

Oxidative C–S Bond Cleavage of Benzyl Thiols Enabled by Visible-Light-Mediated Silver(II) Complexes

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Supporting Information

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1. General Information

1.1. Materials and Instruments

Reactions were performed in a well-dried flask under an oxygen atmosphere (O₂, 99.995%, 1 atm). Solvents were dried over pre-activated molecular sieves (3 Å, pellets, Alfa Aesar) in the microwave oven before using. Unless otherwise noted, all solvents and reagents were purchased from commercial suppliers (Sigma Aldrich, Alfa Aesar, Acros Organics, and TCI) and used without further purifications.

Flash column chromatography was performed with silica gel 60 (particle size range 230-400 mesh) using a mixture of Et₂O/hexane as the eluent. After purification of the product, the fractions were combined and concentrated under reduced pressure.

¹H and ¹³C NMR spectra were, respectively, recorded on Agilent 400 MHz (¹H NMR), 101 MHz (¹³C NMR) spectrometer in deuterated chloroform (CDCl₃) with tetramethylsilane (TMS) as an internal reference. Data are reported as (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet, br = broad; coupling constant(s) in Hz, integration). NMR yields were determined by adding *n*-dodecane (δ = 0.88 ppm, 6H) as an internal standard to the crude reaction mixtures and by integration of diagnostic signals. Infrared spectra were recorded on Agilent Cary 630 or Perkin Elmer Spectrum Two FT-IR spectrometers. The wavenumbers (ν) of recorded IR-signals are reported in cm⁻¹. UV-vis absorption spectra were recorded on Perkin Elmer Lambda 365 spectrometer. The samples were measured in QS quartz cuvettes (chamber volume 1.4 mL, path length 10 mm). Mass spectra were obtained on a Gas Chromatography Mass Spectrometer (Agilent 7890A/5975C GCMS System). X-band Continuous wave EPR spectra were recorded on Bruker EMX plus 6/1 spectrometer or JEOL JES-FA300 ESR spectrometer.

1.2. Light Sources and Photochemical Reactions Setup

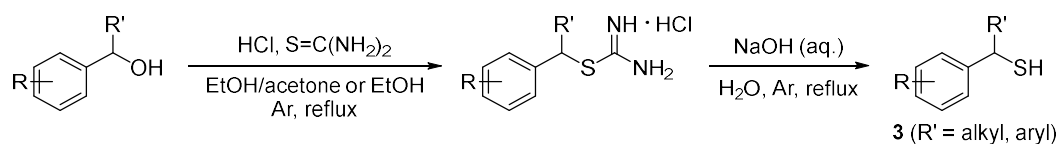
Spotlight-type LED bulbs purchased from CR LIGHTING TECHNOLOGY (Model Number: CR-MR16-5W Cool White LED Bulb ($\lambda_{\text{max}} = 450$ nm, broad spectral range of 500-750 nm), CR-MR16-4W Green LED Bulb ($\lambda_{\text{max}} = 530$ nm), and CR-MR16-4W-B Blue LED Bulb ($\lambda_{\text{max}} = 455$ nm)), OSRAM 20W CFL (Model Number – Duluxstar compact 20W/865), and DAYTIME 20W EFTR20-BLB UV lamp ($\lambda_{\text{max}} = 352$ nm) were used for our study. In each case, the light source was placed around 4 cm from the reaction vessel. The reaction contents were maintained at room temperature (around 23 °C) without using additional cooling instruments.



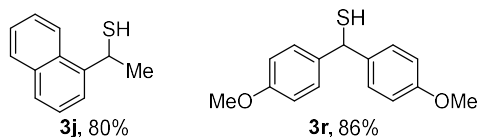
Fig S1. Light lamps and photochemical reactions setup

2. Preparation of the Starting Compounds

The starting thiol compounds **3j** and **3r** were synthesized by following procedure.^[1] Other thiols (**1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, **1o**, **1p**, **1q**, **1r**, **1s**, **1t**, **1u**, **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, **3g**, **3h**, **3i**, **3k**, **3l**, **3m**, **3n**, **3o**, **3p**, **3q**, **3s**, **3t**) are all commercial available.

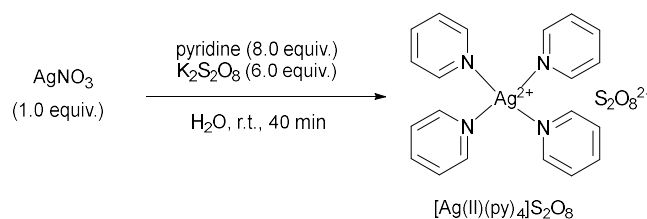


In a well dried two-neck flask equipped with a magnetic stirring bar, the corresponding substituted benzyl alcohol (4.0 mmol, 1.0 equiv.), thiourea (335 mg, 4.4 mmol, 1.1 equiv.), and conc. HCl (1.1 mL, 12.0 mmol, 3.0 equiv.) were dissolved in solvent (**3j** : EtOH/acetone = 1:1, 2 M, 2.0 mL; **3r** : EtOH, 2 M, 2.0 mL). The suspension was stirred and refluxed for 8–12 h. After the resulting solution was cooled to room temperature, 5 M NaOH solution (3.2 mL, 16.0 mmol, 4.0 equiv.) was added to a reaction mixture. The contents were then refluxed for another 2–4 h under argon atmosphere. After lowering the pH to 5 by adding 2 M HCl solution, and the reaction mixture was extracted with CH₂Cl₂ (3×20 mL). The combined organic layer was washed with brine, sodium bicarbonate solution and concentrated under reduced pressure. Purification by column chromatography (**3j**: 20% CH₂Cl₂ in hexane, **3r**: 40% CH₂Cl₂ in hexane) afforded the desired product **3**. The analytical data of thiols were identical in all respects to those previously reported.^{[1],[2]}



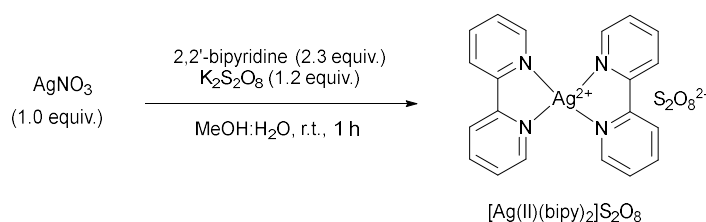
3. Preparation of the Ag(II)–Ligand Complexes

3.1. Preparation of Tetrakis(pyridine)silver(II) peroxydisulfate^[3]



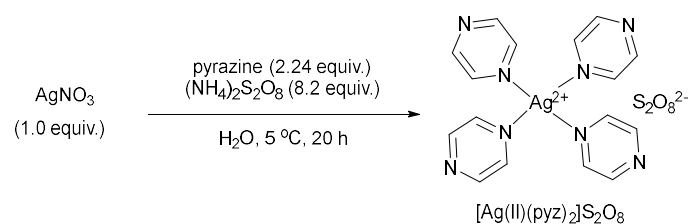
A 100 mL round-bottom-flask equipped with a magnetic stirring bar was charged with $\text{K}_2\text{S}_2\text{O}_8$ (811.0 mg, 3.0 mmol) and 70 mL of ice-cold water. Pyridine (0.32 mL, 4.0 mmol) was added to a solution of AgNO_3 (84.9 mg, 0.5 mmol) in 1.8 mL of water, and the resulting solution was slowly added to the $\text{K}_2\text{S}_2\text{O}_8$ solution. The mixture was stirred for 40 min at room temperature until the precipitation was completed. The precipitate was filtered, washed with ice-cold water (10 mL), ethanol (2×10 mL), and diethyl ether (2×10 mL). The resulting orange solid was dried under reduced pressure and stored in a dark-glass vial. Yield for $[\text{Ag(II)(py)}_4]\text{S}_2\text{O}_8$ was 225 mg (0.365 mmol, 73% yield). The analytical data of the compound were identical in all respects to those previously reported.^[3]

3.2. Preparation of Bis(2,2'-bipyridine)silver(II) peroxydisulfate^[4]



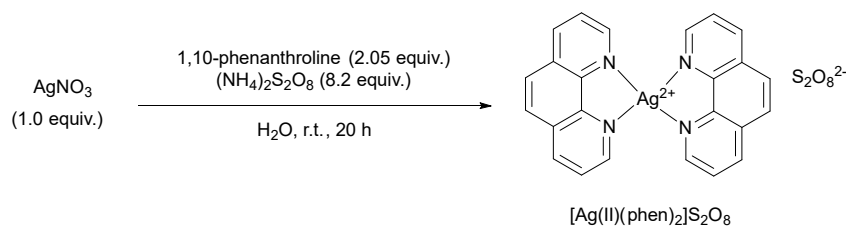
A 250 mL round-bottom-flask equipped with a magnetic stirring bar was charged with $\text{K}_2\text{S}_2\text{O}_8$ (486.6 mg, 1.8 mmol) and 80 mL of ice-cold water. 2,2'-Bipyridine (538.9 mg, 3.45 mmol) was added to a solution of AgNO_3 (254.8 mg, 1.5 mmol) in 20 mL of methanol, and the resulting bright yellow solution was allowed to stir for 30 min. The solvent was removed and the yellow crystalline product ($[\text{Ag(bipy)}_2]\text{NO}_3$) was poured into the $\text{K}_2\text{S}_2\text{O}_8$ solution. The mixture was stirred for 1 h at room temperature until the precipitation was completed. The precipitate was filtered, washed with ice-cold water (2×20 mL), ethanol (2×20 mL), and diethyl ether (2×20 mL). The resulting brown solid was dried under reduced pressure and stored in a dark-glass vial. Yield for $[\text{Ag(II)(bipy)}_2]\text{S}_2\text{O}_8$ was 640.4 mg (1.05 mmol, 70% yield). The analytical data of the compound were identical in all respects to those previously reported.^[4]

3.3. Preparation of Bis(pyrazine)silver(II) peroxydisulfate^[5]



A 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with AgNO₃ (84.9 mg, 0.5 mmol) and 2 mL of water. Pyrazine (89.7 mg, 1.12 mmol) was added to a solution of (NH₄)₂S₂O₈ (935.6 mg, 4.1 mmol) in 4 mL of ice-cold water, and the resulting solution was slowly added to the AgNO₃ solution at 5 °C. The mixture was stirred for 20 h at 5 °C until the precipitation was completed. The precipitate was filtered, washed with ice-cold water (10 mL), ethanol (2 × 10 mL), and diethyl ether (2 × 10 mL). The resulting dark brown solid was dried *in vacuo* over CaCl₂ and stored in a dark-glass vial. Yield for [Ag(II)(pyr)₂]S₂O₈ was 169 mg (0.367 mmol, 73% yield). The analytical data of the compound were identical in all respects to those previously reported.^[5]

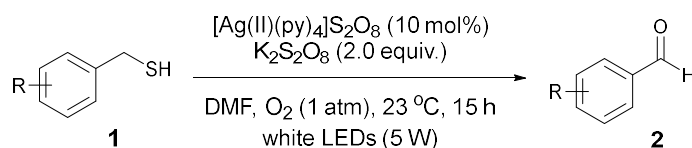
3.4. Preparation of Bis(1,10-phenanthroline)silver(II) peroxydisulfate^[6]



A 100 mL round-bottom-flask equipped with a magnetic stirring bar was charged with 1,10-phenanthroline (184.7 mg, 1.025 mmol), (NH₄)₂S₂O₈ (935.6 mg, 4.1 mmol) and 40 mL of water. On the addition of a solution of AgNO₃ (84.9 mg, 0.5 mmol) in 2 mL of water at room temperature, a yellow solid precipitated. The mixture was stirred for 20 h at room temperature until the precipitation was completed. The precipitate was filtered, washed with ice-cold water (2 × 20 mL), ethanol (2 × 20 mL), and diethyl ether (2 × 20 mL). The resulting brown solid was dried under reduced pressure and stored in a dark-glass vial. Yield for [Ag(II)(phen)₂]S₂O₈ was 263 mg (0.398 mmol, 80% yield). The analytical data of the compound were identical in all respects to those previously reported.^[6]

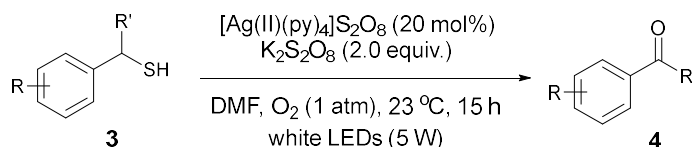
4. General Procedures for the Oxidative C–S Bond Cleavage Reactions

4.1. Standard Reaction Conditions: Aldehydes



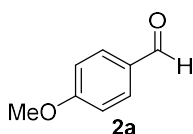
A well dried 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with the corresponding thiol (0.65 mmol, 1.0 equiv.), $[Ag(II)(py)_4]S_2O_8$ (40.1 mg, 0.065 mmol, 0.1 equiv.) and $K_2S_2O_8$ (351.4 mg, 1.3 mmol, 2.0 equiv.). In the absence of light, dry DMF (0.25 M, 2.6 mL) was added. The resulting suspension was degassed and backfilled with O_2 . The reaction mixture was stirred and irradiated with 5 W white LEDs for 18 h at room temperature. After irradiation, the crude mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (Et_2O in hexane: 5 – 60%) afforded the desired products.

4.2. Standard Reaction Conditions: Ketones



A well dried 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with the corresponding thiol (0.65 mmol, 1.0 equiv.), $[Ag(II)(py)_4]S_2O_8$ (80.1 mg, 0.13 mmol, 0.2 equiv.) and $K_2S_2O_8$ (351.4 mg, 1.3 mmol, 2.0 equiv.). In the absence of light, dry DMF (0.25 M, 2.6 mL) was added. The resulting suspension was degassed and backfilled with O_2 . The reaction mixture was stirred and irradiated with 5 W white LEDs for 18 - 36 h at room temperature. After irradiation, the crude mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (Et_2O in hexane: 5 – 60%) afforded the desired products.

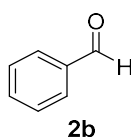
5. Physical Data for the Compounds



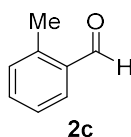
4-Methoxybenzaldehyde (2a)^[7]: Prepared according to the general procedure using 4-methoxybenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (40% Et₂O/hexane, R_f = 0.46) to provide the title compound as a colorless oil (81 mg, 91%). ¹H NMR (400 MHz, CDCl₃) δ 9.87 (s, 1H), 7.84 – 7.81 (m, 2H), 7.01 – 6.97 (m, 2H), 3.87 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 190.8, 164.5, 131.9, 129.9, 114.2, 55.5; IR (neat) 1680, 1595, 1509, 1460, 1426, 1314, 1253, 1156, 1109, 1022, 829, 597, 515 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₈H₈O₂ 136; Found 136.

****4-Methoxybenzaldehyde (2a)**^[7]: 1 mmol reaction scale

A well dried 25 mL round-bottom-flask equipped with a magnetic stirring bar was charged with 4-methoxybenzylthiol (1.0 mmol, 1.0 equiv.), [Ag(II)(py)₄]S₂O₈ (0.1 mmol, 0.1 equiv.) and K₂S₂O₈ (2.0 mmol, 2.0 equiv.). In the absence of light, dry DMF (0.25 M) was added. The resulting suspension was degassed and backfilled with O₂. The reaction mixture was stirred and irradiated with 5 W white LEDs for 18 h at room temperature. After irradiation, the crude mixture was extracted with Et₂O (3 × 30 mL). The combined organic layer was washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. Purification by column chromatography (40% Et₂O/hexane, R_f = 0.46) afforded the desired products (125 mg, 92%).

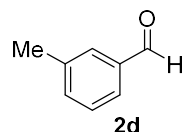


Benzaldehyde (2b)^{[7],[8]}: Prepared according to the general procedure using benzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et₂O/hexane, R_f = 0.42) to provide the title compound as a colorless oil (52 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ 10.03 (s, 1H), 7.91 – 7.88 (m, 2H), 7.66 – 7.62 (m, 1H), 7.56 – 7.52 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 192.4, 136.3, 134.5, 129.7, 129.0; IR (neat) 1693, 1597, 1450, 1391, 1310, 1202, 825, 742, 685, 646, 450 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₇H₆O 106; Found 106.

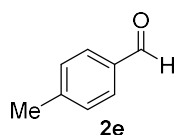


2-Methylbenzaldehyde (2c)^[9]: Prepared according to the general procedure using 2-methylbenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et₂O/hexane, R_f = 0.67) to provide the title compound as a colorless oil (66 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ 10.27 (s, 1H), 7.80 (dd, J = 7.6, 1.5 Hz, 1H), 7.48 (td, J = 7.5, 1.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.27 – 7.25 (m, 1H), 2.68 (s, 3H); ¹³C NMR (101

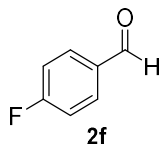
MHz, CDCl₃) δ 192.7, 140.5, 134.1, 133.6, 132.0, 131.7, 126.2, 19.5; IR (neat) 1600, 1461, 1194, 1124, 863, 752, 664, 434 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₈H₈O 120; Found 120.



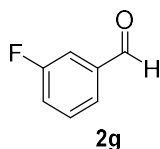
3-Methylbenzaldehyde (2d)^[8]: Prepared according to the general procedure using 3-methylbenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et₂O/hexane, R_f = 0.63) to provide the title compound as a colorless oil (75 mg, 96%). ¹H NMR (400 MHz, CDCl₃) δ 9.99 (s, 1H), 7.69 – 7.67 (m, 2H), 7.46 – 7.40 (m, 2H), 2.44 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 192.6, 138.9, 136.5, 135.3, 130.0, 128.8, 127.2, 21.2; IR (neat) 1699, 1589, 1461, 1381, 1292, 1247, 1143, 778, 685, 430 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₈H₈O 120; Found 120.



4-Methylbenzaldehyde (2e)^{[7],[10]}: Prepared according to the general procedure using 4-methylbenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et₂O/hexane, R_f = 0.54) to provide the title compound as a colorless oil (76 mg, 97%). ¹H NMR (400 MHz, CDCl₃) δ 9.96 (s, 1H), 7.79 – 7.76 (m, 2H), 7.34 – 7.32 (m, 2H), 2.44 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 191.9, 145.5, 134.1, 129.8, 129.7, 21.8; IR (neat) 1690, 1601, 1452, 1387, 1306, 1209, 1169, 807, 758, 600, 481 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₈H₈O 120; Found 120.

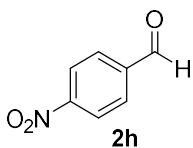


4-Fluorobenzaldehyde (2f)^{[7],[11]}: Prepared according to the general procedure using 4-fluorobenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (30% Et₂O/hexane, R_f = 0.55) to provide the title compound as a colorless oil (65 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ 9.97 (s, 1H), 7.94 – 7.89 (m, 2H), 7.25 – 7.19 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 190.5, 166.5 (d, J_{cf} = 256.7 Hz), 132.9 (d, J_{cf} = 2.9 Hz), 132.2 (d, J_{cf} = 9.6 Hz), 116.3 (d, J_{cf} = 22.2 Hz); IR (neat) 1694, 1594, 1504, 1388, 1297, 1226, 1149, 1094, 829, 773, 596, 506, 421 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₇H₅FO 124; Found 124.

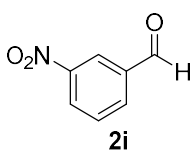


3-Fluorobenzaldehyde (2g)^[8]: Prepared according to the general procedure using 3-fluorobenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (30% Et₂O/hexane, R_f = 0.58) to provide the title compound as a colorless oil (63 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ 10.00 (d, J = 2.0 Hz, 1H), 7.69 (dt, J = 7.6, 1.3 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.37 – 7.32 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 190.8, 163.1 (d, J_{cf} = 249.5 Hz), 138.4 (d, J_{cf} = 6.2 Hz), 130.8 (d, J_{cf} = 7.6 Hz), 126.0 (d, J_{cf} = 3.0 Hz), 121.5 (d, J_{cf} = 21.8 Hz), 115.3 (d, J_{cf} = 22.1 Hz); IR

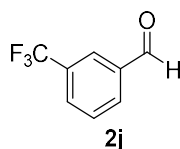
(neat) 1692, 1591, 1451, 1386, 1247, 1128, 929, 881, 787, 747, 676, 520, 441 cm^{-1} ; LRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_7\text{H}_5\text{FO}$ 124; Found 124.



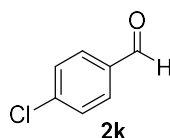
4-Nitrobenzaldehyde (2h)^[7]: Prepared according to the general procedure using 4-nitrobenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (50% Et_2O /hexane, $R_f = 0.46$) to provide the title compound as a white solid (90 mg, 92%). ^1H NMR (400 MHz, CDCl_3) δ 10.17 (s, 1H), 8.42 – 8.39 (m, 2H), 8.11 – 8.08 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 190.3, 151.1, 140.0, 130.4, 124.3; IR (neat) 1707, 1600, 1531, 1344, 1267, 1195, 1105, 1008, 813, 733, 513, 463 cm^{-1} ; LRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_7\text{H}_5\text{NO}_3$ 151; Found 151.



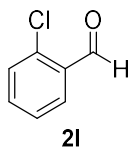
3-Nitrobenzaldehyde (2i)^{[12],[13]}: Prepared according to the general procedure using 3-nitrobenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (60% Et_2O /hexane, $R_f = 0.62$) to provide the title compound as a white solid (69 mg, 70%). ^1H NMR (400 MHz, CDCl_3) δ 10.12 (s, 1H), 8.71 (dd, $J = 2.3, 1.6$ Hz, 1H), 8.50 – 8.47 (m, 1H), 8.25 – 8.22 (m, 1H), 7.79 – 7.75 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 189.7, 148.7, 137.3, 134.6, 130.3, 128.5, 124.3; IR (neat) 1700, 1613, 1529, 1348, 1198, 1085, 903, 812, 728, 667, 528, 471, 424 cm^{-1} ; LRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_7\text{H}_5\text{NO}_3$ 151; Found 151.



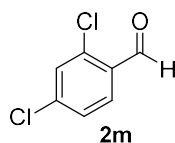
3-(Trifluoromethyl)benzaldehyde (2j)^[14]: Prepared according to the general procedure using 3-trifluoromethylbenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (30% Et_2O /hexane, $R_f = 0.51$) to provide the title compound as a colorless oil (85 mg, 75%). ^1H NMR (400 MHz, CDCl_3) δ 10.09 (s, 1H), 8.15 (s, 1H), 8.09 (d, $J = 7.7$ Hz, 1H), 7.90 (d, $J = 7.9$ Hz, 1H), 7.70 (t, $J = 7.7$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 190.7, 136.7, 132.6 (q, $J_{\text{CF}} = 1.2$ Hz), 131.8 (q, $J_{\text{CF}} = 33.3$ Hz), 130.8 (q, $J_{\text{CF}} = 3.6$ Hz), 129.7, 126.4 (q, $J_{\text{CF}} = 3.8$ Hz), 123.5 (q, $J_{\text{CF}} = 272.5$ Hz); IR (neat) 1705, 1614, 1386, 1325, 1125, 1071, 907, 804, 764, 696 cm^{-1} ; LRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_8\text{H}_5\text{F}_3\text{O}$ 174; Found 174.



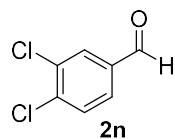
4-Chlorobenzaldehyde (2k)^{[7],[8]}: Prepared according to the general procedure using 4-chlorobenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et_2O /hexane, $R_f = 0.50$) to provide the title compound as a white solid (72 mg, 79%). ^1H NMR (400 MHz, CDCl_3) δ 9.97 (s, 1H), 7.83 – 7.79 (m, 2H), 7.52 – 7.48 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 190.8, 140.9, 134.7, 130.9, 129.4; IR (neat) 1699, 1573, 1485, 1383, 1296, 1203, 1165, 1090, 1011, 815, 541, 483 cm^{-1} ; LRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_7\text{H}_5\text{ClO}$ 140; Found 140.



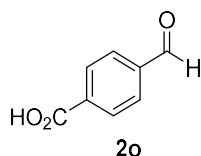
2-Chlorobenzaldehyde (2l)^{[8],[10]}: Prepared according to the general procedure using 2-chlorobenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et₂O/hexane, *R_f* = 0.53) to provide the title compound as a colorless oil (73 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ 10.49 (s, 1H), 7.94 – 7.92 (m, 1H), 7.56 – 7.52 (m, 1H), 7.47 – 7.45 (m, 1H), 7.42 – 7.37 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 189.8, 137.9, 135.1, 132.4, 130.6, 129.4, 127.3; IR (neat) 1695, 1591, 1442, 1270, 1197, 1054, 825, 755, 633, 435 cm⁻¹; LRMS (EI) *m/z*: [M]⁺ Calcd for C₇H₅ClO 140; Found 140.



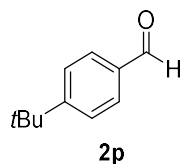
2,4-Dichlorobenzaldehyde (2m)^{[15],[16]}: Prepared according to the general procedure using 2,4-dichlorobenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (5% Et₂O/hexane, *R_f* = 0.50) to provide the title compound as a white solid (84 mg, 74%). ¹H NMR (400 MHz, CDCl₃) δ 10.42 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.40 – 7.37 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 188.5, 141.1, 138.5, 130.9, 130.4, 130.3, 127.9; IR (neat) 1687, 1578, 1463, 1375, 1250, 1196, 1097, 1050, 822, 768, 663, 571, 415 cm⁻¹; LRMS (EI) *m/z*: [M]⁺ Calcd for C₇H₄Cl₂O 174; Found 174.



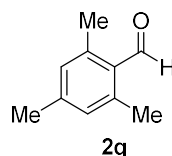
3,4-Dichlorobenzaldehyde (2n)^[18]: Prepared according to the general procedure using 3,4-dichlorobenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (30% Et₂O/hexane, *R_f* = 0.53) to provide the title compound as a white solid (74 mg, 65%). ¹H NMR (400 MHz, CDCl₃) δ 9.95 (s, 1H), 7.96 (d, *J* = 1.9 Hz, 1H), 7.72 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 189.6, 139.1, 135.8, 133.9, 131.3, 131.2, 128.4; IR (neat) 1695, 1584, 1464, 1361, 1261, 1192, 1130, 1031, 879, 821, 740, 553, 416 cm⁻¹; LRMS (EI) *m/z*: [M]⁺ Calcd for C₇H₄Cl₂O 174; Found 174.



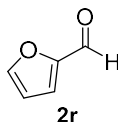
4-Formylbenzoic acid (2o)^[20]: Prepared according to the general procedure using 4-(mercaptomethyl)benzoic acid (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was loaded on silica and purified by flash column chromatography (15% MeOH/CH₂Cl₂, *R_f* = 0.25) to provide the title compound as a white solid (72 mg, 74%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.36 (br, 1H), 10.10 (s, 1H), 8.14 – 8.12 (m, 2H), 8.03 – 8.00 (m, 2H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 193.0, 166.6, 138.9, 135.8, 129.9, 129.6; IR (neat) 1702, 1024, 820, 757, 621, 508 cm⁻¹; LRMS (EI) *m/z*: [M]⁺ Calcd for C₈H₆O₃ 150; Found 150.



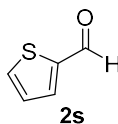
4-(*tert*-Butyl)benzaldehyde (2p)^[16]: Prepared according to the general procedure using 4-*tert*-butylbenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et₂O/hexane, R_f = 0.42) to provide the title compound as a pale yellow oil (92 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 1H), 7.84 – 7.81 (m, 2H), 7.57 – 7.54 (m, 2H), 1.35 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 192.0, 158.4, 134.1, 129.6, 125.9, 35.3, 31.0; IR (neat) 1694, 1606, 1464, 1364, 1310, 1268, 1220, 1175, 1107, 827, 702, 549 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₁₁H₁₄O 162; Found 162.



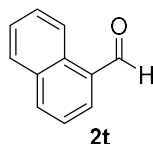
2,4,6-Trimethylbenzaldehyde (2q)^[22]: Prepared according to the general procedure using 2,4,6-trimethylbenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et₂O/hexane, R_f = 0.50) to provide the title compound as a colorless oil (73 mg, 76%). ¹H NMR (400 MHz, CDCl₃) δ 10.55 (s, 1H), 6.89 (s, 2H), 2.57 (s, 6H), 2.31 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 192.9, 143.8, 141.4, 130.5, 129.9, 21.4, 20.4; IR (neat) 1684, 1609, 1437, 1379, 1290, 1209, 1147, 1034, 851, 781 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₁₀H₁₂O 148; Found 148.



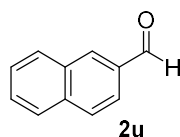
Furan-2-carbaldehyde (2r)^{[9],[15]}: Prepared according to the general procedure using 2-furanmethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (40% Et₂O/hexane, R_f = 0.40) to provide the title compound as a yellow oil (50 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ 9.67 (s, 1H), 7.72 – 7.71 (m, 1H), 7.29 – 7.28 (m, 1H), 6.63 – 6.62 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 177.7, 152.8, 148.0, 121.1, 112.5; IR (neat) 1668, 1566, 1464, 1392, 1276, 1155, 1079, 1016, 928, 881, 746, 592, 501 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₅H₄O₂ 96; Found 96.



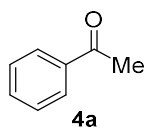
Thiophene-2-carbaldehyde (2s)^{[7],[15]}: Prepared according to the general procedure using 2-thiophenemethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (30% Et₂O/hexane, R_f = 0.40) to provide the title compound as a yellow oil (64 mg, 88%). ¹H NMR (400 MHz, cdcl₃) δ 9.96 (s, 1H), 7.80 – 7.77 (m, 2H), 7.26 – 7.21 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 183.0, 144.0, 136.3, 135.1, 128.3; IR (neat) 1672, 1516, 1418, 1213, 1046, 729, 665 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₅H₄OS 112; found 112.



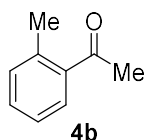
1-Naphthaldehyde (2t)^{[11],[15]}: Prepared according to the general procedure using 1-naphthalenemethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (40% Et₂O/hexane, R_f= 0.58) to provide the title compound as a pale yellow oil (90 mg, 89%). ¹H NMR (400 MHz, CDCl₃) δ 10.36 (s, 1H), 9.25 – 9.22 (m, 1H), 8.07 – 8.04 (m, 1H), 7.94 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.90 – 7.87 (m, 1H), 7.69 – 7.64 (m, 1H), 7.60 – 7.54 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 193.5, 136.6, 135.2, 133.6, 131.3, 130.4, 129.0, 128.4, 126.9, 124.8; IR (neat) 1684, 1572, 1508, 1459, 1215, 1169, 1053, 885, 768, 711, 646, 522, 403 cm⁻¹; LRMS (EI) *m/z*: [M]⁺ Calcd for C₁₁H₈O 156; Found 156.



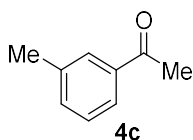
2-Naphthaldehyde (2u)^[8]: Prepared according to the general procedure using 2-naphthalenemethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et₂O/hexane, R_f= 0.53) to provide the title compound as a white solid (95 mg, 94%). ¹H NMR (400 MHz, CDCl₃) δ 10.13 (s, 1H), 8.30 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.95 – 7.92 (m, 1H), 7.91 – 7.87 (m, 2H), 7.64 – 7.60 (m, 1H), 7.59 – 7.54 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 192.1, 136.3, 134.4, 134.0, 132.5, 129.4, 129.0, 129.0, 127.9, 127.0, 122.6; IR (neat) 1687, 1625, 1463, 1345, 1259, 1170, 1115, 859, 816, 743, 605, 473 cm⁻¹; LRMS (EI) *m/z*: [M]⁺ Calcd for C₁₁H₈O 156; found 156.



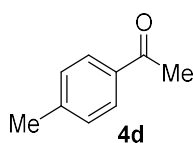
Acetophenone (4a)^{[8],[12]}: Prepared according to the general procedure using 1-phenylethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et₂O/hexane, R_f= 0.44) to provide the title compound as a colorless oil (66 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.93 (m, 2H), 7.57 – 7.53 (m, 1H), 7.47 – 7.42 (m, 2H), 2.58 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 198.0, 136.9, 132.9, 128.4, 128.1, 26.4; IR (neat) 1680, 1598, 1445, 1358, 1260, 954, 758, 687, 587 cm⁻¹; LRMS (EI) *m/z*: [M]⁺ Calcd for C₈H₈O 120; Found 120.



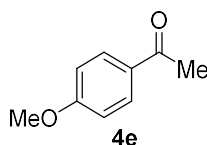
1-(*o*-Tolyl)ethan-1-one (4b)^[24]: Prepared according to the general procedure using 1-(*o*-tolyl)ethane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et₂O/hexane, R_f= 0.45) to provide the title compound as a colorless oil (60 mg, 69%). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.35 (td, *J* = 7.5, 1.4 Hz, 1H), 7.26 – 7.21 (m, 2H), 2.55 (s, 3H), 2.52 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 201.5, 138.2, 137.4, 131.9, 131.3, 129.2, 125.5, 29.3, 21.4; IR (neat) 1684, 1454, 1355, 1247, 1127, 1039, 952, 759, 601 cm⁻¹; LRMS (EI) *m/z*: [M]⁺ Calcd for C₉H₁₀O 134; found 134.



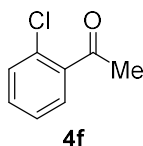
1-(*m*-Tolyl)ethan-1-one (4c)^[24]: Prepared according to the general procedure using 1-(*m*-tolyl)ethane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et₂O/hexane, R_f= 0.39) to provide the title compound as a colorless oil (56 mg, 64%). ¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.72 (m, 2H), 7.37 – 7.30 (m, 2H), 2.57 (s, 3H), 2.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 198.1, 138.1, 137.0, 133.7, 128.6, 128.3, 125.4, 26.5, 21.1; IR (neat) 1680, 1591, 1425, 1355, 1273, 1191, 956, 784, 690, 586, 464 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₉H₁₀O 134; Found 134.



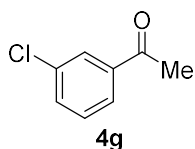
1-(*p*-Tolyl)ethan-1-one (4d)^{[10],[22]}: Prepared according to the general procedure using 1-(*p*-tolyl)ethane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et₂O/hexane, R_f= 0.42) to provide the title compound as a colorless oil (52 mg, 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.85 (m, 2H), 7.27 – 7.25 (m, 2H), 2.58 (s, 3H), 2.41 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 197.9, 143.9, 134.6, 129.2, 128.4, 26.5, 21.6; IR (neat) 1681, 1606, 1357, 1270, 1182, 814, 568 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₉H₁₀O 134; Found 134.



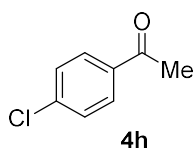
1-(4-Methoxyphenyl)ethan-1-one (4e)^[12]: Prepared according to the general procedure using 1-(4-methoxyphenyl)ethane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et₂O/hexane, R_f= 0.30) to provide the title compound as a colorless oil (78 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.89 (m, 2H), 6.92 – 6.89 (m, 2H), 3.84 (s, 3H), 2.53 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 196.8, 163.4, 130.6, 130.3, 113.6, 55.4, 26.3; IR (neat) 1673, 1597, 1509, 1356, 1247, 1170, 1025, 955, 834, 565 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₉H₁₀O₂ 150; Found 150.



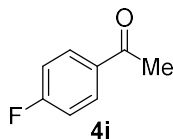
1-(2-Chlorophenyl)ethan-1-one (4f)^[10]: Prepared according to the general procedure using 1-(2-chlorophenyl)ethane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et₂O/hexane, R_f= 0.35) to provide the title compound as a colorless oil (79 mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.54 (m, 1H), 7.44 – 7.37 (m, 2H), 7.35 – 7.31 (m, 1H), 2.65 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 200.5, 139.1, 132.0, 131.3, 130.6, 129.4, 126.9, 30.7; IR (neat) 1698, 1591, 1433, 1358, 1241, 1042, 758, 594 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₈H₇ClO 154; Found 154.



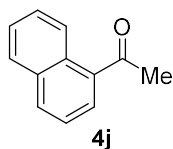
1-(3-Chlorophenyl)ethan-1-one (4g)^[10]: Prepared according to the general procedure using 1-(3-chlorophenyl)ethane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et₂O/hexane, R_f = 0.40) to provide the title compound as a colorless oil (70 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.92 (m, 1H), 7.84 – 7.82 (m, 1H), 7.55 – 7.52 (m, 1H), 7.43 – 7.39 (m, 1H), 2.60 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 196.7, 138.5, 134.9, 133.0, 129.9, 128.4, 126.4, 26.6; IR (neat) 1686, 1570, 1422, 1355, 1247, 1073, 785, 681, 588 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₈H₇ClO 154; Found 154.



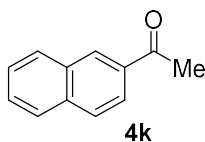
1-(4-Chlorophenyl)ethan-1-one (4h)^{[10],[12]}: Prepared according to the general procedure using 1-(4-chlorophenyl)ethane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et₂O/hexane, R_f = 0.51) to provide the title compound as a colorless oil (68 mg, 68%). ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.88 (m, 2H), 7.45 – 7.41 (m, 2H), 2.59 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 196.7, 139.5, 135.4, 129.7, 128.8, 26.5; IR (neat) 1683, 1587, 1356, 1257, 1092, 1012, 956, 822, 759, 588, 524, 468 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₈H₇ClO 154; Found 154.



