Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Calculated Oxidation Potentials Predict Reactivity in Baeyer-Mills Reactions

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Supplementary Material

(47 pages)

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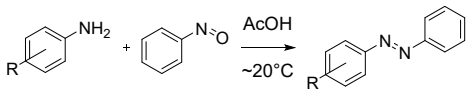
1. General Information

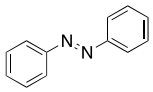
All reagents were obtained from commercial sources and reactions were performed using oven-dried glassware (120°C) under an inert N_2 atmosphere unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless-steel cannula. Organic solutions were concentrated under reduced pressure (~5 Torr) by rotary evaporation. Chromatography was performed using Fisher Chemical™ Silica Gel Sorbent (230–400 Mesh, Grade 60). Compounds purified by chromatography were typically applied to the adsorbent bed using the indicated solvent conditions with a minimum amount of added dichloromethane as needed for solubility. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates (250 μm). Visualization of the developed chromatogram was accomplished by fluorescence quenching or by staining with butanolic ninhydrin, or aqueous ceric ammonium molybdate (CAM).

Nuclear magnetic resonance (NMR) spectra were acquired on either a Bruker 400 operating at 400 and 100 MHz or a Varian 600 operating at 600 and 150 MHz for ^{1}H and ^{13}C, respectively, and are referenced internally according to residual solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectra were obtained using a Thermo Fisher Scientific Q-Exactive HF Orbitrap.

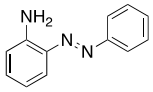
2. Detailed Synthesis Procedures and Experimental Data for all Compounds



General Procedure for Baeyer-Mills Reactions
A flask was sequentially charged with aniline or a substituted aniline (1.00 equiv), nitrosobenzene (1.00 equiv), and acetic acid (0.5 M). The mixture was stirred at ambient temperature for 24 h before being diluted with dichloromethane (40 mL) and 1 M $NaOH_{(aq)}$ (100 mL). The layers were separated, and the aqueous layer further extracted with dichloromethane (2 x 40 mL). The organic extracts were combined, washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The unpurified material was dissolved in an appropriate deuterated solvent, and NMR yields were determined using dibromomethane as an internal standard. The solution was concentrated under reduced pressure, and the residue was purified by chromatography on silica gel.



1,2-diphenyldiazene
Synthesized from aniline (0.093 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes → hexanes/dichloromethane (99:1) to afford 1,2-diphenyldiazene (0.117g, 70%) as an orange solid. The spectral data are consistent with existing literature.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 7.1 Hz, 4H), 7.59–7.48 (m, 6H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.8, 131.1, 129.2, 123.0 ppm.
HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{12}H_{11}N_2^+$ 183.0917, found 183.0924.



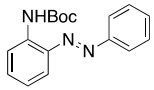
2-(phenyldiazenyl)aniline
A flask was charged with *tert*-butyl-(2-(phenyldiazenyl)phenyl)carbamate (0.170 g, 0.572 mmol, 1.00 equiv) and cooled to 0°C prior to the addition of dichloromethane/trifluoroacetic acid (1:1) (2.00 mL). The solution was slowly warmed to ambient temperature and stirred for 5 h. The solution was poured into 1 M $NaOH_{(aq)}$ (100 mL), and the mixture was extracted with dichloromethane (3 x 40 mL). The organic extracts

were combined, washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel with hexanes/EtOAc (20:1) to afford 2-(phenyldiazenyl)aniline (0.112 g, 99%) as an orange solid. The spectral data are consistent with existing literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 8.2 Hz, 3H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.29–7.23 (m, 1H), 6.91–6.84 (m, 1H), 6.80 (dd, *J* = 8.2, 0.9 Hz, 1H), 5.93 (br s, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.0, 143.0, 137.1, 132.4, 130.1, 129.2, 127.7, 122.3, 117.5, 117.1 ppm.

HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{12}H_{12}N_3^+$ 198.1025, found 198.1029.



***tert*-butyl-(2-(phenyldiazenyl)phenyl)carbamate**

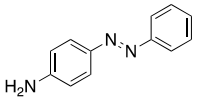
Synthesized from *tert*-butyl (2-aminophenyl)carbamate (0.208 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/EtOAc (50:1) → hexanes/EtOAc (20:1) to afford *tert*-butyl-(2-(phenyldiazenyl)phenyl)carbamate (0.241 g, 81%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.28 (br s, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.84 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.59–7.42 (m, 4H), 7.10 (t, *J* = 7.2 Hz, 1H), 1.60 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.6, 138.8, 137.0, 132.9, 131.2, 129.3, 122.8, 122.1, 120.4, 118.8, 80.8, 27.9 ppm

HRMS (ES^+): *m/z* $[M - C(O)O^tBu + 2H]^+$ calcd for $C_{12}H_{22}N_3^+$ 198.1031, found 198.1029.

LCMS (ES^+): *m/z* [M + H] calcd for $C_{17}H_{20}N_3O_2^+$ 298.1556 found 298.14.



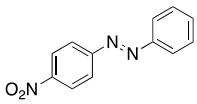
4-(phenyldiazenyl)aniline

Synthesized from 1,4-phenylenediamine (0.108 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/dichloromethane (1:1) → 100% dichloromethane to afford 4-(phenyldiazenyl)aniline (0.052 g, 26%) as an orange solid. The spectral data are consistent with existing literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 7.8 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 2H), 4.04 (br s, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.1, 149.7, 145.6, 129.9, 129.1, 125.2, 122.4, 114.7 ppm.

HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{12}H_{12}N_3^+$ 198.1023, found 198.1029.



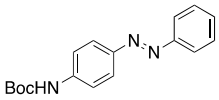
(4-nitrophenyl)-2-phenyldiazene

Synthesized from p-nitroaniline (0.138 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/dichloromethane (5:1) to afford (4-nitrophenyl)-2-phenyldiazene (0.040 g, 18%) as an orange solid. An analytical sample was prepared via recrystallization with hexanes. The spectral data are consistent with existing literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 9.0 Hz, 2H), 8.03 (d, *J* = 9.0 Hz, 2H), 8.00–7.95 (m, 2H), 7.60–7.53 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.8, 152.5, 148.9, 132.6, 129.5, 124.9, 123.6 ppm.

HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{12}H_{10}N_3O_2^+$ 228.0767, found 228.0770.



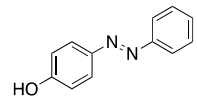
***tert*-butyl-(4-(phenyldiazenyl)phenyl)carbamate**

Synthesized from *tert*-butyl (4-aminophenyl)carbamate (0.208 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/EtOAc (50:1) to afford *tert*-butyl-(4-(phenyldiazenyl)phenyl)carbamate (0.270 g, 91%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94–7.88 (m, 4H), 7.55–7.47 (m, 4H), 7.47–7.42 (m, 1H), 6.80 (br s, 1H), 1.55 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.8, 152.5, 148.4, 141.2, 130.7, 129.2, 125.2, 122.8, 118.4, 81.2, 29.1 ppm.

HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{17}H_{20}N_3O_2^+$ 298.1547, found 298.1553.



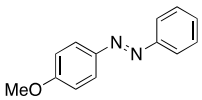
4-(phenyldiazenyl)phenol

Synthesized from *p*-aminophenol (0.109 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions, with the exception that the reaction mixture was diluted in H_2O instead of 1 M $NaOH_{(aq)}$. The residue was chromatographed on silica gel with hexanes/EtOAc (99:1) → hexanes/EtOAc (9:1) to afford 4-(phenyldiazenyl)phenol (0.067 g, 34%) as a yellow solid. The spectral data are consistent with existing literature.[4]

^{1}H NMR (400 MHz, DMSO-d_6) δ = 10.35 (br s, 1H), 7.87–7.78 (m, 4H), 7.58–7.43 (m, 3H), 6.96 (d, *J* = 8.8 Hz, 2H) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ = 161.0, 152.2, 145.3, 130.5, 129.4, 124.9, 122.2, 116.0 ppm.

HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{12}H_{11}N_2O^+$ 199.0865, found 199.0869.



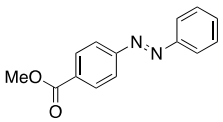
1-(4-methoxyphenyl)-2-phenyldiazene

Synthesized from *p*-anisidine (0.123 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/dichloromethane (3:1) to afford 1-(4-methoxyphenyl)-2-phenyldiazene (0.196 g, 92%) as an orange solid. The spectral data are consistent with existing literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.9 Hz, 2H), 7.96 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.1, 152.8, 147.0, 130.4, 129.1, 124.8, 122.7, 114.3, 55.6 ppm.

HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{13}H_{13}N_2O^+$ 213.1022, found 213.1025.

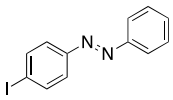


methyl-4-(phenyldiazenyl)benzoate

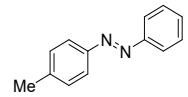
Synthesized from methyl-4-aminobenzoate (0.151 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/EtOAc (99:1) → hexanes/EtOAc (20:1) to afford methyl-4-(phenyldiazenyl)benzoate (0.178 g, 74%) as an orange solid. The spectral data are consistent with existing literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 4H), 7.55–7.48 (m, 3H), 3.95 (s, 3H) ppm.

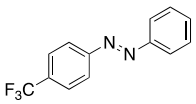
^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.6, 155.2, 152.6, 131.9, 131.8, 130.7, 129.3, 123.2, 122.7, 52.4 ppm.
HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{14}H_{13}N_2O_2^+$ 241.0969, found 241.0974.



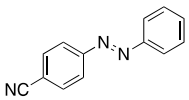
1-(4-iodophenyl)-2-phenyldiazene
Synthesized from 4-iodoaniline (0.219 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes → hexanes/dichloromethane (99:1) to afford 1-(4-iodophenyl)-2-phenyldiazene (0.276 g, 90%) as an orange solid. The spectral data are consistent with existing literature.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.56–7.47 (m, 3H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.5, 152.0, 138.4, 131.4, 129.2, 124.6, 123.1, 97.8 ppm.
HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{12}H_{10}IN_2^+$ 308.9882, found 308.9885.



1-phenyl-2-(*p*-tolyl)diazene
Synthesized from *p*-toluidine (0.107g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/dichloromethane (49:1) → hexanes/dichloromethane (19:1) to afford 1-phenyl-2-(*p*-tolyl)diazene (0.143 g, 73%) as an orange solid. The spectral data are consistent with existing literature.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 7.2 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.60–7.47 (m, 3H), 7.36 (d, *J* = 8.1 Hz, 2H), 2.48 (s, 3H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.8, 150.9, 141.6, 130.8, 129.8, 129.1, 123.0, 122.9, 21.6 ppm.
HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{13}H_{13}N_2^+$ 197.1070, found 197.1076.

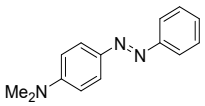


1-phenyl-2-(4-(trifluoromethyl)phenyl)diazene
Synthesized from 4-(trifluoromethyl)aniline (0.161 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/dichloromethane (10:1) → hexanes/dichloromethane (1:1) to afford 1-phenyl-2-(4-(trifluoromethyl)phenyl)diazene (0.207 g, 83%) as an orange solid. The spectral data are consistent with existing literature.[1]
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.00 (dd, *J* = 17.4, 6.9 Hz, 4H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 3H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ = 154.5, 152.5, 132.3 (q, $^2J_{CF}$ = 32.4 Hz), 131.9, 129.3, 126.4 (q, $^3J_{CF}$ = 3.7 Hz), 125.0, 123.3, 123.2 (q, $^1J_{CF}$ = 271.1 Hz) ppm.
HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{13}H_{10}F_3N_2^+$ 251.0790, found 251.0795.



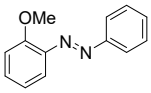
4-(phenyldiazenyl)benzonitrile
Synthesized from p-aminobenzonitrile (0.118 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes → hexanes/EtOAc (49:1) to afford 4-(phenyldiazenyl)benzonitrile (0.092 g, 44%) as an orange solid. The spectral data are consistent with existing literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98–7.91 (m, 4H), 7.8 (d, *J* = 8.5 Hz, 2H), 7.58–7.50 (m, 3H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.4, 152.3, 133.2, 132.3, 129.3, 123.3, 123.3, 118.5, 113.9 ppm.
HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{13}H_{10}N_3^+$ 208.0865, found 208.0872.

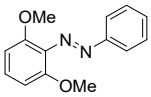


***N,N*-dimethyl-4-(phenyldiazenyl)aniline**
Synthesized from *N,N*-dimethyl-*p*-phenylenediamine (0.136 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/dichloromethane (5:1) → hexanes/dichloromethane (1:2) to afford *N,N*-dimethyl-4-(phenyldiazenyl)aniline (0.076 g, 34%) as an orange solid. The spectral data are consistent with existing literature.[6]

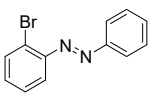
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 9.1 Hz, 2H), 7.87 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 9.1 Hz, 2H), 3.08 (s, 6H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.3, 152.5, 143.8, 129.5, 129.1, 125.1, 122.3, 111.6, 40.4 ppm.
HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{14}H_{16}N_3^+$ 226.1338, found 226.1340.



1-(2-methoxyphenyl)-2-phenyldiazene
Synthesized from 2-methoxyaniline (0.123 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/dichloromethane (4:1) → hexanes/dichloromethane (2:1) to afford *1*-(2-methoxyphenyl)-2-phenyldiazene (0.170 g, 80%) as a red oil. The spectral data are consistent with existing literature.[7]
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 7.6 Hz, 2H), 7.75 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.53–7.43 (m, 2H), 7.14–7.03 (m, 2H), 4.04 (s, 3H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.0, 153.2, 142.3, 132.5, 130.8, 129.0, 123.0, 120.7, 116.9, 112.8, 56.3 ppm.
HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{13}H_{13}N_2O^+$ 213.1028, found 213.1022.

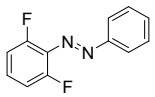


1-(2,6-dimethoxyphenyl)-2-phenyldiazene
Synthesized from 2,6-dimethoxyaniline (0.153 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/dichloromethane (1:1) → hexanes/dichloromethane (1:2) to afford 1-(2,6-dimethoxyphenyl)-2-phenyldiazene (0.108 g, 45%) as an orange solid. The spectral data are consistent with existing literature.[8]
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 7.6 Hz, 2H), 7.57–7.46 (m, 3H), 7.27 (t, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 6H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.4, 152.4, 133.9, 130.9, 129.5, 129.0, 122.7, 105.2, 56.5 ppm.
HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{14}H_{15}N_2O_2^+$ 243.1134, found 243.1132.

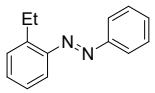


1-(2-bromophenyl)-2-phenyldiazene
Synthesized from 2-bromoaniline (0.172 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/dichloromethane (10:1) →

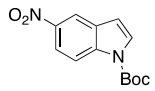
hexanes/dichloromethane (5:1) to afford 1-(2-bromophenyl)-2-phenyldiazene (0.125 g, 48%) as an orange solid. The spectral data are consistent with existing literature.[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.60–7.52 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.7, 149.7, 133.8, 132.0, 131.7, 129.3, 128.1, 125.9, 123.5, 117.9 ppm.
HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{12}H_{10}BrN_2^+$ 261.0027, found 261.0027.



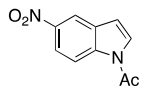
1-(2,6-difluorophenyl)-2-phenyldiazene
Synthesized from 2,6-difluoroaniline (0.129 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/dichloromethane (8:1) to afford 1-(2,6-difluorophenyl)-2-phenyldiazene (0.027 g, 12%) as an orange oil. The spectral data are consistent with existing literature.[9]
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98–7.90 (m, 2H), 7.57–7.50 (m, 3H), 7.36–7.28 (m, 1H), 7.05 (t, *J* = 8.7 Hz, 2H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.9 (dd, $^1J_{CF}$ = 257.0 Hz, 4.4 Hz),153.4, 132.1, 131.6, 130.4 (t, $^2J_{CF}$ = 10.3 Hz), 129.3, 128.8, 123.1, 118.9, 112.7 (m), 111.9 ppm. There is mixture of isomers present in this sample and all peaks are reported.
HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{12}H_9F_2N_2^+$ 219.0734, found 219.0731.



1-(2-ethylphenyl)-2-phenyldiazene
Synthesized from 2-ethylaniline (0.121 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/dichloromethane (4:1) to afford 1-(2-ethylphenyl)-2-phenyldiazene (0.157 g, 75%) as a red oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 2H), 7.59–7.45 (m, 3H), 7.43–7.37 (m, 1H), 3.32 (q, *J* = 7.6 Hz, 2H), 1.46 (t, *J* = 7.6 Hz, 3H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.1, 150.3, 144.3, 131.3, 130.8, 129.9, 129.2, 126.6, 123.1, 115.4, 24.8, 16.6 ppm.
HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{14}H_{15}N_2^+$ 211.1235, found 211.1232.



***tert*-butyl 5-nitro-1*H*-indole-1-carboxylate**
A flask was charged with 5-nitro-1H-indole (1.00 g, 6.17 mmol, 1.00 equiv), di-tert-butyl dicarbonate (2.69 g, 12.3 mmol, 2.00 equiv), 4-dimethylaminopyridine (0.113 g, 0.925 mmol, 0.150 equiv), and THF (44.0 mL). The solution was stirred at ambient temperature for 1 h. The mixture was diluted in water H_2O (200 mL) and extracted with EtOAc (3 x 150 mL). The organic extracts were combined, washed with brine (100 mL), dried over Na_2SO_4, and concentrated under reduced pressure to afford *tert*-butyl 5-nitro-1*H*-indole-1-carboxylate (1.56 g, 96%) as a dark tan solid. The spectral data are consistent with existing literature.[10]
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 (d, *J* = 1.5 Hz, 1H), 8.22–8.06 (m, 2H), 7.69 (d, *J* = 3.5 Hz, 1H), 6.64 (d, *J* = 3.6 Hz, 1H), 1.67 (s, 9H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.9, 143.6, 138.2, 130.3, 128.9, 119.3, 117.1, 115.2, 107.8, 85.2, 28.1 ppm.

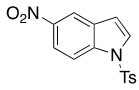


1-(5-nitro-1*H*-indol-1-yl)ethan-1-one

Following a literature procedure,[11] triethylamine (1.27 mL, 9.13 mmol, 1.48 equiv), acetic anhydride (2.45 g, 24.0 mmol, 3.89 equiv), and 4-dimethylaminopyridine (0.151 g, 1.23 mmol, 0.200 equiv) were added to a stirred solution of 5-nitro-1H-indole (1.00 g, 6.17 mmol, 1.00 equiv) in 1,2-dichloroethane (14.2 mL). The flask was equipped with a reflux condenser, placed under N_2 atmosphere, and the solution was stirred at 60°C for 8 h. The solution was diluted with EtOAc (100 mL) and then washed with saturated $NH_4Cl_{(aq)}$ (120 mL). The aqueous layer was further extracted with EtOAc (3 x 50 mL). The organic extracts were combined, washed with brine (100 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was suspended in Et_2O (10 mL), filtered, and washed with additional Et_2O (2 x 10 mL) to afford 1-(5-nitro-1*H*-indol-1-yl)ethan-1-one (1.07 g, 85%) as a brown solid. The spectral data are consistent with existing literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55 (d, *J* = 9.2 Hz, 1H), 8.47 (d, *J* = 2.0 Hz, 1H), 8.22 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.59 (d, *J* = 3.7 Hz, 1H), 6.79 (d, *J* = 3.7 Hz, 1H), 2.69 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.8, 144.4, 138.6, 130.4, 128.2, 120.5, 117.2, 116.9, 109.7, 24.1 ppm.

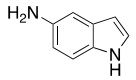


5-nitro-1-tosyl-1*H*-indole

Following a modified procedure,[12] a flask was charged with sodium hydride (60% dispersion in mineral oil) (0.369 g, 9.25 mmol, 1.50 equiv), washed with hexanes, and dried under a stream of N_2. Next, THF (12.0 mL) was added, and the mixture was cooled to 0°C. A solution of 5-nitro-1H-indole (1.00 g, 6.17 mmol, 1.00 equiv) in THF (6.00 mL) was added slowly before warming to ambient temperature and stirring for 1 h. A solution of tosyl chloride (1.76 g, 9.25 mmol, 1.50 equiv) in THF (6.00 mL) was added slowly, and the solution was stirred 24 h at ambient temperature. The mixture was poured into saturated $NaHCO_{3(aq)}$ (100 mL) and extracted with EtOAc (3 x 100 mL). The organic extracts were combined, washed with brine (100 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel with hexanes/EtOAc (9:1) → hexanes/EtOAc (3:2) to afford 5-nitro-1-tosyl-1*H*-indole (1.84 g, 95%) as a brown solid. The spectral data are consistent with existing literature.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.46 (d, *J* = 1.6 Hz, 1H), 8.19 (dd, *J* = 9.4 Hz, *J* = 1.9 Hz, 1H), 8.08 (d, *J* = 9.1 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 3.6 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 3.5 Hz, 1H), 2.36 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.0, 144.2, 137.6, 134.7, 130.6, 130.3, 129.3, 127.0, 119.8, 117.9, 113.7, 109.5, 21.7 ppm.

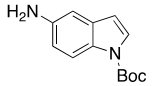


1*H*-indol-5-amine

A flask was sequentially charged with 5-nitro-1*H*-indole (1.00 g, 6.17 mmol, 1.00 equiv), palladium on carbon (10% wt) (0.100 g), and MeOH (30.0 mL). The solution was placed under an H_2 atmosphere and allowed to stir at ambient temperature for 24 h. The mixture was filtered through celite, and the filter cake was washed with MeOH (150 mL). The solution was concentrated under reduced pressure, and the resulting residue was purified by chromatography on silica gel with hexanes/EtOAc (1:1) to afford 1*H*-indol-5-amine (0.493 g, 60%) as a brown solid. The spectral data are consistent with existing literature.[10]

^{1}H NMR (400 MHz, $MeOD_4$) δ = 7.18 (d, *J* = 8.5 Hz, 1H), 7.12 (d, *J* = 3.1 Hz, 1H), 6.96 (d, *J* = 1.8 Hz, 1H), 6.67 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.26 (dd, *J* = 3.1, 0.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $MeOD_4$) δ = 139.6, 133.0, 130.2, 125.9, 114.2, 112.4, 107.5, 101.3 ppm.



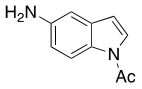
***tert*-butyl 5-amino-1*H*-indole-1-carboxylate**

A flask was sequentially charged with *tert*-butyl 5-nitro-1*H*-indole-1-carboxylate (1.00 g, 3.81 mmol, 1.00 equiv), palladium on carbon (10% wt) (0.100 g), and MeOH (19.0 mL). The solution was placed under an

H_2 atmosphere and allowed to stir at ambient temperature for 14 h. The mixture was filtered through celite, and the filter cake was washed with MeOH (150 mL). The solution was concentrated under reduced pressure, and the resulting residue was purified by chromatography on silica gel with hexanes/EtOAc (4:1) to afford *tert*-butyl 5-amino-1*H*-indole-1-carboxylate (0.715 g, 80%) as a viscous light brown oil. The spectral data are consistent with existing literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 5.5 Hz, 1H), 7.54 (d, *J* = 2.2 Hz, 1H), 6.82 (d, *J* = 2.2 Hz, 1H), 6.72 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.41 (d, *J* = 3.6 Hz, 1H), 3.61 (br s, 2H), 1.67 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.8, 142.1, 131.6, 129.1, 126.2, 115.7, 113.6, 106.8, 105.9, 83.2, 28.2 ppm.



