

Supporting Information

**Iodine Pentoxide-Mediated Oxidative Selenation and
Seleno/Thiocyanation of Electron-Rich Arenes**

Yong-Hao Wang,[†] Yun-Qian Zhang,[†] Chen-Fan Zhou, You-Qin Jiang, Yue Xu, Xiaobao Zeng*
and Gong-Qing Liu*

[†] Y.-H. Wang and Y.-Q. Zhang contributed equally.

*School of Pharmacy and Jiangsu Province Key Laboratory for Inflammation and Molecular Drug
Target, Nantong University, 19 Qixiu Road, Nantong 226001, People's Republic of China*

E-mail: zengxb@ntu.edu.cn; gqliu@ntu.edu.cn

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1. General information

Reagents were used as received without further purification unless otherwise indicated. Solvents were dried and distilled prior to use. Petroleum ether used had a boiling point range of 60–90°C. Diselenides were prepared from the corresponding iodides with elemental selenium according to Braga's report.¹ Chromatographic purification of products was performed as flash column chromatography on silica gel (200–300 meshes). Thin-layer chromatography (TLC) was carried out on silica plates (TLC Silica GF₂₅₄). Visualization of the compounds was accomplished by projecting UV-light onto the developed plates. Nuclear magnetic resonance spectra were recorded at ambient temperature (unless otherwise stated) at 400 MHz (100 MHz for ¹³C) in CDCl₃ or DMSO-*d*₆. Chemical shifts were reported in ppm (δ) using TMS as internal standard, and spin–spin coupling constants (*J*) were given in Hz. Multiplicities of NMR signals are abbreviated as follows: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectrometry (HRMS) analyses were carried out on a Thermo Fisher Q Exactive Mass Spectrometer. Melting points were determined on glass slides using a digital display microscopic melting point apparatus and were presented uncorrected.

2. Photograph of the color of reaction mixture

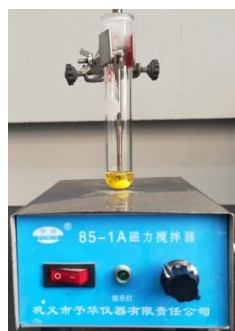


Fig. S1a at the beginning of the reaction

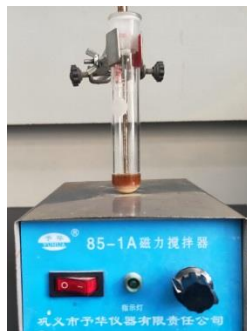


Fig. S1b at the end of the reaction



Fig. S1c after adding an aqueous Na₂S₂O₃

3. General procedure for selenation of electron rich arenes

The reaction was carried out in an open air system at ambient temperature. To a 10 mL vessel with magnetic stir bar were added 0.5 mmol indole/arene, 0.5

mmol diselenide, 0.5 mmol I₂O₅ and 2 mL of CH₃CN. The reaction mixture was stirred for an indicated time. Then, the reaction was quenched with a saturated aqueous Na₂S₂O₃ solution and extracted with EtOAc. The combined organic layers were dried (Na₂SO₄) and concentrated to give a crude residue, which was purified by flash column chromatography.

4. Characterization data

3-(Phenylselanyl)-1H-indole (3aa). Compound **3aa** was prepared according to the general procedure and isolated as a yellow solid (122 mg, 90% yield) after flash chromatography (petroleum ether/ethyl acetate = 20/1). mp=135-136 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.36 (brs, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 2.5 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.13 (m, 3H), 7.13 – 6.97 (m, 4H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 135.3, 132.8, 130.2, 128.9, 127.9, 127.6, 124.5, 121.9, 119.8, 119.3, 110.3, 97.1. The data are in accordance with the literature.²

4-Methyl-3-(phenylselanyl)-1H-indole (3ab). Compound **3ab** was prepared according to the general procedure and isolated as a brown solid (122 mg, 85% yield) after flash chromatography (petroleum ether/ethyl acetate = 25/1). mp=110-112 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.15 (brs, 1H), 7.30 (d, *J* = 2.6 Hz, 1H), 7.25 – 7.14 (m, 3H), 7.14 – 7.01 (m, 4H), 6.87 (d, *J* = 7.1 Hz, 1H), 2.68 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.9, 136.2, 132.6, 132.3, 129.2, 128.2, 127.3, 125.5, 123.1, 122.5, 109.5, 96.8, 19.0. The data are in accordance with the literature.²

5-Methyl-3-(phenylselanyl)-1H-indole (3ac). Compound **3ac** was prepared according to the general procedure and isolated as a brown solid (122 mg, 85% yield) after flash chromatography (petroleum ether/ethyl acetate = 20/1). mp=93-95 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.34 – 7.25 (m, 2H), 7.25 – 7.20 (m, 2H), 7.20 – 7.05 (m, 4H), 3.83 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 137.5, 135.7, 134.2, 130.7, 128.9, 128.6, 125.5, 122.5, 120.5, 120.4, 109.6, 96.0, 33.1. The data are in accordance with the literature.²

6-Methyl-3-(phenylselanyl)-1H-indole (3ad). Compound **3ad** was prepared according to the general procedure and isolated as a brown solid (113 mg, 79% yield)

after flash chromatography (petroleum ether/ethyl acetate = 20/1). mp=136-138 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.21 (brs, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 2.5 Hz, 1H), 7.26 – 7.17 (m, 3H), 7.17 – 7.04 (m, 3H), 6.99 (d, *J* = 8.2 Hz, 1H), 2.46 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.9, 134.0, 132.9, 130.7, 129.0, 128.6, 127.8, 125.6, 122.7, 120.0, 111.4, 97.9, 21.7. The data are in accordance with the literature.²

7-Methyl-3-(phenylselanyl)-1*H*-indole (3ae). Compound **3ae** was prepared according to the general procedure and isolated as a yellow solid (112 mg, 78% yield) after flash chromatography (petroleum ether/ethyl acetate = 25/1). mp=56-57 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.26 (brs, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 2.6 Hz, 1H), 7.29 – 7.19 (m, 2H), 7.15 – 6.96 (m, 5H), 2.49 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.0, 133.9, 131.0, 129.6, 129.0, 128.7, 125.6, 123.5, 121.1, 120.6, 118.1, 98.6, 16.5. The data are in accordance with the literature.²

Methyl 3-(phenylselanyl)-1*H*-indole-4-carboxylate (3af). Compound **3af** was prepared according to the general procedure and isolated as an oil (112 mg, 68% yield) after flash chromatography (petroleum ether/ethyl acetate = 2/1). ¹H NMR (400 MHz, CDCl₃): δ 8.85 (brs, 1H), 7.60 – 7.45 (m, 2H), 7.33 – 7.25 (m, 2H), 7.27 – 7.20 (m, 2H), 7.18 – 7.09 (m, 3H), 3.72 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 169.4, 137.5, 134.1, 132.7, 130.1, 129.0, 126.1, 126.0, 125.1, 122.3, 121.9, 115.0, 98.3, 51.9. The data are in accordance with the literature.³

Methyl 3-(phenylselanyl)-1*H*-indole-5-carboxylate (3ag). Compound **3ag** was prepared according to the general procedure and isolated as white solid (124 mg, 75% yield) after flash chromatography (petroleum ether/ethyl acetate = 2/1). mp=155-157 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.73 (s, 1H), 8.41 (d, *J* = 1.7 Hz, 1H), 7.97 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.55 (d, *J* = 2.5 Hz, 1H), 7.54 – 7.41 (m, 1H), 7.29 – 7.17 (m, 2H), 7.19 – 7.02 (m, 3H), 3.90 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 167.9, 139.0, 133.5, 132.7, 129.8, 129.1, 128.8, 125.8, 124.4, 123.2, 123.1, 111.3, 99.9, 52.0. The data are in accordance with the literature.²

Methyl 3-(phenylselanyl)-1*H*-indole-6-carboxylate (3ah). Compound **3ah** was prepared according to the general procedure and isolated as a white solid (134 mg, 81%

yield) after flash chromatography (petroleum ether/ethyl acetate = 2/1). mp=164-166 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.82 (brs, 1H), 8.22 (d, *J* = 1.4 Hz, 1H), 7.85 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.73 – 7.52 (m, 2H), 7.39 – 7.18 (m, 2H), 7.17 – 6.96 (m, 3H), 3.94 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 168.0, 135.8, 134.3, 133.7, 133.3, 129.1, 128.8, 125.9, 124.8, 121.9, 120.1, 113.8, 98.8, 52.1. The data are in accordance with the literature.³

5-Fluoro-3-(phenylselanyl)-1*H*-indole (3ai). Compound **3ai** was prepared according to the general procedure and isolated as a pink solid (96 mg, 66% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1). mp=116-118 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.41 (brs, 1H), 7.50 (d, *J* = 2.5 Hz, 1H), 7.34 (dd, *J* = 8.8, 4.2 Hz, 1H), 7.27 (dd, *J* = 9.3, 2.5 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.18 – 7.07 (m, 3H), 6.99 (td, *J* = 9.0, 2.6 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 158.7 (d, *J* = 236.5 Hz), 133.4, 132.9, 132.8, 130.9 (d, *J* = 10.2 Hz), 129.1, 128.8, 125.8, 112.2 (d, *J* = 9.6 Hz), 111.5 (d, *J* = 26.7 Hz), 105.4 (d, *J* = 24.2 Hz), 98.3 (d, *J* = 4.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ -122.7. The data are in accordance with the literature.³

5-Chloro-3-(phenylselanyl)-1*H*-indole (3aj). Compound **3aj** was prepared according to the general procedure and isolated as a white solid (115 mg, 75% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1). mp=192-193 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.40 (brs, 1H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.45 (d, *J* = 2.3 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.25 – 7.16 (m, 3H), 7.17 – 7.05 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 134.8, 133.4, 132.6, 131.3, 129.1, 128.7, 126.8, 125.9, 123.4, 119.9, 112.5, 98.0. The data are in accordance with the literature.³

5-Bromo-3-(phenylselanyl)-1*H*-indole (3ak). Compound **3ak** was prepared according to the general procedure and isolated as a white solid (128 mg, 73% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1). mp=97-99 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.45 (brs, 1H), 7.77 (d, *J* = 1.7 Hz, 1H), 7.46 (d, *J* = 2.5 Hz, 1H), 7.39 – 7.27 (m, 2H), 7.25 – 7.17 (m, 2H), 7.17 – 7.09 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 135.1, 133.4, 132.4, 131.9, 129.1, 128.7, 126.0, 125.9, 123.0, 114.4, 112.9, 97.9. The data are in accordance with the literature.³

5-Iodo-3-(phenylselanyl)-1*H*-indole (3al). Compound **3al** was prepared according to

the general procedure and isolated as a white solid (139 mg, 70% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1). mp=128-130 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.43 (brs, 1H), 7.98 (d, *J* = 1.5 Hz, 1H), 7.50 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.24 – 7.10 (m, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 135.5, 133.4, 132.6, 132.1, 131.4, 129.2, 129.1, 128.7, 125.9, 113.4, 97.5, 84.7. The data are in accordance with the literature.⁴

5-Methoxy-3-(phenylselanyl)-1*H*-indole (3am). Compound **3am** was prepared according to the general procedure and isolated as an oil (137 mg, 91% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1). ¹H NMR (400 MHz, CDCl₃): δ 8.37 (brs, 1H), 7.39 (d, *J* = 2.6 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.22 (dt, *J* = 6.0, 1.5 Hz, 2H), 7.17 – 7.02 (m, 4H), 6.90 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.78 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.1, 134.0, 132.0, 131.3, 130.8, 129.0, 128.5, 125.6, 113.5, 112.3, 101.6, 97.6, 55.8. The data are in accordance with the literature.³

3-(Phenylselanyl)-1*H*-indole-5-carbonitrile (3an). Compound **3an** was prepared according to the general procedure and isolated as a white solid (74 mg, 50% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1). mp=151-152 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.86 (brs, 1H), 7.98 (d, *J* = 1.2 Hz, 1H), 7.62 (d, *J* = 2.5 Hz, 1H), 7.55 – 7.43 (m, 2H), 7.29 – 7.20 (m, 2H), 7.19 – 7.07 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 138.2, 133.2, 132.5, 130.0, 129.19, 129.16, 126.2, 126.1, 125.9, 120.3, 112.5, 104.1, 99.8. The data are in accordance with the literature.²

3-(Phenylselanyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (3ao). Compound **3ao** was prepared according to the general procedure and isolated as a pink solid (139 mg, 70% yield) after flash chromatography (petroleum ether/ethyl acetate = 6/1). mp=166-168 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.57 (brs, 1H), 8.21 (d, *J* = 1.1 Hz, 1H), 7.71 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.13 – 7.02 (m, 3H), 1.33 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 138.5, 134.3, 131.8, 129.8, 129.1, 129.0, 128.4, 127.9, 125.5, 110.9, 98.6, 83.6, 24.9. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₀H₂₃BNO₂Se, 400.0982; found, 400.0986.

3-(Phenylselanyl)-6-(trifluoromethyl)-1*H*-indole (3ap). Compound **3ap** was

prepared according to the general procedure and isolated as a brown solid (116 mg, 68% yield) after flash chromatography (petroleum ether/ethyl acetate = 4/1). mp=110-111 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.61 (brs, 1H), 7.84 – 7.64 (m, 2H), 7.59 (d, *J* = 2.6 Hz, 1H), 7.39 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.27 – 7.18 (m, 2H), 7.18 – 7.03 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 135.3, 133.6, 133.1, 132.4, 129.1, 128.9, 126.4, 126.0, 125.2 (q, *J*_{C-F} = 31.9 Hz), 123.7, 120.9, 117.6 (d, *J*_{C-F} = 3.5 Hz), 109.1 (q, *J*_{C-F} = 4.5 Hz), 98.9. ¹⁹F NMR (376 MHz, CDCl₃): δ -60.6. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₁₅H₁₁F₃NSe, 342.0003; found, 342.0014.

3-(Phenylselanyl)-1*H*-indole-7-carbaldehyde (3aq). Compound **3aq** was prepared according to the general procedure and isolated as a white solid (84 mg, 56% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1). mp=110-112 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.39 (brs, 1H), 10.13 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.70 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.16 – 7.03 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 193.4, 134.4, 133.3, 132.9, 131.2, 129.6, 129.1, 128.9, 127.8, 125.9, 120.9, 120.5, 98.8. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₁₅H₁₂N₂OSe, 302.0079; found, 302.0086.

1-Methyl-3-(phenylselanyl)-1*H*-indole (3ar). Compound **3ar** was prepared according to the general procedure and isolated as a brown solid (123 mg, 86% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1). mp=85-87 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.25 – 7.20 (m, 2H), 7.20 – 7.04 (m, 4H), 3.83 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 137.5, 135.7, 134.2, 130.7, 128.9, 128.6, 125.5, 122.5, 120.5, 120.4, 109.6, 96.0, 33.1. The data are in accordance with the literature.²

1-Benzyl-3-(phenylselanyl)-1*H*-indole (3as). Compound **3as** was prepared according to the general procedure and isolated as a white solid (147 mg, 81% yield) after flash chromatography (petroleum ether/ethyl acetate = 80/1). mp=75-77 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.40 (s, 1H), 7.36 – 7.27 (m, 4H), 7.27 – 7.19 (m, 3H), 7.20 – 7.04 (m, 6H), 5.36 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 137.1, 136.7, 135.0, 134.1, 130.9, 129.0, 128.9, 128.5, 127.9, 127.0, 125.5, 122.7, 120.7, 120.6, 110.1, 96.8, 50.4. The data are in accordance with the literature.²

2-Methyl-3-(phenylselanyl)-1H-indole (3at). Compound **3at** was prepared according to the general procedure and isolated as a pink solid (122 mg, 85% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1). mp=90-91 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.26 (brs, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.23 – 6.97 (m, 7H), 2.55 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 140.8, 135.8, 133.9, 131.2, 128.9, 128.3, 125.4, 122.1, 120.6, 119.8, 110.5, 96.3, 13.2. The data are in accordance with the literature.²

2-Phenyl-3-(phenylselanyl)-1H-indole (3au). Compound **3au** was prepared according to the general procedure and isolated as an oil (134 mg, 77% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1). ¹H NMR (400 MHz, CDCl₃): δ 8.54 (s, 1H), 7.70 (d, *J* = 6.8 Hz, 2H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.33 (m, 4H), 7.32 – 7.02 (m, 7H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 142.1, 136.2, 134.1, 132.1, 132.0, 129.1, 128.7, 128.6, 128.3, 125.5, 123.3, 121.1, 120.9, 111.1, 95.8. The data are in accordance with the literature.²

3-Methyl-2-(phenylselanyl)-1H-indole (3av). Compound **3av** was prepared according to the general procedure and isolated as an oil (76 mg, 53% yield) after flash chromatography (petroleum ether/ethyl acetate = 20/1). ¹H NMR (400 MHz, CDCl₃): δ 7.95 (brs, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.18 – 7.01 (m, 7H), 2.34 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.5, 131.0, 128.3, 128.2, 127.2, 125.3, 122.1, 118.9, 118.5, 118.2, 117.0, 109.7, 9.4. The data are in accordance with the literature.⁵

2-Methyl-3-(*p*-tolylselanyl)-1H-indole (3ba). Compound **3ba** was prepared according to the general procedure and isolated as an oil (111 mg, 74% yield) after flash chromatography (petroleum ether/ethyl acetate = 20/1). ¹H NMR (400 MHz, CDCl₃): δ 8.18 (brs, 1H), 7.72 – 7.47 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.02 (m, 4H), 6.93 (d, *J* = 7.9 Hz, 2H), 2.52 (s, 3H), 2.22 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): 140.7, 135.8, 135.2, 131.3, 130.0, 129.8, 128.6, 122.1, 120.6, 119.8, 110.5, 96.6, 20.9, 13.2. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₁₆H₁₆NSe, 302.0442; found, 302.0437.

3-((4-Methoxyphenyl)selanyl)-2-methyl-1H-indole (3bb). Compound **3bb** was

prepared according to the general procedure and isolated as an oil (123 mg, 78% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1). ^1H NMR (400 MHz, CDCl_3): δ 8.21 (brs, 1H), 7.57 (d, $J = 7.6$ Hz, 1H), 7.29 (d, $J = 7.6$ Hz, 2H), 7.22 – 7.02 (m, 4H), 6.69 (d, $J = 8.7$ Hz, 2H), 3.70 (s, 3H), 2.54 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): 158.1, 140.4, 135.7, 131.2, 130.7, 123.7, 122.0, 120.5, 119.8, 114.8, 110.4, 97.4, 55.3, 13.2. The data are in accordance with the literature.⁵

2-Methyl-3-((4-(trifluoromethoxy)phenyl)selanyl)-1H-indole (3bc). Compound **3bc** was prepared according to the general procedure and isolated as an oil (152 mg, 82% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1). ^1H NMR (400 MHz, CDCl_3): δ 8.27 (brs, 1H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.27 – 7.07 (m, 4H), 7.00 – 6.92 (m, 2H), 2.54 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 147.3 (d, $J_{\text{C-F}} = 2.1$ Hz), 141.0, 135.8, 132.45, 131.0, 129.4, 122.3, 121.7, 120.8, 119.6, 117.9 (q, $J_{\text{C-F}} = 256.9$ Hz), 110.6, 96.0, 13.2. ^{19}F NMR (376 MHz, CDCl_3): δ -58.0. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NOSe}$, 372.0109; found, 372.0126.

3-([1,1'-Biphenyl]-4-ylselanyl)-2-methyl-1H-indole (3bd). Compound **3bd** was prepared according to the general procedure and isolated as a brown solid (154 mg, 85% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1). mp=150-151 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 8.30 (brs, 1H), 7.58 (d, $J = 18.0$ Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.42 – 7.26 (m, 6H), 7.23 – 7.11 (m, 4H), 2.58 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 140.9, 140.7, 138.4, 135.8, 133.2, 131.2, 128.7, 128.6, 127.7, 127.1, 126.8, 122.2, 120.7, 119.8, 110.5, 96.1, 13.3. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{18}\text{NSe}$, 364.0599; found, 364.0610.

3-((4-Fluorophenyl)selanyl)-2-methyl-1H-indole (3be). Compound **3be** was prepared according to the general procedure and isolated as a brown solid (122 mg, 80% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1). mp=74-76 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 8.17 (brs, 1H), 7.54 (d, $J = 7.7$ Hz, 1H), 7.29 (d, $J = 7.4$ Hz, 1H), 7.24 – 7.06 (m, 4H), 6.91 – 6.58 (m, 2H), 2.51 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 161.4 (d, $J_{\text{C-F}} = 244.1$ Hz), 140.8, 135.8, 131.1, 130.3 (d, $J_{\text{C-F}} = 7.6$ Hz), 128.2 (d, $J_{\text{C-F}} = 3.3$ Hz), 122.2, 120.8, 119.7, 116.1 (d, $J_{\text{C-F}} = 21.6$ Hz), 110.6,

96.7, 13.2. ^{19}F NMR (376 MHz, CDCl_3): δ -117.6. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{13}\text{FNSe}$, 306.0192; found, 306.0169.

3-((4-Chlorophenyl)selanyl)-2-methyl-1H-indole (3bf). Compound **3bf** was prepared according to the general procedure and isolated as a brown solid (138 mg, 86% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1). mp=81-83 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 8.28 (brs, 1H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.33 (d, $J = 8.1$ Hz, 1H), 7.19 (dd, $J = 8.1, 7.1$ Hz, 1H), 7.13 (dd, $J = 8.1, 7.1$ Hz, 1H), 7.07 (s, 4H), 2.53 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 140.9, 135.8, 132.2, 131.3, 131.0, 129.6, 129.0, 122.3, 120.8, 119.6, 110.6, 96.0, 13.2. The data are in accordance with the literature.⁵

3-(Mesitylselanyl)-2-methyl-1H-indole (3bg). Compound **3bg** was prepared according to the general procedure and isolated as a brown solid (123 mg, 75% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=88-89 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.90 (brs, 1H), 7.36 (d, $J = 7.8$ Hz, 1H), 7.19 (d, $J = 7.8$ Hz, 1H), 7.08 (ddd, $J = 8.0, 7.1, 1.4$ Hz, 1H), 7.02 (dd, $J = 8.2, 7.1, 1.2$ Hz, 1H), 6.82 (s, 2H), 2.44 (s, 6H), 2.37 (s, 3H), 2.20 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): 141.9, 137.9, 137.2, 135.6, 131.0, 128.7, 128.6, 121.5, 120.1, 119.6, 110.3, 98.1, 24.3, 20.9, 13.2. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{NSe}$, 330.0755; found, 330.0779.

3-(Benzo[d][1,3]dioxol-5-ylselanyl)-2-methyl-1H-indole (3bh). Compound **3bh** was prepared according to the general procedure and isolated as a yellow solid (134 mg, 81% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1). mp=86-88 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 8.22 (brs, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.21 – 7.13 (m, 2H), 6.77 (dd, $J = 8.0, 1.7$ Hz, 1H), 6.66 (d, $J = 1.7$ Hz, 1H), 6.62 (d, $J = 8.0$ Hz, 1H), 5.84 (s, 2H), 2.56 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 148.1, 146.2, 140.5, 135.7, 131.1, 125.2, 122.3, 122.1, 120.7, 119.7, 110.5, 110.1, 108.9, 100.9, 97.3, 13.2. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{NO}_2\text{Se}$, 332.0184; found, 332.0186.

2-Methyl-3-(methylnselanyl)-1H-indole (3bi). Compound **3bi** was prepared according to the general procedure and isolated as an oil (86 mg, 77% yield) after

flash chromatography (petroleum ether/ethyl acetate = 8/1). ^1H NMR (400 MHz, CDCl_3): δ 7.98 (brs, 1H), 7.73 – 7.54 (m, 1H), 7.38 – 7.21 (m, 1H), 7.17 – 7.14 (m, 2H), 2.52 (s, 3H), 2.07 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 139.0, 135.6, 131.0, 121.8, 120.2, 119.6, 110.5, 98.1, 13.1, 8.6. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{NSe}$, 226.0129; found, 226.0139.

3-(Ethylselanyl)-2-methyl-1H-indole (3bj). Compound **3bj** was prepared according to the general procedure and isolated as an oil (83 mg, 70% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1). ^1H NMR (400 MHz, CDCl_3): δ 8.04 (brs, 1H), 7.72 – 7.55 (m, 1H), 7.37 – 7.21 (m, 1H), 7.18 – 7.07 (m, 2H), 2.61 (q, $J = 7.5$ Hz, 2H), 2.52 (s, 3H), 1.27 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 139.9, 135.7, 131.7, 121.8, 120.2, 119.7, 110.4, 96.7, 21.8, 16.1, 13.3. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{14}\text{NSe}$, 240.0286; found, 240.0259.

3-(Benzylselanyl)-2-methyl-1H-indole (3bk). Compound **3bk** was prepared according to the general procedure and isolated as an oil (138 mg, 92% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1). ^1H NMR (400 MHz, CDCl_3): δ 7.89 (brs, 1H), 7.67 – 7.56 (m, 1H), 7.26 – 7.17 (m, 1H), 7.17 – 7.13 (m, 2H), 7.11 – 7.08 (m, 3H), 6.96 – 6.87 (m, 2H), 3.73 (s, 2H), 1.98 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 141.2, 140.0, 135.7, 131.4, 128.8, 128.1, 126.3, 121.8, 120.3, 119.6, 110.5, 96.7, 31.5, 12.5, 13.2. The data are in accordance with the literature.⁶

2-Methyl-3-(phenethylselanyl)-1H-indole (3bl). Compound **3bl** was prepared according to the general procedure and isolated as a brown solid (138 mg, 88% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=61-63 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.95 (brs, 1H), 7.64 (dd, $J = 5.9, 3.2$ Hz, 1H), 7.26 – 7.18 (m, 3H), 7.16 – 7.10 (m, 3H), 7.09 – 7.04 (m, 2H), 3.06 – 2.75 (m, 4H), 2.47 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 141.5, 139.9, 135.7, 131.6, 128.45, 128.41, 126.2, 121.9, 120.4, 119.7, 110.5, 96.8, 37.3, 28.9, 13.3. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{18}\text{NSe}$, 316.0599; found, 316.0583.

2-Methyl-3-(pentylselanyl)-1H-indole (3bm). Compound **3bm** was prepared according to the general procedure and isolated as an oil (94 mg, 67% yield) after

flash chromatography (petroleum ether/ethyl acetate = 10/1). ^1H NMR (400 MHz, CDCl_3): δ 8.01 (brs, 1H), 7.65 – 7.62 (m, 1H), 7.26 – 7.23 (m, 1H), 7.20 – 7.06 (m, 2H), 2.60 (t, $J = 7.4$ Hz, 2H), 2.52 (s, 3H), 1.64 – 1.46 (m, 2H), 1.40 – 1.16 (m, 4H), 0.84 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 139.7, 135.7, 131.6, 121.7, 120.2, 119.7, 110.4, 97.1, 31.9, 30.3, 28.5, 22.3, 14.0, 13.3. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{20}\text{NSe}$, 282.0755; found, 282.0744.

3-(Heptylselanyl)-2-methyl-1H-indole (3bn). Compound **3bn** was prepared according to the general procedure and isolated as an oil (102 mg, 66% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1). ^1H NMR (400 MHz, CDCl_3): δ 8.05 (s, 1H), 7.78 – 7.54 (m, 1H), 7.43 – 7.21 (m, 1H), 7.21 – 7.08 (m, 2H), 2.61 (t, $J = 7.4$ Hz, 2H), 2.54 (s, 3H), 1.55 (p, $J = 7.3$ Hz, 2H), 1.35 – 1.30 (m, 2H), 1.29 – 1.16 (m, 6H), 0.85 (t, $J = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 139.6, 135.6, 131.6, 121.7, 120.2, 119.7, 110.3, 97.1, 31.8, 30.6, 29.7, 28.9, 28.5, 22.6, 14.1, 13.3. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{24}\text{NSe}$, 310.1068; found, 310.1075.

3-(Isobutylselanyl)-2-methyl-1H-indole (3bo). Compound **3bo** was prepared according to the general procedure and isolated as an oil (99 mg, 74% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1). ^1H NMR (400 MHz, CDCl_3): δ 7.99 (brs, 1H), 7.71 – 7.58 (m, 1H), 7.31 – 7.21 (m, 1H), 7.20 – 7.10 (m, 2H), 2.83 – 2.35 (m, 5H), 1.69 (dt, $J = 13.4, 6.7$ Hz, 1H), 0.98 (d, $J = 6.6$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 139.4, 135.7, 131.6, 121.7, 120.2, 119.7, 110.4, 97.5, 38.4, 29.0, 22.5, 13.3. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{18}\text{NSe}$, 268.0599; found, 268.0573.

3-(Cyclohexylselanyl)-2-methyl-1H-indole (3bp). Compound **3bp** was prepared according to the general procedure and isolated as an oil (99 mg, 68% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1). ^1H NMR (400 MHz, CDCl_3): δ 8.09 (brs, 1H), 7.70 – 7.53 (m, 1H), 7.35 – 7.20 (m, 1H), 7.23 – 7.01 (m, 2H), 3.05 – 2.92 (m, 1H), 2.54 (s, 3H), 2.13 – 1.78 (m, 2H), 1.69 – 1.66 (m, 2H), 1.56 – 1.34 (m, 3H), 1.29 – 1.03 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 140.3, 135.6, 132.3, 121.7, 120.2, 120.1, 110.3, 96.5, 43.0, 34.5, 27.0, 25.7, 13.4. HRMS

(ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{20}NSe$, 294.0755; found, 294.0751.

Methyl 2-methyl-2-((2-methyl-1H-indol-3-yl)selanyl)propanoate (3bq).

Compound **3bq** was prepared according to the general procedure and isolated as a yellow solid (109 mg, 70% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1). mp=98-100 °C. 1H NMR (400 MHz, $CDCl_3$): δ 8.42 (brs, 1H), 7.70 – 7.44 (m, 1H), 7.23 – 7.18 (m, 1H), 7.16 – 7.05 (m, 2H), 3.56 (s, 3H), 2.48 (d, $J = 0.8$ Hz, 3H), 1.57 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.8, 142.2, 135.5, 132.1, 121.9, 120.4, 119.9, 110.5, 97.3, 52.3, 45.7, 26.2, 13.2. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{18}NO_2Se$, 312.0497; found, 312.0490.

Ethyl (R)-2-((2-methyl-1H-indol-3-yl)selanyl)propanoate (3br).

Compound **3br** was prepared according to the general procedure and isolated as a yellow solid (116 mg, 75% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=65-67 °C. 1H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.60 – 7.39 (m, 1H), 7.16 – 7.10 (m, 1H), 7.08 – 7.00 (m, 2H), 4.09 – 3.75 (m, 2H), 3.48 (q, $J = 7.1$ Hz, 1H), 2.39 (s, 3H), 1.39 (d, $J = 7.1$ Hz, 3H), 1.03 (t, $J = 7.1$ Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.2, 141.8, 135.6, 131.9, 121.9, 120.4, 119.6, 110.5, 95.7, 61.0, 36.7, 17.6, 13.9, 13.1. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{18}NO_2Se$, 312.0497; found, 312.0491.

N-Methyl-4-(phenylselanyl)aniline (5a). Compound **5a** was prepared according to the general procedure and isolated as an oil (92 mg, 70% yield) after flash chromatography (petroleum ether/ethyl acetate = 20/1). 1H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, $J = 8.6$ Hz, 2H), 7.28 – 7.23 (m, 2H), 7.22 – 7.04 (m, 3H), 6.54 (d, $J = 8.6$ Hz, 2H), 3.83 (brs, 1H), 2.82 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.6, 137.4, 134.6, 129.8, 129.1, 125.9, 114.4, 113.3, 30.5. The data are in accordance with the literature.²

3,4,5-Trimethoxy-2-(phenylselanyl)aniline (5b). Compound **5b** was prepared according to the general procedure and isolated as a yellow solid (127 mg, 75% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=66-68 °C. 1H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.09 (m, 5H), 6.21 (s, 1H), 4.32 (s, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.9, 155.7,

146.1, 134.5, 132.6, 129.2, 128.5, 125.8, 99.1, 94.3, 61.4, 61.2, 55.8. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{18}NO_3Se$, 340.0446; found, 340.0460.

6-(Phenylselanyl)benzo[d][1,3]dioxol-5-amine (5c). Compound **5c** was prepared according to the general procedure and isolated as a white solid (99 mg, 68% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1). mp=70-72 °C. 1H NMR (400 MHz, $CDCl_3$): δ 7.16 – 7.06 (m, 5H), 6.98 (s, 1H), 6.33 (s, 1H), 5.83 (s, 2H), 4.07 (brs, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.3, 143.6, 139.3, 131.3, 128.2, 127.8, 125.0, 116.0, 101.3, 100.0, 95.9. The data are in accordance with the literature.⁴

Phenyl(2,4,6-trimethoxyphenyl)selane (5d). Compound **5d** was prepared according to the general procedure and isolated as a white solid (134 mg, 83% yield) after flash chromatography (petroleum ether/ethyl acetate =25/1). mp = 103-105°C. 1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 6.70 (m, 5H), 6.14 (s, 2H), 3.79 (s, 3H), 3.72 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.9, 160.9, 132.5, 127.7, 127.6, 124.2, 96.0, 90.1, 55.3, 54.4. The data are in accordance with the literature.²

3-(Phenylselanyl)imidazo[1,2-a]pyridine (5e). Compound **5e** was prepared according to the general procedure and isolated as a white solid (90 mg, 66% yield) after flash chromatography (petroleum ether/ethyl acetate = 2/1). mp=59-61 °C. 1H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 6.8 Hz, 1H), 7.98 (s, 1H), 7.69 (d, J = 9.0 Hz, 1H), 7.37 – 7.23 (m, 1H), 7.21 – 7.07 (m, 5H), 6.86 (td, J = 6.8, 1.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.3, 143.1, 130.6, 129.5, 129.0, 126.8, 125.7, 125.2, 117.9, 113.1, 106.4. The data are in accordance with the literature.²

1-(Phenylselanyl)naphthalen-2-ol (5f). Compound **5f** was prepared according to the general procedure and isolated as a yellow solid (109 mg, 73% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1). mp=49-51 °C. 1H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.78 (dd, J = 8.0, 1.2 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.44 – 7.26 (m, 2H), 7.17 – 7.04 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.3, 135.8, 132.8, 130.6, 129.5, 129.1, 128.5, 128.0, 127.0, 126.6, 123.8, 116.6, 109.0. The data are in accordance with the literature.⁴

1-(Phenylselanyl)naphthalen-2-amine (5g). Compound **5g** was prepared according

to the general procedure and isolated as a brown solid (91 mg, 61% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1). mp=77-79 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.32 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.31 – 7.22 (m, 1H), 7.17 – 7.08 (m, 5H), 7.05 (d, *J* = 8.8 Hz, 1H), 4.72 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 148.1, 136.9, 131.83, 131.76, 129.2, 128.6, 128.33, 128.32, 127.8, 126.6, 125.8, 122.5, 117.4, 105.5. The data are in accordance with the literature.⁴

6-(Phenylselanyl)-1,2,3,4-tetrahydroquinoline (5h). Compound **5h** was prepared according to the general procedure and isolated as a yellow solid (66 mg, 46% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=47-49 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.37 – 7.06 (m, 7H), 6.41 (d, *J* = 8.0 Hz, 1H), 3.96 (brs, 1H), 3.32 (t, *J* = 5.4 Hz, 2H), 2.73 (t, *J* = 6.4 Hz, 2H), 1.98 – 1.78 (m, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 145.2, 137.4, 134.9, 134.8, 129.7, 129.0, 125.8, 122.4, 114.8, 41.8, 26.8, 21.7. The data are in accordance with the literature.²

2-Phenyl-5-(phenylselanyl)thiophene (5i) Compound **5i** was prepared according to the general procedure and isolated as an oil (121 mg, 77% yield) after flash chromatography (petroleum ether/ethyl acetate = 100/1). ¹H NMR (400 MHz, CDCl₃): δ 7.58 – 7.54 (m, 2H), 7.45 – 7.33 (m, 4H), 7.29 (d, *J* = 3.8 Hz, 2H), 7.28 – 7.16 (m, 4H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 150.8, 138.0, 133.8, 133.4, 130.0, 129.3, 129.0, 128.0, 126.9, 125.9, 124.1, 122.6. The data are in accordance with the literature.⁷

2-Methoxy-5-(phenylselanyl)thiophene (5j) Compound **5j** was prepared according to the general procedure and isolated as an oil (82 mg, 61% yield) after flash chromatography (petroleum ether/ethyl acetate = 200/1). ¹H NMR (400 MHz, CDCl₃): δ 7.31 (d, *J* = 6.9 Hz, 2H), 7.26 – 7.15 (m, 3H), 7.05 (d, *J* = 3.9 Hz, 1H), 6.16 (d, *J* = 3.8 Hz, 1H), 3.89 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 171.2, 136.5, 134.2, 129.2, 129.1, 129.0, 126.4, 107.7, 105.3, 60.2. The data are in accordance with the literature.²

5. General procedure for selenocyanation of electron rich arenes

The reaction was carried out in an open air system at ambient temperature. To a 10 mL vessel with magnetic stir bar were added 0.5 mmol indole, 0.5 mmol KSeCN, 0.5 mmol I₂O₅ and 2 mL of MeOH. The reaction mixture was stirred for an indicated time. Then, the reaction was quenched with a saturated aqueous Na₂S₂O₃ solution and extracted with EtOAc. The combined organic layers were dried (Na₂SO₄) and concentrated to give a crude residue, which was purified by flash column chromatography.

3-Selenocyanato-1H-indole (6a). Compound **6a** was prepared according to the general procedure and isolated as a brown solid (88 mg, 80% yield) after flash chromatography (petroleum ether/ethyl acetate = 6/1). mp=107-109 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.68 (s, 1H), 7.79 – 7.66 (m, 1H), 7.47 (d, *J* = 2.8 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.32 – 7.28 (m, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.0, 131.8, 128.7, 123.8, 121.9, 119.6, 111.9, 101.9, 89.5. The data are in accordance with the literature.⁸

Methyl 3-selenocyanato-1H-indole-4-carboxylate (6b). Compound **6b** was prepared according to the general procedure and isolated as an oil (88 mg, 63% yield) after flash chromatography (petroleum ether/ethyl acetate = 3/1). ¹H NMR (400 MHz, CDCl₃): δ 8.81 (brs, 1H), 7.87 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.64 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.59 (d, *J* = 2.8 Hz, 1H), 7.29 – 7.24 (m, 1H), 3.97 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 168.6, 137.9, 127.2, 125.4, 124.1, 122.3, 120.5, 117.5, 106.7, 92.4, 52.6. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₁₁H₉N₂O₂Se, 280.9824; found, 280.9829.

Methyl 3-selenocyanato-1H-indole-6-carboxylate (6c). Compound **6c** was prepared according to the general procedure and isolated as a yellow solid (92 mg, 66% yield) after flash chromatography (petroleum ether/ethyl acetate = 3/1). mp=166-168 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.94 (brs, 1H), 8.22 (d, *J* = 0.7 Hz, 1H), 7.99 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.79 (d, *J* = 8.4, 0.7 Hz, 1H), 7.71 (d, *J* = 2.9 Hz, 1H), 3.97 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 167.5, 135.4, 134.6, 132.3, 125.8, 122.9, 119.5, 114.2, 101.2, 90.4, 52.3. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₁₁H₉N₂O₂Se,

280.9824; found, 280.9810.

3-Selenocyanato-6-(trifluoromethyl)-1H-indole (6d). Compound **6d** was prepared according to the general procedure and isolated as a yellow solid (79 mg, 55% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=101-103 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.69 (brs, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.74 (s, 1H), 7.66 (d, *J* = 2.8 Hz, 1H), 7.51 (dd, *J* = 8.4, 1.4 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 135.4, 134.9, 131.1, 125.6 (q, *J*_{C-F} = 32.2 Hz), 123.5, 119.9, 118.1 (q, *J*_{C-F} = 3.5 Hz), 109.8 (d, *J*_{C-F} = 4.4 Hz), 101.8, 89.0. ¹⁹F NMR (376 MHz, CDCl₃): δ -60.9. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₁₀H₆F₃N₂Se, 290.9643; found, 290.9642.

5-Fluoro-3-selenocyanato-1H-indole (6e). Compound **6e** was prepared according to the general procedure and isolated as a brown solid (82 mg, 69% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=104-105 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.73 (s, 1H), 7.55 (d, *J* = 2.9 Hz, 1H), 7.47 – 7.27 (m, 2H), 7.05 (td, *J* = 9.0, 2.5 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.1 (d, *J*_{C-F} = 238.7 Hz), 133.4, 132.4, 129.6 (d, *J*_{C-F} = 10.5 Hz), 112.9 (d, *J*_{C-F} = 9.6 Hz), 112.5 (d, *J*_{C-F} = 26.5 Hz), 104.8 (d, *J*_{C-F} = 24.9 Hz), 101.6, 89.6 (d, *J*_{C-F} = 4.7 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ -120.9. The data are in accordance with the literature.⁹

5-Chloro-3-selenocyanato-1H-indole (6f). Compound **6f** was prepared according to the general procedure and isolated as a yellow solid (89 mg, 70% yield) after flash chromatography (petroleum ether/ethyl acetate = 2/1). mp=151-153 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.70 (brs, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.57 (d, *J* = 2.8 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.30 – 7.27 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 134.4, 133.0, 130.0, 128.0, 124.4, 119.3, 112.9, 101.2, 89.5. The data are in accordance with the literature.⁹

5-Bromo-3-selenocyanato-1H-indole (6g). Compound **6g** was prepared according to the general procedure and isolated as a yellow solid (95 mg, 63% yield) after flash chromatography (petroleum ether/ethyl acetate = 3/1). mp=155-156 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.06 (brs, 1H), 7.93 (d, *J* = 2.7 Hz, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.36 (dd, *J* = 8.6, 1.9 Hz, 1H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 135.4, 135.1, 131.0, 125.6, 121.4, 115.0, 113.8, 104.9, 89.5. The data

are in accordance with the literature.⁸

3-Selenocyanato-1*H*-indole-5-carbonitrile (6h). Compound **6h** was prepared according to the general procedure and isolated as a white solid (63 mg, 51% yield) after flash chromatography (petroleum ether/ethyl acetate = 3/1). mp=187-189 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 12.37 (brs, 1H), 8.09 – 8.07 (m, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.61 (dd, *J* = 8.5, 1.6 Hz, 1H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 138.6, 136.3, 129.0, 125.8, 124.7, 120.5, 114.3, 105.0, 103.4, 91.6. The data are in accordance with the literature.⁸

5-Methyl-3-selenocyanato-1*H*-indole (6i). Compound **6i** was prepared according to the general procedure and isolated as a yellow solid (89 mg, 76% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=104-106 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.62 (brs, 1H), 7.51 (s, 1H), 7.40 (d, *J* = 2.8 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.11 (dd, *J* = 8.3, 1.5 Hz, 1H), 2.50 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 134.3, 131.8, 131.4, 128.9, 125.4, 119.1, 111.6, 102.2, 88.8, 21.6. The data are in accordance with the literature.¹⁰

5-Methoxy-3-selenocyanato-1*H*-indole (6j). Compound **6j** was prepared according to the general procedure and isolated as a yellow solid (100 mg, 80% yield) after flash chromatography (petroleum ether/ethyl acetate = 3/1). mp=108-109 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 11.75 (brs, 1H), 7.80 (d, *J* = 2.8 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.82 (s, 3H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 155.1, 134.1, 131.5, 129.8, 113.8, 113.2, 104.7, 100.5, 88.8, 55.9. The data are in accordance with the literature.⁸

1-Methyl-3-selenocyanato-1*H*-indole (6k). Compound **6k** was prepared according to the general procedure and isolated as a yellow solid (96 mg, 82% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1). mp=95-97 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, *J* = 7.5 Hz, 1H), 7.54 – 6.76 (m, 4H), 3.79 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 137.2, 136.0, 129.5, 123.3, 121.5, 119.8, 110.1, 101.9, 87.2, 33.4. The data are in accordance with the literature.⁸

1-Benzyl-3-selenocyanato-1*H*-indole (6l). Compound **6l** was prepared according to the general procedure and isolated as a yellow solid (135 mg, 87% yield) after flash

chromatography (petroleum ether/ethyl acetate = 15/1). mp=88-90 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.90 – 7.58 (m, 2H), 7.38 – 7.20 (m, 6H), 7.14 – 7.11 (m, 2H), 5.29 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.8, 135.9, 135.2, 129.7, 129.1, 128.3, 127.2, 123.5, 121.8, 120.0, 110.6, 101.8, 88.2, 50.7. The data are in accordance with the literature.⁸

2-Phenyl-3-selenocyanato-1H-indole (6m). Compound **6m** was prepared according to the general procedure and isolated as a yellow solid (107 mg, 72% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1). mp=151-153 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 12.25 (brs, 1H), 7.87 (d, *J* = 7.0 Hz, 2H), 7.67 – 7.64 (m, 1H), 7.62 – 7.59 (m, 2H), 7.54 – 7.50 (m, 2H), 7.31 – 7.24 (m, 2H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 143.2, 136.6, 131.4, 130.9, 129.6, 129.4, 129.1, 123.5, 121.5, 119.7, 112.6, 105.2, 88.6. The data are in accordance with the literature.⁹

***N,N*-Dimethyl-4-selenocyanatoaniline (6n)**. Compound **6n** was prepared according to the general procedure and isolated as a yellow solid (92 mg, 82% yield) after flash chromatography (petroleum ether/ethyl acetate = 25/1). mp=81-83 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.50 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 8.9 Hz, 2H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 151.6, 136.5, 136.5, 113.7, 106.5, 105.9., 40.2. The data are in accordance with the literature.⁸

1-Selenocyanatonaphthalen-2-amine (6o). Compound **6o** was prepared according to the general procedure and isolated as an oil (58 mg, 47% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.72 (brs, 2H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.48 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.37 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H). The data are in accordance with the literature.¹¹

1,3,5-Trimethoxy-2-selenocyanatobenzene (6p). Compound **6p** was prepared according to the general procedure and isolated as an oil (75 mg, 55% yield) after flash chromatography (petroleum ether/ethyl acetate = 6/1). ¹H NMR (400 MHz, DMSO-*d*₆): δ 6.37 (s, 2H), 3.86 (s, 6H), 3.84 (s, 3H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 164.3, 161.1, 104.5, 92.1, 90.6, 56.9, 56.1. The data are in accordance with the literature.⁸

6. General procedure for thiocyanation of electron rich arenes

The reaction was carried out in an open air system at ambient temperature. To a 10 mL vessel with magnetic stir bar were added 0.5 mmol indole, 0.5 mmol KSCN, 0.5 mmol I₂O₅ and 2 mL of MeOH. The reaction mixture was stirred for an indicated time. Then, the reaction was quenched with a saturated aqueous Na₂S₂O₃ solution and extracted with EtOAc. The combined organic layers were dried (Na₂SO₄) and concentrated to give a crude residue, which was purified by flash column chromatography.

3-Thiocyanato-1H-indole (7a). Compound **7a** was prepared according to the general procedure and isolated as a red solid (70 mg, 80% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=49-50 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.64 (brs, 1H), 8.02 – 7.68 (m, 1H), 7.53 (d, *J* = 2.8 Hz, 1H), 7.49 – 7.38 (m, 1H), 7.38 – 7.27 (m, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.0, 130.9, 127.7, 124.0, 122.0, 118.9, 112.0, 111.7, 92.6. The data are in accordance with the literature.⁸

5-Fluoro-3-thiocyanato-1H-indole (7b). Compound **7b** was prepared according to the general procedure and isolated as a yellow solid (68 mg, 71% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=87-89 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.22 (brs, 1H), 7.54 (d, *J* = 3.0 Hz, 1H), 7.41 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.36 (dd, *J* = 8.9, 4.2 Hz, 1H), 7.02 (td, *J* = 9.0, 2.5 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): 158.9 (d, *J*_{C-F} = 238.2 Hz), 133.2, 132.8, 128.5 (d, *J*_{C-F} = 10.5 Hz), 113.3 (d, *J*_{C-F} = 9.7 Hz), 112.3, 112.0, 103.7 (d, *J*_{C-F} = 24.8 Hz), 91.2 (d, *J*_{C-F} = 4.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ -121.4. The data are in accordance with the literature.¹²

5-Chloro-3-thiocyanato-1H-indole (7c). Compound **7c** was prepared according to the general procedure and isolated as a white solid (78 mg, 75% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=123-125 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.49 (brs, 1H), 7.74 (d, *J* = 1.9 Hz, 1H), 7.54 (d, *J* = 2.9 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.23 (dd, *J* = 8.7, 2.0 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): 134.8, 133.0, 128.9, 127.5, 123.9, 118.0, 113.5, 111.9, 90.8. The data are in

accordance with the literature.¹³

5-Bromo-3-thiocyanato-1H-indole (7d). Compound **7d** was prepared according to the general procedure and isolated as a brown solid (98 mg, 78% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1). mp=99-101 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 12.21 (brs, 1H), 8.07 (d, *J* = 2.6 Hz, 1H), 7.81 (d, *J* = 1.9 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.40 (dd, *J* = 8.7, 1.9 Hz, 1H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 135.6, 135.2, 129.7, 126.1, 120.4, 115.4, 114.2, 112.6, 89.9. The data are in accordance with the literature.⁸

4-Methyl-3-thiocyanato-1H-indole (7e). Compound **7e** was prepared according to the general procedure and isolated as a white solid (69 mg, 73% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=121-123 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.66 (brs, 1H), 7.46 (d, *J* = 2.8 Hz, 1H), 7.31 – 7.21 (m, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.05 – 6.90 (m, 1H), 2.93 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.5, 132.1, 131.1, 125.6, 124.0, 123.5, 113.4, 110.1, 92.2, 19.2. The data are in accordance with the literature.¹²

5-Methyl-3-thiocyanato-1H-indole (7f). Compound **7f** was prepared according to the general procedure and isolated as a yellow solid (77 mg, 82% yield) after flash chromatography (petroleum ether/ethyl acetate = 3/1). mp=67-69 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.45 (brs, 1H), 7.57 – 7.49 (m, 1H), 7.43 (d, *J* = 2.9 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.08 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.44 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 134.3, 131.6, 130.8, 128.0, 125.6, 118.4, 111.8, 111.6, 91.9, 21.5. The data are in accordance with the literature.¹²

3-Thiocyanato-6-(trifluoromethyl)-1H-indole (7g). Compound **7g** was prepared according to the general procedure and isolated as a yellow solid (102 mg, 84% yield) after flash chromatography (petroleum ether/ethyl acetate = 6/1). mp=84-86 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.07 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.64 (s, 1H), 7.58 (d, *J* = 2.8 Hz, 1H), 7.45 (dd, *J* = 8.4, 1.4 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 134.0, 132.5, 128.9, 125.2 (q, *J*_{C-F} = 33.0 Hz), 122.2, 118.3, 117.6 (d, *J*_{C-F} = 3.4 Hz), 110.6, 108.8 (q, *J*_{C-F} = 4.5 Hz), 91.9. ¹⁹F NMR (376 MHz, CDCl₃): δ -61.0. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₁₀H₆F₃N₂S, 243.0198; found, 243.0213.

3-Thiocyanato-1*H*-indole-7-carbaldehyde (7h). Compound **7h** was prepared according to the general procedure and isolated as a yellow solid (61 mg, 60% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1). mp=152-153 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 12.38 (brs, 1H), 10.21 (s, 1H), 8.07 (dt, *J* = 7.8, 0.9 Hz, 1H), 8.03 (d, *J* = 3.0 Hz, 1H), 7.96 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 193.4, 135.5, 133.1, 130.3, 129.2, 125.4, 122.1, 121.6, 112.6, 92.0. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₁₀H₇N₂OS, 203.0274; found, 203.0260.

2-Methyl-3-thiocyanato-1*H*-indole (7i). Compound **7i** was prepared according to the general procedure and isolated as a pink solid (70 mg, 74% yield) after flash chromatography (petroleum ether/ethyl acetate = 5/1). mp=89-91 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.53 (brs, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.26 – 7.18 (m, 2H), 2.48 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 142.0, 135.1, 128.7, 123.0, 121.6, 118.1, 112.1, 111.2, 88.9, 12.1. The data are in accordance with the literature.⁸

1-Methyl-3-thiocyanato-1*H*-indole (7j). Compound **7j** was prepared according to the general procedure and isolated as a yellow solid (71 mg, 76% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1). mp=61-63 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.85 – 7.65 (m, 1H), 7.43 – 7.27 (m, 4H), 3.79 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 137.2, 135.1, 128.5, 123.5, 121.6, 119.0, 111.9, 110.2, 89.9, 33.5. The data are in accordance with the literature.⁸

1,3,5-Trimethoxy-2-thiocyanatobenzene (7k). Compound **7k** was prepared according to the general procedure and isolated as an oil (57 mg, 51% yield) after flash chromatography (petroleum ether/ethyl acetate = 6/1). ¹H NMR (400 MHz, DMSO-*d*₆): δ 6.39 (s, 2H), 3.90 (s, 6H), 3.85 (s, 3H). ¹³C{¹H} (100 MHz, DMSO-*d*₆): δ 164.7, 161.4, 112.4, 92.4, 88.6, 57.1, 56.3. The data are in accordance with the literature.¹³

1-Thiocyanatonaphthalen-2-amine (7l). Compound **7l** was prepared according to the general procedure and isolated as an oil (42 mg, 42% yield) after flash chromatography (petroleum ether/ethyl acetate = 4/1). ¹H NMR (400 MHz,

DMSO-*d*₆): δ 7.93 (d, $J = 8.1$ Hz, 1H), 7.77 (d, $J = 8.7$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 1H), 7.64 (brs, 2H), 7.58 (d, $J = 8.7$ Hz, 1H), 7.56 – 7.49 (m, 1H), 7.43 – 7.28 (m, 1H). The data are in accordance with the literature.¹¹

***N,N*-Dimethyl-4-thiocyanatoaniline (7m)**. Compound **7m** was prepared according to the general procedure and isolated as an oil (56 mg, 63% yield) after flash chromatography (petroleum ether/ethyl acetate = 40/1). ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.46 (d, $J = 9.0$ Hz, 2H), 6.77 (d, $J = 9.0$ Hz, 2H). ¹³C{¹H} (100 MHz, DMSO-*d*₆): 152.0, 134.8, 113.7, 113.4, 106.1, 40.2. The data are in accordance with the literature.⁸

7. Gram-Scale Reaction for the Synthesis of 3an

To a 50 mL round-bottom flask with magnetic stir bar were added 5-methoxy-1*H*-indole (0.735 g, 5 mmol), Ph₂Se₂ (1.560 g, 5 mmol), I₂O₅ (1.670 g, 5 mmol) and 20 mL of CH₃CN. The reaction mixture was stirred at room temperature in the open air and the reaction was monitored by TLC. After completion of reaction, the reaction was next quenched with a saturated aqueous Na₂S₂O₃ solution and extracted with EtOAc. The combined organic layers were dried (Na₂SO₄) and concentrated to give a crude residue, which was purified by flash column chromatography (silica gel, petroleum ether : ethyl acetate = 10:1) to give **3an** in 82% yield (1.238 g).

8. Control Experiments

To a 10 mL vessel with magnetic stir bar were added N-3-butenylindole **1x** (85.5 mg, 0.5 mmol), Ph₂Se₂ (156.0 mg, 0.5 mmol), I₂O₅ (167.0 mg, 0.5 mmol) and 2 mL of CH₃CN. The reaction mixture was stirred for an indicated time. Then, the reaction was quenched with a saturated aqueous Na₂S₂O₃ solution and extracted with EtOAc. The combined organic layers were dried (Na₂SO₄) and concentrated to give a crude residue, which was purified by flash column chromatography (silica gel, petroleum ether : ethyl acetate = 40:1) to give **3aw** and **3aw'**.

