

Supporting Information

Divergent Synthesis of Selenide-Containing Spirocarbocycles and Phenanthrenes through Cu(OTf)₂-Promoted Selenylation of Alkyne-Containing Phenol-Based Biaryls

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General information

All commercially available reagents were used directly without purification unless otherwise stated. All solvents were used directly without purification. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{19}F NMR spectra were recorded using CDCl_3 or $\text{DMSO}-d_6$ at 500, 126 and 470 MHz Bruker Advanced III instrument respectively. IR spectra were recorded on a FT-IR instrument. The HRMS analysis was obtained on a QTOF mass spectrometer. Melting points were determined with melting points apparatus and are uncorrected. Substrates **1** and **2** were synthesized in the lab by the reported procedures.

General procedure for the synthesis of selenylated spirocyclohexadienones **3**.

Aryl phenol-tethered alkyne **1** (0.12 mmol, 1.0 eq.), diselenide **2** (0.144 mmol, 1.2 eq.), K_2CO_3 (0.24 mmol, 2.0 eq., 33.1 mg) and $\text{Cu}(\text{OTf})_2$ (0.144 mmol, 1.2 eq., 52.1 mg) were added to a reaction tube successively under an air atmosphere, and then MeCN (0.1 M, 1.2 mL) was added via syringe. The mixture was heated in an oil bath at 80 °C for 12 h until reaction completion (monitored by TLC). After completion of the reaction, the mixture was cooled to room temperature. Then, the solvent was removed in a vacuum, and the resulting residue was purified on a silica gel column (petroleum ether/ethyl acetate = 20:1, v/v) to afford the product **3**.

2'-Phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3a**).

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (50 mg, 98% yield). Mp 168-169 °C. IR 3937, 3889, 3842, 3794, 1660, 859, 737 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.23 (m, 10H), 7.20 – 7.13 (m, 4H), 6.59 (d, J = 10.0 Hz, 2H), 6.49 (d, J = 10.0 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.9, 151.6, 148.0, 145.3,

140.8, 134.3, 132.1, 130.9, 129.8, 129.3, 128.8, 128.7, 128.6, 128.1, 127.2, 126.8, 123.5, 123.0, 62.2. HRMS (ESI) calcd for C₂₆H₁₈NaOSe [M + Na]⁺ 449.0417, found 449.0418.

3'-(Phenylselanyl)-2'-(p-tolyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3b**).

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (49.9 mg, 95% yield). Mp 156-157 °C. IR 3926, 3797, 3665, 3504, 3346, 3177, 2934, 1630, 1439, 708 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.30 (m, 2H), 7.28 – 7.08 (m, 11H), 6.59 (d, *J* = 10.1 Hz, 2H), 6.49 (d, *J* = 10.0 Hz, 2H), 2.32 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 186.0, 151.9, 148.2, 145.3, 140.7, 138.7, 131.5, 131.4, 130.9, 130.8, 130.0, 129.2, 128.82, 128.75, 128.4, 127.0, 126.7, 123.4, 122.9, 62.2, 21.3. HRMS (ESI) calcd for C₂₇H₂₀NaOSe [M + Na]⁺ 463.0573, found 463.0575.

2'-(4-Ethylphenyl)-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one

(**3c**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (47.9 mg, 88% yield). Mp 125-126 °C. IR 3864, 3603, 2927, 2346, 1693, 1520 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.08 (m, 13H), 6.63 (d, *J* = 9.9 Hz, 2H), 6.53 (d, *J* = 9.9 Hz, 2H), 2.66 (s, 2H), 1.25 (t, *J* = 7.6 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 186.0, 151.8, 148.3, 145.4, 144.9, 140.6, 131.6, 131.4, 130.9, 130.8, 130.0, 129.2, 128.8, 128.5, 127.6, 127.0, 126.7, 123.4, 123.0, 62.2, 28.6, 15.1. HRMS (ESI) calcd for C₂₈H₂₂NaOSe [M + Na]⁺ 477.0730, found 477.0748.

2'-(4-Methoxyphenyl)-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one

(**3d**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow solid (45.4 mg, 83% yield). Mp 132-133 °C. IR 3838, 3753, 3610, 2916, 1667, 1502 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.31 (m, 4H), 7.28 – 7.16 (m, 6H), 7.13 (d, *J* = 6.9 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 10.1 Hz, 2H), 6.51 (d, *J* = 10.0 Hz, 2H), 3.79 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 186.0, 159.9, 151.5, 148.5, 145.5, 140.5,

130.9, 130.8, 130.7, 130.1, 129.9, 129.3, 128.8, 127.0, 126.74, 126.72, 123.4, 122.9, 113.6, 62.2, 55.2. HRMS (ESI) calcd for C₂₇H₂₀NaO₂Se [M + Na]⁺ 479.0522, found 479.0520.

2'-(4-Fluorophenyl)-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3e). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (48.6 mg, 91% yield). Mp 136-137 °C. IR 3941, 3882, 3805, 3750, 1667, 1502, 1222, 1164, 1006, 829, 745 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.22 (m, 7H), 7.21 – 7.13 (m, 4H), 7.00 – 6.94 (m, 2H), 6.57 (d, *J* = 10.1 Hz, 2H), 6.50 (d, *J* = 10.1 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.7, 162.7 (d, *J*_{C-F} = 249.4 Hz), 150.2, 147.8, 145.1, 140.6, 132.6, 131.1, 131.0, 130.4 (d, *J*_{C-F} = 8.2 Hz), 130.3 (d, *J*_{C-F} = 3.3 Hz), 129.6, 129.3, 128.9, 127.3, 126.9, 123.5, 123.0, 115.20 (d, *J*_{C-F} = 21.6 Hz), 62.2. ¹⁹F NMR (470 MHz, CDCl₃) δ -111.98. HRMS (ESI) calcd for C₂₆H₁₇NaFOSe [M + Na]⁺ 467.0322, found 467.0320.

2'-(4-Chlorophenyl)-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3f). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (48.9 mg, 89% yield). Mp 164-165 °C. IR 3790, 3669, 3357, 2908, 1663, 1450 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.23 (m, 9H), 7.21 – 7.13 (m, 4H), 6.56 (d, *J* = 10.2 Hz, 2H), 6.50 (d, *J* = 10.1 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.7, 149.9, 147.7, 145.1, 140.7, 134.7, 133.0, 132.7, 131.13, 131.11, 129.9, 129.5, 129.3, 128.9, 128.4, 127.4, 127.0, 123.5, 123.1, 62.1. HRMS (ESI) calcd for C₂₆H₁₇ClNaOSe [M + Na]⁺ 483.0024, found 483.0017.

2'-(4-Bromophenyl)-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3g). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (46.8 mg, 77% yield). Mp 152-154 °C. IR 3845, 3735, 3346, 2920, 1675, 1468 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.33 – 7.13 (m, 11H), 6.56 (d, *J* = 10.2 Hz,

2H), 6.50 (d, $J = 10.1$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.7, 149.9, 147.7, 145.1, 140.7, 133.2, 133.0, 131.3, 131.2, 131.1, 130.1, 129.5, 129.3, 128.9, 127.4, 127.1, 123.5, 123.1, 123.0, 62.1. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{BrNaOSe}$ [$\text{M} + \text{Na}$] $^+$ 526.9519, found 526.9512.

3'-(Phenylselanyl)-2'-(4-(trifluoromethyl)phenyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3h). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (42.7 mg, 72% yield). Mp 117-118 °C. IR 3948, 3900, 3838, 3761, 1663, 1325, 1164, 1127, 1053, 1002, 840, 734, 679 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.55 (d, $J = 8.2$ Hz, 2H), 7.44 (d, $J = 8.1$ Hz, 2H), 7.39 – 7.27 (m, 5H), 7.20 (d, $J = 7.4$ Hz, 4H), 6.60 (d, $J = 10.1$ Hz, 2H), 6.52 (d, $J = 10.1$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.6, 149.1, 147.4, 144.9, 140.8, 137.9, 134.2, 131.4, 131.3, 130.5, 130.3, 129.4, 129.2, 129.0, 128.9, 127.7, 127.2, 125.07 (q, $J_{\text{C-F}} = 3.7$ Hz), 123.6, 123.2, 62.2. ^{19}F NMR (470 MHz, CDCl_3) δ -62.75. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{F}_3\text{NaOSe}$ [$\text{M} + \text{Na}$] $^+$ 517.0291, found 517.0294.

2'-(4-Nitrophenyl)-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3i). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow solid (39.3 mg, 70% yield). Mp 166-167 °C. IR 3822, 3805, 2927, 1652, 1527 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.11 (d, $J = 8.8$ Hz, 2H), 7.49 (d, $J = 8.9$ Hz, 2H), 7.40 – 7.29 (m, 5H), 7.18 (t, $J = 7.4$ Hz, 4H), 6.58 (d, $J = 10.2$ Hz, 2H), 6.52 (d, $J = 10.1$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.3, 147.7, 147.4, 147.1, 144.8, 141.0, 140.8, 135.6, 131.5, 131.4, 129.5, 129.4, 129.1, 128.9, 128.0, 127.4, 123.6, 123.33, 123.28, 62.1. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{NNaO}_3\text{Se}$ [$\text{M} + \text{Na}$] $^+$ 494.0267, found 494.0268.

3'-(Phenylselanyl)-2'-(m-tolyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3j). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (43.6 mg, 83% yield). Mp 126-128 °C. IR 3926, 3636, 3349, 2908, 1648, 1468, 723 cm^{-1} . ^1H NMR (500 MHz,

CDCl₃) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.21 (m, 3H), 7.21 – 7.08 (m, 8H), 6.59 (d, *J* = 10.1 Hz, 2H), 6.49 (d, *J* = 10.0 Hz, 2H), 2.29 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 186.0, 151.8, 148.1, 145.3, 140.8, 137.6, 134.3, 132.0, 131.1, 130.9, 129.9, 129.5, 129.3, 129.2, 128.8, 128.0, 127.1, 126.8, 125.6, 123.5, 123.0, 62.3, 21.5. HRMS (ESI) calcd for C₂₇H₂₀NaOSe [M + Na]⁺ 463.0573, found 463.0576.

2'-(3-Fluorophenyl)-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3k**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (45.6 mg, 86% yield). Mp 130-132 °C. IR 3970, 3908, 3772, 3706, 2916, 1656, 1461, 1255, 1178, 1009, 844, 741 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.21 (m, 6H), 7.21 – 7.14 (m, 4H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.06 – 6.96 (m, 2H), 6.59 – 6.54 (m, 2H), 6.53 – 6.48 (m, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.7, 162.2 (d, *J*_{C-F} = 246.7 Hz), 149.6, 147.6, 145.0, 140.7, 136.3 (d, *J*_{C-F} = 8.1 Hz), 133.4, 131.3, 131.1, 129.7 (d, *J*_{C-F} = 8.4 Hz), 129.4, 129.3, 128.9, 127.5, 127.1, 124.4 (d, *J*_{C-F} = 2.9 Hz), 123.5, 123.1, 115.7 (d, *J*_{C-F} = 14.4 Hz), 115.5 (d, *J*_{C-F} = 13.1 Hz), 62.1. ¹⁹F NMR (470 MHz, CDCl₃) δ -112.39. HRMS (ESI) calcd for C₂₆H₁₇NaFOSe [M + Na]⁺ 467.0322, found 467.0319.

2'-(3-Chlorophenyl)-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3l**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (46.4 mg, 84% yield). Mp 157-159 °C. IR 2920, 1660, 1467 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.24 (m, 7H), 7.22 – 7.14 (m, 6H), 6.55 (d, *J* = 10.2 Hz, 2H), 6.50 (d, *J* = 10.1 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.7, 149.2, 147.5, 145.0, 140.7, 136.0, 133.9, 133.7, 131.5, 131.2, 129.4, 129.3, 129.2, 128.9, 128.8, 128.6, 127.5, 127.2, 126.6, 123.5, 123.1, 62.1. HRMS (ESI) calcd for C₂₆H₁₇ClNaOSe [M + Na]⁺ 483.0024, found 483.0036.

2'-(3-Bromophenyl)-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3m**). Purification by column chromatography on silica gel (petroleum ether/ethyl

acetate = 20:1, v/v) afforded the target compound as a yellow solid (39.3 mg, 65% yield). Mp 148-150 °C. IR 3838, 3702, 3625, 1667, 737 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.44 – 7.39 (m, 2H), 7.35 – 7.24 (m, 5H), 7.23 – 7.11 (m, 6H), 6.55 (d, *J* = 10.2 Hz, 2H), 6.50 (d, *J* = 10.2 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.7, 149.0, 147.5, 145.0, 140.7, 136.3, 133.8, 131.7, 131.65, 131.55, 131.2, 129.6, 129.3, 129.2, 128.9, 127.5, 127.2, 127.0, 123.5, 123.1, 122.1, 62.2. HRMS (ESI) calcd for C₂₆H₁₇BrNaOSe [M + Na]⁺ 526.9519, found 526.9512.

2'-(2-Fluorophenyl)-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3n). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (38.9 mg, 73% yield). Mp 145-147 °C. IR 3955, 3897, 3753, 1645, 866, 745 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.37 (m, 2H), 7.35 – 7.26 (m, 4H), 7.24 – 7.17 (m, 4H), 7.12 – 7.03 (m, 3H), 6.62 (d, *J* = 9.0 Hz, 2H), 6.46 (d, *J* = 10.0 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.9, 159.6 (d, *J*_{C-F} = 246.4 Hz), 146.9, 145.1, 144.7, 141.7, 135.9, 131.9, 130.9 (d, *J*_{C-F} = 38.2 Hz), 130.8 (d, *J*_{C-F} = 2.3 Hz), 130.5 (d, *J*_{C-F} = 8.2 Hz), 129.2, 128.9, 128.8, 127.3, 127.1, 123.7 (d, *J*_{C-F} = 3.7 Hz), 123.6, 122.9, 121.8 (d, *J*_{C-F} = 16.1 Hz), 115.8 (d, *J*_{C-F} = 22.4 Hz), 62.7. ¹⁹F NMR (470 MHz, CDCl₃) δ -111.11. HRMS (ESI) calcd for C₂₆H₁₇NaFOSe [M + Na]⁺ 467.0322, found 467.0327.

2'-(2-Chlorophenyl)-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3o). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (39.3 mg, 71% yield). Mp 146-148 °C. IR 3742, 3382, 2927, 1667, 741 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.47 – 7.12 (m, 12H), 7.05 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.78 (dd, *J* = 9.9, 2.8 Hz, 1H), 6.62 (dd, *J* = 9.9, 2.8 Hz, 1H), 6.52 (dd, *J* = 9.9, 1.6 Hz, 1H), 6.38 (dd, *J* = 9.9, 1.6 Hz, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.9, 147.8, 146.6, 145.2, 144.6, 141.6, 135.9, 134.0, 132.7, 132.0, 131.4, 130.9, 130.8, 129.8, 129.7, 129.2, 128.9, 128.8, 127.3, 127.1, 126.2, 123.6, 122.9, 63.2. HRMS (ESI) calcd for C₂₆H₁₇ClNaOSe [M + Na]⁺ 483.0024, found 483.0038.

2'-(Ferrocen-2-yl)-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3p**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a red solid (25.4 mg, 40% yield). Mp 177-179 °C. IR 3728, 3474, 3342, 2931, 1667, 1461 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, *J* = 6.9 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.17 (m, 5H), 7.05 (d, *J* = 7.1 Hz, 1H), 6.71 (d, *J* = 10.0 Hz, 2H), 6.62 (d, *J* = 10.0 Hz, 2H), 5.15 (s, 2H), 4.36 (s, 2H), 4.03 (s, 5H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 186.2, 152.6, 150.7, 147.0, 138.4, 130.8, 129.9, 129.8, 129.5, 129.0, 126.6, 126.4, 125.6, 123.1, 121.8, 78.0, 69.9, 69.8, 69.0, 61.9. HRMS (ESI) calcd for C₃₀H₂₂NaFeOSe [M + Na]⁺ 557.0080, found 557.0067.

4'-Methyl-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3q**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (38 mg, 72% yield). Mp 162-164 °C. IR 3827, 3551, 2934, 1593, 756 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.08 (m, 12H), 7.04 (d, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 9.8 Hz, 2H), 6.44 (d, *J* = 9.8 Hz, 2H), 2.62 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.9, 154.6, 147.8, 141.9, 141.4, 134.8, 133.9, 133.1, 132.3, 131.6, 130.9, 129.4, 129.1, 128.7, 128.4, 127.9, 127.0, 126.2, 121.6, 62.1, 19.3. HRMS (ESI) calcd for C₂₇H₂₀NaOSe [M + Na]⁺ 463.0573, found 463.0578.

4'-Fluoro-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3r**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (39.6 mg, 74% yield). Mp 138-140 °C. IR 3944, 3838, 3753, 1660, 1465, 1252, 1086, 862, 730 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.31 (m, 2H), 7.31 – 7.23 (m, 6H), 7.18 (t, *J* = 2.1 Hz, 2H), 7.17 – 7.16 (m, 1H), 7.05 – 7.02 (m, 1H), 7.01 – 6.99 (m, 1H), 6.63 – 6.57 (m, 2H), 6.52 – 6.47 (m, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.6, 156.7 (d, *J*_{C-F} = 255.1 Hz), 151.6, 147.0, 143.7, 133.9, 131.7, 131.6, 131.1, 130.9 (d, *J*_{C-F} = 2.7 Hz), 129.1, 128.7, 128.67, 128.64, 128.5, 128.0, 126.8, 119.6 (d, *J*_{C-F} = 3.6 Hz),

116.7 (d, $J_{C-F} = 21.1$ Hz), 62.5. ^{19}F NMR (470 MHz, CDCl_3) δ -118.98. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{NaFOSe}$ $[\text{M} + \text{Na}]^+$ 467.0322, found 467.0331.

5'-Methyl-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3s**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (42.7 mg, 81% yield). Mp 133-135 °C. IR 3801, 2912, 1648, 1061, 822 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.25 (m, 7H), 7.17 (d, $J = 32.0$ Hz, 4H), 7.07 (dd, $J = 17.1, 7.6$ Hz, 2H), 6.60 (d, $J = 9.8$ Hz, 2H), 6.49 (d, $J = 9.8$ Hz, 2H), 2.32 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 186.1, 151.9, 148.3, 145.5, 139.0, 137.7, 134.4, 132.1, 130.9, 130.8, 130.0, 129.3, 128.6, 128.6, 128.08, 128.06, 126.8, 123.6, 123.2, 62.0, 21.5. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{20}\text{NaOSe}$ $[\text{M} + \text{Na}]^+$ 463.0573, found 463.0562.

5'-Fluoro-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3t**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (47.1 mg, 89% yield). Mp 143-144 °C. IR 3955, 3893, 3849, 3750, 1660, 1472, 1248, 1160, 726 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.32 (m, 7H), 7.25 – 7.21 (m, 3H), 7.12 (dd, $J = 8.2, 4.8$ Hz, 1H), 7.01 – 6.97 (m, 1H), 6.95 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.62 – 6.58 (m, 2H), 6.54 – 6.50 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.7, 163.5 (d, $J_{C-F} = 246.4$ Hz), 153.7, 147.6, 147.5, 136.2, 136.1, 134.1, 131.2, 131.1, 129.4, 129.3, 128.9, 128.5, 128.2, 127.2, 124.6 (d, $J_{C-F} = 9.3$ Hz), 114.1 (d, $J_{C-F} = 23.7$ Hz), 110.3 (d, $J_{C-F} = 24.8$ Hz), 61.6. ^{19}F NMR (470 MHz, CDCl_3) δ -112.27. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{NaFOSe}$ $[\text{M} + \text{Na}]^+$ 467.0322, found 467.0324.

5'-Chloro-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3u**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (50.5 mg, 92% yield). Mp 123-125 °C. IR 3904, 3706, 3559, 3342, 2931, 1663, 1531 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.34 (d, $J = 9.3$ Hz, 7H), 7.27 (s, 1H), 7.23 (td, $J = 5.7, 5.1, 1.9$ Hz, 4H), 7.09 (d, $J = 8.0$ Hz, 1H), 6.58 (d, $J = 10.1$ Hz, 2H), 6.51 (d, $J = 10.1$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.6, 153.4, 147.2, 147.1, 139.9, 139.6, 139.1, 135.0, 133.9, 131.2, 131.2, 129.4, 129.3, 129.0, 128.5, 128.2, 127.2, 124.5, 123.2, 61.7. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{ClNaOSe}$ $[\text{M} + \text{Na}]^+$ 483.0024, found 483.0037.

6'-Methyl-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3v**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (41.3 mg, 78% yield). Mp 134-136 °C. IR 3900, 3735, 2912, 1660, 1509, 752 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.27 (m, 6H), 7.25 (s, 1H), 7.20 – 7.12 (m, 4H), 7.09 – 7.04 (m, 1H), 6.96 (d, $J = 1.5$ Hz, 1H), 6.63 – 6.57 (m, 2H), 6.51 – 6.46 (m, 2H), 2.33 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 186.0, 150.4, 148.4, 142.8, 140.8, 137.4, 134.5, 131.9, 130.9, 130.8, 129.9, 129.6, 129.2, 128.6, 128.1, 126.8, 124.2, 122.7, 62.1, 21.4. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{20}\text{NaOSe}$ $[\text{M} + \text{Na}]^+$ 463.0573, found 463.0584.

6'-Fluoro-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3w**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (42.5 mg, 80% yield). Mp 139-141 °C. IR 3897, 3820, 3753, 3691, 1663, 1476, 1255, 862, 745 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.29 (m, 7H), 7.22 – 7.17 (m, 4H), 6.96 (td, $J = 8.8, 2.4$ Hz, 1H), 6.88 (dd, $J = 8.0, 2.4$ Hz, 1H), 6.59 (d, $J = 10.1$ Hz, 2H), 6.51 (d, $J = 10.1$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.6, 162.4 (d, $J_{\text{C-F}} = 248.3$ Hz), 151.4, 147.2, 143.1, 143.0, 141.1 (d, $J_{\text{C-F}} = 2.4$ Hz), 134.1, 131.3, 131.1, 129.5, 129.4, 128.8, 128.6, 128.2, 127.0, 124.0 (d, $J_{\text{C-F}} = 8.5$ Hz), 115.9 (d, $J_{\text{C-F}} = 22.9$ Hz), 111.3 (d, $J_{\text{C-F}} = 24.1$ Hz), 62.0. ^{19}F NMR (470 MHz, CDCl_3) δ -113.60. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{NaFOSe}$ $[\text{M} + \text{Na}]^+$ 467.0322, found 467.0323.

6'-Chloro-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3x**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (45.6 mg, 83% yield). Mp 137-138 °C. IR 3831, 3364, 2938, 1663, 1428, 737 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.31 (m, 7H), 7.27 – 7.20 (m, 4H), 7.16 (dd, $J = 11.9, 5.0$ Hz,

2H), 6.60 (d, $J = 10.1$ Hz, 2H), 6.53 (d, $J = 10.1$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.6, 151.9, 147.0, 143.7, 142.6, 134.0, 133.2, 131.4, 131.3, 131.1, 129.4, 129.3, 129.1, 128.9, 128.5, 128.2, 127.1, 123.9, 62.0. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{ClNaOSe}$ $[\text{M} + \text{Na}]^+$ 483.0024, found 483.0027.

2'-Phenyl-3'-(phenylselanyl)-6'-(trifluoromethyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3y). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (52.9 mg, 89% yield). Mp 149-150 °C. IR 3952, 3886, 3772, 1641, 1333, 1171, 1166, 737, 686 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.57 – 7.53 (m, 1H), 7.38 (d, $J = 19.2$ Hz, 9H), 7.23 (dd, $J = 5.1, 1.8$ Hz, 3H), 6.62 – 6.54 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.4, 154.5, 148.5, 146.5, 141.8, 133.8, 131.7, 131.5, 131.2, 129.5, 129.4, 129.20, 129.19, 128.5, 128.3, 127.3, 126.2 (q, $J_{\text{C-F}} = 3.8$ Hz), 123.2, 122.9, 120.4 (q, $J_{\text{C-F}} = 3.7$ Hz), 62.0. ^{19}F NMR (470 MHz, CDCl_3) δ -61.77. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{F}_3\text{NaOSe}$ $[\text{M} + \text{Na}]^+$ 517.0291, found 517.0305.

4-Oxo-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-diene-6'-carbonitrile (3z). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow solid (39 mg, 72% yield). Mp 160-162 °C. IR 3908, 3860, 3797, 3717, 1656, 866, 737 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.55 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.42 – 7.40 (m, 1H), 7.37 – 7.29 (m, 8H), 7.23 – 7.18 (m, 3H), 6.55 (s, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.1, 155.6, 149.5, 145.8, 142.1, 133.4, 133.1, 131.8, 131.2, 129.5, 129.4, 128.9, 128.4, 128.3, 127.4, 126.8, 123.5, 118.5, 110.5, 61.9. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{17}\text{NNaOSe}$ $[\text{M} + \text{Na}]^+$ 474.0369, found 474.0372.

6'-Nitro-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3a'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow solid (43.8 mg, 78% yield). Mp 178-179 °C. IR 3839, 3750, 3669, 3518, 3342, 2908, 1652, 1527 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.15 (dd, $J = 8.5, 2.1$ Hz, 1H), 7.99 (d, $J = 2.0$ Hz, 1H),

7.39 – 7.31 (m, 8H), 7.21 (d, $J = 6.2$ Hz, 3H), 6.57 (s, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.0, 157.1, 151.2, 146.9, 145.5, 142.4, 133.4, 132.0, 131.3, 131.2, 129.54, 129.48, 129.4, 128.8, 128.3, 127.5, 124.9, 123.1, 118.8, 61.9. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{NNaO}_3\text{Se}$ $[\text{M} + \text{Na}]^+$ 494.0267, found 494.0254.

7'-Methyl-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3b'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (35 mg, 66% yield). Mp 144-145 °C. IR 3827, 3761, 3577, 3485, 3364, 2931, 1667, 1427, 1171 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.13 (m, 12H), 7.03 (dd, $J = 6.6, 1.5$ Hz, 1H), 6.60 – 6.51 (m, 4H), 2.19 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.7, 151.4, 146.5, 145.4, 138.4, 135.1, 134.0, 133.1, 132.4, 130.9, 130.1, 129.5, 129.2, 128.9, 128.7, 128.5, 127.9, 126.7, 120.7, 62.7, 16.9. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{20}\text{NaOSe}$ $[\text{M} + \text{Na}]^+$ 463.0573, found 463.0570.

3-Methyl-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3c'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1, v/v) afforded the target compound as a yellow solid (35.1 mg, 67% yield). Mp 108-110 °C. IR 3823, 3353, 2927, 1645, 1432, 1072 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.20 (m, 11H), 7.18 – 7.16 (m, 2H), 7.12 (d, $J = 6.6$ Hz, 1H), 6.56 (dd, $J = 9.7, 2.8$ Hz, 1H), 6.47 (d, $J = 9.7$ Hz, 1H), 6.38 (d, $J = 1.2$ Hz, 1H), 1.94 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 186.6, 152.3, 147.6, 145.2, 142.8, 141.3, 137.6, 134.5, 131.5, 130.9, 130.7, 130.0, 129.3, 128.6, 128.5, 128.0, 127.0, 126.8, 123.3, 123.0, 62.5, 16.1. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{20}\text{NaOSe}$ $[\text{M} + \text{Na}]^+$ 463.0573, found 463.0563.

3-Chloro-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3d'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1, v/v) afforded the target compound as a yellow solid (39 mg, 71% yield). Mp 102-103 °C. IR 3911, 3805, 3673, 1693, 1531 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.33 (m, 5H), 7.30 (dd, $J = 6.9, 2.0$ Hz, 4H), 7.23 – 7.18 (m, 5H),

6.81 (d, $J = 2.5$ Hz, 1H), 6.62 (dd, $J = 9.7, 2.5$ Hz, 1H), 6.58 (d, $J = 9.7$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 178.9, 150.3, 148.1, 145.2, 143.6, 139.6, 134.5, 133.8, 133.0, 131.2, 130.1, 129.5, 129.3, 129.2, 128.9, 128.5, 128.3, 127.4, 127.0, 123.5, 123.3, 63.9. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{ClNaOSe}$ $[\text{M} + \text{Na}]^+$ 483.0024, found 483.0039.

2-Methyl-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3e'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1, v/v) afforded the target compound as a yellow solid (38 mg, 72% yield). Mp 104-106 °C. IR 3698, 3485, 3371, 3213, 3092, 2920, 1652, 752 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.16 (m, 13H), 7.06 (s, 1H), 6.50 (dd, $J = 22.5, 9.2$ Hz, 2H), 6.39 (s, 1H), 1.55 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 186.9, 157.4, 151.8, 148.8, 145.7, 142.4, 134.1, 132.4, 131.0, 130.3, 130.0, 129.8, 129.3, 128.8, 128.7, 128.3, 128.2, 127.3, 126.9, 123.1, 122.7, 64.9, 18.9. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{20}\text{NaOSe}$ $[\text{M} + \text{Na}]^+$ 463.0573, found 463.0570.

2-Chloro-2'-phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3f'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1, v/v) afforded the target compound as a yellow solid (49.7 mg, 90% yield). Mp 115-117 °C. IR 3893, 3735, 3540, 3357, 2920, 1637 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.26 (m, 11H), 7.22 – 7.20 (m, 2H), 7.17 (dd, $J = 5.8, 3.2$ Hz, 1H), 6.70 (d, $J = 1.4$ Hz, 1H), 6.59 (d, $J = 9.7$ Hz, 1H), 6.50 (dd, $J = 9.7, 1.4$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 185.0, 153.9, 150.3, 147.7, 145.6, 141.1, 134.0, 133.5, 131.6, 131.0, 129.8, 129.3, 129.2, 128.9, 128.6, 128.2, 127.5, 126.8, 123.2, 122.7, 66.1. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{17}\text{ClNaOSe}$ $[\text{M} + \text{Na}]^+$ 483.0024, found 483.0025.

(2'-Phenyl-3'-(p-tolylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3ab). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (40.7 mg, 77% yield). Mp 120-121 °C. IR 3853, 3658, 3375, 3169, 2931, 1637, 1450, 1270, 737 cm^{-1} . ^1H NMR

(500 MHz, CDCl₃) δ 7.34 – 7.31 (m, 2H), 7.31 – 7.28 (m, 3H), 7.28 – 7.25 (m, 2H), 7.25 – 7.22 (m, 3H), 7.14 (d, J = 6.8 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.60 – 6.56 (m, 2H), 6.51 – 6.46 (m, 2H), 2.27 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.9, 151.0, 148.1, 145.4, 140.7, 136.9, 134.4, 132.5, 131.3, 130.9, 130.1, 128.8, 128.7, 128.6, 128.1, 127.1, 125.8, 123.4, 123.1, 62.2, 21.0. HRMS (ESI) calcd for C₂₇H₂₀NaOSe [M + Na]⁺ 463.0573, found 463.0576.

3'-((4-Methoxyphenyl)selanyl)-2'-phenylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3ac). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow solid (29.8 mg, 55% yield). Mp 141-142 °C. IR 3834, 3739, 3573, 3313, 2912, 1648, 1468, 1255, 719 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.31 (s, 6H), 7.29 (d, J = 2.2 Hz, 1H), 7.28 (dd, J = 6.5, 1.2 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.13 (d, J = 7.2 Hz, 1H), 6.75 – 6.70 (m, 2H), 6.59 – 6.54 (m, 2H), 6.50 – 6.45 (m, 2H), 3.75 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 186.0, 159.2, 150.1, 148.2, 145.5, 140.8, 134.5, 133.7, 133.3, 130.9, 128.7, 128.6, 128.5, 128.1, 127.0, 123.4, 122.9, 119.3, 115.0, 62.2, 55.2. HRMS (ESI) calcd for C₂₇H₂₀NaO₂Se [M + Na]⁺ 479.0522, found 479.0533.

3'-((4-Chlorophenyl)selanyl)-2'-phenylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3ad). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (40 mg, 73% yield). Mp 147-148 °C. IR 3886, 3357, 2920, 1649, 1439, 715 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.22 (m, 10H), 7.18 – 7.12 (m, 3H), 6.58 (d, J = 10.1 Hz, 2H), 6.49 (d, J = 10.1 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.9, 151.9, 147.7, 144.9, 140.8, 134.1, 133.1, 132.3, 131.9, 131.1, 129.5, 128.9, 128.8, 128.5, 128.1, 127.9, 127.3, 123.7, 122.8, 62.2. HRMS (ESI) calcd for C₂₆H₁₇ClNaOSe [M + Na]⁺ 483.0024, found 483.0018.

3'-((4-Bromophenyl)selanyl)-2'-phenylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3ae). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (42.7 mg, 71%

yield). Mp 152-153 °C. IR 3908, 3709, 3588, 3291, 2908, 1674, 1439 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.24 (m, 10H), 7.20 – 7.14 (m, 3H), 6.58 (d, *J* = 10.0 Hz, 2H), 6.50 (d, *J* = 10.0 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.9, 152.1, 147.7, 144.9, 140.8, 134.1, 132.5, 132.3, 131.7, 131.1, 128.9, 128.8, 128.7, 128.5, 128.2, 127.4, 123.6, 122.9, 121.0, 62.2. HRMS (ESI) calcd for C₂₆H₁₇BrNaOSe [M + Na]⁺ 526.9519, found 526.9524.

4-((4-Oxo-2'-phenylspiro[cyclohexane-1,1'-indene]-2,5-dien-3'-yl)selanyl)benzotrile (3af). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow solid (39.2 mg, 73% yield). Mp 163-165 °C. IR 3820, 3735, 2923, 1660, 1516 cm⁻¹. ¹H NMR (500 MHz, DMSO) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.30 (m, 7H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 1H), 6.91 (d, *J* = 10.0 Hz, 2H), 6.47 (d, *J* = 9.9 Hz, 2H). ¹³C{¹H} NMR (126 MHz, DMSO) δ 185.0, 154.8, 147.9, 144.1, 141.1, 138.1, 133.9, 132.8, 130.7, 129.9, 129.4, 128.9, 128.8, 128.4, 128.0, 127.6, 123.8, 122.1, 118.6, 108.8, 62.0. HRMS (ESI) calcd for C₂₇H₁₇NNaOSe [M + Na]⁺ 474.0369, found 474.0367.

3'-((4-Nitrophenyl)selanyl)-2'-phenylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3ag). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow solid (34.3 mg, 61% yield). Mp 155-156 °C. IR 3878, 3750, 3346, 2912, 1645, 730 cm⁻¹. ¹H NMR (500 MHz, DMSO) δ 8.05 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 8.9 Hz, 2H), 7.40 – 7.31 (m, 7H), 7.23 (dd, *J* = 17.3, 6.9 Hz, 2H), 6.94 (d, *J* = 10.0 Hz, 2H), 6.47 (d, *J* = 9.9 Hz, 2H). ¹³C{¹H} NMR (126 MHz, DMSO) δ 185.0, 155.2, 147.8, 145.8, 144.1, 141.2, 141.0, 133.9, 130.7, 129.8, 129.4, 129.1, 128.8, 128.4, 128.1, 127.7, 124.1, 123.8, 122.1, 62.1. HRMS (ESI) calcd for C₂₆H₁₇NNaO₃Se [M + Na]⁺ 494.0267, found 494.0258.

2'-Phenyl-3'-(m-tolylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3ah). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate =

20:1, v/v) afforded the target compound as a yellow solid (44 mg, 83% yield). Mp 129-130 °C. IR 3658, 2908, 1656, 1450 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.23 (m, 8H), 7.20 – 7.11 (m, 2H), 7.10 (d, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 10.0 Hz, 2H), 6.49 (d, *J* = 10.0 Hz, 2H), 2.25 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.9, 151.3, 148.1, 145.4, 140.7, 139.0, 134.4, 132.3, 131.7, 130.9, 129.5, 129.1, 128.8, 128.6, 128.5, 128.1, 128.0, 127.8, 127.1, 123.4, 123.1, 62.3, 21.3. HRMS (ESI) calcd for C₂₇H₂₀NaOSe [M + Na]⁺ 463.0573, found 463.0578.

3'-((3-Fluorophenyl)selanyl)-2'-phenylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3ai). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (32.5 mg, 61% yield). Mp 135-136 °C. IR 3860, 3753, 3338, 2905, 1656, 1487, 756 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.26 (m, 8H), 7.18 – 7.12 (m, 2H), 7.10 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.01 (ddd, *J* = 8.7, 2.4, 1.6 Hz, 1H), 6.87 (tdd, *J* = 9.3, 2.5, 1.1 Hz, 1H), 6.61 – 6.57 (m, 2H), 6.52 – 6.49 (m, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.9, 162.7 (d, *J*_{C-F} = 250.0 Hz), 152.5, 147.7, 144.9, 140.8, 134.1, 131.7, 131.5, 131.1, 130.5 (d, *J*_{C-F} = 8.2 Hz), 130.4, 128.9, 128.5, 128.2, 127.4, 126.3 (d, *J*_{C-F} = 3.1 Hz), 123.6, 122.9, 117.7 (d, *J*_{C-F} = 22.9 Hz), 113.9 (d, *J*_{C-F} = 21.2 Hz), 62.3. ¹⁹F NMR (470 MHz, CDCl₃) δ -111.41. HRMS (ESI) calcd for C₂₆H₁₇NaFOSe [M + Na]⁺ 467.0322, found 467.0327.

3'-((3-Chlorophenyl)selanyl)-2'-phenylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3aj). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (44.2 mg, 80% yield). Mp 142-144 °C. IR 3871, 3728, 3551, 3353, 2920, 1674, 1520, 1061, 881, 697 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.24 (m, 9H), 7.19 – 7.12 (m, 3H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.59 (d, *J* = 10.1 Hz, 2H), 6.50 (d, *J* = 10.1 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.8, 152.3, 147.7, 144.9, 140.8, 134.9, 134.0, 131.5, 131.4,

131.2, 130.6, 130.2, 129.3, 128.9, 128.8, 128.5, 128.1, 127.4, 127.1, 123.6, 122.8, 62.3. HRMS (ESI) calcd for C₂₆H₁₇ClNaOSe [M + Na]⁺ 483.0024, found 483.0030.

2'-Phenyl-3'-(o-tolylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3ak**).

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (47.5 mg, 90% yield). Mp 150-151 °C. IR 3889, 3856, 3797, 3727, 1667, 1457, 1274, 862, 756 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.31 (m, 2H), 7.29 (dd, J = 5.8, 4.3 Hz, 3H), 7.25 (dt, J = 6.2, 2.2 Hz, 2H), 7.23 – 7.20 (m, 1H), 7.18 – 7.13 (m, 3H), 7.12 – 7.08 (m, 1H), 6.95 (dd, J = 10.7, 4.1 Hz, 1H), 6.60 (t, J = 6.2 Hz, 2H), 6.50 (t, J = 6.2 Hz, 2H), 2.37 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.9, 151.6, 148.0, 145.3, 140.7, 138.3, 134.3, 132.1, 131.0, 130.9, 130.5, 130.3, 128.9, 128.7, 128.4, 128.1, 127.2, 126.9, 126.7, 123.5, 122.9, 62.3, 21.9. HRMS (ESI) calcd for C₂₇H₂₀NaOSe [M + Na]⁺ 463.0573, found 463.0574.

3'-((2-Fluorophenyl)selanyl)-2'-phenylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one

(**3al**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (28 mg, 53% yield). Mp 145-146 °C. IR 3878, 3735, 3665, 3562, 3335, 2901, 1663, 1531, 726 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.24 (m, 8H), 7.21 – 7.14 (m, 3H), 7.02 – 6.97 (m, 1H), 6.95 – 6.91 (m, 1H), 6.59 (d, J = 10.1 Hz, 2H), 6.50 (d, J = 10.1 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.9, 160.9 (d, J_{C-F} = 244.1 Hz), 152.2, 147.8, 145.1, 140.7, 134.2, 132.6 (d, J_{C-F} = 3.0 Hz), 131.1, 130.7 (d, J_{C-F} = 2.1 Hz), 128.98, 128.91, 128.8, 128.5, 128.1, 127.3, 124.9 (d, J_{C-F} = 3.4 Hz), 123.5, 122.7, 116.5 (d, J_{C-F} = 21.8 Hz), 115.7 (d, J_{C-F} = 22.6 Hz), 62.3. ¹⁹F NMR (470 MHz, CDCl₃) δ -104.44. HRMS (ESI) calcd for C₂₆H₁₇NaFOSe [M + Na]⁺ 467.0322, found 467.0322.

3'-((2-Chlorophenyl)selanyl)-2'-phenylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one

(**3am**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (25.5 mg, 46% yield). Mp 139-140 °C. IR 3860, 3761, 3669, 3540, 3338, 3169, 2905, 1630, 1424,

756 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.24 (m, 9H), 7.19 (d, *J* = 6.7 Hz, 1H), 7.14 – 7.09 (m, 1H), 7.07 – 7.04 (m, 1H), 7.02 – 6.97 (m, 1H), 6.63 (d, *J* = 10.1 Hz, 2H), 6.52 (d, *J* = 10.0 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 185.9, 153.6, 147.8, 144.9, 140.9, 134.1, 134.0, 131.1, 130.7, 130.6, 129.7, 129.0, 128.9, 128.3, 128.2, 127.6, 127.5, 127.3, 123.6, 122.9, 62.4. HRMS (ESI) calcd for C₂₆H₁₇ClNaOSe [M + Na]⁺ 483.0024, found 483.0026.

3'-(Naphthalen-1-ylselanyl)-2'-phenylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3an**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow solid (22.4 mg, 39% yield). Mp 165-167 °C. IR 3797, 3684, 3364, 2920, 1637, 1450, 737 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.84 (s, 1H), 7.77 – 7.71 (m, 1H), 7.65 (dd, *J* = 13.4, 5.5 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.38 – 7.33 (m, 3H), 7.32 – 7.26 (m, 4H), 7.24 – 7.20 (m, 2H), 7.15 (dd, *J* = 5.6, 2.8 Hz, 1H), 6.62 (d, *J* = 10.0 Hz, 2H), 6.51 (d, *J* = 10.0 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 186.0, 151.7, 148.0, 145.4, 140.8, 134.3, 133.9, 132.2, 132.1, 131.0, 129.9, 128.9, 128.8, 128.7, 128.6, 128.1, 127.8, 127.3, 127.2, 126.6, 126.1, 123.5, 123.1, 62.3. HRMS (ESI) calcd for C₃₀H₂₀NaOSe [M + Na]⁺ 499.0574, found 499.0578.

3'-(Butylselanyl)-2'-phenylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3ao**). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow oil (45 mg, 93% yield). IR 3886, 3750, 3606, 3493, 3327, 2927, 1663, 1513, 1435, 1226, 741 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 7.5 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.39 – 7.36 (m, 2H), 7.33 – 7.29 (m, 3H), 7.28 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 6.55 – 6.51 (m, 2H), 6.48 – 6.42 (m, 2H), 2.67 – 2.60 (m, 2H), 1.50 (ddd, *J* = 14.9, 8.3, 6.5 Hz, 2H), 1.28 – 1.17 (m, 2H), 0.78 (t, *J* = 7.4 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 186.1, 148.7, 148.4, 146.4, 140.4, 134.8, 132.5, 130.9, 128.6, 128.4, 128.1, 127.1, 125.8, 123.5, 122.3, 62.4, 32.2, 26.7, 22.5, 13.4. HRMS (ESI) calcd for C₂₄H₂₂NaOSe [M + Na]⁺ 429.0729, found 429.0714.

General procedure for the synthesis of selenylated-phenanthrenes 4.

Aryl phenol-tethered alkyne **1** (0.12 mmol, 1.0 eq.), diselenide **2** (0.144 mmol, 1.2 eq.) and Cu(OTf)₂ (0.144 mmol, 1.2 eq., 52.1 mg) were added to a reaction tube successively under an air atmosphere, and then MeCN (0.1 M, 1.2 mL) was added via syringe. The mixture was heated in an oil bath at 80 °C for 12 h until reaction completion (monitored by TLC). After completion of the reaction, the mixture was cooled to room temperature. Then, the solvent was removed in a vacuum, and the resulting residue was purified on a silica gel column (petroleum ether/ethyl acetate = 10:1, v/v) to afford the product **4**.

10-Phenyl-9-(phenylselanyl)phenanthren-2-ol (4a). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow solid (49.9 mg, 98% yield). Mp 171-173 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.73 – 8.70 (m, 1H), 8.70 – 8.66 (m, 2H), 7.68 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.55 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.45 (dd, *J* = 4.9, 1.8 Hz, 3H), 7.28 – 7.24 (m, 3H), 7.09 (s, 5H), 6.84 (d, *J* = 2.7 Hz, 1H), 5.04 (s, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 154.1, 145.8, 141.9, 134.2, 133.6, 131.4, 130.7, 130.6, 129.6, 129.1, 128.9, 128.4, 128.0, 127.3, 127.1, 126.6, 125.5, 125.4, 124.6, 122.1, 117.4, 112.3. HRMS (ESI) calcd for C₂₆H₁₇OSe [M - H]⁻ 425.0450, found 425.0454.

9-(Phenylselanyl)-10-(p-tolyl)phenanthren-2-ol (4b). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (34.1 mg, 65% yield). IR 3827, 3728, 3526, 2934, 1656, 1502 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.63 (d, *J* = 9.0 Hz, 1H), 8.62 – 8.58 (m, 2H), 7.60 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.47 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.22 – 7.18 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.02 (s, 5H), 6.80 (d, *J* = 2.7 Hz, 1H), 4.87 (s, 1H), 2.42 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 154.1, 145.9, 139.0, 137.0, 134.3, 133.8, 131.4, 130.8, 130.7, 129.5, 129.1, 128.9, 128.8, 128.5, 127.1, 126.6,

125.54, 125.46, 124.6, 122.1, 117.3, 112.4, 21.4. HRMS (ESI) calcd for C₂₇H₁₉OSe [M - H]⁻ 439.0607, found 439.0609.

10-(4-Ethylphenyl)-9-(phenylselanyl)phenanthrene-2-ol (4c). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (34.8 mg, 64% yield). IR 3842, 3346, 2916, 1641, 734 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.63 (dd, *J* = 17.4, 8.7 Hz, 3H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 4H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.03 (s, 4H), 6.81 (s, 1H), 4.91 (s, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 154.1, 145.9, 143.2, 139.2, 134.3, 133.8, 131.4, 130.73, 130.65, 129.5, 129.2, 128.9, 128.6, 127.5, 127.1, 126.6, 125.5, 125.4, 124.6, 122.1, 117.3, 112.4, 28.6, 15.3. HRMS (ESI) calcd for C₂₈H₂₁OSe [M - H]⁻ 453.0763, found 453.0768.

10-(4-Methoxyphenyl)-9-(phenylselanyl)phenanthren-2-ol (4d). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1, v/v) afforded the target compound as a yellow solid (30 mg, 55% yield). Mp 110-111 °C. IR 3889, 3691, 3522, 3298, 3198, 1637, 1524, 969, 845, 737 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.66 (d, *J* = 8.9 Hz, 1H), 8.64 – 8.60 (m, 2H), 7.64 – 7.59 (m, 1H), 7.51 – 7.46 (m, 1H), 7.25 (s, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.03 (s, 4H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 2.2 Hz, 1H), 5.00 (s, 1H), 3.86 (s, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 158.8, 154.2, 145.5, 134.4, 134.3, 134.0, 131.5, 130.8, 130.7, 129.2, 129.0, 128.9, 127.1, 126.6, 125.6, 125.5, 124.6, 122.1, 117.4, 113.5, 112.4, 55.3. HRMS (ESI) calcd for C₂₇H₁₉O₂Se [M - H]⁻ 455.0556, found 455.0560.

10-(4-Fluorophenyl)-9-(phenylselanyl)phenanthren-2-ol (4e). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (27.8 mg, 52% yield). IR 3900, 3786, 1604, 1487, 1211, 726 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.64 (dd, *J* = 17.2, 8.4 Hz, 3H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.24 (q, *J* = 5.9, 4.2 Hz, 2H), 7.14 – 6.98 (m, 8H), 6.75 (d, *J* = 2.3 Hz, 1H), 5.00 (s, 1H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ

162.11 (d, J_{C-F} = 246.2 Hz), 154.2, 144.7, 137.7, 134.0, 133.6, 131.4, 131.3 (d, J_{C-F} = 7.9 Hz), 130.8, 130.7, 129.2, 129.1, 128.9, 127.3, 126.7, 125.6, 125.5, 124.7, 122.2, 117.5, 115.1 (d, J_{C-F} = 21.4 Hz), 112.1. ^{19}F NMR (470 MHz, CDCl_3) δ -114.64. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{16}\text{OFSe}$ [$\text{M} - \text{H}$] $^-$ 443.0356, found 443.0358.

10-(4-Chlorophenyl)-9-(phenylselanyl)phenanthren-2-ol (4f). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (33.6 mg, 61% yield). IR 3860, 3728, 3636, 2916, 1645, 1524, 752 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.63 (dd, J = 17.1, 8.5 Hz, 3H), 7.64 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 6.5 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 7.04 – 6.98 (m, 4H), 6.73 (d, J = 2.2 Hz, 1H), 5.02 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.2, 144.5, 140.2, 134.0, 133.4, 133.3, 131.4, 131.0, 130.8, 130.6, 129.2, 129.0, 128.7, 128.3, 127.4, 126.8, 125.7, 125.5, 124.7, 122.2, 117.6, 112.0. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{16}\text{OClSe}$ [$\text{M} - \text{H}$] $^-$ 459.0060, found 459.0062.

10-(4-Bromophenyl)-9-(phenylselanyl)phenanthren-2-ol (4g). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (44 mg, 73% yield). IR 3904, 3805, 1615, 1428, 1208, 730 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.69 (dd, J = 8.3, 0.9 Hz, 1H), 8.63 (dd, J = 15.3, 8.6 Hz, 2H), 7.64 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.28 (t, J = 1.7 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.12 – 7.09 (m, 1H), 7.06 – 7.03 (m, 3H), 7.02 – 6.98 (m, 2H), 6.72 (d, J = 2.6 Hz, 1H), 4.97 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.2, 144.1, 143.8, 133.9, 133.3, 132.7, 131.5, 130.8, 130.7, 130.4, 129.6, 129.5, 129.0, 128.4, 127.4, 126.8, 125.9, 125.5, 124.7, 122.2, 117.6, 112.0. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{16}\text{OBrSe}$ [$\text{M} - \text{H}$] $^-$ 502.9555, found 502.9557.

9-(Phenylselanyl)-10-(4-(trifluoromethyl)phenyl)phenanthren-2-ol (4h). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (45.2 mg, 76% yield). IR 3911, 3812, 3735, 1601, 1446, 1314, 1120, 737 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.74 – 8.57

(m, 3H), 7.65 (dd, $J = 16.5, 7.8$ Hz, 3H), 7.53 (t, $J = 7.1$ Hz, 1H), 7.32 – 7.20 (m, 3H), 7.00 (dd, $J = 30.7, 7.7$ Hz, 5H), 6.64 (d, $J = 2.6$ Hz, 1H), 5.00 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.3, 145.4, 144.2, 133.8, 133.4, 133.1, 131.4, 130.8, 130.6, 130.1, 129.6, 129.3, 129.0, 128.7, 127.6, 126.8, 125.8, 125.7, 125.0 (dd, $J_{\text{C-F}} = 7.4, 3.7$ Hz), 124.8, 122.2, 117.6, 111.8. ^{19}F NMR (470 MHz, CDCl_3) δ -62.28. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{16}\text{OF}_3\text{Se}$ $[\text{M} - \text{H}]^-$ 493.0324, found 493.0327.

10-(4-Nitrophenyl)-9-(phenylselanyl)phenanthren-2-ol (4i). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1, v/v) afforded the target compound as a yellow solid (49 mg, 87% yield). Mp 124-126 °C. IR 3926, 3834, 3651, 3559, 3342, 3188, 2927, 1637, 1624, 730 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.72 – 8.64 (m, 3H), 8.23 (d, $J = 8.6$ Hz, 2H), 7.73 – 7.66 (m, 1H), 7.60 – 7.51 (m, 1H), 7.33 (d, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 8.6$ Hz, 1H), 7.25 (s, 1H), 7.07 – 7.04 (m, 2H), 6.96 (dq, $J = 6.5, 2.3$ Hz, 2H), 6.62 (d, $J = 1.9$ Hz, 1H), 5.18 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.5, 148.7, 147.1, 143.4, 133.6, 132.7, 131.3, 130.9, 130.8, 130.5, 129.2, 129.1, 128.5, 127.8, 127.0, 126.0, 125.6, 125.0, 123.4, 122.3, 117.9, 111.5. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{16}\text{O}_3\text{NSe}$ $[\text{M} - \text{H}]^-$ 470.0301, found 470.0302.

*9-(Phenylselanyl)-10-(*m*-tolyl)phenanthren-2-ol (4j)*. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (40.9 mg, 78% yield). IR 3785, 3366, 2918, 1649, 1452, 1192, 734 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.63 (dd, $J = 15.9, 8.5$ Hz, 3H), 7.62 (t, $J = 7.5$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.29 (t, $J = 7.6$ Hz, 1H), 7.23 – 7.20 (m, 2H), 7.03 (s, 6H), 6.95 (s, 1H), 6.79 (d, $J = 2.1$ Hz, 1H), 4.90 (s, 1H), 2.32 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.1, 145.9, 141.8, 137.6, 134.4, 133.7, 131.5, 130.7, 130.6, 130.4, 129.4, 128.9, 128.5, 128.1, 127.9, 127.1, 126.7, 126.6, 125.5, 124.6, 122.1, 117.4, 112.4, 21.5. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{19}\text{OSe}$ $[\text{M} - \text{H}]^-$ 439.0607, found 439.0604.

10-(3-Fluorophenyl)-9-(phenylselanyl)phenanthren-2-ol (4k). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (47.2 mg, 89% yield). IR 3889, 3801, 3735, 1612, 1435, 1219, 726 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.64 (dd, $J = 17.6, 8.5$ Hz, 3H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.36 (q, $J = 7.7$ Hz, 1H), 7.24 (d, $J = 4.9$ Hz, 2H), 7.13 – 7.07 (m, 1H), 7.05 – 7.01 (m, 4H), 6.97 (d, $J = 7.5$ Hz, 1H), 6.89 (d, $J = 9.3$ Hz, 1H), 6.75 (d, $J = 2.2$ Hz, 1H), 4.95 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 162.6 (d, $J_{\text{C-F}} = 246.8$ Hz), 154.2, 144.4, 143.9 (d, $J_{\text{C-F}} = 7.9$ Hz), 133.9, 133.3, 131.4, 130.8, 130.7, 129.7, 129.6, 129.3, 129.0, 128.7, 127.4, 126.8, 125.8, 125.6, 124.7, 122.2, 117.6, 116.9 (d, $J_{\text{C-F}} = 21.4$ Hz), 114.3 (d, $J_{\text{C-F}} = 20.9$ Hz), 112.0. ^{19}F NMR (470 MHz, CDCl_3) δ -113.15. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{16}\text{OFSe}$ [$\text{M} - \text{H}$] $^-$ 443.0356, found 443.0357.

10-(3-Chlorophenyl)-9-(phenylselanyl)phenanthren-2-ol (4l). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (42.7 mg, 77% yield). IR 3917, 3814, 3614, 2908, 1649, 1539, 710 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.72 – 8.57 (m, 3H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.38 (d, $J = 8.1$ Hz, 1H), 7.31 (t, $J = 7.8$ Hz, 1H), 7.24 (s, 1H), 7.13 (s, 1H), 7.08 – 6.96 (m, 6H), 6.73 (d, $J = 1.9$ Hz, 1H), 4.96 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.2, 144.2, 143.5, 134.0, 133.9, 133.3, 131.4, 130.8, 130.7, 129.9, 129.5, 129.4, 129.1, 129.0, 128.0, 127.5, 127.4, 126.8, 125.8, 125.5, 124.7, 122.2, 117.6, 112.0. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{16}\text{OClSe}$ [$\text{M} - \text{H}$] $^-$ 459.0060, found 459.0063.

10-(3-Bromophenyl)-9-(phenylselanyl)phenanthren-2-ol (4m). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (41.4 mg, 68% yield). IR 3678, 3362, 3199, 2922, 1632, 1455, 1216, 717 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.62 – 8.48 (m, 3H), 7.58 – 7.51 (m, 1H), 7.47 – 7.37 (m, 3H), 7.17 – 7.13 (m, 1H), 6.93 (ddd, $J = 25.2, 6.9, 3.3$ Hz, 7H), 6.65 (d, $J = 2.6$ Hz, 1H), 4.91 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ

154.2, 144.5, 140.7, 134.0, 133.3, 131.4, 131.3, 130.8, 130.6, 129.6, 129.2, 129.0, 128.7, 128.4, 127.4, 126.8, 125.9, 125.7, 125.6, 124.8, 122.2, 121.5, 117.6, 112.0. HRMS (ESI) calcd for C₂₆H₁₆OBrSe [M - H]⁻ 502.9555, found 502.9557.

10-(2-Fluorophenyl)-9-(phenylselanyl)phenanthren-2-ol (4n). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (47.1 mg, 89% yield). IR 3805, 1615, 1446, 1200, 737 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.72 – 8.63 (m, 3H), 7.70 – 7.65 (m, 1H), 7.57 – 7.50 (m, 1H), 7.49 – 7.42 (m, 1H), 7.29 – 7.27 (m, 1H), 7.24 – 7.16 (m, 3H), 7.15 – 7.04 (m, 5H), 6.82 (d, *J* = 1.9 Hz, 1H), 5.04 (s, 1H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 159.95 (d, *J*_{C-F} = 245.6 Hz), 154.4, 139.7, 133.5, 133.2, 131.9 (d, *J*_{C-F} = 3.2 Hz), 131.4, 131.1, 130.7, 130.1, 129.7 (d, *J*_{C-F} = 7.9 Hz), 129.6, 129.3 (d, *J*_{C-F} = 17.0 Hz), 129.0, 127.5, 126.7, 125.8, 125.6, 124.8, 123.9 (d, *J*_{C-F} = 3.5 Hz), 122.3, 117.7, 115.7 (d, *J*_{C-F} = 21.8 Hz), 111.5. ¹⁹F NMR (470 MHz, CDCl₃) δ -113.23. HRMS (ESI) calcd for C₂₆H₁₆OFSe [M - H]⁻ 443.0356, found 443.0357.

10-(2-Chlorophenyl)-9-(phenylselanyl)phenanthren-2-ol (4o). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (43.8 mg, 79% yield). IR 3854, 3730, 3615, 3470, 2904, 1656, 1521, 1206, 849, 752 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.69 – 8.56 (m, 3H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.40 – 7.33 (m, 1H), 7.29 – 7.23 (m, 2H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.09 – 7.00 (m, 5H), 6.65 (d, *J* = 2.2 Hz, 1H), 4.93 (s, 1H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 154.4, 142.9, 140.5, 134.2, 133.5, 132.8, 131.4, 131.3, 131.0, 130.6, 129.6, 129.4, 129.2, 129.1, 128.9, 127.4, 126.61, 126.59, 125.7, 125.6, 124.8, 122.3, 117.6, 111.4. HRMS (ESI) calcd for C₂₆H₁₆OClSe [M - H]⁻ 459.0060, found 459.0062.

7-Methyl-10-phenyl-9-(phenylselanyl)phenanthren-2-ol (4p). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (38.7 mg, 73% yield). IR 3854, 3740, 3605, 2915, 1646, 1525, 1205, 800 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.65 (d, *J* = 9.0 Hz, 1H),

8.58 – 8.45 (m, 2H), 7.54 – 7.39 (m, 4H), 7.30 – 7.17 (m, 3H), 7.08 (s, 5H), 6.79 (d, $J = 2.6$ Hz, 1H), 4.95 (s, 1H), 2.50 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 153.8, 145.7, 142.0, 136.3, 134.4, 133.2, 131.6, 130.1, 129.7, 129.3, 128.9, 128.9, 128.6, 128.3, 128.0, 127.3, 125.6, 125.5, 124.4, 122.1, 117.4, 112.3, 21.6. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{19}\text{OSe}$ $[\text{M} - \text{H}]^-$ 439.0607, found 439.0608.

7-Chloro-10-phenyl-9-(phenylselanyl)phenanthren-2-ol (4q). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (42 mg, 76% yield). IR 3879, 3695, 3542, 3345, 3189, 2929, 1643, 1462, 727 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.68 (d, $J = 1.8$ Hz, 1H), 8.55 (dd, $J = 23.4, 8.9$ Hz, 2H), 7.56 (dd, $J = 8.8, 1.9$ Hz, 1H), 7.40 (d, $J = 5.4$ Hz, 3H), 7.23 (d, $J = 5.9$ Hz, 2H), 7.19 – 7.12 (m, 2H), 7.08 – 6.96 (m, 4H), 6.76 (d, $J = 2.0$ Hz, 1H), 4.92 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.4, 147.0, 141.6, 133.64, 133.60, 132.9, 132.6, 129.8, 129.5, 129.1, 129.0, 128.1, 127.64, 127.61, 127.5, 125.9, 125.1, 124.6, 123.9, 117.8, 112.5. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{16}\text{OClSe}$ $[\text{M} - \text{H}]^-$ 459.0060, found 459.0061.

6-Methyl-10-phenyl-9-(phenylselanyl)phenanthren-2-ol (4r). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (37.6 mg, 71% yield). IR 3899, 3747, 2929, 2693, 1643, 1466, 731 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.64 (d, $J = 9.0$ Hz, 1H), 8.50 (d, $J = 8.4$ Hz, 1H), 8.40 (s, 1H), 7.39 (dd, $J = 4.9, 1.8$ Hz, 3H), 7.31 (dd, $J = 8.5, 1.2$ Hz, 1H), 7.20 (td, $J = 8.3, 7.5, 3.4$ Hz, 3H), 7.02 (s, 5H), 6.74 (d, $J = 2.5$ Hz, 1H), 4.88 (s, 1H), 2.58 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.0, 144.8, 142.0, 137.0, 134.3, 133.8, 130.8, 130.5, 129.7, 129.4, 129.2, 128.9, 128.4, 128.3, 128.0, 127.3, 125.4, 125.3, 124.6, 122.0, 117.2, 112.3, 21.9. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{19}\text{OSe}$ $[\text{M} - \text{H}]^-$ 439.0607, found 439.0608.

6-Chloro-10-phenyl-9-(phenylselanyl)phenanthren-2-ol (4s). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (42.3 mg, 77% yield). IR 3915, 3786, 3731, 3654,

1608, 1483, 1424, 1204, 1083, 1020, 826, 734 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.54 (dd, $J = 8.9, 6.8$ Hz, 3H), 7.40 (dq, $J = 5.9, 2.0$ Hz, 4H), 7.22 – 7.16 (m, 3H), 7.07 – 6.96 (m, 5H), 6.76 (d, $J = 2.5$ Hz, 1H), 5.00 (br, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.7, 146.0, 141.6, 134.0, 133.9, 133.4, 132.4, 131.8, 129.8, 129.6, 129.2, 129.0, 128.1, 128.0, 127.5, 127.0, 125.7, 124.7, 124.5, 121.8, 117.7, 112.5. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{16}\text{OClSe}$ [$\text{M} - \text{H}$] $^-$ 459.0060, found 459.0063.

7-Hydroxy-9-phenyl-10-(phenylselanyl)phenanthrene-3-carbonitrile (4t). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1, v/v) afforded the target compound as a yellow solid (38.8 mg, 72% yield). Mp 170-171 $^\circ\text{C}$. IR 3879, 3376, 2918, 1636, 1452, 1223, 1025, 713 cm^{-1} . ^1H NMR (500 MHz, DMSO) δ 10.09 (s, 1H), 9.37 – 9.30 (m, 1H), 8.92 (d, $J = 9.1$ Hz, 1H), 8.55 (d, $J = 8.6$ Hz, 1H), 7.80 (dd, $J = 8.6, 1.4$ Hz, 1H), 7.53 – 7.40 (m, 3H), 7.34 – 7.23 (m, 3H), 7.16 – 6.97 (m, 5H), 6.73 (d, $J = 2.5$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 157.3, 149.1, 141.2, 133.7, 132.9, 132.6, 130.9, 130.7, 129.4, 129.0, 128.7, 128.2, 127.64, 127.57, 126.3, 126.0, 125.5, 123.0, 119.2, 119.1, 111.8, 109.7. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{16}\text{ONSe}$ [$\text{M} - \text{H}$] $^-$ 450.0403, found 450.0408.

5-Methyl-10-phenyl-9-(phenylselanyl)phenanthren-2-ol (4u). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (22 mg, 42% yield). IR 3854, 3736, 3355, 3203, 2911, 1646, 1445, 727 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.83 (d, $J = 9.2$ Hz, 1H), 8.73 – 8.66 (m, 1H), 7.54 (d, $J = 7.0$ Hz, 1H), 7.47 – 7.39 (m, 4H), 7.26 – 7.19 (m, 3H), 7.06 (dq, $J = 5.7, 3.4, 2.9$ Hz, 5H), 6.86 (d, $J = 2.7$ Hz, 1H), 4.98 (s, 1H), 3.17 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 153.3, 145.8, 142.3, 135.0, 134.5, 134.2, 132.7, 131.9, 131.0, 129.6, 129.5, 129.3, 129.2, 129.1, 128.9, 128.1, 127.3, 126.6, 125.8, 125.4, 115.6, 112.5, 27.3. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{19}\text{OSe}$ [$\text{M} - \text{H}$] $^-$ 439.0607, found 439.0609.

3-Methyl-10-phenyl-9-(phenylselanyl)phenanthren-2-ol (4v). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the

target compound as a yellow oil (32.4 mg, 61% yield). IR 3896, 3830, 3733, 3594, 3497, 3352, 2922, 1646, 1528, 720 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.66 – 8.58 (m, 2H), 8.52 (s, 1H), 7.65 – 7.56 (m, 1H), 7.49 – 7.44 (m, 1H), 7.40 (dd, $J = 5.0, 1.9$ Hz, 3H), 7.21 – 7.15 (m, 2H), 7.02 (d, $J = 1.4$ Hz, 5H), 6.70 (s, 1H), 4.85 (s, 1H), 2.50 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 153.1, 145.7, 142.2, 134.4, 132.1, 131.5, 130.6, 130.5, 129.6, 129.2, 129.1, 128.9, 128.0, 127.3, 127.1, 126.9, 126.6, 126.5, 125.6, 125.4, 124.9, 122.2, 111.8, 16.7. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{19}\text{OSe}$ $[\text{M} - \text{H}]^-$ 439.0607, found 439.0609.

3-Chloro-10-phenyl-9-(phenylselanyl)phenanthren-2-ol (4w). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (36.5 mg, 66% yield). IR 3896, 3712, 3504, 3359, 2929, 1639, 1438, 707 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.65 (s, 1H), 8.56 (d, $J = 8.2$ Hz, 1H), 8.47 (d, $J = 8.2$ Hz, 1H), 7.57 (t, $J = 8.2$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.35 (dd, $J = 5.0, 1.8$ Hz, 3H), 7.18 (s, 1H), 7.11 (dd, $J = 6.4, 3.1$ Hz, 2H), 6.96 (tt, $J = 6.9, 3.8$ Hz, 5H), 5.57 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 149.6, 145.6, 141.5, 134.0, 132.7, 131.7, 130.8, 129.7, 129.5, 129.3, 129.0, 128.9, 128.2, 127.5, 127.4, 127.2, 126.1, 125.6, 123.3, 122.2, 122.1, 113.8. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{16}\text{OClSe}$ $[\text{M} - \text{H}]^-$ 459.0060, found 459.0064.

4-Methyl-10-phenyl-9-(phenylselanyl)phenanthren-2-ol (4x). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (35.9 mg, 68% yield). IR 3868, 3730, 3646, 3535, 3449, 3355, 2918, 1636, 1455, 717 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.76 – 8.65 (m, 2H), 7.64 – 7.52 (m, 1H), 7.48 (ddd, $J = 8.1, 7.0, 1.1$ Hz, 1H), 7.39 (dd, $J = 5.0, 1.8$ Hz, 3H), 7.20 – 7.15 (m, 2H), 7.10 (d, $J = 2.0$ Hz, 1H), 7.02 (s, 5H), 6.68 (d, $J = 2.5$ Hz, 1H), 4.81 (s, 1H), 3.11 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 152.7, 146.3, 142.7, 137.5, 135.3, 134.2, 132.4, 131.9, 130.5, 129.7, 129.2, 128.9, 128.6, 128.1, 127.3, 126.9, 126.0, 125.9, 125.8, 125.5, 121.4, 111.2, 27.3. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{19}\text{OSe}$ $[\text{M} - \text{H}]^-$ 439.0607, found 439.0609.

4-Chloro-10-phenyl-9-(phenylselanyl)phenanthren-2-ol (4y). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (44 mg, 80% yield). IR 3906, 3820, 3736, 3504, 3359, 2929, 1646, 1431, 1275, 745 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 9.76 – 9.64 (m, 1H), 8.69 (dd, $J = 8.3, 1.2$ Hz, 1H), 7.60 (ddd, $J = 8.5, 6.9, 1.4$ Hz, 1H), 7.51 (ddd, $J = 8.2, 7.0, 1.1$ Hz, 1H), 7.41 – 7.35 (m, 3H), 7.33 (d, $J = 2.6$ Hz, 1H), 7.17 – 7.12 (m, 2H), 7.05 – 6.98 (m, 5H), 6.74 (d, $J = 2.7$ Hz, 1H), 4.98 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 152.6, 145.3, 142.1, 136.0, 133.9, 132.4, 132.3, 130.4, 130.3, 130.0, 129.7, 129.4, 129.0, 128.2, 127.5, 127.0, 126.6, 126.1, 125.7, 123.0, 120.9, 112.5. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{16}\text{OClSe}$ $[\text{M} - \text{H}]^-$ 459.0060, found 459.0063.

9-(Phenylselanyl)-10-(thiophen-2-yl)phenanthren-2-ol (4z). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (33.1 mg, 64% yield). IR 3906, 3743, 3632, 3490, 3348, 3206, 2922, 1636, 1435, 693 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.67 – 8.55 (m, 4H), 7.64 – 7.60 (m, 1H), 7.49 – 7.41 (m, 2H), 7.11 (dd, $J = 5.1, 3.4$ Hz, 1H), 7.09 – 7.02 (m, 5H), 7.00 (d, $J = 2.6$ Hz, 1H), 6.92 (dd, $J = 3.4, 1.0$ Hz, 1H), 4.98 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.4, 142.6, 138.1, 134.3, 134.2, 132.1, 131.2, 130.9, 129.3, 129.0, 128.2, 127.7, 126.7, 126.6, 125.8, 125.7, 125.4, 124.6, 122.2, 117.6, 112.1. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{15}\text{OSSe}$ $[\text{M} - \text{H}]^-$ 431.0014, found 431.0015.

10-Butyl-9-(phenylselanyl)phenanthren-2-ol (4a'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow oil (20.9 mg, 43% yield). IR 3872, 3733, 3629, 1660, 1528, 731 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.67 – 8.62 (m, 2H), 8.55 (d, $J = 8.1$ Hz, 1H), 7.58 – 7.52 (m, 2H), 7.45 (ddd, $J = 8.2, 7.0, 1.1$ Hz, 1H), 7.26 (s, 2H), 7.14 – 7.03 (m, 4H), 5.16 (s, 1H), 3.58 – 3.51 (m, 2H), 1.68 – 1.60 (m, 2H), 1.52 (h, $J = 7.2$ Hz, 2H), 0.96 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.4, 144.2, 133.8, 132.4, 132.1, 130.6, 130.2, 129.1, 128.8, 128.3, 126.4, 125.9, 125.5, 125.1,

122.0, 117.2, 110.0, 35.1, 33.0, 23.2, 14.0. HRMS (ESI) calcd for C₂₄H₂₁OSe [M - H]⁻ 405.0763, found 405.0763.

10-Octyl-9-(phenylselanyl)phenanthren-2-ol (4b'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow oil (29.1 mg, 53% yield). IR 3875, 3799, 3730, 3653, 3601, 3293, 2894, 2312, 1646, 1525, 779 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.67 – 8.62 (m, 2H), 8.55 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.45 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.27 (s, 1H), 7.14 – 7.03 (m, 5H), 5.15 (s, 1H), 3.54 (t, *J* = 8.3 Hz, 2H), 1.66 (p, *J* = 7.7 Hz, 2H), 1.49 (p, *J* = 7.2 Hz, 2H), 1.35 – 1.26 (m, 8H), 0.89 – 0.86 (m, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 154.5, 144.3, 133.8, 132.4, 132.1, 131.5, 130.6, 130.2, 129.1, 128.7, 126.4, 125.9, 125.5, 125.1, 122.0, 117.2, 110.0, 35.4, 31.9, 30.9, 30.2, 29.4, 29.3, 22.7, 14.1. HRMS (ESI) calcd for C₂₈H₂₉OSe [M - H]⁻ 461.1389, found 461.1393.

10-Phenyl-9-(p-tolylselanyl)phenanthren-2-ol (4d'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (39.7 mg, 75% yield). IR 3823, 3719, 2922, 1653, 1528 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.73 – 8.59 (m, 3H), 7.71 – 7.59 (m, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.49 – 7.40 (m, 3H), 7.26 (td, *J* = 5.8, 2.6 Hz, 3H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 2.5 Hz, 1H), 4.99 (s, 1H), 2.23 (s, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 154.1, 145.6, 142.0, 135.3, 133.6, 131.4, 130.72, 130.70, 130.3, 129.8, 129.7, 129.3, 128.7, 128.1, 127.3, 127.1, 126.6, 125.5, 124.6, 122.1, 117.3, 112.3, 20.9. HRMS (ESI) calcd for C₂₇H₁₉OSe [M - H]⁻ 439.0607, found 439.0606.

9-((4-Chlorophenyl)selanyl)-10-phenylphenanthren-2-ol (4e'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (48.9 mg, 89% yield). IR 3906, 3712, 3362, 2918, 1639, 1435, 752 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.73 – 8.56 (m, 3H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.59 – 7.38 (m, 4H), 7.25 (dd, *J* = 33.4, 5.4 Hz, 3H), 6.99 (dd, *J* = 36.7,

8.4 Hz, 4H), 6.80 (d, $J = 1.6$ Hz, 1H), 5.02 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.2, 145.9, 141.8, 134.3, 133.6, 132.4, 131.5, 131.2, 130.8, 130.42, 130.38, 129.6, 129.0, 128.1, 127.5, 127.3, 126.8, 125.6, 124.7, 122.3, 117.6, 112.4. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{16}\text{OClSe}$ $[\text{M} - \text{H}]^-$ 459.0060, found 459.0062.

4-((2-Hydroxy-10-phenylphenanthren-9-yl)selanyl)benzotrile (4f'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1, v/v) afforded the target compound as a yellow solid (43.4 mg, 80% yield). Mp 191-193 °C. IR 3861, 3768, 3698, 3476, 3317, 2911, 1653, 1476, 745 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.71 (dd, $J = 14.8, 8.6$ Hz, 2H), 8.53 – 8.45 (m, 1H), 7.75 – 7.65 (m, 1H), 7.57 – 7.49 (m, 1H), 7.46 – 7.42 (m, 2H), 7.34 – 7.27 (m, 4H), 7.22 – 7.15 (m, 2H), 7.10 – 7.04 (m, 2H), 6.81 (d, $J = 2.6$ Hz, 1H), 5.07 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.5, 146.6, 142.4, 141.6, 133.5, 132.2, 131.0, 130.8, 129.9, 129.3, 128.8, 128.2, 127.7, 127.5, 126.9, 126.7, 125.7, 124.7, 122.4, 118.9, 118.1, 112.5, 108.6. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{16}\text{ONSe}$ $[\text{M} - \text{H}]^-$ 450.0403, found 450.0407.