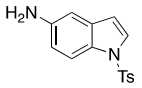
1-(5-amino-1*H*-indol-1-yl)ethan-1-one

A flask was sequentially charged with 1-(5-nitro-1*H*-indol-1-yl)ethan-1-one (0.600 g, 2.94 mmol, 1.00 equiv), palladium on carbon (10% wt) (0.060 g,), and MeOH (14.7 mL). The solution was placed under an H_2 atmosphere and allowed to stir at ambient temperature for 13 h. The mixture was filtered through celite, and the filter cake was washed with MeOH (150 mL). The solution was concentrated under reduced pressure, and the resulting residue was purified by chromatography on silica gel with dichloromethane/EtOAc (20:1) to afford 1-(5-amino-1*H*-indol-1-yl)ethan-1-one (0.284 g, 56%) as a tan solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 5.9 Hz, 1H), 7.31–7.21 (m, 1H), 6.78 (d, *J* = 2.2, 1H), 6.70 (dd, *J* = 6.4, 2.3 Hz, 1H), 6.43 (d, *J* = 3.7 Hz, 1H), 3.67 (br s, 2H), 2.52 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.2, 143.0, 131.6, 129.4, 125.7, 117.1, 114.1, 108.2, 105.7, 23.6 ppm.

HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{10}H_{11}N_2O^+$ 175.0865, found 175.0868.

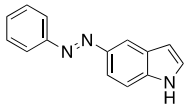


1-tosyl-1*H*-indol-5-amine

Following a modified procedure,[12] a flask was charged with 5-nitro-1-tosyl-1*H*-indole (0.500 g, 1.58 mmol, 1.00 equiv), palladium on carbon (10% wt) (0.050 g), and a MeOH/DMF (5:4) solution (17.2 mL). The solution was placed under an H_2 atmosphere and allowed to stir at ambient temperature for 68 h. The mixture was filtered over celite, and the filter cake was washed with EtOAc (150 mL). The filtrate was added to H_2O (300 mL) and the layers were separated. The aqueous layer was further extracted with EtOAc (2 x 150 mL). The organic layers were combined, washed with brine (2 x 200 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel with hexanes/EtOAc (3:1) → hexanes/EtOAc (3:2) to afford 1-tosyl-1*H*-indol-5-amine (0.322 g, 71%) as a pale yellow semi-solid. The spectral data are consistent with existing literature.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 3.6 Hz, 1H), 7.19 (d. *J* = 8.1 Hz, 2H), 6.76 (d. *J* = 2.1 Hz, 1H), 6.69 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.48 (dd, *J* = 3.6, 0.4 Hz, 1H), 3.60 (br s, 2H), 2.33 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.8, 142.8, 135.4, 132.2, 129.9, 129.1, 127.1, 126.9, 114.5, 114.2, 109.1, 106.1, 21.7 ppm.



5-(phenyldiazenyl)-1*H*-indole

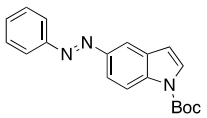
A flask was charged with t*ert*-butyl-5-(phenyldiazenyl)-1*H*-indole-1-carboxylate (0.100 g, 0.311 mmol, 1.00 equiv) and cooled to 0°C prior to the addition of a dichloromethane/trifluoroacetic acid (1:1) solution (2.00 mL). The solution was slowly warmed to ambient temperature and stirred for 1 h. The solution was added to 1 M $NaOH_{(aq)}$ (50 mL) and extracted with dichloromethane (3 x 50 mL). The organic extracts were combined, washed with brine (50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was chromatographed on silica with hexanes/dichloromethane (4:1) → hexanes/dichloromethane

(2:1) to afford 5-(phenyldiazenyl)-1*H*-indole (0.025 g, 36%) as an orange solid. The spectral data are consistent with existing literature.[14]

^{1}H NMR (400 MHz, $MeOD_4$) δ = 8.21 (d, *J* = 1.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.81 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.56–7.42 (m, 4H), 7.33 (d, *J* = 3.1 Hz, 1H), 6.64 (dd, *J* = 3.2, 1.0 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $MeOD_4$) δ = 154.3, 148.1, 139.6, 131.1, 130.1, 129.5, 127.4, 123.3, 120.5, 115.4, 112.7, 104.4 ppm.

HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{14}H_{12}N_3^+$ 222.1025, found 222.1029.



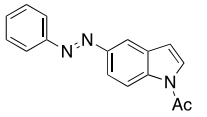
***tert*-butyl-5-(phenyldiazenyl)-1*H*-indole-1-carboxylate**

Synthesized from *tert*-butyl 5-amino-1*H*-indole-1-carboxylate (0.232g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was chromatographed on silica with hexanes/EtOAc (20:1) to afford *tert*-butyl-6-(phenyldiazenyl)-1*H*-indole-1-carboxylate (0.171 g, 53%) as a red oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.30 (d, *J* = 8.7 Hz, 1H), 8.19 (d, *J* = 1.5 Hz, 1H), 8.00 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 3.5 Hz, 1H), 7.57–7.45 (m, 3H), 6.71 (d, *J* = 3.6 Hz, 1H), 1.71 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.9, 149.6, 148.8, 136.9, 131.1, 130.6, 129.1, 127.4, 122.8, 119.0, 117.0, 115.6, 108.3, 84.3, 28.3 ppm.

HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{19}H_{20}N_3O_2^+$ 322.1549, found 322.1555.



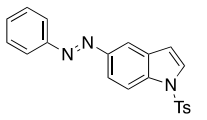
(*E*)-1-(5-(phenyldiazenyl)-1*H*-indol-1-yl)ethan-1-one

Synthesized from 1-tosyl-1*H*-indol-5-amine (0.286g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes → hexanes/EtOAc (9:1) to afford 1-(5-(phenyldiazenyl)-1H-indol-1-yl)ethan-1-one (0.134 g, 51%) as a red solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.54 (d, *J* = 8.8 Hz, 1H), 8.12 (d, *J* = 1.7 Hz, 1H), 8.02–7.93 (m, 3H), 7.56–7.44 (m, 3H), 7.39 (d, *J* = 3.7 Hz, 1H), 6.69 (d, *J* = 3.7 Hz, 1H), 2.57 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.6, 152.7, 149.2, 137.0, 130.9, 130.7, 129.1, 126.6, 122.8, 119.9, 116.9, 116.4, 109.9, 23.9 ppm.

HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{16}H_{14}N_3O^+$ 264.1131, found 264.1135.



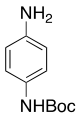
5-(phenyldiazenyl)-1-tosyl-1*H*-indole

Synthesized from 1-tosyl-1*H*-indol-5-amine (0.286 g, 1.00 mmol, 1.00 equiv), nitrosobenzene (0.107 g, 1.00 mmol, 1.00 equiv), and acetic acid (2.00 mL) following the general procedure for Baeyer-Mills reactions. The residue was purified by chromatography on silica gel with hexanes/EtOAc (49:1) → hexanes/EtOAc (9:1) to afford 5-(phenyldiazenyl)-1-tosyl-1H-indole (0.134 g, 46%) as a red solid. The spectral data are consistent with existing literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16–8.11 (m, 2H), 8.00–7.91 (m, 3H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 3.6 Hz, 1H), 7.56–7.44 (m, 3H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.78 (d, *J* = 3.6 Hz, 1H), 2.31 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.7, 149.2, 145.4, 136.3, 135.1, 131.3, 130.9, 130.1, 129.2, 127.8, 126.9, 122.8, 119.0, 117.6, 114.0, 109.9, 21.6 ppm.

HRMS (ES^+): *m/z* $[M + H]^+$ calcd for $C_{21}H_{17}N_3O_2S^+$ 376.1113, found 376.1119.

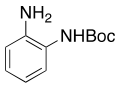


***tert*-butyl (4-aminophenyl)carbamate**

A flask was sequentially charged with 1,4-phenylenediamine (1.00 g, 9.25 mmol, 1.00 equiv), di-tert-butyl dicarbonate (2.02 g, 9.25 mmol, 1.0 equiv), dichloromethane (18.5 mL), and triethylamine (1.29 mL, 9.25 mmol, 1.00 equiv). The solution was stirred at ambient temperature for 18 h. The resulting mixture was added to 1 M $NaOH_{(aq)}$ (200 mL) and extracted with dichloromethane (3 x 100 mL). The organic extracts were combined, washed with brine (200 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel with hexanes/EtOAc (4:1) to afford *tert*-butyl (4-aminophenyl)carbamate (0.987 g, 51%) as an off-white solid. The spectral data are consistent with existing literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 (d, *J* = 7.6 Hz, 2H), 6.58 (d, *J* = 8.7 Hz, 2H), 6.55 (br s, 1H), 3.54 (br s, 2H), 1.49 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.5, 142.4, 129.7, 121.0, 115.6, 79.9, 28.4 ppm.



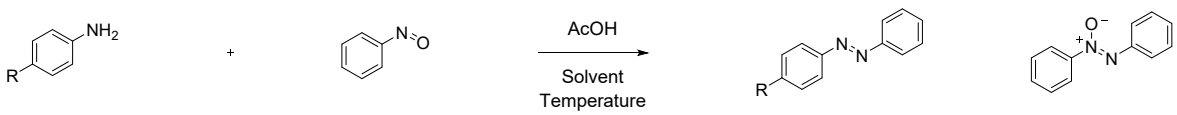
***tert*-butyl (2-aminophenyl)carbamate**

A flask was sequentially charged with 1,2-phenylenediamine (1.00 g, 9.25 mmol, 1.00 equiv), di-tert-butyl dicarbonate (2.02 g, 9.25 mmol, 1.00 equiv), dichloromethane (18.5 mL), and triethylamine (1.29 mL, 9.25 mmol, 1.00 equiv). The solution was stirred at ambient temperature for 18 h. The resulting mixture was added to 1 M $NaOH_{(aq)}$ (200 mL) and extracted with dichloromethane (3 x 100 mL). The organic extracts were combined, washed with brine (200 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel with hexanes/EtOAc (5:1) to afford *tert*-butyl (2-aminophenyl)carbamate (1.332 g, 69%) as an off-white solid. The spectral data are consistent with existing literature.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 7.7 Hz, 1H), 6.99 (td, *J* = 7.7, 1.3 Hz, 1H), 6.81–6.72 (m, 2H), 6.36 (br s, 1H), 3.74 (br s, 2H), 1.52 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.0, 140.1, 126.2, 124.8, 119.6, 117.6, 80.5, 28.4 ppm.

3. Table S1



Entry	R	Solvent	Temperature (°C)	AcOH (equiv)	Azobenzene % Yield[a]	Azoxybenzene % Yield[a]
1	*p*-NO_2	AcOH	Ambient	-	19	≤5
2	*p*-H	AcOH	Ambient	-	≥95	≤5
3	*p*-NH_2	AcOH	Ambient	-	28	43
4	*p*-NO_2	AcOH	80	-	45	38
5	*p*-H	AcOH	80	-	93	7
6	*p*-NH_2	AcOH	80	-	9	37
7	*p*-NO_2	DCM	Ambient	10	7	≤5
8	*p*-H	DCM	Ambient	10	92	≤5
9	*p*-NH_2	DCM	Ambient	10	60	11
10	*p*-NO_2	DCM	40	10	25	9
11	*p*-H	DCM	40	10	90	≤5
12	*p*-NH_2	DCM	40	10	79	14
13	*p*-NO_2	EtOH	Ambient	10	≤5	9

14	*p*-H	EtOH	Ambient	10	89	≤5
15	*p*-NH_2	EtOH	Ambient	10	74	10
16	*p*-NO_2	EtOH	80	10	17	61
17	*p*-H	EtOH	80	10	88	4
18	*p*-NH_2	EtOH	80	10	70	10

Table S1. Reaction of substituted anilines with nitrosobenzene. Reagents and conditions: appropriate aniline (1.0 eq.), nitrosobenzene (1.0 eq.), solvent/AcOH (0.5 M), 24 h. [a]Yield determined by ^{1}H NMR using dibromomethane as an internal standard.

4. Computational Experiments and Table S2

Calculations were performed in Gaussian 16 A.03. A Born-Haber cycle was applied for solvation corrections to the gas phase free energy calculations. All compounds were modeled in their unprotonated state. B3LYP/6-31+G(d,p) was used for all calculations, except in the case of p-iodoaniline where LANL2DZ with an effective core potential was used for the iodine and 6-31+G(d,p) was used for the remaining atoms. The default ultrafine integration grid was utilized. Compounds were first optimized to a minimum in the gas phase and the absence of imaginary frequencies was confirmed in each case. For solvation corrections to free energies, gas phase stationary points were submitted to a single point calculation with the addition of an implicit SMD solvation model for acetic acid. Oxidation potentials were then calculated relative to the standard hydrogen electrode according to equation S1, where *n* is the number of electrons transferred (n=1 in this work), *F* is Faraday's constant (23.061 kcal V^{-1} mol^{-1}), and *SHE* is the standard hydrogen electrode potential (4.28 V). Coordinates for the located stationary points for both neutral molecules and radical cations in the gas phase are included in the provided mol2 files.

$$E_{ox} = -\left(\frac{-\Delta G^{\circ}_{rxn}}{nF} - SHE\right) \quad \text{(S1)}$$

Compound	Neutral Molecule G_{gas} (Hartree)	Neutral Molecule ΔG_{solv} (kcal/mol)	Radical Cation G_{gas} (Hartree)	Radical Cation ΔG_{solv} (kcal/mol)
aniline	-287.543166	-5.45	-287.268563	-51.45
2-aminoanline	-342.889673	-6.84	-342.634169	-51.74
3-aminoaniline	-342.890082	-7.82	-342.636473	-49.62
4-aminoaniline	-342.88709	-8.04	-342.649399	-49.64
2-nitroanline	-492.060279	-3.6	-491.75808	-51.2
3-nitroanline	-492.055655	-4.07	-491.75604	-55
4-nitroanline	-492.059645	-5.85	-491.753854	-55.13
tert-butyl (2-aminophenyl)carbamate	-688.631121	-6.63	-688.378494	-42.58
tert-butyl (3-aminophenyl)carbamate	-688.634	-7.49	-688.374735	-45.8
tert-butyl (4-aminophenyl)carbamate	-688.631312	-7.82	-688.385417	-44.96
2,6-difluoroaniline	-486.04106	-4.09	-485.75183	-51.21
2-bromoaniline	-2858.682723	-5.68	-2858.403413	-48.59
4-iodoaniline	-298.327988	-5.35	-298.057175	-49.94
4-methylaniline	-326.839371	-5.28	-326.57614	-49.38
2-ethylaniline	-366.126643	-5.85	-365.859987	-49.5
4-(trifluoromethyl)aniline	-624.607488	-6.17	-624.311447	-54.76
4-cyanoylaniline	-379.795717	-7.9	-379.501704	-56.12
4-aminophenol	-362.763185	-7.88	-362.505192	-51.87

2-methoxyaniline	-402.04284	-4.64	-401.785701	-45.96
4-methoxyaniline	-402.040172	-5.52	-401.789032	-46.72
2,6-dimethoxyaniline	-516.297078	-3.95	-516.297078	-41.33
methyl 4-aminobenzoate	-515.401282	-5.92	-515.119971	-49.49
N^1,N^1-dimethylbenzene-1,4-diamine	-421.448526	-6.95	-421.223345	-45.33
5-aminoindole	-419.090246	-8.3	-418.842741	-48.45
tert-butyl 5-amino-1H-indole-1-carboxylate	-764.827619	-6.51	-764.578334	-42.79
1-(5-amino-1H-indol-1-yl)ethan-1-one	-571.720384	-7.63	-571.464619	-47.01
1-(phenylsulfonyl)-1H-indol-5-amine	-1198.644791	-8.94	-1198.392119	-45.08

Table S2. Neutral molecule and radical cation Gibbs free energies and solvation free energies as computed per the computational details above. The values were utilized with the necessary unit conversions in the calculation of oxidation potentials using Equation S1 above.

5. Supplemental References

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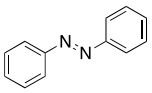
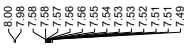
6. ^{1}H and ^{13}C NMR Spectra

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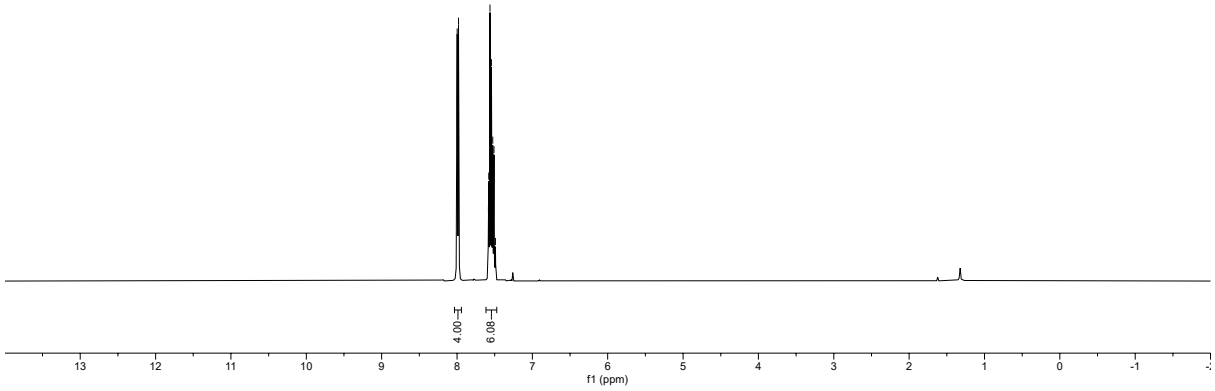
7.51
7.49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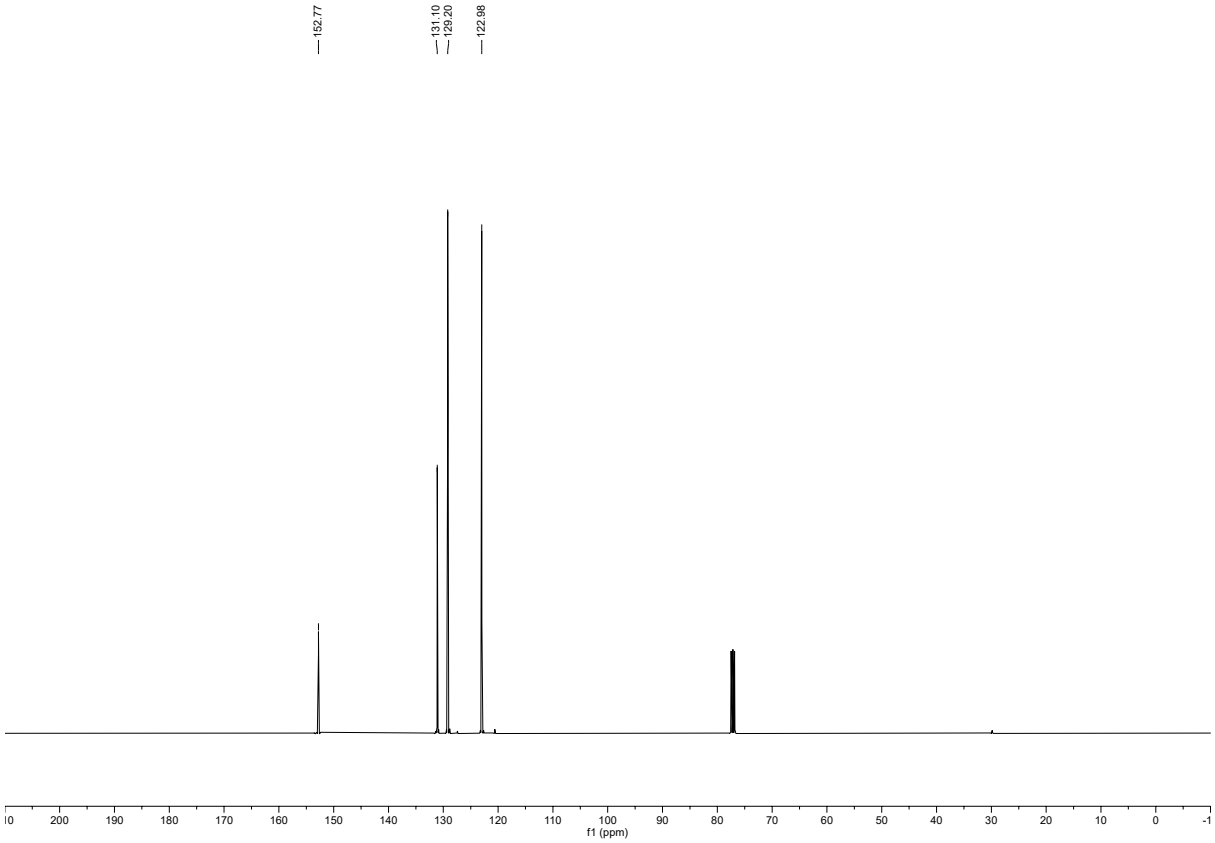
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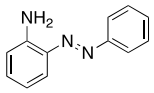
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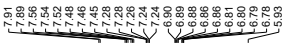
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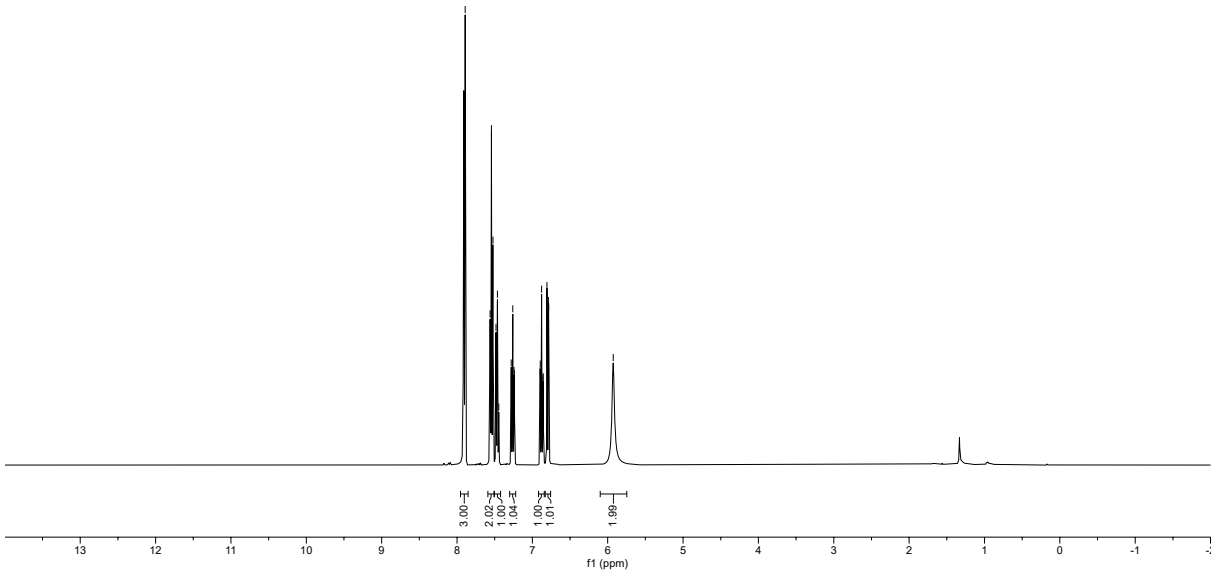
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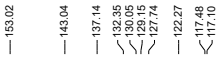
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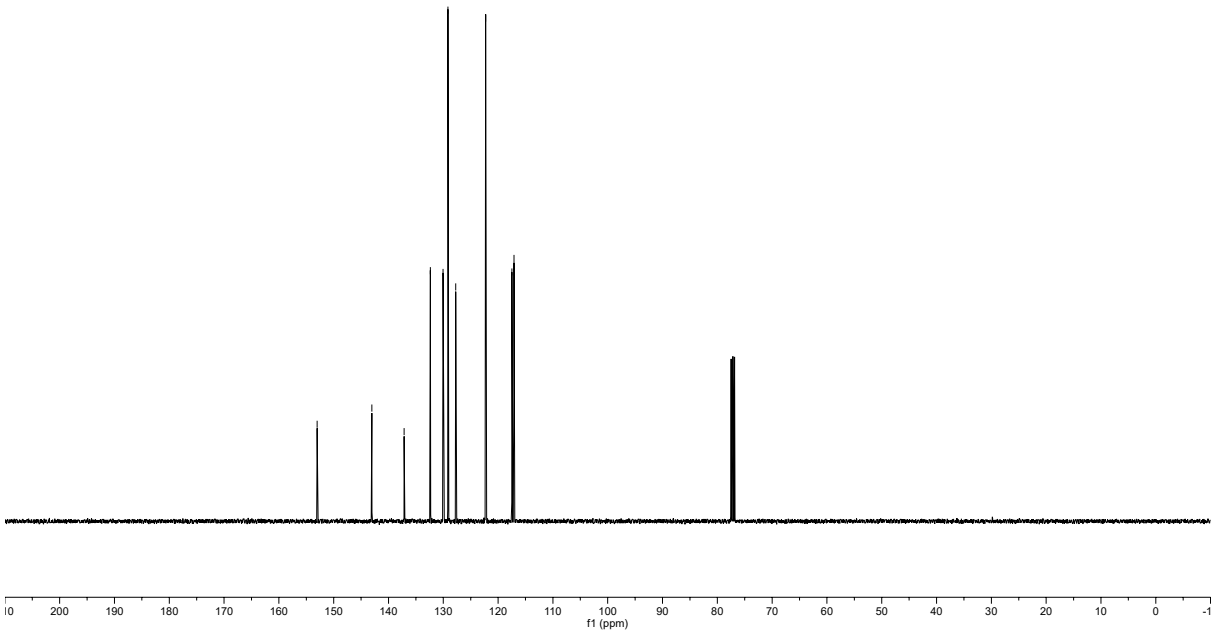
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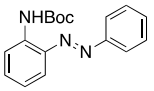
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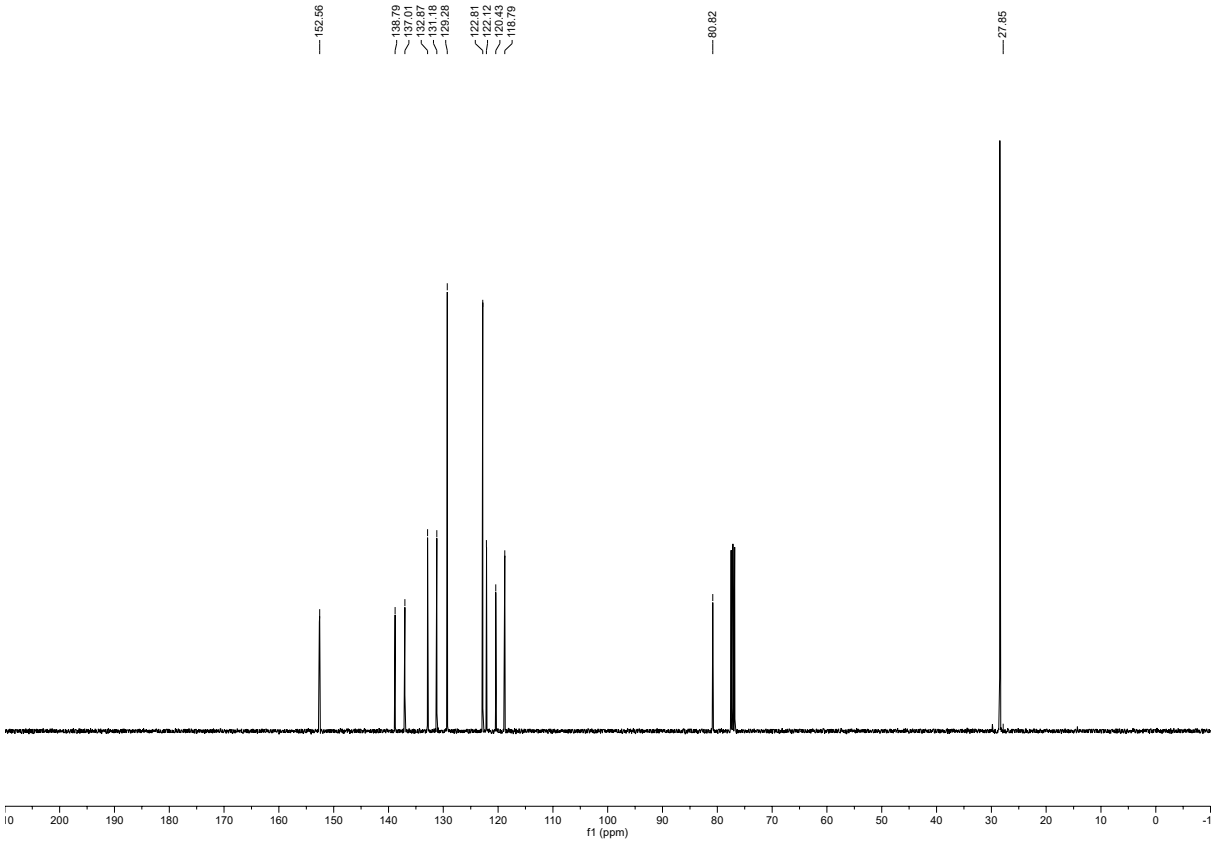
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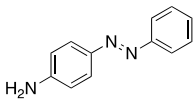


