Predominant Intermolecular Decarbonylative Thioetherification of Carboxylic Acids using Nickel Precatalysts

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List of Known Compounds/General Methods

All starting materials reported in the manuscript have been prepared according to the method reported previously.[1-6] Unless stated otherwise, all compounds reported in this manuscript have been previously reported. Spectroscopic data matched literature values. All experiments involving palladium were performed using standard Schlenk techniques under argon atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ^{1}H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at 500 (^{1}H NMR) and 125 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.27 and 77.2 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (*J*) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5973A inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 220 °C, then hold at 220 °C for 15 min (splitless mode of injection, total run time of 22.0 min). High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument (for HRMS). Melting point was measured on MeltEMP (laboratory devices). All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Information. ^{1}H NMR, ^{13}C NMR and HRMS data are reported for all new compounds.

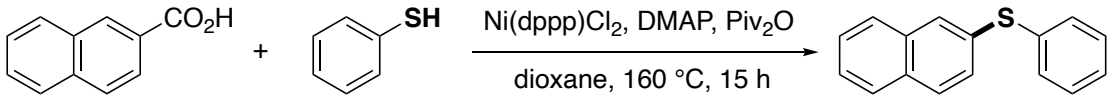
Experimental Procedures and Characterization Data

General Procedure for Decarbonylative Thioetherification of Carboxylic Acids. An oven-dried vial equipped with a stir bar was charged with carboxylic acid substrate (neat, 1.0 equiv), thiol (typically, 2.0 equiv), Ni(dppp)Cl_2 (typically, 20 mol%), 4-dimethylaminopyridine (typically, 1.2 equiv) and trimethylacetic anhydride (typically, 1.2 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. 1,4-Dioxane (typically, 0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time at 160 °C. After the indicated time, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexanes/ethyl acetate) afforded the title product.

Representative Procedure for Decarbonylative Thioetherification of Carboxylic Acids. An oven-dried vial equipped with a stir bar was charged with 2-naphthoic acid (neat, 34.5 mg, 0.20 mmol), thiophenol (2.0 equiv), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. 1,4-Dioxane (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for 15 h at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. A sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexanes/ethyl acetate) afforded the title product. Yield 86% (40.7 mg, 0.172 mmol). Colorless oil. Characterization data are included in the section below.

Characterization Data for Decarbonylative Thioetherification of Carboxylic Acids

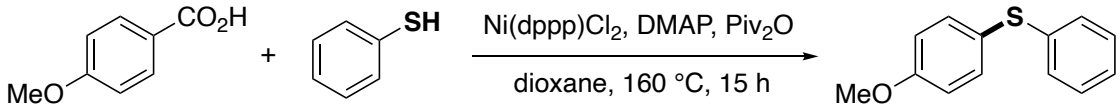
2-Naphthoic acid and thiophenol (Scheme 1, 3a)[1]



1a **2a** **3a**

According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), thiophenol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 86% yield (40.7 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.81 – 7.75 (m, 1H), 7.74 – 7.64 (m, 3H), 7.42 – 7.36 (m, 2H), 7.35 – 7.27 (m, 3H), 7.26 – 7.17 (m, 3H).**^{13}C NMR (101 MHz, Chloroform-d)** δ 134.80, 132.74, 131.95, 131.24, 129.91, 128.84, 128.19, 127.82, 127.71, 126.70, 126.38, 126.03, 125.56, 125.17.

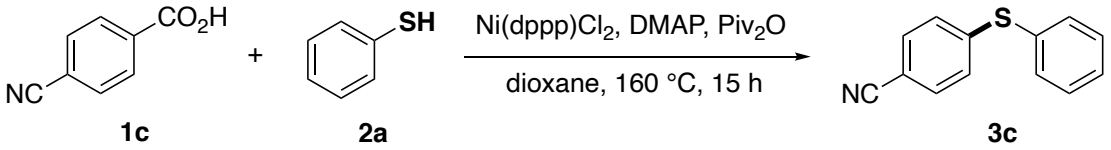
4-Methoxybenzoic acid and thiophenol (Scheme 1, 3b)[1]



1b **2a** **3b**

According to the general procedure, the reaction of 4-methoxybenzoic acid (0.20 mmol), thiophenol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 66% yield (28.6 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.34 (d, J = 8.8 Hz, 2H), 7.18 – 7.14 (m, 2H), 7.12 – 7.01 (m, 3H), 6.86 – 6.79 (m, 2H), 3.75 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-d)** δ 158.79, 137.57, 134.35, 127.89, 127.14, 124.72, 123.24, 113.95, 54.34.

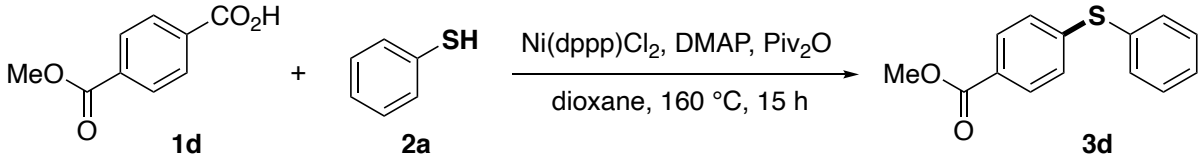
4-Cyanobenzoic acid and thiophenol (Scheme 1, 3c)[1]



1c **2a** **3c**

According to the general procedure, the reaction of 4-cyanobenzoic acid (0.20 mmol), thiophenol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 85% yield (36.0 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.47 – 7.42 (m, 2H), 7.42 – 7.39 (m, 2H), 7.36 (q, J = 3.4, 2.4 Hz, 3H), 7.13 – 7.06 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 144.72, 133.50, 131.35, 129.78, 128.90, 128.38, 126.26, 117.79, 107.65.

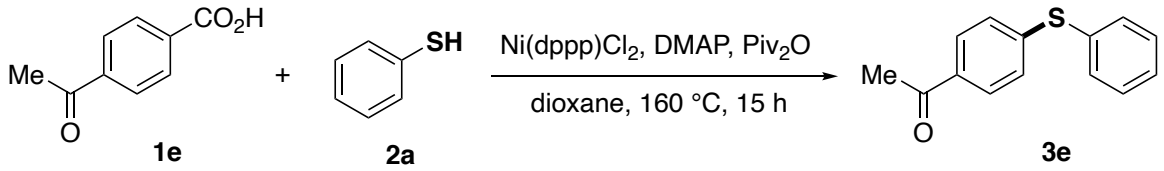
4-(Methoxycarbonyl)benzoic acid and thiophenol (Scheme 1, 3d)[1]



1d **2a** **3d**

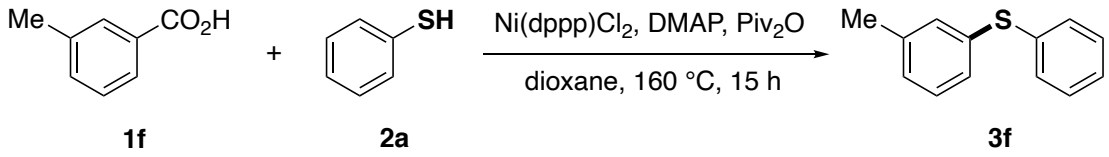
According to the general procedure, the reaction of 4-(methoxycarbonyl)benzoic acid (0.20 mmol), thiophenol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 97% yield (47.4 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.85 – 7.79 (m, 2H), 7.41 (dd, J = 7.6, 2.2 Hz, 2H), 7.31 (dd, J = 5.1, 2.1 Hz, 3H), 7.16 – 7.11 (m, 2H), 3.81 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 165.66, 143.36, 132.68, 131.31, 129.05, 128.61, 127.64, 126.51, 126.42, 51.06.

4-Acetylbenzoic acid and thiophenol (Scheme 1, 3e)[1]



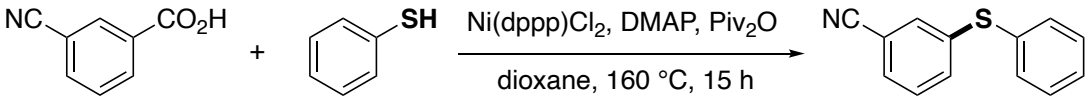
According to the general procedure, the reaction of 4-acetylbenzoic acid (0.20 mmol), thiophenol (0.40 mmol), $Ni(dppp)Cl_2$ (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 94% yield (43.0 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.77 – 7.71 (m, 2H), 7.47 – 7.38 (m, 2H), 7.33 (dd, J = 5.1, 2.1 Hz, 3H), 7.16 – 7.11 (m, 2H), 2.48 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 196.11, 143.91, 133.43, 132.86, 131.03, 128.66, 127.87, 127.78, 126.41, 25.46.

3-Methylbenzoic acid and thiophenol (Scheme 1, 3f)[1]



According to the general procedure, the reaction of 3-methylbenzoic acid (0.20 mmol), thiophenol (0.40 mmol), $Ni(dppp)Cl_2$ (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 64% yield (25.7 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.31 – 7.24 (m, 2H), 7.24 (d, J = 1.0 Hz, 2H), 7.18 – 7.06 (m, 4H), 7.03 – 6.94 (m, 1H), 2.24 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 138.03, 135.06, 134.18, 130.81, 129.71, 128.09, 128.00, 127.30, 126.99, 125.81, 20.27.

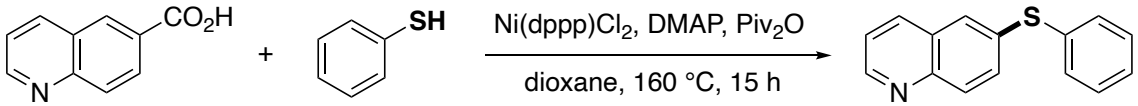
3-Cyanobenzoic acid and thiophenol (Scheme 1, 3g)[1]



1g **2a** **3g**

According to the general procedure, the reaction of 3-cyanobenzoic acid (0.20 mmol), thiophenol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 83% yield (35.1 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.37 (dd, J = 3.7, 1.8 Hz, 3H), 7.34 (ddd, J = 6.9, 3.4, 1.6 Hz, 4H), 7.32 (d, J = 2.3 Hz, 1H), 7.30 – 7.25 (m, 1H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 138.99, 132.38, 131.78, 131.11, 130.54, 128.80, 128.56, 128.48, 127.84, 117.28, 112.26.

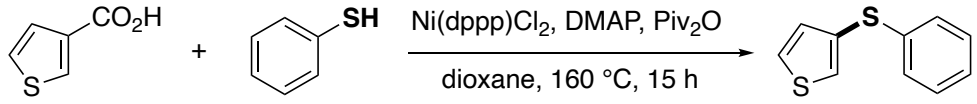
Quinoline-6-carboxylic acid and thiophenol (Scheme 1, 3h)[1]



1h **2a** **3h**

According to the general procedure, the reaction of quinoline-6-carboxylic acid (0.20 mmol), thiophenol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 97% yield (46.1 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.79 (dd, J = 4.2, 1.7 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.62 (d, J = 2.1 Hz, 1H), 7.52 (dd, J = 8.9, 2.2 Hz, 1H), 7.37 (dt, J = 6.0, 1.6 Hz, 2H), 7.33 – 7.24 (m, 4H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 149.27, 146.09, 131.08, 130.45, 129.20, 128.45, 127.64, 126.86 (d, J = 9.6 Hz), 120.65.

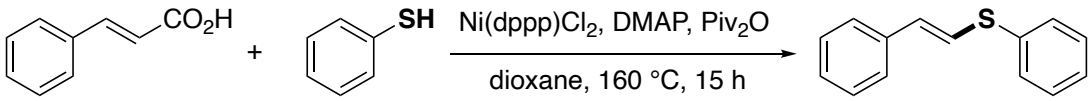
Thiophene-3-carboxylic acid and thiophenol (Scheme 1, 3i)[1]



1i **2a** **3i**

According to the general procedure, the reaction of thiophene-3-carboxylic acid (0.20 mmol), thiophenol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 75% yield (28.9 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.33 – 7.28 (m, 2H), 7.20 – 7.09 (m, 5H), 6.97 (dd, J = 4.5, 1.7 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 136.31, 130.22, 128.27, 127.97, 127.36, 127.20, 125.72, 125.10.

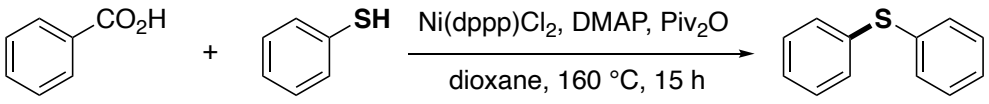
Cinnamic acid and thiophenol (Scheme 1, 3j)[1]



1j **2a** **3j**

According to the general procedure, the reaction of cinnamic acid (0.20 mmol), thiophenol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 86% yield (36.6 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.37 – 7.32 (m, 2H), 7.29 (d, J = 1.4 Hz, 1H), 7.27 – 7.24 (m, 4H), 7.24 – 7.11 (m, 3H), 6.82 (d, J = 15.4 Hz, 1H), 6.67 (d, J = 15.5 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 135.48, 134.19, 130.78, 128.79, 128.13, 127.66, 126.56, 125.92, 124.99, 122.35.

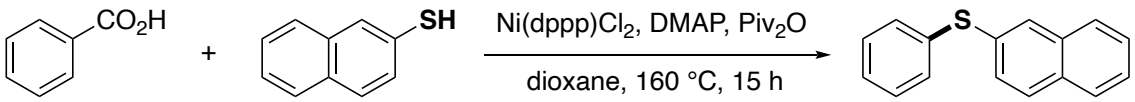
Benzoic acid and thiophenol (Scheme 2, 3k)[1]



1k **2a** **3k**

According to the general procedure, the reaction of benzoic acid (0.20 mmol), thiophenol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 93% yield (34.7 mg). Yellow oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.29 – 7.25 (m, 4H), 7.22 (ddd, J = 8.0, 6.7, 0.9 Hz, 4H), 7.19 – 7.15 (m, 2H).**^{13}C NMR (101 MHz, Chloroform-d)** δ 134.73, 130.00, 128.15, 126.00.

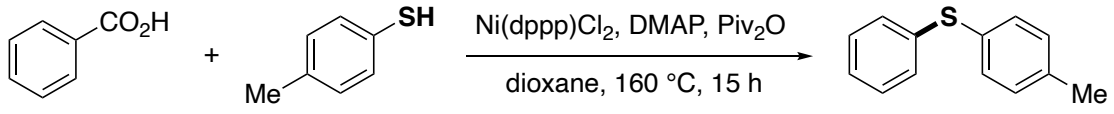
Benzoic acid and naphthalene-2-thiol (Scheme 2, 3a')[1]



1k **2b** **3a'**

According to the general procedure, the reaction of benzoic acid (0.20 mmol), naphthalene-2-thiol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 64% yield (30.3 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.84 (d, J = 1.8 Hz, 1H), 7.82 – 7.72 (m, 3H), 7.49 – 7.46 (m, 2H), 7.44 – 7.35 (m, 3H), 7.34 – 7.25 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 131.07, 130.01, 129.36, 128.93 (d, J = 12.0 Hz), 127.86, 127.55, 127.19, 126.72, 126.34, 77.47, 77.15, 76.83.

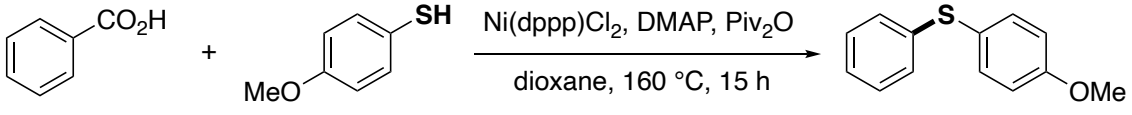
Benzoic acid and 4-methylbenzenethiol (Scheme 2, 3l)[1]



1k **2c** **3l**

According to the general procedure, the reaction of benzoic acid (0.20 mmol), 4-methylbenzenethiol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 68% yield (27.3 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.32 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 4.3 Hz, 4H), 7.20 (q, J = 4.1 Hz, 1H), 7.15 (d, J = 7.9 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 137.74, 132.42, 131.37, 130.20, 129.87, 129.17, 126.52, 77.49, 77.17, 76.85, 21.27.

Benzoic acid and 4-methoxybenzenethiol (Scheme 2, 3b')[1]

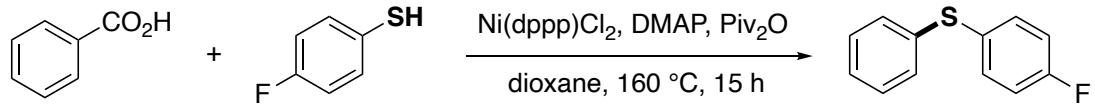


1k **2d** **3b'**

According to the general procedure, the reaction of benzoic acid (0.20 mmol), 4-methoxybenzenethiol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 90% yield (39.0 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.34 (d, J = 8.8 Hz, 2H), 7.18 – 7.14 (m, 2H), 7.12 – 7.01 (m, 3H), 6.86 – 6.79 (m, 2H), 3.75 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 158.79, 137.57, 134.35, 127.89, 127.14, 124.72, 123.24, 113.95, 54.34.

Gram-scale reaction for 3b': According to the general procedure, the reaction of benzoic acid (10.0 mmol), 4-methoxybenzenethiol (20.0 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 71% yield (1.54 g). Colorless oil.

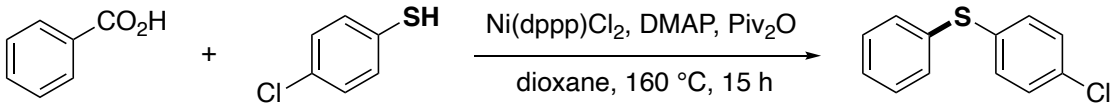
Benzoic acid and 4-fluorobenzenethiol (Scheme 2, 3m)[1]



1k **2e** **3m**

According to the general procedure, the reaction of benzoic acid (0.20 mmol), 4-fluorobenzenethiol (0.40 mmol), $Ni(dppp)Cl_2$ (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 69% yield (28.2 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.30 (dd, J = 8.8, 5.2 Hz, 2H), 7.23 – 7.17 (m, 4H), 7.16 – 7.11 (m, 1H), 6.98 – 6.92 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 135.60, 133.11, 133.02, 128.90, 128.15, 125.72, 115.49, 115.27. **^{19}F NMR (376 MHz, Chloroform-d)** δ -114.01.

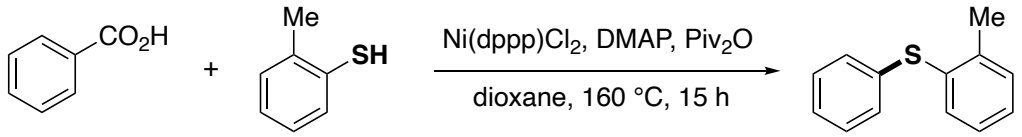
Benzoic acid and 4-chlorobenzenethiol (Scheme 2, 3n)[1]



1k **2f** **3n**

According to the general procedure, the reaction of benzoic acid (0.20 mmol), 4-chlorobenzenethiol (0.40 mmol), $Ni(dppp)Cl_2$ (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 58% yield (25.6 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.03 – 7.98 (m, 2H), 7.61 (d, J = 7.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.43 (s, 4H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 189.79, 136.43, 136.10, 133.99, 129.63, 128.93, 127.62, 125.92.