10-Phenyl-9-(m-tolylselanyl)phenanthren-2-ol (4g'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (38.9 mg, 74% yield). IR 3875, 3688, 3591, 3348, 3175, 3067, 2911, 1646, 1441, 1209, 731 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.67 – 8.55 (m, 3H), 7.61 (ddd, $J = 8.3, 7.0, 1.3$ Hz, 1H), 7.49 (ddd, $J = 8.2, 7.0, 1.1$ Hz, 1H), 7.39 (dd, $J = 4.9, 1.7$ Hz, 3H), 7.21 – 7.16 (m, 3H), 6.92 – 6.86 (m, 2H), 6.83 (d, $J = 7.5$ Hz, 1H), 6.78 – 6.73 (m, 2H), 4.89 (s, 1H), 2.14 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.1, 145.7, 141.9, 138.6, 133.9, 133.7, 131.5, 130.72, 130.70, 129.8, 129.7, 128.7, 128.6, 128.0, 127.3, 127.1, 126.6, 126.5, 126.4, 125.5, 124.6, 122.1, 117.3, 112.3, 21.3. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{19}\text{OSe}$ $[\text{M} - \text{H}]^-$ 439.0607, found 439.0607.

9-((3-Chlorophenyl)selanyl)-10-phenylphenanthren-2-ol (4h'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (43.1 mg, 78% yield). IR 3736, 3355,

2929, 1636, 1445, 707 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.68 – 8.55 (m, 3H), 7.64 (ddd, $J = 8.3, 7.0, 1.3$ Hz, 1H), 7.51 (ddd, $J = 8.2, 7.0, 1.1$ Hz, 1H), 7.40 (qd, $J = 4.6, 3.8, 1.1$ Hz, 3H), 7.25 – 7.22 (m, 1H), 7.19 – 7.15 (m, 2H), 7.03 – 6.98 (m, 2H), 6.95 – 6.89 (m, 1H), 6.84 (dt, $J = 7.8, 1.3$ Hz, 1H), 6.77 (d, $J = 2.6$ Hz, 1H), 4.91 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.2, 146.0, 141.7, 135.9, 134.6, 133.8, 131.2, 130.8, 130.3, 129.9, 129.6, 128.8, 128.1, 127.9, 127.5, 127.3, 127.3, 126.8, 125.8, 125.6, 124.7, 122.3, 117.6, 112.4. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{16}\text{OClSe}$ [$\text{M} - \text{H}$] $^-$ 459.0060, found 459.0064.

10-Phenyl-9-(o-tolylselanyl)phenanthren-2-ol (4i'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (33.2 mg, 63% yield). IR 3875, 3591, 3168, 2922, 1639, 1449, 1199, 755 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.64 (dd, $J = 17.2, 8.6$ Hz, 2H), 8.55 (dd, $J = 8.3, 1.0$ Hz, 1H), 7.62 (ddd, $J = 8.3, 7.0, 1.3$ Hz, 1H), 7.48 (ddd, $J = 8.2, 7.0, 1.1$ Hz, 1H), 7.39 – 7.32 (m, 3H), 7.22 (d, $J = 7.6$ Hz, 1H), 7.16 (dq, $J = 6.5, 2.3, 1.9$ Hz, 2H), 7.03 (d, $J = 7.3$ Hz, 1H), 6.95 (td, $J = 7.4, 1.2$ Hz, 1H), 6.76 – 6.70 (m, 2H), 6.65 (dd, $J = 7.9, 1.1$ Hz, 1H), 4.88 (s, 1H), 2.22 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.1, 146.0, 141.9, 136.5, 135.2, 133.8, 131.6, 130.7, 130.6, 129.7, 129.5, 129.2, 128.6, 128.0, 127.3, 127.2, 126.7, 126.4, 125.5, 125.4, 124.6, 122.2, 117.4, 112.3, 21.6. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{19}\text{OSe}$ [$\text{M} - \text{H}$] $^-$ 439.0607, found 439.0609.

9-((2-Chlorophenyl)selanyl)-10-phenylphenanthren-2-ol (4j'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (25.3 mg, 46% yield). IR 3915, 3055, 2916, 1656, 1457, 1233, 859, 745 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.69 (d, $J = 9.0$ Hz, 1H), 8.65 (d, $J = 8.2$ Hz, 1H), 8.51 (dd, $J = 8.3, 0.9$ Hz, 1H), 7.65 (ddd, $J = 8.3, 7.0, 1.3$ Hz, 1H), 7.49 (ddd, $J = 8.2, 7.0, 1.1$ Hz, 1H), 7.44 – 7.36 (m, 3H), 7.27 (dd, $J = 8.9, 2.6$ Hz, 1H), 7.23 (d, $J = 1.3$ Hz, 1H), 7.22 – 7.16 (m, 2H), 6.97 (td, $J = 7.7, 1.5$ Hz, 1H), 6.82 – 6.75 (m, 2H), 6.55 (dd, $J = 8.0, 1.5$ Hz, 1H), 4.91 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126

MHz, CDCl₃) δ 154.2, 146.6, 141.6, 134.7, 133.7, 132.4, 131.2, 130.8, 130.4, 129.6, 129.3, 129.1, 128.2, 127.7, 127.6, 127.4, 127.1, 126.9, 126.3, 125.7, 124.7, 122.2, 117.7, 112.5. HRMS (ESI) calcd for C₂₆H₁₆OClSe [M - H]⁻ 459.0060, found 459.0063.

9-(Naphthalen-1-ylselanyl)-10-phenylphenanthren-2-ol (4k'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow solid (14 mg, 25% yield). Mp 188-189 °C. IR 3910, 3775, 3345, 3192, 2915, 1643, 1445, 703 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.67 (ddd, *J* = 12.7, 11.6, 8.6 Hz, 3H), 7.69 – 7.59 (m, 2H), 7.54 – 7.43 (m, 4H), 7.42 – 7.32 (m, 5H), 7.28 – 7.25 (m, 1H), 7.21 (d, *J* = 1.7 Hz, 2H), 7.13 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.80 (d, *J* = 2.6 Hz, 1H), 4.89 (s, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 154.2, 145.9, 141.9, 134.0, 133.7, 131.9, 131.6, 131.5, 130.8, 130.6, 129.7, 128.3, 128.2, 128.1, 127.7, 127.4, 127.34, 127.30, 127.2, 127.0, 126.7, 126.2, 125.7, 125.3, 124.7, 122.2, 117.5, 112.4. HRMS (ESI) calcd for C₃₀H₁₉OSe [M - H]⁻ 475.0607, found 475.0610.

9-(Butylselanyl)-10-phenylphenanthren-2-ol (4l'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the target compound as a yellow oil (32.4 mg, 67% yield). IR 3924, 3844, 3698, 3348, 3189, 2915, 1643, 1455, 717 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.87 – 8.77 (m, 1H), 8.61 (d, *J* = 8.6 Hz, 2H), 7.71 – 7.54 (m, 2H), 7.47 (tdd, *J* = 8.6, 6.8, 3.7 Hz, 3H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.23 (s, 1H), 7.18 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.73 (d, *J* = 2.6 Hz, 1H), 4.96 (s, 1H), 2.65 – 2.58 (m, 2H), 1.46 – 1.32 (m, 2H), 1.27 – 1.11 (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 154.1, 144.8, 142.4, 133.5, 131.9, 130.6, 130.5, 130.3, 129.4, 128.0, 127.2, 126.9, 126.4, 125.0, 124.5, 122.3, 116.9, 112.0, 32.2, 29.6, 22.8, 13.4. HRMS (ESI) calcd for C₂₄H₂₁OSe [M - H]⁻ 405.0763, found 405.0767.

9-(Cyclohexylselanyl)-10-phenylphenanthren-2-ol (4m'). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded the

target compound as a yellow oil (25.1 mg, 48% yield). IR 3854, 3757, 3345, 3220, 3060, 2929, 1632, 1452, 1192, 717 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.86 (dd, $J = 8.1, 1.3$ Hz, 1H), 8.68 – 8.53 (m, 2H), 7.74 – 7.55 (m, 2H), 7.51 – 7.44 (m, 3H), 7.25 (d, $J = 5.3$ Hz, 2H), 7.20 (dd, $J = 8.9, 2.6$ Hz, 1H), 6.74 (d, $J = 2.6$ Hz, 1H), 4.85 (s, 1H), 3.05 (tt, $J = 10.6, 3.7$ Hz, 1H), 1.77 – 1.66 (m, 2H), 1.56 (dt, $J = 7.5, 3.2$ Hz, 2H), 1.49 – 1.40 (m, 1H), 1.39 – 1.33 (m, 2H), 1.19 – 1.05 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 154.1, 145.0, 142.4, 133.6, 132.4, 130.8, 130.5, 130.4, 129.5, 127.9, 127.1, 126.9, 126.3, 125.1, 124.5, 122.2, 116.8, 112.1, 44.8, 34.1, 26.7, 25.7. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{23}\text{OSe}$ $[\text{M} - \text{H}]^-$ 431.0920, found 431.0918.

General procedure for the synthesis of ketoxime 5.

The compound **3a** (0.1 mmol, 1.0 eq., 42.5 mg) and methoxyamine hydrochloride (0.25 mmol, 2.5 eq., 21.0 mg) were placed into an oven dried reaction tube with a magnetic stir and a condenser within nitrogen atmosphere. Then, pyridine (1.0 mL) was added and the mixture was allowed to stir in an oil bath at 120 $^\circ\text{C}$ for 20 h. After completion of the reaction, volatiles were removed under reduced pressure and the crude reaction mixture was directly purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100:1, v/v) to provide ketoxime **5** (44.7 mg, 98% yield) as yellow solid.

2'-Phenyl-3'-(phenylselanyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one O-methyl oxime (5). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) afforded the target compound as a yellow solid (44.7 mg, 98% yield). Mp 98-100 $^\circ\text{C}$. IR 3897, 3845, 3728, 1454, 1050, 914, 737 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.39 (dd, $J = 6.3, 2.6$ Hz, 2H), 7.34 – 7.25 (m, 5H), 7.25 – 7.12 (m, 7H), 7.08 (dd, $J = 10.0, 0.8$ Hz, 1H), 6.49 (dd, $J = 9.9, 0.8$ Hz, 1H), 5.91 (dd, $J = 10.1, 1.8$ Hz, 1H), 5.81 (dd, $J = 9.9, 1.8$ Hz, 1H), 3.94 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 155.2, 147.9, 145.5, 144.2, 138.5, 135.1, 134.1, 130.6, 130.3, 129.9, 129.2, 128.8, 128.3, 128.2, 127.9, 126.8, 126.5, 125.1, 123.9, 122.6, 117.6, 62.2, 62.0. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{21}\text{NaNOSe}$ $[\text{M} + \text{Na}]^+$ 478.0682, found 478.0680.

General procedure for the synthesis of selenoxide 6.

The compound **3a** (0.1 mmol, 1.0 eq., 42.5 mg) and DCM (1.0 mL) were placed into an oven dried reaction tube. Then, *m*-CPBA (0.22 mmol, 2.2 eq., 38.1 mg) was added and the mixture was allowed to stir 10 min under 0 °C. After that, the mixture was allowed to stir 12 h under room temperature. After completion of the reaction, volatiles were removed under reduced pressure and the crude reaction mixture was directly purified by silica gel column chromatography (ethyl acetate) to provide ketoxime **6** (36 mg, 82% yield) as yellow solid.

2'-Phenyl-3'-(phenylseleninyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**6**).

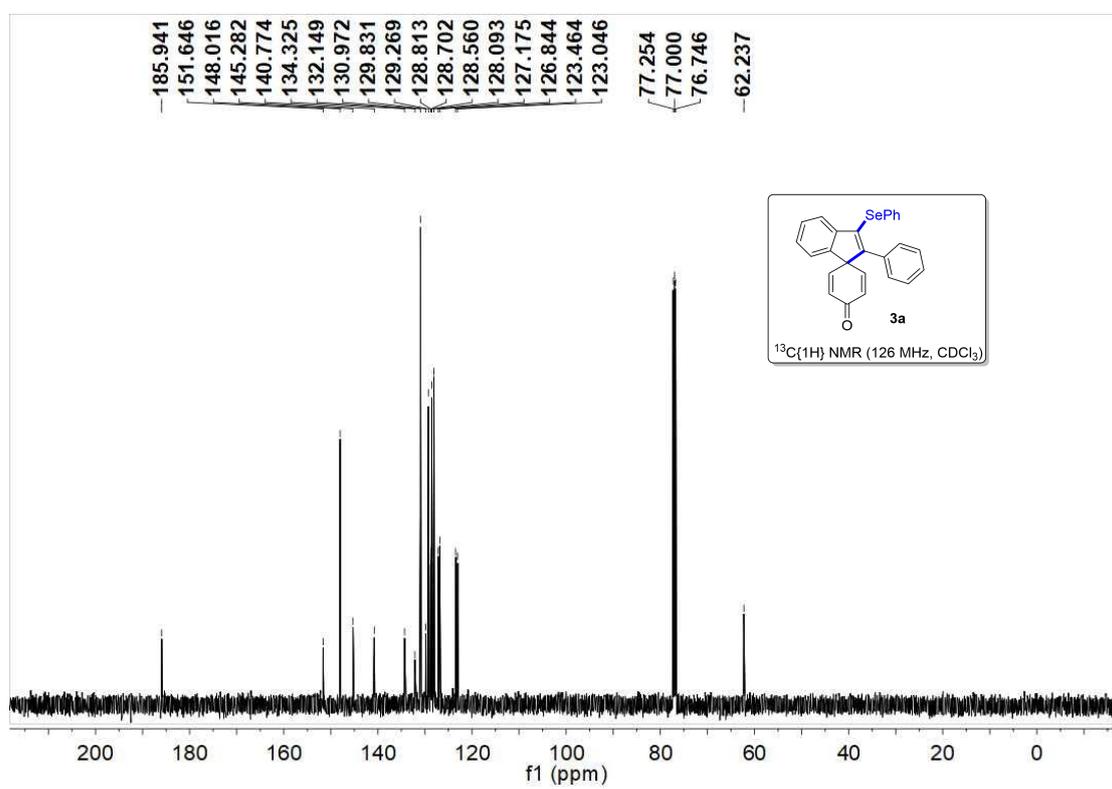
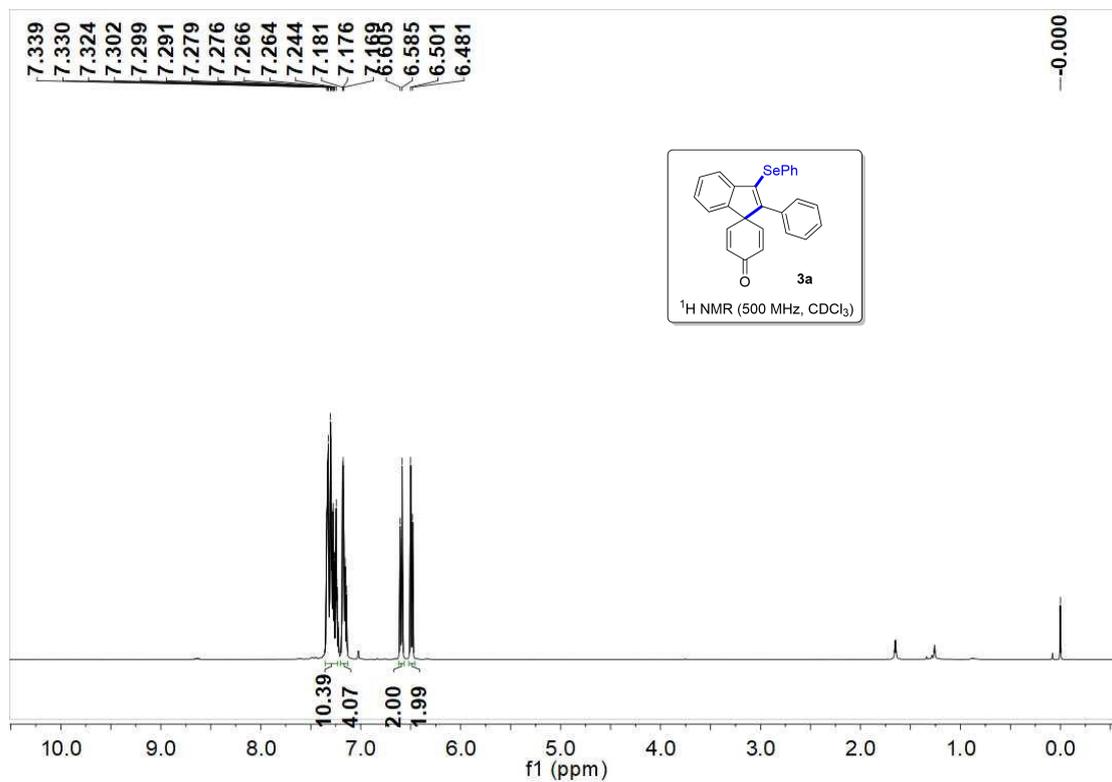
Purification by column chromatography on silica gel (ethyl acetate) afforded the target compound as a yellow solid (36 mg, 82% yield). Mp 167-169 °C. IR 3853, 3720, 1663, 1461, 870, 741 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 8.53 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.45 (m, 4H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.20 (m, 5H), 7.12 (t, *J* = 7.7 Hz, 2H), 6.98 (d, *J* = 7.4 Hz, 2H), 6.42 (s, 4H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 184.9, 155.3, 144.1, 144.0, 142.9, 140.3, 138.9, 133.7, 132.1, 129.8, 129.7, 129.6, 129.5, 128.7, 128.6, 128.0, 126.5, 124.1, 124.0, 62.7. HRMS (ESI) calcd for C₂₆H₁₈NaO₂Se [M + Na]⁺ 465.0366, found 465.0359.

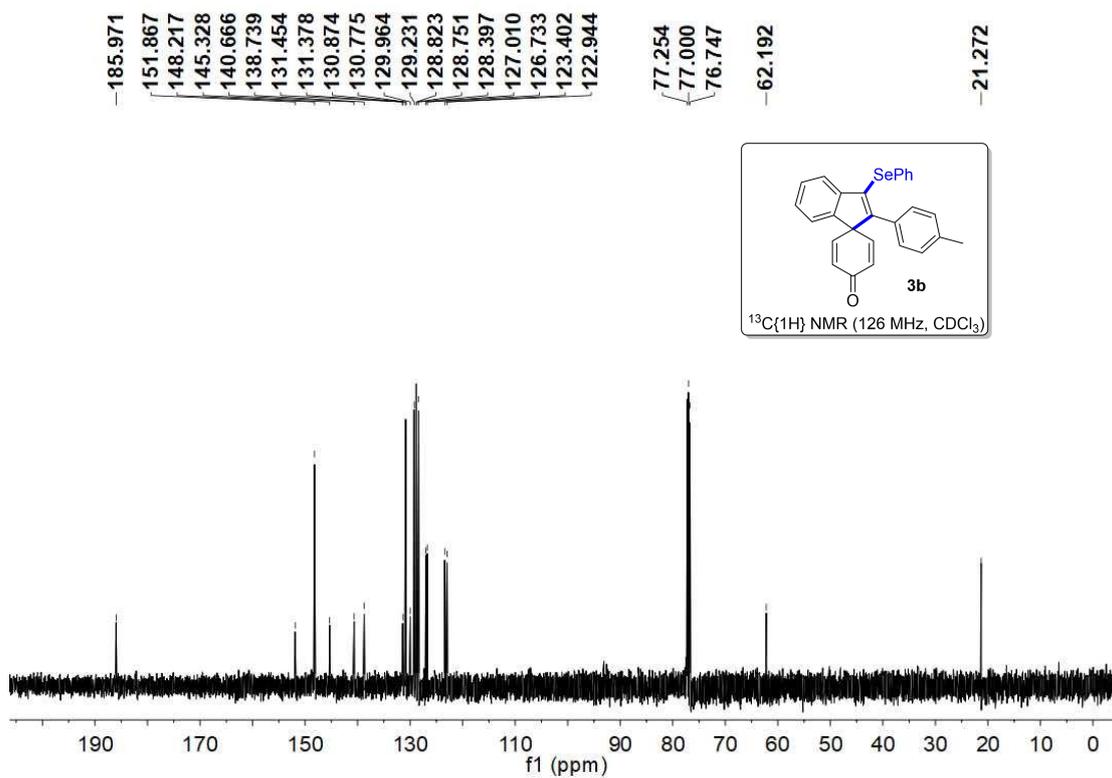
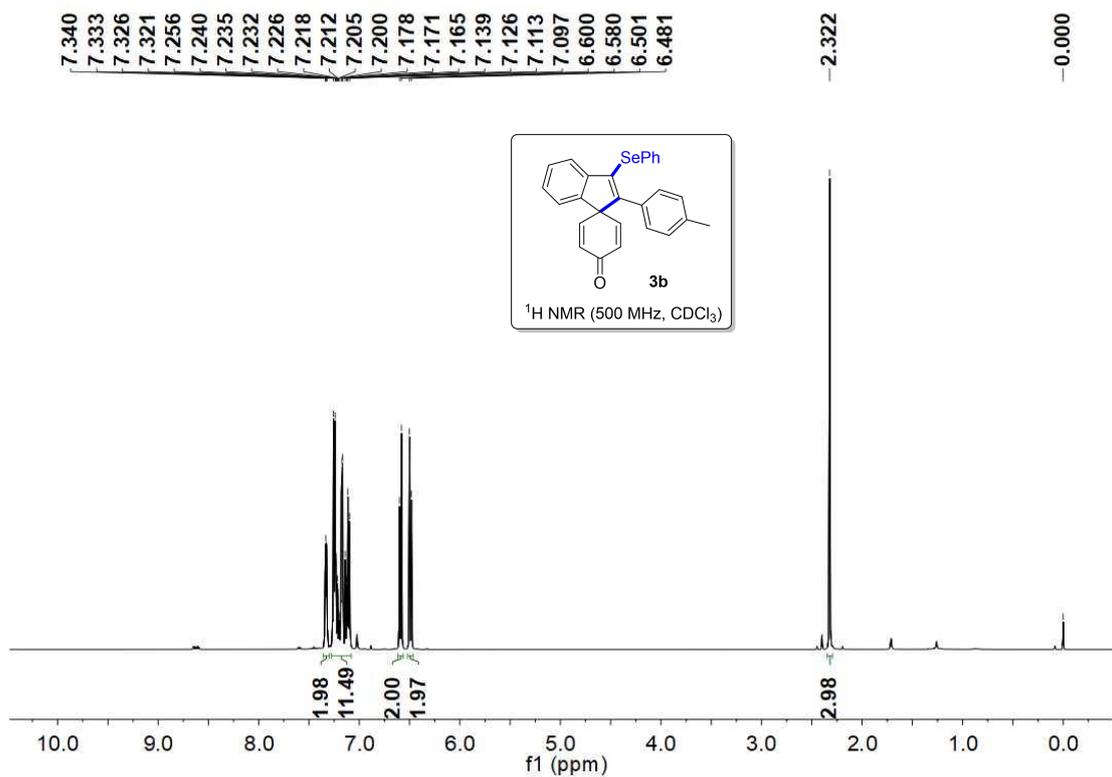
General procedure for the synthesis of compound 7.

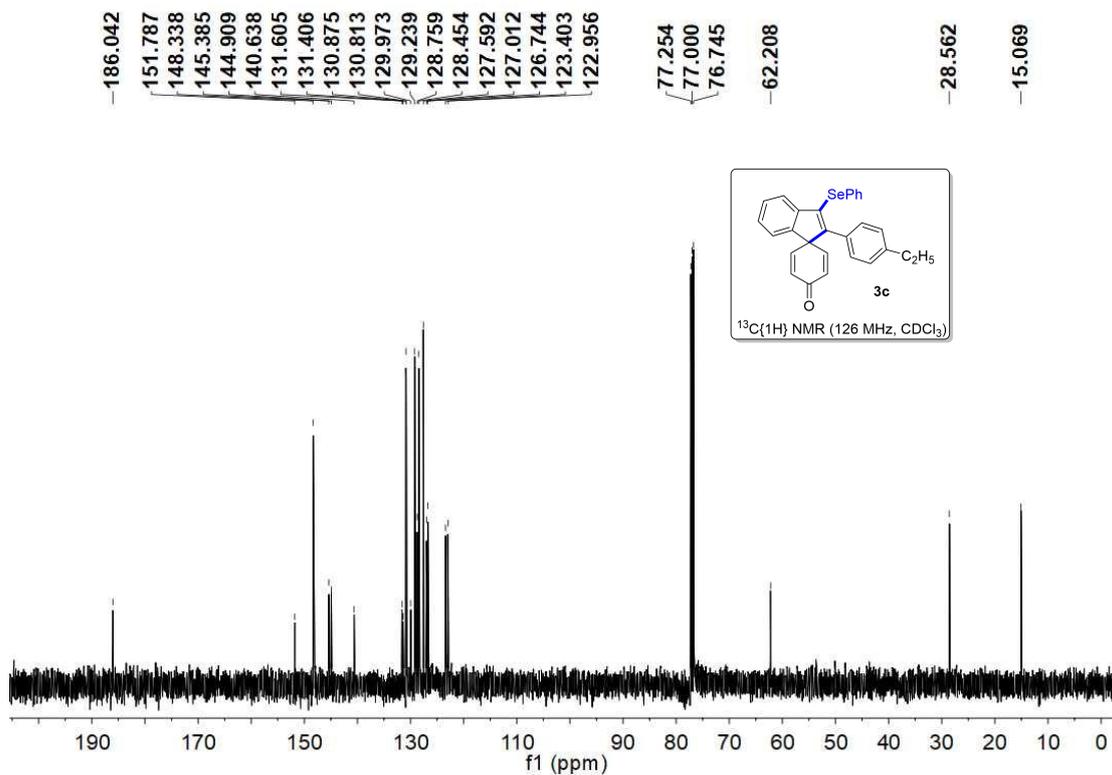
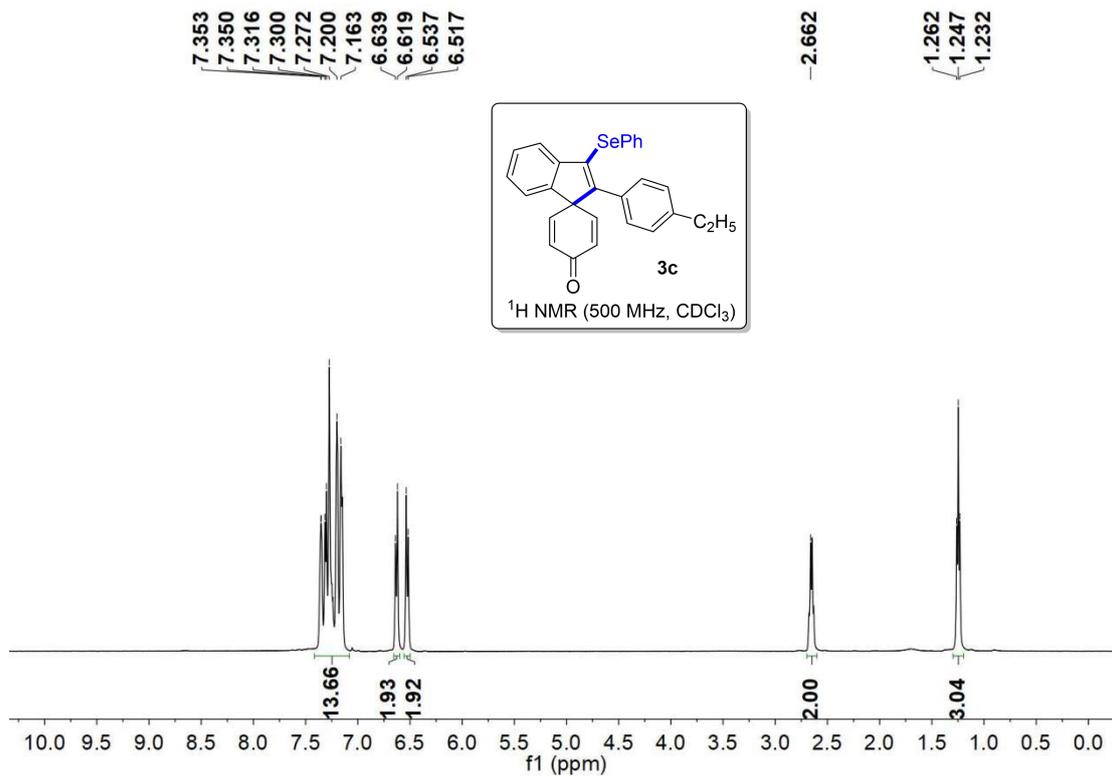
To a stirred solution of **3a** (0.1 mmol, 1.0 eq., 42.5 mg) in MeOH (1.0 mL) at room temperature was added CeCl₃·7H₂O (0.35 mmol, 3.5 eq., 0.131 g). After the reaction was cooled down to 0 °C, NaBH₄ (0.25 mmol, 2.5 eq., 9.5 mg) was added to the reaction, and the reaction was stirred for 30 min, and then the reaction allowed to stir 12 h under room temperature. After completion of the reaction, volatiles were removed under reduced pressure and the crude reaction mixture was directly purified by silica gel column chromatography (ethyl acetate) to provide **7** (32 mg, 78% yield) as yellow oil.

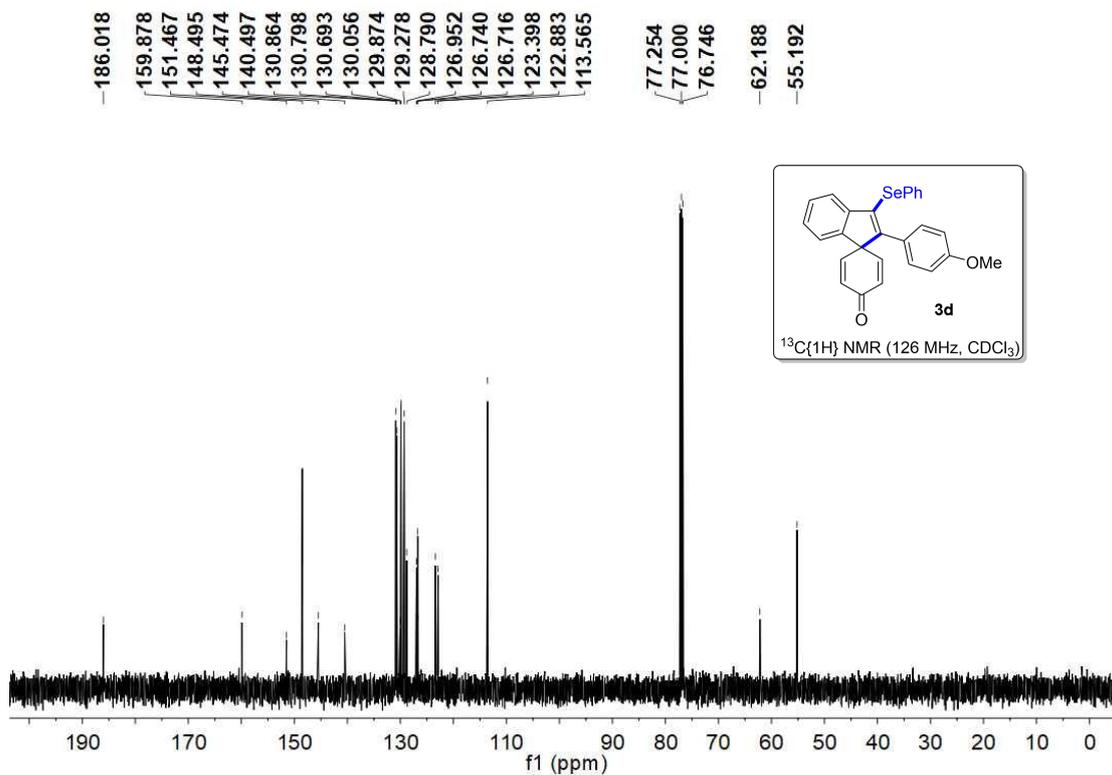
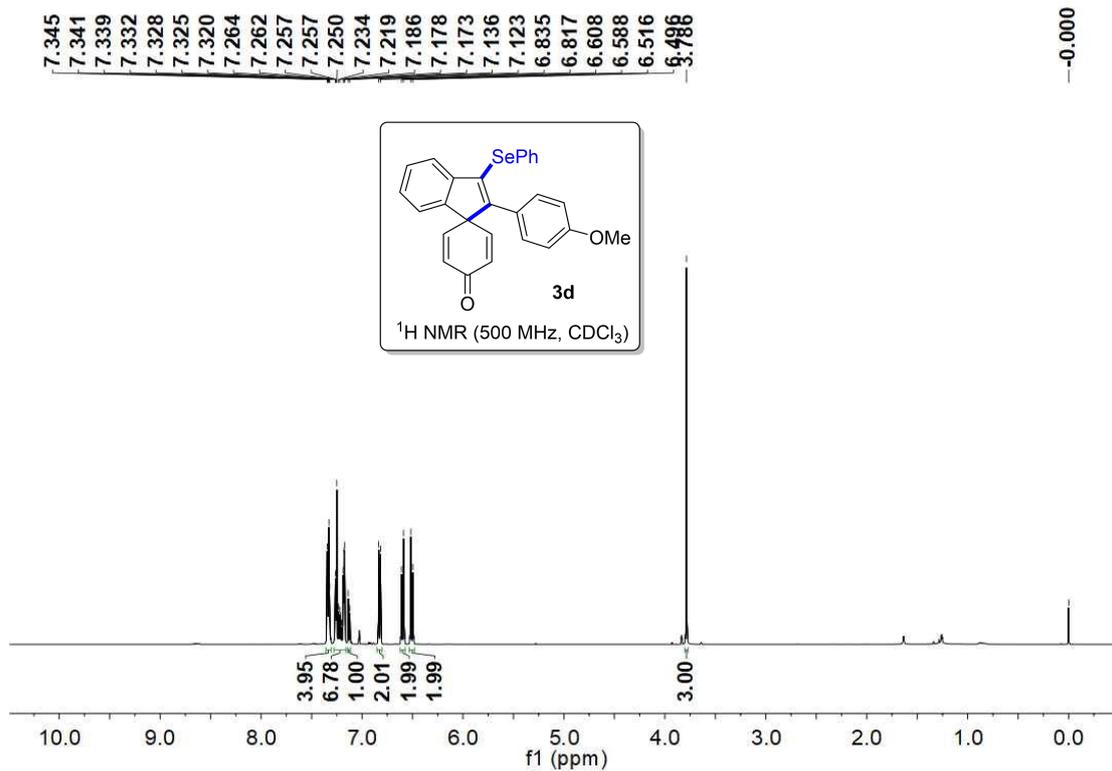
Phenyl(10-phenylphenanthren-9-yl)selane (7). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) afforded the target compound as a yellow oil (32 mg, 78% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.76 (dd, *J* = 11.0, 8.9 Hz, 2H), 8.68 (d, *J* = 8.3 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.48 – 7.40 (m, 5H), 7.23 (s, 2H), 7.03 (s, 5H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 146.8, 141.9, 134.3, 132.5, 132.2, 131.1, 130.7, 130.6, 129.7, 129.2, 128.9, 127.9, 127.7, 127.6, 127.4, 127.3, 127.0, 126.7, 125.5, 122.7, 122.6. HRMS (ESI) calcd for C₂₆H₁₈Se [M]⁺ 410.0568, found 410.0567.

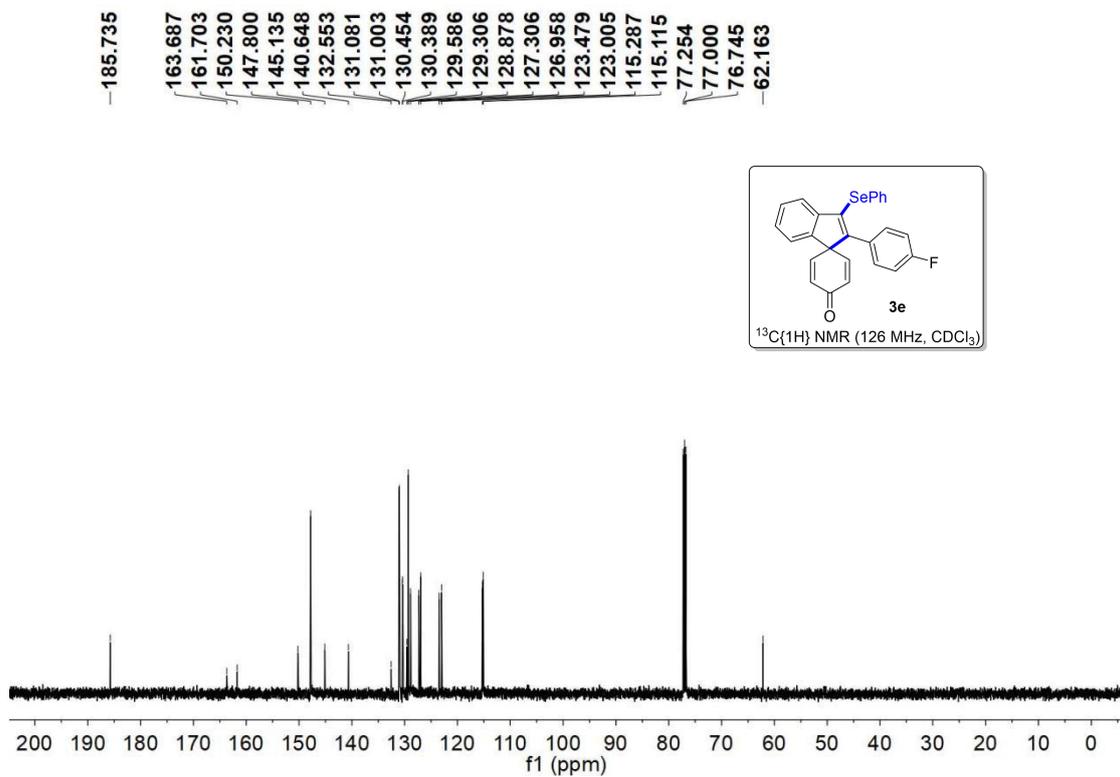
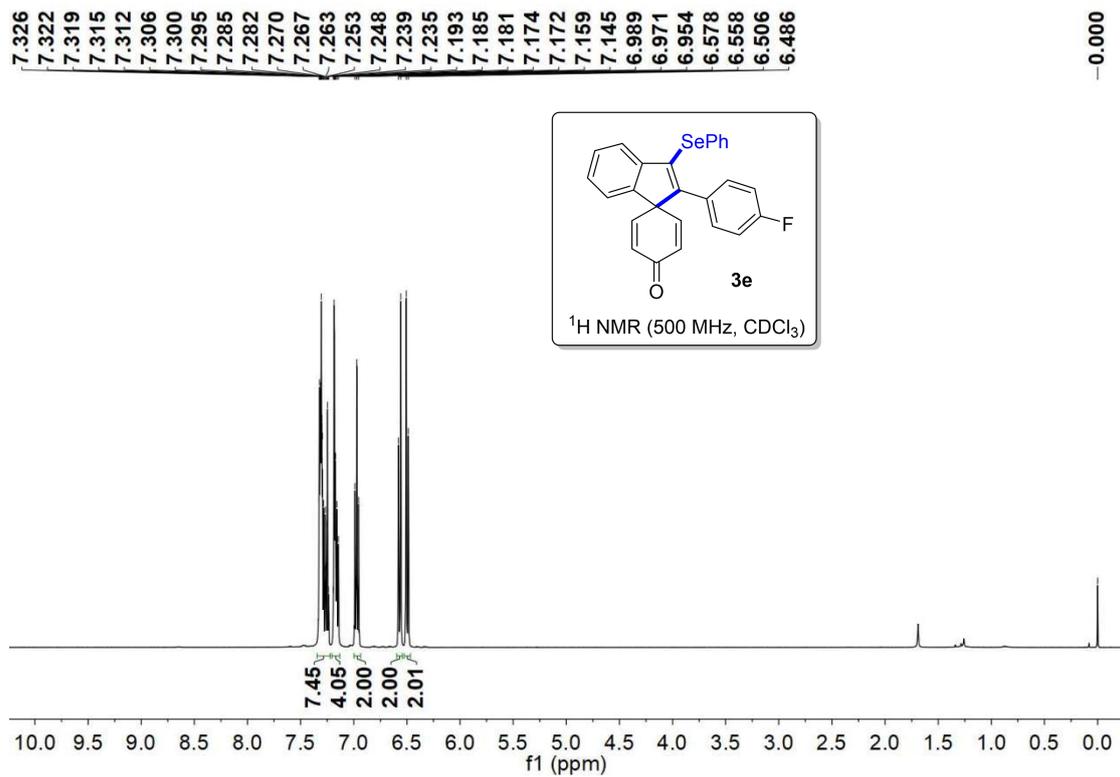
^1H , ^{13}C and ^{19}F NMR spectra

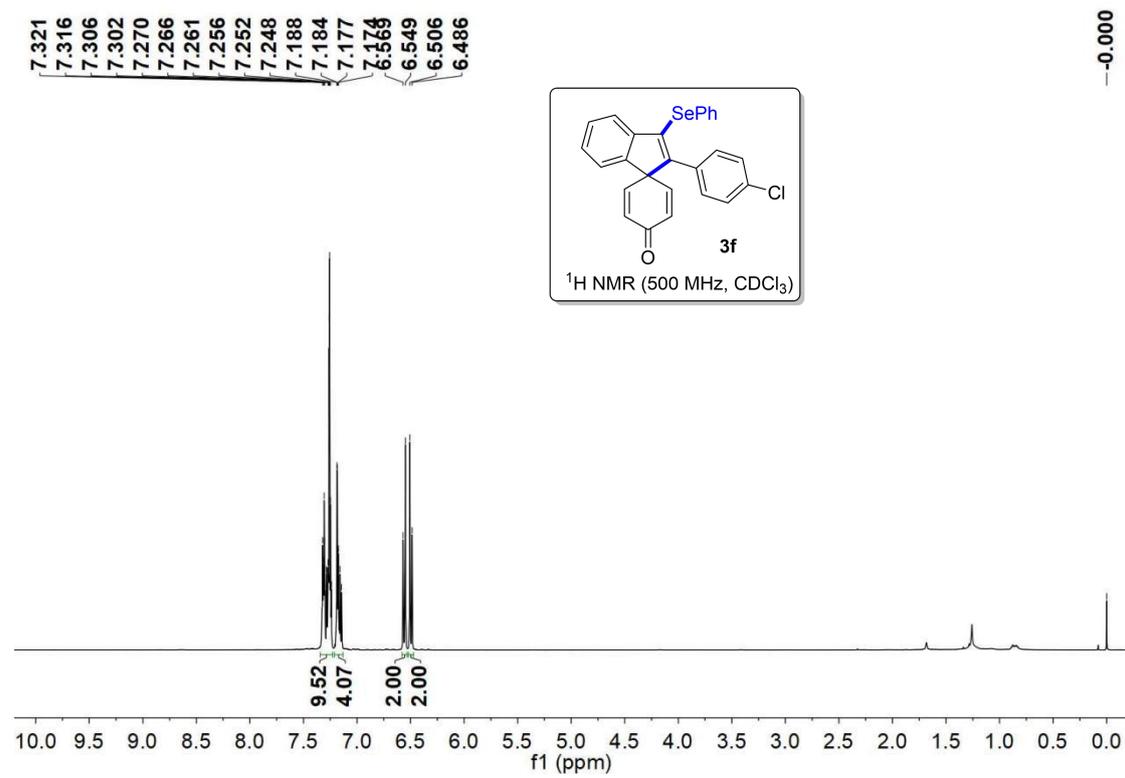
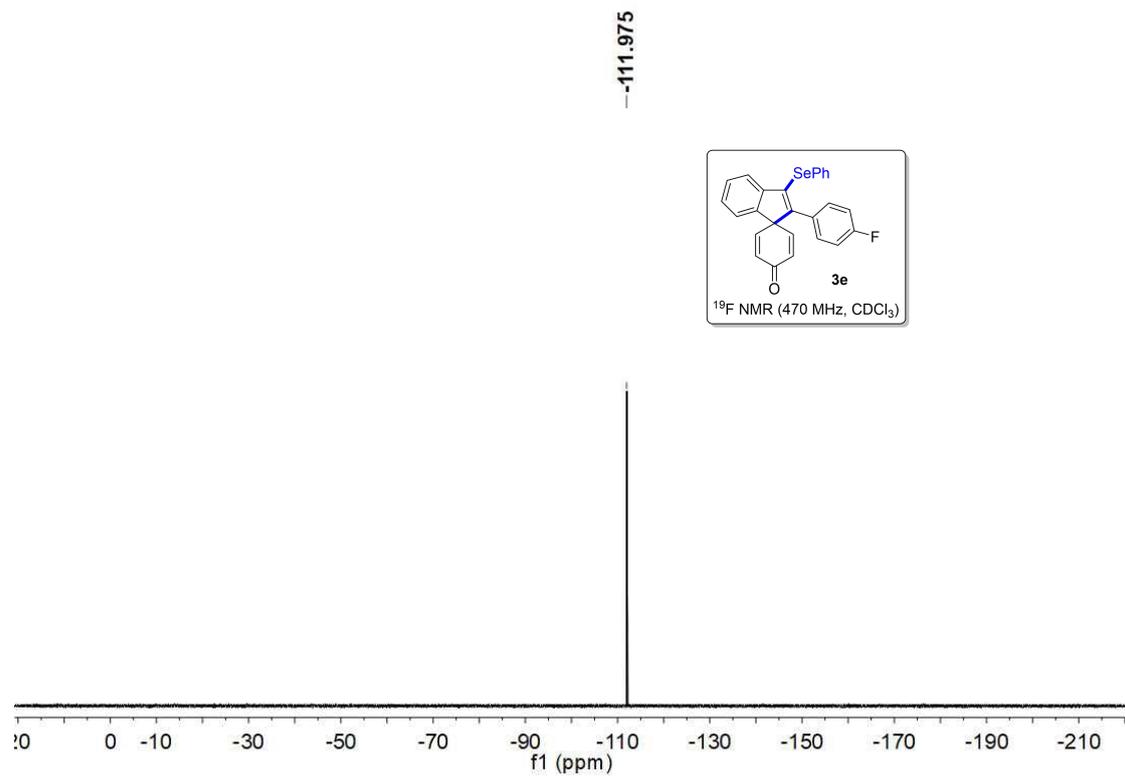


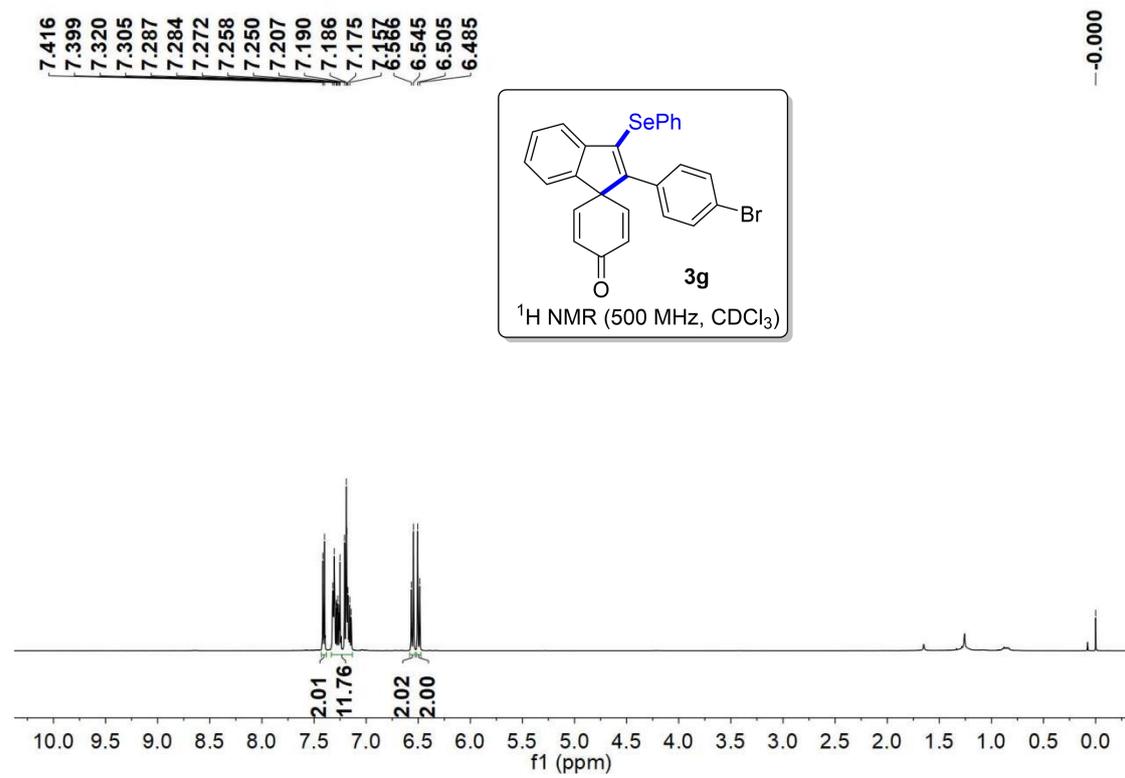
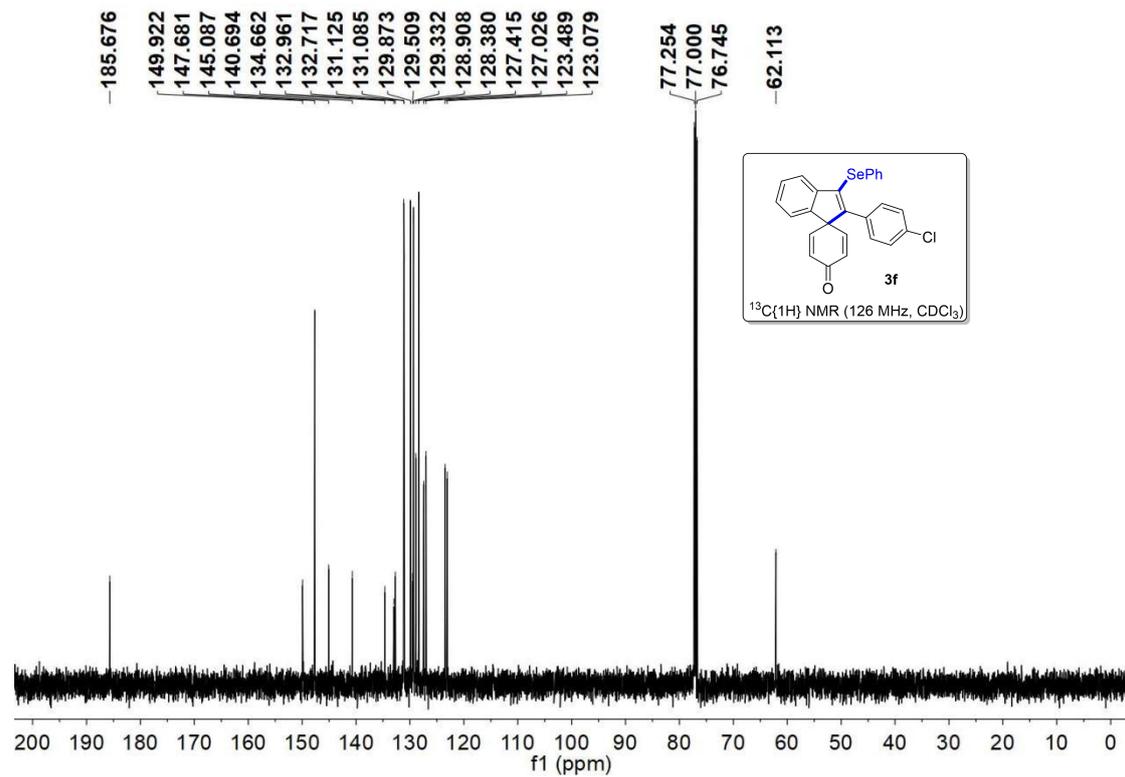


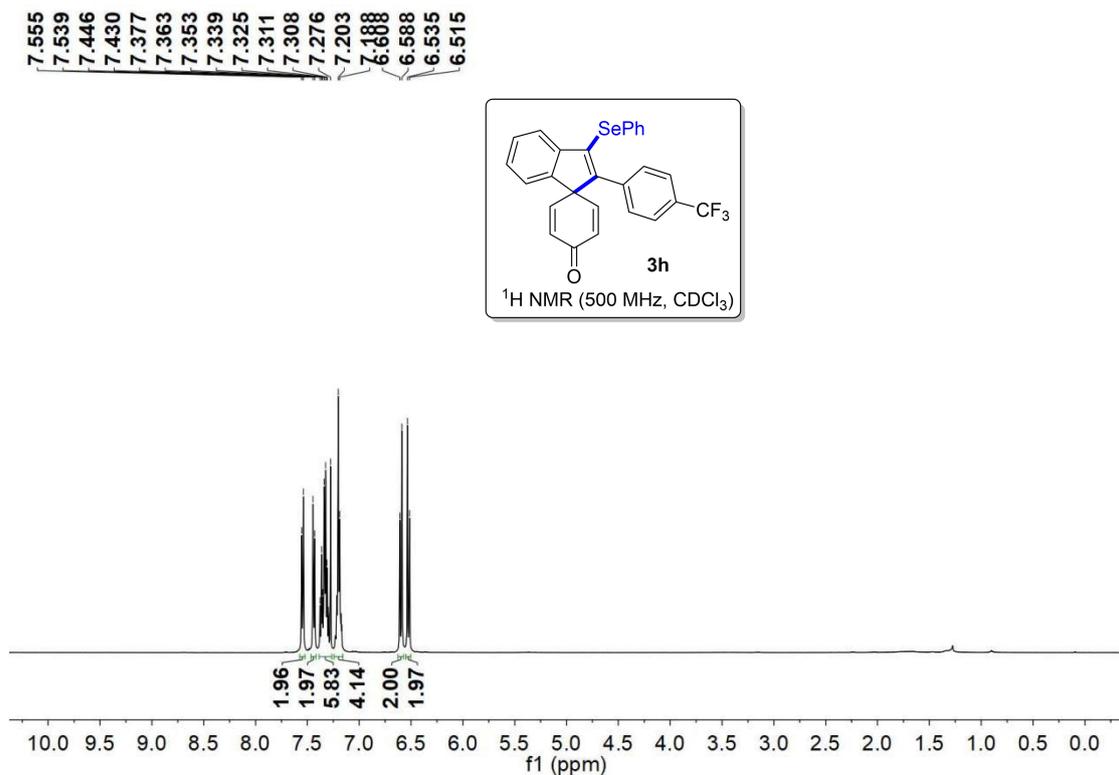
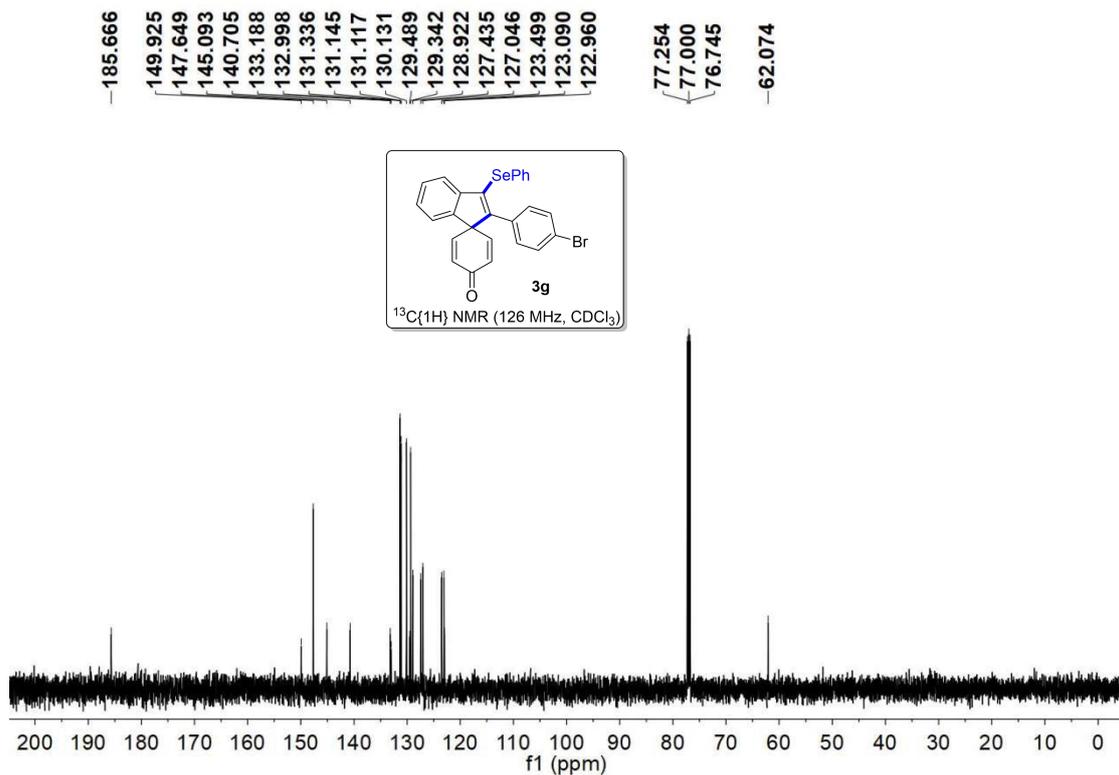


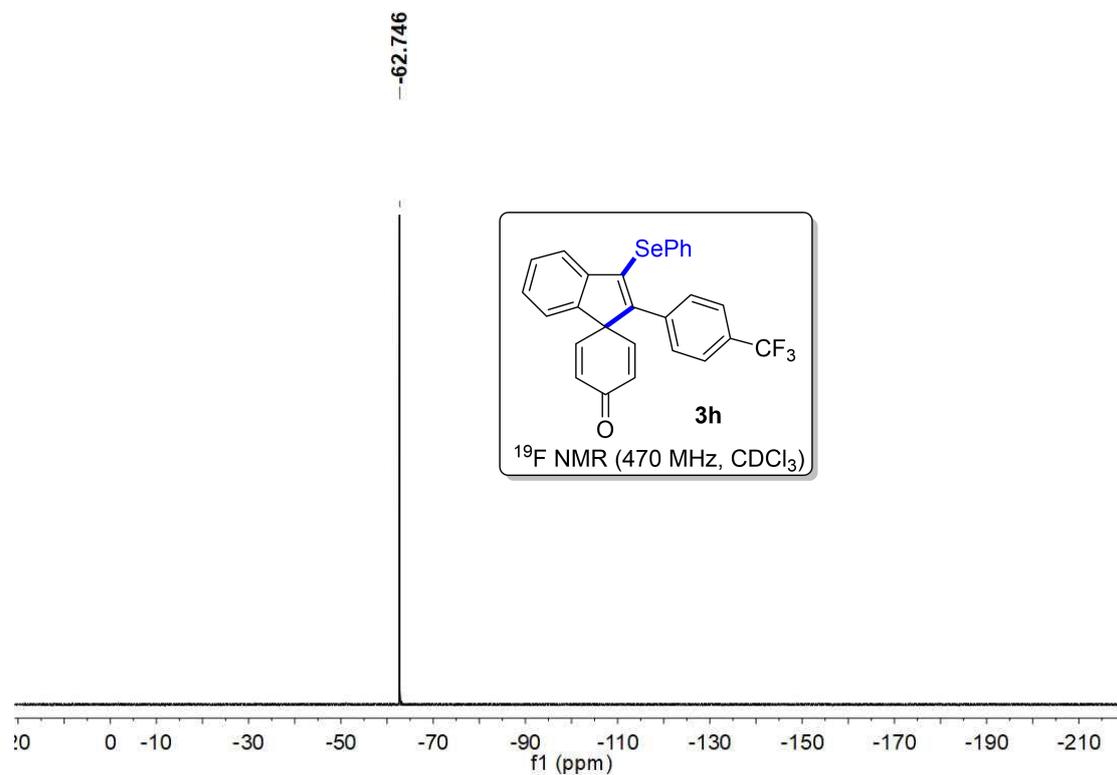
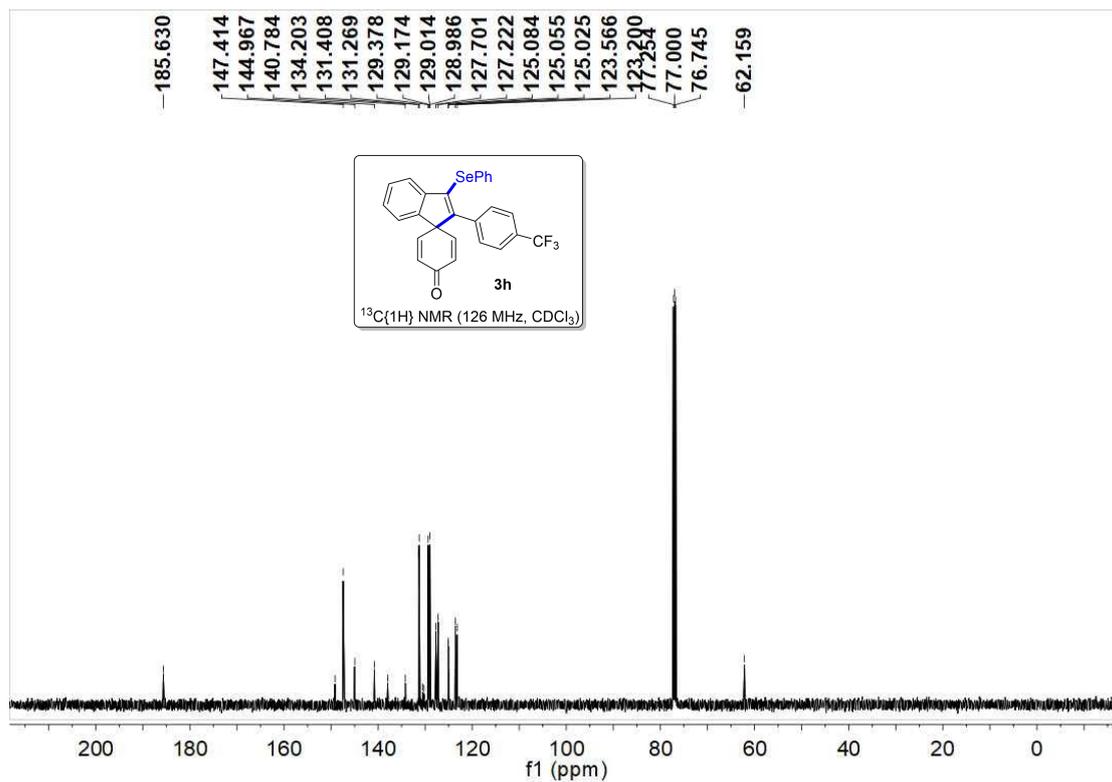


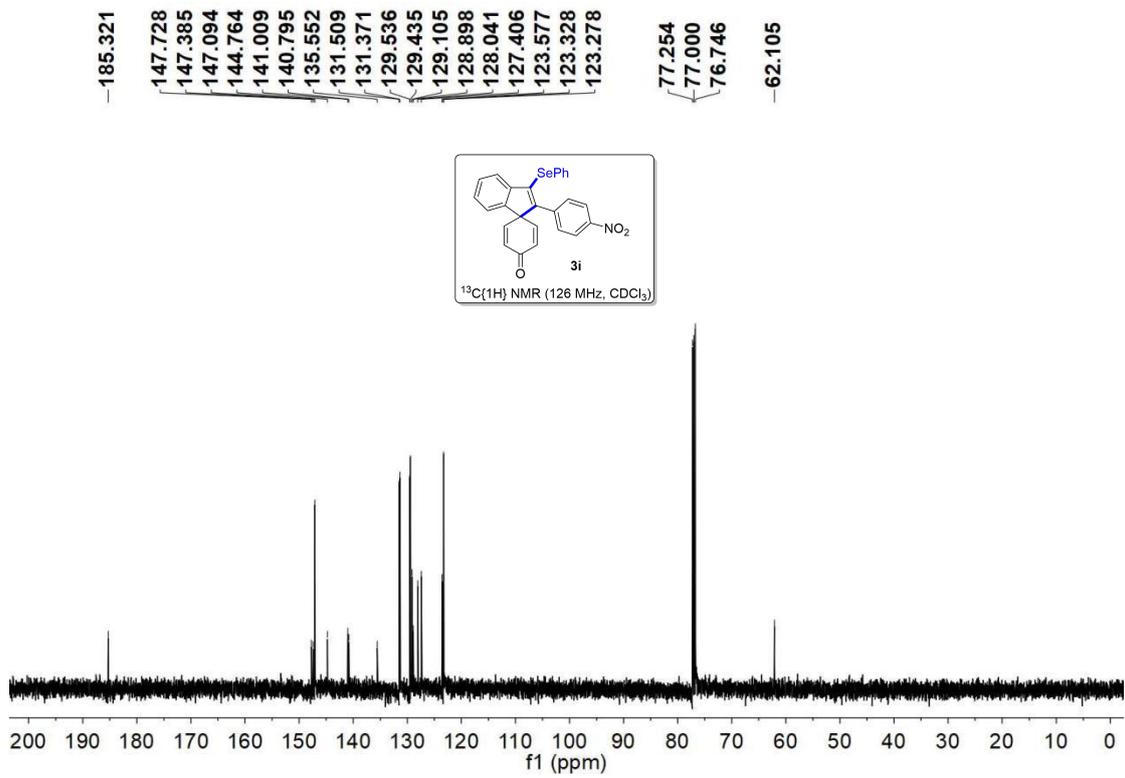
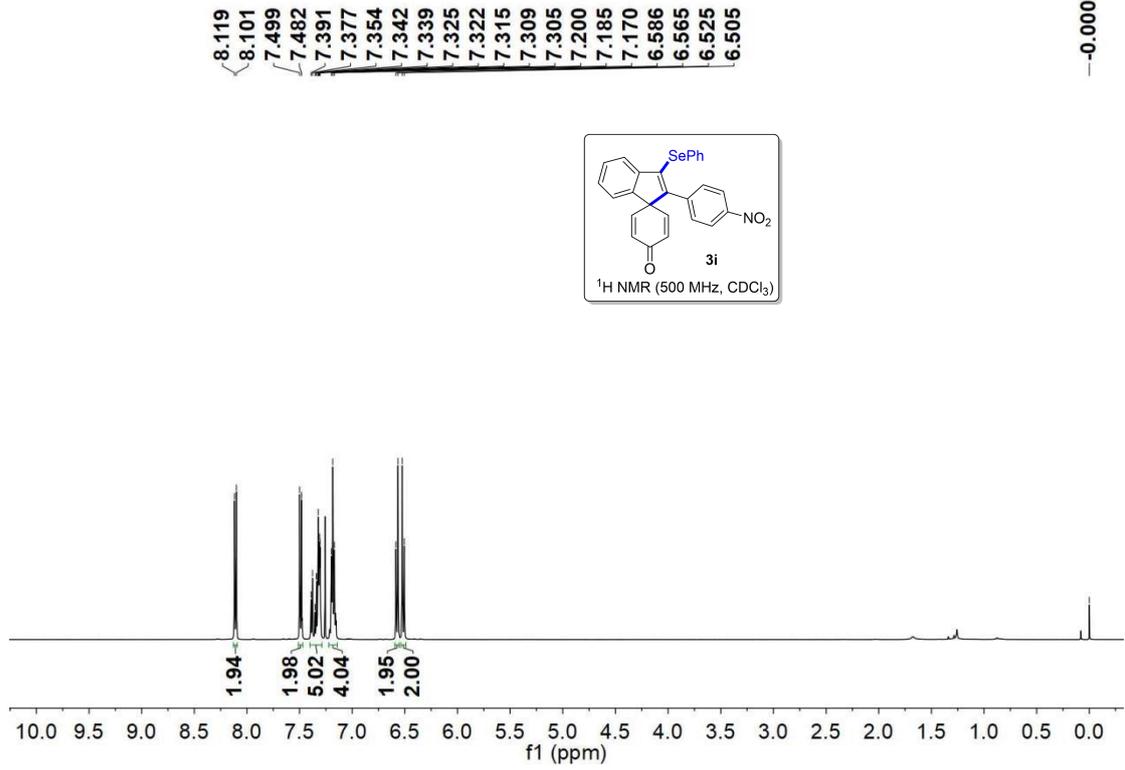


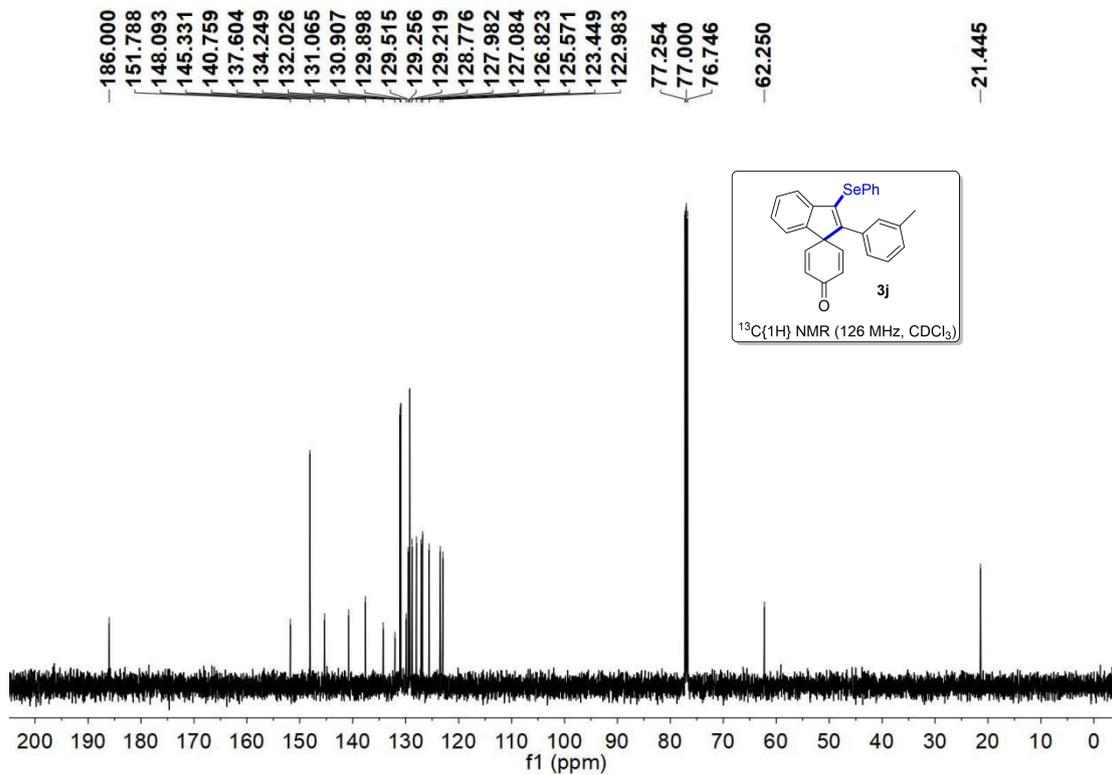
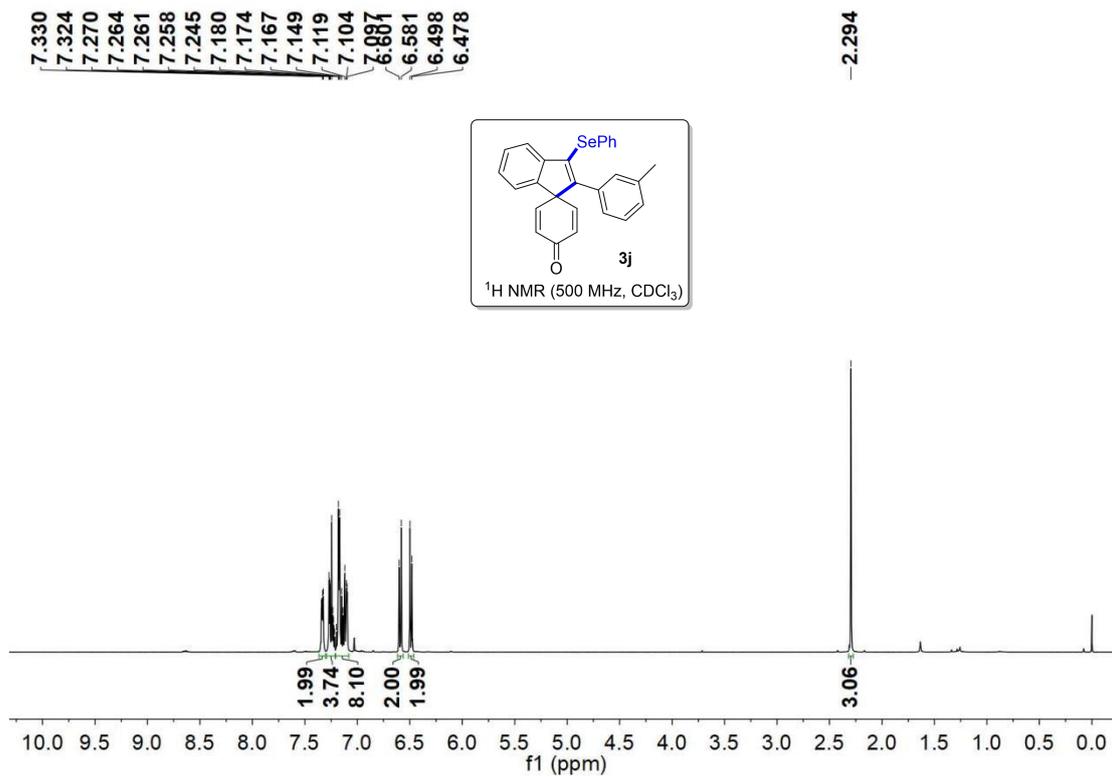