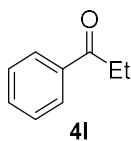
1-(4-Fluorophenyl)ethan-1-one (4i)^{[15],[24]}: Prepared according to the general procedure using 1-(4-fluorophenyl)ethane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et₂O/hexane, R_f = 0.43) to provide the title compound as a colorless oil (55 mg, 61%). ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.96 (m, 2H), 7.16 – 7.10 (m, 2H), 2.59 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 196.4, 165.7 (d, J_{cf} = 254.4 Hz), 133.6 (d, J_{cf} = 3.0 Hz), 130.9 (d, J_{cf} = 9.4 Hz), 115.6 (d, J_{cf} = 21.8 Hz), 26.5; IR (neat) 1683, 1595, 1505, 1358, 1261, 1228, 1156, 959, 837, 564, 493 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₈H₇FO 138; Found 138.



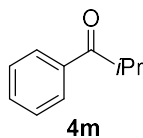
1-(Naphthalen-1-yl)ethan-1-one (4j)^{[24],[25]}: Prepared according to the general procedure using 1-(1-naphthyl)ethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et₂O/hexane, R_f = 0.54) to provide the title compound as a white solid (69 mg, 62%). ¹H NMR (400 MHz, CDCl₃) δ 8.76 – 8.73 (m, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.93 (dd, J = 7.2, 1.2 Hz, 1H), 7.87 – 7.85 (m, 1H), 7.62 – 7.58 (m, 1H), 7.54 – 7.46 (m, 2H), 2.74 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 201.8, 135.4, 133.9, 133.0, 130.1, 128.6, 128.4, 128.0, 126.4, 126.0, 124.3, 29.9; IR (neat) 1674, 1507, 1355, 1239, 1190, 1127, 942, 773, 591, 491 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₁₂H₁₀O 170; Found 170.



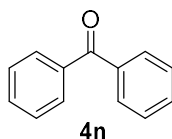
1-(Naphthalen-2-yl)ethan-1-one (4k)^{[12],[24]}: Prepared according to the general procedure using 1-(2-naphthyl)ethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by column flash chromatography (20% Et₂O/hexane, R_f = 0.45) to provide the title compound as a pale yellow solid (97 mg, 88%). ¹H NMR (400 MHz, CDCl₃) δ 8.44 (s, 1H), 8.03 – 8.01 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.60 – 7.52 (m, 2H), 2.71 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 198.0, 135.5, 134.4, 132.4, 130.1, 129.5, 128.4, 128.3, 127.7, 126.7, 123.8, 26.6; IR (neat) 1674, 1627, 1468, 1362, 1279, 1191, 1127, 942, 859, 818, 745, 665, 576, 475 cm⁻¹; LRMS (EI) *m/z*: [M]⁺ Calcd for C₁₂H₁₀O 170; Found 170.



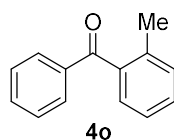
Propiophenone (4l)^{[7],[10]}: Prepared according to the general procedure using 1-phenylpropane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et₂O/hexane, R_f = 0.50) to provide the title compound as a colorless oil (61 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.95 (m, 2H), 7.57 – 7.53 (m, 1H), 7.47 – 7.43 (m, 2H), 3.01 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 200.8, 136.8, 132.8, 128.5, 127.9, 31.7, 8.2; IR (neat) 1684, 1597, 1447, 1351, 1219, 950, 744, 689, 566 cm⁻¹; LRMS (EI) *m/z*: [M]⁺ Calcd for C₉H₁₀O 134; Found 134.



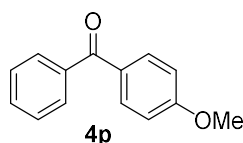
2-Methyl-1-phenylpropan-1-one (4m)^{[10],[12]}: Prepared according to the general procedure using 2-methyl-1-phenylpropane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 36 h, the reaction mixture was purified by flash column chromatography (10% Et₂O/hexane, R_f = 0.50) to provide the title compound as a colorless oil (78 mg, 81%). ¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.95 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 – 7.45 (m, 2H), 3.56 (hept, *J* = 6.8 Hz, 1H), 1.22 (dd, *J* = 6.8, 0.4 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 204.5, 136.2, 132.8, 128.6, 128.3, 35.3, 19.1; IR (neat) 1682, 1596, 1447, 1223, 1163, 979, 701 cm⁻¹; LRMS (EI) *m/z*: [M]⁺ Calcd for C₁₀H₁₂O 148; Found 148.



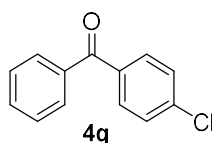
Benzophenone (4n)^{[7],[10]}: Prepared according to the general procedure using diphenylmethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et₂O/hexane, R_f = 0.46) to provide the title compound as a colorless oil (103 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.81 – 7.79 (m, 4H), 7.60 – 7.55 (m, 2H), 7.49 – 7.45 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 196.7, 137.5, 132.3, 130.0, 128.2; IR (neat) 1656, 1597, 1446, 1274, 1150, 919, 762, 695, 638 cm⁻¹; LRMS (EI) *m/z*: [M]⁺ Calcd for C₁₃H₁₀O 182; Found 182.



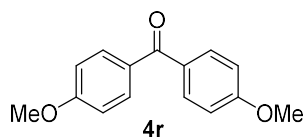
Phenyl(*o*-tolyl)methanone (4o)^[27]: Prepared according to the general procedure using phenyl(*o*-tolyl)methanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 36 h, the reaction mixture was purified by flash column chromatography (5% Et₂O/hexane, $R_f = 0.42$) to provide the title compound as a colorless oil (89 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.81 – 7.78 (m, 2H), 7.58 – 7.54 (m, 1H), 7.46 – 7.41 (m, 2H), 7.40 – 7.36 (m, 1H), 7.31 – 7.21 (m, 3H), 2.33 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 198.5, 138.5, 137.6, 136.6, 133.1, 130.9, 130.2, 130.0, 128.4, 128.4, 125.1, 19.9; IR (neat) 1662, 1597, 1447, 1271, 1154, 924, 701, 639 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₁₄H₁₂O 196; Found 196.



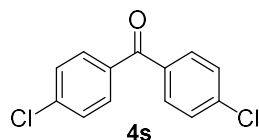
(4-Methoxyphenyl)(phenyl)methanone (4p)^{[28],[29]}: Prepared according to the general procedure using (4-methoxyphenyl)(phenyl)methanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (30% Et₂O/hexane, $R_f = 0.46$) to provide the title compound as a white solid (99 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.81 (m, 2H), 7.77 – 7.74 (m, 2H), 7.59 – 7.54 (m, 1H), 7.49 – 7.45 (m, 2H), 6.98 – 6.95 (m, 2H), 3.89 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 195.6, 163.2, 138.2, 132.5, 131.9, 130.1, 129.7, 128.2, 113.5, 55.5; IR (neat) 1650, 1595, 1507, 1443, 1251, 1170, 1026, 920, 843, 741, 698, 601 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₁₄H₁₂O₂ 212; Found 212.



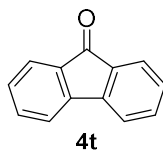
(4-Chlorophenyl)(phenyl)methanone (4q)^[29]: Prepared according to the general procedure using (4-chlorophenyl)(phenyl)methanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (7% Et₂O/hexane, $R_f = 0.46$) to provide the title compound as a white solid (108 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.73 (m, 4H), 7.61 – 7.57 (m, 1H), 7.50 – 7.43 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 195.3, 138.8, 137.1, 135.8, 132.5, 131.4, 129.8, 128.5, 128.3; IR (neat) 1658, 1584, 1271, 1151, 1090, 921, 844, 696, 475 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₁₃H₉ClO 216; Found 216.



Bis(4-methoxyphenyl)methanone (4r)^{[28],[32]}: Prepared according to the general procedure using bis(4-methoxyphenyl)methanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (40% Et₂O/hexane, $R_f = 0.33$) to provide the title compound as a white solid (106 mg, 67%). ¹H NMR (400 MHz, CDCl₃) δ 7.81 – 7.77 (m, 4H), 6.98 – 6.94 (m, 4H), 3.88 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 194.4, 162.8, 132.2, 130.7, 113.4, 55.4; IR (neat) 1645, 1598, 1507, 1304, 1246, 1164, 1028, 927, 850, 770, 586 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₁₅H₁₄O₃ 242; Found 242.



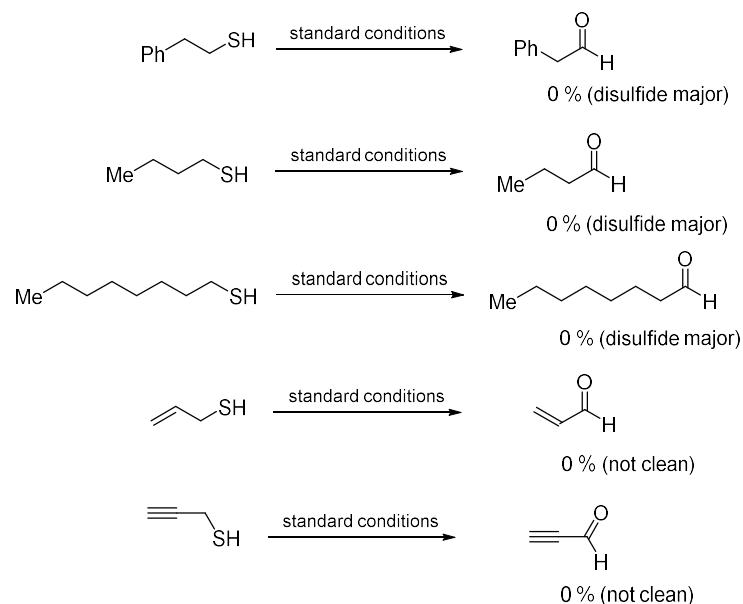
Bis(4-chlorophenyl)methanone (4s)^[32]: Prepared according to the general procedure using bis(4-chlorophenyl)methane-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash chromatography (7% Et₂O/hexane, R_f = 0.53) to provide the title compound as a white solid (127 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.71 (m, 4H), 7.48 – 7.45 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 194.2, 139.1, 135.5, 131.3, 128.7; IR (neat) 1651, 1583, 1397, 1267, 1086, 926, 851, 751, 668, 507, 459 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₁₃H₈Cl₂O 250; Found 250.



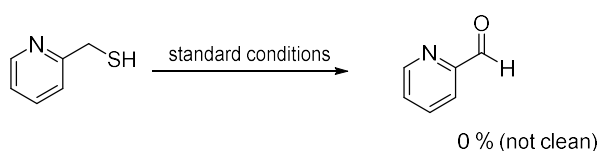
9H-fluoren-9-one (4t)^[34]: Prepared according to the general procedure using 9H-fluorene-9-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash chromatography (20% Et₂O/hexane, R_f = 0.47) to provide the title compound as a yellow solid (111mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.61 (m, 2H), 7.48 – 7.42 (m, 4H), 7.28 – 7.24 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 193.8, 144.3, 134.6, 134.0, 129.0, 124.2, 120.2; IR (neat) 1713, 1610, 1599, 1451, 1298, 1191, 1149, 1097, 948, 916, 811, 731, 668, 650 cm⁻¹; LRMS (EI) m/z: [M]⁺ Calcd for C₁₃H₈O 180; Found 180.

6. Reactions with Non-Benzyllic Substrates

We carried out the reactions with various non-benzylic substrates such as alkyl, allyl, and propargyl thiols. No desired carbonyl product was obtained with these substrates. In the case of alkyl thiols, disulfides were obtained as major compounds. However, the reactions were not clean with allyl and propargyl thiols under the reaction conditions. We assumed that the benzyl group would be crucial for the oxidative cleavage process.

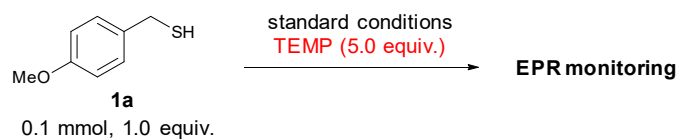


In addition, 2-pyridinemethanethiol was not a suitable substrate for this transformation, probably due to the nitrogen atom effect.



7. Mechanistic Studies

7.1. Determination of Singlet Oxygen Species^[35]



We could confirm the generation of $^1\text{O}_2$ during the reaction by EPR (Fig. S2). A characteristic signal of TEMPO was detected when we employed 2,2,6,6-tetramethylpiperidine (TEMP) to trap $^1\text{O}_2$, indicating that $^1\text{O}_2$ is involved in this transformation.

Irradiation of air-saturated DMF solution of TEMP and the reaction mixture (4-methoxybenzylthiol and $[\text{Ag}(\text{II})(\text{py})_4]\text{S}_2\text{O}_8$ in DMF) under white LEDs resulted in the formation of a strong characteristic signal of $^1\text{O}_2$ adduct with TEMP ($a^{\text{N}} = 16.0 \pm 0.1$ G). A series of stronger characteristic signal of $^1\text{O}_2$ were collected with prolonged irradiation time, indicating that $^1\text{O}_2$ is present during the reaction (Fig S2).

All EPR spectra were collected with the following experimental parameters: frequency: 9.4 GHz; power: 0.9230 mW; modulation width: 0.8 mT; amplitude: 120; time constant: 0.03 sec; sweep time: 30 sec; Number of scans: 1.

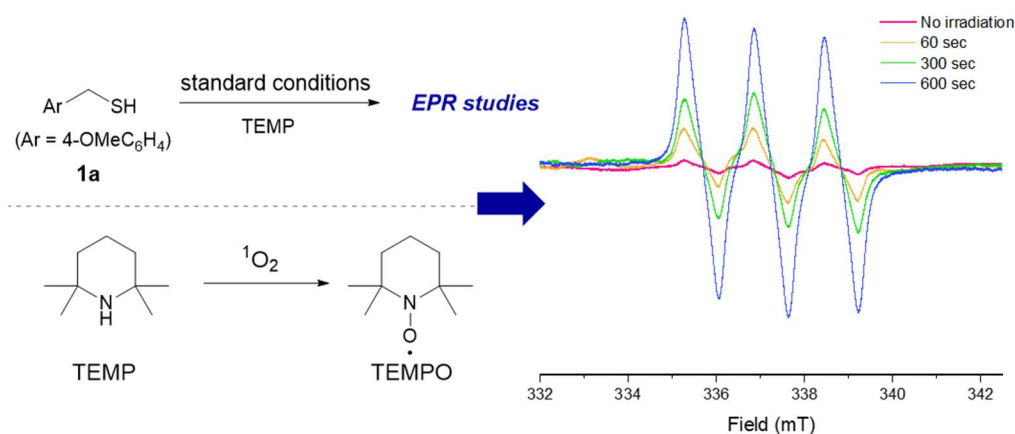


Fig S2. EPR signal of TEMPO free radical

7.2. NMR Studies

To check the reaction intermediates, we carried out the reaction in DMF-d₇. We observed peaks that could correspond to α -hydroperoxy sulfide **I** in the ¹H NMR studies (**Fig. S3**).

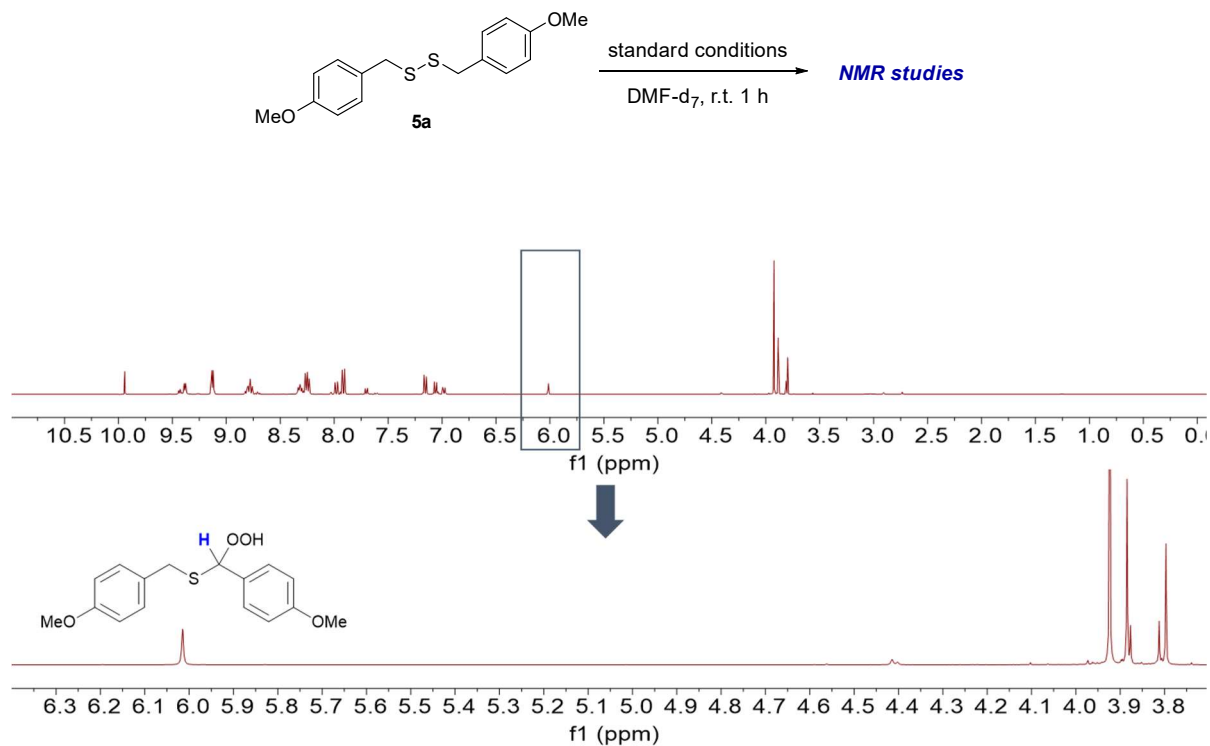
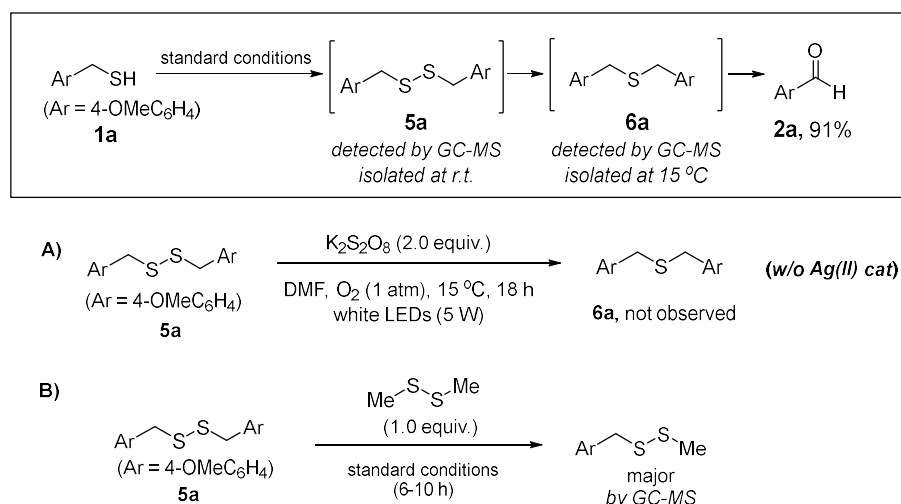


Fig S3. NMR studies

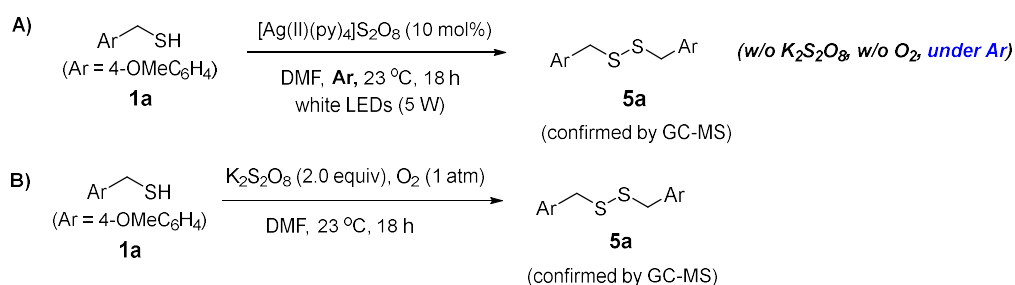
7.3. Control Experiments

To gain further information for the formation of sulfide **6a** from disulfide **5a**, we carried out some additional experiments. The reaction did not take place in the absence of [Ag(II)(py)₄]S₂O₈ (Scheme S1, **A**). This indicates that the use of the silver catalyst is necessary in this process. We assumed that thiyl radical would be involved in the formation of sulfide **6a** from **5a** in the presence of a silver catalyst. To test our hypothesis, we carried out a cross-coupling reaction with disulfide **5a** and dimethyl disulfide under the reaction conditions (Scheme S1, **B**). As expected, the cross-coupled product was obtained as a major compound (analyzed by GC-MS). The reaction between thiyl and benzyl radicals from **5a** could afford sulfide **6a**.



Scheme S1. Control experiments: The formation of sulfide **6**.

Furthermore, disulfide **5a** was obtained from **1a** when we carried out the reaction with [Ag(II)(py)₄]S₂O₈ *under Ar* (Scheme S2, **A**). In addition, we could also confirm the formation of disulfide **5a** from thiol **1a** by oxidation under the reaction conditions (Scheme S2, **B**). On the basis of our results, a proposed reaction pathway is summarized in Scheme 6.

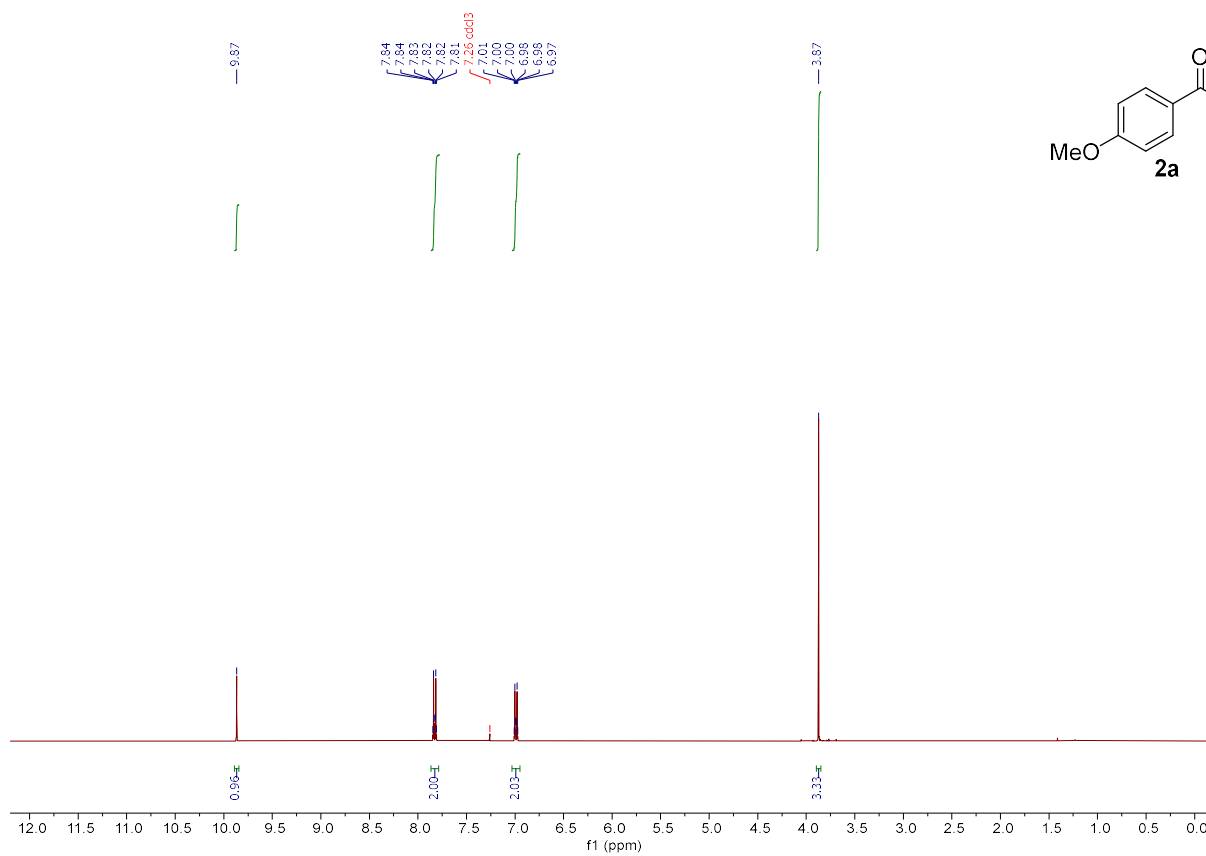
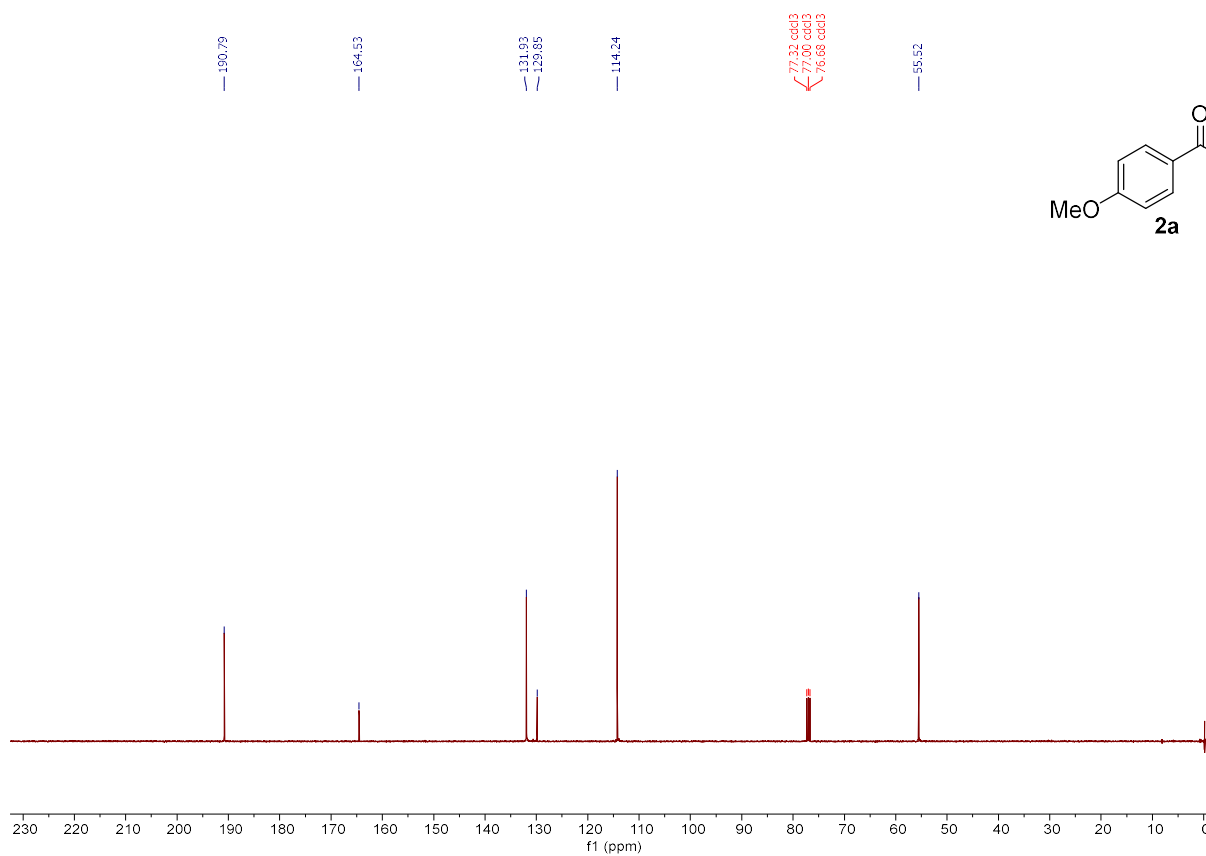


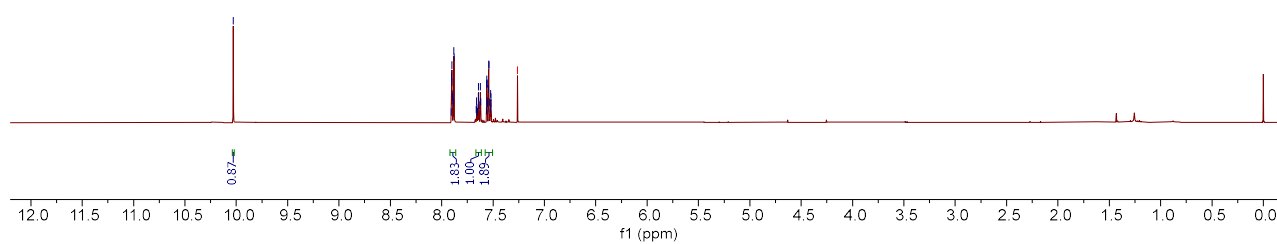
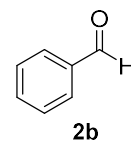
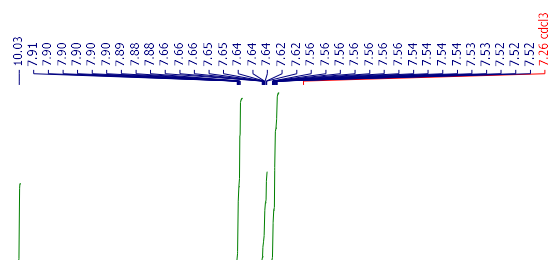
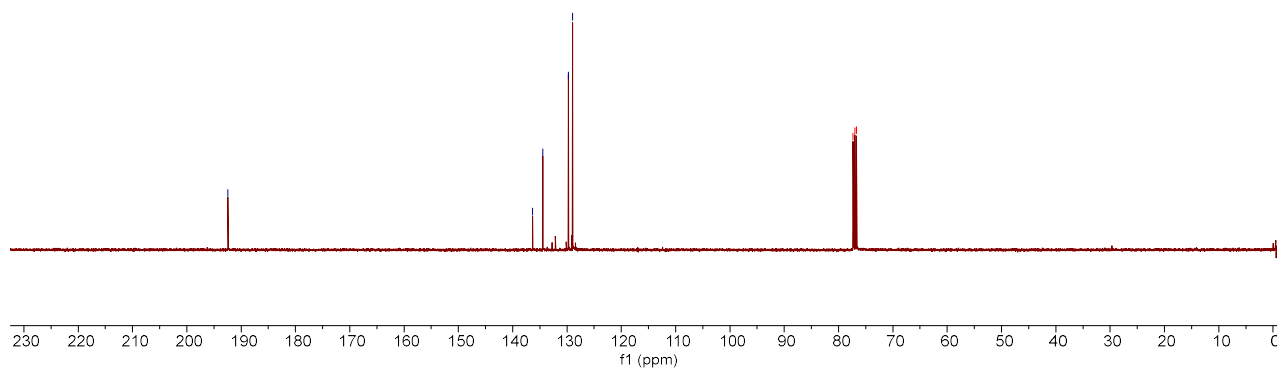
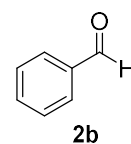
Scheme S2. Control experiments: The formation of disulfide **5**.

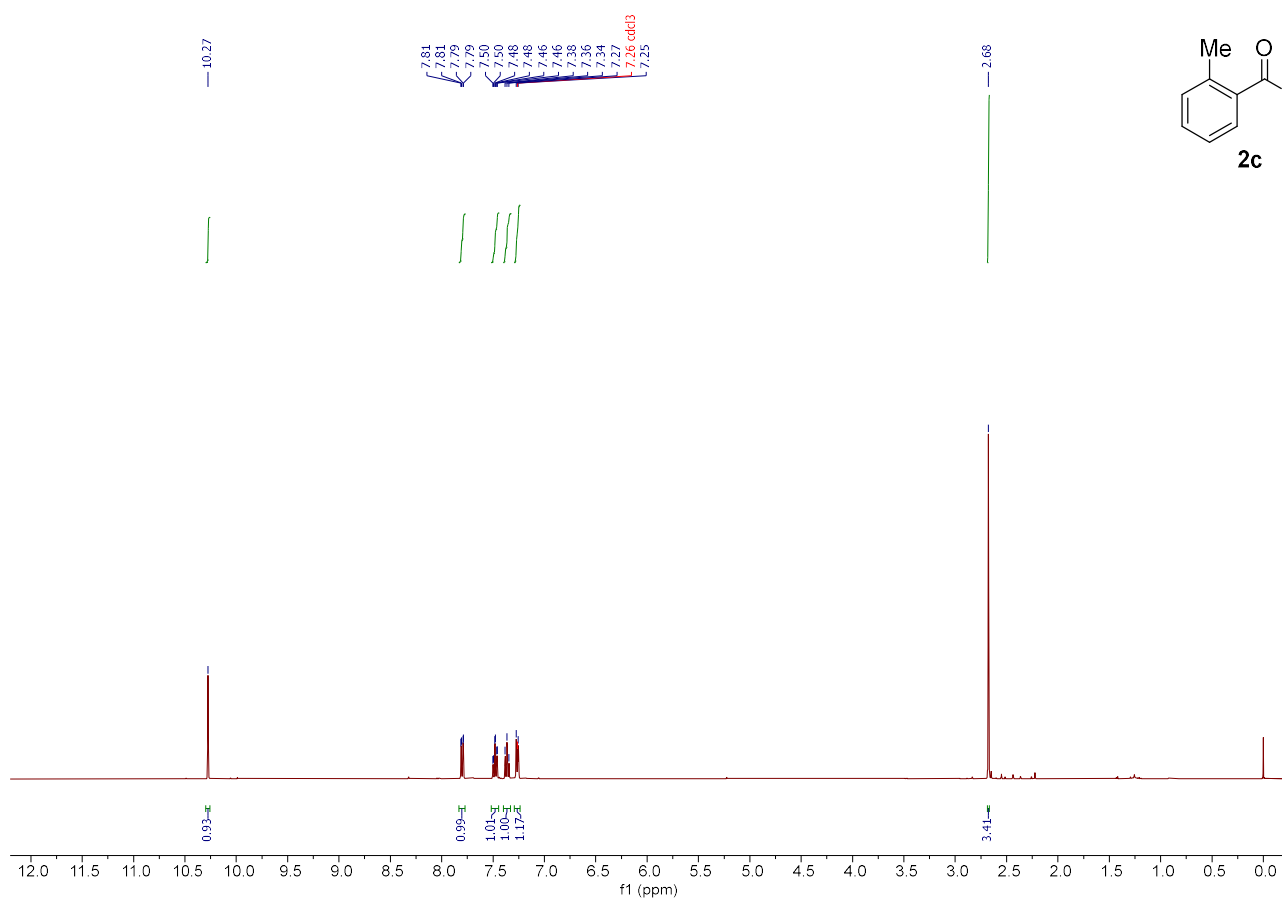
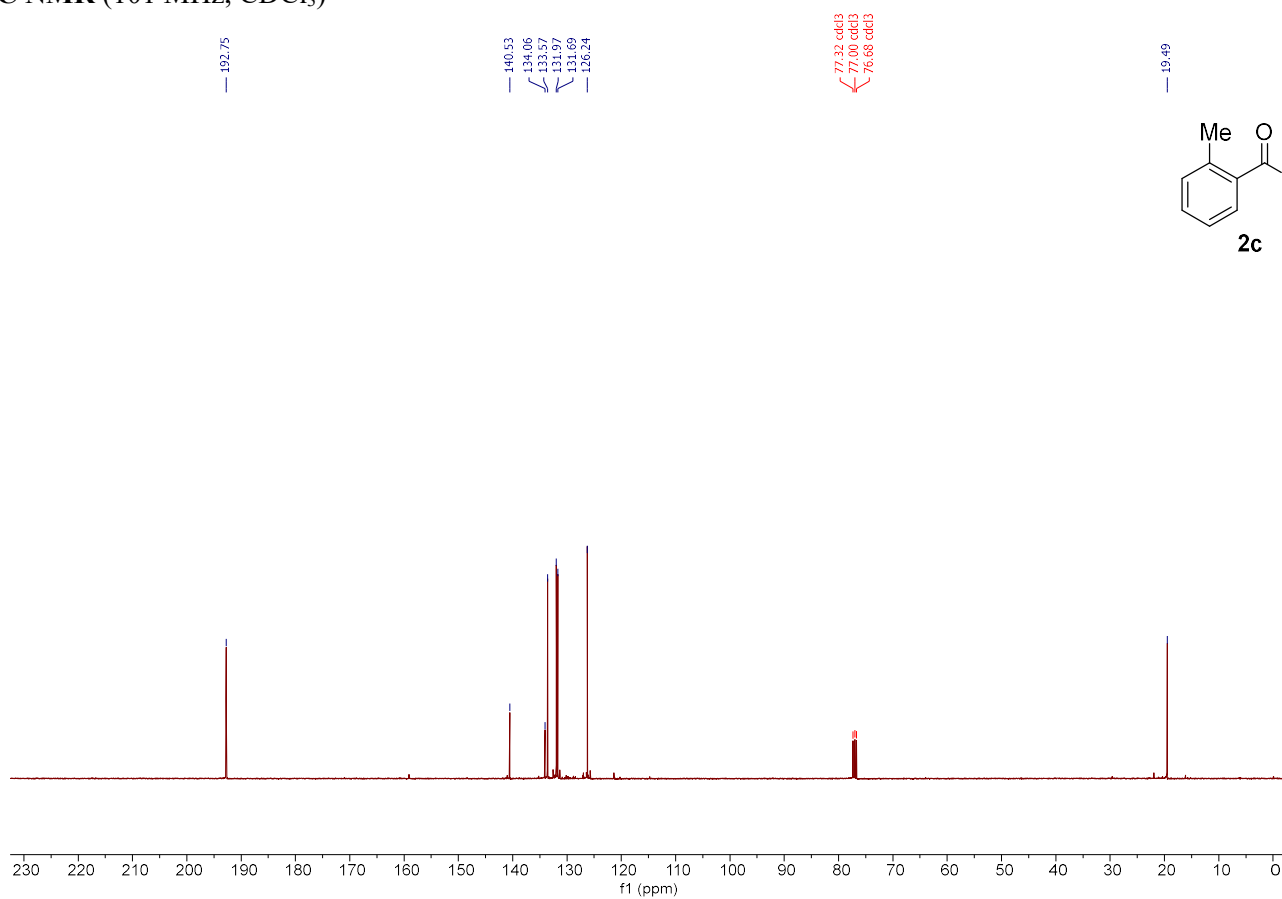
8. References

