Silver-Catalyzed Direct Selanylation of Indoles: Synthesis and Mechanistic Insights

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SUPPORTING INFORMATION

Table of contents

1. General information

Commercially available reagents were used without additional purification, unless otherwise stated. The reaction solvents dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), 1,4-dioxane, isopropanol, THF, toluene, and DCE were dried, purified and degassed by classical methods.[1] The solvents employed in liquid-liquid extraction and as eluents for chromatographic purification were distilled before use. The reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 F_{254} aluminum sheets, and the visualization of the spots was done using UV light (254 nm) or staining with iodine. ^{1}H NMR and ^{13}C{^{1}H} NMR were recorded on a 400 MHz Bruker Nuclear Ascend 400 spectrometer and the chemical shifts (δ) were reported in parts per million (ppm) relative to TMS as an internal standard in $CDCl_3$. Coupling constants (*J*) are reported in hertz. Abbreviations to denote the multiplicity of a particular signal on the NMR spectra are described as s (singlet), d (doublet), t (triplet), m (multiplet, complex pattern), and br s (broad signal). Low-resolution mass spectra were obtained with a Shimadzu GC-MS-QP2010 Plus mass spectrometer. Hydrogen coupling patterns are described as s (singlet), d (doublet), t (triplet), td (triplet of doublets), quartet (q), quintet (quint), sextet (st), m (multiplet) and br s (broad signal) as soon as they appear. Low-resolution mass spectra were obtained with a Shimadzu GC-MS-QP2010 Plus mass spectrometer. High-resolution mass spectra were recorded on a Bruker MicroToF-QII Mass Spectrometer (QTOF-MS) by direct infusion into the electrospray (ESI) source, using positive ion mode.

2. Computational Details

Calculations were performed using M06-2X functional[2] combined with the LANL2DZ basis set for the Ag atom and 6-311++G(d,p) for other atoms. DMSO solvation was implicitly modelled by a solvation model based on density (SMD). TSSs were identified by the presence of a single imaginary frequency whereas only real frequencies were observed for minima. IRC calculations[3] were carried out to confirm reaction pathways. Relative energy barriers were calculated using Gibbs free energies computed at 373.15 K, considering infinitely separated reactants. All calculations were performed in Gaussian16 software.[4] CYLview software[5] was used to generate images of molecular structures.

3. General procedure for preparation of 3a–m

An oven-dried glass tube was charged with indole **1** (0.5 mmol), diorganoyl dichalcogenide **2** (0.25 mmol), Ag_2SO_4 (20 mol%, 0,031 g), and dry DMSO (1 mL). The reaction was stirred for 18 h at 100 °C. After this time, the system was cooled to room temperature, and ethyl acetate (2 mL) was added to the glass tube. Then, the crude reaction mixture was filtered through a silica gel pad under vacuum, and the silica gel was further washed with ethyl acetate (150 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced

pressure. The crude product was purified by column chromatography (hexane/ethyl acetate) on silica gel to afford product **3**.

1-methyl-3-(phenylselanyl)-1*H*-indole (3a):[6,7] Yield: 0.122 g (85 %); white solid, mp 68–70 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.62 (d, *J* = 7.6 Hz, 1H); 7.37 (d, *J* = 7.6 Hz, 1H); 7.32 (s, 1H); 7.28 (td, *J* = 7.6 and 0.8 Hz, 1H); 7.21-7.24 (m, 2H); 7.16 (td, *J* = 7.4 and 1.2 Hz, 1H); 7.05-7.13 (m, 3H); 3.83 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 137.5, 135.6, 134.2, 130.7, 128.9, 128.6, 125.5, 122.4, 120.5, 120.4, 109.5, 95.9, 33.0. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 287 (14), 207 (100), 192 (5), 178 (2), 165 (11), 144 (4), 130 (16), 102 (7), 89 (10), 77 (10).

1-methyl-3-(p-tolylselanyl)-1*H*-indole (3b):[8] Yield: 0.120 g (80 %); white solid, mp 119–122 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.63 (d, *J* = 8.0 Hz, 1H); 7.35 (d, *J* = 8.0 Hz, 1H); 7.25-7.31 (m, 2H), 7.12-7.18 (m, 3H); 6.93 (d, *J* = 8.0 Hz, 2H); 3.81 (s, 3H); 2.22 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 137.4, 135.4, 130.7, 130.2, 129.7, 129.0, 122.3, 120.5, 120.3, 109.5, 96.5, 33.0, 20.9. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 301 (16), 221 (100), 178 (4), 165 (3), 151 (3), 130 (11), 111 (5), 102 (5), 91 (4), 89 (7), 77 (5).

3-((4-methoxyphenyl)selanyl)-1-methyl-1*H*-indole (3c):[9] Yield: 0.139 g (88 %); white solid, mp 55–57 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.65 (d, *J* = 8.0 Hz, 1H); 7.34 (d, *J* = 8.4 Hz, 1H); 7.22-7.30 (m, 4H); 7.16 (td, *J* = 7.4 and 0.8 Hz, 1H); 6.70 (d, *J* = 8.8 Hz, 2H); 3.81 (s, 3H); 3.71 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 158.3, 137.4, 135.0, 131.1, 130.6, 123.8, 122.3, 120.4, 120.3, 114.7, 109.4, 97.3, 55.2, 33.0. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 317 (19), 237 (100), 222 (74), 194 (8), 152 (4), 130 (11), 119 (16), 108 (8), 89 (6), 77 (7).

1-methyl-3-((3-(trifluoromethyl)phenyl)selanyl)-1*H*-indole (3d): Yield: 0.110 g (62 %, 18h); 0.106 g (60 %, 24h); ~~white solid~~yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.58 (d, *J* = 7.6 Hz, 1H); 7.54 (s, 1H); 7.40 (d, *J* = 8.4 Hz, 1H); 7.35 (s, 1H); 7.29-7.33 (m, 3H); 7.16-7.20 (m, 2H); 3.87 (s, 3H).^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 137.5, 135.8, 135.6, 131.7, 131.1 (q, *J* = 32.0 Hz); 130.4, 129.1, 125.0 (q, *J* = 3.8 Hz); 123.8 (q, *J* = 270.9 Hz); 122.7, 122.3 (q, *J* = 3.7 Hz);120.7, 120.2, 109.7, 95.0, 33.1. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 355 (15), 275 (100), 260 (3), 233 (3), 210 (8), 165 (8), 130 (28), 117 (4), 102 (9), 95 (8), 89 (15), 77 (13). HRMS (ESI) *m/z* [M+H]$^+$ calcd for $C_{16}H_{13}F_3NSe$, 356.0165, found, 356.0098.

3-((4-chlorophenyl)selanyl)-1-methyl-1*H*-indole (3e):[10] 0.109 g (68 %, 18h); 0.104 g (65 %, 24h); white solid, mp 119–122 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.58 (d, *J* = 7.6 Hz, 1H); 7.38 (d, *J* = 8.4 Hz, 1H); 7.33 (s, 1H); 7.30 (td, *J* = 7.6 and 0.8 Hz, 1H); 7.18 (td, *J* = 7.6 and 0.8 Hz, 1H); 7.14 (d, *J* = 8.4 Hz, 2H); 7.07 (d, *J* = 8.4 Hz, 2H); 3.85 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 137.5, 135.6, 132.5, 131.5, 130.5, 129.9, 129.0, 122.6, 120.6, 120.3, 109.6, 95.7, 33.1. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 321 (17), 241 (100), 226 (5), 190 (3), 165 (6), 143 (4), 130 (16), 121 (6), 102 (9), 89 (8), 77 (6).

3-(mesitylselanyl)-1-methyl-1*H*-indole (3f): Yield: 0.107 g (65 %); white solid, mp 118–121 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.56 (d, *J* = 8.0 Hz, 1H); 7.26 (d, *J* = 8.0 Hz, 1H); 7.20 (td, *J* = 7.4 and 0.8 Hz, 1H); 7.10 (td, *J* = 7.6 and 0.8 Hz, 1H); 7.02 (s, 1H); 6.86 (s, 2H); 3.72 (s, 3H); 2.57 (s, 6H); 2.22 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 142.5, 137.8, 137.1, 132.7, 130.2, 129.1, 128.6, 121.9, 120.4, 119.7, 109.2, 98.9, 32.9, 24.5, 20.9. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 329 (28), 248 (18), 233 (4), 218 (3), 210 (4), 198 (17), 144 (3), 131 (100), 117 (6), 103 (4), 91 (6), 89 (5), 77 (7). HRMS (ESI) *m/z* [M+H]$^+$ calcd for $C_{18}H_{20}NSe$, 330.0761, found, 330.0778.

1-methyl-3-(naphthalen-1-ylselanyl)-1*H*-indole (3g):[10]Yield: 0,104 g (62 %); white solid, mp 118–120 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.30 (d, *J* = 8.0 Hz, 1H); 7.81 (d, *J* = 8.0 Hz, 1H); 7.55–7.62 (m, 3H); 7.50 (td, *J* = 7.2 and 1.2 Hz, 1H); 7.38 (d, *J* = 8.0 Hz, 1H); 7.36 (s, 1H); 7.29 (td, *J* = 7.6 and 1.2 Hz, 1H); 7.09–7.17 (m, 3H); 3.85 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 137.6, 135.9, 133.8, 132.9, 132.3, 130.7, 128.5, 126.7, 126.1, 126.1, 126.0, 125.6, 122.5, 120.5, 120.5, 109.6, 95.1, 33.1. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 337 (19), 257 (100), 241 (17), 215 (6), 169 (4), 128 (16), 121 (8), 115 (4), 102 (3), 89 (6), 77 (6).

3-(butylselanyl)-1-methyl-1*H*-indole (3h): Yield: 0.051 g (38 %); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.72 (d, *J* = 8.0 Hz, 1H); 7.32 (d, *J* = 8.0 Hz, 1H); 7.26 (td, *J* = 7.6 and 1.2 Hz, 1H); 7.20 (dd, *J* = 7.4 and 1.2 Hz, 1H); 7.17 (s, 1H); 3.78 (s, 3H); 2.66 (t, *J* = 7.6 Hz, 2H); 1.59 (quint, *J* = 7.6 Hz, 2H); 1.38 (sext, *J* = 7.6 Hz, 2H); 0.86 (t, *J* = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 137.3, 134.6, 131.0, 122.1, 120.4, 119.9, 109.3, 96.9, 32.9, 32.7, 28.8, 22.7, 13.6. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 267 (27), 210 (35), 144 (5), 131 (100), 102 (5), 89 (10), 77 (7). HRMS (ESI) *m/z* [M+H]$^+$ calcd for $C_{13}H_{18}NSe$, 268.0604, found, 268.0612.

1-benzyl-3-(phenylselanyl)-1*H*-indole (3i):[10] Yield: 0.130 g (72 %, 18h); 0.167 g (92 %, 24 h); white solid, mp 78–80 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.64 (d, *J* = 7.8 Hz, 1H); 7.39 (s, 1H); 7.27-7.34 (m, 4H); 7.21-7.25 (m, 3H); 7.06-7.18 (m, 6H); 5.35 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 137.1, 136.7, 135.0, 134.1, 130.9, 128.9, 128.9, 128.5, 127.9, 127.0, 125.5, 122.6, 120.6, 120.6, 110.1, 96.9, 50.4. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 363 (24), 283 (87), 272 (6), 192 (35), 165 (16), 91 (100), 77 (7), 65 (16).

3-(phenylselanyl)-1*H*-indole (3j):[6] Yield: 0.098 g (72 %, 18 h); 0,112 g (82 %, 24 h); white solid, mp 133–135 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.38 (br s, 1H); 7.63 (d, *J* = 8.0 Hz, 1H); 7.46 (d, *J* = 2.4 Hz, 1H); 7.42 (d, *J* = 8.0 Hz, 1H); 7.21–7.28 (m, 3H); 7.17 (td, *J* = 7.6 and 0.8 Hz, 1H); 7.06–7.14 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 136.4, 133.8, 131.2, 130.0, 128.9, 128.7, 125.6, 122.9, 120.9, 120.4, 111.3, 98.2. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 273 (21), 193 (100), 165 (12), 116 (6), 104 (6), 89 (14), 77 (8).

1,2-dimethyl-3-(phenylselanyl)-1*H*-indole (3k):[11] Yield: 0.087 g (58 %, 18 h); 0.126 g (84 %, 24 h); colorless crystal, mp 118–121 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.58 (d, *J* = 8.0 Hz, 1H); 7.31 (d, *J* = 8.0 Hz, 1H); 7.22 (td, *J* = 7.6 and 1.2 Hz, 1H); 7.03–7.16 (m, 6H); 3.75 (s, 3H); 2.55 (s, 3H).^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 142.5, 137.3, 134.3, 130.6, 128.9, 128.2, 125.2, 121.6, 120.3, 119.8, 108.9, 95.1, 30.4, 12.0. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 301 (15), 221 (100), 204 (4), 144 (58), 128 (7), 115 (18), 110 (4), 102 (7), 91 (6), 77 (13).

1,3-dimethyl-2-(phenylselanyl)-1*H*-indole (3l): Yield: 0.056 g (37 %, 18 h); 0.096 g (64 %, 24 h); white solid, mp 80–82 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.63 (d, *J* = 8.0 Hz, 1H); 7.32 (d, *J* = 8.0 Hz, 1H); 7.27 (td, *J* = 7.6 and 0.8 Hz, 1H); 7.08–7.18 (m, 6H); 3.74 (s, 3H); 2.47 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 138.3, 132.6, 129.3, 128.7, 127.6, 126.1, 122.9, 119.8, 119.4, 119.0, 109.7, 31.4, 11.0. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 301 (45), 221 (100), 204 (6), 151 (3), 144 (78), 128 (11), 115 (17), 110 (5), 102 (10), 91 (6), 77 (17). HRMS (ESI) *m/z* [M+H]$^+$ calcd for $C_{16}H_{16}NSe$, 302.0448, found, 302.0466.

1-methyl-3-(phenylthio)-1*H*-indole (3m):[12] Yield: 0.042 g (35 %); yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.61 (d, *J* = 8.0 Hz, 1H); 7.38 (d, *J* = 8.0 Hz, 1H); 7.32 (s, 1H); 7.29 (td, *J* = 7.6 and 1.2 Hz, 1H); 7.08-7.18 (m, 5H); 7.03 (t, *J* = 7.2 Hz, 1H); 3.83 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 139.7, 137.5, 135.0, 129.8, 128.6, 125.7, 124.6, 122.5, 120.5, 119.7, 109.7, 100.5, 33.1. MS (EI) (Rel. Int.) *m*/*z*: [M$^+$] 239 (100), 224 (18), 207 (16), 162 (11), 128 (5), 120 (12), 112 (5), 89 (3), 77 (15).

