

A Facile Synthesis of 3,4-Dimercaptofurans via Sulfenylation of (*E*)- β -Chlorovinyl Ketones and 1,2-Sulfur Migration

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General Methods. All reactions were carried out under argon atmosphere with oven-dried glassware. The progress of all reactions was monitored by thin-layer chromatography on Merck KGaA precoated silica gel plates (250 μm) and visualized by ultra-violet light or by staining with KMnO_4 stain. HPLC grade DCM was further dried through alumina columns. Unless otherwise specified, all chemicals were purchased from Sigma Aldrich or Alfa Aesar and all solvents were purchased from Fischer Scientific. The ^1H NMR and ^{13}C NMR spectra were obtained on Varian 600 MHz Fourier transform spectrometers. Chemical Shifts are reported in units of parts per million downfield from either a residual CHCl_3 or tetramethylsilane and all coupling constants are reported in Hertz. The infrared spectra were obtained using a Thermo Nicolet IR 300 Spectrometer. Silica gel (32-64 μ , Merck KGaA) was used for column chromatography. Melting points were recorded on a Buchi-B-450 melting point apparatus and the melting point values were uncorrected.

Preparation of Starting Materials.

(a) Preparation of (*E*)- β -chlorovinyl ketones

(*E*)- β -chlorovinyl ketones were prepared according to literature procedure and spectral data were consistent with literature value.^{1a,b,c}

(b) Preparation of N-(Arylthio)phthalimides

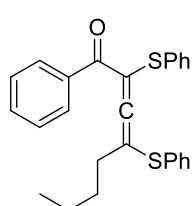
N-(Arylthio)phthalimides were prepared based on a modified method as follows.² To a suspension of N-Chlorophthalimide (10 mmol) in benzene (55 mL) was added thiol (10 mmol, 1M in benzene) at once. After stirring for 5 min at ambient temperature, triethyl amine (1.45 mL, 1.05 M in benzene) was added dropwise over 5 min. After the reaction was complete (1 h), the crude mixture was treated with 1M NaOH to eliminate a phthalimide byproduct and then extracted with DCM (twice, 100 mL each) before drying over MgSO_4 . After removing the three third of solvent under reduced pressure, hexanes was added and the reaction flask was allowed to stand for 20 min. The precipitate (product) was then filtered and washed with hexanes. The spectral data were compared with literature values.³

General Procedure for Sulfonylation of (*E*)- β -Chlorovinyl Ketones.

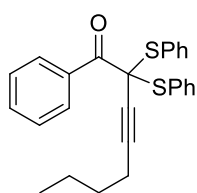
To a flask charged with (*E*)- β -chlorovinyl ketone (1.0 mmol) under argon were added dry DCM (4 mL) and

triethylamine (1.1 mmol) at ambient temperature. The solution was left to stir until the elimination step was complete by TLC (18 h). The reaction was then cooled down to 0 °C and *t*-BuOK (1.1 mmol) was added followed by the addition of *N*-thiophthalimide (2.5 mmol) in 5 min. The reaction solution was allowed to stir at this temperature until the reaction was complete by TLC (1-2 h). The crude mixture was then concentrated under reduced pressure and chromatographed on silica gel (hexanes or 10% EtOAc in hexanes) to afford the title compound.

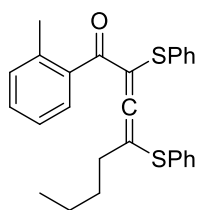
Characterization Data of the Compounds in Table 2.



1-Phenyl-2,4-bis(phenylthio)octa-2,3-dien-1-one (**3a**): 242 mg (58%), yellow oil; ¹H NMR (CDCl₃, 600 MHz) δ 7.69 – 7.65 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.33 (m, 3H), 7.27 – 7.23 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 7.4 Hz, 2H), 2.03 – 1.91 (m, 2H), 1.23 – 1.08 (m, 2H), 1.05 – 0.97 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 206.0, 190.6, 137.6, 134.4, 132.7, 132.3, 132.0, 131.5, 129.0, 128.9, 128.8, 128.5, 128.2, 128.0, 113.0, 112.0, 32.5, 29.6, 21.7, 13.6; IR (neat): 3058, 2956, 2930, 2870, 1679, 1595, 1578, 1446, 1226 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₆H₂₅OS₂ [M+H]⁺ 417.1341 Found 417.1349.

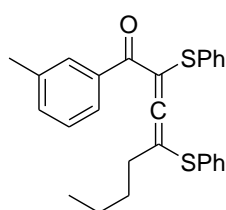


1-Phenyl-2,2-bis(phenylthio)oct-3-yn-1-one (**4a**): 49 mg (12%), yellow oil; ¹H NMR (CDCl₃, 600 MHz) δ 8.29 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 7.3 Hz, 4H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.39 – 7.35 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 4H), 2.04 (t, *J* = 7.0 Hz, 2H), 1.24 – 1.18 (m, 2H), 1.15 – 1.08 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 189.6, 136.7, 134.4, 132.8, 131.5, 130.6, 129.6, 128.4, 127.6, 97.1, 75.9, 67.6, 29.8, 21.7, 18.6, 13.5; IR (neat): 3058, 2956, 2930, 2870, 1680, 1595, 1472, 1438, 1226 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₆H₂₅OS₂ [M+H]⁺ 417.1341 Found 417.1349.



2,4-Bis(phenylthio)-1-o-tolylocta-2,3-dien-1-one (**3b**): 258 mg (60%), yellow oil; ¹H NMR (CDCl₃, 600 MHz): δ 7.48 – 7.45 (m, 2H), 7.37 – 7.31 (m, 4H), 7.24 – 7.20 (m, 3H), 7.19 – 7.13 (m, 3H), 6.89 – 6.86 (m, 2H), 2.33 (s, 3H), 1.87 (t, *J* = 7.5 Hz, 2H), 1.16 – 1.01 (m, 2H), 0.99 – 0.91 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 207.6,

193.4, 138.3, 136.4, 134.5, 132.2, 131.9, 131.6, 130.8, 130.3, 129.0, 128.9, 128.5, 127.9, 127.8, 124.7, 113.5, 112.4, 32.3, 29.5, 21.6, 19.6, 13.7; IR (neat): 3058, 2956, 2929, 2870, 1660, 1581, 1476, 1439, 1250 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{27}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 431.1497 Found 431.1501.



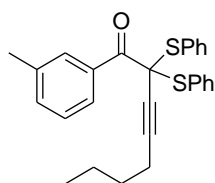
2,4-Bis(phenylthio)-1-m-tolylocta-2,3-dien-1-one (**3c**): 324 mg (75%); yellow oil; ^1H

NMR (CDCl_3 , 600 MHz): δ 7.52 (s, 1H), 7.48 (d, $J = 7.6$ Hz, 1H), 7.45 – 7.42 (m, 2H),

7.35 – 7.30 (m, 4H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.21 (t, $J = 7.3$ Hz, 1H), 7.16 (t, $J = 7.4$ Hz,

2H), 6.98 (d, $J = 7.2$ Hz, 2H), 2.34 (s, 3H), 2.01 – 1.91 (m, 2H), 1.22 – 1.08 (m, 2H),

1.03 – 0.95 (m, 2H), 0.71 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 206.2, 190.8, 137.7, 137.6, 134.4, 133.2, 132.4, 132.0, 131.7, 129.3, 129.0(4), 129.0(1), 128.5, 128.1, 127.9, 126.0, 112.5, 111.9, 32.6, 29.6, 21.8, 21.3, 13.7; IR (neat): 3058, 2956, 2928, 2870, 1654, 1582, 1476, 1272 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{27}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 431.1497 Found 431.1507.



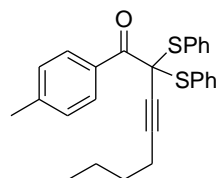
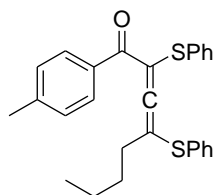
2,2-Bis(phenylthio)-1-m-tolyloct-3-yn-1-one (**4c**): 46 mg (11%), yellow oil; ^1H NMR

(CDCl_3 , 600 MHz): δ 8.14 (d, $J = 7.8$ Hz, 1H), 7.99 (s, 1H), 7.58 – 7.54 (m, 4H), 7.39 –

7.35 (m, 2H), 7.34 – 7.24 (m, 6H), 2.35 (s, 3H), 2.03 (t, $J = 7.0$ Hz, 2H), 1.24 – 1.18 (m,

2H), 1.15 – 1.08 (m, 2H), 0.77 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 151 MHz): δ 189.8,

137.3, 136.8, 134.4, 133.5, 131.6, 131.1, 129.6, 128.3, 127.9, 127.4, 97.1, 76.0, 67.6, 29.8, 21.7, 21.3, 18.6, 13.4; IR (neat): 3058, 2956, 2929, 2870, 1676, 1582, 1472, 1438, 1256, 1169 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{27}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 431.1497 Found 431.1507.



A mixture of **3d** and **4d** was isolated with a 4:1 ratio in 332 mg

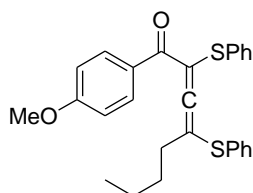
(77%). (2,4-Bis(phenylthio)-1-p-tolylocta-2,3-dien-1-one (**3d**):

yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.60 (d, $J = 8.1$ Hz, 2H),

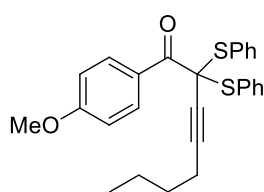
7.44 – 7.40 (m, 2H), 7.32 – 7.28 (m, 3H), 7.20 (t, $J = 7.3$ Hz, 1H),

7.16 (t, $J = 8.5$ Hz, 4H), 7.05 – 7.00 (m, 2H), 2.35 (s, 3H), 2.00 – 1.92 (m, 2H), 1.24 – 1.07 (m, 2H), 1.05 – 0.95 (m, 2H), 0.71 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 205.6, 190.0, 143.2, 136.7, 134.4, 132.7, 132.1, 131.6, 130.9, 129.0(4), 129.0(3), 128.7, 128.4, 128.2, 112.7, 111.9, 32.6, 29.6, 21.8, 21.7, 13.7;

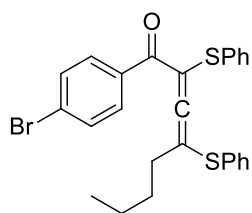
2,2-Bis(phenylthio)-1-p-tolyloct-3-yn-1-one (**4d**): ^1H NMR (CDCl_3 , 600 MHz): δ 8.22 (d, $J = 8.2$ Hz, 2H), 7.57 (d, $J = 7.9$ Hz, 4H), 7.33 (d, $J = 7.4$ Hz, 1H), 7.26 (t, $J = 7.4$ Hz, 3H), 7.20 (t, $J = 7.3$ Hz, 4H), 2.35 (s, 3H), 2.02 (t, $J = 7.1$ Hz, 2H), 1.23 – 1.08 (m, 4H), 0.76 (t, $J = 7.3$ Hz, 3H); 189.1, 143.7, 134.9(25), 134.9(27), 132.1, 129.6, 129.0, 128.5, 128.4, 97.1, 76.2, 67.8, 29.9, 21.7(8), 21.7(5), 18.7, 13.5; IR (neat): 3057, 2956, 2929, 2870, 1919, 1651, 1606, 1475, 1439, 1262, 1180 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{27}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 431.1497 Found 431.1498



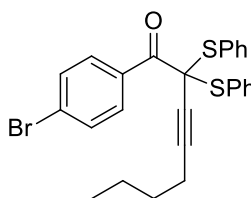
1-(4-Methoxyphenyl)-2,4-bis(phenylthio)octa-2,3-dien-1-one (**3e**): 268 mg (60%), yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.76 – 7.72 (m, 2H), 7.45 – 7.40 (m, 2H), 7.35 – 7.31 (m, 3H), 7.26 – 7.22 (m, 1H), 7.22 – 7.17 (m, 2H), 7.09 – 7.05 (m, 2H), 6.88 – 6.84 (m, 2H), 3.84 (s, 3H), 2.04 – 1.95 (m, 2H), 1.25 – 1.10 (m, 2H), 1.08 – 1.01 (m, 2H), 0.73 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 205.0, 188.7, 163.2, 134.3, 132.5, 132.2, 131.7, 131.3, 130.0, 128.9, 128.9, 128.4, 128.1, 113.3, 112.3, 111.5, 55.4, 32.6, 29.6, 21.8, 13.7; IR (neat): 3057, 2956, 2929, 2869, 2360, 2341, 1647, 1600, 1508, 1254, 1169 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{27}\text{O}_2\text{S}_2$ $[\text{M}+\text{H}]^+$ 447.1447 Found 447.1445.



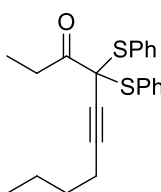
1-(4-Methoxyphenyl)-2,2-bis(phenylthio)oct-3-yn-1-one (**4e**): 54 mg (12%), yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 8.36 – 8.32 (m, 2H), 7.58 – 7.56 (m, 4H), 7.39 – 7.36 (m, 2H), 7.32 – 7.29 (m, 4H), 6.88 – 6.86 (m, 2H), 3.87 (s, 3H), 2.06 (t, $J = 7.0$ Hz, 2H), 1.26 – 1.21 (m, 2H), 1.18 – 1.12 (m, 2H), 0.79 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 188.0, 163.3, 136.7, 133.2, 131.6, 129.5, 128.3, 126.7, 112.8, 96.9, 76.2, 67.7, 55.4, 29.9, 21.7, 18.7, 13.5; IR (neat): 3056, 2956, 2930, 2869, 2360, 2341, 1671, 1598, 1508, 1261, 1172 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{27}\text{O}_2\text{S}_2$ $[\text{M}+\text{H}]^+$ 447.1447 Found 447.1445.



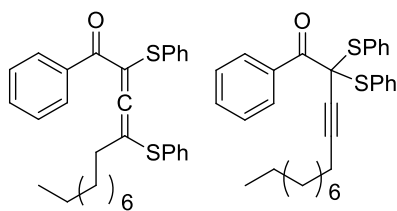
1-(4-Bromophenyl)-2,4-bis(phenylthio)octa-2,3-dien-1-one (**3f**): 260 mg (53%), yellow oil; $^1\text{H NMR}$ (CDCl_3 , 600 MHz): δ 7.51 (s, 4H), 7.42 (dd, $J = 6.5, 3.1$ Hz, 2H), 7.36 – 7.33 (m, 3H), 7.28 – 7.24 (m, 1H), 7.24 – 7.20 (m, 2H), 7.06 – 7.02 (m, 2H), 2.02 – 1.93 (m, 2H), 1.23 – 1.07 (m, 2H), 1.06 – 0.98 (m, 2H), 0.73 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 150 MHz): δ 205.7, 189.5, 136.2, 134.4, 132.8, 131.7, 131.3(2), 131.3(0), 130.3, 129.0(9), 129.0(5), 128.6, 128.4, 127.3, 113.7, 112.1, 32.6, 29.6, 21.8, 13.7; IR (neat): 3058, 2956, 2929, 2360, 2347, 1655, 1584, 1477, 1439, 1261, 1071 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{24}\text{BrOS}_2$ $[\text{M}+\text{H}]^+$ 495.0446 Found 495.0454.



1-(4-Bromophenyl)-2,2-bis(phenylthio)oct-3-yn-1-one (**4f**): 50 mg (10%), yellow solid, m.p. 84-86 °C; $^1\text{H NMR}$ (CDCl_3 , 600 MHz): δ 8.18 – 8.15 (m, 2H), 7.58 – 7.54 (m, 4H), 7.54 – 7.51 (m, 2H), 7.40 – 7.37 (m, 2H), 7.33 – 7.29 (m, 4H), 2.05 (t, $J = 7.0$ Hz, 2H), 1.25 – 1.19 (m, 2H), 1.16 – 1.08 (m, 2H), 0.79 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 150 MHz): δ 188.6, 136.7, 133.0, 132.2, 131.2, 131.0, 129.7, 128.5, 128.0, 97.4, 75.7, 67.4, 29.8, 21.7, 18.6, 13.4; IR (neat): 3058, 2956, 2930, 2870, 2359, 2341, 1660, 1581, 1438, 1234 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{24}\text{BrOS}_2$ $[\text{M}+\text{H}]^+$ 495.0446 Found 495.0455.



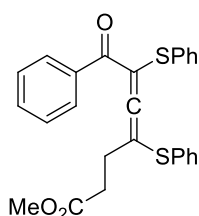
4,4-Bis(phenylthio)dec-5-yn-3-one (**4g**): 151 mg (41%), yellow oil; $^1\text{H NMR}$ (CDCl_3 , 600 MHz) δ 7.57 (d, $J = 7.4$ Hz, 4H), 7.38 (t, $J = 7.3$ Hz, 2H), 7.33 (t, $J = 7.5$ Hz, 4H), 2.84 (m, 2H), 2.06 (t, $J = 7.0$ Hz, 2H), 1.27 – 1.23 (m, 2H), 1.21 – 1.14 (m, 2H), 1.07 (t, $J = 7.2$ Hz, 3H), 0.82 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 150 MHz): δ 200.1, 136.4, 131.6, 129.5, 128.4, 95.2, 75.0, 67.5, 31.5, 30.0, 21.7, 18.5, 13.5, 8.6; IR (neat): 3058, 2957, 2933, 2871, 2360, 2341, 1716, 1438 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{25}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 369.1341 Found 369.1341.



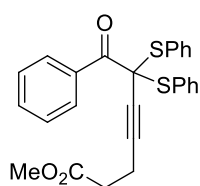
A mixture of **3h** and **4h** was isolated with a 6:1 ratio in 331 mg (68%). 1-Phenyl-2,4-bis(phenylthio)trideca-2,3-dien-1-one (**3h**): yellow oil; $^1\text{H NMR}$ (CDCl_3 , 600 MHz): δ 7.69 – 7.65 (m, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.45 – 7.41 (m, 2H), 7.38 (t, $J = 7.7$ Hz, 2H), 7.35 – 7.32 (m, 3H), 7.24 (t,

$J = 7.4$ Hz, 1H), 7.19 (t, $J = 7.5$ Hz, 2H), 7.02 (d, $J = 7.2$ Hz, 2H), 2.01 – 1.91 (m, 2H), 1.26 – 1.04 (m, 12H), 0.99 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 206.0, 190.5, 137.6, 134.4, 132.7, 132.3, 132.0, 131.5, 129.0, 128.9, 128.8, 128.5, 128.2, 128.0, 113.0, 112.0, 32.9, 31.8, 29.3, 29.2(4), 29.2(1), 28.7, 27.5, 22.6, 14.1;

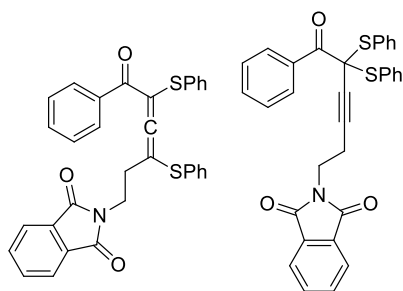
2-Bis(phenylthio)tridec-3-yn-1-one (**4h**): ^1H NMR (CDCl_3 , 600 MHz): δ 8.31 – 8.27 (m, 2H), 7.58 – 7.55 (m, 4H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.36 (dd, $J = 7.3, 2.8$ Hz, 4H), 7.30 (t, $J = 7.5$ Hz, 4H), 2.03 (t, $J = 7.1$ Hz, 2H), 1.33 – 1.17 (m, 14H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 189.61, 136.7, 134.4, 132.8, 131.5, 130.6, 129.6, 128.4, 127.6, 97.2, 75.9, 67.6, 32.9, 31.8, 29.4, 29.2, 29.0, 28.7, 27.8, 22.6, 19.0; IR (neat): 2925, 2853, 2359, 2341, 1657, 1581, 1477, 1439, 1248 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{35}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 487.2123 Found 487.2125.



Methyl 7-oxo-7-phenyl-4,6-bis(phenylthio)hepta-4,5-dienoate (**3i**): 244 mg (55%), yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.72 – 7.69 (m, 2H), 7.57 – 7.52 (m, 1H), 7.48 – 7.45 (m, 2H), 7.42 – 7.36 (m, 5H), 7.27 – 7.23 (m, 1H), 7.22 – 7.18 (m, 2H), 7.03 – 7.00 (m, 2H), 3.55 (s, 3H), 2.35 – 2.20 (m, 2H), 2.18 – 2.02 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 205.4, 190.0, 172.1, 137.2, 134.8, 132.6, 132.4, 131.6, 131.1, 129.1(6), 129.1(1), 128.8(7), 128.8(5), 128.3, 128.1, 113.1, 111.3, 51.7, 31.9, 28.0; IR (neat): 3058, 2950, 1922, 1736, 1653, 1438, 1260 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{23}\text{O}_3\text{S}_2$ $[\text{M}+\text{H}]^+$ 447.1083 Found 447.1087.



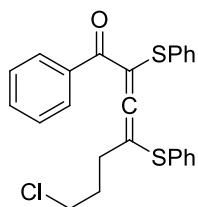
Methyl 7-oxo-7-phenyl-6,6-bis(phenylthio)hept-4-ynoate (**4i**): 14 mg (3%), yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 8.28 – 8.25 (m, 2H), 7.57 – 7.53 (m, 5H), 7.42 – 7.38 (m, 4H), 7.33 – 7.30 (m, 4H), 3.62 (s, 3H), 2.38 – 2.34 (m, 2H), 2.22 – 2.19 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 189.3, 171.8, 136.7, 134.2, 132.9, 131.3, 130.6, 129.8, 128.4, 127.7, 94.6, 76.7, 67.1, 51.7, 32.3, 14.8; IR (neat): 3058, 2950, 2922, 1738, 1681, 1438, 1228, 1172 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{23}\text{O}_3\text{S}_2$ $[\text{M}+\text{H}]^+$ 447.1083 Found 447.1088.



A mixture of **3j** and **4j** was isolated with a 13:1 ratio in 486 mg (91%).

2-(6-Oxo-6-phenyl-3,5-bis(phenylthio)hexa-3,4-dienyl)isoindoline-1,3-dione (**3j**): yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.79 – 7.73 (m, 3H), 7.72 – 7.64 (m, 4H), 7.51 (t, $J = 7.3$ Hz, 1H), 7.44 (d, $J = 6.2$ Hz, 2H), 7.40 – 7.36 (m, 4H), 7.26 (t, $J = 7.1$ Hz, 1H), 7.20 (t, $J = 7.4$ Hz,

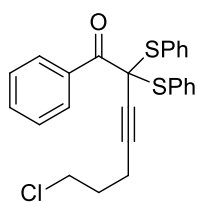
2H), 7.03 (d, $J = 7.5$ Hz, 2H), 3.55 – 3.45 (m, 2H), 2.46 – 2.25 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 205.7, 190.1, 167.7, 137.3, 134.5, 134.2, 133.9, 132.9, 132.5, 131.9, 129.2, 129.1, 128.8, 128.7, 128.5, 128.1, 123.5, 123.2, 112.9, 109.2, 35.8, 31.3; 2-(6-Oxo-6-phenyl-5,5-bis(phenylthio)hex-3-ynyl)isoindoline-1,3-dione (**4j**): ^1H NMR (CDCl_3 , 600 MHz): δ 8.27 – 8.23 (m, 2H), 7.88 – 7.84 (m, 2H), 7.83 – 7.80 (m, 2H), 7.79 – 7.73 (m, 2H), 7.72 – 7.65 (m, 2H), 7.56 – 7.48 (m, 4H), 7.32 – 7.28 (m, 1H), 7.25 (t, $J = 7.1$ Hz, 4H), 3.55 – 3.47 (m, 2H), 2.46 – 2.25 (m, 2H); IR (neat): 3058, 3021, 2943, 1922, 1772, 1715, 1439, 1395, 1364 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{32}\text{H}_{23}\text{NO}_3\text{S}_2$ [$\text{M}+\text{H}$] $^+$ 534.1192 Found 534.1186



7-Chloro-1-phenyl-2,4-bis(phenylthio)hepta-2,3-dien-1-one (**3k**): 230 mg (53%), yellow oil;

^1H NMR (CDCl_3 , 600 MHz) δ 7.68 – 7.66 (m, 2H), 7.56 – 7.53 (m, 1H), 7.48 – 7.45 (m, 2H), 7.42 – 7.36 (m, 5H), 7.28 – 7.25 (m, 1H), 7.22 – 7.18 (m, 2H), 7.02 – 6.99 (m, 2H), 3.17 – 3.09 (m, 2H), 2.17 – 2.09 (m, 2H), 1.68 – 1.54 (m, 2H); ^{13}C NMR (CDCl_3 , 151 MHz):

δ 205.8, 190.5, 137.5, 134.6, 132.7, 132.5, 131.6, 131.0, 129.1(6), 129.1(2), 128.8, 128.7, 128.4, 128.1, 112.7, 111.4, 43.3, 30.1, 29.8; IR (neat): 3058, 2956, 1920, 1655, 1476, 1439, 1262, 1064 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{22}\text{ClOS}_2$ [$\text{M}+\text{H}$] $^+$ 437.0795 Found 437.0804.

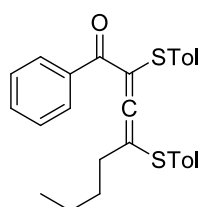


7-Chloro-1-phenyl-2,2-bis(phenylthio)hept-3-yn-1-one (**4k**): 32 mg (7%), yellow oil; ^1H

NMR (CDCl_3 , 600 MHz): δ 8.30 – 8.27 (m, 2H), 7.58 – 7.53 (m, 5H), 7.43 – 7.38 (m, 4H), 7.32 (t, $J = 7.6$ Hz, 4H), 3.22 (t, $J = 6.4$ Hz, 2H), 2.23 (t, $J = 6.7$ Hz, 2H), 1.66 – 1.61 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 189.5, 136.7, 134.3, 132.9, 131.3, 130.5, 129.8, 128.5,

127.7, 94.6, 76.7, 67.1, 43.2, 30.5, 16.3; IR (neat): 3058, 2957, 2923, 2850, 2232, 1680, 1472, 1438, 1227 cm^{-1} ;

HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{22}\text{ClOS}_2$ $[\text{M}+\text{H}]^+$ 437.0795 Found 437.0805.



2,4-Bis(p-tolylthio)-1-phenylocta-2,3-dien-1-one (**3l**): 233 mg (53%), yellow oil; ^1H NMR

(CDCl_3 , 600 MHz): δ 7.66 – 7.62 (m, 2H), 7.53 – 7.49 (m, 1H), 7.37 (t, $J = 7.8$ Hz, 2H),

7.32 (d, $J = 8.1$ Hz, 2H), 7.15 (d, $J = 7.9$ Hz, 2H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.93 (d, $J = 8.1$

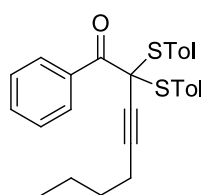
Hz, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 1.95 (t, $J = 7.5$ Hz, 2H), 1.20 – 1.05 (m, 2H), 1.02 –

0.95 (m, 2H), 0.71 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 205.6, 190.8, 138.6, 138.5, 137.7, 134.6,

133.1, 132.2, 129.7(4), 129.7(2), 128.8, 128.3, 127.9, 127.8, 113.7, 112.6, 32.5, 29.6, 21.7, 21.2(9), 21.2(2), 13.7;

IR (neat): 3021, 2956, 2926, 2869, 1918, 1654, 1596, 1491, 1446, 1262, 1062 cm^{-1} ; HRMS (ESI): m/z calcd for

$\text{C}_{28}\text{H}_{29}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 445.1654 Found 445.1661.



2,2-Bis(p-tolylthio)-1-phenyloct-3-yn-1-one (**4l**): 75 mg (17%), yellow oil; ^1H NMR

(CDCl_3 , 600 MHz): δ 8.32 – 8.29 (m, 2H), 7.53 – 7.49 (m, 1H), 7.45 (d, $J = 8.0$ Hz, 4H),

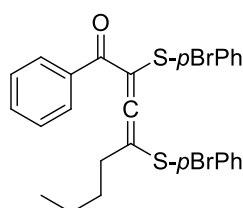
7.38 (t, $J = 7.6$ Hz, 2H), 7.12 – 7.09 (m, 4H), 2.34 (s, 6H), 2.06 (t, $J = 7.0$ Hz, 2H), 1.24 –

1.19 (m, 2H), 1.15 – 1.09 (m, 2H), 0.78 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ

189.7, 139.9, 136.8, 134.5, 132.7, 130.7, 129.2, 127.9, 127.6, 96.7, 76.1, 67.6, 29.9, 21.7, 21.3, 18.7, 13.5; IR

(neat): 3021, 2956, 2929, 2870, 2230, 1680, 1596, 1490, 1446, 1227, 1180, 1018 cm^{-1} ; HRMS (ESI): m/z calcd

for $\text{C}_{28}\text{H}_{29}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 445.1654 Found 445.1660.



2,4-Bis(4-bromophenylthio)-1-phenylocta-2,3-dien-1-one (**3m**): 377 mg (66%), yellow

oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.69 – 7.64 (m, 2H), 7.56 – 7.52 (m, 1H), 7.48 –

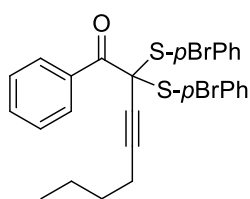
7.44 (m, 2H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.32 – 7.25 (m, 4H), 6.86 – 6.83 (m, 2H), 2.04 –

1.96 (m, 2H), 1.22 – 1.08 (m, 2H), 1.04 – 0.97 (m, 2H), 0.74 (t, $J = 7.3$ Hz, 3H); ^{13}C

NMR (CDCl_3 , 150 MHz): δ 206.2, 190.1, 137.3, 135.7, 133.8, 132.6, 132.2(5), 132.2(2), 131.2, 130.7, 128.7,

128.1, 123.0, 122.5, 112.4, 111.3, 32.5, 29.5, 21.7, 13.7; IR (neat): 2956, 2929, 2870, 1919, 1654, 1471, 1446,

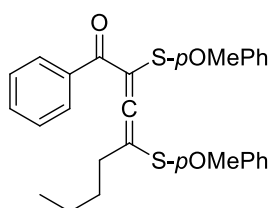
1263, 1067 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{23}\text{Br}_2\text{OS}_2$ $[\text{M}+\text{H}]^+$ 572.9551 Found 572.9561.



2,2-Bis(4-bromophenylthio)-1-phenyloct-3-yn-1-one (**4m**): 52 mg (18%); yellow oil;

^1H NMR (CDCl_3 , 600 MHz): δ 8.29 – 8.25 (m, 2H), 7.57 – 7.53 (m, 1H), 7.45 – 7.43 (m, 4H), 7.41 – 7.38 (m, 6H), 2.08 (t, $J = 7.0$ Hz, 2H), 1.26 – 1.22 (m, 2H), 1.18 – 1.11 (m, 2H), 0.81 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 189.1, 138.0, 134.0,

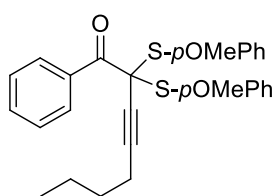
133.1, 131.7, 130.6, 130.3, 127.8, 124.7, 97.8, 75.5, 67.7, 29.8, 21.7, 18.7, 13.5 ; IR (neat): 3064, 2956, 2930, 2870, 2228, 1679, 1471, 1384, 1228, 1068 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{23}\text{Br}_2\text{OS}_2$ [$\text{M}+\text{H}$] $^+$ 572.9551 Found 572.9560.



2,4-Bis(4-methoxyphenylthio)-1-phenylocta-2,3-dien-1-one (**3n**): 228 mg (48%),

yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.65 – 7.62 (m, 2H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.39 – 7.35 (m, 4H), 6.98 – 6.95 (m, 2H), 6.90 – 6.87 (m, 2H), 6.74 – 6.71 (m, 2H), 3.82 (s, 3H), 3.78 (s, 3H), 1.92 (t, $J = 7.5$ Hz, 2H), 1.21 – 1.07 (m, 2H), 1.04 –

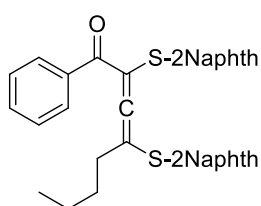
0.97 (m, 2H), 0.73 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 204.5, 190.8, 190.8, 160.3, 160.1, 137.6, 136.8, 135.5, 132.2, 128.7, 127.8, 122.2, 121.5, 115.1, 114.5, 113.9, 55.3(6), 55.3(2), 32.5, 29.6, 21.8, 13.7; IR (neat): 2956, 2931, 2870, 2360, 1651, 1591, 1493, 1462, 1288, 1247, 1172 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{29}\text{O}_3\text{S}_2$ [$\text{M}+\text{H}$] $^+$ 477.1552 Found 477.1557.



