Supplementary Information (SI) for Green Chemistry.

Iron-photocatalyzed Desulfurizing Chlorination with Seawater

Boning, Gu [a], Yinsong, Zhao [a,*], Chengliang Li [a], Xuefeng, Jiang [a,b,*]

[a] Hainan Institute of East China Normal University, State Key Laboratory of Petroleum Molecular & Process Engineering, Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai 200241, China

[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China.

Tables of Contents

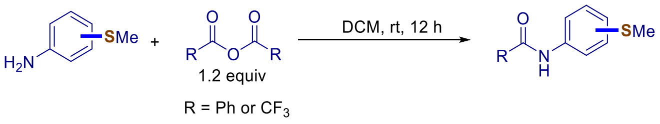
General remarks

All chemicals were obtained from commercial suppliers and used without further purification unless otherwise noted. All elution solvents were purchased from Shanghai Titan Scientific Co., Ltd.. Seawater (35‰ salinity, ~ 0.55 M chloride) was purchased from Beijing Wanjia Shouhua Biotechnology Co., Ltd.. Natural seawater was collected at Sanya Yazhou Bay (109.3534° E, 18.2990° N) with a calculated salinity of 33.26 ‰. ^{1}H NMR spectra were recorded on Bruker AVANCE spectrometers (400 MHz) in $CDCl_3$, DMSO-d_6, or CD_3CN-d_3 solution, ^{13}C NMR were recorded on Bruker AVANCE spectrometers (100 MHz and 125 MHz) in $CDCl_3$, DMSO-d_6, or CD_3CN-d_3 solution, and ^{19}F NMR were recorded on Bruker AVANCE spectrometers (376 MHz) in $CDCl_3$ solution. Data for ^{1}H NMR spectra were reported as follows: chemical shift (δ ppm), multiplicity (br = broad, s = singlet, d = double, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz) and integration were referenced to the residual solvent peak 7.26 ppm for $CDCl_3$, 2.50 ppm for DMSO-d_6, and 1.94 ppm for CD_3CN-d_3. ^{13}C NMR spectra were referenced to the residual solvent peak 77.16 ppm for $CDCl_3$, 39.52 ppm for DMSO-d_6, and 1.32 ppm for CD_3CN-d_3. Mass spectra were recorded on a Shimadzu GCMS-QP2010 Ultra and an HP 5989A mass selective detector with helium (He) as the carrier gas. High resolution mass spectrometry (HR-MS) was performed on a Bruker solarix XR instrument equipped with ParaCell ICR cell using positive electrospray ionization (ESI^+). Salinity of natural seawater was measured on Autosal salinometer 8400B. The photoreactor and CSTR-photoreactor are exclusively designed by hsly-Green Lab (Shanghai, China).[1]

General procedure for the synthesis of thioethers

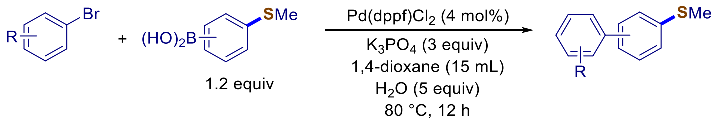
Thioethers **1b-f**, **1i-l**, **1q**, **1t-u**, **1w**, **1y-z**, **1aa**, **1ac-ad**, **1af-ag**, **3a-b** and **5a-c** were purchased from Bide Pharmatech Co., Ltd., and used without further purification. Other thioether models were prepared according to the reported literatures.[2-5]

(i) General procedure A for the synthesis of **1a**, **1g**, **1r**, and **1v** [2]



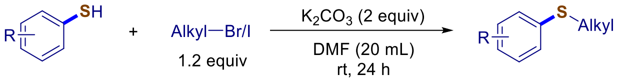
A 50 mL Schlenk bottle was charged with methylthioaniline (5.0 mmol), benzoic anhydride or trifluoroacetic anhydride (6.0 mmol), and dichloromethane (15 mL). The reaction mixture was stirred at room temperature for 12 hours, monitored by TLC until the reaction was complete. The reaction mixture was diluted with dichloromethane (15 mL), washed with saturated NaCl (3*20 mL) for three times, dried with anhydrous Na_2SO_4, and then concentrated in vacuum. The residual was purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to yield the corresponding product.

(ii) General procedure B for the synthesis of **1m**, **1n**, **1s** and **1ab** [3]



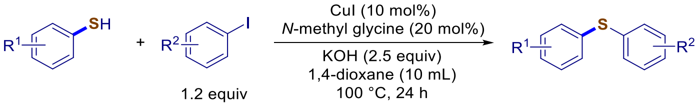
A 50 ml Schlenk bottle was charged with bromobenzene (5.0 mmol), phenylboronic acid (6.0 mmol), $Pd(dppf)Cl_2$ (0.2 mmol, 4 mol%), and K_3PO_4 (15.0 mmol). After evacuated/backfilled with nitrogen for three times, H_2O (25.0 mmol) and 1,4-dioxane (20 mL) was added *via* syringe. The reaction mixture was stirred at 80 °C for 12 hours, and monitored by TLC until the reaction was complete. After cooling to room temperature, the solvent was evaporated. The reaction mixture was diluted with ethyl acetate (30 mL), washed with saturated NaCl (3*20 mL) for three times, dried with anhydrous Na_2SO_4, and concentrated in vacuum. The residual was purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to yield the corresponding product.

(iii) General procedure C for the synthesis of **1x** and **1ae** [4]



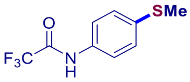
A 50 ml Schlenk bottle was charged with phenylthiophenol (5.0 mmol), K_2CO_3 (10.0 mmol) and DMF (15 mL), then alkyl bromide/iodide (6.0 mmol) was added dropwise while stirring at 0 °C. The reaction mixture was stirred at room temperature for 12 h, monitored by TLC until the reaction was complete. The mixture was diluted with ethyl acetate (100 mL), washed with saturated NaCl (3*100 mL) for three times, dried with anhydrous Na_2SO_4, and concentrated in vacuum. The residual was purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to yield the corresponding product.

(iv) General procedure D for the synthesis of **1aj**, **1ak** and **1al** [5]



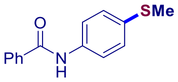
A 50 ml Schlenk bottle was charged with phenylthiophenol (5.0 mmol), iodobenzene (6.0 mmol), CuI (0.5 mmol, 10 mol%), *N*-methyl glycine (1.0 mmol, 20 mol%), KOH (12.5 mmol) and 1,4-dioxane (10 mL). The reaction mixture was stirred at 100 °C for 24 h, monitored by TLC until the reaction was complete. After cooling to room temperature, the solvent was evaporated. The reaction mixture was diluted with ethyl acetate (30 mL), washed with saturated NaCl (3*20 mL) for three times, dried with anhydrous Na_2SO_4, and concentrated in vacuum. The residual was purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent to yield the corresponding product.

Characterization data of the prepared thioethers

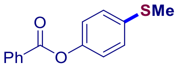


2,2,2-Trifluoro-*N*-(4-(methylthio)phenyl)acetamide (1a): The title compound was isolated (998.8 mg, 85%) as a light yellow solid after chromatography on silica gel

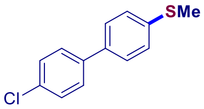
(PE/EA = 50:1 to 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.49 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9 (q, J_{CF} = 37.1 Hz), 136.9, 132.4, 127.5, 121.2, 115.8 (q, J_{CF} = 286.8 Hz), 16.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.7. GC-MS (EI$^+$): calcd for $C_9H_8F_3NOS$ $[M]^+$ 235.03, found 235.05.



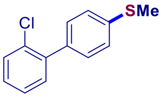
***N*-(4-(Methylthio)phenyl)benzamide (1g):** The title compound was isolated (911.3 mg, 75%) as a yellow solid after chromatography on silica gel (PE/EA = 50:1 to 3:1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.29 (s, 1H), 7.96 (d, J = 7.2 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.58 (t, J = 6.8 Hz, 1H), 7.52 (t, J = 7.2 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.4, 136.7, 134.9, 132.3, 131.6, 128.4, 127.7, 126.9, 121.0, 15.5. GC-MS (EI$^+$): calcd for $C_{14}H_{13}NOS$ $[M]^+$ 243.07, found 243.00.



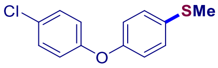
4-(Methylthio)phenyl benzoate (1h):[6] A 50 ml Schlenk bottle was charged with 4-methylthiophenol (5.0 mmol), 10% aqueous sodium hydroxide solution (10 mL). A dichloromethane solution (10 mL) containing tetra-*N*-butylammonium iodide (0.5 mmol, 10 mol%) and benzoyl chloride (6.0 mmol) was then added slowly. The reaction mixture was stirring at room temperature for 12 hours, and monitored by TLC until the reaction was complete. The reaction mixture was diluted with dichloromethane (20 mL), washed with saturated NaCl (3*20 mL) for three times, dried with anhydrous Na_2SO_4, and concentrated in vacuum. The title compound was isolated (854.0 mg, 70%) as a white solid after chromatography on silica gel (PE/EA = 50:1 to 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 7.2 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 148.7, 135.8, 133.8, 130.3, 129.5, 128.7, 128.1, 122.3, 16.6. GC-MS (EI$^+$): calcd for $C_{14}H_{12}O_2S$ $[M]^+$ 244.06, found 244.05.



(4'-Chloro-[1,1'-biphenyl]-4-yl)(methyl)sulfane (1m): The title compound was isolated (830.7 mg, 71%) as a white solid after chromatography on silica gel (PE/EA = 50:1 to 10:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.50-7.47 (m, 4H), 7.40 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 139.1, 138.3, 136.8, 133.4, 129.1, 128.2, 127.4, 127.1, 15.9. GC-MS (EI$^+$): calcd for $C_{13}H_{11}ClS$ [M]$^+$ 234.03, found 233.95.

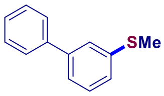


(2'-Chloro-[1,1'-biphenyl]-4-yl)(methyl)sulfane (1n): The title compound was isolated (807.3 mg, 69%) as a light-green thick oil after chromatography on silica gel (PE/EA = 50:1 to 10:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.43-7.34 (m, 5H), 7.29 (d, J = 7,6 Hz, 1H), 7.24-7.18 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 139.7, 139.0, 137.2, 133.7, 130.8, 130.0, 128.5, 128.4, 125.4, 125.0, 16.1. HR-MS (ESI$^+$): calcd for $C_{13}H_{12}ClS$ [M+H]$^+$ 235.0343, found 235.0340.

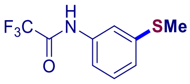


(4-(4-Chlorophenoxy)phenyl)(methyl)sulfane (1o):[7] A 50 ml Schlenk bottle was charged with 4-chlorophenol (5.0 mmol), 4-methylthiobromobenzene (6.0 mmol), copper iodide (0.5 mmol, 10 mol%), 2-pyridinecarboxylic acid (0.5 mmol, 10 mol%), and K_3PO_4 (10.0 mmol), which was then evacuated/backfilled with nitrogen for three times followed by the addition of DMSO (20 mL) *via* syringe. The reaction mixture was stirred at 120 °C for 48 h. After cooling to room temperature, the mixture was diluted with ethyl acetate (100 mL), washed with saturated NaCl (3*100 mL) for three times, dried with anhydrous Na_2SO_4, and then concentrated in vacuum. The title compound was isolated (662.5 mg, 53%) as a white solid after chromatography on silica gel (PE/EA = 50:1 to 10:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35-7.32 (m, 4H), 7.01-6.97 (m, 4H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 156.1, 154.9, 133.1, 129.9, 129.2, 128.3, 119.9, 119.8, 17.1. GC-MS (EI$^+$): calcd for $C_{13}H_{11}ClOS$ [M]$^+$ 250.02, found 250.00.

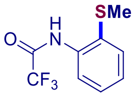
Methyl(4-(methylsulfonyl)phenyl)sulfane (1p):[8] A 50 ml Schlenk bottle was charged with 1-bromo-4-(methylsulfonyl)benzene (5.0 mmol), *S*-methylisothioureasulfate (6.0 mmol), cesium carbonate (12.5 mmol), dry DMSO (20 mL) *via* syringe under an nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 12 h, monitored by TLC until the reaction was complete. After cooling to room temperature, the mixture was diluted with ethyl acetate (100 mL), washed with saturated NaCl (3*100 mL) for three times, dried with anhydrous Na_2SO_4, and then concentrated in vacuum. The title compound was isolated (646.5 mg, 64%) as a light yellow solid after chromatography on silica gel (PE/EA = 50:1 to 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.81 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 3.03 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 147.3, 136.3, 127.8, 125.6, 44.8, 14.9. GC-MS (EI$^+$): calcd for $C_8H_{10}O_2S_2$ [M]$^+$ 202.01, found 202.05.



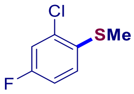
[1,1'-Biphenyl]-3-yl(methyl)sulfane (1r): The title compound was isolated (600.1 mg, 60%) as a yellow oil after chromatography on silica gel (PE/EA = 50:1 to 10:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.59-7.57 (m, 2H), 7.49-7.43 (m, 3H), 7.38-7.36 (m, 3H), 7.27-7.24 (m, 1H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 142.0, 140.9, 139.1, 129.3, 128.9, 127.6, 127.3, 125.4, 124.2, 16.0. GC-MS (EI$^+$): calcd for $C_{13}H_{12}S$ [M]$^+$ 200.07, found 199.85.



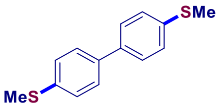
2,2,2-Trifluoro-*N*-(3-(methylthio)phenyl)acetamide (1s): The title compound was isolated (928.3 mg, 79%) as a white solid after chromatography on silica gel (PE/EA = 50:1 to 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.24 (s, 1H), 7.51 (s, 1H), 7.31-7.28 (m, 2H), 7.13-7.10 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 155.2 (q, J_{CF} = 37.2 Hz), 140.5, 135.7, 129.6, 124.2, 118.1, 117.1, 115.8 (q, J_{CF} = 286.7 Hz), 15.5. ^{19}F NMR (376 MHz, CDCl$_3$): δ -75.7. GC-MS (EI$^+$): calcd for $C_9H_8F_3NOS$ [M]$^+$ 235.03, found 234.85.



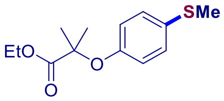
2,2,2-Trifluoro-*N*-(2-(methylthio)phenyl)acetamide (1v): The title compound was isolated (998.8 mg, 85%) as a white solid after chromatography on silica gel (PE/EA = 50:1 to 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.26 (s, 1H), 8.30 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.57 (dd, J = 8.0 Hz, 0.8 Hz, 1H), 7.39-7.35 (m, 1H), 7.20 (td, J = 7.6 Hz, 1.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.8 (q, J_{CF} = 37.1 Hz), 136.1, 133.7, 129.5, 126.7, 126.5, 120.8, 115.9 (q, J_{CF} = 287.0 Hz), 19.3. ^{19}F NMR (376 MHz, CDCl$_3$): δ -75.9. GC-MS (EI$^+$): calcd for $C_9H_8F_3NOS$ [M]$^+$ 235.03, found 234.90.



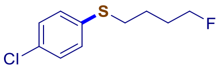
(2-Chloro-4-fluorophenyl)(methyl)sulfane (1x): The title compound was isolated (660.0 mg, 75%) as a colorless oil after chromatography on silica gel (PE/EA = 50:1 to 10:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.19-7.13 (m, 2H), 7.01-6.96 (m, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 160.5 (d, J_{CF} = 248.6 Hz), 133.3 (d, J_{CF} = 10.2 Hz), 133.0 (d, J_{CF} = 3.6 Hz), 127.9 (d, J_{CF} = 8.1 Hz), 117.3 (dt, J_{CF} = 25.0 Hz, 4.2 Hz), 114.7 (d, J_{CF} = 21.4 Hz), 16.1. ^{19}F NMR (376 MHz, CDCl$_3$): δ -116.3. GC-MS (EI$^+$): calcd for C_7H_6ClFS [M]$^+$ 175.99, found 175.95.



4,4'-Bis(methylthio)-1,1'-biphenyl (1ab): The title compound was isolated (787.2 mg, 64%) as a white solid after chromatography on silica gel (PE/EA = 50:1 to 10:1). ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.50 (d, *J* = 8.8 Hz, 4H), 7.32 (d, *J* = 8.8 Hz, 4H), 2.52 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): *δ* 137.7, 137.5, 127.3, 127.1, 16.1. GC-MS (EI$^+$): calcd for $C_{14}H_{14}S_2$ [M]$^+$ 246.05, found 246.00.

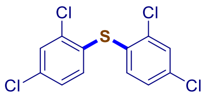


Ethyl 2,2-dimethyl-3-(4-(methylthio)phenyl)propanoate (1ac):[9] A 50 ml Schlenk bottle was charged with 4-methylthiophenol (5.0 mmol), ethyl 2-bromoisobutyrate (6.0 mmol), potassium carbonate (12.5 mmol) and acetonitrile (10 mL). The reaction mixture was stirring at 100 °C for 24 hours, and monitored by TLC until the reaction was complete. The reaction mixture was diluted with dichloromethane (20 mL), washed with saturated NaCl (3*20 mL) for three times, dried with anhydrous Na_2SO_4, and concentrated in vacuum. The title compound was isolated (832.0 mg, 66%) as a yellow oil after chromatography on silica gel (PE/EA = 50:1 to 10:1). ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.17 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.57 (s, 6H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): *δ* 174.3, 153.8, 131.0, 129.0, 120.1, 79.4, 61.6, 25.4, 17.4, 14.2. GC-MS (EI$^+$): calcd for $C_{13}H_{18}O_3S$ [M]$^+$ 254.10, found 254.10.

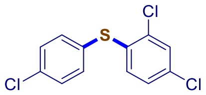


(4-Chlorophenyl)(4-fluorobutyl)sulfane (1af): The title compound was isolated (544.8 mg, 50%) as a colorless oil after chromatography on silica gel (PE/EA = 50:1 to 10:1). ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.26 (s, 4H), 4.52 (t, *J* = 5.6 Hz, 1H), 4.40 (t, *J* = 5.6 Hz, 1H), 2.95 (t, *J* = 7.2 Hz, 2H), 1.90-1.83 (m 1H), 1.80-1.73 (m, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): *δ* 135.0, 132.1, 130.8, 129.2, 83.6 (d, J_{CF} = 165.3 Hz), 33.7, 29.5

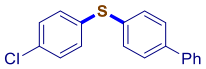
(d, J_{CF} = 19.8 Hz), 25.1 (d, J_{CF} = 4.9 Hz). ^{19}F NMR (376 MHz, CDCl$_3$): δ -218.7. GC-MS (EI$^+$): calcd for $C_{10}H_{12}ClFS$ [M]$^+$ 218.03, found 217.85.



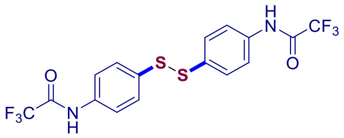
Bis(2,4-dichlorophenyl)sulfane (3c): The title compound was isolated (777.2 mg, 48%) as a yellow thick oil after chromatography on silica gel (PE/EA = 50:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.48 (d, J = 2.0 Hz, 2H), 7.19 (dd, J = 8.8 Hz, 2.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 136.4, 134.5, 133.3, 131.6, 130.3, 128.1. HR-MS (ESI$^+$): calcd for $C_{12}H_7Cl_4S$ [M+H]$^+$ 322.9017, found 322.9011.



(4-Chlorophenyl)(2,4-dichlorophenyl)sulfane (3d): The title compound was isolated (806.0 mg, 56%) as a white solid after chromatography on silica gel (PE/EA = 50:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.42 (d, J = 2.0 Hz, 1H), 7.35-7.33 (m, 4H), 7.12 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 134.9, 134.6, 134.4, 134.3, 134.1, 131.4, 131.2, 130.0, 129.8, 127.8. HR-MS (ESI$^+$): calcd for $C_{12}H_8Cl_3S$ [M+H]$^+$ 288.9407, found 288.9407.



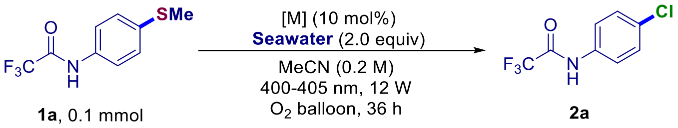
[1,1'-biphenyl]-4-yl(4-chlorophenyl)sulfane (3e): The title compound was isolated (561.8 mg, 38%) as a white solid after chromatography on silica gel (PE/EA = 50:1 to 10:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.59 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.30 (s, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 140.5, 140.3, 134.7, 134.3, 133.2, 132.2, 131.7, 129.5, 129.0, 128.1, 127.7, 127.1. GC-MS (EI$^+$): calcd for $C_{18}H_{13}ClS$ [M]$^+$ 296.04, found 296.00.



***N,N'*-(disulfanediylbis(4,1-phenylene))bis(2,2,2-trifluoroacetamide) (4):**[2] A 50 mL Schlenk bottle was charged with 4-4'-diaminodiphenyl disulfide (5.0 mmol), trifluoroacetic anhydride (12.0 mmol), and dichloromethane (15.0 mL). The reaction mixture was stirred at room temperature for 12 hours, monitored by TLC until the reaction was complete. The mixture was diluted with dichloromethane (20 mL), washed with saturated NaCl (3*20 mL) for three times, dried with anhydrous Na_2SO_4, and then concentrated in vacuum. The title compound was isolated (1.41 g, 64%) as a pink solid after chromatography on silica gel (PE/EA = 50:1 to 1:1). ^1H NMR (400 MHz, DMSO-d_6): δ 11.36 (s, 2H), 7.71 (d, J = 8.8 Hz, 4H), 7.55 (d, J = 8.8 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.5 (q, J_{CF} = 26.9 Hz), 136.2, 132.4, 128.9, 121.8, 115.7 (q, J_{CF} = 287.9 Hz). ^{19}F NMR (376 MHz, DMSO-d_6): δ -74.0. GC-MS (EI$^+$): calcd for $C_{16}H_{10}F_6N_2O_2S_2$ [M]$^+$ 440.01, found 440.05.

Optimization of the reaction conditions

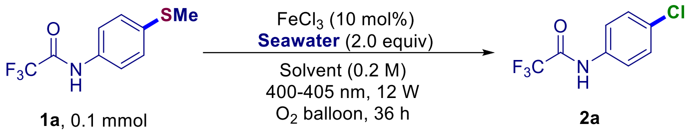
Table S1. The screening of various catalysts



Entry	Variation of catalyst	Yield of **2a** (%)
1	$FeCl_3$	82
2	$FeCl_3 \cdot 6H_2O$	77
3	$Fe(NO_3)_3 \cdot 9H_2O$	52
4	$CuCl_2$	56
5	$BiCl_3$	15
6	$CeCl_3$	nd.
7	*fac*-Ir(ppy)$_3$	nd.
8	$[Ru(bpy)_2Cl]_2$	nd.
9	$PdCl_2$	nd.
10	$MgCl_2$	nd.
11	None	nd.

Conditions: **1a** (0.1 mmol, 23.5 mg), metal catalyst (10 mol%), MeCN (0.5 mL) and seawater (0.2 mmol, ~ 0.55 M chloride, 0.37 mL) were irradiated under blue LEDs (400-405 nm, 12 W) for 36 h in O_2. Isolated yield. ppy = 2-phenylpyridine; bpy = 2,2'-bipyridine. nd. = Not detected..

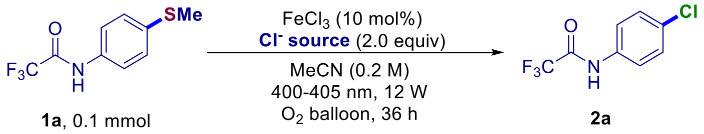
Table S2. The screening of various solvents



Entry	Variation of solvent	Yield of **2a** (%)
1	MeCN	82
2	DMSO	nd.
3	DMF	nd.
4	None	nd.

Conditions: **1a** (0.1 mmol, 23.5 mg), $FeCl_3$ (10 mol%), MeCN (0.5 mL) and seawater (0.2 mmol, ~ 0.55 M chloride, 0.37 mL) were irradiated under blue LEDs (400-405 nm, 12 W) for 36 h in O_2. Isolated yield. nd. = Not detected..

Table S3. The screening of various metal chlorides

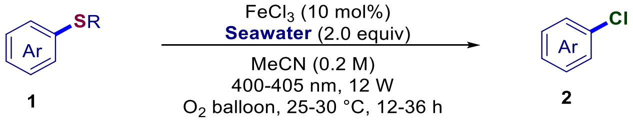


Entry	Variation of chlorides	Yield of **2a** (%)
1	Seawater (0.55 M, 0.2 mmol, 0.37 mL)	82
2	NaCl (solid, 0.2 mmol, 11.7 mg)	65
3	Saturated NaCl (aq., 0.2 mmol, 35 μL)	65
4	NaCl (aq., 0.55 M, 0.37 mL)	79
5	KCl (aq., 0.55 M, 0.37 mL)	83
6	$MgCl_2$ (aq., 0.275 M, 0.37 mL)	72
7	$CaCl_2$ (aq., 0.275 M, 0.37 mL)	75

Conditions: **1a** (0.1 mmol, 23.5 mg), $FeCl_3$ (10 mol%), CH_3CN (0.5 mL) and chloride source were irradiated under blue LEDs (400-405 nm, 12 W) for 36 h in O_2. Isolated yield.

General procedure for the desulfurizing chlorination reaction

(i) General procedure for the desulfurizing chlorination of aryl thioether **1**



A 4 mL screw-capped vial with a stirring bar were added **1** (0.1 mmol), $FeCl_3$ (10 mol%, 0.2 M in CH_3CN solution, 0.5 mL), and seawater (salinity: 35‰, ~ 0.55 M chloride, 370 μL). (Note: *For the reaction of 1mmol* ***1b****, a 20 mL screw-capped vial was used as a reaction vessel*). The vial was then sealed with a cap containing a PTFE septum and linked to an oxygen balloon (*spherical diameter: ~25 cm*). The reaction mixture was stirred under the irradiation of blue LEDs (400-405 nm, 12 W) at 25-30 ºC for the indicated time (12-36 h). See **Figure S1** for details. The resulting solution was concentrated in vacuum and the residue was purified by flash chromatography on silica gel column to provide the product **2**. For cases yielding volatile aryl chlorides, an internal standard (0.1 mmol) was added to the reaction mixture after extraction (Note: *For the reaction of 1mmol **1b**, 1 mmol of internal standard was added*). Then 5 μL of the solution was drawn, diluted immediately with ethyl acetate, and measured by GC-MS analysis to determine the yields of aryl chlorides. See **Figure S3-S14** for details. For cases yielding volatile fluorine-containing aryl chlorides, 100 μL of the organic phase (upper layer) was taken after reaction, diluted with $CDCl_3$ and measured by ^{19}F NMR (376 MHz). See **Figure S25-S28** for details.

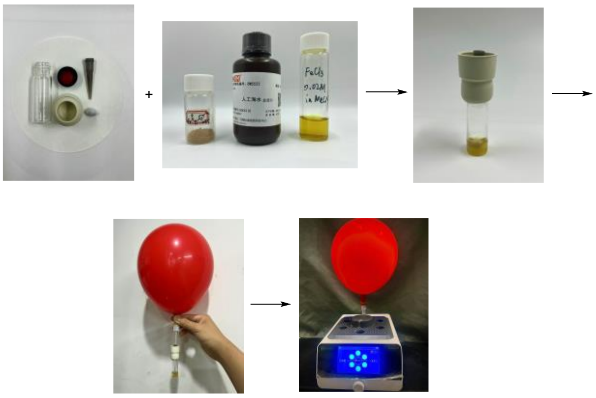
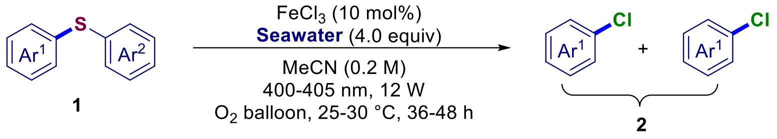


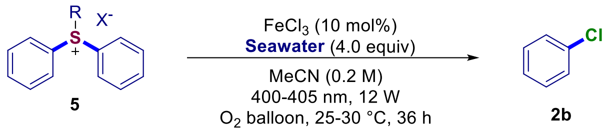
Figure S1. Schematic diagram of the reaction

(ii) General procedure for the desulfurizing chlorination of diaryl thioether **3**



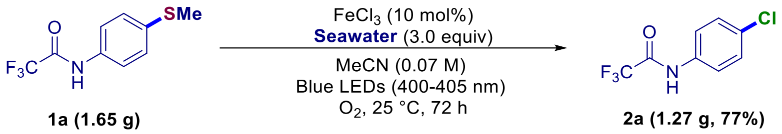
A 4 mL screw-capped vial with a stirring bar were added **3** (**3a**-**3e**, 0.1 mmol), $FeCl_3$ (10 mol%, 0.02 M in CH_3CN solution, 0.5 mL), seawater (salinity: 35‰, ~ 0.55 M chloride, 370 μL, 2.0 eqiuv), and additional sodium chloride (0.2 mmol, 11.7 mg). (Note: *For **3a**, reaction with 0.4 mmol seawater was also attempted.*) The vial was then sealed with a cap containing a PTFE septum and installed a rubber stopper. Then, a thin plastic tube was inserted for the connection to an oxygen balloon. The reaction mixture was stirred under the irradiation of blue LEDs (400-405 nm, 12 W) at 25-30 ºC for the indicated time (36-48 h). The resulting solution was concentrated in vacuum and the residue was purified by flash chromatography on silica gel column using PE/EA, or pure PE as eluent to provide the product **2ai**. For reactions yielding volatile aryl halides **2b**, **2d**, or **2ah**, 0.1 or 0.2 mmol of internal standard was added to the reaction mixture after extraction based on the generated product. Then 5 μL of the solution was drawn, diluted immediately with ethyl acetate, and measured by GC-MS analysis to determine the yields of aryl chlorides. See **Figure S15- S17** and **Figure S19-S21** for details.

(iv) General procedure for the desulfurizing chlorination of sulfonium salts **5**



A 4 mL screw-capped vial with a stirring bar were added **5** (0.1 mmol), $FeCl_3$ (10 mol%, 0.2 M in CH_3CN solution, 0.5 mL), seawater (salinity: 35‰, ~ 0.55 M chloride, 370 μL) and additional sodium chloride (0.2 mmol, 11.7 mg). The vial was then sealed with a cap containing a PTFE septum and linked to an oxygen balloon (*spherical diameter: ~25 cm*). The reaction mixture was stirred under the irradiation of blue LEDs (400-405 nm, 12 W) at 25-30 ºC for 36 h. Then, an internal standard (0.2 or 0.3 mmol) was added to the reaction mixture after extraction. Finally, 5 μL of the solution was drawn, diluted immediately with ethyl acetate, and measured by GC-MS analysis to determine the yields of aryl chlorides. See **Figure S22-S24** for details.

(v) Procedure for the gram-scale reaction using photo-CSTR system



A continuous, multimode photo-CSTR (continuous stirred tank reactor) reactor with recirculation developed by us was used for gram-scale reaction, as shown in **Figure S2**.[1] To the 100 mL three-necked, round-bottomed flask with a stirring bar were added **1a** (1.65 g, 7 mmol), seawater (salinity: ~ 0.55 M chloride, 38 mL), $FeCl_3$ (113.6 mg, 10 mol%) and CH_3CN (40 mL). After stirring for 5 mins, the solution was pumped into the multimode photo-CSTR (8 tanks) reactor at a flow rate of 15 mL/min, while oxygen gas was bubbled in at a rate of 1.5 mL/min. Acetonitrile (60 mL) were then slowly added into flask and pumped into the recirculation system. The reaction mixture was continuously recirculated under the irradiation of blue LEDs (400-405 nm) at 25~30 ºC for 72 hours. Upon completion of the reaction, the photoreactor was flushed with CH_3CN and H_2O (50 mL). The resulting solution was washed out by ethyl acetate, concentrated in vacuum, extracted by ethyl acetate for three times, dried with anhydrous Na_2SO_4, and then concentrated in vacuum. The title compound was isolated (1.27 g, 77%) as a pink solid after chromatography on silica gel (PE/EA = 50:1 to 10:1).

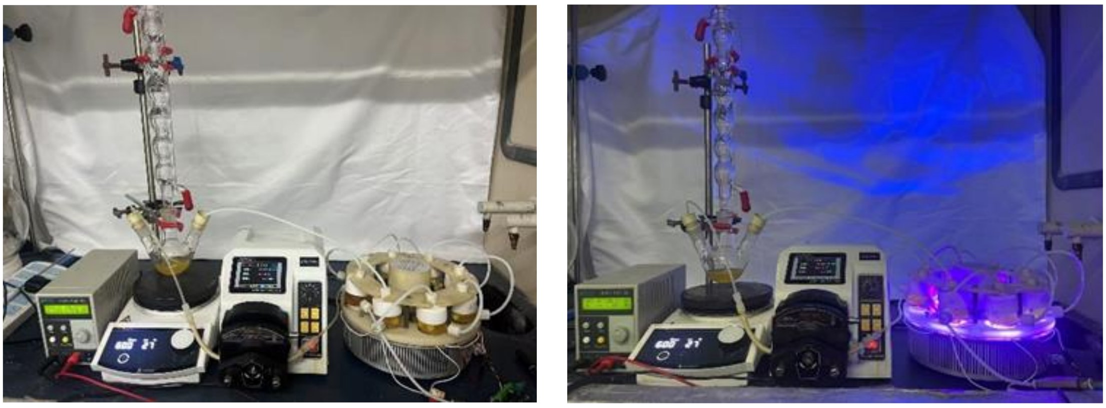
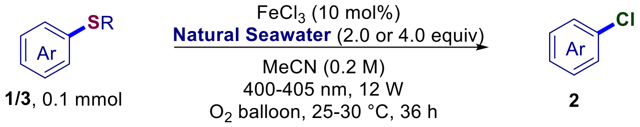

Before reaction
During reaction

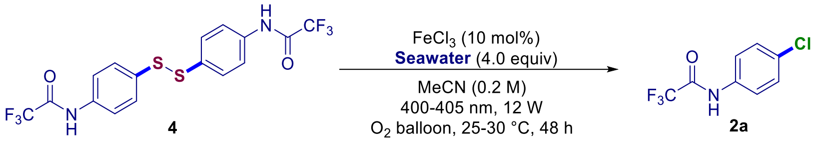
Figure S2. Gram scale reaction using Photo-CSTR system

(vi) General procedure for the desulfurizing chlorination with natural seawater:



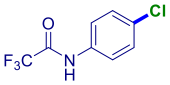
A 4 mL screw-capped vial with a stirring bar were added **1** or **3** (0.1 mmol), $FeCl_3$ (10 mol%, 0.2 M in CH_3CN solution, 0.5 mL), and natural seawater (0.2 mmol, 390 μL) with a calculated salinity of 33.26 ‰ (Note: *For the reaction of diaryl thioethers* ***3b****, 780 μL of natural seawater was added.*). The vial was then sealed with a cap containing a PTFE septum and linked to an oxygen balloon (*spherical diameter: ~25 cm*) The reaction mixture was stirred under the irradiation of blue LEDs (400-405 nm, 12 W) at 25-30 ºC for 36 h. The resulting solution was concentrated in vacuum and the residue was purified by flash chromatography on silica gel column to provide the product **2**. For the reaction of **3b**, 0.2 mmol of internal standard **2b** was added to the reaction mixture after extraction. Then 5 μL of the solution was drawn, diluted immediately with ethyl acetate, and measured by GC-MS analysis to determine the yields of aryl chlorides. See **Figure S18** for details.

(ii) Procedure for the desulfurizing chlorination of disulfide **4**:

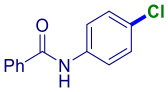


A 4 mL screw-capped vial with a stirring bar were added **4** (0.1 mmol， 44.0 mg), $FeCl_3$ (10 mol%, 0.2 M in CH_3CN solution, 0.5 mL), seawater (salinity: 35‰, ~ 0.55 M chloride, 370 μL) and additional sodium chloride (0.2 mmol, 11.7 mg). The vial was then sealed with a cap containing a PTFE septum and installed a rubber stopper. Then, a thin plastic tube was inserted for the connection to an oxygen balloon. The reaction mixture was stirred under the irradiation of blue LEDs (400-405 nm, 12 W) at 25-30 ºC for 48 h. The resulting solution was concentrated in vacuum and the residue was purified by flash chromatography on silica gel column using PE/EA (PE/EA = 50:1 to 10:1) as eluent to provide the product **2a** in 66% yield.

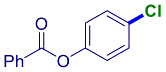
a) Characterization data of the aryl chlorides



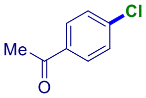
***N*-(4-Chlorophenyl)-2,2,2-trifluoroacetamide (2a):** The title compound was isolated as a white solid after chromatography on silica gel (PE/EA = 10:1) with the yield of (18.3 mg, 82%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether, and (16.5 mg, 74%) after reaction for 36 h according to general procedure for the desulfurizing chlorination with natural seawater. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0 (q, J_{CF} = 37.5 Hz), 133.7, 131.9, 129.6, 121.9, 115.7 (q, J_{CF} = 286.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.7. GC-MS (EI$^+$): calcd for $C_8H_5ClF_3NO$ $[M]^+$ 223.00, found 222.90.



N-(4-Chlorophenyl)benzamide (2g): The title compound was isolated as a white solid after chromatography on silica gel (PE/EA = 5:1) with the yield of (14.1 mg, 61%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether, and (12.2 mg, 53%) after reaction for 36 h according to general procedure for the desulfurizing chlorination with natural seawater. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 10.39 (s, 1H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 165.7, 138.2, 134.7, 131.7, 128.5, 128.4, 127.7, 127.3, 121.9. GC-MS (EI$^+$): calcd for $C_{13}H_{10}ClNO$ [M]$^+$ 231.05, found 231.00.

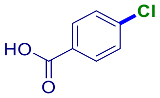


4-Chlorophenyl benzoate (2h): The title compound was isolated as a white solid after chromatography on silica gel (PE/EA = 10:1) with the yield of (16.9 mg, 73%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether, and (13.9 mg, 60%) after reaction for 36 h according to general procedure for the desulfurizing chlorination with natural seawater. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.20 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 165.1, 149.5, 133.9, 131.4, 130.3, 129.7, 129.3, 128.8, 123.2. GC-MS (EI$^+$): calcd for $C_{13}H_9ClO_2$ [M]$^+$ 232.03, found 232.00.

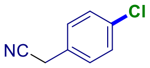


4-Chlorophenyl benzoate (2i): The title compound was isolated (11.4 mg, 74%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether as a colorless oil after chromatography on silica gel (PE/EA = 10:1). ^{1}H

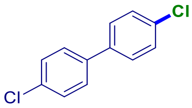
NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 139.7, 135.5, 129.8, 129.0, 26.7. GC-MS (EI^+): calcd for C_8H_7ClO $[M]^+$ 154.02, found 154.05.



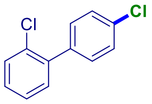
4-Chlorobenzoic acid (2j): The title compound was isolated (14.2 mg, 91%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether as a white solid after chromatography on silica gel (PE/EA/Acetic acid = 50:25:1). ^1H NMR (400 MHz, DMSO-d_6): δ 13.18 (br, s, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.5, 137.9, 131.2, 129.7, 128.8. GC-MS (EI^+): calcd for $C_7H_5ClO_2$ $[M]^+$ 156.00, found 156.00.



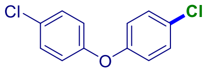
2-(4-Chlorophenyl)acetonitrile (2l): The title compound was isolated (6.4 mg, 42%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether as a pink oil after chromatography on silica gel (PE/EA = 3:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 3.72 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.2, 129.4, 129.4, 128.5, 117.6, 23.2. GC-MS (EI^+): calcd for C_8H_6ClN $[M]^+$ 151.02, found 151.05.



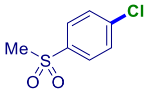
4,4'-Dichloro-1,1'-biphenyl (2m): The title compound was isolated as a white solid after chromatography on silica gel (PE/EA = 50:1) with the yield of (16.9 mg, 76%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether, (12.4 mg, 56%) after reaction of **1ab** for 36 h according to general procedure for the desulfurizing chlorination of diaryl thioether, and (17.3 mg, 78%) after reaction for 36 h according to general procedure for the desulfurizing chlorination with natural seawater. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 8.4 Hz, 4H), 7.41 (d, J = 8.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 133.9, 129.2, 128.4. GC-MS (EI$^+$): calcd for $C_{12}H_8Cl_2$ $[M]^+$ 222.00, found 221.95.



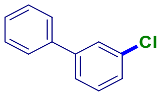
2,4'-Dichloro-1,1'-biphenyl (2n): The title compound was isolated (20.9 mg, 94%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether as a colorless thick oil after chromatography on silica gel (PE/EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 1H), 7.43-7.37 (m, 4H), 7.32-7.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 137.9, 133.9, 132.6, 131.3, 130.9, 130.2, 129.0, 128.4, 127.1. GC-MS (EI$^+$): calcd for $C_{12}H_8Cl_2$ $[M]^+$ 222.00, found 221.95.



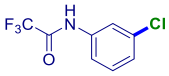
4,4'-Oxybis(chlorobenzene) (2o): The title compound was isolated (13.8 mg, 58%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether as a colorless oil after chromatography on silica gel (PE/EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.8 Hz, 4H), 6.93 (d, J = 8.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 130.0, 128.8, 120.2. GC-MS (EI$^+$): calcd for $C_{12}H_8Cl_2O$ $[M]^+$ 238.00, found 237.95.



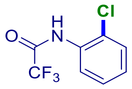
1-Chloro-4-(methylsulfonyl)benzene (2p): The title compound was isolated (7.0 mg, 37%) after reaction for 12 h according to general procedure for the desulfurizing chlorination of aryl thioether as a white solid after chromatography on silica gel (PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 3.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 139.1, 129.9, 129.1, 44.7. GC-MS (EI$^+$): calcd for $C_7H_7ClO_2S$ $[M]^+$ 189.99, found 189.95.



3-Chloro-1,1'-biphenyl (2r): The title compound was isolated (8.5 mg, 45%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether as a yellow oil after chromatography on silica gel (PE/EA = 50:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.59-7.56 (m, 3H), 7.49-7.43 (m, 3H), 7.40-7.32 (m, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 143.2, 140.0, 137.6, 134.8, 130.1, 129.0, 128.0, 127.4, 127.4, 125.4. GC-MS (EI$^+$): calcd for $C_{12}H_9Cl$ [M]$^+$ 188.04, found 187.95.

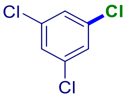


***N*-(3-Chlorophenyl)-2,2,2-trifluoroacetamide (2s):** The title compound was isolated (12.3 mg, 55%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether as a white acicular solid after chromatography on silica gel (PE/EA = 10:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.03 (s, 1H), 7.68 (t, J = 2.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 155.0 (q, J_{CF} = 37.4 Hz), 136.3, 135.3, 130.5, 126.7, 120.9, 118.7, 115.7 (q, J_{CF} = 287.1 Hz). ^{19}F NMR (376 MHz, CDCl$_3$): δ -75.7. GC-MS (EI$^+$): calcd for $C_8H_5ClF_3NO$ [M]$^+$ 223.00, found 222.95.

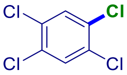


***N*-(2-Chlorophenyl)-2,2,2-trifluoroacetamide (2v):** The title compound was isolated (14.5 mg, 65%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether as a white acicular solid after chromatography on silica gel (PE/EA = 10:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.44 (s, 1H), 8.31 (dd, J = 8.4, 1.6 Hz, 1H), 7.44 (dd, J = 8.0, 1.6 Hz, 1H), 7.34 (td, J = 8.0, 2.0 Hz, 1H), 7.18 (td, J = 8.0, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.8 (q, J_{CF} = 37.5 Hz), 132.2, 129.5, 128.2, 126.9, 123.9, 122.0, 115.7 (q, J_{CF} = 286.8 Hz). ^{19}F NMR

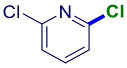
(376 MHz, $CDCl_3$): δ -75.8. GC-MS (EI^+): calcd for $C_8H_5ClF_3NO$ $[M]^+$ 223.00, found 222.90.



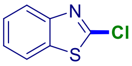
1,3,5-Trichlorobenzene (2w): The title compound was isolated (13.9 mg, 77%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether as a white solid after chromatography on silica gel (PE/EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.7, 127.4. GC-MS (EI^+): calcd for $C_6H_3Cl_3$ $[M]^+$ 179.93, found 179.95.



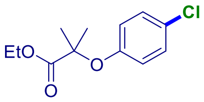
1,2,4,5-Tetrachlorobenzene (2y): The title compound was isolated (15.3 mg, 71%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether as a white solid after chromatography on silica gel (PE/EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.8, 131.4. GC-MS (EI^+): calcd for $C_6H_2Cl_4$ $[M]^+$ 215.89, found 215.95.



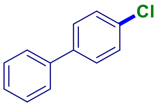
2,6-Dichloropyridine (2z): The title compound was isolated (6.5 mg, 44%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether as a white solid after chromatography on silica gel (PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 140.8, 123.0. GC-MS (EI^+): calcd for $C_5H_3Cl_2N$ $[M]^+$ 146.96, found 147.05.



2-Chlorobenzo[d]thiazole (2aa): The title compound was isolated (6.9 mg, 41%) after reaction for 24 h according to general procedure for the desulfurizing chlorination of aryl thioether as a pink oil after chromatography on silica gel (PE/EA = 50:1 to 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, J = 8.0, 0.8 Hz, 1H), 7.76 (dd, J = 8.0, 0.8 Hz, 1H), 7.47 (td, J = 7.6, 1.6 Hz, 1H), 7.39 (td, J = 8.0, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 151.1, 136.2, 126.8, 125.9, 123.0, 121.2. GC-MS (EI$^+$): calcd for C_7H_4ClNS $[M]^+$ 168.98, found 169.00.



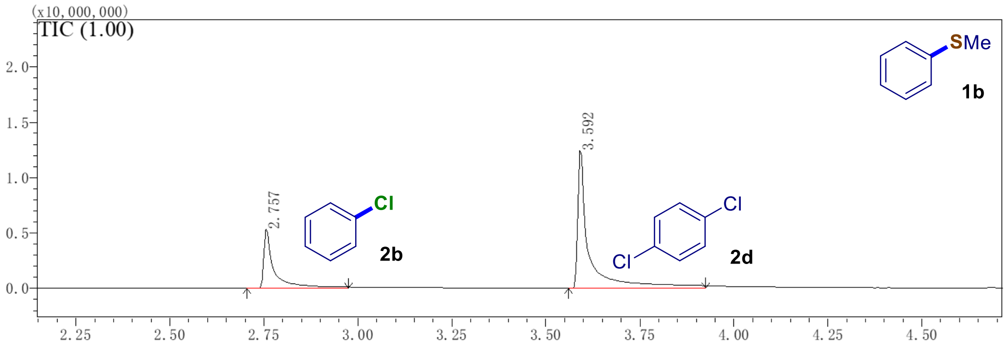
Ethyl 3-(4-chlorophenyl)-2,2-dimethylpropanoate (2ac): The title compound was isolated (10.8 mg, 45%) after reaction for 36 h according to general procedure for the desulfurizing chlorination of aryl thioether as a yellow oil after chromatography on silica gel (PE/EA = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, J = 9.2 Hz, 2H), 6.77 (d, J = 9.2 Hz, 2H), 4.22 (q, J = 7.2 Hz, 2H), 1.57 (s, 6H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 154.1, 129.2, 127.3, 120.6, 79.5, 61.6, 25.4, 14.2. GC-MS (EI$^+$): calcd for $C_{12}H_{15}ClO_3$ $[M]^+$ 242.07, found 242.05.