4. General procedures of control experiments (Scheme 1)

4.1 General procedure of Scheme 1a

An oven-dried glass tube was charged with indole **1a** (0.5 mmol, 0.146 g), diphenyl diselenide (**2a**) (0.25 mmol, 0.078 g), Ag_2SO_4 (20 mol%, 0,031 g), the selected radical scavenger (0.5 mmol) and dry DMSO (1 mL). The reaction was stirred for 18 h at 100°C. After this time, the system was cooled to room temperature, and ethyl acetate (2 mL) was added to the glass tube. Then, the crude reaction mixture was filtered through a silica gel pad under vacuum, and the silica gel was further washed with ethyl acetate (150 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/ethyl acetate) on silica gel to afford the product **3a**. BHT (yield: 83 %, 0.119 g). TEMPO (yield: 44%, 0.063 g). TEMPO and 0.5 mmol of **2a** (yield: 70%, 0.100 g).

4.2 General procedure of Scheme 1b

An oven-dried glass tube was charged with indole **1a** (0.5 mmol, 0.146 g), diphenyl diselenide (**2a**) (0.25 mmol, 0.078 g), Ag_2SO_4 (20 mol%, 0,031 g), KBr (0.5 mmol, 0.060 g) and dry DMSO (1 mL). The reaction was stirred for 18 h at 100°C. After this time, the system was cooled to

room temperature, and ethyl acetate (2 mL) was added to the glass tube. Then, the crude reaction mixture was filtered through a silica gel pad under vacuum, and the silica gel was further washed with ethyl acetate (150 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/ethyl acetate) on silica gel to afford the product **3a**. Yield: 11%, 0.015 g.

4.3 General procedure of Scheme 1c

An oven-dried glass tube was charged with indole **1a** (0.5 mmol, 0.146 g), diphenyl diselenide (**2a**) (0.25 mmol, 0.078 g), Ag_2SO_4 (20 mol%, 0,031 g) and dry DMSO (1 mL) under inert atmosphere. The reaction was stirred for 18 h at 100°C. After this time, the system was cooled to room temperature, and ethyl acetate (2 mL) was added to the glass tube. Then, the crude reaction mixture was filtered through a silica gel pad under vacuum, and the silica gel was further washed with ethyl acetate (150 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/ethyl acetate) on silica gel to afford the product **3a**. Yield: 35%, 0.050 g.

4.4 General procedure of Scheme 1d

An oven-dried glass tube was charged with indole **1a** (0.5 mmol, 0.146 g), diphenyl diselenide (**2a**) (0.25 mmol, 0.078 g), Ag_2SO_4 (20 mol%, 0,031 g) and dry DMF (1 mL) using specific atmosphere conditions. The reaction was stirred for 18 h at 100°C. After this time, the system was cooled to room temperature, and ethyl acetate (2 mL) was added to the glass tube. Then, the crude reaction mixture was filtered through a silica gel pad under vacuum, and the silica gel was further washed with ethyl acetate (150 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/ethyl acetate) on silica gel to afford the product **3a**. O_2 atmosphere (yield: 45%, 0.064 g). Air atmosphere (yield: 37%, 0.053 g). Inert atmosphere (argon) and 10 equivalents of DMSO (5 mmol, 0.391 g) (yield: 28%, 0.040 g).

5. Computational Data

5.1 Electrophilic aromatic substitution using Ag(I)-phenylselenolate as a base in the second step

Considering the mechanistic proposal (ii), we have also investigated whether Ag(I)-phenylselenolate could promote the deprotonation of INT(ii). As presented in Figure S1, a 30.9 kcal mol^{-1} barrier was observed for such event (TSS_2(ii-b))— turning the second step as the rate determining — confirming that sulfate ion acting as a base should be expected.

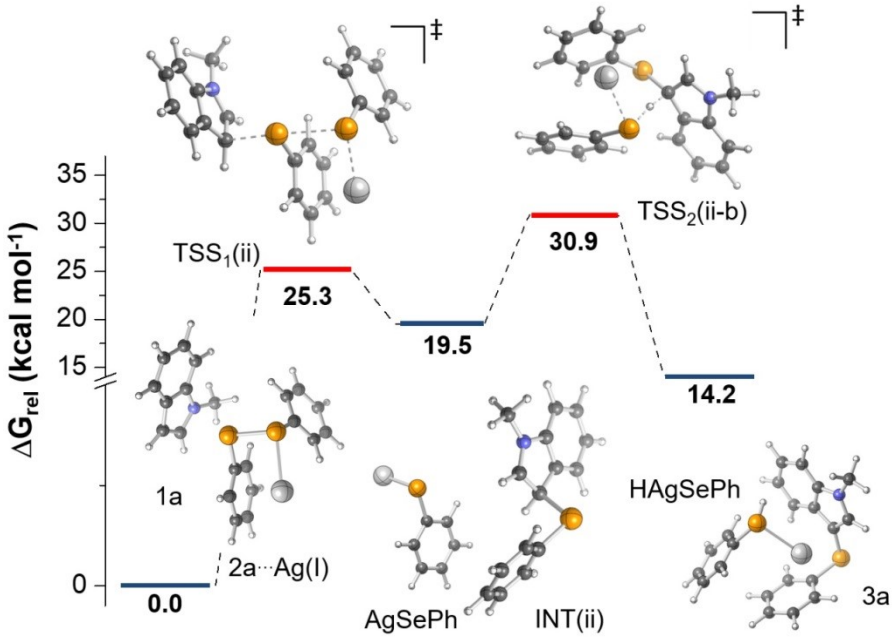

Figure S1: Potential energy surface (PES) of the electrophilic substitution mechanism (ii) proposed for the formation of **3a** considering Ag(I)-phenylselenolate as base obtained using M06-2X functional combined with LANL2DZ (for Ag atom) and 6-311++G(d,p) (for additional atoms).

5.2 Energy and Cartesian coordinates

5.2.1 Energy and coordinates of 1a

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found
Sum of electronic and thermal Free Energies = -402.954395 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.726787	1.888884	-0.000011
2	6	0	0.388184	0.985634	-0.000016
3	6	0	-1.856460	1.113547	0.000027
4	6	0	-0.153669	-0.325776	0.000007
5	6	0	1.784660	1.141473	-0.000014
6	7	0	-1.521571	-0.218021	0.000055
7	1	0	-2.897803	1.401742	-0.000010
8	6	0	0.652091	-1.470448	0.000017
9	6	0	2.585407	0.012274	-0.000006
10	1	0	2.226201	2.132405	-0.000038
11	6	0	2.023936	-1.281715	0.000008
12	1	0	0.218685	-2.464417	-0.000005
13	1	0	3.664247	0.119487	-0.000006
14	1	0	2.680012	-2.144798	0.000013
15	6	0	-2.445269	-1.336520	-0.000042
16	1	0	-2.298031	-1.951119	-0.890452
17	1	0	-2.297258	-1.951850	0.889729
18	1	0	-3.461910	-0.947174	0.000565

19	1	0	-0.695709	2.967748	-0.000001

5.2.2 Energy and coordinates of 2a···Ag

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found
Sum of electronic and thermal Free Energies = -5411.790661 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.217999	0.764916	0.340942
2	6	0	-3.286010	-0.259674	0.220117
3	6	0	-2.052624	0.000643	-0.378252
4	6	0	-1.751569	1.273429	-0.861152
5	6	0	-2.694287	2.292142	-0.740775
6	6	0	-3.923217	2.039635	-0.139342
7	1	0	-5.176655	0.565444	0.805777
8	1	0	-3.511618	-1.253229	0.590233
9	1	0	-0.792183	1.474346	-1.327497
10	1	0	-2.463224	3.282227	-1.116496
11	1	0	-4.654105	2.834710	-0.046942
12	34	0	-0.781530	-1.439165	-0.533575
13	34	0	0.126613	-1.394932	1.650130
14	6	0	1.174457	0.204406	1.413963
15	6	0	2.476736	0.115018	0.902025
16	6	0	0.601338	1.446429	1.677128
17	6	0	3.181261	1.283973	0.614655
18	1	0	2.933675	-0.856687	0.741662
19	6	0	1.321156	2.608548	1.399498
20	1	0	-0.404001	1.506127	2.078227
21	6	0	2.599363	2.529264	0.858708
22	1	0	4.188229	1.219413	0.218627
23	1	0	0.872377	3.575289	1.597396
24	1	0	3.150425	3.435138	0.634459
25	47	0	1.437290	-0.110975	-1.574115

5.2.3 Energy and coordinates of INT(ii)

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found
Sum of electronic and thermal Free Energies = -3035.869986 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.268642	-1.762429	0.854178
2	6	0	-3.626453	-2.047458	0.706196
3	6	0	-4.528646	-1.079556	0.259356
4	6	0	-4.107567	0.211994	-0.053964
5	6	0	-2.758902	0.465704	0.107285
6	6	0	-1.840995	-0.480623	0.552134
7	6	0	-0.490516	0.168172	0.579417
8	6	0	-0.805324	1.555124	0.154048
9	7	0	-2.058163	1.688314	-0.125997

10	1	0	-1.569878	-2.518548	1.192070
11	1	0	-3.988896	-3.041515	0.939356
12	1	0	-5.576011	-1.334661	0.152697
13	1	0	-4.798223	0.970459	-0.401601
14	1	0	-0.108751	2.377349	0.044365
15	34	0	0.675400	-0.649143	-0.803393
16	6	0	2.418310	-0.176754	-0.134343
17	6	0	3.471085	-0.983899	-0.571107
18	6	0	2.667613	0.909099	0.702713
19	6	0	4.771776	-0.699209	-0.170570
20	1	0	3.274708	-1.834353	-1.215362
21	6	0	3.973366	1.173737	1.111274
22	1	0	1.869351	1.556664	1.044229
23	6	0	5.027071	0.377252	0.675440
24	1	0	5.584394	-1.329088	-0.514172
25	1	0	4.161704	2.015169	1.768302
26	1	0	6.040546	0.592465	0.992916
27	1	0	0.043719	0.115648	1.529801
28	6	0	-2.714109	2.894433	-0.623902
29	1	0	-3.152926	2.671310	-1.596181
30	1	0	-3.494772	3.176367	0.081822
31	1	0	-1.969808	3.681885	-0.709817

5.2.4 Energy and coordinates of HAgSePh

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found
Sum of electronic and thermal Free Energies = -2779.265158 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	34	0	0.271951	1.359180	0.177263
2	6	0	-1.358895	0.318891	0.092307
3	47	0	2.051884	-0.630164	-0.158059
4	6	0	-1.388036	-1.006881	0.520526
5	6	0	-2.497749	0.922997	-0.431666
6	6	0	-2.574516	-1.727634	0.431887
7	1	0	-0.491219	-1.471056	0.917847
8	6	0	-3.678770	0.188932	-0.527811
9	1	0	-2.467486	1.955350	-0.759660
10	6	0	-3.718937	-1.132197	-0.094891
11	1	0	-2.601033	-2.757826	0.767786
12	1	0	-4.566193	0.656158	-0.938883
13	1	0	-4.639215	-1.699827	-0.169396
14	1	0	0.381708	1.338117	1.642029

5.2.5 Energy and coordinates of TSS_1(ii)

M06-2X/6-311++G(d,p)
Imaginary frequencies: -127.5287
Sum of electronic and thermal Free Energies = -5814.704724 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.218632	3.954709	-0.503784
2	6	0	0.959769	2.762764	-1.174369
3	6	0	1.859097	1.694060	-1.091258
4	6	0	3.028764	1.849394	-0.341269
5	6	0	3.284835	3.044538	0.325956
6	6	0	2.379576	4.100032	0.253038
7	1	0	0.508110	4.771259	-0.572806
8	1	0	0.049319	2.656399	-1.754072
9	1	0	3.737360	1.030074	-0.267924
10	1	0	4.193837	3.145617	0.908901
11	1	0	2.577894	5.027690	0.777448
12	34	0	1.425006	0.038943	-1.968907
13	34	0	-0.882500	-0.441601	-0.245871
14	6	0	0.381932	-0.633148	1.200520
15	6	0	0.854646	-1.911422	1.527367
16	6	0	0.870535	0.488265	1.864297
17	6	0	1.850597	-2.052586	2.493045
18	1	0	0.446906	-2.784287	1.027534
19	6	0	1.859183	0.336829	2.838112
20	1	0	0.499682	1.475773	1.610963
21	6	0	2.357396	-0.924164	3.142668
22	1	0	2.218862	-3.040774	2.744162
23	1	0	2.245904	1.212739	3.346775
24	1	0	3.133228	-1.035468	3.891269
25	47	0	2.805923	-1.622012	-0.384312
26	6	0	-2.578123	-0.922515	1.057818
27	6	0	-3.748350	-0.927065	0.166663
28	6	0	-2.683353	0.328991	1.757386
29	1	0	-2.221318	-1.809186	1.567058
30	6	0	-4.373043	0.318436	0.301474
31	6	0	-4.244033	-1.846572	-0.752598
32	7	0	-3.682802	1.046979	1.290814
33	1	0	-2.040979	0.711514	2.539902
34	6	0	-5.478918	0.700707	-0.444710
35	6	0	-5.361737	-1.489151	-1.499698
36	1	0	-3.771015	-2.813255	-0.881296
37	6	0	-5.967240	-0.234252	-1.350966
38	1	0	-5.940197	1.673956	-0.326406
39	1	0	-5.771431	-2.191814	-2.215798
40	1	0	-6.832696	0.013855	-1.953792
41	6	0	-4.017084	2.414559	1.666163
42	1	0	-3.878846	3.067355	0.803566
43	1	0	-5.056572	2.448902	1.991733
44	1	0	-3.360493	2.721287	2.477099

5.2.6 Energy and coordinates of TSS_2(ii-b)

M06-2X/6-311++G(d,p)
Imaginary frequencies: -1144.3216
Sum of electronic and thermal Free Energies = -5814.695820 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.192353	1.671987	0.645819
2	6	0	-4.357631	2.080592	0.011425
3	6	0	-5.123437	1.189570	-0.758333