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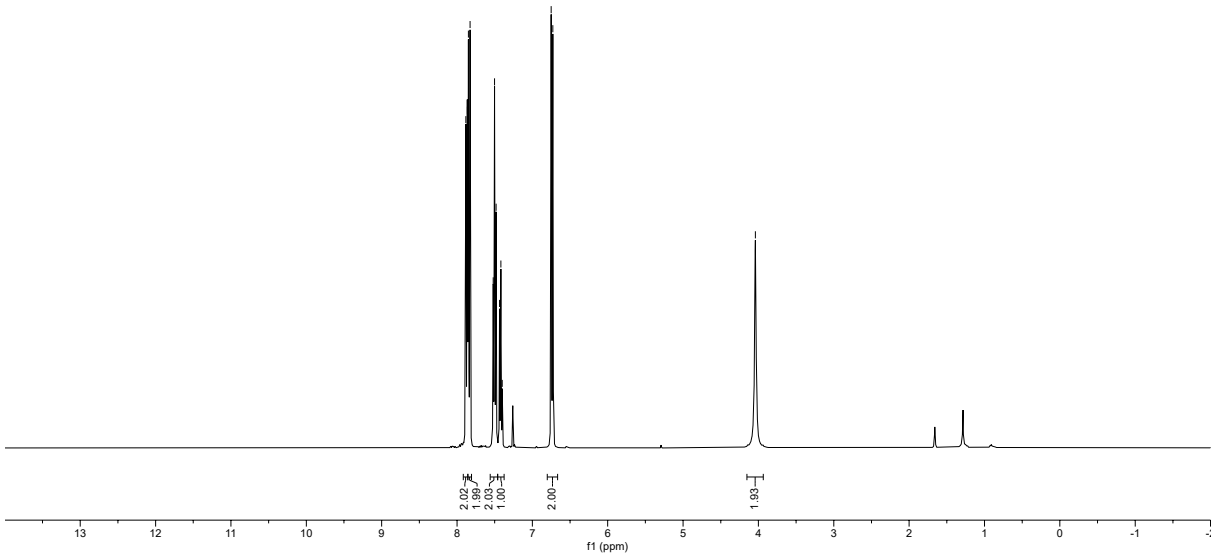
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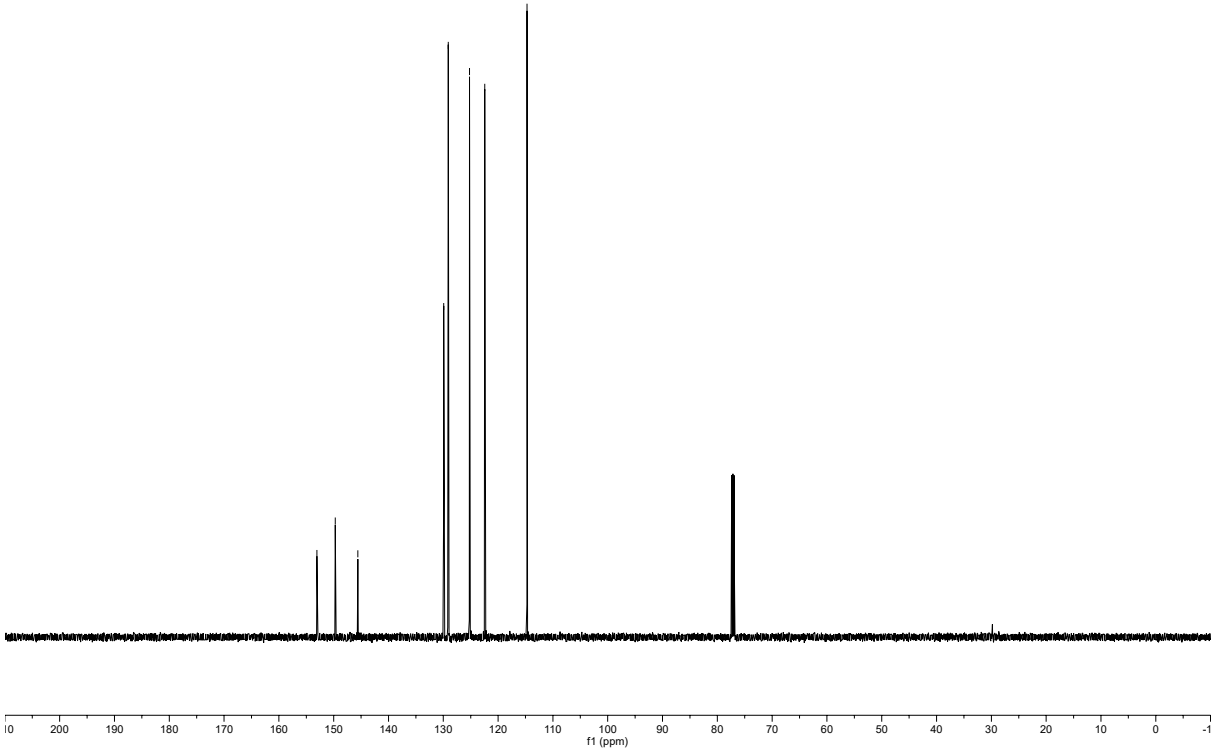
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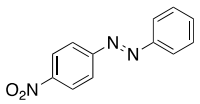
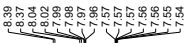
f1 (ppm)


N
N
O2N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8.37
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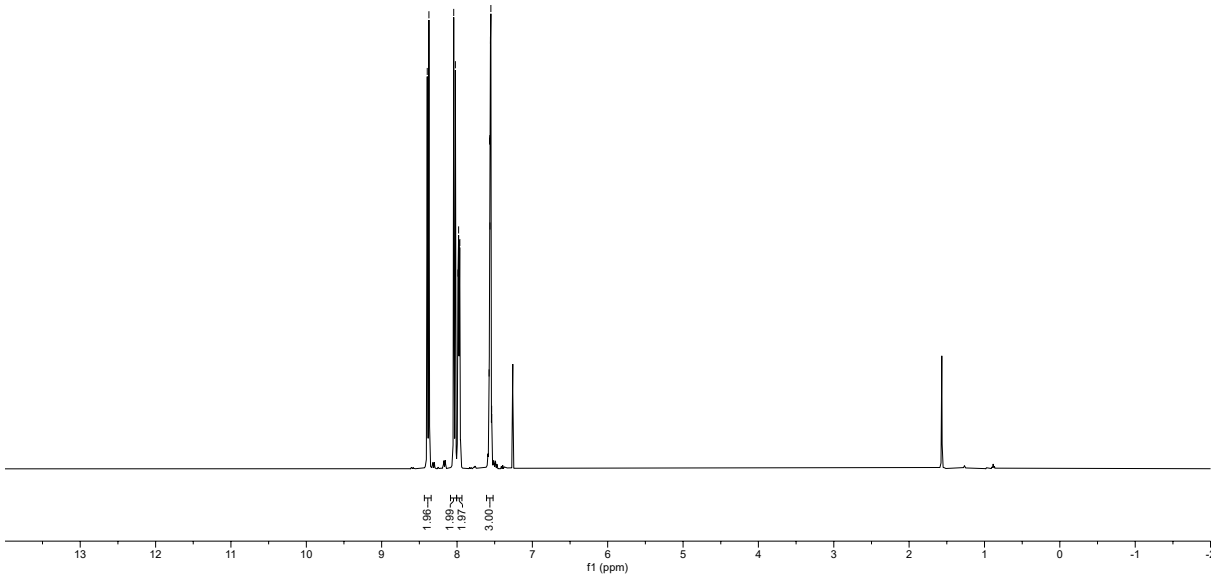
7.97
7.96
7.57
7.57
7.57
7.56
7.56
7.55
7.54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1.99
1.97
3.00
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10
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8
7
6
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4
3
2
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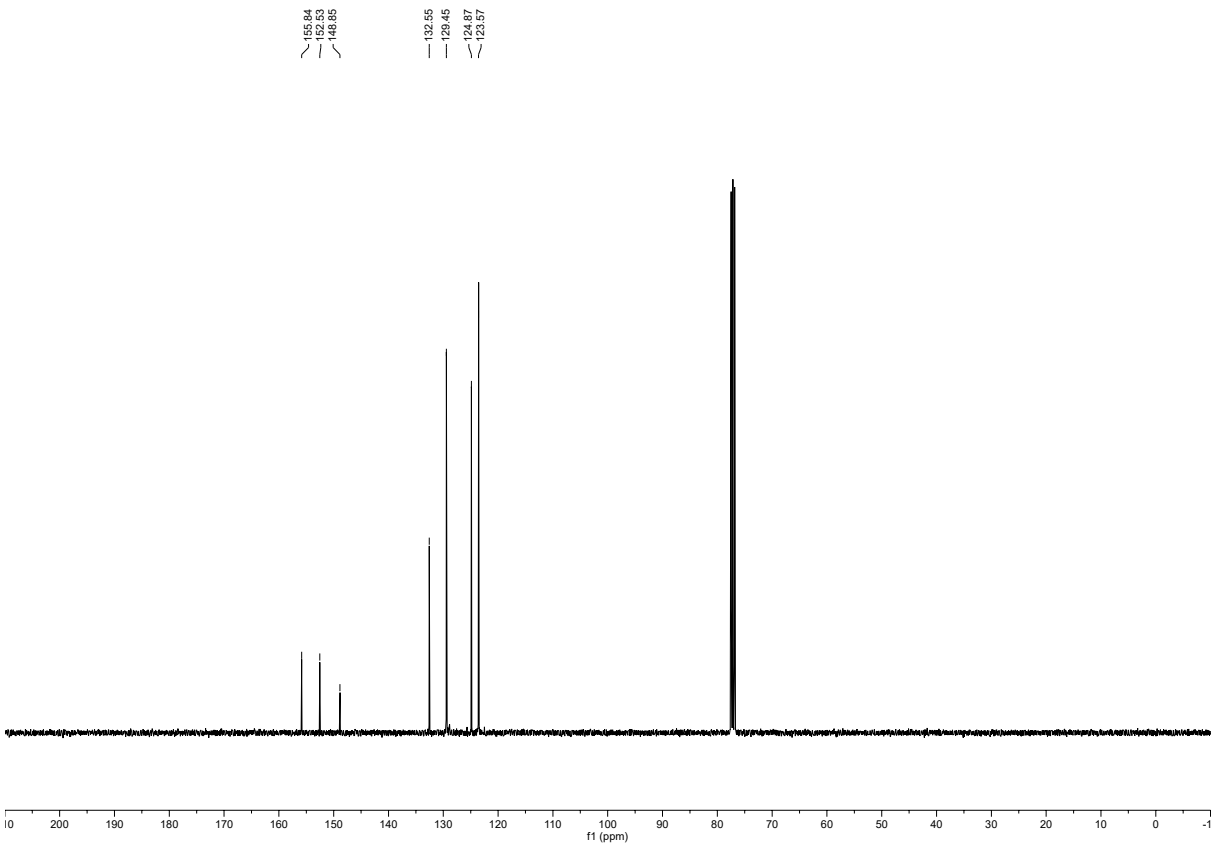
0
-1
f1 (ppm)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152.53
148.85
132.55
129.45
124.87
123.57
200
190
180
170
160
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120
110
100
90
80
70
60
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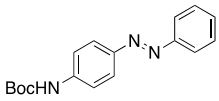
40
30
20
10
0
-1
f1 (ppm)


BocHN
N
N

7.93
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7.90
7.89
7.89
7.54
7.53
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7.52
7.51
7.51
7.49
7.46
7.46
7.46
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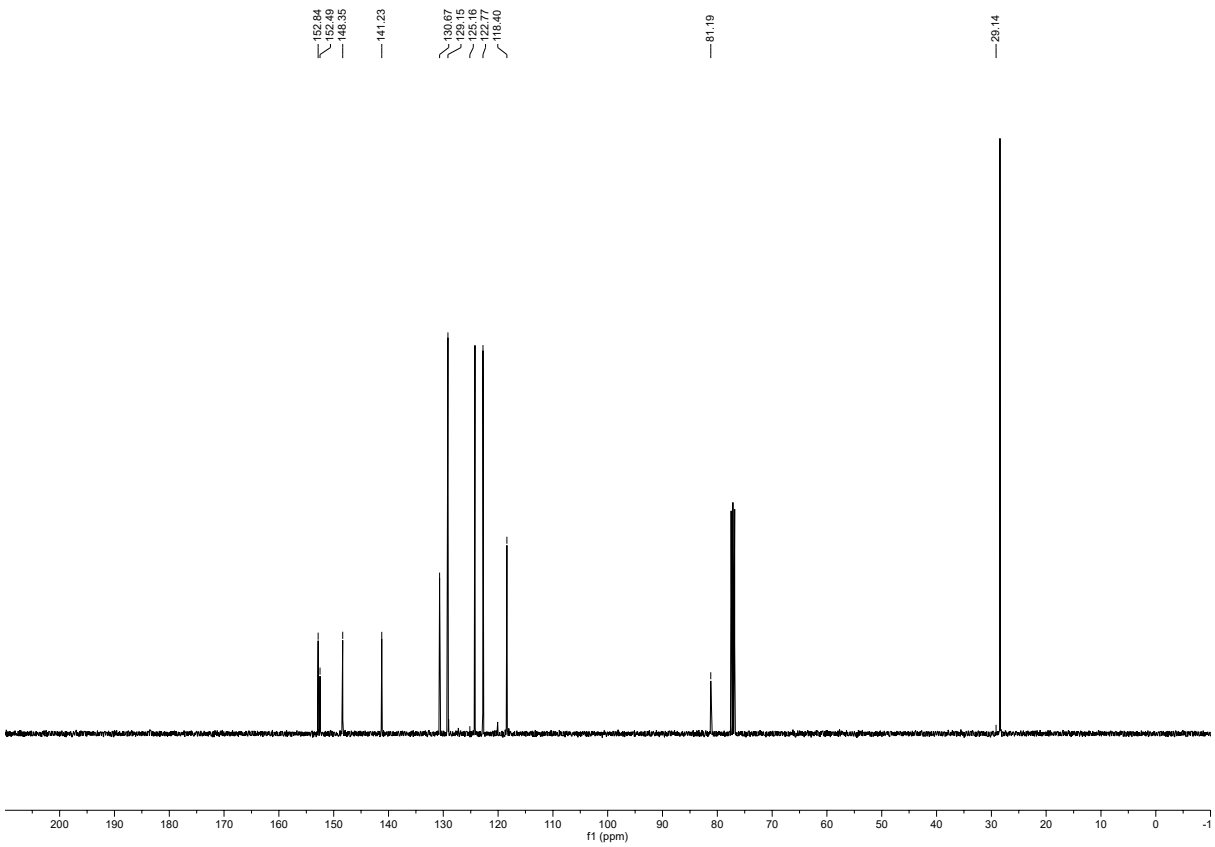
7.44
7.42
6.80
1.55
4.00
4.01
1.02
0.95
9.06
f1 (ppm)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152.49
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141.23
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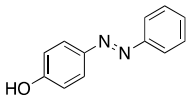
129.15
125.16
122.77
118.40
81.19
29.14
f1 (ppm)


HO
N
N

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7.83
7.82
7.80
7.55
7.54
7.53
7.52
7.49
7.47
7.45
6.97
6.97
6.96
6.95
0.98
4.00
3.00
1.99
13
12
11
10
9
8
7
6
5
4
3
2
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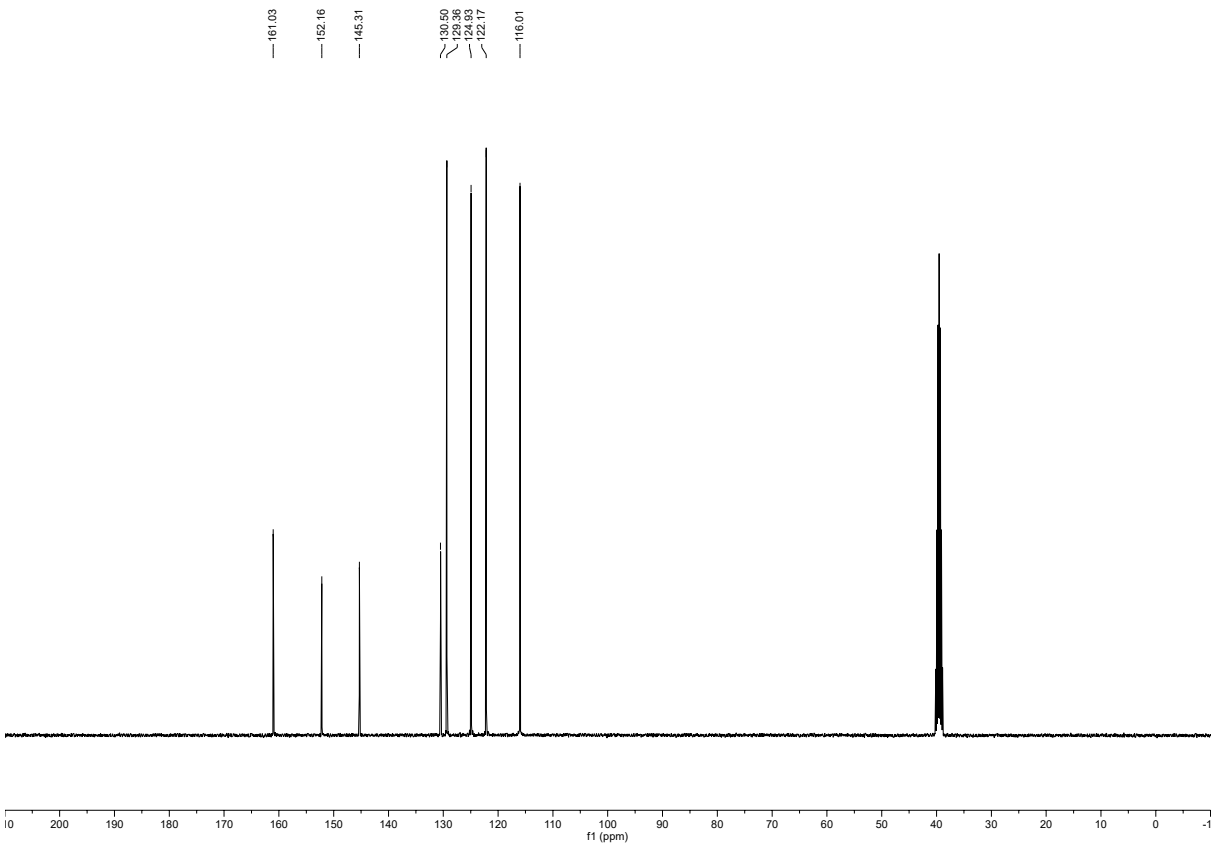
0
-1
f1 (ppm)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152.16
145.31
130.50
129.36
124.93
122.17
116.01
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190
180
170
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140
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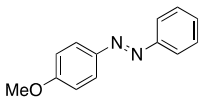
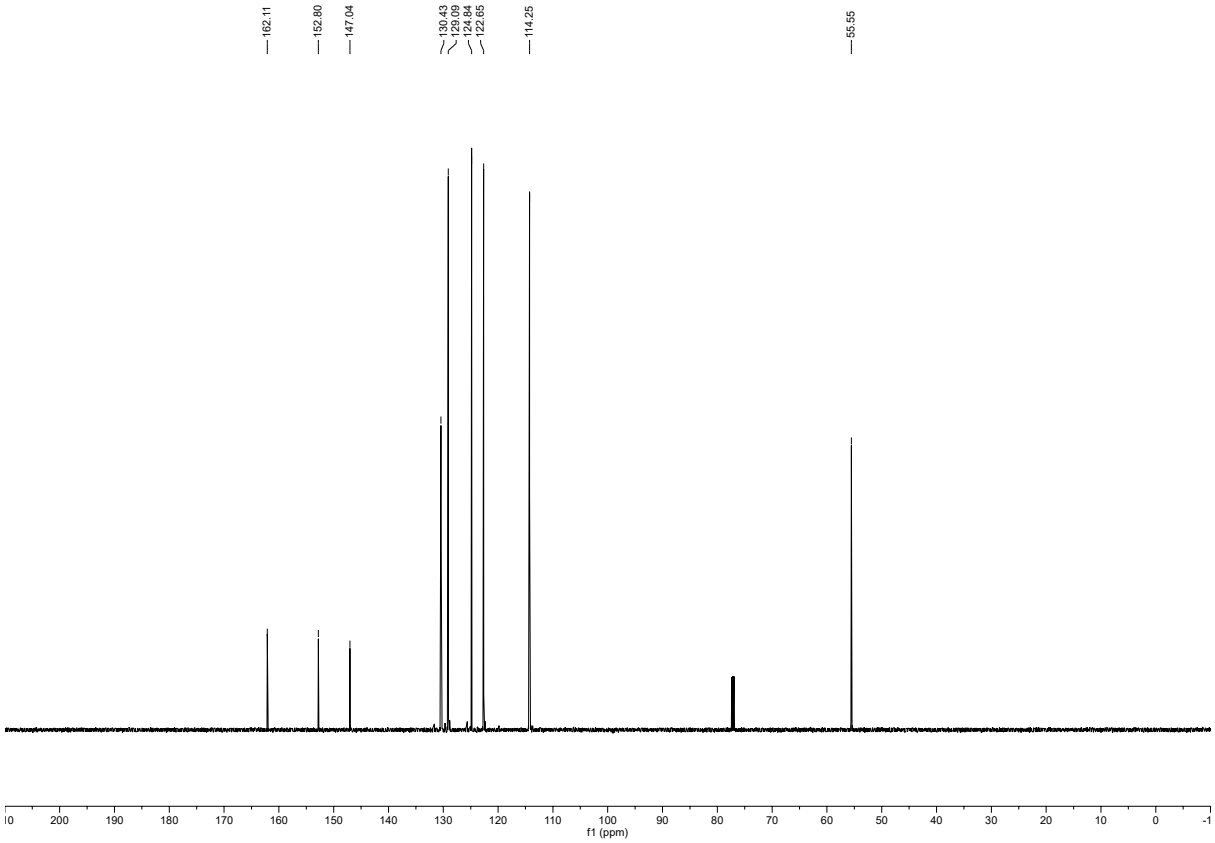
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


