

Supporting Information

(NH₄)₂S₂O₈-Promoted cross-coupling of thiols/diselenides and sulfoxides for the synthesis of unsymmetrical disulfides/selenosulfides

Yang-Tong Ma, Chao Lin, Xiao-Bo Huang, Miao-Chang Liu, * Yun-Bing Zhou, *
and Hua-Yue Wu

College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou,
325035, P. R. of China.

CONTENTS:

| | |
|--|----|
| 1. General Information..... | 2 |
| 2. Substrate Preparation..... | 3 |
| 2.1 Synthesis of Diselenides..... | 3 |
| 2.2 Characterization of Diselenides in Details..... | 3 |
| 3. Reaction Optimization..... | 8 |
| Table S1 Reaction Optimization..... | 8 |
| Table S2 The Influence of the amount of DMSO on the Yield of 2a | 8 |
| Table S3 Reaction Optimization for the Synthesis of 2w | 9 |
| Table S4 Reaction Optimization for the Synthesis of 5a | 9 |
| 4. General Procedure for the Synthetic of Unsymmetrical Disulfides and Selenosulfides..... | 10 |
| 4.1 Synthesis of Unsymmetrical Disulfides..... | 10 |
| 4.2 Synthesis of Unsymmetrical Selenosulfides..... | 10 |
| 4.3 The reaction between diselenide 4s and selenoxide 6a | 10 |
| 4.4 Gram-Scale Synthesis of 1a | 11 |
| 5. Preliminary Mechanistic Studies..... | 12 |
| 5.1 GC-MS..... | 12 |
| 5.2 Kinetic Isotope Effect Experiments..... | 17 |
| 5.3 Competitive Reaction between 2a and 2a-d₃ | 17 |
| 6. Characterization of Products in Details..... | 19 |
| 7. Reference:..... | 33 |
| 8. ¹ H, ¹³ C and ¹⁹ F NMR Spectra of Products..... | 35 |

1. General Information

All reactions were conducted under an inert N₂ atmosphere with oven-dried glassware fitted with a magnetic stirrer bar, unless otherwise stated.

All reagents and solvents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros and Meryer. All commercial reagents were used as supplied unless otherwise stated. Organic solutions were concentrated by rotary evaporation below 45°C. All reactions were monitored by TLC, GC-MS. Analytical thin-layer chromatography was performed using Merck Kieselgel 60 F254 0.20 mm precoated glass-backed silica gel plates. Visualization of the chromatogram was performed by UV absorbance (λ_{max} = 254 nm) and/or by staining with aqueous potassium permanganate. Flash column chromatography was performed using silica gel (EM 60 F254 300 - 400 mesh) with the appropriate solvent system.

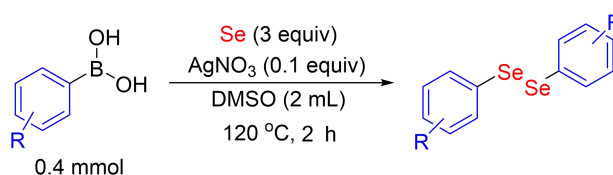
Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker DPX 400 (400 MHz) or Avance 500 (500 MHz) spectrometer. Chemical shifts (δ) are recorded in parts per million (ppm) and are quoted to the nearest 0.01 ppm relative to the residual solvent protons (CDCl₃ = 7.26 ppm, DMSO-*d*₆ = 2.50 ppm). Coupling constants (*J*) are quoted in Hertz (Hz), and data reported as follows: Chemical shift (multiplicity, coupling constant, number of protons). Coupling constants were reported to the nearest 0.1 Hz and multiplicity reported according to the following: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet m = multiplet, br = broad, with associated combinations e.g. dd = doublet of doublets.

Carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on a Bruker AVANCE 500 (125 MHz) spectrometer. Chemical shifts (δ) are recorded in parts per million (ppm) and are quoted to the nearest 0.1 ppm relative to the residual solvent protons (CDCl₃ = 77.2 ppm, DMSO-*d*₆ = 29.8 ppm). High-resolution mass spectra were recorded on a micrOTOF-Q II 10410 mass spectrometer.

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification.

2. Substrate Preparation

2.1 Synthesis of Diselenides

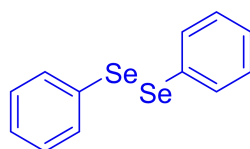


Scheme S1

General Procedure A:^[1] To a Schlenk tube were added arylboronic acid (0.4 mmol), selenium (1.2 mmol), AgNO₃ (0.04 mmol), and DMSO (2.0 mL). The mixture was stirred in a heating mantle preheated to 120 °C for 2 h. After cooled to room temperature, the reaction mixture was diluted with H₂O (10 mL), and extracted with EtOAc (3×10 mL). The combined organic phase was washed with water and brine (30 mL), dried over anhydrous Na₂SO₄, and then evaporated under reduced pressure. The residue was purified by column chromatography to give the desired diselenides (**4a-4v**).

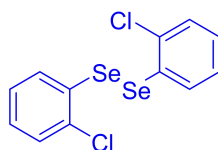
2.2 Characterization of Diselenides in Details

1,2-diphenyldiselenane (**4a**)^[1]



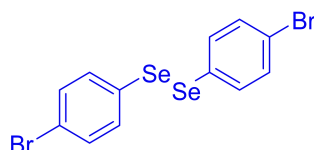
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4a** as yellow oil (60 mg, 96%). **M.p.:** 62.8 - 64.2 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.61 (d, *J* = 6.9 Hz, 4H), 7.26 (d, *J* = 6.9 Hz, 6H); **¹³C NMR** (125 MHz, CDCl₃) δ 131.5, 130.9, 129.2, 127.7.

1,2-bis(2-chlorophenyl)diselenane (**4b**)^[2]



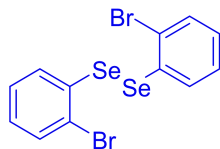
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4b** as yellow solid (69 mg, 90%). **M.p.:** 73.1 - 74.8 °C **¹H NMR** (500 MHz, CDCl₃) δ 7.62 - 7.56 (m, 2H), 7.31 - 7.15 (m, 6H); **¹³C NMR** (125 MHz, CDCl₃) δ 133.3, 130.7, 129.3, 129.2, 128.4, 127.9.

1,2-bis(4-bromophenyl)diselenane (**4c**)^[2]



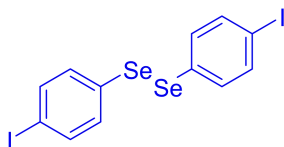
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4c** as red solid (86 mg, 92%). **M.p.:** 72.8 - 74.2 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.43 (d, *J* = 8.5 Hz, 4H), 7.37 (d, *J* = 8.5 Hz, 4H); **¹³C NMR** (125 MHz, CDCl₃) δ 133.4, 132.3, 129.5, 122.4.

1,2-bis(2-bromophenyl)diselane (4d) [3]



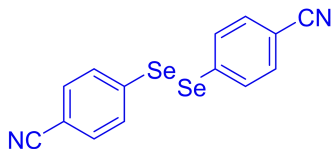
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4d** as yellow solid (69 mg, 73%). **M.p.:** 75.8 - 77.4 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.59 - 7.57 (m, 2H), 7.50 - 7.48 (m, 2H), 7.22 - 7.19 (m, 2H), 7.10 - 7.06 (m, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 132.5, 131.4, 130.5, 128.6, 128.4, 122.9.

1,2-bis(4-iodophenyl)diselane (4e) [4]



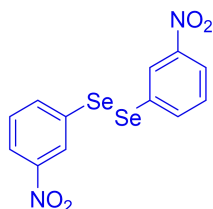
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4e** as red solid (96 mg, 85%). **M.p.:** 72.8 - 74.2 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.57 (d, *J* = 8.4 Hz, 4H), 7.30 (d, *J* = 8.4 Hz, 4H); **¹³C NMR** (125 MHz, CDCl₃) δ 138.2, 133.4, 130.4, 93.7.

4,4'-diselanediyldibenzonitrile (4f) [5]



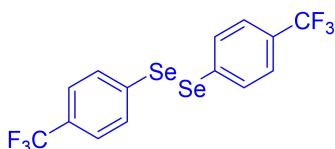
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4f** as red solid (62 mg, 85%). **M.p.:** 70.4 - 72.2 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.68 (dd, *J*₁ = 8.2 Hz, *J*₂ = 1.9 Hz, 4H), 7.58 - 7.53 (m, 4H). **¹³C NMR** (125 MHz, CDCl₃) δ 136.4, 132.7, 130.5, 118.2, 111.4.

1,2-bis(3-nitrophenyl)diselane (4g) [6]



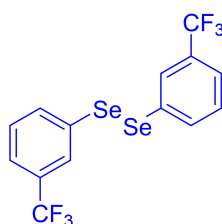
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4g** as yellow solid (64 mg, 80%). **M.p.:** 75.2 - 80.4 °C. **¹H NMR** (500 MHz, CDCl₃) δ 8.46 (d, *J* = 2.4 Hz, 2H), 8.11 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 148.5, 136.8, 131.8, 130.2, 125.9, 123.0.

1,2-bis(4-(trifluoromethyl)phenyl)diselane (4h) [5]



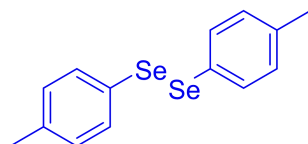
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4h** as yellow solid (76 mg, 85%). **M.p.:** 69.2 - 71.4 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.70 (d, *J* = 8.0 Hz, 4H), 7.52 (d, *J* = 8.0 Hz, 4H). **¹³C NMR** (125 MHz, CDCl₃) δ 134.8, 130.7, 129.94 (q, *J* = 32.6 Hz), 126.13 (q, *J* = 3.7 Hz), 123.85 (q, *J* = 272.1 Hz). **¹⁹F NMR** (470 MHz, CDCl₃) δ -62.6.

1,2-bis(3-(trifluoromethyl)phenyl)diselane (4i) ^[7]



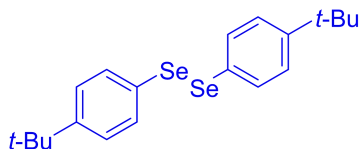
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4i** as yellow solid (75 mg, 84%). **M.p.:** 70.1 - 71.8 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.85 (s, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.9 Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 134.9, 131.6 (q, *J* = 32.5 Hz), 131.3 (m), 129.7, 128.3 (q, *J* = 4.1 Hz), 124.9 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.8 Hz). **¹⁹F NMR** (470 MHz, CDCl₃) δ -62.8.

1,2-di-*p*-tolyl diselane (4j) ^[5]



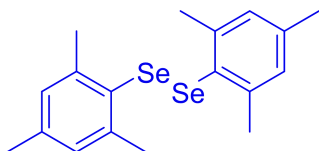
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4j** as yellow solid (56 mg, 83%). **M.p.:** 45.1 - 47.5 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.48 (d, *J* = 8.1 Hz, 4H), 7.07 (d, *J* = 7.9 Hz, 4H), 2.33 (s, 6H). **¹³C NMR** (125 MHz, CDCl₃) δ 137.9, 133.0, 132.3, 129.9, 21.1.

1,2-bis(4-(tert-butyl)phenyl)diselane (4k) ^[8]



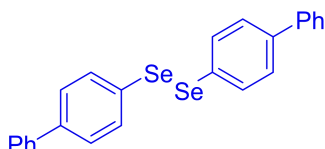
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4k** as yellow solid (55 mg, 65%). **M.p.:** 74.1 - 76.2 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.55 (d, *J* = 8.3 Hz, 4H), 7.29 (d, *J* = 8.3 Hz, 4H), 1.30 (s, 18H); **¹³C NMR** (125 MHz, CDCl₃) δ 133.0, 131.6, 127.7, 126.3, 34.6, 31.3.

1,2-dimesityl diselane (4l) ^[8]



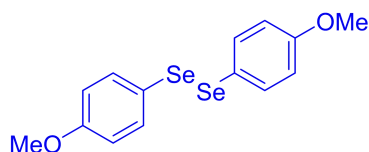
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4l** as yellow solid (67 mg, 84%). **M.p.:** 114.0 - 116.8 °C. **¹H NMR** (500 MHz, CDCl₃) δ 6.82 (s, 4H), 2.25 (s, 6H), 2.22 (s, 12H); **¹³C NMR** (125 MHz, CDCl₃) δ 143.7, 139.1, 128.8, 128.3, 24.2, 21.1.

1,2-di([1,1'-biphenyl]-4-yl)diselane (4m) ^[5]



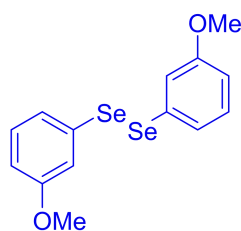
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4m** as yellow solid (78 mg, 84%). **M.p.:** 183.5 - 185.8 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.72 - 7.69 (m, 4H), 7.59 - 7.55 (m, 4H), 7.52 - 7.50 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.36 (d, *J* = 7.4 Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 140.9, 140.2, 132.2, 129.9, 128.9, 127.9, 127.6, 127.0.

1,2-bis(4-methoxyphenyl)diselane (4n) ^[6]



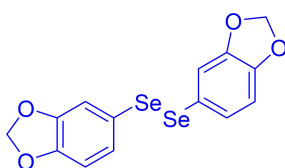
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4n** as yellow solid (49 mg, 66%). **M.p.:** 52.5 - 55.0 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.50 (d, *J* = 8.4 Hz, 4H), 6.81 (d, *J* = 8.3 Hz, 4H), 3.81 (s, 6H); **¹³C NMR** (126 MHz, CDCl₃) δ 160.1, 135.5, 121.9, 114.7, 55.4.

1,2-bis(3-methoxyphenyl)diselane (4o) ^[2]



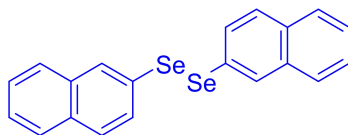
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4o** as white solid (41 mg, 55%). **M.p.:** 193.8 - 195.2 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.23 - 7.15 (m, 6H), 6.79 (d, *J* = 7.6 Hz, 2H), 3.77 (s, 6H); **¹³C NMR** (125 MHz, CDCl₃) δ 159.9, 131.9, 129.9, 123.5, 116.6, 113.8, 55.3.

1,2-bis(benzo[d][1,3]dioxol-5-yl)diselane (4p) ^[9]



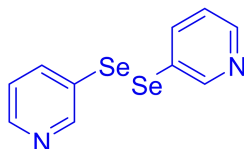
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4p** as yellow solid (50 mg, 63%). **M.p.**: 99.3 - 111.5 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.00 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.7$ Hz, 2H), 6.93 (d, $J = 1.7$ Hz, 2H), 6.73 (d, $J = 8.0$ Hz, 2H), 5.94 (s, 4H); **¹³C NMR** (125 MHz, CDCl₃) δ 148.3, 147.5, 126.9, 123.0, 113.7, 109.1, 101.2.

1,2-di(naphthalen-2-yl)diselane (4q) ^[5]



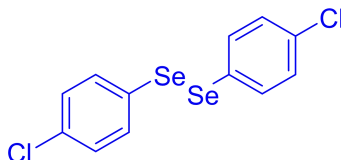
The **General Procedure A** was followed, and hexane was used as the eluant to afford **4q** as yellow solid (62 mg, 75%). **M.p.**: 126.2 - 127.8 °C. **¹H NMR** (500 MHz, CDCl₃) δ 8.17 (d, $J = 8.4$ Hz, 2H), 7.79 - 7.70 (m, 6H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.36 (t, $J = 7.7$ Hz, 2H), 7.21 (t, $J = 7.6$ Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 134.1, 134.1, 134.0, 130.1, 129.9, 128.6, 128.0, 126.7, 126.4, 125.7.

1,2-di(pyridin-3-yl)diselane (4r) ^[2]



The **General Procedure A** was followed, and hexane was used as the eluant to afford **4r** as yellow oil (47 mg, 75%). **¹H NMR** (500 MHz, CDCl₃) δ 8.76 (s, 2H), 8.51 (d, $J = 4.9$ Hz, 2H), 7.90 (dt, $J_1 = 7.9$ Hz, $J_2 = 2.1$ Hz, 2H), 7.24 (d, $J = 6.7$ Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 152.5, 149.3, 140.2, 127.8, 124.3.

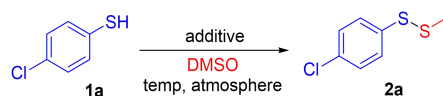
1,2-bis(4-chlorophenyl)diselane (4v) ^[2]



The **General Procedure A** was followed, and hexane was used as the eluant to afford **4v** as yellow solid (71 mg, 93%). **¹H NMR** (500 MHz, CDCl₃) δ 7.50 - 7.48 (m, 4H), 7.23 - 7.21 (m, 4H); **¹³C NMR** (125 MHz, CDCl₃) δ 134.4, 133.3, 129.4, 128.8.

3. Reaction Optimization

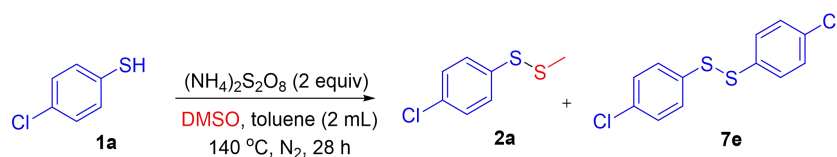
Table S1 Reaction optimization^a



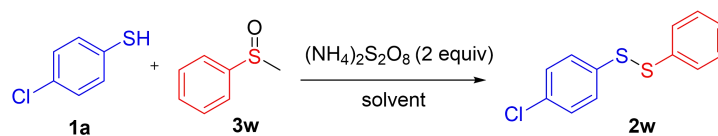
| entry | Additive (x equiv) | T (°C) | atmosphere | yield (%) |
|-------|---|--------|----------------|-----------|
| 1 | K ₂ S ₂ O ₈ (2) | 140 | N ₂ | 31 |
| 2 | (NH ₄) ₂ S ₂ O ₈ (2) | 140 | N ₂ | 93 |
| 3 | Na ₂ S ₂ O ₈ (2) | 140 | N ₂ | trace |
| 4 | PhI(OAc) ₂ (2) | 140 | N ₂ | trace |
| 5 | TBHP (2) | 140 | N ₂ | 22 |
| 6 | (NH ₄) ₂ SO ₄ (2) | 140 | N ₂ | 62 |
| 7 | NH ₄ Cl (2) | 140 | N ₂ | 86 |
| 8 | CH ₃ COOH (2) | 140 | N ₂ | 85 |
| 9 | CF ₃ COOH (2) | 140 | N ₂ | 58 |
| 10 | (NH ₄) ₂ S ₂ O ₈ (2) | 150 | N ₂ | 82 |
| 11 | (NH ₄) ₂ S ₂ O ₈ (2) | 130 | N ₂ | 78 |
| 12 | (NH ₄) ₂ S ₂ O ₈ (2) | 120 | N ₂ | 66 |
| 13 | (NH ₄) ₂ S ₂ O ₈ (1.5) | 140 | N ₂ | 66 |
| 14 | (NH ₄) ₂ S ₂ O ₈ (2) | 140 | N ₂ | 25 |
| 15 | (NH ₄) ₂ S ₂ O ₈ (2) | 140 | air | 70 |
| 16 | (NH ₄) ₂ S ₂ O ₈ (2) | 140 | O ₂ | 73 |

^aReactions conditions: **1a** (0.2 mmol), DMSO (2.0 mL), additive (2 equiv), 28 h, N₂ atmosphere, isolated yields.

Table S2 The Influence of the amount of DMSO on the Yield of **2a**



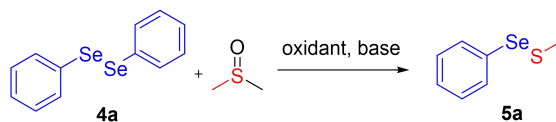
| entry | DMSO (equiv.) | Yield of 2a /% | Yield of 7e /% |
|-------|---------------|-----------------------|-----------------------|
| 1 | 3 | 25 | 67 |
| 2 | 5 | 34 | 59 |
| 3 | 7 | 46 | 50 |
| 4 | 9 | 58 | 35 |

Table S3 Reaction Optimization for the Synthesis of **2w**^a

| entry | solvent | temp/°C | time/h | yields/% |
|-----------------|-------------------|---------|--------|----------|
| 1 | toluene | 130 | 12 | <5 |
| 2 | xylene | 130 | 12 | N.R. |
| 3 | PhCl | 130 | 12 | N.R. |
| 4 | DMF | 130 | 12 | trace |
| 5 | NMP | 130 | 12 | trace |
| 6 | PhCF ₃ | 130 | 12 | N.R. |
| 7 | toluene | 140 | 12 | 3 |
| 8 | toluene | 150 | 12 | 14 |
| 9 | toluene | 160 | 12 | 13 |
| 10 ^b | toluene | 150 | 12 | 29 |
| 11 ^c | toluene | 150 | 12 | 25 |
| 14 ^b | toluene | 150 | 24 | 39 |
| 15 ^c | toluene | 150 | 24 | 63 |

^aReactions conditions: **1a** (0.2 mmol), **3w** (0.6 mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.4 mmol), N₂, isolated yields.

^b**3w** (1.0 mmol). ^c**3w** (1.8 mmol).

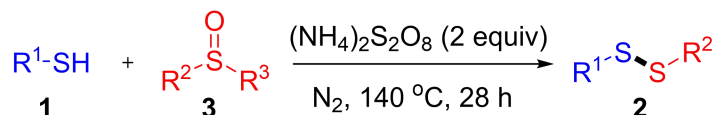
Table S4 Reaction Optimization for the Synthesis of **5a**^a

| entry | oxidant | base | temp/°C | time/h | yields/% |
|-----------------|---|--------------------------------|---------|--------|----------|
| 1 ^b | $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | K ₃ PO ₄ | 140 | 24 | 47 |
| 2 ^c | $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | K ₃ PO ₄ | 140 | 24 | 41 |
| 3 | $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | K ₃ PO ₄ | 140 | 24 | 62 |
| 4 | $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | <i>t</i> -BuOK | 140 | 24 | 64 |
| 5 | $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | KOH | 140 | 24 | 64 |
| 6 | $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | CH ₃ ONa | 140 | 24 | 50 |
| 7 | Na ₂ S ₂ O ₈ | <i>t</i> -BuOK | 150 | 24 | NR |
| 8 | K ₂ S ₂ O ₈ | <i>t</i> -BuOK | 150 | 24 | trace |
| 9 | $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | - | 140 | 24 | 4 |
| 10 ^d | $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | <i>t</i> -BuOK | 140 | 24 | 71 |
| 11 | - | <i>t</i> -BuOK | 150 | 24 | trace |
| 12 ^e | $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | <i>t</i> -BuOK | 150 | 24 | 68 |
| 13 ^f | $(\text{NH}_4)_2\text{S}_2\text{O}_8$ | <i>t</i> -BuOK | 150 | 12 | 72 |

^aReactions conditions: **4a** (0.2 mmol), oxidant (1.0 mmol), base (0.6 mmol), DMSO (2.0 mL), 140 °C, N₂, 12 h, isolated yields. ^bAir atmosphere. ^cO₂ atmosphere. ^dBase (0.8 mmol). ^eOxidant (0.6 mmol). ^fOxidant (0.6 mmol), base (0.8 mmol).

4. General Procedure for the Synthetic of Unsymmetrical Disulfides and Selenosulfides

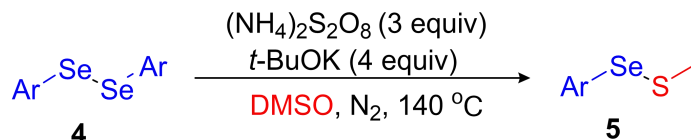
4.1 Synthesis of Unsymmetrical Disulfides



Scheme S2

General Procedure B: To a Schlenk tube were added thiols (0.2 mmol), sulfoxide (2 mL), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (91 mg, 0.4 mmol). The mixture was stirred in a heating mantle preheated to 140 °C for 28 h under N_2 atmosphere. After cooled to room temperature, the reaction mixture was diluted with H_2O (10 mL), and extracted with EtOAc (3×10 mL). The combined organic phase was washed with water and brine (30 mL), dried over anhydrous Na_2SO_4 , and then evaporated under reduced pressure. The residue was purified by column chromatography to give the desired unsymmetrical disulfides.

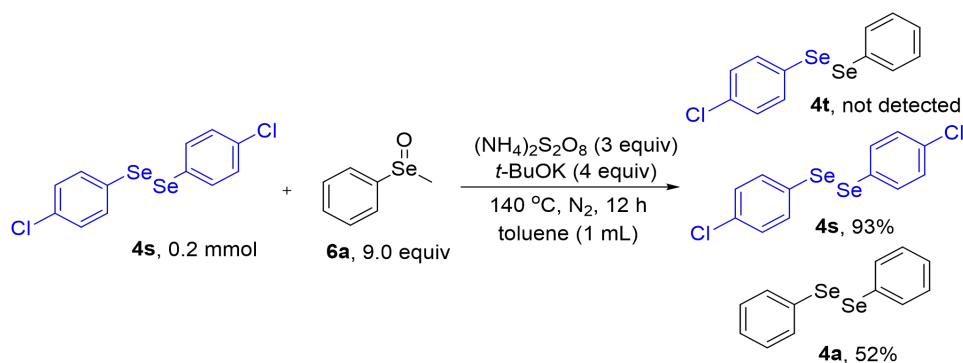
4.2 Synthesis of Unsymmetrical Selenosulfides



Scheme S3

General Procedure C: To a Schlenk tube were added diselenide (0.2 mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (137 mg, 0.6 mmol), *t*-BuOK (90 mg, 0.8 mmol) and DMSO (2 mL). The mixture was stirred in a heating mantle preheated to 140 °C for 12 h under N_2 atmosphere. After cooled to room temperature, the reaction mixture was diluted with H_2O (10 mL), and extracted with EtOAc (3×10 mL). The combined organic phase was washed with water and brine (30 mL), dried over anhydrous Na_2SO_4 , and then evaporated under reduced pressure. The residue was purified by column chromatography to give the desired unsymmetrical selenosulfides.

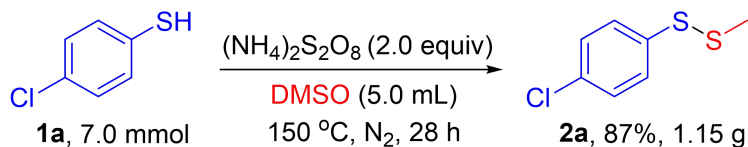
4.3 The reaction between diselenide **4s** and selenoxide **6a**.



Scheme S4

To a Schlenk tube were added diselenide **4s** (0.2 mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (137 mg, 0.6 mmol), *t*-BuOK (90 mg, 0.8 mmol), **6a** (337 mg, 1.8 mmol) and toluene (1 mL). The mixture was stirred in a heating mantle preheated to 140 °C for 12 h under N_2 atmosphere. After cooled to room temperature, the reaction mixture was diluted with H_2O (10 mL), and extracted with EtOAc (3×10 mL). The combined organic phase was washed with water and brine (30 mL), dried over anhydrous Na_2SO_4 , and then evaporated under reduced pressure. The residue was purified by column chromatography to give the desired products.

4.4 Gram-Scale Synthesis of **1a**

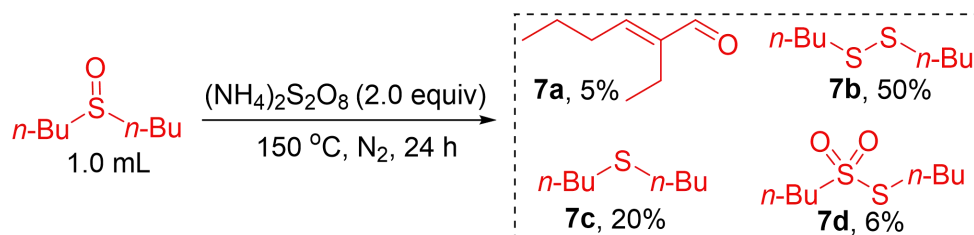


Scheme S5

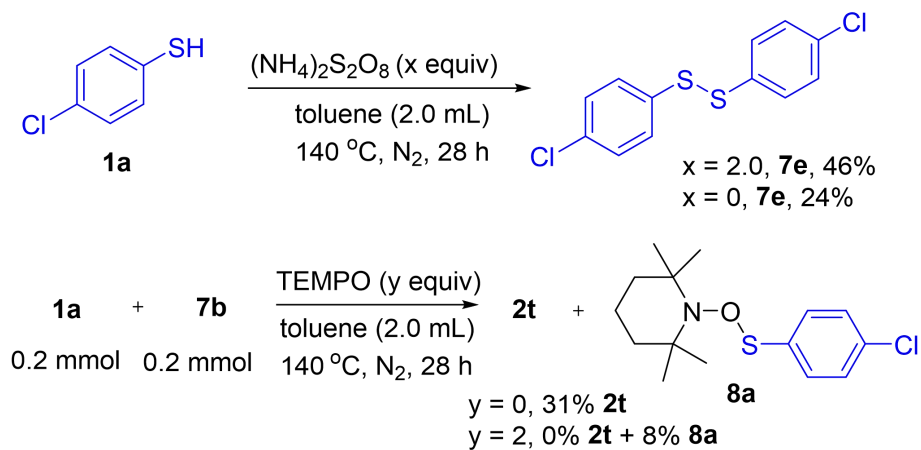
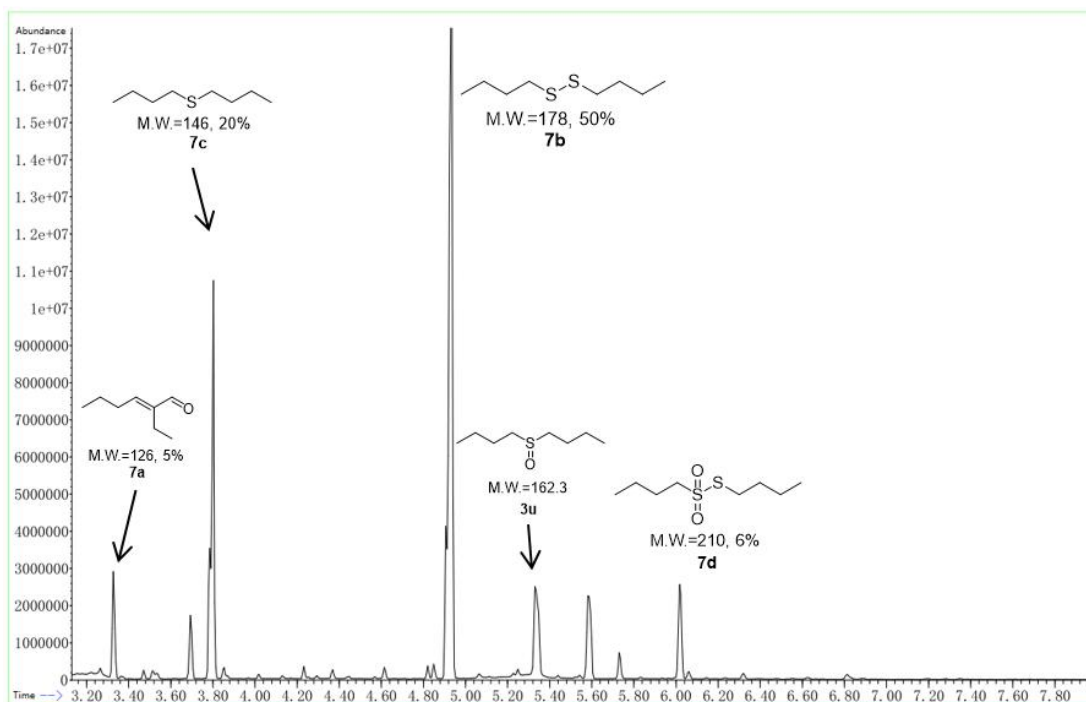
To a Schlenk tube were added **1a** (1.01 g, 7.0 mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (3.2 g, 14 mmol), and DMSO (5 mL). The mixture was stirred in a heating mantle preheated to 140 °C for 28 h under N_2 atmosphere. After cooled to room temperature, the reaction mixture was diluted with H_2O (10 mL), extracted with EtOAc (3×20 mL). The combined organic phase was washed with water and brine (150 mL), dried over anhydrous Na_2SO_4 , and then evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether) to afford **2a** (1.15 g, 87 %) as yellow oil.

5. Preliminary Mechanistic Studies

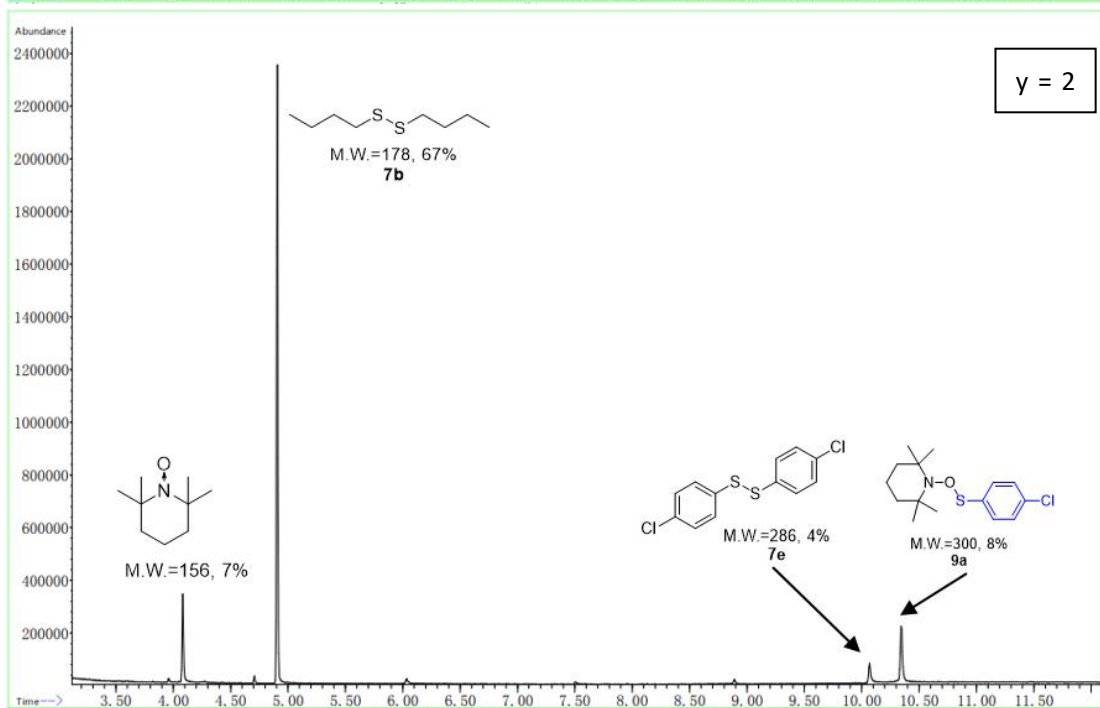
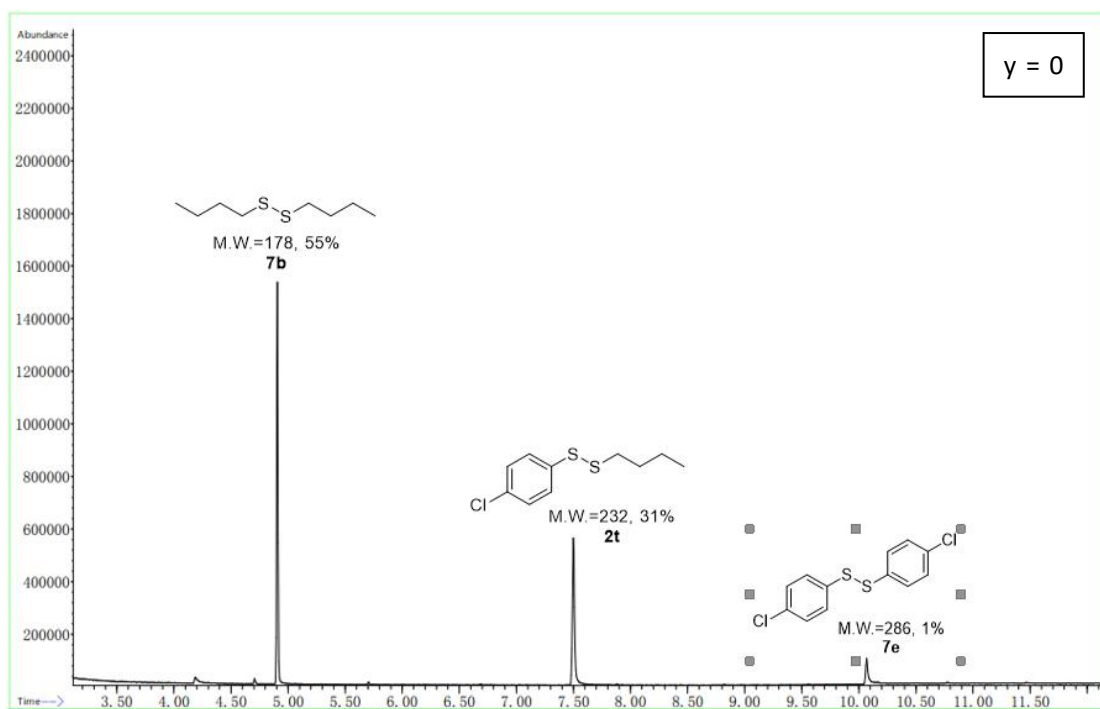
5.1 GC-MS

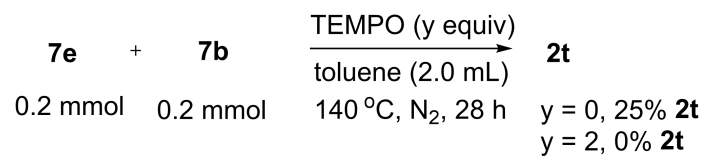


Scheme S6

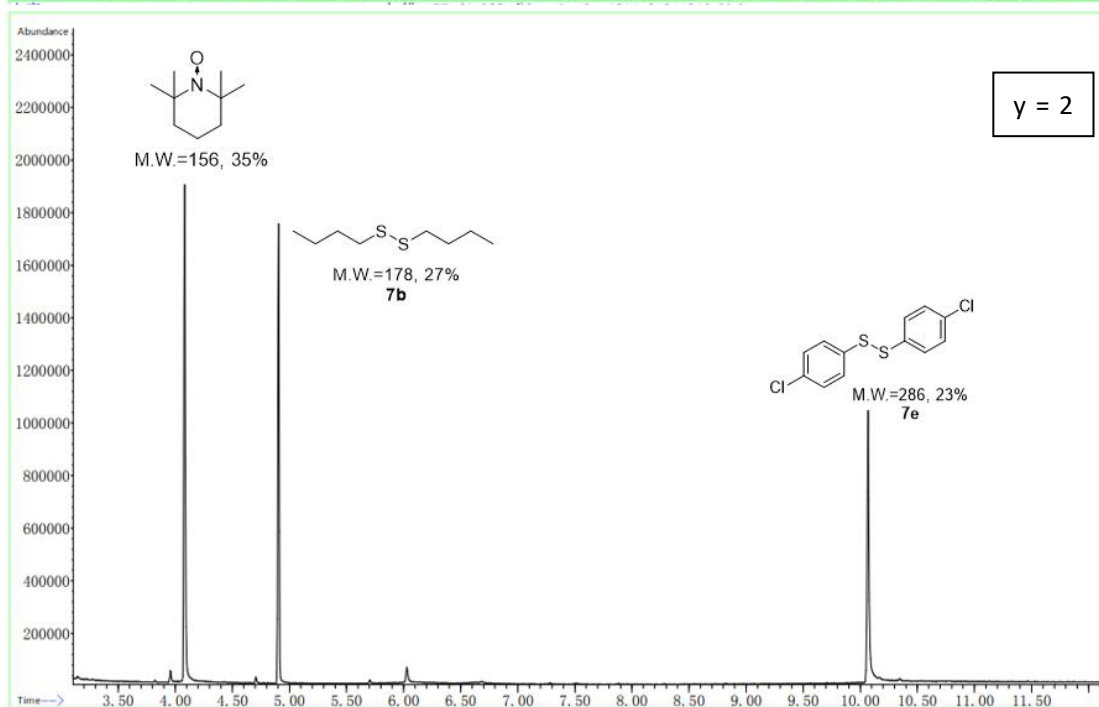
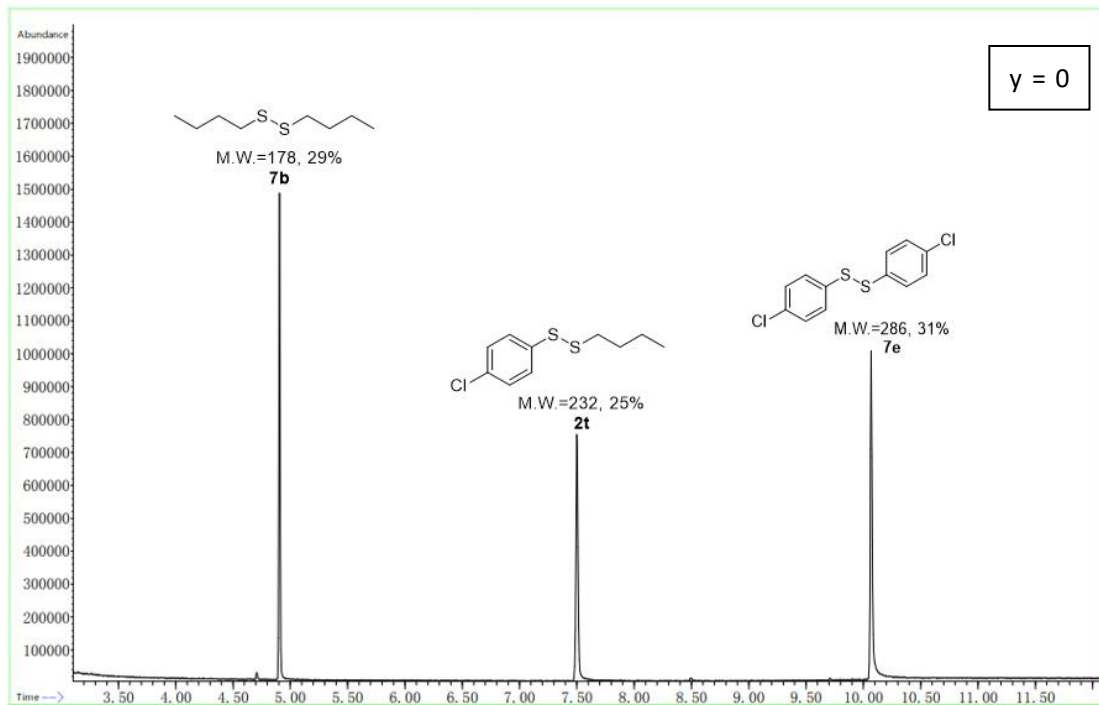


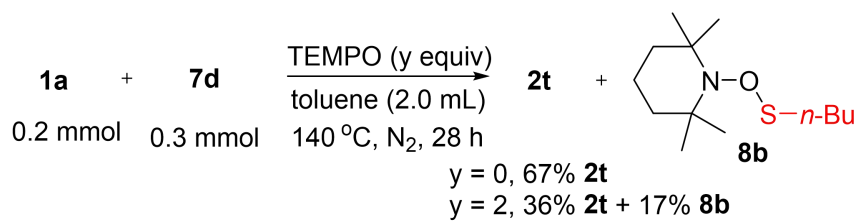
Scheme S7



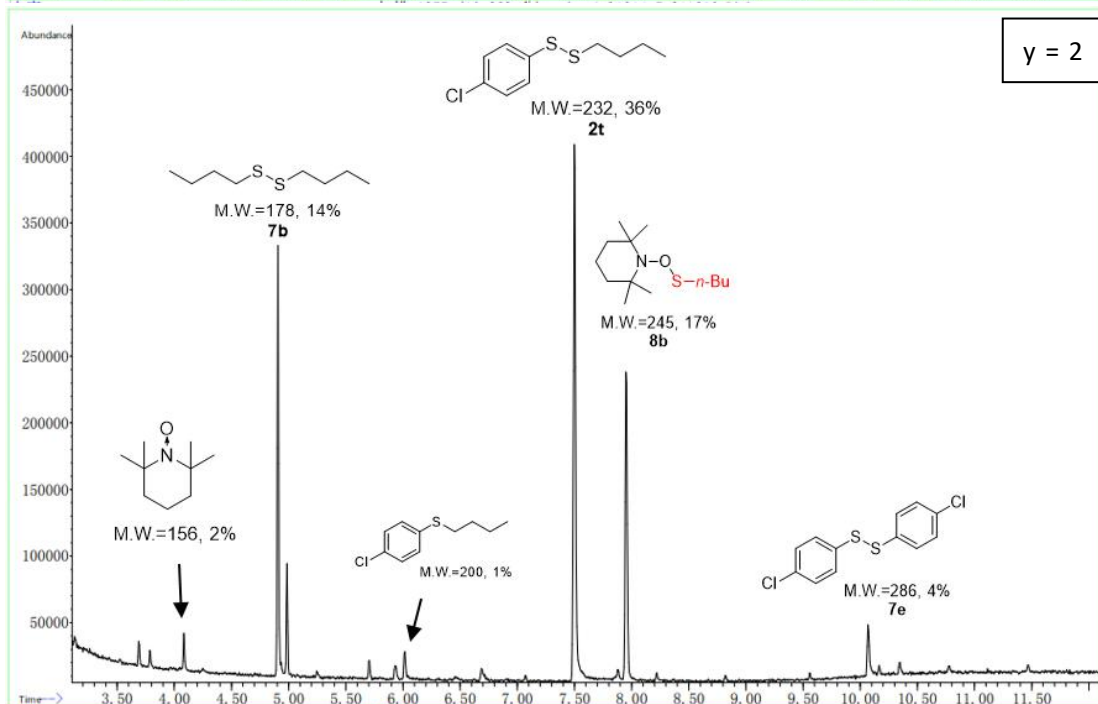
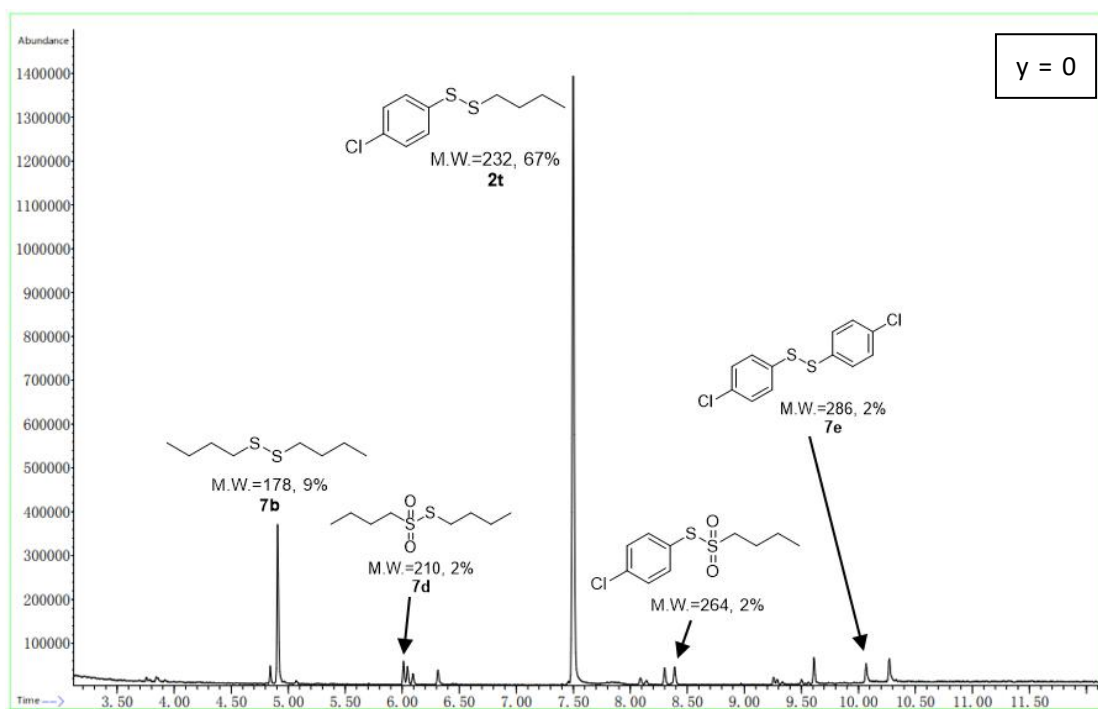


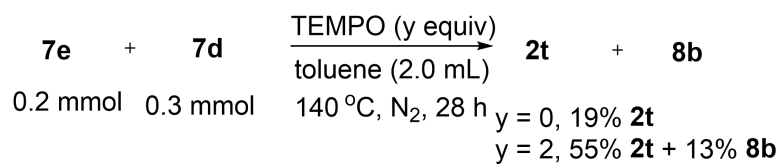
Scheme S8



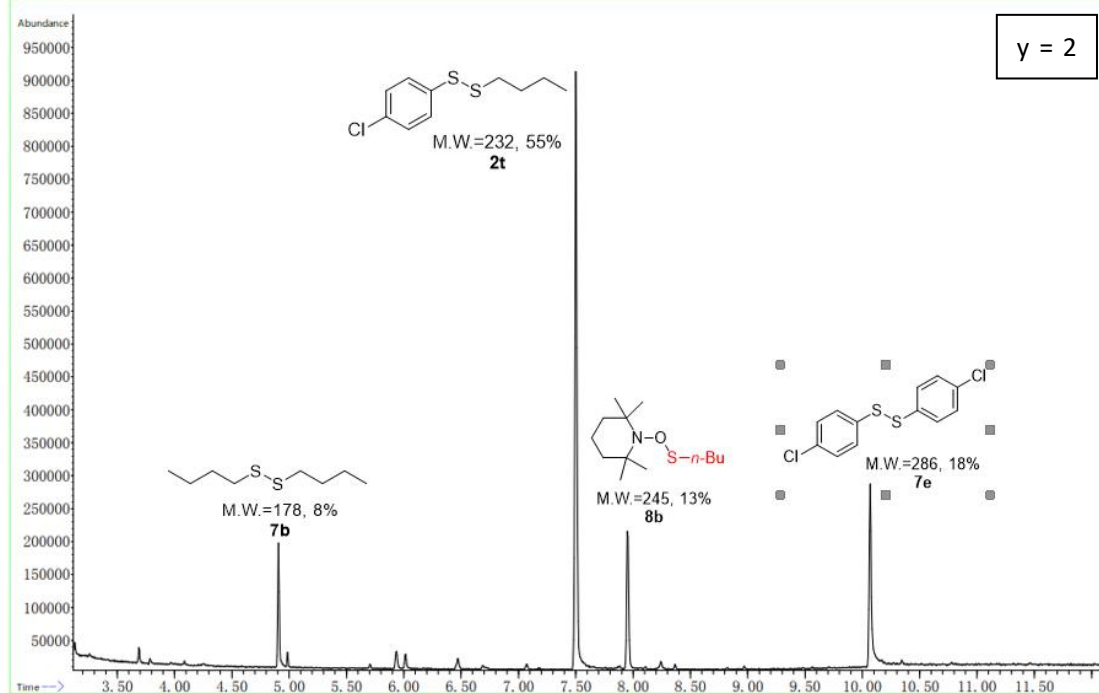
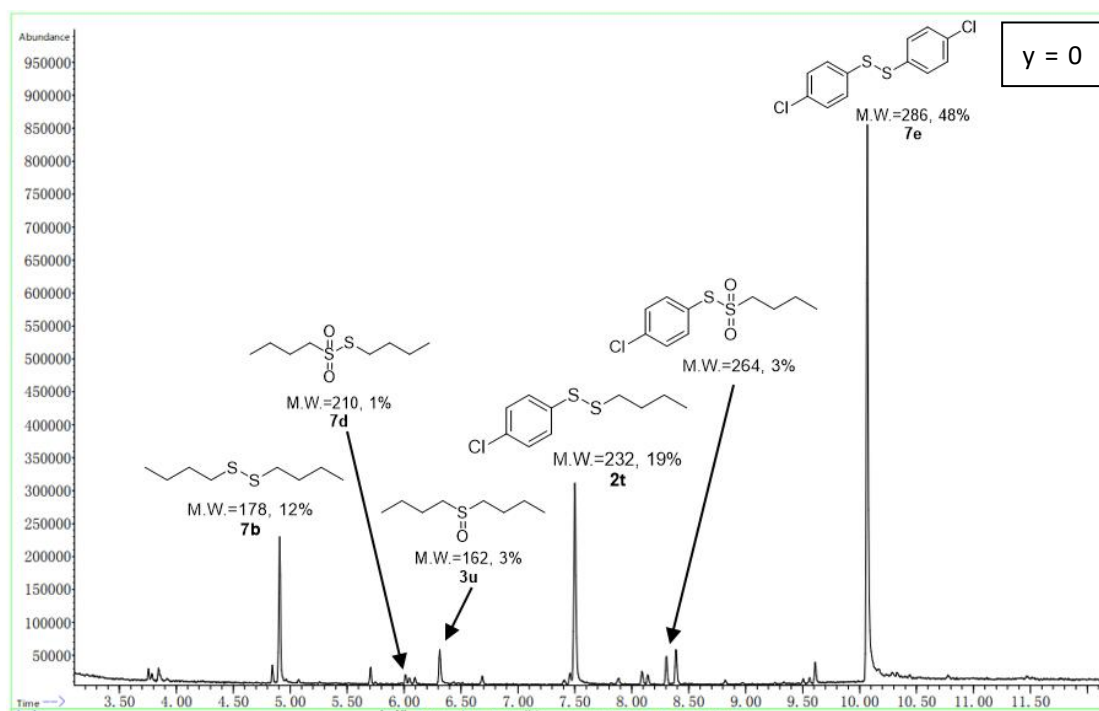


Scheme S9

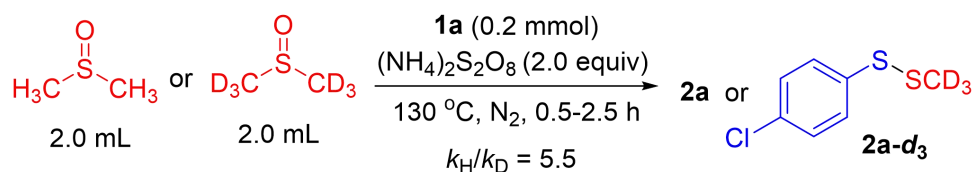




Scheme S10

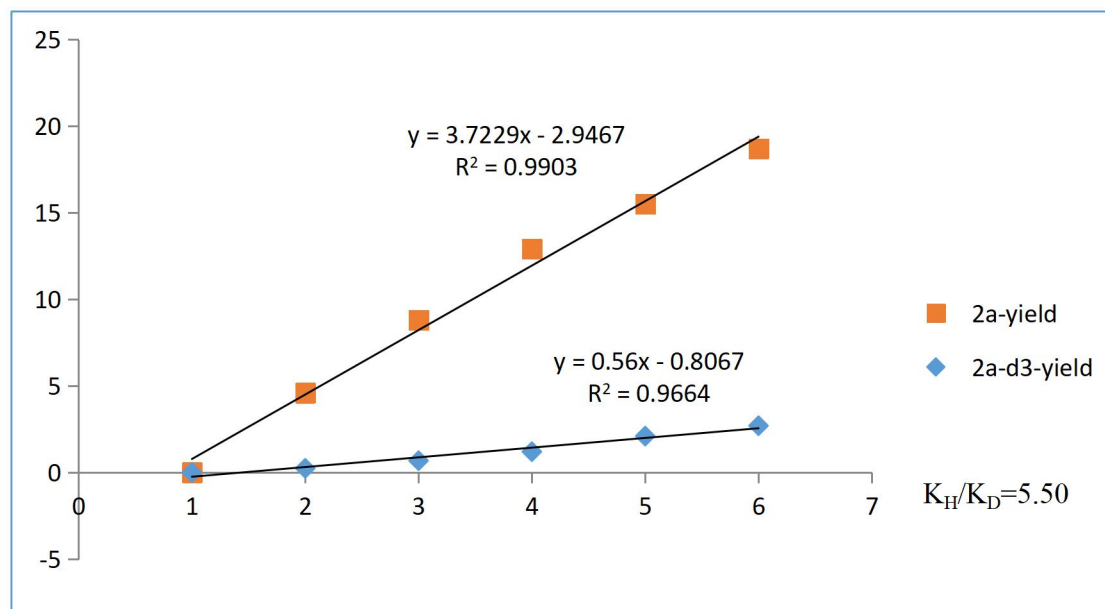


5.2 Kinetic Isotope Effect Experiments

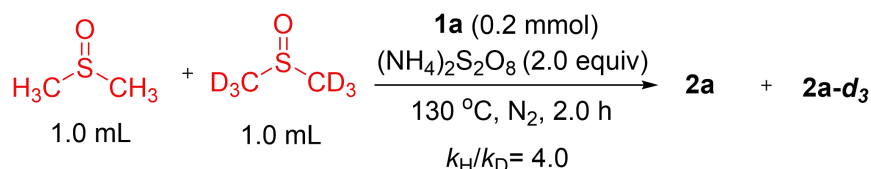


Scheme S11

Preparing five identical 20 mL-Schlenk tubes and each one equipped with a stir bar was charged with **1a** (0.2 mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.4 mmol). Each tube was fitted with a rubber septum, then evacuated and refilled with nitrogen three times. Under nitrogen, DMSO (2 mL) was added in turn to the Schlenk tube through the rubber septum using syringes, and then the rubber septum was replaced by a Teflon screwcap under nitrogen flow. In the other five identical 25 mL-Schlenk tubes, DMSO-*d*₆ was used instead of DMSO. In each group, 30, 60, 90, 120 and 150 min was chosen the reaction time respectively and the corresponding yield was obtained by flash chromatography. A kinetic isotope effect value $K_{\text{H}}/K_{\text{D}} = 3.7229/0.5600 = 5.5$ was obtained.