4-Chloro-1,1'-biphenyl (2ai): The title compound was isolated (10.0 mg, 53%) after reaction for 48 h according to general procedure for the desulfurizing chlorination of diaryl thioether as a white solid after chromatography on silica gel (PE/EA = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.55 (m, 2H), 7.55-7.52 (m, 2H), 7.48-7.44 (m, 2H), 7.43-7.41 (m, 2H), 7.40-7.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 139.8, 133.5, 129.1, 129.0, 128.5, 127.7, 127.1. GC-MS (EI$^+$): calcd for $C_{12}H_9Cl$ $[M]^+$ 188.04, found 188.00.

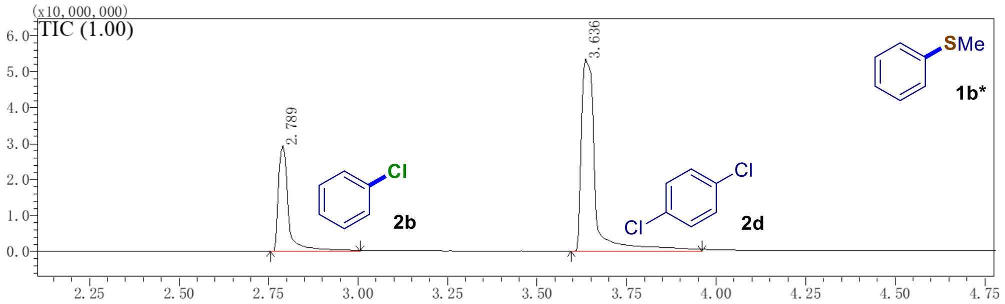
b) Selected GC-MS data for the volatile aryl chlorides

GC measuring method: Helium gas was used as carrier gas at a constant flow rate of 1.0 mL/min. Before the separation, the temperature of the chromatographic column was progressively increased as follows: (i) initial temperature at 50 ºC for 1 min, (ii) 50 ºC to 280 ºC at a rate of 35 ºC/min, and (iii) holding for 2 mins at 280 ºC. The reactions were carried according to the general procedure for iron-photocatalyzed desulfurizing chlorination of aryl thioethers. The reactions (**1b**, **1d-1e**, **1k**, **1q**, **1ad-1ah**, **3d-3e**, **6**) required 0.1 mmol (1 mmol) internal standard, while (**3a-3c**, **5a-5b**) required 0.2 mmol internal standard, and (**5c**) required 0.3 mmol. The yields were obtained according to the equation (P = peak area, A = Amount of substance): (i) $P_{2d/2b} = 2.1135{*}A_{2d/2b} - 0.0267$, $R^2 = 0.9983$, (ii) $P_{2d/2e} = 1.3622{*}A_{2d/2e} - 0.0608$, $R^2 = 0.9900$, (iii) $P_{2d/2k} = 0.9447{*}A_{2d/2k} + 0.2768$, $R^2 = 0.9985$, (iv) $P_{2b/2q} = 0.3720{*}A_{2b/2q} + 0.0922$, $R^2 = 0.9973$, (v) $P_{2b/2t} = 0.3398{*}A_{2b/2t} + 0.1229$, $R^2 = 0.9928$, (vi) $P_{2b/2ah} = 0.4662{*}A_{2b/2ah} + 0.0068$, $R^2 = 0.9993$.



	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.757	10119100	28.89	86
2d	3.592	24910254	71.11	/

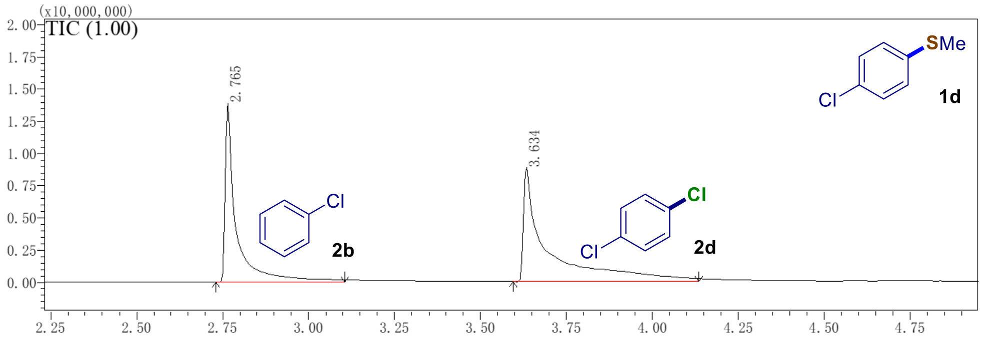
Figure S3. GC spectra for standard reaction of **1b** with internal standard **2d** for 12 h



	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.789	58591320	28.32	82

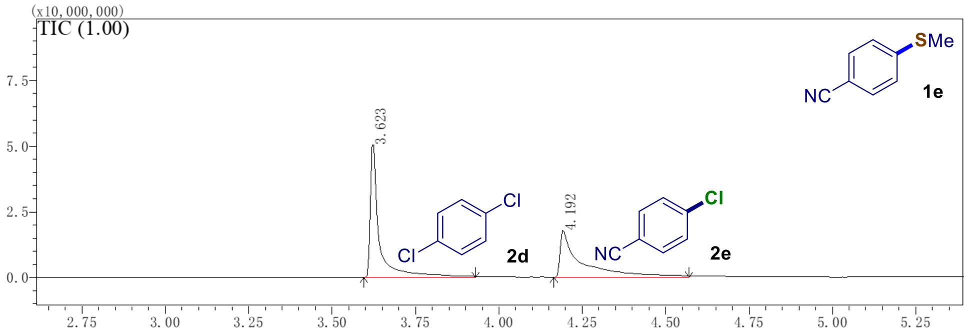
2d	3.636	148298934	71.68	/

Figure S4. GC spectra for the reaction of **1b** (1.0 mmol) with internal standard **2d** for 24 h



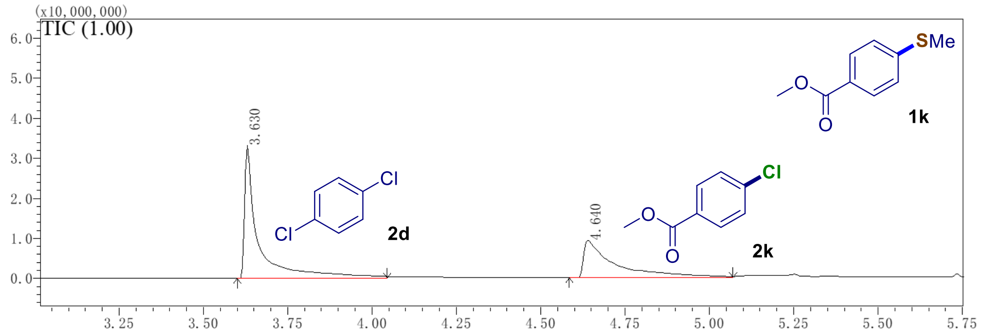
	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.765	31184529	40.92	/
2d	3.634	45026845	59.08	83

Figure S5. GC spectra for standard reaction of **1d** with internal standard **2b** for 24 h



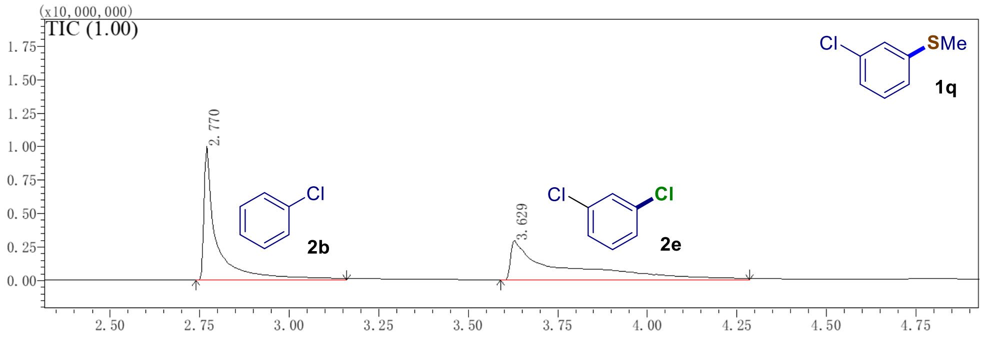
	Peak time	Peak area	Peak area (%)	GC yield (%)
2d	3.623	98258557	64.86	/
2e	4.192	53234747	35.14	68

Figure S6. GC spectra for standard reaction of **1e** with internal standard **2d** for 24 h



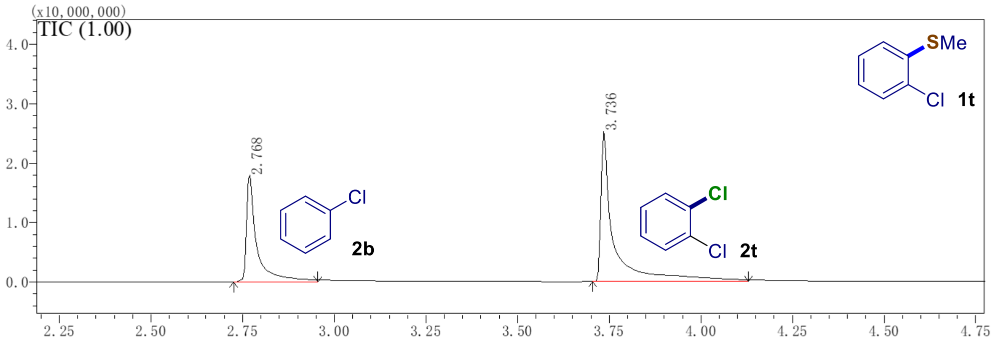
	Peak time	Peak area	Peak area (%)	GC yield (%)
2d	3.630	98177014	57.52	/
2k	4.640	72506251	42.48	87

Figure S7. GC spectra for standard reaction of **1k** with internal standard **2d** for 24 h



	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.770	25624032	41.45	/
2q	3.629	36195104	58.55	64

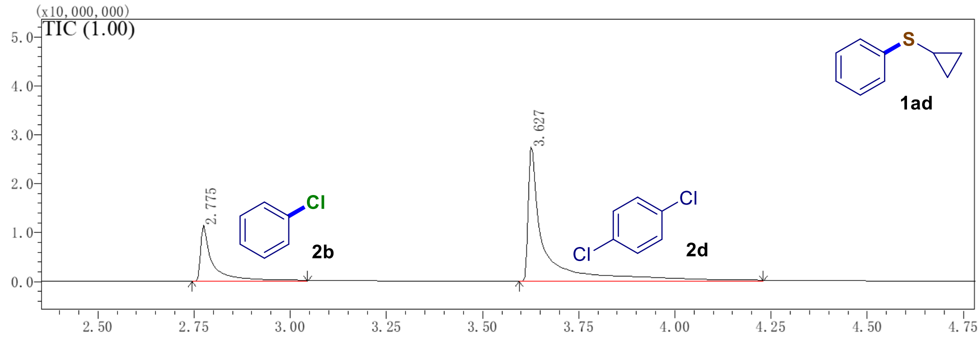
Figure S8. GC spectra for standard reaction of **1q** with internal standard **2b** for 24 h



	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.768	33389534	33.48	/

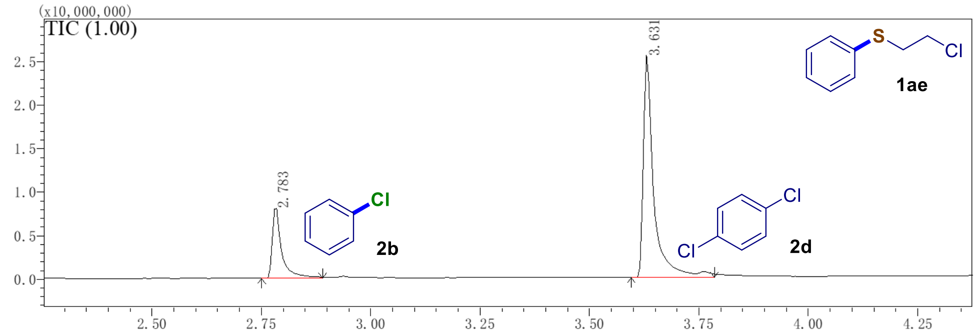
2t	3.736	66340256	66.52	90

Figure S9. GC spectra for standard reaction of **1t** with internal standard **2b** for 24 h



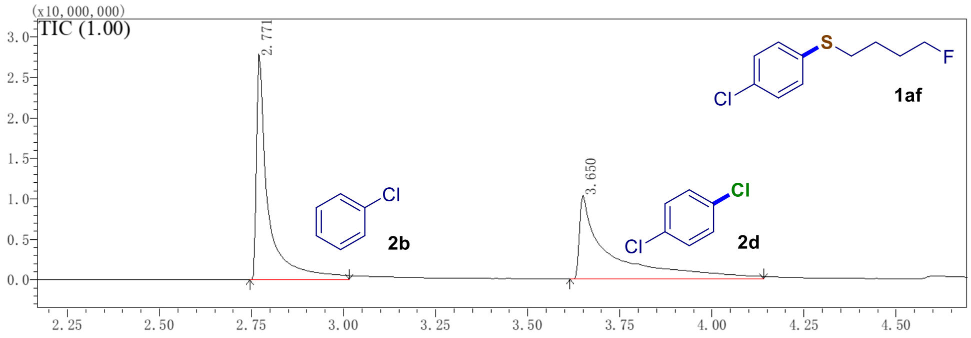
	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.775	27922145	25.87	72
2d	3.627	80010383	74.13	/

Figure S10. GC spectra for standard reaction of **1ad** and internal standard **2d** for 24 h



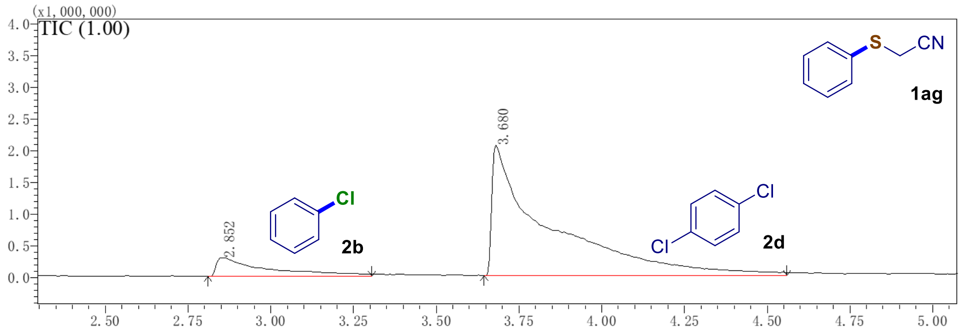
	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.783	12258634	23.43	66
2d	3.631	40061613	76.57	/

Figure S11. GC spectra for standard reaction of **1ae** and internal standard **2d** for 24 h



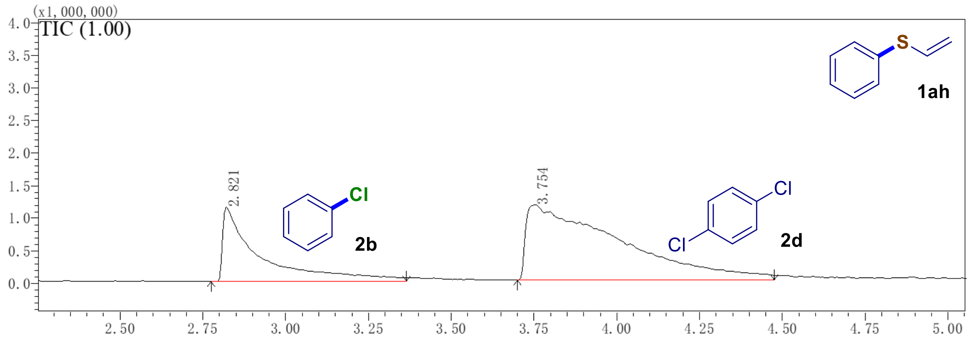
	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.771	62203742	51.29	/
2d	3.650	59074756	48.71	52

Figure S12. GC spectra for standard reaction of **1af** and internal standard **2b** for 24 h



	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.852	1504763	14.05	34
2d	3.680	9205294	85.95	/

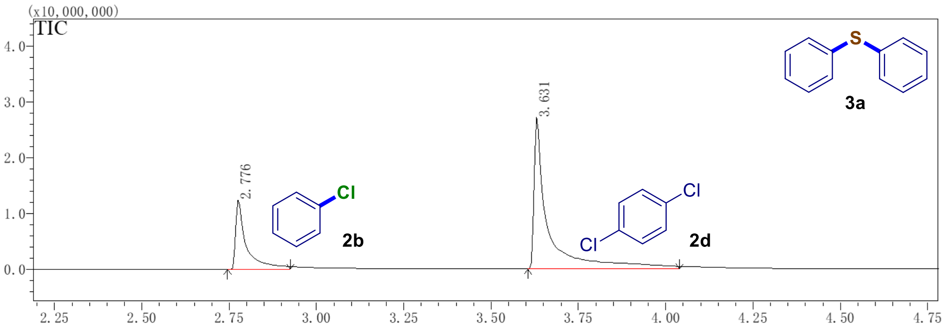
Figure S13. GC spectra for standard reaction of **1ag** and internal standard **2d** for 24 h



	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.821	8886269	28.27	80

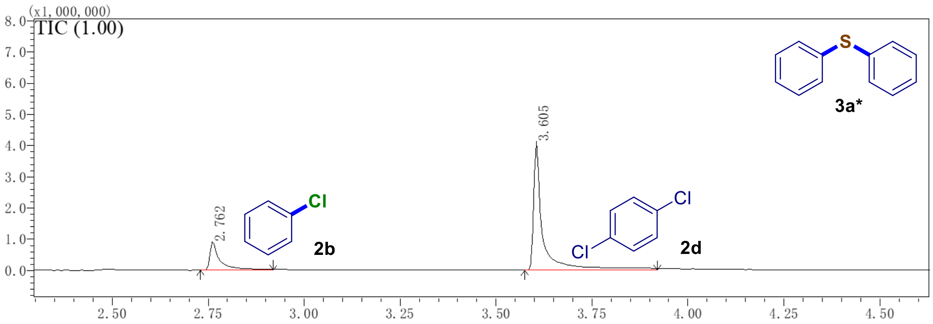
2d	3.754	22547296	71.73	/

Figure S14. GC spectra for standard reaction of **1ah** and internal standard **2d** for 24 h



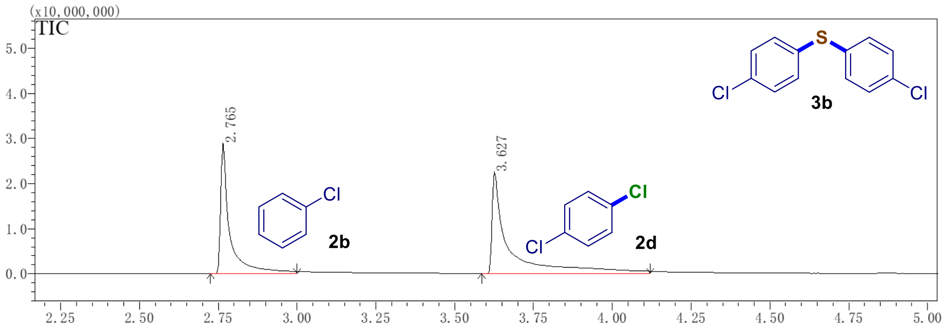
	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.776	26694226	26.95	78
2d	3.631	72356705	73.05	/

Figure S15. GC spectra for standard reaction of **3a** with internal standard **2d** for 36 h



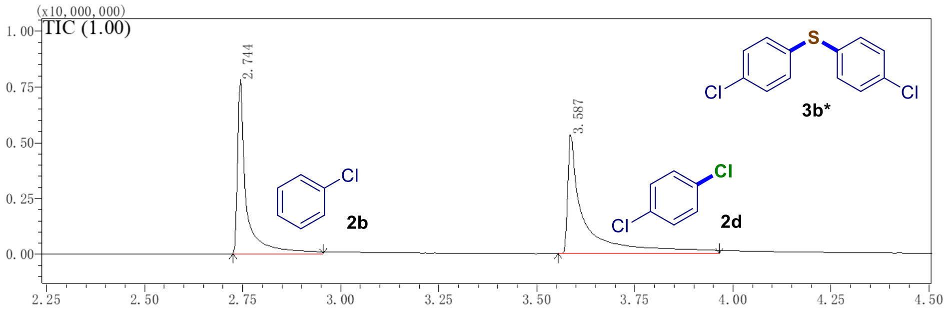
	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.762	1762724	23.68	65
2d	3.605	5681212	76.32	/

Figure S16. GC spectra for the reaction of **3a** by seawater (4.0 equiv) with internal standard **2d** for 36 h



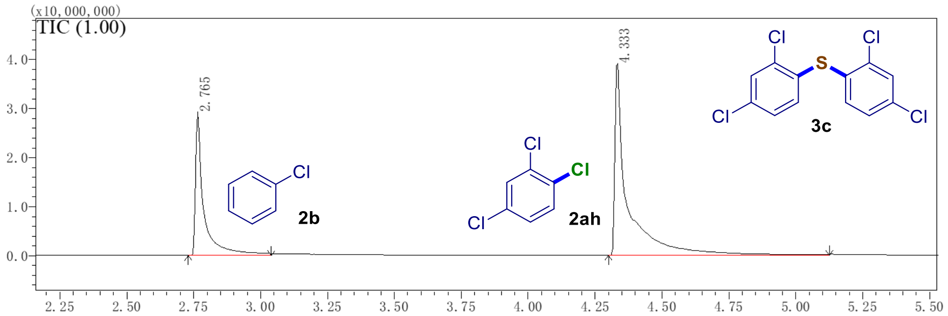
	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.765	59519458	41.42	/
2d	3.627	84177929	58.58	78

Figure S17. GC spectra for standard reaction of **3d** with internal standard **2b** for 36 h



	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.744	12331539	43.24	/
2d	3.587	16188416	56.76	72

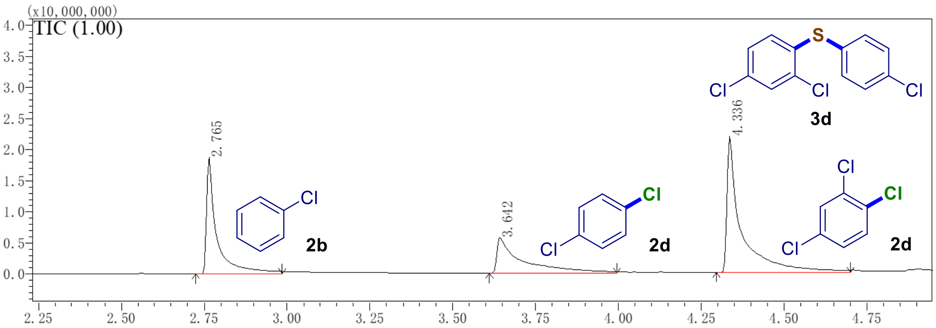
Figure S18. GC spectra of the reaction of **3b** by natural seawater with internal standard **2b** for 36 h



	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.765	63467312	34.46	/

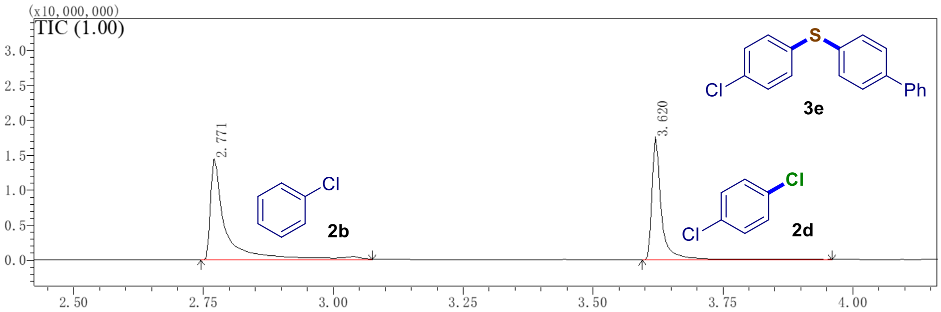
2ah	4.333	120709449	65.54	92

Figure S19. GC spectra for the reaction of **3c** with internal standard **2b** for 36 h



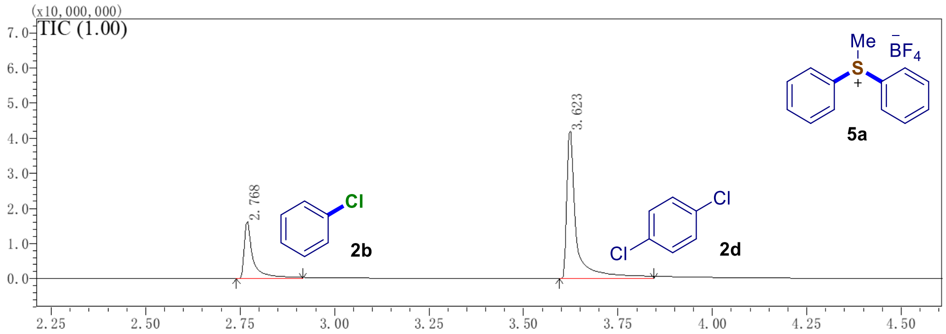
	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.765	33954426	29.26	/
2d	3.642	29953149	21.93	45
2ah	4.336	66652778	48.81	73

Figure S20. GC spectra for standard reaction of **3d** with internal standard **2b** for 36 h



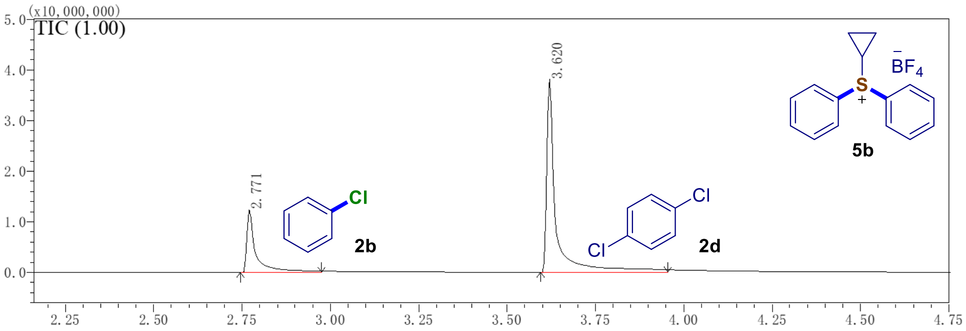
	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.771	30901406	56.91	/
2d	3.620	23395806	43.09	45

Figure S21. GC spectra for standard reaction of **3e** with internal standard **2b** for 48 h



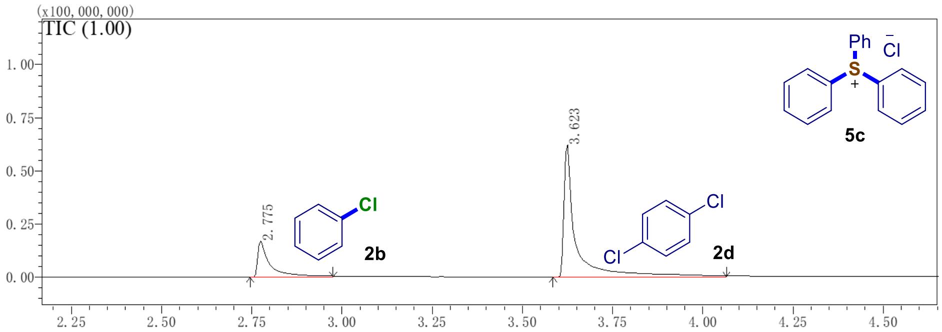
	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.768	27545972	27.82	80
2d	3.623	71469024	72.18	/

Figure S22. GC spectra for standard reaction of **5a** with internal standard **2d** for 36 h



	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.771	22370045	24.27	69
2d	3.620	66529453	72.18	/

Figure S23. GC spectra for standard reaction of **5b** with internal standard **2d** for 36 h



	Peak time	Peak area	Peak area (%)	GC yield (%)
2b	2.775	26548827	23.88	66

2d	3.623	84627166	76.12	/

Figure S24. GC spectra for standard reaction of **5c** with internal standard **2d** for 36 h

c) Selected ^{19}F NMR data for volatile fluorine-containing aryl chlorides

The reactions were carried according to the general procedure for iron-photocatalyzed desulfurizing chlorination of aryl thioethers. 100 µL of the organic phase (upper layer) was taken after reaction, diluted with $CDCl_3$ and measured by ^{19}F NMR (376 MHz). The reactions (**1c**, **1u**, **1x**) required 0.1 mmol *para*-fluorotoluene added as the internal standard, while **1f** required 0.05 mmol 1,4-bis(trifluoromethyl)-benzene as the internal standard.

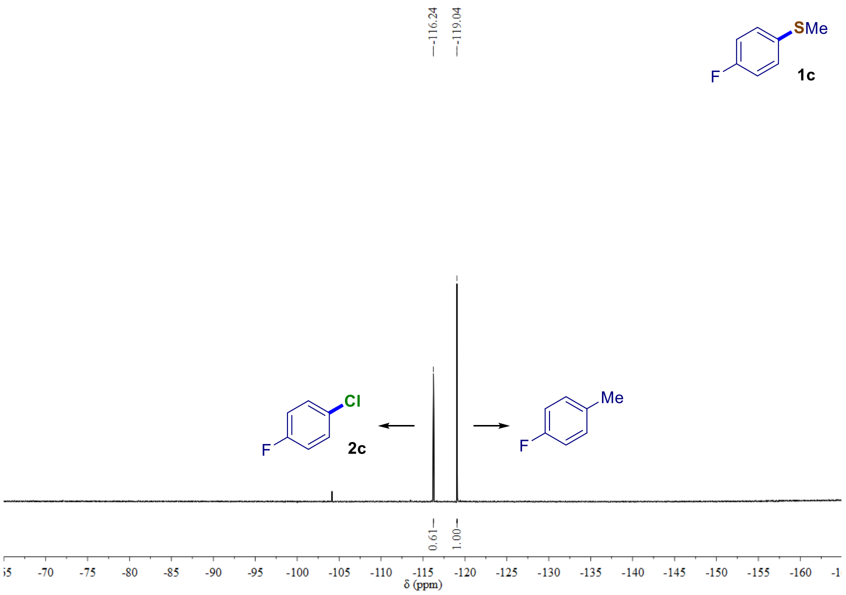


Figure S25. ^{19}F NMR spectra for the reaction of **1c** with 4-fluorotoluene for 24 h

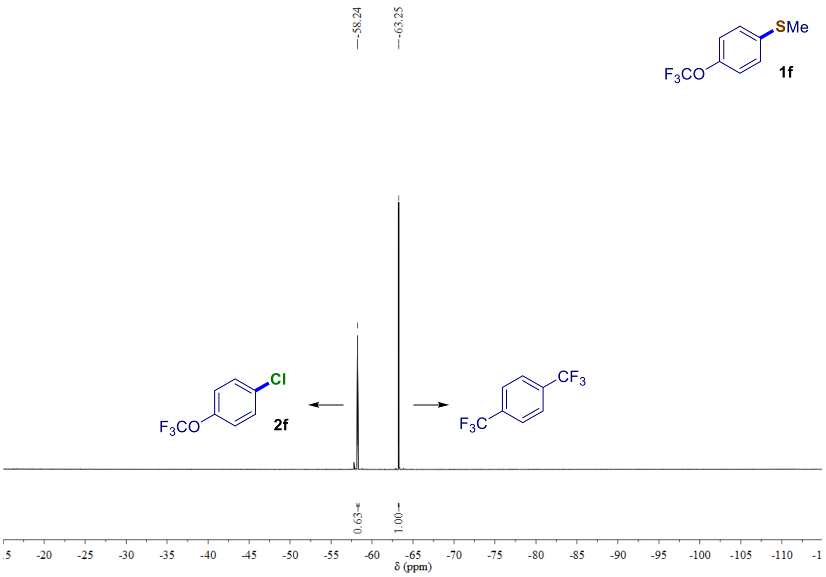


Figure S26. ^{19}F NMR spectra for the reaction of **1f** with 1,4-bis(trifluoromethyl)-benzene for 24 h

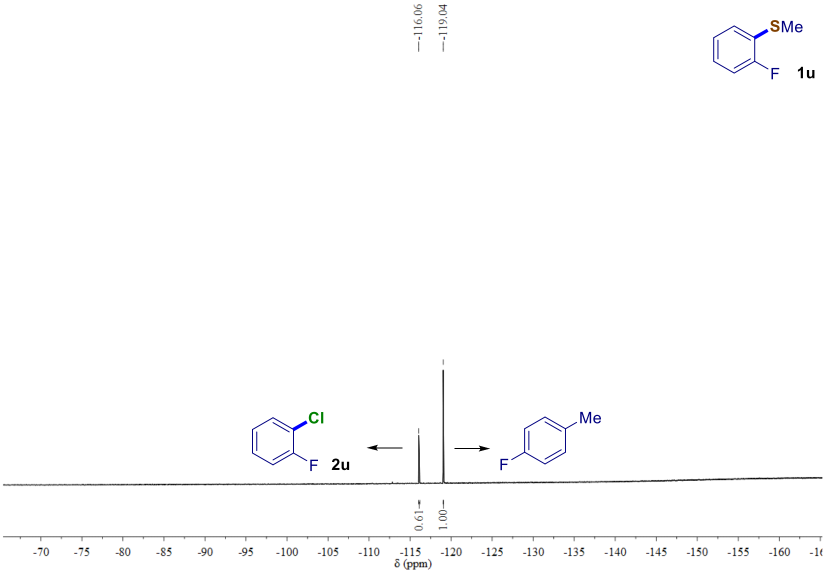


Figure S27. ^{19}F NMR spectra for the reaction of **1u** with 4-fluorotoluene for 24 h

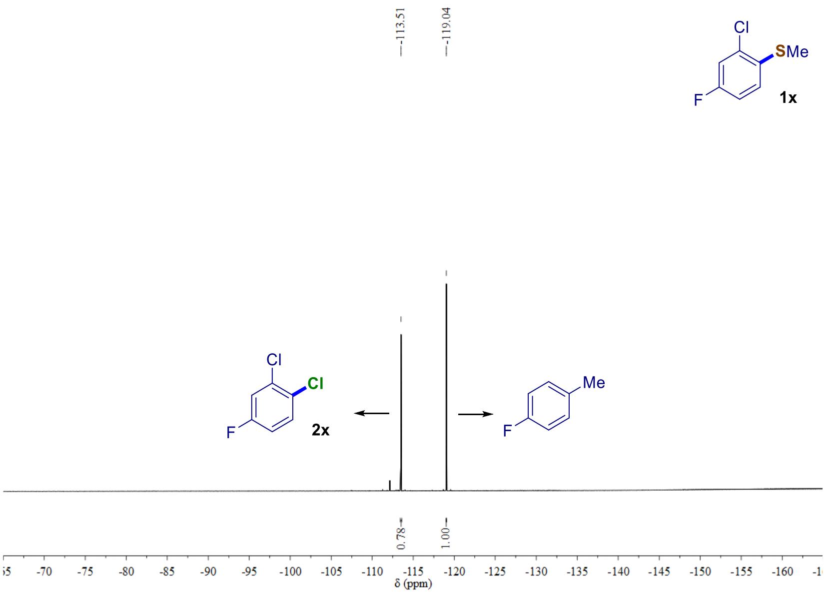
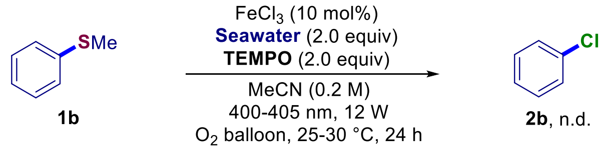


Figure S28. ^{19}F NMR spectra for the reaction of **1x** with 4-fluorotoluene for 36 h

Mechanism study

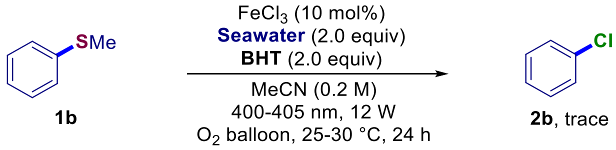
a) Radical quenching experiments

(i) The reaction of **1b** with 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO)



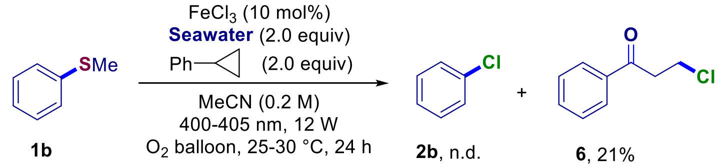
According to general procedure for iron-photocatalyzed desulfurizing chlorination of aryl thioethers, **1b** (0.1 mmol), $FeCl_3$ (10 mol%, 0.02 M in CH_3CN, 0.5 mL), seawater (0.2 mmol, salinity: 35‰, ~ 0.55 M chloride, 370 μL), and TEMPO (0.2 mmol, 31.3 mg) were used. No **2b** was obtained as detected by GC-MS.

(ii) The reaction of **1b** with butylated hydroxytoluene (BHT)



For iron-photocatalyzed desulfurizing chlorination of thioethers, **1b** (0.1 mmol), $FeCl_3$ (10 mol%, 0.02 M in CH_3CN, 0.5 mL), seawater (0.2 mmol, salinity: 35‰, ~ 0.55 M chloride, 370 μL), and BHT (0.2 mmol, 44.2 mg) were used. Trace amount of **2b** was obtained as detected by GC-MS.

(iii) the reaction of **1b** with the addition of cyclopropyl benzene



According to general procedure for the desulfurizing chlorination of aryl thioethers, **1b** (0.1 mmol), $FeCl_3$ (10 mol%, 500 μL of 0.02 M $FeCl_3$ in CH_3CN solution), seawater (salinity: 35‰, ~ 0.55 M chloride, 370 μL), and cyclopropylbenzene (0.2 mmol, 23.6 mg) were added. The reaction mixture was stirred under blue LEDs (400-405 nm, 12 W) at 25-30 ºC for 24 h. No **2b** was obtained as detected by GC-MS, while 3-chloropropiophenone **6** was isolated (7.0 mg, 21%) as a white solid by chromatography on silica gel (PE/EA = 50:1 to 10:1), suggesting the generation of chlorine radicals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 7.2 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 3.93 (t, J = 6.8 Hz, 2H), 3.47 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 136.5, 133.7, 128.9, 128.2, 41.4, 38.8. GC-MS (EI$^+$): calcd for C_9H_9ClO $[M]^+$ 168.03, found 168.00.

b) EPR experiments

The samples for EPR experiments were transferred into a capillary column (20 cm), sealed with high vacuum grease, which was then put into a quartz tube and measured at room temperature. (Data was acquired on a BrukerA300 spectrometer operating at 9.449 GHz with a microwave power of 0.629 mW and a modulation amplitude of 1 Gauss.).

(i) Detection of the chlorine radical and hydroxide radical

According to general procedure for the desulfurizing chlorination of aryl thioethers, **1a** (0.1 mmol), $FeCl_3$ (10 mol%, 500 μL of 0.02 M $FeCl_3$ in CH_3CN solution), seawater (salinity: 35‰, ~ 0.55 M chloride, 370 μL), and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, 0.12 mmol) were used. The reaction mixture was measured by EPR before irradiation and no obvious signal was obtained (**Figure S29**, top). Then the reaction mixture was stirred under the irradiation of blue LEDs (400-405 nm, 12 W) at 25-30 ºC for 10 mins, followed by the addition of H_2O (5.0 mL). Further EPR experiment indicated generations of the chloride radical and hydroxide radical (**Figure S29**, bottom).

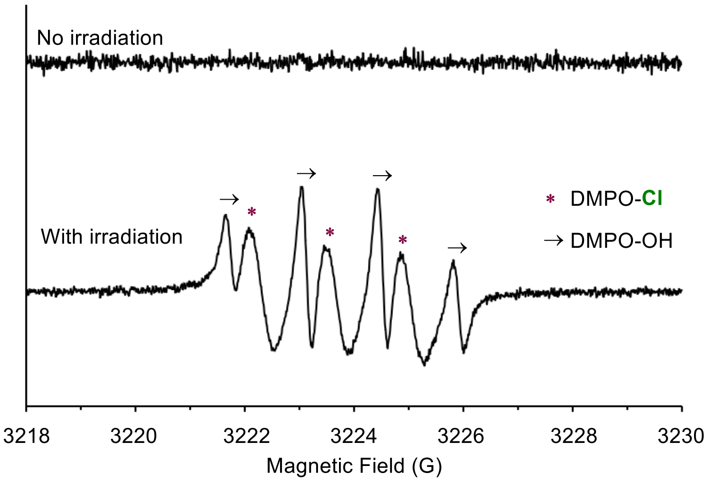


Figure S29. EPR spectrum for detection of chloride radicals

(ii) Detection of superoxide radicals

According to general procedure for the desulfurizing chlorination of aryl thioethers, **1a** (0.1 mmol), $FeCl_3$ (10 mol%, 500 μL of 0.02 M $FeCl_3$ in CH_3CN solution), seawater (salinity: 35‰, ~ 0.55 M chloride, 370 μL), and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, 0.12 mmol). The reaction mixture was measured by EPR before irradiation and no obvious signal was obtained (**Figure S30**, top). Then the reaction mixture was stirred under the irradiation of blue LEDs (400-405 nm, 12 W) at 25-30 ºC for 10 mins, followed by the addition of methanol (2.0 mL). Further EPR experiment indicated generation of the superoxide radical (**Figure S30**, bottom).

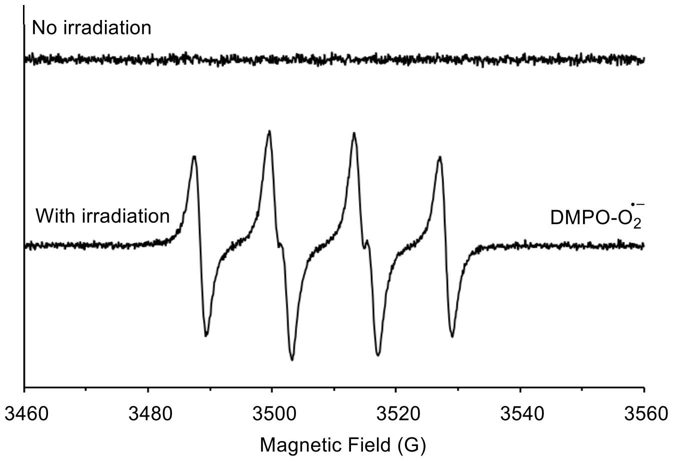


Figure S30. EPR spectrum for detection of superoxide radicals

c) UV-Vis spectra:

$FeCl_3$ and **1a** were dissolved in CH_3CN, seawater, or CH_3CN/seawater mixed solution (5:4, v/v) with the concentration of $1*10^{-4}$ M. UV-Vis spectroscopy for the solutions of **1a**, $FeCl_3$, $FeCl_3$+**1a** in CH_3CN/seawater mixed solution and $FeCl_3$ in CH_3CN or seawater were obtained in Figure S31. UV-Vis spectroscopy revealed two emission peaks (λ_{max}) at 312 nm and 363 nm for $FeCl_3$ in CH_3CN, whereas such peaks were observed with sharp decreased intensity for iron chloride in seawater and mixed solution. Further experiments indicated that no interaction occurred between **1a** and $FeCl_3$. These results demonstrated that the reaction might involve an immiscible liquid-liquid interface model, with iron chloride as the photosensitizer.

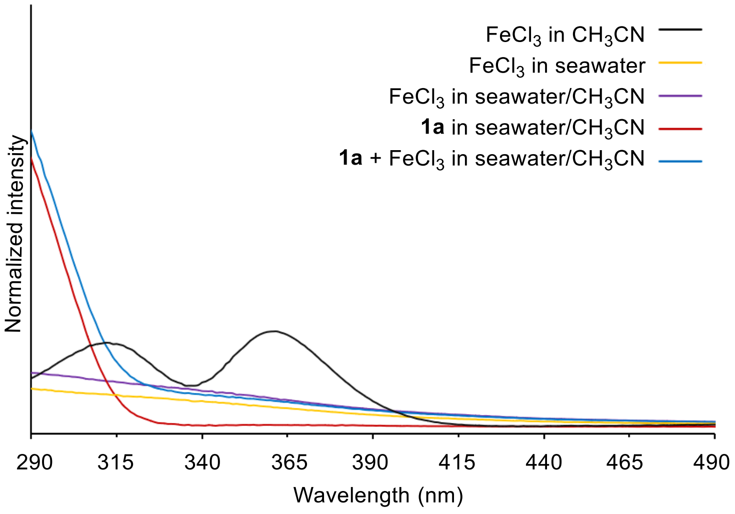


Figure S31. UV-Vis absorption spectrums

d) Light-on-off experiments:

According to general procedure for the desulfurizing chlorination of aryl thioethers, **1a** (0.1 mmol), $FeCl_3$ (10 mol%, 500 μL of 0.02 M $FeCl_3$ in CH_3CN solution), seawater (salinity: 35‰, ~ 0.55 M chloride, 370 μL), and internal standard **1d** (0.1 mmol) were added. The reaction mixture was stirred with or without irradiation under blue LEDs (400-405 nm, 12 W) at 25-30 ℃. 5 μL of the solution was drawn at intervals for 1 hours, diluted immediately with ethyl acetate and measured by GC-MS analysis to determine the yields of **2a**. The results were summarized in **Figure S32**, excluding the radical chain mechanism of this reaction. The yields were obtained according to the equation (P = peak area, A = Amount of substance): $P_{\mathbf{2a/2d}} = 1.1064*A_{\mathbf{2d/2a}}-0.0971$, $R^2 = 0.9927$.