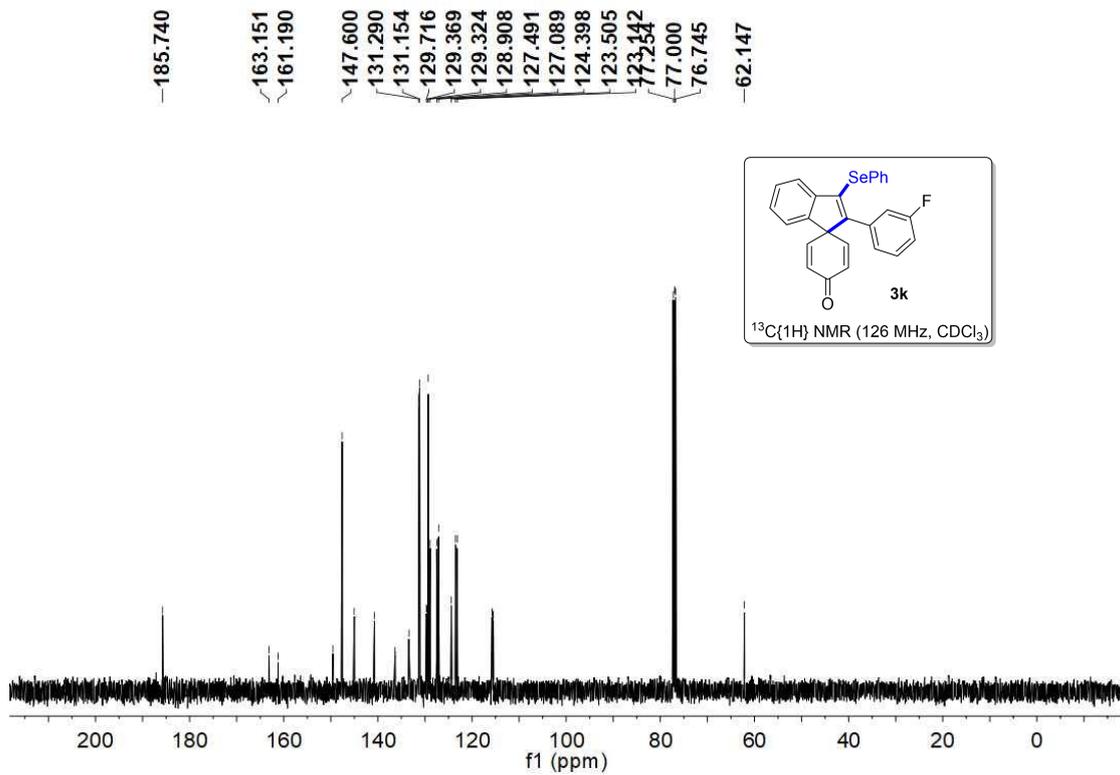
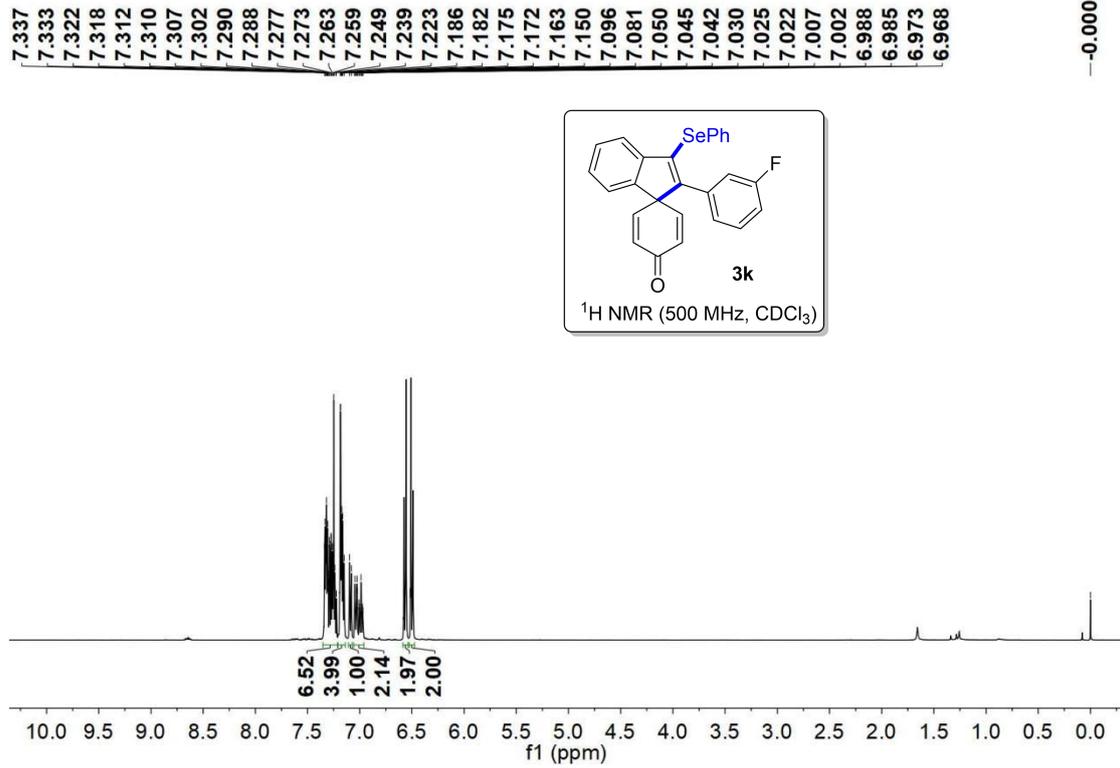


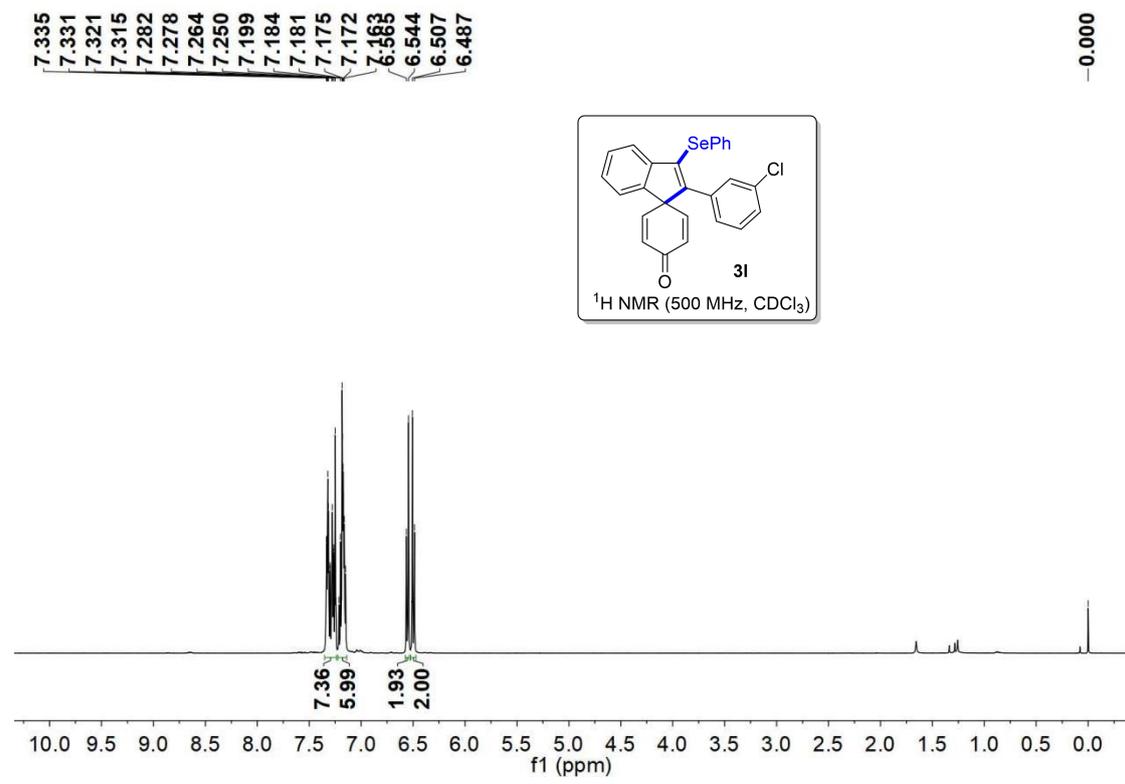
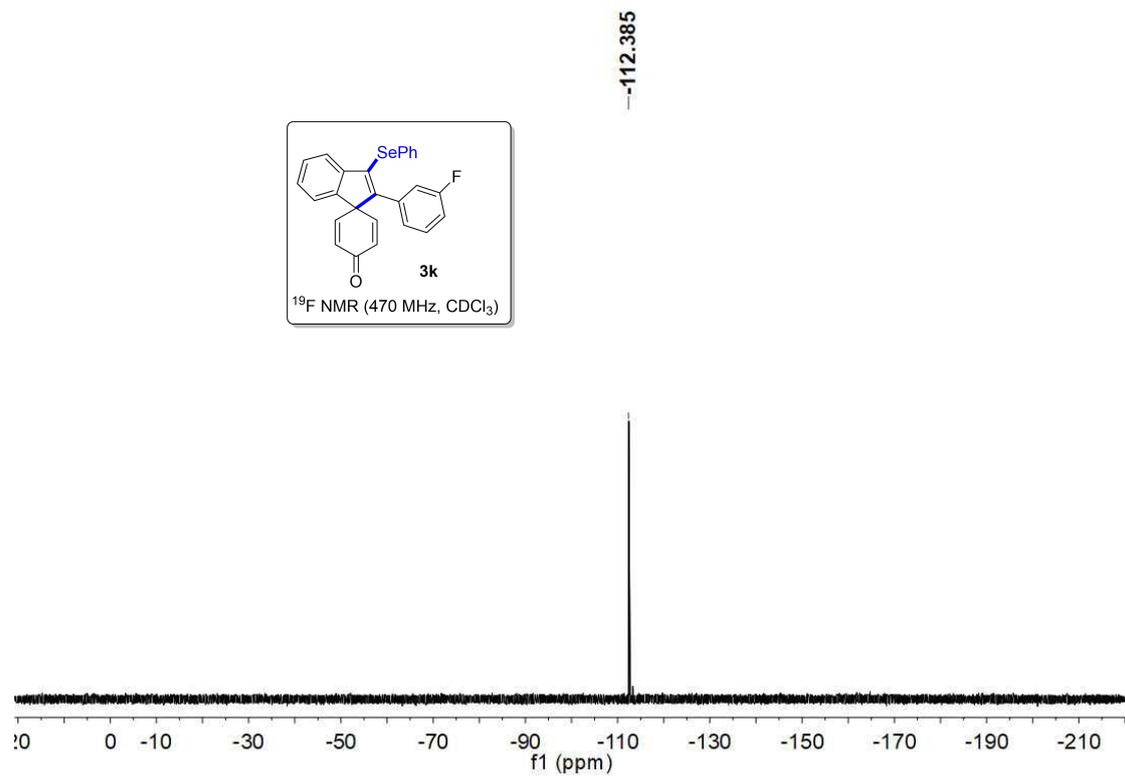


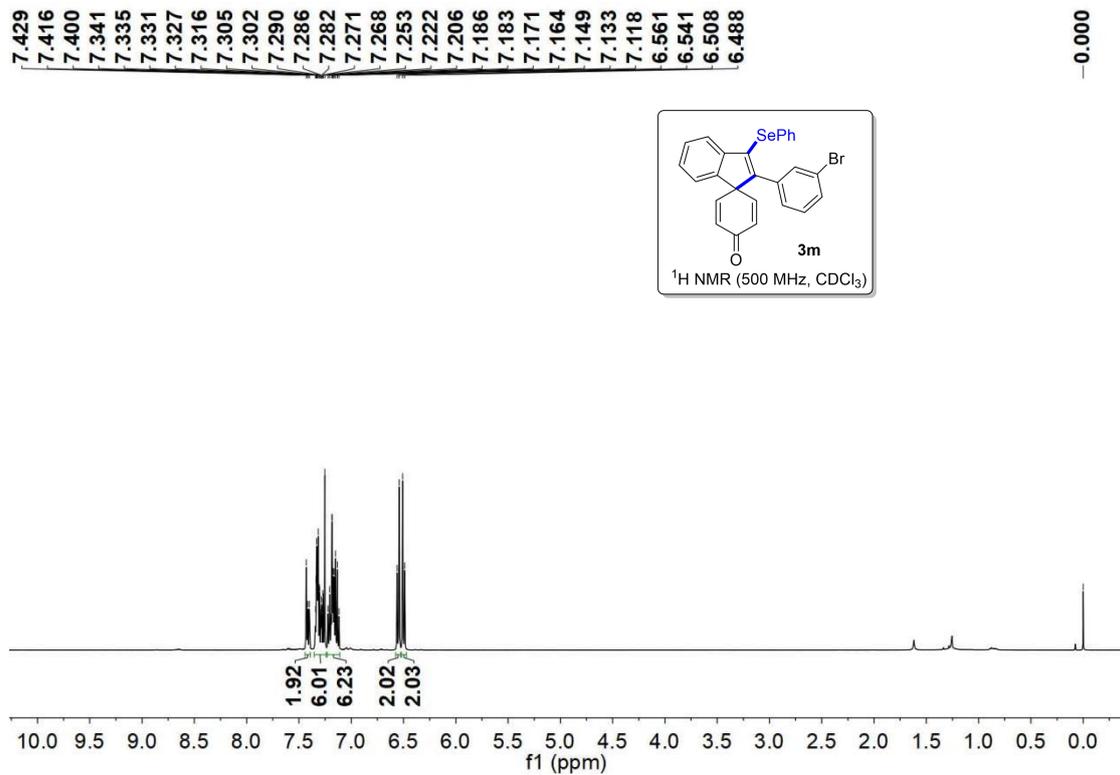
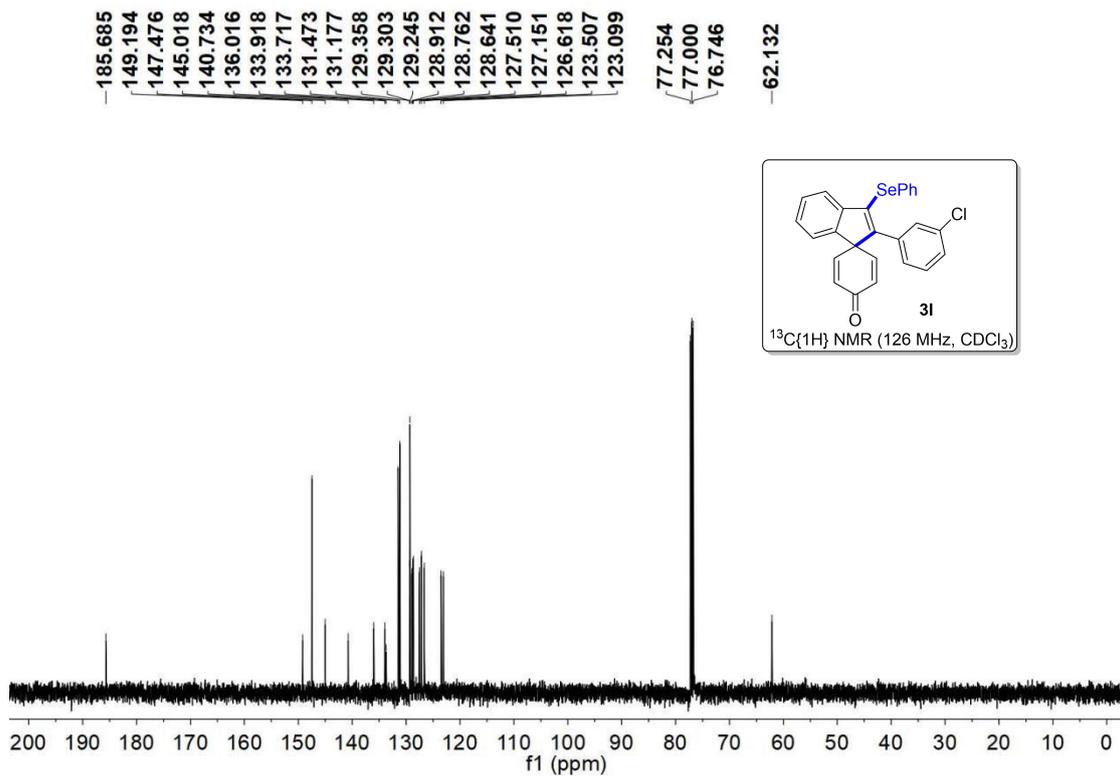


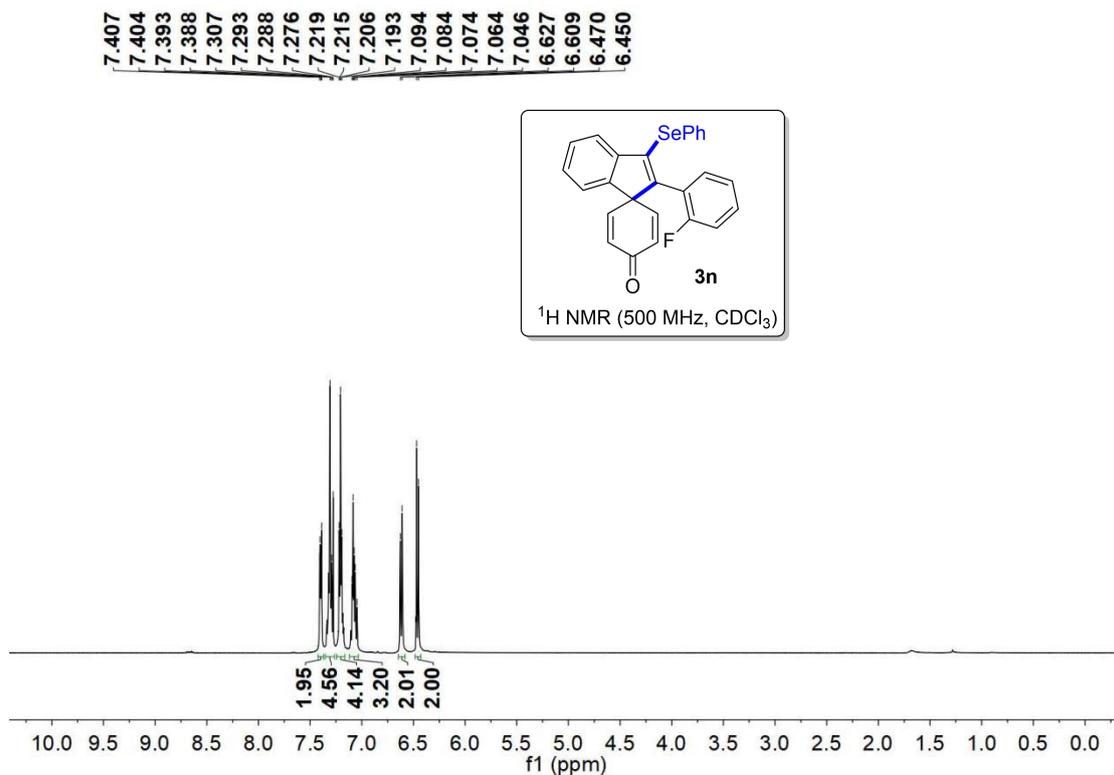
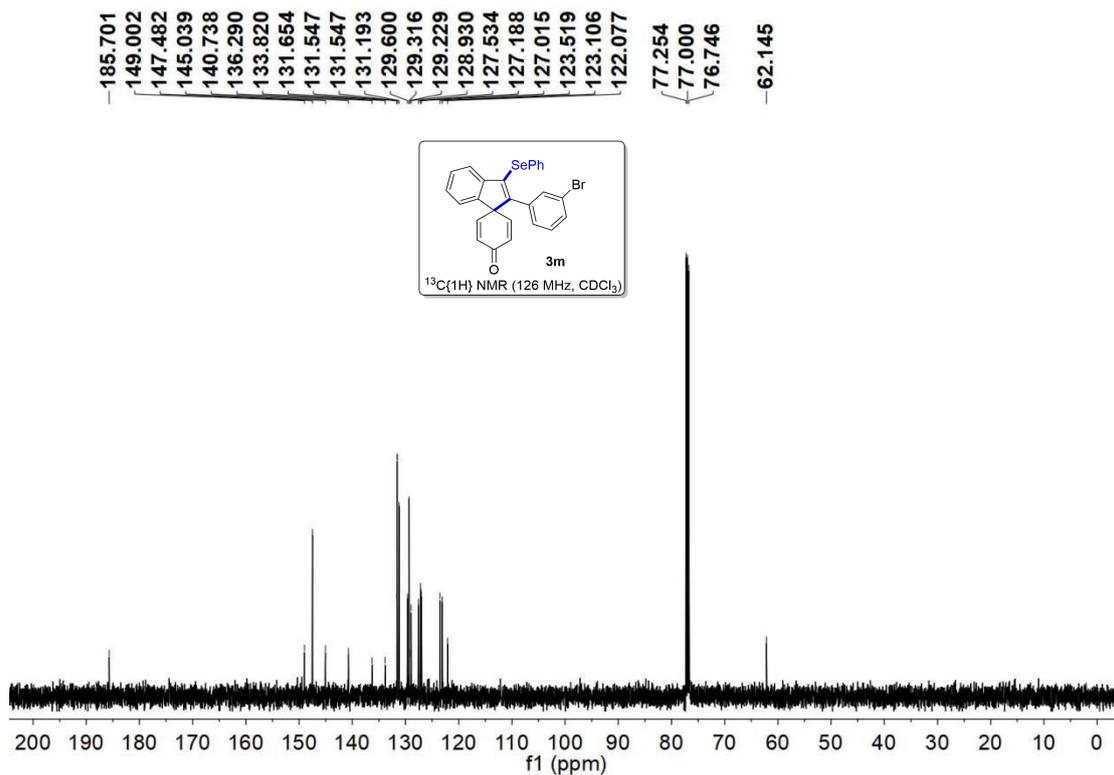


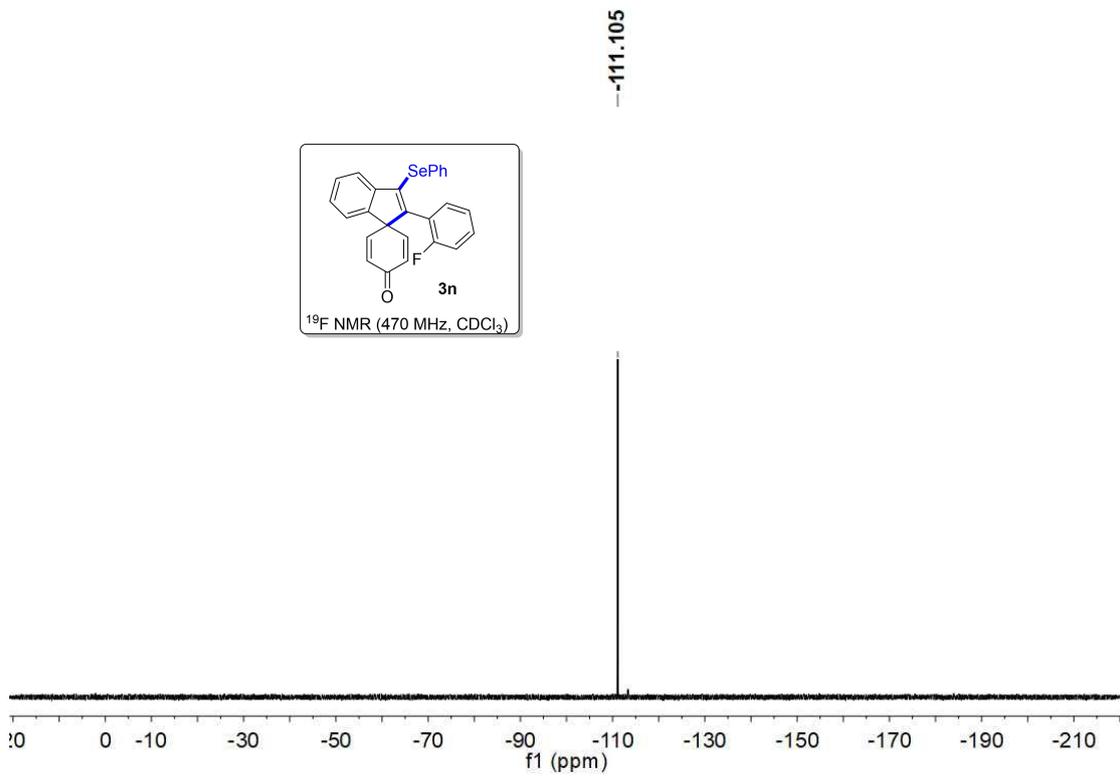
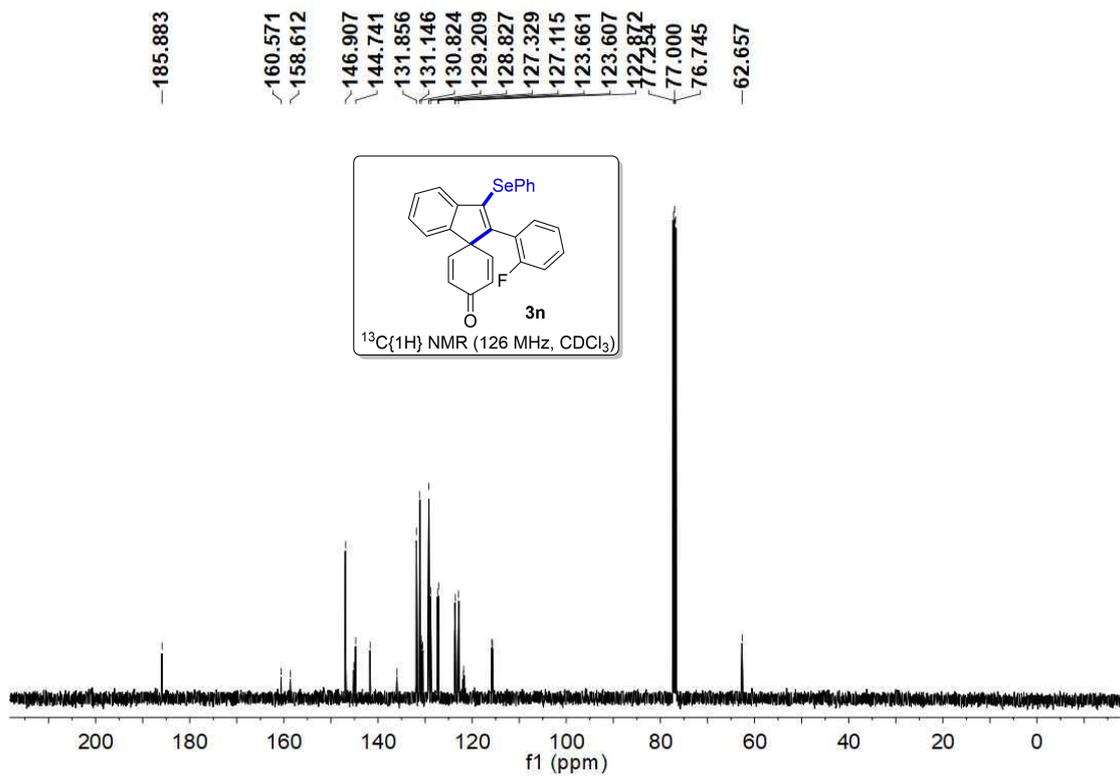


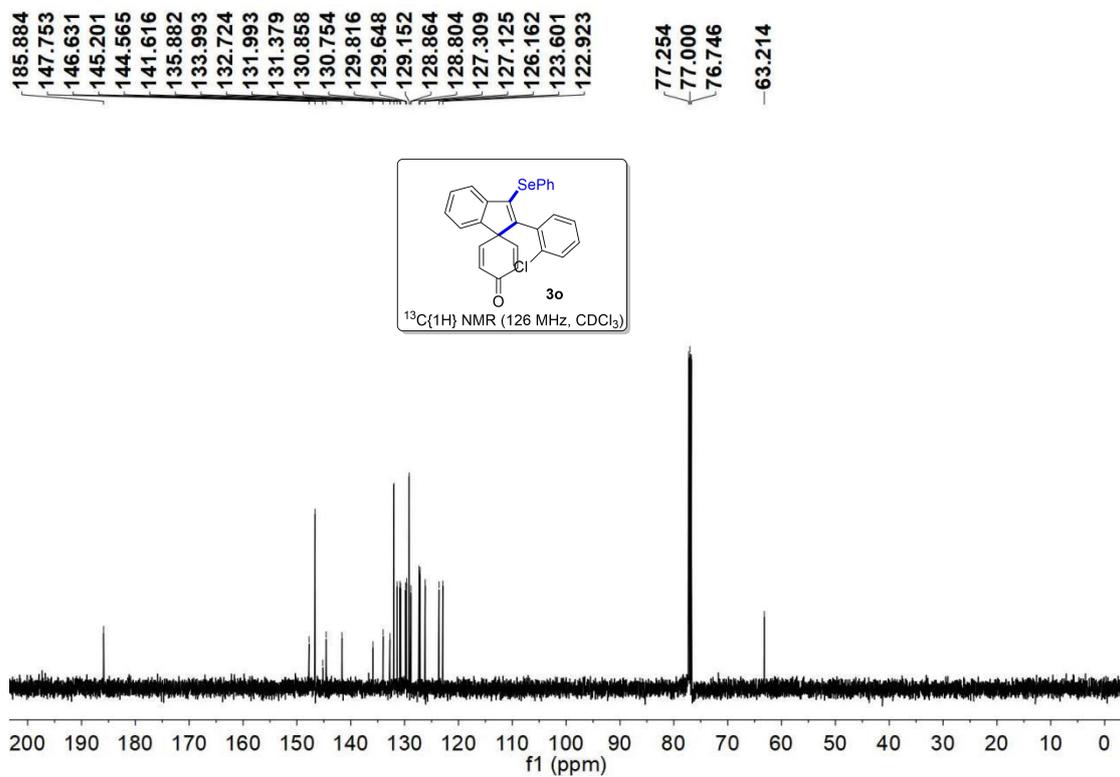
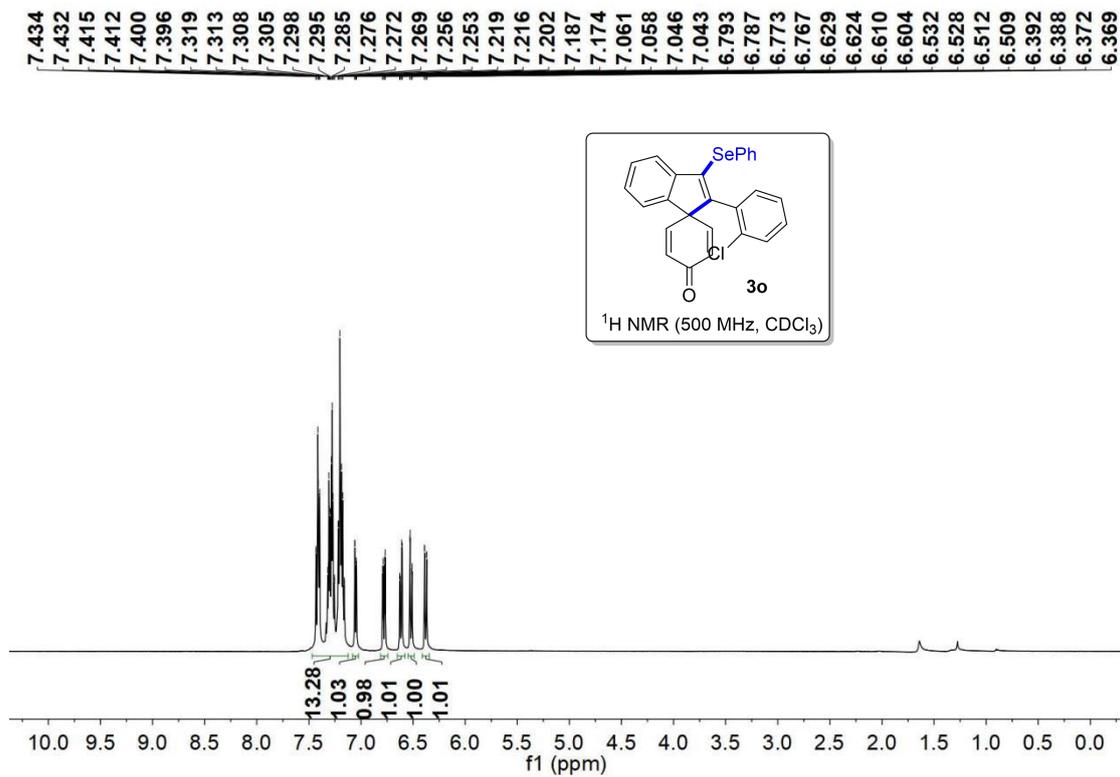


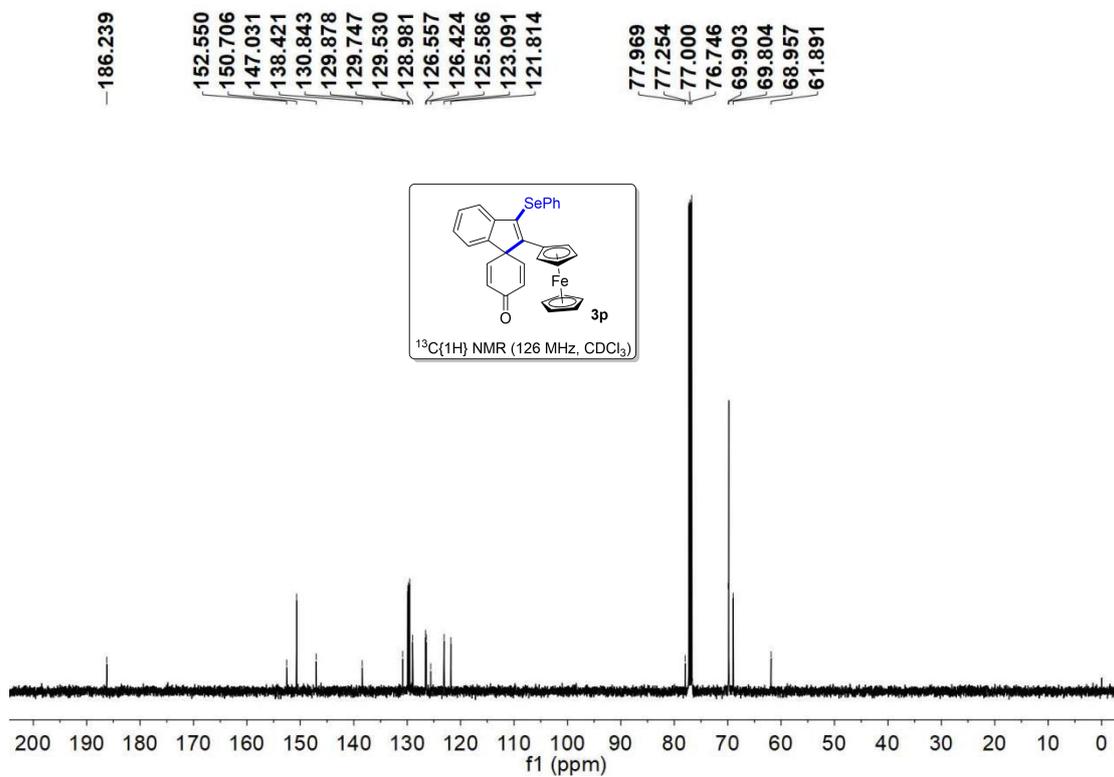
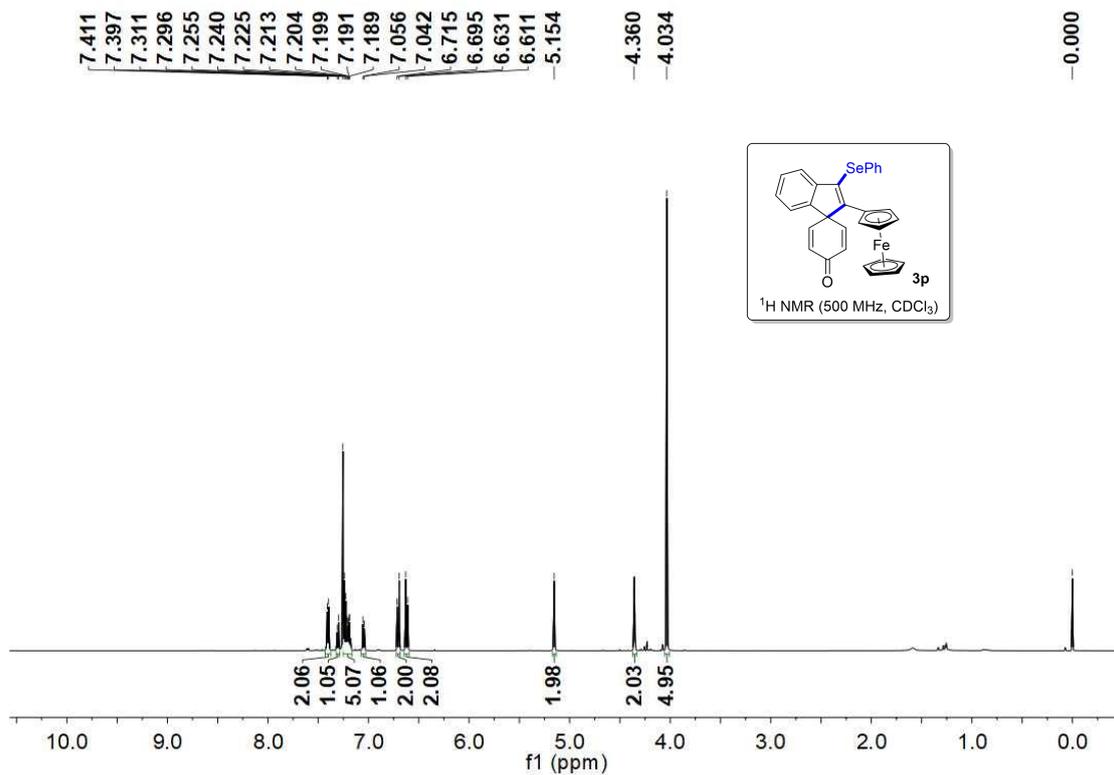


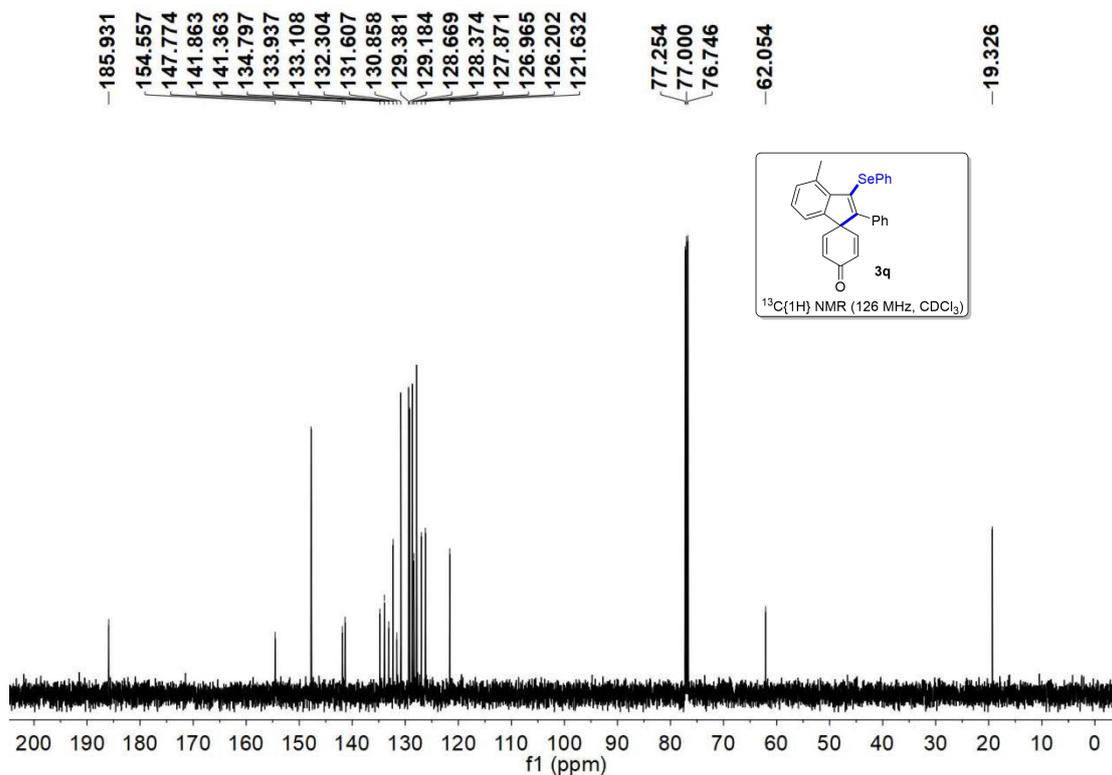
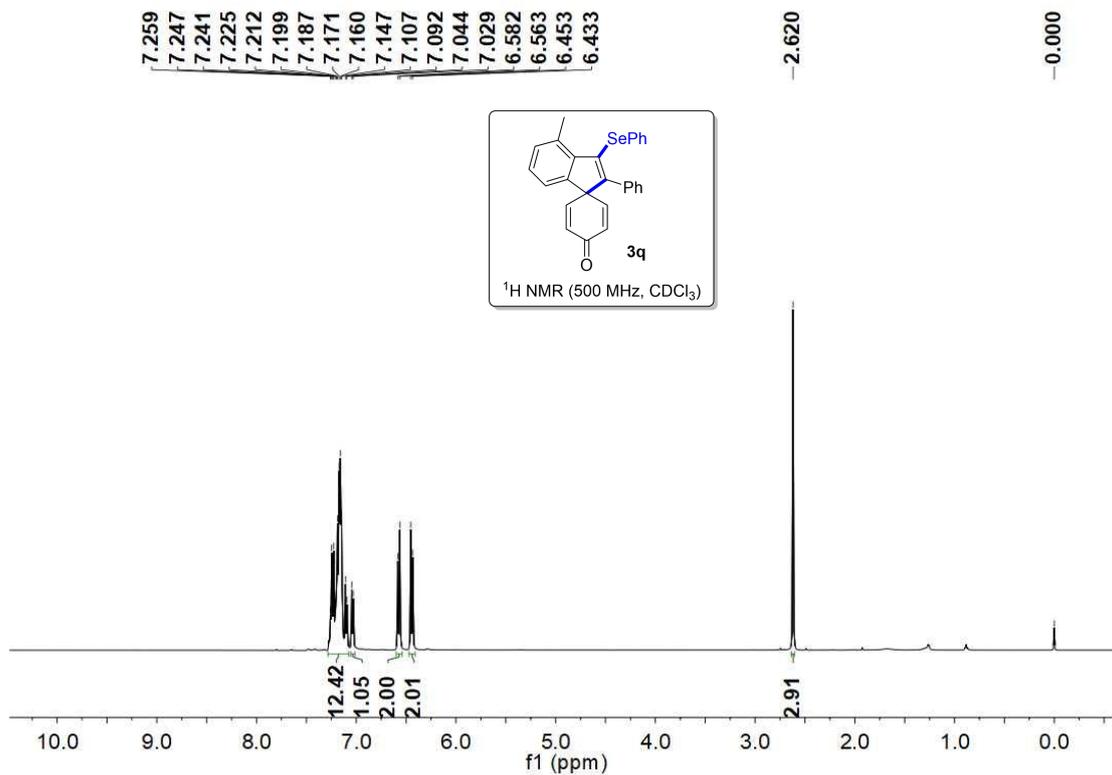


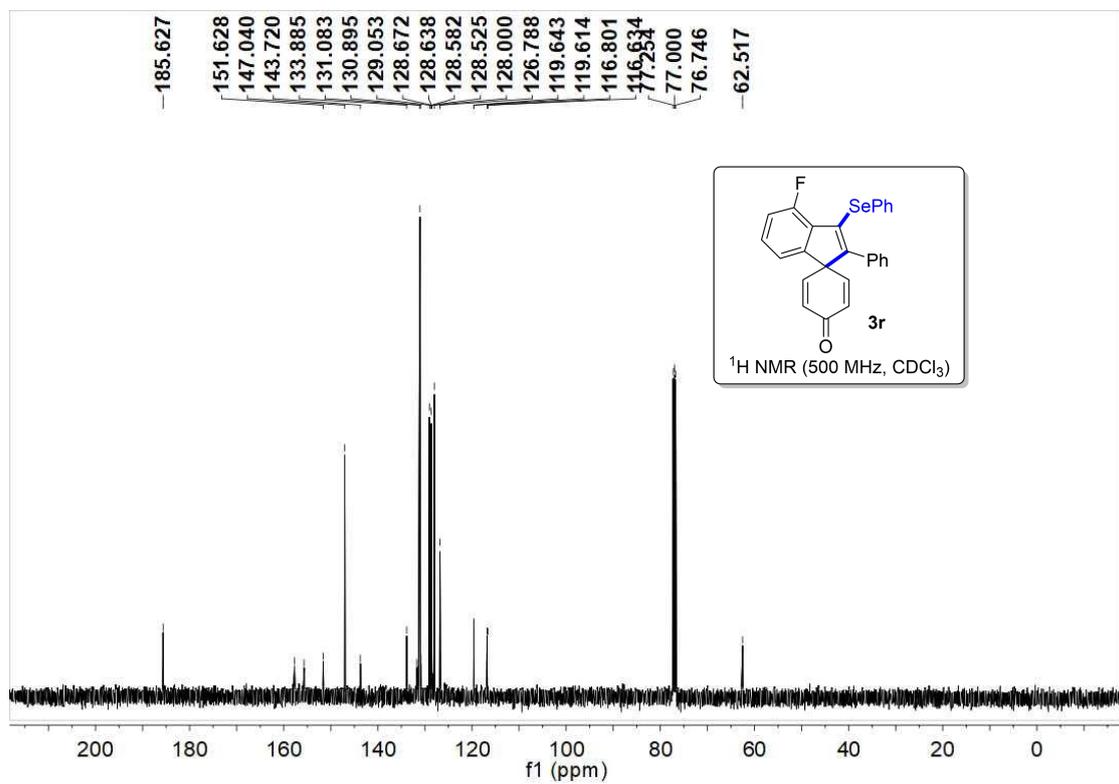
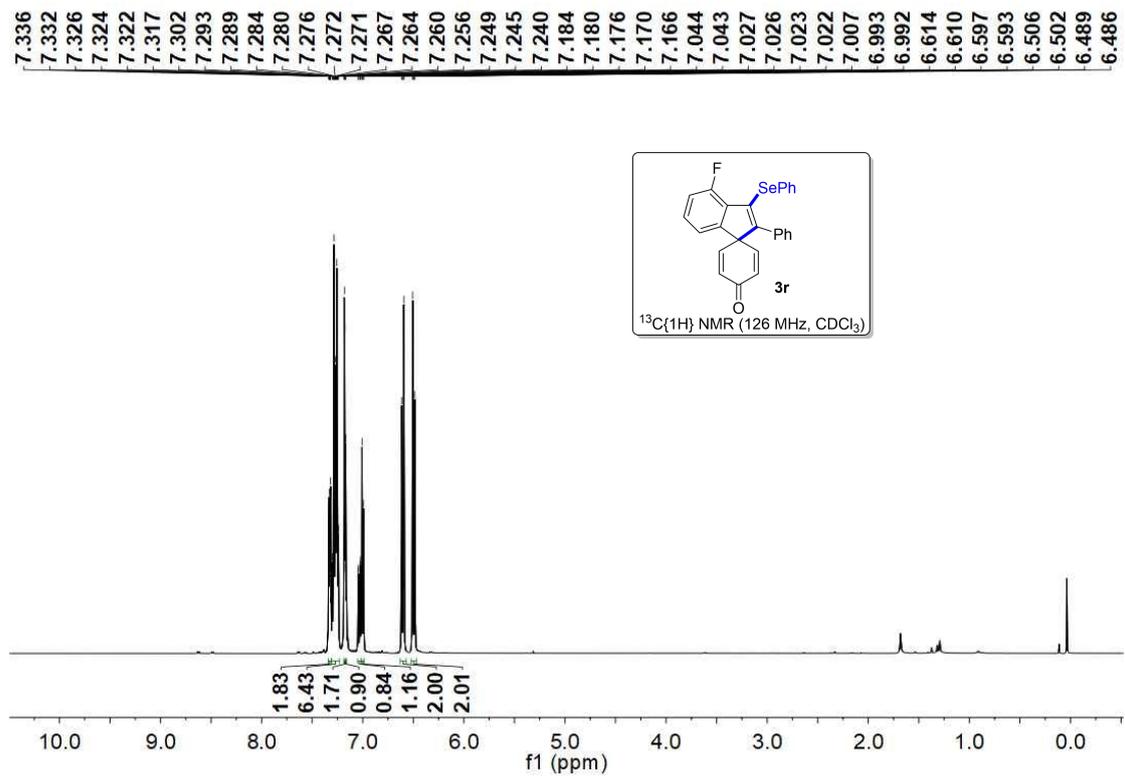


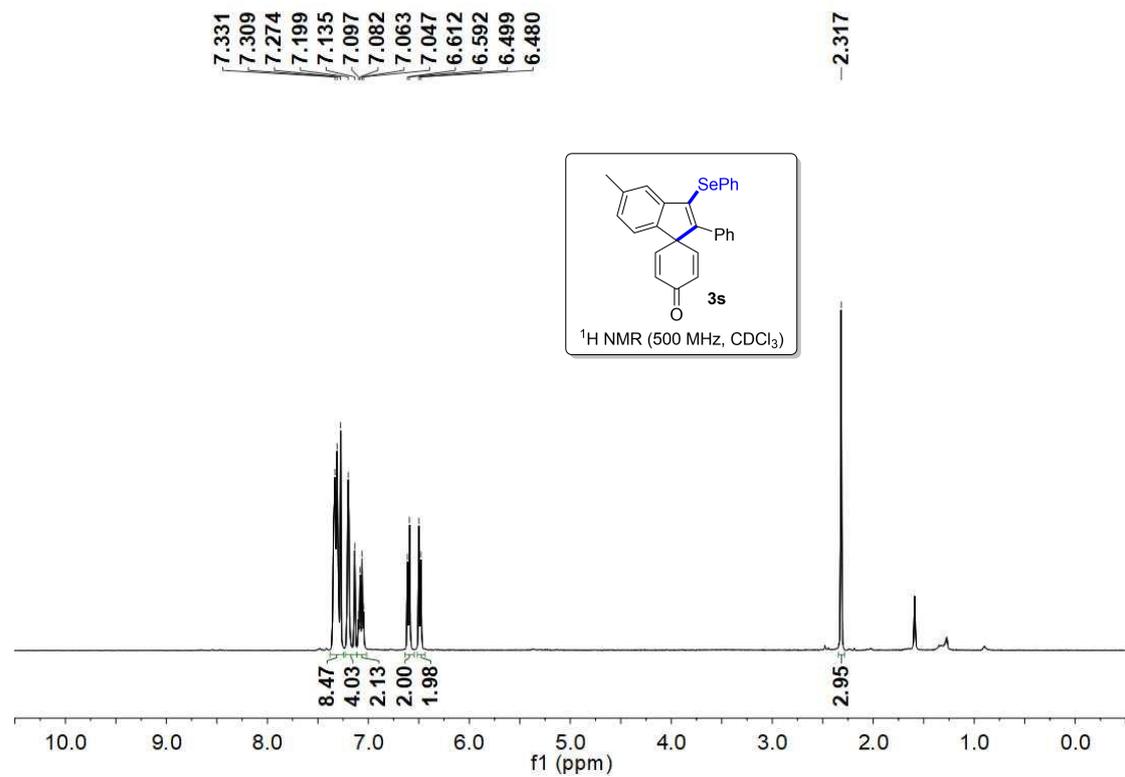
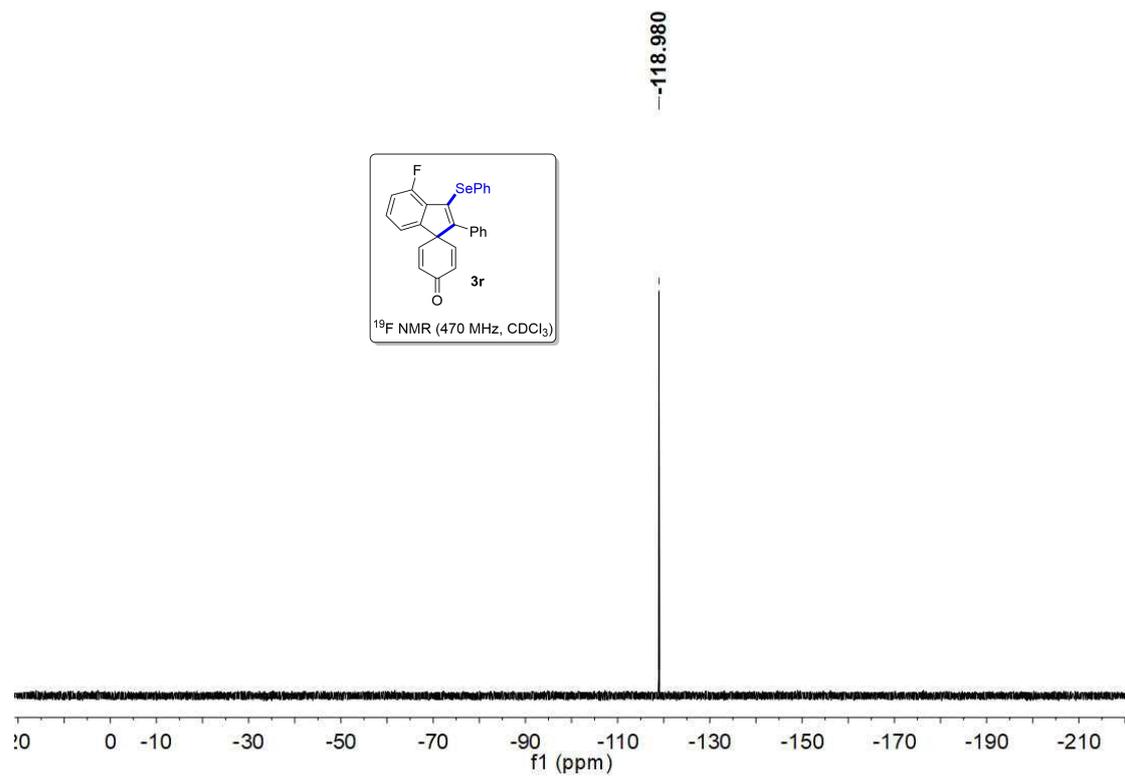


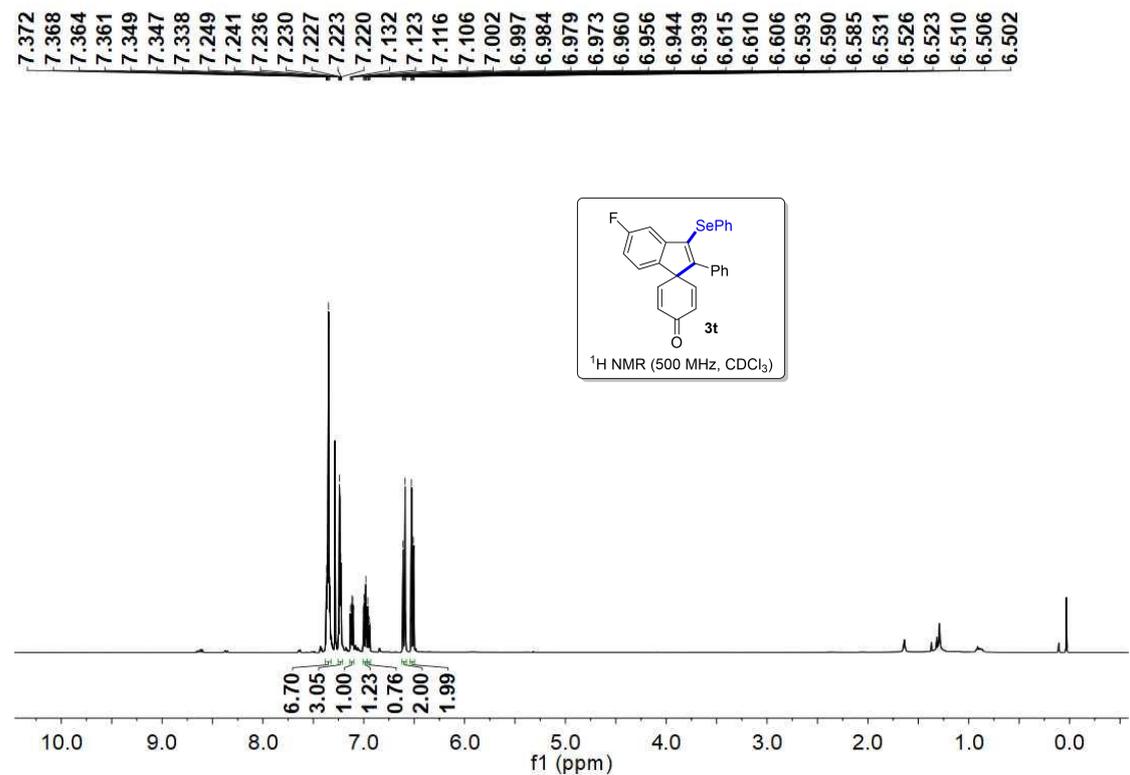
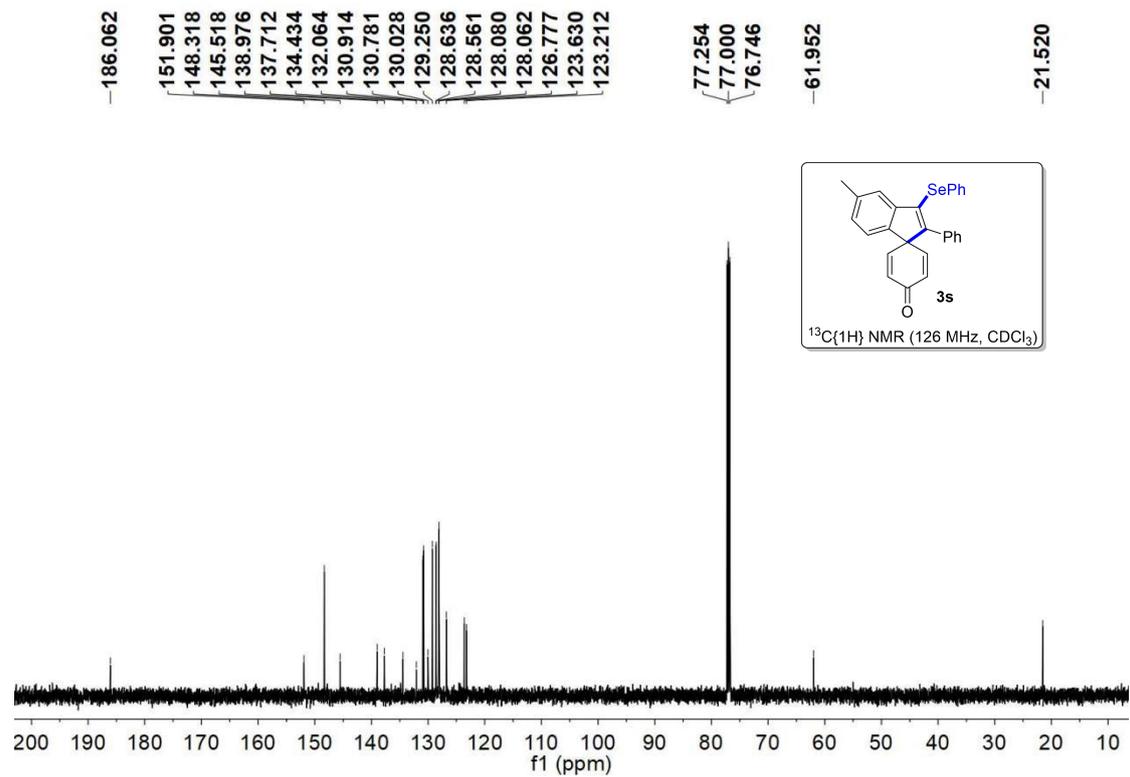


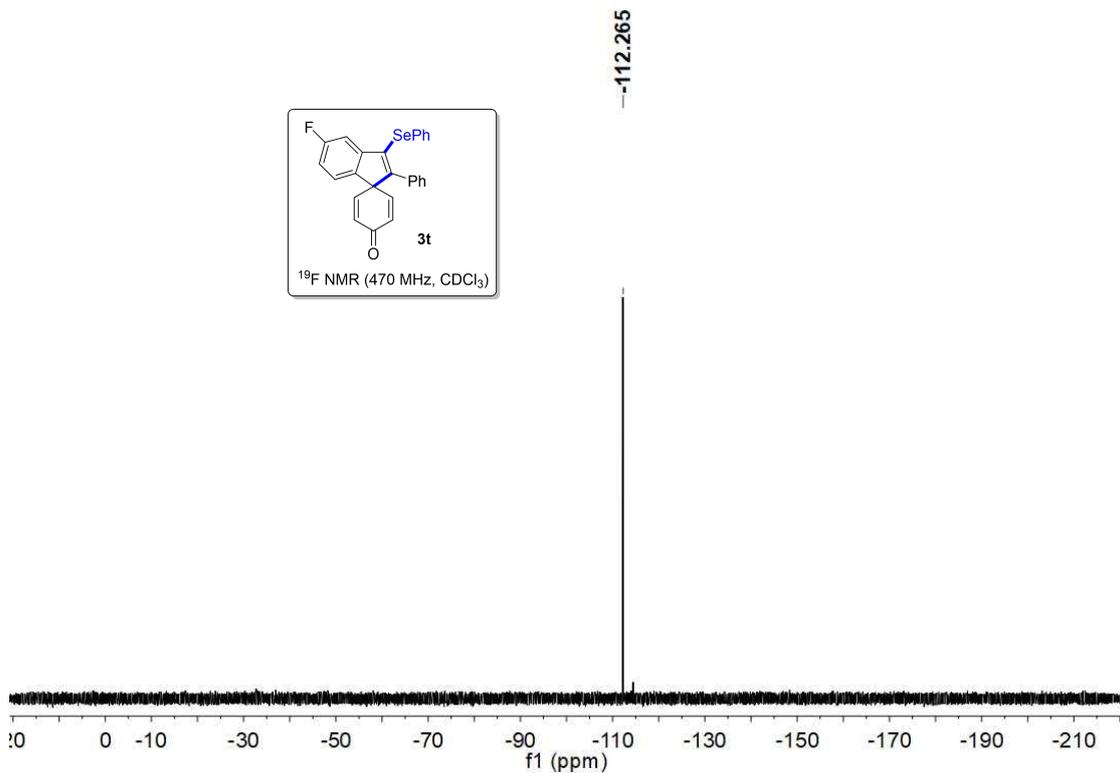
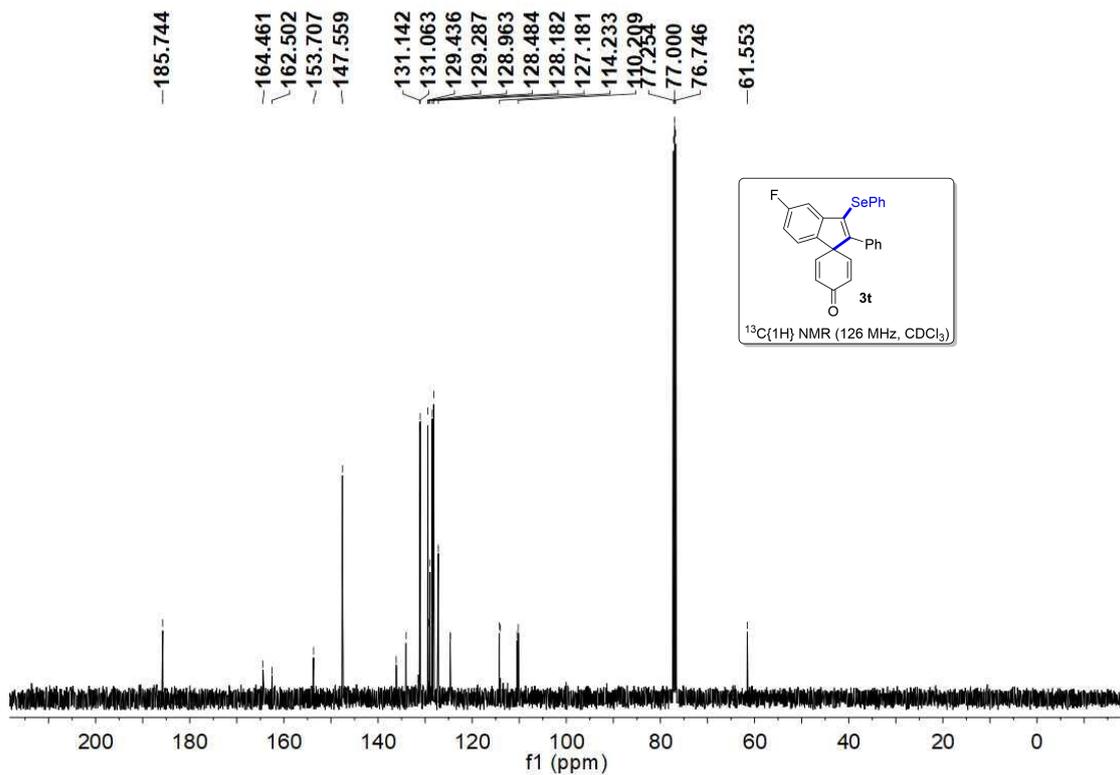


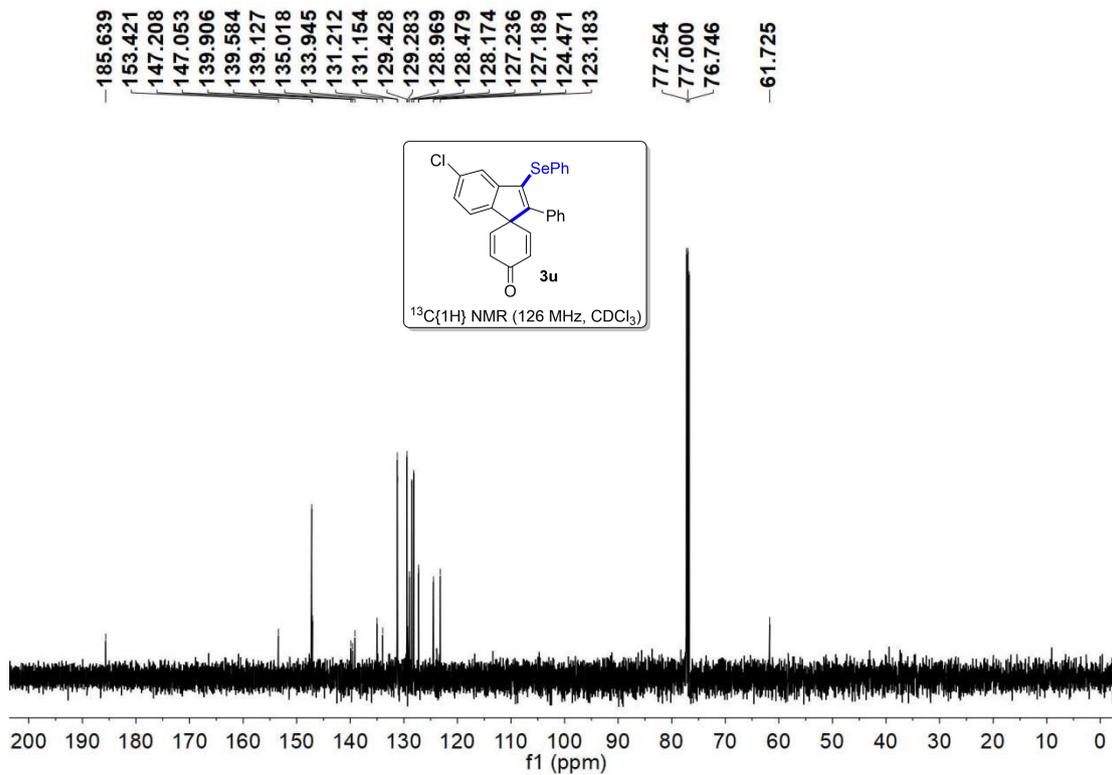
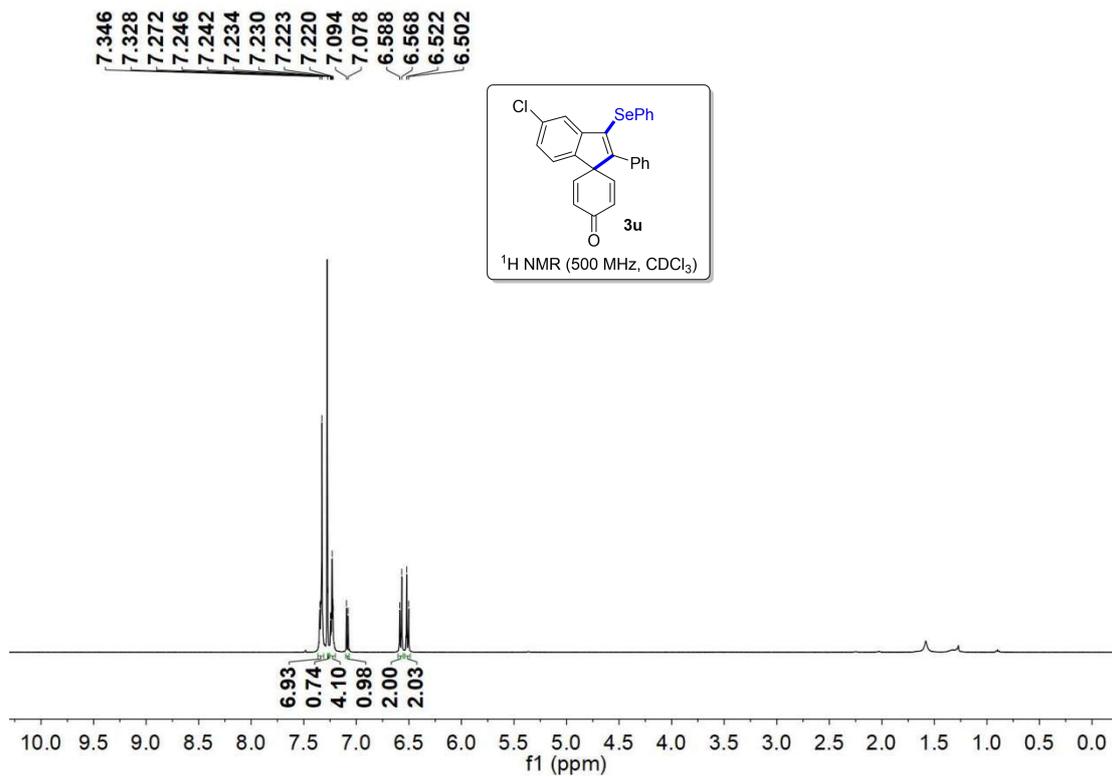


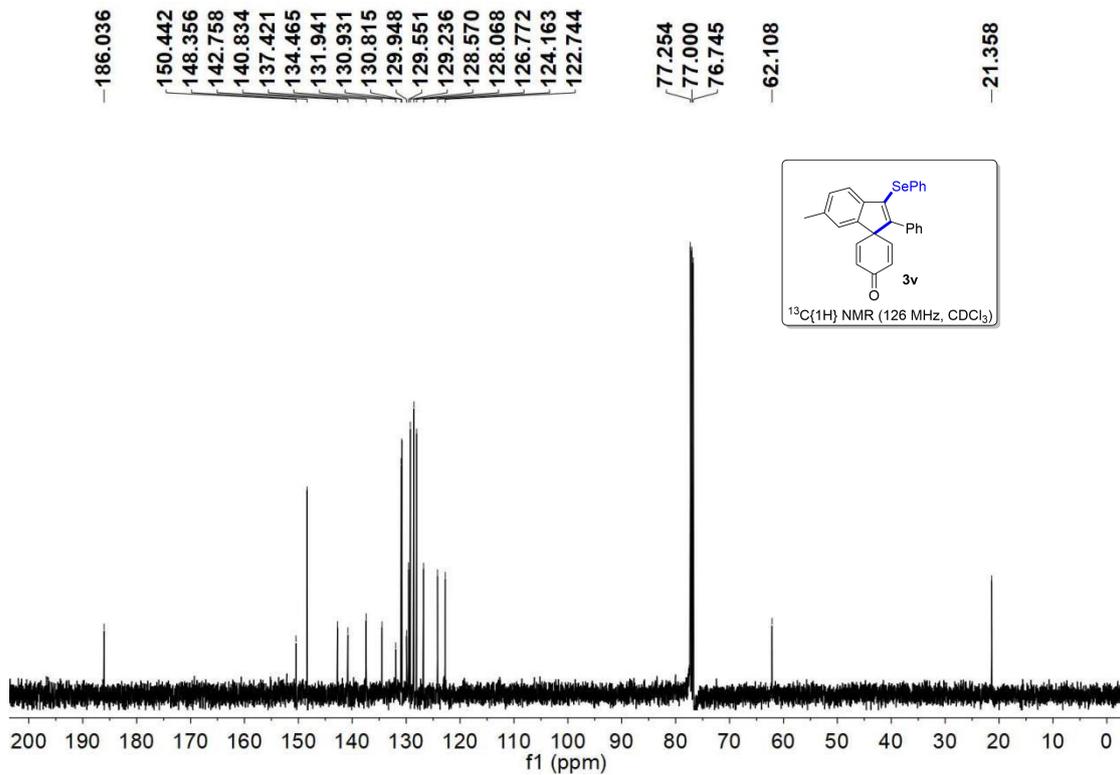
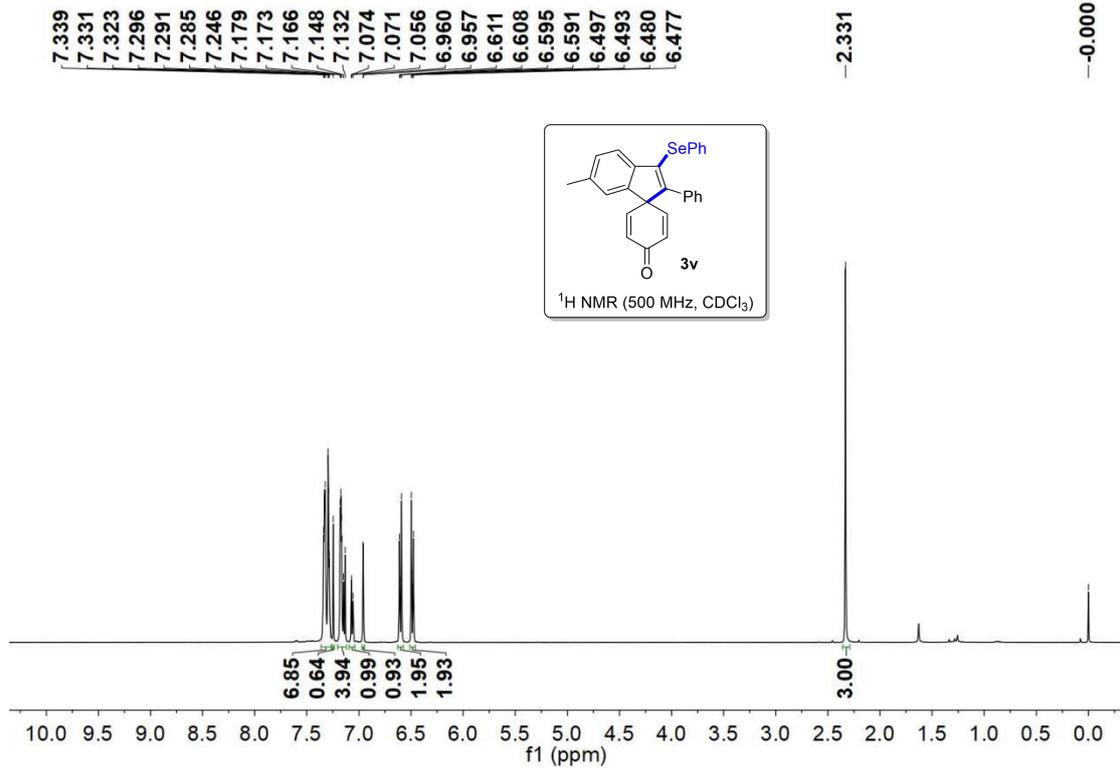


