Supporting Information

Iron-Catalyzed Ligand-Free Diazidation of Alkenes Controlled by the Ratio of TBHP to $TMSN_3$

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1. General considerations.

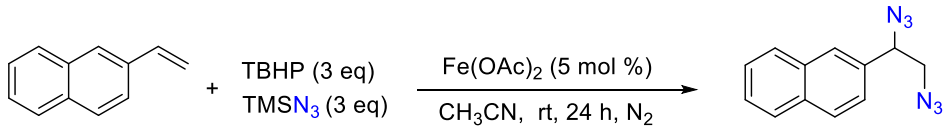
All commercially available compounds were purchased from Aldrich, Alfa Aesar or Adamas. NMR spectra were recorded on Varian Inova 400 and Agilent 400 (600 MHz for ^{1}H, 150 MHz for ^{13}C) spectrometer. The chemical shifts (δ) are given in parts per million relative to $CDCl_3$ (7.26 ppm for ^{1}H) and $CDCl_3$ (77.0 ppm for ^{13}C). Flash column chromatography was performed on silica gel (particle size 200-300 mesh, purchased from Canada) and eluted with EA/PE. Solvent was purified according to the procedure from the book named —Purification of Laboratory Chemicals.

2. Optimization of the reaction conditions

2.1 Optimization of oxidant.

These reactions were performed according to the general procedure on a 0.1 mmol scale and the results were listed in Table S1.

Table S1. Optimization of oxidant[a, b]



Entry	Oxidant	Yield
1	TBHP	trace
2	TBPB	trace
3	DTPB	n.d.
4	BPO	trace
5	$K_2S_2O_8$	n.d.
6	$PhI(OAc)_2$	trace

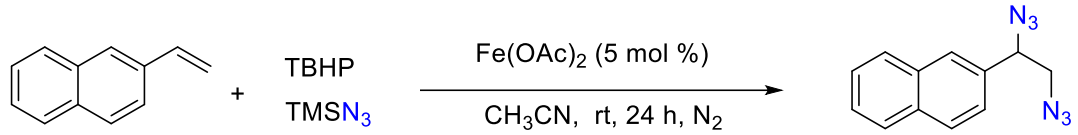
[a] All reactions were run on 0.1 mmol scale in CH_3CN (1 mL) at room temperature under nitrogen atmosphere. [b] Isolated yield.

2.2 Optimization of the ratio of $^{t}BuOOH$ to $TMSN_3$

These reactions were performed according to the general procedure on a 0.1 mmol

scale and the results were listed in Table S2.

Table S2. Optimization of the ratio of ^{t}BuOOH to $TMSN_3$[a, b]



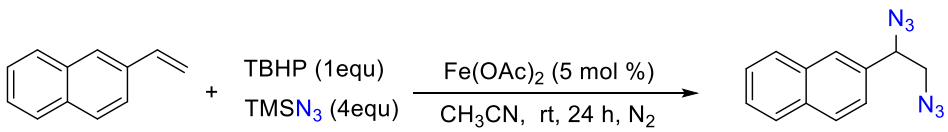
Entry	TBHP:$TMSN_3$	Yield
1	2 :3	36%
2	1 : 3	70%
3	3 : 3	trace
4	4 : 3	trace
5	1 : 2	30%
6	1 : 4	80%

[a] All reactions were run on 0.1 mmol scale in CH_3CN (1 mL) at room temperature under nitrogen atmosphere. [b] Isolated yield.

2.3 Optimization of solvents.

These reactions were performed according to the general procedure on a 0.1 mmol scale and the results were listed in Table S3.

Table S3. Optimization of solvents [a, b]



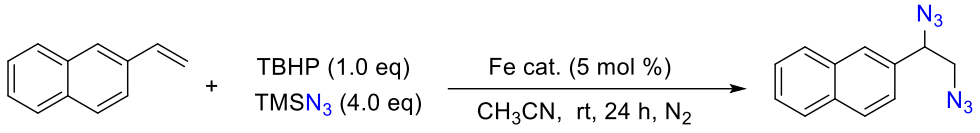
Entry	Solvent	Yield
1	DCE	21%
2	DCM	18%
3	CH_3CN	80%
4	$PhCF_3$	trace
5	PhCl	trace
6	CH_3Cl_3	trace
7	MTBE	trace
8	DMF	trace
9	CH_3CN(0.5mL)	61%
10	CH_3CN(2mL)	65%

[a] All reactions were run on 0.1 mmol scale in solvent (1 mL) at room temperature under nitrogen atmosphere. [b] Isolated yield.

2.4 Optimization of iron catalyst.

These reactions were performed according to the general procedure on a 0.1 mmol scale and the results were listed in Table S4.

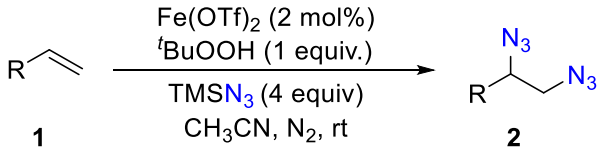
Table S4. Optimization of iron catalyst [a, b]



Entry	Fe cat.	Yield
1	\	0 %
2	$Fe(OTf)_2$	88%
3	$FeCl_3$	86%
4	$FeCl_2$	70%
5	FeF_3	30%
6	$Fe(OAC)_2$	80%
7	$Fe(OTf)_2$ (1 mol%)	60%
8	$Fe(OTf)_2$ (2 mol%)	88%

[a] All reactions were run on 0.1 mmol scale in solvent (1 mL) at room temperature under nitrogen atmosphere. [b] Isolated yield.

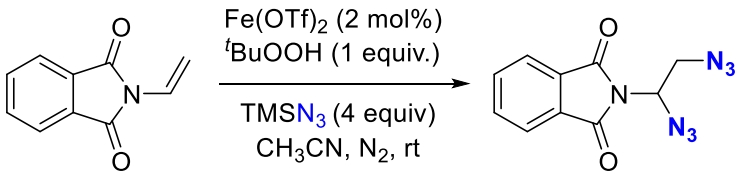
3. General experimental procedures for the diazidition of alkenes



1 **2**

In a dried sealed tube, $Fe(OTf)_2$ (1.4 mg, 0.004 mmol, 2 mol%) was dissolved in CH_3CN (2 mL) under the atmosphere of nitrogen. Then substrates **1** (0.2 mmol, 1.0 equiv.), ^{t}BuOOH (0.2 mmol, 5.5 M in decane, 1 equiv.) and $TMSN_3$ (92 mg, 0.8 mmol, 4.0 equiv.) were added sequentially. The mixture was stirred at room temperature for 24 h. After the reaction was completed, the product was purified by flash column chromatography on silica gel with gradient of petroleum ether/ethyl acetate.

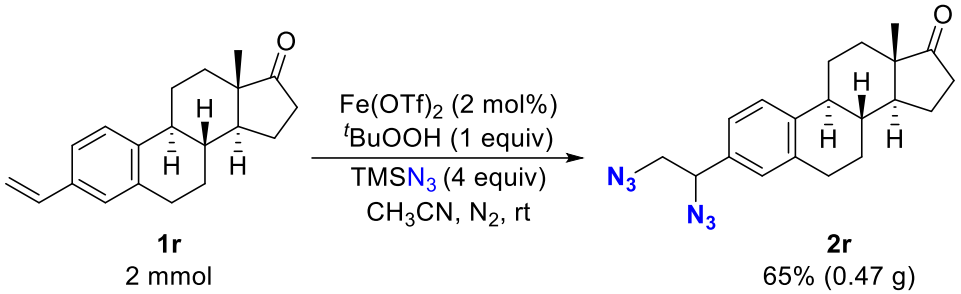
4. Scale-up reaction



1t
6 mmol

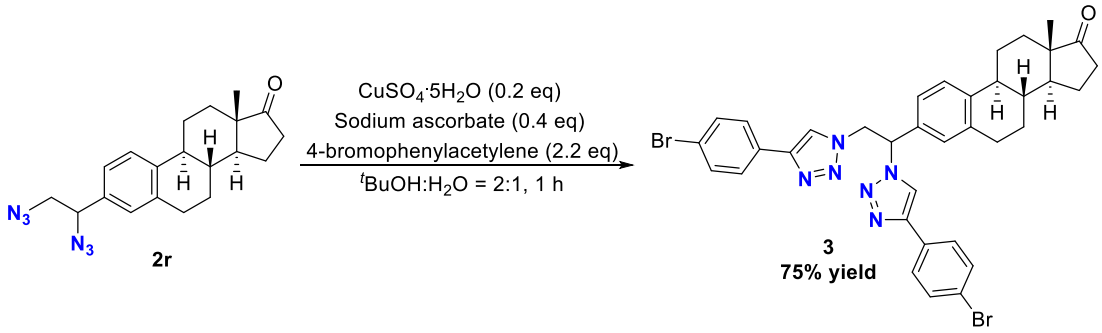
2t
82% (1.26 g)

To a 250 mL double-necked bottle, $Fe(OTf)_2$ (42.4 mg, 0.12 mmol, 2 mol%) was dissolved in CH_3CN (60 mL) under the atmosphere of nitrogen. Then substrates **1t** (1.04 g, 6 mmol, 1.0 equiv.), ^{t}BuOOH (6 mmol, 5.5 M in decane, 1 equiv.) and $TMSN_3$ (3.2 mL, 24 mmol, 4.0 equiv.) were added sequentially. The mixture was stirred at room temperature for 24 h. After the reaction was completed, the product was purified by flash column chromatography on silica gel with gradient of petroleum ether/ethyl acetate to afford 1.26 g product **2t** in 82% yield.



To a 50 mL sealed tube, $Fe(OTf)_2$ (14.2 mg, 0.04 mmol, 2 mol%) was dissolved in CH_3CN (20 mL) under the atmosphere of nitrogen. Then substrates **1r** (0.56 g, 2 mmol, 1.0 equiv.), ^{t}BuOOH (2 mmol, 5.5 M in decane, 1 equiv.) and $TMSN_3$ (1.04 mL, 8 mmol, 4.0 equiv.) were added sequentially. The mixture was stirred at room temperature for 24 h. After the reaction was completed, the product was purified by flash column chromatography on silica gel with gradient of petroleum ether/ethyl acetate to afford 0.47 g product **2r** in 65% yield.

5. Further transformations of products

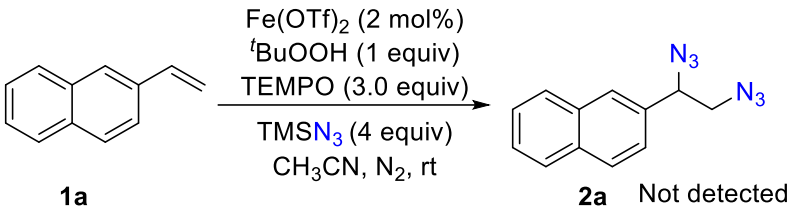


Alkyl diazide **2r** (72.8 mg, 0.2 mmol) was dissolved in a 2:1 mixture of ^{t}BuOH and water (0.6 mL), 4-Bromophenylacetylene (79.2 mg, 0.44 mmol), $CuSO_4 \cdot 5H_2O$ (10.0 mg, 0.04 mol), sodium ascorbate (15.9 mg, 0.08 mmol) were added and the solution was stirred at room temperature for 1H. The reaction mixture was diluted with water

(20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated. The resulting solid was washed with ether (2 × 3 mL) and bistriazole **3** was isolated as a white solid (108.6 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 5.4 Hz, 2H), 7.60 (dd, J = 15.6, 8.4 Hz, 4H), 7.49 (t, J = 6.6 Hz, 4H), 7.34 (dd, J = 8.4, 4.2Hz, 1H), 7.18 (t, J = 8.4 Hz, 1H), 7.13 (d, J = 12.6 Hz, 1H), 6.11 (dd, J = 9.6, 4.2Hz, 1H), 5.65 (dd, J = 14.4, 10.2Hz, 1H), 5.14 (dd, J = 14.4, 4.2Hz, 1H), 2.91-2.88 (m, 2H), 2.53 (dd, J = 18.6, 8.4 Hz, 1H), 2.41-1.96 (m, 7H), 1.62-1.40 (m, 5H), 0.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.5, 147.1, 146.6, 141.6 (d, *J* = 5.8 Hz), 138.0 (d, *J* = 3.4 Hz), 138.0 (d, J = 3.4 Hz), 132.8, 132.0, 131.9, 129.0, 128.8, 127.3 (d, *J* = 8.2 Hz), 127.2, 127.1, 126.5 (d, *J* = 4.6 Hz), 124.0 (d, *J* = 7.0 Hz), 122.4, 122.2, 121.4, 120.9, 65.1 (d, *J* = 5.6 Hz), 53.3 (d, *J* = 2.2 Hz), 50.4, 47.8, 44.3, 37.8, 35.8, 31.5, 29.3 (d, *J* = 4.8 Hz), 26.2 (d, *J* = 2.2 Hz), 25.6, 21.5, 13.8; HRMS (EI) m/z $[M+H]^+$ calculated for $C_{36}H_{35}Br_2N_6O^+$: 725.1234, found: 725.1238.

6. Mechanistic study

6.1 With TEMPO as Radical Scavenger

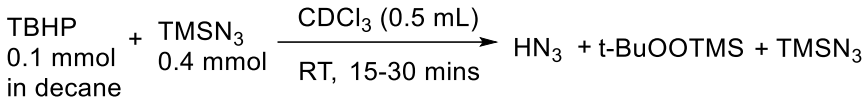


In a dried sealed tube, $Fe(OTf)_2$ (1.4 mg, 0.004 mmol, 2 mol%) was dissolved in CH_3CN (2 mL) under the atmosphere of nitrogen. Then substrates **1a** (0.2 mmol, 1.0 equiv.), ^{t}BuOOH (0.2 mmol, 5.5 M in decane, 1 equiv.), $TMSN_3$ (92 mg, 0.4 mmol, 4.0 equiv.) and TEMPO (0.6 mmol) were added sequentially. The mixture was stirred at room temperature for 24 h. After the reaction was completed, solvent was evaporated under reduced pressure. The mixture was analyzed by ^{1}H-NMR with CH_2Br_2 (0.1 mmol) as internal standard.

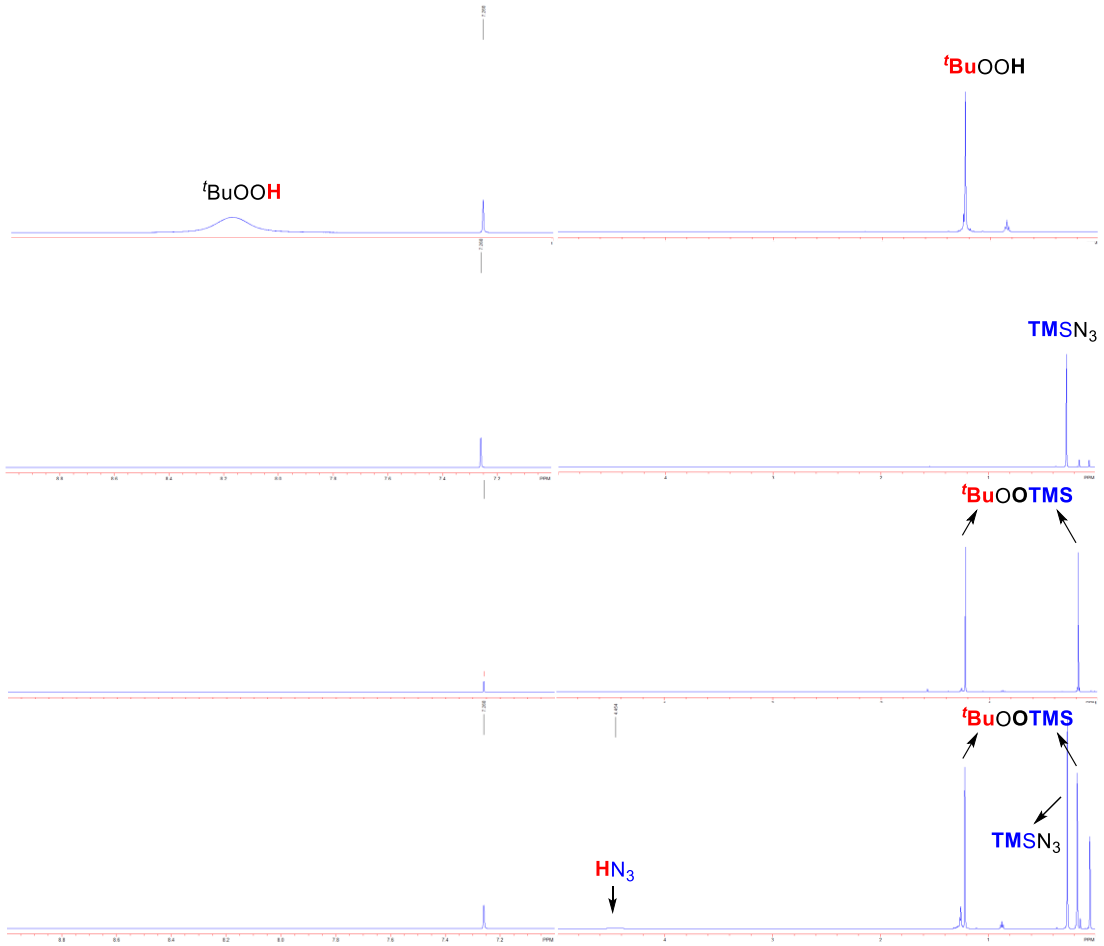
6.2 Control experiments between $TMSN_3$ and TBHP

To a dried sealed tube, **TMSCN** (0.4 mmol) was dissolved in anhydrous and oxygen-

free $CDCl_3$ (0.5 mL) under the atmosphere of argon, then TBHP (0.1 mmol, 1.0 equiv, 5.5 mol/L in decane) was added to the mixture solvent. The reaction was stirred at room temperature for 15 to 30 mins. After that, the reaction result was identified through NMR.



Through the reaction result, we drawn a preliminary conclusion: TBHP would react with $TMSN_3$ to release and produce the real oxidant ^{t}BuOOTMS and HN_3. It reasonably explained when we use equivalent TBHP (in decane) and $TMSN_3$ for our reaction just got trace desired product, due to the disappearance of $TMSN_3$ in the reaction. And the result also further explained that ^{t}BuOOH to TMSN3 ratio was essential for the diazidation reaction



6.3 Experiments to confirm intermediat

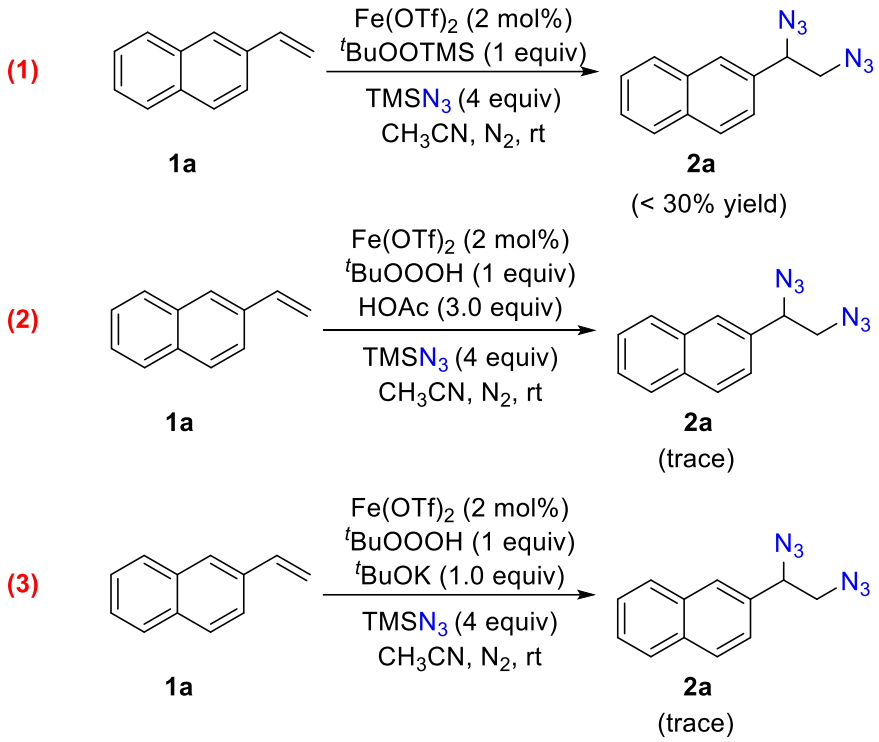
These reactions were conducted following general procedure in a 0.1 mmol scale with **1a** as limiting reagent.

Reaction (1): In a dried sealed tube, $Fe(OTf)_2$ (1.4 mg, 0.004 mmol, 2 mol%) was dissolved in CH_3CN (2 mL) under the atmosphere of nitrogen. Then substrates **1a** (0.2 mmol, 1.0 equiv.), ^{t}BuOOTMS (32.4 mg, 0.2 mmol, 1 equiv.) and $TMSN_3$ (92 mg, 0.8 mmol, 4.0 equiv.) were added sequentially. The mixture was stirred at room temperature for 24 h. After the reaction was completed, solvent was evaporated under reduced pressure. The mixture was analyzed by ^{1}H-NMR with CH_2Br_2 (0.1 mmol) as internal standard.

