

**Inexpensive NaX (X = I, Br, Cl) as a halogen donor in the practical
Ag/Cu-mediated decarboxylative halogenation of
aryl carboxylic acids under aerobic conditions**

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General considerations. The Reagents used for experiments were commercially available and were used as received unless otherwise noted. DMSO were distilled from CaH₂ under reduced pressure and stored under nitrogen. All Reactions were performed under dioxygen with the strict exclusion of moisture using Schlenk techniques. Column chromatography was performed on silica gel 300-400 mesh. The yields reported are the isolated yields and the average of two runs. ¹H, ¹³C and ¹⁹F NMR spectra of compounds (**1a-14a**, **1b-14b** and **1c-14c**) were recorded at 400, 100 and 377 MHz with CDCl₃ as solvent respectively, ¹H and ¹³C NMR spectra of compounds (**15** and **16**) were recorded at 400 and 100 MHz with d₆-DMSO as solvent respectively. All coupling constants (*J* values) were reported in Hertz (Hz). HRMS were performed by Shanghai Mass Spectrometry Centre, Shanghai Institute of Organic Chemistry, CAS (Chinese Academic of Sciences).

General procedure for silver-catalyzed decarboxylative iodination of aryl carboxylic acids (Procedure A). An oven-dried Schlenk tube equipped with a stir bar was charged with aryl carboxylic acid (0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time (unless otherwise specified), and then cooled down to room temperature. The resultant mixture was filtered through a short plug of silica gel and then concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

General procedure for silver-catalyzed decarboxylative bromination and chlorination of aryl carboxylic acids (Procedure B). An oven-dried Schlenk tube equipped with a stir bar was charged with aryl carboxylic acid (0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaX (0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time (unless otherwise specified), and then cooled down to room temperature. The resultant mixture was filtered through a short plug of silica gel and then concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

General procedure for silver-catalyzed decarboxylative halogenation of 2-chloro-5-nitrobenzoic acid (Procedure C). An oven-dried Schlenk tube equipped with a stir bar was charged with aryl carboxylic acid (0.2 mmol), Ag₂SO₄ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv) and NaX (0.24 mmol, 1.2 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (2 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time (unless otherwise specified), and then cooled down to room temperature. The resultant mixture was filtered through a short plug of silica gel and then concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

General procedure for silver-catalyzed decarboxylative iodination of electron-rich aryl carboxylic acids (Procedure D). An oven-dried Schlenk tube equipped with a stir bar was charged with aryl carboxylic acid (0.2 mmol), Ag₂SO₄ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv) and NaI (149.9 mg, 1 mmol, 5 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (1 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time (unless otherwise specified), and then cooled down to room temperature. The resultant mixture was filtered through a short plug of silica gel and then concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

1-Iodo-4,5-dimethoxy-2-nitrobenzene (1a). Procedure A was followed using 4,5-dimethoxy-2-nitrobenzoic acid (45.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (10% ether in hexane) to afford 37.1 mg (60%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.^{1,2} ¹H NMR (400 MHz, CDCl₃): δ 7.61 (s, 1 H), 7.39 (s, 1 H), 3.96 (s, 3 H), 3.93 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 152.7, 149.1, 145.1, 123.1, 109.0, 77.2, 56.7, 56.4. HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₈H₈INO₄ 308.9498; Found: 308.9496.

1-Bromo-4,5-dimethoxy-2-nitrobenzene (1b). Procedure B was followed using 4,5-dimethoxy-2-nitrobenzoic acid (45.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaBr (30.9 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (10%

ether in hexane) to afford 25.9 mg (49%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.^{1,3} ¹H NMR (400 MHz, CDCl₃): δ 7.57 (s, 1 H), 7.12 (s, 1 H), 3.96 (s, 3 H), 3.94 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 152.8, 148.2, 141.8, 116.5, 109.0, 107.5, 56.7, 56.5. HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₈H₈BrNO₄ 260.9637; Found: 260.9636.

1-Chloro-4,5-dimethoxy-2-nitrobenzene (1c). Procedure B was followed using 4,5-dimethoxy-2-nitrobenzoic acid (45.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaCl (17.5 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (10% ether in hexane) to afford 22.6 mg (52%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.^{1,3} ¹H NMR (400 MHz, CDCl₃): δ 7.55 (s, 1 H), 6.93 (s, 1 H), 3.95 (s, 3 H), 3.93 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 152.9, 147.6, 139.7, 121.1, 113.4, 108.6, 56.7, 56.5. HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₈H₈ClNO₄ 217.0142; Found: 217.0142.

2-Iodo-4-methoxy-1-nitrobenzene (2a). Procedure A was followed using 5-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (3% ether in hexane) to afford 35.2 mg (63%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.^{1,4} ¹H NMR (400 MHz, CDCl₃): δ 7.99 (d, *J* = 9.1 Hz, 1 H), 7.53 (d, *J* = 2.6 Hz, 1 H), 6.95 (dd, *J* = 2.5, 9.1 Hz, 1 H), 3.88 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 162.5, 145.4, 127.4, 127.1, 114.1, 88.1, 56.1. HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₇H₆INO₃ 278.9392; Found: 278.9391.

2-Bromo-4-methoxy-1-nitrobenzene (2b). Procedure B was followed using 5-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv) 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (3% ether in hexane) to afford 20.4 mg (44%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.^{1,3} ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 9.1 Hz, 1 H), 7.21 (d, *J* = 2.3 Hz, 1 H), 6.91 (dd, *J* = 2.2, 9.1 Hz, 1 H), 3.88 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 162.8, 142.5, 127.9, 120.2, 116.7, 113.5, 56.2. HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₇H₆BrNO₃ 230.9531; Found: 230.9529.

2-Chloro-4-methoxy-1-nitrobenzene (2c). Procedure B was followed using 5-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaCl (17.5 mg, 0.3 mmol, 1.5 equiv)

and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (3% ether in hexane) to afford 25.1 mg (67%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.^{1,3} ¹H NMR (400 MHz, CDCl₃): δ 7.98 (d, J = 9.4 Hz, 1 H), 7.00 (d, J = 2.2 Hz, 1 H), 6.86 (dd, J = 2.1, 9.1 Hz, 1 H), 3.88 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 163.0, 140.6, 129.6, 128.0, 116.8, 113.0, 56.2. HRMS (MALDI-TOF) m/z : [M]⁺ Calcd for C₇H₆ClNO₃ 187.0036; Found: 187.0038.

1-Iodo-4-methoxy-2-nitrobenzene (3a). Procedure A was followed using 4-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (3% ether in hexane) to afford 35.2 mg (63%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.^{1,5} ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, J = 8.8 Hz, 1 H), 7.37 (d, J = 2.9 Hz, 1 H), 6.85 (dd, J = 2.9, 8.7 Hz, 1 H), 3.84 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 160.2, 153.5, 142.1, 120.4, 110.0, 74.4, 56.0. HRMS (MALDI-TOF) m/z : [M]⁺ Calcd for C₇H₆INO₃ 278.9392; Found: 278.9394.

1-Bromo-4-methoxy-2-nitrobenzene (3b). Procedure B was followed using 4-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaBr (30.9 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 31.1 mg (67%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, J = 8.9 Hz, 1 H), 7.35 (d, J = 2.8 Hz, 1 H), 6.98 (dd, J = 8.9, 2.9 Hz, 1 H), 3.85 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 159.2, 150.1, 135.4, 119.8, 110.8, 104.4, 56.1. HRMS (MALDI-TOF) m/z : [M]⁺ Calcd for C₇H₆BrNO₃ 230.9531; Found: 230.9533.

1-Chloro-4-methoxy-2-nitrobenzene (3c). Procedure B was followed using 4-methoxy-2-nitrobenzoic acid (39.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaCl (17.5 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 19.8 mg (53%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, J = 8.9 Hz, 1 H), 7.39 (d, J = 2.8 Hz, 1 H), 7.06 (dd, J = 2.9, 8.9 Hz, 1 H), 3.86 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 158.5, 148.2, 132.4, 119.8, 118.1, 110.4, 56.1. HRMS (MALDI-TOF) m/z : [M]⁺ Calcd for C₇H₆ClNO₃ 187.0036; Found: 187.0038.

1-Iodo-4-methyl-2-nitrobenzene (4a). Procedure A was followed using 4-methyl-2-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 27.9 mg (53%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.^{1,5} ¹H NMR (400 MHz, CDCl₃): δ 7.87 (d, *J* = 8.1 Hz, 1 H), 7.67 (s, 1 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 2.39 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 152.8, 141.5, 139.9, 134.4, 125.9, 82.0, 20.8. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₇H₆INO₂ 262.9443; Found: 262.9447.

1-Bromo-4-methyl-2-nitrobenzene (4b). Procedure B was followed using 4-methyl-2-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 29.8 mg (69%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 7.64 (s, 1 H), 7.59 (d, *J* = 8.2 Hz, 1 H), 7.23 (d, *J* = 8.2 Hz, 1 H), 2.39 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 149.6, 139.0, 134.6, 134.1, 125.9, 110.9, 20.7. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₇H₆BrNO₂ 214.9582; Found: 214.9580.

1-Chloro-4-methyl-2-nitrobenzene (4c). Procedure B was followed using 4-methyl-2-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaCl (17.5 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 17.4 mg (51%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 7.58 (s, 1 H), 7.30 (m, 2 H), 2.34 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 147.5, 138.5, 134.0, 131.3, 125.7, 123.5, 20.5. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₇H₆ClNO₂ 171.0087; Found: 171.0089.

2-Iodo-1-methyl-3-nitrobenzene (5a). Procedure A was followed using 2-methyl-6-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 14.2 mg (27%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.^{1,6} ¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, *J* = 7.7 Hz, 1 H), 7.36 - 7.31 (m, 1 H), 2.58 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 145.2, 132.3, 128.6, 121.8, 110.0, 92.4, 29.7. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₇H₆INO₂ 262.9443; Found: 262.9441.

2-Bromo-1-methyl-3-nitrobenzene (5b). Procedure B was followed using 2-methyl-6-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 13.0 mg (30%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.^{1,7} ¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, *J* = 7.9 Hz, 1 H), 7.43 (d, *J* = 7.4 Hz, 1 H), 7.33 (t, *J* = 7.8 Hz, 1 H), 2.52 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 151.3, 141.3, 133.5, 127.6, 122.3, 115.8, 23.6. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₇H₆BrNO₂ 214.9582; Found: 214.9584.

2-Chloro-1-methyl-3-nitrobenzene (5c). Procedure B was followed using 2-methyl-6-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaCl (17.5 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 14.7 mg (43%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.³ ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 8.0 Hz, 1 H), 7.44 (d, *J* = 8.0 Hz, 1 H), 7.29 (t, *J* = 8.0 Hz, 1 H), 2.46 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 149.0, 139.4, 134.0, 126.8, 125.9, 122.5, 20.3. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₇H₆ClNO₂ 171.0087; Found: 171.0089.

1-Iodo-2-nitrobenzene (6a). Procedure A was followed using 2-nitrobenzoic acid (33.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaI (45 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 19.6 mg (39%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 8.04 (dd, *J* = 1.0, 7.9 Hz, 1 H), 7.85 (dd, *J* = 1.3, 8.1 Hz, 1 H), 7.51 - 7.47 (m, 1 H), 7.28 - 7.24 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 153.0, 141.9, 133.4, 129.1, 125.4, 86.2. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆H₄INO₂ 248.9287; Found: 248.9285.

1-Bromo-2-nitrobenzene (6b). Procedure B was followed using 2-nitrobenzoic acid (33.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 20.2 mg (50%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.^{1,3} ¹H NMR (400 MHz, CDCl₃): δ 7.84 (dd, *J* = 1.8, 7.4 Hz, 1 H), 7.75 (dd, *J* = 1.5, 7.2 Hz, 1 H), 7.52 - 7.37 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 149.8, 135.0, 133.2, 128.3, 125.6, 114.4. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆H₄BrNO₂ 200.9425; Found: 200.9424.

1-Chloro-2-nitrobenzene (6c). Procedure B was followed using 2-nitrobenzoic acid (33.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaCl (17.5 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 14.1 mg (45%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.^{1,3} ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 8.0 Hz, 1 H), 7.56 - 7.50 (m, 2 H), 7.44 - 7.39 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 147.9, 133.3, 131.8, 127.7, 126.8, 125.5. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆H₄ClNO₂ 156.9931; Found: 156.9931.

1-Iodo-2-nitro-4-(trifluoromethyl)benzene (7a). Procedure A was followed using 1-iodo-2-nitro-4-(trifluoromethyl)benzoic acid (47.0 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 29.8 mg (47%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.^{1,5} ¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, *J* = 8.3 Hz, 1 H), 8.11 (d, *J* = 1.2 Hz, 1 H), 7.52 (dd, *J* = 1.5, 8.3 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 153.1, 143.1, 131.9 (q, *J* = 34.9 Hz), 129.6 (q, *J* = 3.0 Hz), 122.6 (q, *J* = 271.6 Hz), 122.3 (q, *J* = 3.8 Hz), 90.9. ¹⁹F NMR (377 MHz, CDCl₃): δ - 63.3 (s, 3 F). HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₇H₃F₃INO₂ 316.9161; Found: 316.9159.

1-Bromo-2-nitro-4-(trifluoromethyl)benzene (7b). Procedure B was followed using 2-nitro-4-(trifluoromethyl)benzoic acid (47.0 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaBr (30.9 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 16.2 mg (30%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 8.11 (s, 1 H), 7.91 (d, *J* = 8.4 Hz, 1 H), 7.69 (d, *J* = 8.3 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 149.9, 136.1, 131.1 (q, *J* = 34.1 Hz), 129.5 (q, *J* = 3.8 Hz), 122.8 (q, *J* = 3.8 Hz), 122.5 (q, *J* = 271.6 Hz), 118.4. ¹⁹F NMR (377 MHz, CDCl₃): δ - 63.1 (s, 1 F). HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₇H₃BrF₃NO₂ 268.9299; Found: 268.9301.

1-Chloro-2-nitro-4-(trifluoromethyl)benzene (7c). Procedure B was followed using 2-nitro-4-(trifluoromethyl)benzoic acid (47.0 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaCl (17.5 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 7.2 mg (16%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.^{1,8} ¹H NMR (400 MHz,

CDCl₃): δ 8.11 (s, 1H), 7.80 - 7.72 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 147.8, 132.9, 130.9, 130.3 (q, J = 34.9 Hz), 129.6 (q, J = 3.8 Hz), 122.8 (q, J = 3.8 Hz), 122.4 (q, J = 270.9 Hz). ¹⁹F NMR (377 MHz, CDCl₃): δ - 63.0 (s, 3 F). HRMS (MALDI-TOF) m/z : [M]⁺ Calcd for C₇H₃ClF₃NO₂ 224.9804; Found: 224.9807.

4-Fluoro-1-iodo-2-nitrobenzene (8a). Procedure A was followed using 4-fluoro-2-nitrobenzoic acid (37.0 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 35.2 mg (66%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 8.02 (q, J = 4.0 Hz, 1 H), 7.64 (dd, J = 2.8, 8.0 Hz, 1 H), 7.07 (ddd, J = 2.8, 7.5, 8.6 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 162.2 (d, J = 251.9 Hz), 153.4, 143.1 (d, J = 7.6 Hz), 121.2 (d, J = 21.2 Hz), 113.6 (d, J = 26.5 Hz), 79.6 (d, J = 3.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃): δ - 109.6 - - 109.7 (m, 1 F). HRMS (MALDI-TOF) m/z : [M]⁺ Calcd for C₆H₃FINO₂ 266.9192; Found: 266.9196.

1-Bromo-4-fluoro-2-nitrobenzene (8b). Procedure B was followed using 4-fluoro-2-nitrobenzoic acid (37.0 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 21.2 mg (48%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.^{1,9} ¹H NMR (400 MHz, CDCl₃): δ 7.73 (q, J = 4.0 Hz, 1 H), 7.60 (dd, J = 2.6, 7.7 Hz, 1 H), 7.21 (td, J = 4.0, 8.0 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 161.1 (d, J = 251.1 Hz), 150.0, 136.4 (d, J = 7.6 Hz), 120.9 (d, J = 21.2 Hz), 113.5 (d, J = 27.3 Hz), 109.1 (d, J = 4.6 Hz). ¹⁹F NMR (377 MHz, CDCl₃): δ - 110.2 (dd, J = 7.4, 12.7 Hz, 1 F). HRMS (MALDI-TOF) m/z : [M]⁺ Calcd for C₆H₃BrFNO₂ 218.9331; Found: 218.9333.

1-Chloro-4-fluoro-2-nitrobenzene (8c). Procedure B was followed using 4-fluoro-2-nitrobenzoic acid (37.0 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaCl (17.5 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 14.7 mg (42%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 7.62 (dd, J = 2.2, 7.5 Hz, 1 H), 7.54 (q, J = 4.0 Hz, 1 H), 7.27 (dd, J = 2.3, 7.6 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 160.4 (d, J = 251.2 Hz), 148.1, 133.2 (d, J = 7.6 Hz), 122.5 (d, J = 3.8 Hz), 120.8 (d, J = 22.0 Hz), 113.3 (d, J = 27.3 Hz). ¹⁹F NMR (377 MHz, CDCl₃): δ - 110.7 - - 110.6 (m, 1 F). HRMS (MALDI-TOF) m/z : [M]⁺ Calcd for C₆H₃ClFNO₂ 174.9836; Found: 174.9830.

4-Chloro-2-iodo-1-nitrobenzene (9a). Procedure A was followed using 5-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 43 mg (76%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 8.04 (d, *J* = 2.1 Hz, 1 H), 7.84 (d, *J* = 8.7 Hz, 1 H), 7.46 (dd, *J* = 2.1, 8.7 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 151.2, 141.4, 139.3, 129.2, 126.3, 87.1. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆H₃ClINO₂ 282.8897; Found: 282.8895.

2-Bromo-4-chloro-1-nitrobenzene (9b). Procedure B was followed using 5-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaBr (30.9 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 32.6 mg (69%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.³ ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, *J* = 8.0 Hz, 1 H), 7.76 (s, 1 H), 7.44 (d, *J* = 8.0 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 148.1, 139.2, 134.8, 128.5, 126.7, 115.6. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆H₃BrClNO₂ 234.9036; Found: 234.9038.

2,4-Dichloro-1-nitrobenzene (9c). Procedure B was followed using 5-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaCl (17.5 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 24.7 mg (64%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.^{1,3} ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 8.7 Hz, 1 H), 7.55 (d, *J* = 1.8 Hz, 1 H), 7.40 (dd, *J* = 1.7, 8.7 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 146.2, 139.3, 131.8, 128.5, 127.9, 126.7. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆H₃Cl₂NO₂ 190.9541; Found: 190.9542.

4-Chloro-1-iodo-2-nitrobenzene (10a). Procedure A was followed using 4-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 40.8 mg (72%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.^{1,5} ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, *J* = 8.5 Hz, 1 H), 7.84 (d, *J* = 2.0 Hz, 1 H), 7.28 - 7.25 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 153.2, 142.7, 135.3, 133.7, 125.6, 83.8. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆H₃ClINO₂ 282.8897; Found: 282.8902.

1-Bromo-4-chloro-2-nitrobenzene (10b). Procedure B was followed using 4-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 30.2 mg (64%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, *J* = 2.1 Hz, 1 H), 7.67 (d, *J* = 8.6 Hz, 1 H), 7.42 (dd, *J* = 2.2, 8.5 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 150.0, 135.9, 134.3, 133.3, 125.7, 112.5. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆H₃BrClNO₂ 234.9036; Found: 234.9033.

1,4-Dichloro-2-nitrobenzene (10c). Procedure B was followed using 4-chloro-2-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and NaCl (17.5 mg, 0.3 mmol, 1.5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 20.7 mg (54%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.^{1,10} ¹H NMR (400 MHz, CDCl₃): δ 7.87 (s, 1 H), 7.50 (d, *J* = 0.8 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 148.1, 133.5, 133.3, 132.8, 125.6, 125.5. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆H₃Cl₂NO₂ 190.9541; Found: 190.9543.

1-Chloro-2-iodo-4-nitrobenzene (11a). Procedure C was followed using 2-Chloro-5-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv) and NaI (36 mg, 0.24 mmol, 1.2 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford a mixture of the desired decarboxylative iodination product 15.8 mg (28%) and by-product 2,4-dichloro-1-nitrobenzene **9c** 14.8 mg (39%) as a white solid. Exhibited spectral data in accordance with previous report.^{11,12} 1-Chloro-2-iodo-4-nitrobenzene ¹H NMR (400 MHz, CDCl₃): δ 8.70 (s, 1 H), 8.16 (d, *J* = 8 Hz, 1 H), 7.61 (d, *J* = 8 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 135.1, 129.6, 124.1. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆H₃ClINO₂ 282.8897; Found: 282.8895. By-product 2,4-dichloro-1-nitrobenzene ¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, *J* = 8.7 Hz, 1 H), 7.58 (d, *J* = 1.8 Hz, 1 H), 7.40 (dd, *J* = 1.7, 8.7 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 131.8, 127.9, 126.7. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆H₃ClINO₂ 282.8897; Found: 282.8895.

2-Bromo-1-chloro-4-nitrobenzene (11b). Procedure C was followed using 2-chloro-5-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv) and NaBr (24.7 mg, 0.24 mmol, 1.2 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 17.0 mg (36%) of the product as a white solid. Exhibited spectral data in accordance with previous report.¹³ ¹H NMR (400 MHz, CDCl₃): δ 8.51 (s, 1 H), 8.13 (d, *J* = 8.0 Hz, 1 H), 7.64 (d, *J* = 8.0 Hz, 1 H). ¹³C NMR

(100 MHz, CDCl₃): δ 146.6, 141.8, 130.8, 128.8, 123.3, 123.2. HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₆H₃BrClNO₂ 234.9036; Found: 234.9039.

1,2-Dichloro-4-nitrobenzene (11c). Procedure C was followed using 2-chloro-5-nitrobenzoic acid (40.3 mg, 0.2 mmol), Ag₂SO₄ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv) and NaCl (14.0 mg, 0.24 mmol, 1.2 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 15.0 mg (39%) of the product as a white solid. Exhibited spectral data in accordance with previous report.¹⁴ ¹H NMR (400 MHz, CDCl₃): δ 8.51 (s, 1 H), 8.09 (d, *J* = 12.0 Hz, 1 H), 7.65 (d, *J* = 12.0 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 146.7, 139.8, 133.9, 131.0, 125.5, 122.5. HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₆H₃Cl₂NO₂ 190.9541; Found: 190.9546.

1-Iodo-2,4,5-trimethoxybenzene (12a). Procedure D was followed using 2,4,5-trimethoxybenzoic acid (42.4 mg, 0.2 mmol), Ag₂SO₄ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv) and NaI (149.9 mg, 1 mmol, 5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (10 % ether in hexane) to afford 21.8 mg (37%) of the product as a white solid. Exhibited spectral data in accordance with previous report.^{1,15} ¹H NMR (400 MHz, CDCl₃): δ 7.20 (s, 1 H), 6.51 (s, 1 H), 3.89 (s, 3 H), 3.85 (s, 3 H), 3.83 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 153.0, 150.2, 144.2, 121.8, 97.7, 72.9, 57.3, 56.7, 56.1. HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₉H₁₁IO₃ 293.9753; Found: 293.9751.

2-Iodo-1,3,5-trimethoxybenzene (13a). Procedure D was followed using 2,4,6-trimethoxybenzoic acid (42.4 mg, 0.2 mmol), Ag₂SO₄ (3.1 mg, 0.01 mmol, 0.05 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv) and NaI (149.9 mg, 1 mmol, 5 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (10 % ether in hexane) to afford 46.5 mg (79%) of the product as a white solid. Exhibited spectral data in accordance with previous report.^{1,16} ¹H NMR (400 MHz, CDCl₃): δ 6.14 (s, 2 H), 3.86 (s, 6 H), 3.83 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ 162.1, 159.8, 91.2, 66.7, 56.5, 55.5. HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₉H₁₁IO₃ 293.9753; Found: 293.9755.

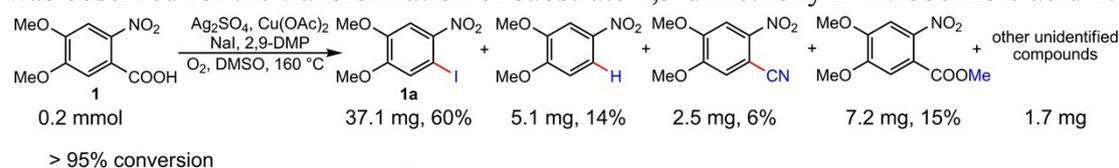
3-Chloro-2-iodobenzo[*b*]thiophene (14a). Procedure A was followed using 3-chlorobenzo[*b*]thiophene-2-carboxylic acid (42.5 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 41.2 mg (70%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 7.76 (dd, *J* = 8.0, 20.0 Hz, 2 H), 7.44 - 7.32 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 142.1, 135.8, 128.6, 125.4, 125.2, 122.0, 121.9, 78.7. HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₈H₄ClIS 293.8767; Found: 293.8771.

2-Bromo-3-chlorobenzo[*b*]thiophene (14b). Procedure B was followed using 3-chlorobenzo[*b*]thiophene-2-carboxylic acid (42.5 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaBr (30.9 mg, 0.3 mmol, 1.5equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 37.5 mg (76%) of the product as a white solid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 7.78 - 7.69 (m, 2 H), 7.50 - 7.33 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 138.0, 135.8, 125.7, 125.4, 123.3, 122.0, 121.8, 111.7. HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₈H₄BrClS 245.8906; Found: 245.8907.

2,3-Dichlorobenzo[*b*]thiophene (14c). Procedure B was followed using 3-chlorobenzo[*b*]thiophene-2-carboxylic acid (42.5 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (36.3 mg, 0.2 mmol, 1 equiv), NaCl (17.5 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 27.6 mg (68%) of the product as a white solid. Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.64 - 7.55 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 139.1, 134.5, 129.0, 126.4, 123.6, 122.9, 112.4, 105.5. HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₈H₄Cl₂S 201.9411; Found: 201.9414.

The quantitative data of mass balance for the model reaction

The model reaction was performed in an oven-dried Schlenk tube with a stir bar at 160 °C for 20 hours, which was charged with 4,5-dimethoxy-2-nitrobenzoic acid **1** (45.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv) and DMSO (4 mL) under aerobic conditions. After 20 hours of heating at the indicated temperature, the residue was purified by flash chromatography on silica gel to provide the desired iododecarboxylation product 1-iodo-4,5-dimethoxy-2-nitrobenzene **1a** 37.1 mg (60% yield) and by-products that contained protodecarboxylation 5.1 mg (14% yield), decarboxylative cyanation 2.5 mg (6% yield), methyl benzoate 7.2 mg (15% yield) and other unidentified compounds 1.7 mg. Therefore, it's more than 95% conversion was observed for the transformation of substrate 4,5-dimethoxy-2-nitrobenzoic acid **1**.



Besides the corresponding decarboxylative product, by-products containing protodecarboxylation, decarboxylative cyanation, methyl benzoate and other unidentified compounds were also detected for other aryl carboxylic acid substrate in this Ag/Cu-mediated decarboxylative halogenation protocol.

Gram-scale synthesis of 4-chloro-1-iodo-2-nitrobenzene 10a

Procedure A was followed using 4-chloro-2-nitrobenzoic acid (1.21 g, 6 mmol), Ag₂SO₄ (187.2 mg, 0.6 mmol, 0.1 equiv), Cu(OAc)₂ (654 mg, 3.6 mmol, 0.6 equiv), NaI (1.35 g, 9 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (375 mg, 1.8 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford product **10a** (1.20 g, 71%) as a yellow solid.

Three-step synthesis of iniparib 16

1) Decarboxylative iodination of 4-methyl-2-nitrobenzoic acid 4 with NaI under standard conditions

Procedure A was followed using 4-methyl-2-nitrobenzoic acid (36.2 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The reaction mixtures were purified by flash column chromatography on silica gel (1% ether in hexane) to afford 27.9 mg (53%) of the product as a yellow solid.

2) Oxidation of 4-methyl-2-nitrobenzoic acid 4a to 4-iodo-3-nitrobenzoic acid 15 by CrO₃/ H₅IO₆ under mild conditions¹⁷

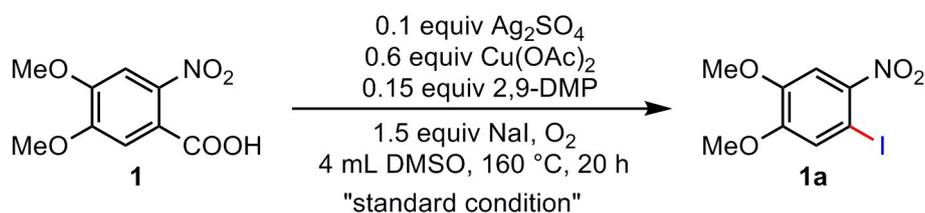
An oven-dried Schlenk tube equipped with a stir bar was charged with 4-methyl-2-nitrobenzoic acid **4a** (168.6 mg, 0.6 mmol), CrO₃ (30 mg, 0.3 mmol, 0.5 equiv), H₅IO₆ (34.2 mg, 0.3 mmol, 0.5 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, CH₃CN (5 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 60 °C for overnight, and then cooled down to room temperature. The reaction mixtures were purified by flash column chromatography on silica gel (2% methanol in dichloromethane) to afford 40.3 mg (23%) of the product (**15**) as a yellow solid. Exhibited spectral data in accordance with previous report.¹⁸ ¹H NMR (400 MHz, DMSO-d₆): δ 8.32 (s, 1 H), 8.26 (d, *J* = 8.1 Hz, 1 H), 7.86 (d, *J* = 8.1 Hz, 1 H); ¹³C NMR (100 MHz, DMSO-d₆): δ 165.6, 153.7, 142.4, 133.8, 132.6, 125.6, 94.4. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₇H₄INO₄ 292.9185; Found: 292.9183.