2,2-Bis(4-methoxyphenylthio)-1-phenyloct-3-yn-1-one (**4n**): 76 mg (16%), yellow

oil; ^1H NMR (CDCl_3 , 600 MHz) δ 8.32 – 8.27 (m, 2H), 7.54 – 7.51 (m, 1H), 7.50 – 7.47 (m, 4H), 7.39 (t, $J = 7.9$ Hz, 2H), 6.85 – 6.82 (m, 4H), 3.80 (s, 6H), 2.07 (t, $J =$

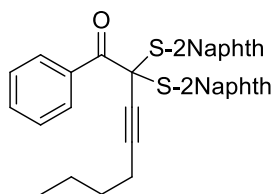
7.0 Hz, 2H), 1.27 – 1.22 (m, 2H), 1.17 – 1.11 (m, 2H), 0.79 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 151 MHz): δ 190.0, 161.0, 138.7, 134.6, 132.7, 130.6, 127.6, 122.2, 113.9, 96.8, 76.1, 67.9, 55.2, 29.9, 21.7, 18.7, 13.4; IR (neat): 2956, 2931, 2870, 2359, 2341, 1678, 1590, 1492, 1288, 1249, 1172 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{29}\text{O}_3\text{S}_2$ [$\text{M}+\text{H}$] $^+$ 477.1552 Found 477.1560.



2,4-Bis(naphthalen-2-ylthio)-1-phenylocta-2,3-dien-1-one (**3o**): 256 mg (50%),

yellow oil; ^1H NMR (CDCl_3 , 600 MHz) δ 7.95 – 7.93 (s, 1H), 7.83 – 7.81 (m, 1H), 7.77 – 7.68 (m, 5H), 7.56 – 7.47 (m, 5H), 7.46 – 7.41 (m, 4H), 7.39 – 7.35 (m, 2H),

6.87 (dd, $J = 8.5, 1.8$ Hz, 1H), 1.98 – 1.90 (m, 2H), 1.14 – 0.99 (m, 2H), 0.90 – 0.84 (m, 2H), 0.58 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 206.6, 190.6, 137.5, 133.6, 133.5(7), 133.5(6), 133.3, 132.9, 132.5, 132.4, 131.4, 130.8, 129.4, 129.2, 128.9, 128.8, 128.5, 128.0, 127.7(8), 127.7(3), 127.7(2), 127.4, 126.7, 126.6(4), 126.6(2), 126.5, 112.4, 111.4, 32.6, 29.5, 21.6, 13.5; IR (neat): 3053, 2956, 2928, 1918, 1654, 1500, 1340, 1264 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{34}\text{H}_{29}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 517.1654 Found 517.1664.



2,2-Bis(naphthalen-2-ylthio)-1-phenyloct-3-yn-1-one (**4o**): 83 mg (16%), yellow oil;

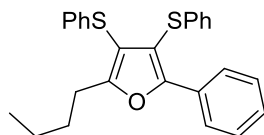
^1H NMR (CDCl_3 , 600 MHz): δ 8.33 – 8.28 (m, 2H), 8.06 (s, 2H), 7.82 (d, $J = 8.0$ Hz, 2H), 7.77 – 7.74 (m, 4H), 7.67 – 7.64 (m, 2H), 7.53 – 7.46 (m, 5H), 7.39 – 7.35 (m, 2H), 1.94 (t, $J = 7.0$ Hz, 2H), 1.06 – 0.99 (m, 2H), 0.96 – 0.91 (m, 2H), 0.58 (t, $J =$

7.3 Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 189.7, 137.1, 134.5, 133.6, 133.2, 132.9, 132.8, 130.7, 128.9, 128.1, 127.8, 127.7, 127.6, 127.0, 126.2, 97.5, 76.0, 67.9, 29.7, 21.6, 18.7, 13.3; IR (neat): 3053, 2956, 2928, 2869, 2359, 1676, 1226 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{34}\text{H}_{29}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 517.1654 Found 517.1661.

General Procedure for Synthesis of Furan via 1,2-Sulfur Migration.

To a suspension of CuCl (0.02 mmol, 10 mol%, 2 mg) in dry dichloromethane (0.5 mL) was added α, γ -dithio allenyl and α, α -dithio propargyl ketones (0.2 mmol) under argon at ambient temperature. The resulting solution was stirred for 1-2 h at this temperature, after which it was concentrated under reduced pressure and purified by column chromatography on silica gel (10-20% dichloromethane in hexanes) to give the desired products.

Characterization Data of the Compounds in Scheme 4.

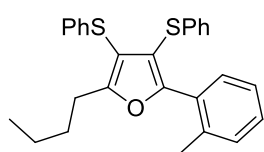


2-Butyl-5-phenyl-3,4-bis(phenylthio)furan (**9a**): 67 mg (81%), white solid, m.p. 50-

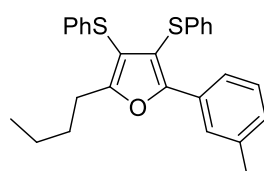
53 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 600 MHz): δ 8.07 (d, $J = 7.8$ Hz, 2H), 7.36 (t, $J = 7.7$ Hz, 2H), 7.28 (t, $J = 7.4$ Hz, 1H), 7.13 – 6.96 (m, 10H), 2.86 (t, $J = 7.6$ Hz, 2H), 1.72 –

1.65 (m, 2H), 1.40 – 1.33 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 161.0, 154.9, 137.3, 136.7, 129.9, 128.7, 128.6, 128.5, 128.4, 126.7, 126.6, 125.9, 125.3, 125.2, 115.2, 113.2, 30.2, 26.7, 22.3, 13.8;

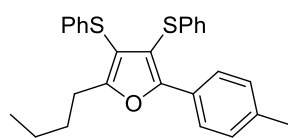
IR (neat): 3058, 2956, 2928, 2870, 1582, 1478, 1439, 1024 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{25}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 417.1341 Found 417.1303.



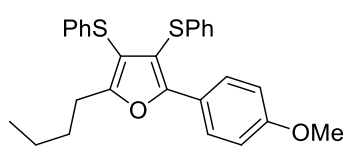
2-Butyl-3,4-bis(phenylthio)-5-o-tolylfuran (**9b**): 71 mg (83%), pale yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.42 (d, $J = 7.4$ Hz, 1H), 7.29 – 7.22 (m, 2H), 7.18 – 7.11 (m, 3H), 7.09 – 7.03 (m, 5H), 7.02 – 6.97 (m, 3H), 2.84 (t, $J = 7.5$ Hz, 2H), 2.37 (s, 3H), 1.72 – 1.62 (m, 2H), 1.39 – 1.30 (m, 2H), 0.89 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 161.3, 156.9, 137.6, 137.3, 137.2, 130.6, 130.4, 129.3, 129.2, 128.6, 128.5, 126.9, 126.7, 125.4, 125.3, 125.2, 114.8, 113.6, 30.2, 26.6, 22.2, 20.6, 13.7; IR (neat): 3058, 2956, 2927, 2870, 1582, 1477, 1439, 1084, 1024 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{25}\text{OS}_2$ $[\text{M}-\text{H}]^-$ 429.1341 Found 429.1322.



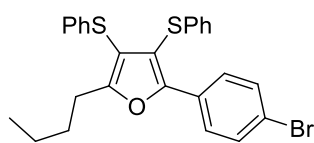
2-Butyl-3,4-bis(phenylthio)-5-m-tolylfuran (**9c**): 79 mg (92%), pale yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.90 – 7.84 (m, 2H), 7.25 (t, $J = 7.7$ Hz, 1H), 7.13 – 6.98 (m, 11H), 2.88 – 2.82 (m, 2H), 2.34 (s, 3H), 1.74 – 1.65 (m, 2H), 1.41 – 1.33 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 160.9, 155.0, 138.0, 137.4, 136.8, 129.8, 129.2, 128.7, 128.6, 128.4, 126.7(7), 126.7(1), 126.5, 125.3, 125.2, 123.1, 115.1, 113.2, 30.2, 26.7, 22.3, 21.5, 13.8; IR (neat): 3057, 2956, 2927, 2870, 1582, 1477, 1439, 1082 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{25}\text{OS}_2$ $[\text{M}-\text{H}]^-$ 429.1341 Found 429.1322.



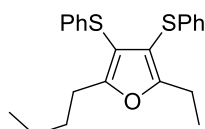
2-Butyl-3,4-bis(phenylthio)-5-p-tolylfuran (**9d**): 65 mg (76%), white solid, m.p. 57-58 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 600 MHz): δ 7.97 – 7.93 (m, 2H), 7.18 (d, $J = 8.1$ Hz, 2H), 7.12 – 7.07 (m, 4H), 7.07 – 7.00 (m, 6H), 2.85 (t, $J = 7.8$ Hz, 2H), 2.35 (s, 3H), 1.73 – 1.64 (m, 2H), 1.42 – 1.33 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 160.69, 155.2, 138.4, 137.3, 136.9, 129.1, 128.7, 128.5, 127.1, 126.7, 126.5, 125.8, 125.2, 125.2, 115.0, 112.2, 30.2, 26.6, 22.3, 21.3, 13.7; IR (neat): 3058, 2956, 2927, 2870, 1582, 1496, 1477, 1439, 1089, 1023 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{25}\text{OS}_2$ $[\text{M}-\text{H}]^-$ 429.1341 Found 429.1322.



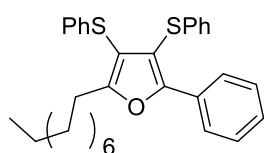
2-Butyl-5-(4-methoxyphenyl)-3,4-bis(phenylthio)furan (**9e**): 71 mg (80%), yellow oil; $^1\text{H NMR}$ (CDCl_3 , 600 MHz): δ 8.02 – 7.97 (m, 2H), 7.11 – 7.07 (m, 4H), 7.07 – 6.98 (m, 6H), 6.92 – 6.87 (m, 2H), 3.79 (s, 3H), 2.85 (t, $J = 7.8$ Hz, 2H), 1.72 – 1.64 (m, 2H), 1.41 – 1.33 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 151 MHz): δ 160.3, 159.7, 155.2, 137.4, 137.0, 128.7, 128.6, 127.4, 126.7, 126.4, 125.2(1), 125.2(0), 122.8, 114.9, 113.9, 111.1, 55.2, 30.2, 26.6, 22.3, 13.7; IR (neat): 3058, 2956, 2928, 2870, 1609, 1581, 1496, 1252, 1178 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{26}\text{O}_2\text{S}_2$ $[\text{M}+\text{H}]^+$ 447.1447 Found 447.1452.



2-(4-Bromophenyl)-5-butyl-3,4-bis(phenylthio)furan (**9f**): 74 mg (75%), white solid, m.p. 80-84 $^\circ\text{C}$; $^1\text{H NMR}$ (CDCl_3 , 600 MHz): δ 7.97 – 7.93 (m, 2H), 7.50 – 7.46 (m, 2H), 7.12 – 7.07 (m, 4H), 7.06 – 7.00 (m, 6H), 2.85 (t, $J = 7.2$ Hz, 2H), 1.71 – 1.65 (m, 2H), 1.41 – 1.33 (m, 2H), 0.91 (d, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 150 MHz): δ 161.2, 153.7, 137.0, 136.2, 131.6, 128.8, 128.7, 128.6, 127.2, 126.8, 126.6, 125.5, 125.3, 122.4, 115.6, 114.0, 30.1, 26.6, 22.3, 13.7; IR (neat): 3058, 2956, 2927, 2870, 1742, 1581, 1477, 1438 cm^{-1} ; MS (EI) $m/z = 495.6$ (M^+).

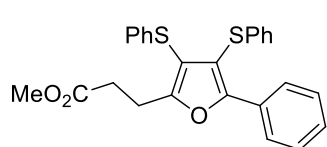


2-Butyl-5-ethyl-3,4-bis(phenylthio)furan (**9g**): 41 mg (56%), pale yellow oil; $^1\text{H NMR}$ (CDCl_3 , 600 MHz): δ 7.12 – 7.07 (m, 4H), 7.04 – 6.98 (m, 6H), 2.80 – 2.74 (m, 4H), 1.65 – 1.59 (m, 2H), 1.36 – 1.29 (m, 2H), 1.21 (t, $J = 7.6$ Hz, 3H), 0.89 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 150 MHz): δ 161.1, 160.2, 137.6, 137.5, 128.5(6), 128.5(3), 126.7, 126.6, 125.1(1), 125.1(0), 112.2, 111.6, 30.2, 26.5, 22.2, 20.3, 13.7, 12.6; IR (neat): 3059, 2956, 2929, 2871, 1582, 1477, 1439, 1059, 1024 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{25}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 369.1341 Found 369.1356.



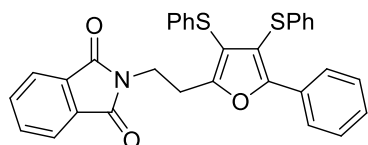
2-Nonyl-5-phenyl-3,4-bis(phenylthio)furan (**9h**): 88 mg (90%), pale yellow sticky oil; $^1\text{H NMR}$ (CDCl_3 , 600 MHz): δ 8.09 – 8.05 (m, 2H), 7.39 – 7.35 (m, 2H), 7.31 – 7.27 (m, 1H), 7.11 – 7.08 (m, 4H), 7.07 – 7.00 (m, 6H), 2.85 (t, $J = 7.5$ Hz, 2H), 1.74 – 1.67 (m, 2H), 1.35 – 1.21 (m, 12H), 0.87 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 150 MHz): δ 161.0, 154.8,

137.3, 136.7, 129.8, 128.7, 128.5, 128.4, 128.3, 126.7, 126.5, 125.8, 125.2(8), 125.2(3), 115.2, 113.2, 31.8, 29.4, 29.2(5), 29.2(3), 29.1, 28.0, 26.9, 22.6, 14.1; IR (neat): 3059, 2925, 2853, 1582, 1478, 1439, 1024 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{35}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 487.2123 Found 487.2133.



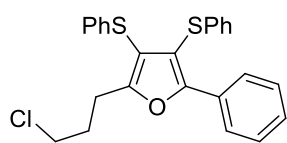
Methyl 3-(5-phenyl-3,4-bis(phenylthio)furan-2-yl)propanoate (**9i**): 71 mg

(79%), pale yellow solid, m.p. 65-66 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 8.07 – 8.03 (m, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.28 (m, 1H), 7.13 – 7.08 (m, 4H), 7.07 – 7.01 (m, 6H), 3.67 (s, 3H), 3.21 (t, $J = 7.8$ Hz, 2H), 2.73 (t, $J = 7.8$ Hz, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 172.4, 158.2, 155.3, 136.7, 136.4, 129.6, 128.7(8), 128.7(1), 128.6, 128.5, 126.9, 126.7, 125.9, 125.4(8), 125.4(2), 116.2, 113.5, 51.8, 32.1, 22.6; IR (neat): 3058, 2949, 1739, 1582, 1478, 1438, 1197, 1071 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{23}\text{O}_3\text{S}_2$ $[\text{M}+\text{H}]^+$ 447.1083 Found 447.1099.



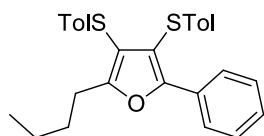
2-(2-(5-Phenyl-3,4-bis(phenylthio)furan-2-yl)ethyl)isoindoline-1,3-dione

(**9j**): 97 mg (91%), yellow solid, m.p. 122-123 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 7.91 – 7.88 (m, 2H), 7.76 (dd, $J = 5.4, 3.1$ Hz, 2H), 7.66 (dd, $J = 5.5, 3.0$ Hz, 2H), 7.29 – 7.24 (m, 3H), 7.14 – 7.10 (m, 2H), 7.05 – 6.99 (m, 7H), 6.98 – 6.94 (m, 1H), 4.04 (t, $J = 6.4$ Hz, 2H), 3.27 (t, $J = 6.4$ Hz, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 167.9, 156.6, 155.9, 136.6(8), 136.6(4), 133.8, 132.0, 129.4, 128.7, 128.6, 128.5, 128.3, 126.8, 126.3, 125.9, 125.4, 125.2, 123.2, 117.6, 113.1, 36.3, 25.9; IR (neat): 3058, 1771, 1715, 1478, 1394 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{32}\text{H}_{24}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$ 534.1192 Found 534.1176.

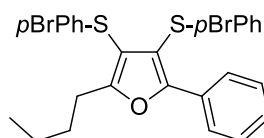


2-(3-Chloropropyl)-5-phenyl-3,4-bis(phenylthio)furan (**9k**): 81 mg (93%), yellow solid, m.p. 79-80 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 8.08 – 8.05 (m, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.28 (m, 1H), 7.13 – 7.08 (m, 4H), 7.08 – 7.01 (m, 6H), 3.56 (t,

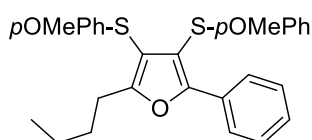
$J = 6.5$ Hz, 2H), 3.05 – 3.00 (m, 2H), 2.20 – 2.14 (m, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 158.9, 155.3, 136.8, 136.49, 129.6, 128.8, 128.7, 128.6, 128.5, 126.9, 126.7, 125.9, 125.5, 125.4, 116.4, 113.5, 44., 30.9, 24.5; IR (neat): 3058, 2957, 1581, 1478, 1439, 1070, 1023 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{22}\text{ClOS}_2$ $[\text{M}+\text{H}]^+$ 437.0795 Found 437.0782.



3,4-Bis(p-tolylthio)-2-butyl-5-phenylfuran (**9l**): 80 mg (90%), pale yellow solid, m.p. 71-72 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 8.10 – 8.05 (m, 2H), 7.36 (t, $J = 7.8$ Hz, 2H), 7.31 – 7.25 (m, 1H), 6.98 – 6.92 (m, 4H), 6.89 (d, $J = 7.8$ Hz, 4H), 2.85 (t, $J = 7.2$ Hz, 2H), 2.22 (d, $J = 5.8$ Hz, 6H), 1.72 – 1.64 (m, 2H), 1.42 – 1.33 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 160.7, 154.6, 135.1, 135.0, 133.6, 133.1, 130.0, 129.5, 129.3, 128.4, 128.3, 127.2, 126.9, 125.9, 115.8, 113.8, 30.2, 26.7, 22.3, 20.9(35), 20.9(31), 13.8; IR (neat): 3018, 2956, 2925, 2870, 1576, 1490, 1445, 1085, 1016 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{29}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 445.1654 Found 445.1633.

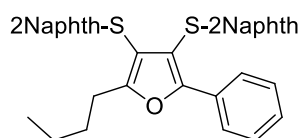


3,4-bis(4-bromophenylthio)-2-butyl-5-phenylfuran (**9m**): 99 mg (86%); white solid; m.p. 105-106 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 8.06 – 8.02 (m, 2H), 7.38 (t, $J = 7.6$ Hz, 2H), 7.34 – 7.30 (m, 1H), 7.20 – 7.16 (m, 4H), 6.87 – 6.83 (m, 4H), 2.86 (t, $J = 7.6$ Hz, 2H), 1.73 – 1.67 (m, 2H), 1.42 – 1.34 (m, 2H), 0.93 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 151 MHz) δ 161.3, 155.3, 136.1, 135.5, 131.7, 131.6, 129.5, 128.7, 128.6, 128.4, 128.3, 125.8, 119.3, 119.2, 114.6, 112.5, 30.2, 26.6, 22.3, 13.7; IR (neat): 2956, 2928, 2870, 1576, 1471, 1385, 1069, 1007 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{23}\text{Br}_2\text{OS}_2$ $[\text{M}+\text{H}]^+$ 572.9551 Found 572.9523



3,4-Bis(4-methoxyphenylthio)-2-butyl-5-phenylfuran (**9n**): 88 mg (92%); yellow solid; m.p. 59-60 °C; ^1H NMR (CDCl_3 , 600 MHz): δ 8.12 – 8.07 (m, 2H), 7.37 (t, $J = 15.5$ Hz, 2H), 7.27 (s, 1H), 7.03 – 6.98 (m, 4H), 6.61 (d, $J = 4.5$ Hz, 4H), 3.70 (s, 3H), 3.69 (s, 3H), 2.86 (t, $J = 7.6$ Hz, 2H), 1.72 – 1.65 (m, 2H), 1.42 – 1.34 (m, 2H), 0.92 (t, $J = 7.4$ Hz,

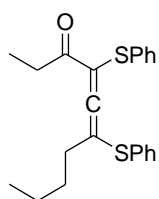
3H); ^{13}C NMR (CDCl_3 , 151 MHz) δ 160.3, 158.0, 158.0, 154.1, 130.1, 129.7, 129.2, 128.4, 128.2, 127.5, 127.1, 125.8, 116.6, 114.5, 114.4, 114.2, 55.2, 55.1, 30.3, 26.6, 22.3, 13.8; IR (neat): 2956, 2870, 2834, 1592, 1442, 1245, 1173, 1071, 1006 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{29}\text{O}_3\text{S}_2$ $[\text{M}+\text{H}]^+$ 477.1552 Found 477.1532



2-Butyl-4-(naphthalen-2-ylthio)-3-(naphthalen-3-ylthio)-5-phenylfuran (**9o**): 90 mg (87%); pale yellow sticky solid; ^1H NMR (CDCl_3 , 600 MHz): δ 8.13 (d, $J = 8.0$ Hz, 2H), 7.49 (d, $J = 7.4$ Hz, 2H), 7.40 – 7.34 (m, 8H), 7.29 – 7.21 (m, 5H),

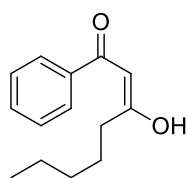
7.15 – 7.07 (m, 2H), 2.92 (t, $J = 7.5$ Hz, 2H), 1.78 – 1.71 (m, 2H), 1.44 – 1.36 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 151 MHz) δ 161.2, 155.2, 134.3, 133.9, 133.5, 133.4, 131.4(6), 131.4(4), 130.0, 128.6(5), 128.6(0), 128.3, 128.1, 127.5(6), 127.5(5), 126.8(7), 126.8(4), 126.2(3), 126.2(2), 126.0, 125.3, 125.2(3), 125.2(1), 125.1(5), 125.1(0), 124.7, 115.5, 113.3, 30.3, 26.8, 22.4, 13.8; IR (neat): 3052, 2956, 2928, 2870, 1624, 1590, 1501, 1484, 1132 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{34}\text{H}_{29}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 517.1654 Found 517.1630

Characterization Data of the Additional Compounds.



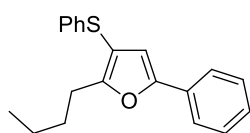
4,6-Bis(phenylthio)deca-4,5-dien-3-one (**3g**): yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 8.35 – 8.27 (m, 8H), 8.24 – 8.20 (m, 2H), 3.58 – 3.40 (m, 2H), 3.06 (t, $J = 7.6$ Hz, 2H), 2.32 – 2.21 (m, 4H), 2.03 (t, $J = 7.4$ Hz, 3H), 1.84 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, cdCl_3) δ 202.82, 197.91, 136.57, 134.59, 133.84, 131.94, 131.13, 129.02, 128.85, 128.80, 128.76, 128.44,

115.19, 114.14, 32.90, 32.75, 30.00, 22.12, 13.72, 8.52; IR (neat): 3058, 2957, 2931, 2871, 1687, 1475, 1439, 1154 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{25}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 369.1341 Found 369.1337.



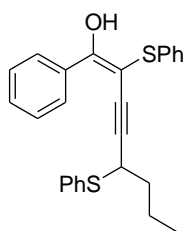
3-Hydroxy-1-phenyloct-2-en-1-one (**5a**): yellow oil; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.⁴ ^1H NMR (CDCl_3 , 600 MHz): δ 7.90 – 7.86 (m, 2H), 7.52 (t, $J = 7.0$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 2H), 6.17 (s, 1H),

2.42 (t, $J = 7.2$ Hz, 2H), 1.73 – 1.66 (m, 2H), 1.40 – 1.32 (m, 4H), 0.91 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (CDCl_3 , 151 MHz) δ 196.9, 183.4, 135.09, 132.1, 128.5, 126.9, 96.0, 39.2, 31.4, 25.5, 22.4, 13.9.



2-Butyl-5-phenyl-3-(phenylthio)furan (**6a**): colorless oil; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with the previously reported literature data.⁵

^1H NMR (CDCl_3 , 600 MHz): δ 7.66 – 7.62 (m, 2H), 7.39 (t, $J = 7.8$ Hz, 2H), 7.28 – 7.22 (m, 3H), 7.20 – 7.16 (m, 2H), 7.12 (t, $J = 7.3$ Hz, 1H), 6.63 (s, 1H), 2.81 (t, $J = 7.5$ Hz, 2H), 1.68 (m, 2H), 1.38 (m, 2H), 0.92 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 151 MHz) δ 160.2, 152.5, 138.1, 130.4, 128.8, 128.6, 127.4, 126.3, 125.1, 123.4, 110.3, 109.6, 30.4, 25.9, 22.2, 13.7.

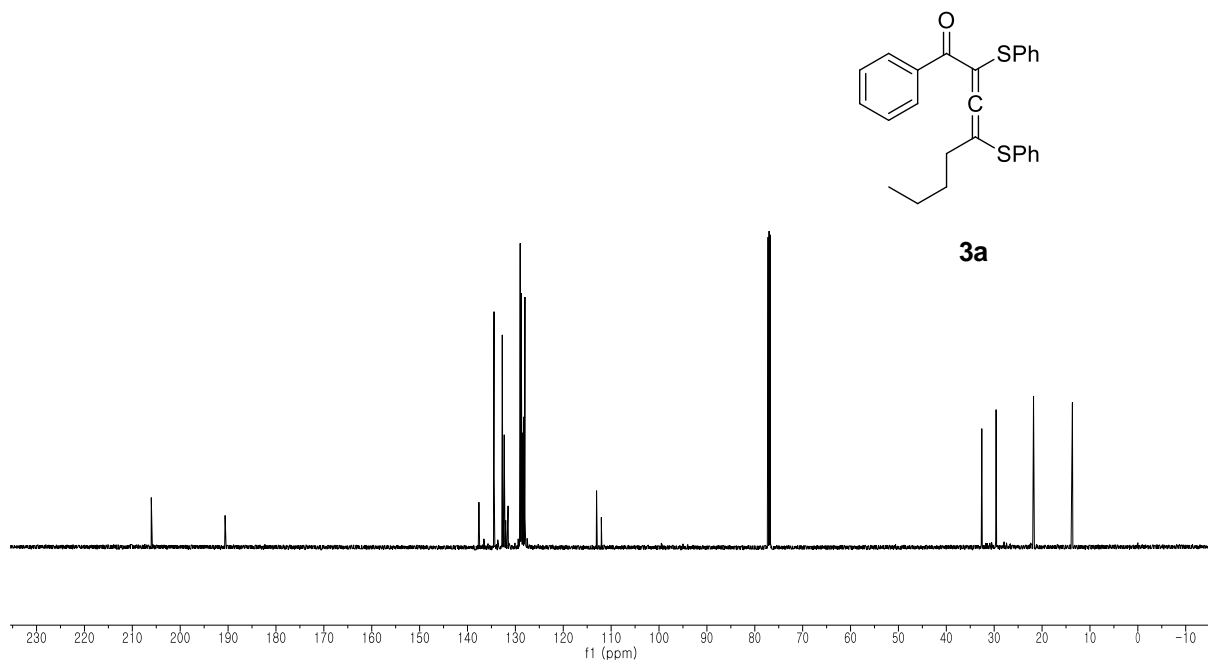
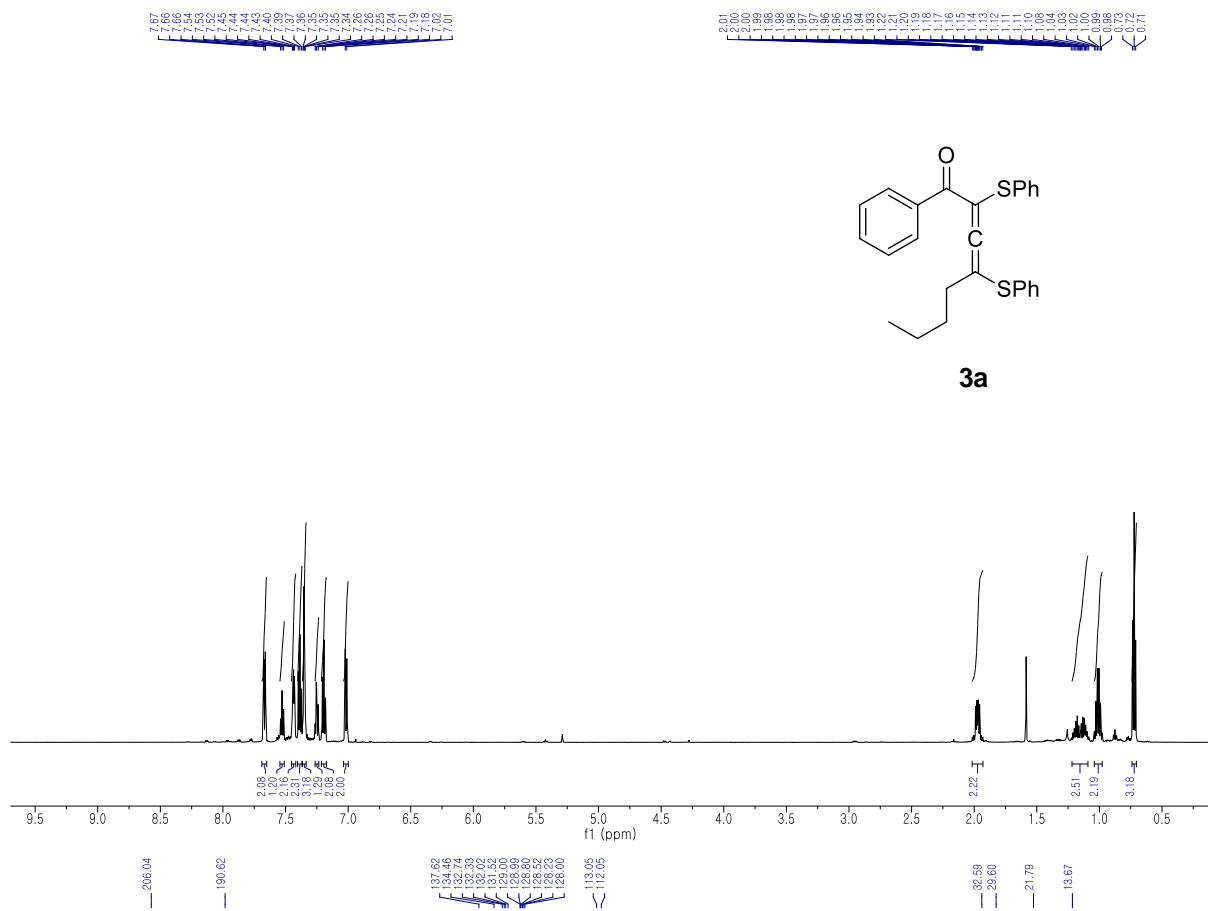