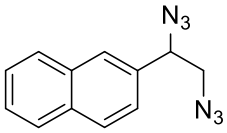
Reaction (2): In a dried sealed tube, $Fe(OTf)_2$ (1.4 mg, 0.004 mmol, 2 mol%) was dissolved in CH_3CN (2 mL) under the atmosphere of nitrogen. Then substrates **1a** (0.2 mmol, 1.0 equiv.), ^{t}BuOOH (0.2 mmol, 5.5 M in decane, 1 equiv.), HOAc (36.2 mg, 3.0 equiv.) and $TMSN_3$ (92 mg, 0.8 mmol, 4.0 equiv.) were added sequentially. The mixture was stirred at room temperature for 24 h. After the reaction was completed, solvent was evaporated under reduced pressure. The mixture was analyzed by ^{1}H-NMR with CH_2Br_2 (0.1 mmol) as internal standard.

Reaction (3): In a dried sealed tube, $Fe(OTf)_2$ (1.4 mg, 0.004 mmol, 2 mol%) was dissolved in CH_3CN (2 mL) under the atmosphere of nitrogen. Then ^{t}BuOOH (0.2 mmol, 5.5 M in decane, 1 equiv.) and $TMSN_3$ (0.8 mmol, 4.0 equiv.) were added sequentially. After 10 minutes, substrates **1a** (0.2 mmol, 1.0 equiv.) and ^{t}BuOK (22.4 mg, 1.0 equiv.) were added to the reaction mixture. The mixture was stirred at room temperature for 24 h. After the reaction was completed, solvent was evaporated under reduced pressure. The mixture was analyzed by ^{1}H-NMR with CH_2Br_2 (0.1 mmol) as internal standard.

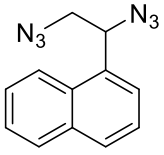
On the basis of above reaction result, we can confirm ^{t}BuOOTMS was the main reaction intermediates, $TMSN_3$ and HN_3 are necessary for the reaction.



7. Analytical data for compounds

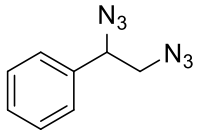


2-(1,2-diazidoethyl)naphthalene (2a): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (41.9 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, J = 8.4 Hz, 1H), 7.89-7.84 (m, 2H), 7.81 (s, 1H), 7.56-7.49 (m, 2H), 7.43 (dd, J = 8.4, 1.8 Hz, 1H), 4.85 (dd, J = 8.4, 4.8 Hz, 1H), 3.64-3.50 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 133.7, 133.5, 133.2, 129.2, 128.1, 127.8, 126.8, 126.6, 124.0, 65.8, 55.9; HRMS (EI) m/z $[M+H-N_4]^+$ calculated for $C_{12}H_{11}N_2^+$: 183.0917, found: 183.0916.

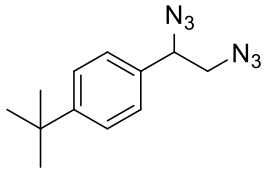


1-(1,2-diazidoethyl)naphthalene (2b): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (33.8 mg, 71%). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz,

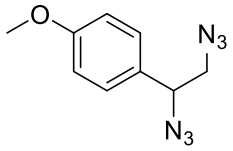
1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.67-7.47 (m, 4H), 5.47 (dd, J = 7.8, 4.8 Hz, 1H), 3.70-3.60 (m, 2H); ^{13}C-NMR (150MHz, $CDCl_3$) δ 134.0, 131.9, 130.3, 129.6, 129.4, 127.0, 126.2, 125.4, 125.0, 122.3, 62.8, 55.6; HRMS (EI) m/z $[M+H]^+$ calculated for $C_{12}H_{11}N_6^+$: 239.1038, found:239.1040.



(1,2-diazidoethyl)benzene (2c): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (28.2 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (t, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 8.4 Hz, 1H), 7.34 (t, *J* = 6.6 Hz, 2H), 4.68 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.55-3.40 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.4, 129.1, 129.1, 127.0, 65.5, 56.0; HRMS (EI) m/z $[M+H]^+$ calculated for $C_8H_9N_6^+$: 189.0883, found: 189.0884.

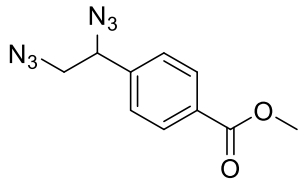


1-(tert-butyl)-4-(1,2-diazidoethyl)benzene (2d): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (39.0 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.65 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.55-3.37 (m, 2H), 1.32 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.2, 133.3, 126.7, 126.0, 65.3, 56.0, 34.7, 31.3; HRMS (EI) m/z $[M+H-N_4]^+$ calculated for $C_{12}H_{17}N_2^+$: 189.1386, found: 189.1385.

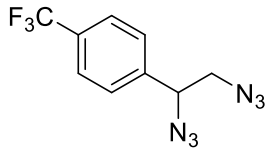


1-(1,2-diazidoethyl)-4-methoxybenzene (2e): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (36.6 mg, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 9 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 4.62 (dd, *J* = 8.4, 5.4 Hz, 1H), 3.82 (s, 3H), 3.51-3.36 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 128.3, 114.4, 65.00,

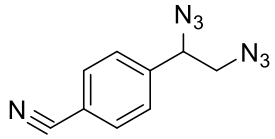
55.8, 55.3; HRMS (EI) m/z $[M+H]^+$ calculated for $C_9H_{11}N_6O^+$: 219.0989, found: 219.0986.



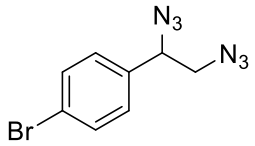
methyl 4-(1,2-diazidoethyl)benzoate (2f): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (44.3 mg, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 4.73 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.91 (s, 3H), 3.55-3.43 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 141.3, 130.8, 130.4, 127.0, 65.1, 55.9, 52.3; HRMS (EI) m/z $[M+H]^+$ calculated for $C_{10}H_{11}N_6O_2^+$: 247.0938, found: 247.0936.



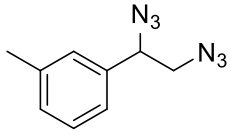
1-(1,2-diazidoethyl)-4-(trifluoromethyl)benzene (2g): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (47.1 mg, 92 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 4.75 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.55-3.42 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.4, 131.2 (q, *J* = 32.4 Hz), 127.4, 126.1 (q, *J* = 3.3 Hz), 123.8 (q, *J* = 270.7 Hz), 64.9, 55.9; HRMS (EI) m/z $[M+H]^+$ calculated for $C_9H_8F_3N_6^+$: 257.0757, found: 257.0758.



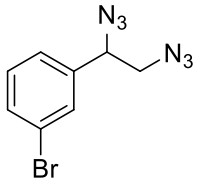
4-(1,2-diazidoethyl)benzonitrile (2h): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (30.2 mg, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 4.74 (dd, *J* = 7.2, 5.4 Hz, 1H), 3.55-3.42 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.7, 132.9, 127.8, 118.2, 113.0, 64.77, 55.8; HRMS (EI) m/z $[M+H]^+$ calculated for $C_9H_8N_7^+$: 214.0836, found: 214.0835.



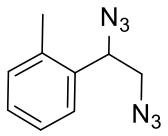
1-bromo-4-(1,2-diazidoethyl)benzene (2i): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (40.0 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.64 (dd, *J* =8.4, 5.4 Hz, 1H), 3.51-3.40 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.4, 132.3, 128.6, 123.1, 64.9, 55.8; HRMS (EI) m/z $[M+H-N_4]^+$ calculated for $C_8H_8BrN_2^+$: 210.9865, found: 210.9865.



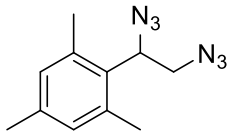
1-(1,2-diazidoethyl)-3-methylbenzene (2j): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (31.8 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.2Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.13(d, *J* = 8.4 Hz, 2H), 4.64 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.54-3.40 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.4, 134.5, 131.1, 128.8, 126.8, 126.5, 62.1, 55.2, 19.2; HRMS (EI) m/z $[M+H]^+$ calculated for $C_9H_{11}N_6^+$: 203.1040, found: 203.1038.



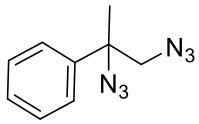
1-bromo-3-(1,2-diazidoethyl)benzene (2k): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (46.8 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60-7.45 (m, 2H), 7.32-7.24 (m, 2H), 4.63 (dd, *J* =7.8, 4.8 Hz, 1H), 3.52-3.40 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.7, 132.2, 130.7, 130.1, 125.5, 123.2, 64.9, 55.9; HRMS (EI) m/z $[M+H-N_4]^+$ calculated for $C_8H_8BrN_2^+$: 210.9865, found: 210.9865.



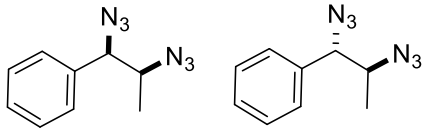
1-(1,2-diazidoethyl)-2-methylbenzene (2l): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (32.7 mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.35 (m, 1H), 7.28-7.20 (m, 3H), 4.92 (dd, *J* = 9, 4.2Hz, 1H), 3.52-3.37 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.0, 136.3, 129.9, 129.0, 127.6, 124.0, 65.6, 56.0, 21.5; HRMS (EI) m/z $[M+H]^+$ calculated for $C_9H_{11}N_6^+$: 203.1040, found: 203.1040.



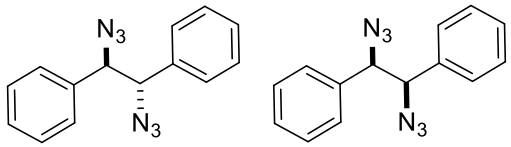
2-(1,2-diazidoethyl)-1,3,5-trimethylbenzene (2m): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (42.3 mg, 92%).^{1}H NMR (600 MHz, $CDCl_3$) δ 6.88 (s, 2H), 5.18 (d, *J* = 3.6 Hz, 1H), 3.70 (t, *J* = 10.8 Hz, 1H), 3.35 (d, *J* = 9.0 Hz, 1H), 2.41 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.3, 136.7, 130.6, 129.1, 62.1, 53.4, 20.8, 20.7; HRMS (EI) m/z $[M+H]^+$ calculated for $C_{11}H_{15}N_6^+$: 231.1353, found: 231.1352.



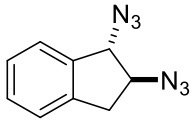
(1,2-diazidopropan-2-yl)benzene (2n): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (24.6 mg, 61%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50-7.39 (m, 4 H), 7.35 (d, *J* = 7.2Hz, 1H), 3.52-3.38 (m, 2 H), 1.77 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.6, 128.9, 128.3, 125.8, 66.6, 61.0, 22.3; HRMS (EI) m/z $[M+Na]^+$ calculated for $C_9H_{10}N_6Na^+$: 225.0859, found: 225.0857.



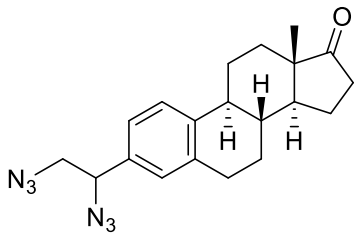
(1,2-diazidopropyl)benzene (2o): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (33.1 mg, 82%) (dr = 1.3:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46-7.40 (m, 3 H), 7.40-7.30 (m, 2H), 4.53 (d, *J* = 6.0 Hz, 0.57H),4.37 (d, *J* = 7.8 Hz, 0.43H), 3.72-3.61 (m, 1H), 1.26 (d, *J* = 6.6 Hz, 1.85H), 1.11 (d, *J* = 6.6 Hz, 1.35H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.2, 136.0, 128.9, 128.8, 128.8, 127.5, 70.7, 69.6, 61.5, 61.0, 16.7, 15.0; HRMS (EI) m/z $[M+H]^+$ calculated for $C_9H_{11}N_6^+$: 203.1040, found: 203.1036.



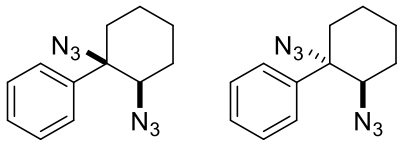
1,2-diazido-1,2-diphenylethane (2p): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (49.1 mg, 93%) (dr = 2:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.32 (m, 2H), 7.30-7.04 (m, 8H), 4.68 (s, 0.66H), 4.63 (s, 1.34H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.9, 135.8, 129.0, 128.8, 128.7, 128.6, 128.0, 127.7, 70.8, 69.7; HRMS (EI) m/z $[M+H]^+$ calculated for $C_{14}H_{13}N_6^+$: 265.1196, found: 265.1194.



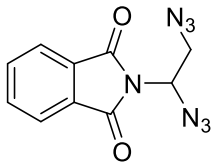
1,2-diazido-2,3-dihydro-1H-indene (2q): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (35.2 mg, 88%) (dr > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.6 Hz, 1H), 7.36-7.29 (m, 2H), 7.26 (d, *J* = 6.6 Hz, 1H), 4.77 (d, *J* = 5.4 Hz, 1H), 4.17 (q, *J* = 6.6 Hz, 1H), 3.37 (dd, *J* = 16.2, 6.6 Hz, 1H), 2.96 (dd, *J* = 15.6, 6.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1, 137.8, 129.5, 127.8, 125.2, 124.6, 70.3, 67.7, 36.1; HRMS (EI) m/z $[M+H]^+$ calculated for $C_9H_9N_6^+$: 201.0883, found: 201.0887.



(8R,9S,13S,14S)-3-(1,2-diazidoethyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (2r): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (47.3 mg, 65%). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.05(s, 1H), 4.61 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.51 (dd, *J* = 12.6, 8.6 Hz, 1H), 3.44 (dd, *J* =12.6, 4.8 Hz, 1H), 2.96-2.90 (m, 2H), 2.53 (dd, *J* = 19.2, 8.4 Hz, 1H), 2.45-2.40 (m, 1H), 2.34-2.28 (m, 1H), 2.20-2.11 (m,1H), 2.10-2.00 (m, 2H), 2.00-1.94 (m, 1H), 1.68-1.42 (m, 6H), 0.92 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ 220.8, 140.8, 137.4, 133.7, 127.6, 127.5, 126.1, 124.3,, 65.3, 55.9, 50.5, 48.0, 44.4, 38.0, 35.8, 31.6, 29.4, 26.4, 25.6, 21.6, 13.8; HRMS (EI) m/z $[M+H]^+$ calculated for $C_{20}H_{25}N_6O^+$: 365.2084, found: 365.2083.

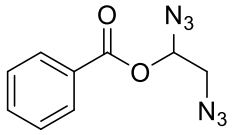


(1,2-diazidocyclohexyl)benzene (2s): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as white solid (32.9 mg, 68%) (dr = 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51-7.41 (m, 4H), 7.39-7.32 (m, 1H), 3.85-3.55 (m, 1H), 2.40-2.33 (m, 0.8H), 2.14-2.06 (m, 1H), 2.05-1.89 (m, 1.82H), 1.87-1.81 (m, 0.8H), 1.80-1.65 (m, 2H), 1.62-1.50 (m, 1.6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.5, 141.0, 128.9, 128.8, 128.4, 128.0, 126.5, 125.8, 69.9, 67.7, 66.0, 65.2, 36.3, 27.5, 27.4, 26.5, 24.2, 21.3, 21.1, 19.3. HRMS (EI) m/z $[M+H]^+$ calculated for $C_{12}H_{15}N_6^+$: 243.1353, found: 243.1353.

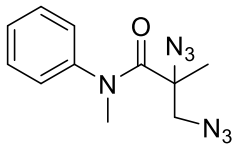


2-(1,2-diazidoethyl)isoindoline-1,3-dione (2t): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title

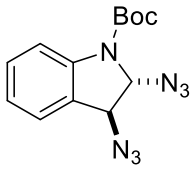
compound as white solid (39.1 mg, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95-7.89 (m, 2H), 7.83-7.78 (m, 2H), 5.68 (t, *J* = 7.2 Hz, 1H), 4.07-3.97 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.0, 134.9, 131.3, 124.1, 65.2, 50.6. HRMS (EI) m/z $[M+H-N_4]^+$ calculated for $C_{10}H_8N_3O_2^+$: 202.0611, found: 202.0610.



1,2-diazidoethyl benzoate (2u): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as yellow oil (32.5 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 6.25 (t, *J* = 4.8 Hz, 1H), 3.58-3.50 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 134.1, 130.1, 128.7, 128.4, 83.9, 52.9; HRMS (EI) m/z $[M+H]^+$ calculated for $C_9H_9N_6O_2^+$: 233.0781, found: 233.0786.

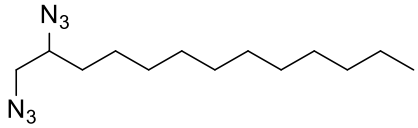


2,3-diazido-N,2-dimethyl-N-phenylpropanamide (2v): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (37.4 mg, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.2Hz, 1H), 7.30-7.24 (m, 2H), 3.67 (d, *J* = 12.6Hz, 1H), 3.43 (d, *J* = 12.6Hz, 1H), 3.28 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 143.4, 129.7, 128.2, 127.3, 67.0, 59.0, 41.1, 21.4; HRMS (EI) m/z $[M+H]^+$ calculated for $C_{11}H_{14}N_7O^+$: 260.1254, found: 260.1253.

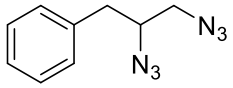


tert-butyl 2,3-diazidoindoline-1-carboxylate (2w): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (33.1 mg, 55%) (dr > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.42 (t, *J* = 7.8Hz, 1H), 7.36 (d, *J* = 7.8Hz, 1H), 7.13 (d, *J* = 7.8Hz, 1H), 5.66 (s, 1H), 4.52 (s, 1H), 1.62 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ

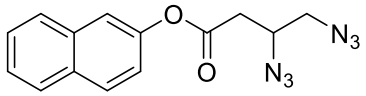
150.8, 141.6, 131.2, 125.4, 124.8, 123.6, 116.0, 83.5, 80.1, 65.3, 28.2; HRMS (EI) m/z $[M+H-N_4]^+$ calculated for $C_{13}H_{16}N_3O_2^+$: 246.1237, found: 246.1235.



1,2-diazidotridecane (2x): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (33.1 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.49-3.49 (m, 1H), 3.40-3.27 (m, 2H), 1.55 (q, *J* = 7.8 Hz, 2H), 1.36-1.20 (m, 18 H), 0.88 (t, *J* = 7.2Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 62.1, 54.8, 31.9, 31.8, 29.7, 29.6, 29.5, 29.4, 29.3, 25.9, 22.7, 14.1; HRMS (EI) m/z $[M+H-N_4]^+$ calculated for $C_{13}H_{27}N_2^+$: 211.2169, found: 211.2168.

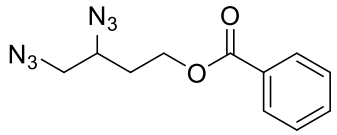


(2,3-diazidopropyl)benzene (2y): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (24.6 mg, 61%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.2Hz, 2H), 7.28 (t, *J* = 7.2Hz, 1H), 7.22 (d, *J* = 7.2Hz, 2H), 3.75-3.69 (m, 1H), 3.41 (dd, *J* = 12.6, 4.2Hz, 1H), 3.31 (dd, *J* = 12.6, 6.6 Hz, 1H), 2.88 (d, *J* = 7.2Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.3, 129.3, 128.8, 127.2, 62.9, 53.9, 38.0; HRMS (EI) m/z $[M+H]^+$ calculated for $C_9H_{11}N_6^+$: 203.1040, found: 203.1039.

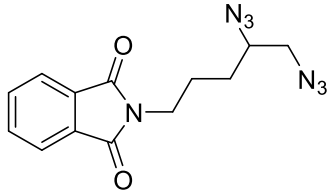


naphthalen-2-yl 3,4-diazidobutanoate (2z): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as pale-yellow liquid (29.6 mg, 50%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.54-7.46 (m, 2H), 7.26 (dd, J = 8.4, 2.4 Hz, 1H), 4.20-4.10 (m, 1H), 3.58-3.50 (m, 2H), 2.94-2.82 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 147.9, 133.7, 131.6, 129.7, 127.8, 127.7, 126.8, 126.0, 120.7,118.5, 58.05, 54.2, 36.9; HRMS (EI) m/z $[M+H]^+$ calculated for

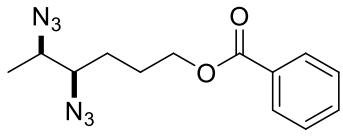
$C_{14}H_{13}N_6^+$: 297.1095, found: 297.1096.



3,4-diazidobutyl benzoate (2aa): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as yellow oil (31.7 mg, 61%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 4.54-4.40 (m, 2H), 3.78-3.68 (m, 1H), 3.51 (dd, J = 12.6, 4.2 Hz, 1H), 3.44 (dd, J = 12.6, 7.2 Hz, 1H), 2.10-1.88 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 133.3, 129.8, 129.6, 128.5, 61.1, 59.2, 54.9, 31.1; HRMS (EI) m/z $[M+H]^+$ calculated for $C_{11}H_{13}N_6O_2^+$: 261.1095, found: 261.1094.

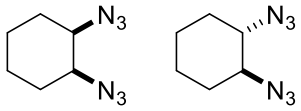


2-(4,5-diazidopentyl)isoindoline-1,3-dione (2ab): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as yellow oil (34.7 mg, 58%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87-7.82 (m, 2H), 7.75-7.70 (m, 2H), 3.72 (t, *J* = 7.2 Hz, 2H), 3.57-3.53 (m, 1H), 3.41 (dd, J = 12.6, 3.6 Hz, 1H), 3.40 (dd, J = 12.6, 7.2Hz, 1H), 1.92-1.83 (m, 1H), 1.82-1.72 (m, 1H) 1.60-1.51 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 134.1, 132.0, 123.3, 61.5, 54.8, 37.2, 29.1, 25.1. HRMS (EI) m/z $[M+H-N_4]^+$ calculated for $C_{13}H_{14}N_3O_2^+$: 244.1081, found: 244.1079.