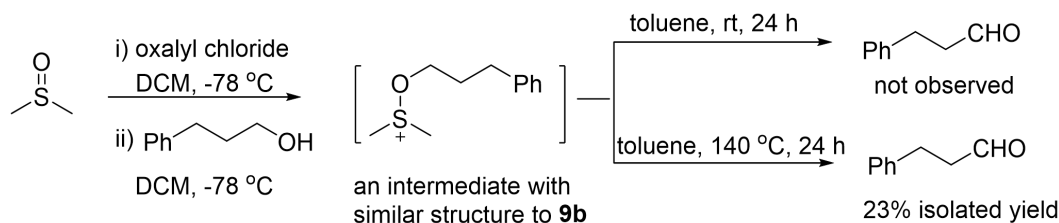
5.3 Competitive Reaction between **2a** and **2a-d₃**



Scheme S12

To a Schlenk tube were added **1a** (0.2 mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.4 mmol), DMSO (1.0 mL) and DMSO- d_6 (1.0 mL). The mixture was stirred in a heating mantle preheated to 130 °C for 2 h under N_2 atmosphere. After cooled to room temperature, the reaction mixture was diluted with H_2O (10 mL), extracted with EtOAc (3×20 mL). The combined organic phase was washed with water and brine (150 mL), dried over anhydrous Na_2SO_4 , and then evaporated under reduced pressure. The residue was detected by GC-MS and the ratio of **2a** to **2a- d_3** (4:1) was obtained.

5.4 A Control Experiment for the Identification of Butoxydibutylsulfonium Salt **9b**

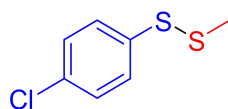


Scheme S13

For the identification of butoxydibutylsulfonium salt **9b**, a control experiment involving an intermediate with similar structure to **9b** was conducted. This intermediate was generated in-situ from swern oxidation of phenylpropanol, the general procedure for this control experiment was as followed: to a Schlenk tube were added DMSO (6.0 eq, 213 μL) and DCM (1.0 mL). Oxalyl chloride (5.0 eq, 212 μL) was added through a syringe at -78 °C, and the mixture was stirred at -78 °C for 10 min. Then phenylpropanol (1.0 eq, 68 μL) was added through a syringe, and the mixture was stirred at -78 °C for 1 h. After the removal of the DCM under reduced pressure followed by the addition of toluene (2 mL). When the resulting mixture was conducted at room temperature for 24 h, no formation of the desired phenylpropionaldehyde. When the resulting mixture was conducted at 140 °C for 24 h, 23% yield of phenylpropionaldehyde was isolated.

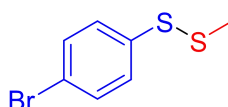
6. Characterization of Products in Details

1-(4-chlorophenyl)-2-methyldisulfane (**2a**)^[10]



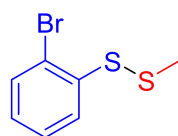
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2a** as yellow oil (36 mg, 93%). ¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, *J* = 7.1 Hz, 2H), 7.31 (d, *J* = 6.6 Hz, 2H), 2.44 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 135.6, 133.0, 129.2, 129.1, 22.8.

1-(4-bromophenyl)-2-methyldisulfane (**2b**)



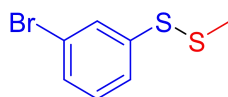
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2b** as white solid (37 mg, 78%). **M.p.** 42.4 - 47.7. ¹H NMR (500 MHz, CDCl₃) δ 7.48 - 7.42 (m, 2H), 7.42 - 7.36 (m, 2H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 136.3, 132.1, 129.2, 120.8, 22.8. **HRMS** (ESI): calculated for C₇H₇BrS₂H [M+H]⁺ 234.9245, found 234.9248.

1-(2-bromophenyl)-2-methyldisulfane (**2c**)



The **General Procedure B** was followed, and hexane was used as the eluant to afford **2c** as a colorless oil (39 mg, 83%). ¹H NMR (500 MHz, CDCl₃) δ 7.78 (dd, *J*₁=8.0 Hz, *J*₂=1.6 Hz, 1H), 7.52 (dd, *J*₁=7.9 Hz, *J*₂=1.3 Hz, 1H), 7.39 - 7.35 (m, 1H), 7.10 - 7.07 (m, 1H), 2.45 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.4, 133.0, 127.9, 127.5, 126.8, 121.5, 22.5. **HRMS** (ESI): calculated for C₇H₇BrS₂H [M+H]⁺ 234.9245, found 234.9250.

1-(3-bromophenyl)-2-methyldisulfane (**2d**)



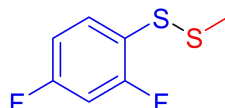
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2d** as a colorless oil (39 mg, 83%). **¹H NMR** (500 MHz, CDCl₃) δ 7.69 - 7.68 (m, 1H), 7.44 - 7.42 (m, 1H), 7.36 - 7.34 (m, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 2.45 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 139.4, 130.3, 129.8, 129.6, 125.7, 123.1, 22.9. **HRMS** (ESI): calculated for C₇H₇BrS₂H [M+H]⁺ 234.9245, found 234.9247.

1-(2-fluorophenyl)-2-methyldisulfane (**2e**)



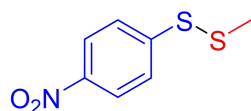
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2e** as a colorless oil (20 mg, 58%). **¹H NMR** (500 MHz, CDCl₃) δ 7.68 - 7.64 (m, 1H), 7.25 (q, *J* = 7.1 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.09 - 7.02 (m, 1H), 2.46 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 160.6 (d, *J* = 245.5 Hz), 130.8, 129.2 (d, *J* = 7.6 Hz), 124.7 (d, *J* = 3.6 Hz), 124.1 (d, *J* = 17.5 Hz), 115.8 (d, *J* = 21.9 Hz), 23.0 (d, *J* = 4.7 Hz); **¹⁹F NMR** (470 MHz, CDCl₃) δ -110.4 (s, 1F). **HRMS** (ESI): calculated for C₇H₇FS₂H [M+H]⁺ 175.0046, found 175.0051.

1-(2,4-difluorophenyl)-2-methyldisulfane (**2f**)



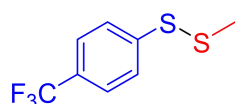
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2f** as a colorless oil (28 mg, 72%). **¹H NMR** (500 MHz, CDCl₃) δ 7.64 - 7.59 (m, 1H), 6.96 - 6.71 (m, 2H), 2.48 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 163.20 (dd, *J*₁ = 208.2 Hz, *J*₂ = 11.7 Hz), 162.16 - 160.26 (m), 133.46 (dd, *J*₁ = 9.5 Hz, *J*₂ = 2.6 Hz), 119.81 (dd, *J*₁ = 18.4 Hz, *J*₂ = 4.1 Hz), 112.00 (dd, *J*₁ = 21.7 Hz, *J*₂ = 3.7 Hz), 104.61 (t, *J* = 26.1 Hz), 23.13 (d, *J* = 3.4 Hz). **¹⁹F NMR** (470 MHz, CDCl₃) δ -104.3 (s, 1F), -109.1 (s, 1F). **HRMS** (ESI): calculated for C₇H₆F₂S₂H [M+H]⁺ 191.9879, found 191.9875.

1-methyl-2-(4-nitrophenyl)disulfane (**2g**)^[11]



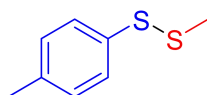
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2g** as a yellow oil (37 mg, 93%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.23 - 8.10 (m, 2H), 7.73 - 7.56 (m, 2H), 2.48 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 146.4, 146.3, 125.8, 124.1, 22.7.

1-methyl-2-(4-(trifluoromethyl)phenyl)disulfane (**2h**)



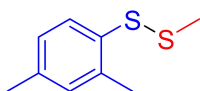
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2h** as a colorless oil (32.3 mg, 72%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 - 7.57 (m, 4H), 2.46 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 142.3 - 141.7 (m), 126.7 - 126.6 (m), 126.4, 126.1 (t, $J = 4.1$ Hz), 125.9 (q, $J = 3.8$ Hz), 22.8. $^{19}\text{F NMR}$ (470 MHz, CDCl_3) δ -62.4 (s, 3F). **HRMS** (ESI): calculated for $\text{C}_8\text{H}_7\text{F}_3\text{S}_2\text{H}$ $[\text{M}+\text{H}]^+$ 223.9941, found 223.9938.

1-methyl-2-(*p*-tolyl)disulfane (**2i**)^[12]



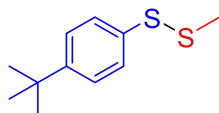
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2i** as a colorless oil (14 mg, 41%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.43 (d, $J = 8.1$ Hz, 2H), 7.15 (d, $J = 7.9$ Hz, 2H), 2.44 (s, 3H), 2.35 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 137.3, 133.6, 129.8, 128.7, 22.9, 21.0.

1-(2,4-dimethylphenyl)-2-methyldisulfane (**2j**)



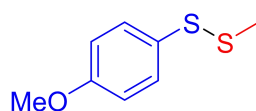
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2j** as a colorless oil (21 mg, 56%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.56 (d, $J = 8.5$ Hz, 1H), 7.03 (d, $J = 6.3$ Hz, 2H), 2.42 (s, 3H), 2.41 (s, 3H), 2.32 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 138.1, 137.6, 131.9, 131.5, 129.8, 127.3, 22.6, 20.9, 20.1. **HRMS** (ESI): calculated for $\text{C}_9\text{H}_{12}\text{S}_2\text{H}$ $[\text{M}+\text{H}]^+$ 184.0380, found 184.0390.

1-(4-(tert-butyl)phenyl)-2-methyldisulfane (**2k**)



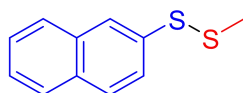
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2k** as a colorless oil (28 mg, 65%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.49 - 7.42 (m, 2H), 7.38 - 7.30 (m, 2H), 2.45 (s, 3H), 1.31 (s, 9H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 150.5, 133.6, 128.2, 126.1, 34.6, 31.3, 23.0. **HRMS** (ESI): calculated for $\text{C}_{11}\text{H}_{16}\text{S}_2\text{H}$ $[\text{M}+\text{H}]^+$ 212.0693, found 212.0688.

1-(4-methoxyphenyl)-2-methyldisulfane (**2l**)^[13]



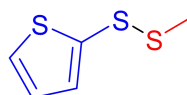
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2l** as a yellow oil (14 mg, 38%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.48 (d, $J = 8.6$ Hz, 2H), 6.87 (d, $J = 8.3$ Hz, 2H), 3.81 (s, 3H), 2.43 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 159.6, 132.0, 127.7, 114.6, 55.3, 55.3, 22.8.

1-methyl-2-(naphthalen-2-yl)disulfane (**2m**)^[13]



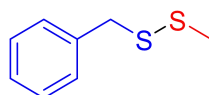
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2m** as a yellow solid (34 mg, 82%). **M.p.** 52.5 - 53.5. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.00 (s, 1H), 7.85 - 7.77 (m, 4H), 7.65 - 7.60 (m, 1H), 7.54 - 7.38 (m, 3H), 2.49 (s, 1H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 134.2, 133.6, 132.4, 128.9, 127.8, 127.4, 126.7, 126.3, 126.1, 125.8, 22.9.

2-(methyldisulfaneyl)thiophene (**2n**)^[13]



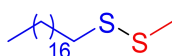
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2n** as a yellow oil (15 mg, 46%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.4 (d, $J = 5.3$ Hz, 1H), 7.3 - 7.2 (m, 1H), 7.0 (dd, $J_1 = 5.4$, $J_2 = 3.2$ Hz, 1H), 2.5 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 136.4, 134.2, 130.9, 127.7, 23.2.

1-benzyl-2-methyldisulfane (**2o**)^[13]



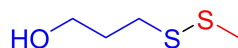
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2o** as a yellow oil (13 mg, 38%). ¹H NMR (500 MHz, CDCl₃) δ 7.34 - 7.26 (m, 5H), 3.88 (s, 2H), 2.08 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.6, 129.4, 128.6, 127.5, 43.0, 23.1.

1-methyl-2-octadecyldisulfane (**2p**)



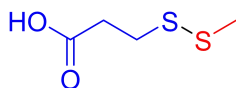
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2p** as a white solid (38 mg, 57%). **M.p.** 63.2 - 65.6. ¹H NMR (400 MHz, CDCl₃) δ 2.68 (t, *J* = 7.3, 2H), 1.70 - 1.56 (m, 2H), 1.56 (s, 3H), 1.38 (t, *J* = 7.4 Hz, 2H), 1.26 (s, 28H), 0.88 (t, *J* = 6.7 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 39.2, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 28.5, 22.7, 14.1. **HRMS** (ESI): calculated for C₁₉H₄₀S₂H [M+H]⁺ 332.2571, found 332.2575.

3-(methyldisulfaneyl)propan-1-ol (**2q**)^[14]



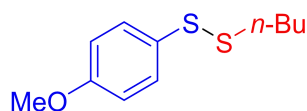
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2q** as a colorless oil (12 mg, 45%). ¹H NMR δ 3.76 (t, *J* = 6.2 Hz, 2H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.42 (d, *J* = 2.2 Hz, 3H), 2.17 (s, 1H), 1.97 (qui, *J* = 6.6 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 60.9, 34.4, 31.8, 23.1.

3-(methyldisulfaneyl)propanoic acid (**2r**)^[15]



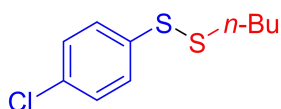
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2r** as a colorless oil (24 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ 11.21 (s, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 178.4, 34.0, 31.9, 23.2.

1-butyl-2-(4-methoxyphenyl)disulfane (**2s**)^[15]



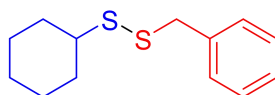
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2s** as a yellow oil (32 mg, 71%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.5 - 7.4 (m, 2H), 6.9 - 6.8 (m, 2H), 3.8 (s, 3H), 2.7 (t, $J = 7.4$ Hz, 2H), 1.68 - 1.60 (m, 2H), 1.4 (q, $J = 7.5$ Hz, 2H), 0.9 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 159.5, 131.6, 128.5, 114.6, 55.4, 38.5, 30.8, 21.7, 13.7.

1-butyl-2-(4-chlorophenyl)disulfane (**2t**)^[16]



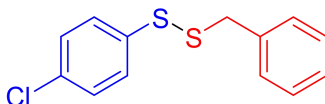
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2t** as a yellow oil (30 mg, 65%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 - 7.38 (m, , 2H), 7.30 - 7.26 (m, 2H), 2.70 (q, $J = 7.2$ Hz, 2H), 1.66 (m, $J = 7.6$ Hz, 2H), 1.42 (m, $J = 7.3$ Hz, 2H), 0.93 (q, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 135.1, 133.6, 129.3, 129.0, 38.9, 31.3, 21.7, 13.7.

1-benzyl-2-cyclohexyldisulfane (**2u**)^[17]



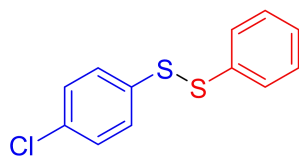
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2u** as a yellow oil (40 mg, 83%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.31 - 7.25 (m, 4H), 7.23 (m, 1H), 3.85 (s, 2H), 2.35 (tt, $J = 10.9, 3.8$ Hz, 1H), 1.90 (d, $J = 12.4$ Hz, 2H), 1.70 (dd, $J_1 = 9.7, J_2 = 5.1$ Hz, 2H), 1.28 - 1.12 (m, 5H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 137.7, 129.3, 128.5, 127.4, 49.3, 44.7, 32.8, 26.1, 25.7.

1-benzyl-2-(4-chlorophenyl)disulfane (**2v**)^[18]



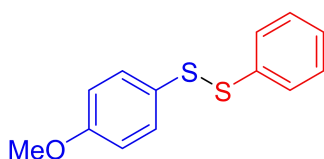
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2v** as a yellow oil (43 mg, 80%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.31 - 7.28 (m, 2H), 7.25 - 7.16 (m, 7H), 3.90 (s, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 136.4, 132.8, 129.4, 129.1, 129.0, 128.6, 127.6, 43.5.

1-(4-chlorophenyl)-2-phenyldisulfane (**2w**)^[19]



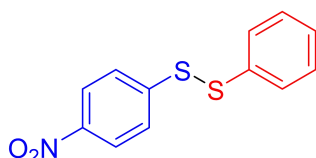
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2w** as a yellow oil (32 mg, 80%). ¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 136.6, 135.6, 133.3, 129.2, 129.2, 129.0, 127.8, 127.5.

1-(4-methoxyphenyl)-2-phenyldisulfane (**2x**)^[8]



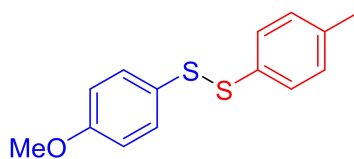
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2w** as a yellow oil (21 mg, 43%). ¹H NMR (500 MHz, CDCl₃) δ 7.4 (dd, *J*₁ = 11.1 Hz, *J*₂ = 8.4 Hz, 4H), 7.3 (d, *J* = 8.3 Hz, 2H), 6.8 (d, *J* = 8.4 Hz, 2H), 3.8 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 160.1, 136.1, 133.4, 132.2, 129.8, 129.2, 127.6, 114.8, 55.4.

1-(4-nitrophenyl)-2-phenyldisulfane (**2y**)^[24]



The **General Procedure B** was followed, and hexane was used as the eluant to afford **2y** as a yellow oil (33 mg, 62%). ¹H NMR (500 MHz, CDCl₃) δ 8.2 - 8.1 (m, 2H), 7.7 - 7.6 (m, 2H), 7.5 - 7.4 (m, 2H), 7.3 (t, *J* = 7.6 Hz, 2H), 7.3 - 7.2 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 146.5, 146.2, 135.3, 129.4, 128.0, 127.8, 126.2, 124.2.

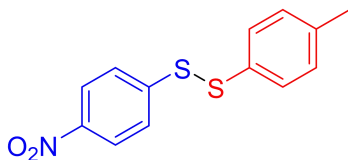
1-(4-methoxyphenyl)-2-(*p*-tolyl)disulfane (**2z**)^[21]



The **General Procedure B** was followed, and hexane was used as the eluant to afford **2z** as a yellow solid (27 mg, 52%). **M.p.** 43.2 - 45.3. ¹H NMR (500 MHz, CDCl₃) δ

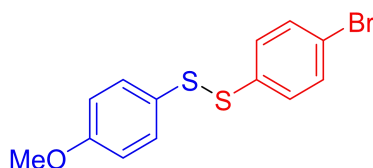
7.44 - 7.36 (m, 4H), 7.12 (d, $J = 7.7$ Hz, 2H), 6.87 - 6.77 (m, 2H), 3.79 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.8, 137.6, 134.1, 131.9, 129.8, 129.1, 128.31, 114.7, 55.4, 21.1.

1-(4-nitrophenyl)-2-(p-tolyl)disulfane (2aa)^[22]



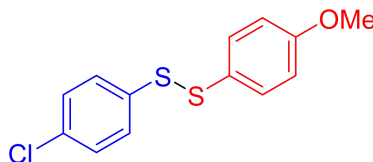
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2aa** as a yellow solid (28 mg, 50%). **M.p.** 63.0 -63.5. ^1H NMR (400 MHz, CDCl_3) δ 8.20 - 8.12 (m, 2H), 7.69 - 7.61 (m, 2H), 7.37 (d, $J = 7.8$ Hz, 2H), 7.13 (d, $J = 7.8$ Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 146.5, 146.4, 138.5, 131.9, 130.2, 128.7, 126.2, 124.1, 21.1.

1-(4-bromophenyl)-2-(4-methoxyphenyl)disulfane (2bb)^[20]



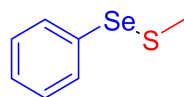
The **General Procedure B** was followed, and hexane was used as the eluant to afford **2x** as a yellow oil (20 mg, 31%). ^1H NMR (400 MHz, CDCl_3) δ 7.46 - 7.32 (m, 6H), 6.83 (d, $J = 8.4$ Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.0, 136.7, 132.1, 132.1, 129.9, 127.5, 121.3, 114.8, 55.4.

1-(4-chlorophenyl)-2-(4-methoxyphenyl)disulfane (2cc)^[6]



The **General Procedure B** was followed, and hexane was used as the eluant to afford **2cc** as a yellow oil (40 mg, 71%). ^1H NMR (400 MHz, CDCl_3) δ 7.4 (dd, $J_1 = 11.1$ Hz, $J_2 = 8.4$ Hz, 4H), 7.3 (d, $J = 8.3$ Hz, 2H), 6.8 (d, $J = 8.4$ Hz, 2H), 3.8 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.1, 136.1, 133.4, 132.2, 129.8, 129.2, 127.6, 114.8, 55.4.

methyl(phenylselanyl)sulfane (5a)^[23]



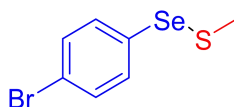
The **General Procedure C** was followed, and hexane was used as the eluant to afford **5a** as a yellow oil (29 mg, 72%). **¹H NMR** (500 MHz, CDCl₃) δ 7.65 - 7.58 (m, 2H), 7.31 (m, 2H), 7.26 (m, 1H), 2.61 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 131.7, 130.2, 129.2, 127.5, 22.3.

((2-chlorophenyl)selanyl)(methyl)sulfane (5b)



The **General Procedure C** was followed, and hexane was used as the eluant to afford **5b** as a yellow oil (41 mg, 86%). **¹H NMR** (500 MHz, CDCl₃) δ 7.84 - 7.82 (m, 1H), 7.34 - 7.29 (m, 2H), 7.21 - 7.18 (m 1H), 2.60 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) 132.8, 131.1, 129.5, 128.1, 127.8, 127.6, 22.0. **HRMS** (ESI): calculated for C₇H₇ClSSeH [M+H]⁺ 238.9195, found 238.9199.

((4-bromophenyl)selanyl)(methyl)sulfane (5c)



The **General Procedure C** was followed, and hexane was used as the eluant to afford **5c** as a yellow oil (36 mg, 63%). **¹H NMR** (500 MHz, CDCl₃) δ 7.50 - 7.48 (m, 2H), 7.46 - 7.42 (m, 2H), 2.61 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 132.2, 131.7, 130.6, 121.6, 22.3. **HRMS** (ESI): calculated for C₇H₇BrSSeH [M+H]⁺ 282.8690, found 282.8698.

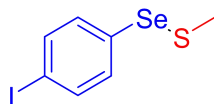
((2-bromophenyl)selanyl)(methyl)sulfane (5d)



The **General Procedure C** was followed, and hexane was used as the eluant to afford **5d** as a yellow oil (37 mg, 65%). **¹H NMR** (500 MHz, CDCl₃) δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 2.61 (s,

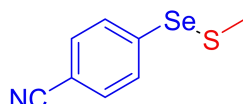
3H); ^{13}C NMR (125 MHz, CDCl_3) δ 132.2, 131.7, 130.6, 121.6, 22.3. **HRMS** (ESI): calculated for $\text{C}_7\text{H}_7\text{BrSSeH}$ $[\text{M}+\text{H}]^+$ 282.8690, found 282.8698.

((4-iodophenyl)selanyl)(methyl)sulfane (5e)



The **General Procedure C** was followed, and hexane was used as the eluant to afford, **5e** as a yellow oil (53 mg, 81%). ^1H NMR (500 MHz, CDCl_3) δ 7.55 (d, $J = 8.5$ Hz, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 137.9, 132.1, 131.8, 91.0, 7.3. **HRMS** (ESI): calculated for $\text{C}_7\text{H}_7\text{ISseH}$ $[\text{M}+\text{H}]^+$ 330.8551, found 330.8560.

4-((methylthio)selanyl)benzonitrile (5f)



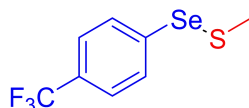
The **General Procedure C** was followed, and hexane was used as the eluant to afford **5f** as a yellow oil (28 mg, 62%). ^1H NMR (500 MHz, CDCl_3) δ 7.71 (dd, $J_1 = 8.4$, $J_2 = 1.6$ Hz, 2H), 7.64 - 7.54 (m, 2H), 2.63 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) 138.9, 132.5, 128.8, 118.5, 110.5, 22.3. **HRMS** (ESI): calculated for $\text{C}_8\text{H}_7\text{NssseH}$ $[\text{M}+\text{H}]^+$ 229.9537, found 229.9544.

methyl((3-nitrophenyl)selanyl)sulfane (5g)



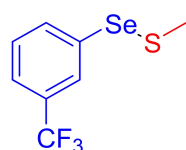
The **General Procedure C** was followed, and hexane was used as the eluant to afford **5g** as a yellow oil (38 mg, 76%). ^1H NMR (500 MHz, CDCl_3) δ 8.48 (d, $J = 1.9$ Hz, 1H), 8.11 - 8.09 (m, 1H), 7.93 - 7.91 (m, 1H), 7.50 (t, $J = 8.0$ Hz, 1H), 2.66 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 148.8, 134.8, 134.1, 129.8, 123.8, 122.1, 22.5. **HRMS** (ESI): calculated for $\text{C}_7\text{H}_8\text{NO}_2\text{SseH}$ $[\text{M}+\text{H}]^+$ 249.9435, found 249.9428.

methyl((4-(trifluoromethyl)phenyl)selanyl)sulfane (5h)



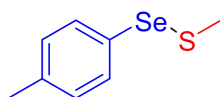
The **General Procedure C** was followed, and hexane was used as the eluant to afford **5h** as a yellow oil (46 mg, 85%). **¹H NMR** (500 MHz, CDCl₃) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 2.63 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 136.7, 129.0, 126.1, 126.0, 125.9 (q, *J* = 12.5 Hz), 125.9, 22.3. **¹⁹F NMR** (470 MHz, CDCl₃) δ -62.5 (s, 3F). **HRMS** (ESI): calculated for C₈H₇F₃SSeH [M+H]⁺ 272.9459, found 272.9455.

methyl((3-(trifluoromethyl)phenyl)selanyl)sulfane (5i)



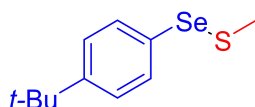
The **General Procedure C** was followed, and hexane was used as the eluant to afford **5i** as a yellow oil (33 mg, 61 %). **¹H NMR** (500 MHz, CDCl₃) δ 7.88 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 2.63 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 132.9, 132.7, 131.6 (q, *J* = 37.5 Hz), 129.5, 126.1 (q, *J* = 4.0 Hz), 124.1 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 275 Hz), 22.4. **¹⁹F NMR** (470 MHz, CDCl₃) δ -62.7 (s, 3F). **HRMS** (ESI): calculated for C₈H₇F₃SSeH [M+H]⁺ 272.9459, found 272.9455.

methyl(*p*-tolylselanyl)sulfane (5j)



The **General Procedure C** was followed, and hexane was used as the eluant to afford **5j** as a yellow oil (29 mg, 66%). **¹H NMR** (500 MHz, CDCl₃) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 2.59 (s, 3H), 2.34 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 137.8, 131.1, 130.0, 128.2, 22.3, 21.1. **HRMS** (ESI): calculated for C₈H₁₀SSeH [M+H]⁺ 218.9741, found 218.9738.

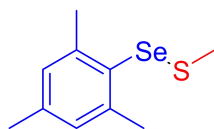
((4-(*tert*-butyl)phenyl)selanyl)(methyl)sulfane (5k)



The **General Procedure C** was followed, and hexane was used as the eluant to afford **5k** as a yellow oil (42 mg, 81%). **¹H NMR** (500 MHz, CDCl₃) δ 7.56 (d, *J* = 8.2 Hz,

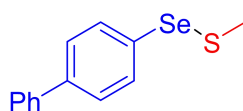
2H), 7.35 (d, $J = 8.2$ Hz, 2H), 2.62 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 151.0, 130.6, 128.3, 126.3, 34.6, 31.3, 22.4. **HRMS** (ESI): calculated for $\text{C}_{11}\text{H}_{16}\text{SSeH}$ $[\text{M}+\text{H}]^+$ 261.0211, found 2610207.

(mesitylselanyl)(methyl)sulfane (5l)



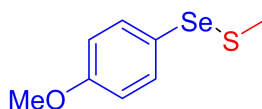
The **General Procedure C** was followed, and hexane was used as the eluant to afford **5l** as a yellow oil (24 mg, 48%). ^1H NMR (500 MHz, CDCl_3) δ 6.97 - 6.95 (m, 2H), 2.58 (s, 9H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.9, 139.3, 129.8, 128.8, 24.4, 21.9, 21.0. **HRMS** (ESI): calculated for $\text{C}_{10}\text{H}_{15}\text{SSeH}$ $[\text{M}+\text{H}]^+$ 247.0054, found 247.0061.

([1,1'-biphenyl]-4-ylselanyl)(methyl)sulfane (5m)



The **General Procedure C** was followed, and hexane was used as the eluant to afford **5m** as a yellow oil (29 mg, 51%). ^1H NMR (500 MHz, CDCl_3) δ 7.68 (d, $J = 8.3$ Hz, 2H), 7.59 - 7.51 (m, 4H), 7.42 (dd, $J_1 = 8.4$, $J_2 = 6.9$ Hz, 2H), 7.37 - 7.31 (m, 1H), 2.63 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 140.7, 140.4, 130.8, 130.8, 128.9, 128.0, 127.6, 127.1, 22.4. **HRMS** (ESI): calculated for $\text{C}_{13}\text{H}_{12}\text{SSeH}$ $[\text{M}+\text{H}]^+$ 280.9898, found 280.9891.

((4-methoxyphenyl)selanyl)(methyl)sulfane (5n)



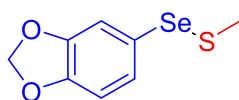
The **General Procedure C** was followed, and hexane was used as the eluant to afford **5n** as a yellow oil (16 mg, 35%). ^1H NMR (500 MHz, CDCl_3) δ 7.58 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.7$ Hz, 2H), 3.81 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.0, 134.1, 122.2, 114.9, 55.4, 22.2. **HRMS** (ESI): calculated for $\text{C}_8\text{H}_{10}\text{OSSeH}$ $[\text{M}+\text{H}]^+$ 234.9690, found 234.9696.

((3-methoxyphenyl)selanyl)(methyl)sulfane (5o)



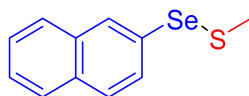
The **General Procedure C** was followed, and hexane was used as the eluant to afford **5o** as a yellow oil (24 mg, 52%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.26 - 7.15 (m, 3H), 6.81 - 6.79 (m, 1H), 3.82 (s, 3H), 2.61 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 160.2, 132.8, 129.9, 122.0, 115.1, 113.3, 55.3, 22.4. **HRMS** (ESI): calculated for $\text{C}_8\text{H}_{10}\text{OSSeH}$ $[\text{M}+\text{H}]^+$ 234.9690, found 234.9696.

5-((methylthio)selanyl)benzo[d][1,3]dioxole (**5p**)



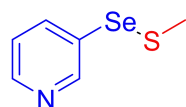
The **General Procedure C** was followed, and hexane was used as the eluant to afford **5p** as a yellow oil (26 mg, 53%). $^1\text{H NMR}$ (500 MHz, CDCl_3) 7.16 (d, $J = 1.7$ Hz, 1H), 7.11 (dd, $J_1 = 8.0$, $J_2 = 1.7$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 5.98 (s, 2H), 2.61 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 148.3, 148.1, 125.9, 123.4, 112.6, 108.9, 101.3, 22.2. **HRMS** (ESI): calculated for $\text{C}_8\text{H}_8\text{O}_2\text{SSeH}$ $[\text{M}+\text{H}]^+$ 248.9483, found 248.9488.

methyl(naphthalen-2-ylselanyl)sulfane (**5q**)



The **General Procedure C** was followed, and hexane was used as the eluant to afford **5q** as a yellow soild (29 mg, 57%). **M.p.** 52.5 - 54.6. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.28 (d, $J = 8.3$ Hz, 1H), 8.05 (dd, $J_1 = 7.1\text{Hz}$, $J_2 = 1.3$ Hz, 1H), 7.89 - 7.82 (m, 2H), 7.62 - 7.52 (m, 2H), 7.48 - 7.43 (m, 1H), 2.62 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 134.2, 130.5, 130.1, 129.0, 128.7, 126.7, 126.3, 125.8, 22.1. **HRMS** (ESI): calculated for $\text{C}_{11}\text{H}_{11}\text{SSeH}$ $[\text{M}+\text{H}]^+$ 254.9741, found 254.9735.

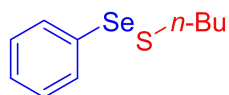
3-((methylthio)selanyl)pyridine (**5r**)



The **General Procedure C** was followed, and hexane was used as the eluant to afford **5r** as a yellow oil (23 mg, 51%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.81 (s, 1H), 8.52 (s,

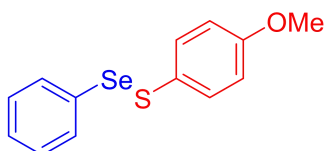
1H), 7.99 - 7.96 (m, 1H), 7.28 (s, 1H), 2.63 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 151.0, 148.6, 138.3, 124.3, 22.4. HRMS (ESI): calculated for $\text{C}_6\text{H}_7\text{NSSeH}$ $[\text{M}+\text{H}]^+$ 205.9537, found 205.9545.

butyl(phenylselanyl)sulfane (5s)^[15]



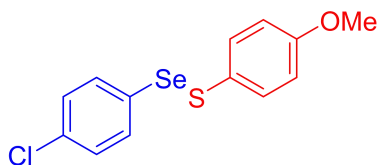
The **General Procedure C** was followed, and hexane was used as the eluant to afford **5s** as a yellow oil (60 mg, 61%). ^1H NMR (500 MHz, CDCl_3) δ 7.6 (d, $J = 7.6$ Hz, 2H), 7.3 (t, $J = 7.5$ Hz, 3H), 2.8 (t, $J = 7.4$ Hz, 2H), 1.6 (q, $J = 7.4$ Hz, 2H), 1.4 (p, $J = 7.4$ Hz, 2H), 0.9 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 132.4, 130.9, 129.9, 129.1, 127.2, 38.0, 32.3, 21.6, 13.6.

(4-methoxyphenyl)(phenylselanyl)sulfane (5u)^[25]



The **General Procedure C** was followed, and hexane was used as the eluant to afford **5u** as a yellow oil (77 mg, 65%; 41 mg, 35%). ^1H NMR (500 MHz, CDCl_3) δ 7.7 - 7.5 (m, 2H), 7.4 (dd, $J_1 = 10.6\text{Hz}$, $J_2 = 8.6$ Hz, 2H), 7.3 - 7.2 (m, 3H), 6.9 - 6.8 (m, 2H), 3.8 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.3, 133.9, 133.0, 131.9, 131.3, 129.6, 128.8, 115.0, 55.7.

((4-chlorophenyl)selanyl)(4-methoxyphenyl)sulfane (5v)



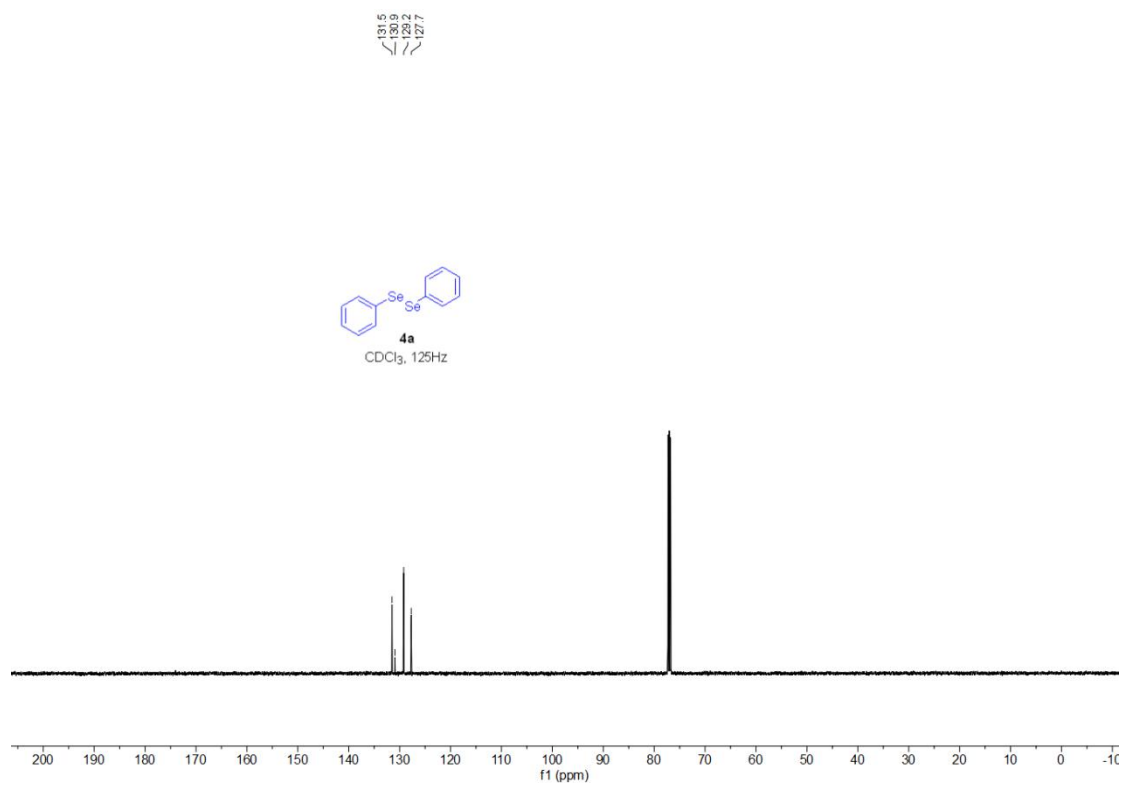
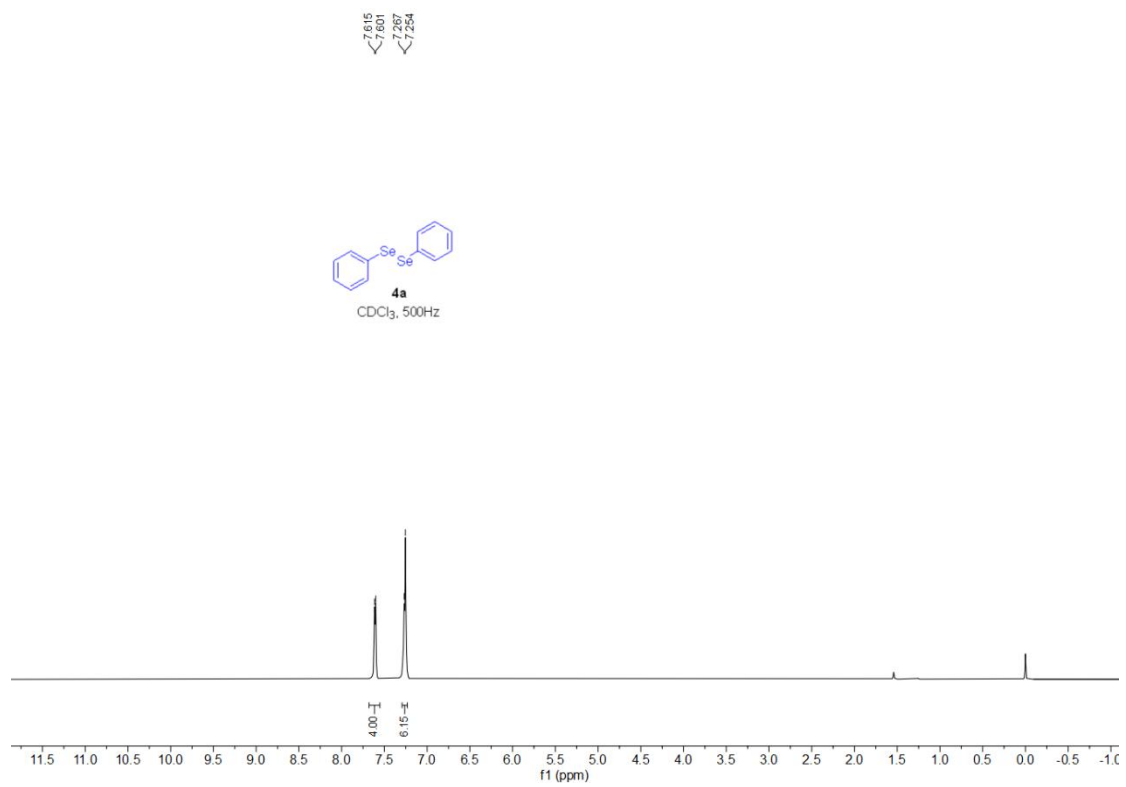
The **General Procedure C** was followed, and hexane was used as the eluant to afford **5v** as a yellow oil (91 mg, 69%; 62 mg, 47%). ^1H NMR (500 MHz, CDCl_3) δ 7.5 (d, $J = 8.4$ Hz, 2H), 7.4 - 7.4 (m, 2H), 7.3 (d, $J = 8.4$ Hz, 2H), 6.8 (d, $J = 8.7$ Hz, 2H), 3.8 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.2, 134.1, 133.8, 132.5, 131.0, 129.3, 127.5, 114.7, 55.4. HRMS (ESI): calculated for $\text{C}_{13}\text{H}_{11}\text{ClOSSeH}$ $[\text{M}+\text{H}]^+$ 329.9384, found 329.9388.

7. Reference:

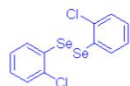
- [1] Leng, T.; Wu, G.; Zhou, Y.-B.; Gao, W.; Ding, J.; Huang, X.; Liu, M.; Wu, H. Silver-Catalyzed One-Pot Three-Component Selective Synthesis of β -Hydroxy Selenides. *Adv. Synth. Catal.* **2018**, *360*, 4336-4340.
- [2] Singh, D.; Deobald, A. M.; Camargo, L. R. S.; Tabarelli, G.; Rodrigues, O. E. D.; Braga, A. L. An Efficient One-Pot Synthesis of Symmetrical Diselenides or Ditellurides from Halides with CuO Nanopowder/Se⁰ or Te⁰/Base. *Org. Lett.* **2010**, *12*, 3288-3291.
- [3] Sébastien, R.; Anne, R. O. K.; Julie, B.; Patrice, V. Metal-Free ipso-Selenocyanation of Arylboronic Acids Using Malononitrile and Selenium Dioxide. *Synthesis* **2019**, *51*, 3758-3764.
- [4] Zhang, Y.; Jia, X.; Zhou, X. Samarium Diiodide-Induced Reduction of Amorphous Selenium: A Facile Synthesis of Diaryl Diselenides. *Synth. Commun.* **1994**, *24*, 1247-1252.
- [5] Kommula, D.; Li, Q.; Ning S.; Liu W.; Wang Q.; Zhao, K. Z. Iodine mediated synthesis of diaryl diselenides using SeO₂ as a selenium source. *Synth. Commun.* **2020**, *50*, 1026-1034.
- [6] Yao, H.-F.; Li, F.-H.; Li, J.; Wang, S.-Y.; Ji, S.-J. Iron(III) chloride-promoted cyclization of α,β -alkynic tosylhydrazones with diselenides: synthesis of 4-(arylselanyl)-1*H*-pyrazoles. *Org. Biomol. Chem.* **2020**, *18*, 1987-1993.
- [7] Curran, S. P.; Connon, S. J. Selenide Ions as Catalysts for Homo- and Crossed-Tishchenko Reactions of Expanded Scope. *Org. Lett.* **2012**, *14*, 1074-1077.
- [8] Li, F.; Wang, D.; Chen H.; He, Z.; Zhou, L.; Zeng Q. Transition metal-free coupling reactions of benzylic trimethylammonium salts with di(hetero)aryl disulfides and diselenides. *Chem. Commun.* **2020**, *56*, 13029-13032.
- [9] Saravanan, P.; Anbarasan, P. Trifluoromethylthiolative 1,2-difunctionalization of alkenes with diselenides and AgSCF₃. *Chem. Commun.* **2019**, *55*, 4639-4642.
- [10] Tsutsumi, N.; Itoh, T.; Ohsawa, A. Cleavage of S-S Bond by Nitric Oxide (NO) in the Presence of Oxygen: A Disproportionation Reaction of Two Disulfides. *Pharma. Bull.* **2000**, *48*, 1524-1528.
- [11] Turos, E.; Revell, K. D.; Ramaraju, P.; Gergeres, D. A.; Greenhalgh, K.; Young, A. Unsymmetric aryl-alkyl disulfide growth inhibitors of methicillin-resistant *Staphylococcus aureus* and *Bacillus anthracis*. *Bio. Med. Chem.* **2008**, *16*, 6501-6508.
- [12] Taniguchi, N. Unsymmetrical disulfide and sulfenamide synthesis via reactions of thiosulfonates with thiols or amines. *Tetrahedron* **2017**, *73*, 2030-2035.
- [13] Guo, J.; Zha, J.; Zhang, T.; Ding, C.-H.; Tan, Q.; Xu, B. PdCl₂/DMSO-Catalyzed Thiol-Disulfide Exchange: Synthesis of Unsymmetrical Disulfide. *Org. Lett.* **2021**, *23*, 3167-3172.
- [14] Arisawa, M.; Suwa, A.; Yamaguchi, M. RhCl₃-catalyzed disulfide exchange reaction using water solvent in homogeneous and heterogeneous systems. *J. Org. Chem.* **2006**, *691*, 1159-1168.