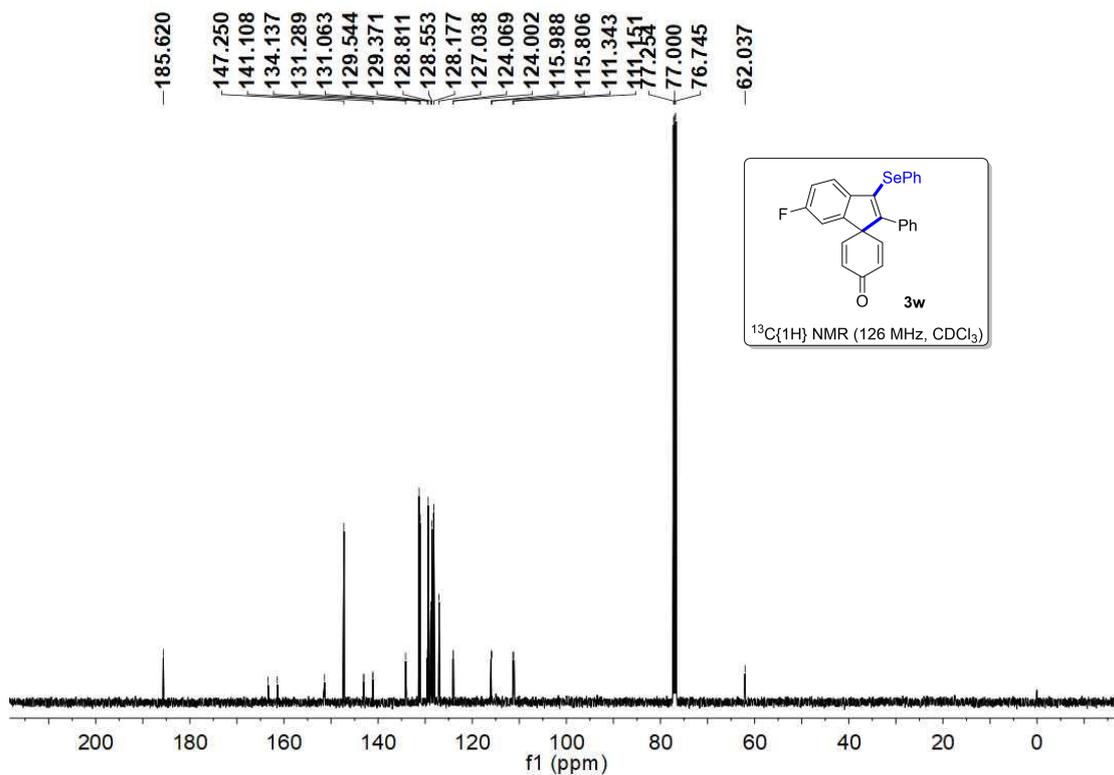
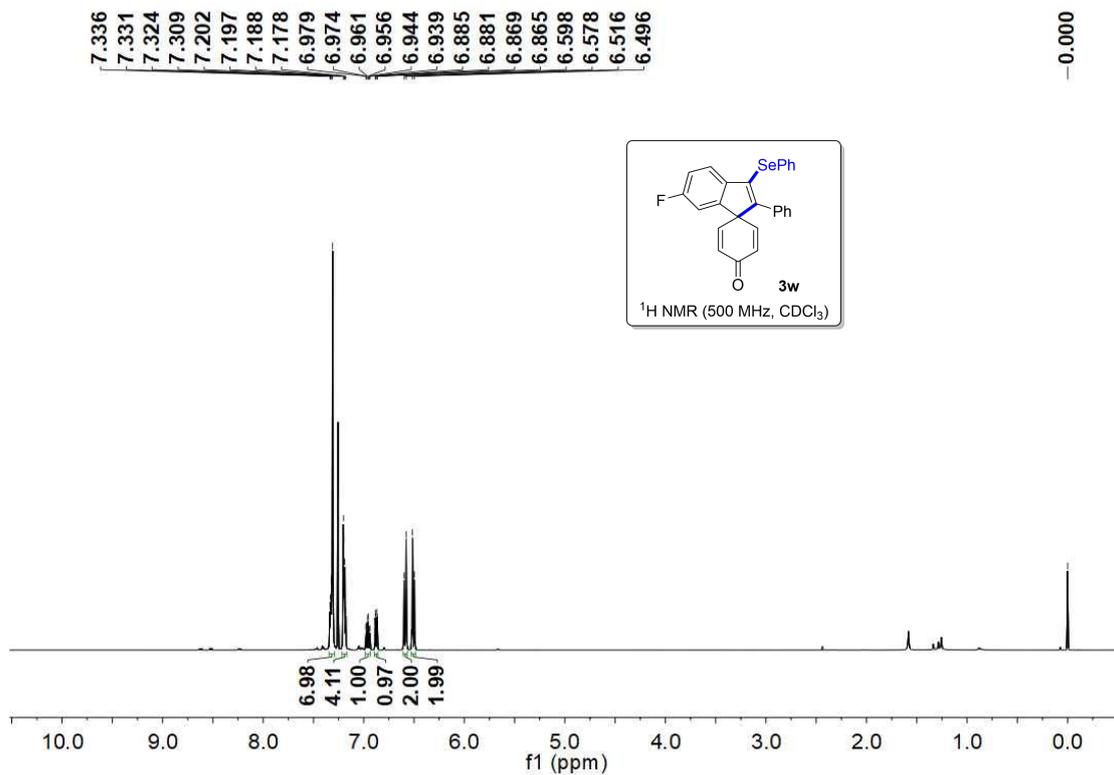


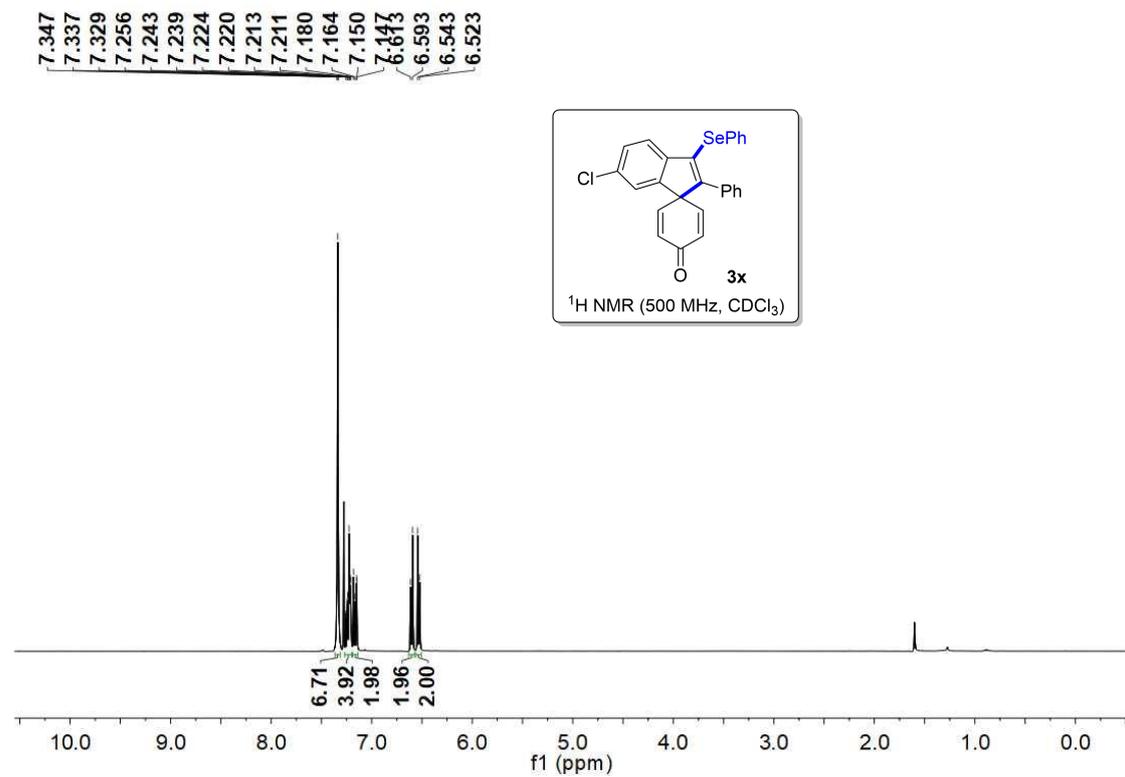
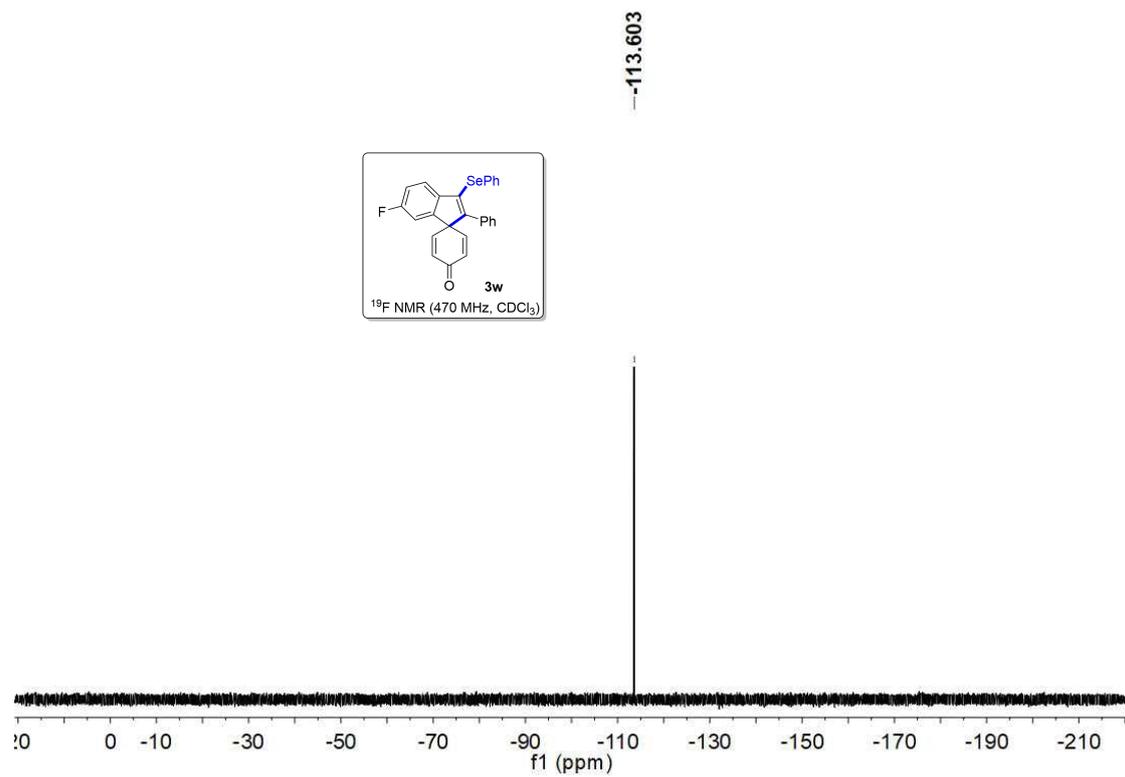


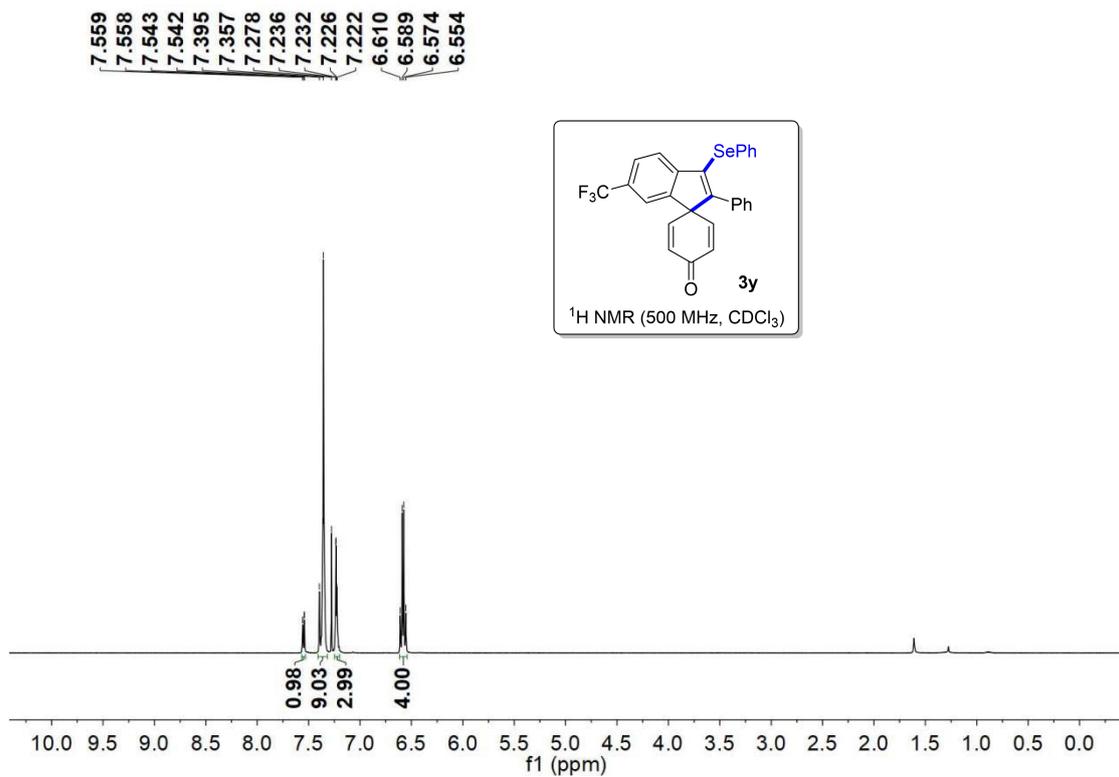
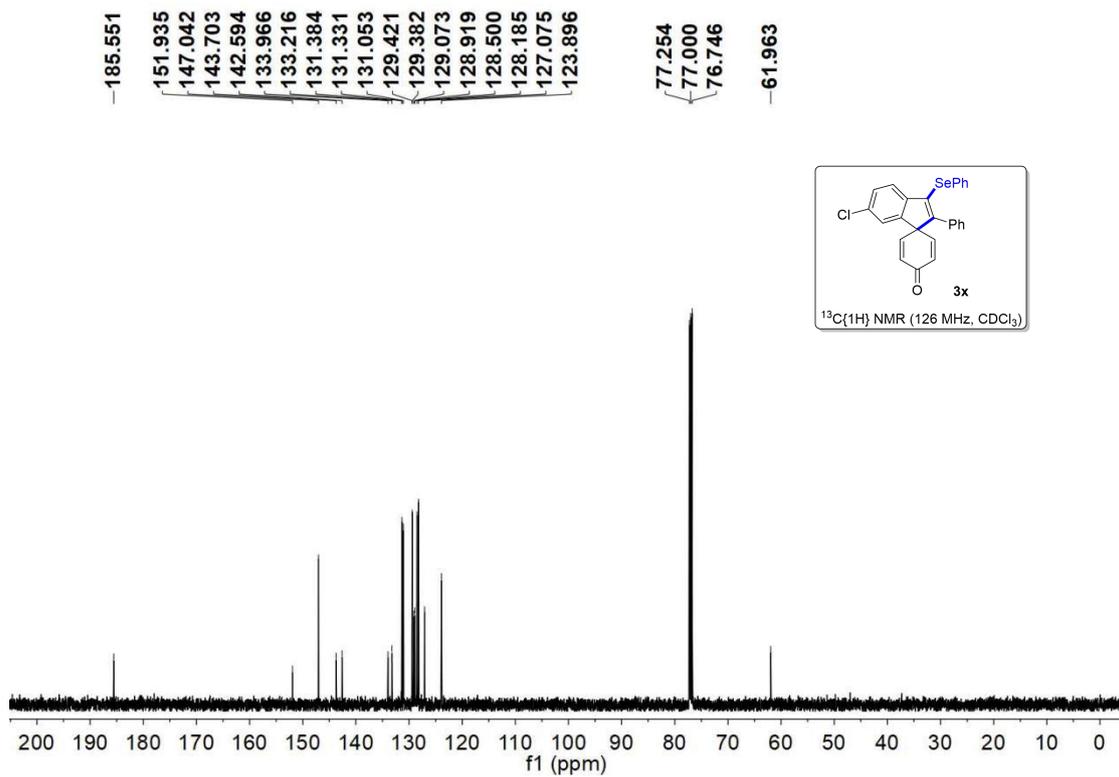


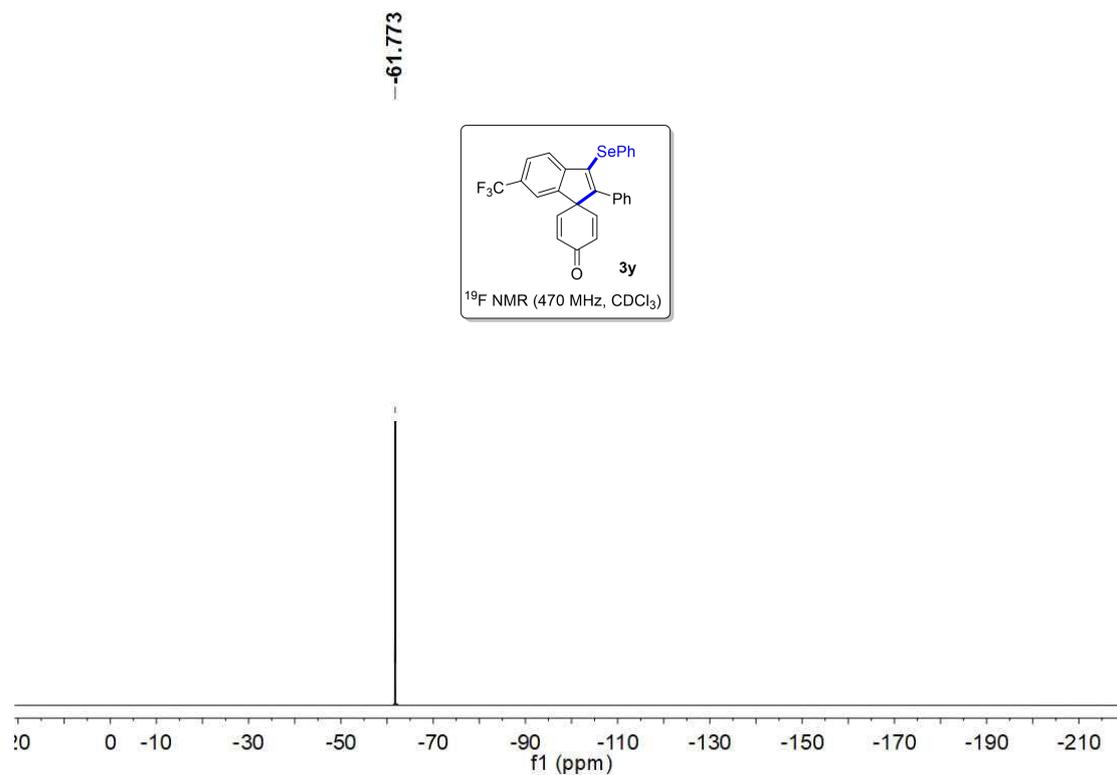
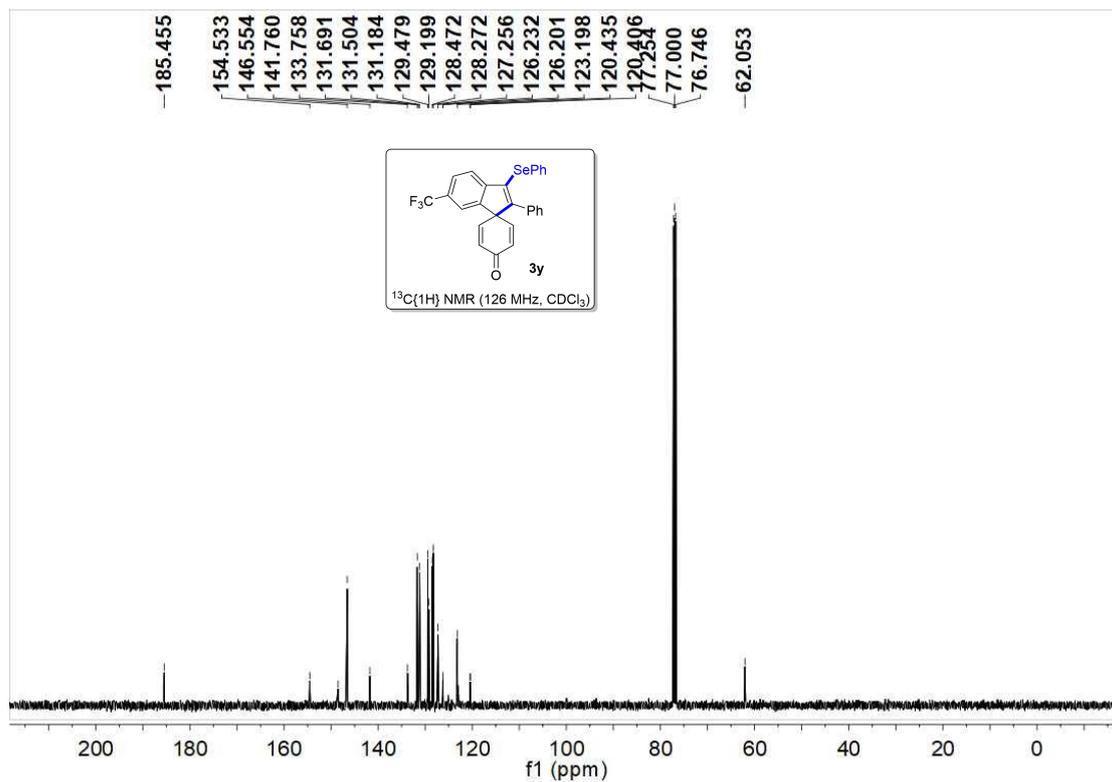


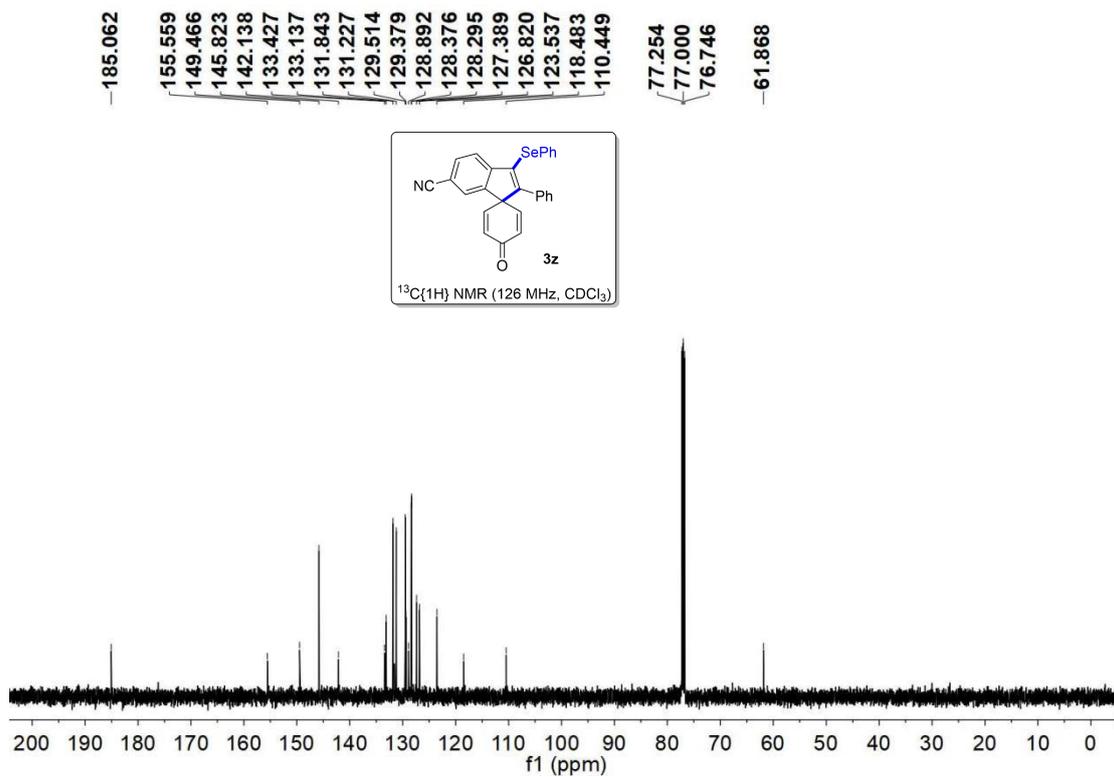
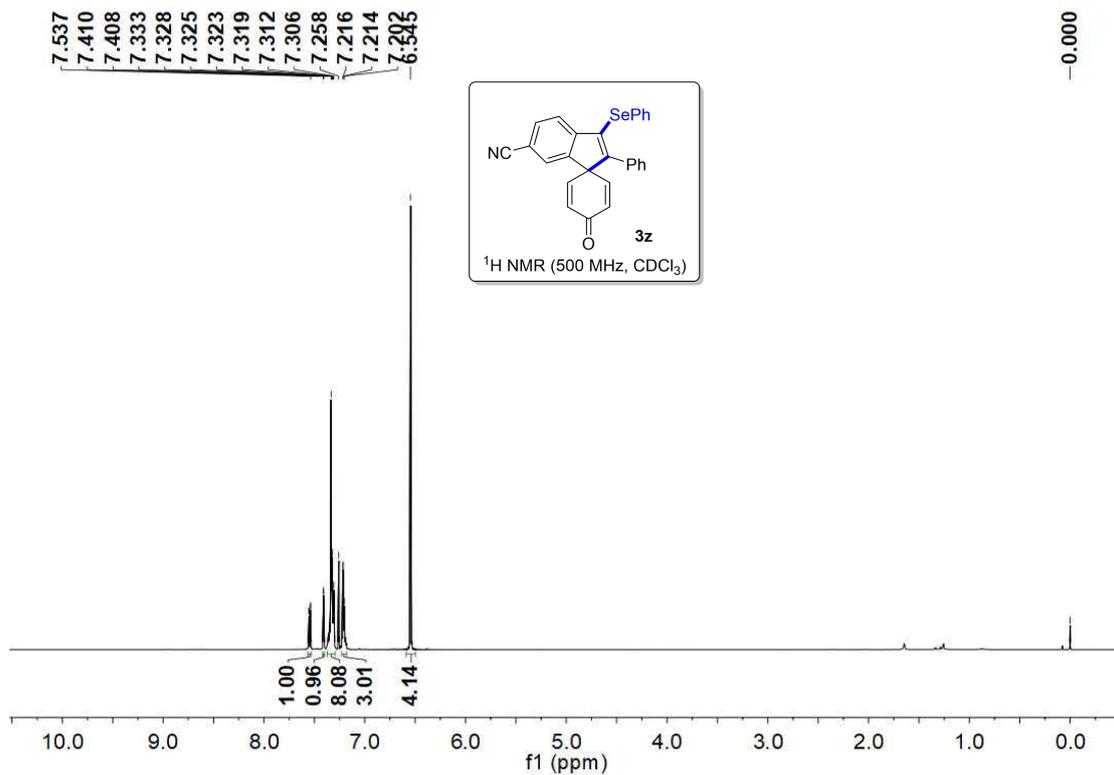


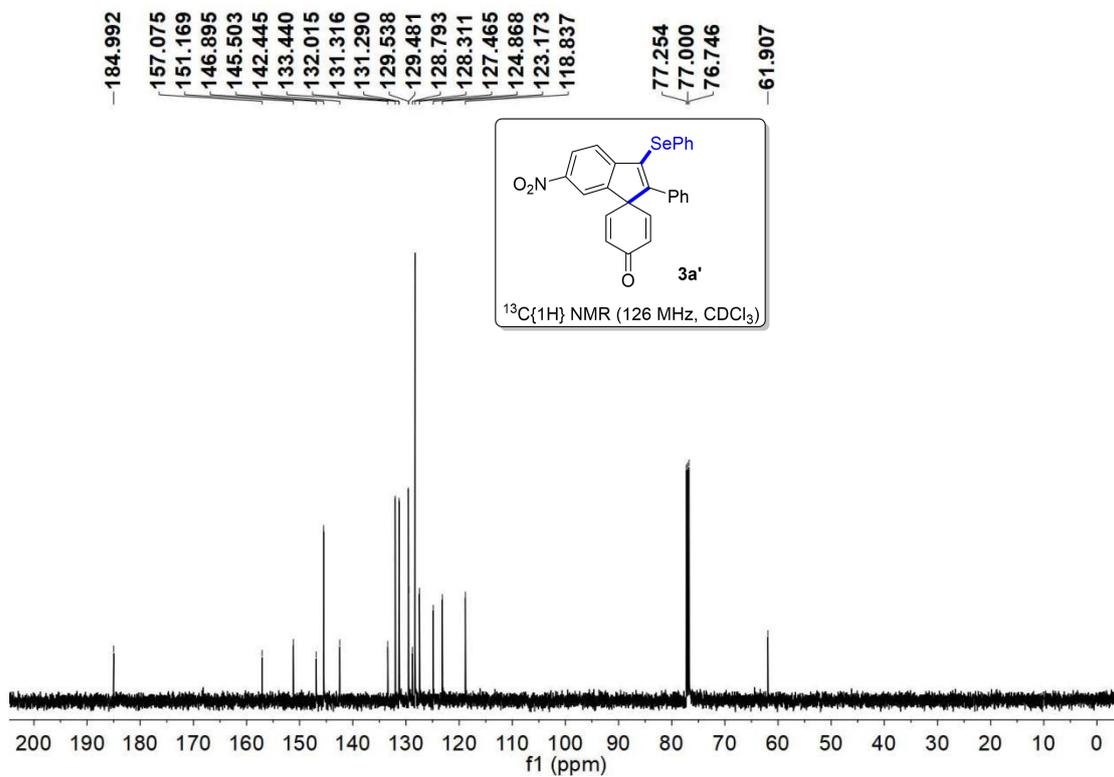
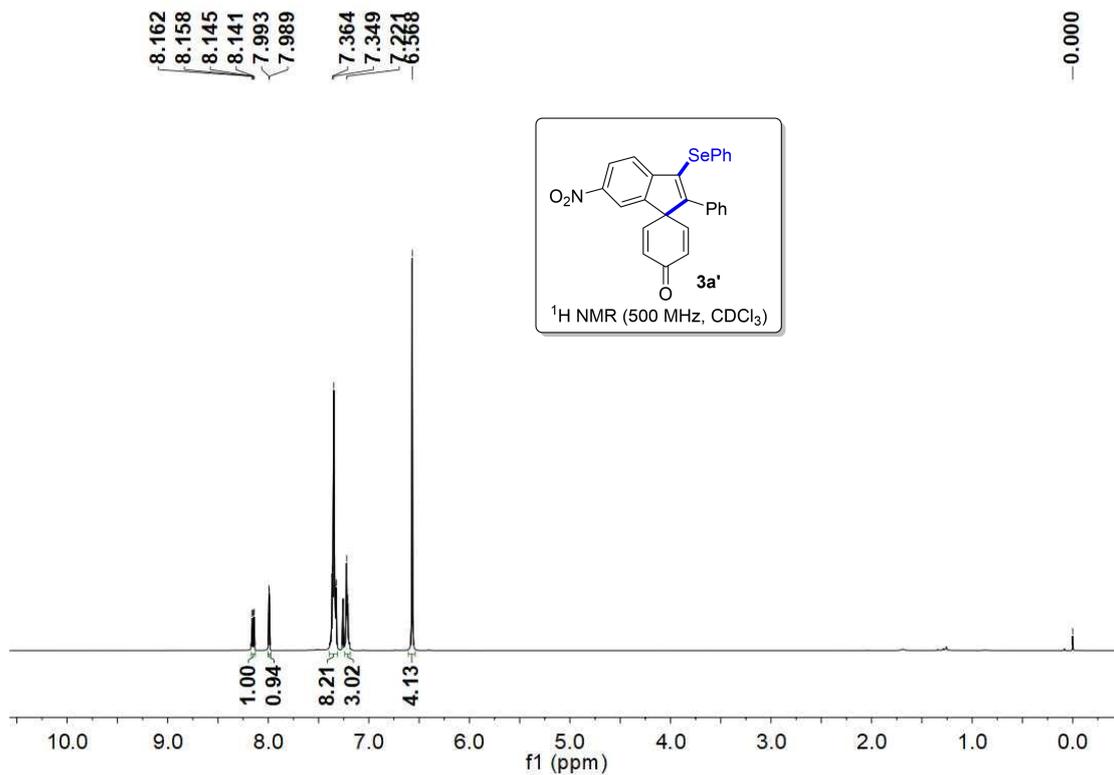


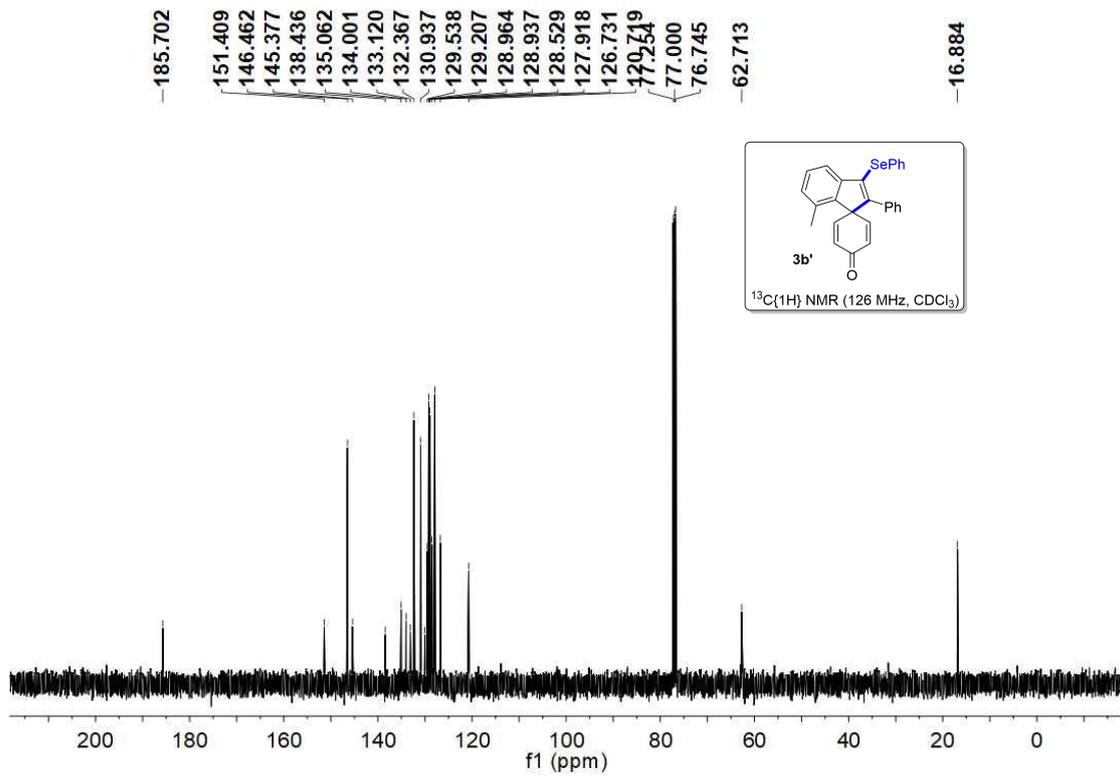
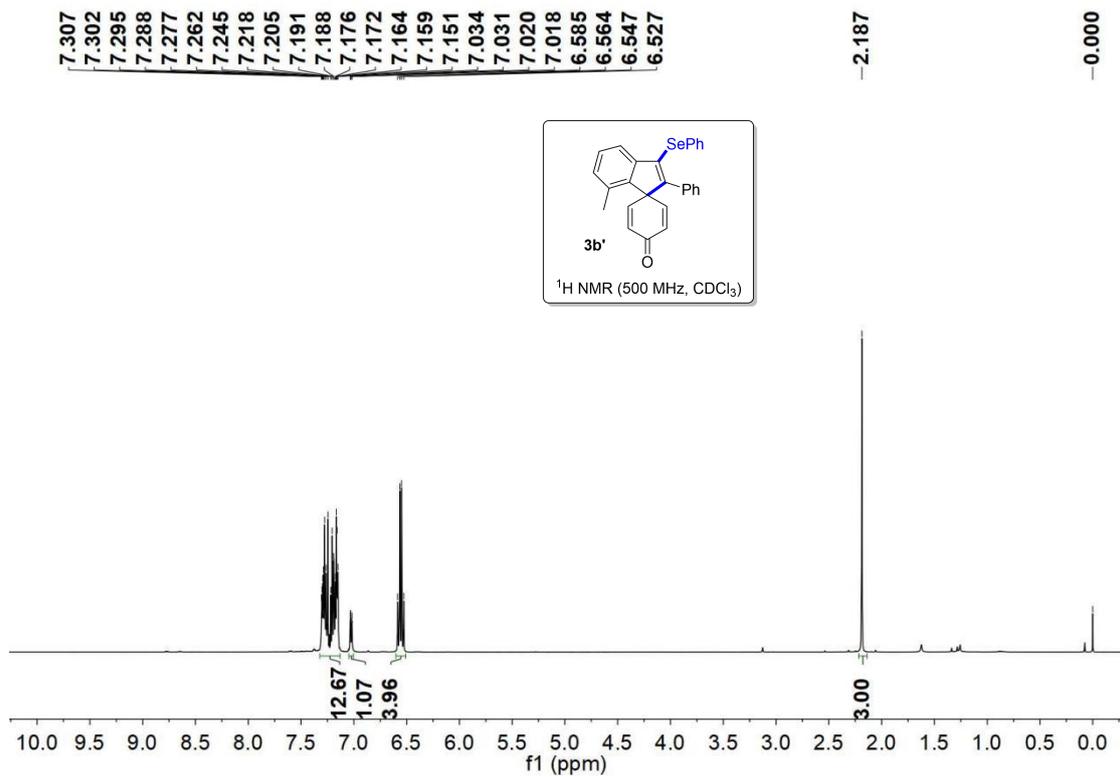


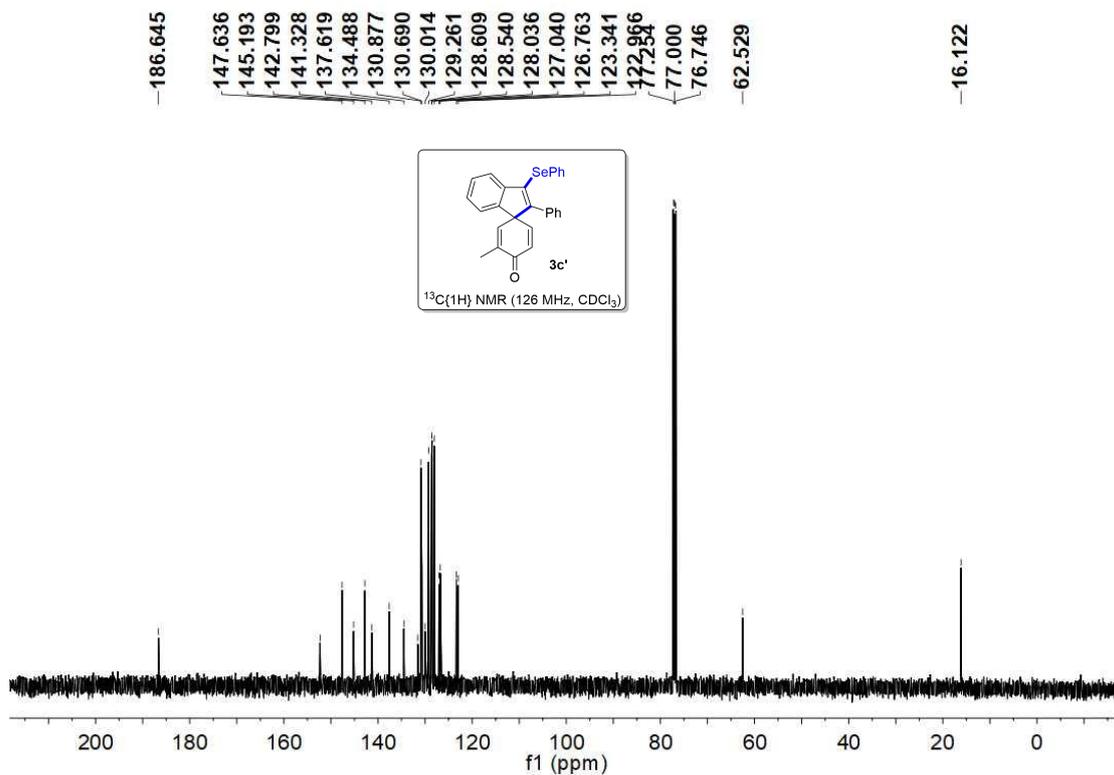
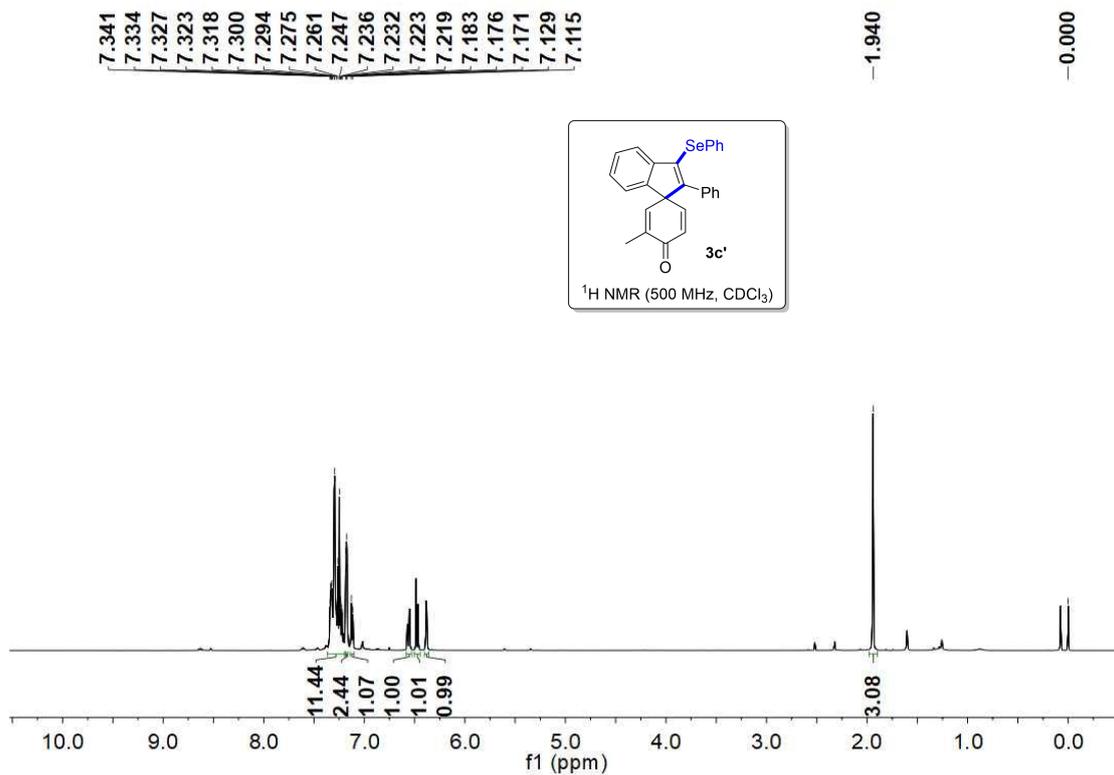


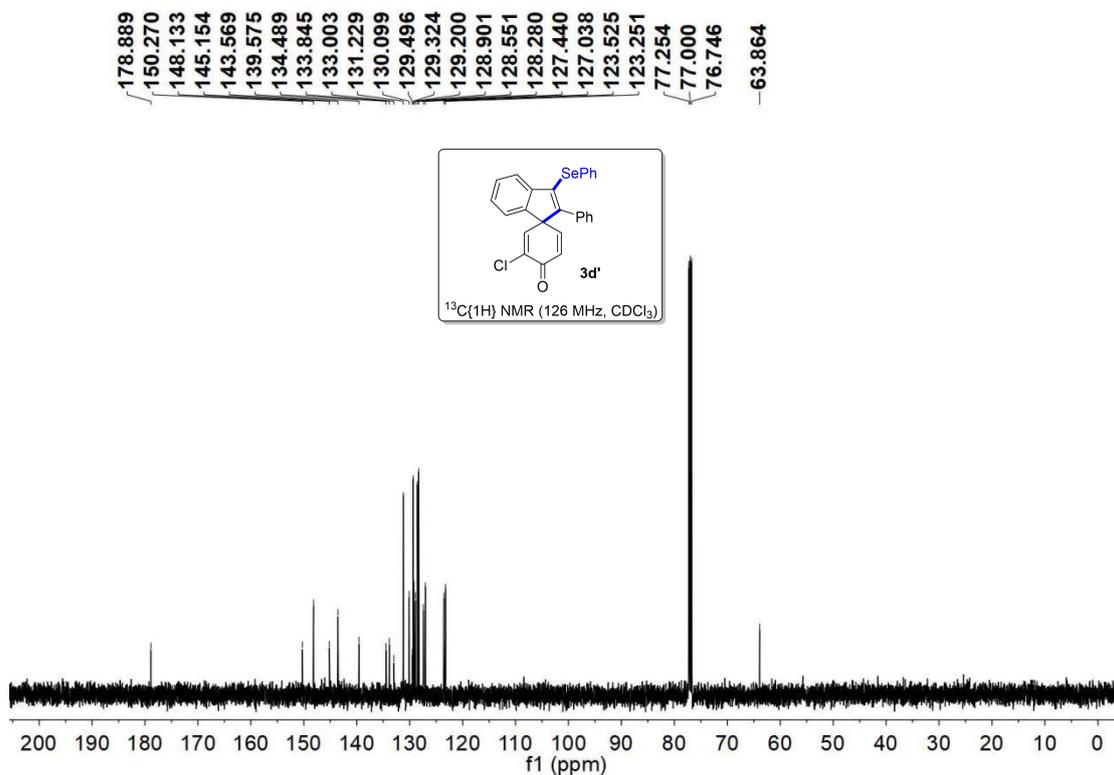
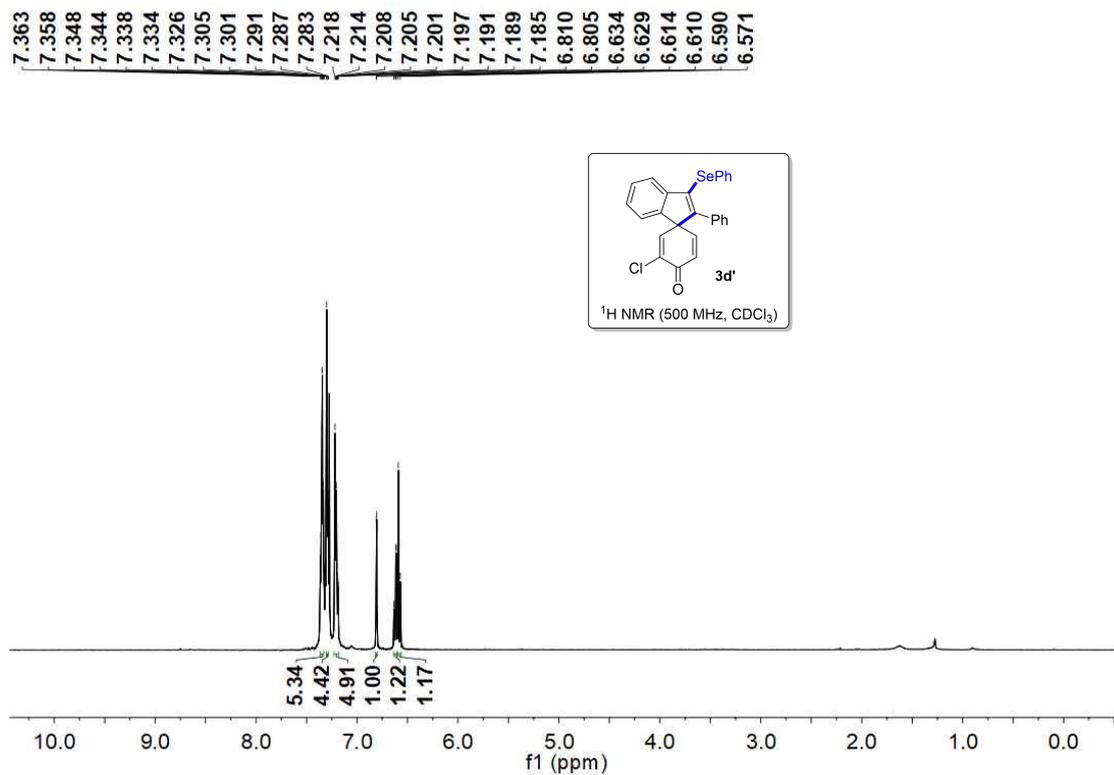


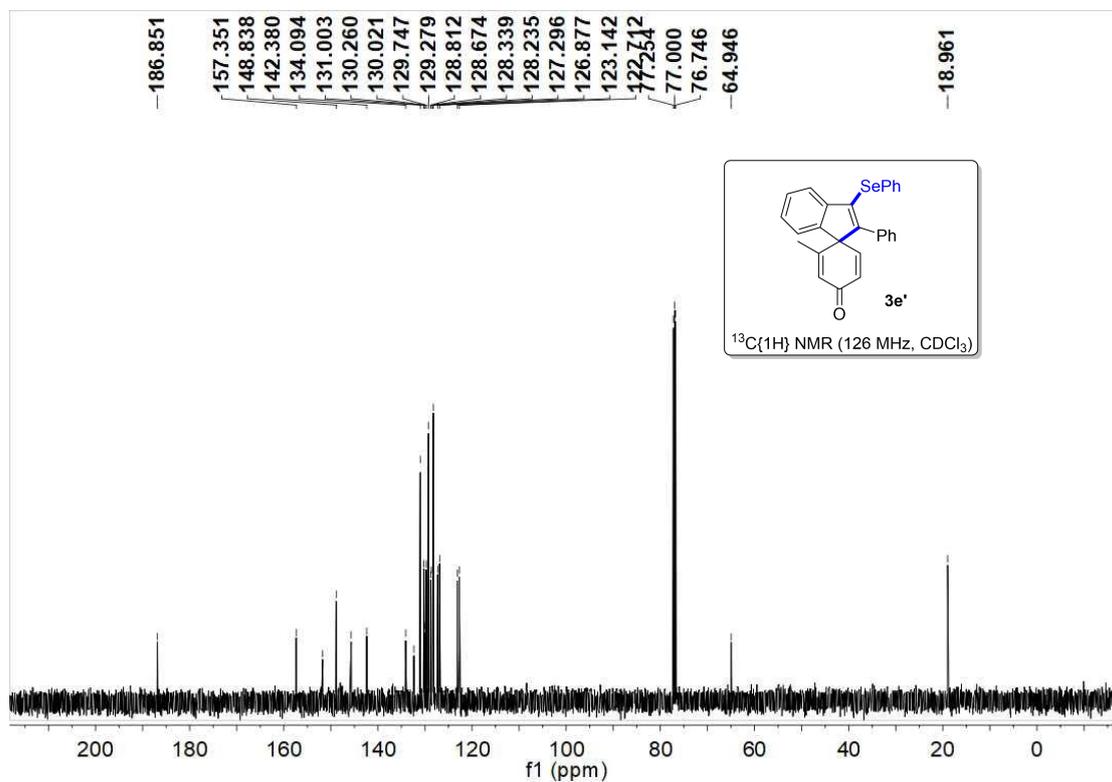
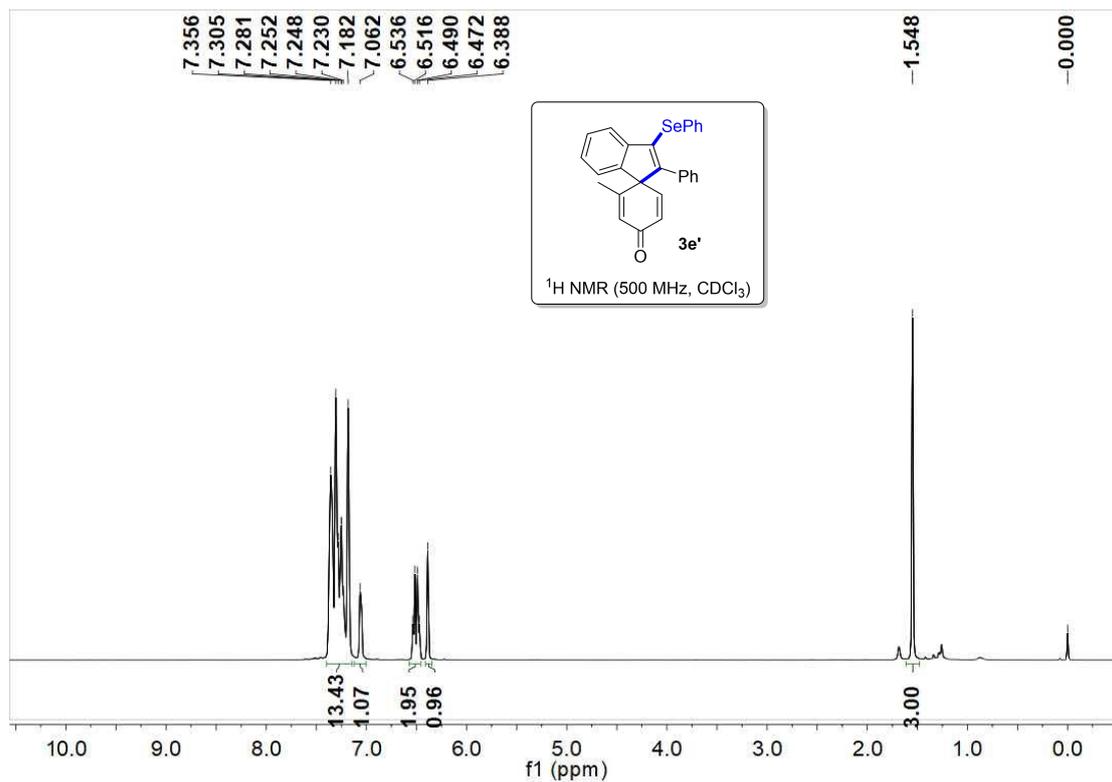


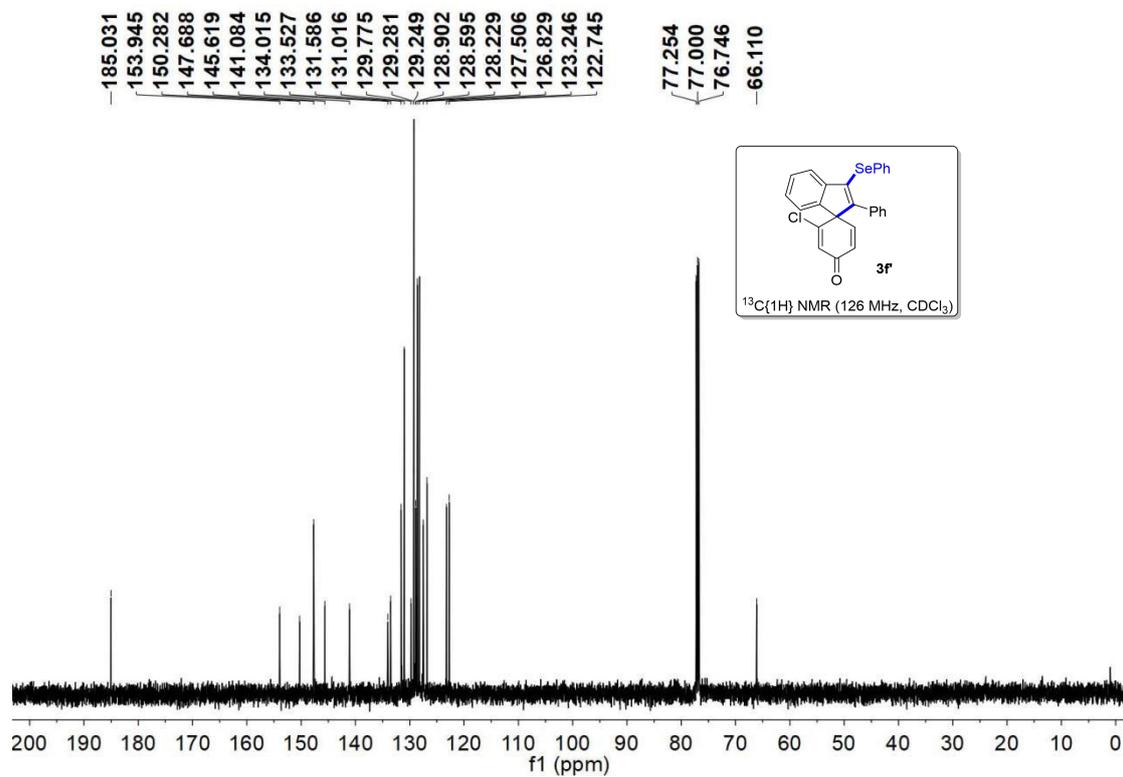
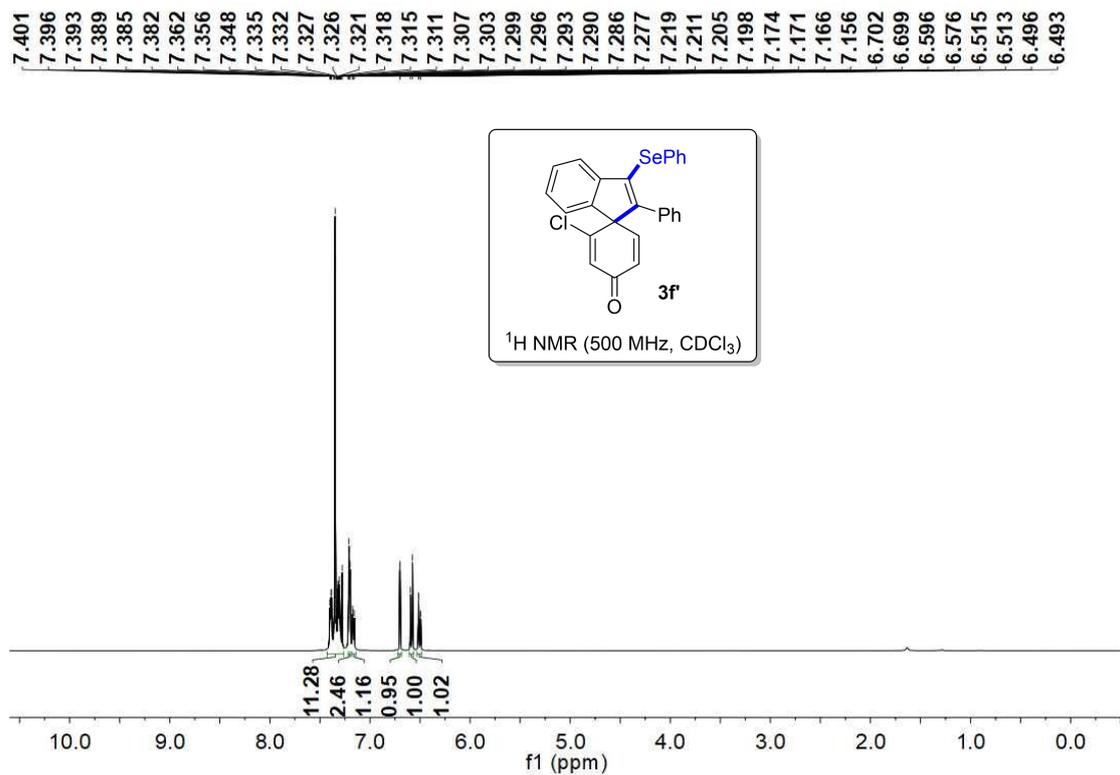


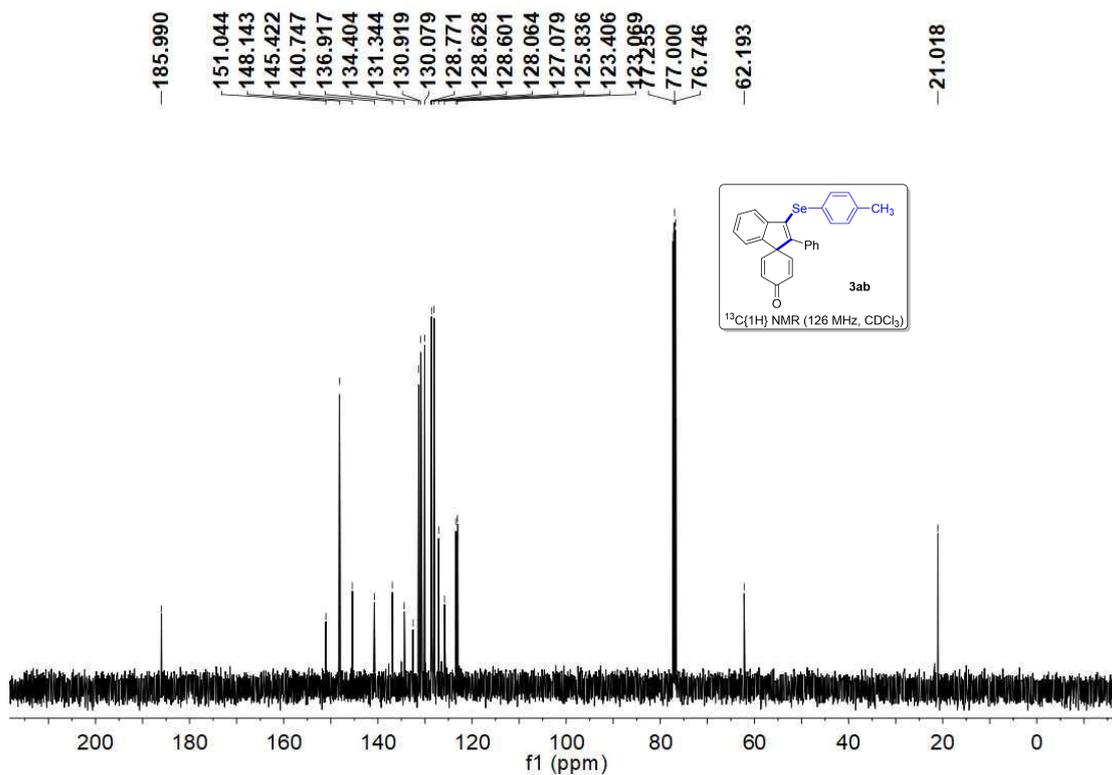
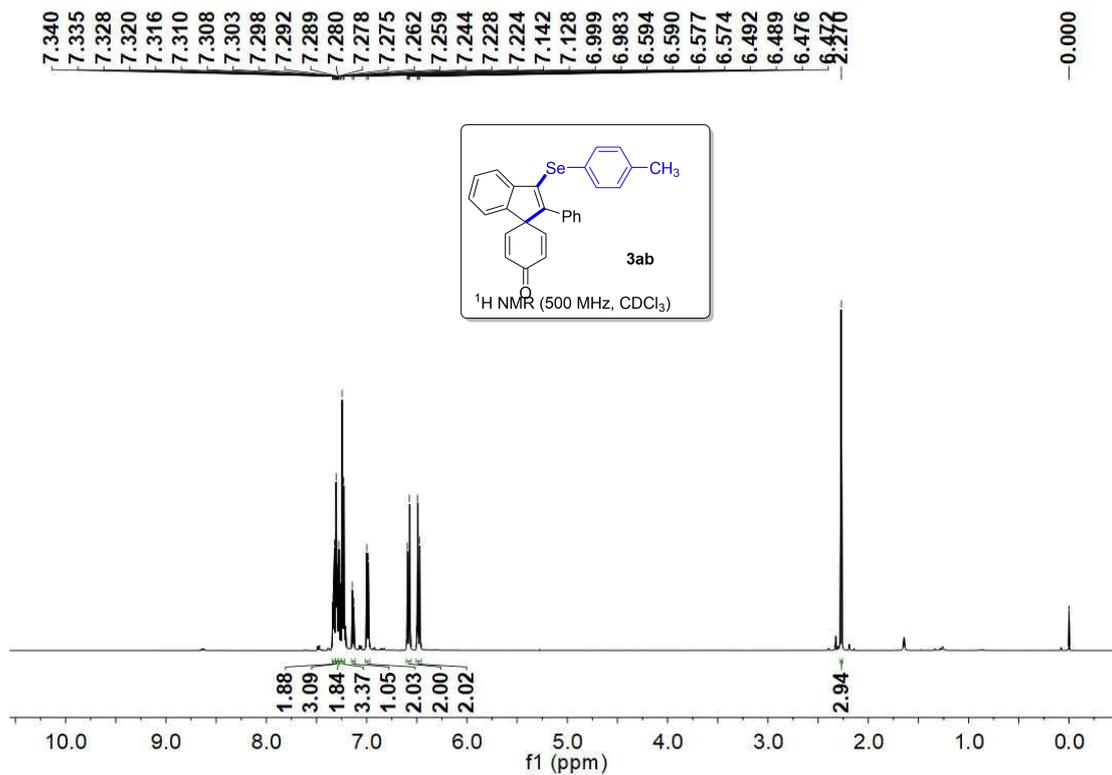


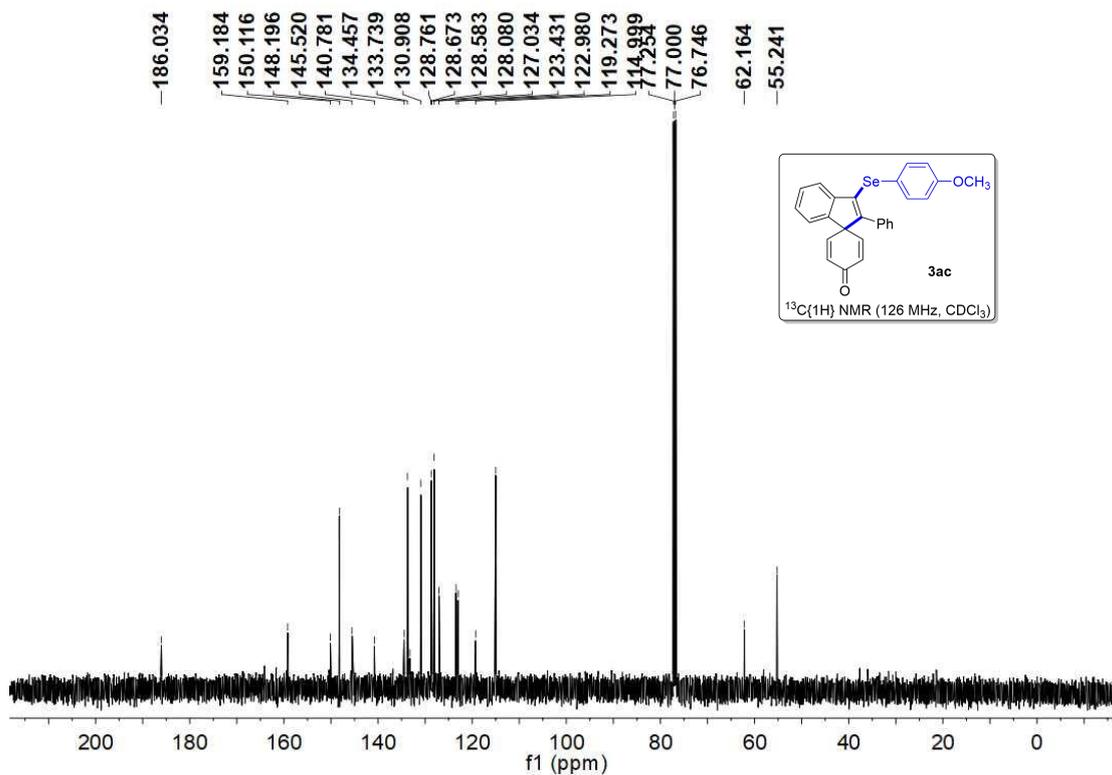
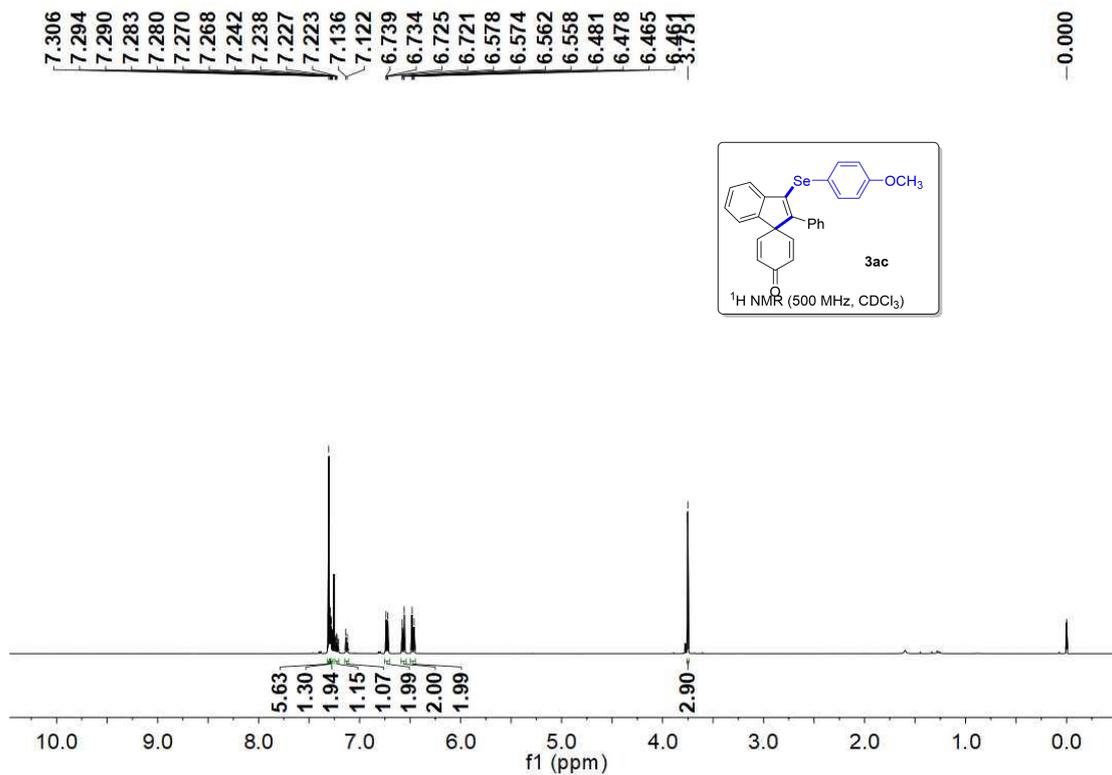


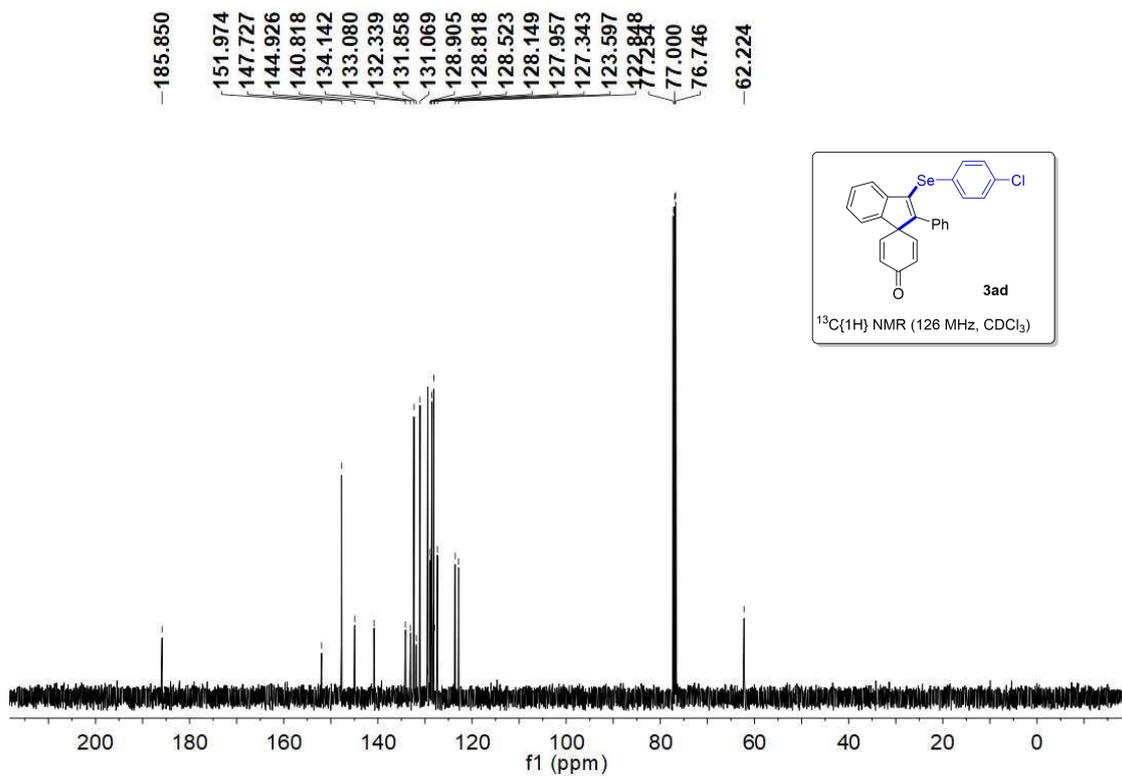
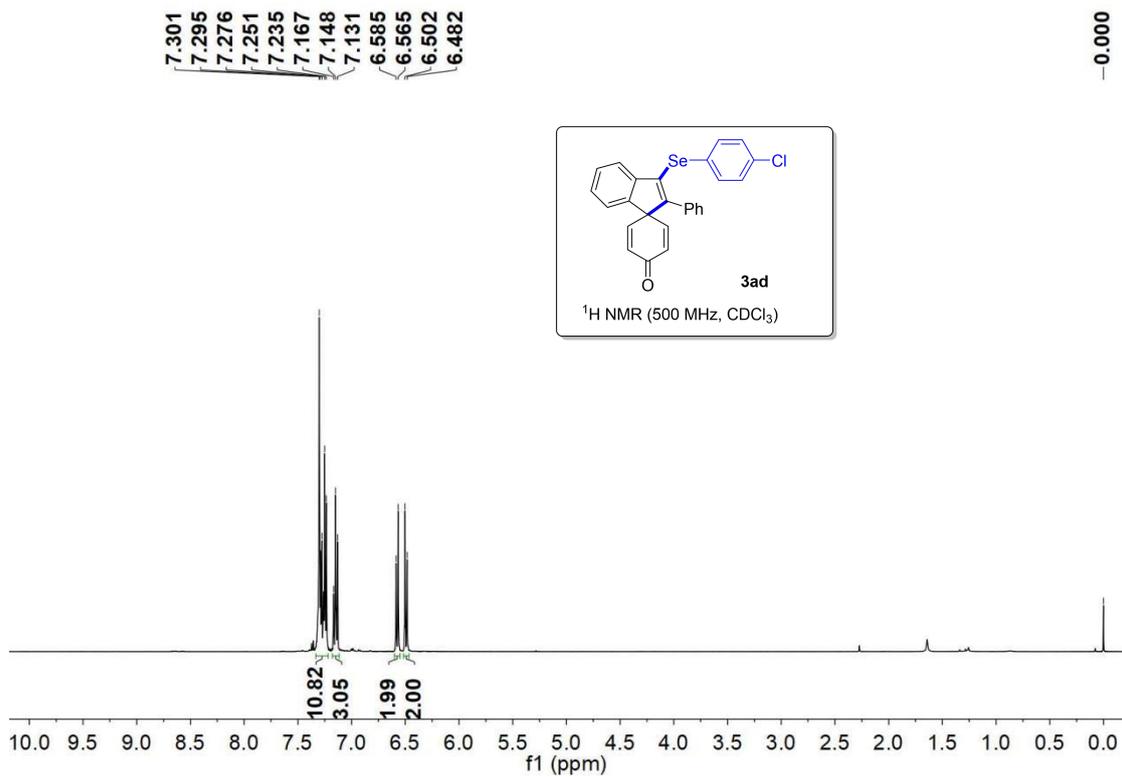