4,5-diazidohexyl benzoate (2ac): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as yellow oil (30.1 mg, 52%) (dr = 17:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.2Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 4.41-4.32 (m, 2H), 3.63-3.55 (m, 1H), 3.41-3.35 (m, 1H), 2.06-1.96 (m, 1H), 1.90-1.81 (m, 1H), 1.78-1.70 (m, 1H), 1.67-1.60 (m, 1H), 1.34 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6, 133.1, 130.1,

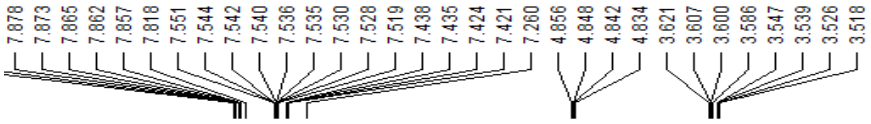
129.6, 128.4, 66.0, 64.2, 60.3, 27.5, 25.7, 14.8; HRMS (EI) m/z $[M+H]^+$ calculated for $C_{13}H_{17}N_6O_2^+$: 289.1408, found: 289.1409.

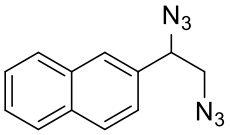


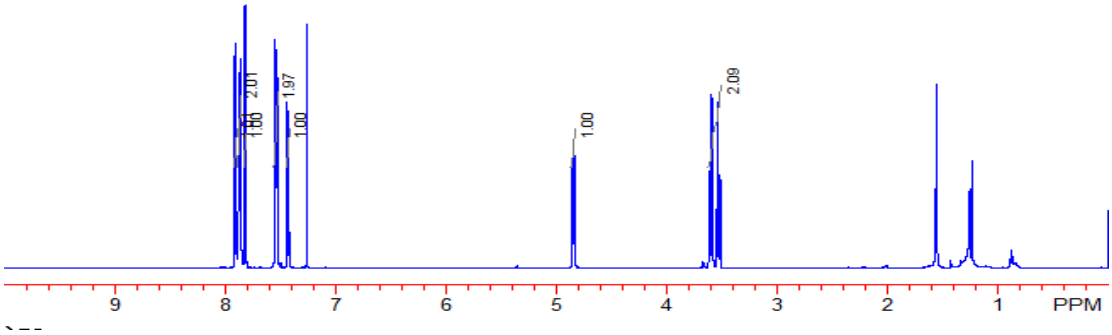
1,2-diazidocyclohexane (2ad): Following general procedure and purified by silica gel column chromatography, eluting with PE/EA afforded the title compound as yellow oil (30.1 mg, 52%) (dr = 2:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.68-3.57 (m, 0.65H), 3.25-3.15 (m, 1.30H), 2.11-2.05 (m, 1.33H), 1.91-1.84 (m, 0.68H), 1.80-1.75 (m, 1.32H), 1.70-1.63 (m, 1.38H), 1.45-1.24 (m, 3.44H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 64.4, 61.4, 30.6, 27.4, 23.7, 21.7; HRMS (EI) m/z $[M+H]^+$ calculated for $C_6H_{11}N_6^+$: 167.1040, found: 167.1042.

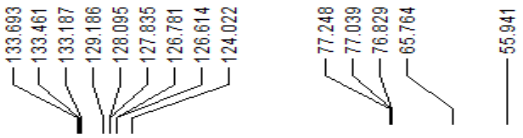
8. NMR spectra of compounds

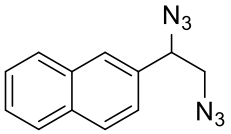
2-(1,2-diazidoethyl)naphthalene (2a) [$CDCl_3$, 600M]

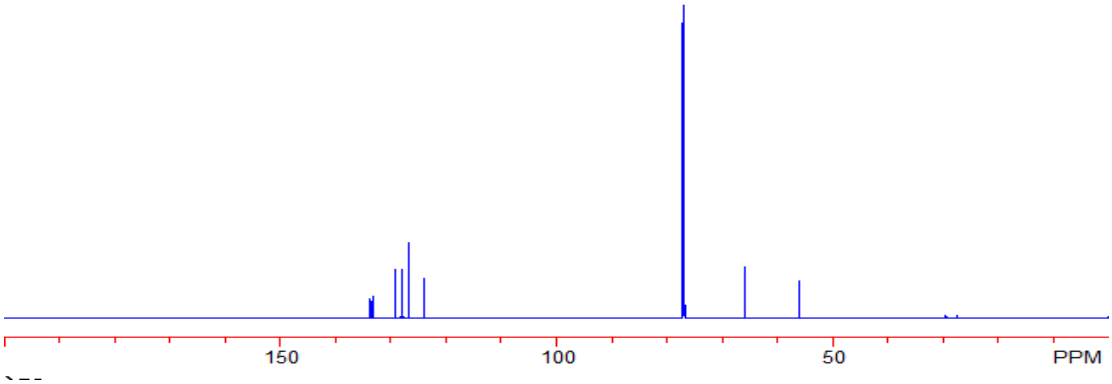




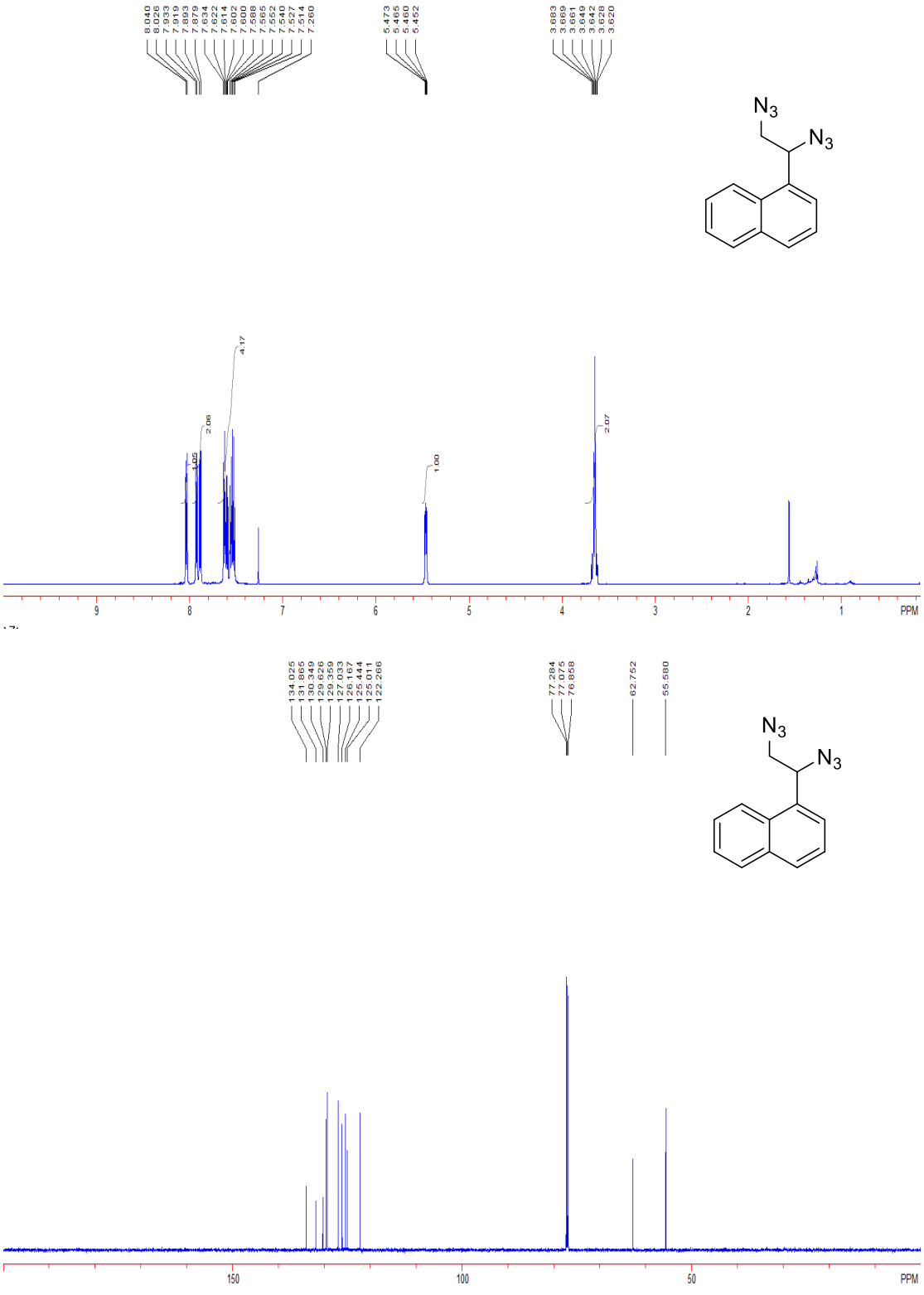




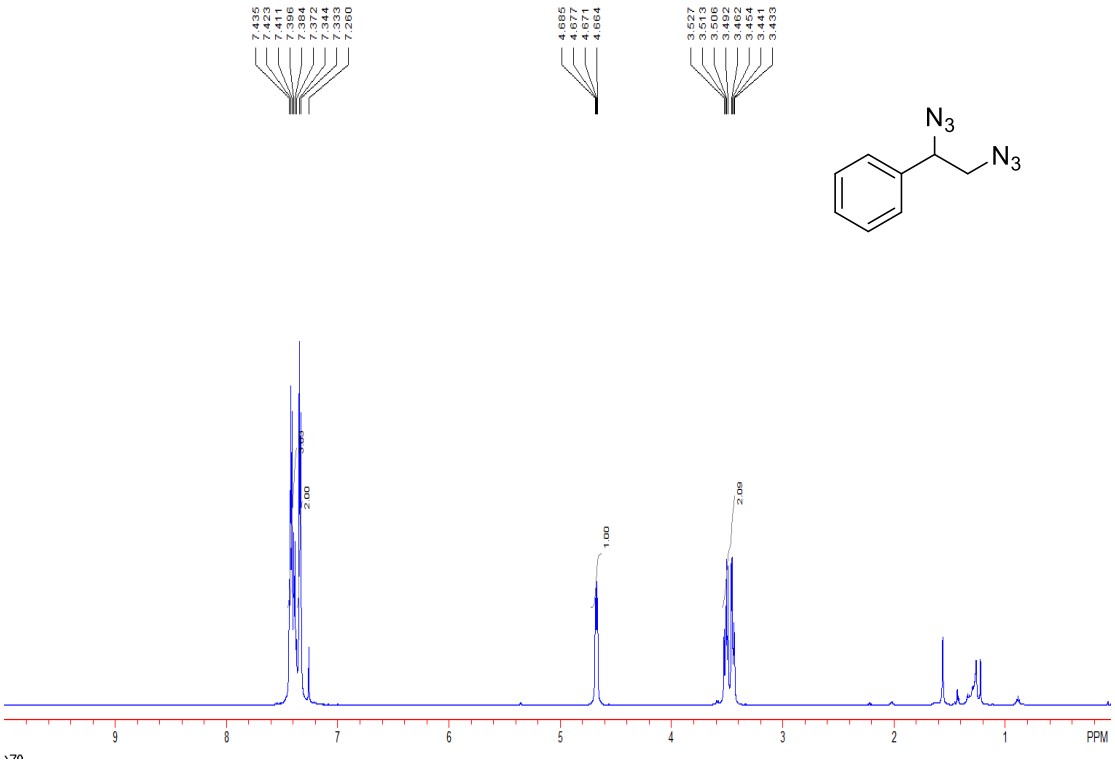


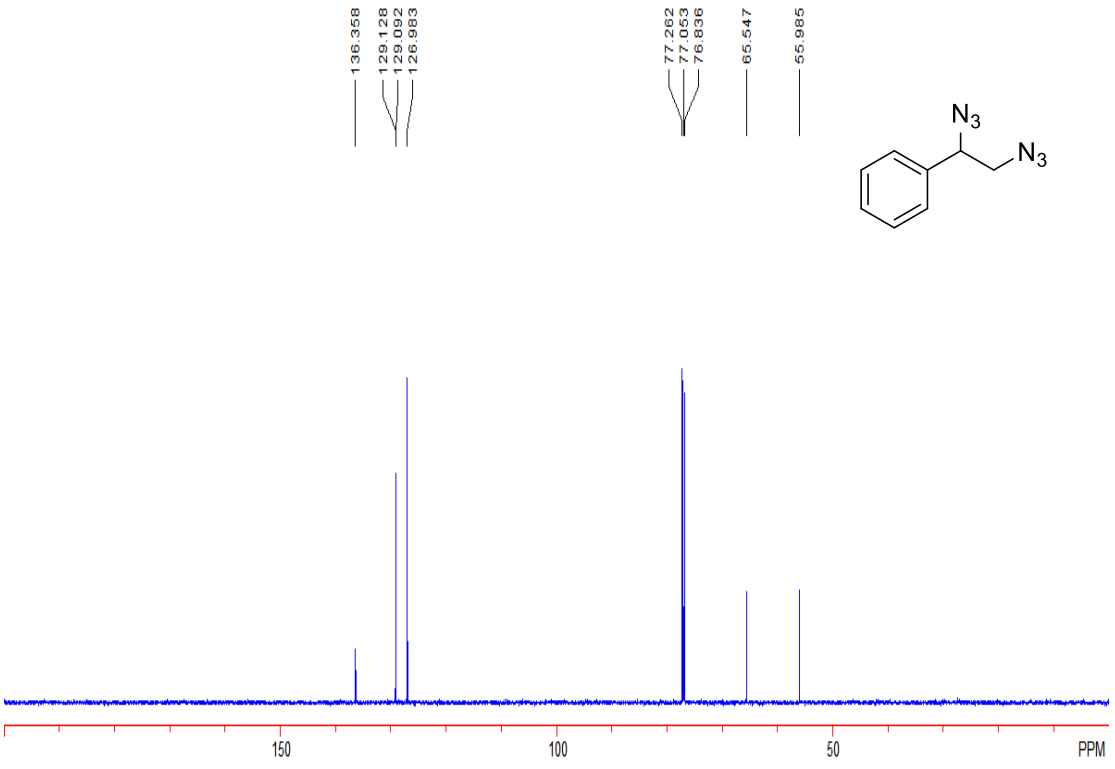


1-(1,2-diazidoethyl)naphthalene (2b) [$CDCl_3$, 600M]

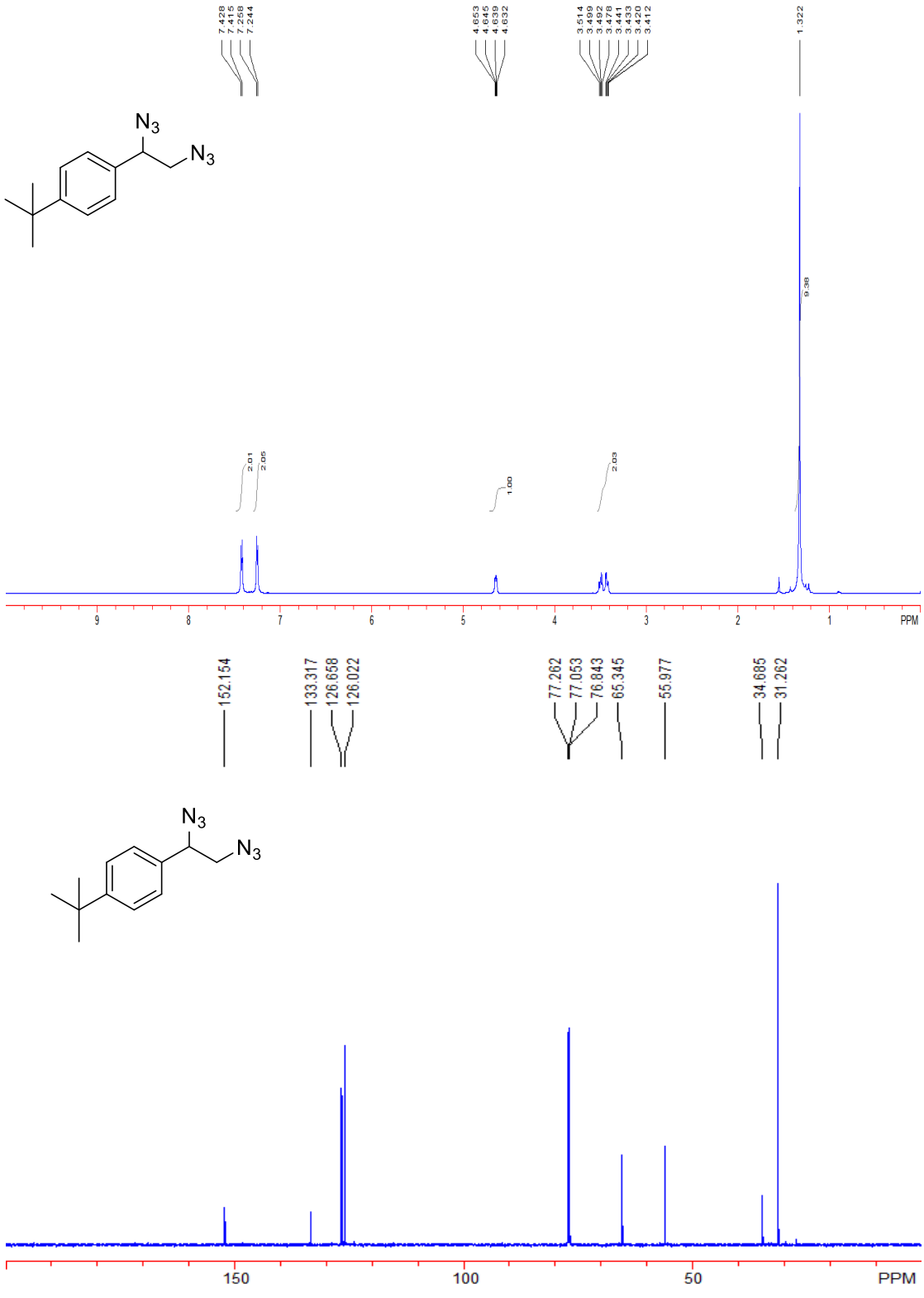


(1,2-diazidoethyl)benzene (2c) [$CDCl_3$, 600M]