MeO
N
N

8.01
7.99
7.97
7.95
7.56
7.55
7.53
7.49
7.48
7.46
7.06
7.03
3.87
1.90
2.01
2.09
1.00
1.98
3.00
f1 (ppm)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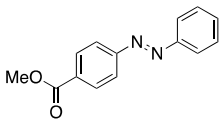
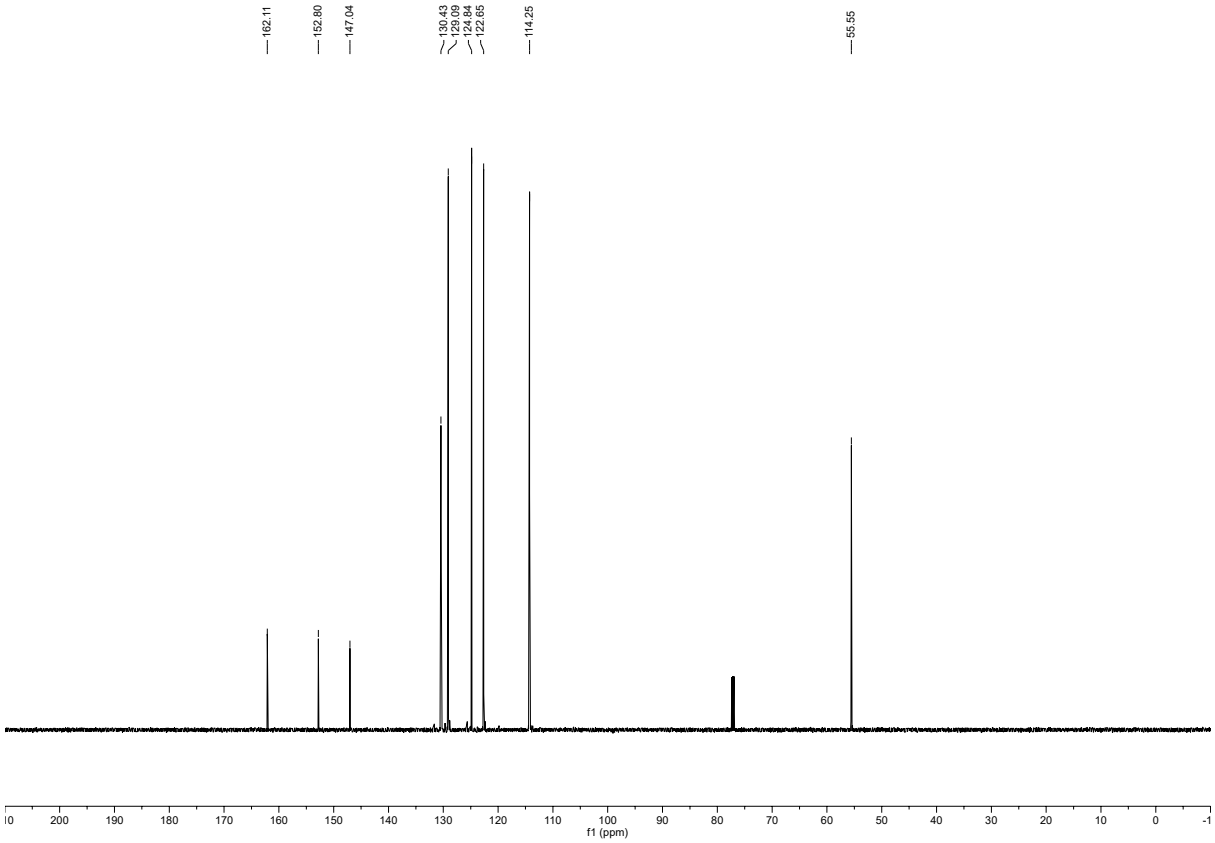
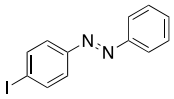
152.80
147.04
130.43
129.09
124.84
122.65
114.25
55.55
f1 (ppm)


MeO
O
N
N

8.01
7.99
7.97
7.95
7.56
7.55
7.53
7.49
7.48
7.46
7.06
7.03
3.87
1.90
2.01
2.09
1.00
1.98
3.00
f1 (ppm)


162.11
152.80
147.04
130.43
129.09
124.84
122.65
114.25
55.55
f1 (ppm)



7.95
7.95
7.93
7.93
7.88
7.86
7.68
7.66
7.56
7.55
7.55
7.54
7.52
7.51
7.50
7.49
7.48
2.02
1.98
1.98
3.00
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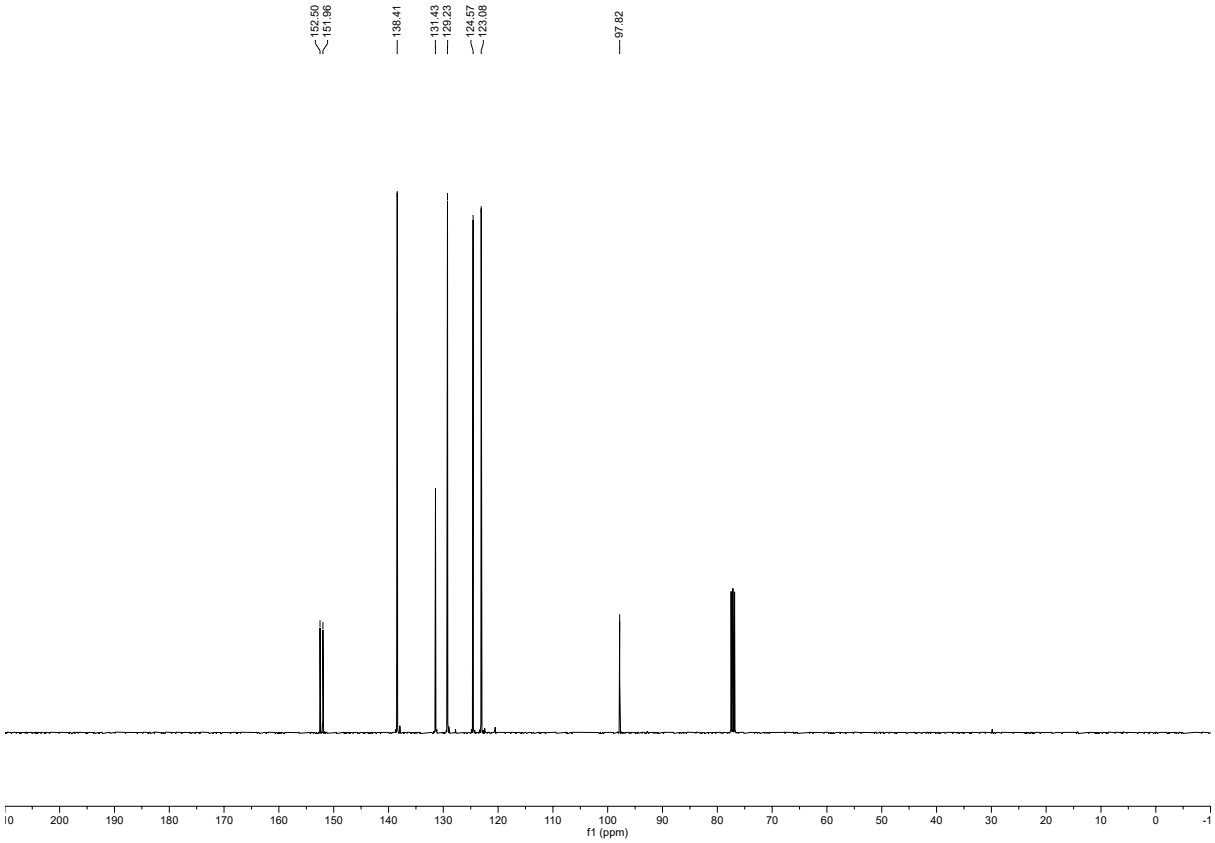
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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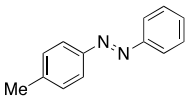
151.96
138.41
131.43
129.23
124.57
123.08
97.82
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


Me
N
N

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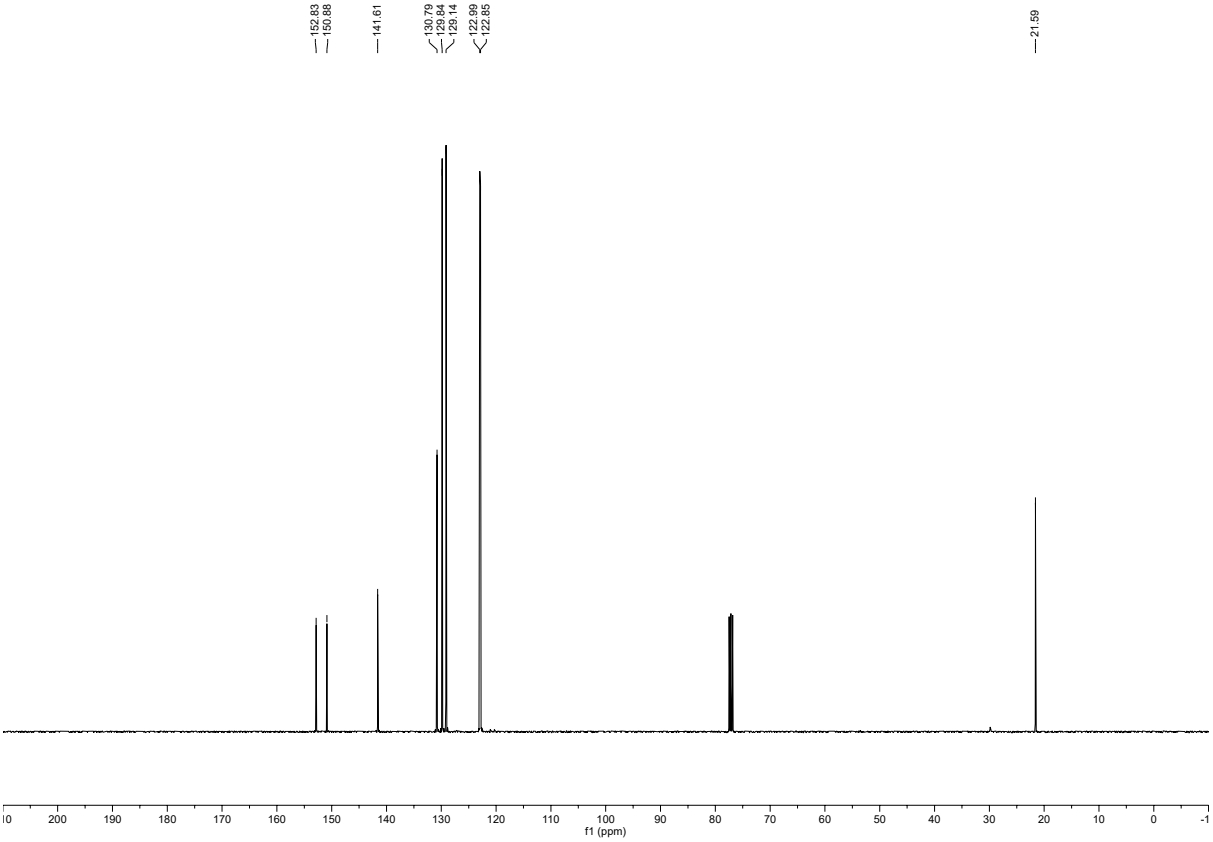
7.93
7.91
7.58
7.56
7.54
7.52
7.50
7.48
7.37
7.35
2.48
2.01
1.97
3.00
1.99
3.00
f1 (ppm)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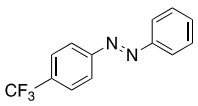
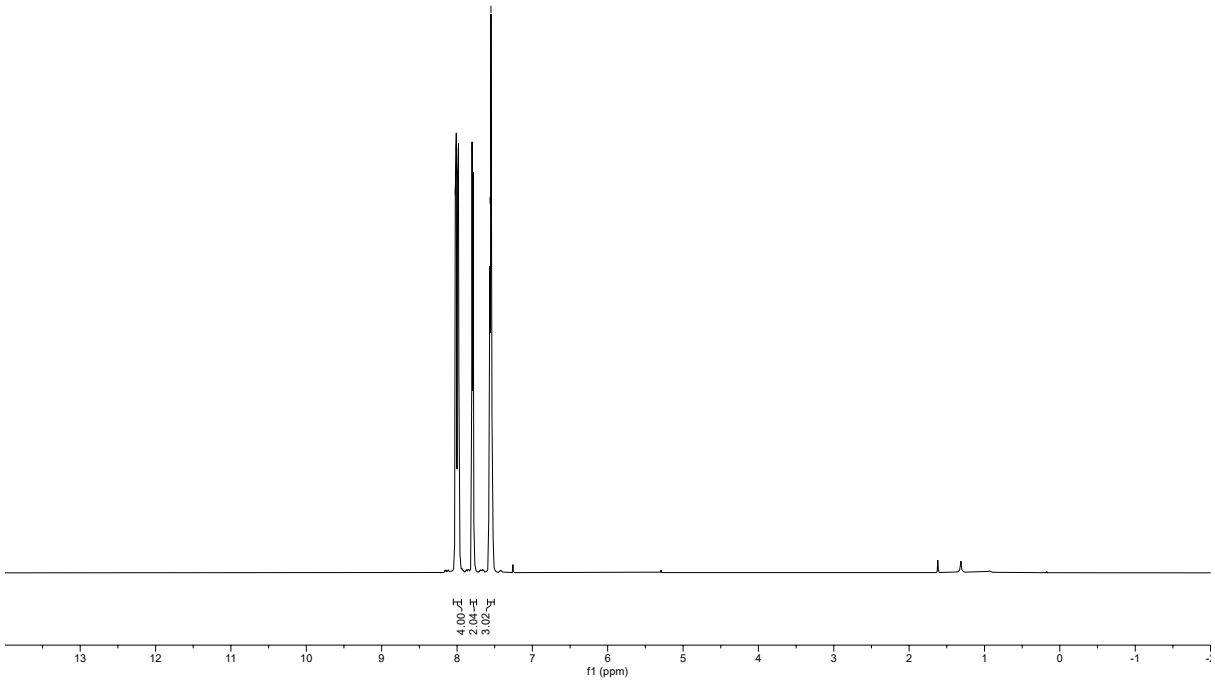
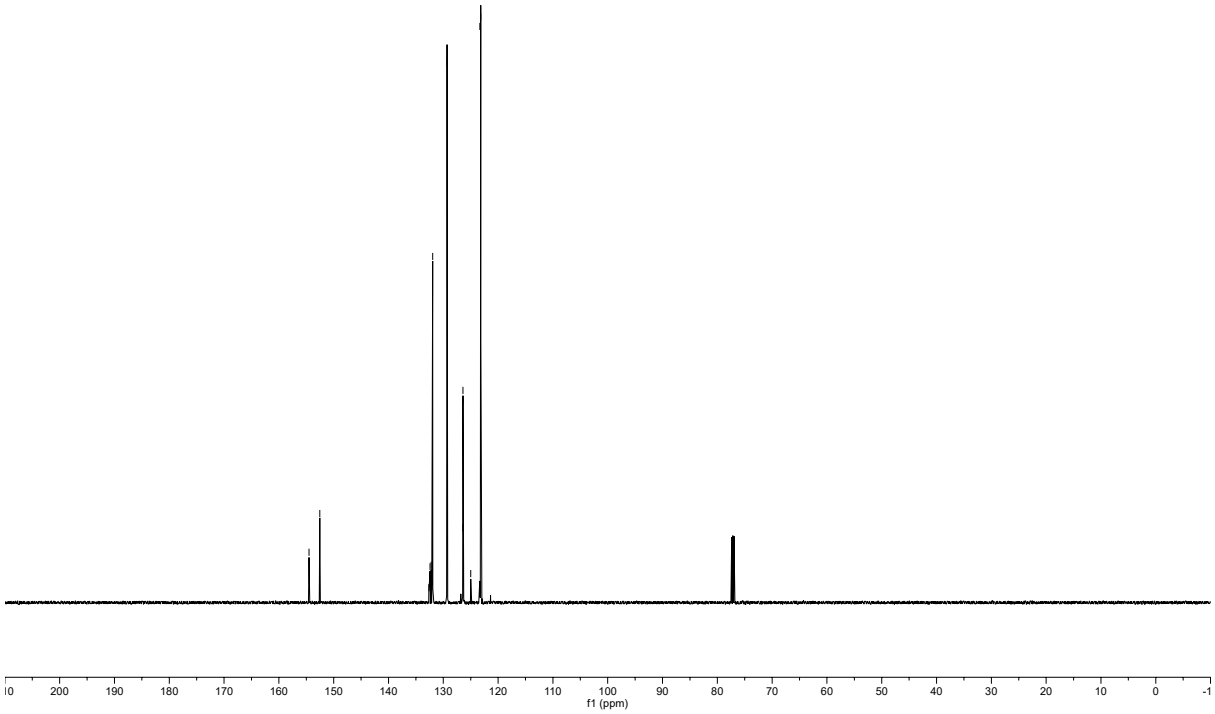
129.84
129.14
122.99
122.85
21.59
f1 (ppm)

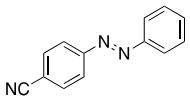

N
N
CF3


8.02
8.01
7.99
7.98
7.60
7.59
7.56
7.55


4.00
2.04
3.02
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


154.51
152.53
132.64
132.43
132.21
132.00
131.94
129.32
126.43
126.41
126.38
126.36
125.00
123.33
123.16


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


N
N
NC


7.96
7.95
7.94
7.94
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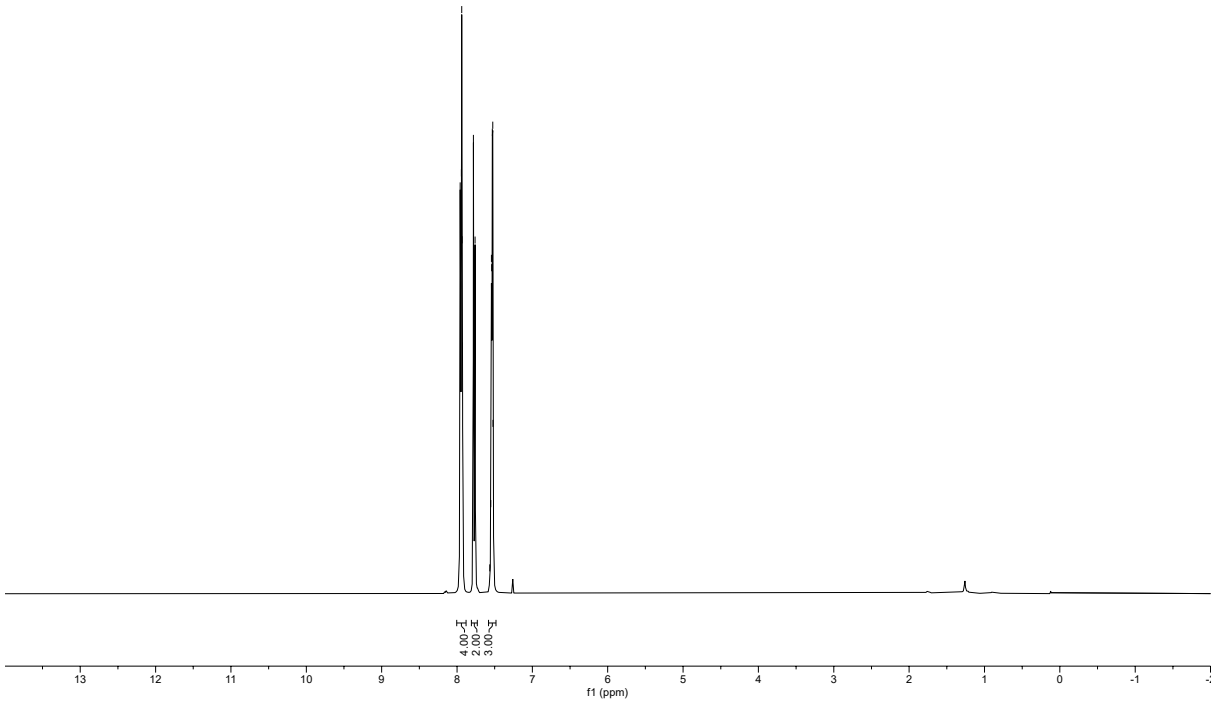
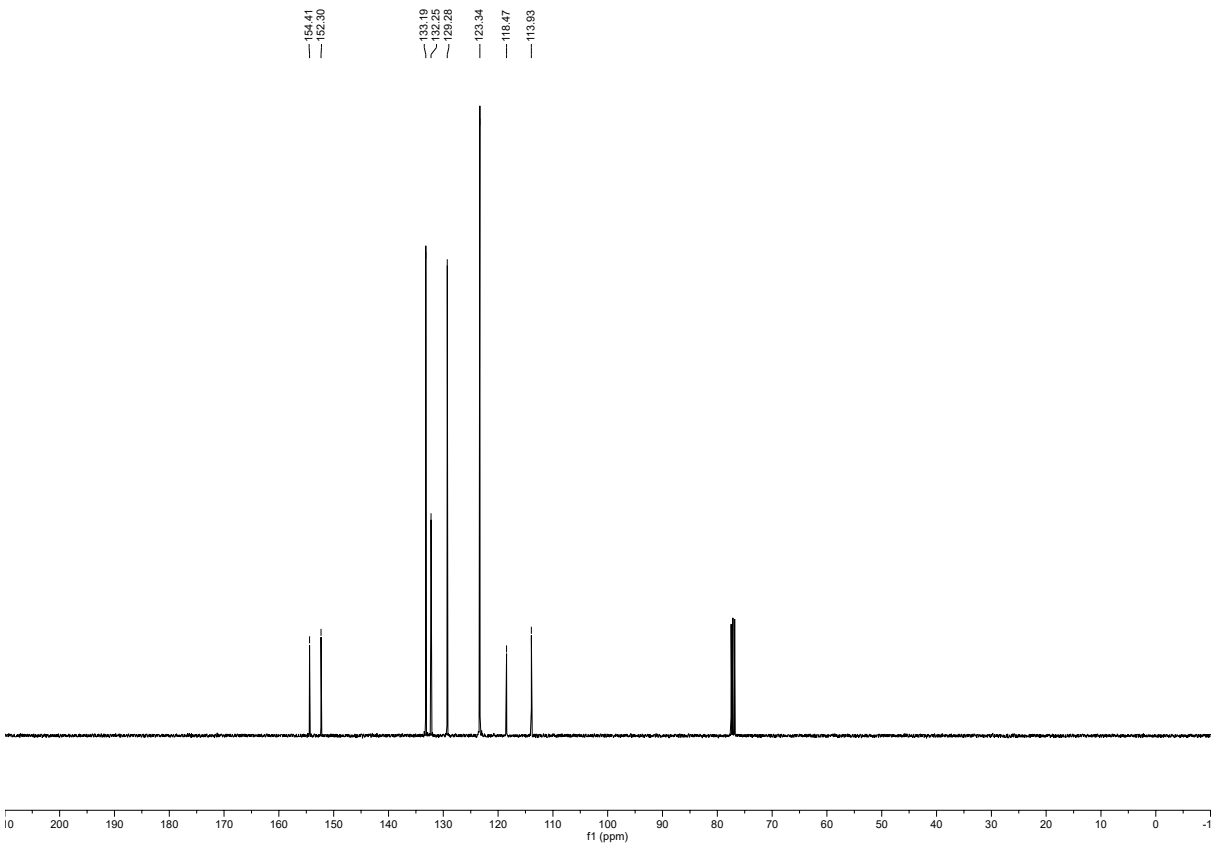
7.93
7.78
7.76
7.56
7.55
7.54
7.54
7.53
7.53
7.52