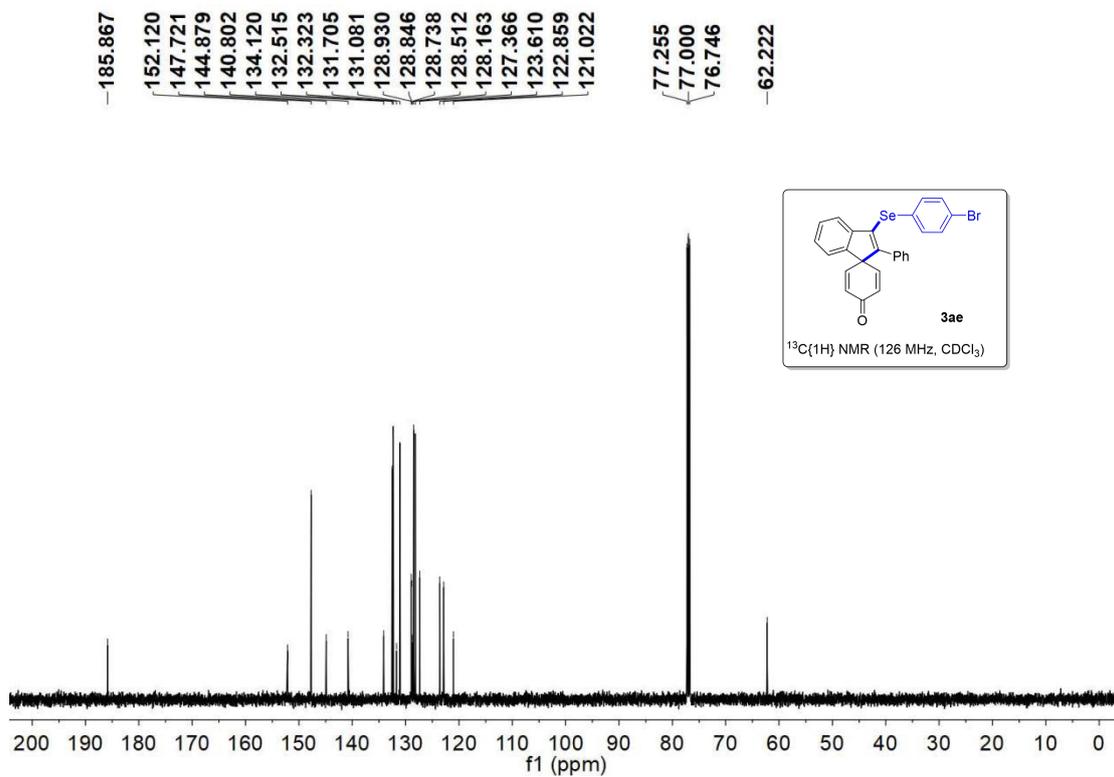
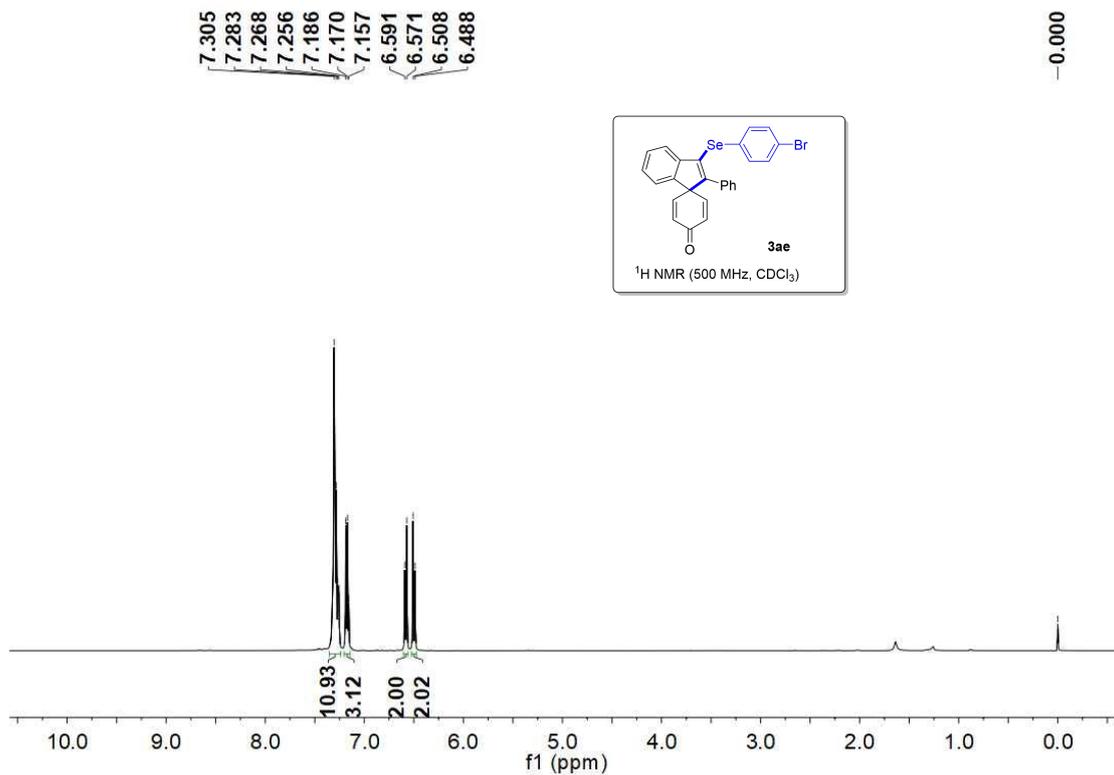


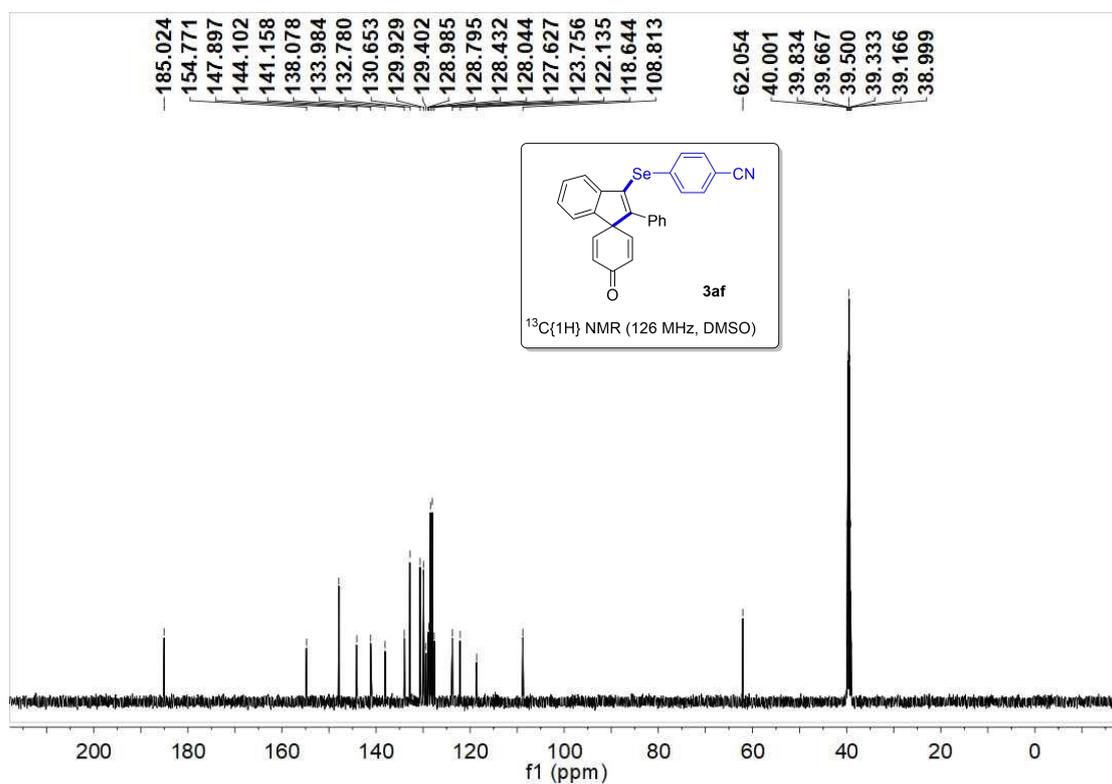
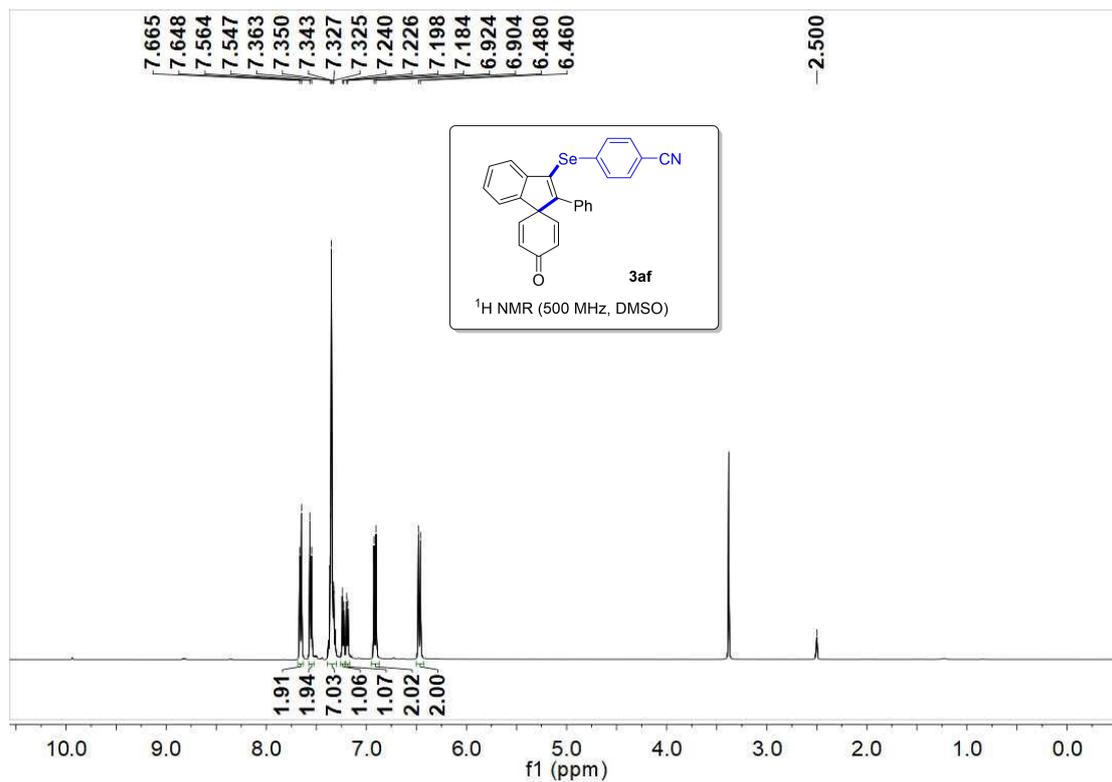


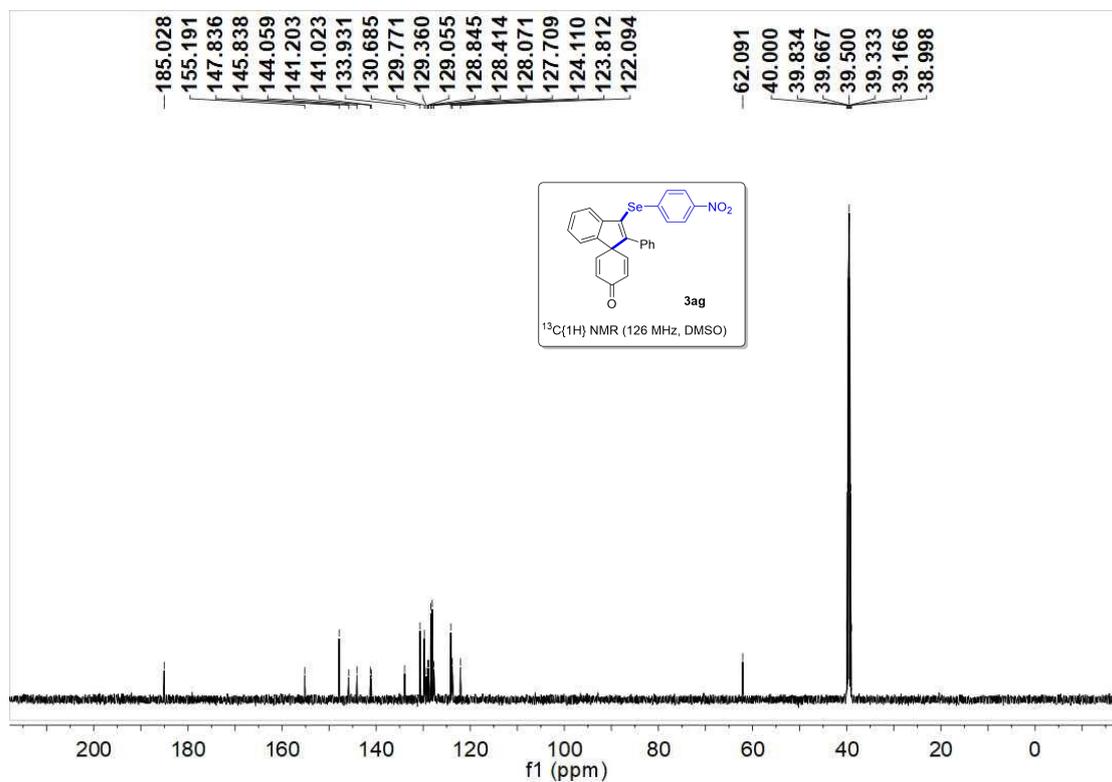
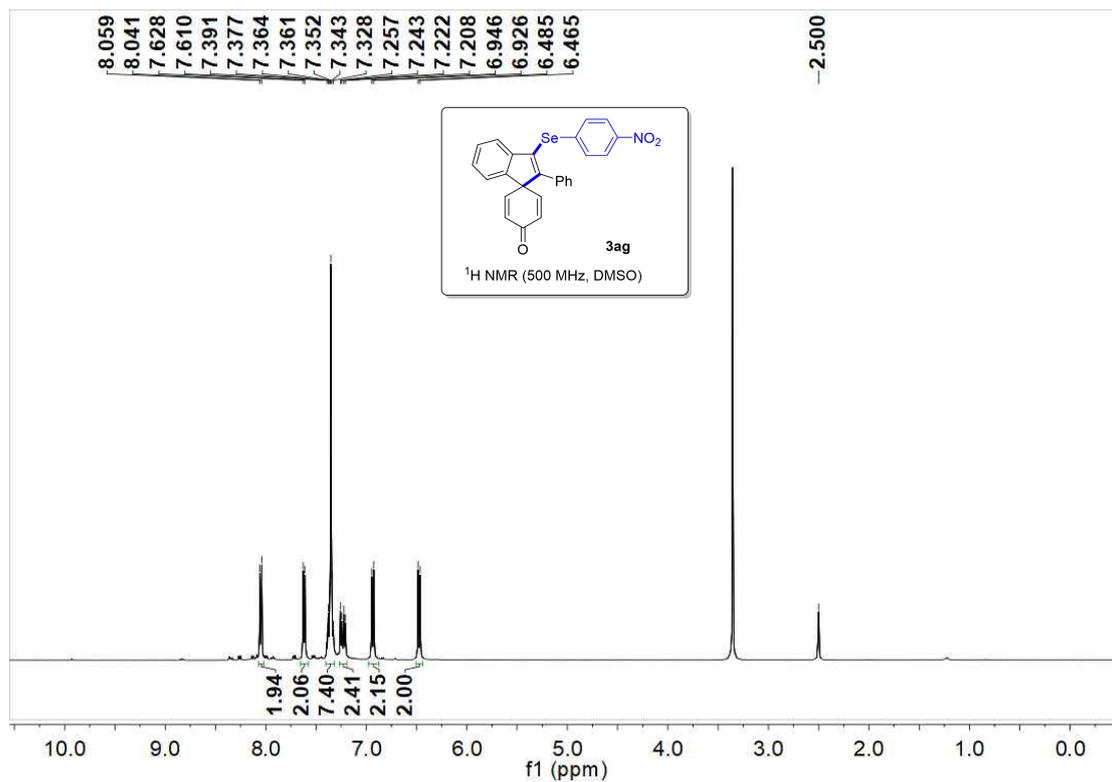


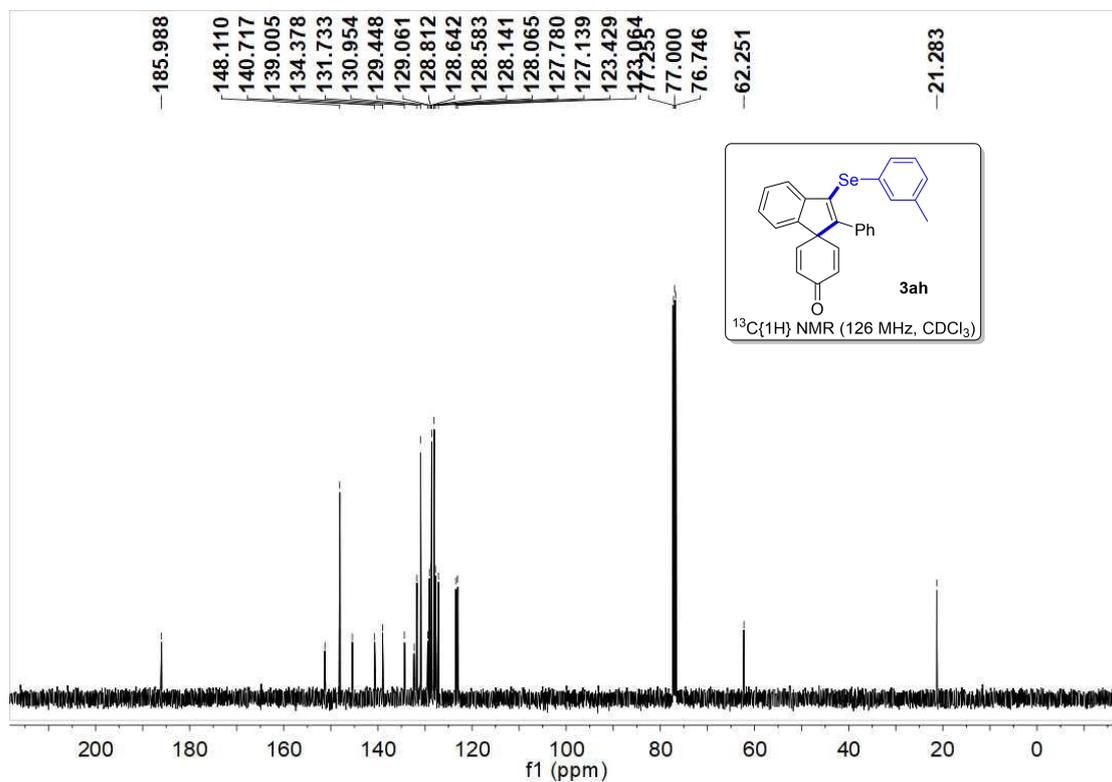
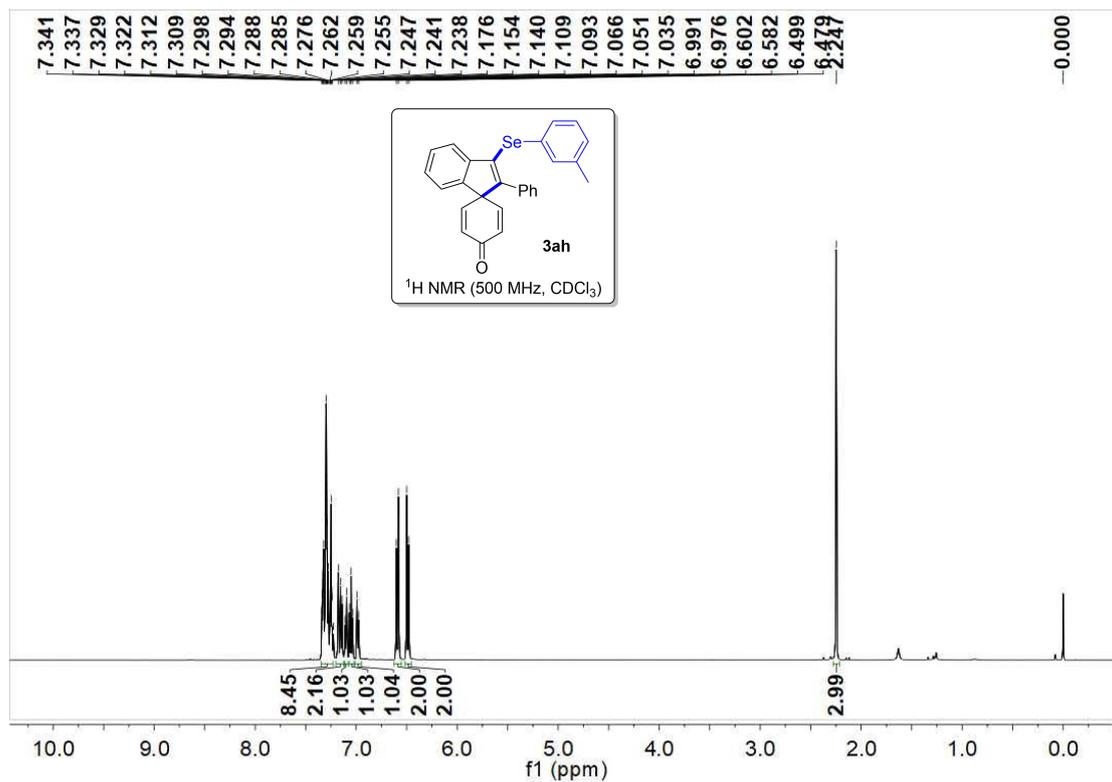


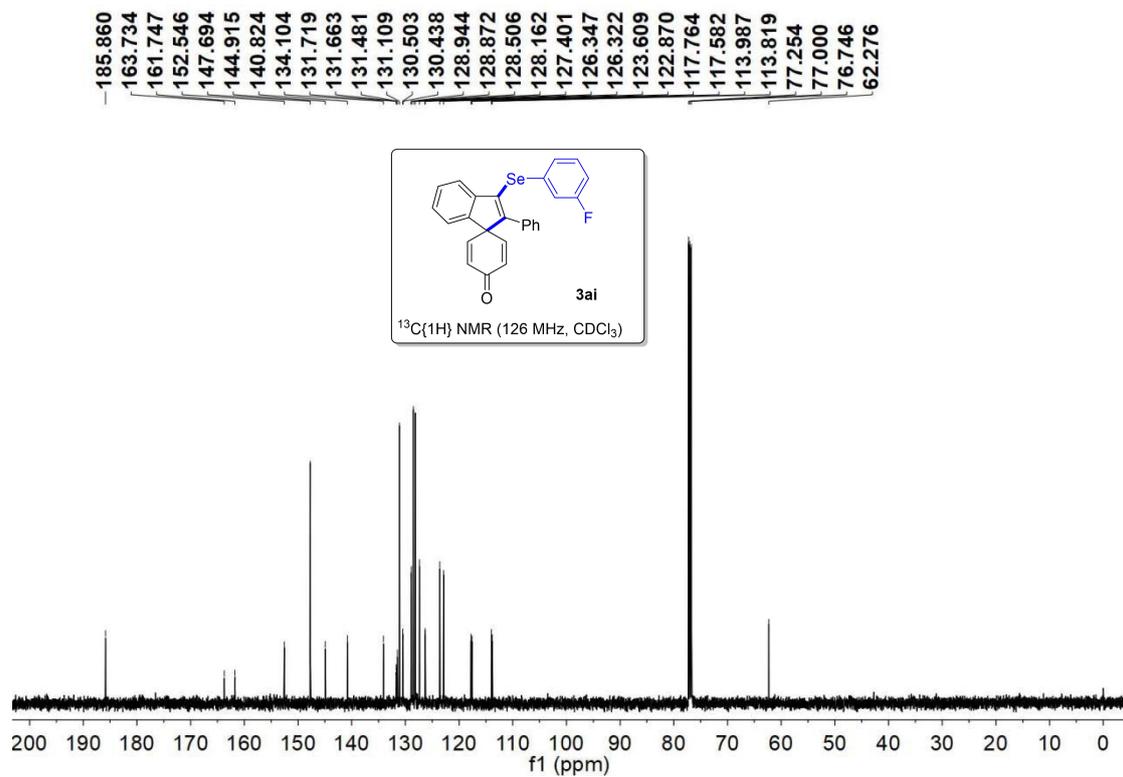
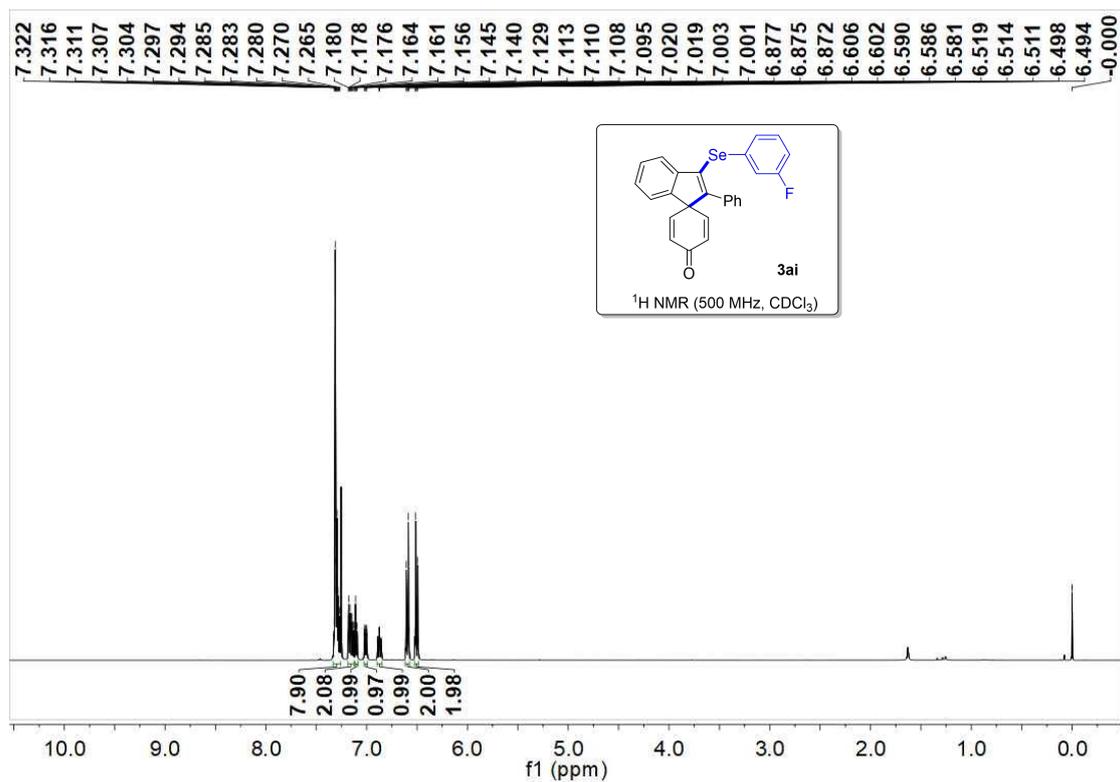


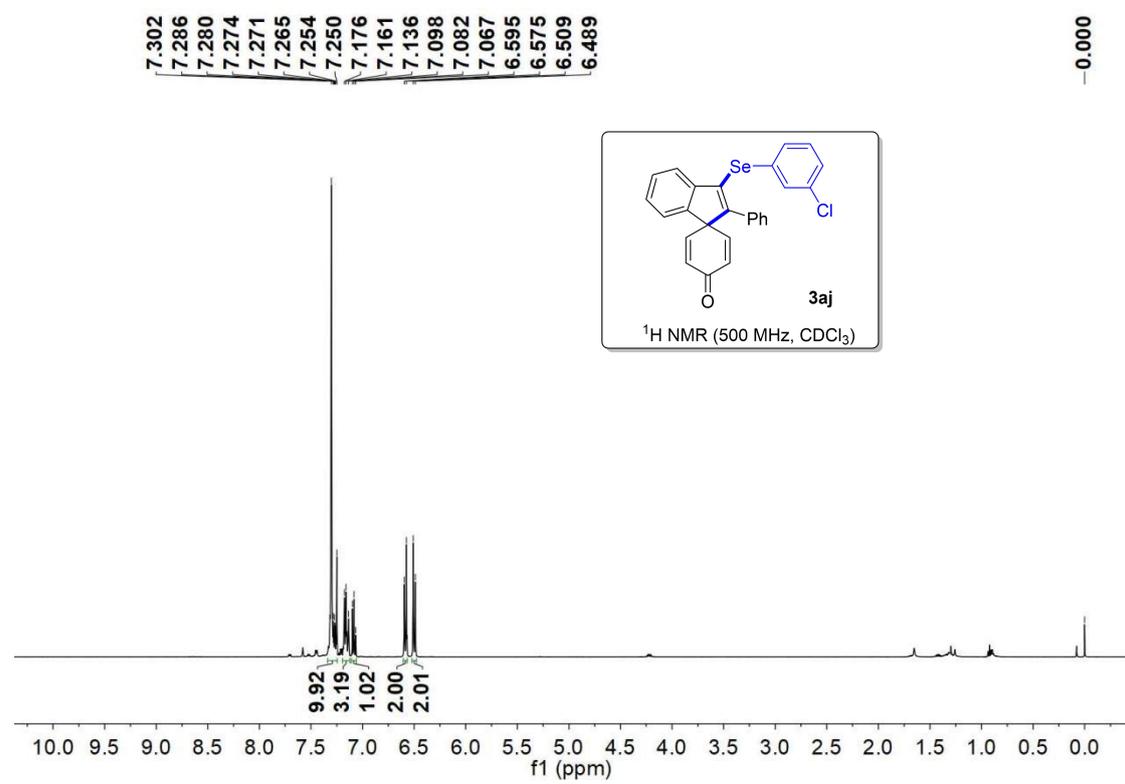
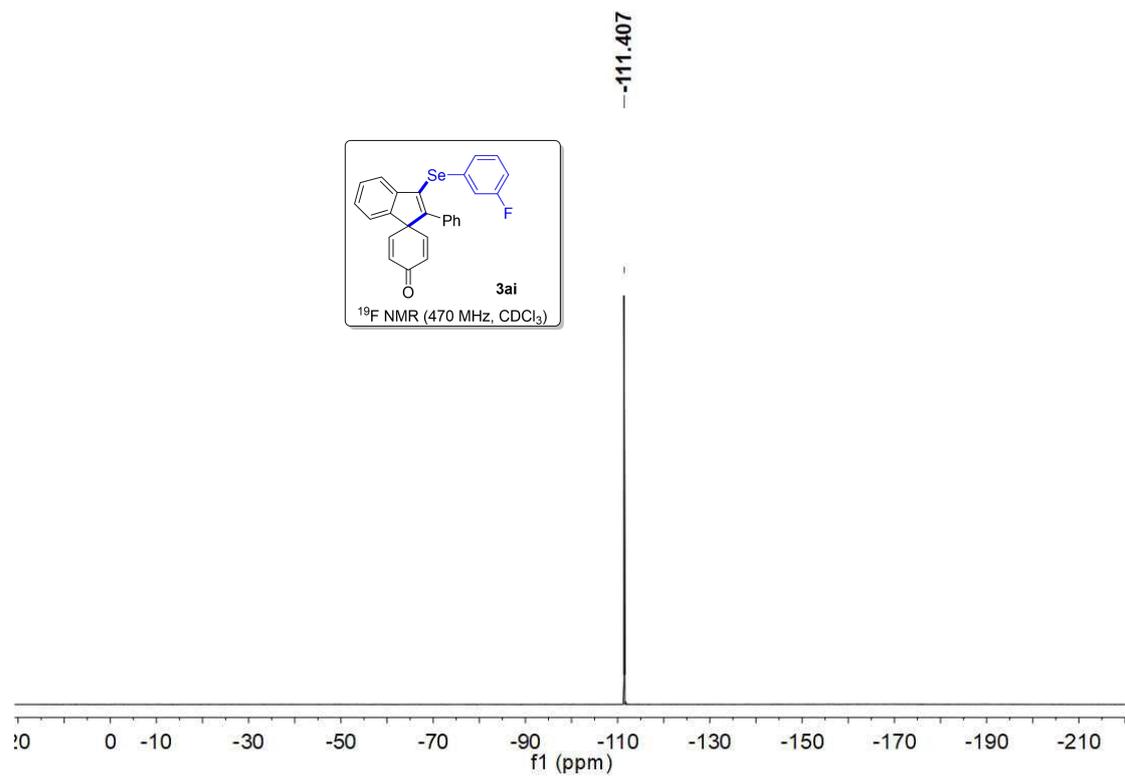


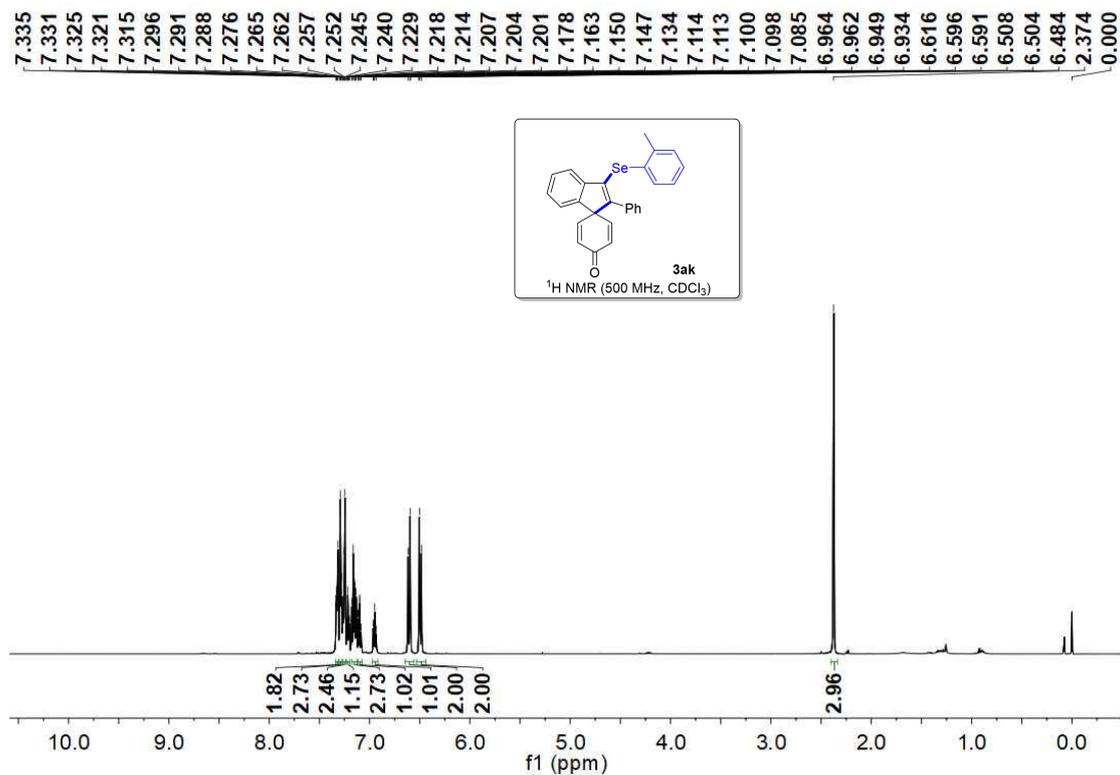
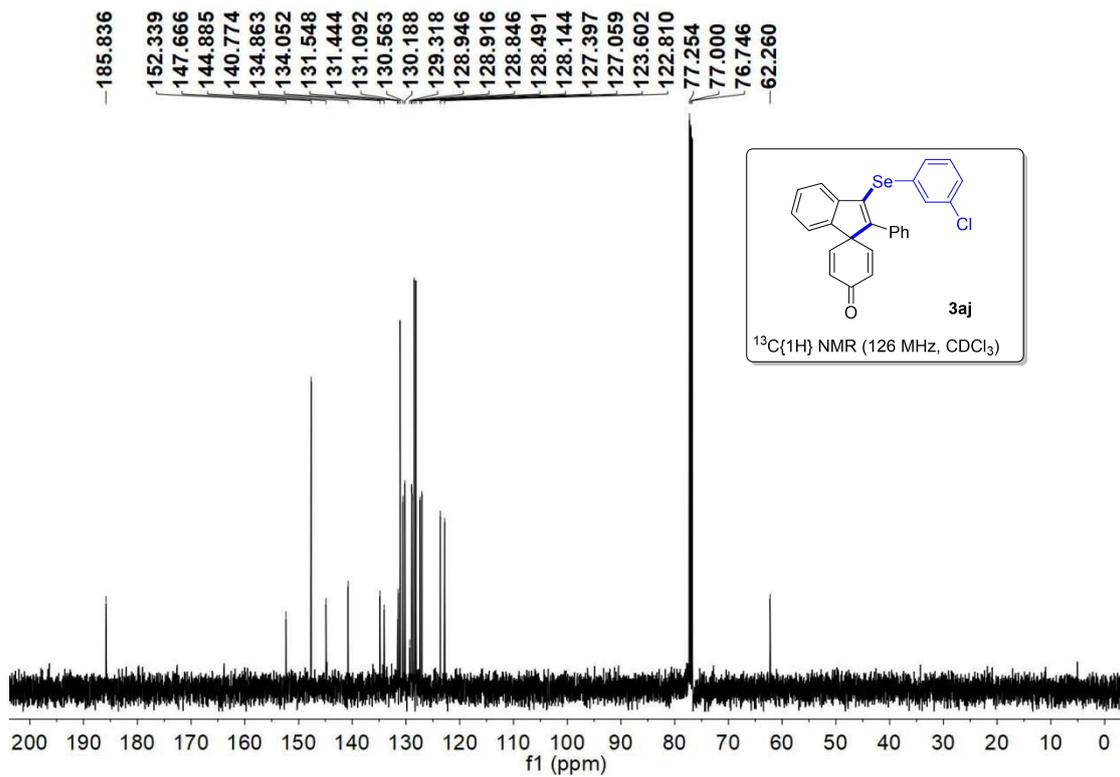


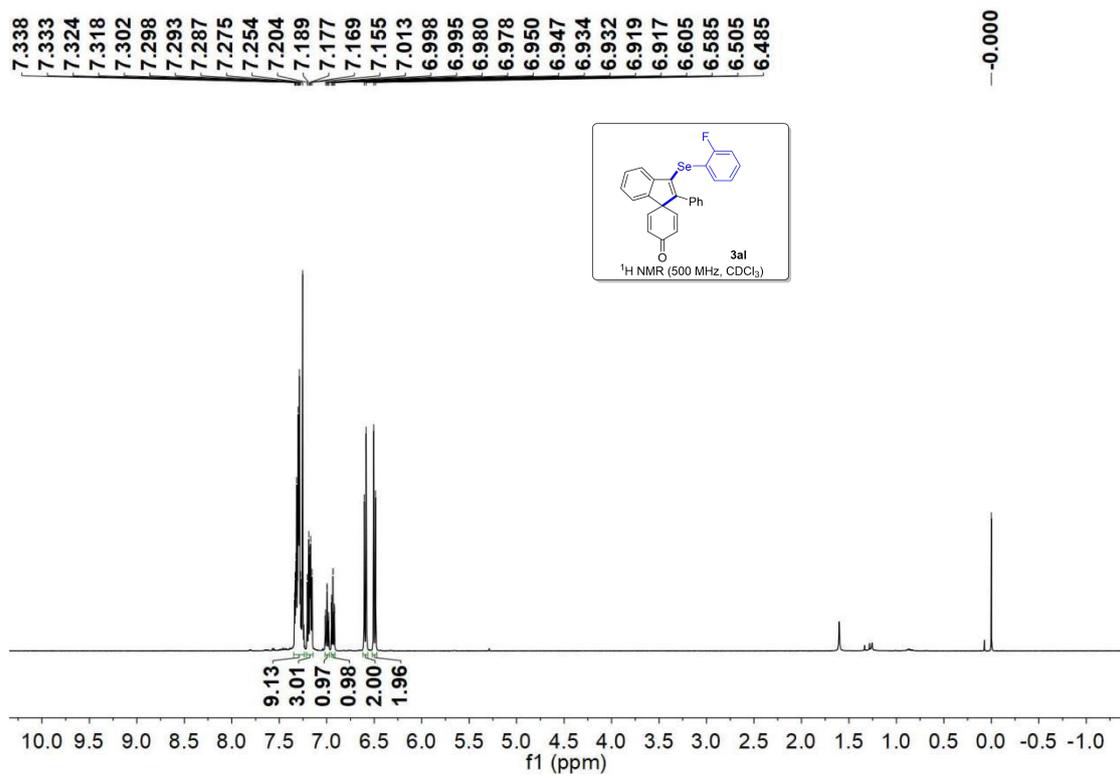
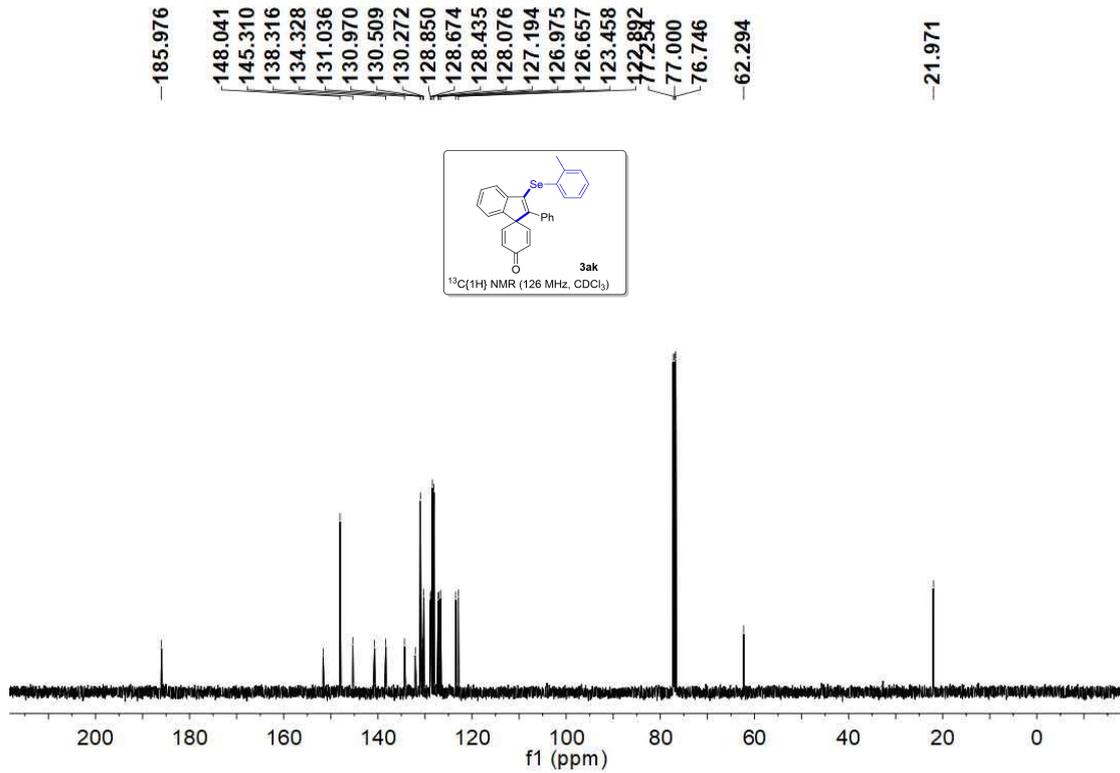


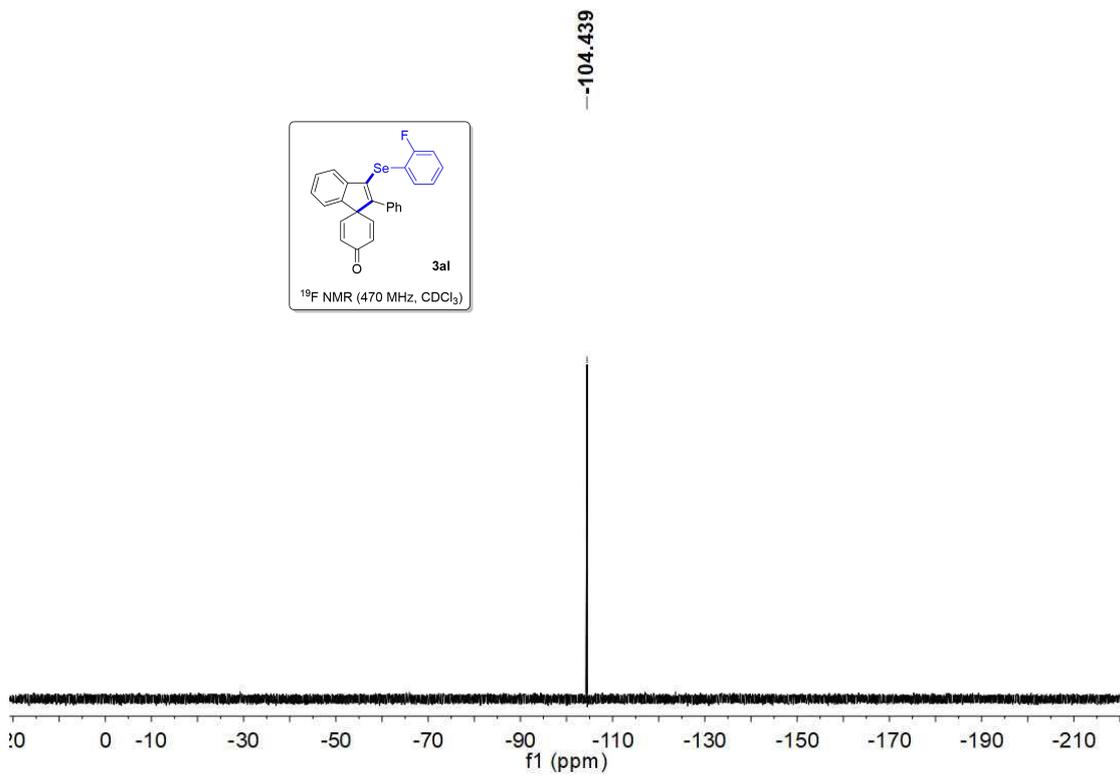
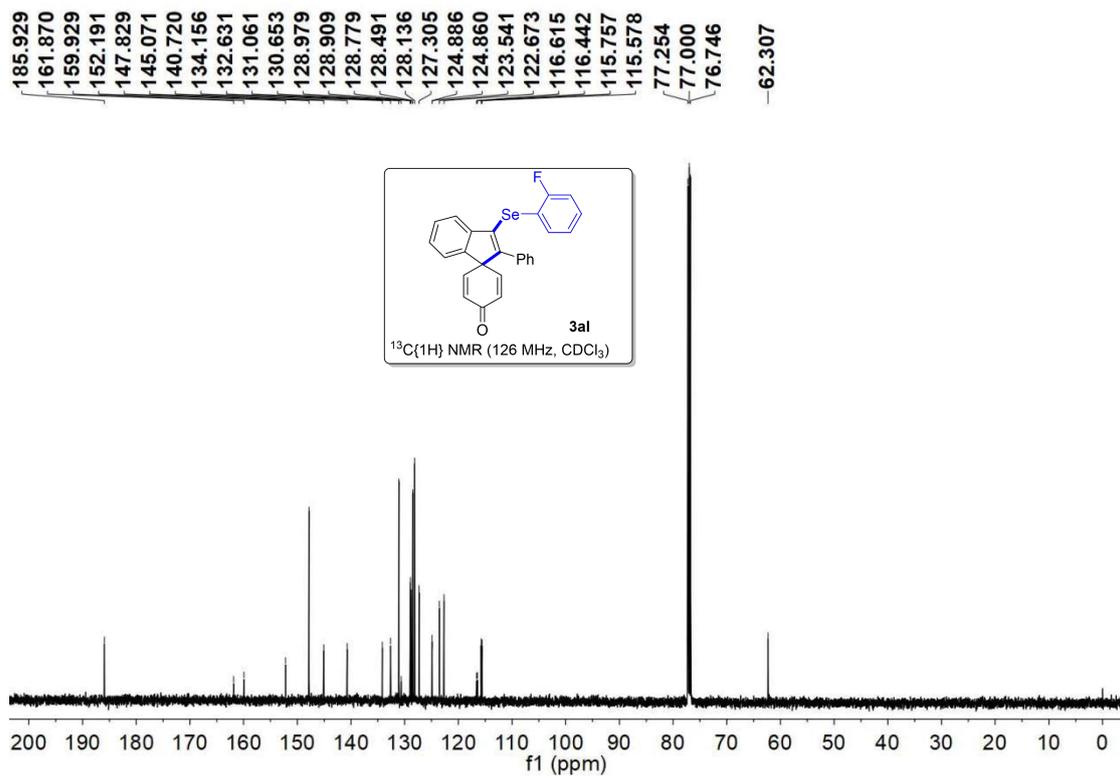


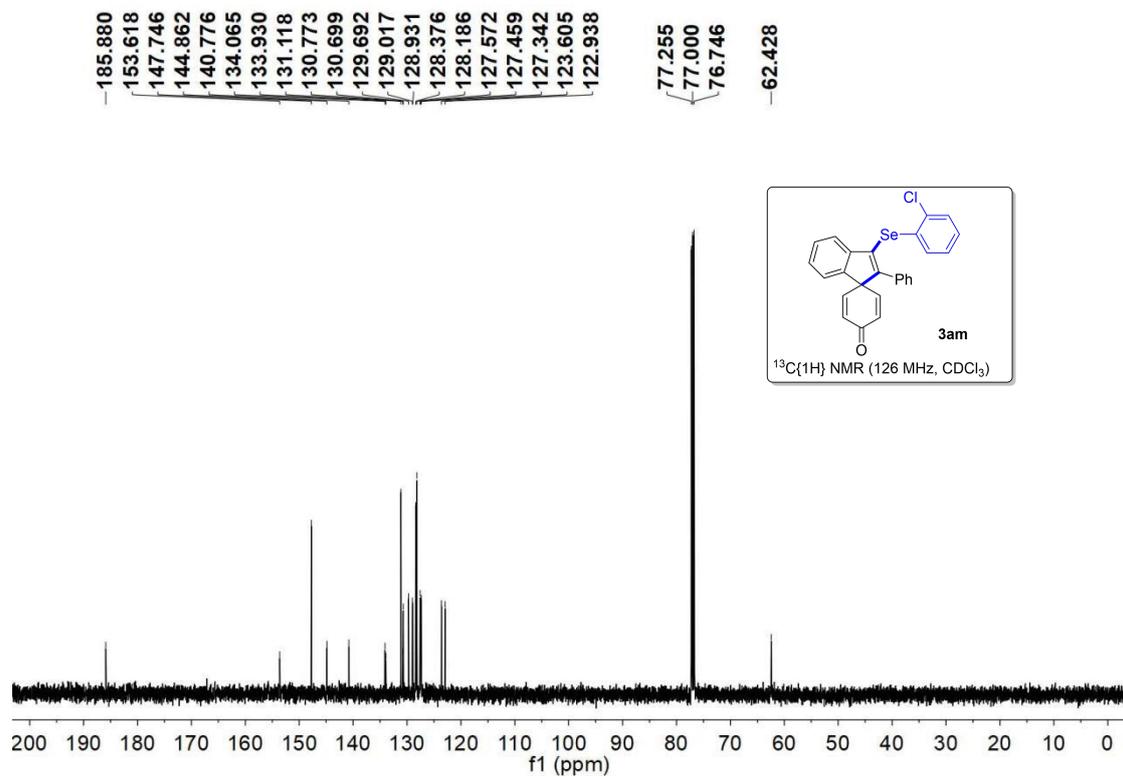
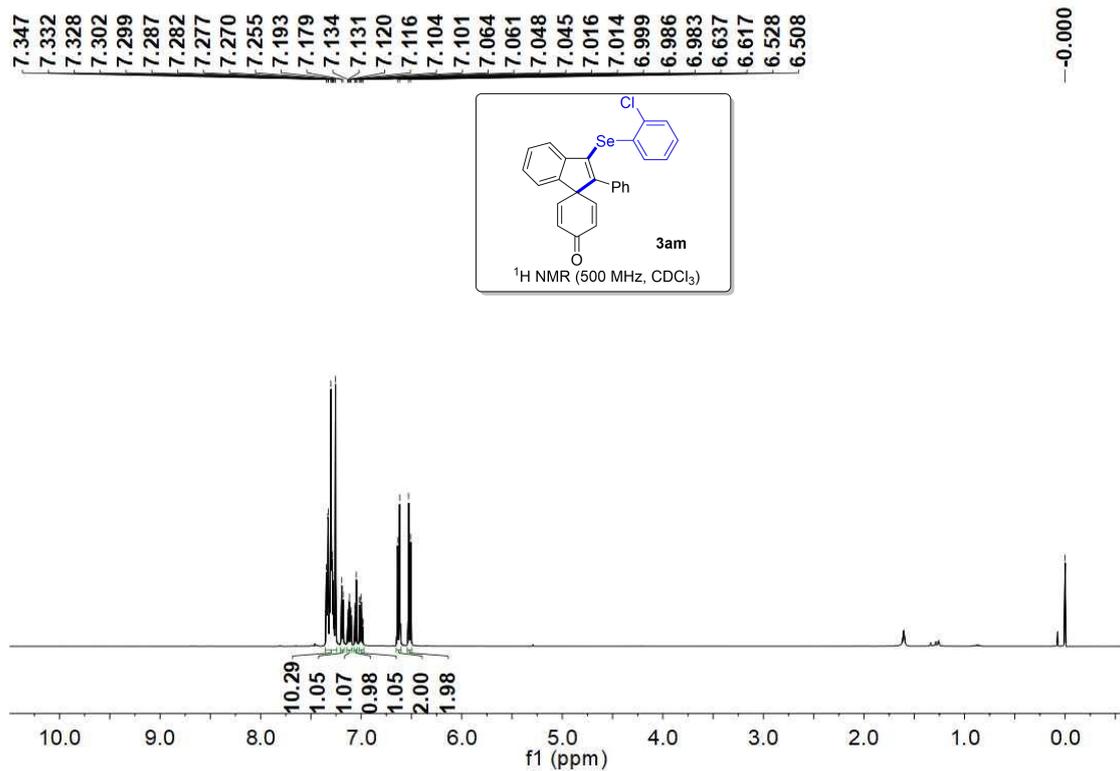


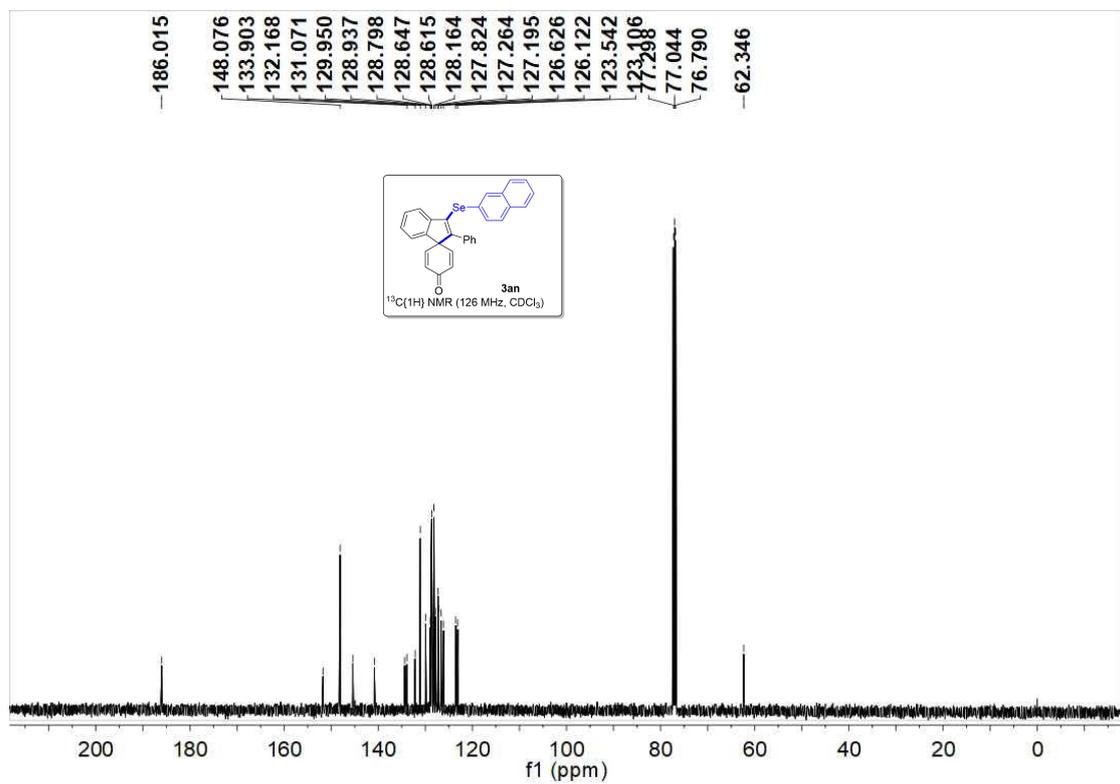
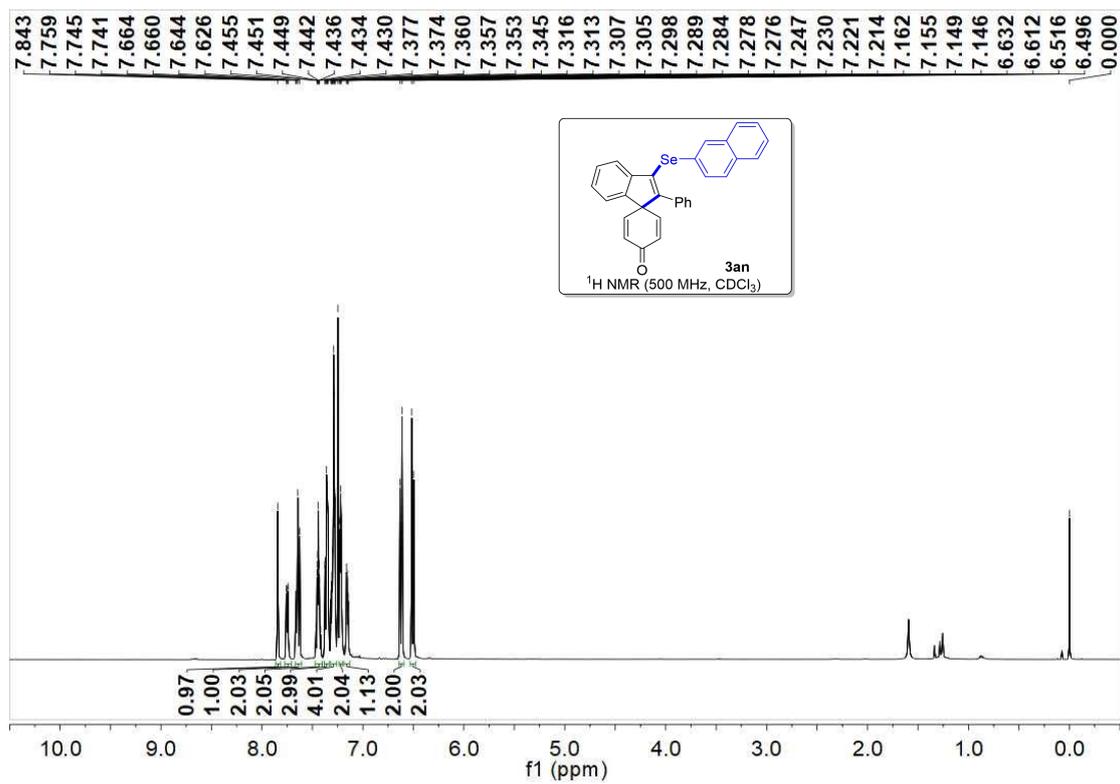


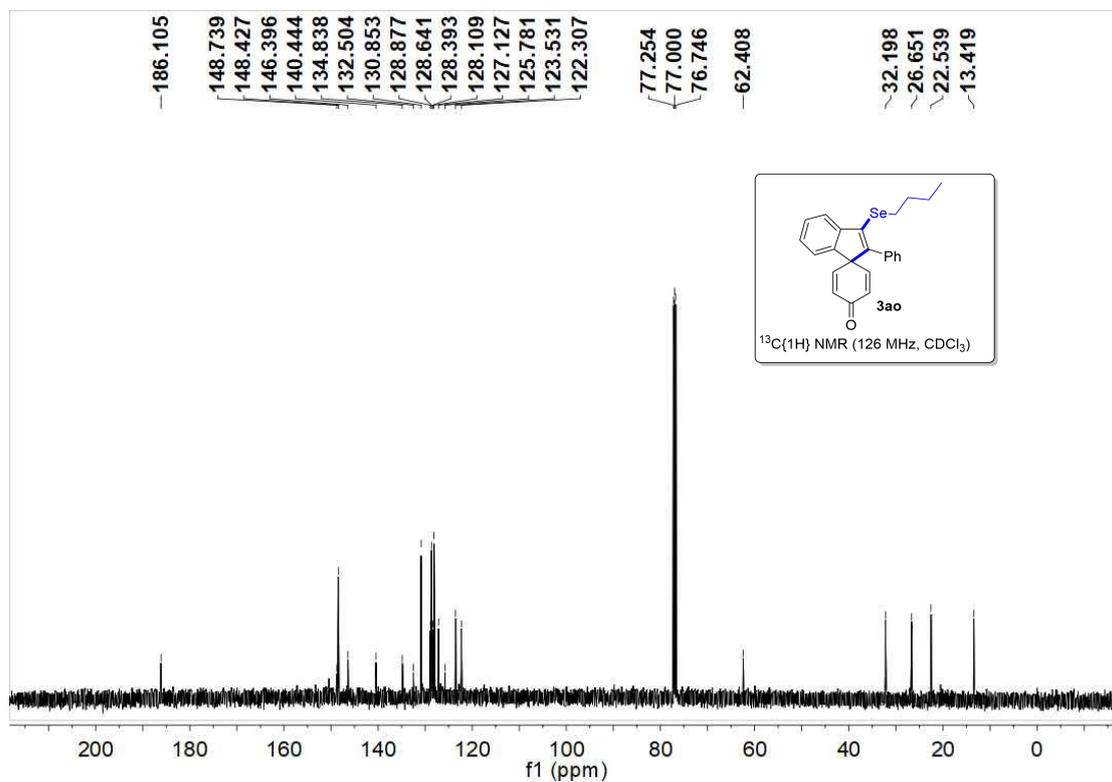
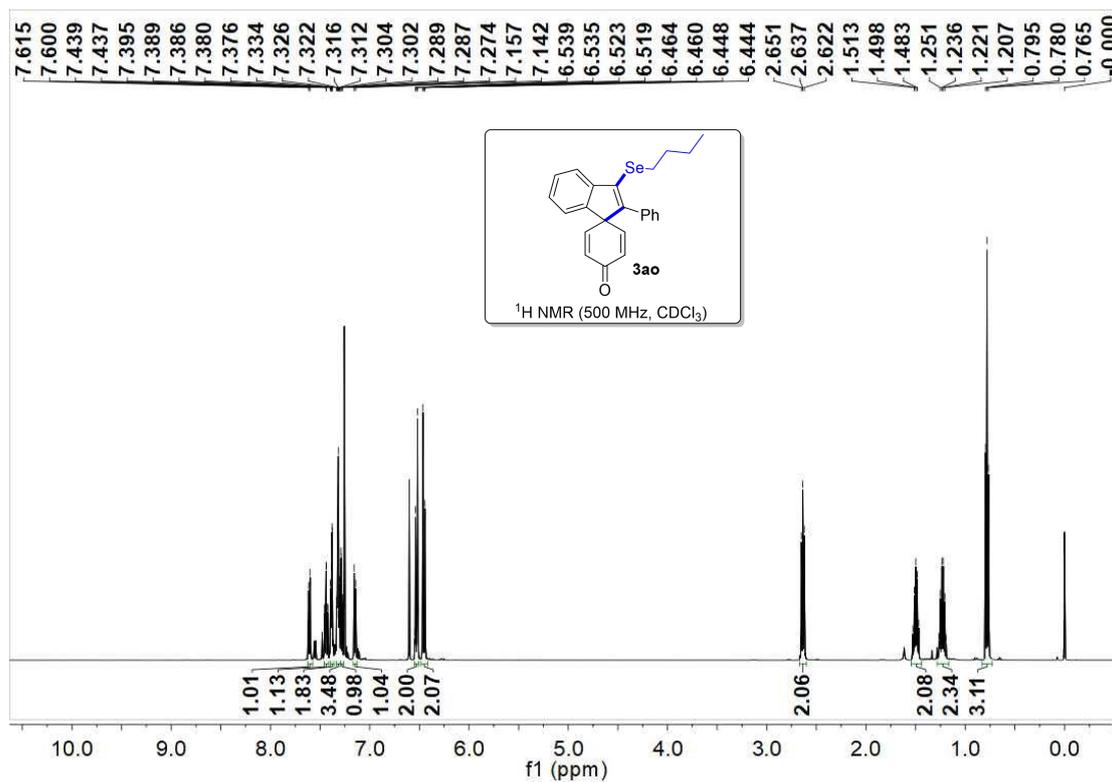


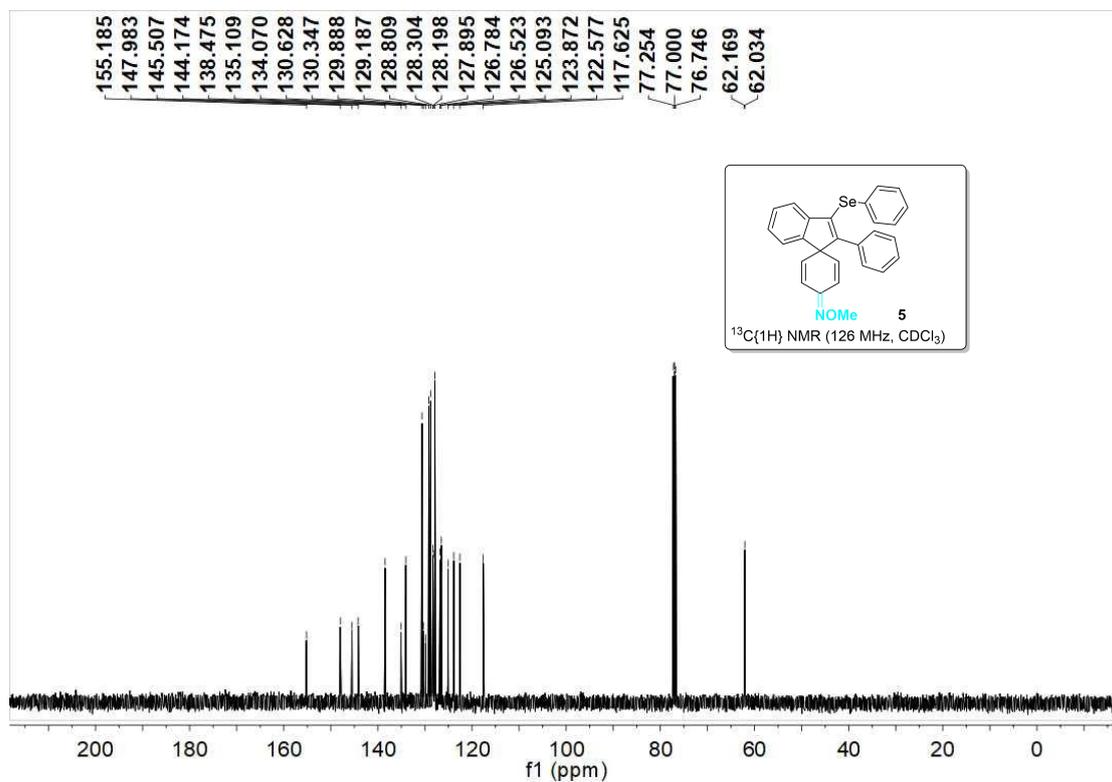
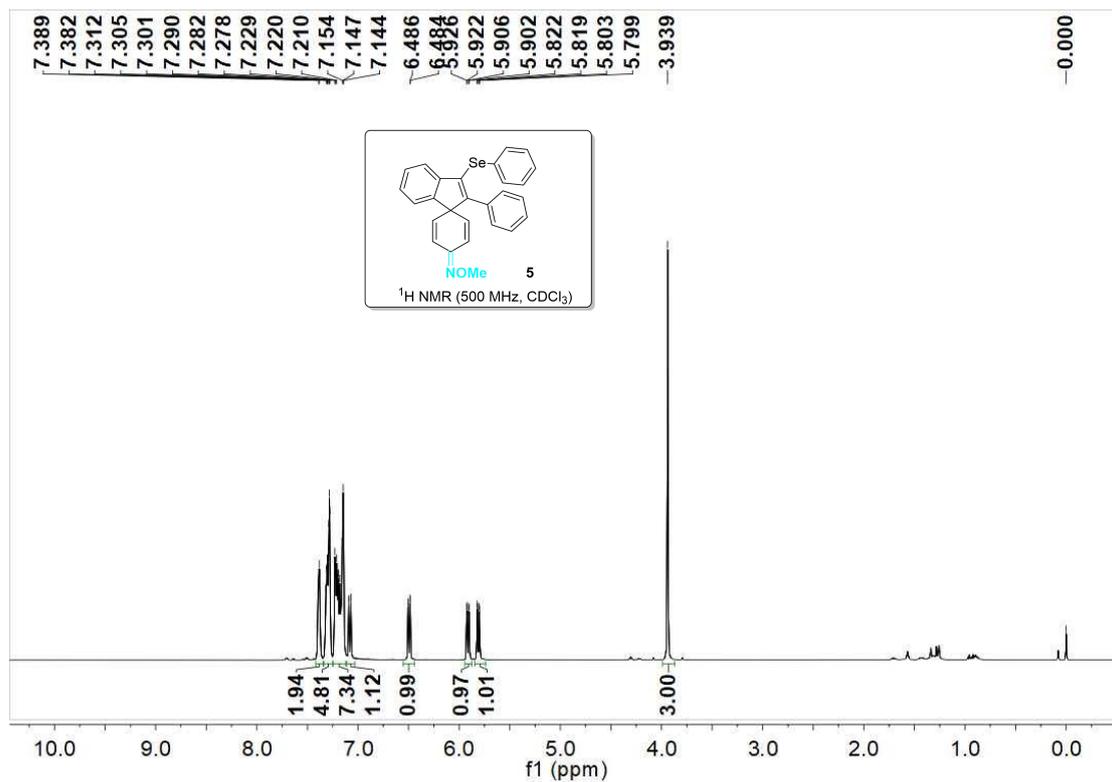


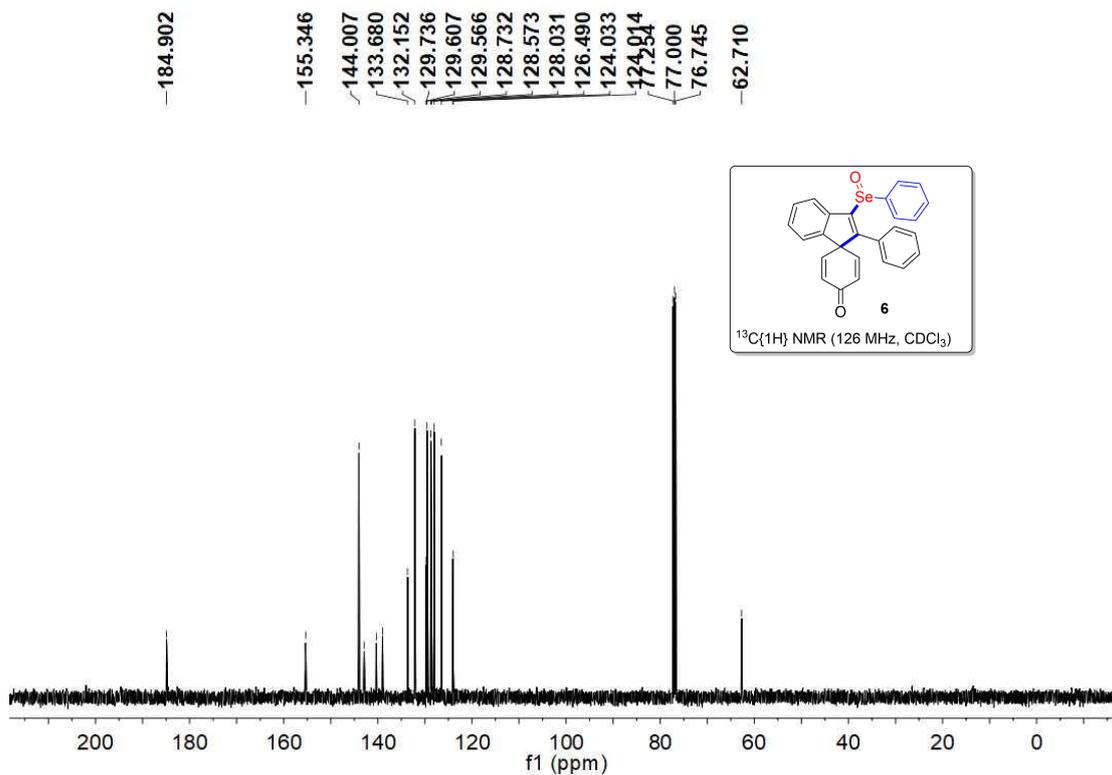
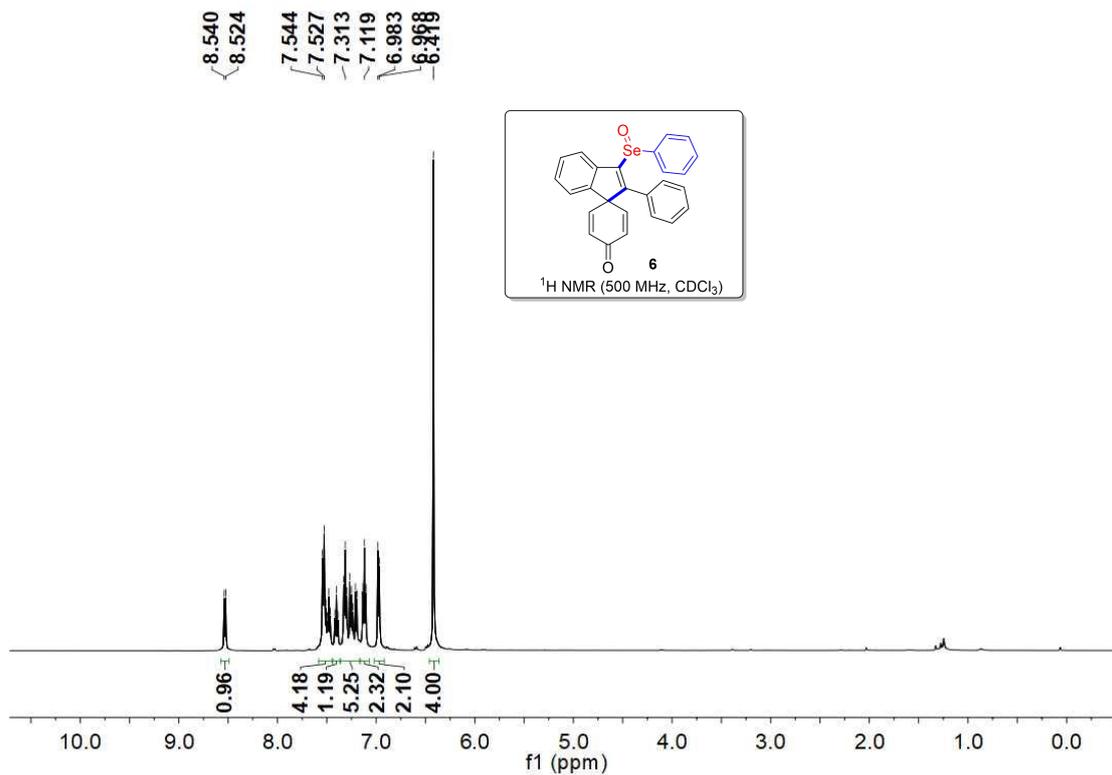