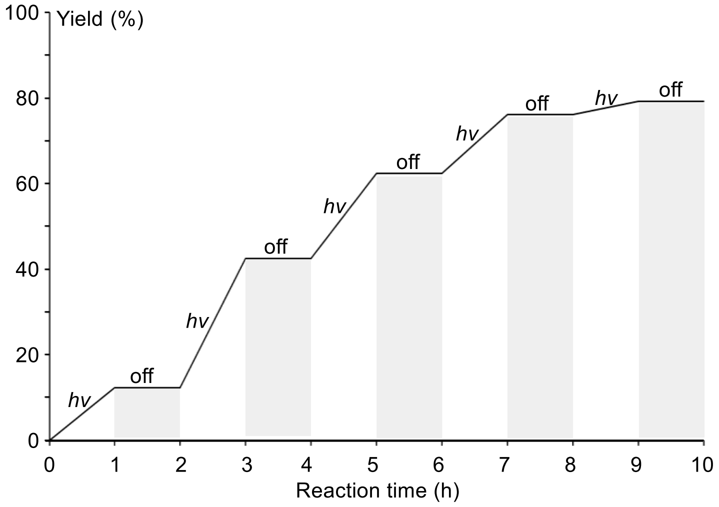
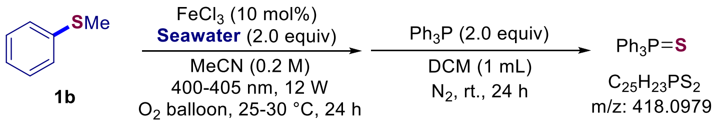


Figure S32. Reaction profile for the reaction of **1a** with light on/off

e) Control experiments to trap the leaving sulfur

(i) Detection of sulfur by GC-MS:



According to general procedure for the desulfurizing chlorination of aryl thioethers, **1b** (0.1 mmol), $FeCl_3$ (10 mol%, 500 μL of 0.02 M $FeCl_3$ in CH_3CN solution), and seawater (salinity: 35‰, ~ 0.55 M chloride, 370 μL). The reaction mixture was stirred under blue LEDs (400-405 nm, 12 W) at 25-30 ℃ for 24 h. After removing the solvent, triphenylphosphine (0.2 mmol, 52.4 mg) and dichloromethane (1 mL) was added under a N_2 atmosphere. The mixture was stirred for another 24 h at room temperature. Triphenylphosphine sulfide was detected by GC-MS (**Figure S33**), which probably indicated that S (0) was formed in the reaction.[10]

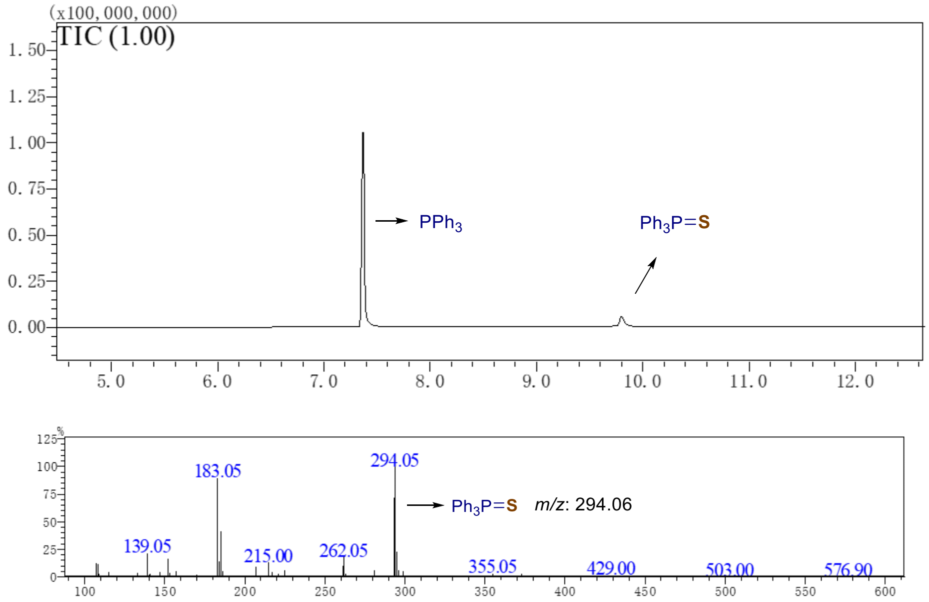
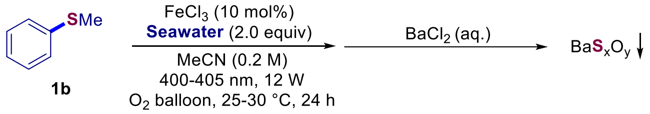


Figure S33. Detection of triphenylphosphine sulfide by GC-MS

(ii) Detection of hypervalent sulfur-containing anions



According to general procedure for the desulfurizing chlorination of aryl thioethers, **1b** (0.1 mmol), $FeCl_3$ (10 mol%, 500 μL of 0.02 M $FeCl_3$ in CH_3CN solution), NaCl (11.7 mg, 0.2 mmol, 2 equiv) and distilled water (370 μL) were added. Several control reactions were performed (**Figure S34**).

(a) Before light irradiation, no precipitate was generated when treating the reaction mixture with $BaCl_2$ solution (0.5 M, 1 mL).

(b) After light irradiation for 24 h, white precipitate was formed rapidly when treating the reaction mixture with $BaCl_2$ solution (0.5 M, 1 mL), which cannot be dissolved in HCl (1.0 M, 1 mL).

(c) After light irradiation for 24 h, no precipitate was observed when treating the residual organic layer with $BaCl_2$ solution (0.5 M, 1 mL).

(d) After the solution without **1b** was performed under light irradiation for 24 h, the aqueous phase (lower layer) was treated with $BaCl_2$ solution (0.5 M, 1 mL). No precipitate was observed.

These results that hypervalent sulfur-containing anion species ($S_xO_y^{2-}$) were probably produced via further oxidation of leaving "RS" group.

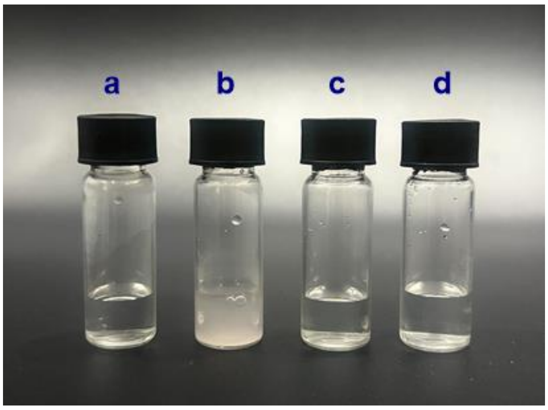
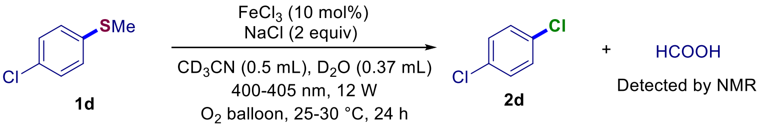


Figure S34. Detection of hypervalent sulfur-containing anion species by $BaCl_2$

f) Control experiments to trap the leaving "RS" group

(i) Detection of formic acid by NMR



According to general procedure for the desulfurizing chlorination of aryl thioethers, **1d** (0.1 mmol), $FeCl_3$ (10 mol%, 500 μL of 0.02 M $FeCl_3$ in CD_3CN-*d*$_3$ solution), NaCl (11.7 mg, 0.2 mmol, 2 equiv) and D_2O (370 μL) were added. The reaction mixture was stirred under blue LEDs (400-405 nm, 12 W) at 25-30 ºC for 24 h, and then examined by ^1H NMR and ^{13}C NMR analysis, respectively. The peaks observed at 8.05 ppm for ^1H NMR spectrum and 162.6 ppm for ^{13}C NMR spectrum were assigned to formic acid (**Figure S35** and **S36**).

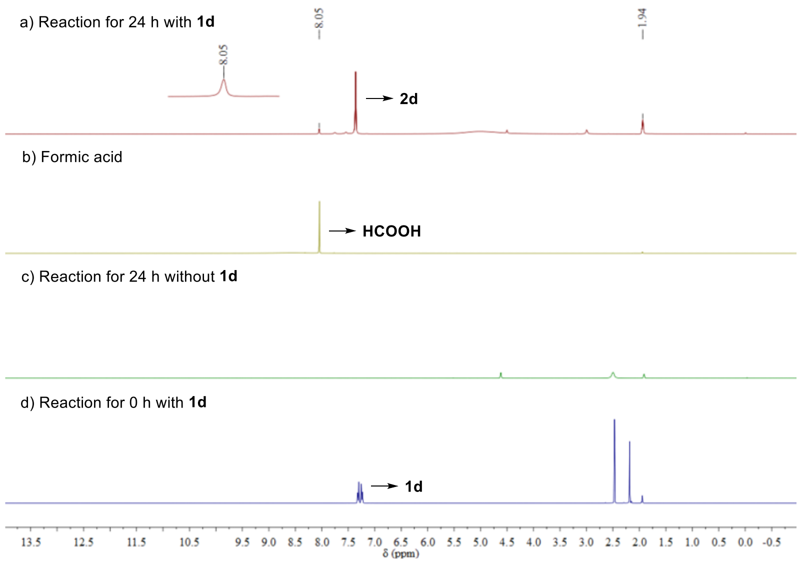


Figure S35. Detection of formic acid by ^{1}H NMR (400 MHz)

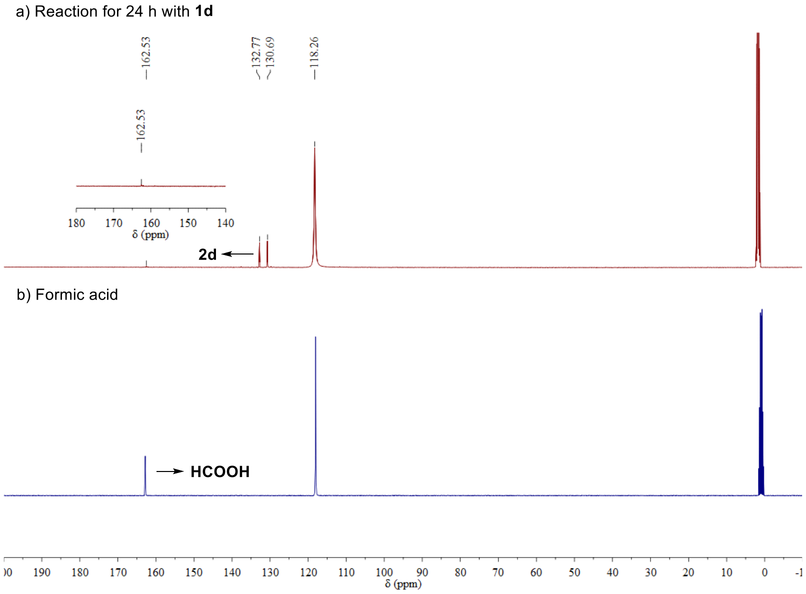


Figure S36. Detection of formic acid by ^{13}C NMR (125 MHz)

(ii) pH test of the residual aqueous phase

According to general procedure for the desulfurizing chlorination of aryl thioethers, **1b** (0.1 mmol), $FeCl_3$ (10 mol%, 500 μL of 0.02 M $FeCl_3$ in CH_3CN solution), and seawater (salinity: 35‰, ~ 0.55 M chloride, 370 μL) were added. The residual aqueous phase was tested.

(a) The reaction mixture of **1b** performed without $FeCl_3$ under irradiation for 24 h: neutral solution; (b) The reaction mixture of **1b** before irradiation: weakly acidic solution; (c) The reaction mixture of **1b** performed under the standard conditions:

enhanced acidic solution; and (d) The reaction mixture of **3a** performed under the standard conditions: weakly acidic solution. These results showed that the reactions involving aryl methyl thioethers produced an increasingly acidic solution, consistent with further oxidation of the departing RS group (**Figure S37**).

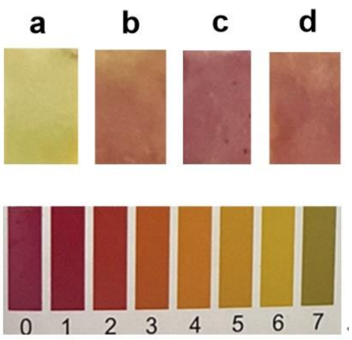


Figure S37. pH test for the reaction of **1b** and **3a**

(iii) ^{19}F NMR analysis of the reaction of **1ae**

According to general procedure for the desulfurizing chlorination of aryl thioethers, **1ae** (0.1 mmol), $FeCl_3$ (10 mol%, 500 μL of 0.02 M $FeCl_3$ in CH_3CN solution), and seawater (salinity: 35‰, ~ 0.55 M chloride, 370 μL) were added. ^{19}F NMR analysis of the reaction mixture were showed in Figure S38, which indicated that the leaving (4-fluorobutyl)thio group were converted into mixed F-containing side-products.

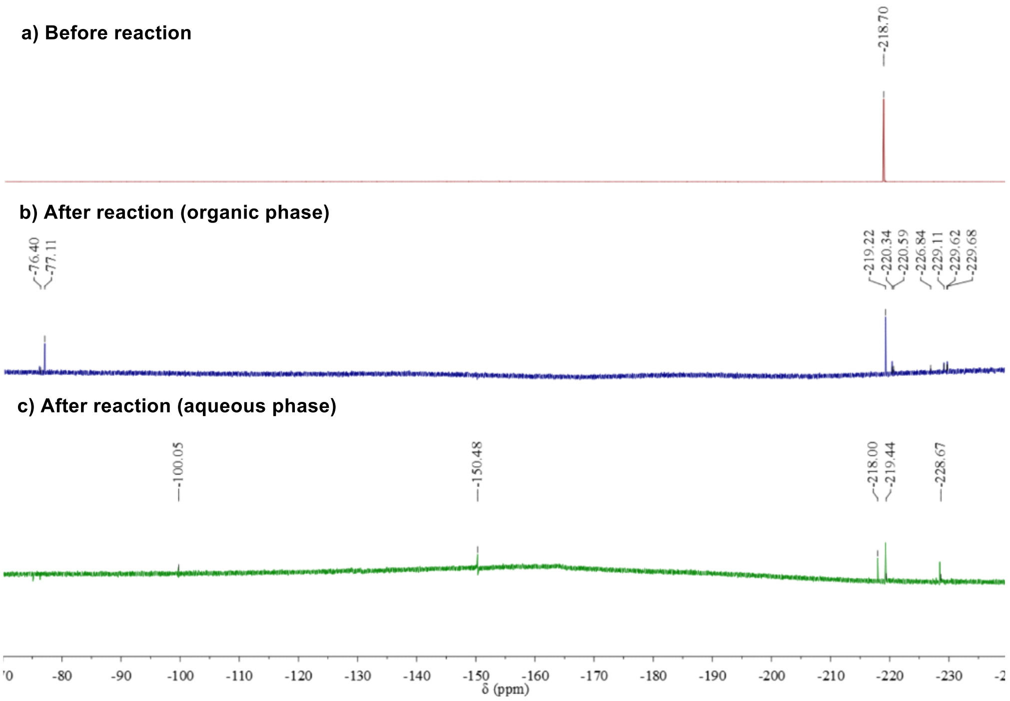


Figure S38. Detection of mixed F-containing products by ^{19}F NMR (376 MHz)

g) Other proposed catalytic pathways

(i) Proposed catalytic cycle of diaryl thioether **3**

As shown in **Figure S39**, the reaction of diaryl thioether **3** with chlorine radical generated the intermediate **II**, which underwent a HAS to give the an aryl chloride and an aryl thiyl radical. The aryl thiyl radical could reacted with a chlorine radical to yield highly reactive aryl hypochlorothioite, rapidly yielding aryl chlorides via iron-photoinduced LMCT & HAS processes. Alternatively, dimerization of the aryl thiyl radicals might also occurred to give 1,2-diaryldisulfanes **4`**, followed by iron-photoinduced LMCT & HAS processes to afford the aryl chlorides.

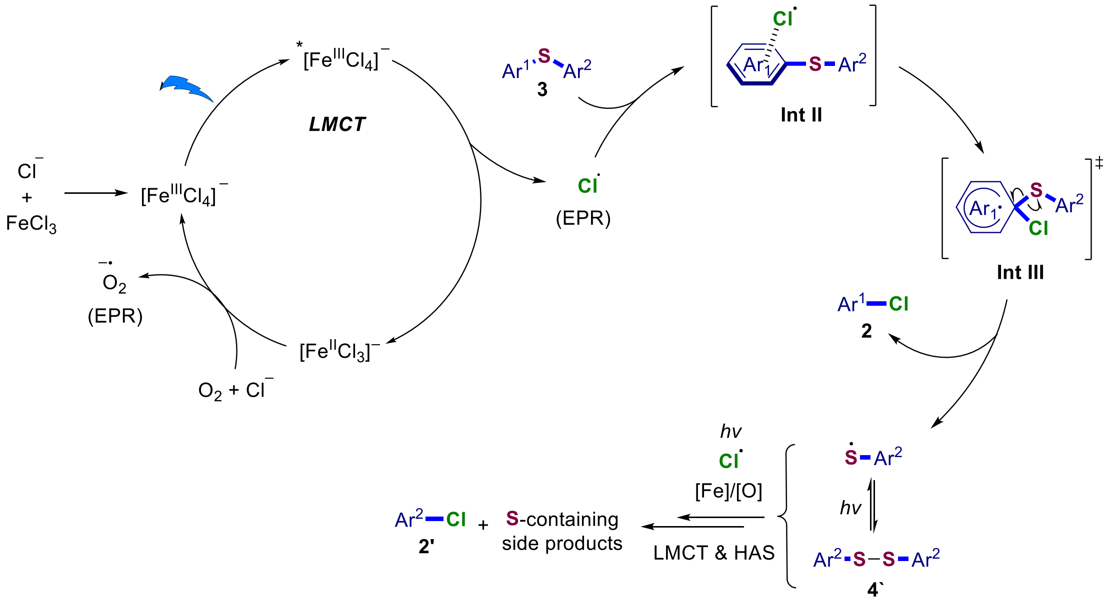


Figure S39. Catalytic cycle of **3**

(ii) Proposed catalytic cycle of aryl sulfonium salts **5**

As shown in **Figure S40**, the reaction of aryl sulfonium salts **5** with chlorine radical generated the intermediate **IV**, which underwent a HAS to give the an aryl chloride and intermediate **VI**. Intermediate **VI** proceeded a SET process in the presence of $[Fe^{II}Cl_3]^-$ species to form aryl thioethers **1** or **3** and $[Fe^{III}Cl_4]^-$ species. The desulfurizing chlorination of **1** or **3** afforded the final aryl chlorides.

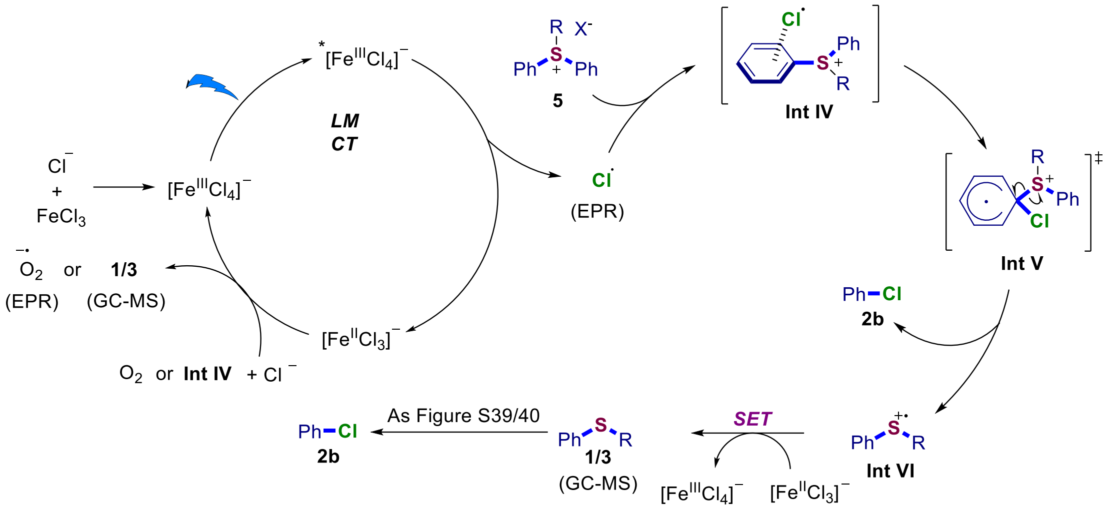
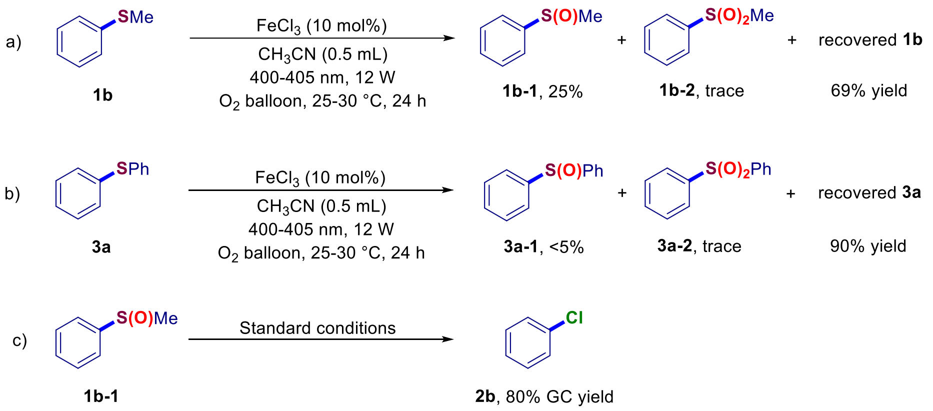


Figure S40. Proposed catalytic cycle of **5**

(iii) Proposed catalytic cycle via sulfoxide from oxidation of thioether



When the reaction of **1b** was performed in the absence of seawater, sulfoxide **1b-1** was obtained in 25% yield, while that of **3a** gave <5% yield of corresponding **3a-1**. Besides, only trace amount of sulfone **1b-2** or **3b-2** was detected. Further experiments showed that **1b-1** could give **2b** in 80% GC yield, indicating that sulfoxide generated from photooxidation of thioethers could undergo similar homolytic aromatic substitution to yield aryl chlorides (**Figure S41**). The reaction of **1-1** with chlorine radical generated the intermediate **I-1**, which underwent a HAS to give the aryl chlorides **2** and the sulfinyl radical. Cascade transformation of the sulfinyl radical furnished the S-containing side products.

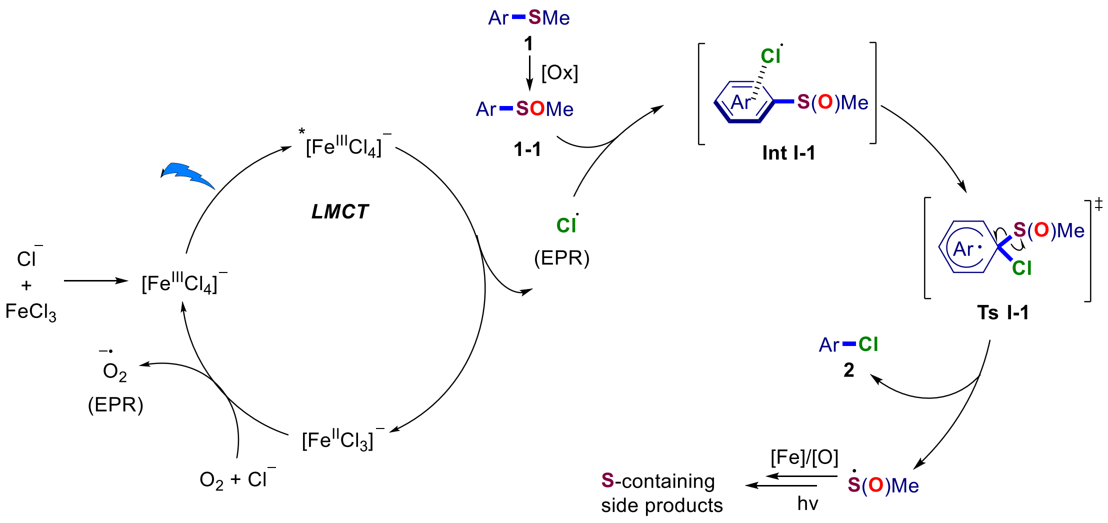


Figure S41. Proposed catalytic cycle of aryl sulfoxides

h) DFT calculations

All calculations were performed with the Gaussian 16 package.[11] Geometry optimizations were performed with PBE0-D3(BJ)[12] set with the PCM[13] (H_2O:MeCN = 1:1, eps = 57.0215, epsinf = 1.7875) solvation model. The def2-SVP[14] basis set was used for all atoms. All optimized structures were verified by frequency calculations and only one imaginary frequency was found in the transition states, while the other structures had no imaginary frequency. Besides, the thermal correction to Gibbs free energy were obtained after frequency calculations. Intrinsic Reaction Coordinate (IRC)[15] were utilized to confirm the reaction pathway. In addition, the single point calculations considering solvation effect were performed with ωB97XD[16] and ma-def2-TZVP[17] basis set with the PCM (H_2O:MeCN = 1:1, eps = 57.0215, epsinf = 1.7875) solvation model. All optimized structures were visualized using VMD 1.9.3[18] and Multiwfn[19] program.

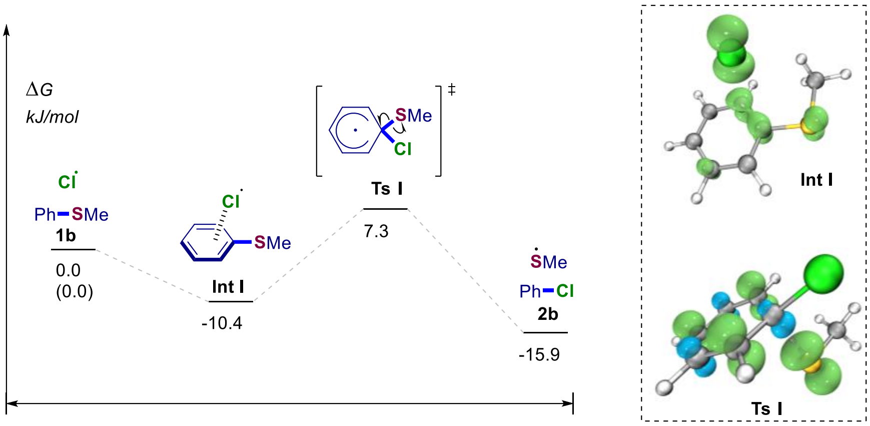


Figure S42. DFT calculations for desulfurizing chlorination of **1**

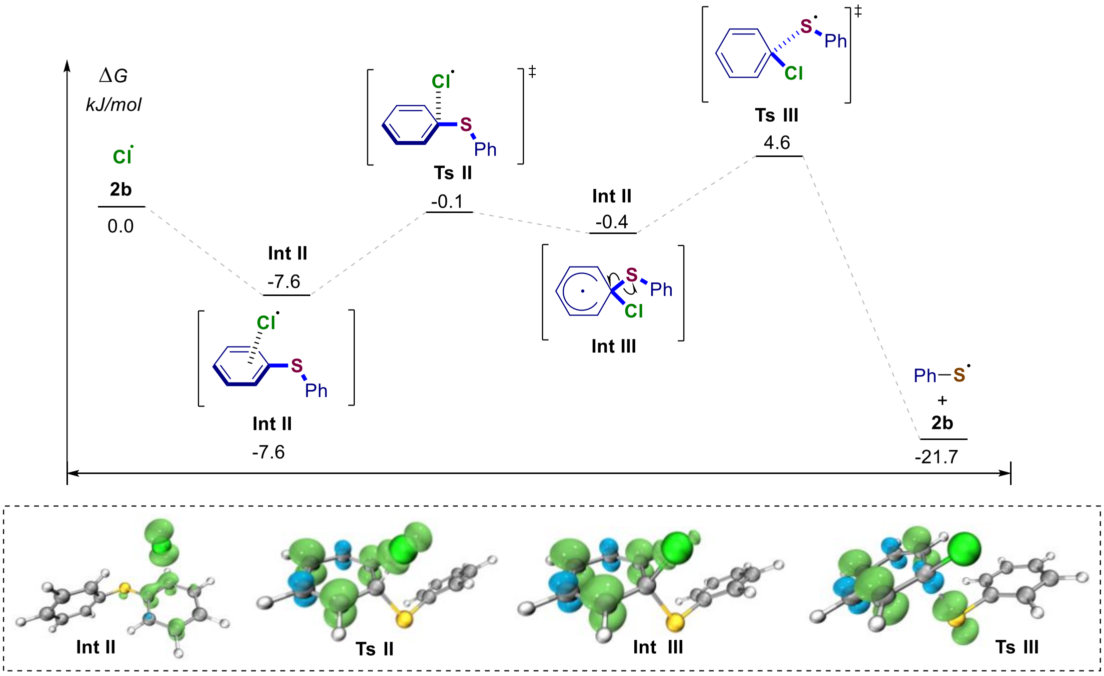
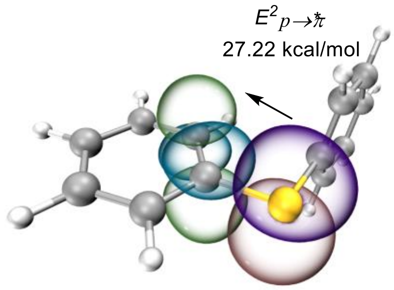


Figure S43. DFT calculations for desulfurizing chlorination of **3**



Second-order perturbation theory analysis in NBO for diphenyl sulfide gives $E^2_{p\to\pi^*}$ to be 27.22 kcal/mol, indicating enhanced conjugation between the lone pair electrons in *p*-orbital of the sulfur atom and aromatic π* systems.

Figure S44. Second-order perturbation theory analysis in NBO for diphenyl sulfide.

Cartesian coordinates for optimized structure

1b

C	-1.69450400	1.37375700	-0.00000400
C	-0.32625800	1.09696600	0.00000200
C	0.11909100	-0.23078600	0.00000900
C	-0.82661200	-1.27002900	0.00001000
C	-2.18726000	-0.98175700	0.00000400
C	-2.63126000	0.34277700	-0.00000200
H	-2.02583500	2.41529200	-0.00000900
H	0.38322300	1.92508000	0.00000000
H	-0.48862800	-2.31001000	0.00001600
H	-2.90869600	-1.80266100	0.00000500
H	-3.70016700	0.56695800	-0.00000700
S	1.81691400	-0.70950500	0.00001500
C	2.70149300	0.85681400	0.00002200
H	2.48338900	1.44727500	0.90130100
H	3.76748600	0.59227800	0.00003200
H	2.48340600	1.44727500	-0.90126100

Int I

C	1.71486100	0.58966000	1.04676500
C	0.33421300	0.35041400	0.84960800
C	-0.07740300	-0.73714300	0.02573300
C	0.90037400	-1.49662600	-0.64715900
C	2.24128200	-1.21446900	-0.46533000
C	2.65659200	-0.17263800	0.39321400
H	2.01436700	1.39916300	1.71497500
H	-0.38580000	0.85414200	1.49247200
H	0.59261500	-2.31455800	-1.30275500
H	2.98967500	-1.81264500	-0.99015600
H	3.72139300	0.02047700	0.53694700
S	-1.72842100	-1.20401600	-0.20132500
C	-2.66610000	0.06441800	0.65792200
H	-2.37237200	1.05276600	0.27510200
H	-3.71930600	-0.13514400	0.42179600
H	-2.52235900	0.00408100	1.74569600
Cl	-0.19316900	2.14509500	-0.81321800

Ts I

C	1.77288300	-0.69426300	1.26577200
C	0.52627000	-0.09543200	1.23783100
C	0.07163300	0.54863700	0.03732200
C	1.02997400	0.78409400	-1.00940600
C	2.26072300	0.16710200	-0.95505100
C	2.63803300	-0.59220400	0.16866200
H	2.08783200	-1.23144700	2.16310600
H	-0.14424900	-0.14066100	2.09785500
H	0.73165700	1.39503600	-1.86316100
H	2.96086800	0.29632300	-1.78354500
H	3.62148900	-1.06506600	0.20099800
S	-1.10852400	-1.10167900	-0.89357300
C	-2.35341500	-1.33523900	0.38492300
H	-2.77409600	-0.36657800	0.69546000
H	-3.16172300	-1.93172200	-0.06629500
H	-1.96450100	-1.87736000	1.25846900
Cl	-1.15380700	1.80217200	0.25527700

MeS•

S	-0.68625600	0.00902400	-0.02470300
C	1.10038900	-0.00182700	0.02434100
H	1.52092900	1.01389700	-0.00447900
H	1.48684100	-0.55789400	0.89084000
H	1.43519000	-0.52848500	-0.88754100

3a

C	-2.31414000	1.77252900	-0.20804700
C	-1.20980000	0.92304300	-0.13960200
C	-1.40132300	-0.45303200	0.02297600
C	-2.70366900	-0.96583200	0.11376400
C	-3.79755500	-0.10787400	0.04125300
C	-3.61004100	1.26626600	-0.11910500
H	-2.15286100	2.84615000	-0.33382000
H	-0.20067500	1.33243500	-0.21233900
H	-2.85874200	-2.04041800	0.24317300
H	-4.80712000	-0.51995800	0.11340600
H	-4.46979500	1.93761000	-0.17357100
S	-0.07859200	-1.63322400	0.11505200
C	1.37393400	-0.61039500	0.07496700
C	2.01995700	-0.36574400	-1.14102400

C	1.89261500	-0.08580900	1.26375800
C	3.17842400	0.40984300	-1.16653700
H	1.60868300	-0.78267500	-2.06289700
C	3.04908200	0.69127800	1.23139100
H	1.38419200	-0.28818100	2.20898100
C	3.69206100	0.93904400	0.01769500
H	3.68168200	0.60102600	-2.11713800
H	3.45212000	1.10202200	2.16003000
H	4.60004200	1.54625700	-0.00456400

Int II

C	-1.92276500	-1.57210900	-1.46919400
C	-0.82436000	-1.23799400	-0.69006400
C	-1.01362900	-0.53846700	0.50868500
C	-2.32594000	-0.11862200	0.87530900
C	-3.43195700	-0.51931500	0.09052800
C	-3.23088800	-1.22560800	-1.07692400
H	-1.76835500	-2.13337700	-2.39371400
H	0.17945200	-1.53887800	-0.99376100
H	-2.48742200	0.34103500	1.85194400
H	-4.43670200	-0.23854700	0.41151400
H	-4.07955200	-1.52078300	-1.69691600
S	0.27383500	-0.15874200	1.62426300
Cl	-1.99528300	2.16348700	-0.05350500
C	1.68410800	-0.03979900	0.55285400
C	2.80165200	-0.84165700	0.79389000
C	1.68973400	0.90459600	-0.48182600
C	3.93239900	-0.70109800	-0.01128000
H	2.78178200	-1.57611400	1.60193700
C	2.81741700	1.02388100	-1.28840100
H	0.80701900	1.52925800	-0.64558400
C	3.93959800	0.22536500	-1.05295900
H	4.80799700	-1.32751800	0.17342200
H	2.82468700	1.75356300	-2.10144100
H	4.82413900	0.32801200	-1.68570600

Ts II

C	-2.15392200	-1.55664800	-1.28660400
C	-1.06628600	-0.86779000	-0.80996100
C	-1.21601000	0.12982100	0.24710200
C	-2.54362500	0.23299700	0.85456400
C	-3.60637400	-0.47340100	0.34971200
C	-3.43472000	-1.36468200	-0.72932300
H	-2.01868900	-2.27446000	-2.09880600
H	-0.07007100	-1.02366400	-1.22843800
H	-2.66510800	0.91625100	1.69837900
H	-4.59358500	-0.35153800	0.80092200
H	-4.28907700	-1.92165600	-1.11848100
S	0.05145200	0.15591100	1.52812400
Cl	-1.04883200	1.88723600	-0.78670900
C	1.55938000	-0.01592200	0.60513100
C	2.15874200	-1.27508700	0.49123300
C	2.17204800	1.11097700	0.04502000
C	3.36546000	-1.40764500	-0.19407500
H	1.67339300	-2.14554800	0.93795500
C	3.37529000	0.96876100	-0.64318000
H	1.69509200	2.08711000	0.14360500
C	3.97198200	-0.28732900	-0.76255900
H	3.83251400	-2.39101300	-0.28396000
H	3.85302600	1.84674400	-1.08414800
H	4.91762600	-0.39268200	-1.29951500

Int III

C	-2.24071400	-1.62119000	-1.07496000
C	-1.14587300	-0.84804800	-0.79315000
C	-1.23264900	0.30885700	0.12007800
C	-2.56348400	0.52261400	0.73101900
C	-3.63012800	-0.27612600	0.41694500
C	-3.49695600	-1.35408900	-0.48679300
H	-2.13478300	-2.46251600	-1.76396200
H	-0.17475800	-1.05533000	-1.24745300
H	-2.66133300	1.35450900	1.43254400
H	-4.59939200	-0.07526800	0.87945700
H	-4.35860600	-1.98060100	-0.72351900
S	-0.01493500	0.24155100	1.49379700
Cl	-0.86455800	1.84412300	-0.93591700
C	1.51980500	-0.04338100	0.64776200
C	2.01628000	-1.34688200	0.53059100
C	2.25388700	1.03633800	0.14212400
C	3.23799800	-1.56962700	-0.10246400
H	1.43902000	-2.18056800	0.93613000
C	3.47200900	0.80537900	-0.49394500
H	1.86130000	2.04898900	0.24639400
C	3.96400300	-0.49490500	-0.61680500
H	3.62367000	-2.58760800	-0.19373700
H	4.04337500	1.64760800	-0.89110100
H	4.92141200	-0.67099100	-1.11285700

Ts III

C	-2.29347900	-1.64164700	-0.93045400
C	-1.29092100	-0.69888800	-1.03092400
C	-1.35608000	0.51228300	-0.24527500
C	-2.60880300	0.81282200	0.41326300
C	-3.58251300	-0.15477600	0.50405700
C	-3.43128200	-1.39636400	-0.14581000
H	-2.20391400	-2.57875700	-1.48441200
H	-0.40891300	-0.86824800	-1.65127900
H	-2.72196000	1.78794700	0.89055400
H	-4.49735000	0.05764800	1.06200400
H	-4.21884500	-2.14877700	-0.07293600
S	-0.12281300	0.02837700	1.46319400
Cl	-0.54010400	1.90570200	-0.97125500
C	1.43974300	-0.17435700	0.69539700
C	1.84095800	-1.43228200	0.21389300
C	2.30589300	0.92388600	0.55725400
C	3.08306000	-1.58505600	-0.39647900
H	1.16740400	-2.28453600	0.32760000
C	3.54964000	0.76290800	-0.04727000
H	1.98923900	1.89943900	0.93099700
C	3.93895600	-0.48920800	-0.52734100
H	3.38769900	-2.56588500	-0.76932300
H	4.21964500	1.62026200	-0.14653000
H	4.91452900	-0.61242000	-1.00365600

PhCl

C	-1.56642900	1.20675900	0.00000200
C	-0.17213100	1.21541300	0.00000000
C	0.51140100	0.00000300	-0.00000200
C	-0.17212500	-1.21541000	0.00000000
C	-1.56642300	-1.20676300	0.00000200
C	-2.26628600	-0.00000300	0.00000200
H	-2.10733500	2.15596300	0.00000300
H	0.38467000	2.15397800	0.00000000
H	0.38468100	-2.15397200	0.00000000
H	-2.10732500	-2.15597000	0.00000300
H	-3.35839300	-0.00000600	0.00000300
Cl	2.24962100	0.00000800	-0.00000200

PhS•

C	-1.53293900	-1.20381400	0.00000400
C	-0.13967000	-1.21377000	0.00000300
C	0.56594100	0.00000000	0.00001500
C	-0.13966900	1.21377000	0.00000600
C	-1.53293800	1.20381500	0.00000200
C	-2.23750500	0.00000100	0.00000600
H	-2.07086800	-2.15508000	0.00000100
H	0.39977500	-2.16374300	-0.00000400
H	0.39977700	2.16374300	0.00000100
H	-2.07086600	2.15508100	-0.00000400
H	-3.32951100	0.00000100	0.00000300
S	2.31819600	-0.00000100	-0.00000500

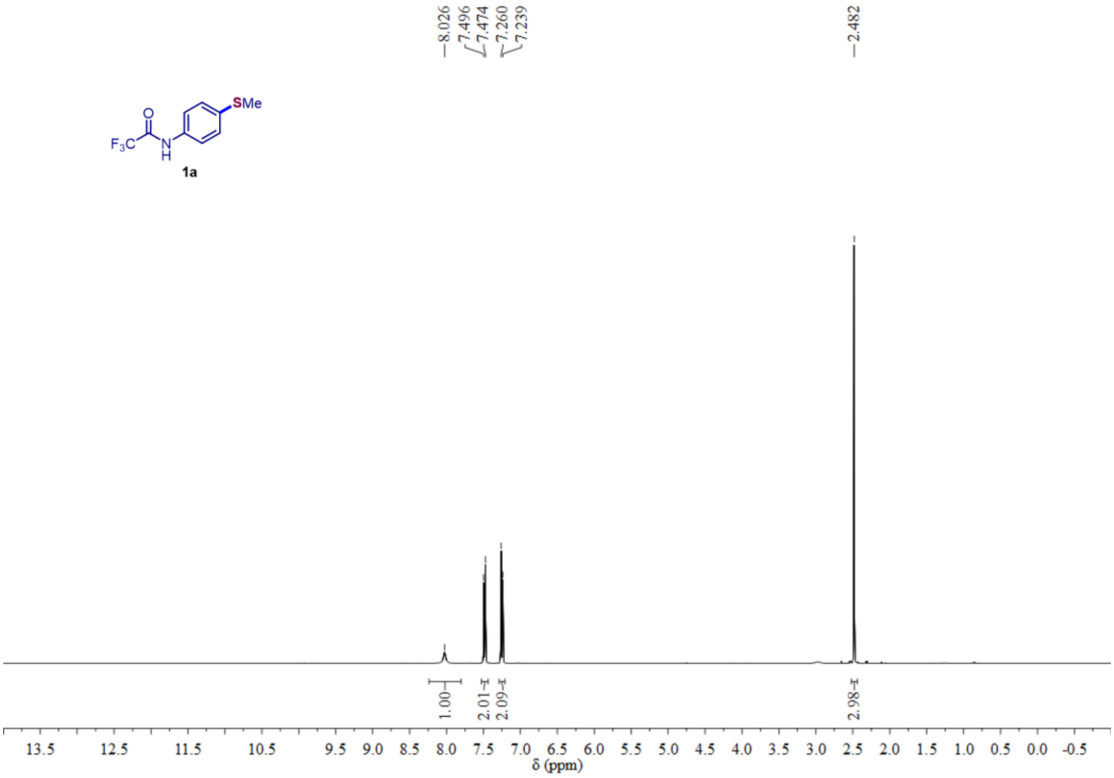
References

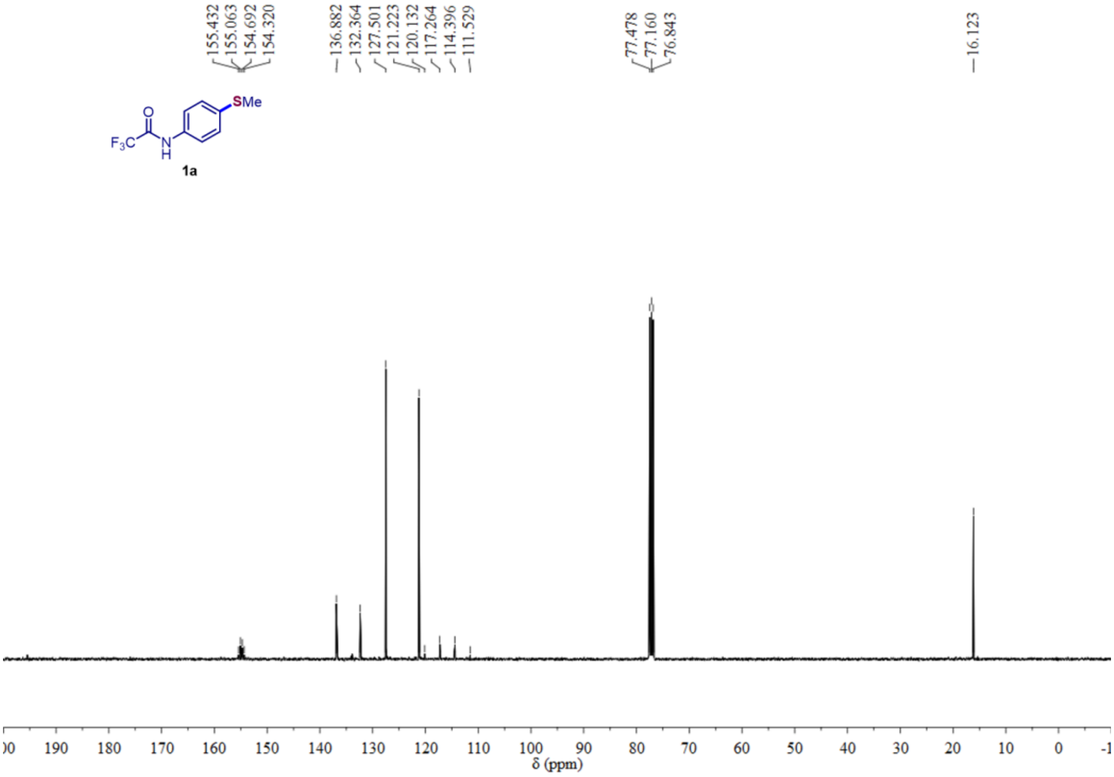
1. R. S. Aal E Ali, Y.-L. Zhou, K. Gong and X.-F. Jiang, *Green Synth. Catal.*, **2023**, *4*, 169-172.
2. A. Augurusa, M. Mehta, M. Perez, J.-T. Zhu and D. W. Stephan, *Chem. Commun.*, **2016**, *52*, 12195-12198.
3. M. J. Westa and A. J. B. Watson, *Org. Biomol. Chem.*, **2019**, *17*, 5055-5059.
4. A. E. Shiely, C. N. Slattery, A. Ford, K. S. Eccles, S. E. Lawrence and A. R. Maguire, *Org. Biomol. Chem.*, **2017**,*15*, 2609-2628.
5. W. Deng, Y. Zou, Y.-F. Wang, L. Liu and Q.-X. Guo. *Synlett*, **2004**, *7*, 1254-1258.
6. A. M. Simion, I. Hashimoto, Y. Mitoma, N. Egashira and C. Simion, *Synth. Commun.*, **2012**, *42*, 921-931.
7. I. Güell and X. Ribas, *Eur. J. Org. Chem.*, **2014**, *15*, 3188-3195.
8. C.-Y. Zhang, Y. Zhou, J.-T. Huang, C.-H. Tu, X.-A. Zhou and G.-D. Yin, *Org. Biomol. Chem.*, **2018**, *16*, 6316-6321.
9. T. Delcaillau, A. Woenckhaus-Alvarez and B. Morandi, *Org. Lett.* **2021**, *23*, 7018-7022.
10. J.-X. Shen, J.-C. Li, M.-J. Chen, X.-R. Yue and X. Shi, *Org. Lett.* **2024**, *26*, 1495–1500
11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R.

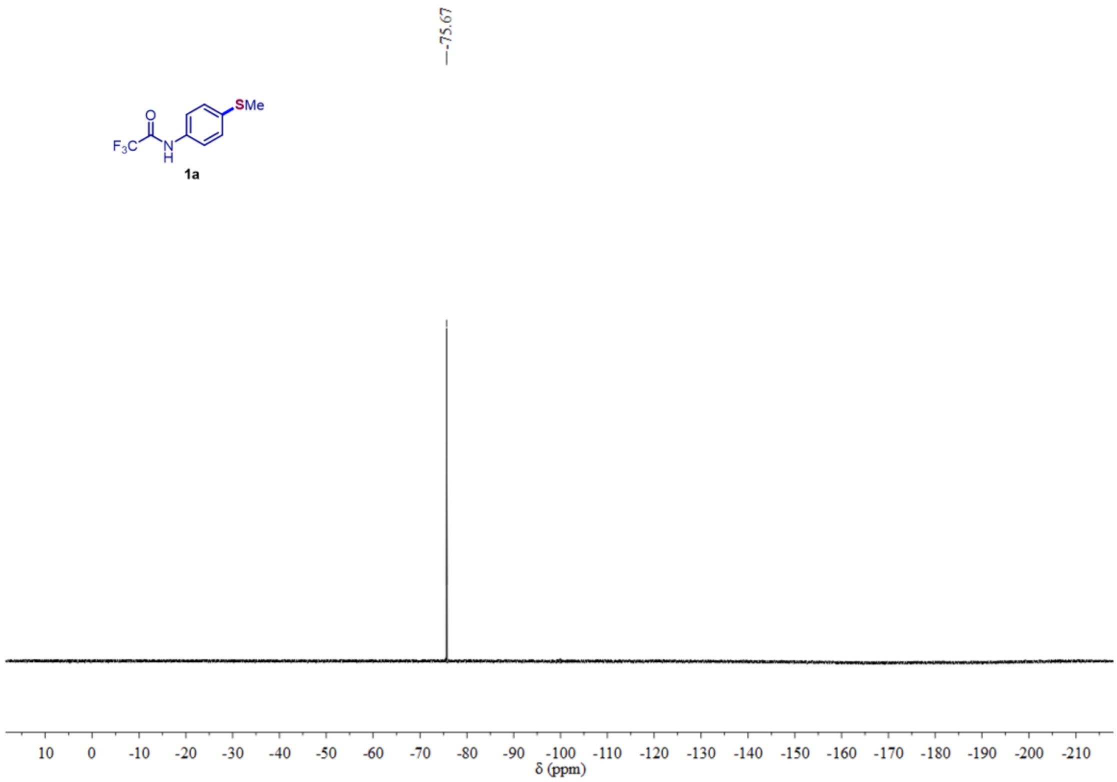
Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

12. (a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865-3868. (b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396. (c) C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158-6169. (d) M. Ernzerhof, G. E. Scuseria, *J. Chem. Phys.* **1999**, *110*, 5029-5036. (e) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.
13. (a) S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117-129. (b) S. Miertuš, J. Tomasi, *Chem. Phys.* **1982**, *65*, 239-245. (c) J. L. Pascual-Ahuir, E. Silla, I. Tuñón, *J. Comp. Chem.* **1994**, *15*, 1127-1138. (d) J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999-3093.
14. (a) A. Schaefer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571-2577. (b) A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829-5835. (c) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305. (d) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.
15. (a) K. Fukui, *Acc. Chem. Res.* **1981**, *14*, 363-368. (b) H. P. Hratchian, H. B. Schlegel, in Theory and Applications of Computational Chemistry: The First 40 Years, Ed. C. E. Dykstra, G. Frenking, K. S. Kim, G. Scuseria (Elsevier, Amsterdam, **2005**) 195-249.
16. J. D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615-6620.
17. (a) E. Papajak, J. Zheng, X. Xu, H. R. Leverentz, D. G. Truhlar, *J. Chem. Theory Comput.* **2011**, *7, 10*, 3027-3034. (b) J. Zheng, X. Xu, D. G. Truhlar, *Theor Chem Acc*, **2011**, *128*, 295-305.
18. W. Humphrey, A. Dalke, K. Schulten, *J. Molec. Graphics*, **1996**, *14*, 33-38.
19. (a) T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592. (b) T. Lu, F. Chen, *J. Mol. Graph. Model.* **2012**, *38*, 314.