1-(But-3-en-1-yl)-3-(phenylselanyl)-1*H*-indole (3aw). Oil, 72 mg, 44% yield. ¹H

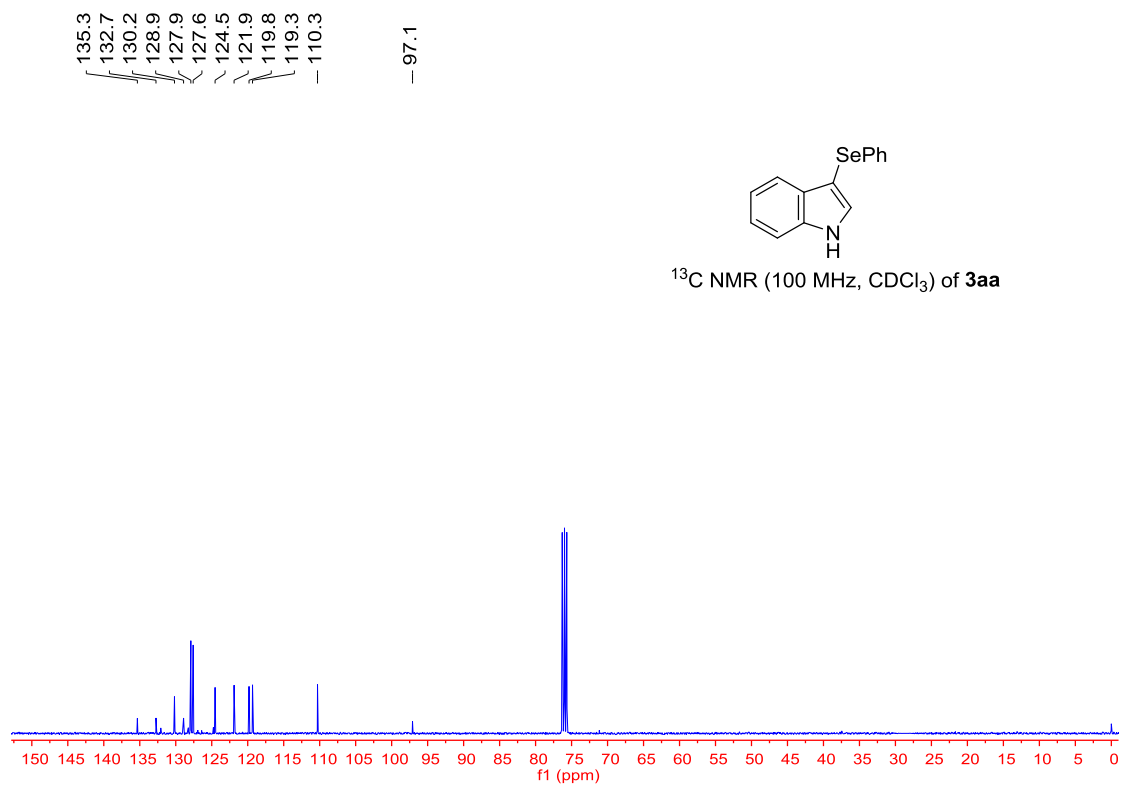
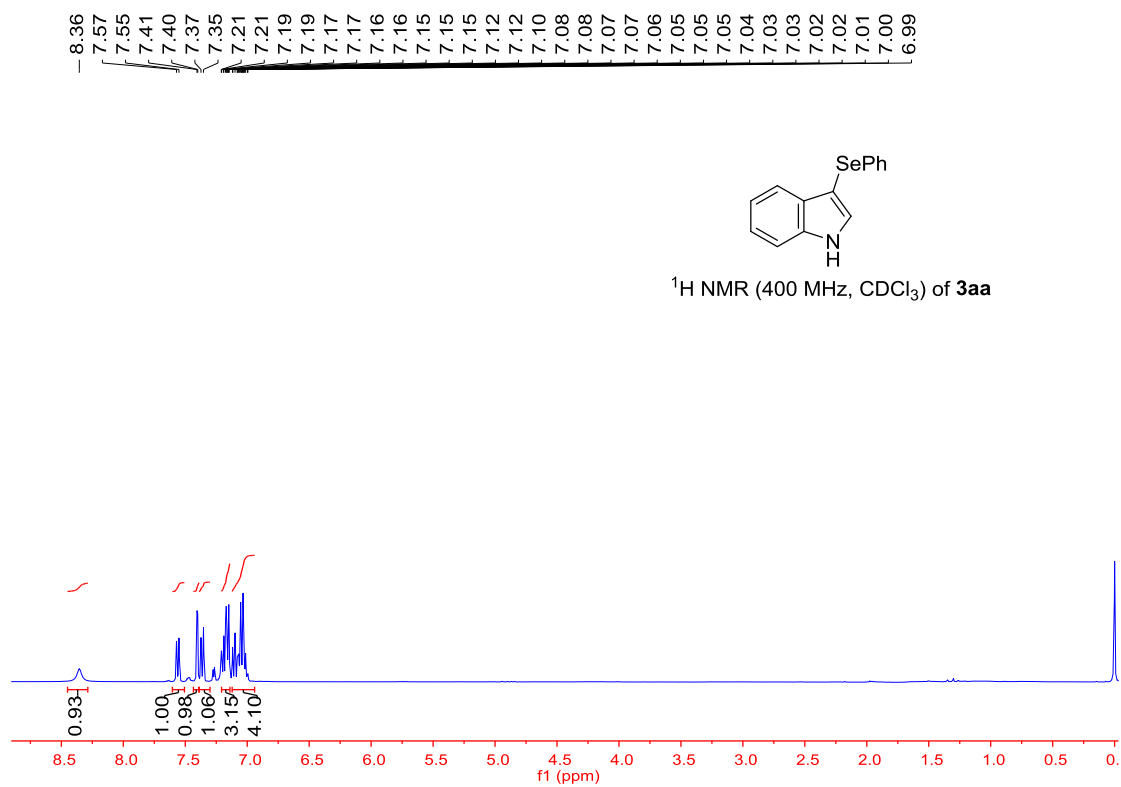
NMR (400 MHz, CDCl₃): δ 7.54 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.25 (m, 2H), 7.21 – 7.19 (m, 1H), 7.16 – 7.07 (m, 3H), 7.06 – 6.98 (m, 3H), 5.96 – 5.61 (m, 1H), 5.02 – 4.98 (m, 1H), 4.97 (t, *J* = 1.5 Hz, 1H), 4.14 (t, *J* = 7.1 Hz, 2H), 2.53 (qt, *J* = 7.0, 1.3 Hz, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 135.6, 133.7, 133.2, 133.1, 129.7, 127.8, 127.4, 127.3, 124.4, 121.3, 119.5, 119.4, 116.8, 108.6, 94.9, 45.2, 33.4. The data are in accordance with the literature.¹⁴

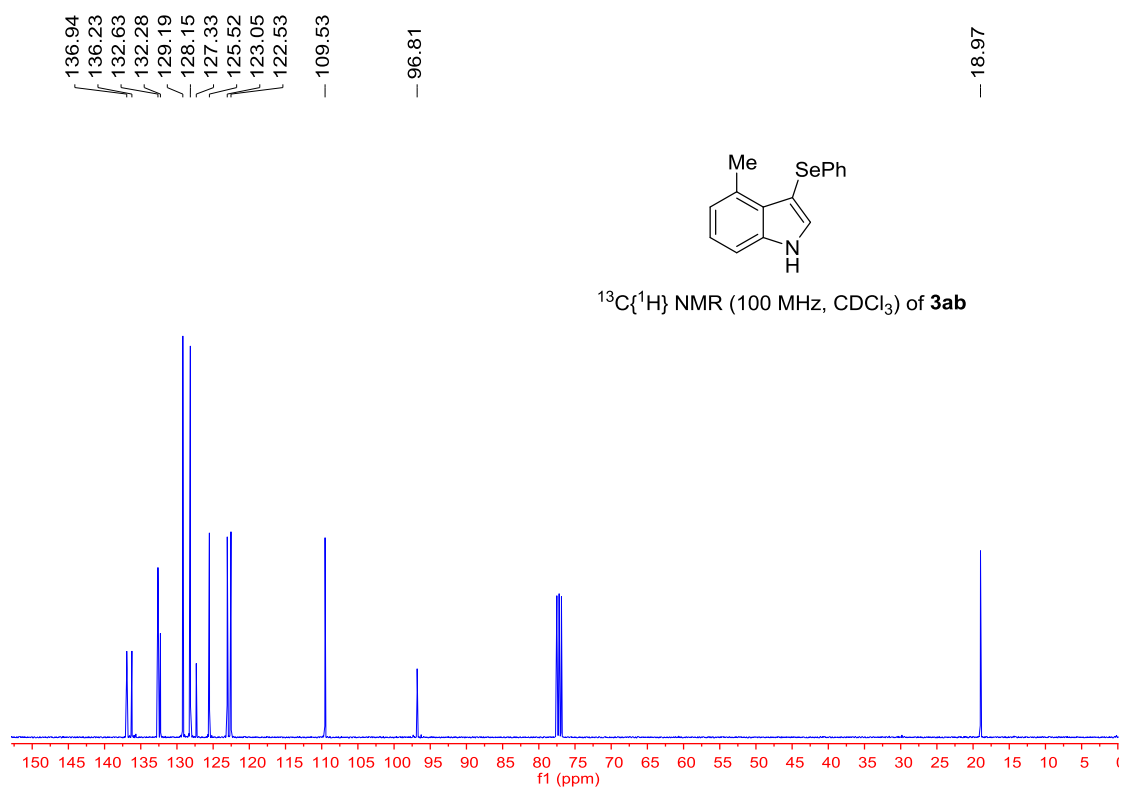
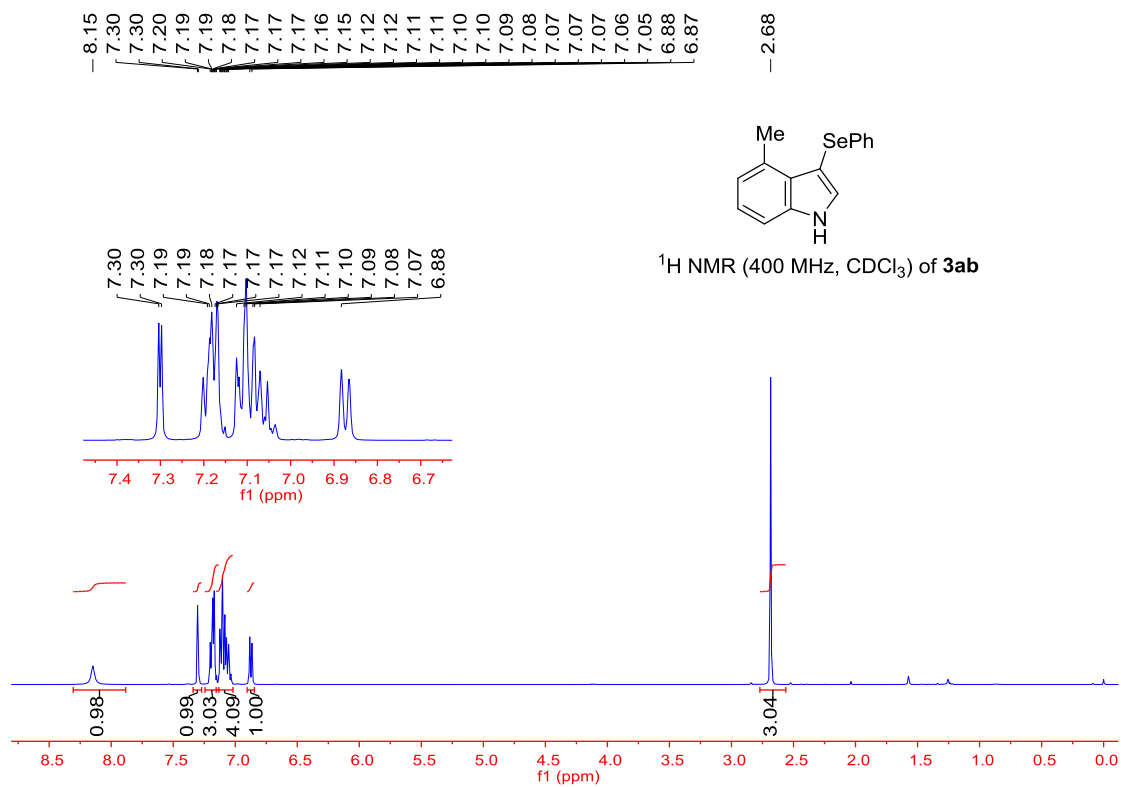
9-(Phenylselanyl)-1-((phenylselanyl)methyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indole (3aw’). Oil, 29 mg, 12% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.20 (m, 5H), 7.18 – 7.06 (m, 6H), 4.35 – 4.22 (m, 1H), 4.10 – 4.02 (m, 1H), 3.75 – 3.69 (m, 1H), 3.51 (dd, *J* = 17.2, 4.9 Hz, 1H), 3.15 (dd, *J* = 17.2, 7.9 Hz, 1H), 2.52 – 2.37 (m, 1H), 2.28 – 2.18 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 140.7, 136.6, 135.5, 134.0, 130.9, 129.2, 129.0, 128.4, 128.2, 127.7, 125.4, 121.6, 120.9, 119.6, 109.0, 93.8, 41.6, 35.9, 30.7, 29.7. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₄H₂₂NSe₂, 484.0077; found, 484.0075.

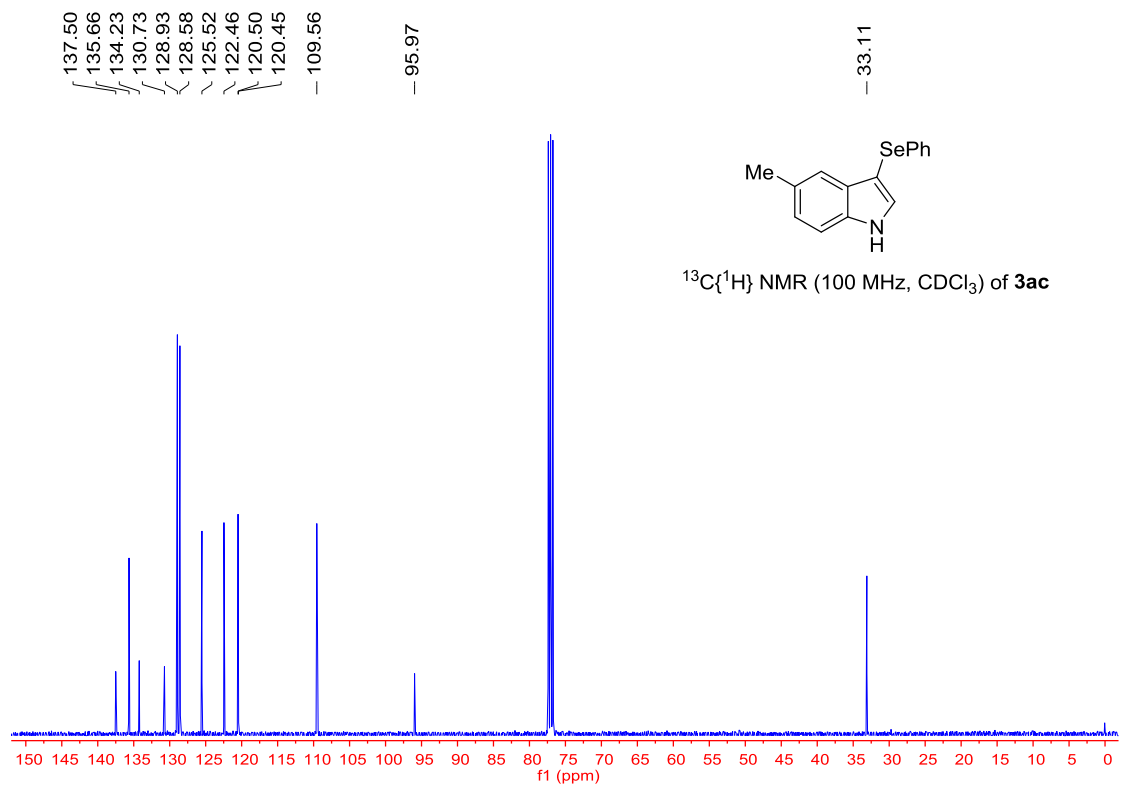
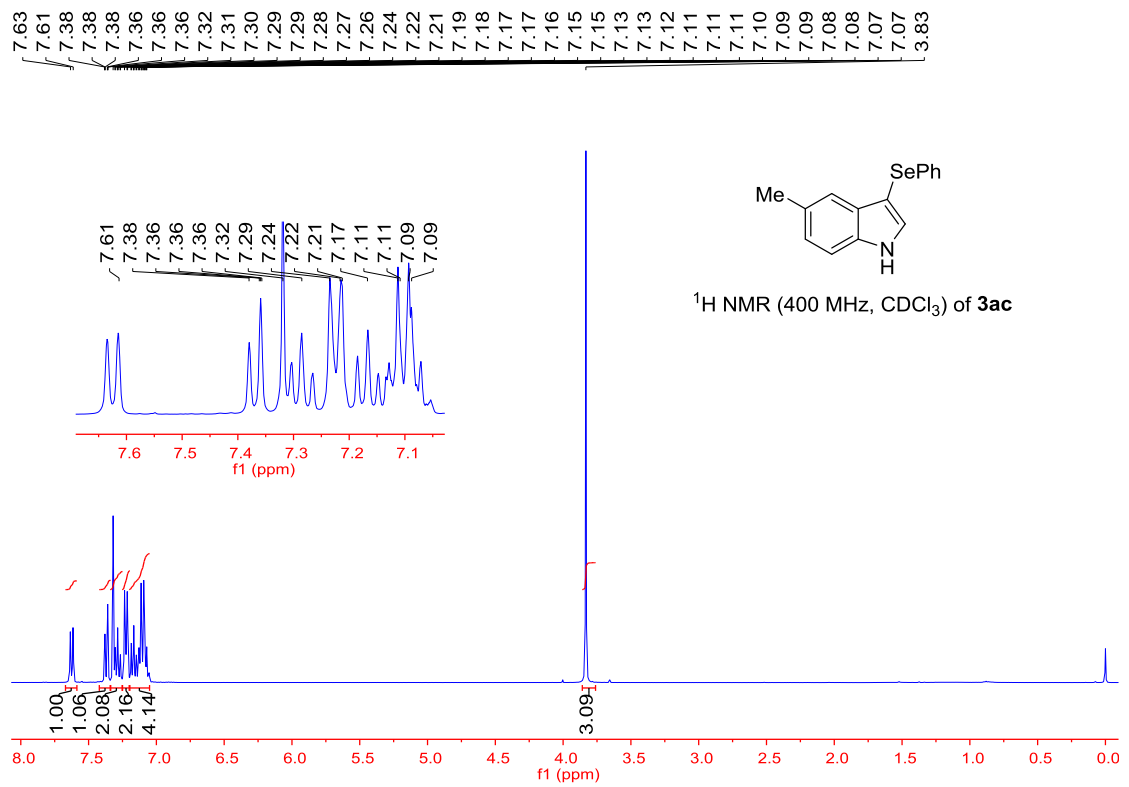
9. References

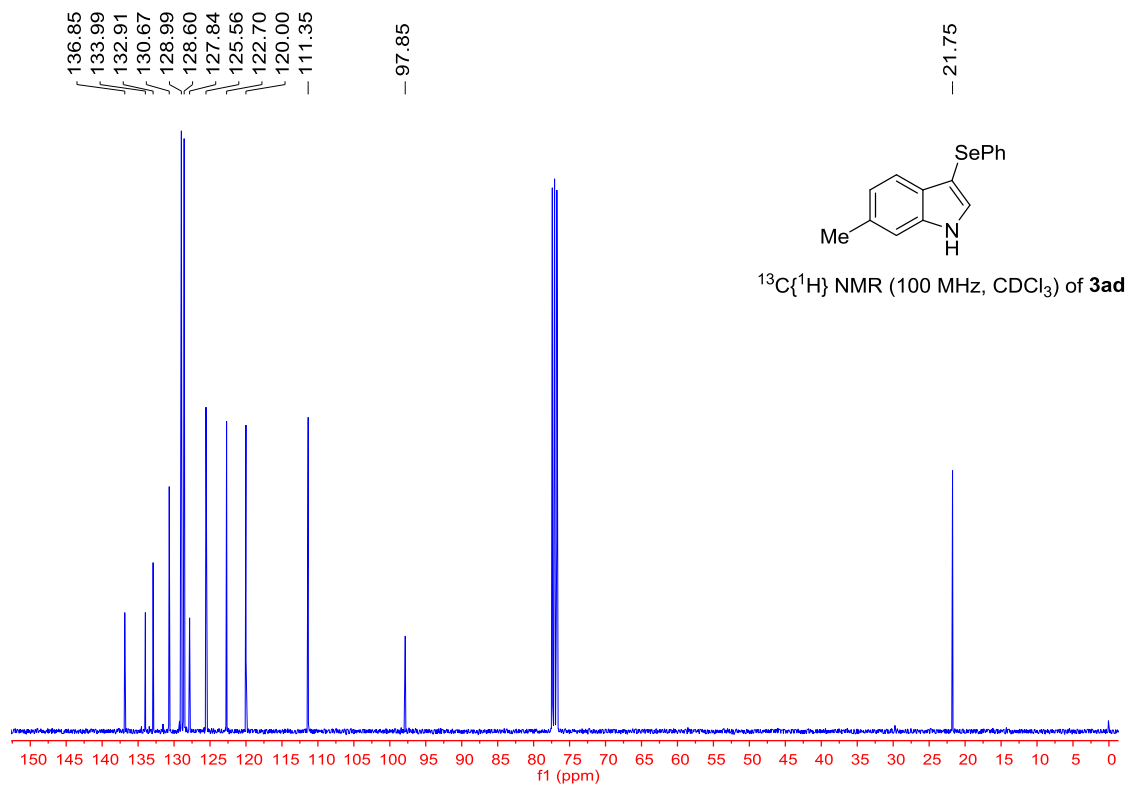
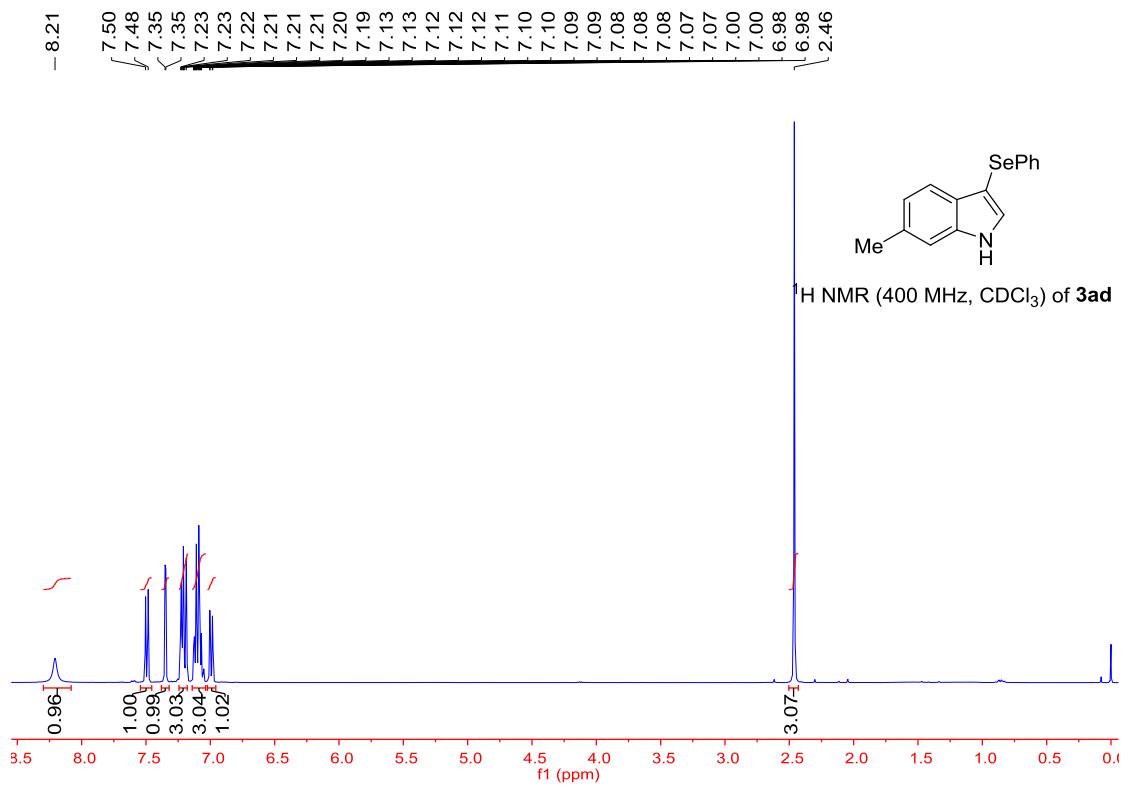
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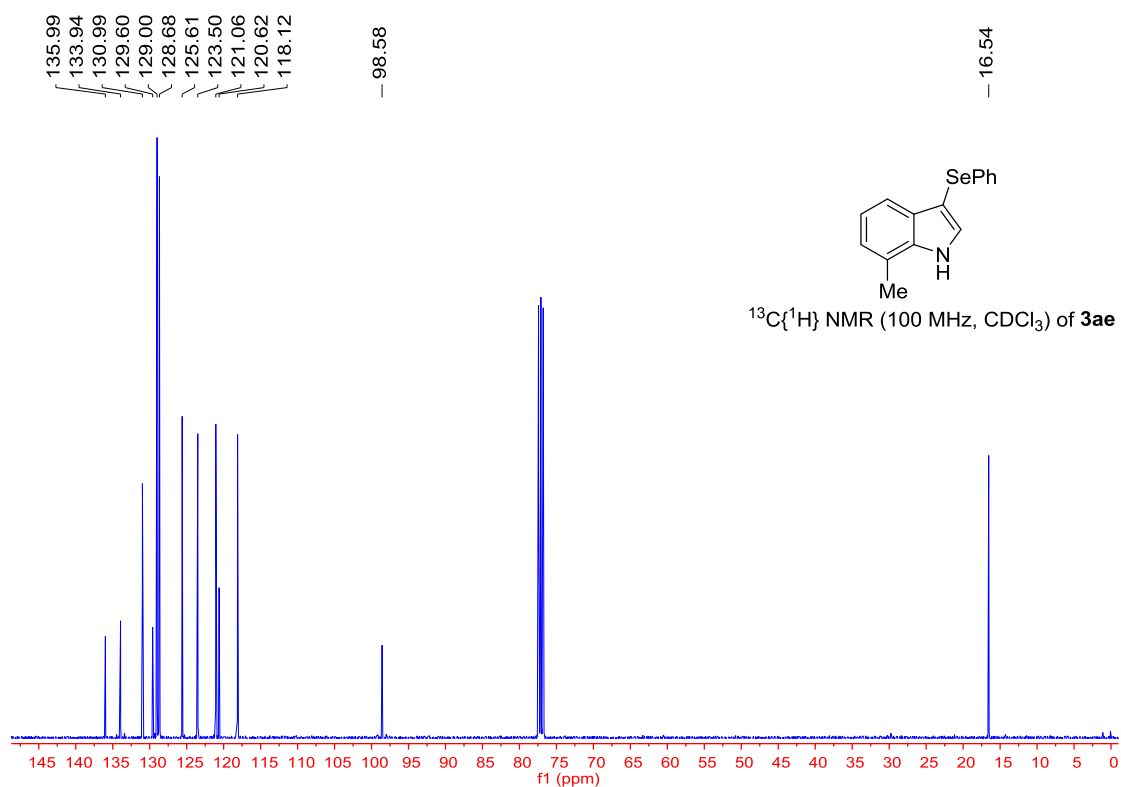
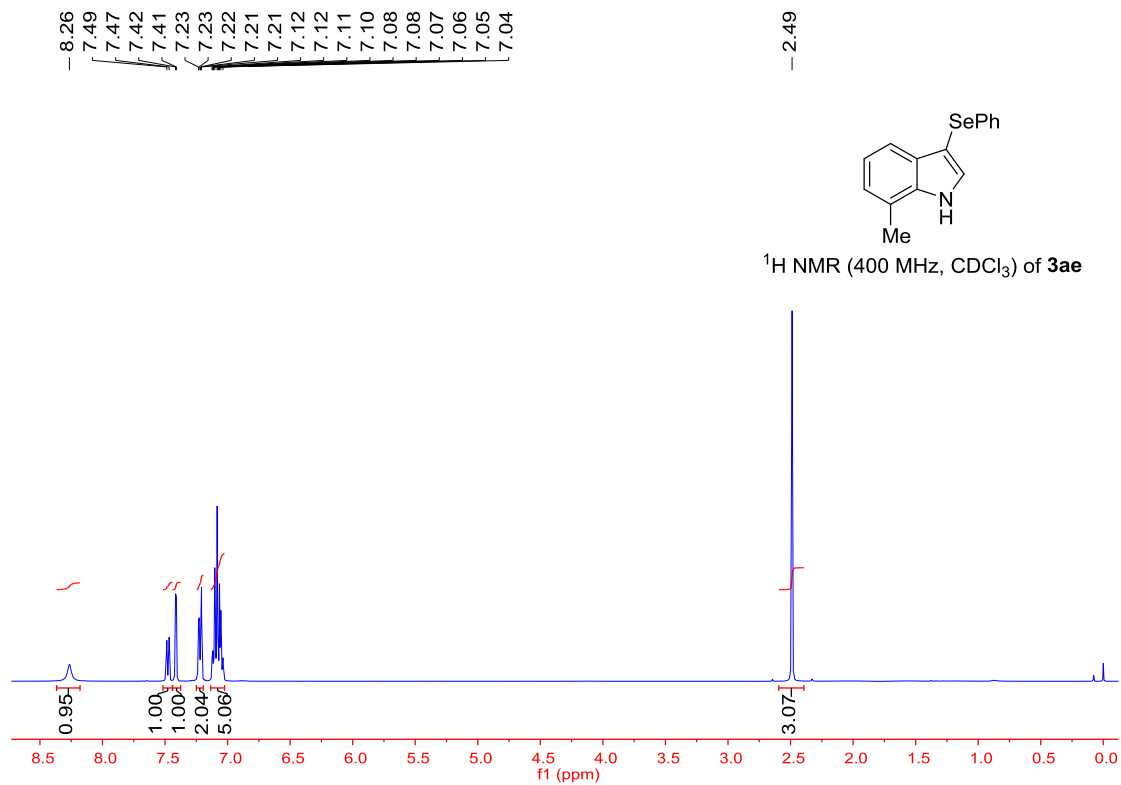
10. Copies of NMR spectra

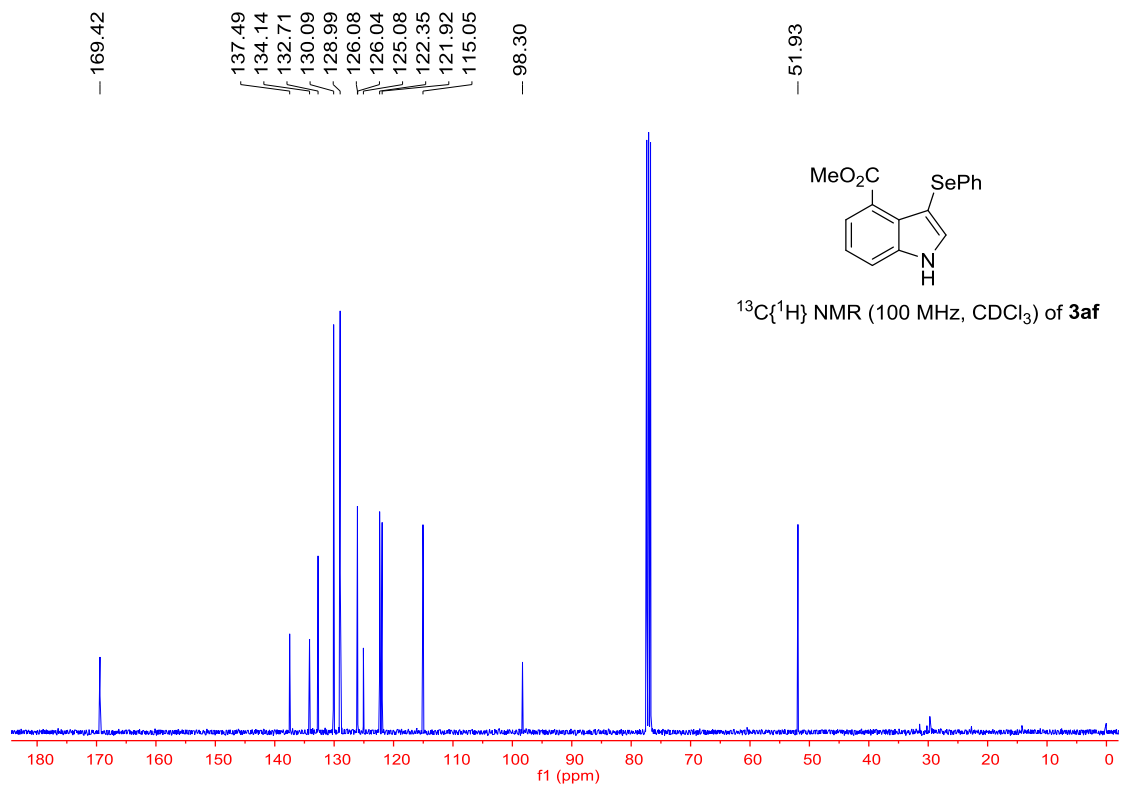
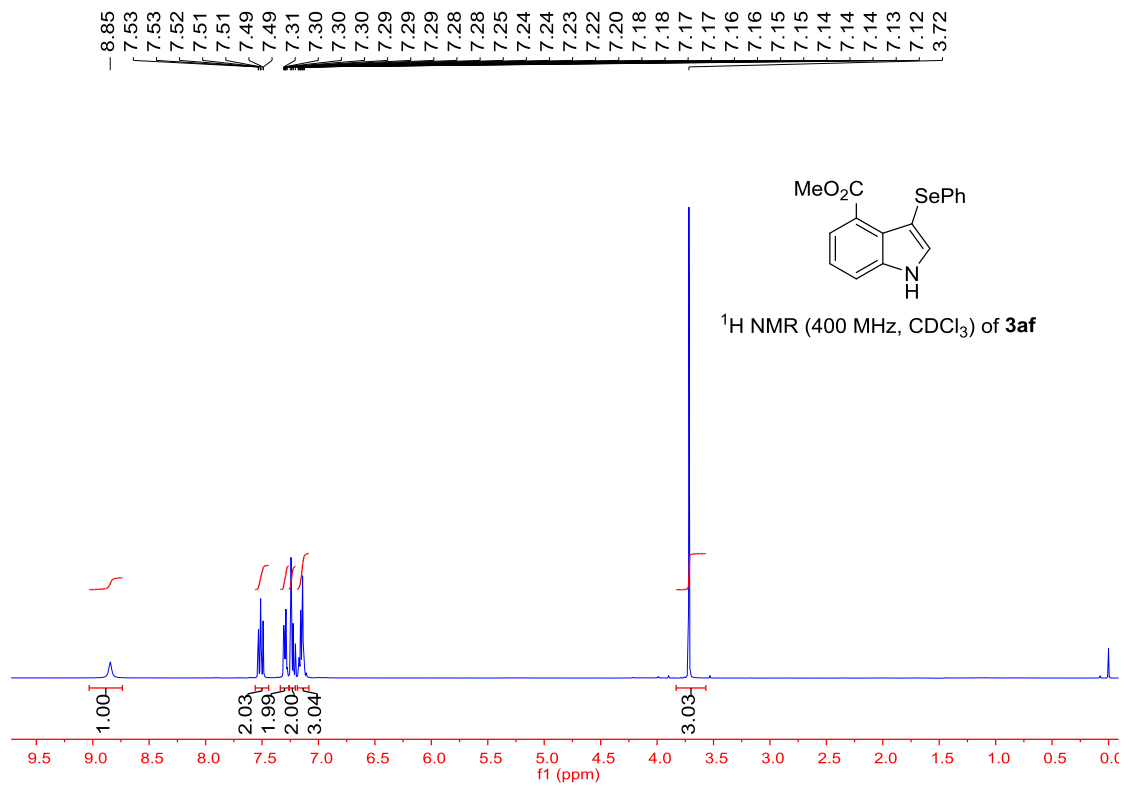


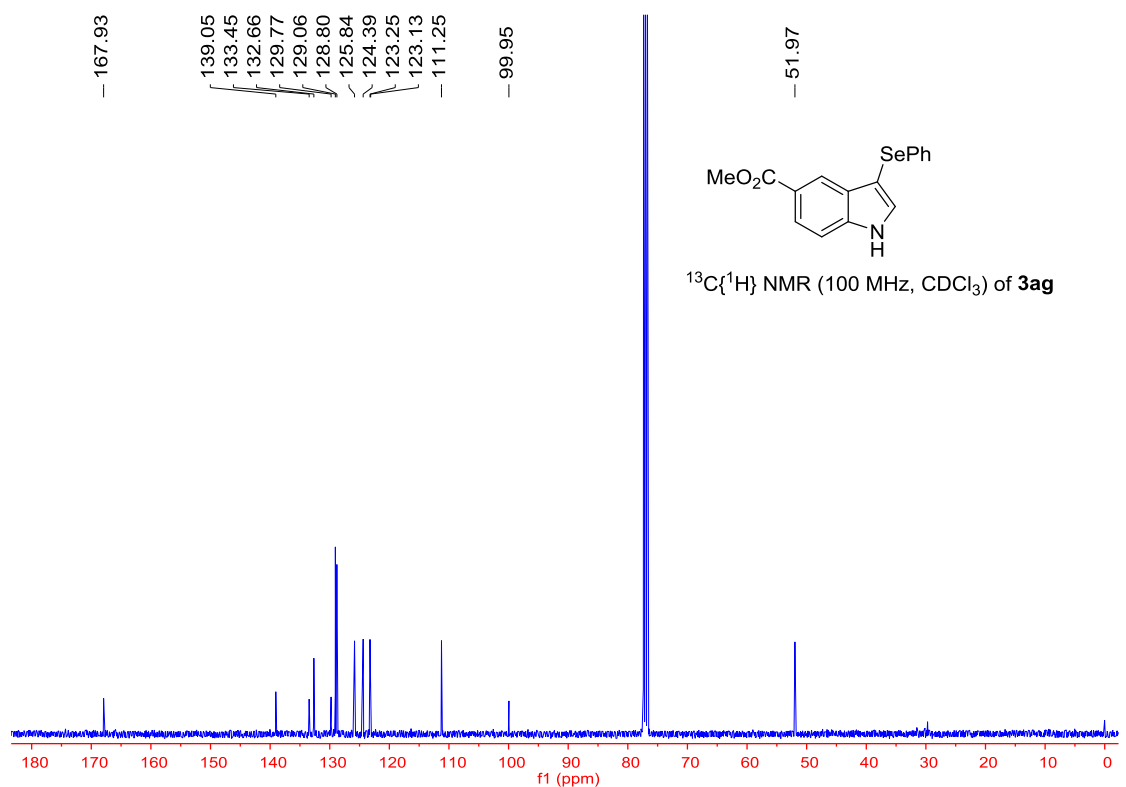
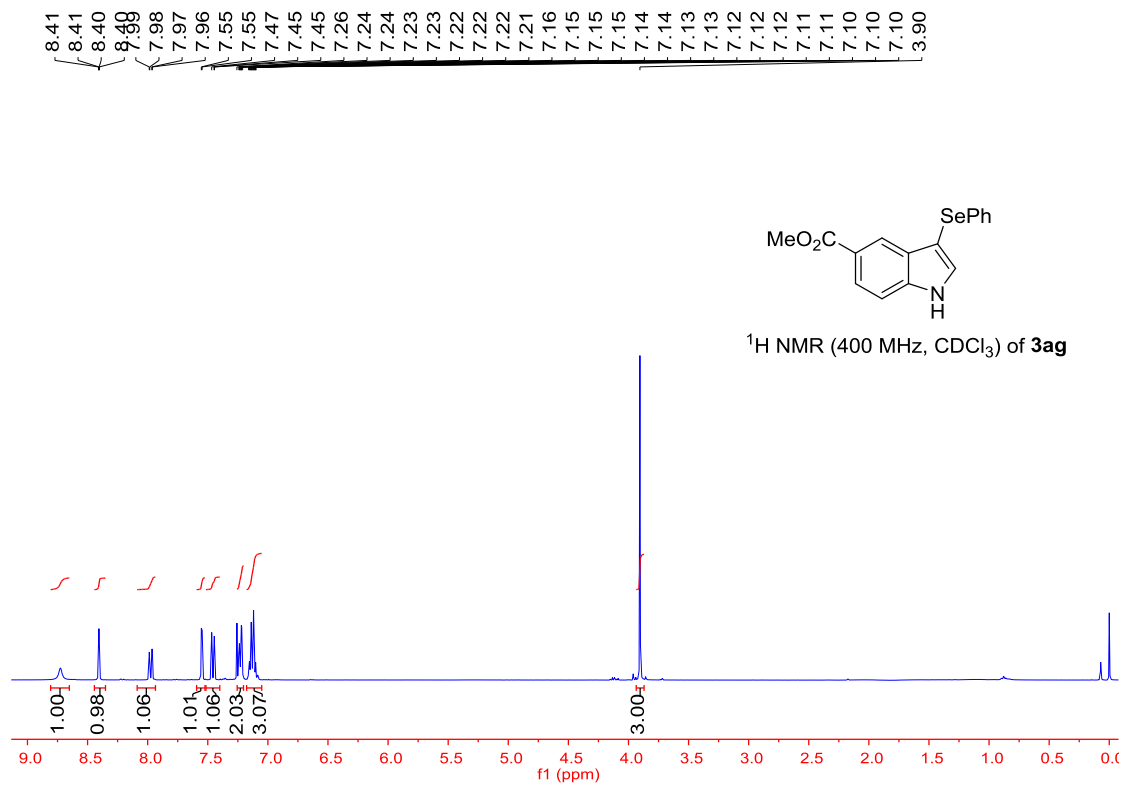


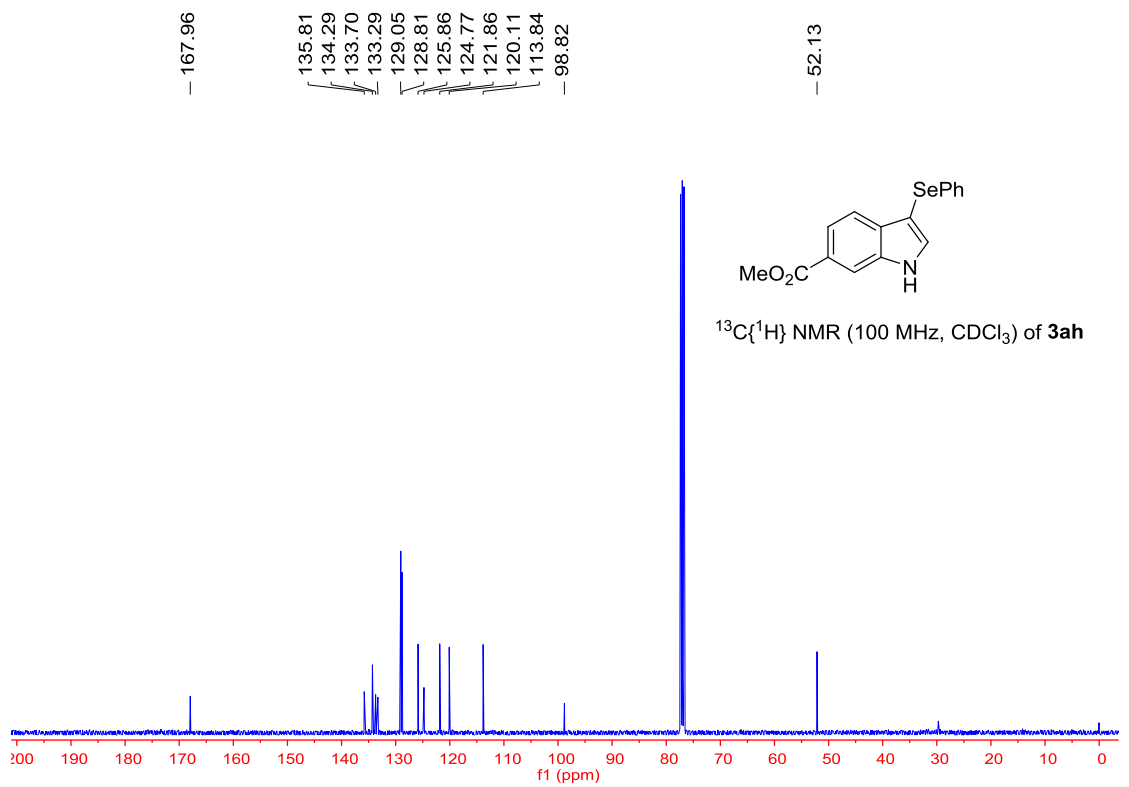
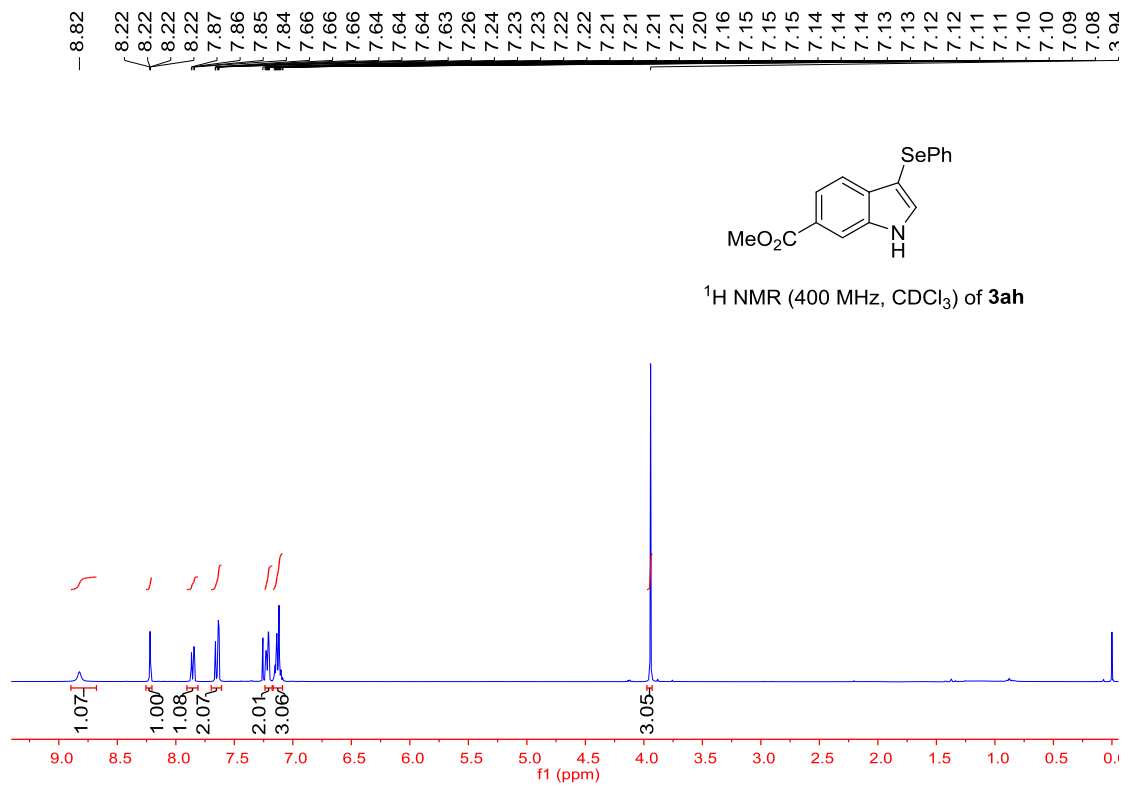


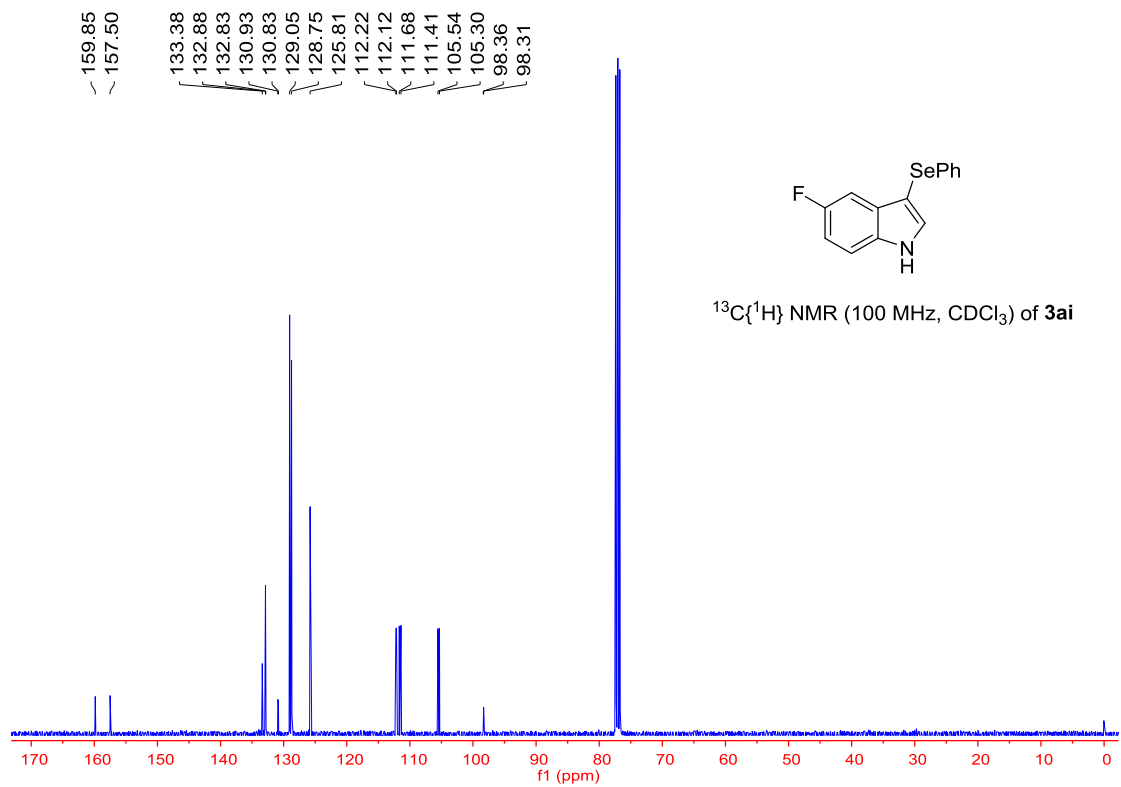
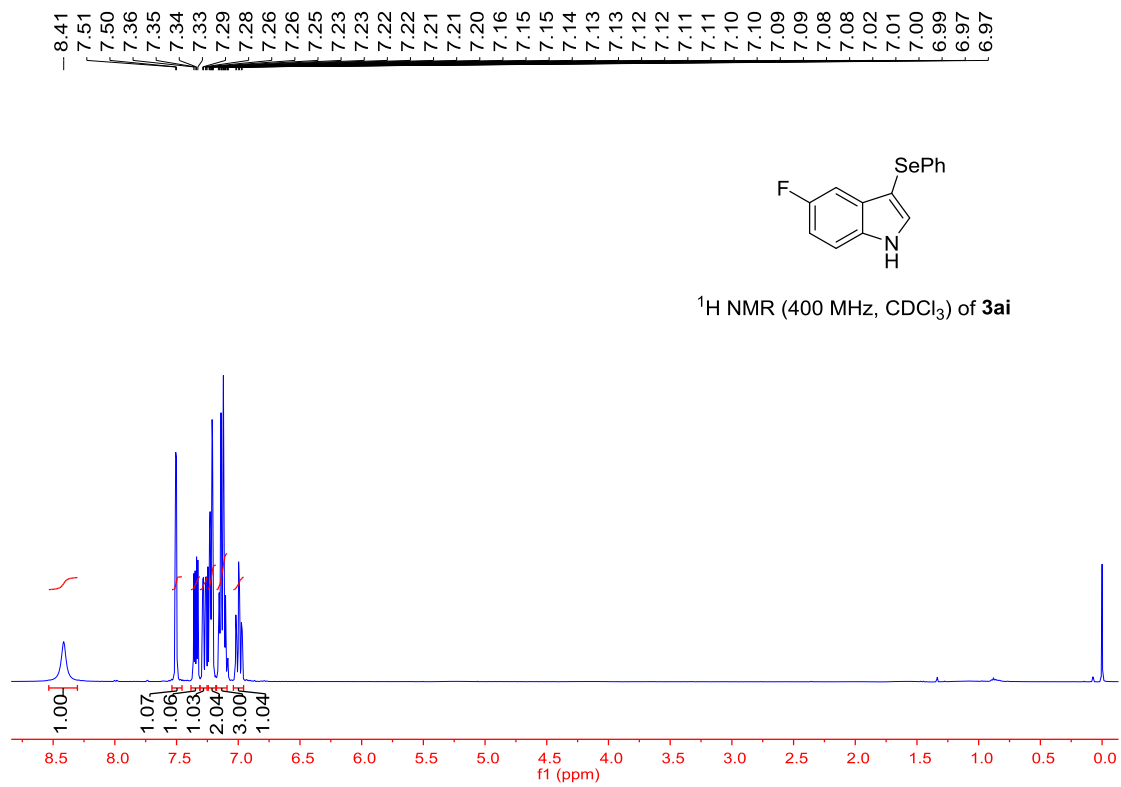


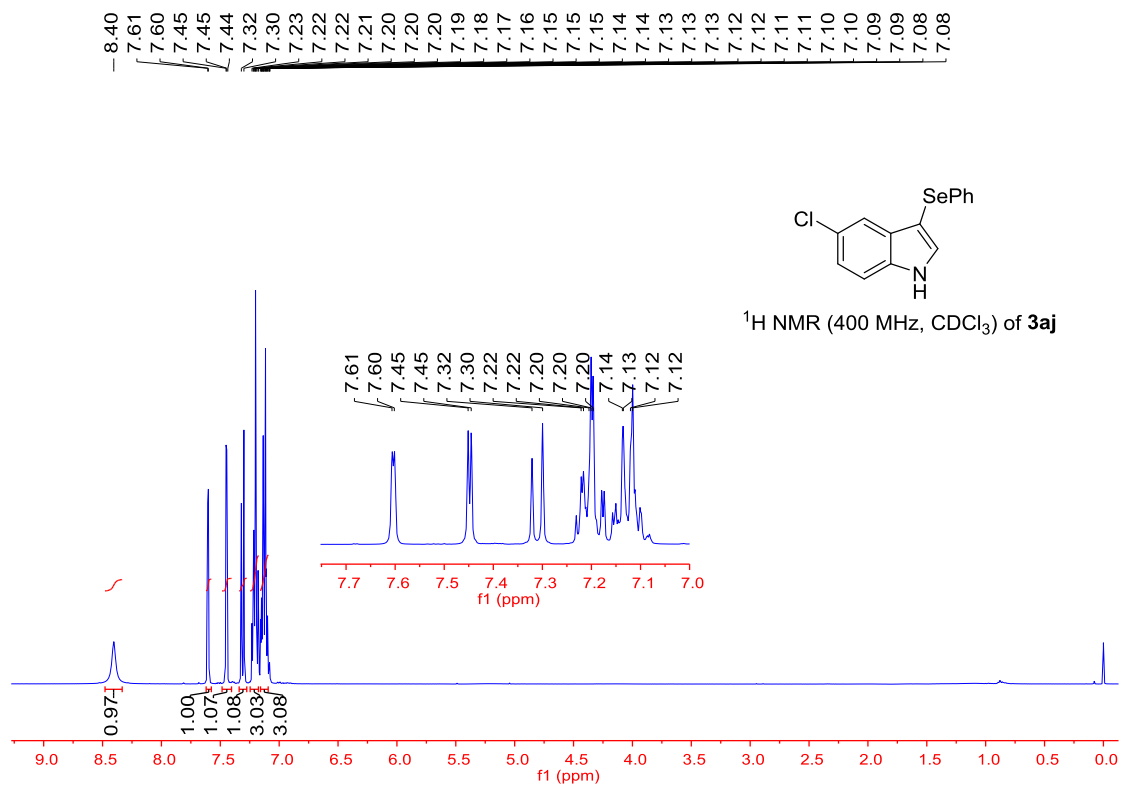
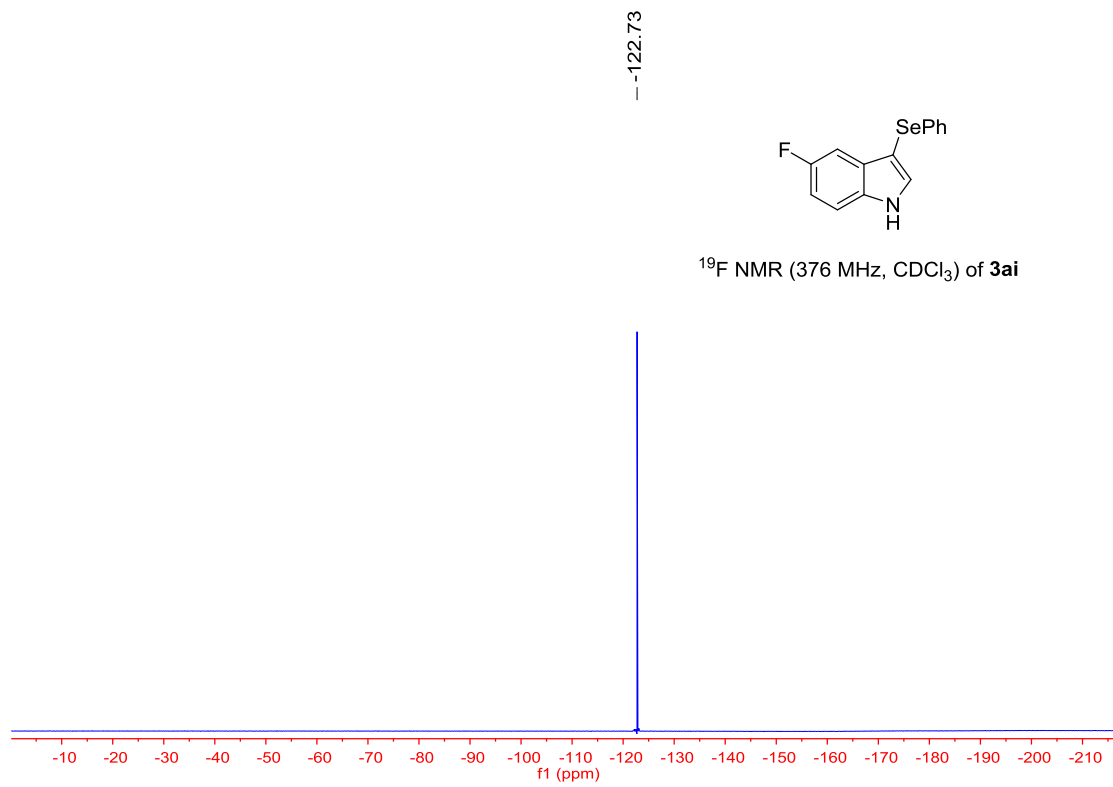






