Cp*Rh(III) Catalyzed *Ortho*-Halogenation of *N*-Nitrosoanilines by Solvent-Controlled Regioselective C-H Functionalization

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Supporting Information

Contents

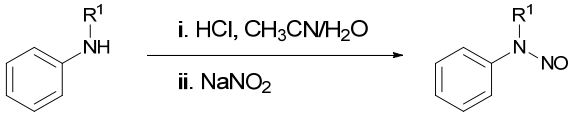
1. General information and materials

Reagent: All the reactions were carried out under air atmosphere. All the solvents used for the reactions were dried according to standard procedures. All commercial materials were used as received unless otherwise noted. $[RhCp^*Cl_2]_2$, $AgSbF_6$, $Zn(NTf_2)_2$, NBS, NIS were used in Rh-catalyzed reactions. The starting materials N-nitrosoanilines[1-4] were prepared according to the reported procedure.. All the reactions were monitored by thin layer chromatography (TLC, Silica gel Merck 60 F_{254}); The spots were visualized by UV light. Purification of products was conducted by flash chromatography on silica gel (particle size 40-63 μm, 230-400 mesh SiliaFlash® P60 (Silicycle Inc.)).

Instruments: NMR spectra were recorded on Bruker Ultrashield™ 500 MHz. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR), DMSO-d_6 (2.50 ppm for ^1H NMR, 39.52 ppm for ^{13}C NMR); For the characterization of the observed signal multiplicities, the following abbreviations were applied: s (singlet), d (doublet), dd (double doublet), t (triplet), td (triple doublet), q (quartet), m (multiplet), as well as br (broad); High resolution ESI mass experiments were operated on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument.

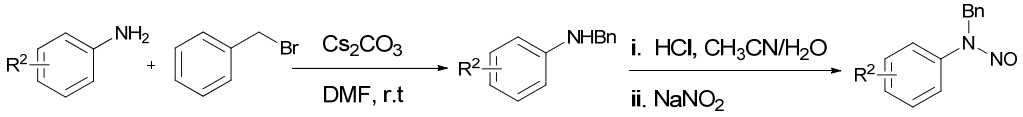
2. Synthesis of Substrates

2.1 General procedure A for preparation of N-nitroso aniline substrates[1]



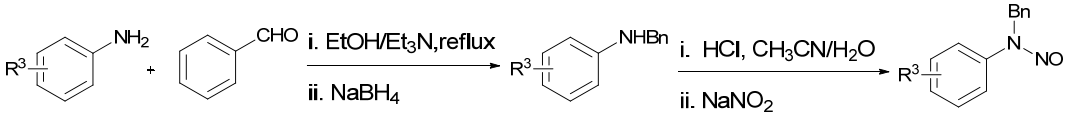
The aniline (5.0 mmol, 1.0 equiv.) was dissolved in a 1:2 mixture of acetonitrile and water (15 mL) and cooled to 0 ºC (ice bath). Concentrated aqueous HCl (2.0 mL, 24.0 mmol) was added dropwise. The mixture was stirred vigorously for half an hour, while maintained at 0 ºC. To this mixture was added an aqueous solution (5.0 mL) of $NaNO_2$ (0.35 g, 5.0 mmol) over the course of 10 min. The reaction was allowed to proceed for 1 h. The mixture was then extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash silica gel column chromatography (petroleum ether / ethyl acetate = 20:1) to give the corresponding N-nitroso aniline substrates 1.

2.2 General procedure B for preparation of N-nitroso aniline substrates[2]



A mixture of cesium carbonate (0.5 equiv.) and the amine (7.0 mmol, 1.0 equiv.) in anhydrous DMF (5.0 mL) was stirred at 25 ºC for 30 min. Then added the benzyl bromide (1.0 equiv.) in one portion, and the resulting reaction mixture was stirred for overnight. The mixture was then poured into a lot of water and extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash silica gel column chromatography (petroleum ether / ethyl acetate = 20:1) to give the N-benzylaniline substrates. The N-benzylaniline (2.0 mmol, 1.0 equiv.) was dissolved in a 1:2 mixture of acetonitrile and water (15.0 mL) and cooled to 0 ºC (ice bath). Concentrated aqueous HCl (0.8 mL, 1.0 mmol) was added dropwise. The mixture was stirred vigorously for half an hour, while maintained at 0 ºC. To this mixture was added an aqueous solution (5 mL) of $NaNO_2$ (0.14 g, 2.0 mmol) over the course of 10 min. The reaction was allowed to proceed for 1 h. The mixture was then extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, concentrated under reduced pressure to afford corresponding N-benzyl-N-phenylnitrous amide substrates. They were pure enough to be used without further purification.

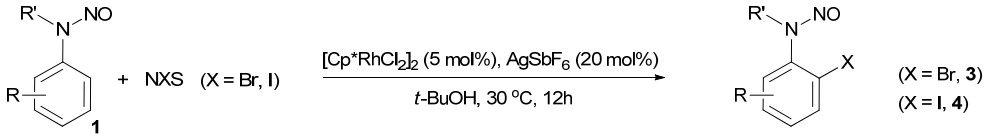
2.3 General procedure C for preparation of N-nitroso aniline substrates[3-4]



A mixture of aniline (7.0 mmol, 1.0 equiv.) and benzaldehyde (0.71mL, 1.0 equiv.), in ethanol (10 mL) was stirred at room temperature. Triethylamine (1.16 mL, 1.2 equiv.) was added to the mixture and refluxed overnight. The solution was then cooled to 0 ºC, and $NaBH_4$ (1.5 equiv.) was added slowly. The resulting solution was allowed to warm to r.t and stirred until the intermediate imine had been completely consumed, as judged by TLC analysis. The reaction mixture was diluted with water and acidified with AcOH to pH 5, then extracted with EtOAc. The combined

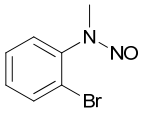
organic layers were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash silica gel column chromatography to give the N-benzylaniline substrates. The N-benzylaniline (2.0 mmol, 1.0 equiv.) was dissolved in a 1:2 mixture of acetonitrile and water (15 mL) and cooled to 0 °C (ice bath). Concentrated aqueous HCl (0.80 mL, 1.0 mmol) was added dropwise. The mixture was stirred vigorously for half an hour, while maintained at 0 °C. To this mixture was added an aqueous solution (5 mL) of $NaNO_2$ (0.14 g, 2.0 mmol) over the course of 10 min. The reaction was allowed to proceed for 1 h. The mixture was then extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, concentrated under reduced pressure to afford corresponding N-benzyl-N-phenylnitrous amide substrates. They were pure enough to be used without further purification.

3. Preparation and characterization Data of Products



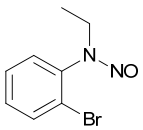
1a (27.2 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %), $AgSbF_6$ (13.8 mg, 20 mol %), and NXS (1.2 eq) were weighed into a pressure tube, to which was added t-BuOH (1.0 mL) under air. The reaction mixture was stirred for 12 h at 30 °C. Purification was performed by flash column chromatography on silica gel using n-hexane and tetrahydrofuran to afford the product **3a** as a pale yellow liquid (38.3 mg, 89%).

***N*-(2-Bromophenyl)-*N*-methylnitrous amide (3a)**



Pale yellow liquid (89% yield, 38.3 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1: 0.11. **^{1}H NMR (500 MHZ,$CDCl_3$)** (*syn* and *anti* isomers) δ 7.75 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H × 0.11), 7.47 (td, *J* = 7.8 Hz, 1.1 Hz, 1H), 7.40-7.38 (m, 1H + 1H × 0.11), 7.36 (td, *J* = 7.9 Hz, 1.5 Hz, 1H), 7.29 (td, *J* = 8.0 Hz, 1.4 Hz, 1H × 0.11), 7.03 (dd, *J* = 1.3 Hz, 1H × 0.11), 4.09 (s, 3H × 0.11), 3.40 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 141.70, 133.98, 133.69, 131.02, 130.74, 128.72, 128.53, 128.37, 128.34, 120.74, 120.03, 40.05, 35.37. **HRMS (ESI) m/z** calculated for $C_7H_8BrN_2O$ $[M+H]^+$, 214.9820, found 214.9820.

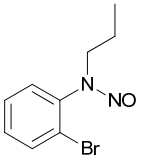
***N*-(2-Bromophenyl)-*N*-ethylnitrous amide (3b)**



Pale yellow liquid (93% yield, 42.6 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be

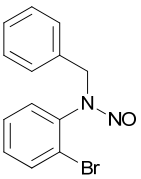
approximately 1:0.45. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H × 0.45), 7.47 (t, *J* = 7.5 Hz, 1H), 7.42-7.34 (m, 2H + 1H × 0.45), 7.29 (t, *J* = 7.8 Hz, 1H × 0.45), 6.99 (d, *J* = 7.7 Hz, 1H × 0.45), 4.67-4.64 (m, 1H × 0.45), 4.44-4.42 (m, 1H × 0.45), 4.01 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H × 0.45), 1.08 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 140.20, 137.64, 133.96, 133.72, 130.90, 130.81, 129.55, 129,29, 128.40 (overlapped), 121.50, 121.40, 48.39, 41.73, 14.11, 11.14. **HRMS (ESI) m/z** calculated for $C_8H_{10}BrN_2O$ $[M+H]^+$, 228.9971, found 228.9978.

***N*-(2-Bromophenyl)-*N*-propylnitrous amide (3c)**



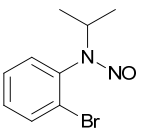
Yellow liquid (82% yield, 40.0 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.53. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.76 (dd, *J* = 8.5 Hz, 0.9 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H × 0.53), 7.47 (td, *J* = 7.6 Hz, 0.6 Hz, 1H), 7.41-7.34 (m, 2H + 1H × 0.53), 7.29 (td, *J* = 8.1 Hz, 1.0 Hz, 1H × 0.53), 6.99 (dd, *J* = 7.8 Hz, 0.8 Hz, 1H × 0.53), 4.59-4.54 (m, 1H × 0.53), 4.31-4.28 (m, 1H × 0.53), 3.91 (t, *J* = 7.7 Hz, 2H), 1.83-1.77 (m, 2H × 0.53), 1.54-1.46 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H × 0.53), 0.88 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 140.58, 137.93, 134.01, 133.76, 130.85, 130.72, 129.38, 129.20, 128.38 (overlapped), 121.36, 121.25, 55.07, 48.20, 21.86, 19.62, 11.57, 11.24. **HRMS (ESI) m/z** calculated for $C_9H_{12}BrN_2O$ $[M+H]^+$, 243.0128, found 243.0128.

***N*-Benzyl-*N*-(2-bromophenyl)nitrous amide (3d)**



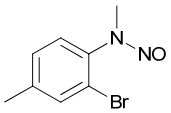
Yellow liquid (89% yield, 51.8 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.44. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.74 (dd, *J* = 7.4 Hz, 1.6 Hz, 1H), 7.65 (dd, *J* = 7.9 Hz, 1.4 Hz, 1H × 0.44), 7.34-7.29 (m, 3H + 3H × 0.44), 7.26-7.24 (m, 2H + 2H × 0.44), 7.22-7.16 (m, 2H × 0.44), 7.12-7.08 (m, 3H), 6.50 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H × 0.44), 6.07 (d, *J* = 14.5 Hz, 1H × 0.44), 5.21-5.16 (m, 2H + 1H × 0.44). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 140.08, 137.32, 134.59 (overlapped), 133.89, 133.58, 130.91, 130.83, 130.02, 129.78, 129.19, 129.10, 128.85, 128.63, 128.60, 128.23, 128.07, 127.98, 121.28, 121.17, 57.20, 49.57. **HRMS (ESI) m/z** calculated for $C_{13}H_{12}BrN_2O$ $[M+H]^+$, 291.0127, found 291.0143.

***N*-(2-Bromophenyl)-*N*-isopropylnitrous amide (3e)**



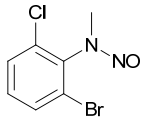
Yellow liquid (41% yield, 20.0 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.47. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.79 (d, *J* = 7.9 Hz, 1H × 0.47), 7.69 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H × 0.47), 7.41-7.33 (m, 1H + 2H × 0.47), 7.29 (td, *J* = 7.9 Hz, 0.7 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 5.11-5.06 (m, 1H × 0.47), 4.85-4.80 (m, 1H), 1.69 (d, *J* = 6.8 Hz, 6H × 0.47), 1.51 (d, *J* = 6.7 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 137.70, 134.10, 133.79, 130.95, 130.80, 129.98, 129.38, 128.28, 128.07, 124.05, 122.17, 56.82, 48.05, 22.70, 21.52, 19.52. **HRMS (ESI) m/z** calculated for $C_9H_{12}BrN_2O$ $[M+H]^+$, 243.0128, found 243.0129.

***N*-(2-Bromo-4-methylphenyl)-*N*-methylnitrous amide (3g)**



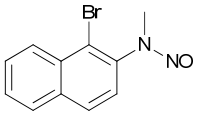
Yellow liquid (85% yield, 38.9 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.12. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.55 (s, 1H), 7.49 (s, 1H × 0.12), 7.28-7.24 (m, 2H), 7.20 (d, *J* = 7.8 Hz, 1H × 0.12), 6.90 (d, *J* = 8.0 Hz, 1H × 0.12), 4.07 (s, 3H × 0.12), 3.38 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H × 0.12). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 141.38, 139.19 (overlapped), 134.26, 134.08, 129.47, 129.17, 127.96, 127.82, 120.27, 119.70, 40.15, 35.45, 20.96, 20.90. **HRMS (ESI) m/z** calculated for $C_8H_{10}BrN_2O$ $[M+H]^+$, 228.9971, found 228.9977.

***N*-(2-Bromo-6-chlorophenyl)-*N*-methylnitrous amide (3r)**



Yellow liquid (30% yield, 15.0 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.23. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.68 (dd, *J* = 8.1 Hz, 0.9 Hz, 1H), 7.57-7.53 (m, 1H + 1H× 0.23), 7.44 (dd, *J* = 8.1 Hz, 0.8 Hz, 1H × 0.23), 7.32 (t, *J* = 8.2 Hz, 1H), 7.24 (t, *J* = 8.2 Hz, 1H × 0.23), 4.09 (s, 3H× 0.23), 3.33 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 139.23, 134.49, 132.96, 132.11, 131.88, 131.67, 131.61, 129.62, 129.36, 124.08, 122.31, 38.33, 33.85. **HRMS (ESI) m/z** calculated for $C_7H_7BrClN_2O$ $[M+H]^+$, 250.9403, found 250.9411.

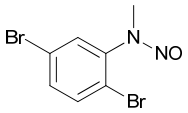
***N*-(1-Bromonaphthalen-2-yl)-*N*-methylnitrous amide (3t)**



Brown liquid (51% yield, 27.0 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.15. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 8.40 (d, *J* = 8.5 Hz, 1H), 8.31 (d, *J* = 8.2 Hz, 1H × 0.15), 7.97-7.92 (m, 2H), 7.90-7.86 (m, 2H × 0.15), 7.70 (t, *J* = 8.2 Hz, 1H),

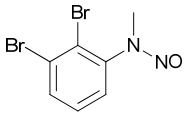
7.66-7.61 (m, 1H + 2H × 0.15), 7.47 (d, *J* = 8.6 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 1H × 0.15), 4.19 (s, 3H × 0.15), 3.50 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 139.71, 134.30, 134.16, 132.62, 131.71, 129.43, 129.07, 128.47 (overlapped), 128.33, 128.30, 128.13, 127.93, 127.84, 127.69, 124.96, 124.19, 121.53, 120.94, 39.87, 35.56. **HRMS (ESI) m/z** calculated for $C_{11}H_{10}BrN_2O$ $[M+H]^+$, 264.9971, found 264.9981.

***N*-(2,5-Dibromophenyl)-*N*-methylnitrous amide (3u)**



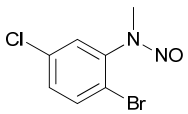
White solid (70% yield, 41.2 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.12. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 7.61 (d, *J* = 8.6 Hz, 1H), 7.56-7.52 (m, 1H + 1H × 0.12), 7.49 (dd, *J* = 8.5 Hz, 1.9 Hz, 1H), 7.42 (dd, *J* = 8.3 Hz, 1.6 Hz, 1H × 0.12), 7.17 (d, *J* = 1.9 Hz, 1H × 0.12), 4.09 (s, 3H × 0.12), 3.38 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 142.72, 135.03, 134.75, 134.06, 133.66, 131.39, 131.31, 121.70 (overlapped), 119.81, 118.73, 39.86, 35.22. **HRMS (ESI) m/z** calculated for $C_7H_7Br_2N_2O$ $[M+H]^+$, 294.8899, found 294.8914.

***N*-(2,3-Dibromophenyl)-*N*-methylnitrous amide (3u')**



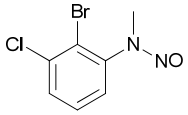
Yellow liquid (20% yield, 11.8 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.15. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 7.78-7.76 (m, 1H), 7.70 (dd, *J* = 8.1 Hz, 1.3 Hz, 1H × 0.15), 7.35-7.34 (m, 2H), 7.30-7.26 (m, 1H × 0.15), 6.97 (dd, *J* = 7.8 Hz, 1.3 Hz, 1H × 0.15), 4.10 (s, 3H × 0.15), 3.38 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 143.47, 134.73, 134.52, 129.27, 129.05, 127.24, 127.08, 126.92 (overlapped), 123.76 (overlapped), 39.83, 35.29. **HRMS (ESI) m/z**calculated for $C_7H_7Br_2N_2O$ $[M+H]^+$, 294.8899, found 294.8914.

***N*-(2-Bromo-5-chlorophenyl)-*N*-methylnitrous amide (3v)**



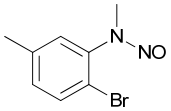
White solid (59% yield, 29.4 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.12. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 7.68 (d, *J* = 8.6 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H × 0.12), 7.42 (d, *J* = 2.3 Hz, 1H), 7.36 (dd, *J* = 8.6 Hz, 2.4 Hz, 1H), 7.29 (dd, *J* = 8.6 Hz, 2.4 Hz, 1H × 0.12), 7.03 (d, *J* = 2.4 Hz, 1H × 0.12), 4.09 (s, 3H × 0.12), 3.39 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 142.55, 134.76, 134.47, 134.33, 134.28, 131.16, 130.72, 128.58, 128.48, 117.94 (overlapped), 39.83, 35.20. **HRMS (ESI) m/z** calculated for $C_7H_7BrClN_2O$, $[M+H]^+$, 250.9403, found 250.9412.

***N*-(2-Bromo-3-chlorophenyl)-*N*-methylnitrous amide (3v')**



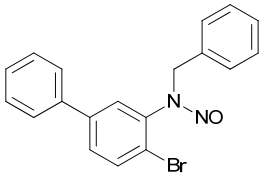
Yellow liquid (27% yield, 13.5 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.17. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.62 (dd, *J* = 8.1 Hz, 1.3 Hz, 1H), 7.54 (dd, *J* = 8.1 Hz, 1.1 Hz, 1H × 0.17), 7.42 (t, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H × 0.17), 7.31 (dd, *J* = 7.9 Hz, 1.3 Hz, 1H), 6.94 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H × 0.17), 4.10 (s, 3H × 0.17), 3.39 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 143.59, 136.75, 136.65, 131.37, 131.12, 128.98, 128.73, 126.59, 126.46, 121.46 (overlapped), 39.85, 35.31. **HRMS (ESI) m/z** calculated for $C_7H_7BrClN_2O$ $[M+H]^+$, 250.9403, found 250.9412.

***N*-(2-Bromo-5-methylphenyl)-*N*-methylnitrous amide (3w)**



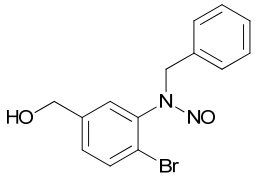
White solid (97% yield, 44.4 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.11. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.59 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H × 0.11), 7.20 (s, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H × 0.11), 6.82 (s, 1H × 0.11), 4.07 (s, 3H × 0.11), 3.38 (s, 3H). 2.37 (s, 3H), 2.31 (s, 3H × 0.11). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 141.33, 139.18, 138.99, 133.54, 133.26, 131.90, 131.54, 128.99, 128.72, 117.04, 116.36, 40.09, 35.38, 20.79 (overlapped). **HRMS (ESI) m/z** calculated for $C_8H_{10}BrN_2O$ $[M+H]^+$, 228.9971, found 228.9979.

***N*-Benzyl-*N*-(4-bromo-[1,1'-biphenyl]-3-yl)nitrous amide (3x)**



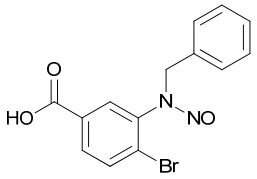
Yellow liquid (92% yield, 67.4 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.42. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.79 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H × 0.42), 7.54 (dd, *J* = 8.3 Hz, 2.1 Hz, 1H), 7.43-7.42 (m, 3H + 3H × 0.42), 7.40-7.33 (m, 3H + 3H × 0.42), 7.30-7.27 (m, 3H + 3H × 0.42), 7.25-7.23 (m, 2H × 0.42), 7.18-7.17 (m, 2H), 6.67 (d, *J* = 2.0 Hz, 1H × 0.42). 6.13 (d, *J* = 14.4 Hz, 1H × 0.42), 5.26-5.22 (m, 2H + 1H × 0.42). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 141.72, 141.52, 140.35, 138.61, 138.58, 137.67, 134.67, 134.13, 133.94, 133.76, 129.45, 129.40, 129.32, 129.30, 129.23 (overlapped), 129.08, 128.95, 128.71, 128.57, 128.30 (overlapped), 128.11, 128.07, 126.94, 126.81, 119.93 (overlapped), 57.32, 49.65. **HRMS (ESI) m/z** calculated for $C_{19}H_{16}BrN_2O$ $[M+H]^+$, 367.0440, found 367.0460.

***N*-Benzyl-*N*-(2-bromo-5-(hydroxymethyl)phenyl)nitrous amide (3zb)**



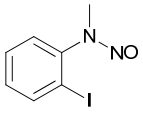
Yellow liquid (78% yield, 50.1 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.44. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 7.66 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H × 0.44), 7.31-7.30 (m, 1H + 1H × 0.44), 7.26-7.22 (m, 4H + 2H × 0.44), 7.16 (d, *J* = 8.1 Hz, 1H × 0.44), 7.10-7.09 (m, 2H + 2H × 0.44), 6.50 (d, *J* = 0.9 Hz, 1H × 0.44), 5.96 (d, *J* = 14.6 Hz, 1H × 0.44), 5.26 (d, *J* = 14.6 Hz, 1H × 0.44), 5.13 (s, 2H), 4.54 (s, 2H), 4.40 (s, 2H × 0.44). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 141.99, 141.81, 139.98, 137.23, 134.33, 133.82, 133.72, 133.49, 129.21, 129.20, 129.05, 128.99, 128.84, 128.63, 128.00 (overlapped), 127.90, 127.64, 119.61, 119.58, 63.51 (overlapped), 57.37, 49.84. **HRMS (ESI) m/z** calculated for $C_{14}H_{14}BrN_2O_2$ $[M+H]^+$, 321.0233, found 321.0249.

3-(Benzyl(nitroso)amino)-4-bromobenzoic acid (3zc)



White solid (37% yield, 24.8 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.60. **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** (*syn* and *anti* isomers) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.93 (dd, *J* = 8.3 Hz, 1.7 Hz, 1H), 7.86-7.82 (m, 1H + 2H × 0.60), 7.35-7.33 (m, 2H + 3H × 0.60), 7.29-7.23 (m, 1H + 3H × 0.60), 7.15 (d, *J* = 6.8 Hz, 2H), 5.94 (d, *J* = 14.8 Hz, 1H × 0.60), 5.55 (d, *J* = 14.8 Hz, 1H × 0.60), 5.18 (s, 2H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** (*syn* and *anti* isomers) δ 166.17, 166.07, 140.18, 137.88, 134.77, 134.20, 134.01 (overlapped), 132.12, 132.04, 132.00, 131.95, 130.20, 130.17, 129.68, 129.28, 129.16, 128.99, 128.91, 128.34, 126.78, 126.49, 57.00, 49.91. **HRMS (ESI) m/z** calculated for $C_{14}H_{12}BrN_2O_3$ $[M+H]^+$, 335.0025, found 335.0046.

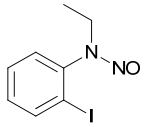
***N*-(2-Iodophenyl)-*N*-methylnitrous amide (4a)**



Pale yellow liquid (95% yield, 49.8 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.12. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H × 0.12), 7.50 (td, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H × 0.12), 7.34 (dd, *J* = 7.8 Hz, 1.3 Hz, 1H), 7.20 (td, *J* = 7.9 Hz, 1.4 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1.4 Hz, 1H × 0.12), 6.98 (d, *J* = 7.8 Hz, 1H × 0.12), 4.09 (s, 3H × 0.12), 3.38 (s, 3H). **^{13}C NMR (125**

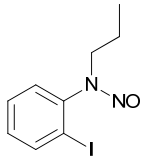
MHz, $CDCl_3$) (*syn* and *anti* isomers) δ 145.11, 140.32, 140.02, 131.01, 130.92, 129.66, 129.44, 127.96, 127.75, 95.43, 95.17, 40.13, 35.54. **HRMS (ESI) m/z** calculated for $C_7H_8IN_2O$ $[M+H]^+$, 262.9675, found 262.9688.

***N*-Ethyl-*N*-(2-iodophenyl)nitrous amide (4b)**



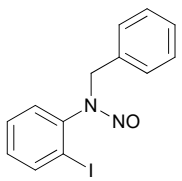
Pale yellow liquid (94% yield, 52.0 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^1H NMR to be approximately 1:0.44. **^1H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 8.02 (dd, *J* = 8.0 Hz, 1.1 Hz, 1H), 7.93 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H × 0.44), 7.50 (td, *J* = 7.7 Hz, 1.2 Hz, 1H), 7.43 (td, *J* = 7.6 Hz, 1.1 Hz, 1H × 0.44), 7.30 (dd, *J* = 7.8 Hz, 1.0 Hz, 1H), 7.20 (td, *J* = 7.8 Hz, 1.4 Hz, 1H), 7.13 (td, *J* = 7.8 Hz, 1.3 Hz, 1H × 0.44), 6.93 (dd, *J* = 7.8 Hz, 1.1 Hz, 1H × 0.44), 4.73-4.66 (m, 1H × 0.44), 4.40-4.33 (m, 1H × 0.44), 3.98 (q, *J* = 7.3 Hz, 2H), 1.45 (t, *J* = 7.3 Hz, 3H × 0.44), 1.08 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 143.54, 141.63, 140.33, 140.12, 130.93, 130.89, 129.25 (overlapped), 129.04, 128.96, 96.83, 96.41, 48.45, 42.01, 14.30, 11.13. **HRMS (ESI) m/z** calculated for $C_8H_{10}IN_2O$ $[M+H]^+$, 276.9832, found 276.9846.

***N*-(2-Iodophenyl)-*N*-propylnitrous amide (4c)**



Pale yellow liquid (80% yield, 46.5 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^1H NMR to be approximately 1:0.50. **^1H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H × 0.50), 7.49 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H × 0.50), 7.30 (dd, *J* = 7.7 Hz, 0.7 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.12 (td, *J* = 7.8 Hz, 0.9 Hz, 1H × 0.50), 6.92 (d, *J* = 7.8 Hz, 1H × 0.50), 4.62-4.57 (m, 1H × 0.50), 4.26-4.21 (m, 1H × 0.50), 3.88 (t, *J* = 7.8 Hz, 2H), 1.88-1.75 (m, 2H × 0.50), 1.54-1.46 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H × 0.50), 0.88 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 143.91, 141.91, 140.39, 140.17, 130.85 (overlapped), 129.23, 129.21, 128.89 (overlapped), 96.61, 96.22, 55.12, 48.54, 22.00, 19.59, 11.62, 11.29. **HRMS (ESI) m/z** calculated for $C_9H_{12}IN_2O$ $[M+H]^+$, 290.9989, found 290.9994.

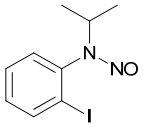
***N*-Benzyl-*N*-(2-iodophenyl)nitrous amide (4d)**



Yellow liquid (97% yield, 65.6 mg). The title compound was obtained as an inseparable mixture of

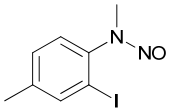
syn and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.44. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 7.98 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.88 (dd, *J* = 7.9 Hz, 0.8 Hz, 1H × 0.44), 7.35-7.31 (m, 2H + 1H × 0.44), 7.27-7.23 (m, 3H + 2H × 0.44), 7.18 (td, *J* = 7.7 Hz, 1.1 Hz, 1H × 0.44), 7.15-7.09 (m, 2H + 2H × 0.44), 7.03 (td, *J* = 7.9 Hz, 1.4 Hz, 1H × 0.44), 6.99 (dd, *J* = 7.8 Hz, 1.3 Hz, 1H), 6.36 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H × 0.44), 6.08 (d, *J* = 14.5 Hz, 1H × 0.44), 5.14-5.10 (m, 2H + 1H × 0.44). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 143.39, 141.25, 140.28, 139.98, 134.59, 133.80, 130.96, 130.93, 129.60, 129.46, 129.30, 129.05, 128.92, 128.88, 128.66, 128.64, 128.04 (overlapped), 96.70, 96.14, 57.26, 49.91. **HRMS (ESI) m/z** calculated for $C_{13}H_{12}IN_2O$ $[M+H]^+$, 338.9988, found 339.0002.

***N*-(2-Iodophenyl)-*N*-isopropylnitrous amide (4e)**



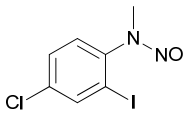
Yellow liquid (69% yield, 40.0 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.55. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 8.04 (dd, *J* = 7.9 Hz, 0.8 Hz, 1H × 0.55), 7.94 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.49 (td, *J* = 7.8 Hz, 1.1 Hz, 1H × 0.55), 7.42 (td, *J* = 7.8 Hz, 1.0 Hz, 1H), 7.32 (dd, *J* = 7.8 Hz, 1.1 Hz, 1H × 0.55), 7.20 (td, *J* = 7.9 Hz, 1.3 Hz, 1H × 0.55), 7.12 (td, *J* = 7.9 Hz, 1.3 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1.1 Hz, 1H), 5.07-5.02 (m, 1H × 0.55), 4.75-4.70 (m, 1H), 1.77 (d, *J* = 6.8 Hz, 6H × 0.55), 1.53 (d, *J* = 6.7 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 142.12, 141.97, 140.50, 140.26, 130.98, 130.74, 129.11 (overlapped), 128.98, 128.94, 97.19 (overlapped), 56.91, 48.07, 22.84, 21.78, 19.67. **HRMS (ESI) m/z** calculated for $C_9H_{12}IN_2O$ $[M+H]^+$, 290.9989, found 290.9992.

***N*-(2-Iodo-4-methylphenyl)-*N*-methylnitrous amide (4g)**



Yellow liquid (82% yield, 45.3 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.12. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 7.81 (s, 1H), 7.73 (s, 1H × 0.12), 7.29 (d, *J* = 7.9 Hz, 1H), 7.23-7.19 (m, 1H + 1H × 0.12), 6.84 (d, *J* = 8.0 Hz, 1H × 0.12), 4.07 (s, 3H × 0.12), 3.35 (s, 3H), 2.39 (s, 3H), 2.33 (s, 3H × 0.12). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 142.67, 141.46 (overlapped), 140.59, 140.42, 130.44, 130.10, 127.47, 127.18, 95.12, 95.02, 40.23, 35.63, 20.73, 20.68. **HRMS (ESI) m/z** calculated for $C_8H_{10}IN_2O$ $[M+H]^+$, 276.9832, found 276.9844.

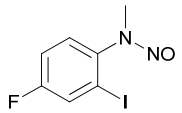
***N*-(4-Chloro-2-iodophenyl)-*N*-methylnitrous amide (4h)**



Yellow liquid (84% yield, 49.8 mg). The title compound was obtained as an inseparable mixture of

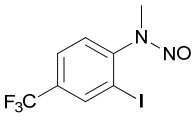
syn and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.14. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 8.00 (d, *J* = 1.7 Hz, 1H), 7.91 (d, *J* = 1.6 Hz, 1H × 0.14), 7.50 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.43 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H × 0.14), 7.28 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H × 0.14), 4.08 (s, 3H × 0.14), 3.36 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 143.89, 141.80, 139.66, 139.49, 136.04, 135.92, 129.92, 129.59, 128.43, 128.39, 95.93, 95.49, 39.97, 35.42. **HRMS (ESI) m/z** calculated for $C_7H_7ClIN_2O$ $[M+H]^+$, 296.9286, found 296.9295.

***N*-(4-Fluoro-2-iodophenyl)-*N*-methylnitrous amide (4i)**



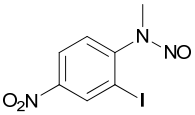
Yellow liquid (96% yield, 53.8 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.14. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 7.72 (dd, *J* = 7.6 Hz, 2.2 Hz, 1H), 7.63 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H × 0.14), 7.33-7.30 (m, 1H), 7.21 (td, *J* = 8.7 Hz, 2.4 Hz, 1H), 7.15 (td, *J* = 8.7 Hz, 2.2 Hz, 1H × 0.14), 6.95-6.92 (m, 1H × 0.14), 4.08 (s, 3H × 0.14), 3.35 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 163.10 (d, $J_{C\text{-}F}$ = 253.5 Hz), 163.07 (d, $J_{C\text{-}F}$ = 253.3 Hz), 141.73 (d, $J_{C\text{-}F}$ = 3.4 Hz), 139.31 (d, $J_{C\text{-}F}$ = 3.8 Hz), 128.90 (d, $J_{C\text{-}F}$ = 8.9 Hz), 128.80 (d, $J_{C\text{-}F}$ = 9.1 Hz), 127.25 (d, $J_{C\text{-}F}$ = 24.7 Hz), 127.19 (d, $J_{C\text{-}F}$ = 24.6 Hz), 116.96 (d, $J_{C\text{-}F}$ = 22.3 Hz), 116.54 (d, $J_{C\text{-}F}$ = 22.3 Hz), 95.55 (d, $J_{C\text{-}F}$ = 8.7 Hz) (overlapped), 40.12, 35.50. **HRMS (ESI) m/z** calculated for $C_7H_7FIN_2O$ $[M+H]^+$, 280.9581, found 280.9593.

***N*-(2-Iodo-4-(trifluoromethyl)phenyl)-*N*-methylnitrous amide (4j)**



Yellow liquid (93% yield, 61.4 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.12. The ^{13}C NMR data listed here represent peak information only for the major syn isomer. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 8.25 (s, 1H), 8.15 (s, 1H × 0.12), 7.78 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H × 0.12), 7.46 (d, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H × 0.12), 4.12 (s, 3H × 0.12), 3.40 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 148.11, 137.49 (q, $J_{C\text{-}F}$ = 3.7 Hz), 132.82 (q, $J_{C\text{-}F}$ = 33.2 Hz), 127.97, 126.55 (q, $J_{C\text{-}F}$ = 3.5 Hz), 123.52 (q, $J_{C\text{-}F}$ = 271.3 Hz), 94.83, 35.30. **HRMS (ESI) m/z** calculated for $C_8H_7F_3IN_2O$ $[M+H]^+$, 330.9549, found 330.9570.

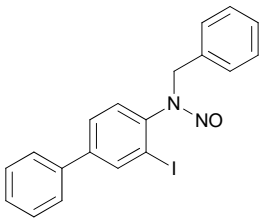
***N*-(2-iodo-4-nitrophenyl)-*N*-methylnitrous amide (4l)**



Yellow liquid (97% yield, 59.7 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.12. The ^{13}C NMR data listed here represent peak information only for the major syn isomer. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 8.84 (d, *J* = 2.3 Hz, 1H), 8.73 (d, *J* = 2.3 Hz,

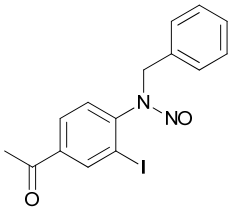
1H × 0.12), 8.37 (dd, *J* = 8.6 Hz, 2.4 Hz, 1H), 8.30 (dd, *J* = 8.6 Hz, 2.3 Hz, 1H × 0.12), 7.51 (d, *J* = 8.6 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 1H × 0.12), 4.14 (s, 3H × 0.12), 3.41 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 150.23, 147.73, 135.60, 127.82, 124.46, 94.11, 35.37. **HRMS (ESI) m/z** calculated for $C_7H_7IN_3O_3$ $[M+H]^+$, 307.9527, found 307.9533.

***N*-Benzyl-*N*-(3-iodo-[1,1'-biphenyl]-4-yl)nitrous amide (4m)**



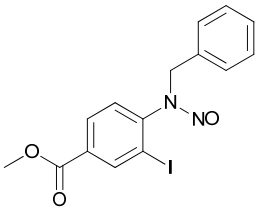
Yellow liquid (85% yield, 70.4 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.45. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 8.21 (d, *J* = 1.7 Hz, 1H), 8.11 (d, *J* = 1.7 Hz, 1H × 0.45), 7.57-7.54 (m, 2H + 2H × 0.45), 7.50-7.34 (m, 5H + 8H × 0.45), 7.29-7.28 (m, 2H + 1H × 0.45), 7.18-7.17 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.46 (d, *J* = 8.2 Hz, 1H × 0.45), 6.14 (d, *J* = 14.6 Hz, 1H × 0.45), 5.21-5.17 (m, 2H + 1H × 0.45). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 144.11, 144.09, 142.38, 140.14, 138.72, 138.46, 138.39, 138.28, 134.67, 133.89, 129.50, 129.43, 129.32 (overlapped), 129.08, 128.99, 128.92, 128.70, 128.67, 128.47, 128.38, 128.06, 127.68, 127.65, 127.21, 127.19, 97.05, 96.56, 57.36, 49.98. **HRMS (ESI) m/z** calculated for $C_{19}H_{16}IN_2O$ $[M+H]^+$, 415.0301, found 415.0323.

***N*-(4-Acetyl-2-iodophenyl)-*N*-benzylnitrous amide (4n)**



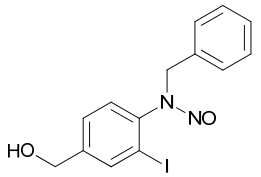
Yellow liquid (78% yield, 59.3 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.45. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 8.53 (d, *J* = 1.6 Hz, 1H), 8.42 (d, *J* = 1.4 Hz, 1H × 0.45), 7.91 (dd, *J* = 8.1 Hz, 1.6 Hz, 1H), 7.75 (dd, *J* = 8.1 Hz, 1.5 Hz, 1H × 0.45), 7.35-7.33 (m, 1H + 1H × 0.45), 7.28-7.24 (m, 2H + 4H × 0.45), 7.10-7.08 (m, 3H), 6.48 (d, *J* = 8.2 Hz, 1H × 0.45), 6.10 (d, *J* = 14.6 Hz, 1H × 0.45), 5.20 (d, *J* = 14.6 Hz, 1H × 0.45), 5.14 (s, 2H), 2.61 (s, 3H), 2.54 (s, 3H × 0.45). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 195. 57, 195.51, 146.91, 145.38, 140.31, 139.77, 138.78, 138.62, 134.19, 133.44, 129.67, 129.31, 129.26, 129.21, 128.99, 128.82, 128.81, 128.76, 128.56, 128.22, 96.73, 96.62, 57.03, 49.50, 26.66, 26.58. **HRMS (ESI) m/z** calculated for $C_{15}H_{14}IN_2O_2$ $[M+H]^+$, 381.0094, found 381.0113.

Methyl 4-(benzyl(nitroso)amino)-3-iodobenzoate (4o)



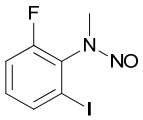
Yellow liquid (84% yield, 66.6 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.45. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 8.63 (d, *J* = 1.6 Hz, 1H), 8.52 (d, *J* = 1.4 Hz, 1H × 0.45), 8.00 (dd, *J* = 8.2 Hz, 1.7 Hz, 1H), 7.84 (dd, *J* = 8.2 Hz, 1.6 Hz, 1H × 0.45), 7.33-7.32 (m, 1H + 1H × 0.45), 7.26-7.23 (m, 2H + 4H × 0.45), 7.09-7.05 (m, 3H), 6.45 (d, *J* = 8.2 Hz, 1H × 0.45), 6.08 (d, *J* = 14.6 Hz, 1H × 0.45), 5.19 (d, *J* = 14.6 Hz, 1H × 0.45), 5.13 (s, 2H), 3.92 (s, 3H), 3.88 (s, 3H × 0.45). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 164.65 (overlapped), 146.89, 145.36, 141.49, 140.99, 134.18, 133.43, 132.39, 132.24, 130.17, 129.95, 129.42, 129.28, 129.23, 129.08, 128.98, 128.81, 128.75, 128.21, 96.13, 96.07, 57.04, 52.73, 52.66, 49.54. **HRMS (ESI) m/z** calculated for $C_{15}H_{14}IN_2O_3$ $[M+H]^+$, 397.0043, found 397.0061.

***N*-Benzyl-*N*-(4-(hydroxymethyl)-2-iodophenyl)nitrous amide (4p)**



Yellow liquid (84% yield, 61.9 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.49. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.98 (s, 1H), 7.88 (s, 1H × 0.49), 7.33-7.24 (m, 4H + 5H × 0.49), 7.15-7.10 (m, 2H + 1H × 0.49), 6.95 (d, *J* = 7.9 Hz, 1H), 6.33 (d, *J* = 8.0 Hz, 1H × 0.49), 6.06 (d, *J* = 14.5 Hz, 1H × 0.49), 5.15-5.10 (m, 2H + 1H × 0.49), 4.67 (s, 2H), 4.59 (s, 2H × 0.49). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 144.27, 144.26, 142.33, 140.09, 138.19, 137.94, 134.44, 133.70, 129.34, 129.31 (2C, overlapped), 129.20, 128.89, 128.67 (overlapped), 128.06, 127.14, 127.08, 96.67, 96.10, 63.47, 63.44, 57.38, 50.00. **HRMS (ESI) m/z** calculated for $C_{14}H_{14}IN_2O_2$ $[M+H]^+$, 369.0094, found 369.0111.

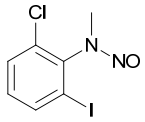
***N*-(2-Fluoro-6-iodophenyl)-*N*-methylnitrous amide (4q)**



Yellow liquid (45% yield, 25.4 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.30. The ^{13}C NMR data listed here represent peak information only for the major syn isomer. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.68-7.67 (m, 1H × 0.30), 7.28-7.25 (m, 1H), 7.24-7.19 (m, 1H), 7.16-7.14 (m, 2H × 0.30), 4.09 (s, 3H × 0.30), 3.33 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 159.01 (d, $J_{C\text{-}F}$ = 254.6 Hz), 135.27 (d, $J_{C\text{-}F}$ = 3.8 Hz), 133.57 (d, $J_{C\text{-}F}$ =13.6 Hz), 132.45 (d, $J_{C\text{-}F}$ =8.3 Hz), 117.00 (d, $J_{C\text{-}F}$ = 20.4 Hz), 98.09, 34.45.

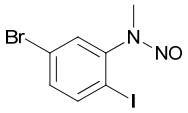
HRMS (ESI) m/z calculated for $C_7H_7FIN_2O$ $[M+H]^+$, 280.9581, found 280.9594.

***N*-(2-Chloro-6-iodophenyl)-*N*-methylnitrous amide (4r)**



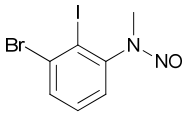
Yellow liquid (43% yield, 25.5 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.31. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H × 0.31), 7.57 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H × 0.31), 7.16 (t, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 8.1 Hz, 1H × 0.31), 4.10 (s, 3H × 0.31), 3.32 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 142.34, 140.50, 138.37, 138.22, 133.53 (overlapped), 132.06, 131.98, 130.53, 130.27, 98.84, 96.69, 38.25, 33.89. **HRMS (ESI) m/z** calculated for $C_7H_7ClIN_2O$ $[M+H]^+$, 296.9286, found 296.9298.

***N*-(5-Bromo-2-iodophenyl)-*N*-methylnitrous amide (4u)**



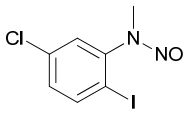
White solid (81% yield, 55.2 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.12. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.85 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H × 0.12), 7.49 (d, *J* = 2.1 Hz, 1H), 7.34 (dd, *J* = 8.5 Hz, 2.1 Hz, 1H), 7.25-7.24 (m, 1H × 0.12), 7.11 (d, *J* = 2.1 Hz, 1H × 0.12), 4.08 (s, 3H × 0.12), 3.36 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 146.21, 141.29, 141.02, 134.15, 133.95, 131.01, 130.87, 123.01, 122.94, 93.29 (overlapped), 39.95, 35.42. **HRMS (ESI) m/z** calculated for $C_7H_7BrIN_2O$ $[M+H]^+$, 340.8780, found 340.8795.

***N*-(3-Bromo-2-iodophenyl)-*N*-methylnitrous amide (4u')**



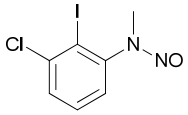
White solid (17% yield, 11.7 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.16. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H × 0.16), 7.38 (t, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H × 0.16), 7.26-7.24 (m, 1H), 6.89 (d, *J* = 7.9 Hz, 1H × 0.16), 4.10 (s, 3H × 0.16), 3.36 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 147.28, 133.55 (overlapped), 132.11, 132.00, 130.49, 130.20, 126.45, 126.05, 104.46 (overlapped), 39.88, 35.47. **HRMS (ESI) m/z** calculated for $C_7H_7BrIN_2O$ $[M+H]^+$, 340.8780, found 340.8794.

***N*-(5-Chloro-2-iodophenyl)-*N*-methylnitrous amide (4v)**



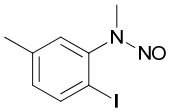
White solid (67% yield, 39.7 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.12. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 7.92 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H × 0.12), 7.35 (d, *J* = 2.2 Hz, 1H), 7.21 (dd, *J* = 8.5 Hz, 2.2 Hz, 1H), 7.13 (dd, *J* = 8.5 Hz, 2.1 Hz, 1H × 0.12), 6.98 (d, *J* = 2.2 Hz, 1H × 0.12), 4.09 (s, 3H × 0.12), 3.36 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 146.09, 141.04, 140.76, 135.52, 135.43, 131.23, 131.01, 128.20, 128.10, 92.96, 92.35, 39.89, 35.35. **HRMS (ESI) m/z** calculated for $C_7H_7ClIN_2O$ $[M+H]^+$, 296.9286, found 296.9295.