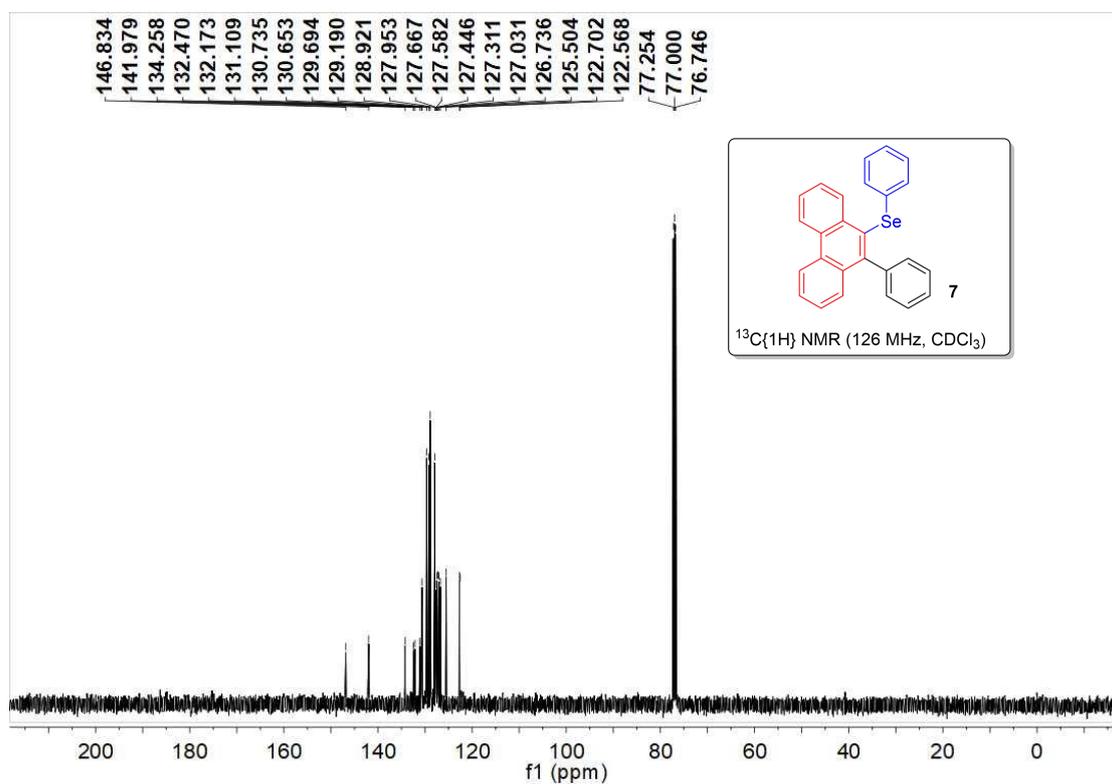
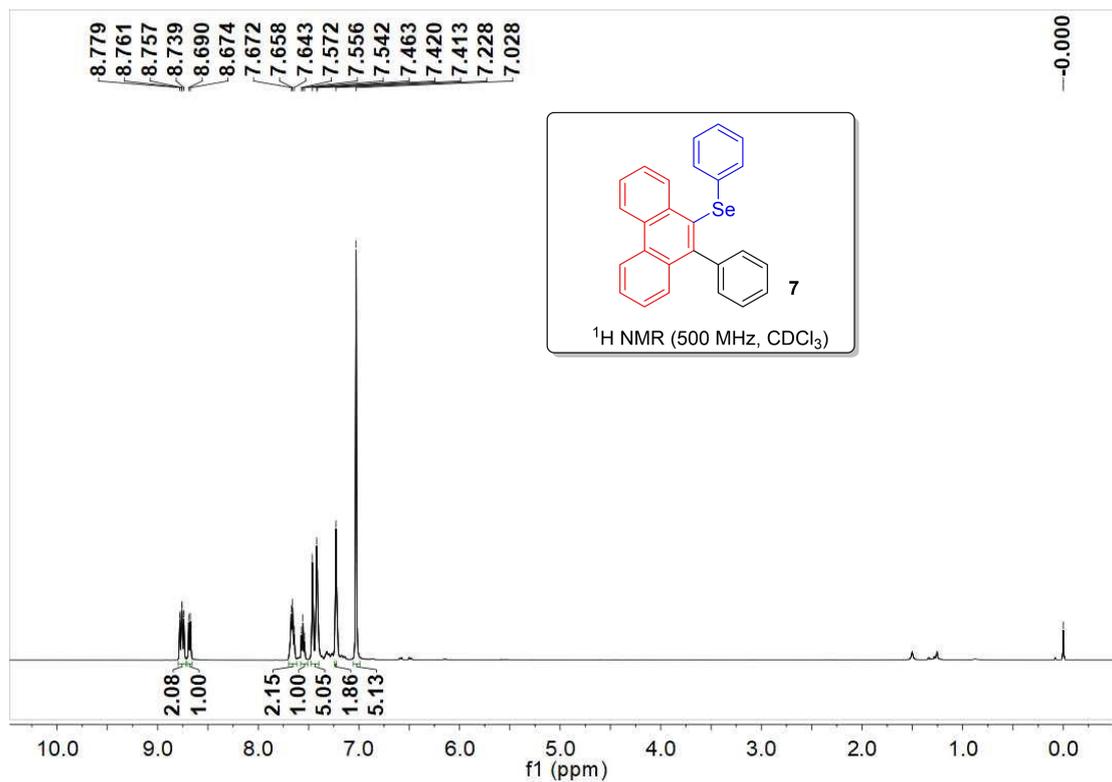


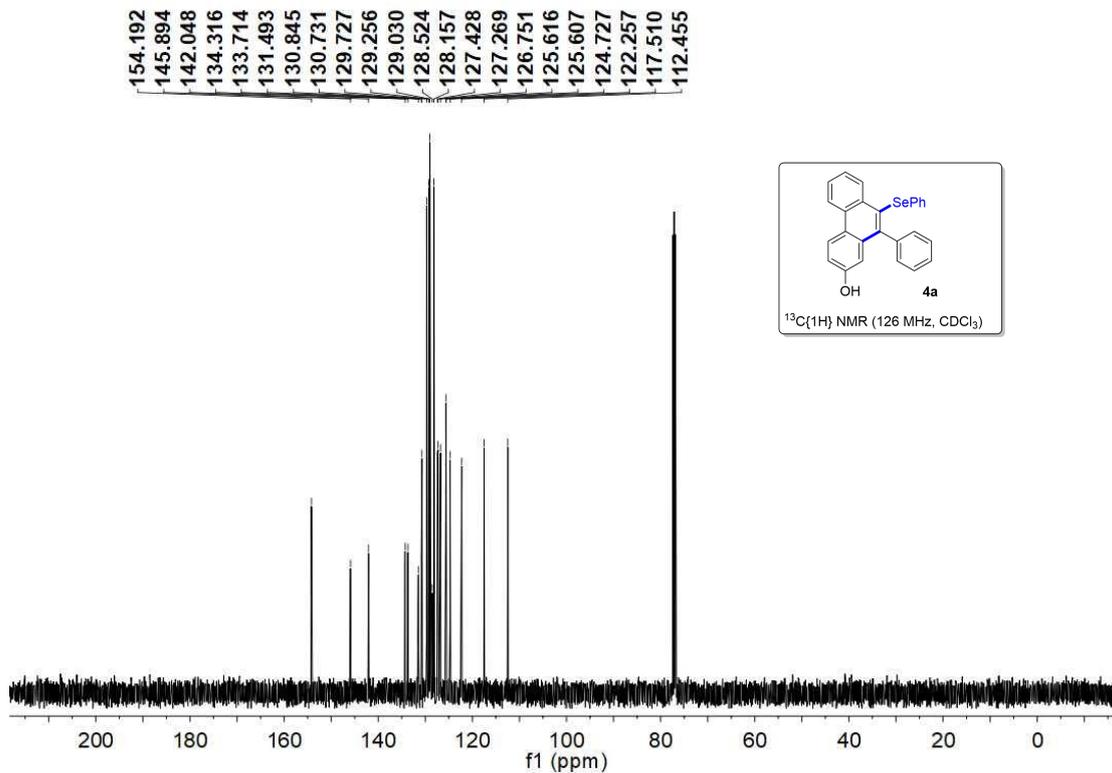
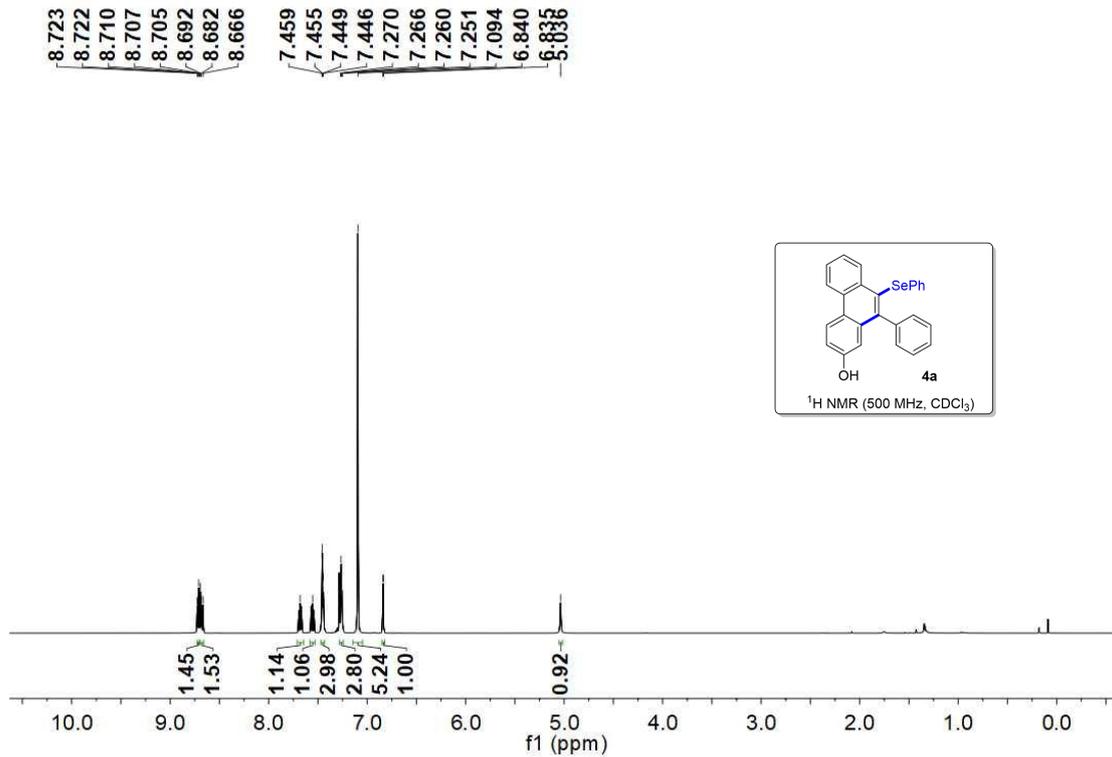


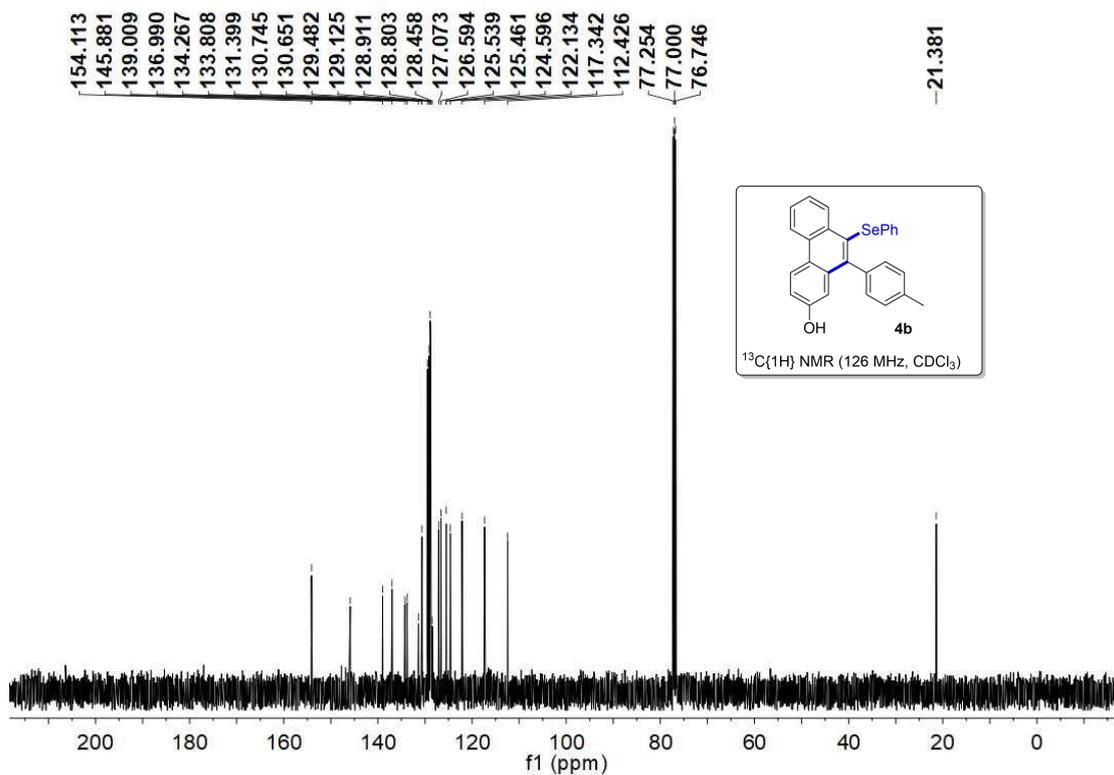
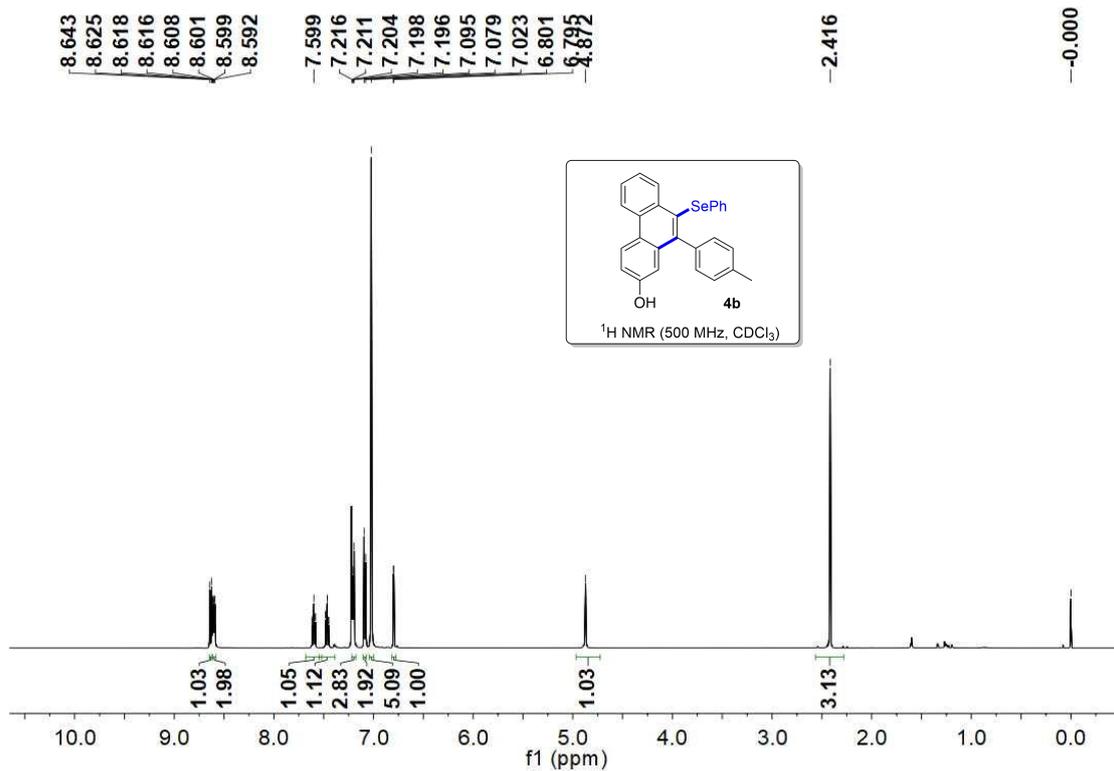


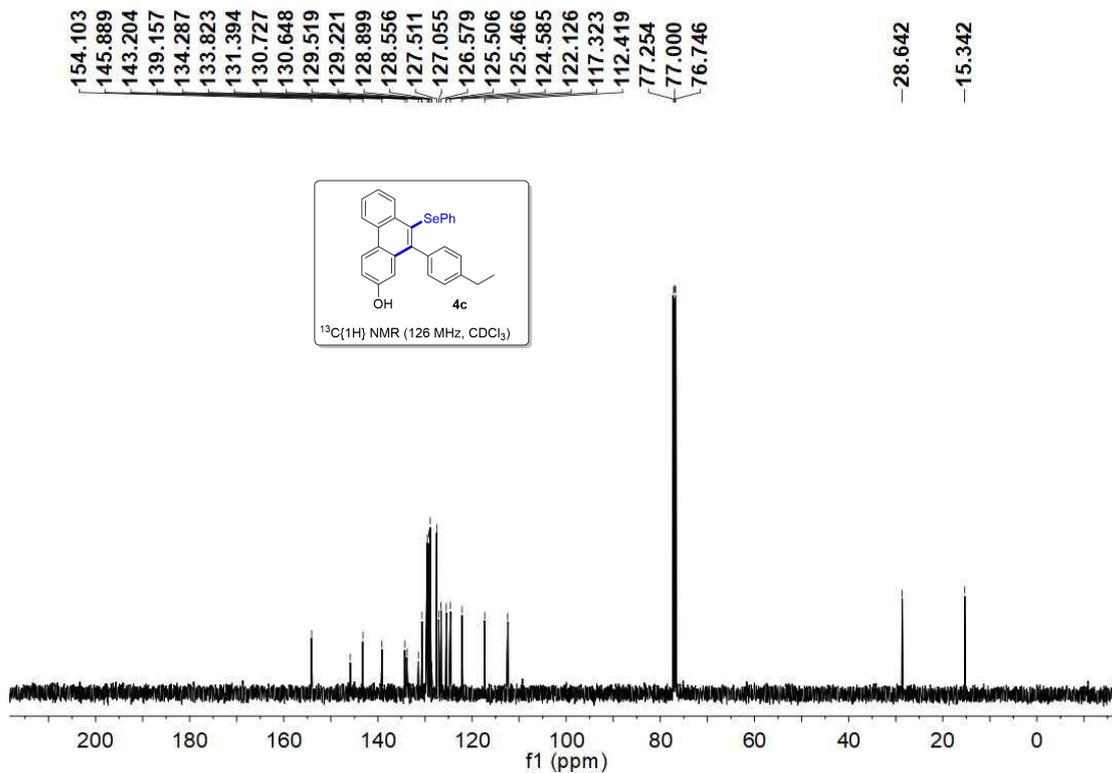
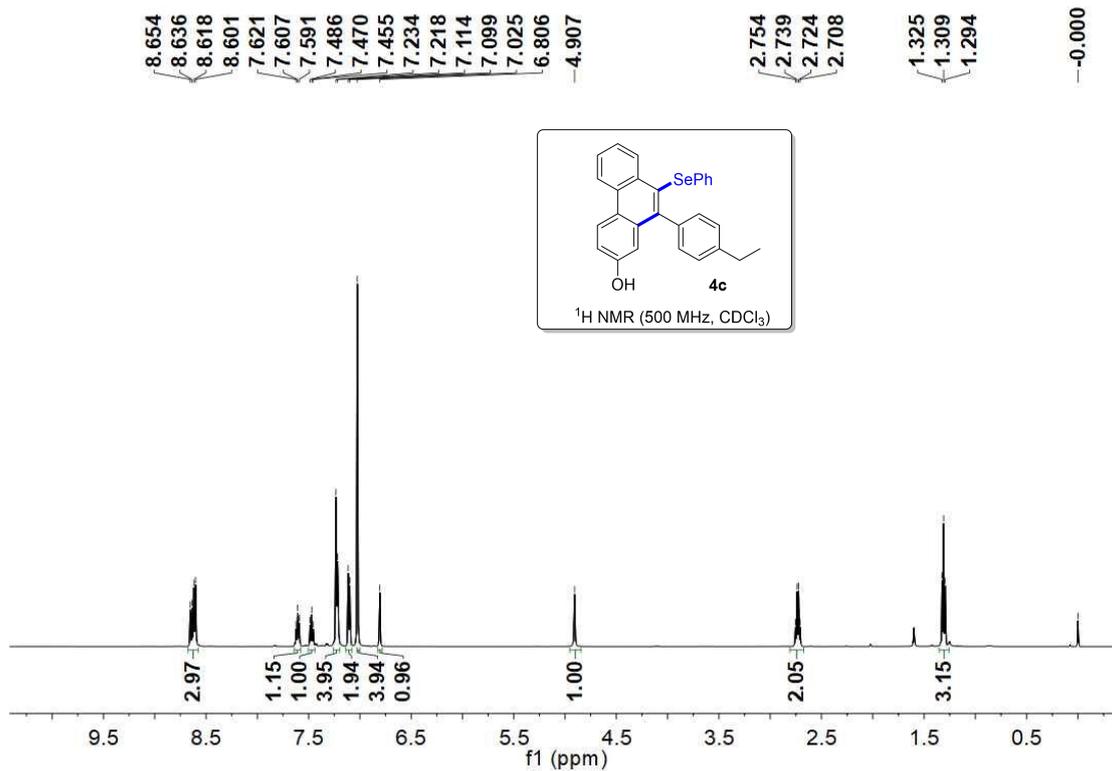


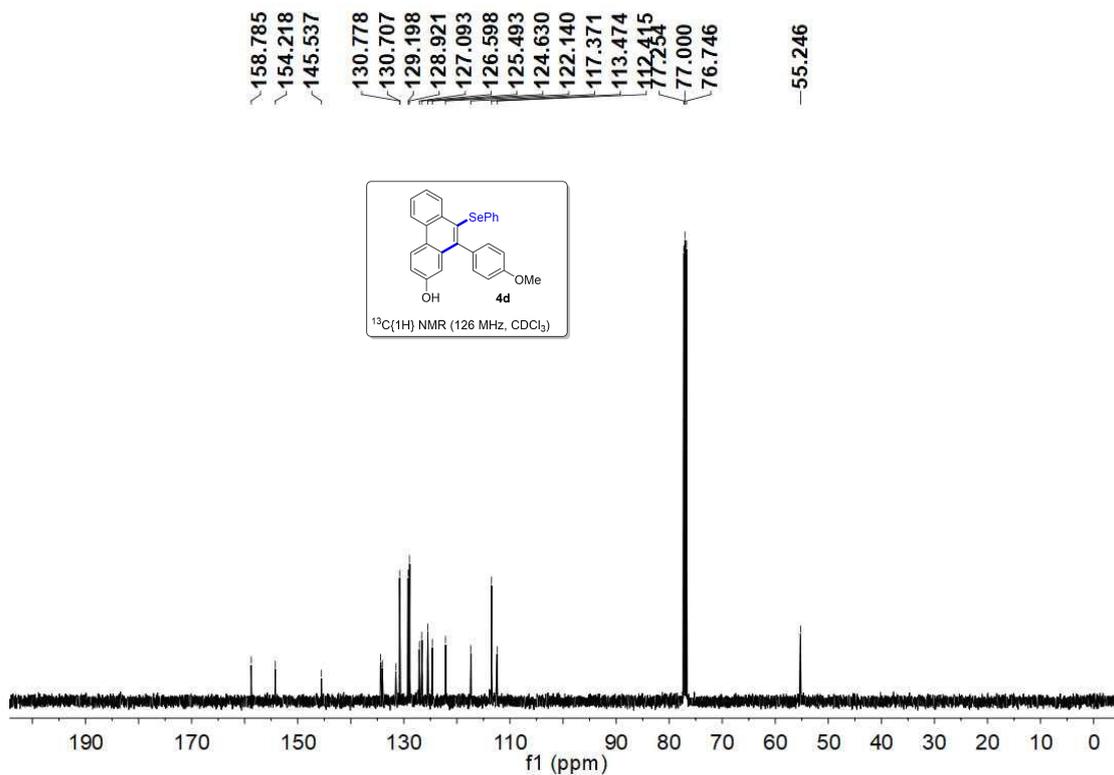
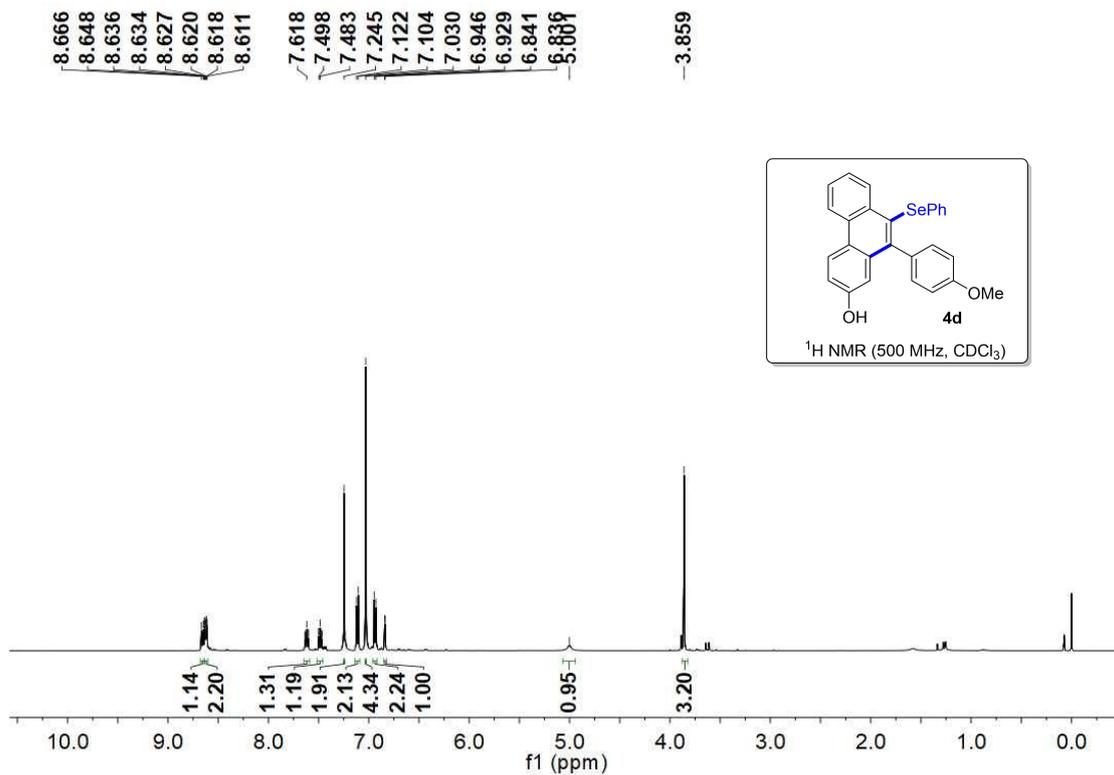


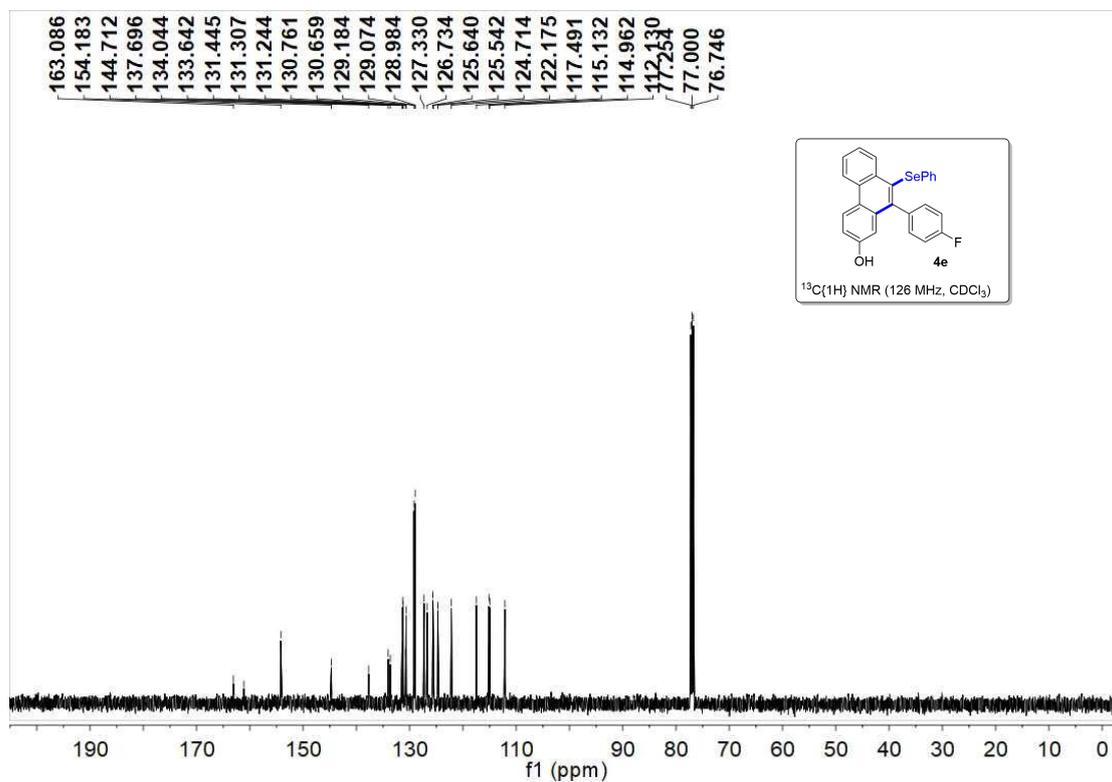
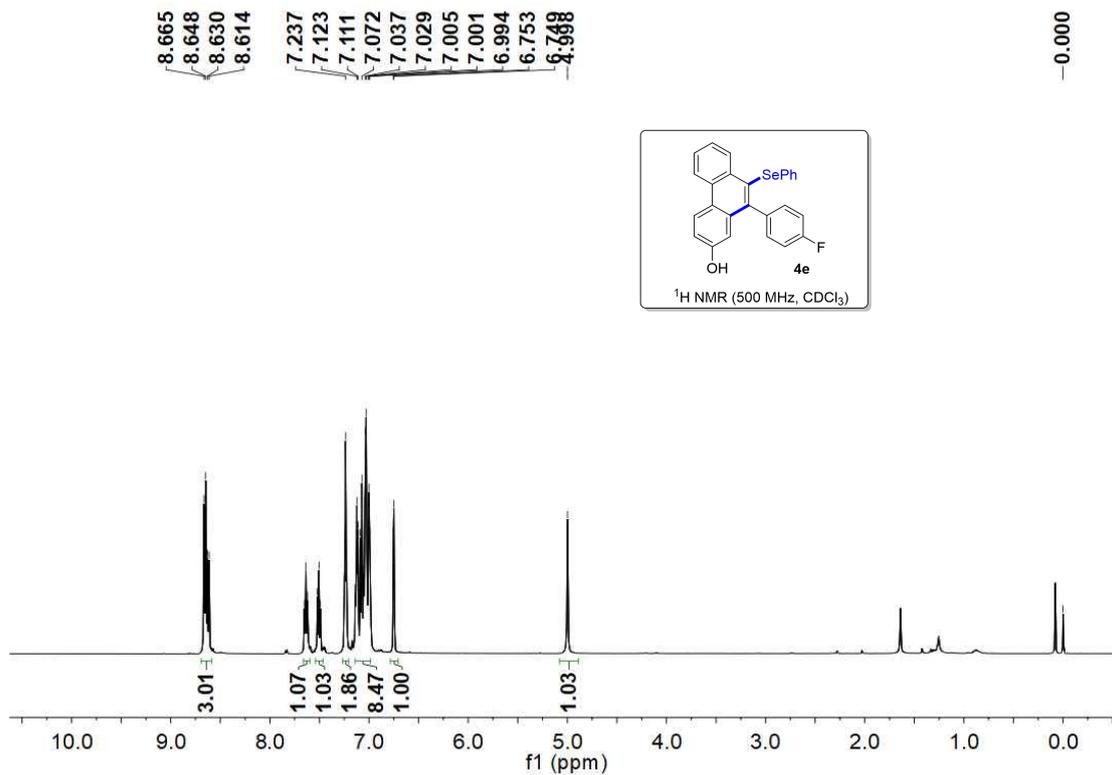


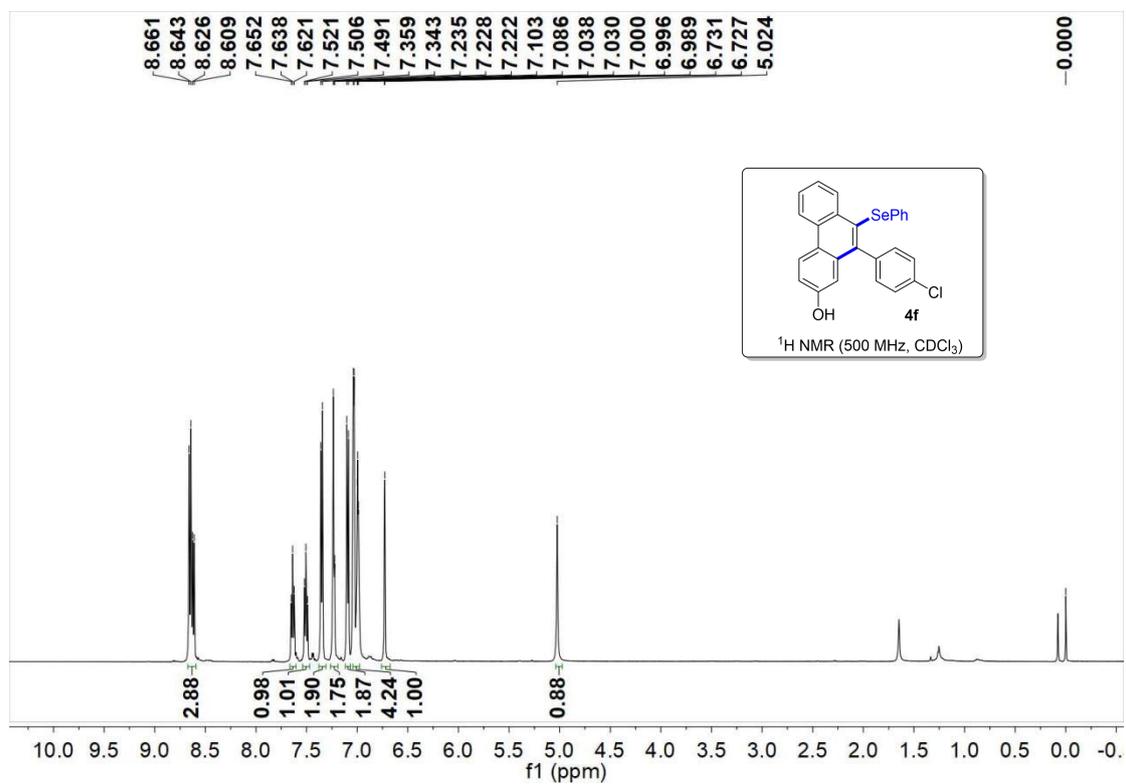
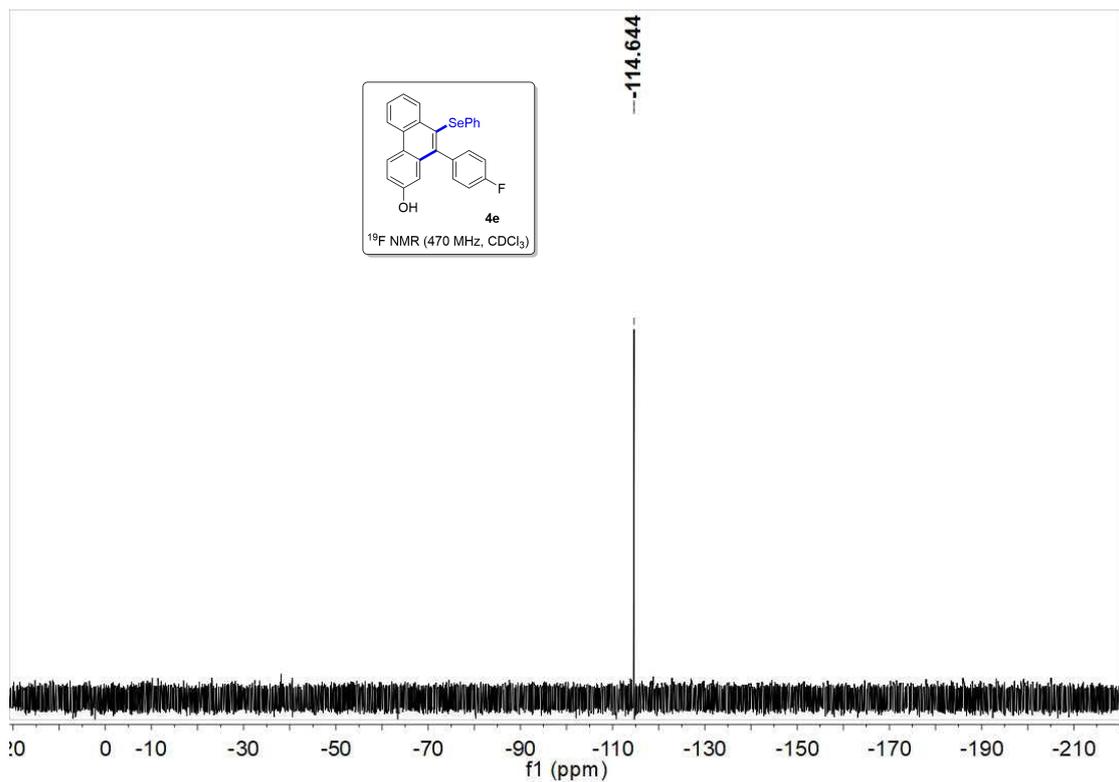


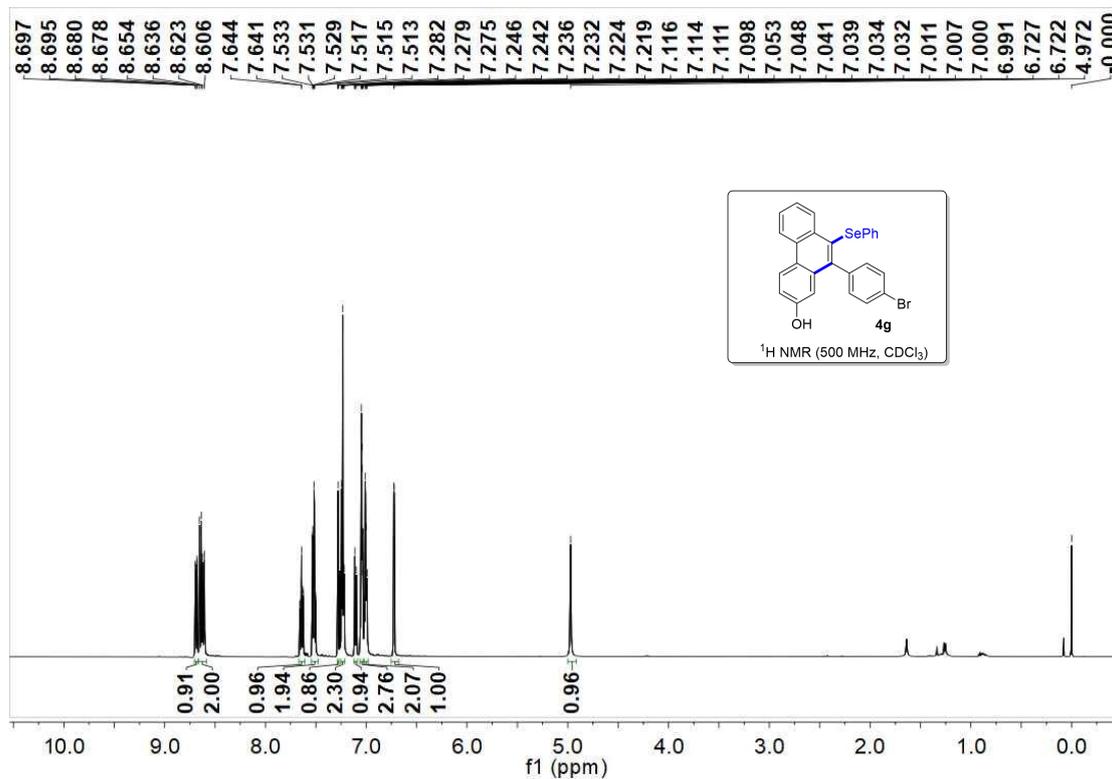
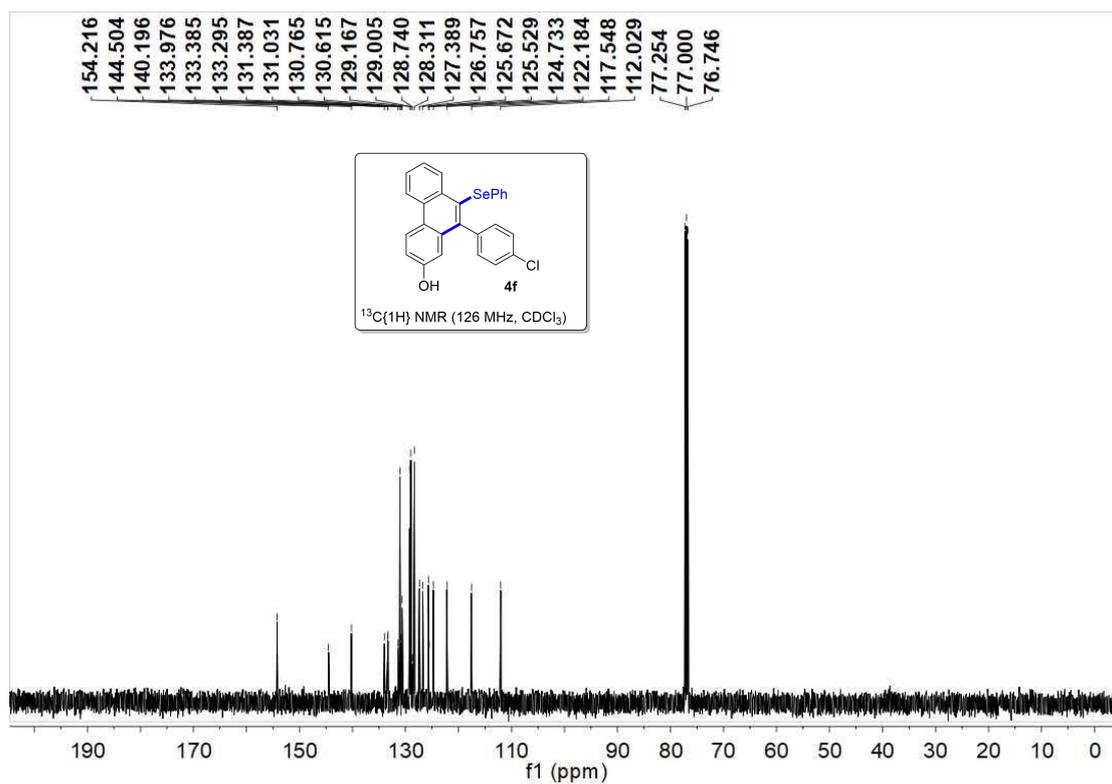


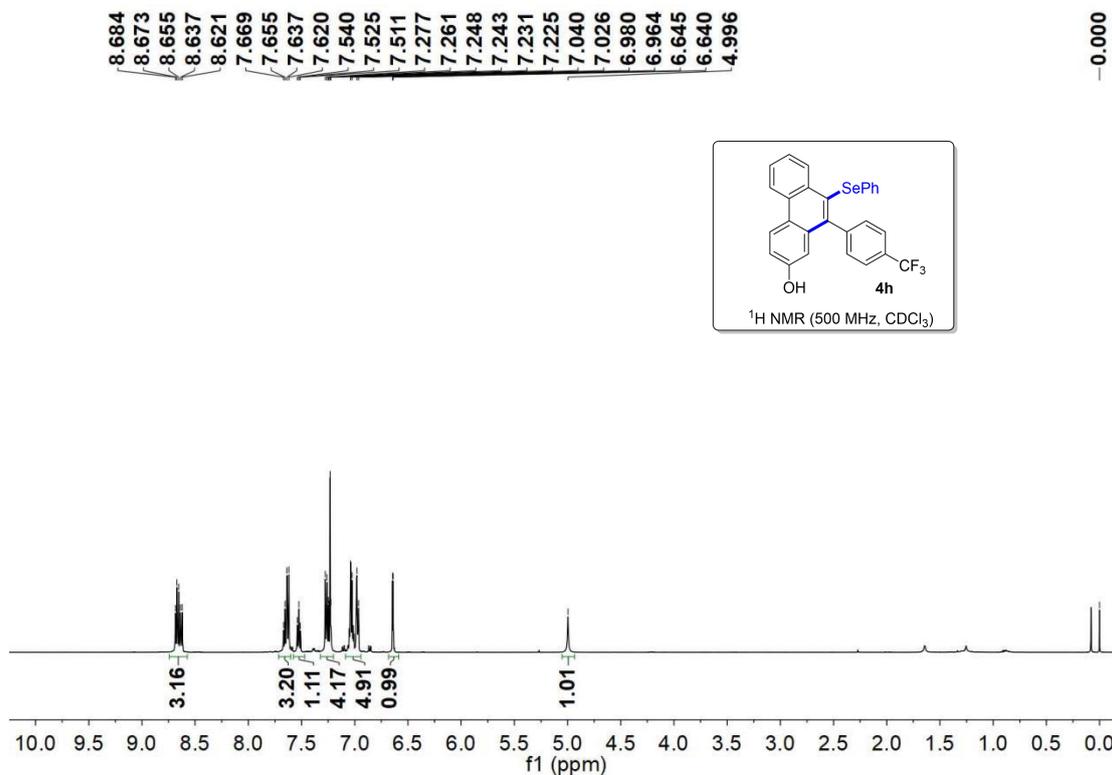
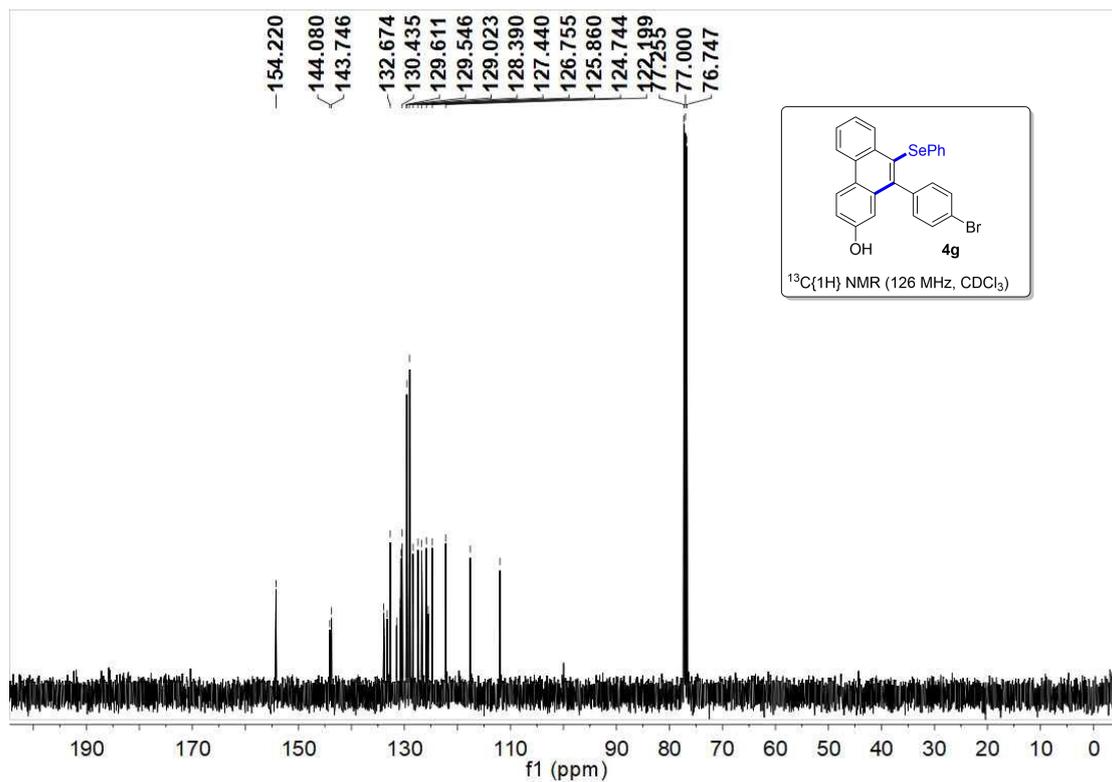


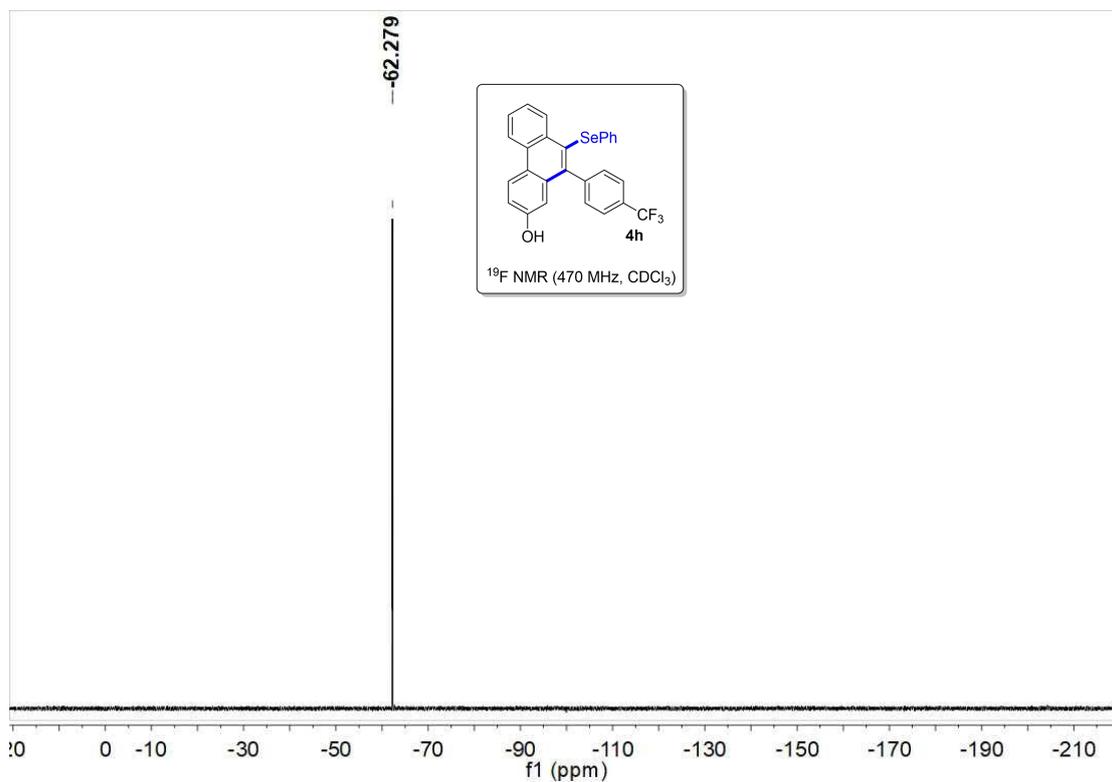
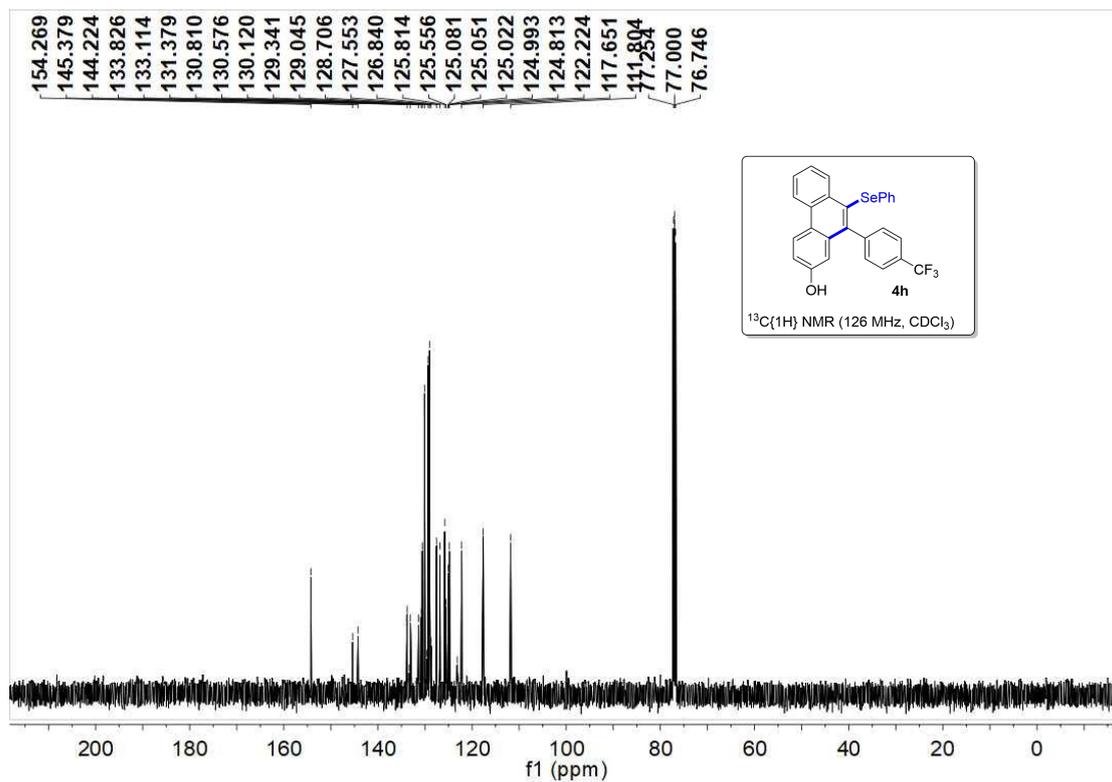


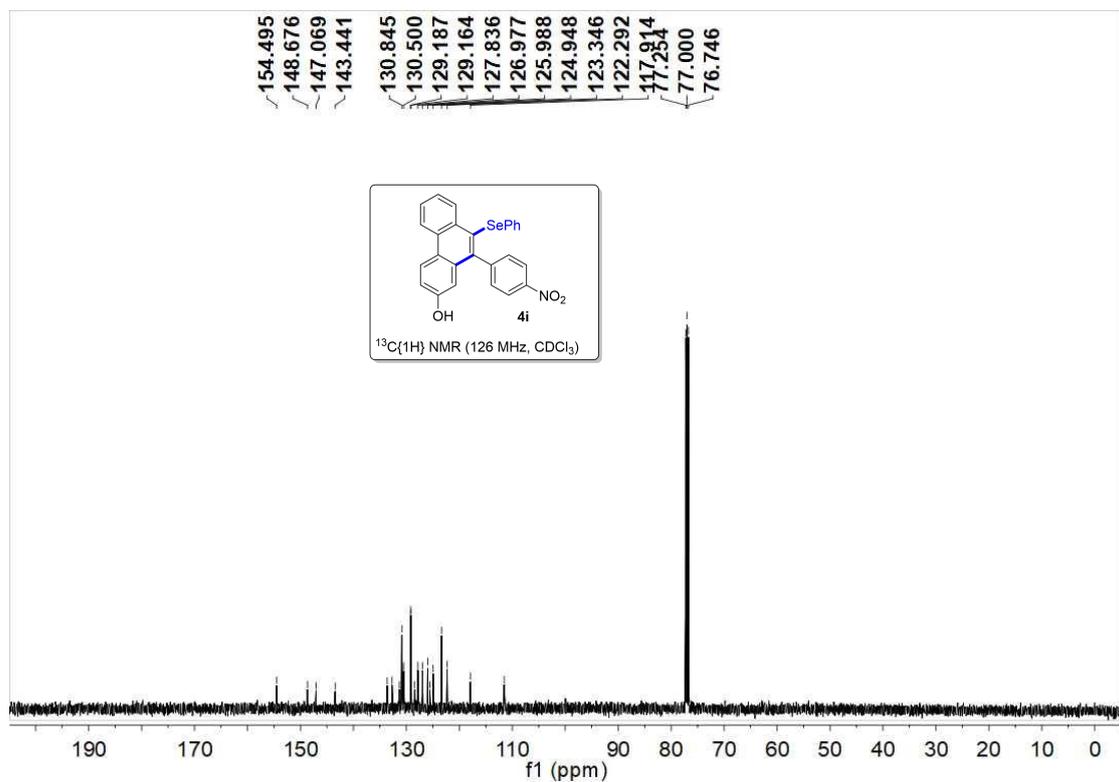
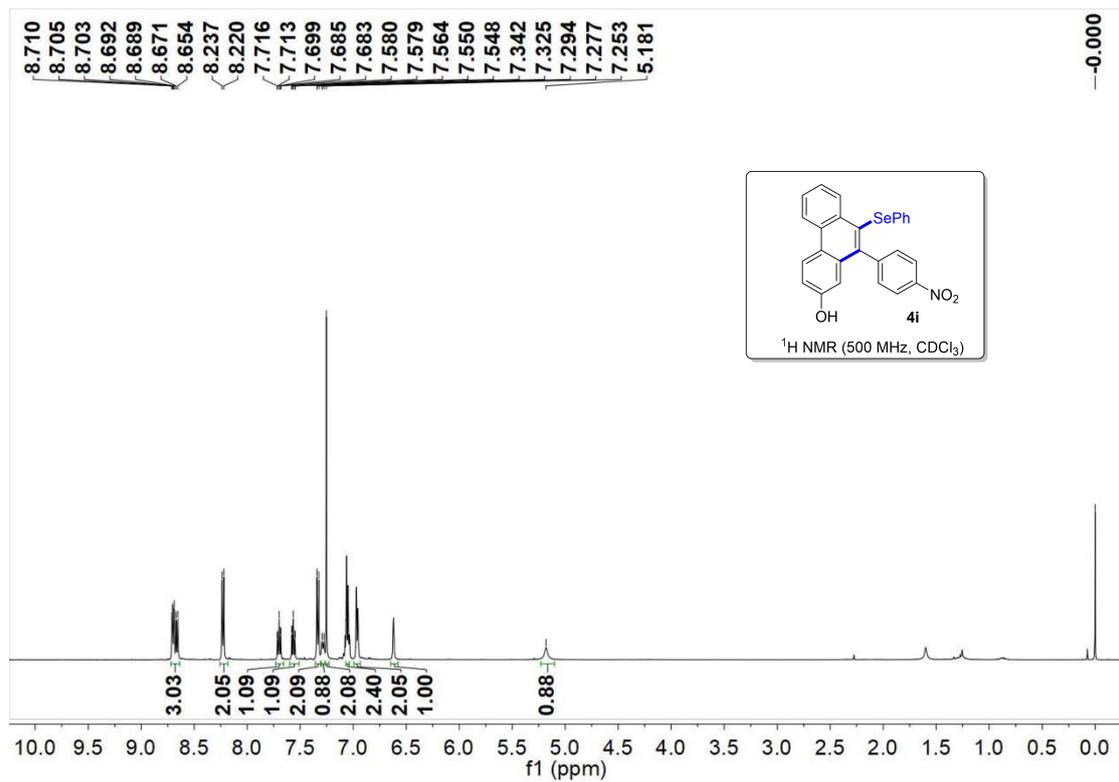


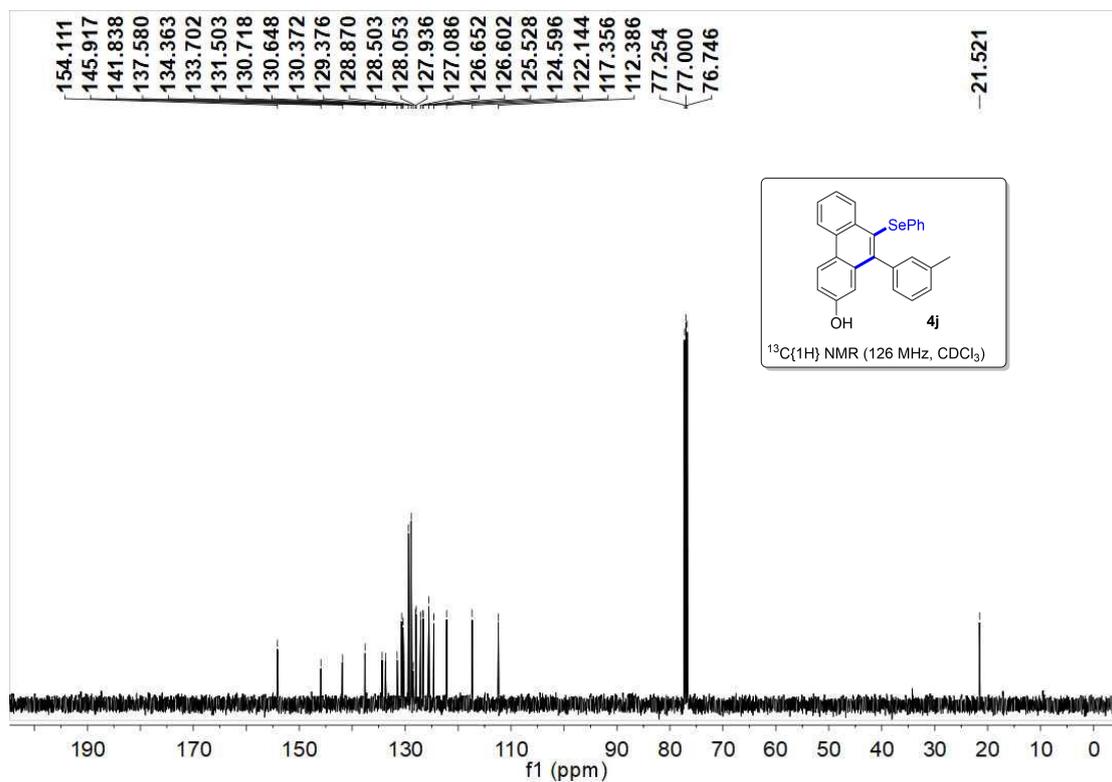
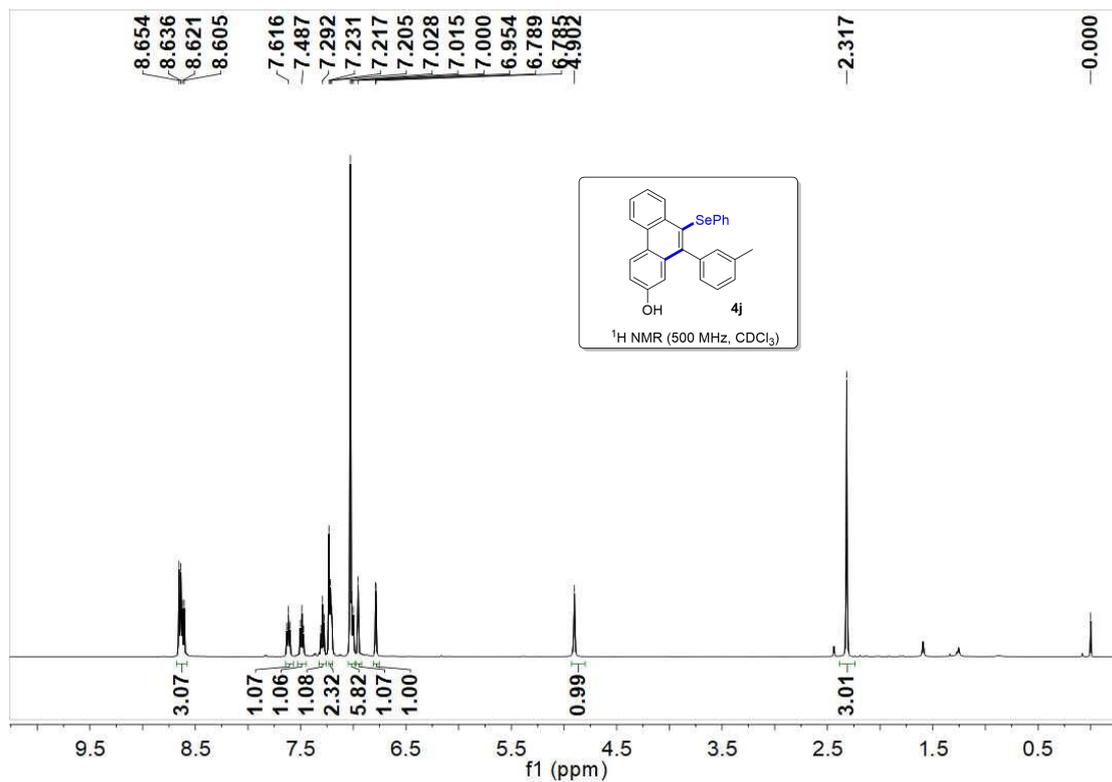


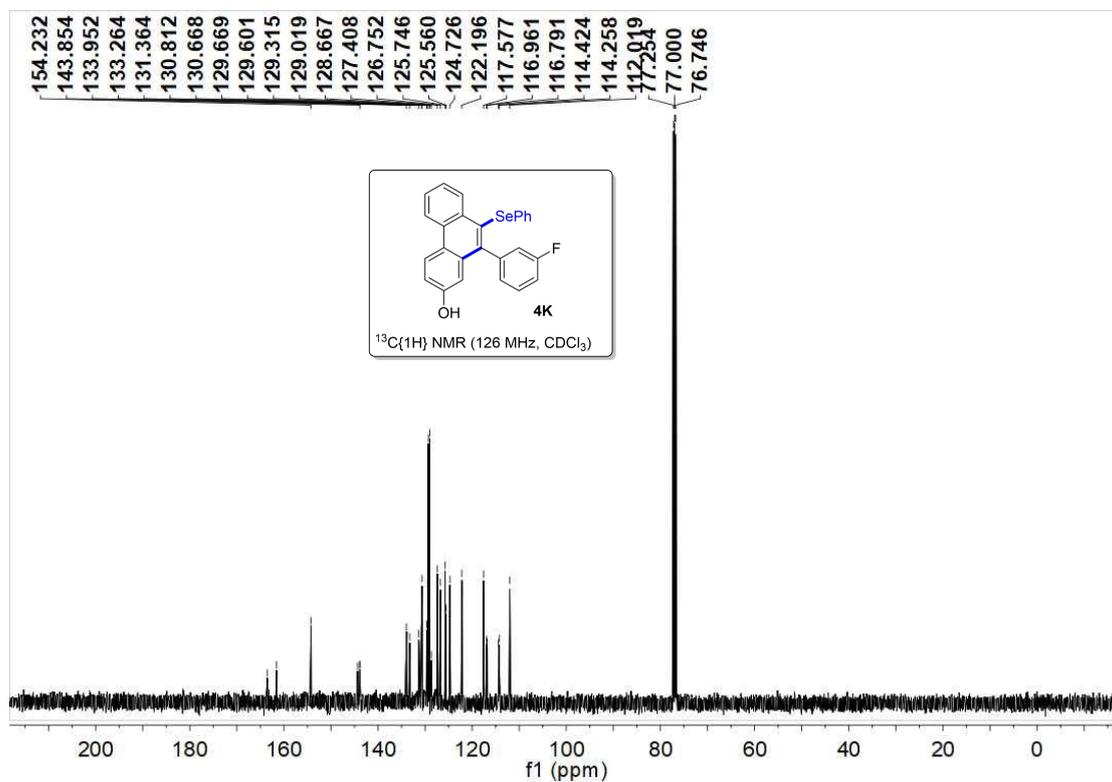
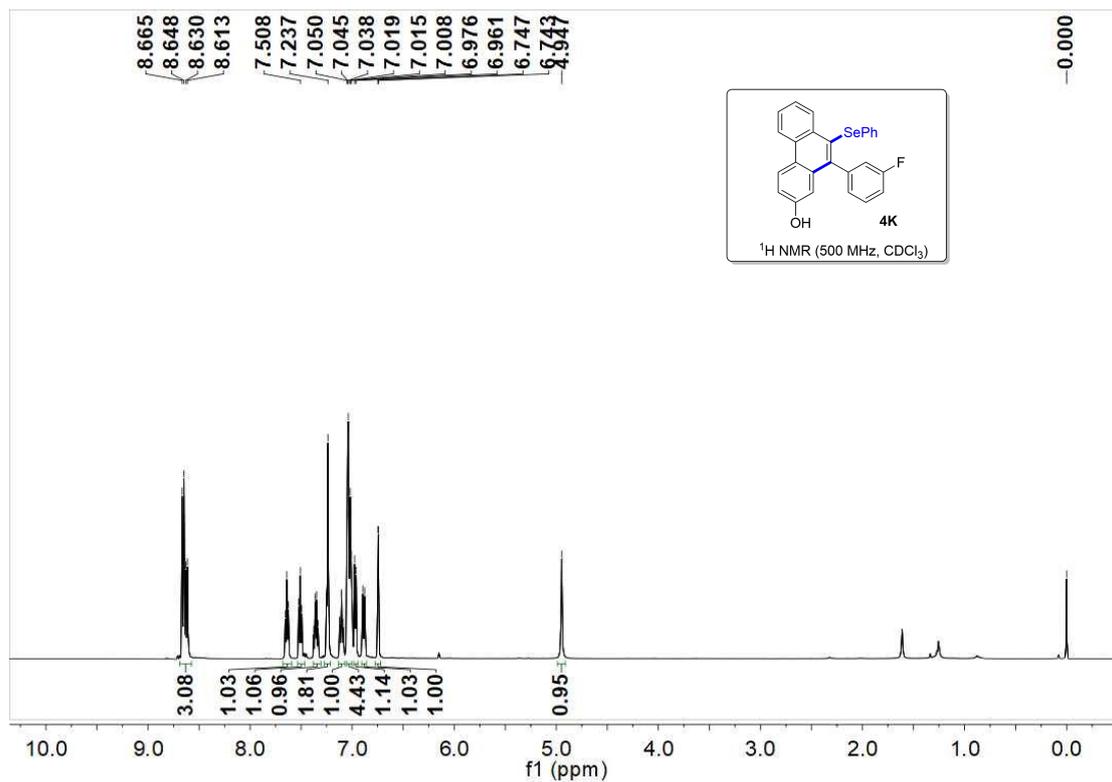


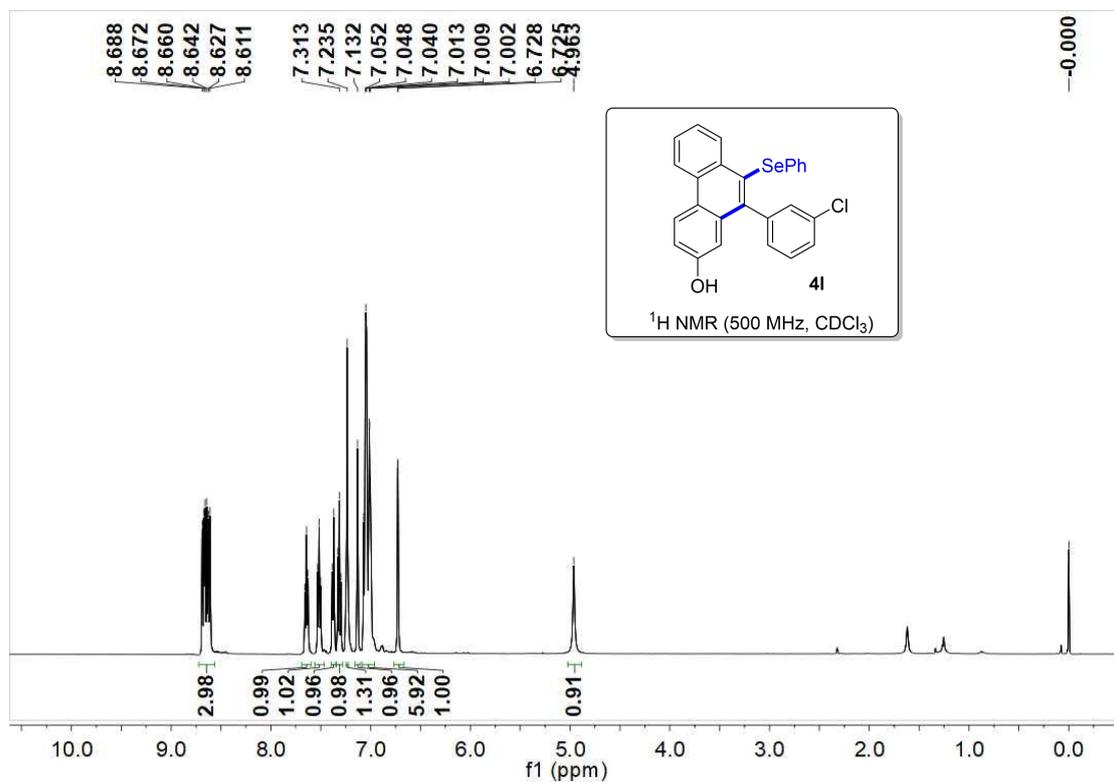
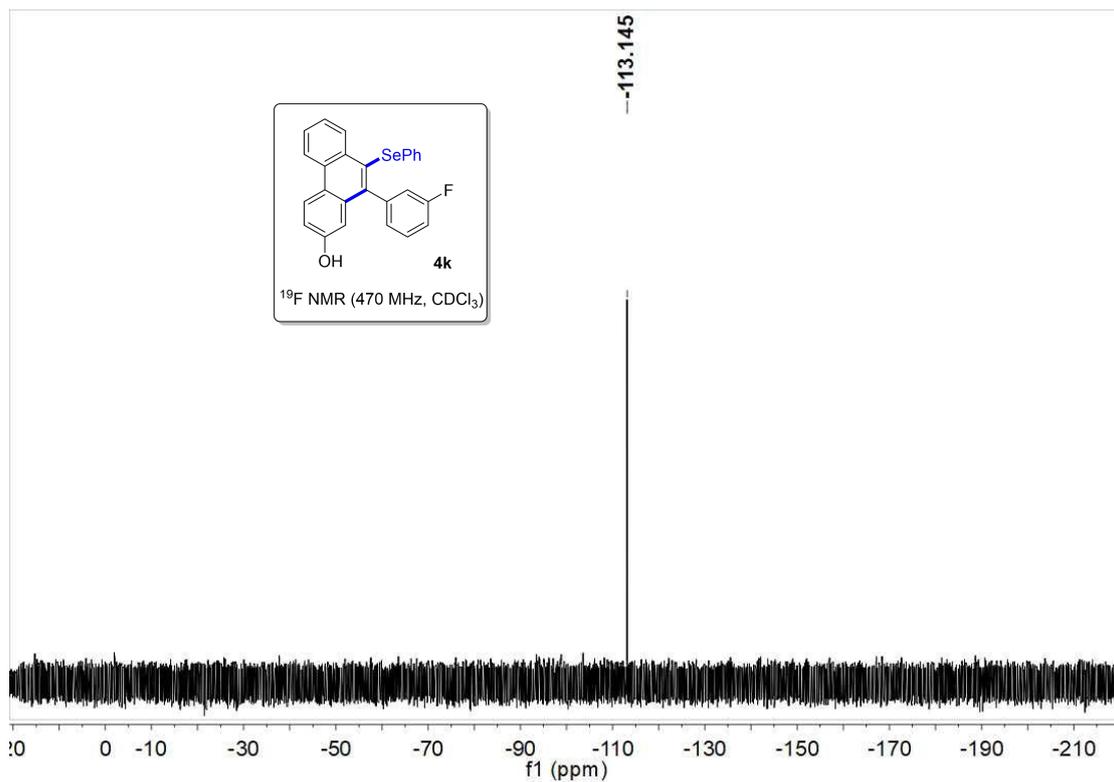