4.00
2.00
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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133.19
132.25
129.28
123.34
118.47
113.93
210
200
190
180
170
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150
140
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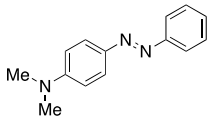
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


Me
N
Me
N
N

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7.88
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7.51
7.49
7.47
7.41
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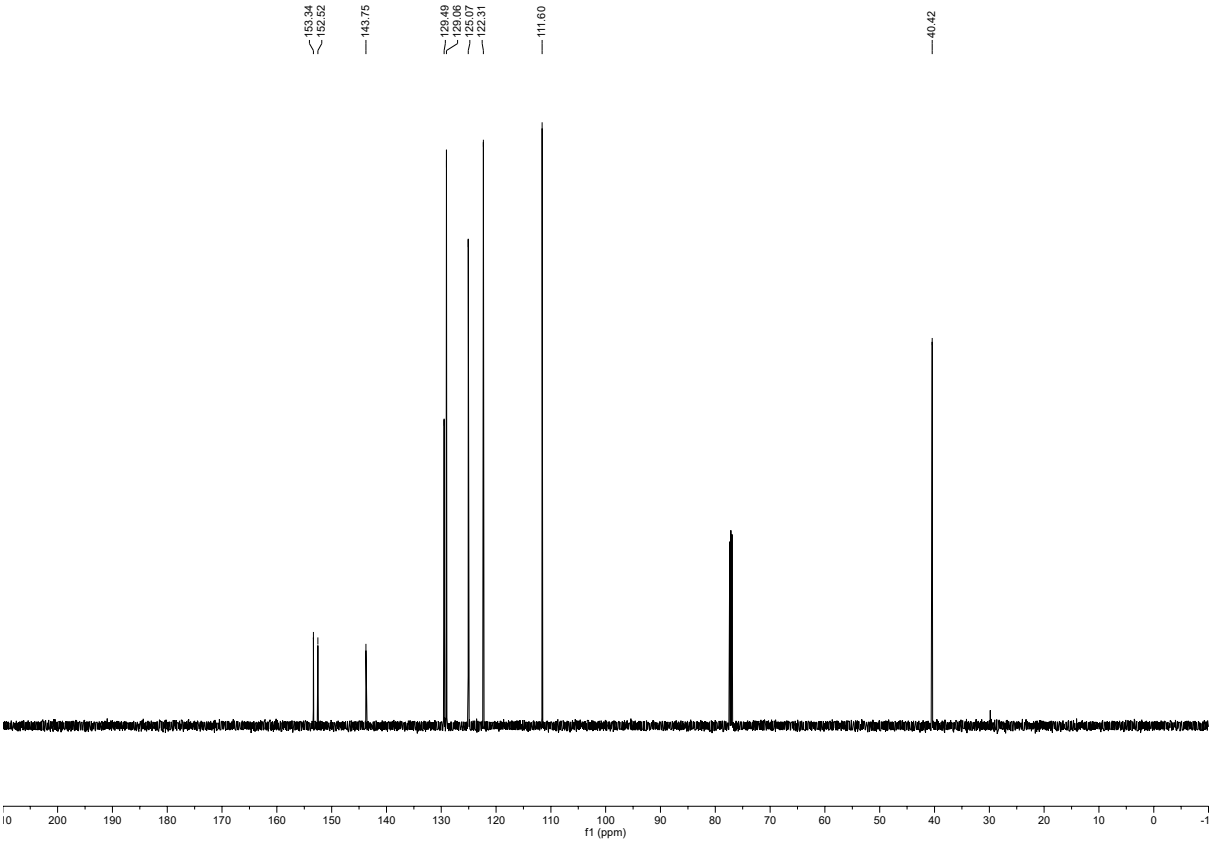
7.37
6.78
6.76
3.08
2.00
1.99
1.99
0.97
2.00
6.00
f1 (ppm)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152.52
143.75
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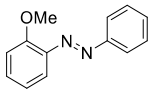
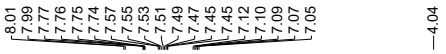
129.06
125.07
122.31
111.60
40.42
f1 (ppm)


OMe
N
N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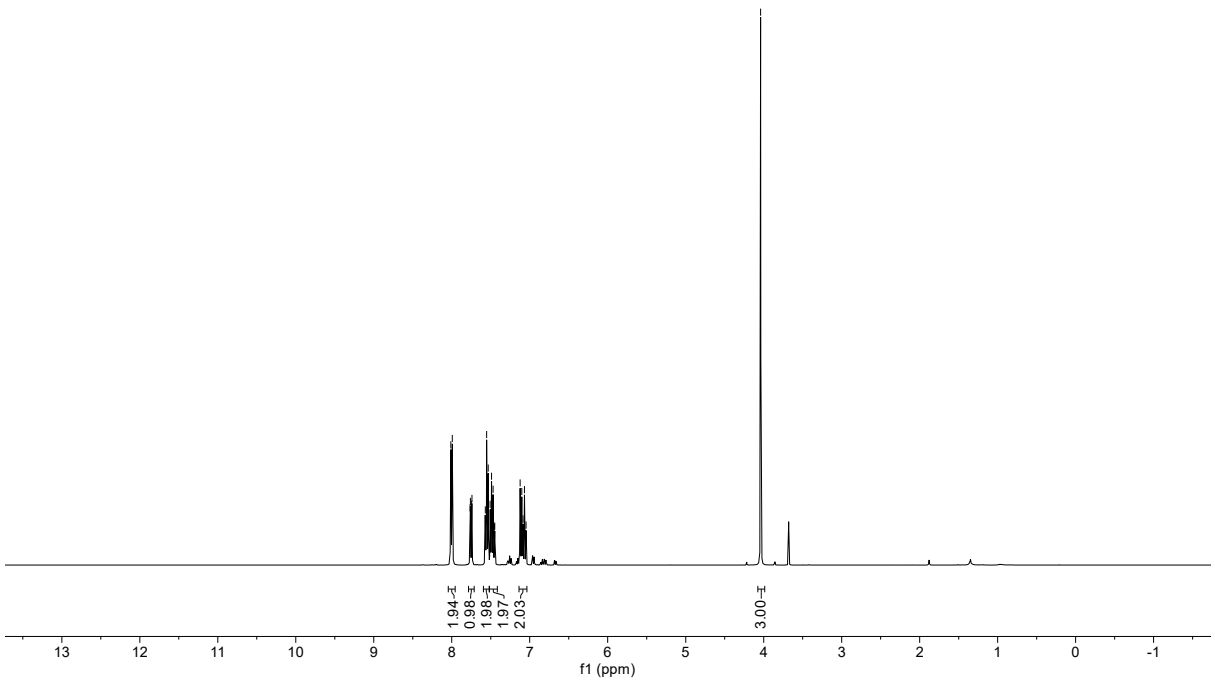
7.99
7.77
7.76
7.75
7.74
7.57
7.55
7.53
7.51
7.49
7.47
7.45
7.45
7.12
7.10
7.09
7.07
7.05
4.04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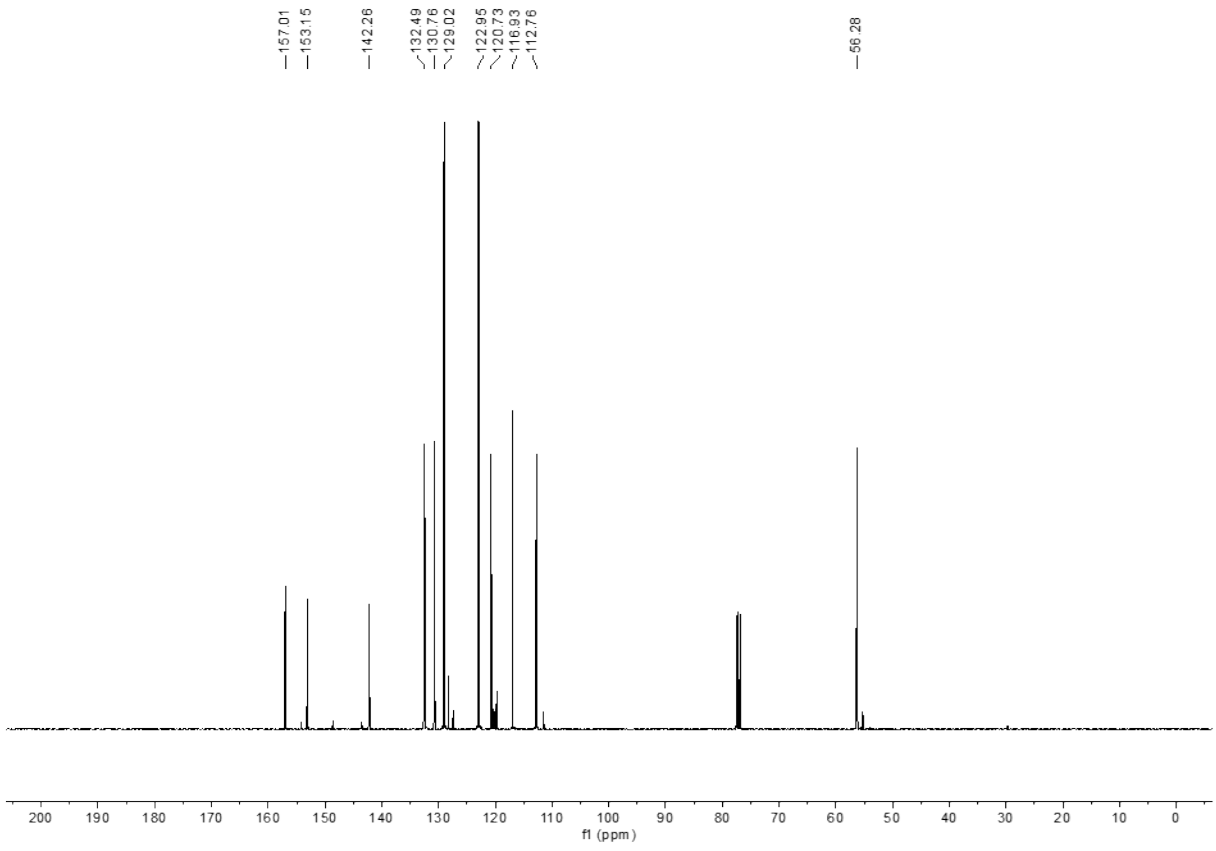
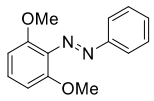
0.98
1.98
1.97
2.03
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


157.01
153.15
142.26
132.49
130.76
129.02
122.95
120.73
116.93
112.76
56.28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
N
N
OMe

7.95
7.93
7.56
7.54
7.52
7.51
7.49
7.30
7.27
7.25
6.72
6.70
3.85
1.94
2.97
1.02
2.00
6.06
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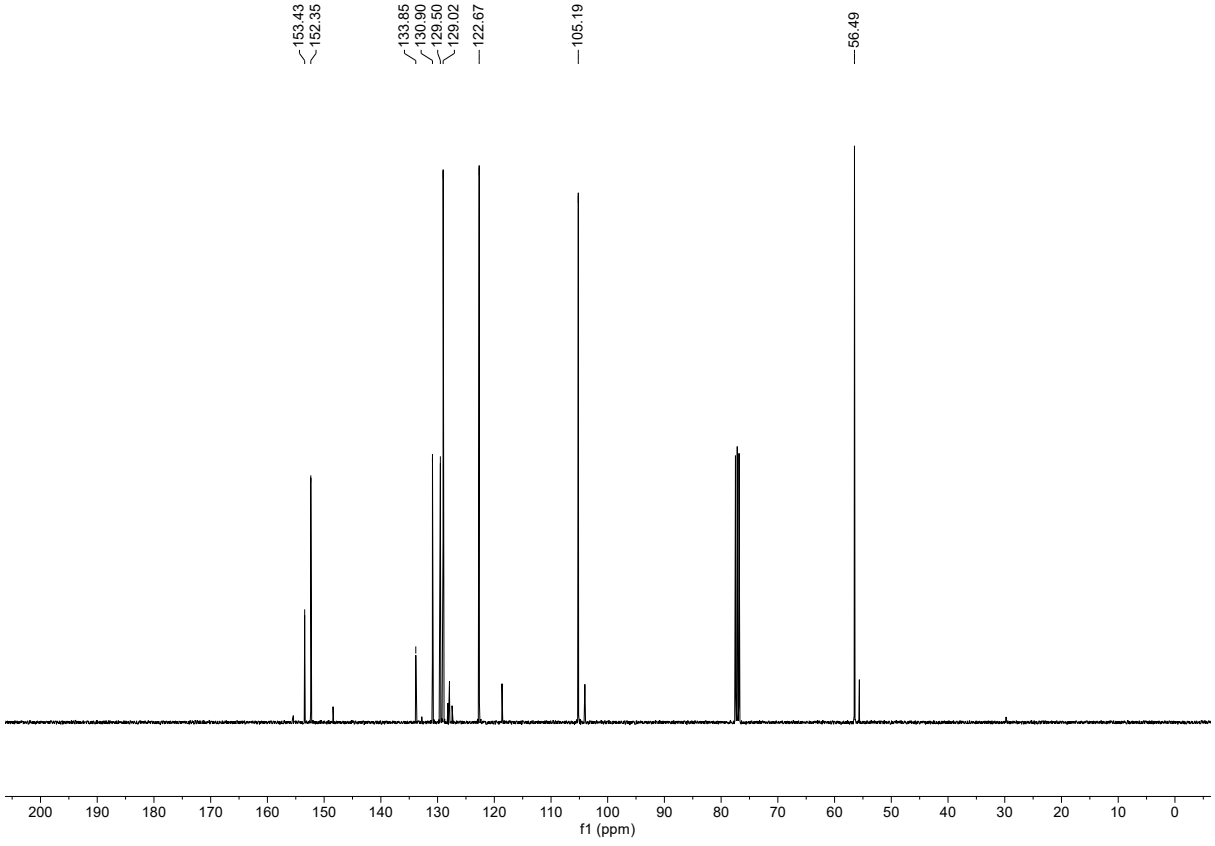
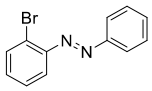
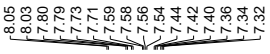
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


153.43
152.35
133.85
130.90
129.50
129.02
122.67
105.19
56.49
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
N
N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7.58
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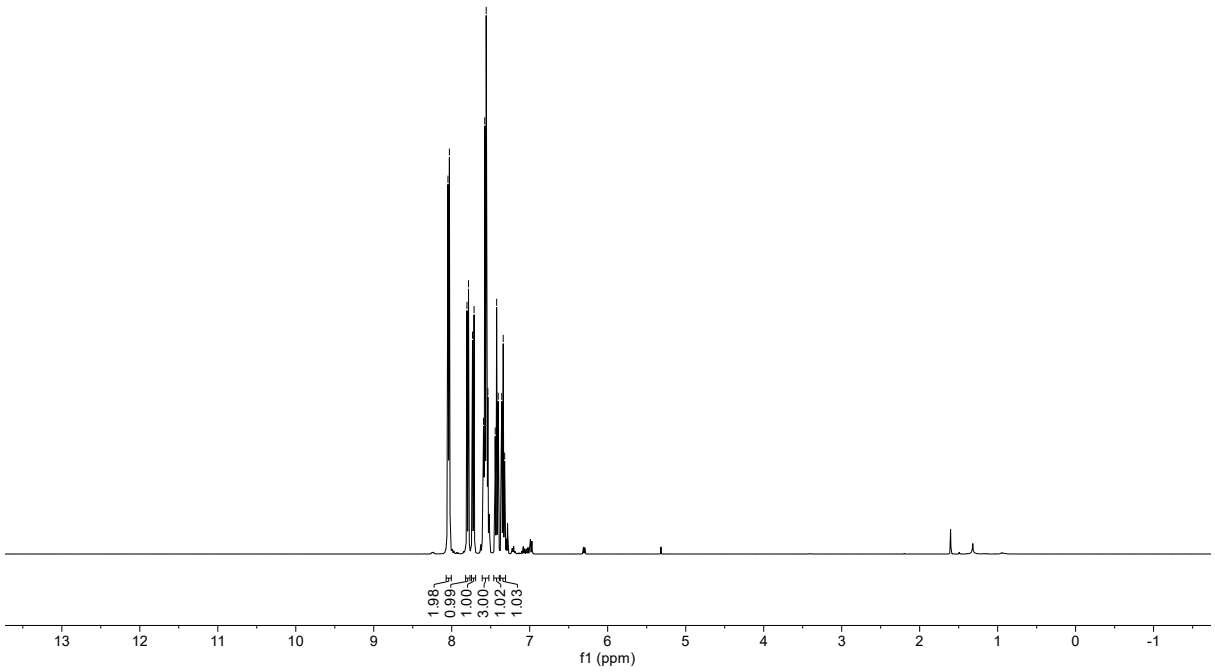
7.54
7.44
7.42
7.40
7.36
7.34
7.32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1.00
3.00
1.02
1.03
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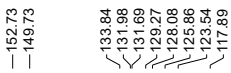
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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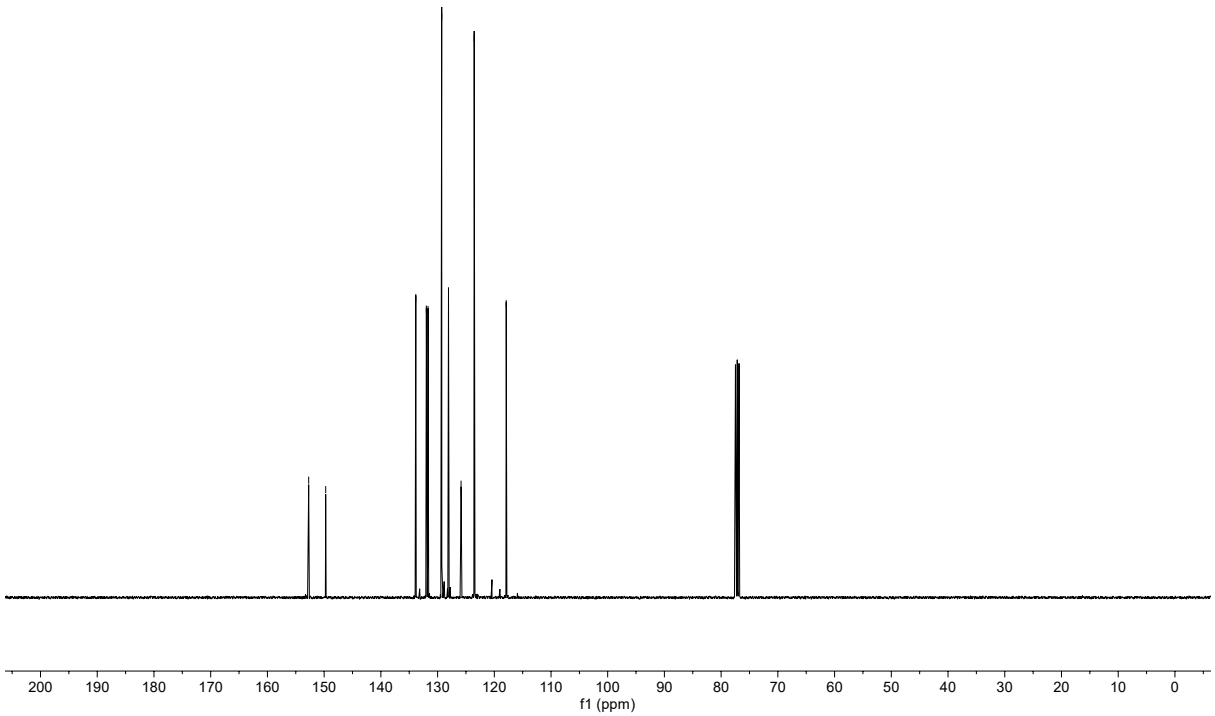
131.69
129.27
128.08
125.86
123.54
117.89


200
190
180
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100
90
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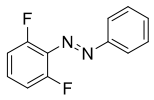
50
40
30
20
10
0
f1 (ppm)


F
N
N
F

7.95
7.95
7.94
7.93
7.93
7.54
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7.53
7.52
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7.34
7.33
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7.05
7.03
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6.77
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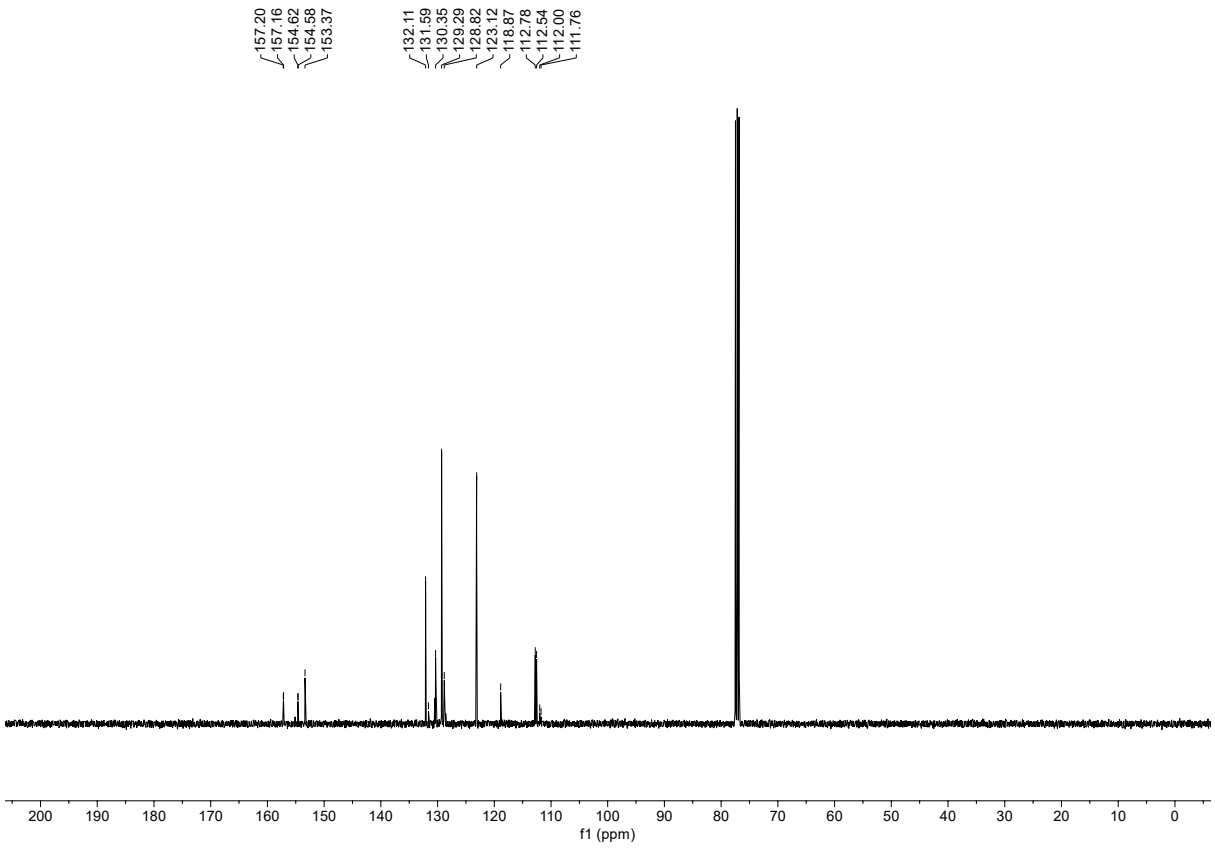
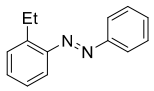
1.19
2.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