***N*-(3-Chloro-2-iodophenyl)-*N*-methylnitrous amide (4v')**



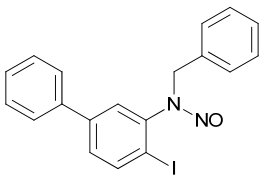
White solid (27% yield, 16.0 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.16. The ^{13}C NMR data listed here represent peak information only for the major syn isomer. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 7.59 (dd, *J* = 8.1 Hz, 1.1 Hz, 1H), 7.50 (dd, *J* = 8.1 Hz, 1.2 Hz, 1H × 0.16), 7.45 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H × 0.16), 7.22 (dd, *J* = 7.8 Hz, 1.1 Hz, 1H), 6.85 (dd, *J* = 7.8 Hz, 1.1 Hz, 1H × 0.16), 4.11 (s, 3H × 0.16), 3.37 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 147.32, 140.81, 130.10, 129.98, 125.98, 101.31, 35.48. **HRMS (ESI) m/z** calculated for $C_7H_7ClIN_2O$ $[M+H]^+$, 296.9286, found 296.9296.

***N*-(2-Iodo-5-methylphenyl)-*N*-methylnitrous amide (4w)**



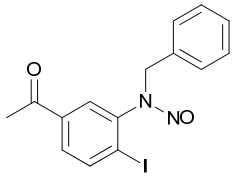
White solid (98% yield, 54.1 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.11. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H × 0.11), 7.15 (s, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H × 0.11), 6.78 (s, 1H × 0.11), 4.07 (s, 3H × 0.11), 3.36 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H × 0.11). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ144.89, 140.21, 139.98, 139.90, 139.62, 132.04, 131.87, 128.75, 128.30, 90.98, 90.75, 40.14, 35.54, 27.65, 20.82. **HRMS (ESI) m/z** calculated for $C_8H_{10}IN_2O$ $[M+H]^+$, 276.9832, found 276.9845.

***N*-Benzyl-*N*-(4-iodo-[1,1'-biphenyl]-3-yl)nitrous amide (4x)**



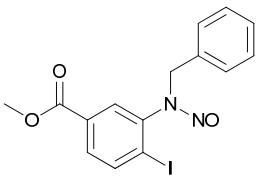
Yellow liquid (94% yield, 77.9 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.42. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H × 0.42), 7.42-7.34 (m, 6H + 8H × 0.42), 7.30-7.28 (m, 3H + 1H × 0.42), 7.21-7.18 (m, 3H + 2H × 0.42), 6.55 (d, *J* = 2.0 Hz, 1H × 0.42), 6.16 (d, *J* = 14.5 Hz, 1H × 0.42), 5.21-5.19 (m, 2H + 1H × 0.42). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 143.76, 142.53, 142.35, 141.73, 140.51, 140.15, 138.62, 138.60, 134.71, 133.88, 129.52, 129.48, 129.46 (overlapped), 129.08, 128.98, 128.94, 128.73, 128.33, 128.22, 128.14 (overlapped), 128.09 (overlapped), 126.89, 126.75, 94.94, 94.46, 57.36, 49.95. **HRMS (ESI) m/z** calculated for $C_{19}H_{16}IN_2O$ $[M+H]^+$, 415.0301, found 415.0320.

***N*-(5-Acetyl-2-iodophenyl)-*N*-benzylnitrous amide (4y)**



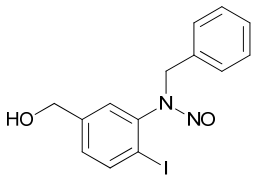
Yellow liquid (85% yield, 64.6 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.52. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 8.11 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H × 0.52), 7.69 (dd, *J* = 8.2 Hz, 1.4 Hz, 1H), 7.61 (dd, *J* = 8.3 Hz, 1.4 Hz, 1H × 0.52), 7.47 (d, *J* = 1.4 Hz, 1H), 7.36-7.35 (m, 1H + 1H × 0.52), 7.29-7.26 (m, 2H +4H × 0.52), 7.12-7.11 (m, 2H), 6.82 (d, *J* = 1.4 Hz, 1H × 0.52), 6.12 (d, *J* = 14.5 Hz, 1H × 0.52), 5.19-5.14 (m, 2H + 1H × 0.52), 2.44 (s, 3H), 2.28 (s, 3H × 0.52). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 195.91, 143.79, 141.75, 140.79, 140.41, 137.81, 137.68, 134.27, 133.47, 129.82, 129.81, 129.41, 129.37, 129.08, 129.00, 128.88, 128.82, 128.77, 128.28, 103.40, 103.15, 57.22, 49.61, 26.40, 26.18. **HRMS (ESI) m/z** calculated for $C_{15}H_{14}IN_2O_2$ $[M+H]^+$, 381.0094, found 381.0106.

Methyl 3-(benzyl(nitroso)amino)-4-iodobenzoate (4za)



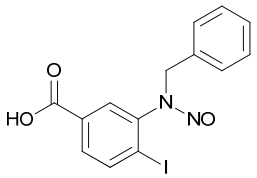
Yellow liquid (85% yield, 67.4 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.44. **^{1}H NMR (500 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 8.08 (dd, *J* = 8.2 Hz, 1.5 Hz, 1H), 7.97 (dd, *J* = 8.2 Hz, 1.5 Hz, 1H × 0.44), 7.77 (d, *J* = 8.3 Hz, 1H), 7.68-7.67 (m, 1H + 1H × 0.44), 7.34 (br, 1H + 1H × 0.44), 7.29-7.25 (m, 2H + 4H × 0.44), 7.12-7.09 (m, 2H +1H × 0.44), 6.01 (d, *J* = 14.6 Hz, 1H × 0.44), 5.30 (d, *J* = 14.6 Hz, 1H × 0.44), 5.14 (s, 2H), 3.88 (s, 3H), 3.81 (s, 3H × 0.44). **^{13}C NMR (125 MHz, $CDCl_3$)** (*syn* and *anti* isomers) δ 165.38, 165.25, 143.77, 141.71, 140.67, 140.27, 134.11, 133.34, 131.43, 131.34, 131.32, 131.26, 130.11, 129.85, 129.32, 129.28, 128.96, 128.78, 128.75, 128.20, 103.12, 103.01, 57.29, 52.60, 52.46, 49.87. **HRMS (ESI) m/z** calculated for $C_{15}H_{14}IN_2O_3$ $[M+H]^+$, 397.0043, found 397.0058.

***N*-Benzyl-*N*-(5-(hydroxymethyl)-2-iodophenyl)nitrous amide (4zb)**



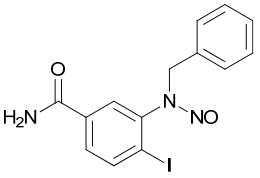
Yellow liquid (94% yield, 69.2 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.44. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H × 0.44), 7.32-7.31 (m, 1H + 1H × 0.44), 7.26-7.23 (m, 3H + 2H × 0.44), 7.12-7.09 (m, 2H + 2H × 0.44), 7.01 (br, 1H + 1H × 0.44), 6.38 (s, 1H × 0.44), 6.00 (d, *J* = 14.5 Hz, 1H × 0.44), 5.20 (d, *J* = 14.6 Hz, 1H × 0.44), 5.10 (s, 2H), 4.54 (s, 2H), 4.39 (s, 2H × 0.44). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 143.40, 142.88, 142.71, 141.30, 140.23, 139.93, 134.36, 133.63, 129.35, 129.28, 129.25, 129.16, 128.87, 128.69, 128.65, 128.06, 127.53, 127.41, 94.67, 94.23, 63.59 (overlapped), 57.43, 50.16. **HRMS (ESI) m/z** calculated for $C_{14}H_{14}IN_2O_2$ $[M+H]^+$, 369.0094, found 369.0108.

3-(Benzyl(nitroso)amino)-4-iodobenzoic acid (4zc)



White solid (93% yield, 71.1 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.54. **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** (*syn* and *anti* isomers) δ 13.26 (br, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H × 0.54), 7.74-7.71 (m, 2H), 7.64 (dd, *J* = 8.2 Hz, 1.6 Hz, 1H × 0.54), 7.35-7.34 (m, 2H + 1H × 0.54), 7.30-7.23 (m, 1H + 4H × 0.54), 7.15-7.14 (m, 2H), 7.12 (d, *J* = 1.5 Hz, 1H × 0.54), 5.99 (d, *J* = 14.7 Hz, 1H × 0.54), 5.43 (d, *J* = 14.7 Hz, 1H × 0.54), 5.16 (s, 2H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** (*syn* and *anti* isomers) δ 166.41, 166.29, 143.72, 142.05, 141.12, 140.62, 134.82, 133.95, 132.46, 132.33, 131.70 (overlapped), 129.77, 129.61, 129.45, 129.28, 129.18, 128.99, 128.92, 128.35, 104.63, 104.53, 57.07, 50.10. **HRMS (ESI) m/z** calculated for $C_{14}H_{12}IN_2O_3$ $[M+H]^+$, 382.9887, found 382.9912.

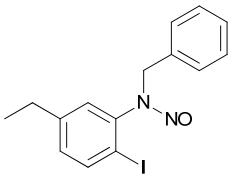
3-(Benzyl(nitroso)amino)-4-iodobenzamide (4zd)



White solid (86% yield, 65.6 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.47. **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** (*syn* and *anti* isomers) δ 8.15-8.13 (m, 2H), 8.02-8.00 (m,

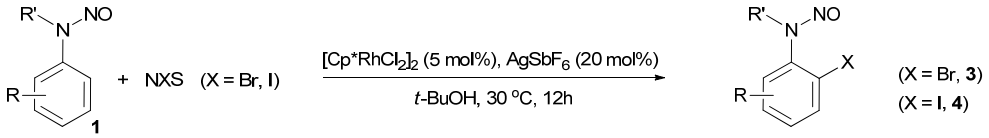
2H × 0.47), 7.82 (d, *J* = 1.7, 1H), 7.72 (dd, *J* = 8.1 Hz, 1.4 Hz, 1H), 7.62 (dd, *J* = 8.1 Hz, 1.3 Hz, 1H × 0.47), 7.57 (br, 1H), 7.48 (br, 1H × 0.47), 7.33 (br, 2H + 1H × 0.47), 7.29-7.24 (m, 1H + 5H × 0.47), 7.16-7.15 (m, 2H), 5.90 (d, *J* = 14.7 Hz, 1H × 0.47), 5.53 (d, *J* = 14.7 Hz, 1H × 0.47), 5.17 (s, 2H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** (*syn* and *anti* isomers) δ 166.59, 166.52, 143.53, 141.85, 140.65, 140.05, 135.80, 135.71, 134.74, 133.92, 130.12, 130.01, 129.82, 129.42, 129.11, 128.94, 128.86, 128.29, 128.22, 127.88, 102.18, 102.07, 57.17, 50.18. **HRMS (ESI) m/z** calculated for $C_{14}H_{13}IN_3O_2$ $[M+H]^+$, 382.0046, found 382.0062.

***N*-Benzyl-*N*-(5-ethyl-2-iodophenyl)nitrous amide (4ze)**



Yellow liquid (85% yield, 62.3 mg). The title compound was obtained as an inseparable mixture of *syn* and *anti* isomers, and the *syn*:*anti* ratio was determined by ^{1}H NMR to be approximately 1:0.40. **^{1}H NMR (500 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H × 0.40), 7.34-7.33 (m, 1H + 1H × 0.40), 7.28-7.25 (m, 2H + 4H × 0.40), 7.13-7.12 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H × 0.40), 6.81 (s, 1H), 6.15 (s, 1H × 0.40), 6.09 (d, *J* = 14.4 Hz, 1H × 0.40), 5.12-5.10 (m, 2H + 1H × 0.40), 2.55 (q, *J* = 7.6 Hz, 2H), 2.41 (q, *J* = 7.6 Hz, 2H × 0.40), 1.12 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H × 0.40). **^{13}C NMR (125 MHz, CDCl$_3$)** (*syn* and *anti* isomers) δ 145.84, 145.59, 143.19, 141.15, 139.89, 139.56, 134.67, 133.89, 130.77, 130.75, 129.44, 129.41, 129.32, 128.98, 128.80, 128.58, 127.99 (overlapped), 92.55, 91.93, 57.33, 49.92, 28.06, 27.96, 15.08, 14.83. **HRMS (ESI) m/z** calculated for $C_{15}H_{16}IN_2O$ $[M+H]^+$,367.0301, found 367.0320.

4. 1 mmol-scale reaction



1a (136.0 mg, 1.0 mmol), $[Cp^*RhCl_2]_2$ (30.9 mg, 5 mol %), $AgSbF_6$ (68.8 mg, 20 mol %), and NXS (1.2 eq) were weighed into a pressure tube, to which was added t-BuOH (5.0 mL) under air. The reaction mixture was stirred for 12 h at 30 °C. Purification was performed by flash column chromatography on silica gel using n-hexane and tetrahydrofuran to afford the product **3a/4a** as a pale yellow liquid (189.2 mg, 88%/243.7 mg, 93%).

5. Optimization of the denitrosation process

We have chosen 4a as model substrate to investigate the denitrosation process of halogenated N-nitrosamine. Condition screening showed that $SnCl_2{\cdot}2H_2O$/HCl (table1, entry 2) gave the best results while CuCl/HCl, $NiCl_2{\cdot}6H_2O$/NaBH4 and $TiCl_4$/$NaBH_4$ were found to be inferior (entries 1, 3, 4). Therefor we used $SnCl_2{\cdot}2H_2O$/HCl system as the optimized condition to remove the nitroso

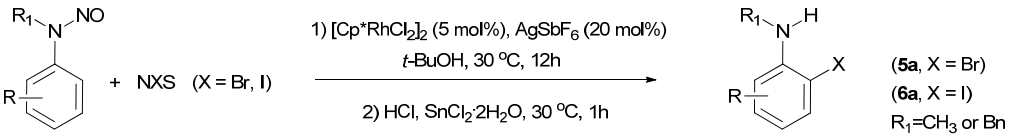
group.

4a **6a**

Entry	Denitrosation Condition	Solvent	Yield (%)[e]
1[a]	CuCl/HCl	MeOH	55
2[b]	$SnCl_2{\cdot}2H_2O$/HCl	MeOH	81
3[c]	$NiCl_2{\cdot}6H_2O/NaBH_4$	THF	15
4[d]	$TiCl_4/NaBH_4$	DME	10

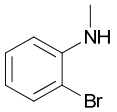
[a]Reaction conditions: **4a** (0.20 mmol), concentrated HCl (2.0 mL), CuCl (20 mol %), MeOH (2.0 mL), 30 °C, 1 h. Then using NaOH to pH=9~10. [b]$SnCl_2{\cdot}2H_2O$ (0.50 mmol) instead of CuCl. [c]$NiCl_2{\cdot}6H_2O$ (0.40 mmol), $NaBH_4$ (0.80 mmol), THF (5.0 mL), 30 °C, 6 h. [d]$TiCl_4$ (0.40 mmol) instead of $NiCl_2{\cdot}6H_2O$, DME (5.0 mL) instead of THF, 14 h. [e]Yield of isolated product.

6. Removal of the NO-directing group with one-pot procedure



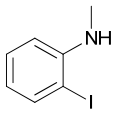
1a (136.0 mg, 1.0 mmol), $[Cp^*RhCl_2]_2$ (30.9 mg, 5 mol %), $AgSbF_6$ (68.8 mg, 20 mol %), and NXS (1.2 eq) were weighed into a pressure tube, to which was added t-BuOH (5.0 mL) under air. The reaction mixture was stirred for 12 h at 30 °C. After that, MeOH (5.0 mL) and $SnCl_2{\cdot}2H_2O$ (565.0 mg, 2.5 mmol) was added followed by addition of HCl (12 N, 6.0 mL). The mixture was stirred at 30 °C for 1h. 10 mol/L NaOH was added slowly at 0 °C to pH 9~10. Then extracted with EA. The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, purification was performed by flash column chromatography on silica gel using n-hexane and tetrahydrofuran to afford the desired product **5a** as a pale yellow liquid (134.7 mg, 72% yield).

2-Bromo-*N*-methylaniline (5a)



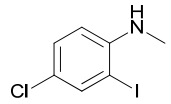
Pale yellow liquid (72% yield, 134.7 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 7.8 Hz, 1H), δ 7.22 (t, *J* = 7.5 Hz, 1H), δ 6.65 (d, *J* = 8.0 Hz, 1H), δ 6.59 (t, *J* = 7.5 Hz, 1H), δ 4.50 (br, 1H), δ 2.90 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 145.92, 132.31, 128.60, 117.69, 110.83, 109.67, 30.67. **HRMS (ESI) m/z** calculated for C_7H_8BrN $[M+H]^+$,185.9913, found 185.9918.

2-Iodo-*N*-methylaniline (6a)



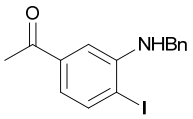
Pale yellow liquid (74% yield, 172.4 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.69 (dd, *J* = 7.8 Hz, 0.9 Hz, 1H), δ 7.26 (t, *J* = 8.3 Hz, 1H), δ 6.59 (d, *J* = 8.0 Hz, 1H), δ 6.47 (t, *J* = 7.7 Hz, 1H), δ 4.22 (br, 1H), δ 2.90 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.22, 138.93, 129.54, 118.54, 110.07, 85.21, 31.05. **HRMS (ESI) m/z** calculated for C_7H_8IN $[M+H]^+$,233.9768, found 233.9774.

4-chloro-2-iodo-*N*-methylaniline (6h)



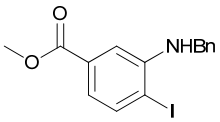
Yellow liquid (60% yield, 32.1 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 2.2 Hz, 1H), δ 7.21 (dd, *J* = 8.7 Hz, 2.2 Hz, 1H), δ 6.46 (d, *J* = 8.7 Hz, 1H), δ 4.18 (br, 1H), δ 2.87 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 146.99, 137.77, 129.28, 121.83, 110.25, 84.37, 31.17. **HRMS (ESI) m/z** calculated for C_7H_8ClIN $[M+H]^+$,267.9384, found 267.9389.

1-(3-(benzylamino)-4-iodophenyl)ethenone (6y)



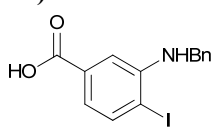
Yellow solid (80% yield, 56.2 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.1 Hz, 1H), δ 7.38-7.35 (m, 4H), δ 7.31-7.29 (m, 1H), δ 7.12 (d, *J* = 1.5 Hz, 1H), δ 7.01 (dd, *J* = 8.0 Hz, 1.7 Hz, 1H), δ 4.72 (br, 1H), δ 4.45 (s, 2H), δ 2.49 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 197.96, 147.30, 139.19, 138.29, 138.08, 128.87, 127.62, 127.44, 118.69, 109.50, 91.71, 48.42, 26.62. **HRMS (ESI) m/z** calculated for $C_{15}H_{15}INO$ $[M+H]^+$,352.0193, found 352.0219.

Methyl 3-(benzylamino)-4-iodobenzoate (6za)



Yellow solid (84% yield, 61.7 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.1 Hz, 1H), δ 7.39-7.36 (m, 4H), δ 7.32-7.30 (m, 1H), δ 7.23 (d, *J* = 1.5 Hz, 1H), δ 7.01 (dd, *J* = 8.2 Hz, 1.8 Hz, 1H), δ 4.65 (br, 1H), δ 4.44 (s, 2H), δ 3.87 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 167.09, 147.20, 139.07, 138.15, 131.42, 128.85, 127.60, 127.49, 119.56, 111.13, 91.23, 52.21, 48.41. **HRMS (ESI) m/z** calculated for $C_{15}H_{15}INO_2$ $[M+H]^+$,368.0142, found 368.0150.

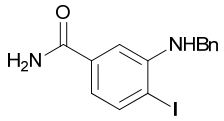
3-(benzylamino)-4-iodobenzoic acid (6zc)



Yellow solid (75% yield, 52.6 mg). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 12.82 (br, 1H), δ 7.78 (d, *J* = 8.0 Hz, 1H), δ 7.34-7.31 (m, 4H), δ 7.25-7.22 (m, 1H), δ 6.98 (s, 1H), δ 6.95 (d, *J* = 8.0 Hz, 1H),

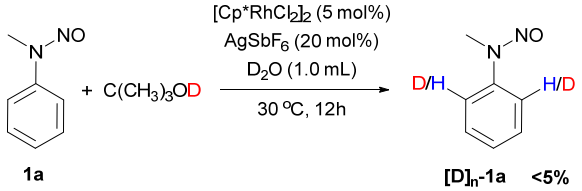
δ 5.81 (t, *J* = 5.3 Hz, 1H), δ 4.47 (d, *J* = 5.4 Hz, 2H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 167.82, 147.96, 139.70, 139.55, 132.19, 128.95, 127.30, 127.20, 119.10, 111.28, 90.96, 47.13. **HRMS (ESI) m/z** calculated for $C_{14}H_{13}INO_2$ $[M+H]^+$,353.9985, found 353.9987.

3-(benzylamino)-4-iodobenzamide (6zd)

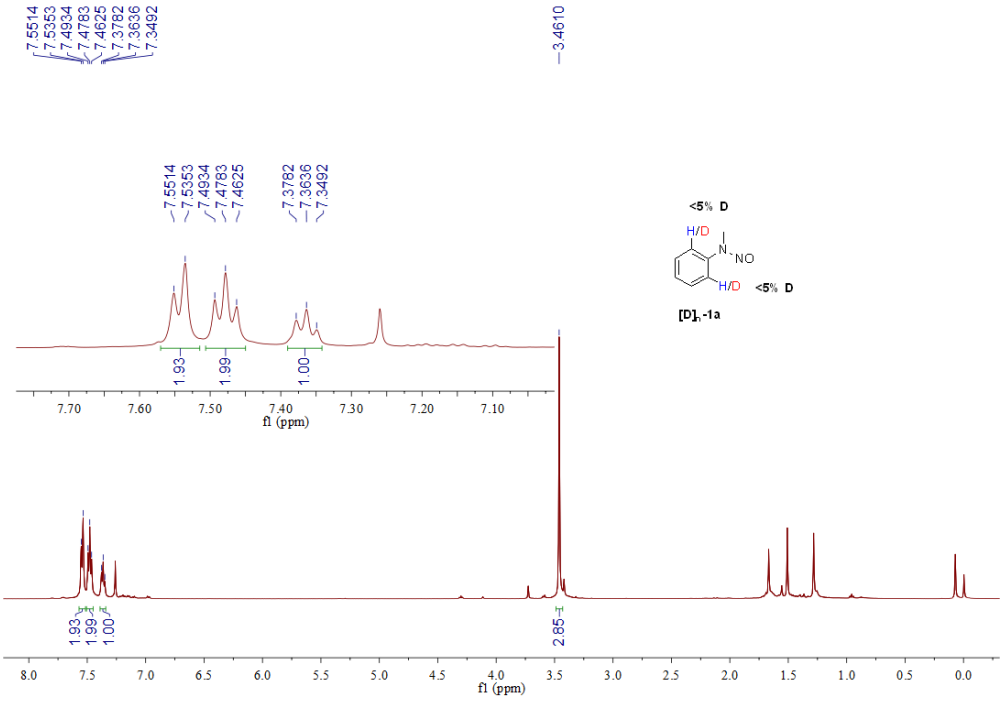


White solid (73% yield, 51.5 mg). **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 7.85 (br, 1H), δ 7.70 (d, *J* = 8.1 Hz, 1H), δ 7.33-7.31 (m, 4H), δ 7.25-7.21 (m, 2H), δ 6.97 (d, *J* = 1.3 Hz, 1H), δ 6.87 (dd, *J* = 8.1 Hz, 1.6 Hz, 1H), δ 5.61 (t, *J* = 6.0 Hz, 1H), δ 4.47 (d, *J* = 6.0 Hz, 2H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 168.23, 147.75, 139.92, 139.06, 135.79, 128.89, 127.35, 127.26, 117.41, 110.14, 88.79, 46.97. **HRMS (ESI) m/z** calculated for $C_{14}H_{14}IN_2O$ $[M+H]^+$,353.0145, found 353.0150.

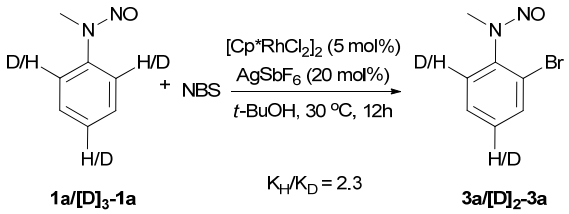
7. Rh-catalyzed H/D exchange of 1a with $C(CH_3)_3OD$



A sealed tube was charged with **1a** (27.2 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %), $AgSbF_6$ (13.8 mg, 20 mol %) and 1.0 mL of $C(CH_3)_3OD$. The reaction mixture was stirred for 12 h at 30 °C, then added 1.0 mL D_2O to continue the reaction for another 12 h. Filtered through a pad of celite and then washed with EtOAc. Then solution was concentrated under vacuum and the residue was purified by flash chromatography. The extents of deuterium incorporation was measured with ^{1}H NMR.



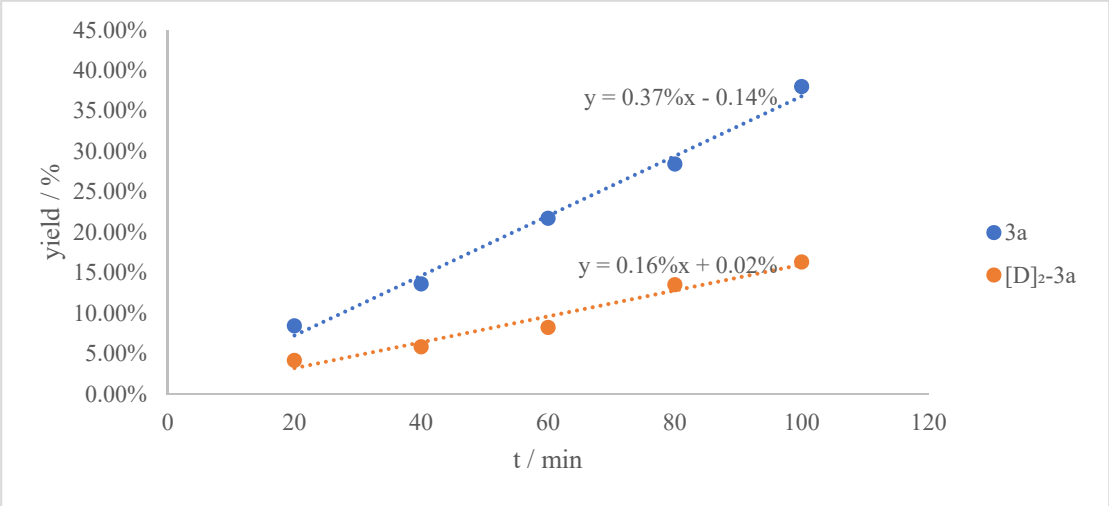
8. Kinetic isotopic effect (KIE) study



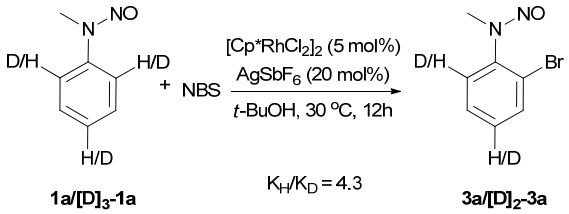
1a/[D]$_3$-1a **3a/[D]$_2$-3a**

N-nitrosoanilines **1a** or its deuterated analogue [D]$_3$-**1a** (0.2 mmol) was added to five separate sealed tubes containing NBS (42.7 mg, 0.24 mmol), [Cp*RhCl$_2$]$_2$ (6.2 mg, 5 mol %), AgSbF$_6$ (13.8 mg, 20 mol %) and t-BuOH (1.0 mL). Each reaction mixture was stirred at 30 °C for 20 min, 40 min, 60 min, 80 min, or 100 min before they were passed through a pad of celite and washed with EtOAc. The resultant solutions were concentrated under reduced pressure and each of the residues was analyzed by ^{1}H NMR using 3,4,5-trichloropyridine as an internal standard to provide the yields for all reactions. Based on these results k_H/k_D was determined to be 2.3.

t/min	**3a** (%)	**[D]$_2$-3a** (%)
20	8.44	4.17
40	13.63	5.85
60	21.74	8.25
80	28.44	13.53
100	38.02	16.34



KIE experiment (intermolecular competition)



N-nitrosoanilines **1a** (0.1 mmol) and its deuterated analogue $[D]_3$-**1a** (0.1 mmol) was added to a 10 mL sealed tube containing NBS (21.4 mg, 0.12 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol %), $AgSbF_6$ (6.9 mg, 20 mol %) and t-BuOH (1.0 mL). The mixture was stirred at 30 °C for 60 min. The product was purified by silica gel flash chromatography (Hexane:THF, 100:1). The ratio of **3a:** $[D]_2$-**3a** = 4.3 was determined by ^1H NMR (500 MHz, $CDCl_3$).

9. References

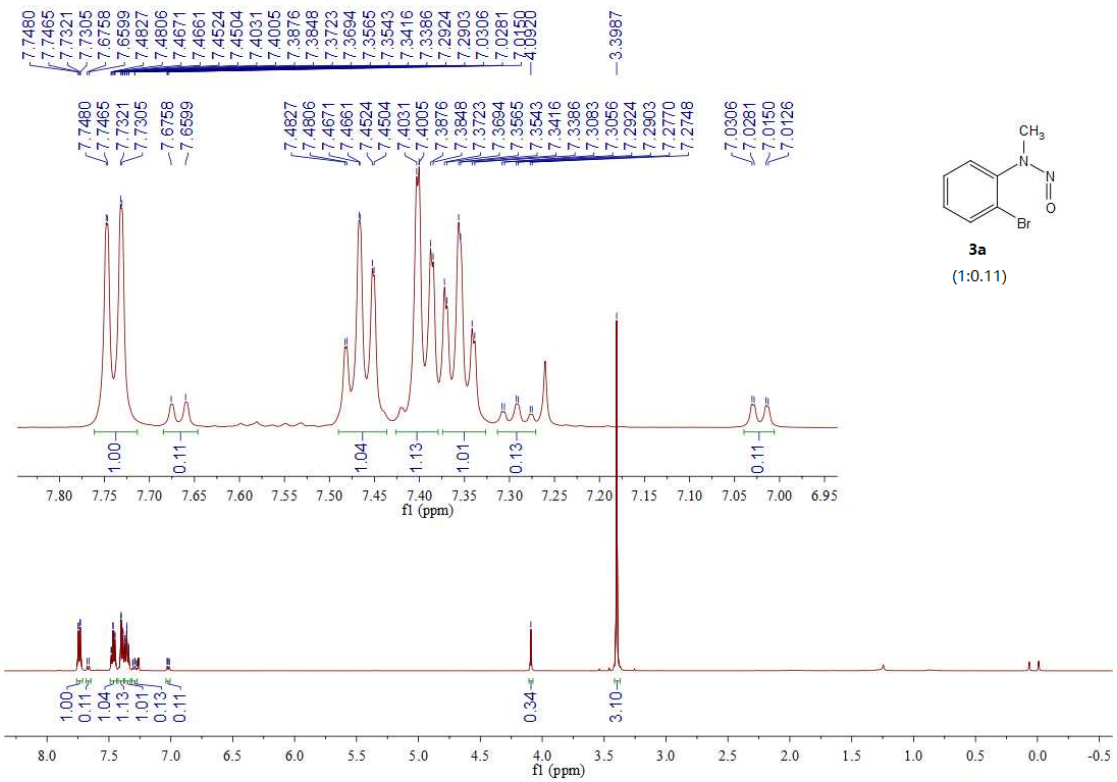
[1] B. Liu, Y. Fan, Y. Gao, C. Sun, C. Xu, J. Zhu, *J. Am. Chem. Soc*., **2013**, *135*, 468.

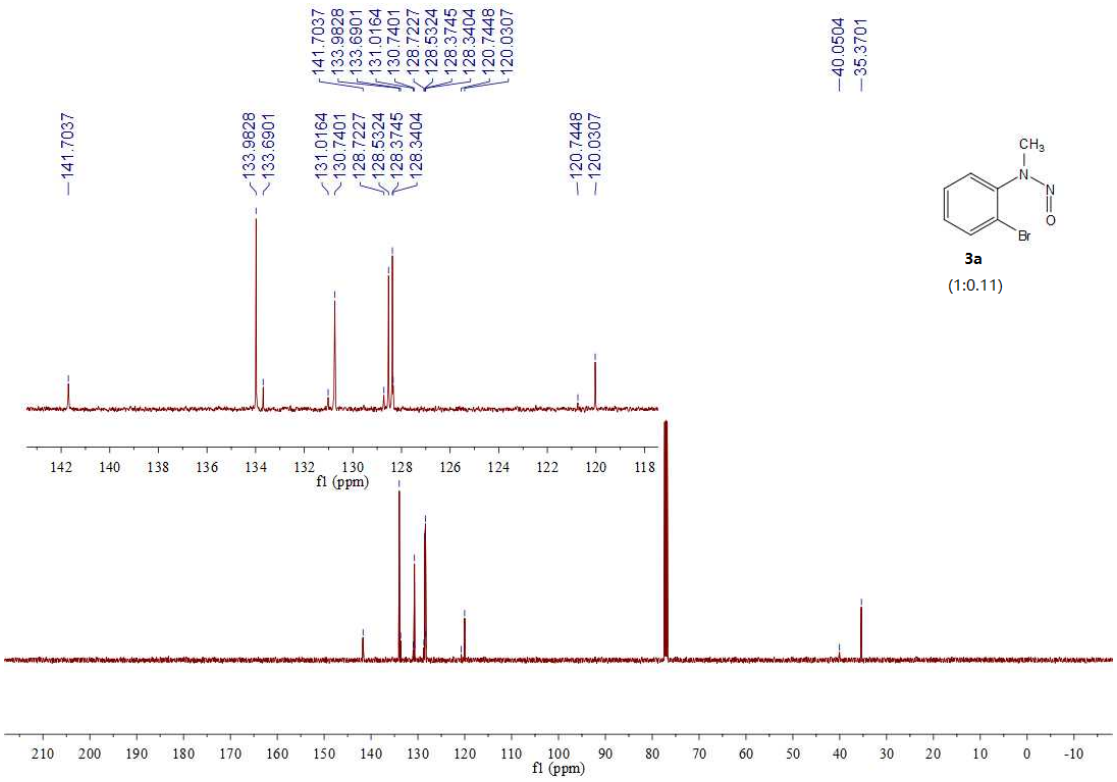
[2] J. Castillo, J. Orrego-Hernández, J. Portilla, *Eur. J. Org. Chem.*, **2016**, *22*, 3824.

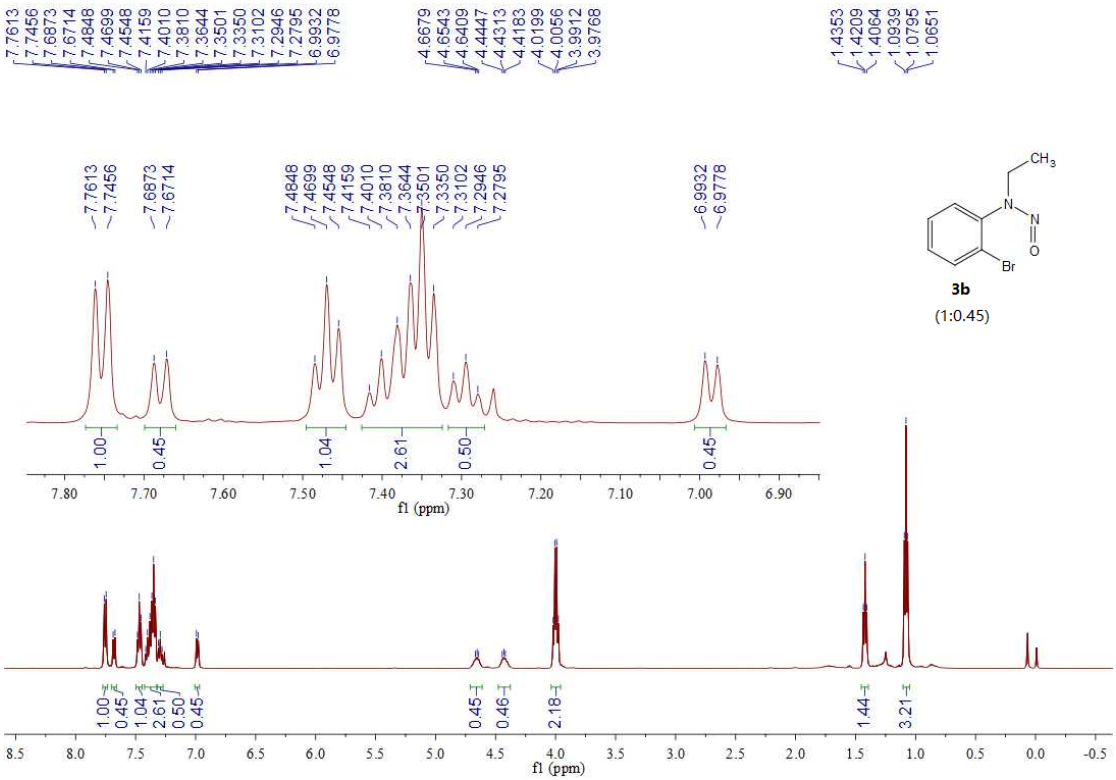
[3] R. K. Everett, J. P. Wolfe, *J. Org. Chem*, **2015**, *80*, 9041.

[4] M. Gupta, M. Ahmad, R. Singh, *Polyhedron*, **2015**, *101*, 86.

10.Copies of ^{1}H and ^{13}C NMR spectrum of products



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7.3350
7.3102
7.2946
7.2795
6.9932
6.9778
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4.0056
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3.9768
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1.4209
1.4064
1.0939
1.0795
1.0651
1.00
0.45
1.04
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0.50
0.45
0.45
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3.21
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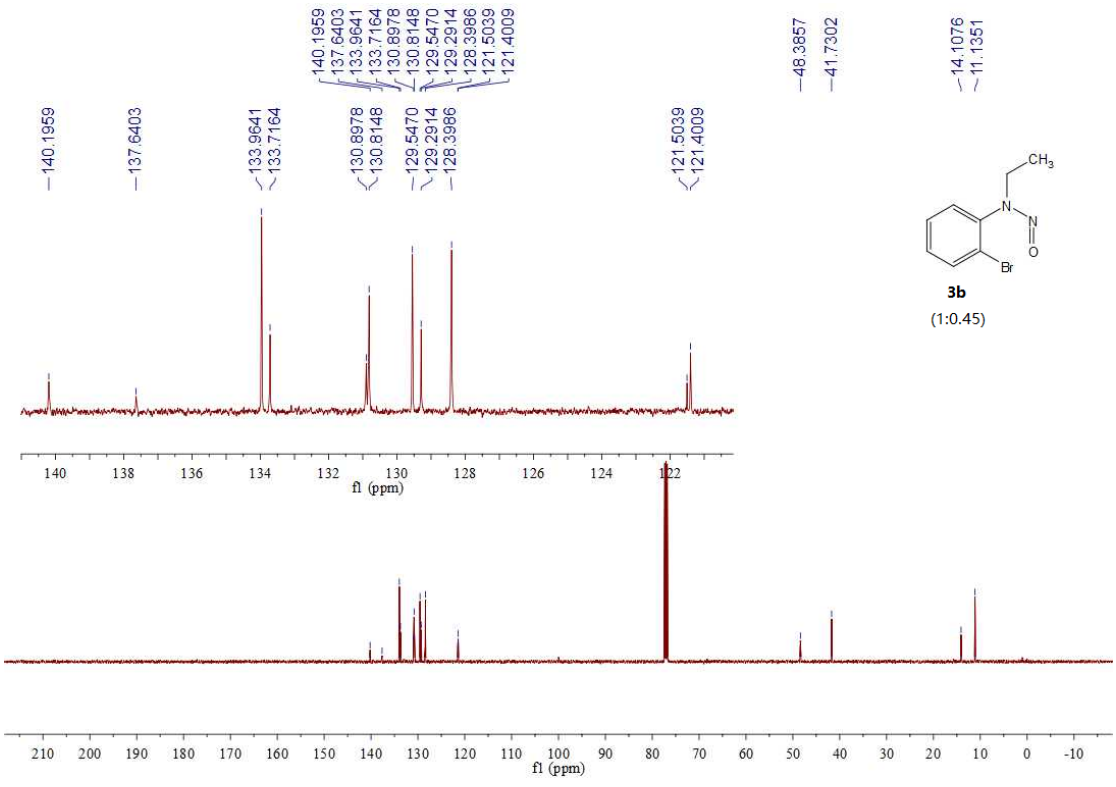
3b
(1:0.45)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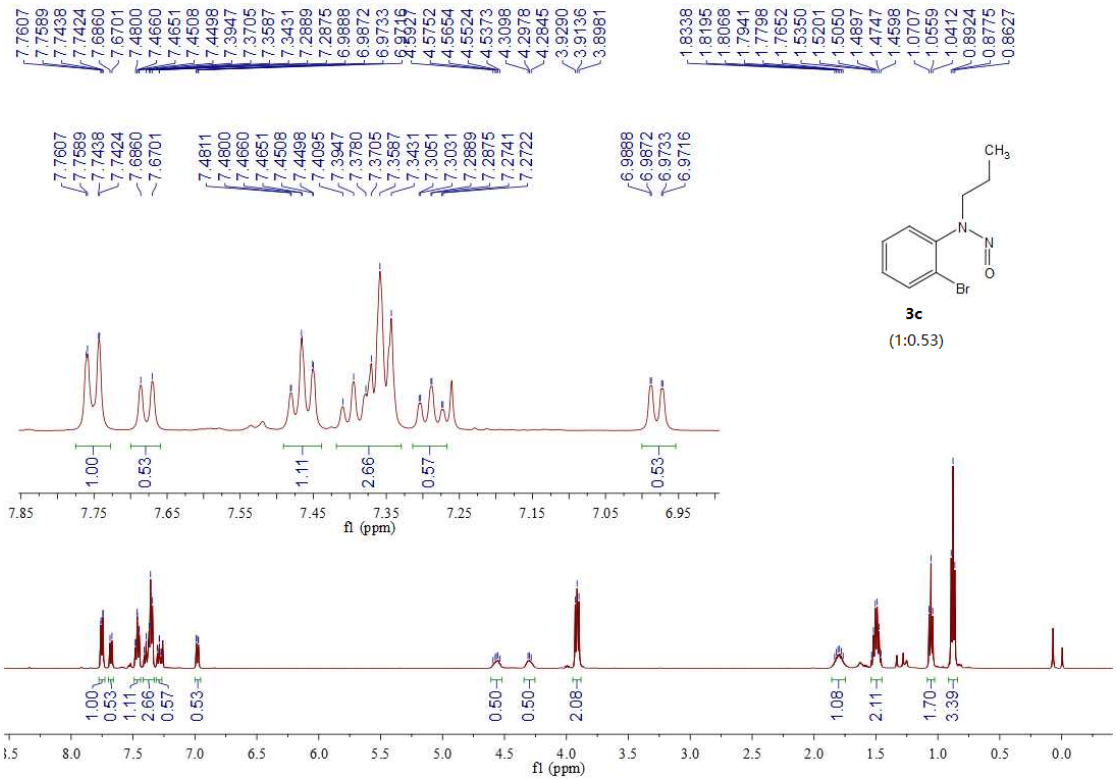
41.7302
14.1076
11.1351
f1 (ppm)
3b
(1:0.45)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7.3587
7.3431
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6.9716
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1.8068
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1.0412
0.8924
0.8775
0.8627
1.00
0.53
1.11
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0.57
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1.08
2.11
1.70
3.39
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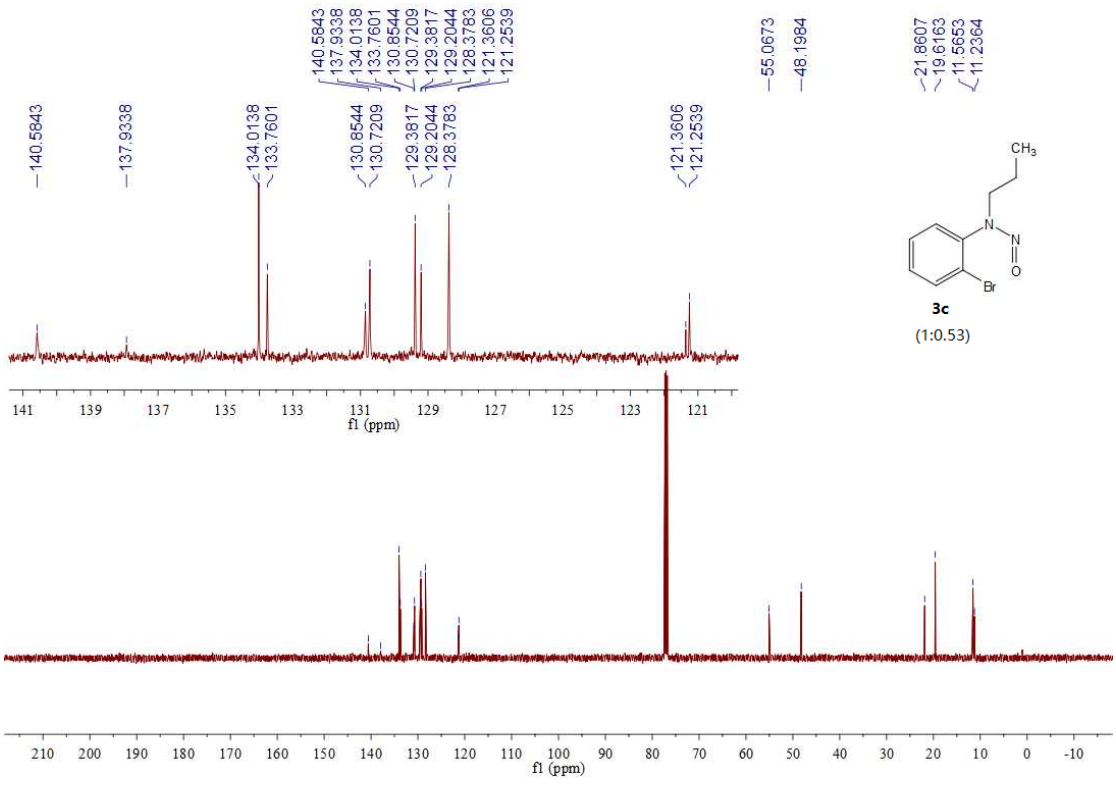
3c
(1:0.53)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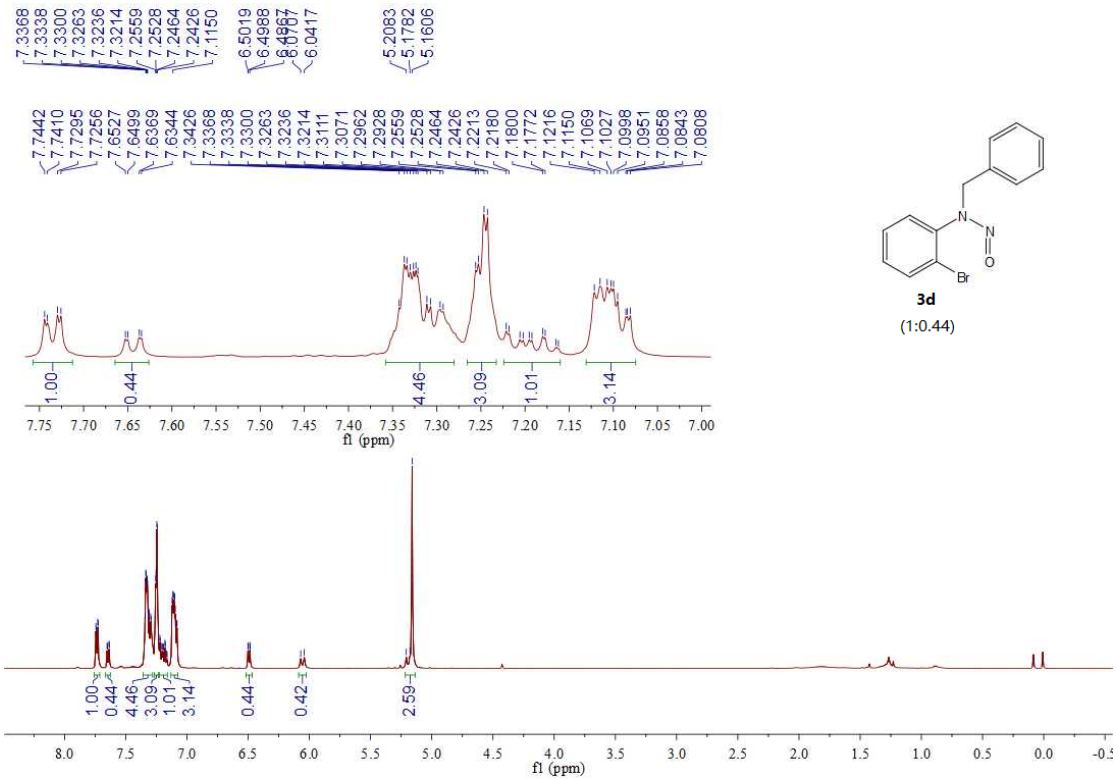
3c
(1:0.53)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6.4988
6.0417
5.2083
5.1782
5.1606
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7.7410
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7.7256
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7.2559
7.2528
7.2464
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7.2213
7.2180
7.1800
7.1772
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7.1069
7.1027
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7.0951
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7.0808
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0.44
4.46
3.09
1.01
3.14
f1 (ppm)
3d
(1:0.44)