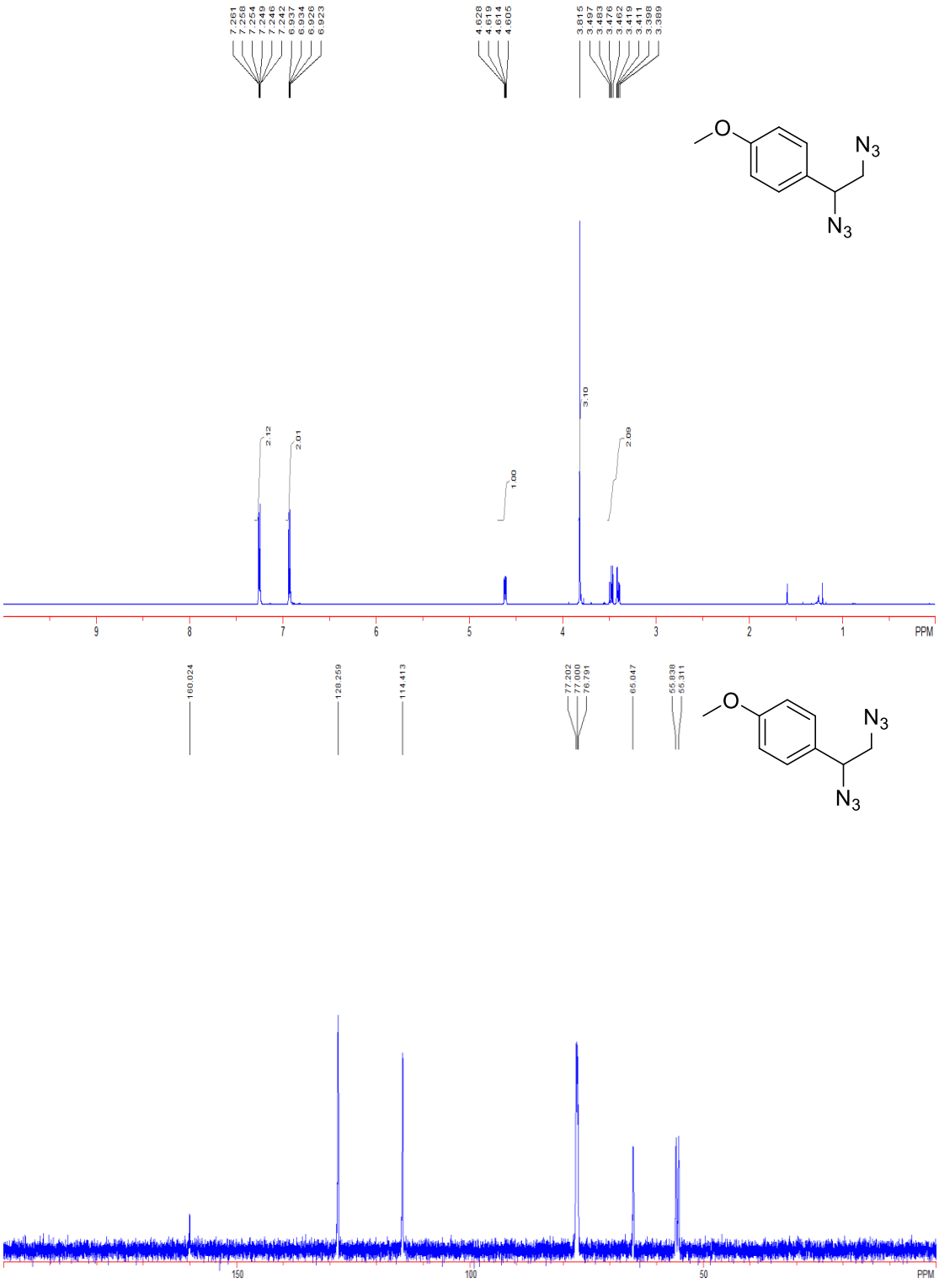




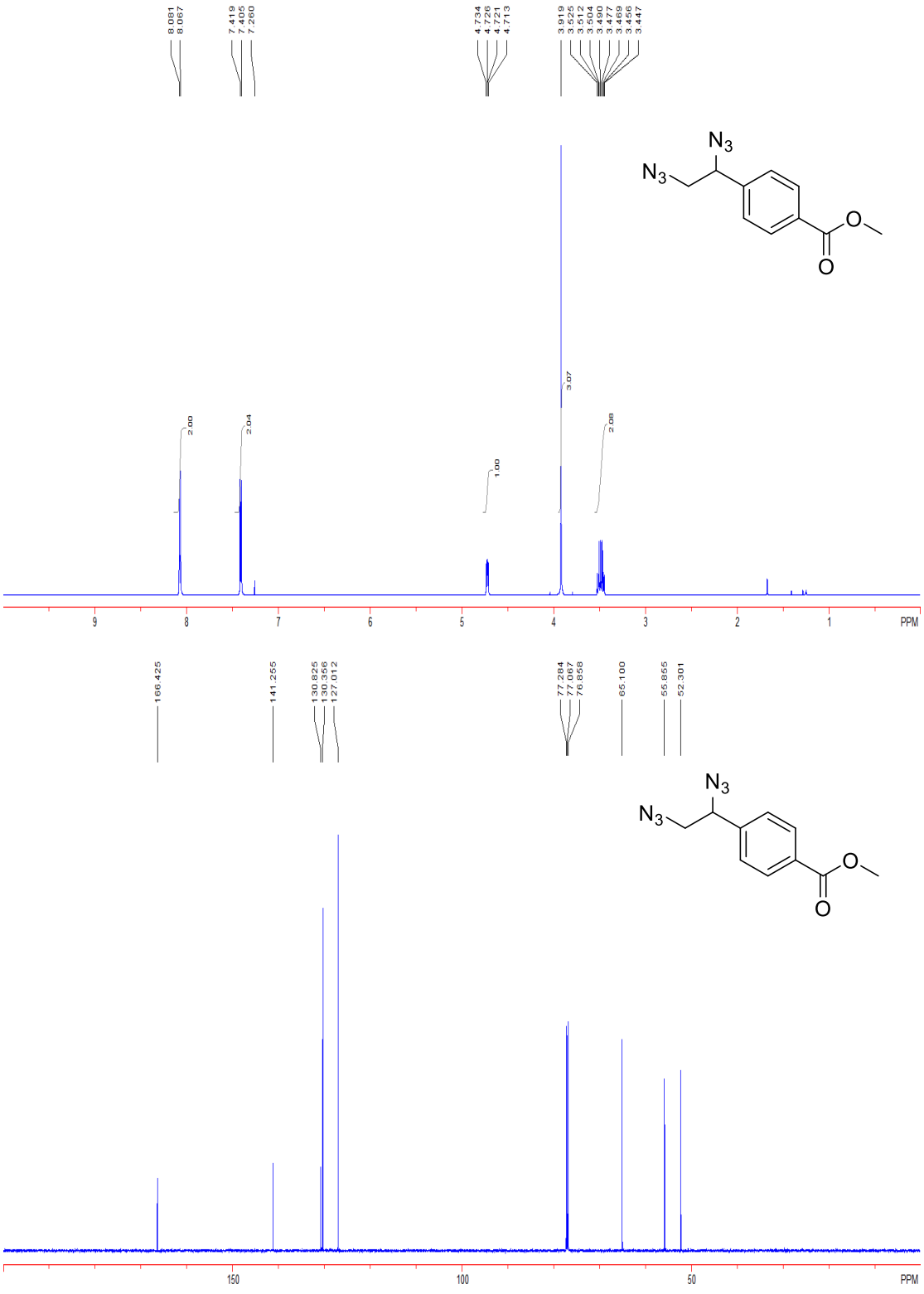
1-(tert-butyl)-4-(1,2-diazidoethyl)benzene (2d) [$CDCl_3$, 600M]



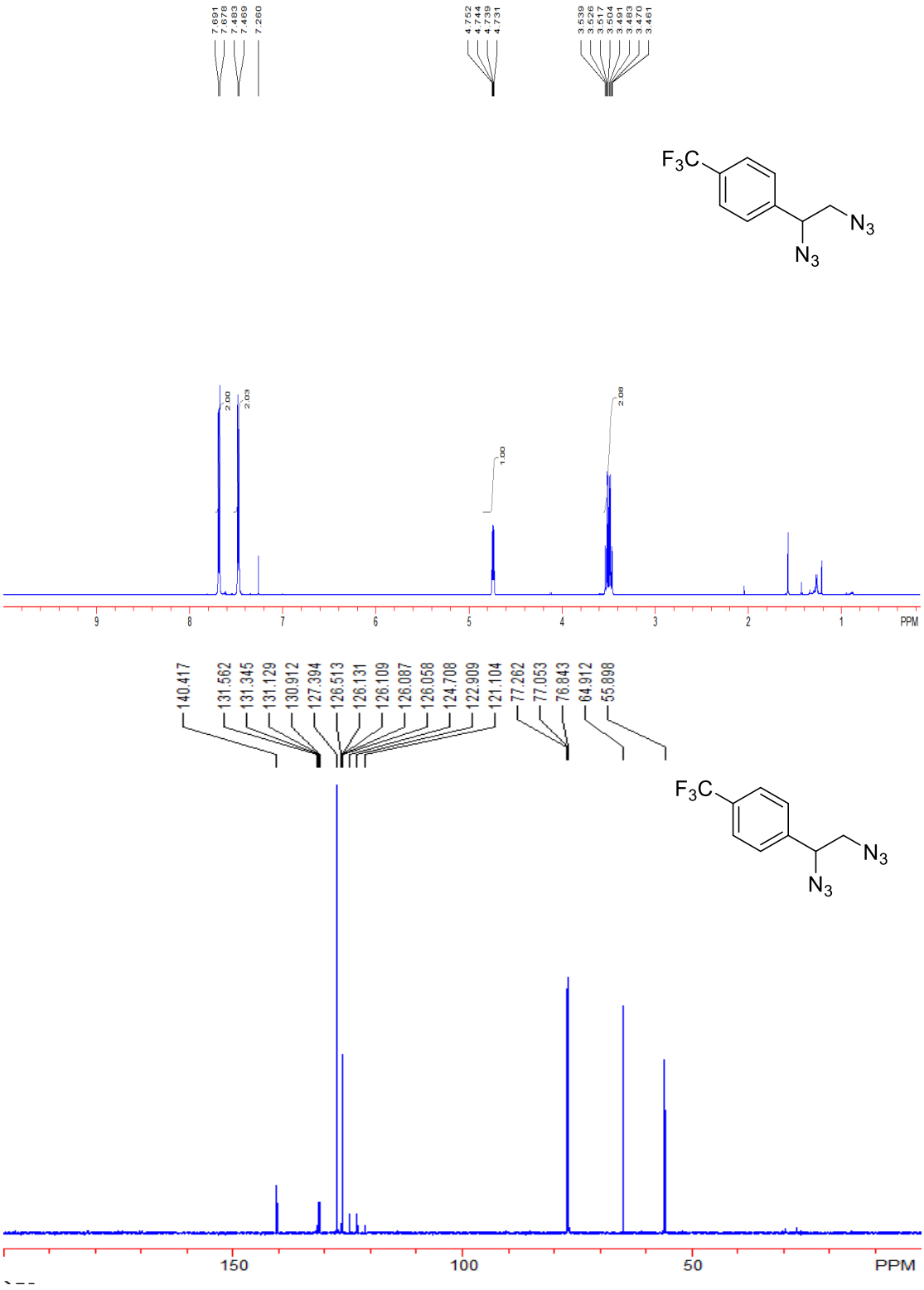
1-(1,2-diazidoethyl)-4-methoxybenzene (2e) [$CDCl_3$, 600M]



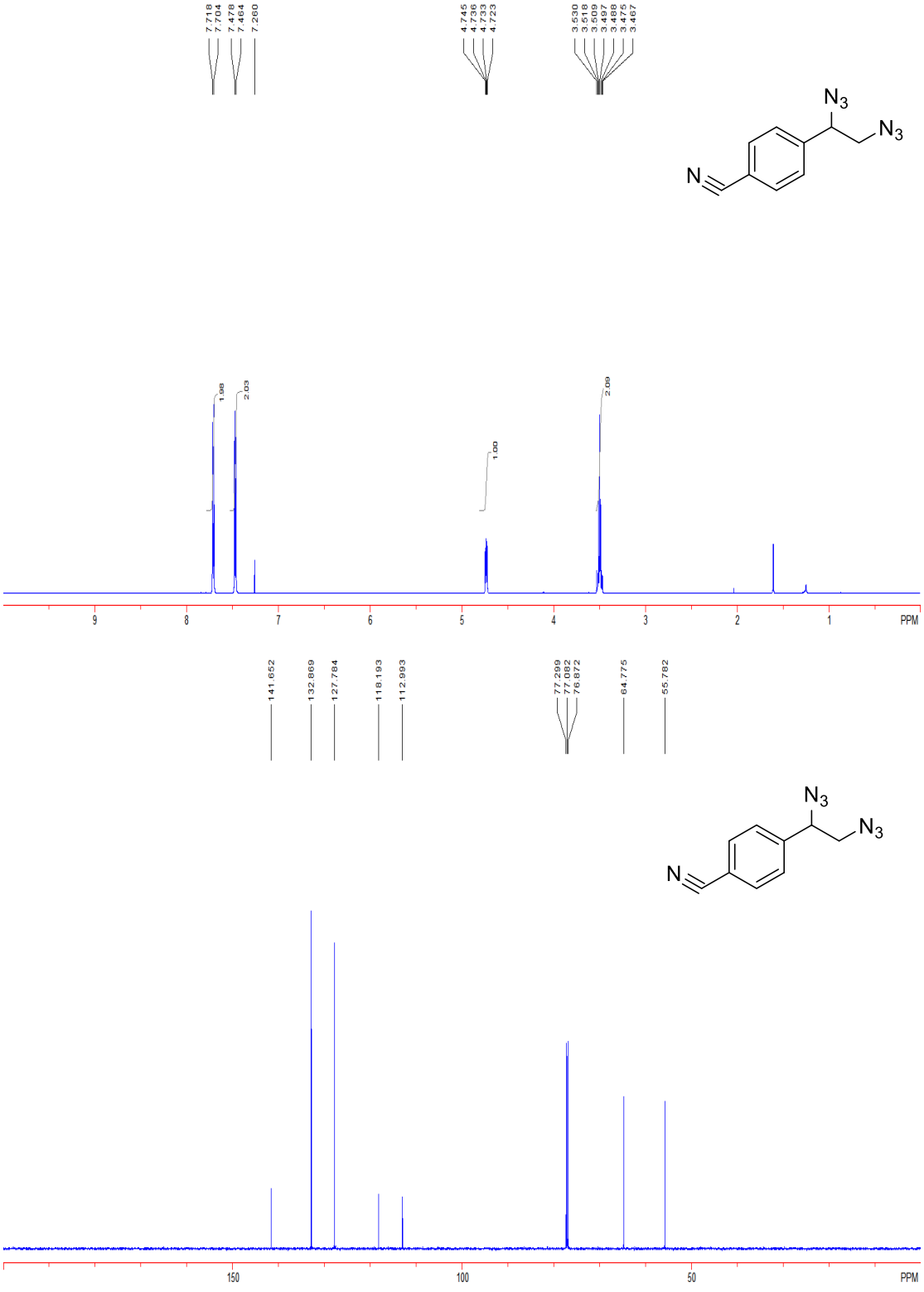
methyl 4-(1,2-diazidoethyl)benzoate (2f) [$CDCl_3$, 600M]



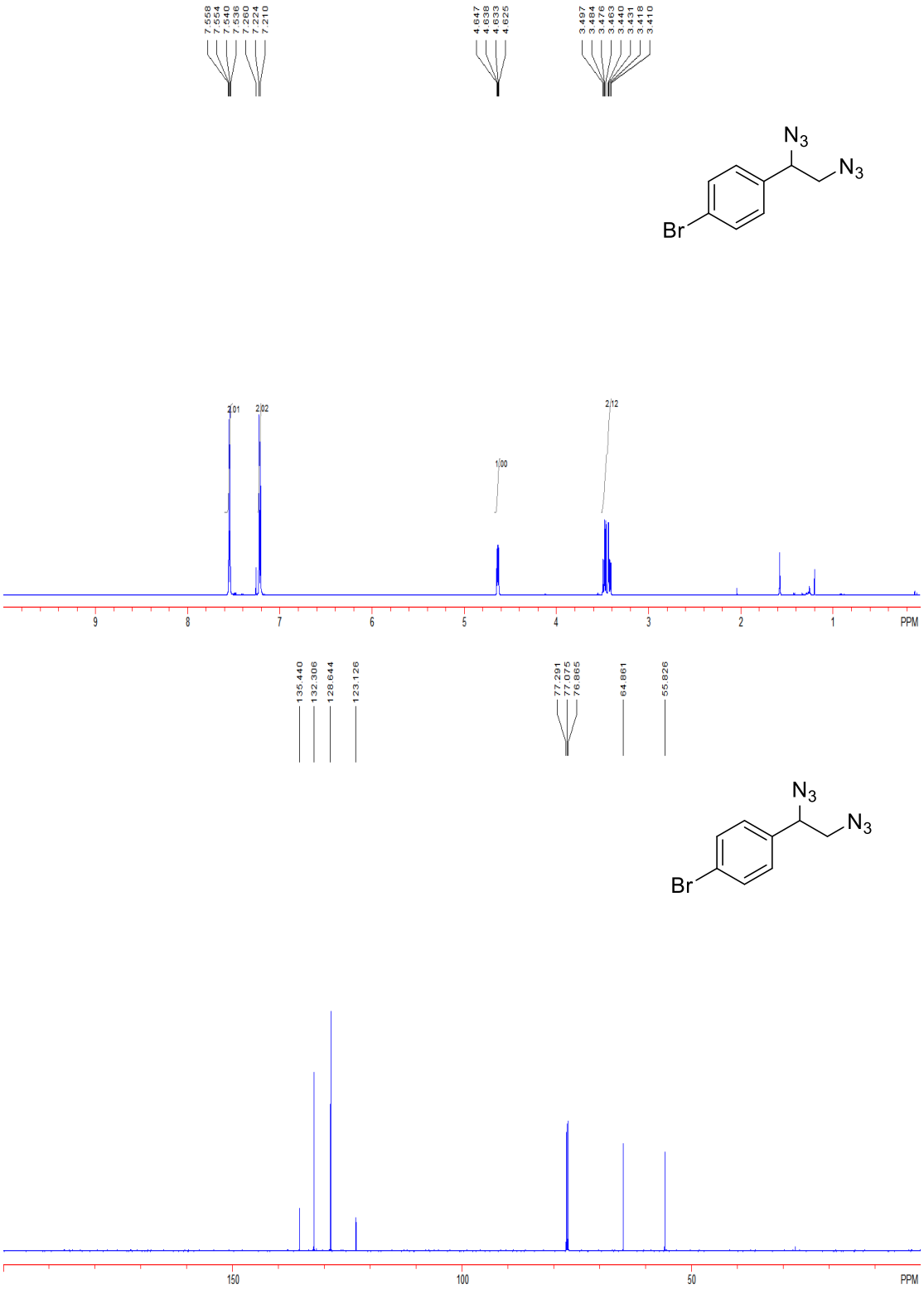
1-(1,2-diazidoethyl)-4-(trifluoromethyl)benzene (2g) [$CDCl_3$, 600M]



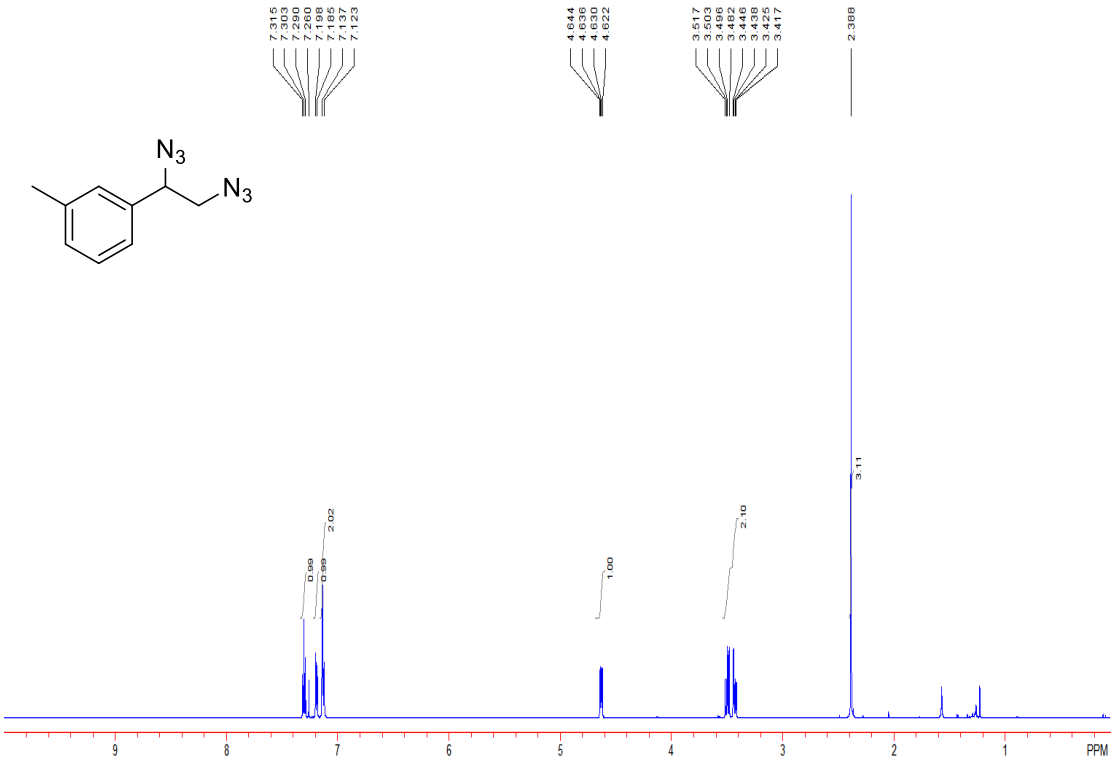
4-(1,2-diazidoethyl)benzonitrile (2h) [$CDCl_3$, 600M]

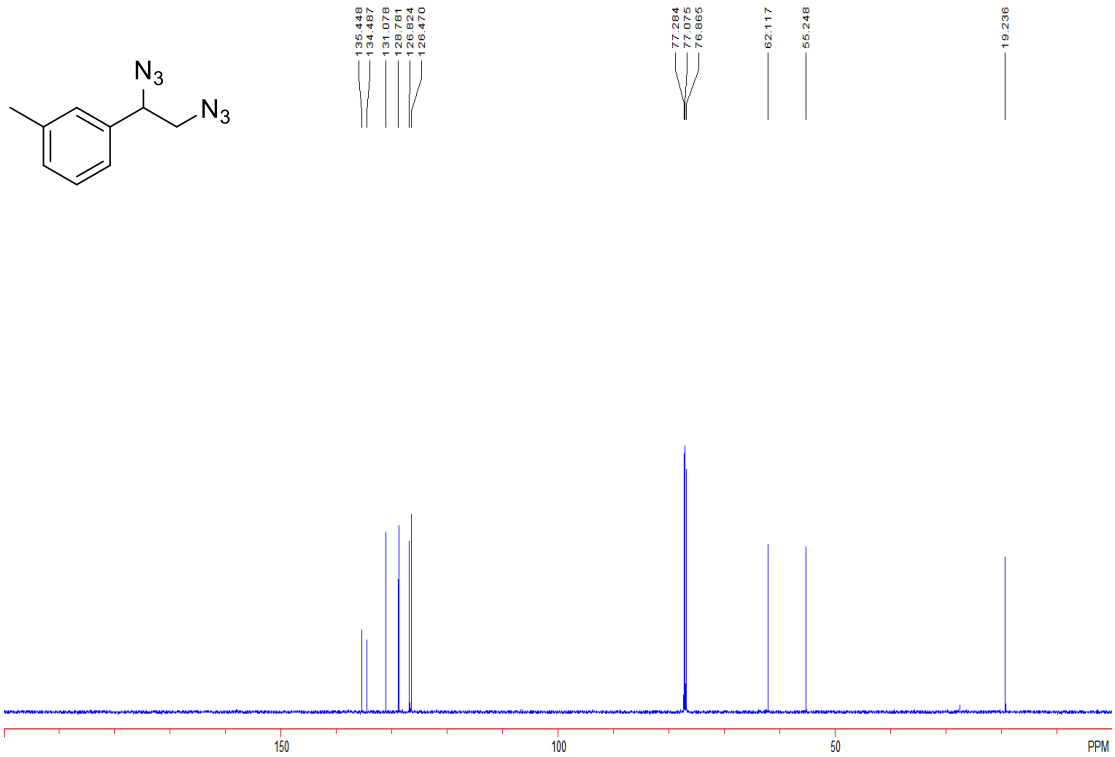


1-bromo-4-(1,2-diazidoethyl)benzene (2i) [$CDCl_3$, 600M]