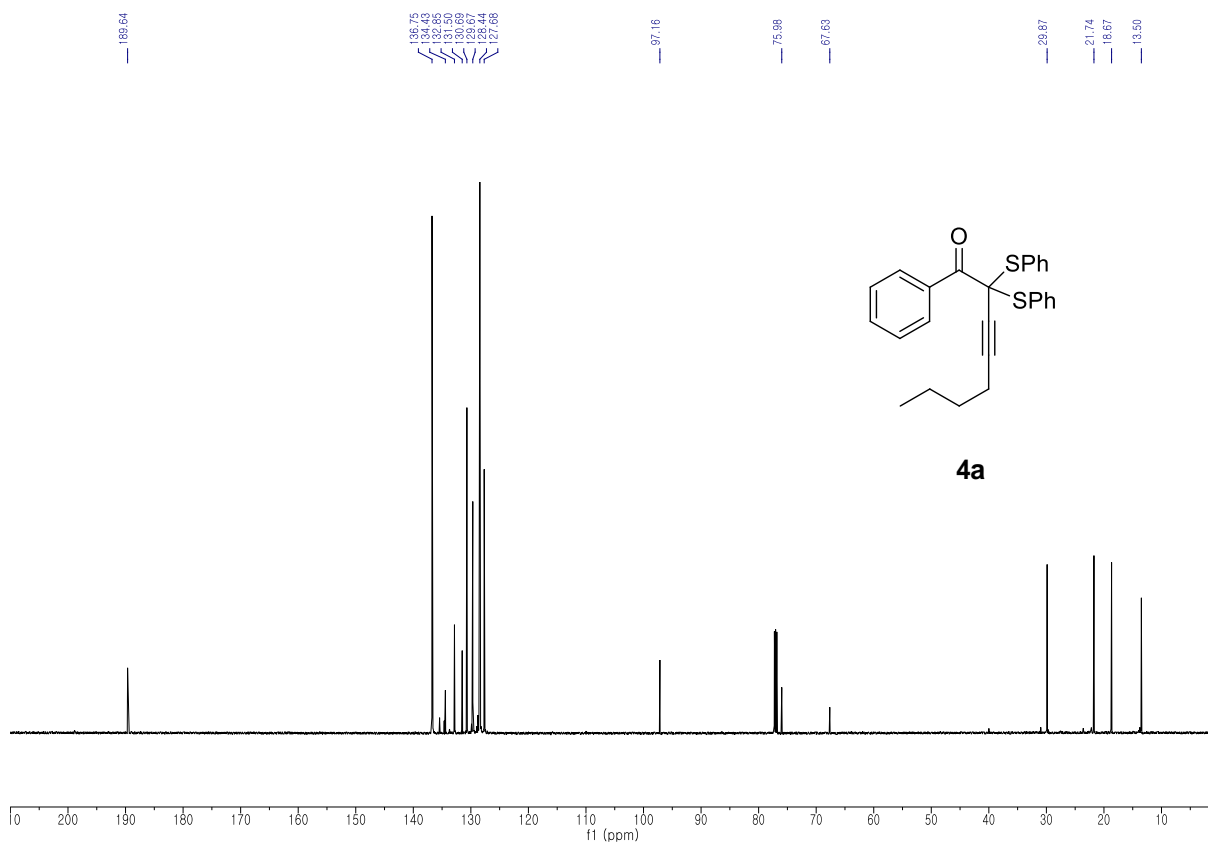
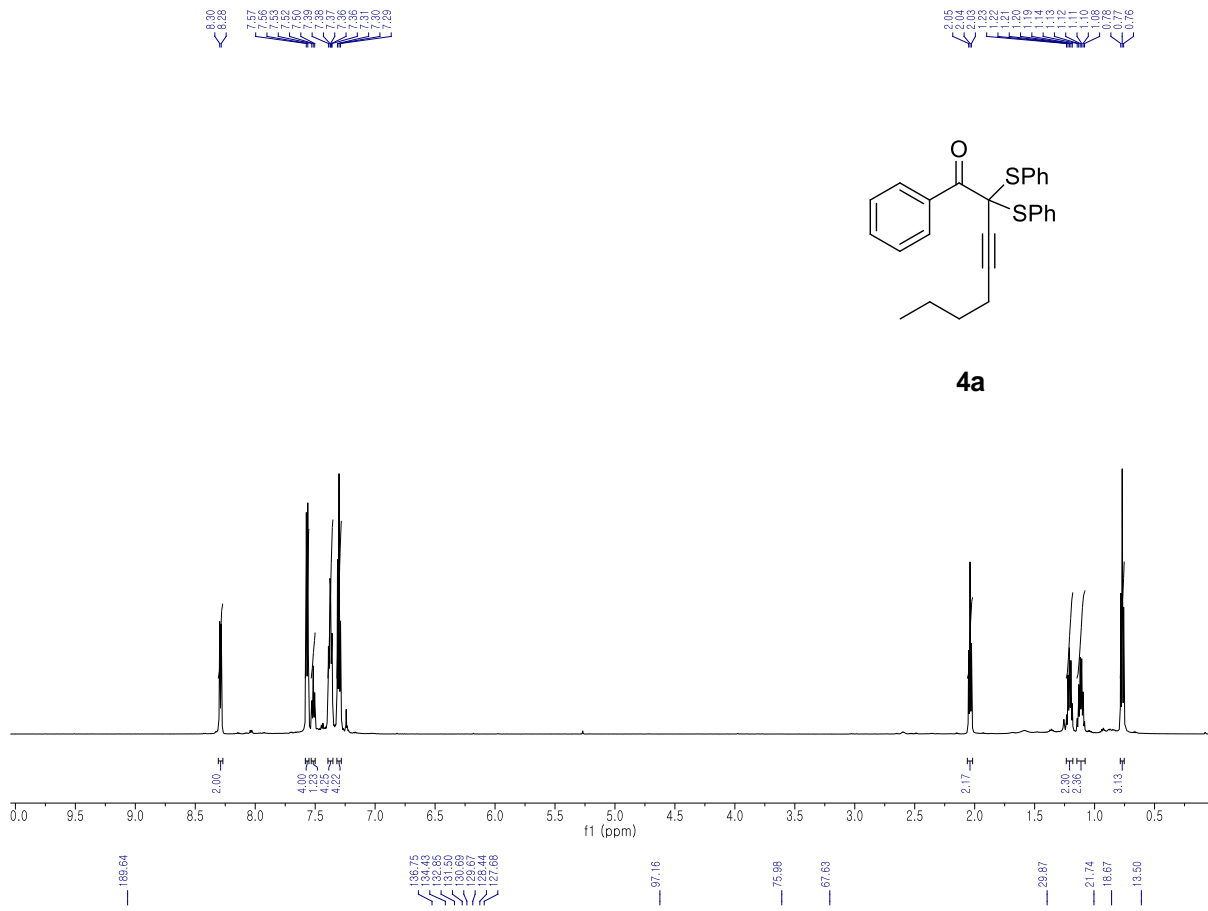
1-Phenyl-2,5-bis(phenylthio)oct-1-en-3-yn-1-ol (**10a**): yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.94 – 7.90 (m, 2H), 7.38 – 7.33 (m, 4H), 7.30 – 7.26 (m, 1H), 7.25 – 7.20 (m, 5H), 7.14 – 7.09 (m, 3H), 6.02 (s, 1H), 4.20 (t, $J = 7.5$ Hz, 1H), 2.04 – 1.88 (m, 2H), 1.58 – 1.44 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 151 MHz) δ 154.1, 153.4, 136.9, 133.8,

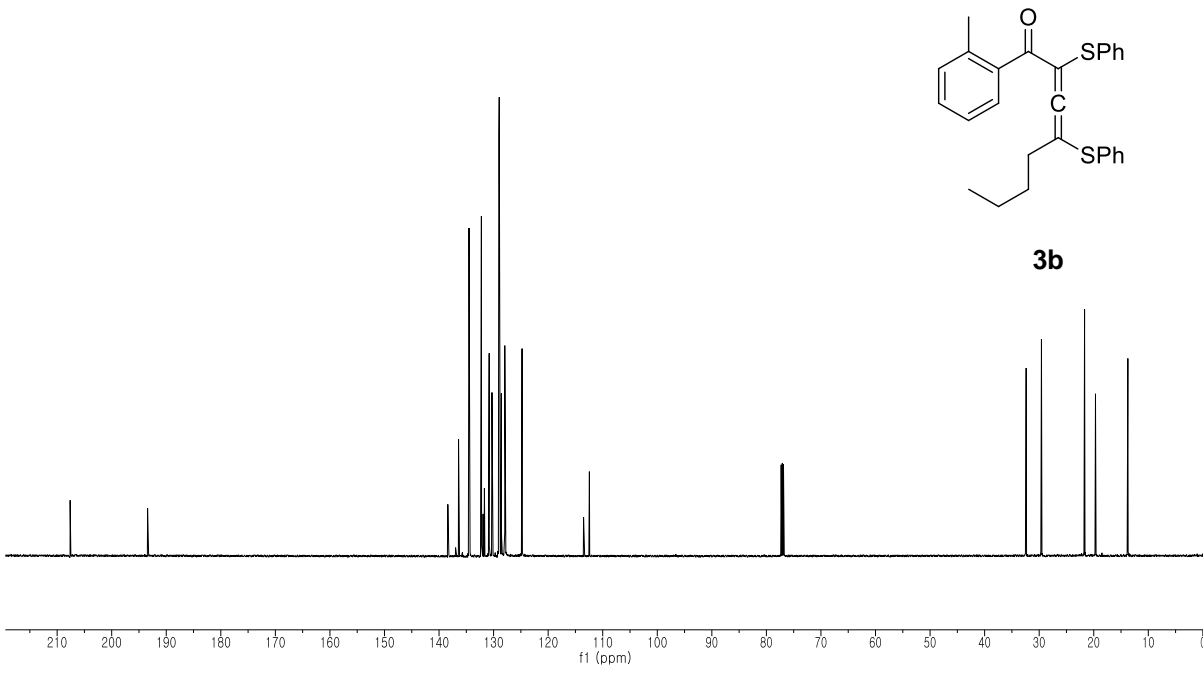
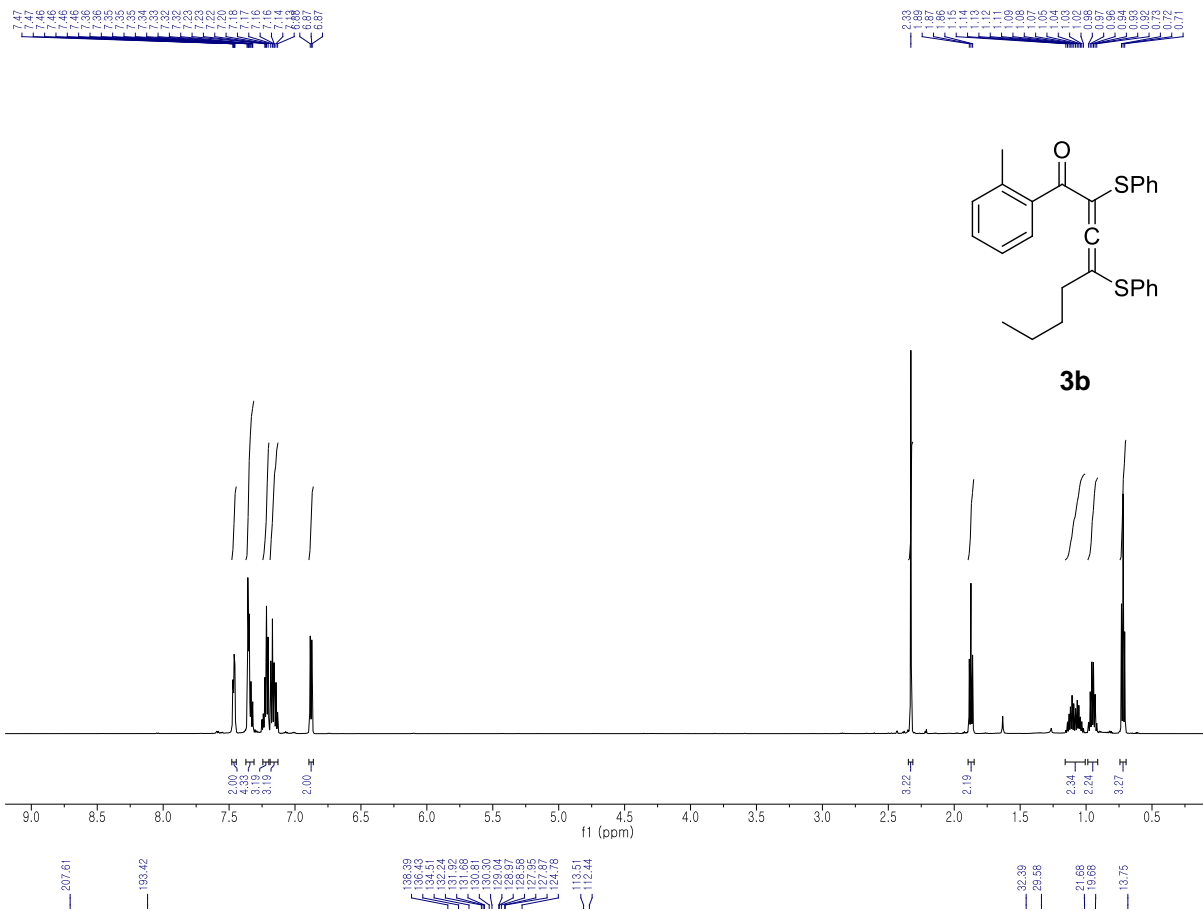
133.6, 130.0, 128.9, 128.7, 128.3, 127.9(9), 127.7(9), 126.8, 125.8, 125.5, 114.7, 109.3, 46.5, 35.3, 20.7, 13.6; IR (neat): 3057, 2957, 2930, 2870, 1582, 1478, 1438 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{24}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 417.1341 Found 417.1340

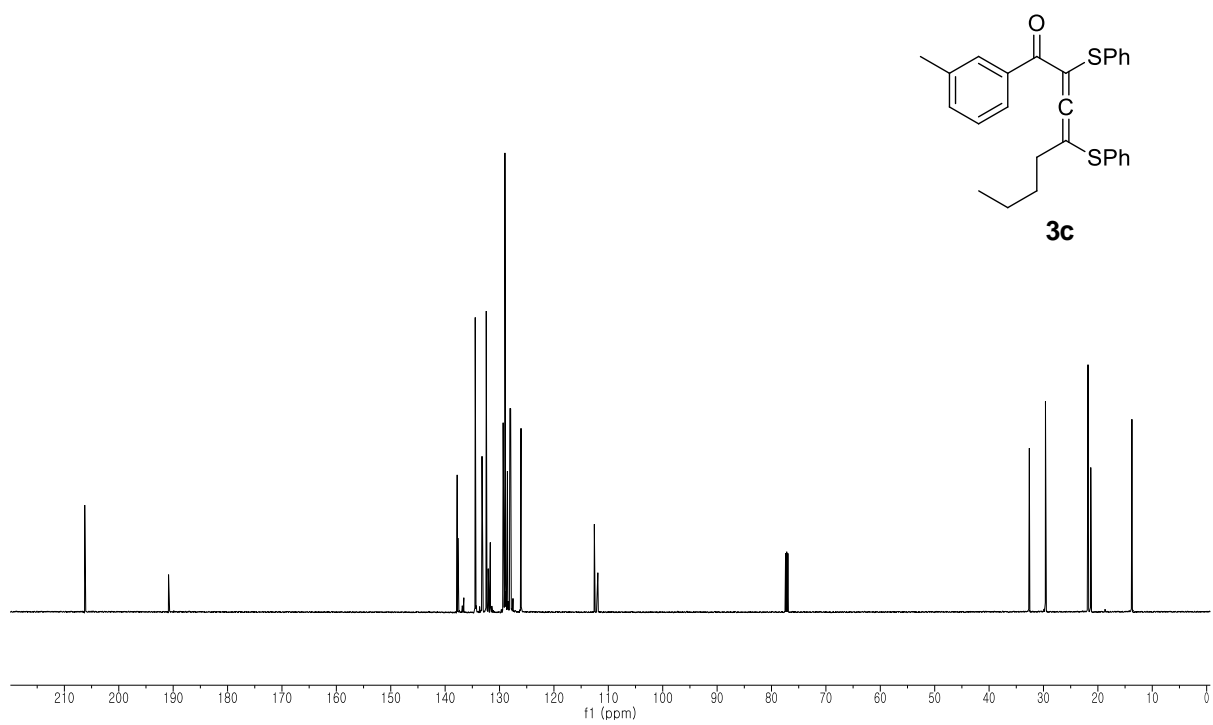
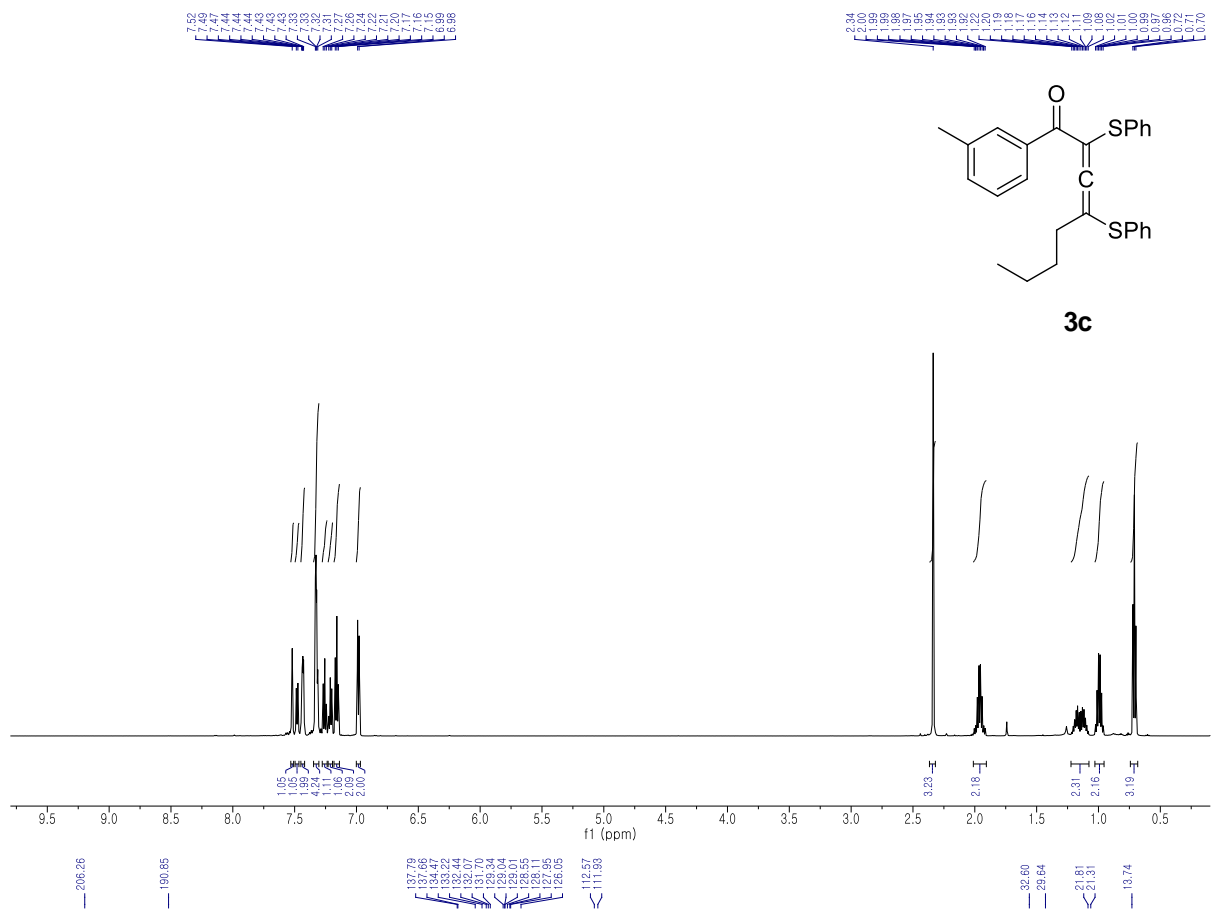
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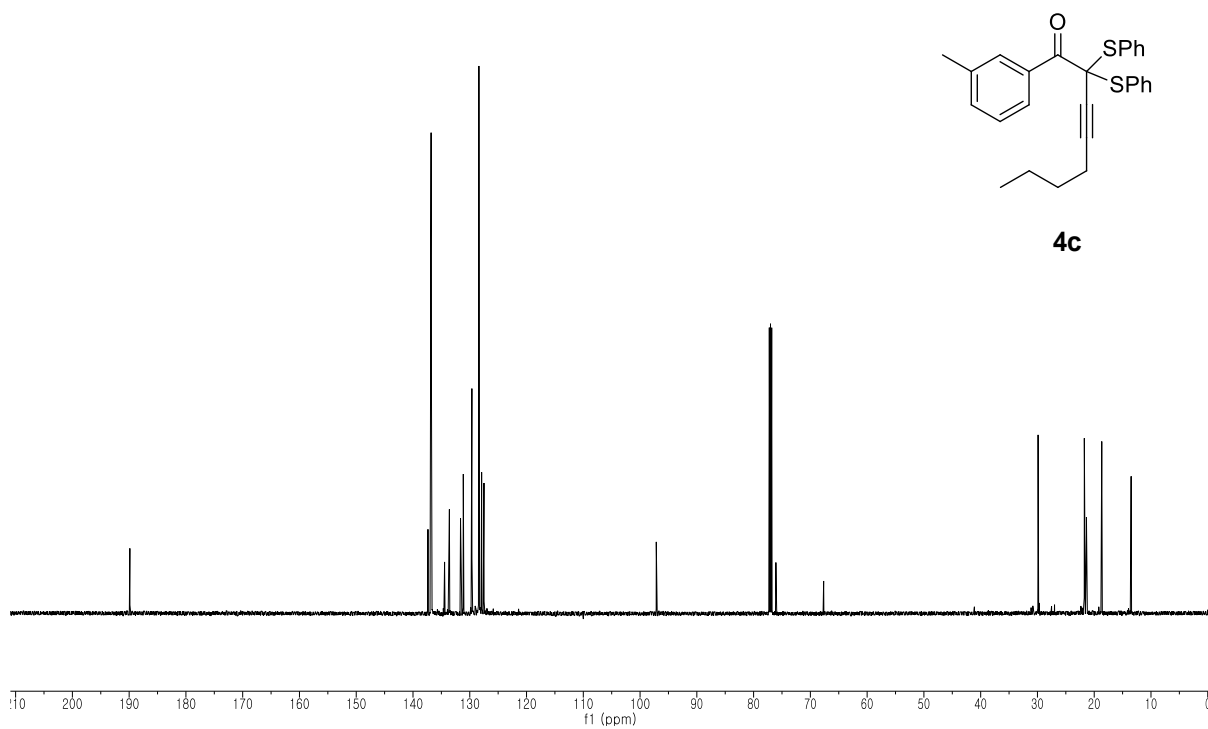
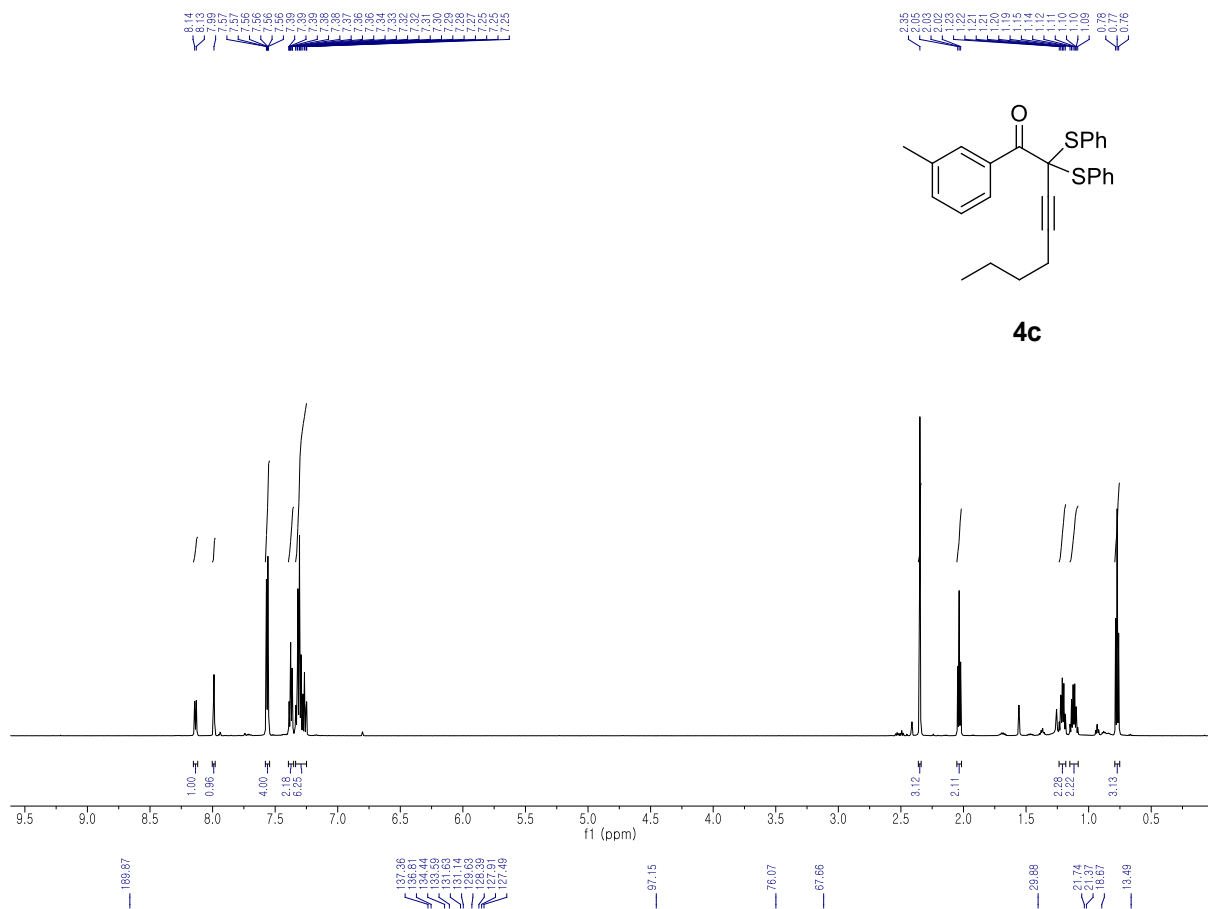
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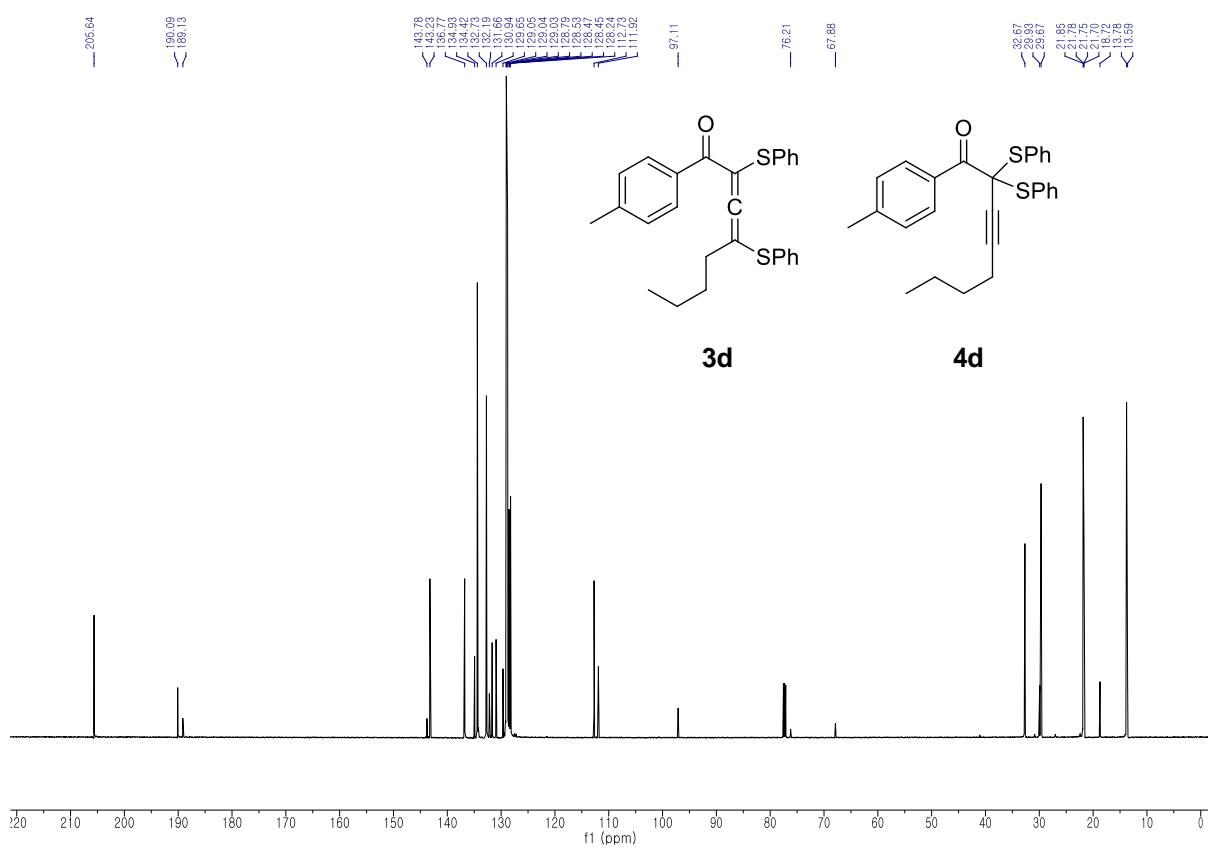
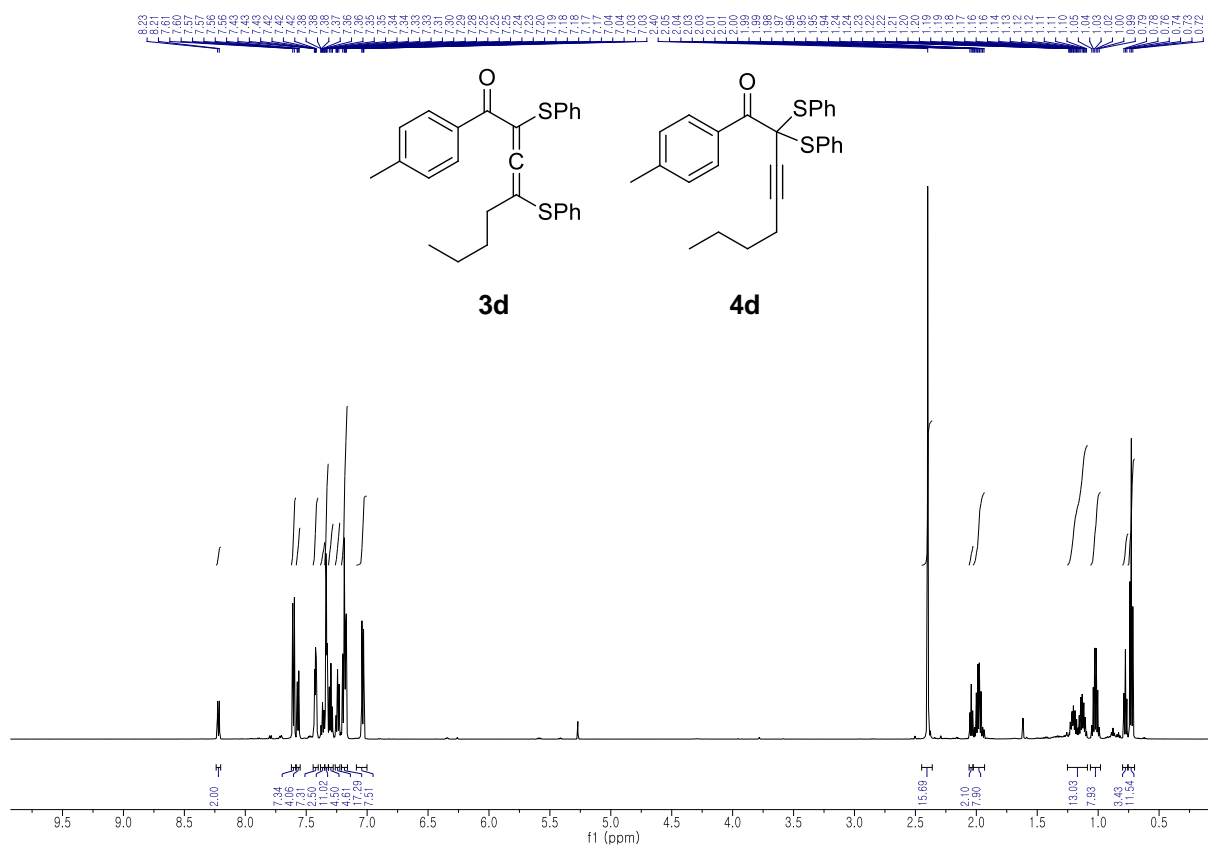