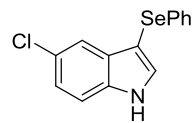




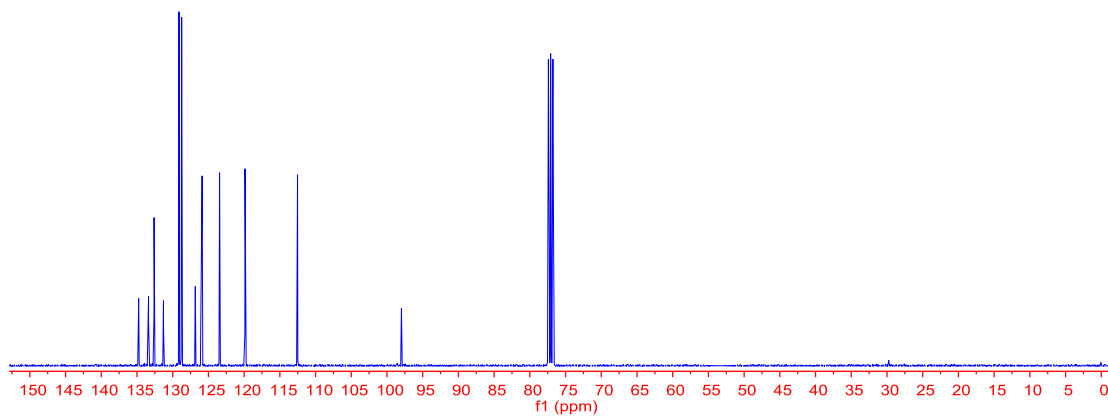


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128.74
126.84
125.88
123.44
119.88
- 112.52

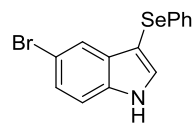
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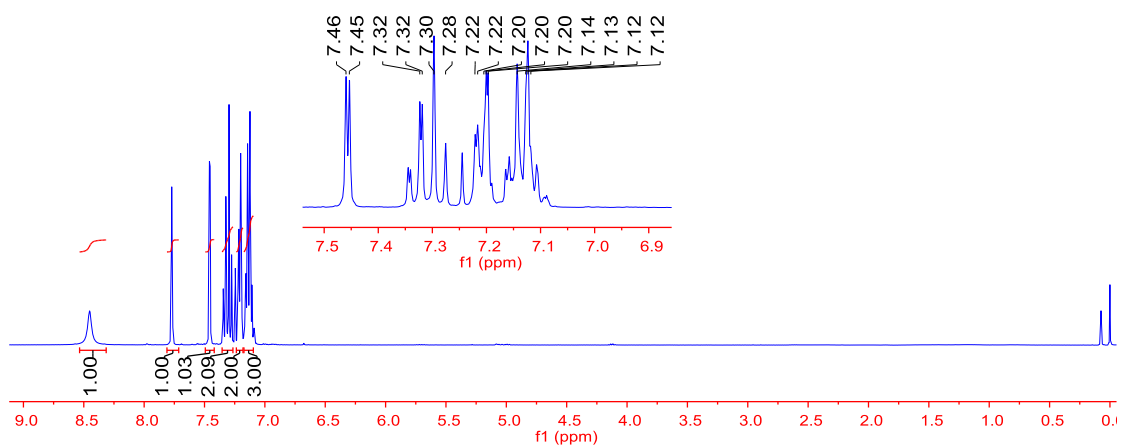
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **3aj**

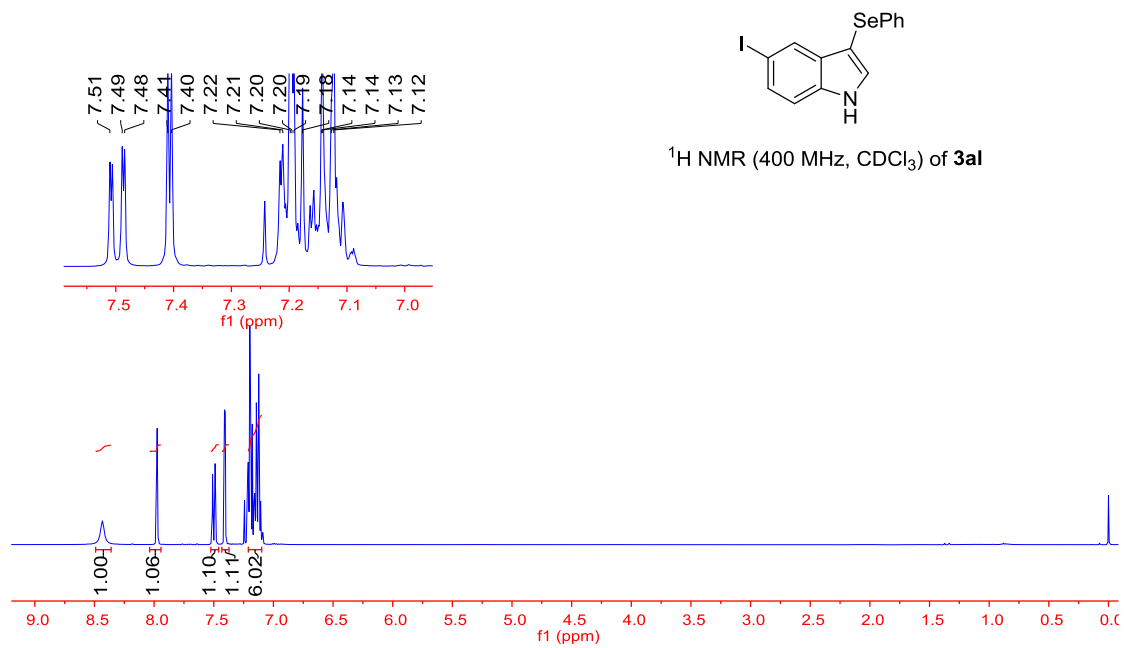
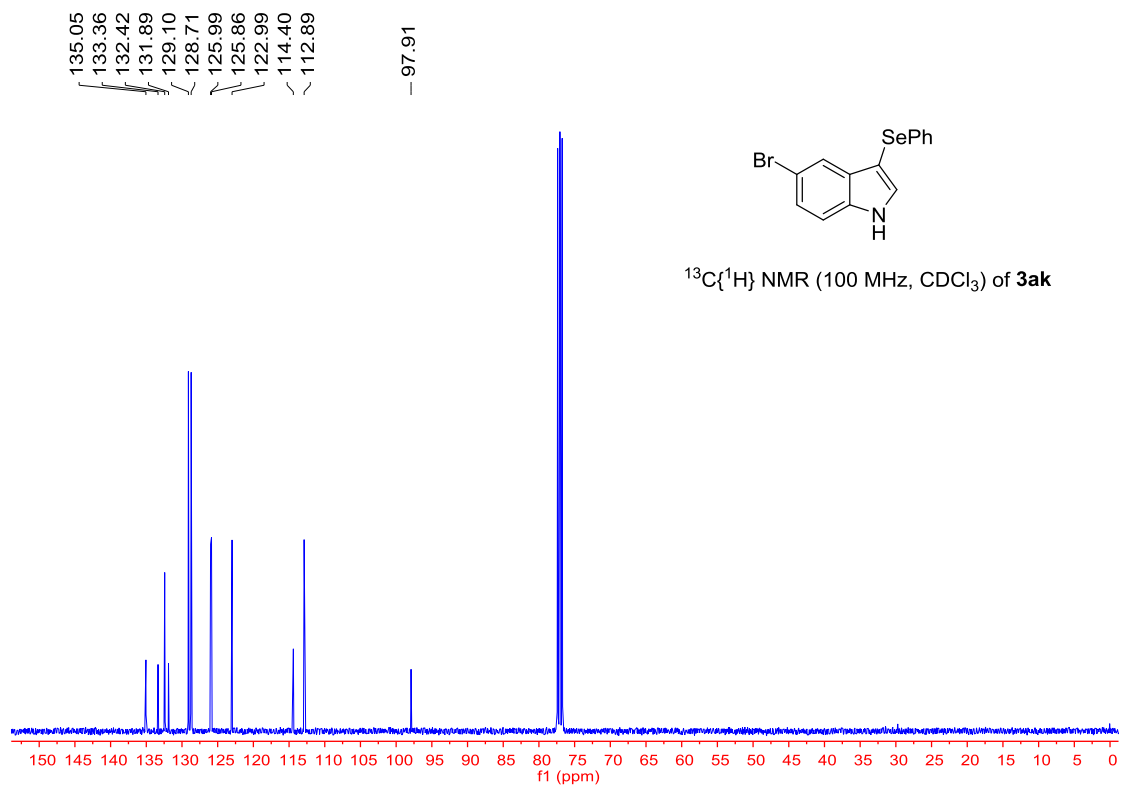


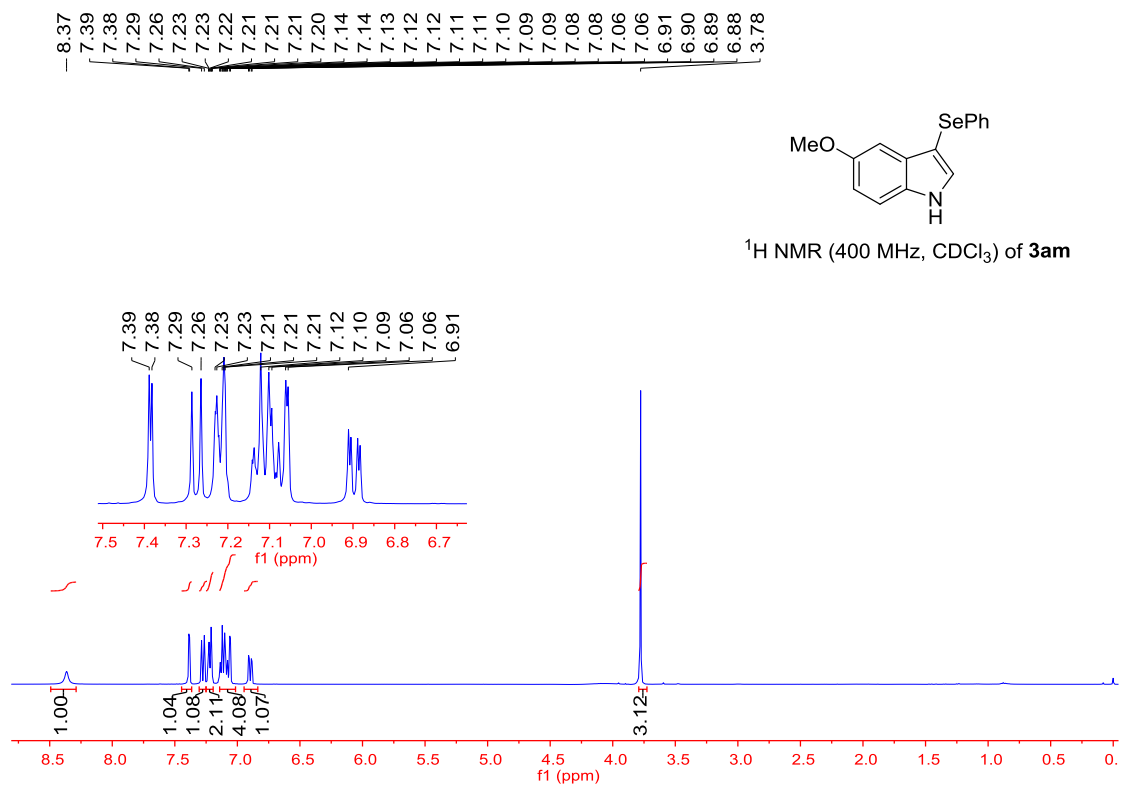
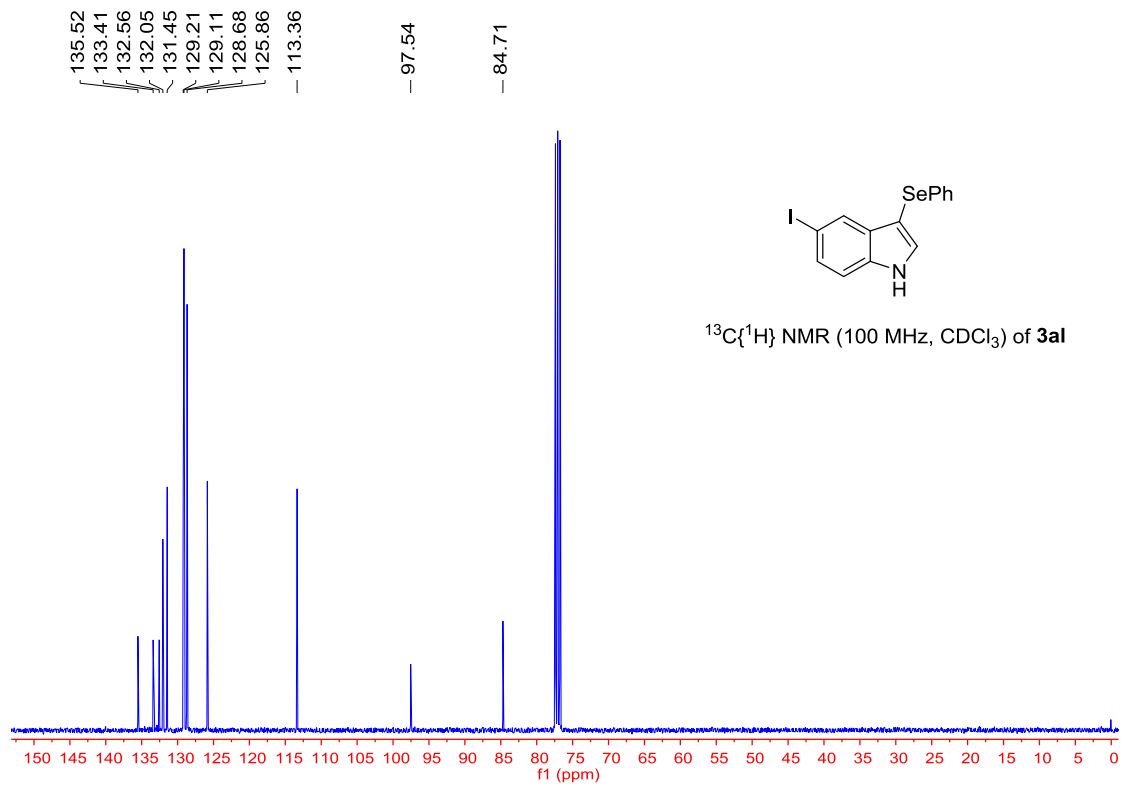
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7.22
7.21
7.20
7.20
7.20
7.19
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7.13
7.12
7.12
7.11
7.11
7.11

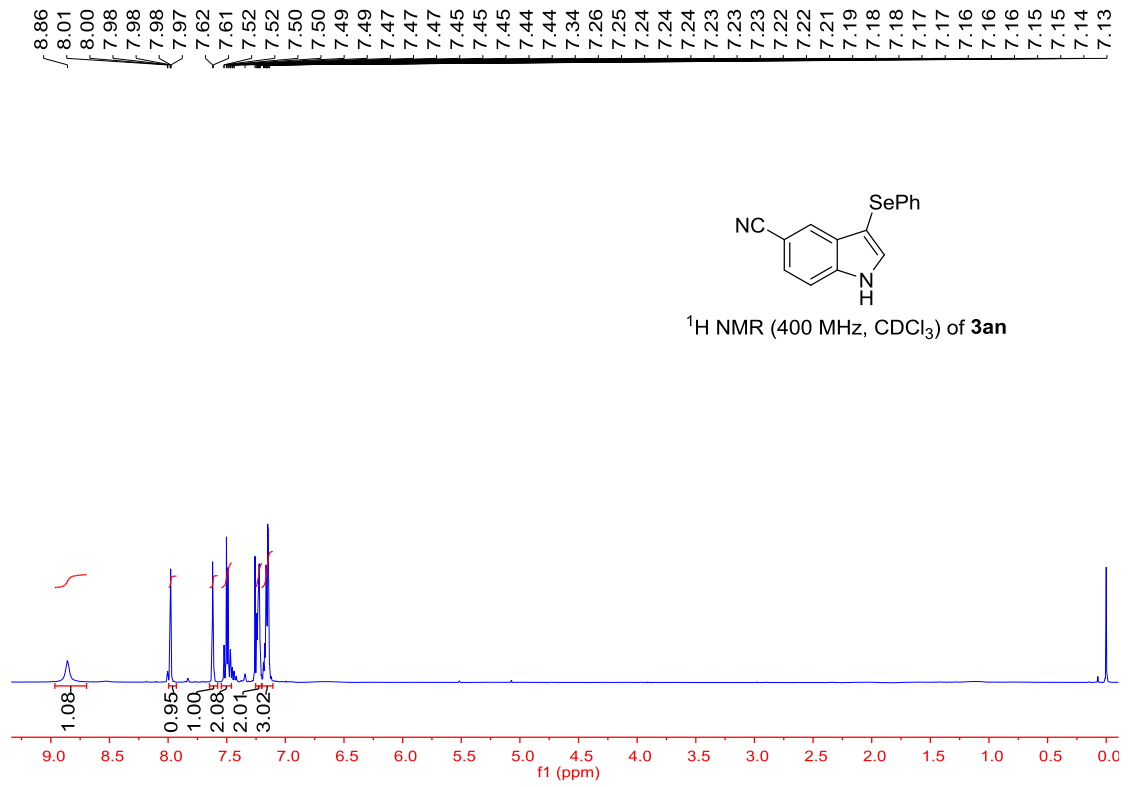
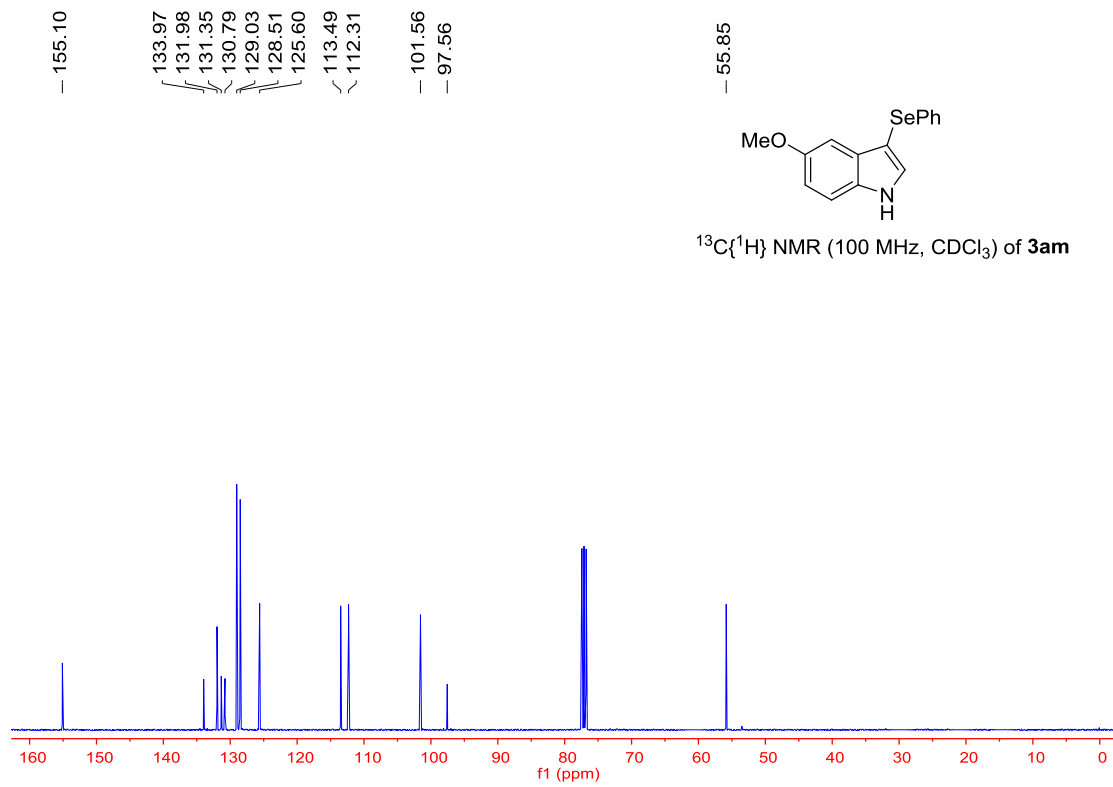


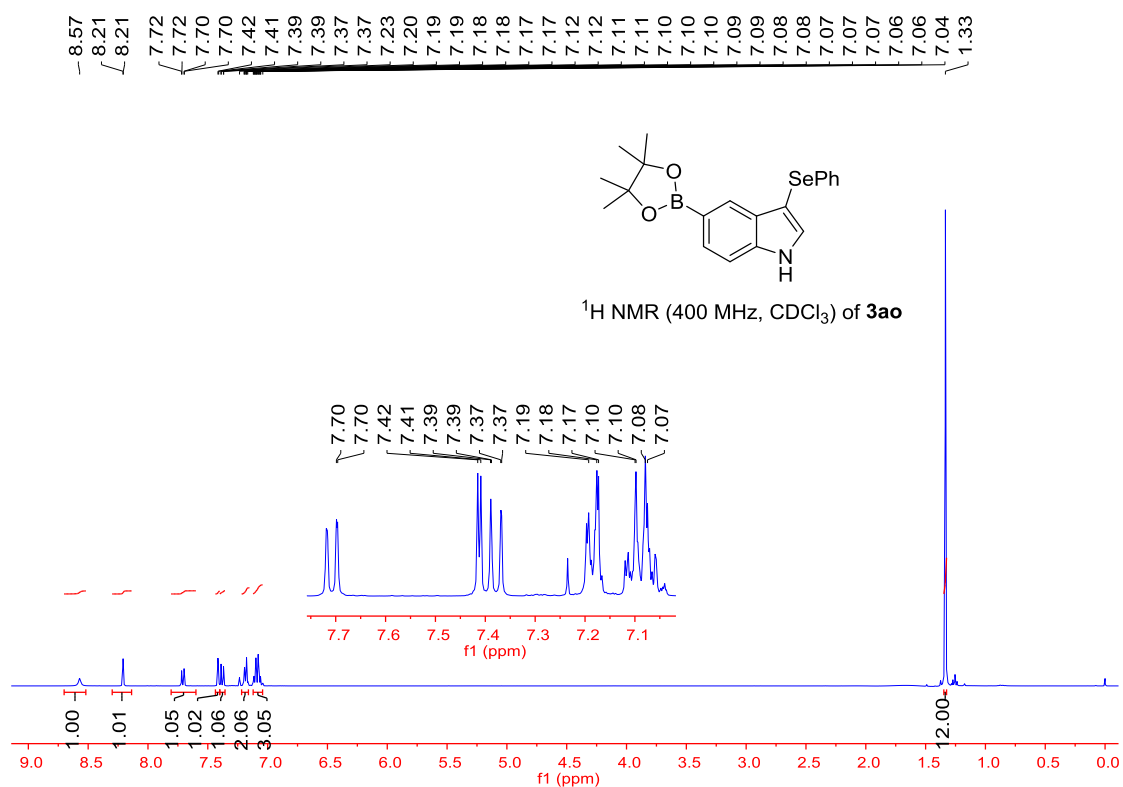
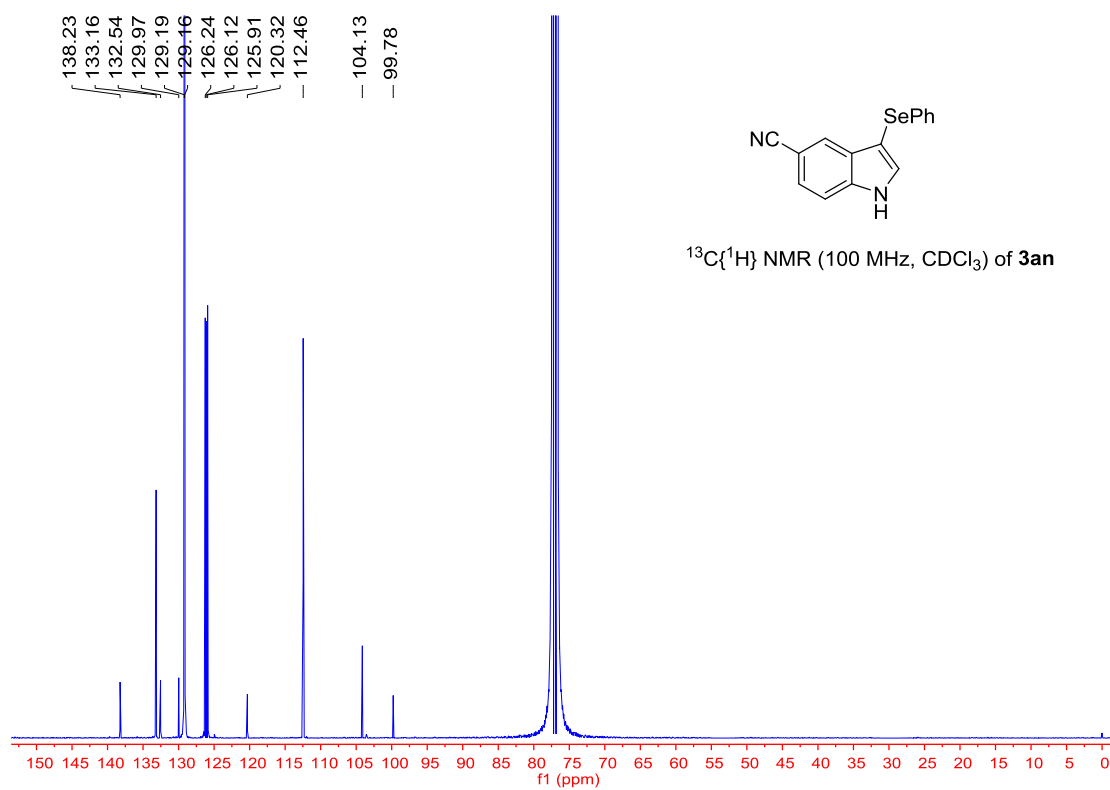
^1H NMR (400 MHz, CDCl_3) of **3ak**

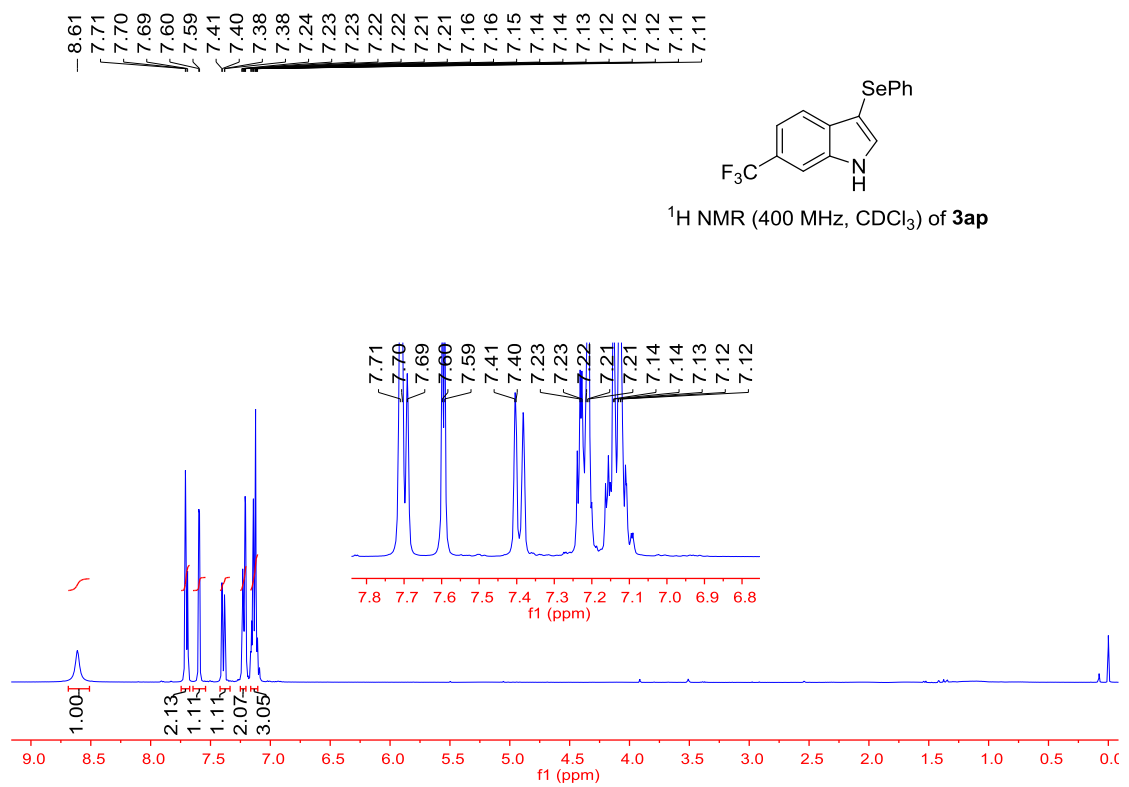
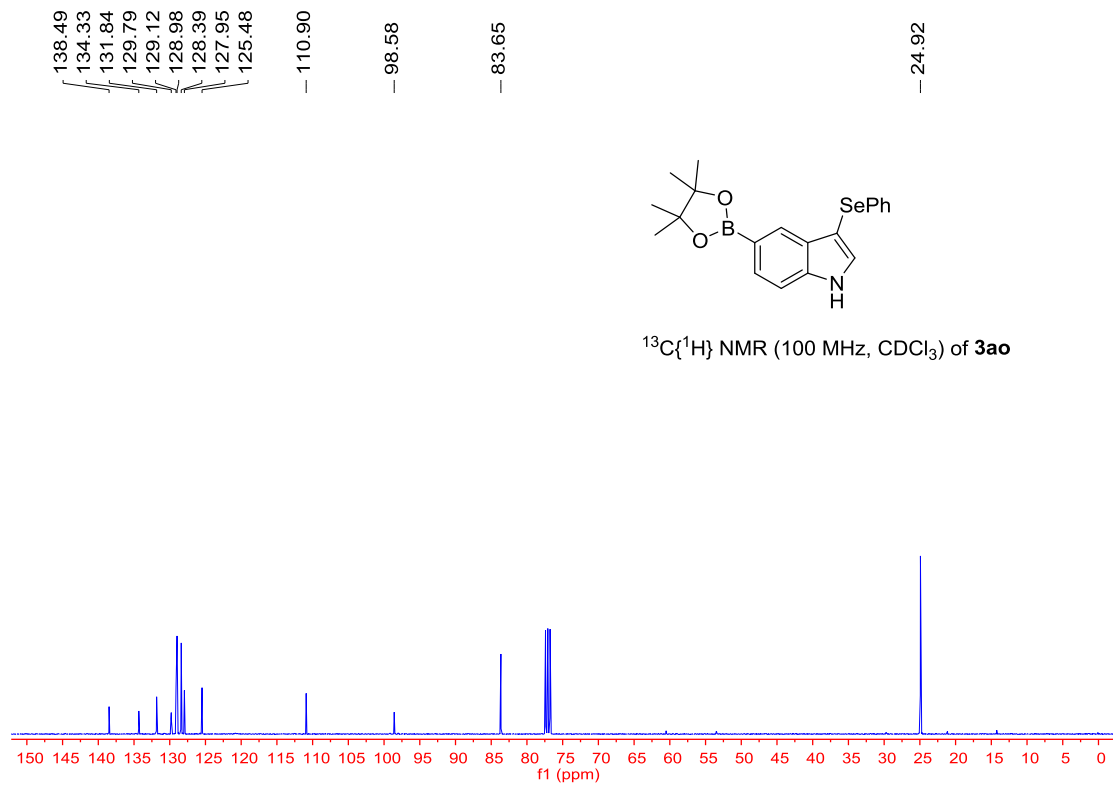




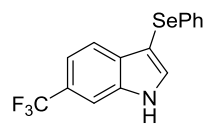




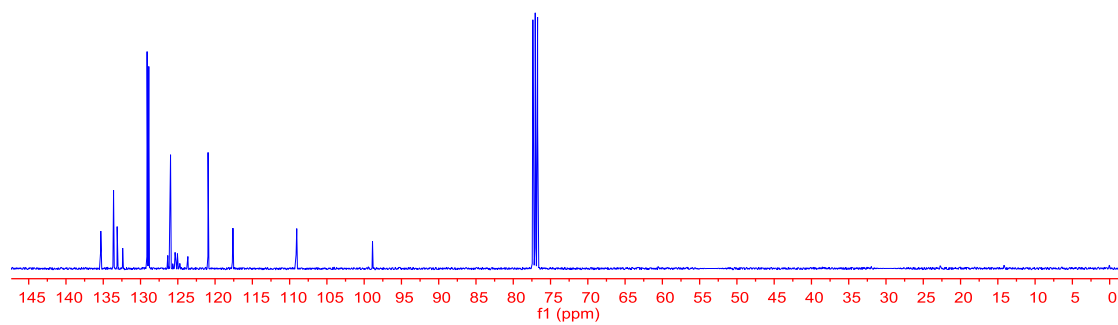




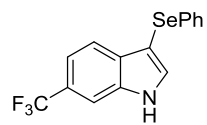
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109.13
109.09
109.05
109.00
98.88



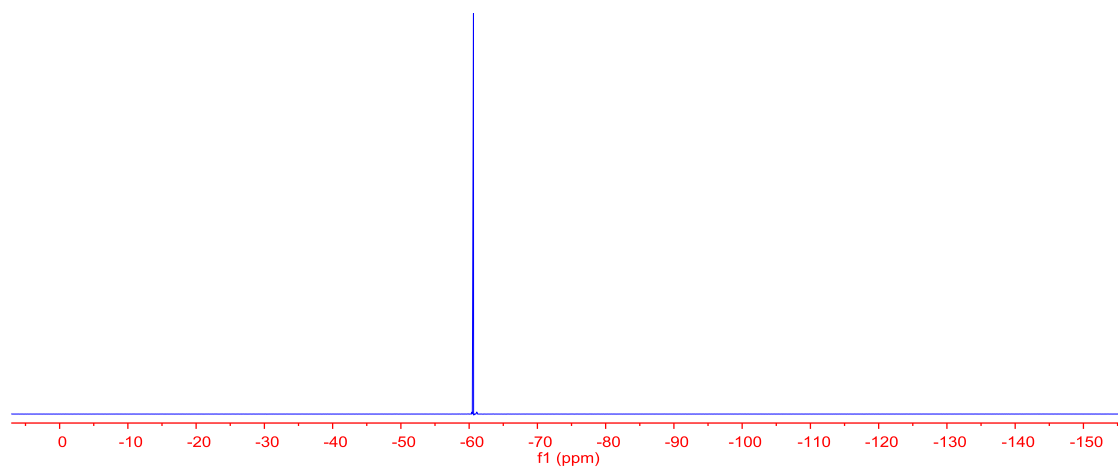
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **3ap**

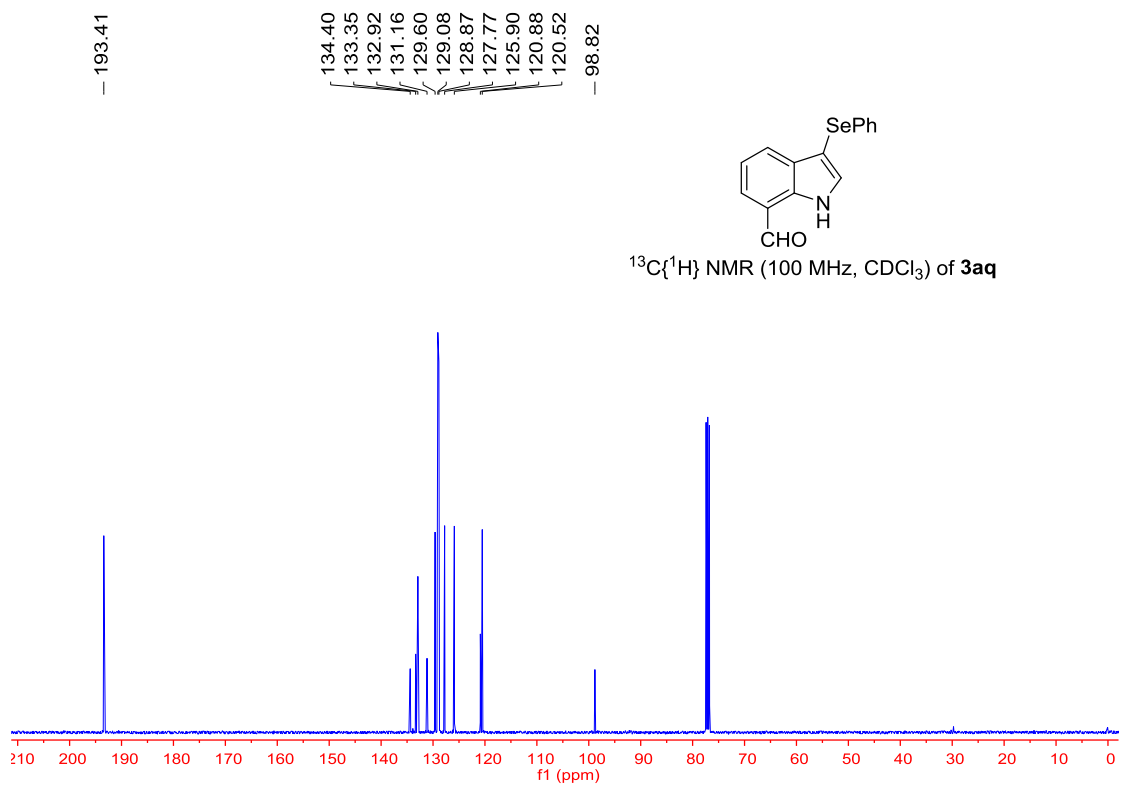
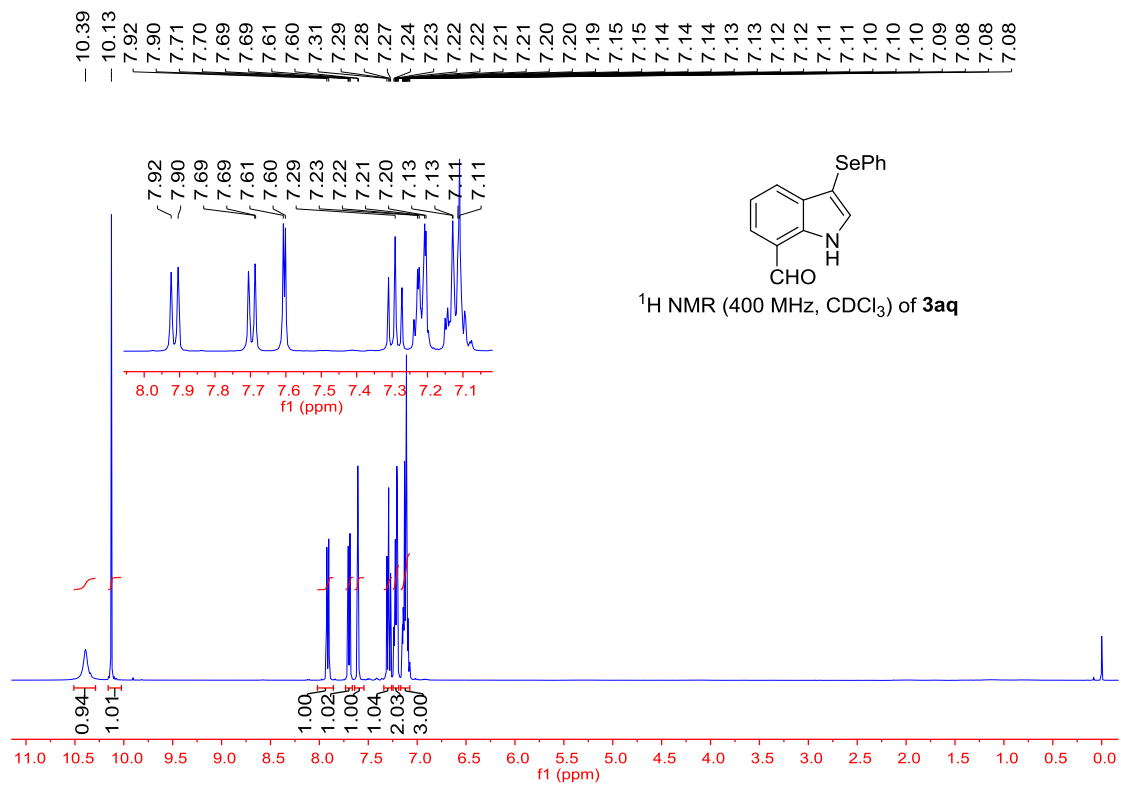


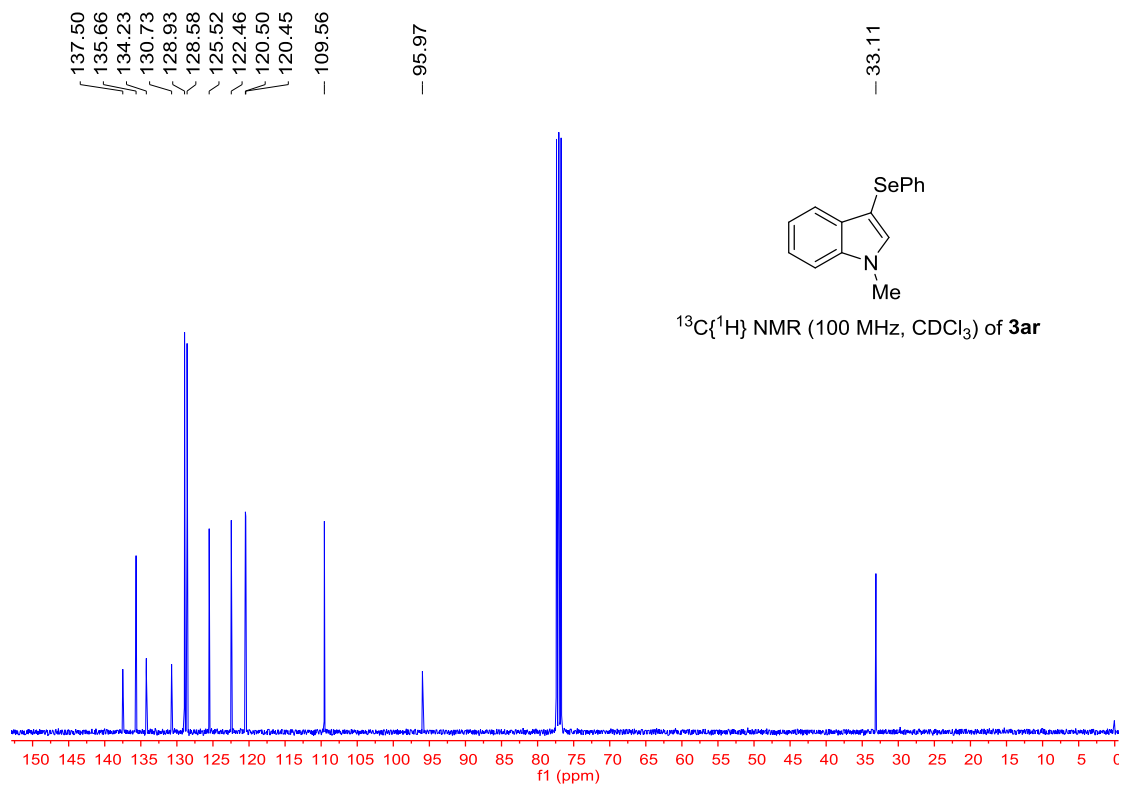
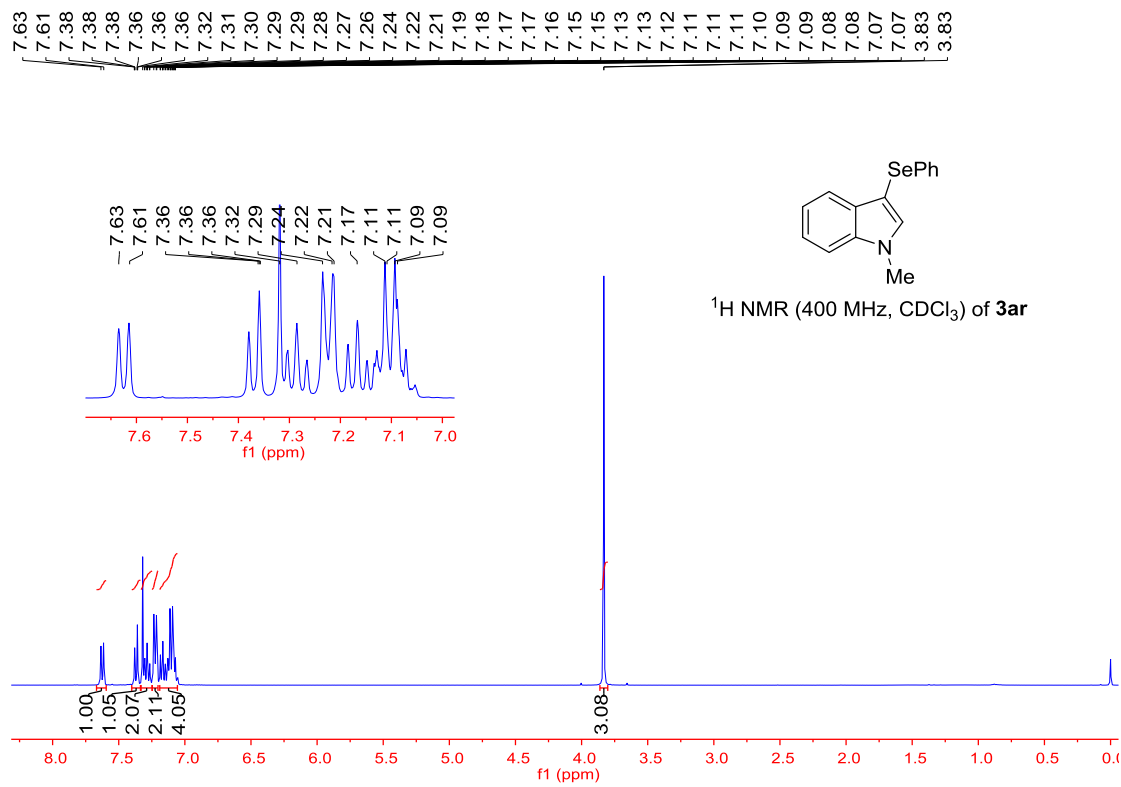
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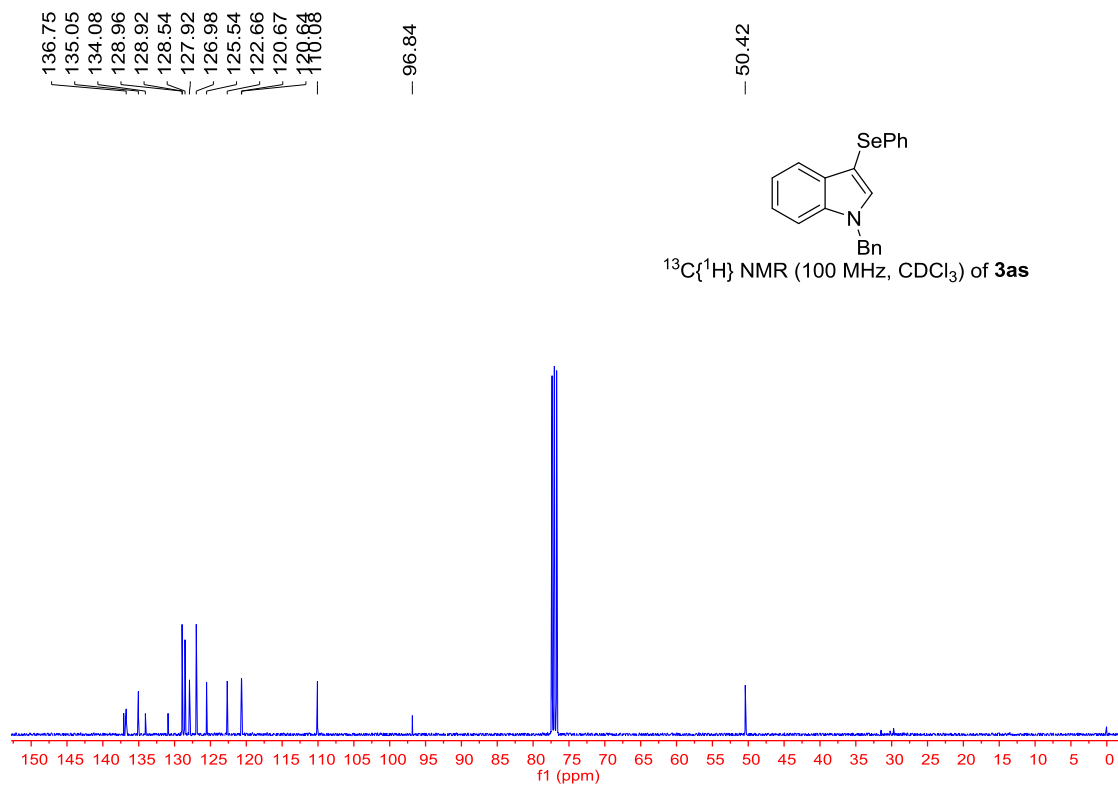
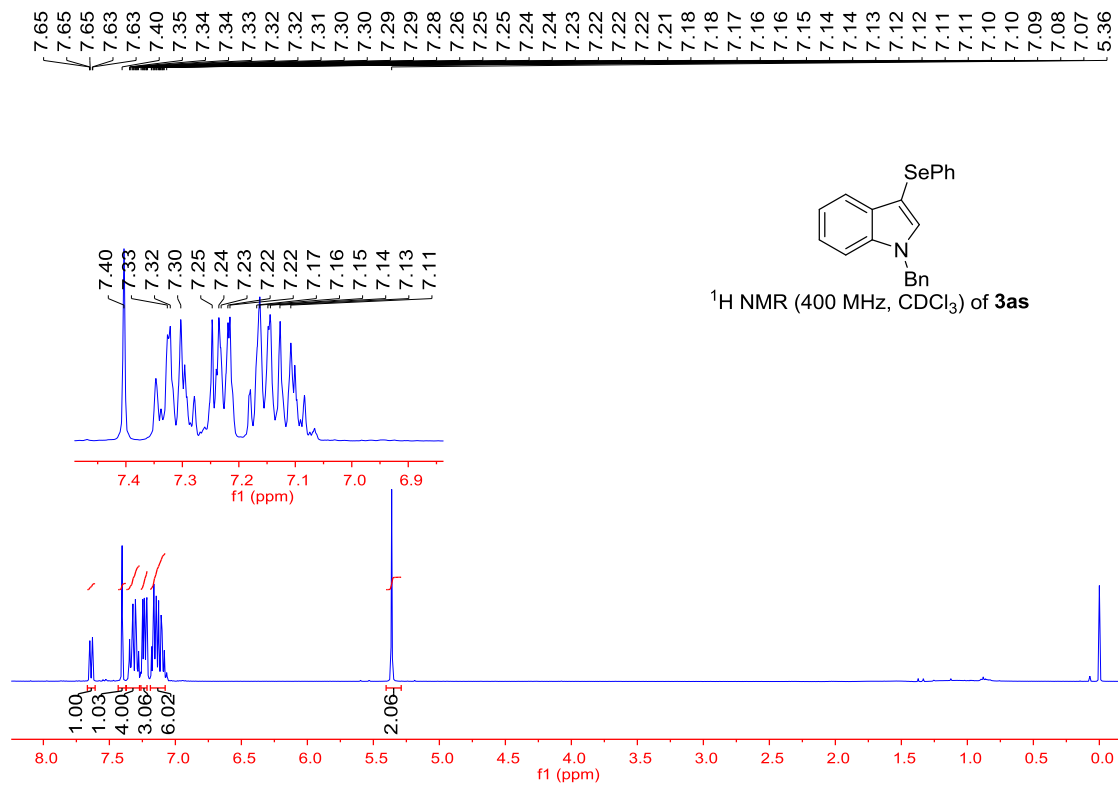


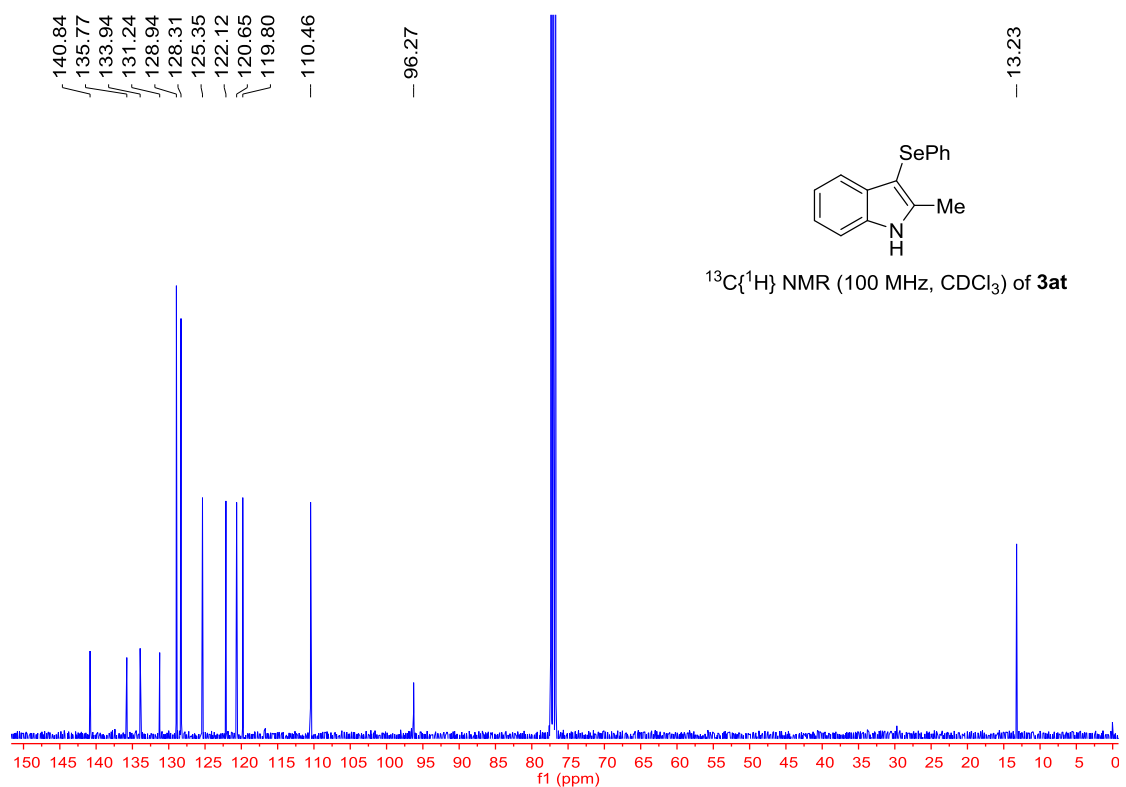
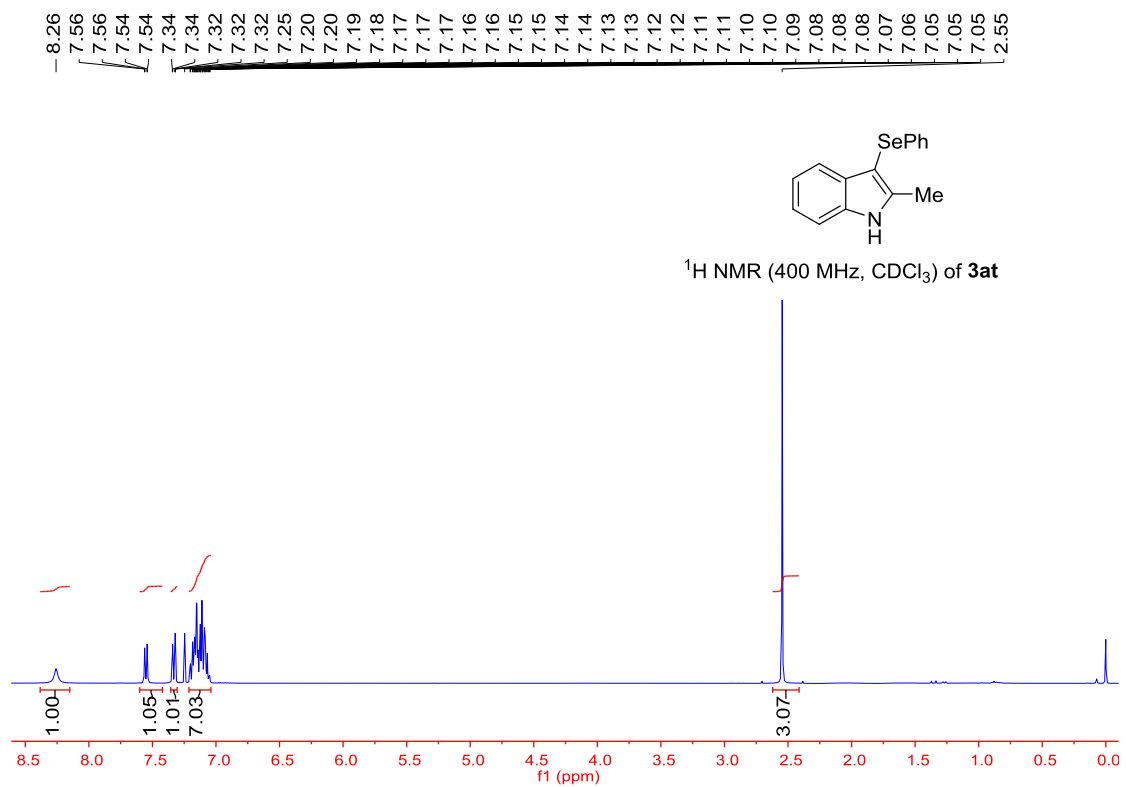
^{19}F NMR (376 MHz, CDCl_3) of **3ap**