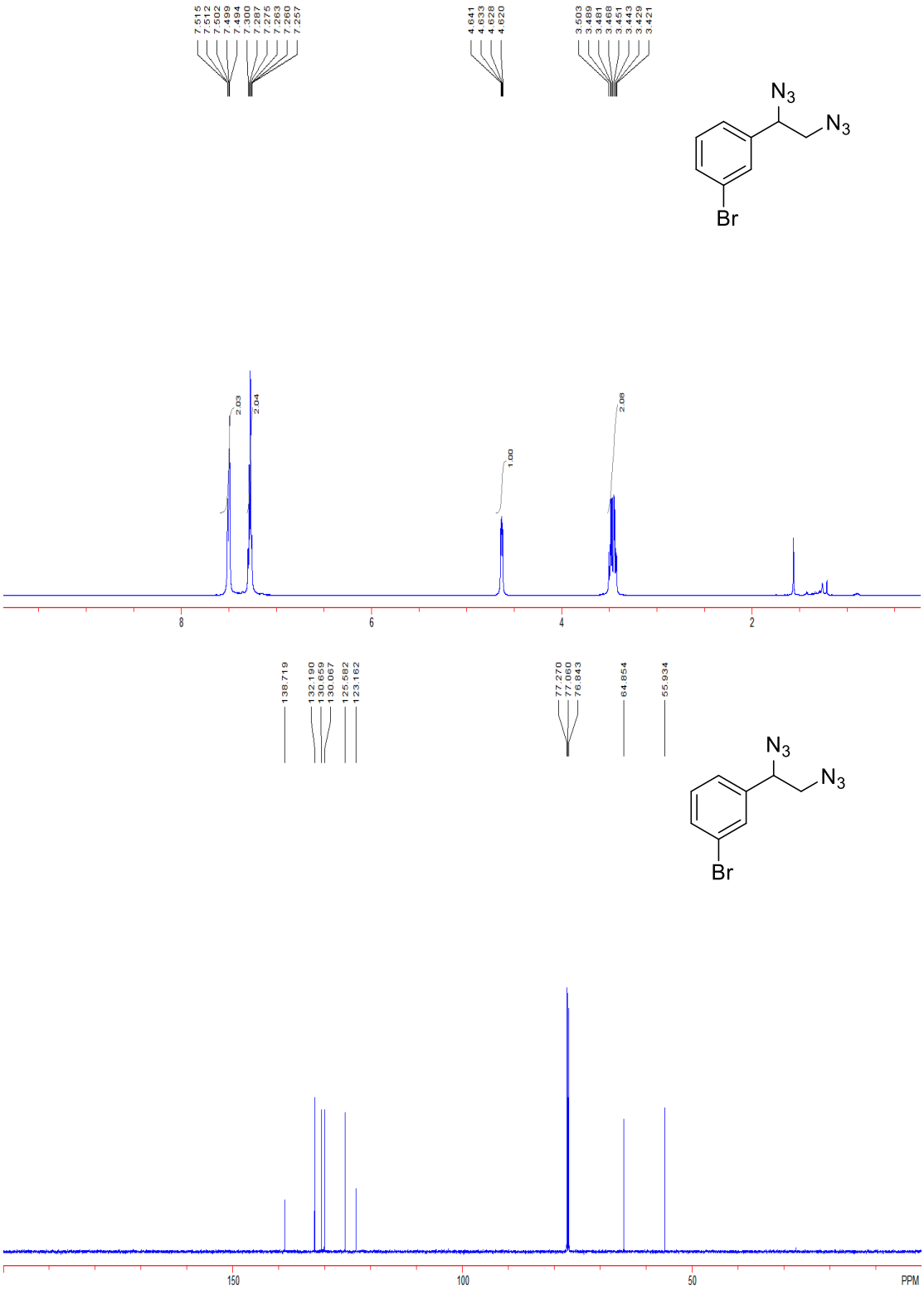


1-(1,2-diazidoethyl)-3-methylbenzene (2j) [$CDCl_3$, 600M]

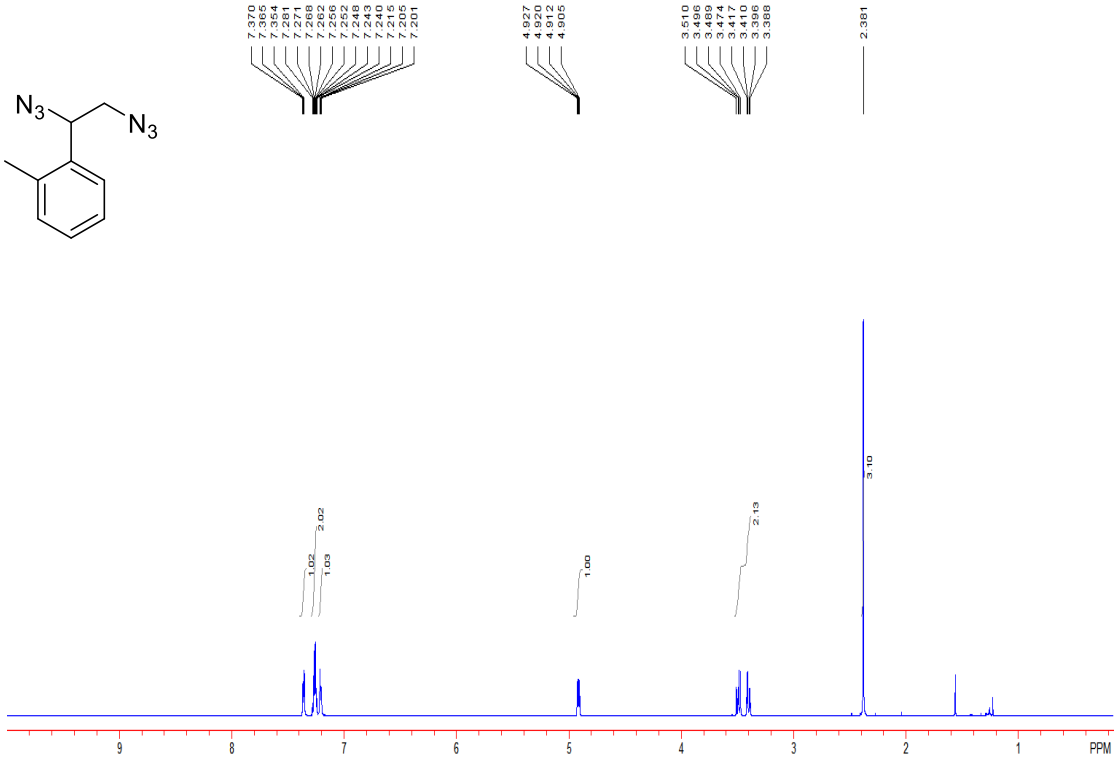


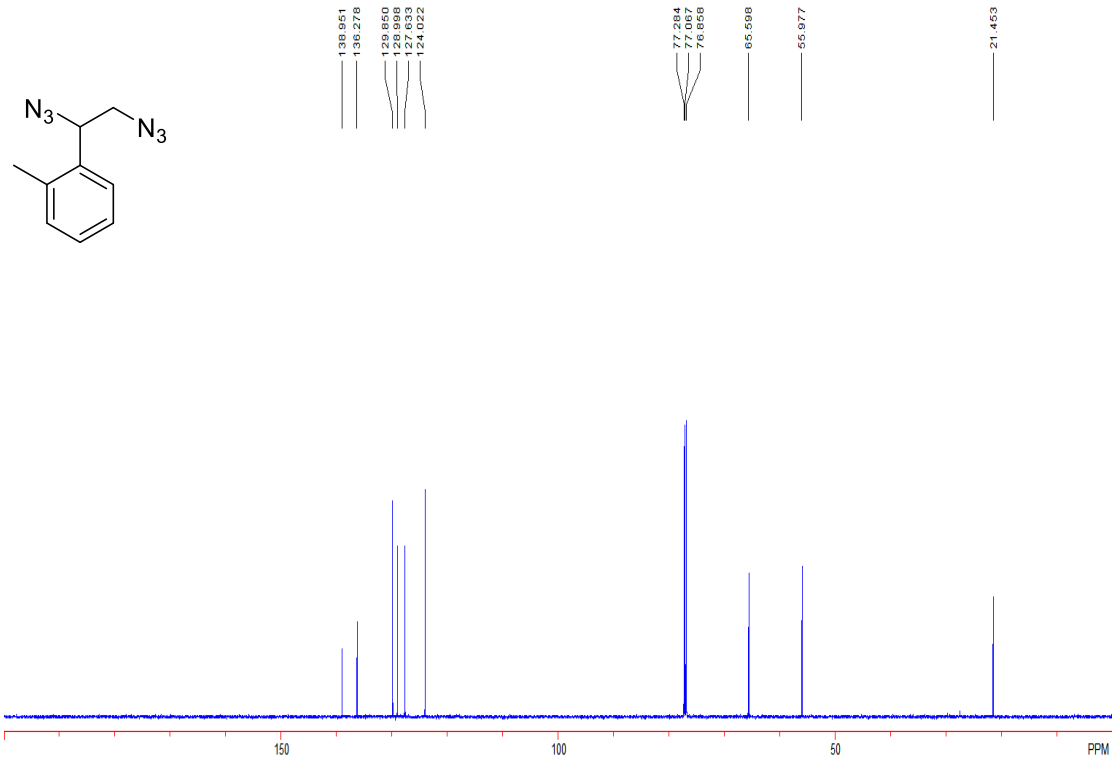


1-bromo-3-(1,2-diazidoethyl)benzene (2k) [$CDCl_3$, 600M]

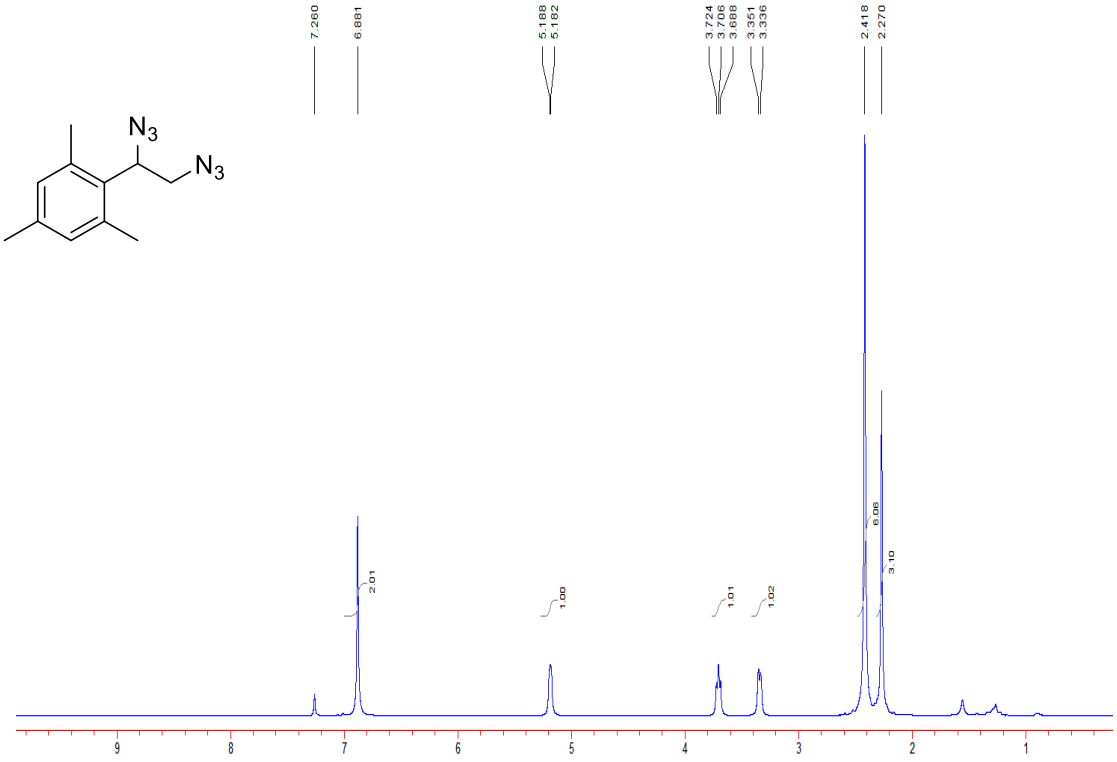


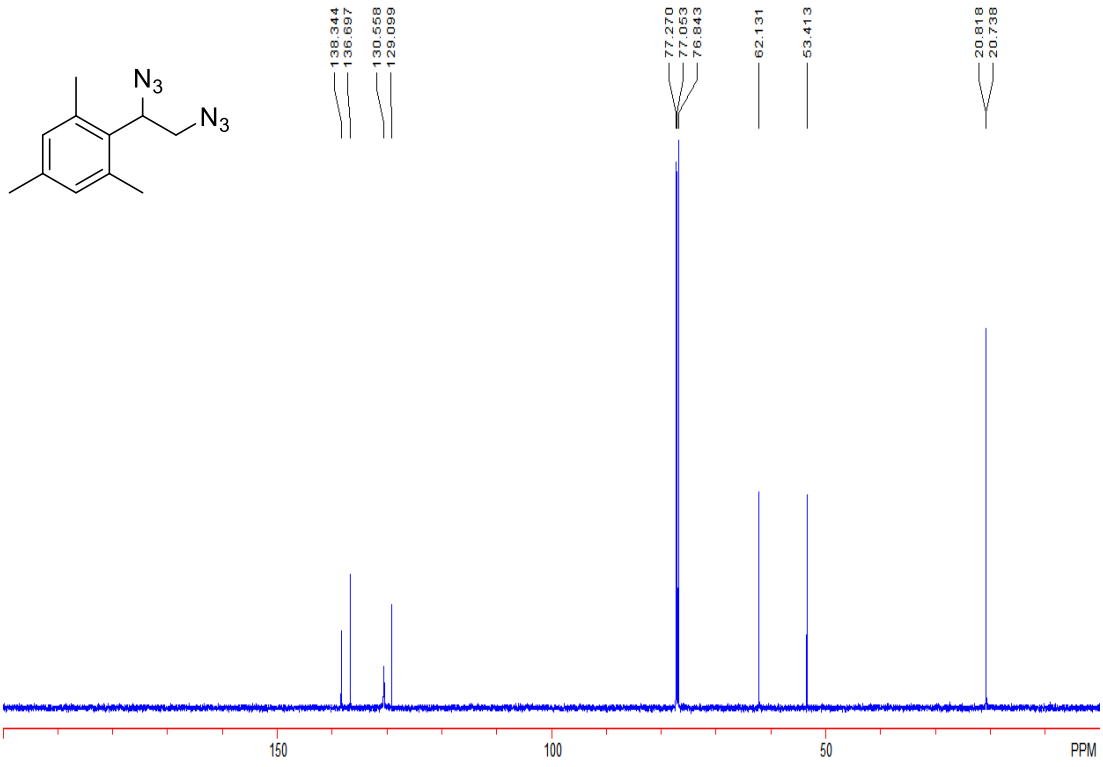
1-(1,2-diazidoethyl)-2-methylbenzene (2l) [$CDCl_3$, 600M]



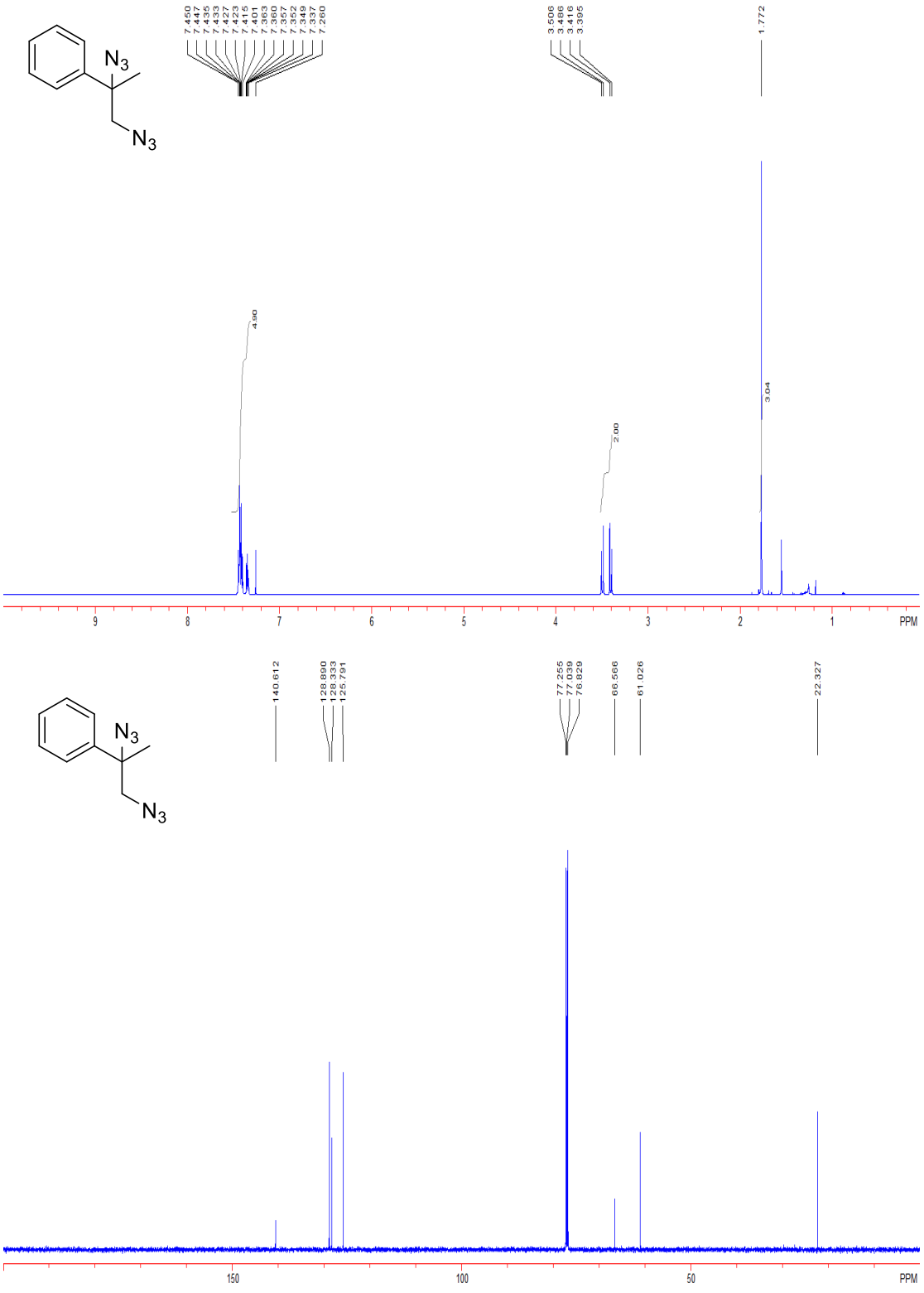


2-(1,2-diazidoethyl)-1,3,5-trimethylbenzene (2m) [$CDCl_3$, 600M]