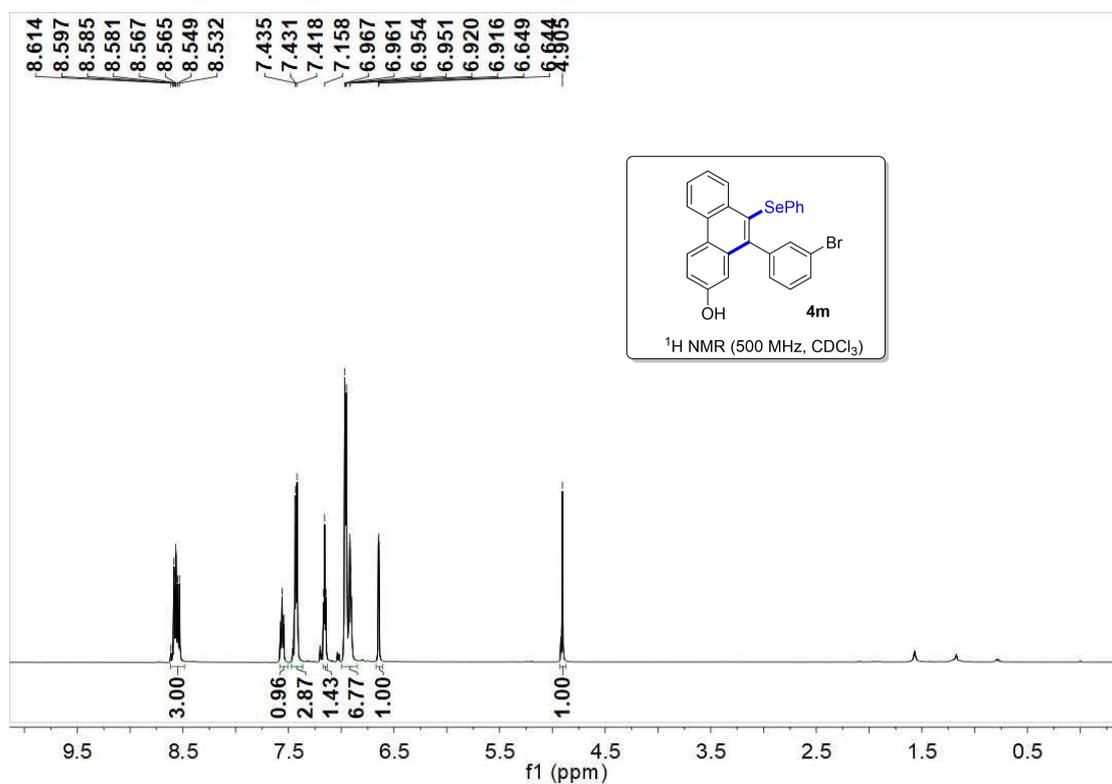
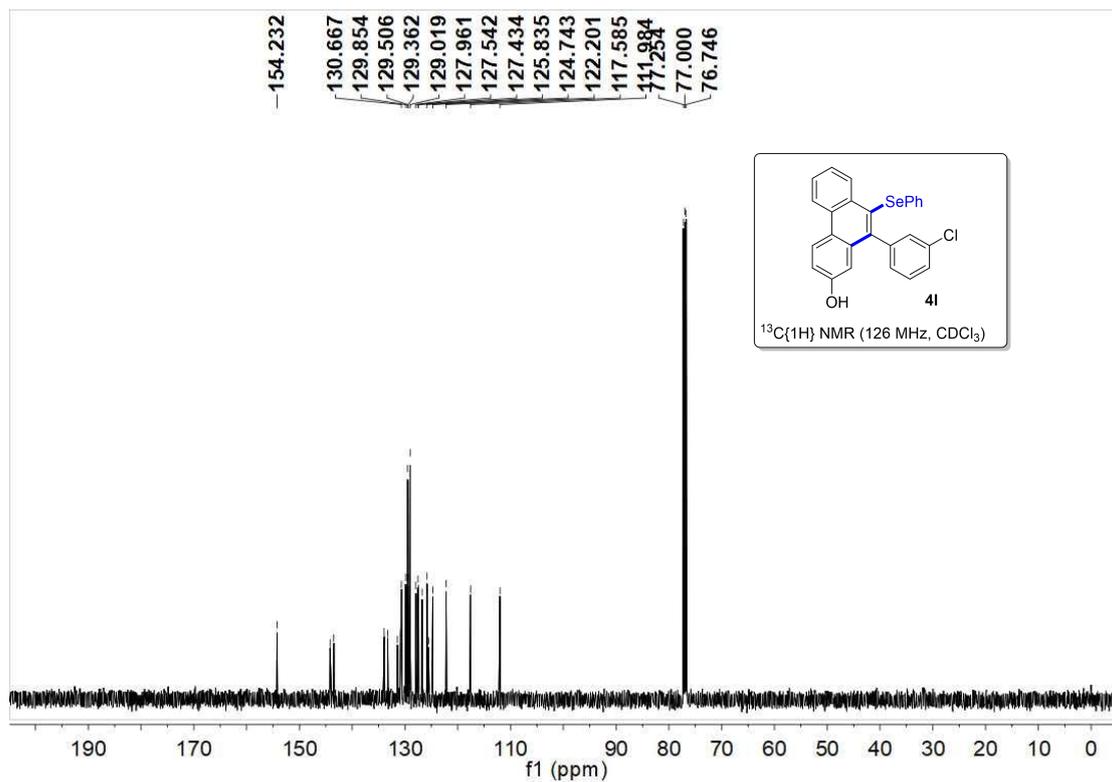


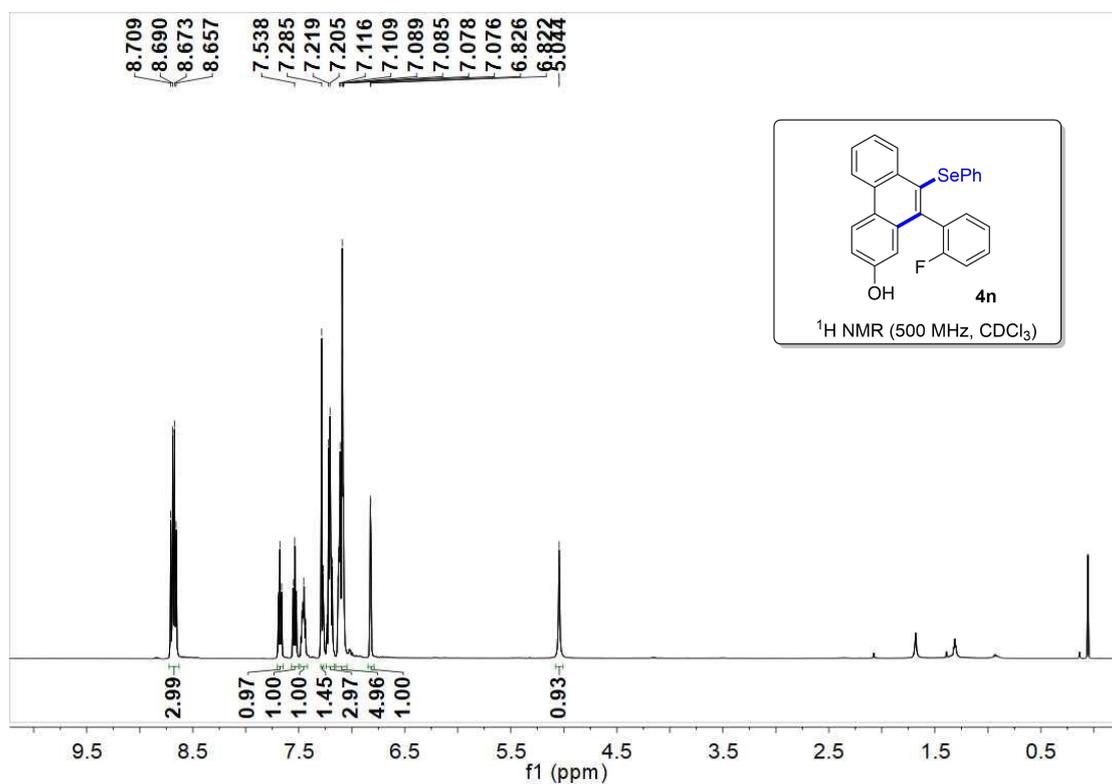
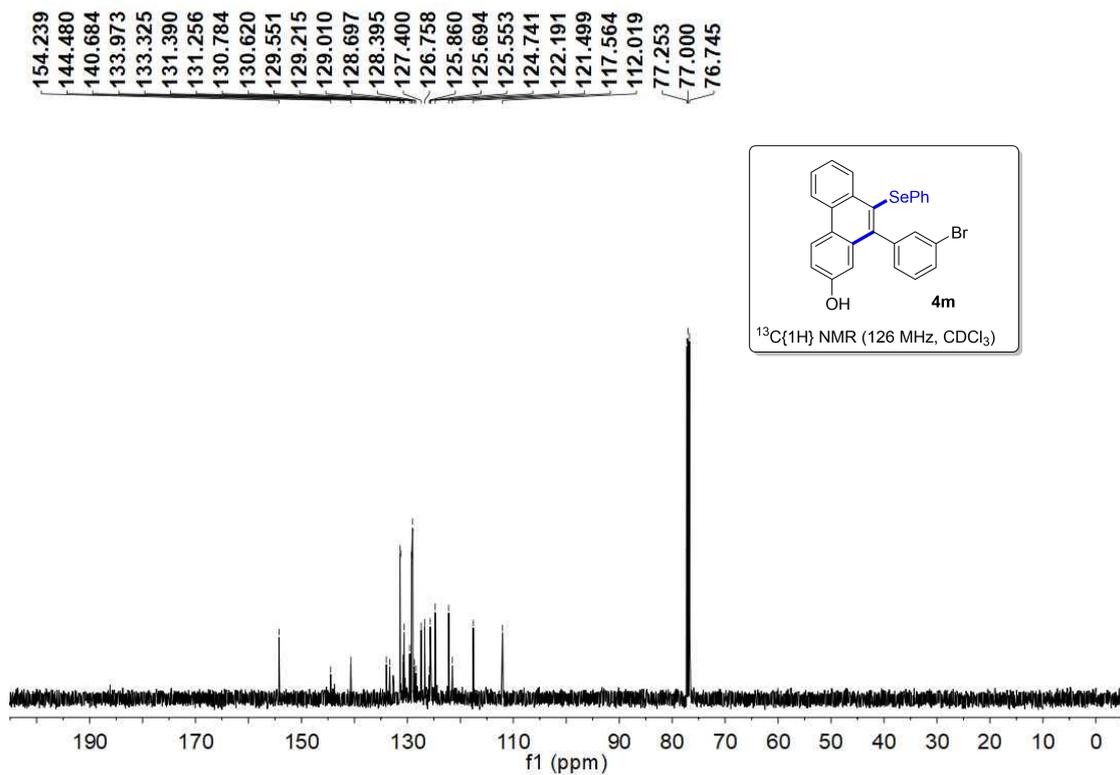


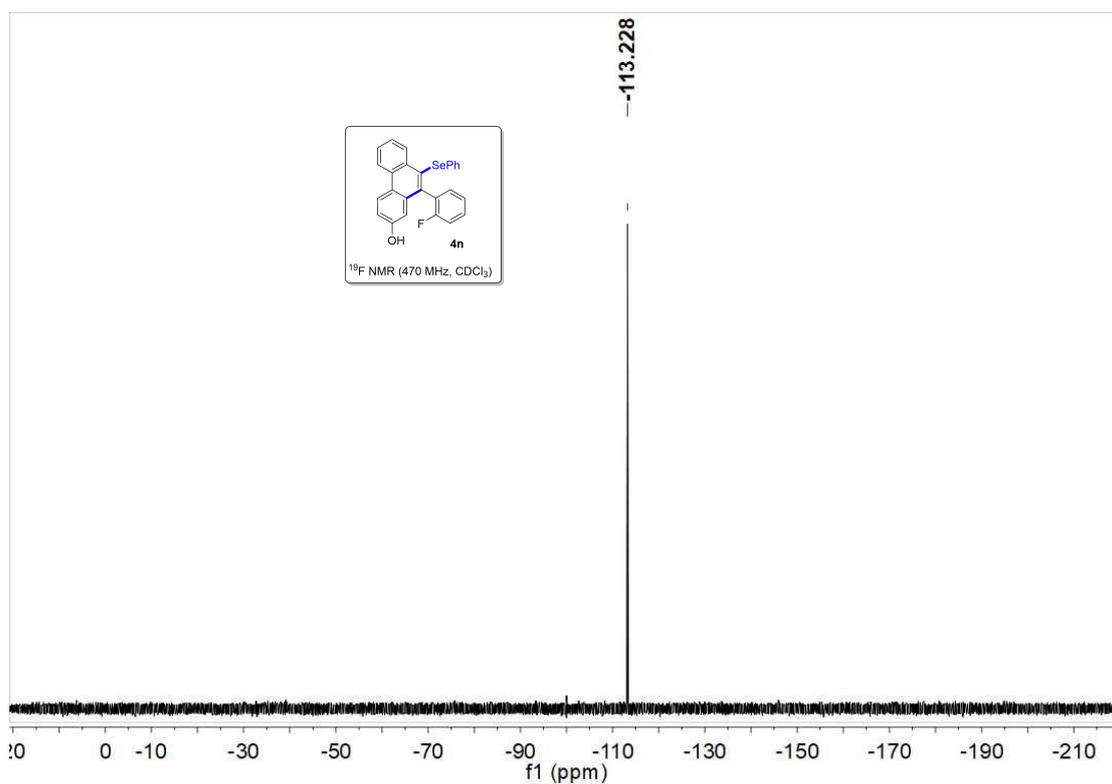
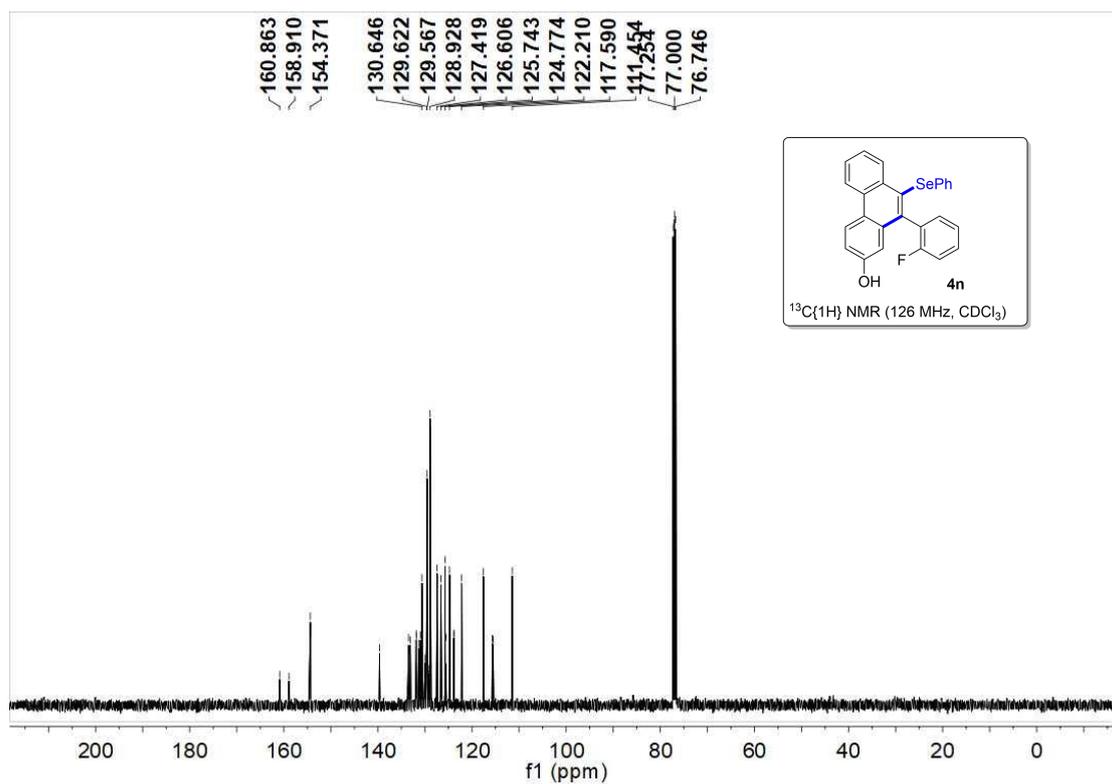


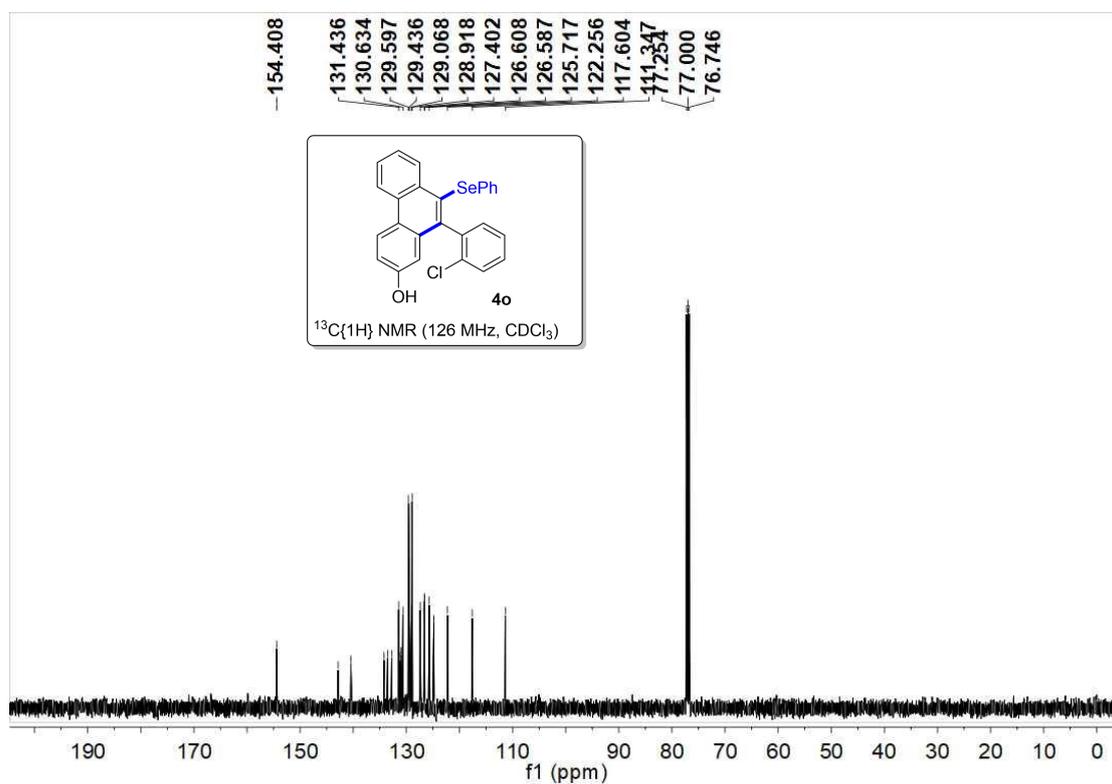
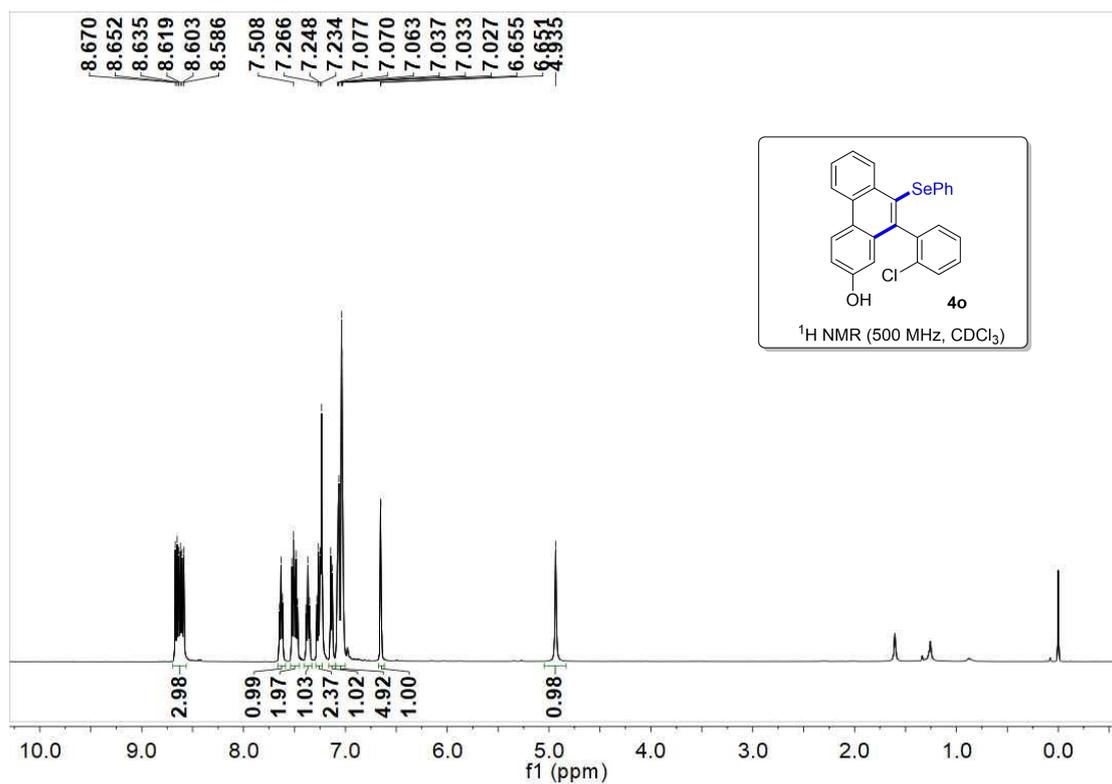


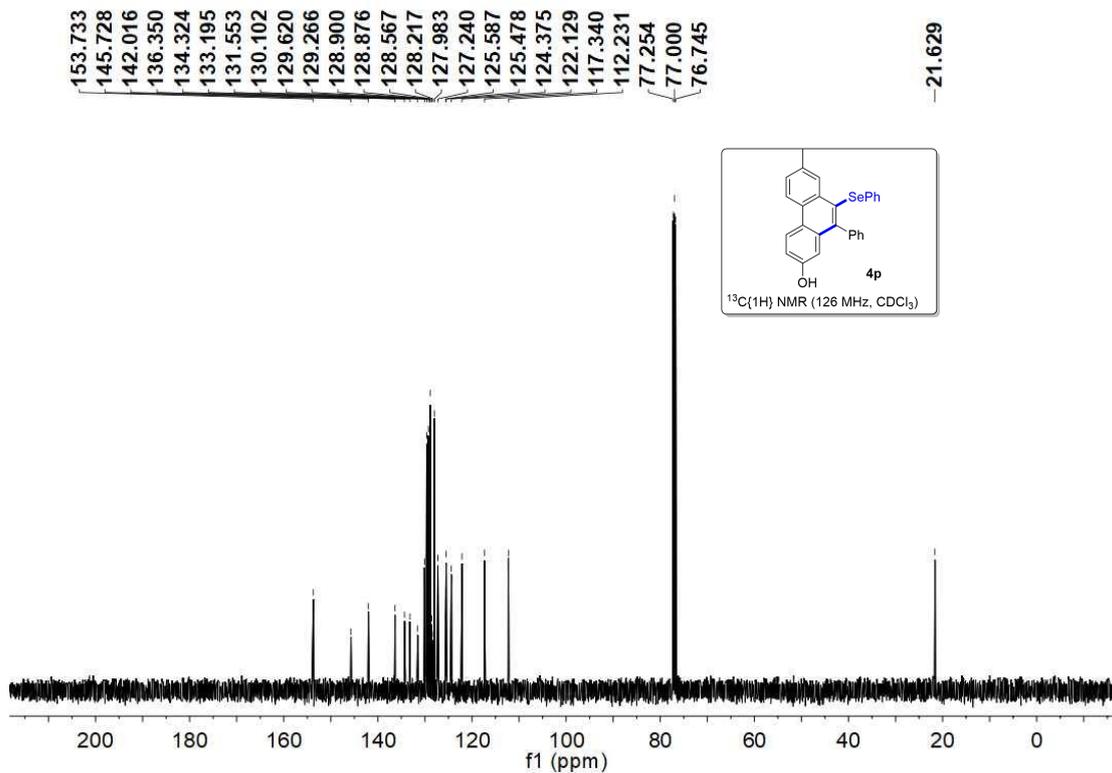
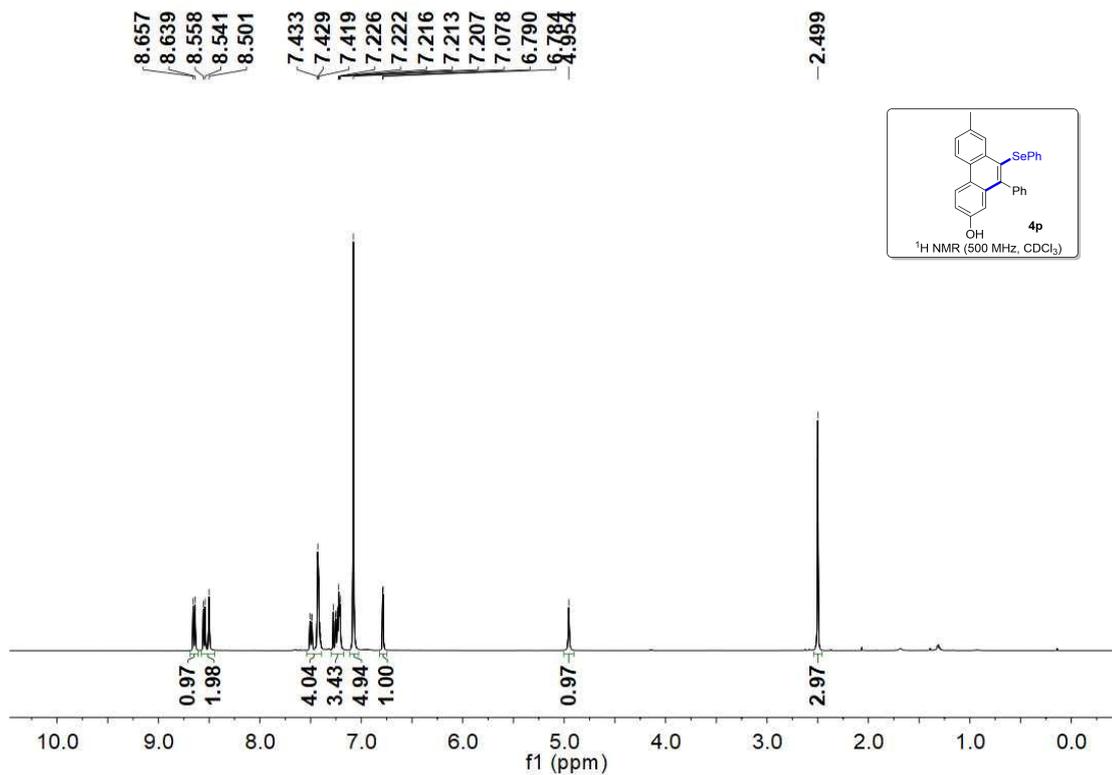


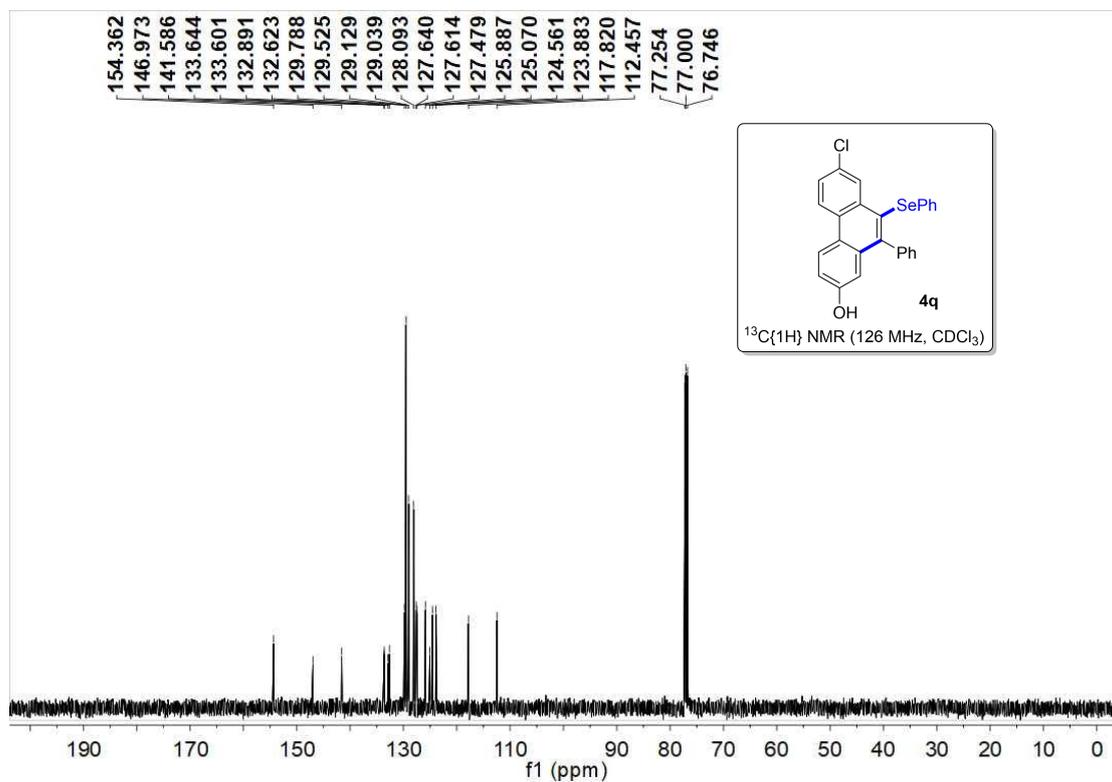
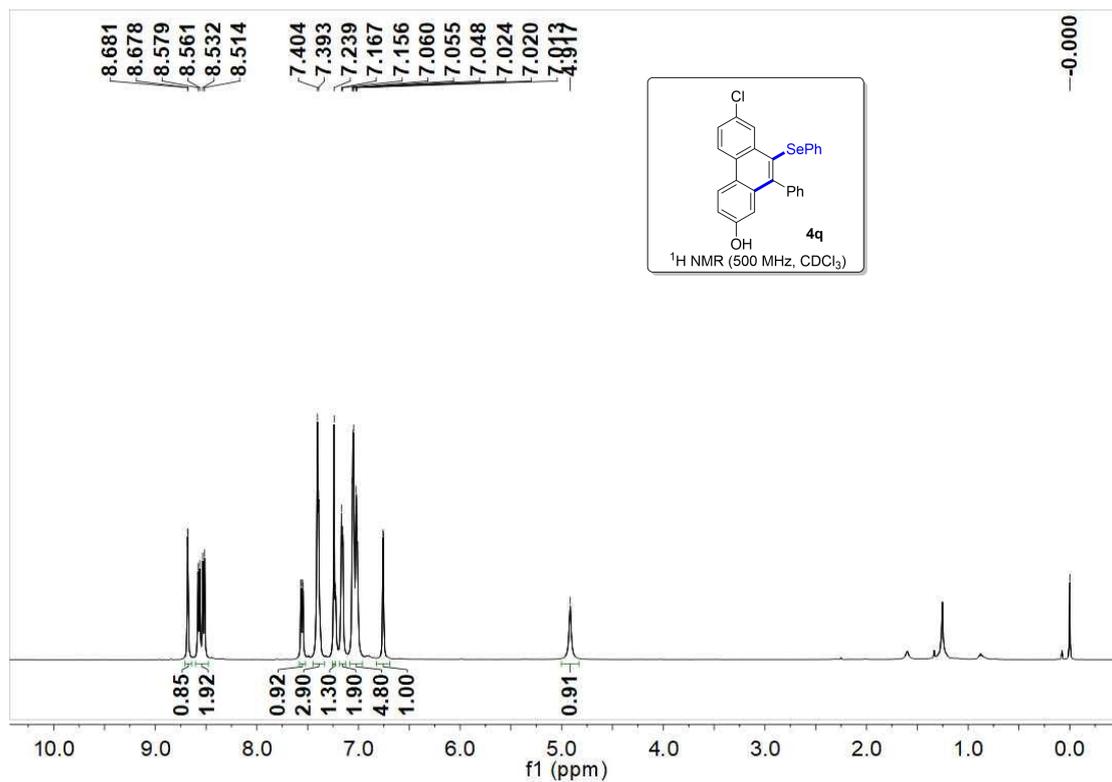


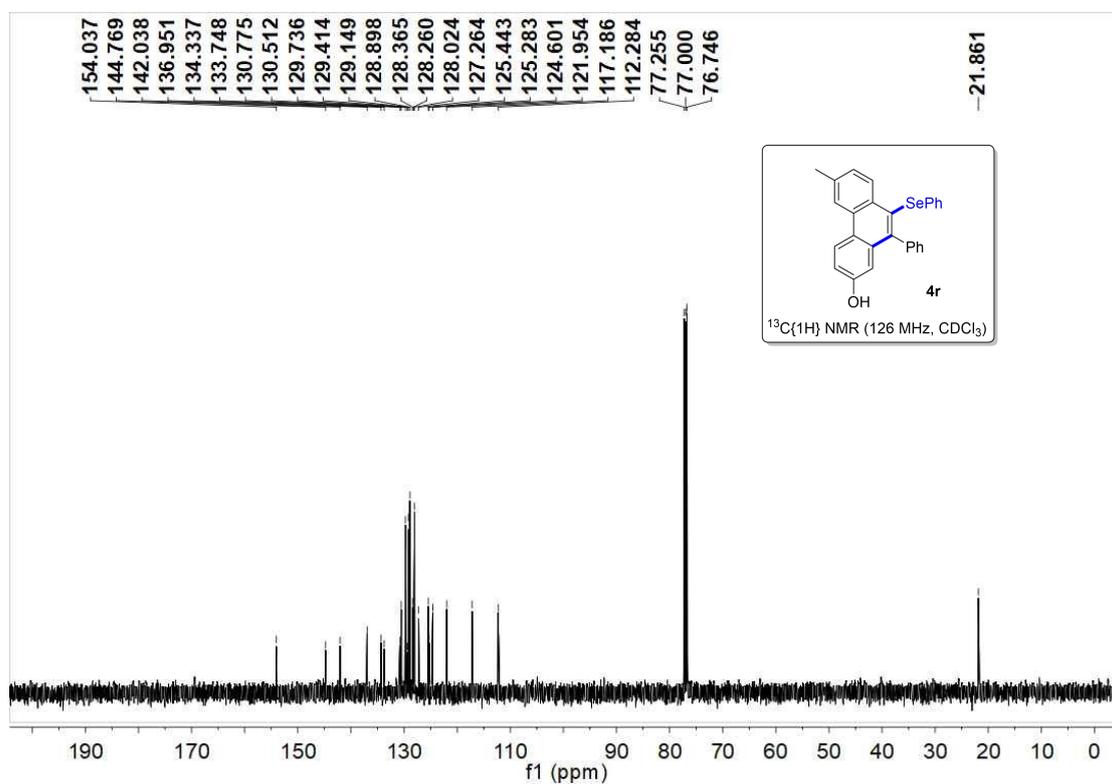
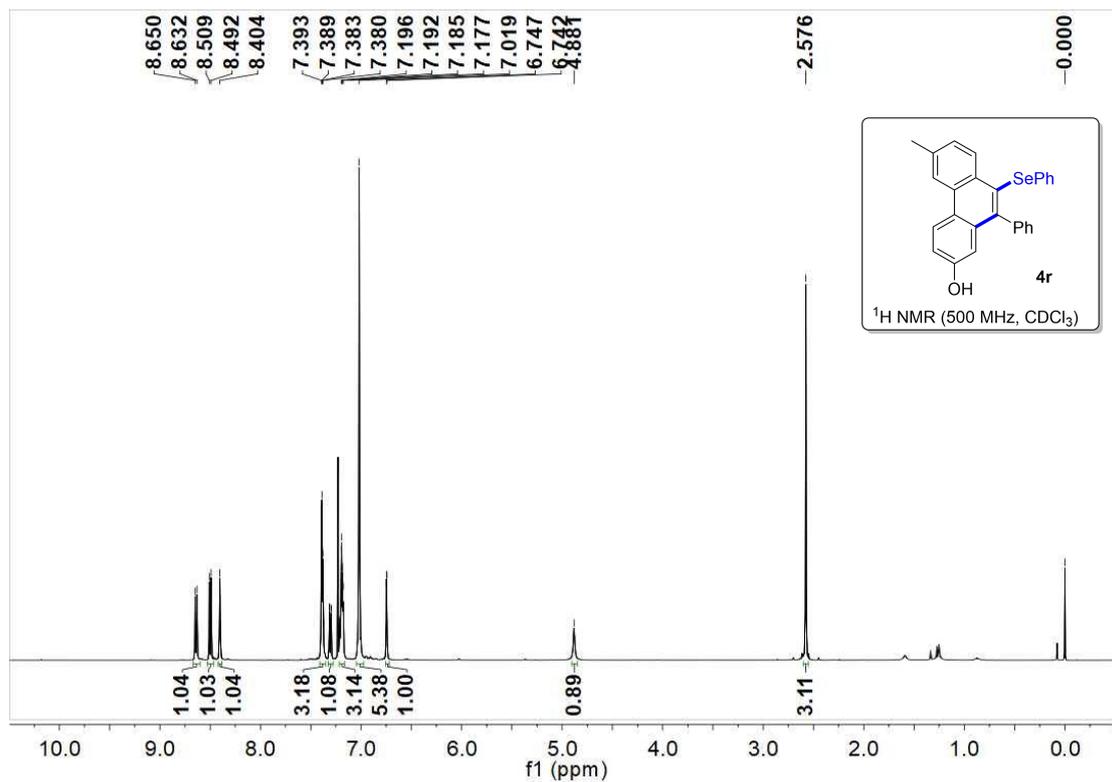


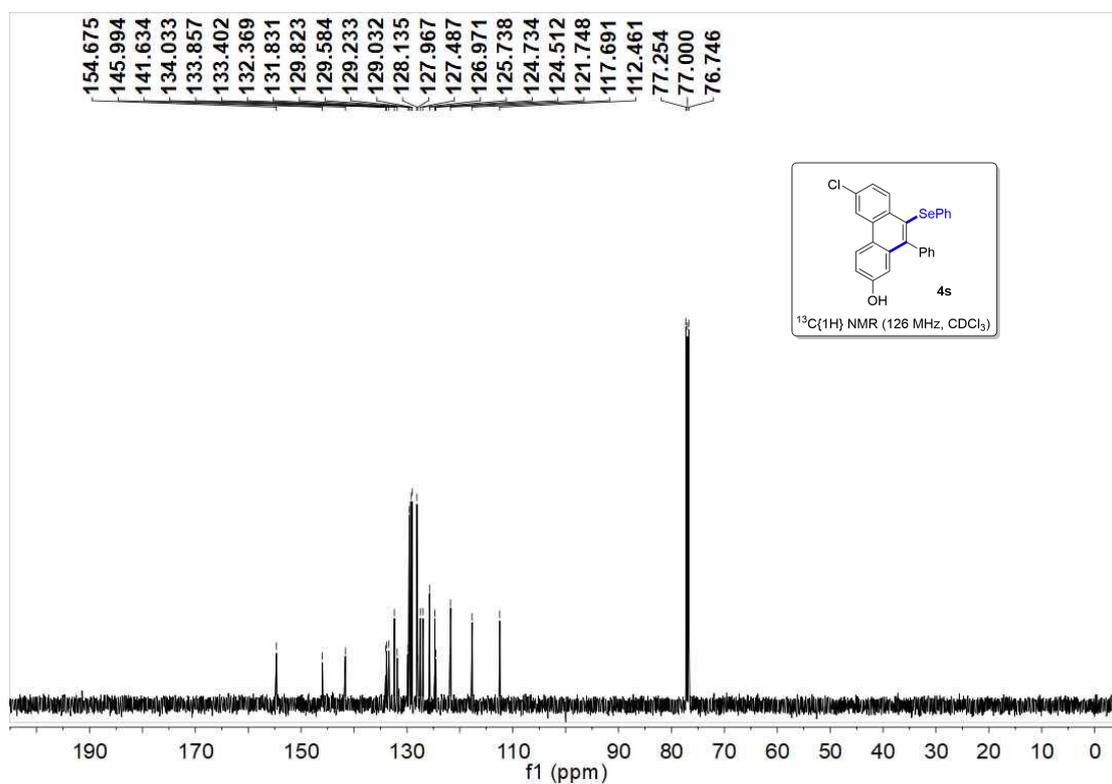
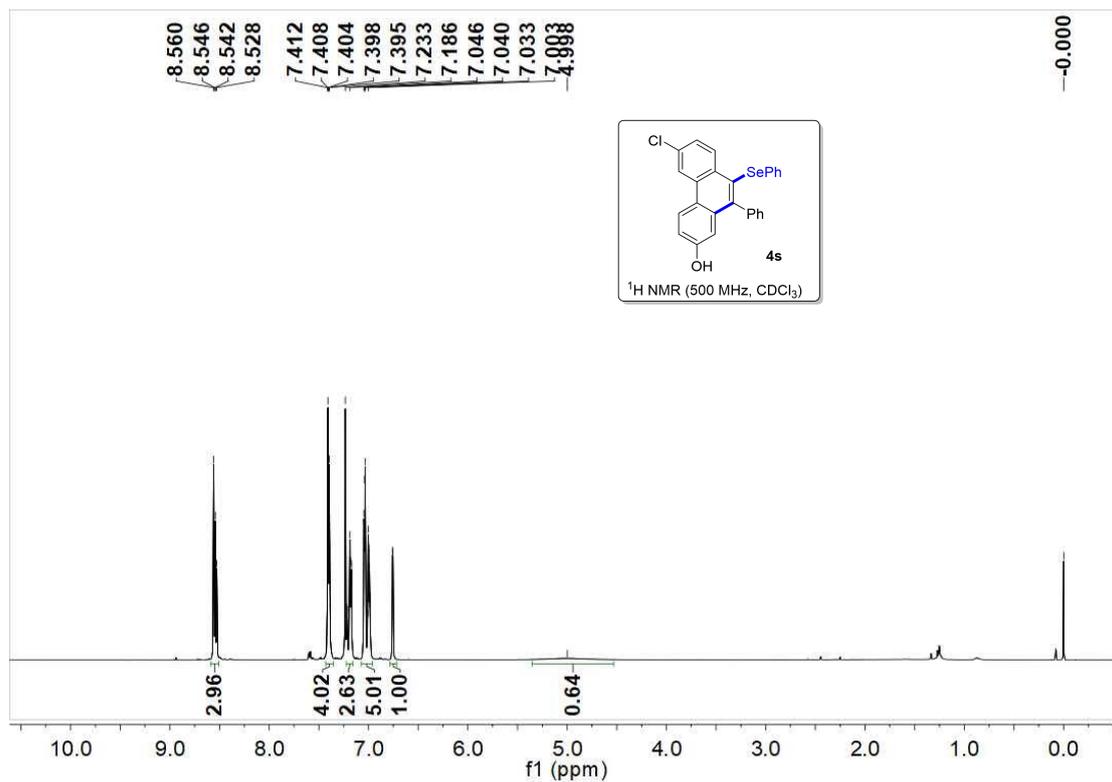


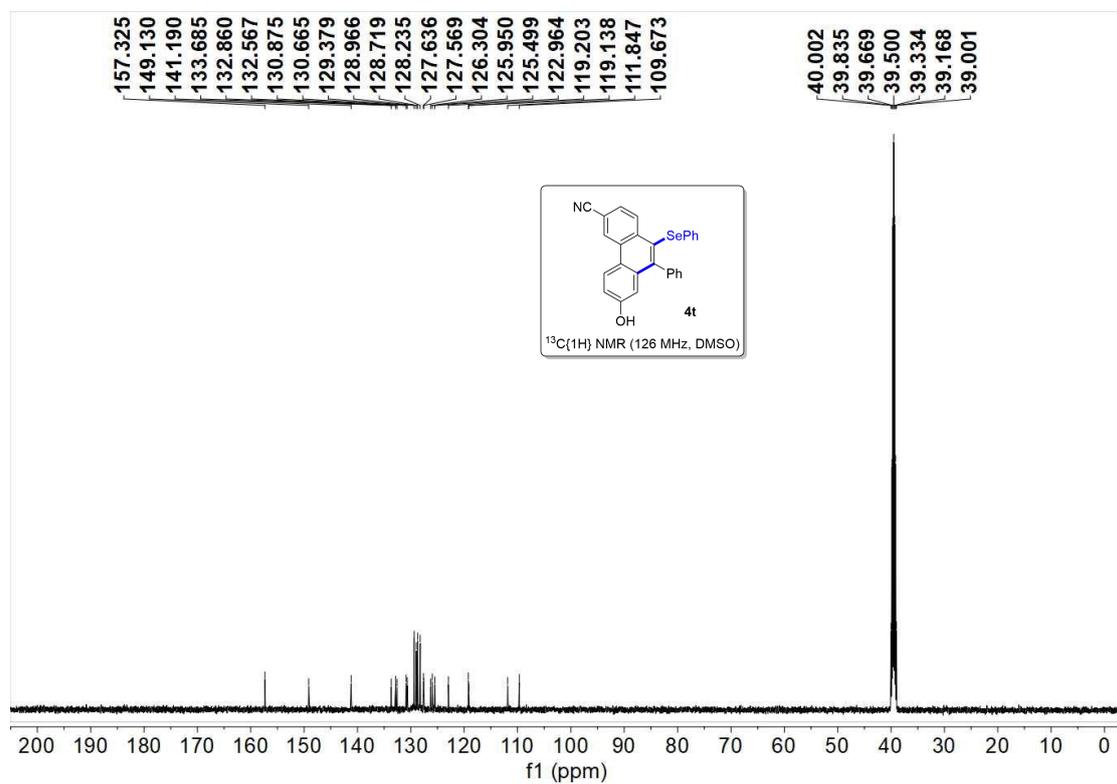
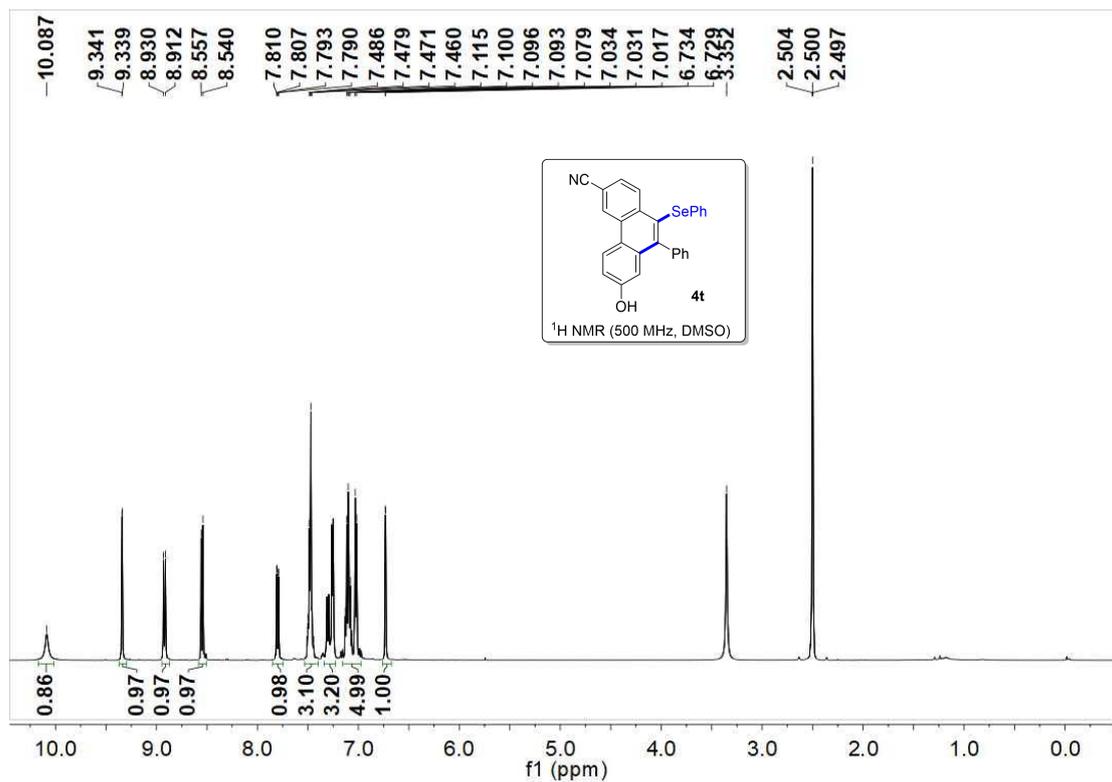


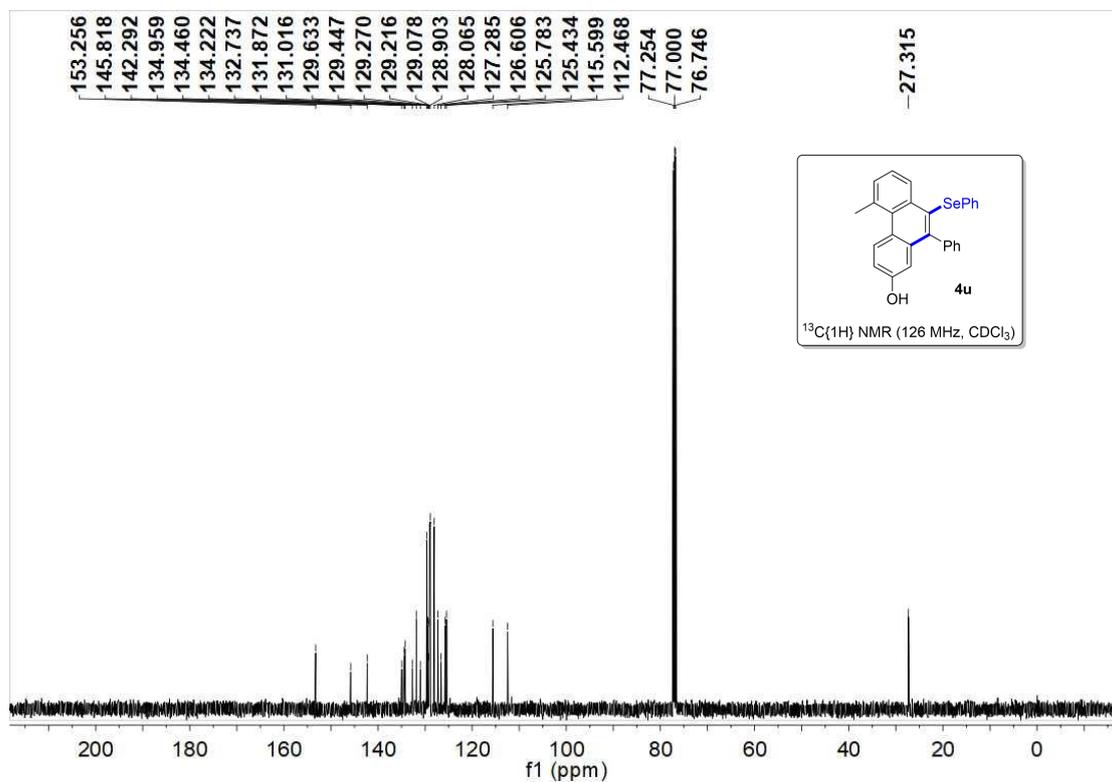
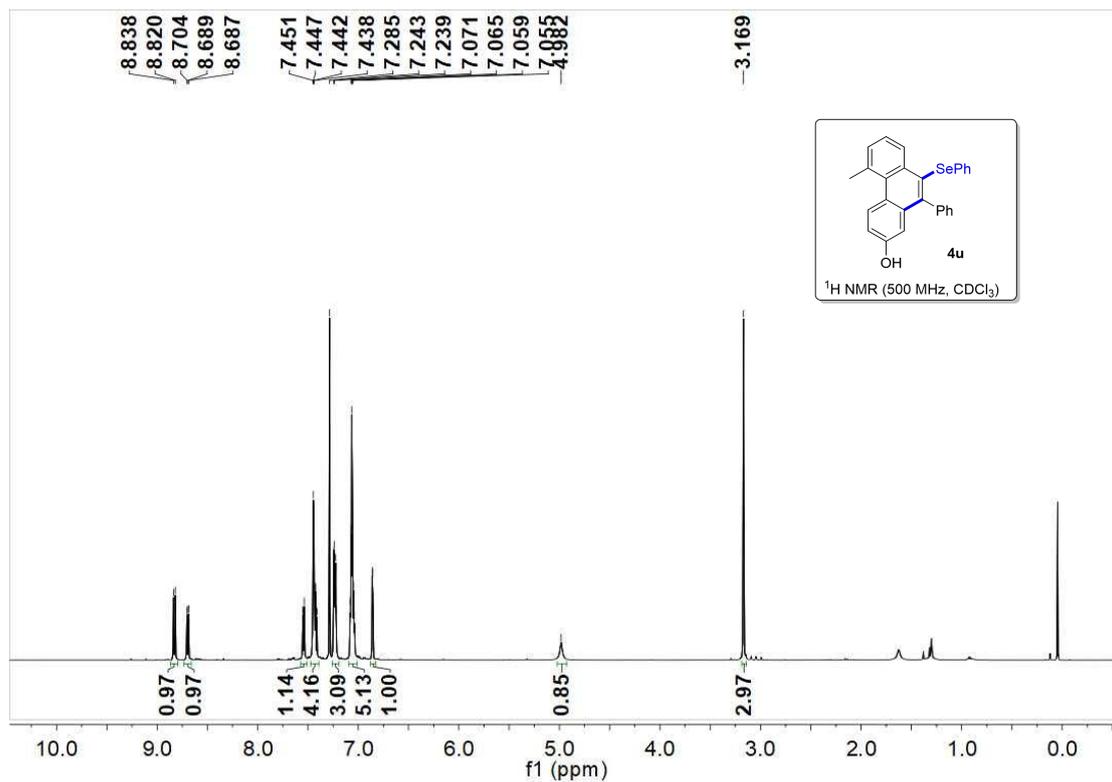


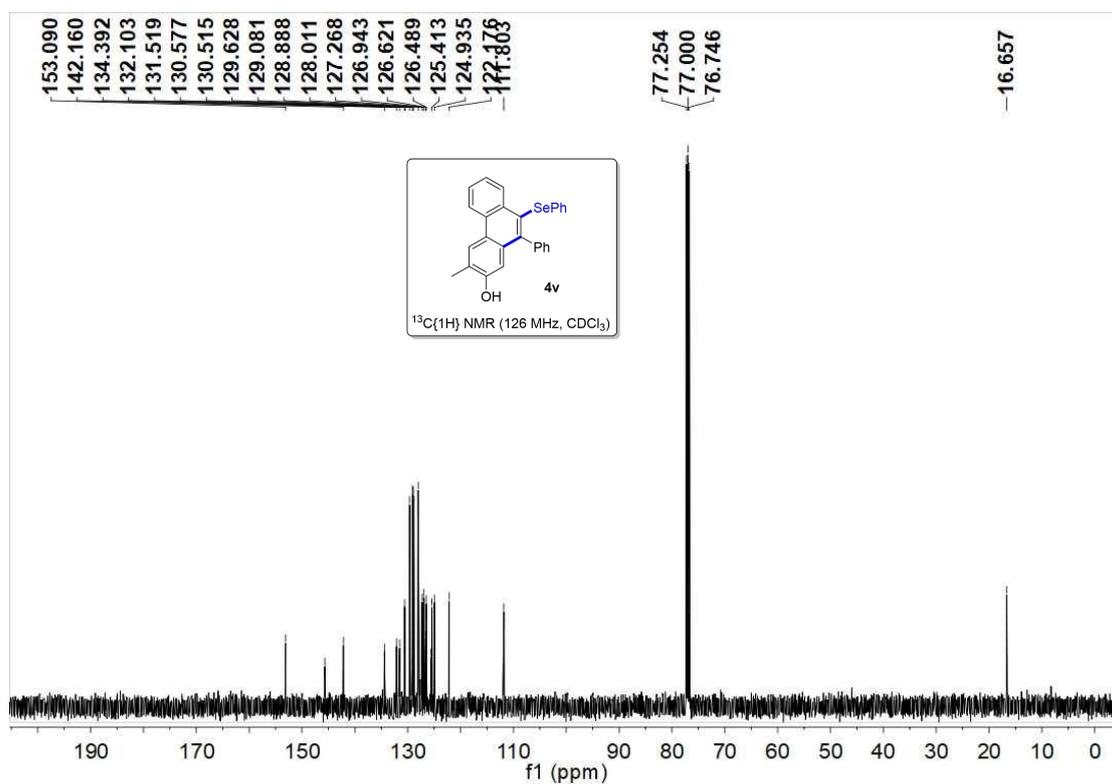
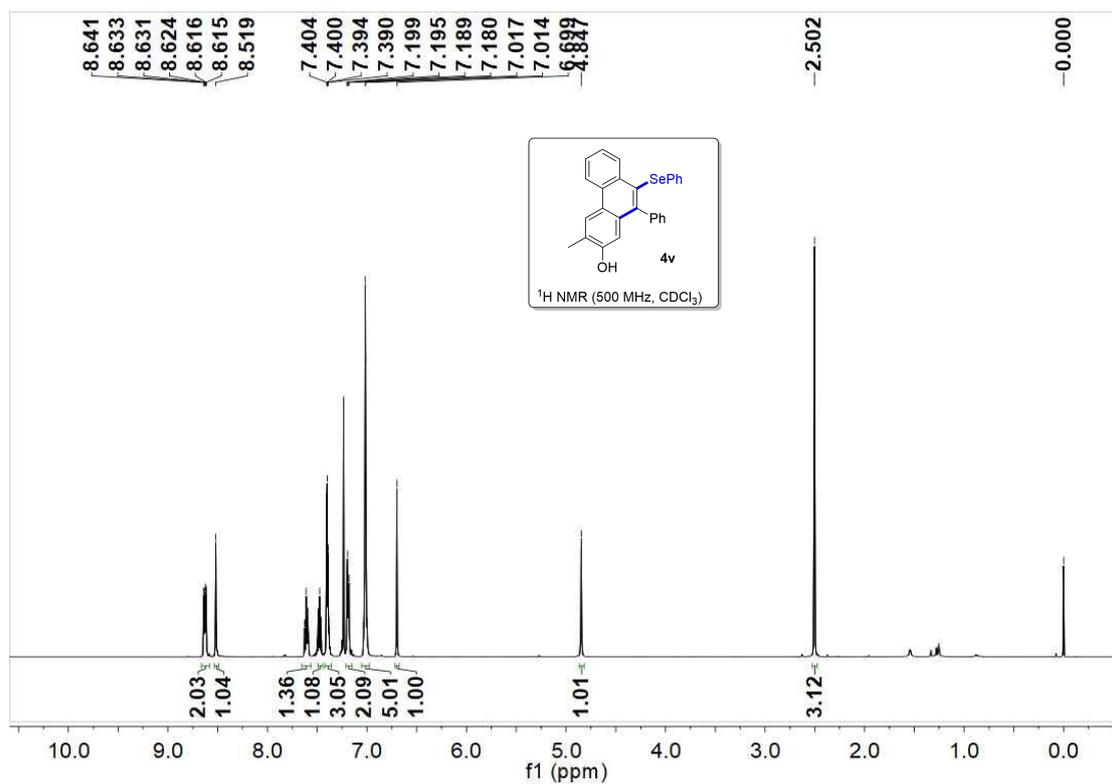


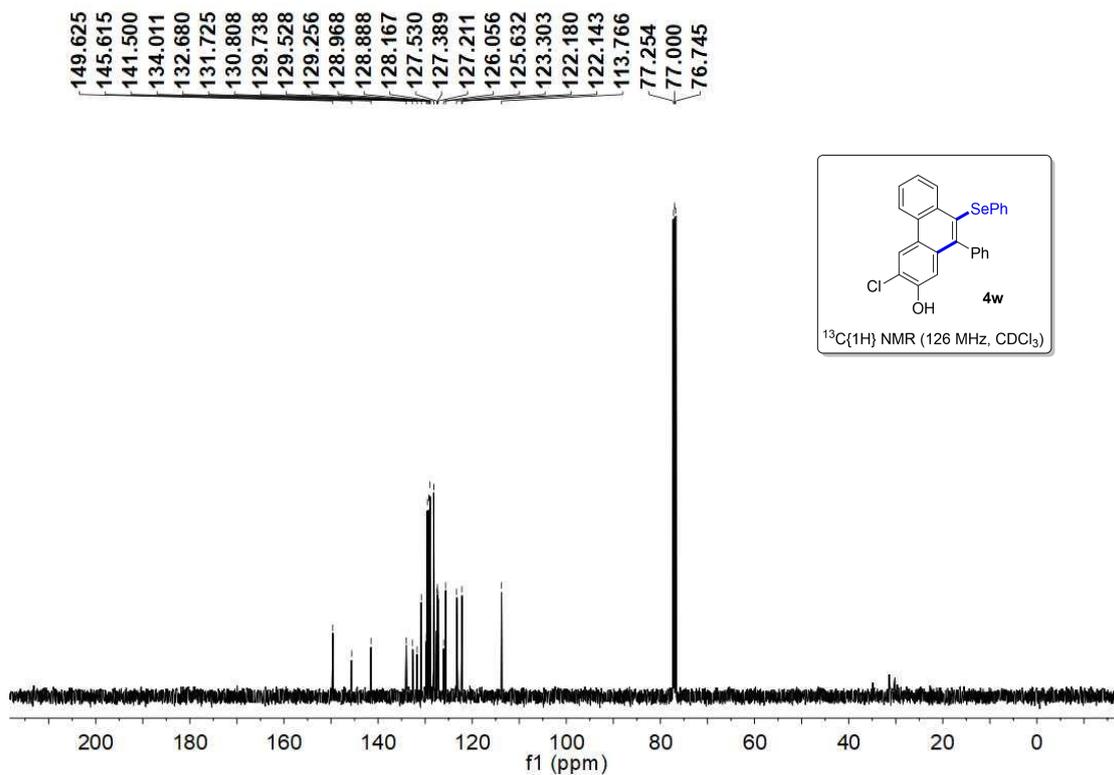
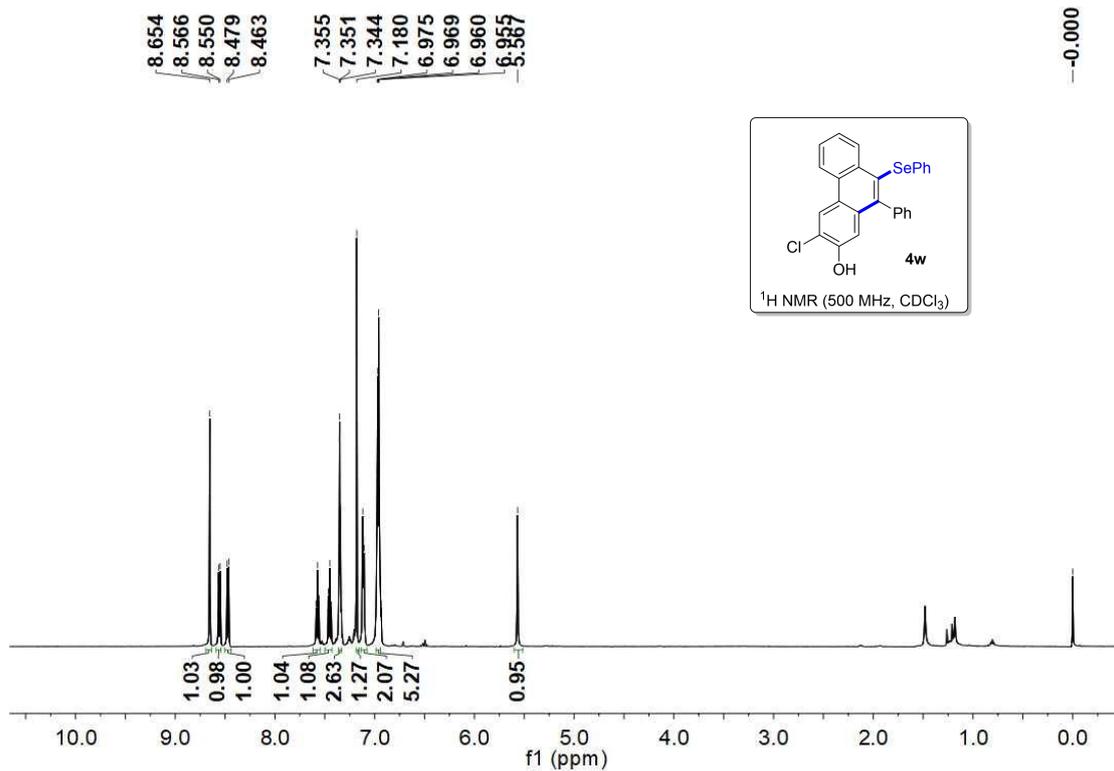


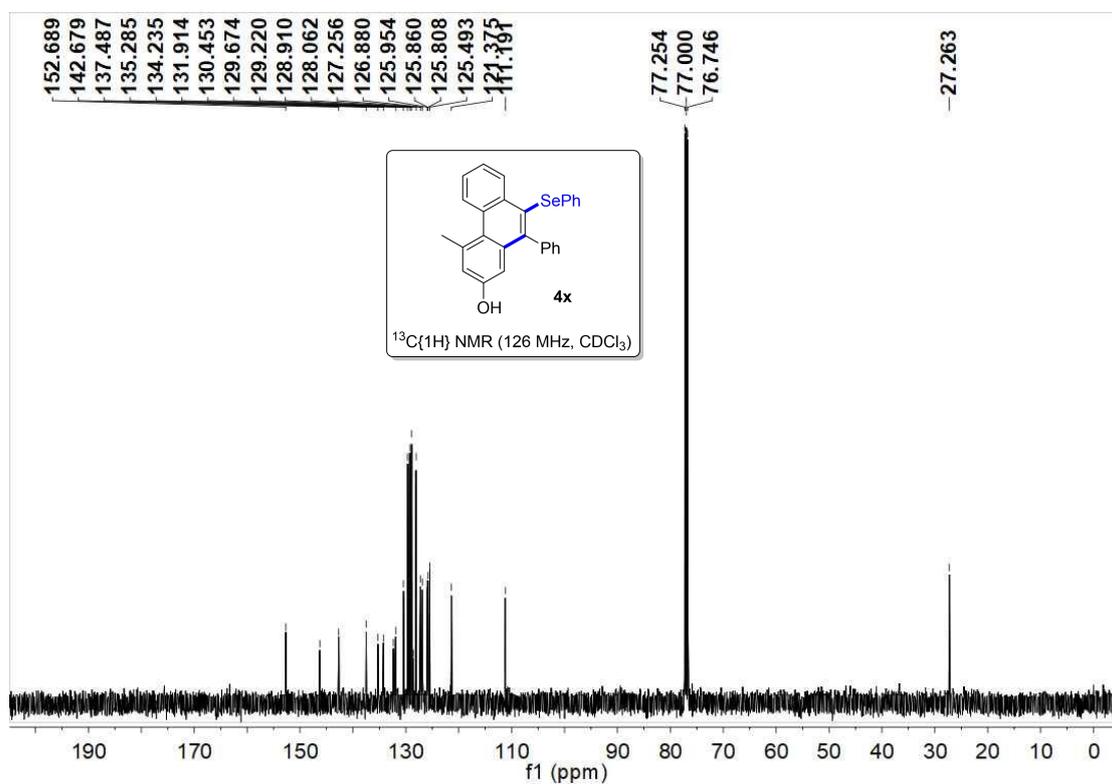
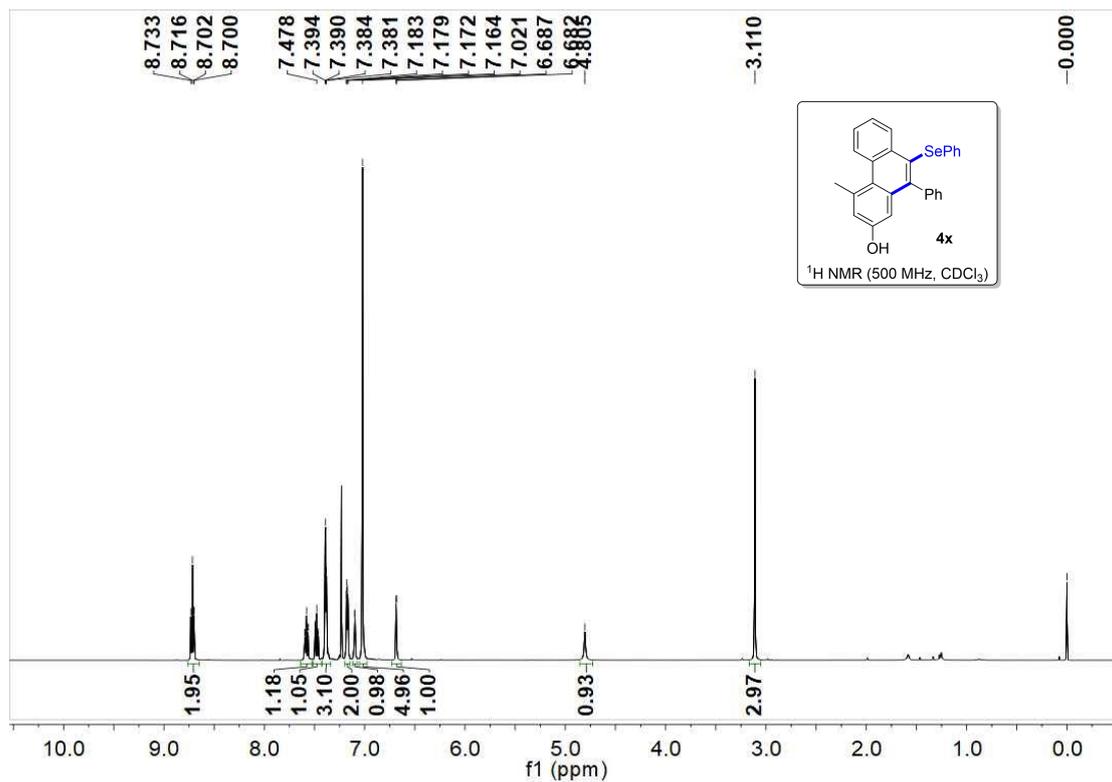


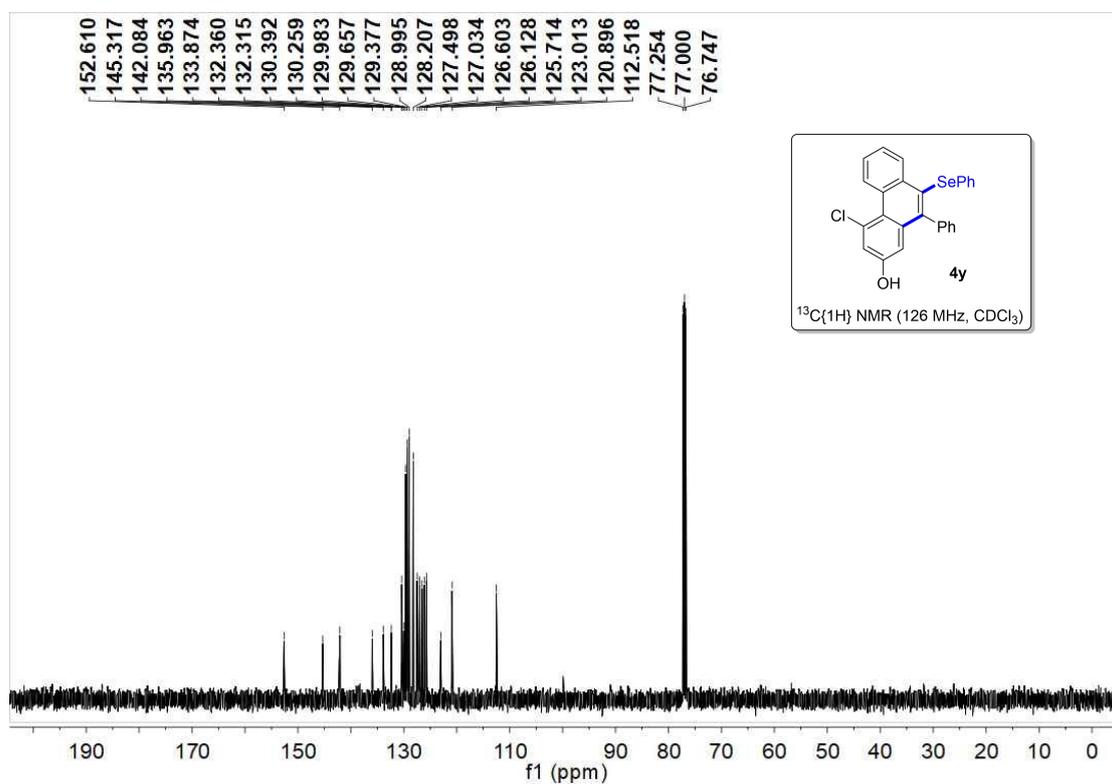
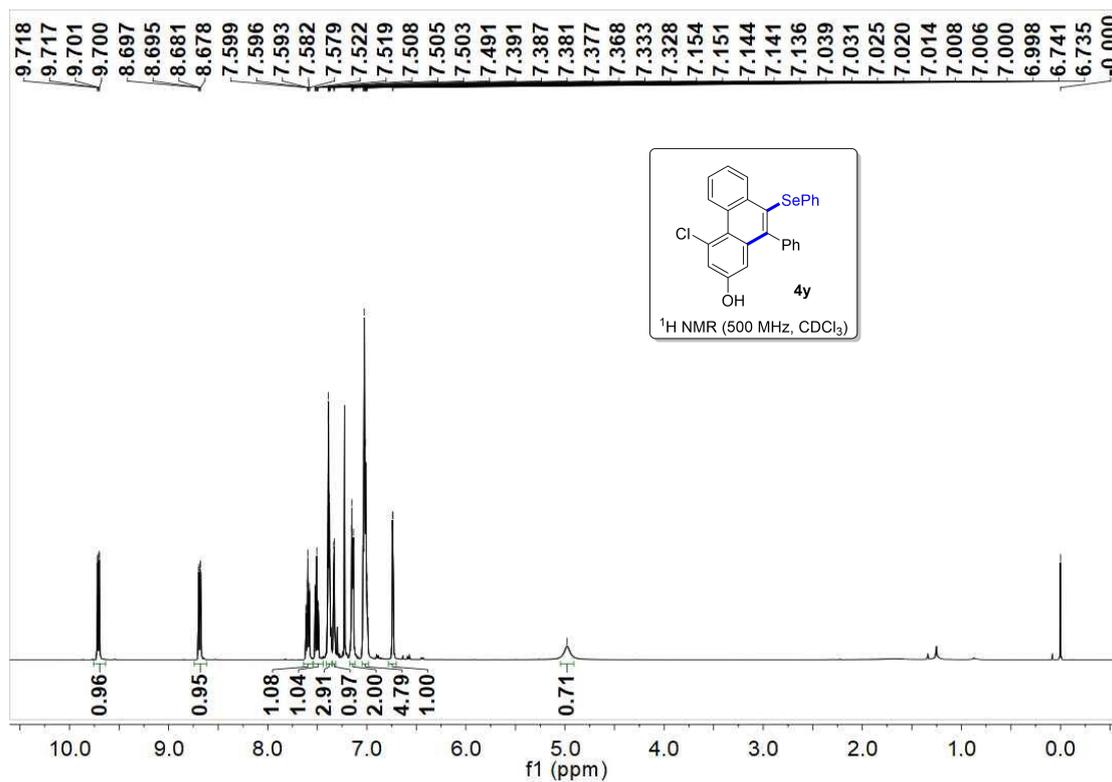