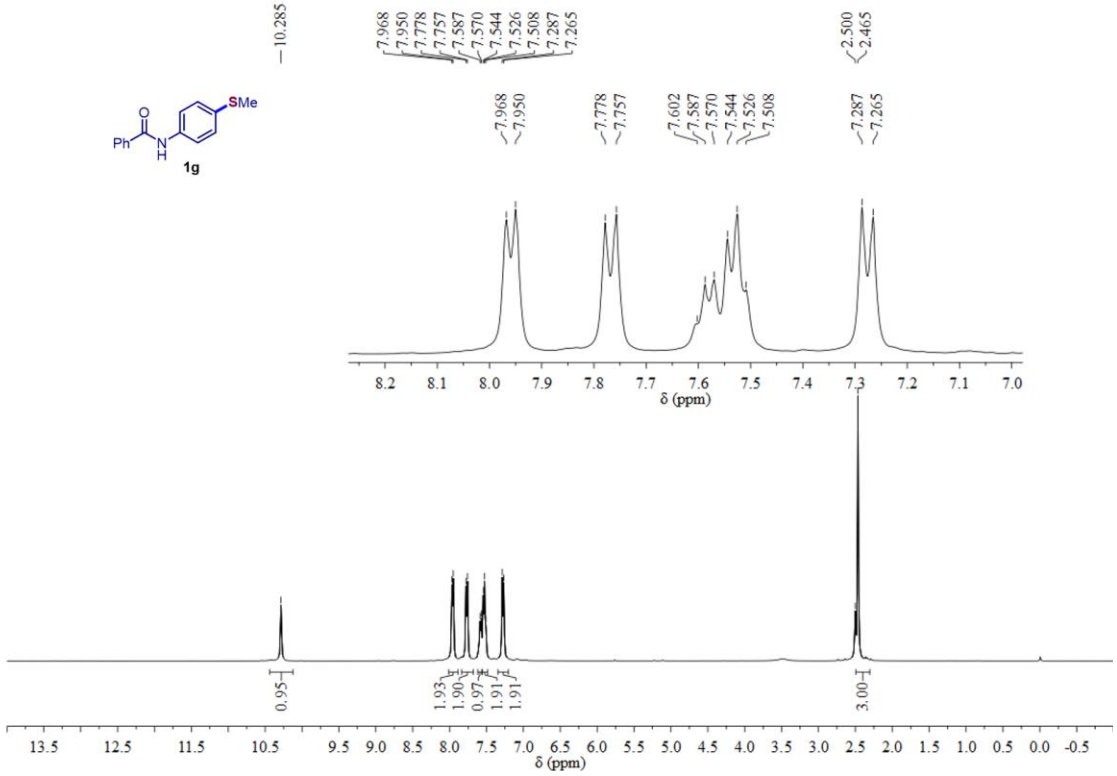
NMR spectra


8.026
7.496
7.474
7.260
7.239
2.482
SMe
O
F3C
N
H
1a
1.00
2.01
2.09
2.98
13.5
12.5
11.5
10.5
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
δ (ppm)

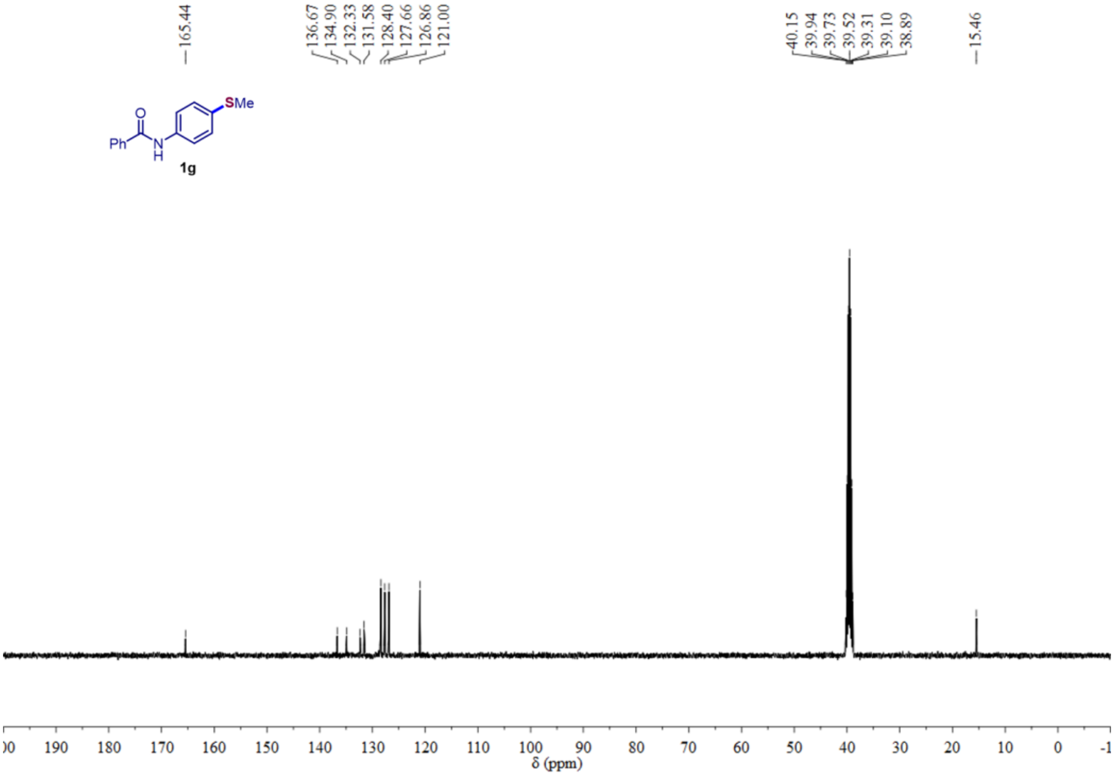

155.432
155.063
154.692
154.320
136.882
132.364
127.501
121.223
120.132
117.264
114.396
111.529
77.478
77.160
76.843
16.123
SMe
O
F3C
N
H
1a
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

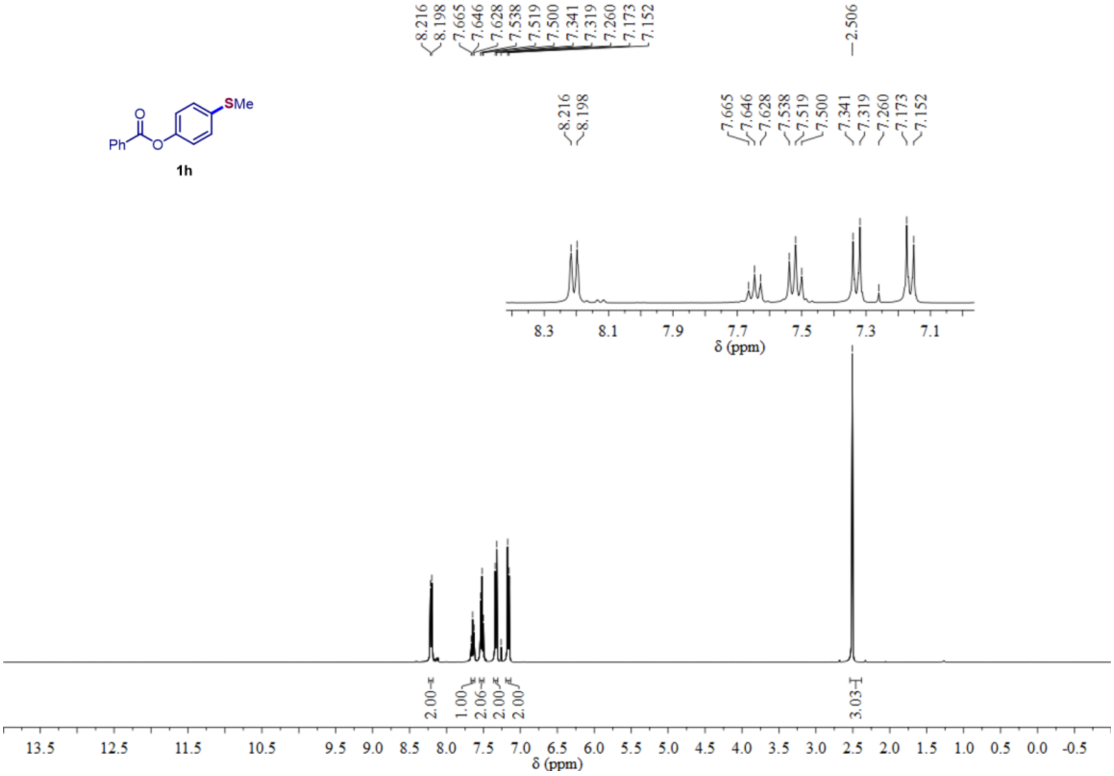

-75.67
SMe
O
F3C
N
H
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
δ (ppm)

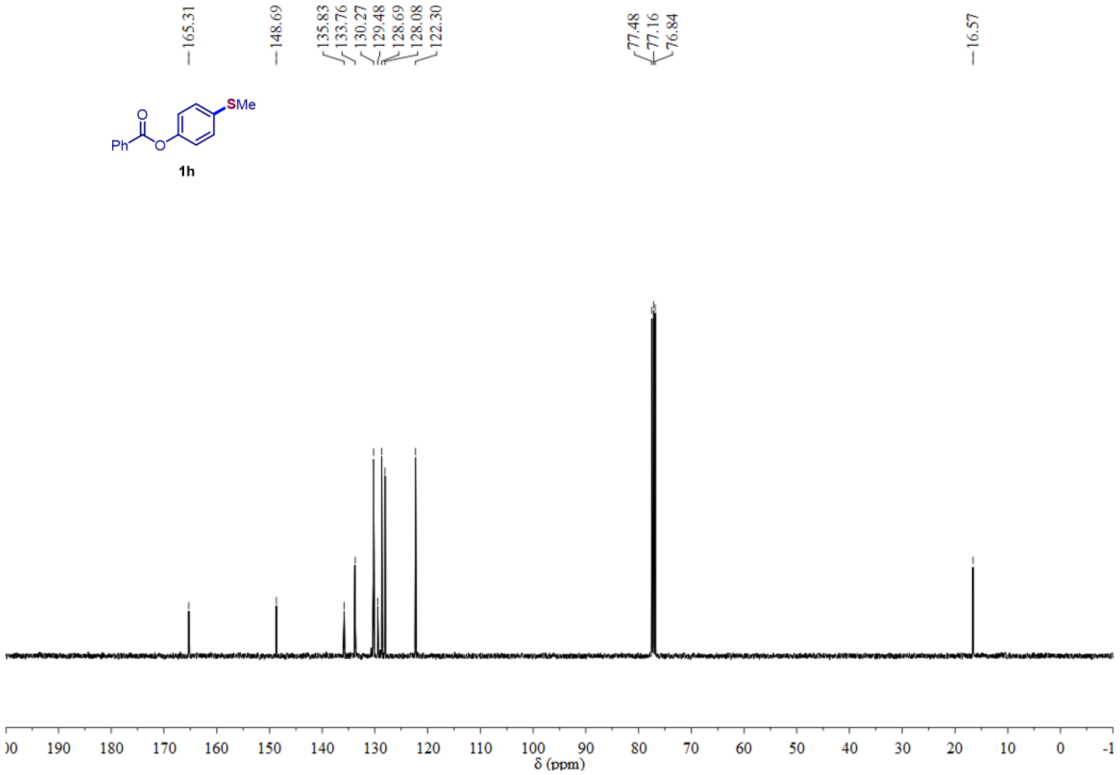
1a

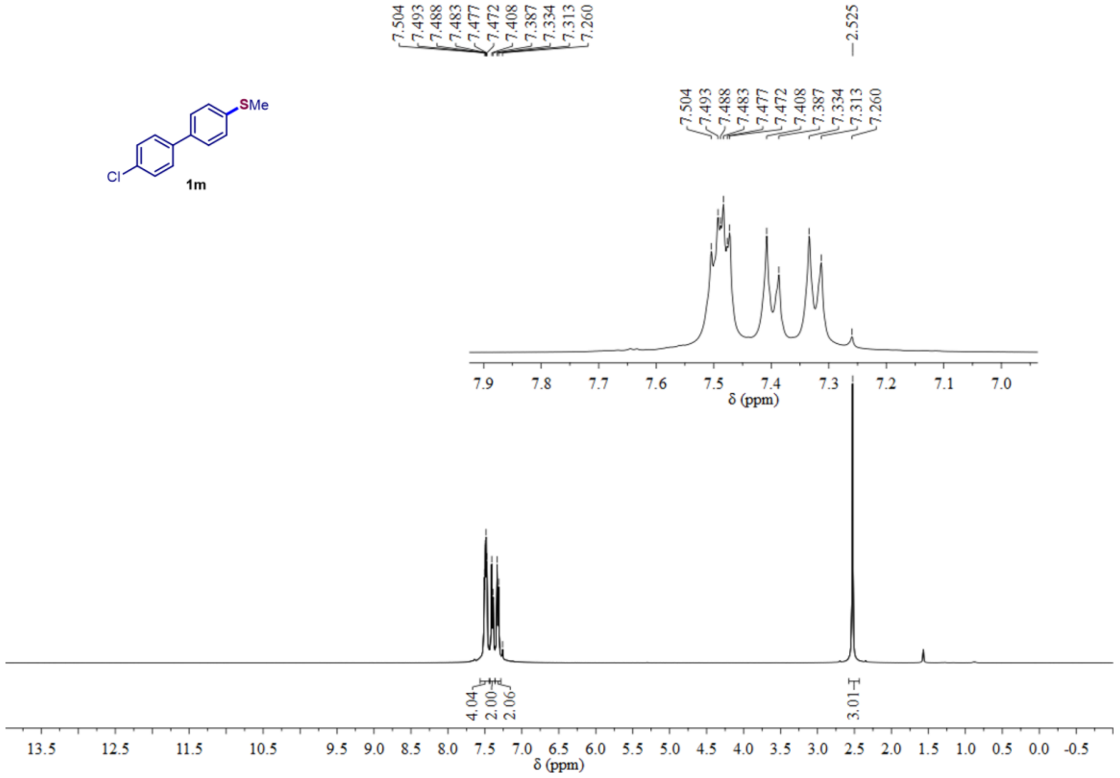

10.285
7.968
7.950
7.778
7.757
7.587
7.570
7.544
7.526
7.508
7.287
7.265
2.500
2.465
SMe
O
Ph
N
H
7.968
7.950
7.778
7.757
7.602
7.587
7.570
7.544
7.526
7.508
7.287
7.265
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
δ (ppm)
0.95
1.93
1.90
0.97
1.91
1.91
3.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
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
δ (ppm)

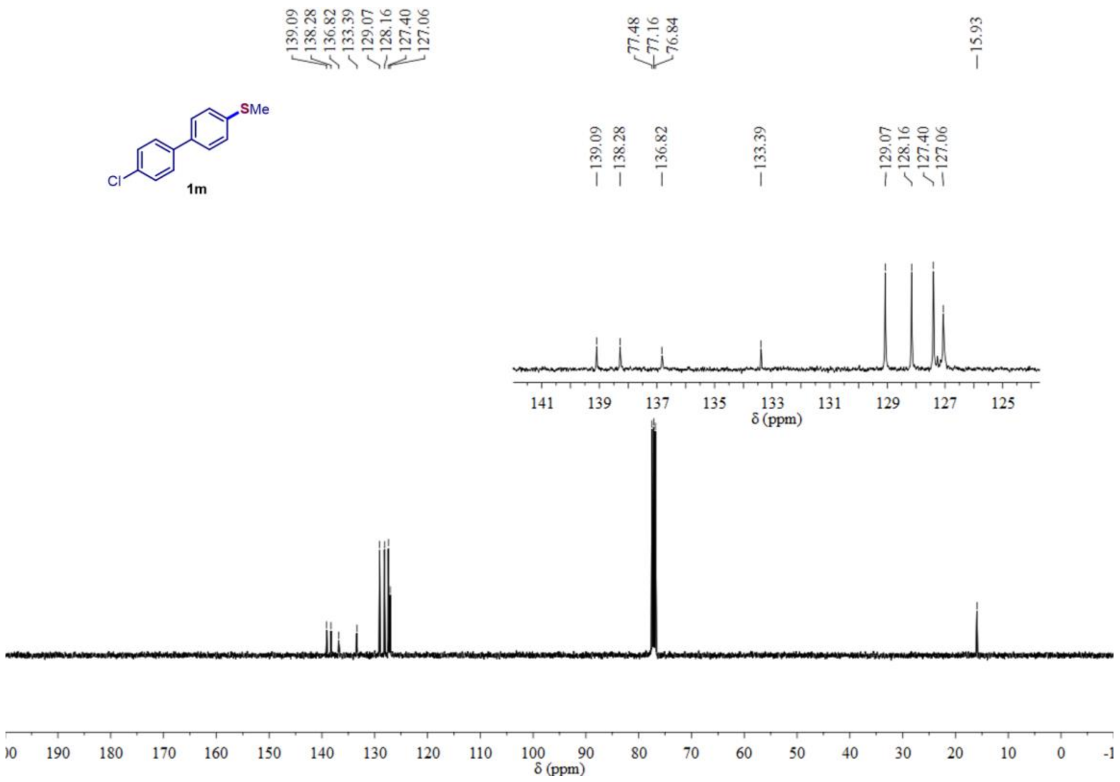
1g


1g
165.44
136.67
134.90
132.33
131.58
128.40
127.66
126.86
121.00
40.15
39.94
39.73
39.52
39.31
39.10
38.89
15.46
SMe
O
Ph
N
H
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

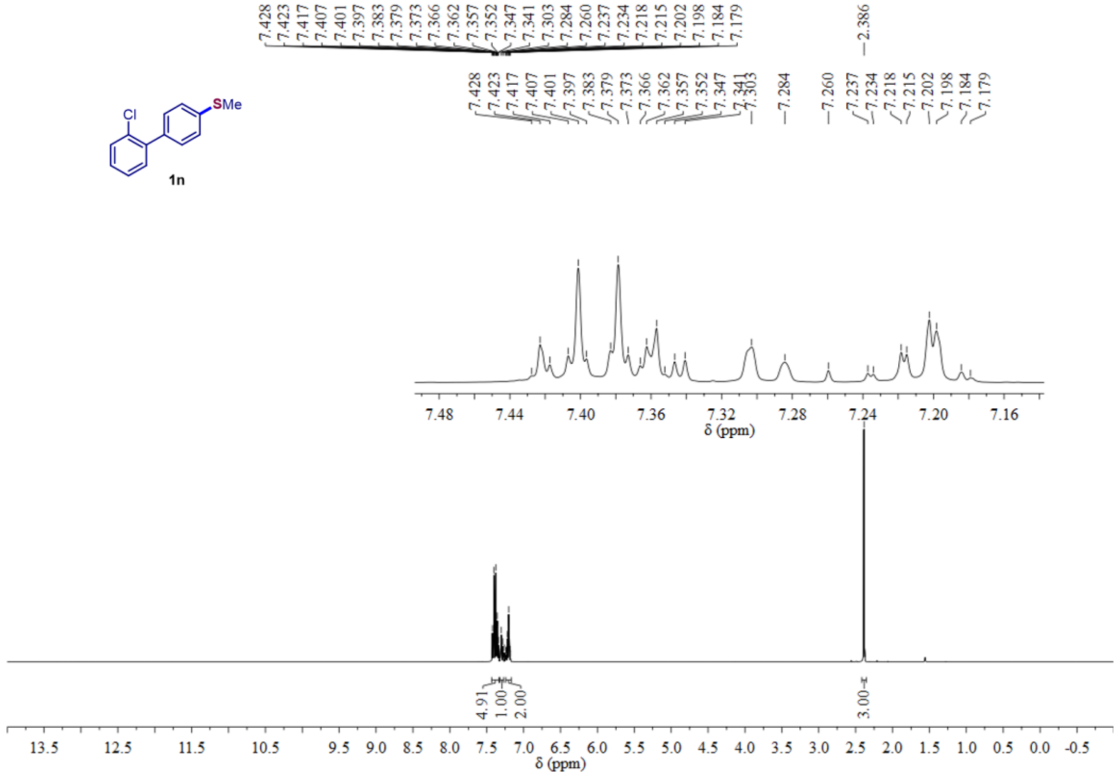

1h
8.216
8.198
7.665
7.646
7.628
7.538
7.519
7.500
7.341
7.319
7.260
7.173
7.152
2.506
SMe
O
Ph
O
8.3
8.1
7.9
7.7
7.5
7.3
7.1
δ (ppm)
2.00
1.00
2.06
2.00
2.00
3.03
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)


165.31
148.69
135.83
133.76
130.27
129.48
128.69
128.08
122.30
77.48
77.16
76.84
16.57
Ph
O
O
SMe
1h
)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

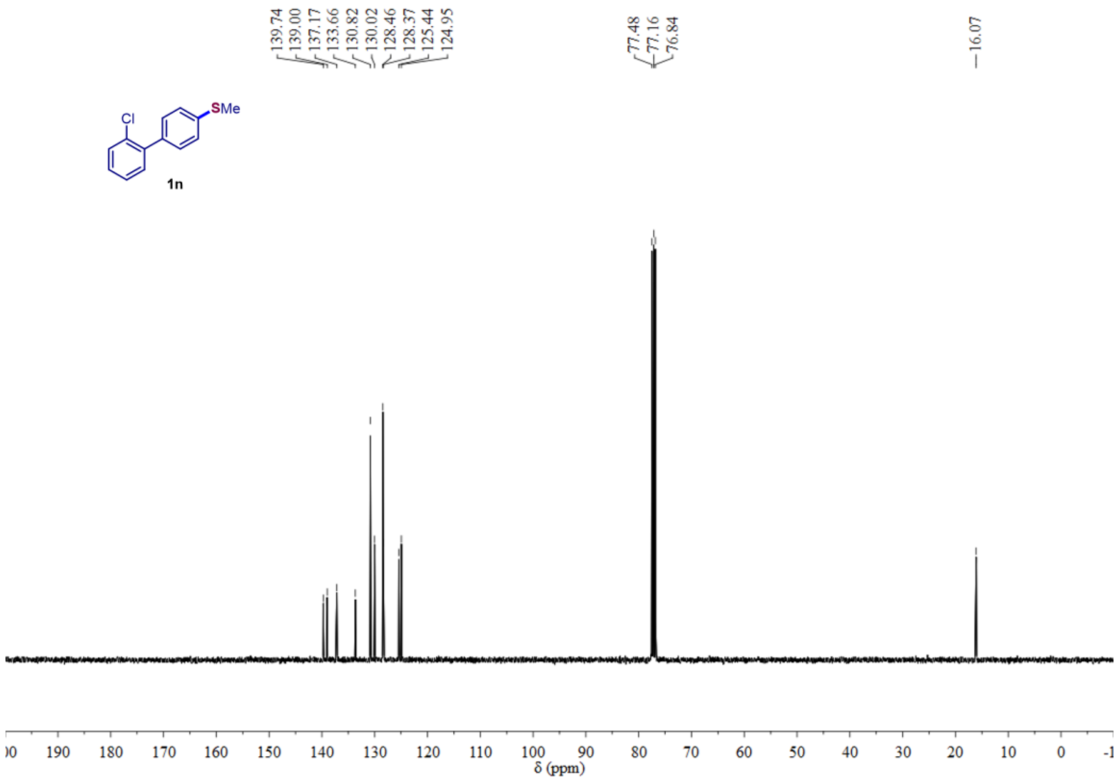

7.504
7.493
7.488
7.483
7.477
7.472
7.408
7.387
7.334
7.313
7.260
2.525
Cl
SMe
1m
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
δ (ppm)
4.04
2.00
2.06
3.01
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)


SMe
Cl
139.09
138.28
136.82
133.39
129.07
128.16
127.40
127.06
77.48
77.16
76.84
15.93
141
139
137
135
133
131
129
127
125
δ (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

1m

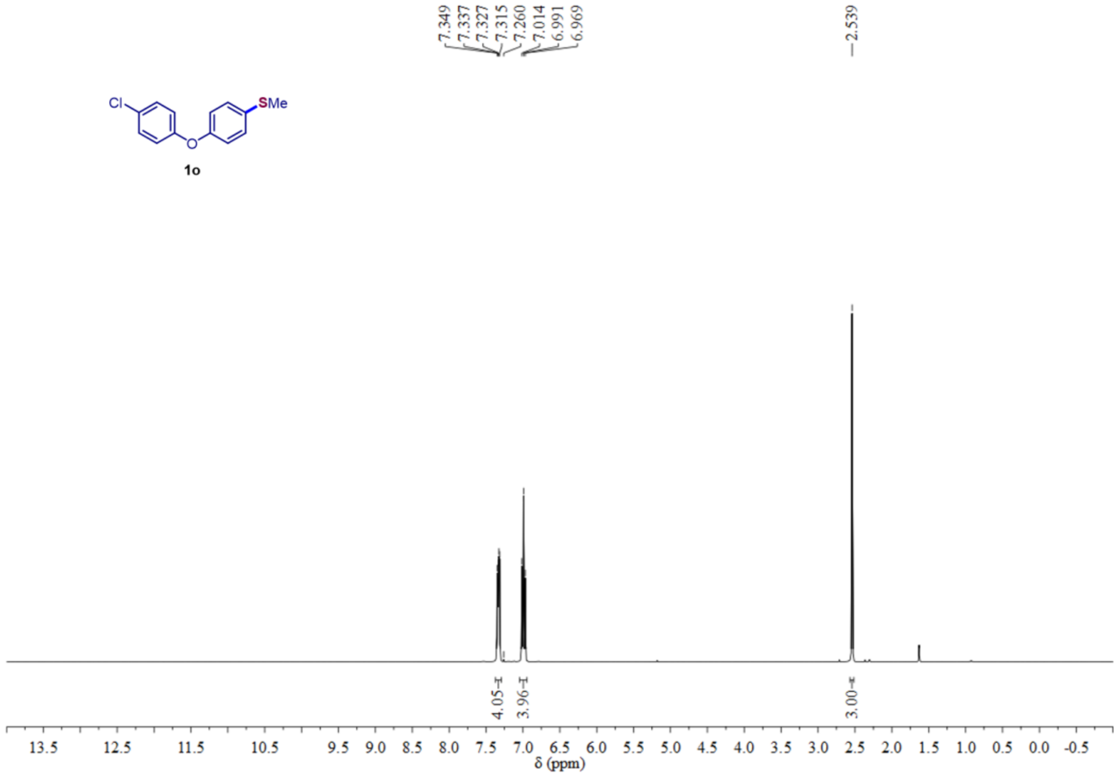

Cl
SMe
7.428
7.423
7.417
7.407
7.401
7.397
7.383
7.379
7.373
7.366
7.362
7.357
7.352
7.347
7.341
7.303
7.284
7.260
7.237
7.234
7.218
7.215
7.202
7.198
7.184
7.179
2.386
7.48
7.44
7.40
7.36
7.32
7.28
7.24
7.20
7.16
δ (ppm)
4.91
1.00
2.00
3.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)

1n



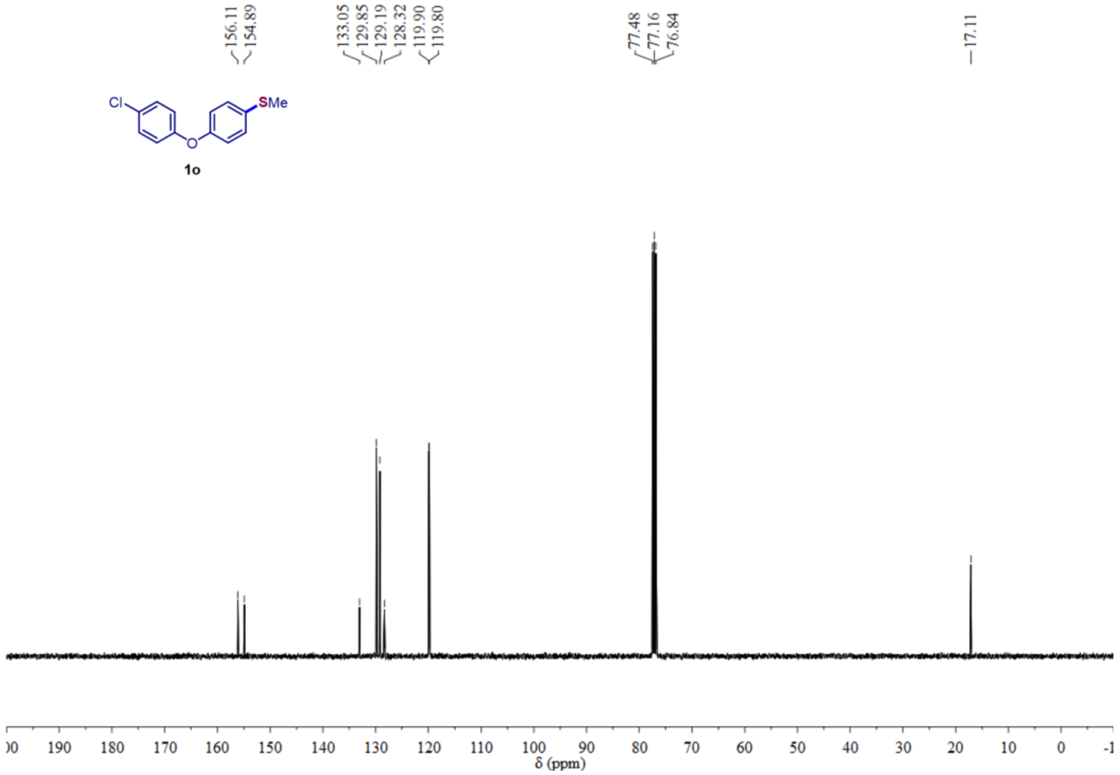
1n

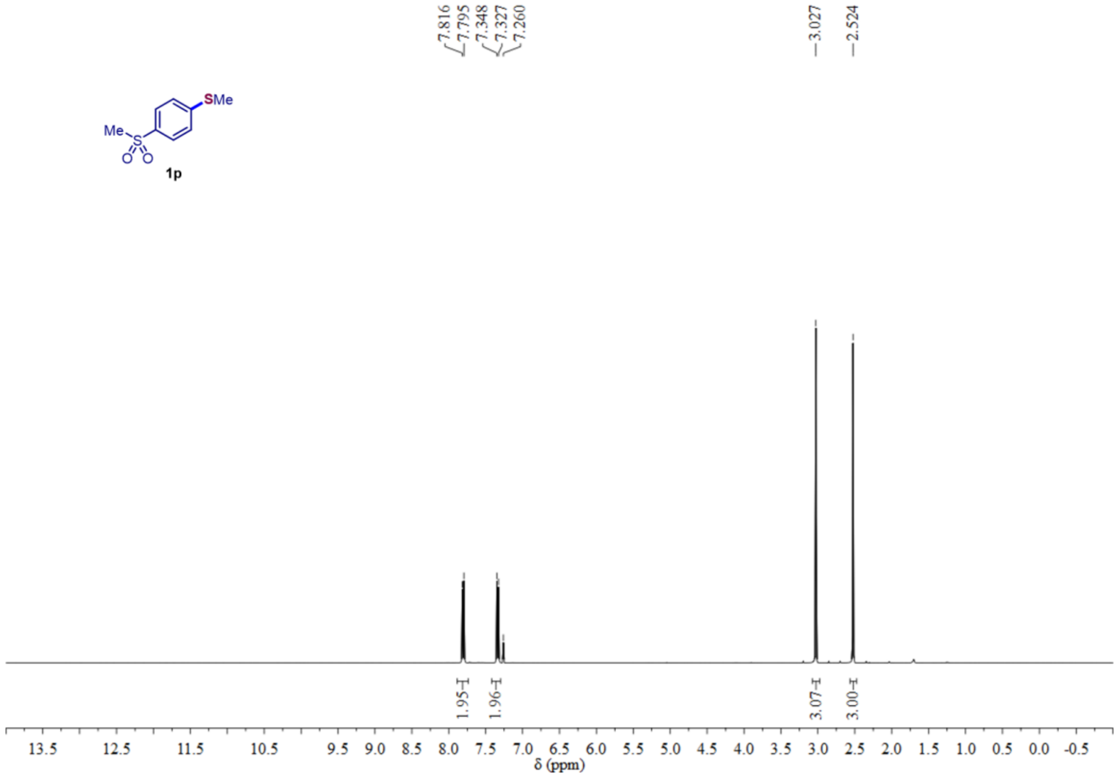
139.74
139.00
137.17
133.66
130.82
130.02
128.46
128.37
125.44
124.95
77.48
77.16
76.84
16.07
Cl
SMe
δ (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

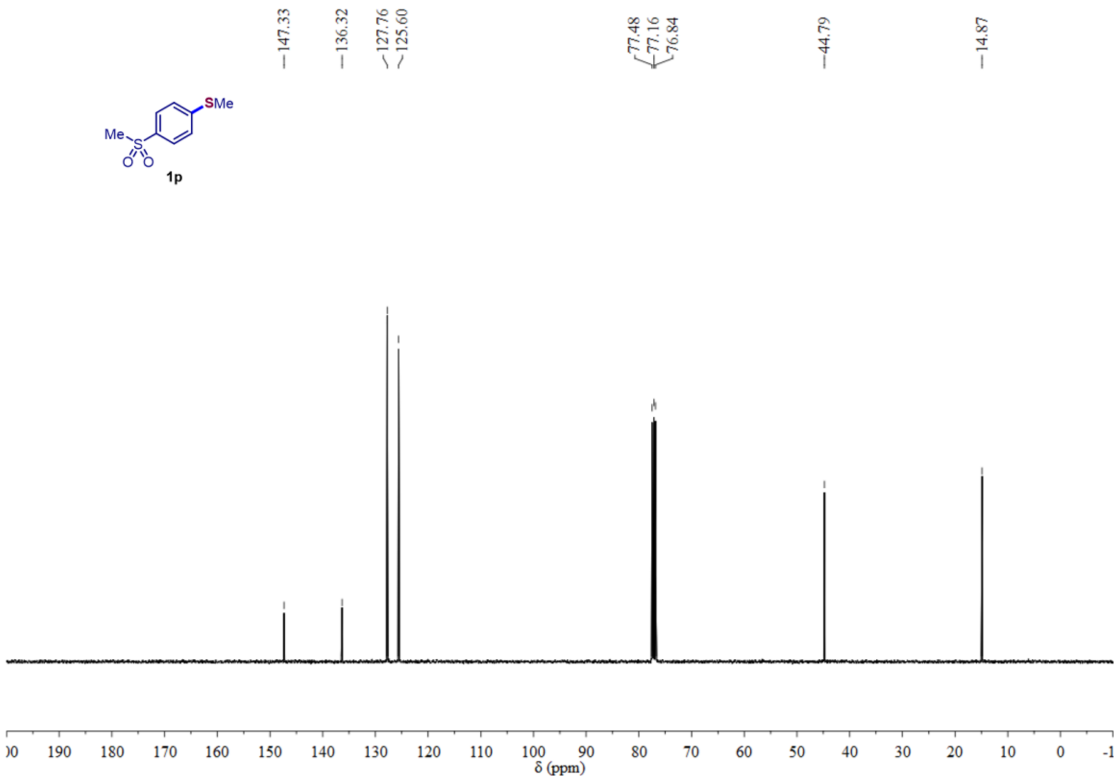


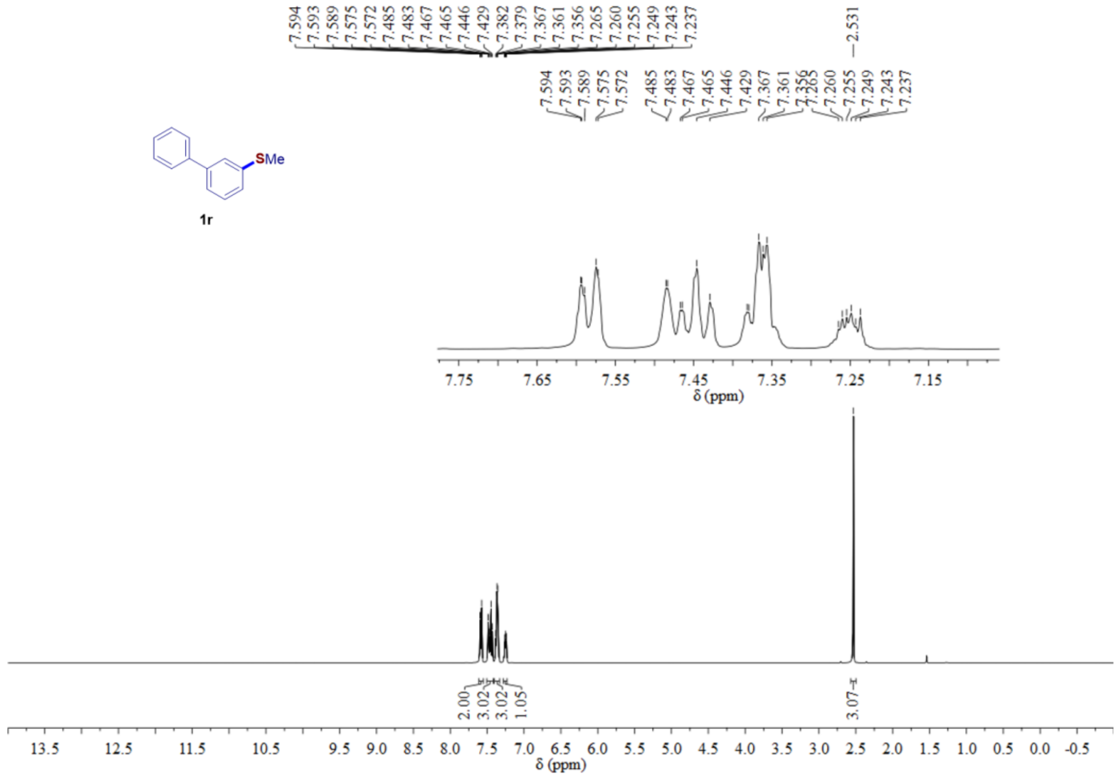
1o

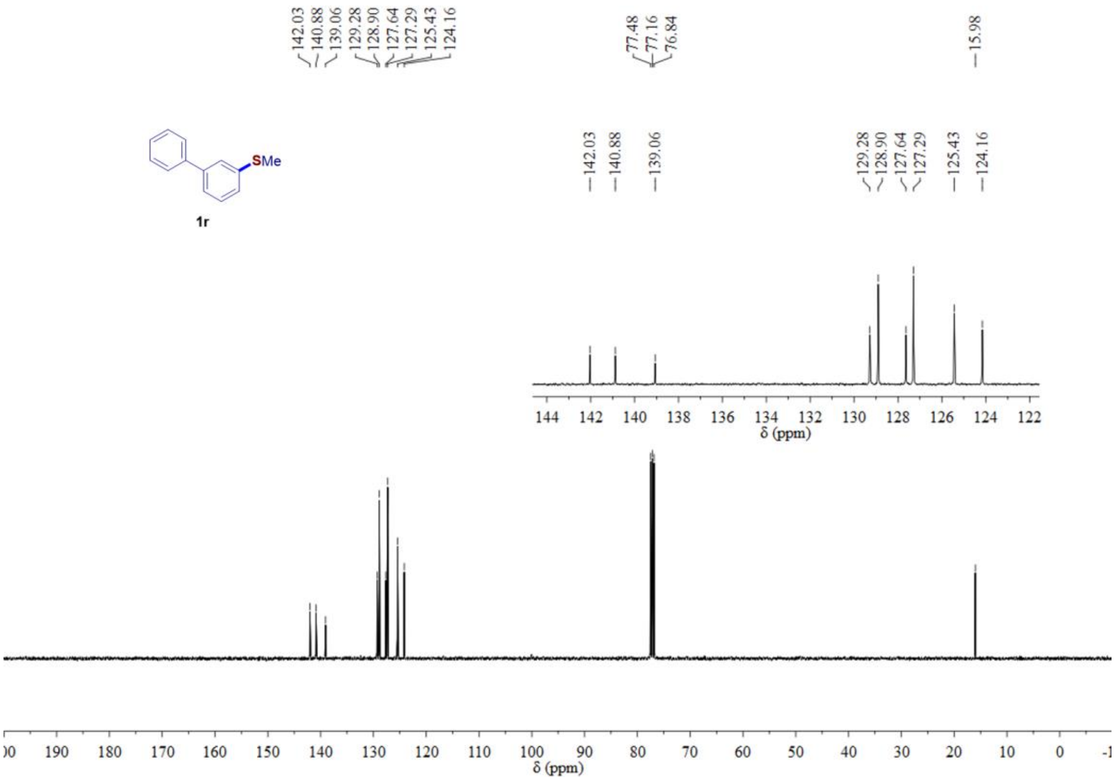
7.349
7.337
7.327
7.315
7.260
7.014
6.991
6.969
2.539
Cl
O
SMe
4.05
3.96
3.00
δ (ppm)
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


156.11
154.89
133.05
129.85
129.19
128.32
119.90
119.80
77.48
77.16
76.84
17.11
Cl
O
SMe
1o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

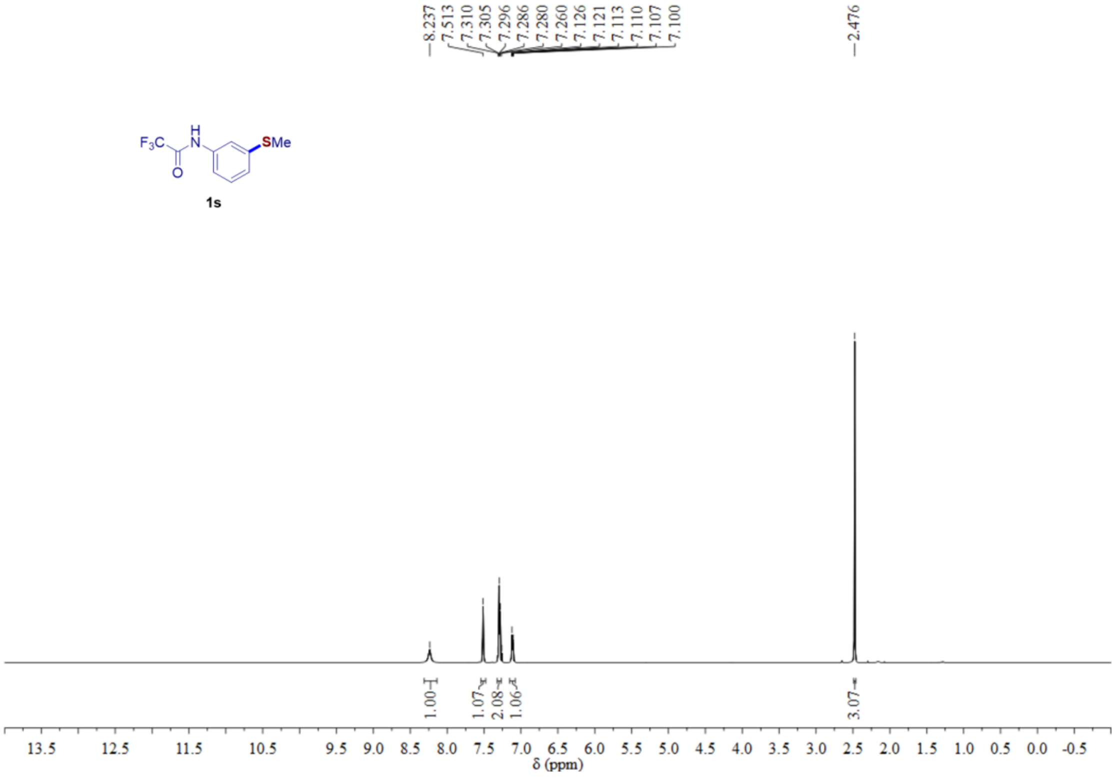

7.816
7.795
7.348
7.327
7.260
3.027
2.524
SMe
Me
S
O
O
1p
1.95
1.96
3.07
3.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)


147.33
136.32
127.76
125.60
77.48
77.16
76.84
44.79
14.87
SMe
Me
S
O
O
1p
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

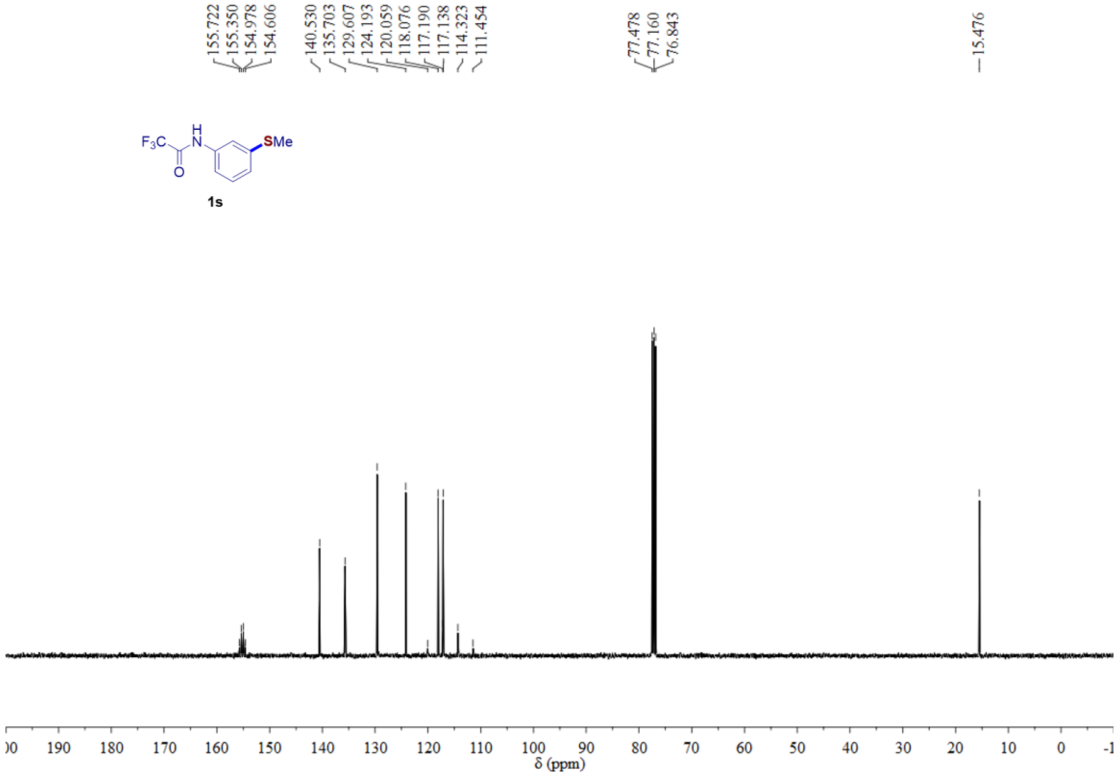

7.594
7.593
7.589
7.575
7.572
7.485
7.483
7.467
7.465
7.446
7.429
7.382
7.379
7.367
7.361
7.356
7.265
7.260
7.255
7.249
7.243
7.237
2.531
SMe
1r
7.75
7.65
7.55
7.45
7.35
7.25
7.15
δ (ppm)
2.00
3.02
3.02
1.05
3.07
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)