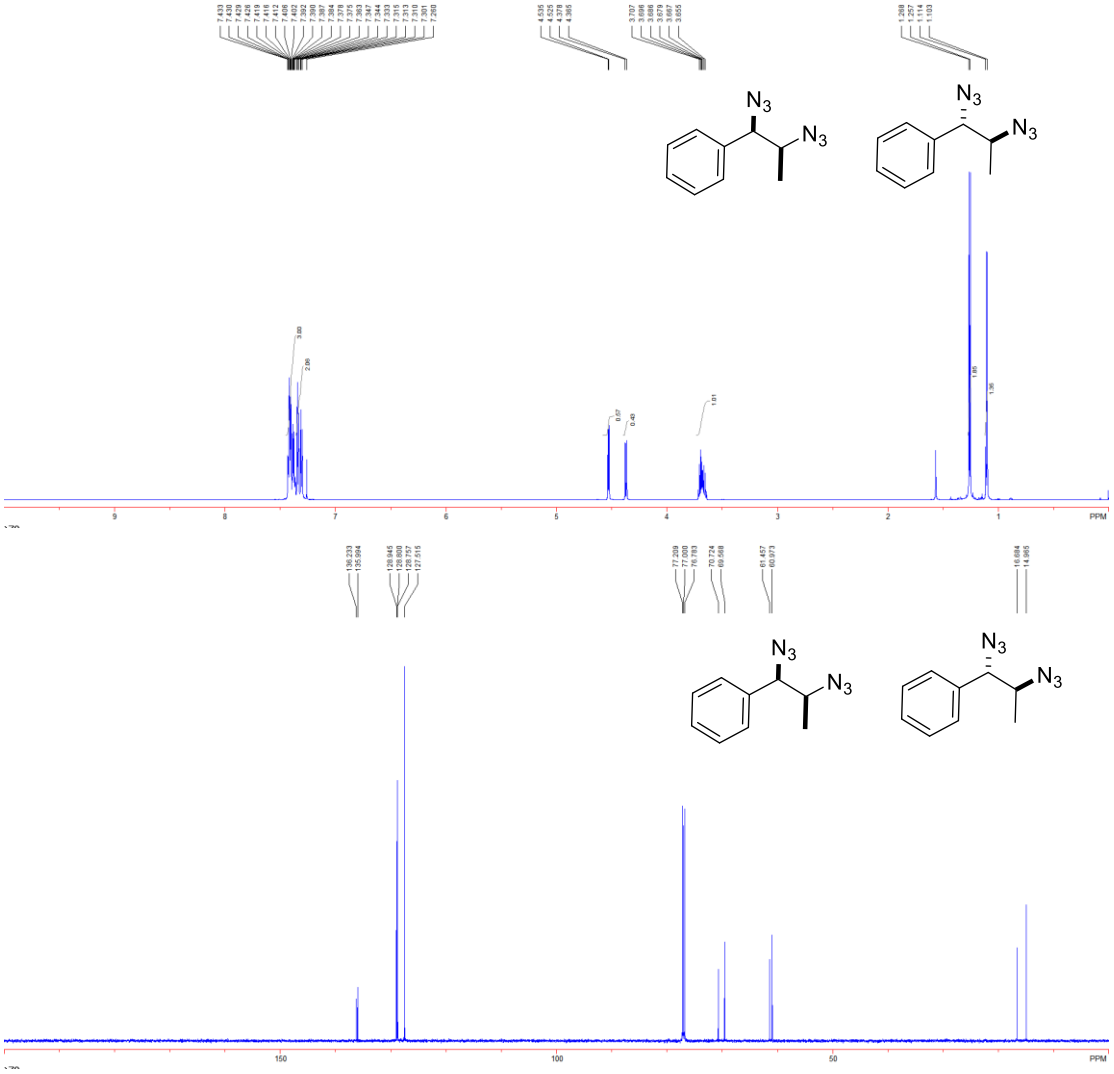




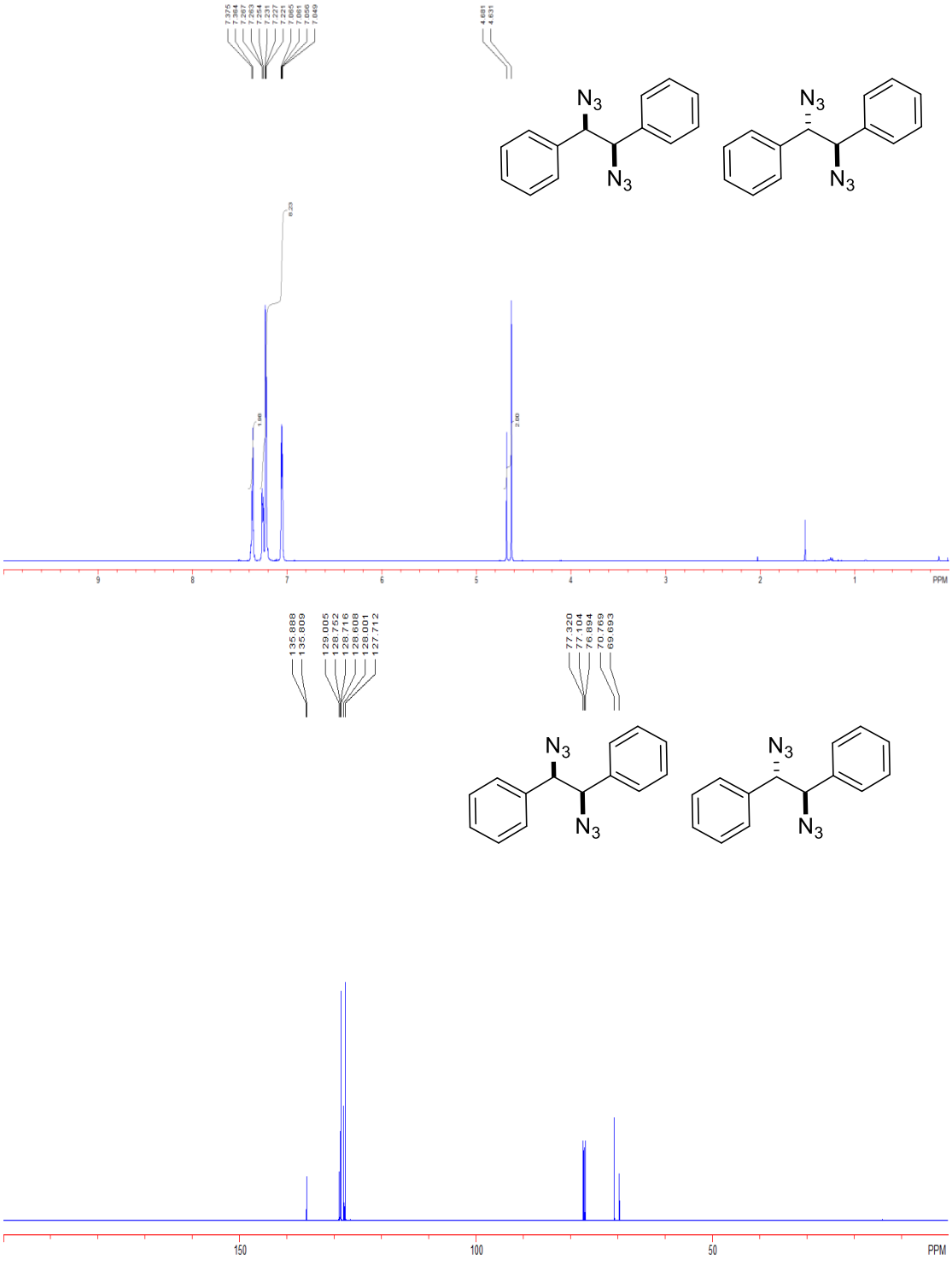
(1,2-diazidopropan-2-yl)benzene (2n) [$CDCl_3$, 600M]



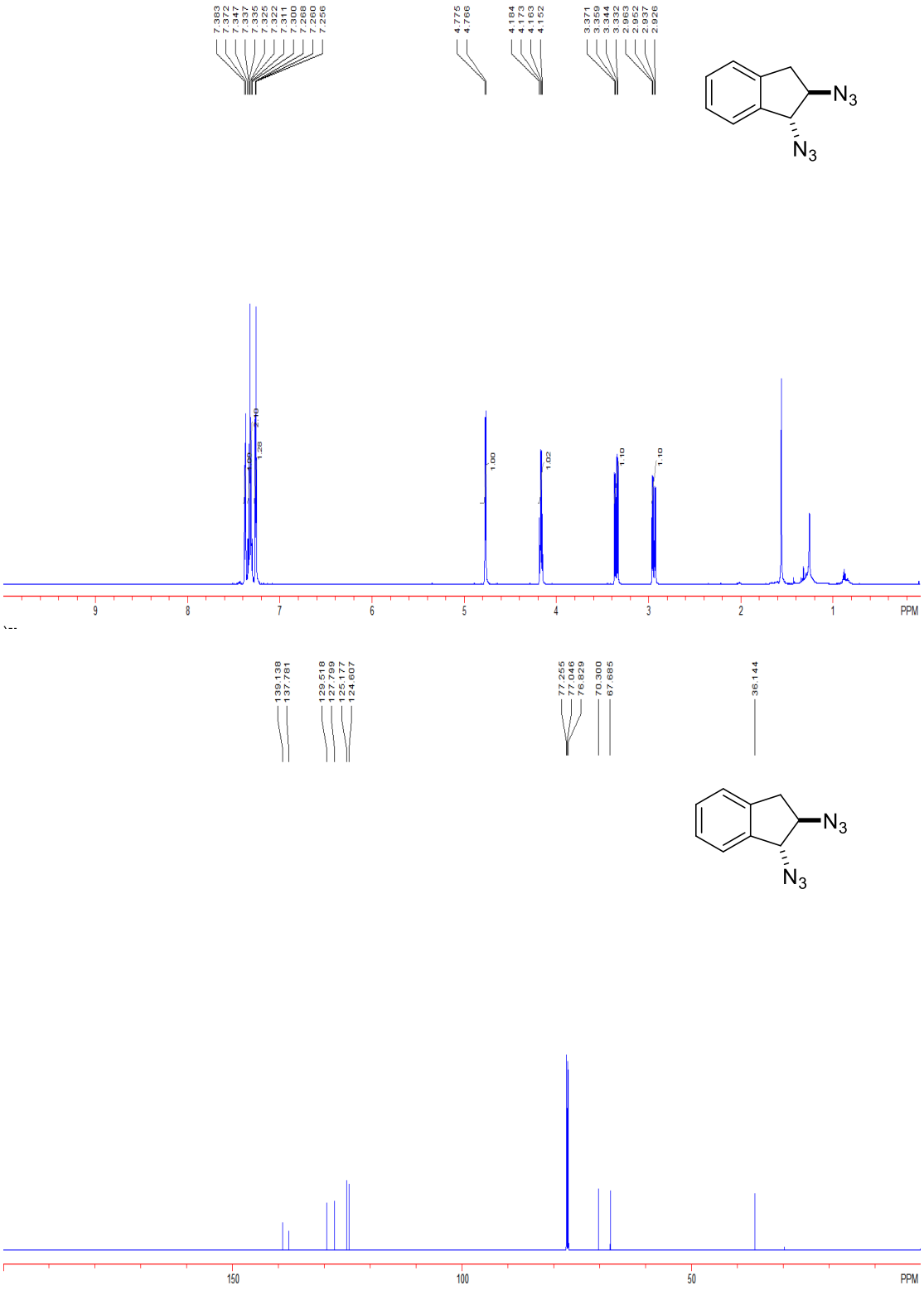
(1,2-diazidopropyl)benzene (2o) [$CDCl_3$, 600M]



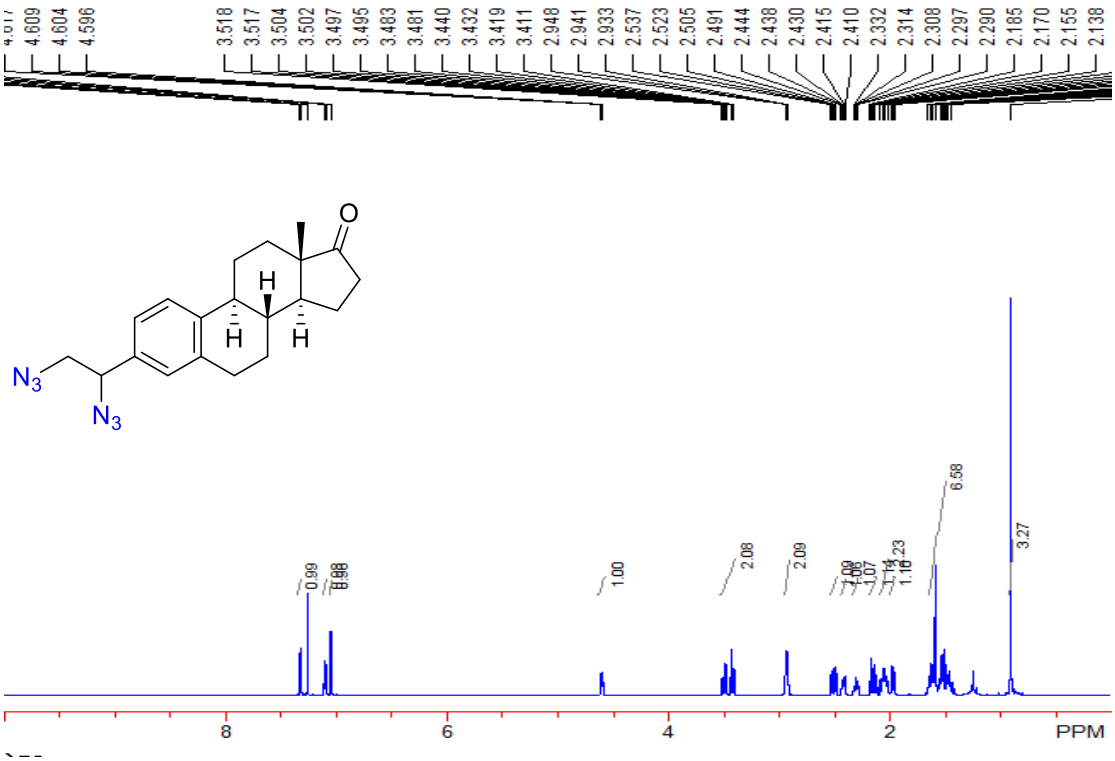
1,2-diazido-1,2-diphenylethane (2p) [$CDCl_3$, 600M]

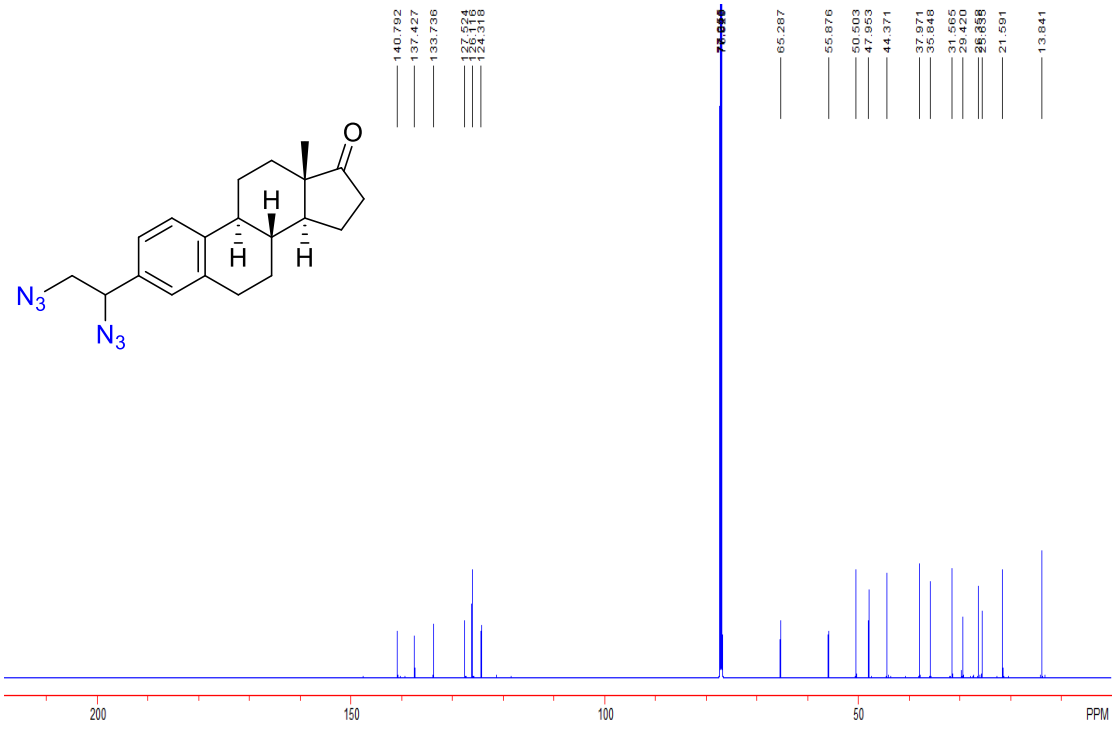


1,2-diazido-2,3-dihydro-1H-indene (2q) [$CDCl_3$, 600M]

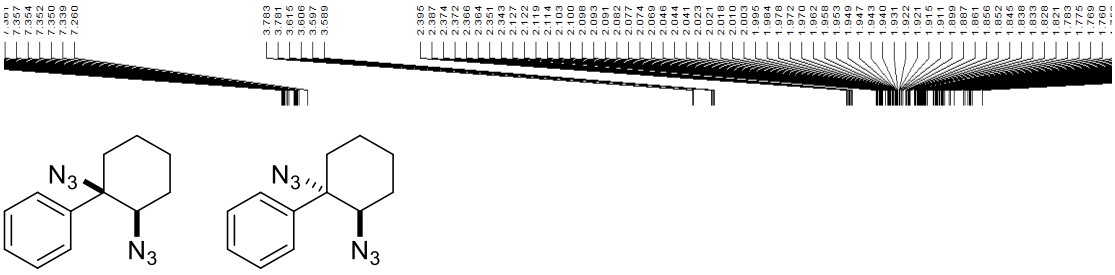


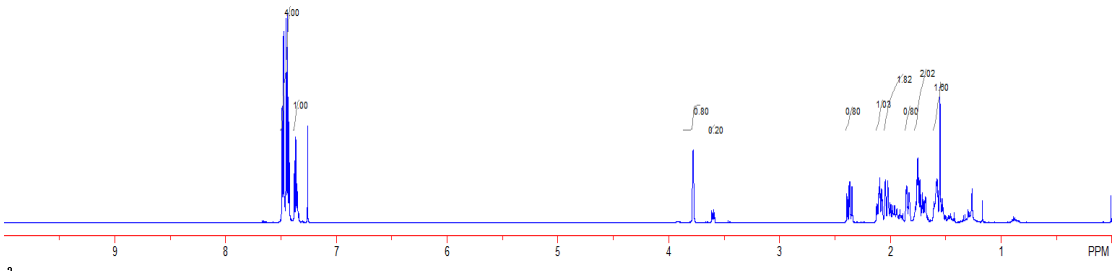
(8R,9S,13S,14S)-3-(1,2-diazidoethyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (2r) [$CDCl_3$, 600M]

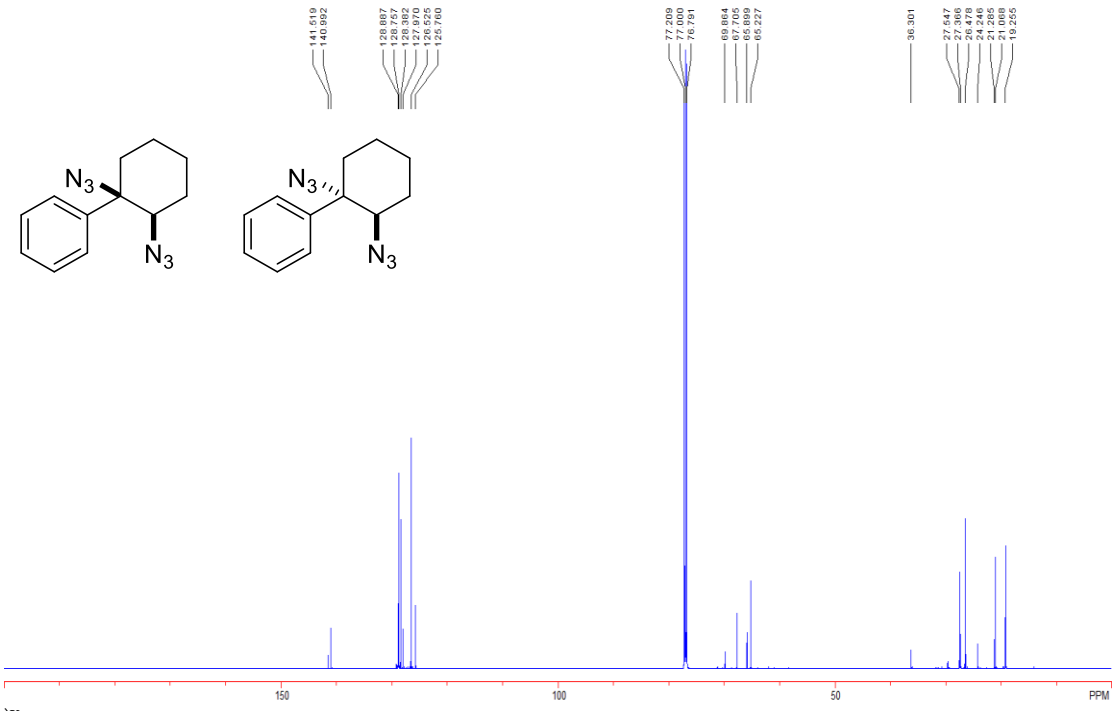




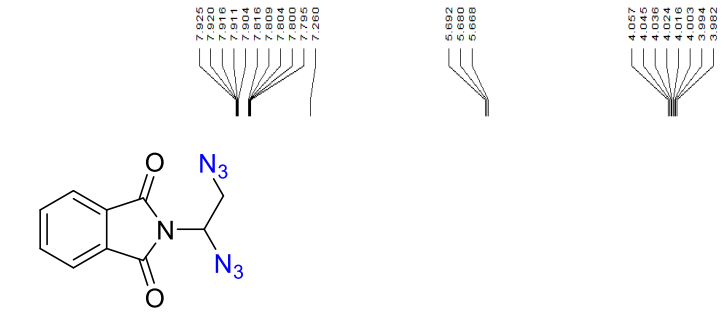
(1,2-diazidocyclohexyl)benzene (2s) [$CDCl_3$, 600M]