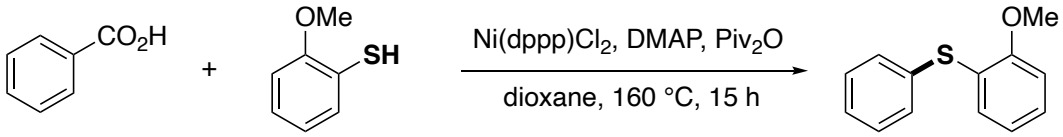
Benzoic acid and 2-methylbenzenethiol (Scheme 2, 3o)[1]



1k **2g** **3o**

According to the general procedure, the reaction of benzoic acid (0.20 mmol), 2-methylbenzenethiol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 72% yield (28.9 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.24 – 7.17 (m, 4H), 7.17 – 7.11 (m, 4H), 7.08 (dd, J = 7.4, 1.9 Hz, 1H), 2.30 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 138.94, 135.09, 132.71, 131.95, 129.56, 128.59, 128.09, 126.86, 125.68, 125.31, 19.56.

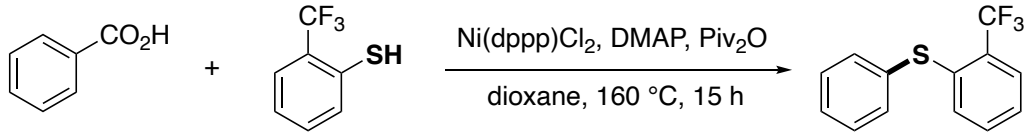
Benzoic acid and 2-methoxybenzenethiol (Scheme 2, 3p)[1]



1k **2h** **3p**

According to the general procedure, the reaction of benzoic acid (0.20 mmol), 2-methoxybenzenethiol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 64% yield (27.7 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.08 – 8.02 (m, 2H), 7.61 – 7.56 (m, 1H), 7.46 (dddd, J = 9.2, 7.4, 5.5, 1.9 Hz, 4H), 7.06 – 7.00 (m, 2H), 3.85 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 137.38, 133.58, 131.93, 128.76, 127.72, 121.28, 115.47, 111.72, 77.45, 77.13, 76.82, 56.15.

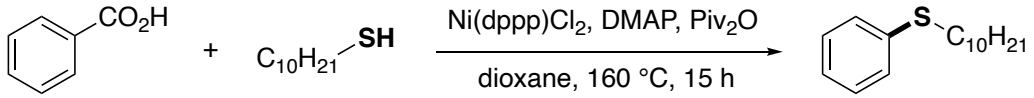
Benzoic acid and 2-(trifluoromethyl)benzenethiol (Scheme 2, 3q)[1]



1k **2i** **3q**

According to the general procedure, the reaction of benzoic acid (0.20 mmol), 2-(trifluoromethyl)benzenethiol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 57% yield (29.0 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.71 – 7.65 (m, 1H), 7.44 – 7.38 (m, 2H), 7.38 – 7.31 (m, 4H), 7.28 (dt, J = 7.7, 0.8 Hz, 1H), 7.18 (ddd, J = 8.4, 1.3, 0.7 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 133.87, 133.15, 132.45, 132.18, 129.63, 128.30, 126.79, 126.36, 77.44, 77.12, 76.80. **^{19}F NMR** (376 MHz, Chloroform-d) δ -60.77.

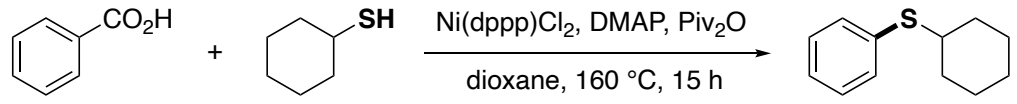
Benzoic acid and decane-1-thiol (Scheme 2, 3r)[1]



1k **2j** **3r**

According to the general procedure, the reaction of benzoic acid (0.20 mmol), decane-1-thiol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 65% yield (32.6 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.30 – 7.17 (m, 4H), 7.09 (d, J = 7.1 Hz, 1H), 2.89 – 2.81 (m, 2H), 1.56 (q, J = 7.6 Hz, 2H), 1.37 – 1.30 (m, 2H), 1.19 (d, J = 3.7 Hz, 12H), 0.81 (t, J = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 136.02, 127.77, 124.57, 32.52, 30.87, 28.50 (d, J = 3.3 Hz), 28.29, 28.13 (d, J = 3.8 Hz), 27.83, 21.66, 13.10.

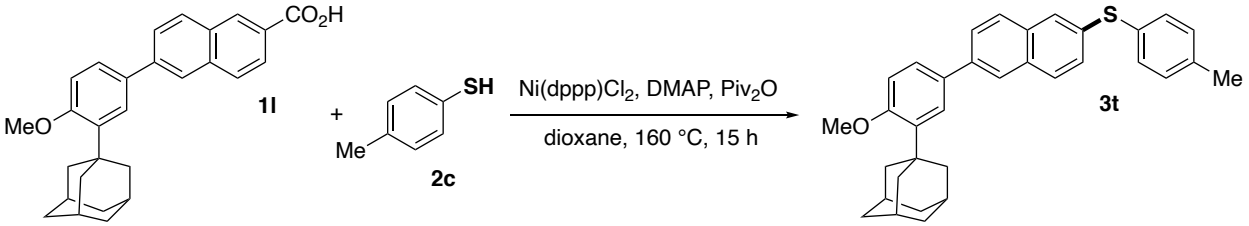
Benzoic acid and cyclohexanethiol (Scheme 2, 3s)[1]



1k **2k** **3s**

According to the general procedure, the reaction of benzoic acid (0.20 mmol), cyclohexanethiol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 62% yield (23.9 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.97 – 7.92 (m, 2H), 7.59 – 7.51 (m, 1H), 7.42 (t, J = 7.7 Hz, 2H), 3.72 (s, 1H), 2.01 (dt, J = 8.8, 3.8 Hz, 2H), 1.74 (dt, J = 9.2, 4.1 Hz, 2H), 1.63 – 1.43 (m, 6H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 137.55, 133.23, 128.62, 127.25, 42.63, 33.26, 26.12, 25.71.

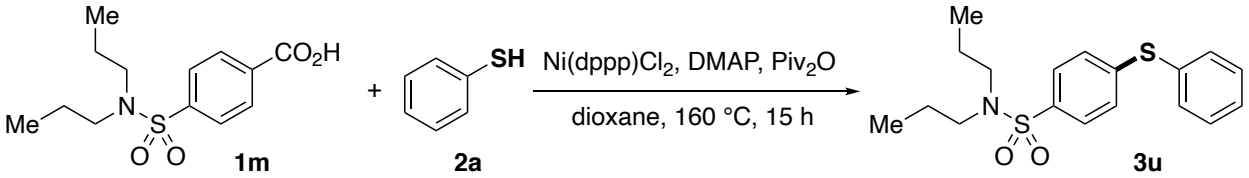
6-(3-((3r,5r,7r)-Adamantan-1-yl)-4-methoxyphenyl)-2-naphthoic acid and 4-methylbenzene thiol (Scheme 3, 3t)[1]



1l **2c** **3t**

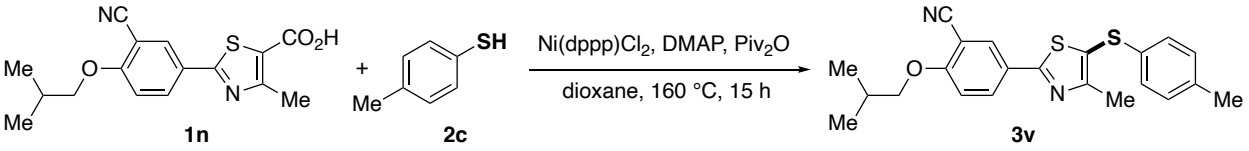
According to the general procedure, the reaction of 6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoic acid (0.20 mmol), 4-methylbenzenethiol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 66% yield (64.8 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.91 (s, 1H), 7.80 – 7.69 (m, 4H), 7.56 – 7.48 (m, 2H), 7.34 (dd, J = 16.4, 8.2 Hz, 3H), 7.14 (d, J = 7.9 Hz, 2H), 6.97 (d, J = 8.4 Hz, 1H), 3.88 (s, 3H), 2.35 (s, 3H), 2.17 (s, 6H), 1.79 (s, 6H), 1.56 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 158.71, 139.21, 138.98, 137.57, 133.72, 133.00, 132.63, 132.52, 131.96, 130.18, 128.95, 128.58, 128.51, 127.76, 126.46, 125.93, 125.64, 124.91, 112.15, 55.26, 40.67, 37.22, 29.81, 29.19, 21.25.

4-(*N,N*-Dipropylsulfamoyl)benzoic acid and thiophenol (Scheme 3, 3u)[1]



According to the general procedure, the reaction of 4-(*N,N*-dipropylsulfamoyl)benzoic acid (0.20 mmol), thiophenol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (68.5 mg). Yellow oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 7.60 – 7.54 (m, 2H), 7.50 – 7.38 (m, 2H), 7.34 (dd, J = 5.1, 1.9 Hz, 3H), 7.18 – 7.13 (m, 2H), 3.00 – 2.94 (m, 4H), 1.52 – 1.43 (m, 4H), 0.79 (t, J = 7.4 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 143.06, 136.13, 132.98, 130.66, 128.76, 127.98, 126.62, 126.54, 49.04, 21.04, 10.17.

2-(3-Cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylic acid and 4-methylbenzene thiol (Scheme 3, 3v)[1]



According to the general procedure, the reaction of 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylic acid (0.20 mmol), 4-methylbenzenethiol (0.40 mmol), Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 61% yield (48.2 mg). Colorless oil. **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.09 (d, J = 2.3 Hz, 1H), 8.00 (dd, J = 8.9, 2.3 Hz, 1H), 7.13 – 7.06 (m, 4H), 6.97 (d, J = 8.9 Hz, 1H), 3.87 (d, J = 6.5 Hz, 2H), 2.51 (s, 3H), 2.30 (s, 3H), 2.18 (dt, J = 13.3, 6.7 Hz, 1H), 1.07 (d, J = 6.7 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 166.97, 162.12, 159.35, 136.83, 133.34, 132.20, 131.71, 130.11, 128.04, 126.65, 122.04, 115.65, 112.62, 102.90, 75.71, 28.25, 21.09, 19.16, 15.81.

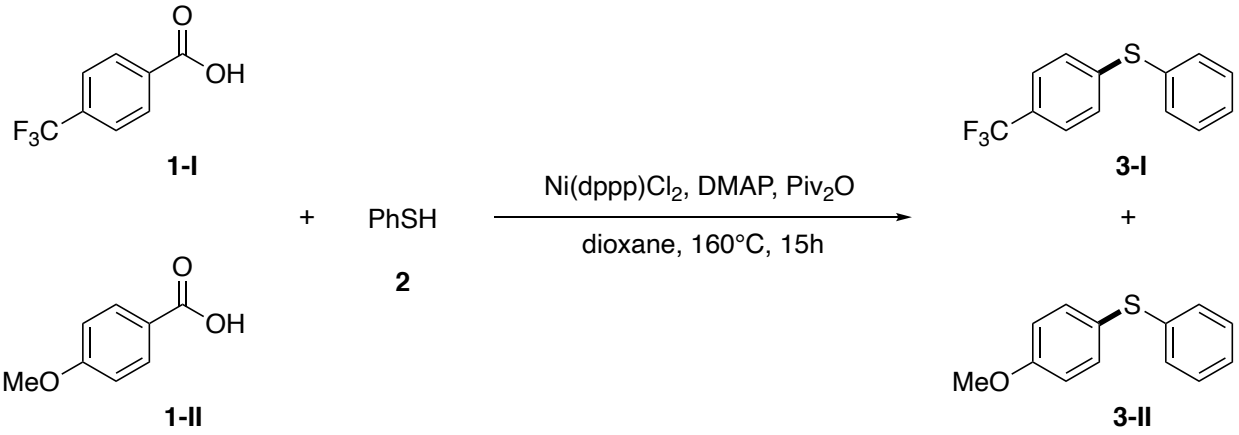
Selectivity Studies – Decarbonylative Thioetherification of Carboxylic Acids

General Procedure.

An oven-dried vial equipped with a stir bar was charged with two carboxylic acid substrates (each 0.2 mmol, 1.0 equiv), thiophenol (0.1 mmol, 0.5 equiv), Ni(dppp)Cl_2 (0.20 equiv), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. 1,4-Dioxane (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time at 160 °C.

Work-up: After the indicated time, the reaction mixture was cooled down to room temperature. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

Table SI-1. Selectivity Study in Decarbonylative Thioetherification of Carboxylic Acids.[a]



Entry	**1-I**	**1-II**	Acid (equiv)	**3-I**:**3-II**
1	4-CF_3	4-OMe	2.0	2.25:1

[a]Conditions: Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv), trimethylacetic anhydride (1.2 equiv), 1,4-dioxane (0.20 M), 160 °C. All reactions carried out using standard Schlenk techniques under argon. [b]Determined by ^{1}H NMR and/or GC-MS.

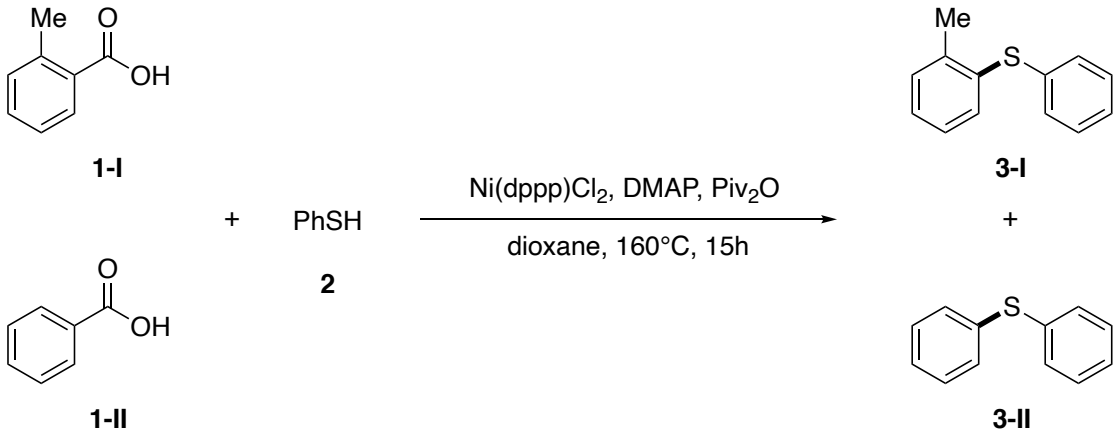
Selectivity Studies – Decarbonylative Thioetherification of Carboxylic Acids

General Procedure.

An oven-dried vial equipped with a stir bar was charged with two carboxylic acid substrates (each 0.2 mmol, 1.0 equiv), thiophenol (0.1 mmol, 0.5 equiv), Ni(dppp)Cl_2 (0.20 equiv), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. 1,4-Dioxane (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time at 160 °C.

Work-up: After the indicated time, the reaction mixture was cooled down to room temperature. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

Table SI-2. Selectivity Study in Decarbonylative Thioetherification of Carboxylic Acids.[a]



Entry	**1-I**	**1-II**	Acid (equiv)	**3-I**:**3-II**
1	2-Me	H	2.0	1.17:1

[a]Conditions: Ni(dppp)Cl_2 (20 mol%), 4-dimethylaminopyridine (1.2 equiv), trimethylacetic anhydride (1.2 equiv), 1,4-dioxane (0.20 M), 160 °C. All reactions carried out using standard Schlenk techniques under argon. [b]Determined by ^{1}H NMR and/or GC-MS.

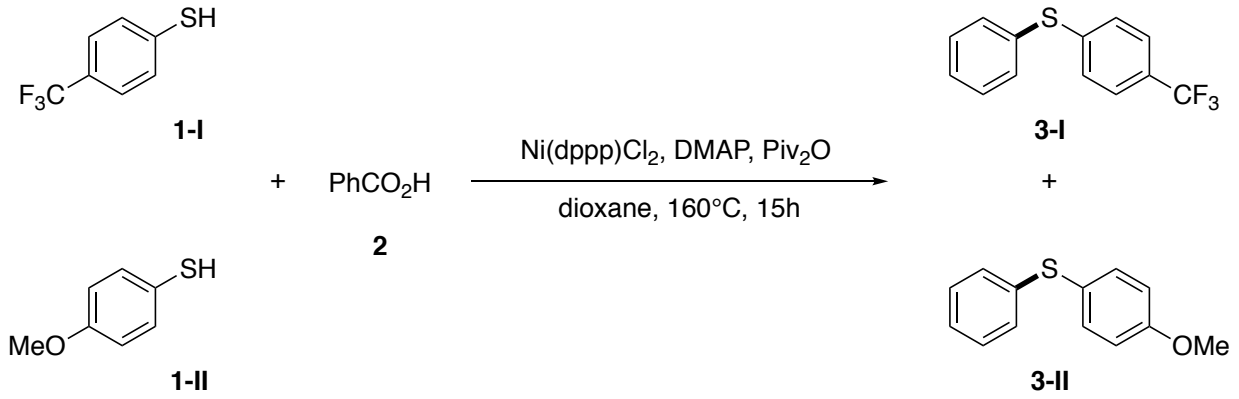
Selectivity Studies – Decarbonylative Thioetherification of Carboxylic Acids

General Procedure.

An oven-dried vial equipped with a stir bar was charged with two thiol substrates (each 0.2 mmol, 1.0 equiv), benzoic acid (0.1 mmol, 0.5 equiv), $Ni(dppp)Cl_2$ (0.20 equiv), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. 1,4-Dioxane (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time at 160 °C.

Work-up: After the indicated time, the reaction mixture was cooled down to room temperature. The sample was analyzed by ^1H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

Table SI-3. Selectivity Study in Decarbonylative Thioetherification of Carboxylic Acids.[a]



Entry	**1-I**	**1-II**	Thiol (equiv)	**3-I**:**3-II**
1	4-CF_3	4-OMe	2.0	2.05:1

[a]Conditions: $Ni(dppp)Cl_2$ (20 mol%), 4-dimethylaminopyridine (1.2 equiv), trimethylacetic anhydride (1.2 equiv), 1,4-dioxane (0.20 M), 160 °C. All reactions carried out using standard Schlenk techniques under argon. [b]Determined by ^1H NMR and/or GC-MS.

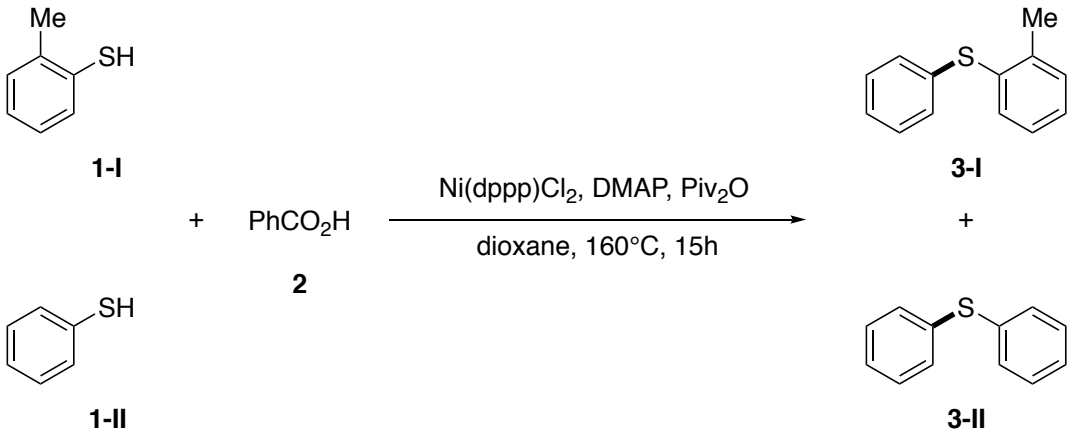
Selectivity Studies – Decarbonylative Thioetherification of Carboxylic Acids

General Procedure.