4	6	0	-4.751824	-0.139332	-0.903612
5	6	0	-3.590845	-0.537605	-0.247787
6	6	0	-2.801231	0.339635	0.511241
7	6	0	-1.623525	-0.421038	0.933763
8	6	0	-1.911325	-1.761650	0.559408
9	7	0	-2.996971	-1.804815	-0.200383
10	1	0	-2.606788	2.362954	1.242022
11	1	0	-4.686839	3.108244	0.112002
12	1	0	-6.024600	1.545323	-1.243477
13	1	0	-5.337707	-0.833723	-1.494155
14	1	0	-1.317906	-2.650710	0.728101
15	34	0	-0.602401	0.104887	2.487867
16	6	0	1.168734	-0.412734	1.922476
17	6	0	2.148673	0.562763	1.750469
18	6	0	1.475719	-1.761977	1.725460
19	6	0	3.431798	0.194310	1.349063
20	1	0	1.908122	1.609210	1.904788
21	6	0	2.757808	-2.127344	1.302324
22	1	0	0.727685	-2.524992	1.906424
23	6	0	3.735257	-1.142960	1.105625
24	1	0	4.189049	0.957162	1.209532
25	1	0	3.002782	-3.175702	1.169373
26	1	0	4.731958	-1.428397	0.789788
27	1	0	-0.830348	-0.179455	-0.186378
28	34	0	-0.006308	0.164736	-1.771486
29	6	0	0.922349	1.742055	-1.161664
30	47	0	1.904222	-1.577220	-1.113999
31	6	0	0.226813	2.718945	-0.447505
32	6	0	2.283643	1.913570	-1.419584
33	6	0	0.895750	3.844896	0.027500
34	1	0	-0.833216	2.596744	-0.257338
35	6	0	2.944671	3.044937	-0.950352
36	1	0	2.829717	1.151650	-1.966654
37	6	0	2.256232	4.010407	-0.218512
38	1	0	0.348766	4.592589	0.591403
39	1	0	4.003926	3.165640	-1.149623
40	1	0	2.775677	4.886052	0.153360
41	6	0	-3.521515	-2.975999	-0.891952
42	1	0	-4.540440	-3.164400	-0.553215
43	1	0	-3.518260	-2.792400	-1.966551
44	1	0	-2.887671	-3.828084	-0.657353

5.2.7 Energy and coordinates of $AgSO_4^-$

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found
Sum of electronic and thermal Free Energies = -844.908258 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.329824	-1.227999	-0.001612
2	16	0	1.491834	-0.000036	0.000023
3	8	0	0.565951	0.002141	-1.212923
4	8	0	2.330214	1.227679	0.002159
5	8	0	0.565400	-0.001677	1.212166
6	47	0	-1.493627	-0.000012	0.000028

5.2.8 Energy and coordinates of INT(i)

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found
Sum of electronic and thermal Free Energies = -548.034599 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.378264	0.430594	0.000009
2	6	0	0.746903	-0.480357	0.000164
3	6	0	0.210995	1.674284	-0.000287
4	6	0	1.949667	0.281202	-0.000005
5	6	0	0.851276	-1.881309	0.000203
6	7	0	1.596997	1.601968	-0.000402
7	1	0	-0.238906	2.659094	-0.000337
8	6	0	3.219059	-0.310086	-0.000171
9	6	0	2.103576	-2.476351	0.000034
10	1	0	-0.049741	-2.489093	0.000362
11	6	0	3.277698	-1.695472	-0.000087
12	1	0	4.122095	0.291282	-0.000297
13	1	0	2.187647	-3.557522	-0.000007
14	1	0	4.243855	-2.187949	-0.000222
15	6	0	2.522785	2.715647	0.000378
16	1	0	3.157277	2.689945	0.889746
17	1	0	3.157238	2.691318	-0.889061
18	1	0	1.951350	3.642981	0.001110
19	47	0	-2.483659	-0.095803	0.000002

5.2.9 Energy and coordinates of $PhSe^-$

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found
Sum of electronic and thermal Free Energies = -2633.258131 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	34	0	-1.859897	0.000000	0.000112
2	6	0	0.063631	-0.000012	-0.000050
3	6	0	0.787750	1.201854	-0.000618
4	6	0	0.787754	-1.201857	-0.000617
5	6	0	2.180580	1.200621	-0.000082
6	1	0	0.253900	2.145843	-0.000143
7	6	0	2.180598	-1.200610	-0.000082
8	1	0	0.253931	-2.145862	-0.000145
9	6	0	2.887426	0.000003	0.000568
10	1	0	2.715350	2.144776	0.000662
11	1	0	2.715361	-2.144769	0.000662
12	1	0	3.971504	0.000017	0.000437

5.2.10 Energy and coordinates of $HAgSO_4$

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found

Sum of electronic and thermal Free Energies = -845.361231 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.784714	1.002356	0.002763
2	16	0	1.576080	-0.095878	-0.000040
3	8	0	1.717466	-0.869632	1.228951
4	8	0	1.719986	-0.865468	-1.231383
5	8	0	0.403248	0.813621	0.000517
6	47	0	-1.741567	0.007532	-0.000073
7	1	0	3.633061	0.533037	-0.002722

5.2.11 Energy and coordinates of TSS_1(i)

M06-2X/6-311++G(d,p)
Imaginary frequencies: -466.2813
Sum of electronic and thermal Free Energies = -1247.818227 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.609990	-0.437895	0.580325
2	6	0	-1.486072	0.598613	0.053284
3	6	0	-1.503844	-1.390184	1.043120
4	6	0	-2.835970	0.209990	0.254146
5	6	0	-1.230143	1.838738	-0.555245
6	7	0	-2.819710	-1.019047	0.865302
7	1	0	-1.311628	-2.339650	1.528446
8	6	0	-3.919690	1.005002	-0.135245
9	6	0	-2.297787	2.635338	-0.943493
10	1	0	-0.199746	2.153045	-0.701469
11	6	0	-3.629247	2.220927	-0.737089
12	1	0	-4.944187	0.686999	0.026714
13	1	0	-2.112040	3.594877	-1.413952
14	1	0	-4.442070	2.865889	-1.052499
15	6	0	-3.996157	-1.775173	1.244900
16	1	0	-4.603723	-1.208251	1.954119
17	1	0	-4.601242	-2.010582	0.366100
18	1	0	-3.676670	-2.704159	1.715025
19	47	0	0.927710	-1.354682	-0.910891
20	1	0	0.756367	0.003537	1.173090
21	8	0	1.698834	0.402055	1.640518
22	16	0	2.750788	0.868604	0.560930
23	8	0	2.996559	-0.324922	-0.316480
24	8	0	3.955222	1.257216	1.303131
25	8	0	2.138299	1.969637	-0.207661

5.2.12 Energy and coordinates of TSS_2(i)

M06-2X/6-311++G(d,p)
Imaginary frequencies: -172.4453
Sum of electronic and thermal Free Energies = -6514.025736 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.915126	-2.030790	-0.115350
2	6	0	1.844944	-1.690512	0.952185
3	6	0	1.758195	-2.368193	-1.179160
4	6	0	3.161806	-1.826030	0.457862
5	6	0	1.666651	-1.225674	2.259990
6	7	0	3.069454	-2.258240	-0.854481
7	1	0	1.495767	-2.650597	-2.190957
8	6	0	4.294408	-1.513383	1.209629
9	6	0	2.783106	-0.907762	3.021212
10	1	0	0.664672	-1.102149	2.661746
11	6	0	4.083011	-1.049656	2.501503
12	1	0	5.294488	-1.623524	0.804563
13	1	0	2.656905	-0.540891	4.033807
14	1	0	4.934815	-0.792484	3.120971
15	6	0	4.204018	-2.476036	-1.731996
16	1	0	4.810299	-1.568827	-1.785000
17	1	0	4.818428	-3.298540	-1.360371
18	1	0	3.833357	-2.721244	-2.726007
19	47	0	-1.191815	-2.617335	0.265860
20	34	0	-0.096816	-0.024800	-0.939922
21	34	0	-1.349485	2.255552	-1.633652
22	6	0	1.630158	0.831105	-0.840461
23	6	0	-0.937540	3.161519	0.009494
24	6	0	2.545640	0.691236	-1.882910
25	6	0	1.987564	1.523863	0.318834
26	6	0	-0.062743	4.251547	0.003648
27	6	0	-1.452154	2.700134	1.226184
28	6	0	3.821440	1.238040	-1.762053
29	1	0	2.267302	0.147241	-2.779267
30	6	0	3.263934	2.067567	0.434243
31	1	0	1.275101	1.627065	1.129973
32	6	0	0.298100	4.869110	1.199332
33	1	0	0.347591	4.607939	-0.934882
34	6	0	-1.083383	3.319158	2.417471
35	1	0	-2.124857	1.847980	1.242339
36	6	0	4.183203	1.920550	-0.602599
37	1	0	4.532779	1.125985	-2.572834
38	1	0	3.540278	2.599842	1.337967
39	6	0	-0.205496	4.402229	2.410523
40	1	0	0.981558	5.711176	1.181688
41	1	0	-1.482725	2.950657	3.356399
42	1	0	5.179223	2.338429	-0.508090
43	1	0	0.080658	4.879142	3.341077
44	1	0	-2.972379	0.402029	-1.025116
45	8	0	-3.350268	-0.498976	-1.089144
46	16	0	-3.971058	-0.971691	0.343505
47	8	0	-3.435811	-0.028448	1.326902
48	8	0	-5.418272	-0.963007	0.188016
49	8	0	-3.432262	-2.352499	0.488965

5.2.13 Energy and coordinates of AgSePh

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found
Sum of electronic and thermal Free Energies = -2778.843974 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	34	0	0.283457	1.303944	0.050739
2	6	0	-1.356647	0.295426	0.017437
3	47	0	2.097233	-0.571879	-0.034271
4	6	0	-2.569071	0.989969	-0.084466
5	6	0	-1.393183	-1.101197	0.101005
6	6	0	-3.781068	0.306170	-0.103825
7	1	0	-2.563171	2.072480	-0.150089
8	6	0	-2.608306	-1.781505	0.079952
9	1	0	-0.468351	-1.663058	0.184076
10	6	0	-3.809046	-1.083975	-0.021950
11	1	0	-4.706726	0.865834	-0.184037
12	1	0	-2.612246	-2.864253	0.144886
13	1	0	-4.753056	-1.616088	-0.038141

5.2.14 Energy and coordinates of SO_4^{2-}

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found
Sum of electronic and thermal Free Energies = -699.316483 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.210087	-0.608190	-1.360806
2	16	0	-0.000025	0.000114	0.000023
3	8	0	1.185041	0.927666	-0.042321
4	8	0	0.253771	-1.092725	1.003878
5	8	0	-1.228676	0.773022	0.399203

5.2.15 Energy and coordinates of HSO_4

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found
Sum of electronic and thermal Free Energies = -699.693059 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.912266	1.209677	0.013469
2	16	0	0.147878	-0.030407	0.000754
3	8	0	0.223840	-0.834742	1.224640
4	8	0	0.244371	-0.821291	-1.230189
5	8	0	-1.427919	0.537943	-0.008486
6	1	0	-1.986521	-0.246191	-0.007534

5.2.16 Energy and coordinates of 3a

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found
Sum of electronic and thermal Free Energies = -3035.457253 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.656686	-0.906290	-0.222884
2	6	0	-1.395483	0.290566	-0.514171
3	6	0	-1.426512	-1.648283	0.640904
4	6	0	-2.605448	0.196191	0.214163
5	6	0	-1.145381	1.430325	-1.290987
6	7	0	-2.598588	-0.996299	0.901916
7	1	0	-1.222807	-2.608239	1.093449
8	6	0	-3.577214	1.201233	0.176485
9	6	0	-2.103965	2.428693	-1.329368
10	1	0	-0.218257	1.520167	-1.848176
11	6	0	-3.307387	2.313749	-0.603631
12	1	0	-4.500835	1.113685	0.737542
13	1	0	-1.930354	3.317285	-1.925459
14	1	0	-4.035917	3.114731	-0.656403
15	6	0	-3.671542	-1.467256	1.759729
16	1	0	-3.844868	-0.756203	2.569394
17	1	0	-4.590145	-1.589665	1.182923
18	1	0	-3.381386	-2.427722	2.181908
19	34	0	1.025367	-1.405733	-0.923829
20	6	0	2.166509	-0.169149	0.024991
21	6	0	1.728900	0.566512	1.123919
22	6	0	3.481740	-0.041199	-0.425482
23	6	0	2.610848	1.432807	1.767072
24	1	0	0.709796	0.467180	1.480588
25	6	0	4.356566	0.820534	0.228211
26	1	0	3.820100	-0.609444	-1.285827
27	6	0	3.924199	1.562932	1.324963
28	1	0	2.264995	2.005671	2.620384
29	1	0	5.376914	0.915109	-0.126237
30	1	0	4.605538	2.238267	1.829198

5.2.17 Energy and coordinates of PhSeSePh

M06-2X/6-311++G(d,p)
Imaginary frequencies: none found
Sum of electronic and thermal Free Energies = -5266.218796 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	34	0	0.811534	-1.603711	0.857515
2	34	0	-0.811252	-1.603806	-0.857545
3	6	0	1.656759	0.059617	0.380761
4	6	0	-1.656768	0.059358	-0.380761
5	6	0	2.551104	0.122802	-0.688642
6	6	0	1.329297	1.210363	1.097091
7	6	0	-1.329677	1.210139	-1.097208
8	6	0	-2.550944	0.122410	0.688797
9	6	0	3.114622	1.344552	-1.040951
10	1	0	2.795739	-0.775099	-1.244822
11	6	0	1.904294	2.429568	0.742839
12	1	0	0.622493	1.155911	1.917761
13	6	0	-1.904893	2.429237	-0.742935

14	1	0	-0.622981	1.155799	-1.917979
15	6	0	-3.114693	1.344047	1.041117
16	1	0	-2.795275	-0.775525	1.245059
17	6	0	2.792766	2.497492	-0.325605
18	1	0	3.807919	1.395993	-1.872837
19	1	0	1.648409	3.324824	1.298135
20	6	0	-2.793216	2.497014	0.325639
21	1	0	-1.649308	3.324521	-1.298322
22	1	0	-3.807854	1.395390	1.873120
23	1	0	3.235069	3.447371	-0.603507
24	1	0	-3.235705	3.446806	0.603544

5.2.18 Energy and coordinates of TSS_2(ii)

M06-2X/6-311++G(d,p)
Imaginary frequencies: -387.9450
Sum of electronic and thermal Free Energies = -3735.188994 Hartrees
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.890926	-2.050807	-1.416351
2	6	0	3.234474	-2.269011	-1.716295
3	6	0	4.252944	-1.698482	-0.945753
4	6	0	3.960289	-0.900025	0.157214
5	6	0	2.618556	-0.715746	0.446860
6	6	0	1.585584	-1.262558	-0.315311
7	6	0	0.307810	-0.733510	0.234542
8	6	0	0.738651	-0.038905	1.443599
9	7	0	2.038163	0.018481	1.509130
10	1	0	1.104278	-2.486578	-2.021941
11	1	0	3.496587	-2.889667	-2.565247
12	1	0	5.288053	-1.880745	-1.209198
13	1	0	4.742172	-0.447289	0.755074
14	1	0	0.117794	0.440458	2.185146
15	34	0	-1.183013	-1.970594	0.345435
16	6	0	-2.676831	-0.781698	0.102389
17	6	0	-3.892066	-1.378519	-0.239951
18	6	0	-2.598269	0.595311	0.304040
19	6	0	-5.031557	-0.593987	-0.384895
20	1	0	-3.947378	-2.450419	-0.399643
21	6	0	-3.745468	1.370483	0.140039
22	1	0	-1.664701	1.086358	0.561049
23	6	0	-4.961877	0.784742	-0.198415
24	1	0	-5.971853	-1.062982	-0.652318
25	1	0	-3.680903	2.443543	0.285925
26	1	0	-5.848336	1.396752	-0.318616
27	1	0	0.054892	0.185879	-0.506485
28	6	0	2.809763	0.853299	2.416821
29	1	0	3.628771	0.269452	2.835796
30	1	0	3.188385	1.697198	1.837402
31	1	0	2.152139	1.203771	3.209044
32	8	0	0.081396	1.428382	-1.375613
33	16	0	0.686400	2.573285	-0.549406
34	8	0	0.364036	3.862587	-1.210041
35	8	0	2.159516	2.359757	-0.442452
36	8	0	0.064482	2.487900	0.817434