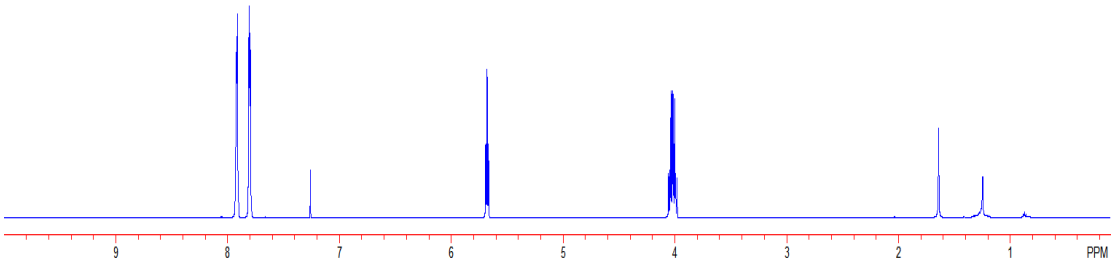


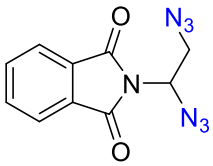


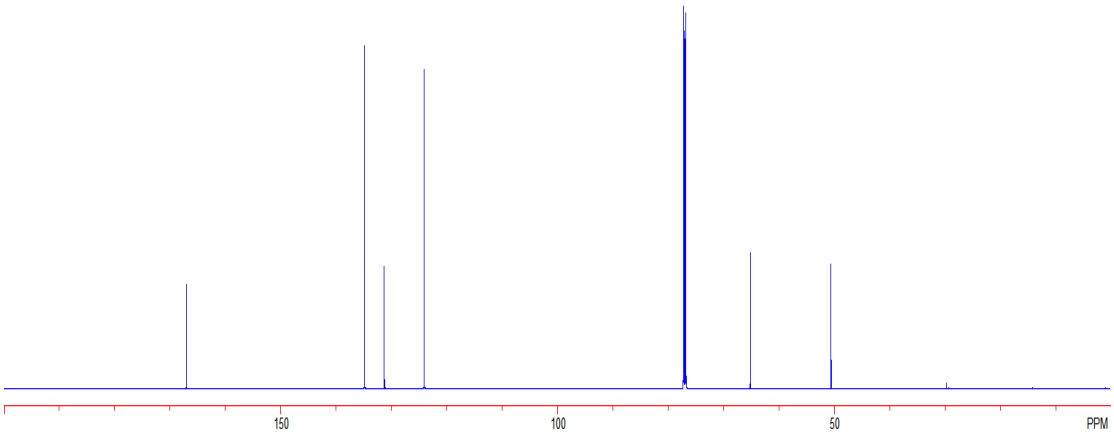


2-(1,2-diazidoethyl)isoindoline-1,3-dione (2t) [$CDCl_3$, 600M]

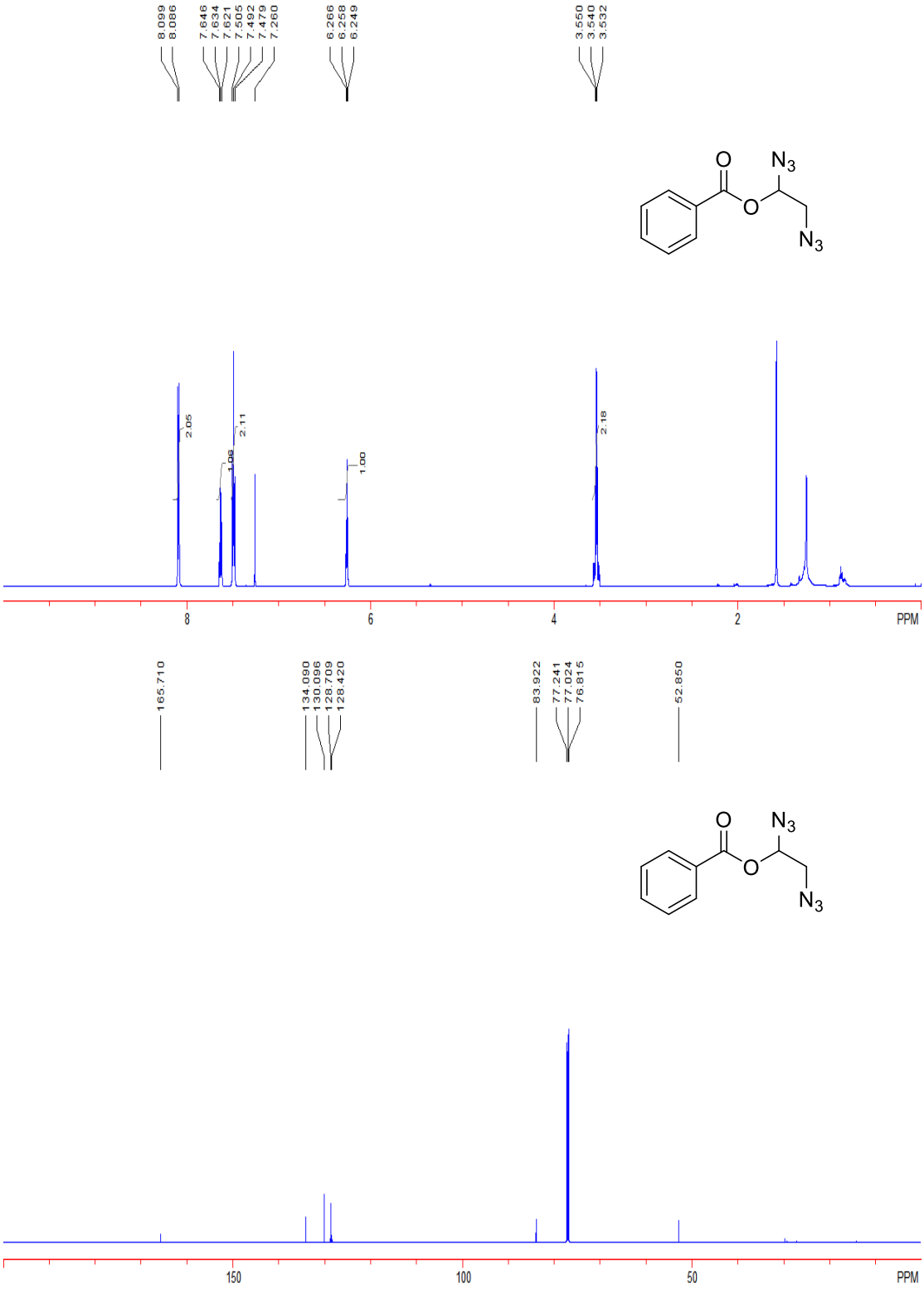




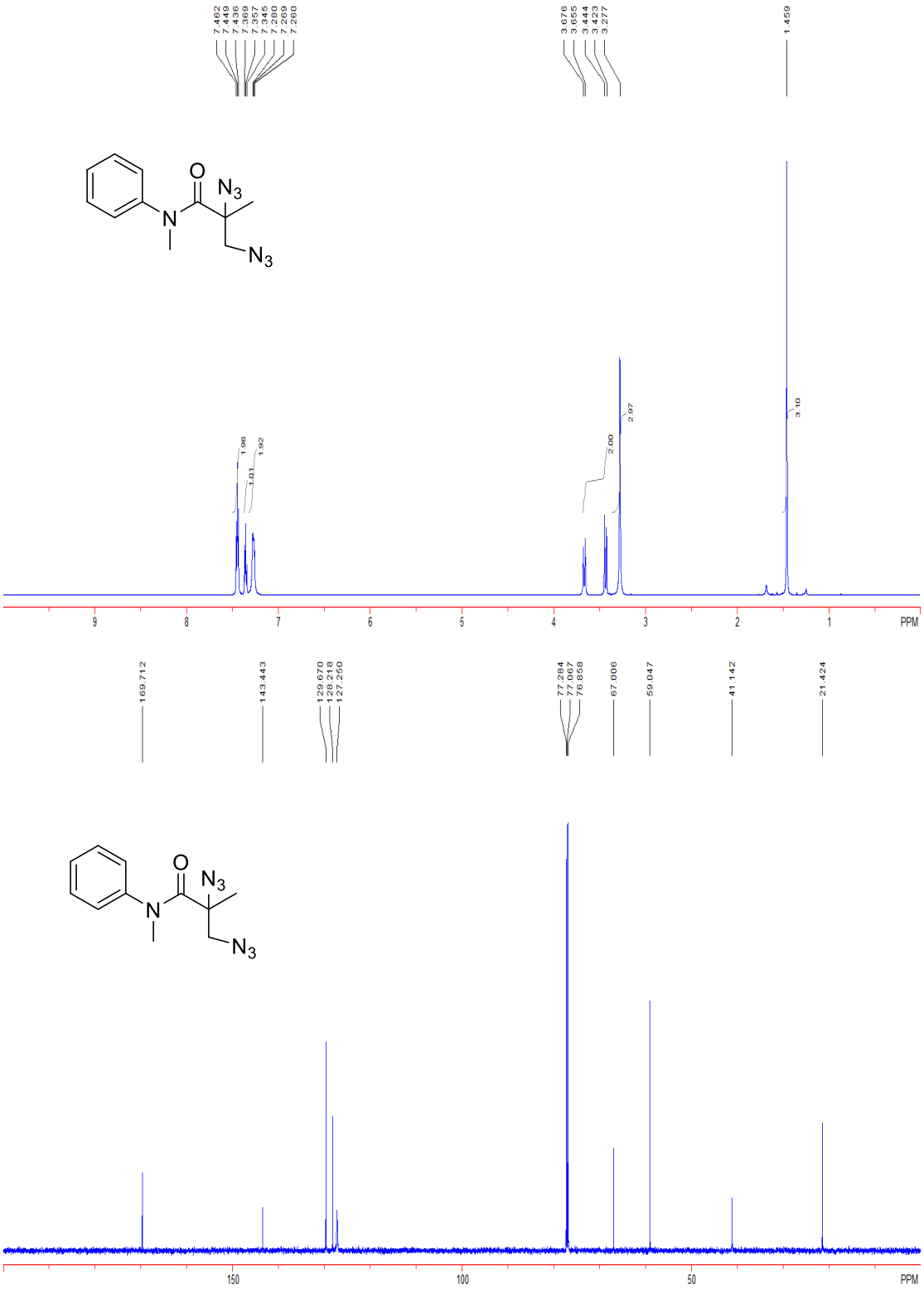




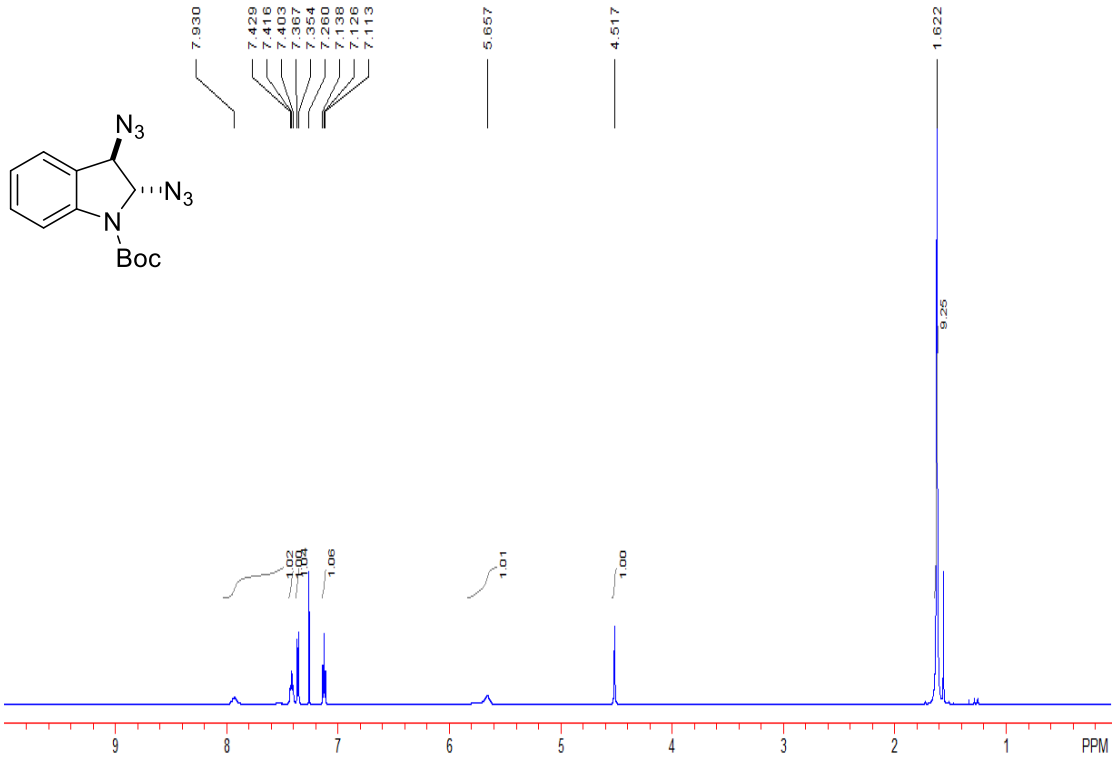
1,2-diazidoethyl benzoate (2u) [$CDCl_3$, 600M]

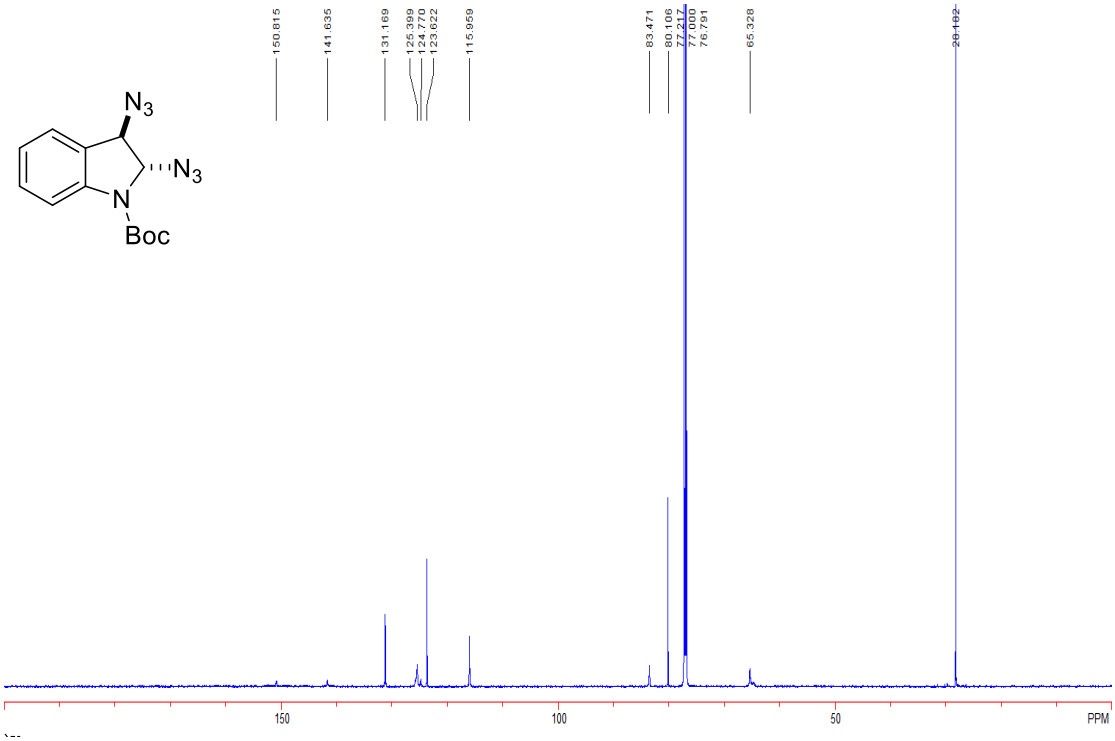


2,3-diazido-N,2-dimethyl-N-phenylpropanamide (2v) [$CDCl_3$, 600M]

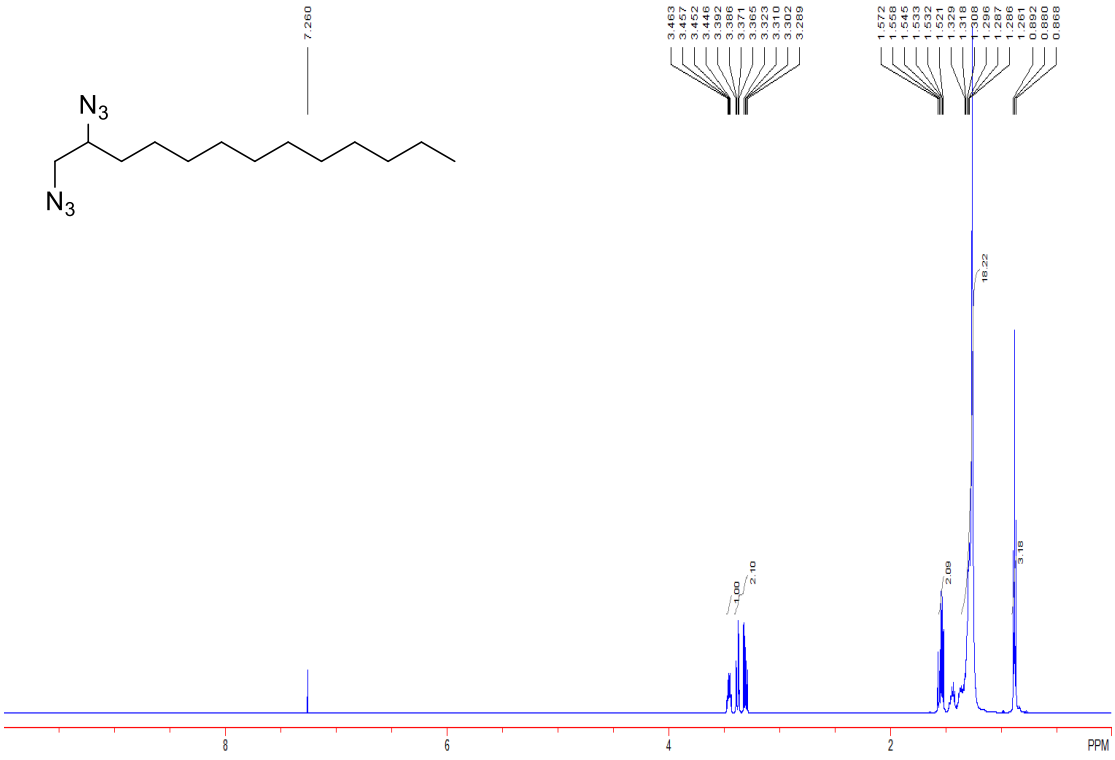


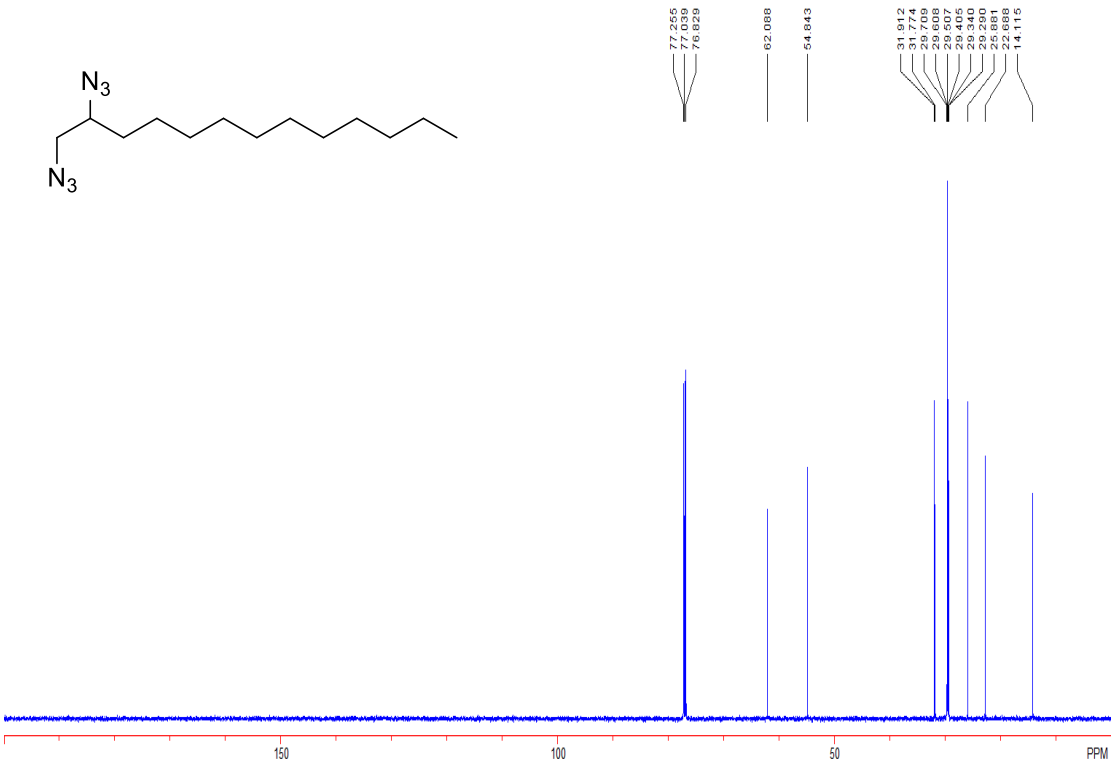
tert-butyl 2,3-diazidoindoline-1-carboxylate (2w) [$CDCl_3$, 600M]