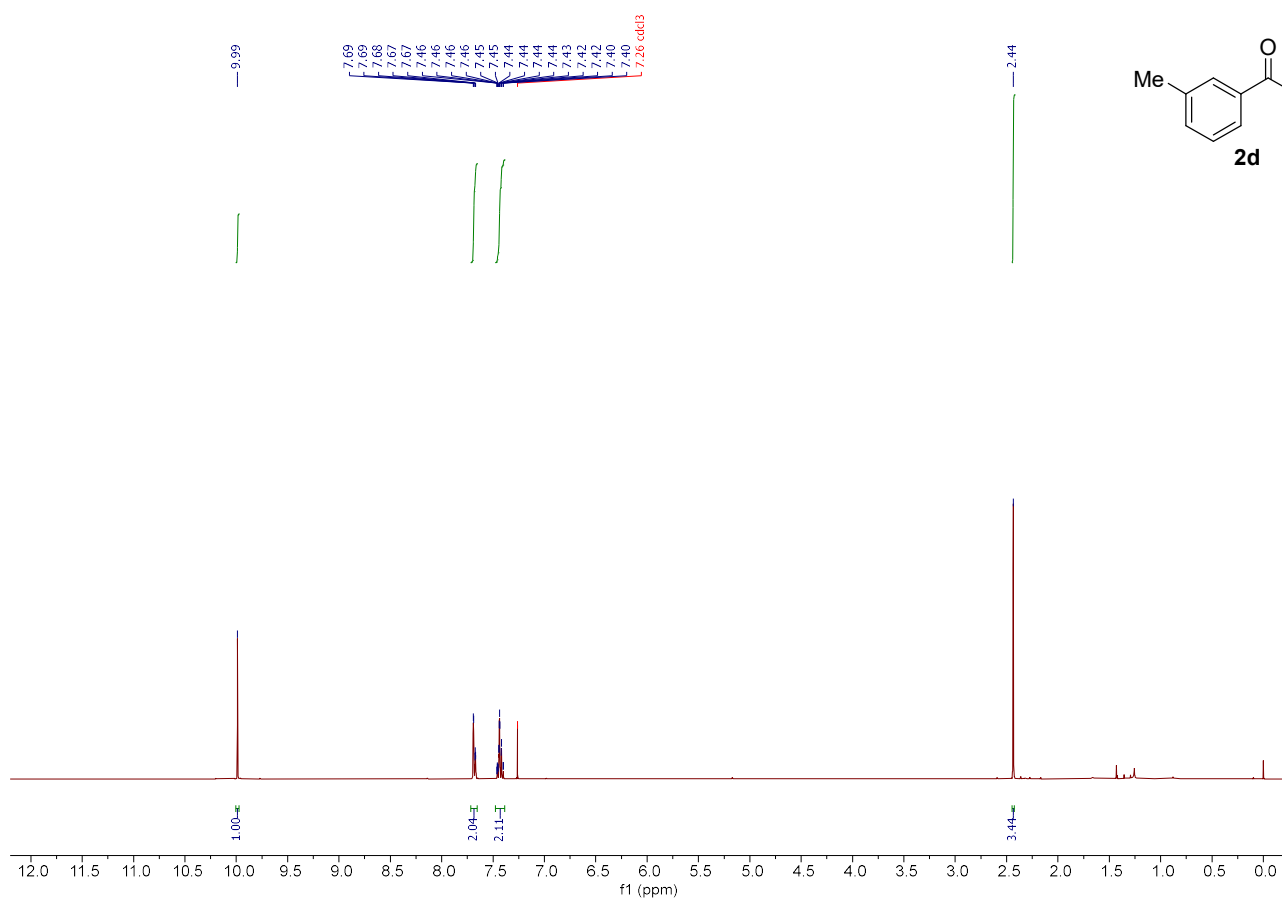
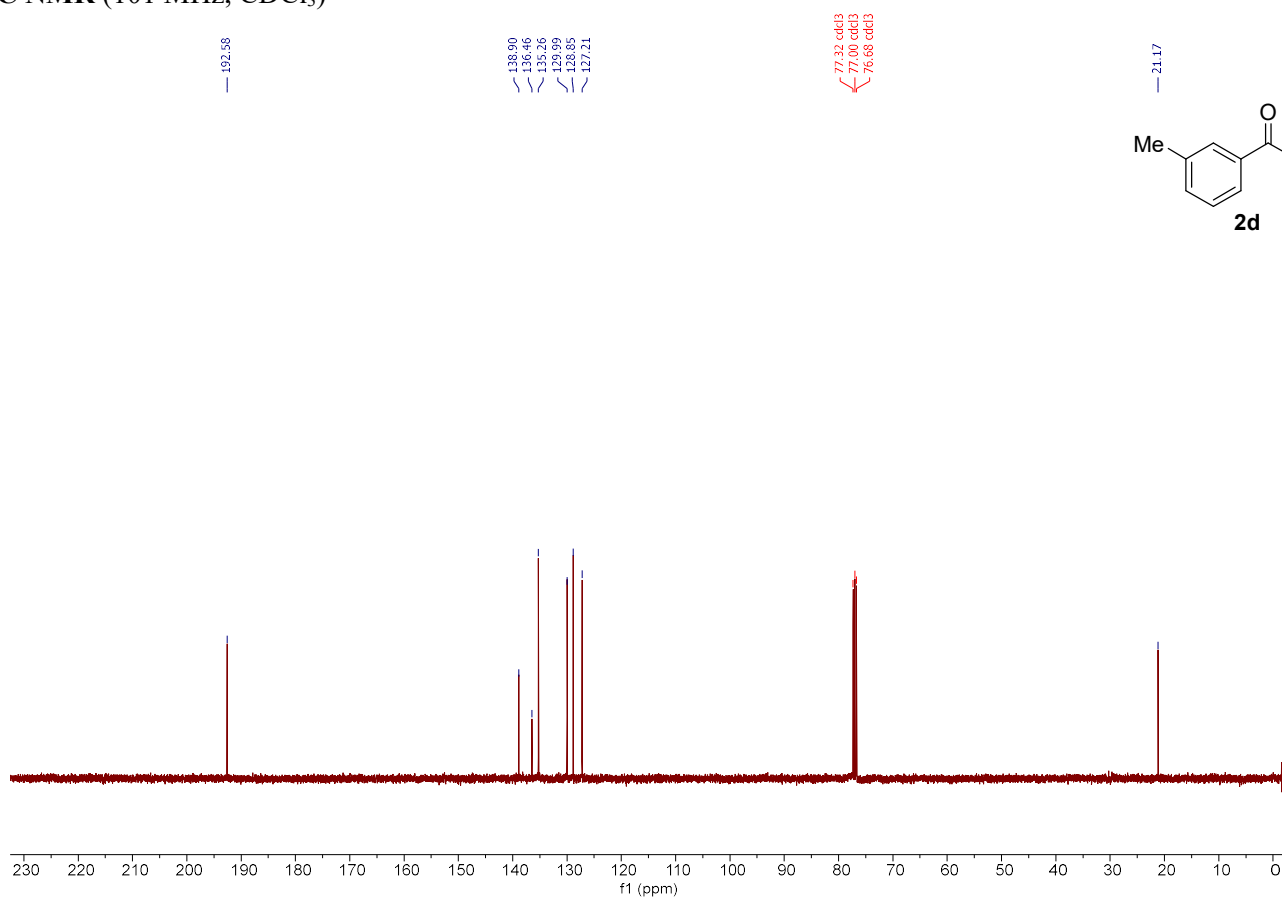
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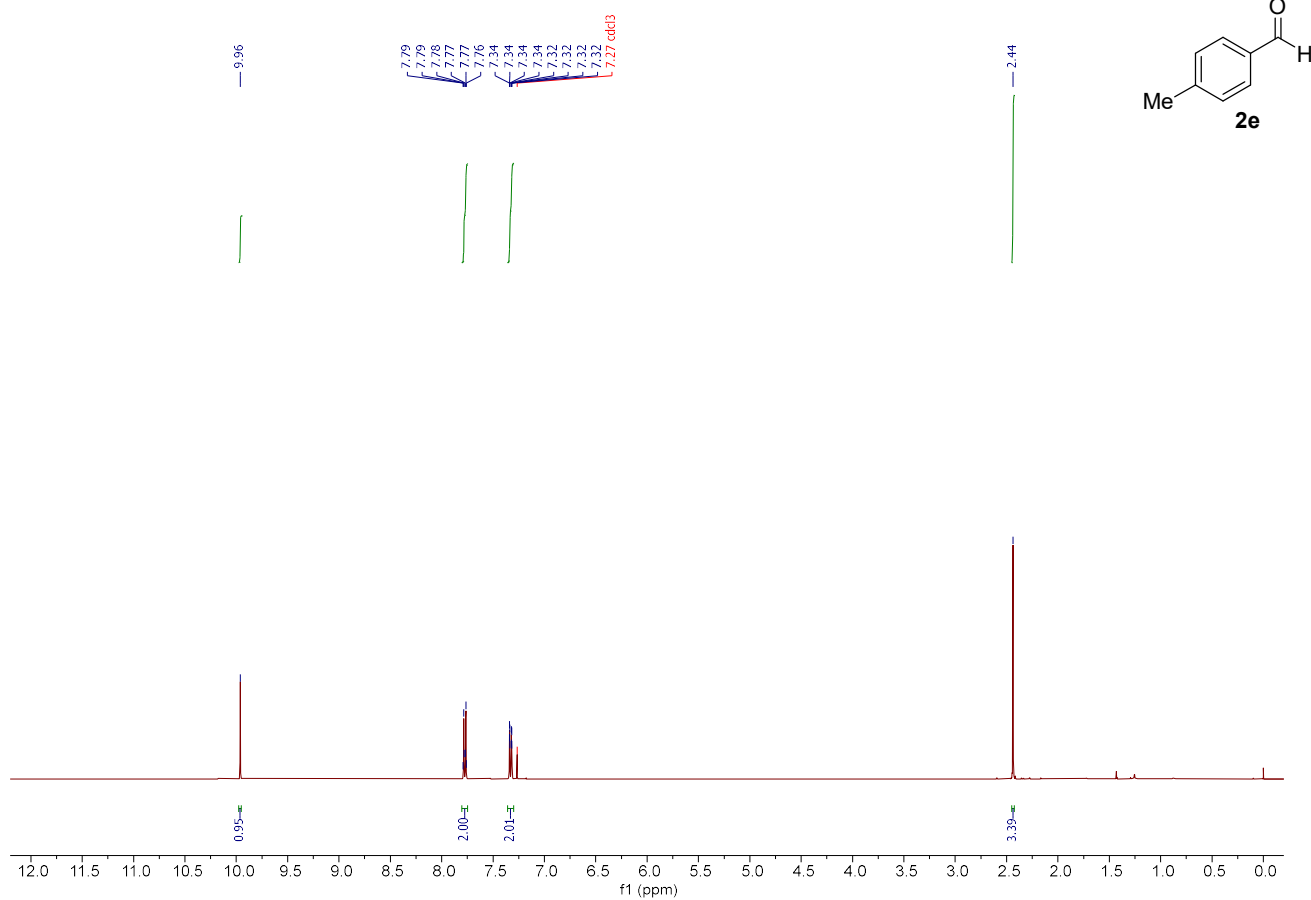
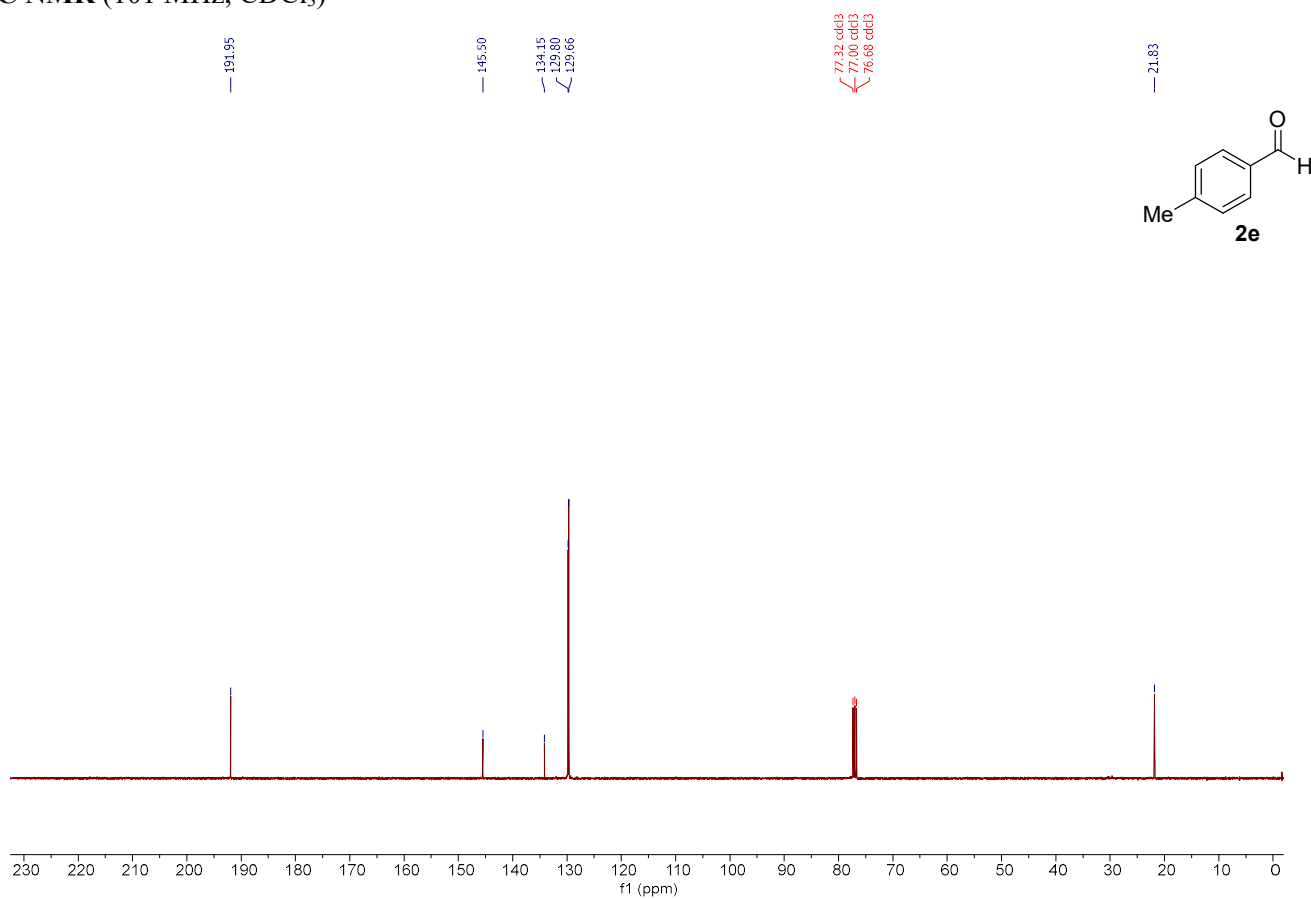
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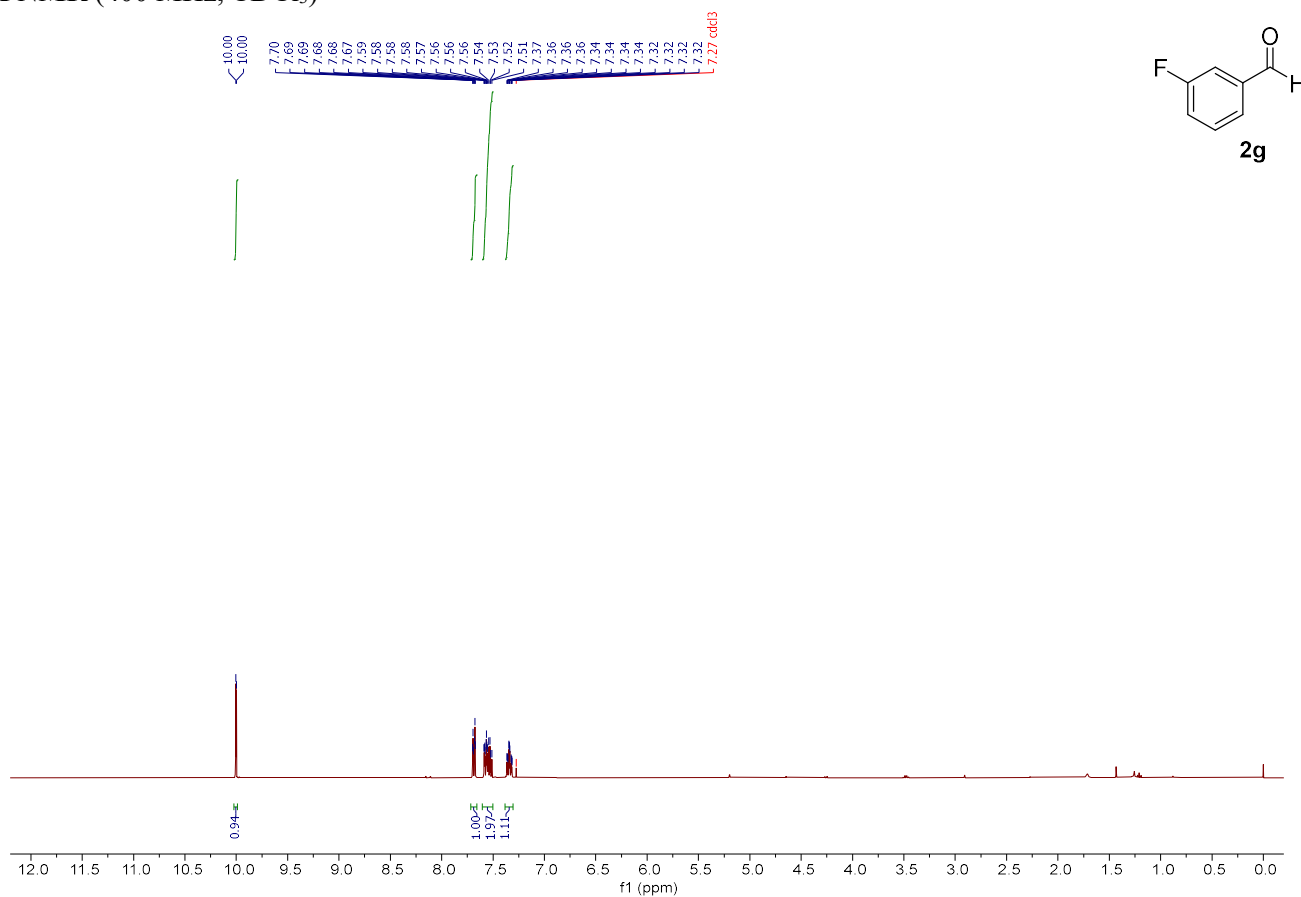
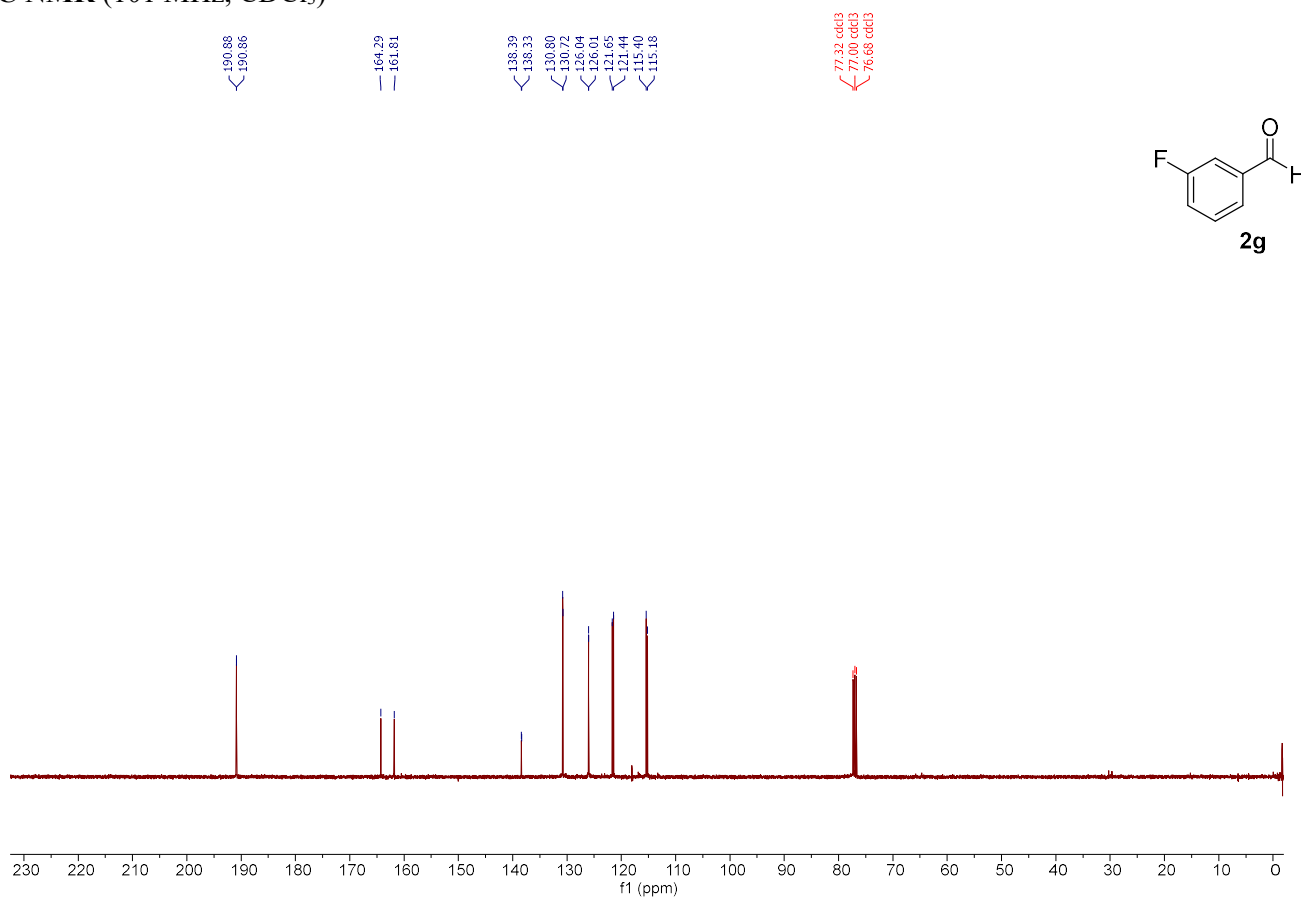
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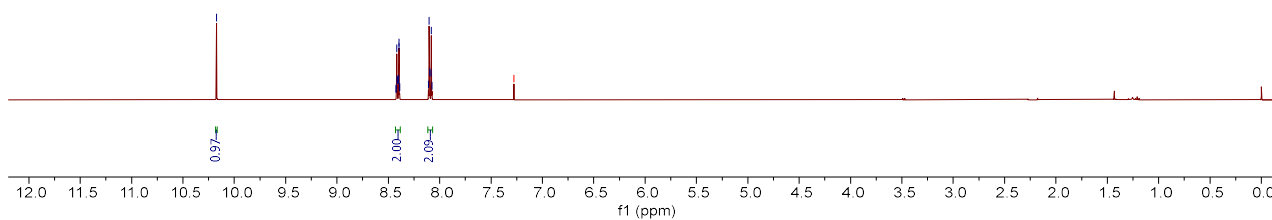
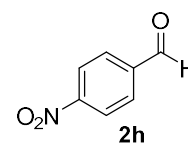
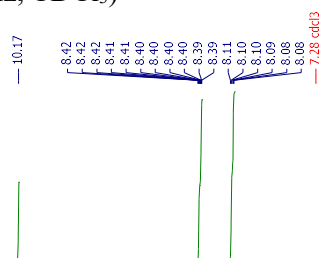
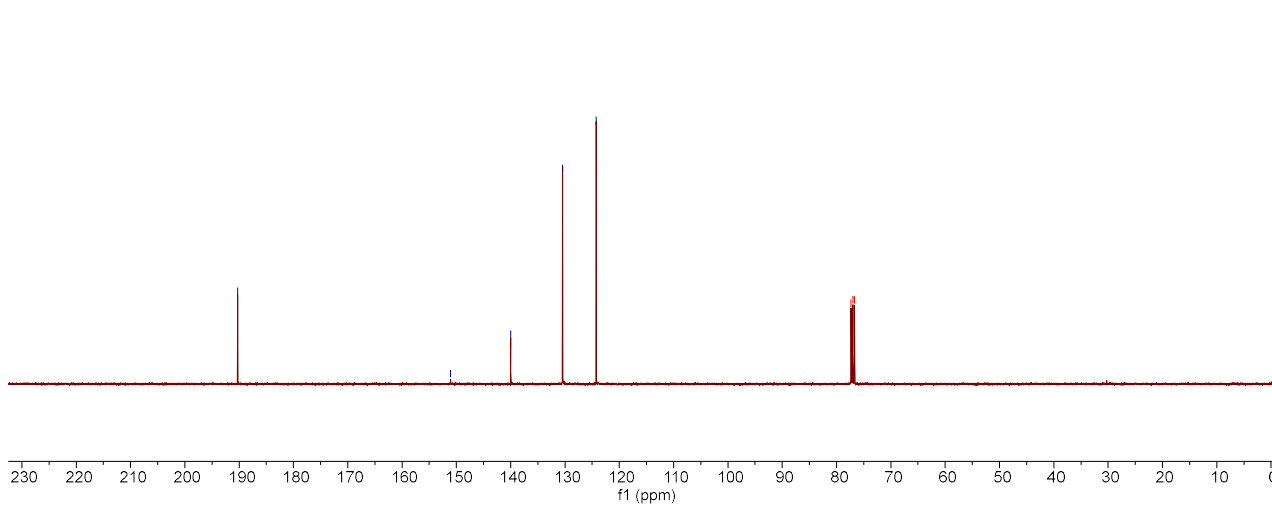
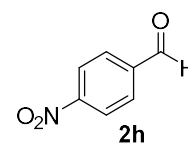
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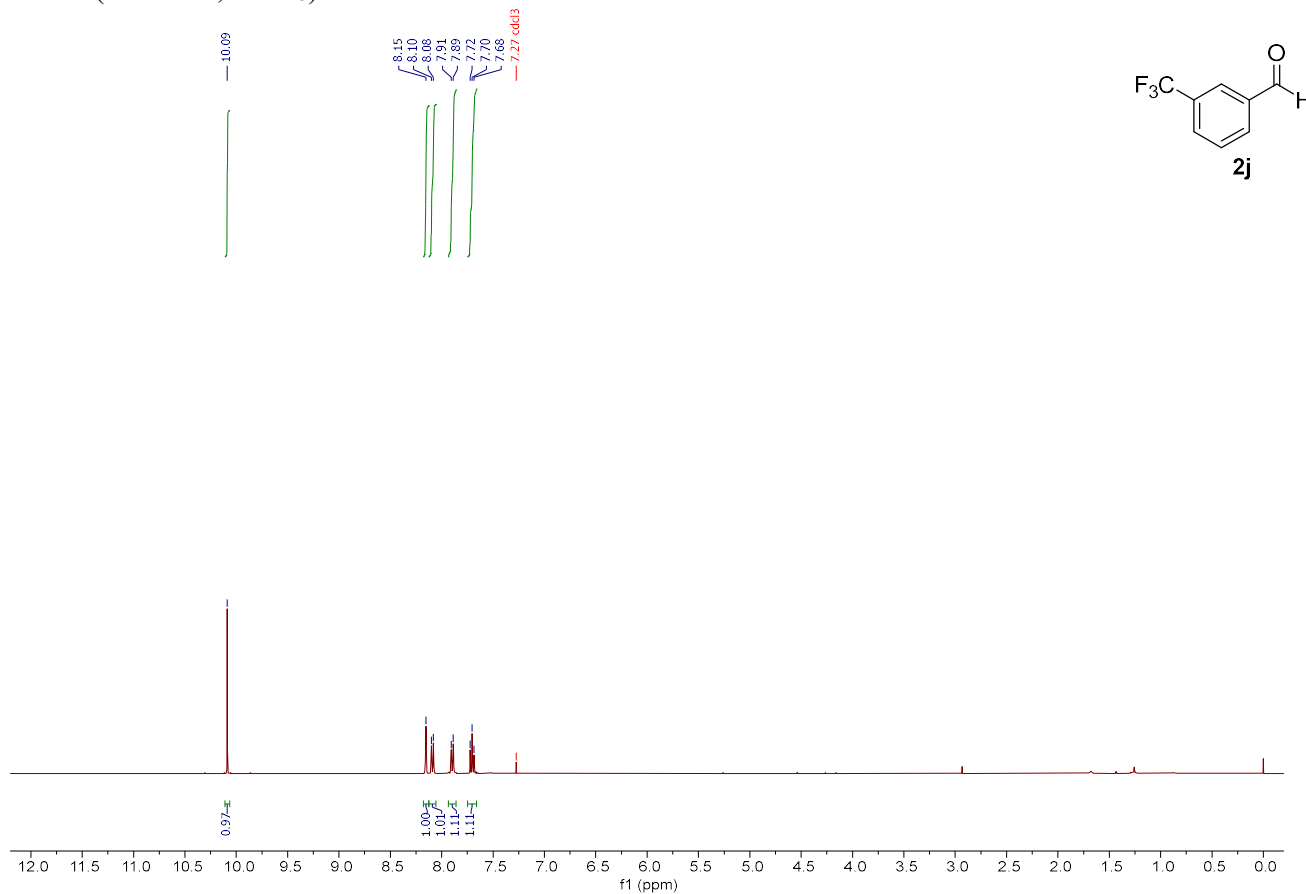
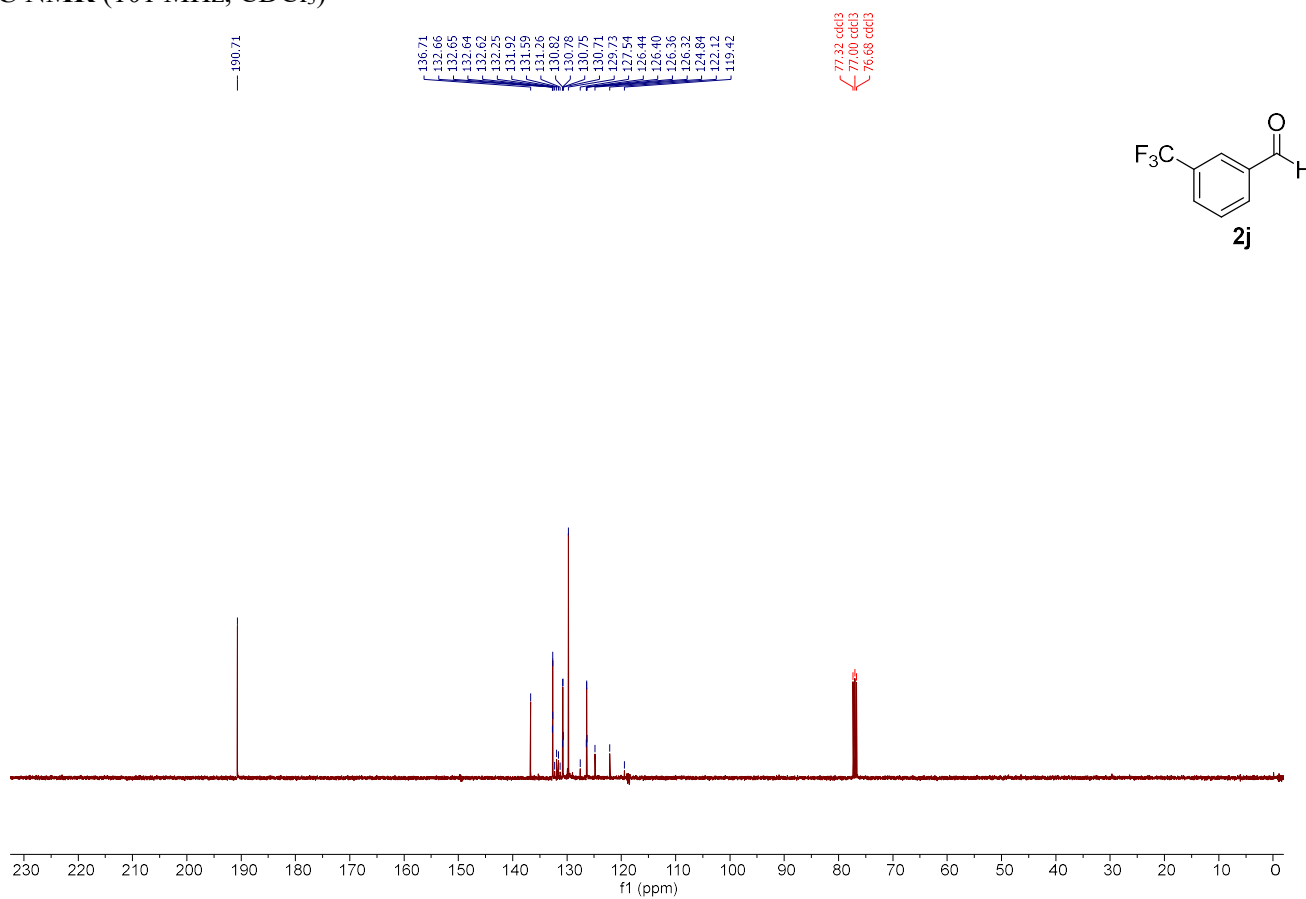