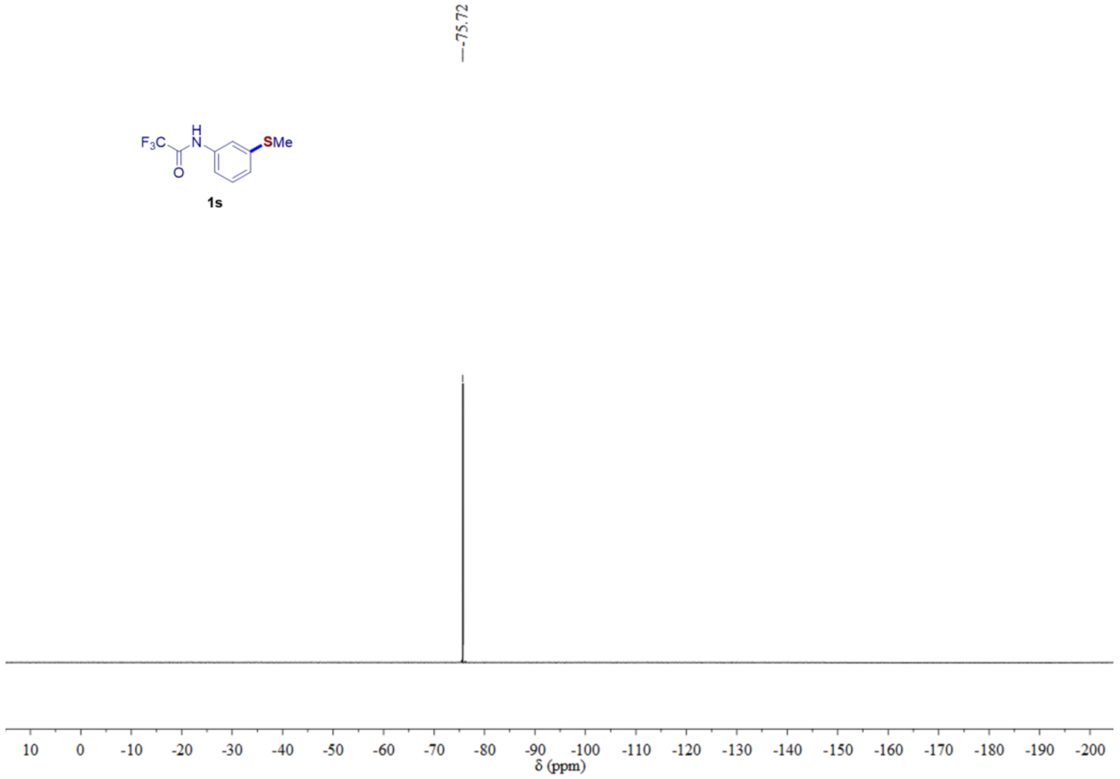

142.03
140.88
139.06
129.28
128.90
127.64
127.29
125.43
124.16
77.48
77.16
76.84
15.98
SMe
142.03
140.88
139.06
129.28
128.90
127.64
127.29
125.43
124.16
144 142 140 138 136 134 132 130 128 126 124 122
δ (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

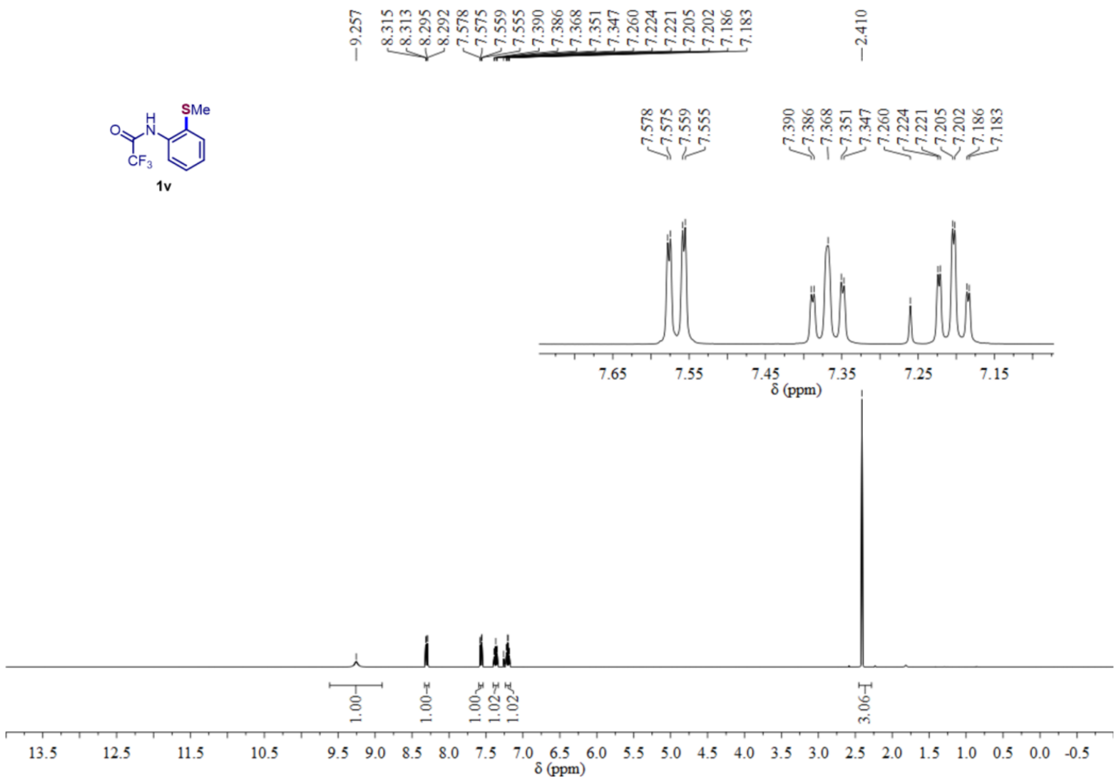
1r

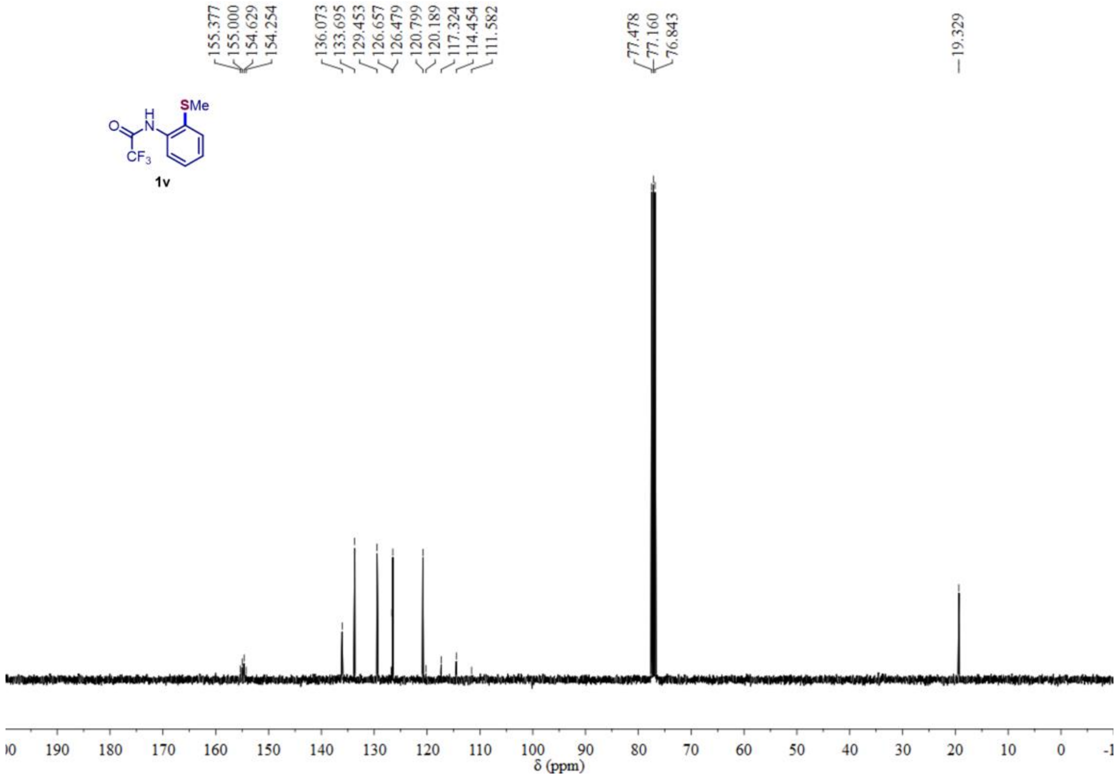

8.237
7.513
7.310
7.305
7.296
7.286
7.280
7.260
7.126
7.121
7.113
7.110
7.107
7.100
2.476
F3C
H
N
O
SMe
1.00
1.07
2.08
1.06
3.07
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

1s


155.722
155.350
154.978
154.606
140.530
135.703
129.607
124.193
120.059
118.076
117.190
117.138
114.323
111.454
77.478
77.160
76.843
15.476
F$_3$C
H
N
O
SMe
1s
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

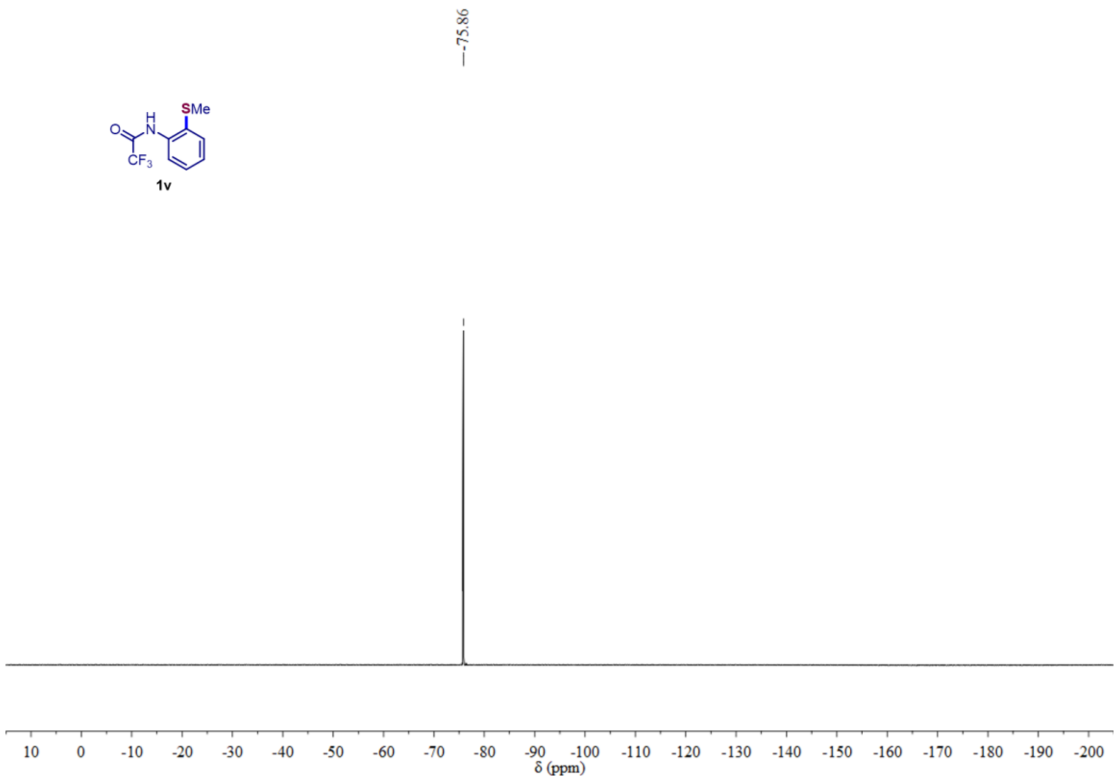

-75.72
F$_3$C
H
N
O
SMe
1s
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
δ (ppm)


9.257
8.315
8.313
8.295
8.292
7.578
7.575
7.559
7.555
7.390
7.386
7.368
7.351
7.347
7.260
7.224
7.221
7.205
7.202
7.186
7.183
2.410
SMe
H
N
O
CF3
1v
7.65
7.55
7.45
7.35
7.25
7.15
δ (ppm)
1.00
1.00
1.00
1.02
1.02
3.06
13.5
12.5
11.5
10.5
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
δ (ppm)


155.377
155.000
154.629
154.254
136.073
133.695
129.453
126.657
126.479
120.799
120.189
117.324
114.454
111.582
77.478
77.160
76.843
19.329
SMe
H
N
O
CF3
1v
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

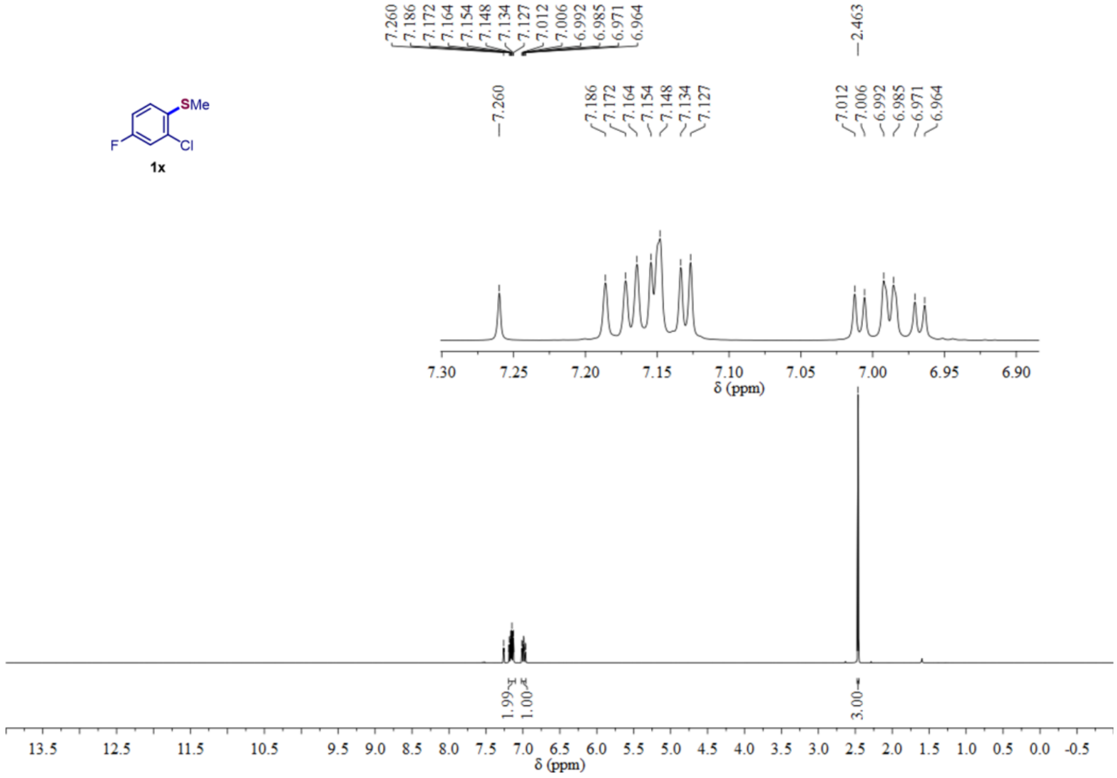
SMe
H
N
O
CF3

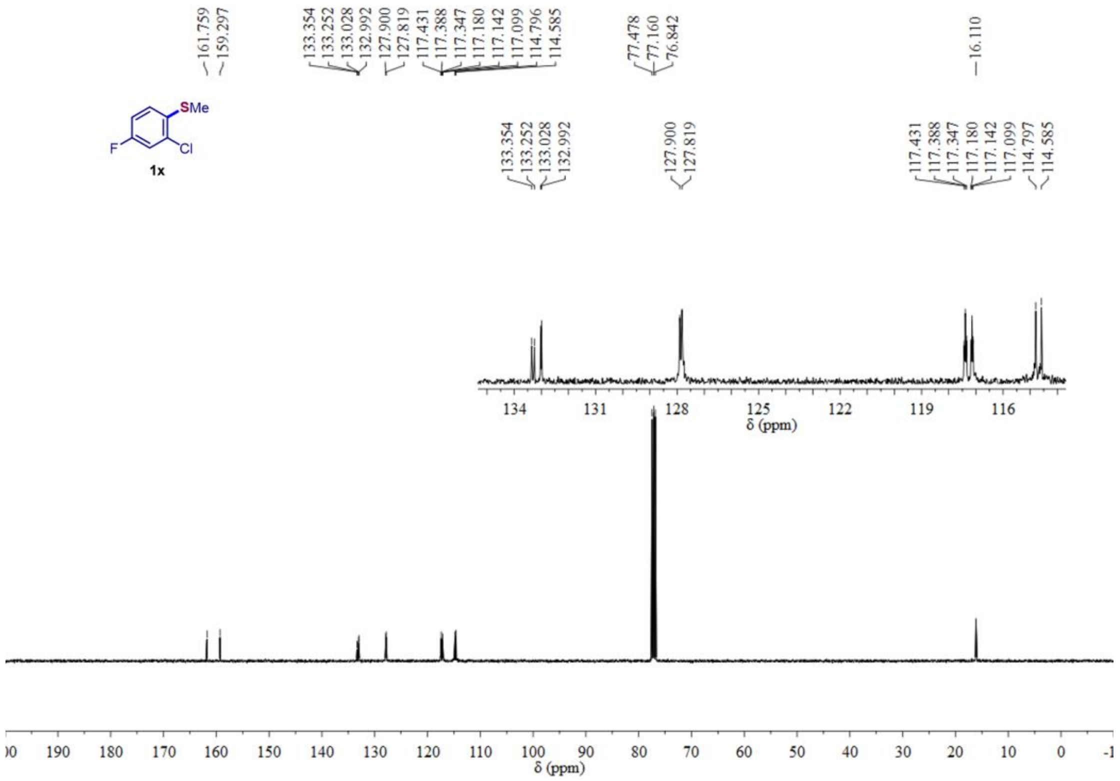
1v

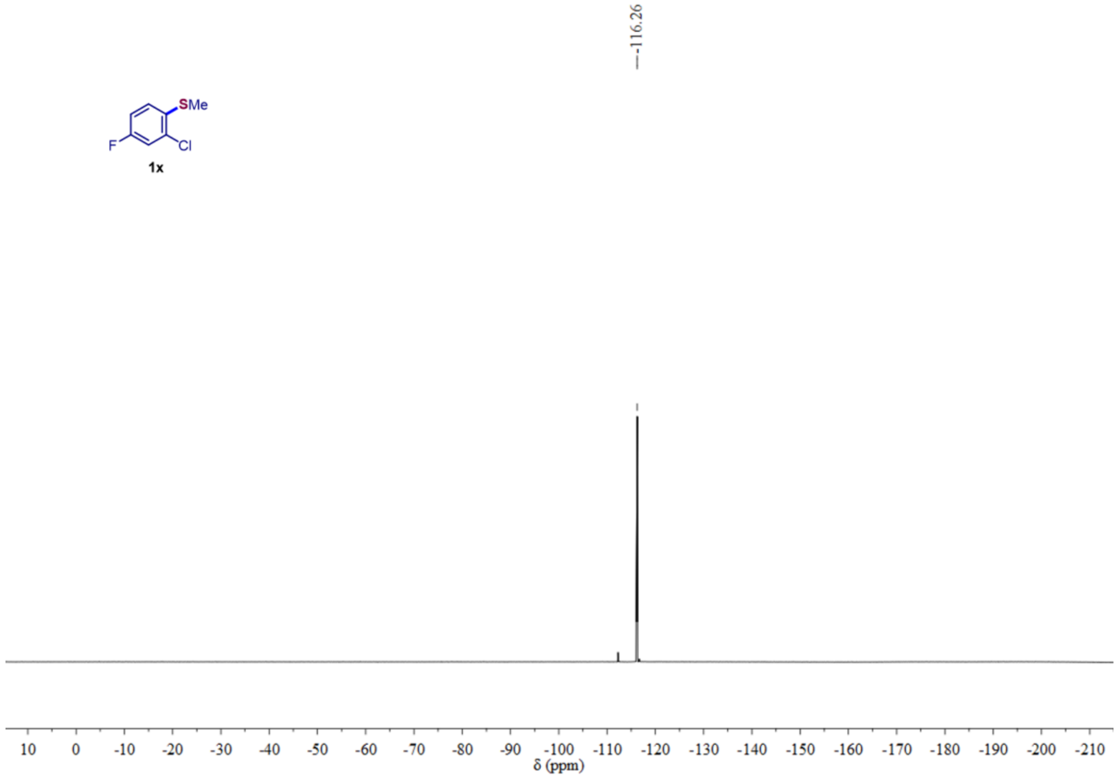

-75.86
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
δ (ppm)

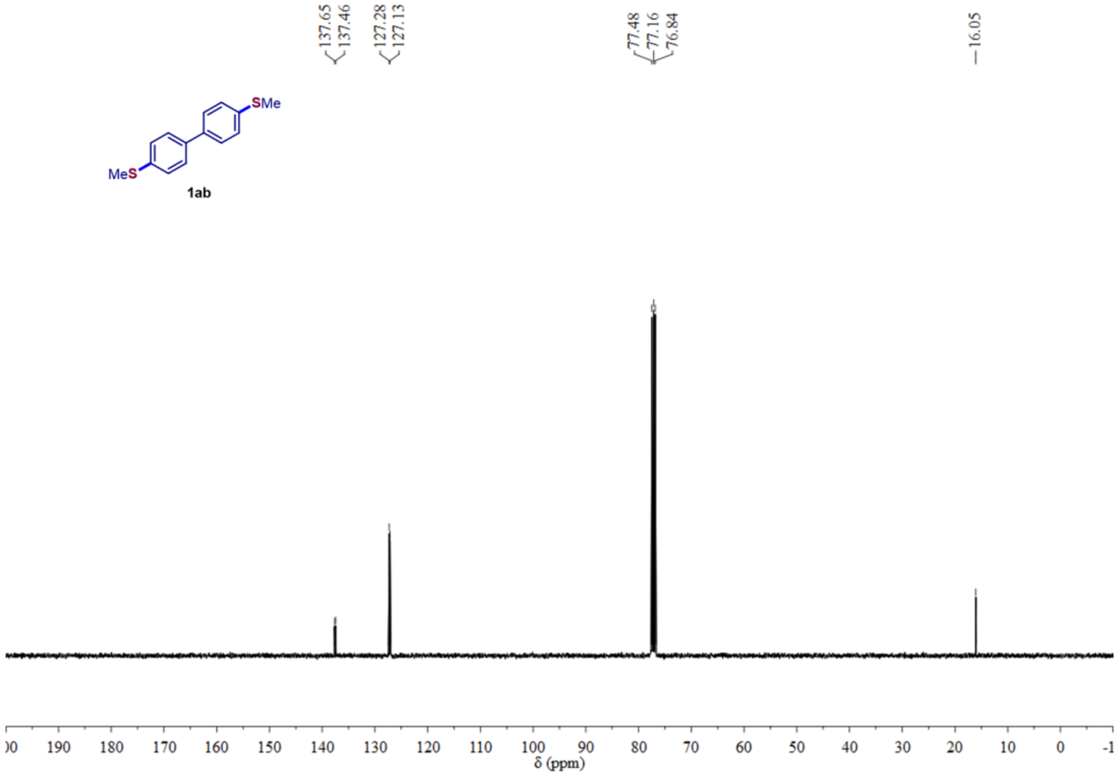
SMe
F
Cl

1x


7.260
7.186
7.172
7.164
7.154
7.148
7.134
7.127
7.012
7.006
6.992
6.985
6.971
6.964
2.463
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
δ (ppm)
1.99
1.00
3.00
13.5
12.5
11.5
10.5
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
δ (ppm)

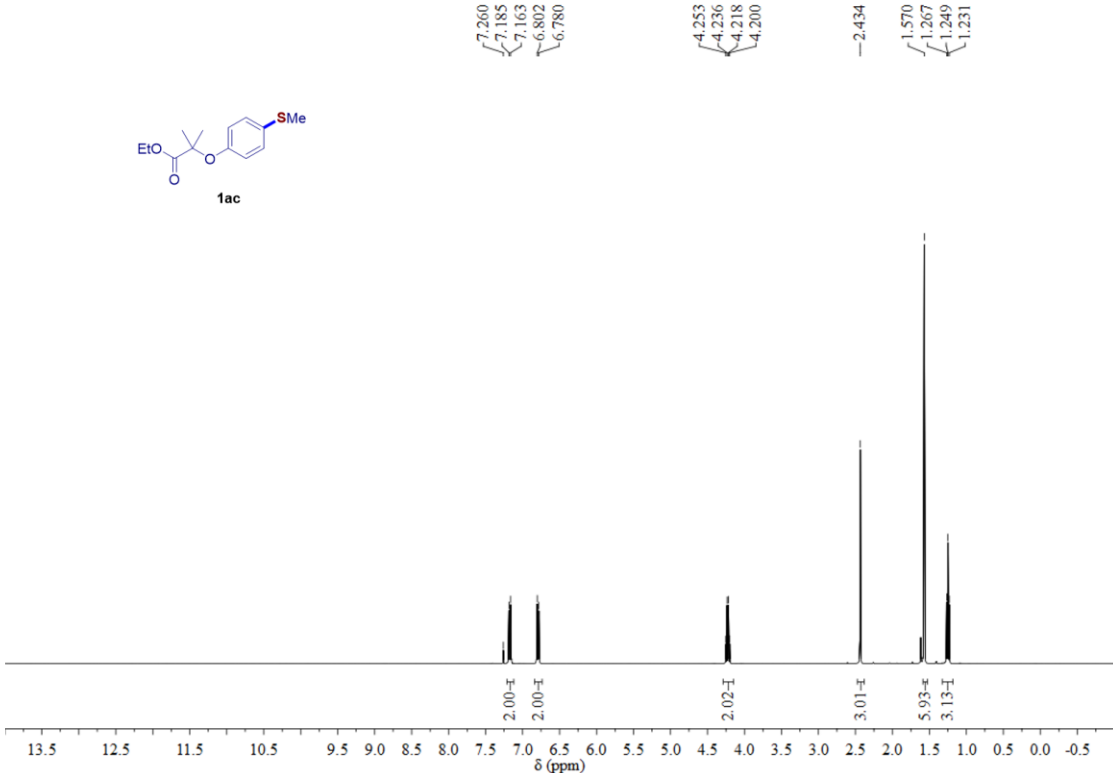

161.759
159.297
133.354
133.252
133.028
132.992
127.900
127.819
117.431
117.388
117.347
117.180
117.142
117.099
114.796
114.585
77.478
77.160
76.842
16.110
SMe
F
Cl
1x
133.354
133.252
133.028
132.992
127.900
127.819
117.431
117.388
117.347
117.180
117.142
117.099
114.797
114.585
134
131
128
125
122
119
116
δ (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


-116.26
SMe
F
Cl
1x
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
δ (ppm)



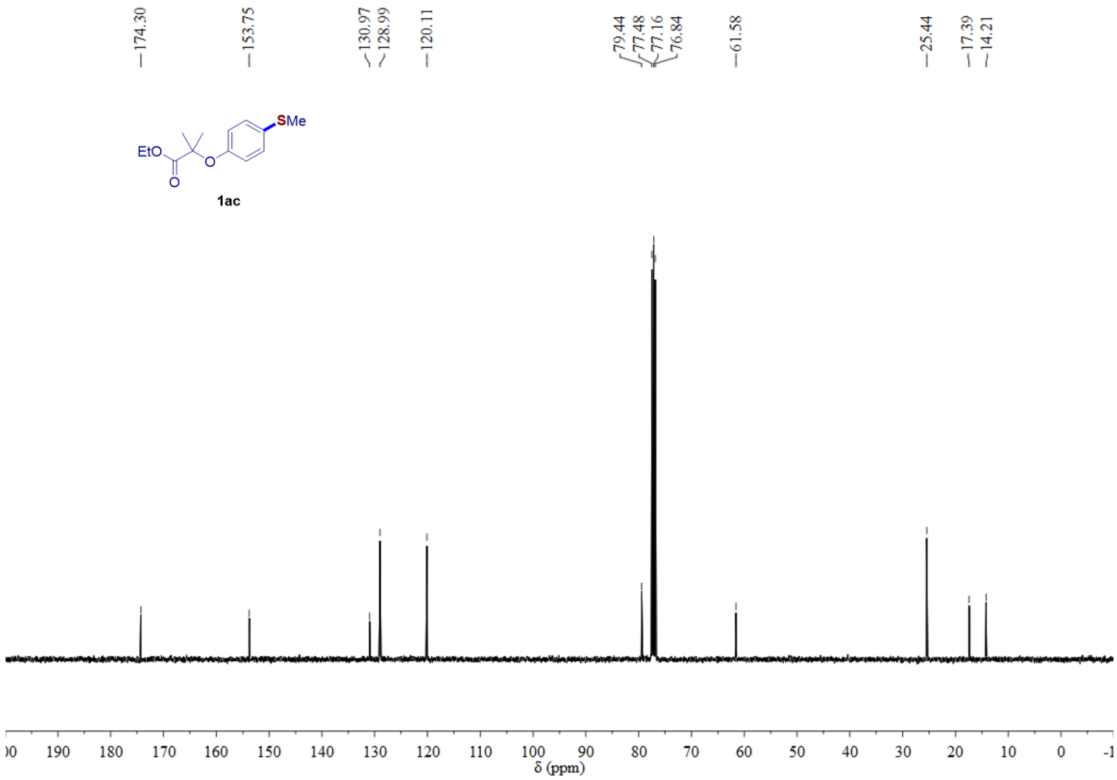
1ab

137.65
137.46
127.28
127.13
77.48
77.16
76.84
16.05
MeS
SMe
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

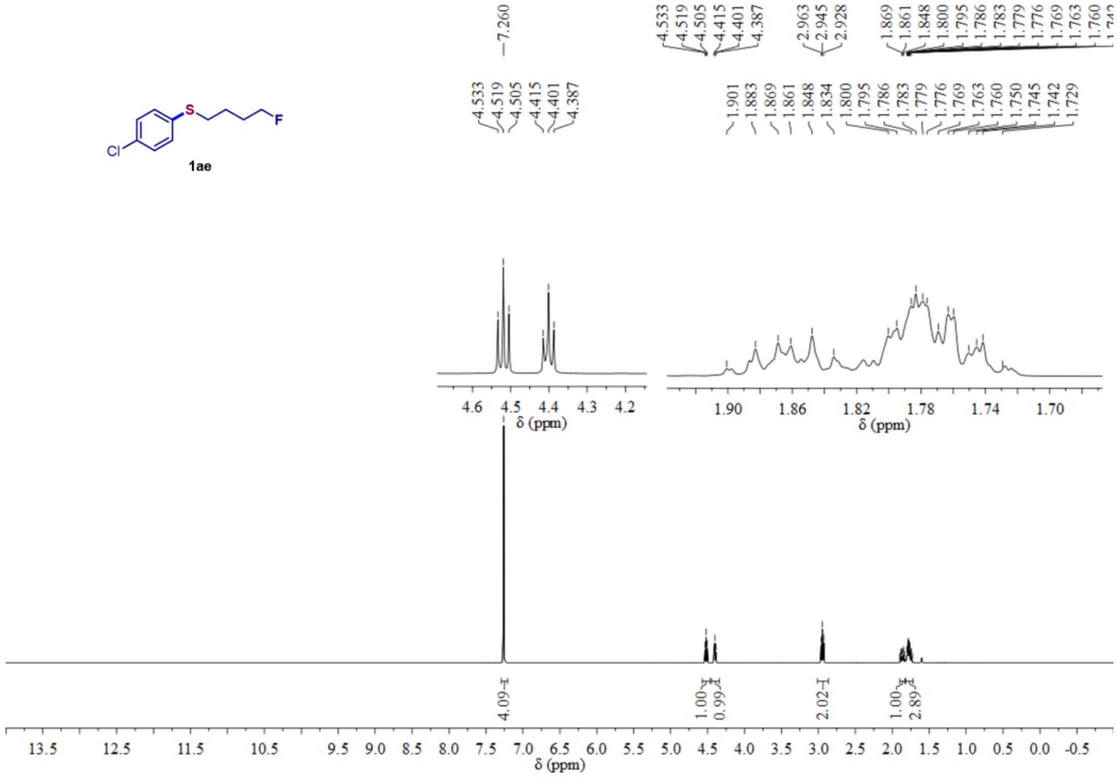


1ac

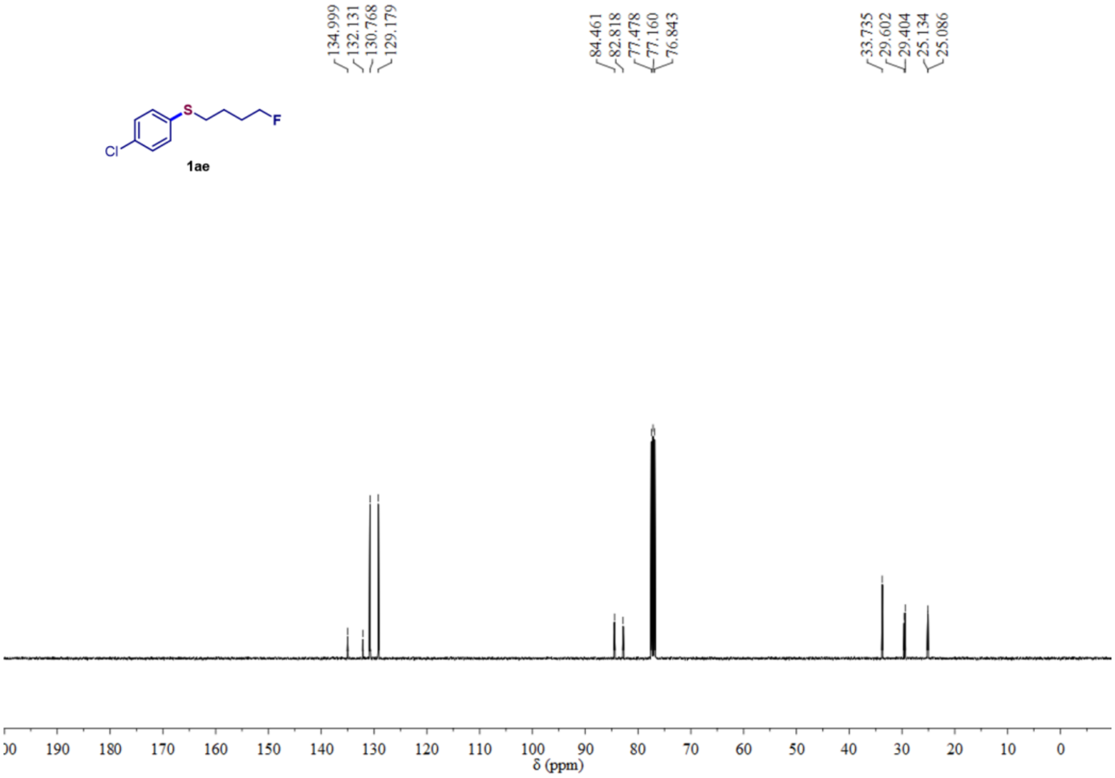
7.260
7.185
7.163
6.802
6.780
4.253
4.236
4.218
4.200
2.434
1.570
1.267
1.249
1.231
EtO
O
O
SMe
2.00
2.00
2.02
3.01
5.93
3.13
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)

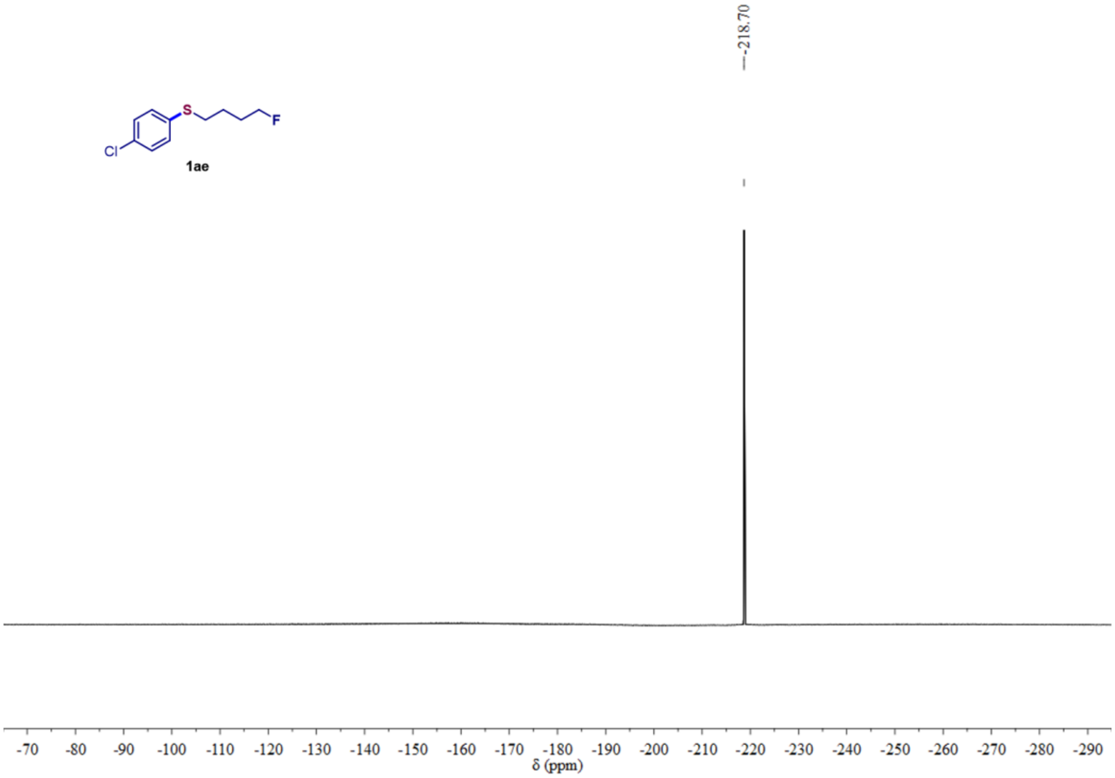

174.30
153.75
130.97
128.99
120.11
79.44
77.48
77.16
76.84
61.58
25.44
17.39
14.21
EtO
O
O
SMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

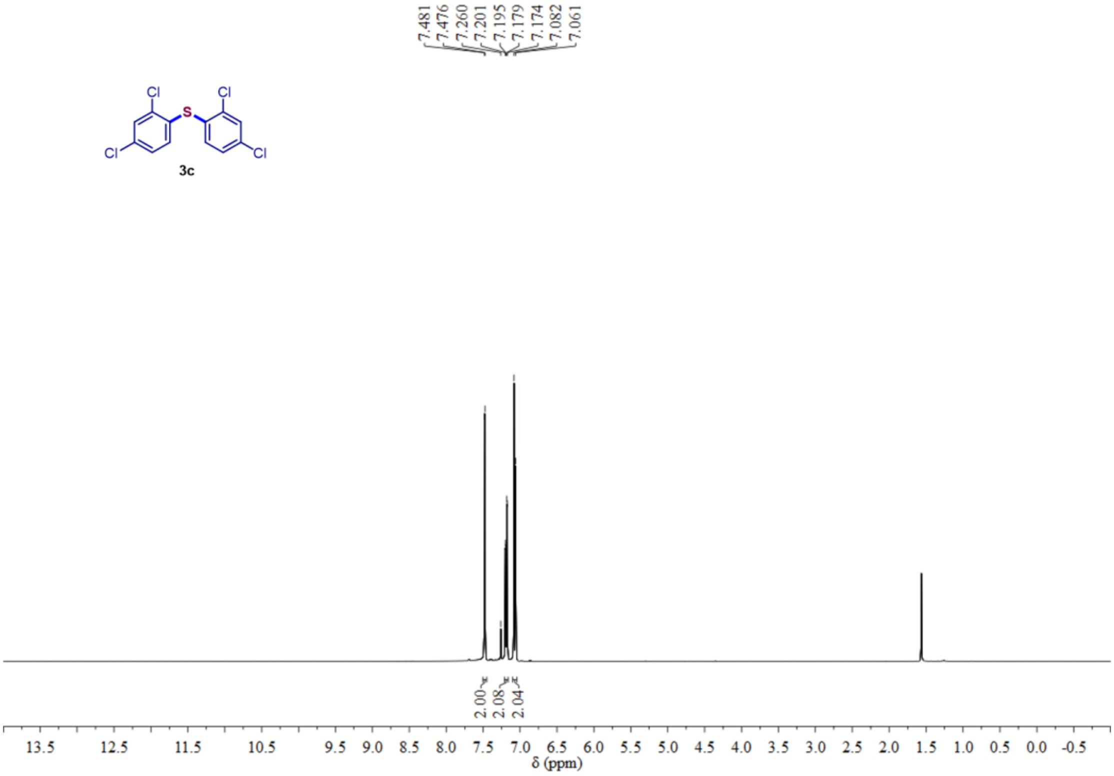
1ac

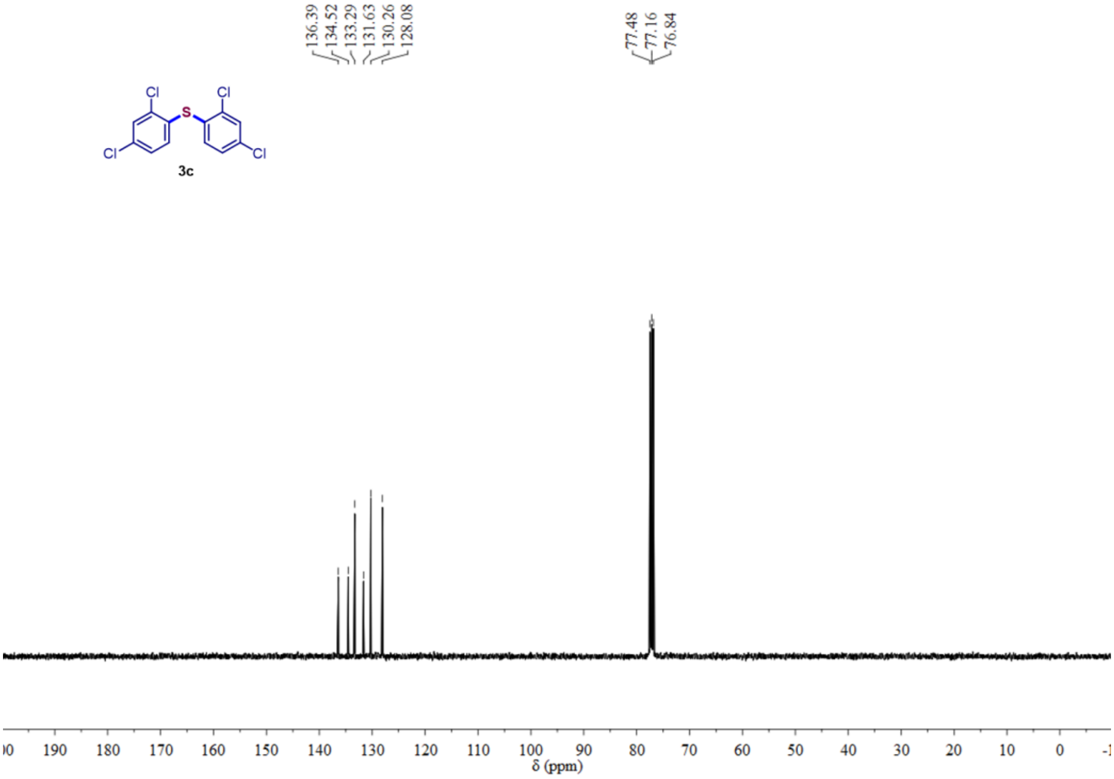

7.260
4.533
4.519
4.505
4.415
4.401
4.387
2.963
2.945
2.928
1.901
1.883
1.869
1.861
1.848
1.834
1.800
1.795
1.786
1.783
1.779
1.776
1.769
1.763
1.760
1.750
1.745
1.742
1.729
Cl
S
F
4.6
4.5
4.4
4.3
4.2
δ (ppm)
1.90
1.86
1.82
1.78
1.74
1.70
δ (ppm)
4.09
1.00
0.99
2.02
1.00
2.89
13.5
12.5
11.5
10.5
9.5
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
δ (ppm)

1ae


134.999
132.131
130.768
129.179
84.461
82.818
77.478
77.160
76.843
33.735
29.602
29.404
25.134
25.086
S
F
Cl
1ae
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

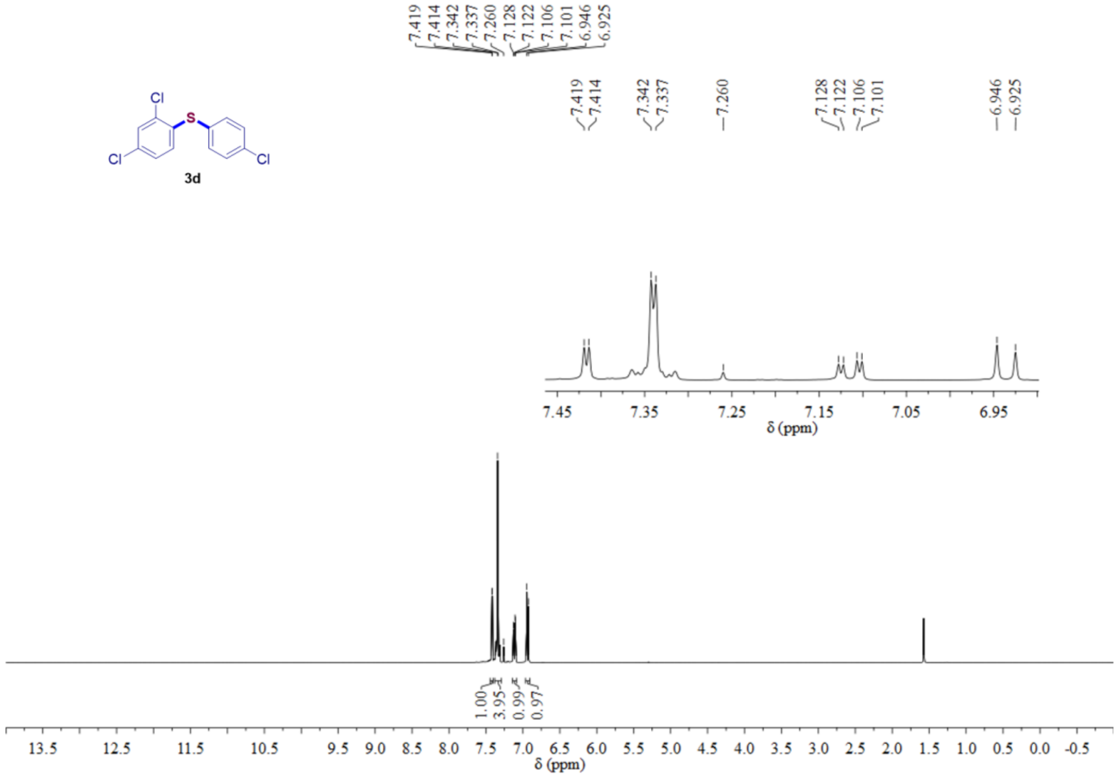

-218.70
S
F
Cl
1ae
-70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290
δ (ppm)