- [15] Tanaka, K.; Ajiki, K. Phosphine-free cationic rhodium(I) complex-catalyzed disulfide exchange reaction: convenient synthesis of unsymmetrical disulfides. *Tetrahedron Letters* **2004**, *45*, 5677-5679.
- [16] Kiyoshi T.; Xing C.; Fumio Y. Oxidation of thiol with 5-arylidene-1,3-dimethylbarbituric acid: application to synthesis of unsymmetrical disulfide. *Tetrahedron*, **1988**, *11*, 3241-3249.
- [17] Wu, Z.; Pratt, D. A. Radical Substitution Provides a Unique Route to Disulfides. *J. Am. Chem. Soc.* **2020**, *142*, 10284-10290.
- [18] Xiao, X.; Feng, M.; Jiang, X. New Design of a Disulfurating Reagent: Facile and Straightforward Pathway to Unsymmetrical Disulfanes by Copper-Catalyzed Oxidative Cross-Coupling. *Angew. Chem. Int. Ed.* **2016**, *55*, 14121-14125.
- [19] Zou, J.; Chen, J.; Shi, T.; Hou, Y.; Cao, F.; Wang, Y. Phthalimide-Carried Disulfur Transfer To Synthesize Unsymmetrical Disulfanes via Copper Catalysis. *ACS Catal.* **2019**, *9*, 11426-11430.
- [20] Wang, Y.; Deng, J.; Chen, J.; Cao, F.; Hou, Y.; Yang, Y. Dechalcogenization of Aryl Dichalcogenides to Synthesize Aryl Chalcogenides via Copper Catalysis. *ACS Catal.* **2020**, *10*, 2707-2712.
- [21] Bizzini, L. D.; Zwick, P.; Mayor, M. Preparation of Unsymmetrical Disulfides from Thioacetates and Thiosulfonates. *Eur. J. Org. Chem.* **2019** 2019 6956-6960.
- [22] Dethlefsen, D. H.; Srivastava, A.; Dherange, B. D.; Kumar, B. V. Unsymmetrical Disulfide Synthesis through Photoredox Catalysis. *Adv. Synth. Catal.* **2018**, *360*, 3020-3025.
- [23] Detty, M. R. Mild reductions of oxides of the Group 6a elements sulfur, selenium, and tellurium with (phenylseleno)trimethylsilane. *J. Org. Chem.* **1979**, *44*, 4528-4531.
- [24] Li, H.; Tao, C.; Xie, Y.; Wang, A.; Chang, Y.; Yu, H. Transformation of arylboronic acids with sodium thiosulfate into organodisulfides catalyzed by a recyclable polyoxometalate-based Cr catalyst. *Green Chem.* **2021**, *23*, 6059-6064.
- [25] Chen, J.; Tang, Z.; Qiu, R.; He, Y.; Wang X.,; Li, N. Cesium-Catalyzed Regioselective Synthesis of Trisubstituted Heteroatom Alkenes: A New Strategy for the Preparation of Functional Alkenes. *Org. Lett.* **2015**, *17*, 2162-2165.

8. ^1H , ^{13}C and ^{19}F NMR Spectra of Products

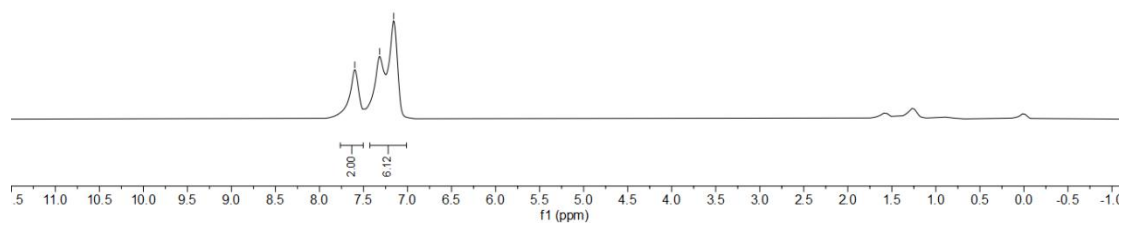


7.599
7.317
7.157

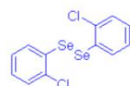


4b

CDCl₃, 500Hz

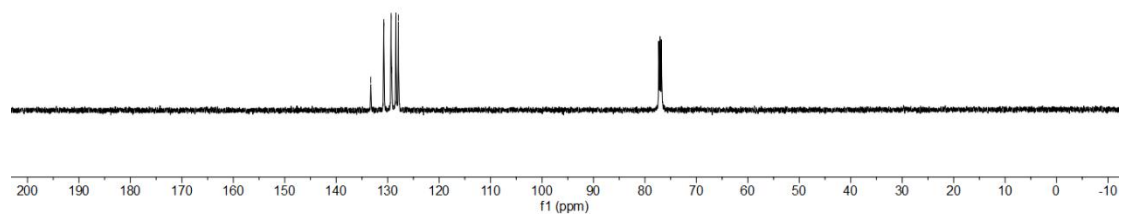


133.3
130.7
129.3
128.4
127.9

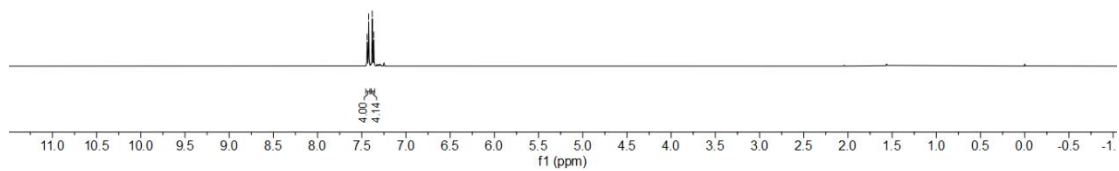
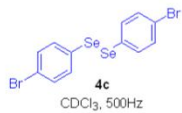


4b

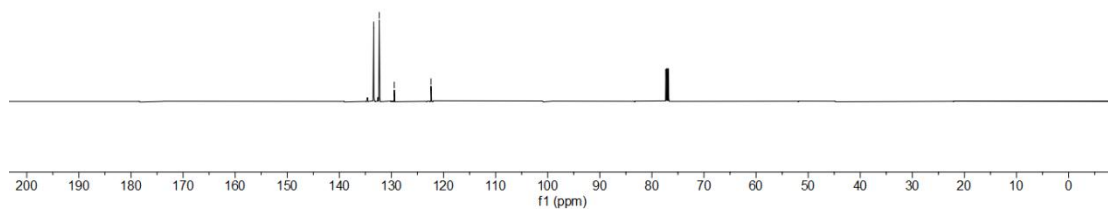
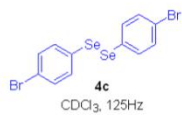
CDCl₃, 125Hz



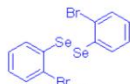
7.439
7.382
7.377
7.365



133.4
132.3
128.5
122.4

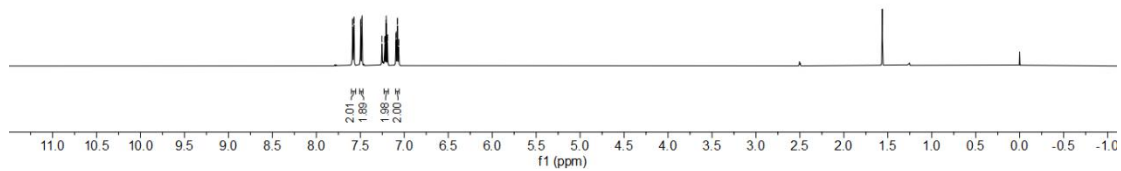


7.688
7.676
7.570
7.498
7.486
7.483
7.254
7.223
7.220
7.205
7.192
7.190
7.099
7.080
7.077
7.065
7.062

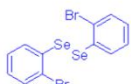


4d

CDCl₃, 500Hz

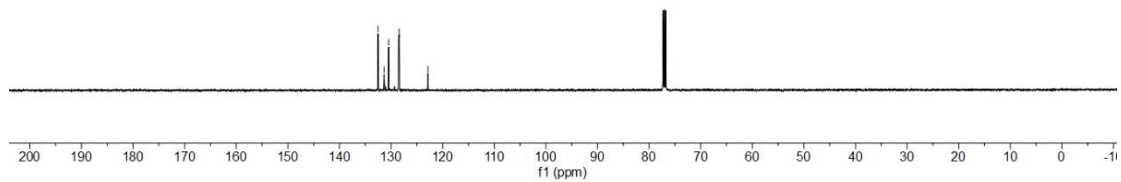


133.5
131.4
129.6
128.4
122.9

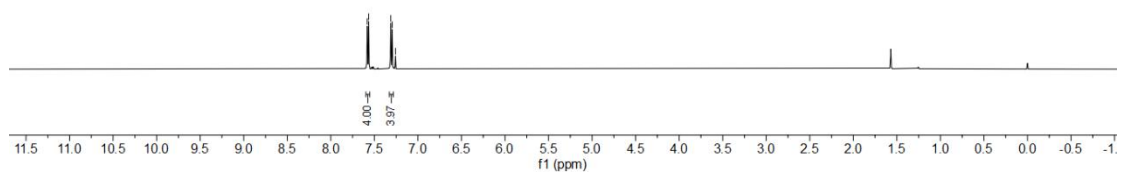
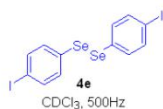


4d

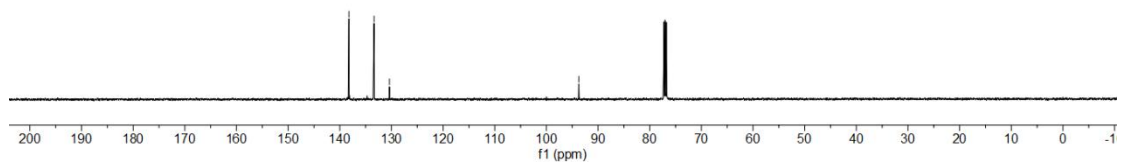
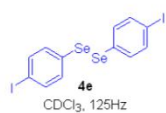
CDCl₃, 125Hz



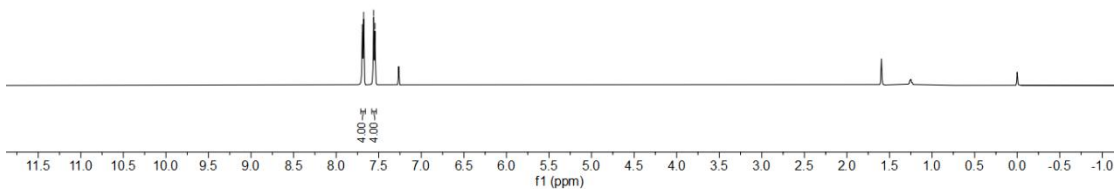
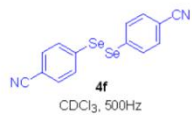
7.682
7.605
7.311
7.294
7.258



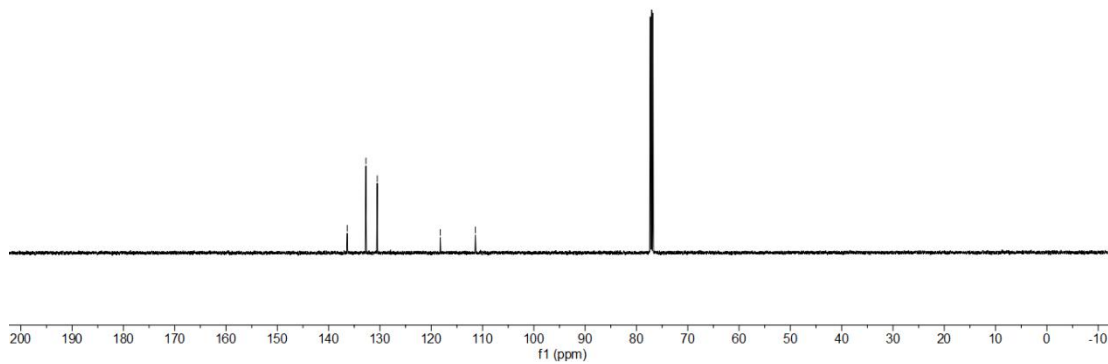
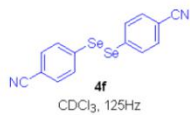
138.2
137.4
136.4
-88.7



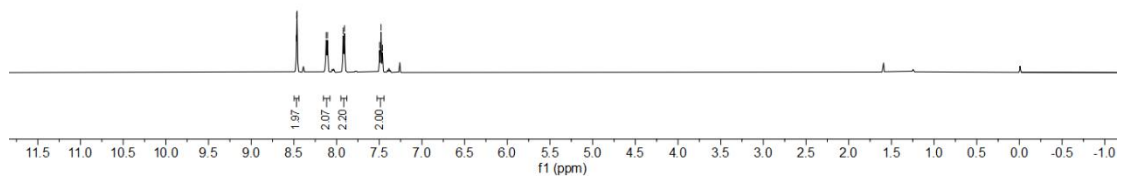
7.693
7.690
7.673
7.561
7.544



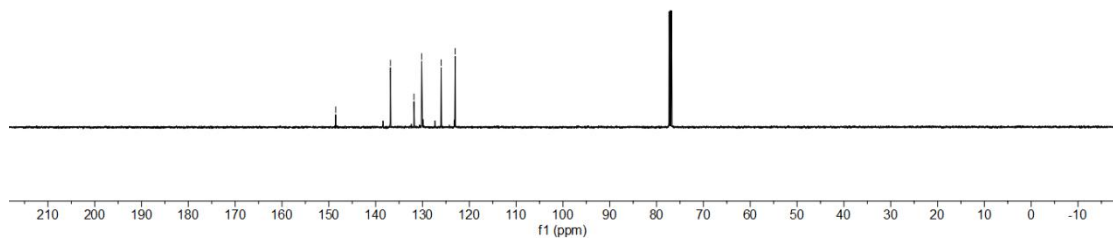
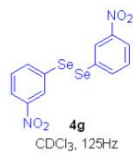
138.4
137.7
130.5
118.2
111.4



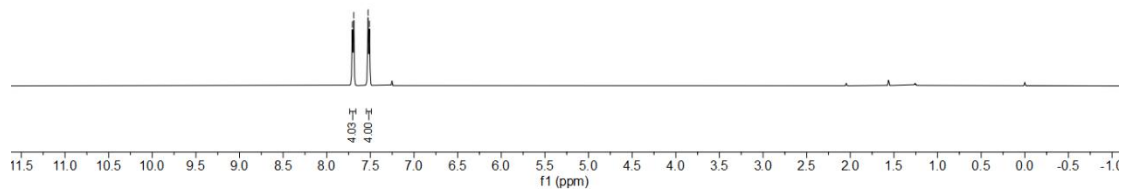
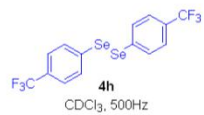
8.470
8.462
8.122
8.106
7.806
7.485
7.479
7.463



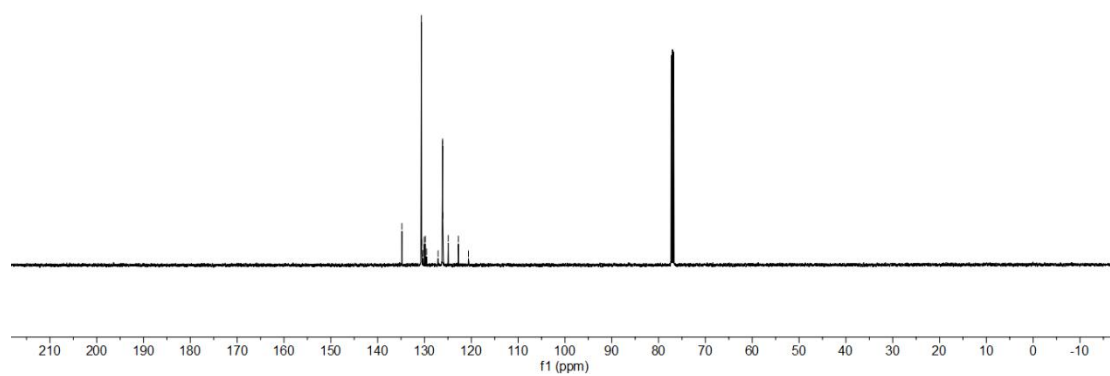
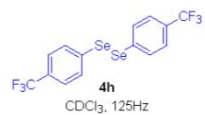
148.5
136.8
131.8
129.2
123.0
123.0



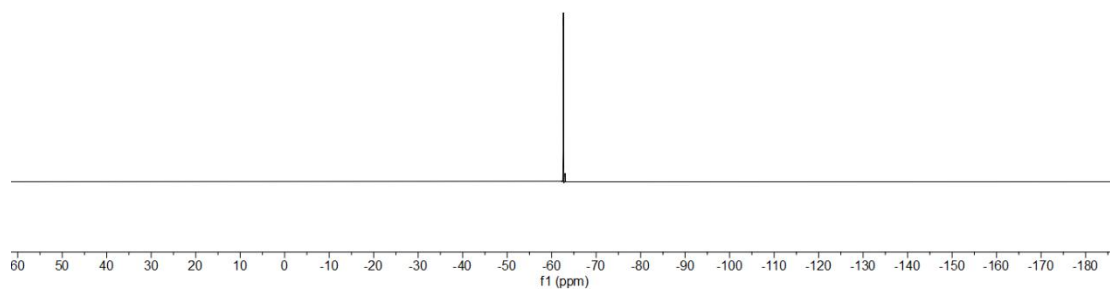
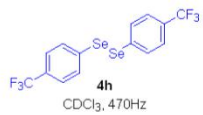
7.707
7.694
7.526
7.510



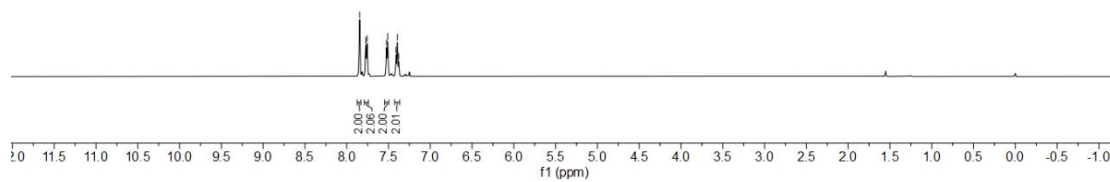
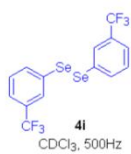
134.9
133.6
133.0
130.3
129.8
129.8
129.1
126.2
126.1
126.1
124.9
122.8
120.6



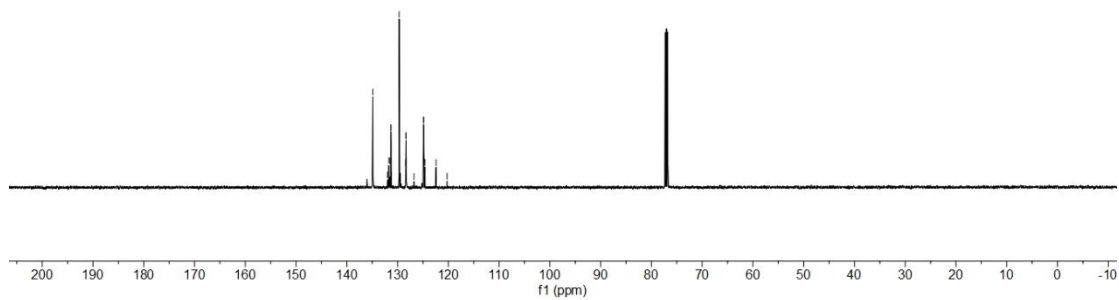
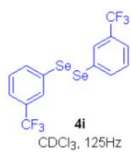
9.23



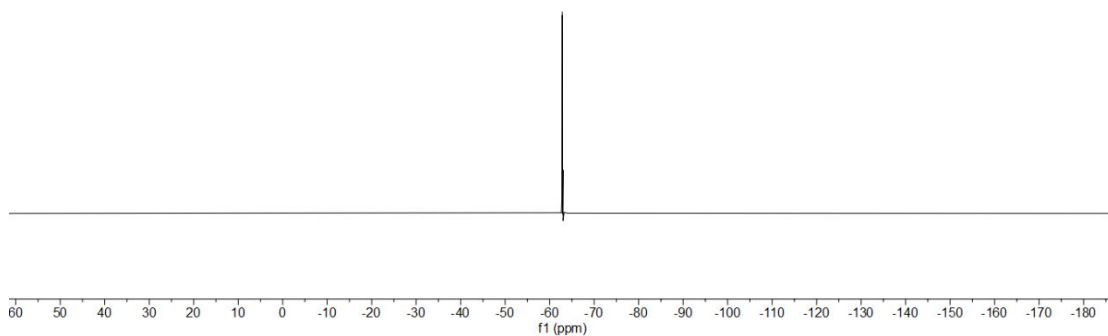
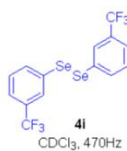
7.846
7.772
7.728
7.524
7.408
7.398
7.378



134.9
132.0
131.7
131.5
131.3
131.2
129.7
128.4
128.3
128.3
128.8
128.8
124.9
124.8
124.6
124.6
120.3

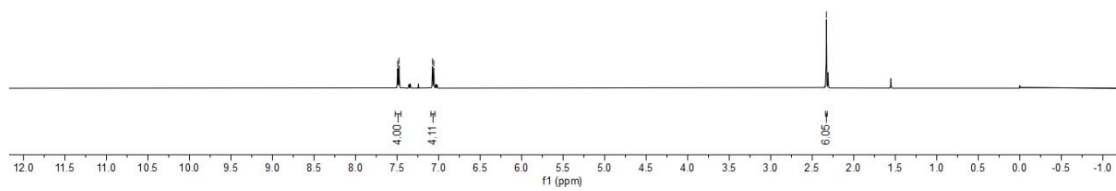
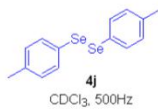


77.8



7.489
7.476
7.074
7.058

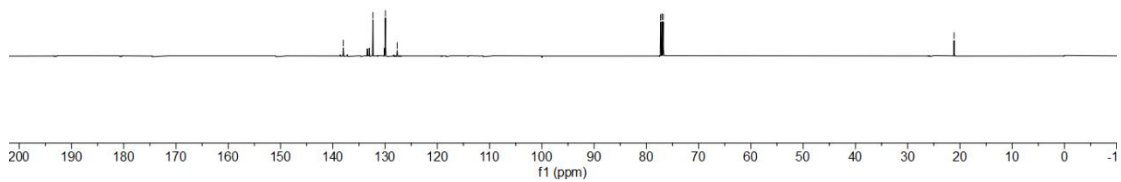
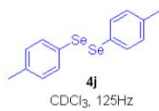
2.330

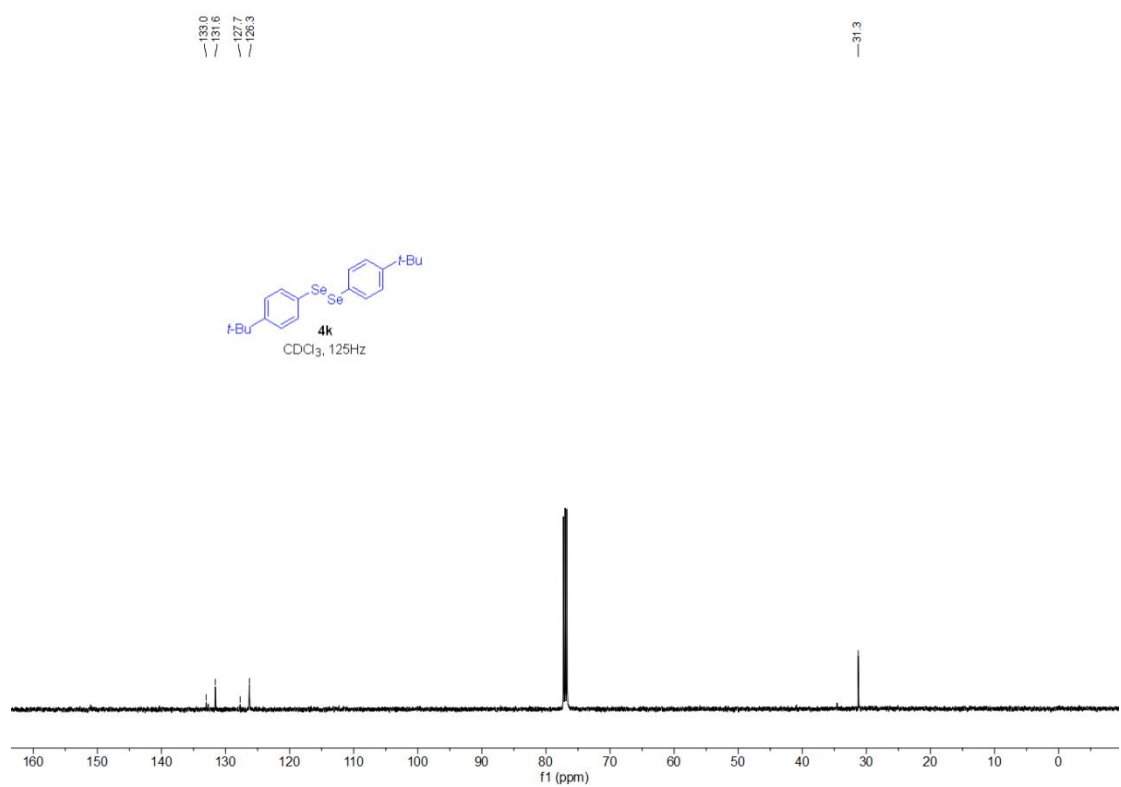
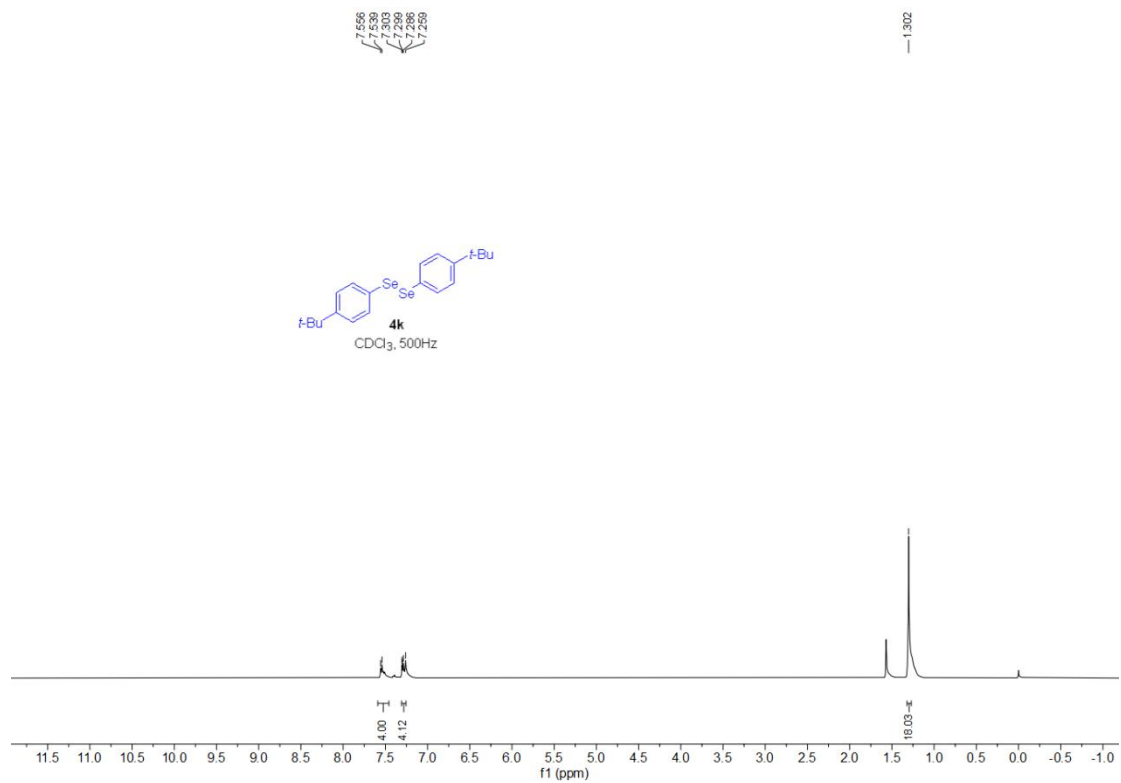


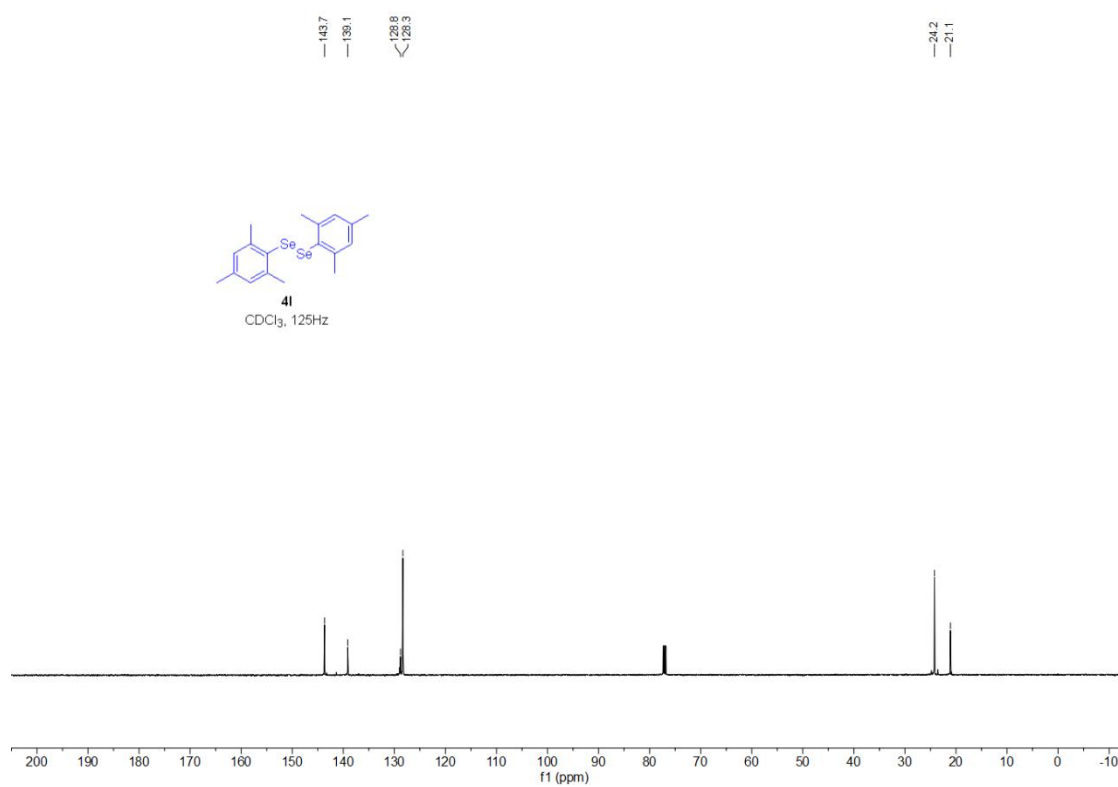
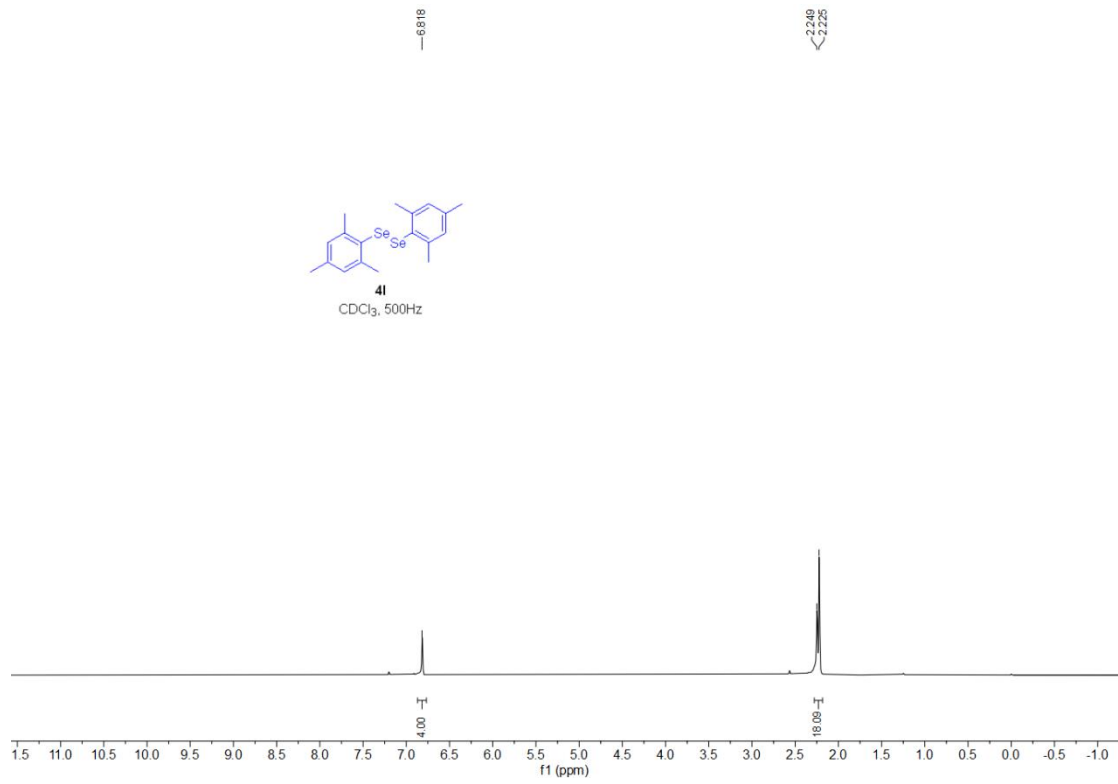
139.0
137.3
129.9
127.7

77.3
77.0
76.8

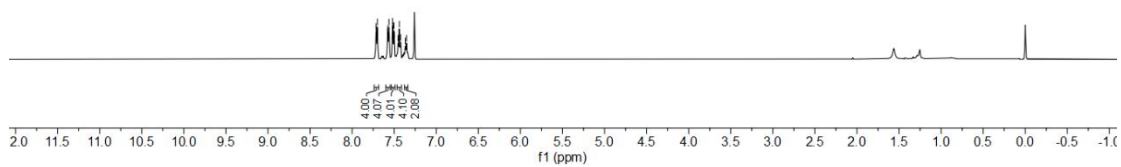
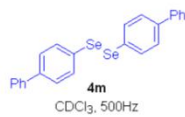
21.1



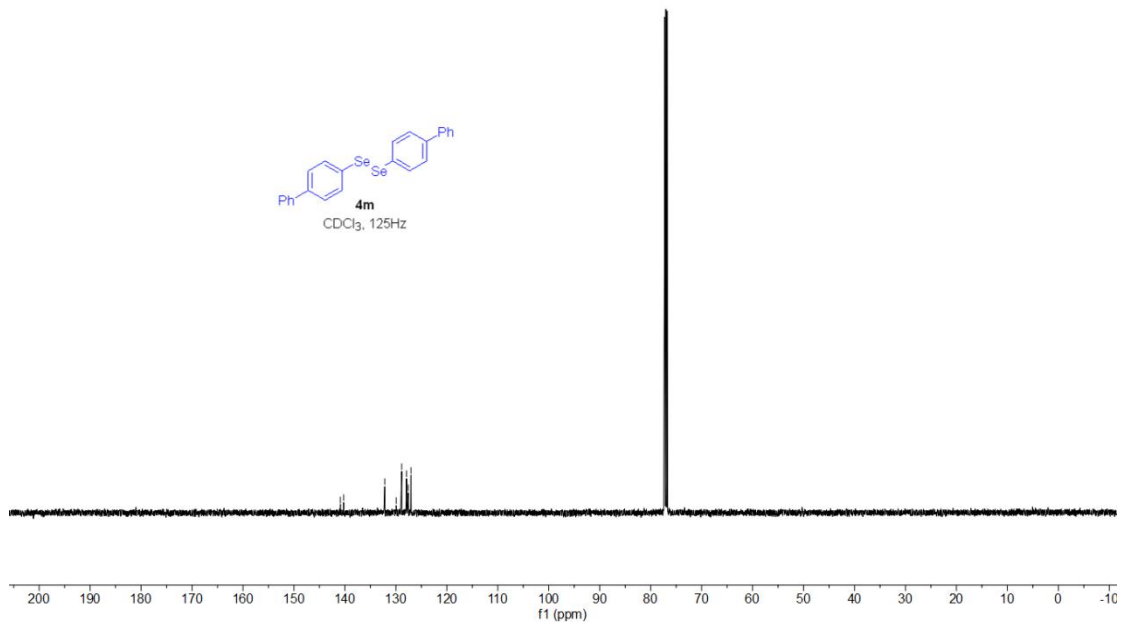
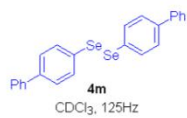


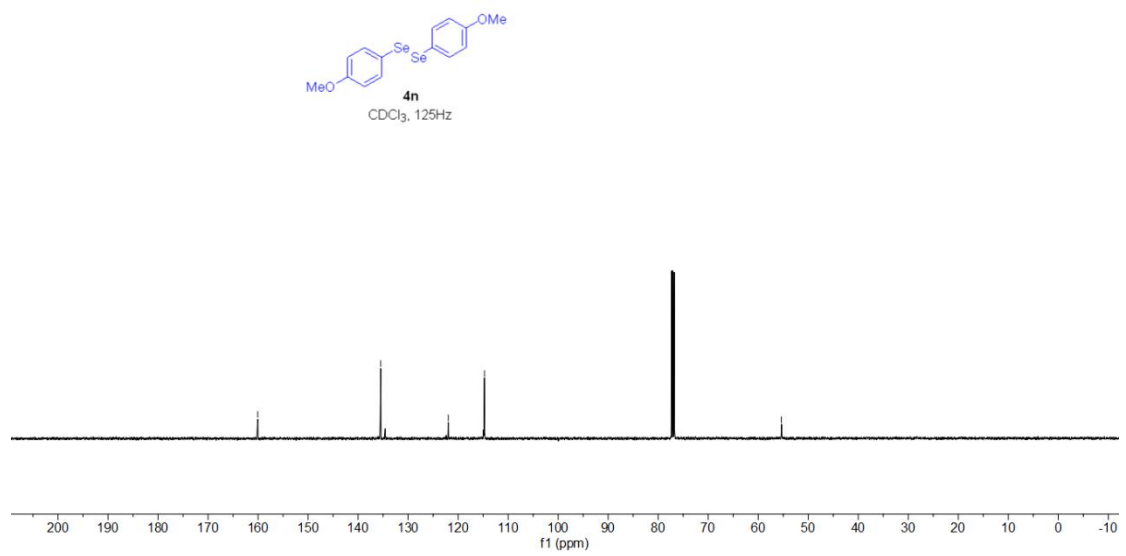
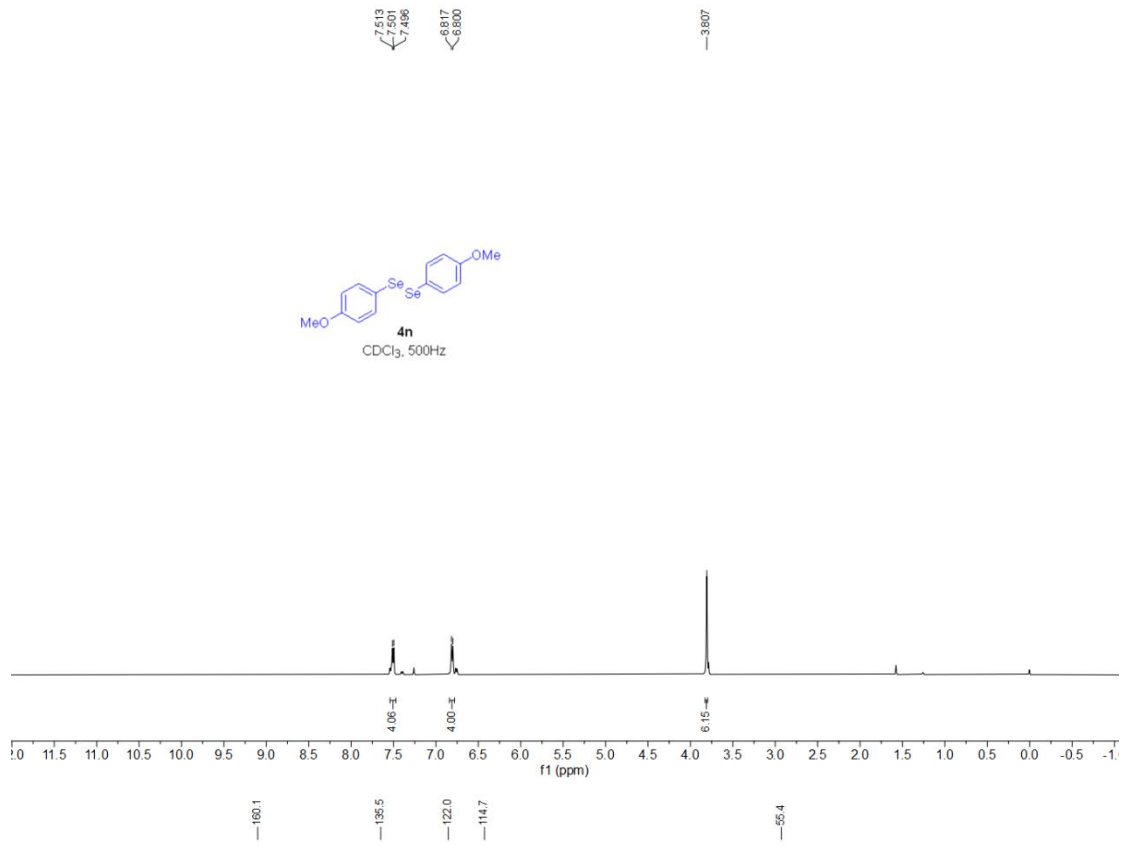


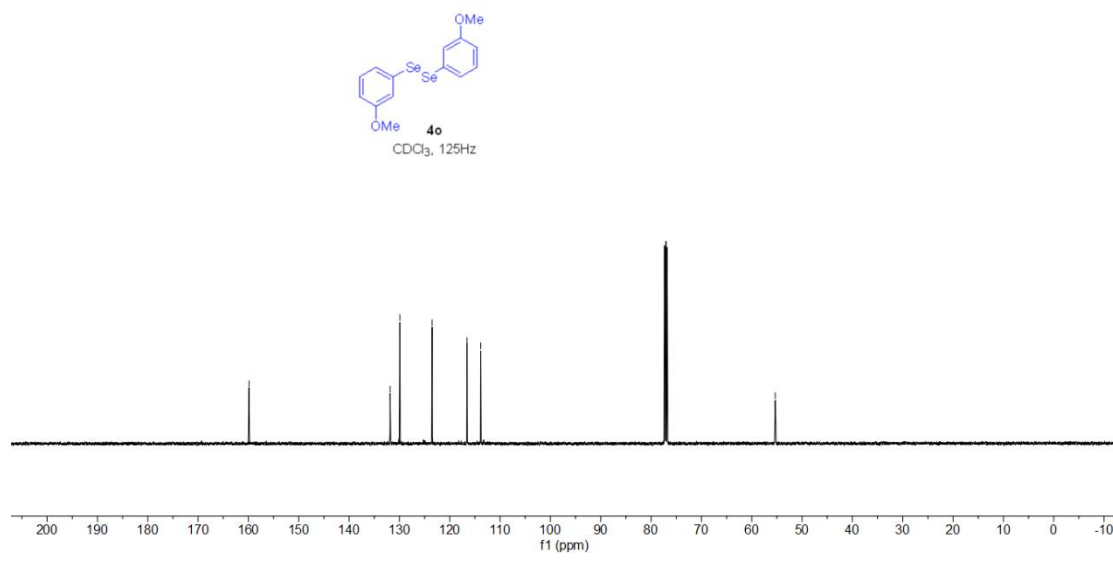
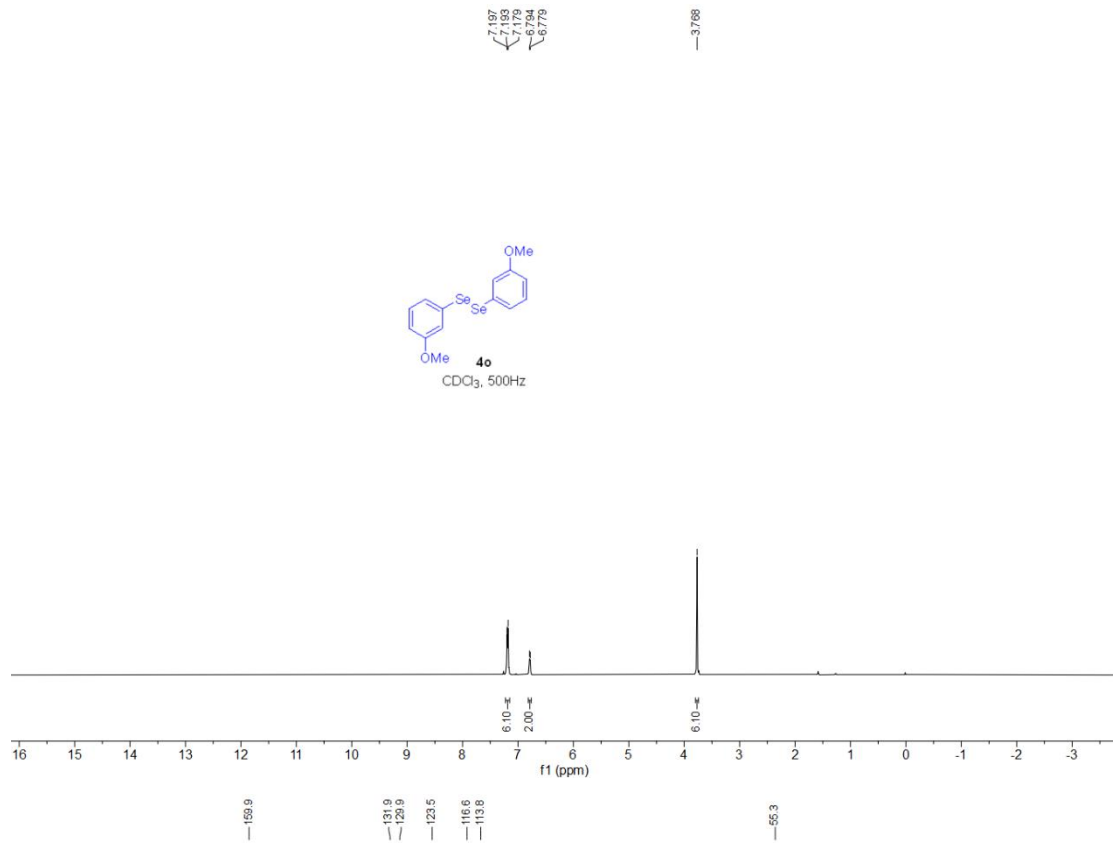
7.716
7.710
7.704
7.696
7.686
7.576
7.562
7.523
7.519
7.510
7.507
7.502
7.486
7.489
7.423
7.368
7.353



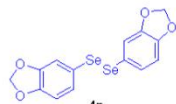
140.9
140.2
132.2
129.9
129.8
127.6
127.0





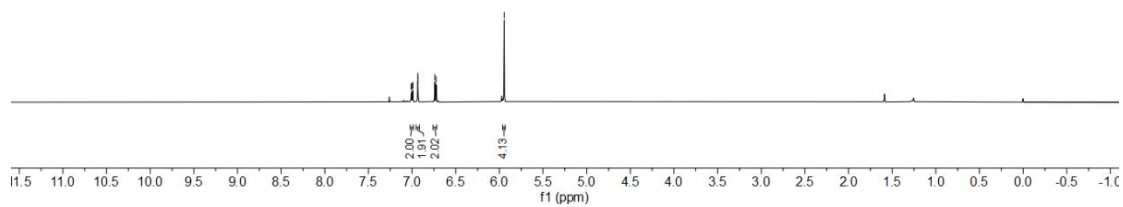


7.010
6.994
6.891
6.835
6.831
6.729
-5.944

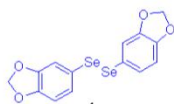


4p

CDCl₃, 500Hz

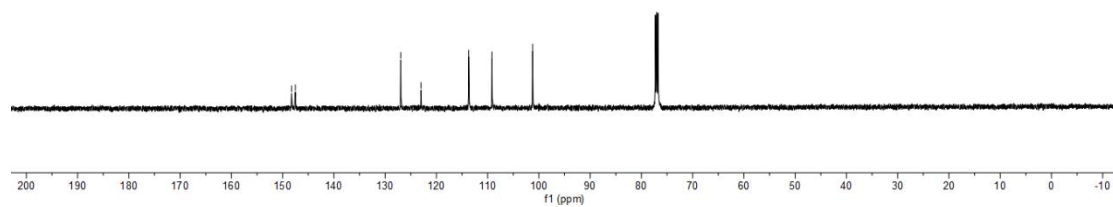


148.3
147.5
127.0
123.0
113.7
109.2
101.2

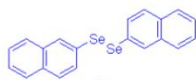


4p

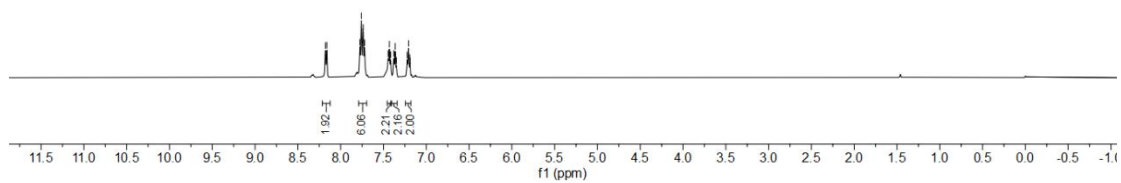
CDCl₃, 125Hz



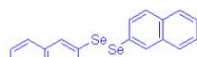
8.179
8.162
7.756
7.741
7.736
7.720
7.705
7.435
7.415
7.379
7.363
7.323
7.207
7.188
7.188



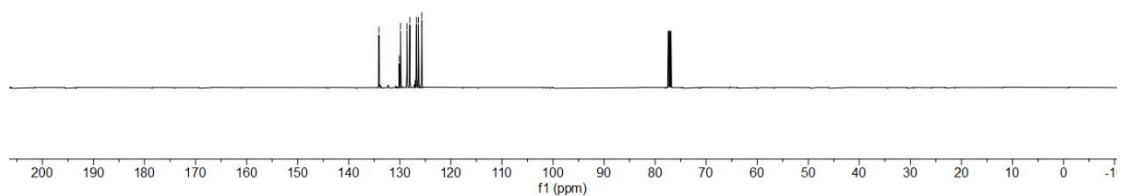
4q
CDCl₃, 500Hz



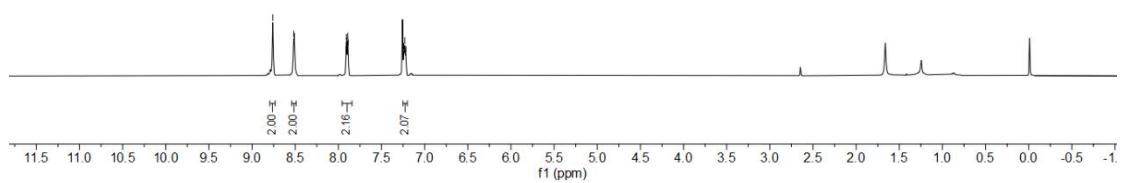
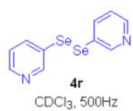
134.1
134.1
134.0
130.1
129.9
129.8
128.0
126.7
126.4
125.7