6. References

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7. NMR spectra

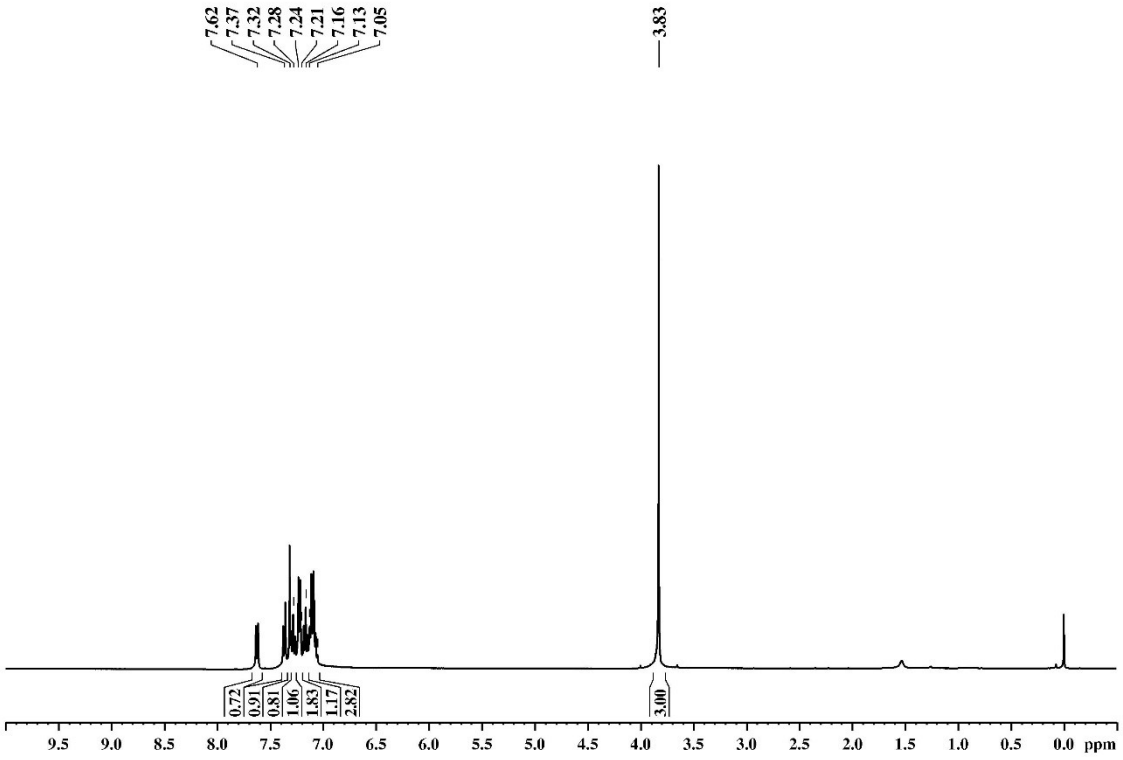

Figure S2: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**.

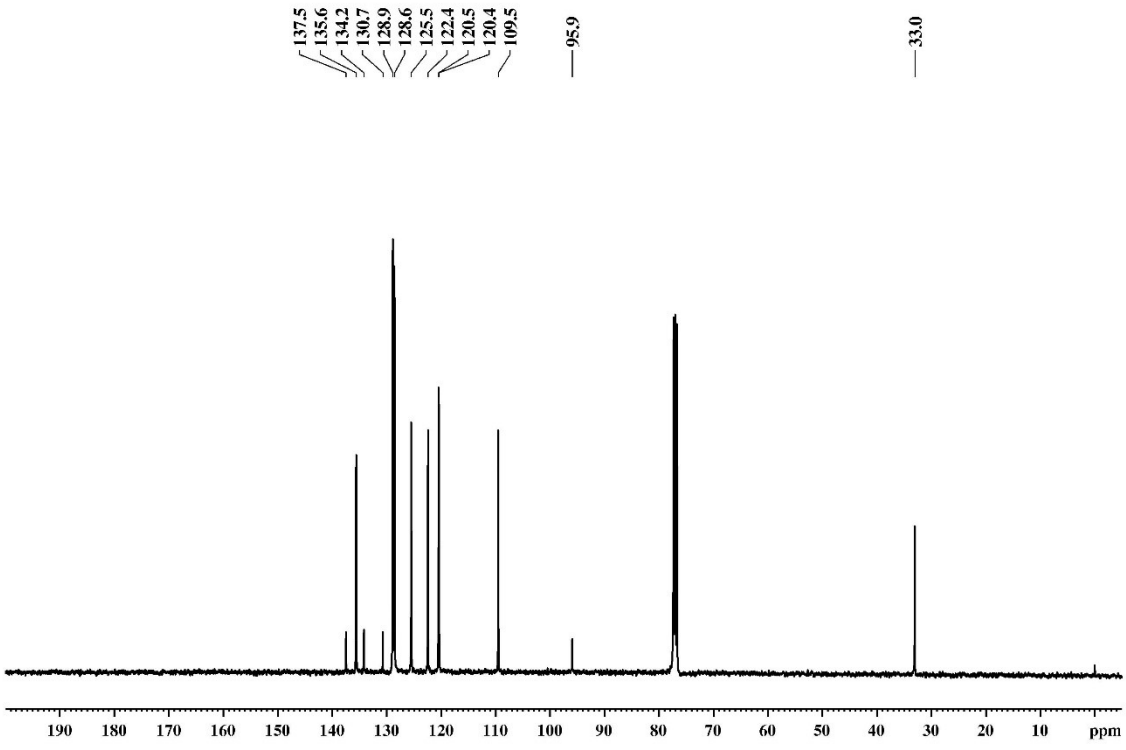

Figure S3: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3a**.

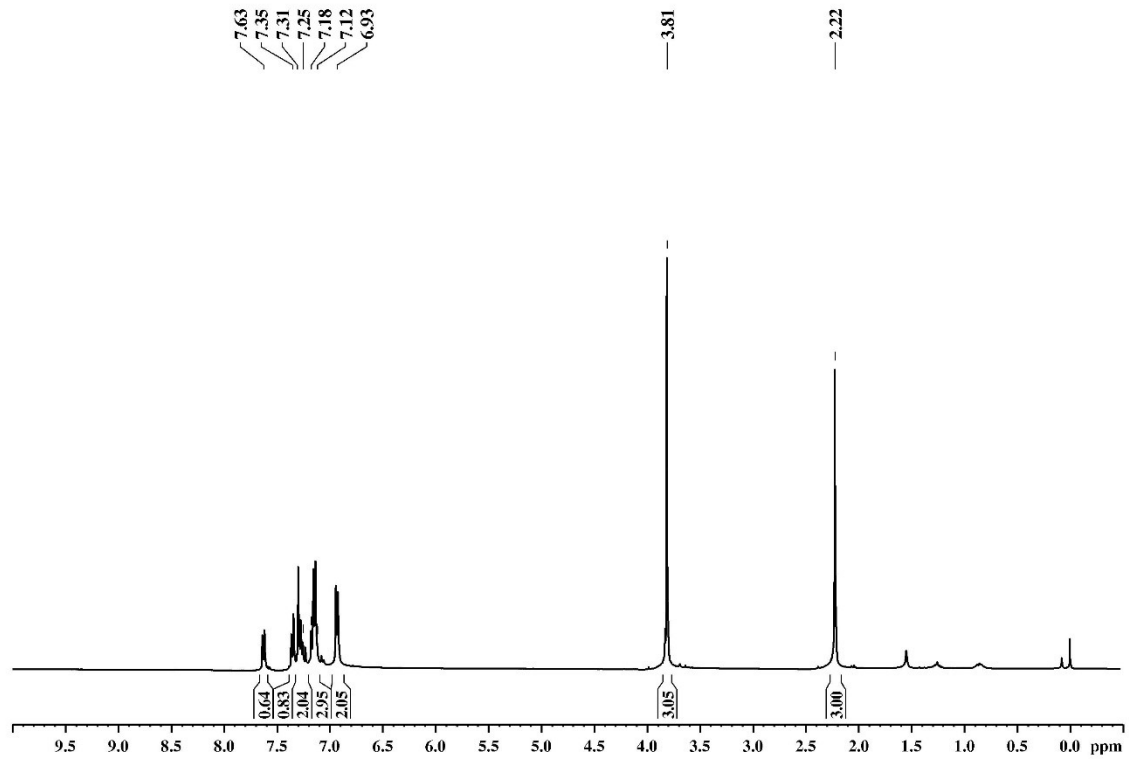

Figure S4: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**.

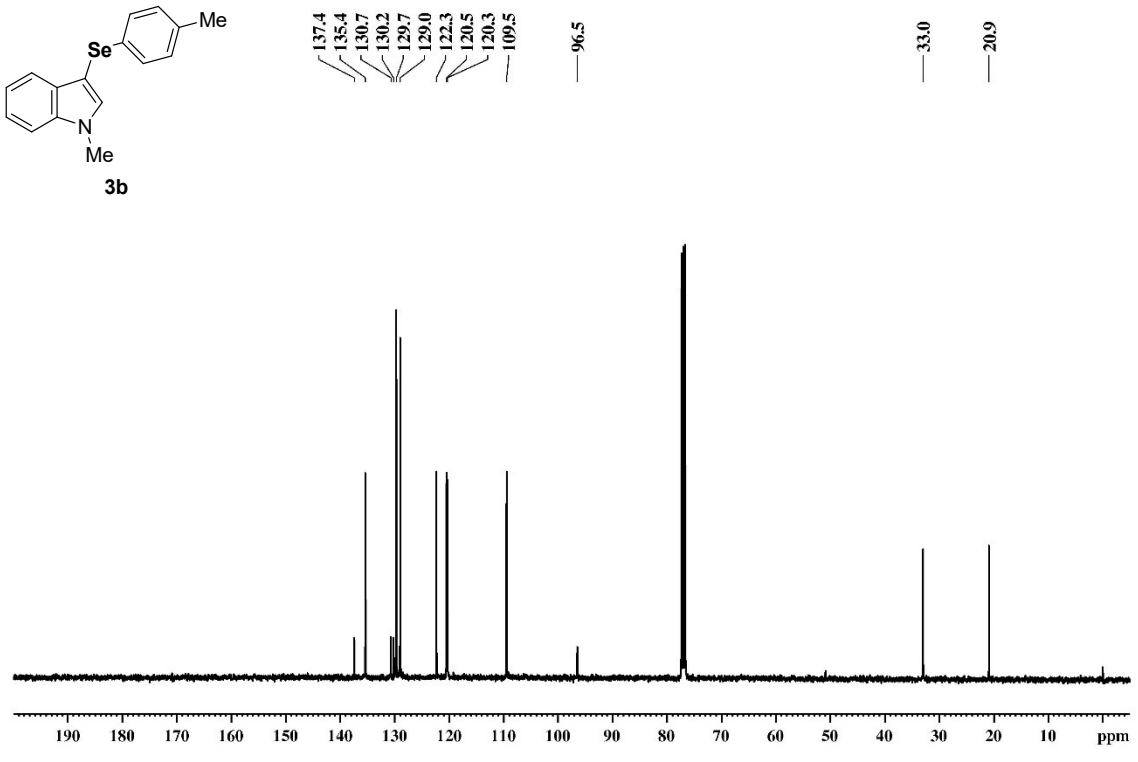

Figure S5: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3b**.

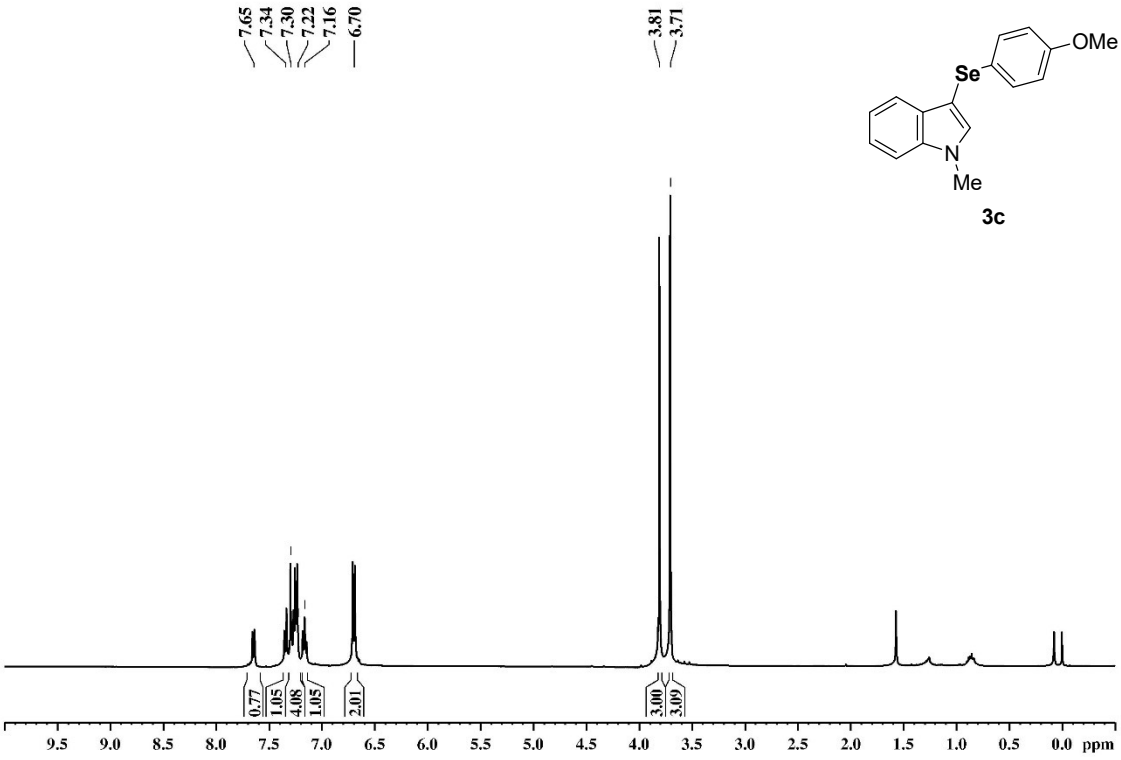

Figure S6: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**.