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0.44
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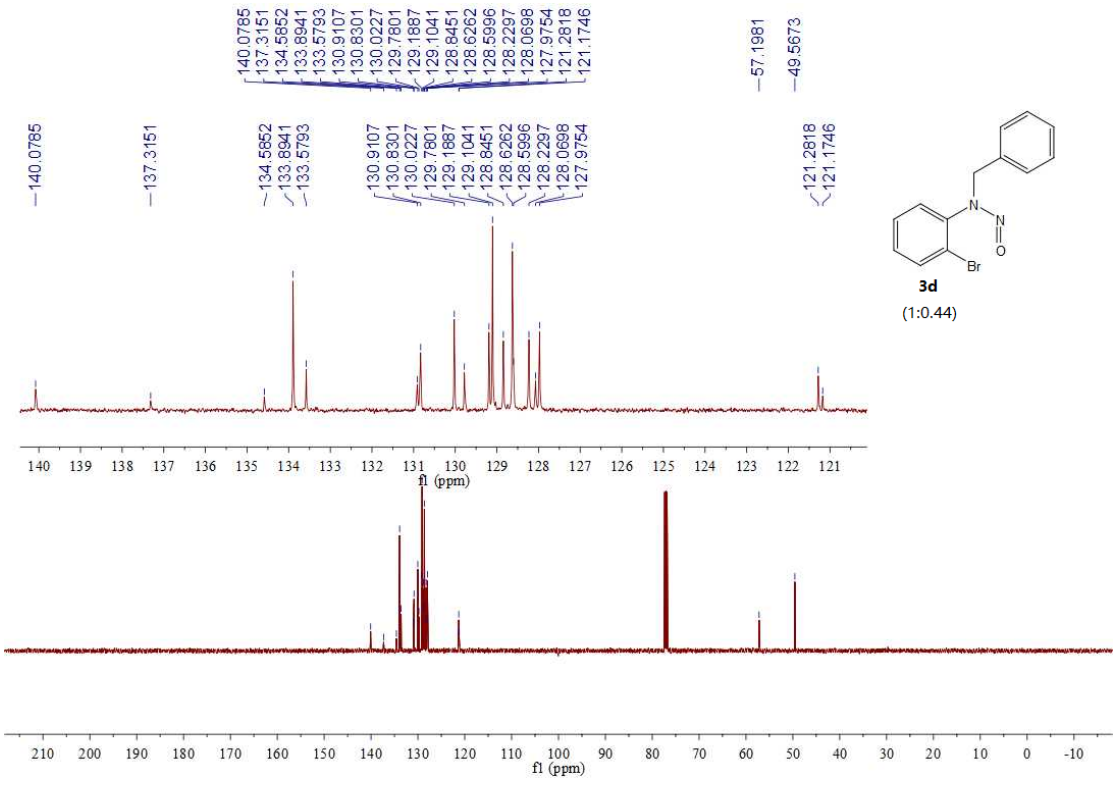
2.59
f1 (ppm)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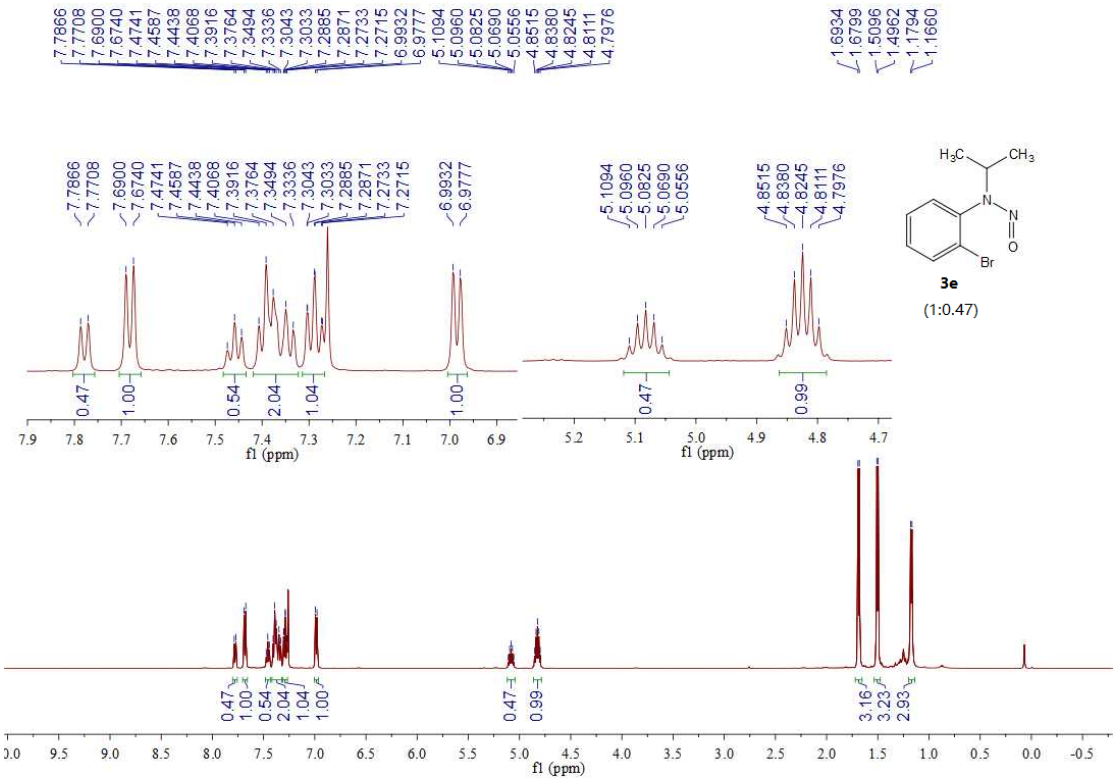
3d
(1:0.44)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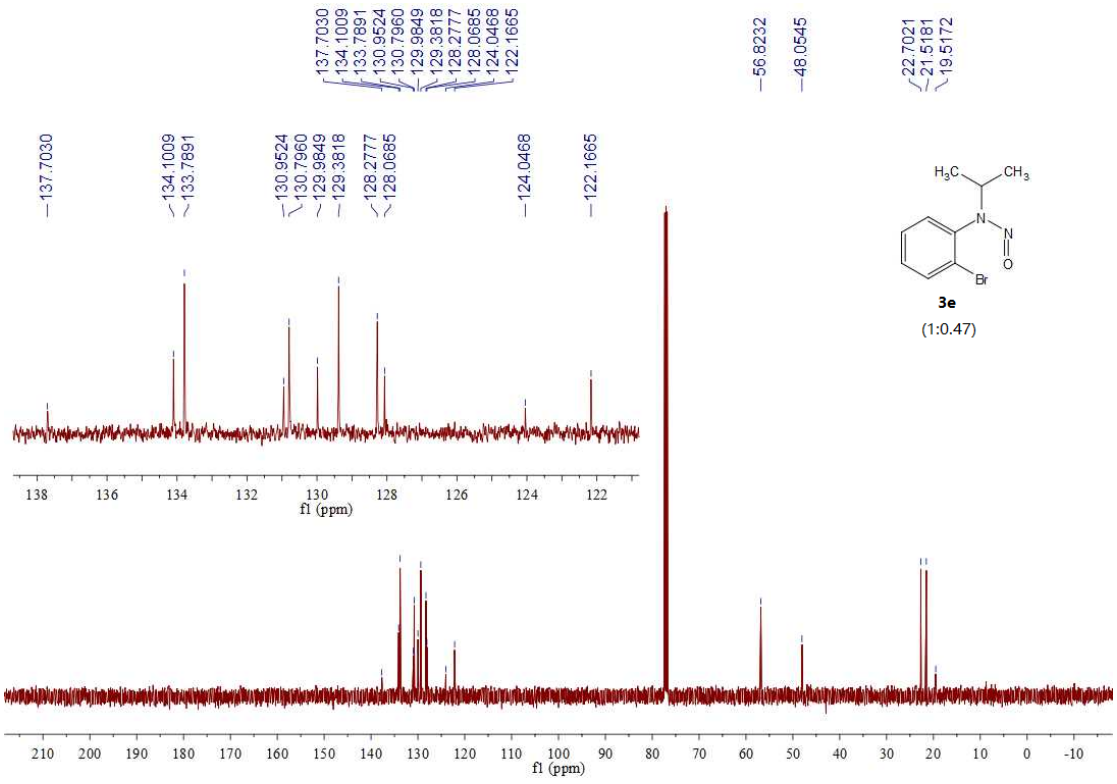
3e
(1:0.47)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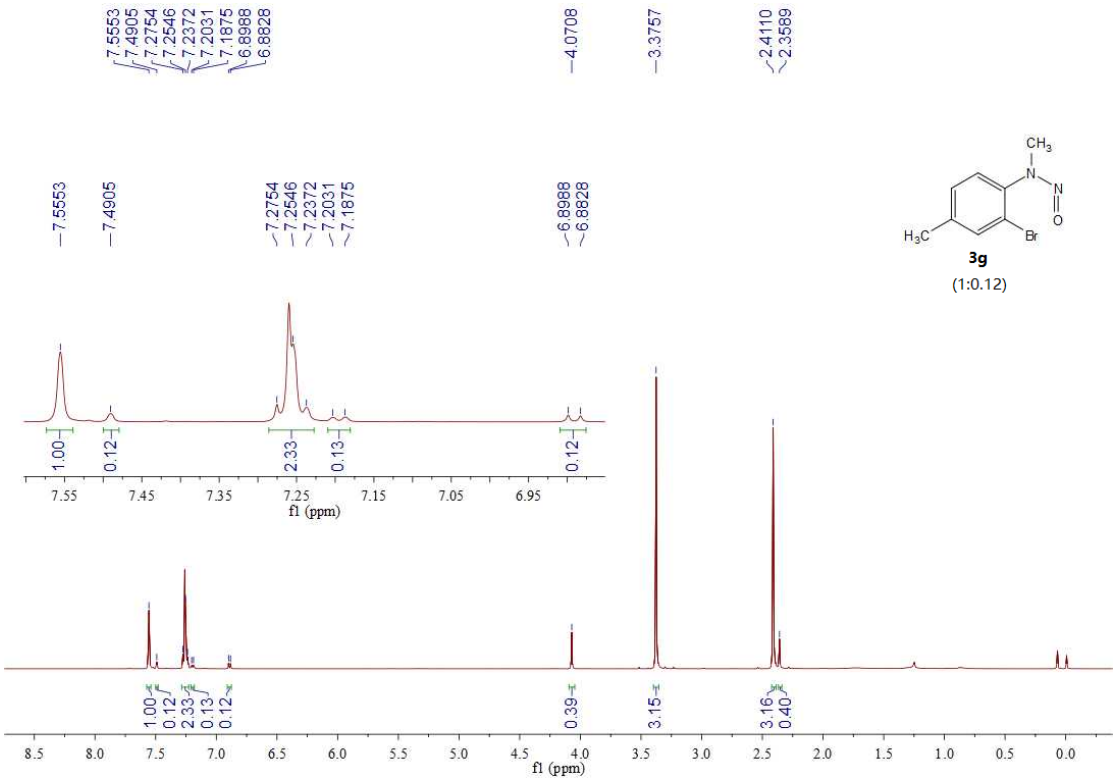
3e
(1:0.47)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N
O
H3C
Br
3g
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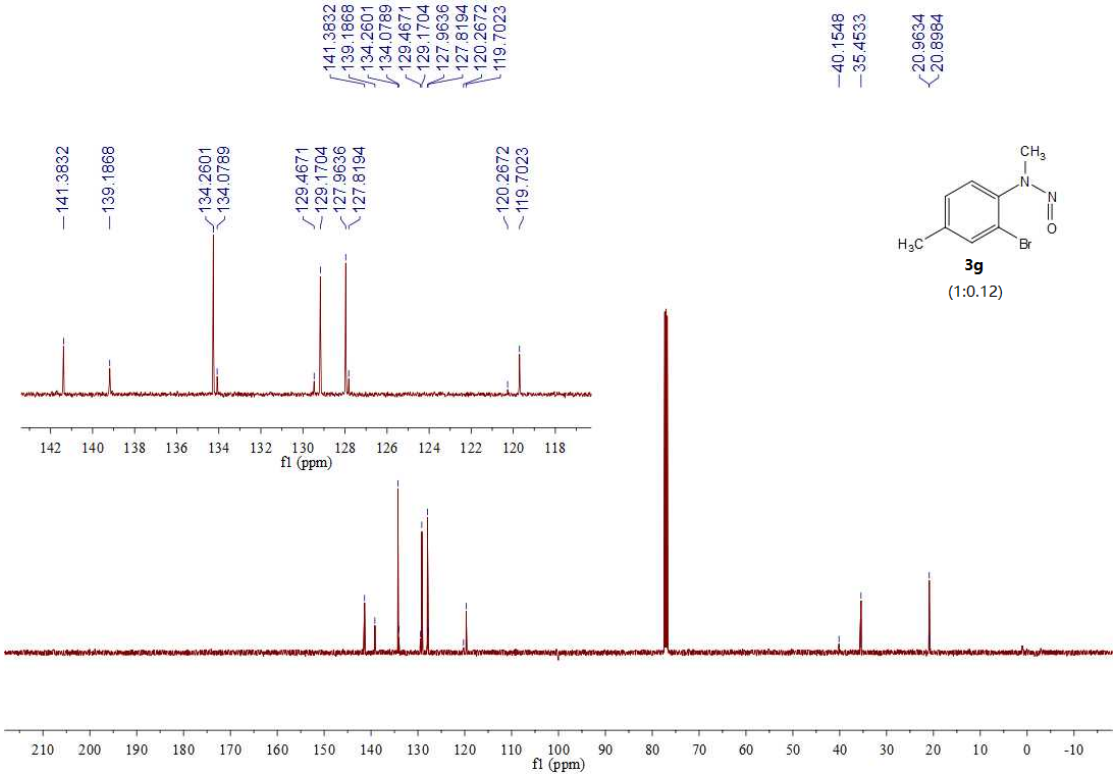
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Br
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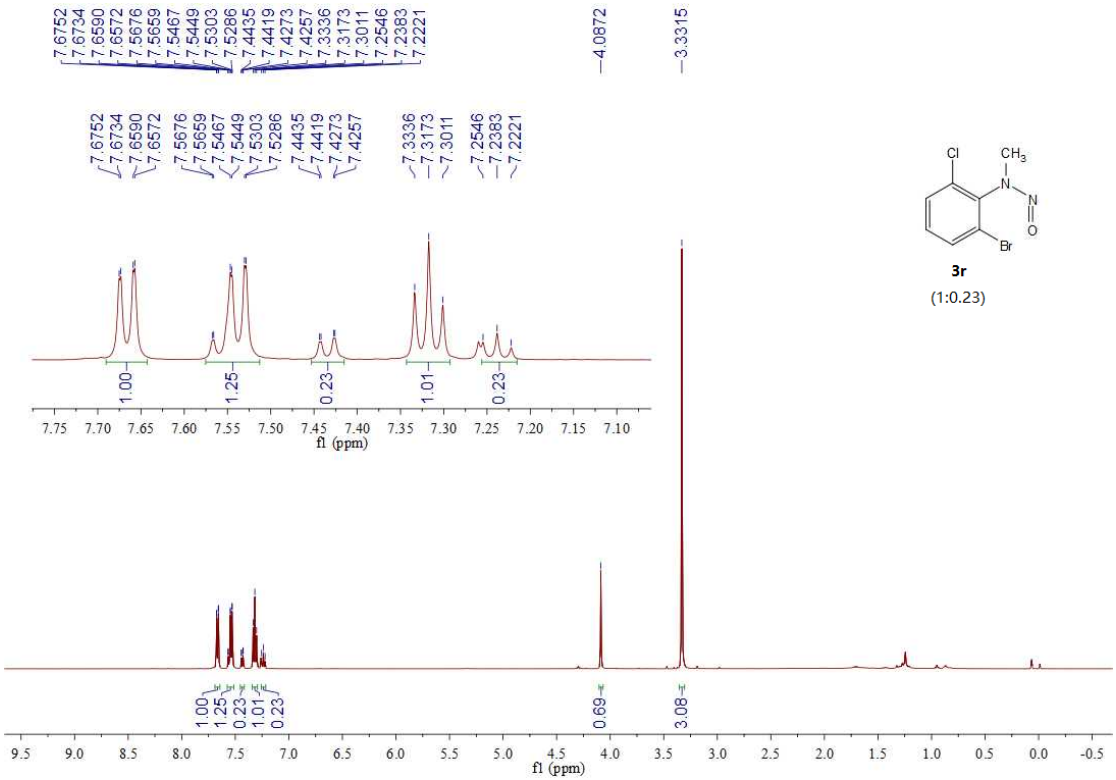
f1 (ppm)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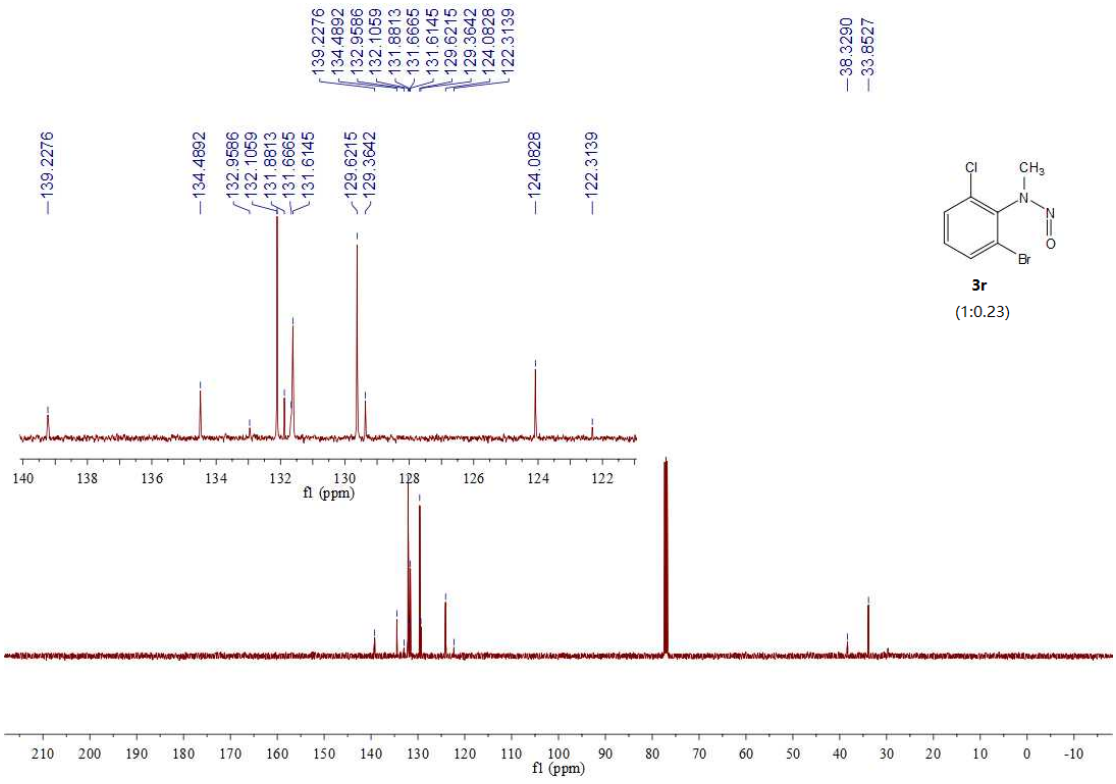
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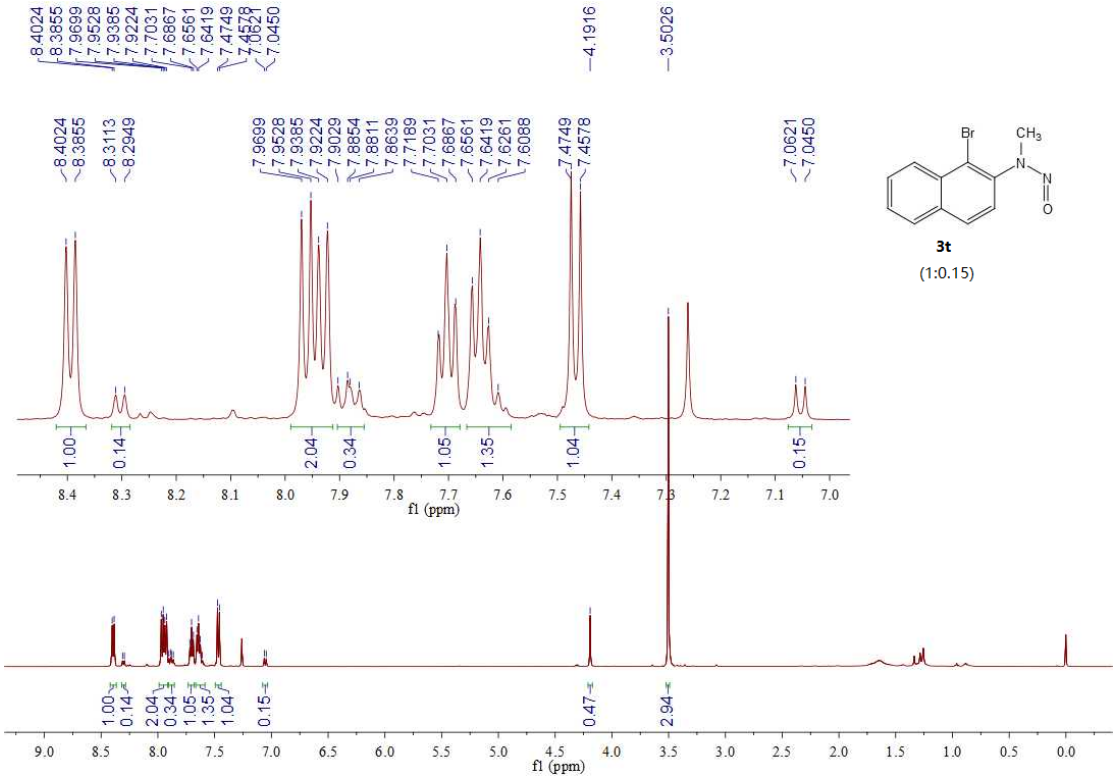
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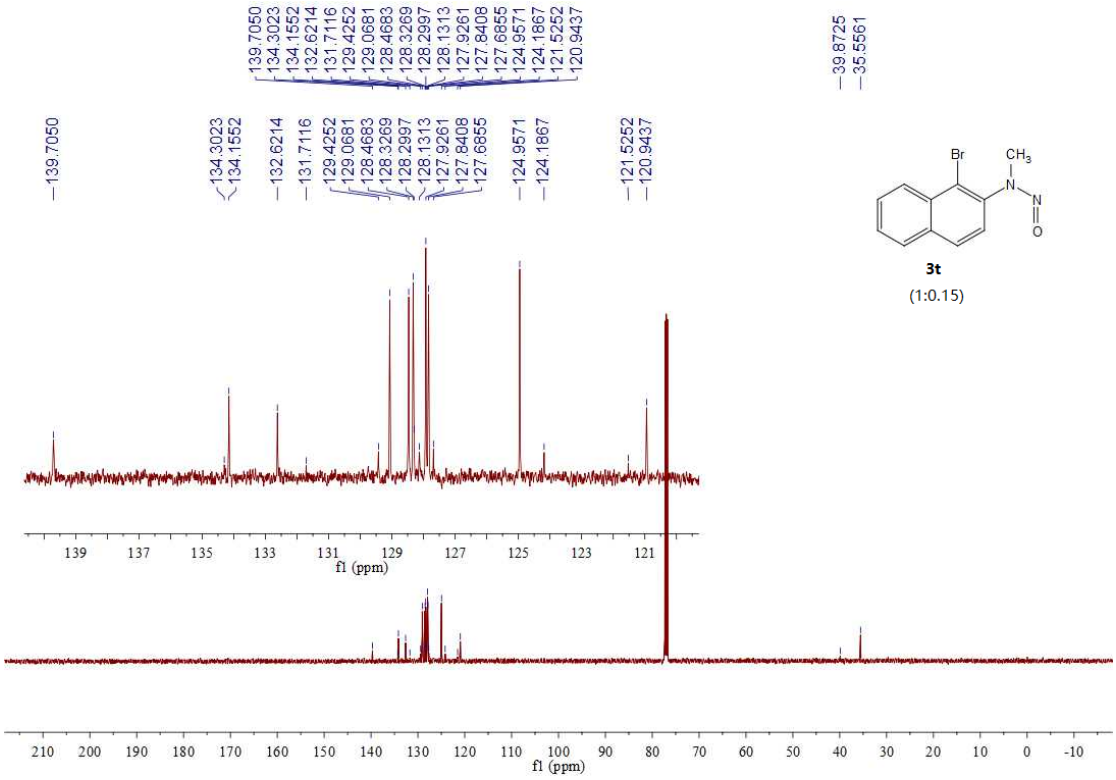
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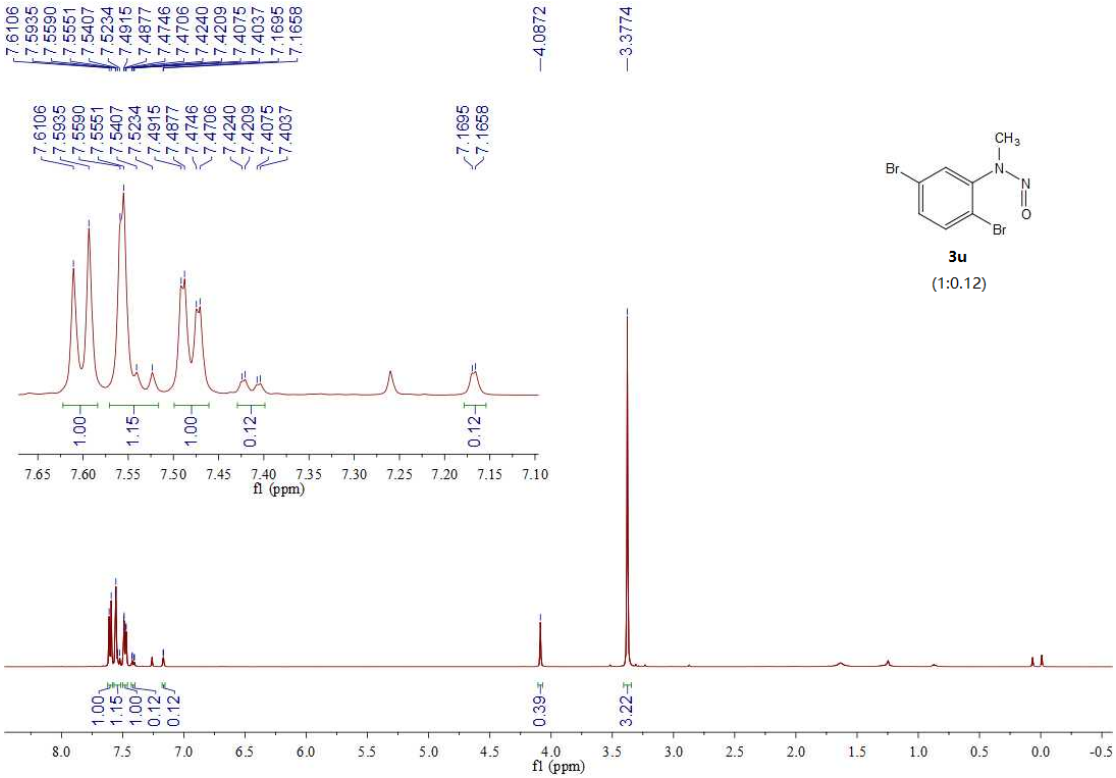
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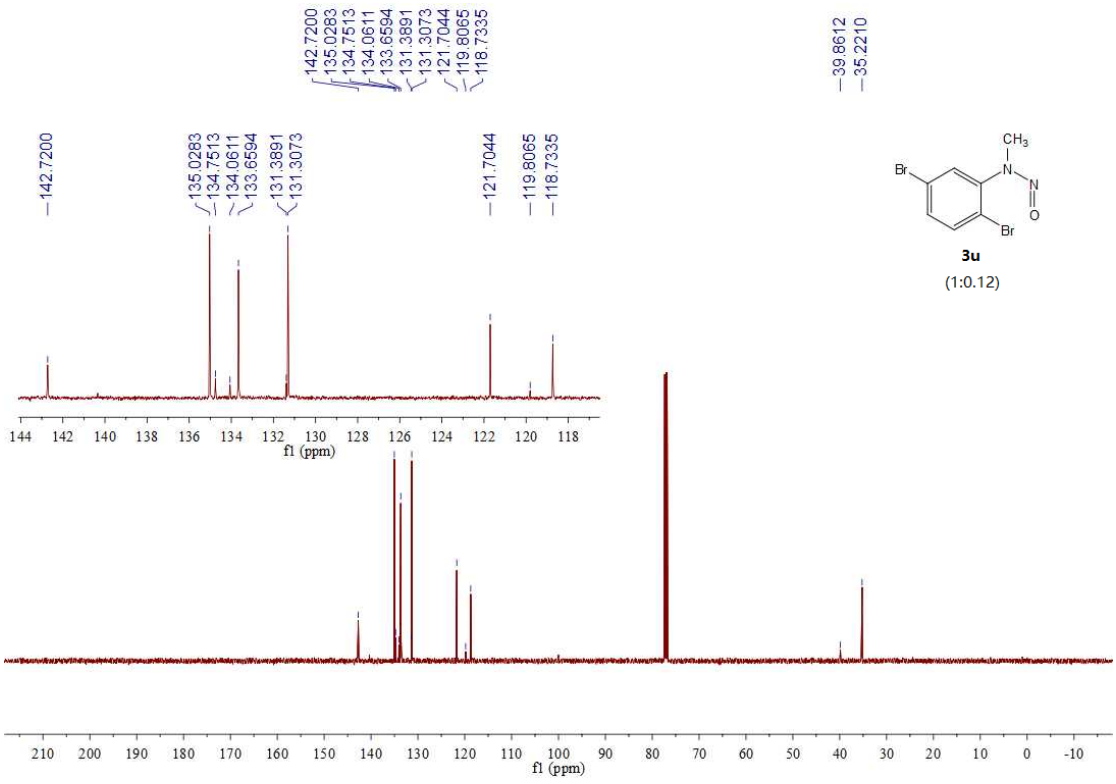
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Br
Br
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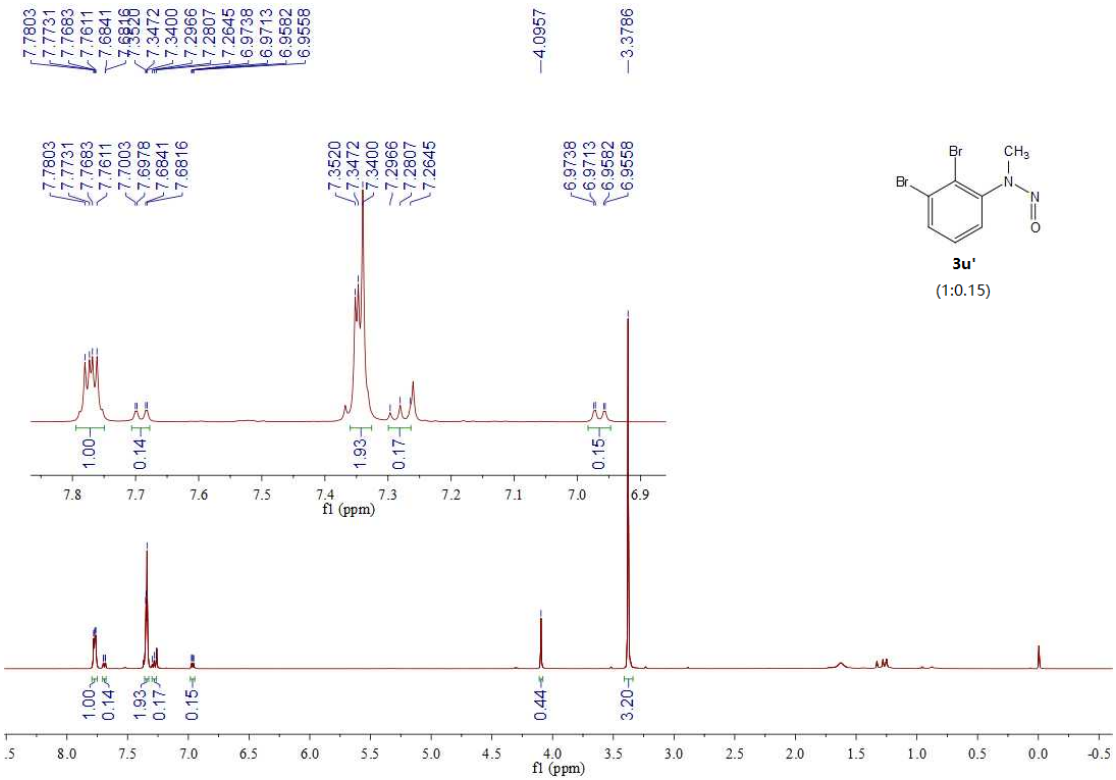
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0.17
0.15
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CH3
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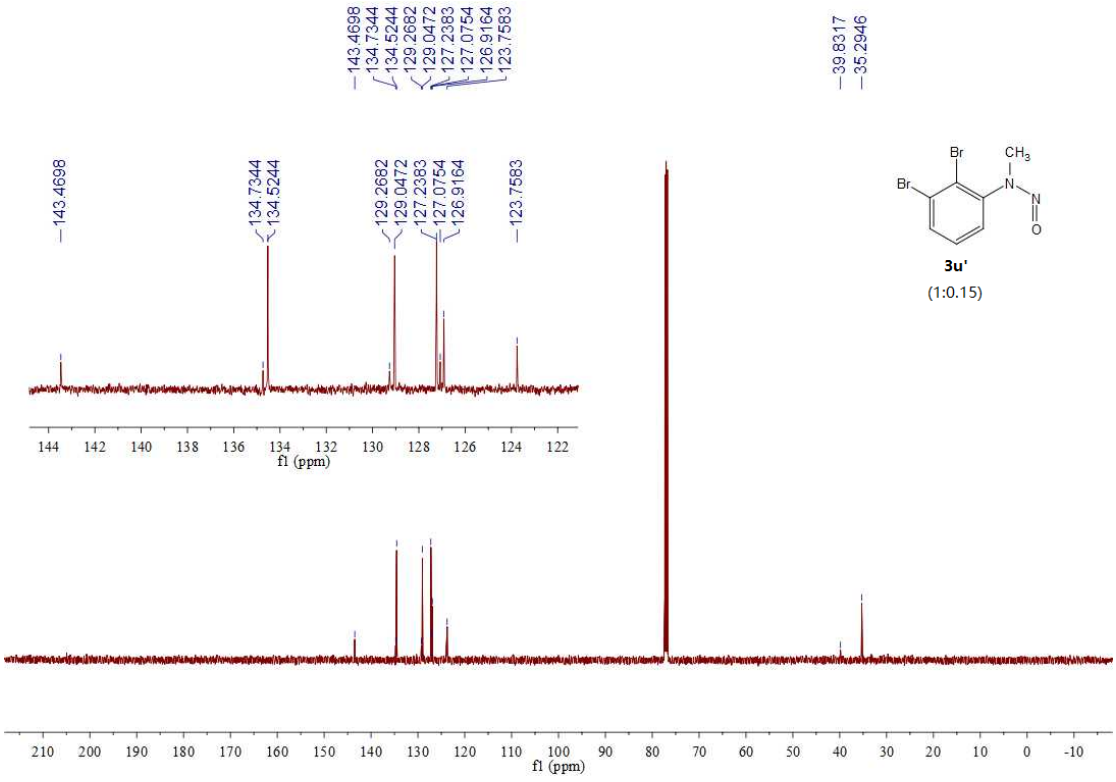
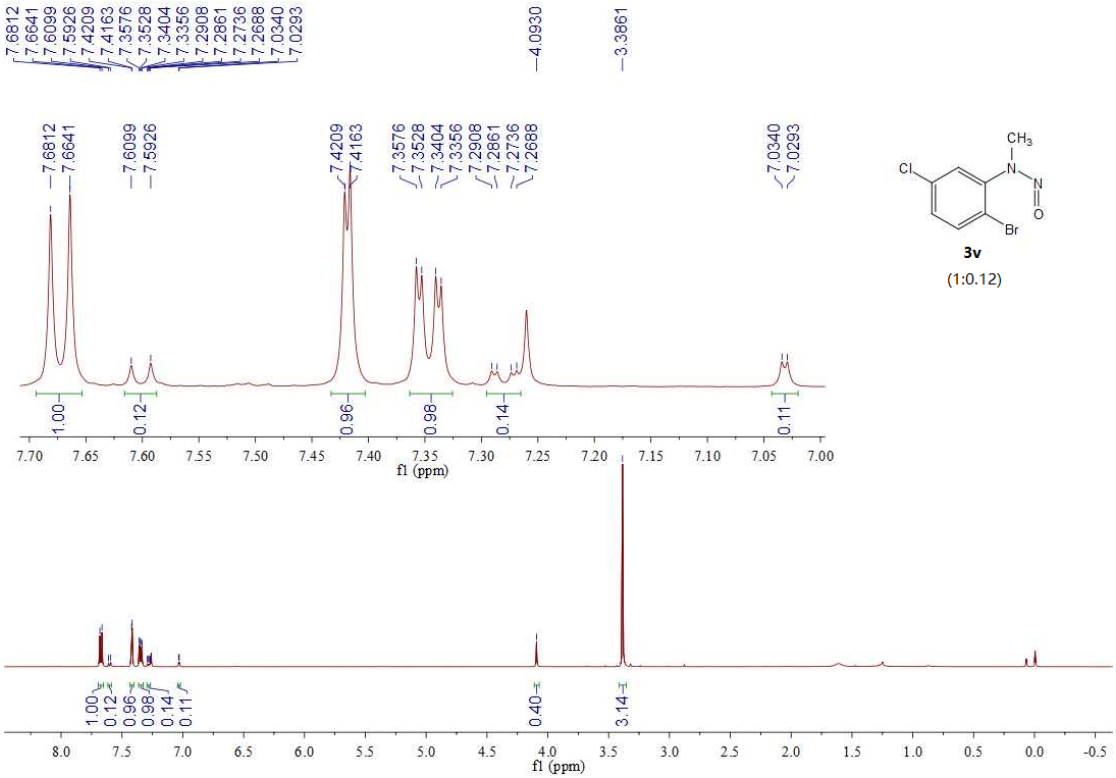
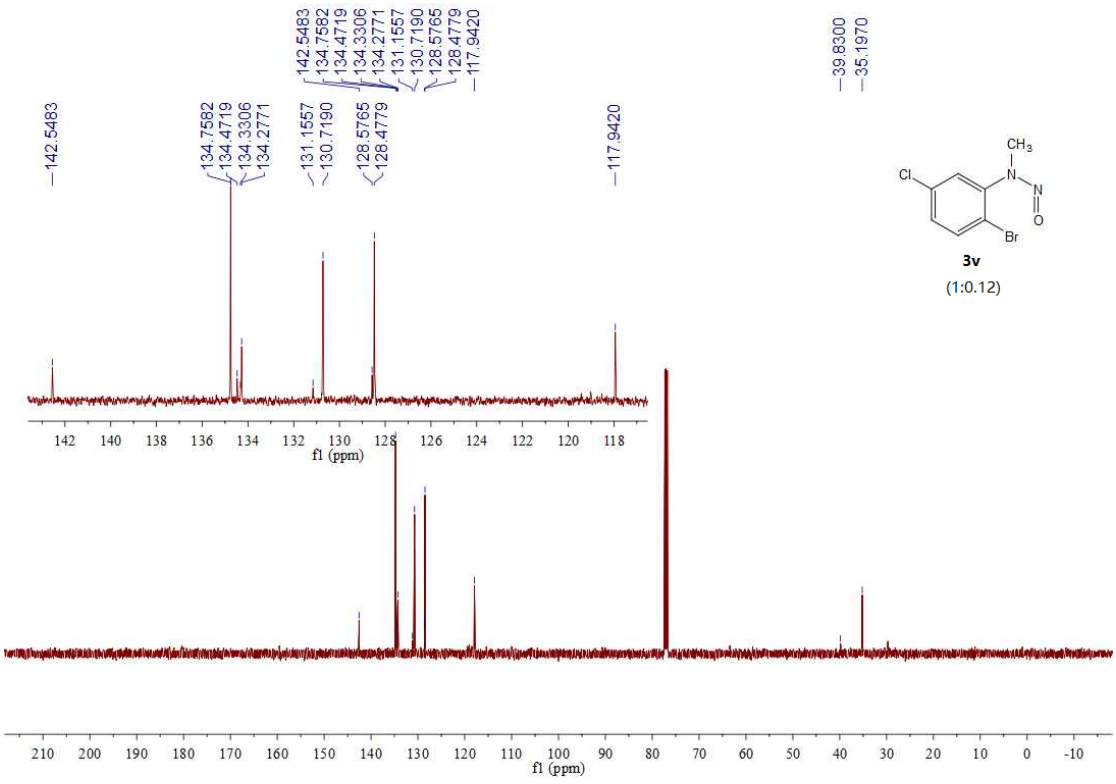
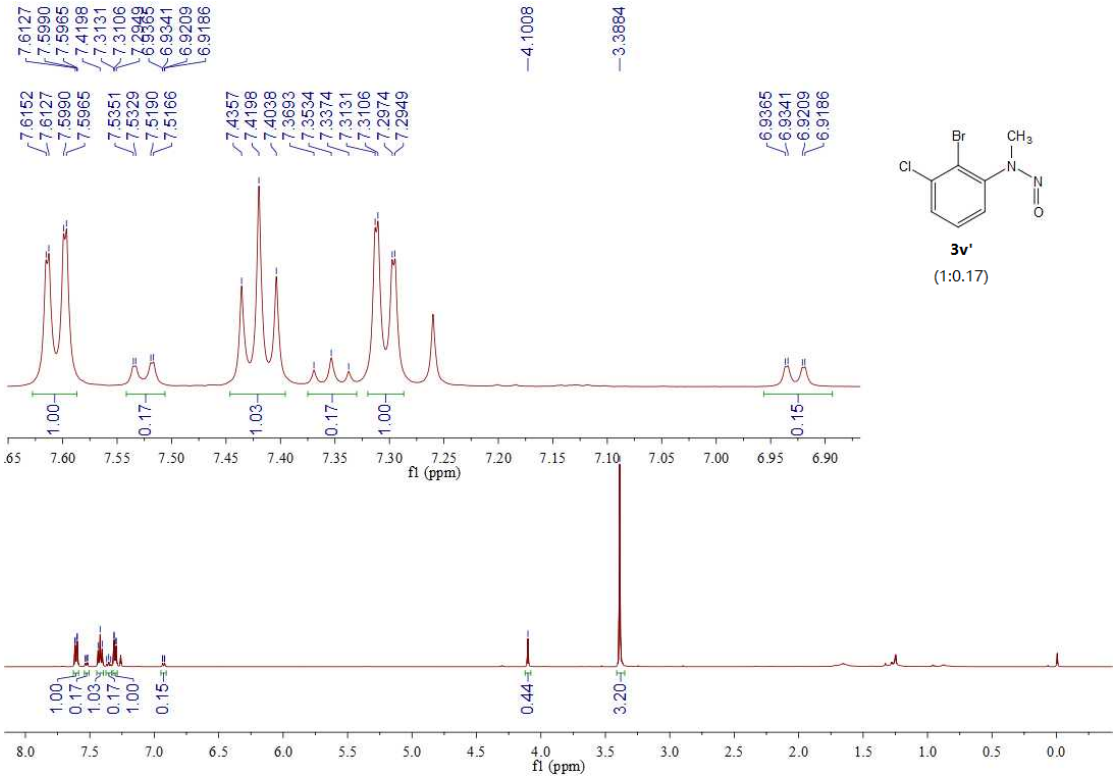
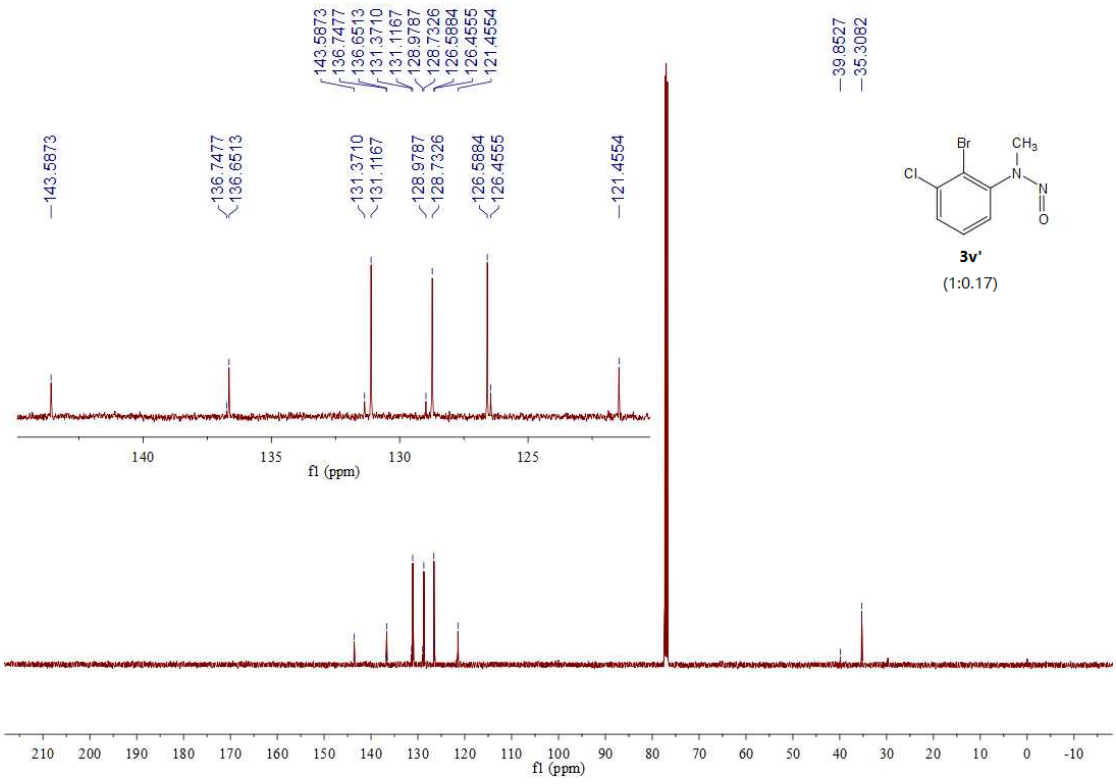
N
O
3u'
(1:0.15)