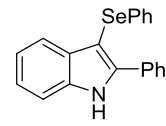
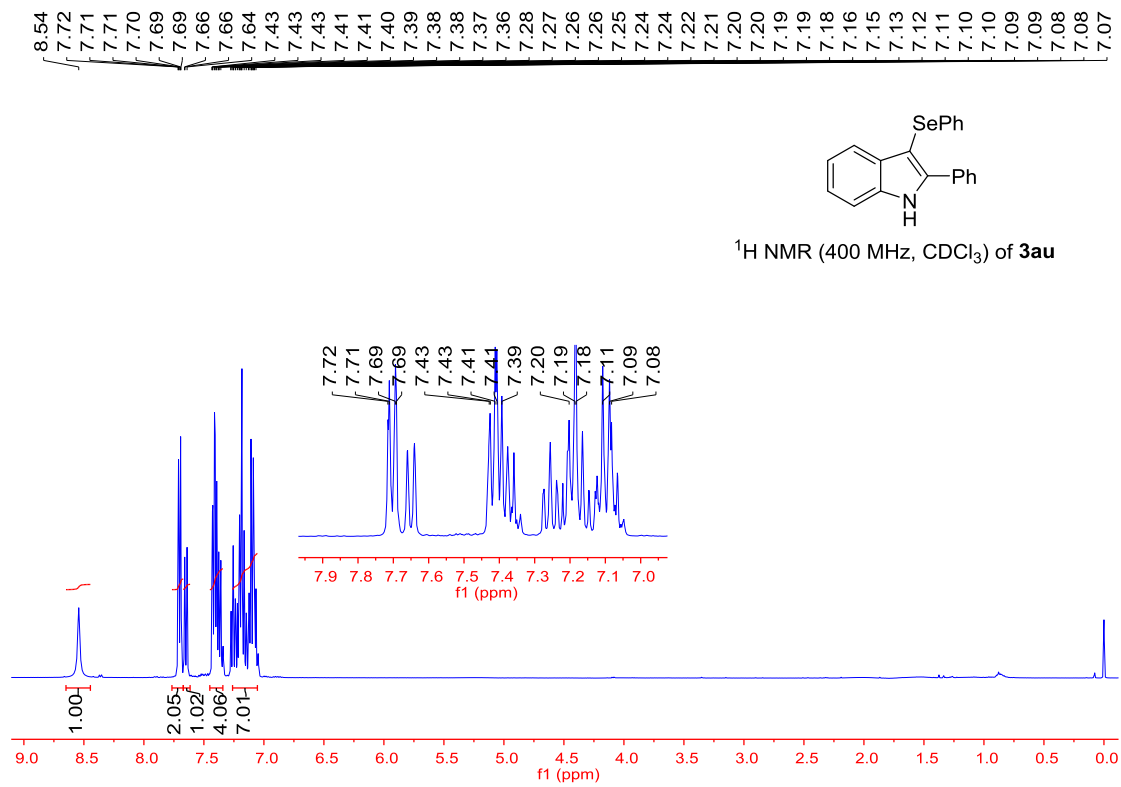




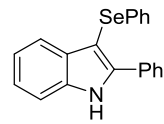
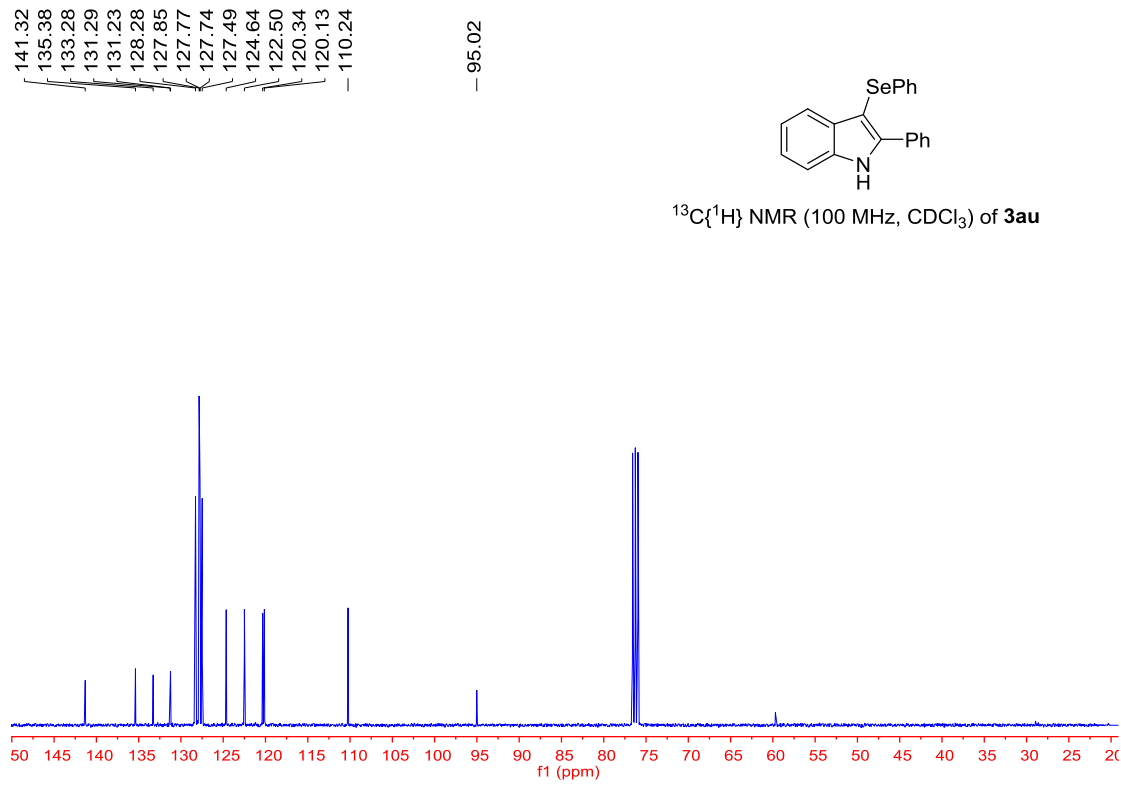




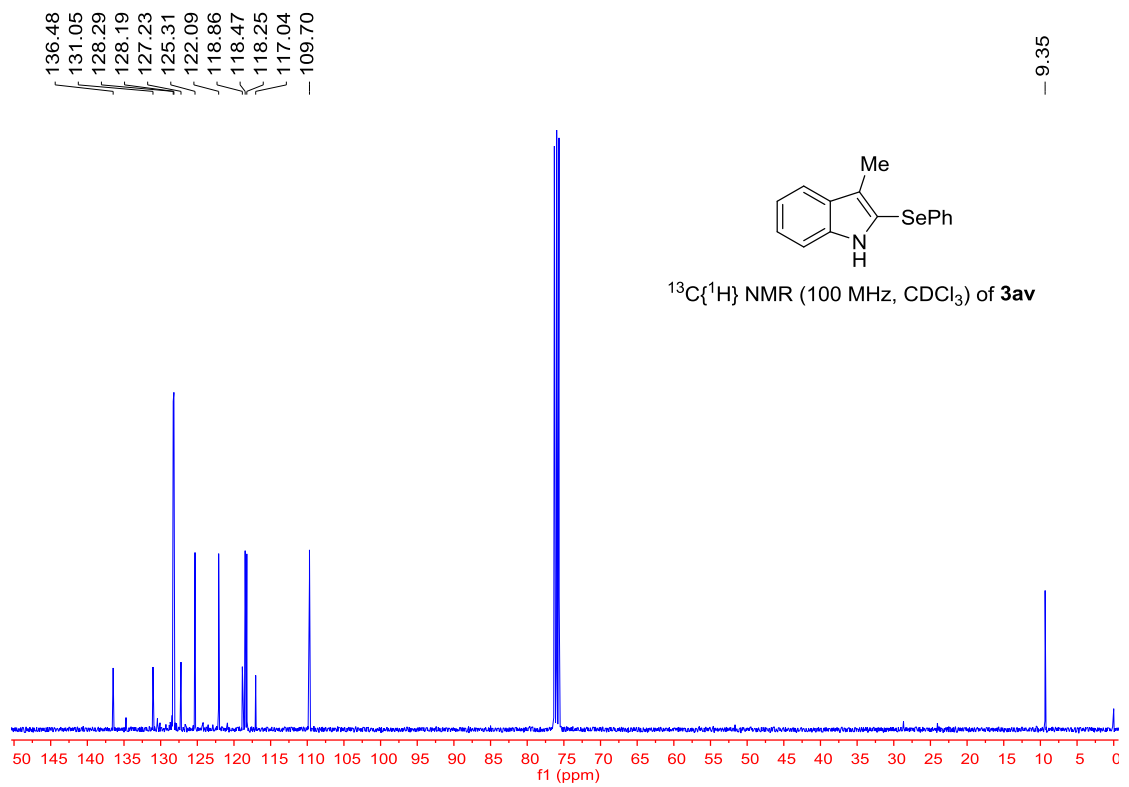
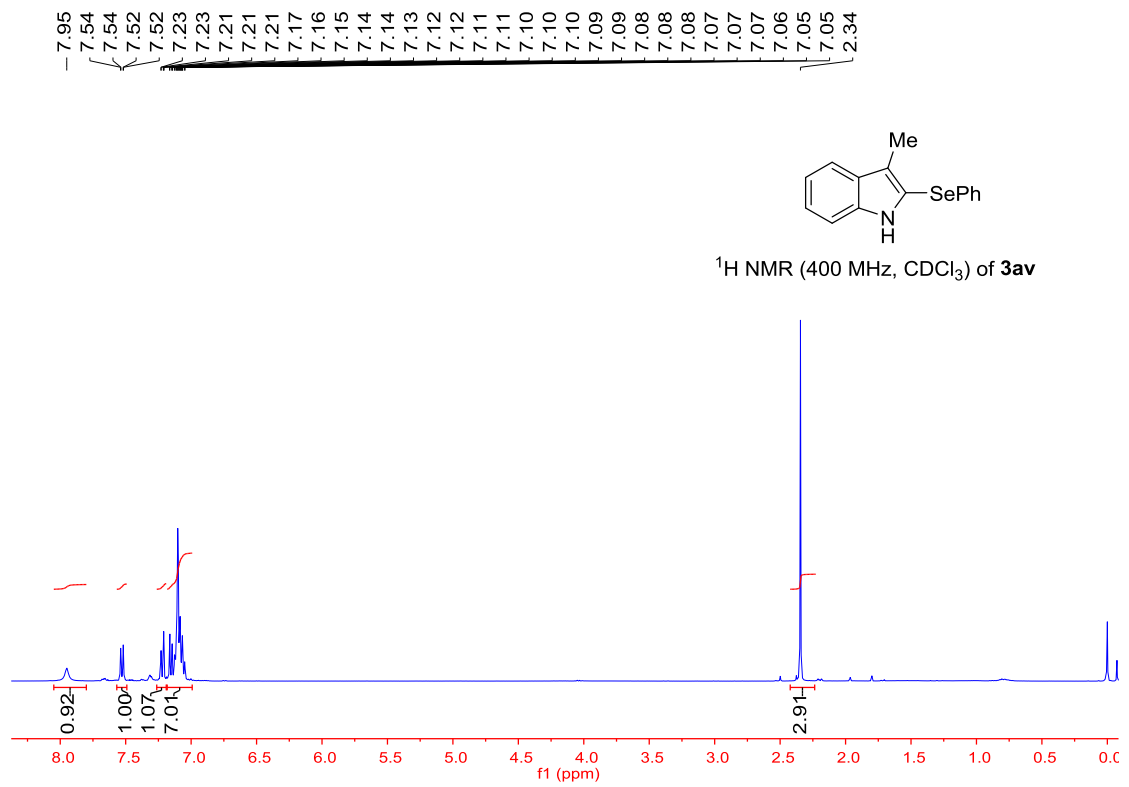


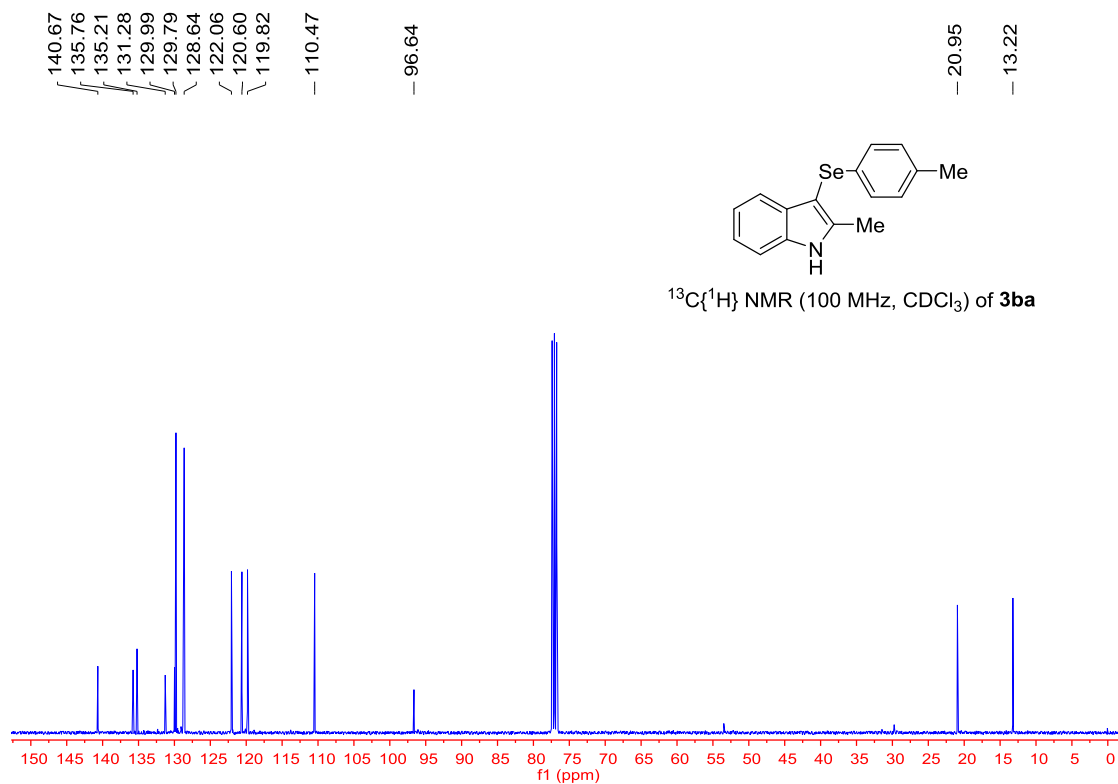
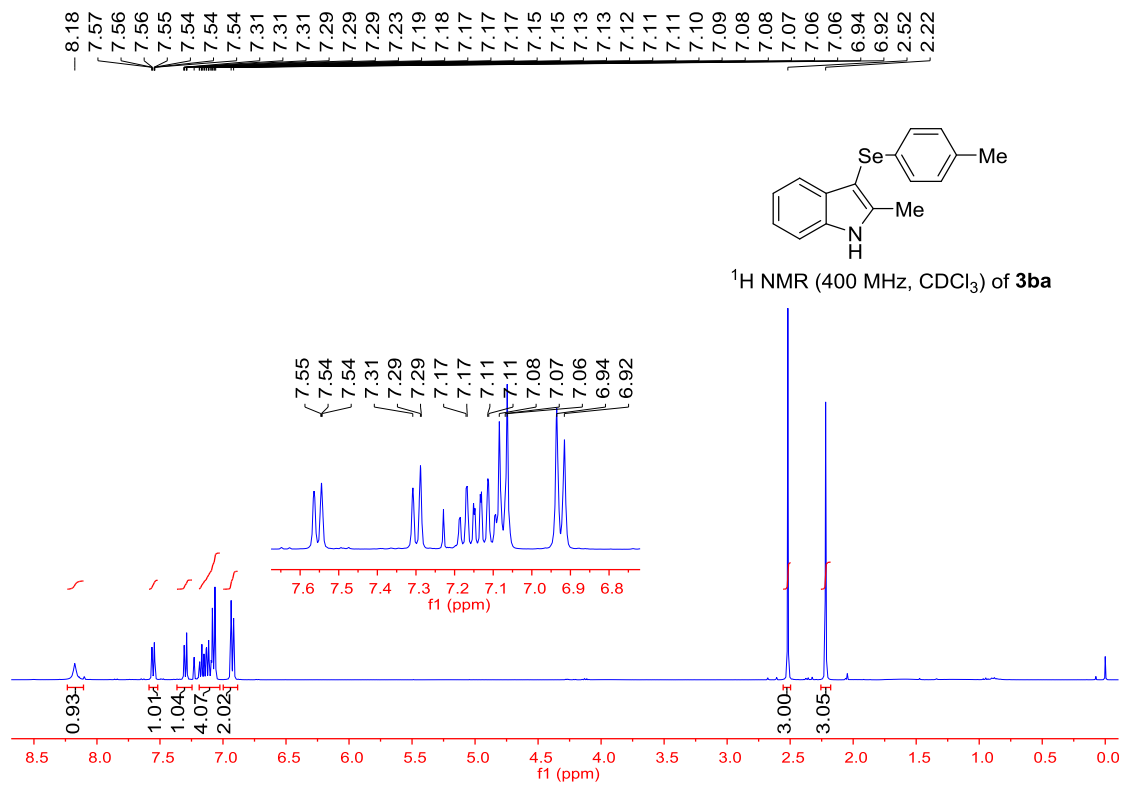


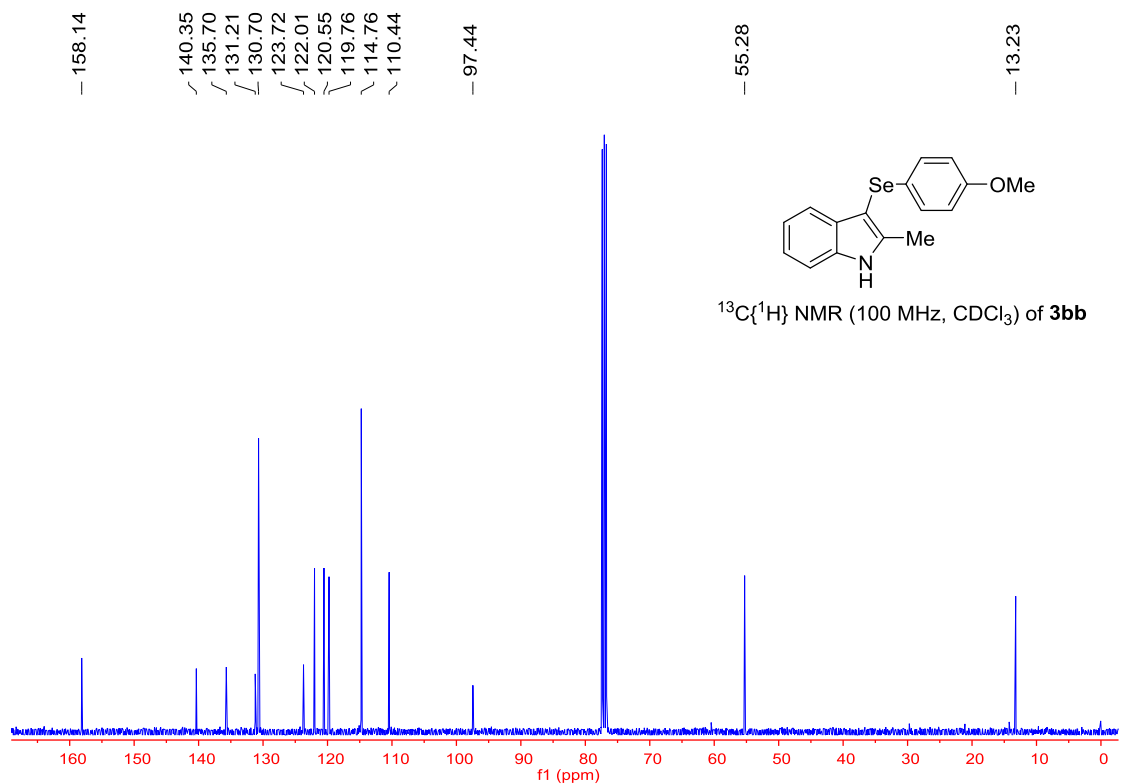
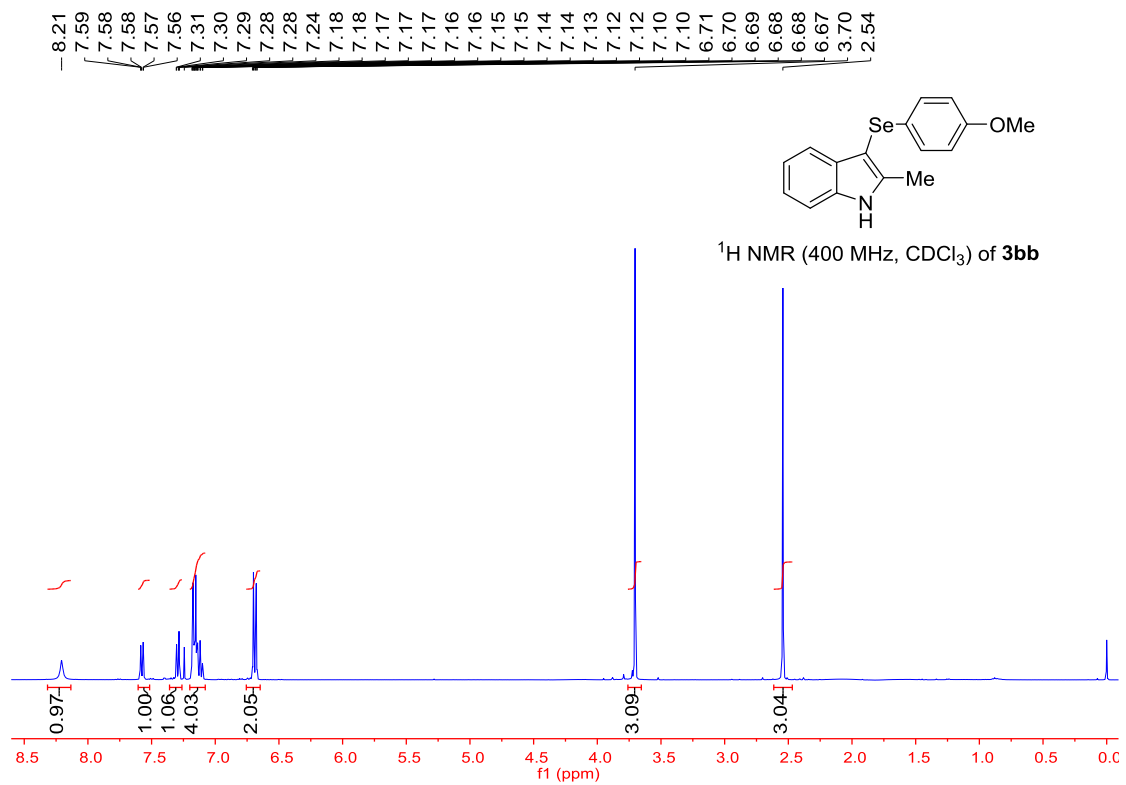
¹H NMR (400 MHz, CDCl₃) of **3au**

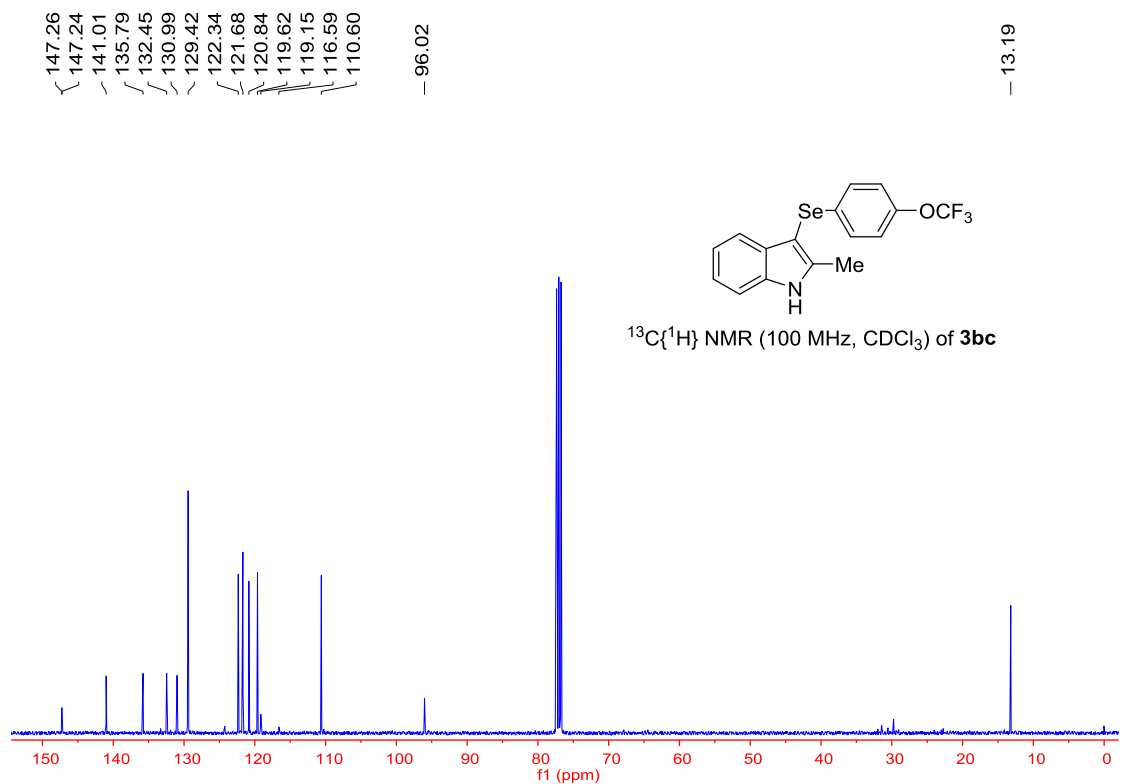
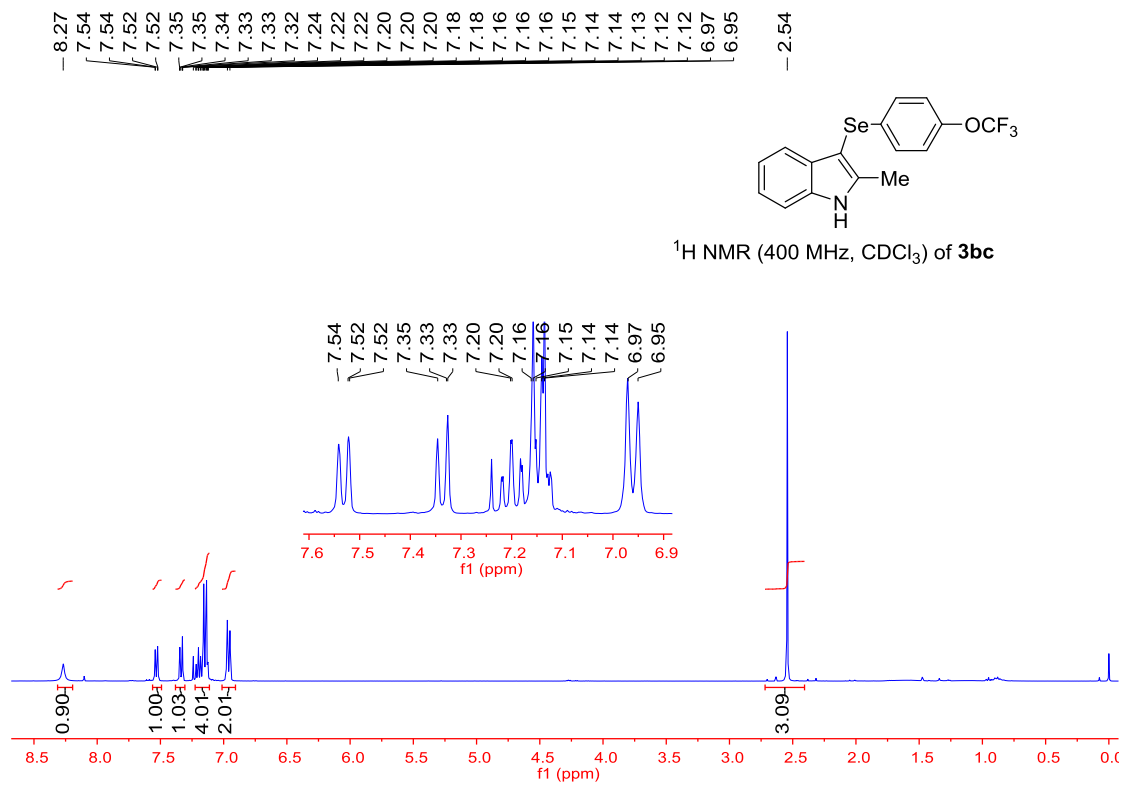


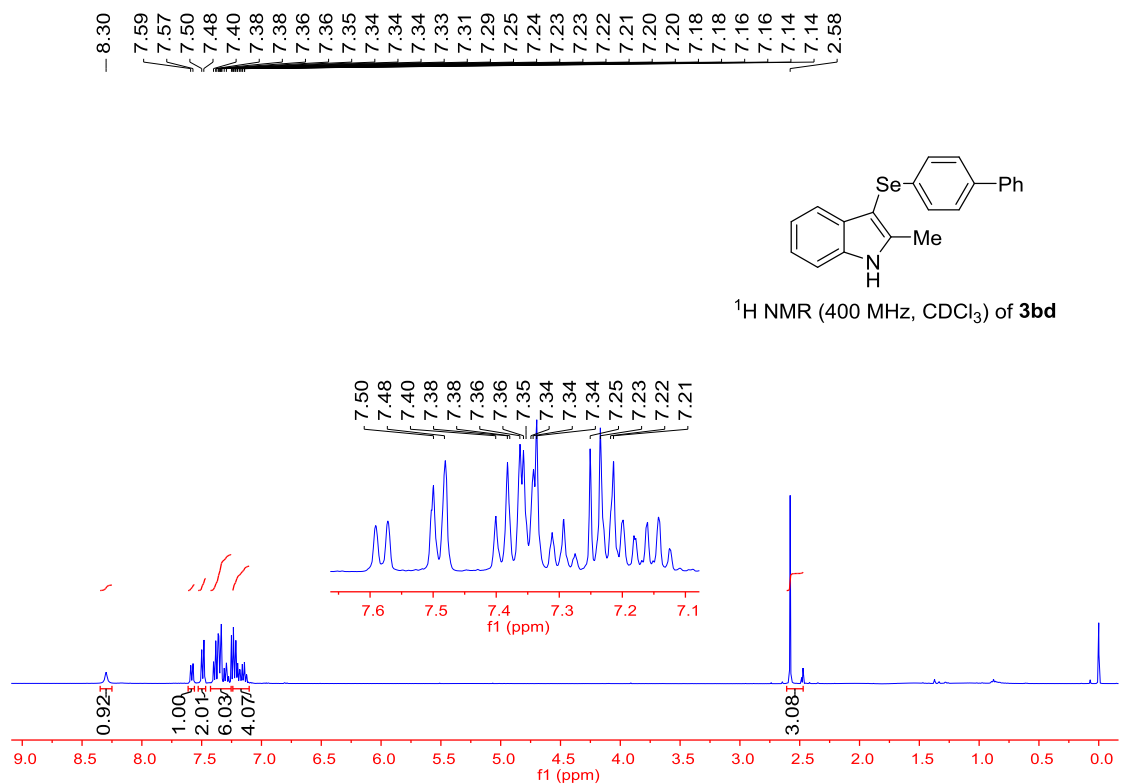
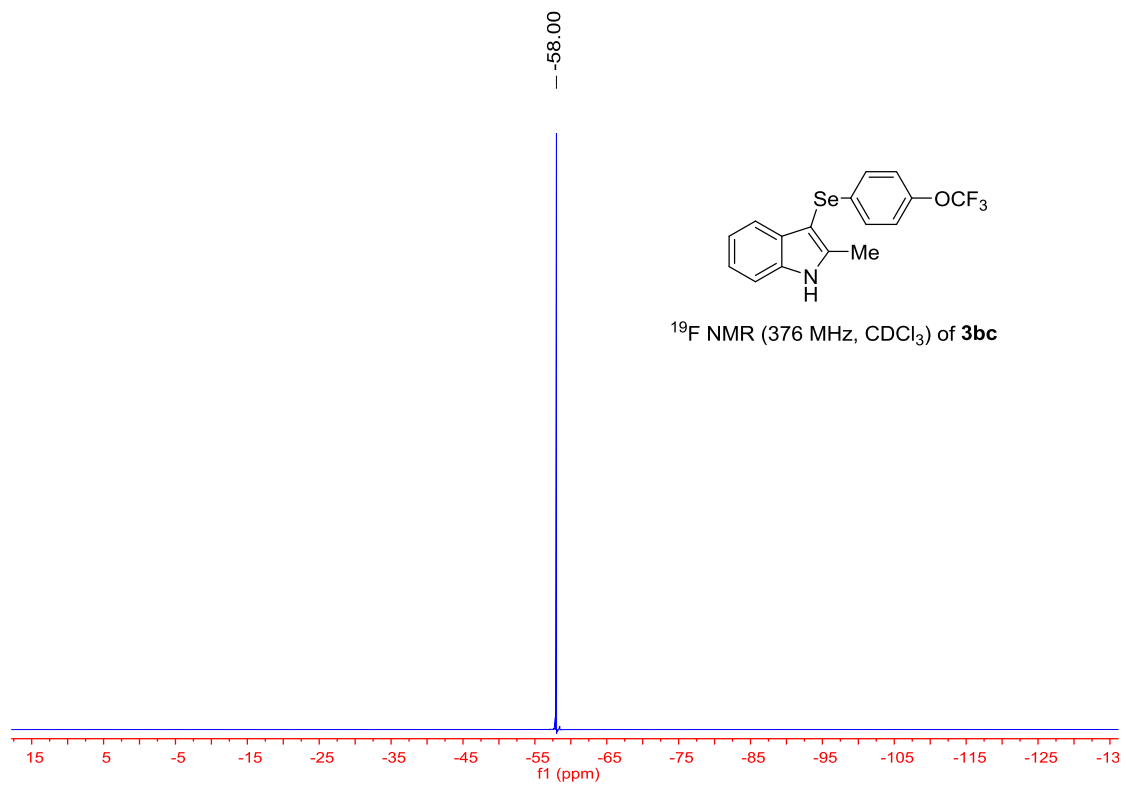
¹³C{¹H} NMR (100 MHz, CDCl₃) of **3au**

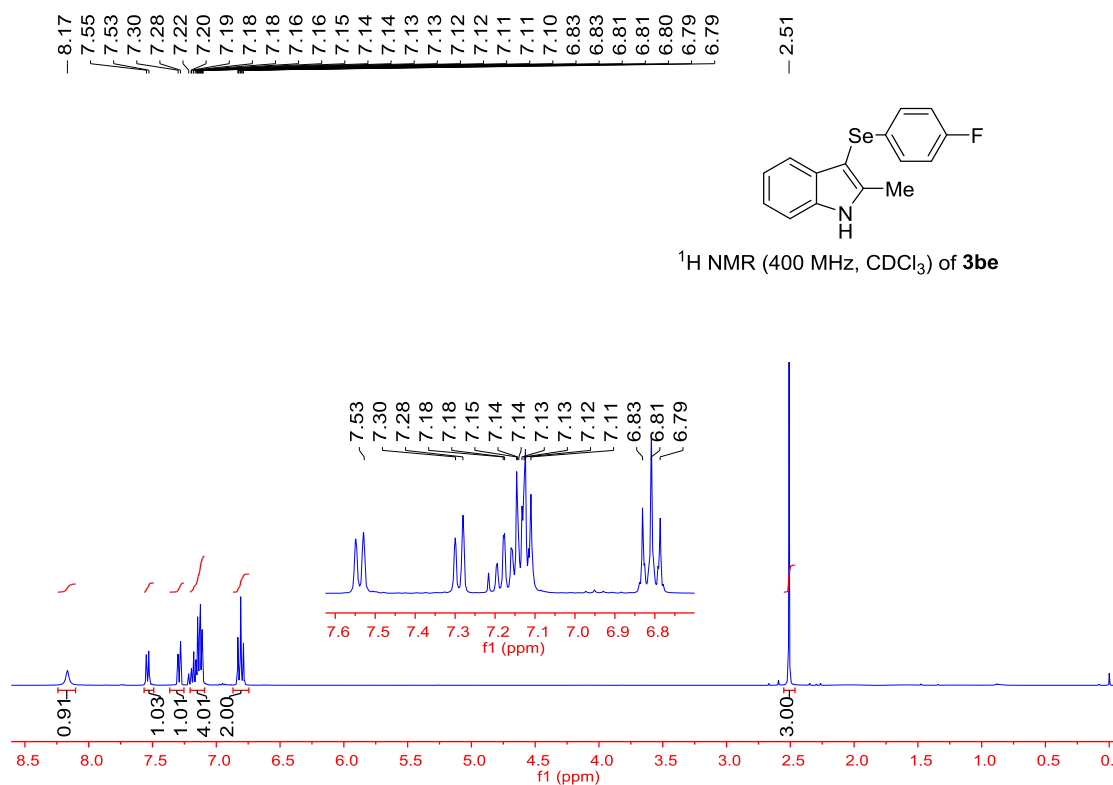
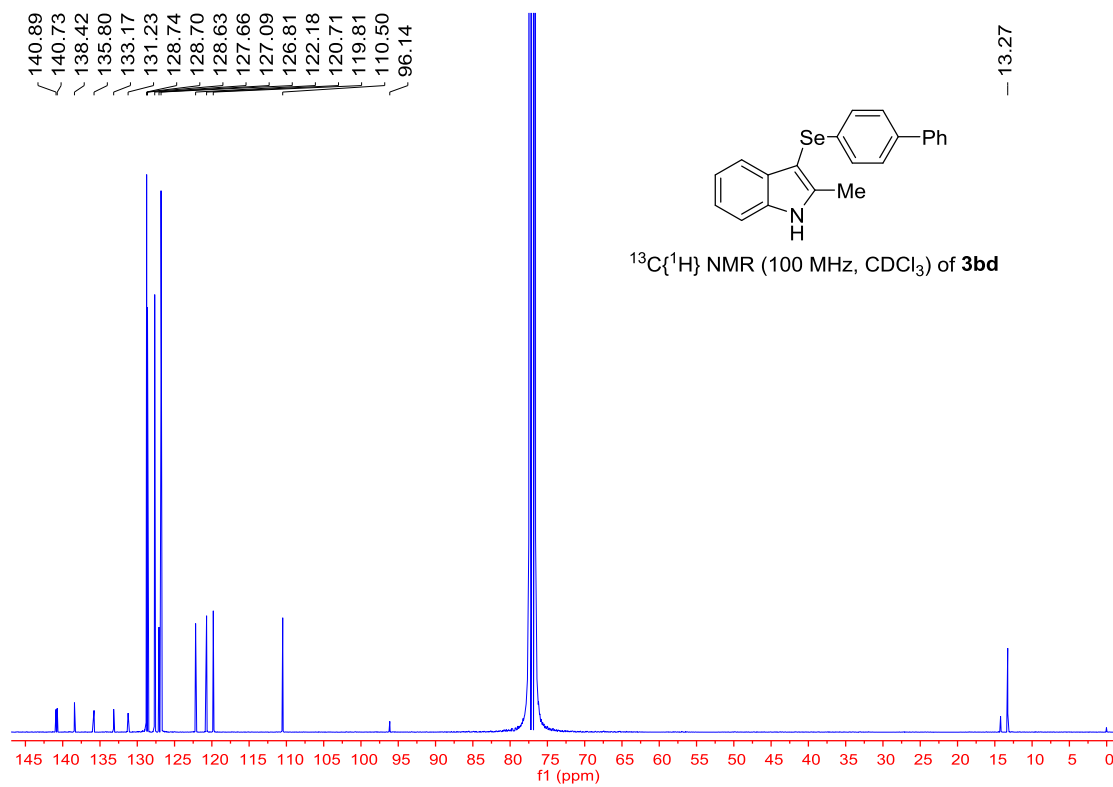






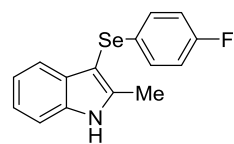




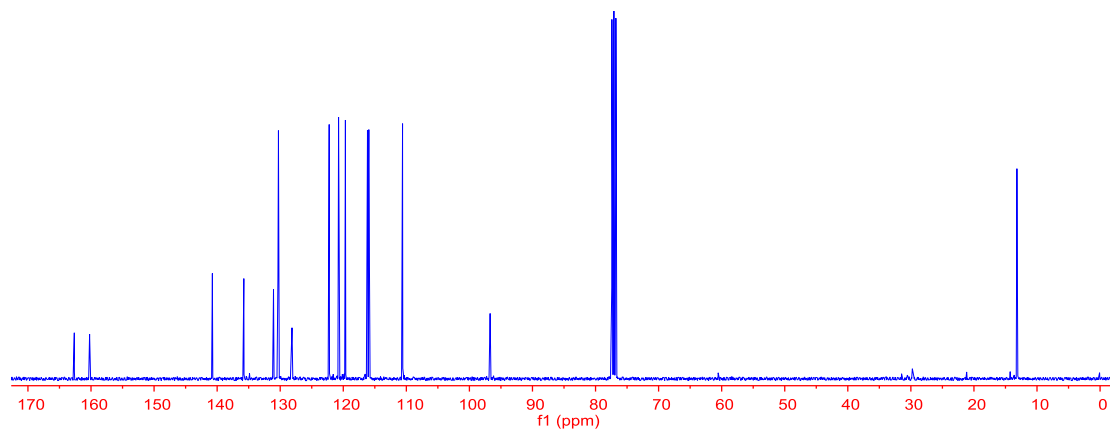


162.65
160.22
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96.72

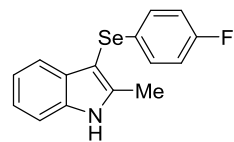
13.19



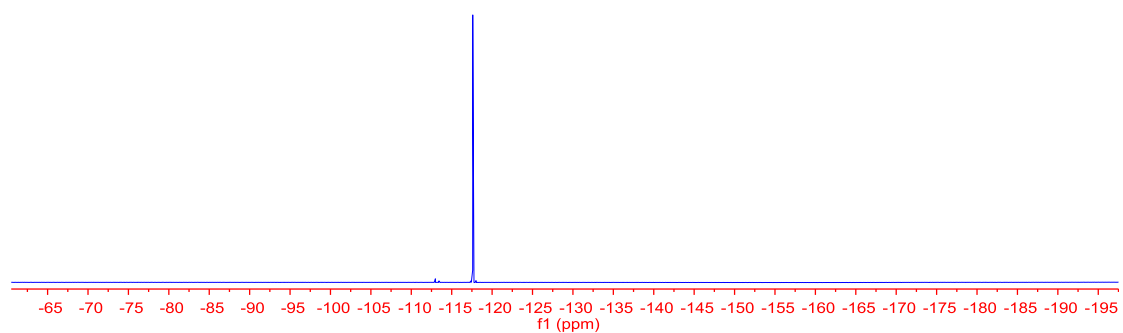
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **3be**

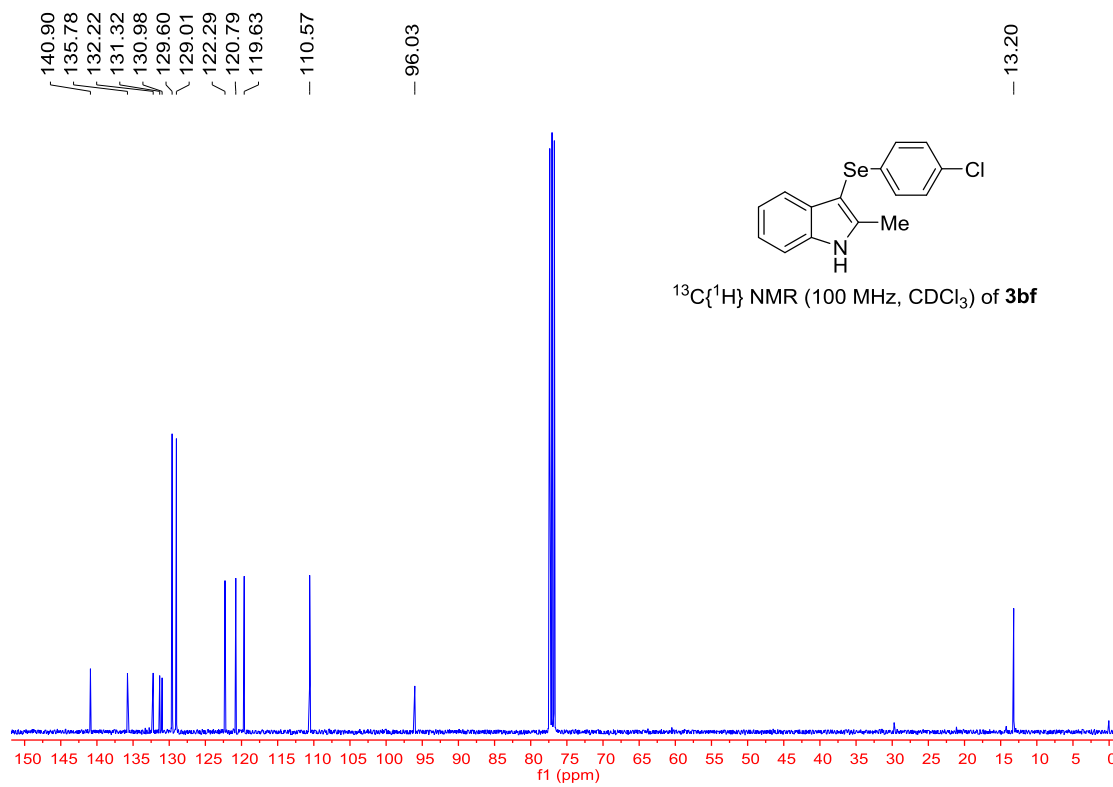
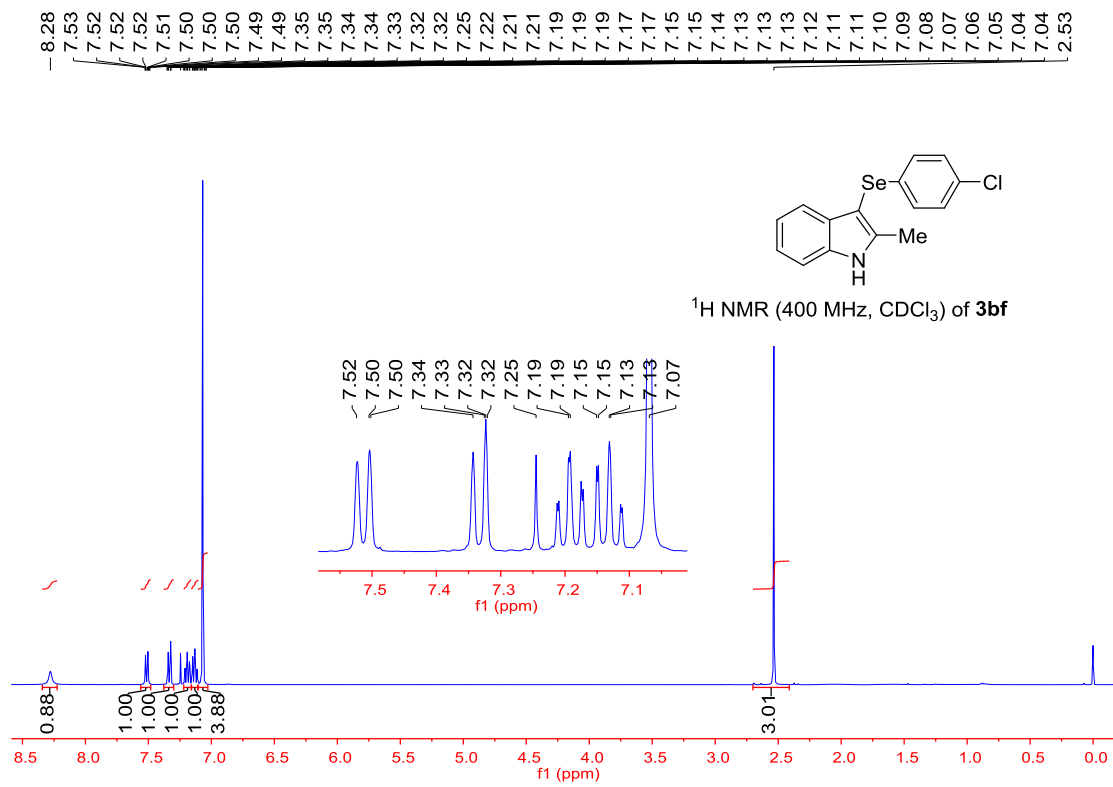


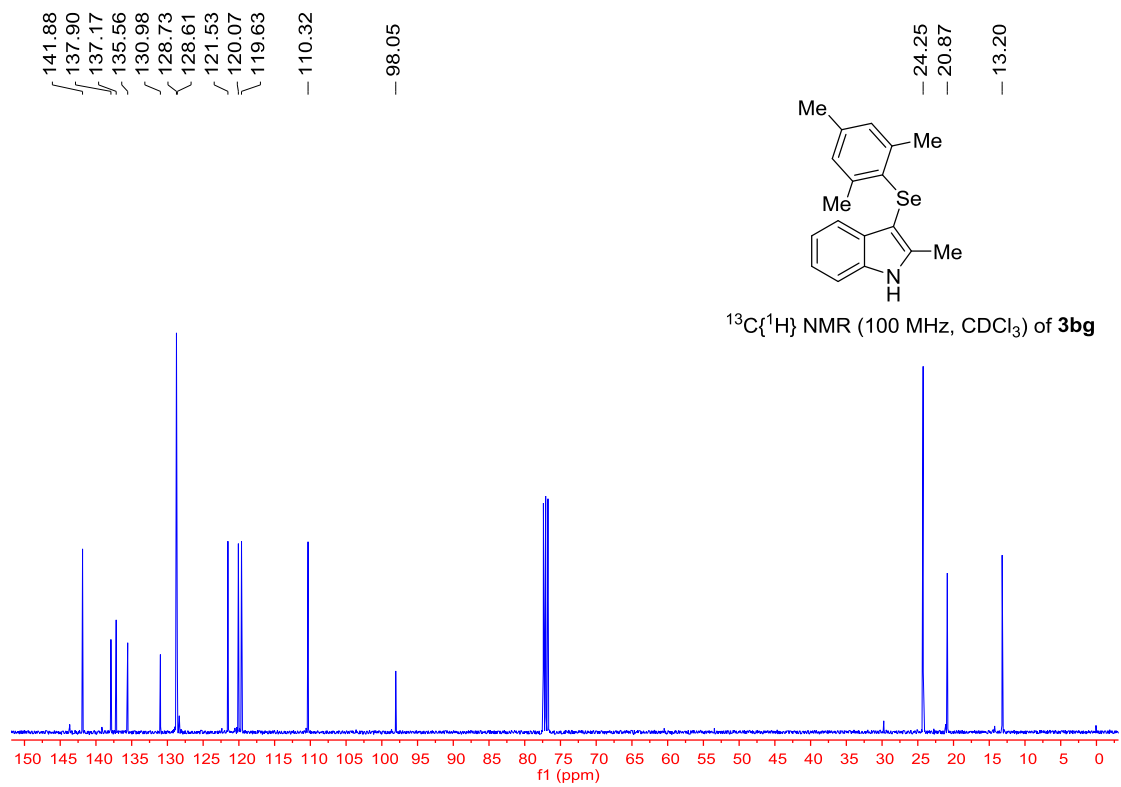
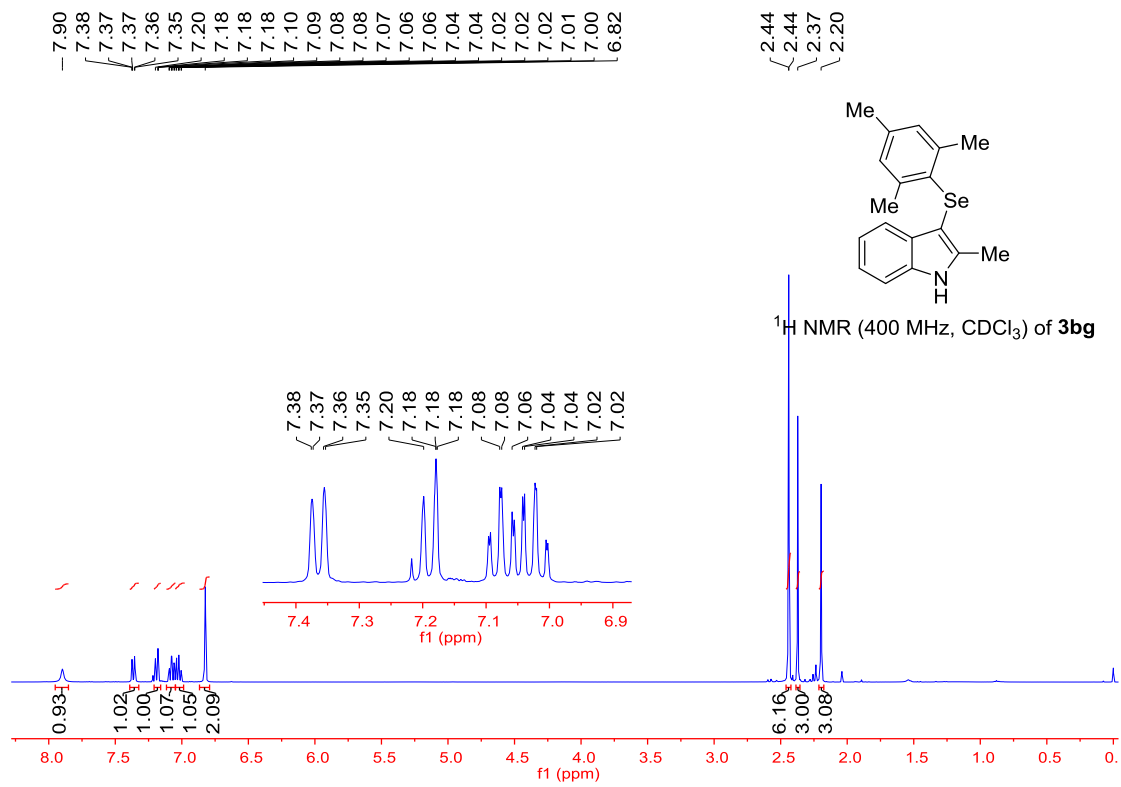
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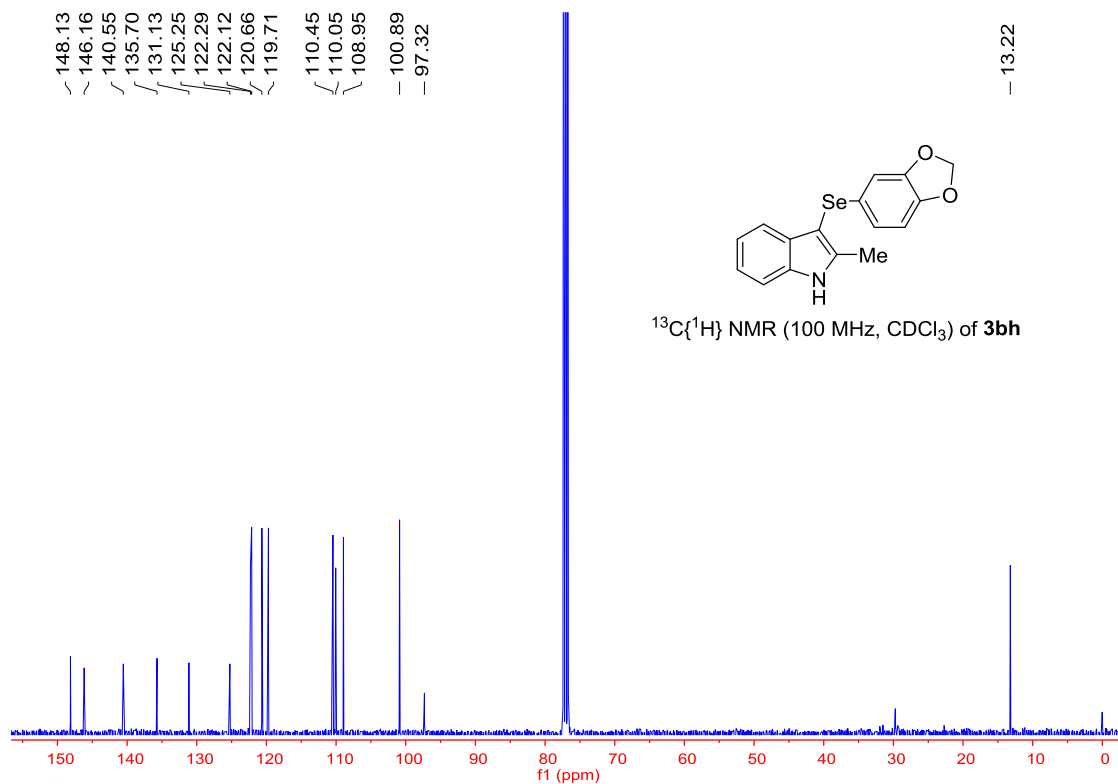
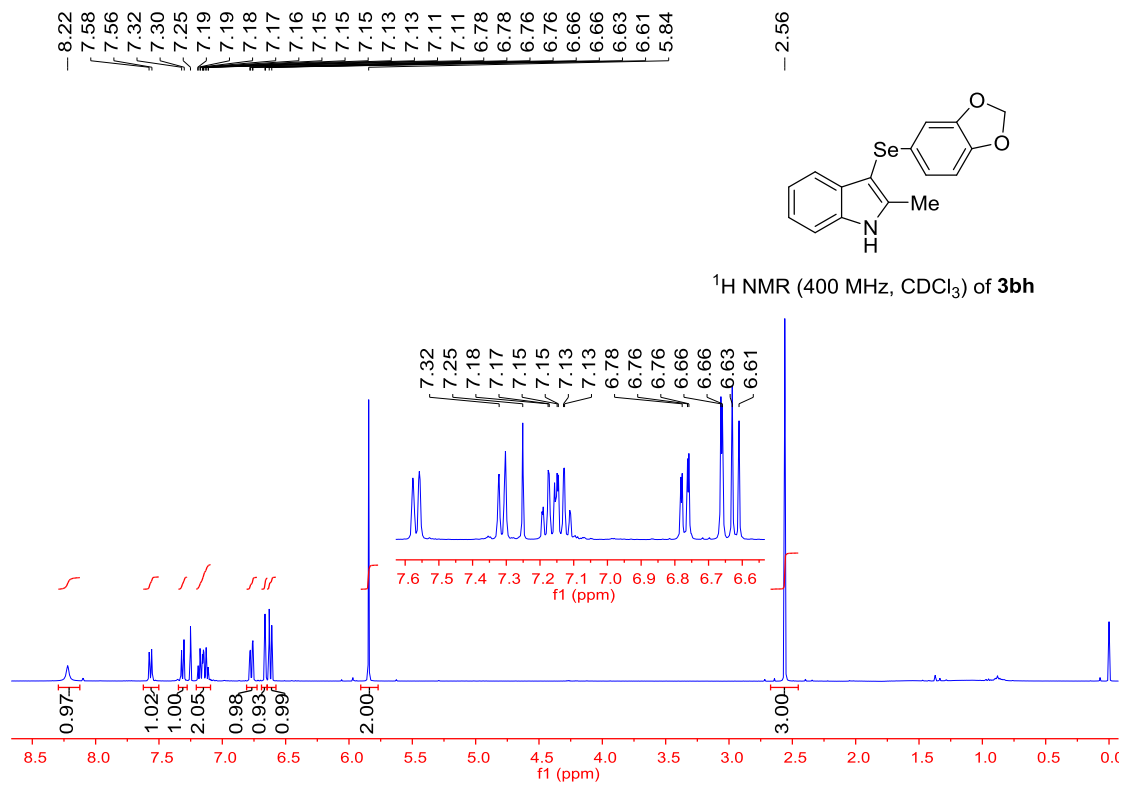