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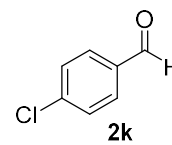
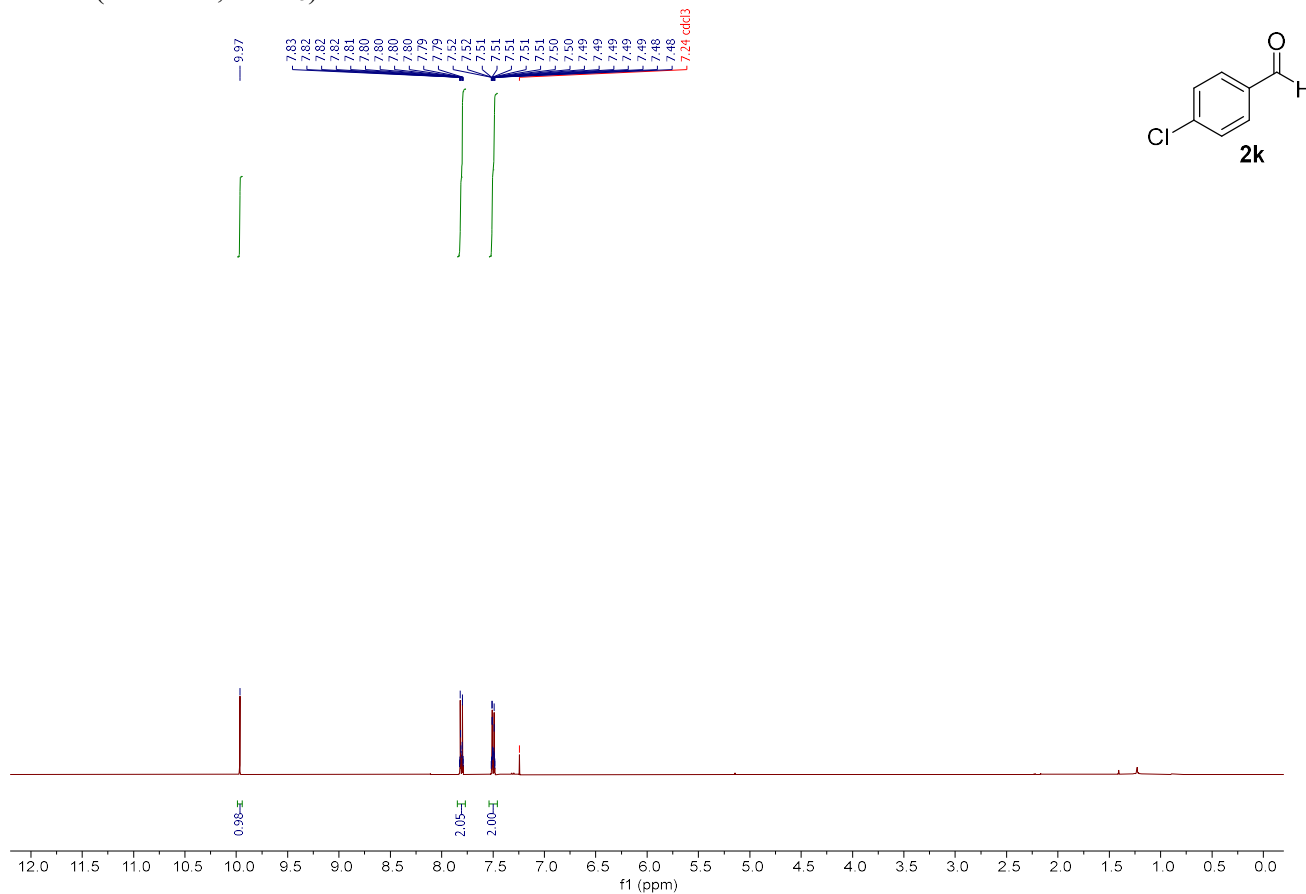
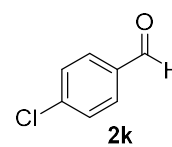
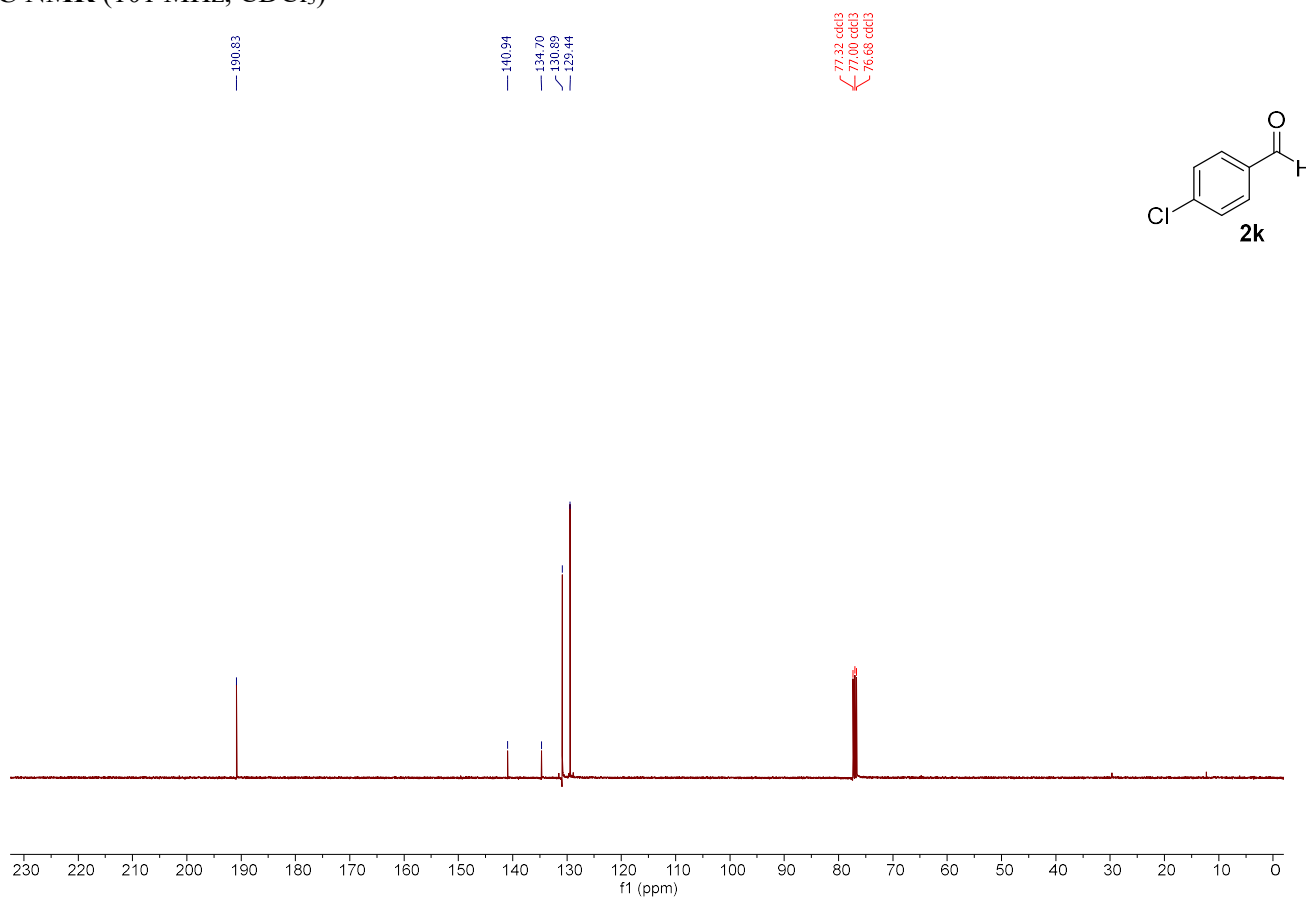
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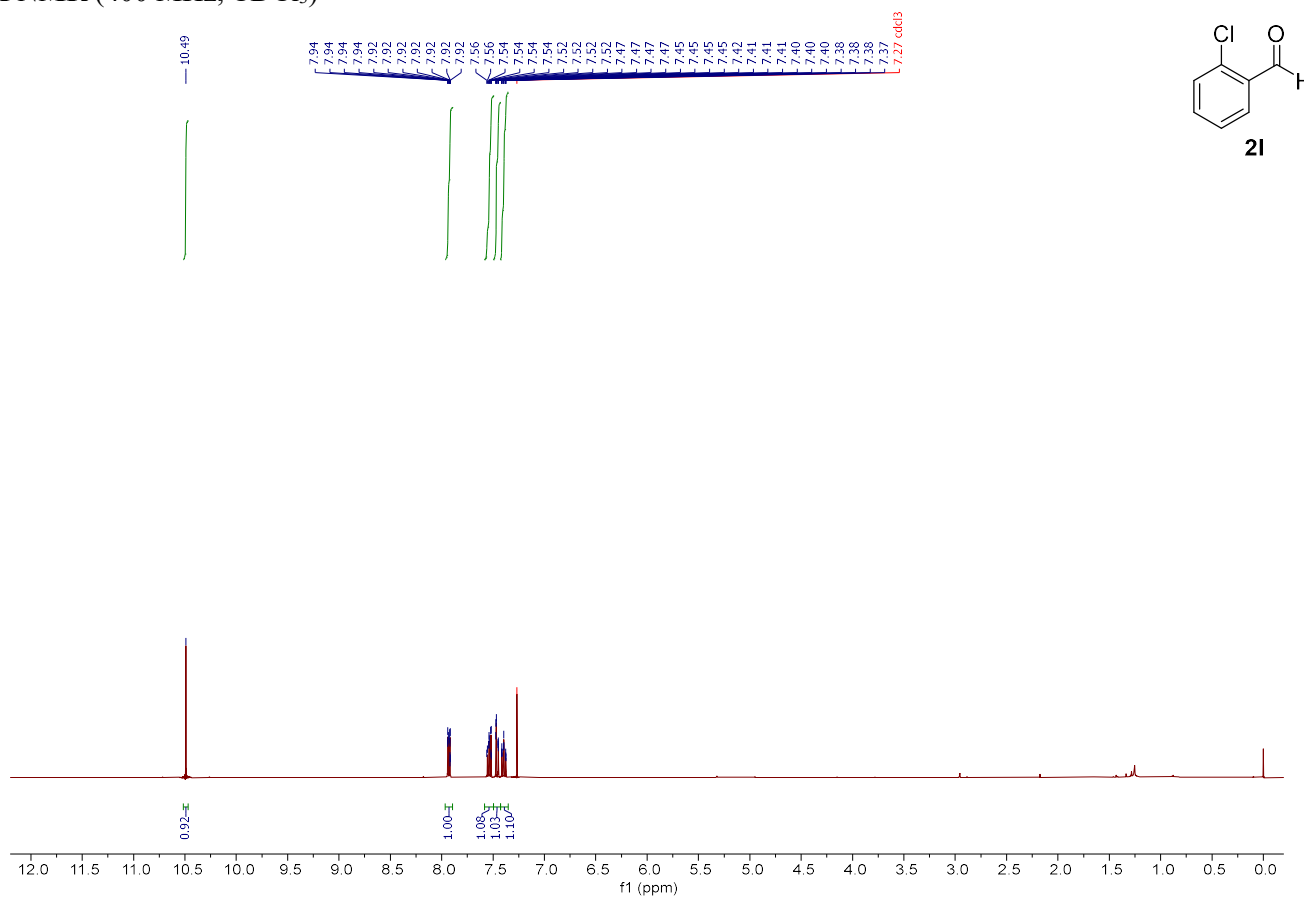
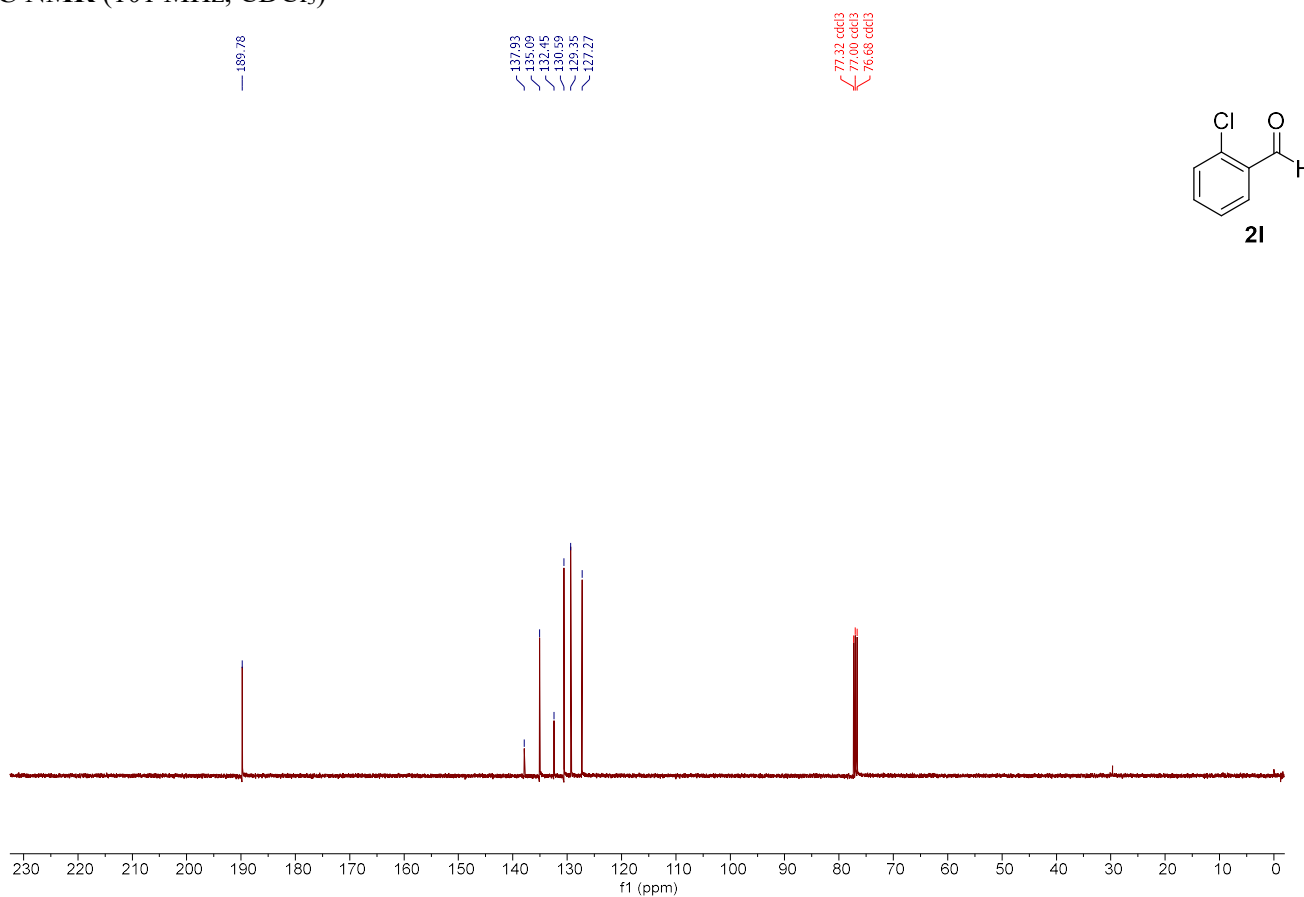
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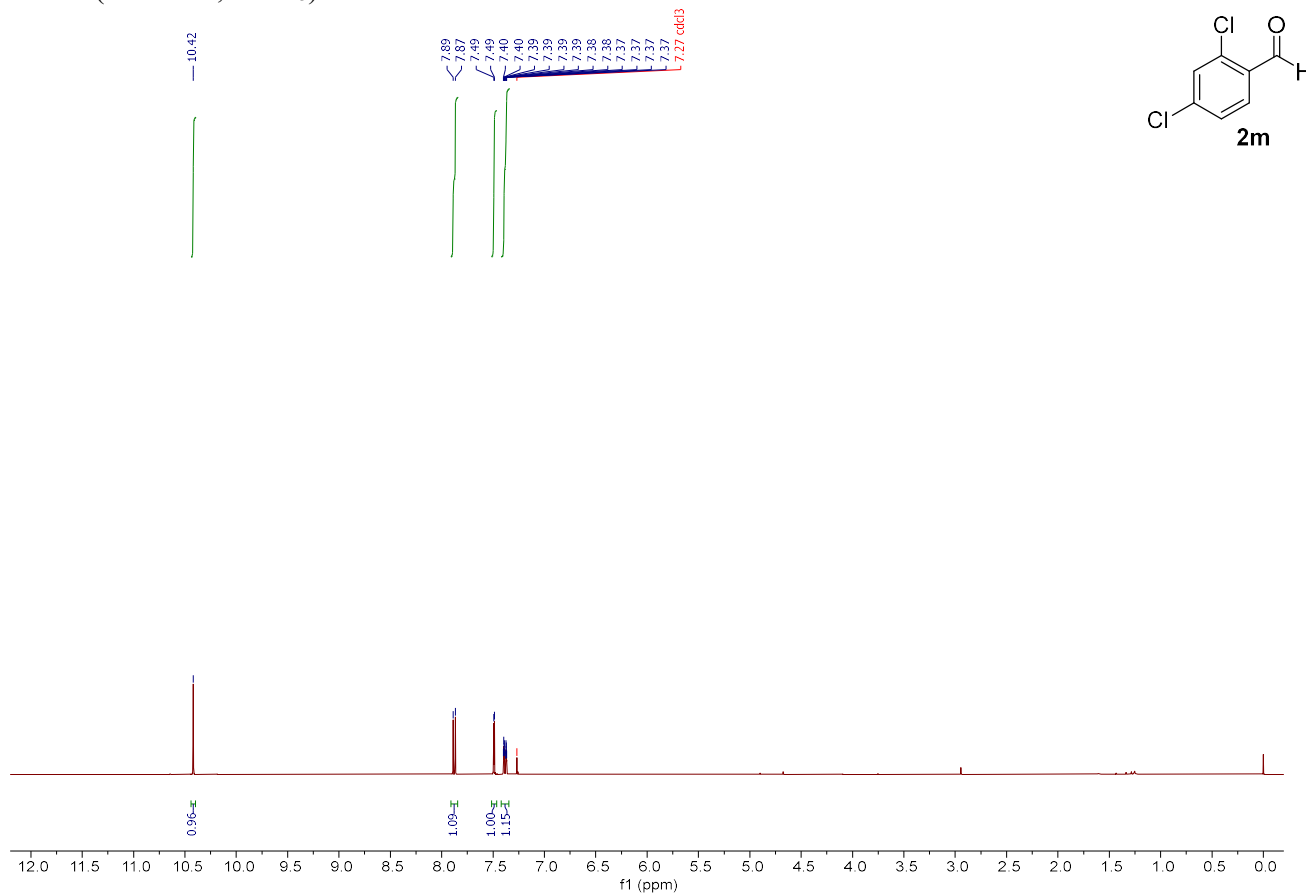
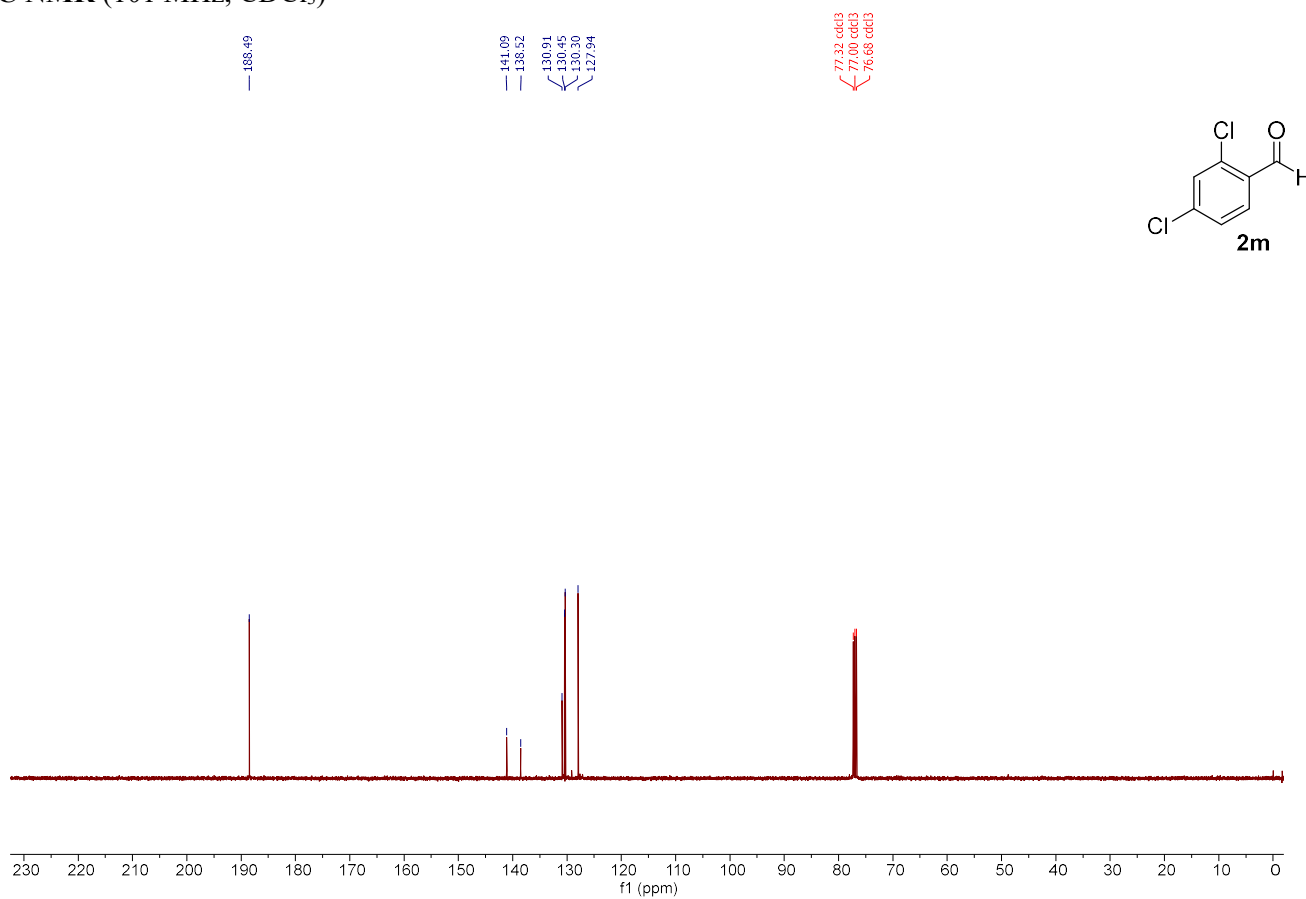
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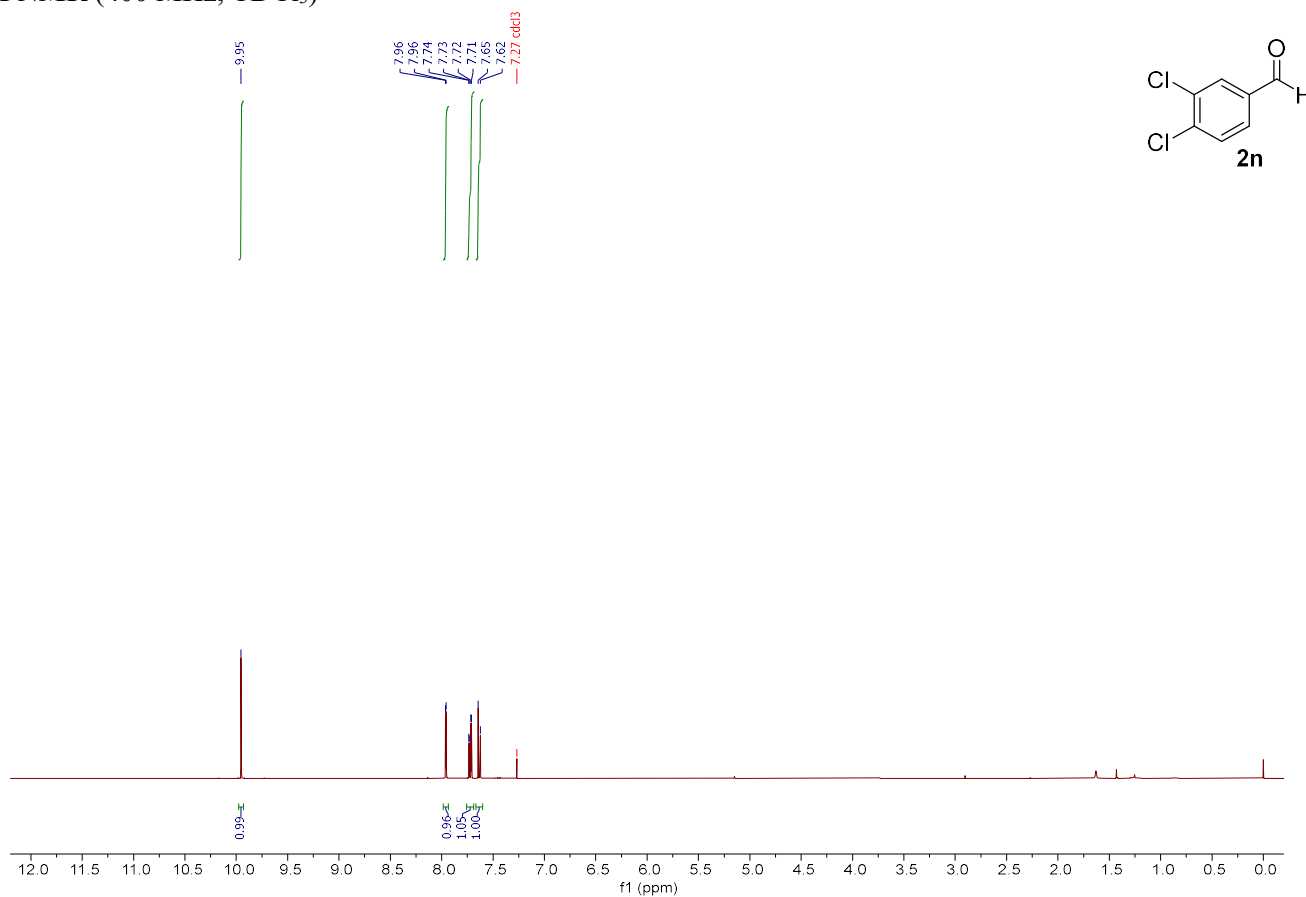
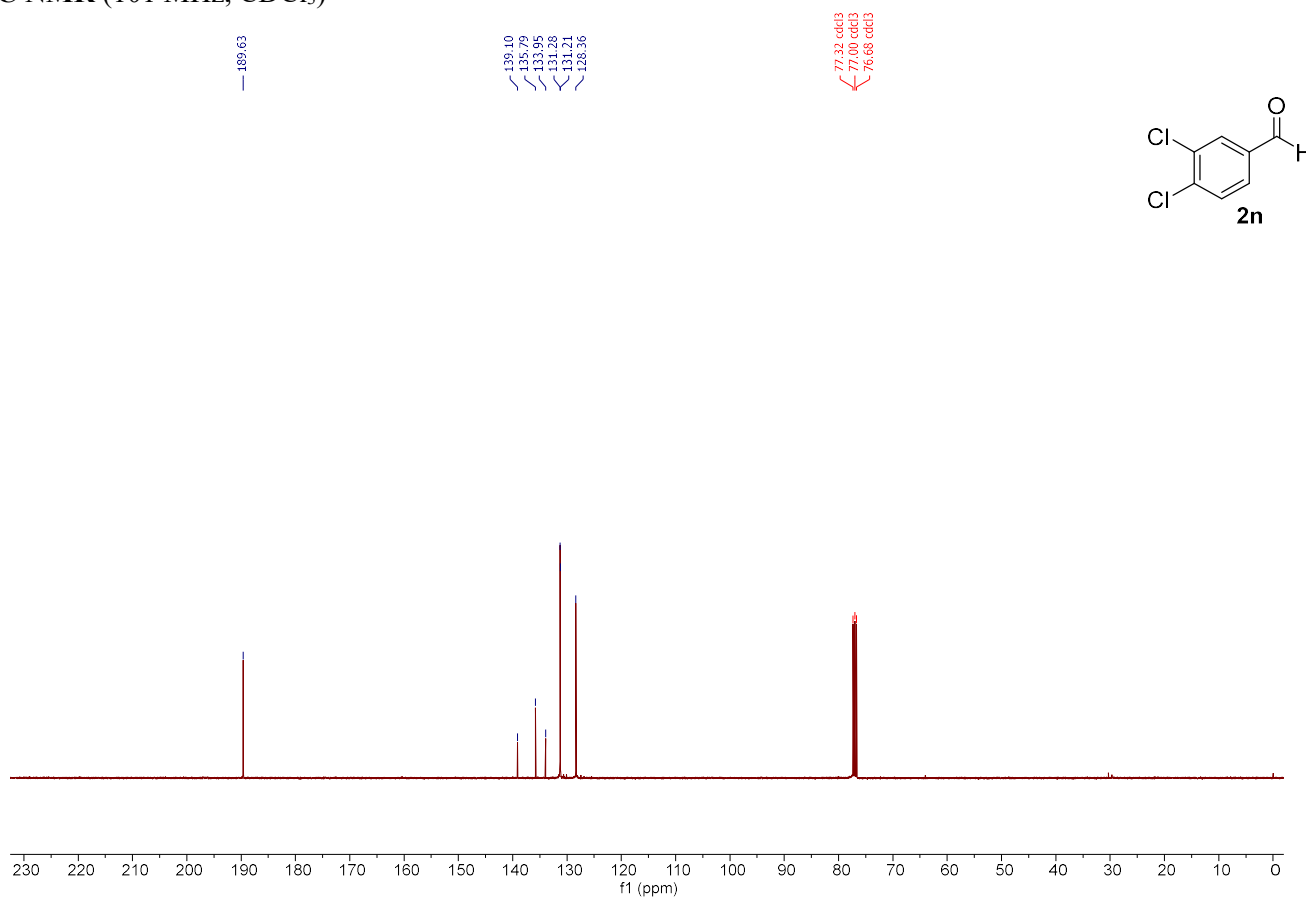
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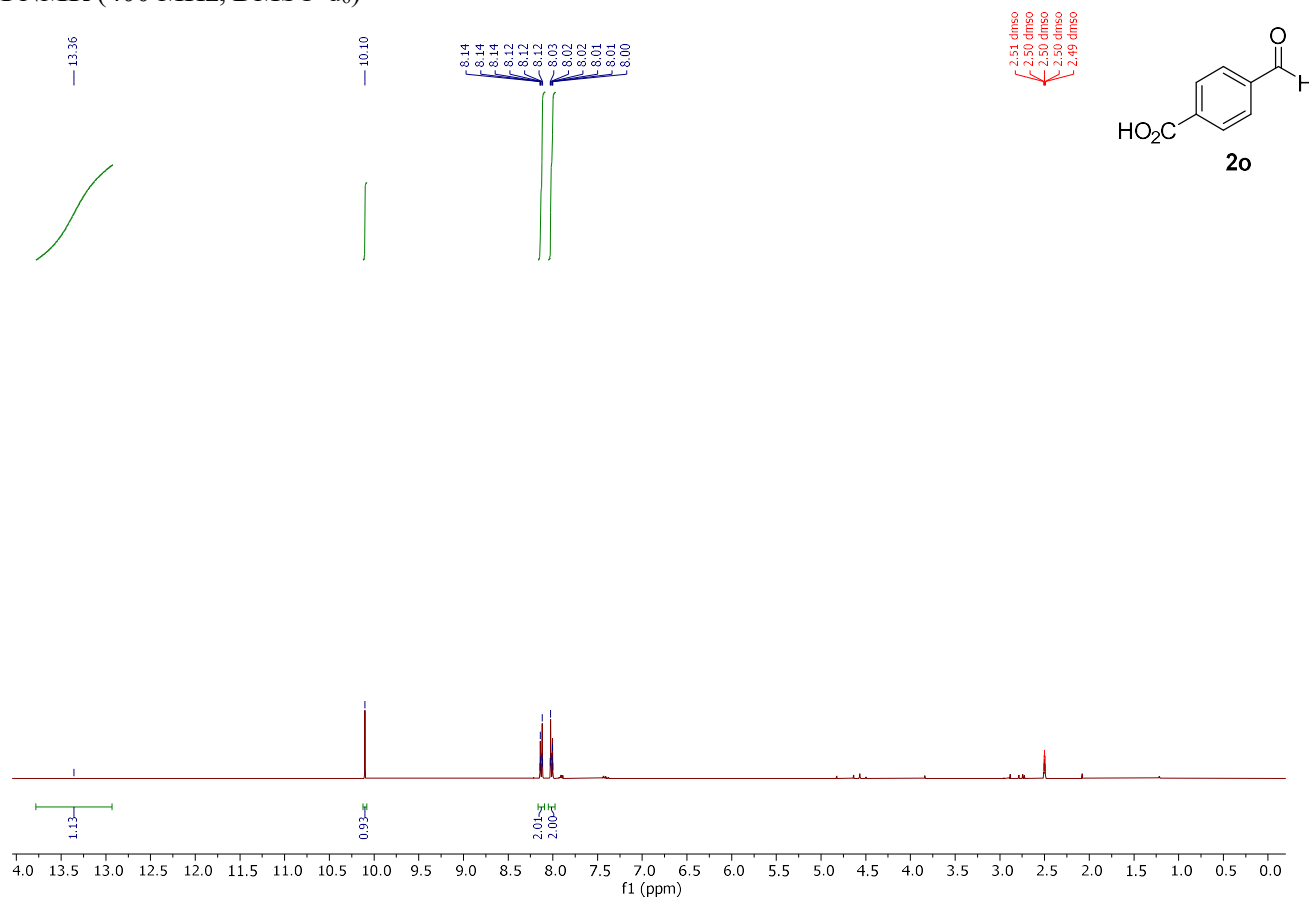
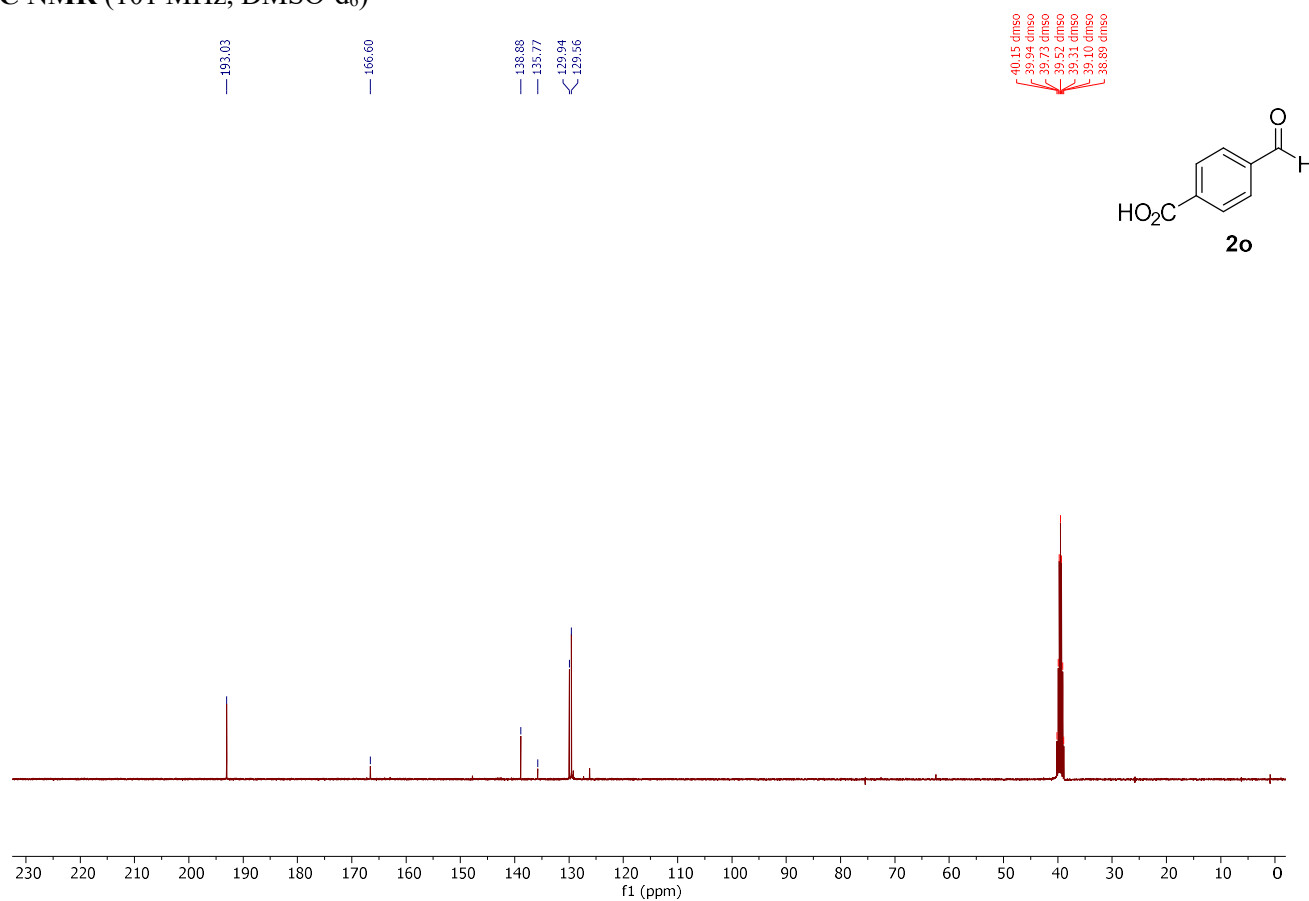