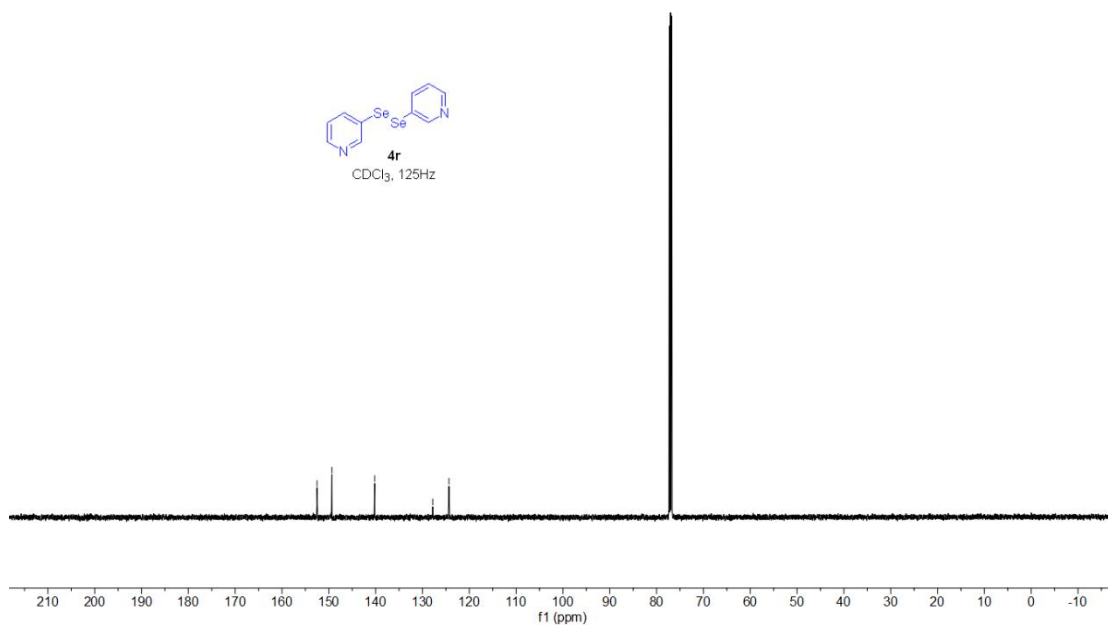
4q
CDCl₃, 125Hz

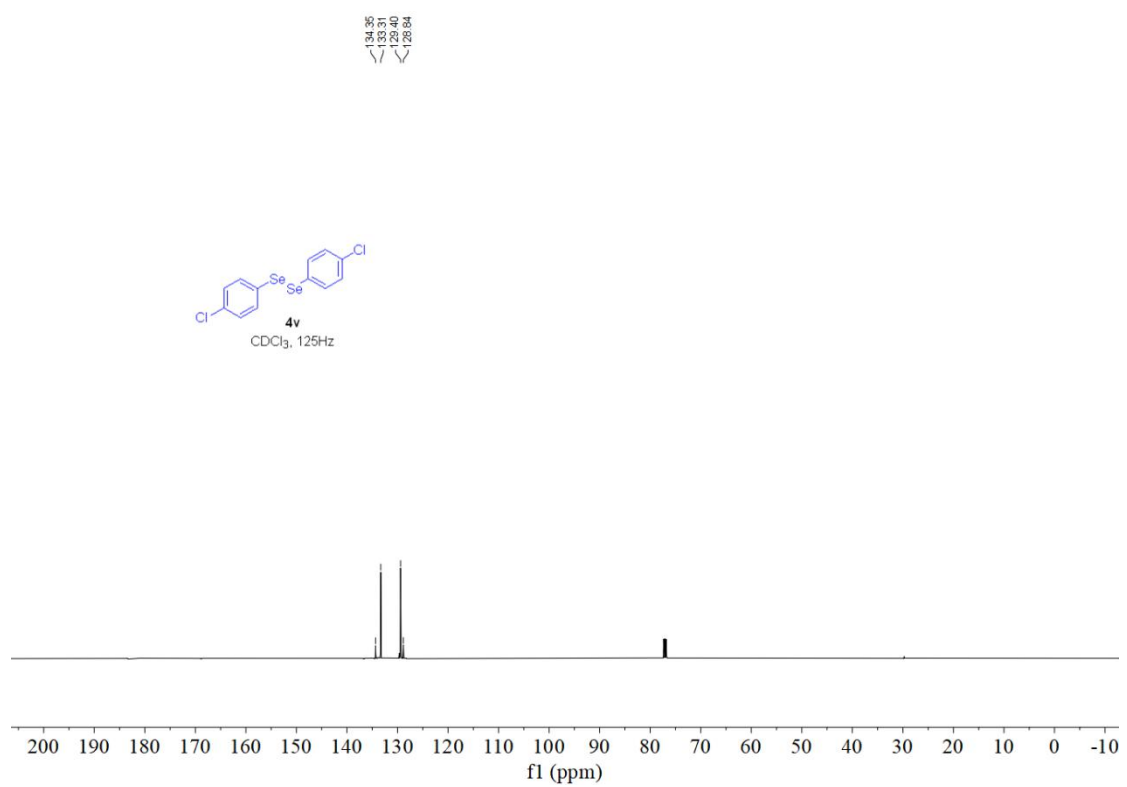
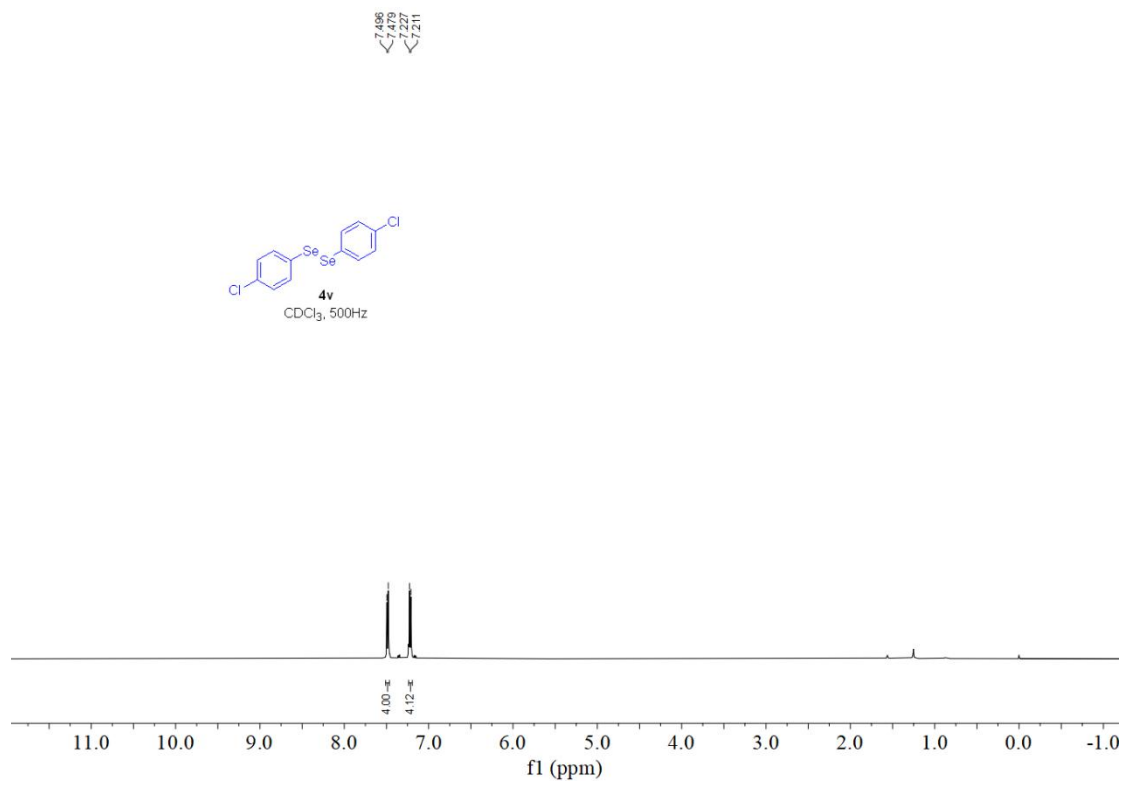


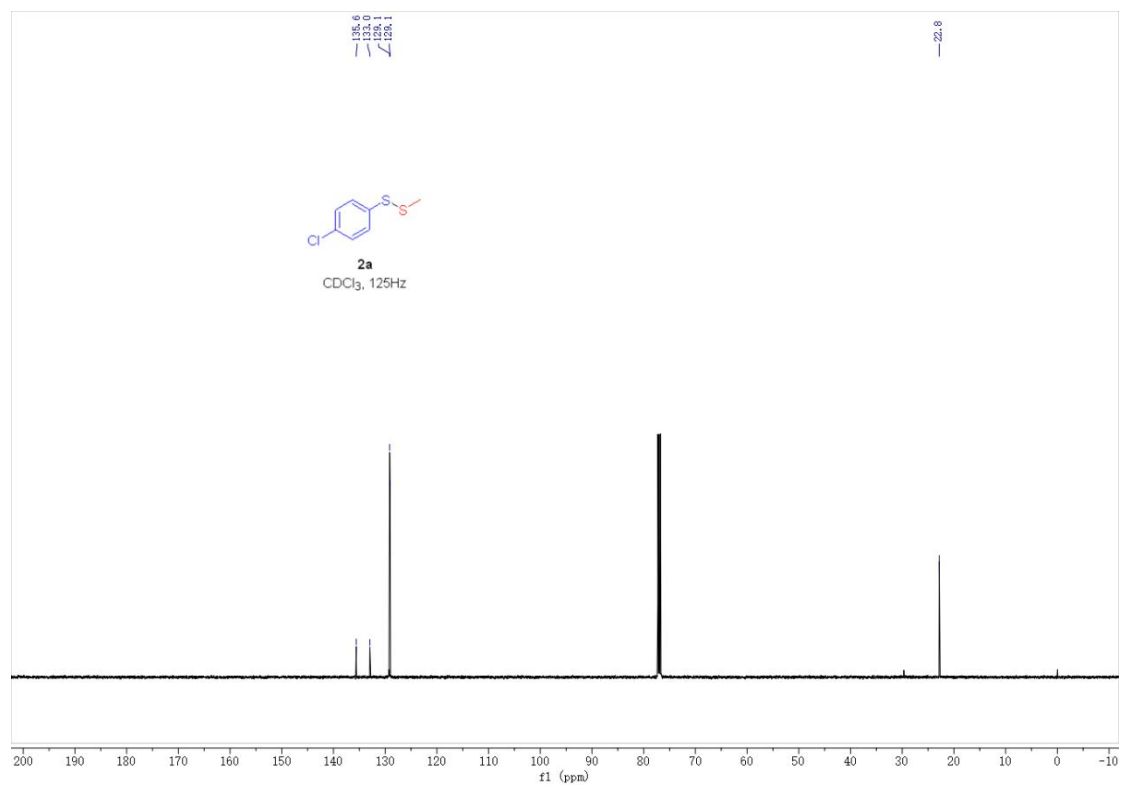
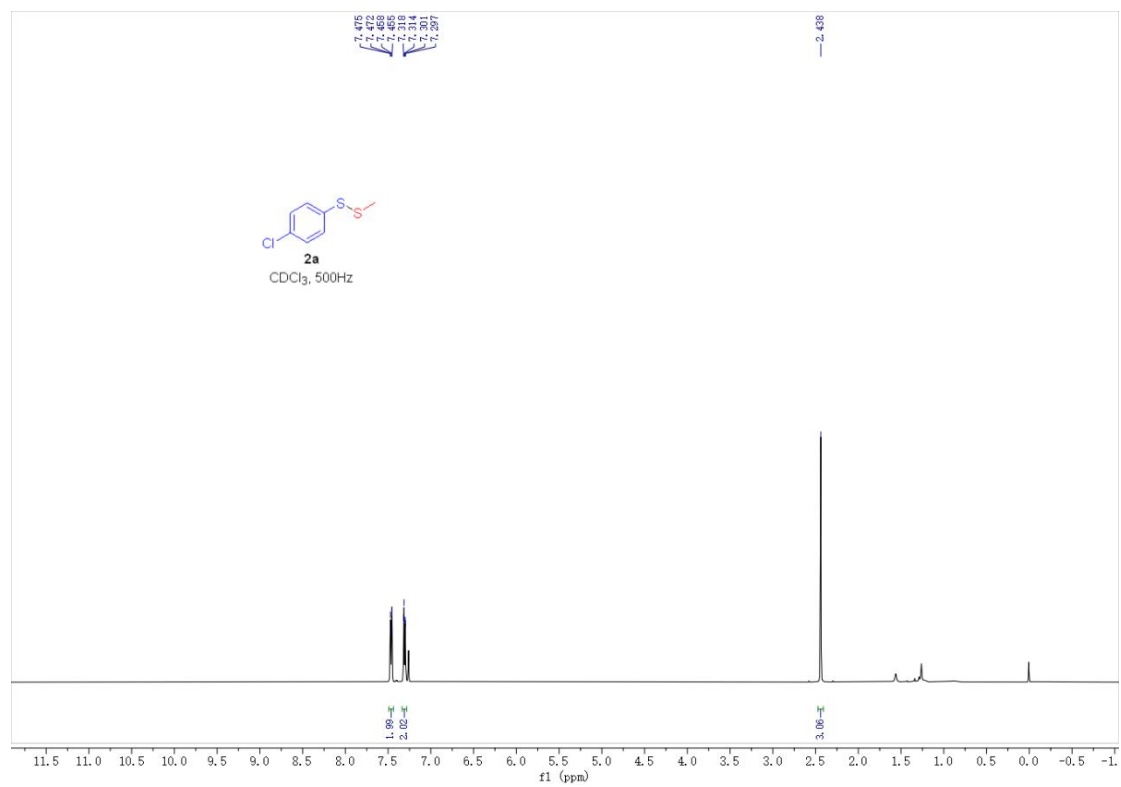
8.760
8.618
8.509
7.911
7.907
7.900
7.895
7.891
7.887
7.249
7.217

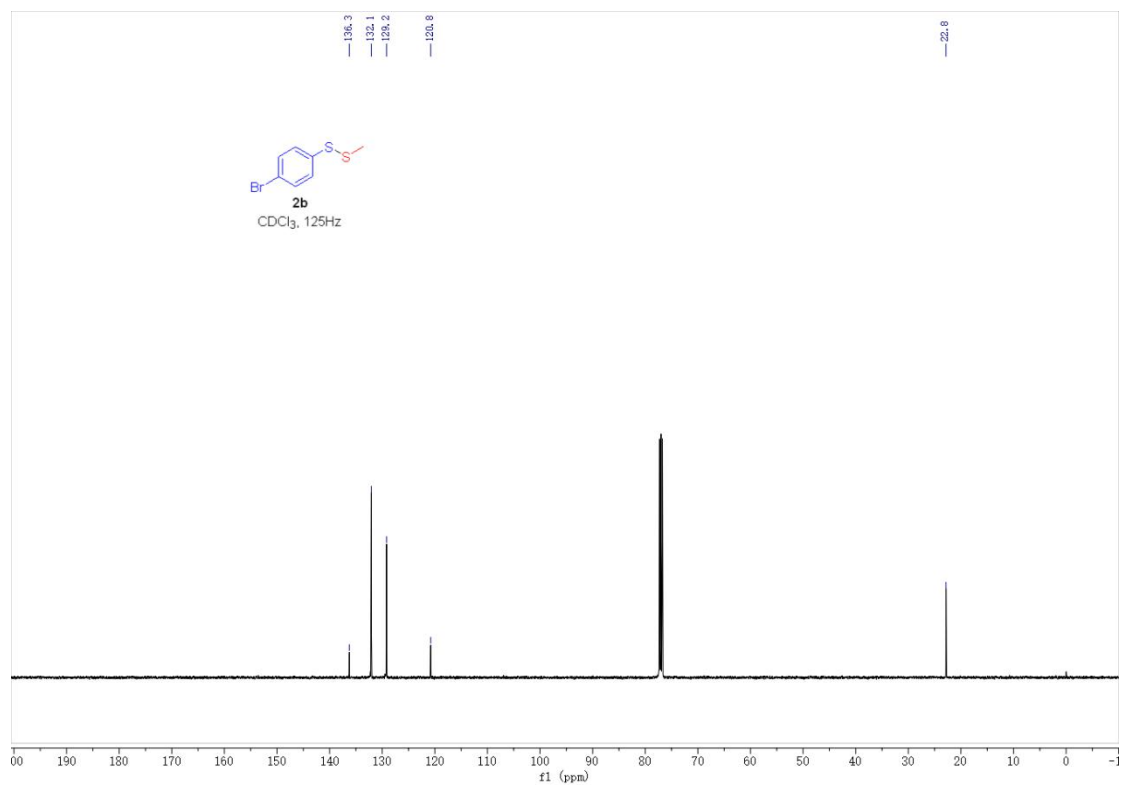
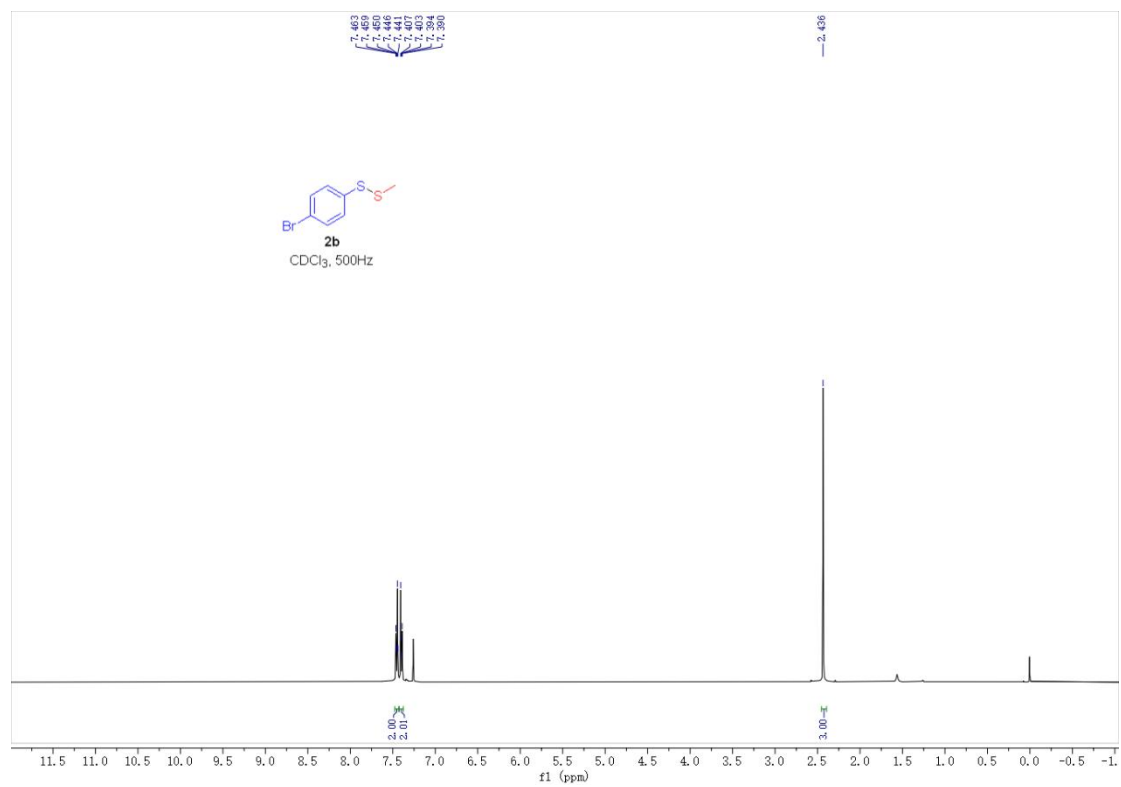


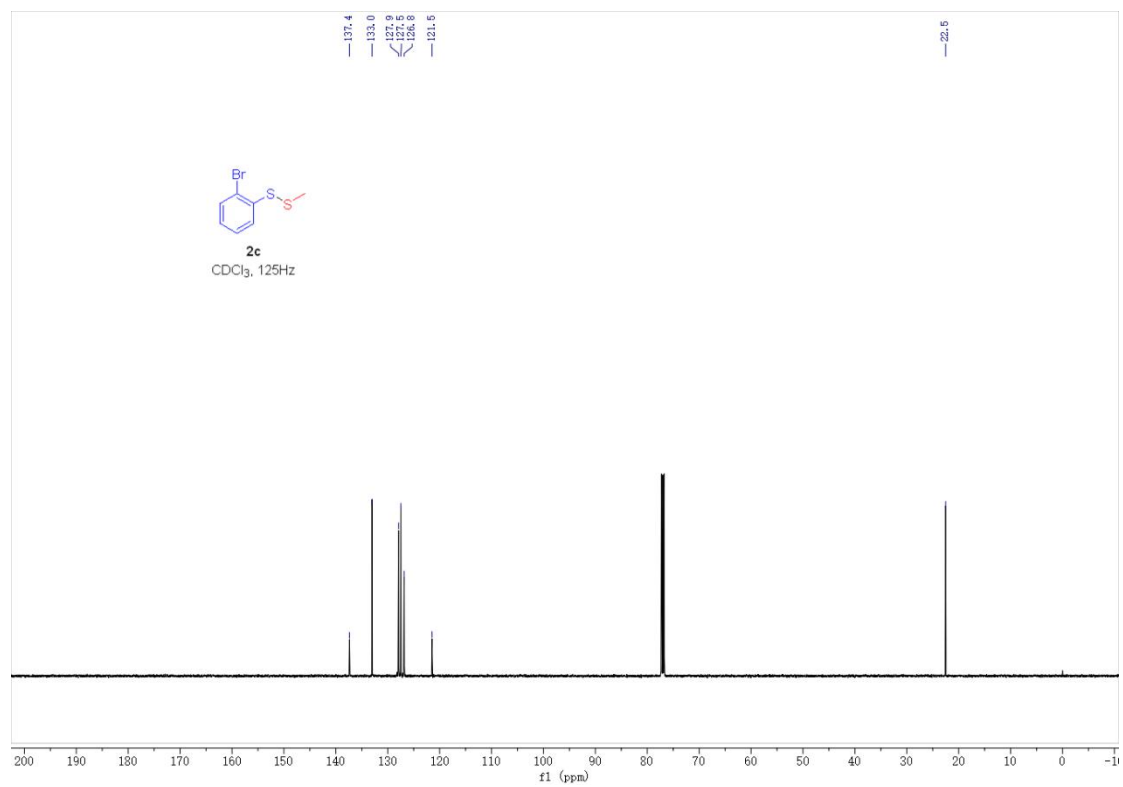
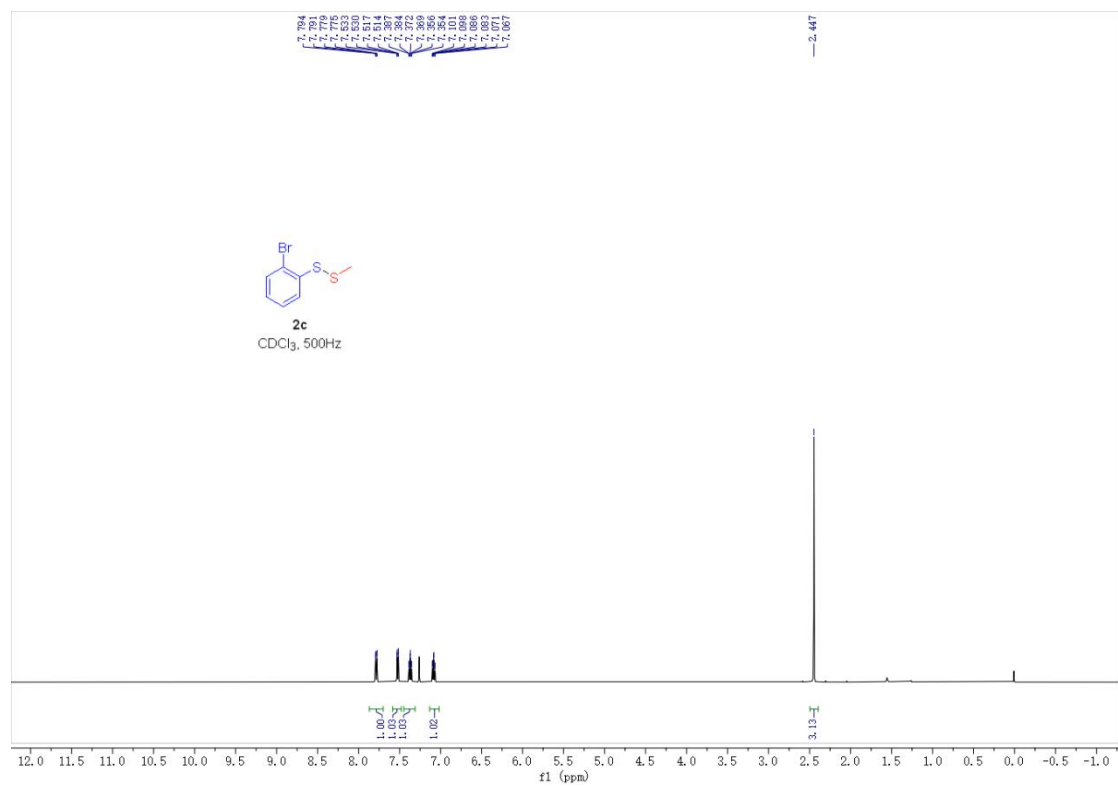
153.5
148.3
140.2
127.8
124.3

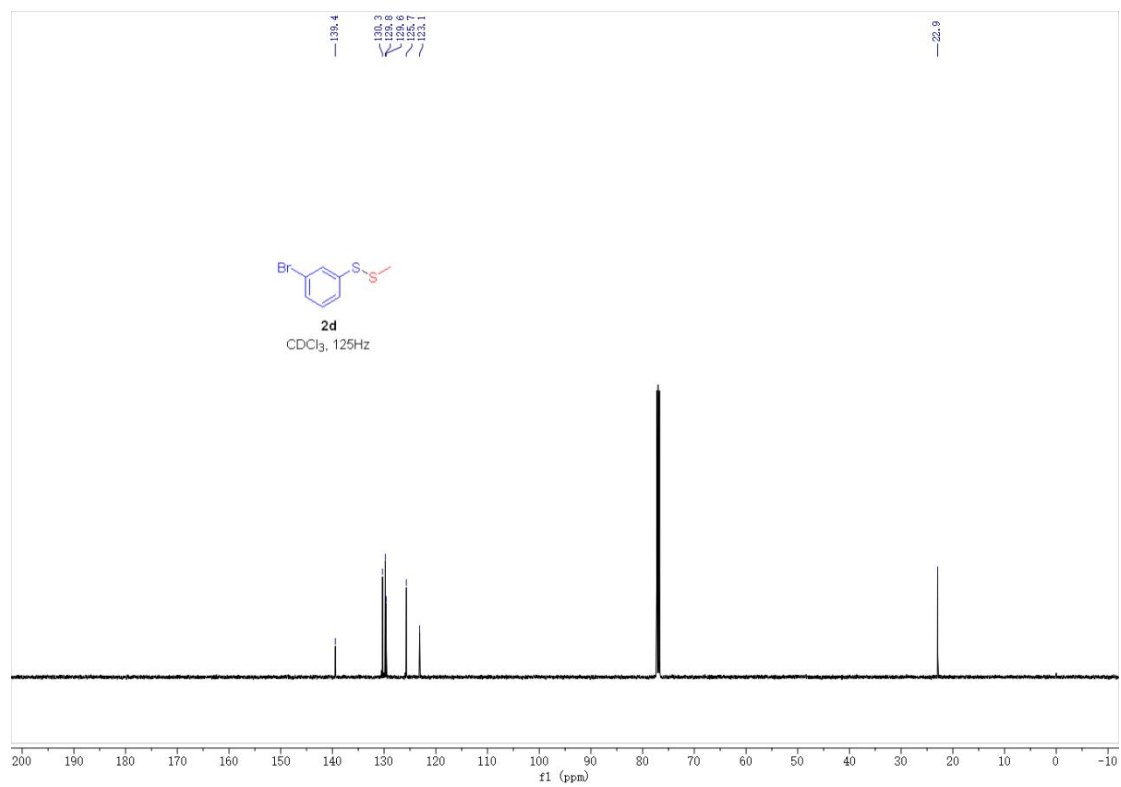
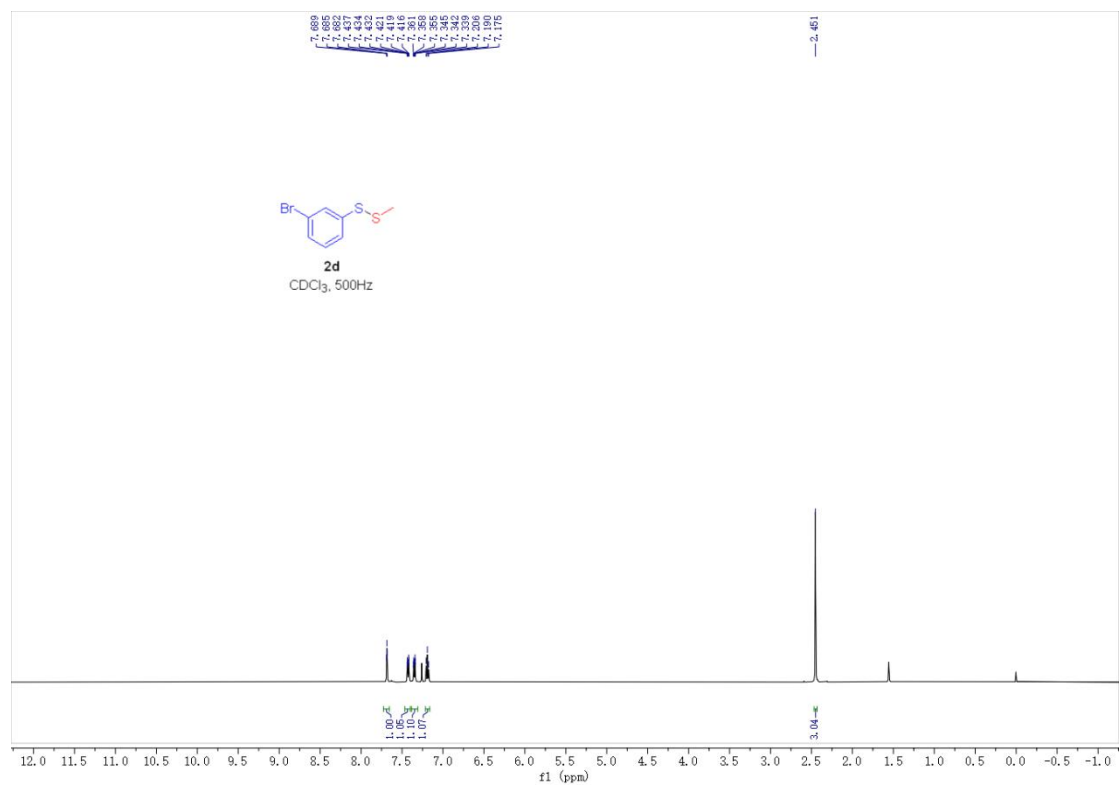


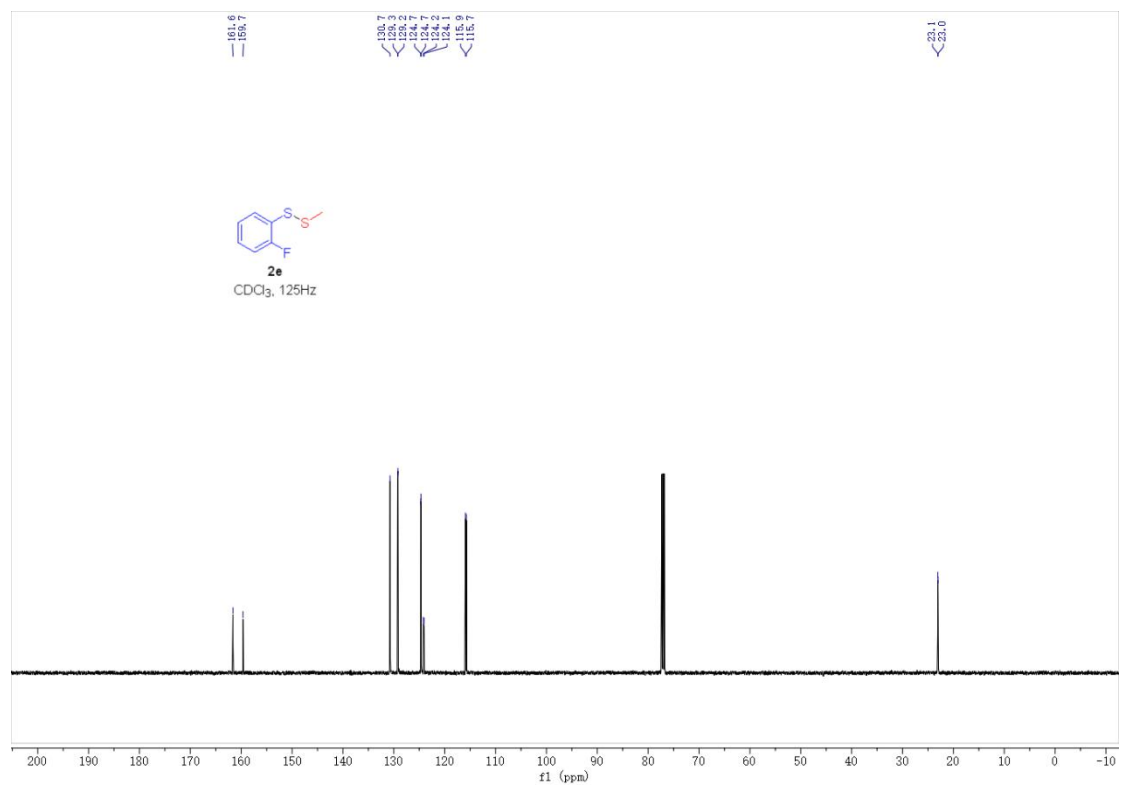
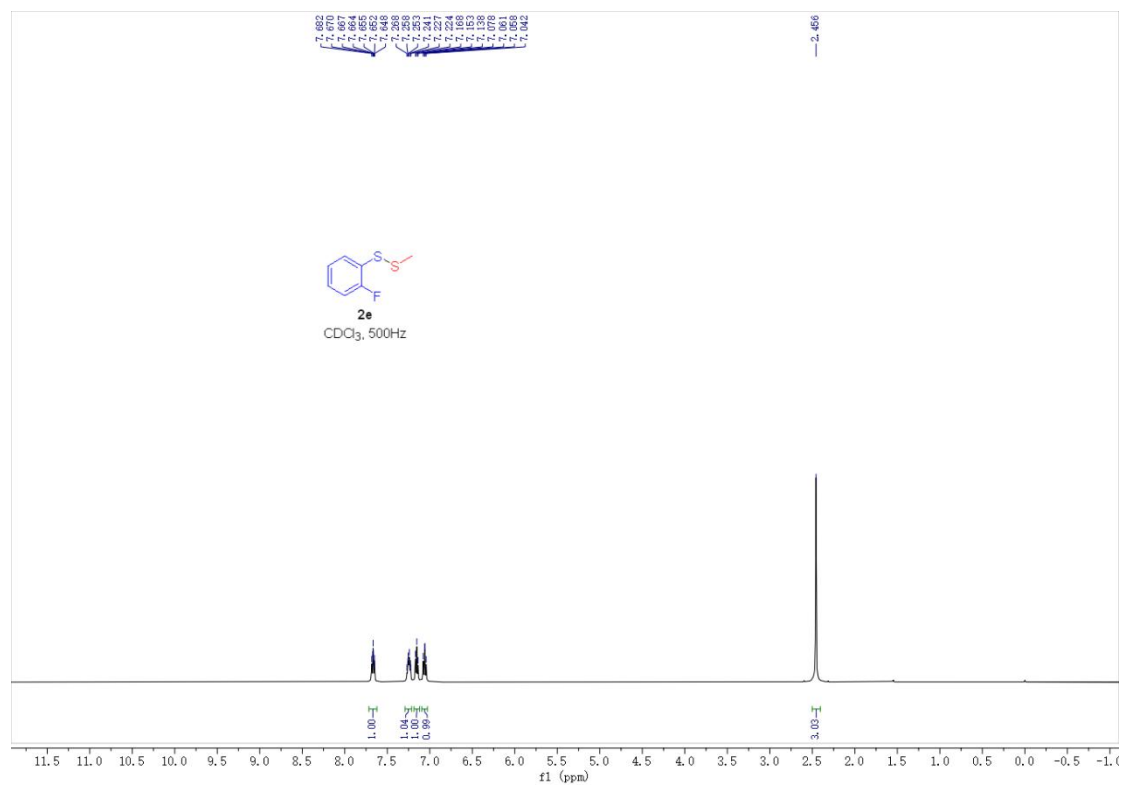


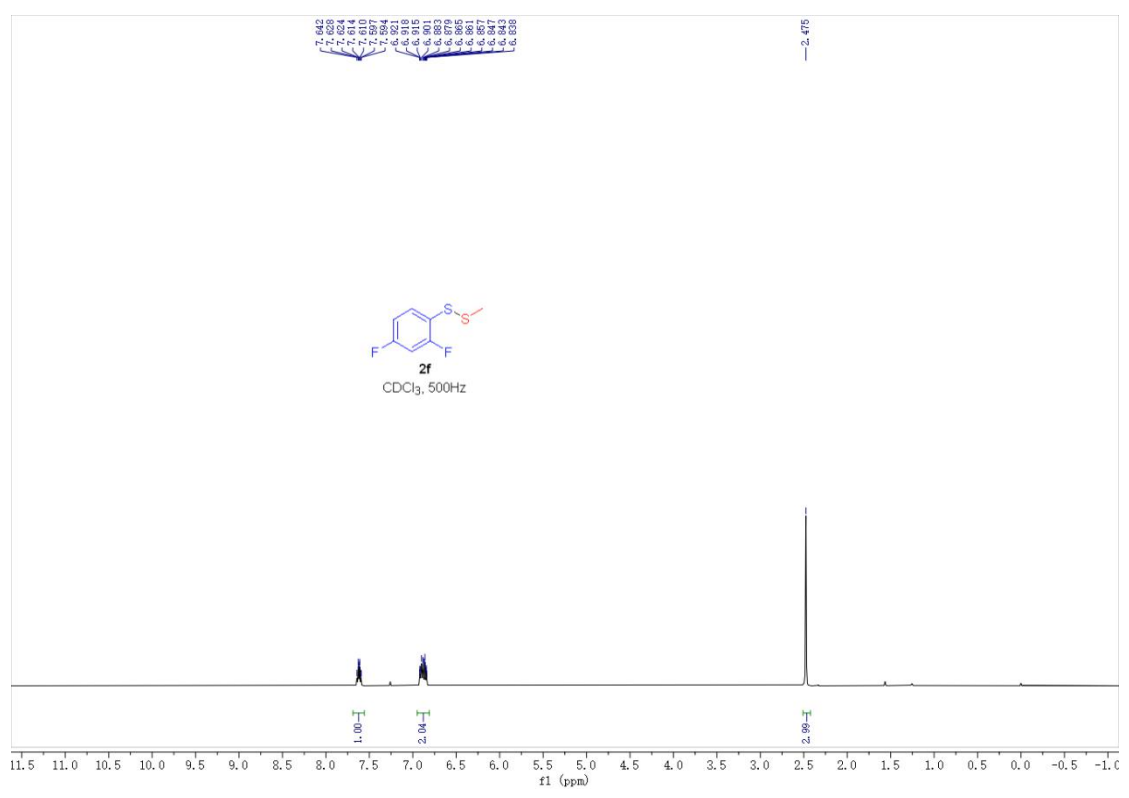
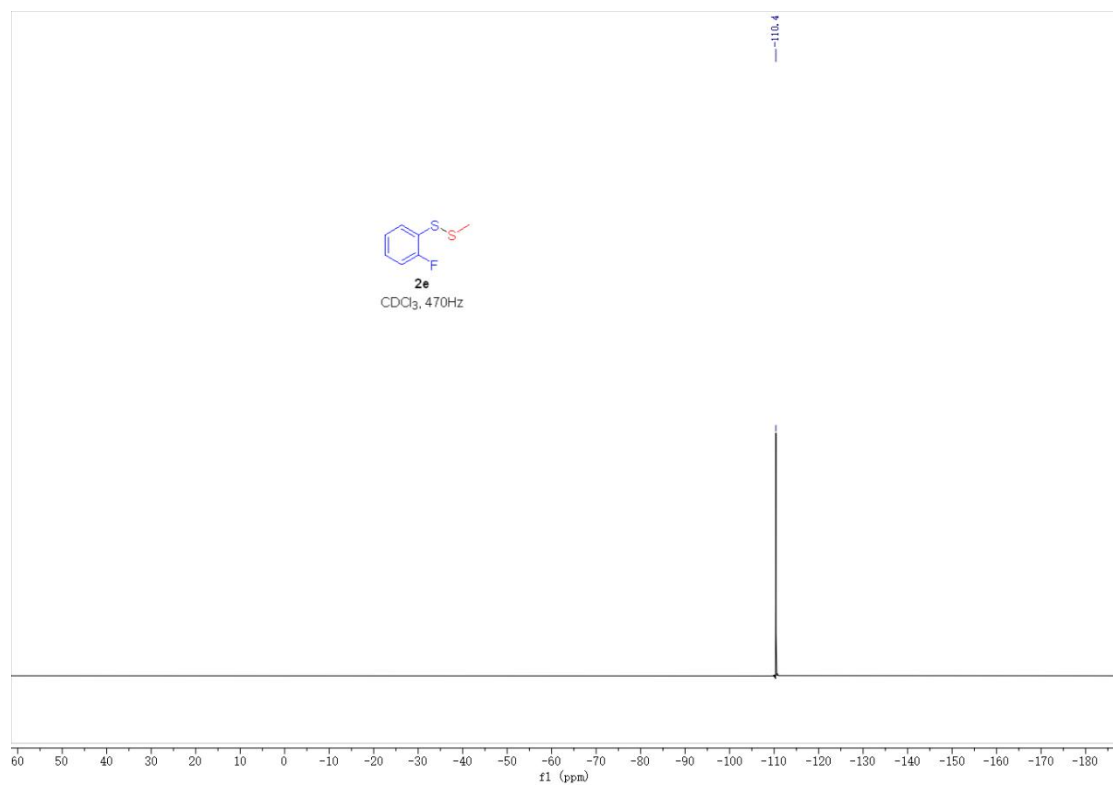


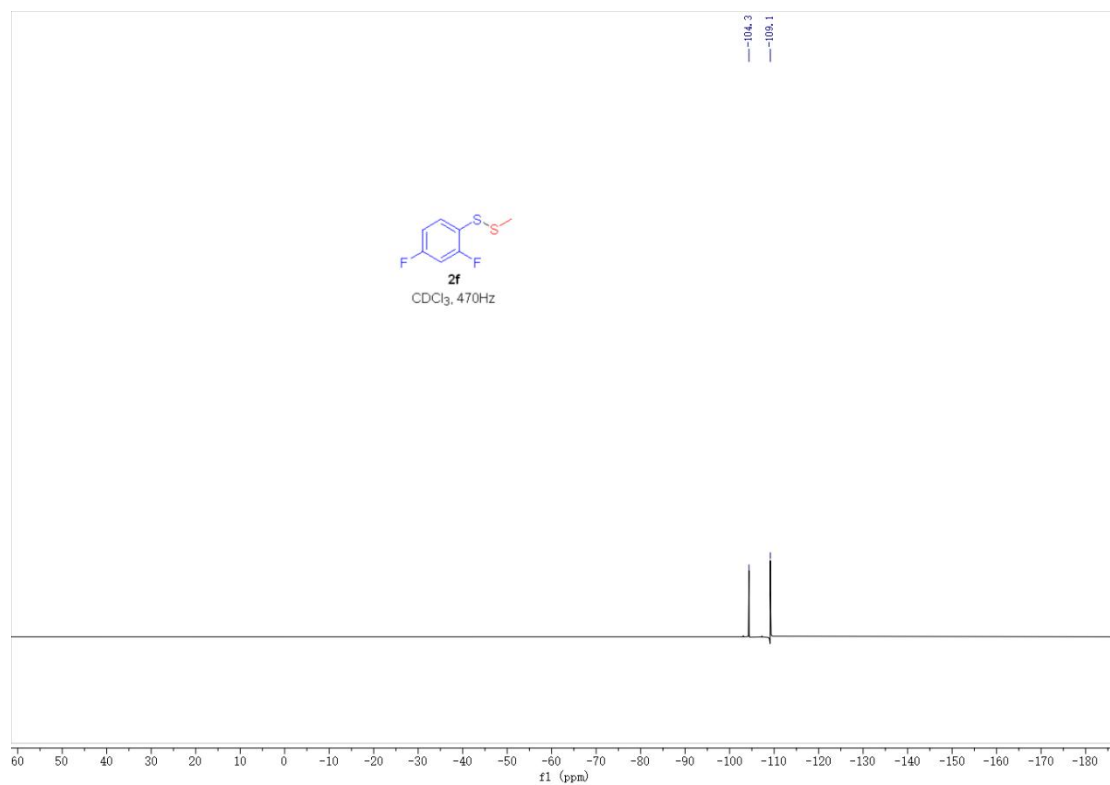
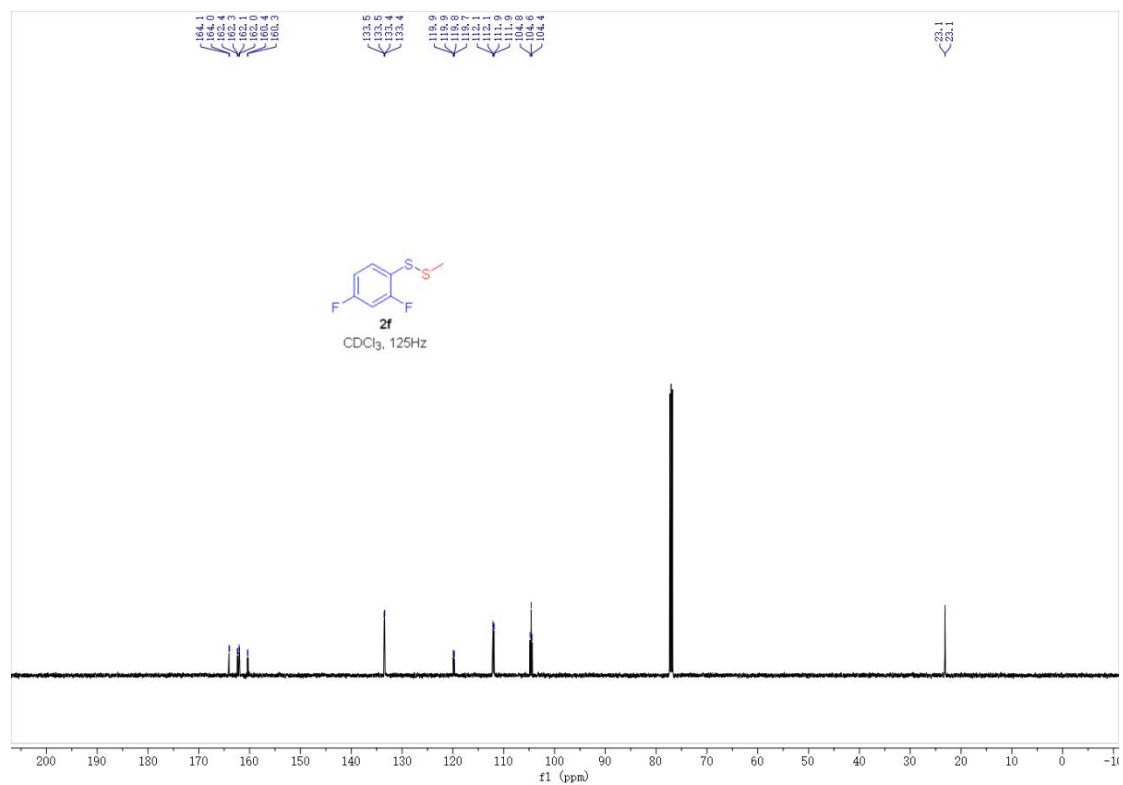


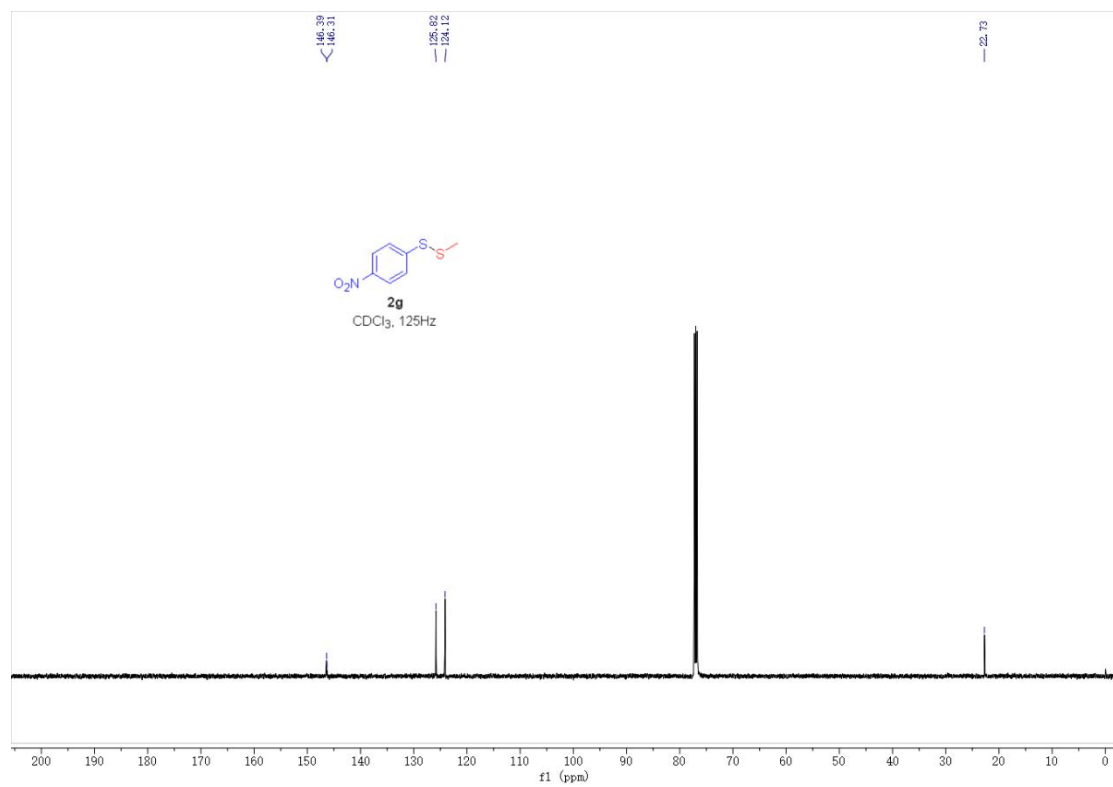
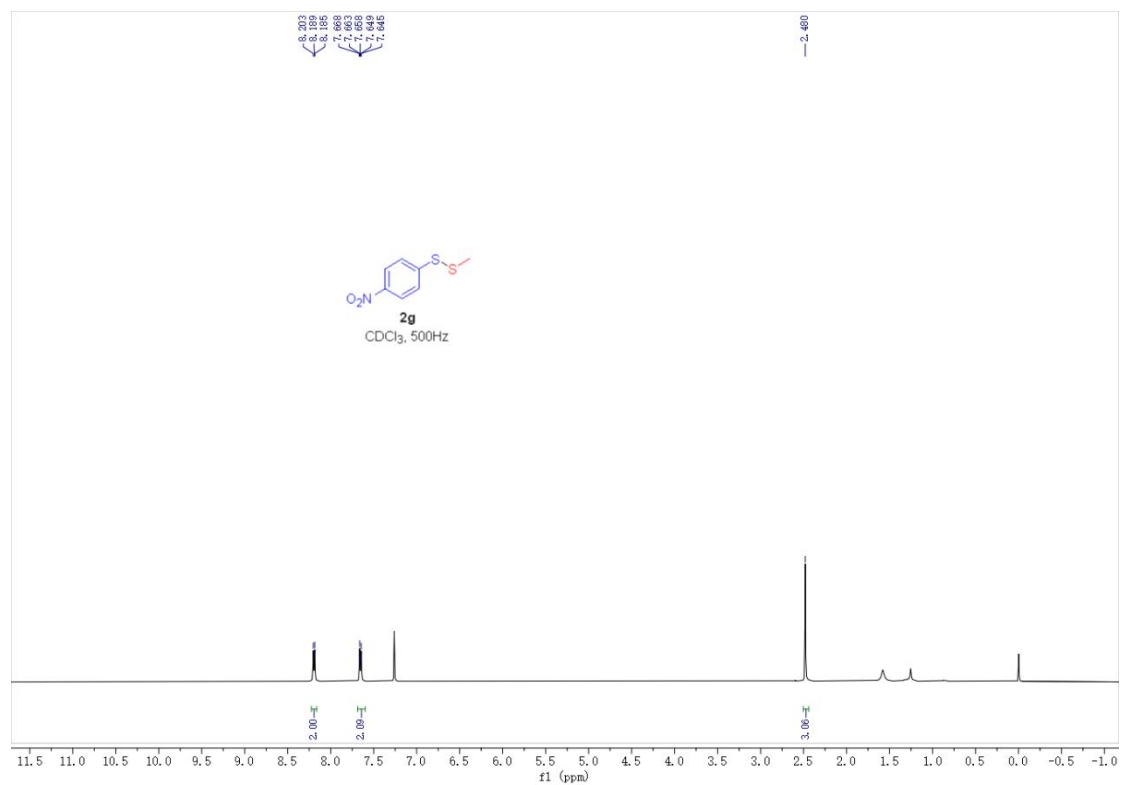