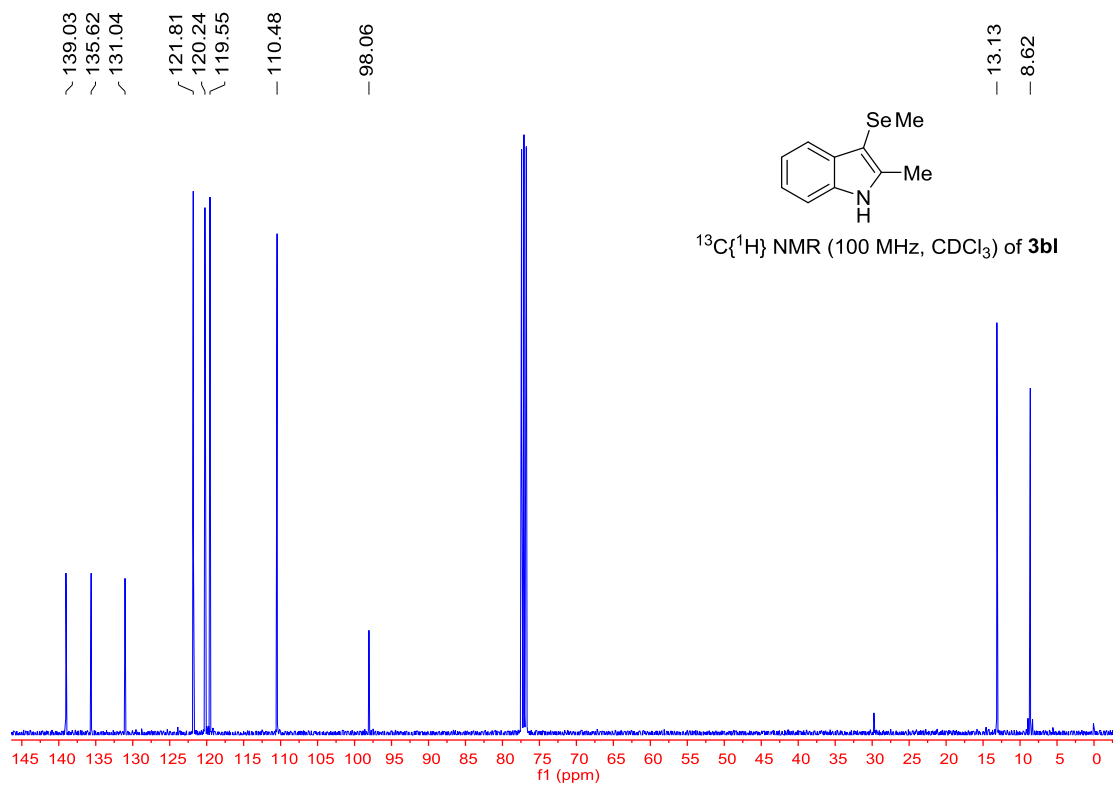
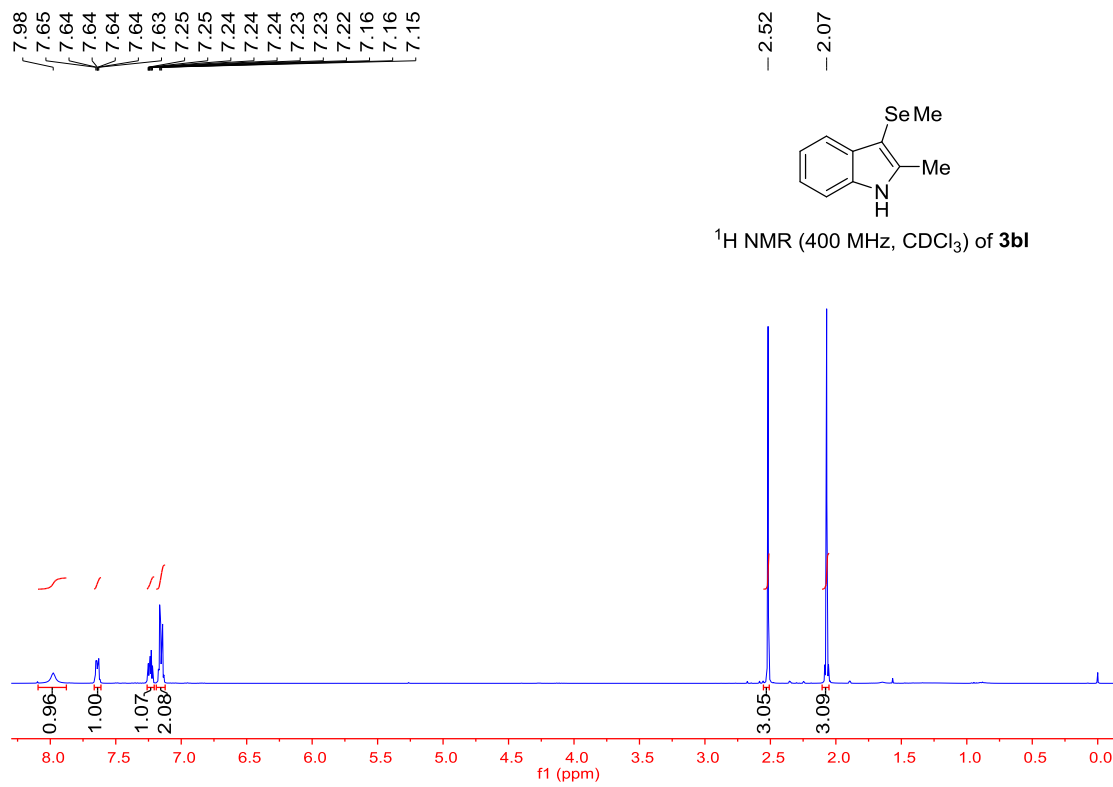
^{19}H NMR (376 MHz, CDCl_3) of **3be**

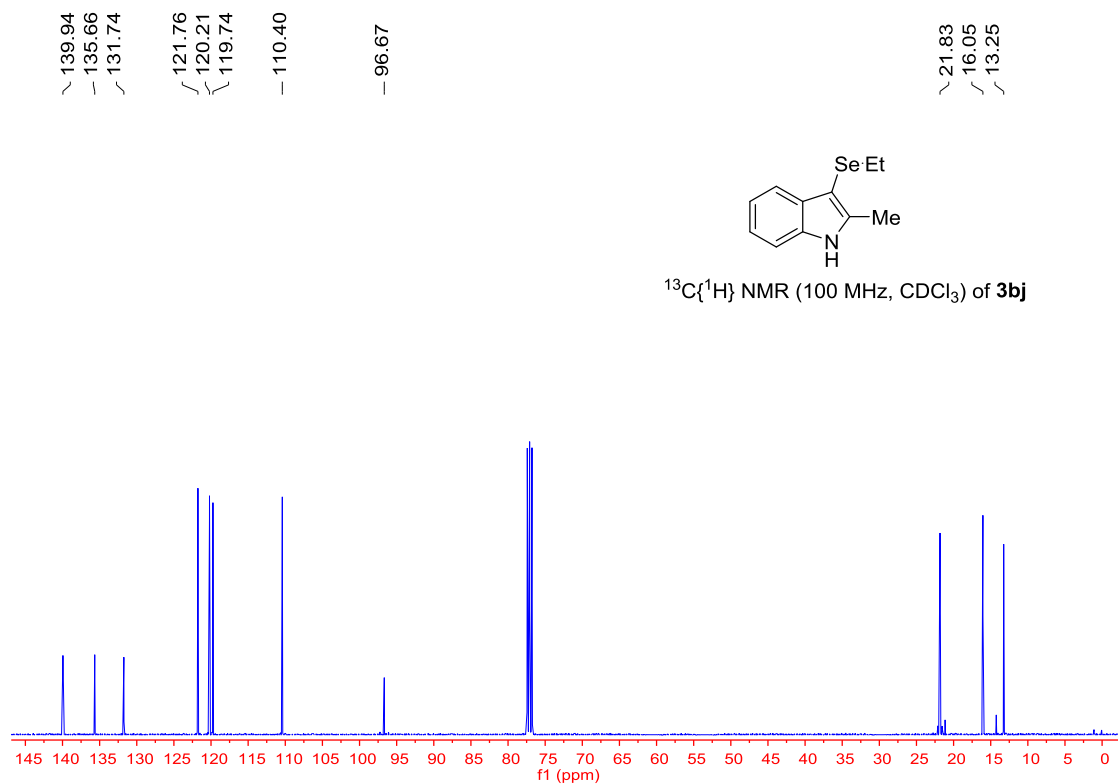
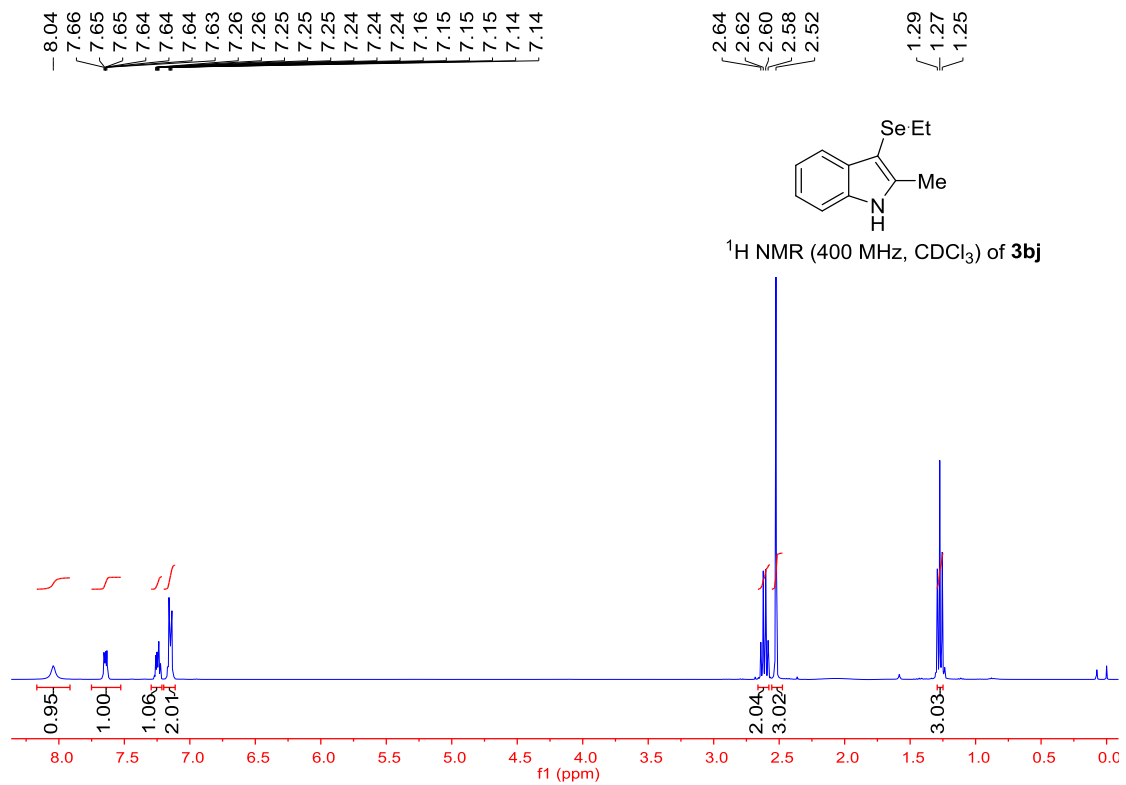


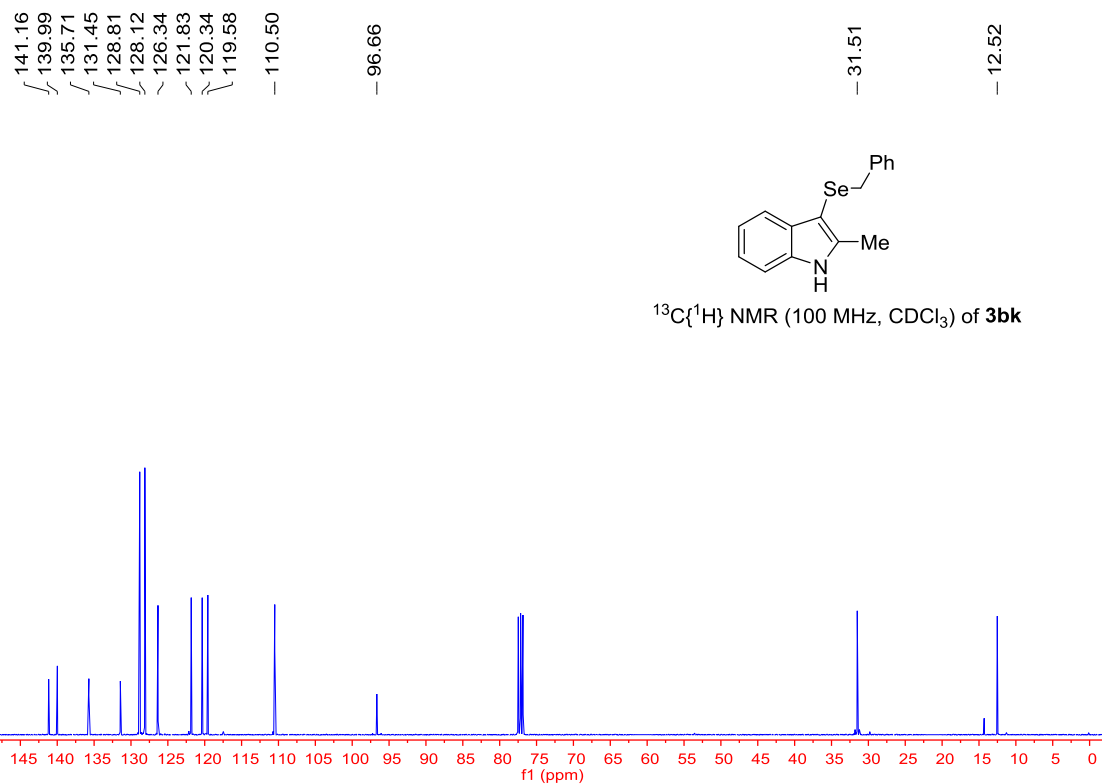
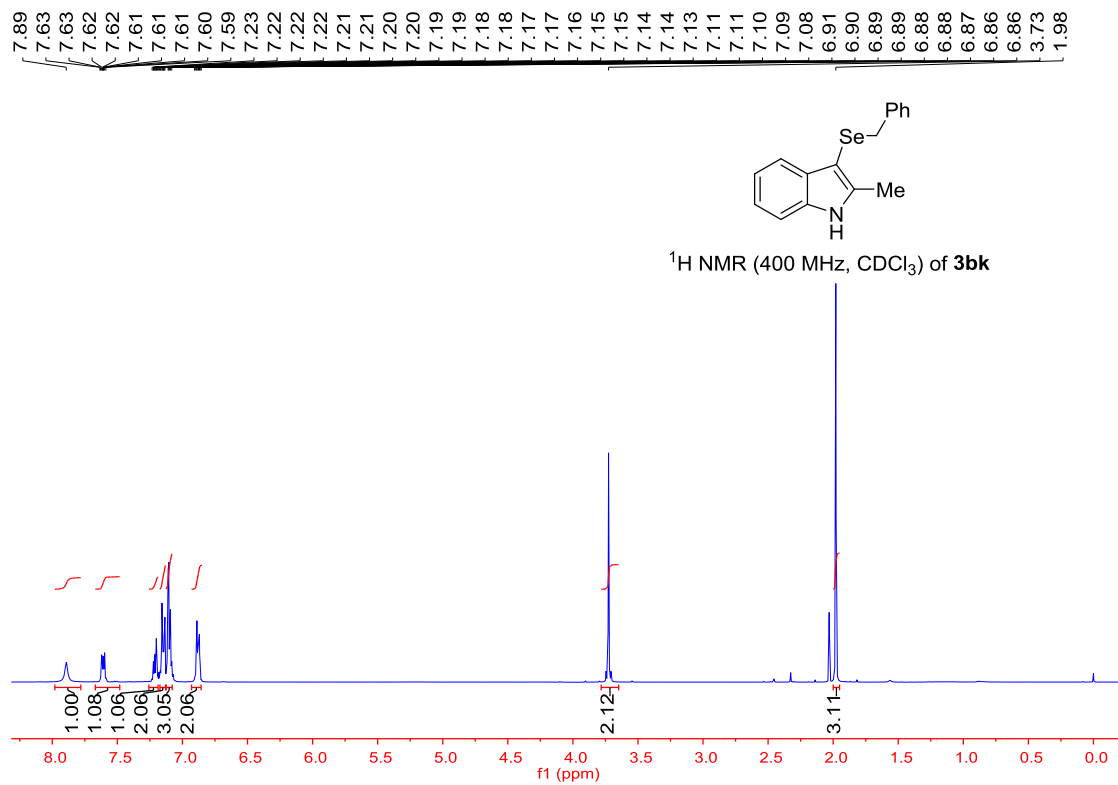


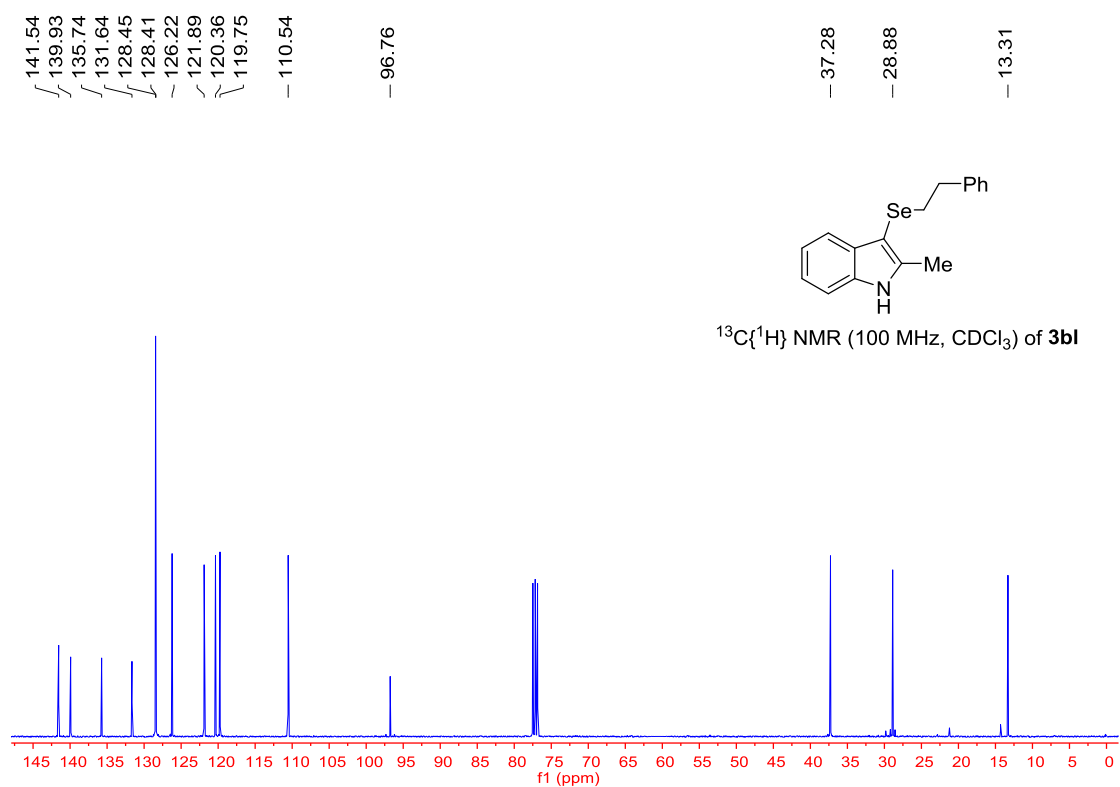
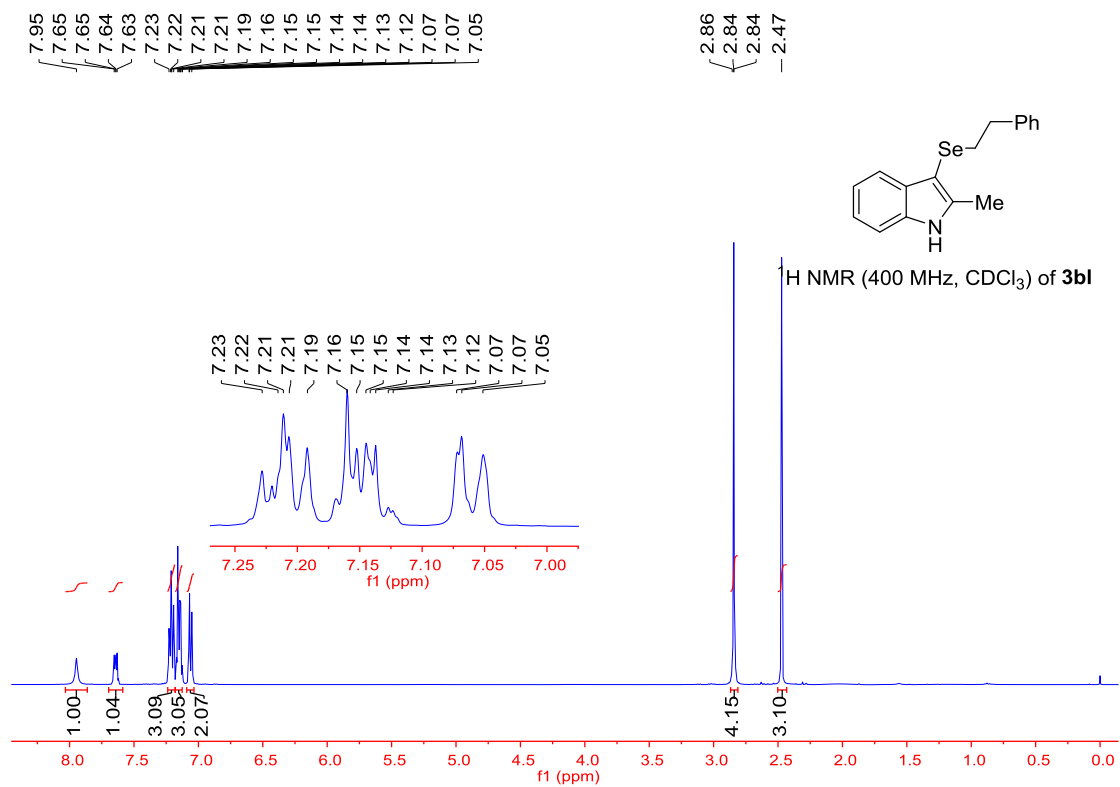


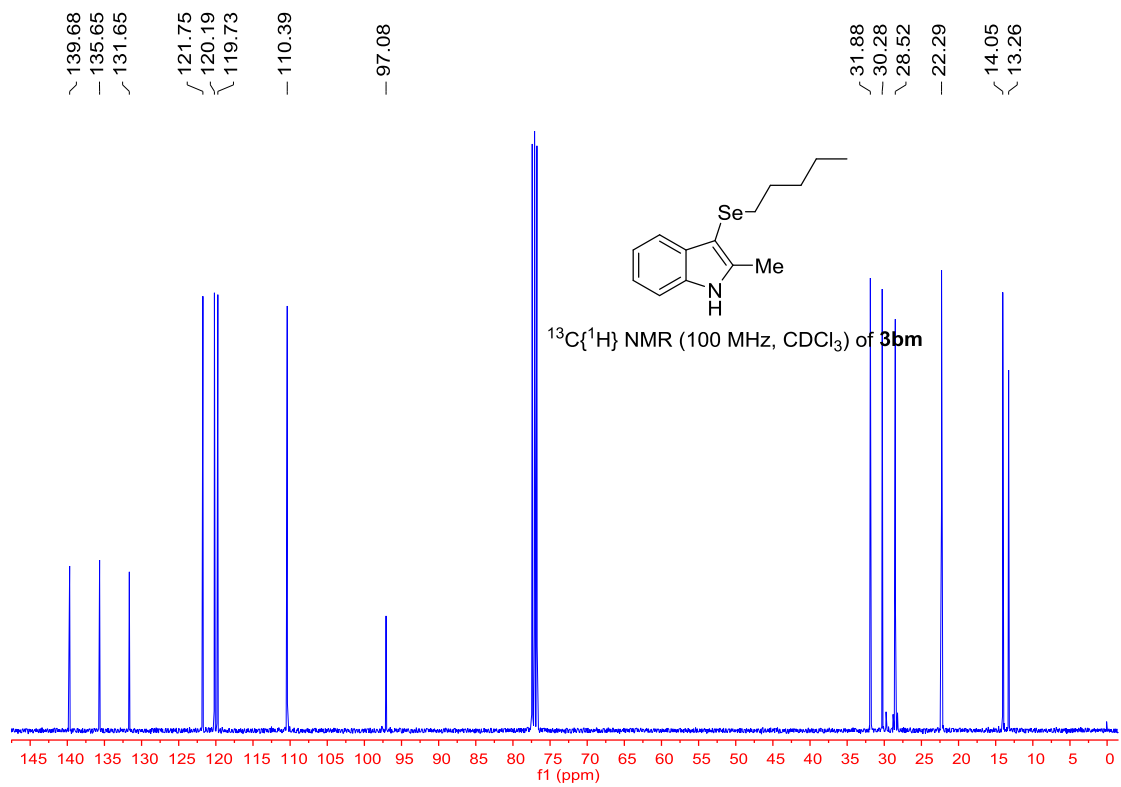
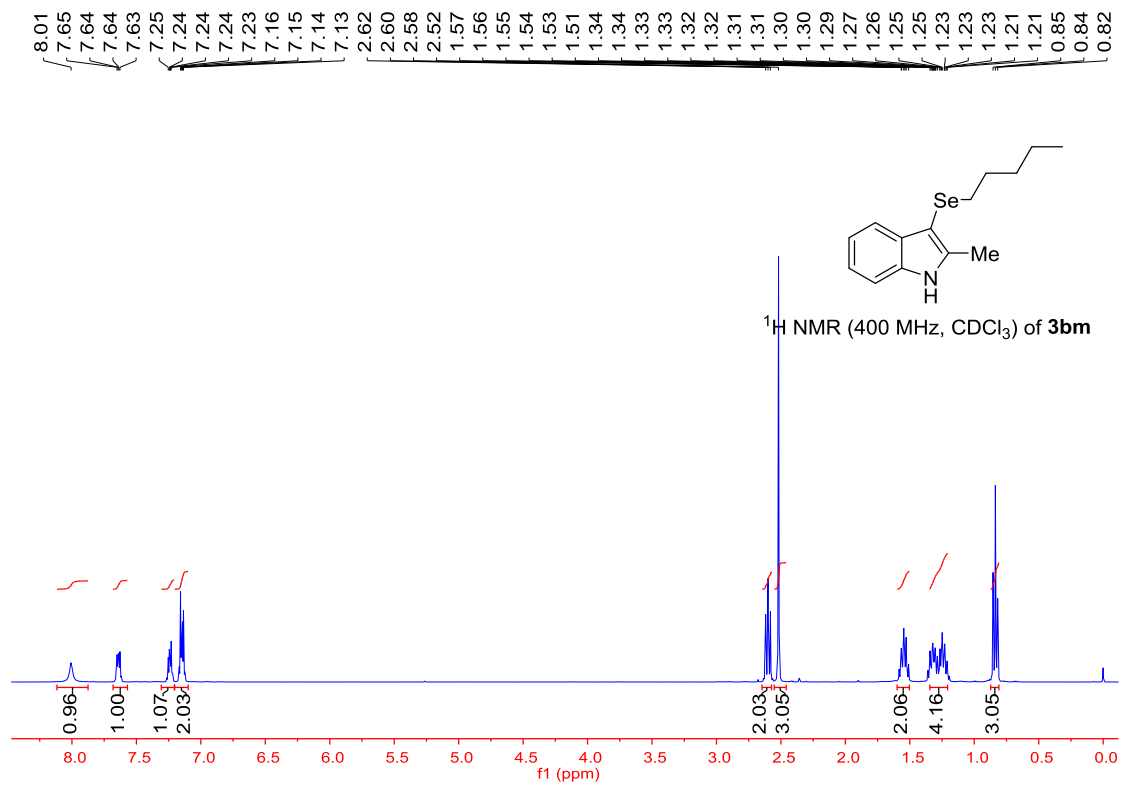


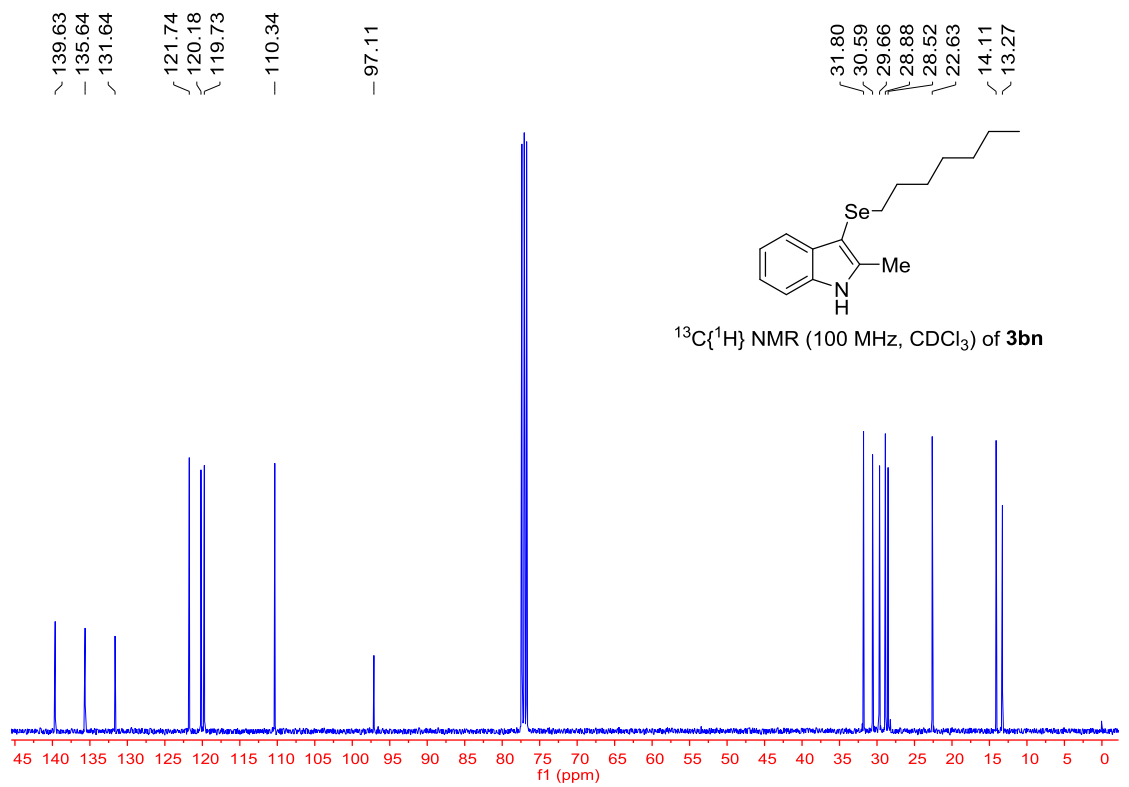
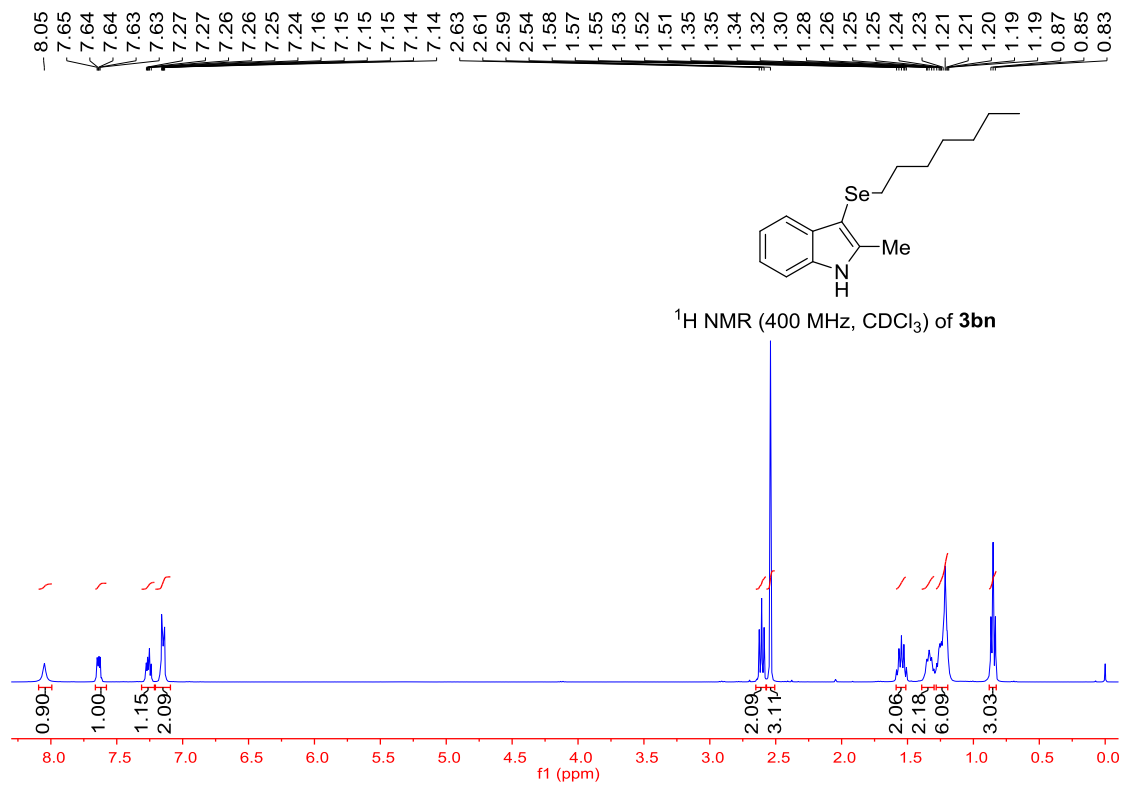


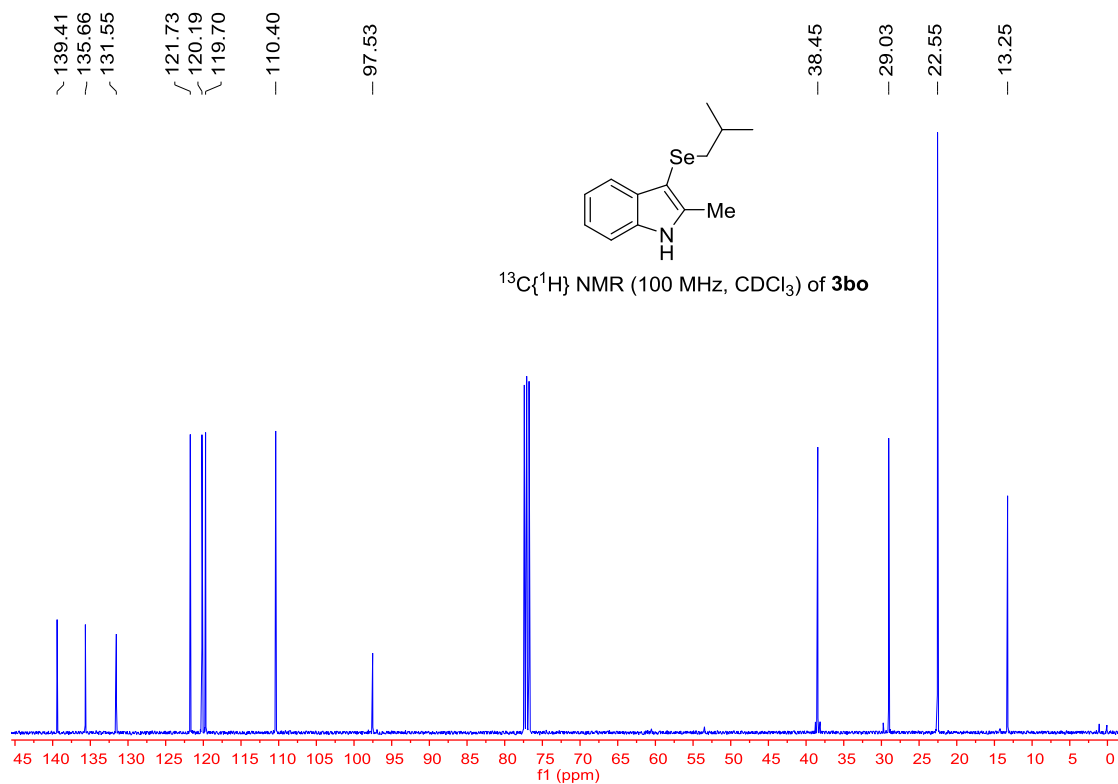
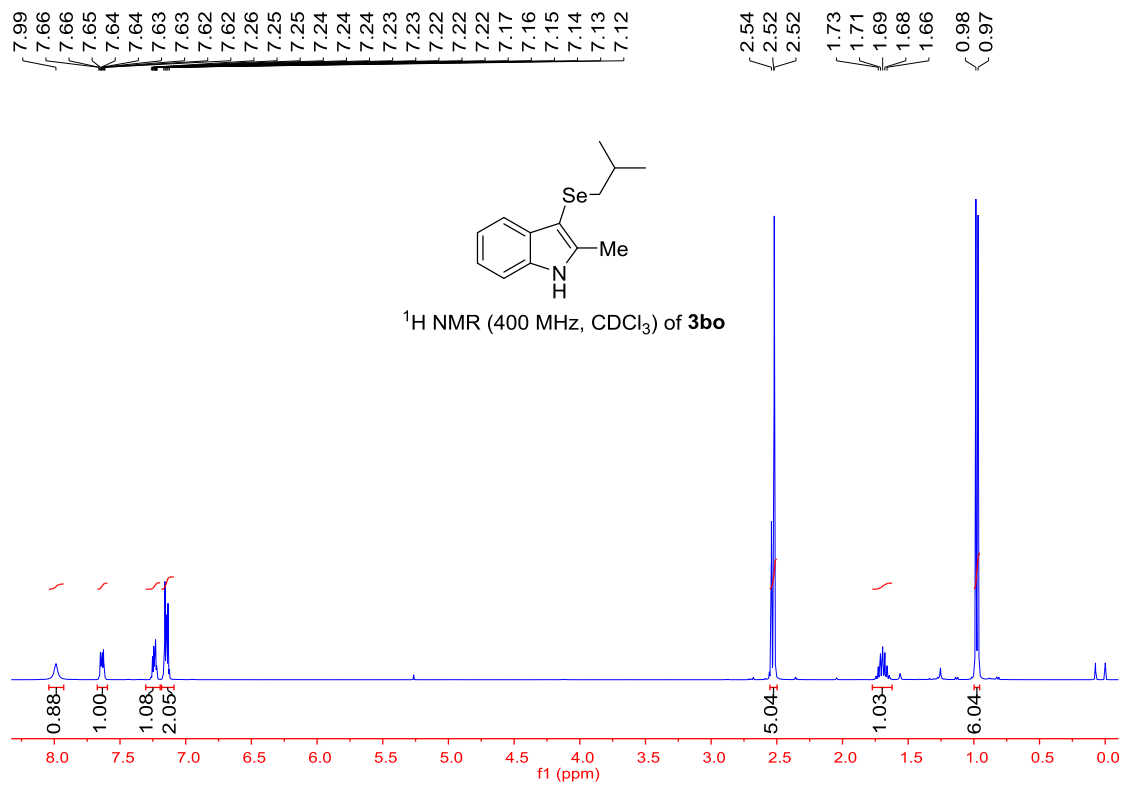


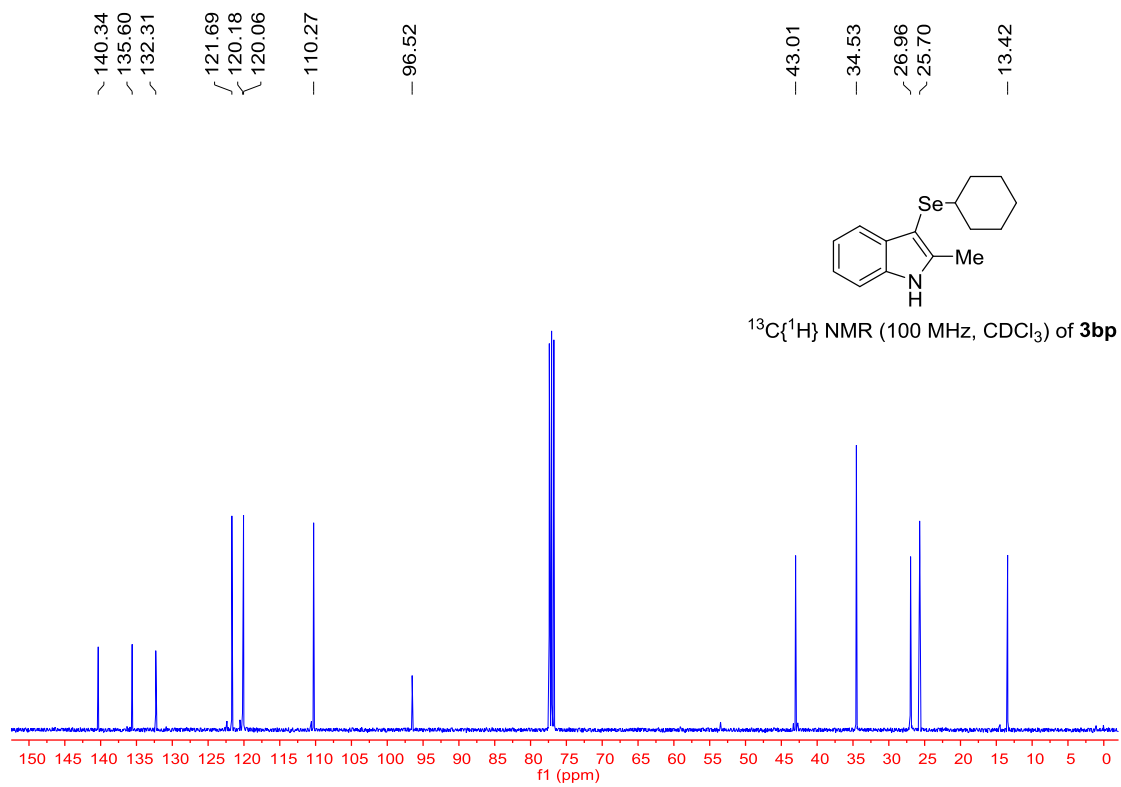
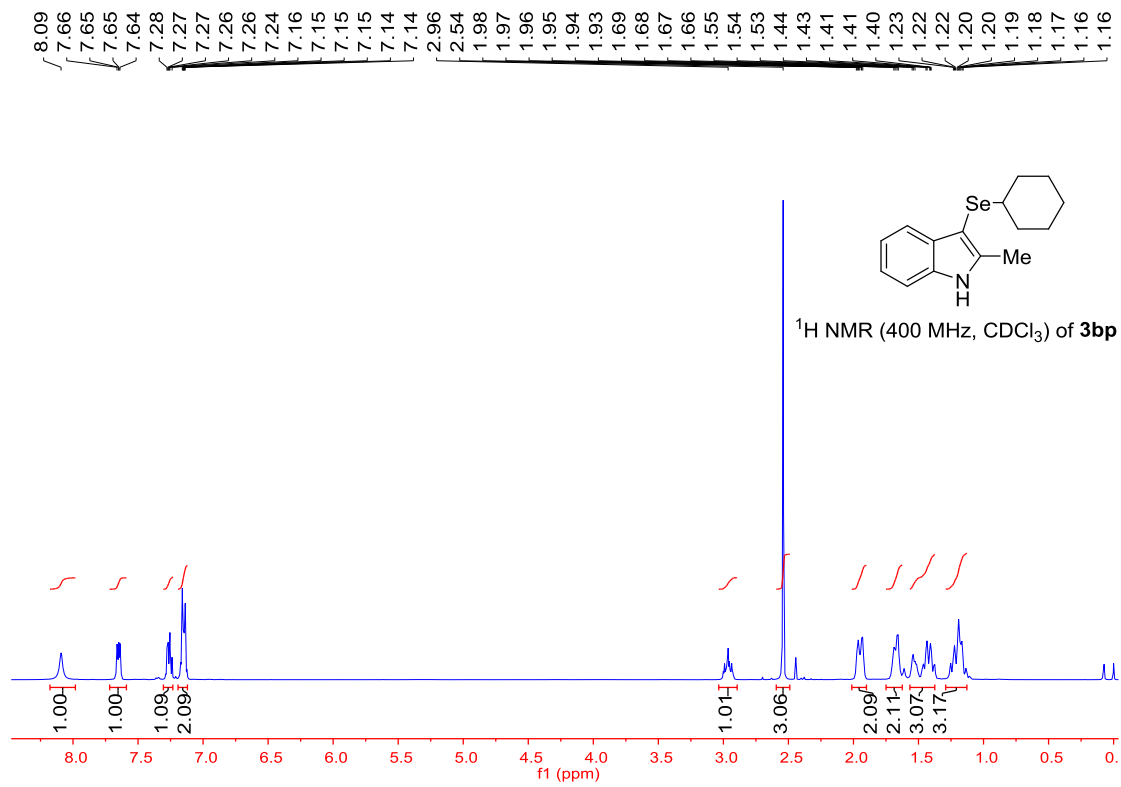


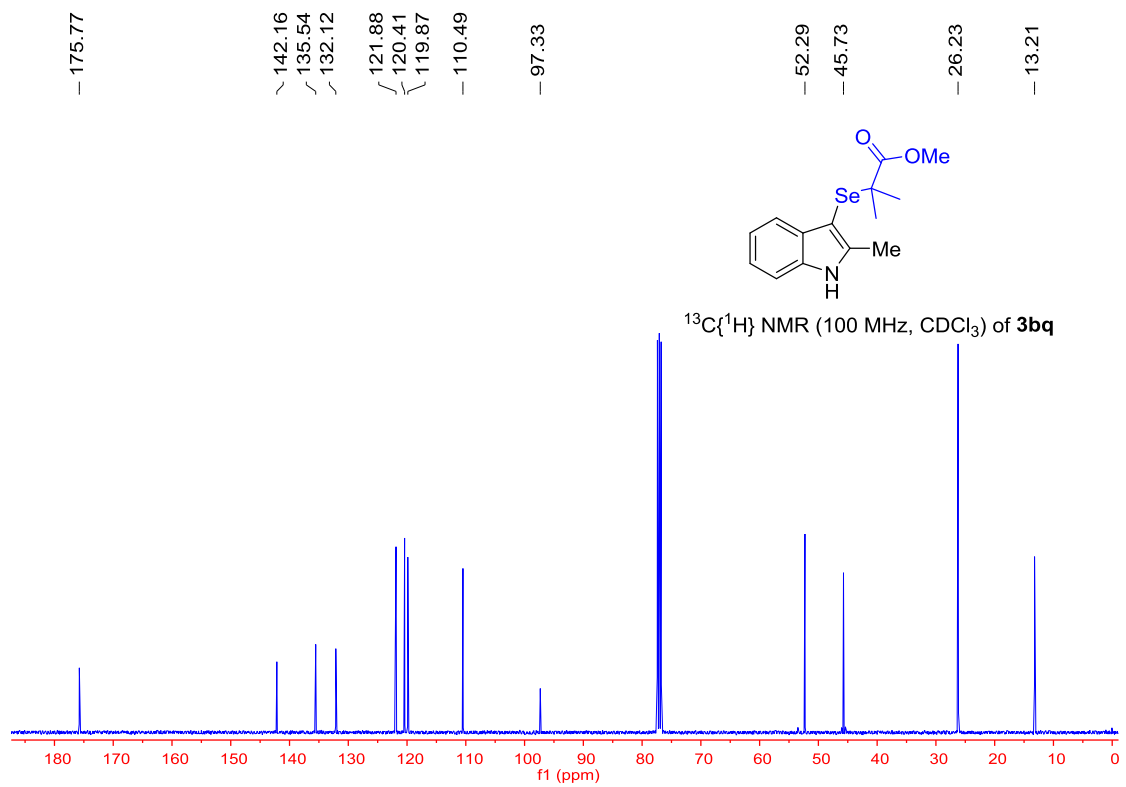
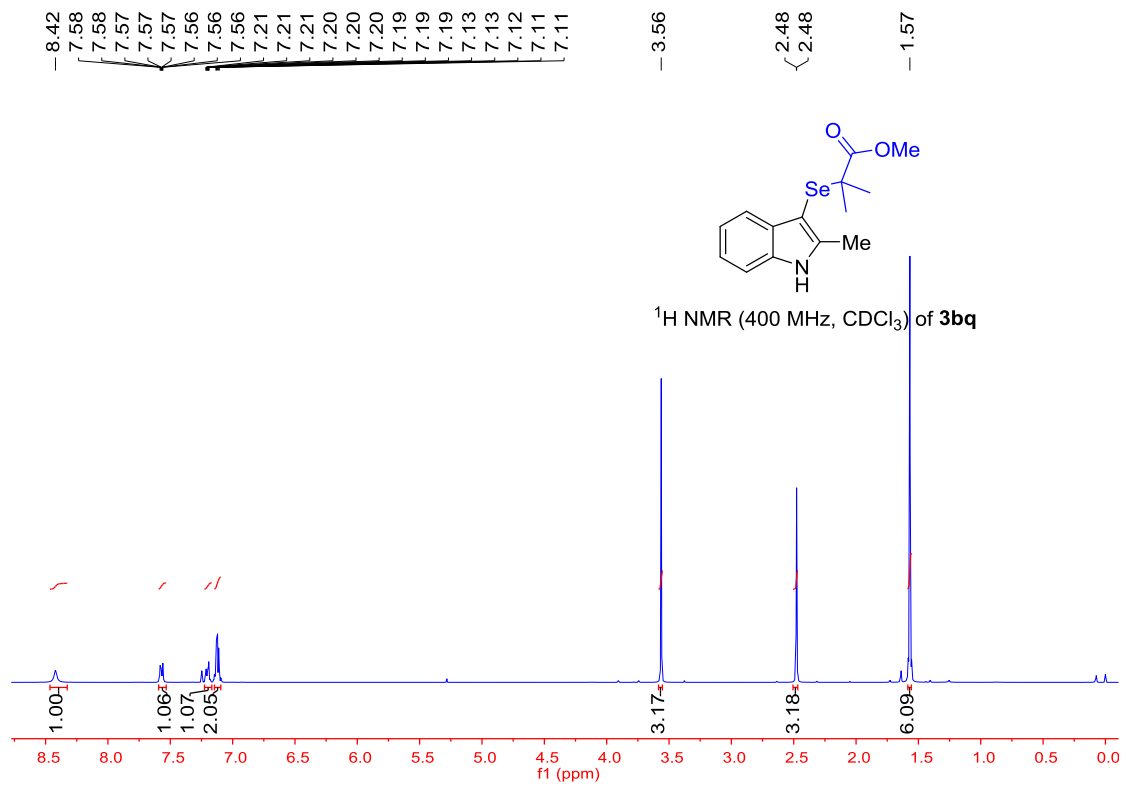