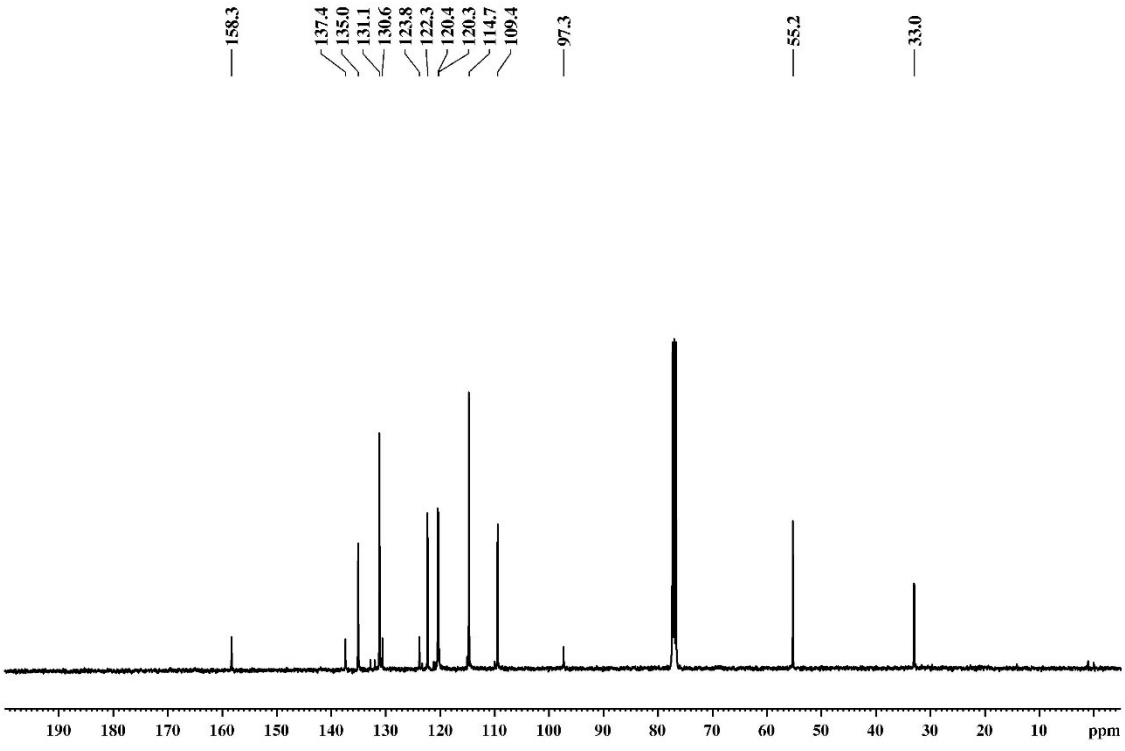

Figure S7: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3c**.

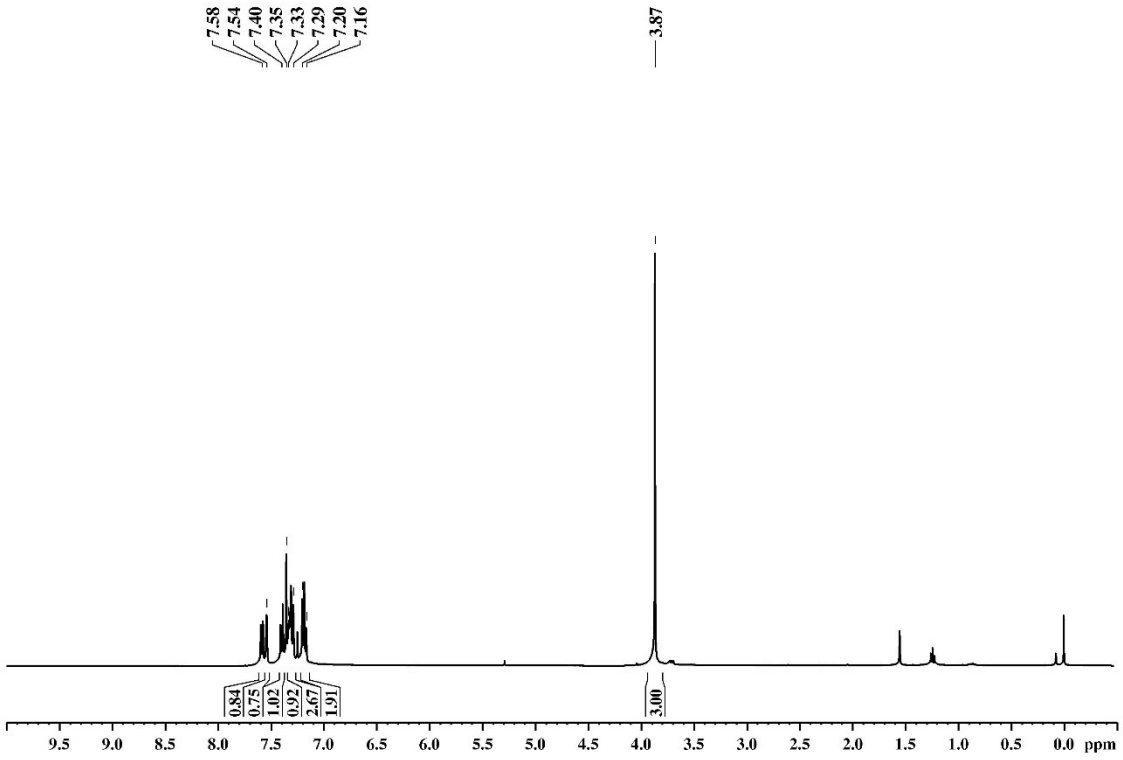

Figure S8: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**.

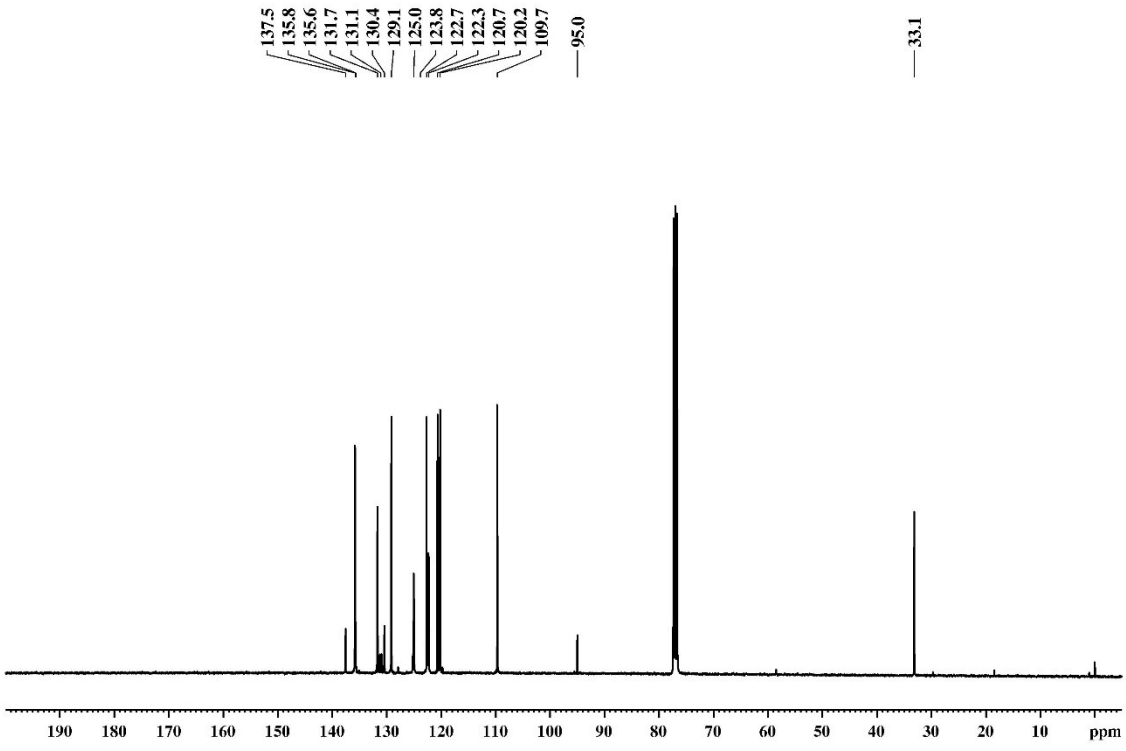

Figure S9: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3d**.

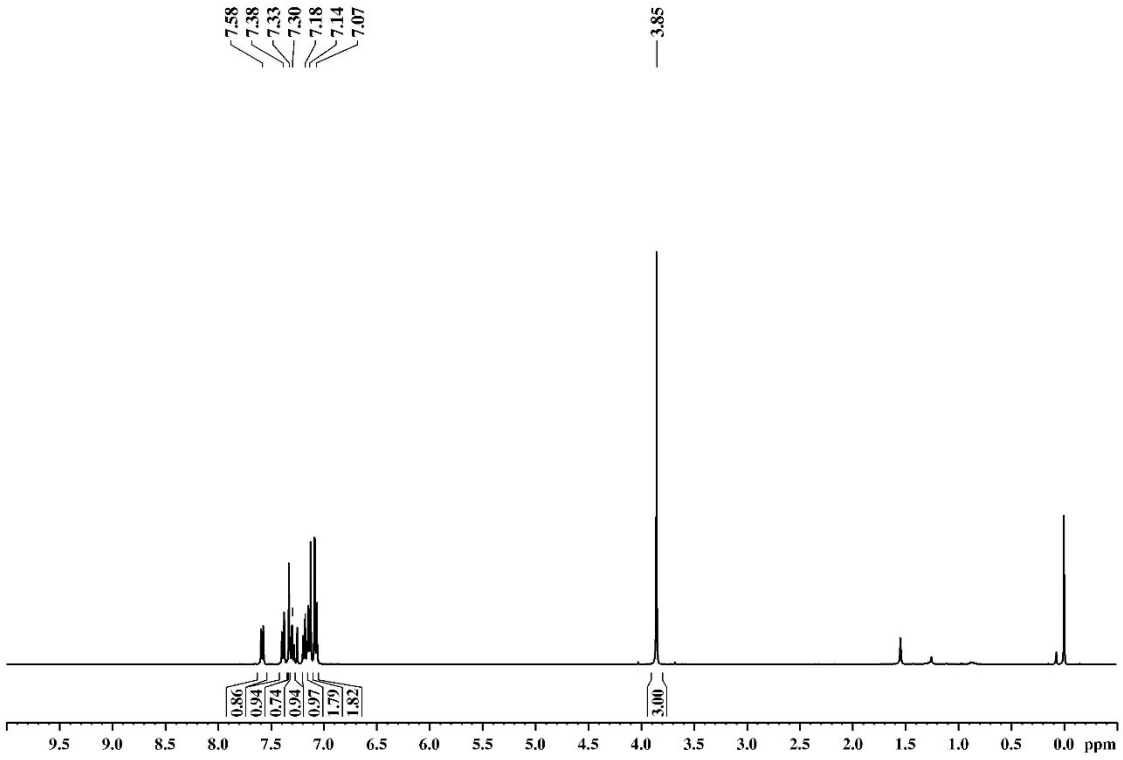

Figure S10: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**.

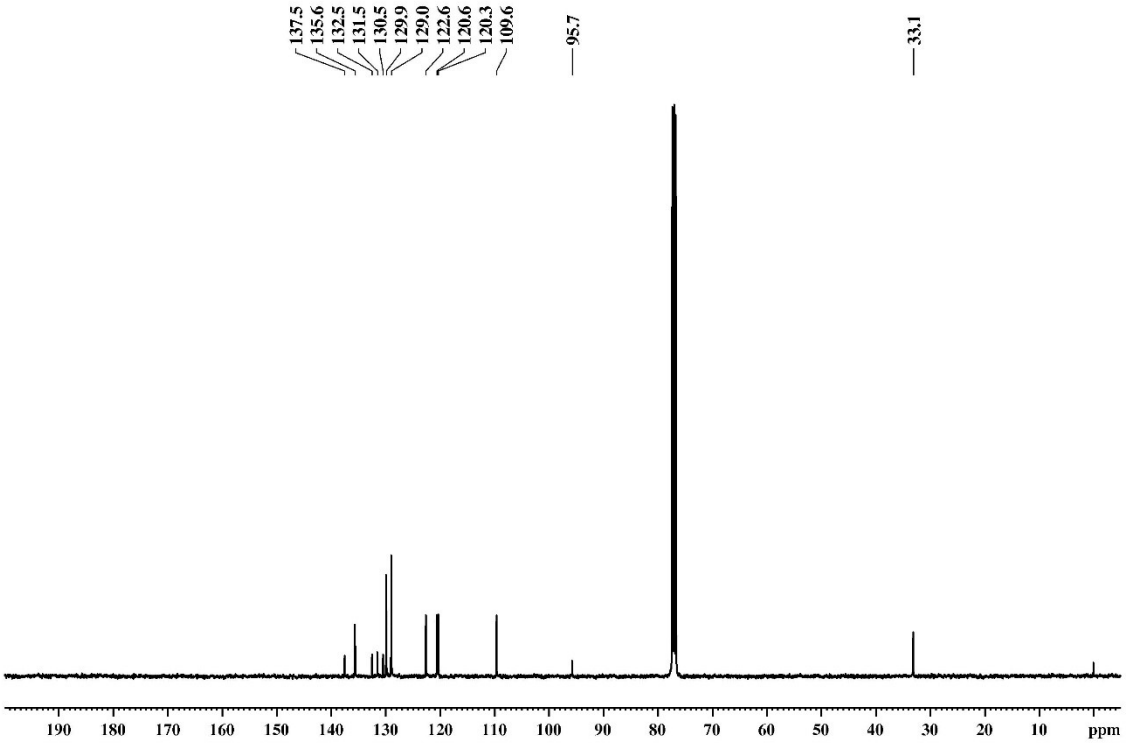

Figure S11: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3e**.