7.481
7.476
7.260
7.201
7.195
7.179
7.174
7.082
7.061
Cl
S
Cl
Cl
Cl
3c
2.00
2.08
2.04
13.5
12.5
11.5
10.5
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
δ (ppm)


136.39
134.52
133.29
131.63
130.26
128.08
77.48
77.16
76.84
Cl
S
Cl
Cl
Cl
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

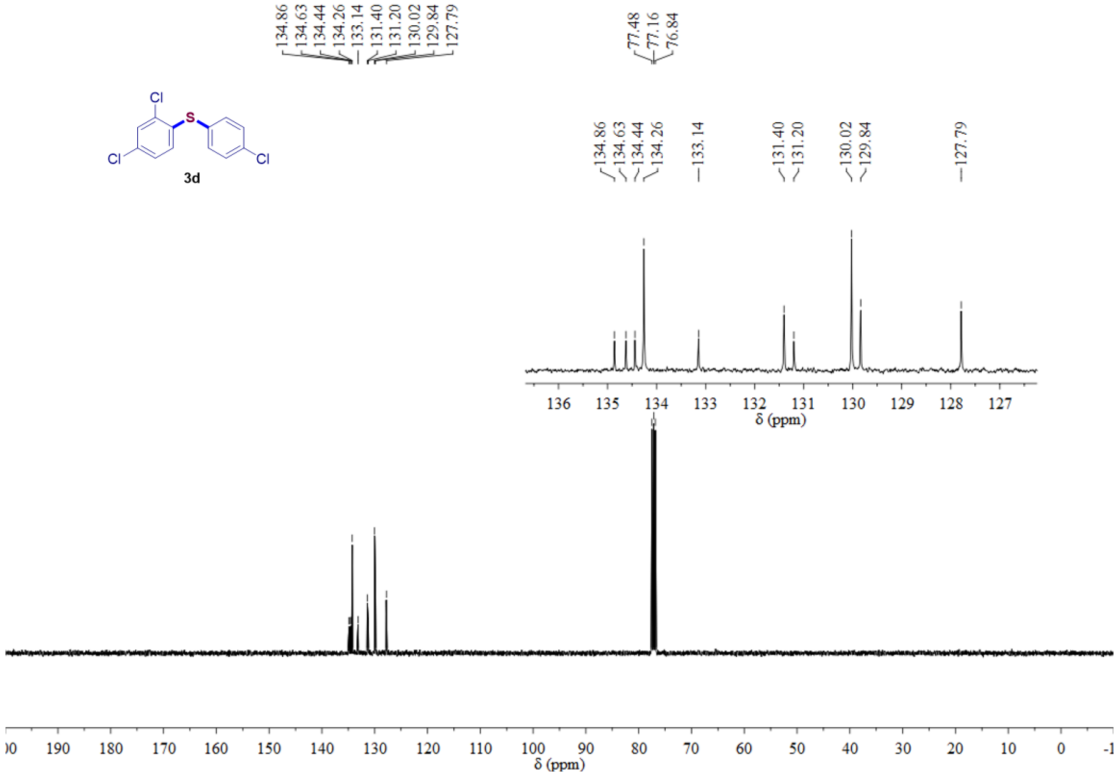
Cl
S
Cl
Cl

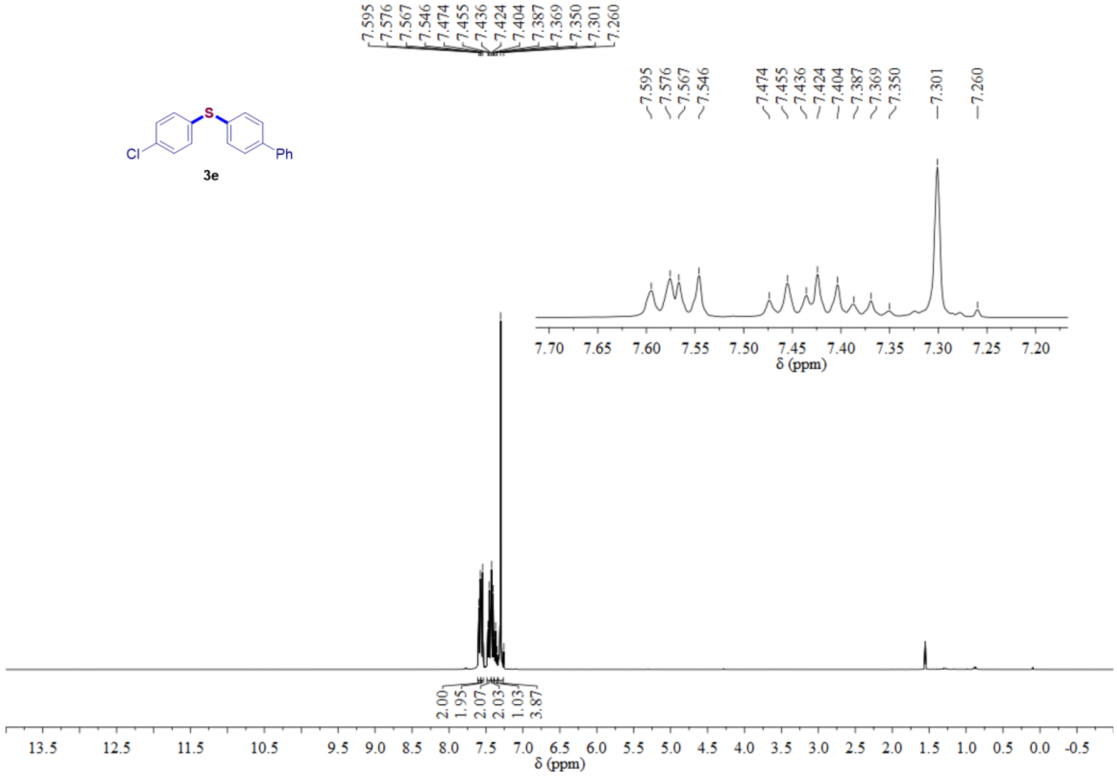
3d

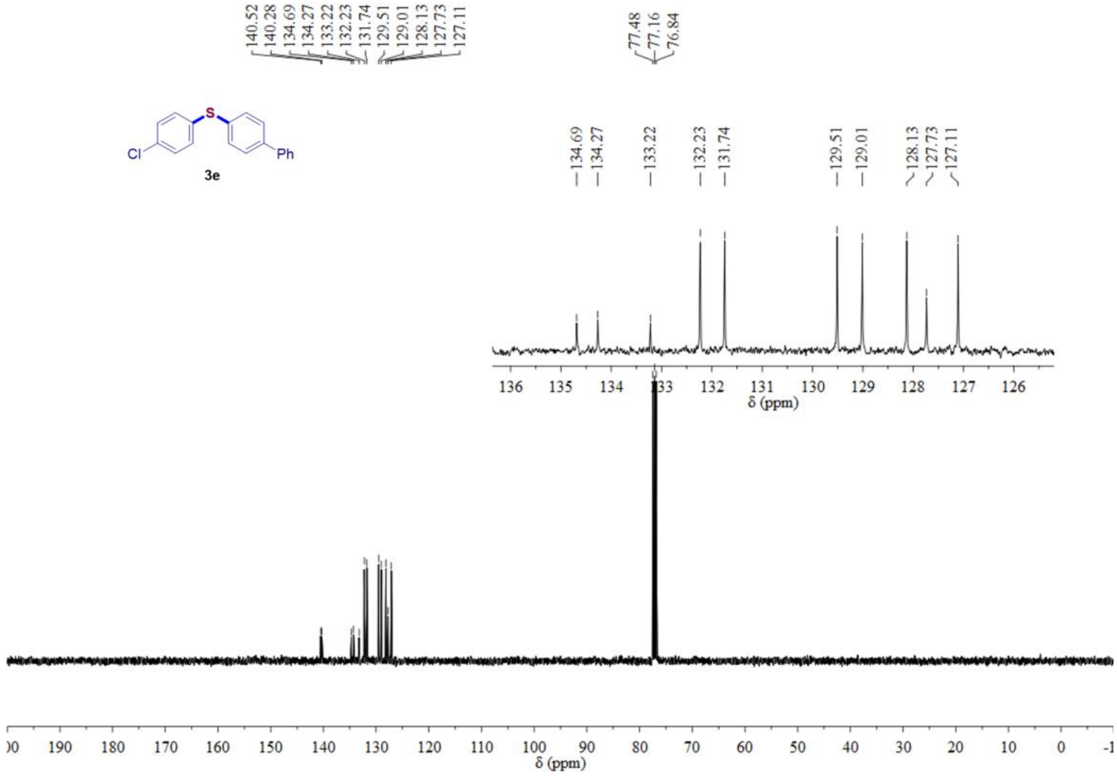

7.419
7.414
7.342
7.337
7.260
7.128
7.122
7.106
7.101
6.946
6.925
7.45
7.35
7.25
7.15
7.05
6.95
δ (ppm)
1.00
3.95
0.99
0.97
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)

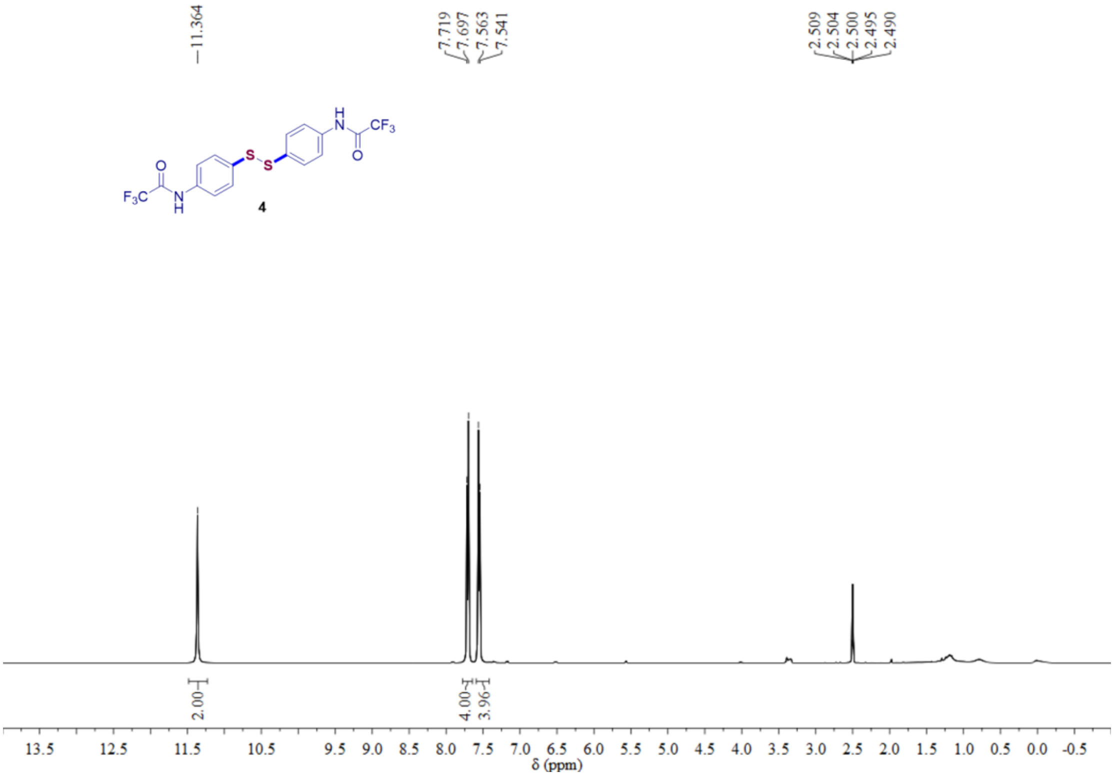
Cl
S
Cl
Cl

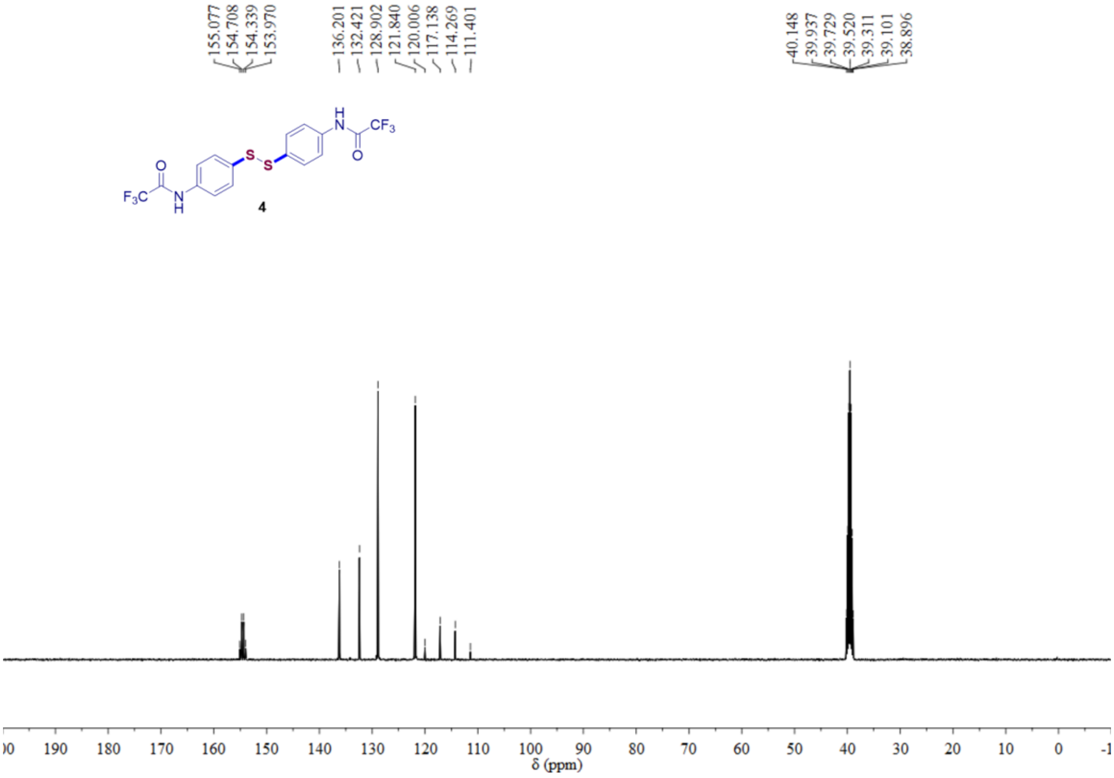
3d

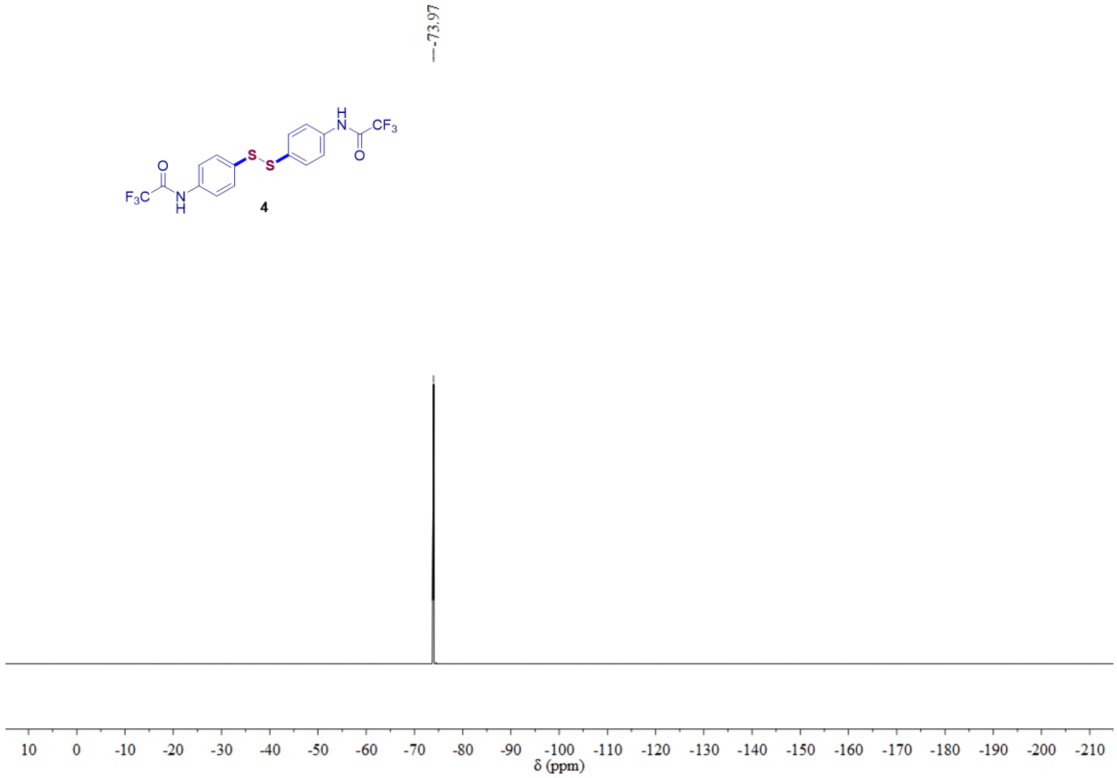

134.86
134.63
134.44
134.26
133.14
131.40
131.20
130.02
129.84
127.79
77.48
77.16
76.84
136
135
134
133
132
131
130
129
128
127
δ (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

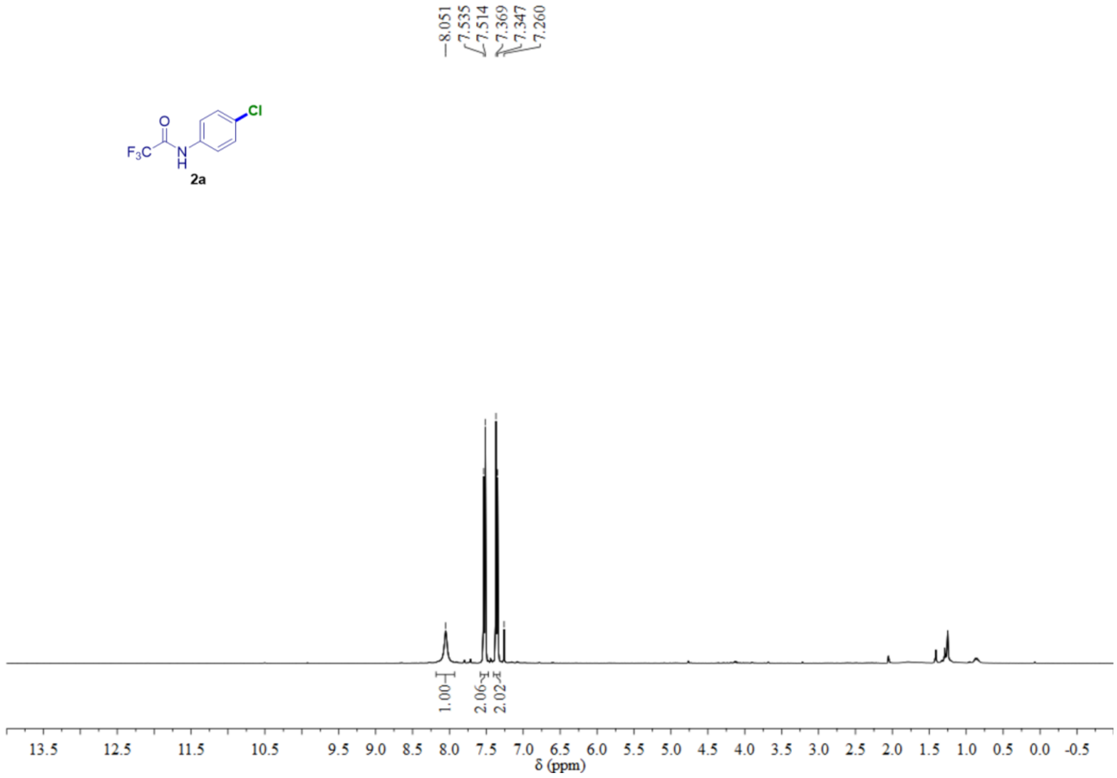

7.595
7.576
7.567
7.546
7.474
7.455
7.436
7.424
7.404
7.387
7.369
7.350
7.301
7.260
Cl
S
Ph
3e
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
δ (ppm)
2.00
1.95
2.07
2.03
1.03
3.87
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

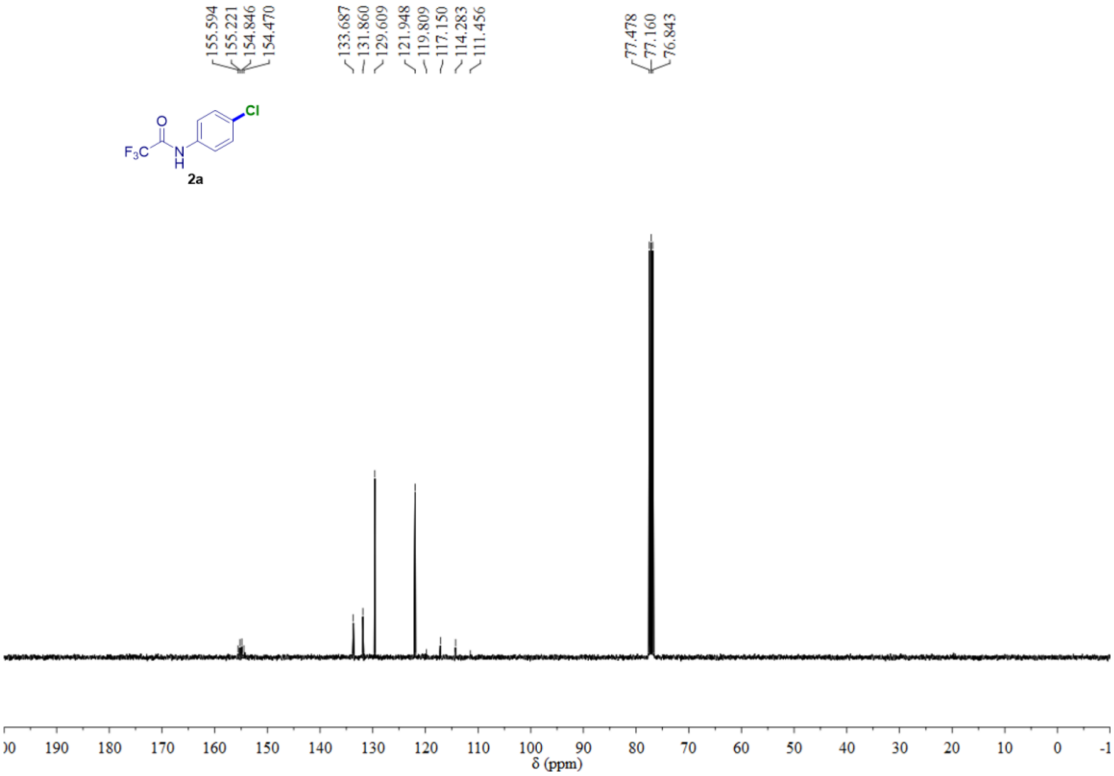

140.52
140.28
134.69
134.27
133.22
132.23
131.74
129.51
129.01
128.13
127.73
127.11
77.48
77.16
76.84
Cl
S
Ph
3e
136 135 134 133 132 131 130 129 128 127 126
δ (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

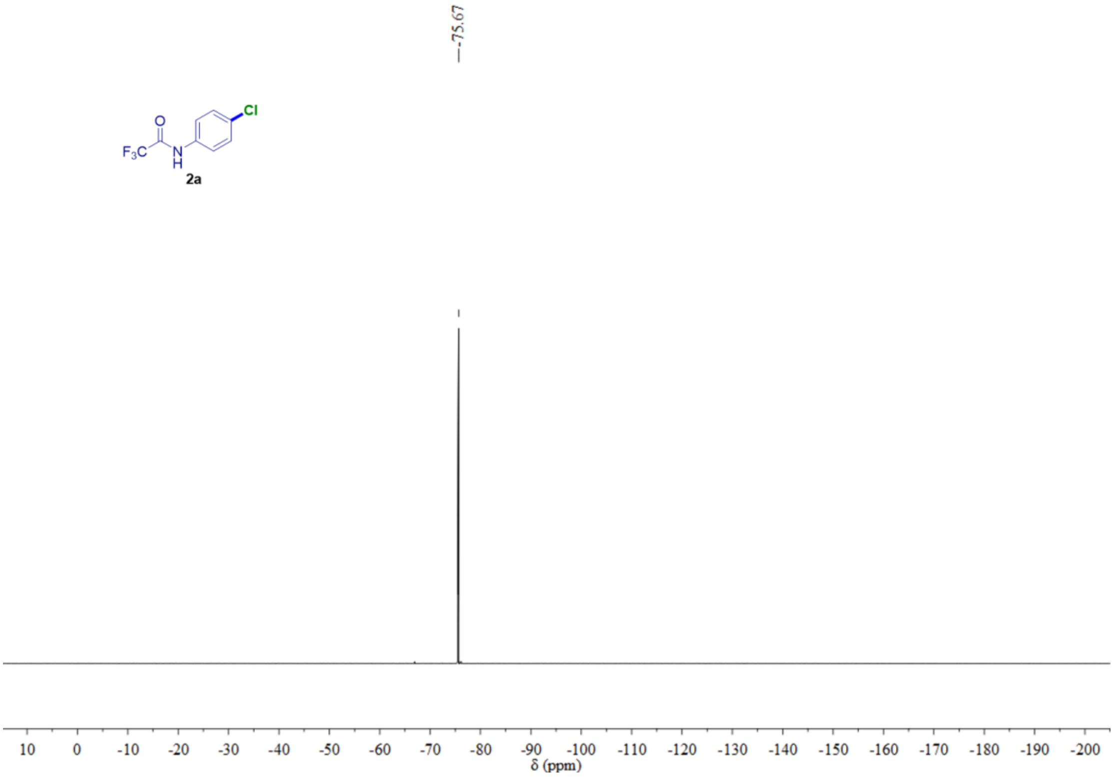

11.364
7.719
7.697
7.563
7.541
2.509
2.504
2.500
2.495
2.490
4
2.00
4.00
3.96
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

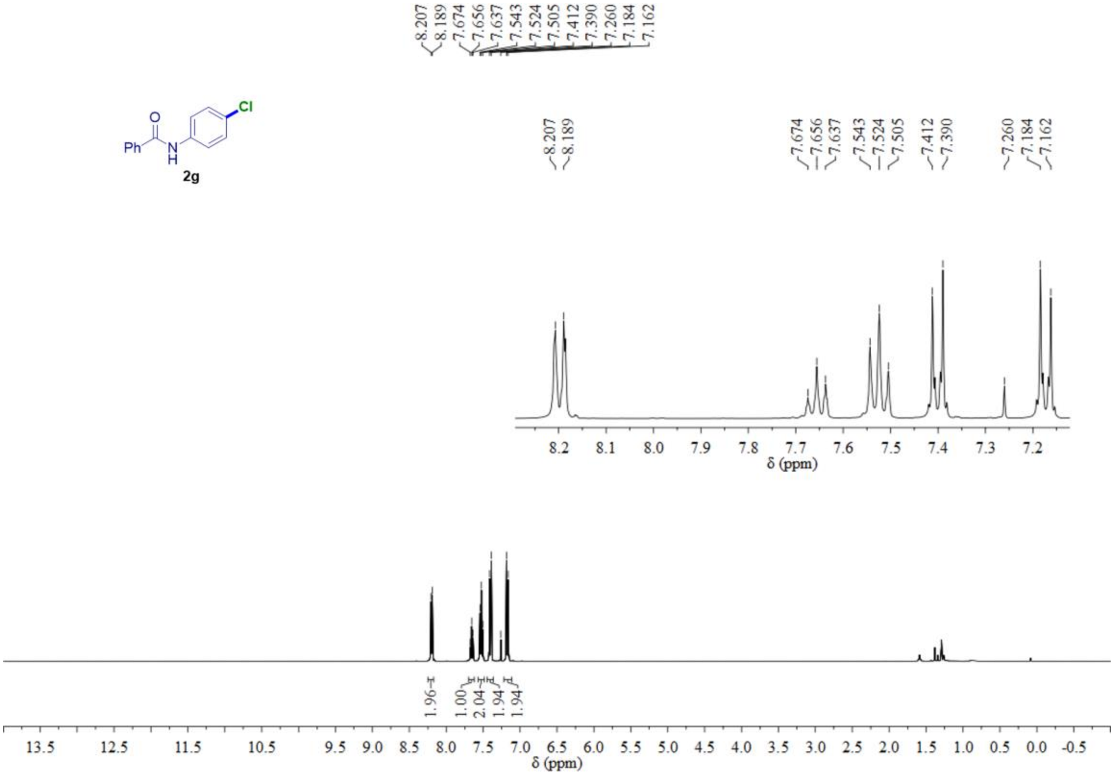

155.077
154.708
154.339
153.970
136.201
132.421
128.902
121.840
120.006
117.138
114.269
111.401
40.148
39.937
39.729
39.520
39.311
39.101
38.896
4
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

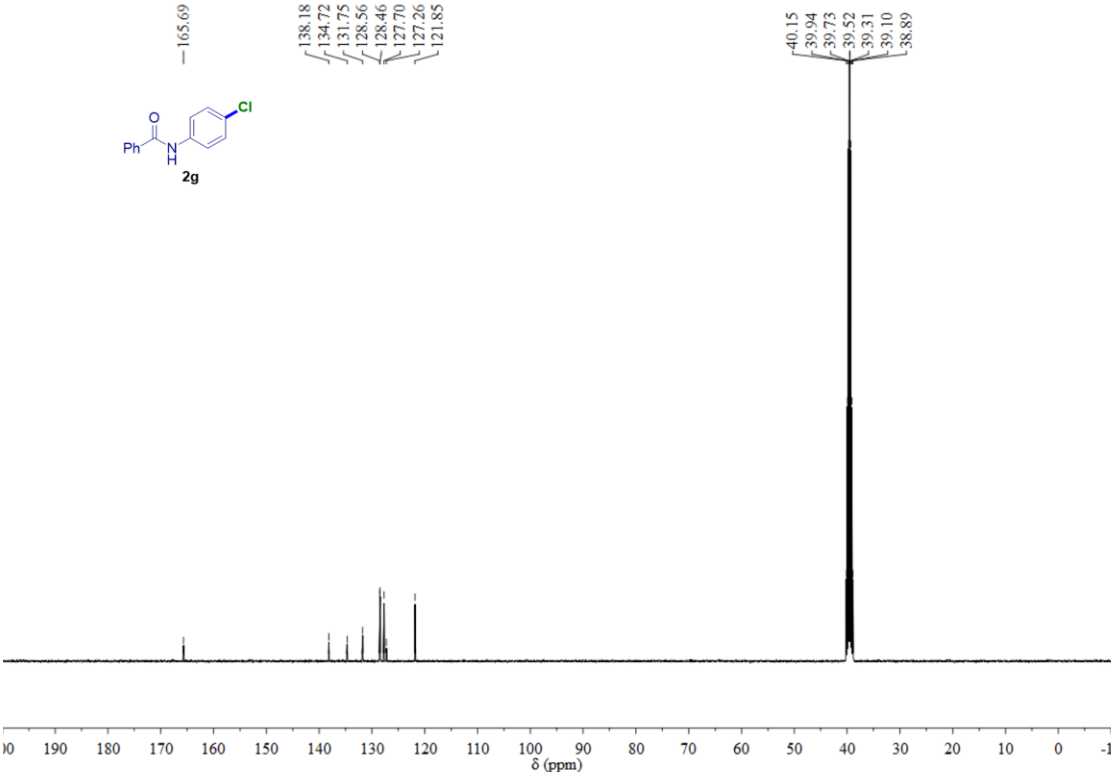

-73.97
F3C
O
N
H
S
S
N
H
CF3
O
4
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
δ (ppm)

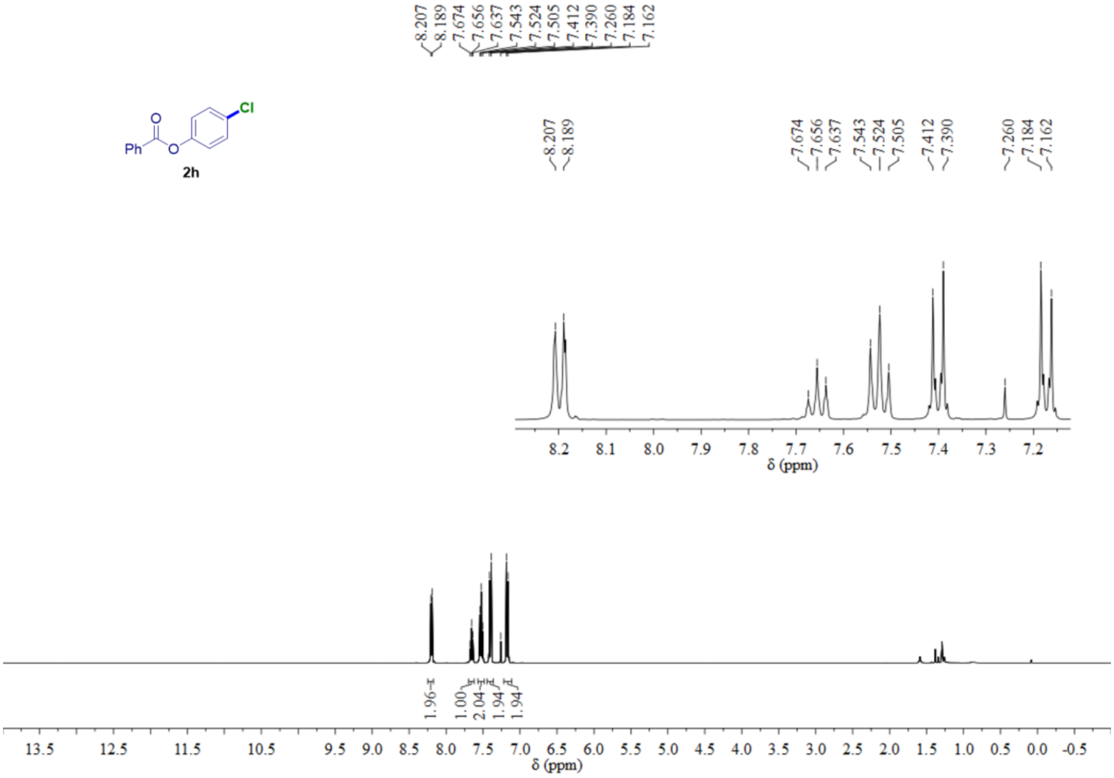

8.051
7.535
7.514
7.369
7.347
7.260
F3C
O
N
H
Cl
2a
1.00
2.06
2.02
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)

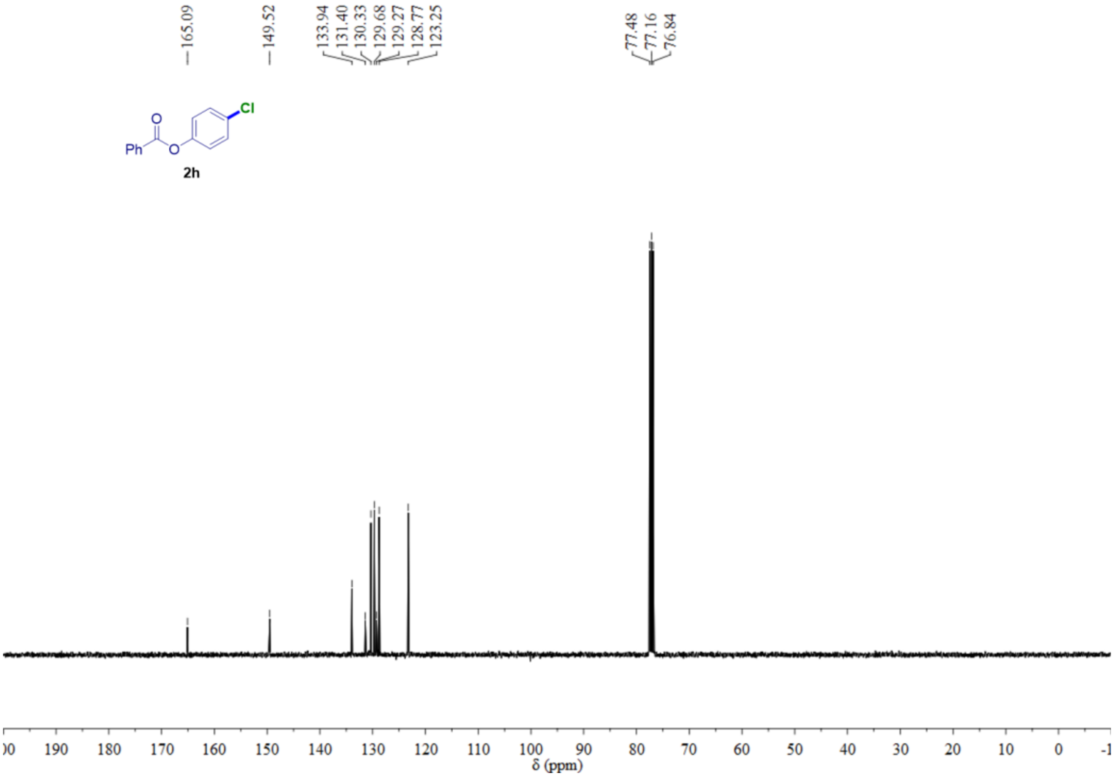

155.594
155.221
154.846
154.470
133.687
131.860
129.609
121.948
119.809
117.150
114.283
111.456
77.478
77.160
76.843
O
Cl
F3C
N
H
2a
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

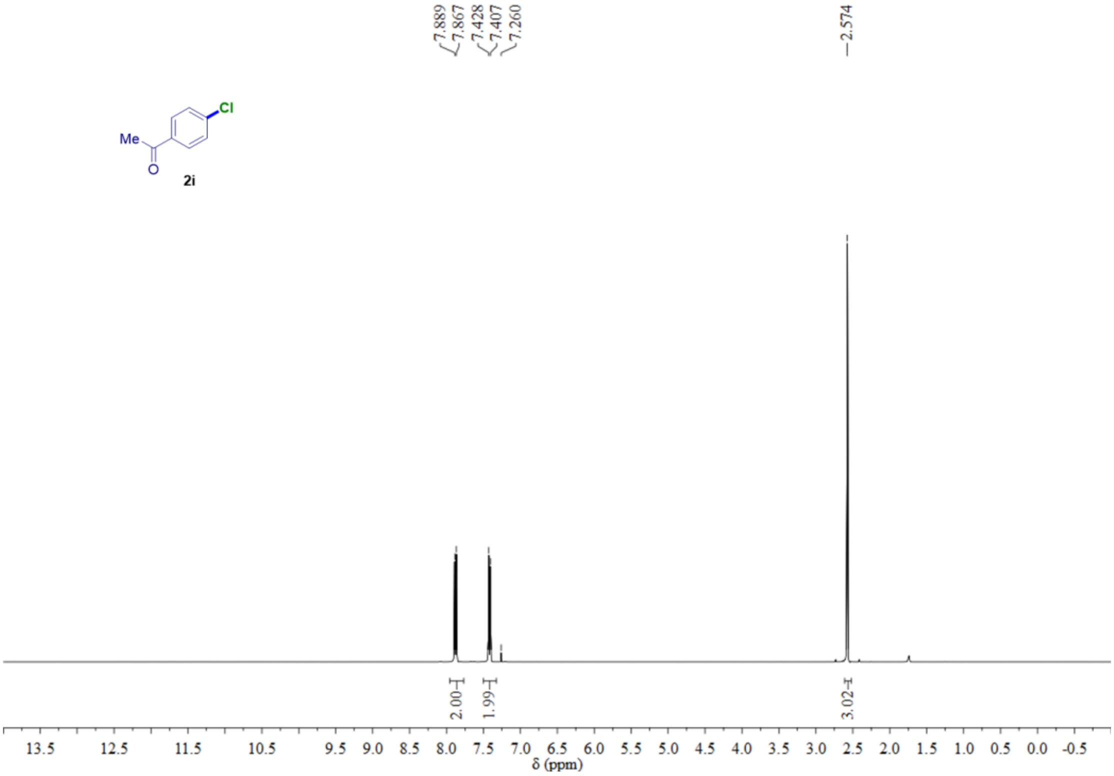

-75.67
O
Cl
F3C
N
H
2a
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
δ (ppm)

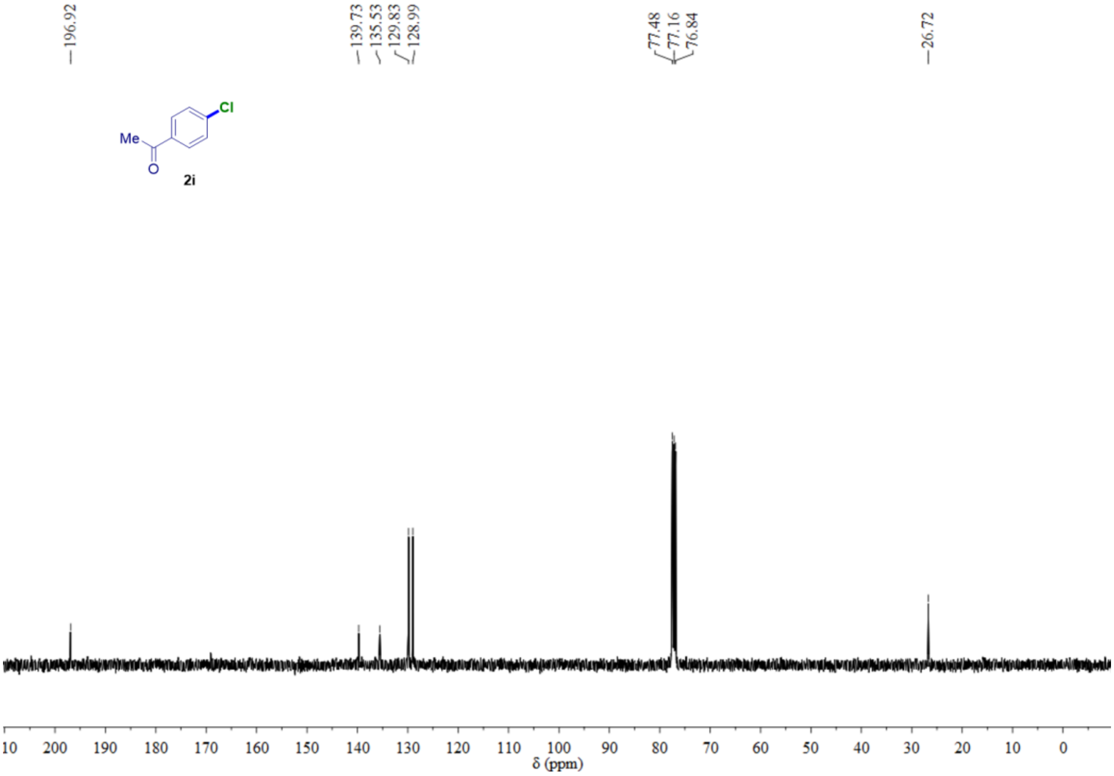

8.207
8.189
7.674
7.656
7.637
7.543
7.524
7.505
7.412
7.390
7.260
7.184
7.162
Ph
O
N
H
Cl
2g
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
δ (ppm)
1.96
1.00
2.04
1.94
1.94
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

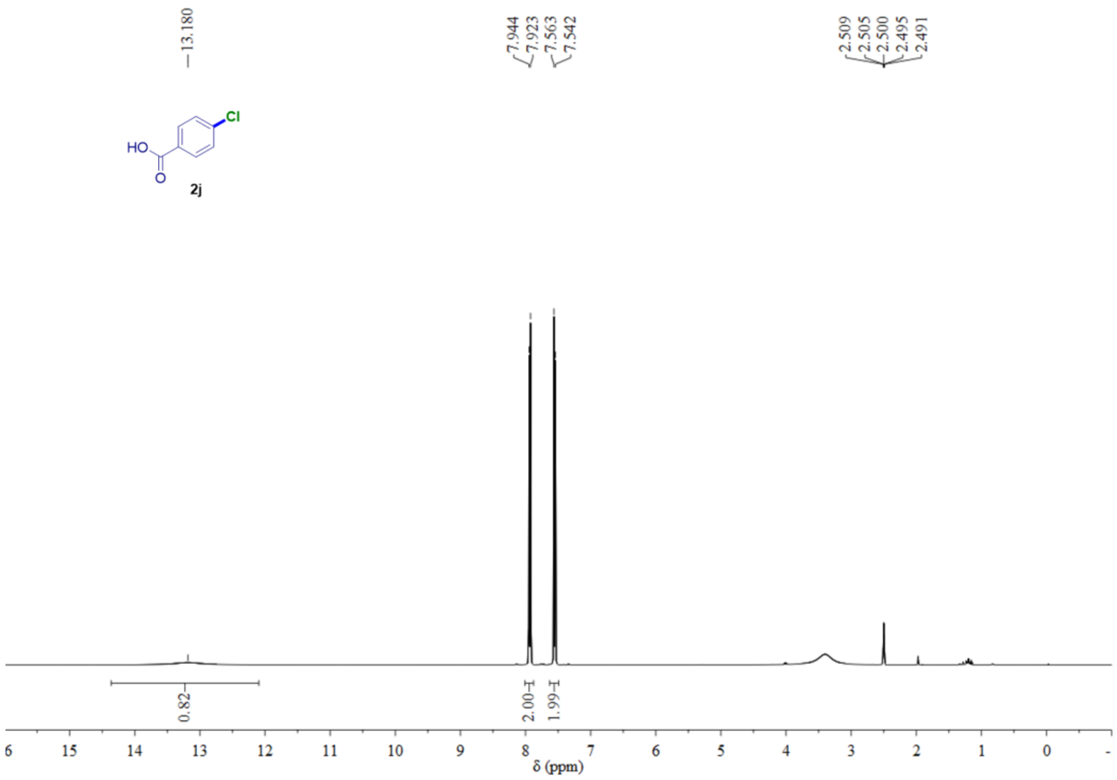

165.69
138.18
134.72
131.75
128.56
128.46
127.70
127.26
121.85
40.15
39.94
39.73
39.52
39.31
39.10
38.89
Ph
O
N
H
Cl
2g
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