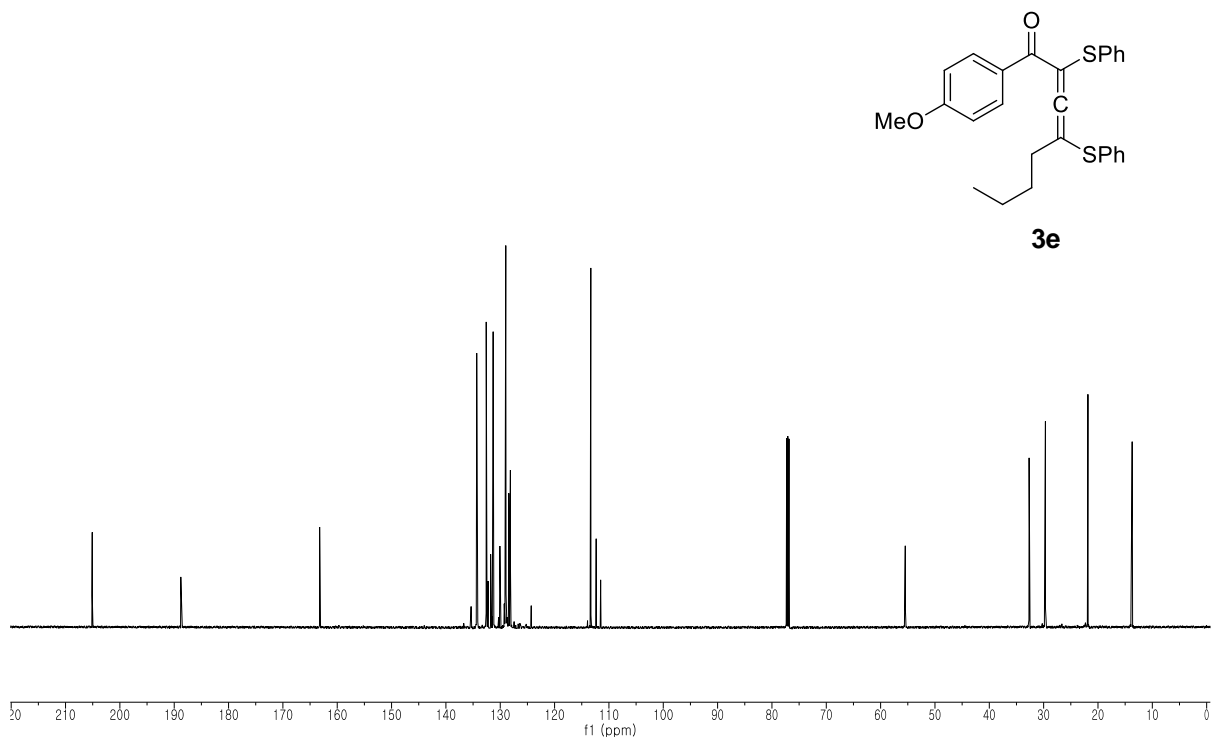
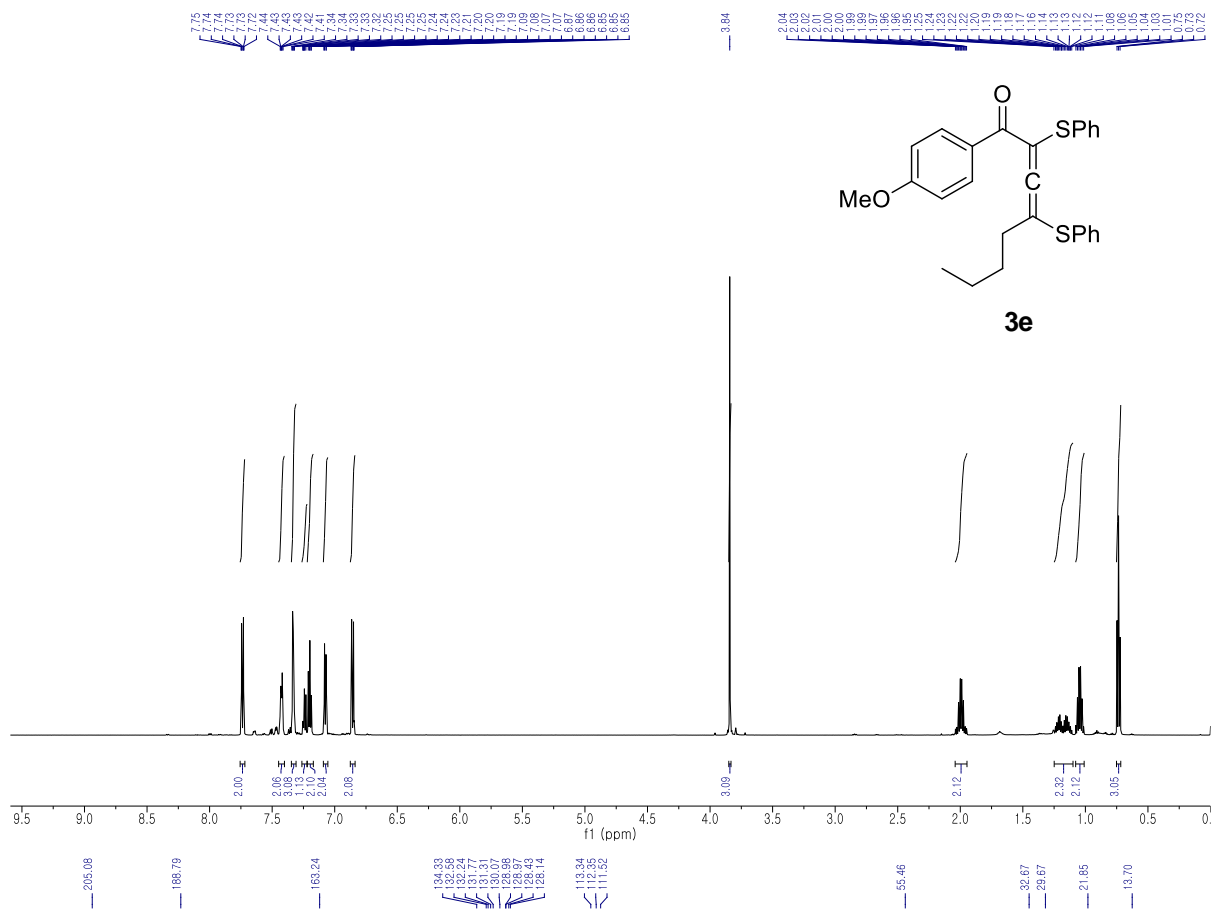


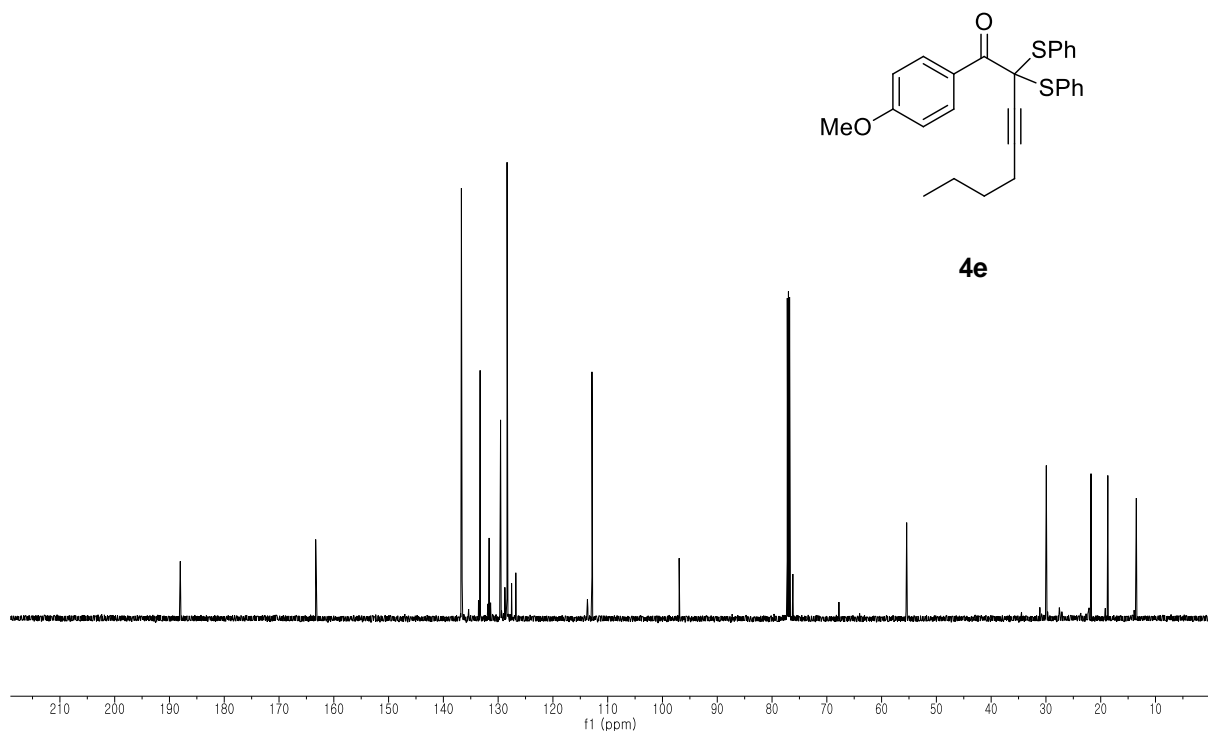
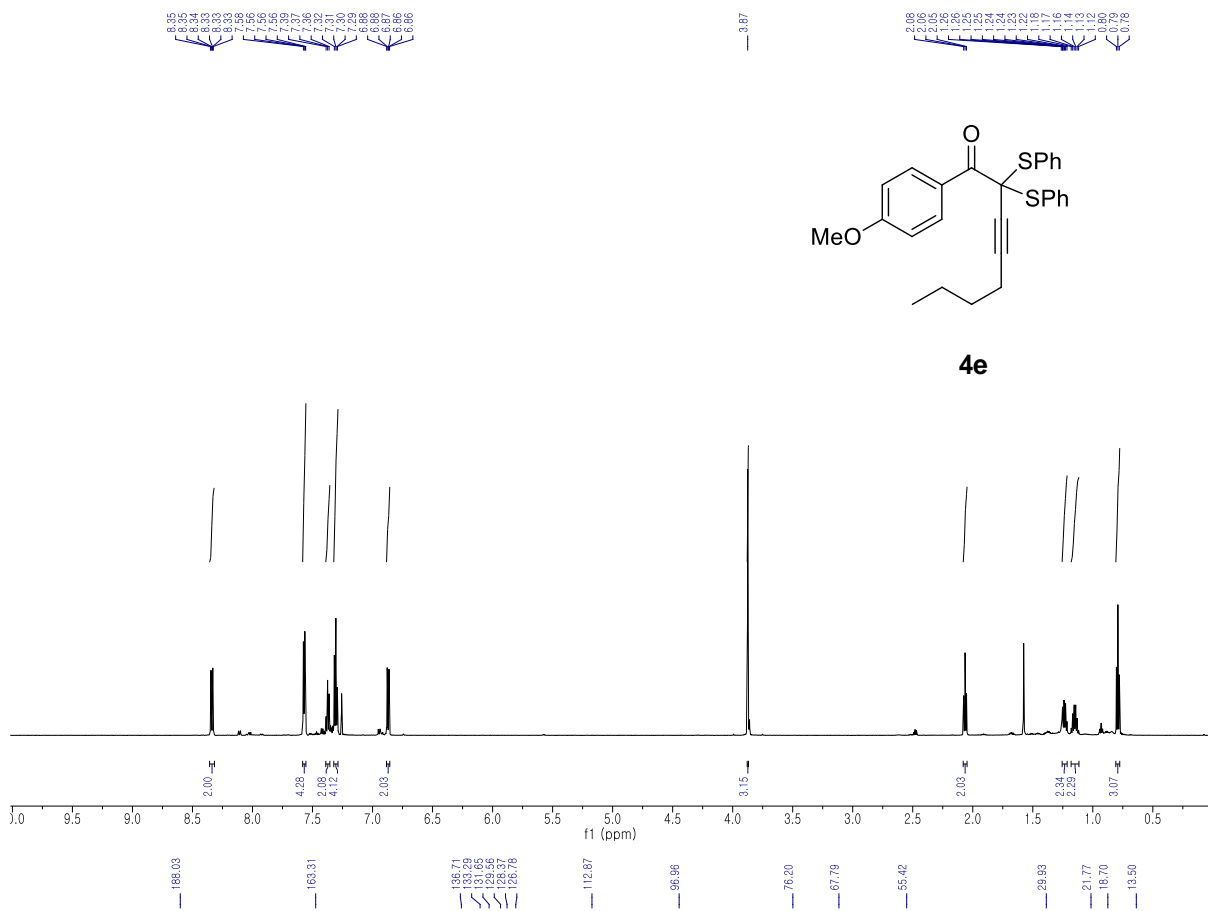


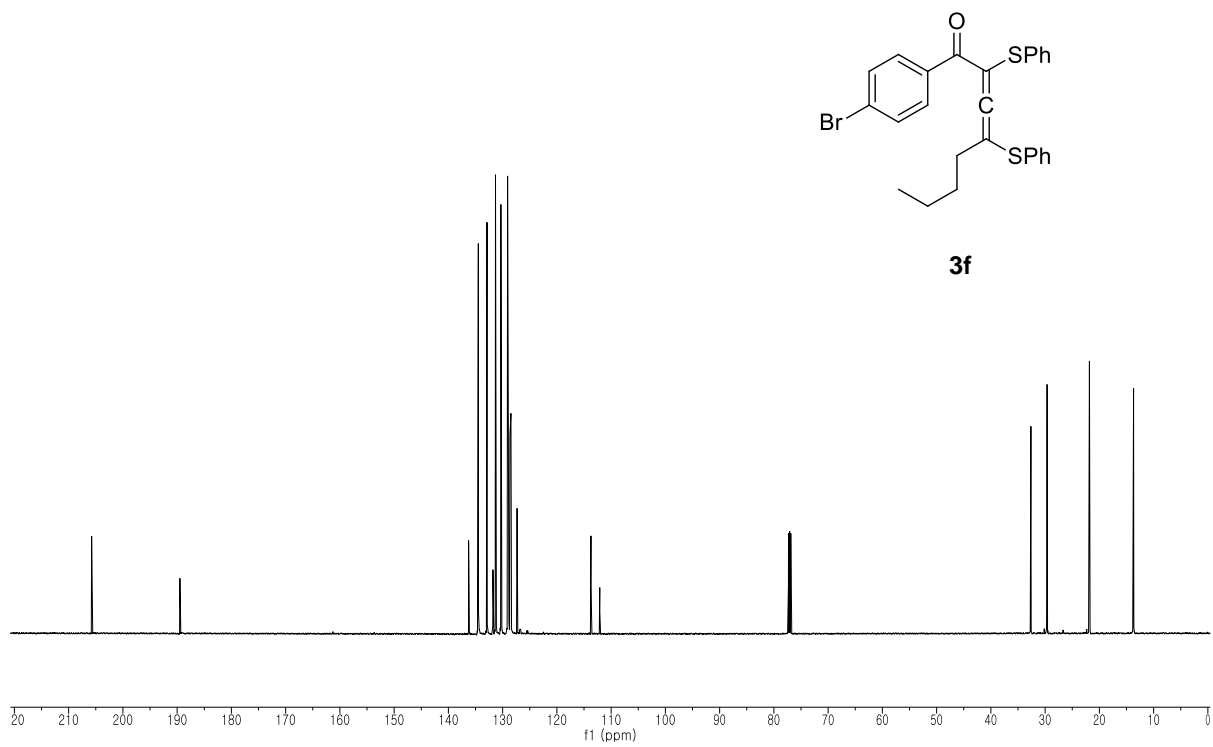
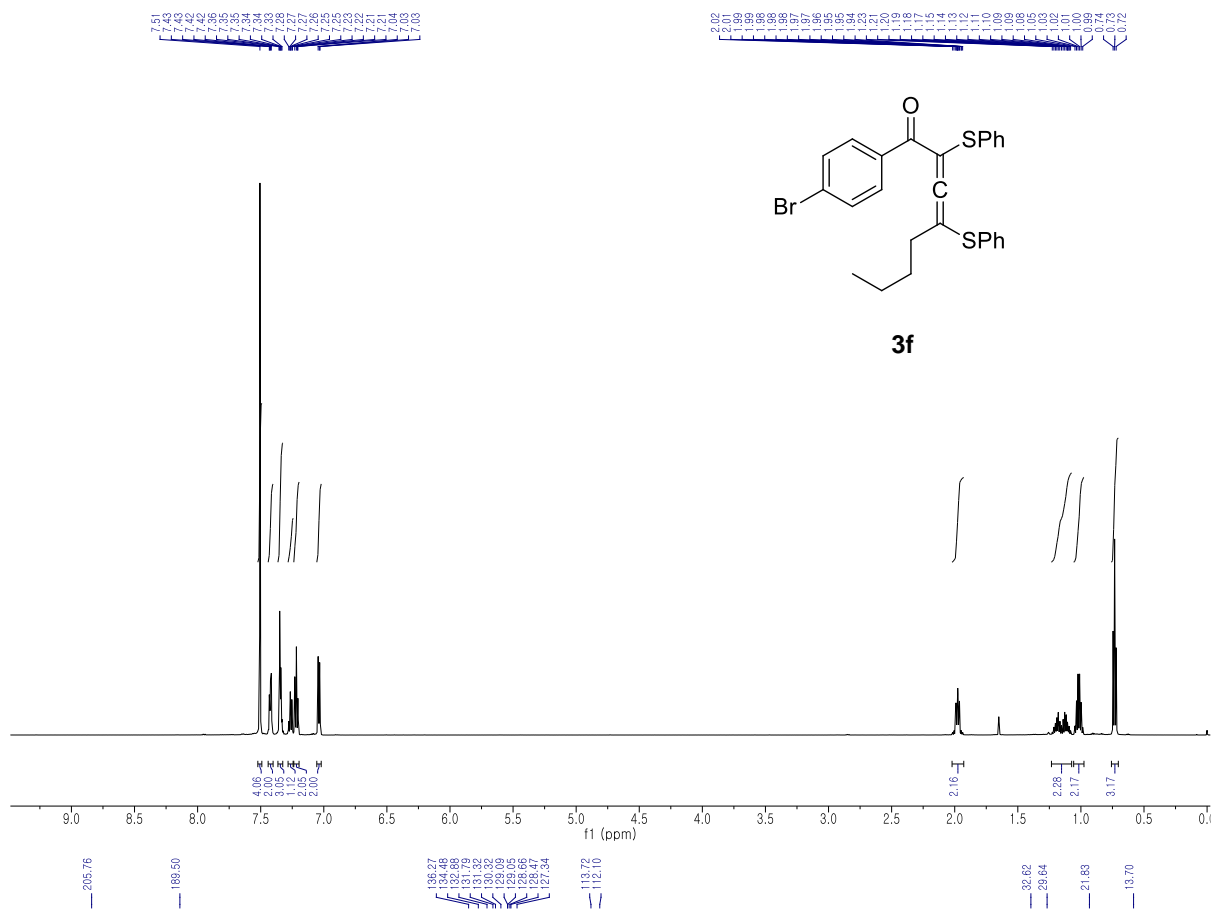


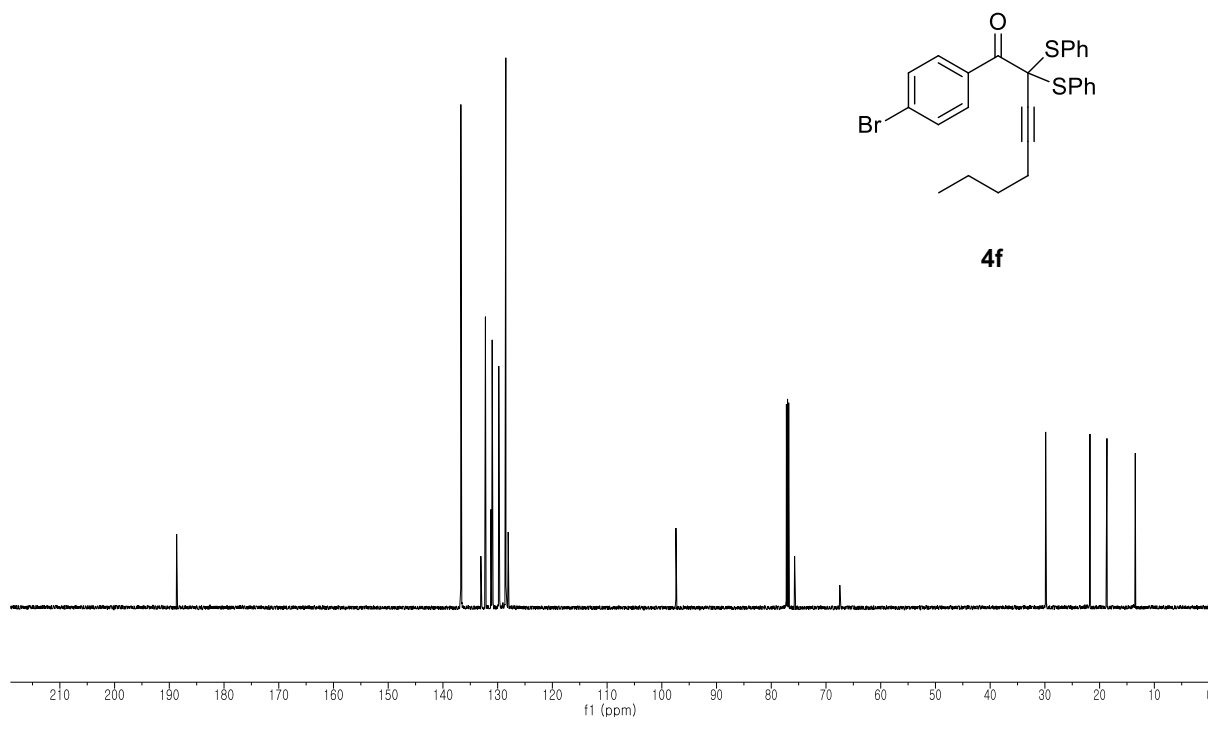
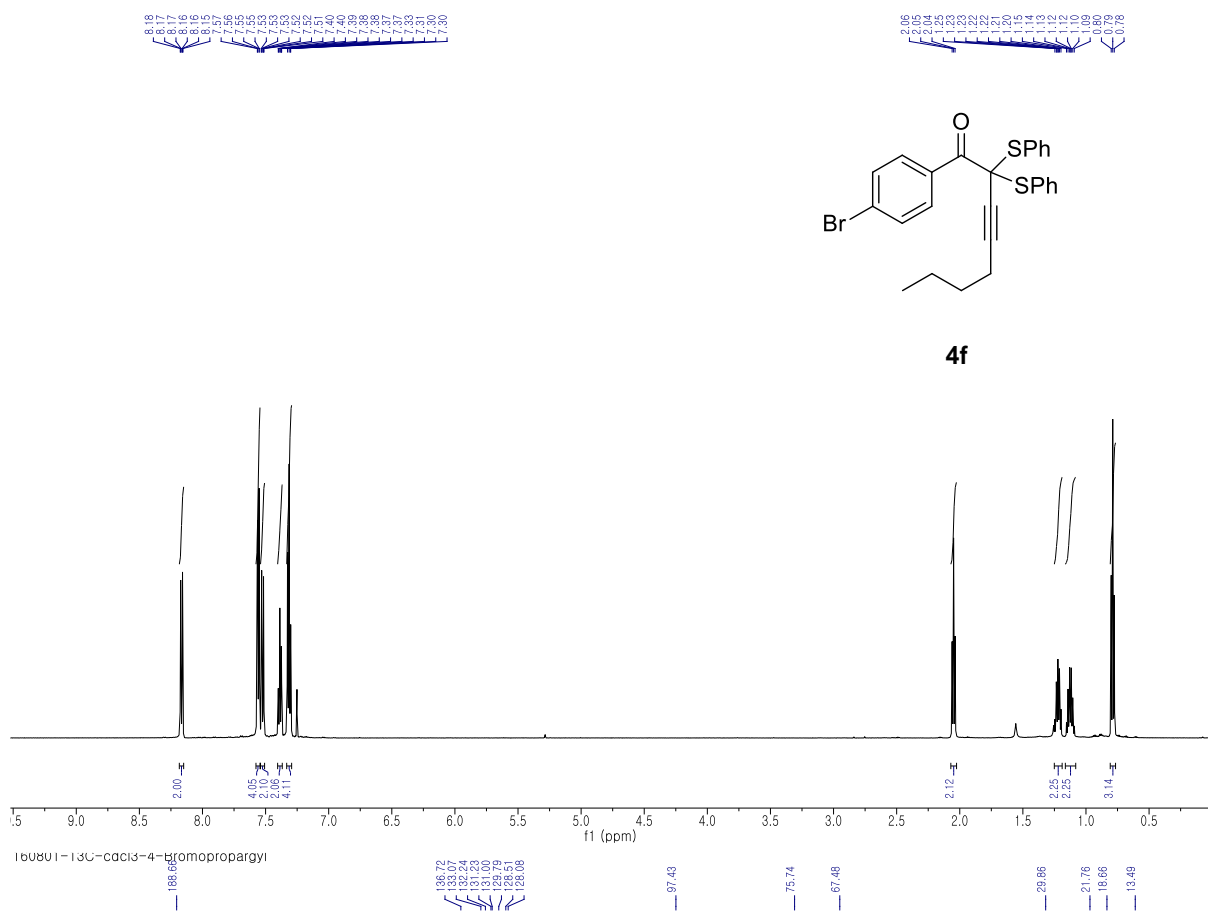


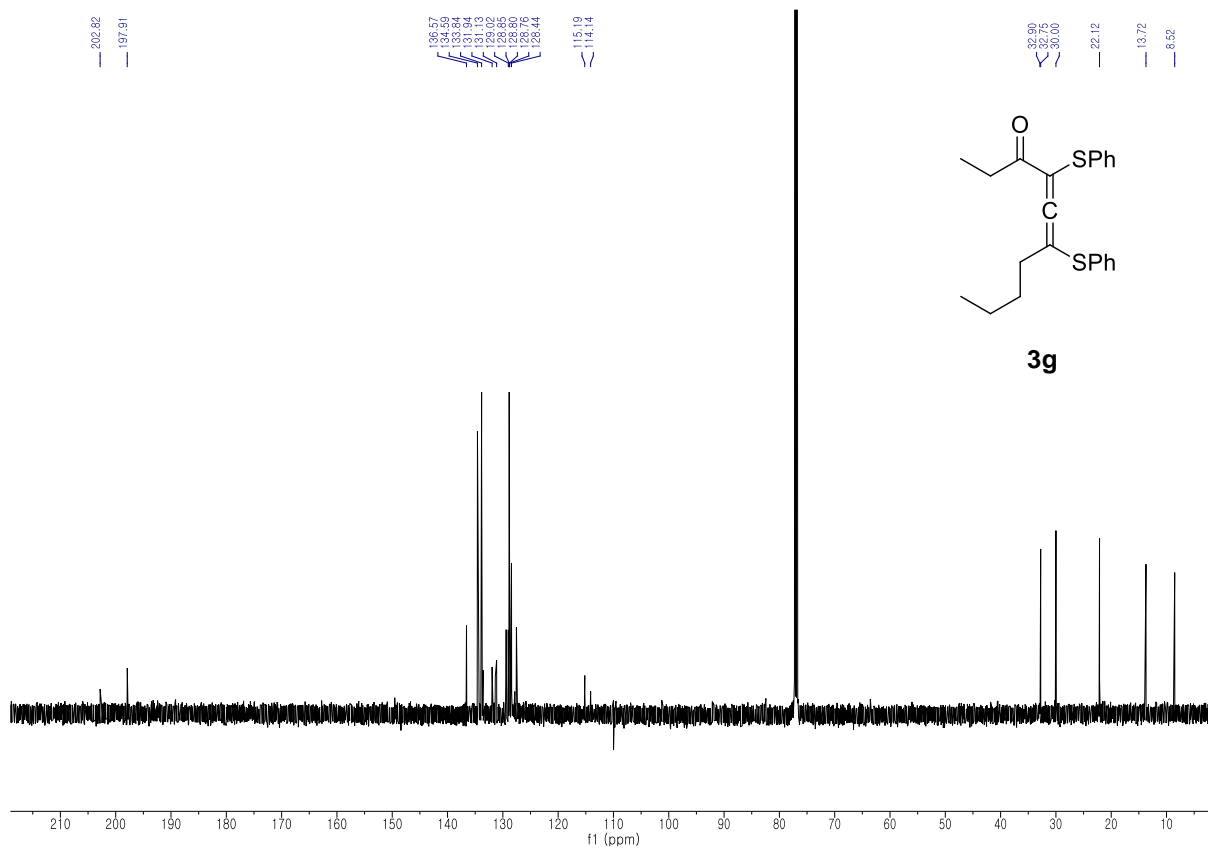
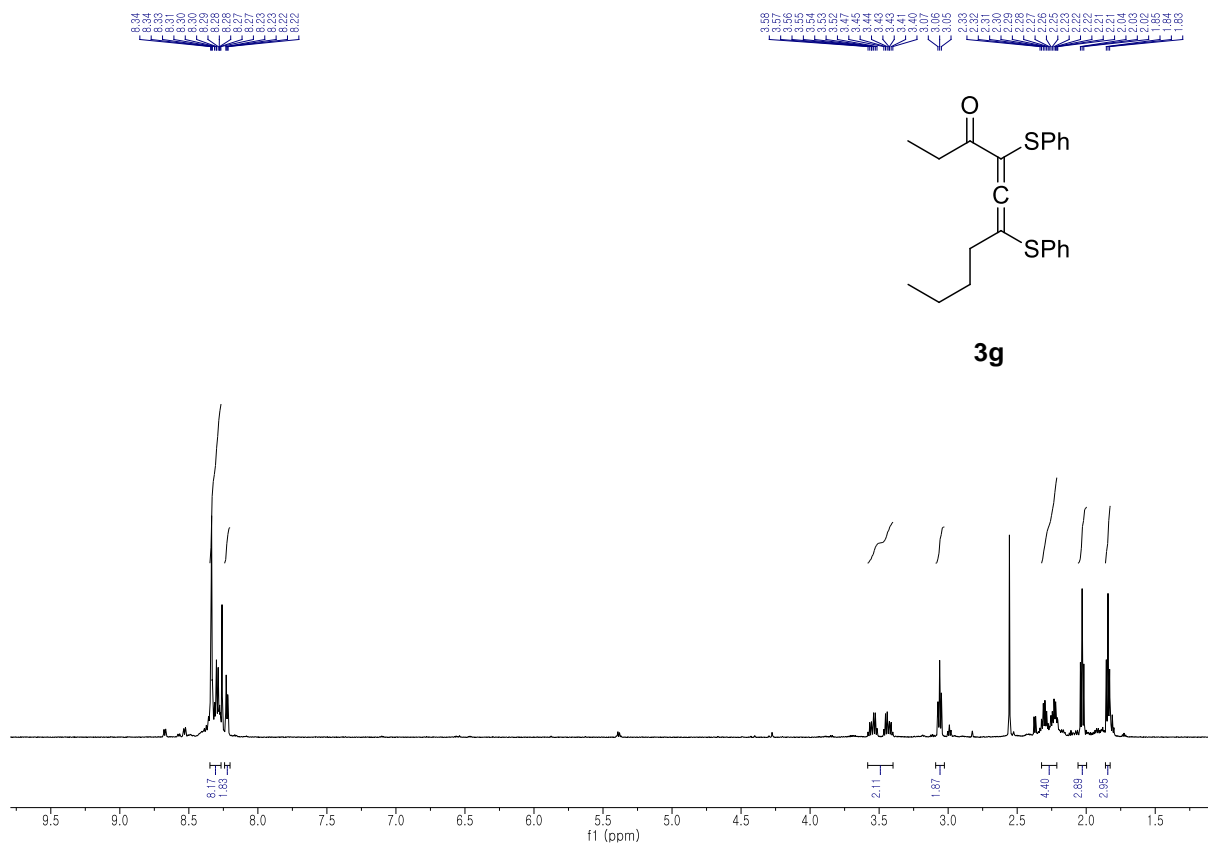