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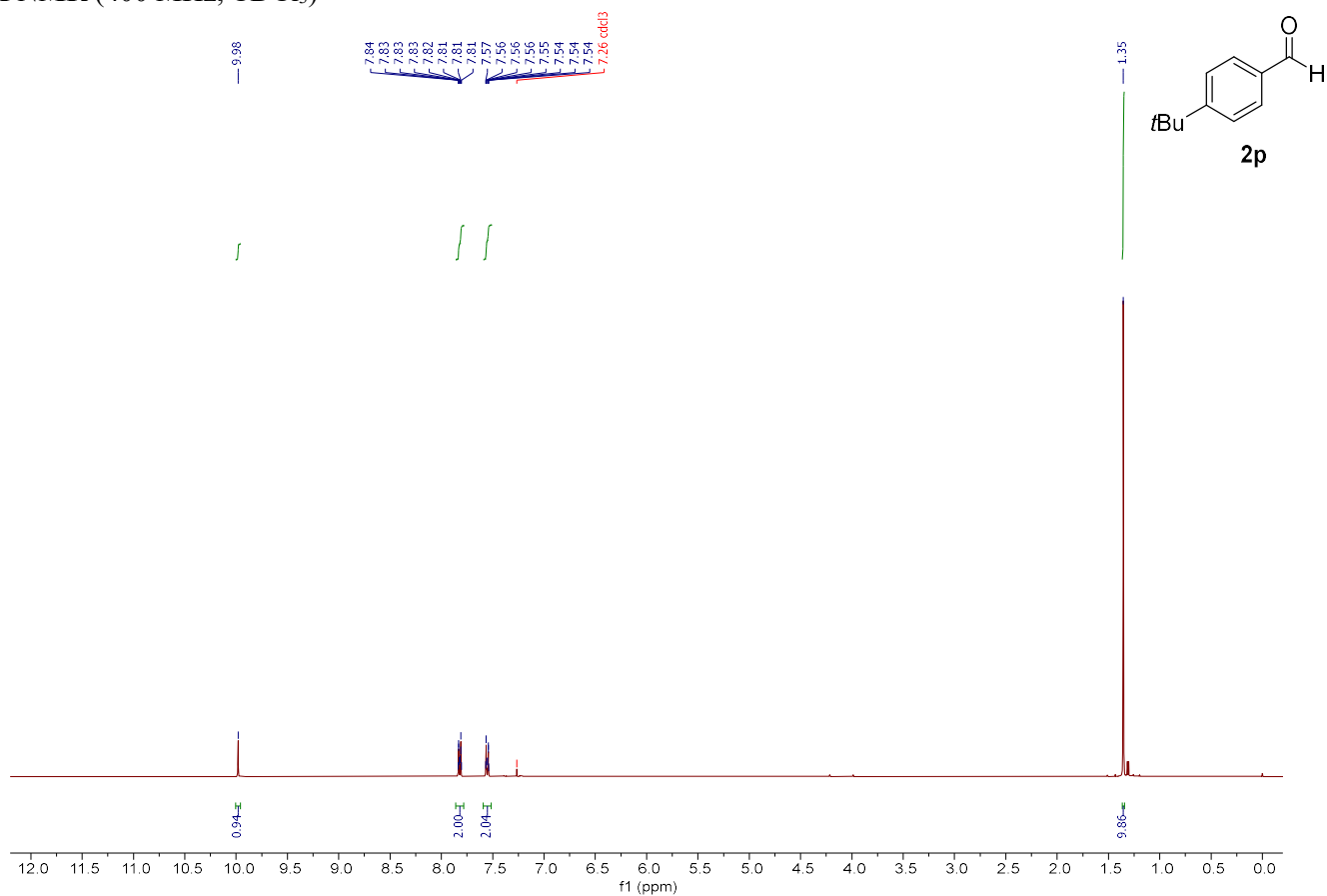
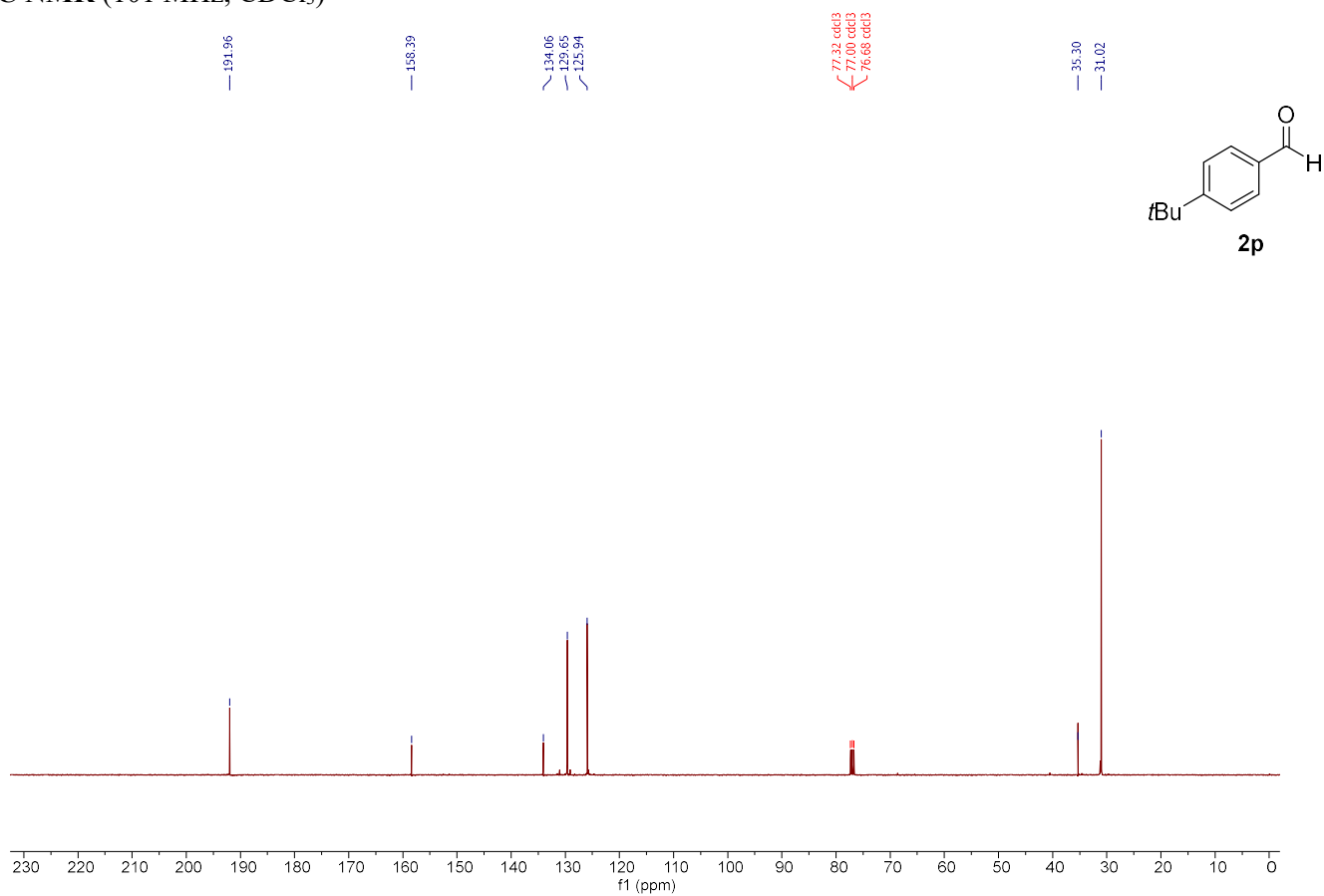
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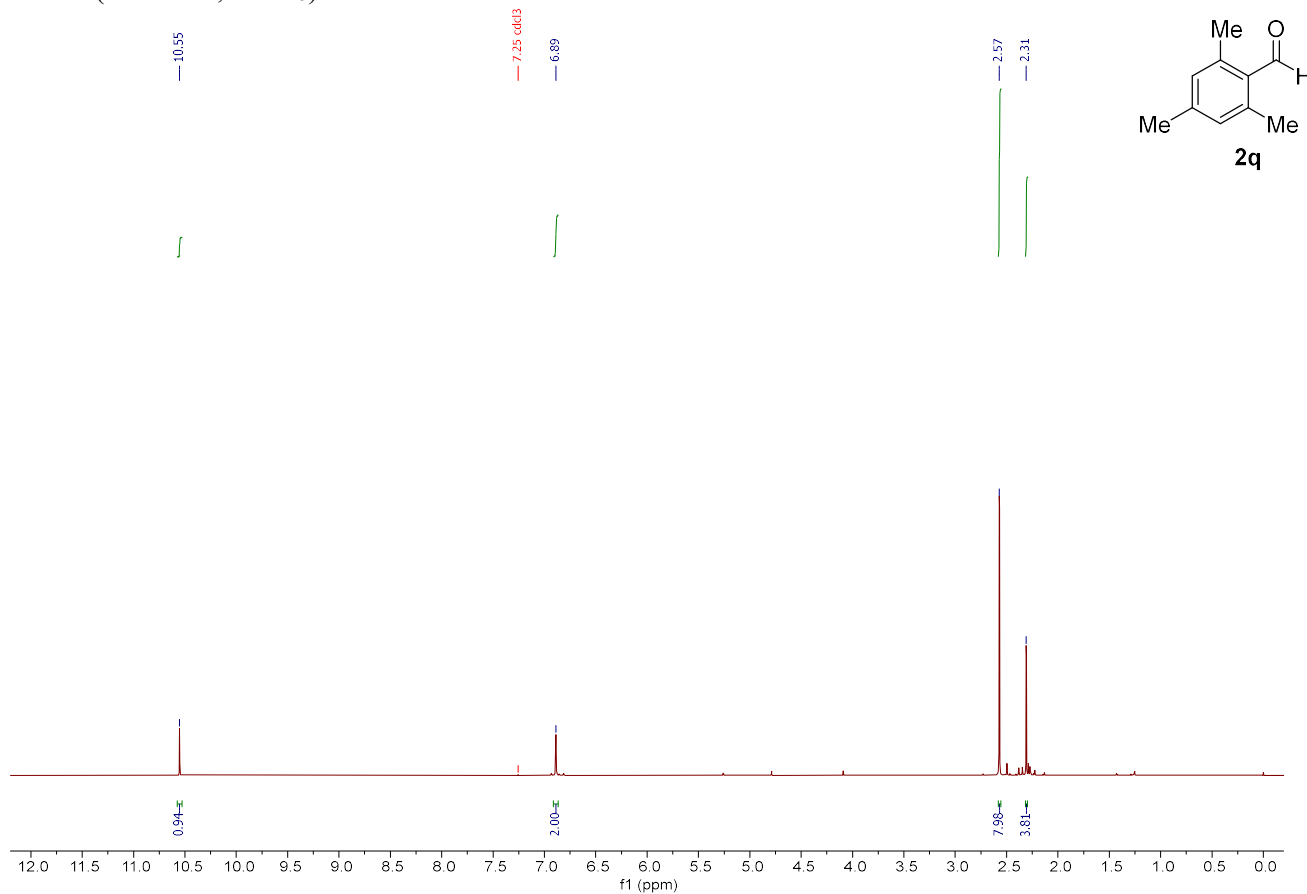
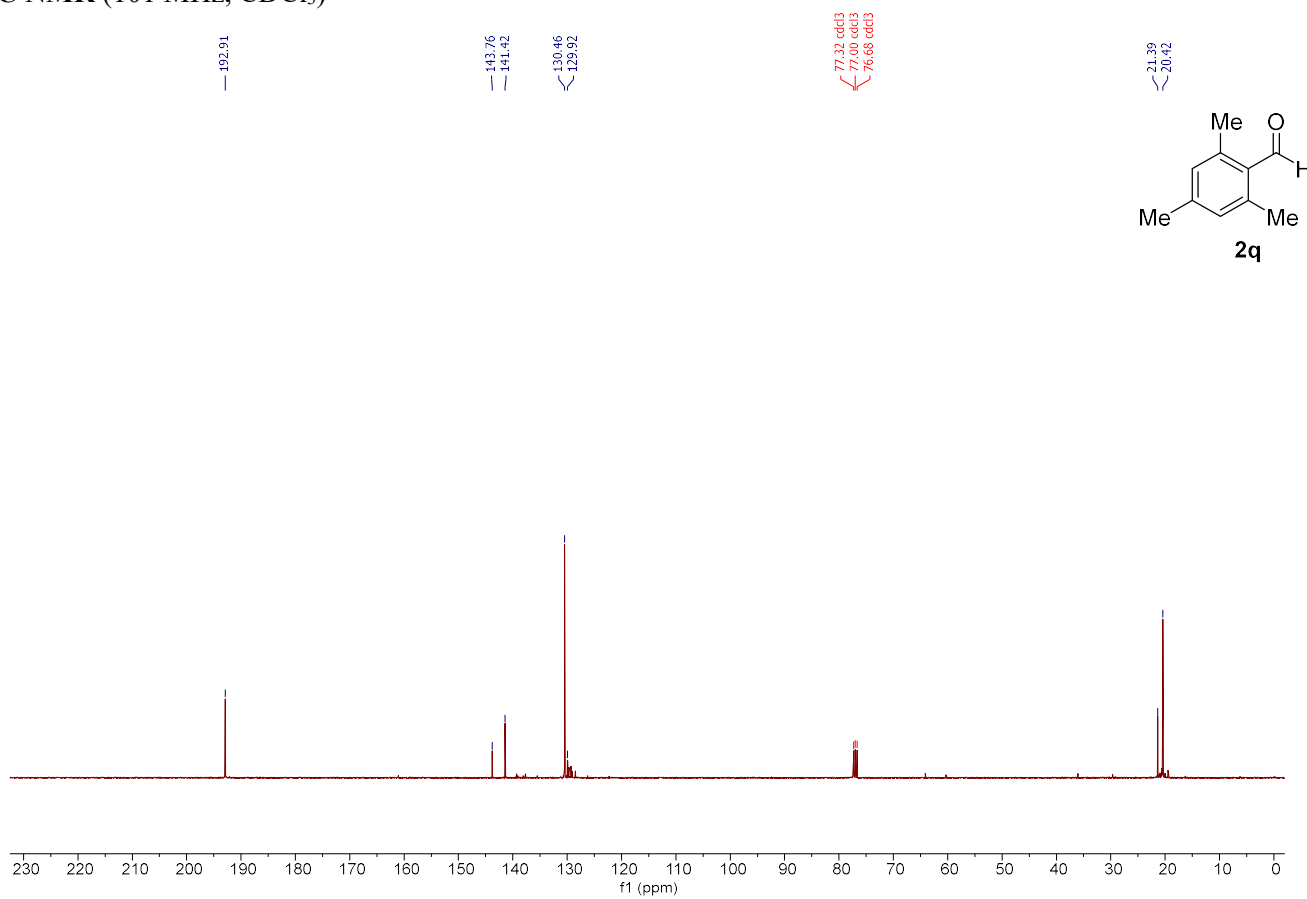
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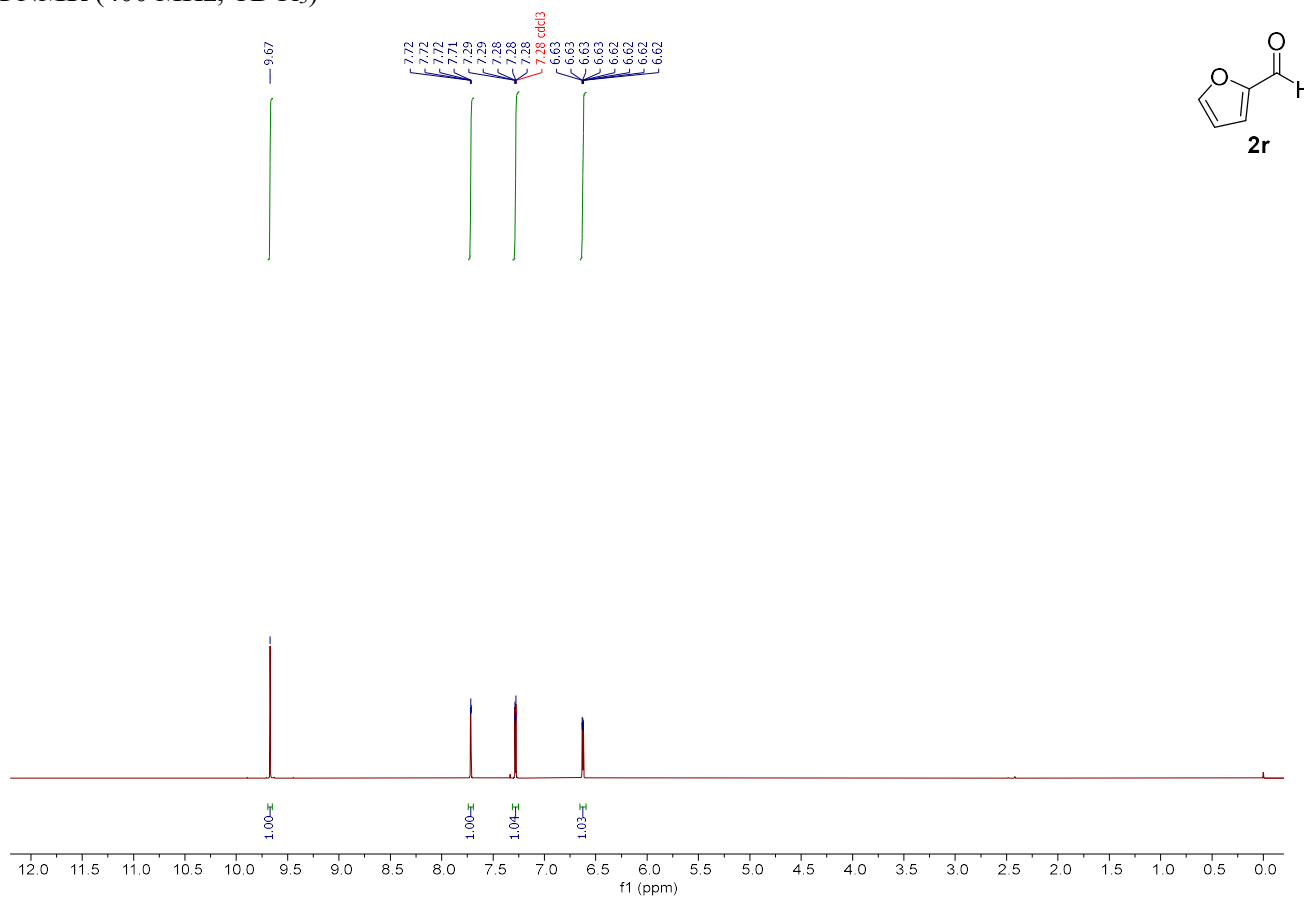
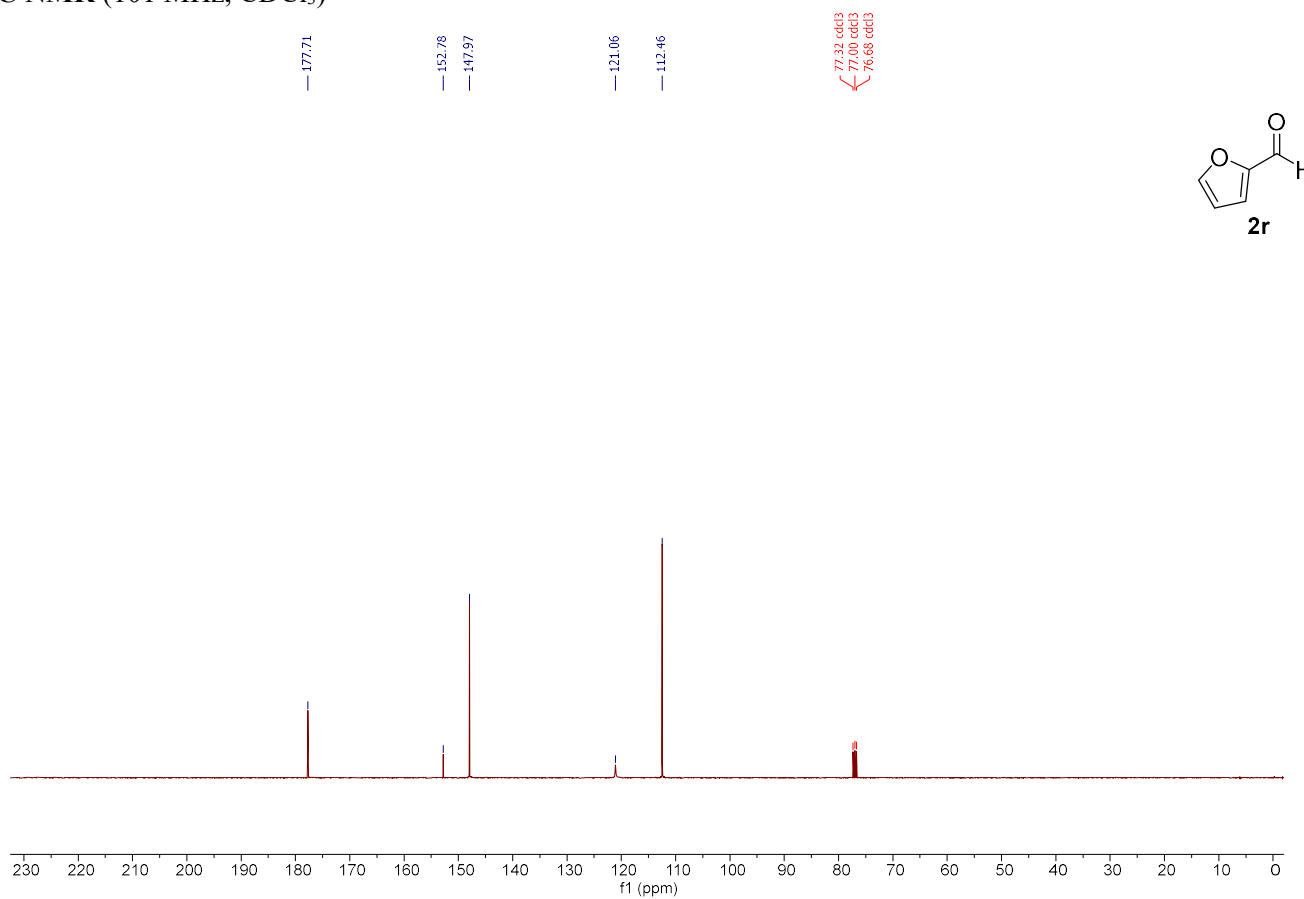
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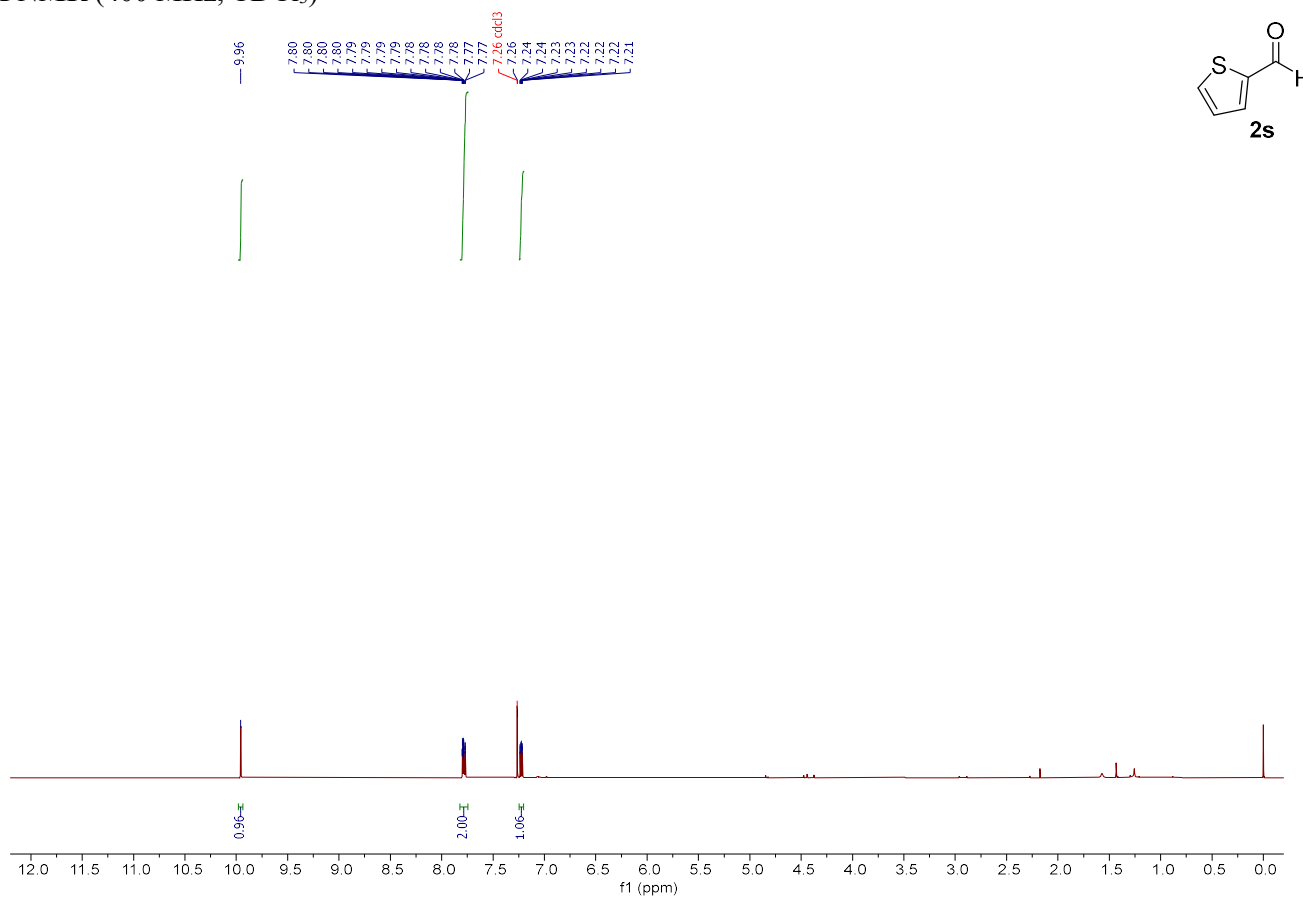
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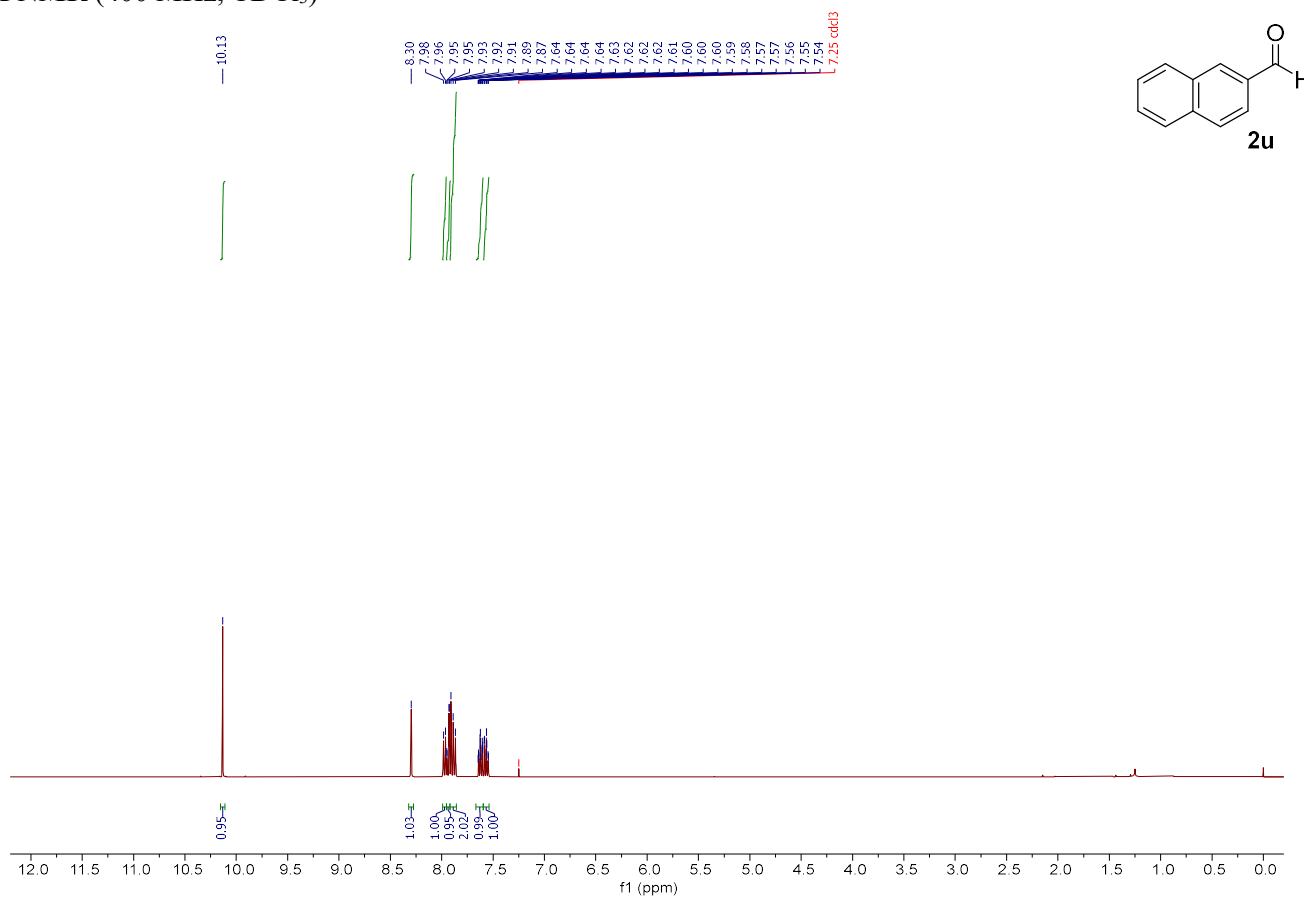
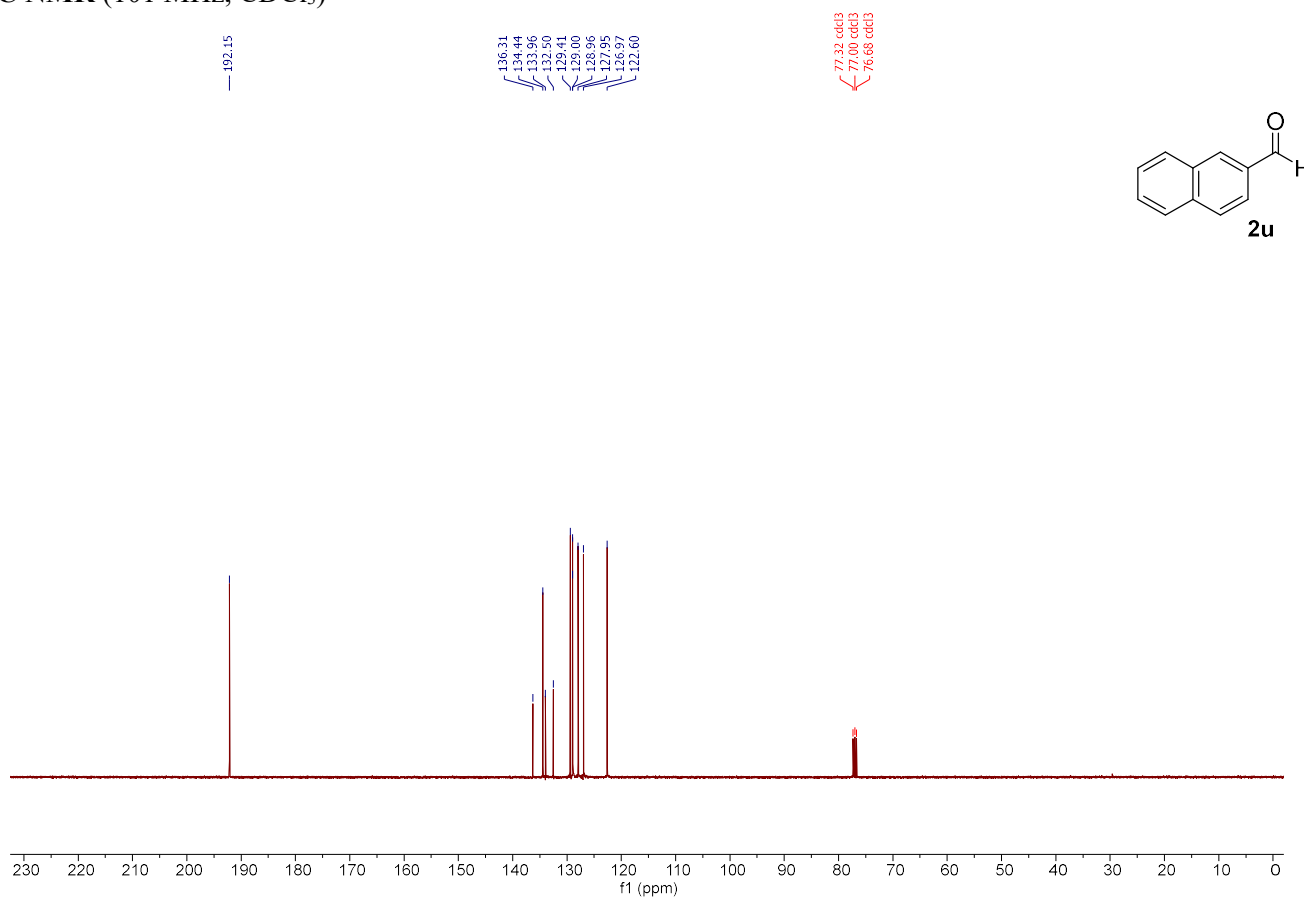
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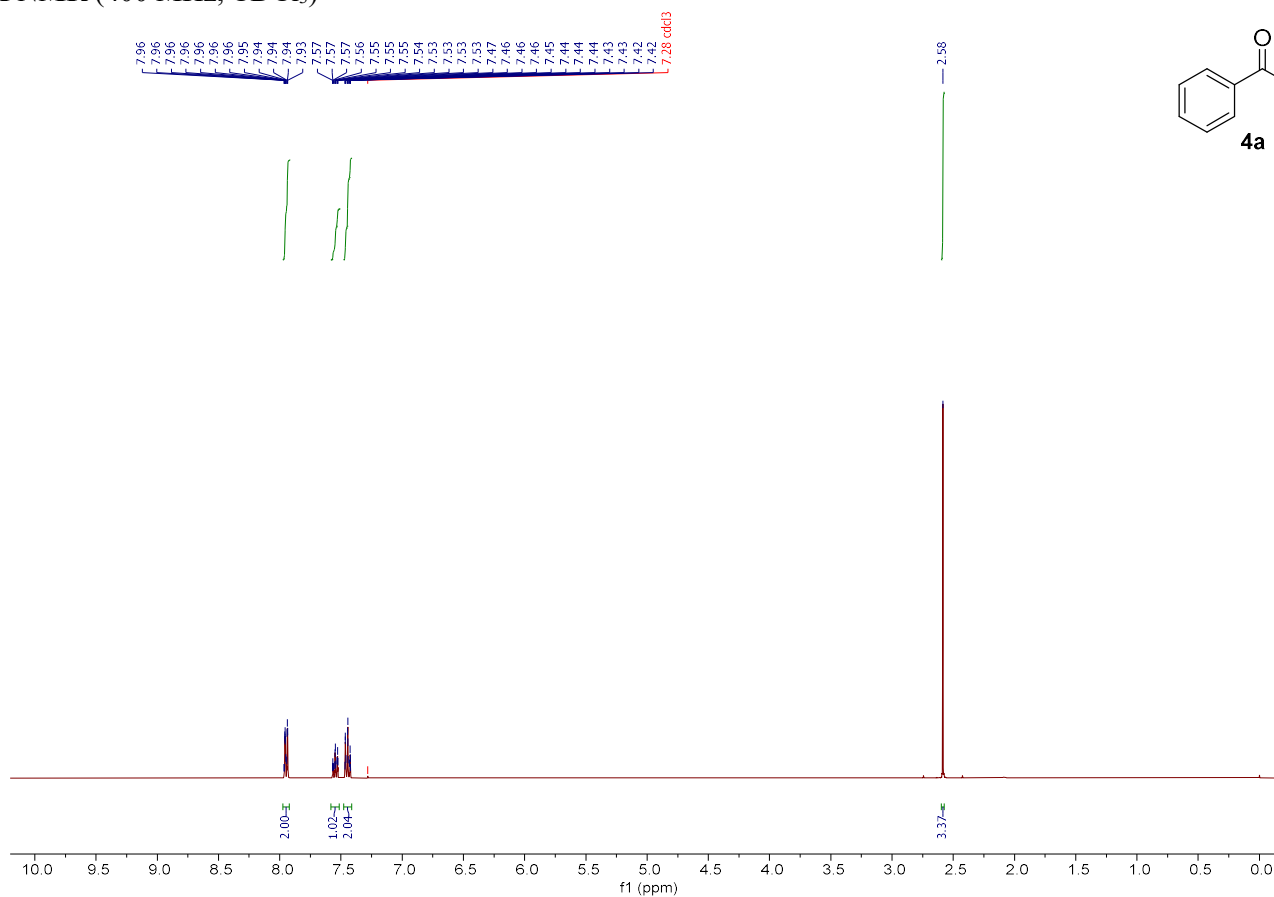
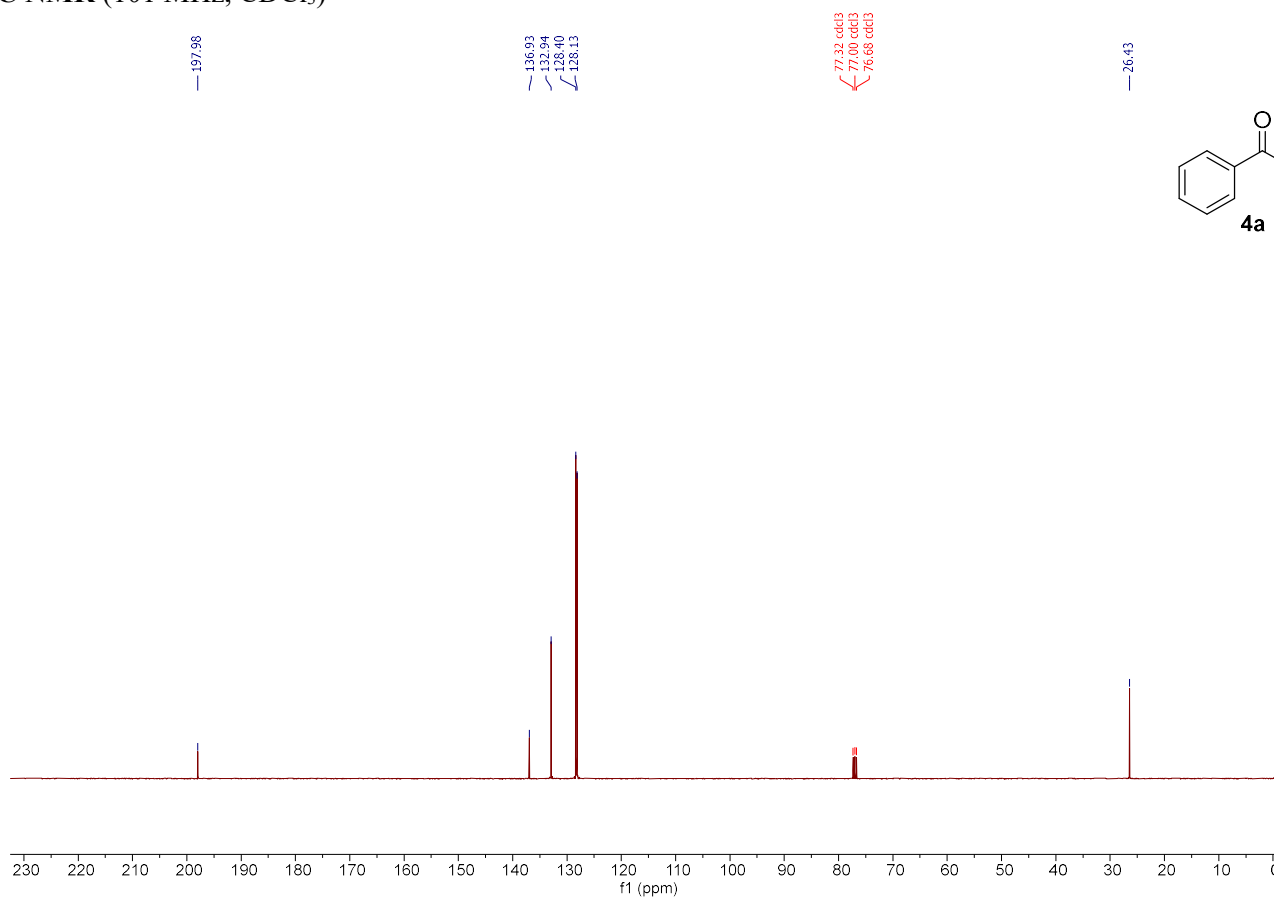