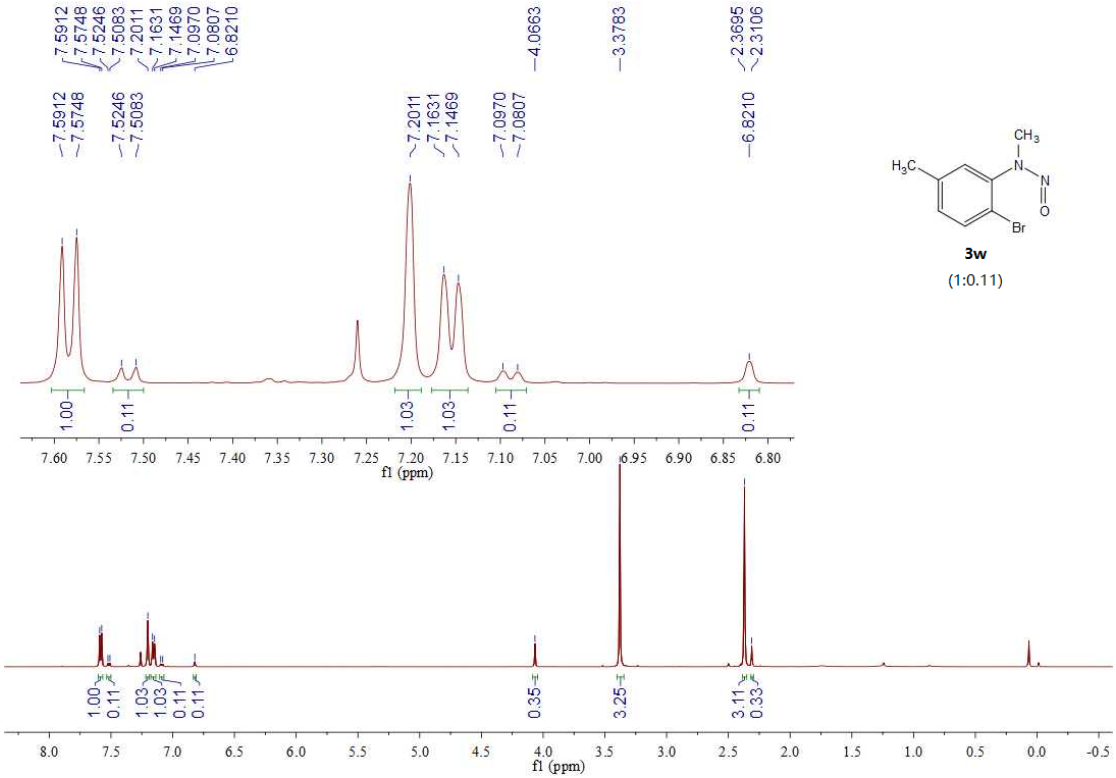

143.4698
134.7344
134.5244
129.2682
129.0472
127.2383
127.0754
126.9164
123.7583
39.8317
35.2946
f1 (ppm)
Br
CH3
N
N
O
3u'
(1:0.15)

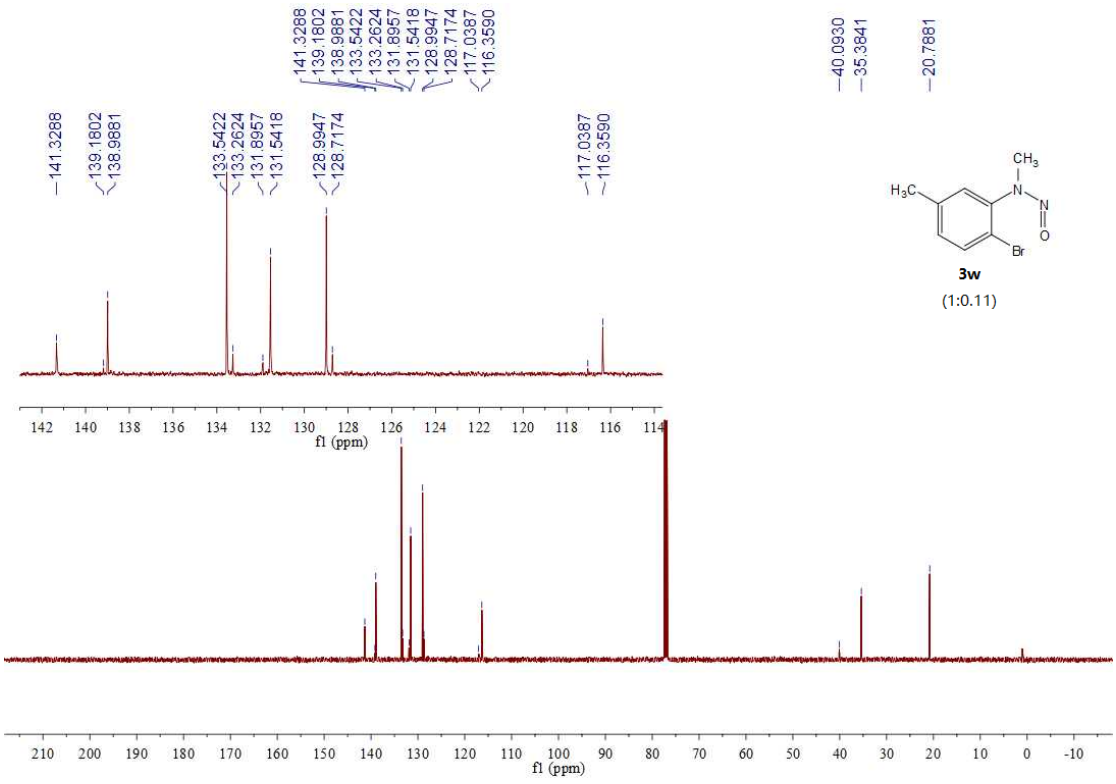

7.6812
7.6641
7.6099
7.5926
7.4209
7.4163
7.3576
7.3528
7.3404
7.3356
7.2908
7.2861
7.2736
7.2688
7.0340
7.0293
4.0930
3.3861
1.00
0.12
0.96
0.98
0.14
0.11
0.40
3.14
f1 (ppm)
Cl
Br
N
O
CH3
3v
(1:0.12)

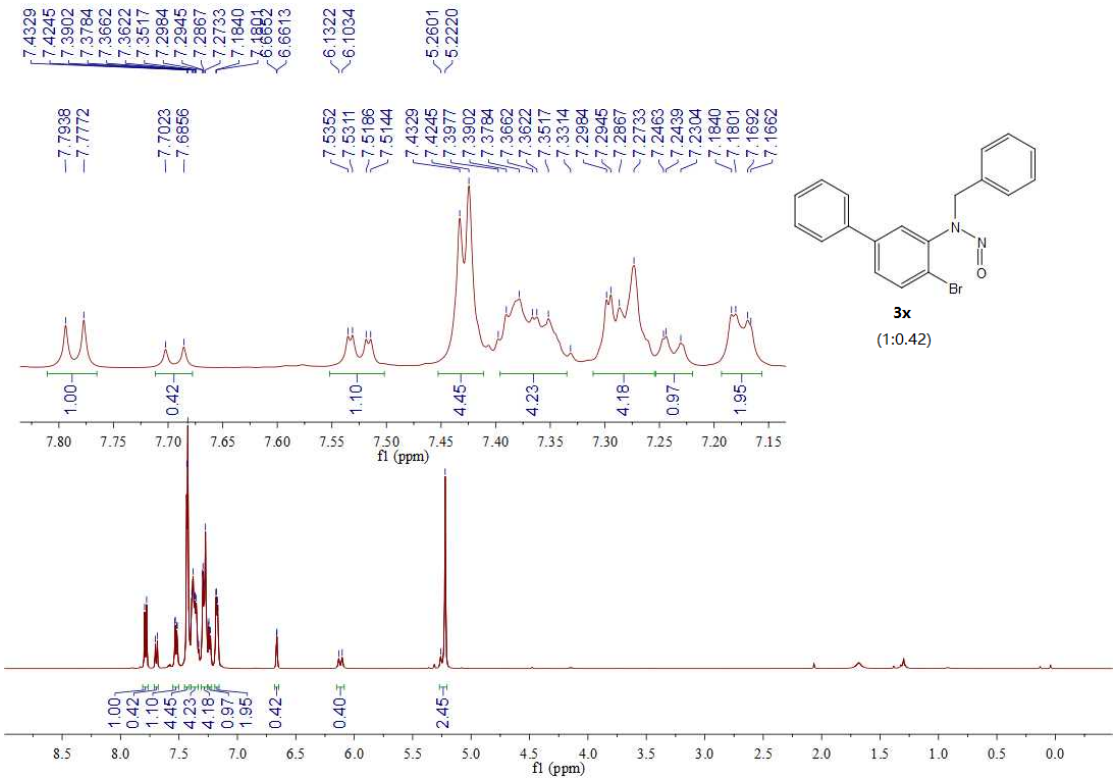

142.5483
134.7582
134.4719
134.3306
134.2771
131.1557
130.7190
128.5765
128.4779
117.9420
39.8300
35.1970
f1 (ppm)
Cl
Br
N
O
CH3
3v
(1:0.12)

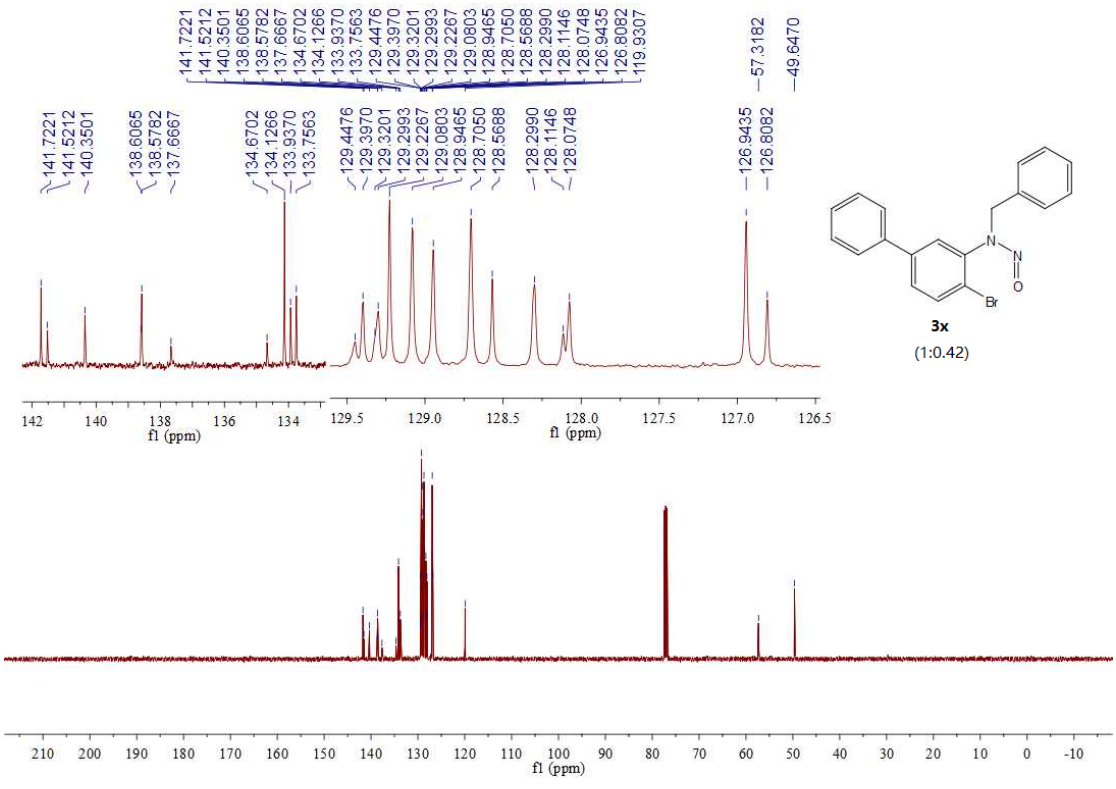

7.6127
7.5990
7.5965
7.4198
7.3131
7.3106
7.2949
6.9365
6.9341
6.9209
6.9186
4.1008
3.3884
7.6152
7.6127
7.5990
7.5965
7.5351
7.5329
7.5190
7.5166
7.4357
7.4198
7.4038
7.3693
7.3534
7.3374
7.3131
7.3106
7.2974
7.2949
6.9365
6.9341
6.9209
6.9186
1.00
0.17
1.03
0.17
1.00
0.15
0.44
3.20
f1 (ppm)
Br
CH3
Cl
N
N
O
3v'
(1:0.17)

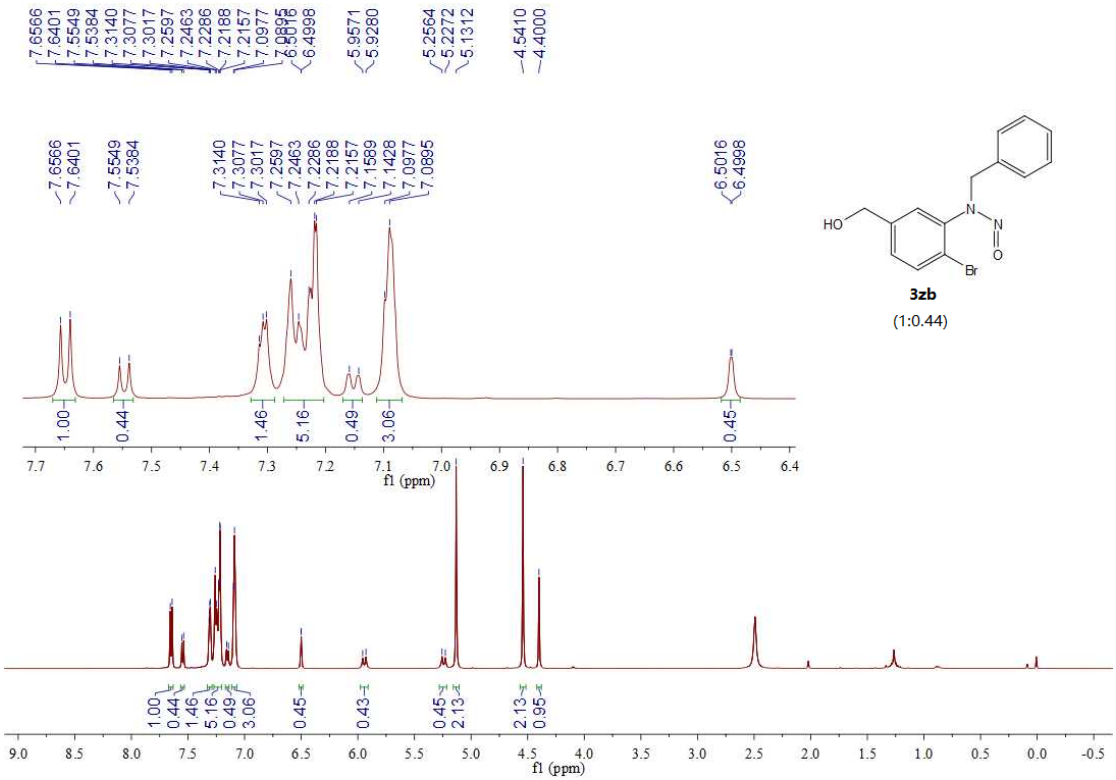

143.5873
136.7477
136.6513
131.3710
131.1167
128.9787
128.7326
126.5884
126.4555
121.4554
39.8527
35.3082
f1 (ppm)
Br
CH3
Cl
N
N
O
3v'
(1:0.17)


7.5912
7.5748
7.5246
7.5083
7.2011
7.1631
7.1469
7.0970
7.0807
6.8210
4.0663
3.3783
2.3695
2.3106
1.00
0.11
1.03
1.03
0.11
0.11
f1 (ppm)
0.35
3.25
3.11
0.33
CH3
H3C
N
N
O
Br
3w
(1:0.11)


141.3288
139.1802
138.9881
133.5422
133.2624
131.8957
131.5418
128.9947
128.7174
117.0387
116.3590
40.0930
35.3841
20.7881
f1 (ppm)
CH3
H3C
N
N
O
Br
3w
(1:0.11)

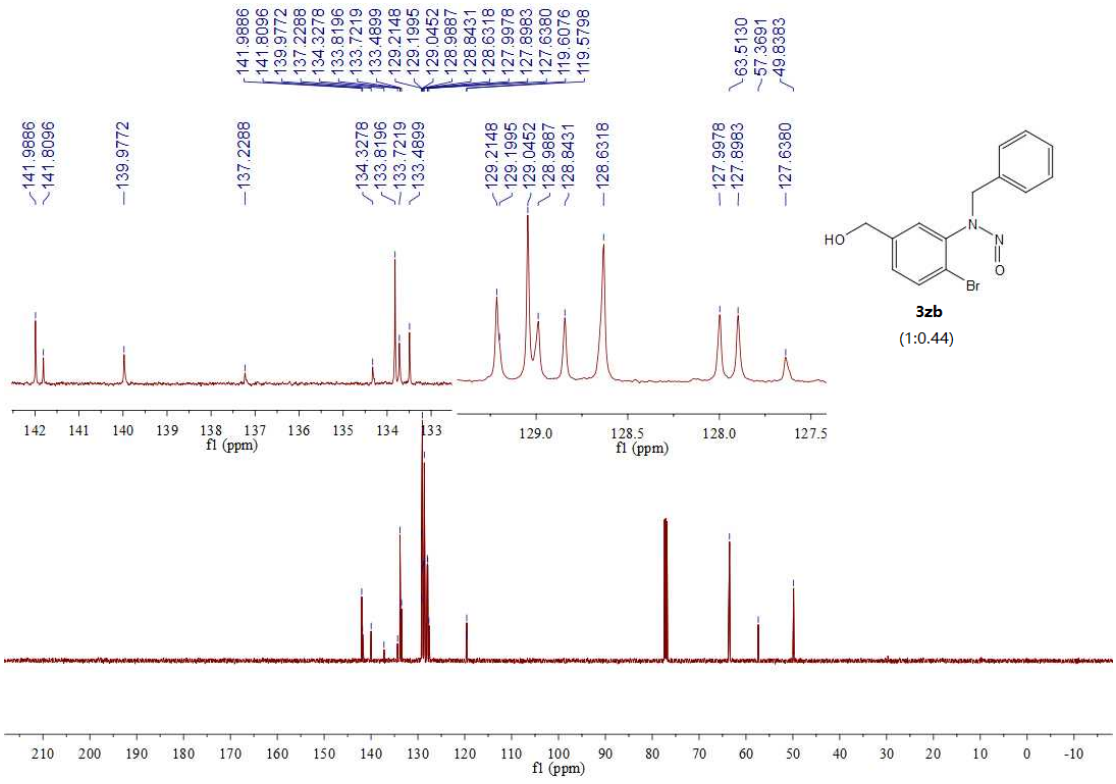

7.4329
7.4245
7.3902
7.3784
7.3662
7.3622
7.3517
7.2984
7.2945
7.2867
7.2733
7.1840
6.6852
6.6613
6.1322
6.1034
5.2601
5.2220
7.7938
7.7772
7.7023
7.6856
7.5352
7.5311
7.5186
7.5144
7.4329
7.4245
7.3977
7.3902
7.3784
7.3662
7.3622
7.3517
7.3314
7.2984
7.2945
7.2867
7.2733
7.2463
7.2439
7.2304
7.1840
7.1801
7.1692
7.1662
1.00
0.42
1.10
4.45
4.23
4.18
0.97
1.95
f1 (ppm)
Br
3x
(1:0.42)


141.7221
141.5212
140.3501
138.6065
138.5782
137.6667
134.6702
134.1266
133.9370
133.7563
129.4476
129.3970
129.3201
129.2993
129.2267
129.0803
128.9465
128.7050
128.5688
128.2990
128.1146
128.0748
126.9435
126.8082
119.9307
57.3182
49.6470
f1 (ppm)
Br
3x
(1:0.42)



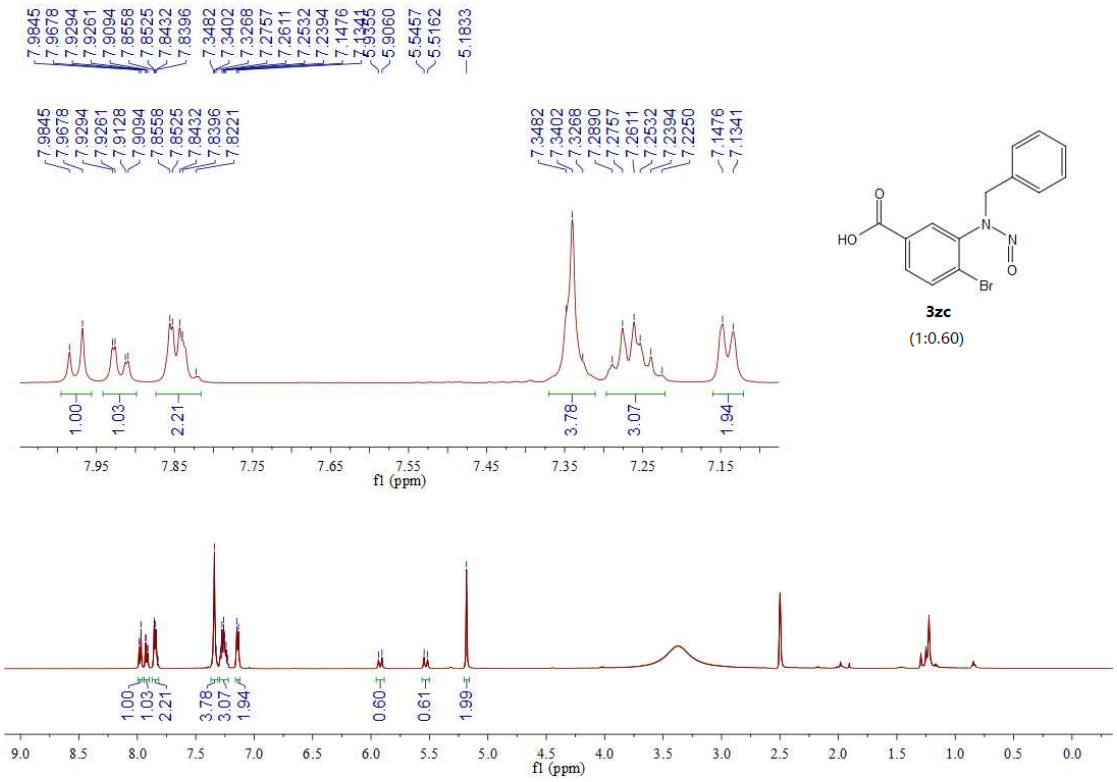
3zb

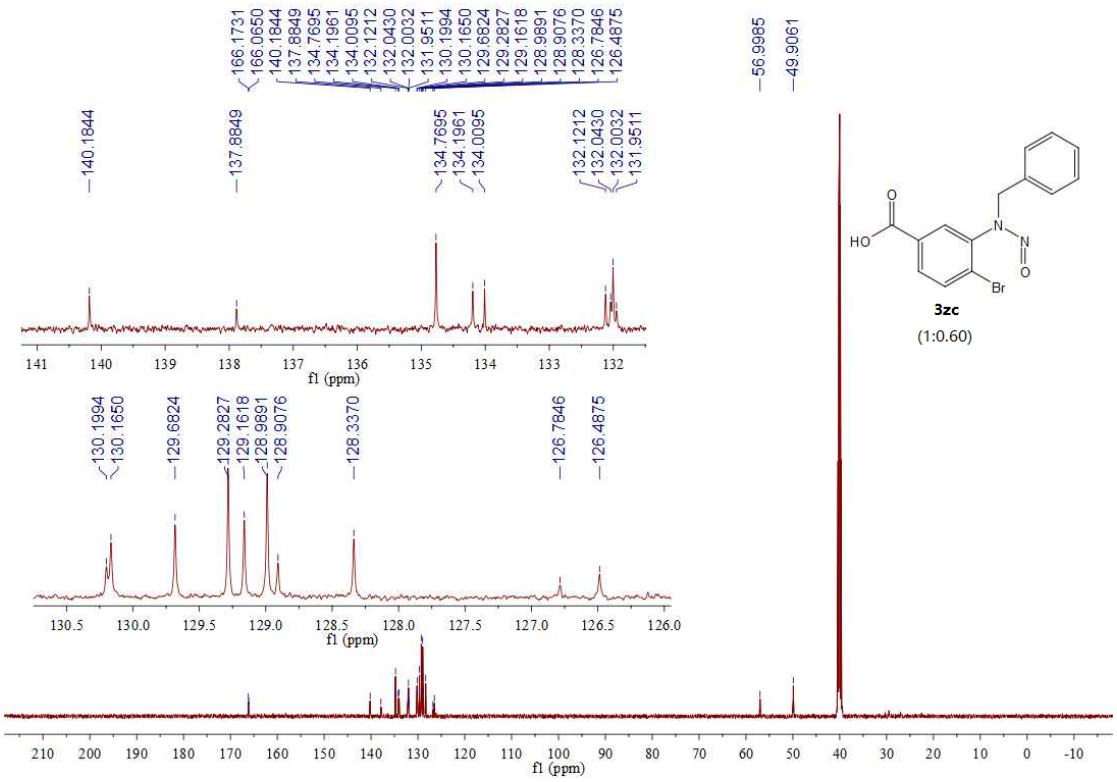
(1:0.44)

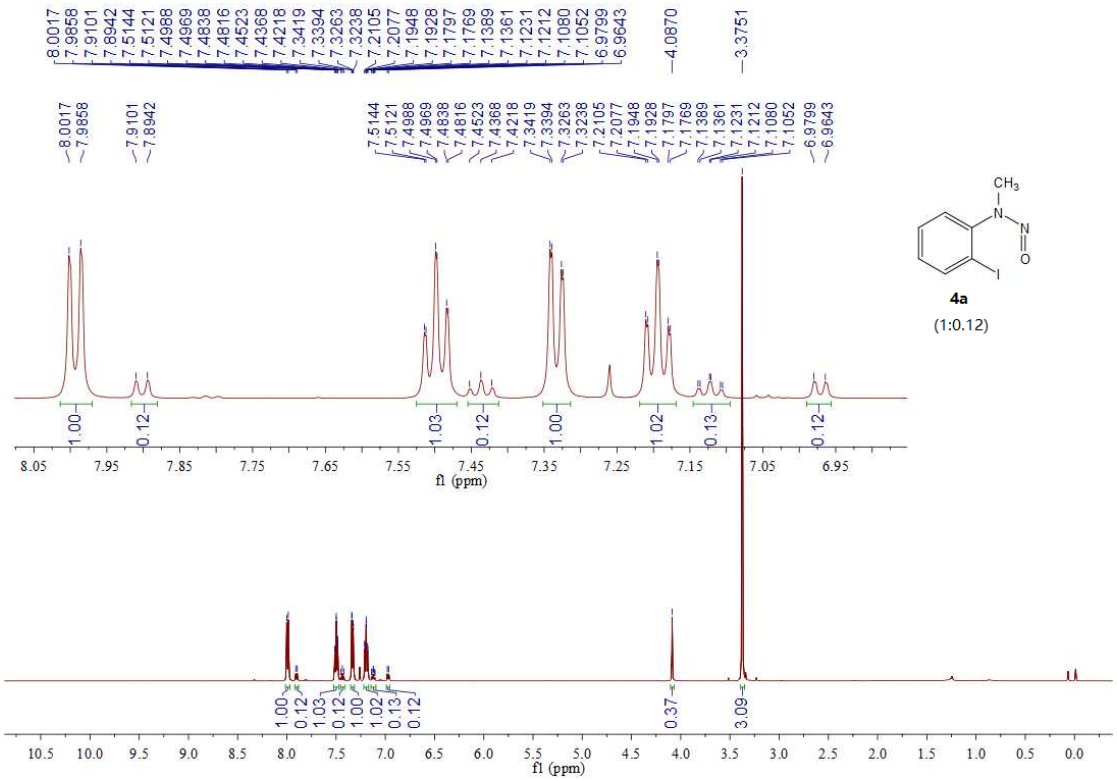


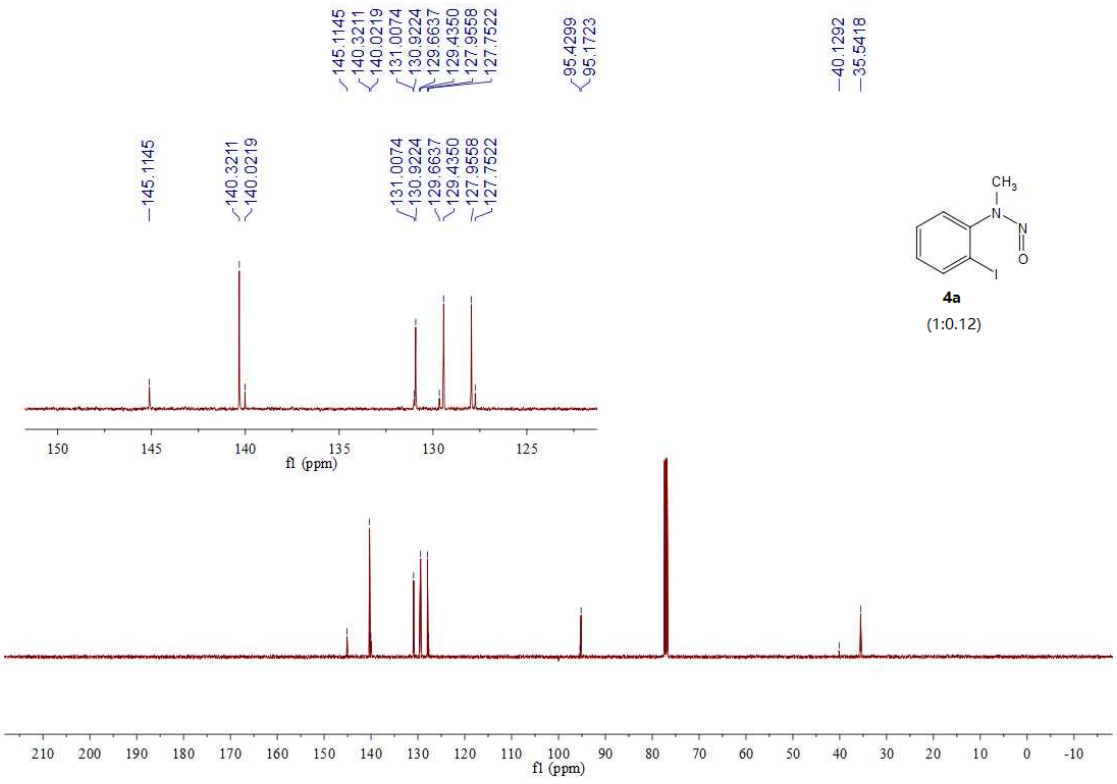
3zb

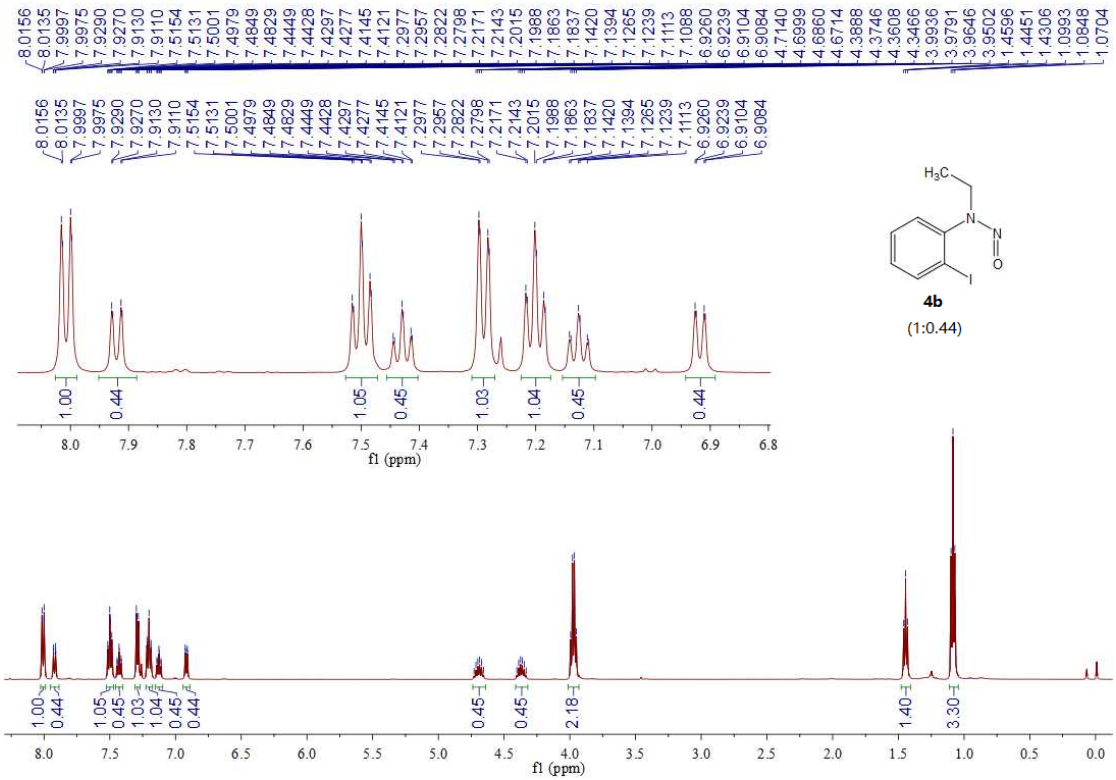
(1:0.44)

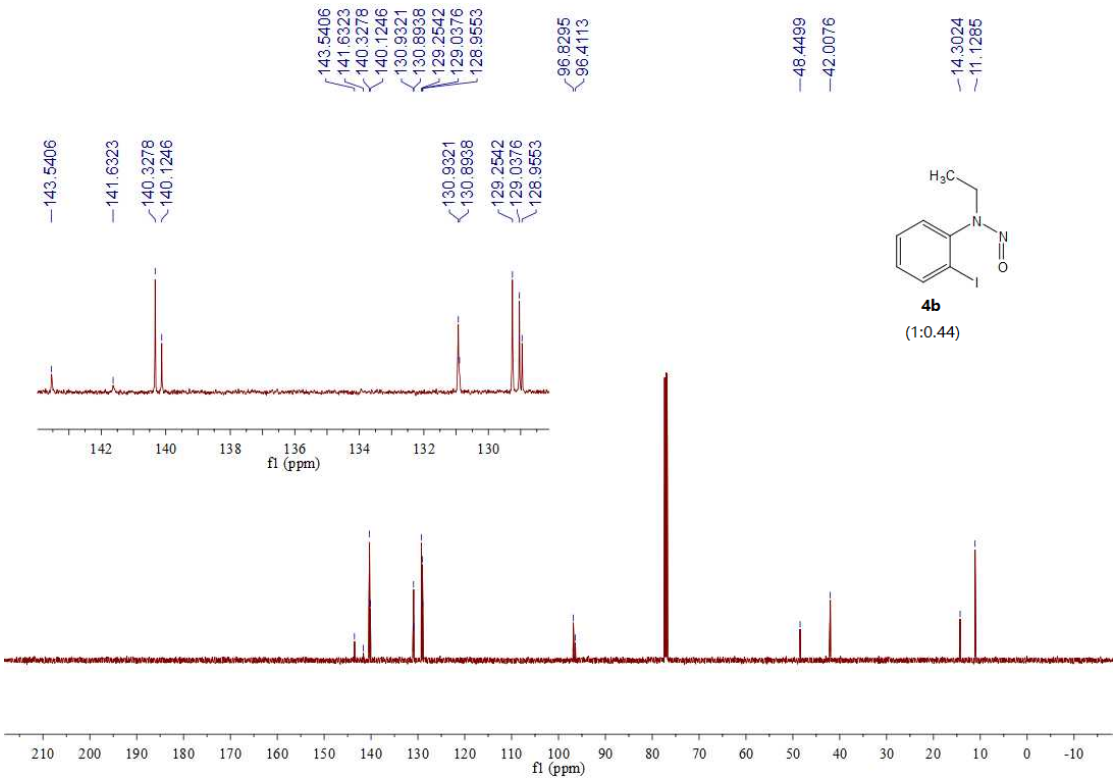

7.9845
7.9678
7.9294
7.9261
7.9094
7.8558
7.8525
7.8432
7.8396
7.3482
7.3402
7.3268
7.2757
7.2611
7.2532
7.2394
7.1476
7.1341
5.9355
5.9060
5.5457
5.5162
5.1833
1.00
1.03
2.21
3.78
3.07
1.94
0.60
0.61
1.99
fl (ppm)
HO
O
N
N
O
Br
3zc
(1:0.60)

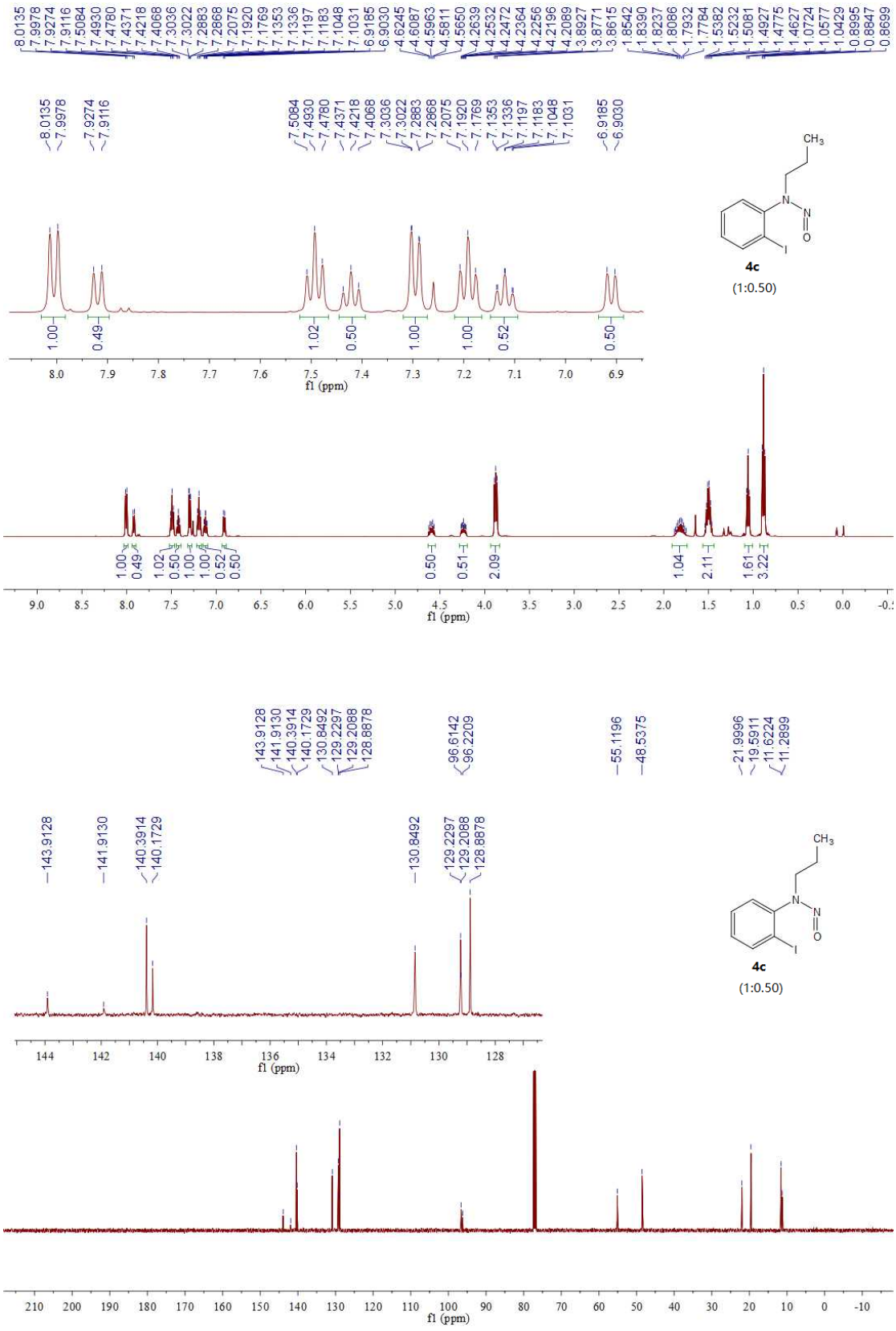

166.1731
166.0650
140.1844
137.8849
134.7695
134.1961
134.0095
132.1212
132.0430
132.0032
131.9511
130.1994
130.1650
129.6824
129.2827
129.1618
128.9891
128.9076
128.3370
126.7846
126.4875
56.9985
49.9061
fl (ppm)
HO
O
N
N
O
Br
3zc
(1:0.60)

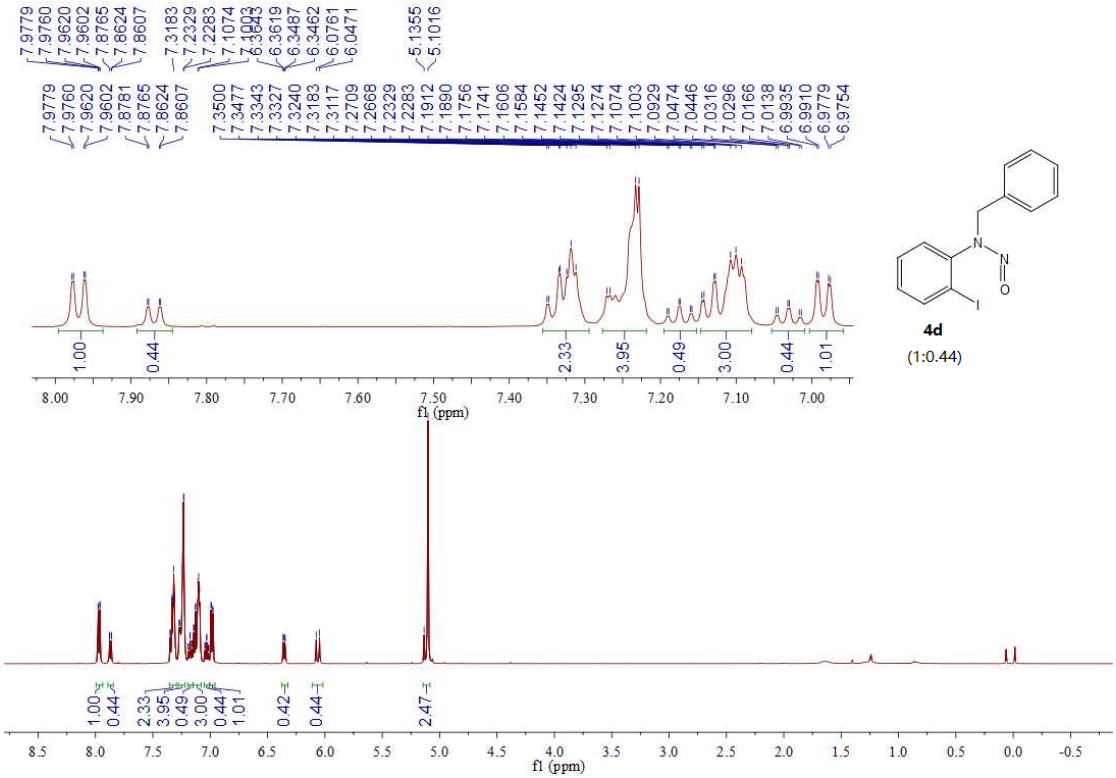

8.0017
7.9858
7.9101
7.8942
7.5144
7.5121
7.4988
7.4969
7.4838
7.4816
7.4523
7.4368
7.4218
7.3419
7.3394
7.3263
7.3238
7.2105
7.2077
7.1948
7.1928
7.1797
7.1769
7.1389
7.1361
7.1231
7.1212
7.1080
7.1052
6.9799
6.9643
4.0870
3.3751
1.00
0.12
1.03
0.12
1.00
1.02
0.13
0.12
0.37
3.09
f1 (ppm)
4a
(1:0.12)

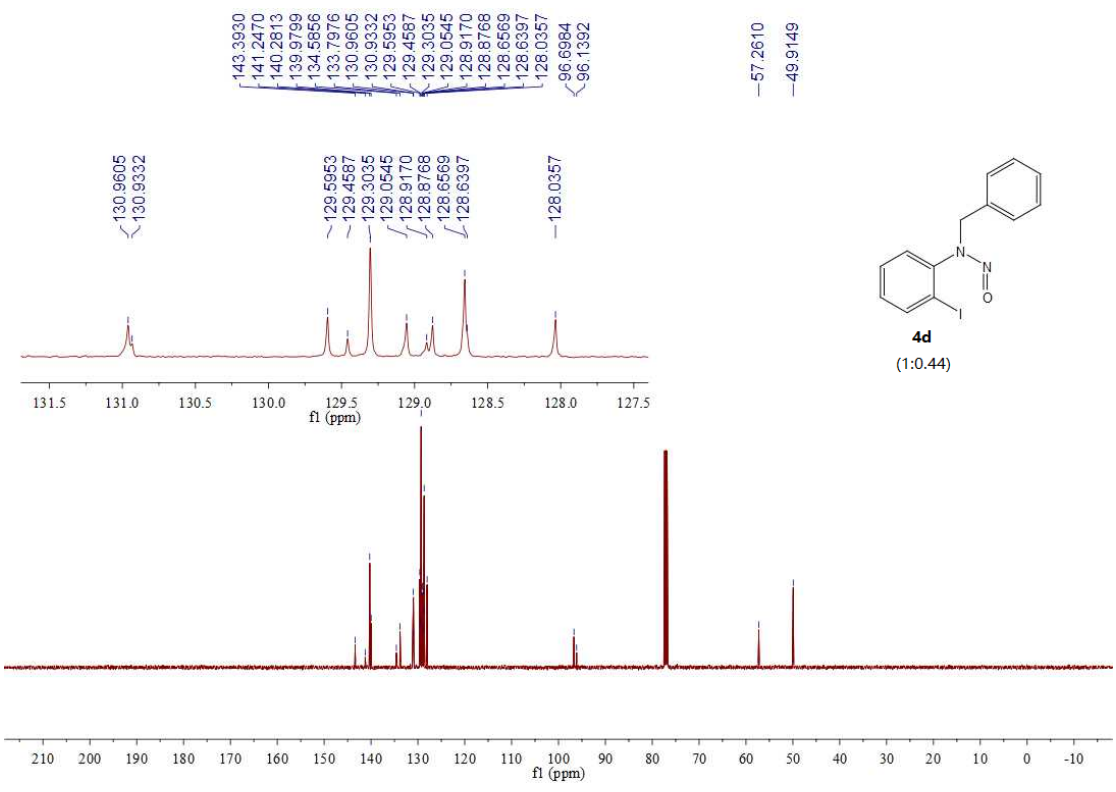

145.1145
140.3211
140.0219
131.0074
130.9224
129.6637
129.4350
127.9558
127.7522
95.4299
95.1723
40.1292
35.5418
f1 (ppm)
4a
(1:0.12)