3) Conversion of 4-iodo-3-nitrobenzoic acid 15 to iniparib 16¹⁹

An oven-dried Schlenk tube equipped with a stir bar was charged with 4-iodo-3-nitrobenzoic acid **15** (58.6 mg, 0.2 mmol), thionyl chloride (0.05 mL, 0.7 mmol, 3.5 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with nitrogen three times. Under nitrogen, toluene (2.0 mL)/ THF (1.0 mL) were added via syringes. The mixture was heated to 80 °C for 2 h. After 2 h, the reaction was allowed to cool, solvents and thionyl chloride were removed under vacuum.

Subsequently, solution of ammonium hydroxide (30% as NH₃, 0.6 mL, 9.0 equiv) and THF (2.0 mL) were added into the tube with *in situ* generated acyl chloride via syringes, and the reaction was allowed to stir for 1 h under nitrogen. The phases were separated and the aqueous layer was extracted with ethyl acetate. The organic phases were combined and purified by flash column chromatography on silica gel (ether) to afford 36.2 mg (62%) of the product (**16**) as a yellow solid. Exhibited spectral data in accordance with previous report.¹⁹ ¹H NMR (400 MHz, DMSO-d₆): δ 7.71 (s, 1 H), 7.85 (dd, *J* = 2.0, 8.5, 1 H), 8.22 (d, *J* = 8.5, 1 H), 8.24 (s, 1 H), 8.35 (d, *J* = 2.0, 1 H); ¹³C NMR (100 MHz, DMSO-d₆): δ 165.7, 153.7, 142.0, 135.8, 132.5, 124.1, 92.3. HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₇H₅IN₂O₃ 291.9345; Found: 291.9345.

Experiments to understand reaction mechanism



Entry	Change of standard conditions	Isolated yield (%)
1	none [entry 15, Table 1]	60
2	0.75 equiv I ₂ [instead of NaI]	0
3	0.75 equiv I ₂ [instead of NaI, no Ag/Cu]	0
4	1 equiv K ₃ PO ₄ , 2 equiv I ₂ , 1 mL CH ₃ CN, 100 °C [instead of standard condition]	0
5	no Ag	39
6	no Cu	0
7	2 equiv TEMPO was added as radical scavenger	9
8	2 equiv BHT was added as radical scavenger	5

1) Decarboxylative iodination of 4,5-dimethoxy-2-nitrobenzoic acid **1** with I₂ in the presence of Ag/Cu (entry 2, Table 2)

An oven-dried Schlenk tube equipped with a stir bar was charged with 4,5-dimethoxy-2-nitrobenzoic acid **1** (45.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), I₂ (38.1 mg, 0.15 mmol, 0.75 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time, and then cooled down to room temperature. However, no product was detected via thin layer chromatography (TLC).

2) Decarboxylative iodination of 4,5-dimethoxy-2-nitrobenzoic acid 1 with I₂ in the absence of Ag/Cu (entry 3, Table 2)

An oven-dried Schlenk tube equipped with a stir bar was charged with 4,5-dimethoxy-2-nitrobenzoic acid **1** (45.4 mg, 0.2 mmol), I₂ (38.1 mg, 1.5 mmol, 0.75 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time, and then cooled down to room temperature. However, no product was detected via thin layer chromatography (TLC).

3) Decarboxylative iodination of 4,5-dimethoxy-2-nitrobenzoic acid 1 under Larrosa's metal-free iododecarboxylation condition²⁰ (entry 4, Table 2)

A oven-dried Schlenk tube equipped with a stir bar was charged with I₂ (101.5 mg, 0.4 mmol, 2 equiv), capped and flushed with N₂. The tube was transferred to a glove box, then 4,5-dimethoxy-2-nitrobenzoic acid **1** (45.4 mg, 0.2 mmol), anhydrous K₃PO₄ (42.4 mg, 0.2 mmol, 1 equiv) and anhydrous MeCN (1 mL) were added. The tube was capped, transferred out of the glove box and stirred at 100 °C for 20 hours, and then cooled down to room temperature. However, no product was detected via TLC.

4) Cu-Catalyzed decarboxylative iodination of 4,5-dimethoxy-2-nitrobenzoic acid 1 with NaI in the absence of Ag (entry 5, Table 2)

An oven-dried Schlenk tube equipped with a stir bar was charged with 4,5-dimethoxy-2-nitrobenzoic acid **1** (45.4 mg, 0.2 mmol), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time, and then cooled down to room temperature. The reaction mixtures were purified by flash column chromatography on silica gel (10% ether in hexane) to afford 24.1 mg (39%) of the product as a yellow solid.

5) Ag-Catalyzed decarboxylative iodination of 4,5-dimethoxy-2-nitrobenzoic acid 1 with NaI in the absence of Cu (entry 6, Table 2)

An oven-dried Schlenk tube equipped with a stir bar was charged with 4,5-dimethoxy-2-nitrobenzoic acid **1** (45.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), NaI (45 mg, 0.3 mmol, 1.5 equiv) and 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced

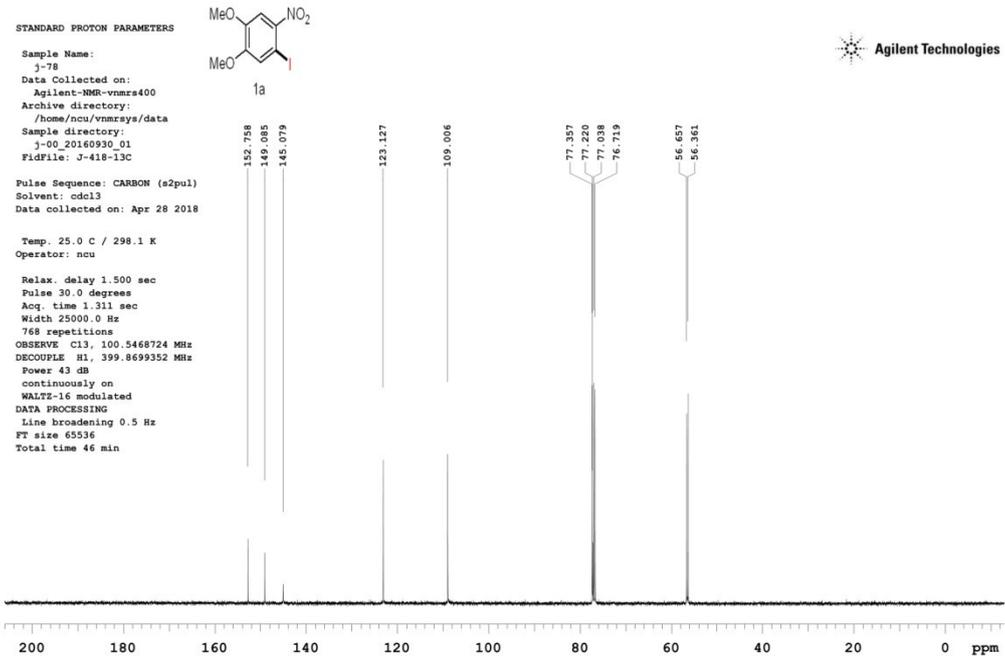
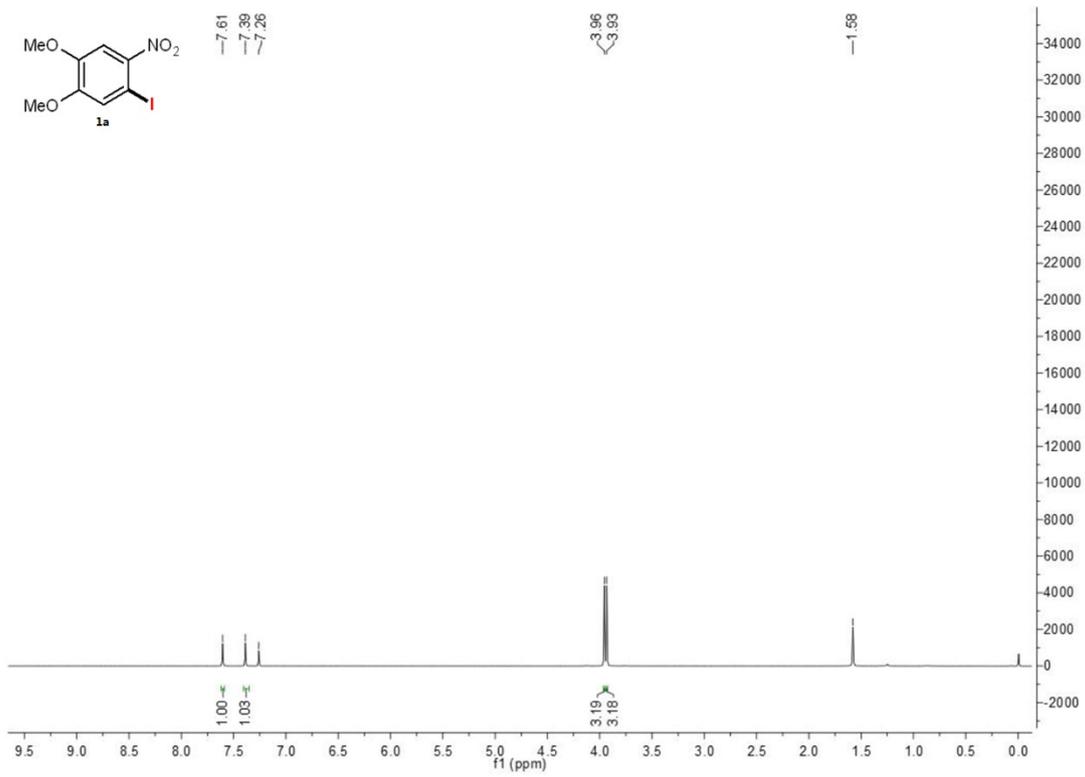
with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time, and then cooled down to room temperature. However, no product was detected via thin layer chromatography (TLC).

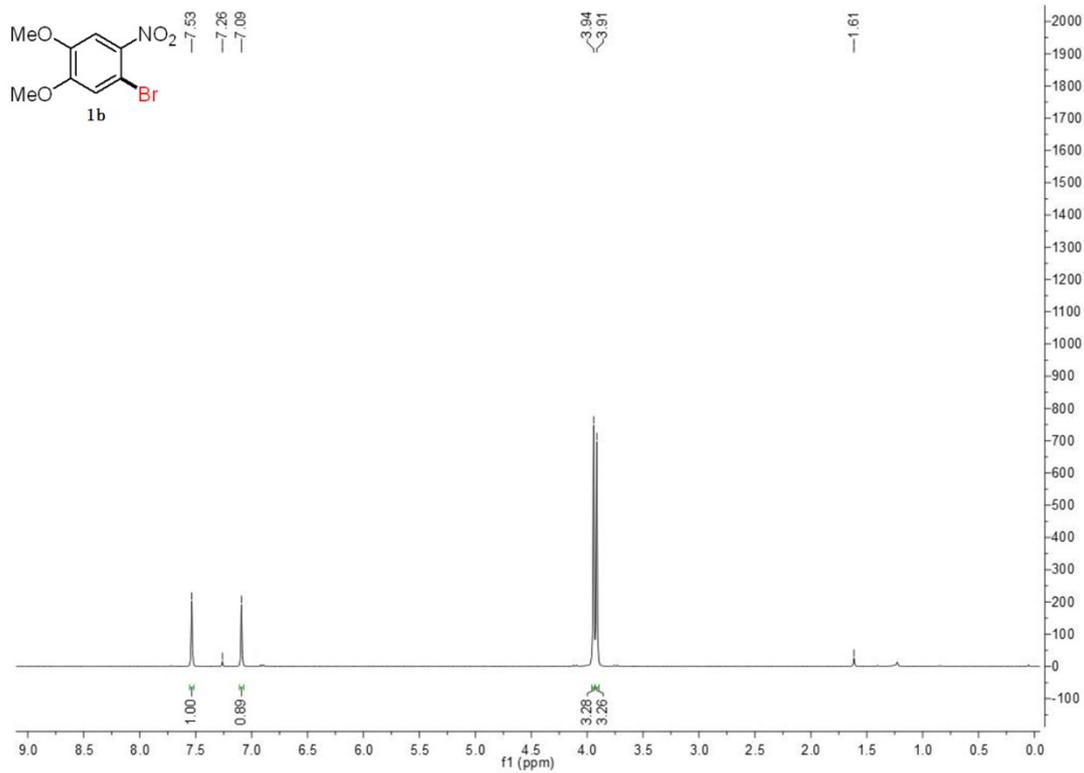
6) The model reaction with radical scavenger (entries 7 and 8, Table 2)

An oven-dried Schlenk tube equipped with a stir bar was charged with 4,5-dimethoxy-2-nitrobenzoic acid **1** (45.4 mg, 0.2 mmol), Ag₂SO₄ (6.2 mg, 0.02 mmol, 0.1 equiv), Cu(OAc)₂ (21.8 mg, 0.12 mmol, 0.6 equiv), NaI (45 mg 0.3 mmol, 1.5 equiv), 2,9-dimethyl-1,10-phenanthroline (12.5 mg, 0.06 mmol, 0.3 equiv), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv) or BHT (88.1 mg, 0.4 mmol, 2.0 equiv). The tube was fitted with a rubber septum, and then it was evacuated and refilled with dioxygen three times. Under dioxygen, DMSO (4 mL) was added via syringe. The rubber septum was replaced with a Teflon screwcap under dioxygen flow, and the Schlenk tube was pressurized to 1 atm. With stirring, the reaction mixtures were heated at 160 °C for the indicated amount of time (unless otherwise specified), and then cooled down to room temperature. The resultant mixture was filtered through a short plug of silica gel and then concentrated in vacuo. The residue was then purified by flash chromatography on silica gel to provide the corresponding product **1a**.

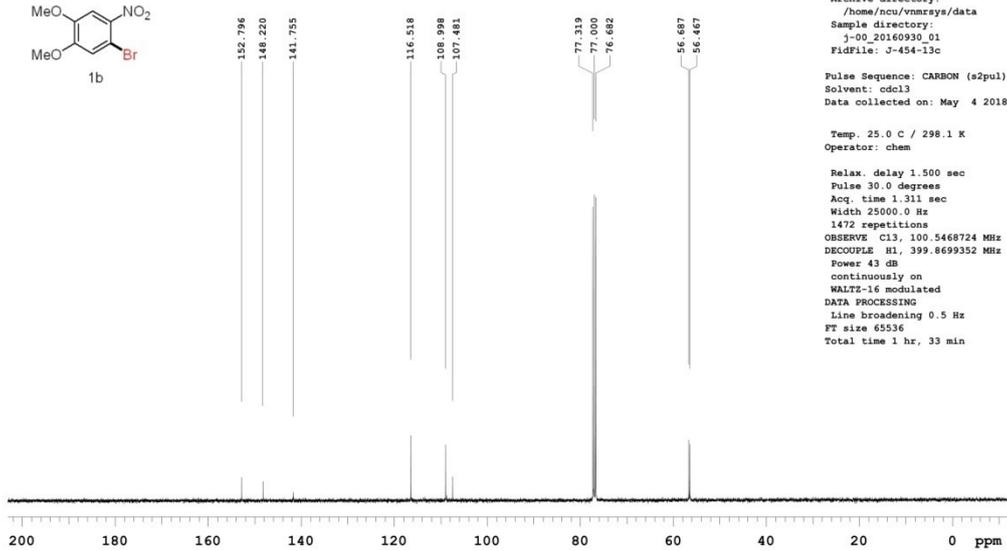
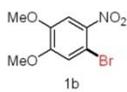
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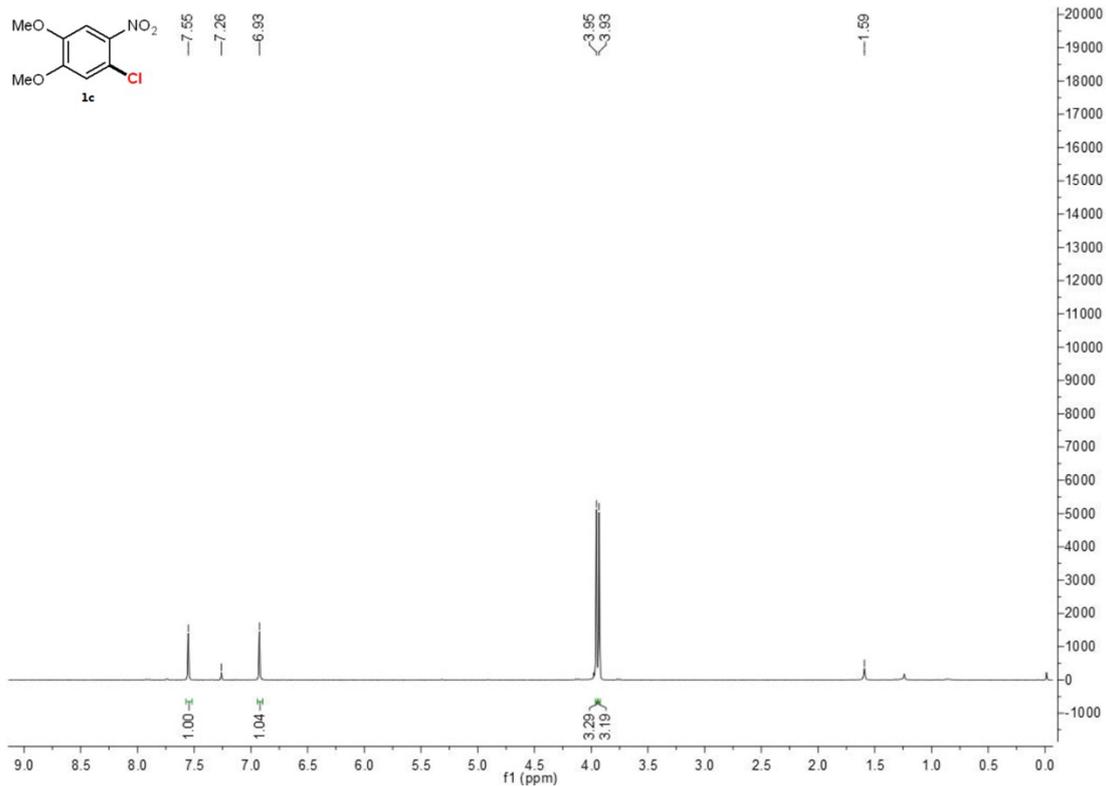


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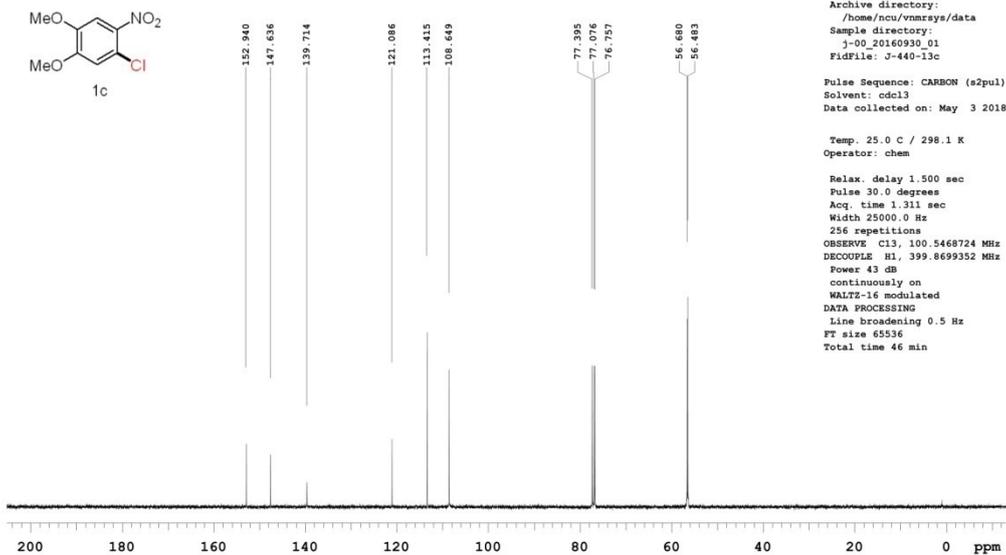
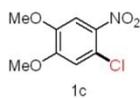


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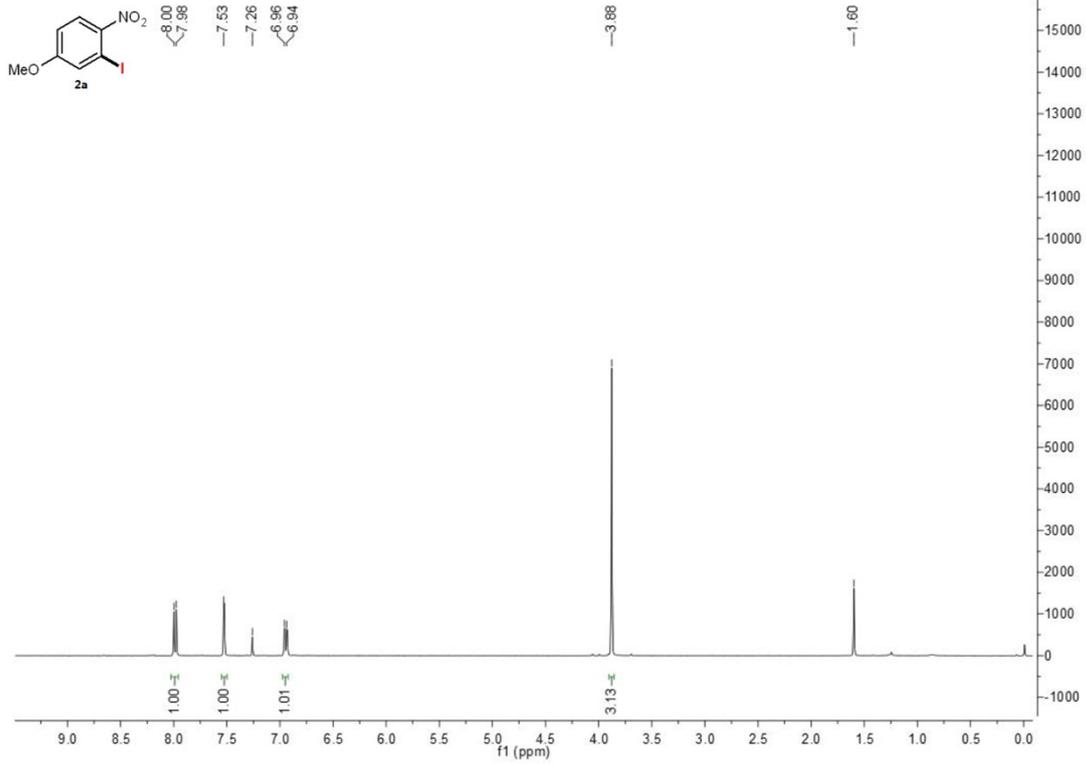


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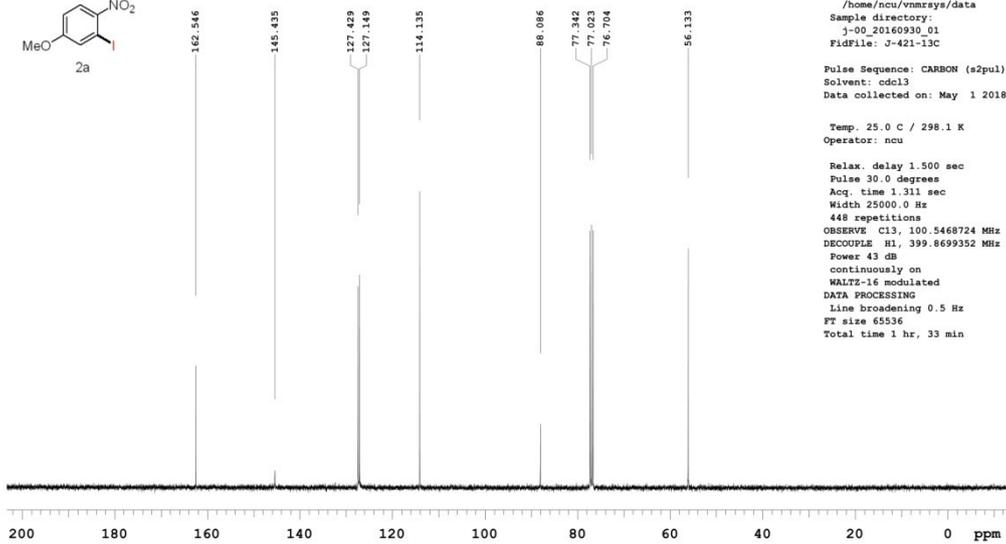
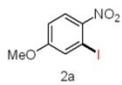


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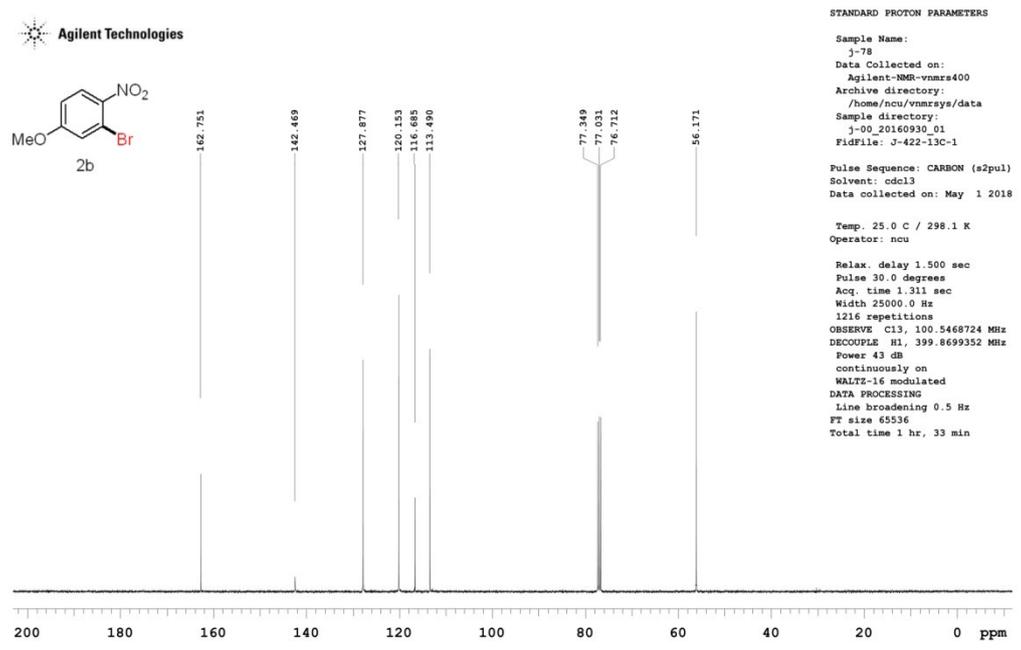
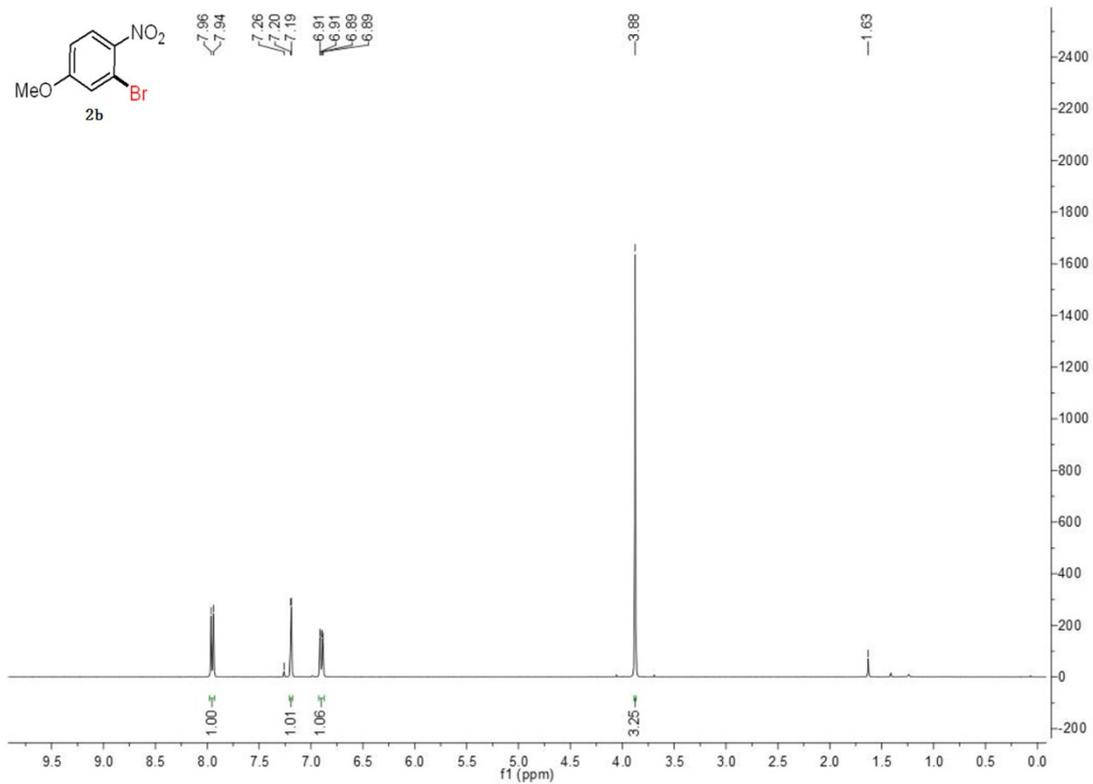