An oven-dried vial equipped with a stir bar was charged with two thiol substrates (each 0.2 mmol, 1.0 equiv), benzoic acid (0.1 mmol, 0.5 equiv), $Ni(dppp)Cl_2$ (0.20 equiv), 4-dimethylaminopyridine (1.2 equiv) and trimethylacetic anhydride (1.2 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. 1,4-Dioxane (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time at 160 °C.

Work-up: After the indicated time, the reaction mixture was cooled down to room temperature. The sample was analyzed by ^1H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

Table SI-4. Selectivity Study in Decarbonylative Thioetherification of Carboxylic Acids.[a]



Entry	**1-I**	**1-II**	Thiol (equiv)	**3-I**:**3-II**
1	2-Me	H	2.0	1:1.27

[a]Conditions: $Ni(dppp)Cl_2$ (20 mol%), 4-dimethylaminopyridine (1.2 equiv), trimethylacetic anhydride (1.2 equiv), 1,4-dioxane (0.20 M), 160 °C. All reactions carried out using standard Schlenk techniques under argon. [b]Determined by ^1H NMR and/or GC-MS.

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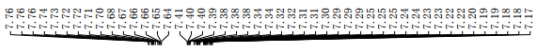
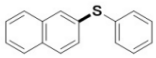
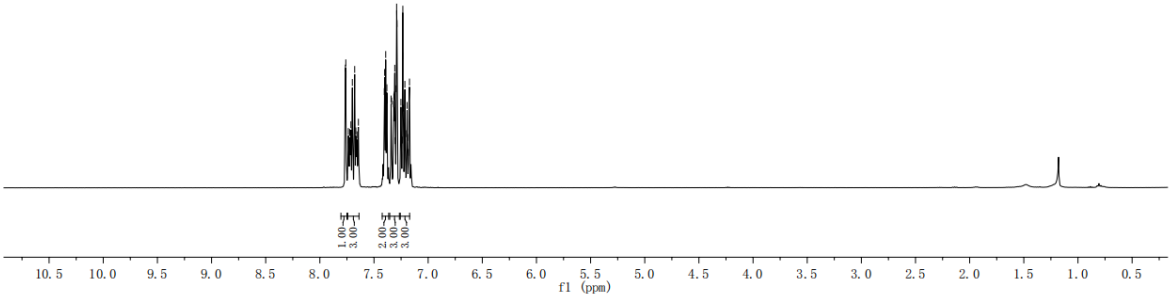
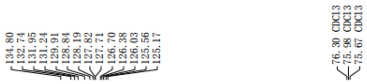
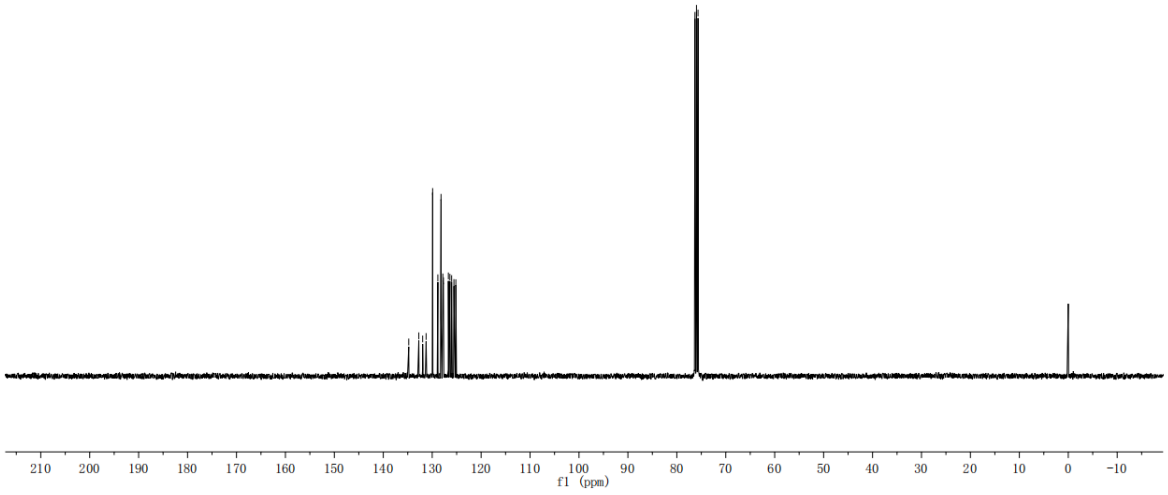


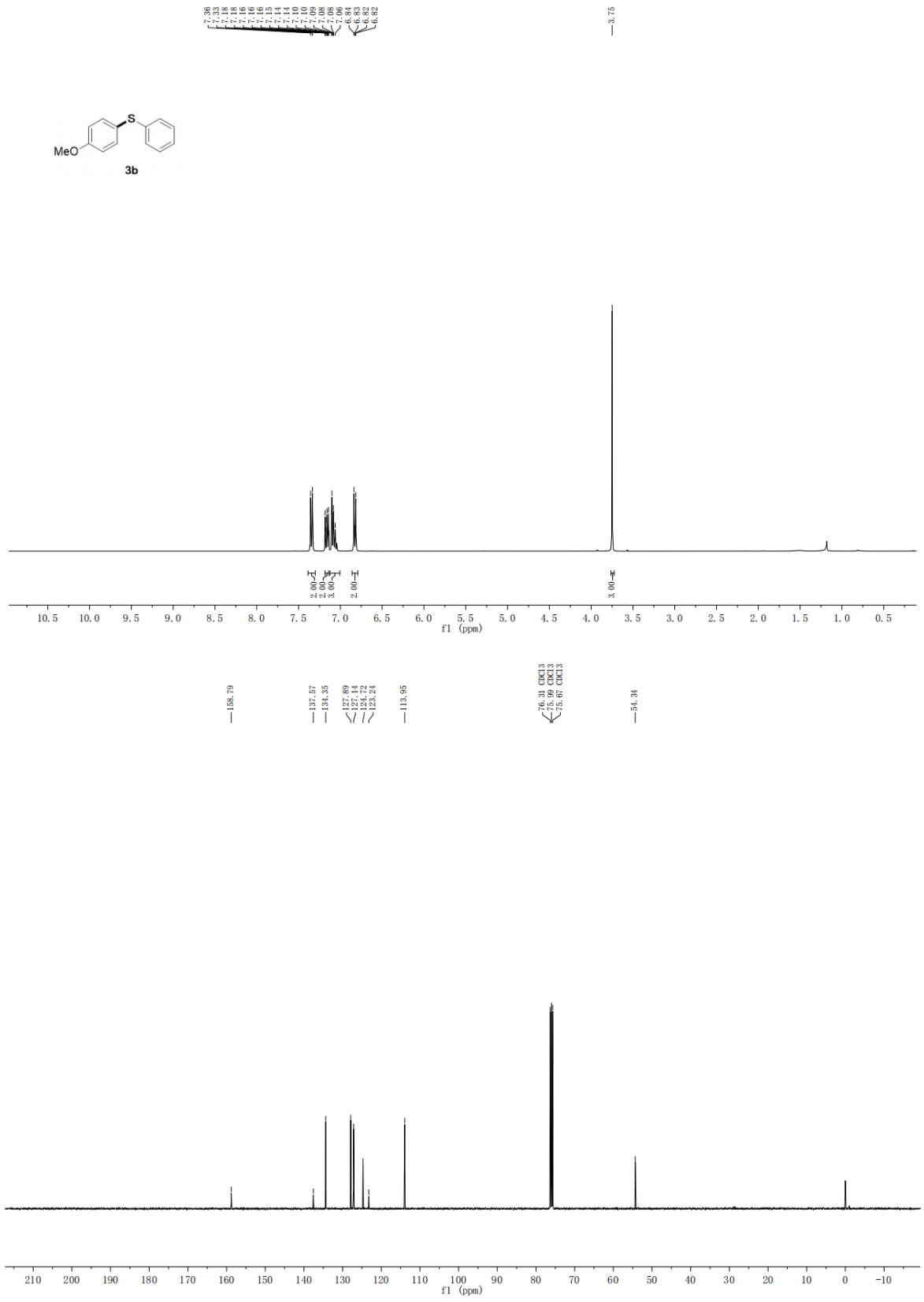


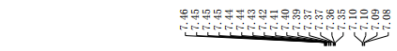
3a








7.36
7.33
7.18
7.18
7.16
7.16
7.16
7.15
7.14
7.10
7.10
7.09
7.08
7.08
7.06
6.84
6.83
6.82
6.82
3.75
MeO
S
3b
2.00
2.00
3.00
2.00
3.00
f1 (ppm)
158.79
137.57
134.35
127.89
127.14
124.72
123.24
113.95
76.31 CDCl3
75.99 CDCl3
75.67 CDCl3
54.34
f1 (ppm)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7.45
7.45
7.45
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7.44
7.43
7.42
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7.40
7.39
7.37
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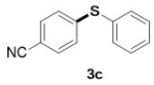
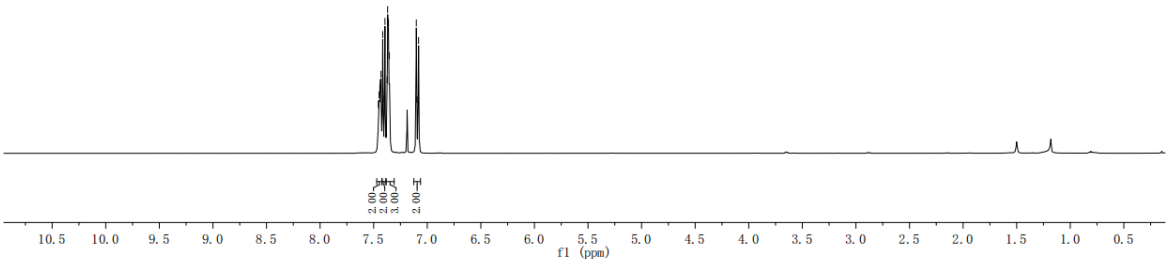
7.36
7.35
7.10
7.09
7.08


S
NC

3c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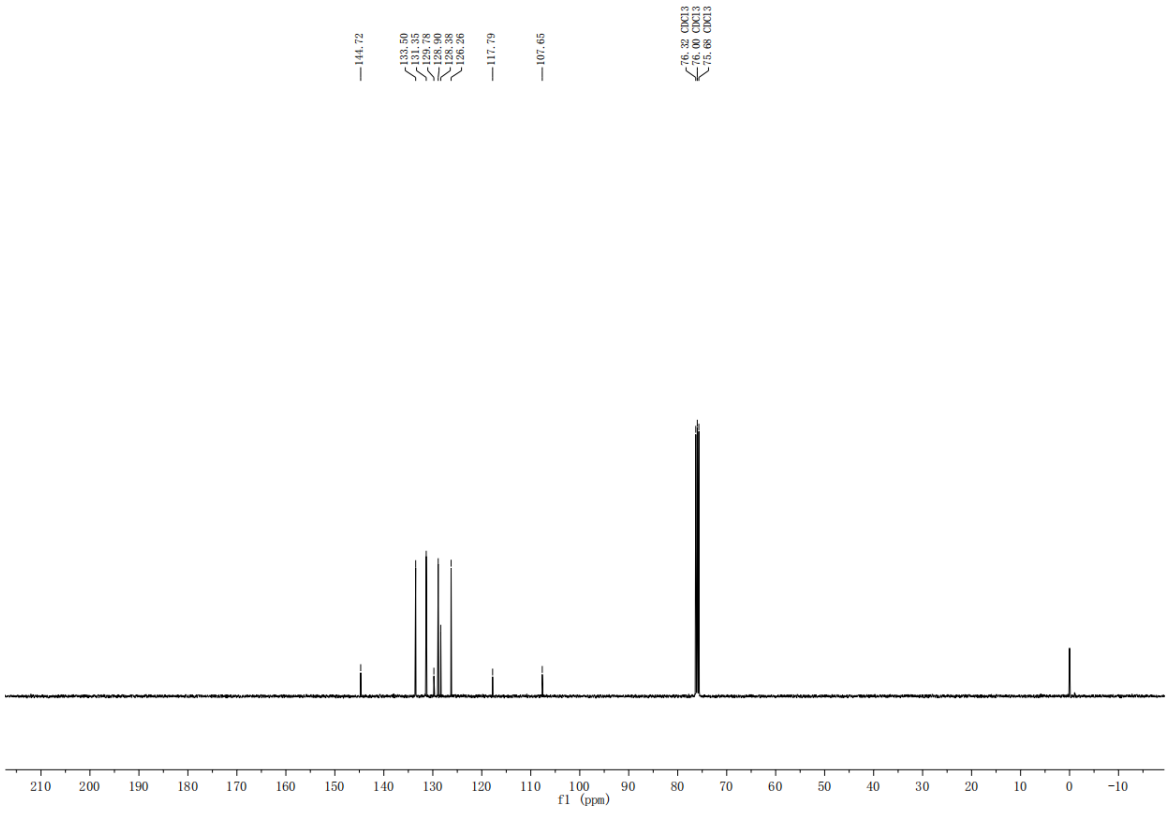
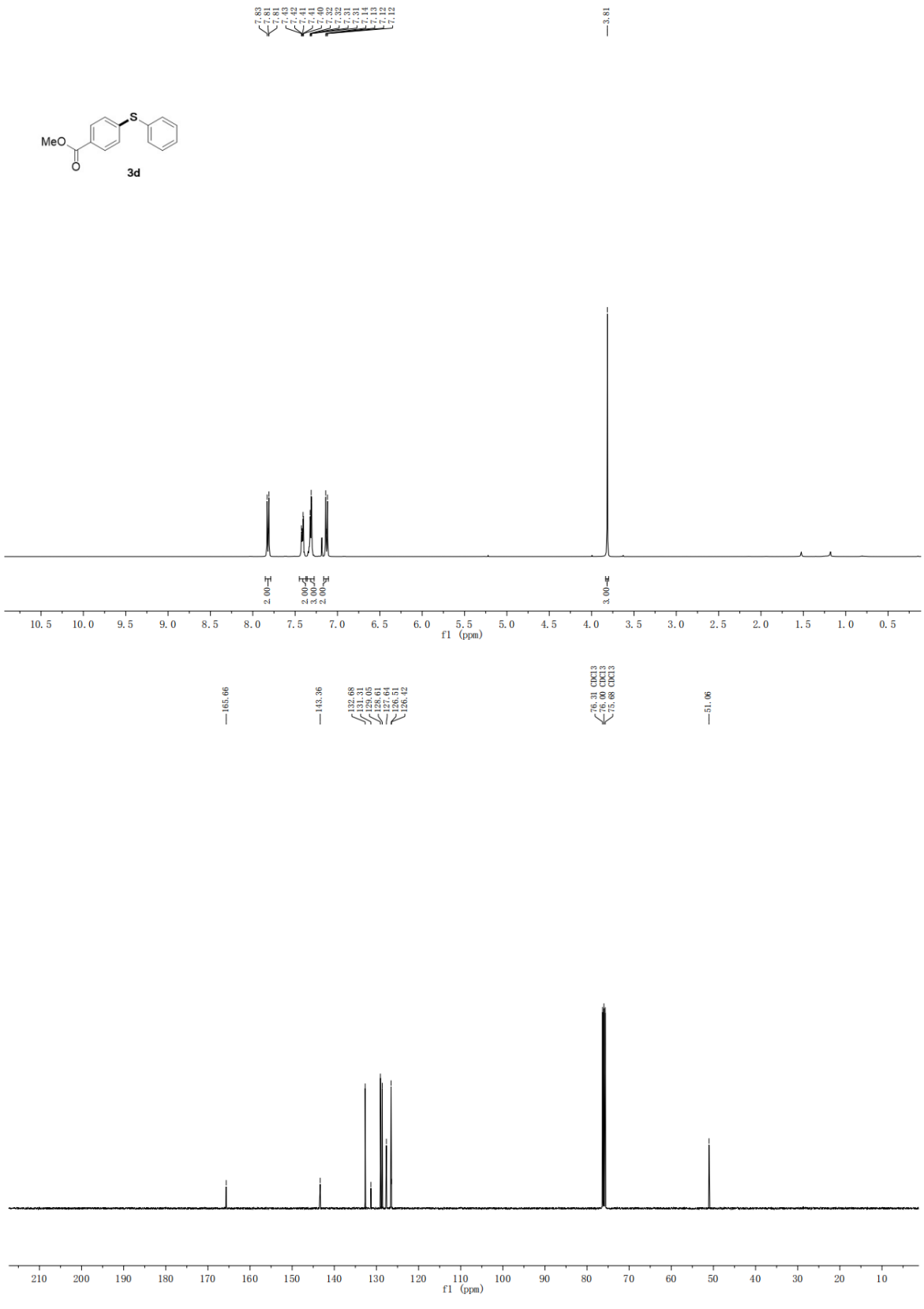
2.03
2.00
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