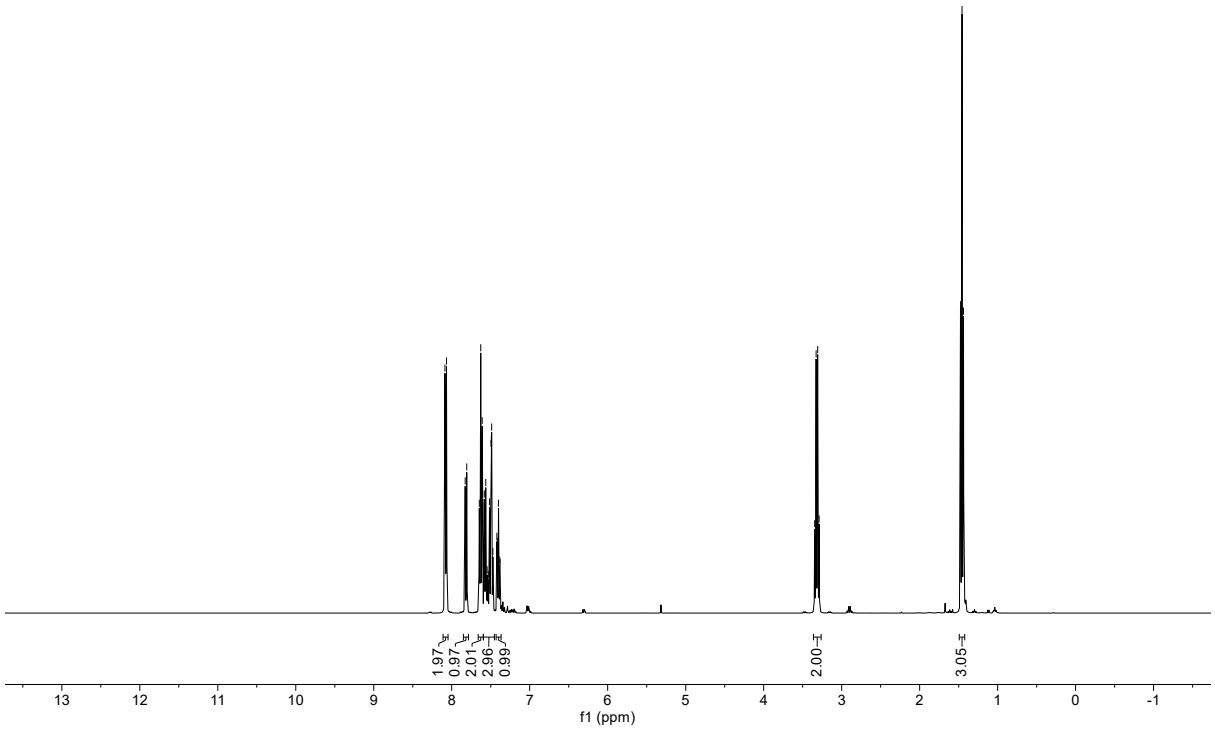

157.20
157.16
154.62
154.58
153.37
132.11
131.59
130.35
129.29
128.82
123.12
118.87
112.78
112.54
112.00
111.76
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



8.09
8.07
7.83
7.81
7.65
7.63
7.61
7.58
7.56
7.55
7.53
7.52
7.50
7.49
7.49
7.47
7.42
7.42
7.40
7.38
7.38

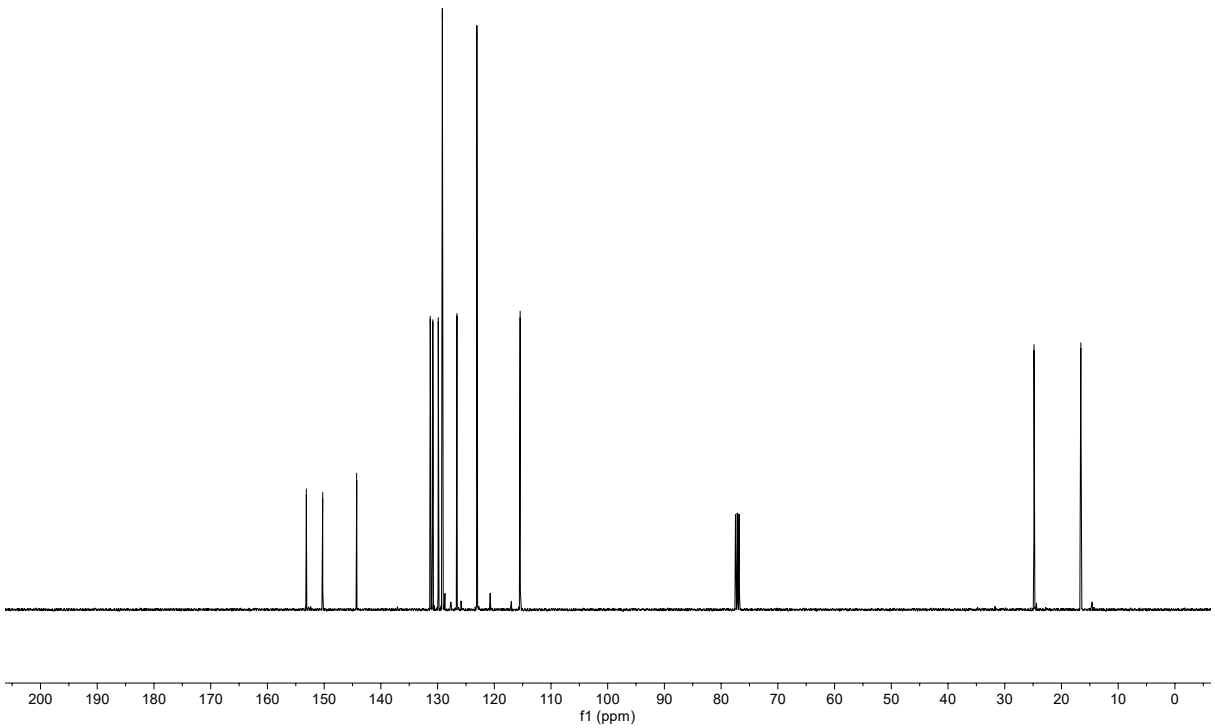
3.35
3.33
3.31
3.29

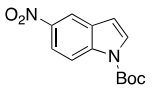
1.48
1.46
1.44



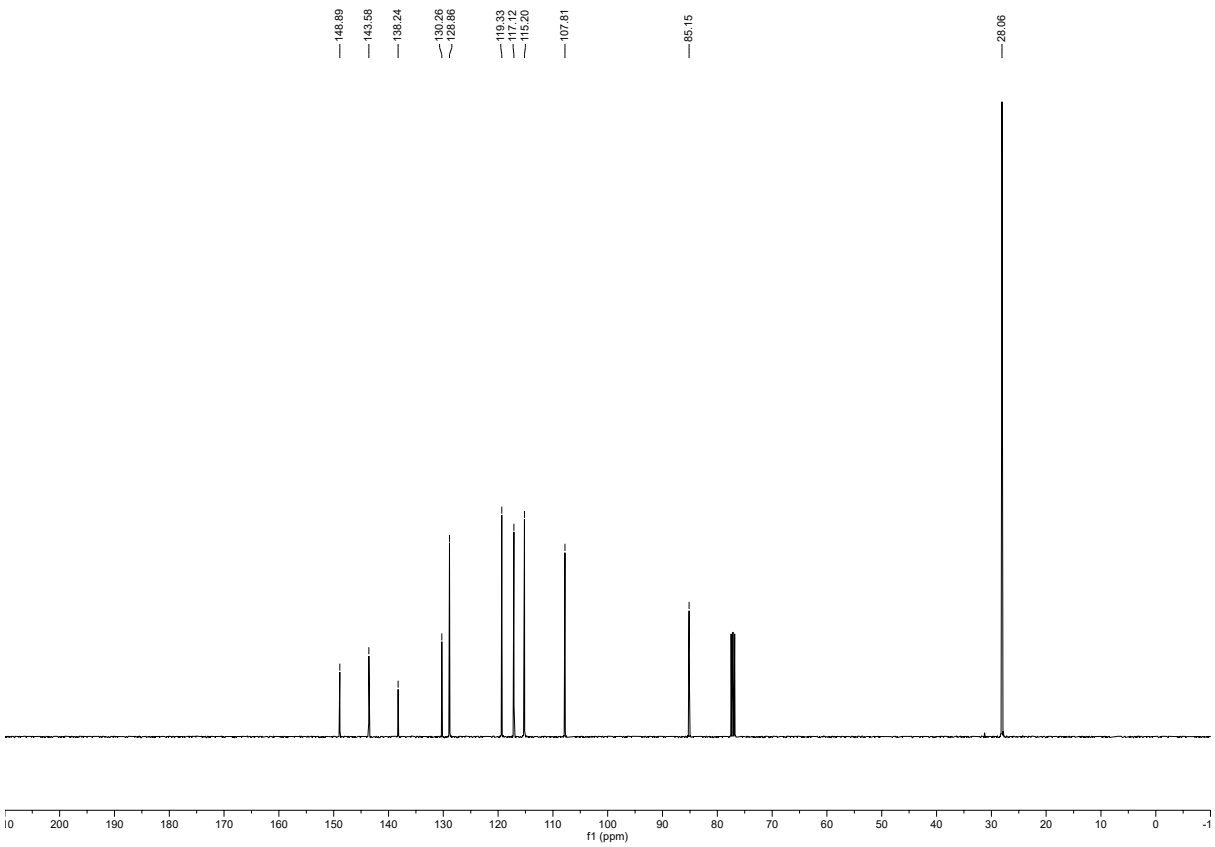
153.13
150.26
144.26
131.29
130.84
129.88
129.16
126.58
123.06
115.44

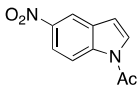
24.84
16.58



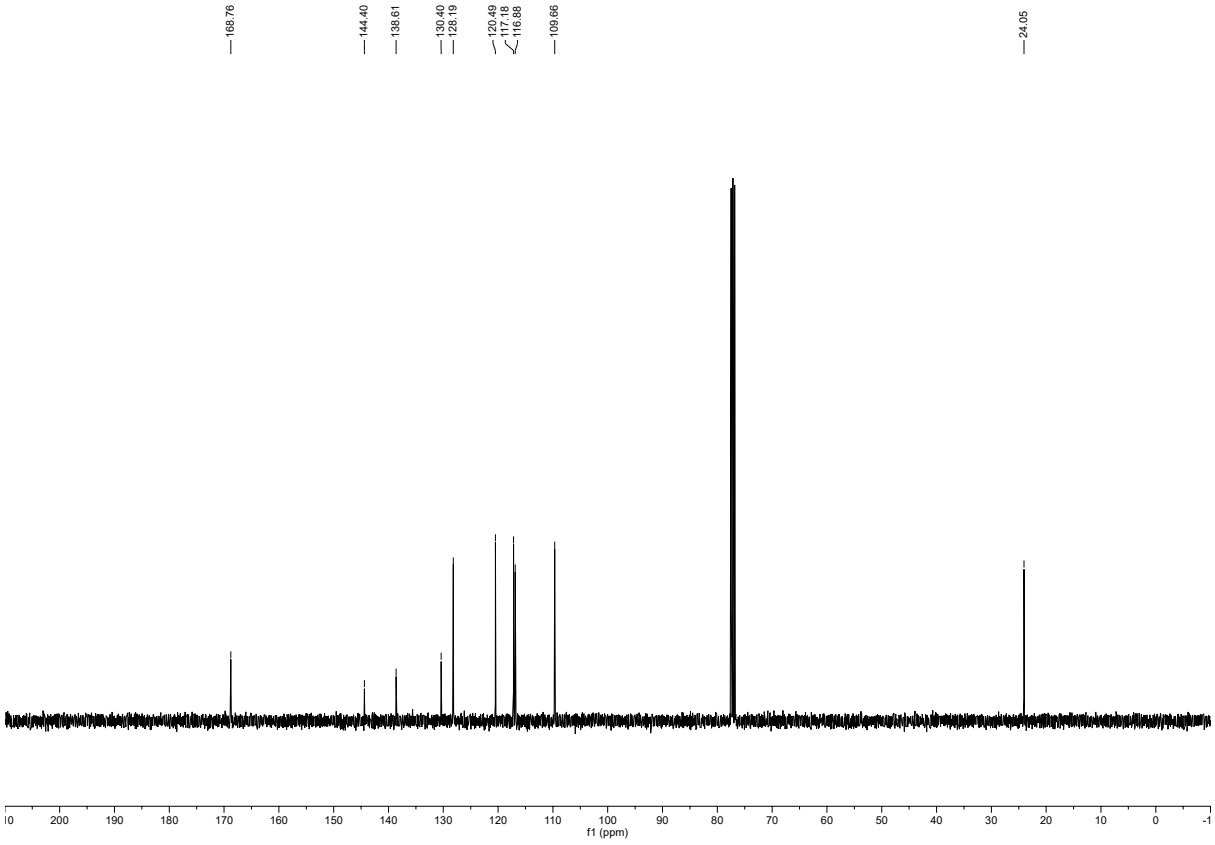

O2N
N
Boc

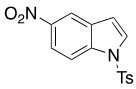
8.38
8.37
8.19
8.17
8.12
8.11
8.09
8.09
7.69
7.68
6.65
6.64
1.67
1.00
2.05
1.02
1.02
9.08
f1 (ppm)


148.89
143.58
138.24
130.26
128.86
119.33
117.12
115.20
107.81
85.15
28.06
f1 (ppm)

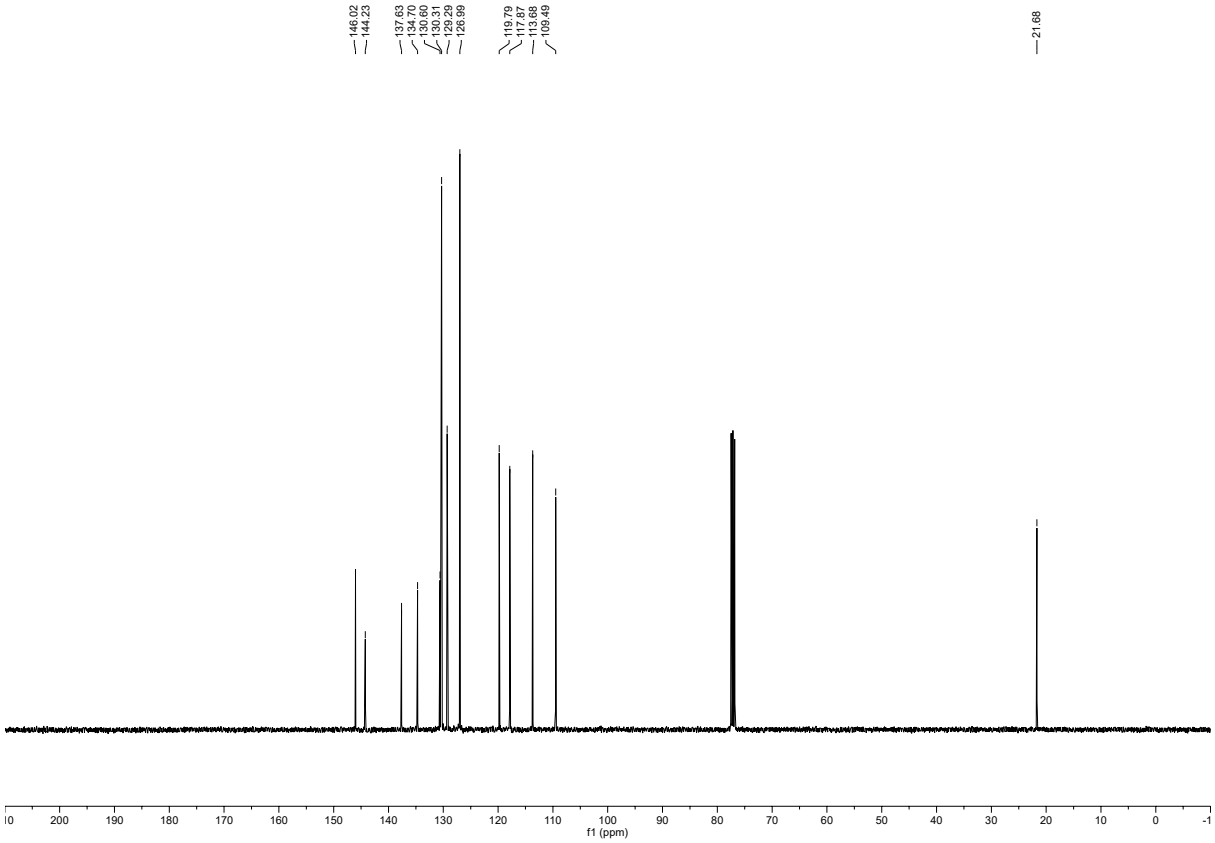

O_2N
N
Ac

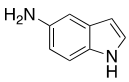
8.57
8.54
8.47
8.47
8.23
8.23
8.21
8.20
7.60
7.59
6.79
6.78
2.69
1.00
0.99
1.00
1.00
1.00
3.06
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


168.76
144.40
138.61
130.40
128.19
120.49
117.18
116.88
109.66
24.05
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

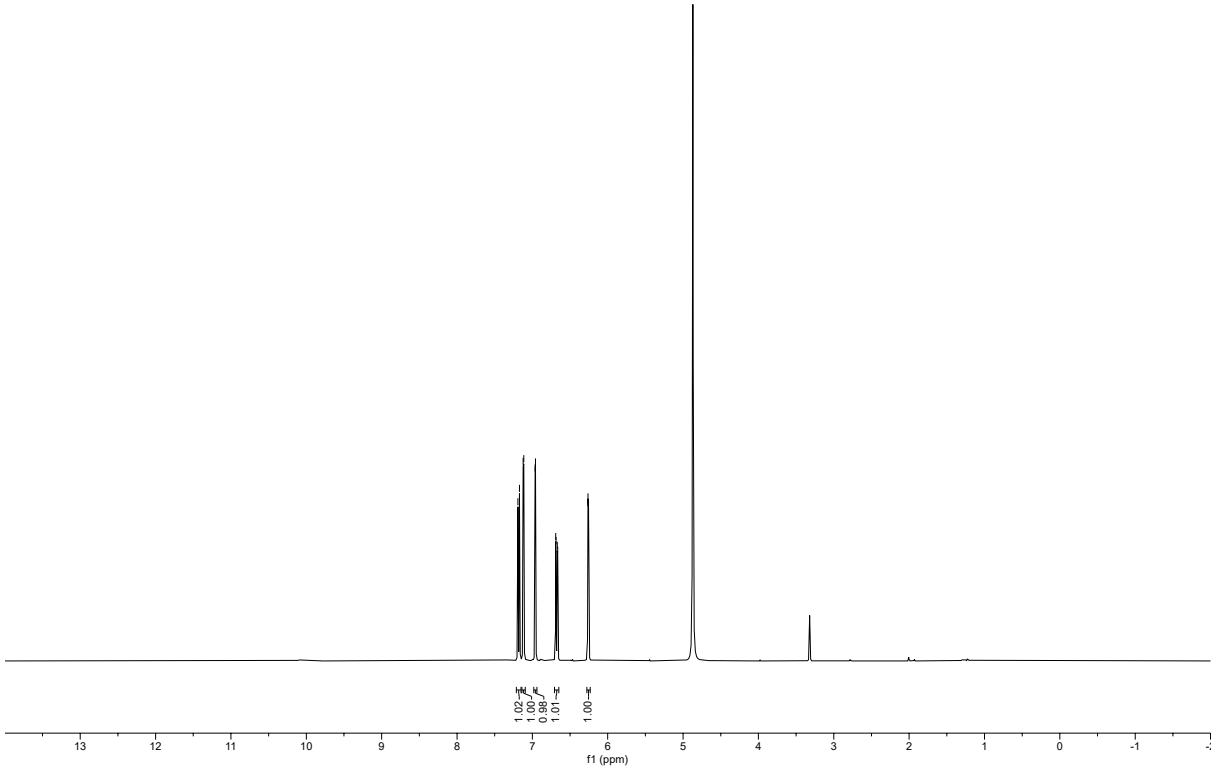

O_2N
N
Ts

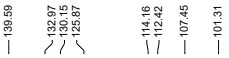
8.46
8.45
8.21
8.20
8.19
8.18
8.09
8.07
7.81
7.79
7.75
7.74
7.29
7.27
6.81
6.80
2.36
0.98
1.00
1.07
1.97
0.97
2.01
0.98
3.00
f1 (ppm)

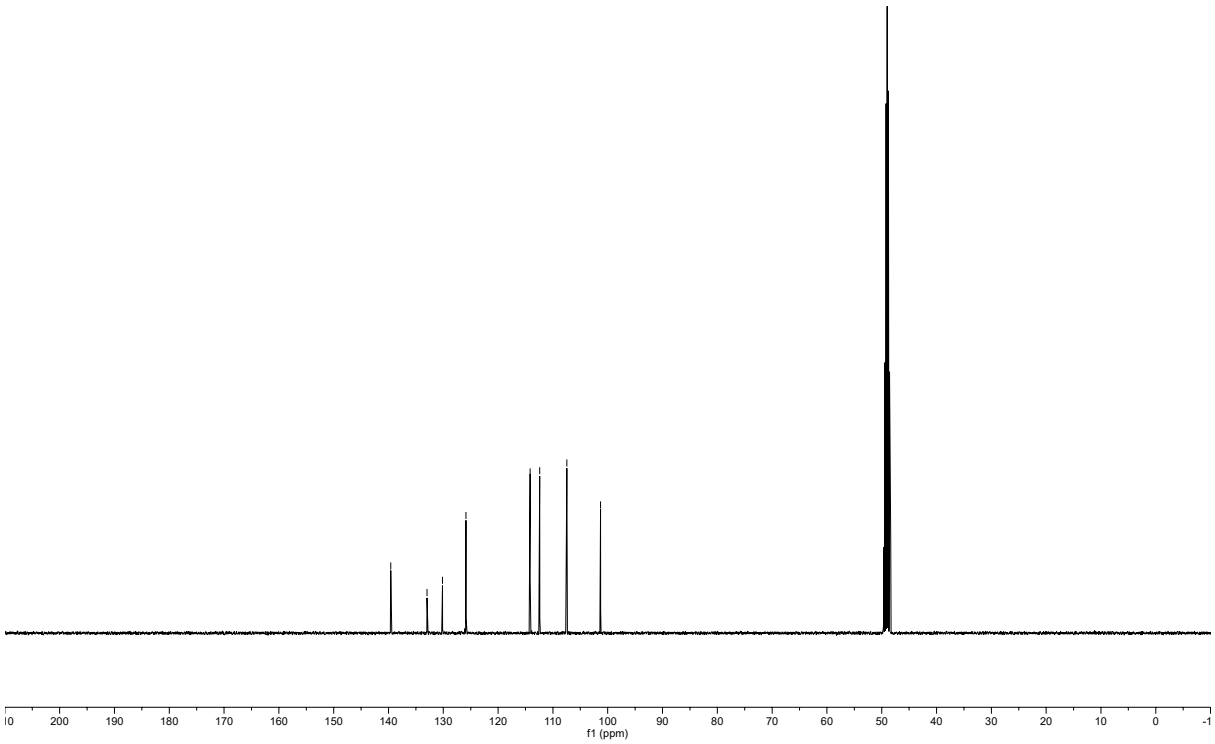

146.02
144.23
137.63
134.70
130.60
130.31
129.29
126.99
119.79
117.87
113.88
109.49
21.68
f1 (ppm)