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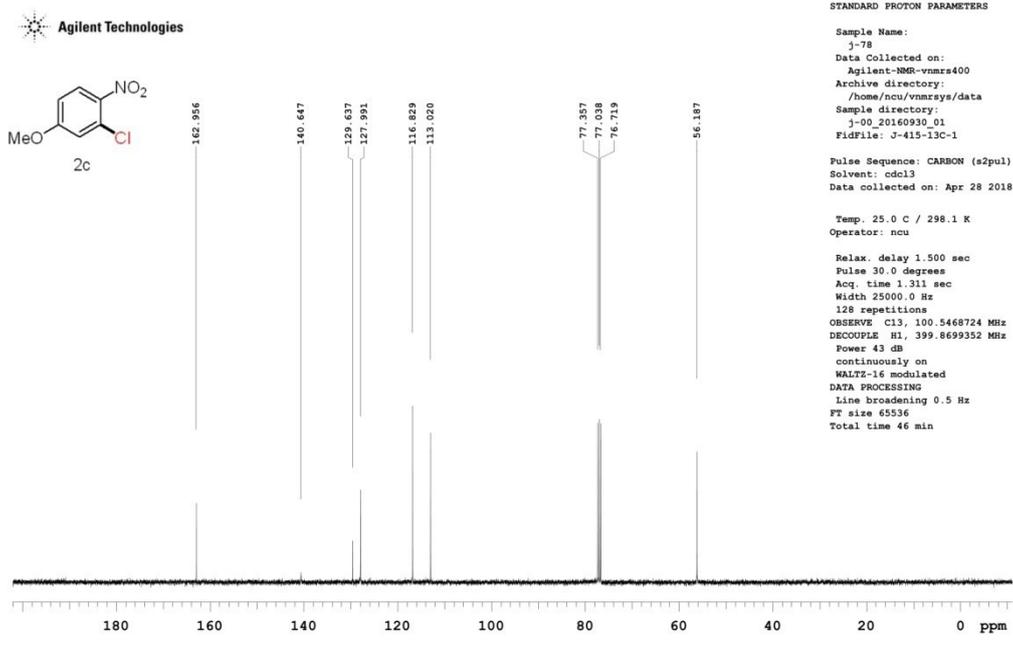
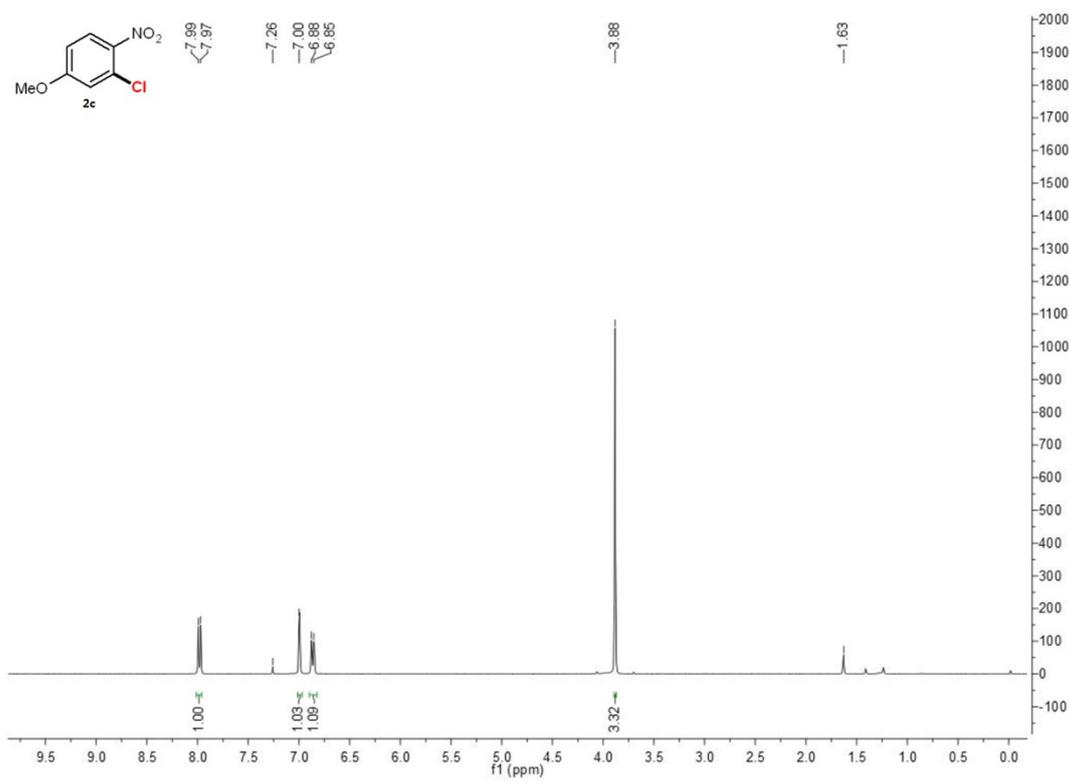
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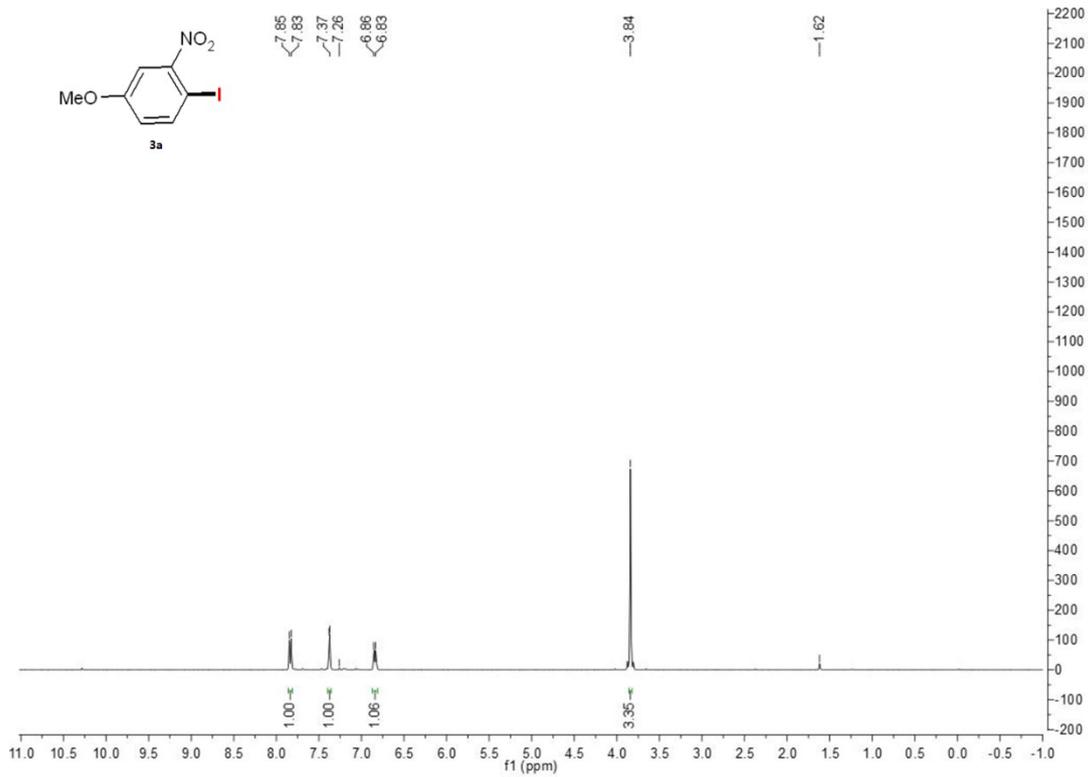
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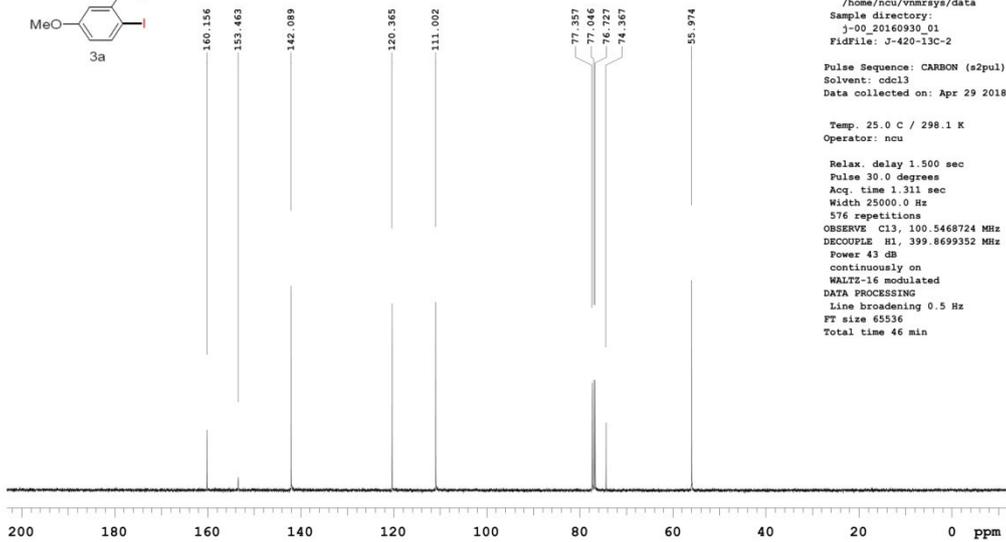
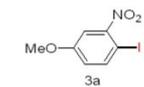
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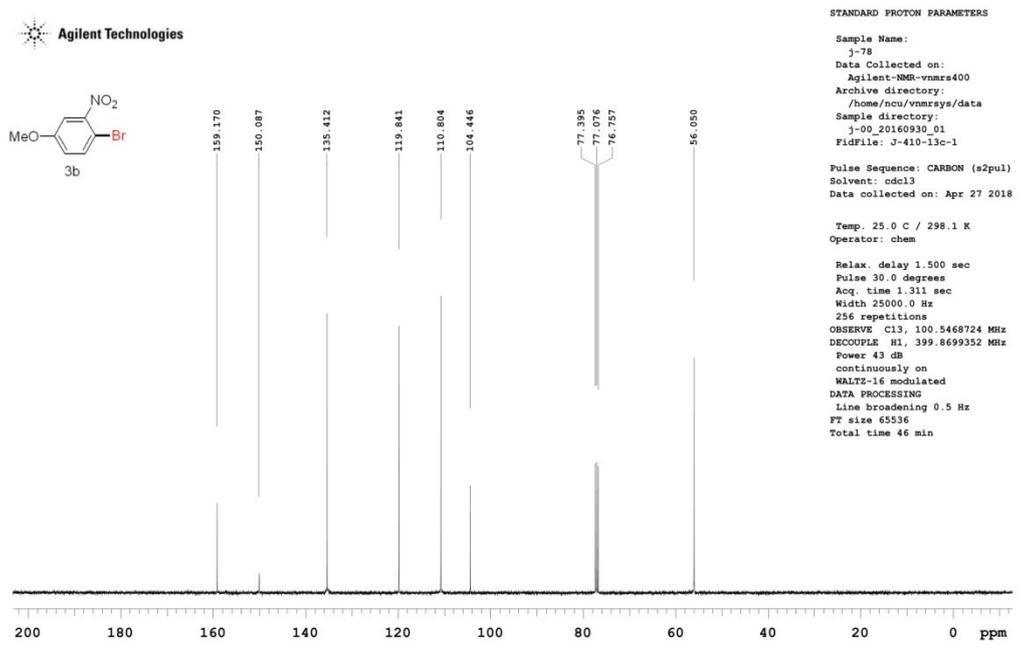
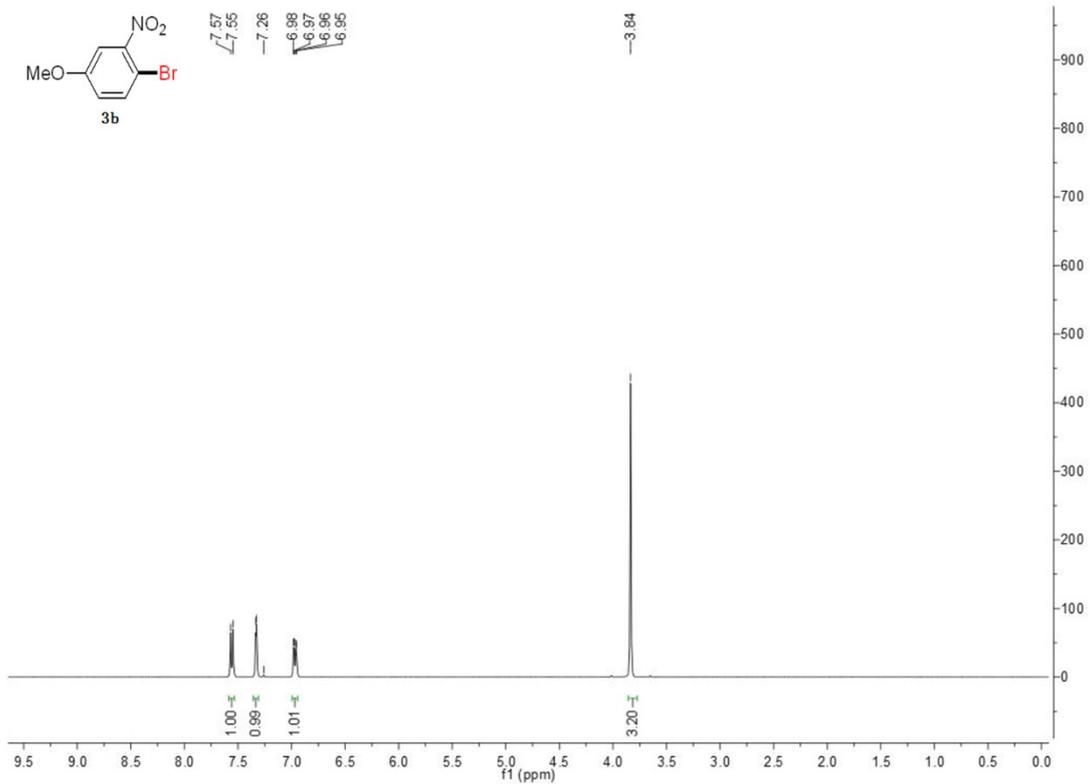
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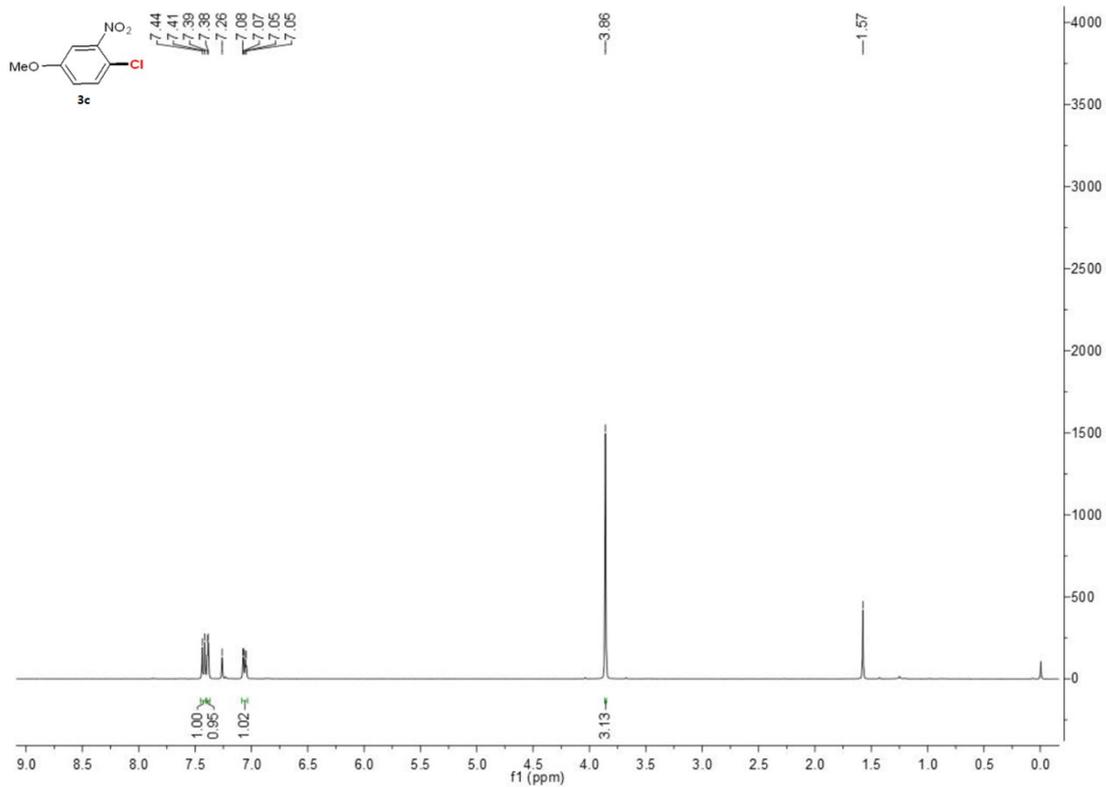




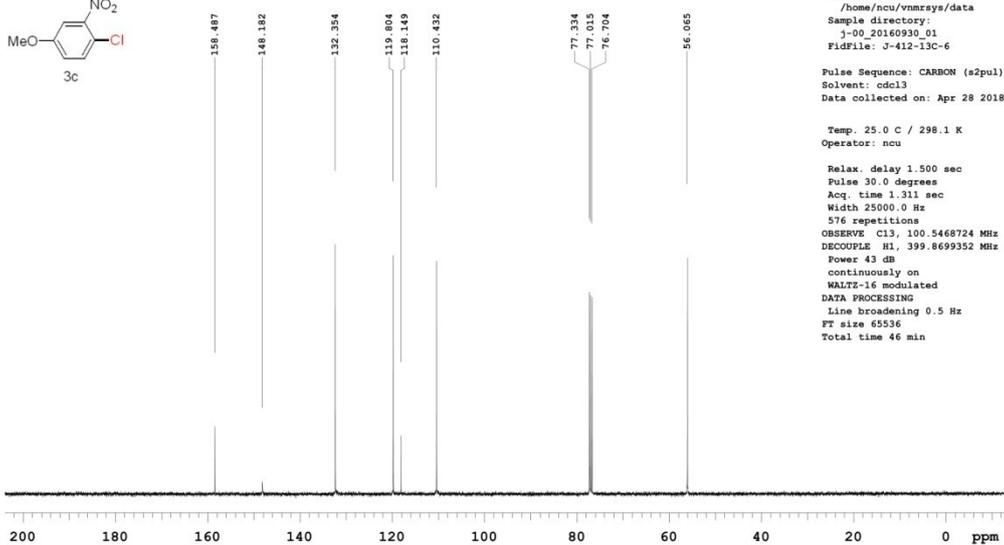
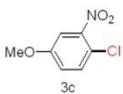
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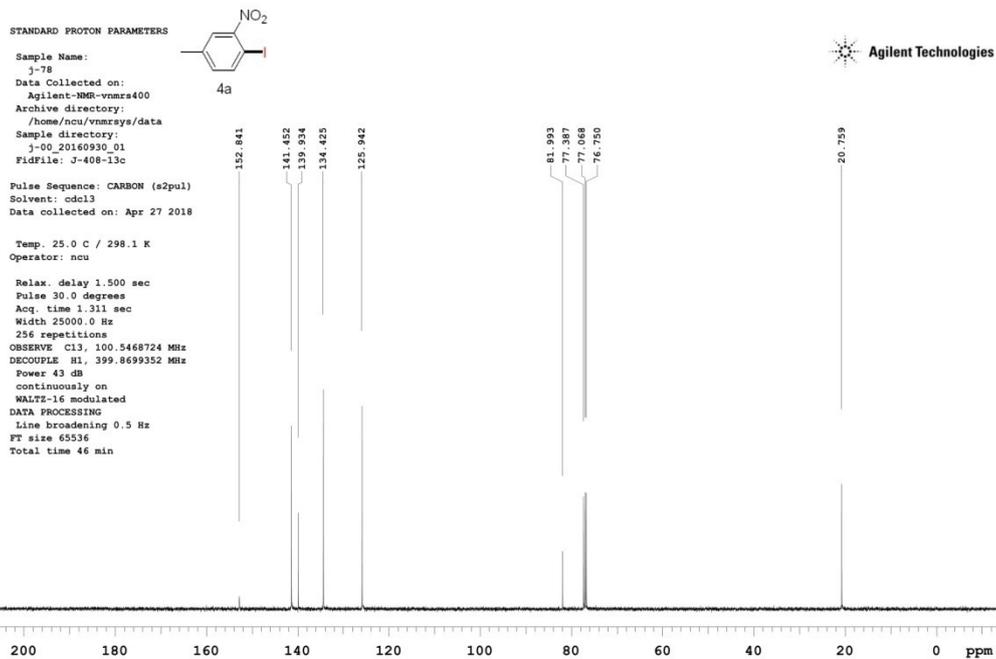
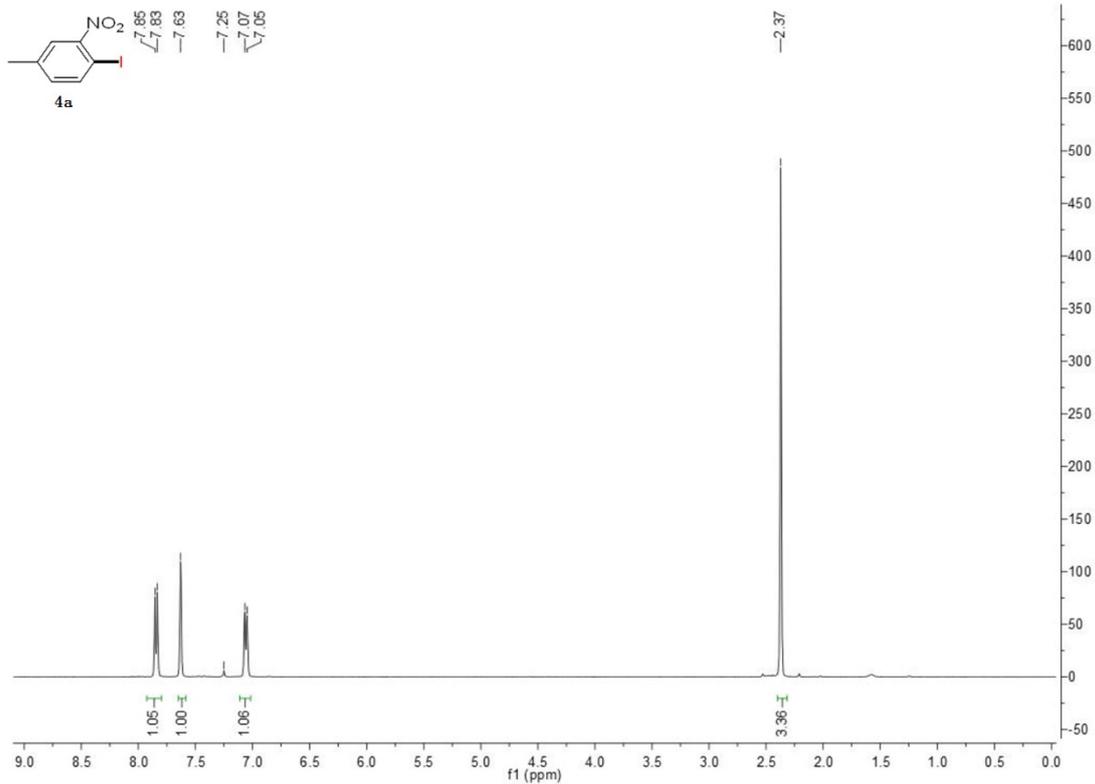
STANDARD PROTON PARAMETERS

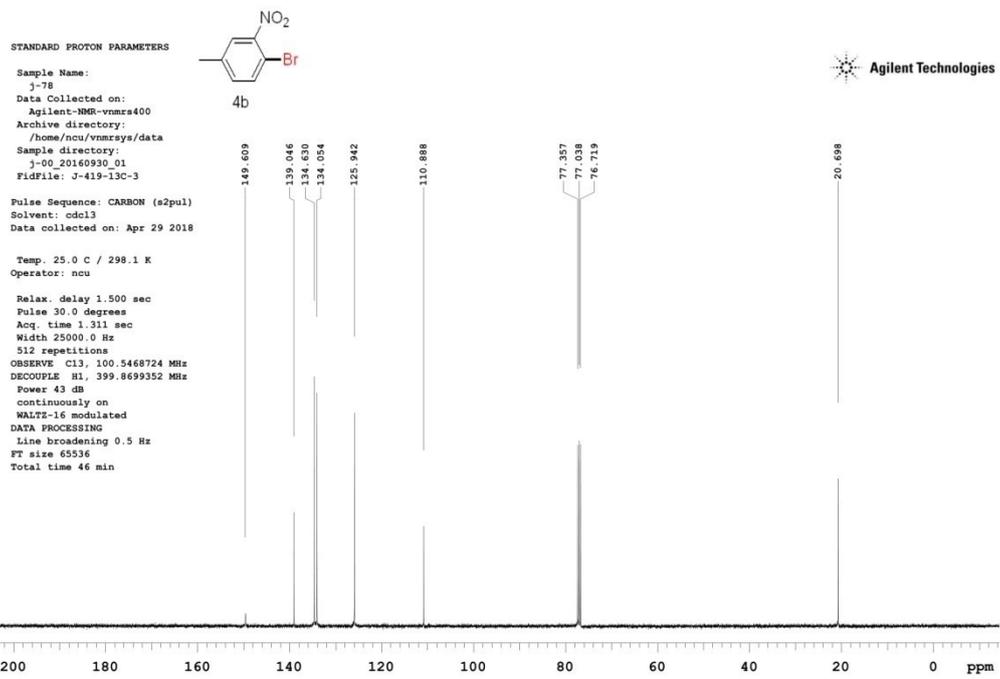
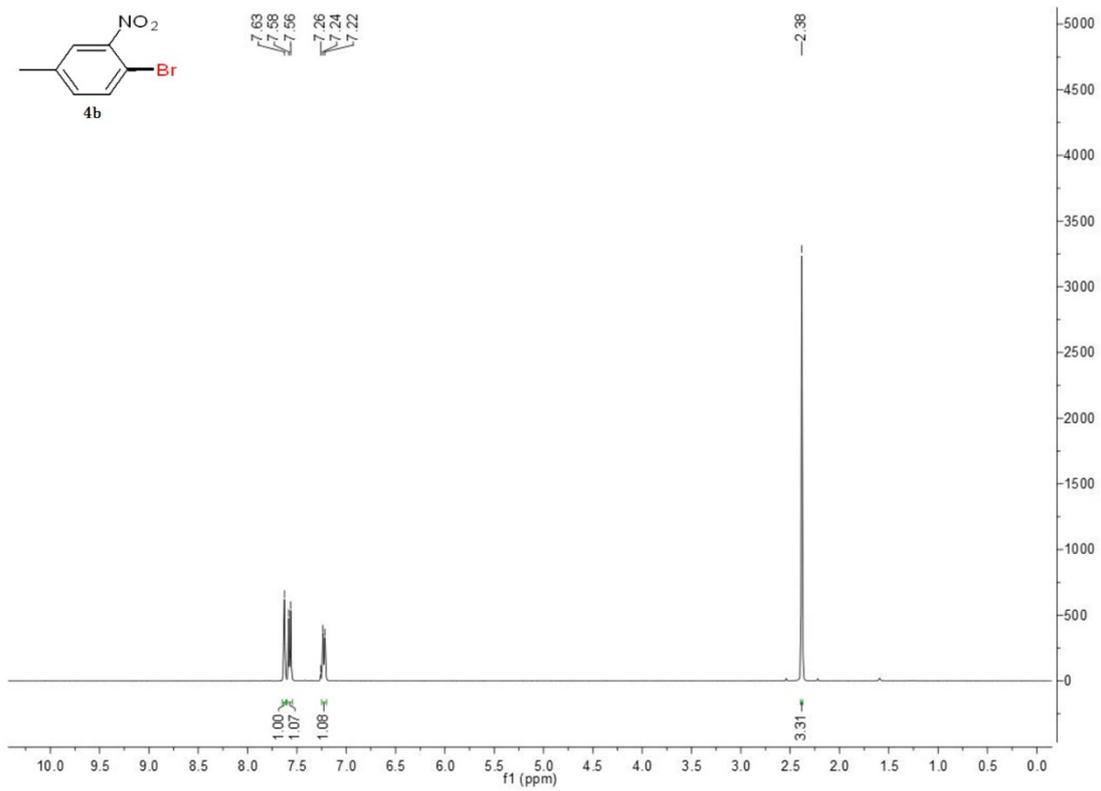
Sample Name: j-78
 Data Collected on: Agilent-NMR-vnmrs400
 Archive directory: /home/ncu/vnmrsys/data
 Sample directory: j-00_20160930_01
 FidFile: J-412-13C-6