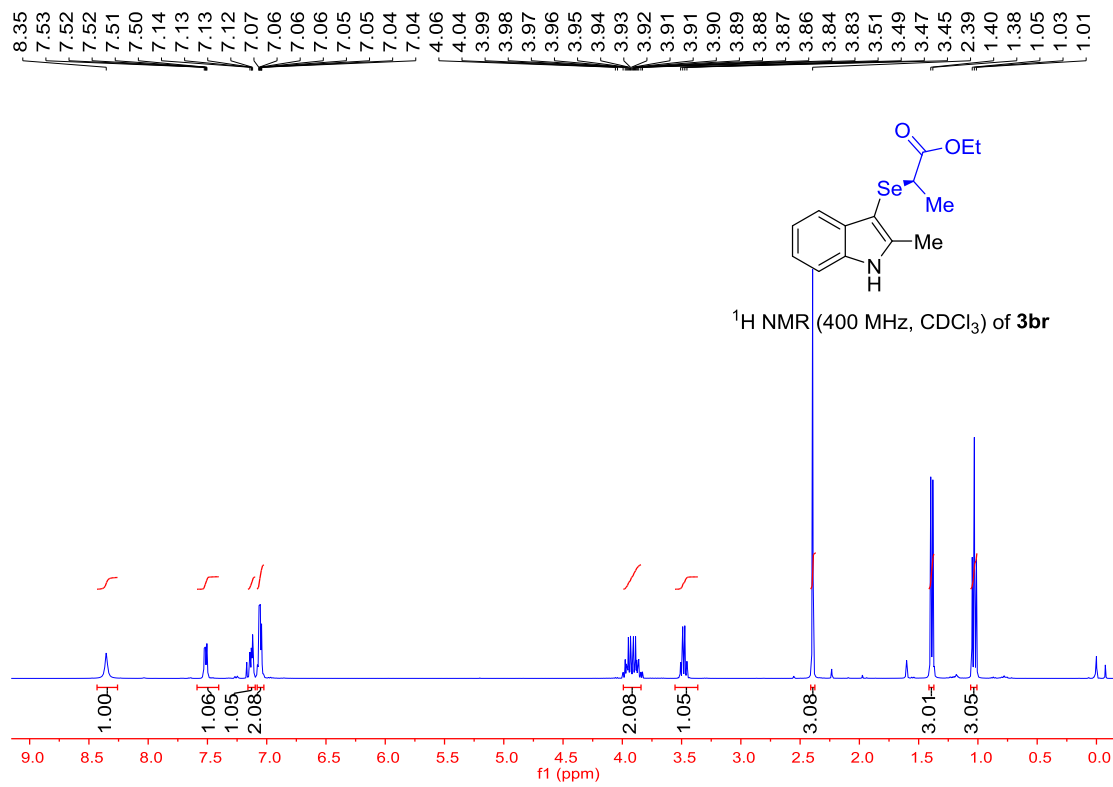




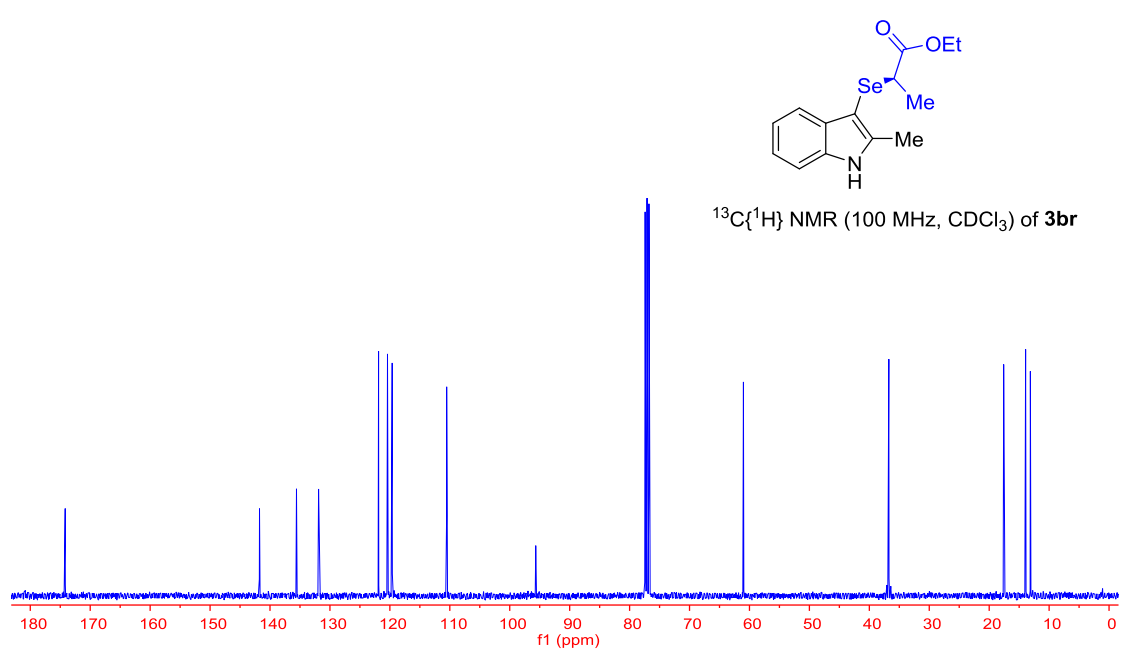


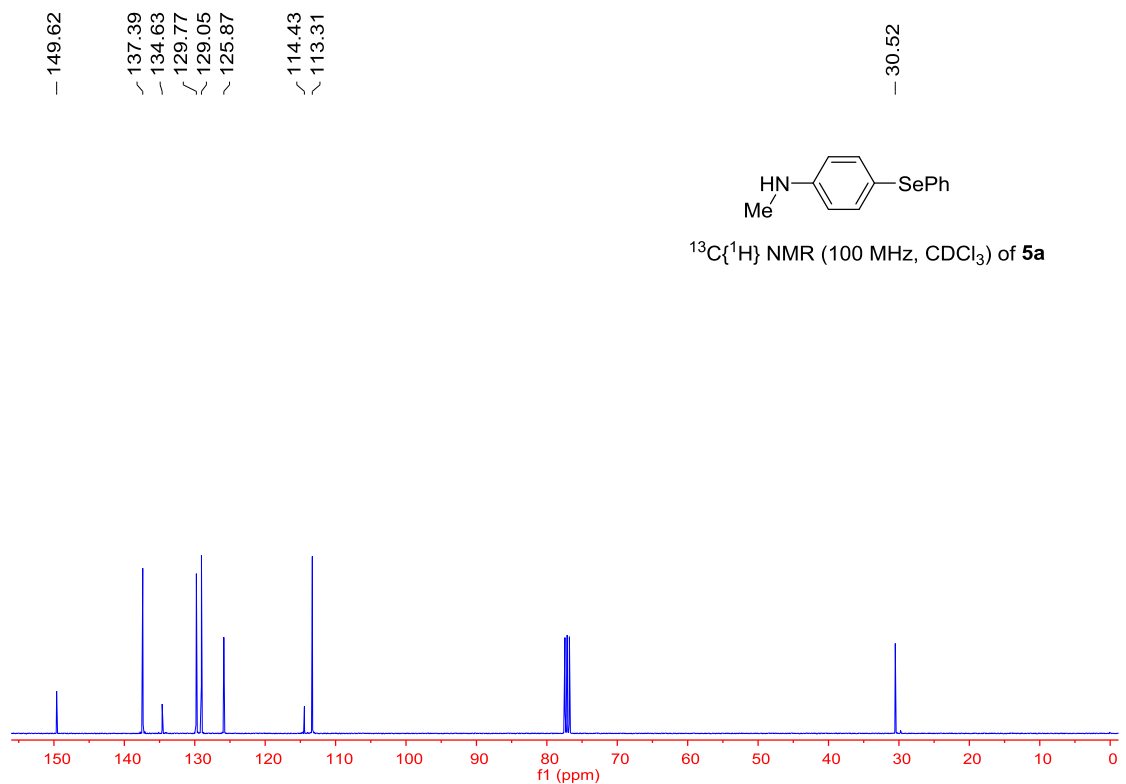
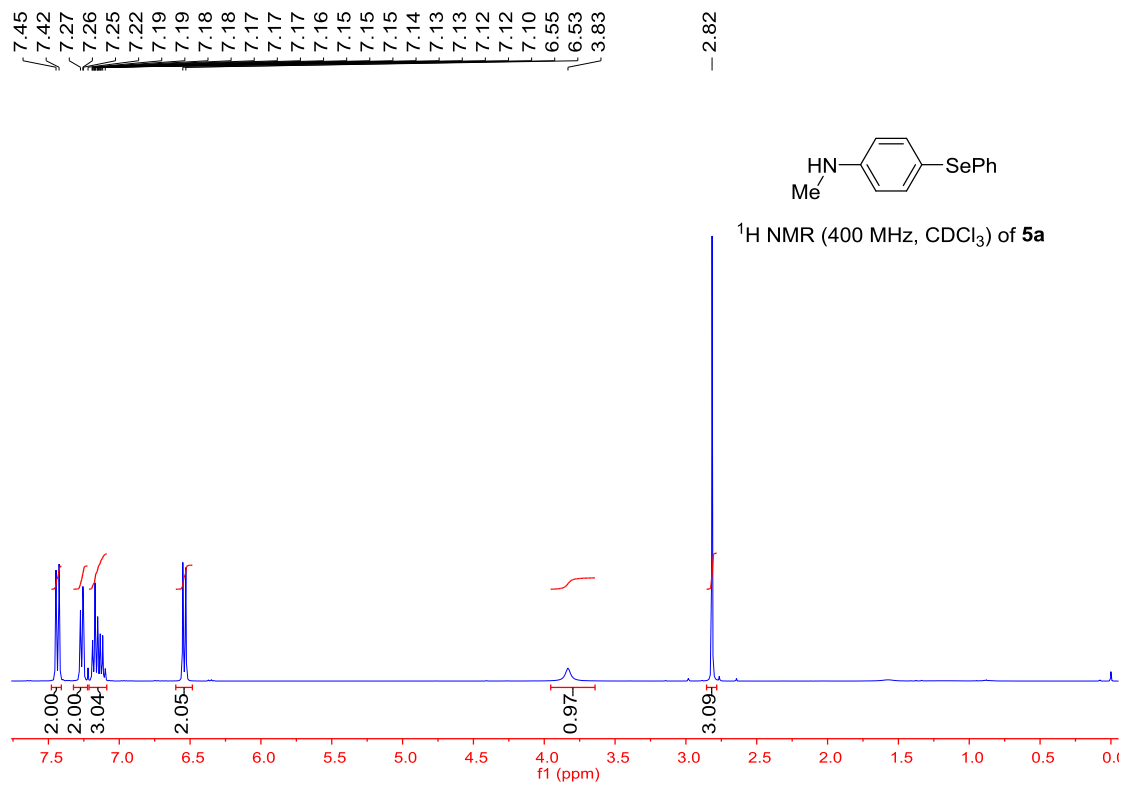


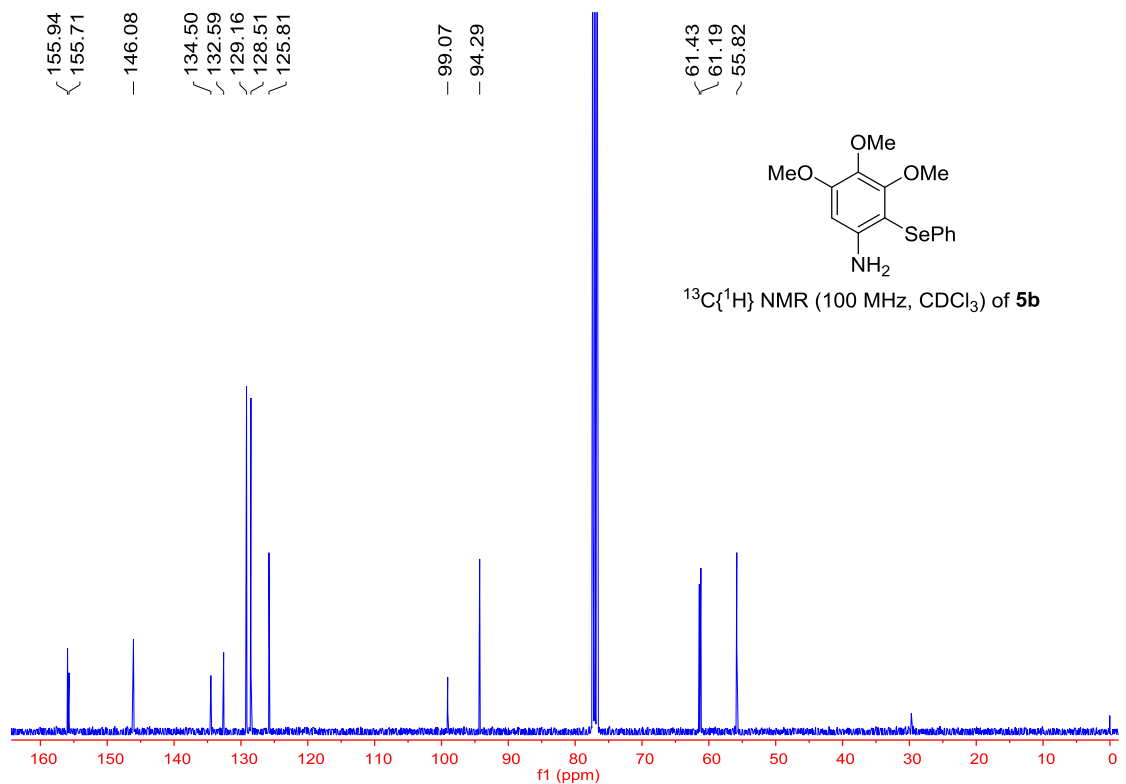
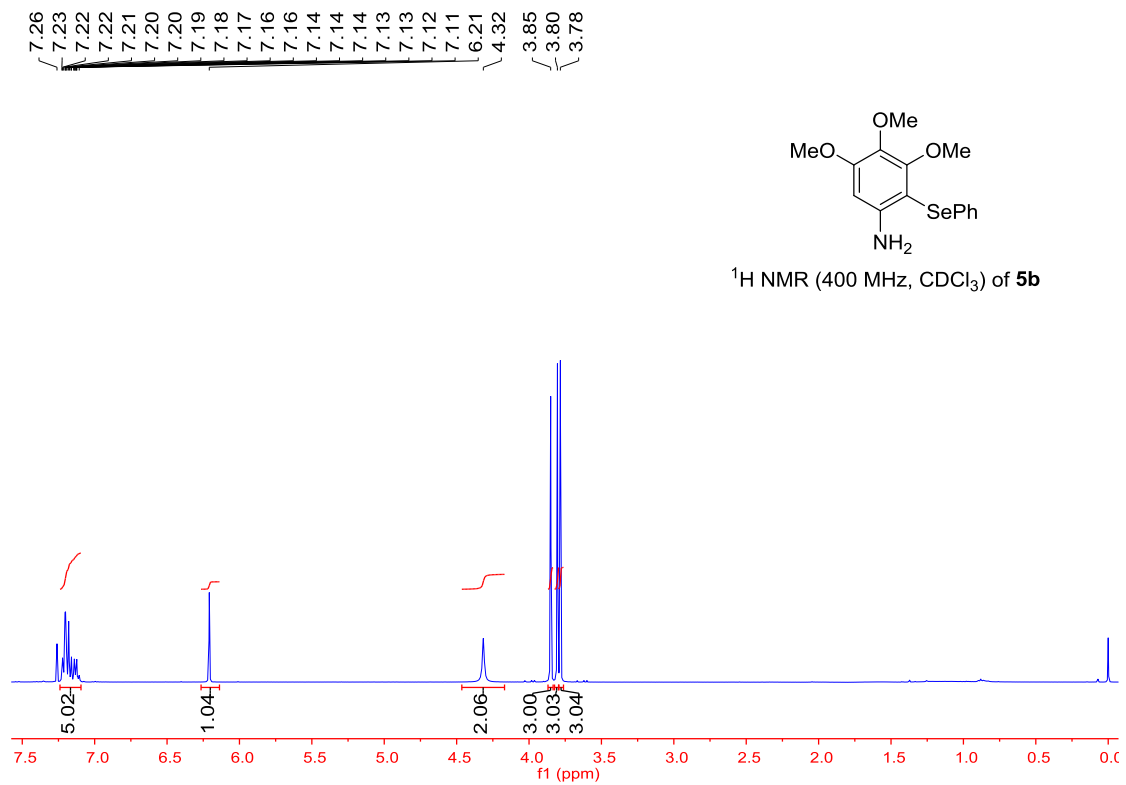




- 174.17
- 141.76
- 135.58
- 131.90
- 121.88
- 120.40
- 119.61
- 110.52
- 95.66
- 61.01
- 36.75
- 17.58
- 13.92
- 13.13

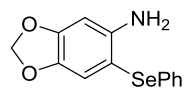




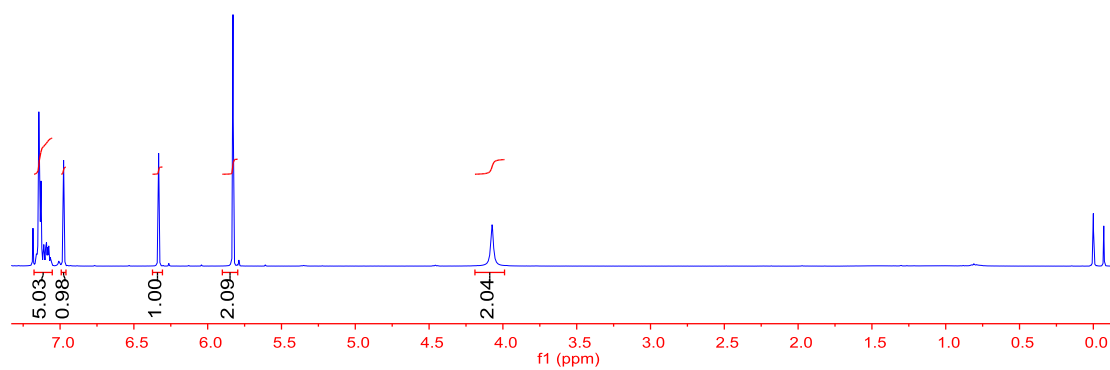


7.16
7.14
7.14
7.13
7.11
7.11
7.10
7.09
7.09
7.08
7.07
6.98
6.33
5.83

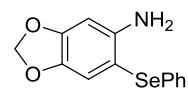
— 4.07



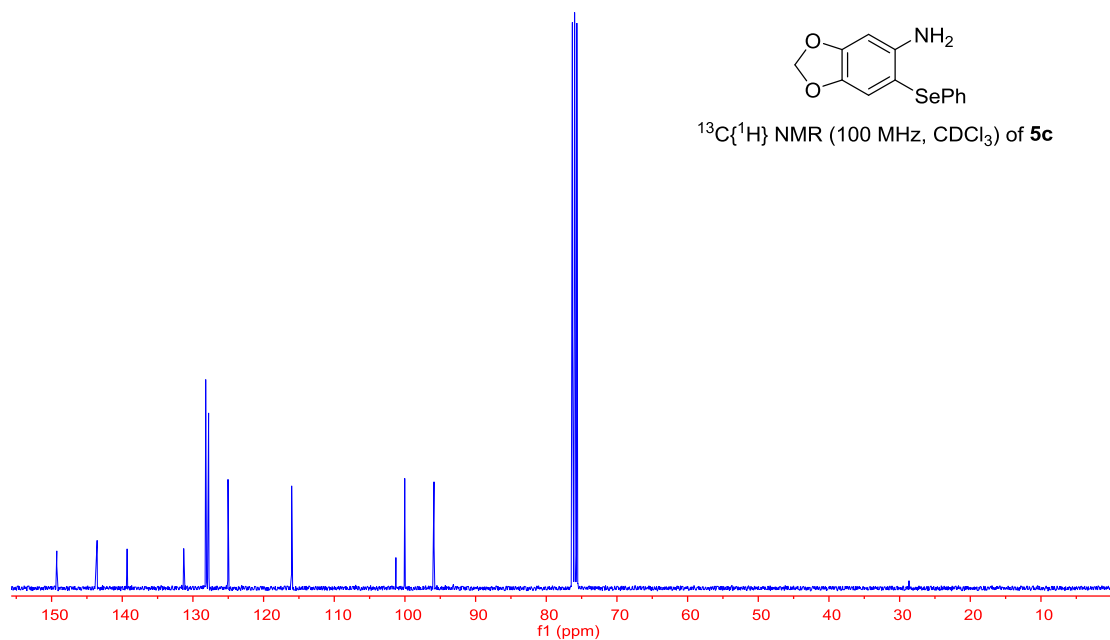
^1H NMR (400 MHz, CDCl_3) of **5c**



149.27
143.56
139.31
131.30
128.19
127.78
125.04
— 116.03
101.28
100.03
95.89

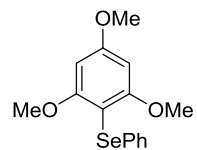


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **5c**

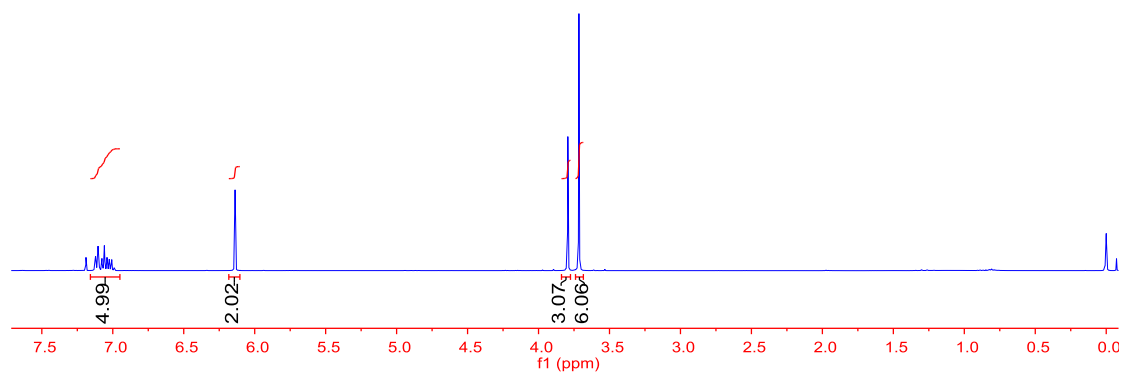


7.19
7.13
7.12
7.11
7.10
7.10
7.08
7.08
7.06
7.06
7.05
7.04
7.04
7.04
7.03
7.02
7.02
7.01
6.14

3.79
3.72



^1H NMR (400 MHz, CDCl_3) of **5d**

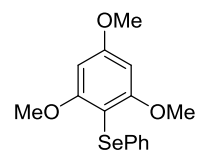


161.9
160.9

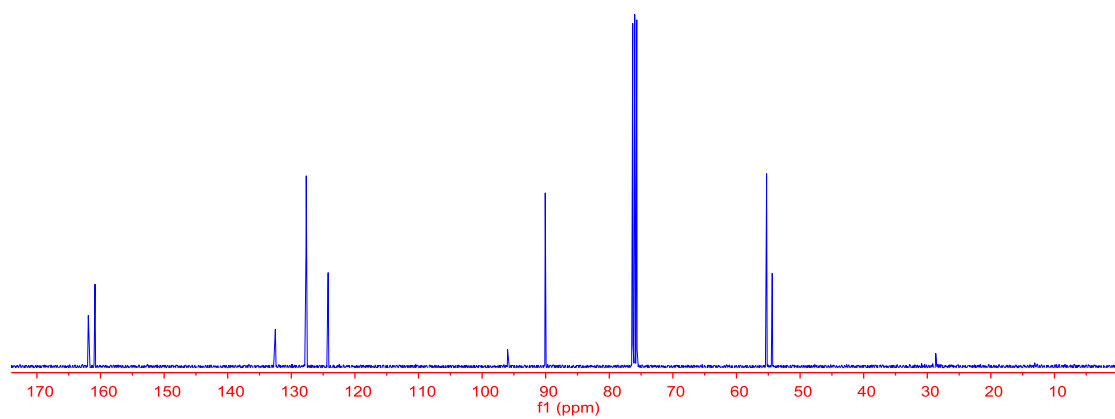
132.5
127.7
127.7
124.2

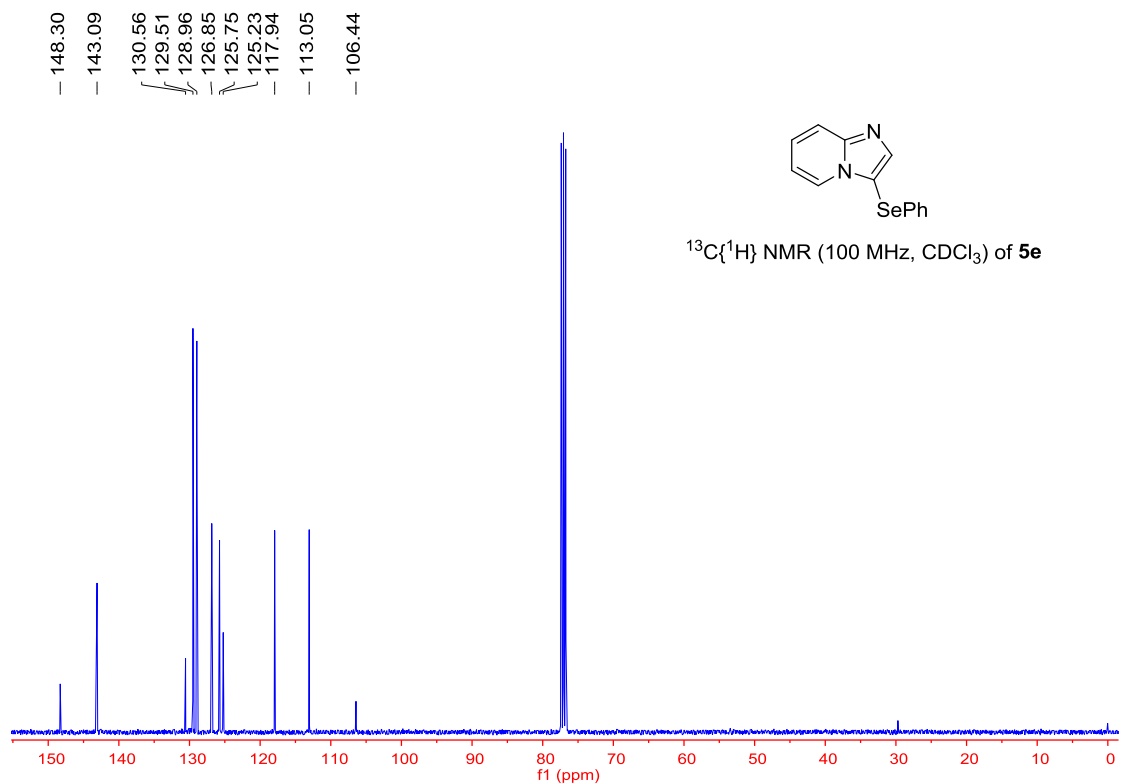
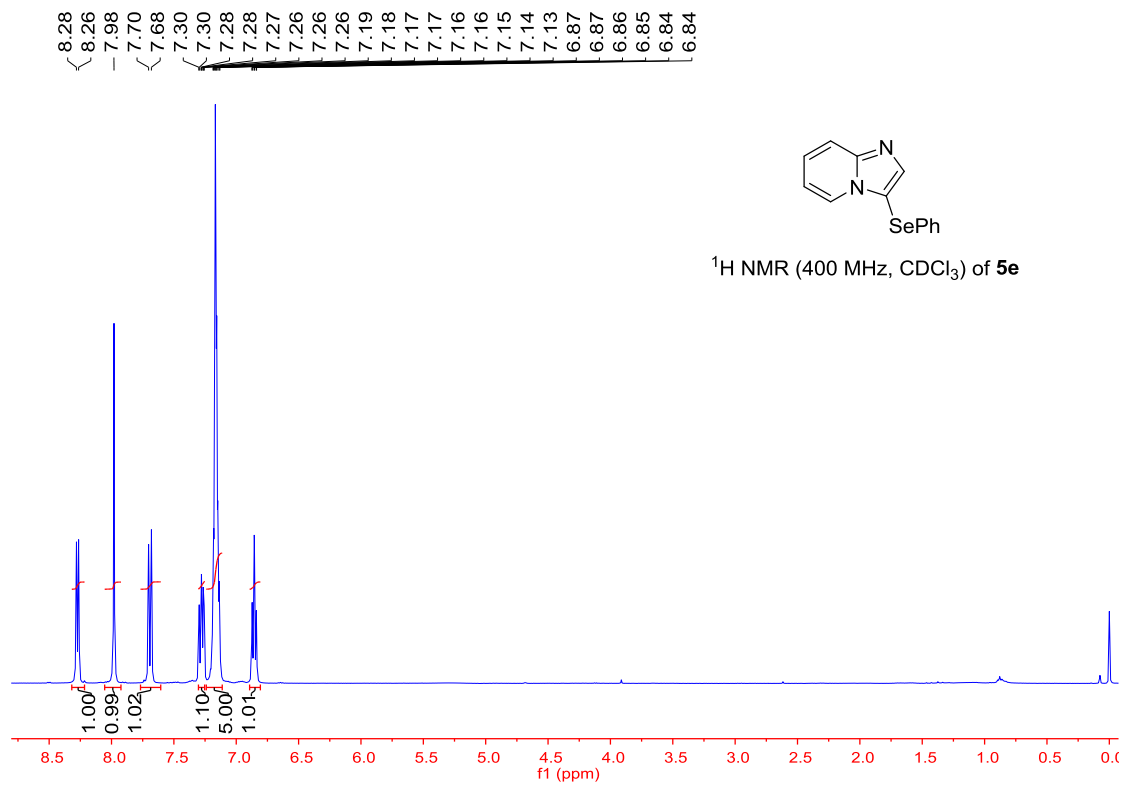
96.0
90.1

55.3
54.4

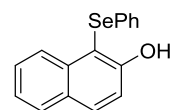


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **5d**

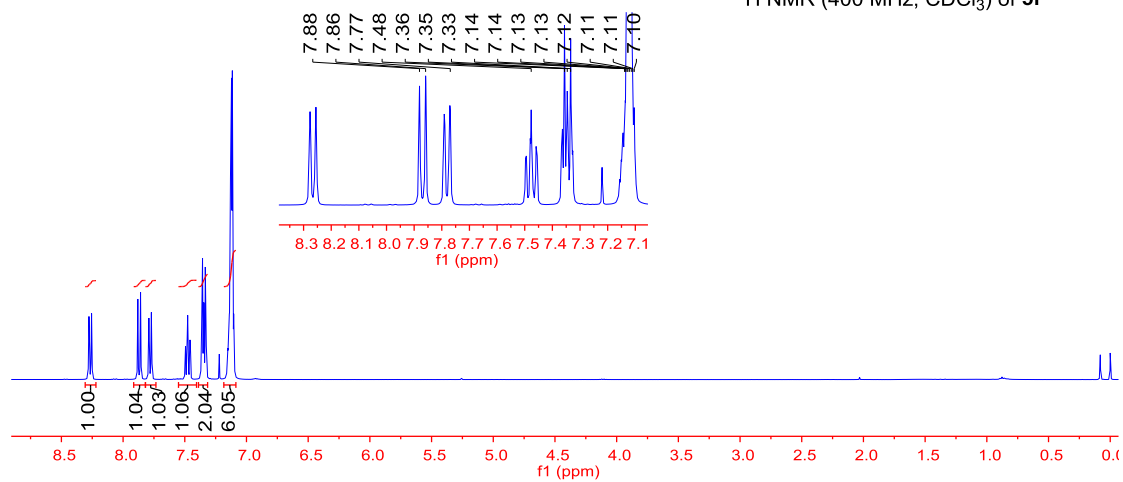




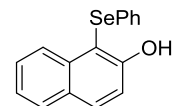
8.28
8.28
8.26
8.25
7.88
7.86
7.79
7.79
7.77
7.77
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.33
7.15
7.14
7.14
7.14
7.13
7.12
7.11
7.11
7.10



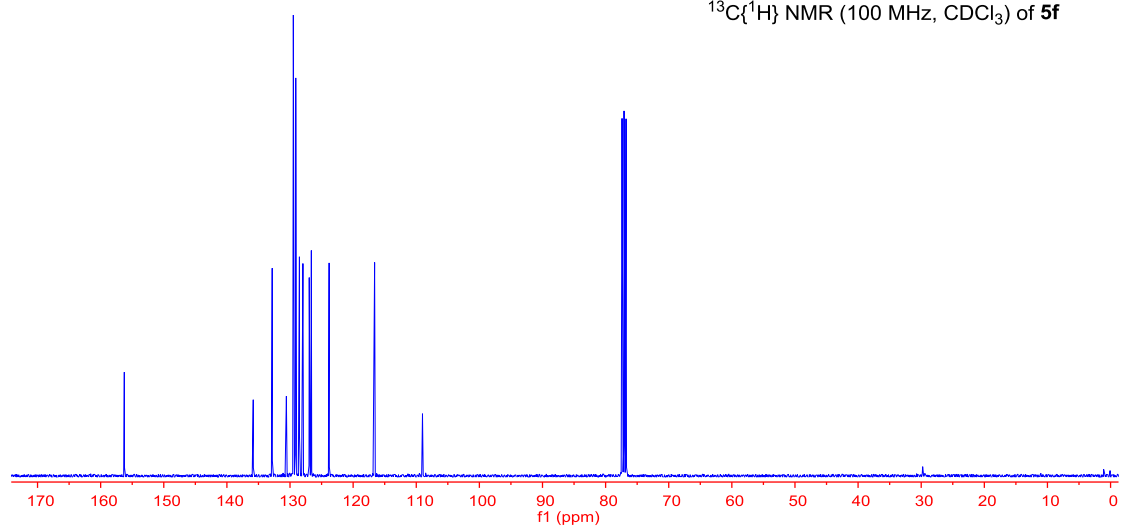
^1H NMR (400 MHz, CDCl_3) of **5f**

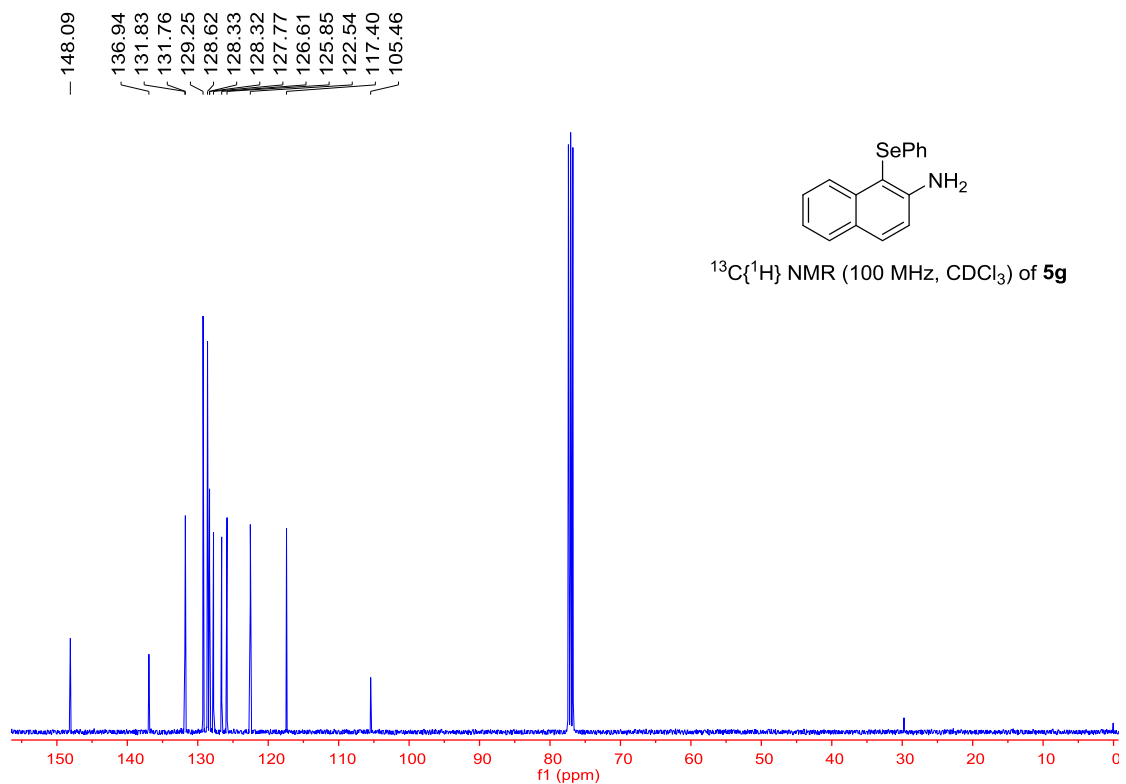
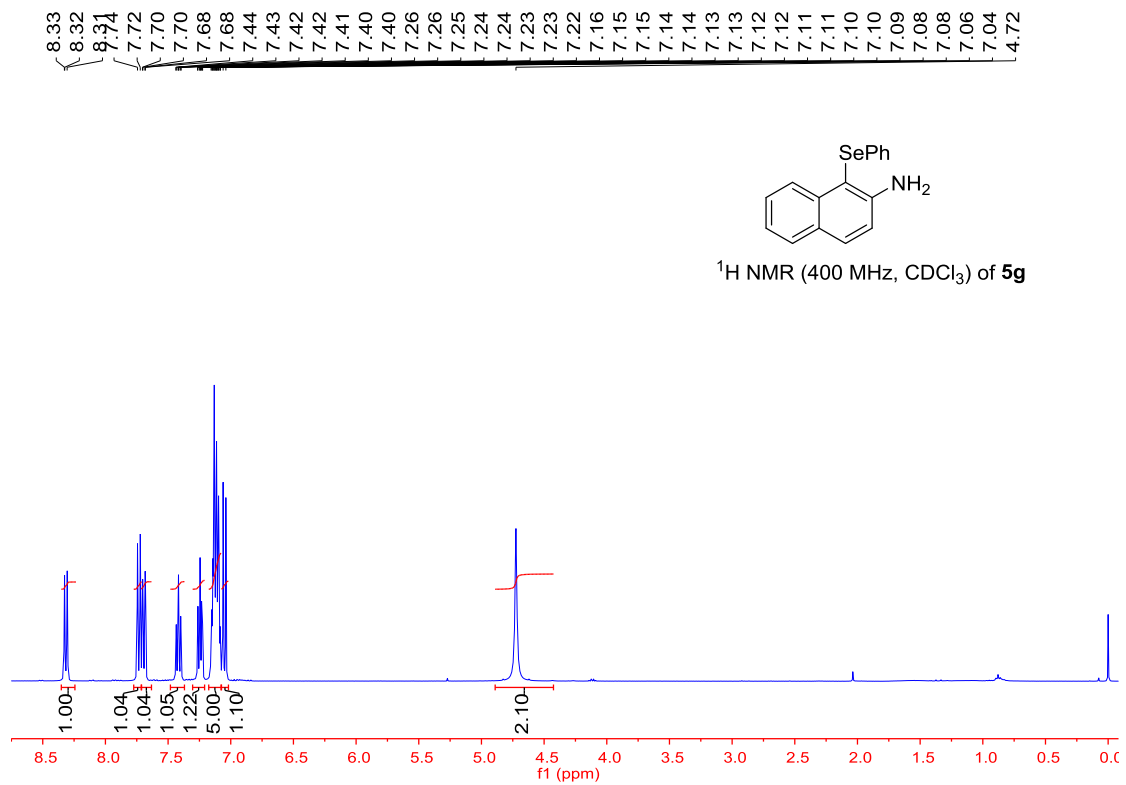


156.25
135.83
132.82
130.58
129.48
129.09
128.51
127.96
126.95
126.62
123.81
116.60
109.01

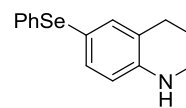


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **5f**

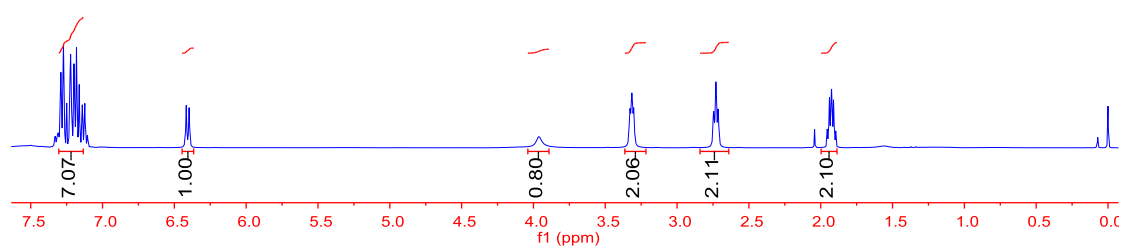




7.33
7.33
7.32
7.31
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.23
7.22
7.22
7.20
7.19
7.18
7.16
7.14
7.14
7.14
7.13
7.12
7.12
7.11
7.11
7.10
6.42
6.40
3.96
3.96
3.33
3.32
3.30
2.75
2.73
2.71
1.95
1.94
1.93
1.92
1.91
1.90

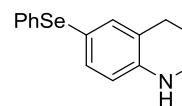


^1H NMR (400 MHz, CDCl_3) of **5h**

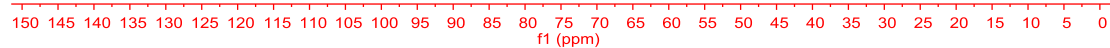


- 145.21
137.40
134.92
134.75
129.71
128.97
125.75
122.39
- 114.83

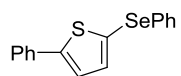
- 41.81
- 26.84
- 21.72



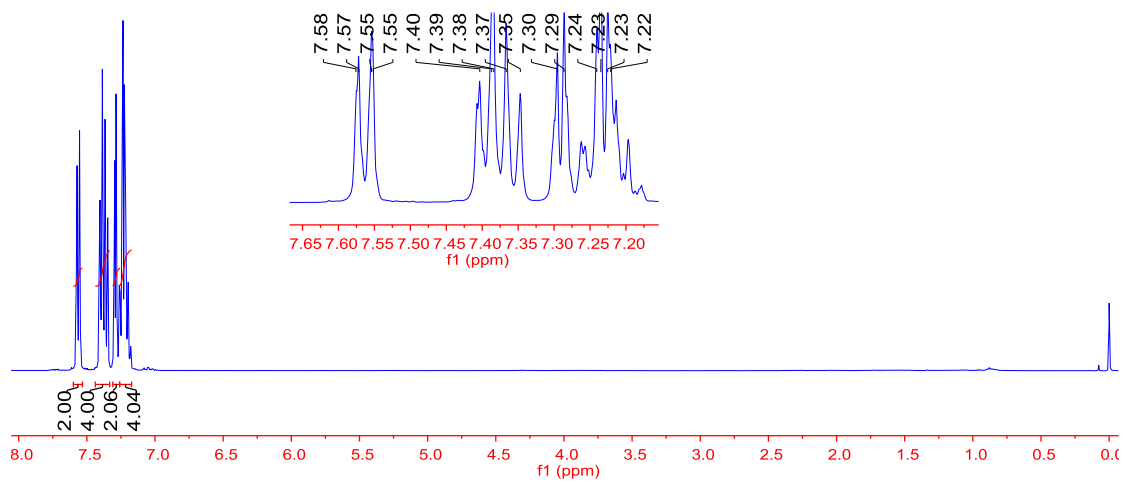
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **5h**



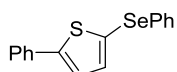
7.58
7.57
7.57
7.56
7.55
7.55
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.35
7.35
7.30
7.30
7.29
7.28
7.26
7.26
7.24
7.23
7.23
7.22
7.21
7.21
7.20



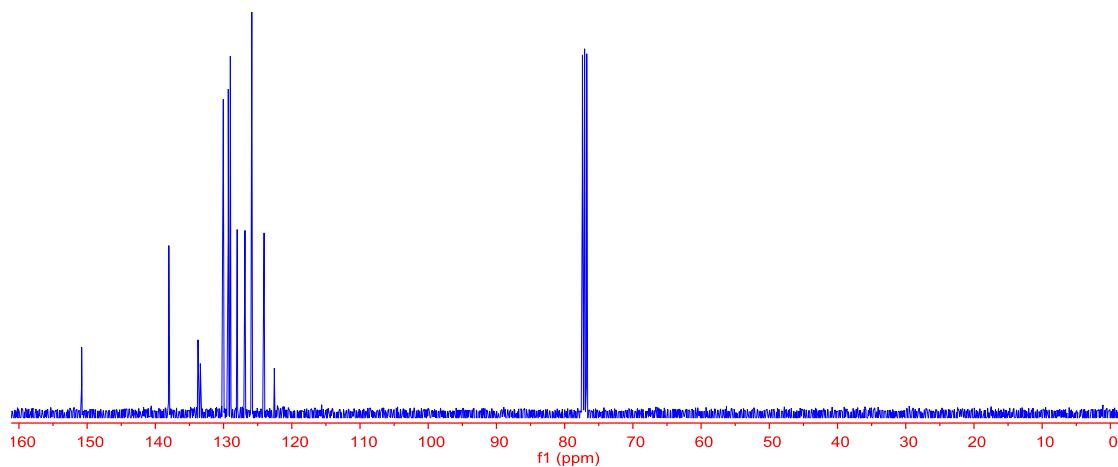
^1H NMR (400 MHz, CDCl_3) of **5i**

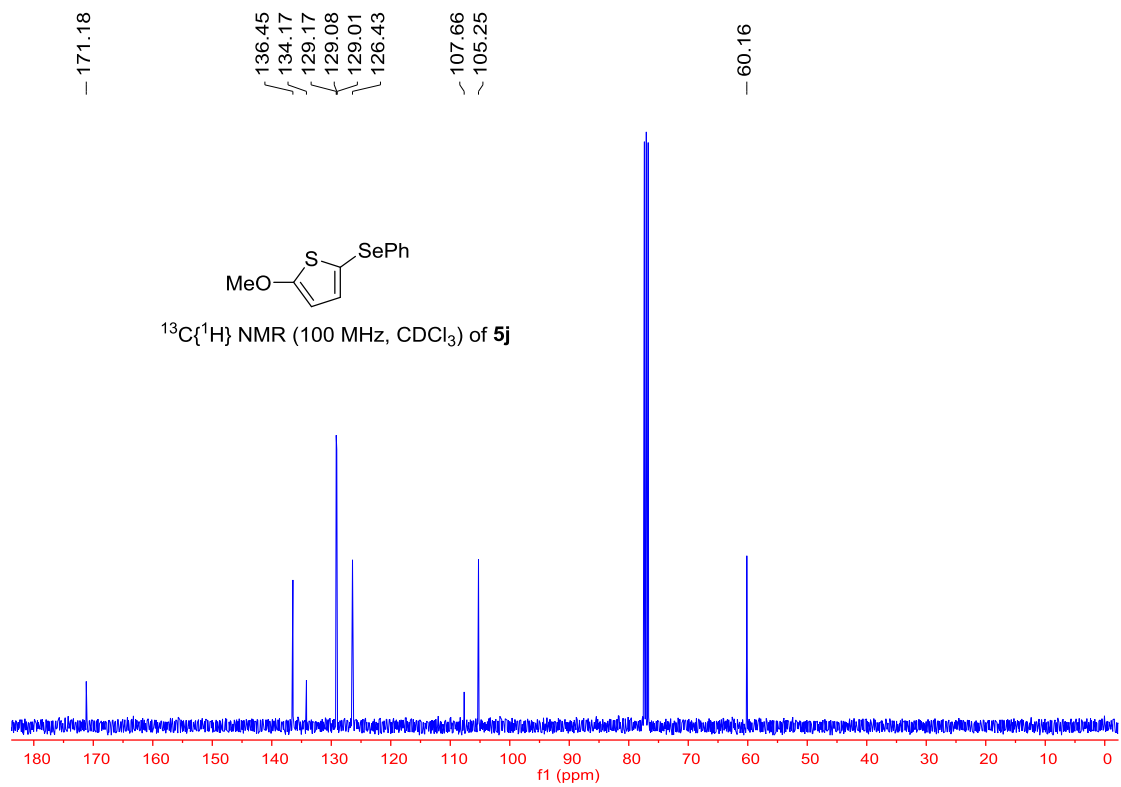
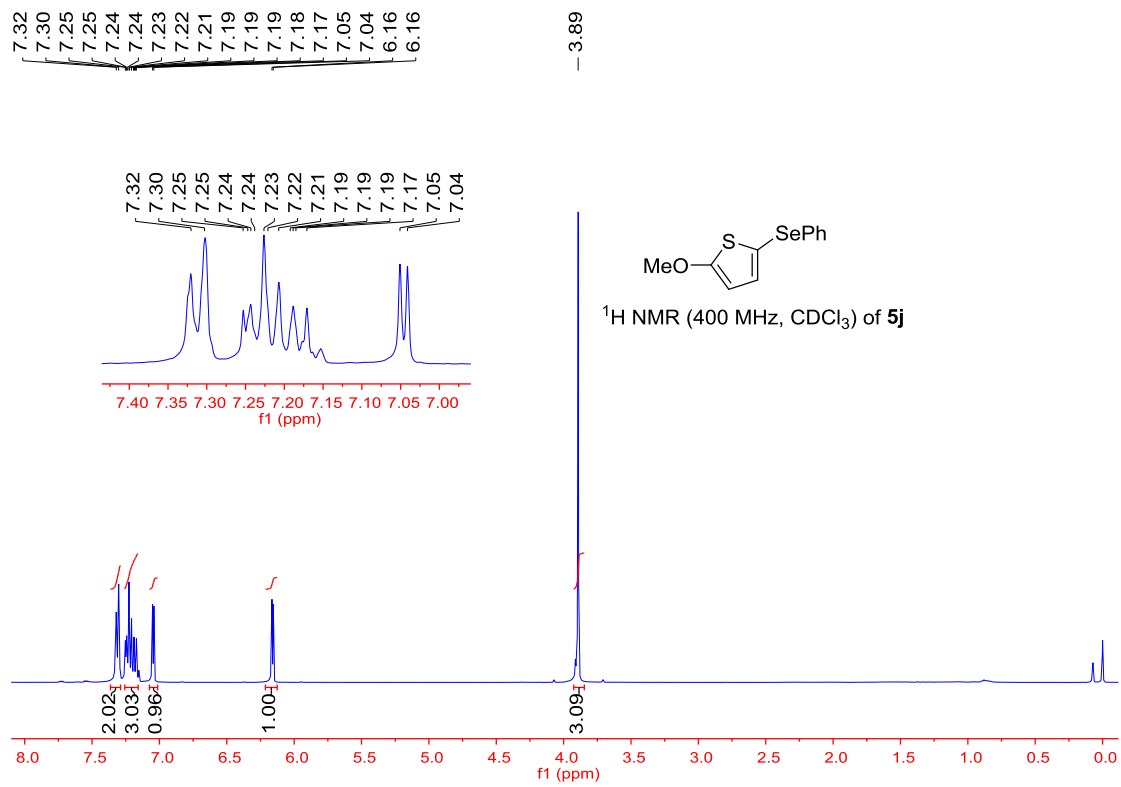


150.80
138.03
133.75
133.41
130.04
129.32
129.01
128.01
126.86
125.86
124.07
122.56

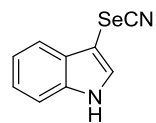


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **5i**

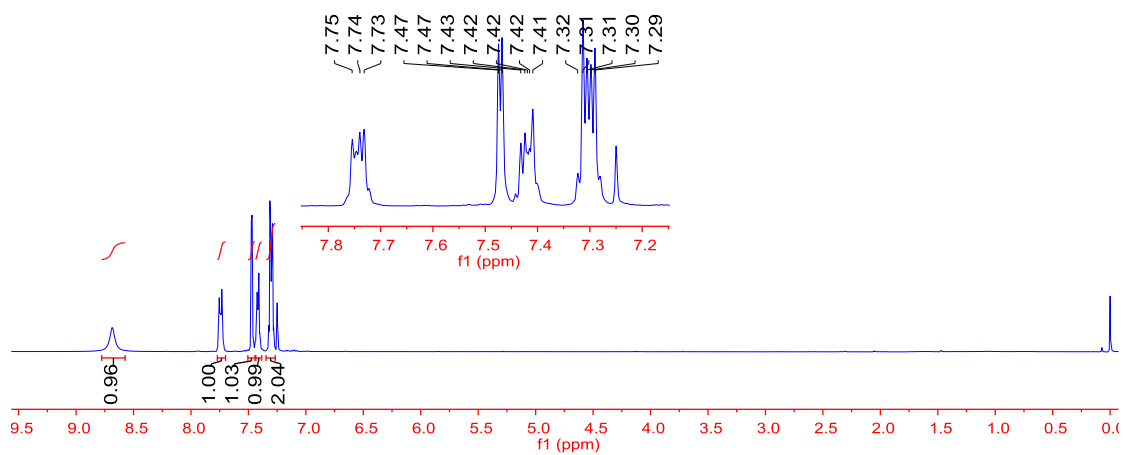




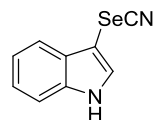
8.68
7.75
7.74
7.73
7.47
7.47
7.43
7.42
7.42
7.41
7.32
7.31
7.30
7.29
7.28



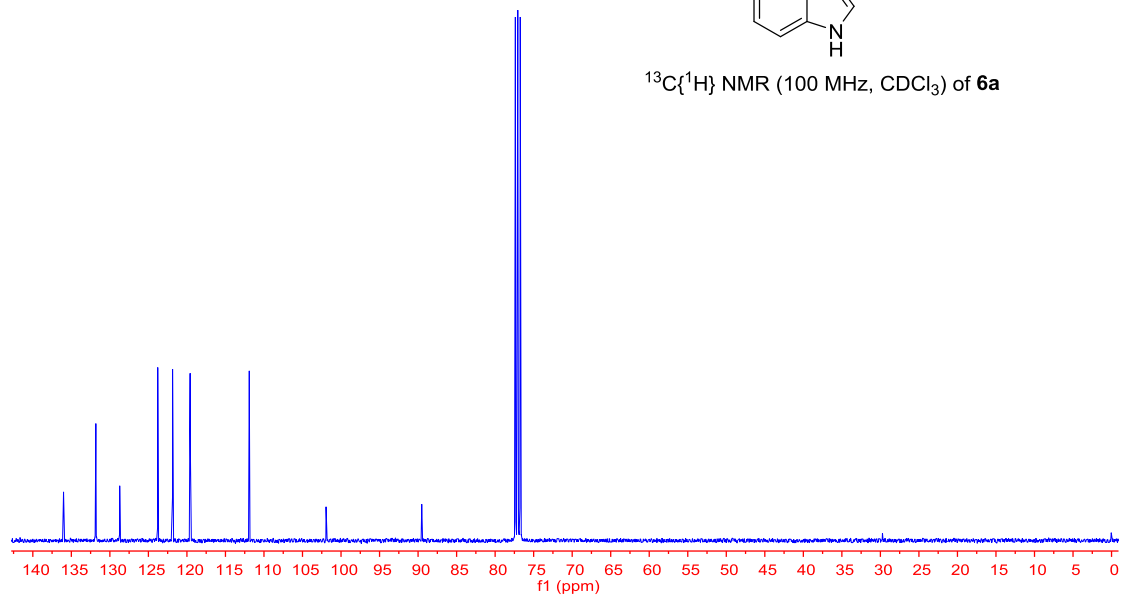
^1H NMR (400 MHz, CDCl_3) of **6a**

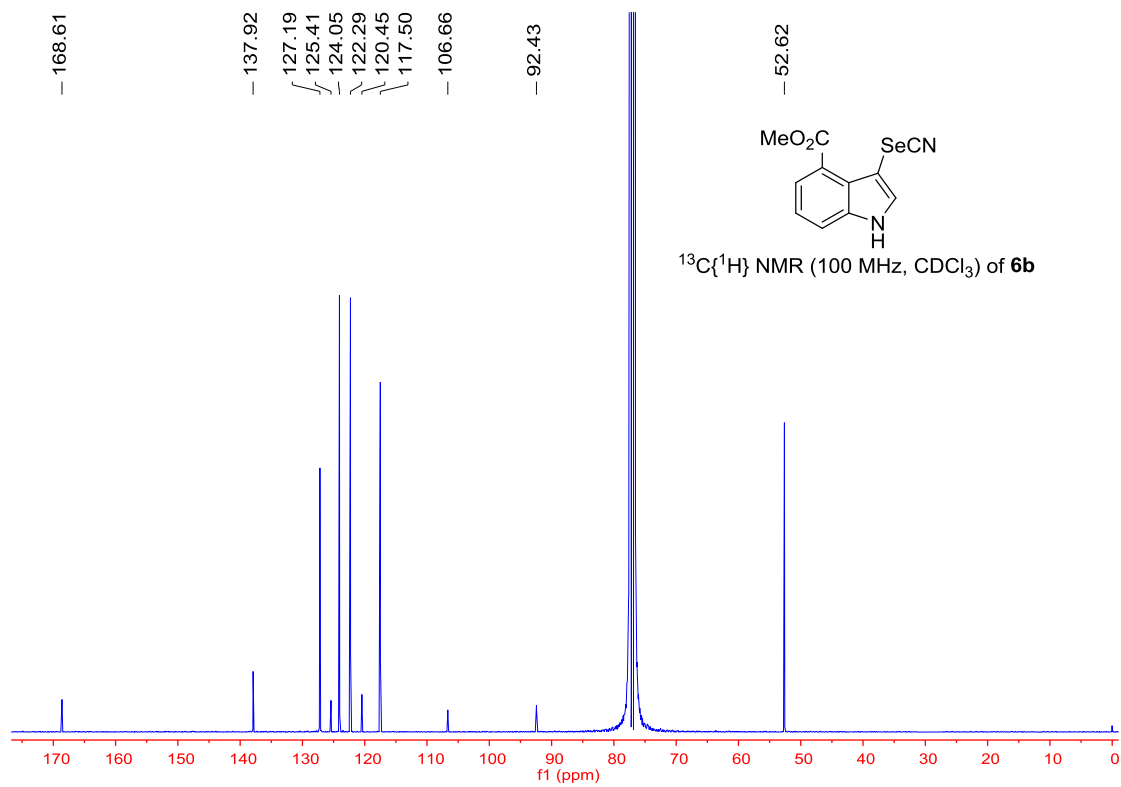
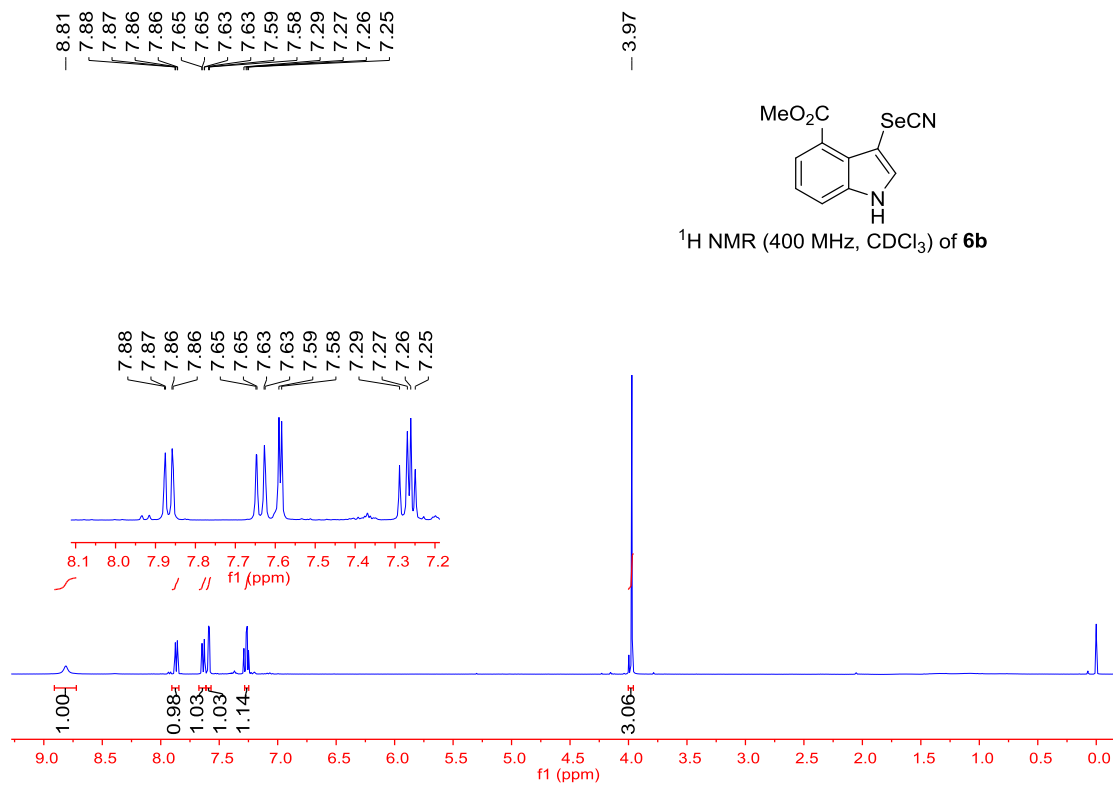