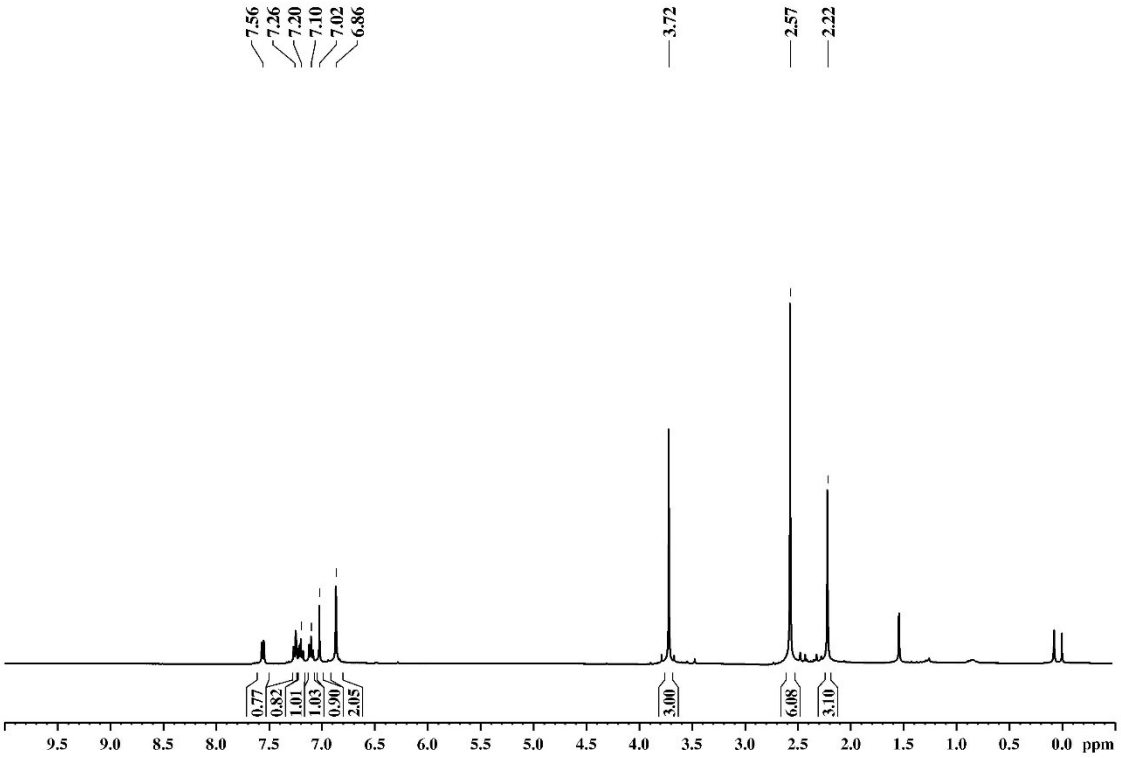

Figure S12: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**.

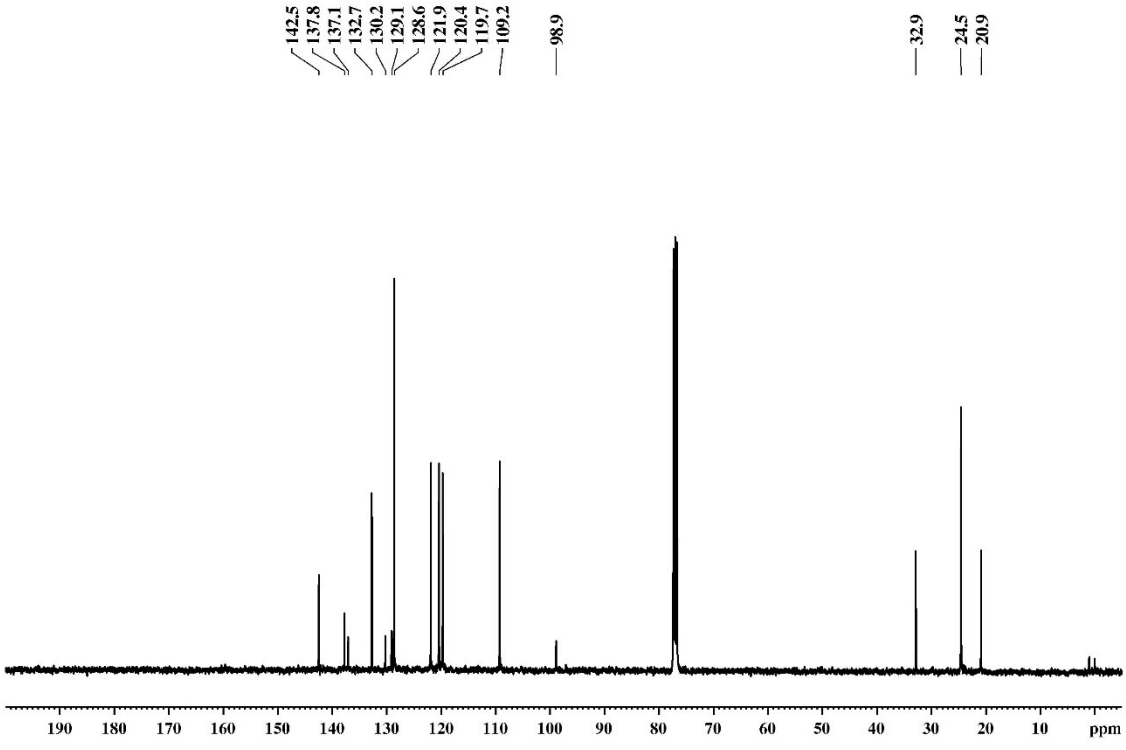

Figure S13: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3f**.

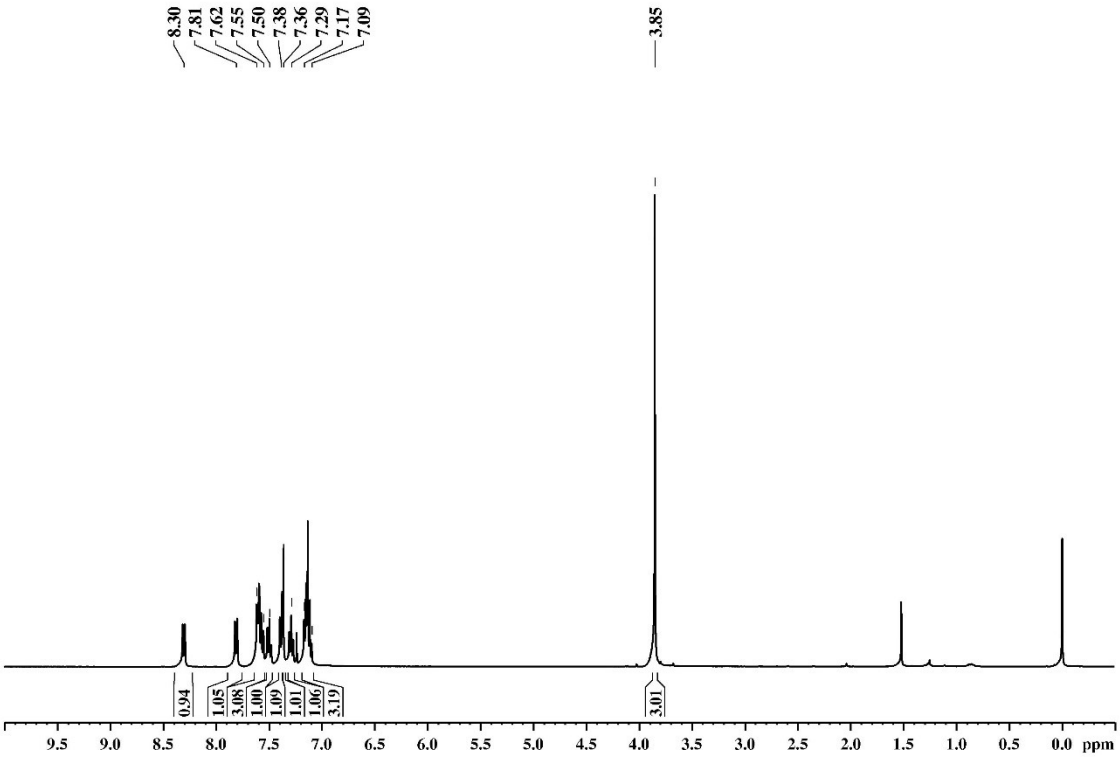

Figure S14: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**.

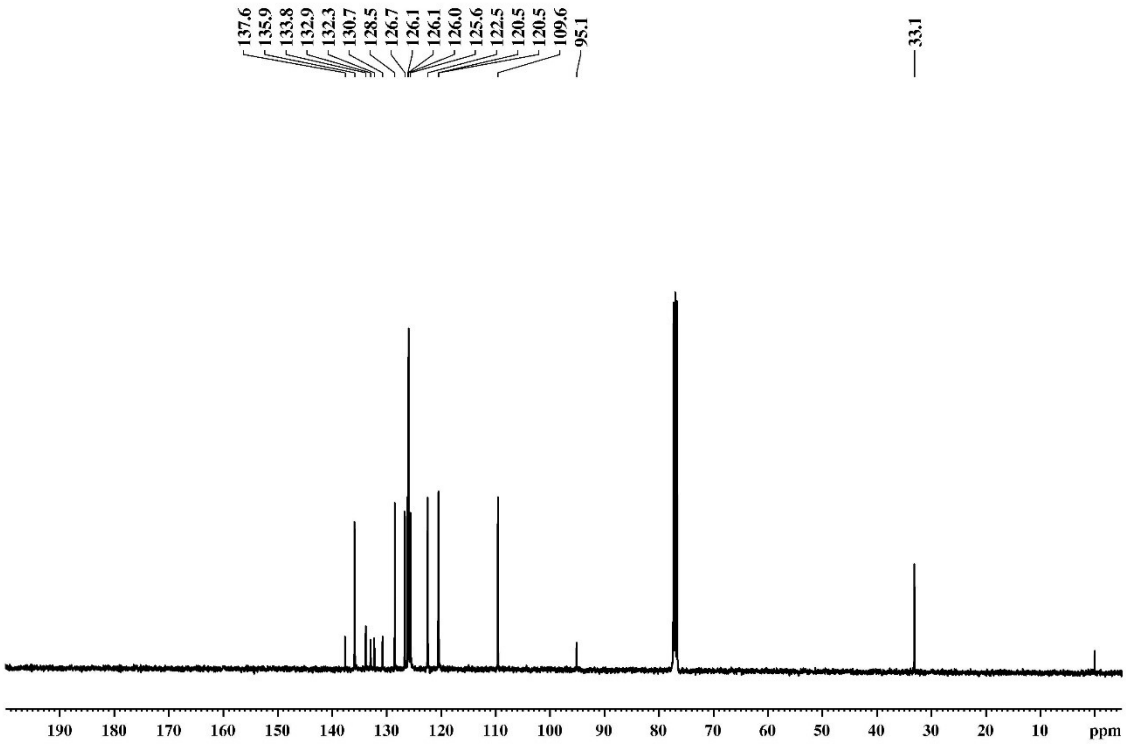

Figure S15: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3g**.

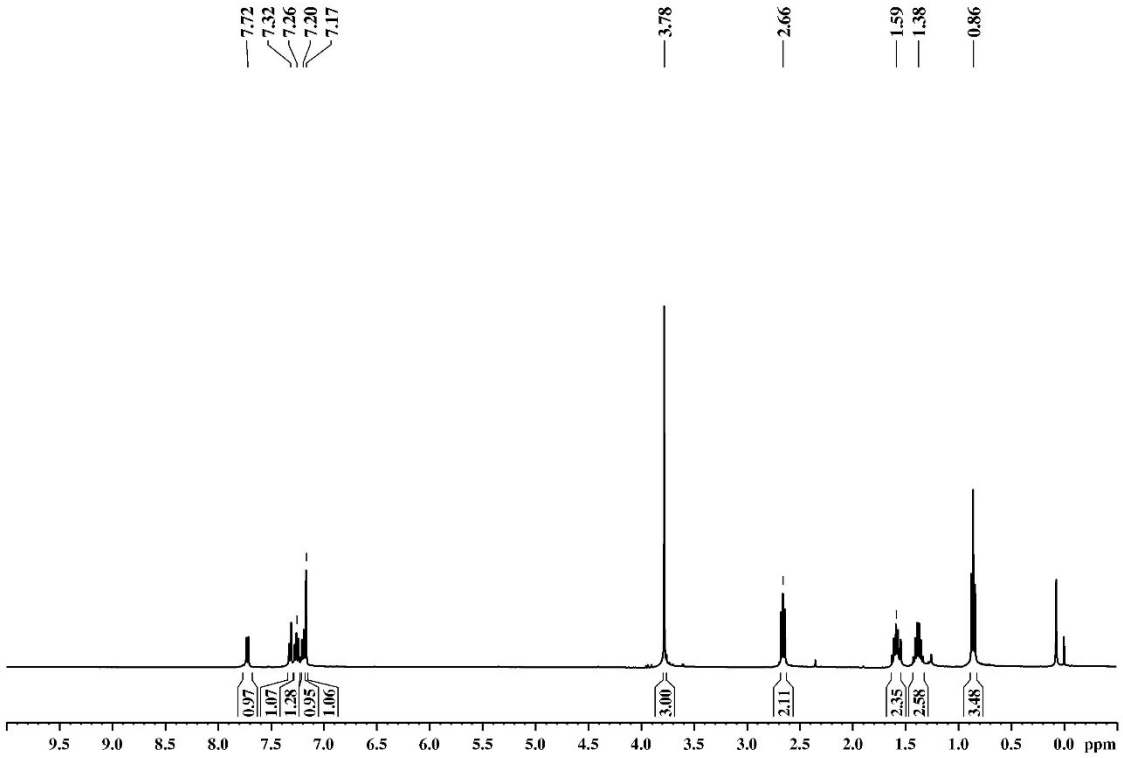

Figure S16: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**.