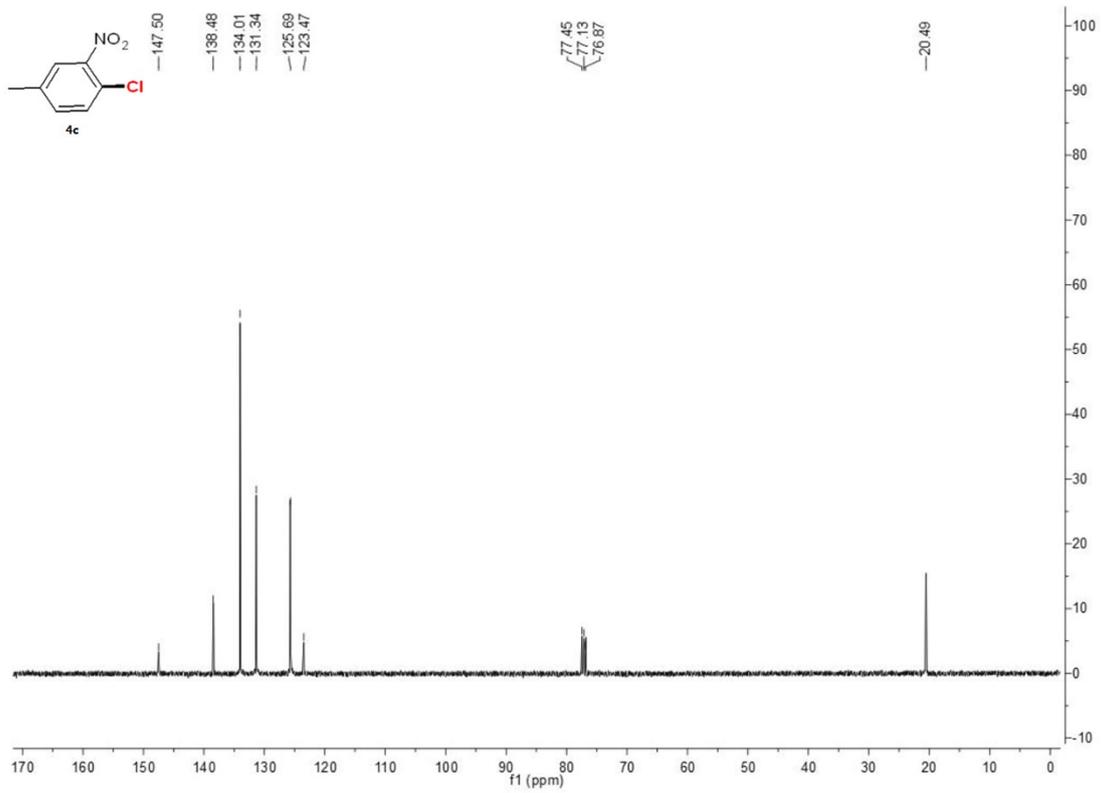
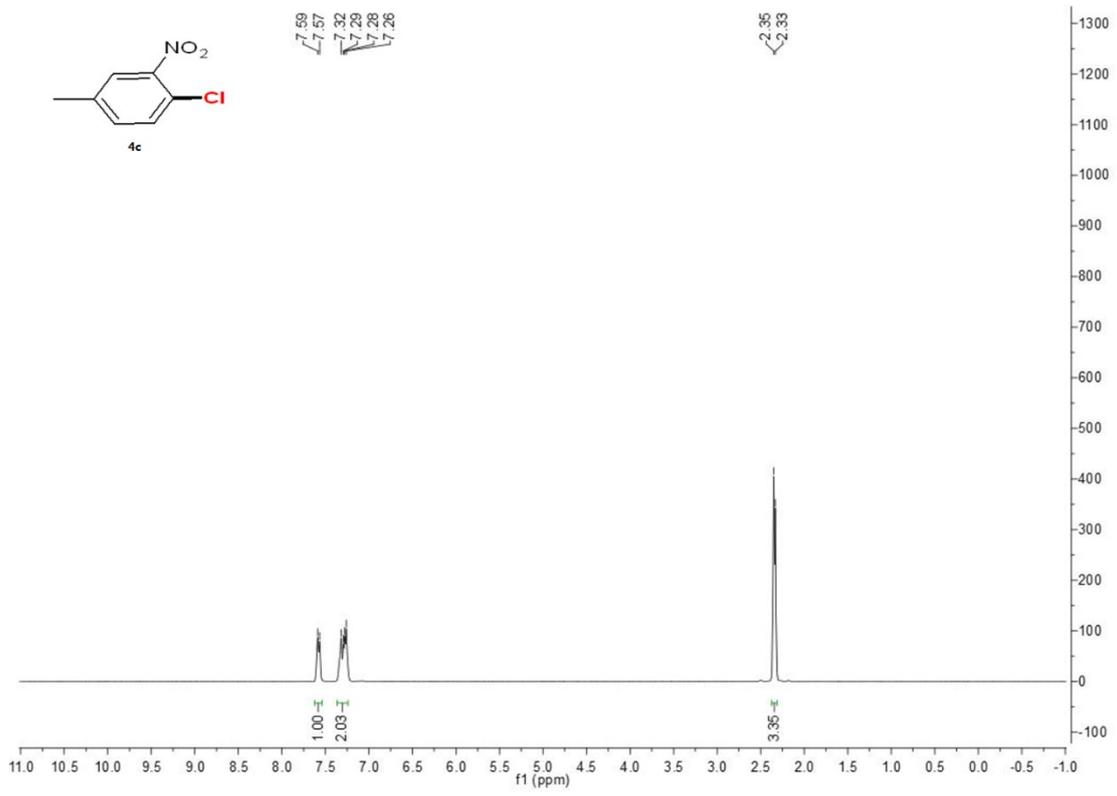
Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Apr 28 2018

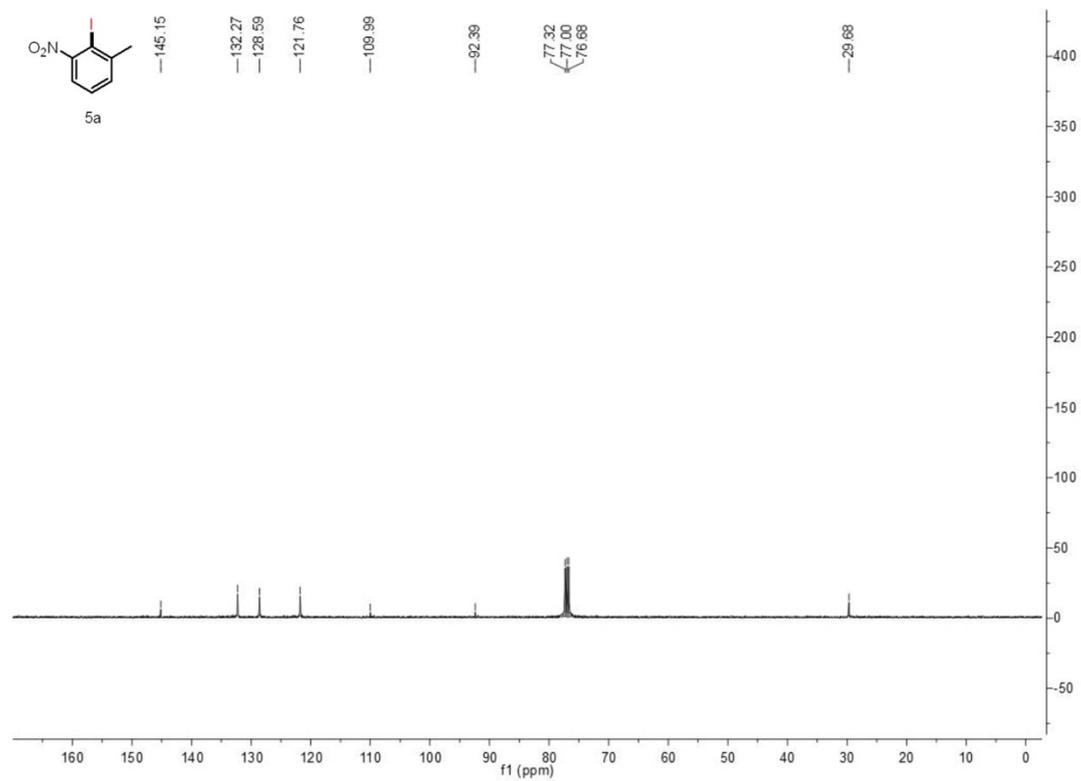
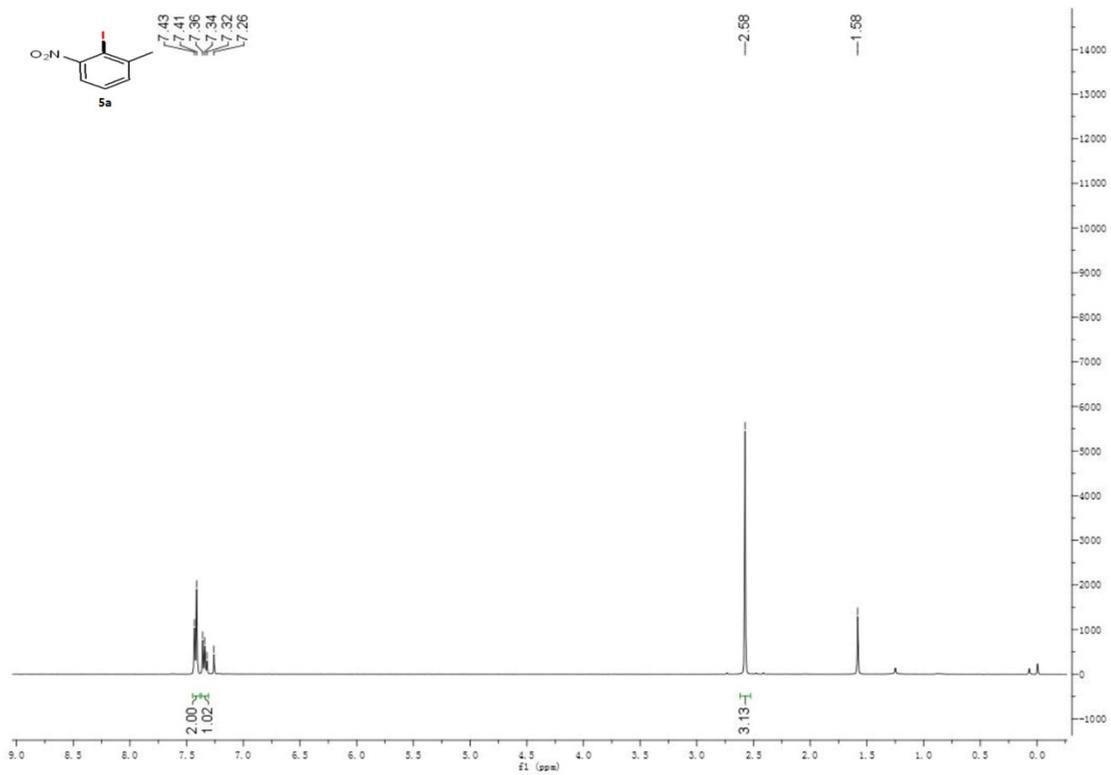
Temp. 25.0 C / 298.1 K
 Operator: ncu

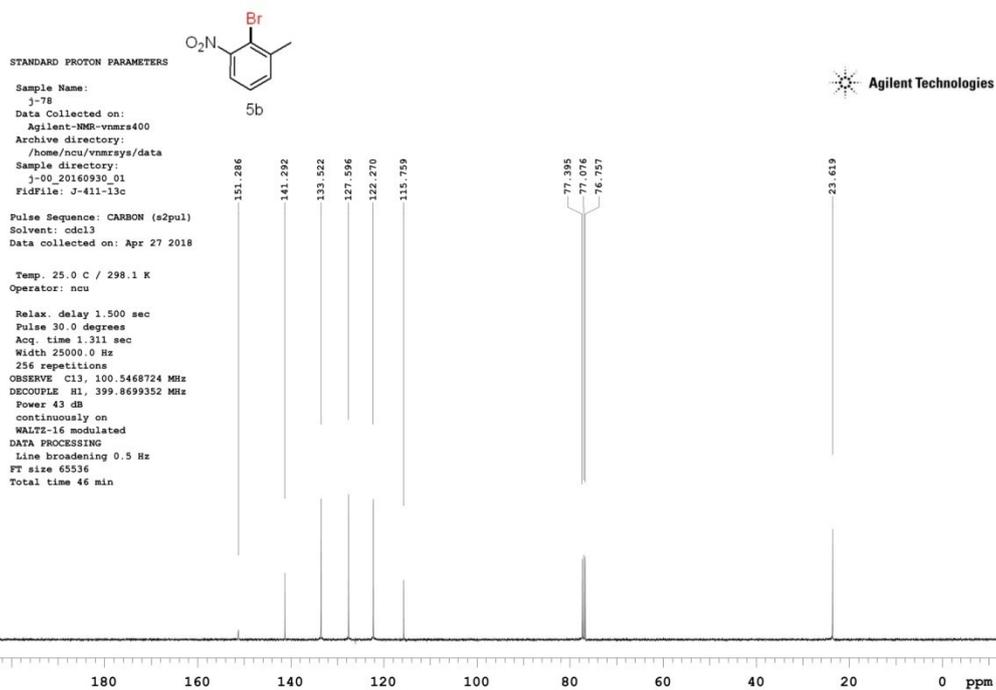
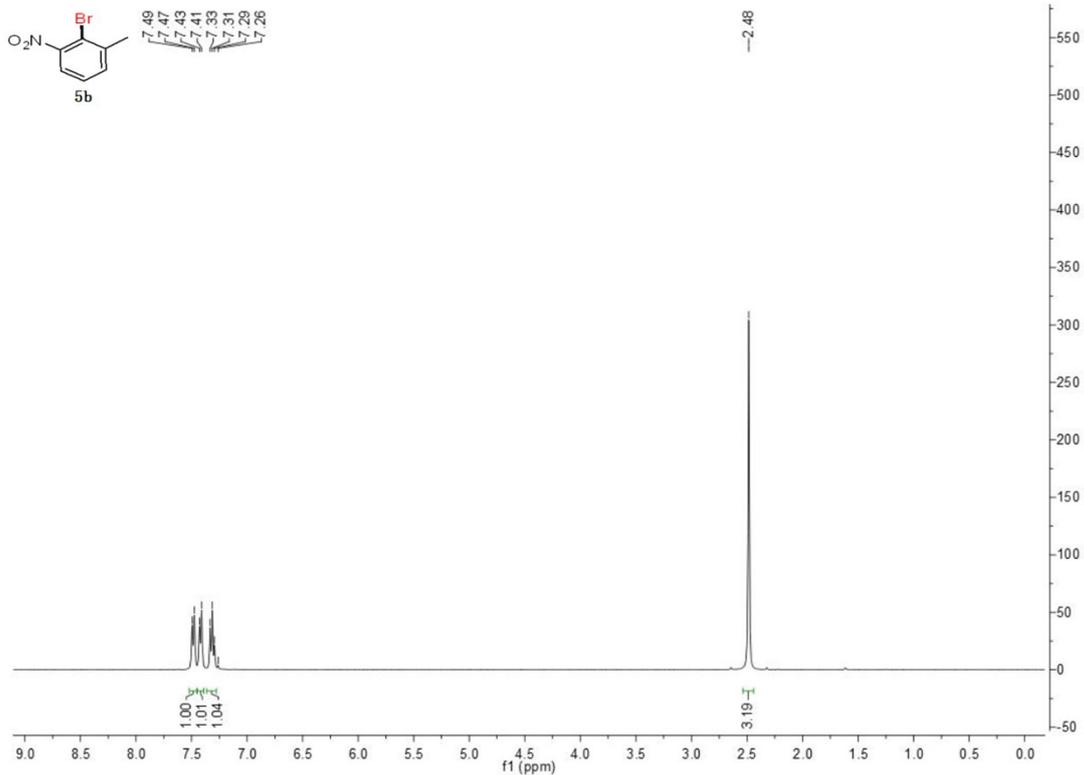
Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 576 repetitions
 OBSERVE C13, 100.5468724 MHz
 DECOUPLE H1, 399.8699352 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 46 min

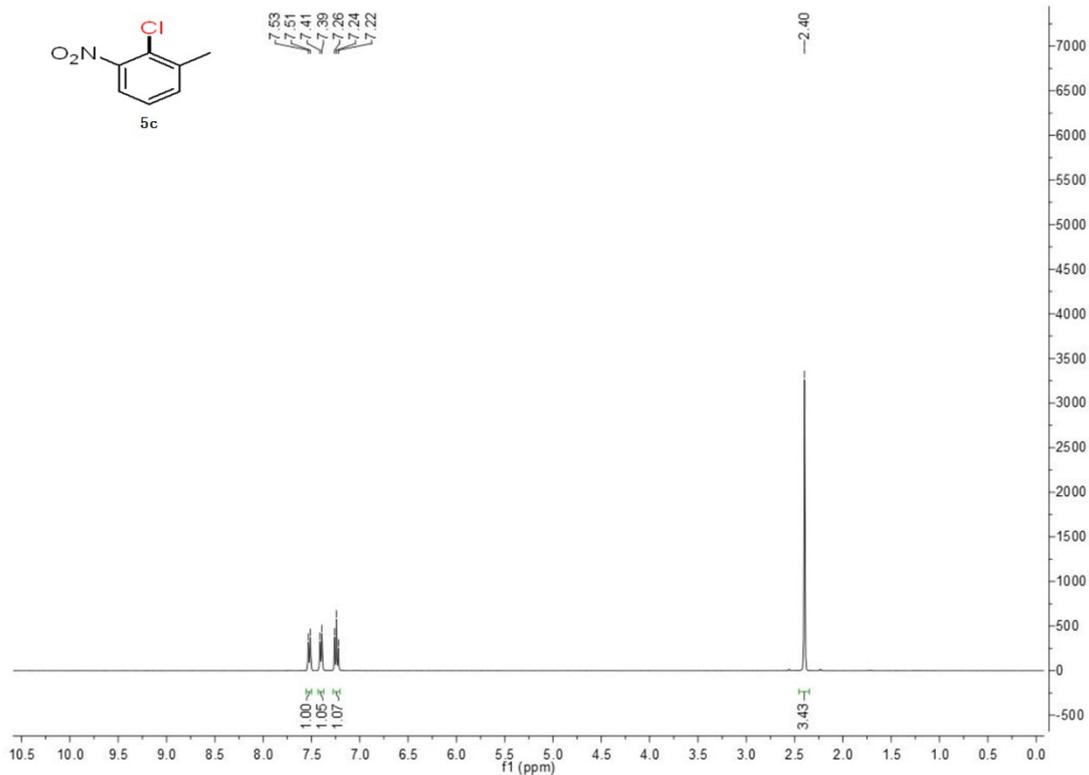






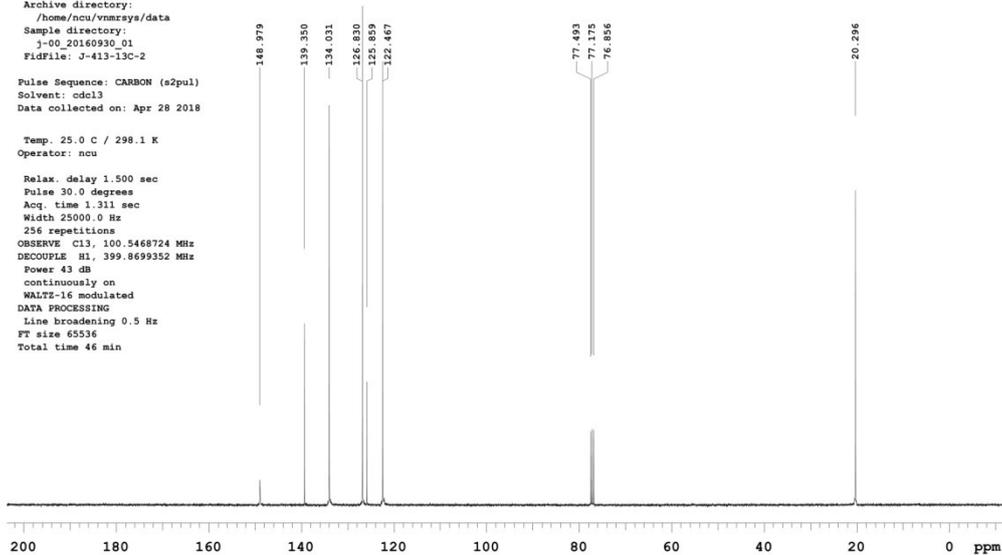
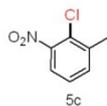


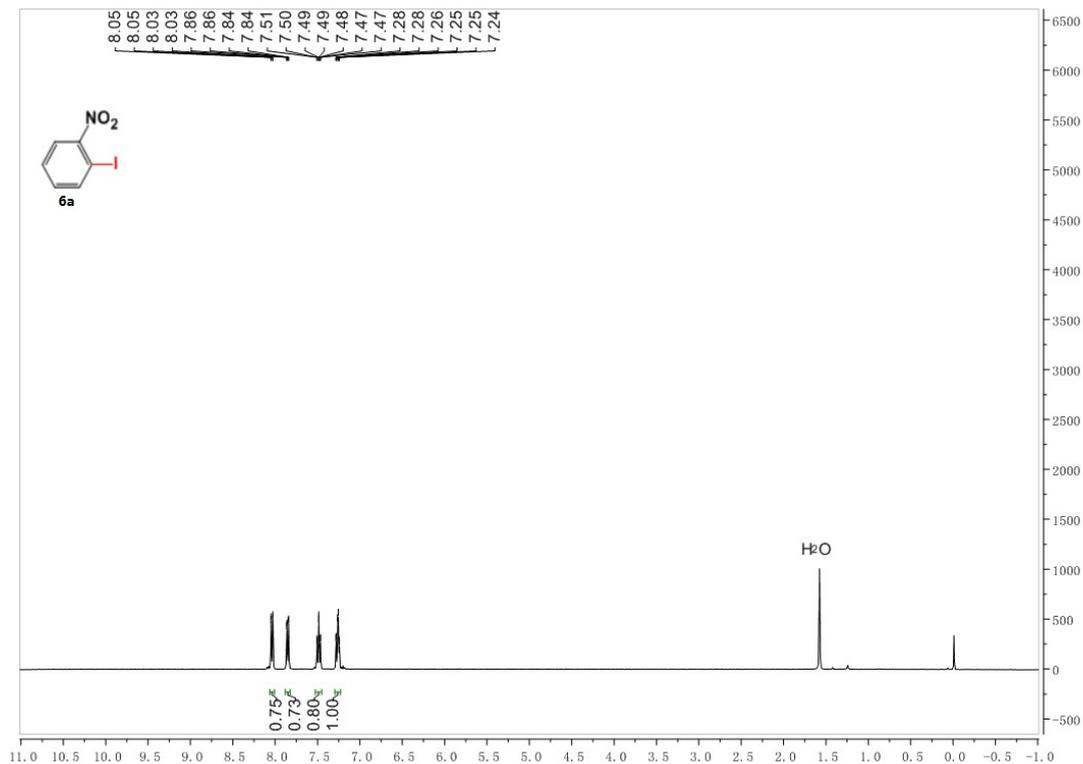




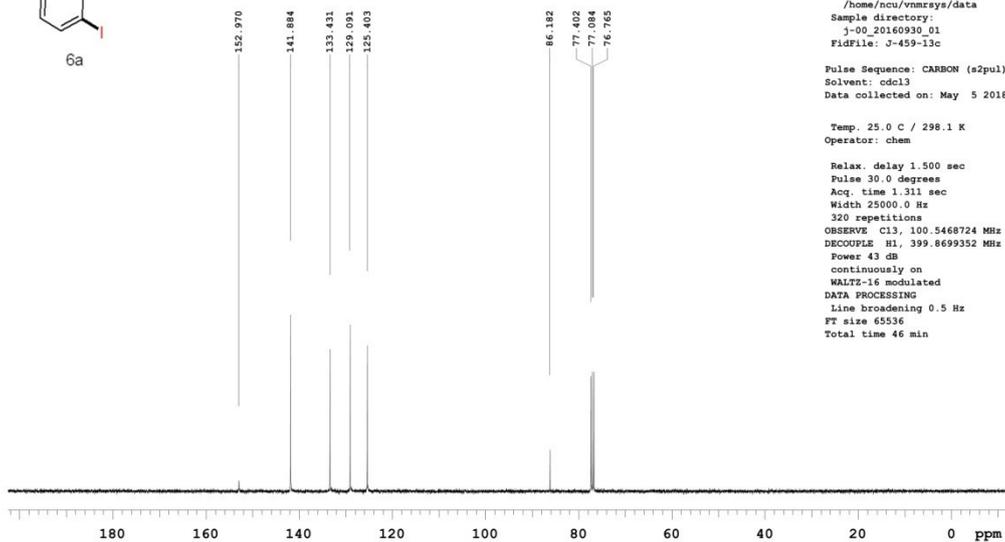
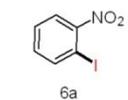
STANDARD PROTON PARAMETERS

Sample Name: j-78
 Data Collected on: Agilent-NMR-vnmrs400
 Archive directory: /home/ncu/vnmrsys/data
 Sample directory: j-00_20160930_01
 FidFile: J-413-13C-2
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Apr 28 2018
 Temp. 25.0 C / 298.1 K
 Operator: ncu
 Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 256 repetitions
 OBSERVE C13, 100.5468724 MHz
 DECOUPLE H1, 399.8699352 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 46 min





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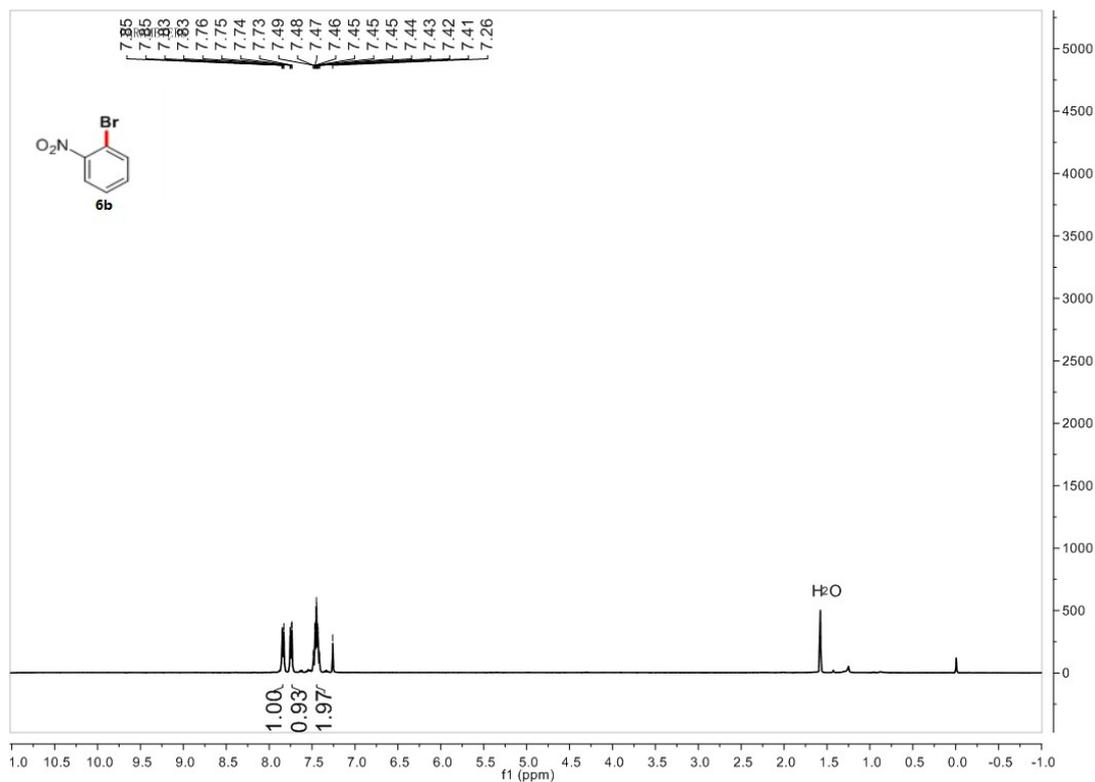
STANDARD PROTON PARAMETERS

