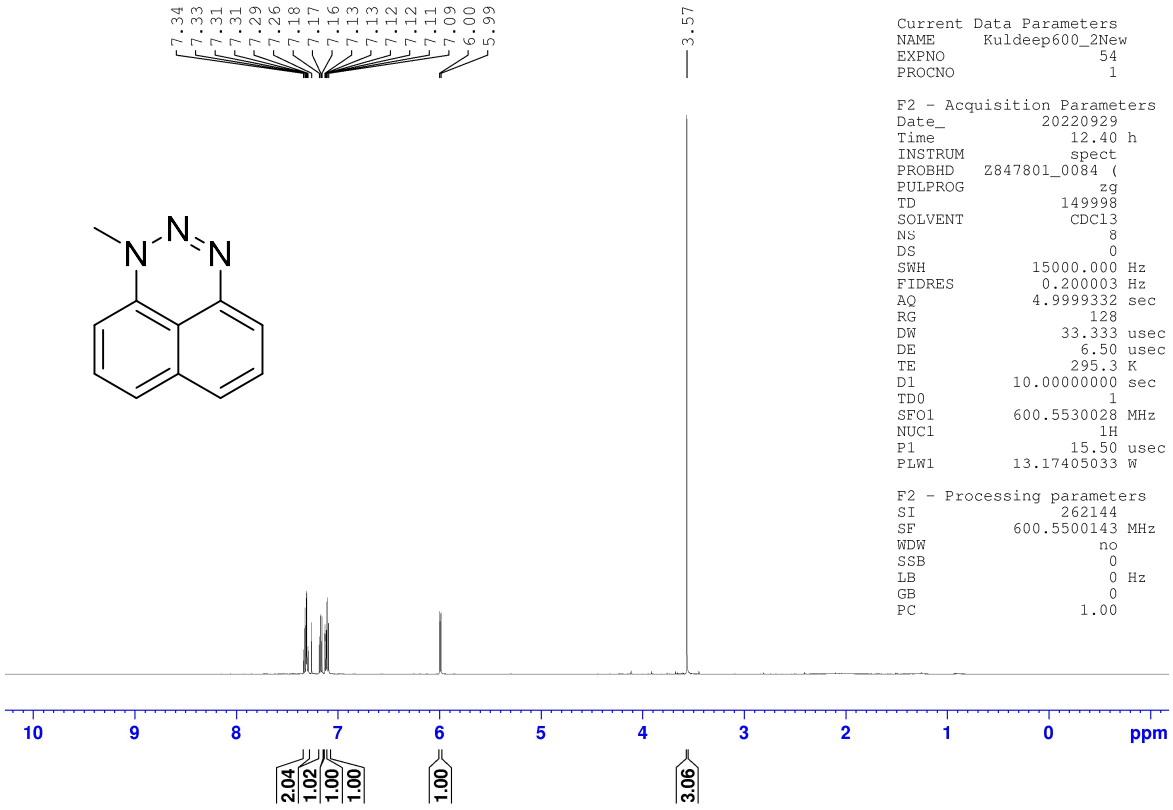

```
Current Data Parameters
NAME      Kuldeep600_2New
EXPNO                  37
PROCNO                  1

F2 - Acquisition Parameters
Date_           20220825
Time               15.03 h
INSTRUM             spect
PROBHD   Z847801_0084 (
PULPROG               zg
TD                299998
SOLVENT             CDCl3
NS                      8
DS                      0
SWH            15000.000 Hz
FIDRES             0.100001 Hz
AQ              9.9999332 sec
RG                   71.8
DW                33.333 usec
DE                  6.50 usec
TE                 295.5 K
D1           20.00000000 sec
TD0                     1
SFO1          600.5530028 MHz
NUC1                   1H
P1                  15.50 usec
PLW1          13.17405033 W

F2 - Processing parameters
SI                 262144
SF            600.5500188 MHz
WDW                    no
SSB                     0
LB                      0 Hz
GB                      0
PC                   1.00
```

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):