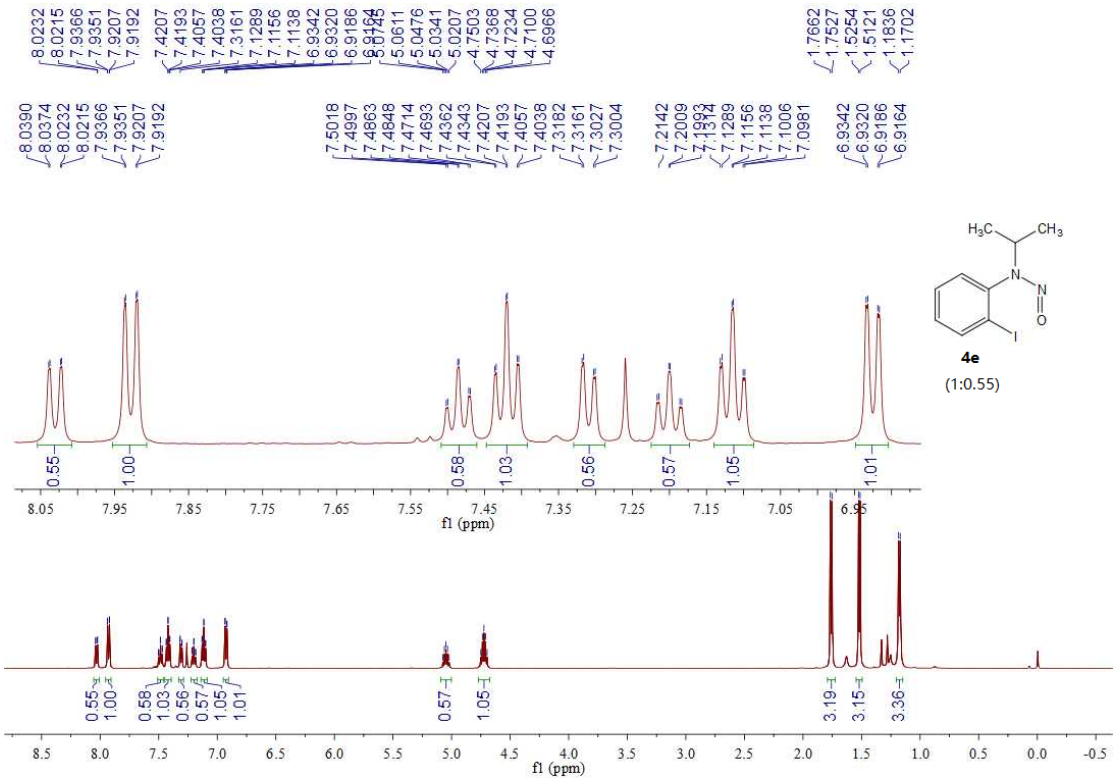

4b
(1:0.44)
f1 (ppm)

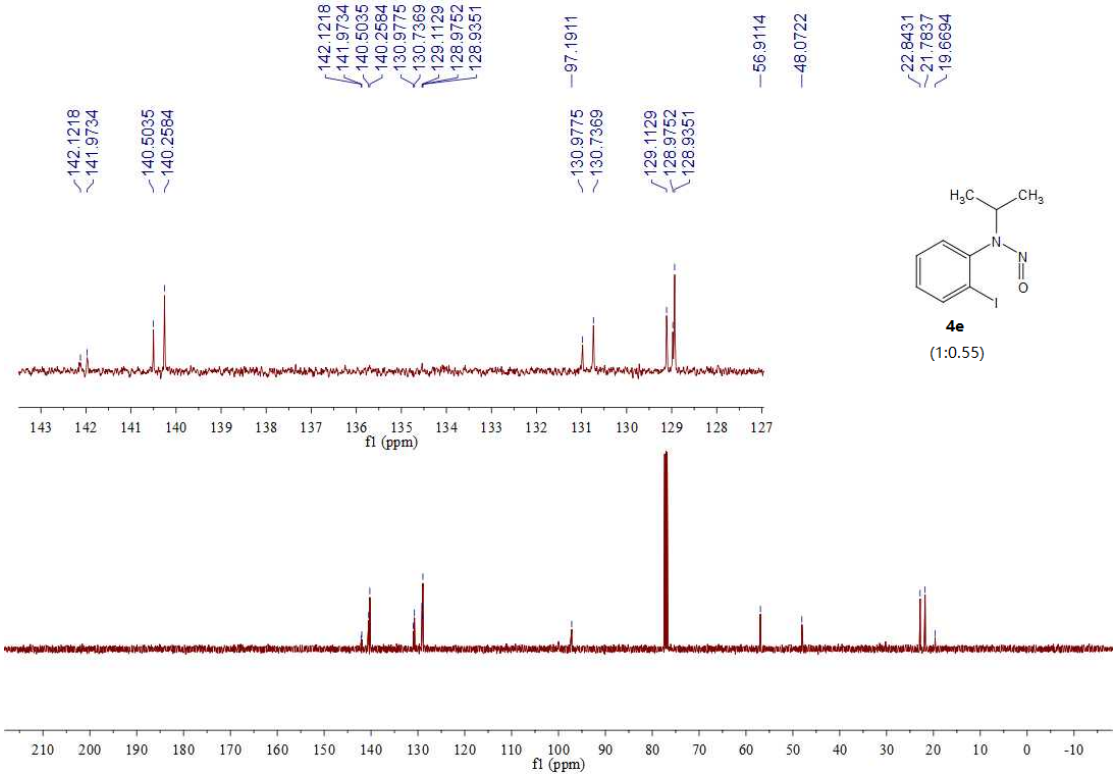

4b
(1:0.44)
f1 (ppm)

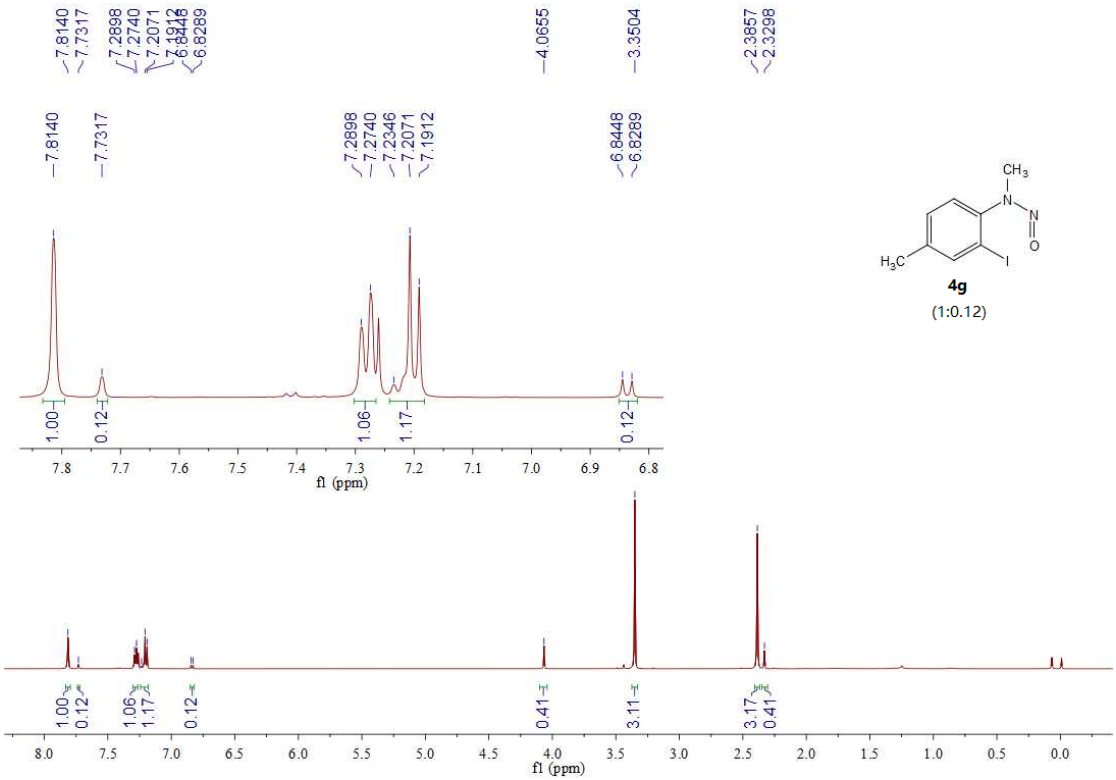

8.0135
7.9978
7.9274
7.9116
7.5084
7.4930
7.4780
7.4371
7.4218
7.4068
7.3036
7.3022
7.2883
7.2868
7.2075
7.1920
7.1769
7.1353
7.1336
7.1197
7.1183
7.1048
7.1031
6.9185
6.9030
4.6245
4.6087
4.5963
4.5811
4.5650
4.2639
4.2532
4.2472
4.2364
4.2256
4.2196
4.2089
3.8927
3.8771
3.8615
1.8542
1.8390
1.8237
1.8086
1.7932
1.7784
1.5382
1.5232
1.5081
1.4927
1.4775
1.4627
1.0724
1.0577
1.0429
0.8995
0.8847
0.8699
1.00
0.49
1.02
0.50
1.00
1.00
0.52
0.50
f1 (ppm)
CH3
N
N
O
I
4c
(1:0.50)
1.00
0.49
1.02
0.50
1.00
1.00
0.52
0.50
0.50
0.51
2.09
1.04
2.11
1.61
3.22
f1 (ppm)
143.9128
141.9130
140.3914
140.1729
130.8492
129.2297
129.2088
128.8878
96.6142
96.2209
55.1196
48.5375
21.9996
19.5911
11.6224
11.2899
f1 (ppm)
CH3
N
N
O
I
4c
(1:0.50)
f1 (ppm)

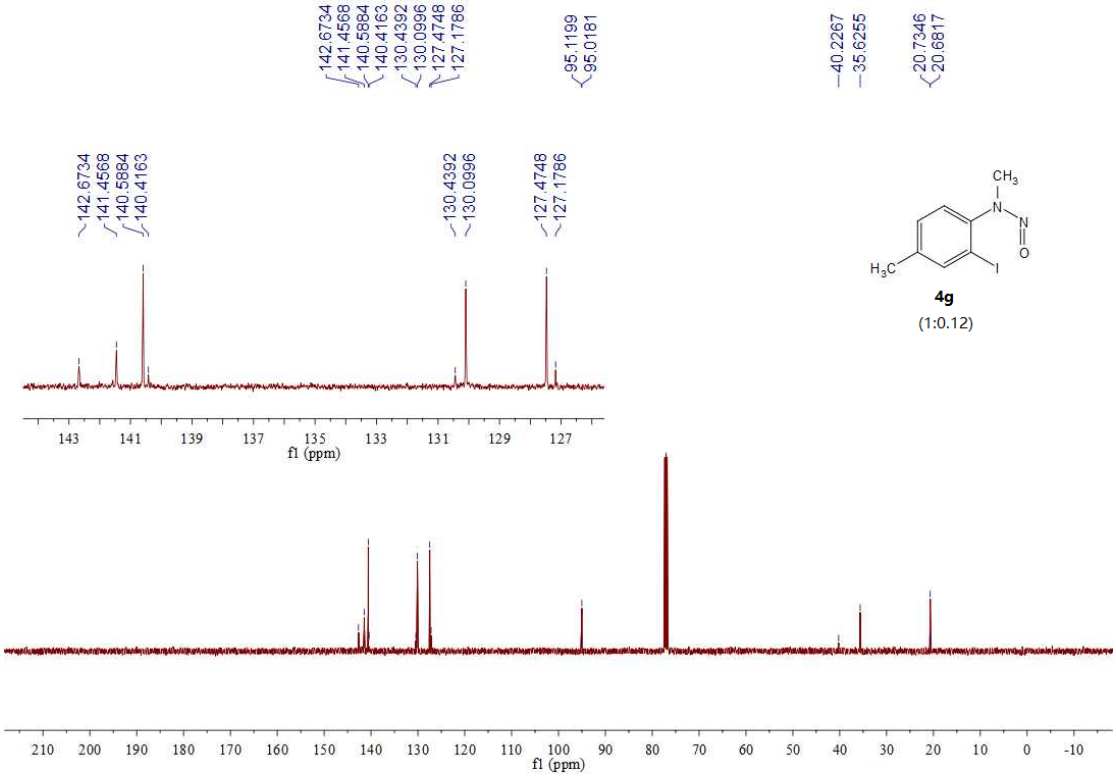

7.9779
7.9760
7.9620
7.9602
7.8765
7.8624
7.8607
7.3183
7.2329
7.2283
7.1074
7.1003
6.3619
6.3487
6.3462
6.0761
6.0471
5.1355
5.1016
7.3500
7.3477
7.3343
7.3327
7.3240
7.3183
7.3117
7.2709
7.2668
7.2329
7.2283
7.1912
7.1890
7.1756
7.1741
7.1606
7.1584
7.1452
7.1424
7.1295
7.1274
7.1074
7.1003
7.0929
7.0474
7.0446
7.0316
7.0296
7.0166
7.0138
6.9935
6.9910
6.9779
6.9754
1.00
0.44
2.33
3.95
0.49
3.00
0.44
1.01
f1 (ppm)
4d
(1:0.44)

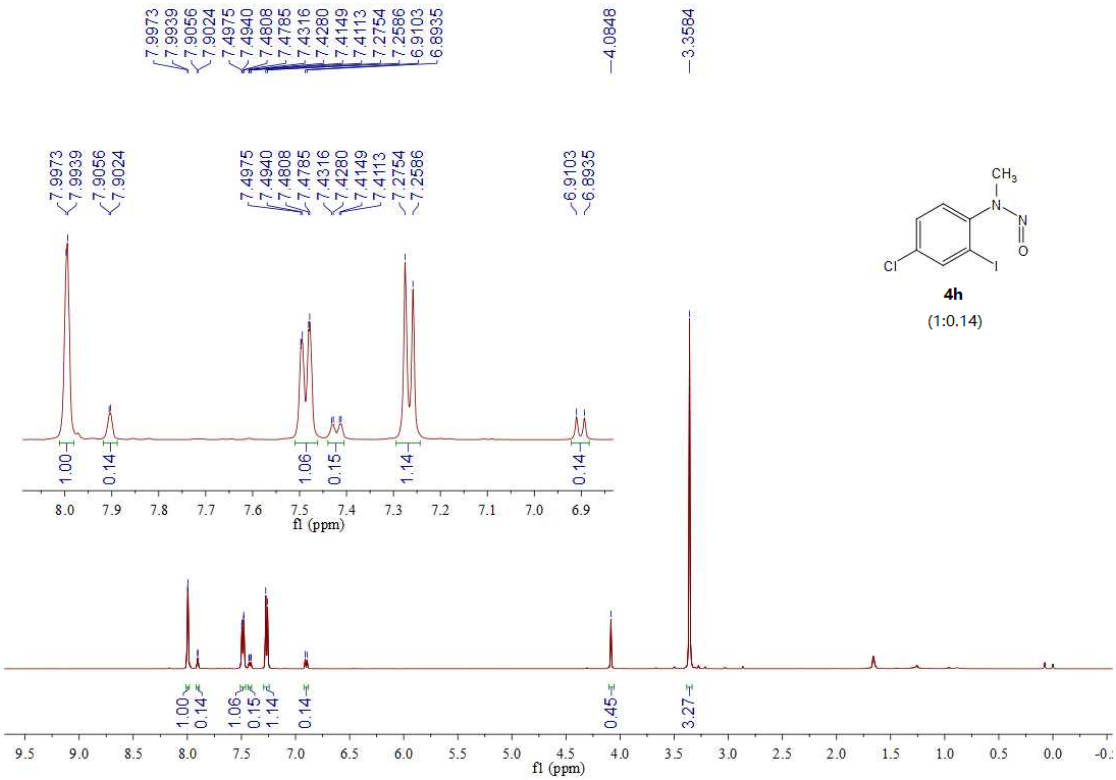

143.3930
141.2470
140.2813
139.9799
134.5856
133.7976
130.9605
130.9332
129.5953
129.4587
129.3035
129.0545
128.9170
128.8768
128.6569
128.6397
128.0357
96.6984
96.1392
57.2610
49.9149
130.9605
130.9332
129.5953
129.4587
129.3035
129.0545
128.9170
128.8768
128.6569
128.6397
128.0357
f1 (ppm)
4d
(1:0.44)

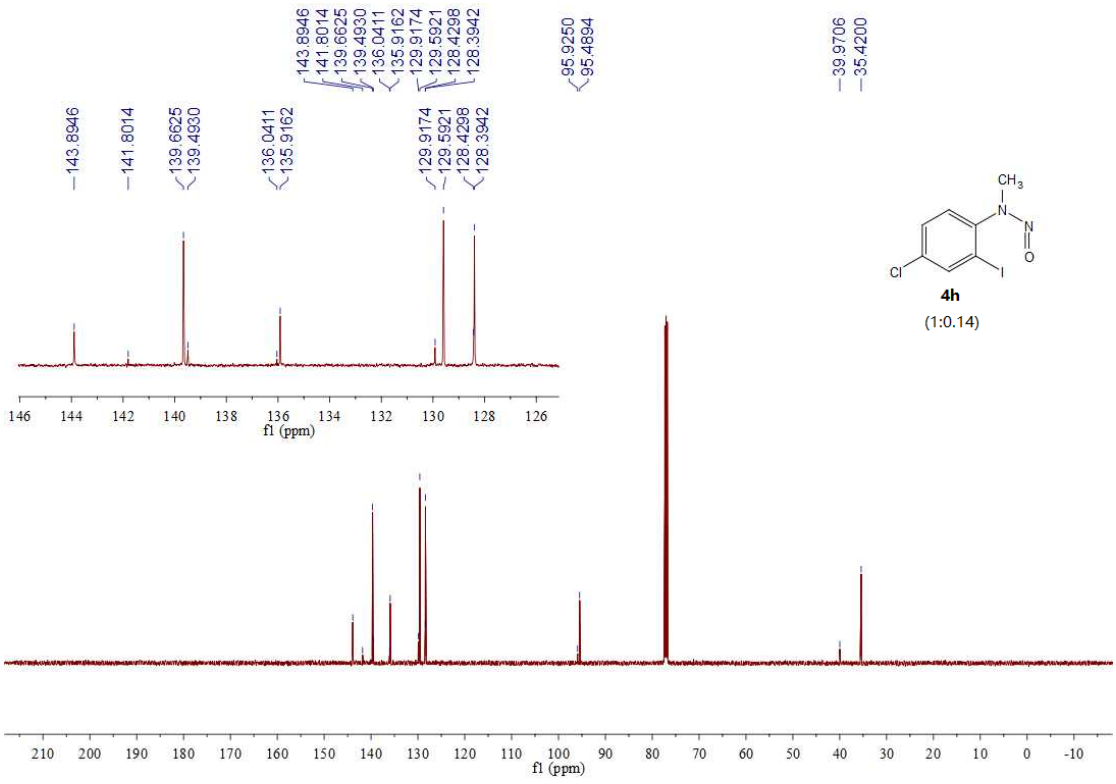

4e
(1:0.55)
f1 (ppm)

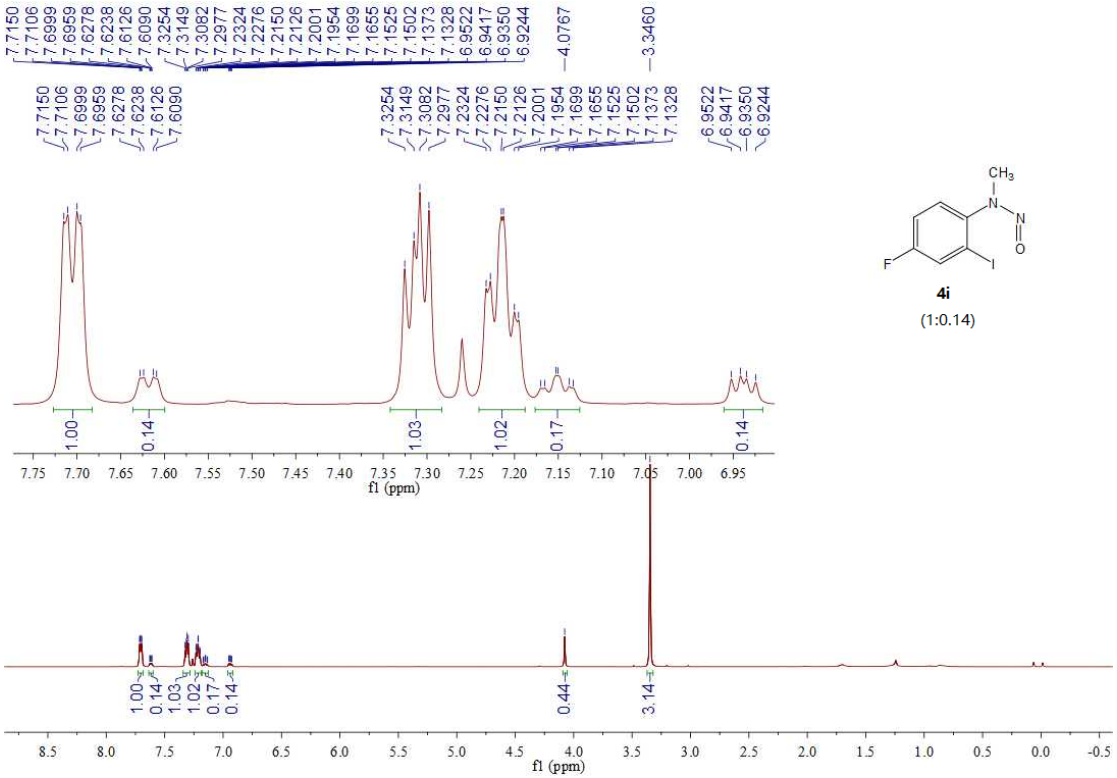

4e
(1:0.55)
f1 (ppm)


7.8140
7.7317
7.2898
7.2740
7.2346
7.2071
7.1912
6.8448
6.8289
4.0655
3.3504
2.3857
2.3298
1.00
0.12
1.06
1.17
0.12
0.41
3.11
3.17
0.41
fl (ppm)
4g
(1:0.12)


142.6734
141.4568
140.5884
140.4163
130.4392
130.0996
127.4748
127.1786
95.1199
95.0181
40.2267
35.6255
20.7346
20.6817
fl (ppm)
4g
(1:0.12)

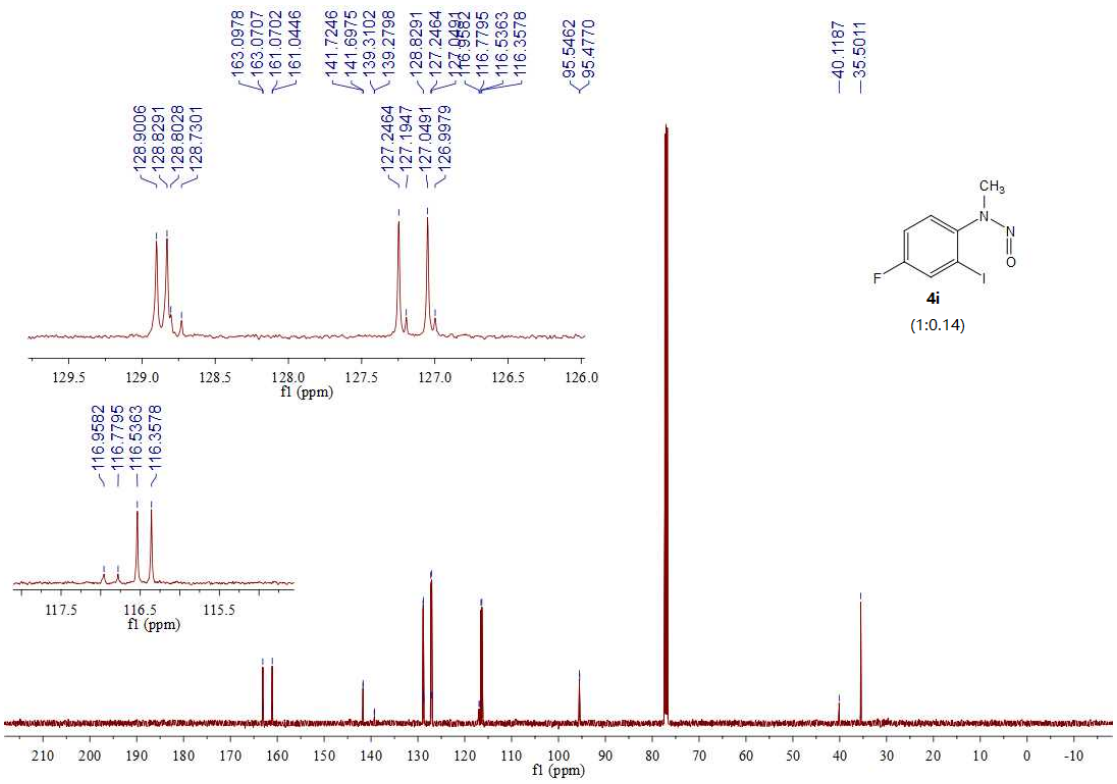

7.9973
7.9939
7.9056
7.9024
7.4975
7.4940
7.4808
7.4785
7.4316
7.4280
7.4149
7.4113
7.2754
7.2586
6.9103
6.8935
4.0848
3.3584
1.00
0.14
1.06
0.15
1.14
0.14
0.45
3.27
f1 (ppm)
CH3
N
N
O
Cl
I
4h
(1:0.14)


143.8946
141.8014
139.6625
139.4930
136.0411
135.9162
129.9174
129.5921
128.4298
128.3942
95.9250
95.4894
39.9706
35.4200
f1 (ppm)
CH3
N
N
O
Cl
I
4h
(1:0.14)



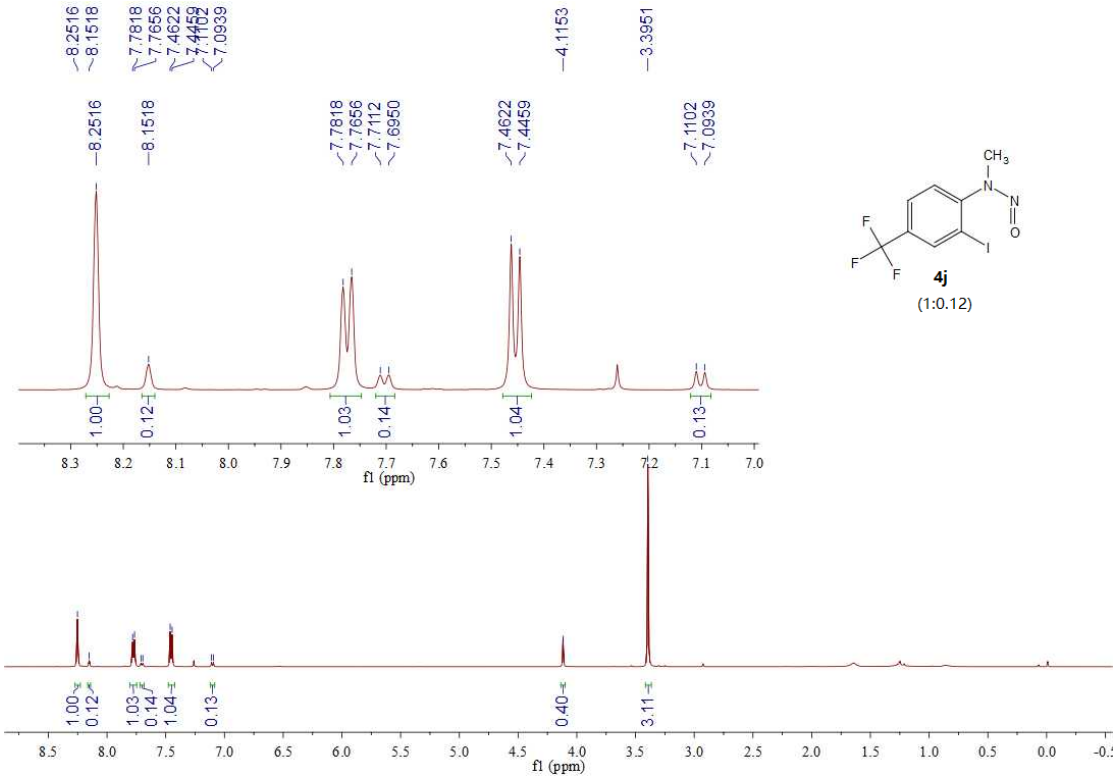
4i

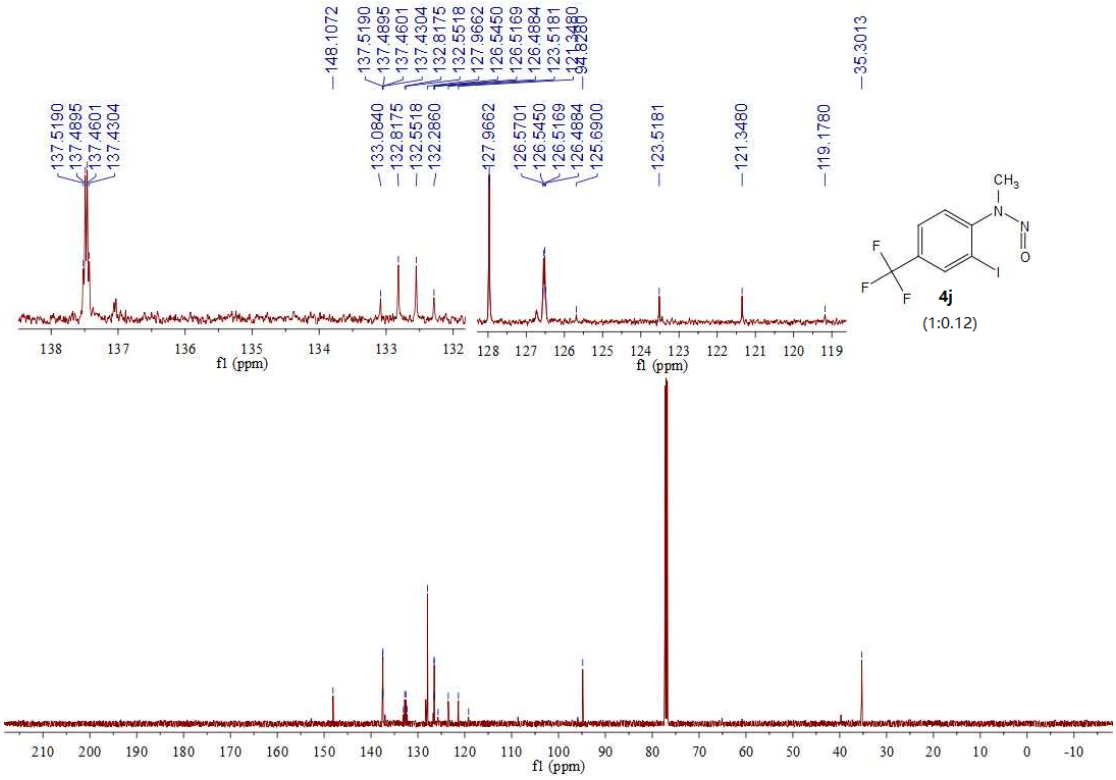
(1:0.14)

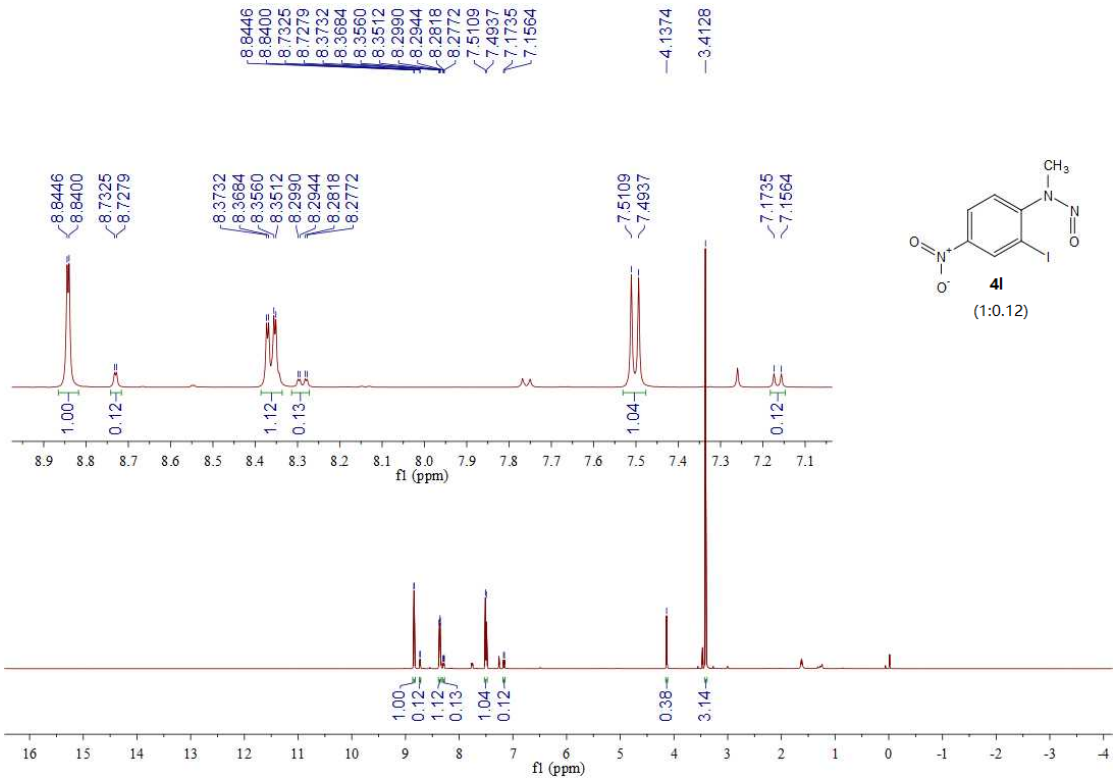


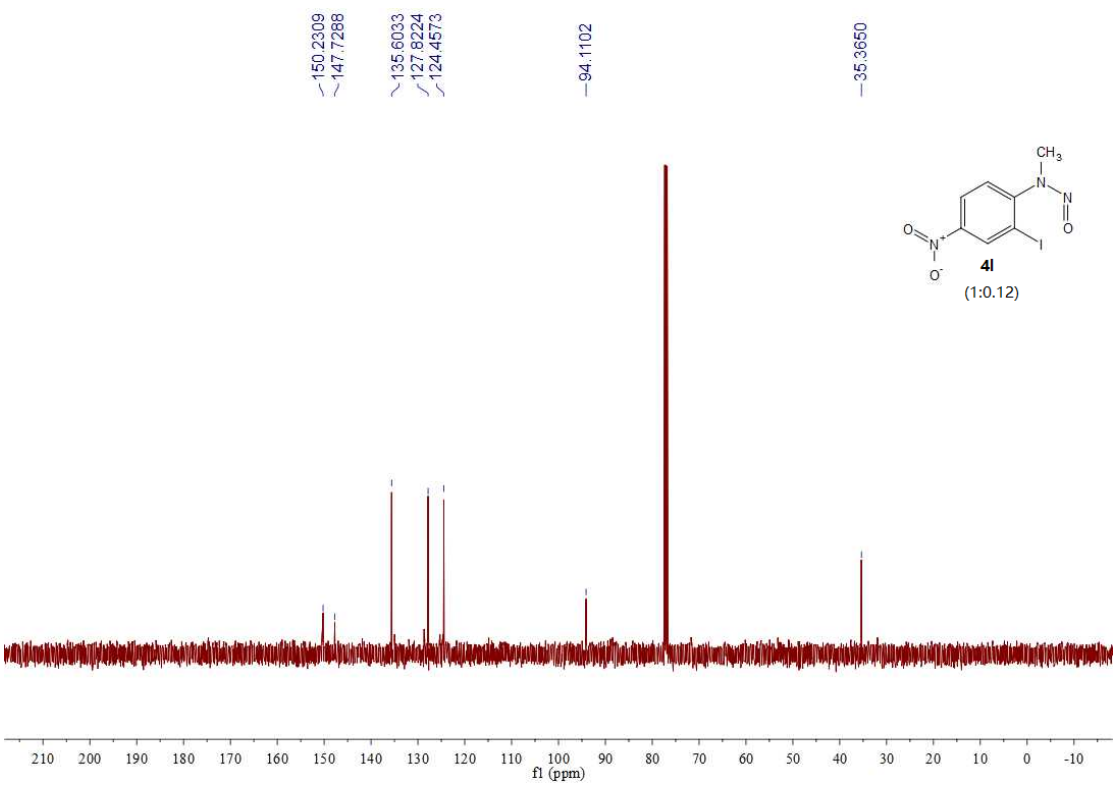
4i

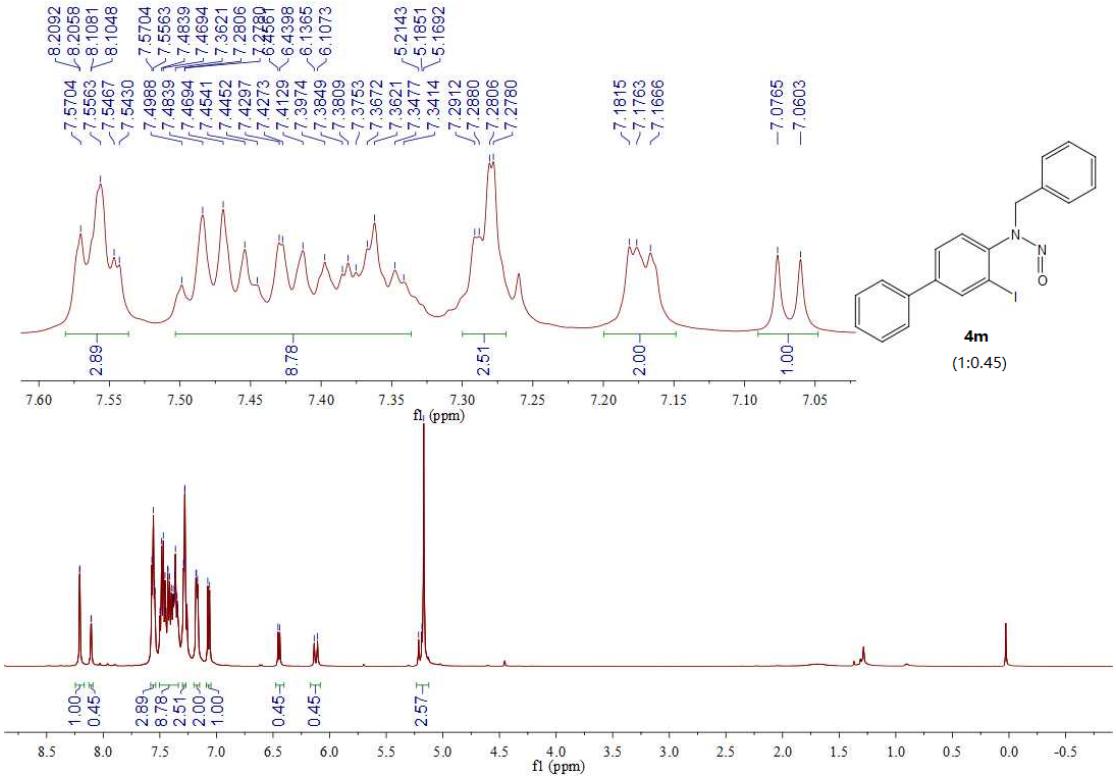
(1:0.14)

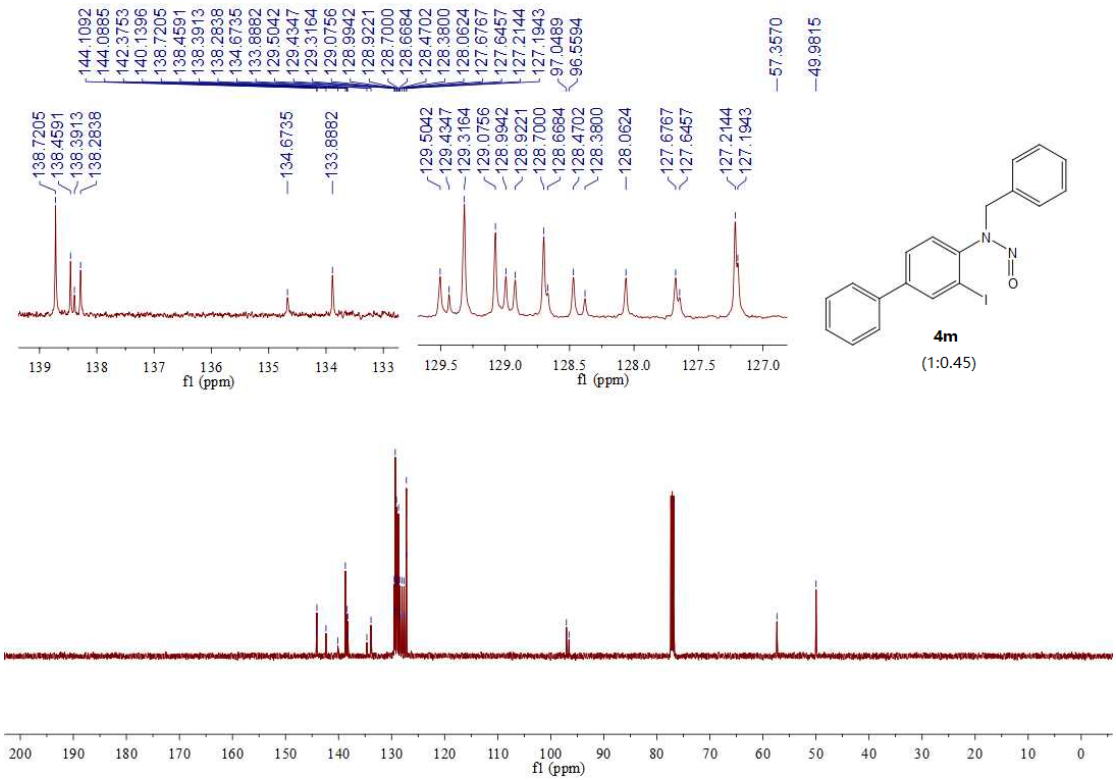

8.2516
8.1518
7.7818
7.7656
7.7112
7.6950
7.4622
7.4459
7.1102
7.0939
4.1153
3.3951
1.00
0.12
1.03
0.14
1.04
0.13
0.40
3.11
f1 (ppm)
4j
(1:0.12)

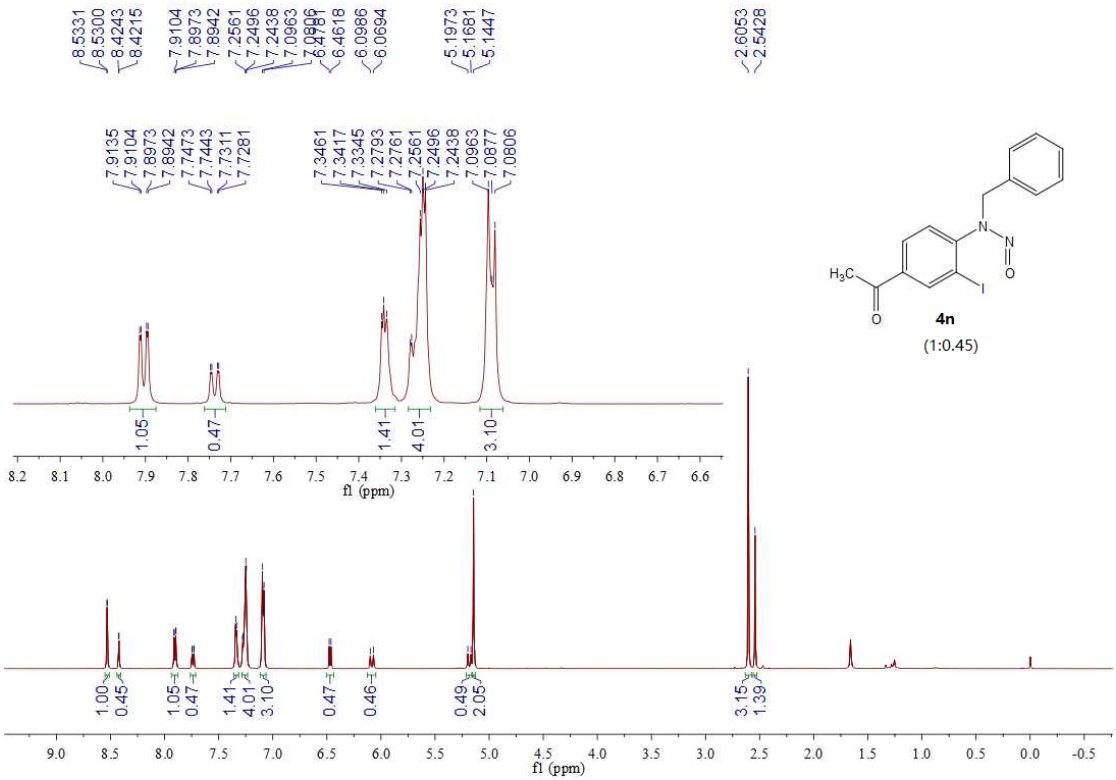

148.1072
137.5190
137.4895
137.4601
137.4304
132.8175
132.5518
132.2860
127.9662
126.5450
126.5169
126.4884
123.5181
121.3480
119.1780
35.3013
f1 (ppm)
4j
(1:0.12)