Sample Name: j-78
 Data Collected on: Agilent-NMR-vnmr400
 Archive directory: /home/ncu/vnmrsys/data
 Sample directory: j-00_20160930_01
 Fidfile: J-459-13c

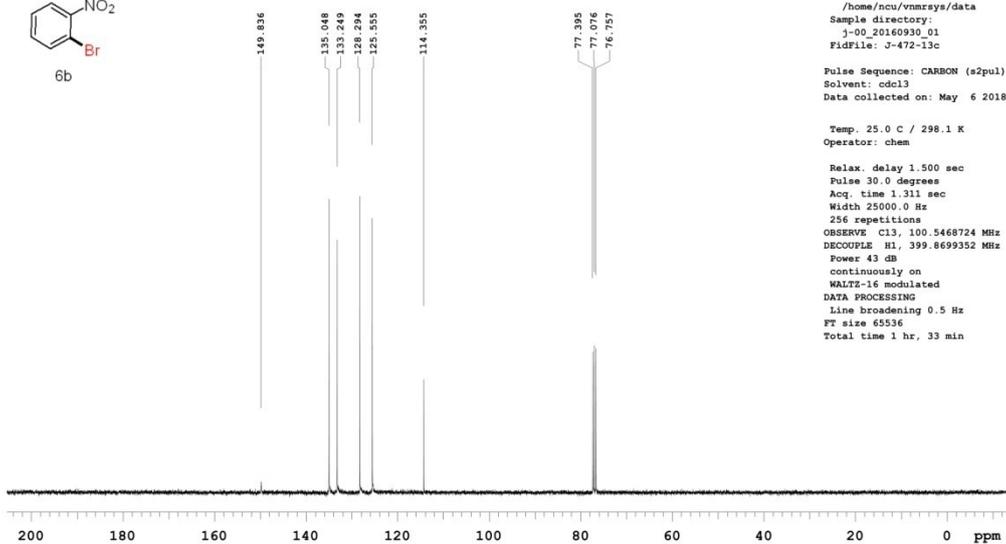
Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: May 5 2018

Temp. 25.0 C / 298.1 K
 Operator: chem

Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 320 repetitions
 OBSERVE C13, 100.5468724 MHz
 DECOUPLE H1, 399.8699352 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 46 min

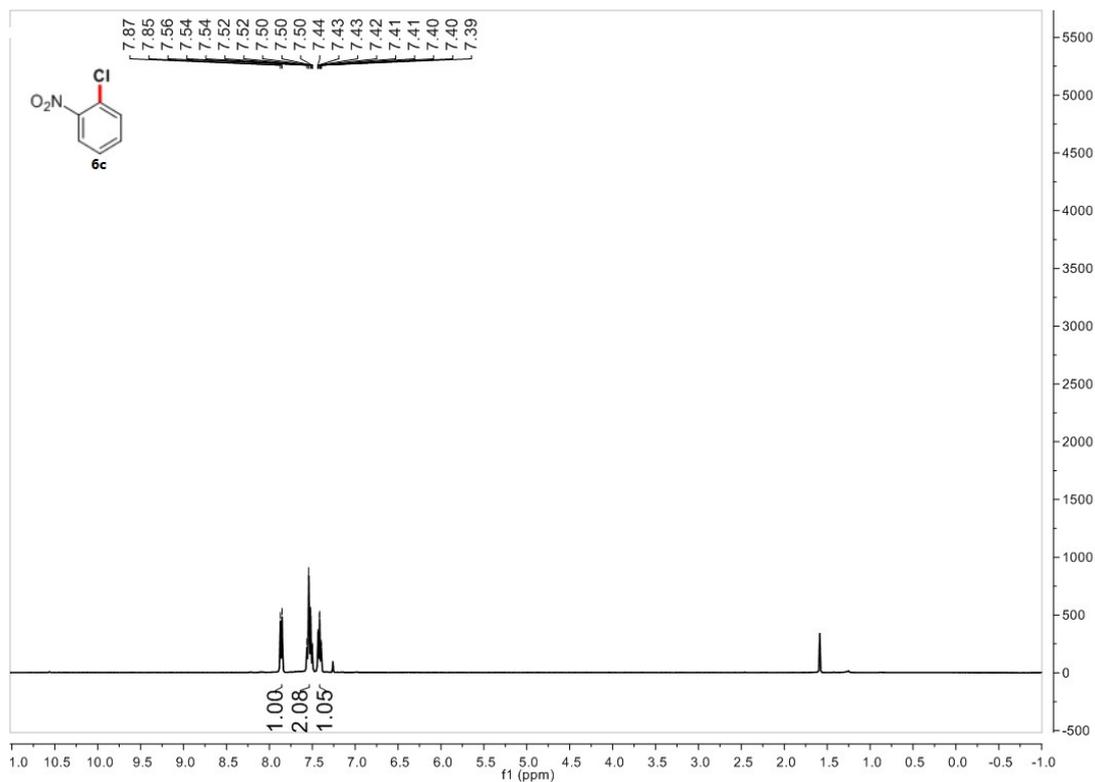


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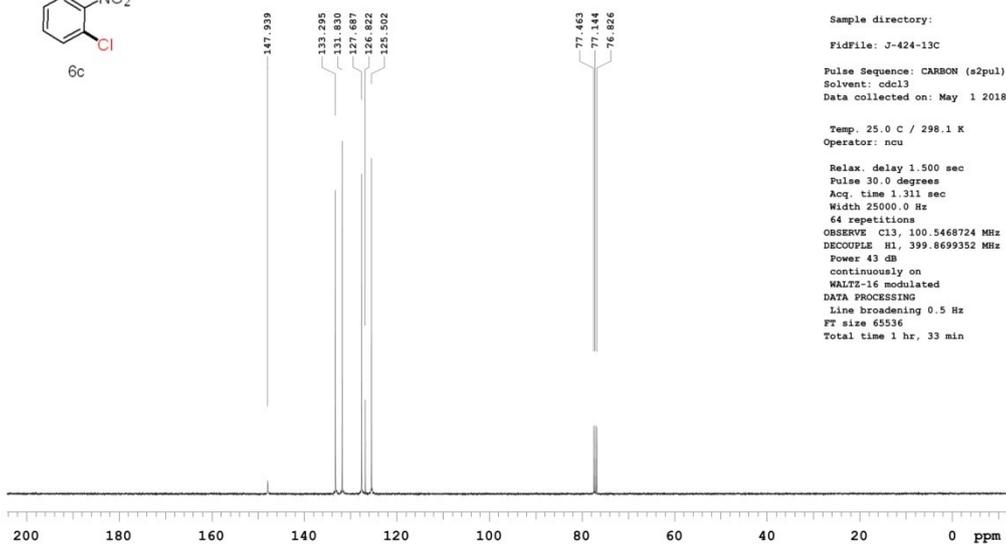


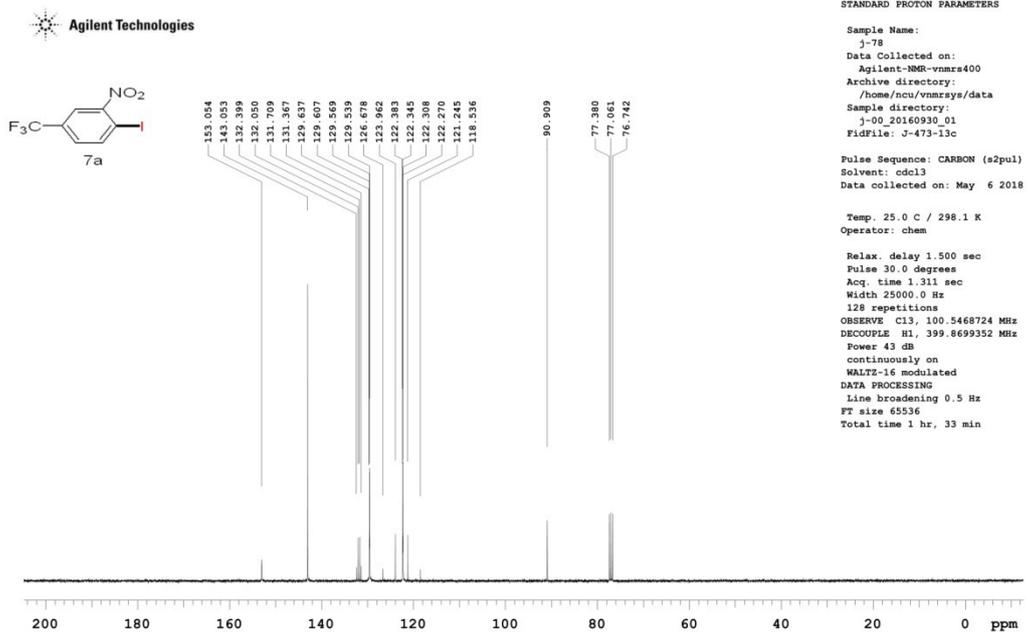
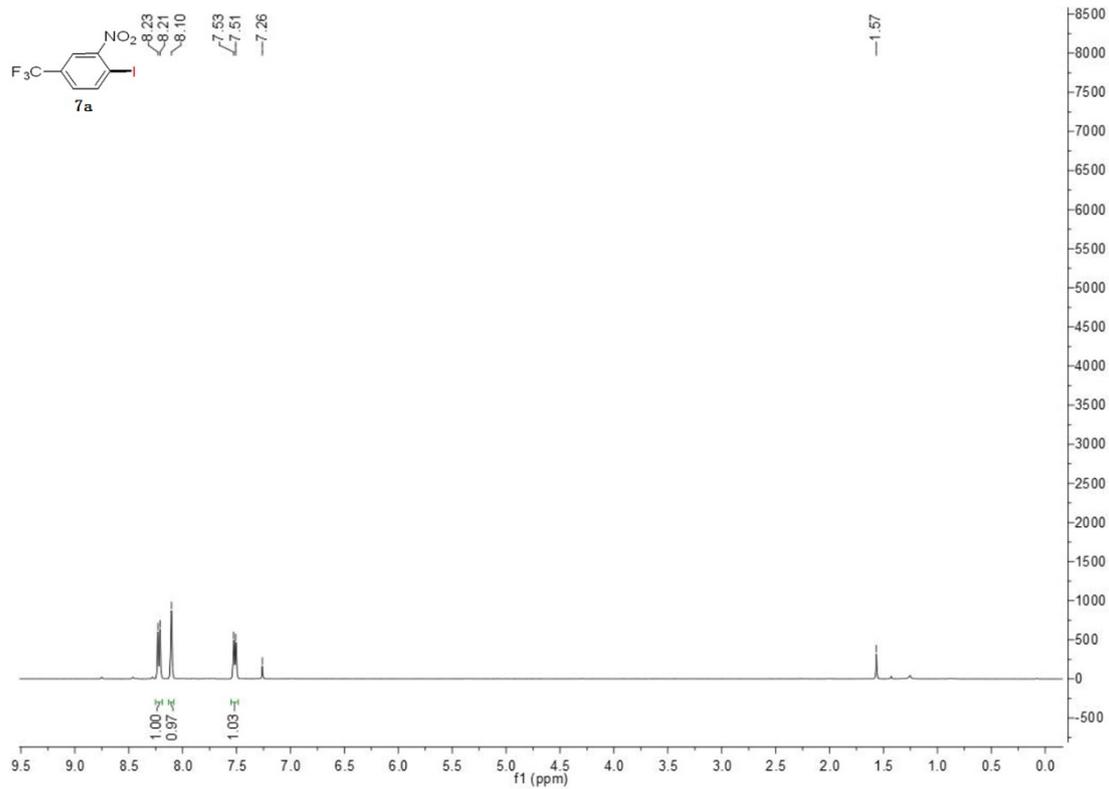
STANDARD PROTON PARAMETERS

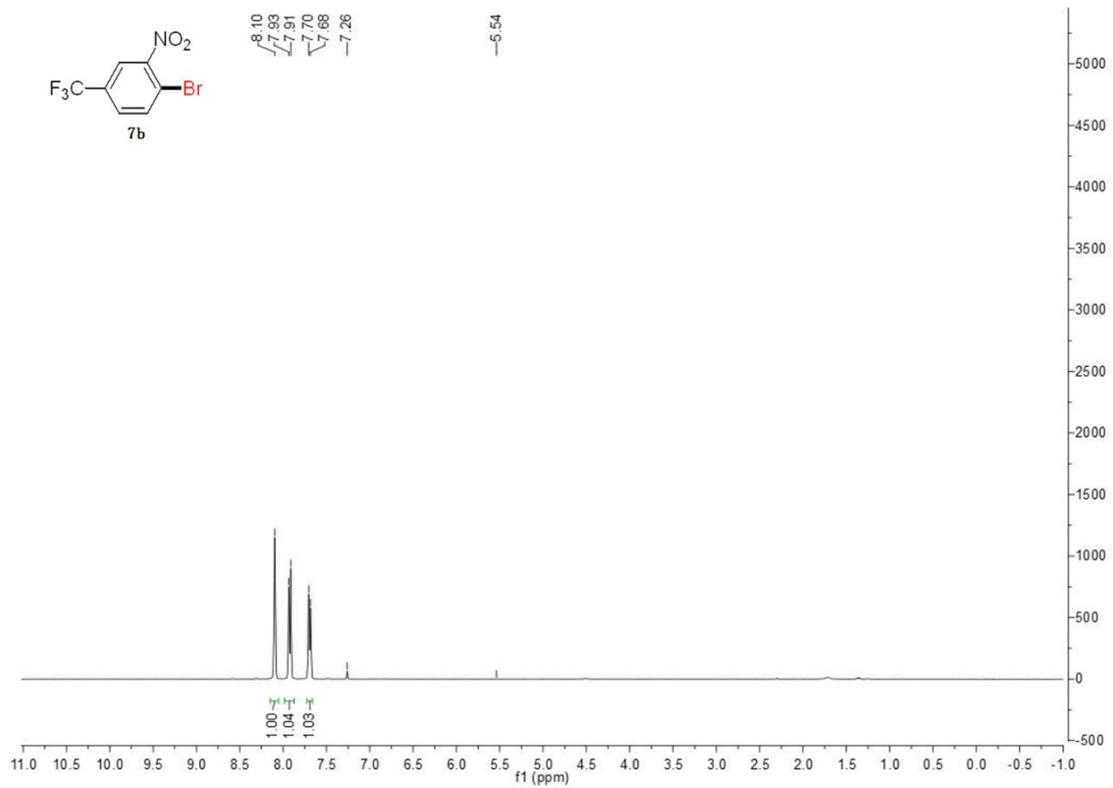
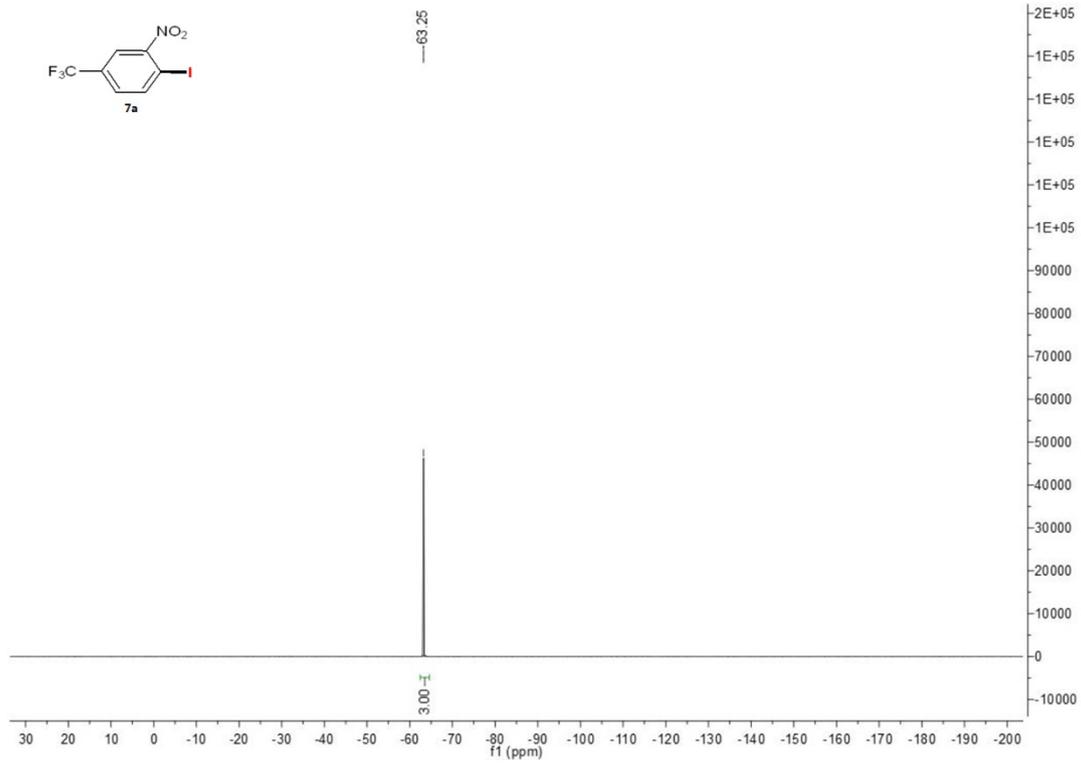
Sample Name: j-78
 Data Collected on: Agilent-NMR-vnmr400
 Archive directory: /home/ncu/vnmrsys/data
 Sample directory: j-00_20160930_01
 FidFile: J-472-13c
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: May 6 2018
 Temp. 25.0 C / 298.1 K
 Operator: chem
 Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 256 repetitions
 OBSERVE C13, 100.5468724 MHz
 DECOUPLE H1, 399.8699352 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 1 hr, 33 min

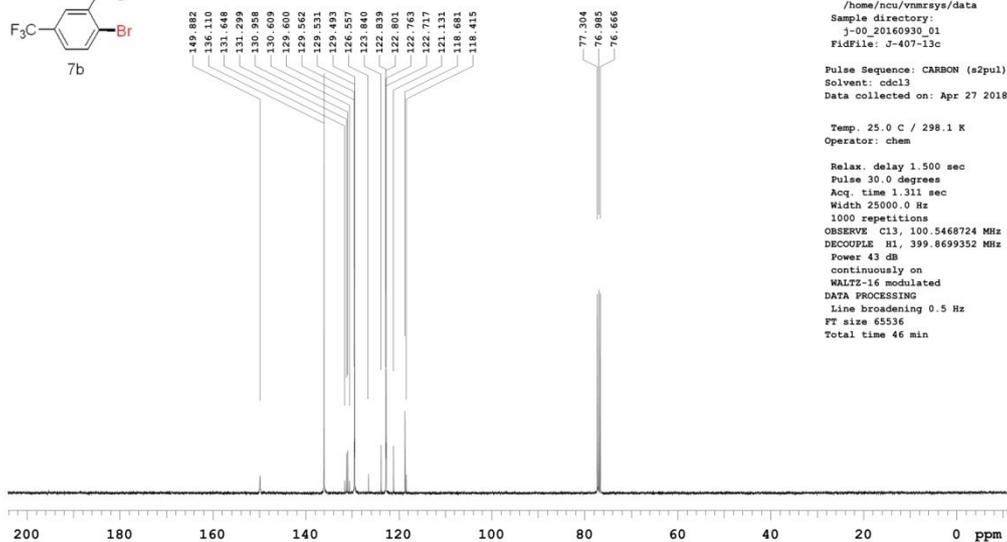
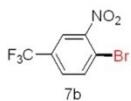


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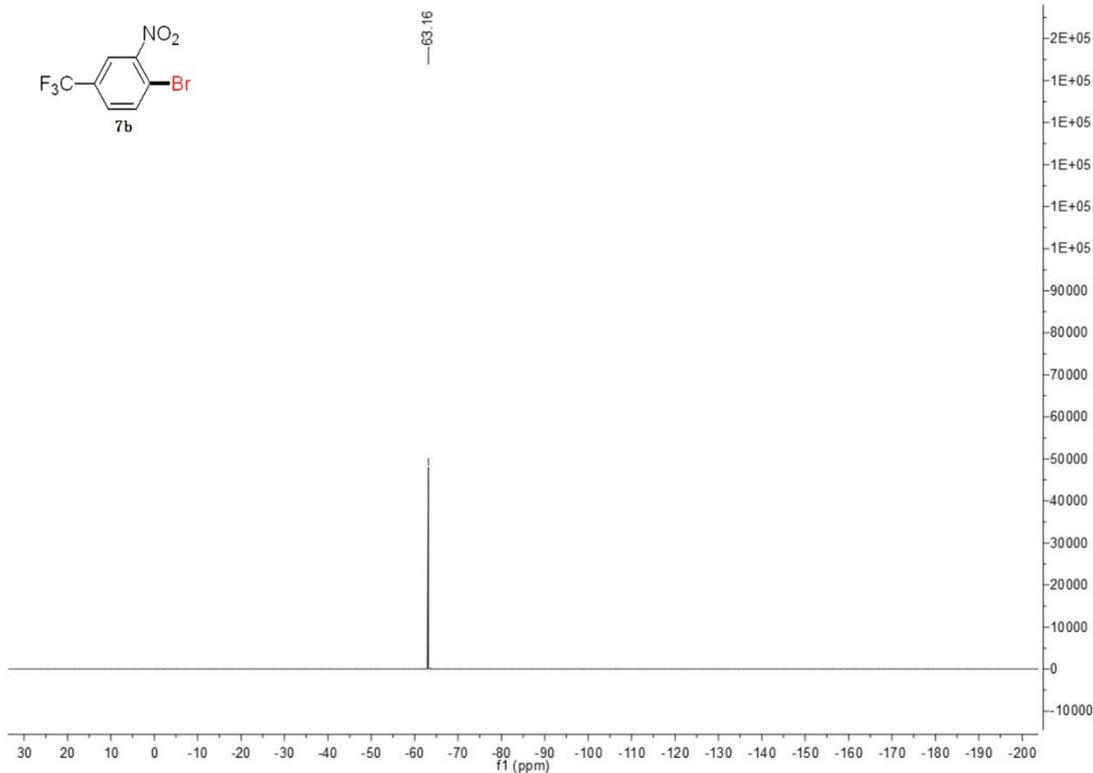
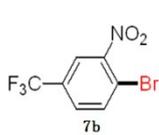


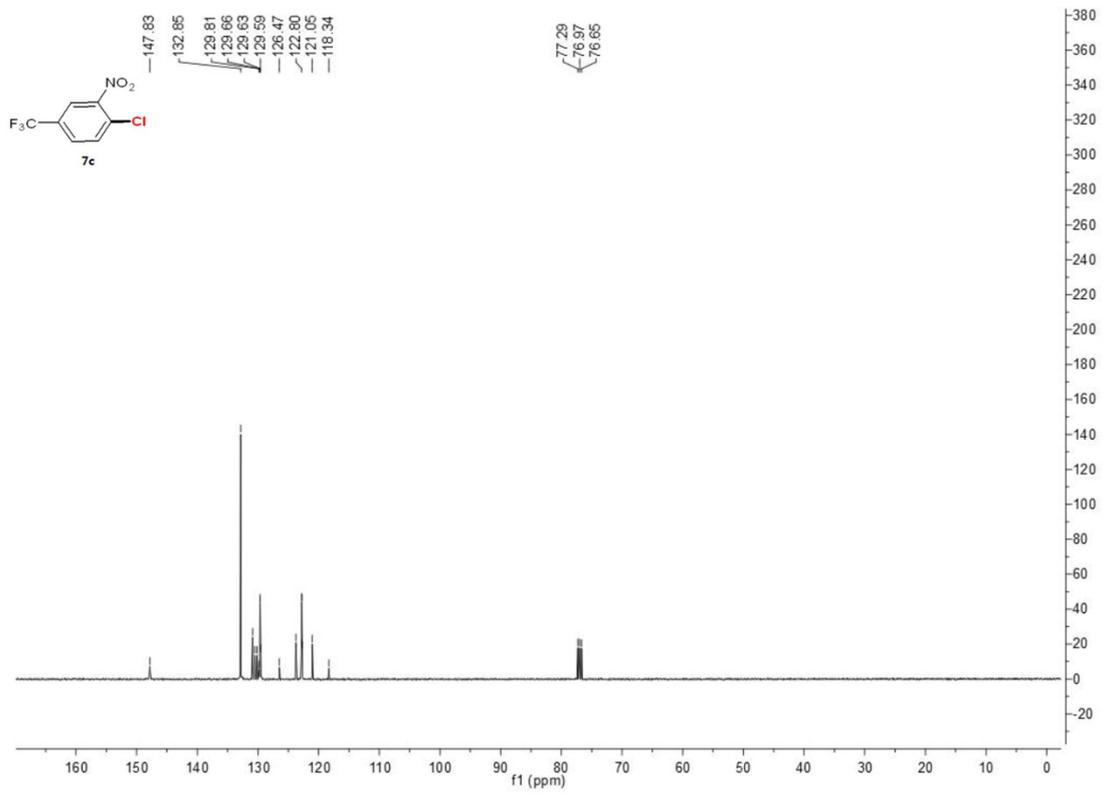
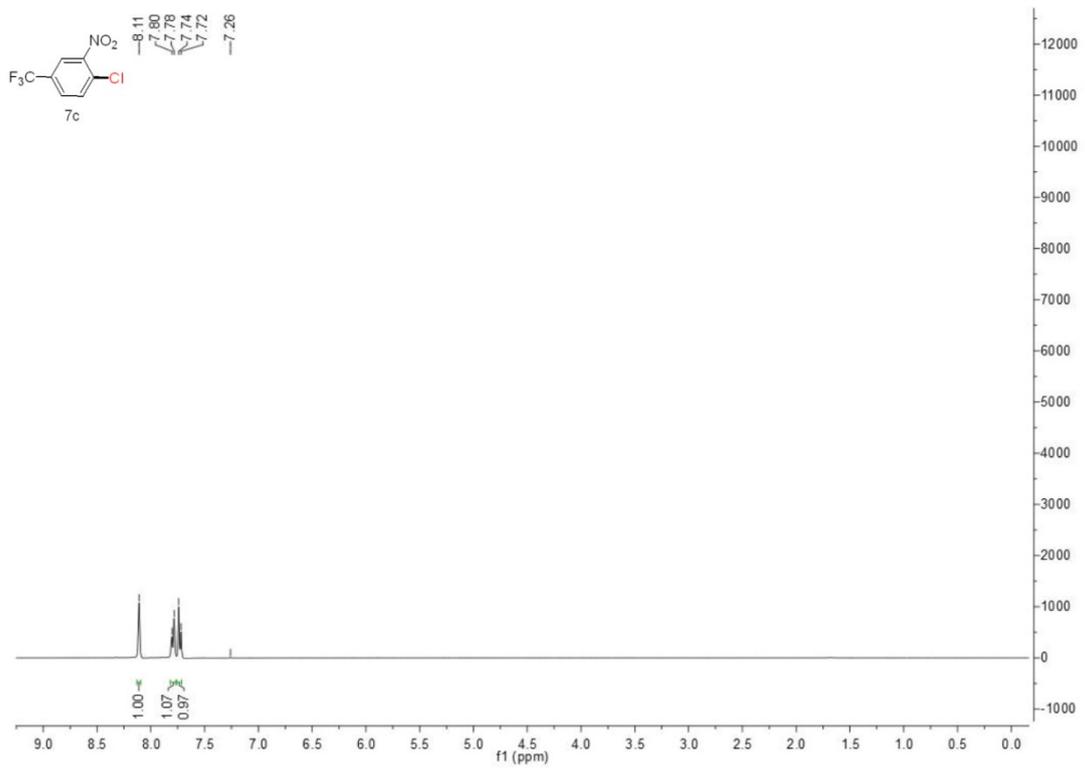