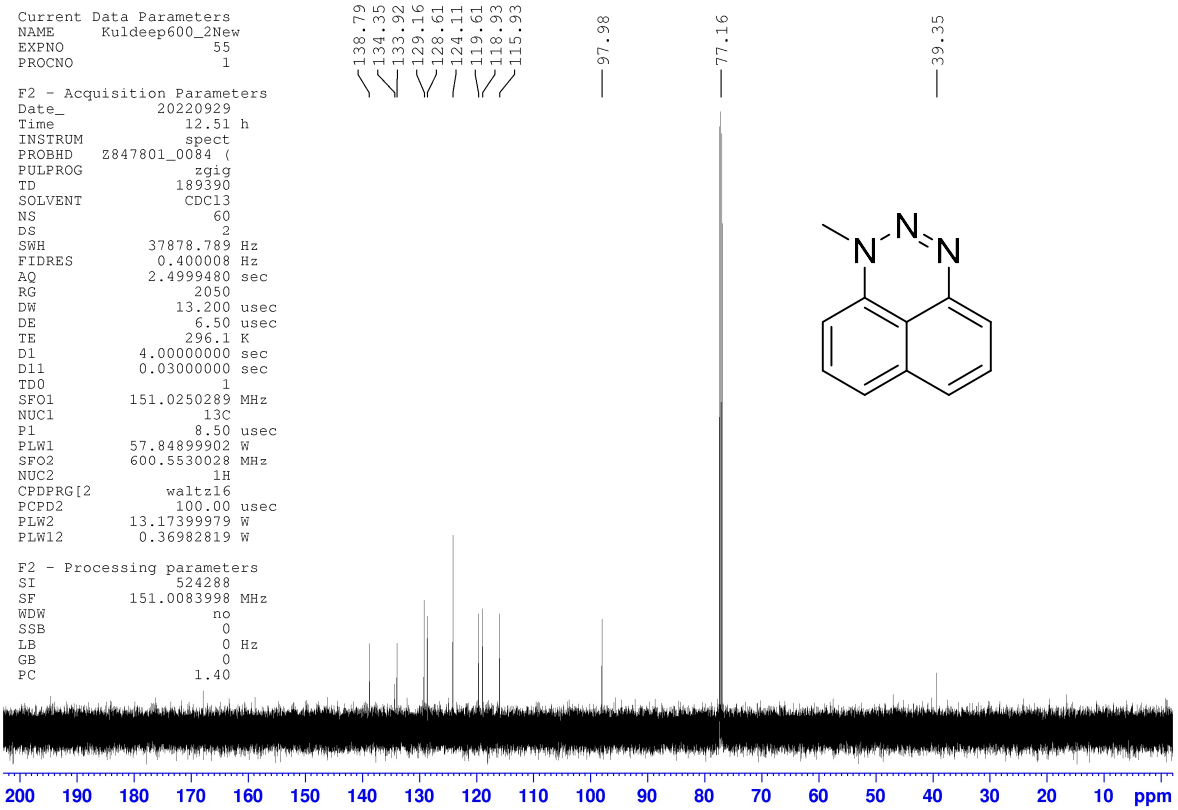



```
Current Data Parameters
NAME      Kuldeep600_2New
EXPNO                  38
PROCNO                  1

F2 - Acquisition Parameters
Date_           20220825
Time               15.15 h
INSTRUM             spect
PROBHD   Z847801_0084 (
PULPROG             zgig
TD                189390
SOLVENT             CDCl3
NS                      64
DS                       2
SWH            37878.789 Hz
FIDRES             0.400008 Hz
AQ              2.4999480 sec
RG                    2050
DW                13.200 usec
DE                  6.50 usec
TE                 296.3 K
D1           4.00000000 sec
D11          0.03000000 sec
TD0                     1
SFO1          151.0250289 MHz
NUC1                   13C
P1                   8.50 usec
PLW1          57.84899902 W
SFO2          600.5530028 MHz
NUC2                   1H
CPDPRG[2         waltz16
PCPD2              100.00 usec
PLW2          13.17399979 W
PLW12          0.36982819 W

F2 - Processing parameters
SI                 524288
SF            151.0084010 MHz
WDW                    no
SSB                     0
LB                      0 Hz
GB                      0
PC                   1.40
```

1*N*-methylnaphthotriazine **1a** – **^{1}H NMR** (600 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):



4. Crystallographic data

Table S1. Crystallographic data for all crystallized materials.