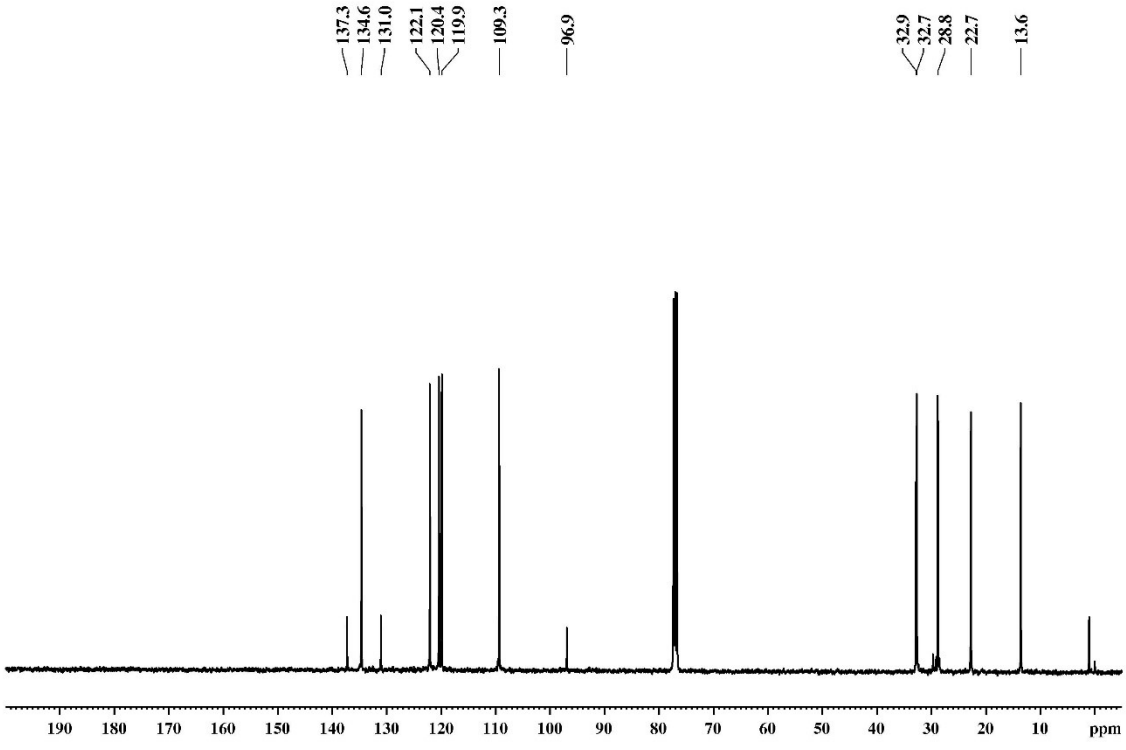

Figure S17: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3h**.

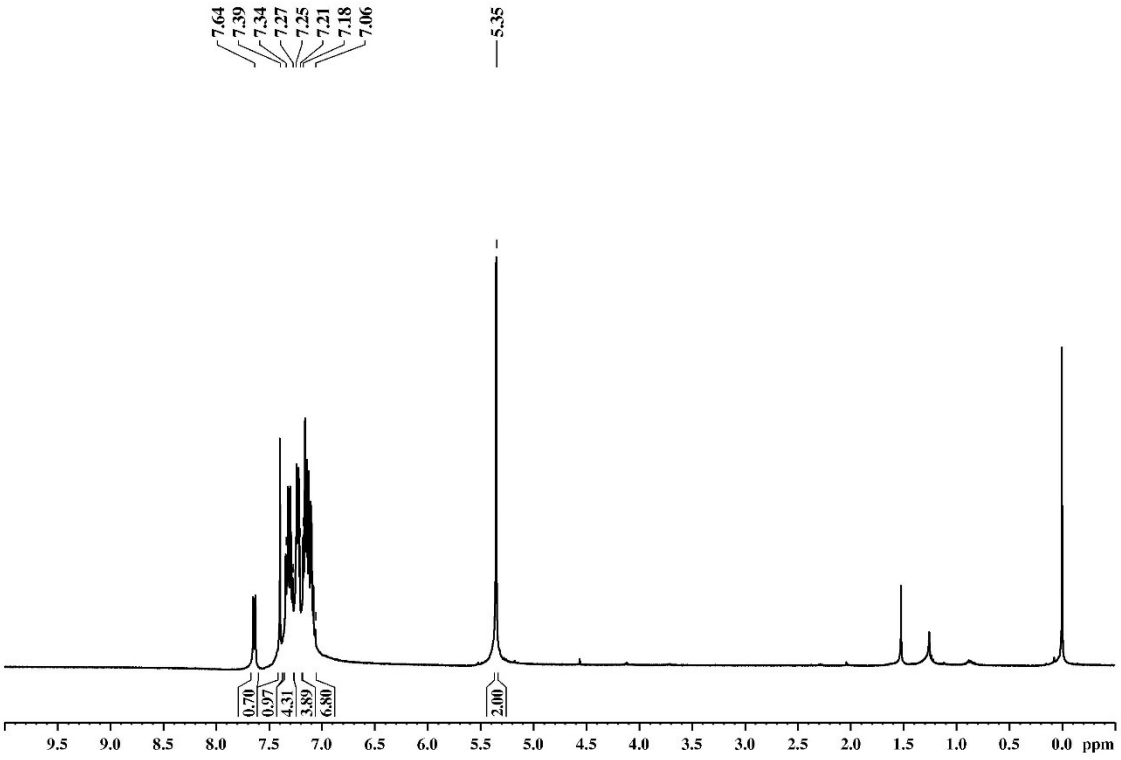

Figure S18: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**.

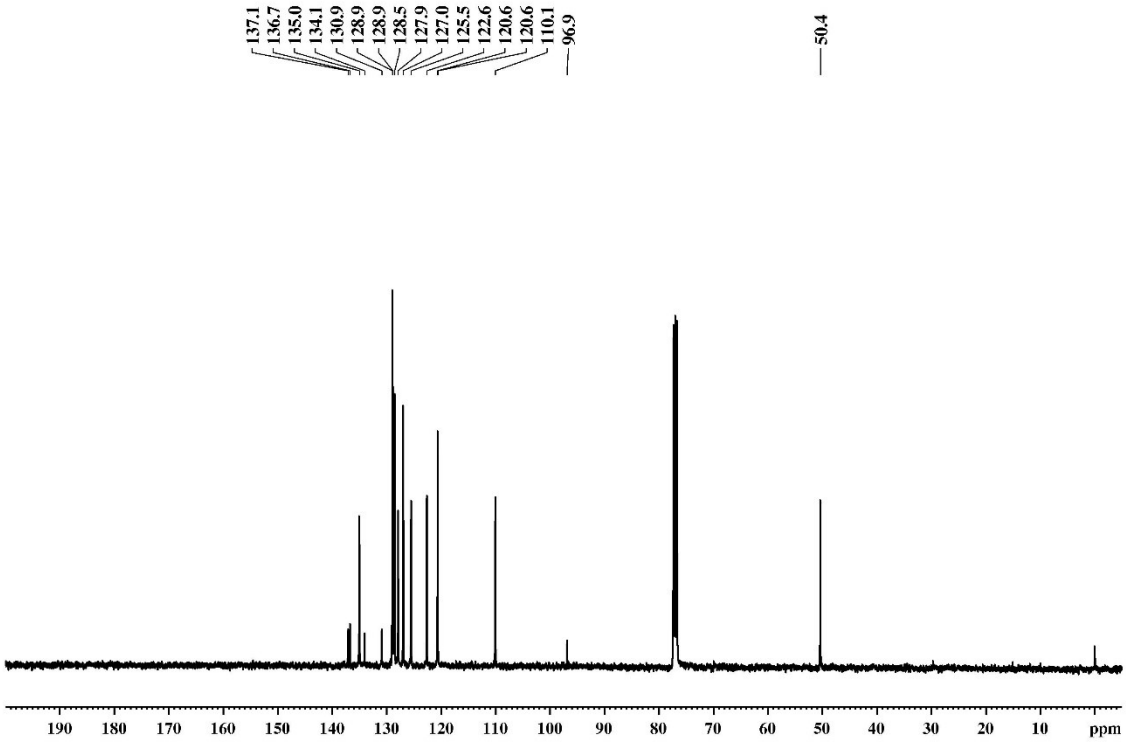

Figure S19: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3i**.

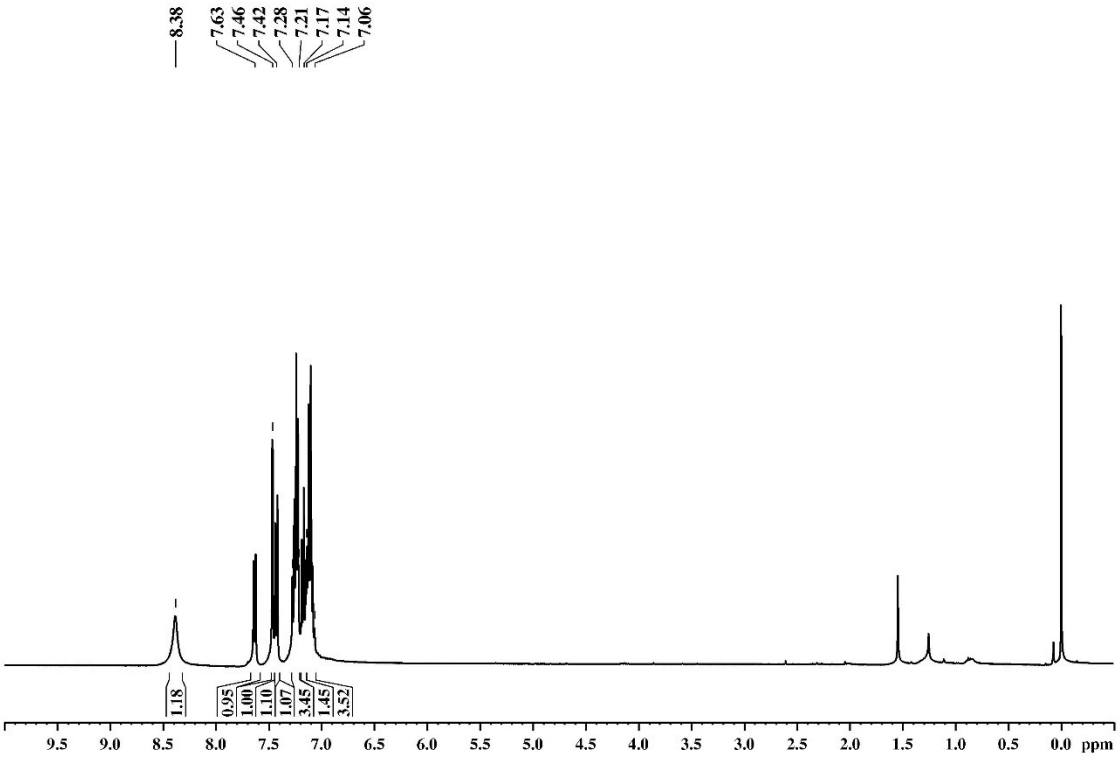

Figure S20: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**.

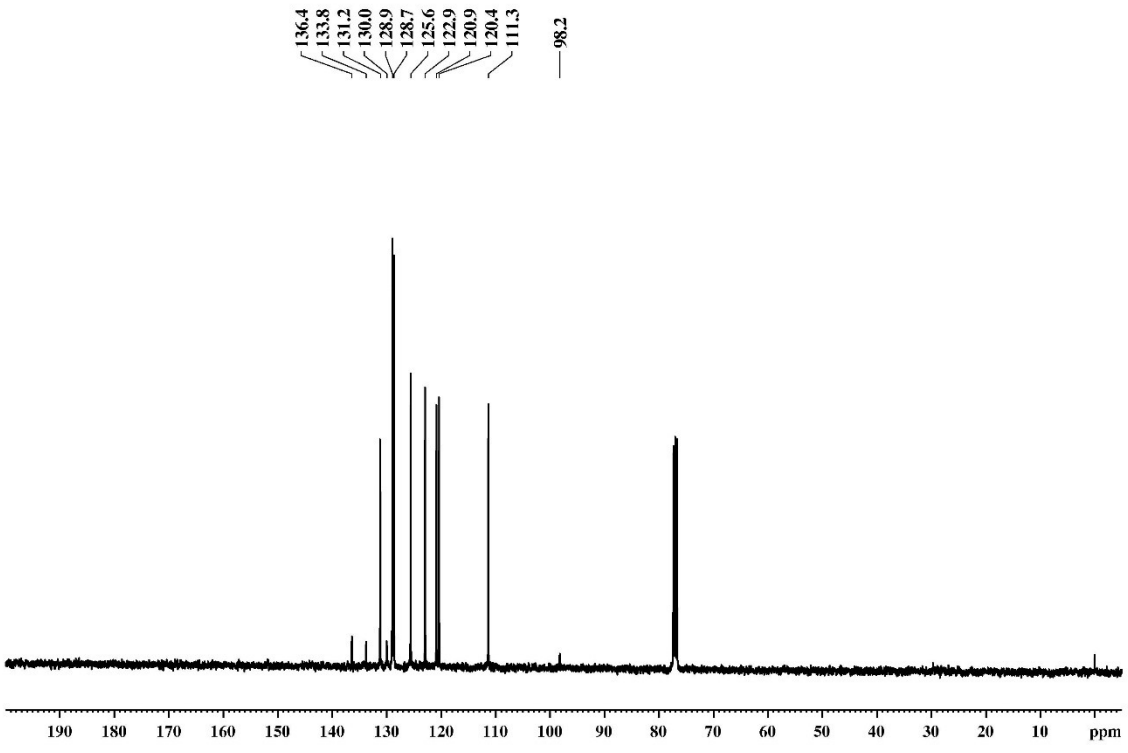

Figure S21: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3j**.

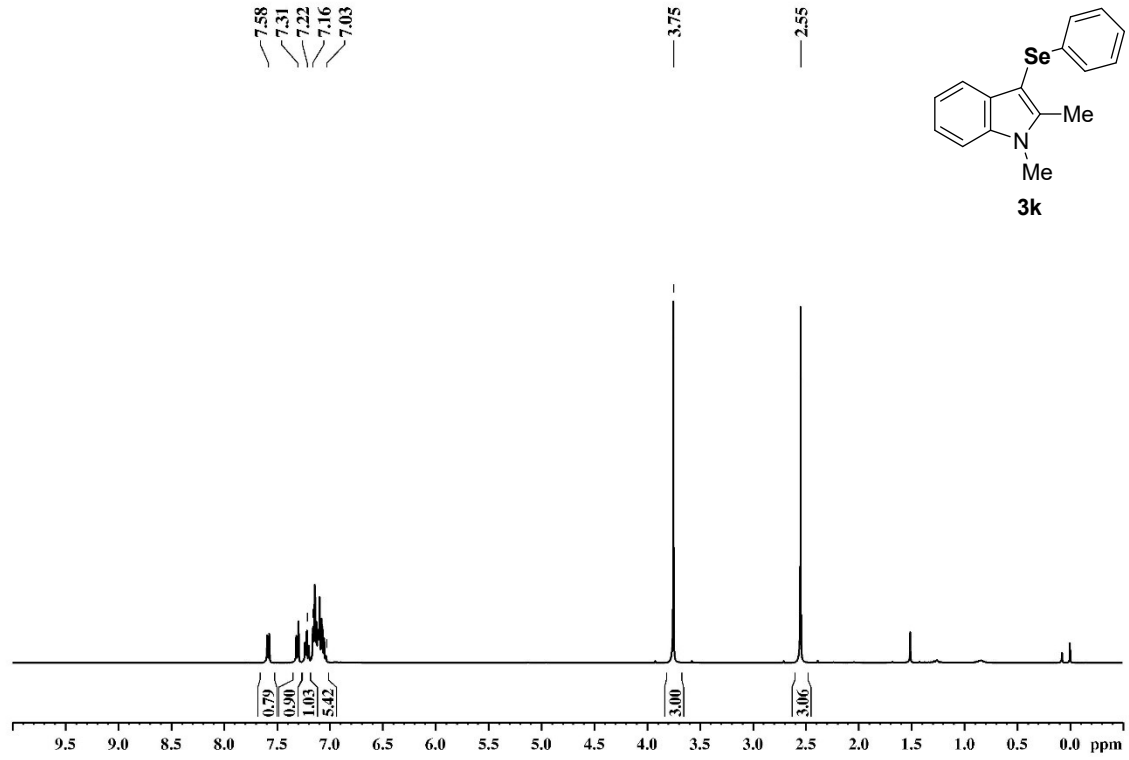

Figure S22: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k**.