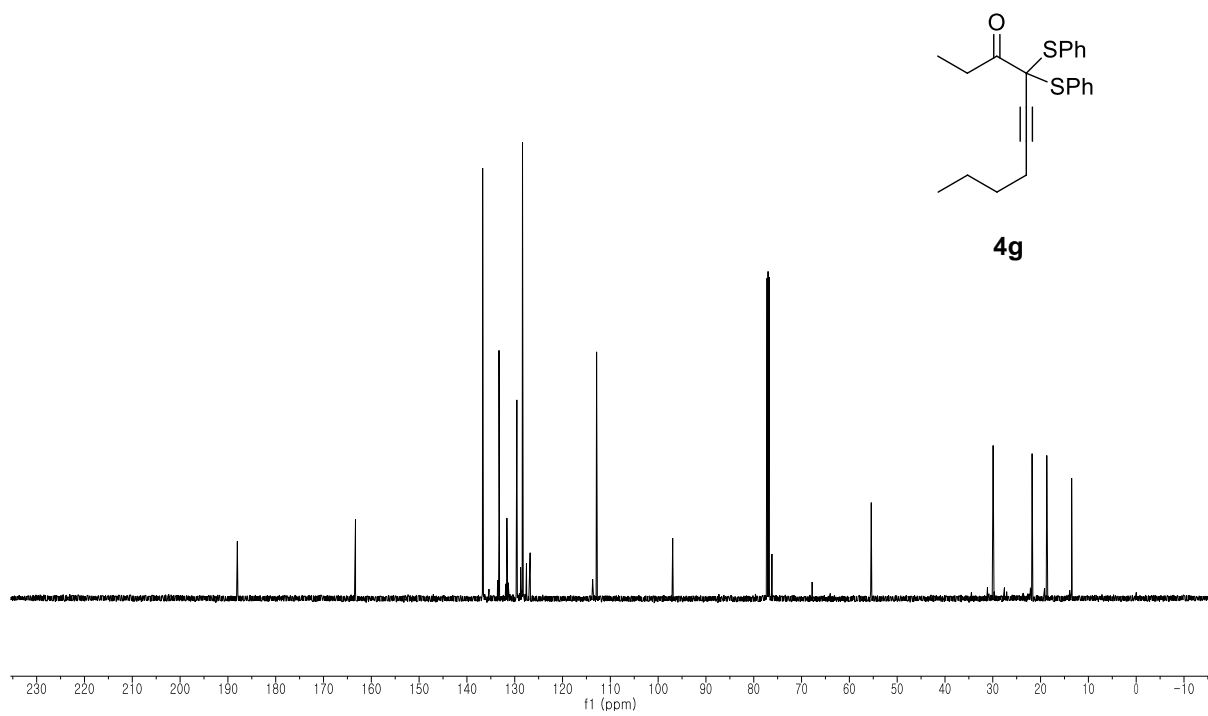
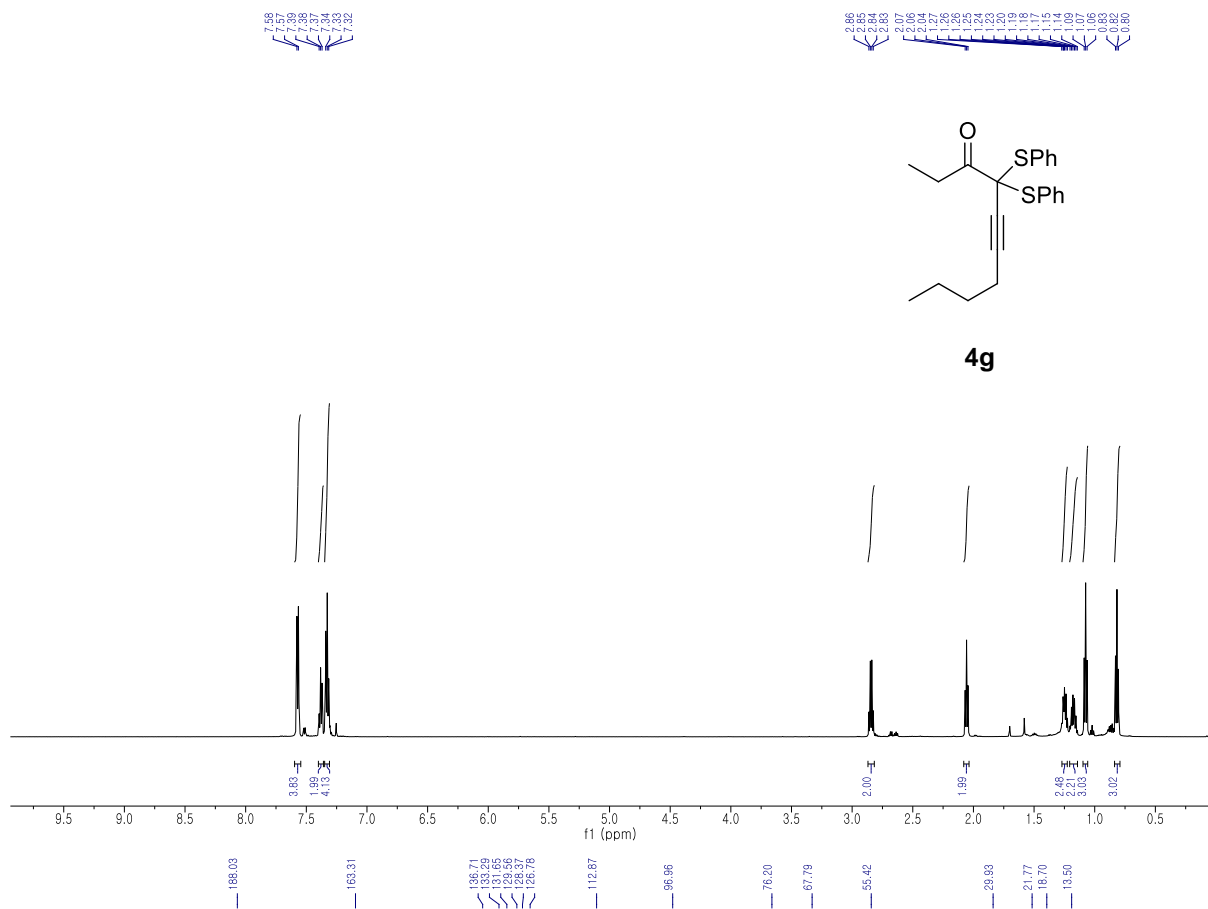


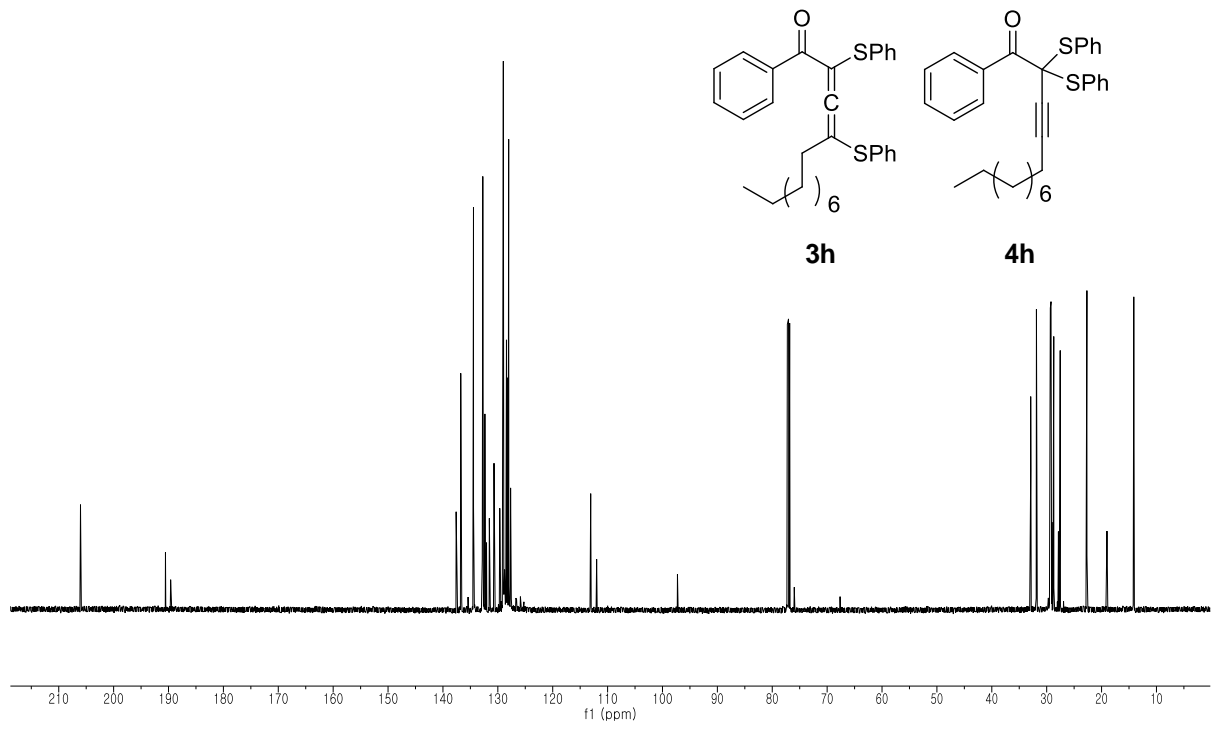
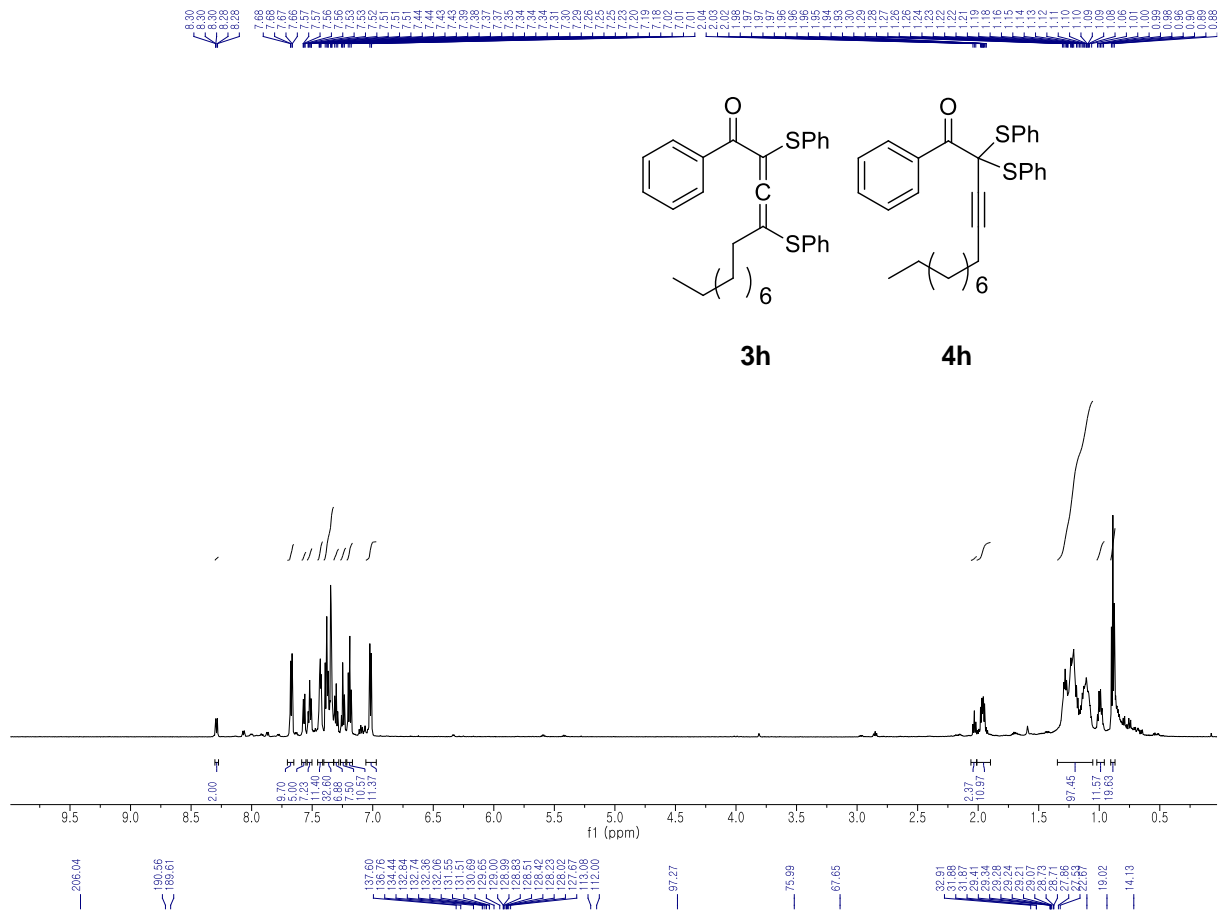


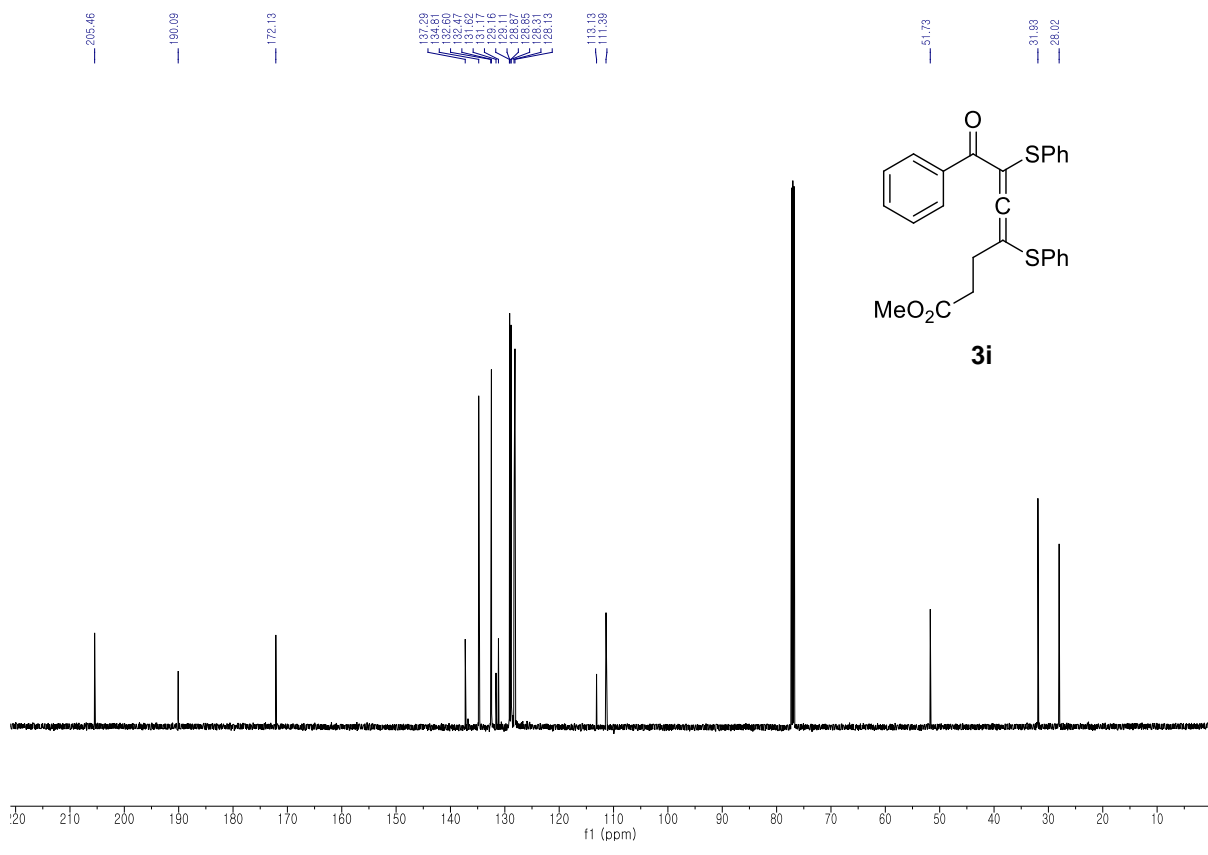
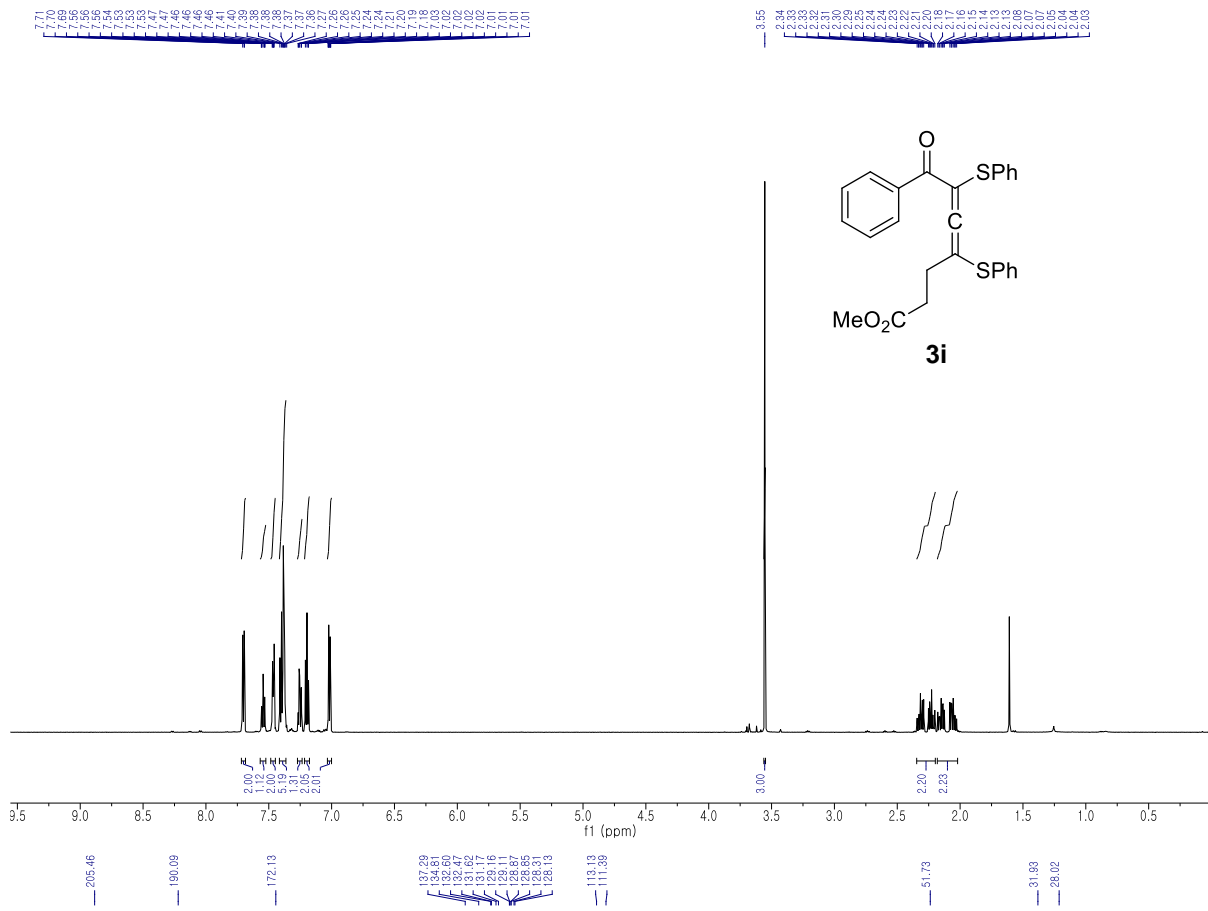


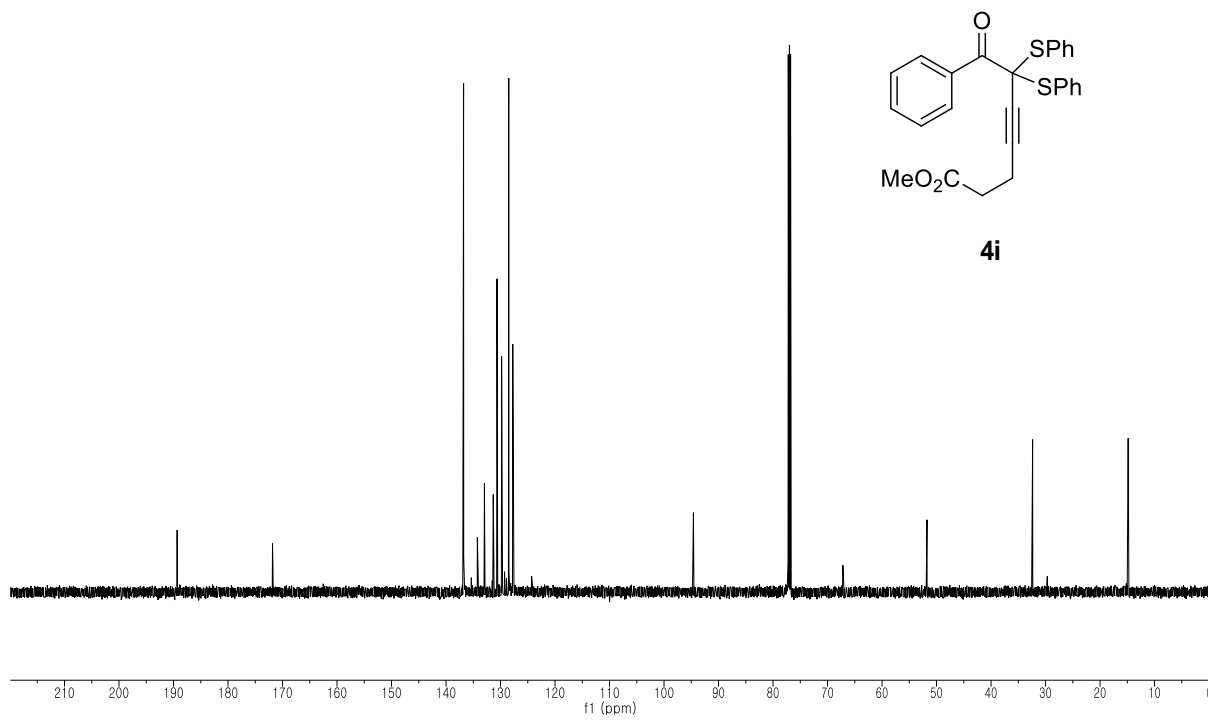
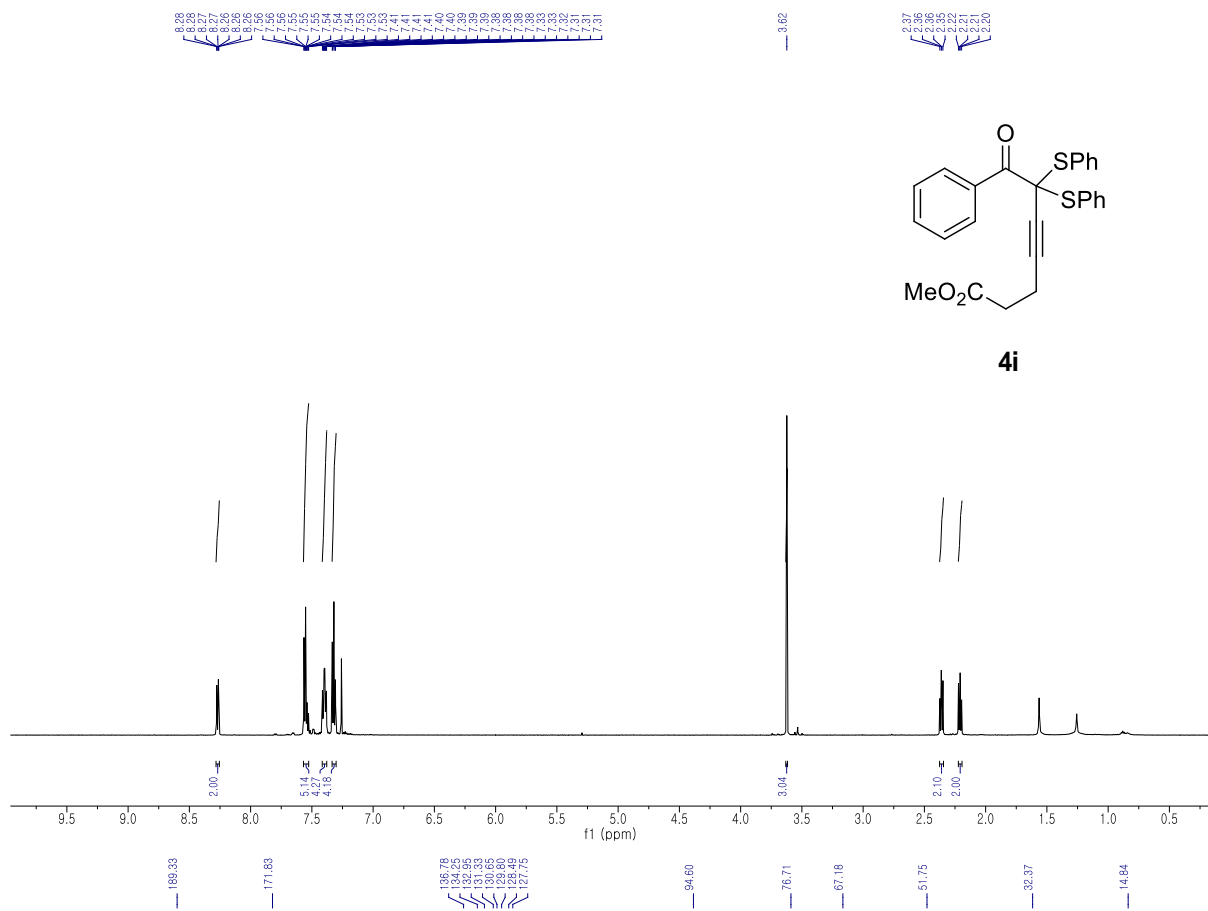


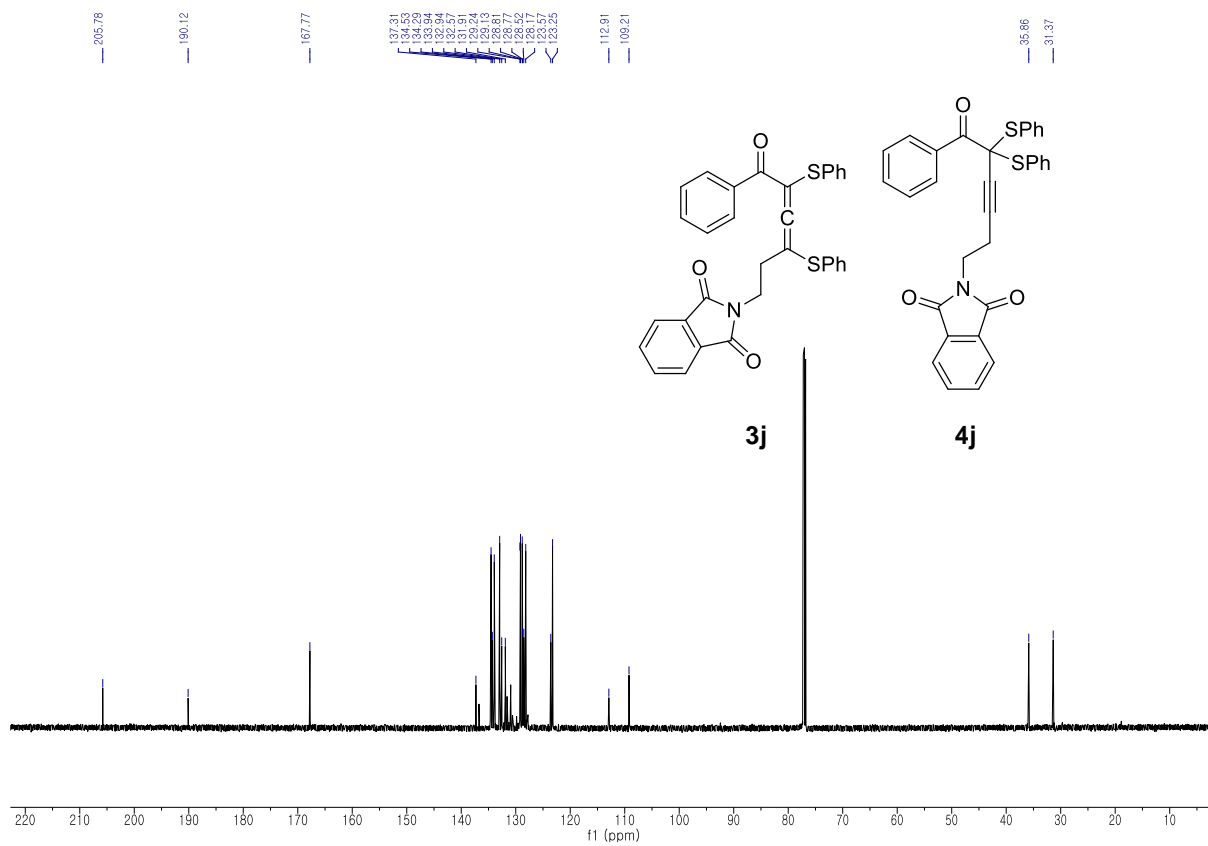
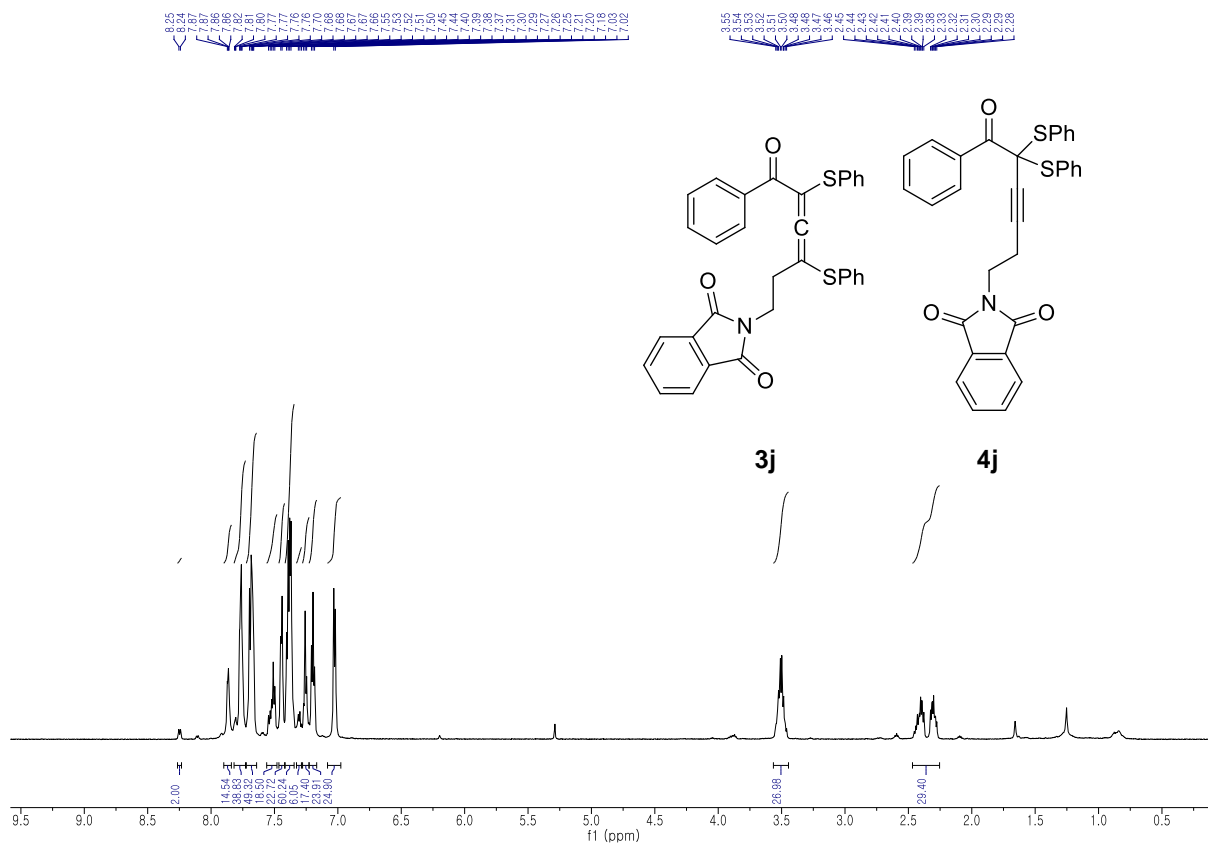