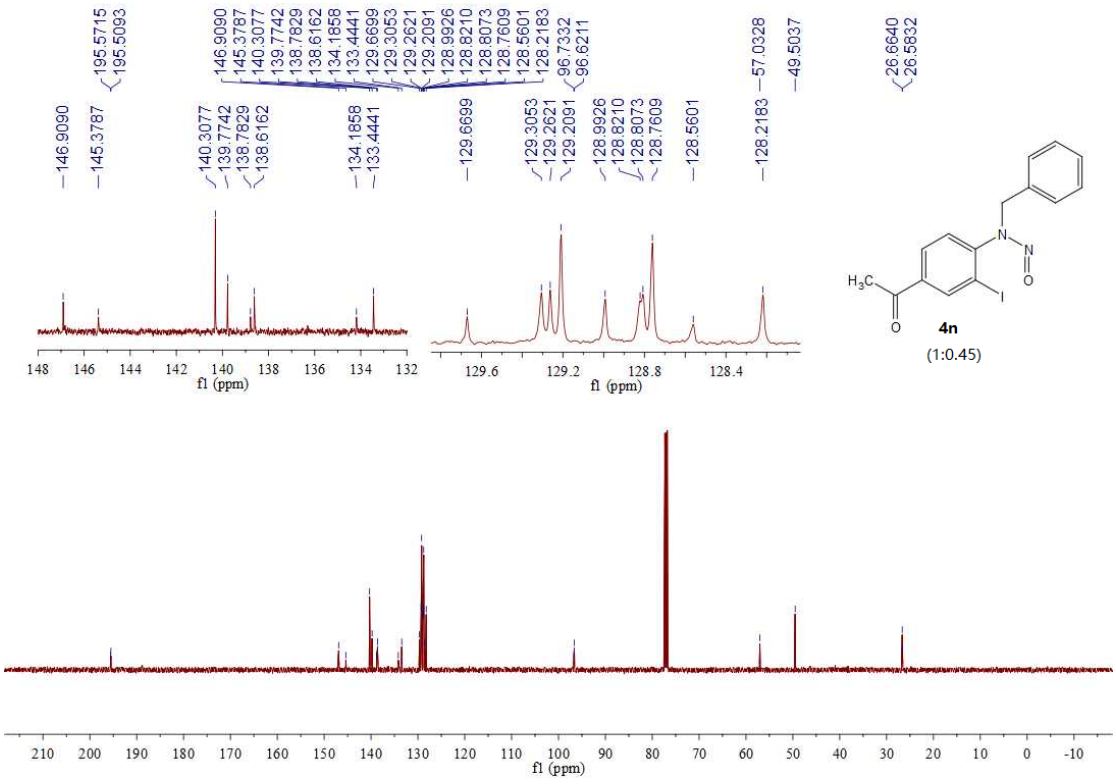

8.8446
8.8400
8.7325
8.7279
8.3732
8.3684
8.3560
8.3512
8.2990
8.2944
8.2818
8.2772
7.5109
7.4937
7.1735
7.1564
4.1374
3.4128
1.00
0.12
1.12
0.13
1.04
0.12
0.38
3.14
f1 (ppm)
4l
(1:0.12)

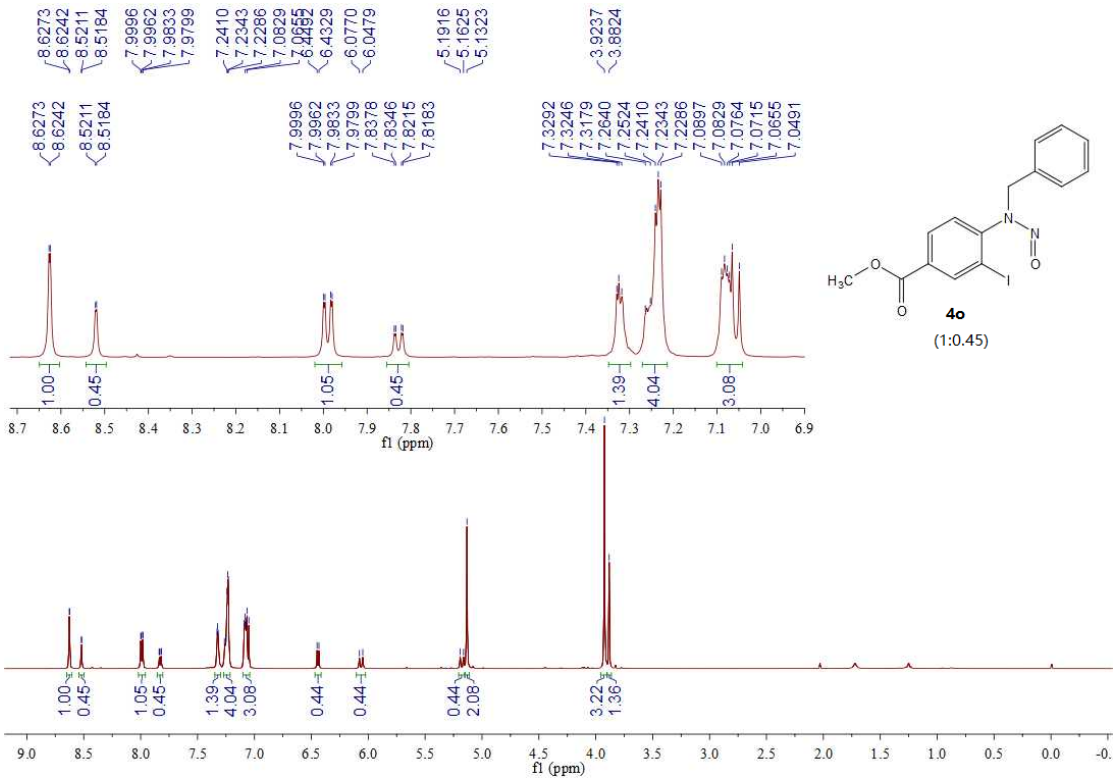

150.2309
147.7288
135.6033
127.8224
124.4573
94.1102
35.3650
f1 (ppm)
4l
(1:0.12)

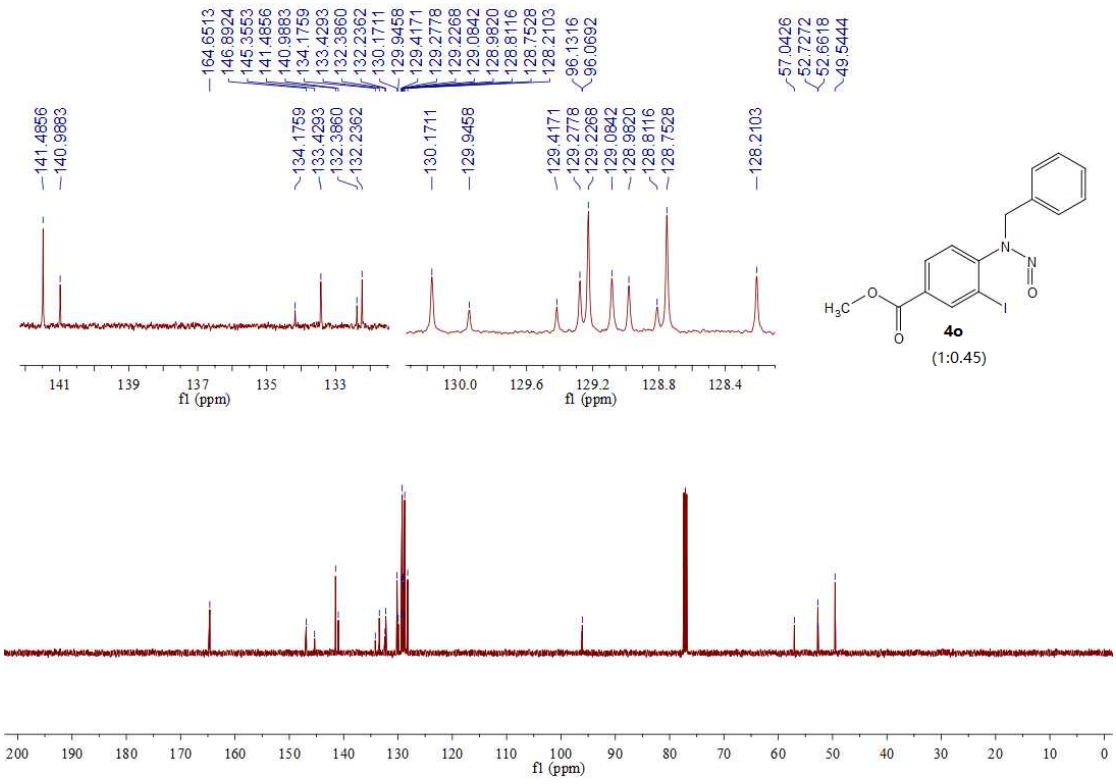

4m
(1:0.45)
f1 (ppm)

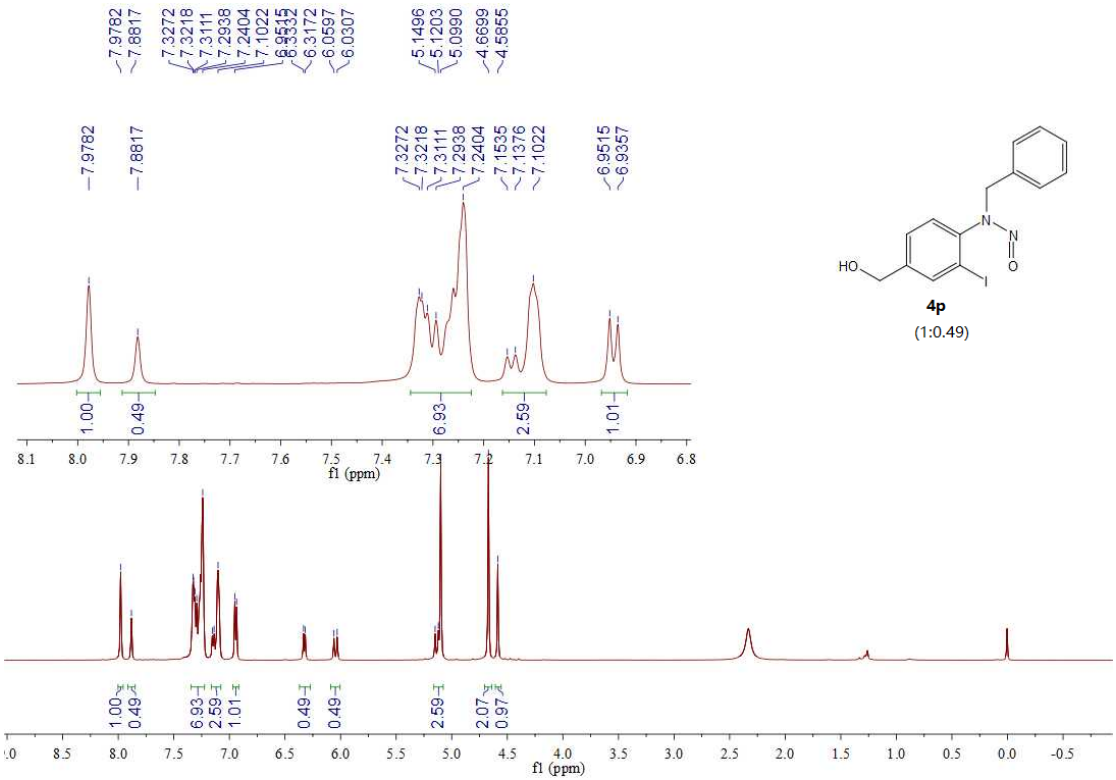

4m
(1:0.45)
f1 (ppm)

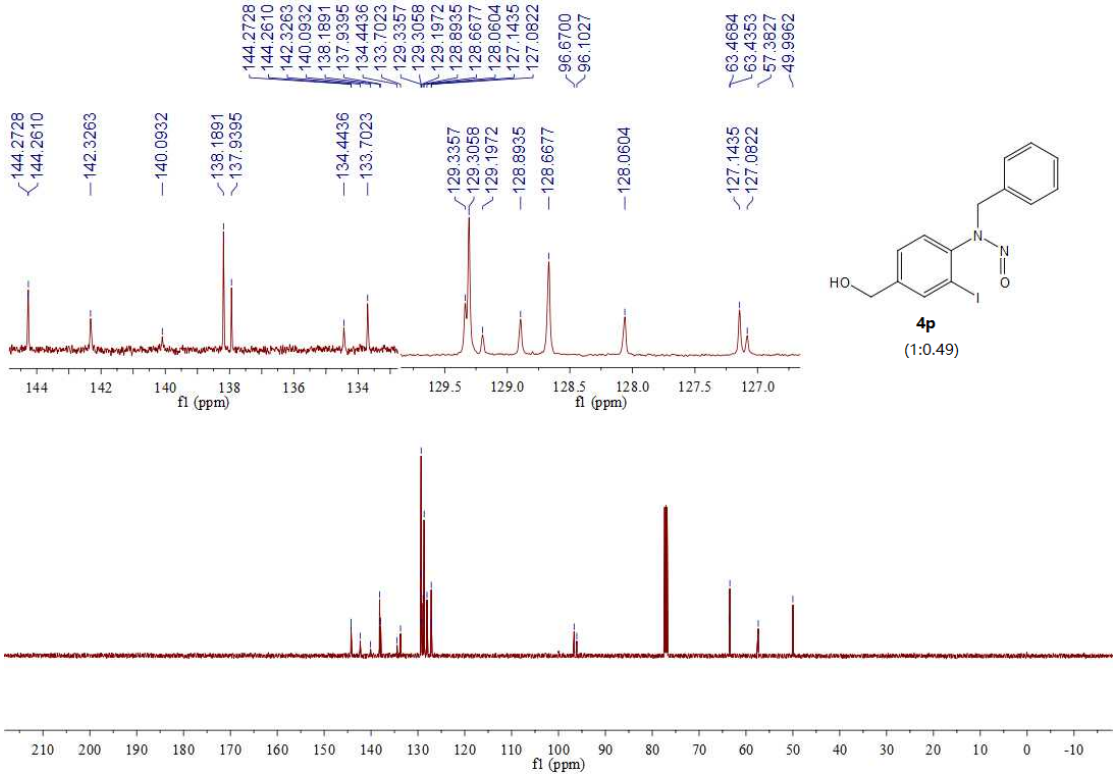

8.5331
8.5300
8.4243
8.4215
7.9104
7.8973
7.8942
7.2561
7.2496
7.2438
7.0963
6.4618
6.0986
6.0694
5.1973
5.1681
5.1447
2.6053
2.5428
1.05
0.47
1.41
4.01
3.10
1.00
0.45
1.05
0.47
1.41
4.01
3.10
0.47
0.46
0.49
2.05
3.15
1.39
f1 (ppm)
4n
(1:0.45)

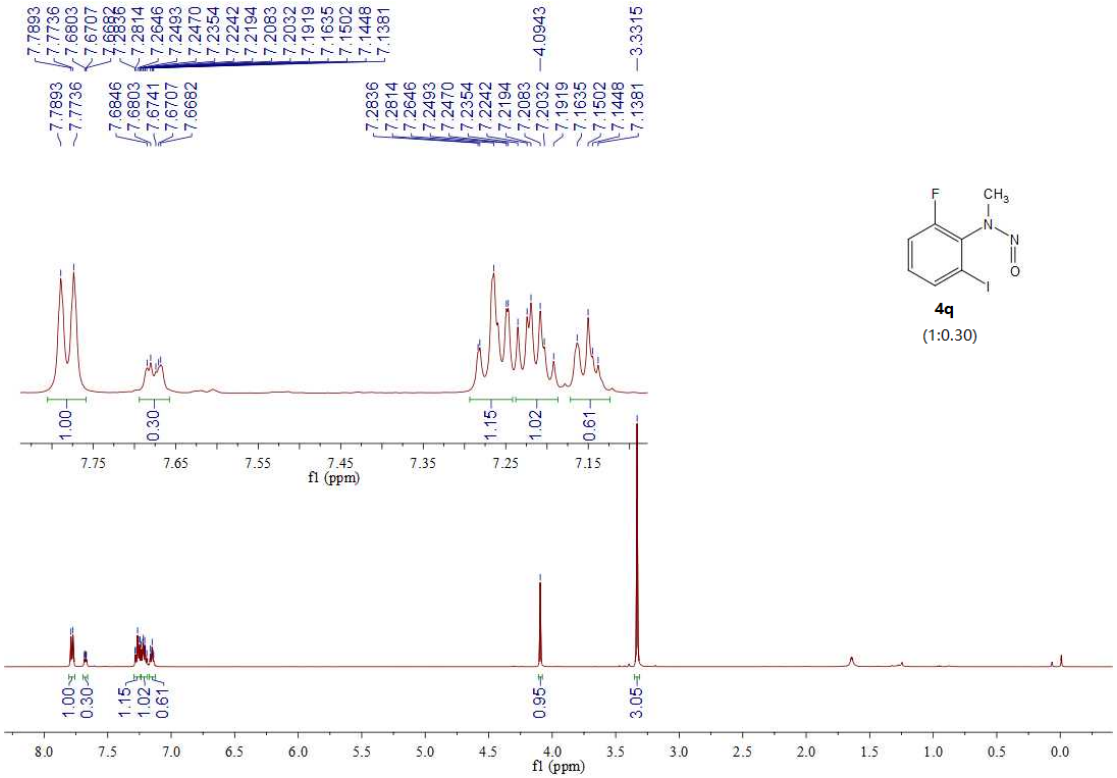

195.5715
195.5093
146.9090
145.3787
140.3077
139.7742
138.7829
138.6162
134.1858
133.4441
129.6699
129.3053
129.2621
129.2091
128.9926
128.8210
128.8073
128.7609
128.5601
128.2183
96.7332
96.6211
57.0328
49.5037
26.6640
26.5832
f1 (ppm)
4n
(1:0.45)

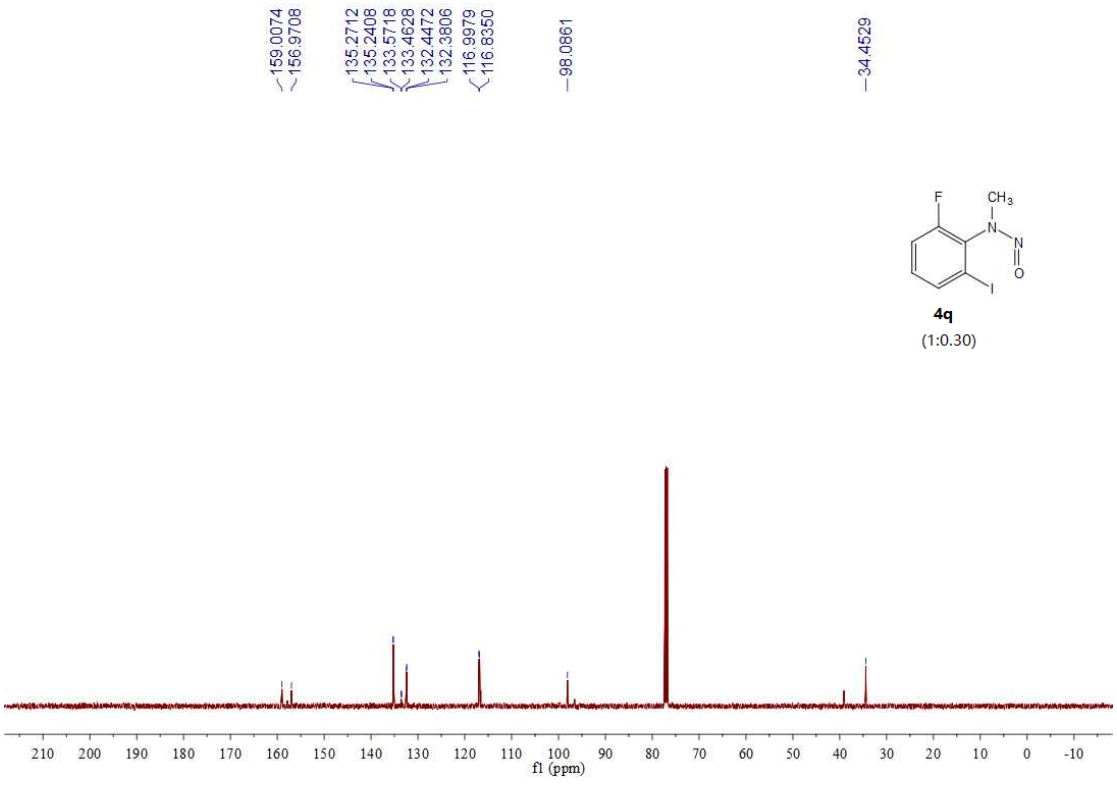

8.6273
8.6242
8.5211
8.5184
7.9996
7.9962
7.9833
7.9799
7.2410
7.2343
7.2286
7.0829
6.4329
6.0770
6.0479
5.1916
5.1625
5.1323
3.9237
3.8824
7.8378
7.8346
7.8215
7.8183
7.3292
7.3246
7.3179
7.2640
7.2524
7.0897
7.0764
7.0715
7.0655
7.0491
1.00
0.45
1.05
0.45
1.39
4.04
3.08
0.44
0.44
0.44
2.08
3.22
1.36
fl (ppm)
4o
(1:0.45)

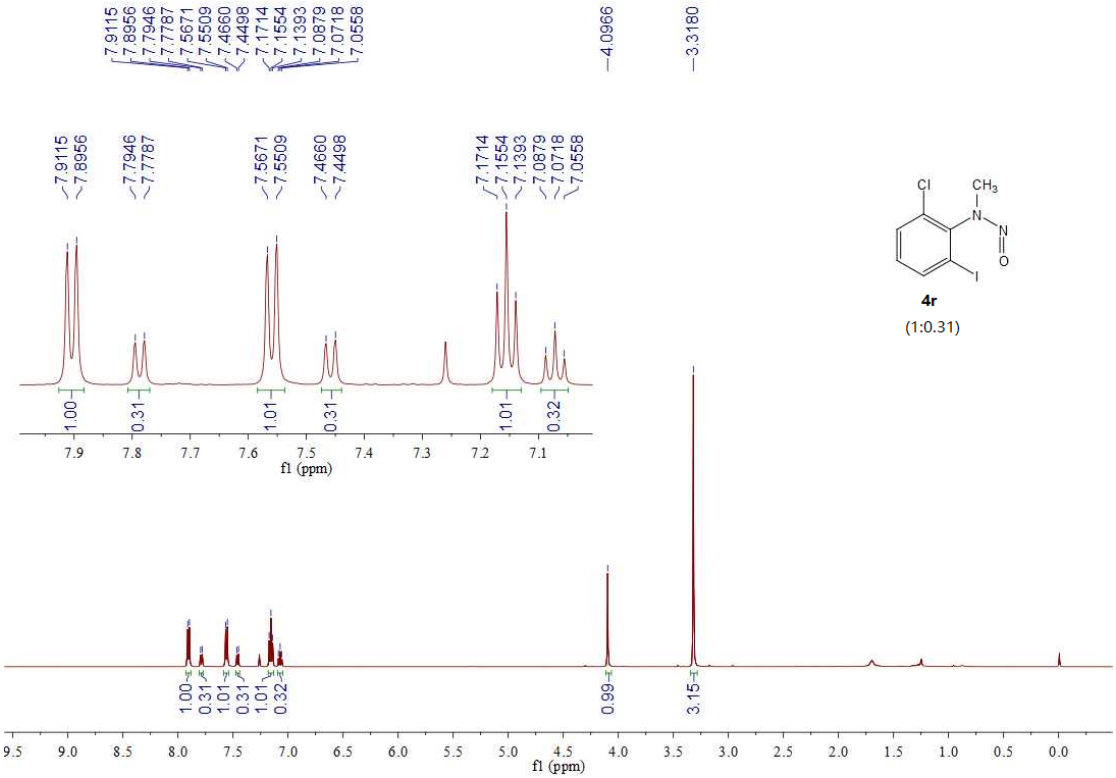

164.6513
146.8924
145.3553
141.4856
140.9883
134.1759
133.4293
132.3860
132.2362
130.1711
129.9458
129.4171
129.2778
129.2268
129.0842
128.9820
128.8116
128.7528
128.2103
96.1316
96.0692
57.0426
52.7272
52.6618
49.5444
fl (ppm)
4o
(1:0.45)

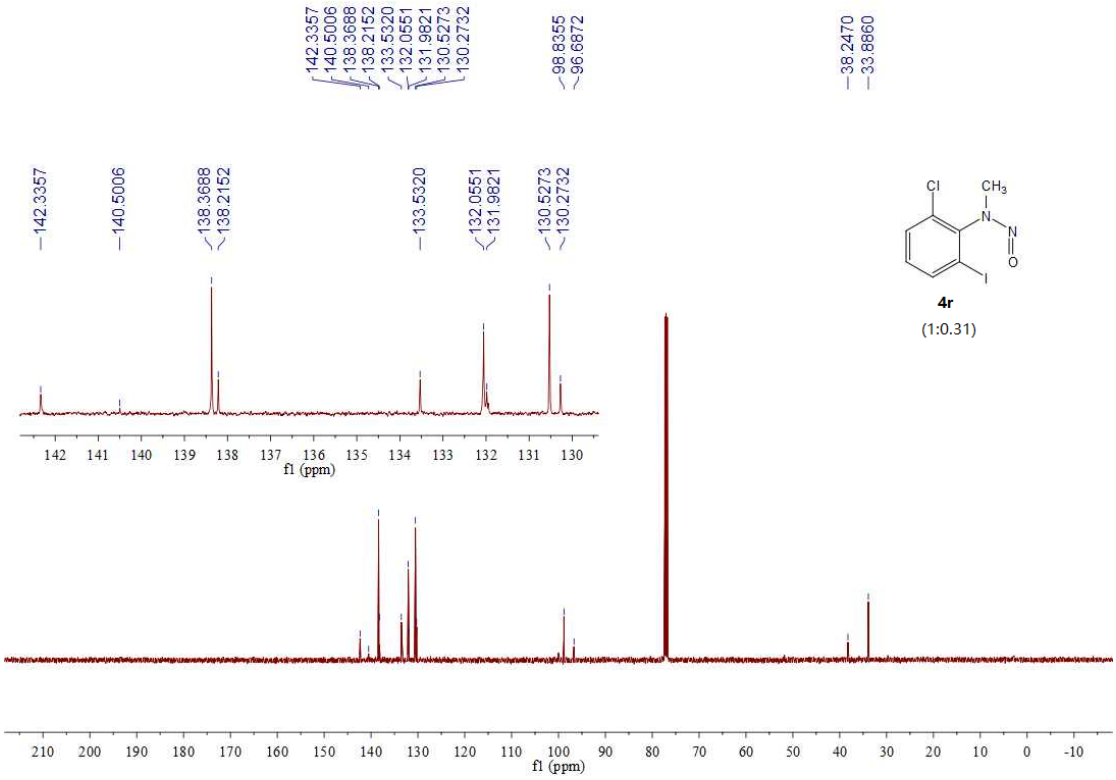

7.9782
7.8817
7.3272
7.3218
7.3111
7.2938
7.2404
7.1022
6.9515
6.9357
6.3172
6.0597
6.0307
5.1496
5.1203
5.0990
4.6699
4.5855
1.00
0.49
6.93
2.59
1.01
f1 (ppm)
HO
N
N
O
I
4p
(1:0.49)

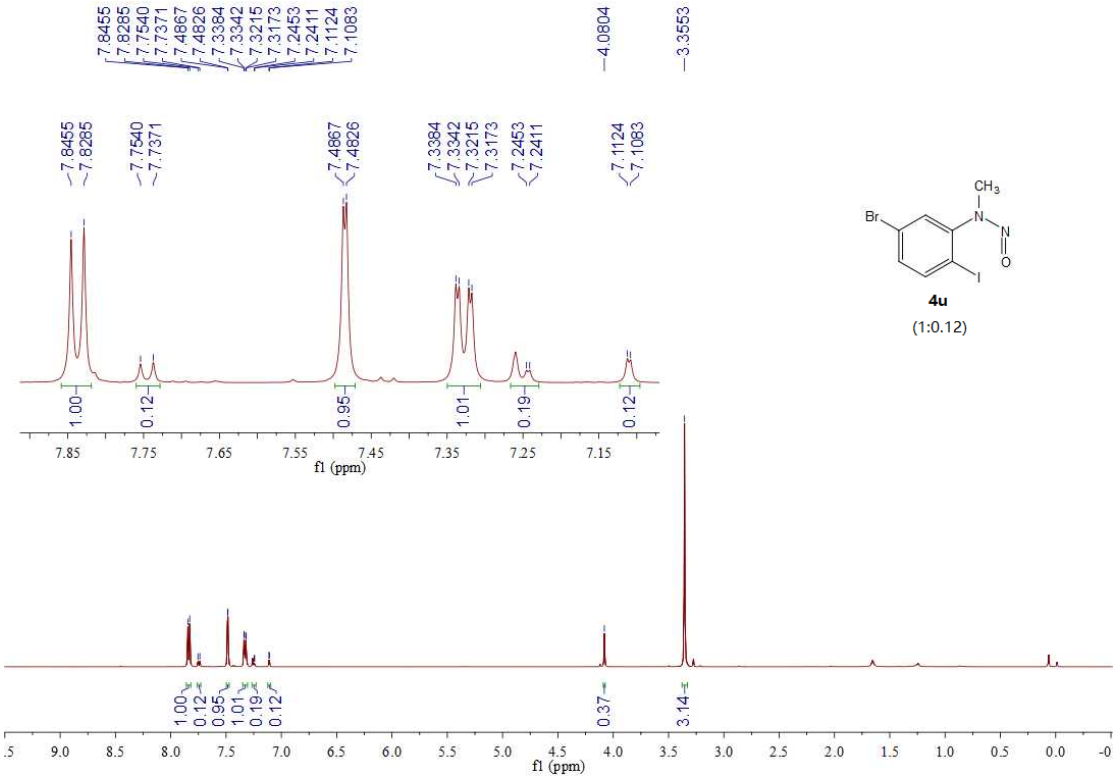

144.2728
144.2610
142.3263
140.0932
138.1891
137.9395
134.4436
133.7023
129.3357
129.3058
129.1972
128.8935
128.6677
128.0604
127.1435
127.0822
96.6700
96.1027
63.4684
63.4353
57.3827
49.9962
f1 (ppm)
HO
N
N
O
I
4p
(1:0.49)

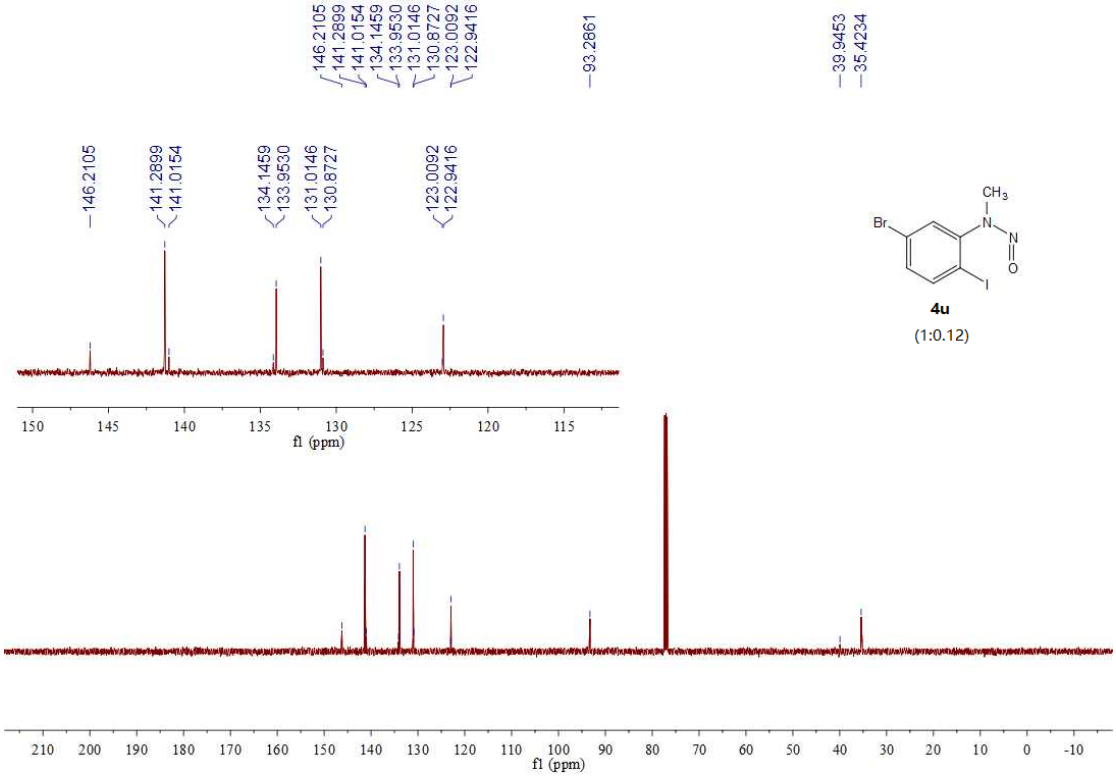

7.7893
7.7736
7.6803
7.6707
7.6682
7.2814
7.2646
7.2493
7.2470
7.2354
7.2242
7.2194
7.2083
7.2032
7.1919
7.1635
7.1502
7.1448
7.1381
4.0943
3.3315
F
CH3
N
N
O
I
4q
(1:0.30)
1.00
0.30
1.15
1.02
0.61
0.95
3.05
f1 (ppm)

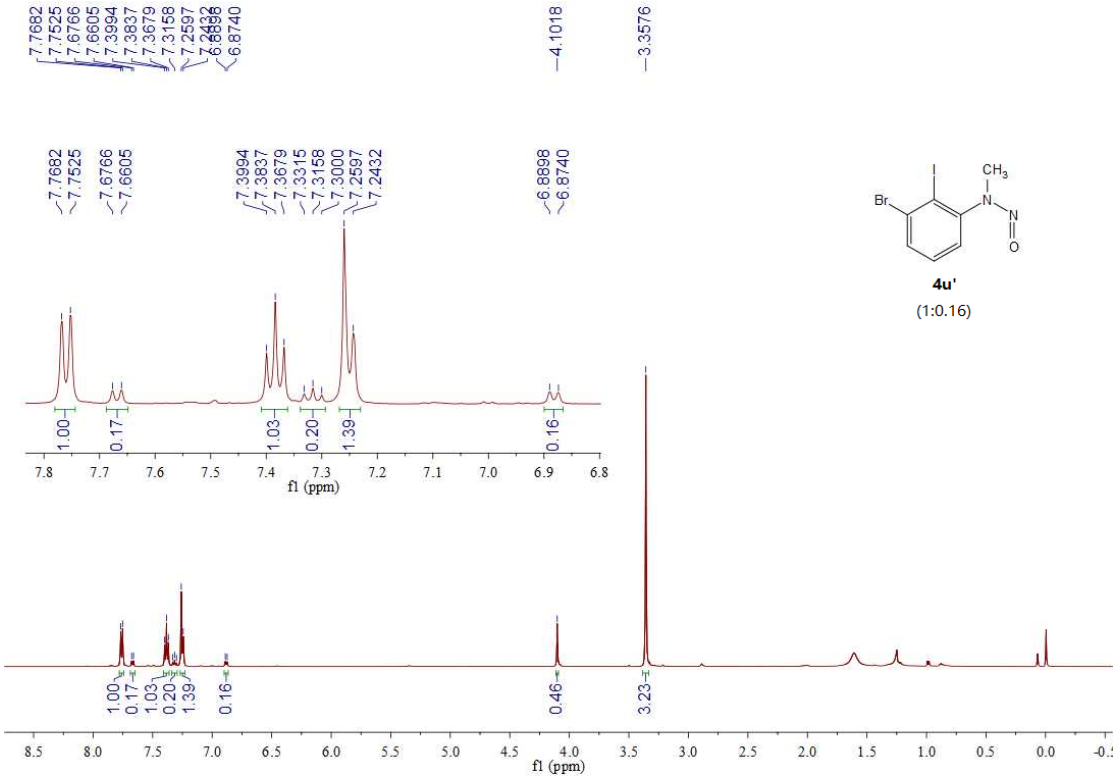

159.0074
156.9708
135.2712
135.2408
133.5718
133.4628
132.4472
132.3806
116.9979
116.8350
98.0861
34.4529
F
CH3
N
N
O
I
4q
(1:0.30)
f1 (ppm)

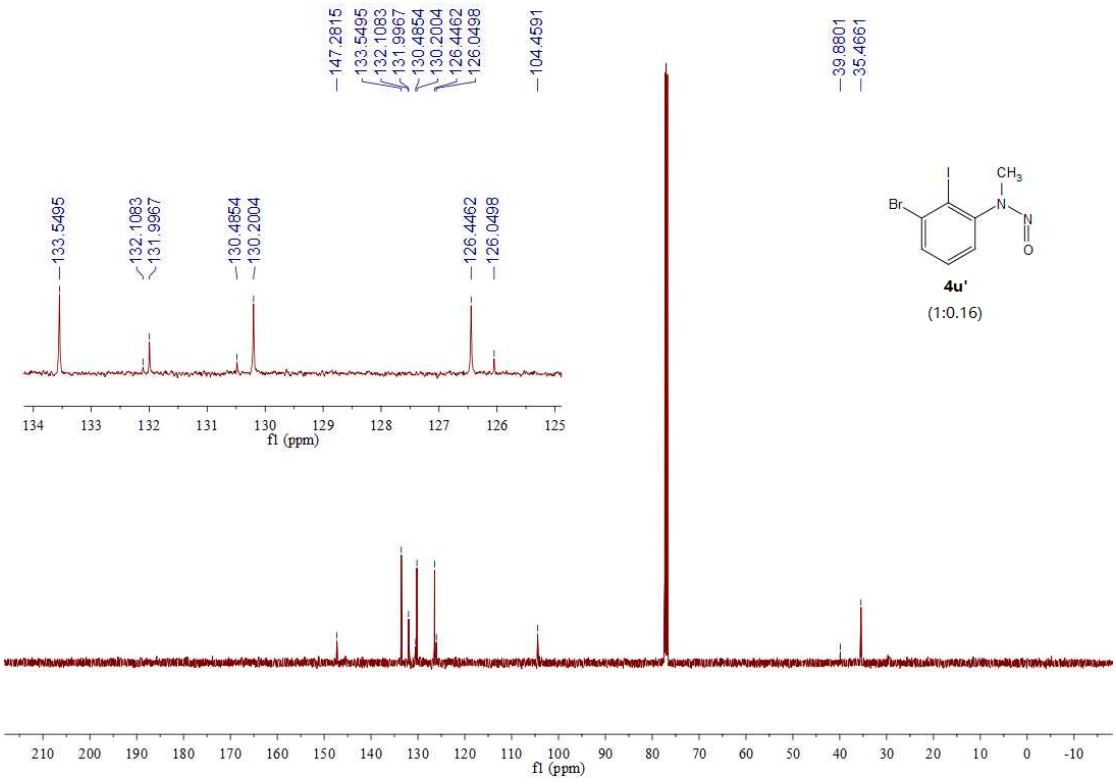

7.9115
7.8956
7.7946
7.7787
7.5671
7.5509
7.4660
7.4498
7.1714
7.1554
7.1393
7.0879
7.0718
7.0558
4.0966
3.3180
Cl
CH3
N
N
O
I
4r
(1:0.31)
1.00
0.31
1.01
0.31
1.01
0.32
0.99
3.15
f1 (ppm)

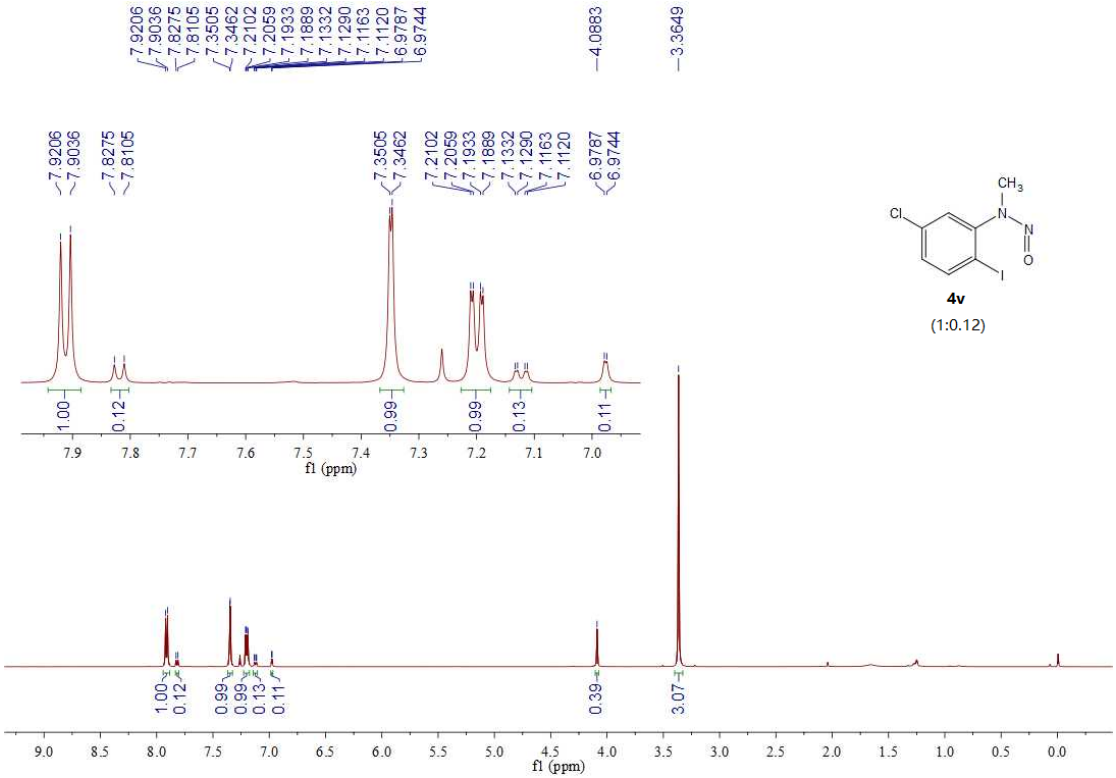

142.3357
140.5006
138.3688
138.2152
133.5320
132.0551
131.9821
130.5273
130.2732
98.8355
96.6872
38.2470
33.8860
Cl
CH3
N
N
O
I
4r
(1:0.31)
f1 (ppm)

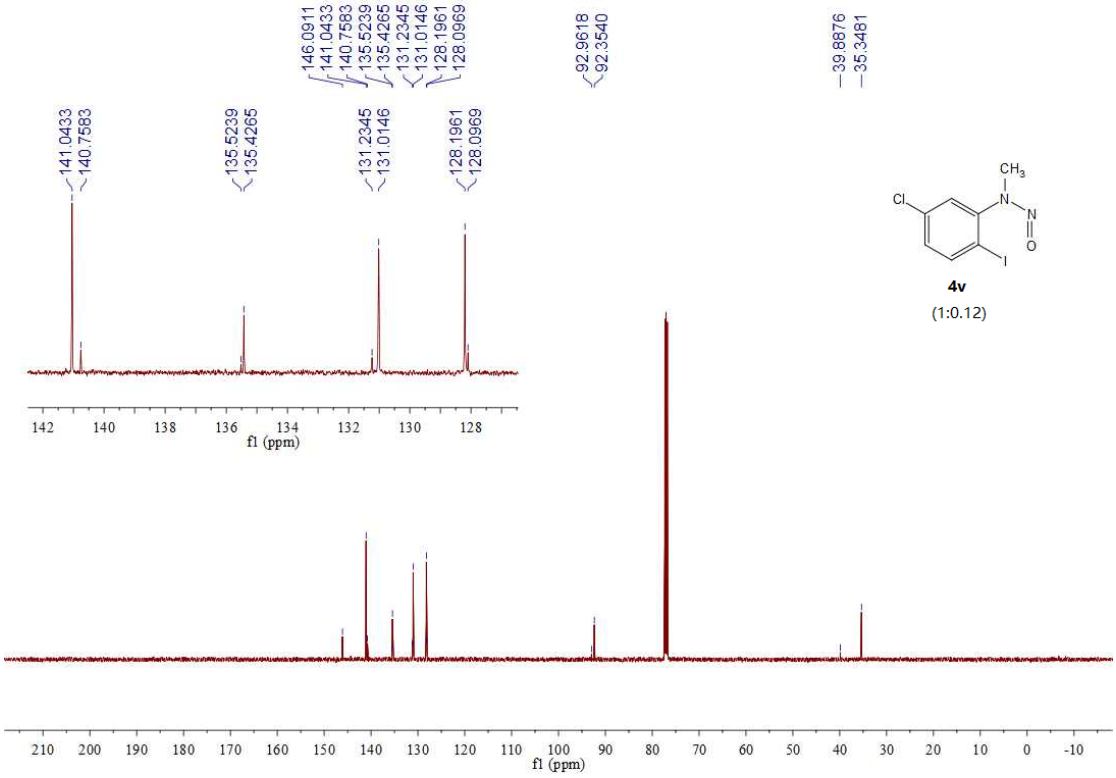

7.8455
7.8285
7.7540
7.7371
7.4867
7.4826
7.3384
7.3342
7.3215
7.3173
7.2453
7.2411
7.1124
7.1083
4.0804
3.3553
1.00
0.12
0.95
1.01
0.19
0.12
0.37
3.14
f1 (ppm)
Br
CH3
N
N
O
I
4u
(1:0.12)

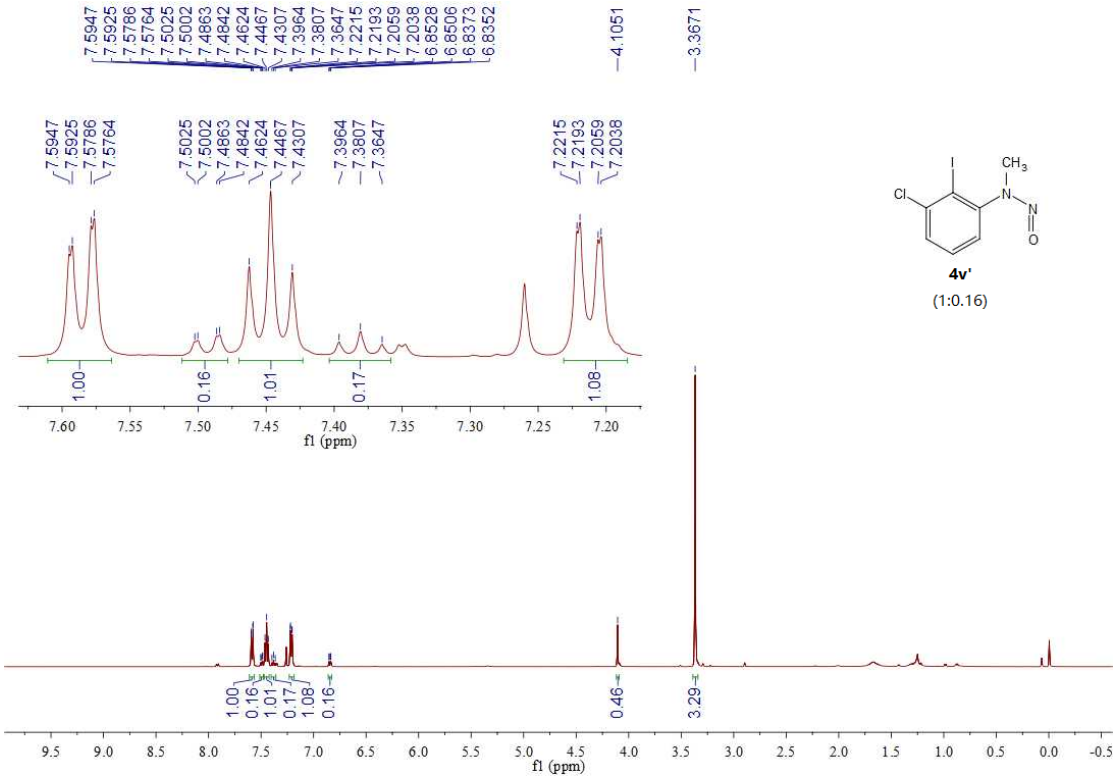

146.2105
141.2899
141.0154
134.1459
133.9530
131.0146
130.8727
123.0092
122.9416
93.2861
39.9453
35.4234
f1 (ppm)
Br
CH3
N
N
O
I
4u
(1:0.12)