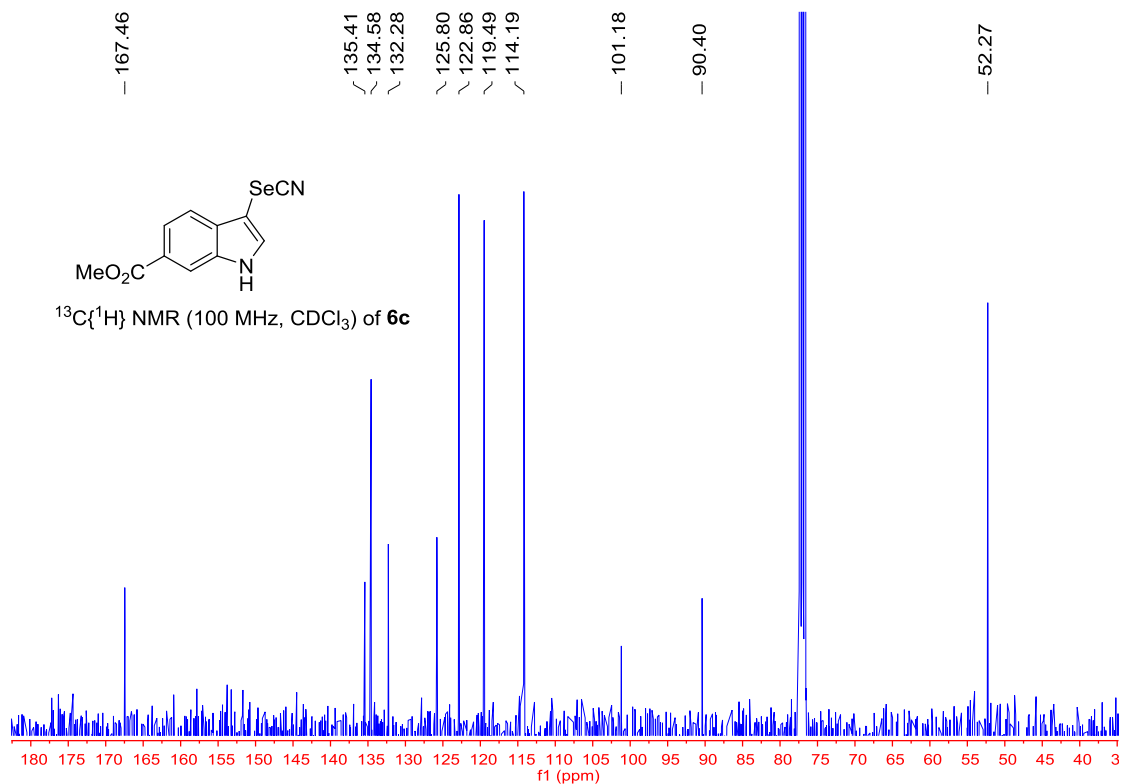
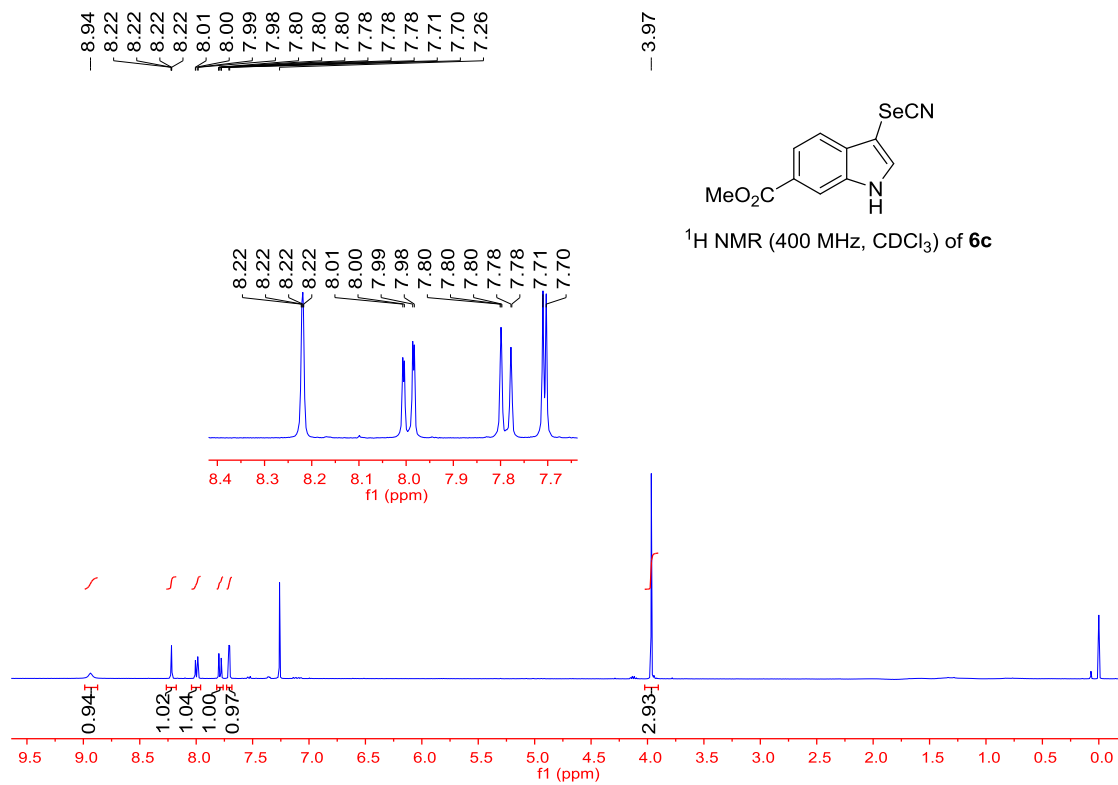
136.01
131.82
128.72
123.79
121.86
119.58
111.91
101.94
89.52



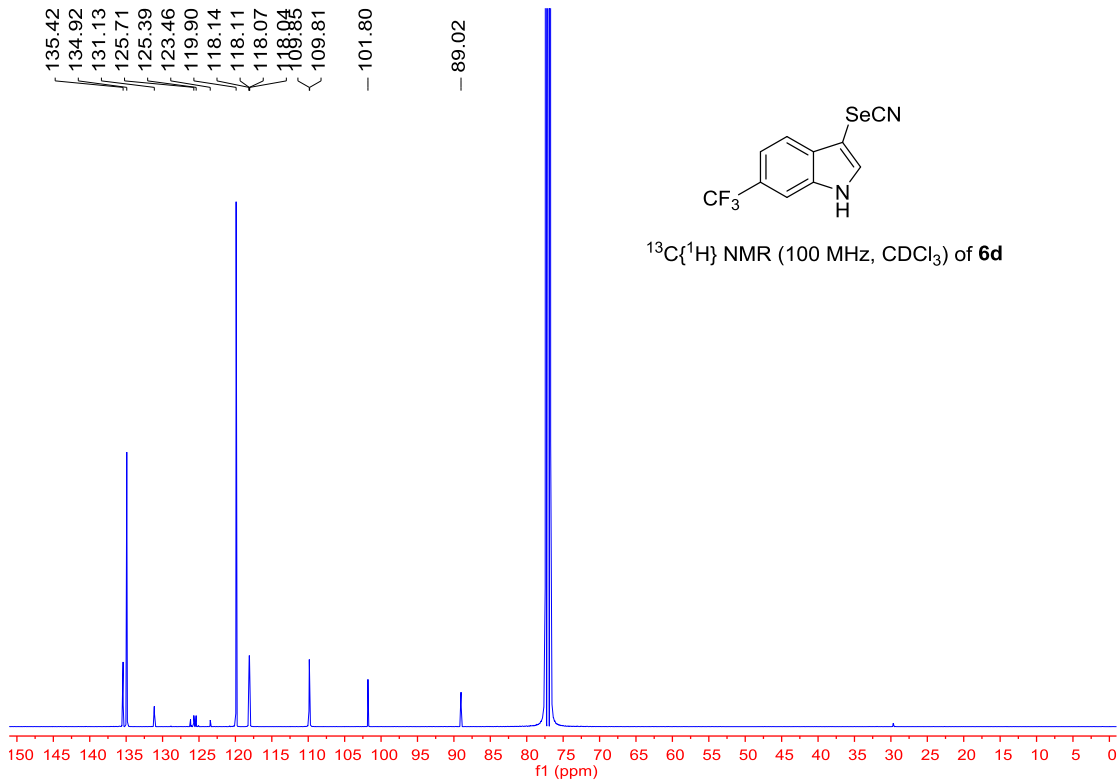
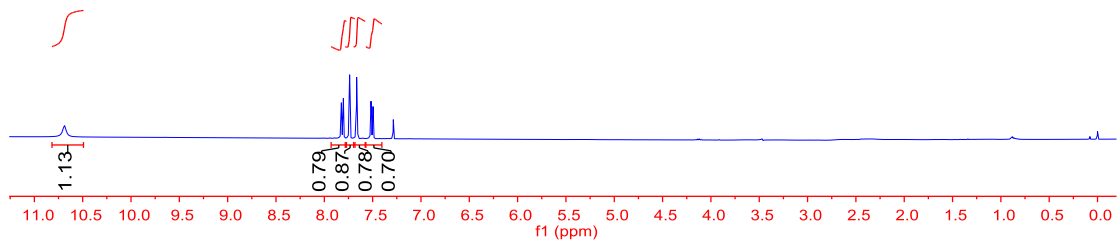
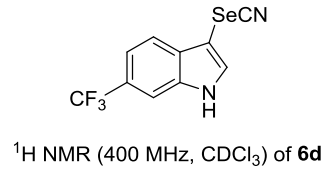
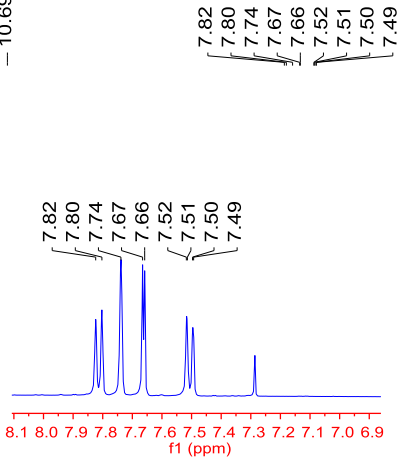
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **6a**

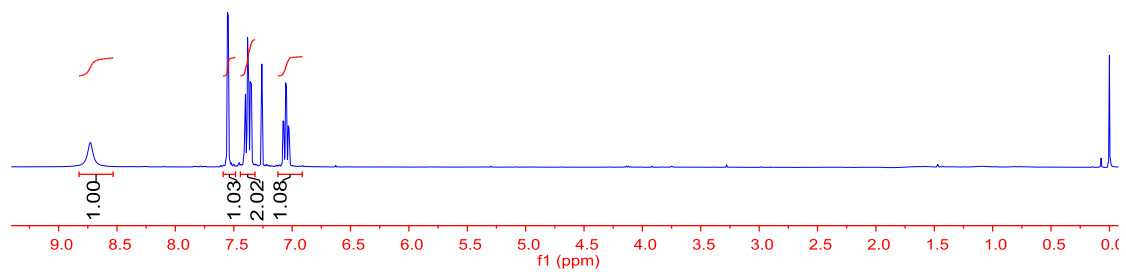
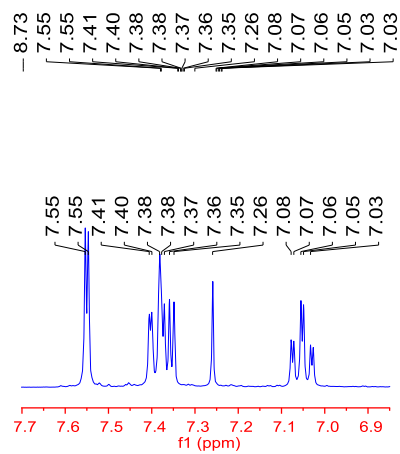
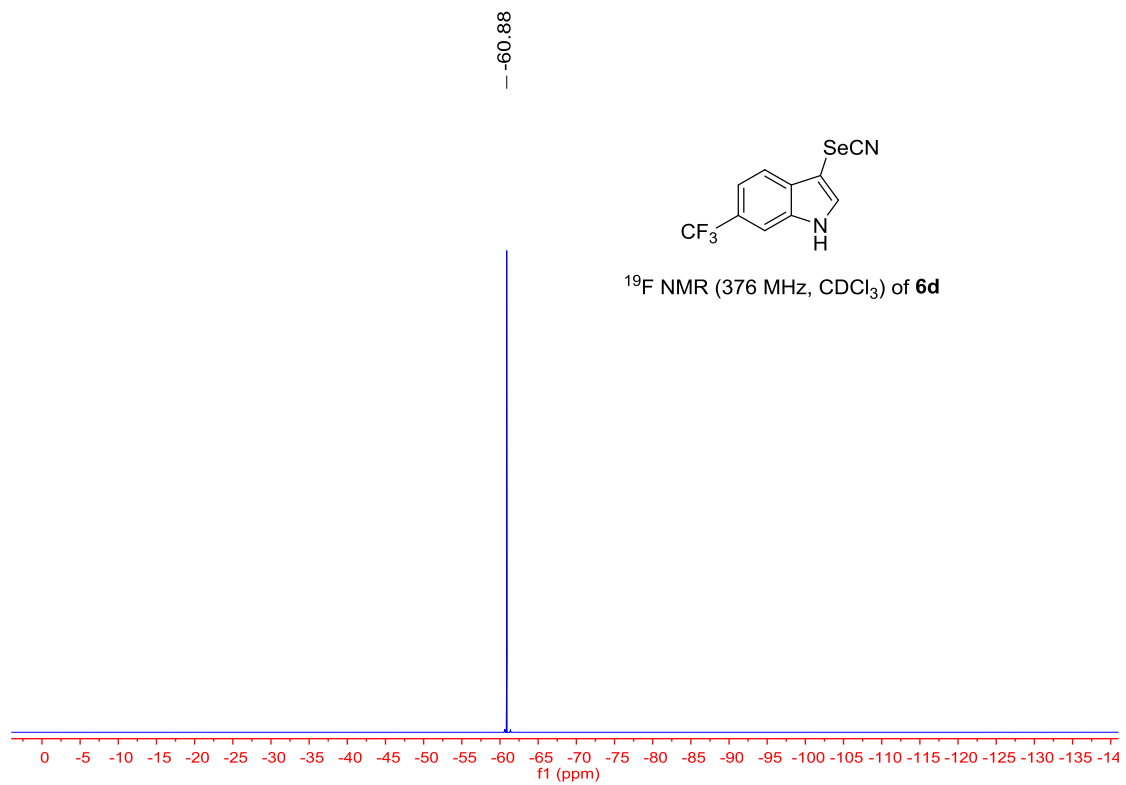


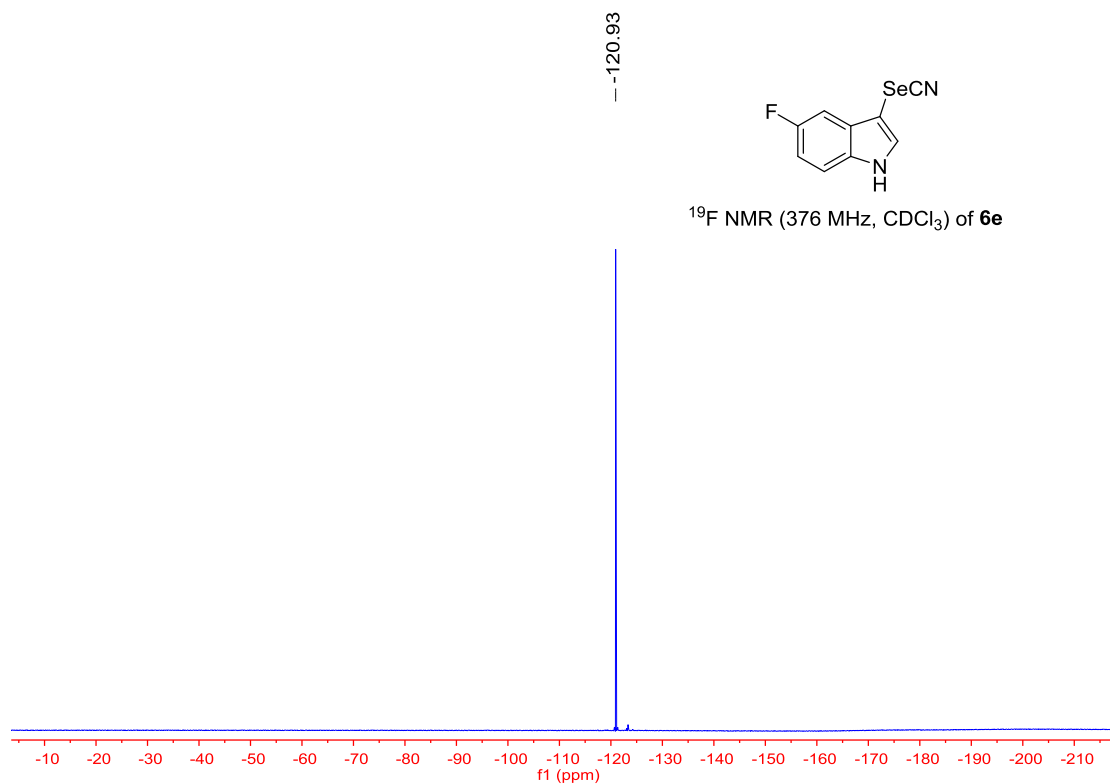
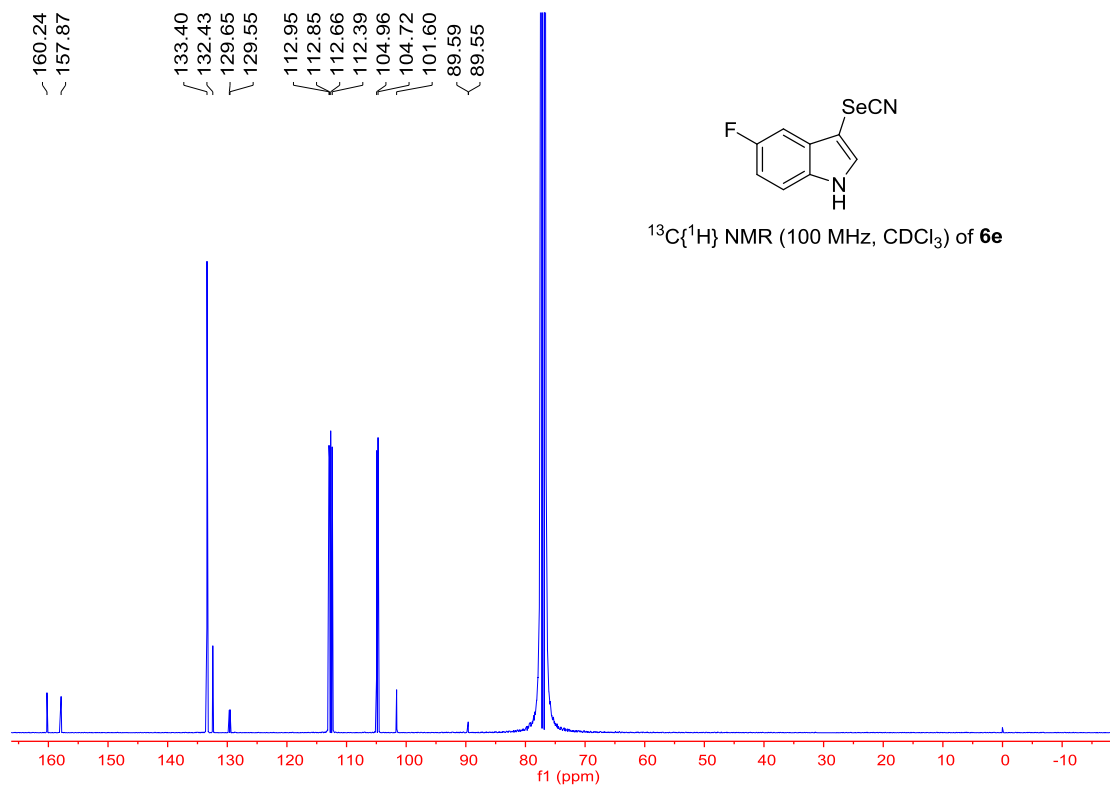


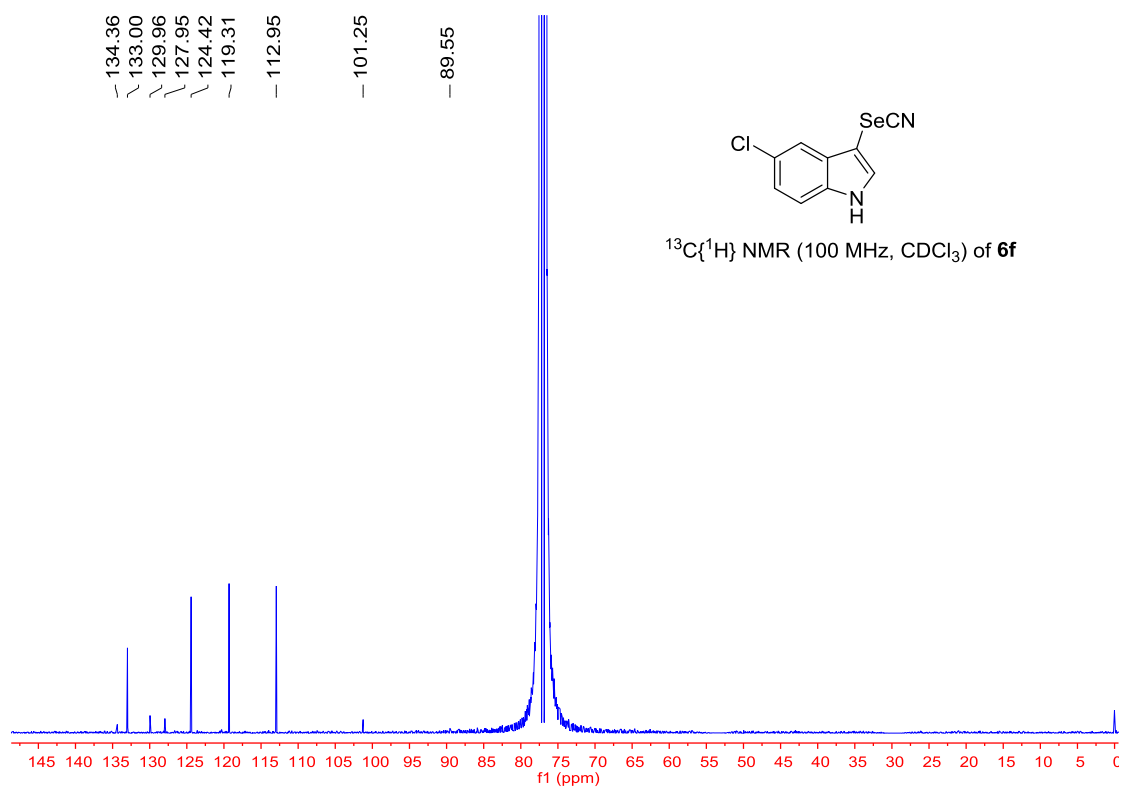
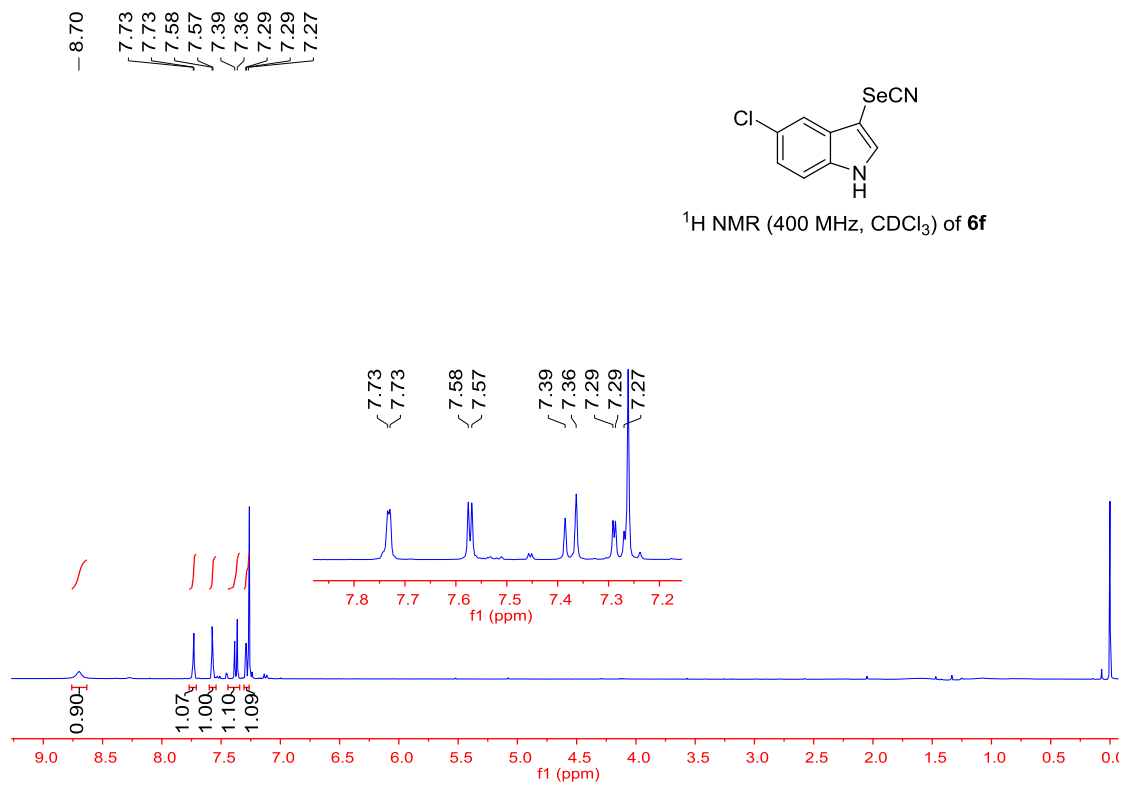


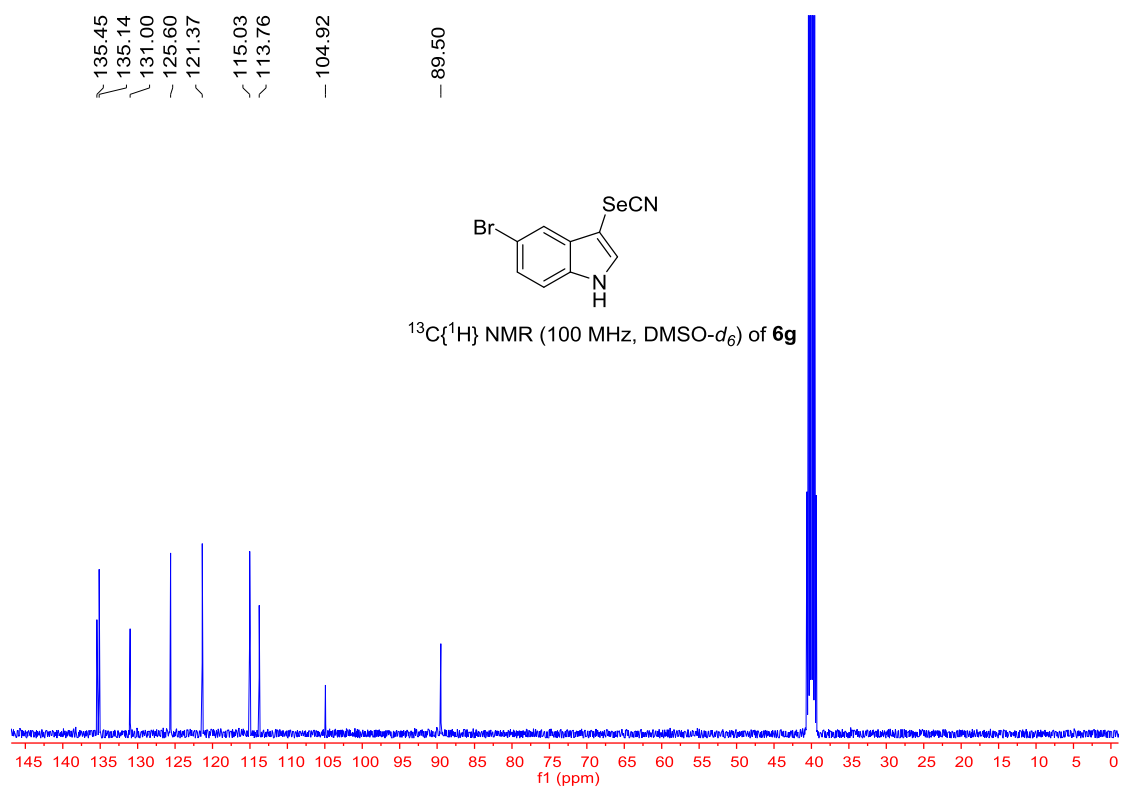
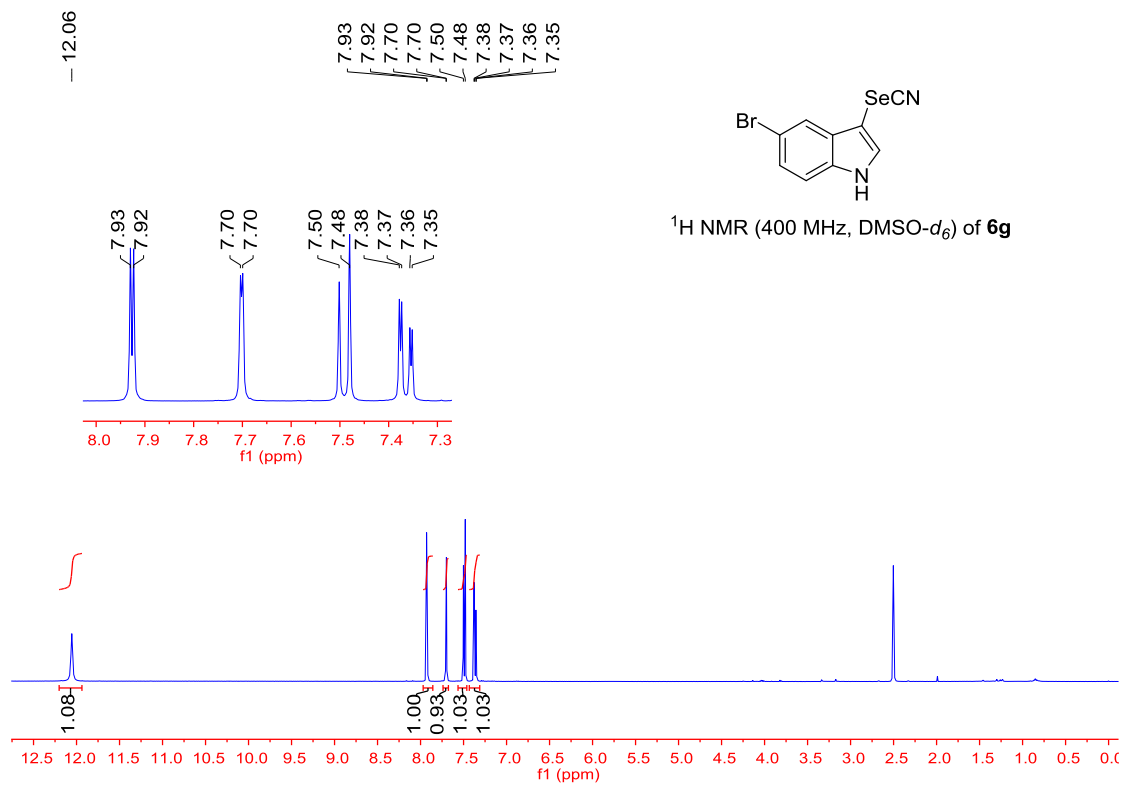
- 10.69

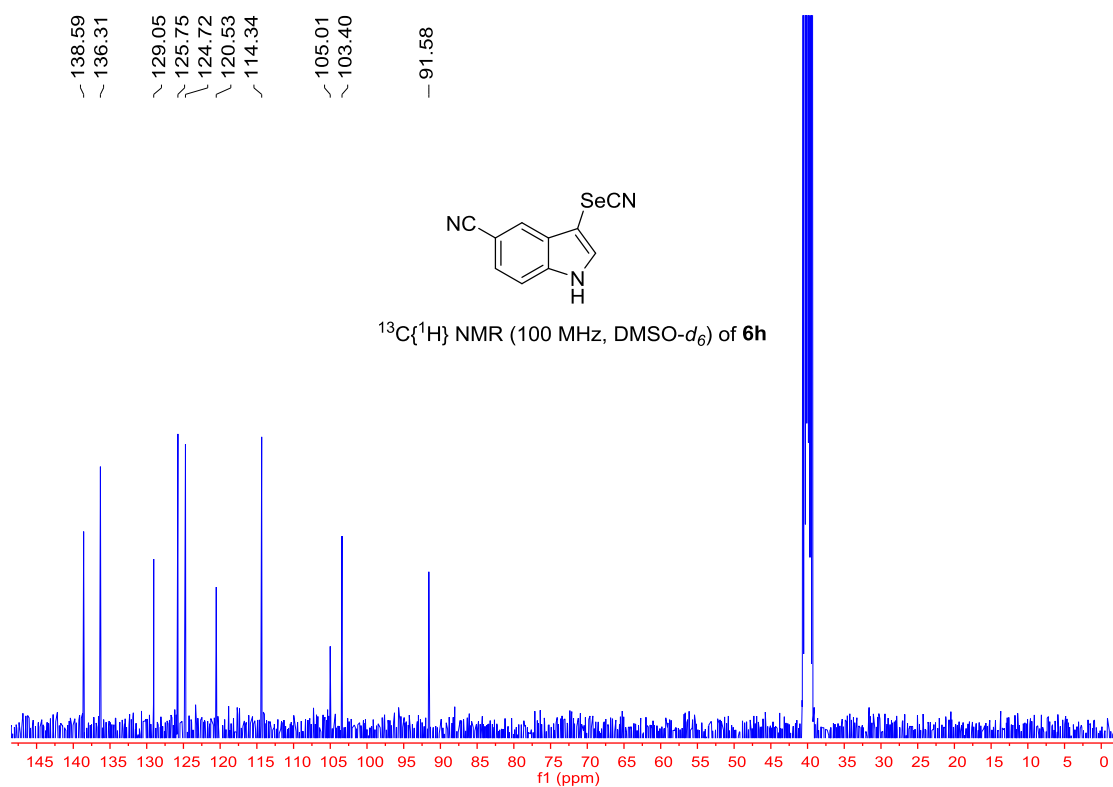
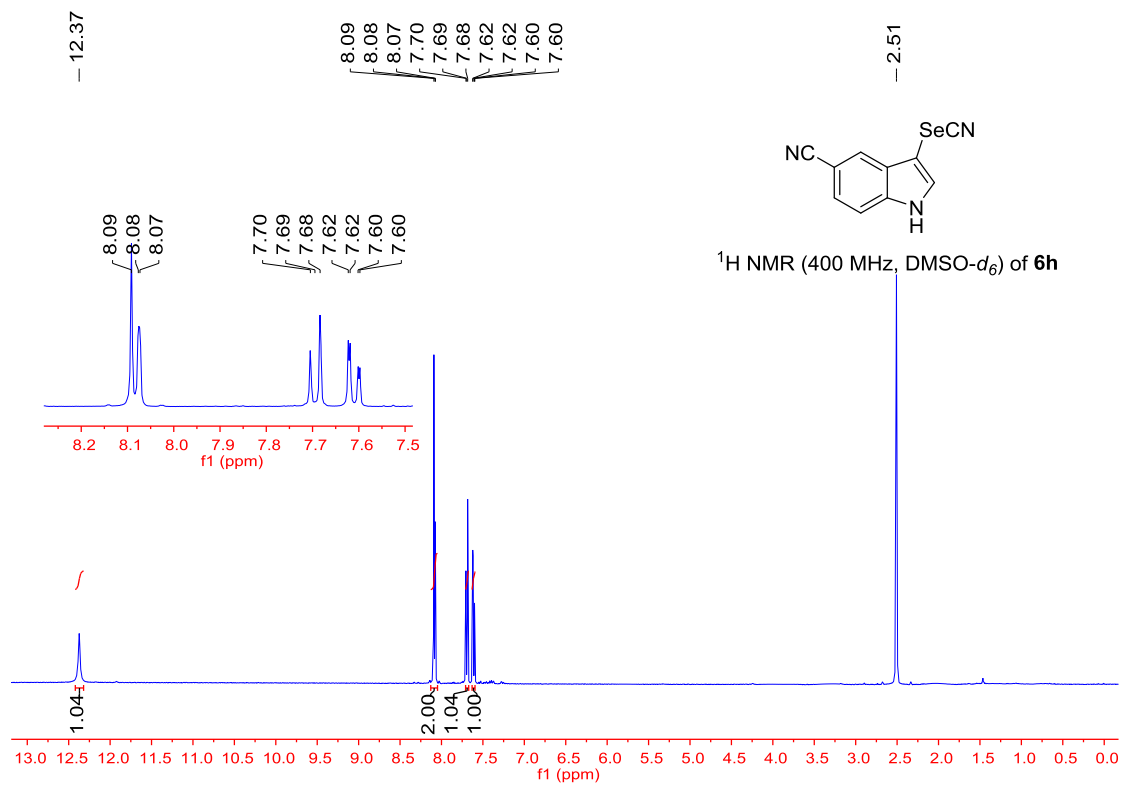


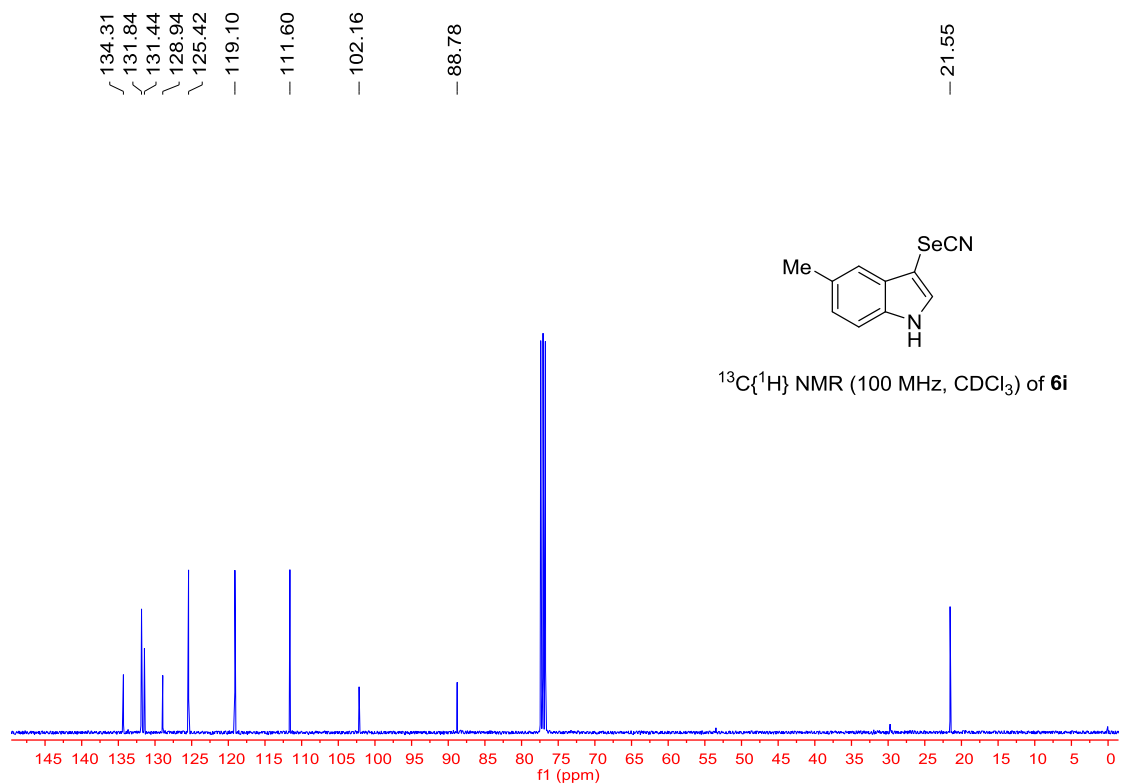
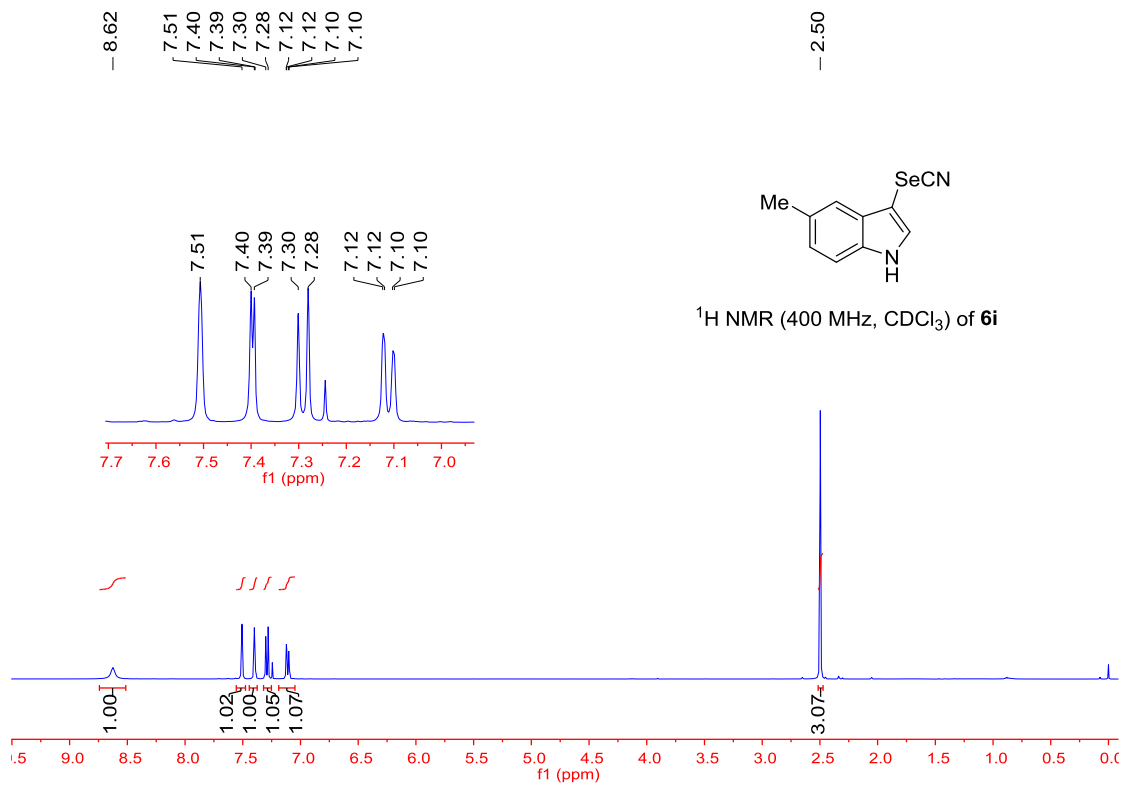


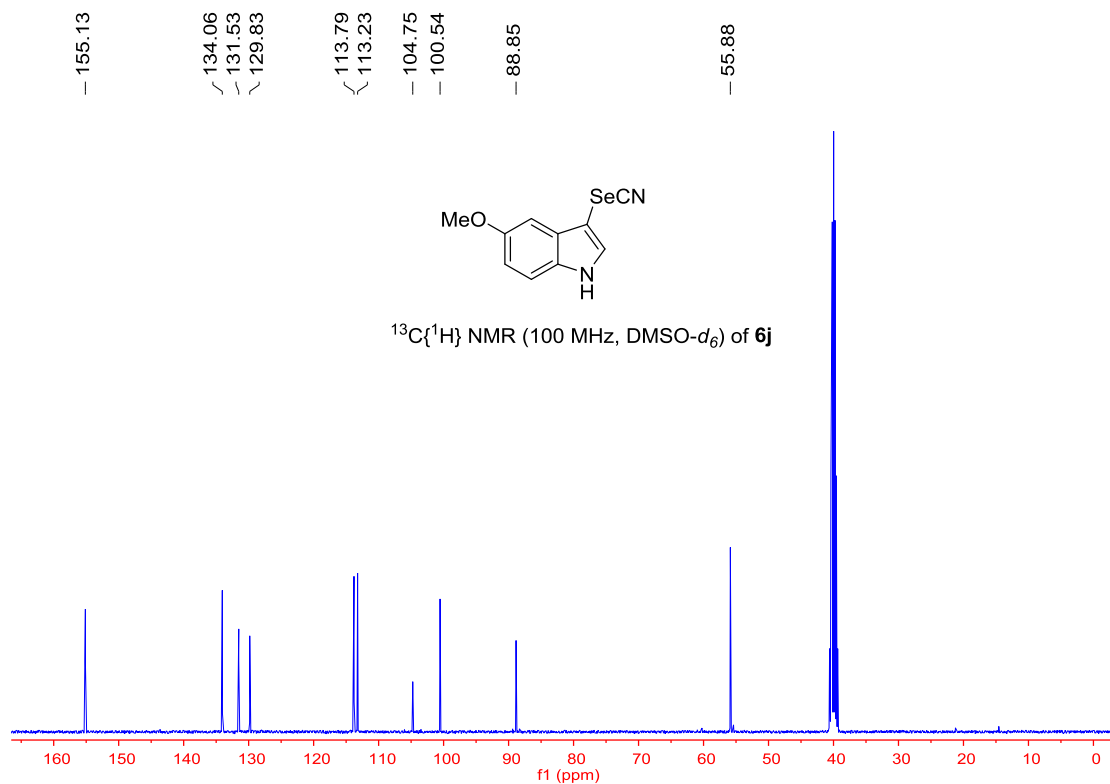
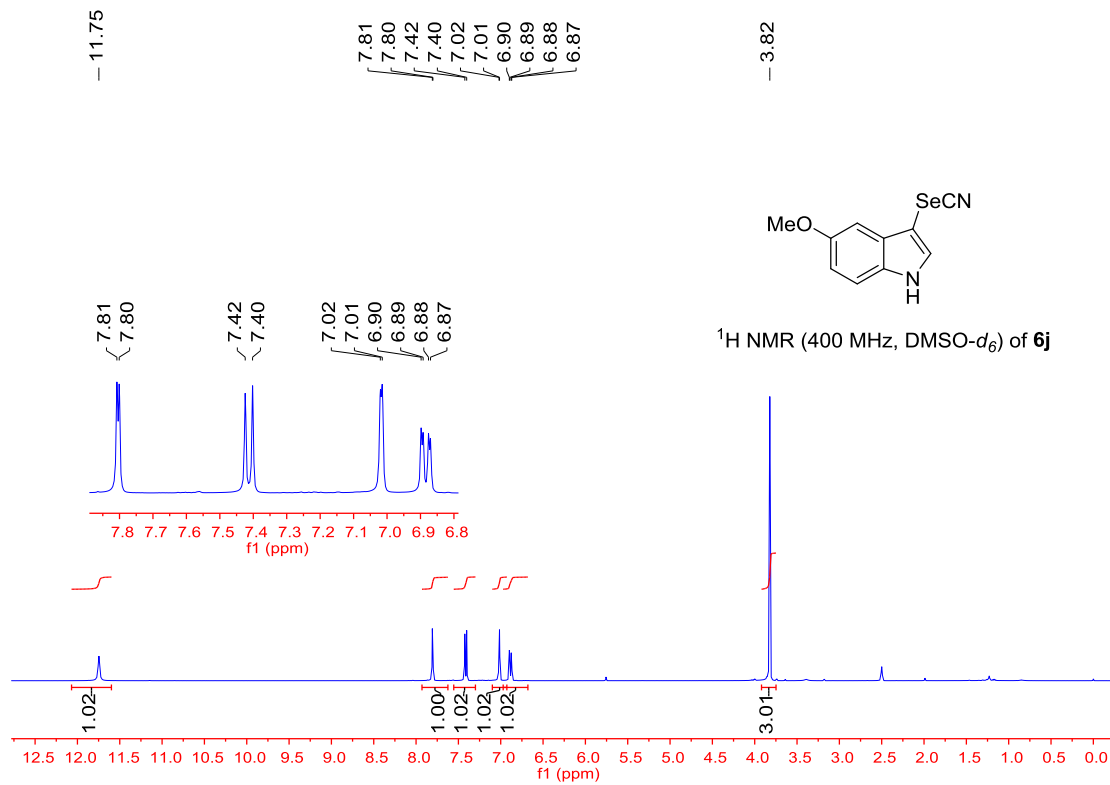


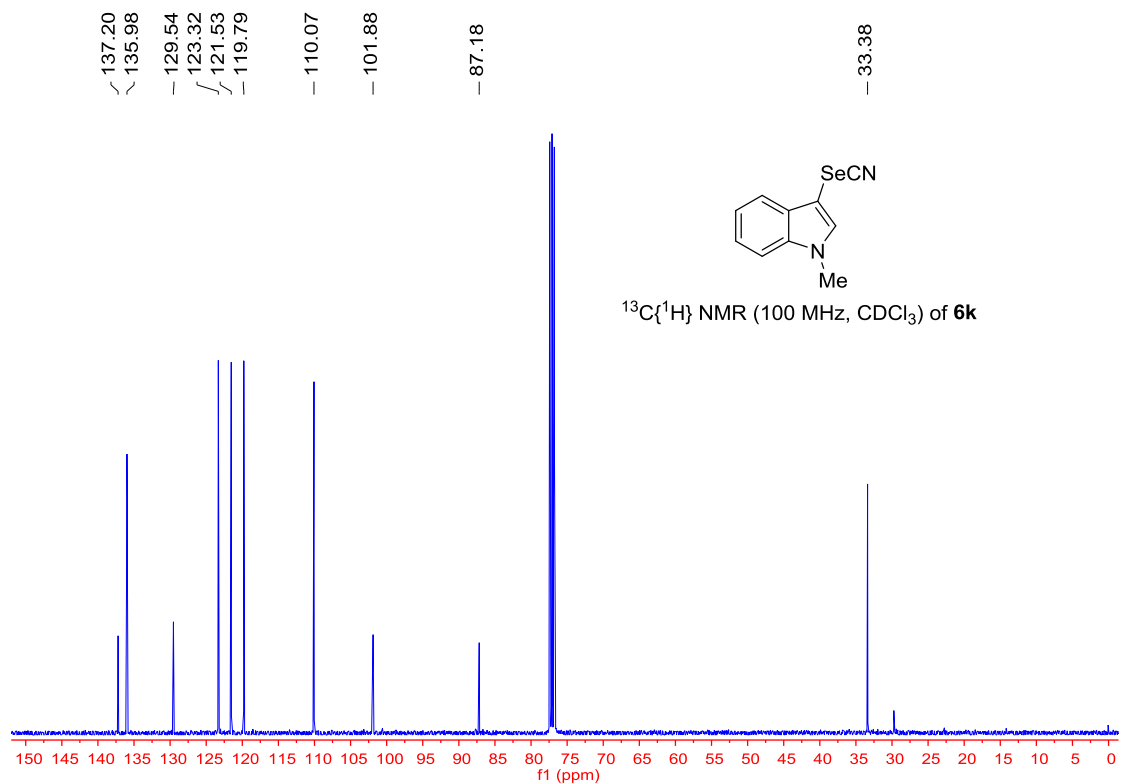
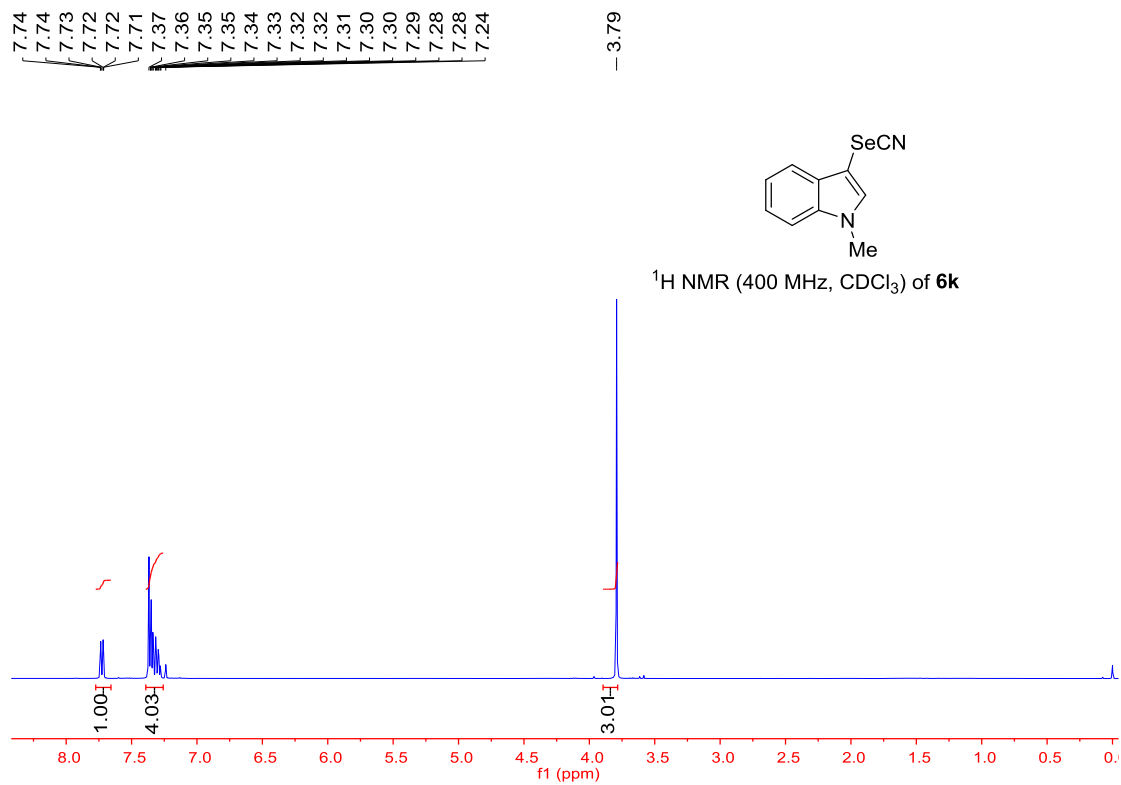




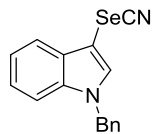




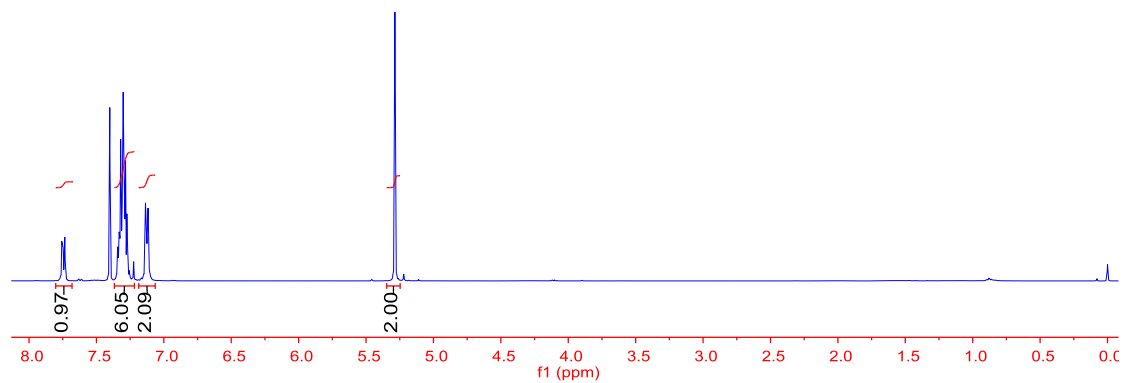




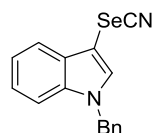
7.76
7.75
7.75
7.74
7.73
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.27
7.27
7.14
7.13
7.12
7.11
5.29