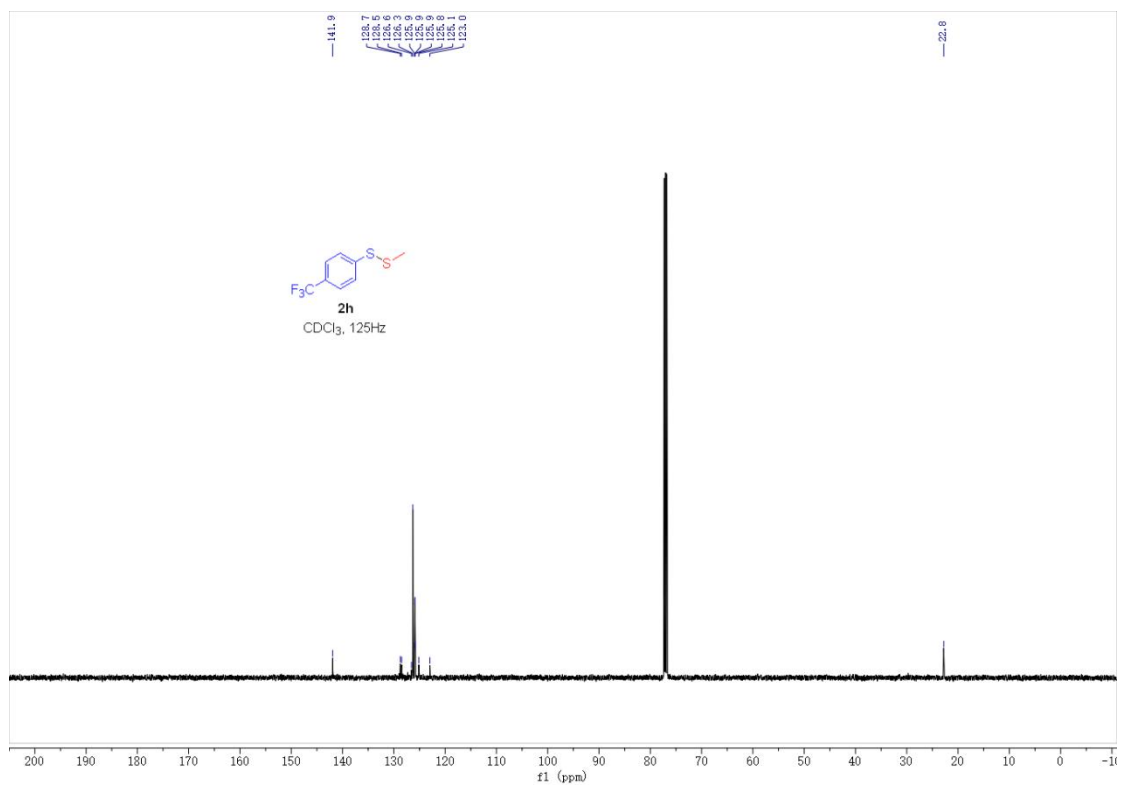
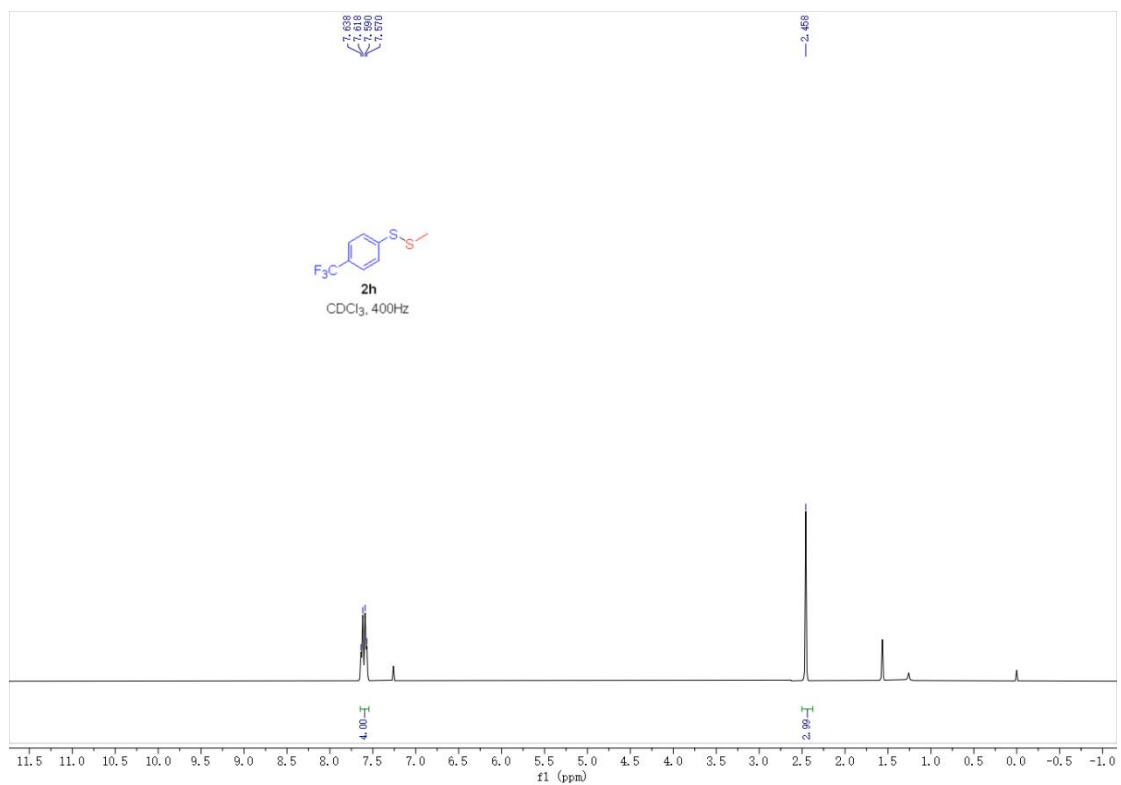


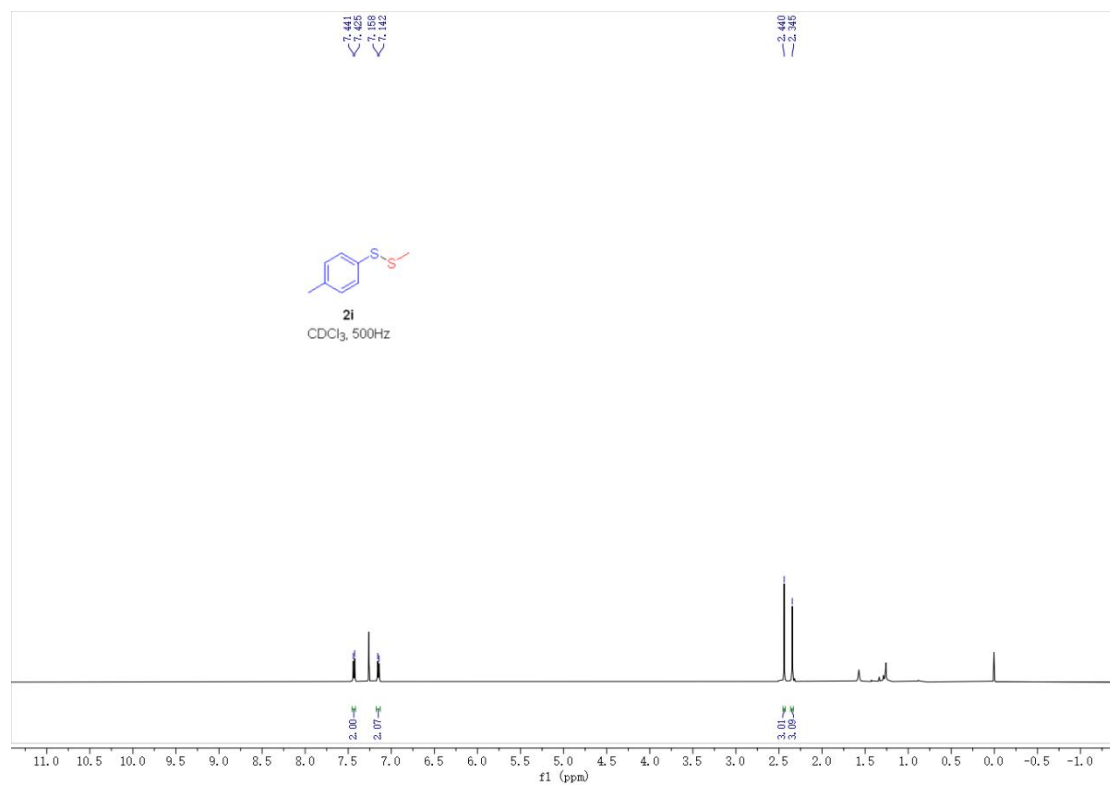
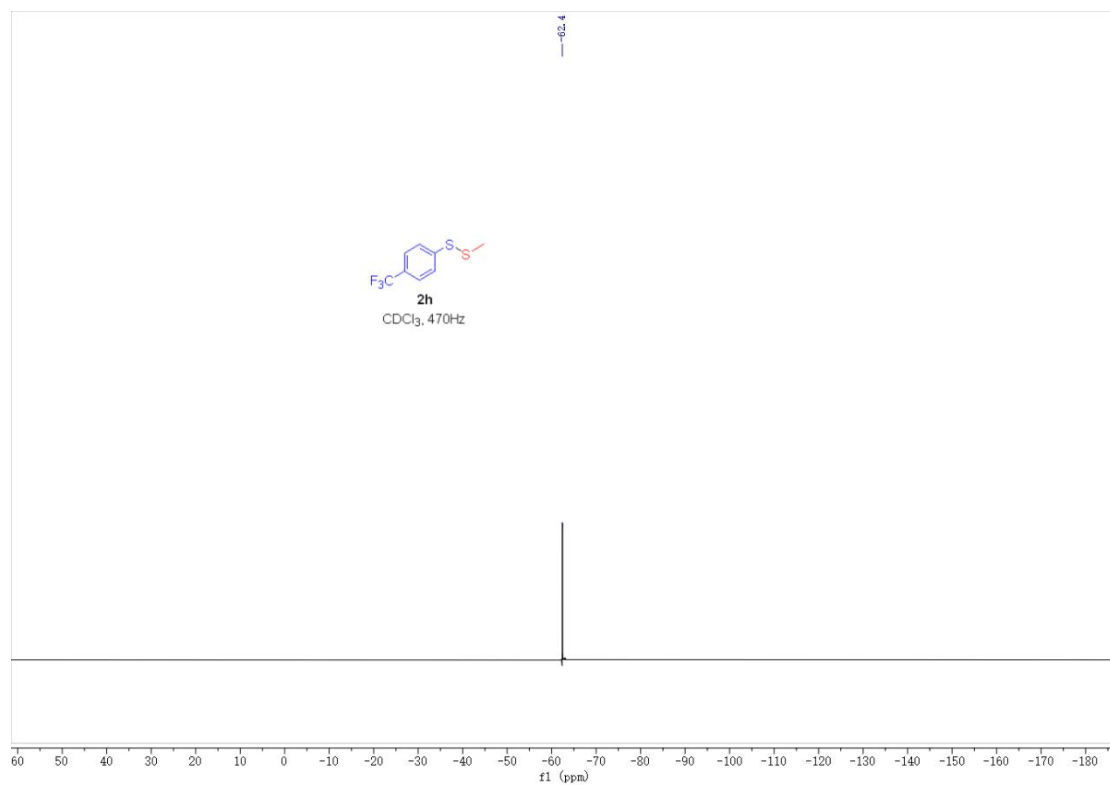


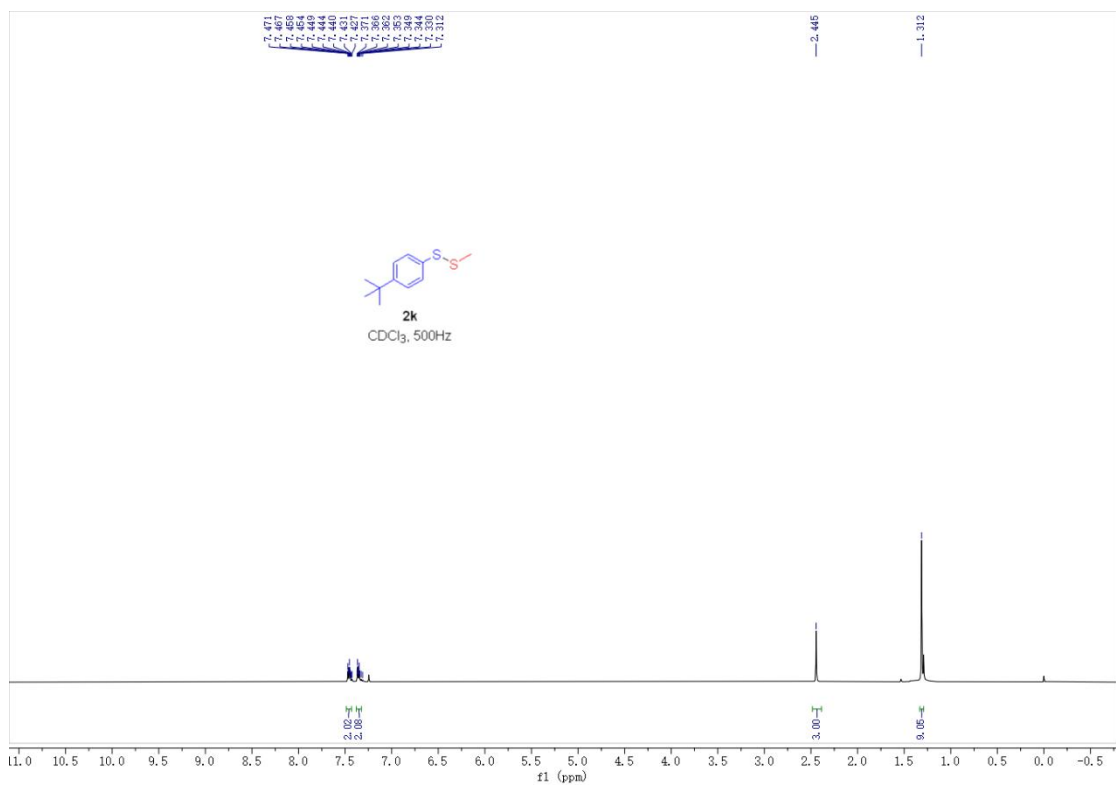
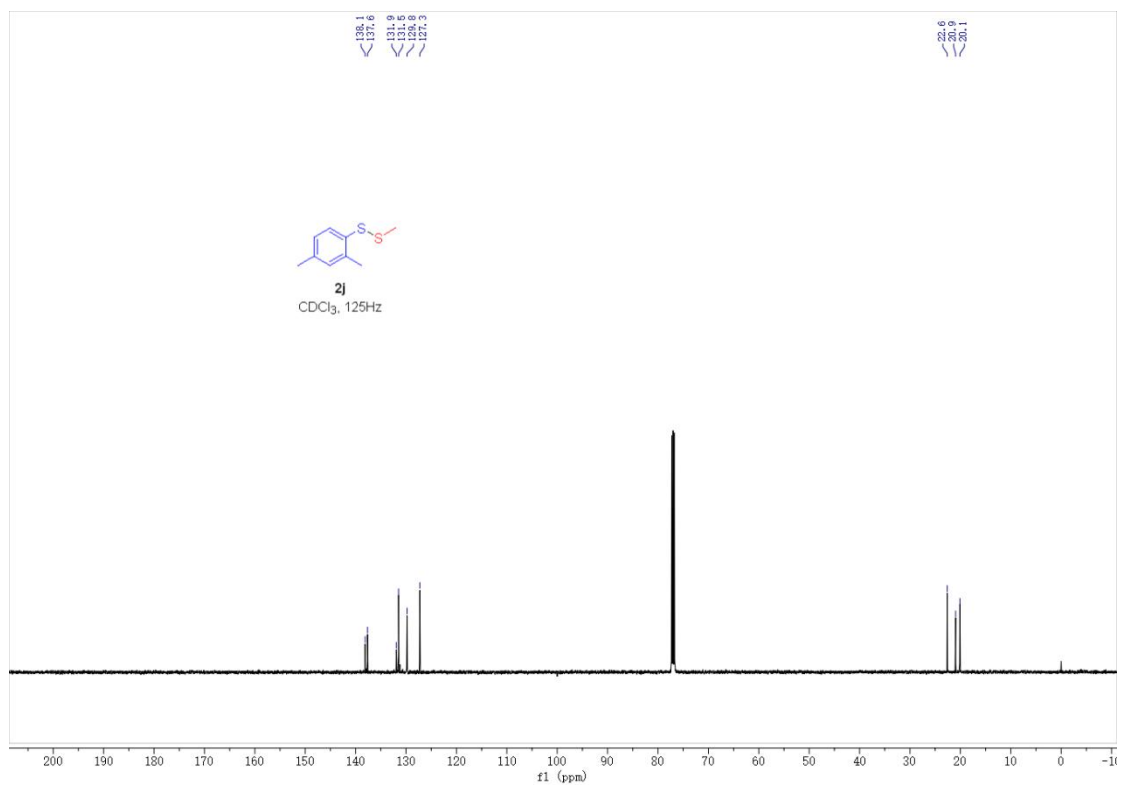


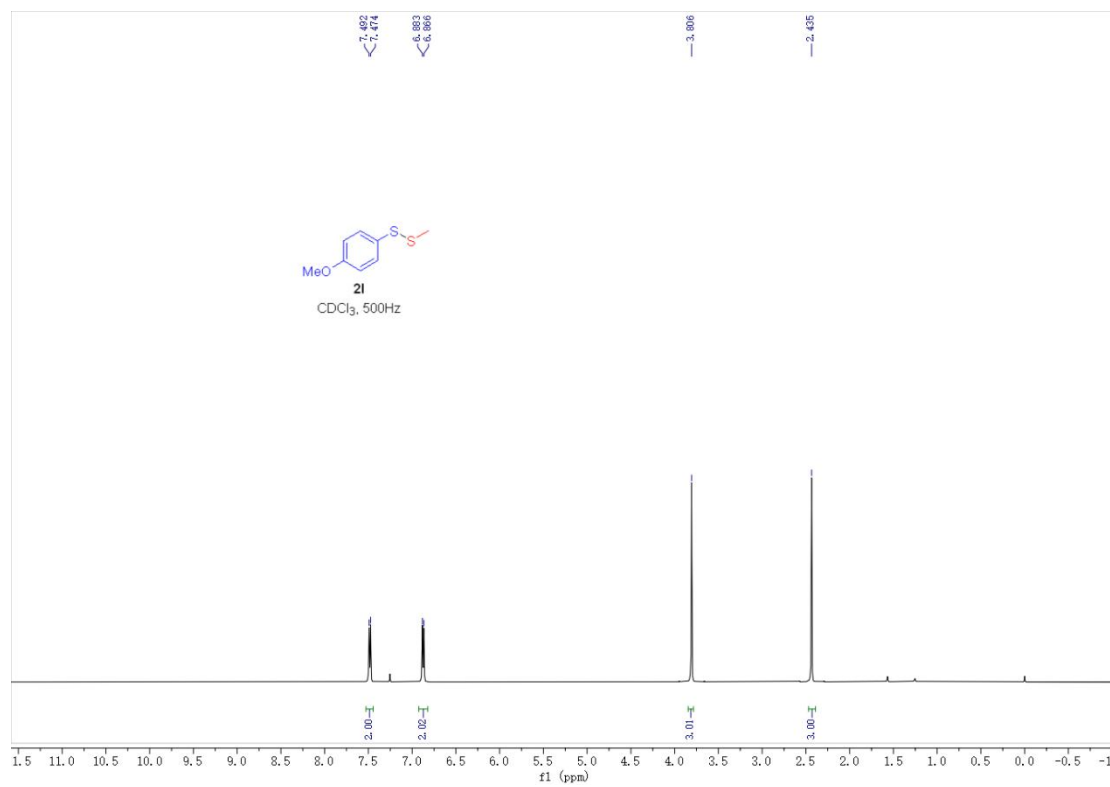
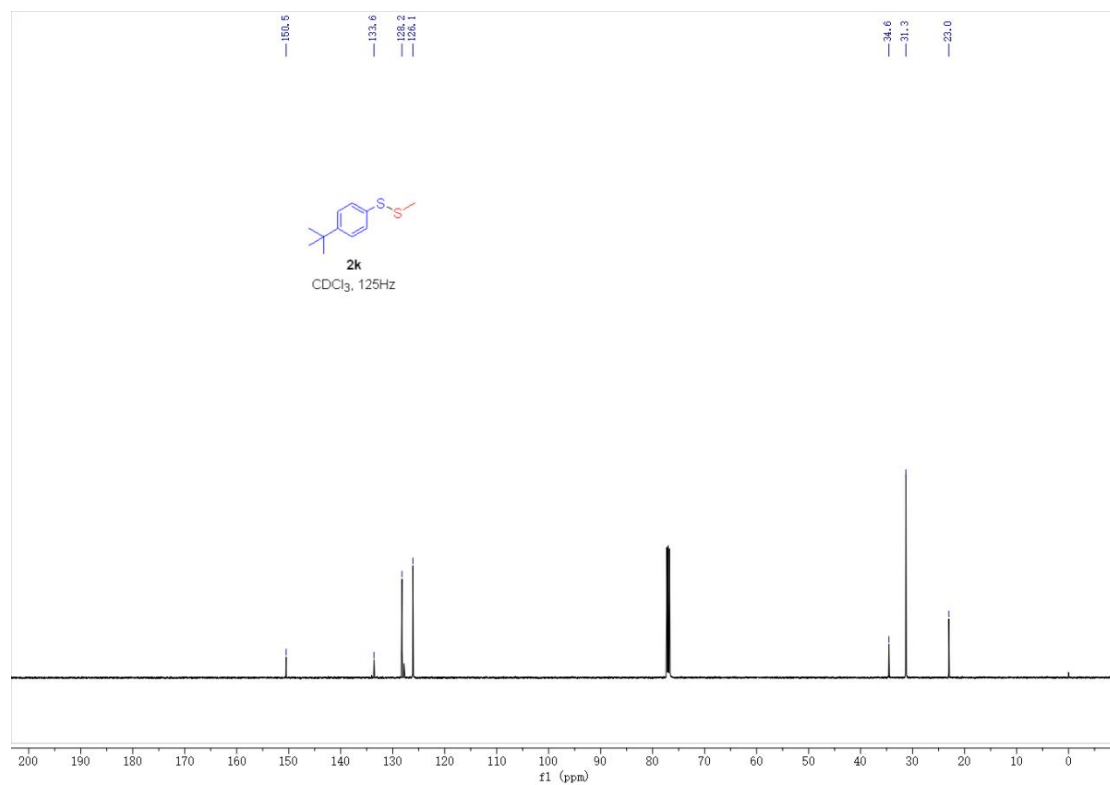


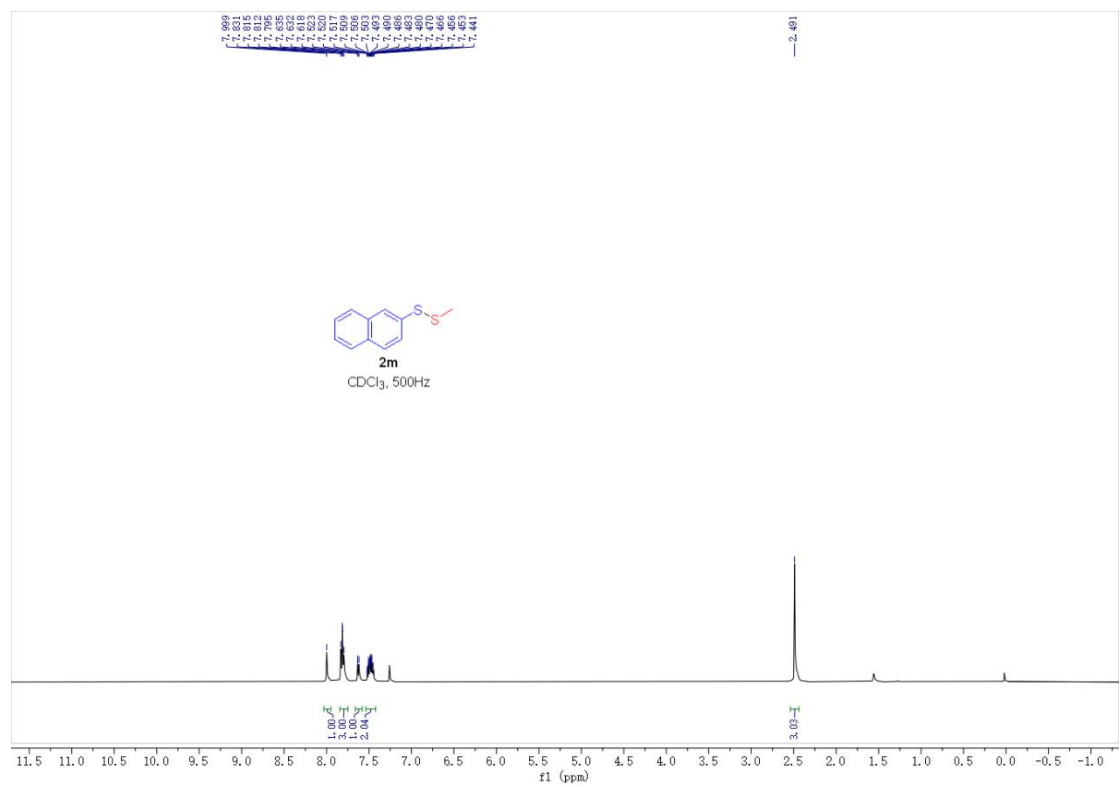
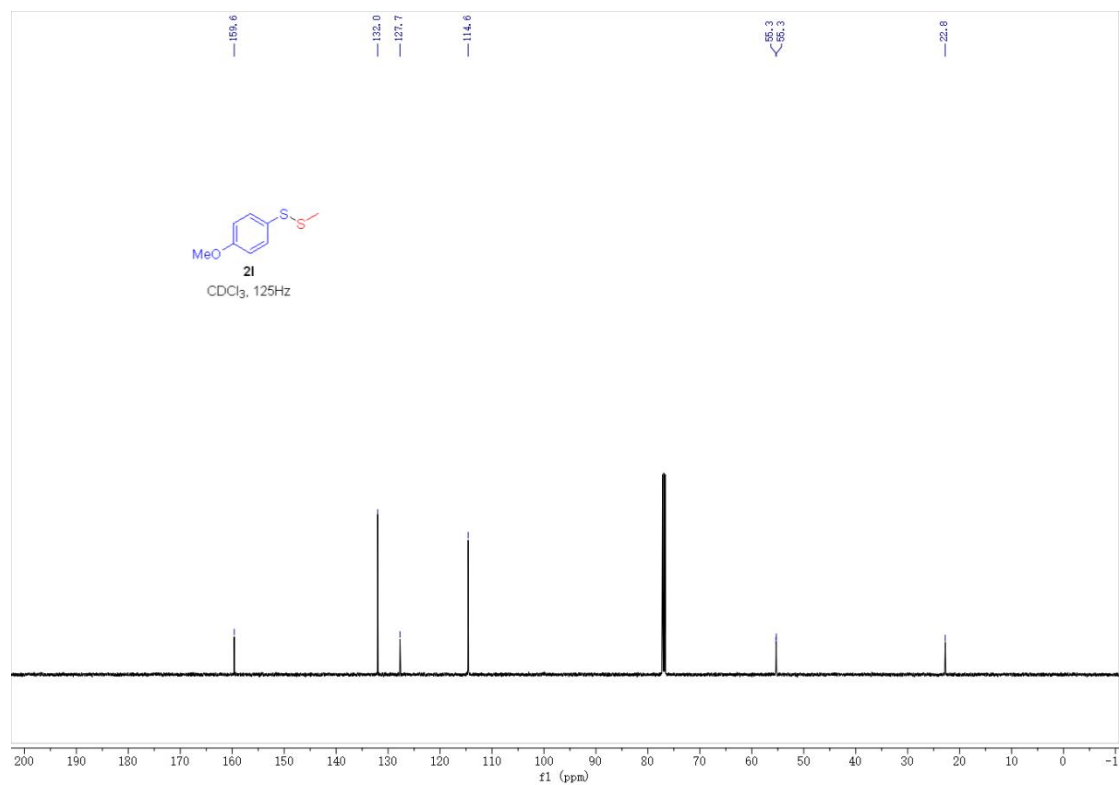


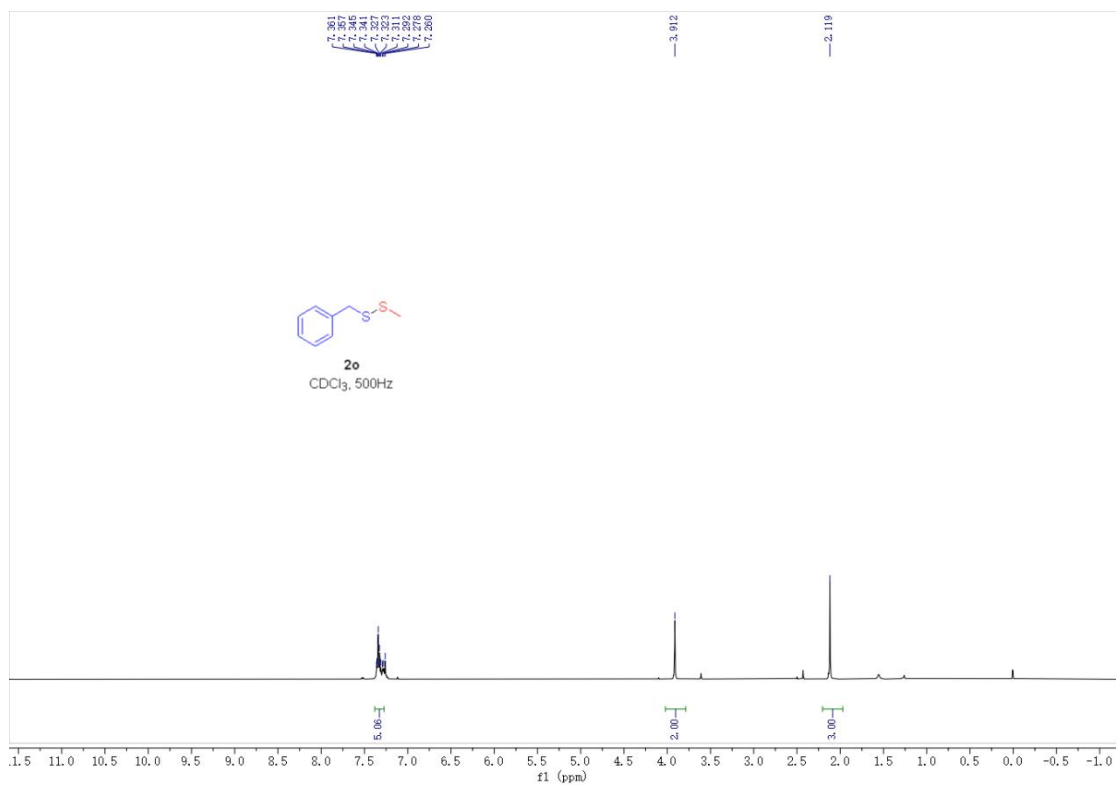
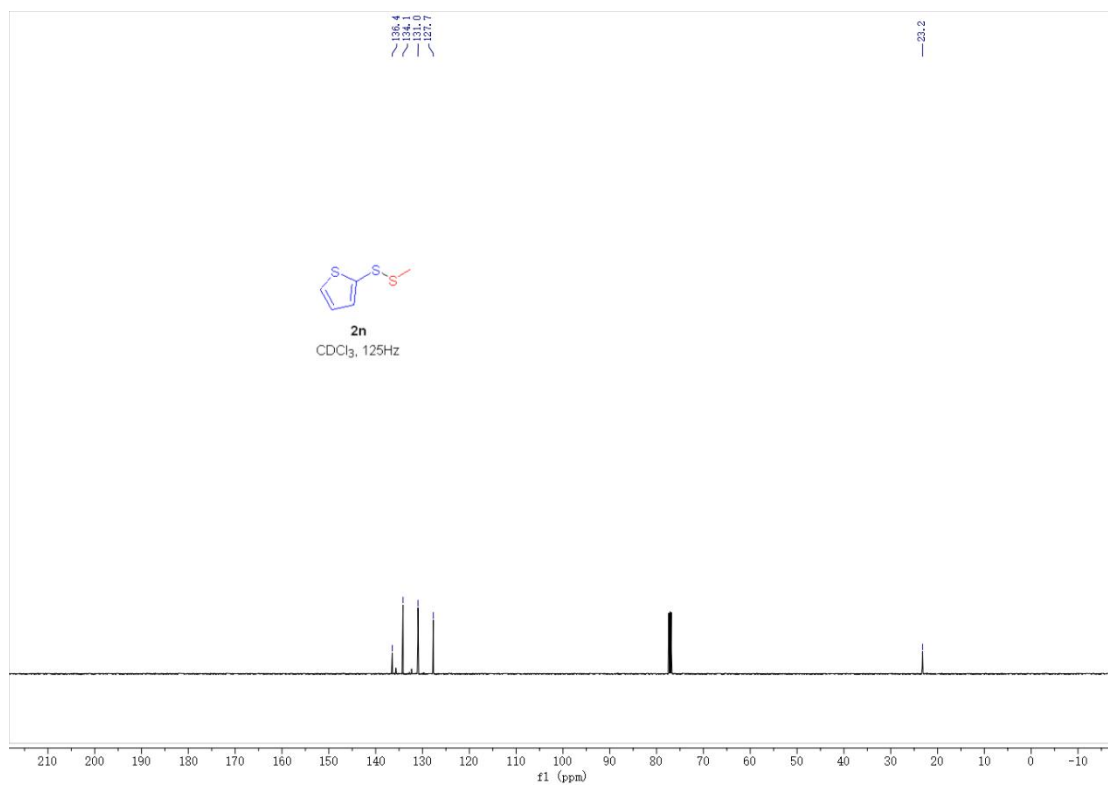


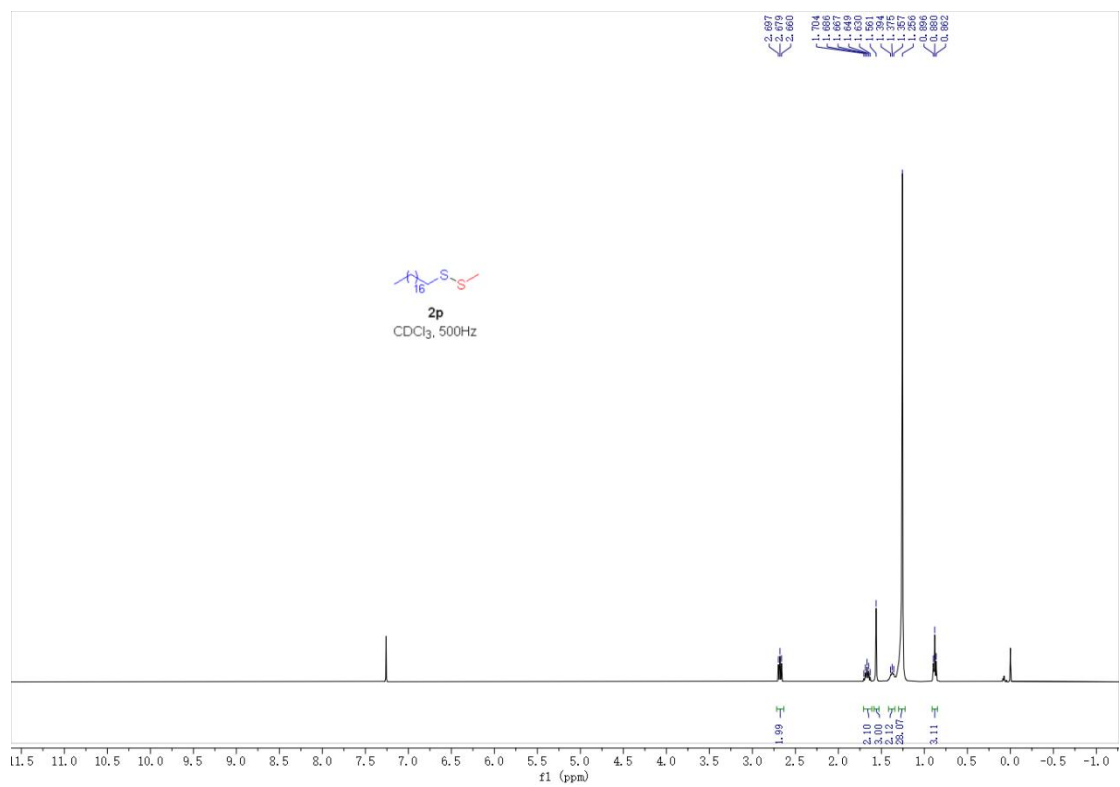
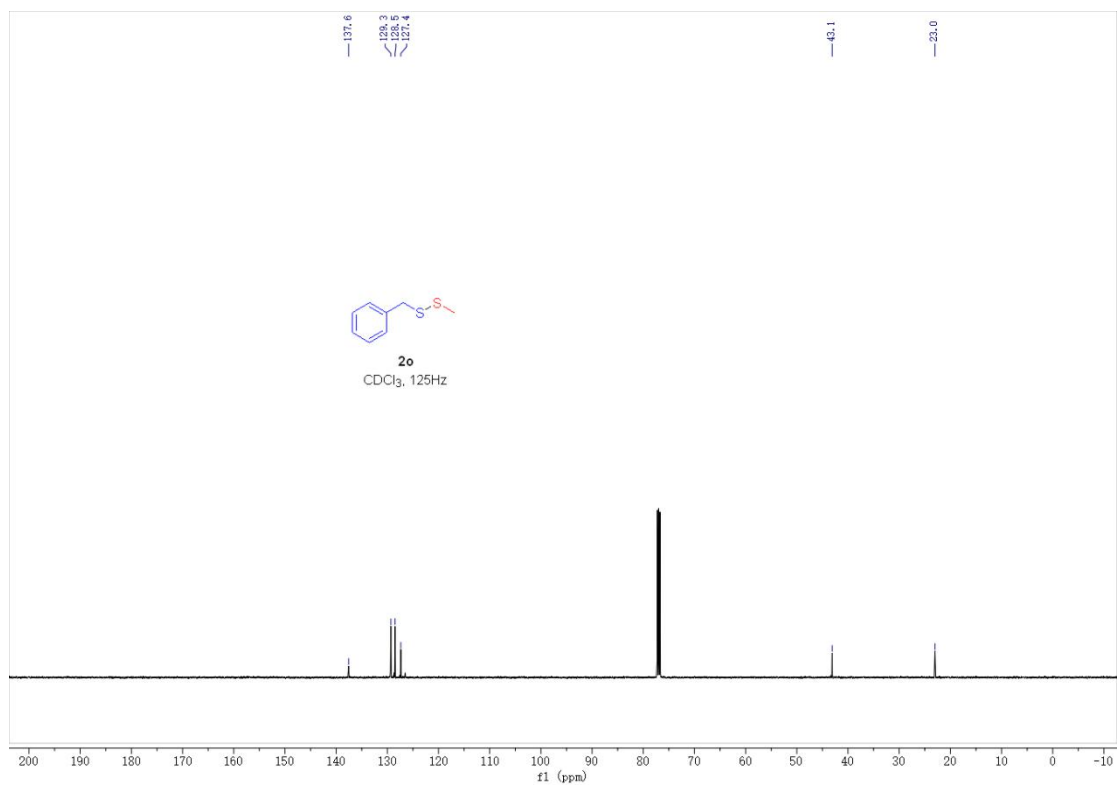


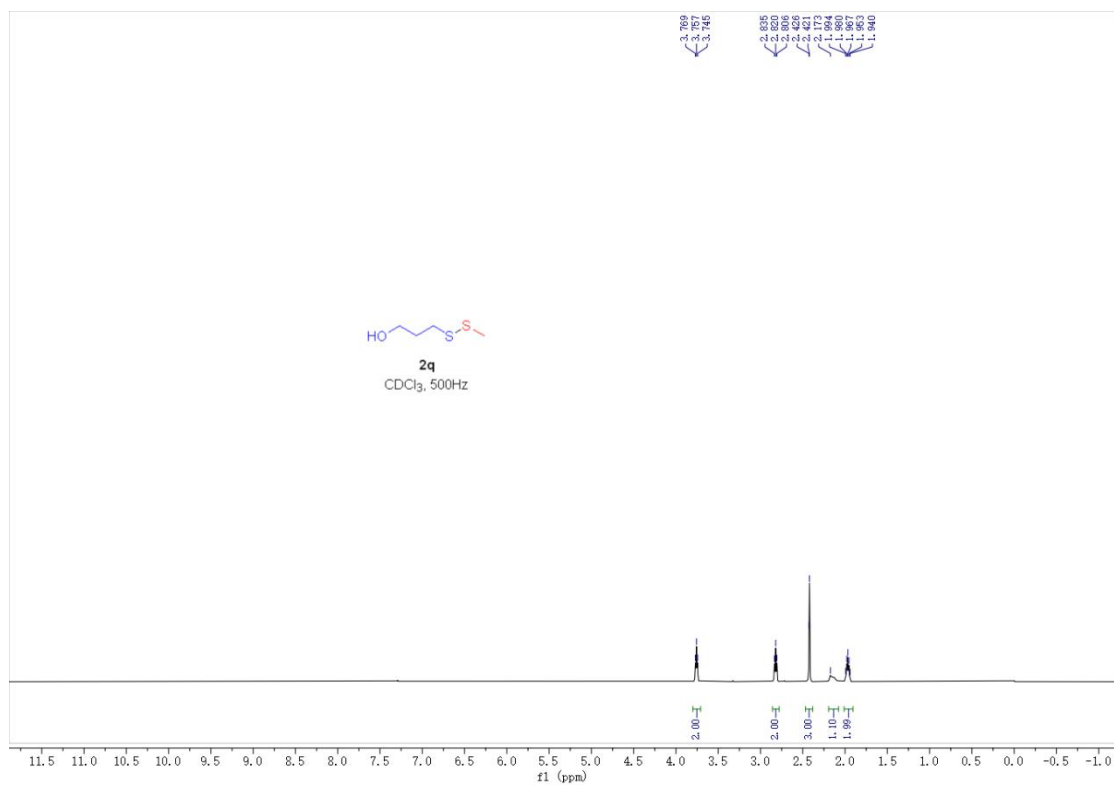
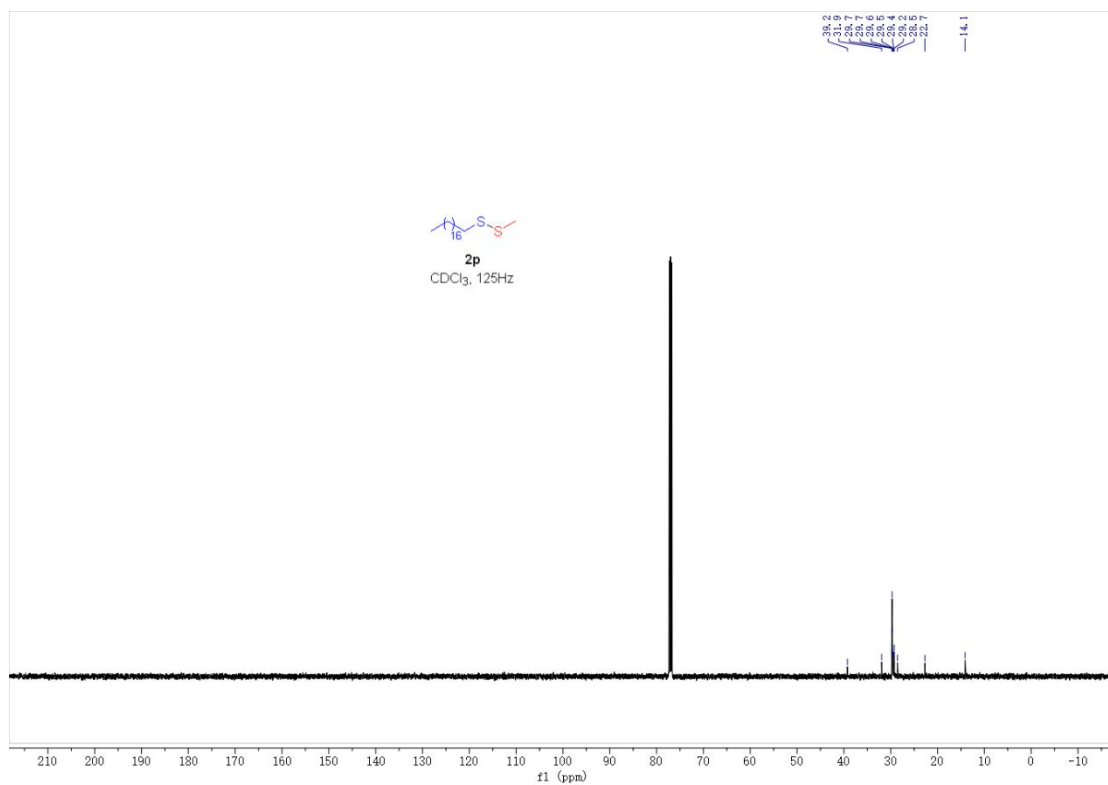


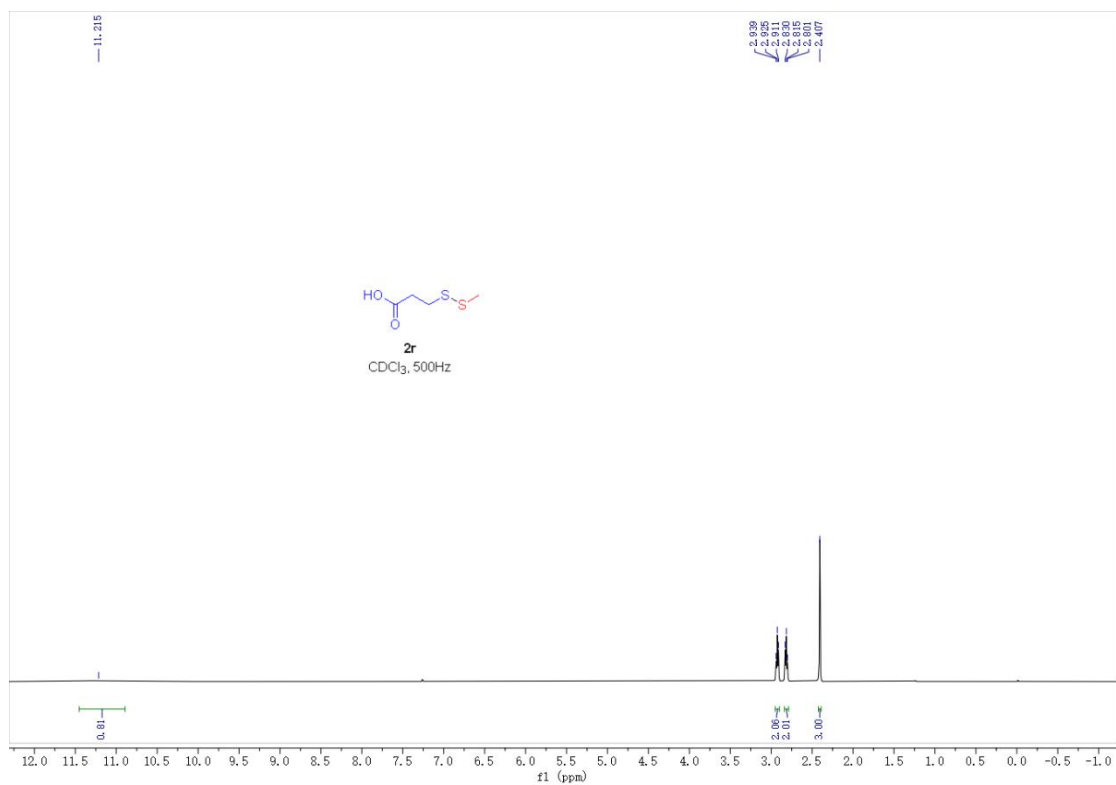
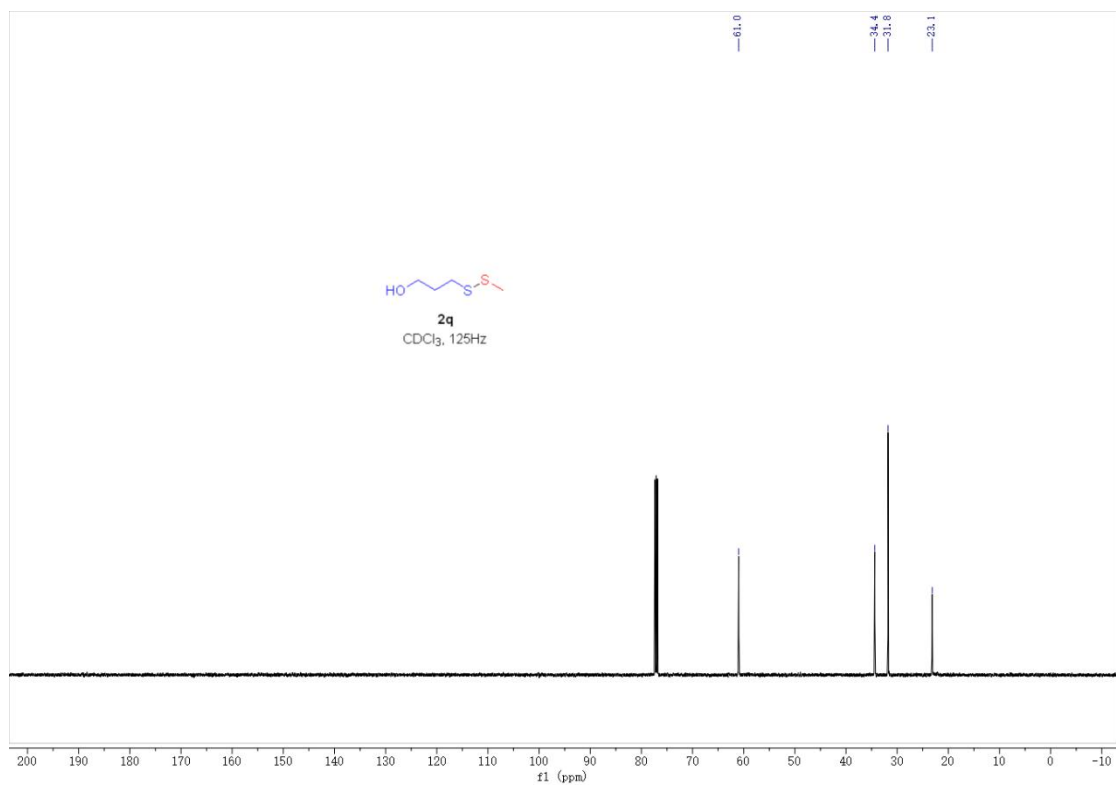