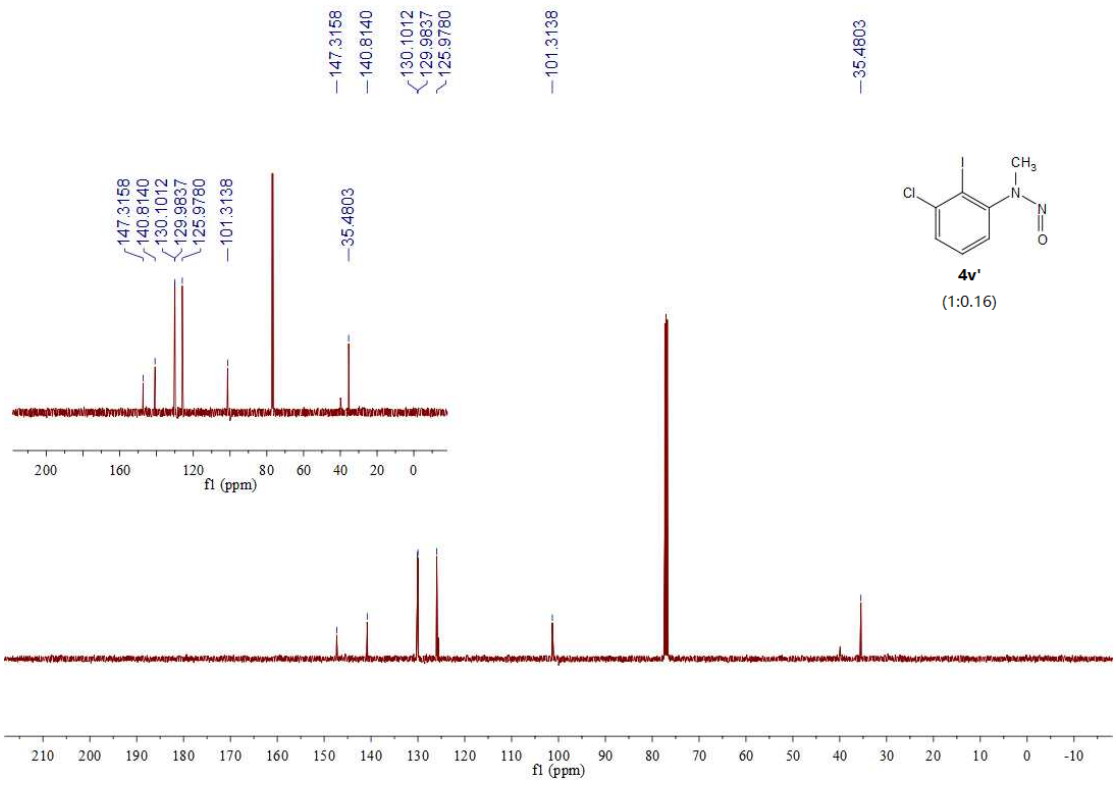

7.7682
7.7525
7.6766
7.6605
7.3994
7.3837
7.3679
7.3315
7.3158
7.3000
7.2597
7.2432
6.8898
6.8740
4.1018
3.3576
1.00
0.17
1.03
0.20
1.39
0.16
0.46
3.23
f1 (ppm)
Br
I
CH3
N
N
O
4u'
(1:0.16)

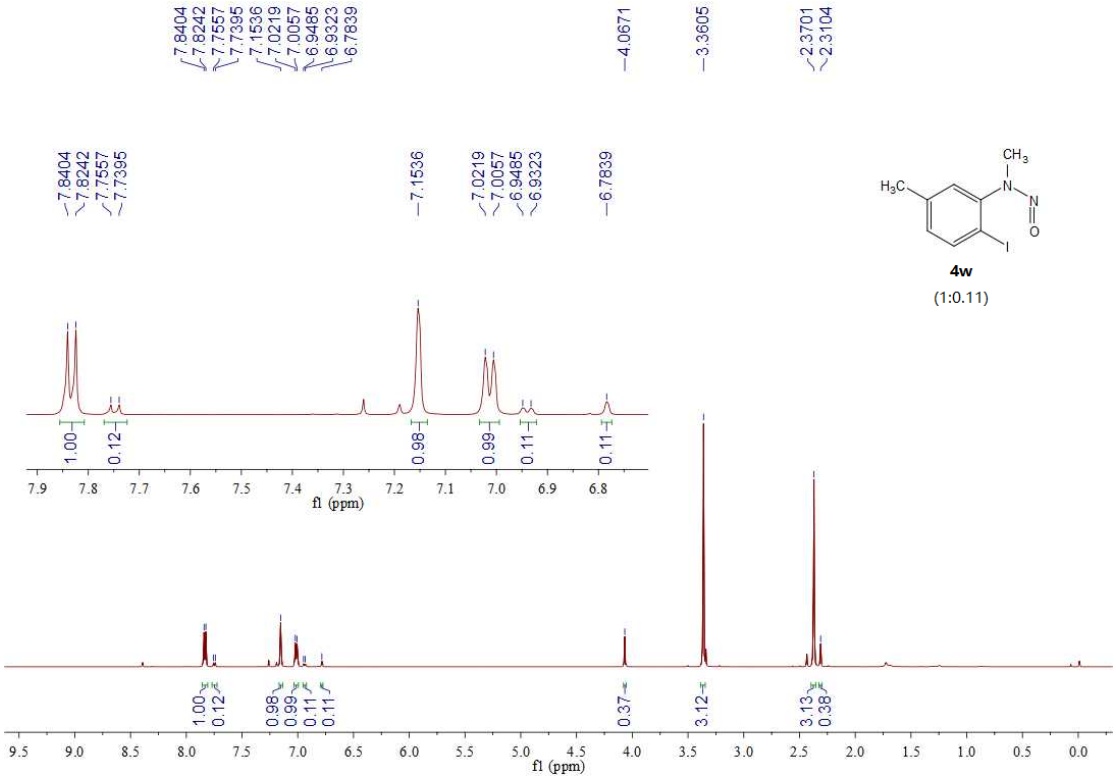

147.2815
133.5495
132.1083
131.9967
130.4854
130.2004
126.4462
126.0498
104.4591
39.8801
35.4661
f1 (ppm)
Br
I
CH3
N
N
O
4u'
(1:0.16)

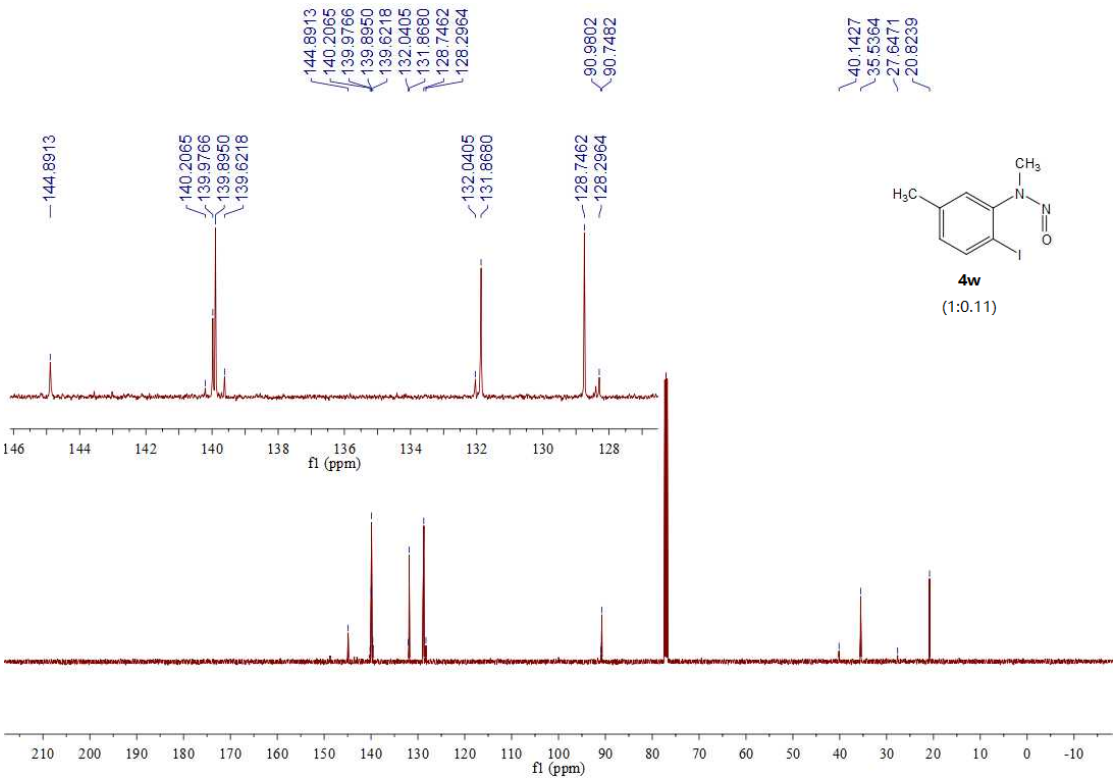

7.9206
7.9036
7.8275
7.8105
7.3505
7.3462
7.2102
7.2059
7.1933
7.1889
7.1332
7.1290
7.1163
7.1120
6.9787
6.9744
4.0883
3.3649
1.00
0.12
0.99
0.99
0.13
0.11
0.39
3.07
f1 (ppm)
4v
(1:0.12)

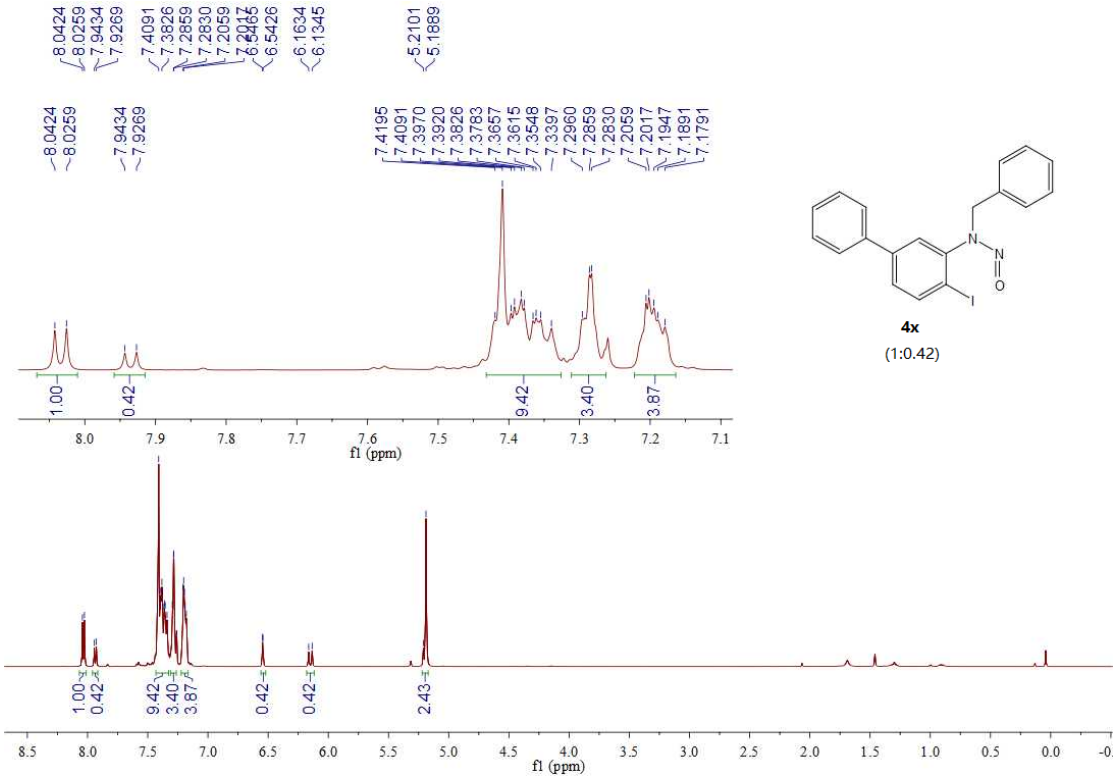

146.0911
141.0433
140.7583
135.5239
135.4265
131.2345
131.0146
128.1961
128.0969
92.9618
92.3540
39.8876
35.3481
f1 (ppm)
4v
(1:0.12)

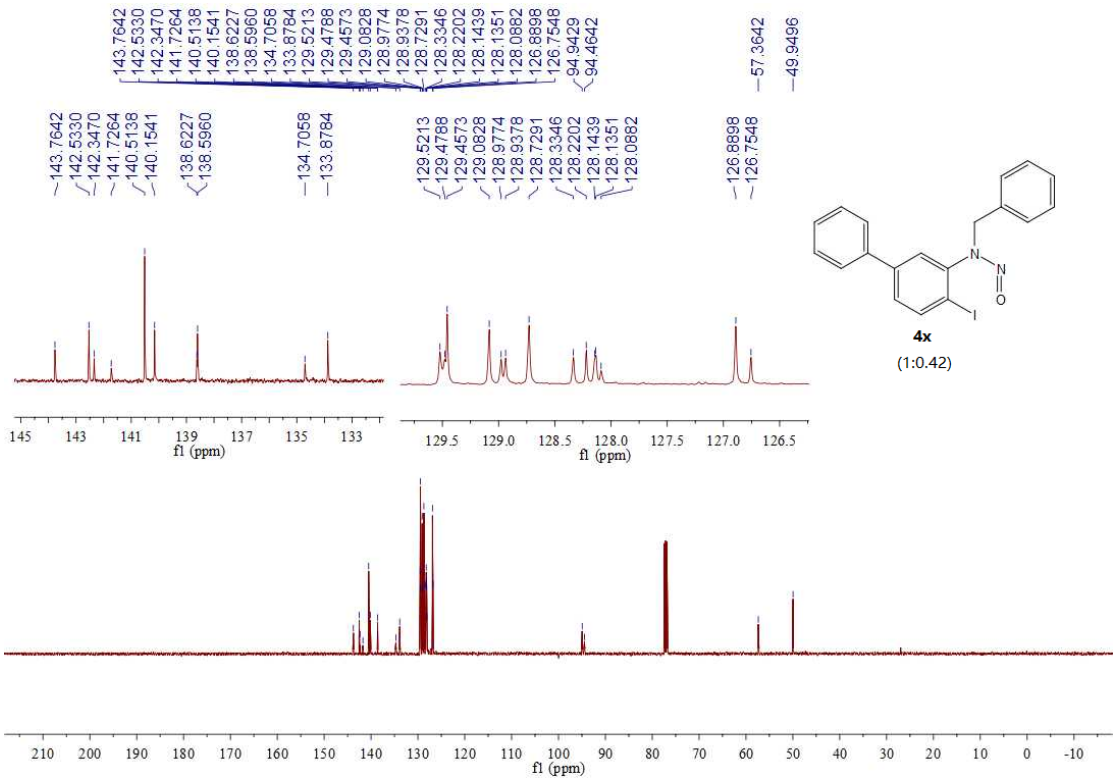

7.5947
7.5925
7.5786
7.5764
7.5025
7.5002
7.4863
7.4842
7.4624
7.4467
7.4307
7.3964
7.3807
7.3647
7.2215
7.2193
7.2059
7.2038
6.8528
6.8506
6.8373
6.8352
4.1051
3.3671
1.00
0.16
1.01
0.17
1.08
0.46
3.29
f1 (ppm)
4v'
(1:0.16)

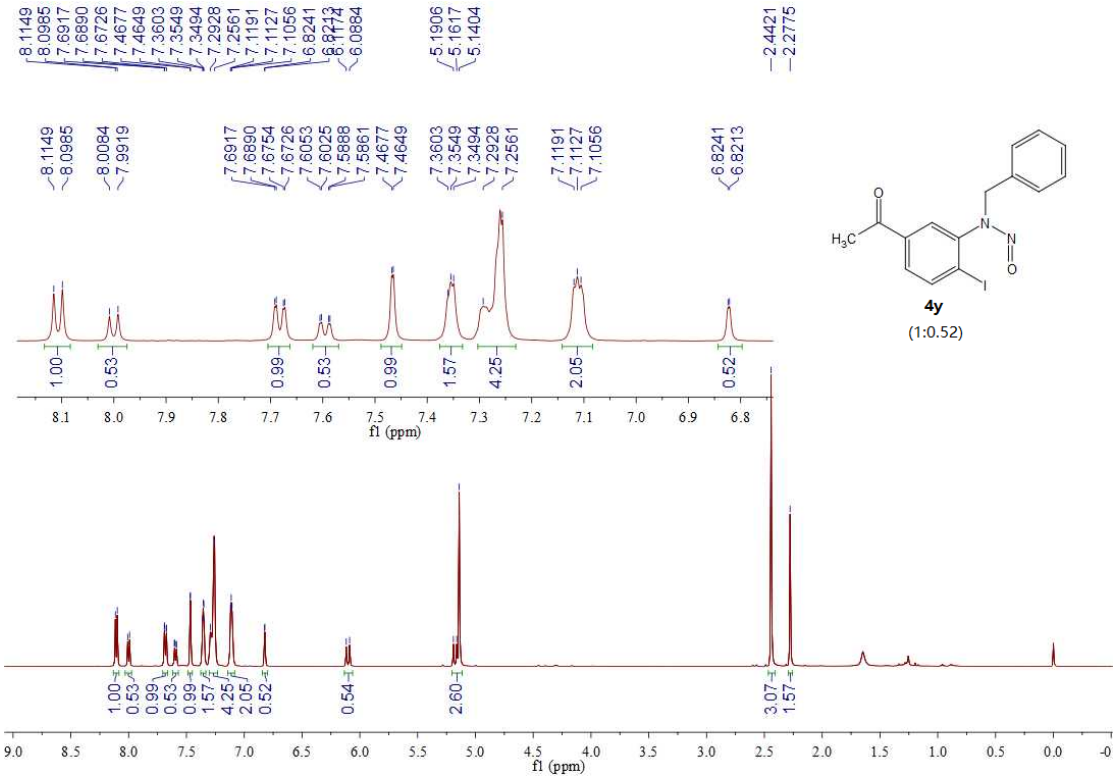

147.3158
140.8140
130.1012
129.9837
125.9780
101.3138
35.4803
f1 (ppm)
4v'
(1:0.16)

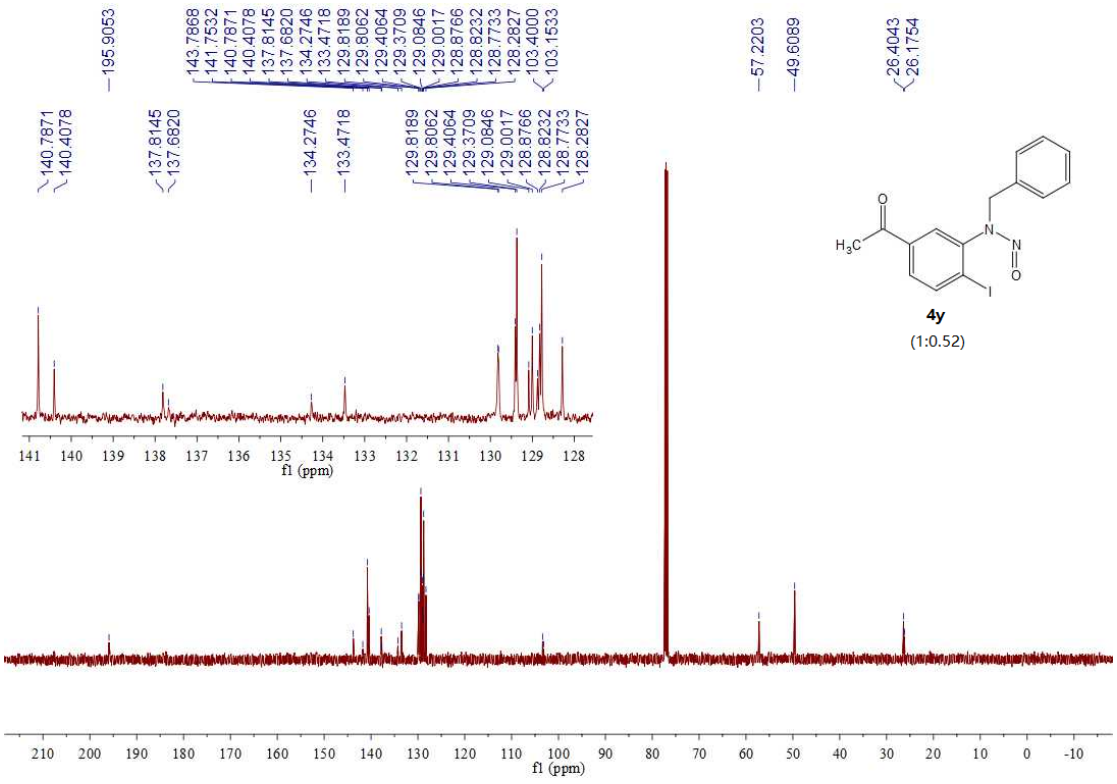

7.8404
7.8242
7.7557
7.7395
7.1536
7.0219
7.0057
6.9485
6.9323
6.7839
4.0671
3.3605
2.3701
2.3104
4w
(1:0.11)
fl (ppm)

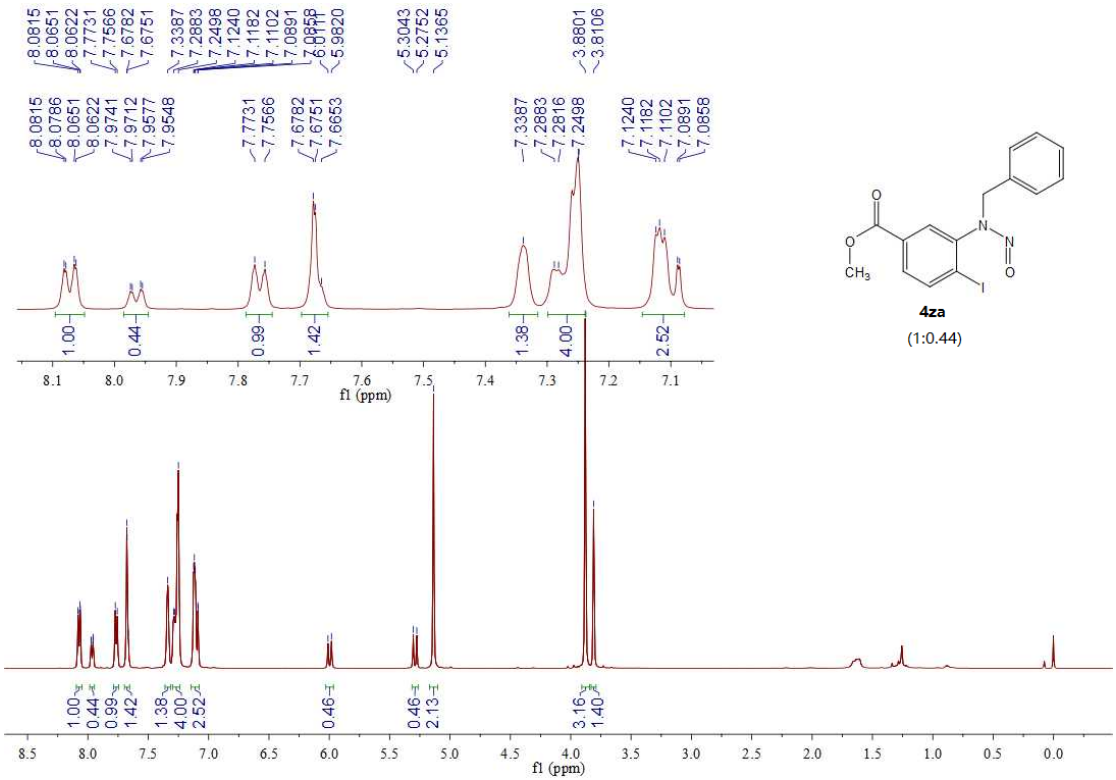

144.8913
140.2065
139.9766
139.8950
139.6218
132.0405
131.8680
128.7462
128.2964
90.9802
90.7482
40.1427
35.5364
27.6471
20.8239
4w
(1:0.11)
fl (ppm)


8.0424
8.0259
7.9434
7.9269
7.4091
7.3826
7.2859
7.2830
7.2059
6.5426
6.1634
6.1345
5.2101
5.1889
7.4195
7.4091
7.3970
7.3920
7.3826
7.3783
7.3657
7.3615
7.3548
7.3397
7.2960
7.2859
7.2830
7.2059
7.2017
7.1947
7.1891
7.1791
1.00
0.42
9.42
3.40
3.87
f1 (ppm)
1.00
0.42
9.42
3.40
3.87
0.42
0.42
2.43
f1 (ppm)
4x
(1:0.42)


143.7642
142.5330
142.3470
141.7264
140.5138
140.1541
138.6227
138.5960
134.7058
133.8784
129.5213
129.4788
129.4573
129.0828
128.9774
128.9378
128.7291
128.3346
128.2202
128.1439
128.1351
128.0882
126.8898
126.7548
94.9429
94.4642
57.3642
49.9496
f1 (ppm)
f1 (ppm)
4x
(1:0.42)

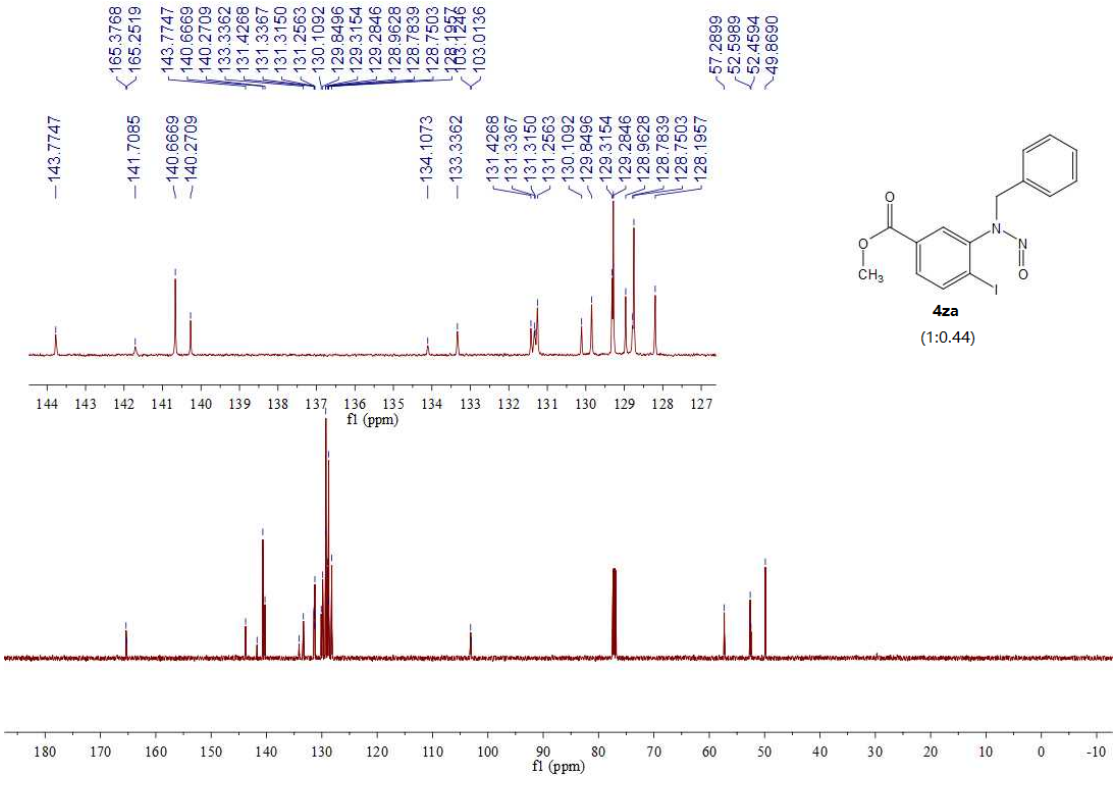

8.1149
8.0985
7.6917
7.6890
7.6726
7.4677
7.4649
7.3603
7.3549
7.3494
7.2928
7.2561
7.1191
7.1127
7.1056
6.8241
6.8213
6.1774
6.0884
5.1906
5.1617
5.1404
2.4421
2.2775
1.00
0.53
0.99
0.53
0.99
1.57
4.25
2.05
0.52
0.54
2.60
3.07
1.57
f1 (ppm)
4y
(1:0.52)


195.9053
143.7868
141.7532
140.7871
140.4078
137.8145
137.6820
134.2746
133.4718
129.8189
129.8062
129.4064
129.3709
129.0846
129.0017
128.8766
128.8232
128.7733
128.2827
103.4000
103.1533
57.2203
49.6089
26.4043
26.1754
f1 (ppm)
4y
(1:0.52)



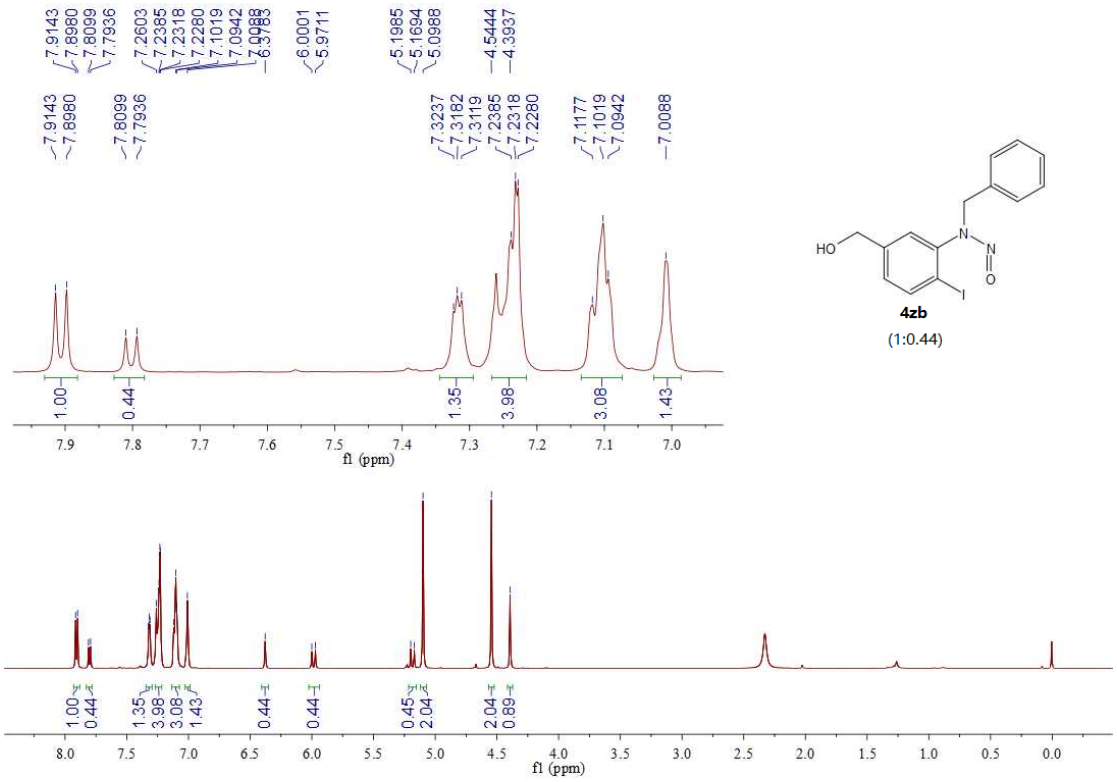
4za

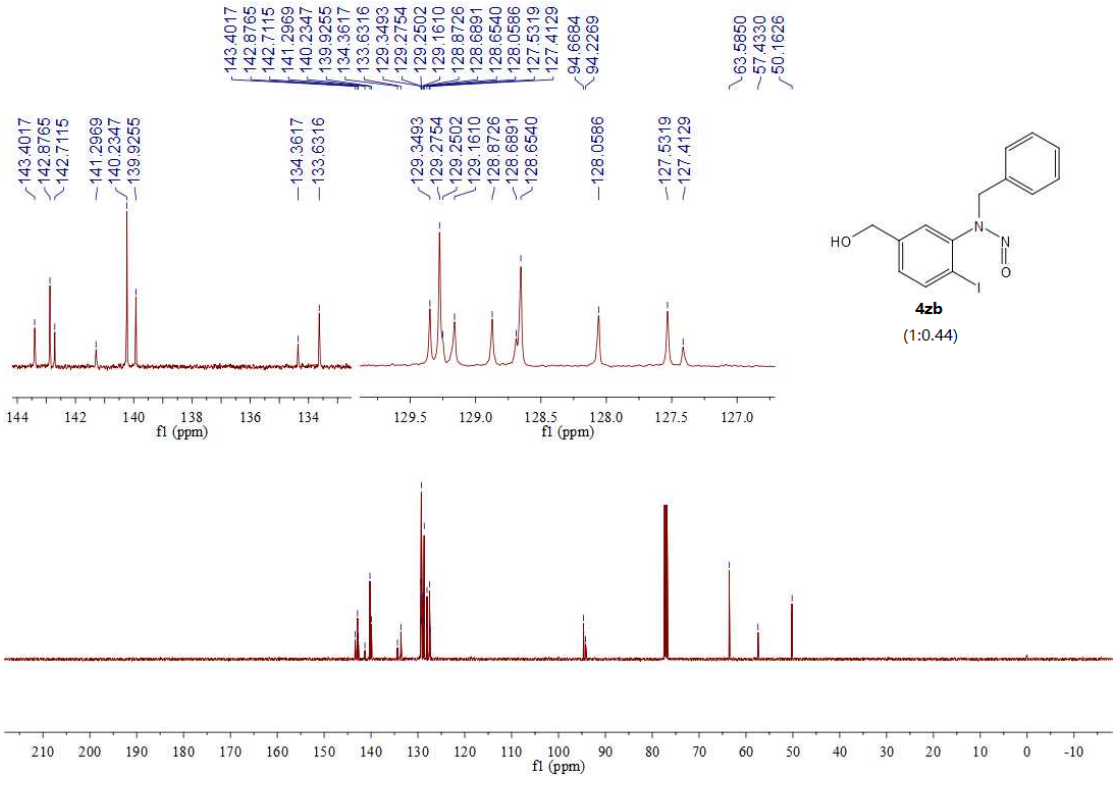
(1:0.44)

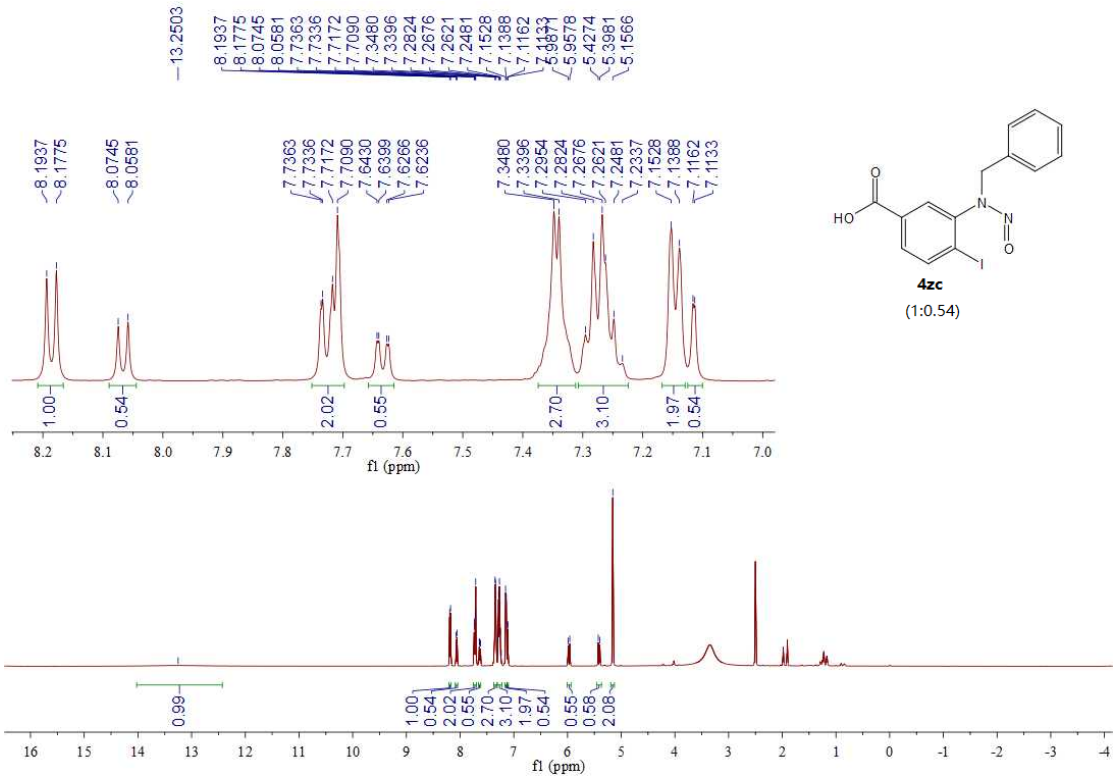


4za

(1:0.44)

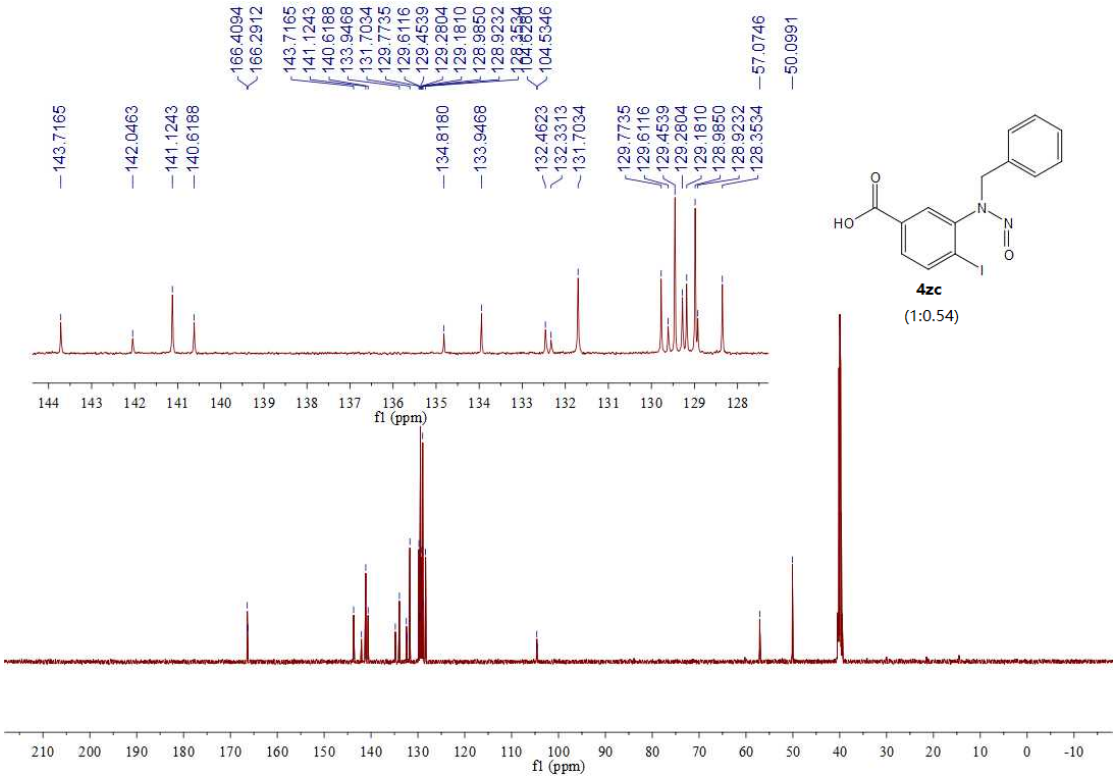

7.9143
7.8980
7.8099
7.7936
7.2603
7.2385
7.2318
7.2280
7.1019
7.0942
6.0001
5.9711
5.1985
5.1694
5.0988
4.5444
4.3937
7.3237
7.3182
7.3119
7.1177
7.0088
1.00
0.44
1.35
3.98
3.08
1.43
0.45
2.04
0.89
fl (ppm)
HO
N
N
O
I
4zb
(1:0.44)


143.4017
142.8765
142.7115
141.2969
140.2347
139.9255
134.3617
133.6316
129.3493
129.2754
129.2502
129.1610
128.8726
128.6891
128.6540
128.0586
127.5319
127.4129
94.6684
94.2269
63.5850
57.4330
50.1626
fl (ppm)
HO
N
N
O
I
4zb
(1:0.44)



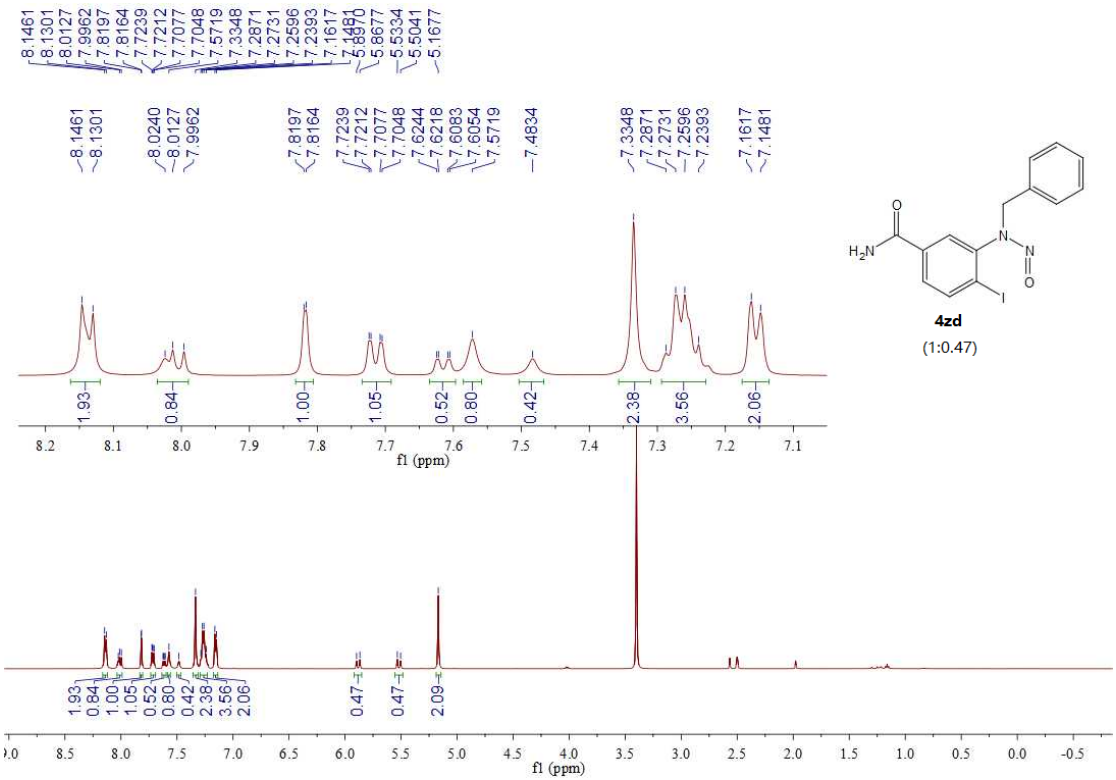
4zc

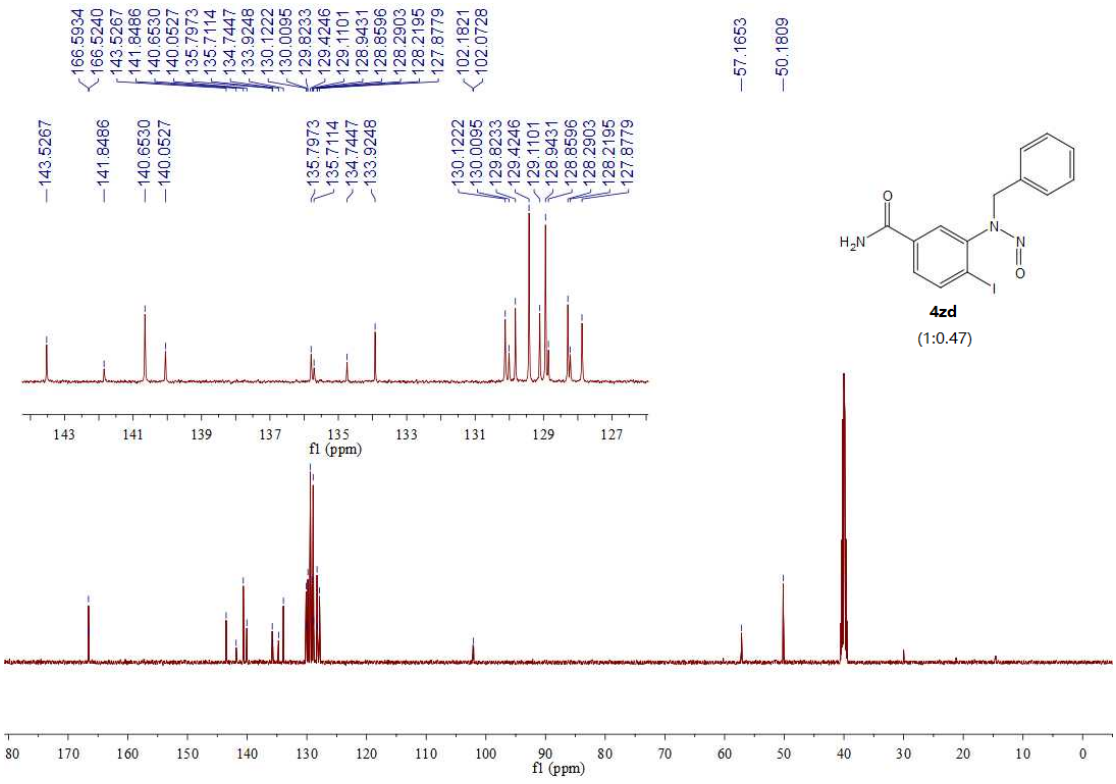
(1:0.54)