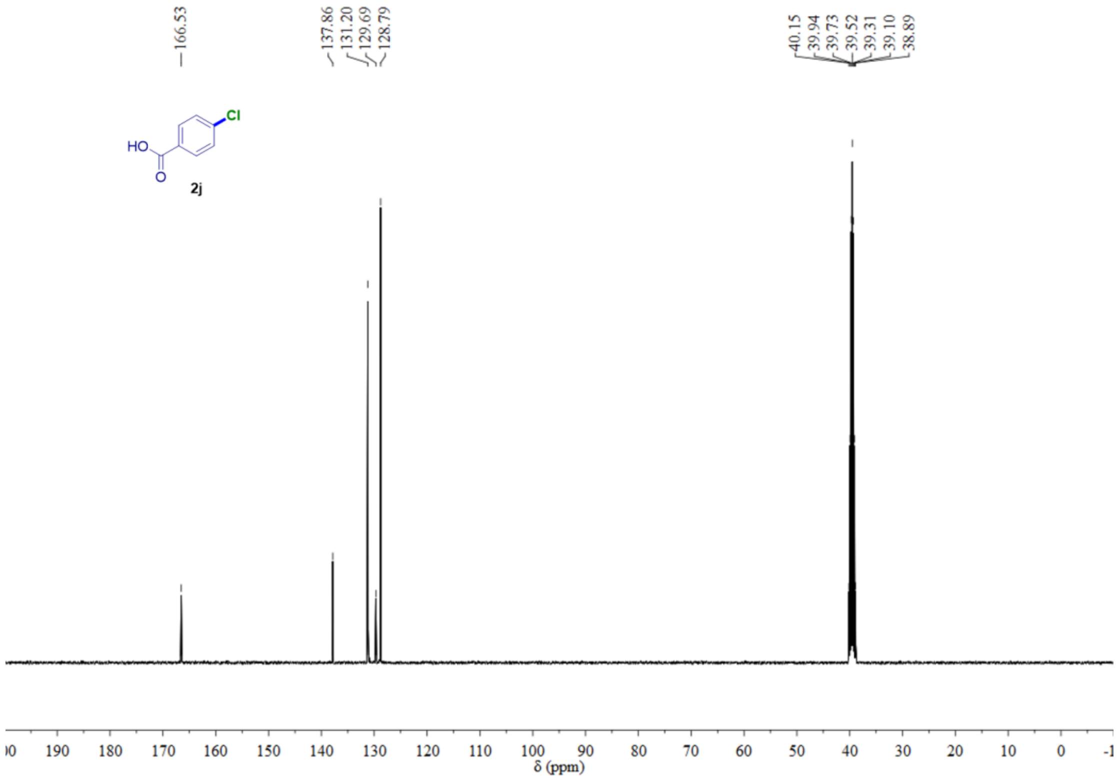

8.207
8.189
7.674
7.656
7.637
7.543
7.524
7.505
7.412
7.390
7.260
7.184
7.162
Cl
O
Ph
O
2h
1.96
1.00
2.04
1.94
1.94
δ (ppm)
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2

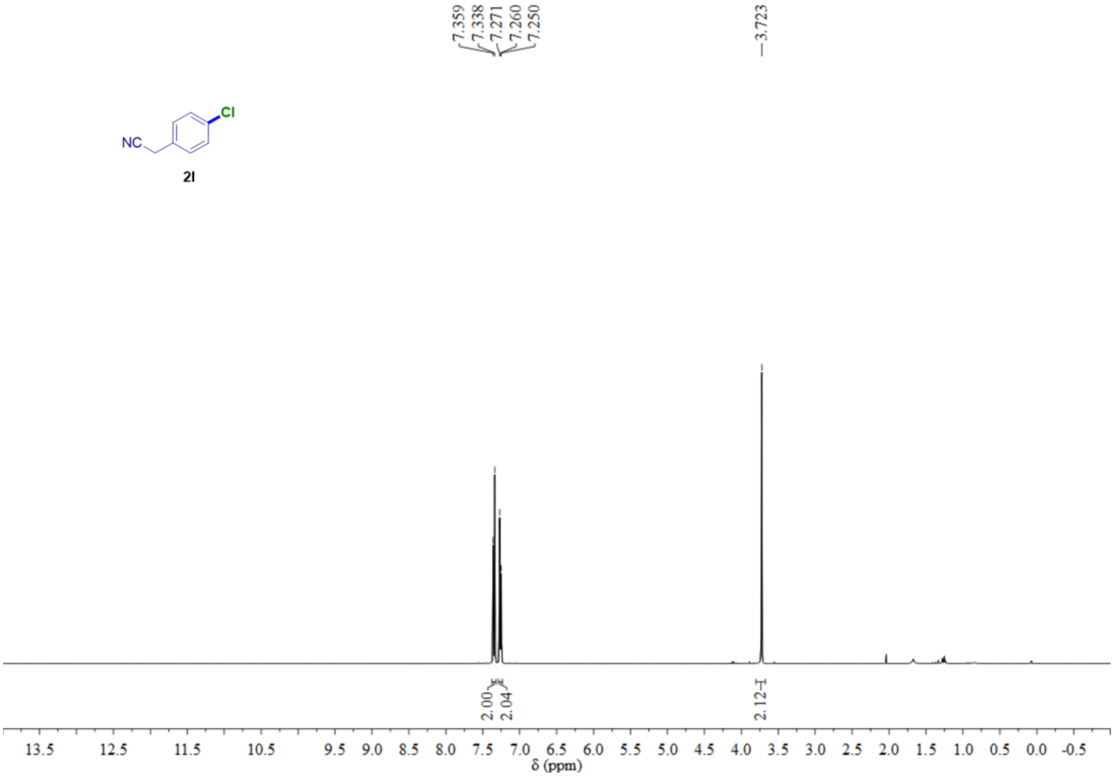

165.09
149.52
133.94
131.40
130.33
129.68
129.27
128.77
123.25
77.48
77.16
76.84
Cl
O
Ph
O
2h
δ (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

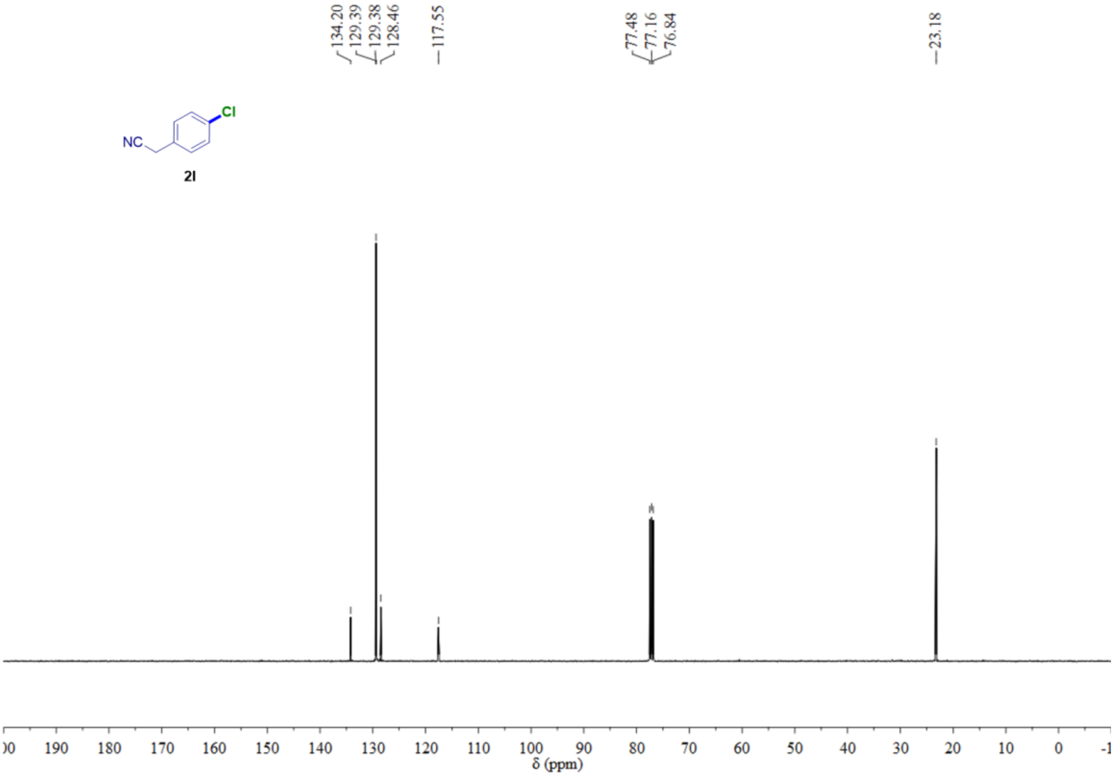

7.889
7.867
7.428
7.407
7.260
2.574
Me
O
Cl
2i
2.00
1.99
3.02
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)

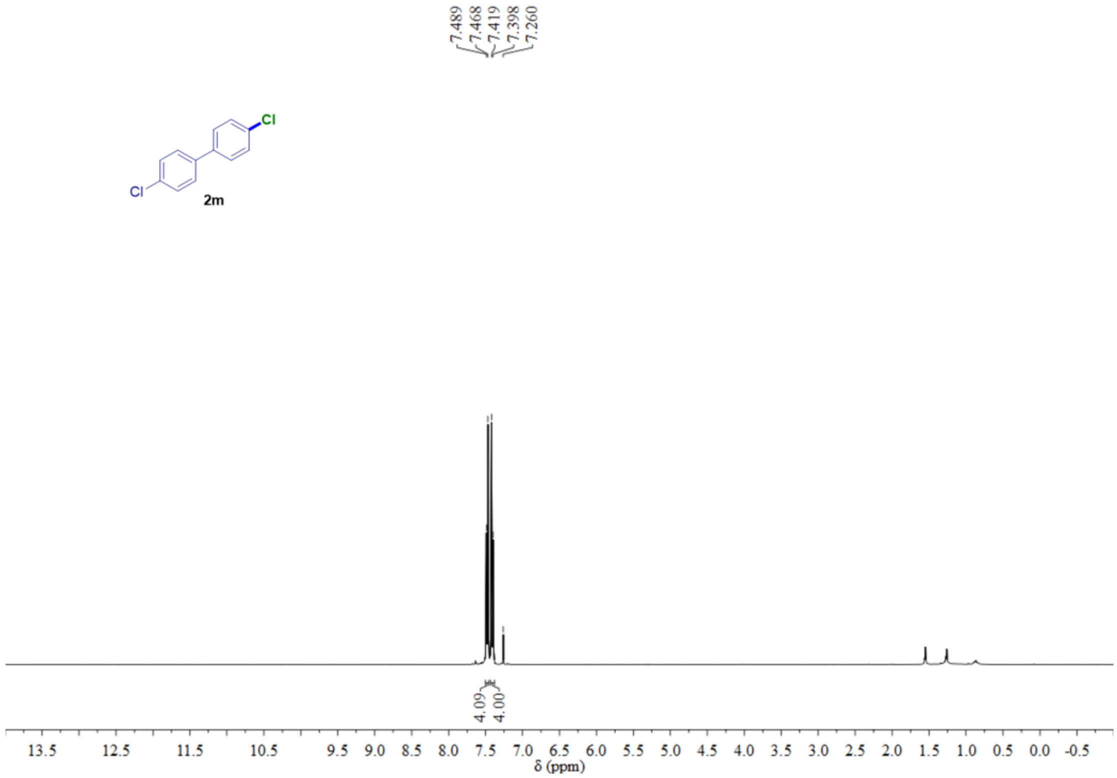

196.92
139.73
135.53
129.83
128.99
77.48
77.16
76.84
26.72
Me
O
Cl
2i
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

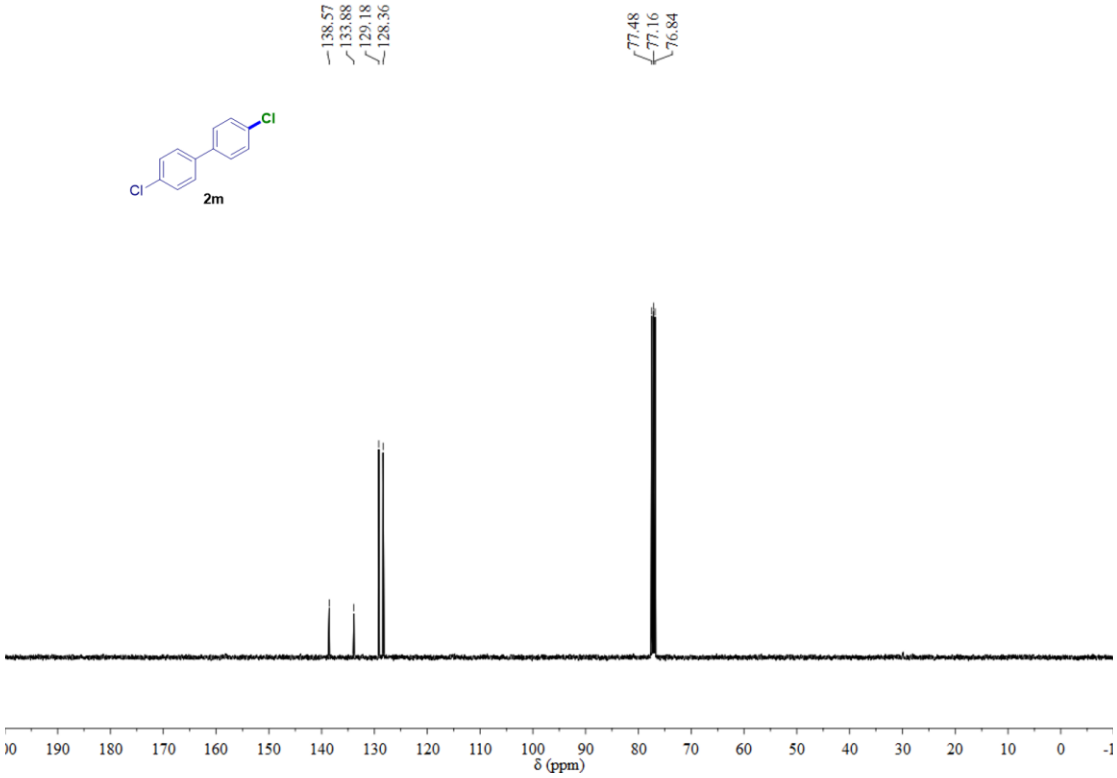

13.180
7.944
7.923
7.563
7.542
2.509
2.505
2.500
2.495
2.491
HO
O
Cl
2j
0.82
2.00
1.99
6
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

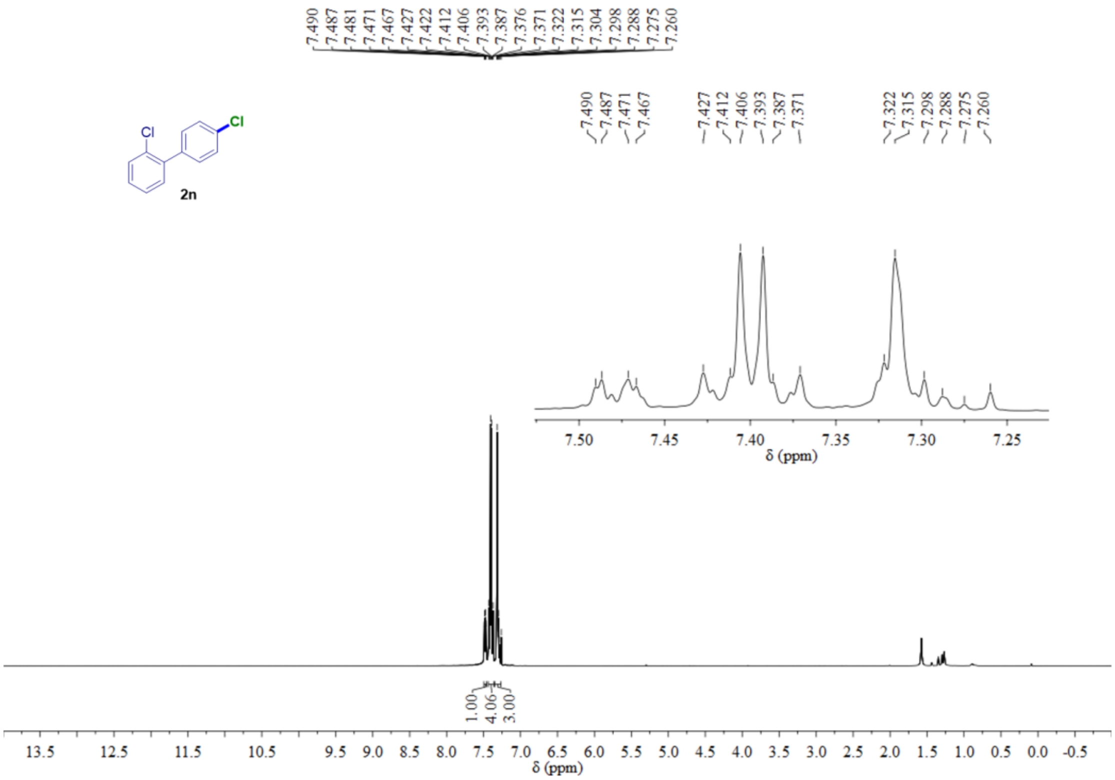

166.53
137.86
131.20
129.69
128.79
40.15
39.94
39.73
39.52
39.31
39.10
38.89
HO
O
Cl
2j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

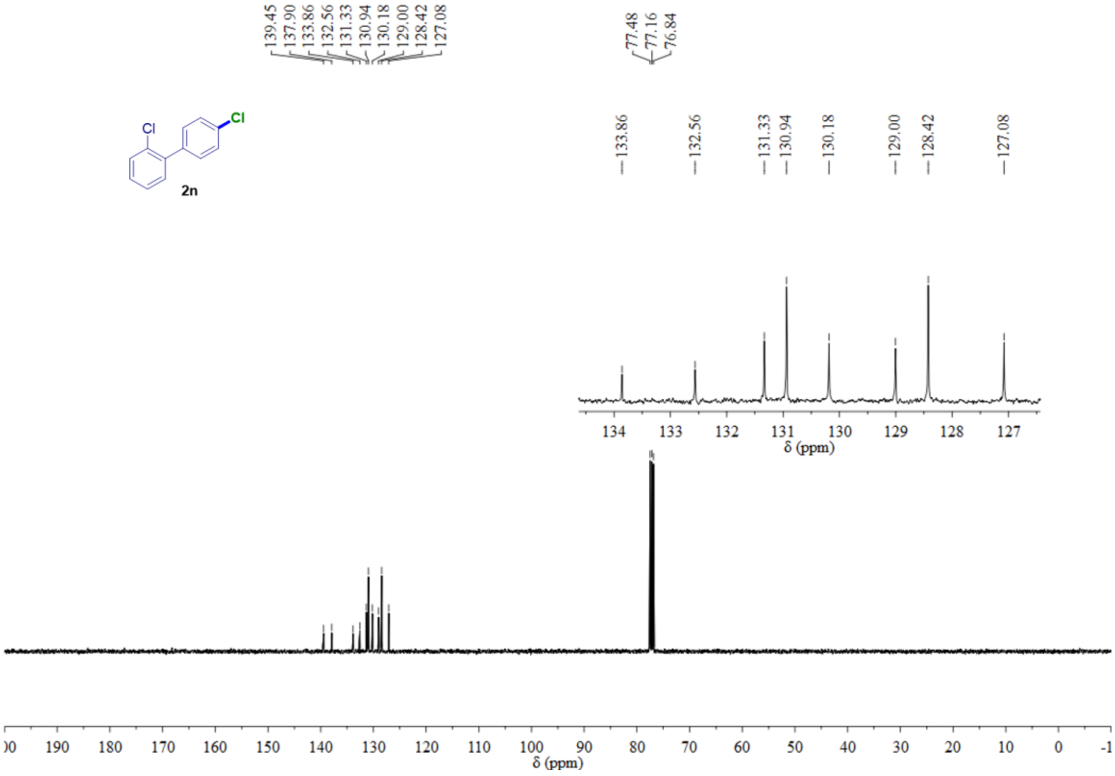

7.359
7.338
7.271
7.260
7.250
3.723
NC
Cl
2l
2.00
2.04
2.12
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)

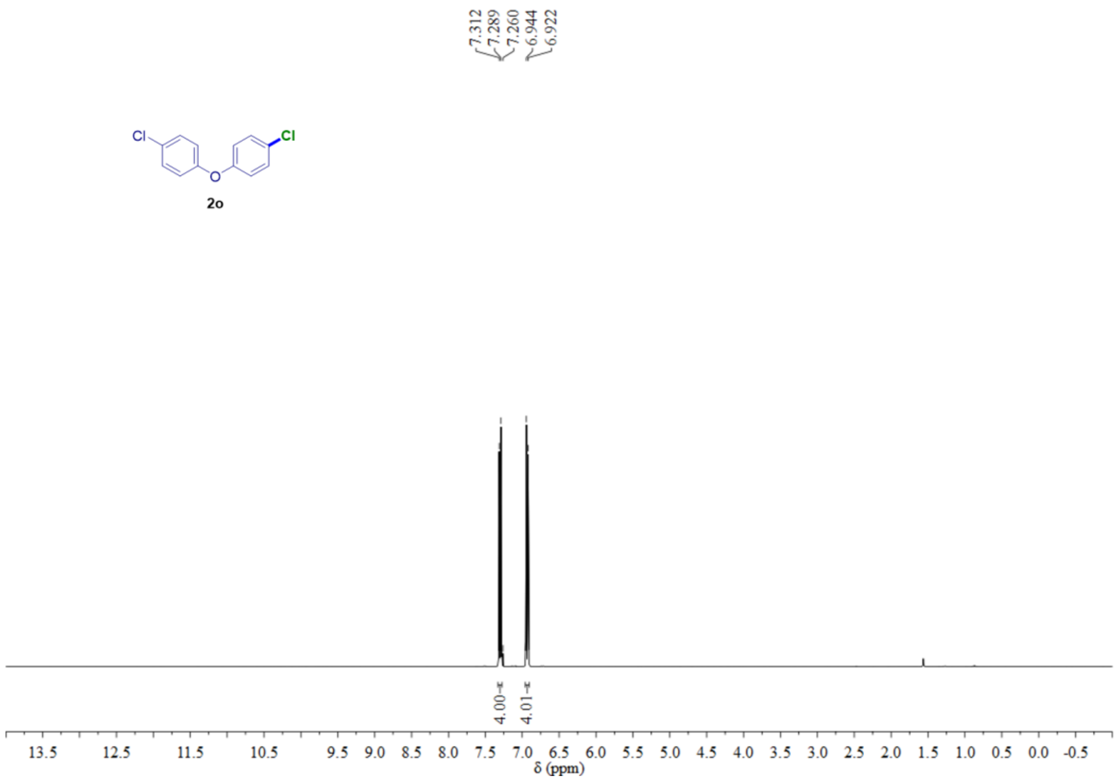

134.20
129.39
129.38
128.46
117.55
77.48
77.16
76.84
23.18
NC
Cl
2l
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

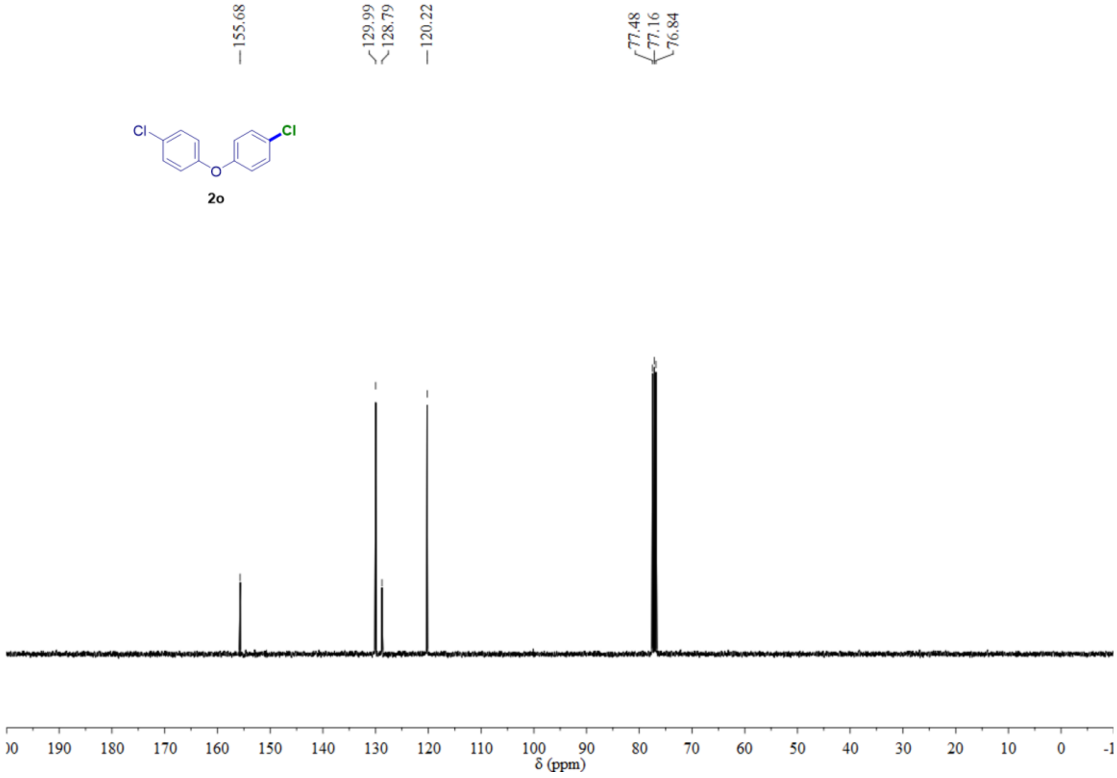

7.489
7.468
7.419
7.398
7.260
Cl
Cl
2m
4.09
4.00
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

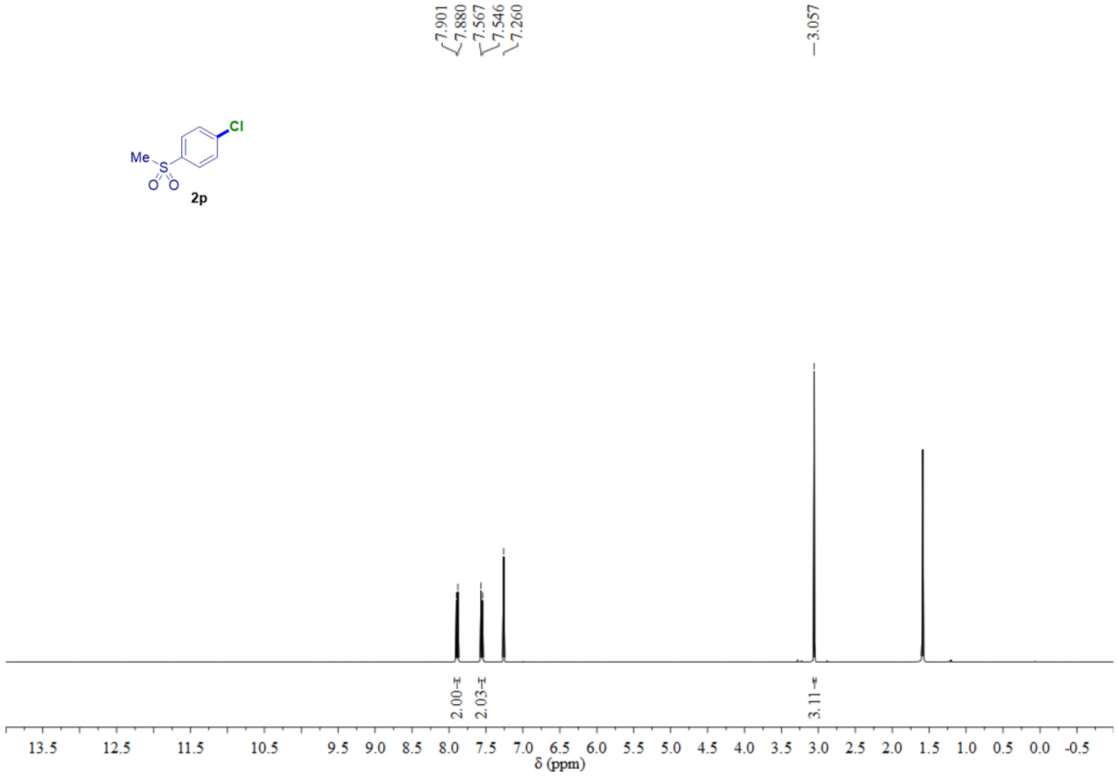

138.57
133.88
129.18
128.36
77.48
77.16
76.84
Cl
Cl
2m
)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

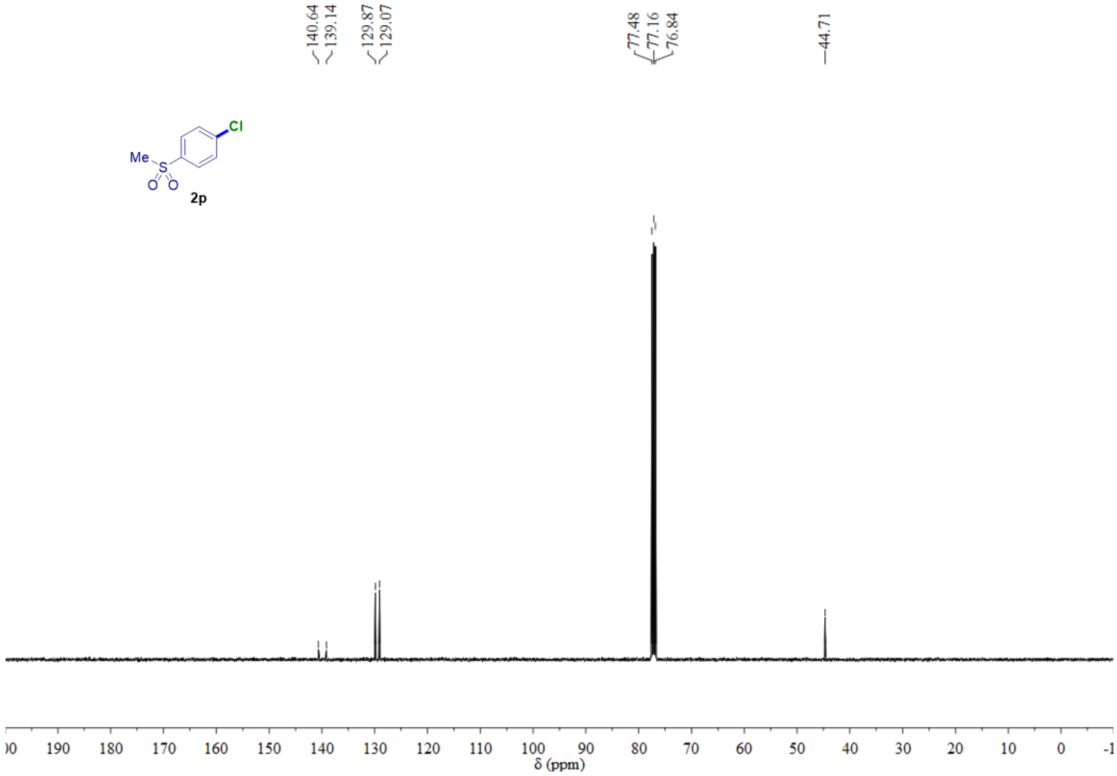

7.490
7.487
7.481
7.471
7.467
7.427
7.422
7.412
7.406
7.393
7.387
7.376
7.371
7.322
7.315
7.304
7.298
7.288
7.275
7.260
Cl
Cl
2n
7.490
7.487
7.471
7.467
7.427
7.412
7.406
7.393
7.387
7.371
7.322
7.315
7.298
7.288
7.275
7.260
7.50
7.45
7.40
7.35
7.30
7.25
δ (ppm)
1.00
4.06
3.00
13.5
12.5
11.5
10.5
9.5
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
δ (ppm)

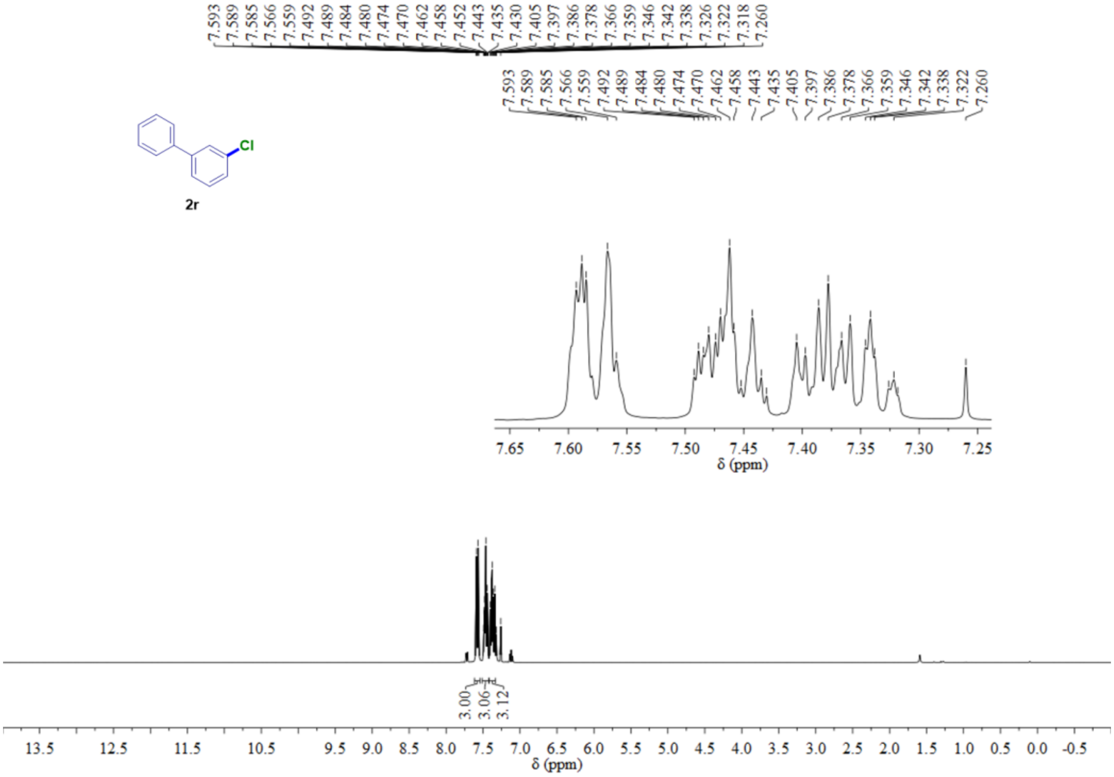

139.45
137.90
133.86
132.56
131.33
130.94
130.18
129.00
128.42
127.08
77.48
77.16
76.84
Cl
Cl
2n
133.86
132.56
131.33
130.94
130.18
129.00
128.42
127.08
134
133
132
131
130
129
128
127
δ (ppm)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

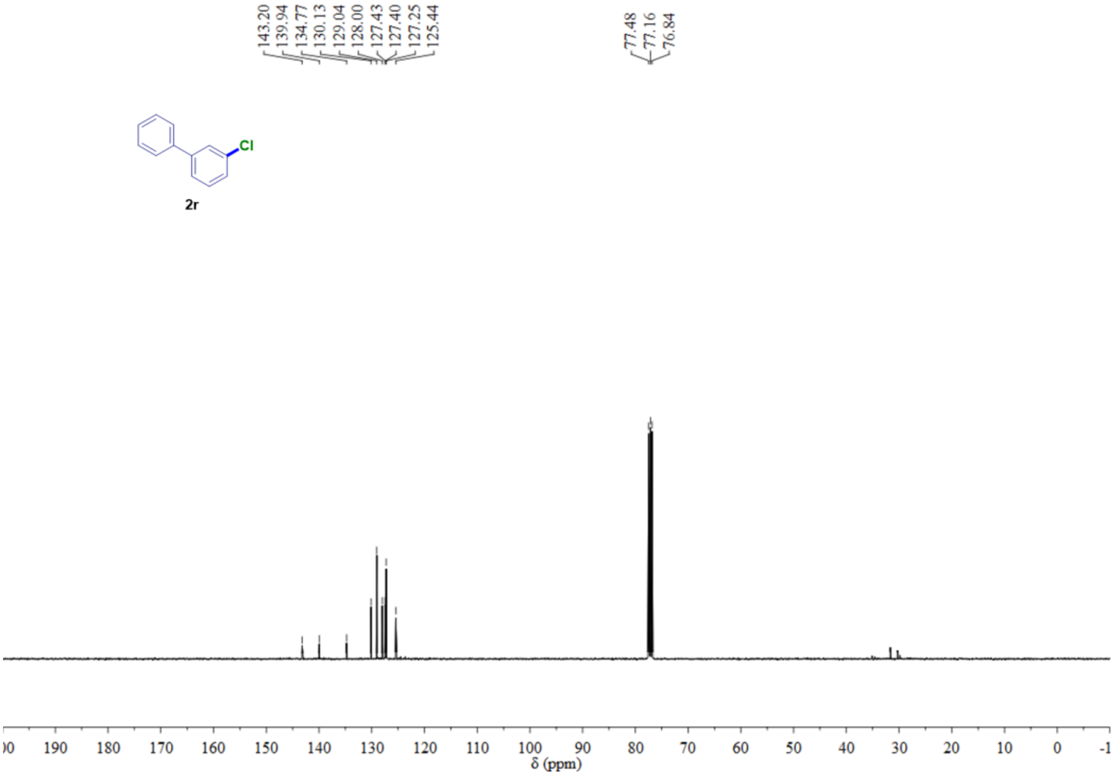

7.312
7.289
7.260
6.944
6.922
Cl
O
Cl
2o
4.00
4.01
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

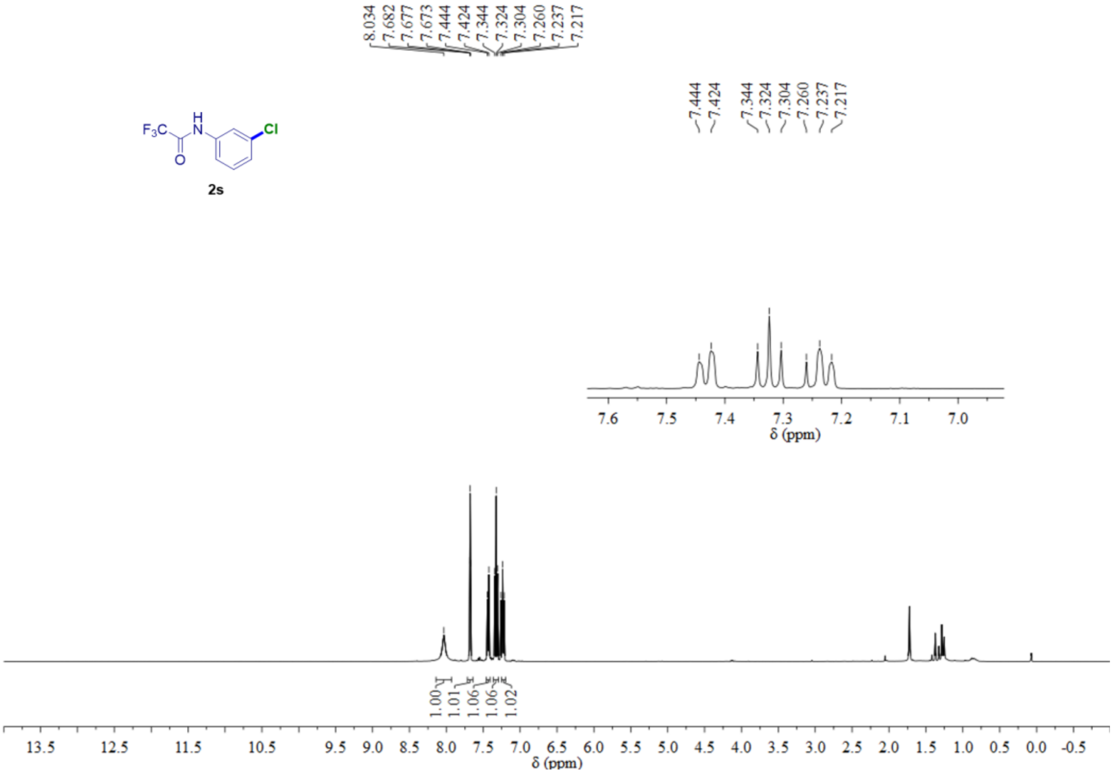

155.68
129.99
128.79
120.22
77.48
77.16
76.84
Cl
O
Cl
2o
)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)


7.901
7.880
7.567
7.546
7.260
3.057
Me
S
O O
Cl
2p
2.00
2.03
3.11
13.5 12.5 11.5 10.5 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
δ (ppm)

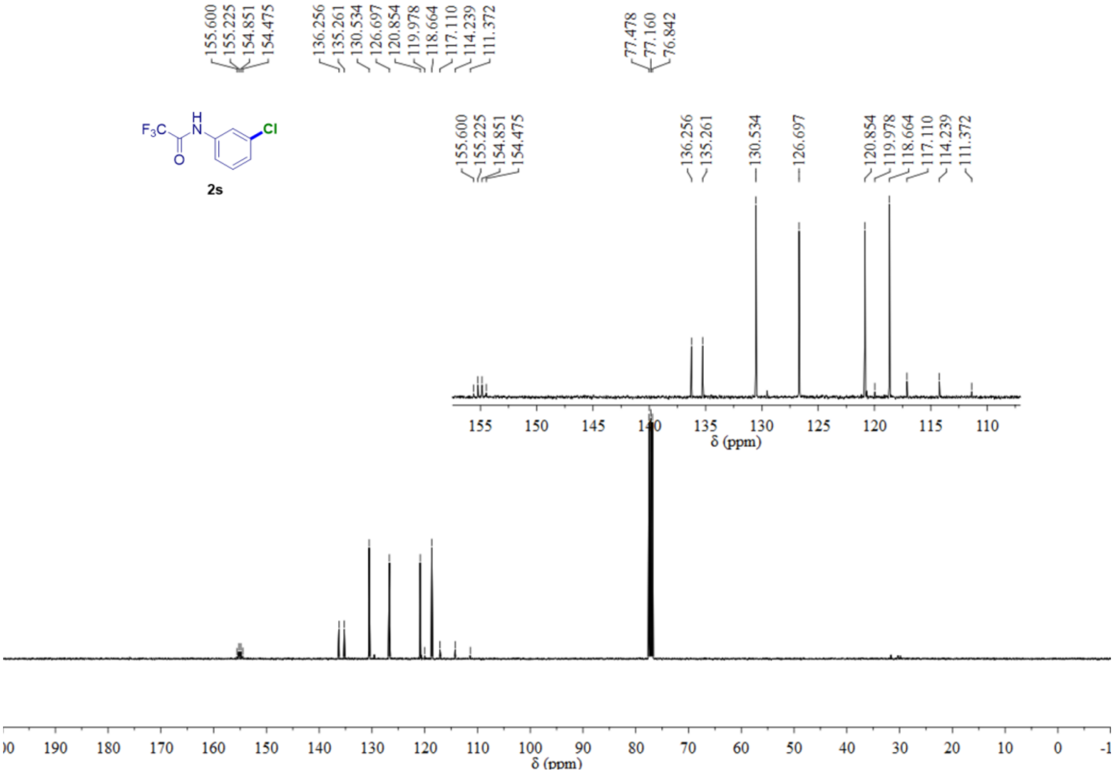

140.64
139.14
129.87
129.07
77.48
77.16
76.84
44.71
Me
S
O O
Cl
2p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.593
7.589
7.585
7.566
7.559
7.492
7.489
7.484
7.480
7.474
7.470
7.462
7.458
7.452
7.443
7.435
7.430
7.405
7.397
7.386
7.378
7.366
7.359
7.346
7.342
7.338
7.326
7.322
7.318
7.260
Cl
2r
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25
δ (ppm)
3.00
3.06
3.12
13.5 12.5 11.5 10.5 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
δ (ppm)

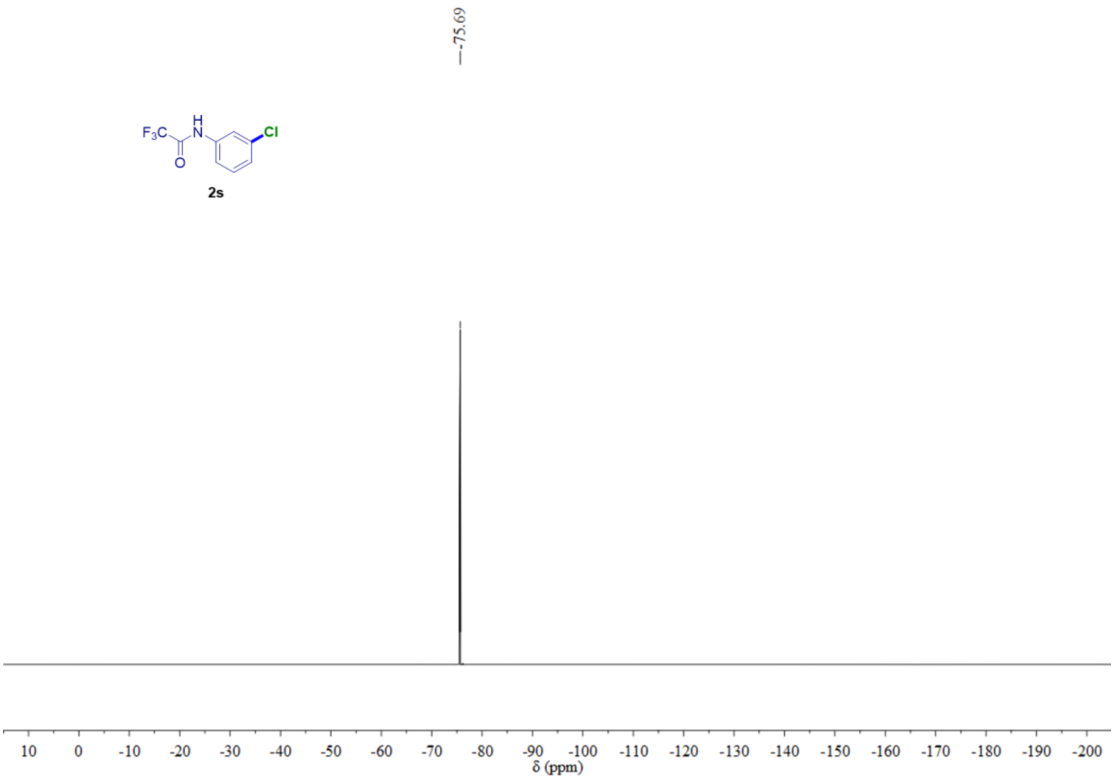

143.20
139.94
134.77
130.13
129.04
128.00
127.43
127.40
127.25
125.44
77.48
77.16
76.84
Cl
2r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


2s

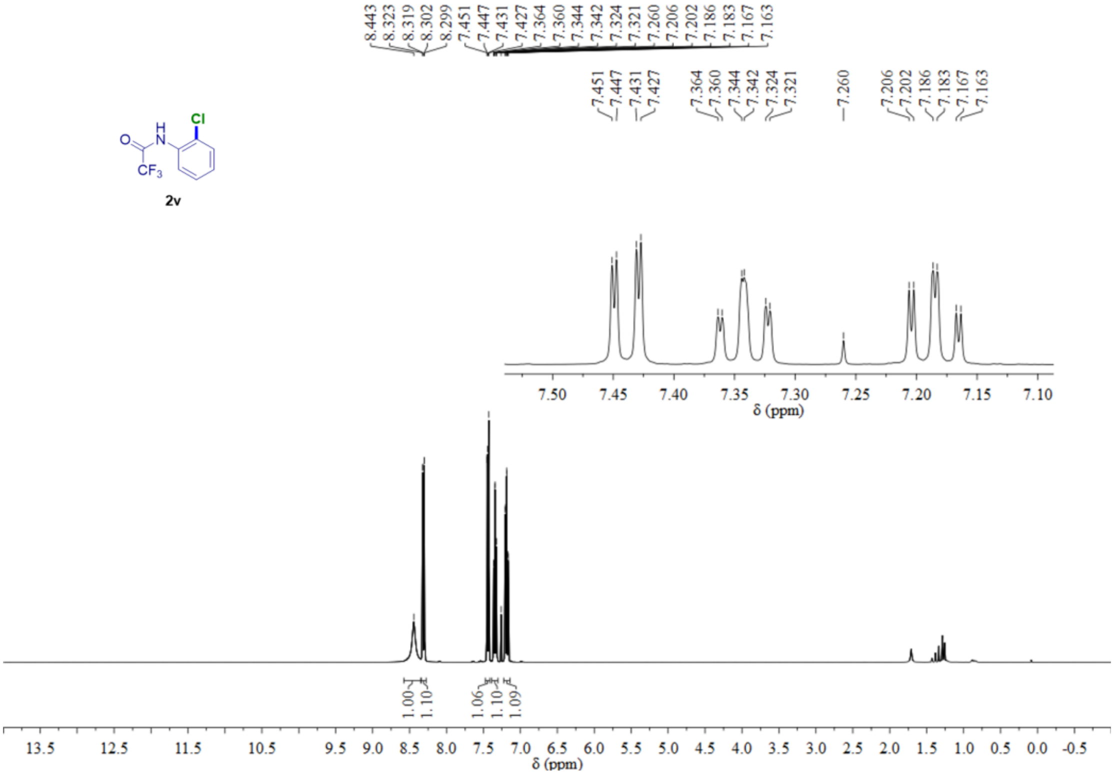
8.034
7.682
7.677
7.673
7.444
7.424
7.344
7.324
7.304
7.260
7.237
7.217
F3C
H
N
O
Cl
7.444
7.424
7.344
7.324
7.304
7.260
7.237
7.217
7.6 7.5 7.4 7.3 7.2 7.1 7.0
δ (ppm)
1.00
1.01
1.06
1.06
1.02
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)