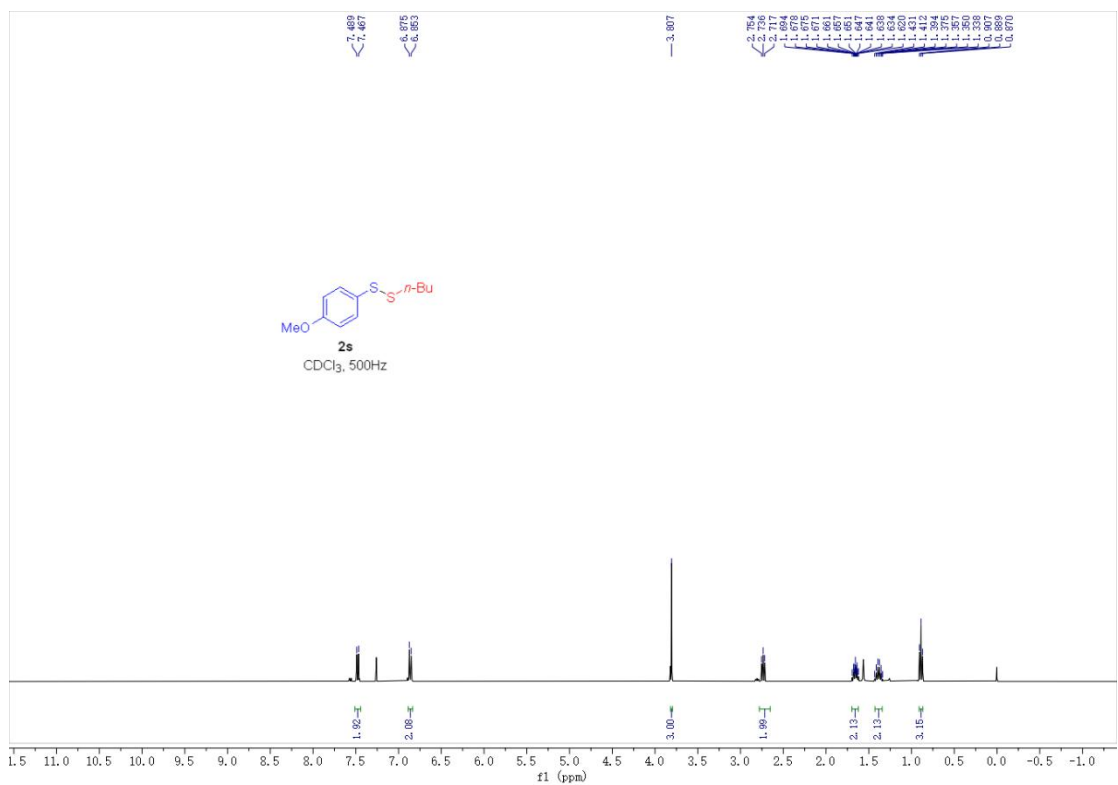
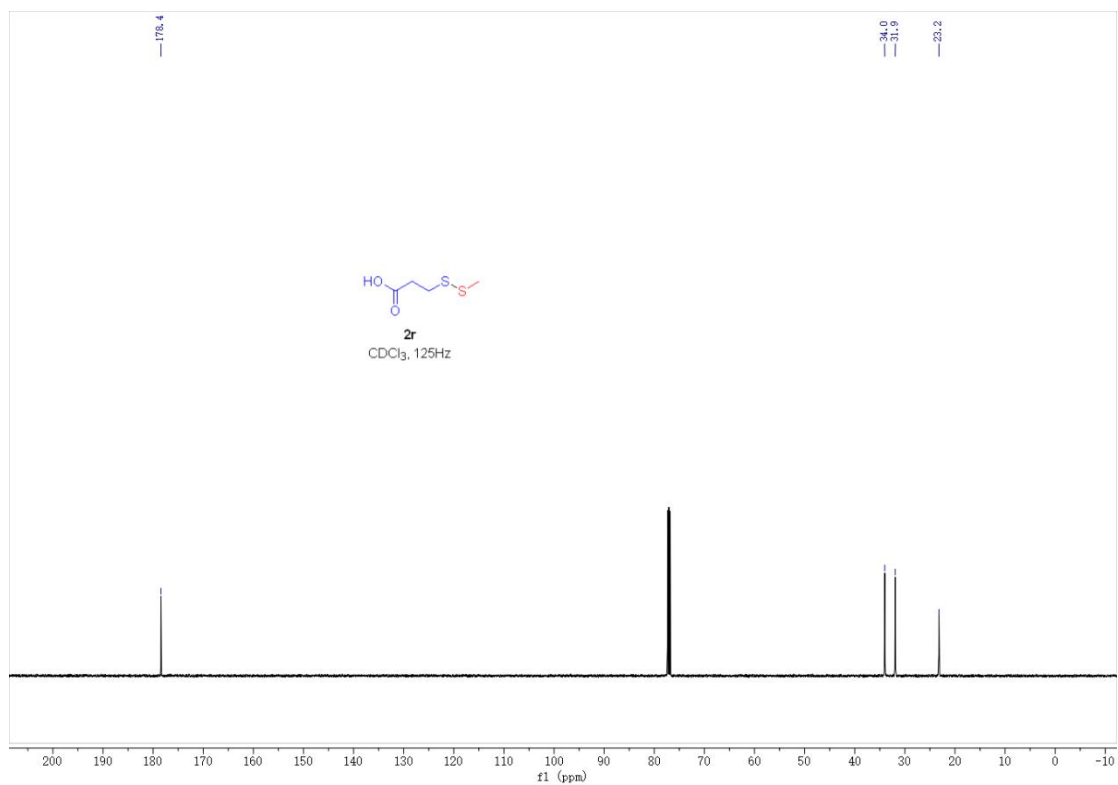


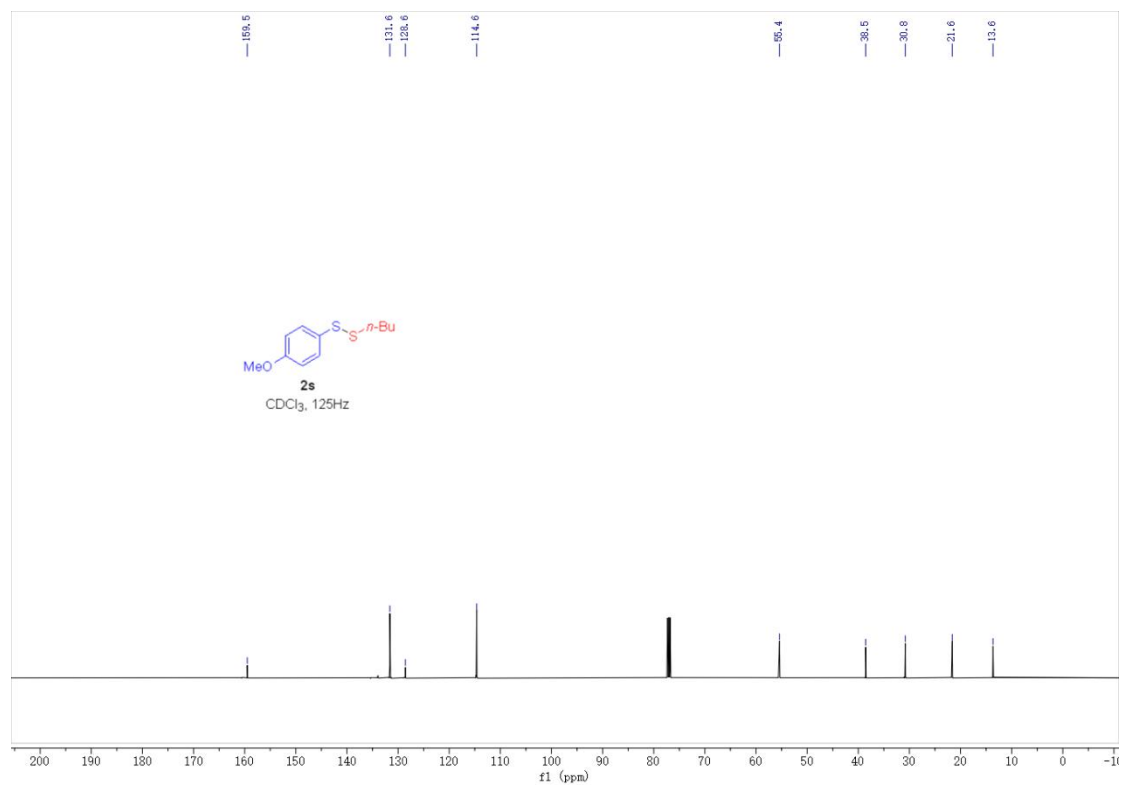






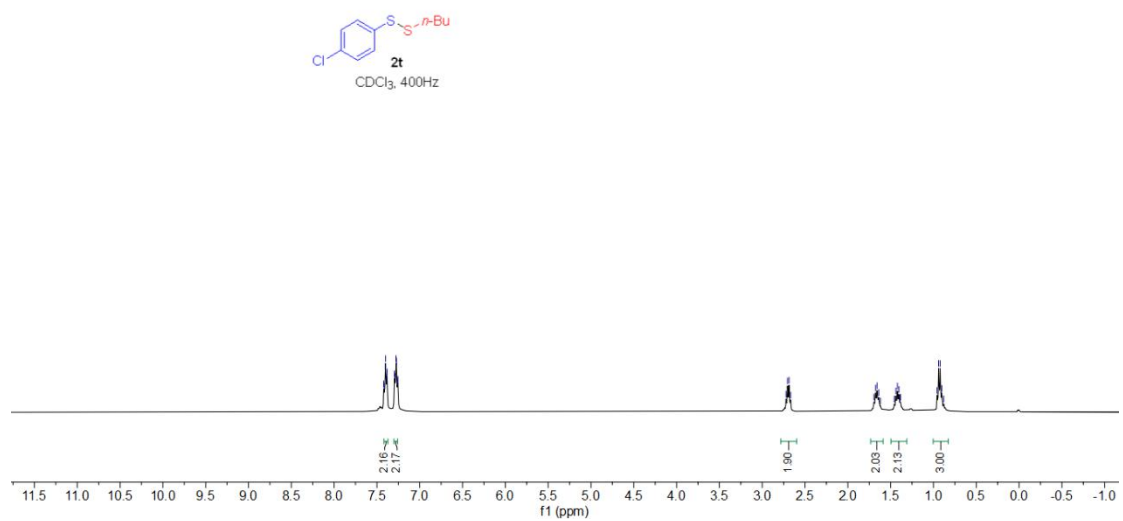


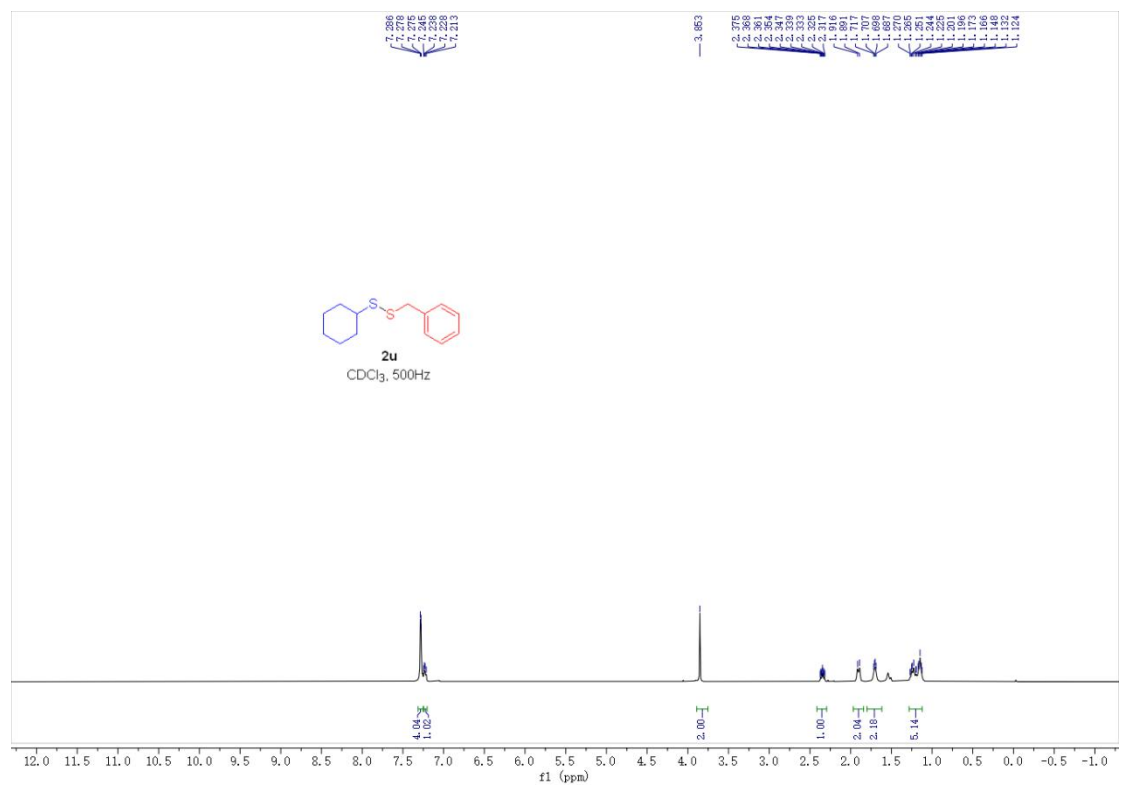
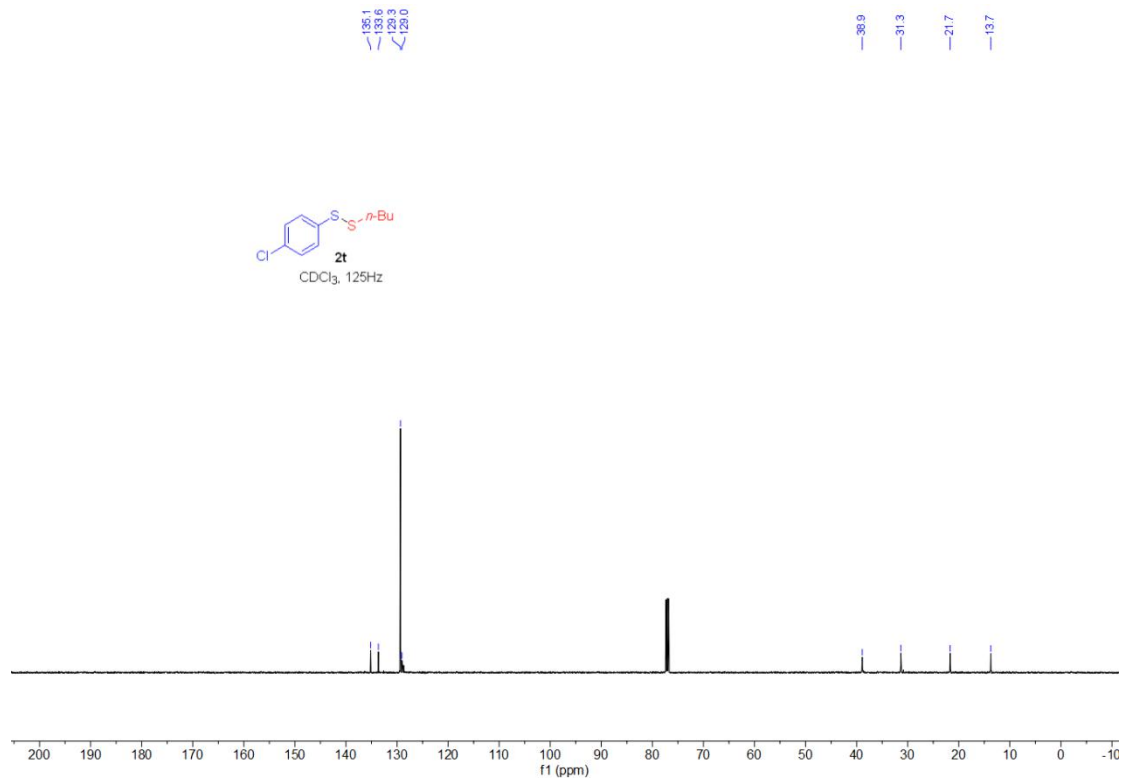


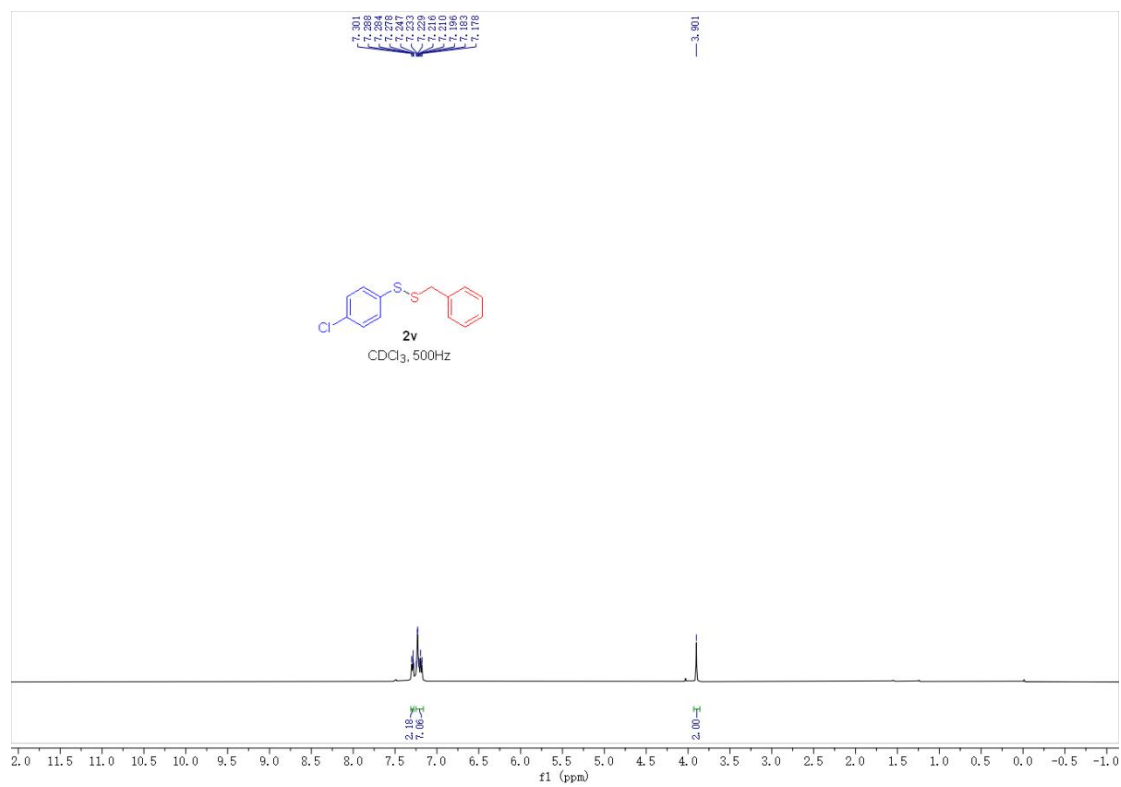
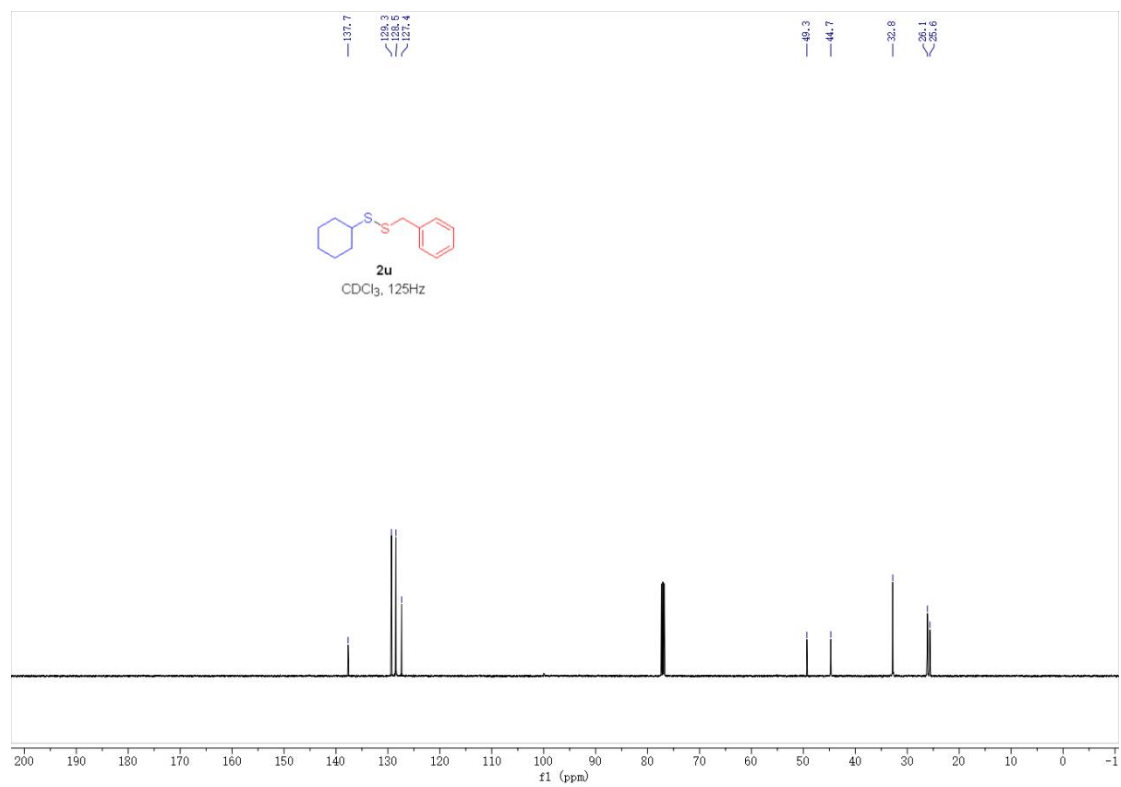


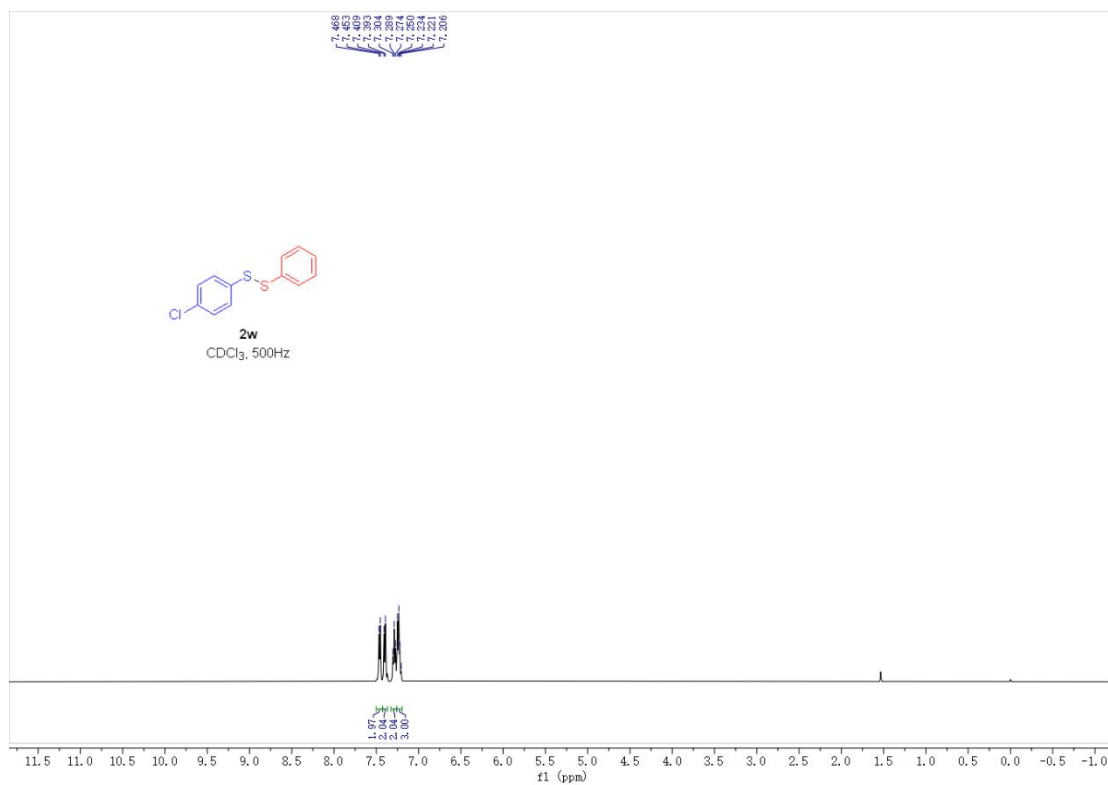
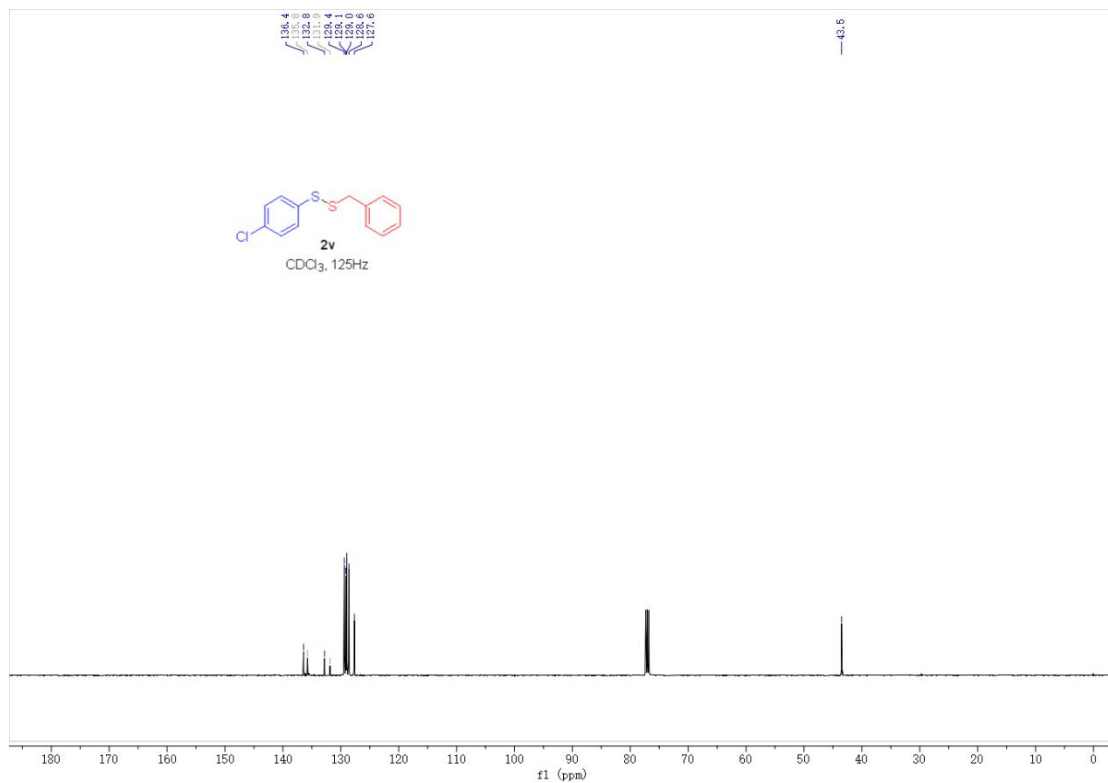
7.421
7.416
7.403
7.388
7.382
7.356
7.339
7.277
7.273
7.261
7.255

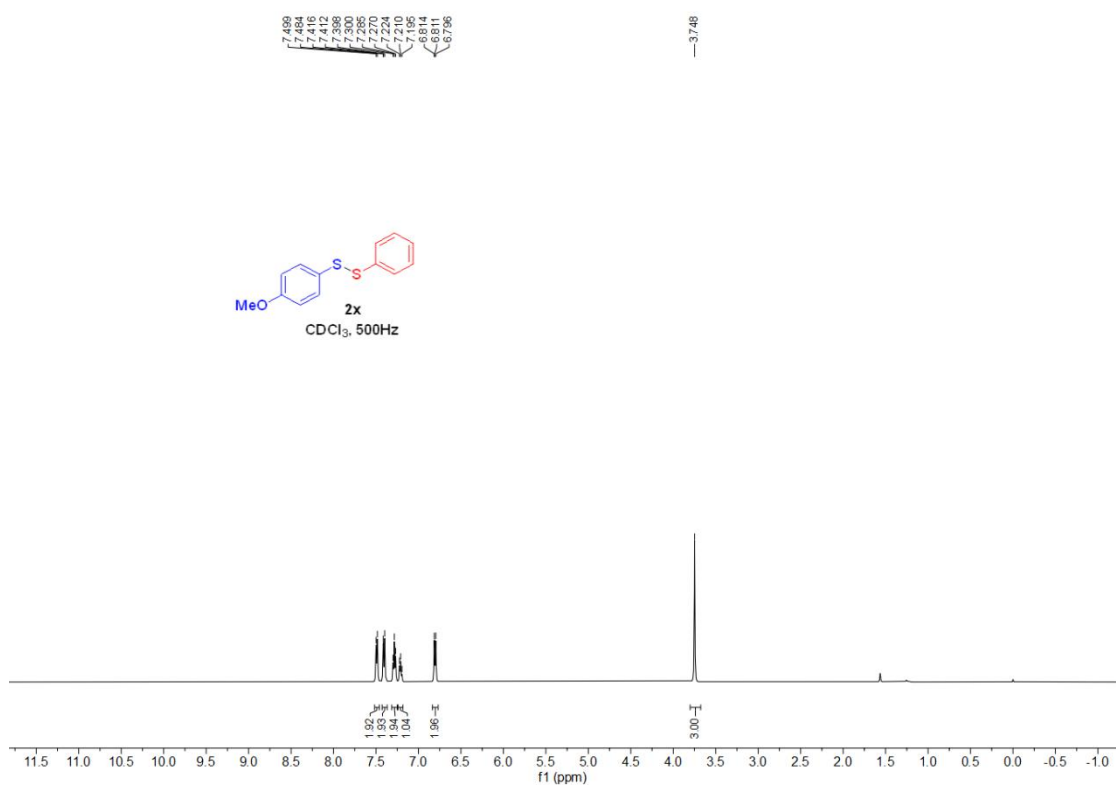
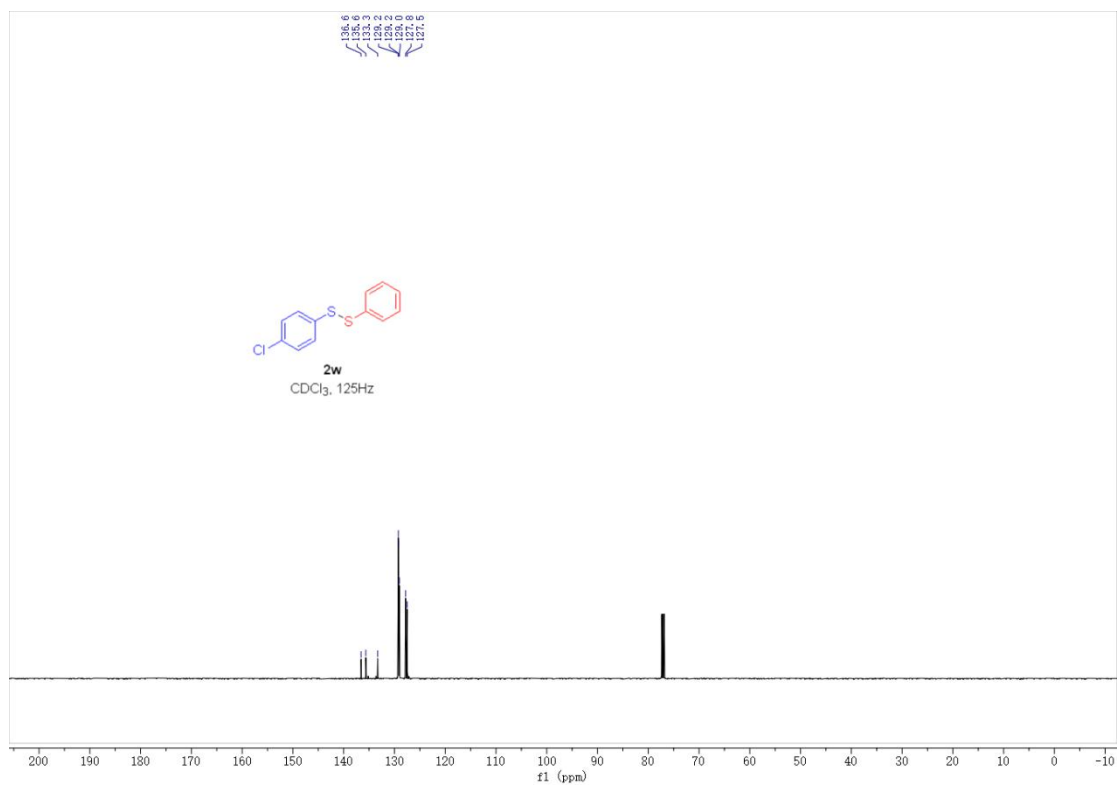
2.722
2.704
2.688
2.673
1.976
1.659
1.640
1.627
1.439
1.421
1.402
1.384
0.959
0.940
0.922
0.887

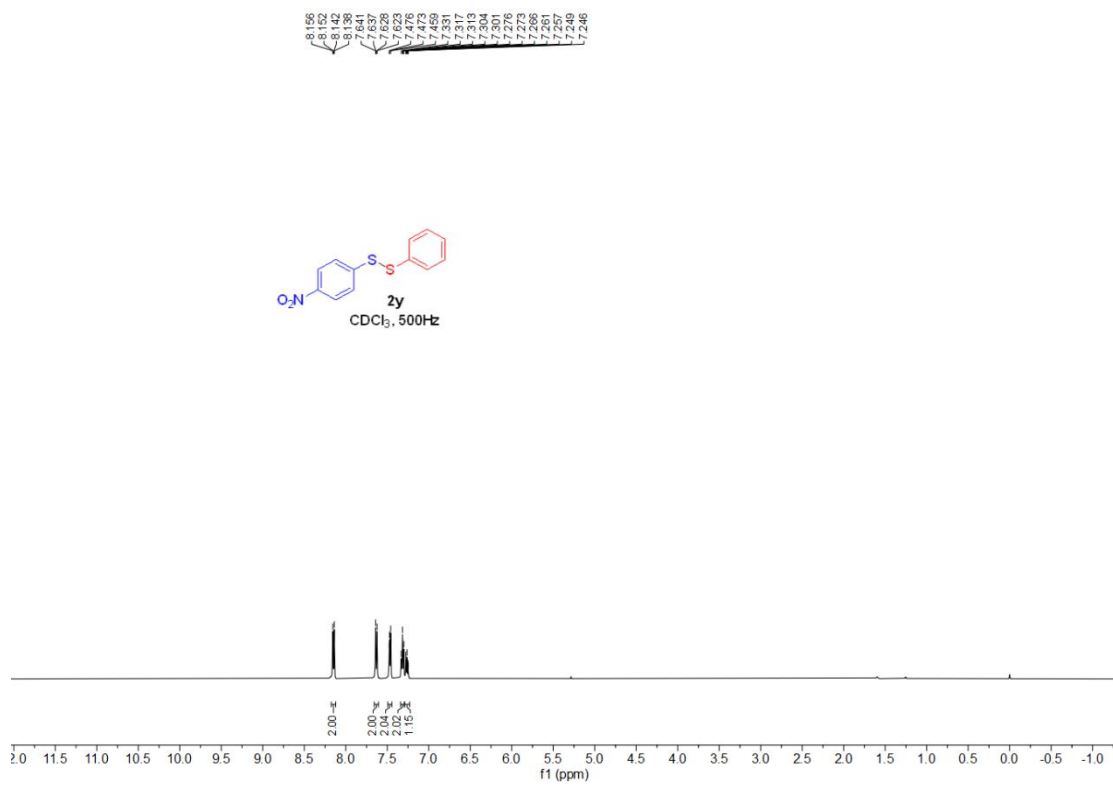
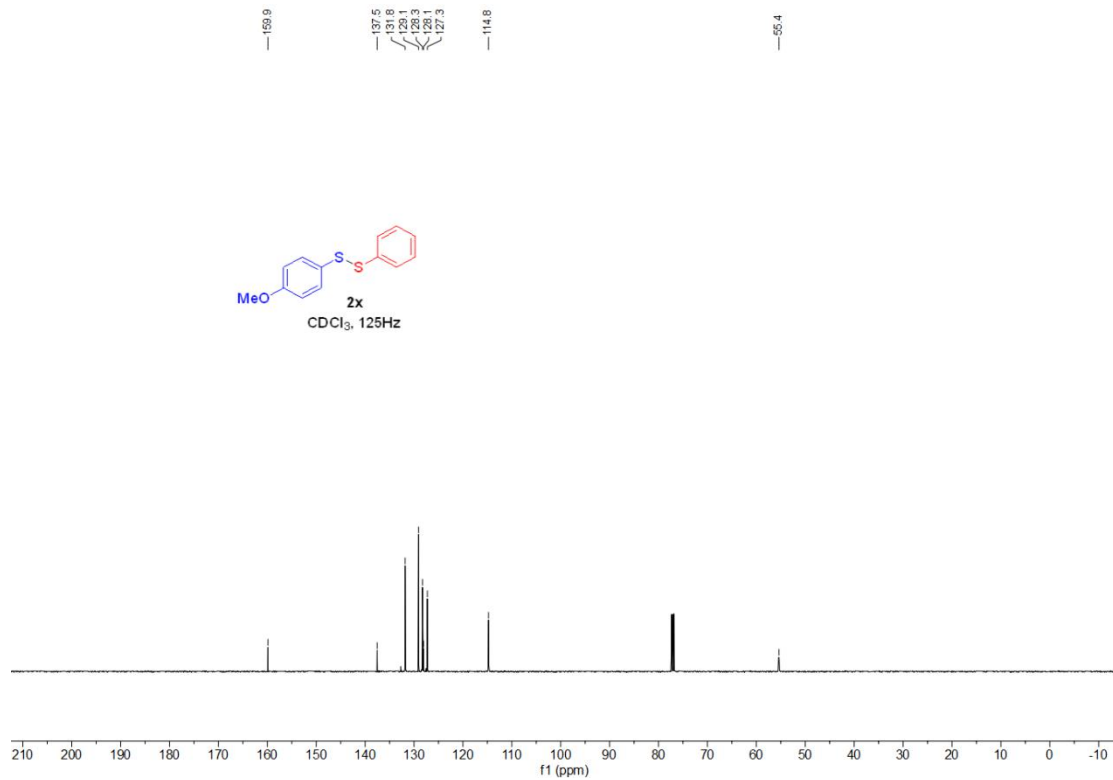


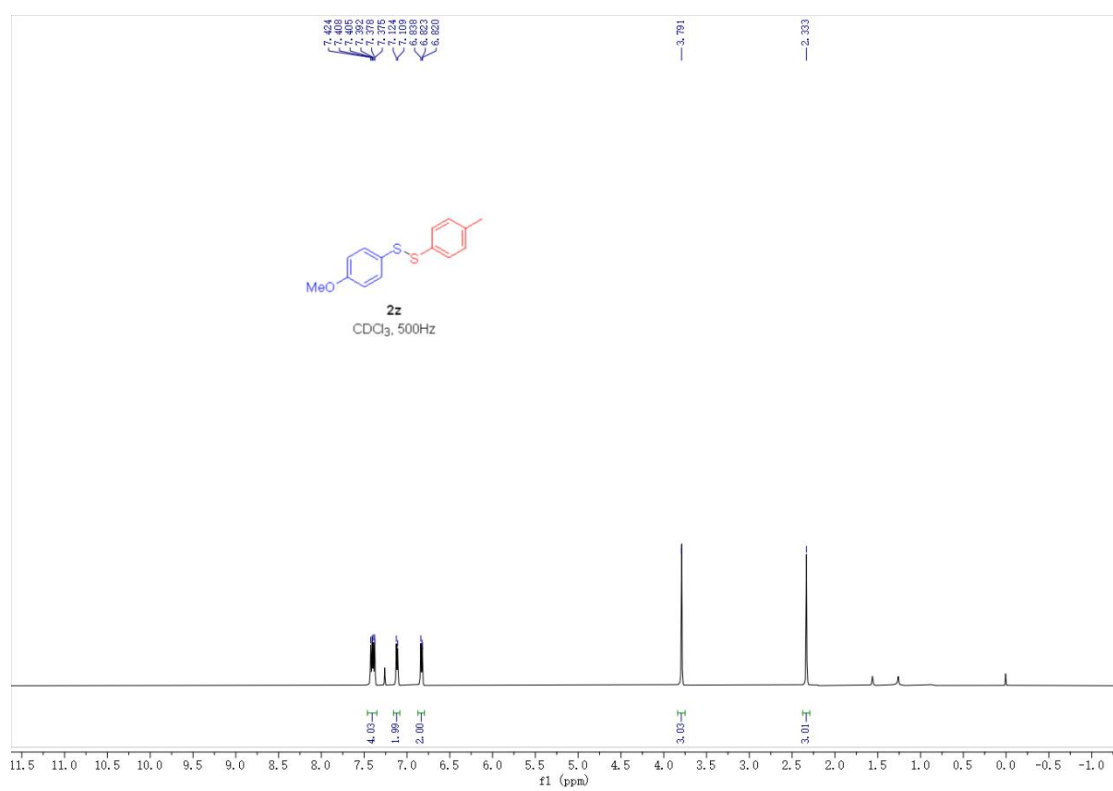
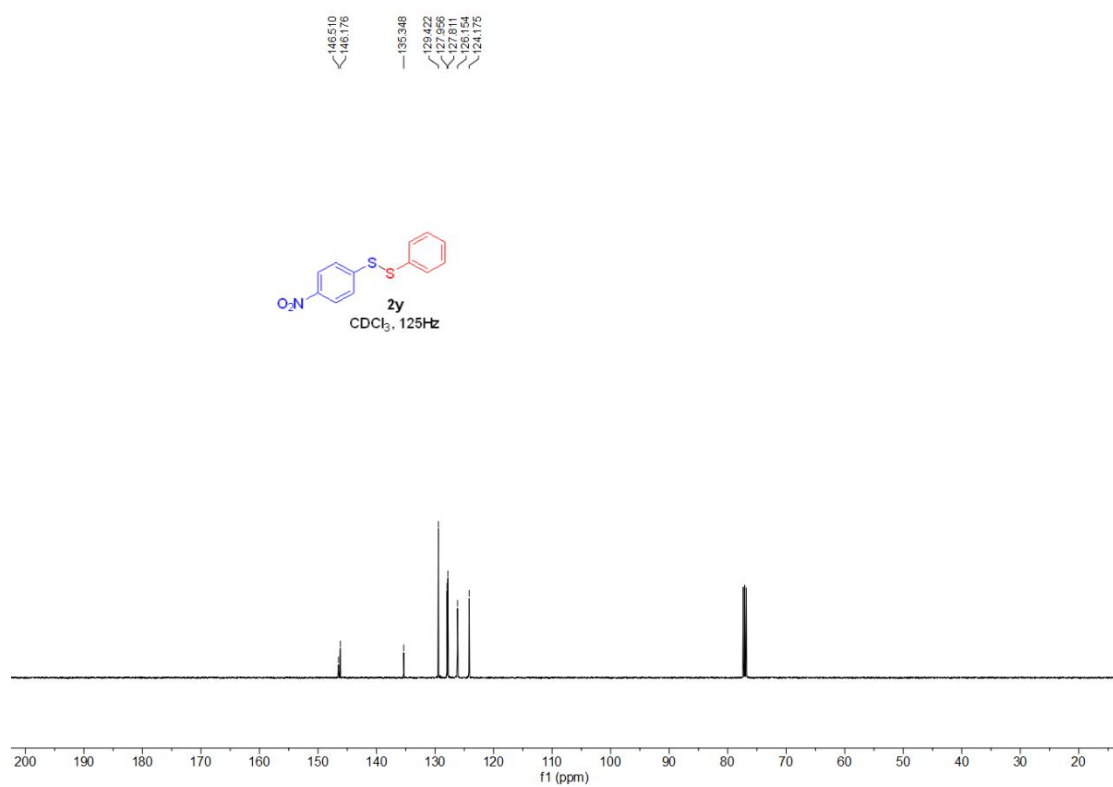


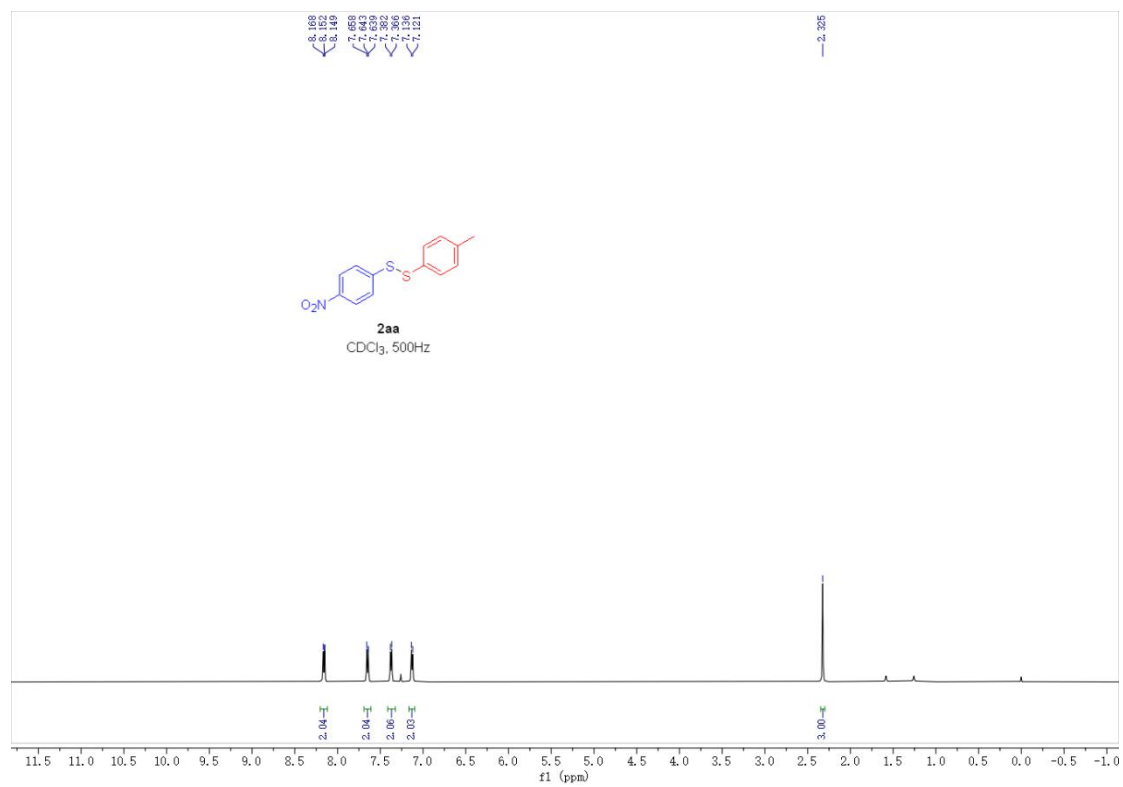
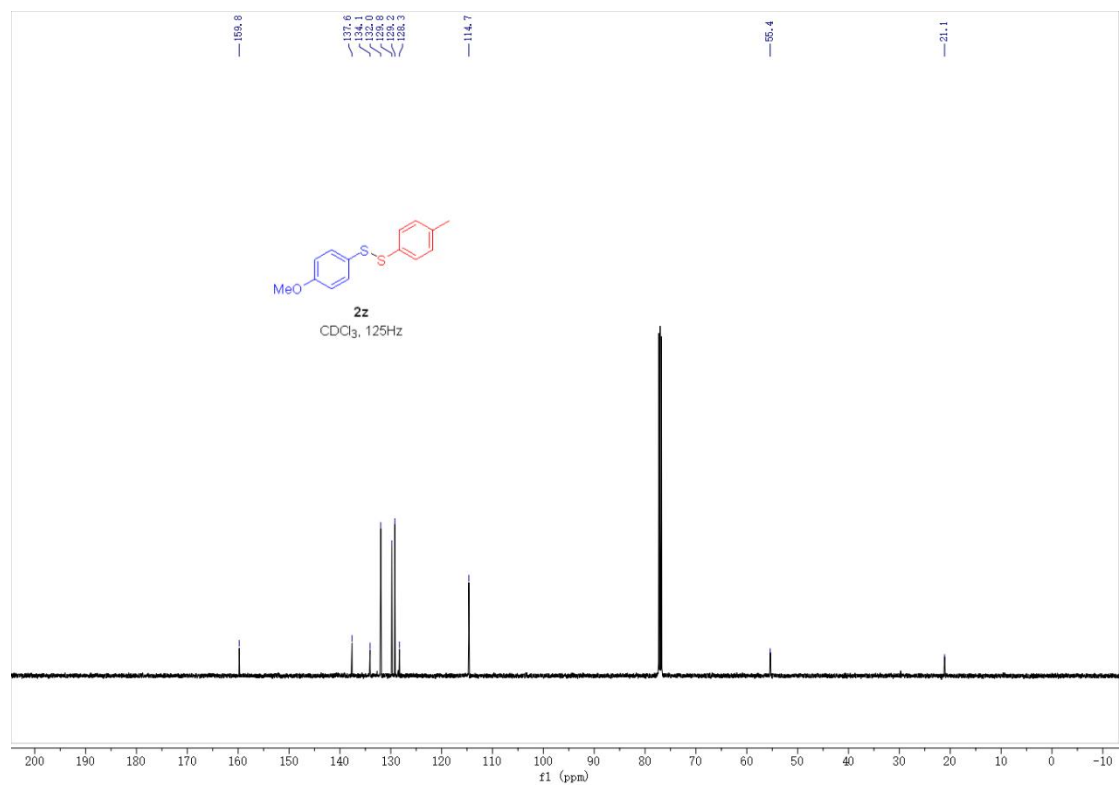


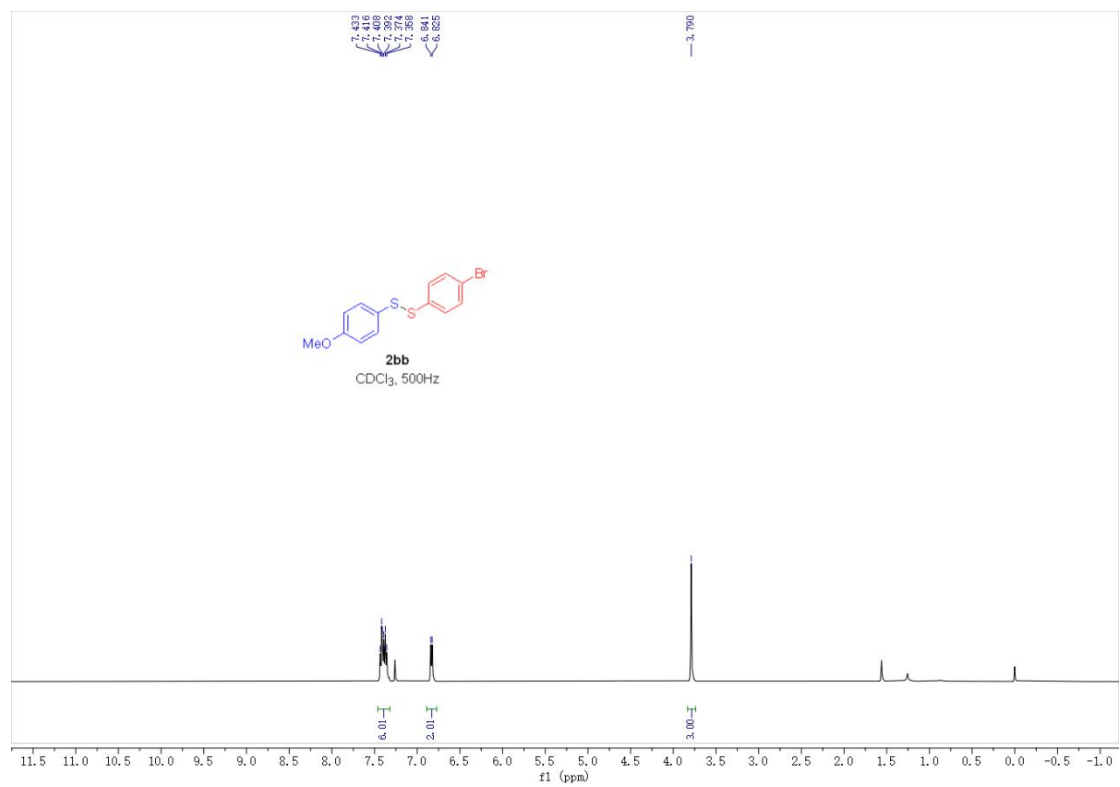
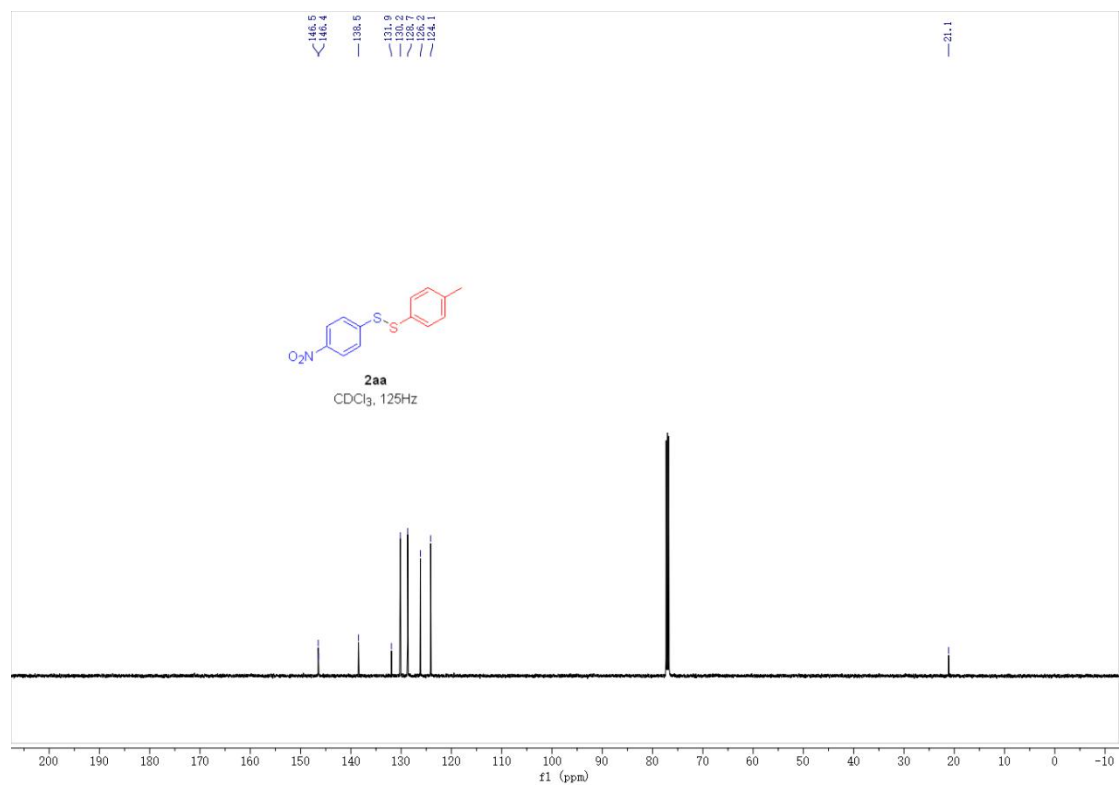