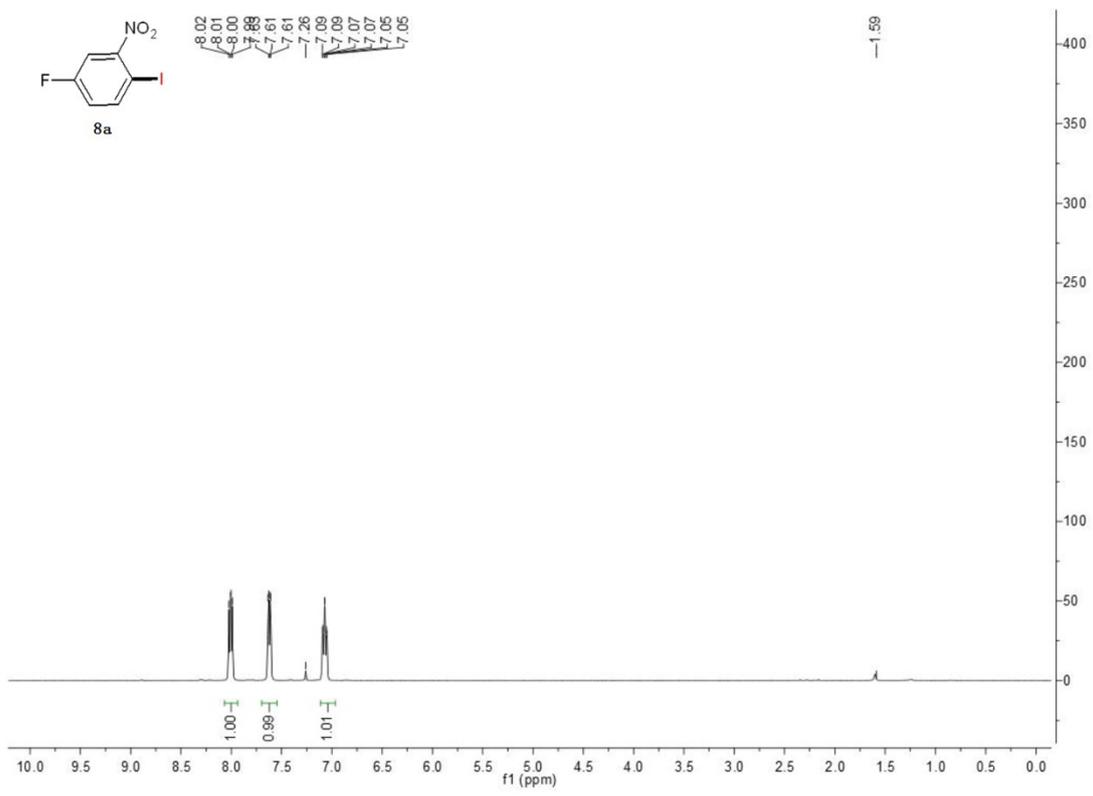
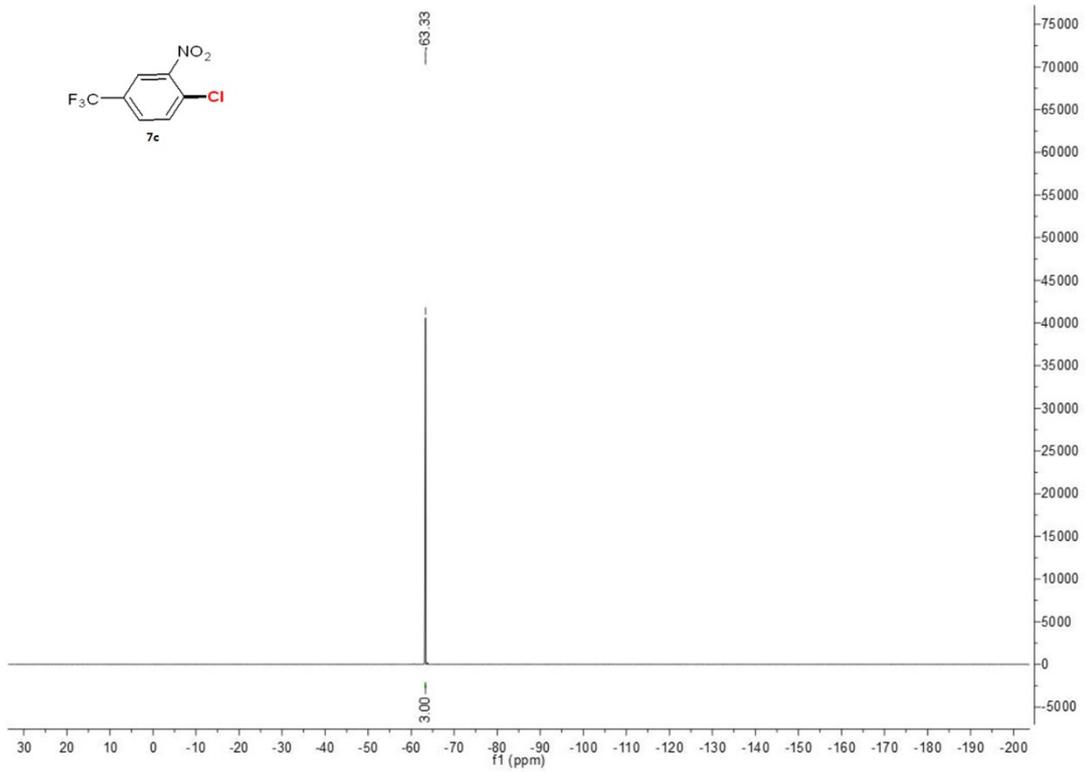
STANDARD PROTON PARAMETERS

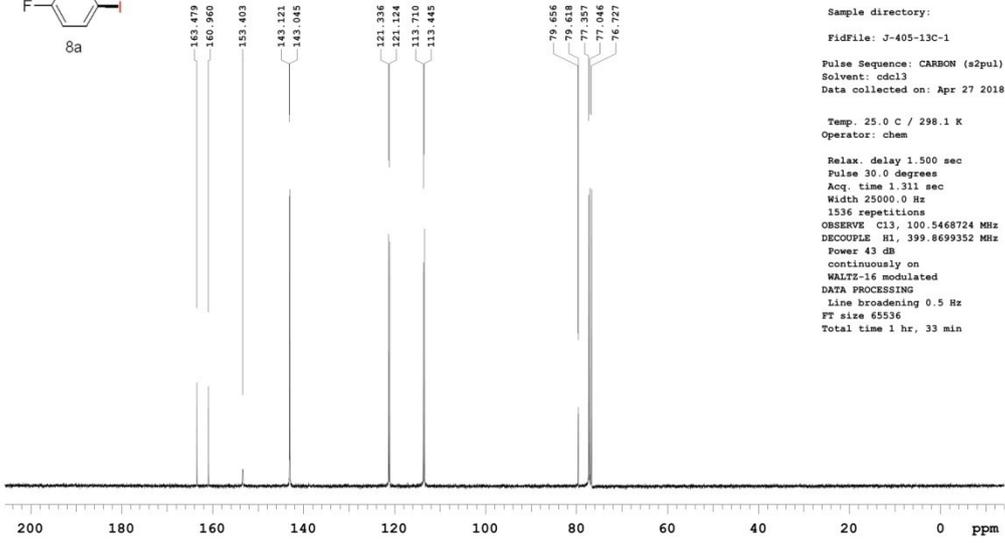
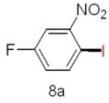
Sample Name: j-78
 Data Collected on: Agilent-VMS-vnmrs400
 Archive directory: /home/ncu/vnmrsys/data
 Sample directory: j-00_20160930_01
 FidFile: J-407-13c
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Apr 27 2018

Temp. 25.0 C / 298.1 K
 Operator: chem
 Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 1000 repetitions
 OBSERVE C13, 100.5468724 MHz
 DECOUPLE H1, 399.8699352 MHz
 Power 43 dB
 continuously on
 MALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 46 min

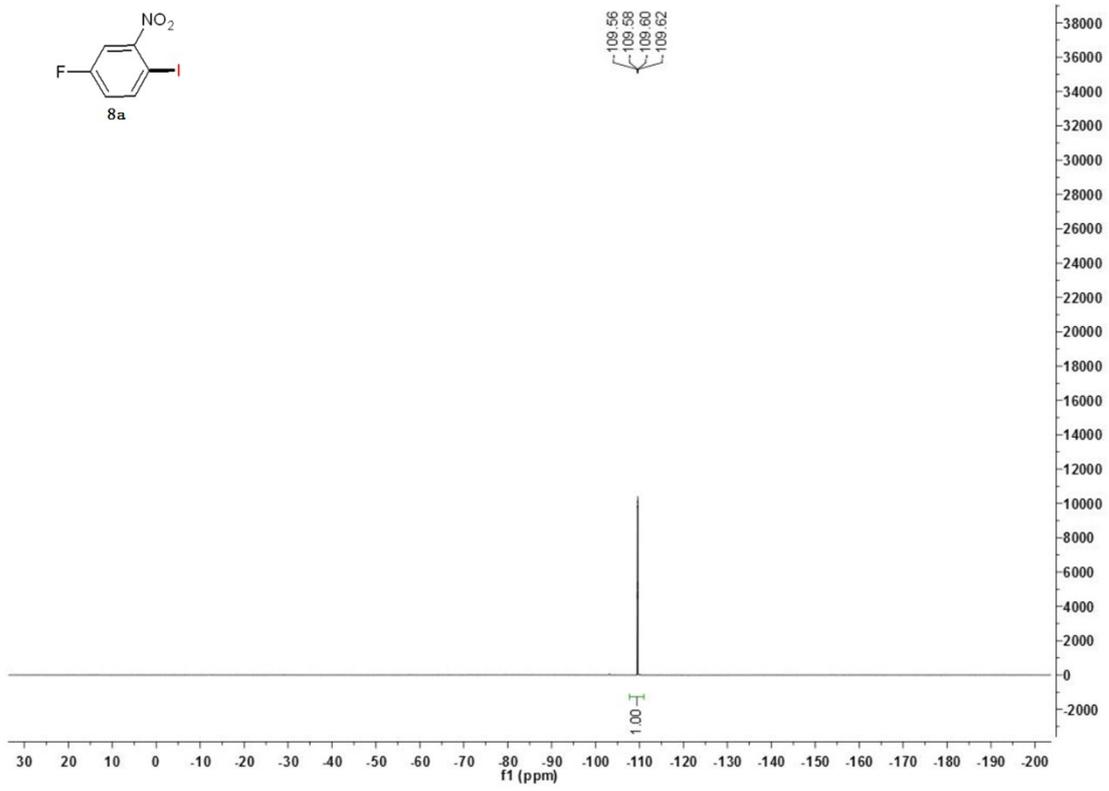
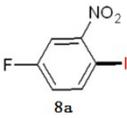


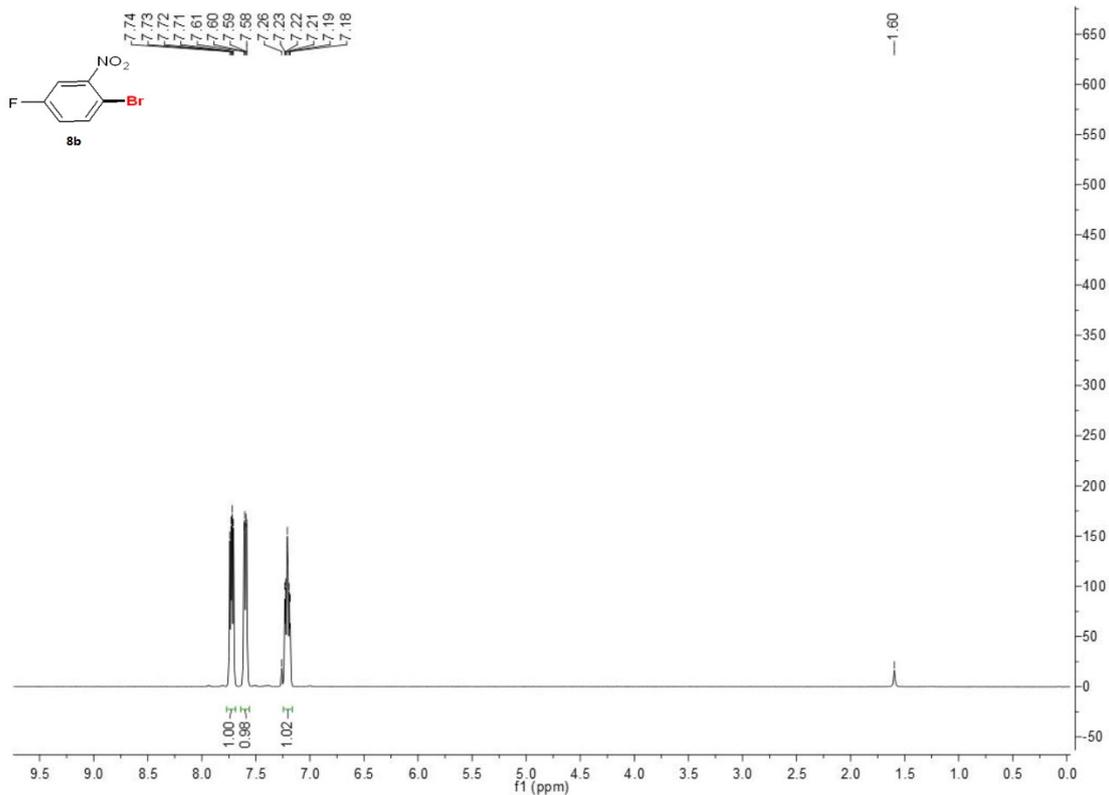




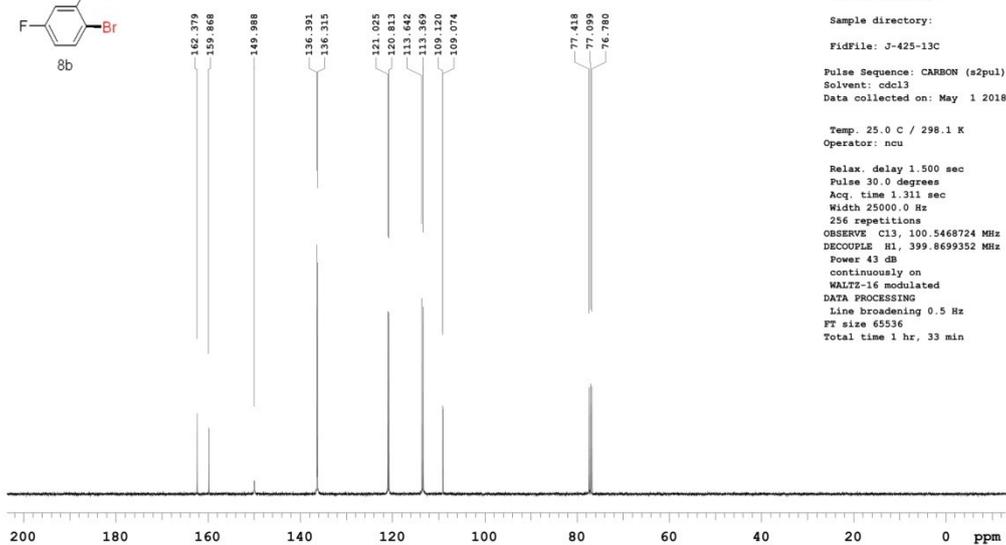
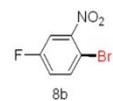


Sample Name:
 Data Collected on:
 Agilent-NMR-vnmrz400
 Archive directory:
 Sample directory:
 FidFile: J-405-13C-1
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Apr 27 2018
 Temp. 25.0 C / 298.1 K
 Operator: chem
 Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 1536 repetitions
 OBSERVE C13, 100.5468724 MHz
 DECOUPLE H1, 399.8699352 MHz
 Power 43 dB
 continuously on
 MLT-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 1 hr, 33 min

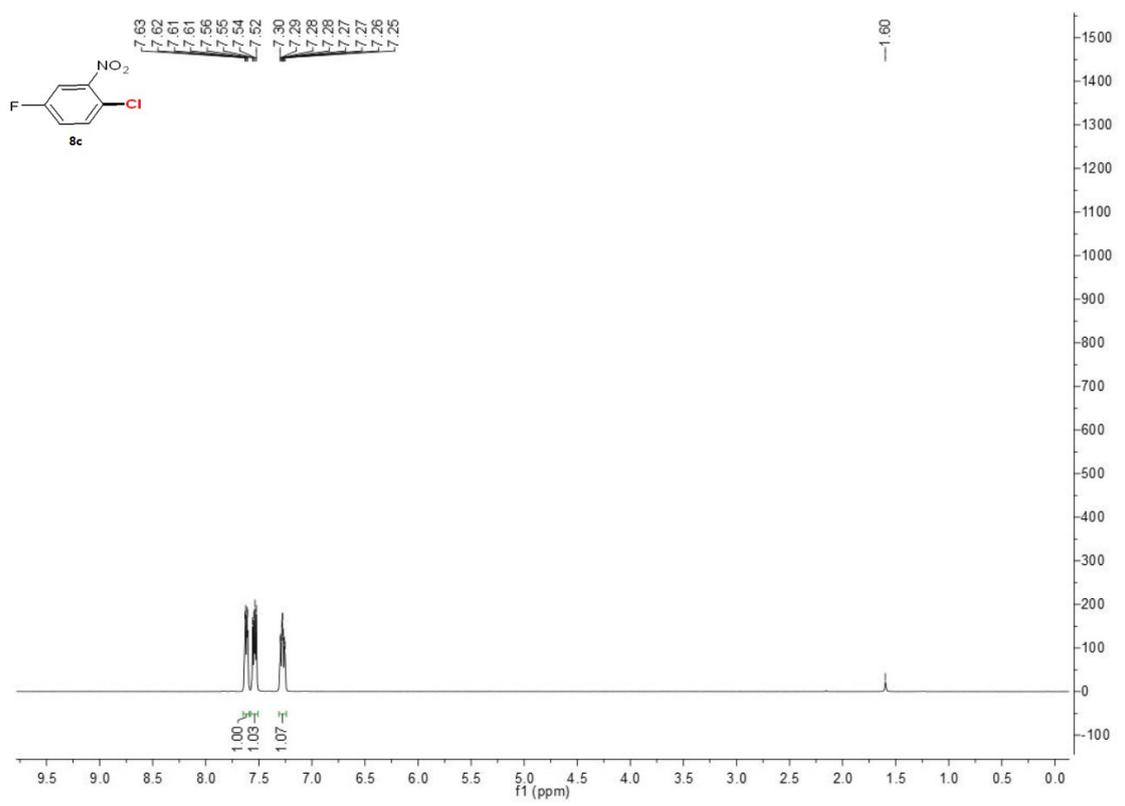
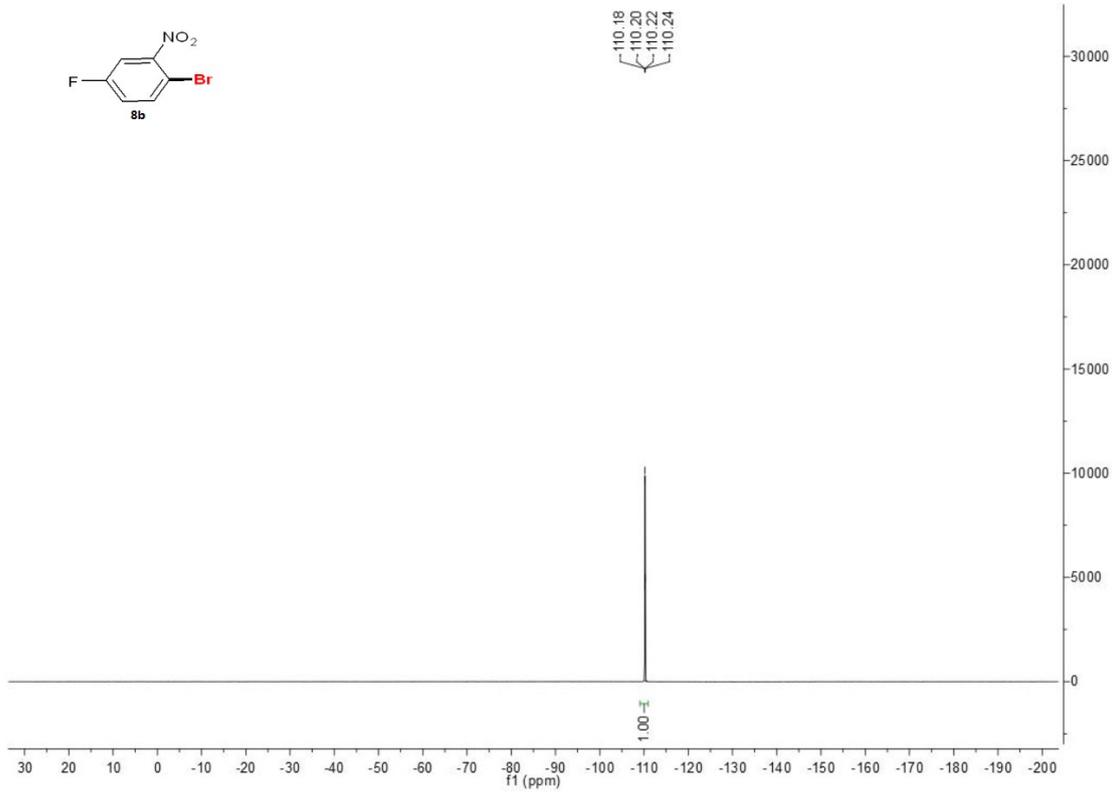




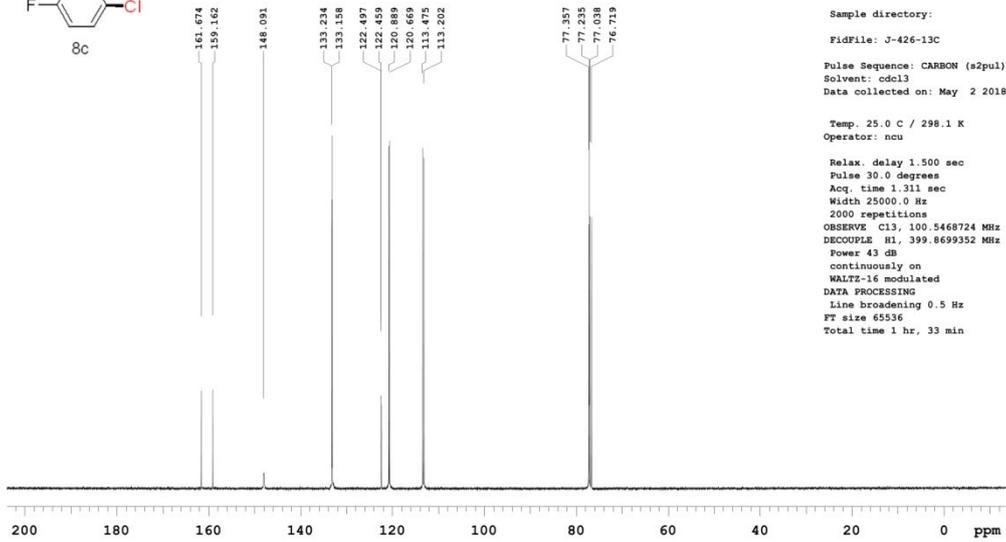
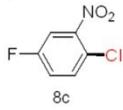
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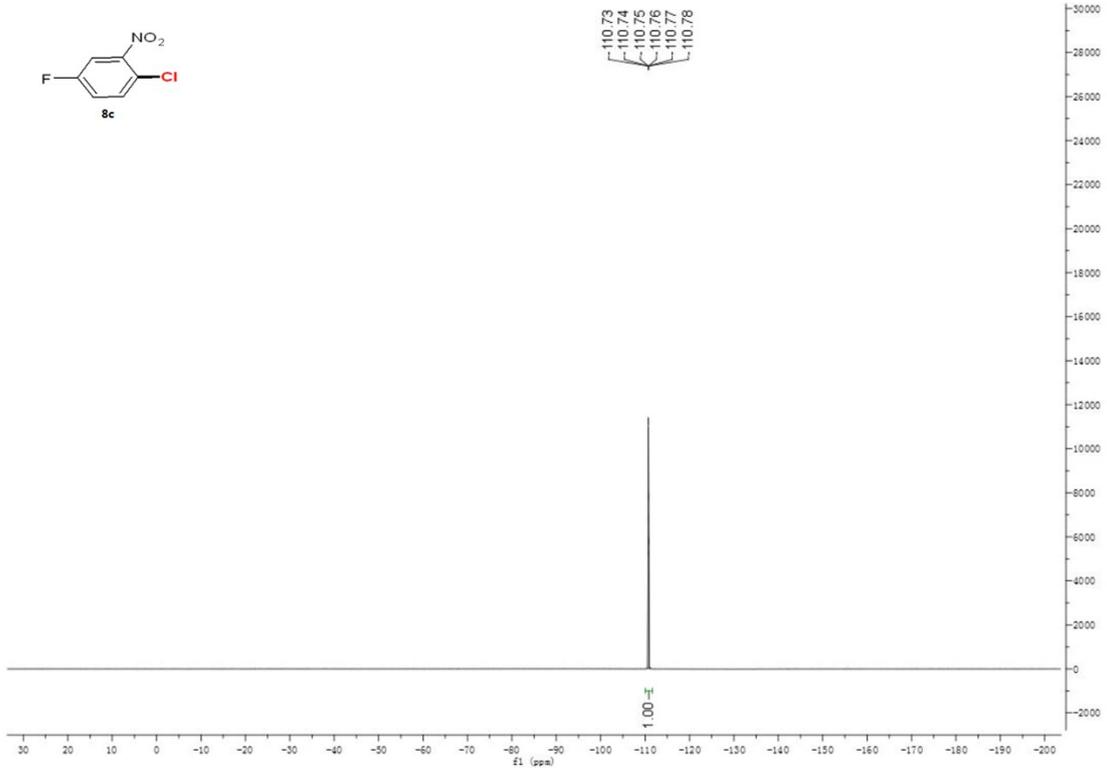
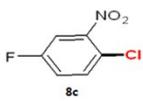
Sample Name: J-425
 Data Collected on: Agilent-NMR-vnmr400
 Archive directory:
 Sample directory:
 FidFile: J-425-13C
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: May 1 2018
 Temp. 25.0 C / 298.1 K
 Operator: ncu
 Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 256 repetitions
 OBSERVE C13, 100.626124 MHz
 DECOUPLE H1, 399.8699352 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 1 hr, 33 min

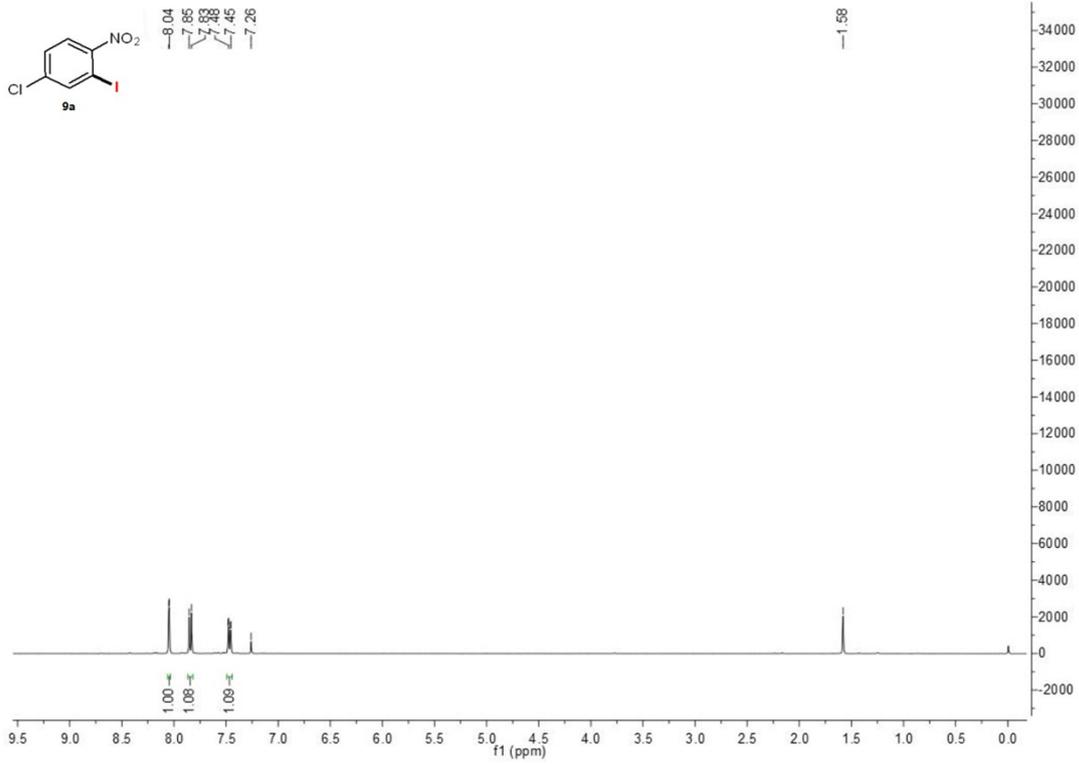


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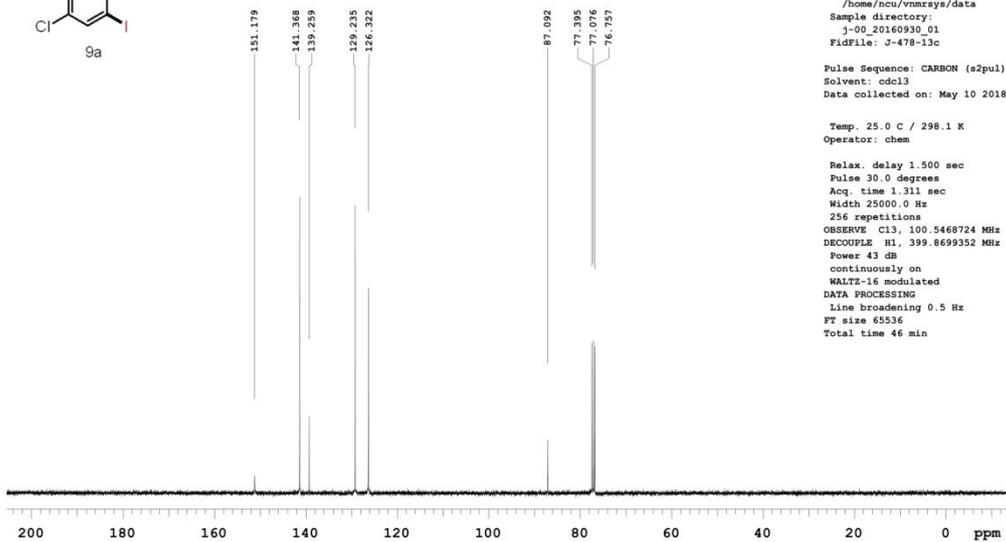
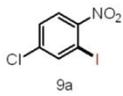