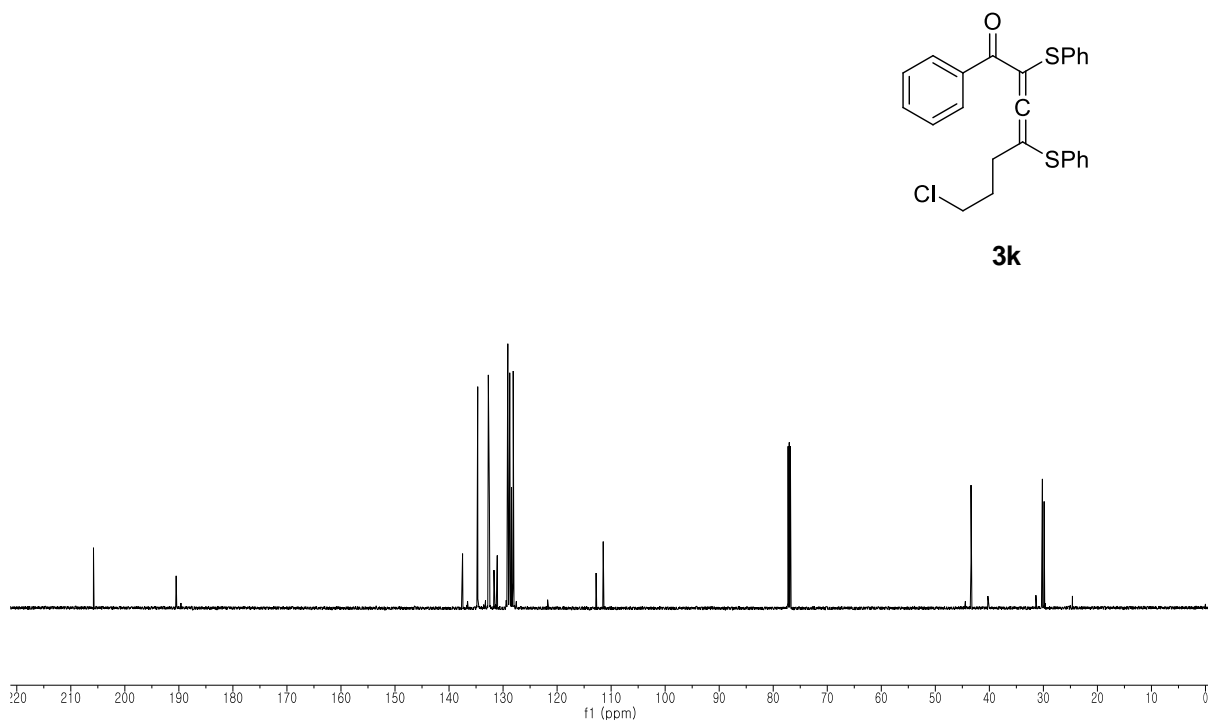
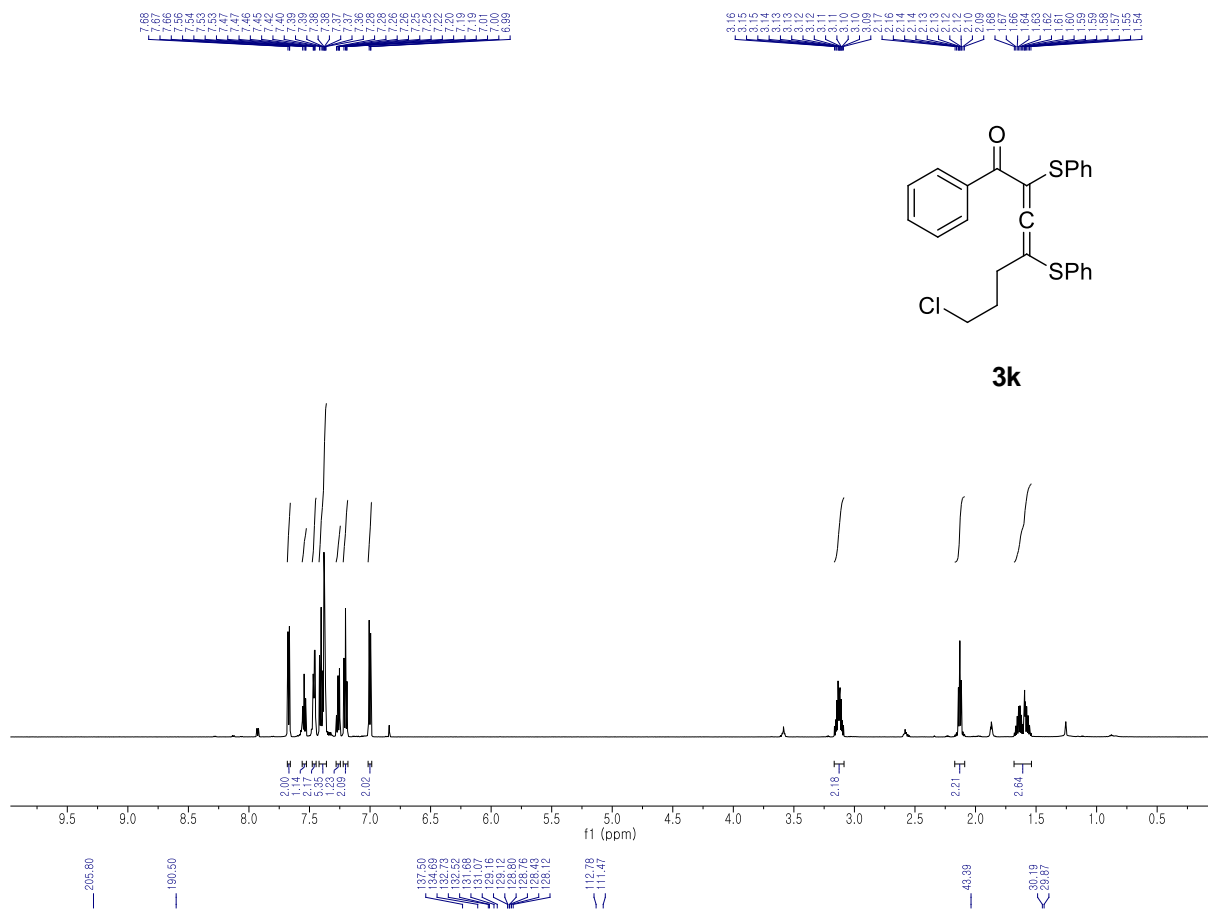


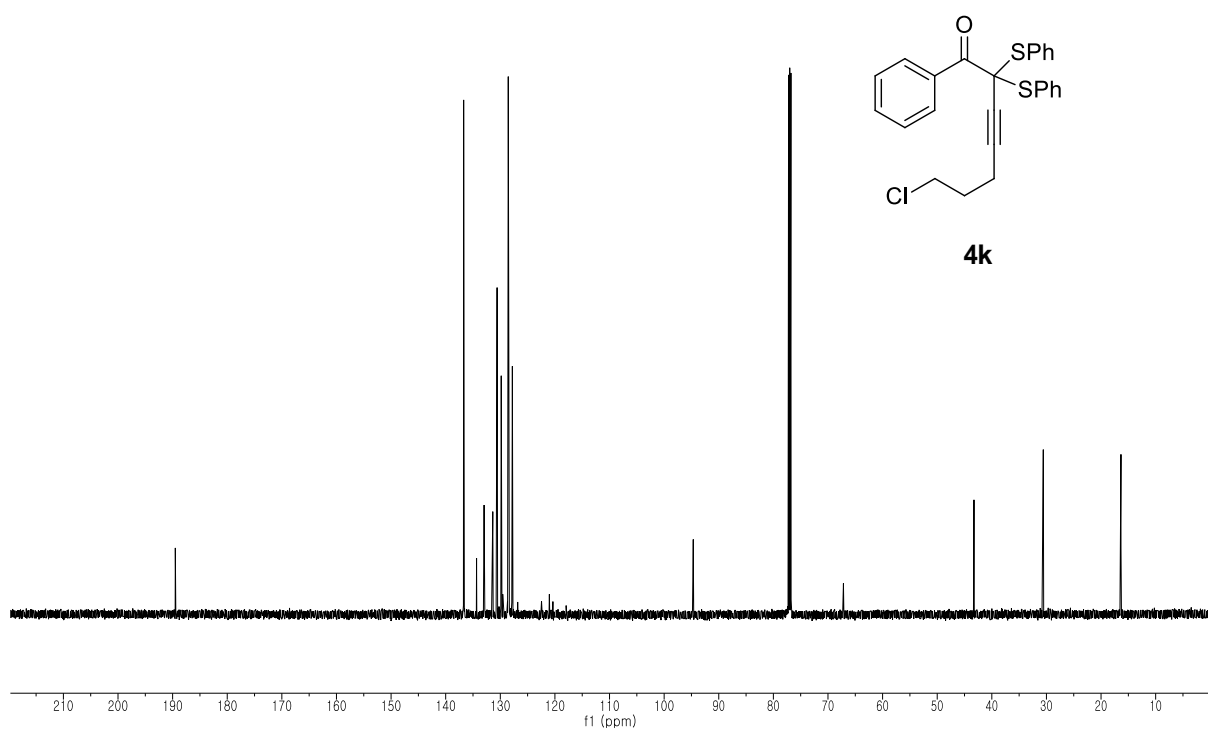
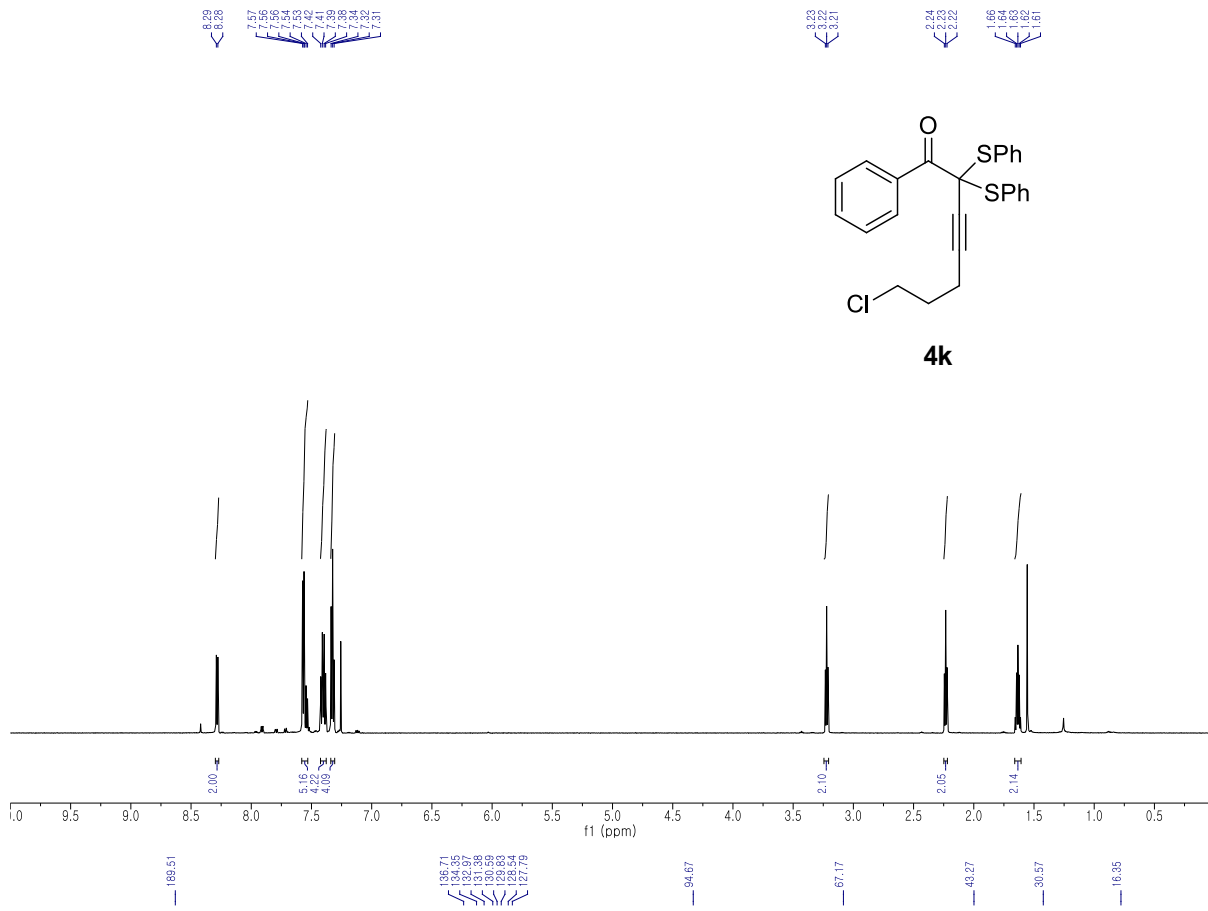


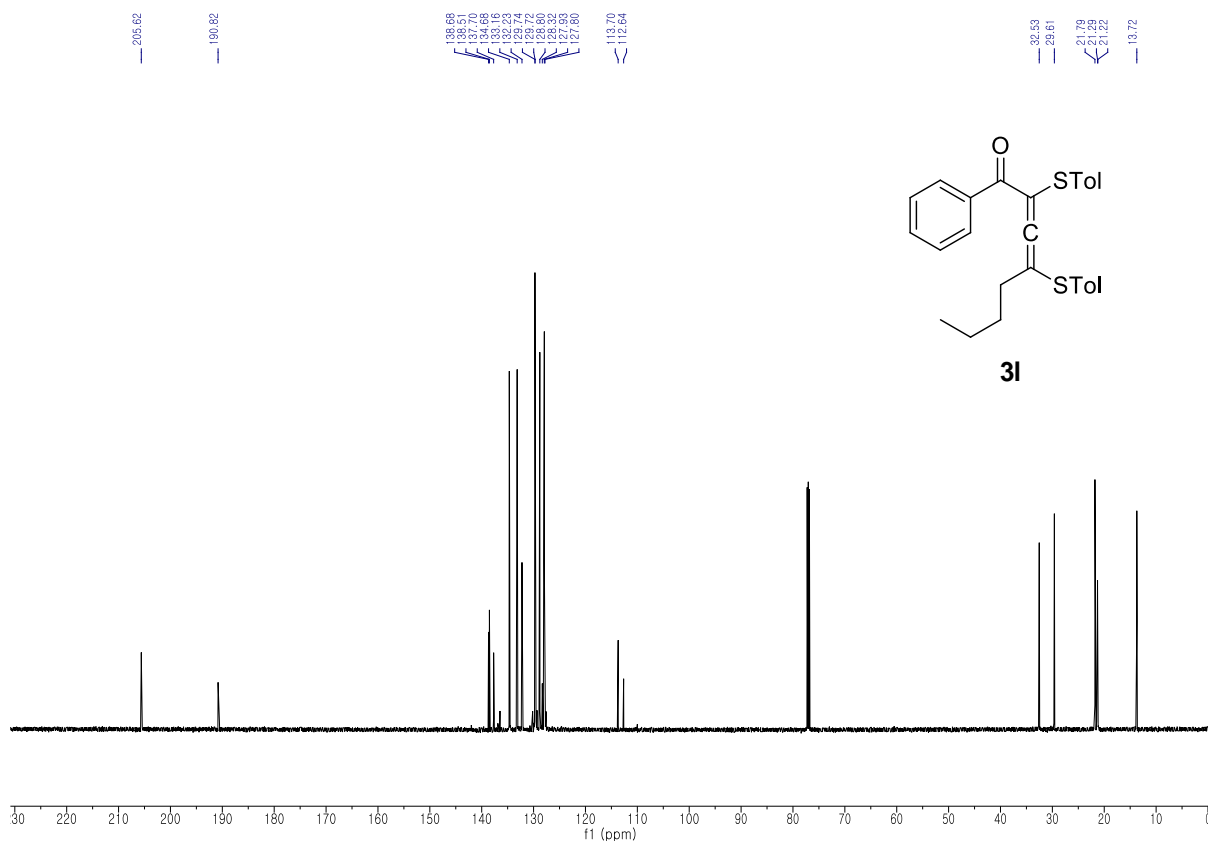
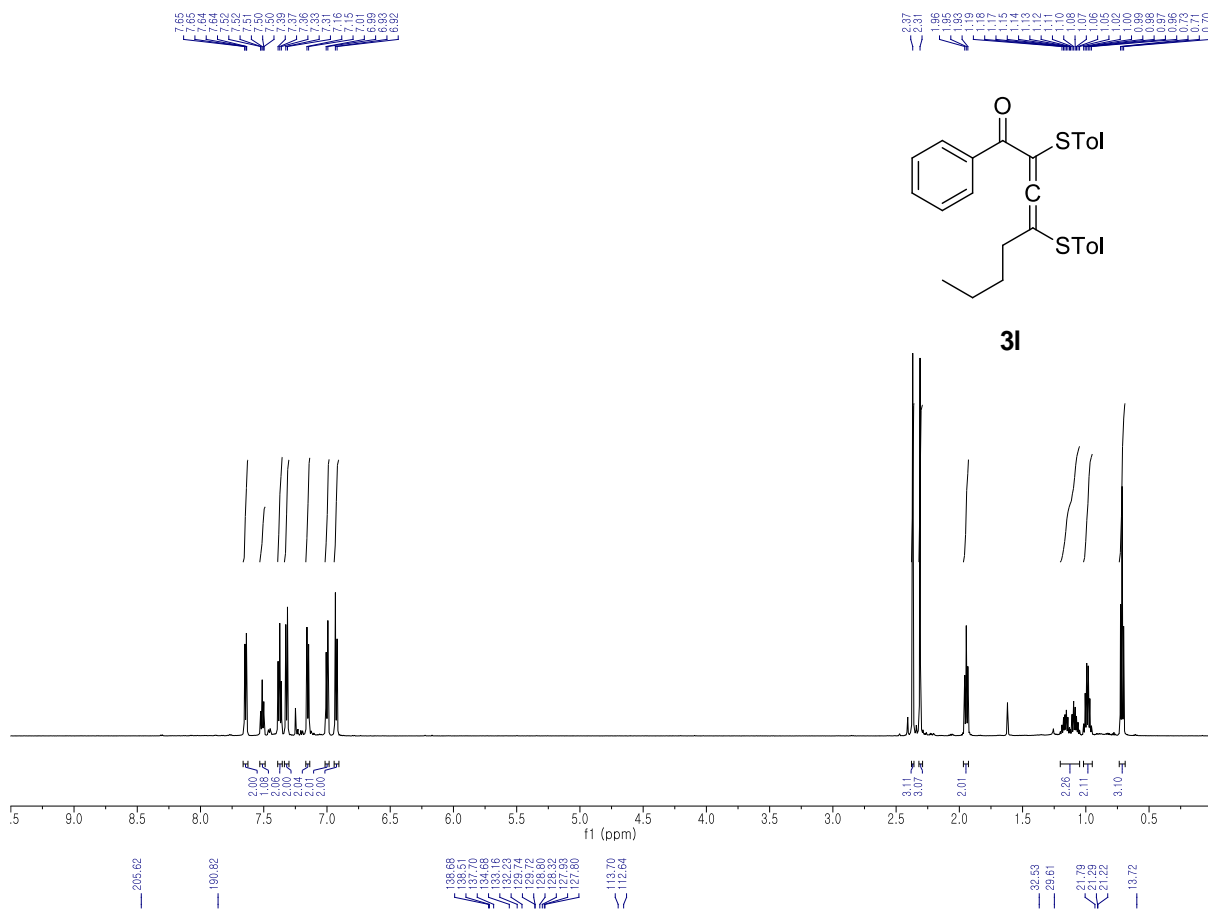


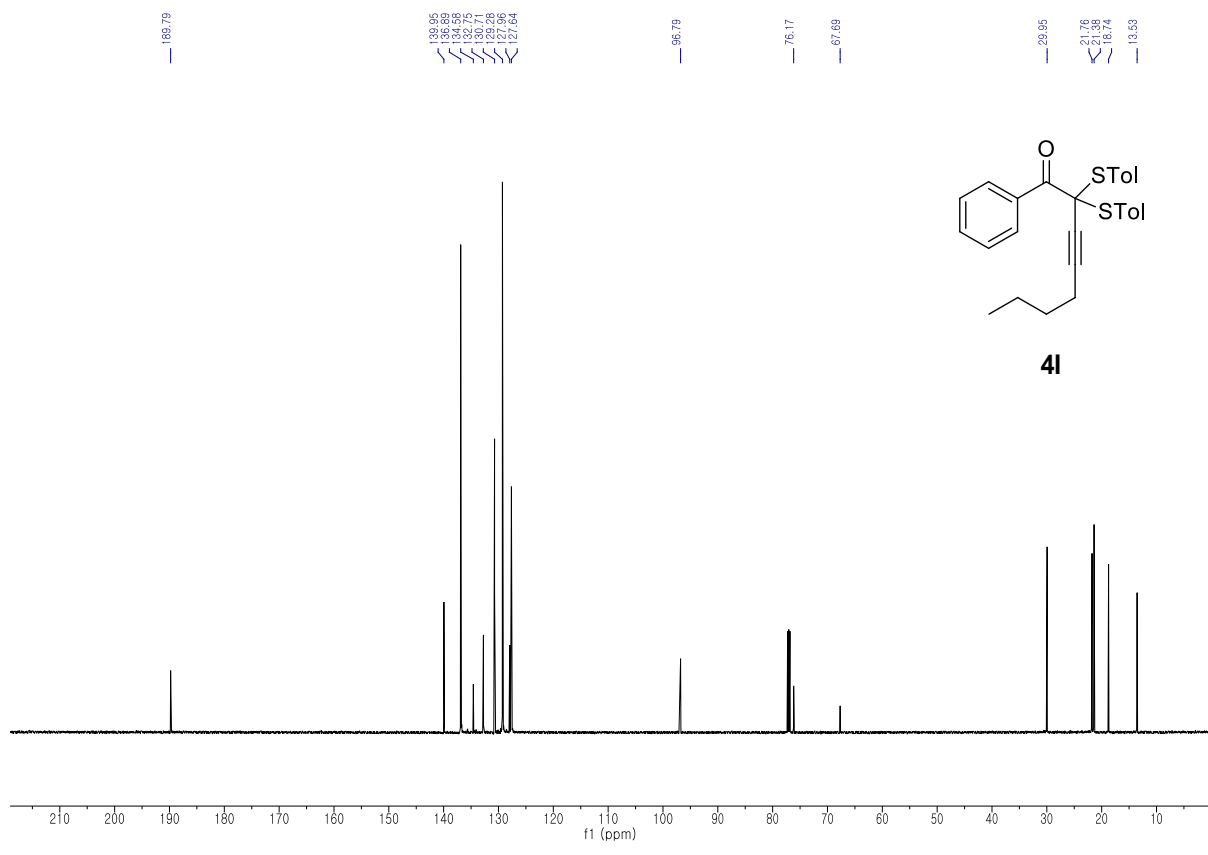
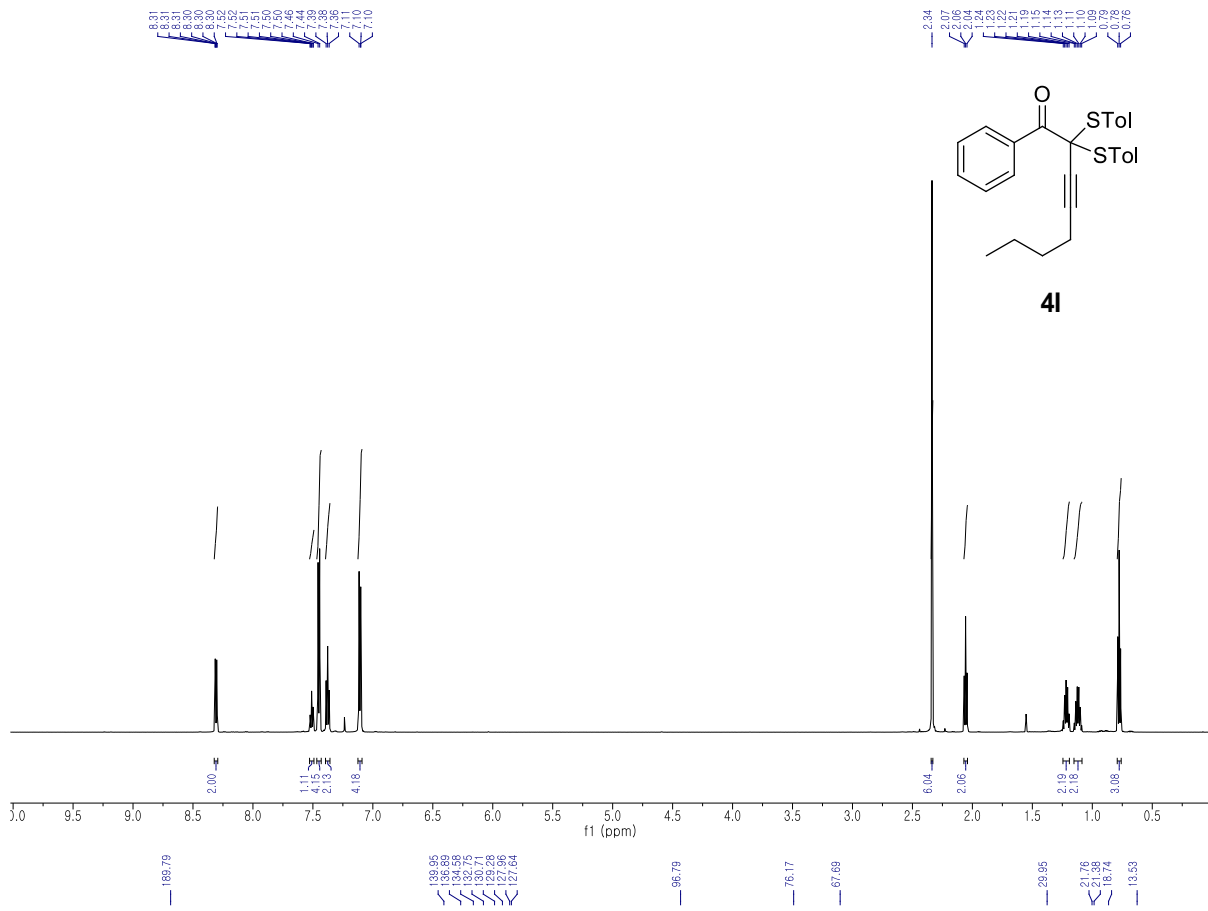


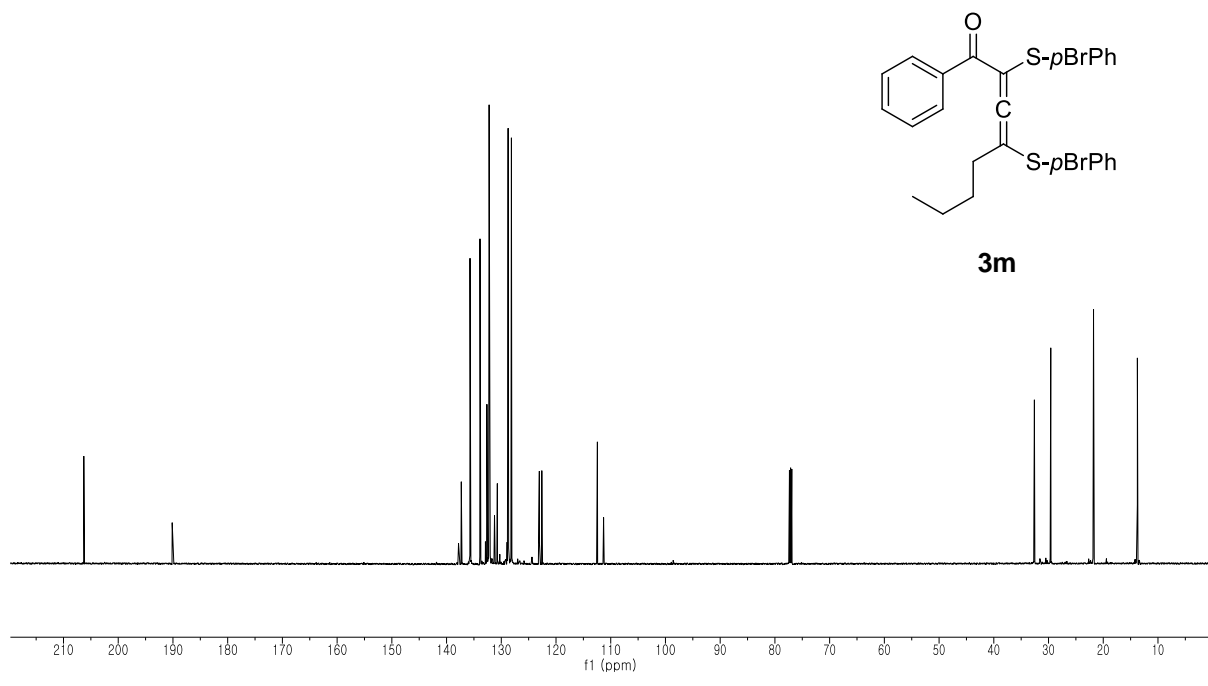
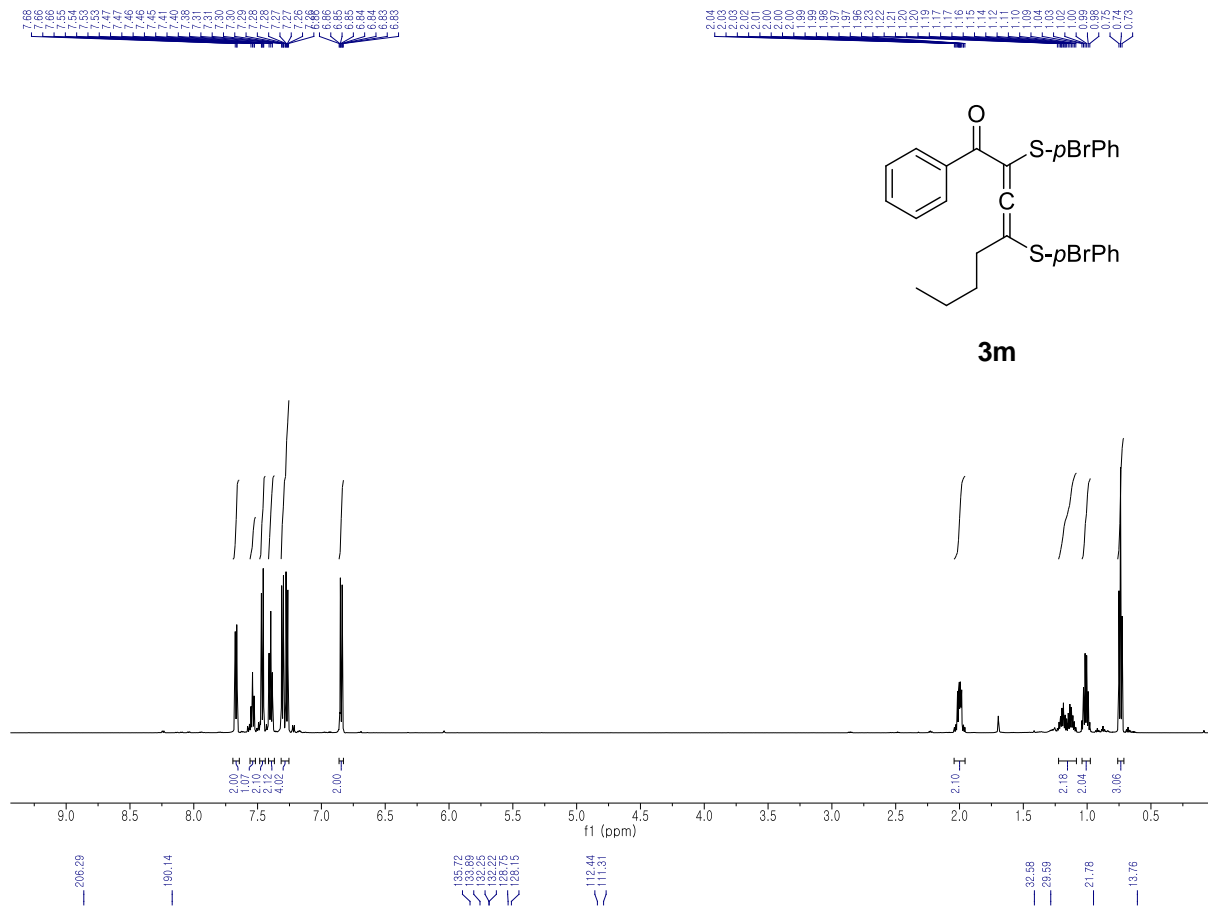