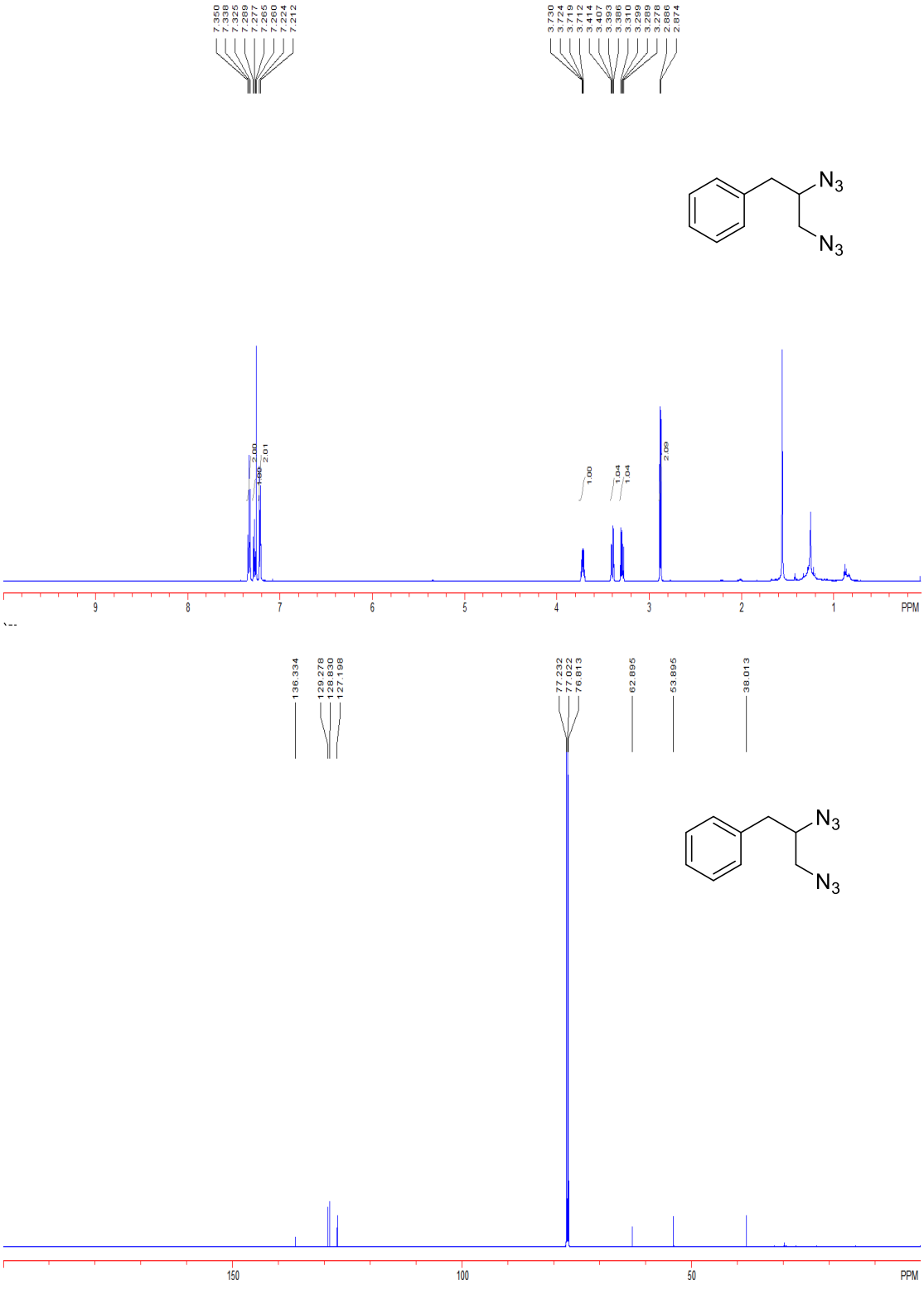


1,2-diazidotridecane (2x) [$CDCl_3$, 600M]

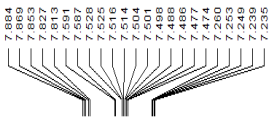


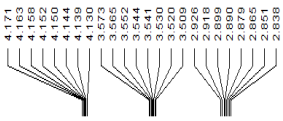


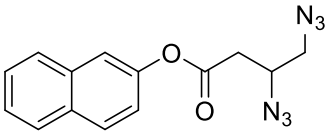
(2,3-diazidopropyl)benzene (2y) [$CDCl_3$, 600M]

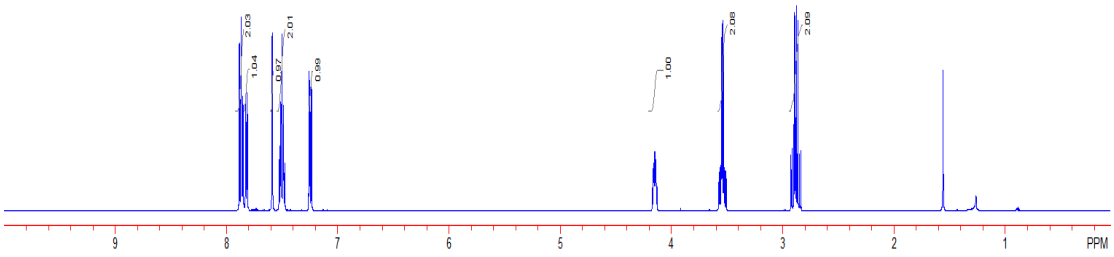


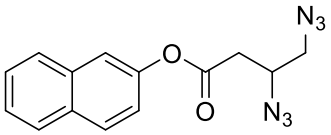
naphthalen-2-yl 3,4-diazidobutanoate (2z) [$CDCl_3$, 600M]

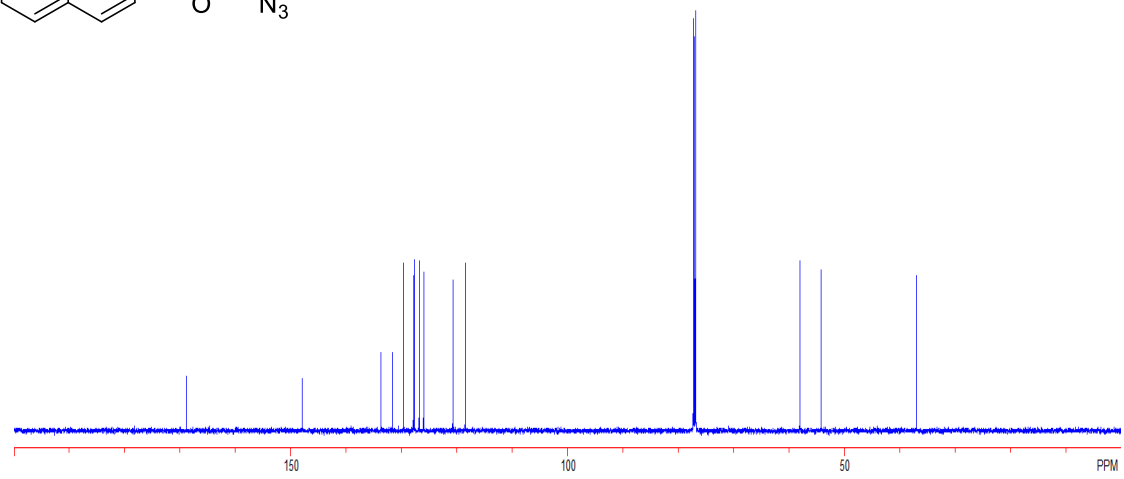




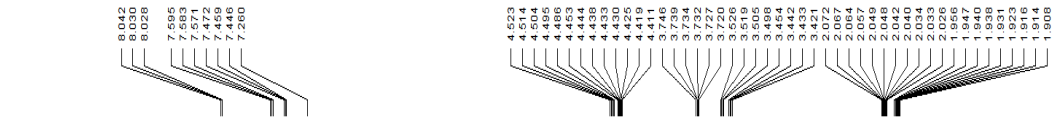


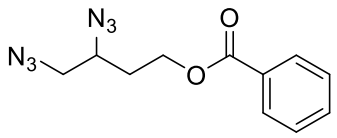


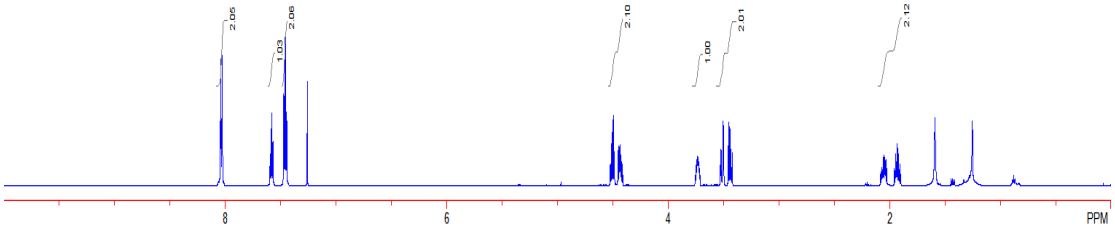


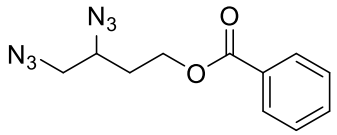


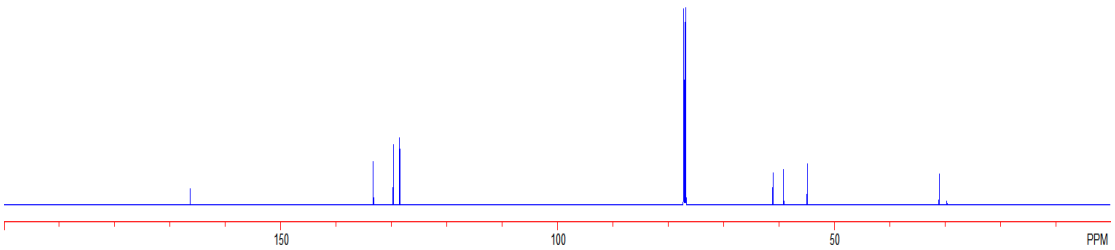
3,4-diazidobutyl benzoate (2aa) [$CDCl_3$, 600M]



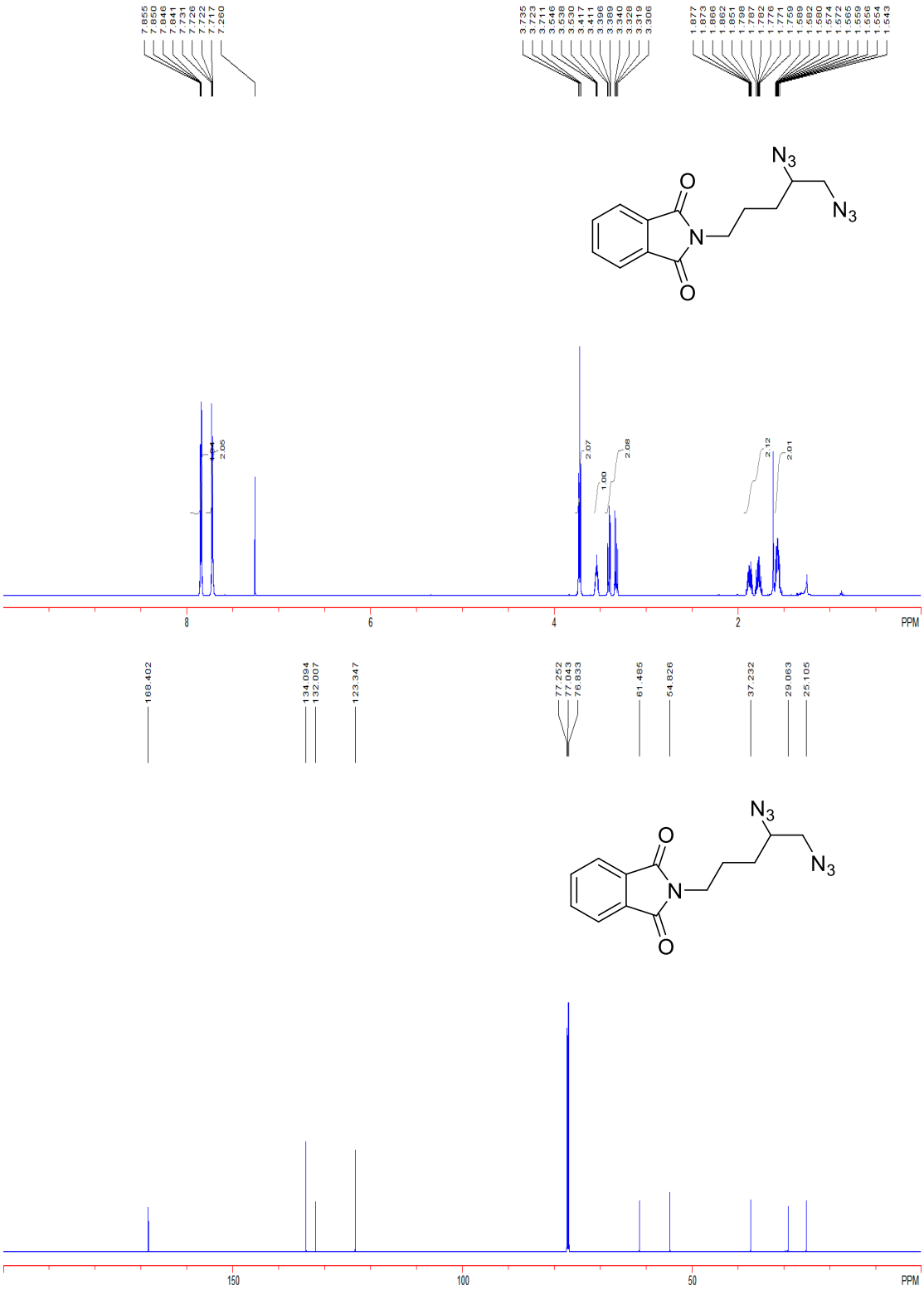




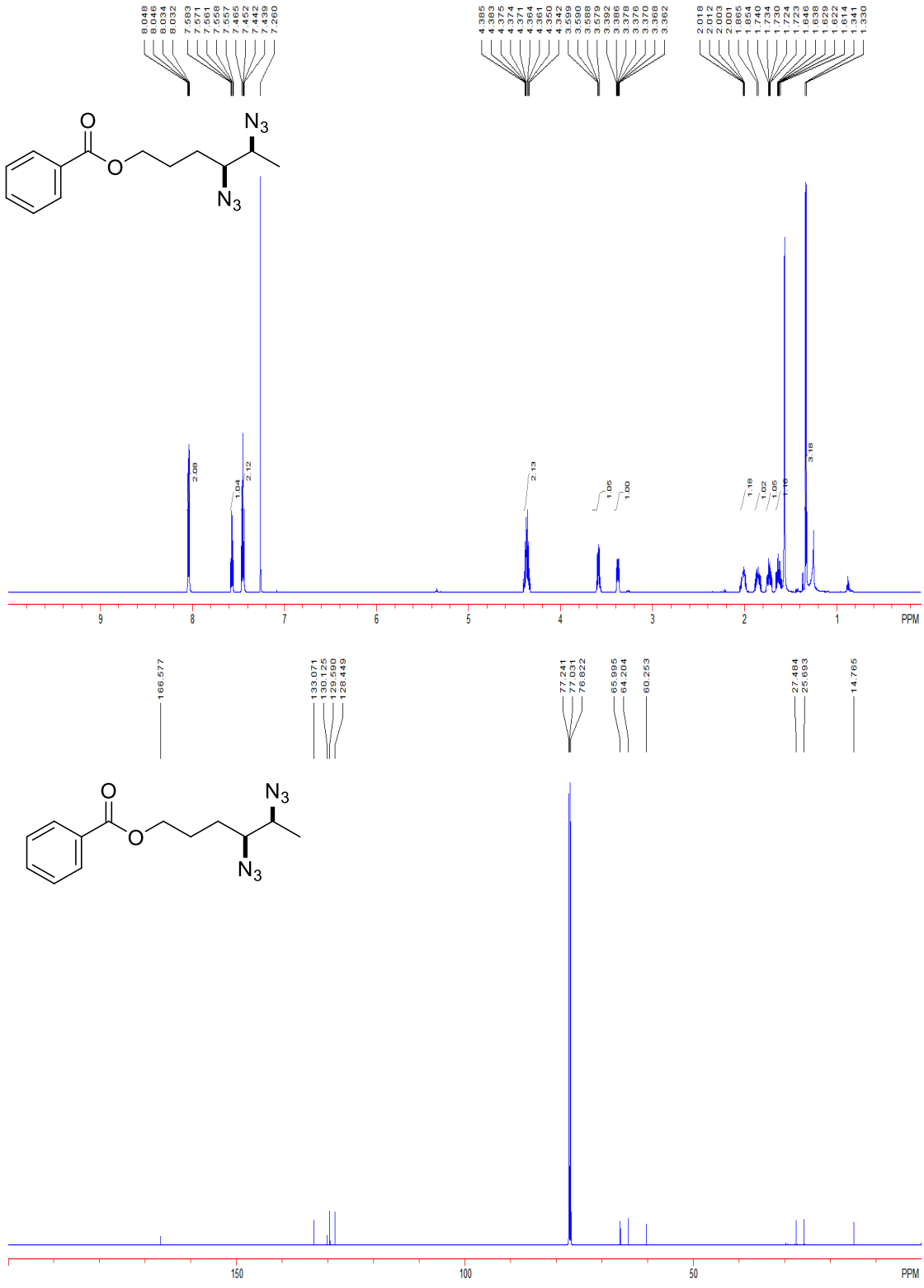




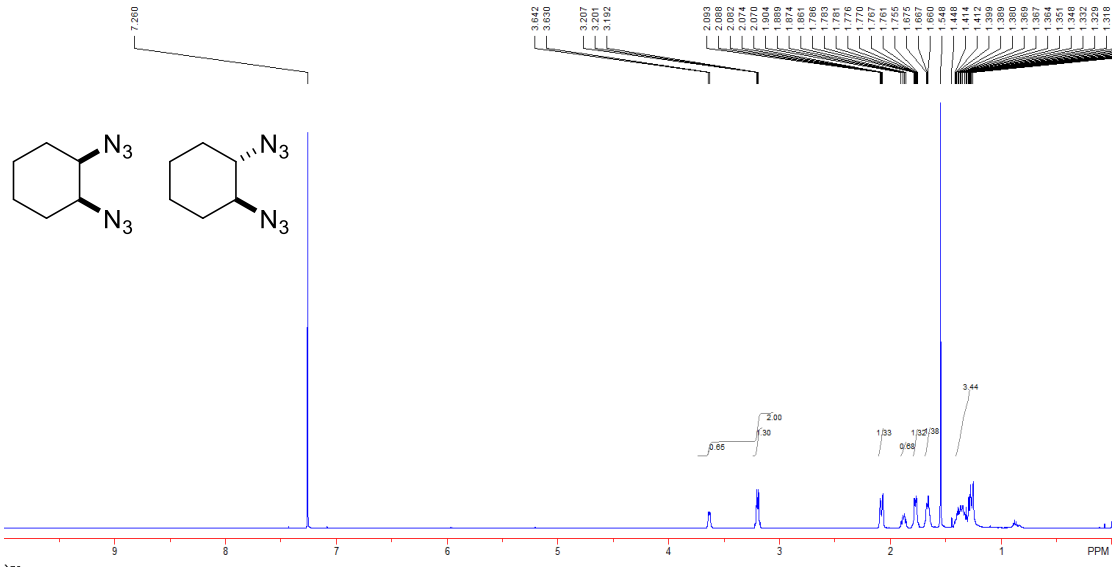
2-(4,5-diazidopentyl)isoindoline-1,3-dione (2ab) [$CDCl_3$, 600M]

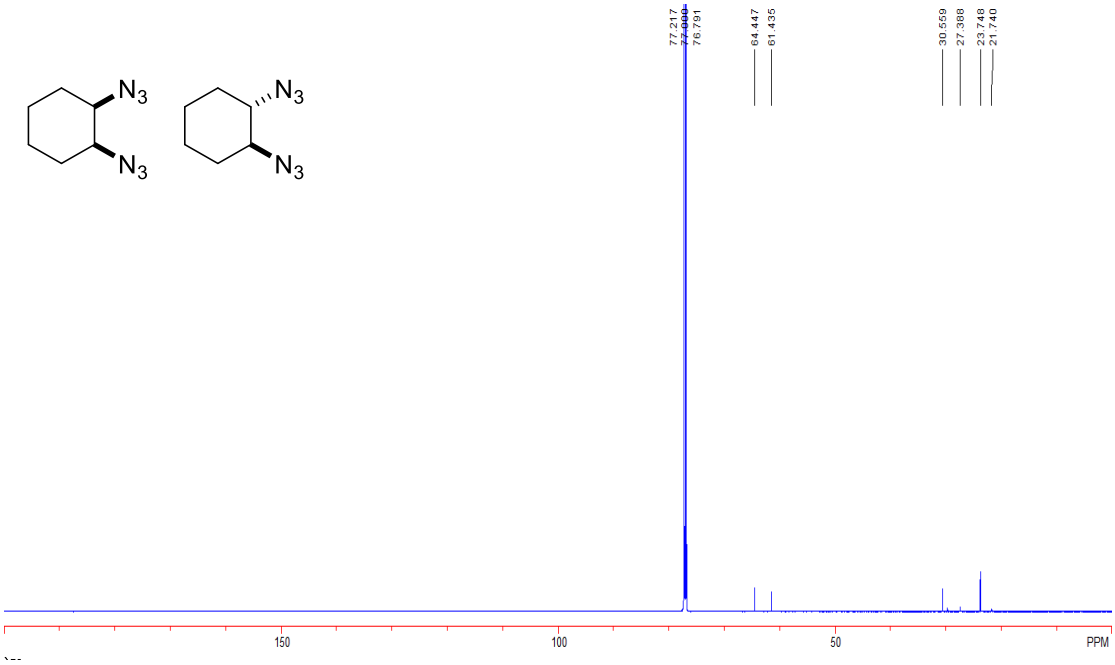


4,5-diazidohexyl benzoate (2ac) [$CDCl_3$, 600M]



1,2-diazidocyclohexane (2ad) [$CDCl_3$, 600M]





Compound 3 [$CDCl_3$, 600M]