144.72
133.50
131.35
129.78
128.86
128.38
126.26
117.79
107.65
76.32 CDCl3
76.00 CDCl3
75.68 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.81
7.81
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7.41
7.40
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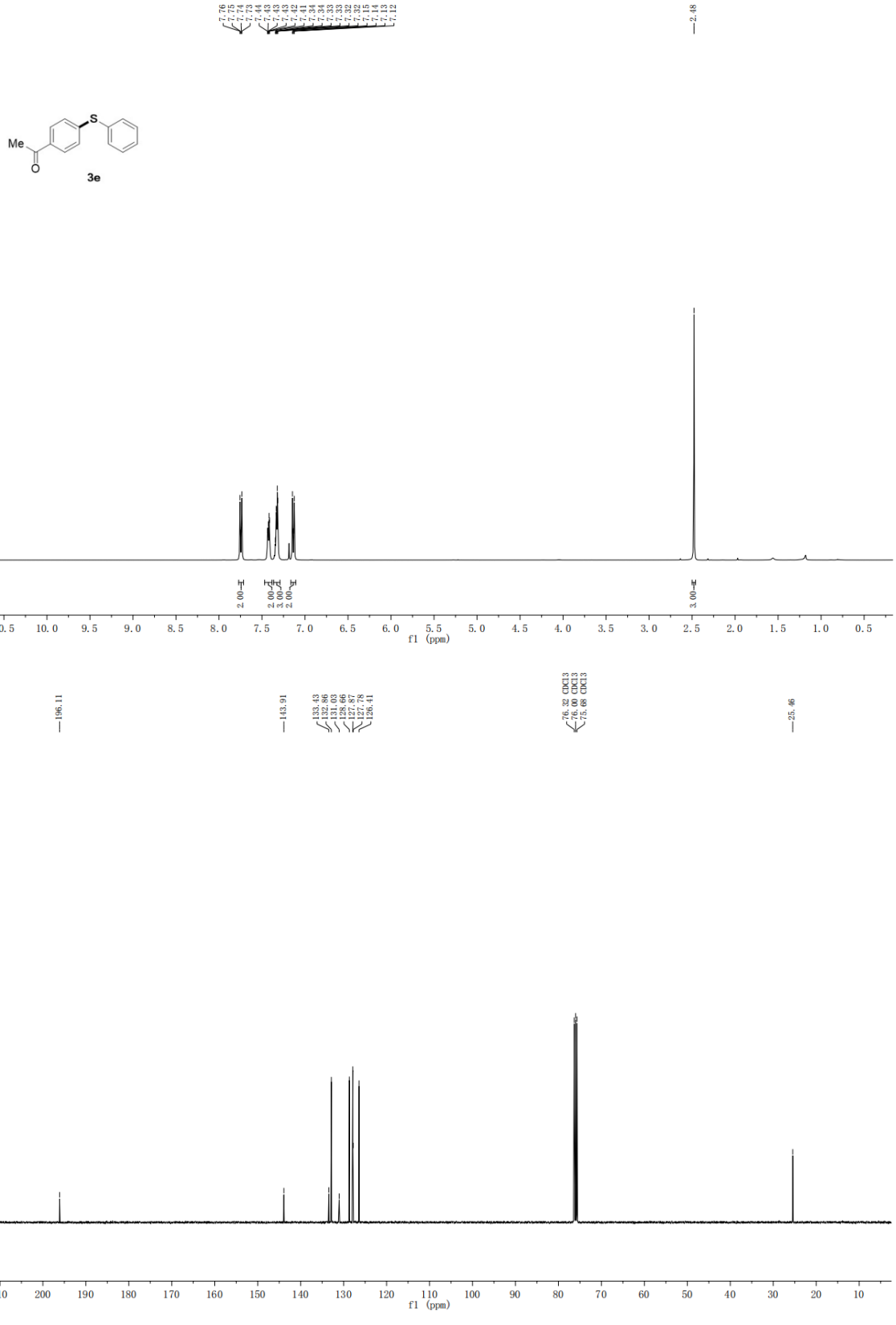
7.32
7.31
7.31
7.14
7.13
7.12
7.12
3.81
MeO
S
O
3d
2.00
2.00
2.00
2.00
3.00
f1 (ppm)
165.66
143.36
132.68
131.31
129.05
128.61
127.64
126.51
126.42
76.31 CDCl3
76.00 CDCl3
75.68 CDCl3
51.06
f1 (ppm)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7.75
7.74
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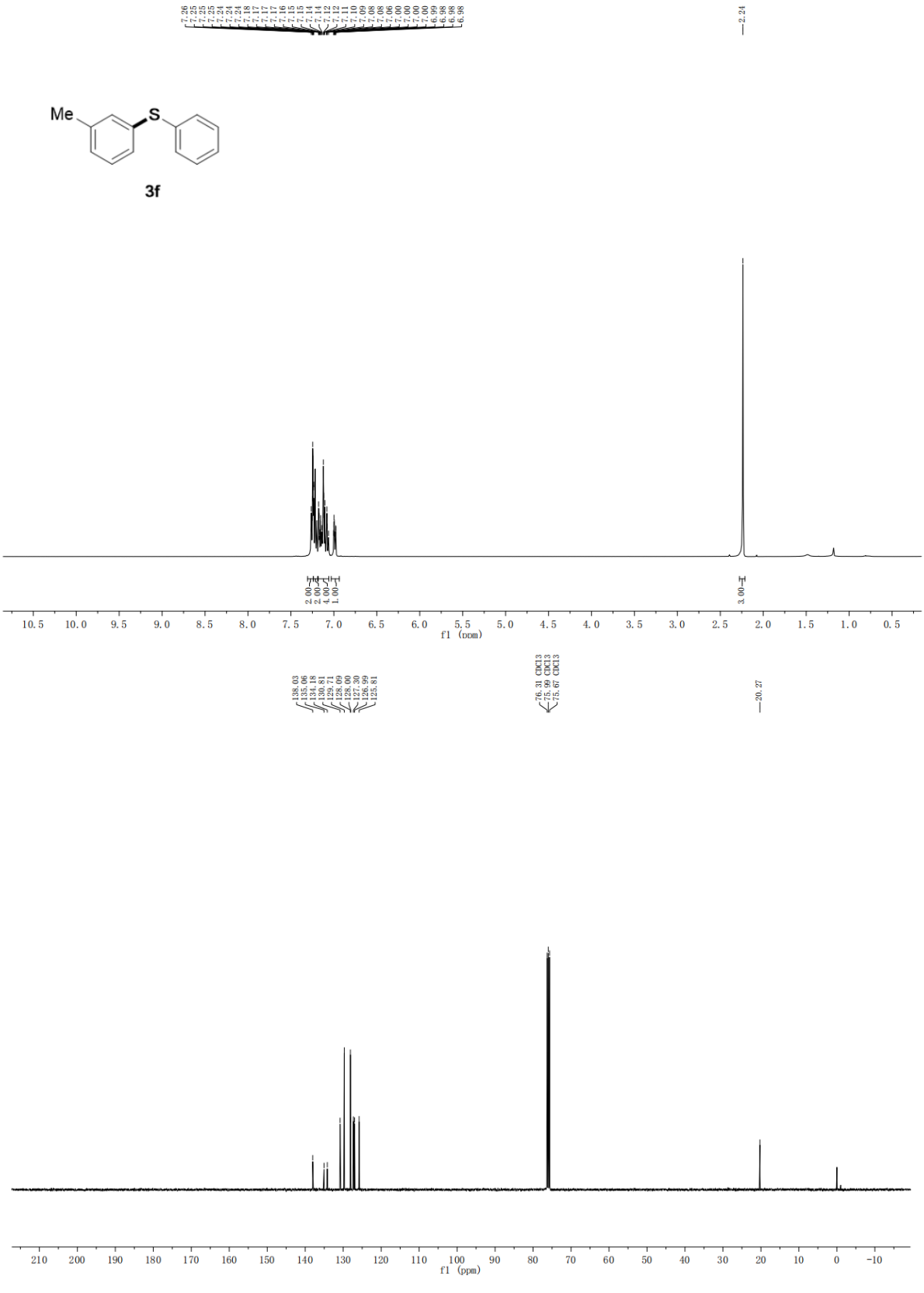
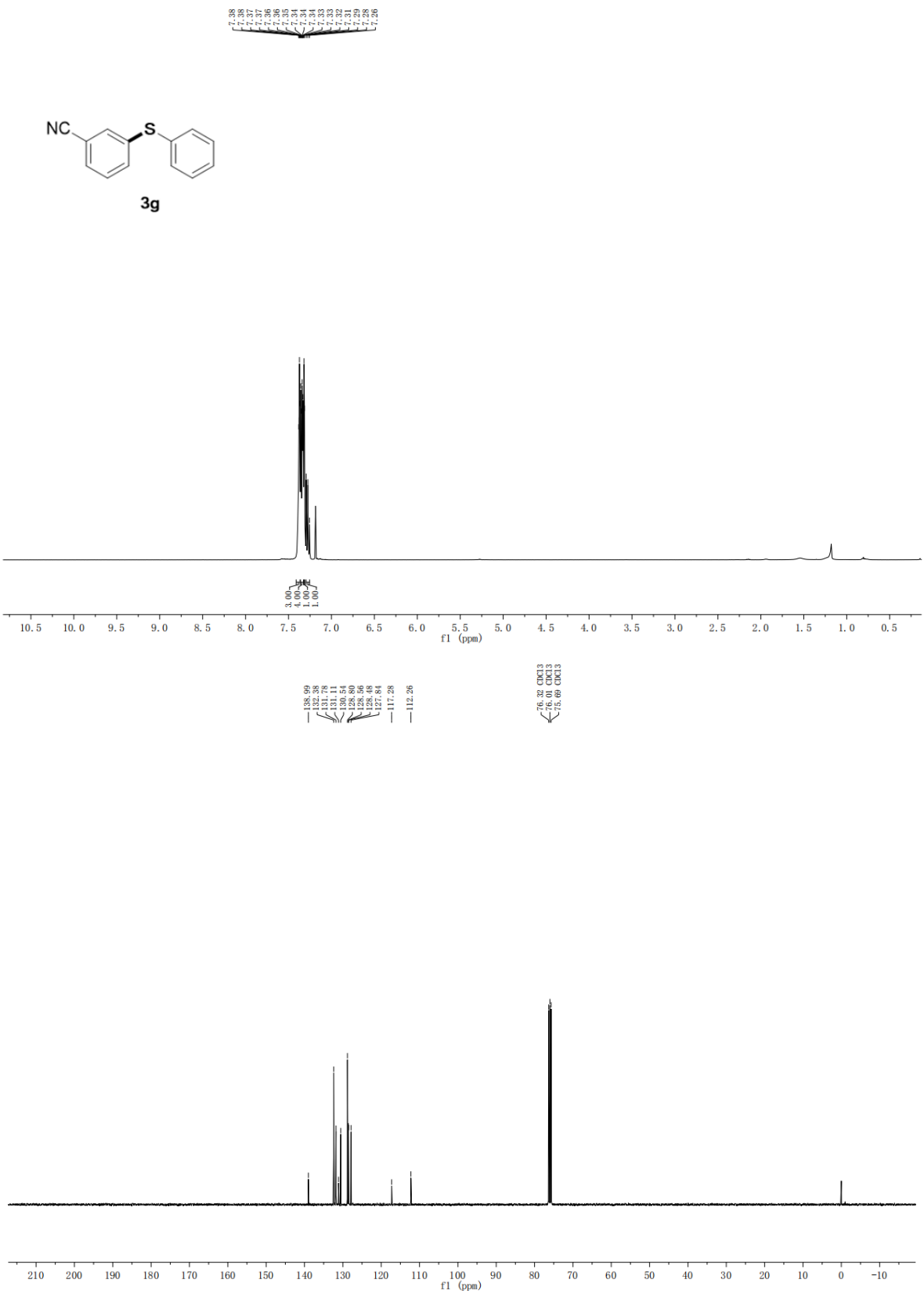
7.44
7.43
7.43
7.43
7.42
7.41
7.34
7.34
7.33
7.33
7.32
7.32
7.15
7.14
7.13
7.12
2.48
Me
O
S
3e
2.00
2.00
3.00
2.00
3.00
f1 (ppm)
196.11
143.91
133.43
132.86
131.03
128.66
127.87
127.78
126.41
76.32 CDCl3
76.00 CDCl3
75.68 CDCl3
25.46
f1 (ppm)


Me
S
3f
f1 (ppm)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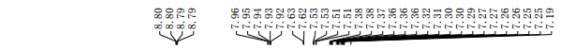
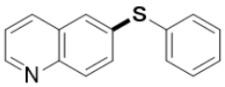
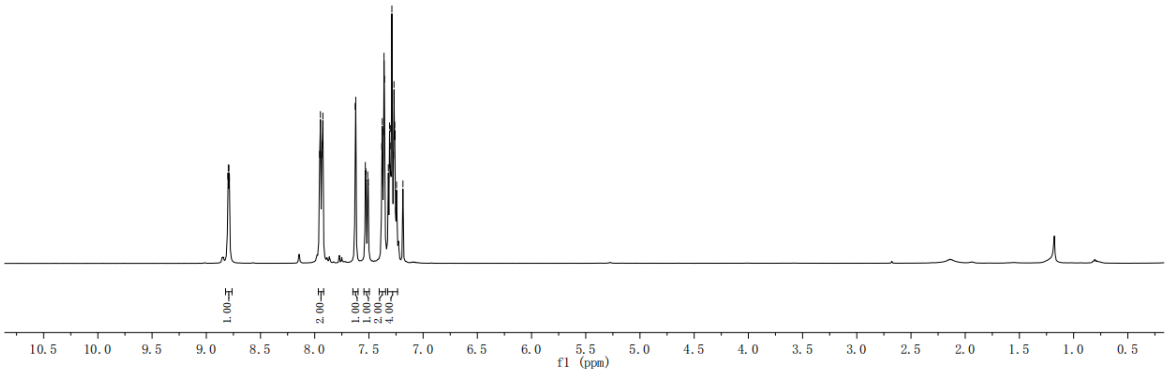
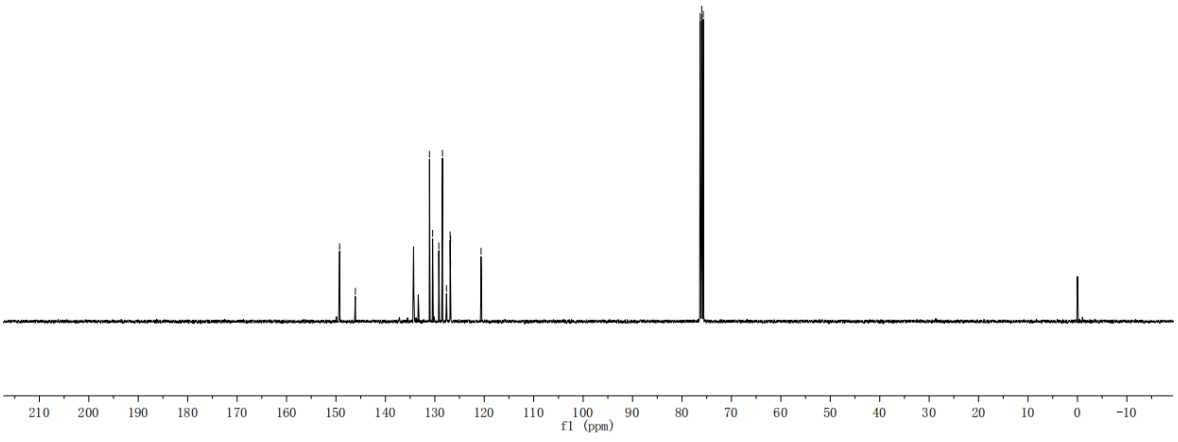
7.36
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.31
7.29
7.28
7.26
NC
S
3g
3.00
4.00
1.00
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
138.99
132.38
131.78
131.11
130.54
128.80
128.56
128.44
127.84
117.28
112.26
76.32 CDCl3
76.01 CDCl3
75.69 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)





3h






7.31
7.31
7.30
7.30
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7.19
7.18
7.18
7.17
7.17
7.15
7.14
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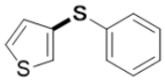
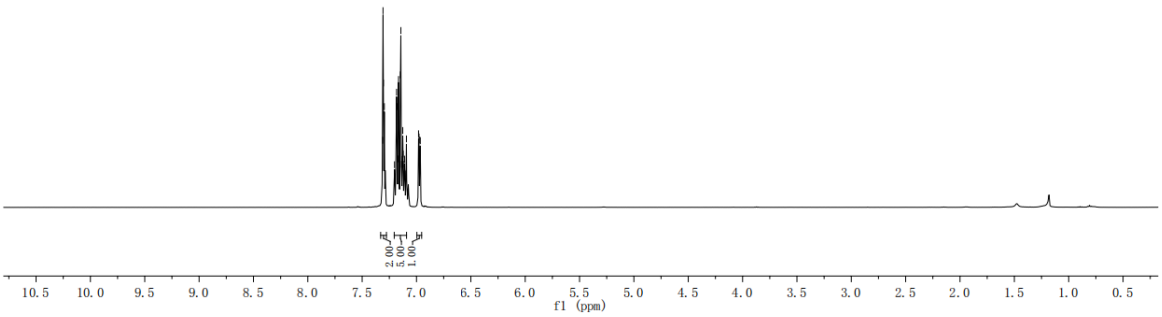
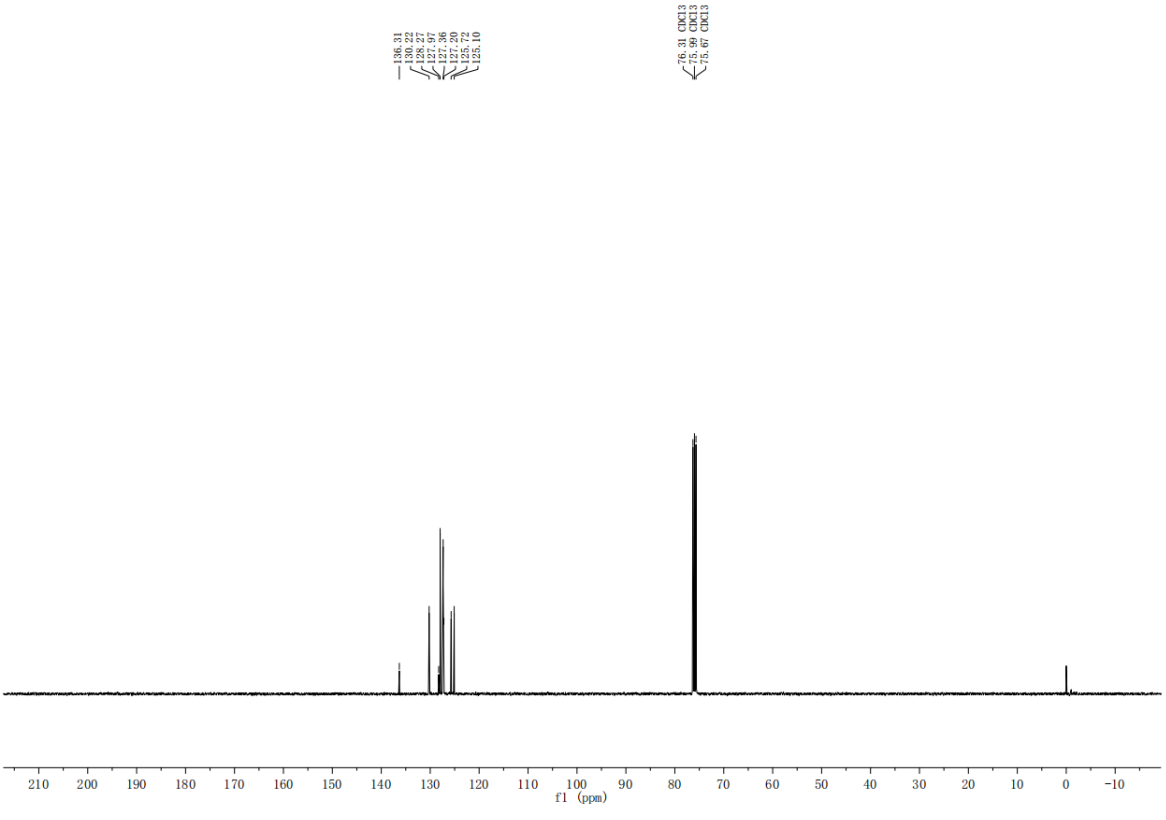
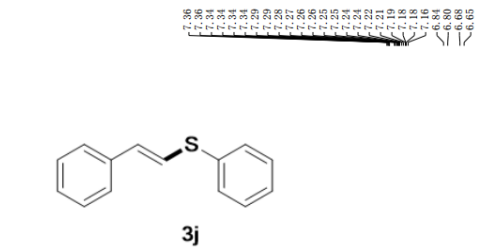
7.10
7.09
6.98
6.98
6.97
6.97