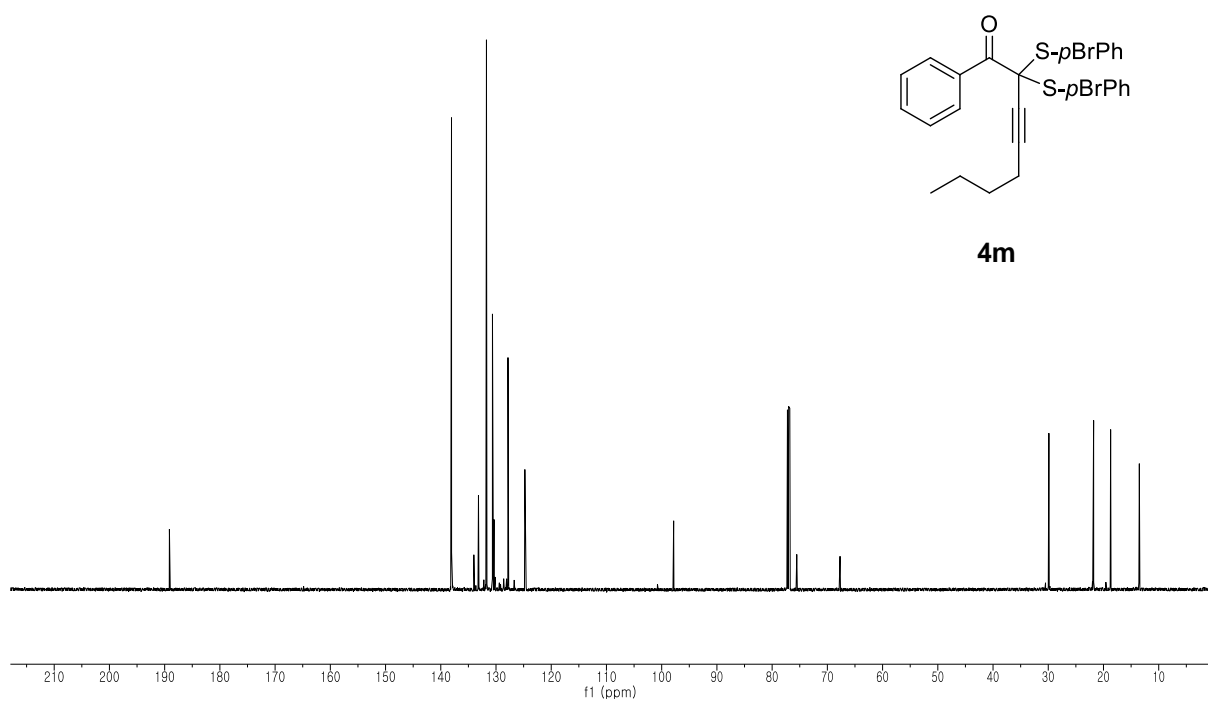
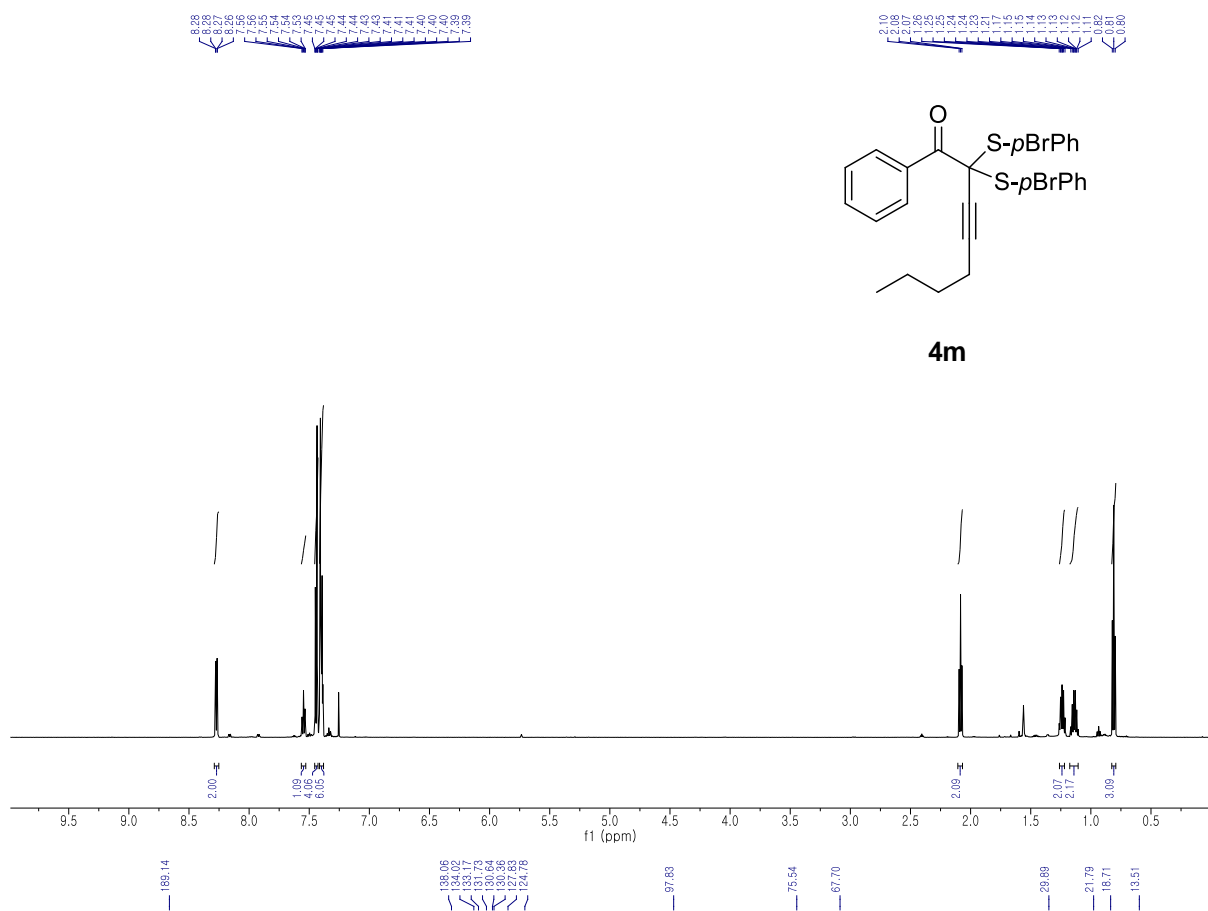


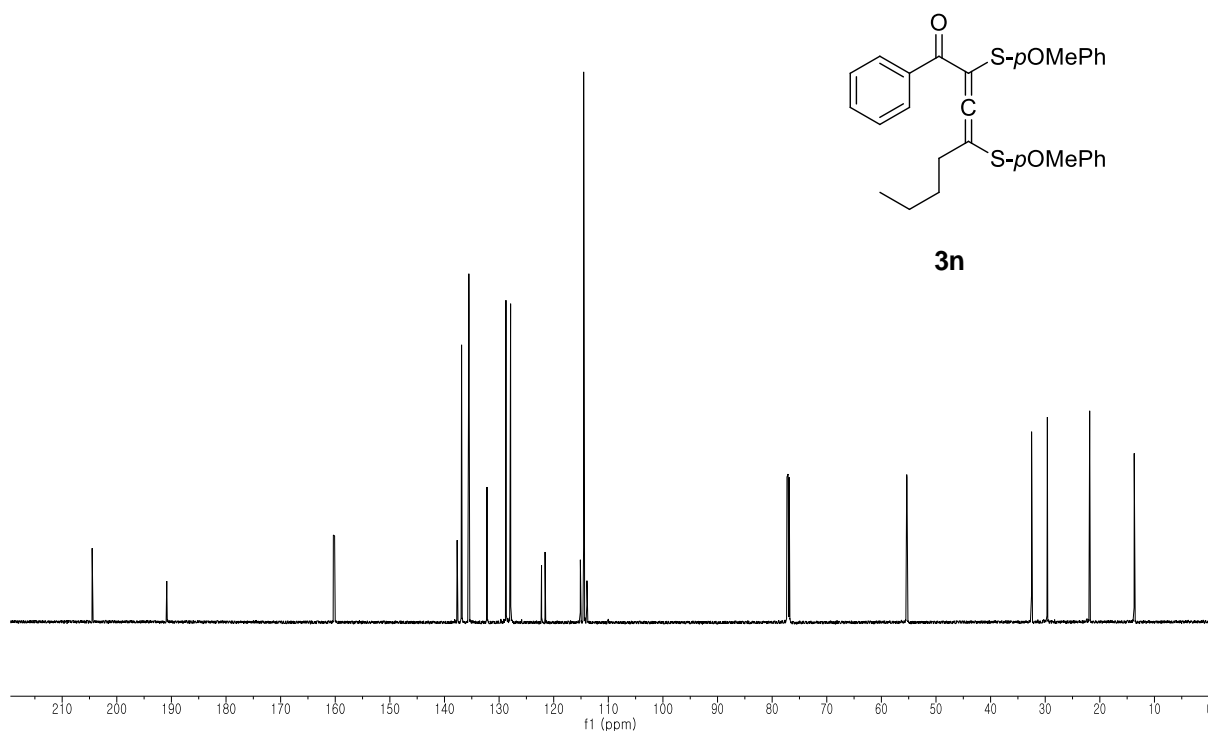
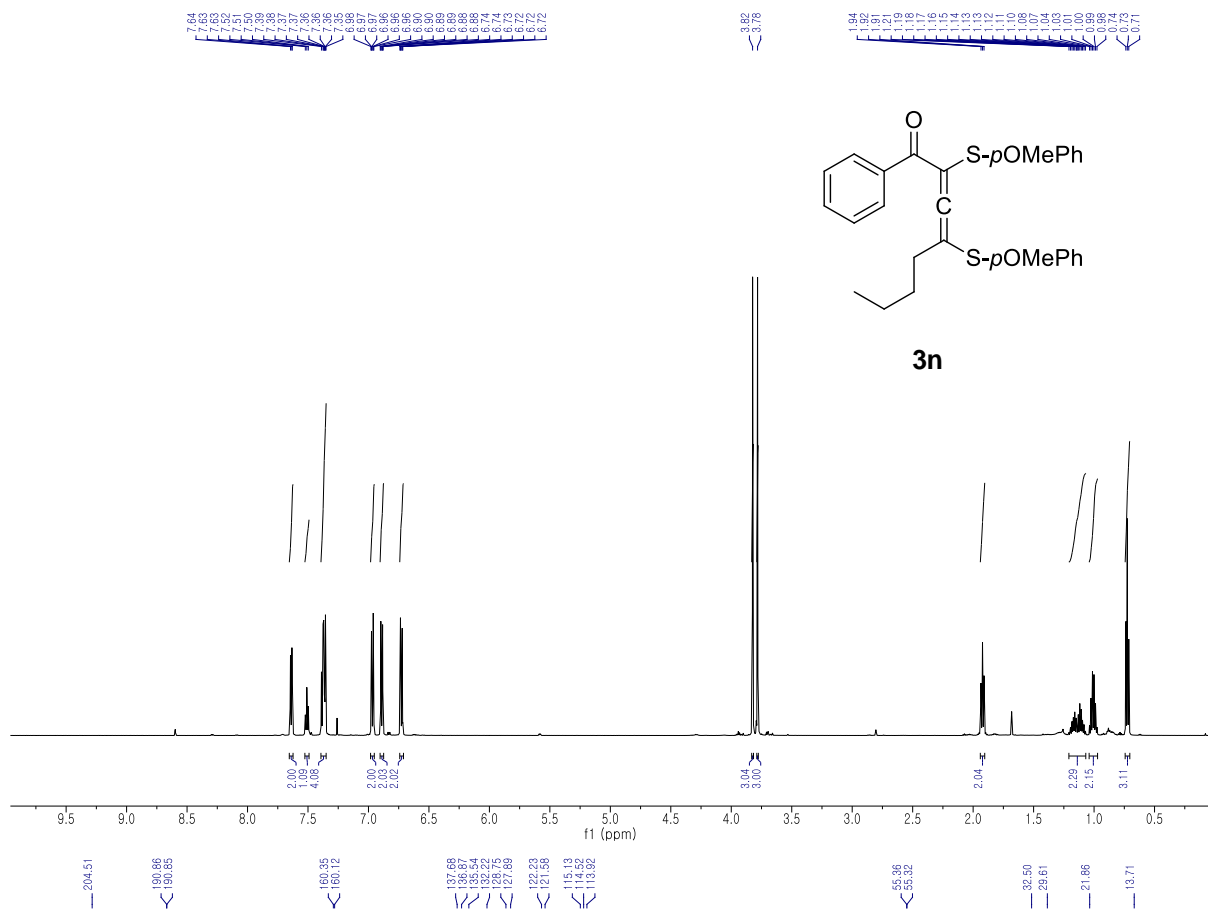


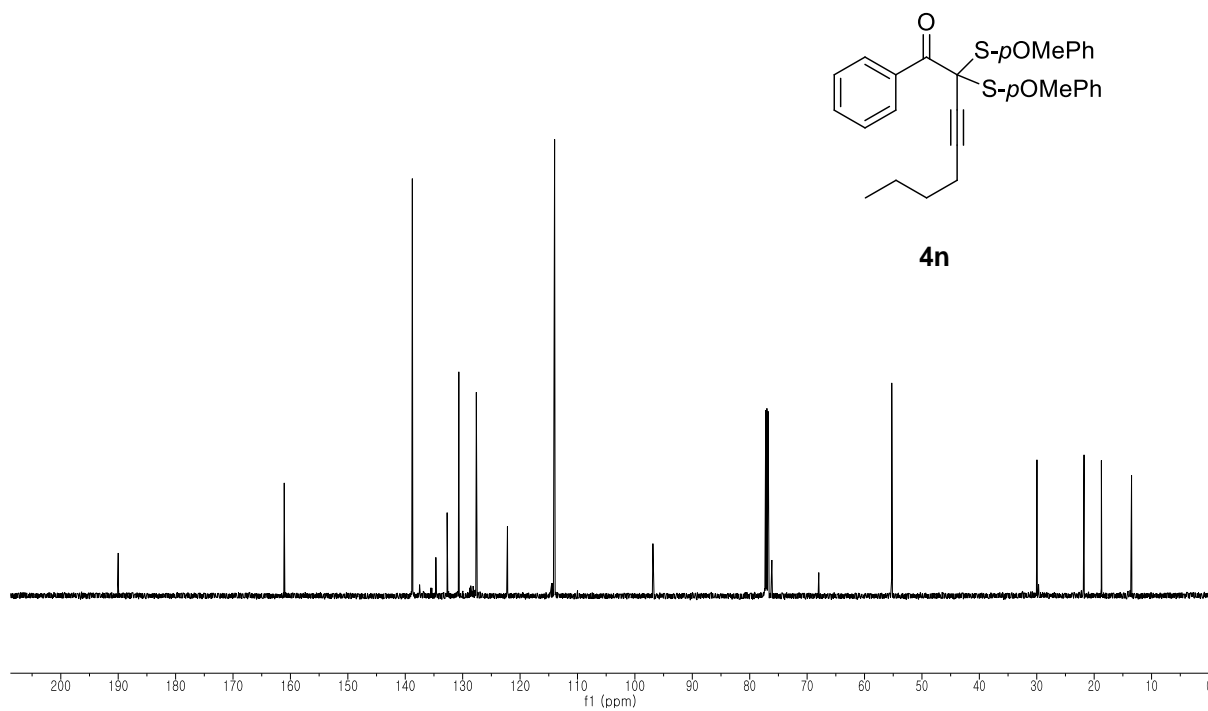
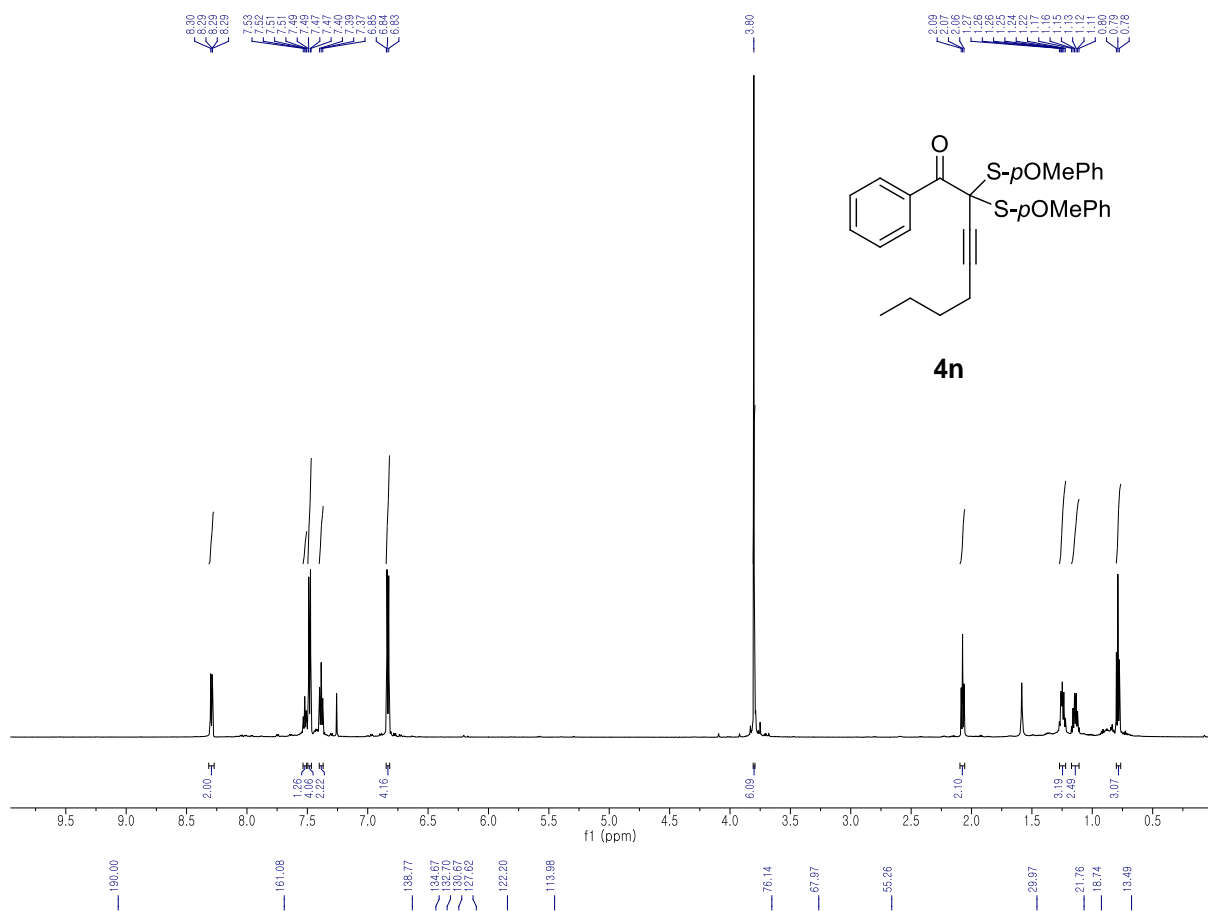


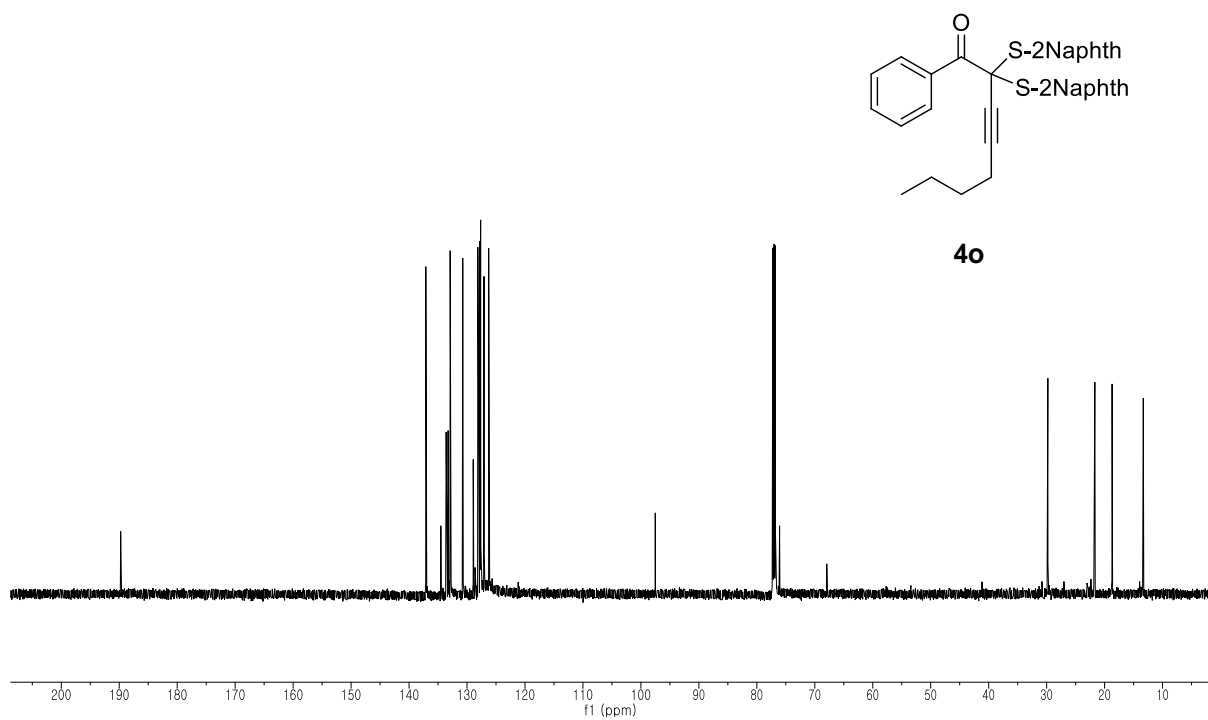
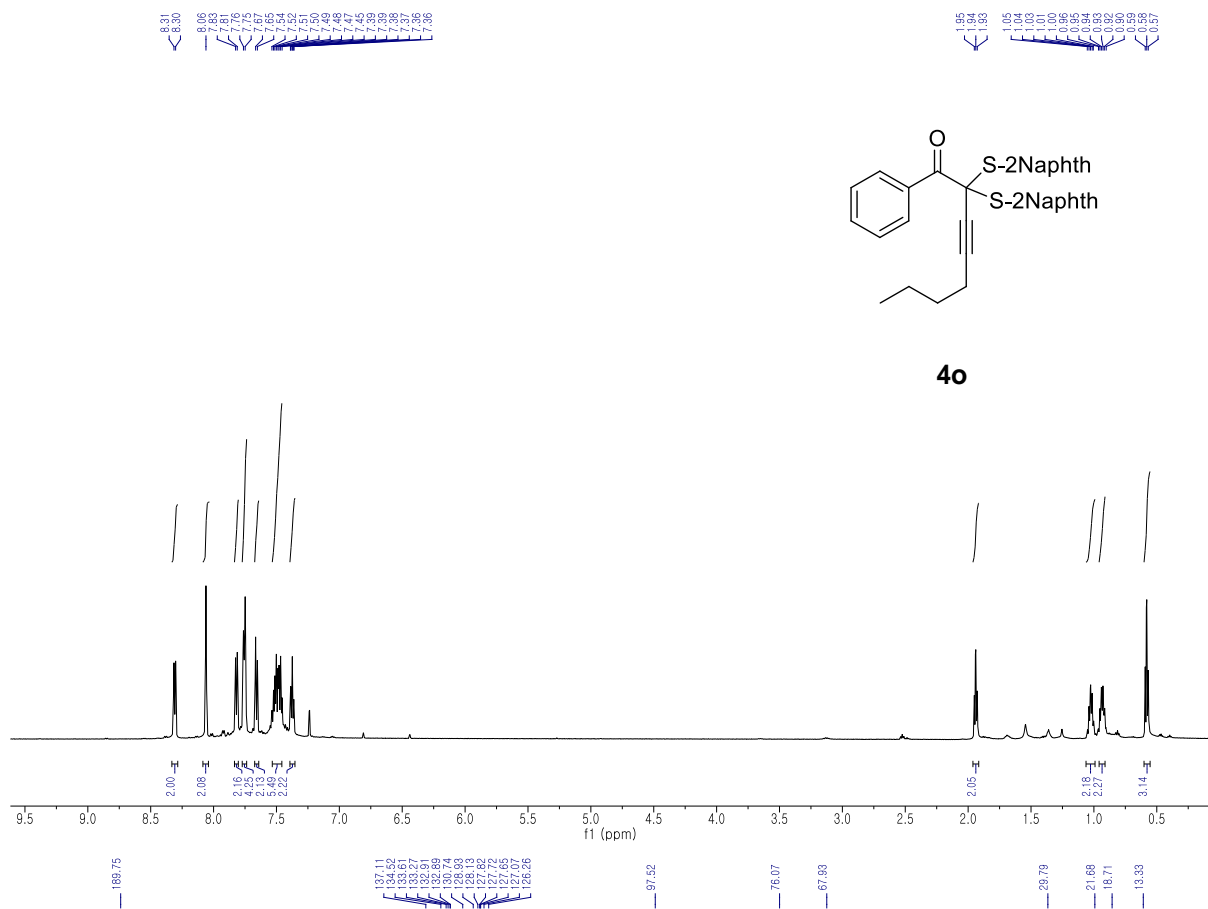


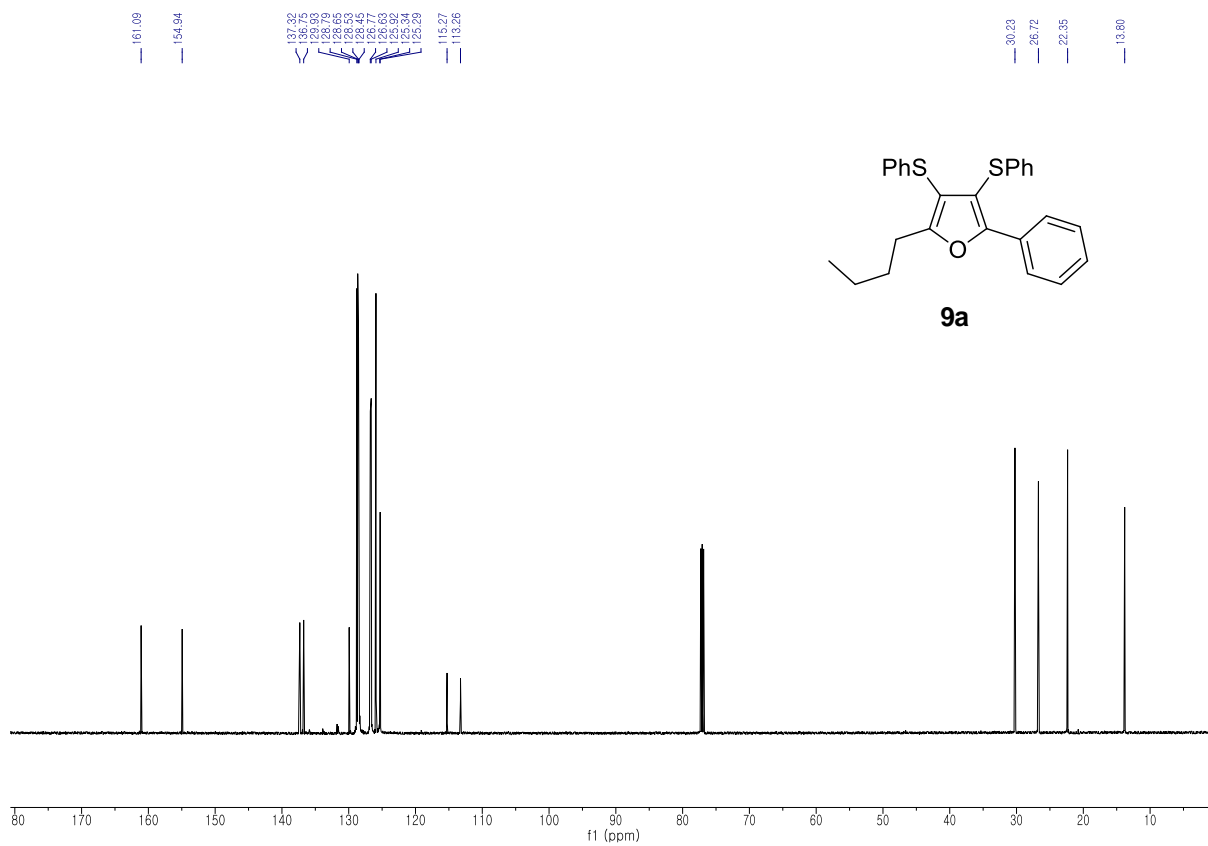
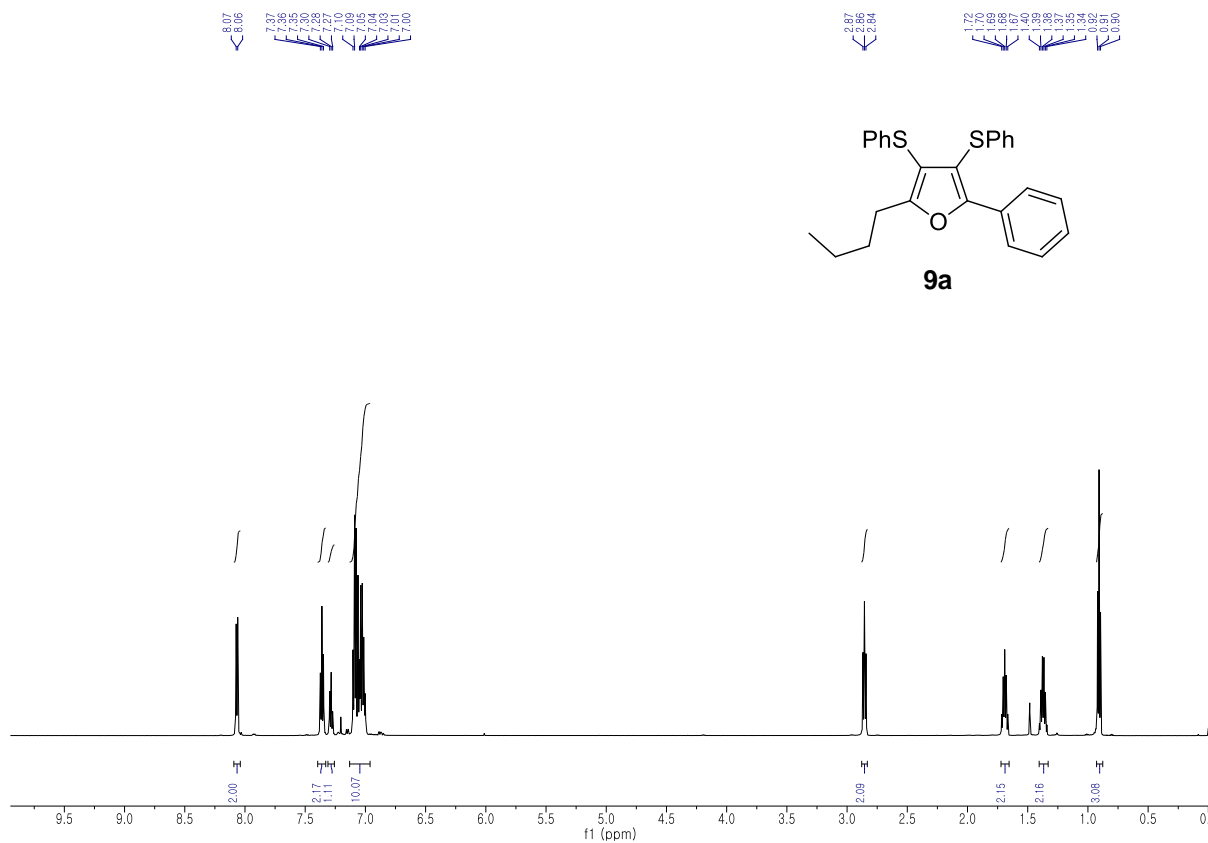