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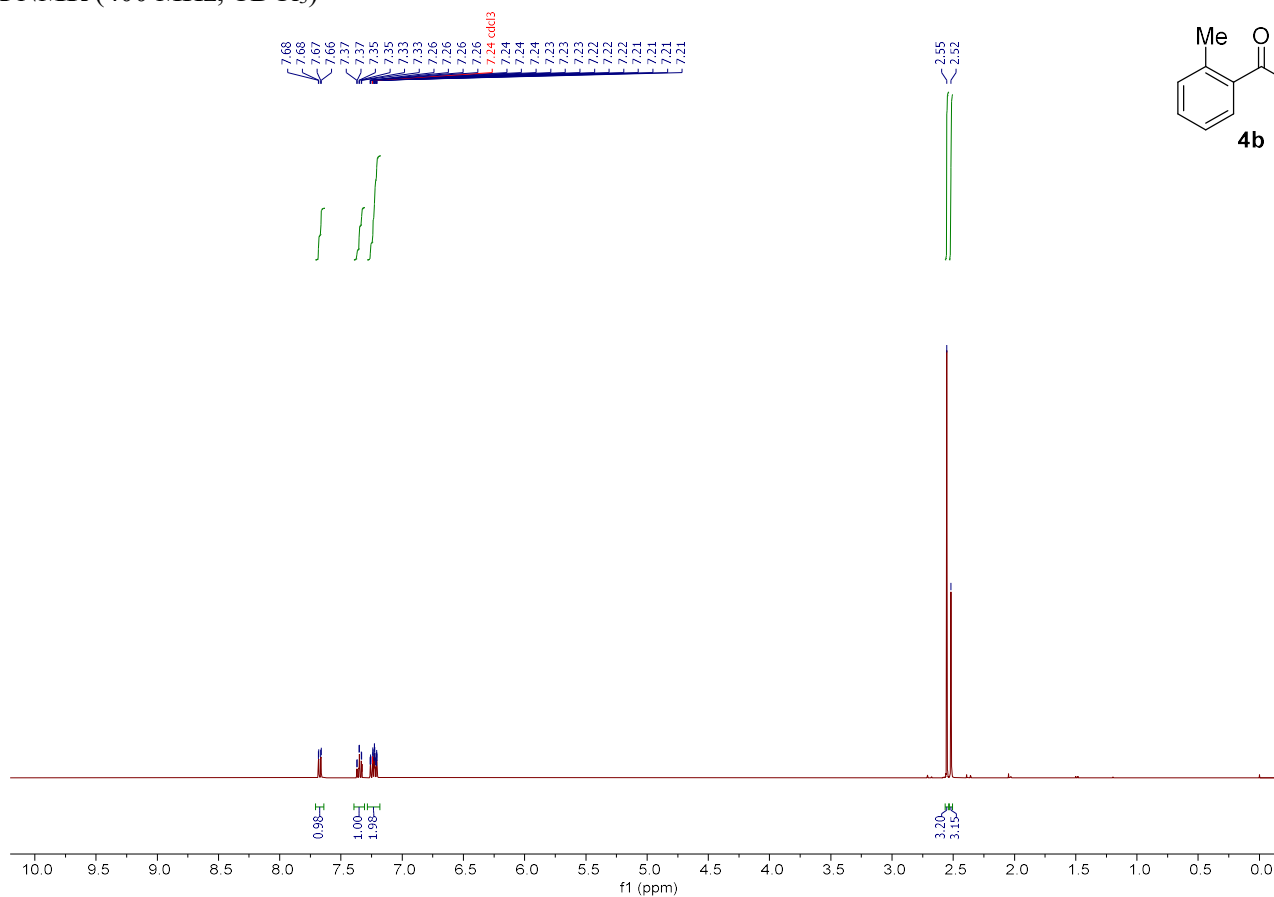
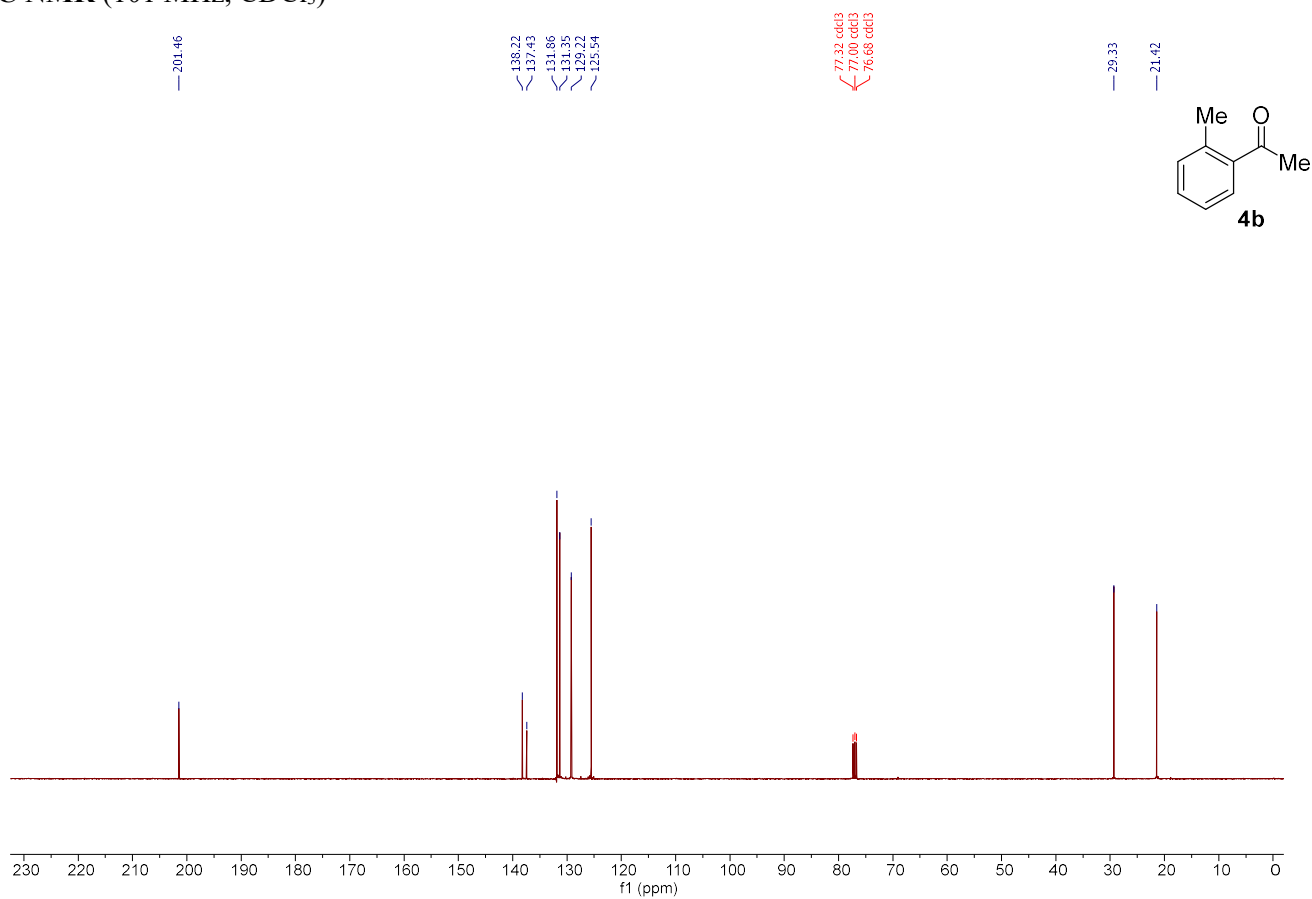
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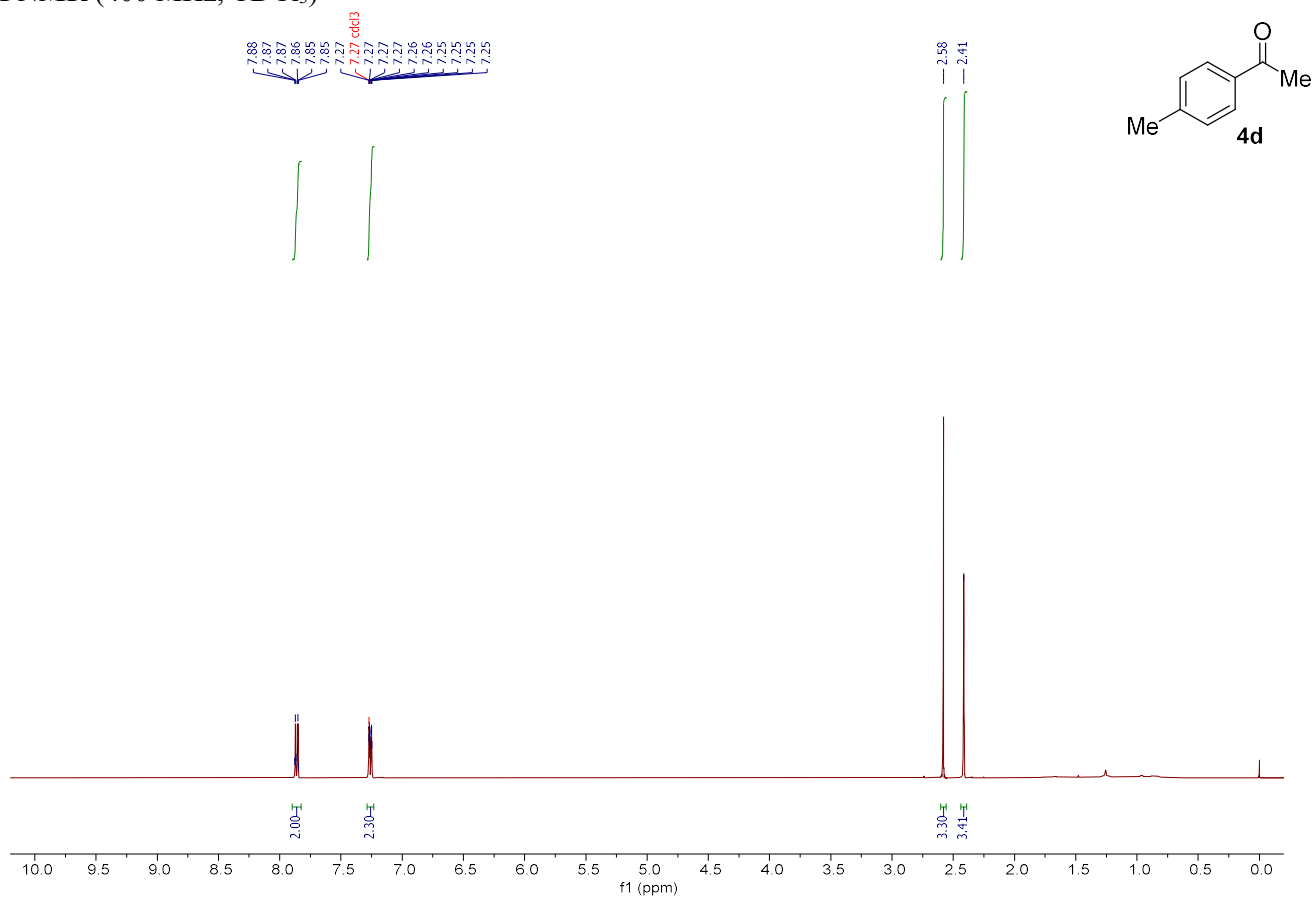
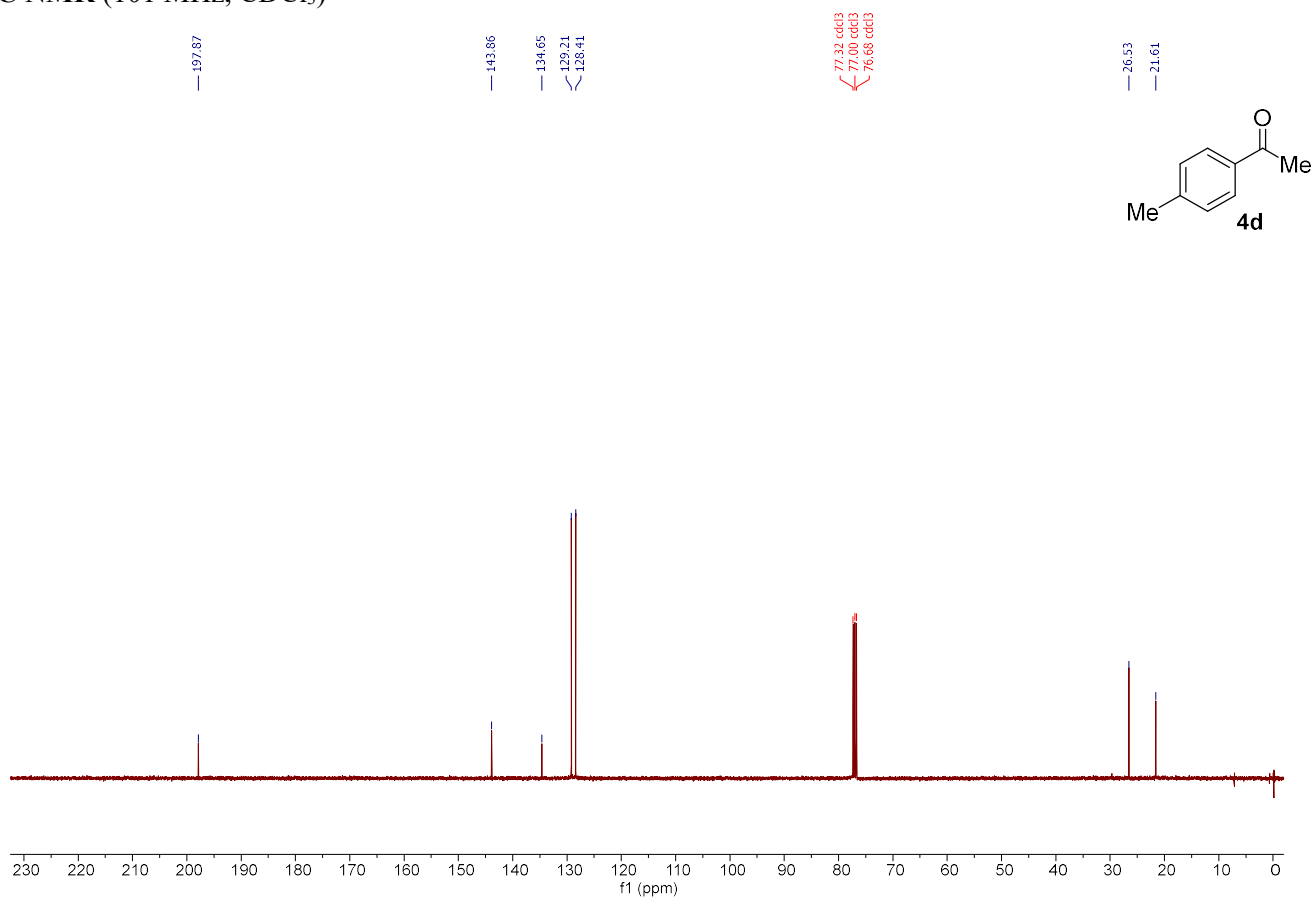
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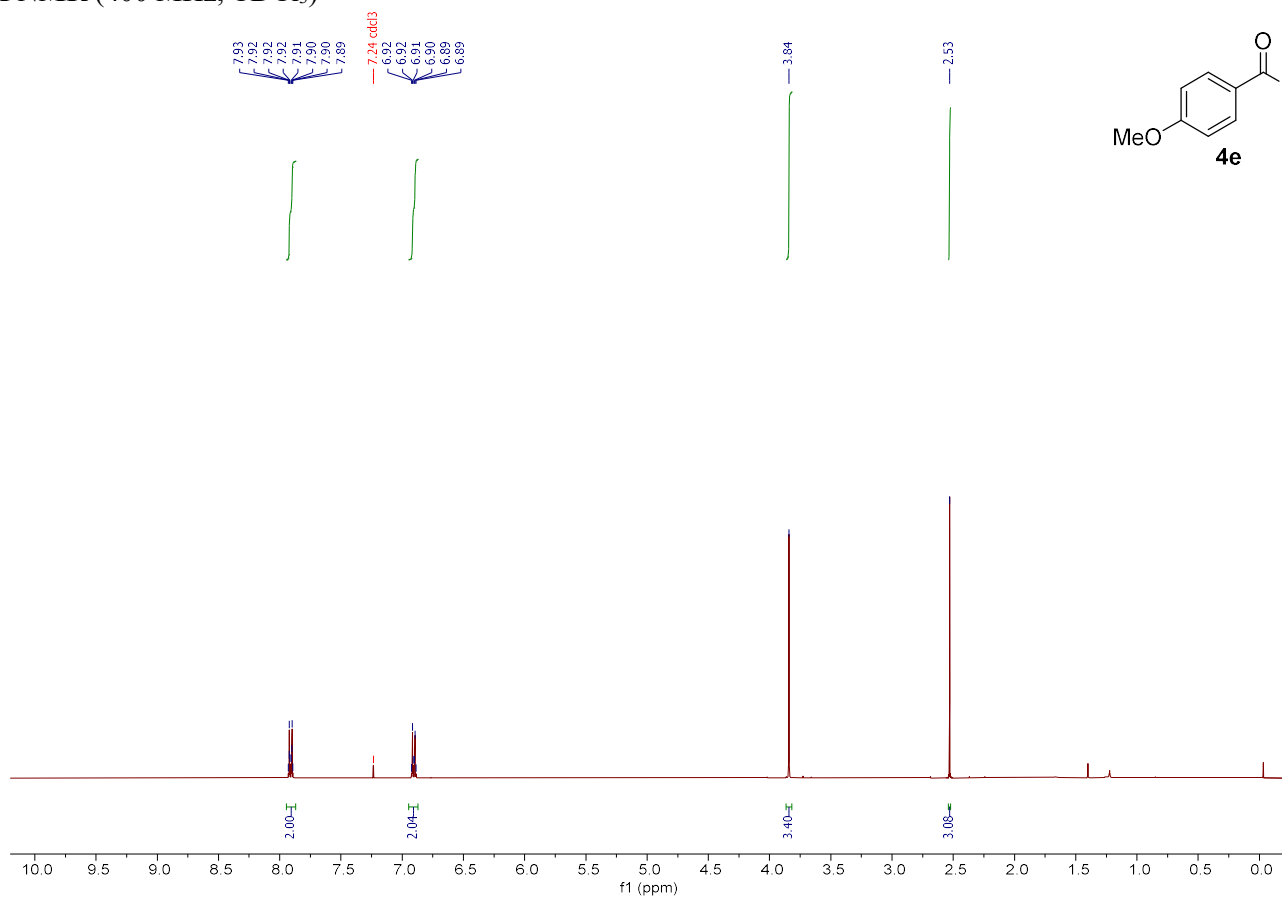
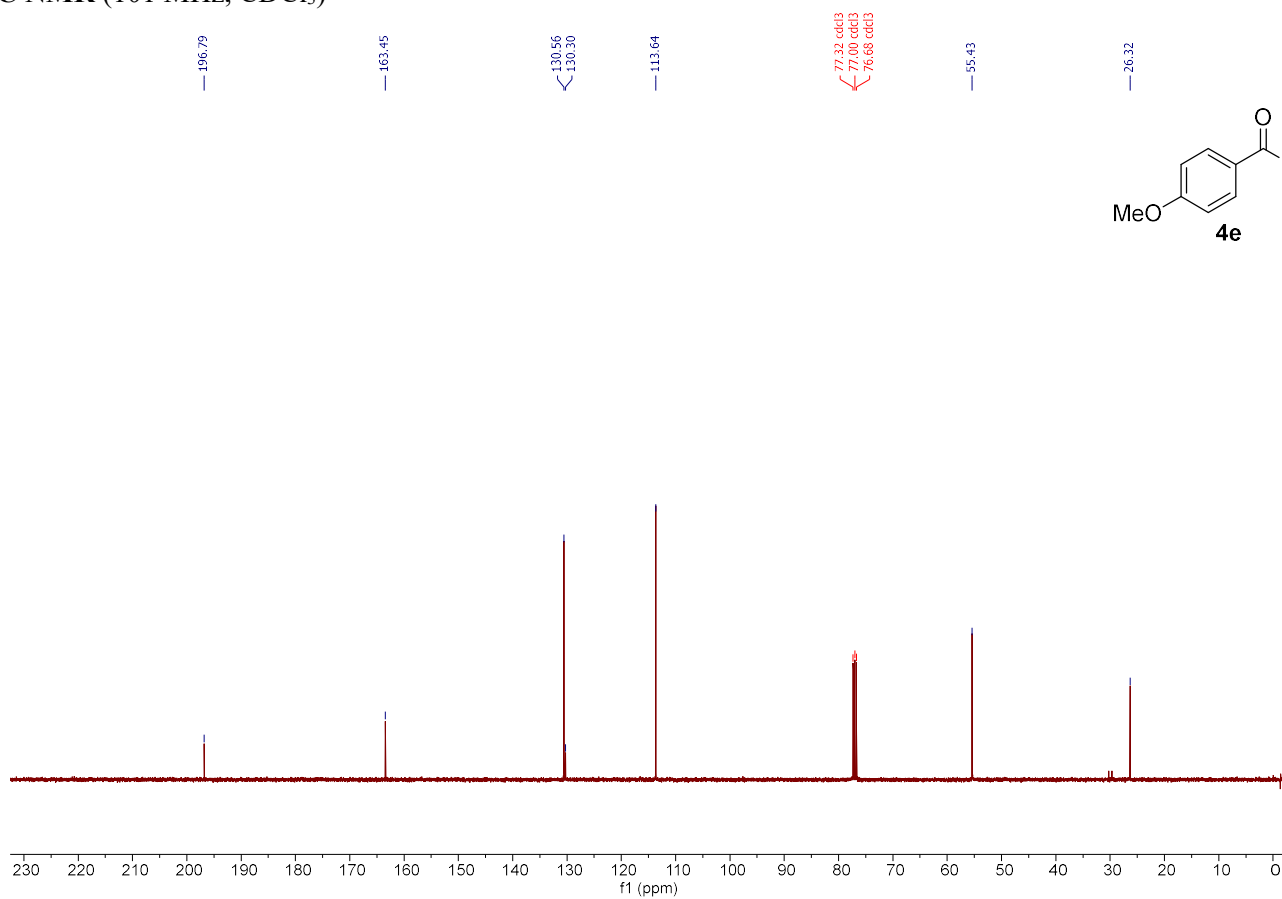
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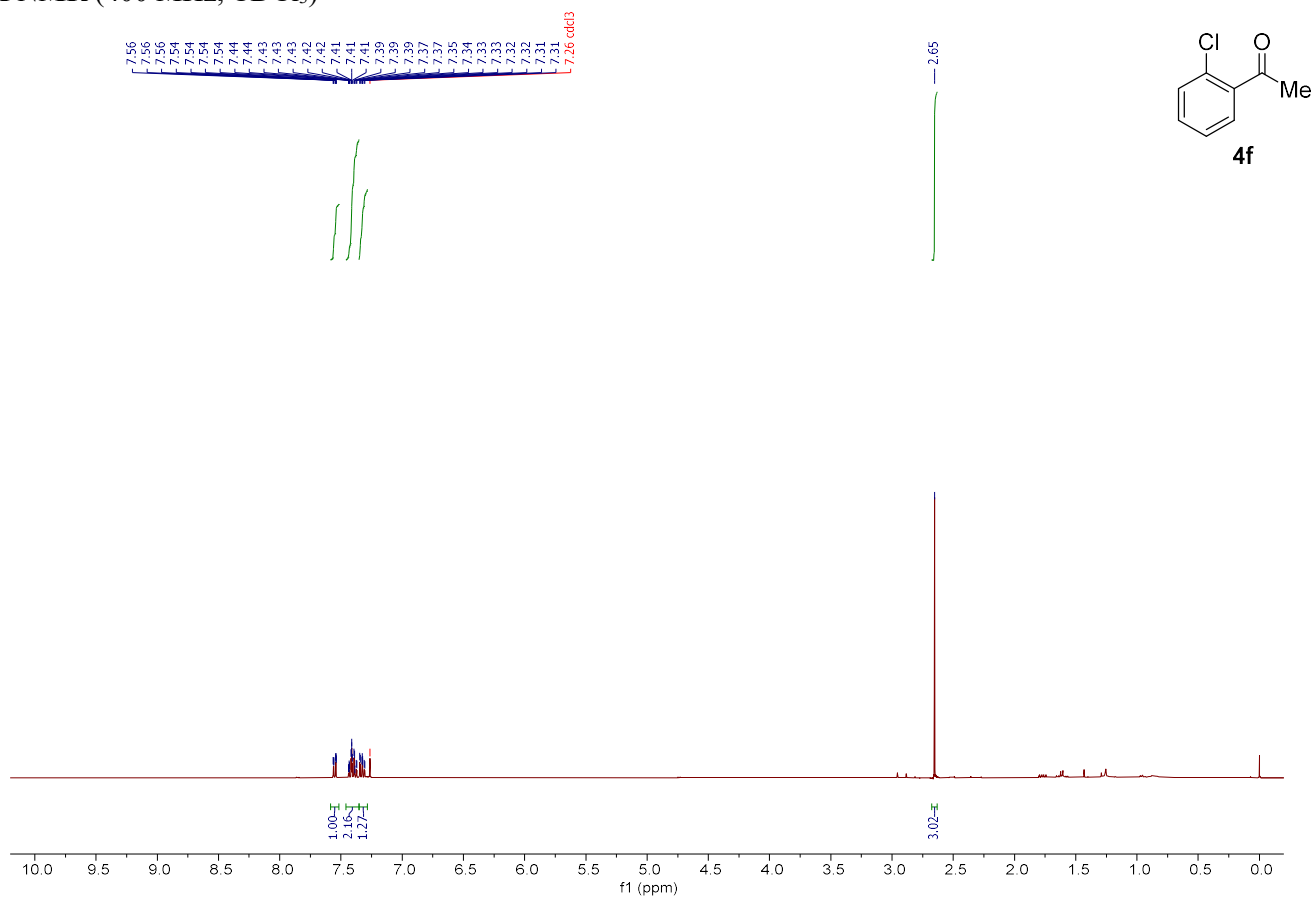
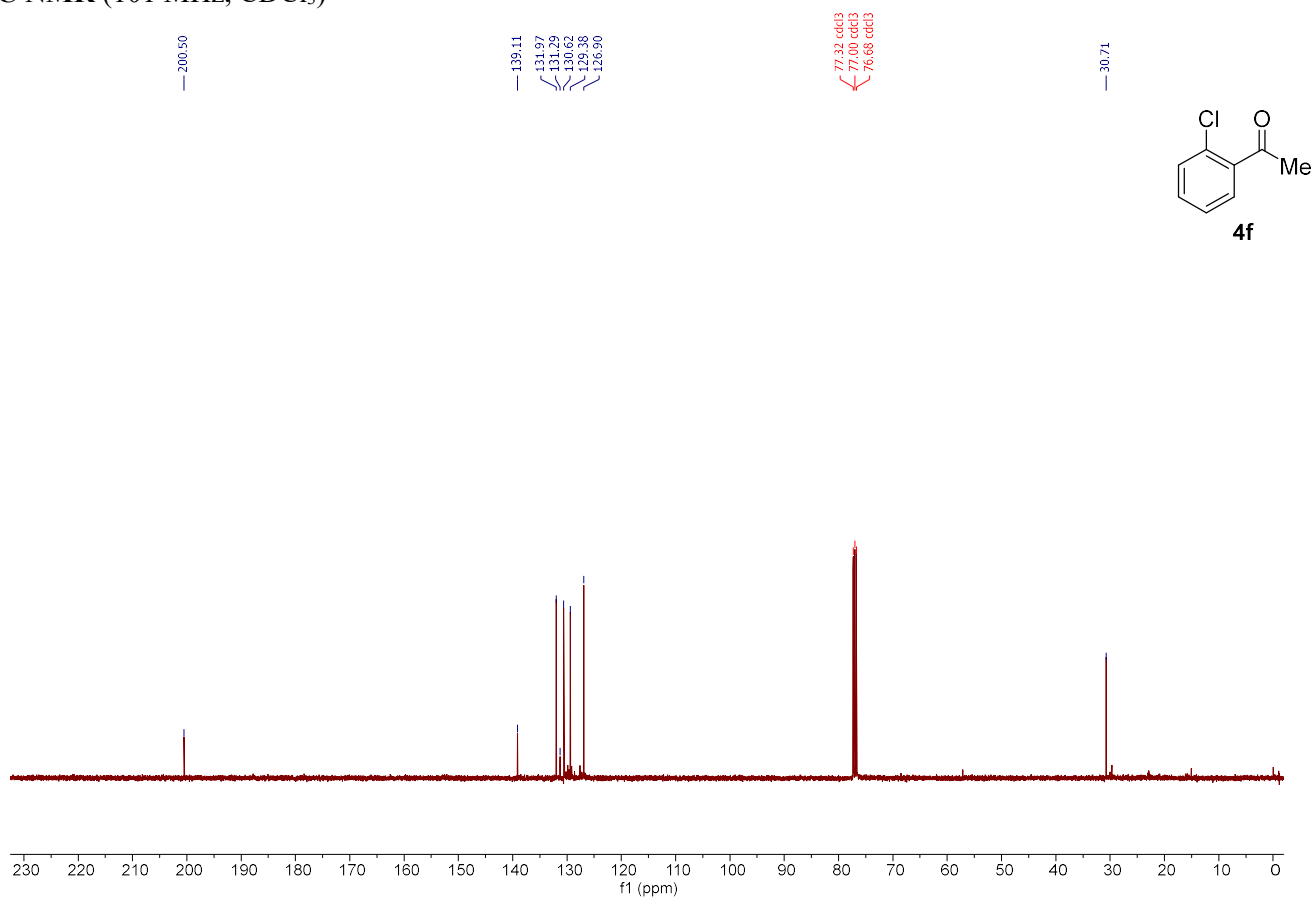
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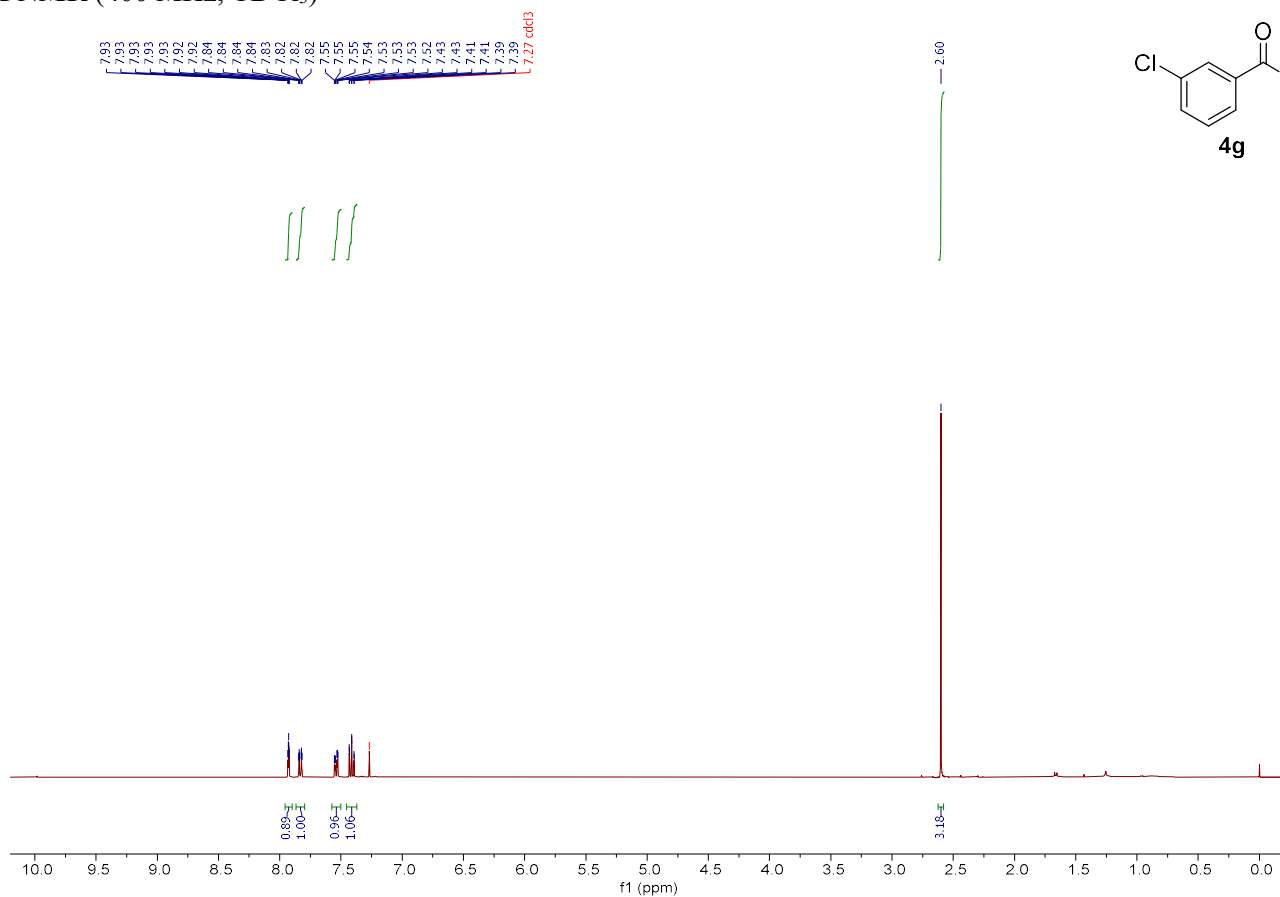
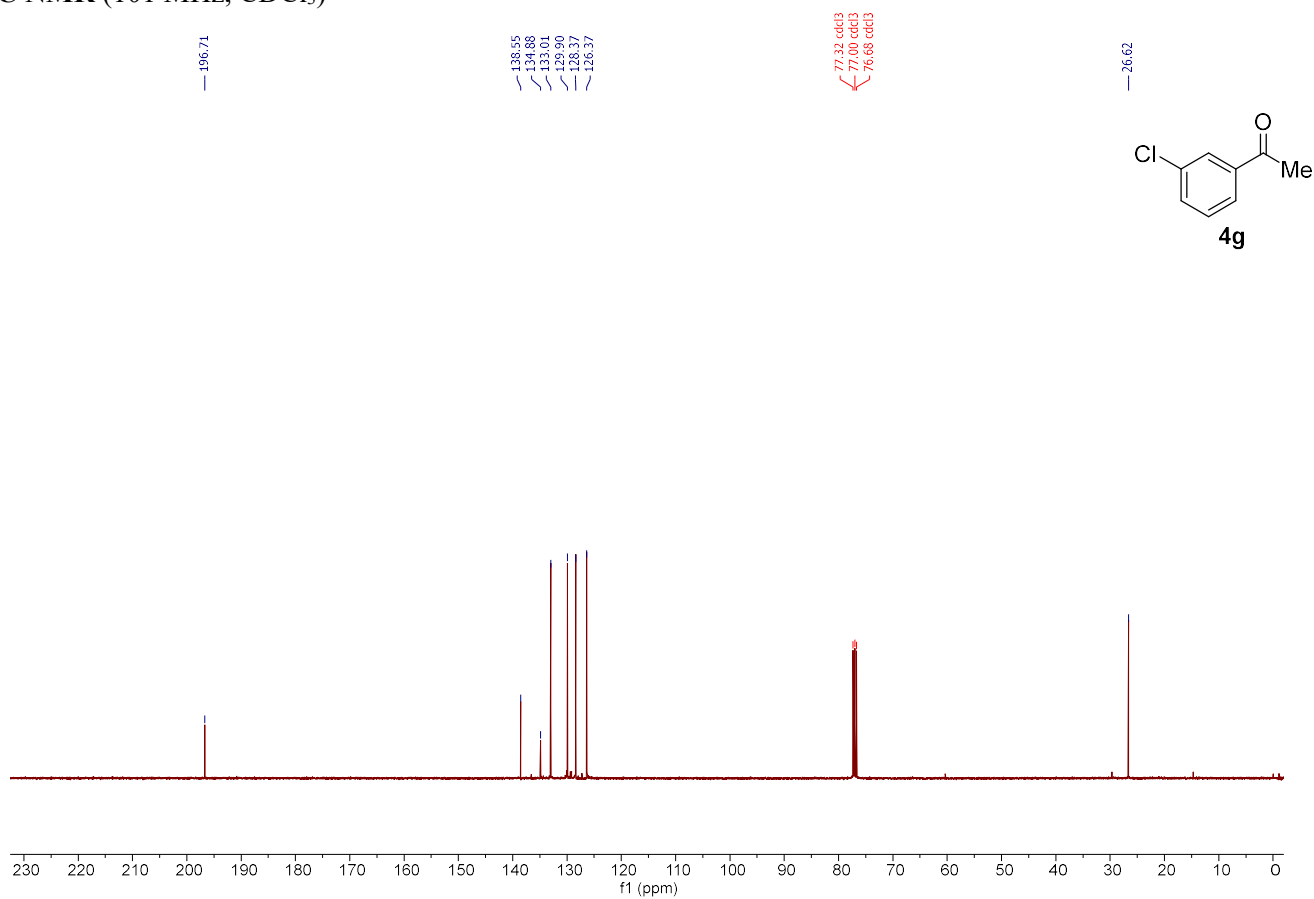
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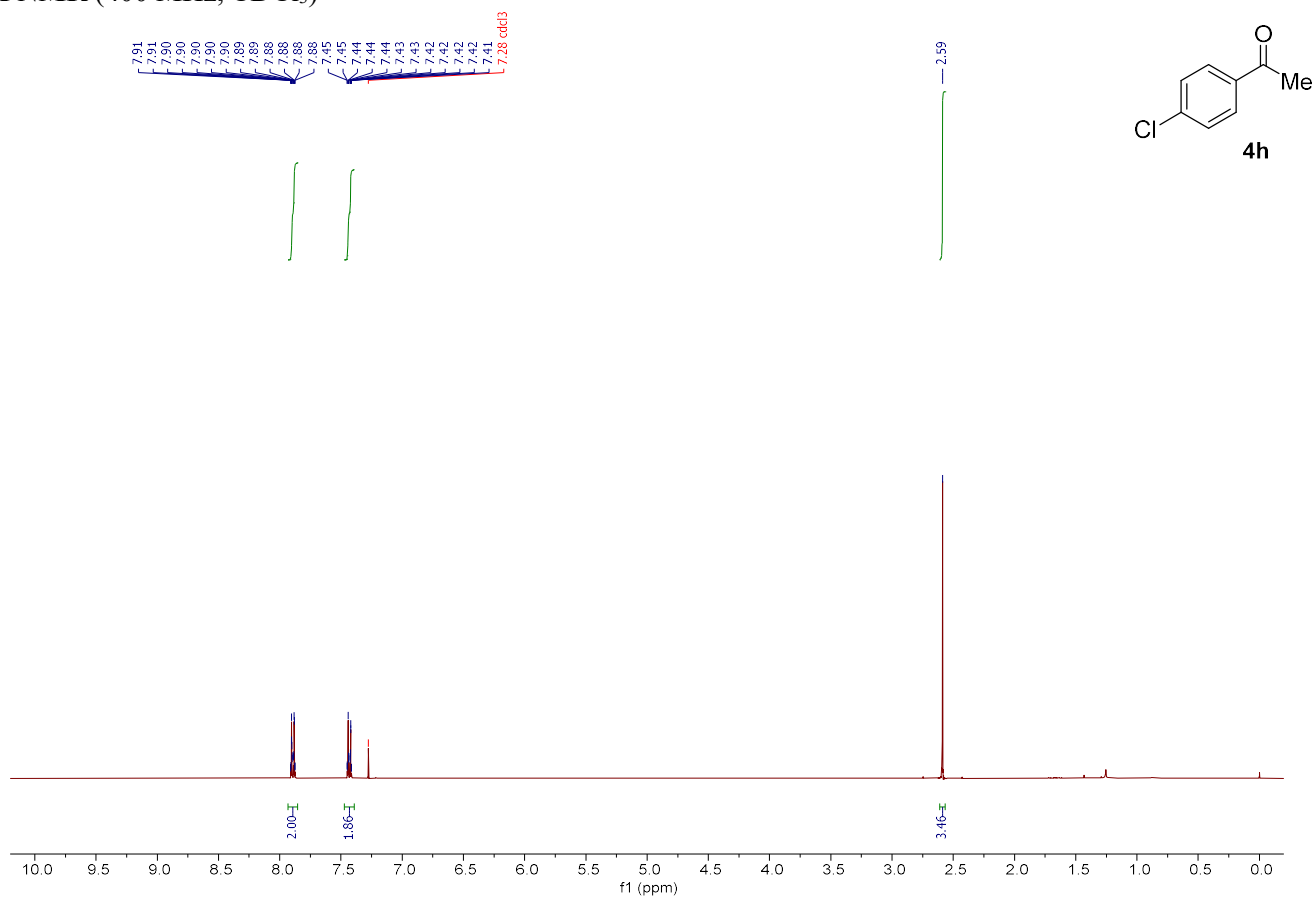