	2a+LiI	**2d**	**2i**
Empirical formula	$6(C_{13}H_{15}N_3)\cdot I_8Li_8$	$C_{15}H_{19}N_3$	$C_{18}H_{17}N_3$
Formula weight	2350.39	241.33	275.34
Temperature (K)	200.15	200.15	200.15
Wavelength (Å)	0.71073	0.71073	0.71073
Color	Colorless	Colorless	Colorless
Crystal system	Trigonal	Triclinic	Orthorhombic
Space group	R-3	P-1	$P2_12_12_1$
a (Å)	17.321(3)	7.8040(16)	9.832(3)
b, (Å)	17.321(3)	8.7759(18)	11.907(4)
c (Å)	25.467(5)	11.326(2)	12.610(4)
α (deg)	90	76.189(2)	90
β (deg)	90	73.494(3)	90
γ (deg)	120	64.373(4)	90
Volume ($Å^3$)	6617(3)	664.5(2)	1476.3(8)
Z	3	2	4
Calculated density (g/cm^3)	1.769	1.206	1.239
Absorption coefficient (mm^{-1})	2.864	0.073	0.075
F(000)	3396.0	260.0	584.0
Crystal size (mm)	0.21 × 0.18 × 0.18	0.21 × 0.18 × 0.18	0.33 x 0.12 x 0.09
2θ range (deg)	3.152 to 50.128	5.196 to 50.464	4.704 to 50.146
No. of measured reflections	6203	5202	9170
No. of independent reflections	2591	2392	2601
R_{int}	0.0768	0.0281	0.0509
Completeness (%)	98.9	99.4	99.0
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Data/restraints/parameters	2591 / 0 / 172	2392 / 0 / 167	2601 / 203 / 192
Goodness of fit on F^2	0.875	0.966	1.083
R_1, wR_2 ($I > 2\sigma(I)$)	0.0387, 0.0616	0.0406, 0.0954	0.0612, 0.1250
R_1, wR_2 (all data)	0.0741, 0.0685	0.0789, 0.1137	0.1291, 0.1544
Largest diff. peak and hole $eÅ^{-3}$	0.77 / -1.21	0.14 / -0.21	0.34 / -0.20
Diffractometer	Bruker APEX II	Bruker APEX II	Bruker APEX II

	2p
Empirical formula	$C_{24}H_{21}N_3$
Formula weight	351.44
Temperature (K)	200.15
Wavelength (Å)	0.71073
Color	Colorless
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	12.4541(11)
b, (Å)	14.0752(12)
c (Å)	11.4174(10)
α (deg)	90
β (deg)	113.841(2)
γ (deg)	90
Volume ($Å^3$)	1830.6(3)
Z	4
Calculated density (g/cm^3)	1.275
Absorption coefficient (mm^{-1})	0.076
F(000)	744.0
Crystal size (mm)	0.24 × 0.21 × 0.21
2θ range (deg)	3.576 to 50.2
No. of measured reflections	18653
No. of independent reflections	3244
R_{int}	0.1134
Completeness (%)	99.6
Absorption correction	Multi-scan
Data/restraints/parameters	3244 / 0 / 246
Goodness of fit on F^2	1.013
R_1, wR_2 ($I > 2\sigma(I)$)	0.0642, 0.1295
R_1, wR_2 (all data)	0.1209, 0.1556
Largest diff. peak and hole $eÅ^{-3}$	0.17 / -0.31
Diffractometer	Bruker APEX II

Crystal structure determination of **2a**+LiI**, 2d, 2i** and **2p**

The single-crystal materials were immersed in Paratone–N oil. The crystals were mounted on a Bruker APEX II diffractometer. The structures: **2a**+LiI, **2d**, **2i** and **2p** were measured at 200K. Data collection was performed using monochromated Mo Kα radiation, λ=0.71073 Å, using φ and ω scans to cover the Ewald sphere. Accurate cell parameters were obtained with the amount of indicated reflections. Using Olex2[4], the structure was solved with the olex2.solve[5] structure solution program using Charge Flipping and refined with the SHELXL[6] refinement package using Least Squares minimization. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Software used for molecular graphics: Mercury 2020.3.0.[7]

Additional information

Accession code: The X-ray crystallographic coordinates for structures **2a**+LiI, **2d**, **2i** and **2p** reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers: 2221687-2221690.

These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

5. References

1. B. D. Shepherd, D. R. Powell and R. West, Synthesis, geometrical isomerism, and crystal structure of a highly hindered disilene, *Organometallics*, 1989, **8**, 2664-2669.
2. S. Fernandez, M. A. Ganiek, M. Karpacheva, F. C. Hanusch, S. Reuter, T. Bein, F. Auras and P. Knochel, Synthesis and Reactivity of Triazaphenanthrenes, *Org. Lett.*, 2016, **18**, 3158-3161.
3. A. Pogoreltsev, Y. Tulchinsky, N. Fridman and M. Gandelman, Nitrogen Lewis Acids, *J. Am. Chem. Soc.*, 2017, **139**, 4062-4067.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
5. L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment - Olex2 dissected, *Acta Crystallogr. A*, 2015, **71**, 59-75.
6. G. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr. C*, 2015, **71**, 3-8.
7. Mercury Software from CCDC: http://www.ccdc.cam.ac.uk/Solutions/CSDSystem/Pages/Mercury.aspx.