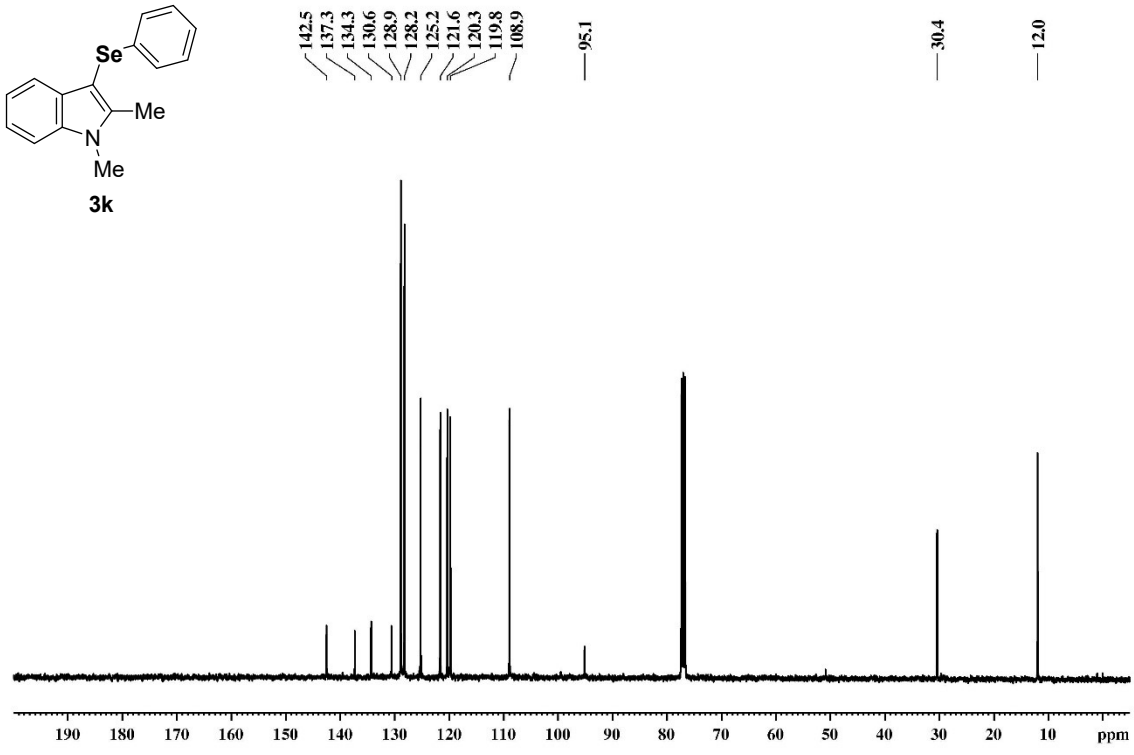

Figure S23: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3k.**

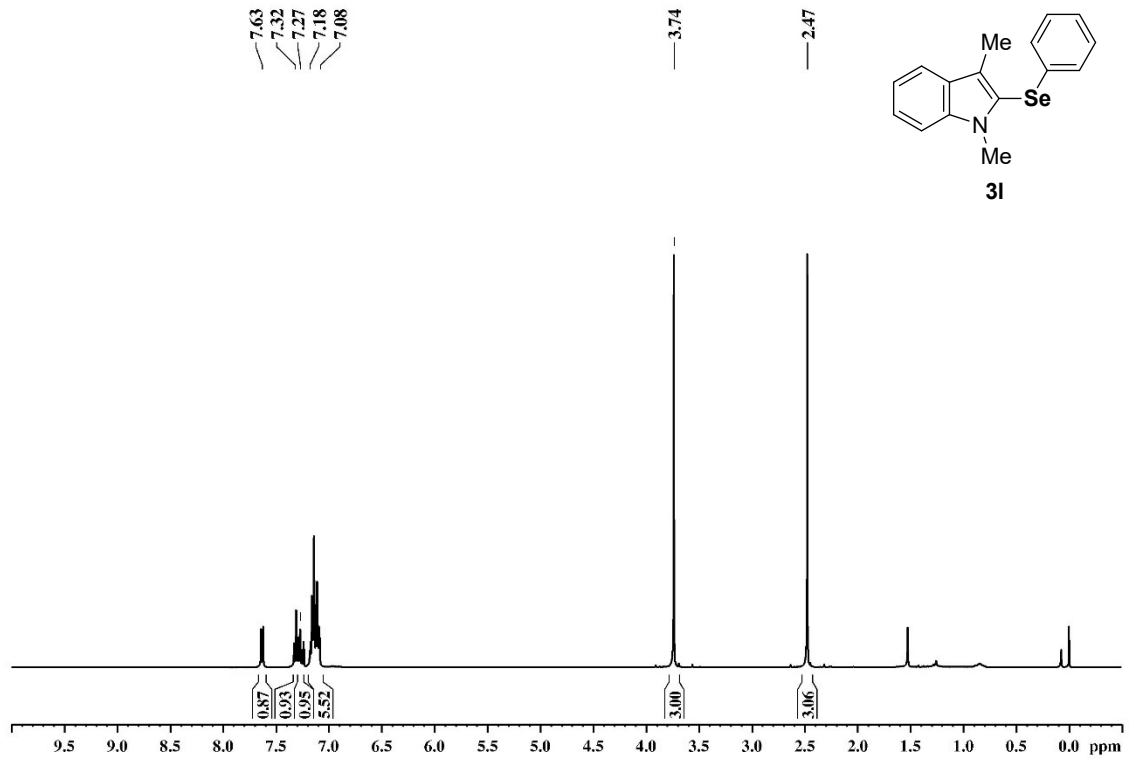

Figure S24: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l**.

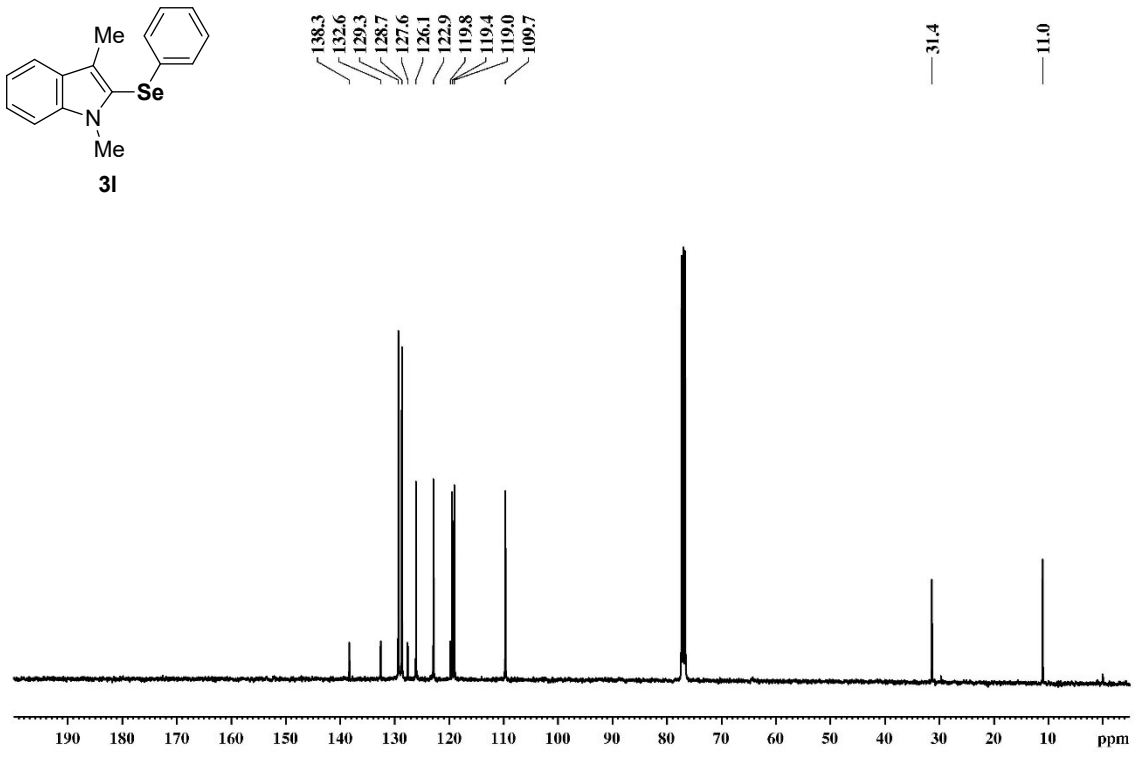

Figure S25: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3k**.

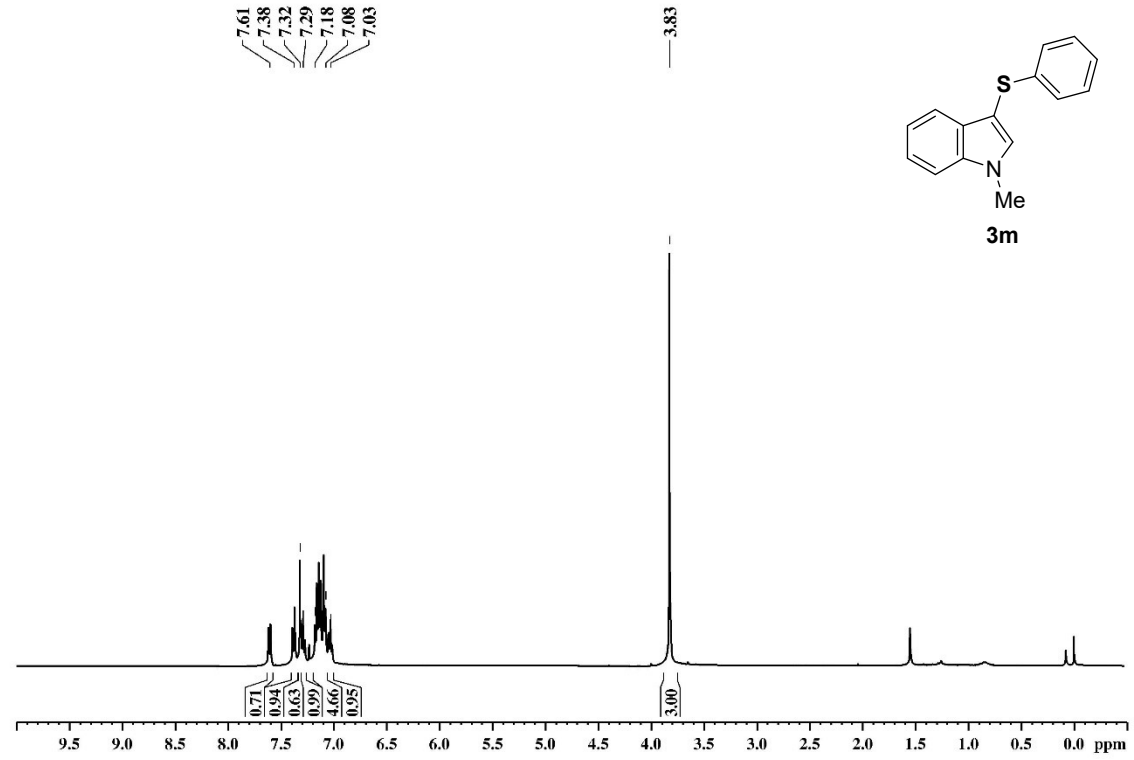

Figure S26: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m**.

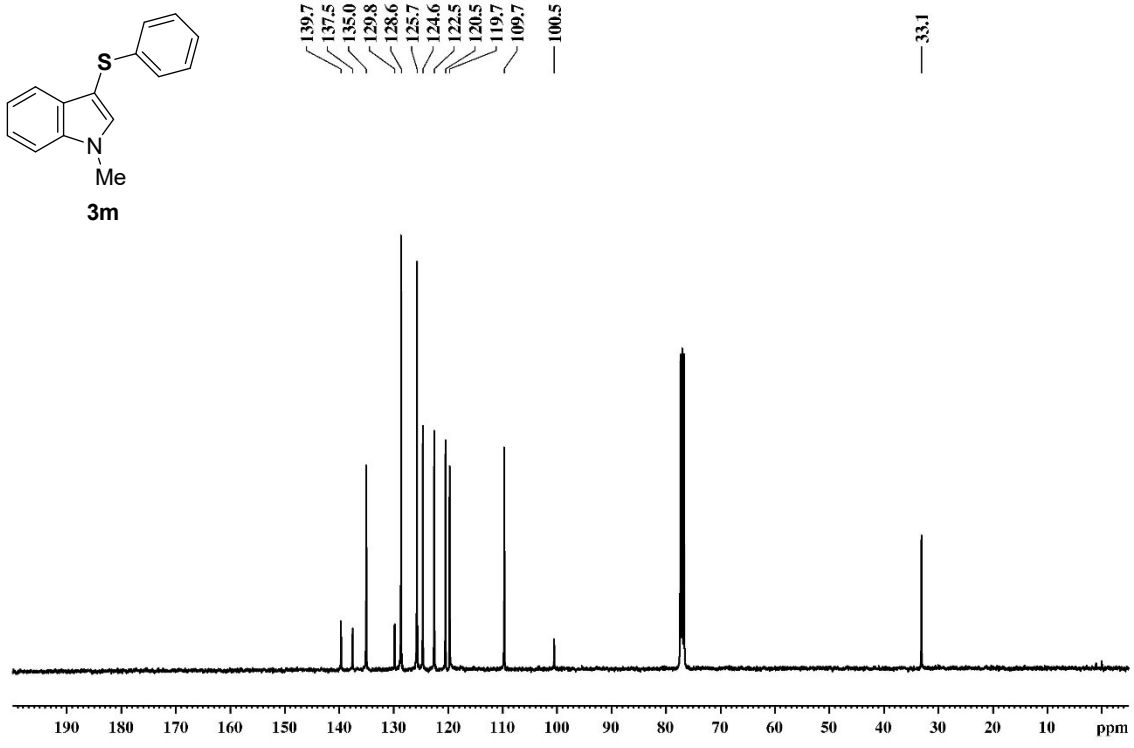

Figure S27: $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) of compound **3m**.