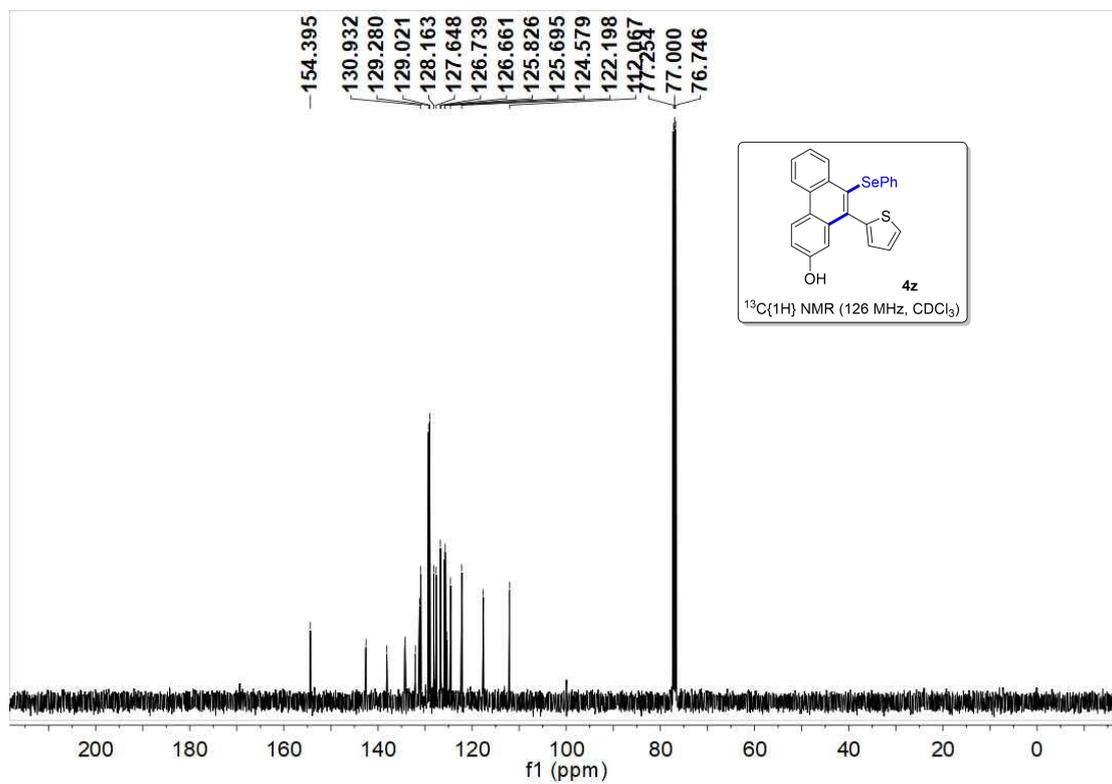
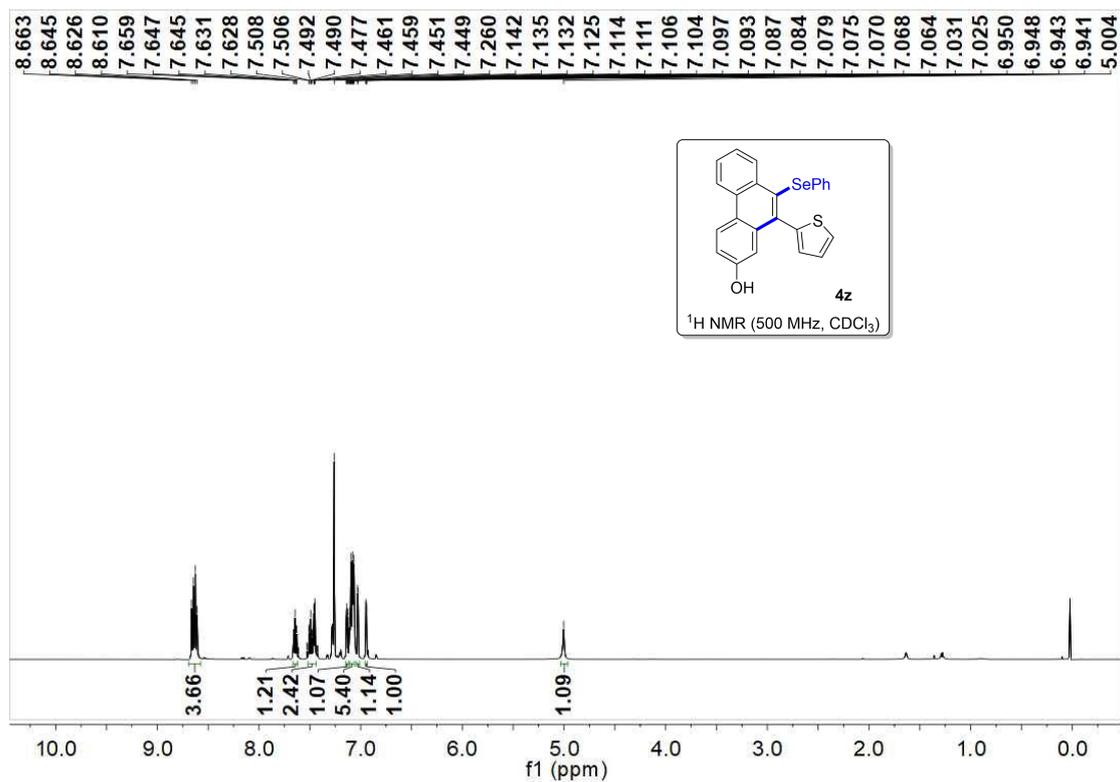


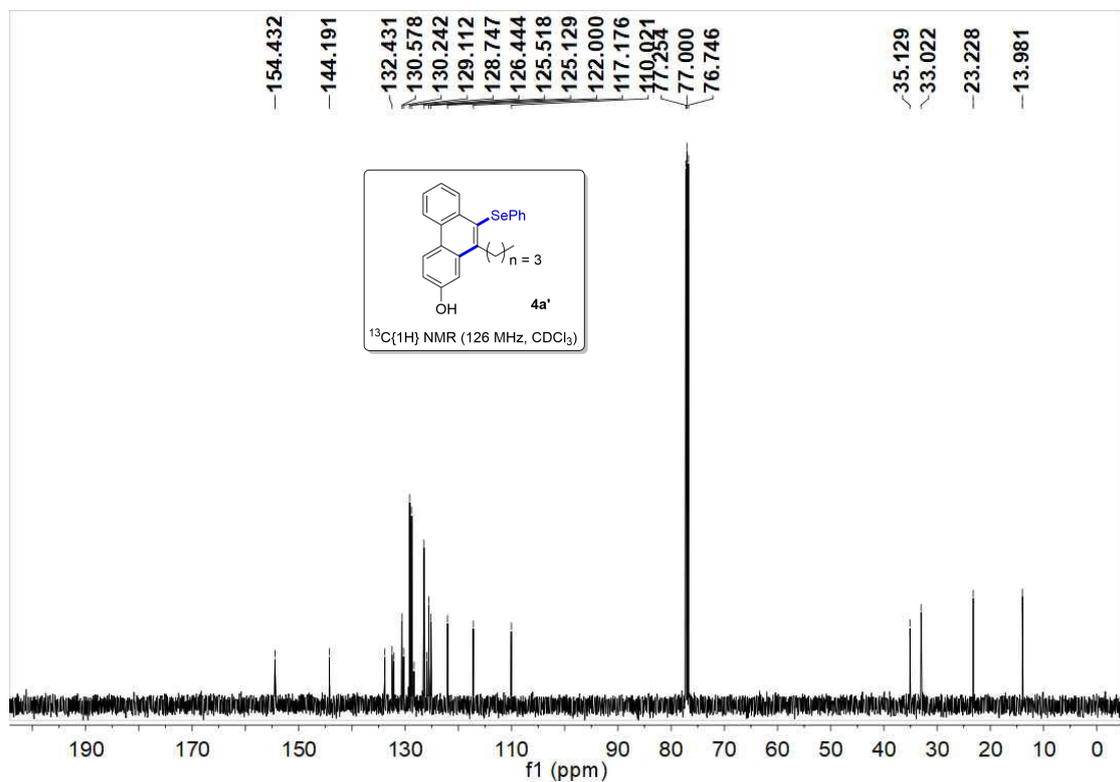
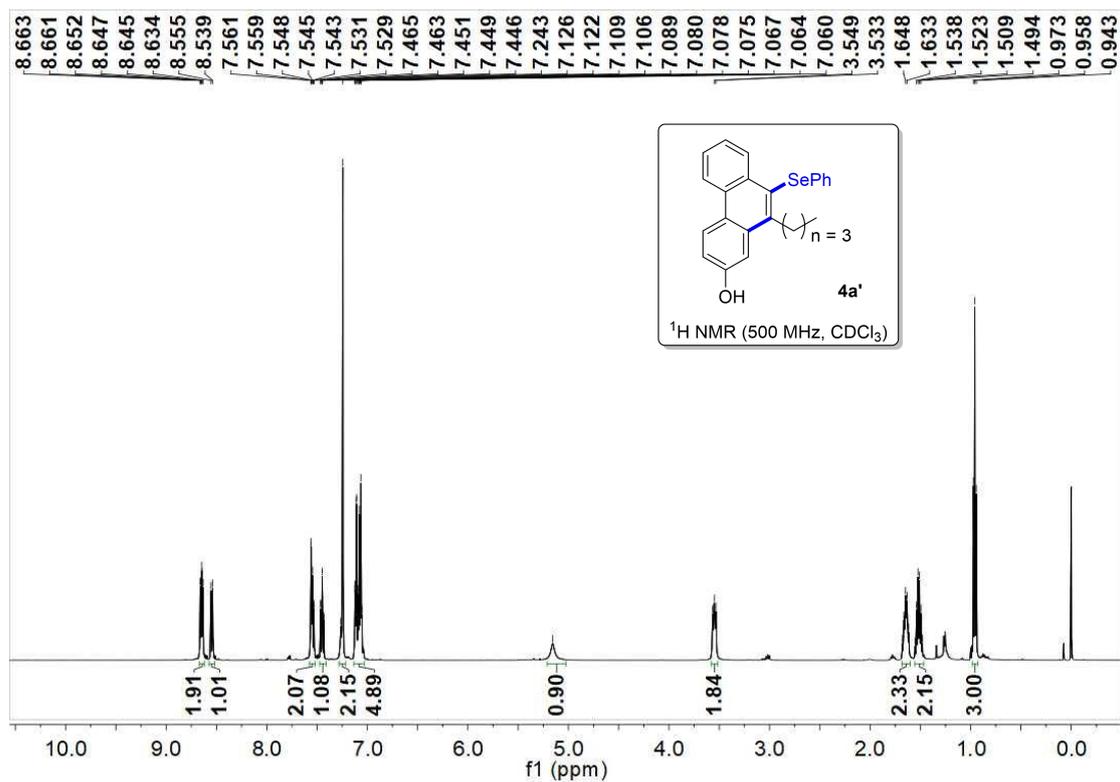


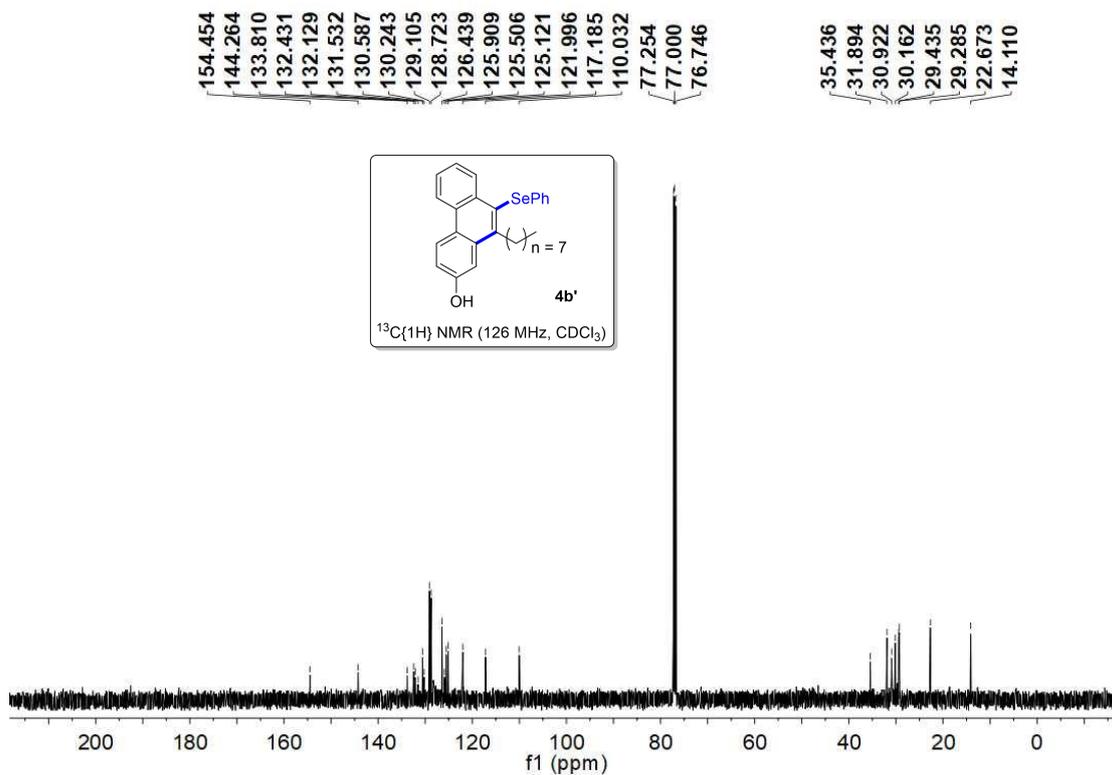
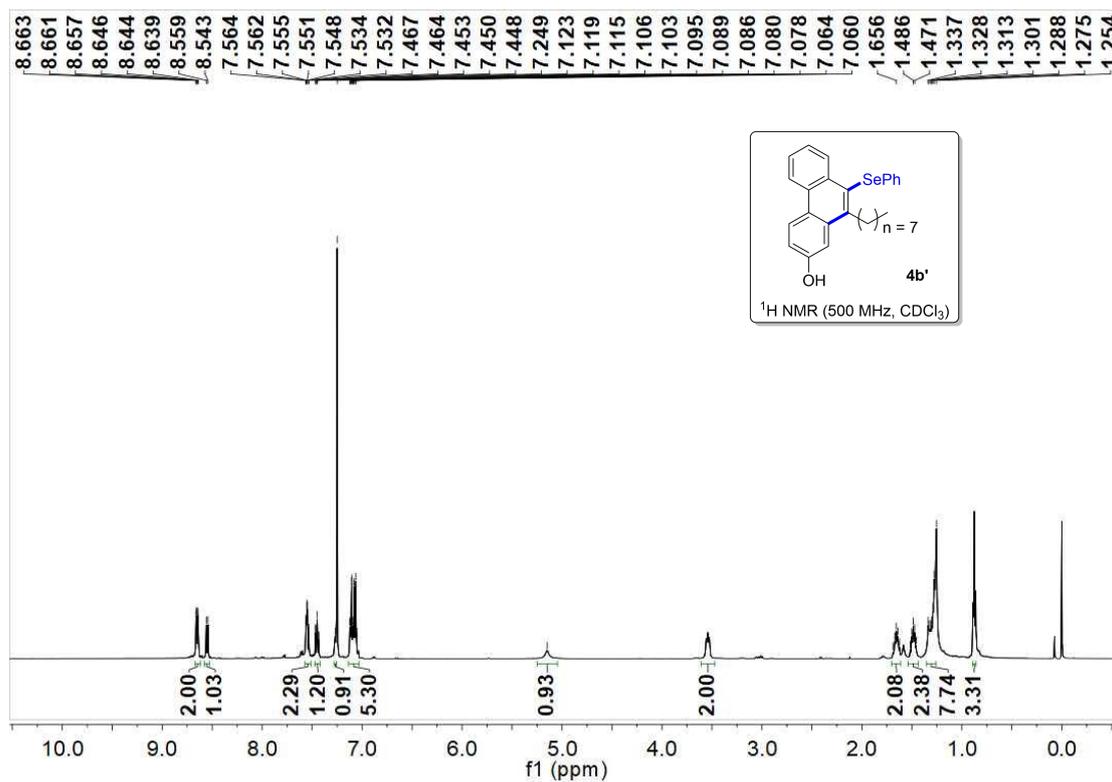


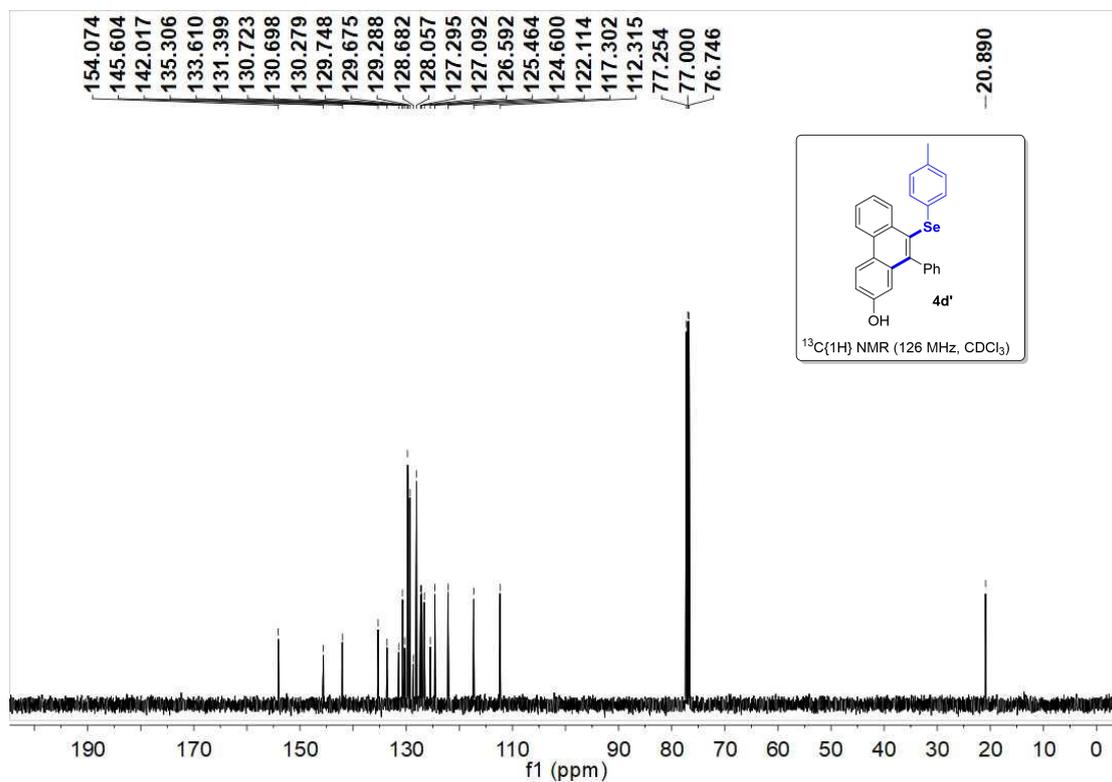
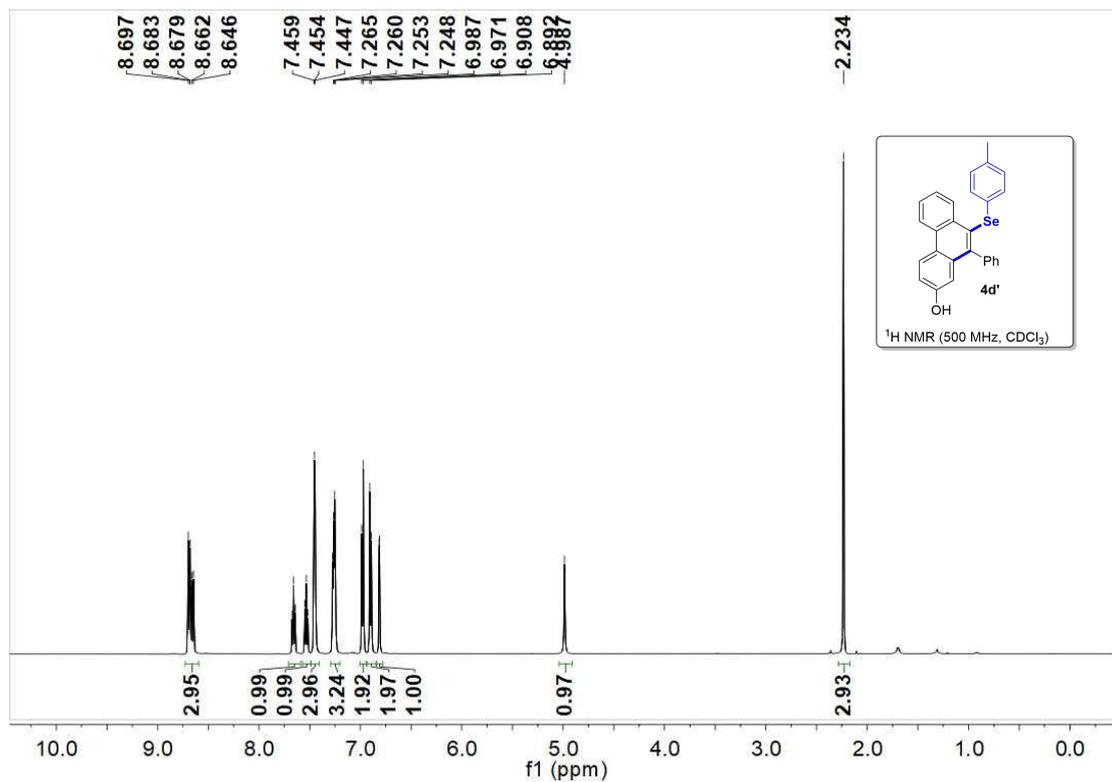


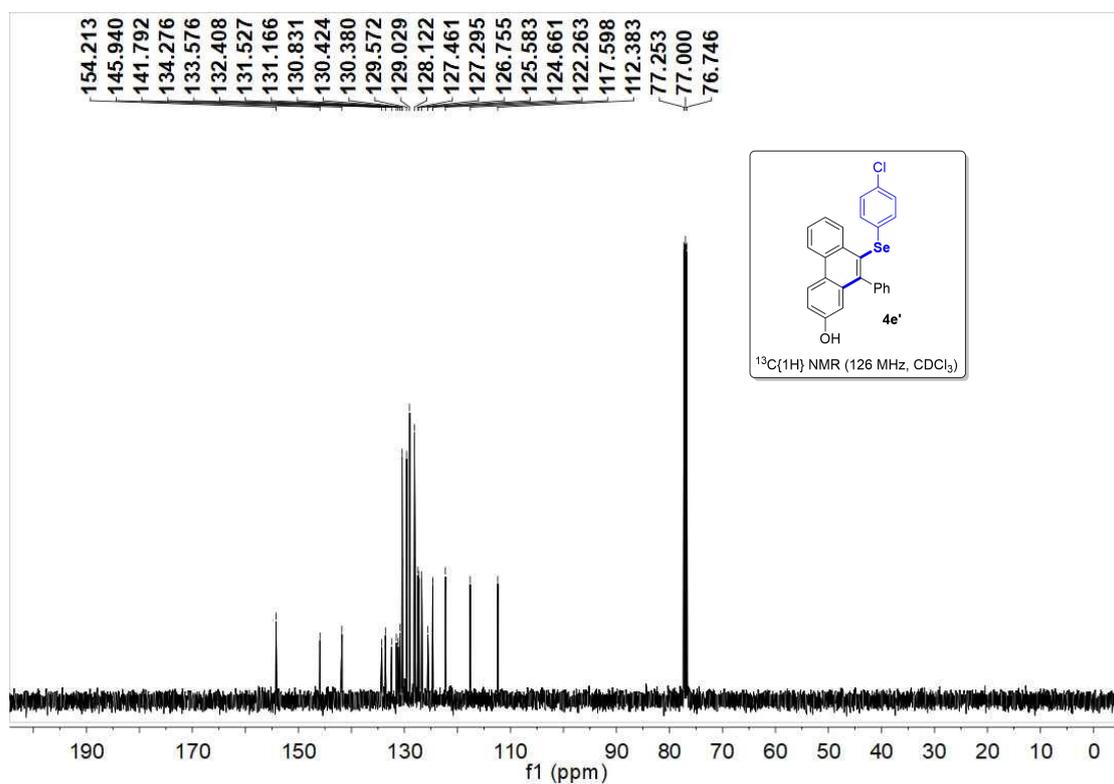
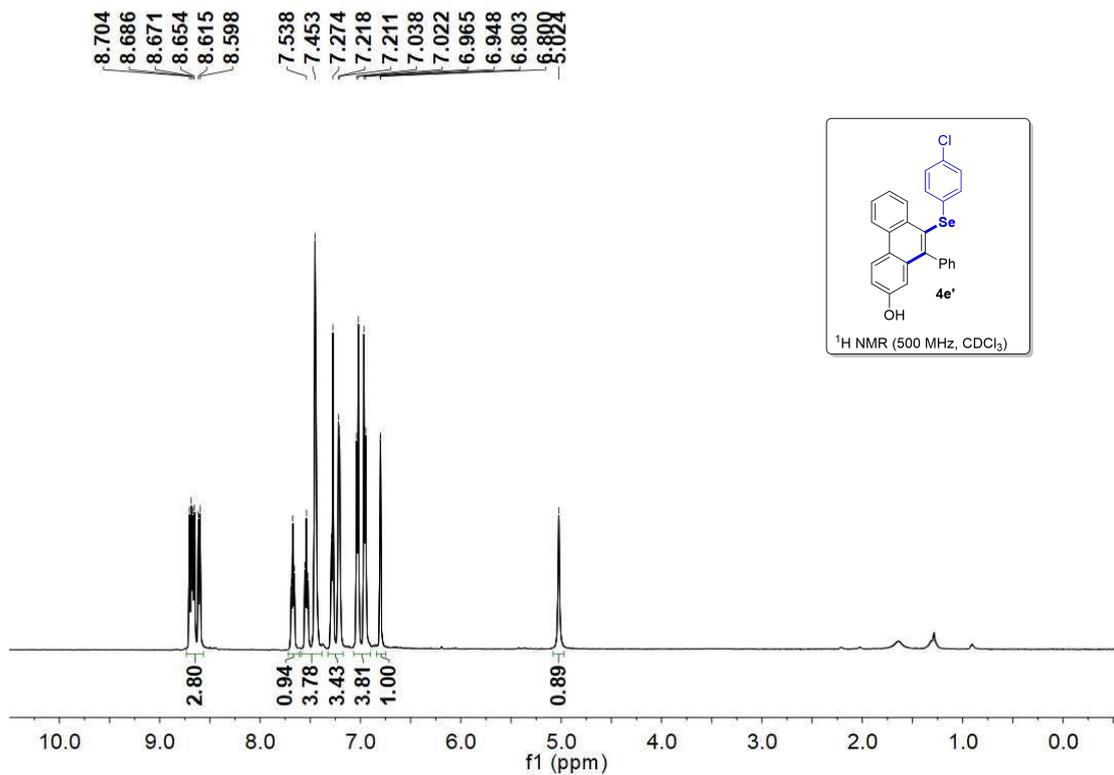


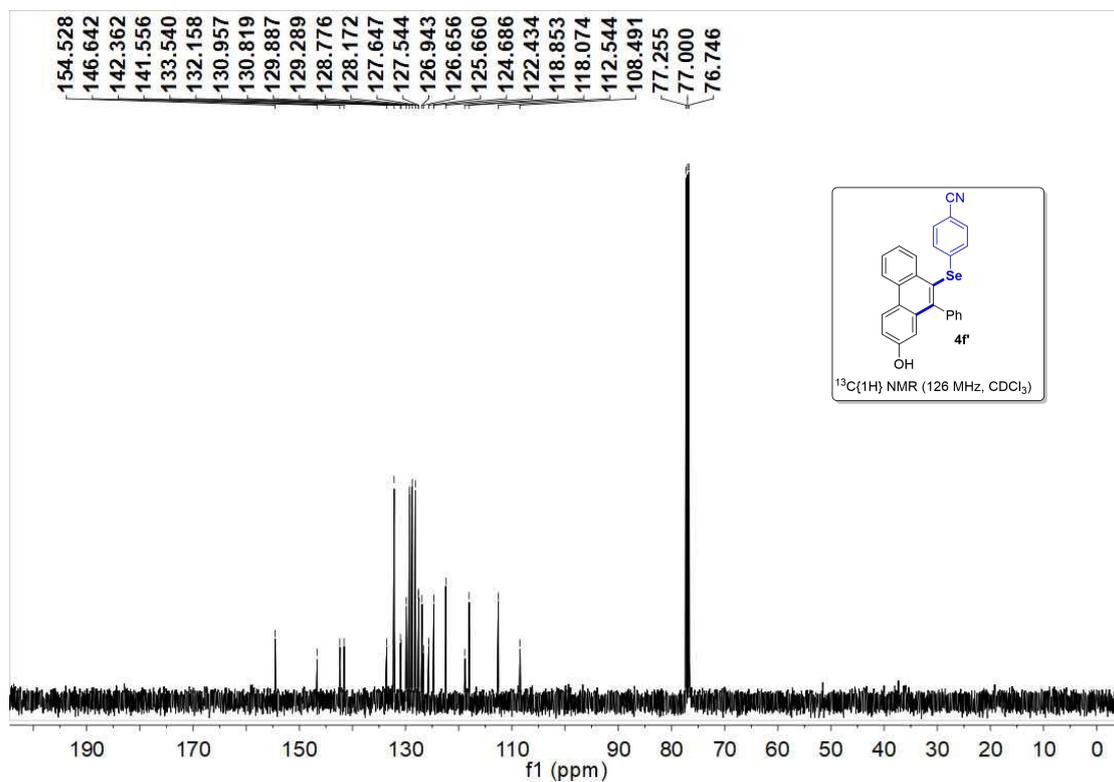
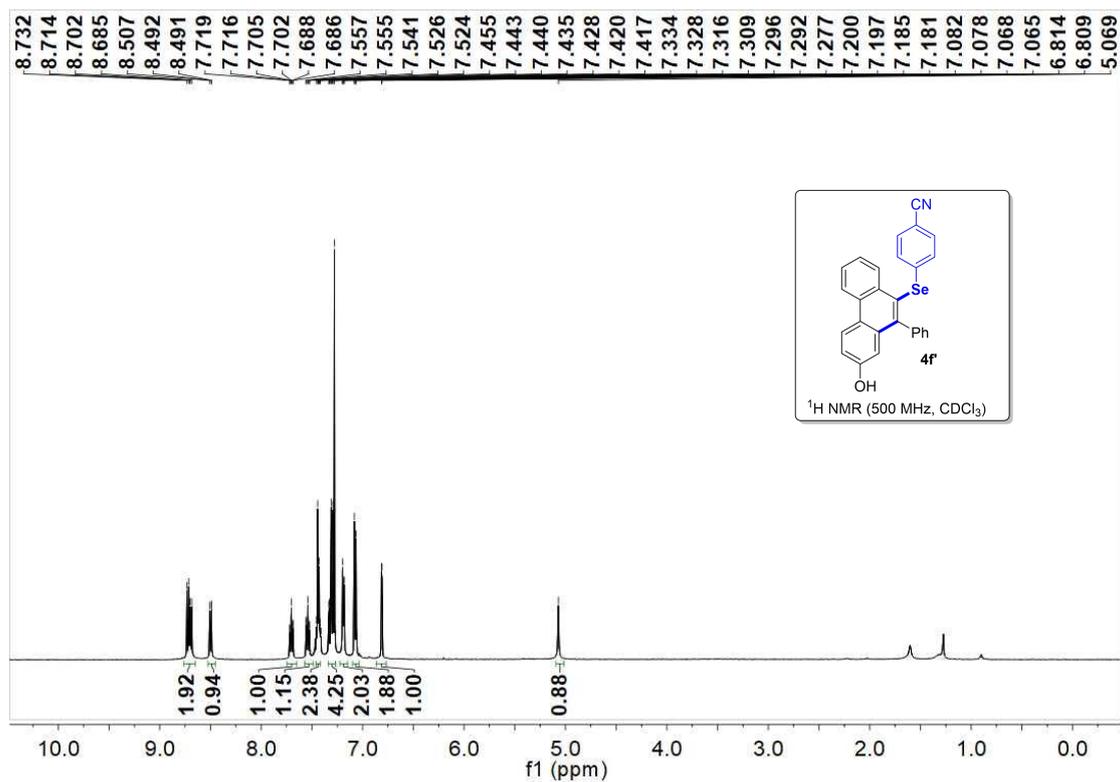


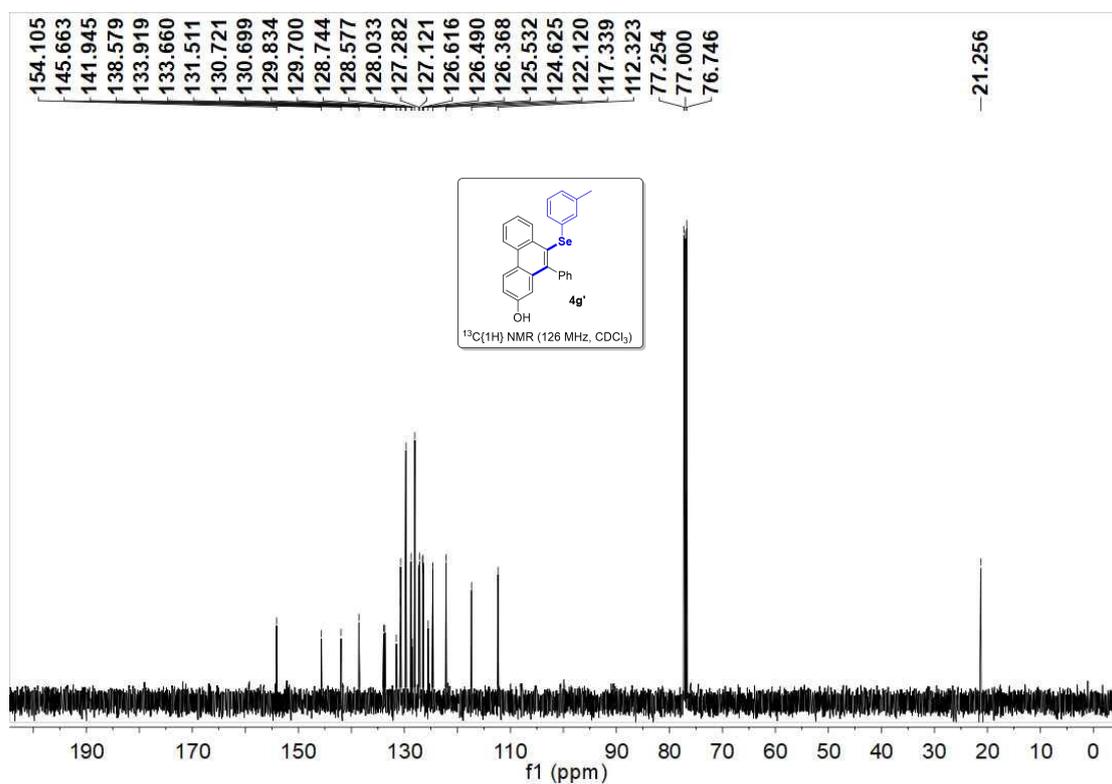
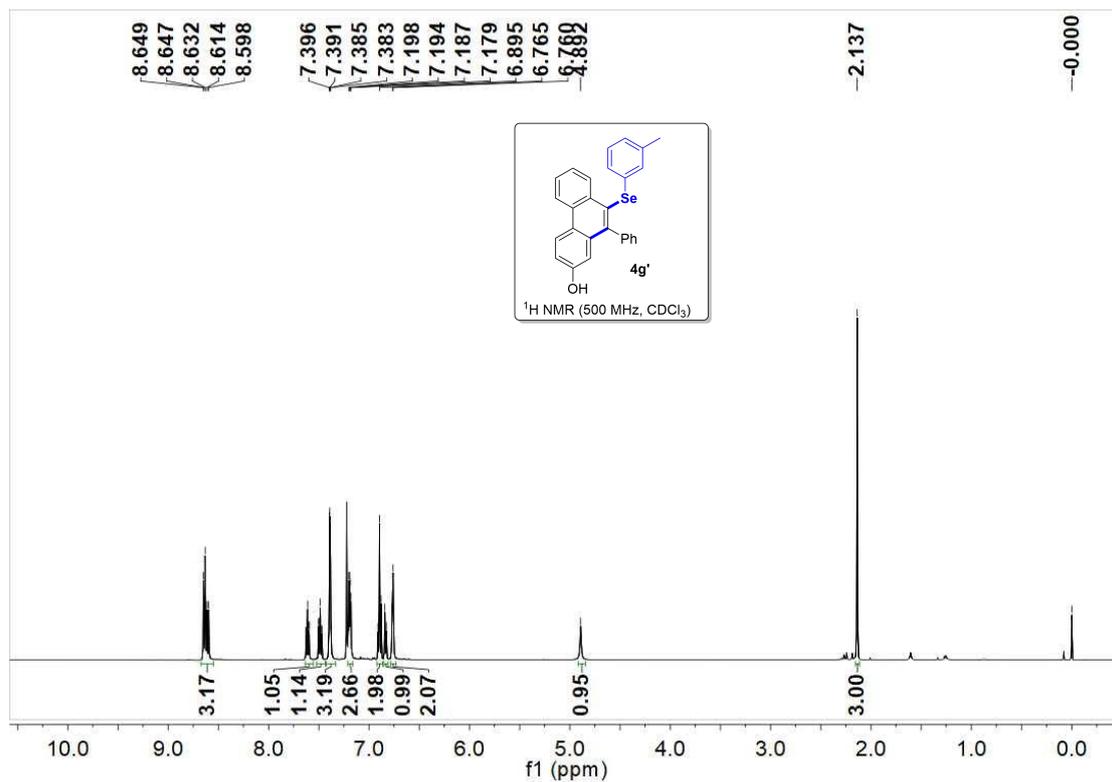


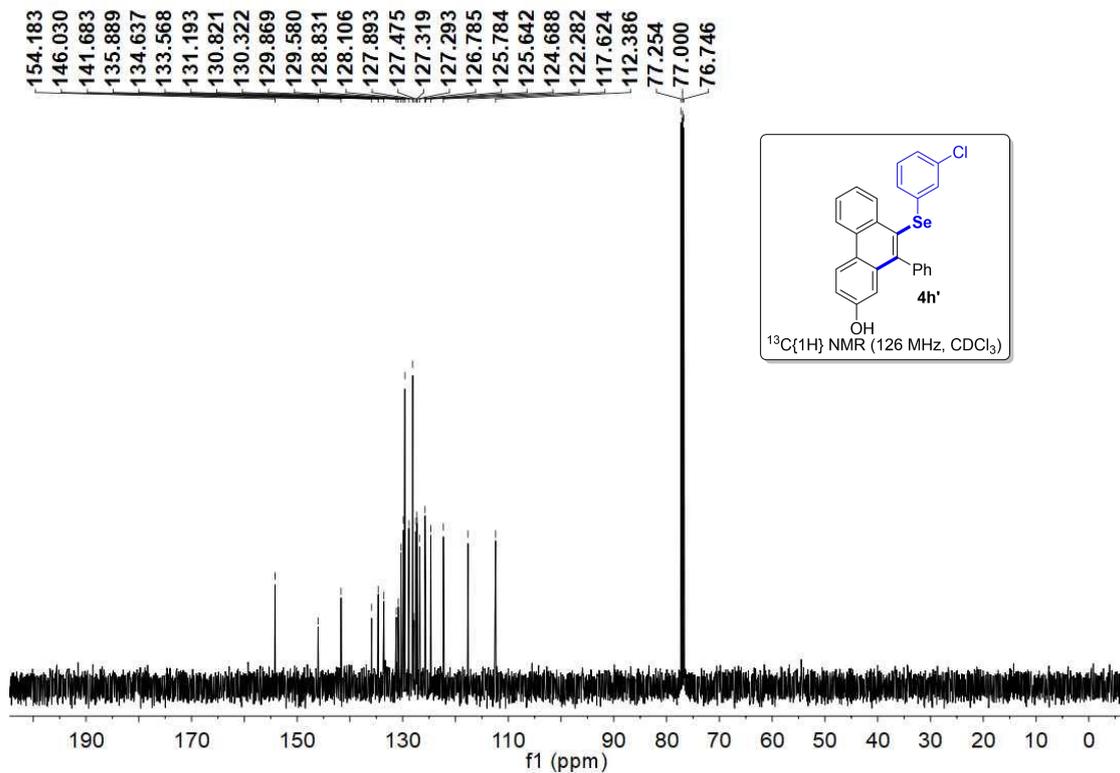
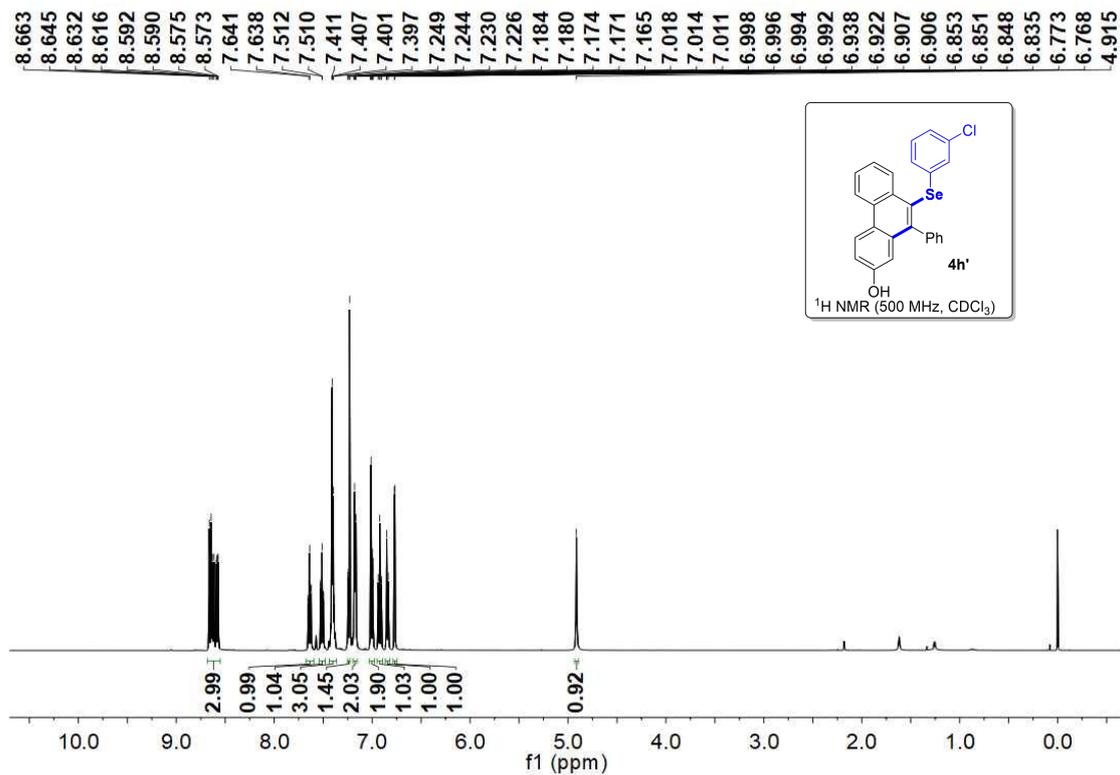


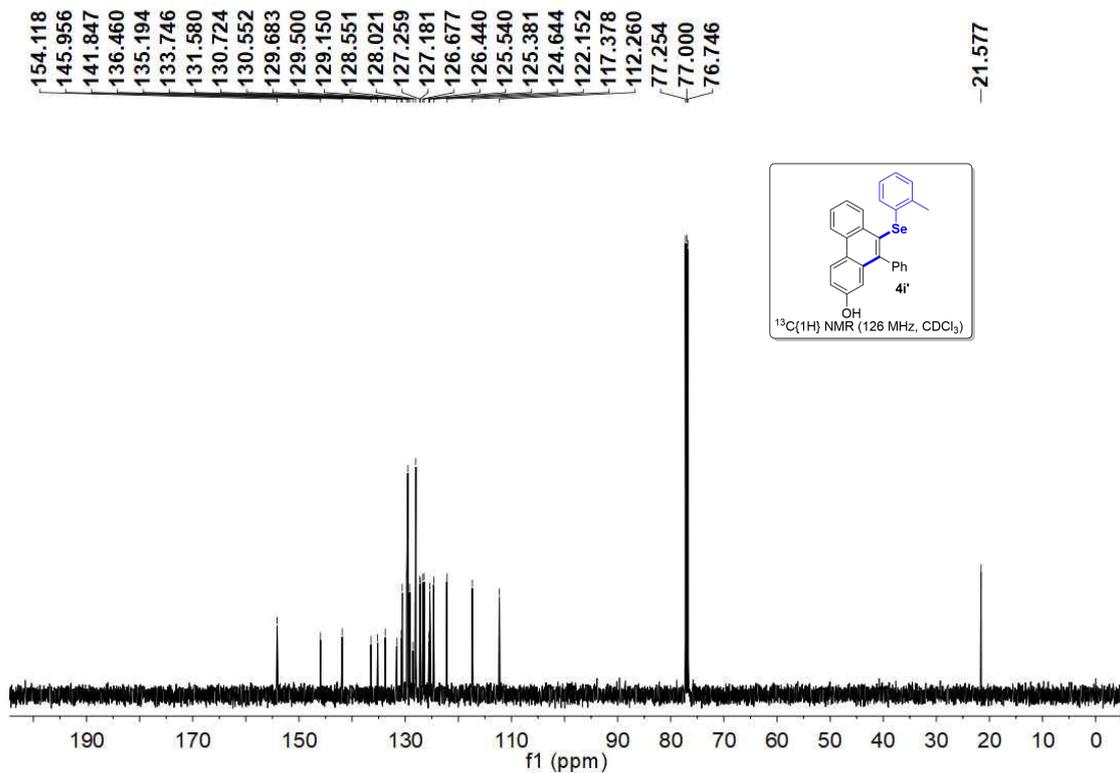
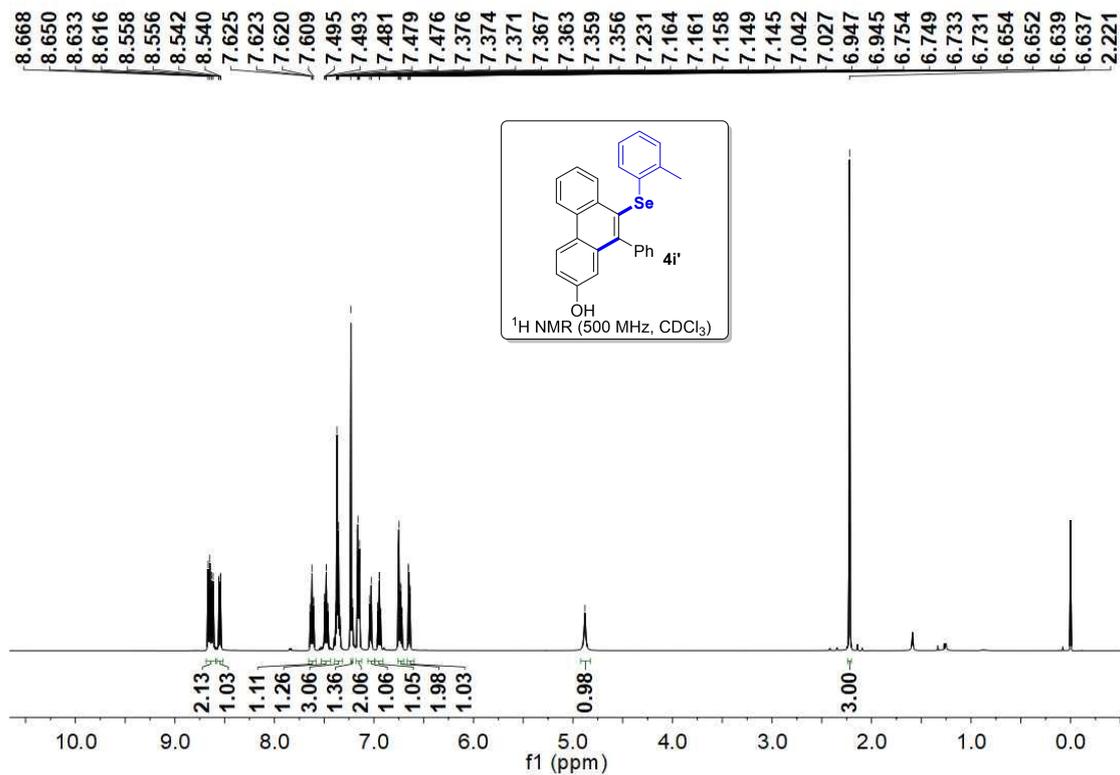


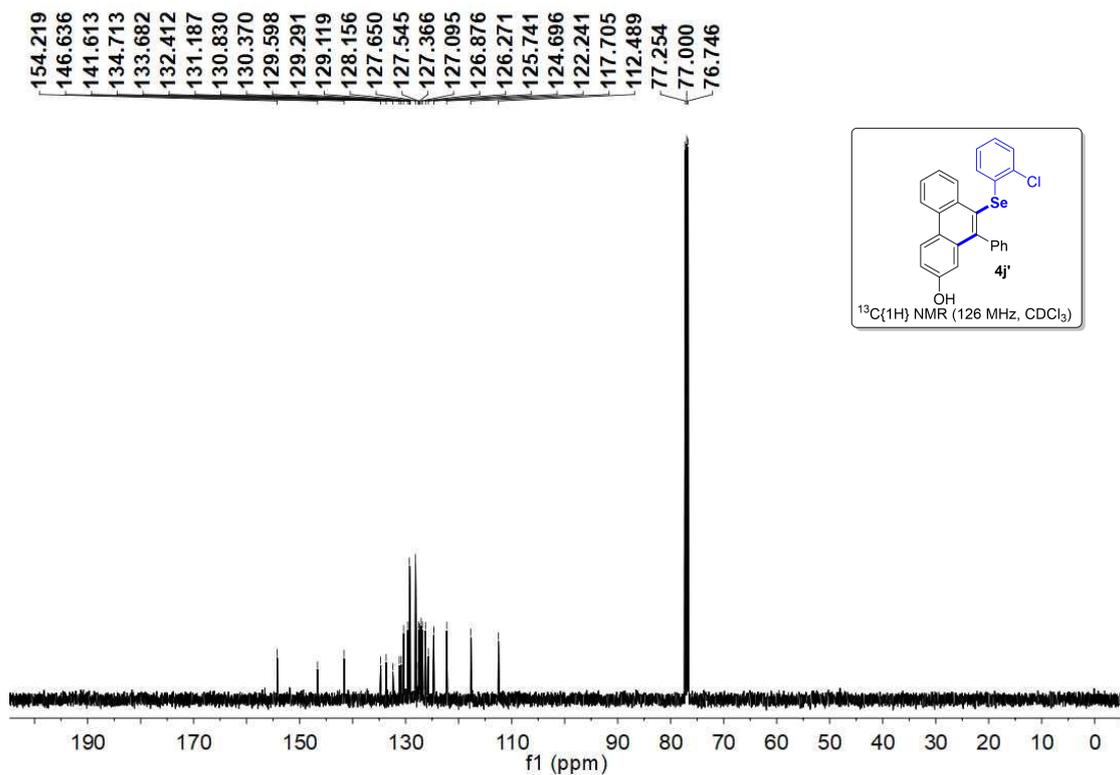
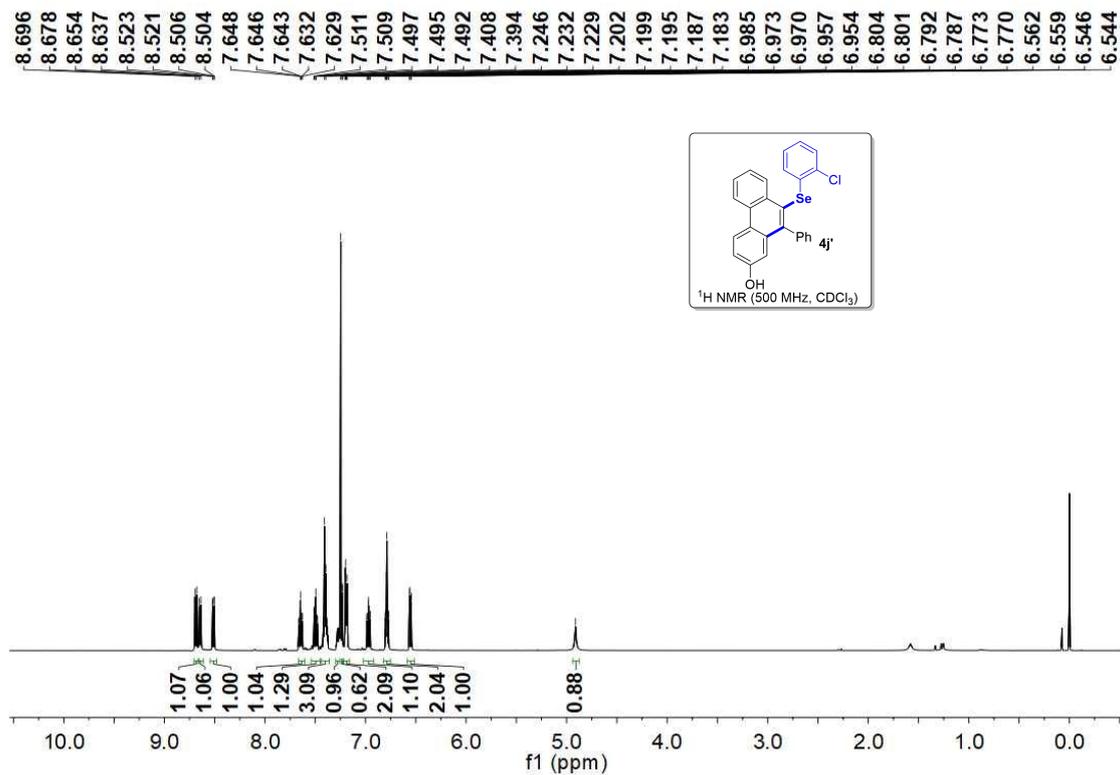


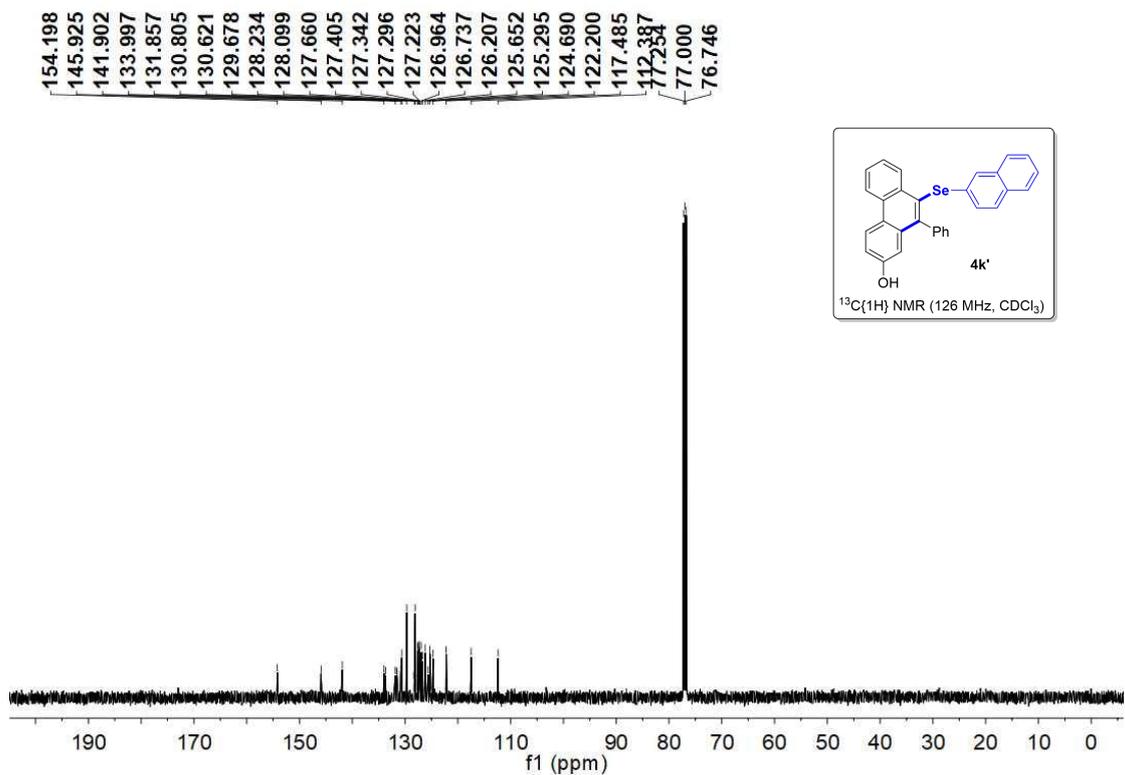
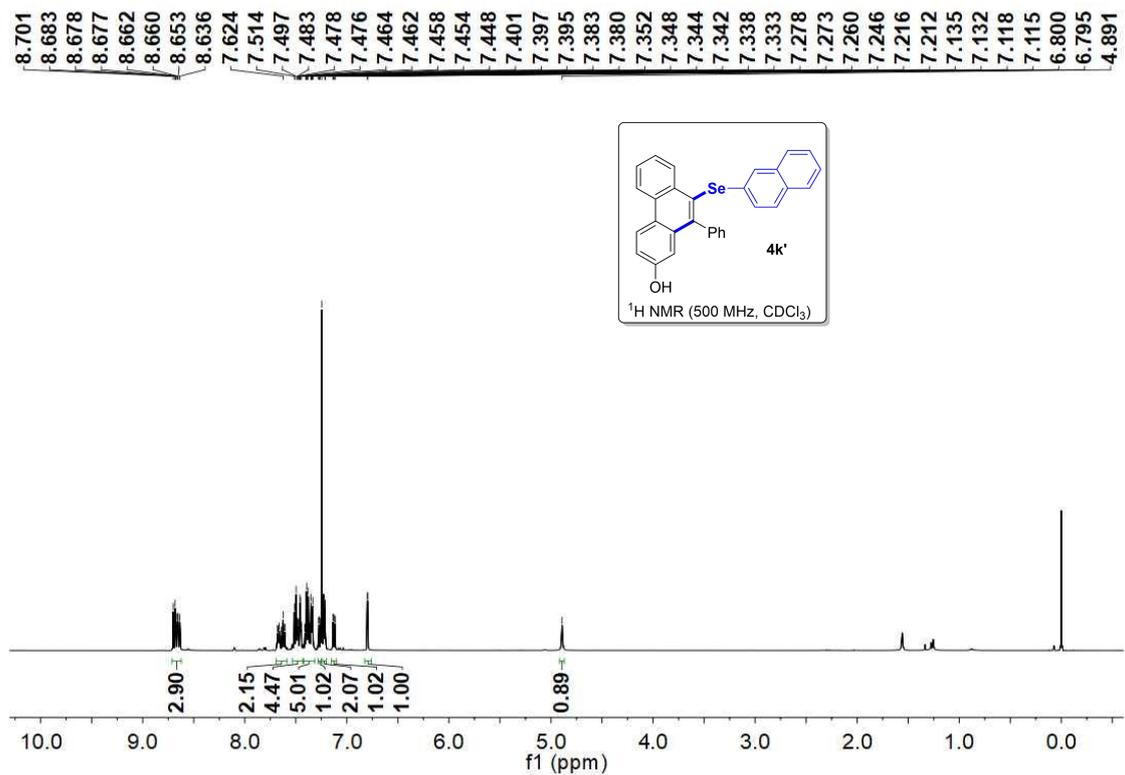


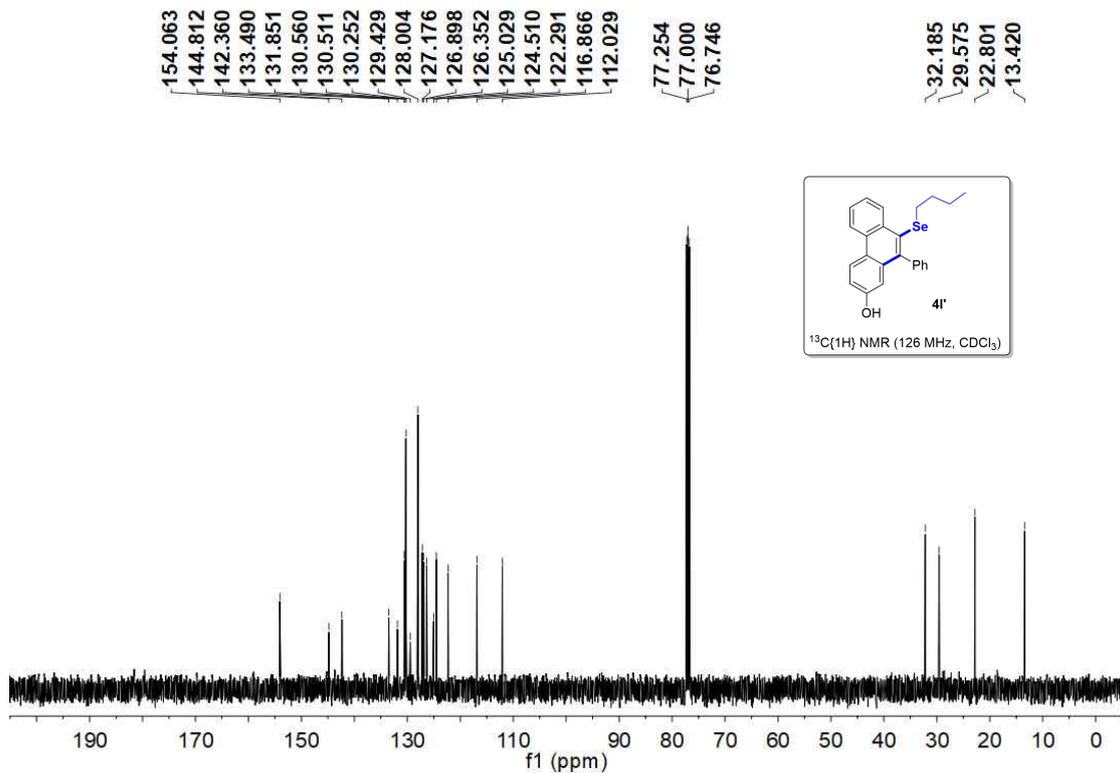
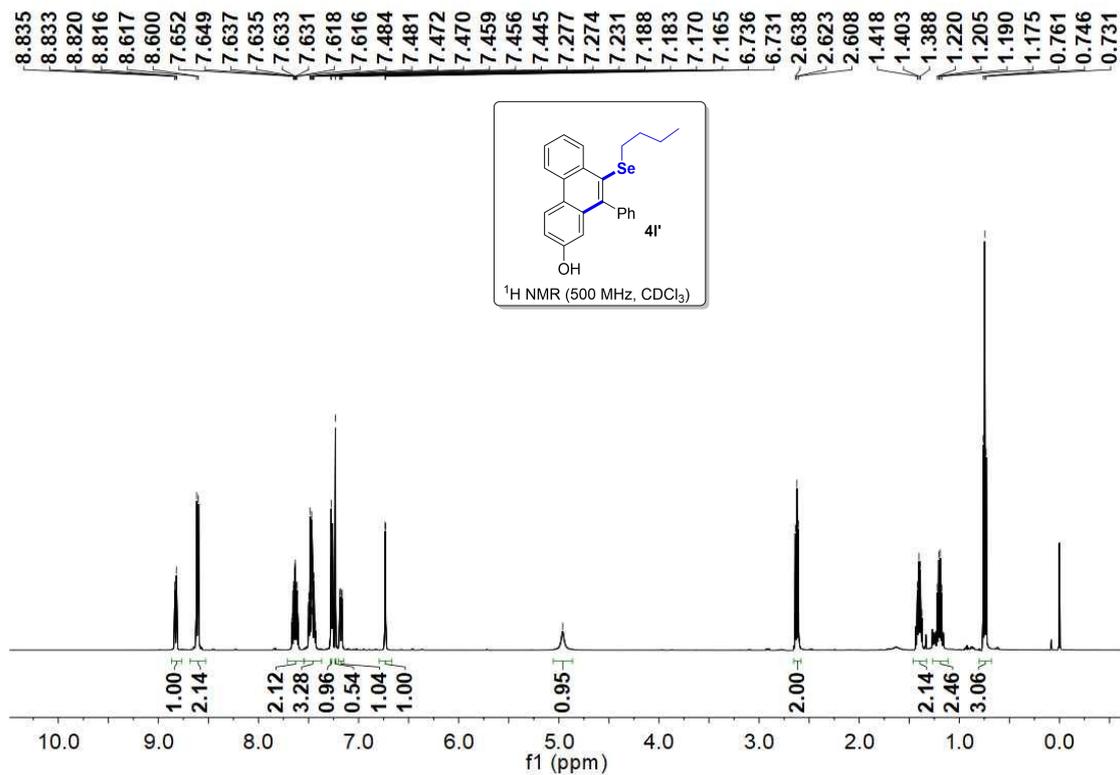


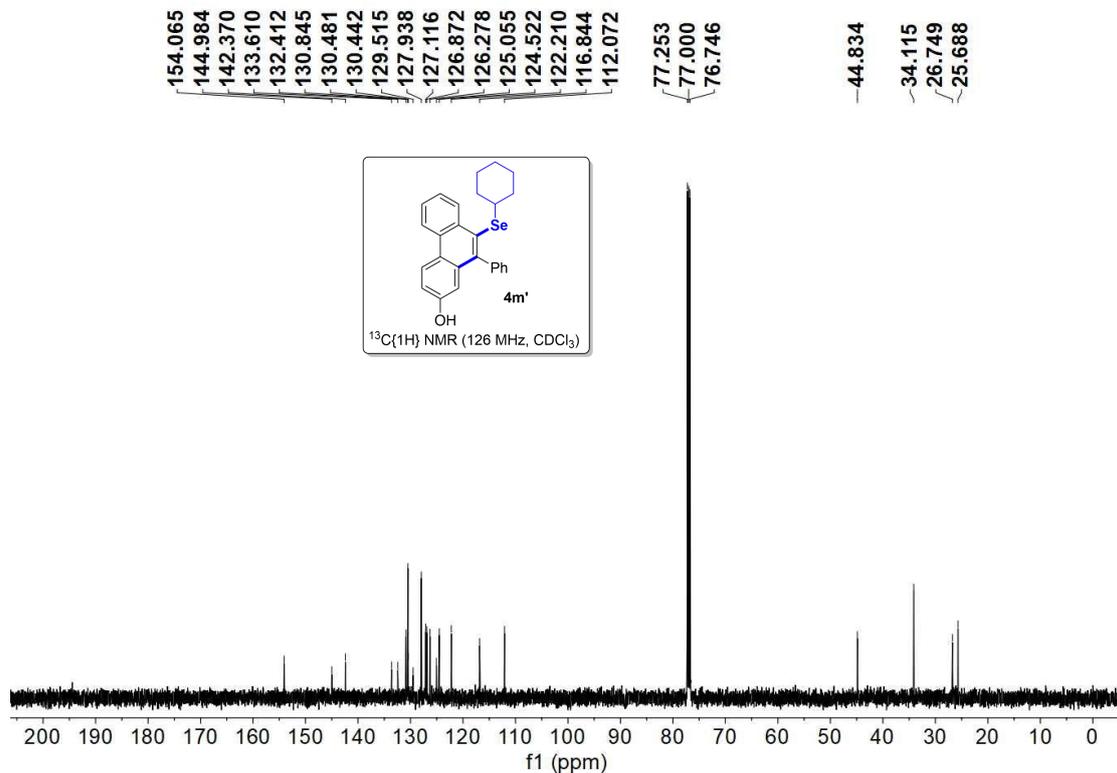
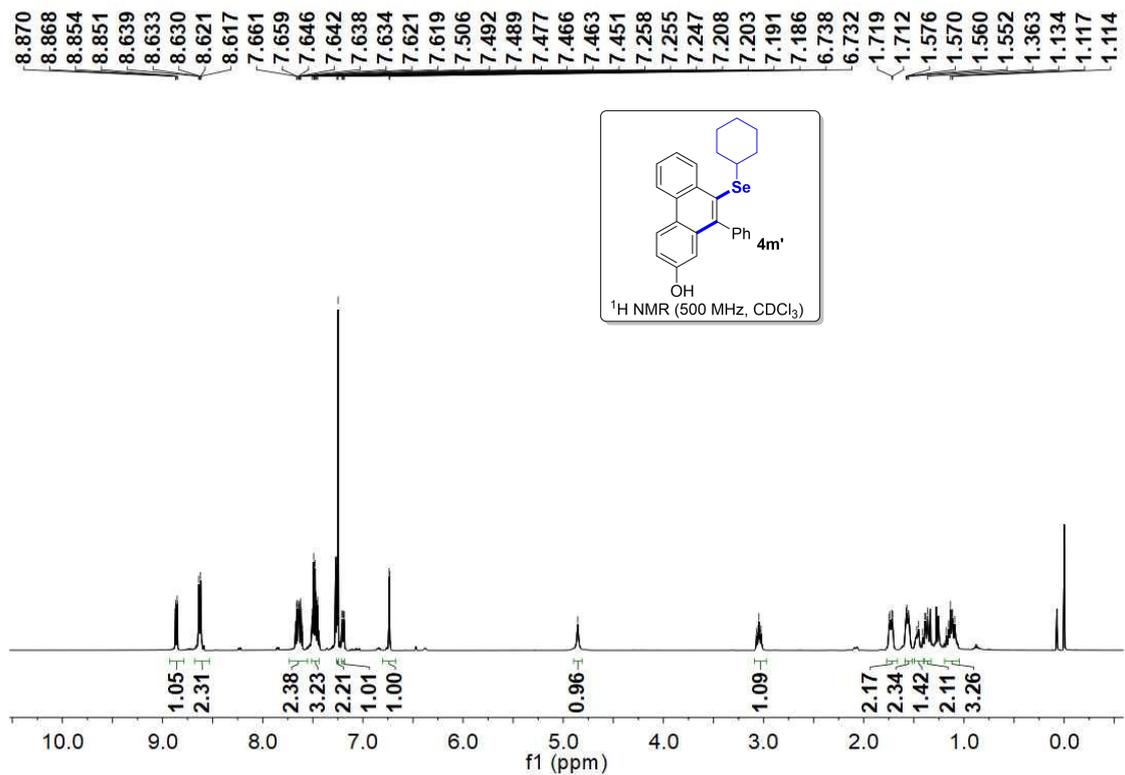












Single-crystal X-ray structure of 3t and 4a

The crystal of products **3t** and **4a** were obtained by slow evaporation in *n*-hexane and dichloromethane. The single crystal X-ray analysis determined the structure of products **3t** and **4a** as expected (Figure S1 and S2).

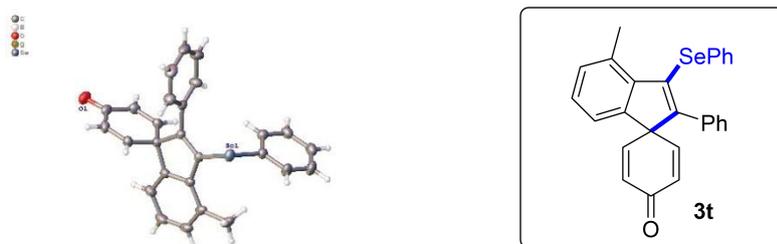


Figure S1. ORTEP illustration of compound 3t with thermal ellipsoids drawn at 50% probability level.

Bond precision:	C-C = 0.0029 Å	Wavelength=1.54184	
Cell:	a=10.2238(3)	b=10.1572(3)	c=21.0271(8)
	alpha=90	beta=104.016(4)	gamma=90
Temperature:	250 K		
	Calculated	Reported	
Volume	2118.55(12)	2118.56(13)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C ₂₇ H ₂₀ O Se	C ₂₇ H ₂₀ O Se	
Sum formula	C ₂₇ H ₂₀ O Se	C ₂₇ H ₂₀ O Se	
Mr	439.39	439.39	
D _x , g cm ⁻³	1.378	1.378	
Z	4	4	
Mu (mm ⁻¹)	2.501	2.501	
F ₀₀₀	896.0	896.0	
F ₀₀₀ '	894.85		
h,k,lmax	12,12,26	12,12,25	

Nref 4275 4179
 Tmin,Tmax 0.759,0.779 0.789,1.000
 Tmin' 0.688
 Correction method= # Reported T Limits: Tmin=0.789 Tmax=1.000
 AbsCorr = MULTI-SCAN
 Data completeness= 0.978 Theta(max)= 73.626
 R(reflections)= 0.0308(3798) wR2(reflections)=
 0.0838(4179)
 S = 1.065 Npar= 263

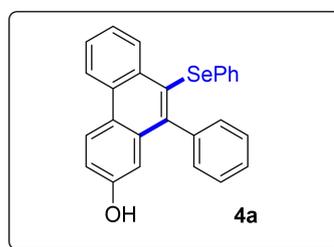


Figure S2. ORTEP illustration of compound 4a with thermal ellipsoids drawn at 50% probability level.

Bond precision:	C-C = 0.0091 Å	Wavelength=0.71073	
Cell:	a=26.615(3)	b=9.7502(10)	c=35.915(6)
	alpha=90	beta=112.221(16)	gamma=90
Temperature:	220 K		
	Calculated	Reported	
Volume	8628(2)	8628(2)	
Space group	C 2/c	C 1 2/c 1	
Hall group	-C 2yc	-C 2yc	
Moiety formula	C ₂₆ H ₁₈ O Se [+ solvent]	C ₂₆ H ₁₈ O Se	
Sum formula	C ₂₆ H ₁₈ O Se [+ solvent]	C ₂₆ H ₁₈ O Se	
Mr	425.36	425.36	
Dx,g cm ⁻³	1.310	1.310	
Z	16	16	

Mu (mm-1)	1.753	1.753
F000	3456.0	3456.0
F000'	3455.71	
h,k,lmax	31,11,42	31,11,42
Nref	7604	7580
Tmin,Tmax	0.810,0.854	0.579,1.000
Tmin'	0.810	
Correction method= # Reported T Limits: Tmin=0.579 Tmax=1.000		
AbsCorr = MULTI-SCAN		
Data completeness= 0.997		Theta(max)= 24.999
R(reflections)= 0.0634(3699)		wR2(reflections)=
0.1417(7580)		
S = 1.000		Npar = 506