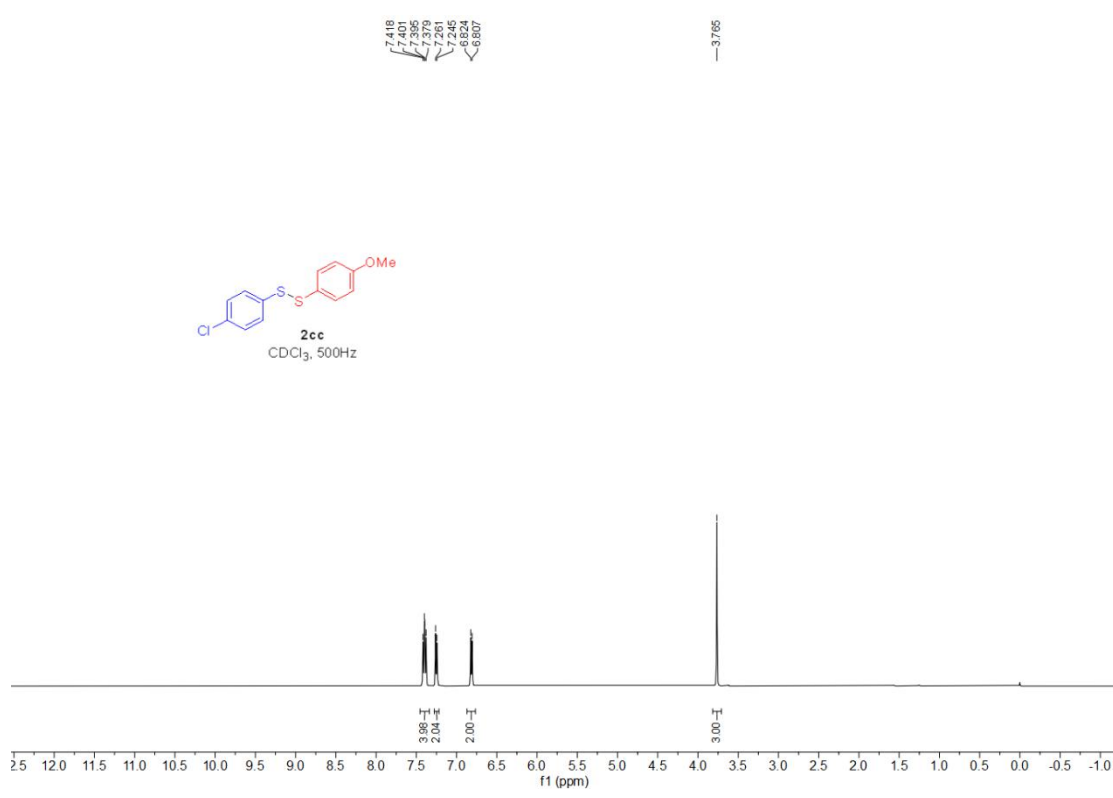
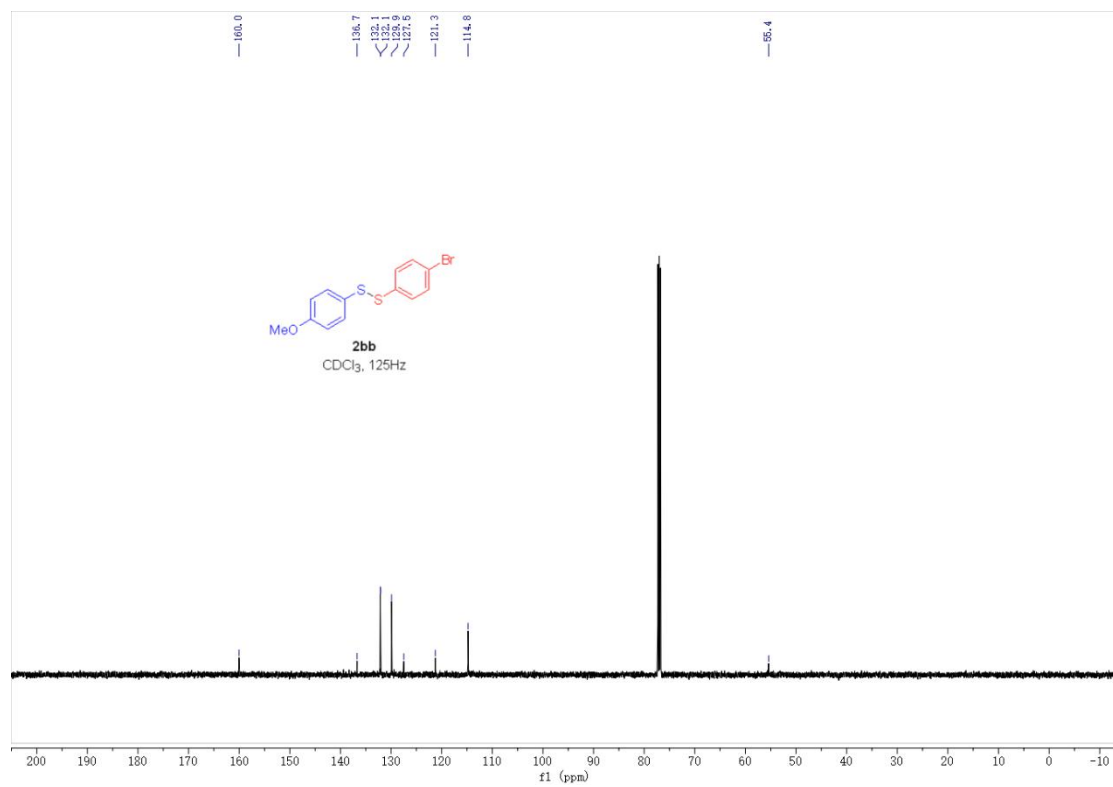


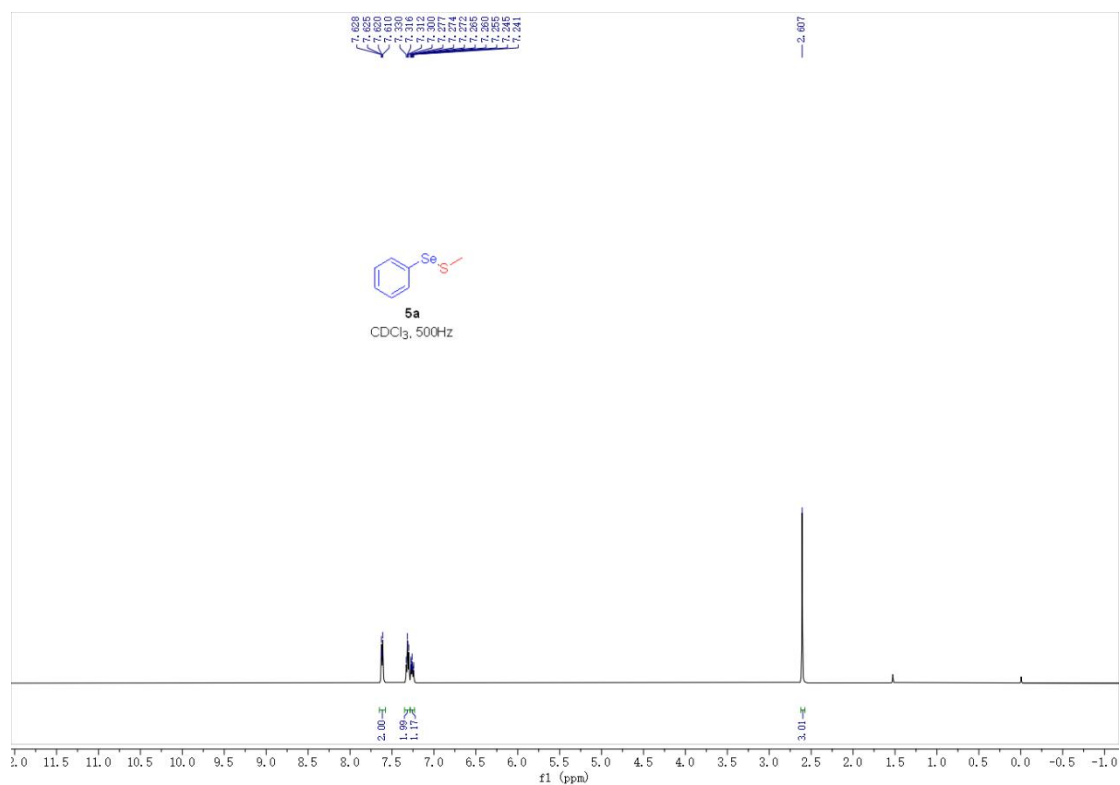
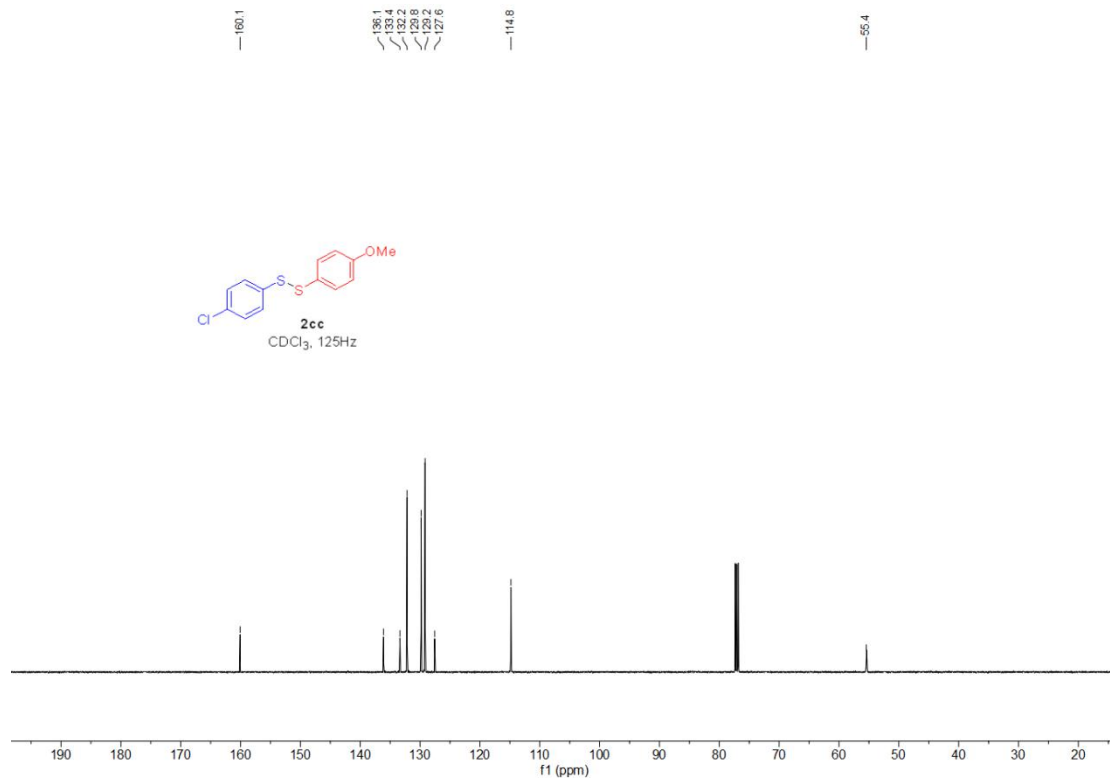


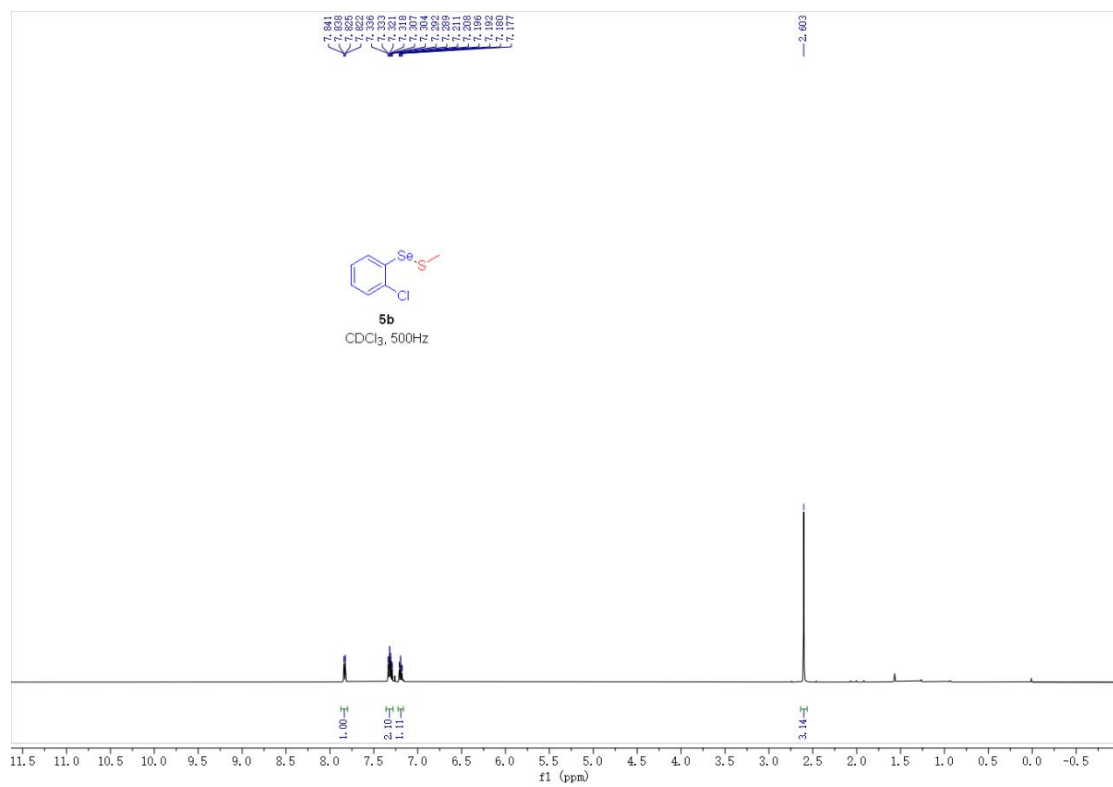
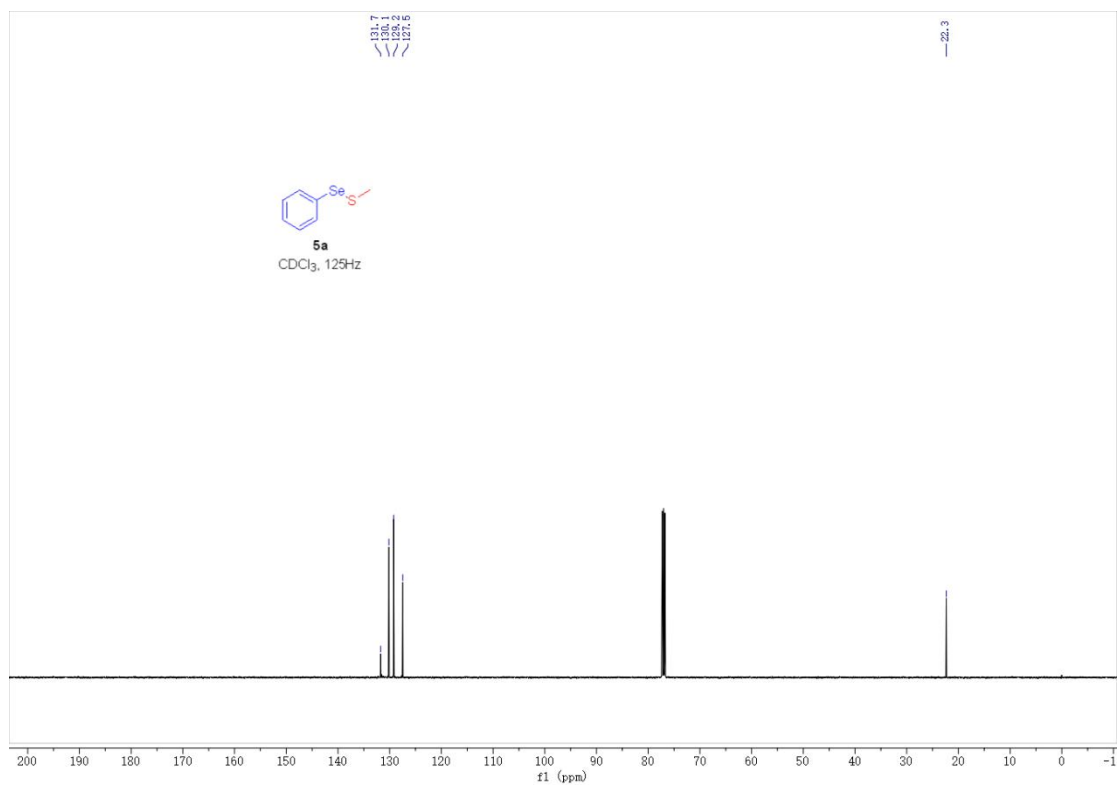


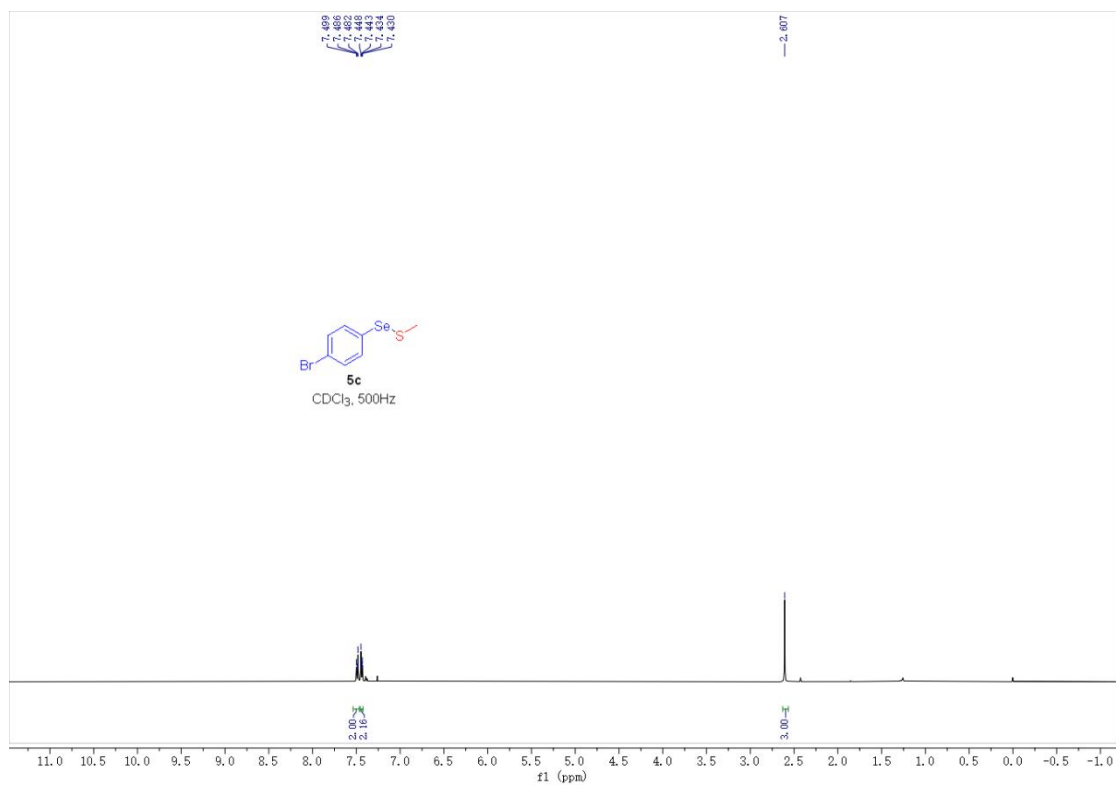
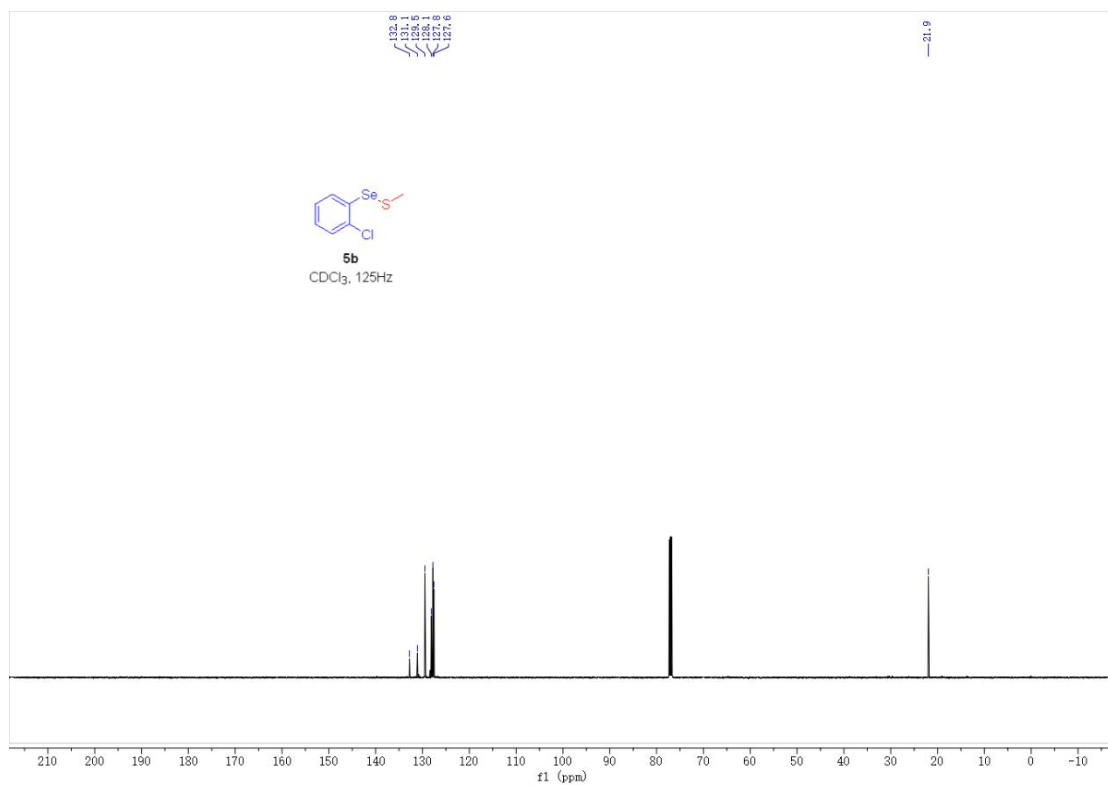


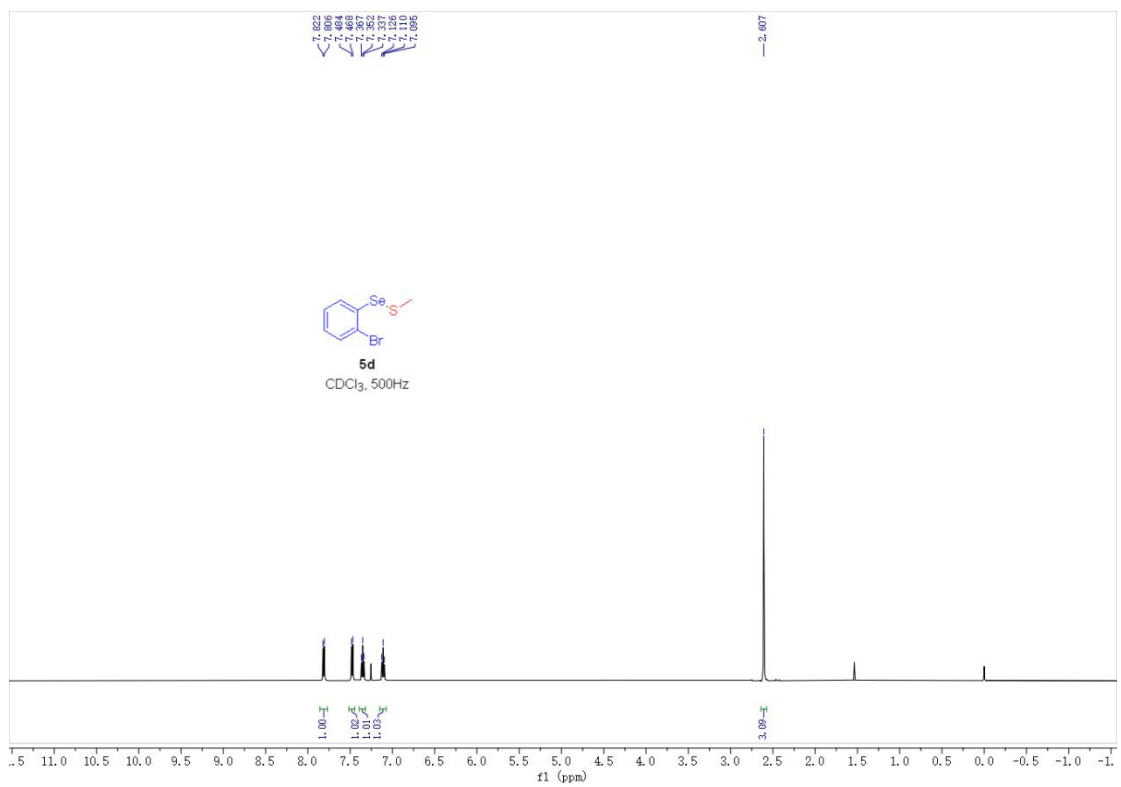
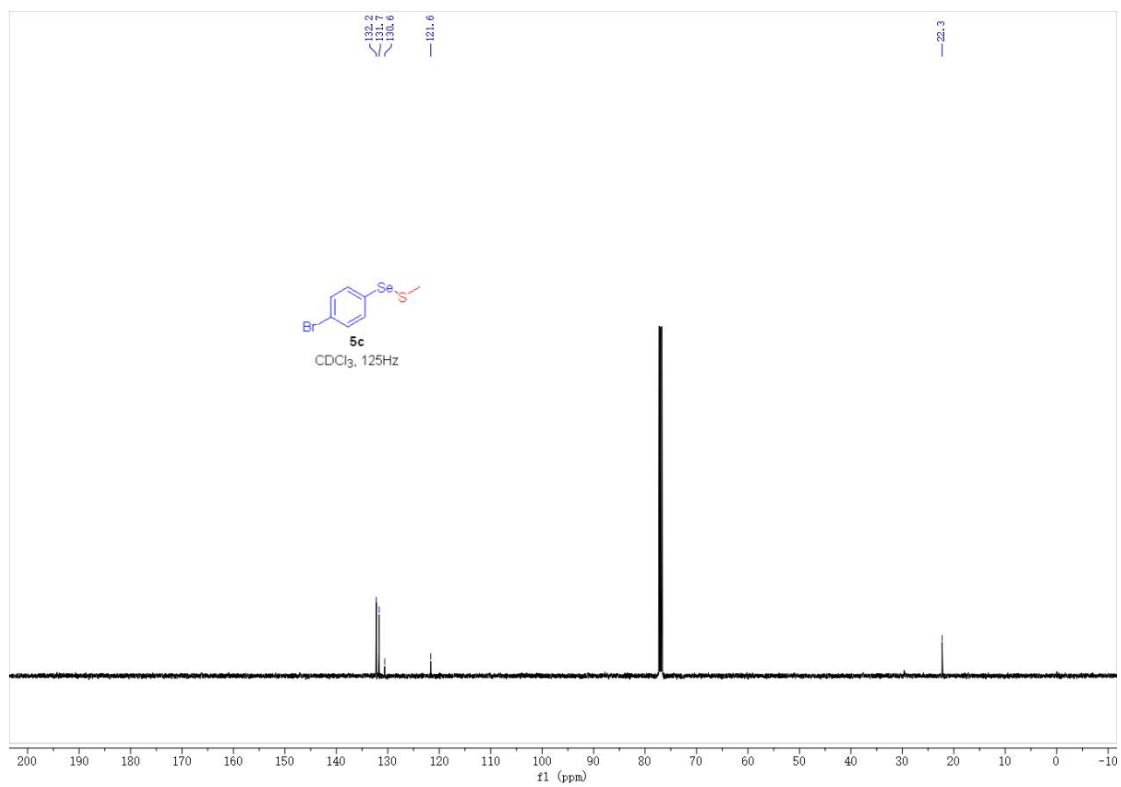


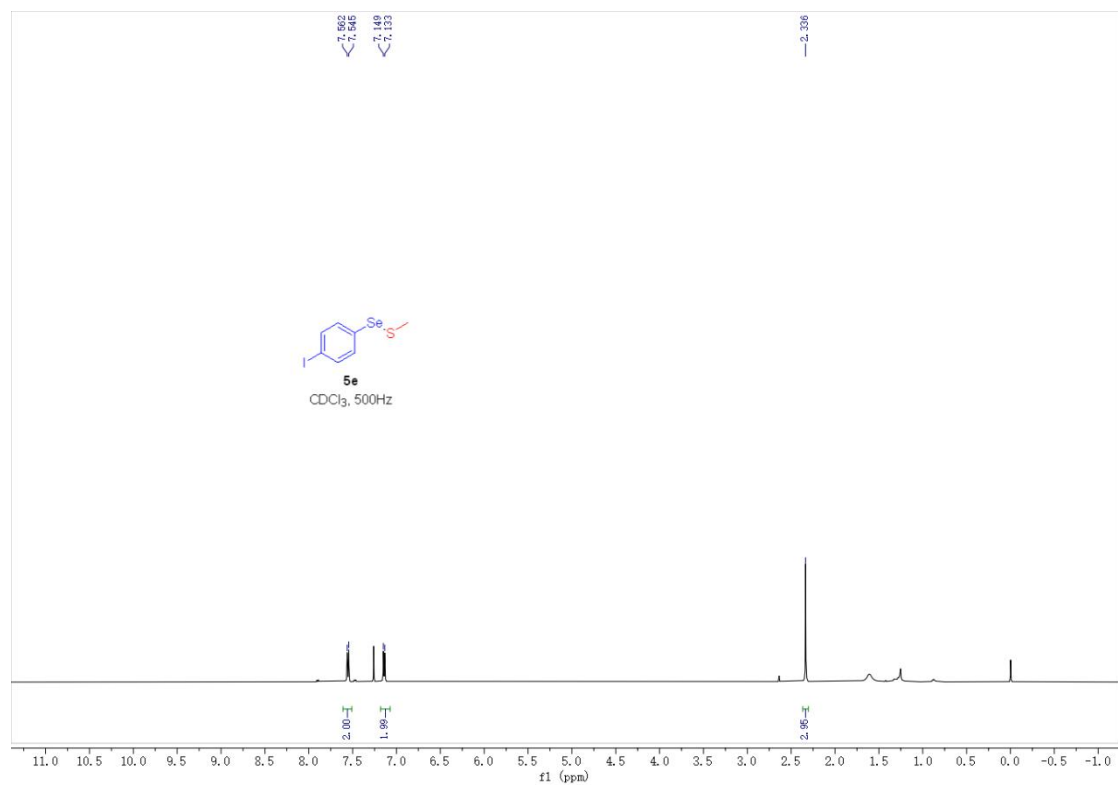
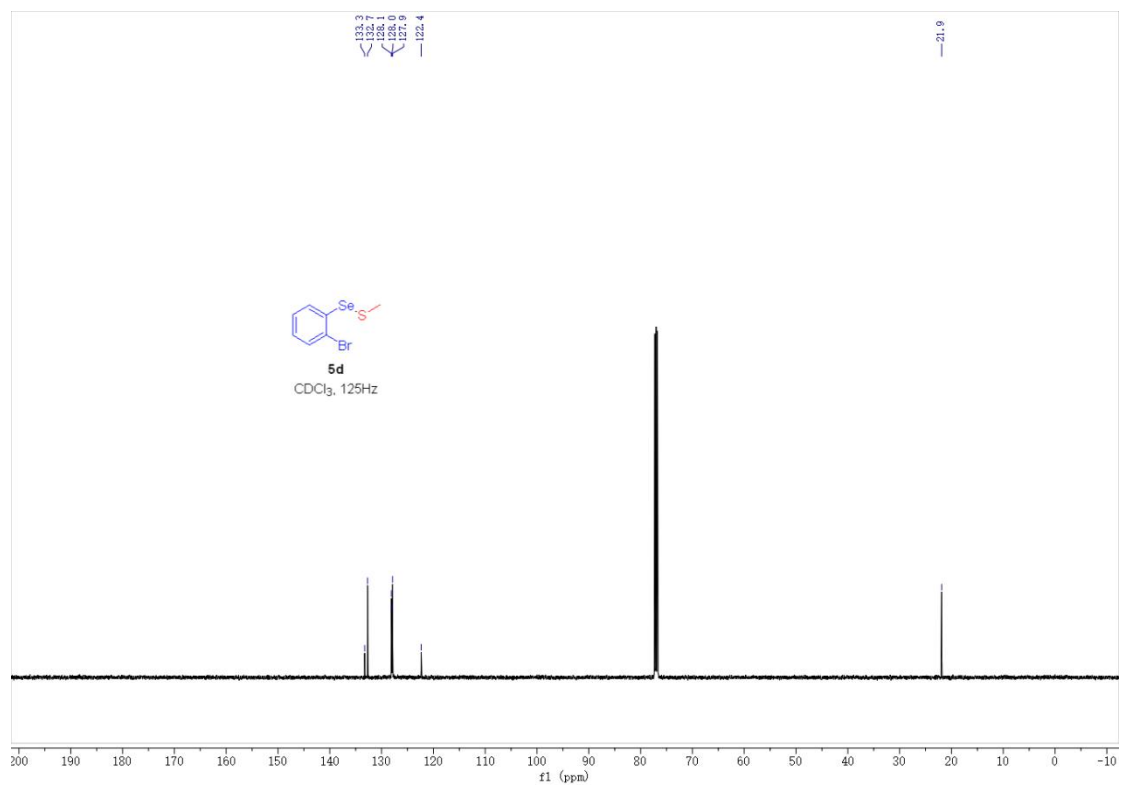


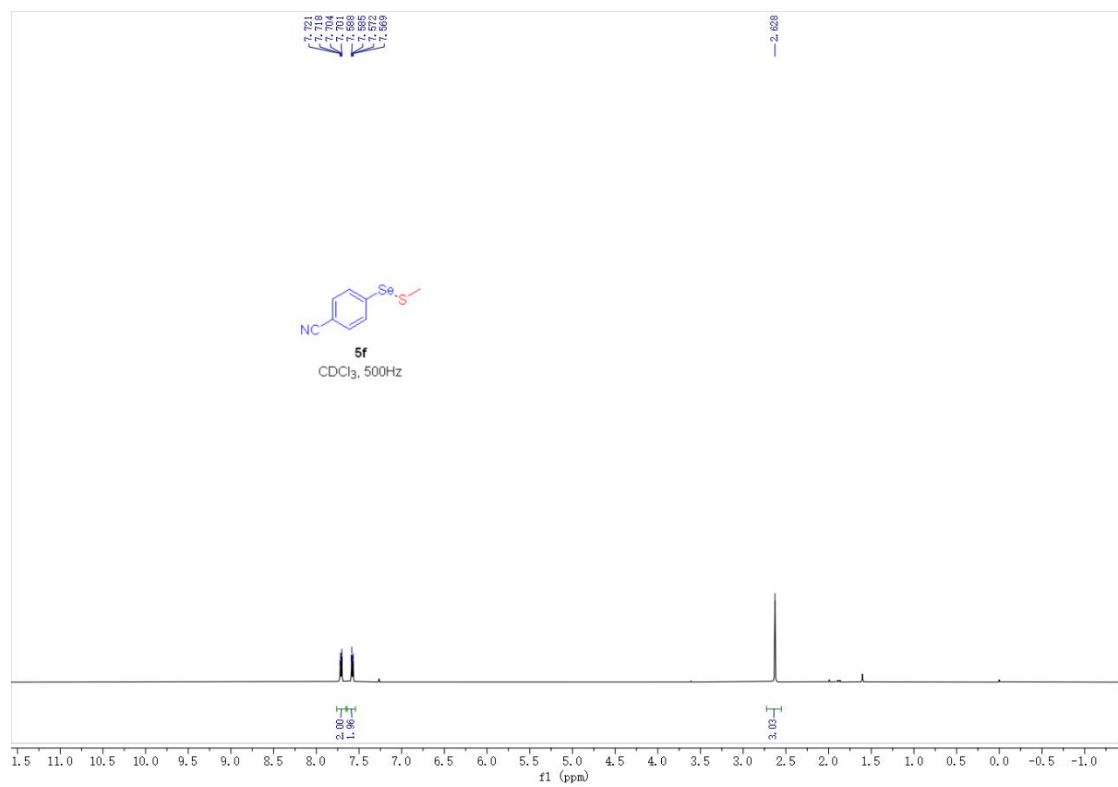
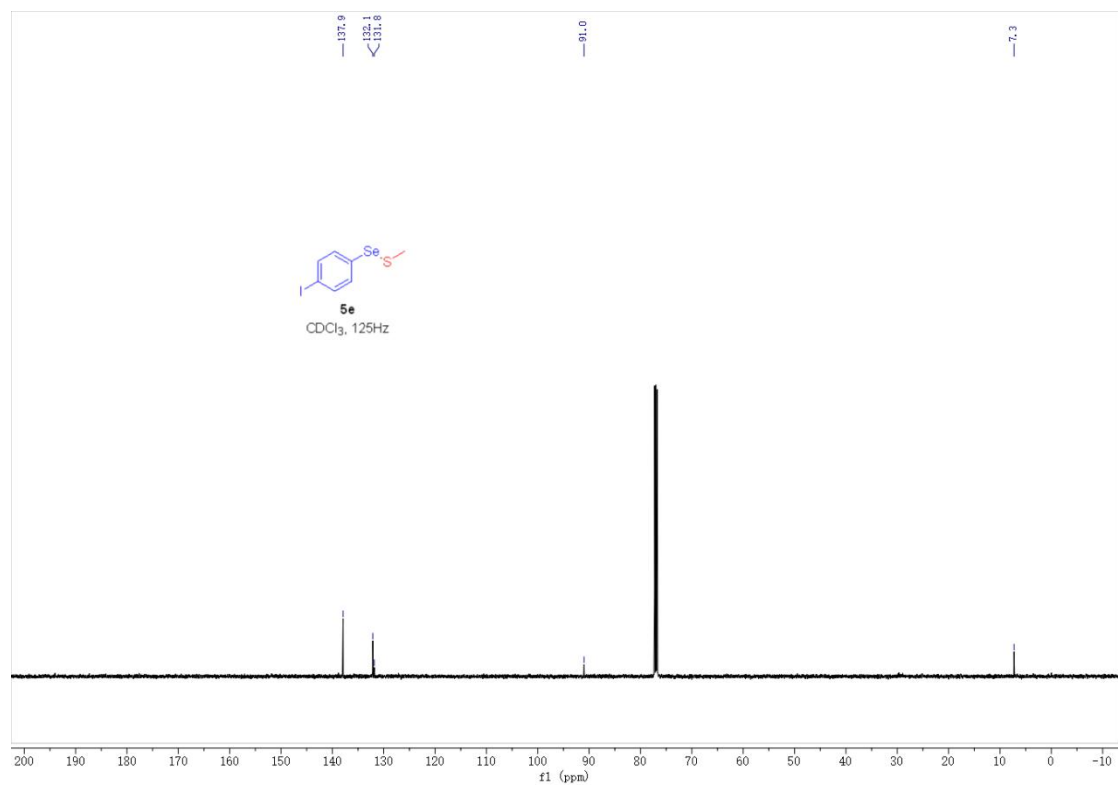


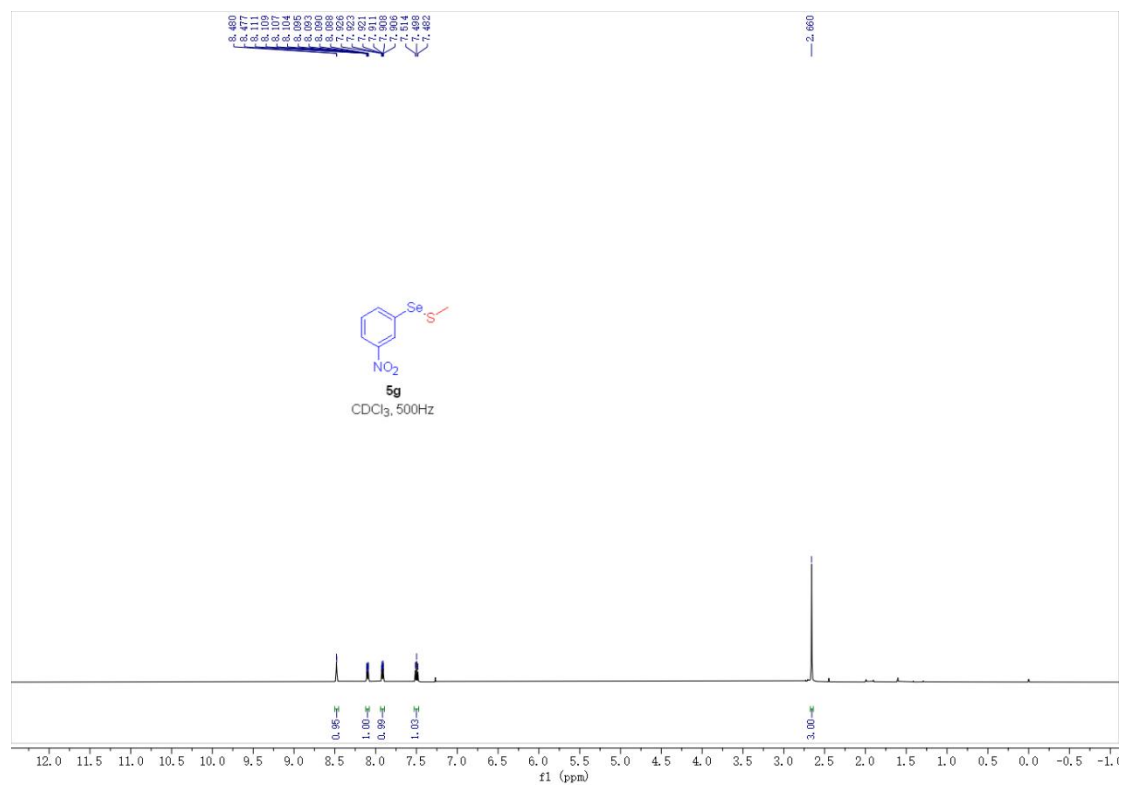
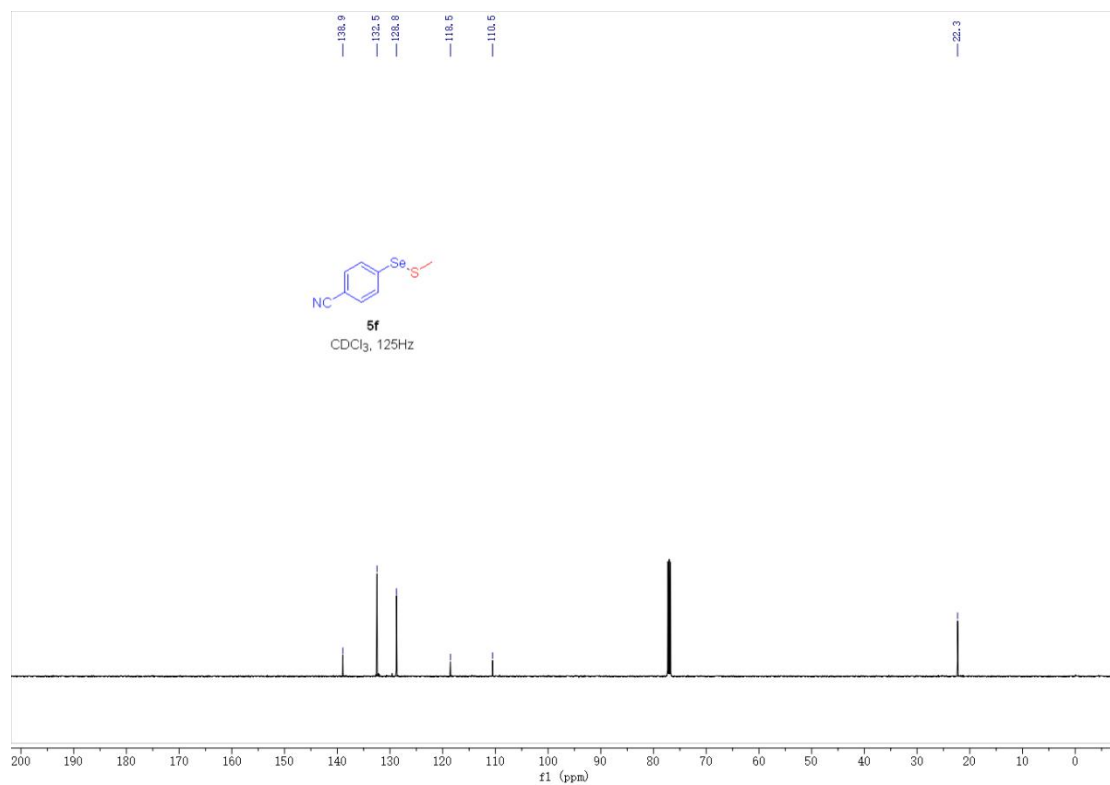


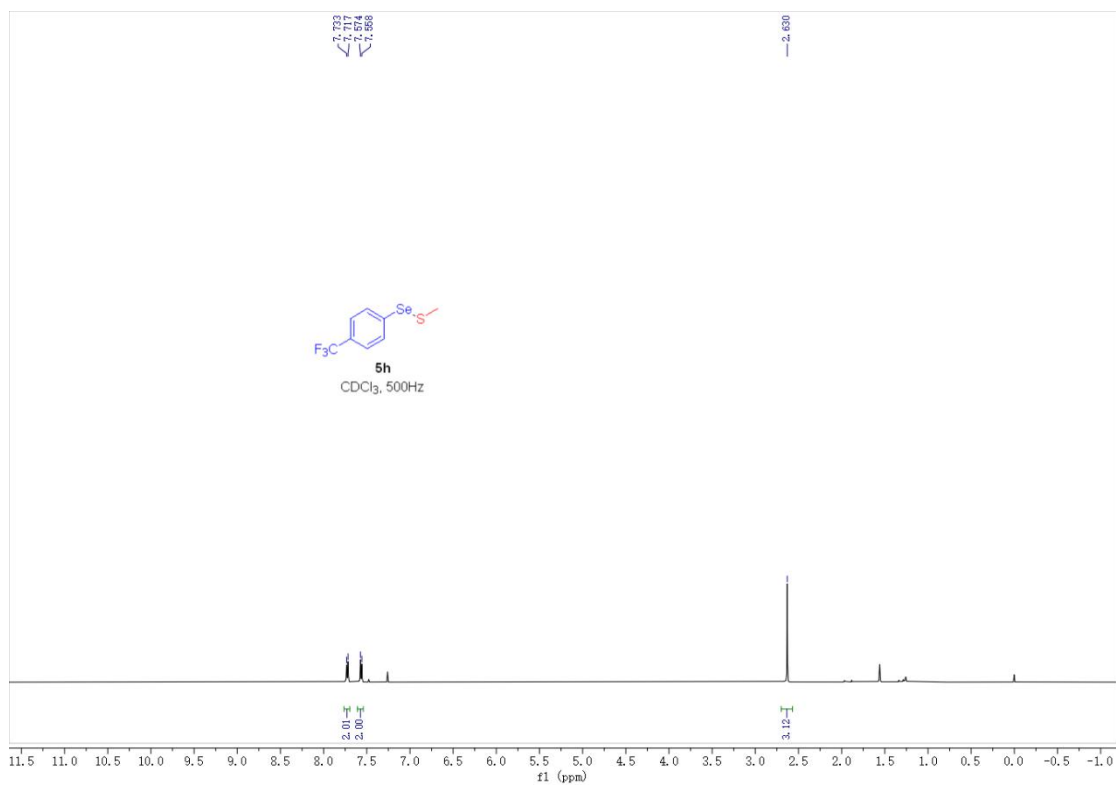
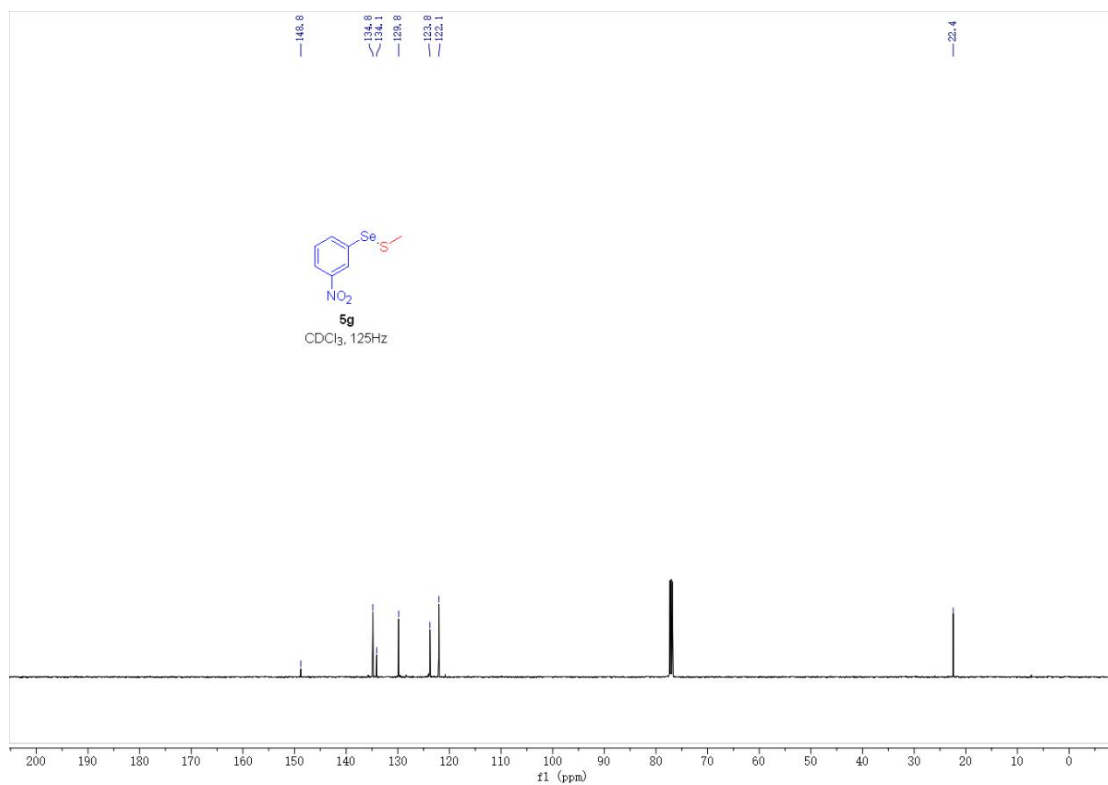