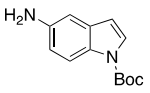



7.19
7.17
7.12
7.11
6.96
6.96
6.69
6.69
6.67
6.66
6.26
6.26
6.26
6.25

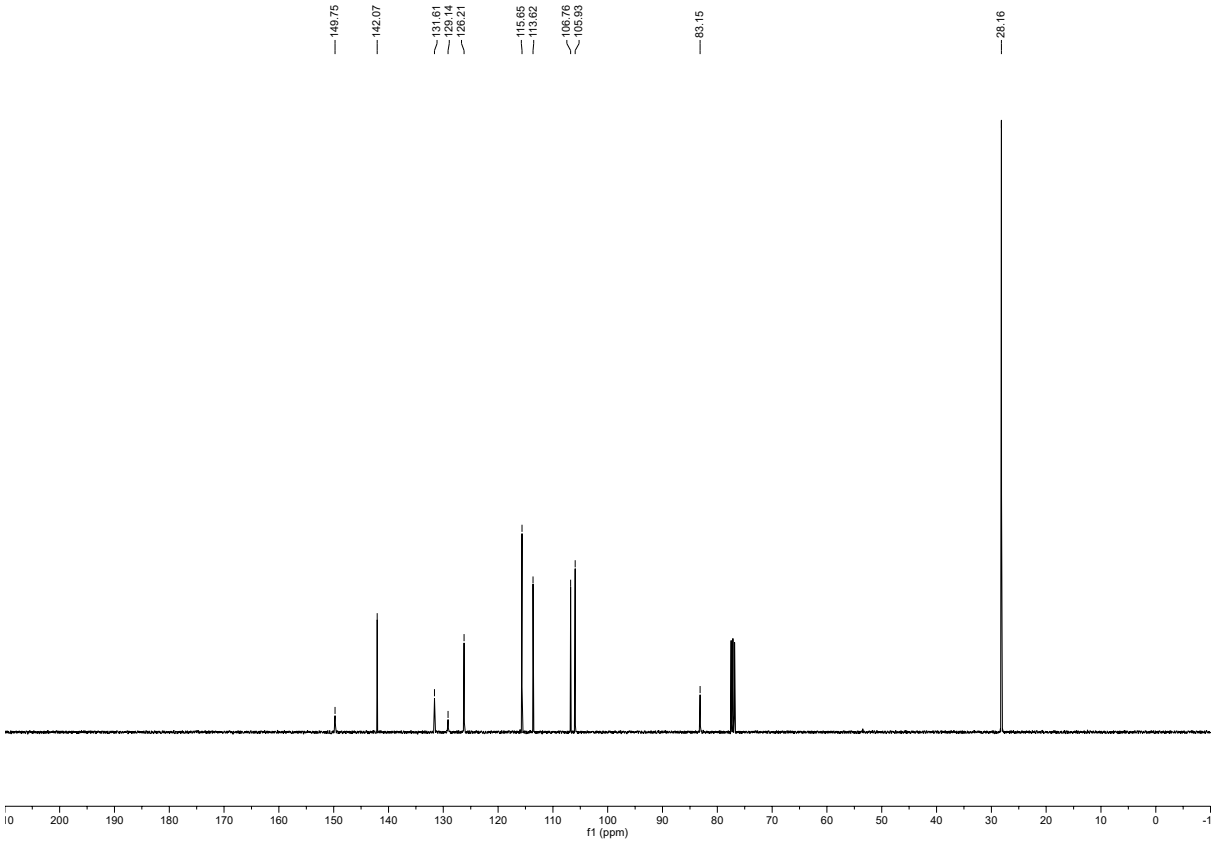

1.02
1.00
0.98
1.01
1.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

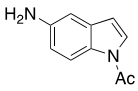

139.59
132.97
130.15
125.87
114.16
112.42
107.45
101.31


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

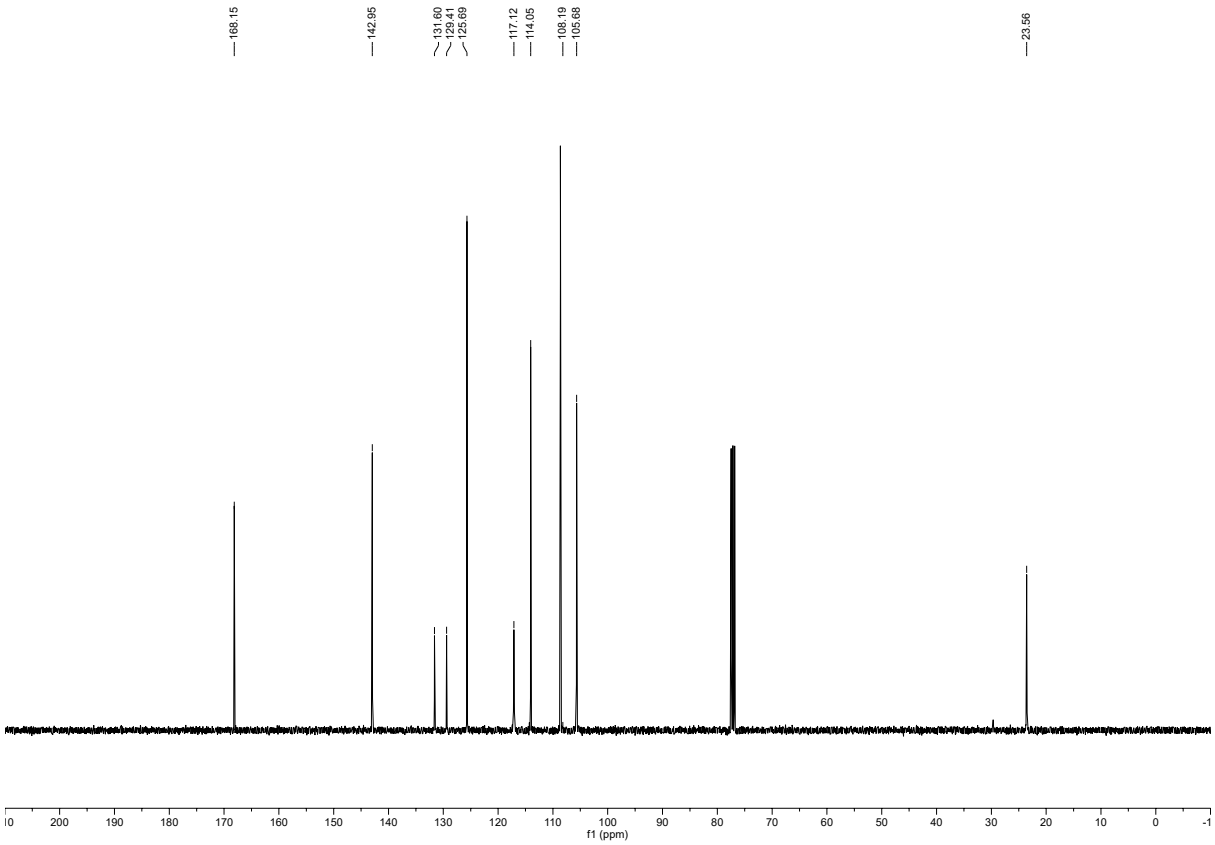

H2N
N
Boc

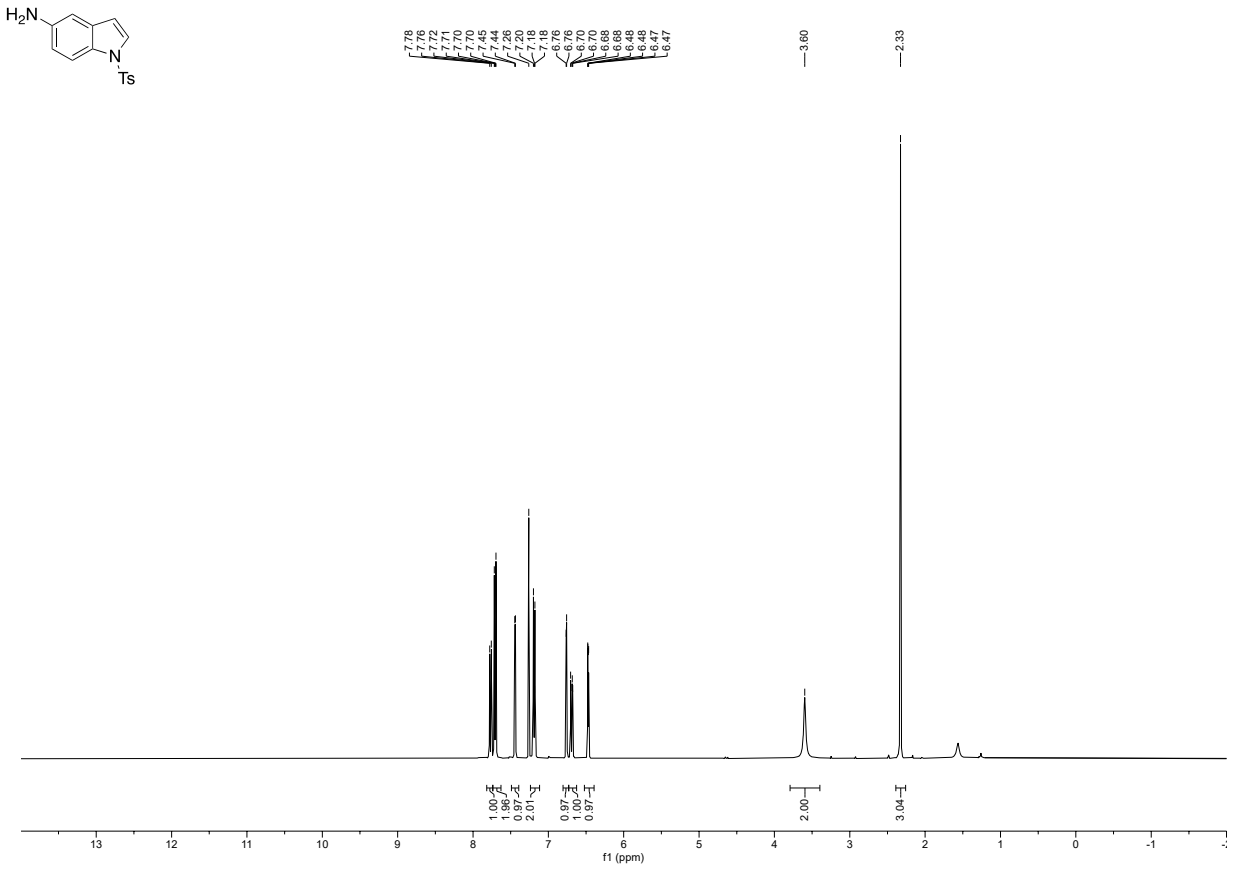
7.96
7.94
7.55
7.54
6.83
6.82
6.73
6.72
6.71
6.70
6.42
6.41
3.61
1.67
0.96
1.00
1.05
1.07
1.05
1.96
9.26
f1 (ppm)

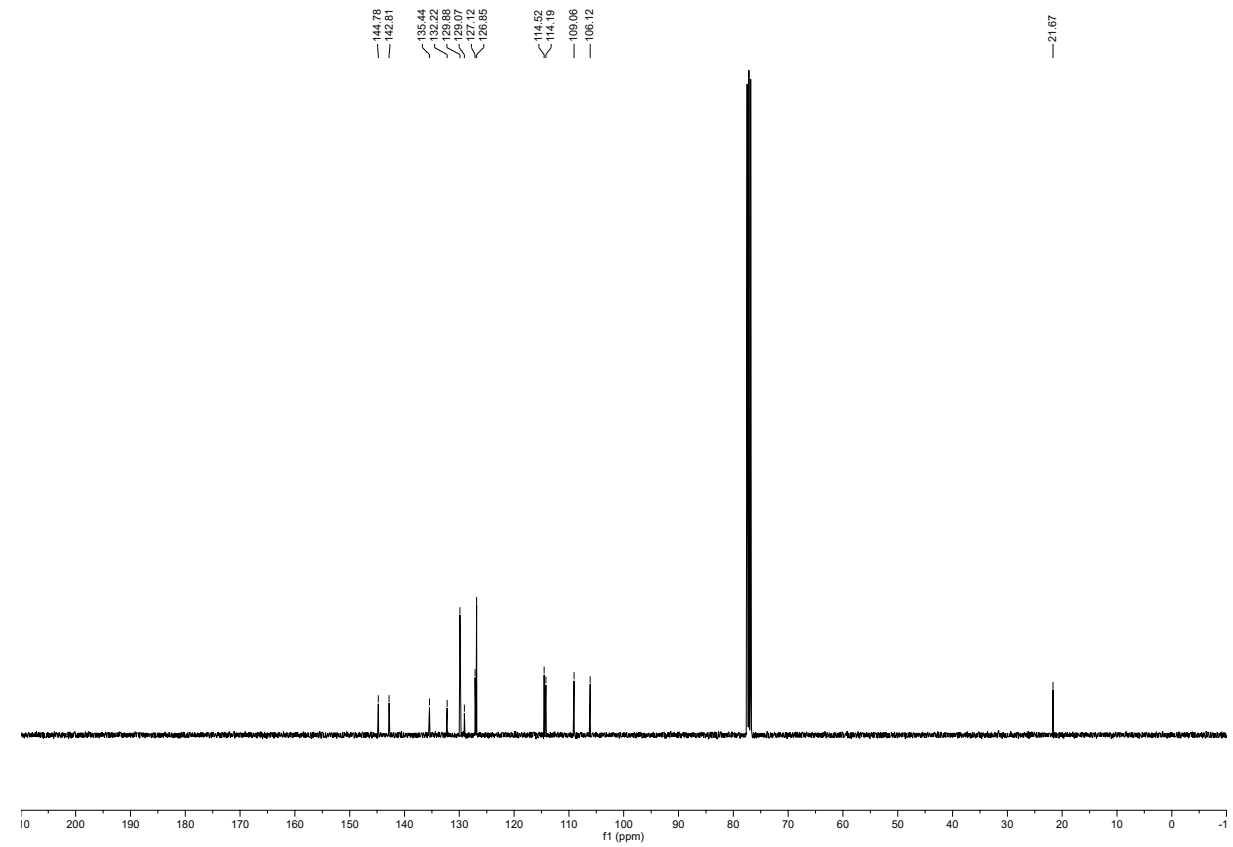

149.75
142.07
131.61
129.14
126.21
115.65
113.62
106.76
105.93
83.15
28.16
f1 (ppm)

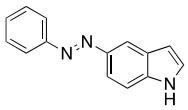

H_2N
N
Ac

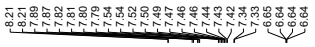
8.22
8.20
7.26
6.79
6.78
6.71
6.70
6.69
6.68
6.43
6.42
3.67
2.52
0.94
1.01
1.01
1.04
1.00
1.95
3.05
f1 (ppm)

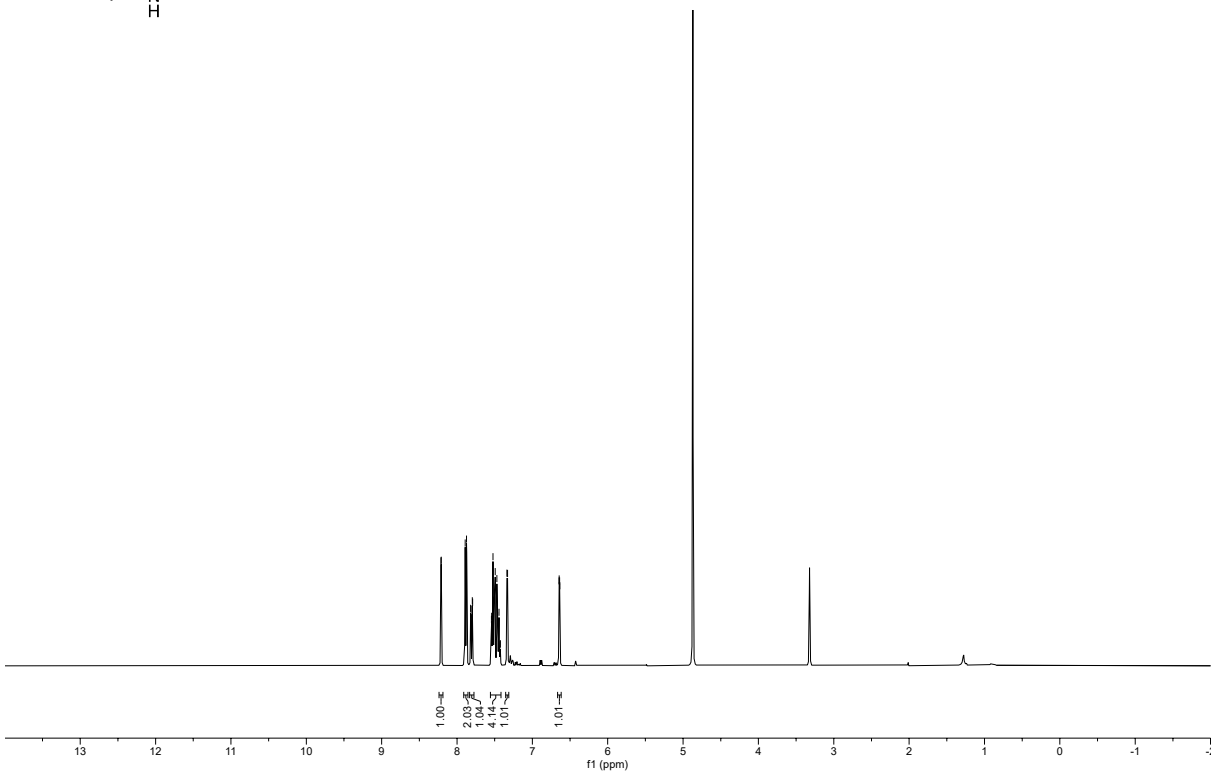

168.15
142.95
131.60
129.41
125.69
117.12
114.05
108.19
105.68
23.56
f1 (ppm)

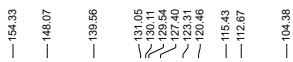

H2N
N
Ts
7.78
7.76
7.72
7.71
7.70
7.70
7.45
7.44
7.26
7.20
7.18
6.76
6.76
6.70
6.70
6.68
6.68
6.48
6.48
6.47
6.47
3.60
2.33
1.00
1.96
0.97
2.01
0.97
1.00
0.97
2.00
3.04
f1 (ppm)

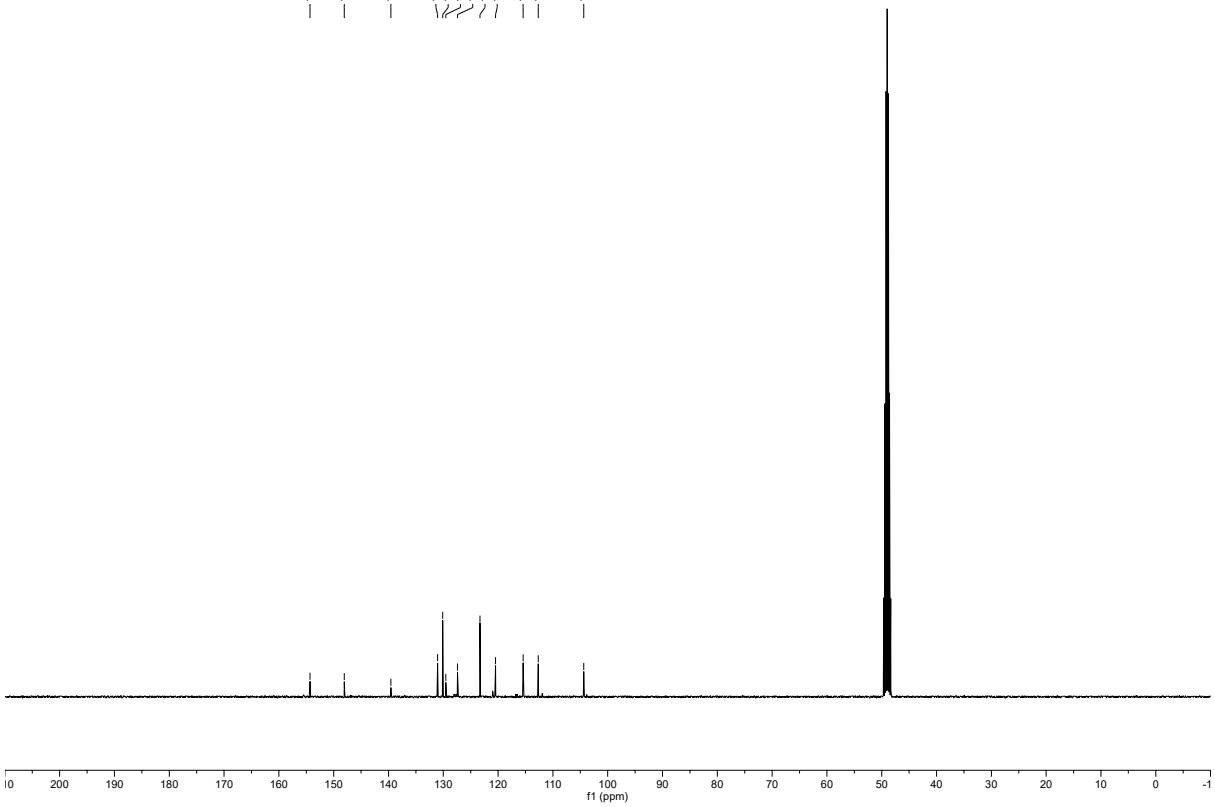

144.78
142.81
135.44
132.22
129.88
129.07
127.12
126.85
114.52
114.19
109.06
106.12
21.67
f1 (ppm)

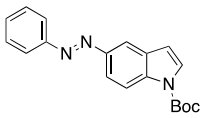



8.21
8.21
7.89
7.87
7.82
7.81
7.80
7.79
7.54
7.54
7.52
7.50
7.49
7.47
7.46
7.46
7.44
7.43
7.42
7.34
7.33
6.65
6.64
6.64
6.64


1.00
2.03
1.04
4.14
1.01
1.01
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