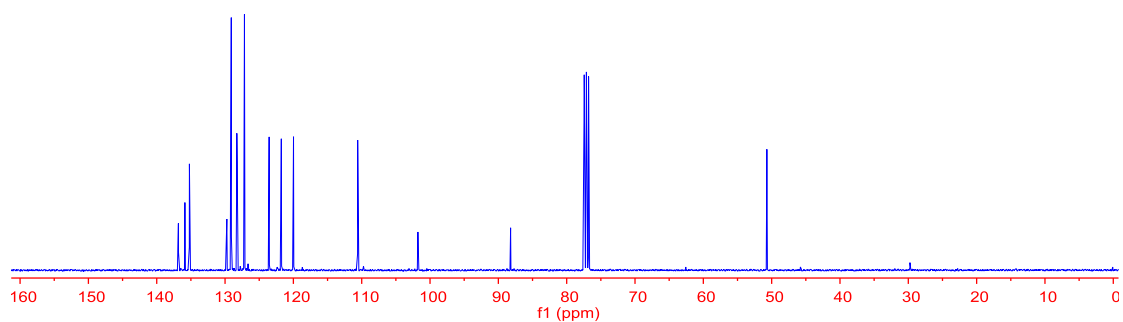
^1H NMR (400 MHz, CDCl_3) of **6I**

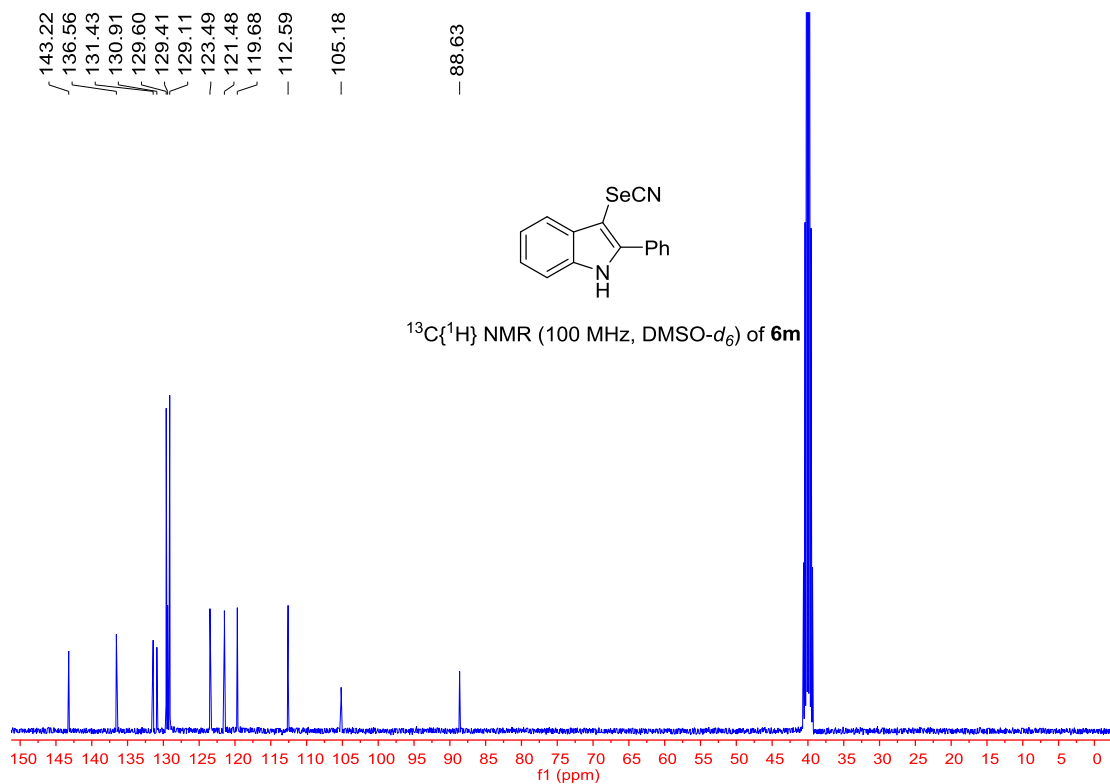
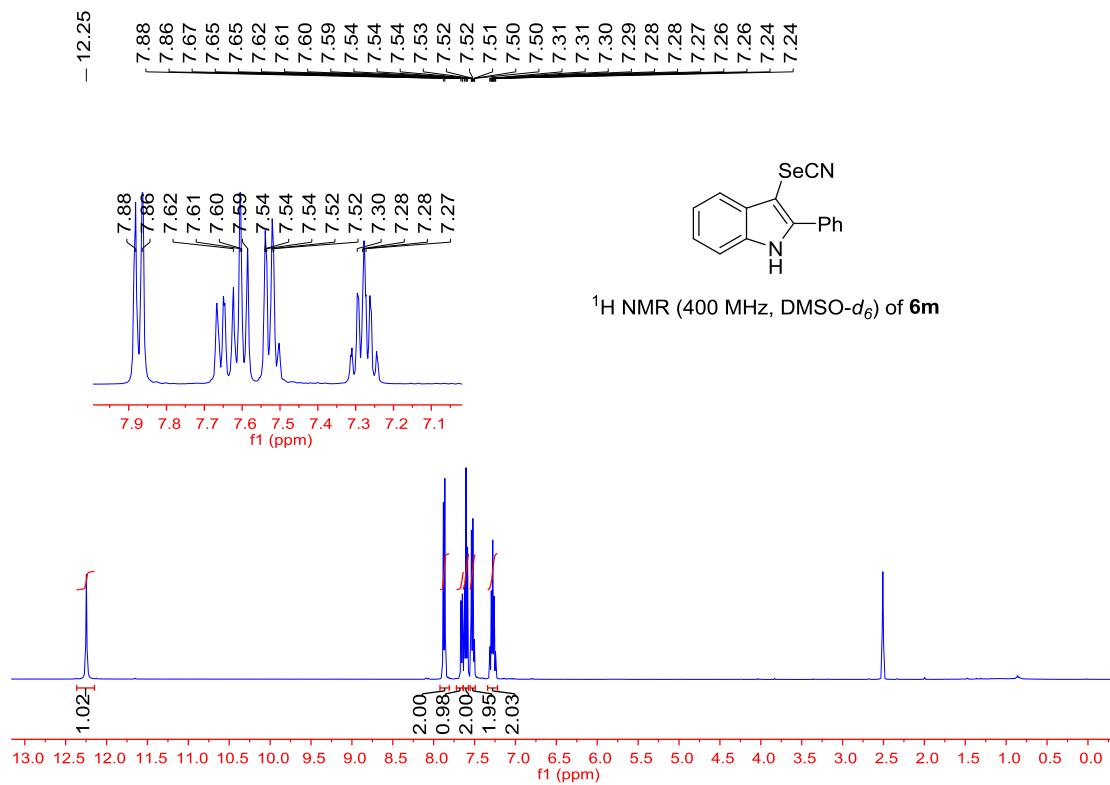


136.83
135.88
135.22
129.74
129.09
128.28
127.16
123.55
121.77
119.98
110.59
101.77
88.21
50.70



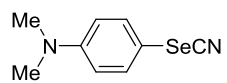
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **6I**



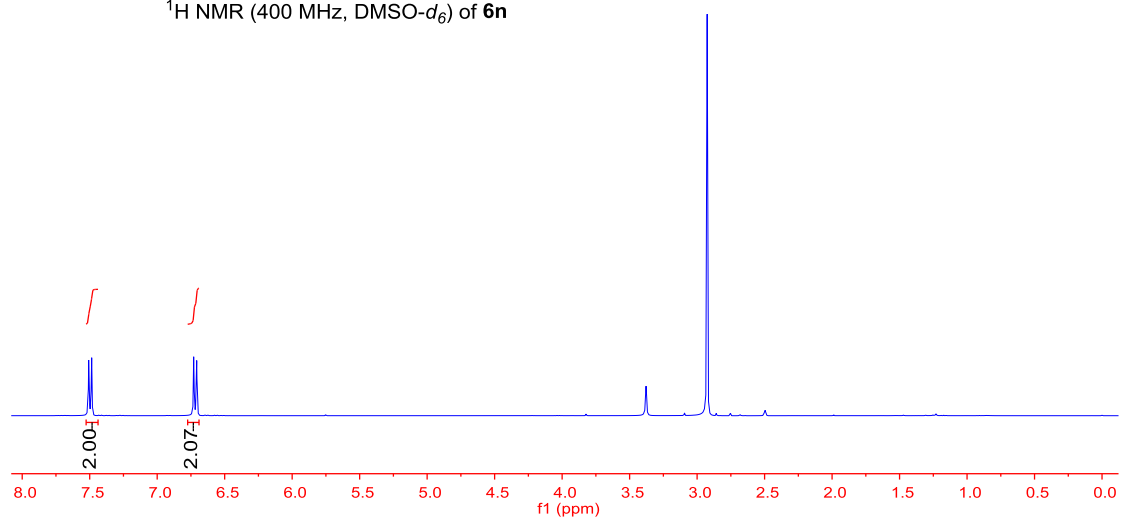


7.51
7.49

6.73
6.71



^1H NMR (400 MHz, $\text{DMSO-}d_6$) of **6n**



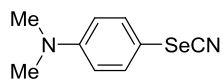
151.62

136.54
136.49

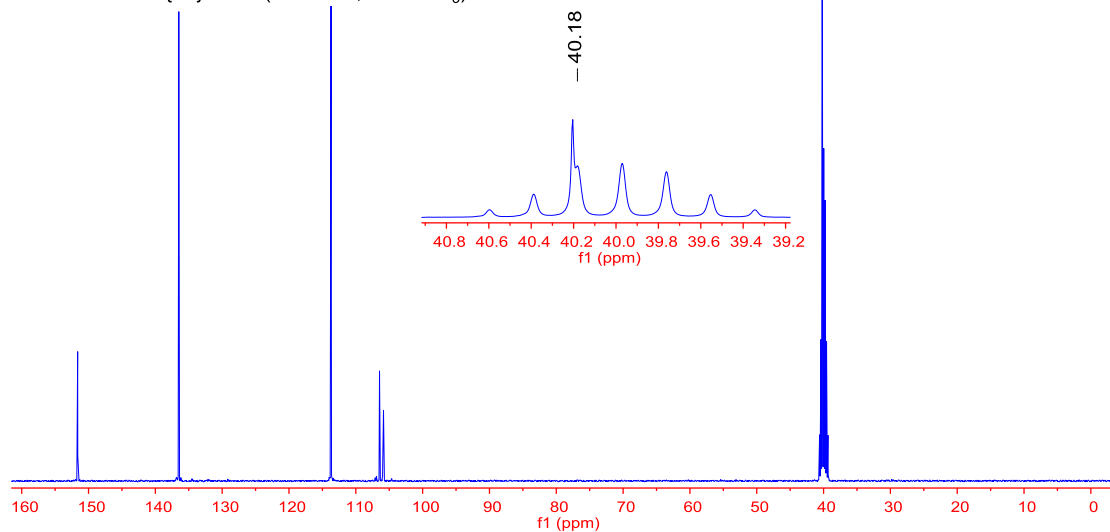
113.71

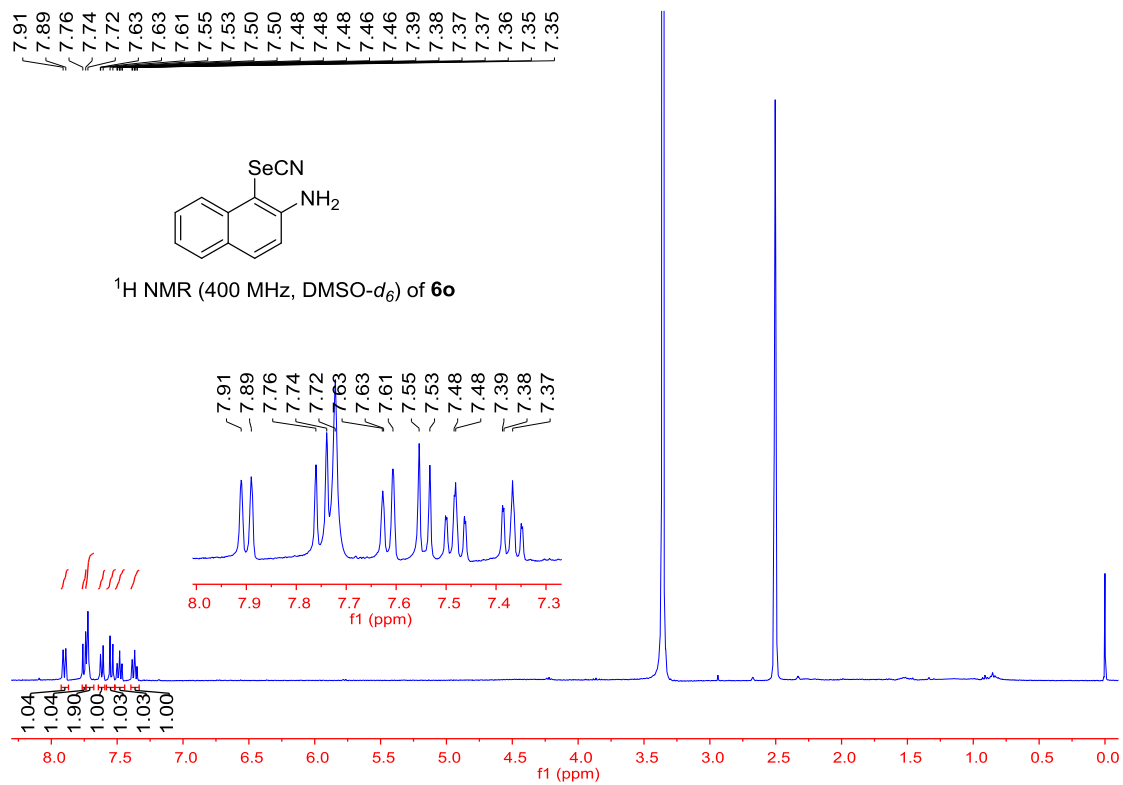
106.45
105.86

40.18



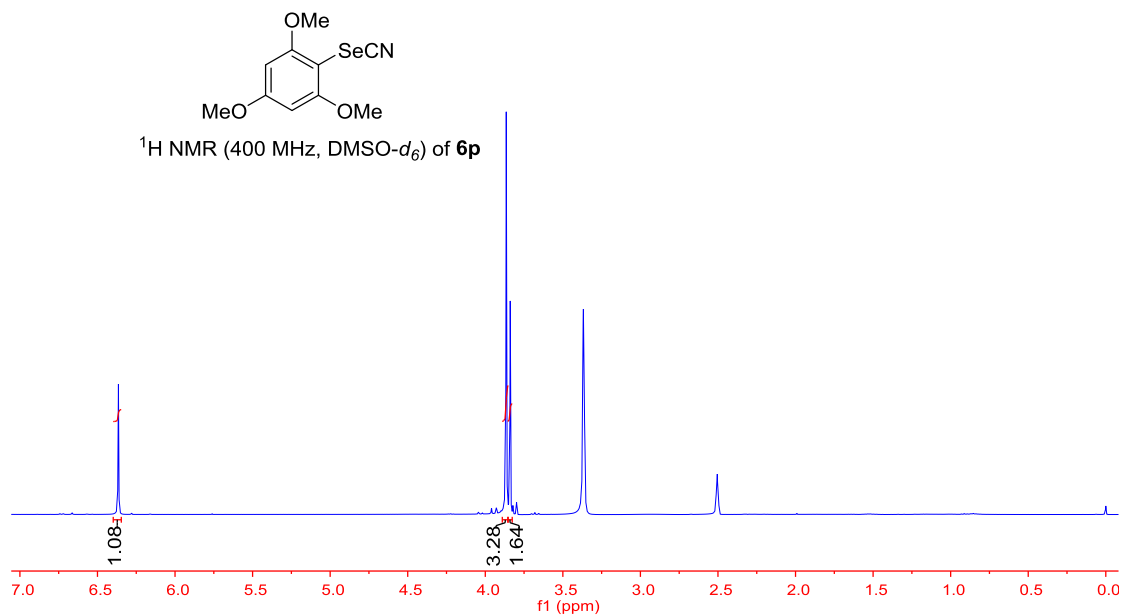
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) of **6n**

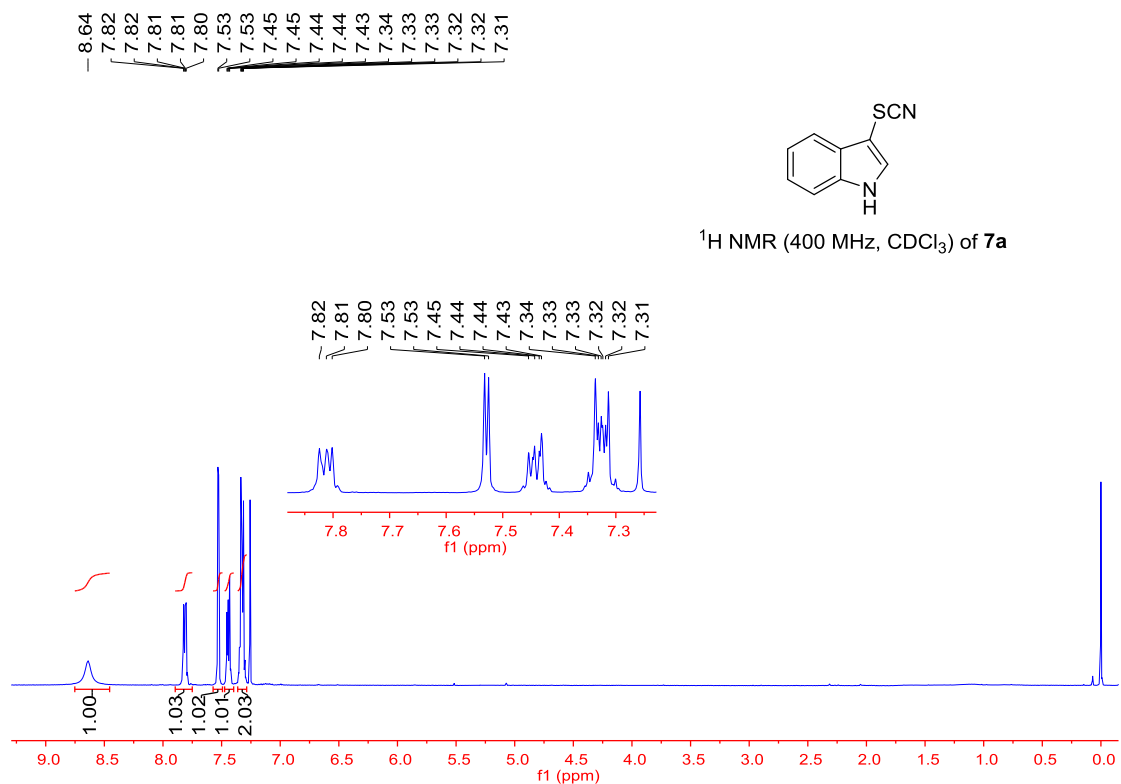
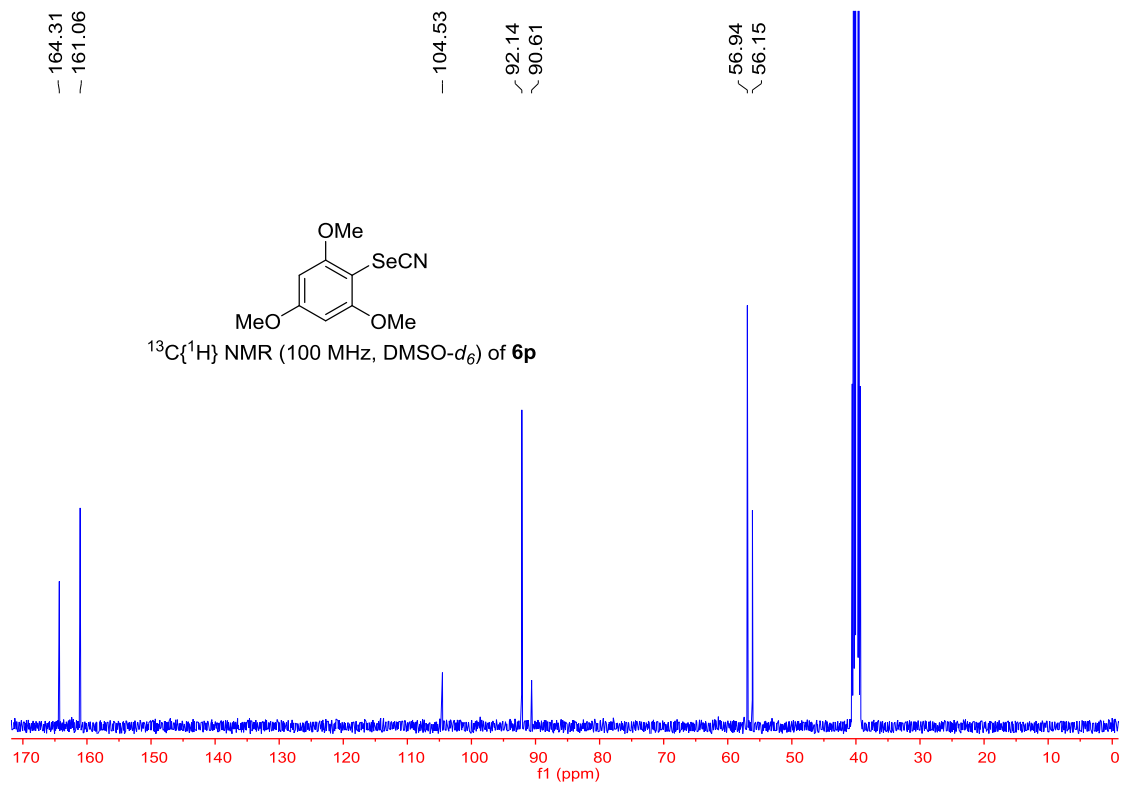


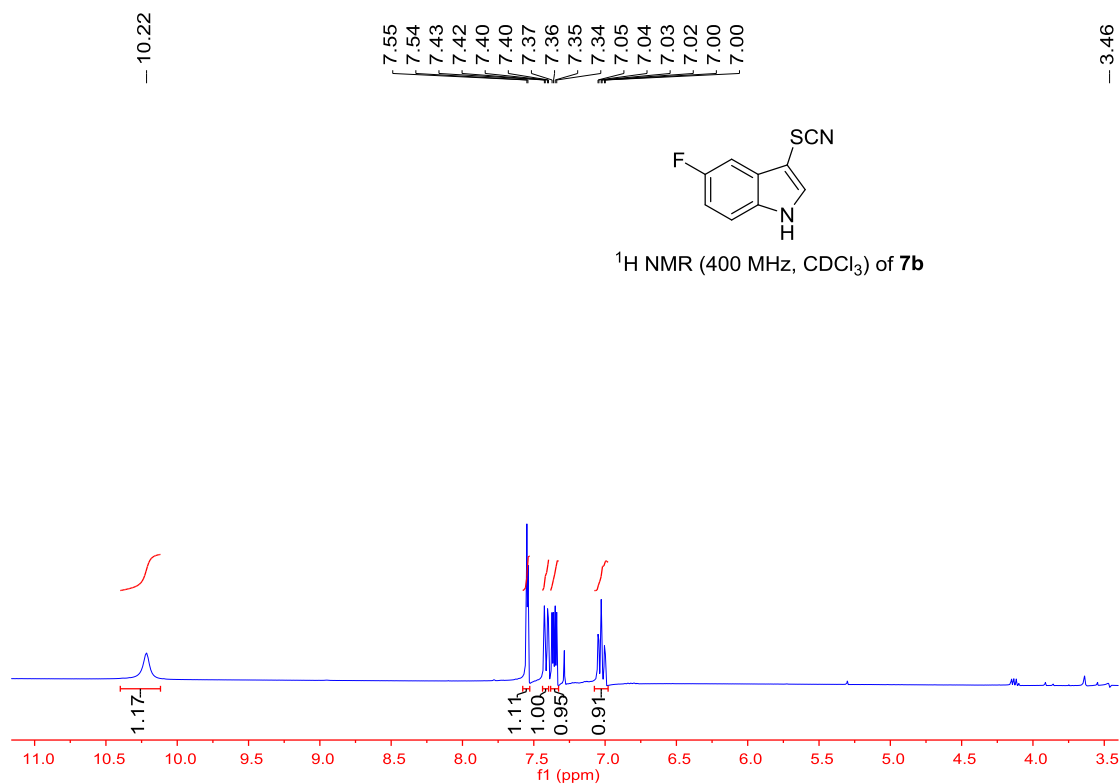
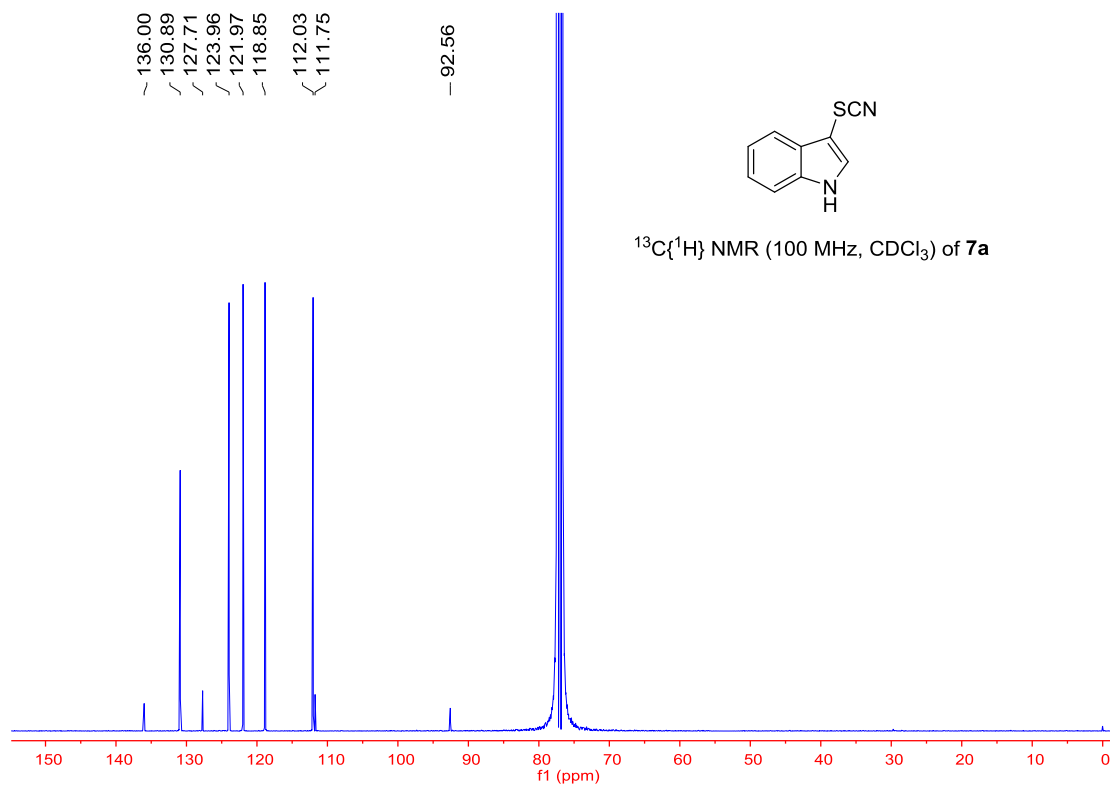


6.37

3.86
3.84



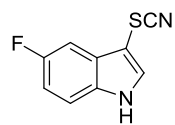




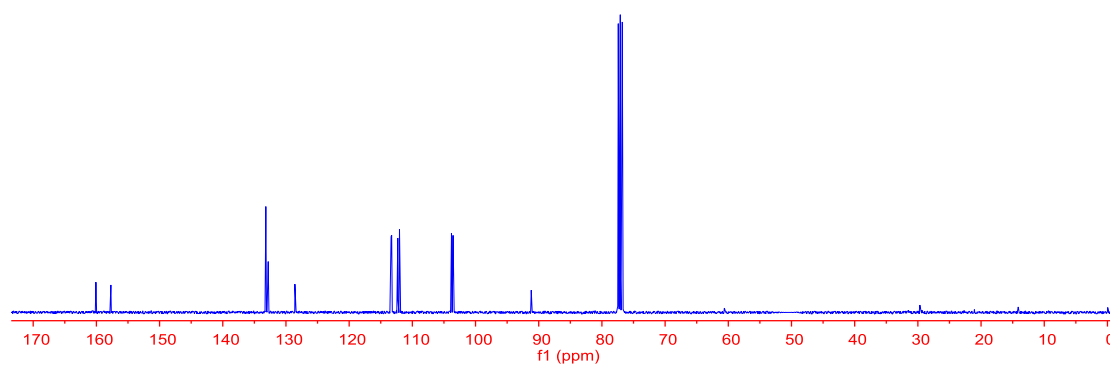
160.07
157.71

133.19
132.81
128.59
128.48
113.37
113.27
112.30
112.04
103.81
103.56

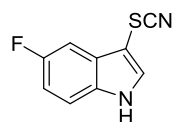
91.18
91.14



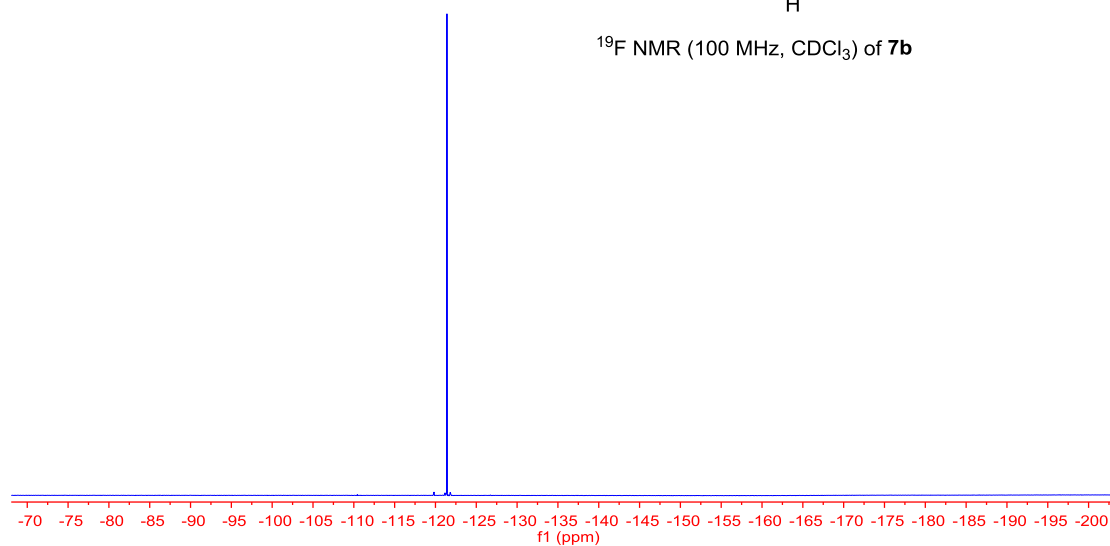
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **7b**



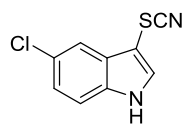
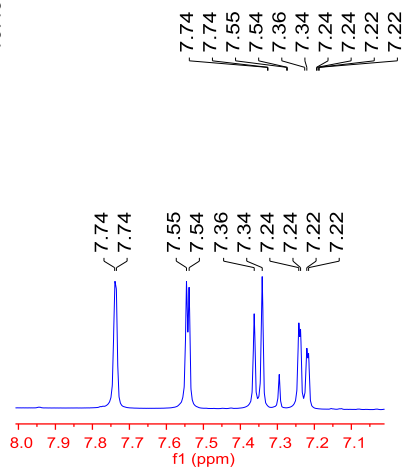
-121.41



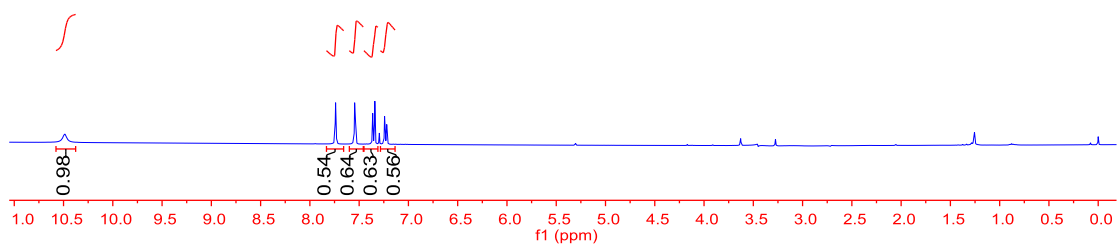
^{19}F NMR (100 MHz, CDCl_3) of **7b**



- 10.49

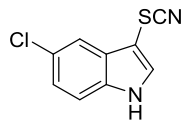


^1H NMR (400 MHz, CDCl_3) of **7c**

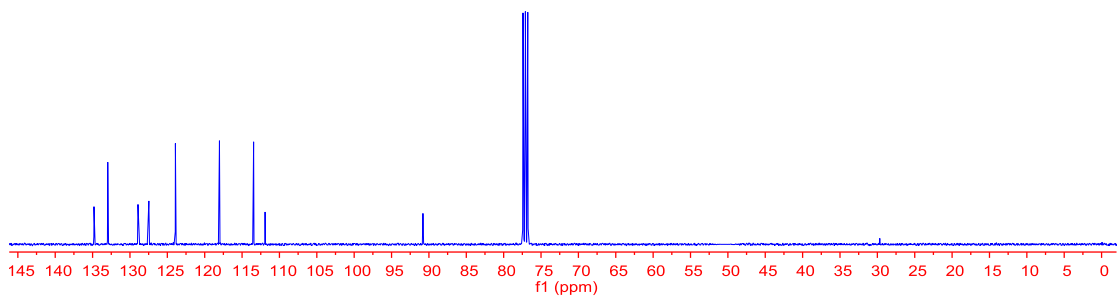


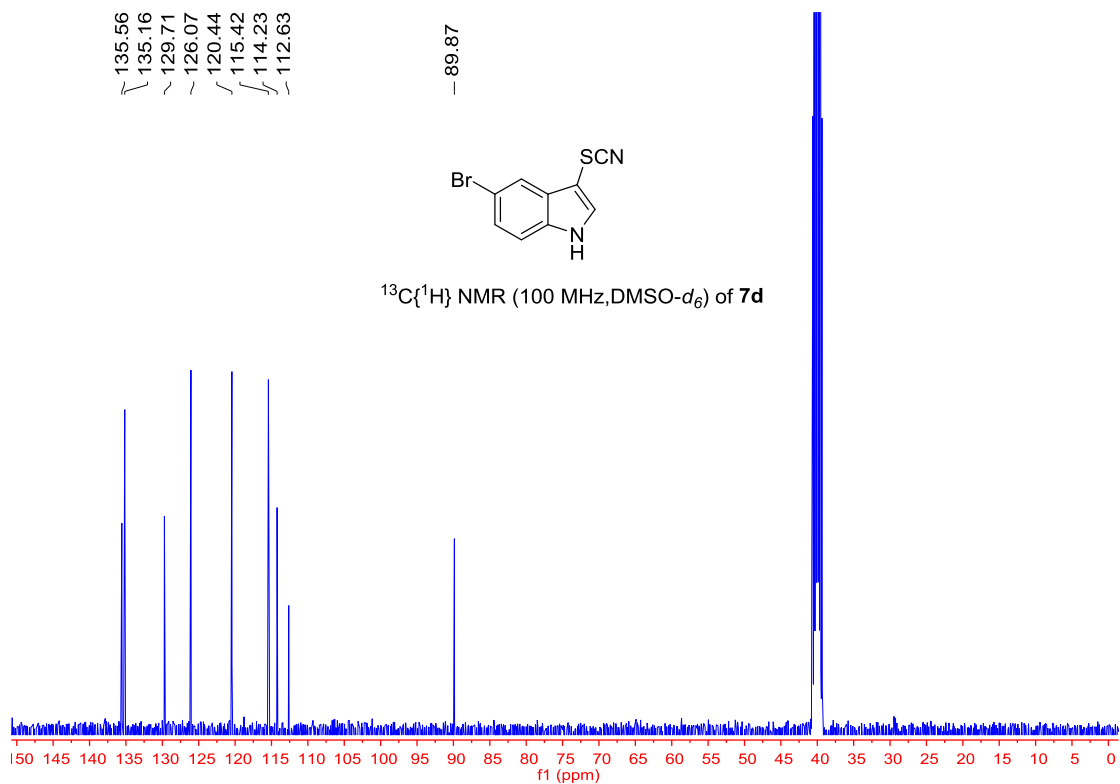
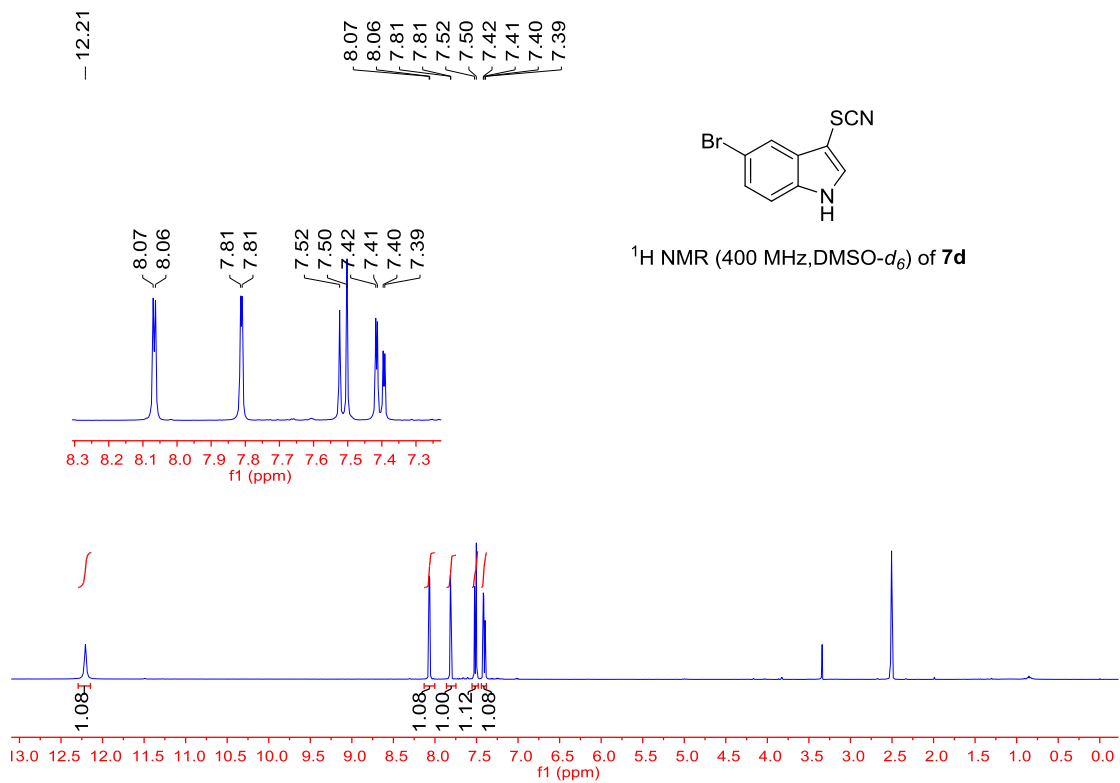
134.81
132.97
128.93
127.47
123.92
118.03
113.46
111.92

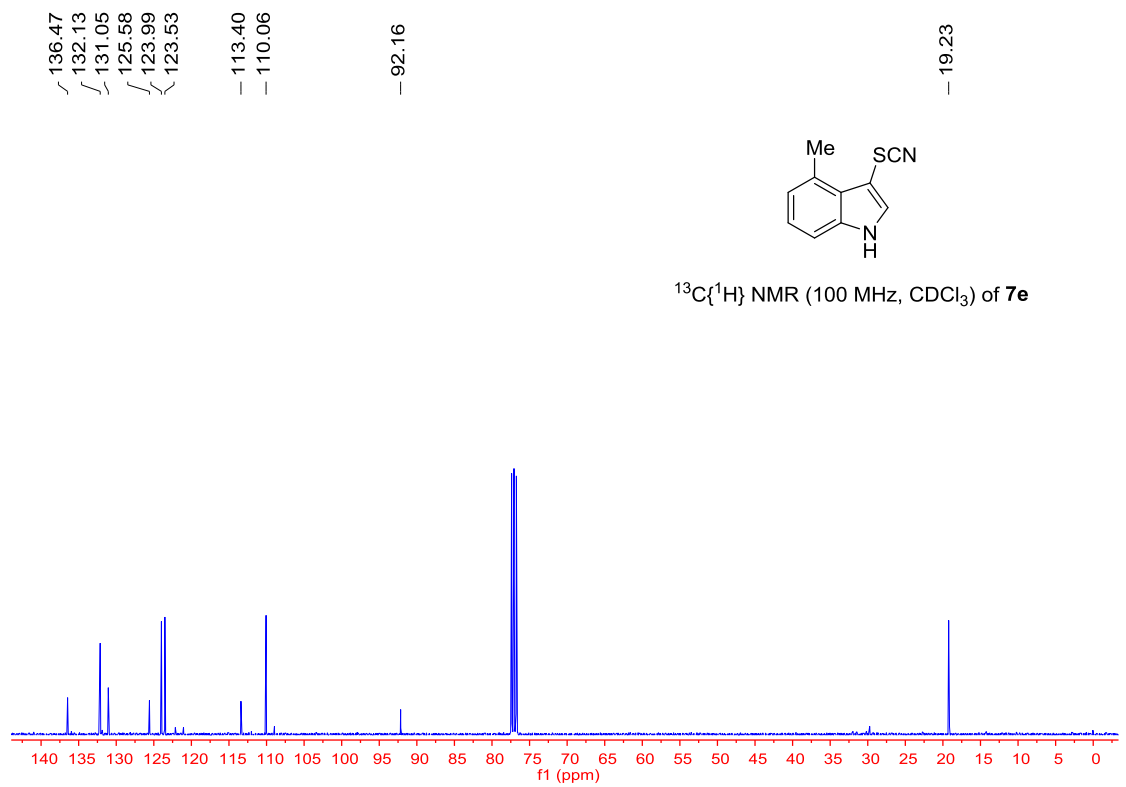
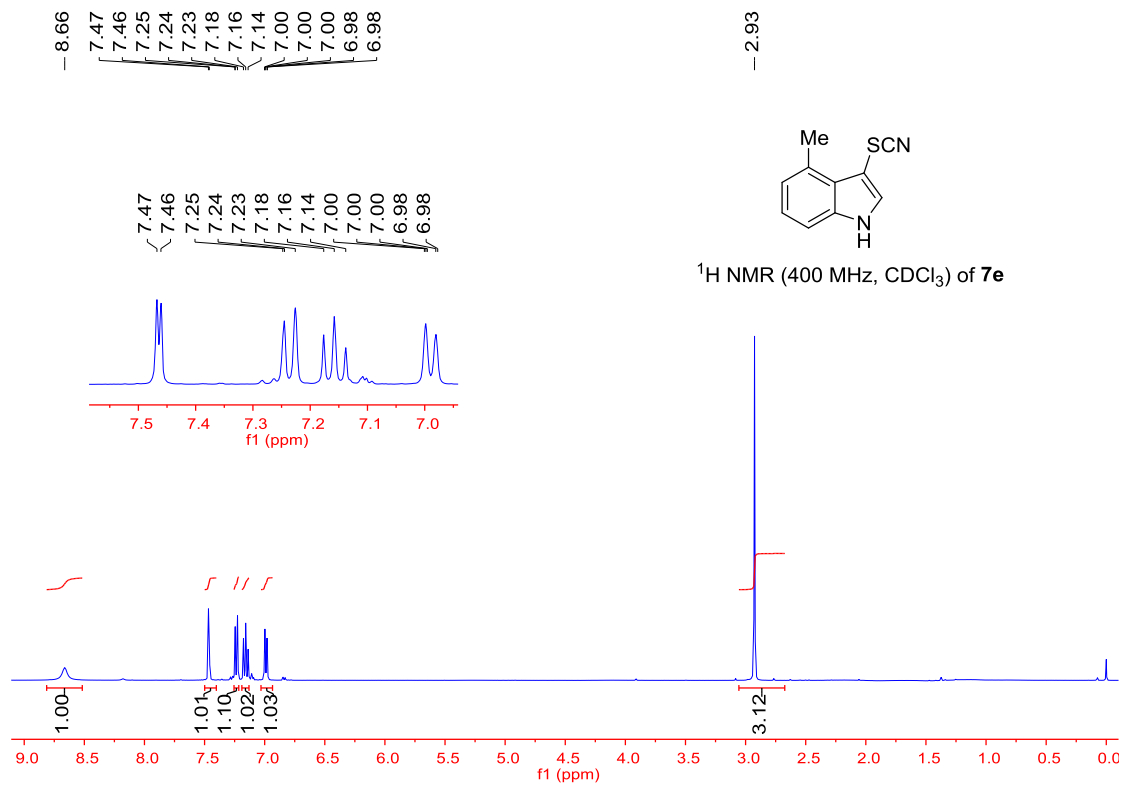
- 90.80

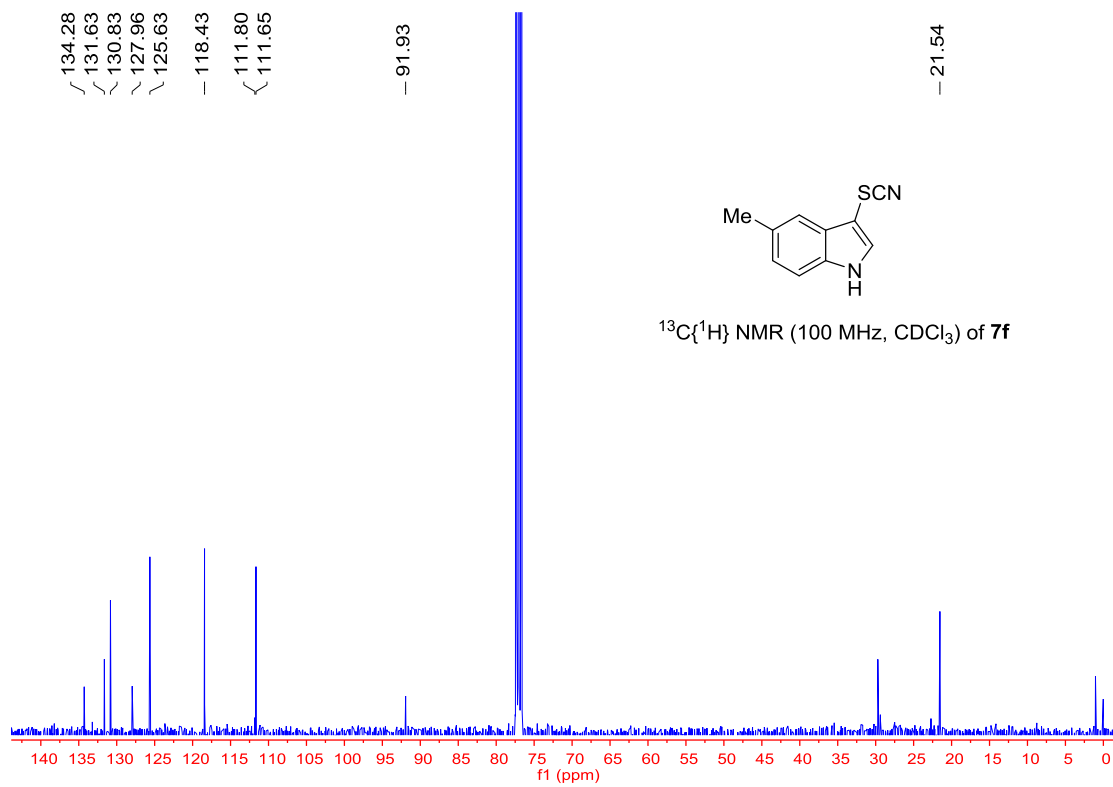
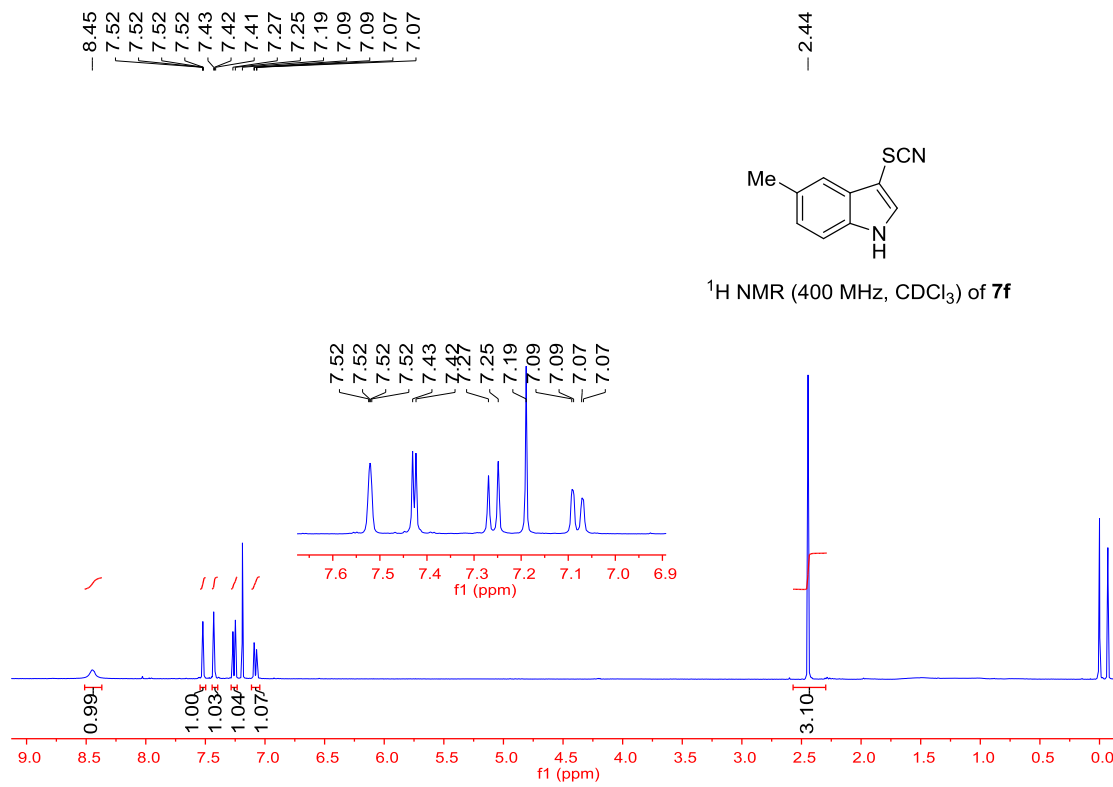


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **7c**

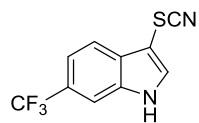




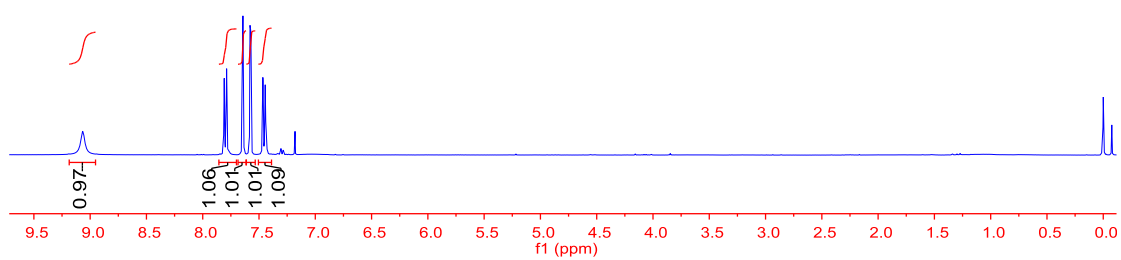




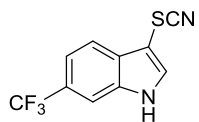
9.07
7.81
7.79
7.64
7.58
7.57
7.47
7.46
7.45
7.44
7.43



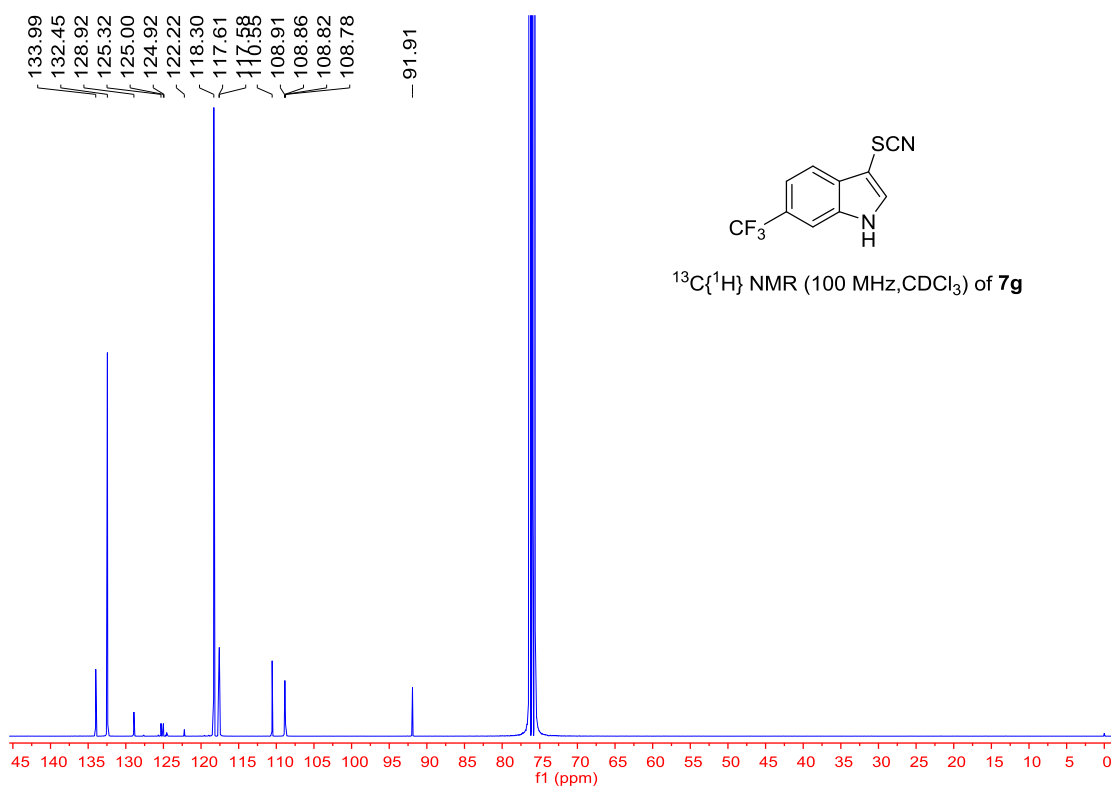
^1H NMR (400 MHz, CDCl_3) of **7g**

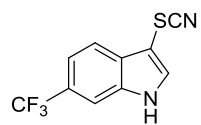


133.99
132.45
128.92
125.32
125.00
124.92
122.22
118.30
117.61
116.58
116.55
108.91
108.86
108.82
108.78
- 91.91

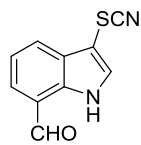
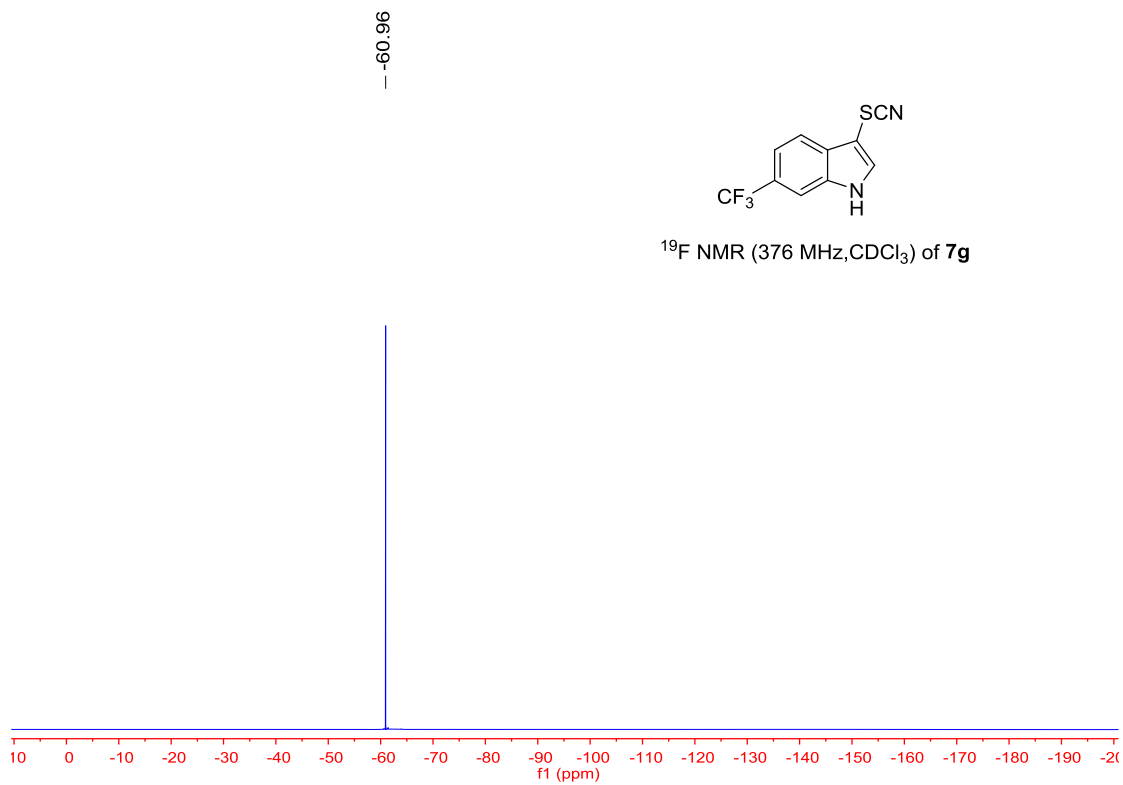


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of **7g**





¹⁹F NMR (376 MHz, CDCl₃) of **7g**



¹H NMR (400 MHz, DMSO-*d*₆) of **7h**