Sample Name:
J-425
Data Collected on:
Agilent-MS-vnmr400
Archive directory:
Sample directory:
FidFile: J-426-13C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 2 2018
Temp: 25.0 C / 298.1 K
Operator: ncu
Relax. delay 1.500 sec
Pulse 30.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
2000 repetitions
OBSERVE C13, 100.5468724 MHz
DECOUPLE H1, 399.8699352 MHz
Power 43 dB
continuously on
MLT2-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 33 min





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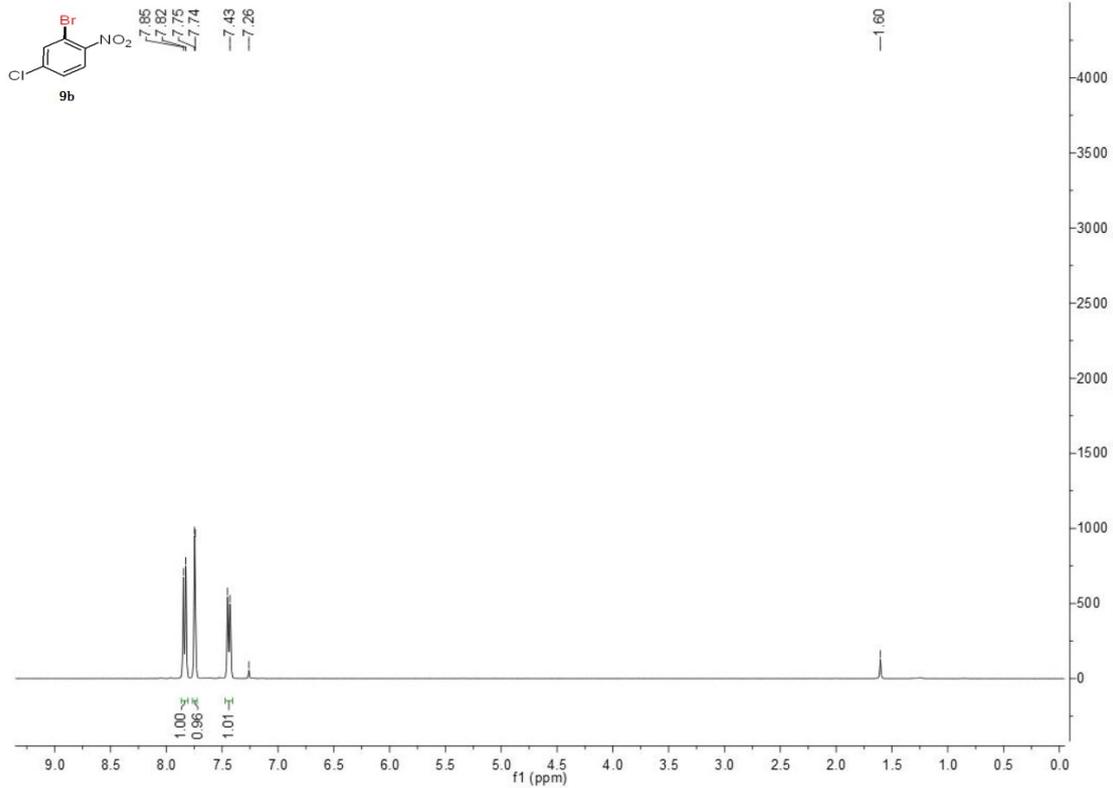
STANDARD PROTON PARAMETERS

Sample Name: j-78
 Data Collected on: Agilent-NMR-vnmrs400
 Archive directory: /home/nca/vnmrsys/data
 Sample directory: j-00_20160930_01
 FidFile: J-478-13c

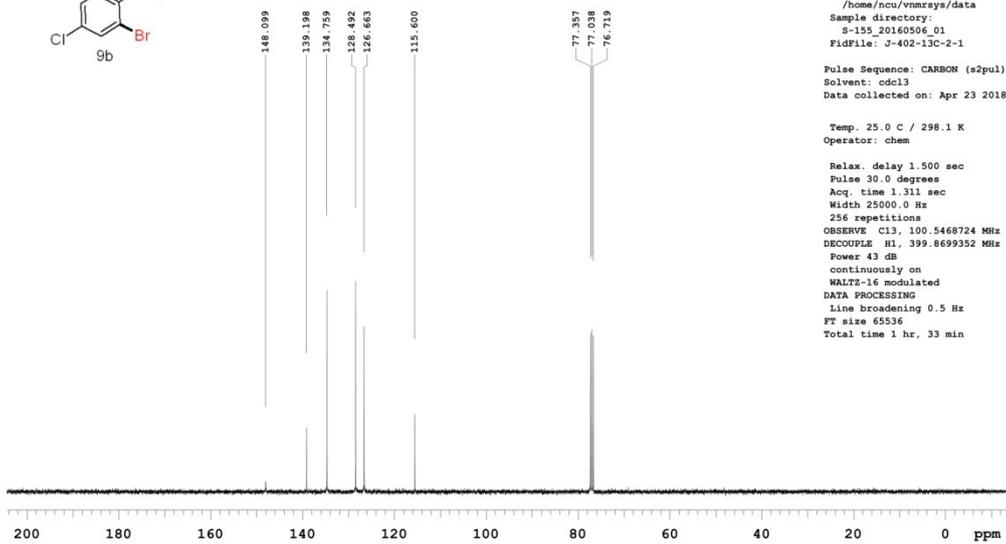
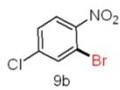
Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: May 10 2018

Temp. 25.0 C / 298.1 K
 Operator: chem

Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 256 repetitions
 OBSERVE C13, 100.5468724 MHz
 DECOUPLE H1, 399.869352 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 46 min

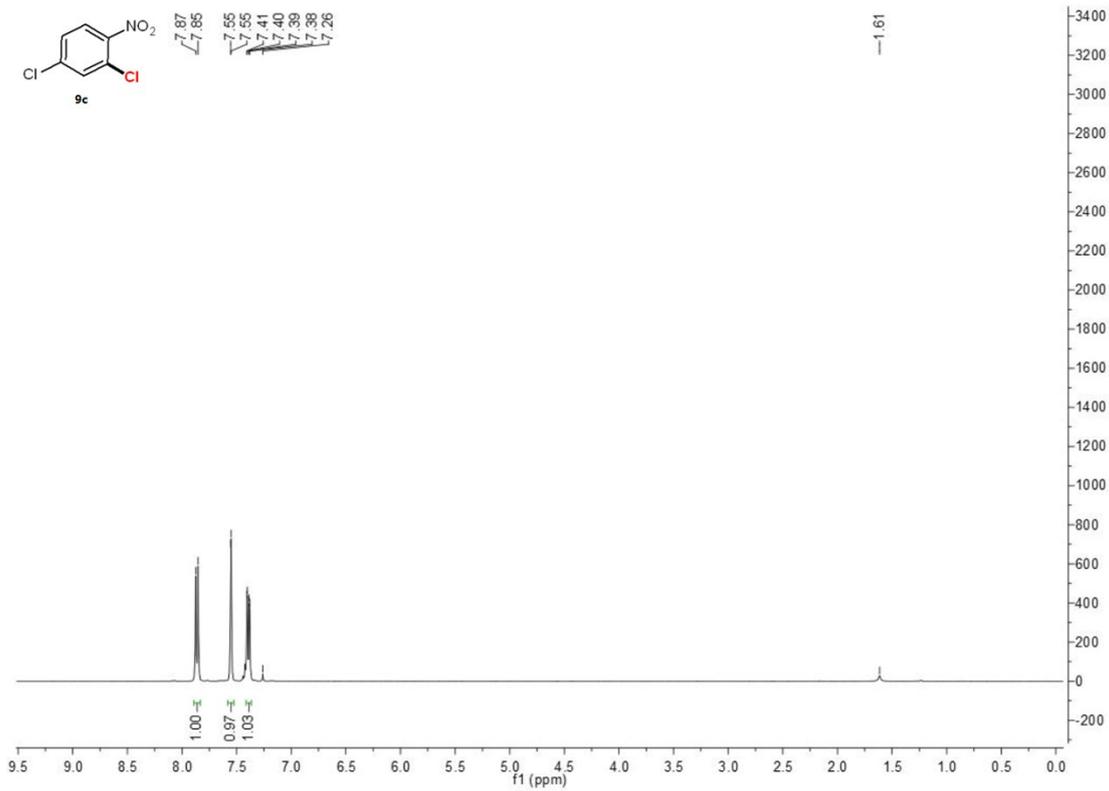


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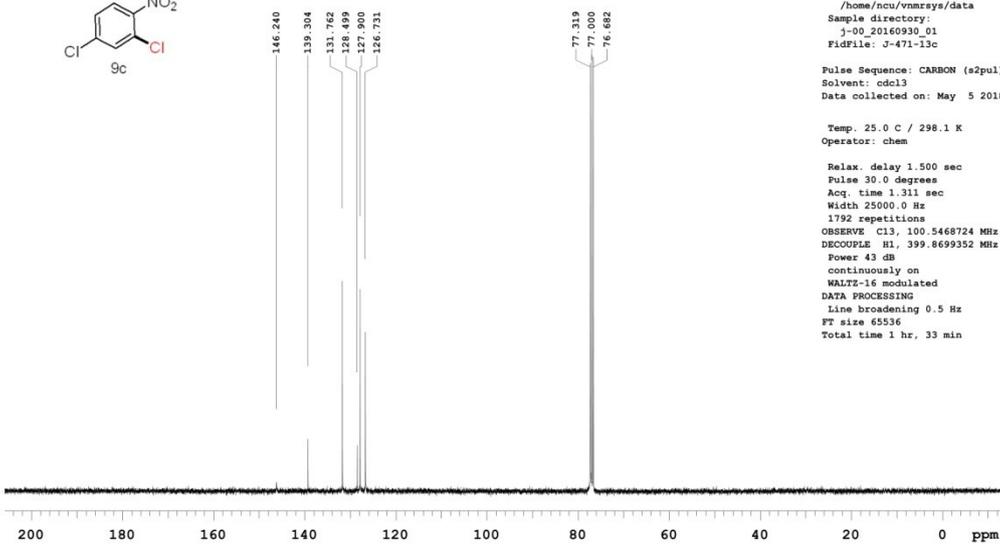
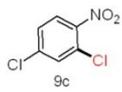


STANDARD PROTON PARAMETERS

Sample Name: HD-64
 Data Collected on: Agilent-NMR-vnmrs400
 Archive directory: /home/ncu/vnmrsys/data
 Sample directory: S-155_20160506_01
 Fidfile: J-402-13C-2-1
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Apr 23 2018
 Temp. 25.0 C / 298.1 K
 Operator: chem
 Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 256 repetitions
 OBSERVE C13, 100.5468724 MHz
 DECOUPLE H1, 399.8699352 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 1 hr, 33 min



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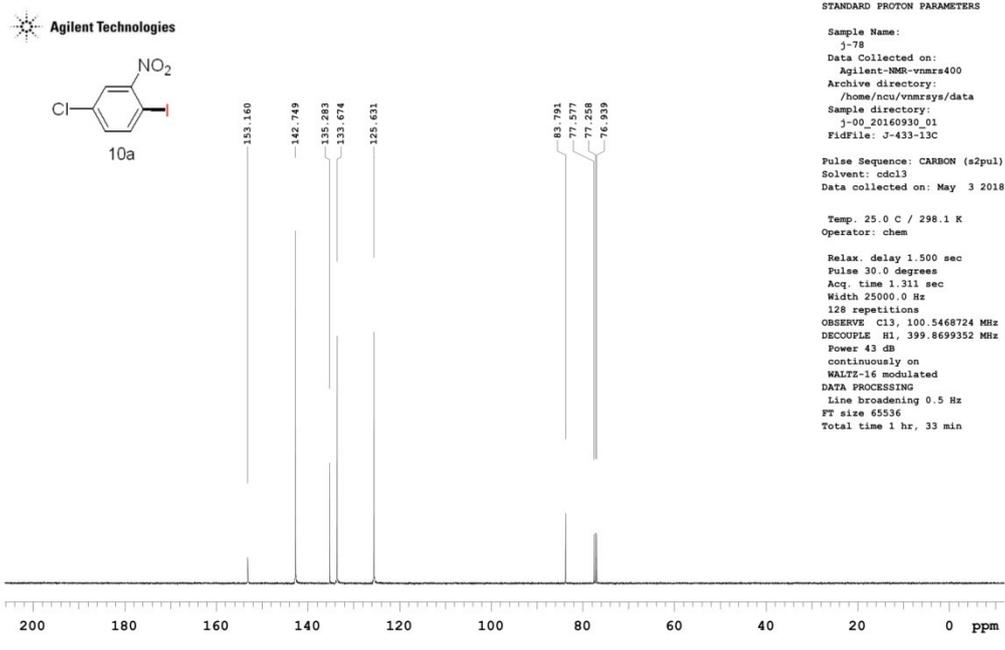
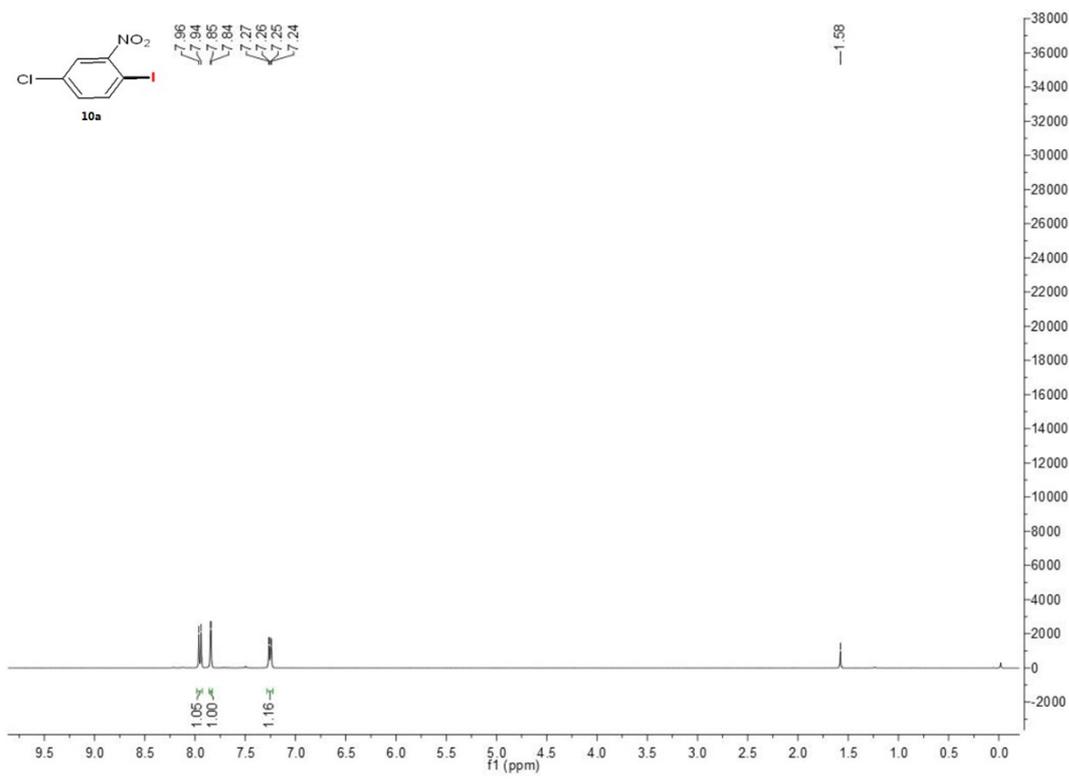
STANDARD PROTON PARAMETERS

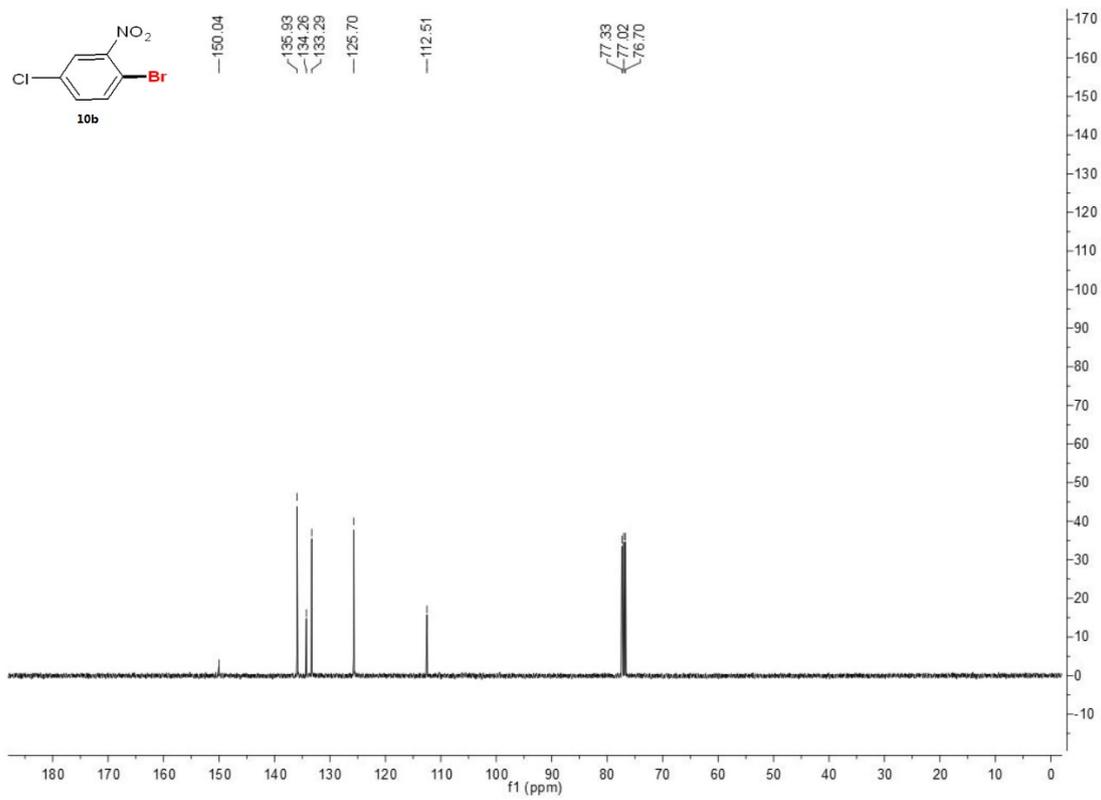
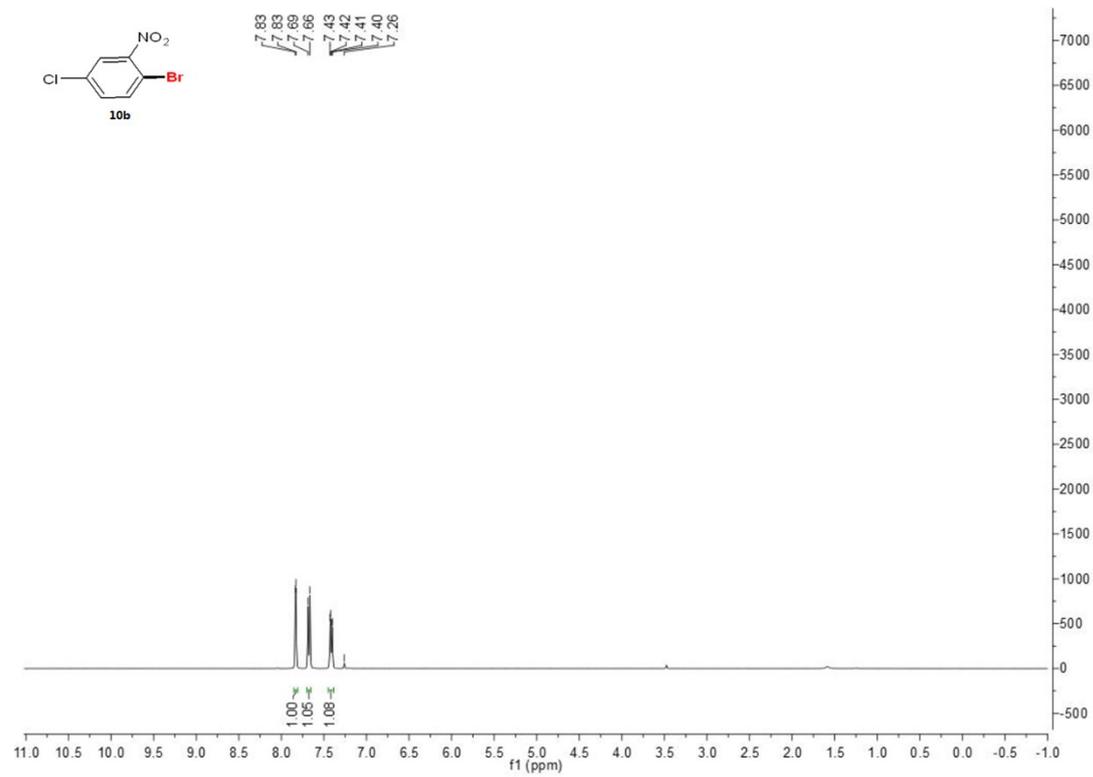
Sample Name: j-78
 Data Collected on: Agilent-NMR-vnmr400
 Archive directory: /home/ncu/vnmr400/data
 Sample directory: j-00_20160930_01
 FidFile: J-471-13c

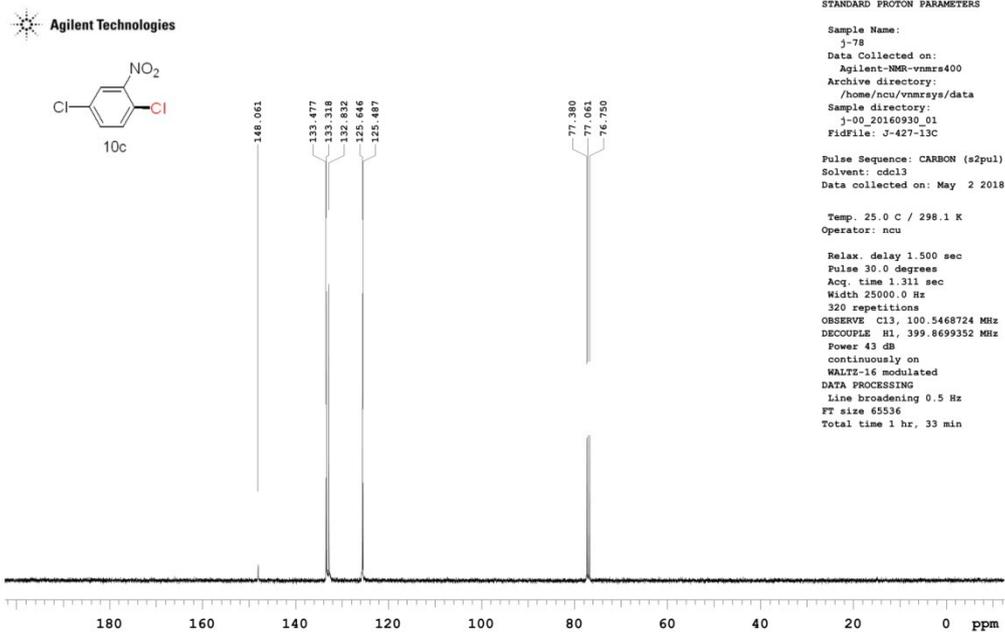
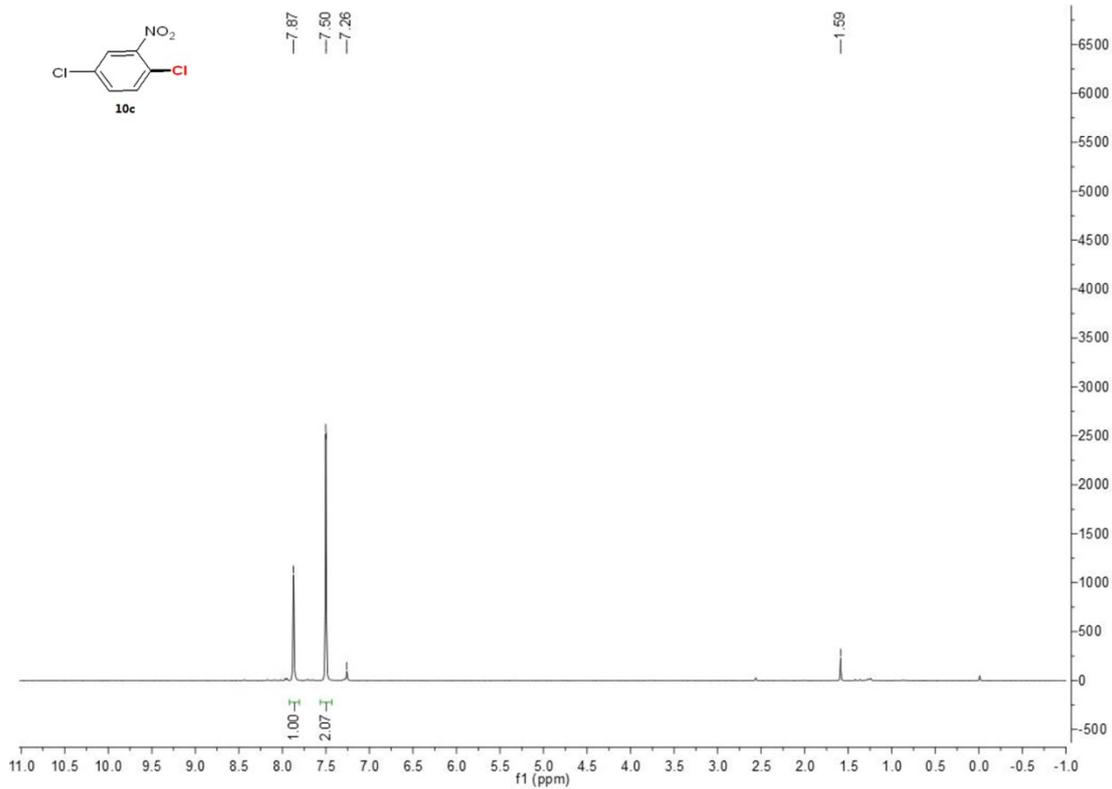
Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: May 5 2018

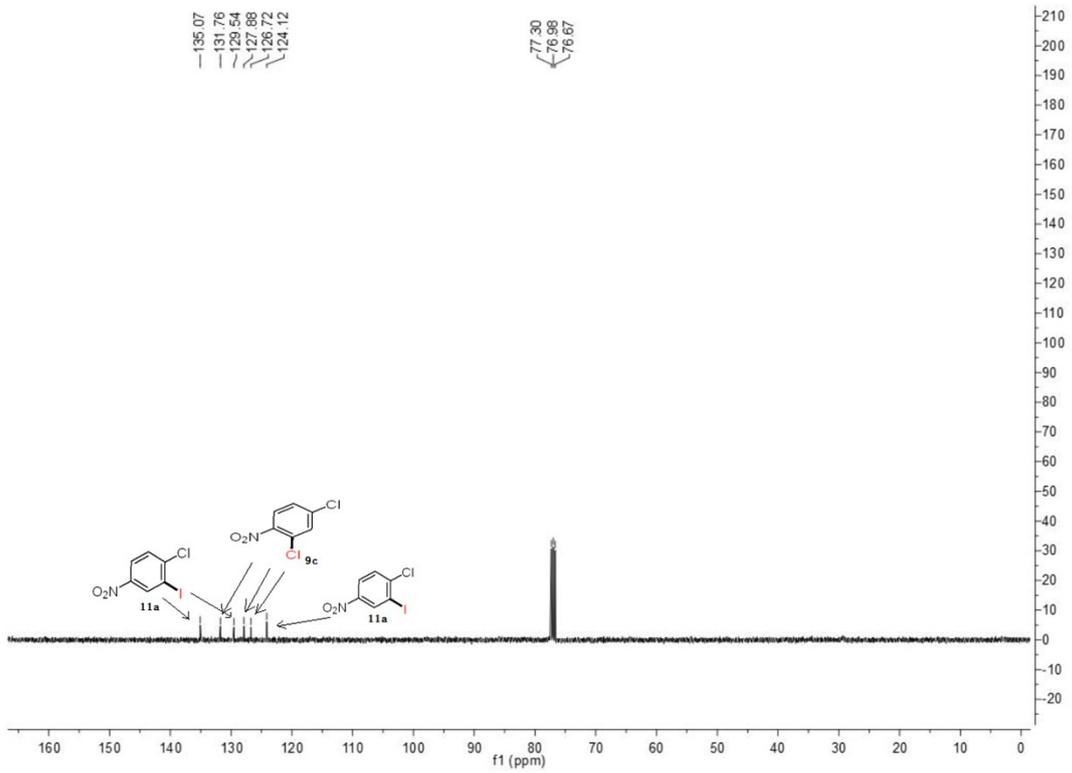
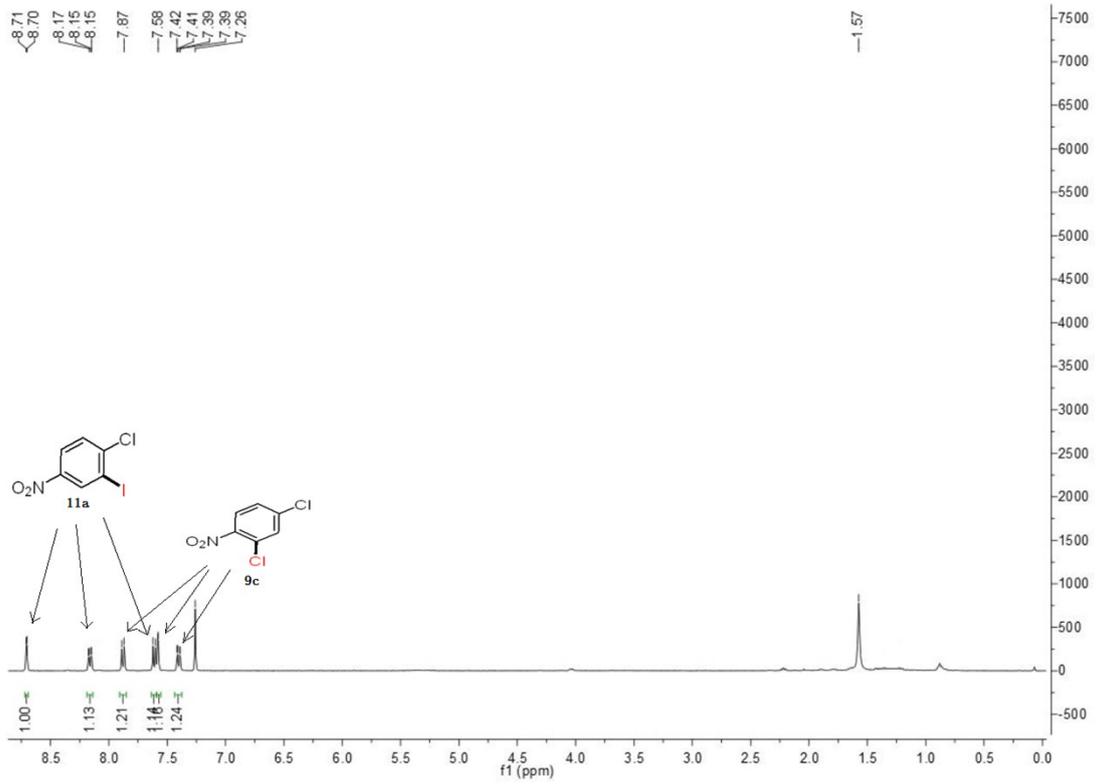
Temp. 25.0 C / 298.1 K
 Operator: chem