S
S

3i


2.00
5.00
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


136.31
130.22
128.27
127.97
127.36
127.20
125.72
125.10
76.31 CDCl3
75.99 CDCl3
75.67 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.25
7.24
7.24
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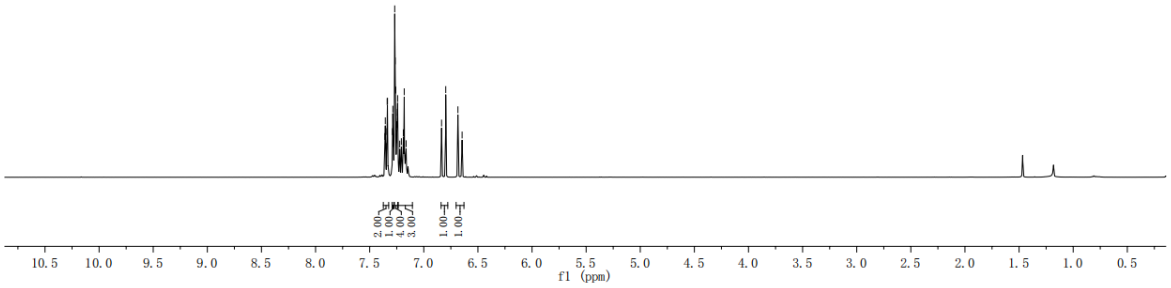
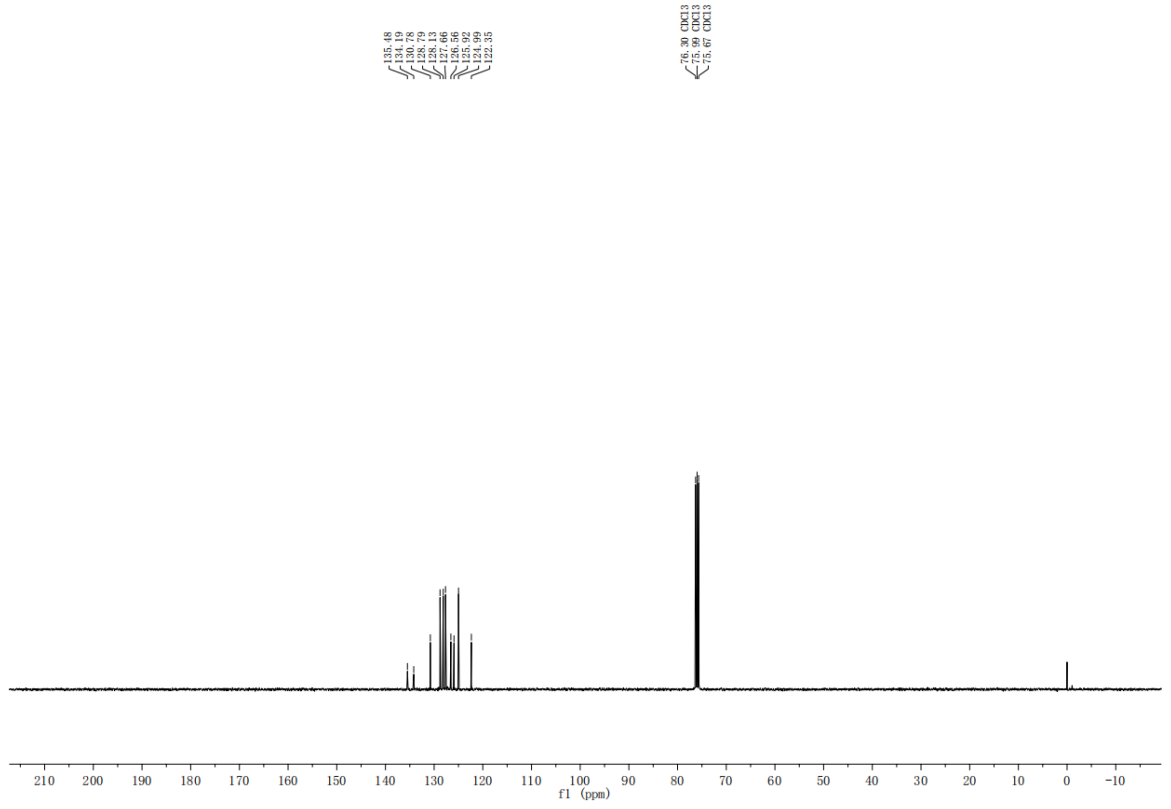
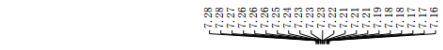
6.84
6.80
6.68
6.65
S
3j


2.00
1.00
4.00
3.00
1.00
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


135.48
134.19
130.78
128.79
128.13
127.66
126.66
125.92
124.99
122.35
76.30 CDCl3
75.99 CDCl3
75.67 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.19
7.18
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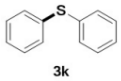
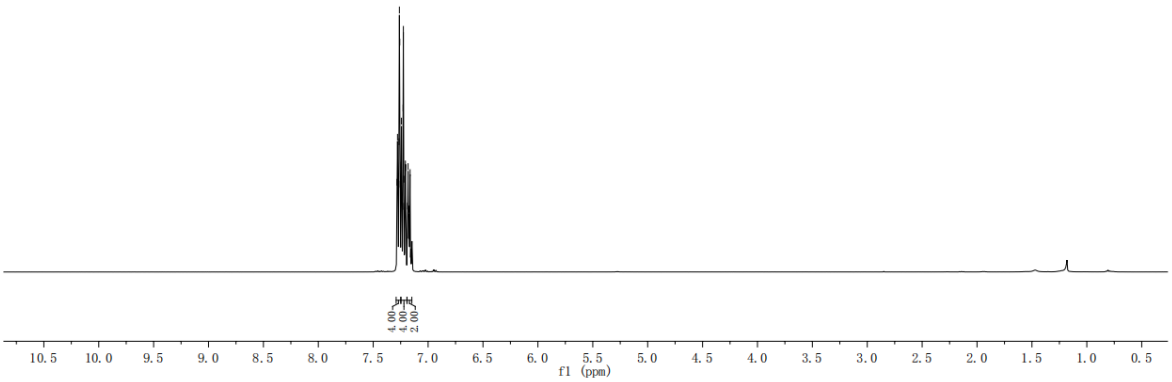
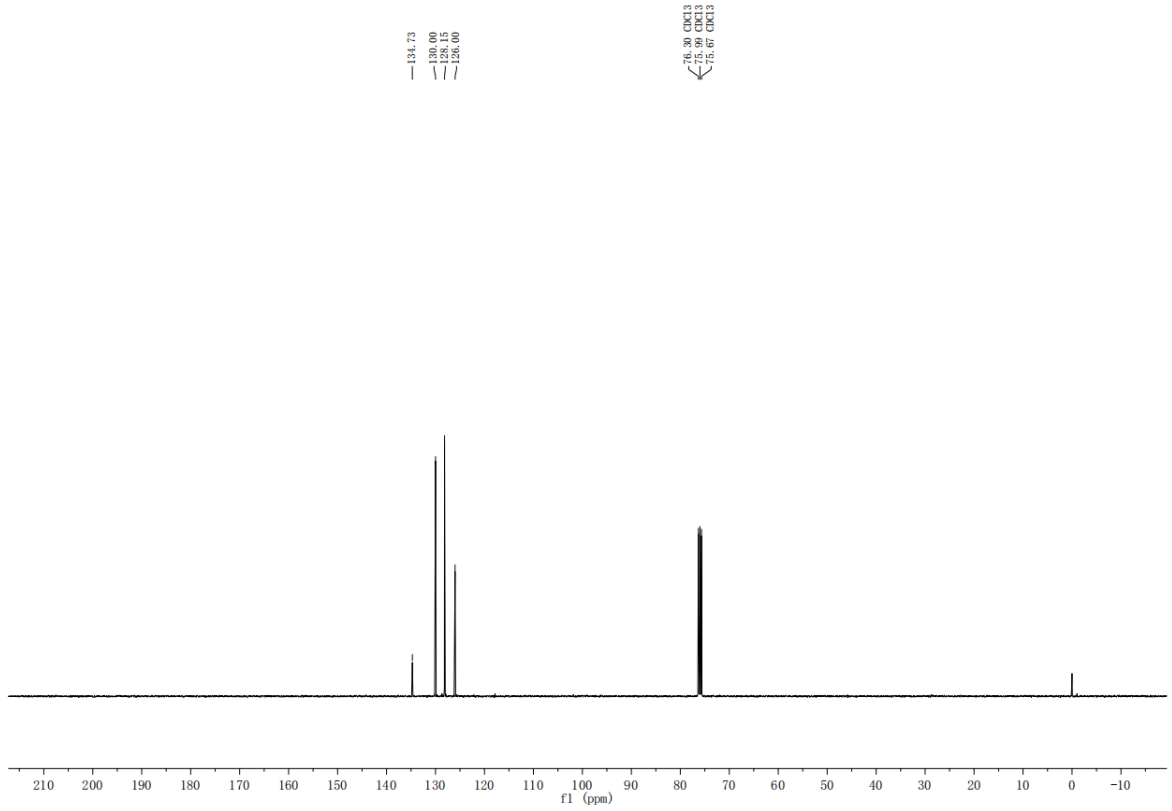
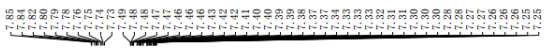
7.17
7.17
7.16

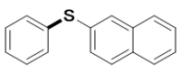

S

3k

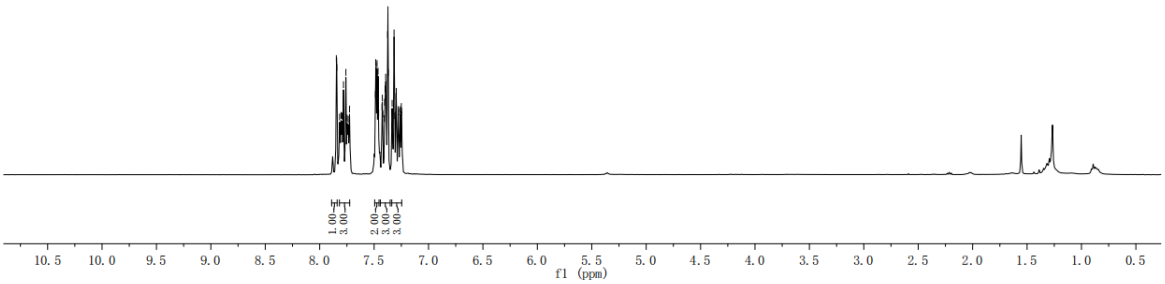

4.00
4.00
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

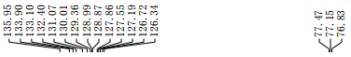

134.73
130.00
128.15
126.00
76.30 CDCl3
75.99 CDCl3
75.67 CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

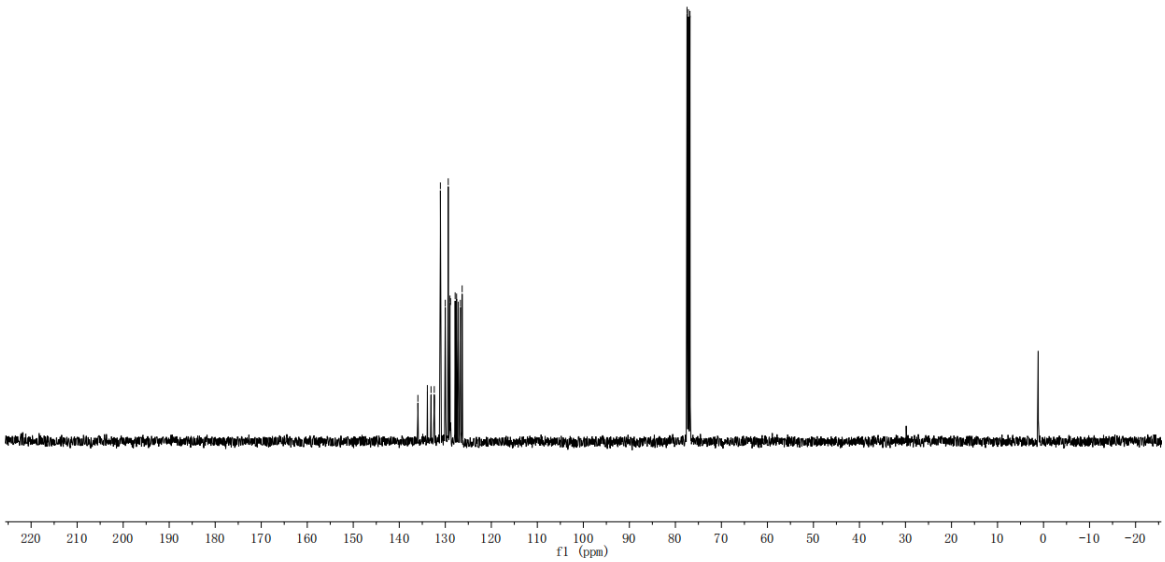


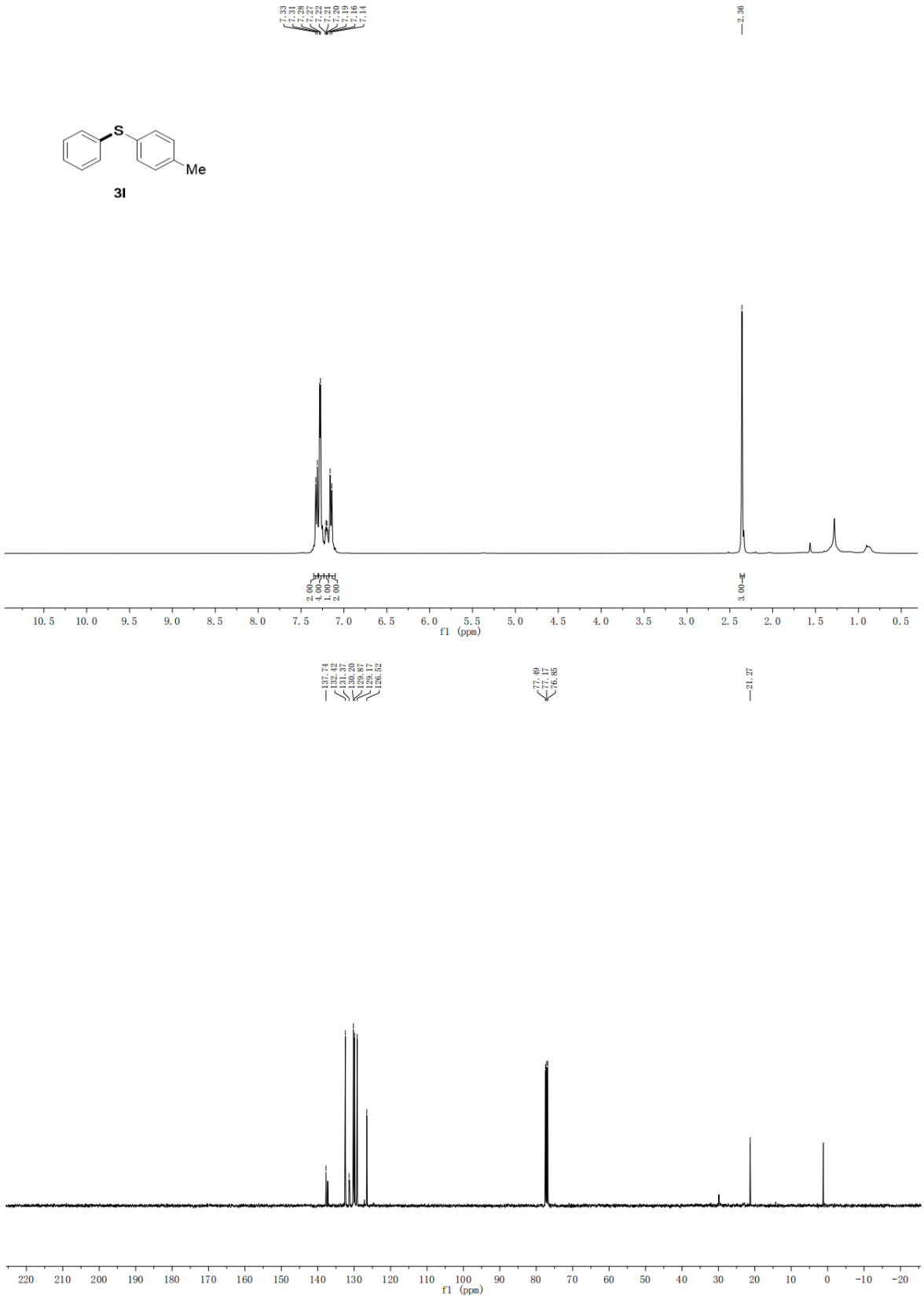


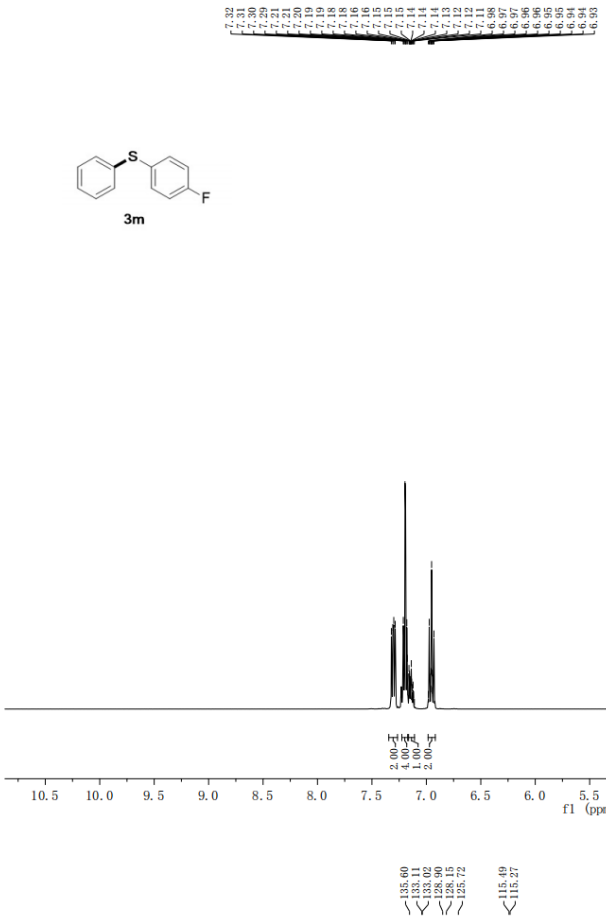
3a'