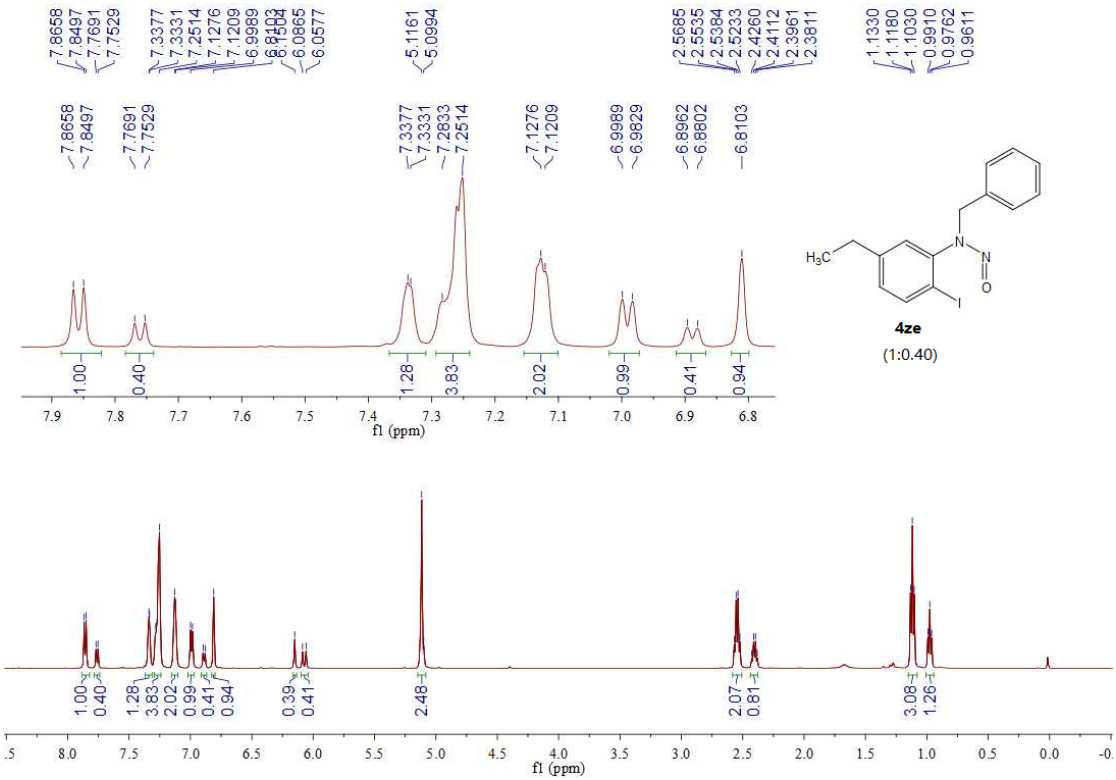


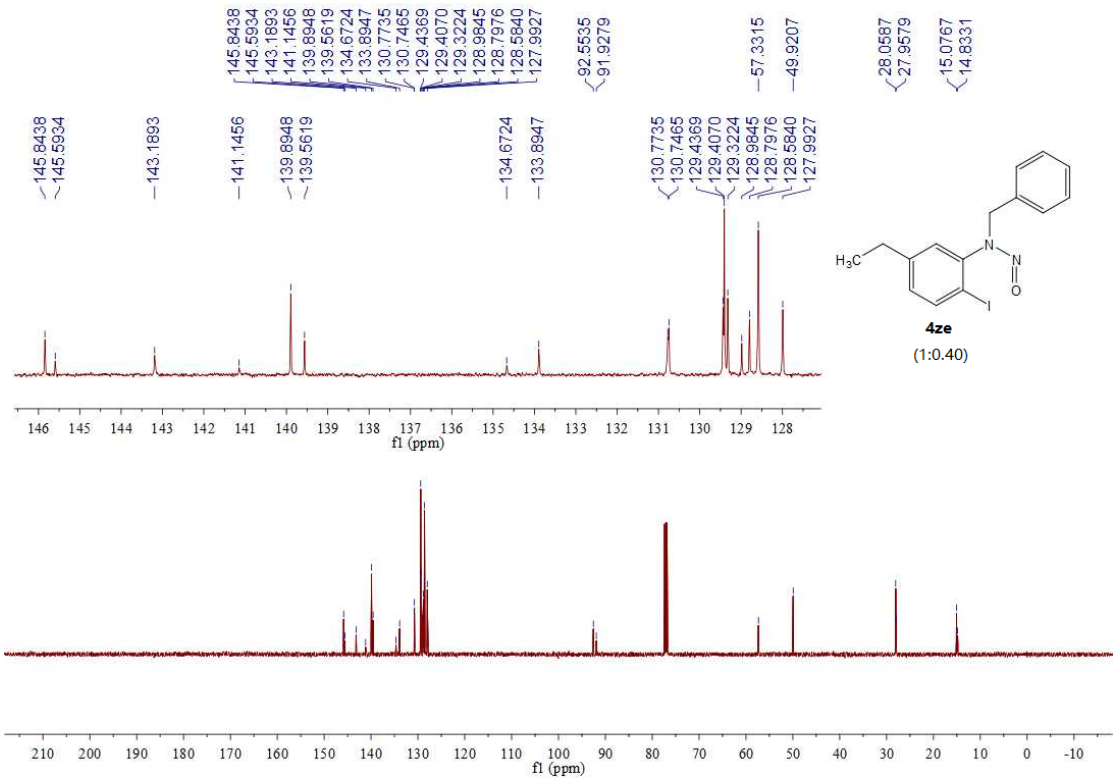
4zc

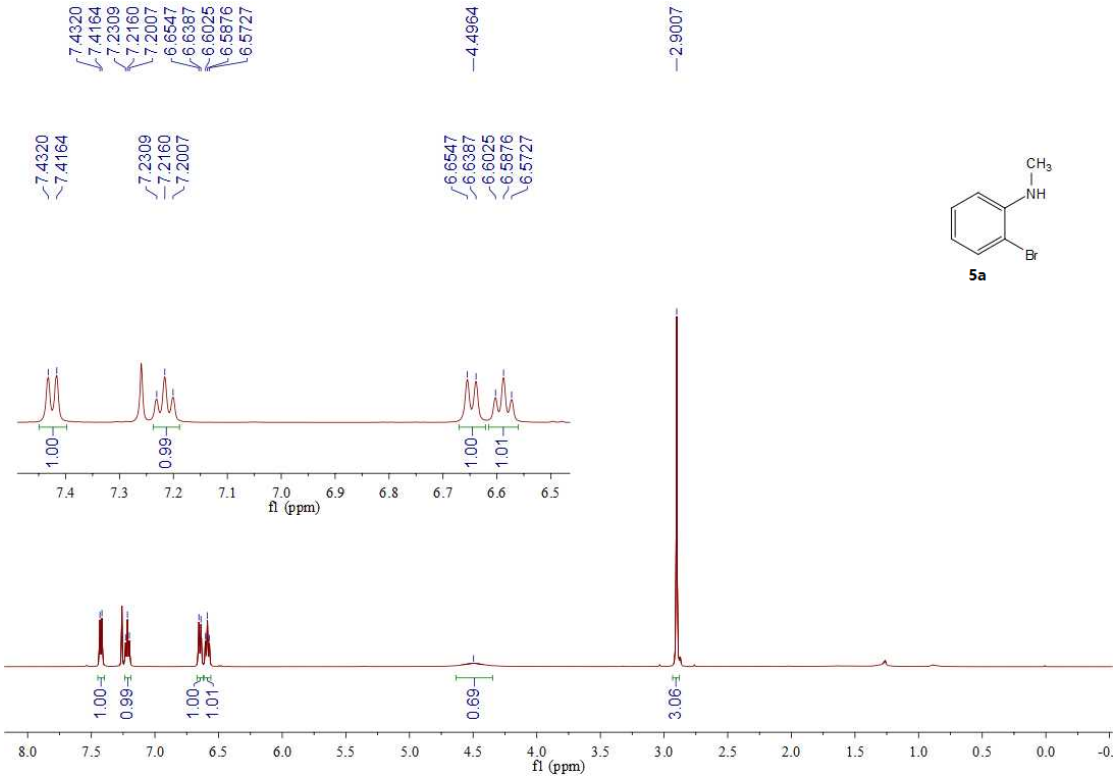
(1:0.54)

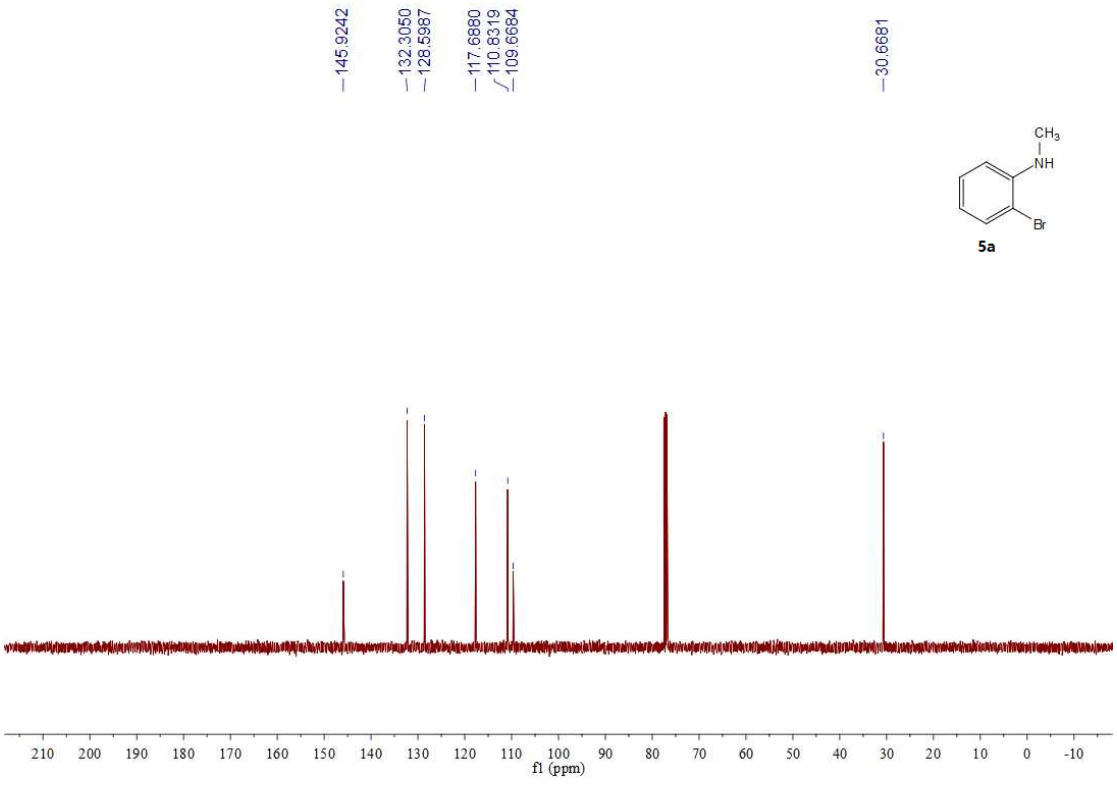

8.1461
8.1301
8.0127
7.9962
7.8197
7.8164
7.7239
7.7212
7.7077
7.7048
7.5719
7.3348
7.2871
7.2731
7.2596
7.2393
7.1617
7.1481
5.8970
5.8677
5.5334
5.5041
5.1677
1.93
0.84
1.00
1.05
0.52
0.80
0.42
2.38
3.56
2.06
0.47
0.47
2.09
f1 (ppm)
4zd
(1:0.47)

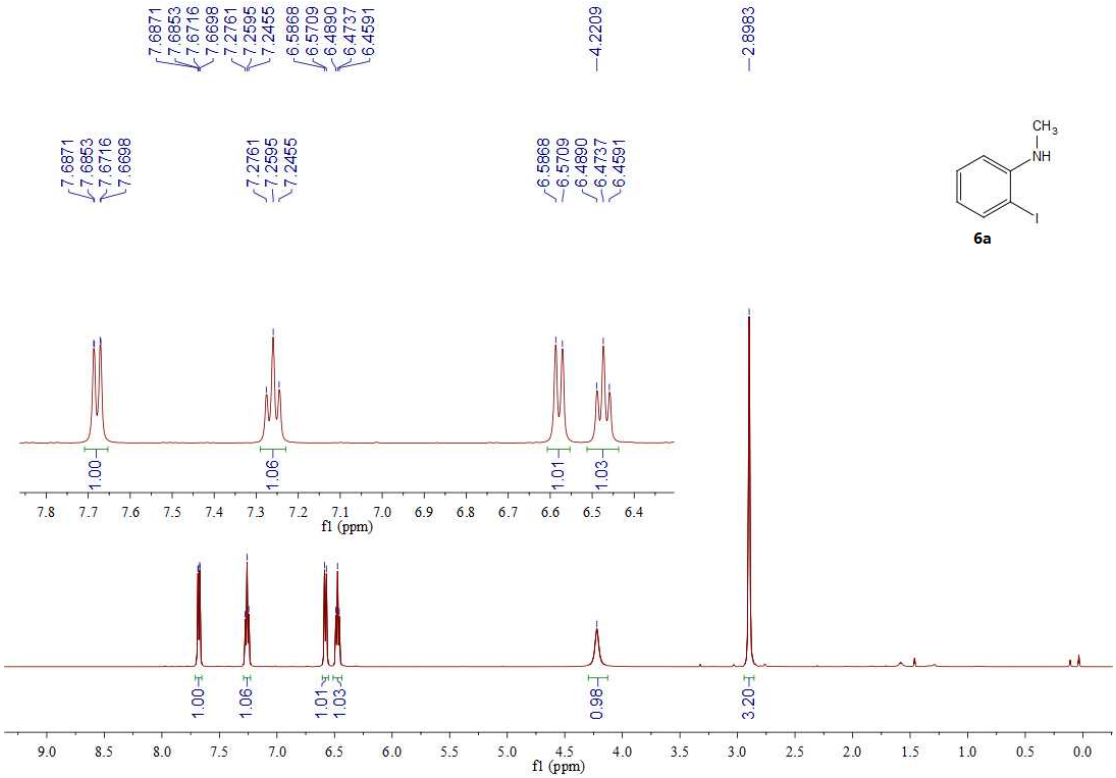

166.5934
166.5240
143.5267
141.8486
140.6530
140.0527
135.7973
135.7114
134.7447
133.9248
130.1222
130.0095
129.8233
129.4246
129.1101
128.9431
128.8596
128.2903
128.2195
127.8779
102.1821
102.0728
57.1653
50.1809
f1 (ppm)
4zd
(1:0.47)

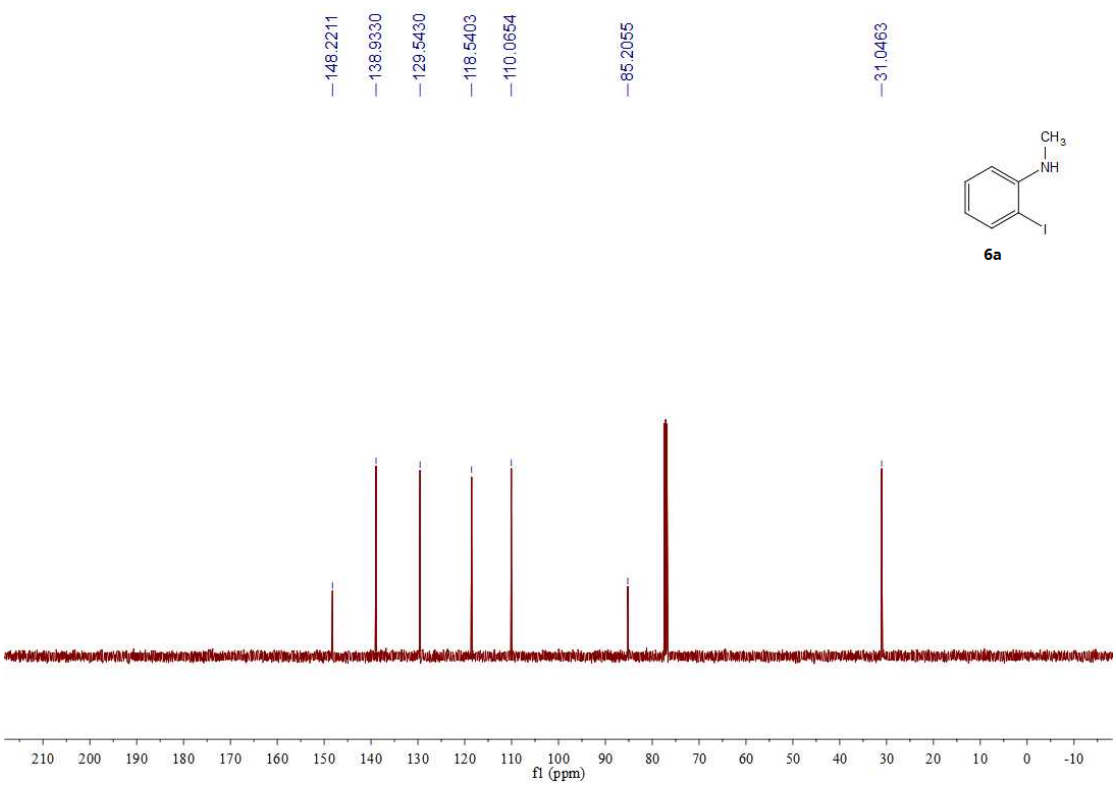

7.8658
7.8497
7.7691
7.7529
7.3377
7.3331
7.2514
7.1276
7.1209
6.9989
6.9629
6.8962
6.8802
6.8103
5.1161
5.0994
2.5685
2.5535
2.5384
2.5233
2.4260
2.4112
2.3961
2.3811
1.1330
1.1180
1.1030
0.9910
0.9762
0.9611
1.00
0.40
1.28
3.83
2.02
0.99
0.41
0.94
0.39
0.41
2.48
2.07
0.81
3.08
1.26
f1 (ppm)
4ze
(1:0.40)

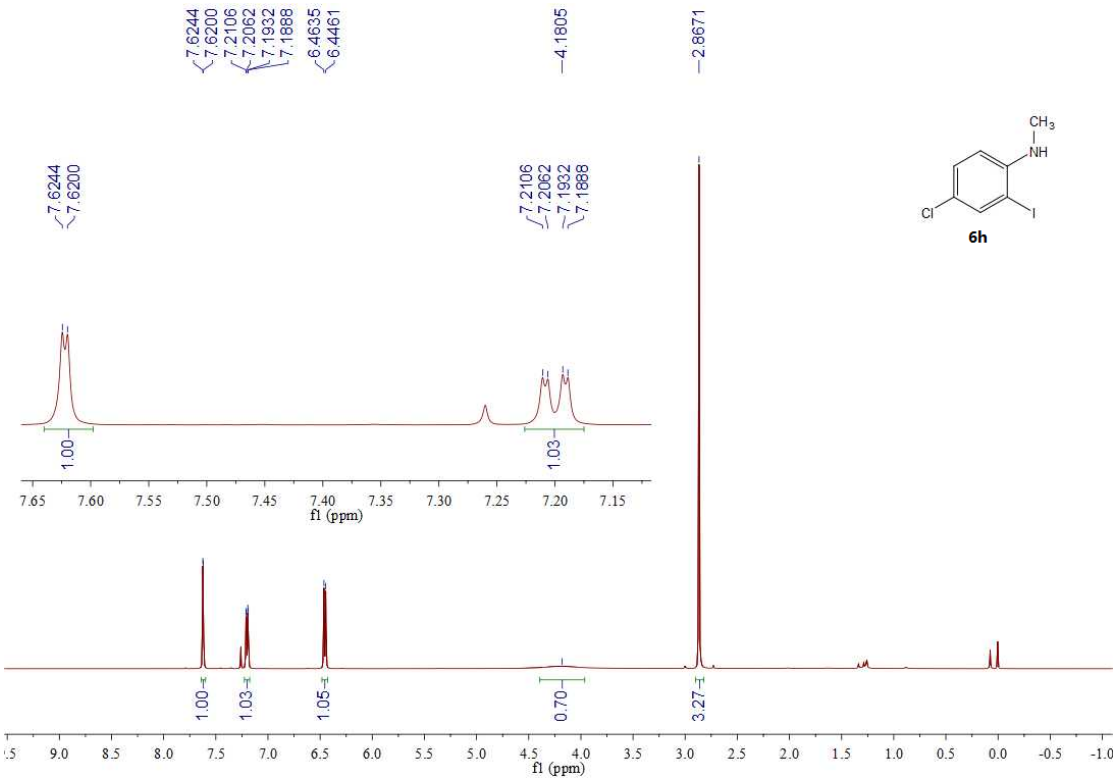

145.8438
145.5934
143.1893
141.1456
139.8948
139.5619
134.6724
133.8947
130.7735
130.7465
129.4369
129.4070
129.3224
128.9845
128.7976
128.5840
127.9927
92.5535
91.9279
57.3315
49.9207
28.0587
27.9579
15.0767
14.8331
f1 (ppm)
4ze
(1:0.40)

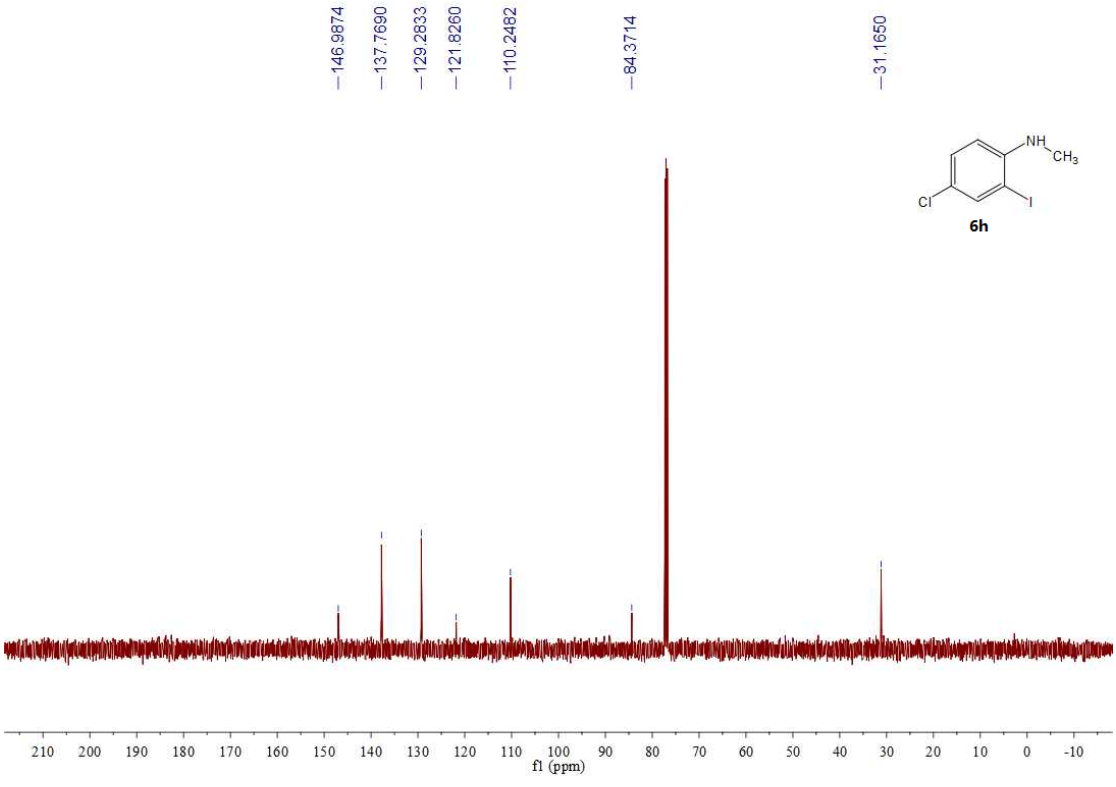

7.4320
7.4164
7.2309
7.2160
7.2007
6.6547
6.6387
6.6025
6.5876
6.5727
4.4964
2.9907
CH3
NH
Br
5a
1.00
0.99
1.00
1.01
0.69
3.06
f1 (ppm)

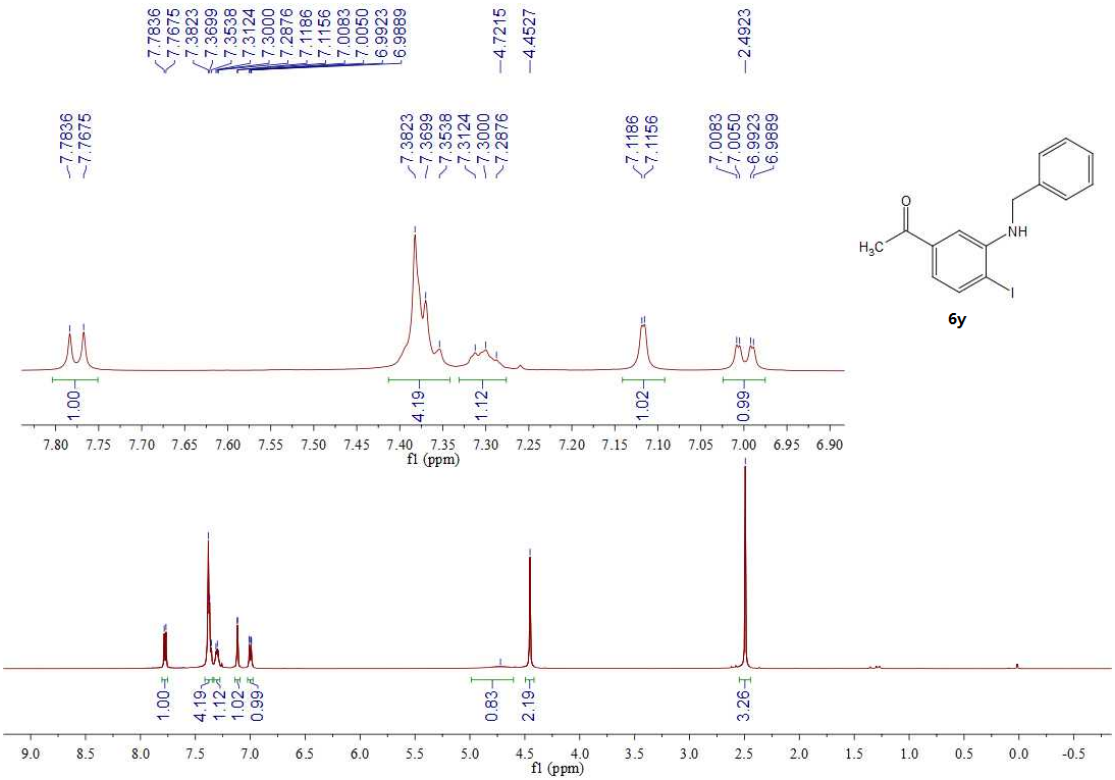

145.9242
132.3050
128.5987
117.6880
110.8319
109.6684
30.6681
CH3
NH
Br
5a
f1 (ppm)

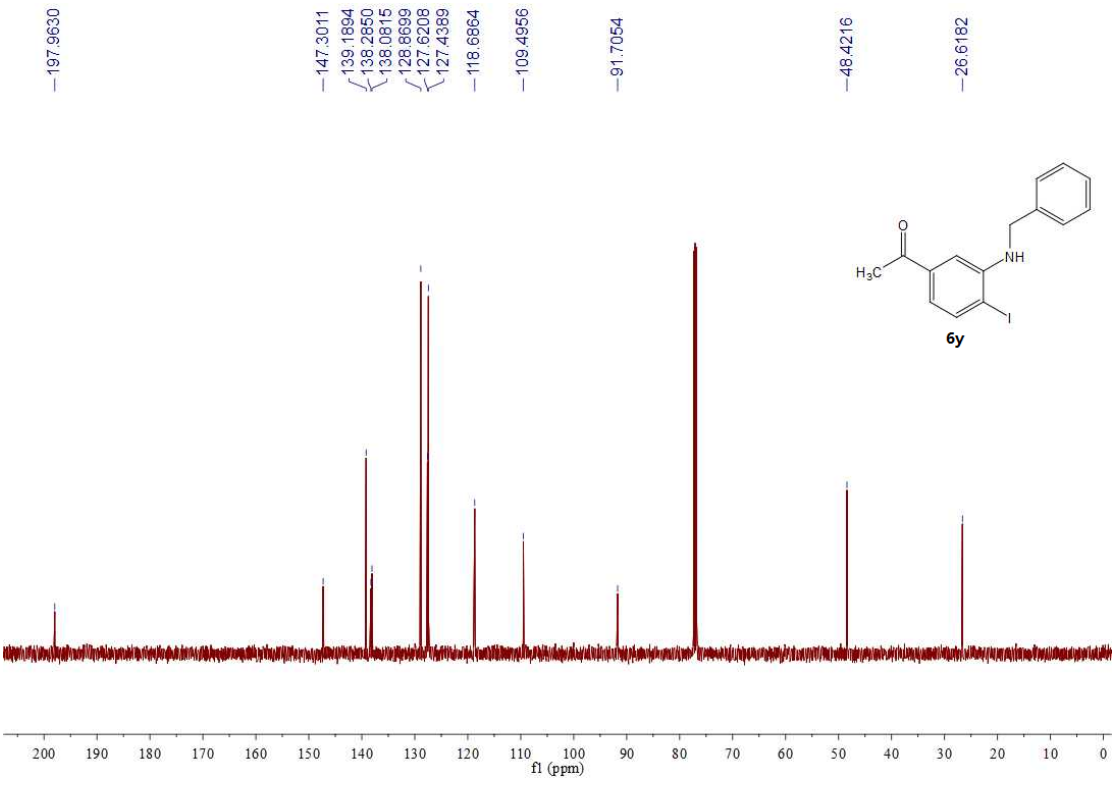

7.6871
7.6853
7.6716
7.6698
7.2761
7.2595
7.2455
6.5868
6.5709
6.4890
6.4737
6.4591
4.2209
2.8983
CH3
NH
I
6a
1.00
1.06
1.01
1.03
0.98
3.20
f1 (ppm)

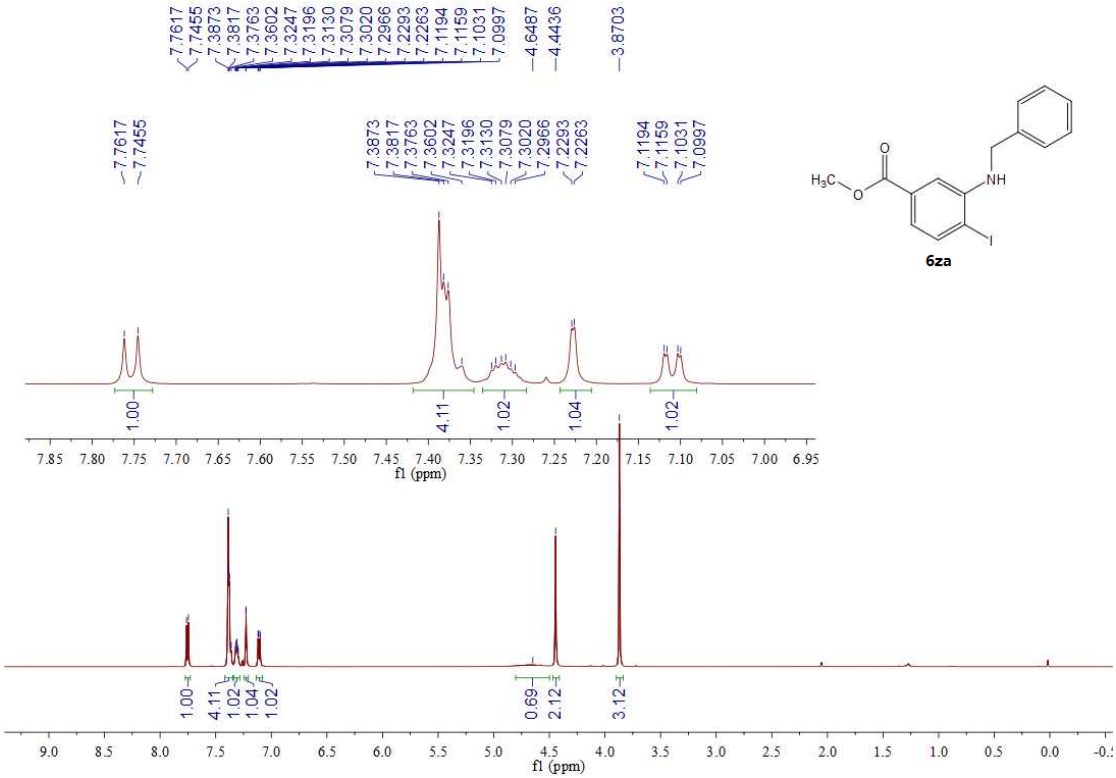

148.2211
138.9330
129.5430
118.5403
110.0654
85.2055
31.0463
CH3
NH
I
6a
f1 (ppm)

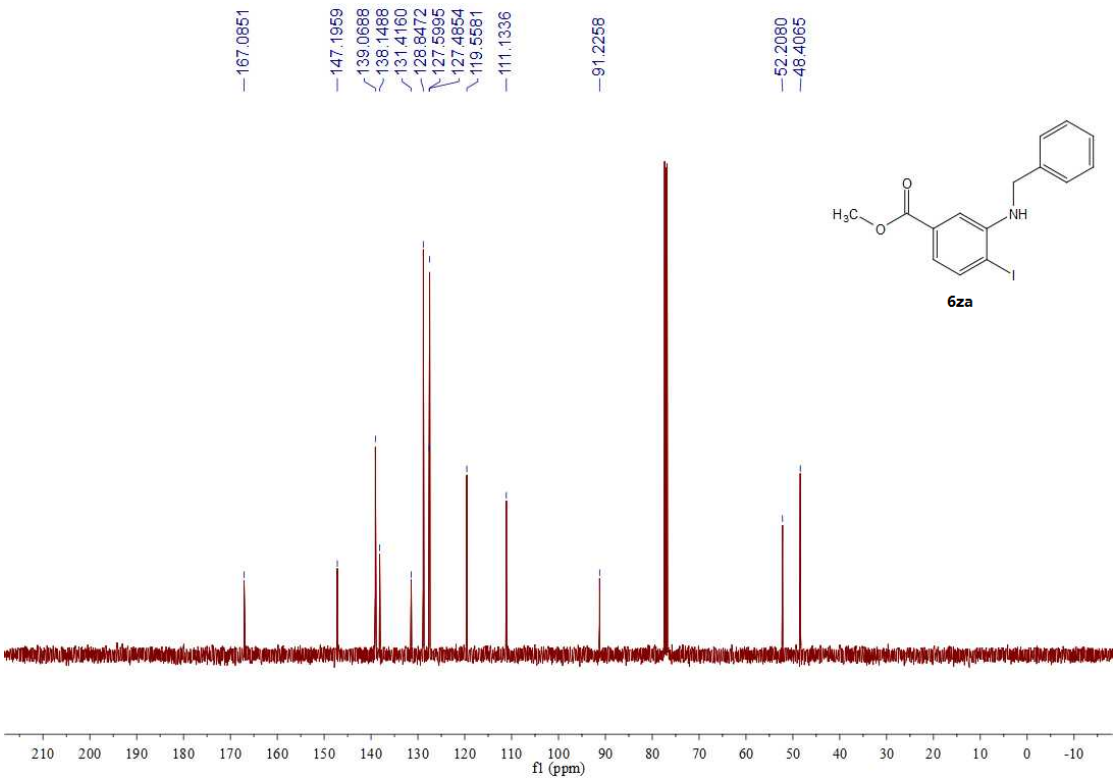

7.6244
7.6200
7.2106
7.2062
7.1932
7.1888
6.4635
6.4461
4.1805
2.8671
CH3
NH
Cl
I
6h
1.00
1.03
f1 (ppm)
1.00
1.03
1.05
0.70
3.27
f1 (ppm)

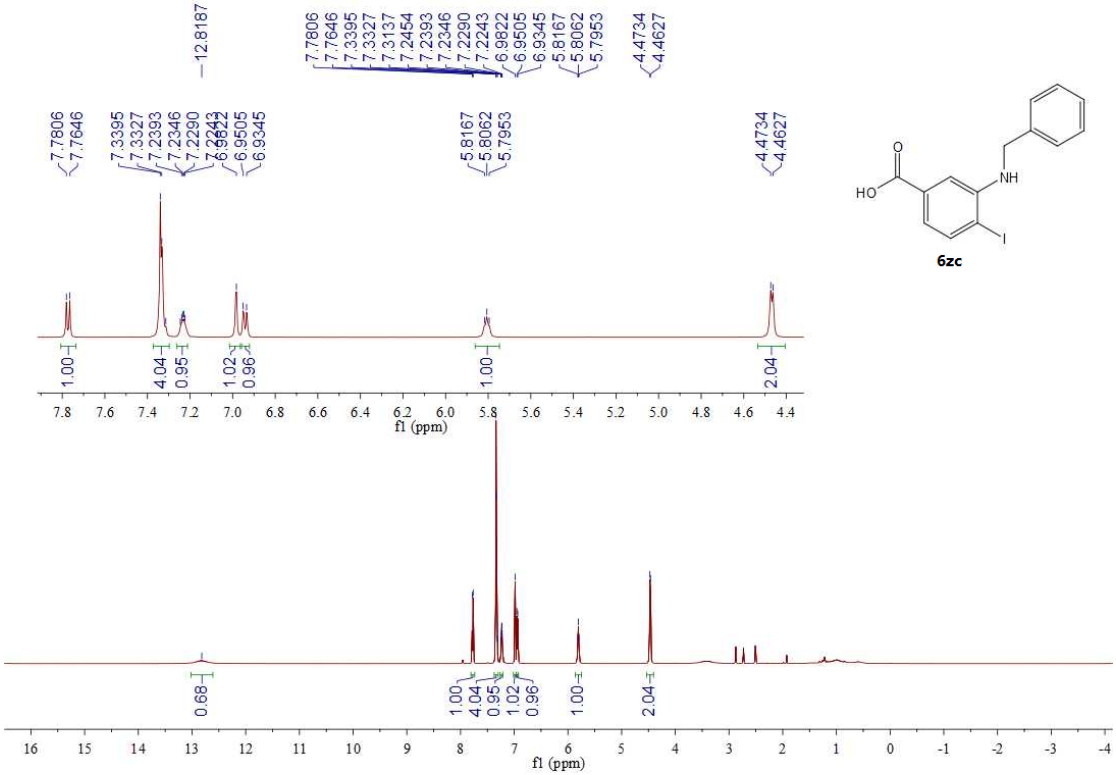

146.9874
137.7690
129.2833
121.8260
110.2482
84.3714
31.1650
NH
CH3
Cl
I
6h
f1 (ppm)

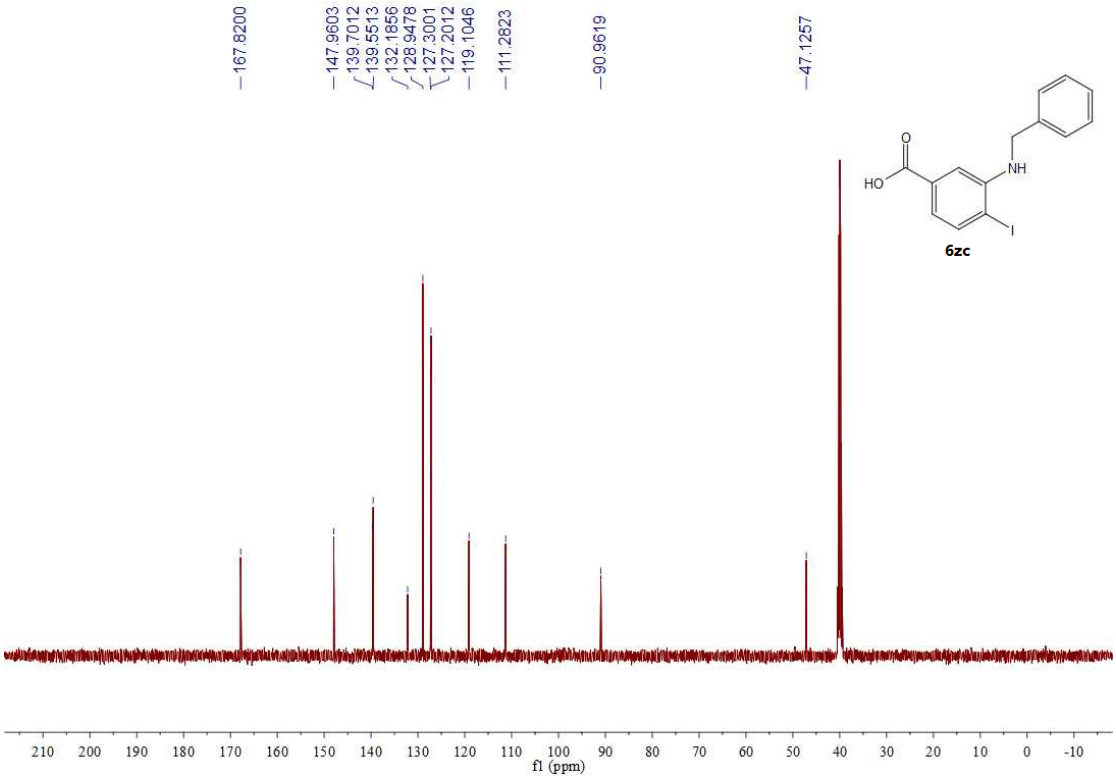

7.7836
7.7675
7.3823
7.3699
7.3538
7.3124
7.3000
7.2876
7.1186
7.1156
7.0083
7.0050
6.9923
6.9889
4.7215
4.4527
2.4923
1.00
4.19
1.12
1.02
0.99
0.83
2.19
3.26
f1 (ppm)
O
NH
H3C
I
6y

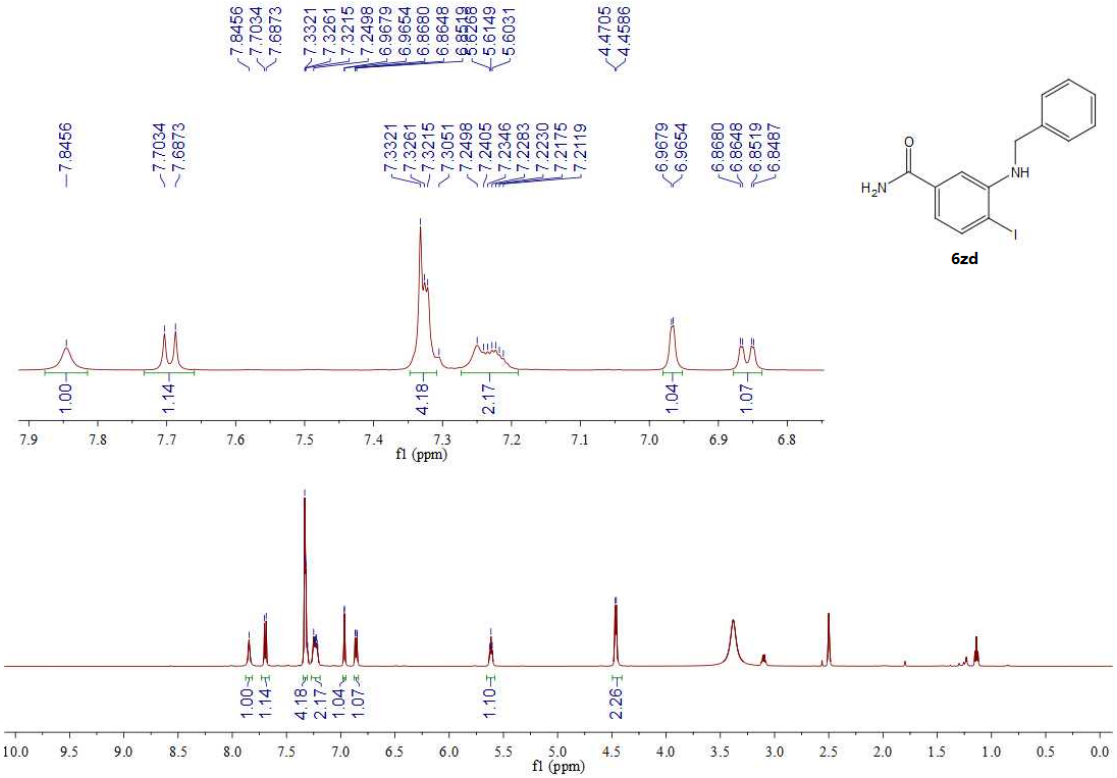

197.9630
147.3011
139.1894
138.2850
138.0815
128.8699
127.6208
127.4389
118.6864
109.4956
91.7054
48.4216
26.6182
f1 (ppm)
O
NH
H3C
I
6y


7.7617
7.7455
7.3873
7.3817
7.3763
7.3602
7.3247
7.3196
7.3130
7.3079
7.3020
7.2966
7.2293
7.2263
7.1194
7.1159
7.1031
7.0997
4.6487
4.4436
3.8703
1.00
4.11
1.02
1.04
1.02
0.69
2.12
3.12
f1 (ppm)
6za


167.0851
147.1959
139.0688
138.1488
131.4160
128.8472
127.5995
127.4854
119.5581
111.1336
91.2258
52.2080
48.4065
f1 (ppm)
6za


12.8187
7.7806
7.7646
7.3395
7.3327
7.3137
7.2454
7.2393
7.2346
7.2290
7.2243
6.9822
6.9505
6.9345
5.8167
5.8062
5.7953
4.4734
4.4627
1.00
4.04
0.95
1.02
0.96
1.00
2.04
0.68
fl (ppm)
HO
O
NH
I
6zc


167.8200
147.9603
139.7012
139.5513
132.1856
128.9478
127.3001
127.2012
119.1046
111.2823
90.9619
47.1257
fl (ppm)
HO
O
NH
I
6zc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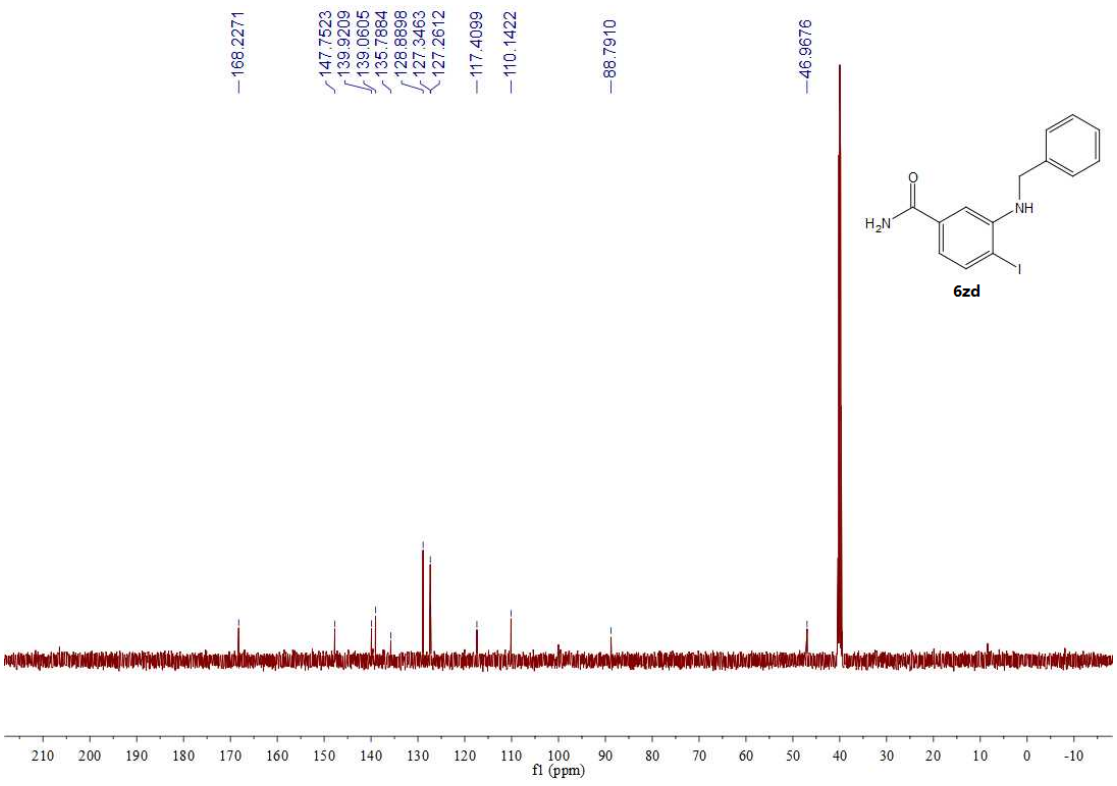
7.7034
7.6873
7.3321
7.3261
7.3215
7.2498
6.9679
6.9654
6.8680
6.8648
6.8519
5.6149
5.6031
4.4705
4.4586
1.00
1.14
4.18
2.17
1.04
1.07
1.10
2.26
f1 (ppm)
6zd


168.2271
147.7523
139.9209
139.0605
135.7884
128.8898
127.3463
127.2612
117.4099
110.1422
88.7910
46.9676
f1 (ppm)
6zd