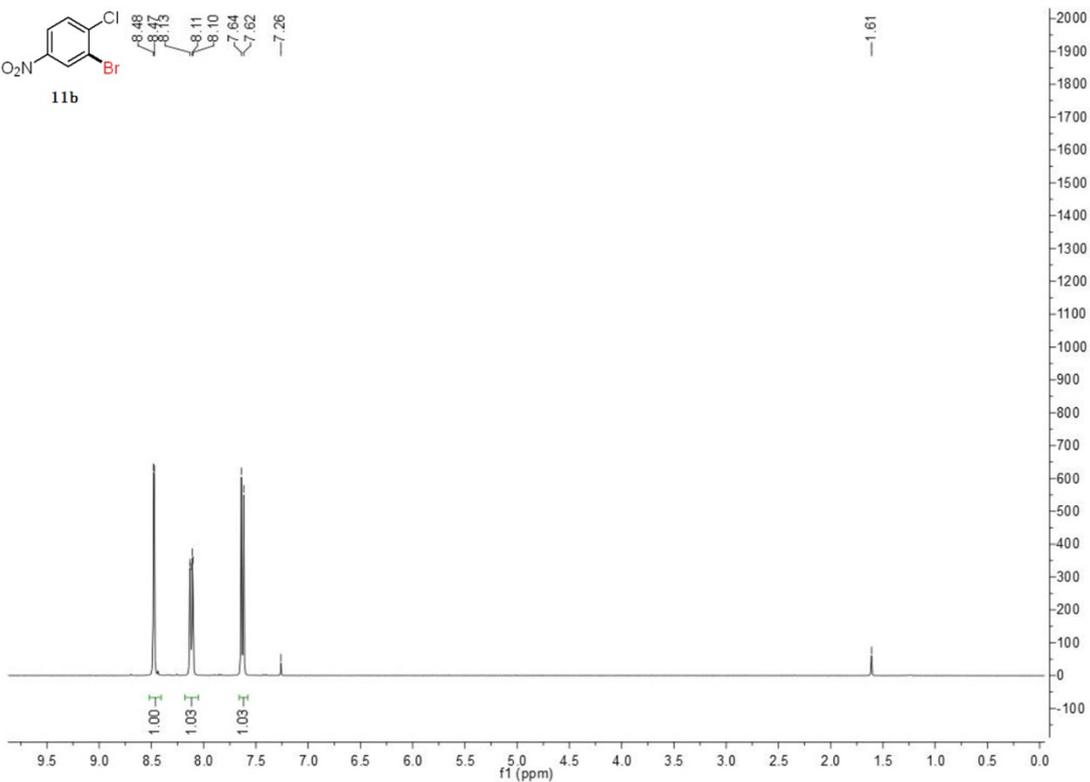
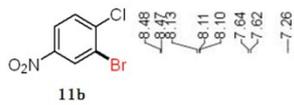
Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 1792 repetitions
 OBSERVE C13, 100.5468724 MHz
 DECOUPLE H1, 399.8699352 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 1 hr, 33 min



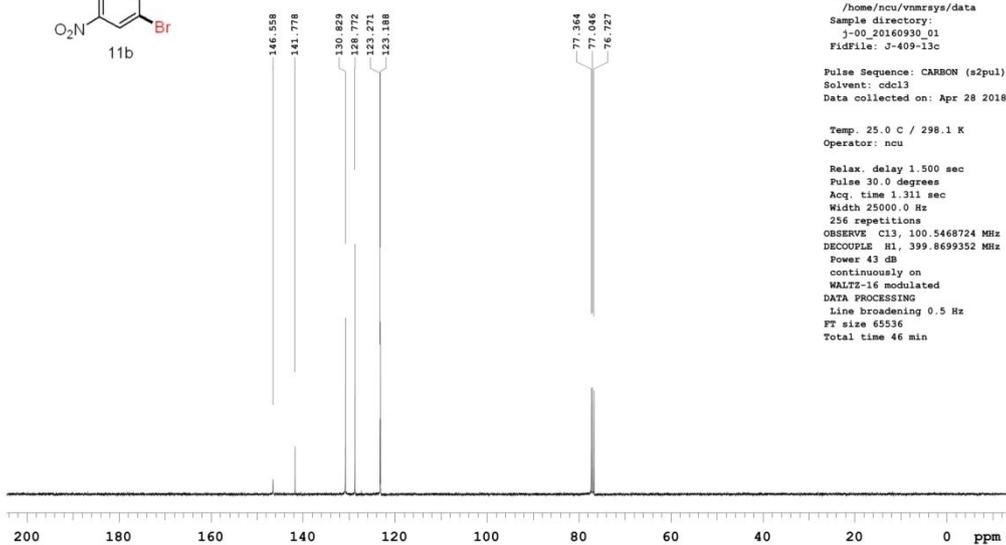
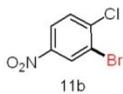






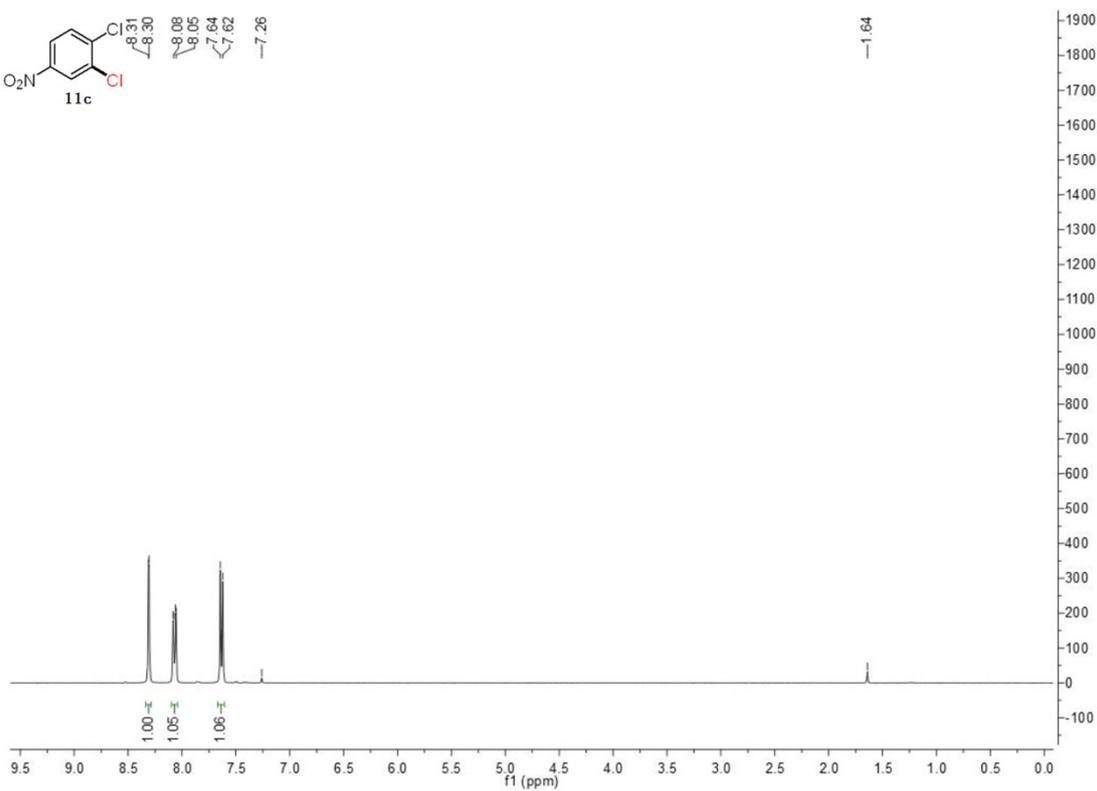
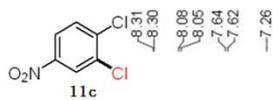


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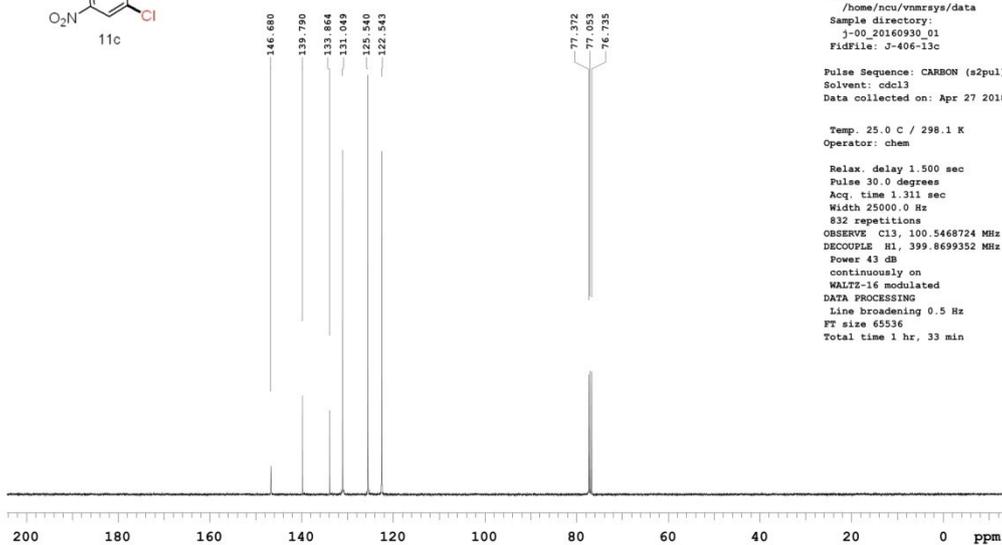
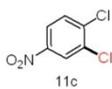


STANDARD PROTON PARAMETERS

Sample Name: j-78
 Data Collected on: Agilent-NMR-vnmrs400
 Archive directory: /home/ncu/vnmrsys/data
 Sample directory: j-00_20160930_01
 FidFile: J-409-13c
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Apr 28 2018
 Temp. 25.0 C / 298.1 K
 Operator: ncu
 Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 256 repetitions
 OBSERVE C13, 100.5468724 MHz
 DECOUPLE H1, 399.8699352 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 46 min

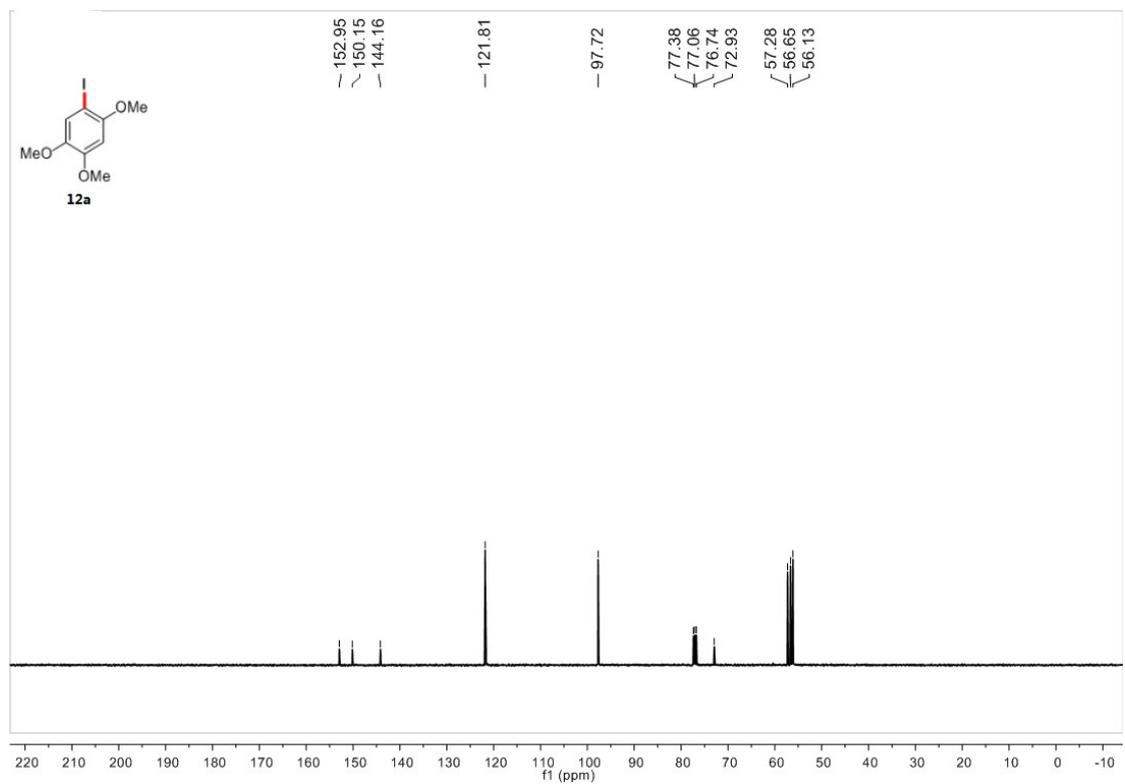
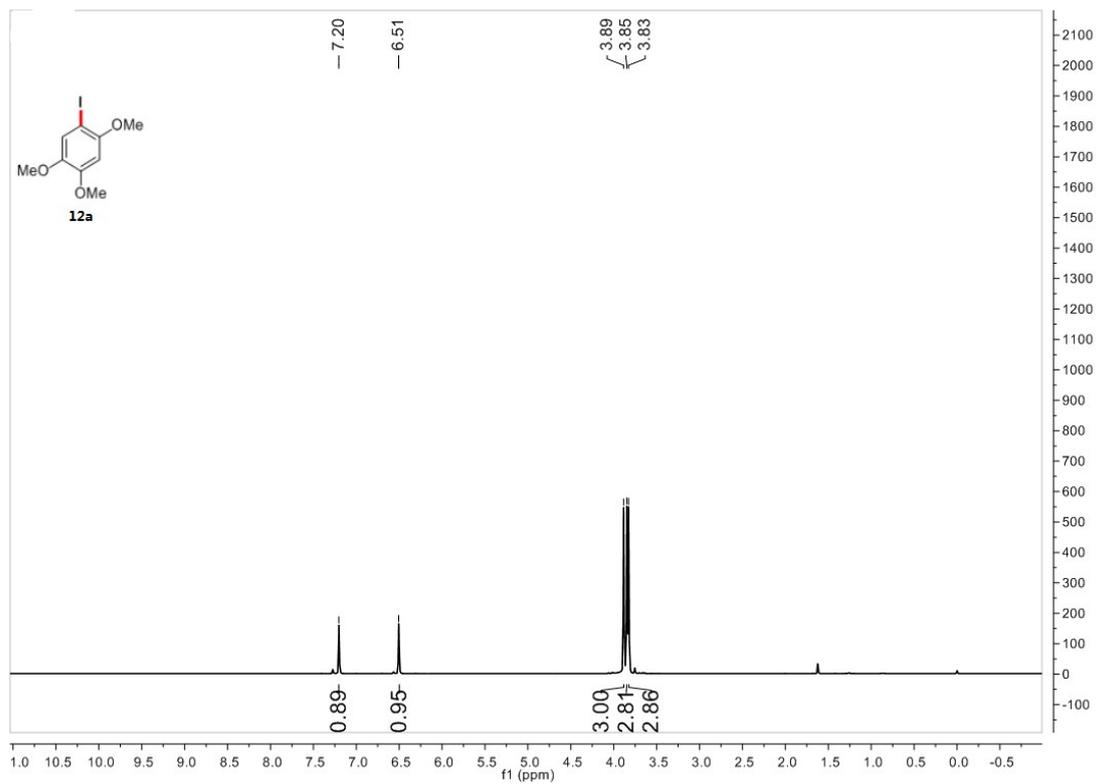


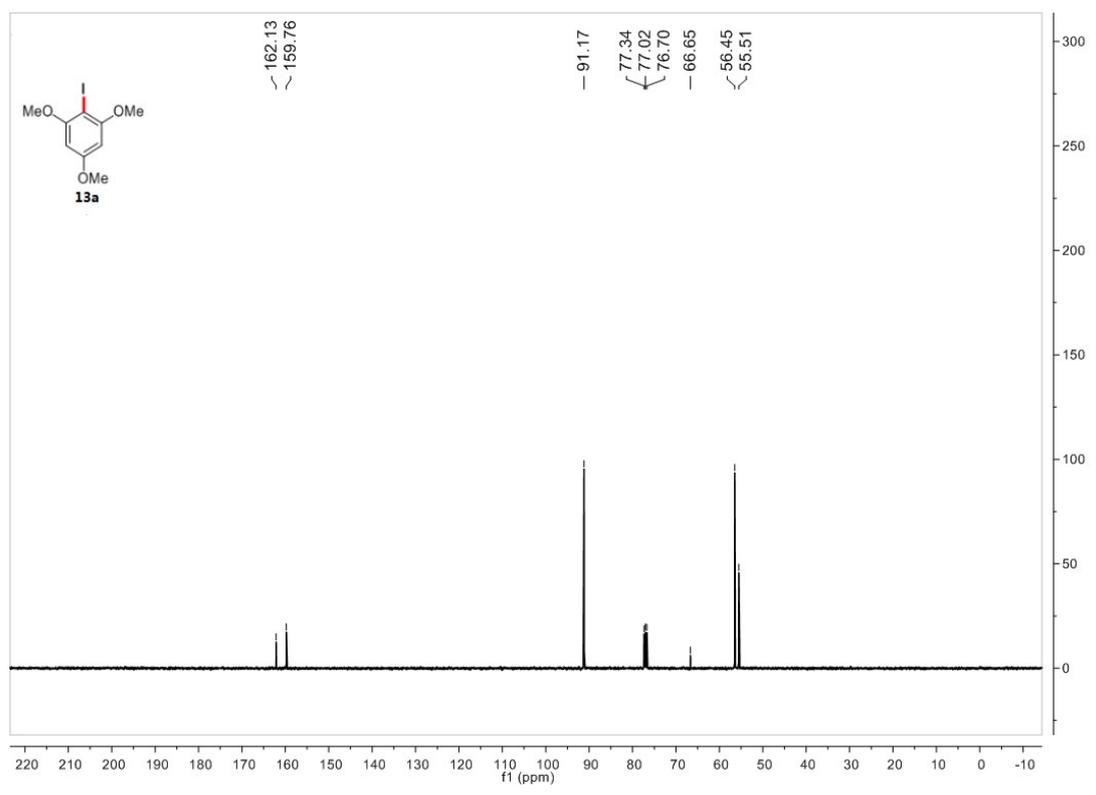
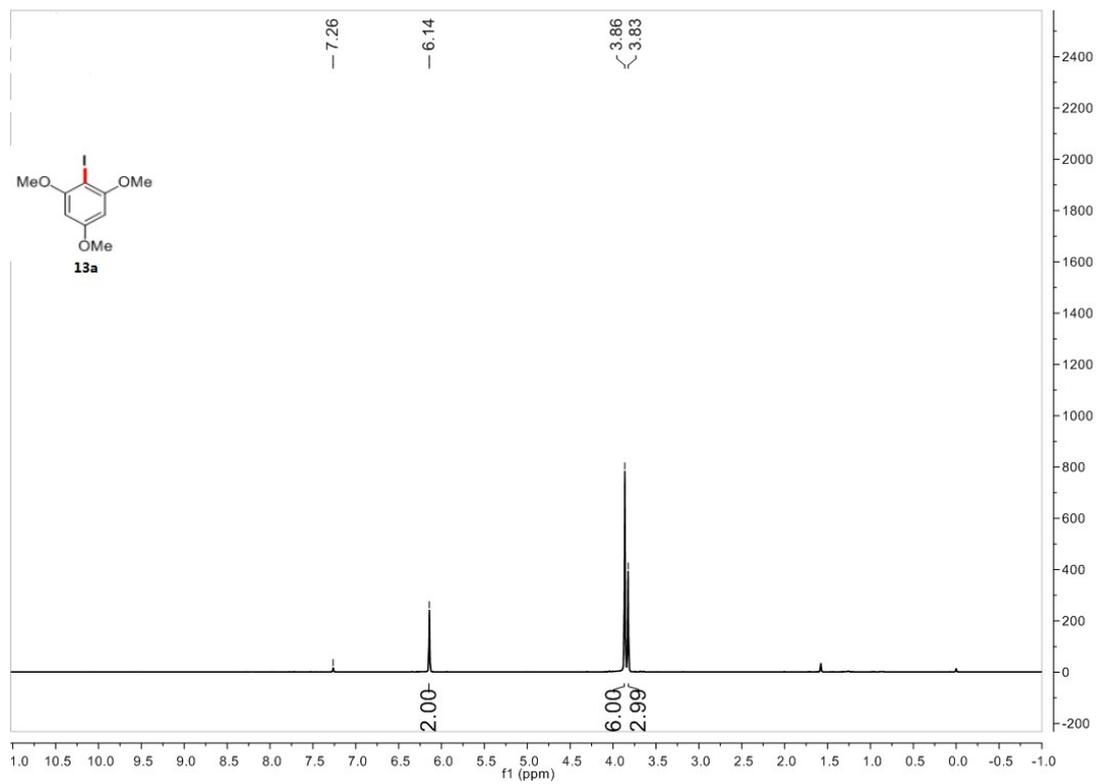
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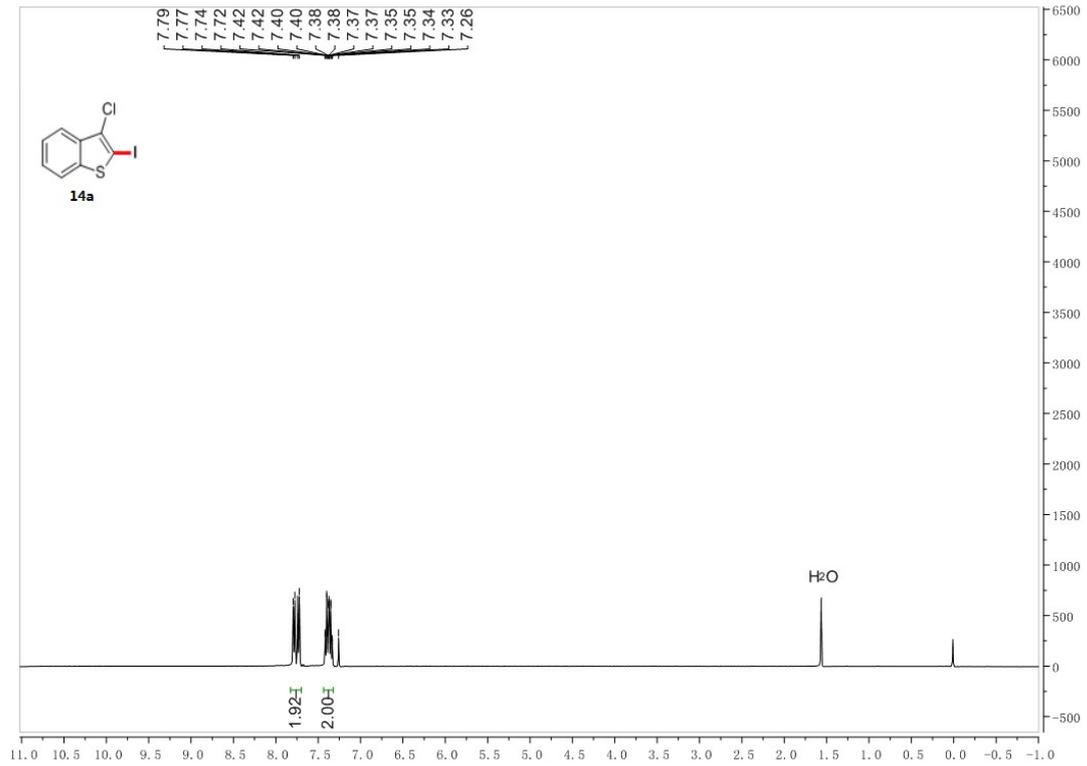


STANDARD PROTON PARAMETERS

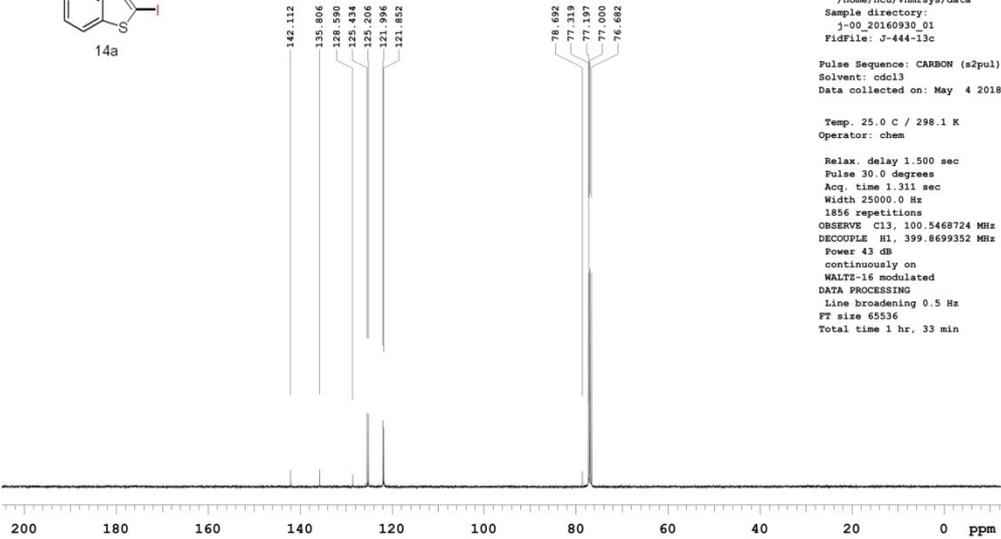
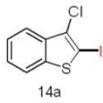
Sample Name: j-78
 Data Collected on: Agilent-NMR-vnmrs400
 Archive directory: /home/ncu/vnmrsys/data
 Sample directory: j-00_20160930_01
 FidFile: J-406-13c
 Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: Apr 27 2018
 Temp. 25.0 C / 298.1 K
 Operator: chem
 Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 832 repetitions
 OBSERVE C13, 100.5468724 MHz
 DECOUPLE H1, 399.8699352 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 1 hr, 33 min







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STANDARD PROTON PARAMETERS

Sample Name: j-78
 Data Collected on: Agilent-NMR-vnmr400
 Archive directory: /home/ncu/vnmrsys/data
 Sample directory: j-00_20160930_01
 FidFile: J-444-13c

Pulse Sequence: CARBON (s2pul)
 Solvent: cdcl3
 Data collected on: May 4 2018

Temp. 25.0 C / 298.1 K
 Operator: chem

Relax. delay 1.500 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 1856 repetitions
 OBSERVE C13, 100.5468724 MHz
 DECOUPLE H1, 399.8699352 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 1 hr, 33 min