7.33
7.31
7.28
7.27
7.22
7.21
7.20
7.19
7.16
7.14
2.36
S
Me
3l
2.00
4.00
1.00
2.00
3.00
f1 (ppm)
137.74
132.42
131.37
130.20
129.87
129.17
126.52
77.49
77.17
76.85
21.27
f1 (ppm)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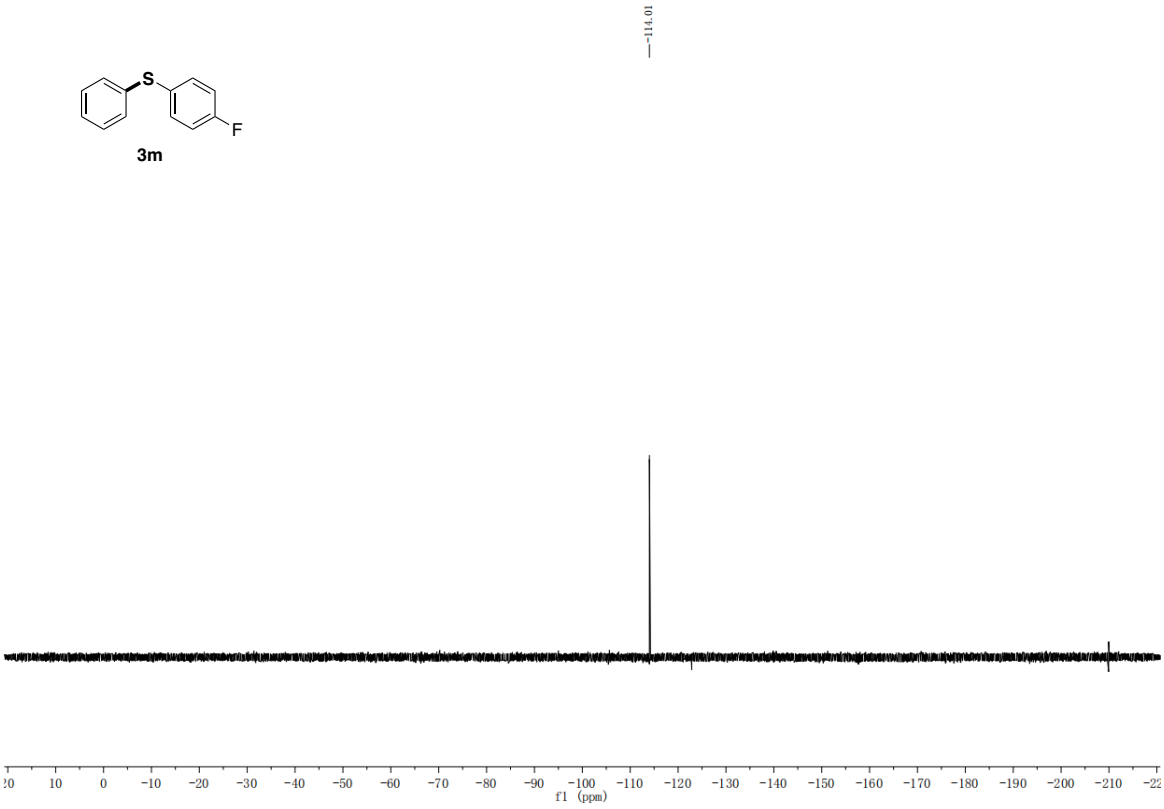
7.15
7.15
7.14
7.14
7.13
7.12
7.12
7.11
6.98
6.97
6.97
6.96
6.96
6.95
6.95
6.94
6.94
6.93
S
F
3m
2.00
4.00
1.00
2.00
f1 (ppm)
135.60
133.11
133.02
128.90
128.15
125.72
115.49
115.27
76.31 CDCl3
75.99 CDCl3
75.67 CDCl3
f1 (ppm)


S
F
3m
-114.01
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
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-120
-130
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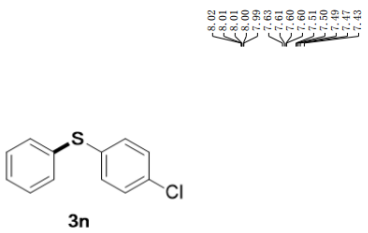
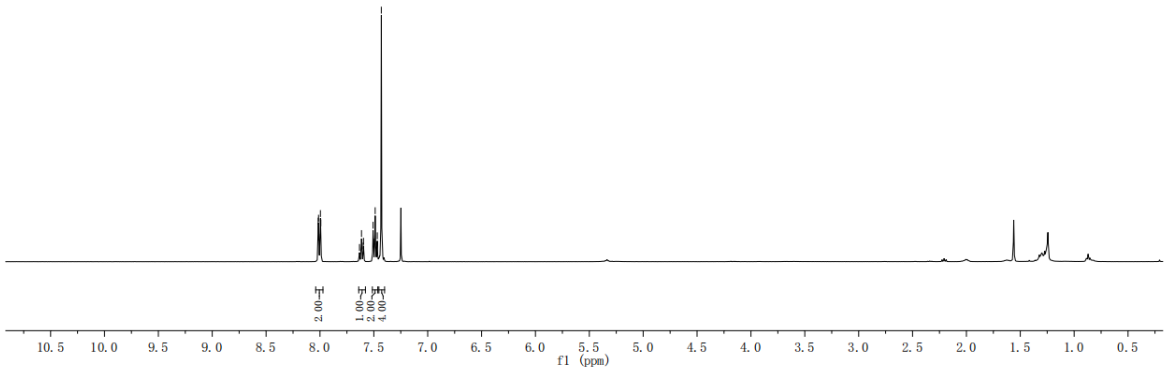
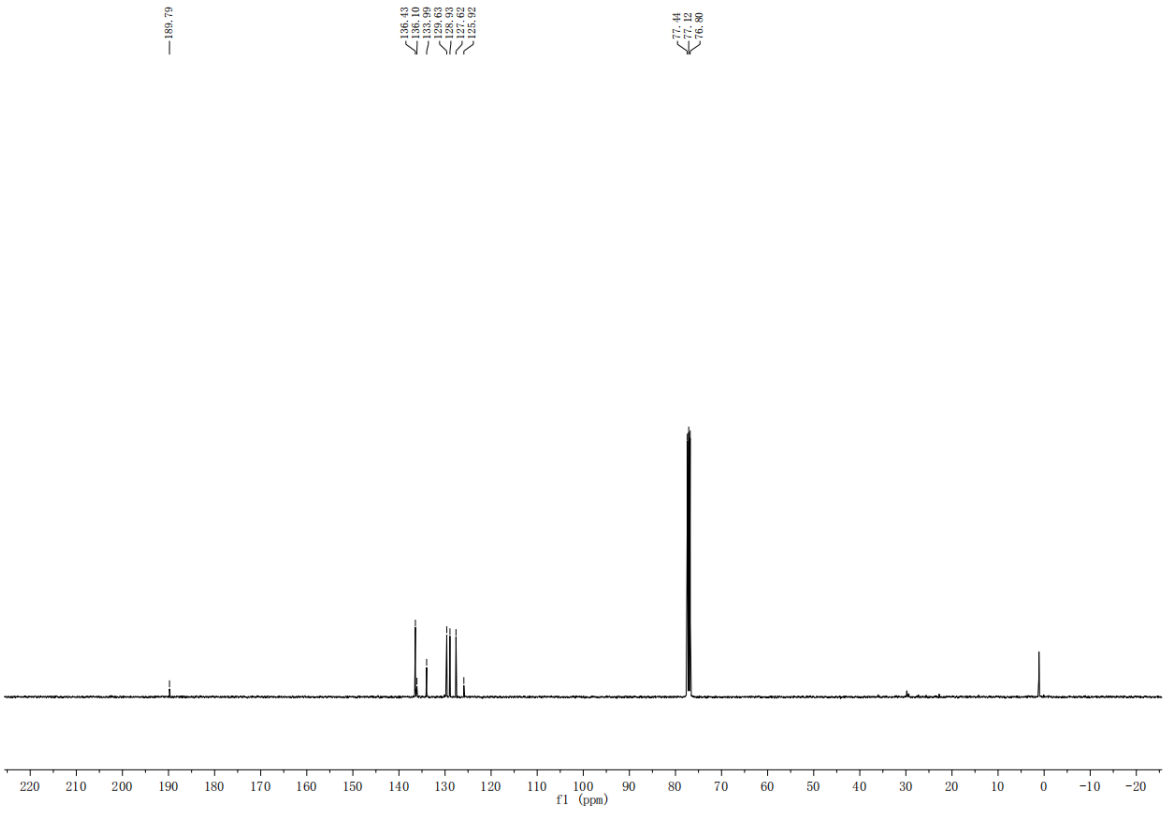
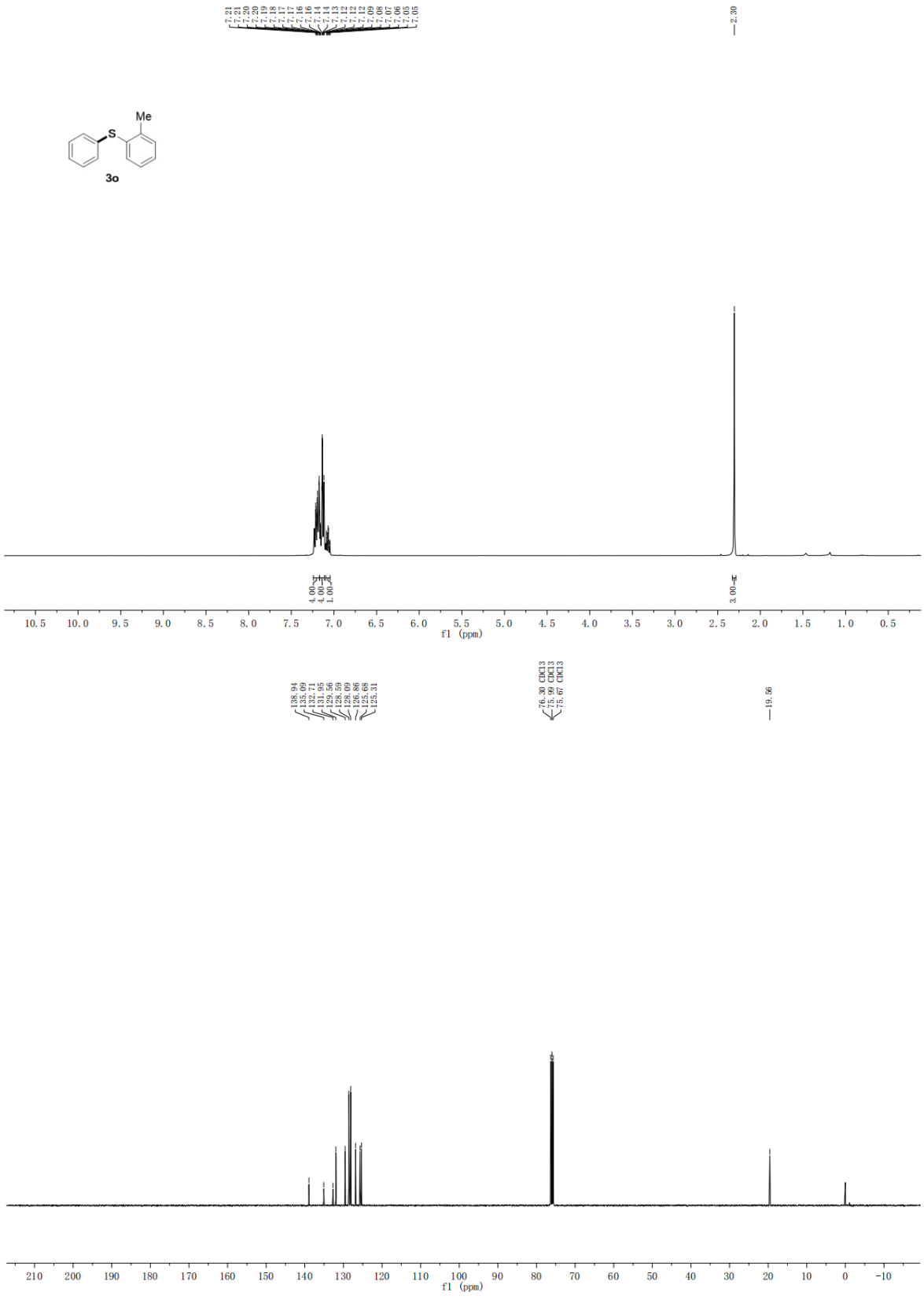
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.02
8.01
8.01
8.00
7.99
7.63
7.61
7.60
7.60
7.51
7.50
7.49
7.47
7.43
S
Cl

3n


2.00
1.00
2.09
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


189.79
136.43
136.10
133.99
129.63
129.53
127.62
125.92
77.44
77.12
76.80
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.20
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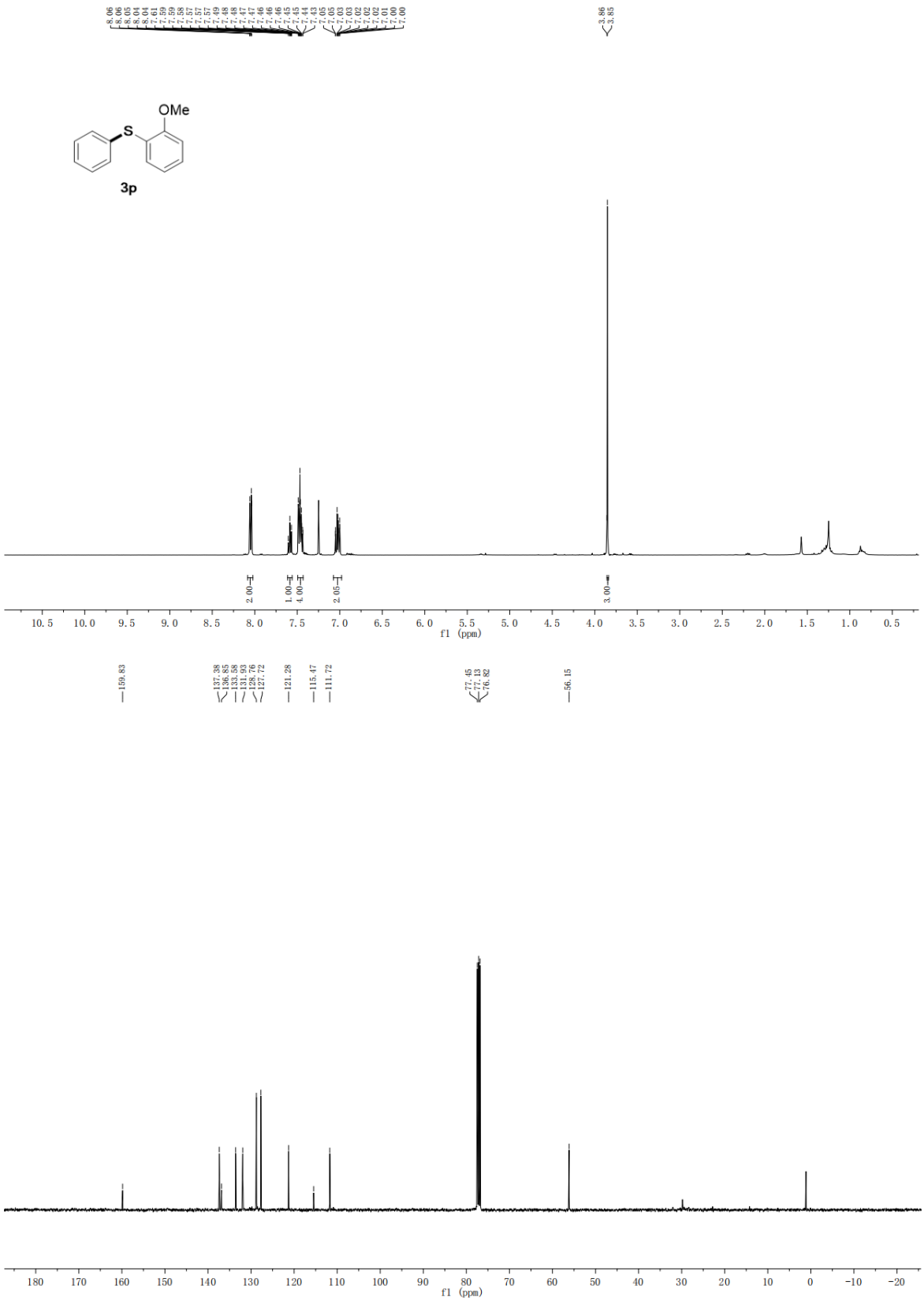
7.14
7.13
7.12
7.12
7.12
7.09
7.08
7.07
7.06
7.05
7.05
2.30
Me
S
3o
4.00
4.00
1.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
138.94
135.09
132.71
131.95
129.56
128.59
128.09
126.86
125.68
125.31
76.30 CDCl3
75.99 CDCl3
75.67 CDCl3
19.96
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.04
8.04
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7.46
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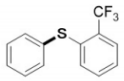
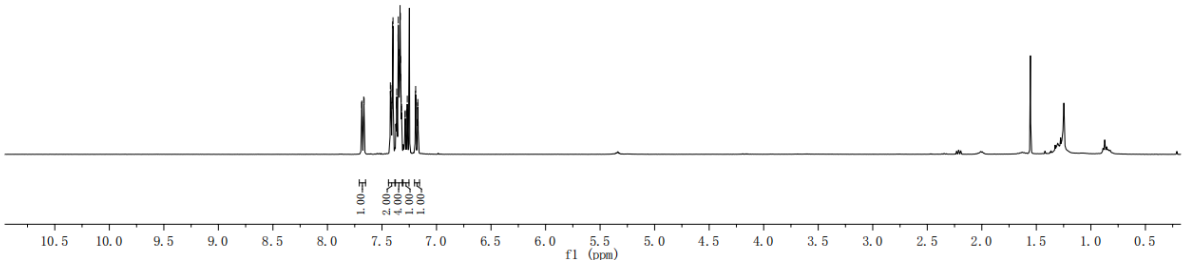
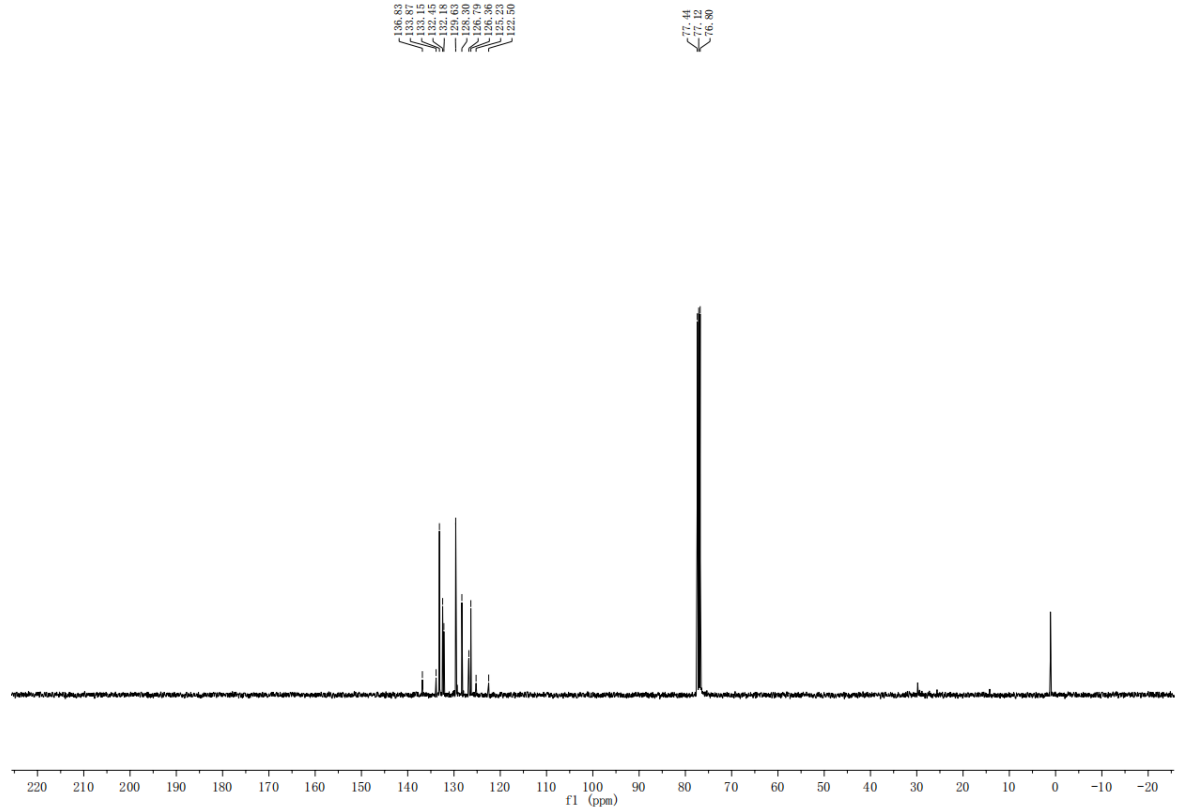
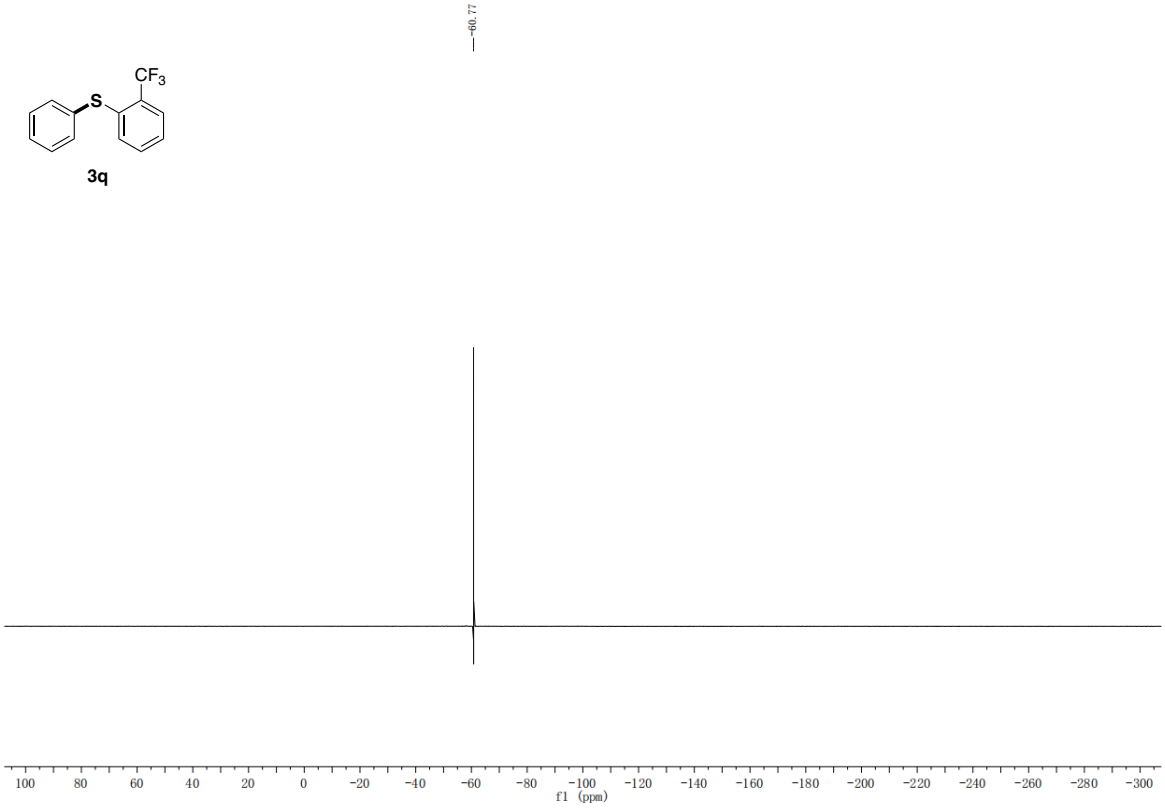
7.45
7.44
7.43
7.05
7.03
7.03
7.02
7.02
7.02
7.01
7.00
7.00
3.86
3.85
OMe
S
3p
2.00
1.00
4.00
2.05
3.00
f1 (ppm)
159.83
137.38
136.85
133.58
131.93
128.76
127.72
121.28
115.47
111.72
77.45
77.13
76.82
56.15
f1 (ppm)