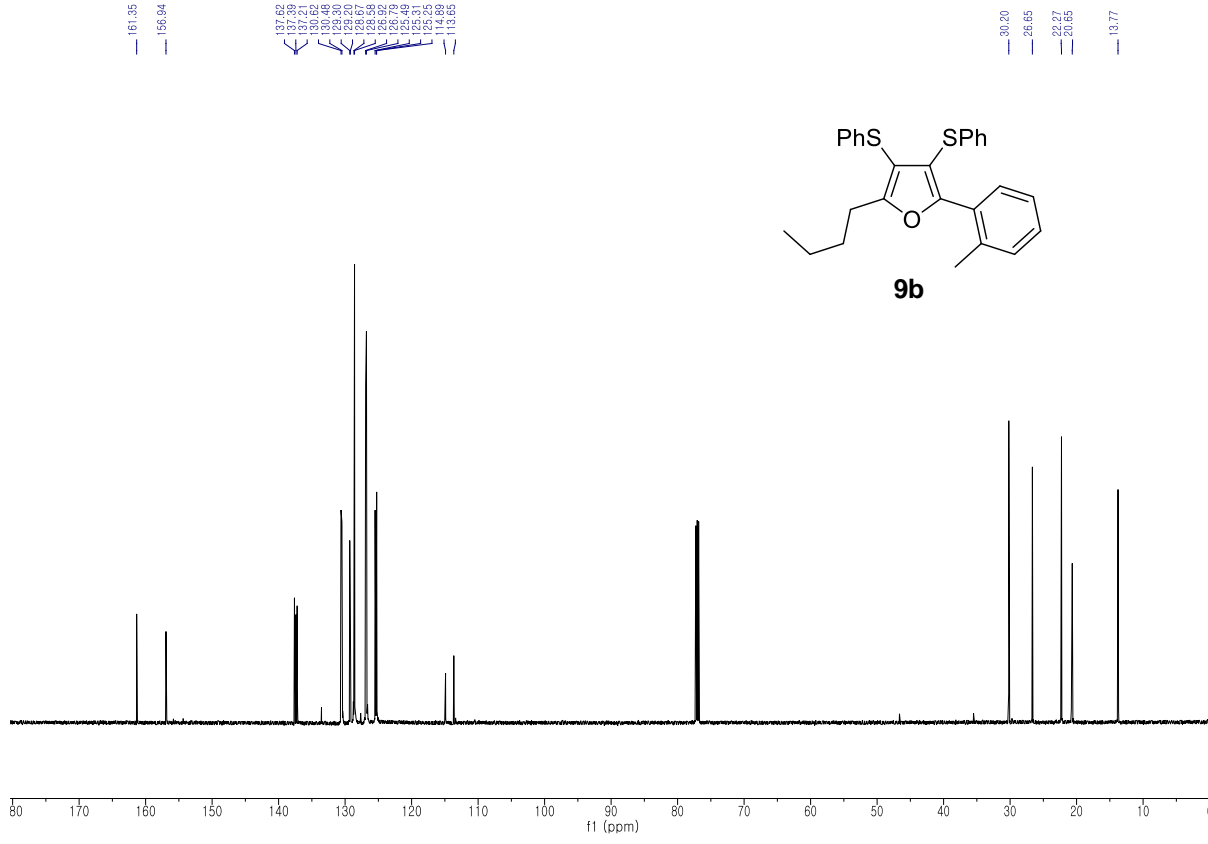
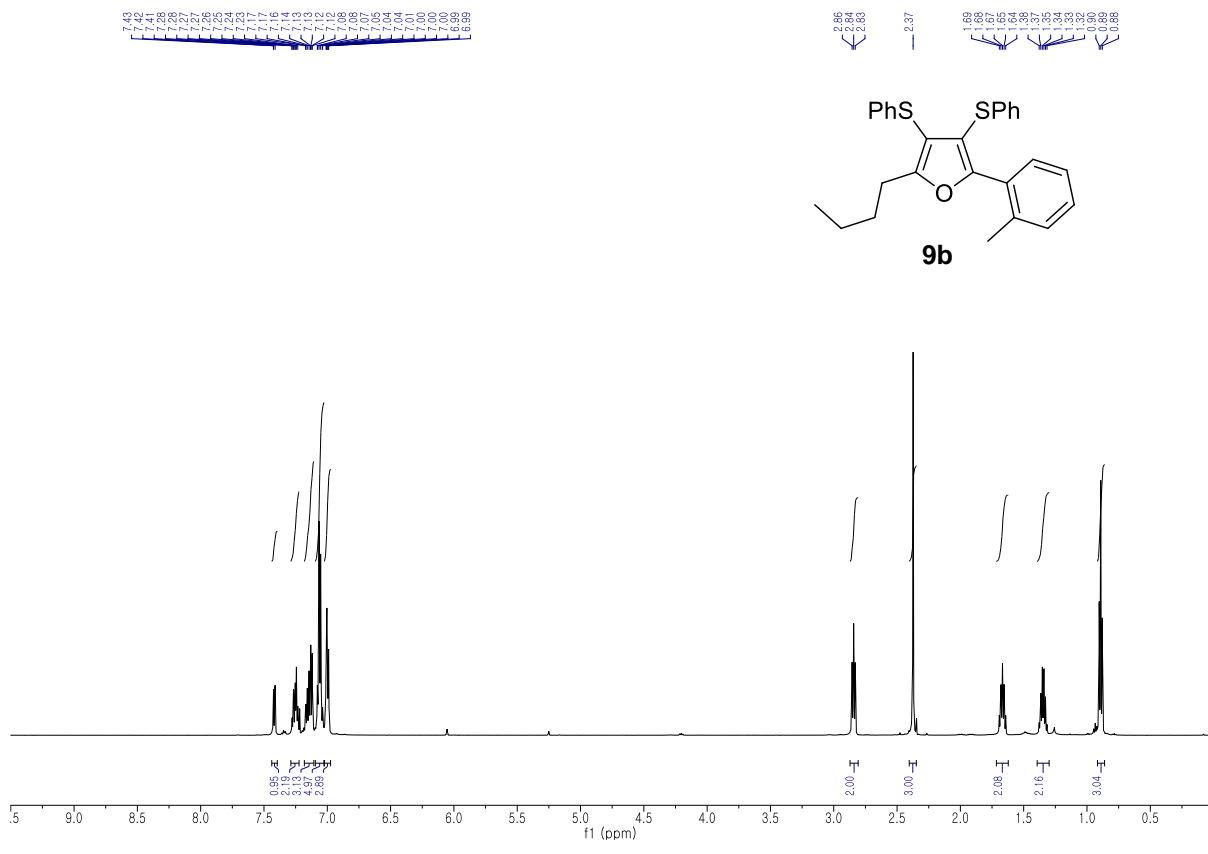


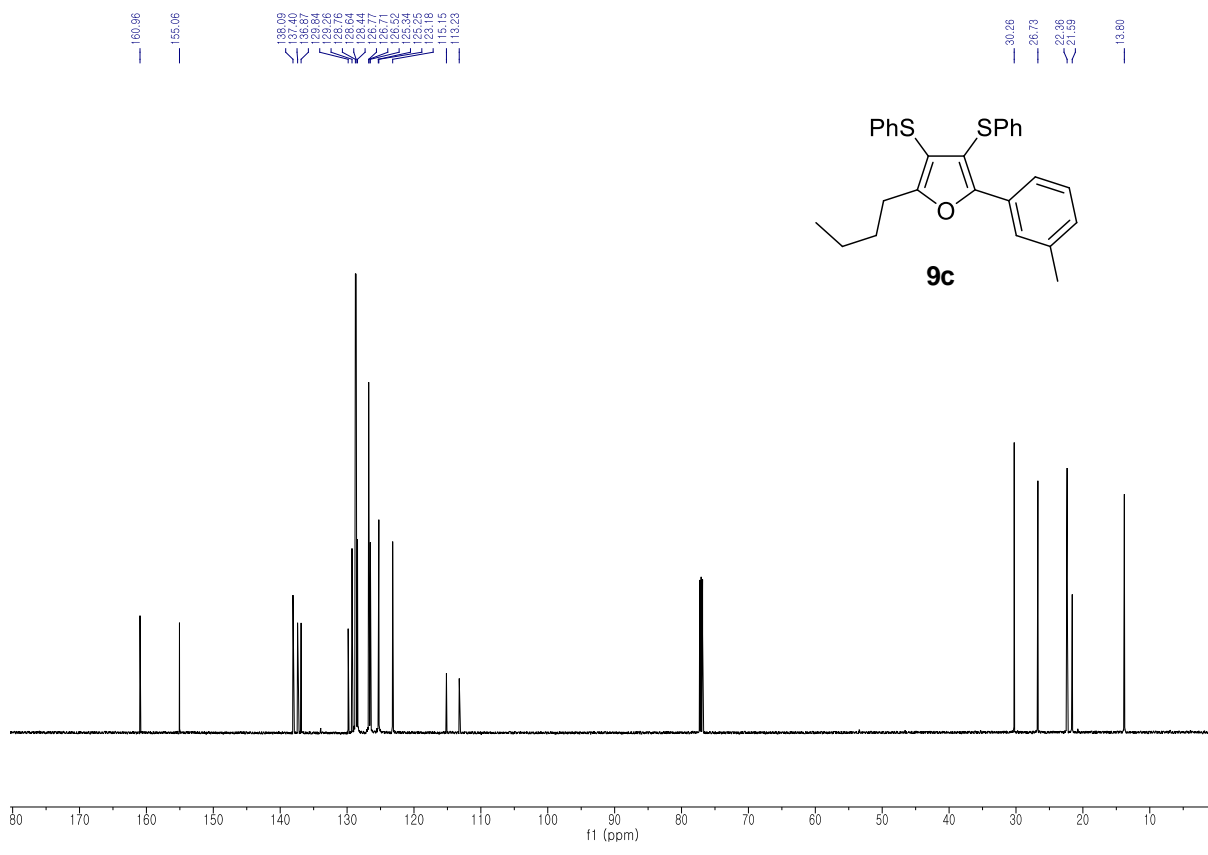
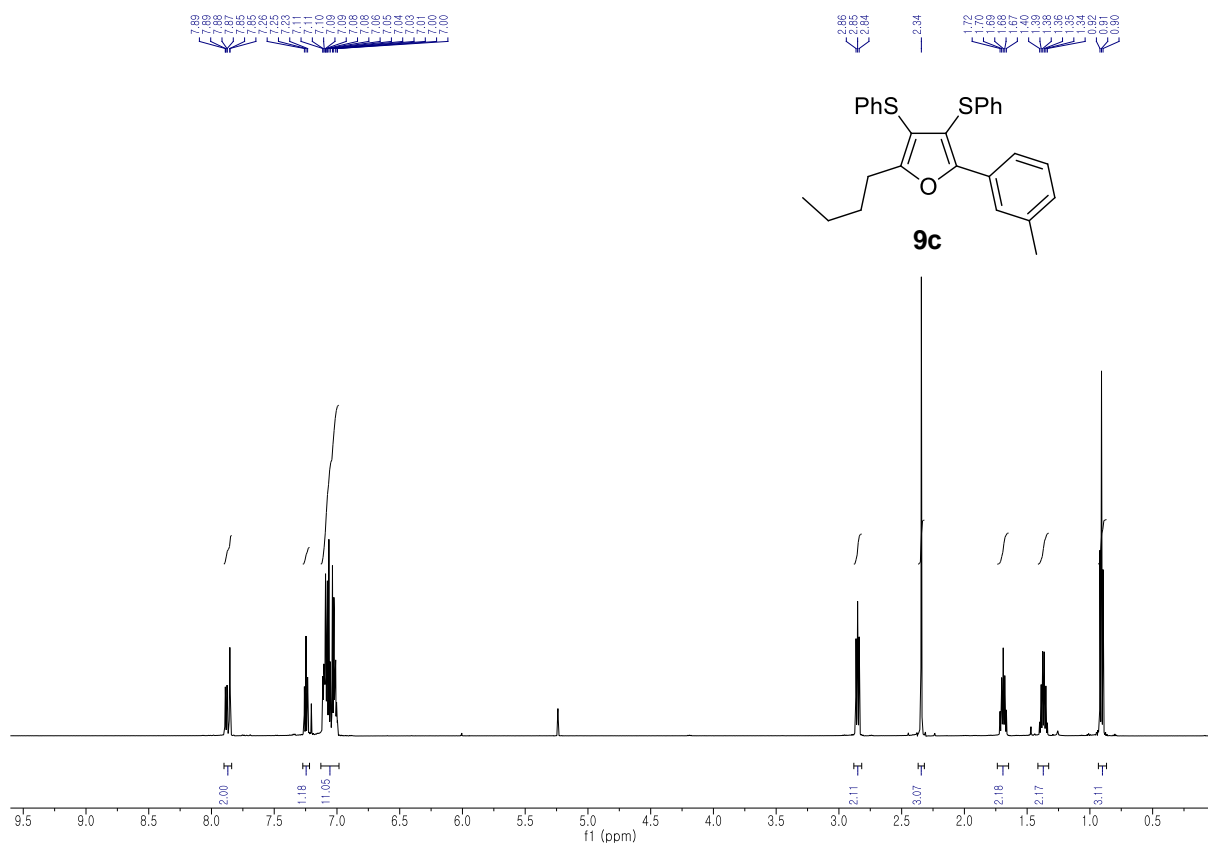


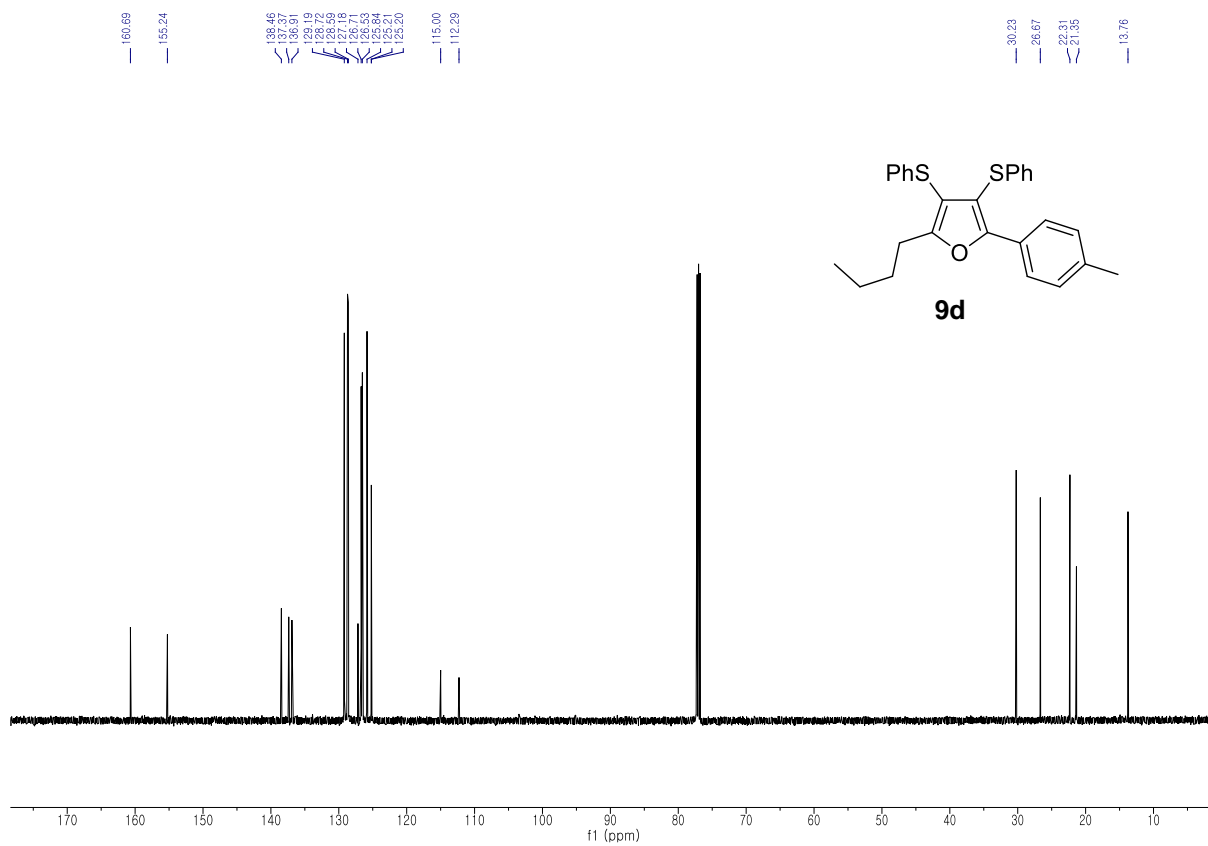
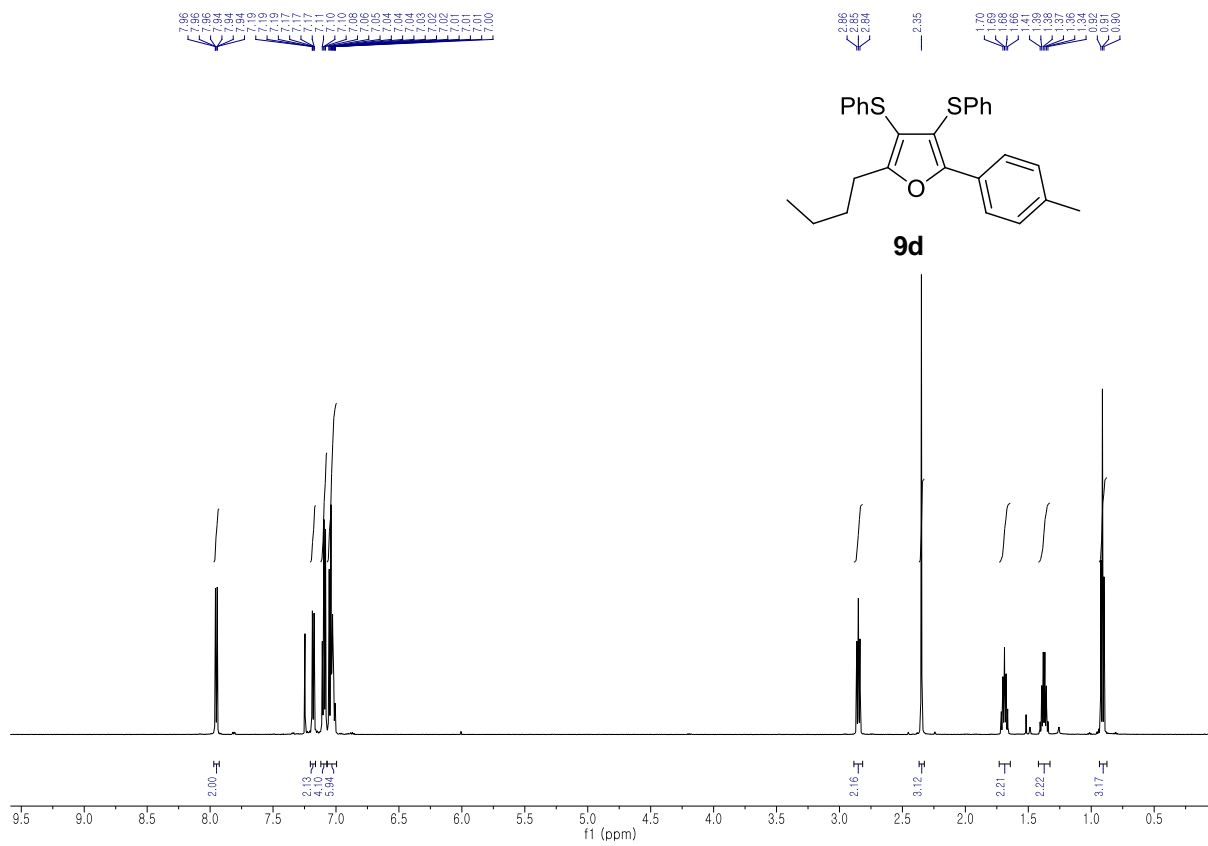


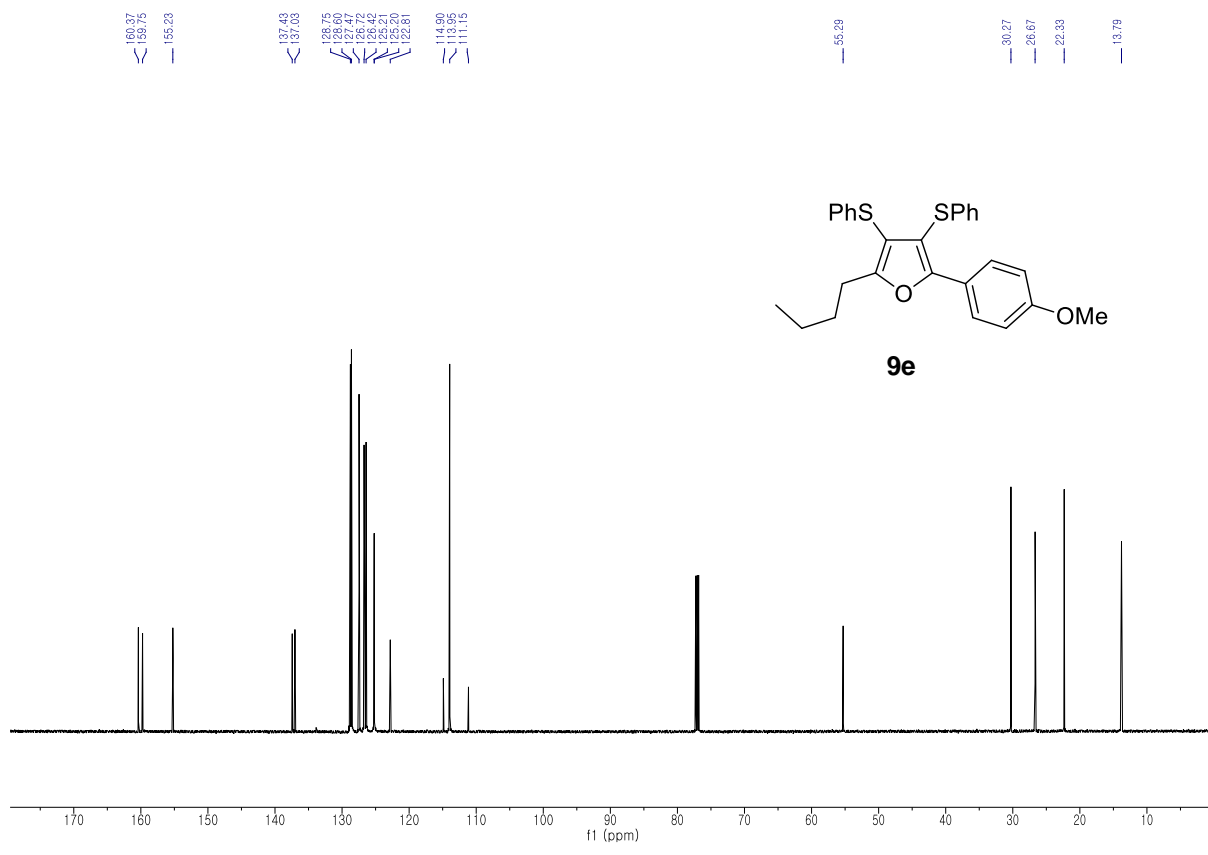
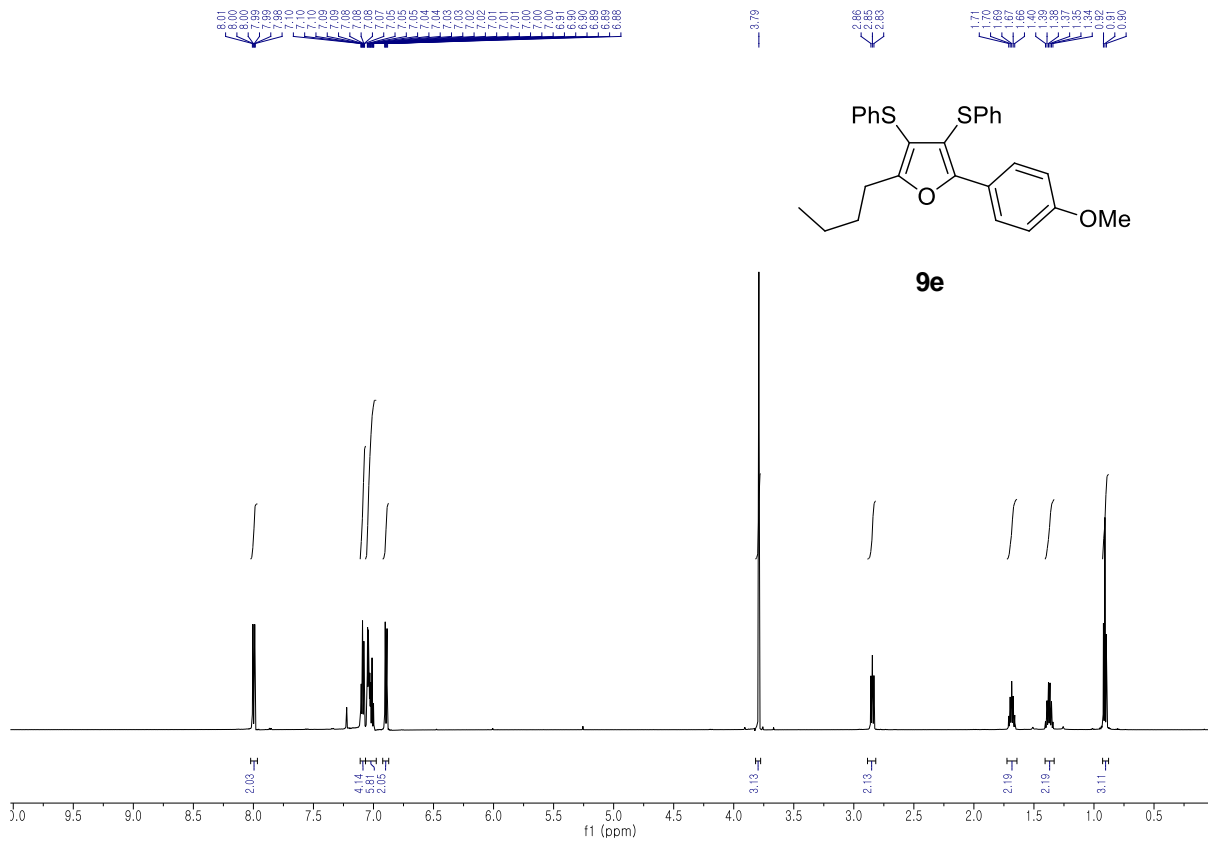


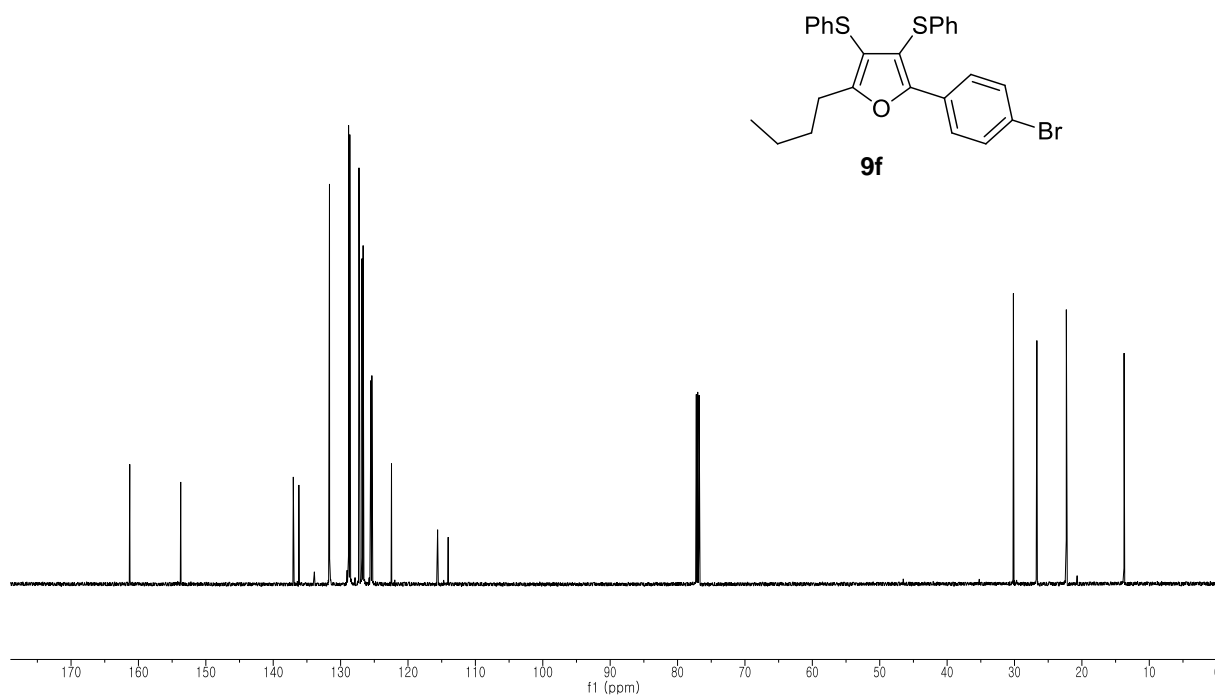
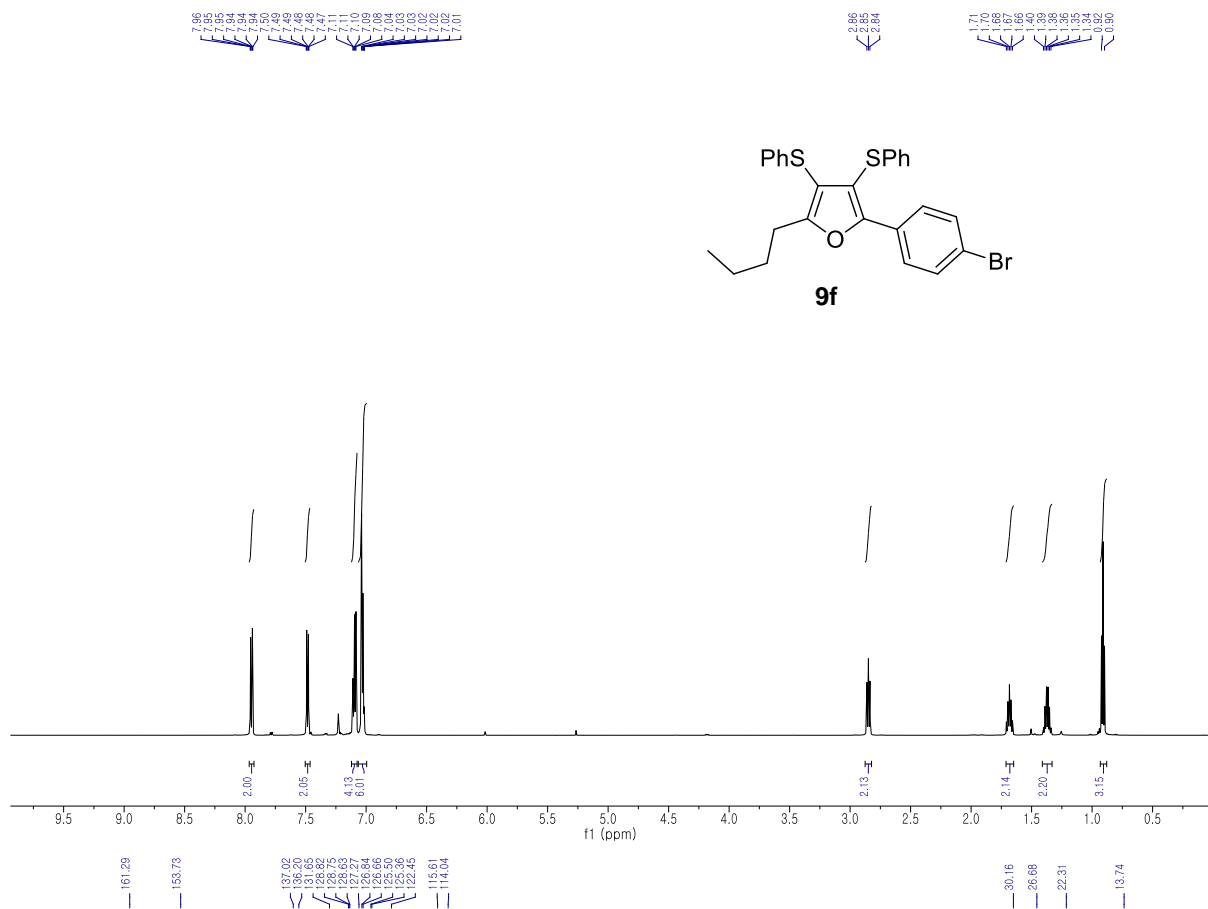






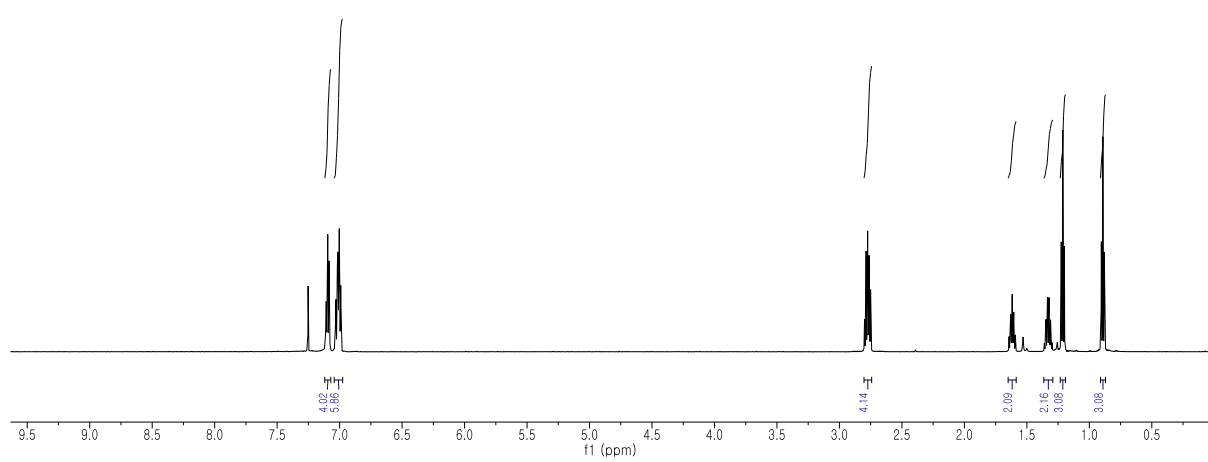
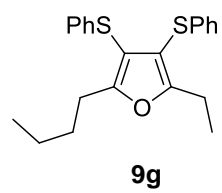






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