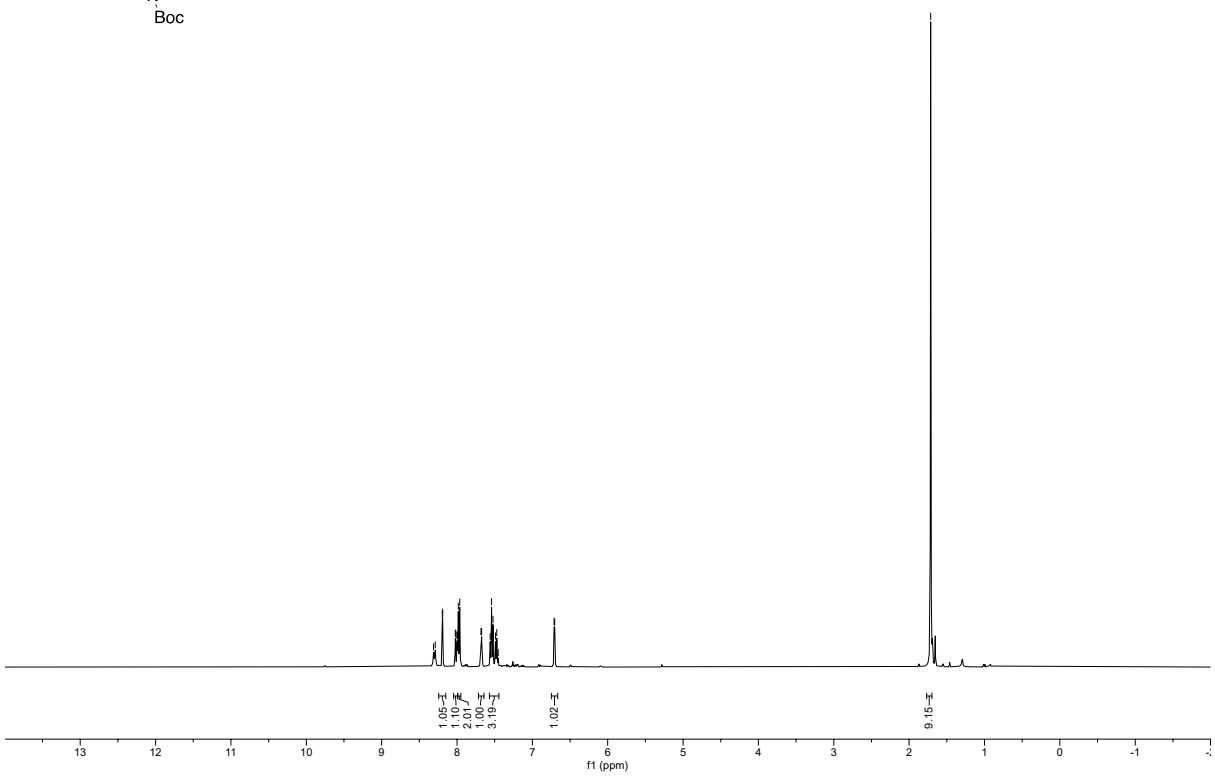

154.33
148.07
139.56
131.05
130.11
129.54
127.40
123.31
120.46
115.43
112.67
104.38


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

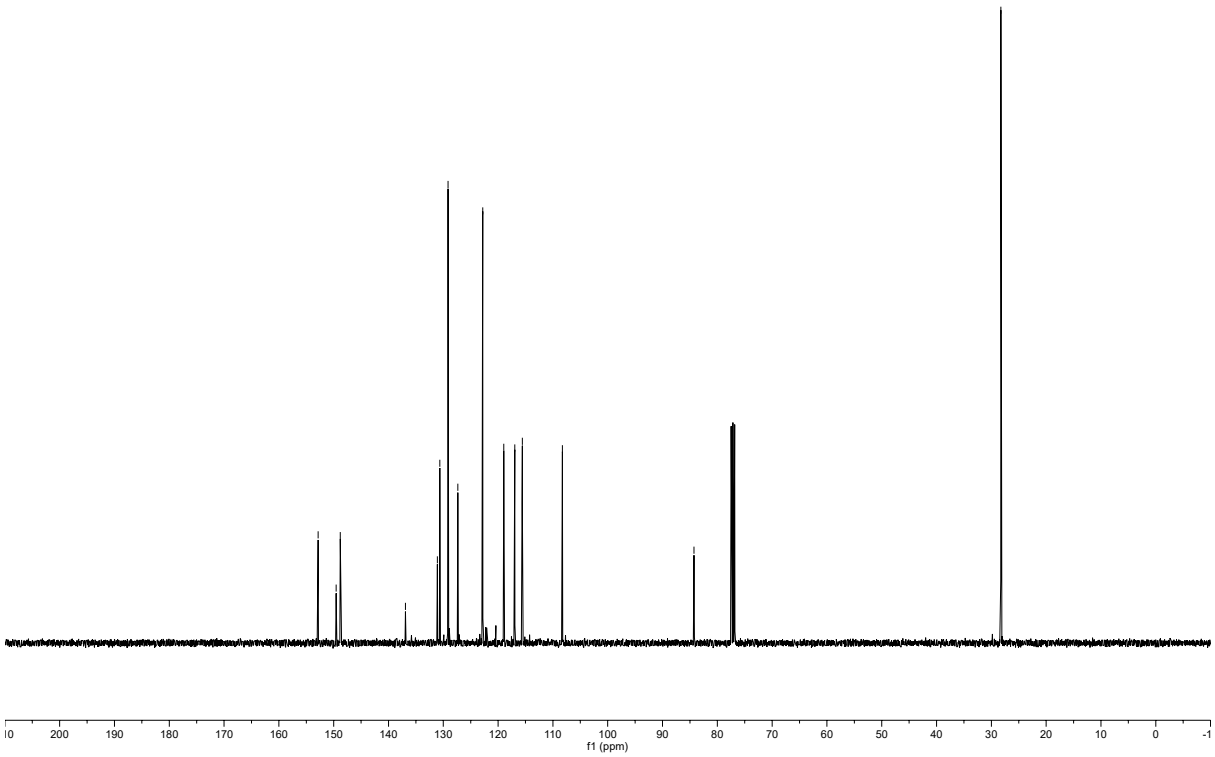

N
N
N
Boc

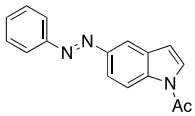

8.31
8.29
8.19
8.19
8.02
8.02
8.00
8.00
7.98
7.96
7.68
7.67
7.56
7.54
7.52
7.49
7.47
6.71
6.70

1.71

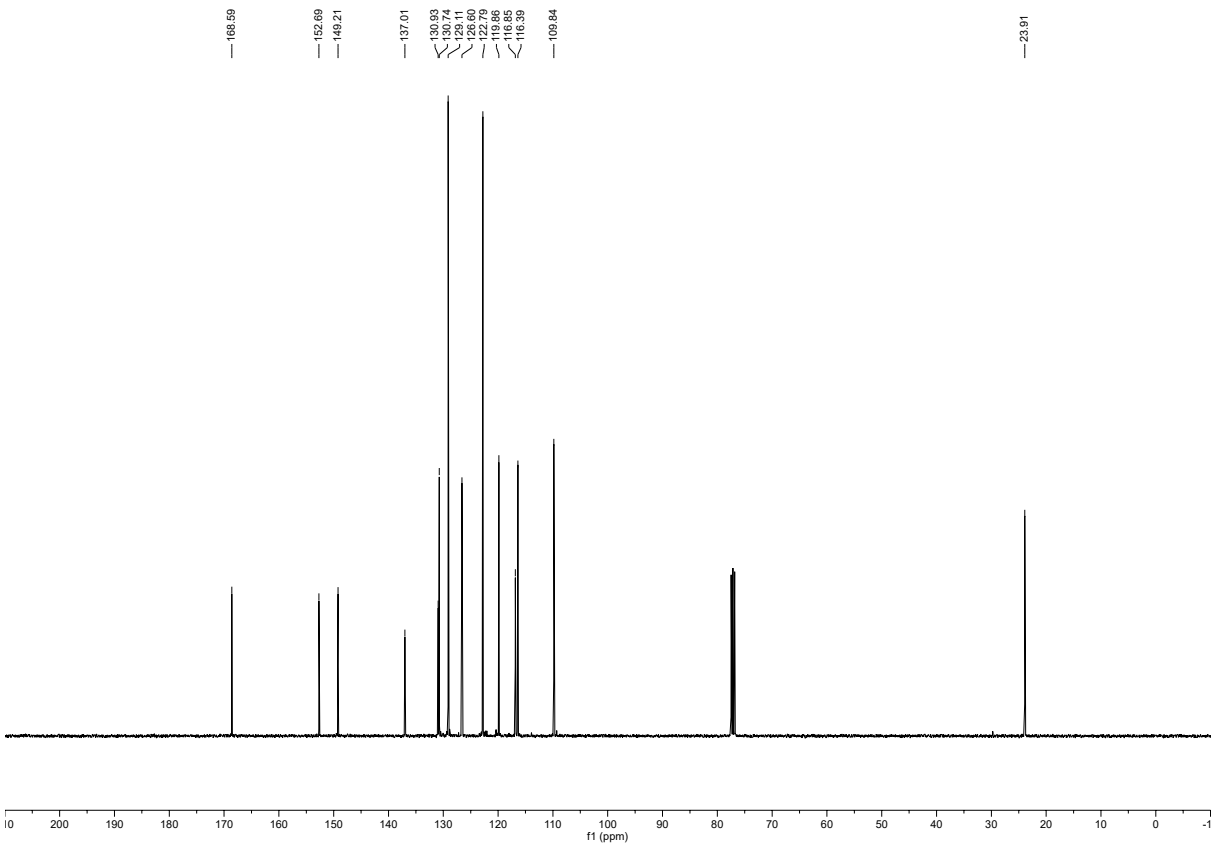

1.05
1.10
2.01
1.00
3.19
1.02
9.15
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

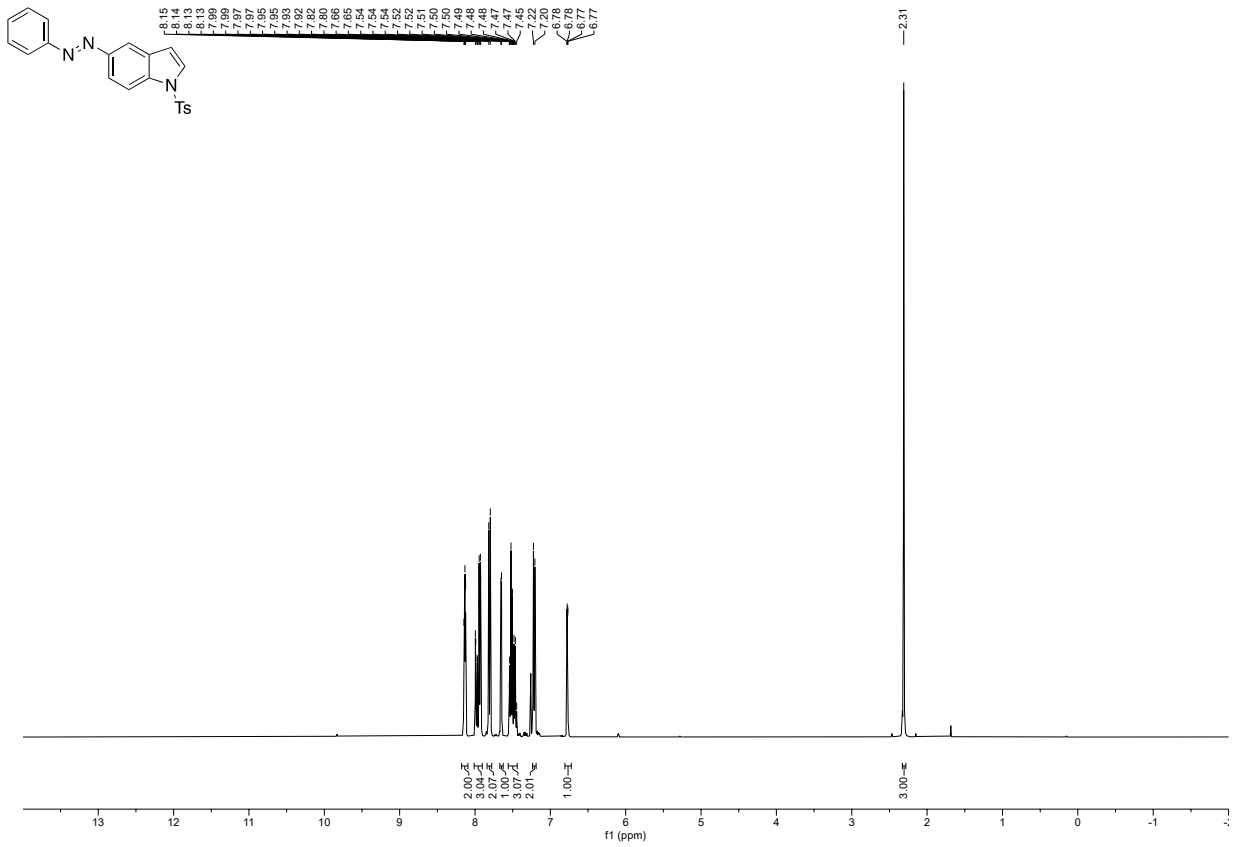

152.85
149.55
148.81
136.90
131.09
130.64
129.14
127.35
122.80
118.96
116.96
115.57
108.26
84.26
28.26

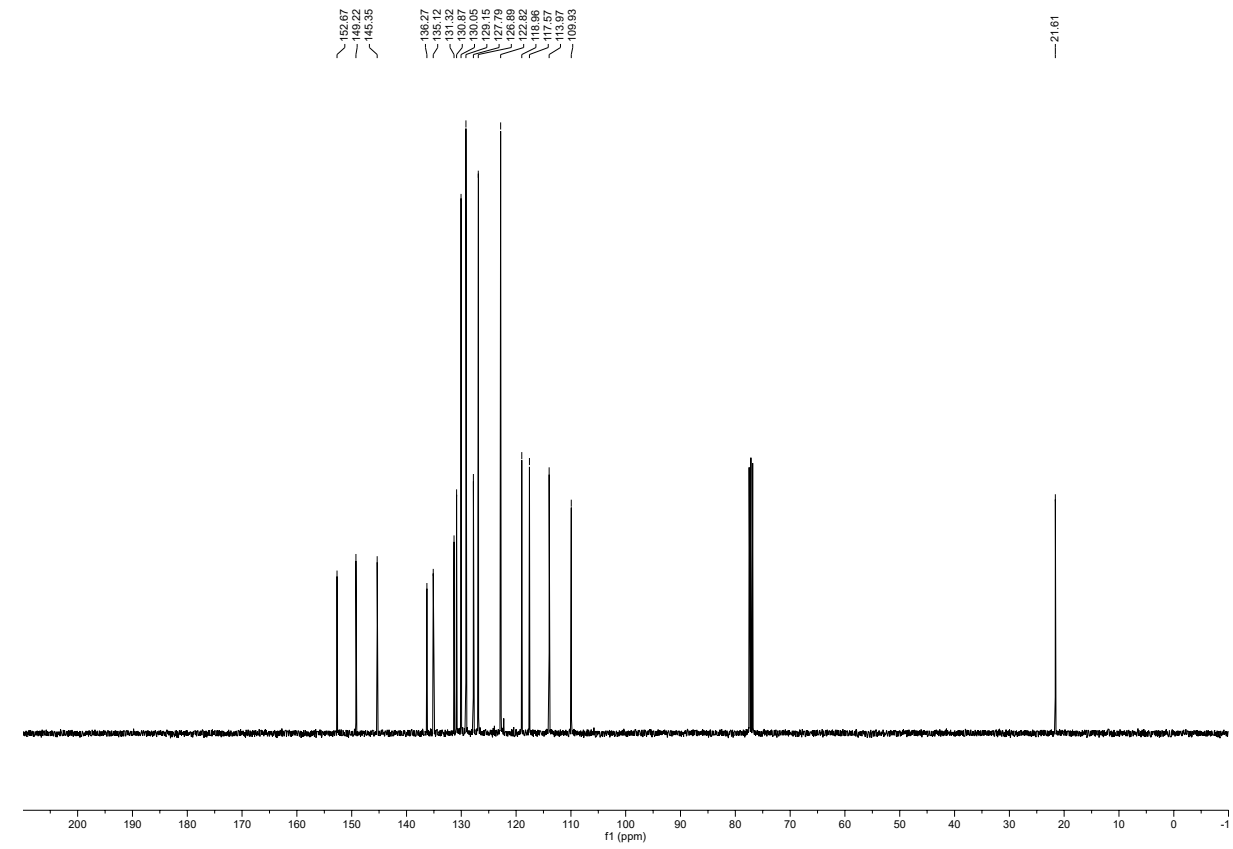

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

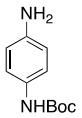

N
N
N
Ac

8.55
8.53
8.12
8.12
8.00
8.00
7.98
7.98
7.97
7.96
7.95
7.94
7.54
7.53
7.52
7.51
7.51
7.48
7.48
7.48
7.47
7.46
7.44
7.39
7.38
6.69
6.68
2.57
1.00
1.00
3.05
3.12
1.03
1.01
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

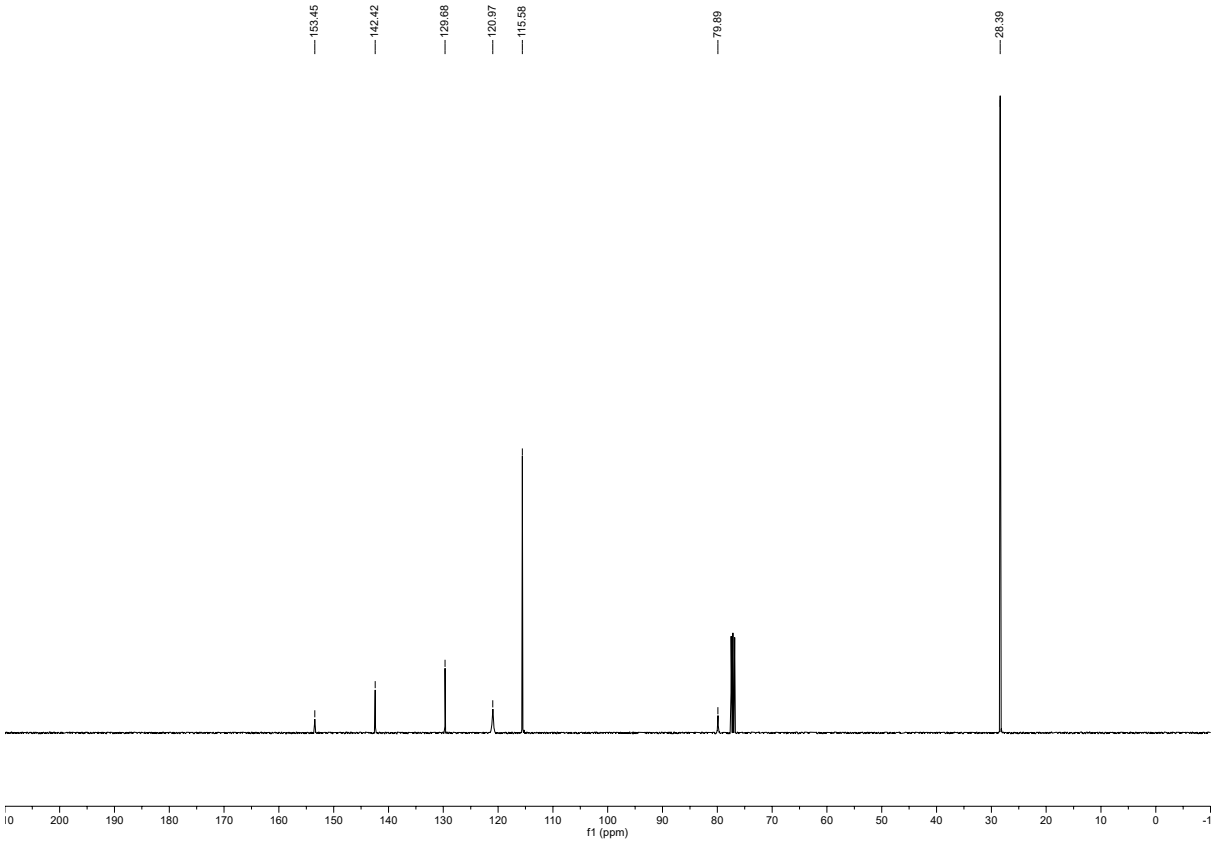

168.59
152.69
149.21
137.01
130.93
130.74
129.11
126.60
122.79
119.86
116.85
116.39
109.84
23.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

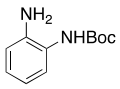

8.15
8.14
8.13
8.13
7.99
7.99
7.97
7.97
7.95
7.93
7.92
7.82
7.80
7.66
7.65
7.54
7.54
7.54
7.52
7.51
7.50
7.50
7.49
7.48
7.48
7.47
7.47
7.45
7.22
6.78
6.78
6.77
6.77
2.31
Ts
2.00
3.04
2.07
1.00
3.07
2.01
1.00
3.00
f1 (ppm)


152.67
149.22
146.35
136.27
135.12
131.32
130.87
130.05
129.15
127.79
126.89
122.82
118.96
117.57
113.97
109.93
21.61
f1 (ppm)

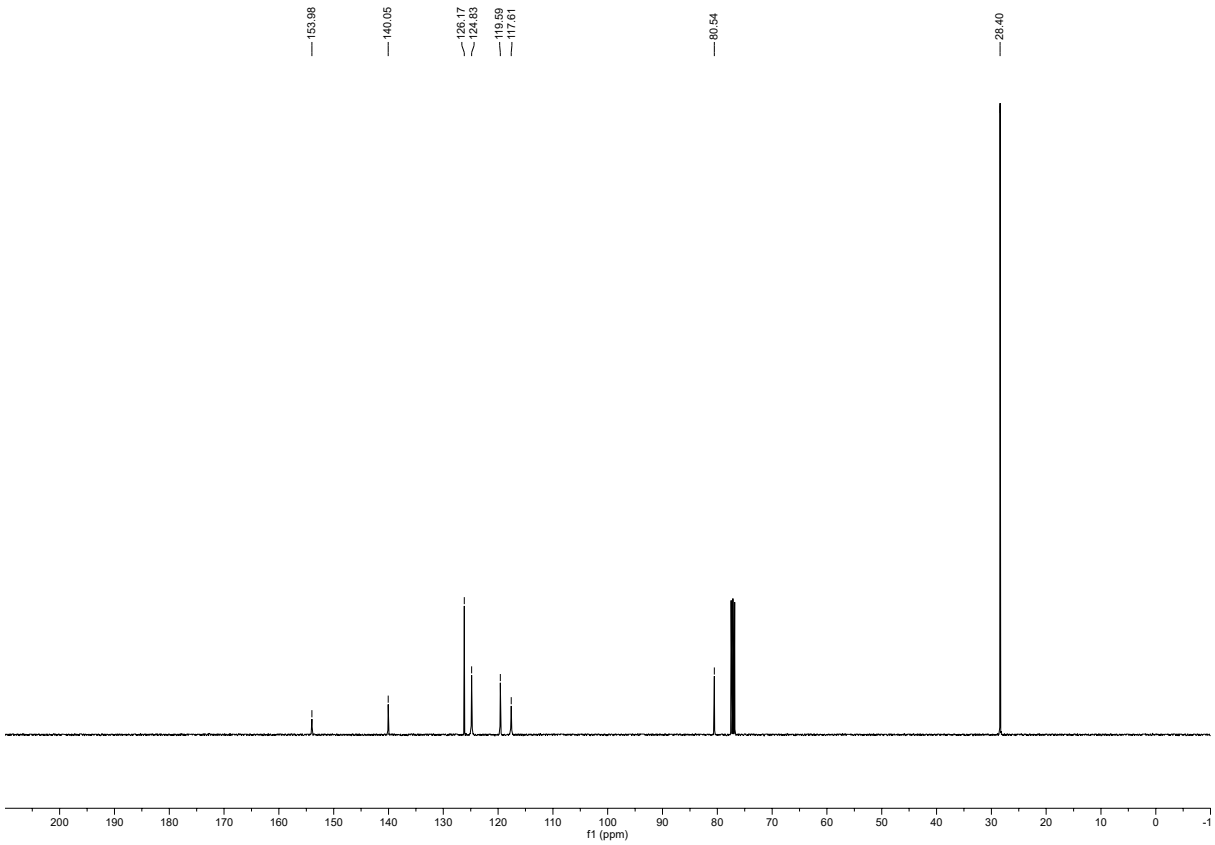

NH2
NHBoc

7.11
7.09
6.59
6.57
6.55
3.54
1.49
1.87
2.04
0.95
1.98
9.00
f1 (ppm)


153.45
142.42
129.68
120.97
115.58
79.69
28.39
f1 (ppm)


NH2
NHBoc

7.27
7.25
7.01
7.00
6.99
6.98
6.97
6.97
6.80
6.79
6.79
6.77
6.75
6.75
6.73
6.73
6.36
3.74
1.52
0.98
0.98
1.96
0.88
1.92
9.00
f1 (ppm)


153.98
140.05
126.17
124.83
119.59
117.61
80.54
28.40
f1 (ppm)