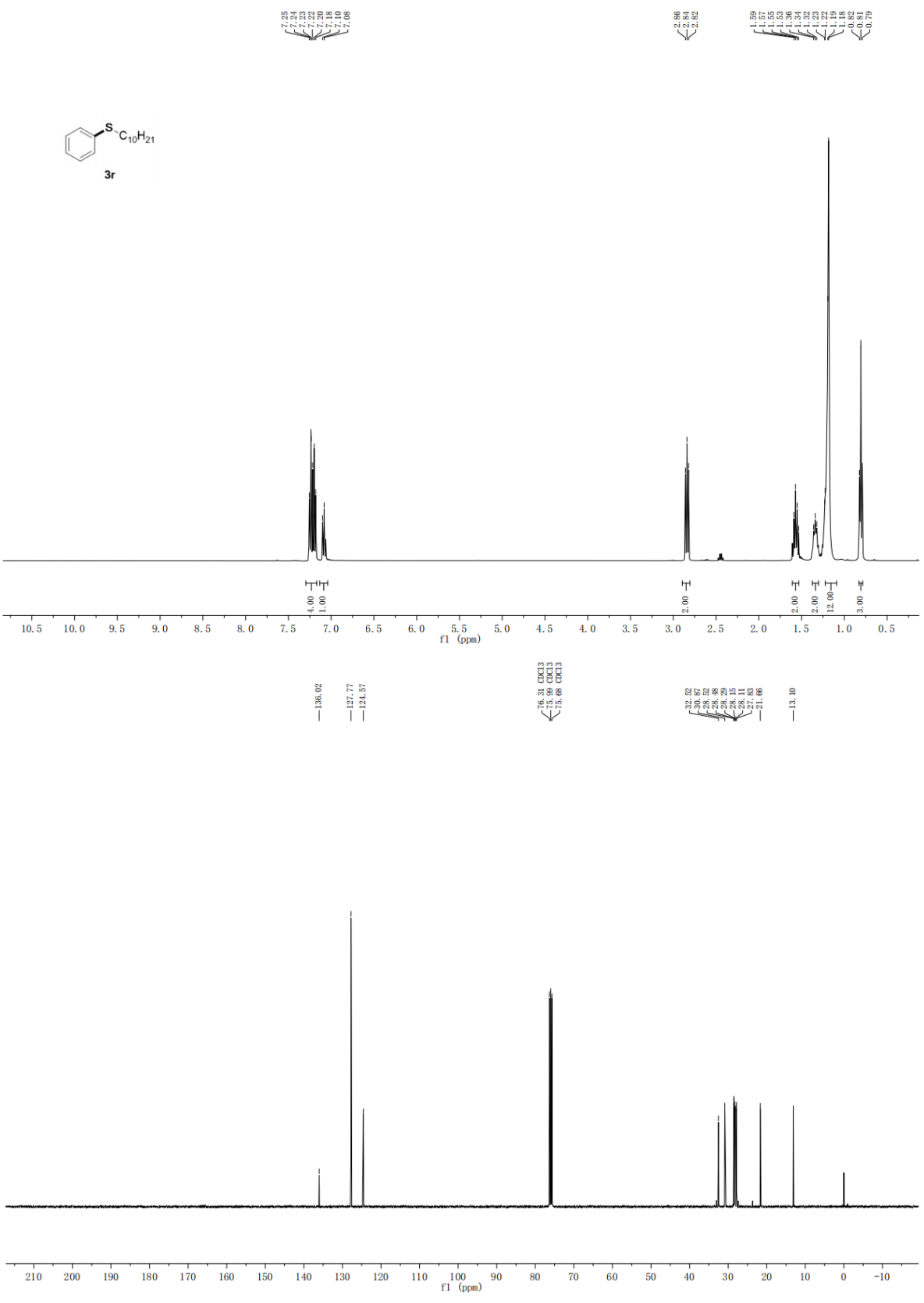


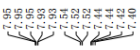
3q

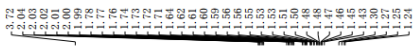


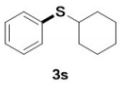



-60.77
CF3
S
3q
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

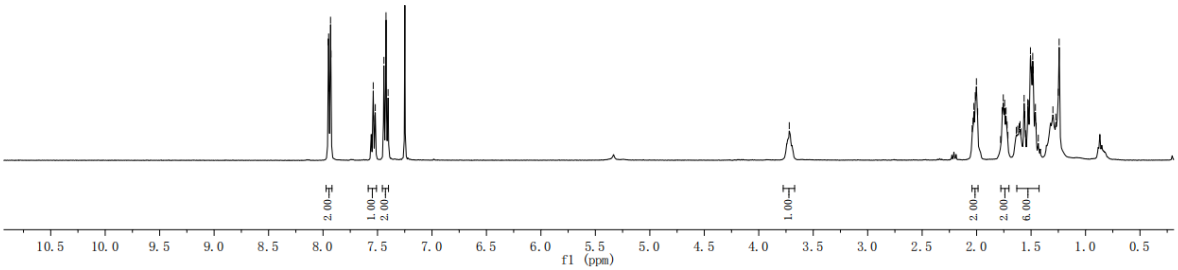

7.25
7.24
7.23
7.22
7.20
7.18
7.10
7.08
2.86
2.84
2.82
1.59
1.57
1.55
1.53
1.36
1.34
1.32
1.23
1.22
1.19
1.18
0.82
0.81
0.79
S
C10H21
3r
4.00
1.00
2.00
2.00
2.00
12.00
3.00
f1 (ppm)
136.02
127.77
124.57
76.31 CDCl3
75.99 CDCl3
75.68 CDCl3
32.52
30.67
29.52
28.48
28.29
28.15
28.11
27.83
21.66
13.10
f1 (ppm)

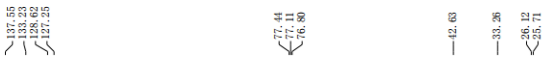

7.95
7.95
7.95
7.93
7.93
7.54
7.52
7.52
7.44
7.44
7.42
7.40

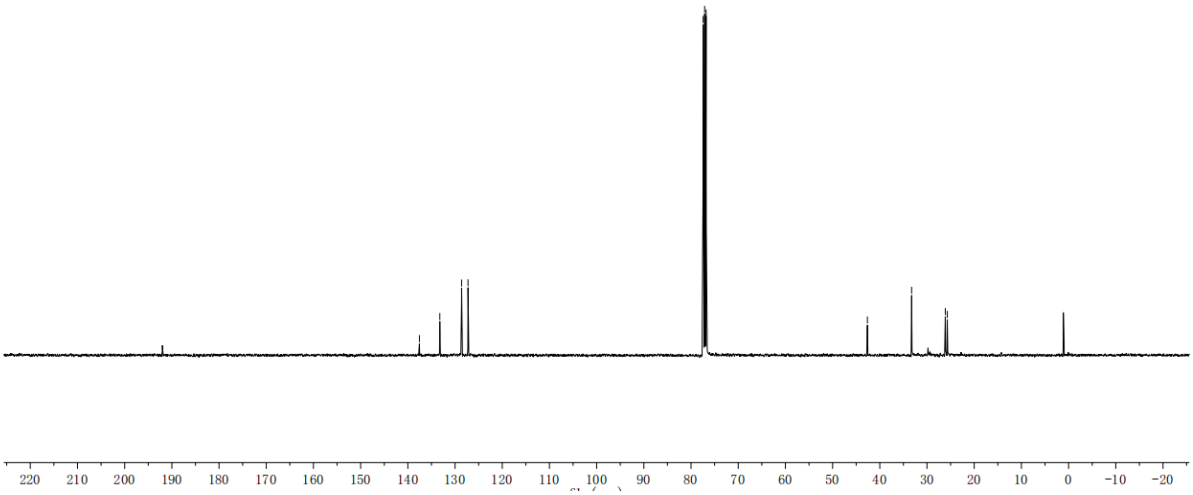

3.72
2.04
2.03
2.02
2.01
2.00
1.99
1.78
1.77
1.76
1.74
1.73
1.72
1.71
1.64
1.62
1.61
1.60
1.59
1.56
1.56
1.55
1.53
1.53
1.51
1.50
1.48
1.48
1.47
1.46
1.45
1.43
1.30
1.27
1.25
1.24