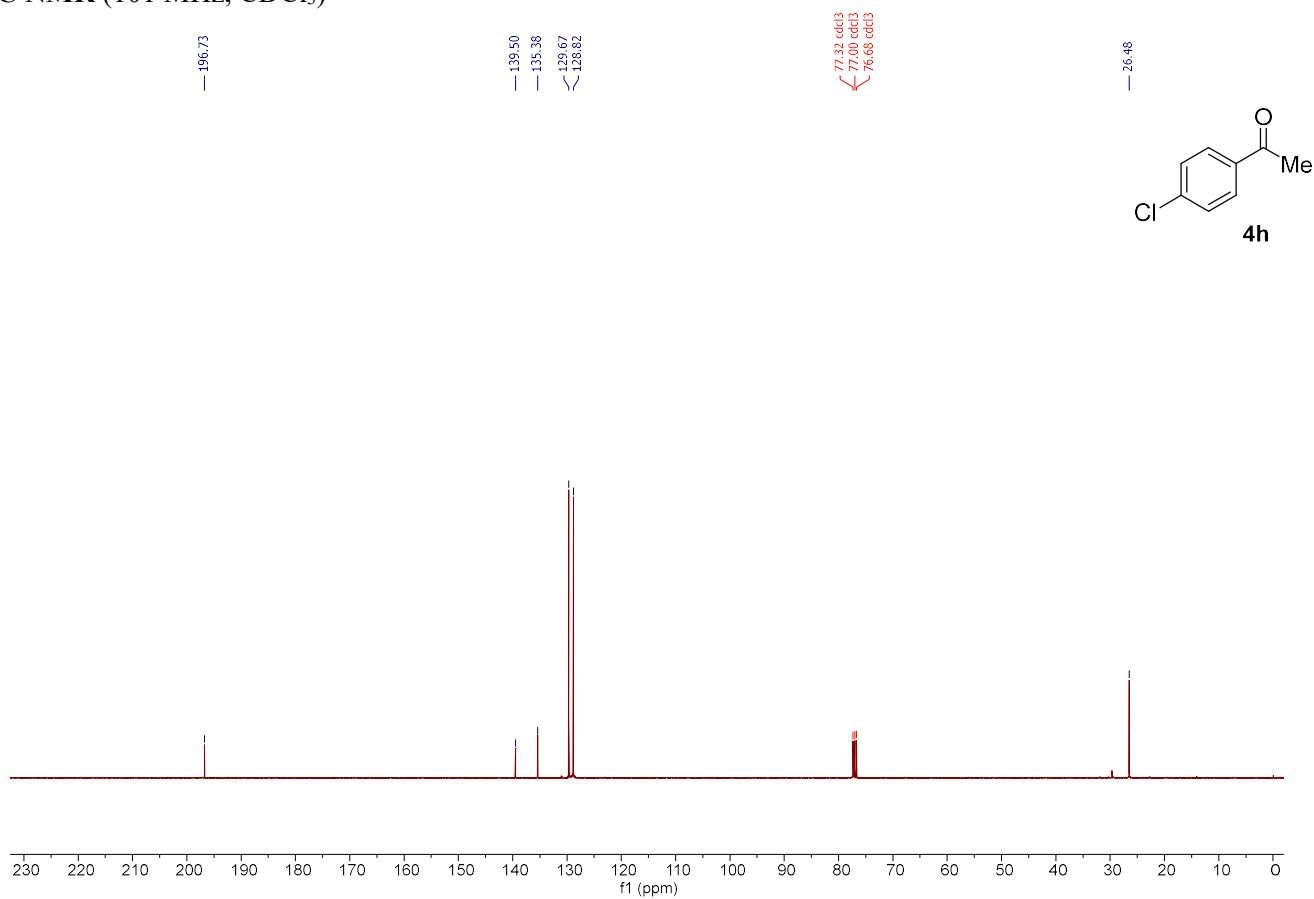
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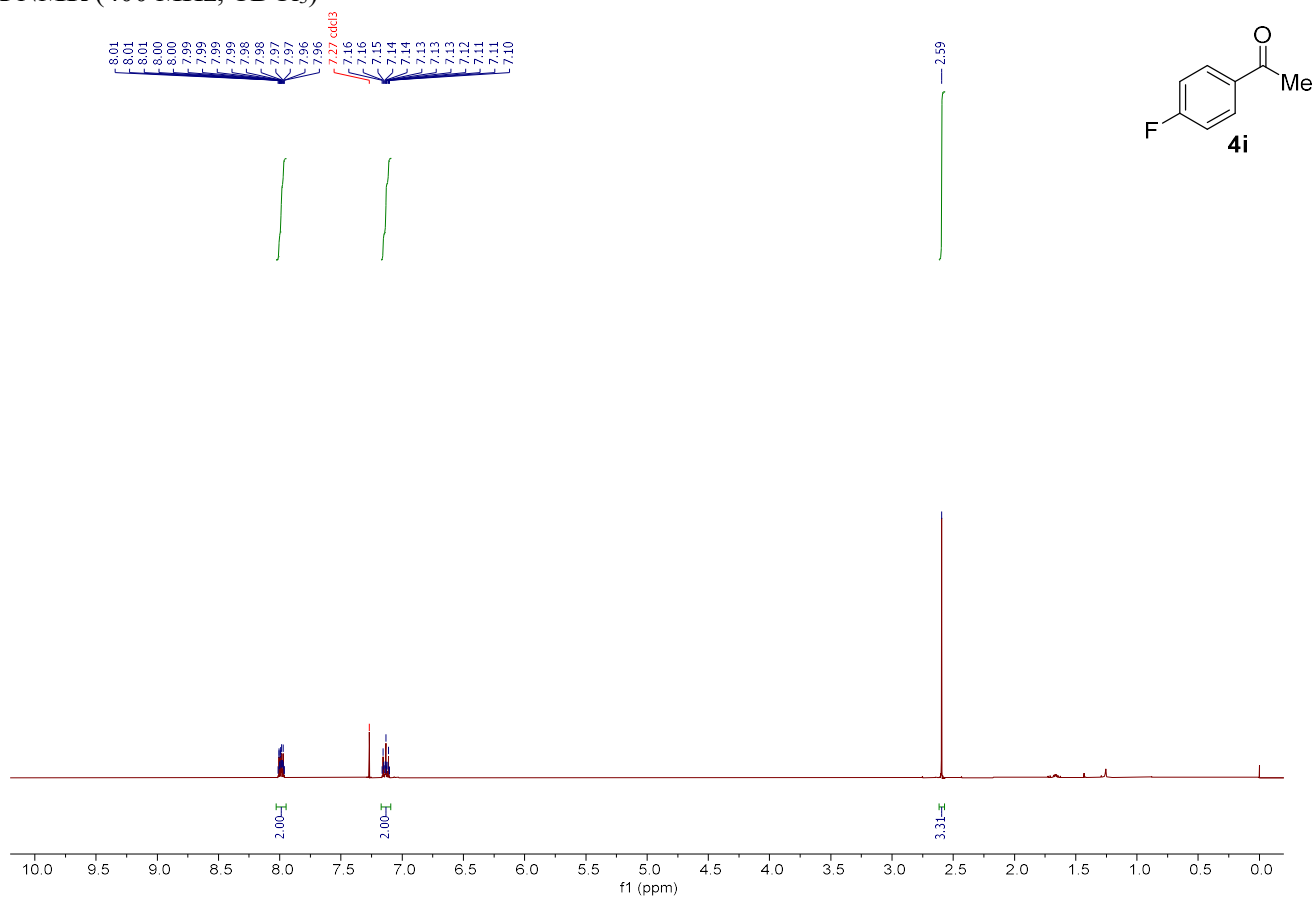
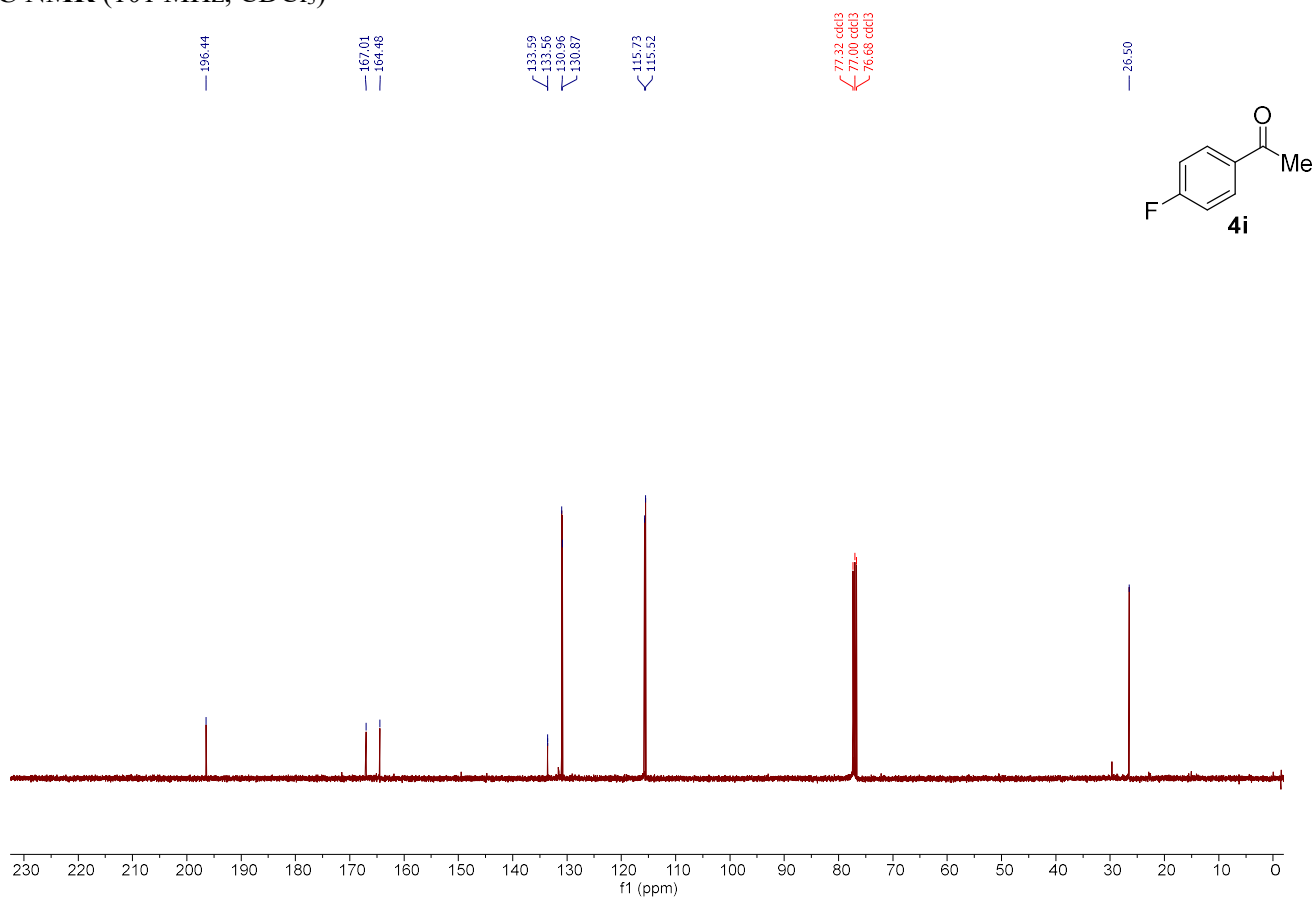
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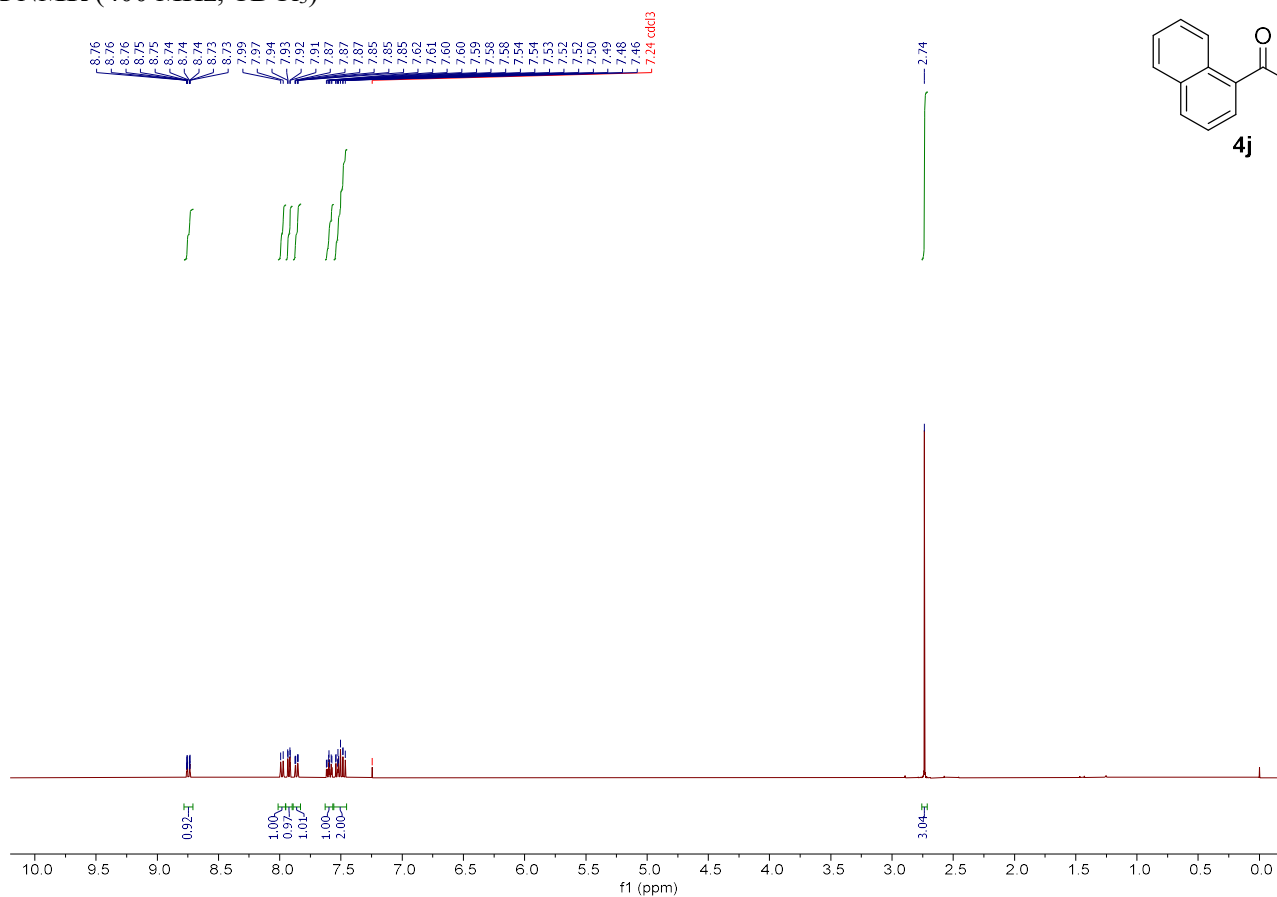
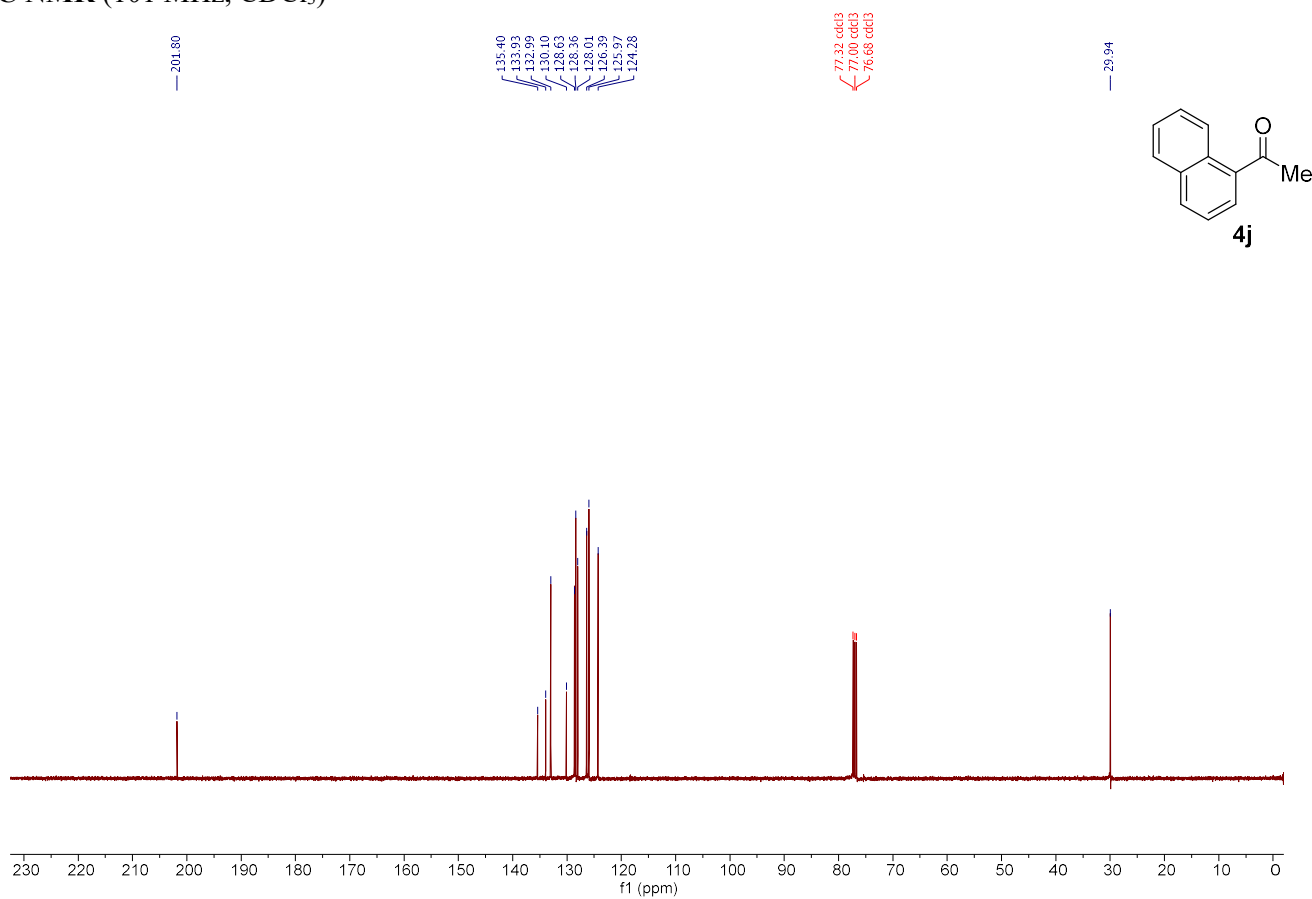
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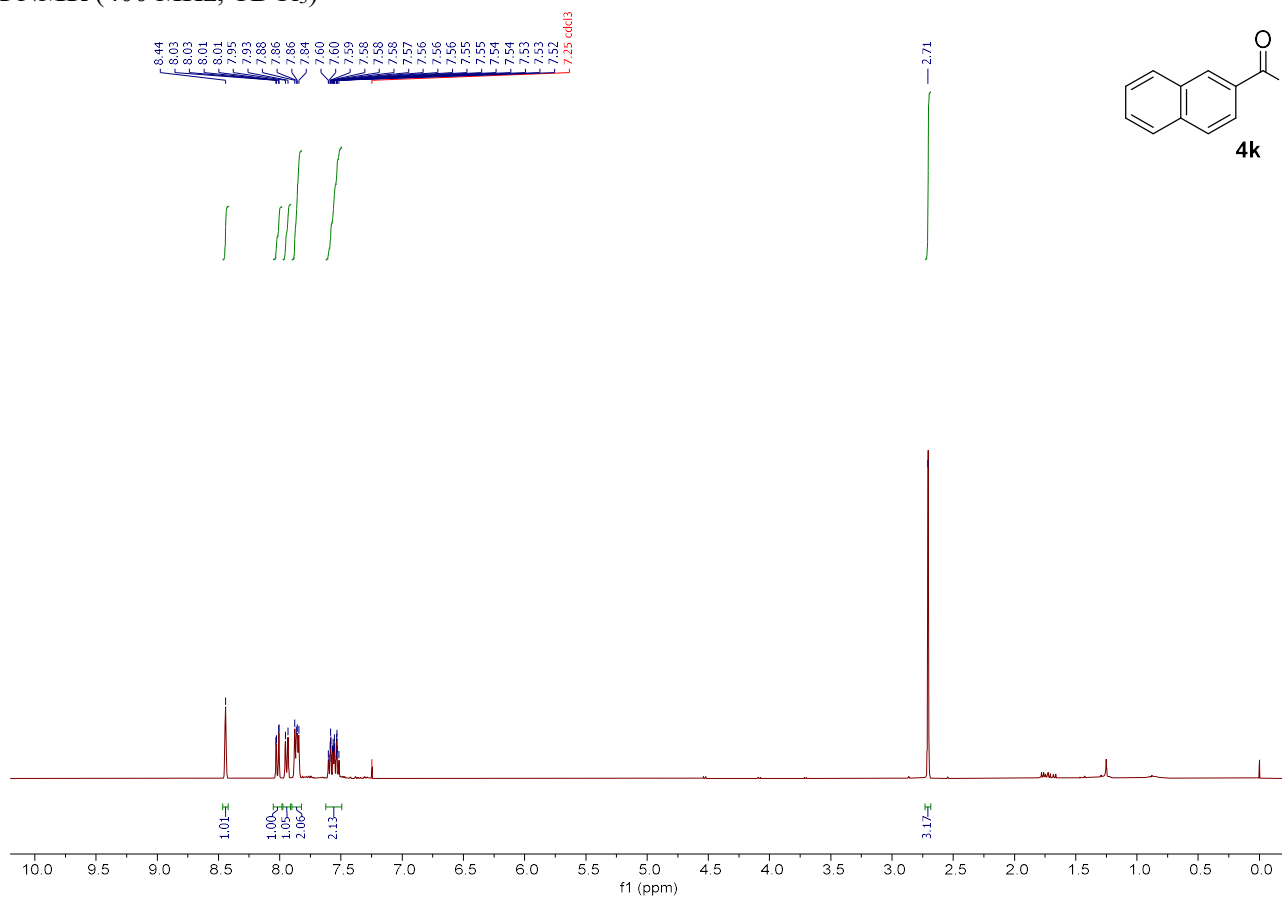
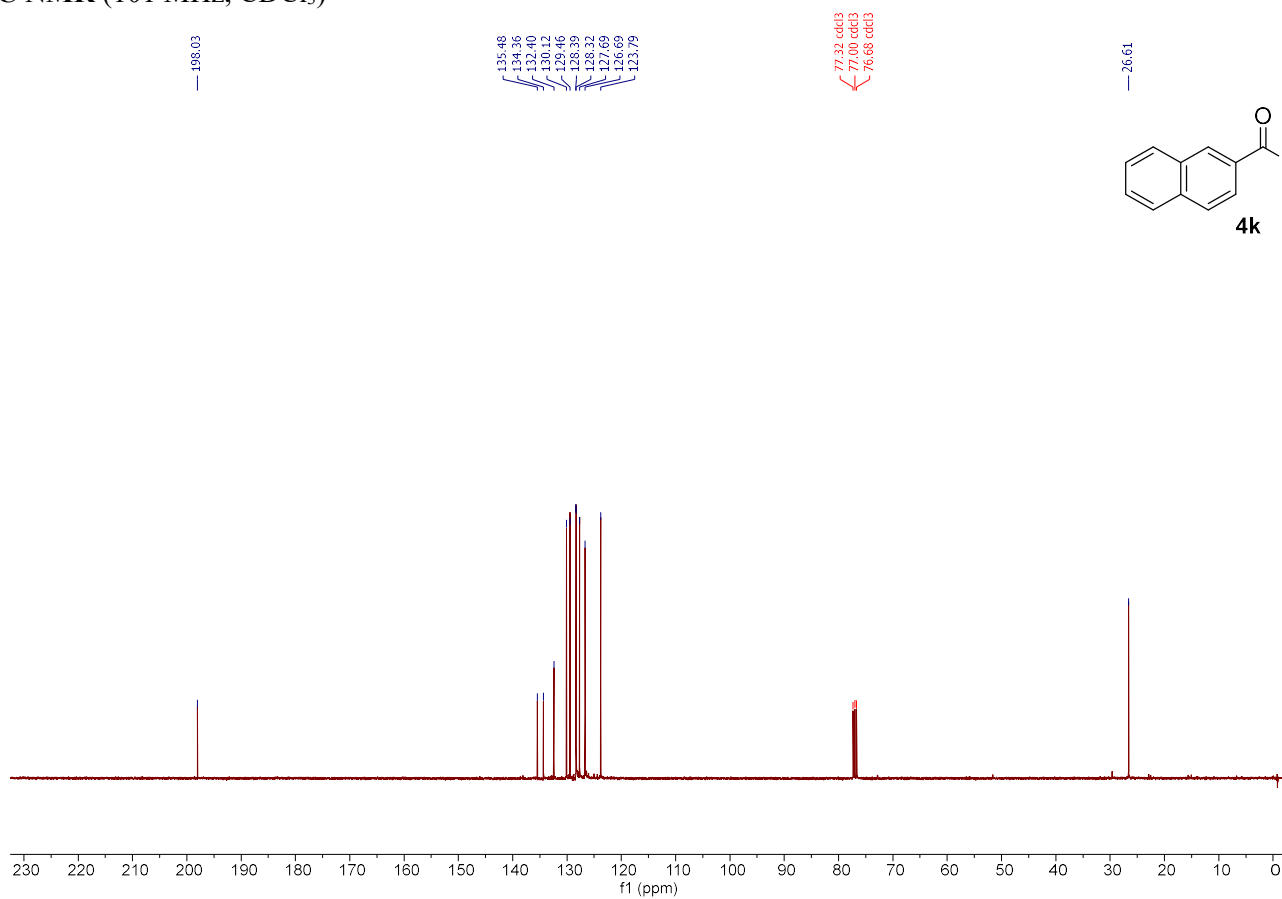
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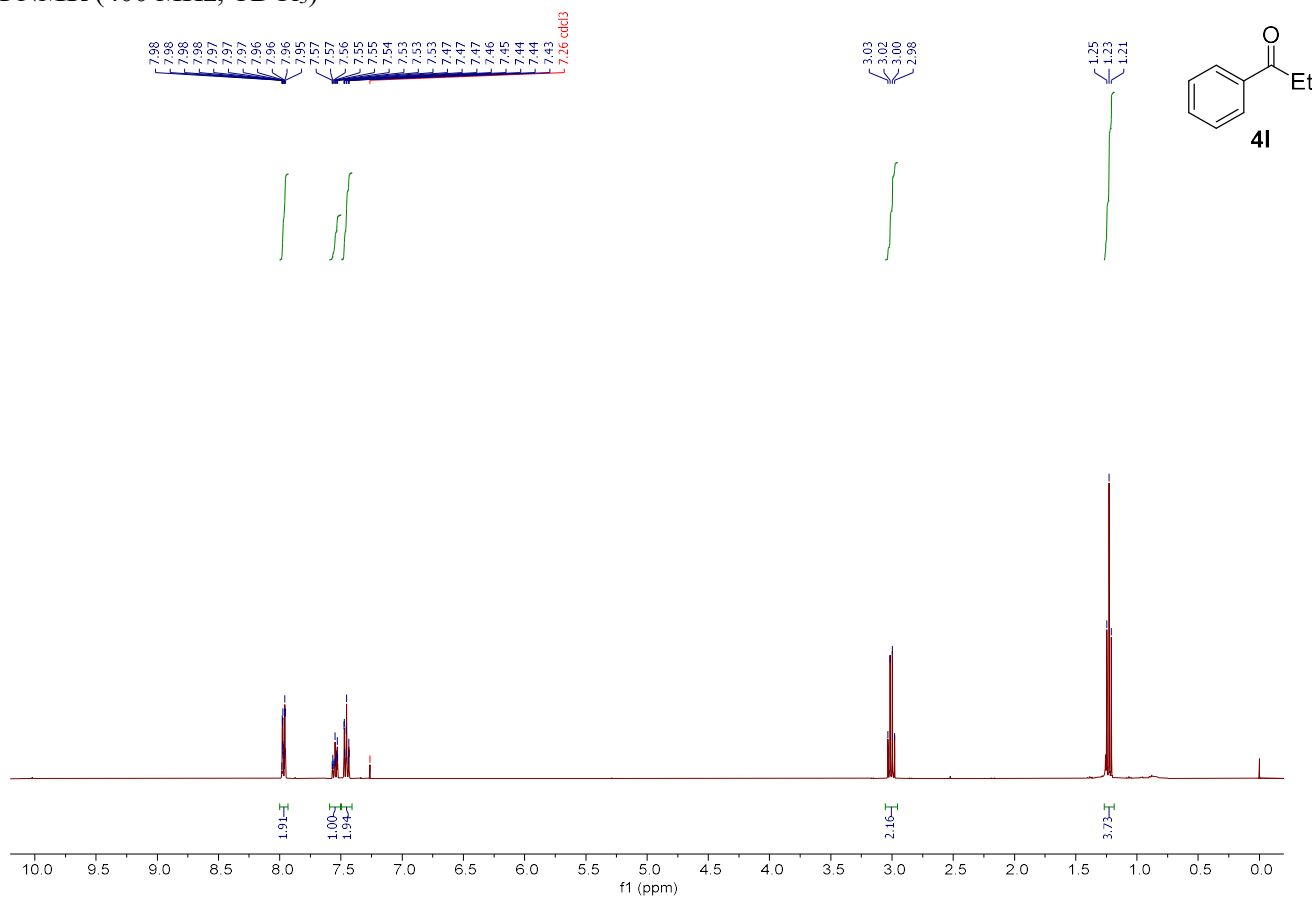
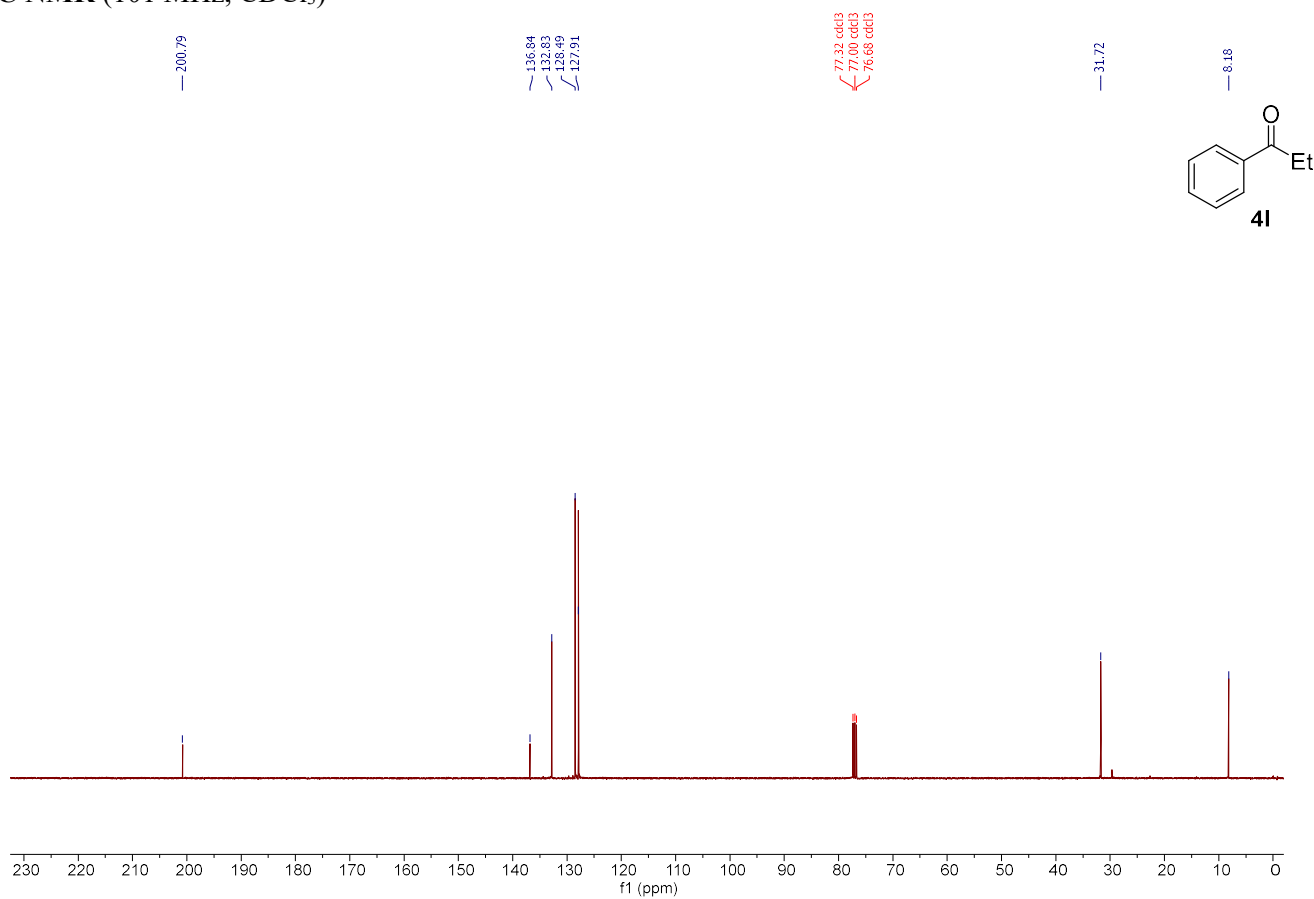
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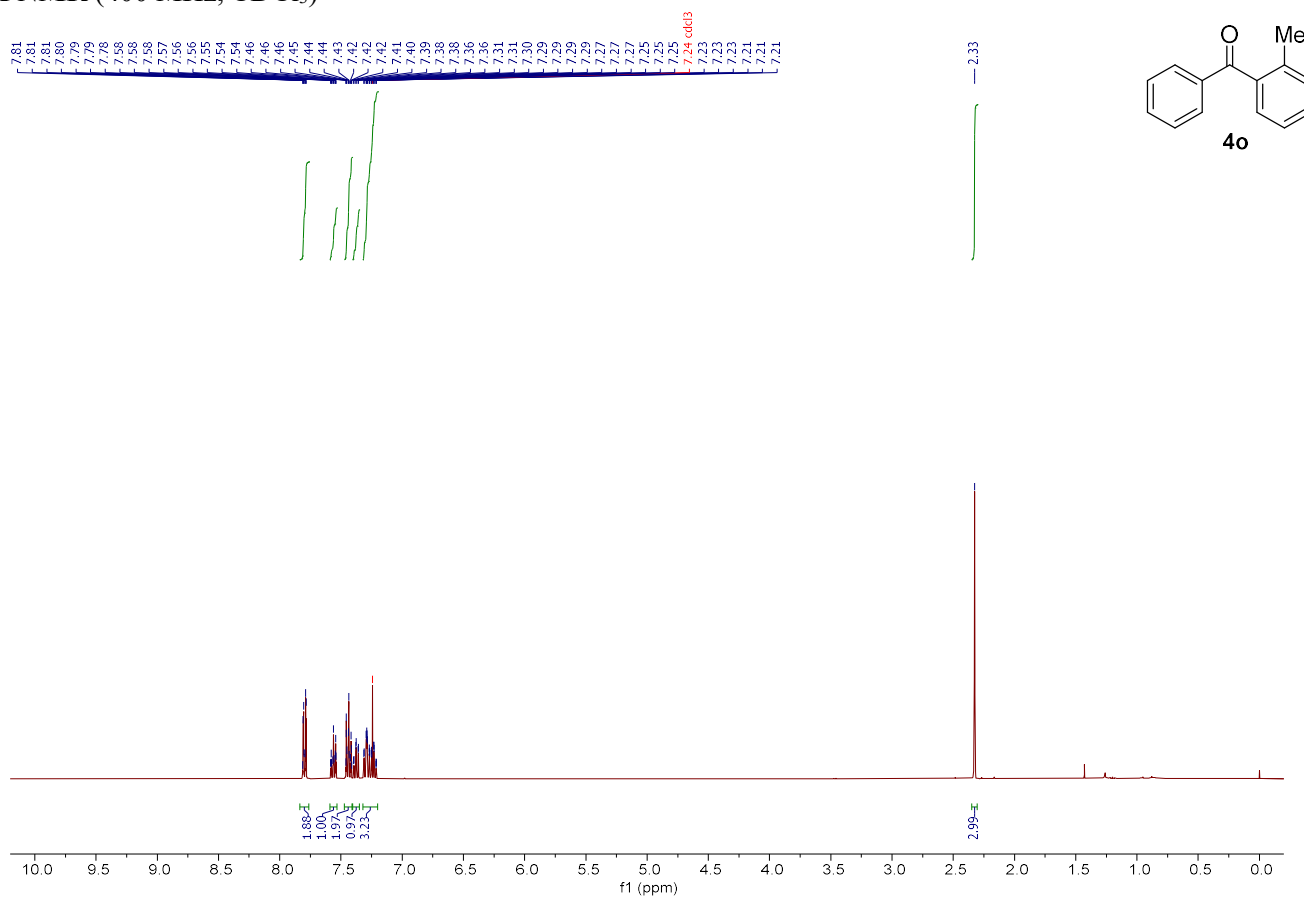
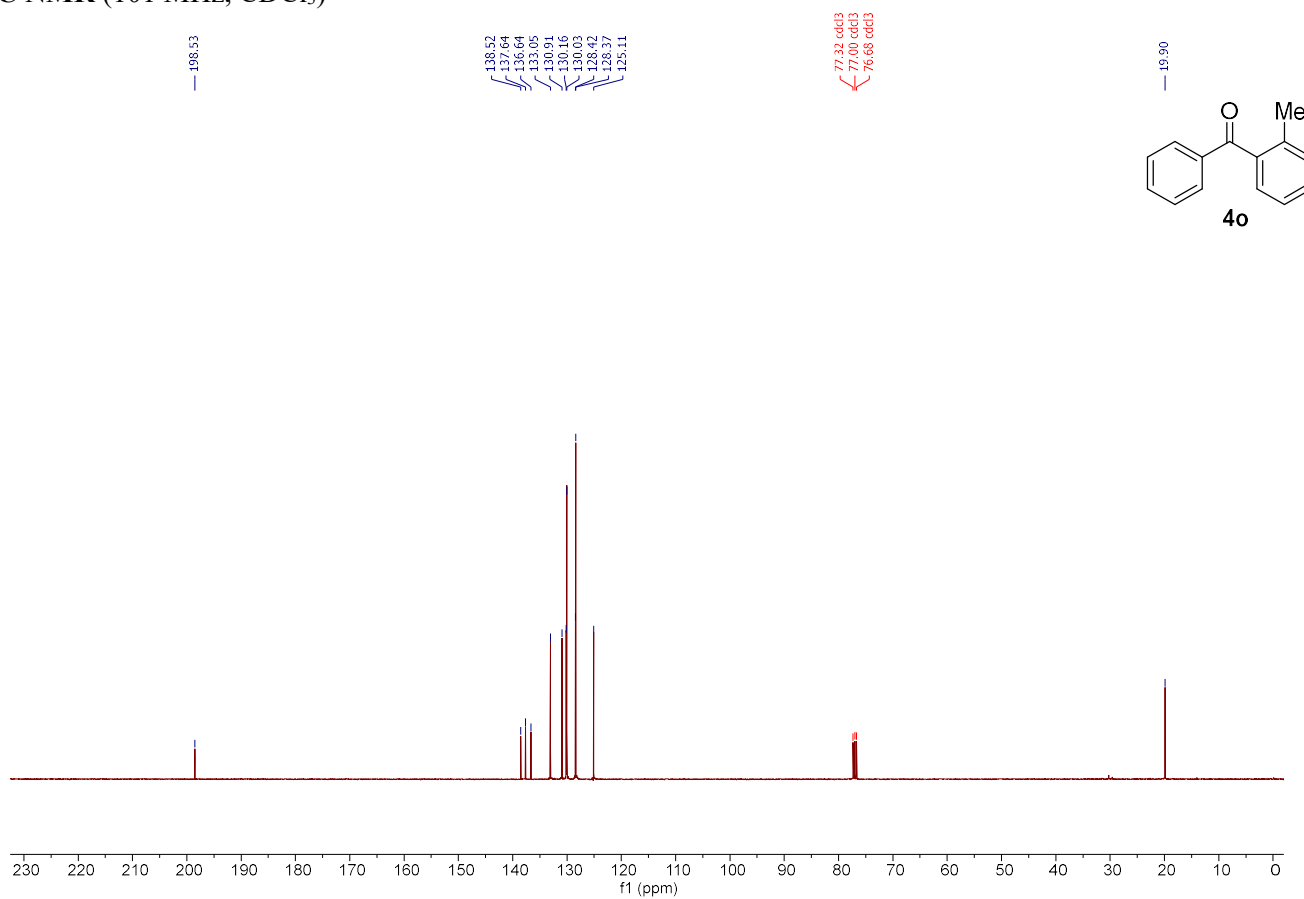
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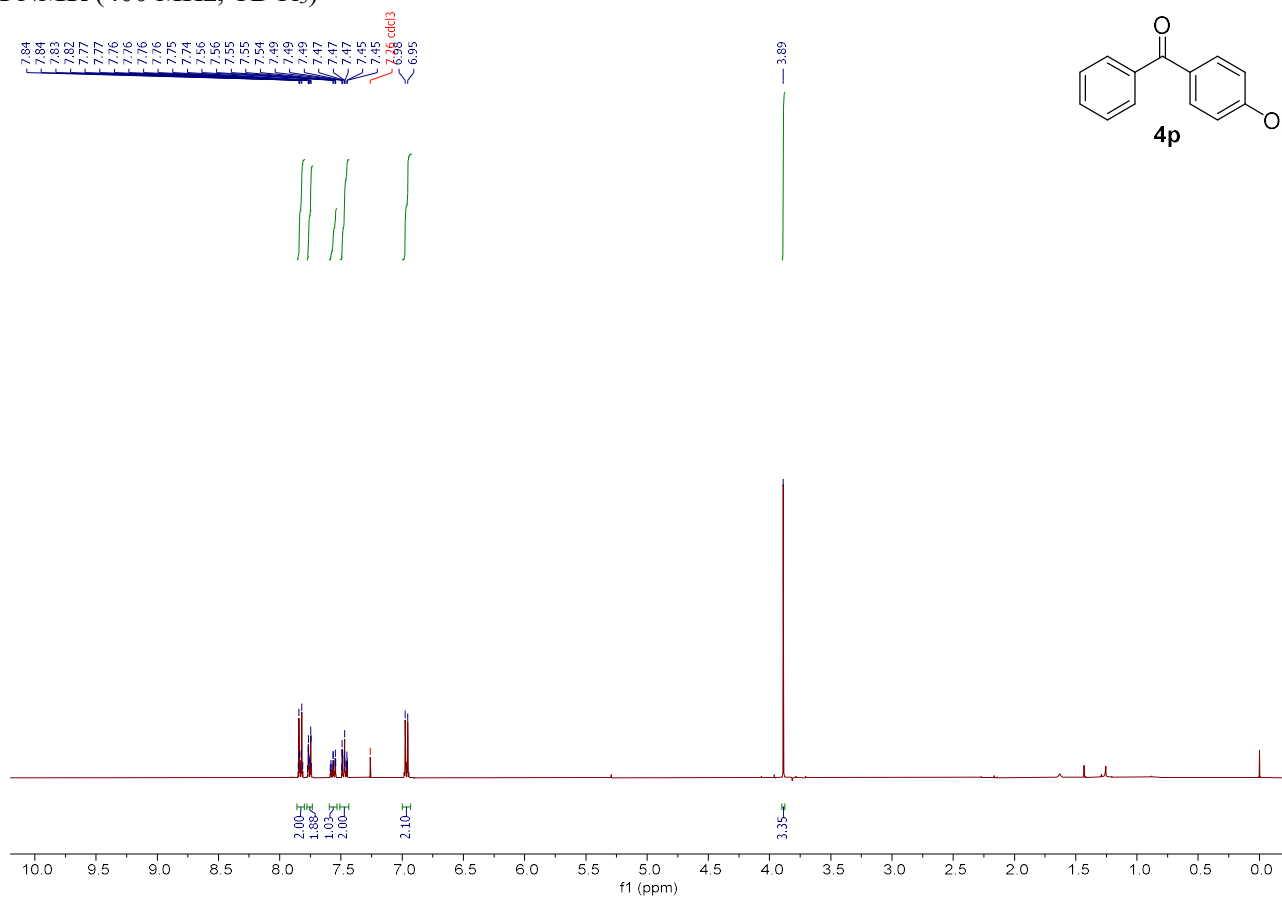