2s

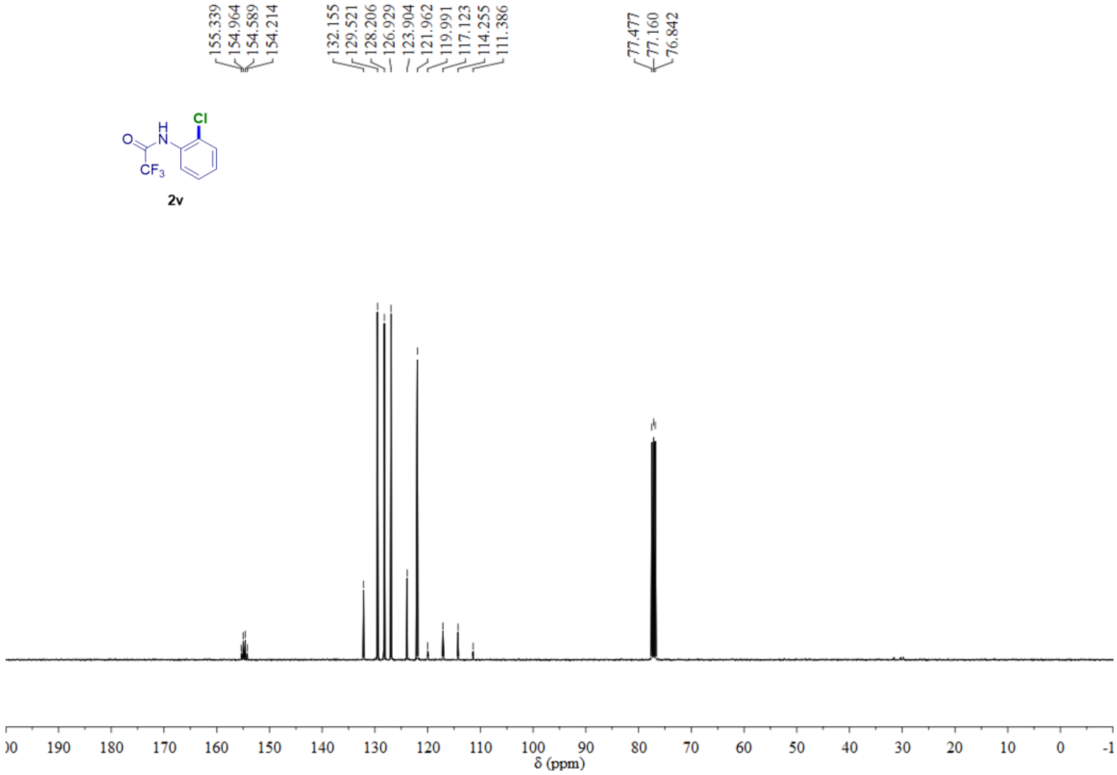
155.600
155.225
154.851
154.475
136.256
135.261
130.534
126.697
120.854
119.978
118.664
117.110
114.239
111.372
77.478
77.160
76.842
F3C
H
N
O
Cl
155.600
155.225
154.851
154.475
136.256
135.261
130.534
126.697
120.854
119.978
118.664
117.110
114.239
111.372
155 150 145 140 135 130 125 120 115 110
δ (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

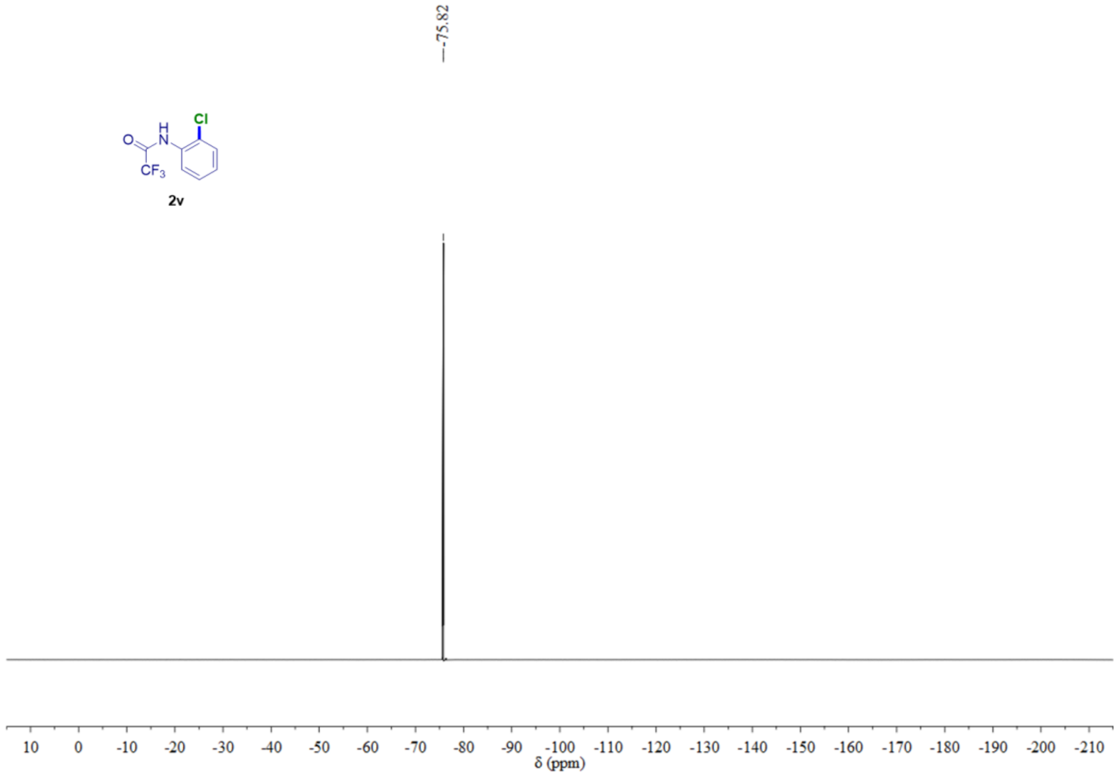

-75.69
F3C
N
H
O
Cl
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
δ (ppm)

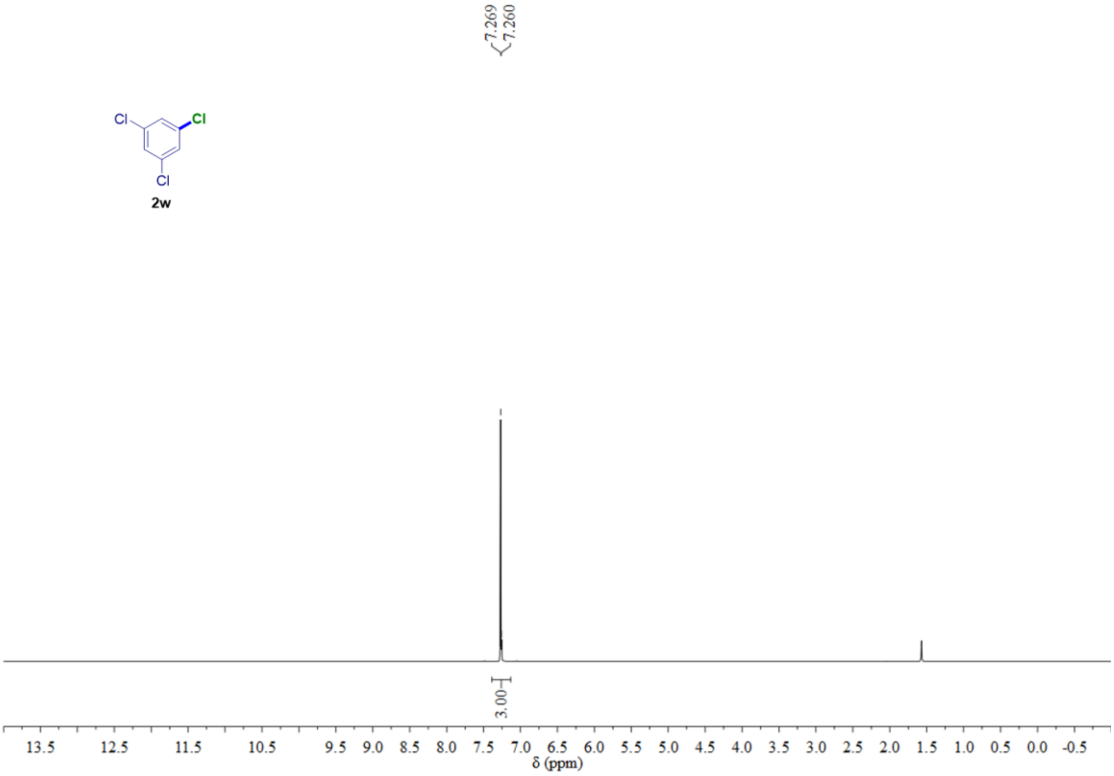
2s


8.443
8.323
8.319
8.302
8.299
7.451
7.447
7.431
7.427
7.364
7.360
7.344
7.342
7.324
7.321
7.260
7.206
7.202
7.186
7.183
7.167
7.163
O
N
H
Cl
CF3
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
δ (ppm)
1.00
1.10
1.06
1.10
1.09
13.5 12.5 11.5 10.5 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
δ (ppm)

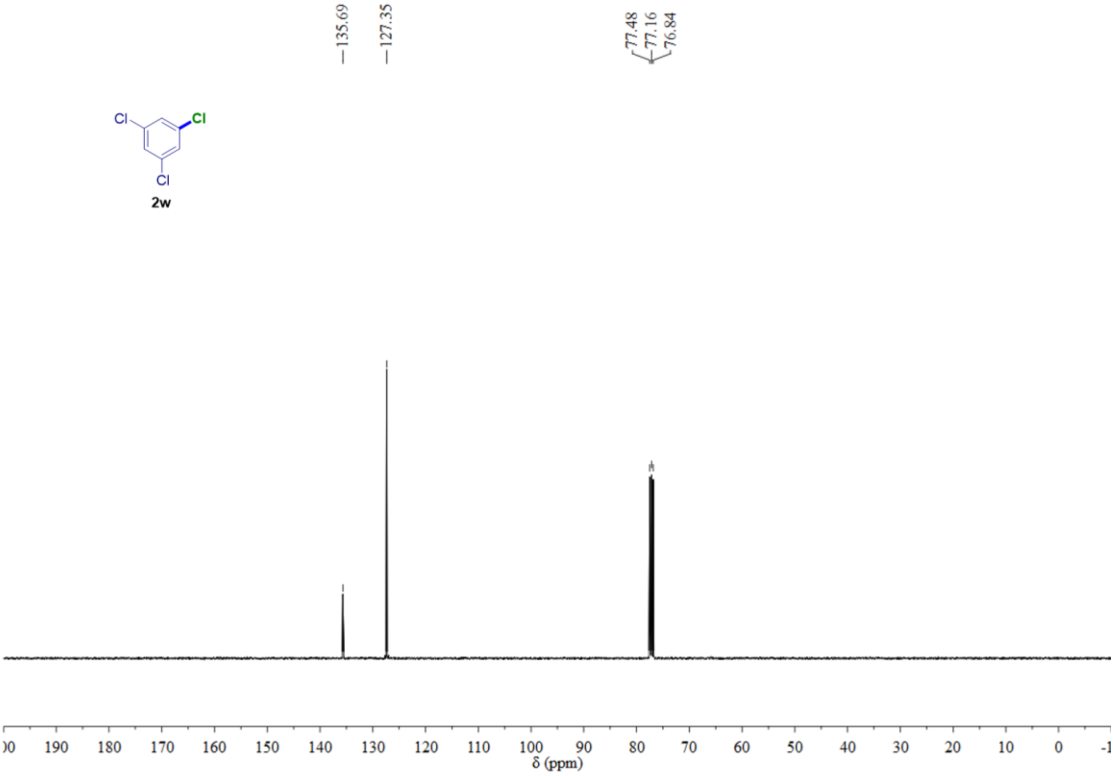
2v


155.339
154.964
154.589
154.214
132.155
129.521
128.206
126.929
123.904
121.962
119.991
117.123
114.255
111.386
77.477
77.160
76.842
O
H
N
Cl
CF3
2v
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

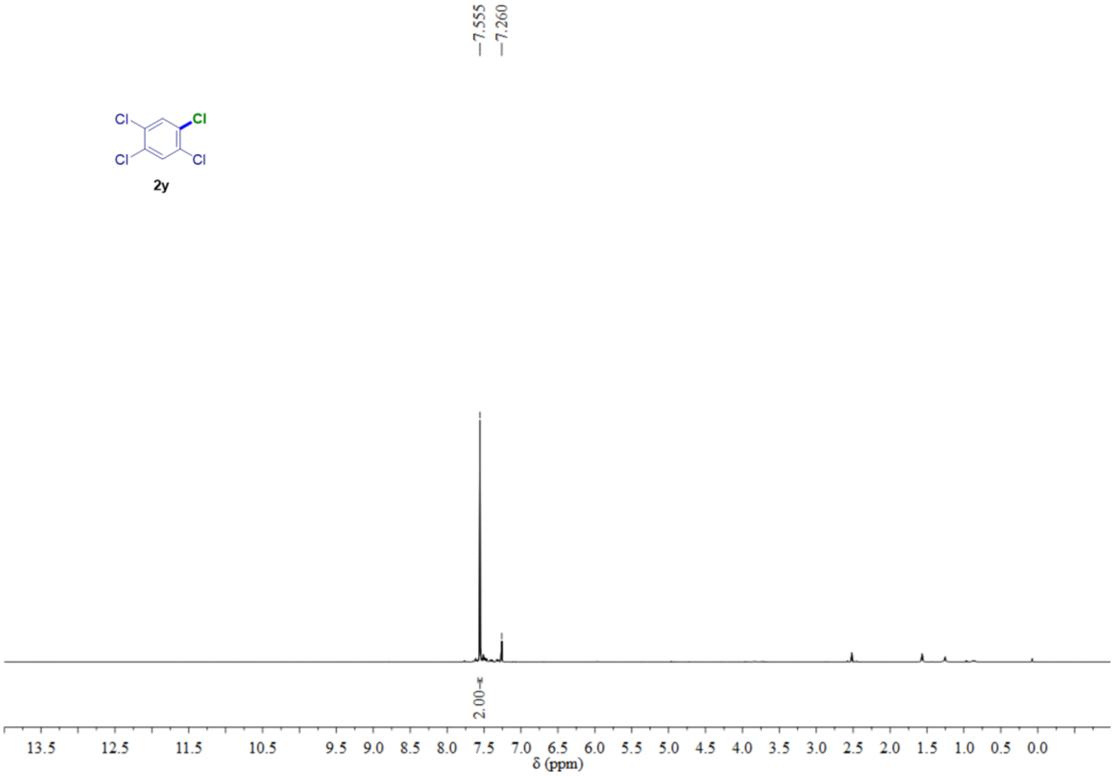

-75.82
O
H
N
Cl
CF3
2v
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
δ (ppm)


7.269
7.260
Cl
Cl
Cl
3.00
13.5
12.5
11.5
10.5
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
δ (ppm)

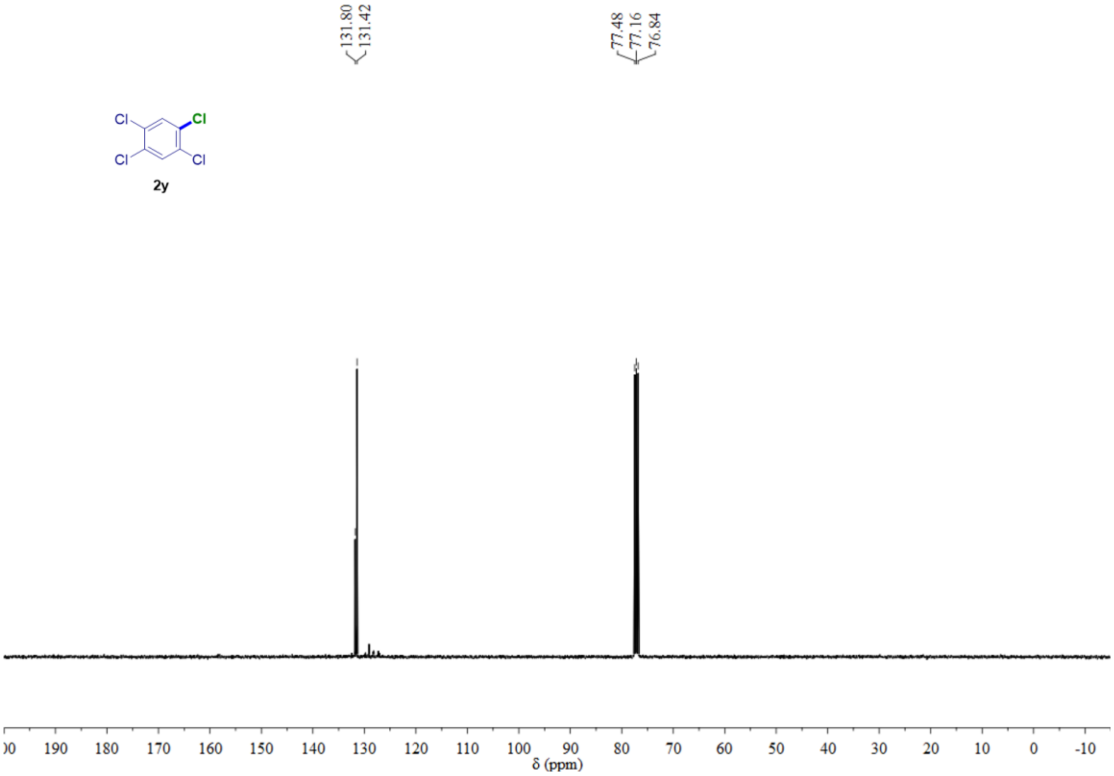
2w


135.69
127.35
77.48
77.16
76.84
Cl
Cl
Cl
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

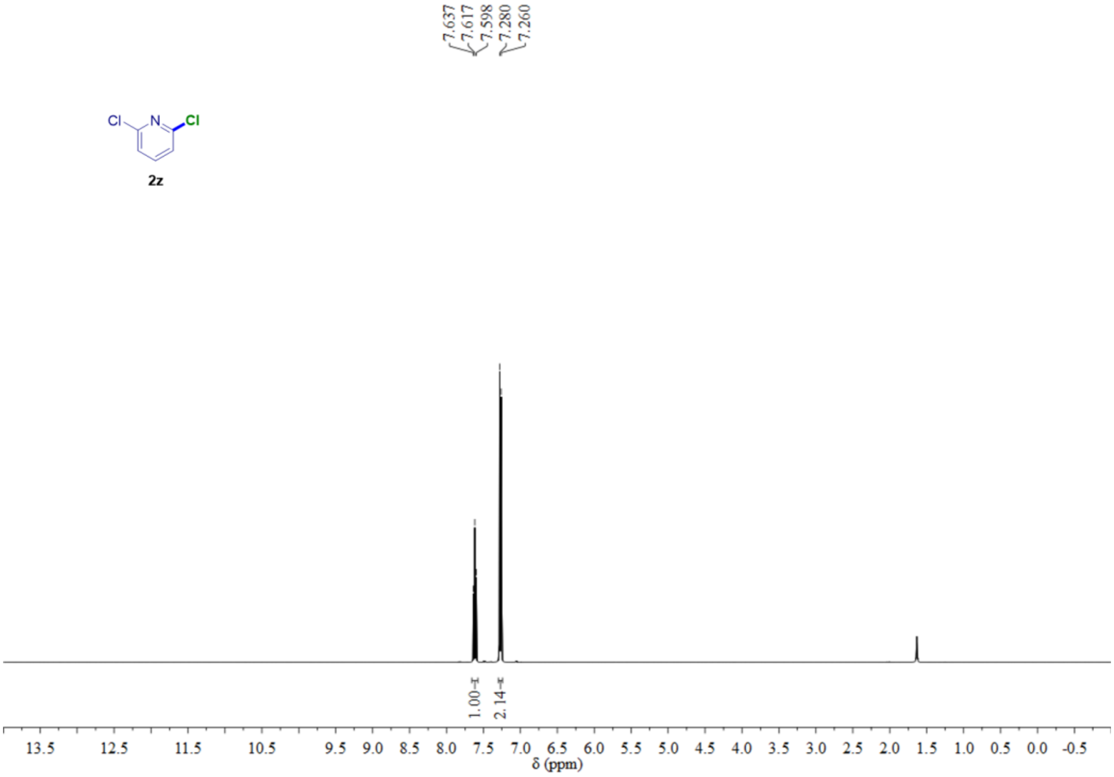
2w

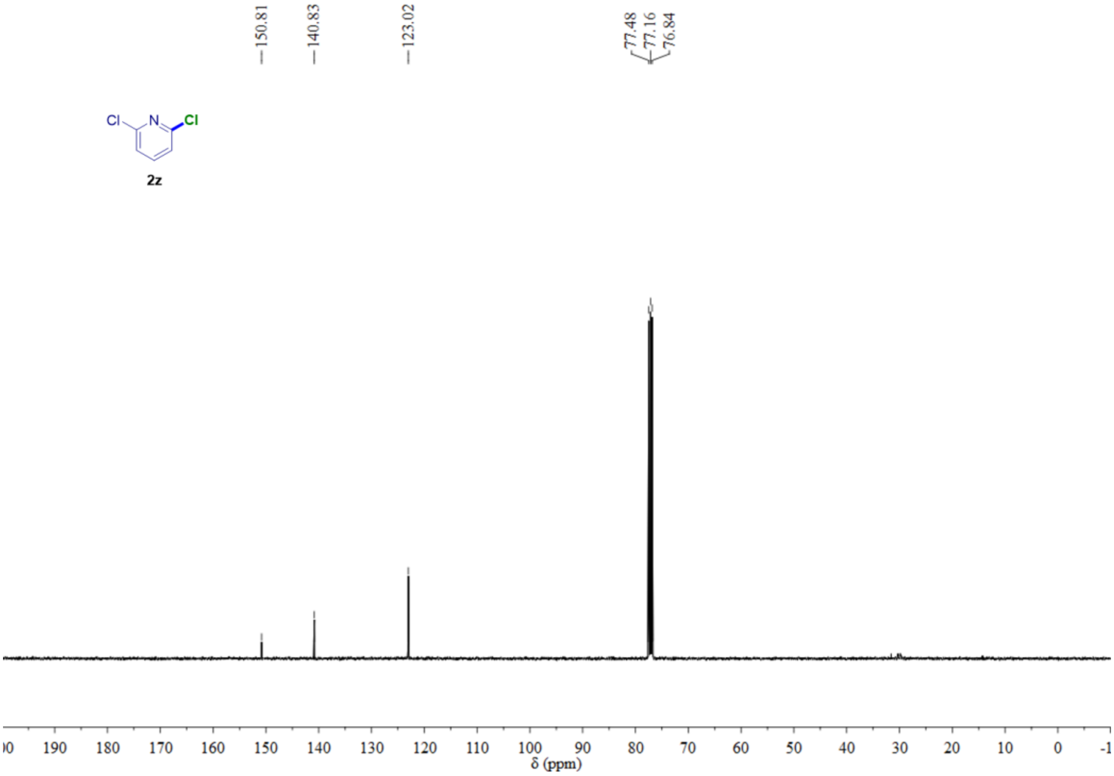


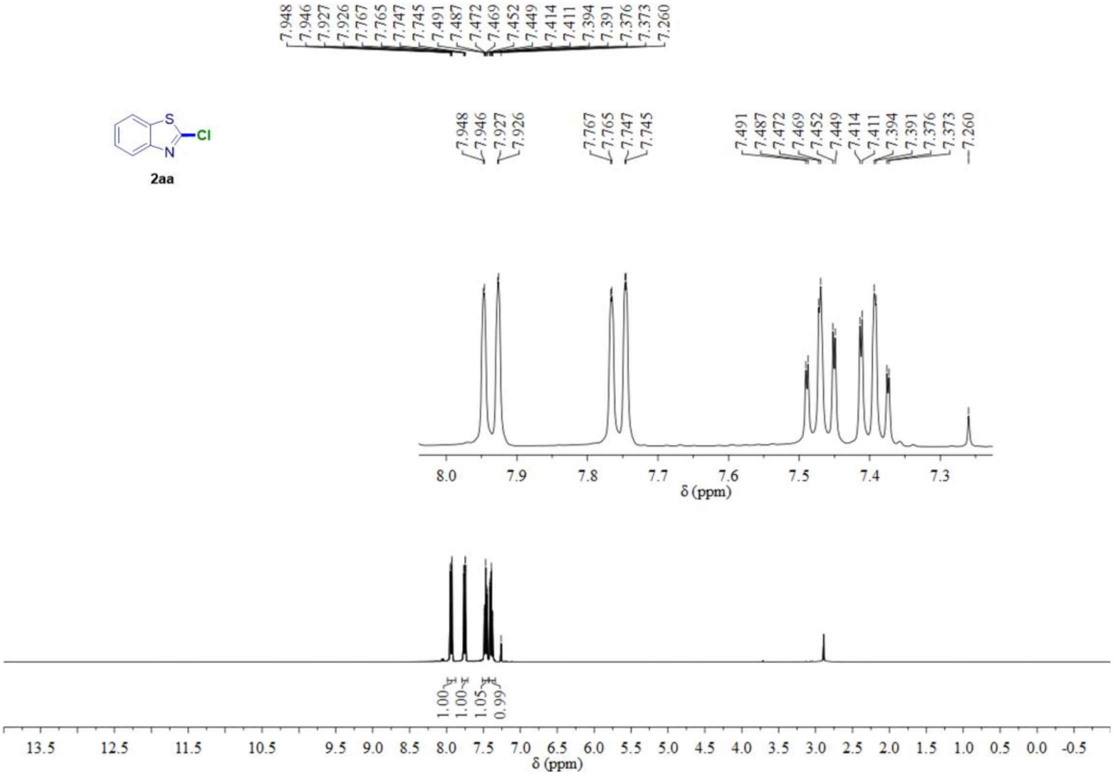
7.555
7.260
Cl
Cl
Cl
Cl
2y
2.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

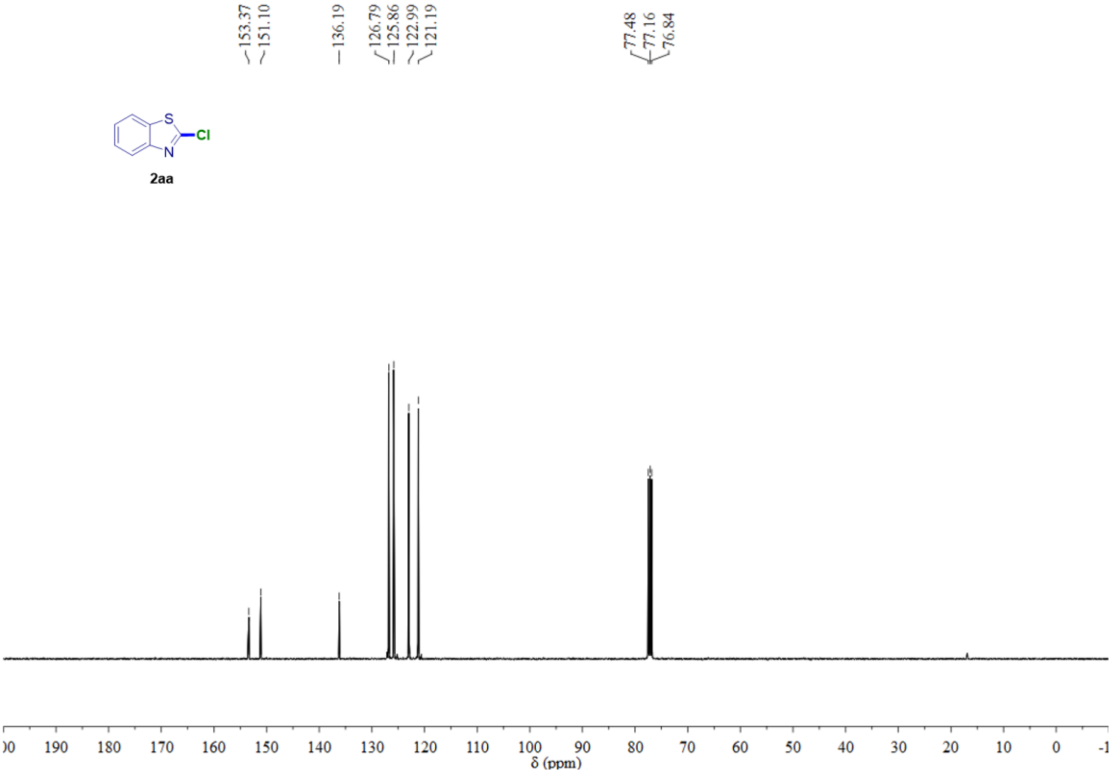


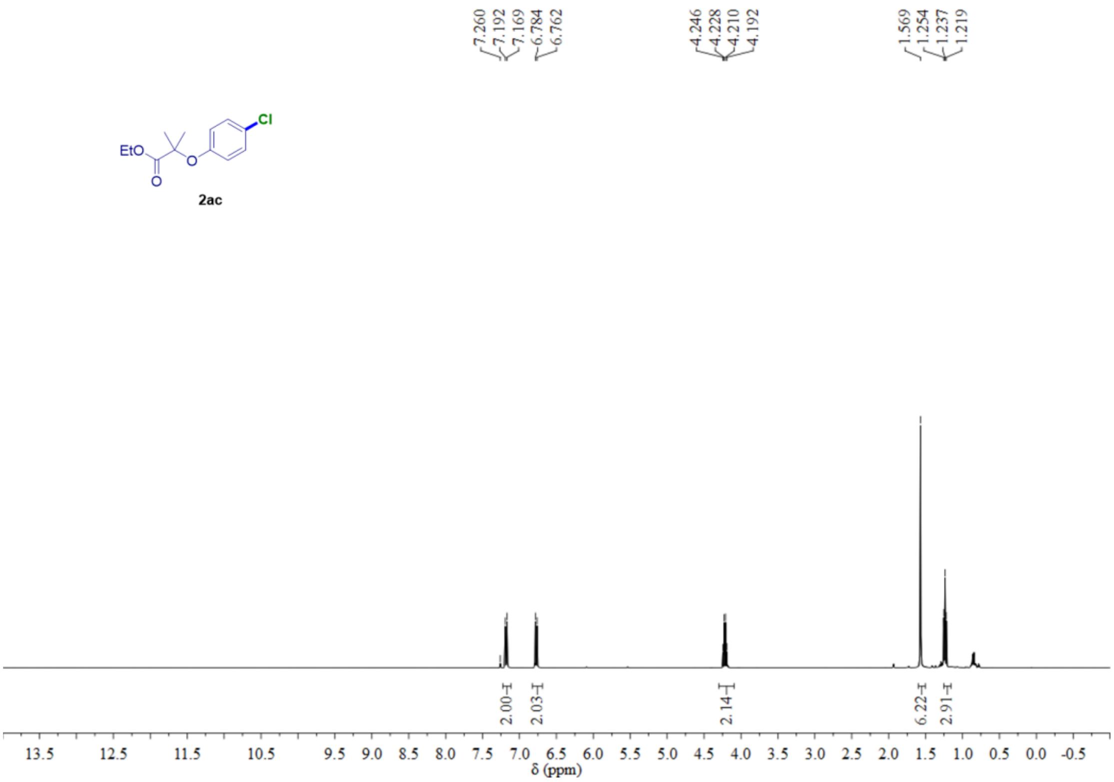
131.80
131.42
77.48
77.16
76.84
Cl
Cl
Cl
Cl
2y
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

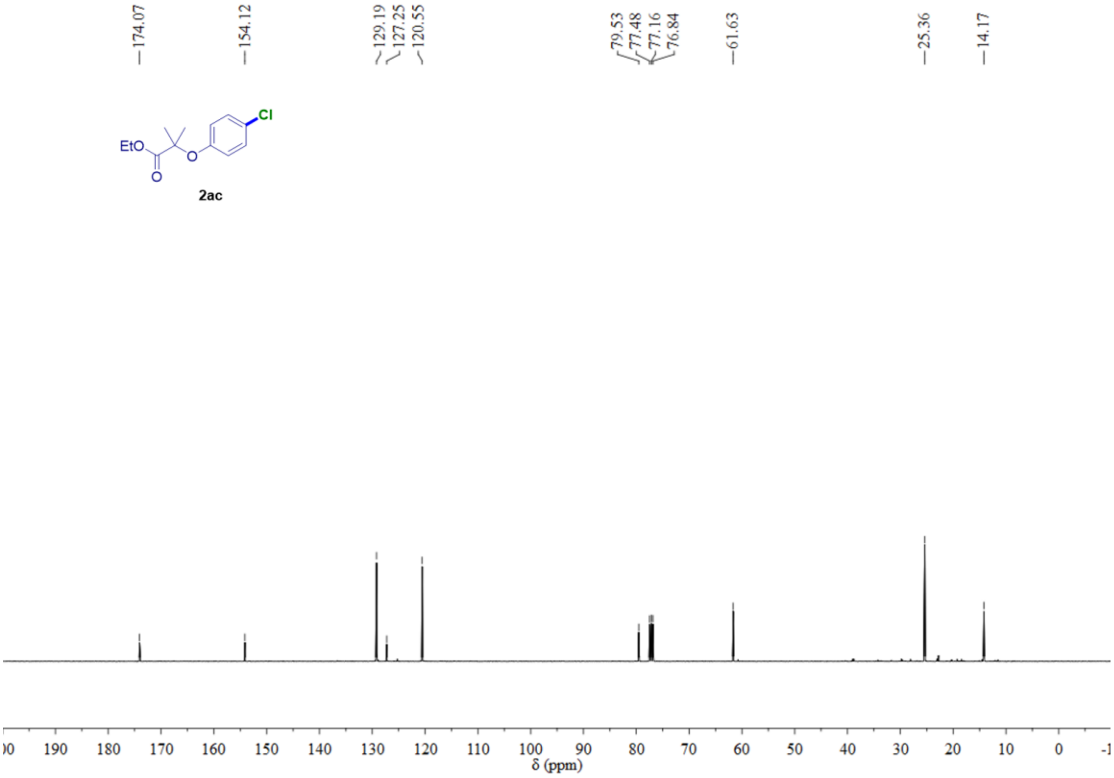

2z
7.637
7.617
7.598
7.280
7.260
Cl
N
Cl
1.00
2.14
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)

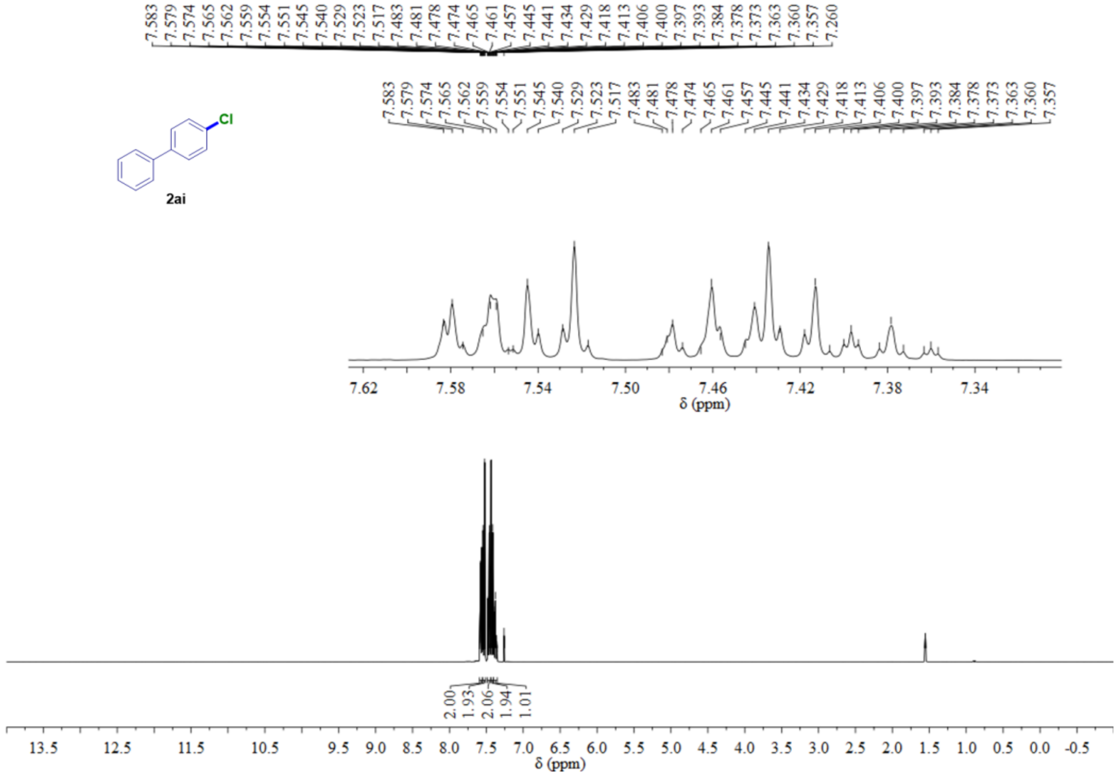

2z
150.81
140.83
123.02
77.48
77.16
76.84
Cl
N
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

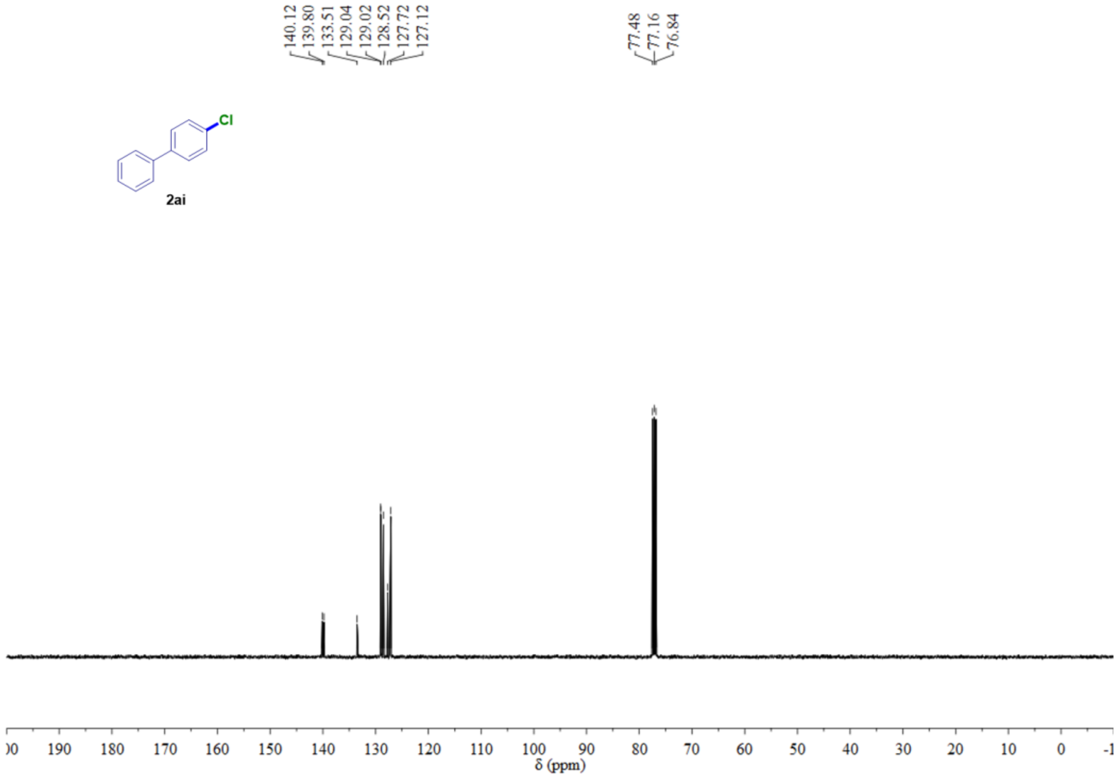

7.948
7.946
7.927
7.926
7.767
7.765
7.747
7.745
7.491
7.487
7.472
7.469
7.452
7.449
7.414
7.411
7.394
7.391
7.376
7.373
7.260
S
Cl
N
2aa
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
δ (ppm)
1.00
1.00
1.05
0.99
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)

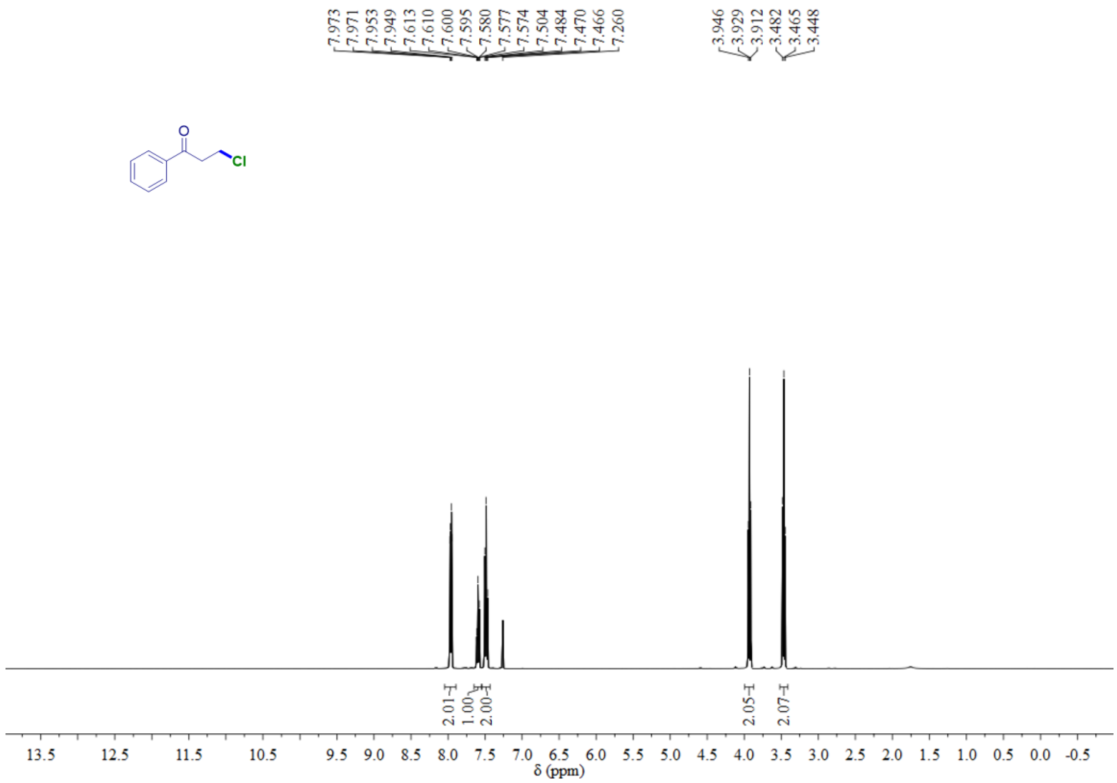

153.37
151.10
136.19
126.79
125.86
122.99
121.19
77.48
77.16
76.84
S
Cl
N
2aa
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

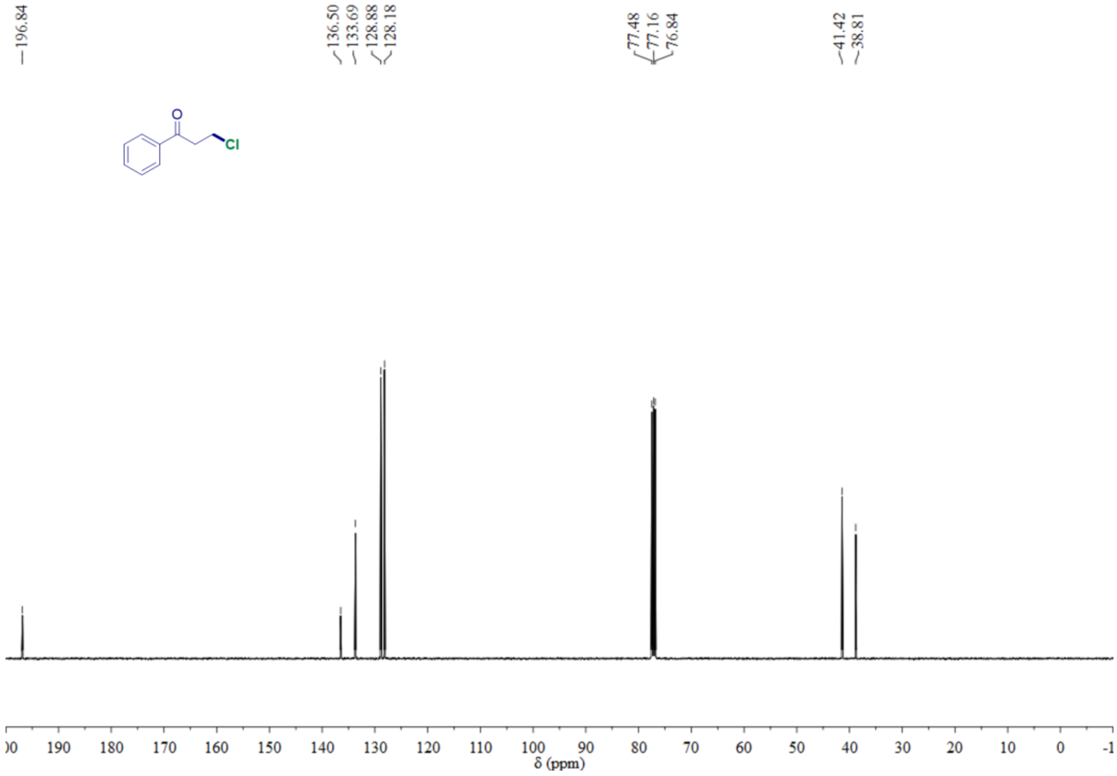

7.260
7.192
7.169
6.784
6.762
4.246
4.228
4.210
4.192
1.569
1.254
1.237
1.219
EtO
O
O
Cl
2ac
2.00
2.03
2.14
6.22
2.91
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)


174.07
154.12
129.19
127.25
120.55
79.53
77.48
77.16
76.84
61.63
25.36
14.17
EtO
O
O
Cl
2ac
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)


7.583
7.579
7.574
7.565
7.562
7.559
7.554
7.551
7.545
7.540
7.529
7.523
7.517
7.483
7.481
7.478
7.474
7.465
7.461
7.457
7.445
7.441
7.434
7.429
7.418
7.413
7.406
7.400
7.397
7.393
7.384
7.378
7.373
7.363
7.360
7.357
7.260
Cl
2ai
7.62
7.58
7.54
7.50
7.46
7.42
7.38
7.34
δ (ppm)
2.00
1.93
2.06
1.94
1.01
13.5
12.5
11.5
10.5
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
δ (ppm)


140.12
139.80
133.51
129.04
129.02
128.52
127.72
127.12
77.48
77.16
76.84
Cl
2ai
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)


7.973
7.971
7.953
7.949
7.613
7.610
7.600
7.595
7.580
7.577
7.574
7.504
7.484
7.470
7.466
7.260
3.946
3.929
3.912
3.482
3.465
3.448
O
Cl
2.01
1.00
2.00
2.05
2.07
13.5
12.5
11.5
10.5
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
δ (ppm)


196.84
136.50
133.69
128.88
128.18
77.48
77.16
76.84
41.42
38.81
O
Cl
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)