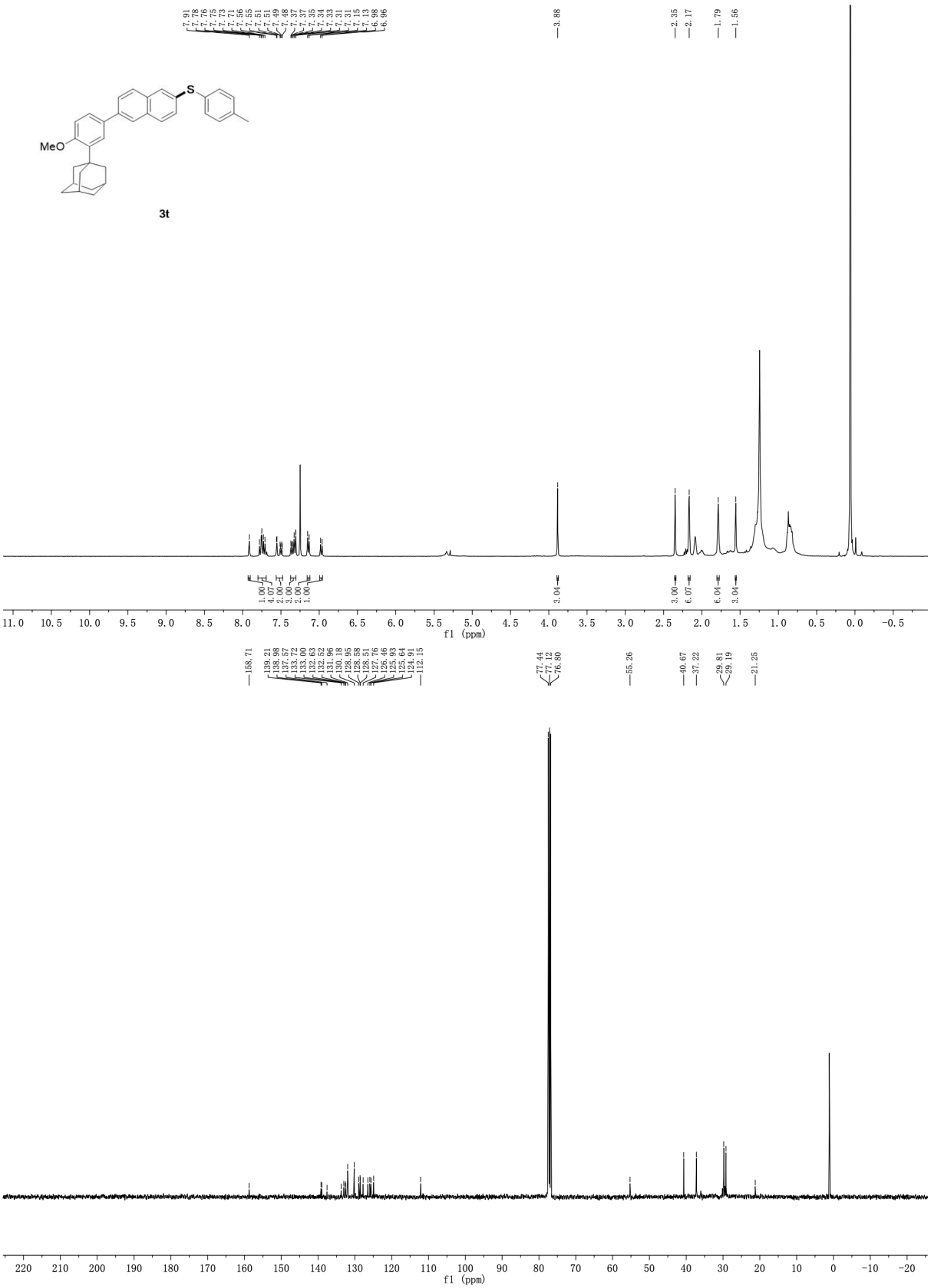

S

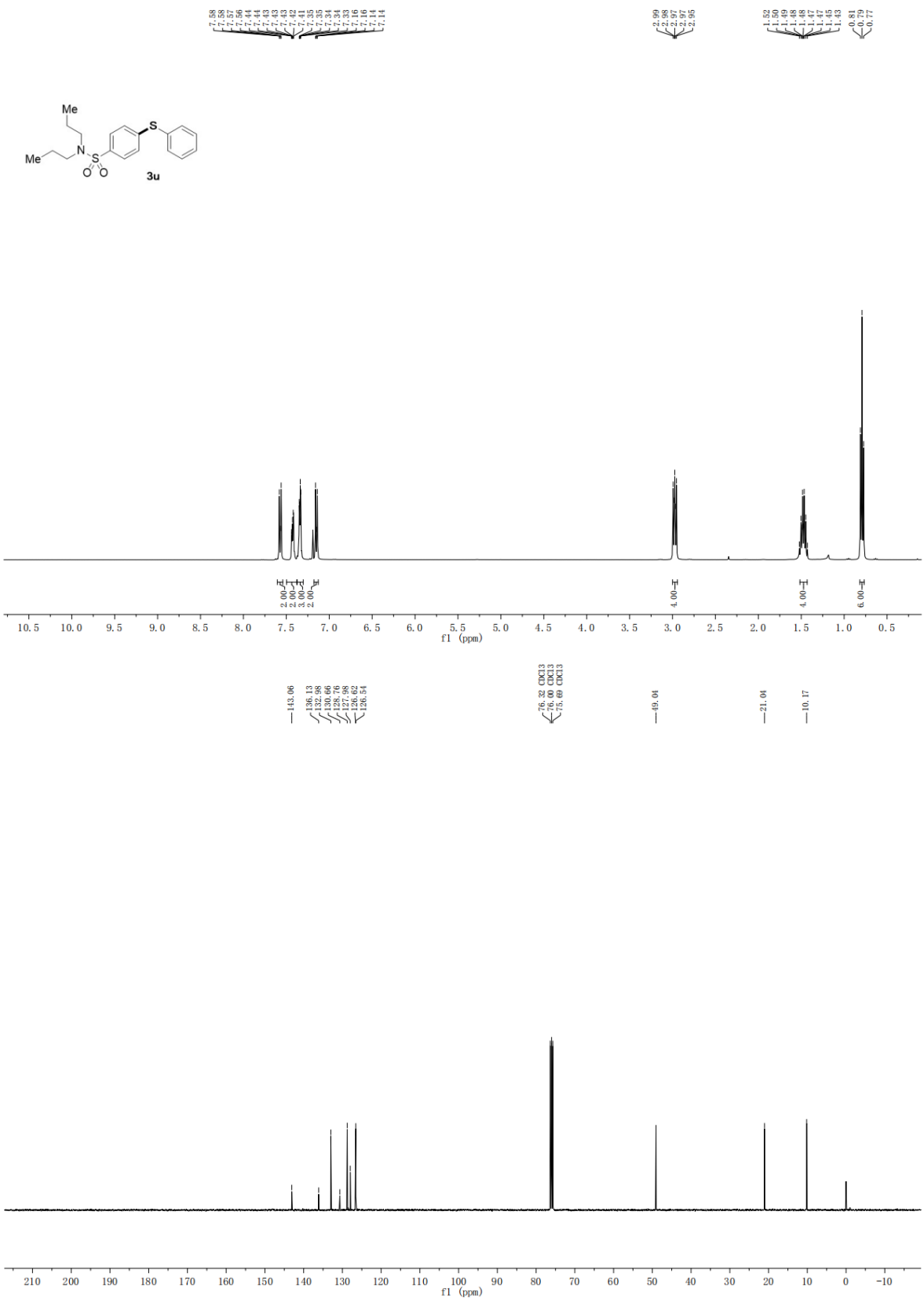
3s

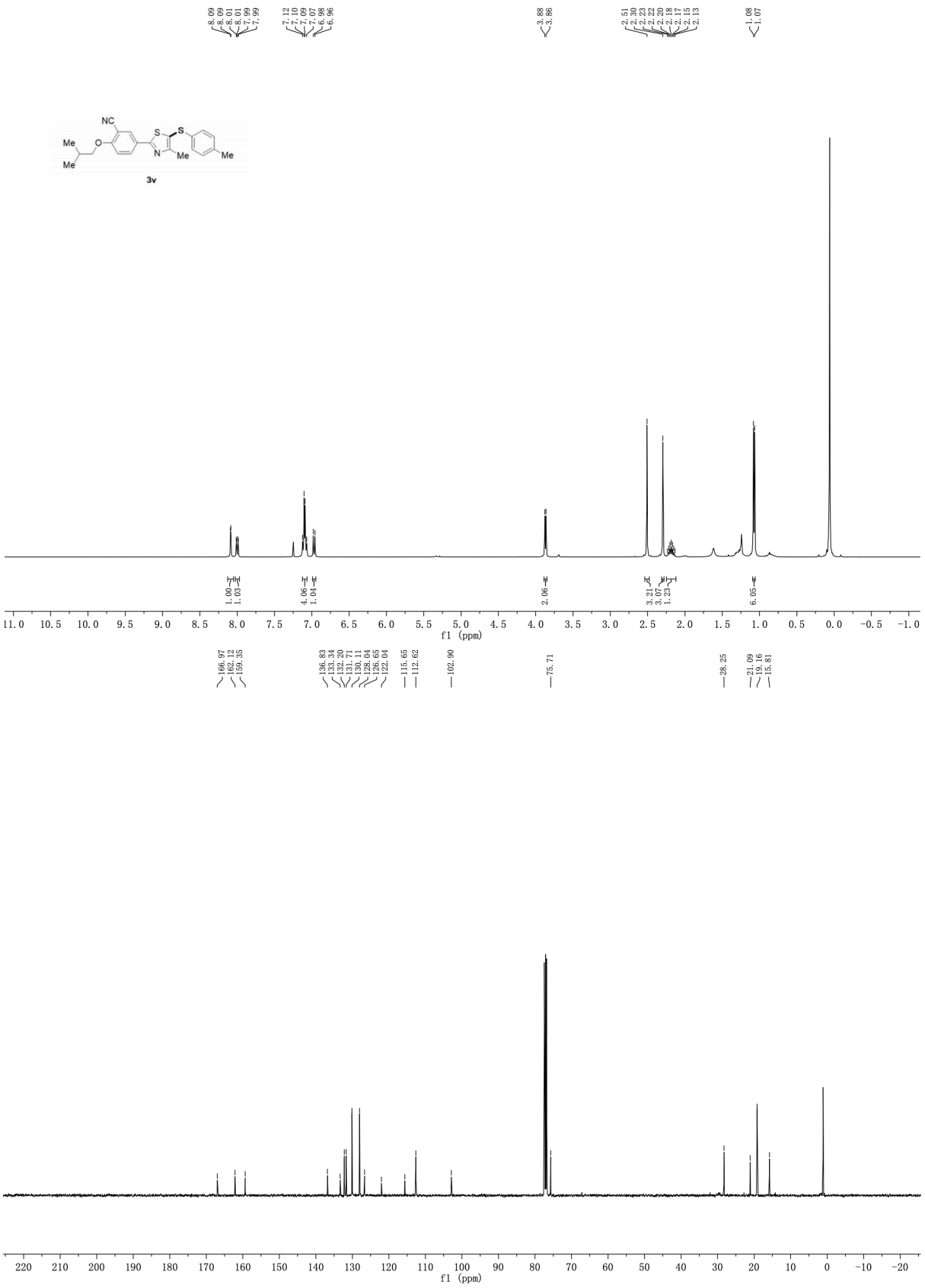

2.00
1.00
2.00
1.00
2.00
2.00
6.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

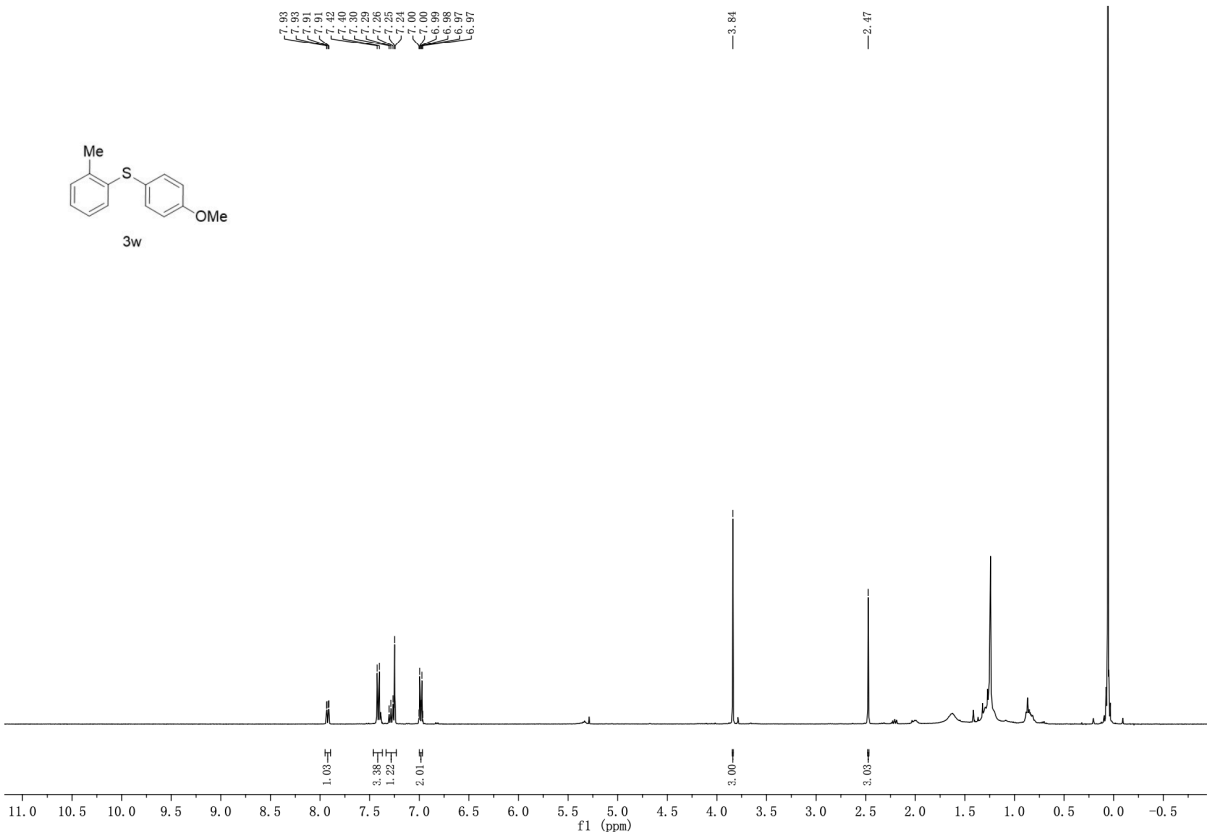

137.55
133.23
128.62
127.25
77.44
77.11
76.80
42.63
33.26
26.12
25.71

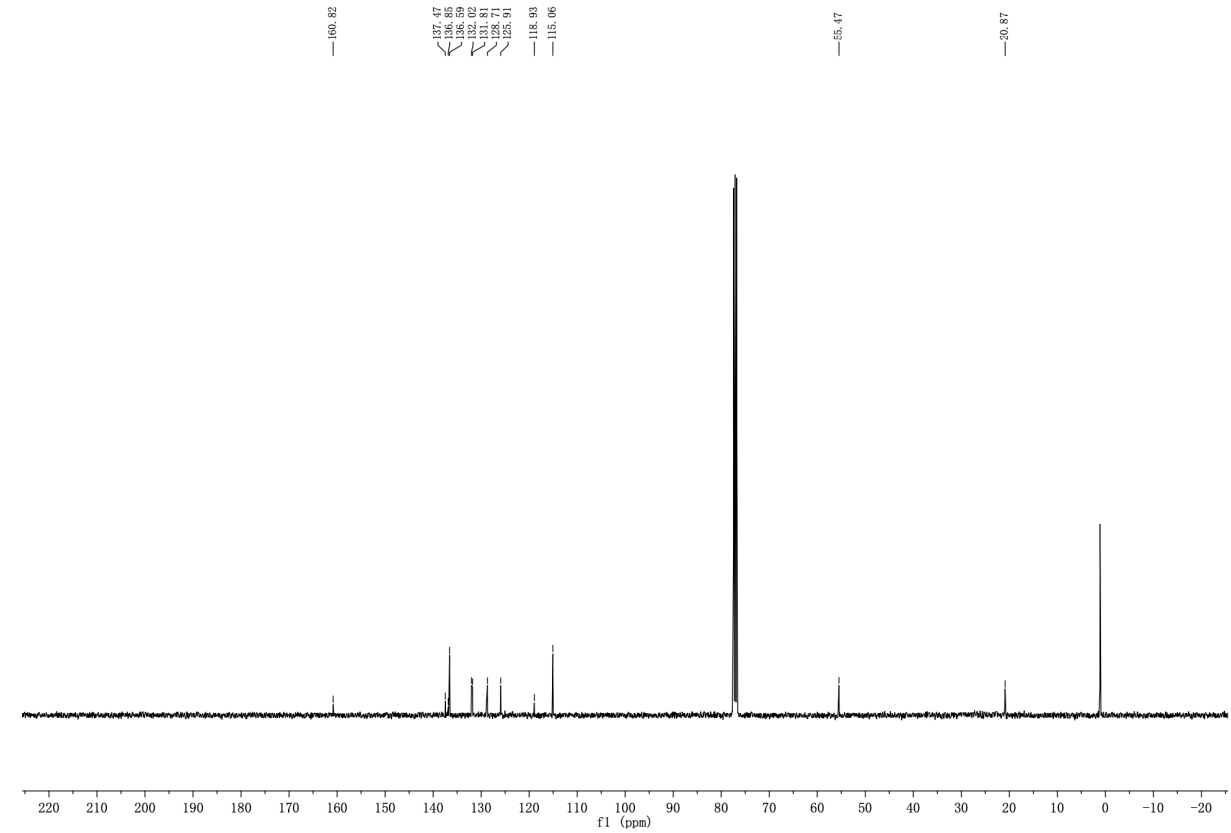

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

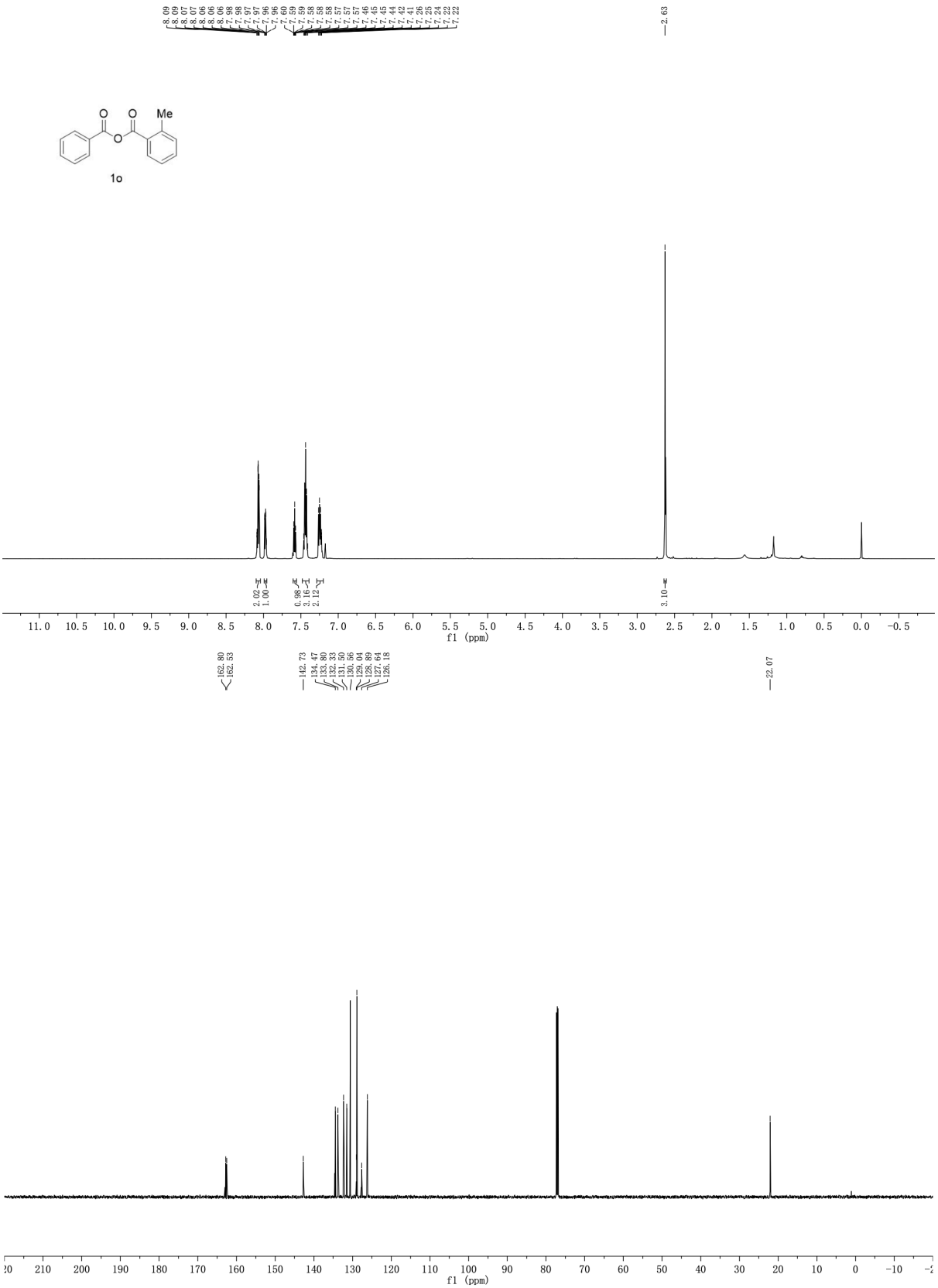

MeO
S
3t
f1 (ppm)
f1 (ppm)

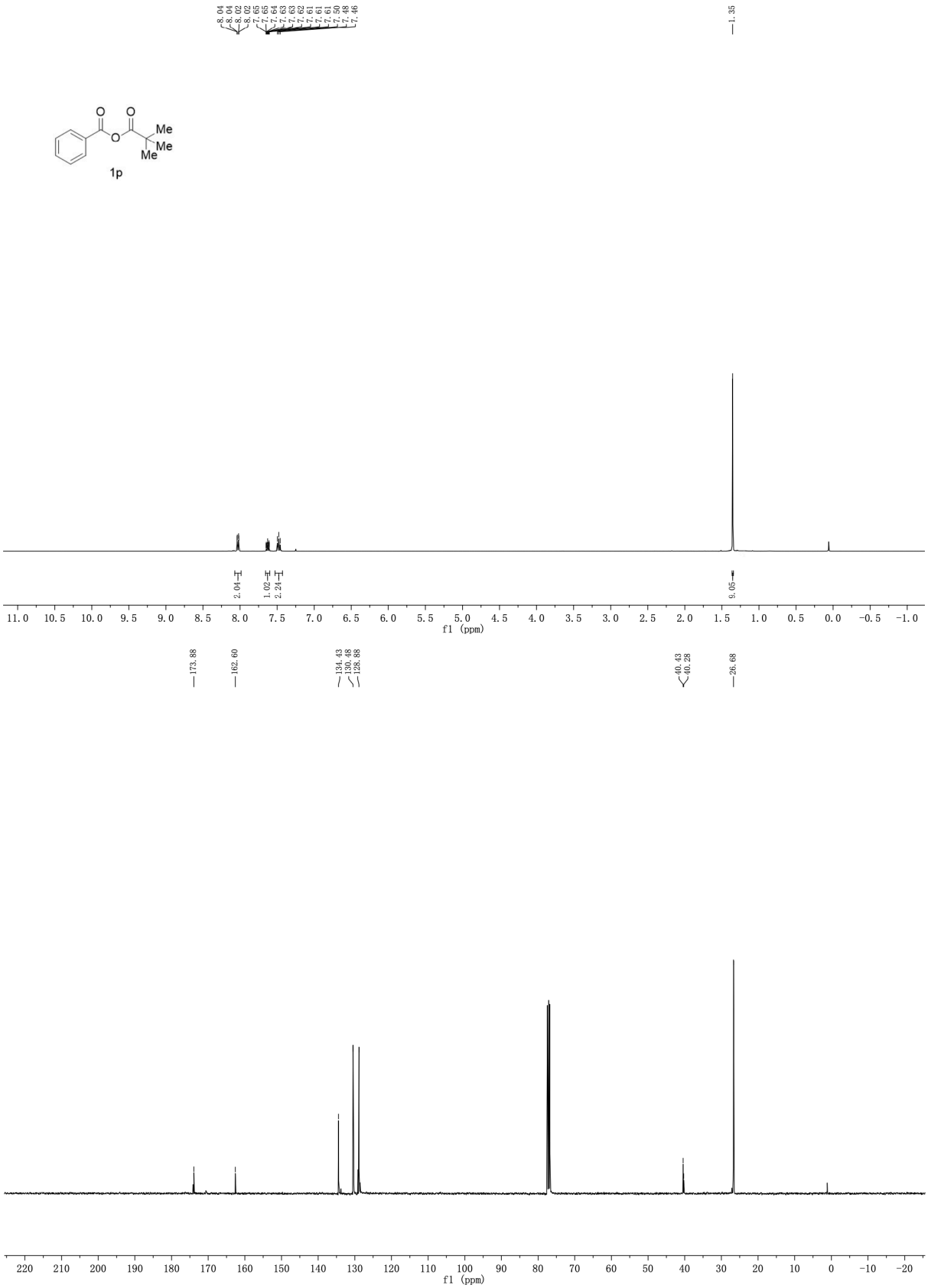

Me
Me
N
S
O
O
S
3u
f1 (ppm)
f1 (ppm)


8.09
8.09
8.01
8.01
7.99
7.99
7.12
7.10
7.09
7.07
6.98
6.96
3.88
3.86
2.51
2.30
2.23
2.22
2.20
2.18
2.17
2.15
2.13
1.08
1.07
NC
Me
O
Me
S
S
N
Me
Me
3v
1.00
1.03
4.06
1.04
2.06
3.21
3.07
1.23
6.05
f1 (ppm)
166.97
162.12
159.35
136.83
133.34
132.20
131.71
130.11
128.04
126.65
122.04
115.65
112.62
102.90
75.71
28.25
21.09
19.15
15.81
f1 (ppm)


7.93
7.93
7.91
7.91
7.42
7.40
7.30
7.29
7.26
7.25
7.24
7.00
7.00
6.99
6.98
6.97
6.97
3.84
2.47
Me
S
OMe
3w
1.03
3.38
1.22
2.01
3.00
3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


160.82
137.47
135.85
136.59
132.02
131.81
128.71
125.91
118.93
115.06
55.47
20.87
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.09
8.09
8.07
8.07
8.06
8.06
8.06
7.98
7.98
7.97
7.97
7.96
7.96
7.60
7.59
7.59
7.58
7.58
7.58
7.57
7.57
7.57
7.46
7.45
7.44
7.42
7.41
7.25
7.24
7.22
7.22
2.63
O
O
O
Me
1o
2.02
1.00
0.98
3.16
2.12
3.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
162.80
162.53
142.73
134.47
133.80
132.33
131.50
130.56
129.04
128.89
127.64
126.18
22.07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.04
8.04
8.02
8.02
7.65
7.64
7.64
7.63
7.63
7.62
7.61
7.61
7.61
7.50
7.48
7.46
1.35
O
O
O
Me
Me
Me
1p
2.04
1.02
2.24
9.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
173.88
162.60
134.43
130.48
128.88
40.43
40.28
26.68
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)