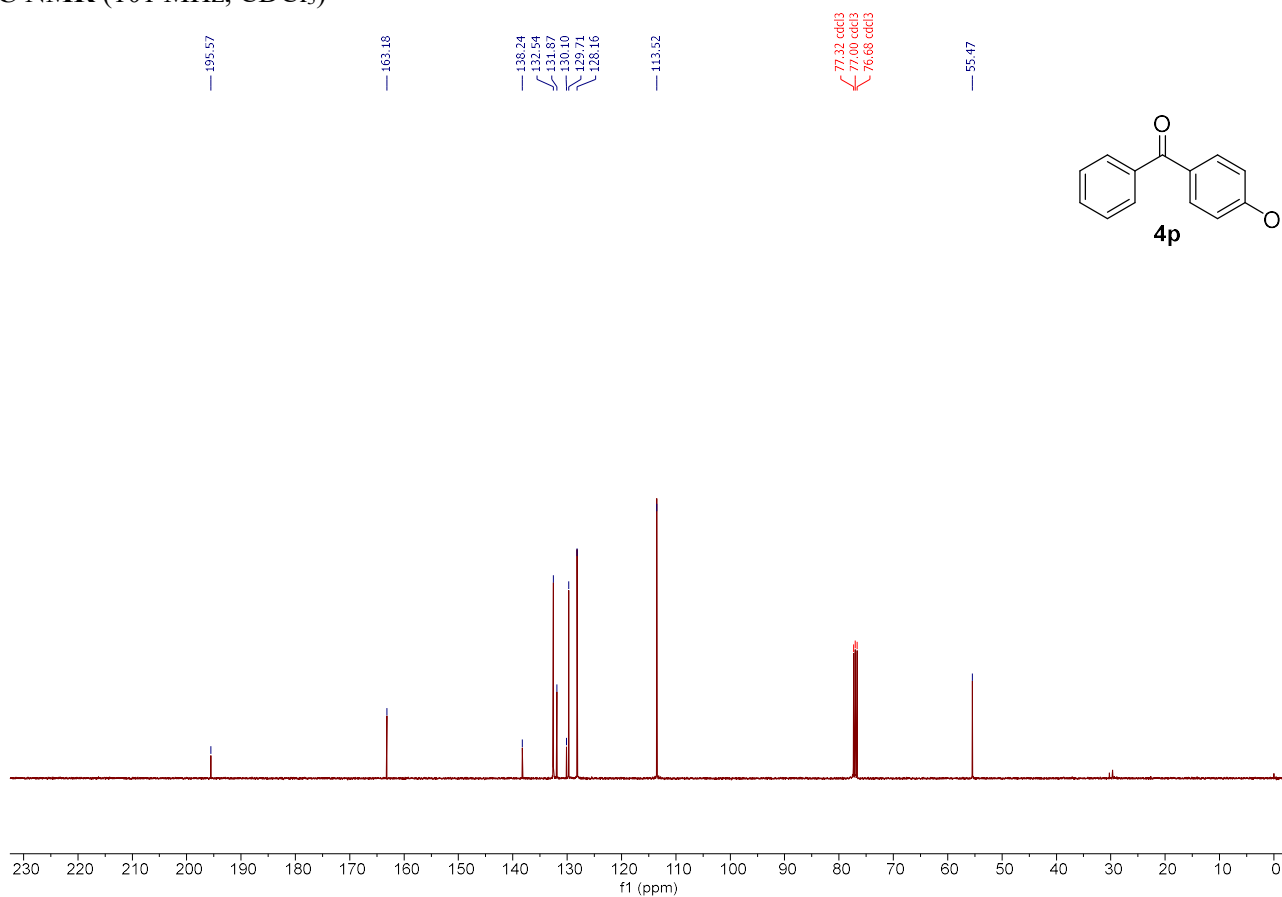
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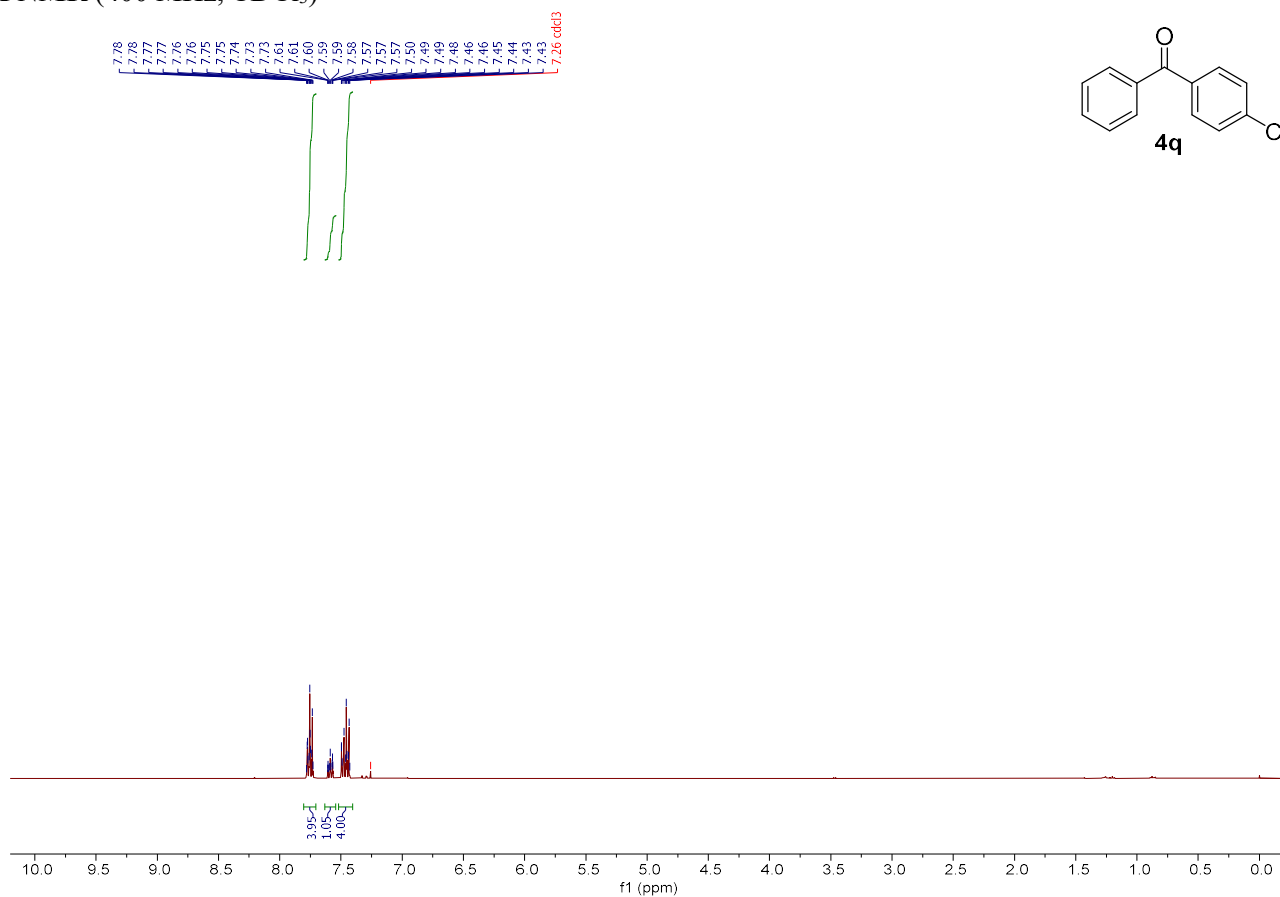
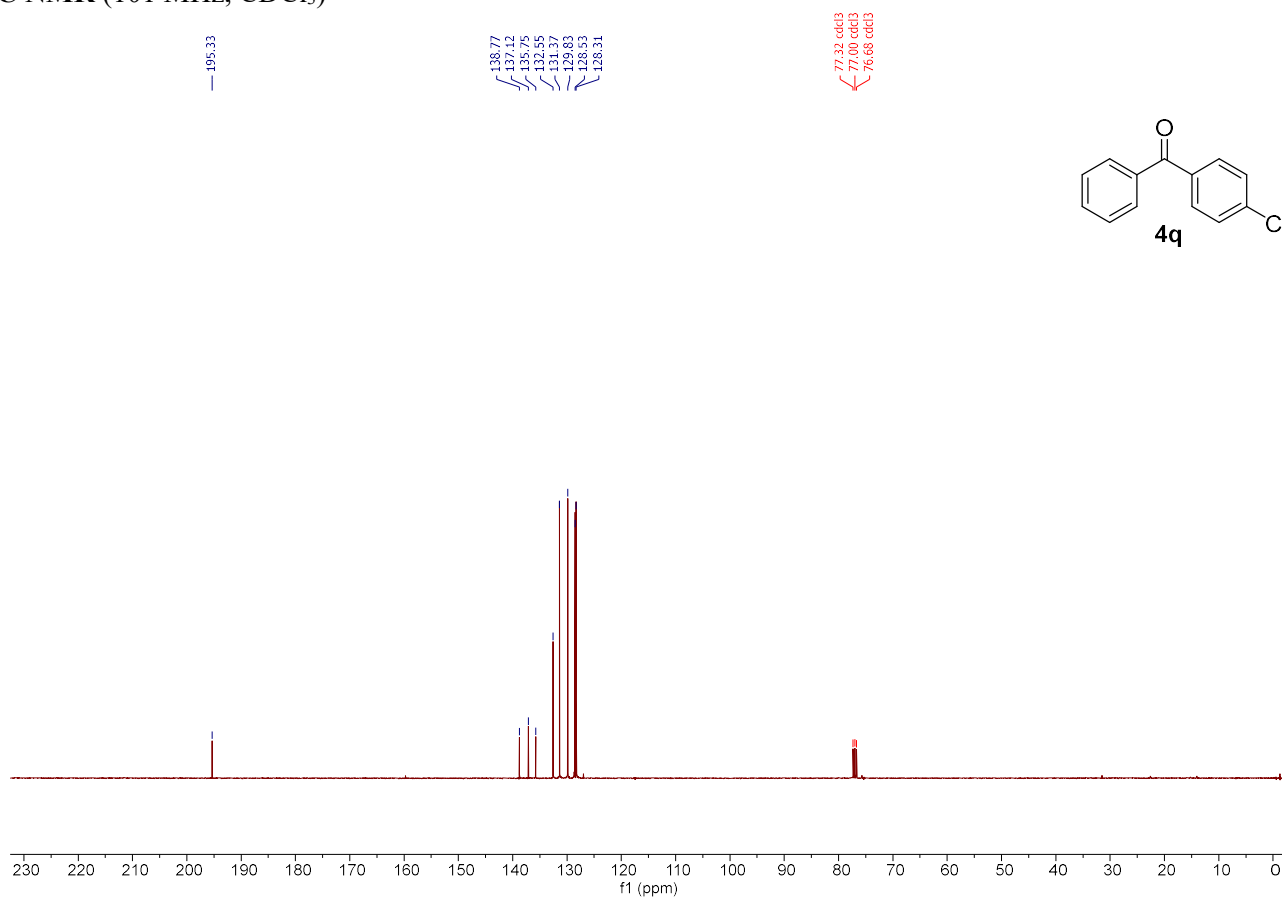
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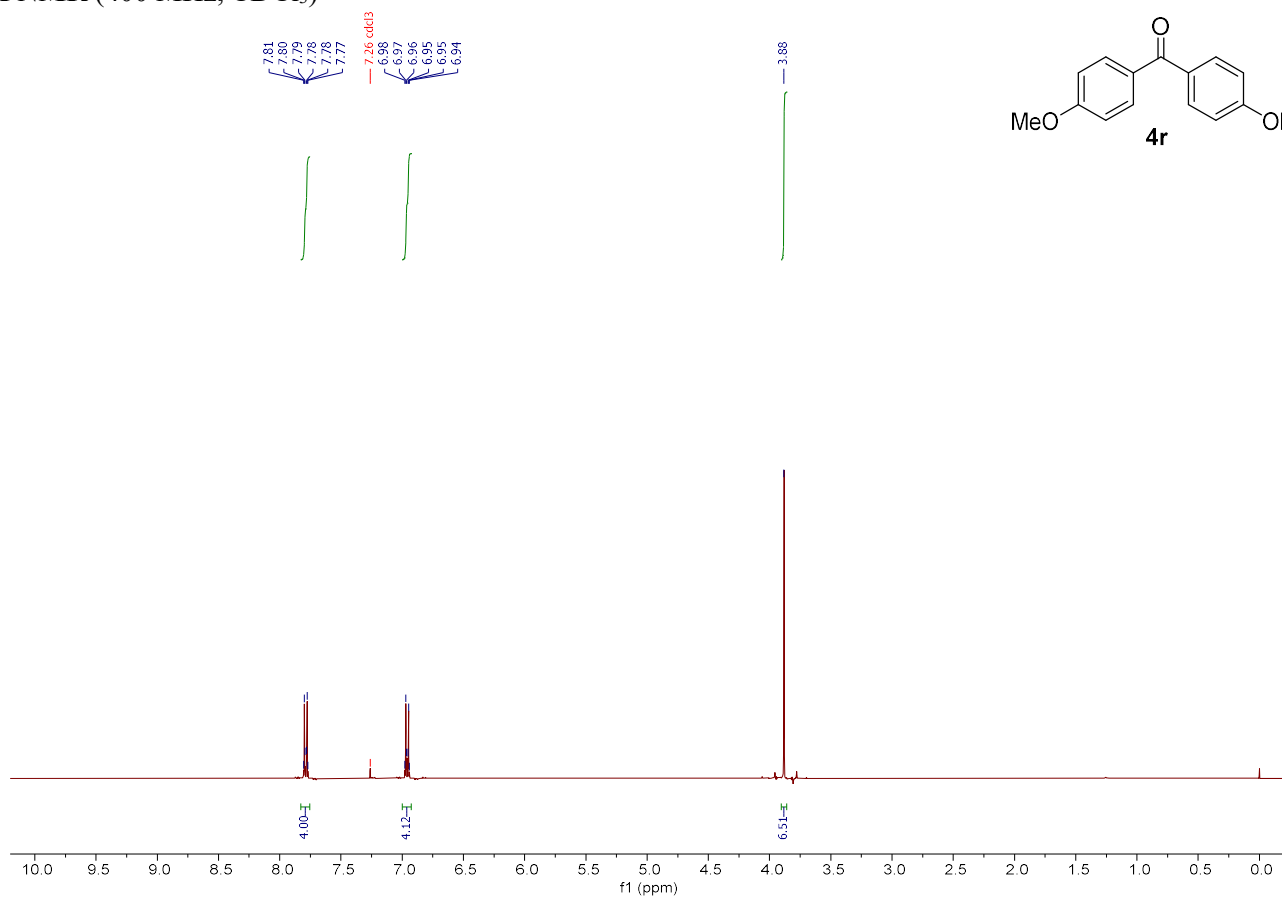
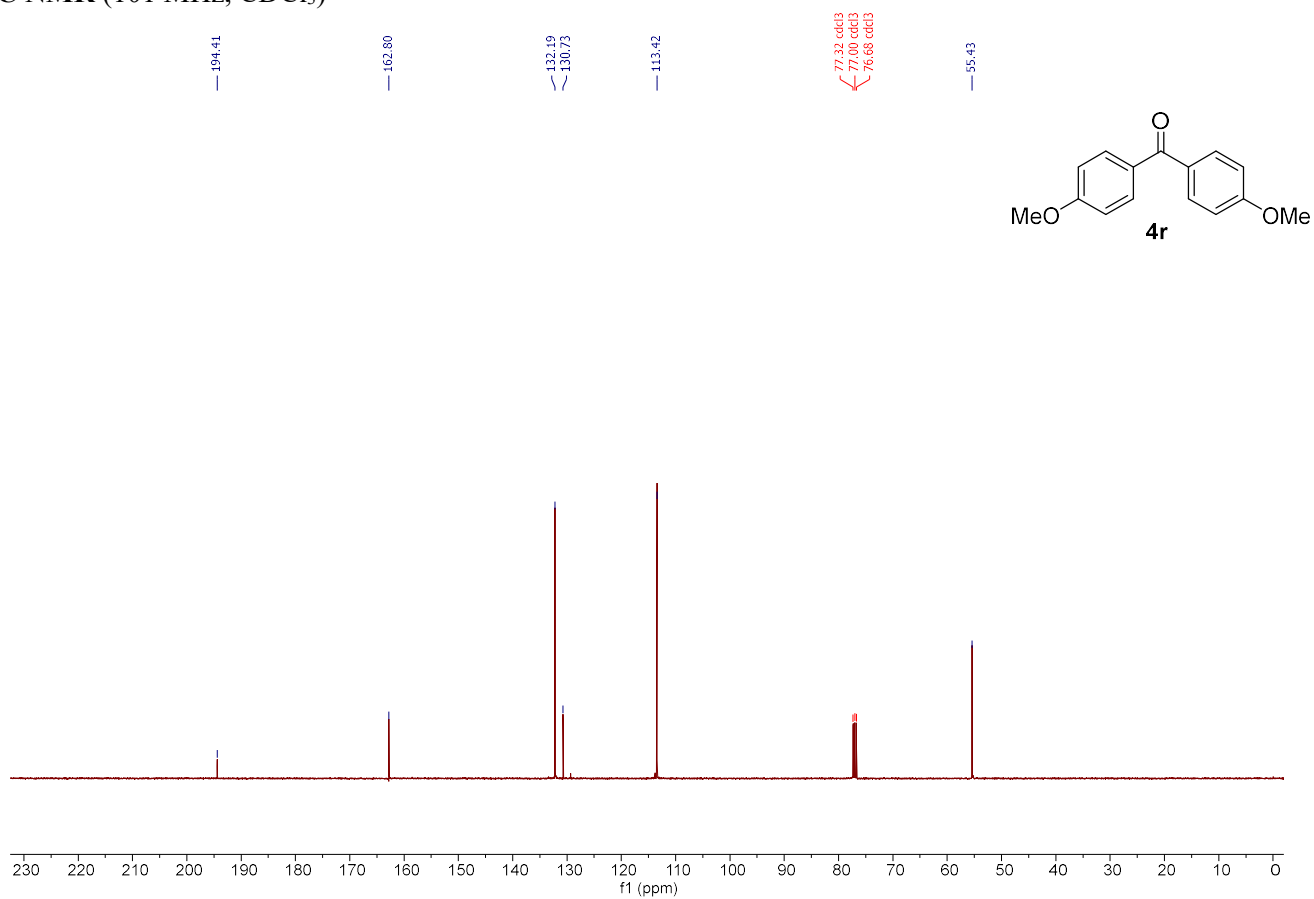
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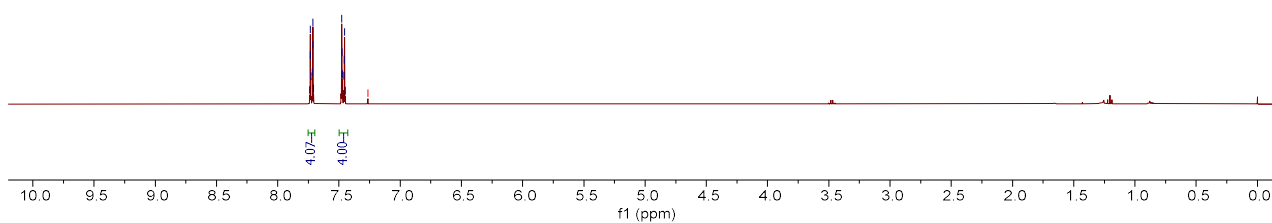
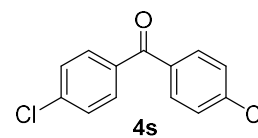
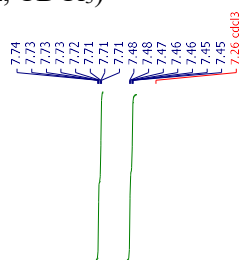
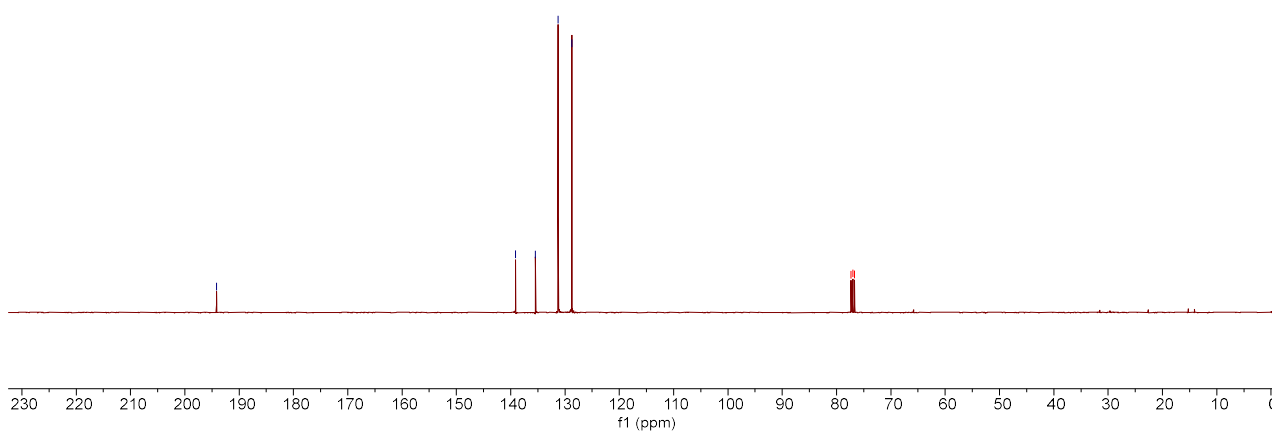
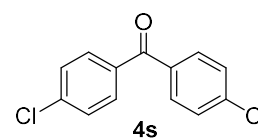
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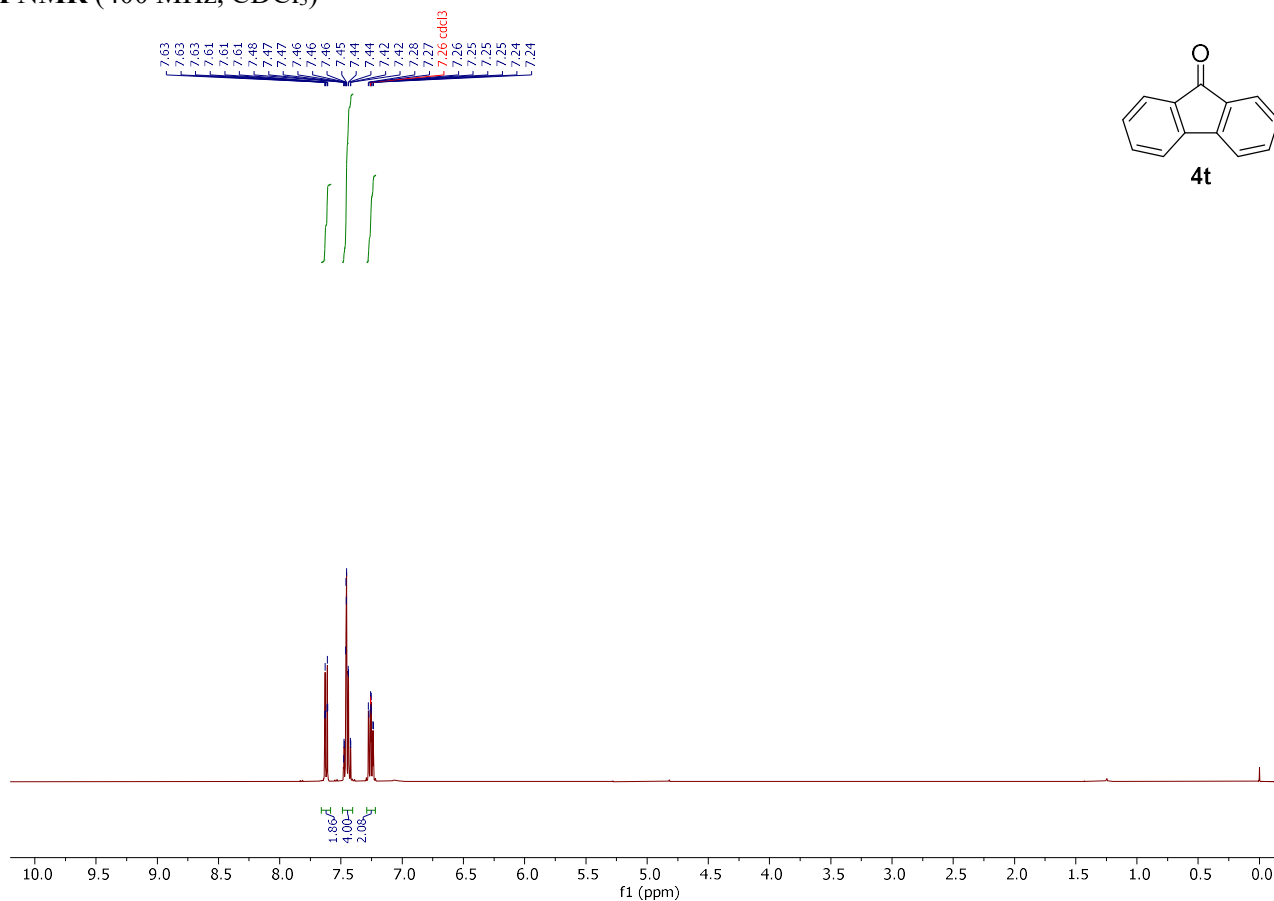
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