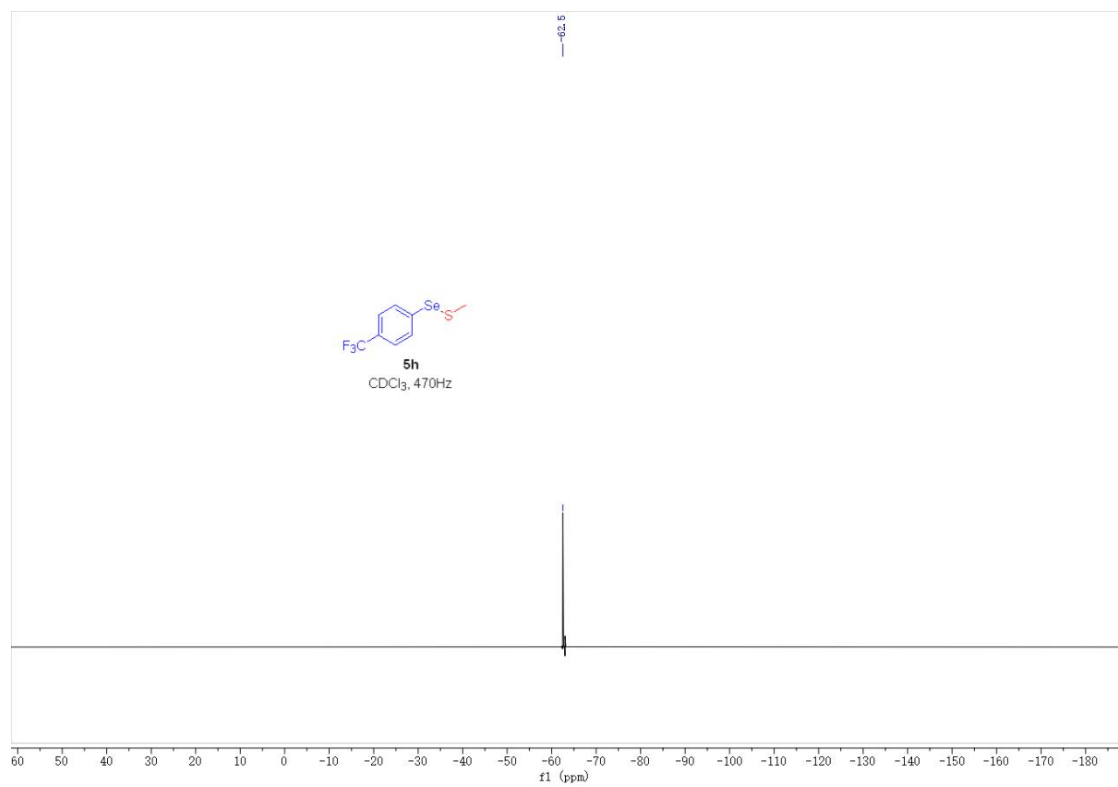
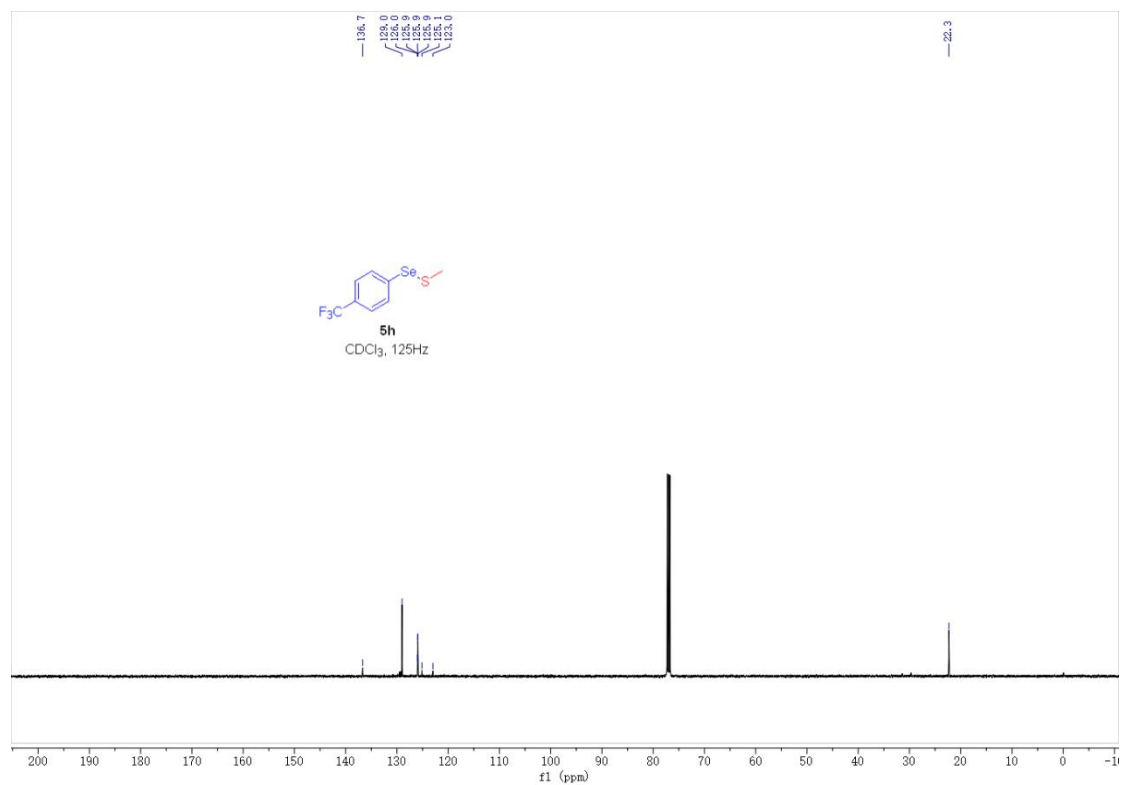


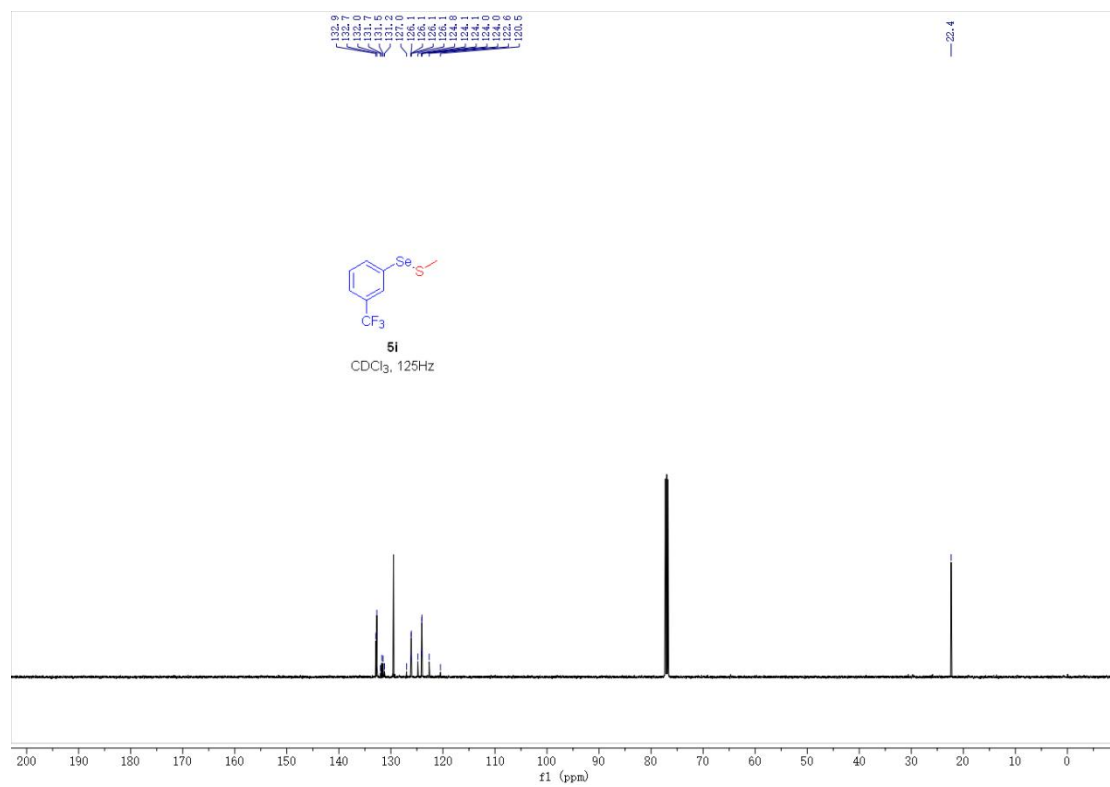
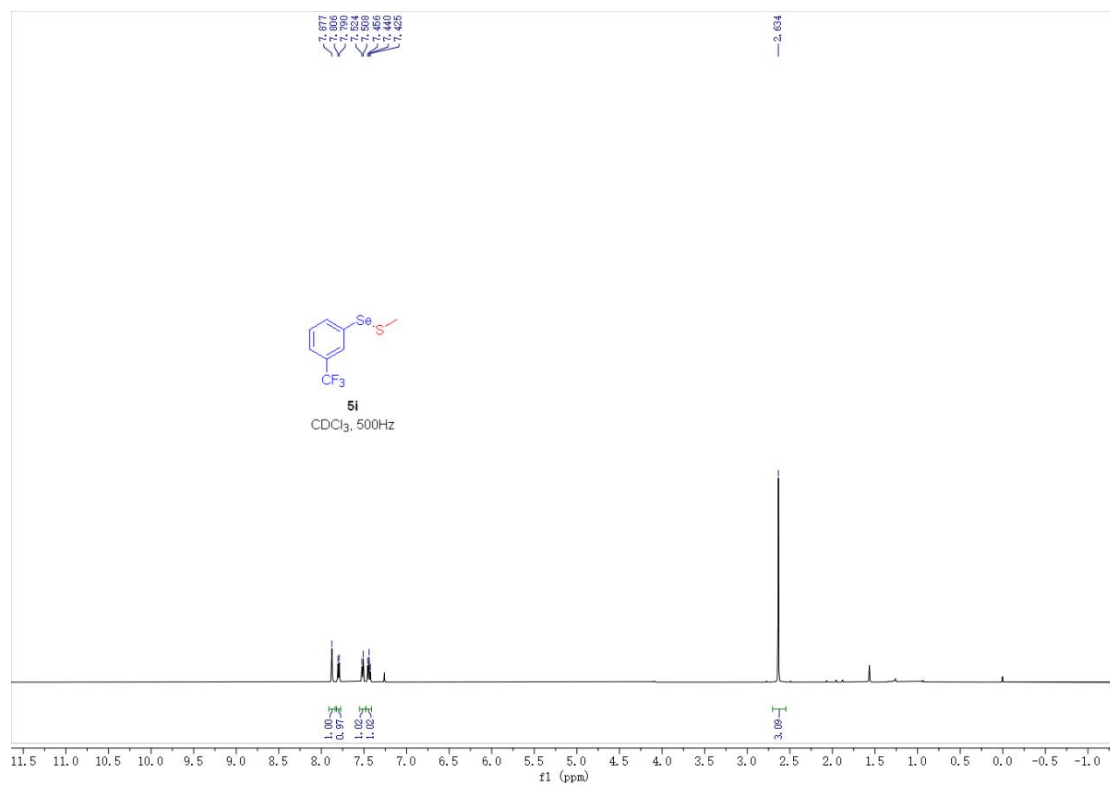


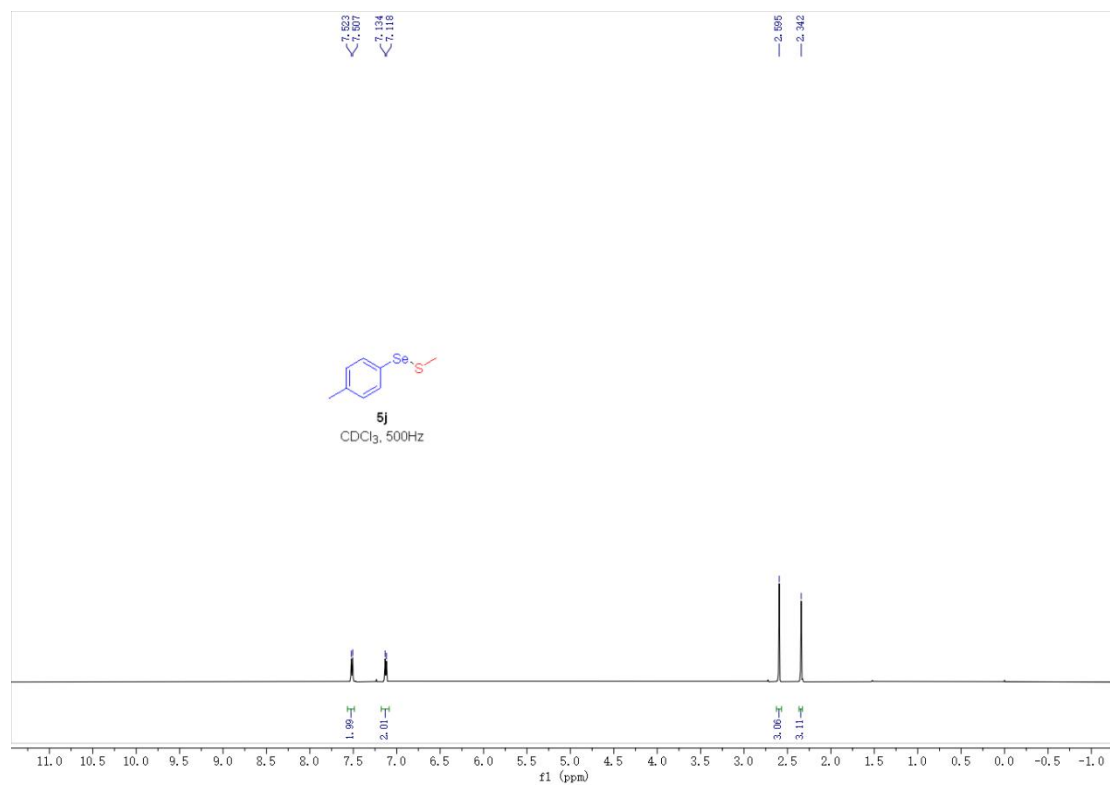
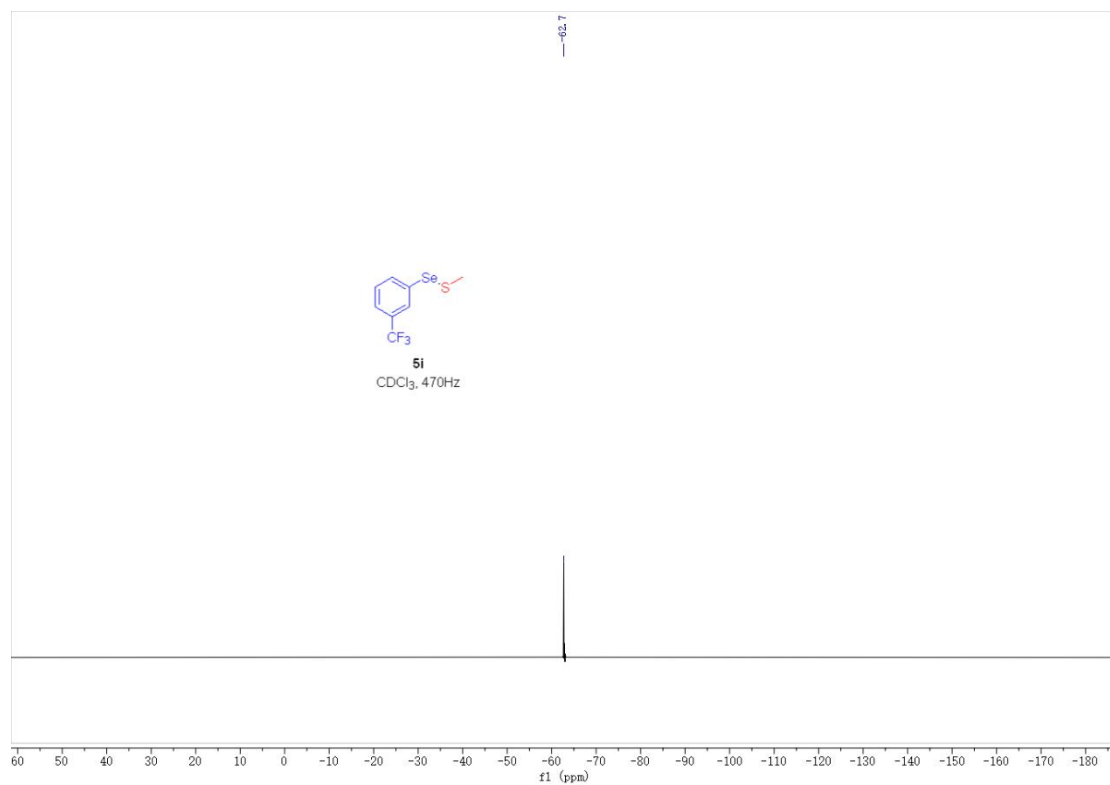


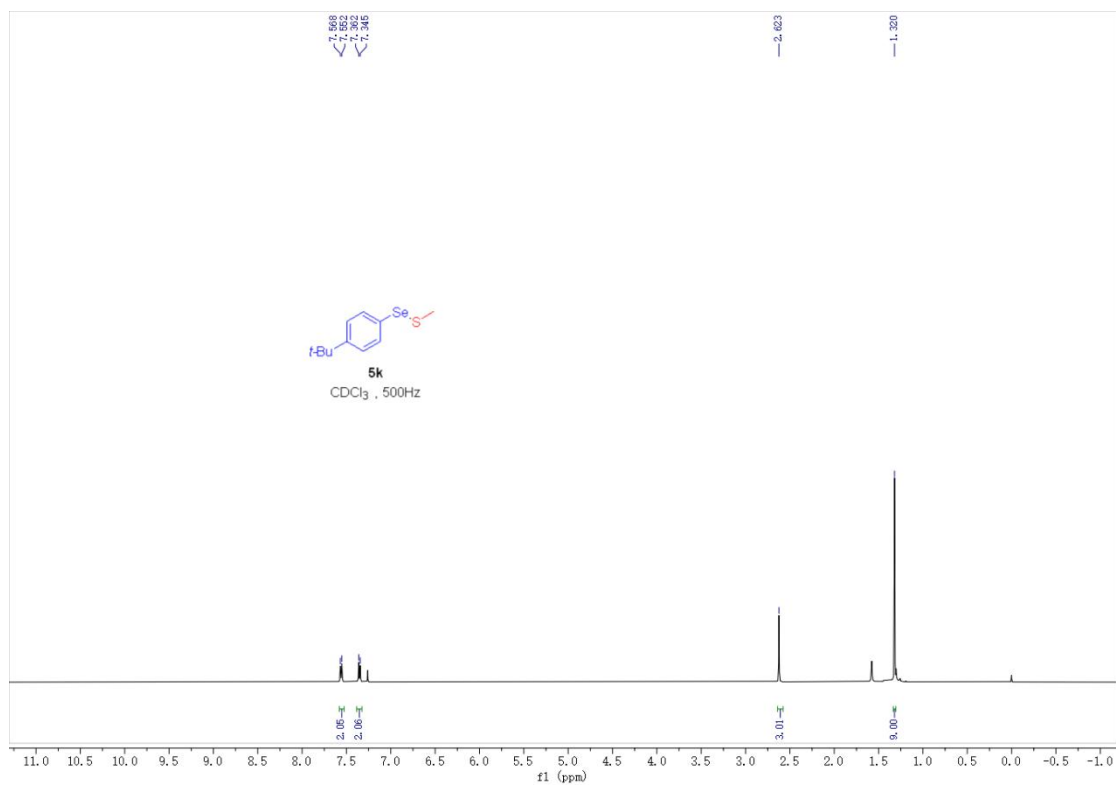
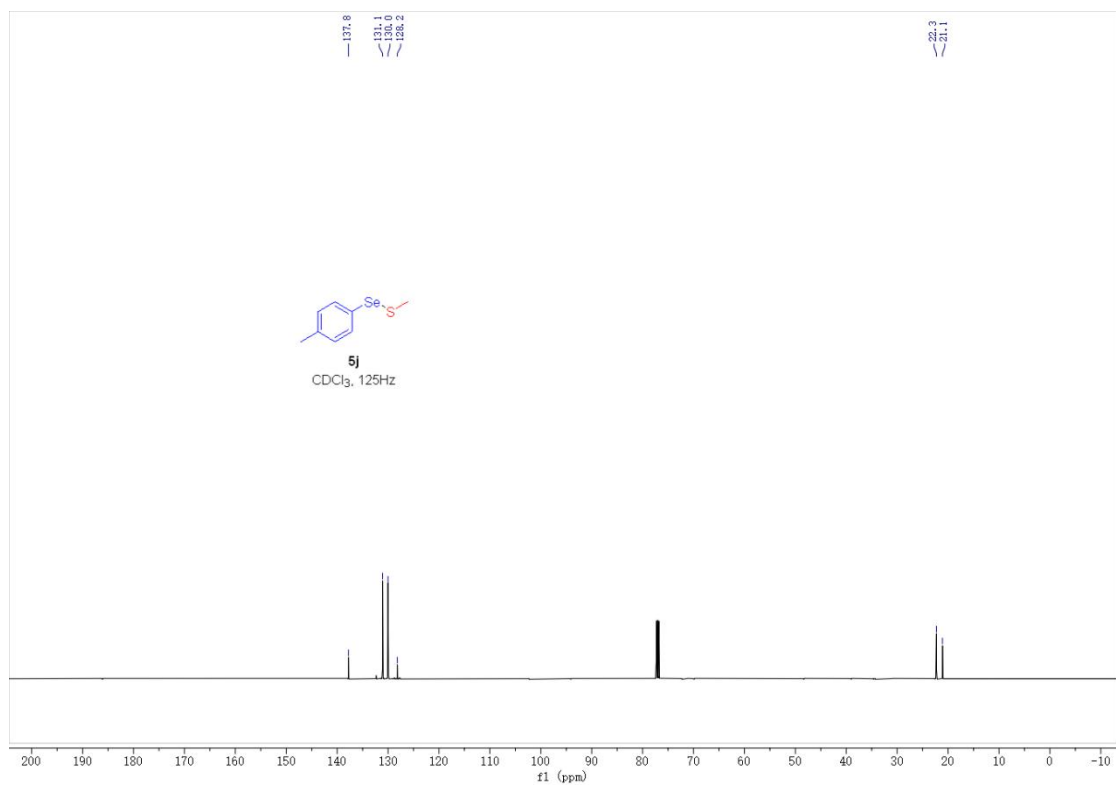


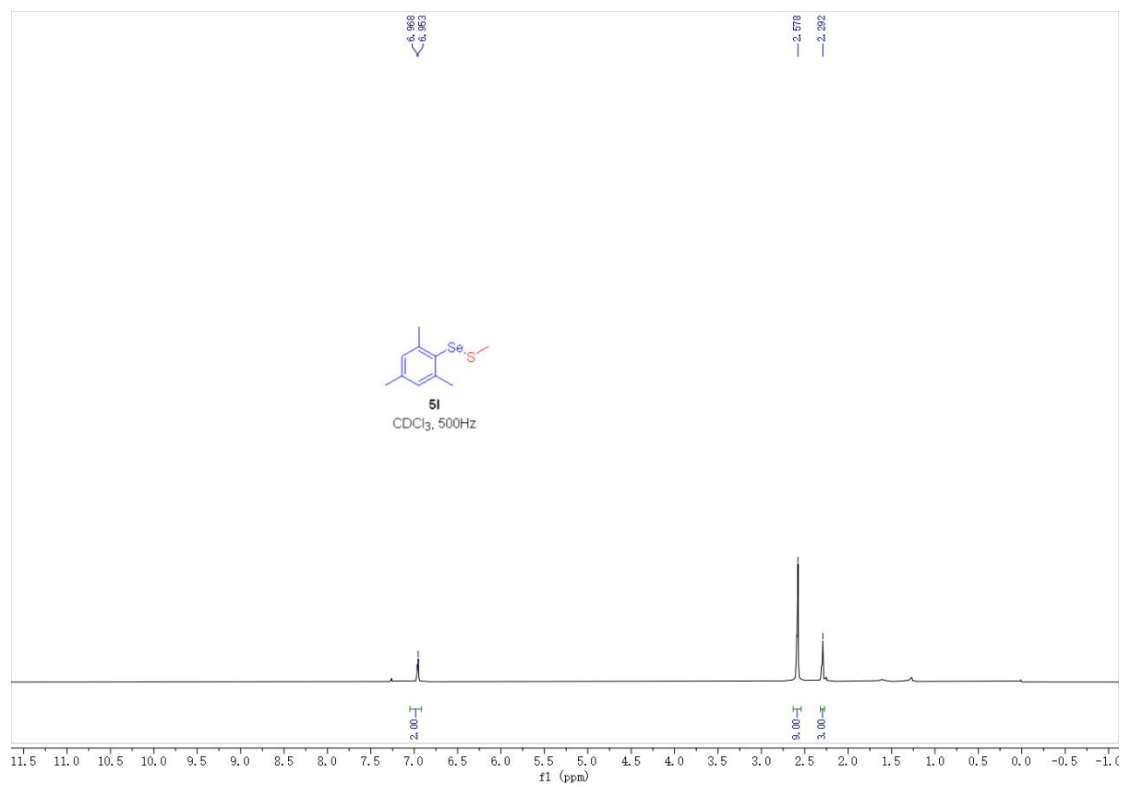
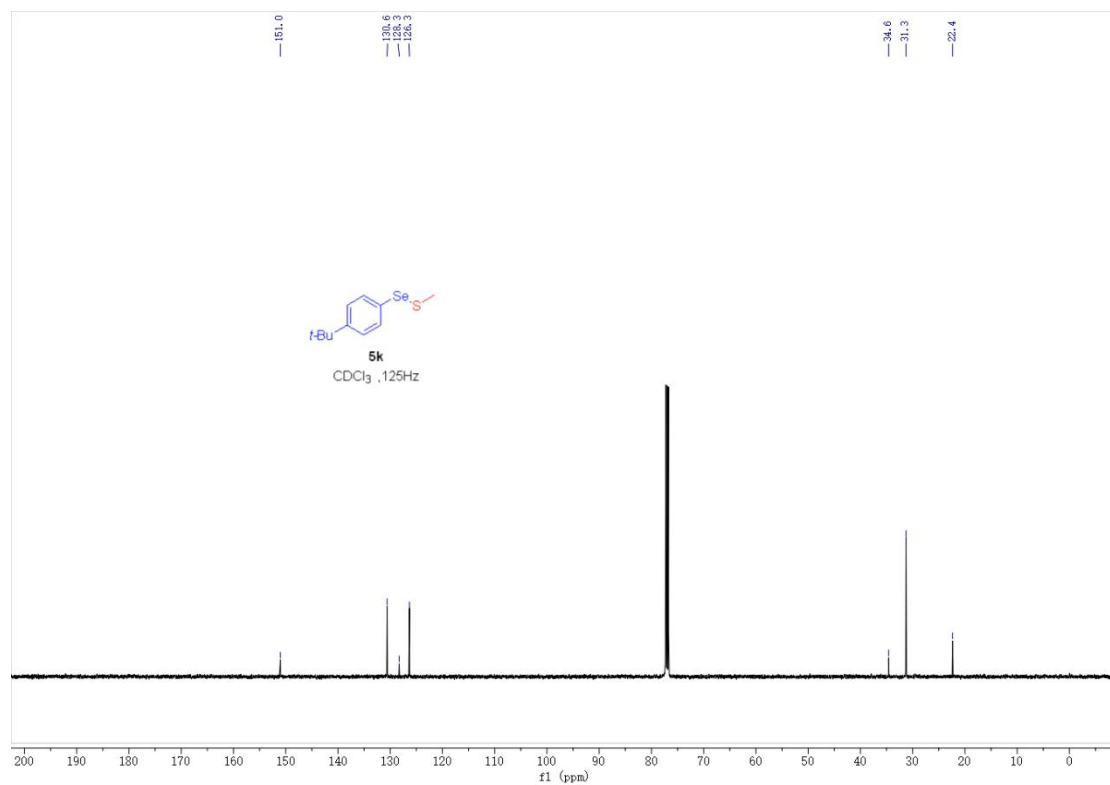


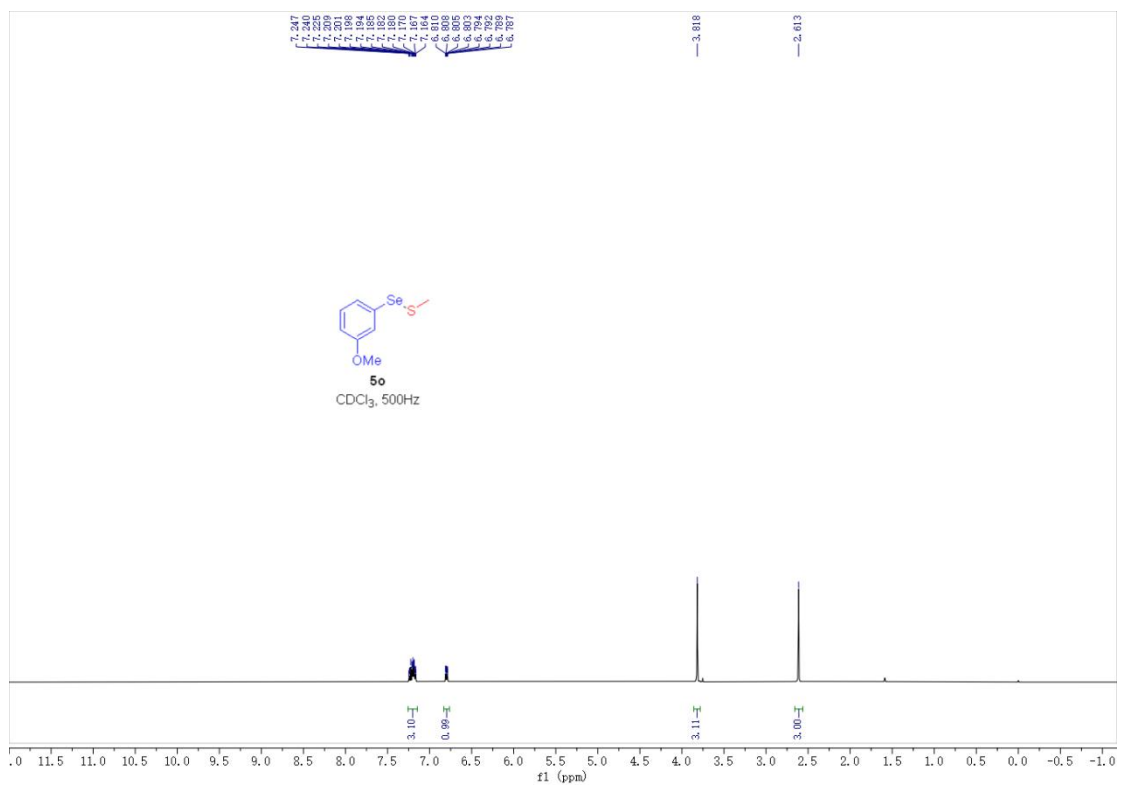
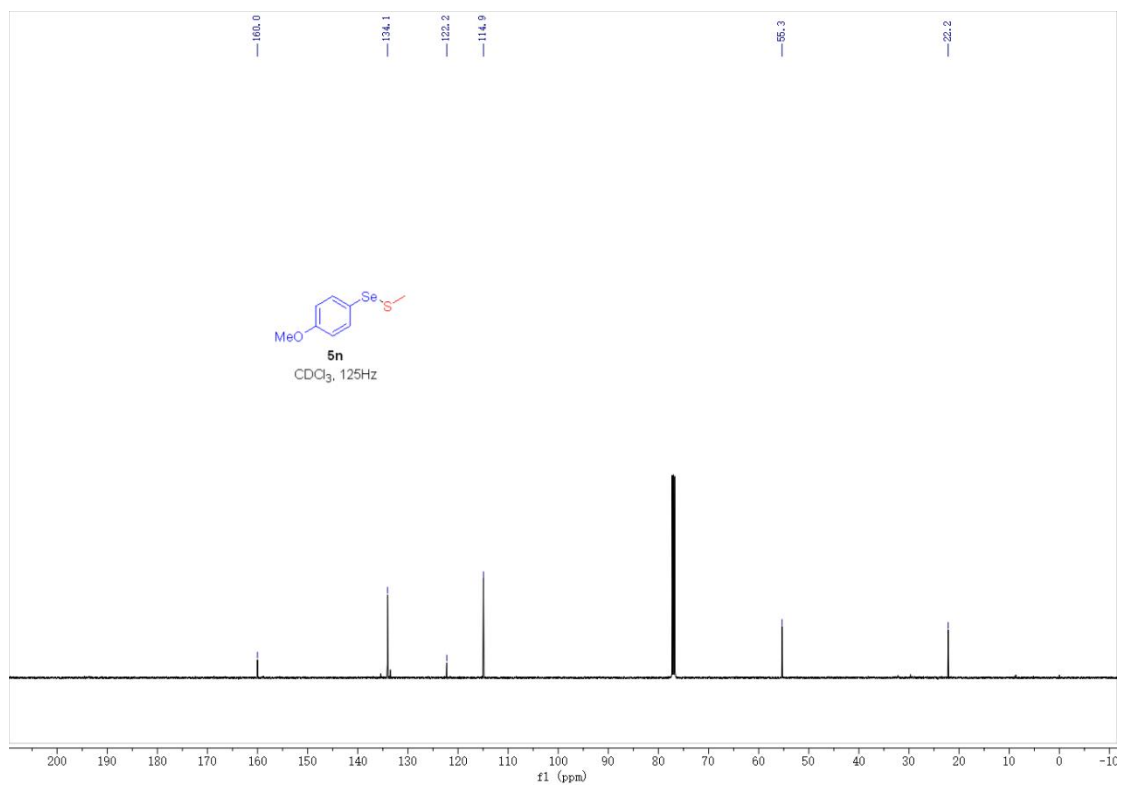


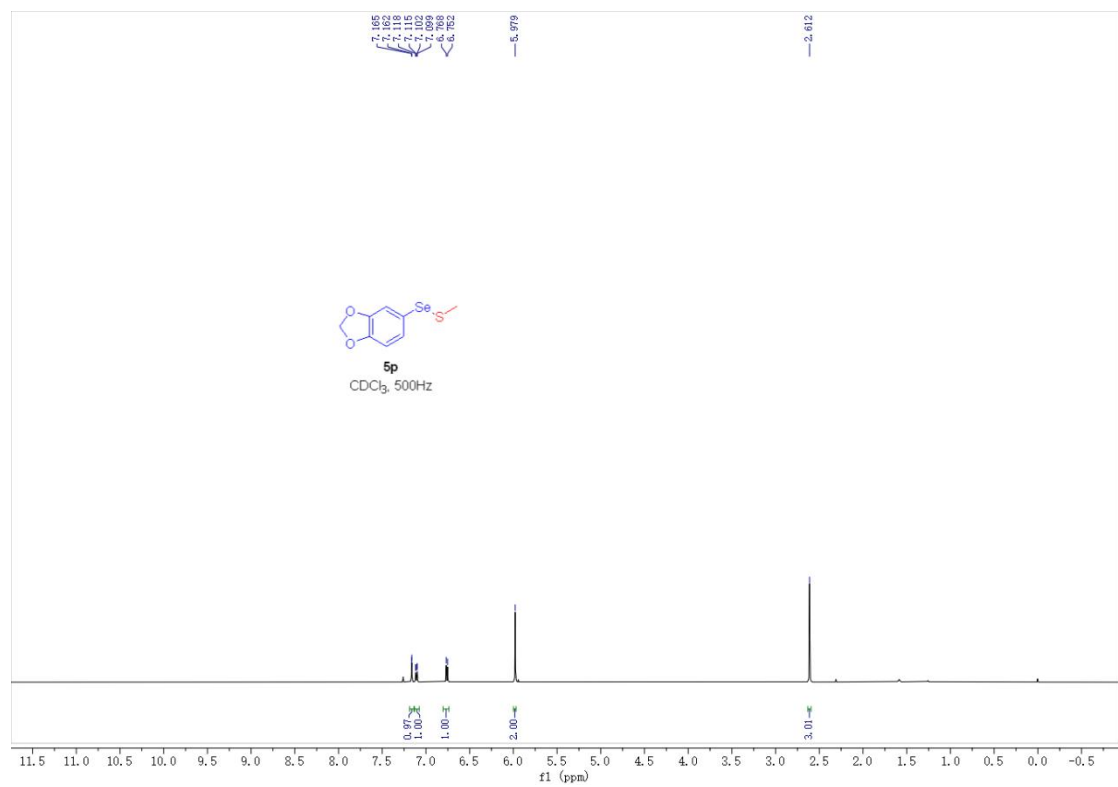
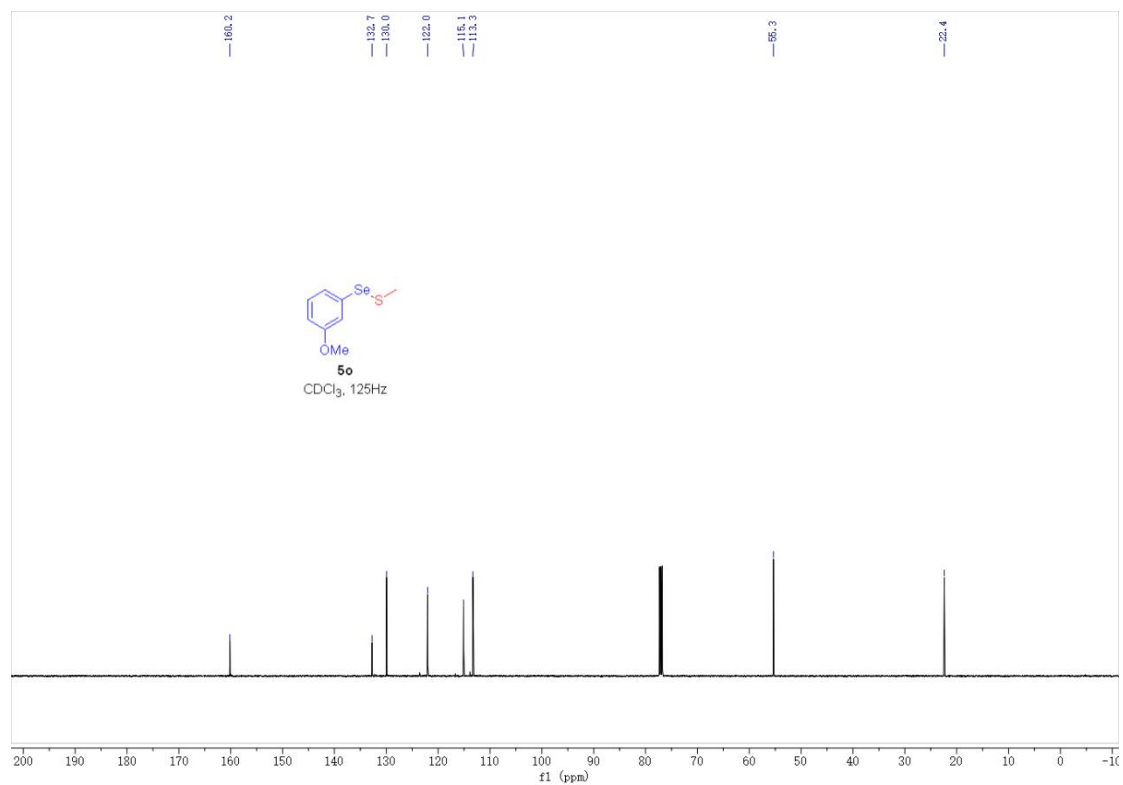


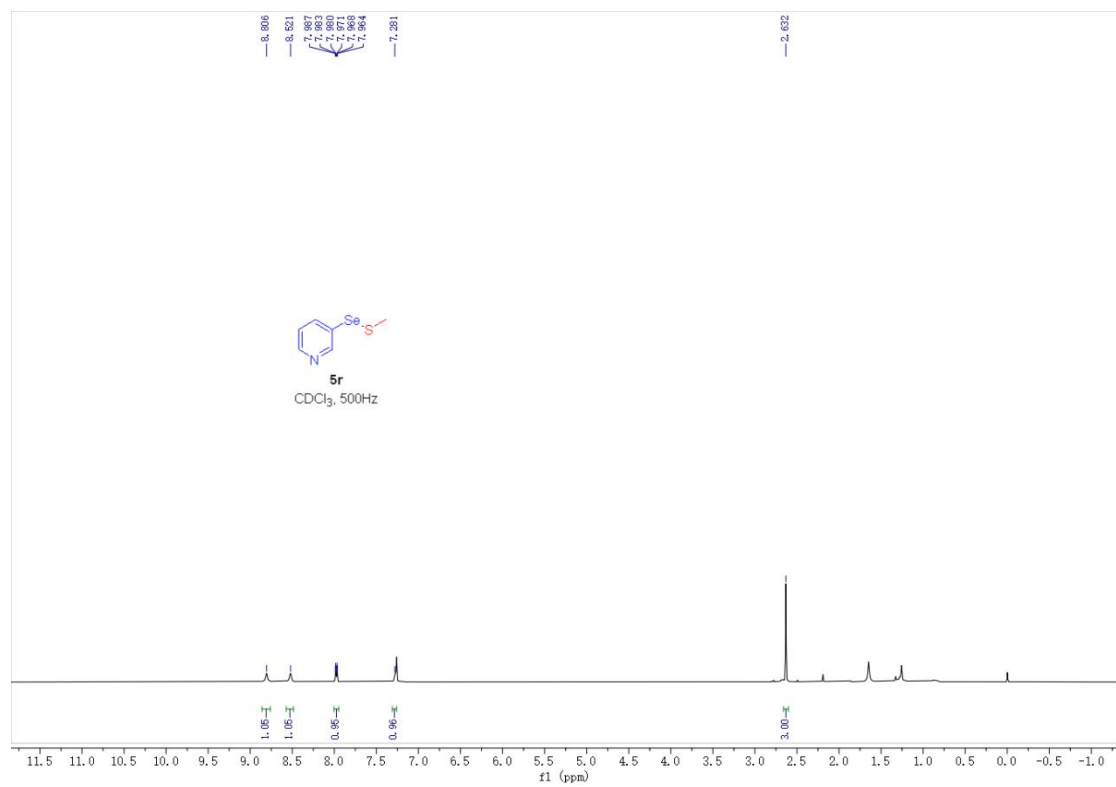
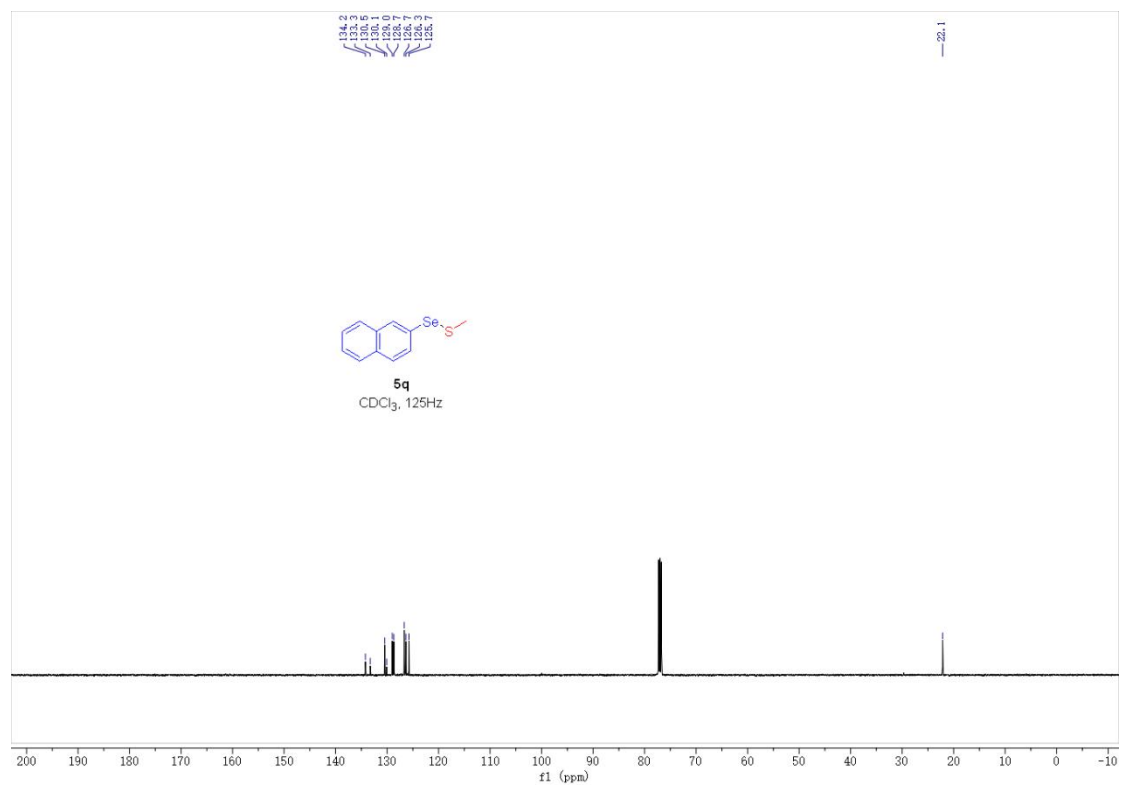


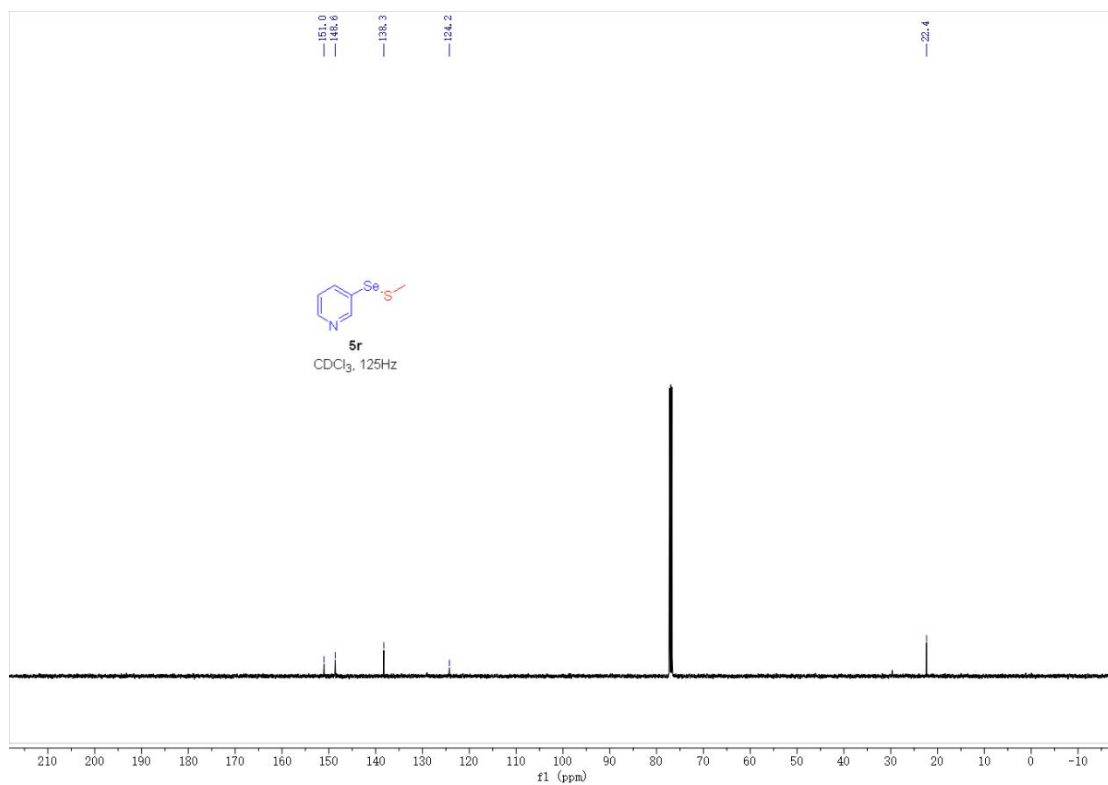






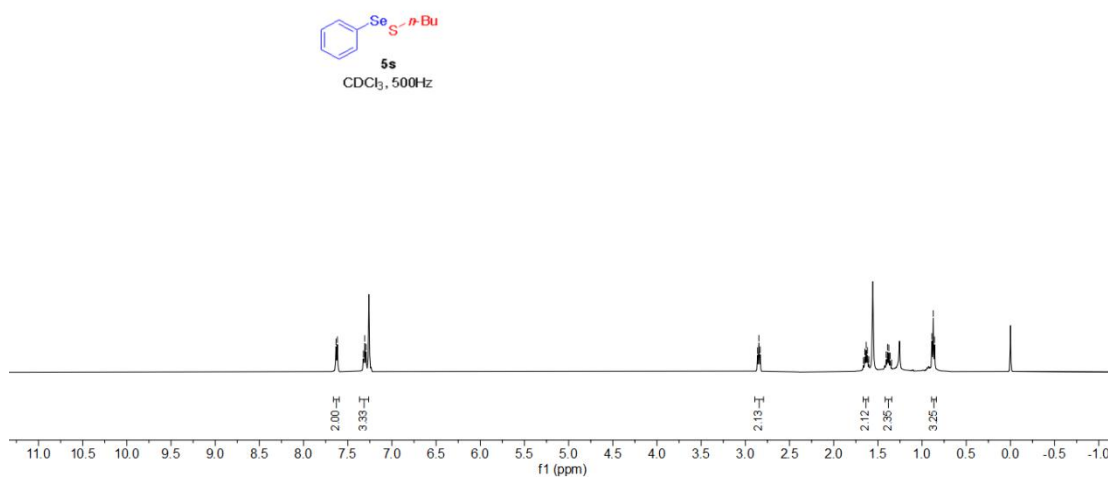






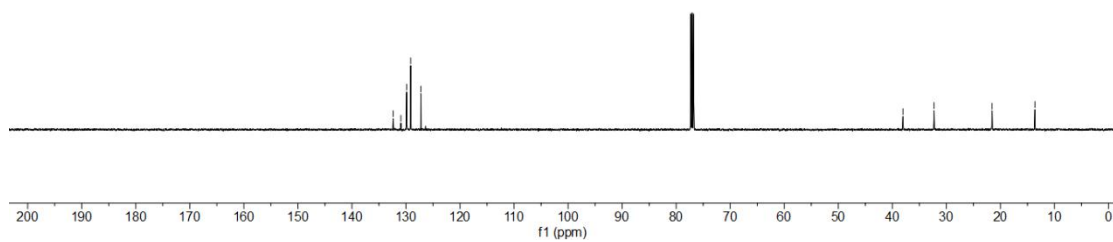
7.633
 7.518
 7.323
 7.300
 7.293

2.862
 2.848
 2.633
 1.663
 1.648
 1.633
 1.618
 1.603
 1.408
 1.391
 1.376
 1.361
 1.346
 0.889
 0.873
 0.859



132.4
130.9
128.9
127.2

—38.0
—32.3
—21.6
—13.6



7.616
7.611
7.606
7.598
7.593
7.593
7.590
7.585
7.578
7.572
7.564
7.552
7.549
7.549
7.539
6.835
6.822
6.802
6.795
—3.793

