

Supporting Information

Synthesis of Multisubstituted Allenes, Furans, and Pyrroles *via* Tandem Palladium-Catalyzed Substitution and Cycloisomerization

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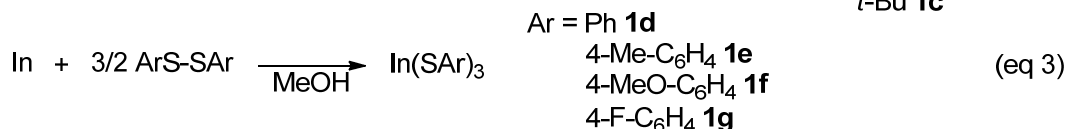
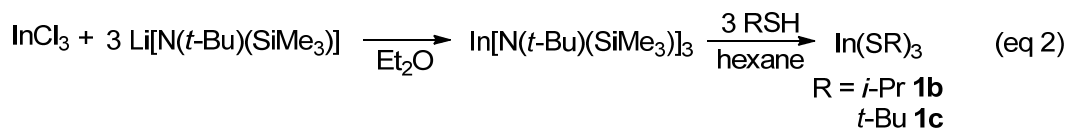
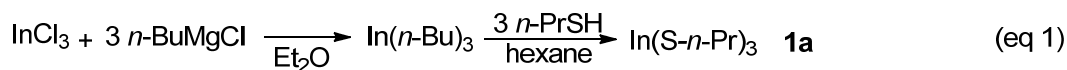
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Experimental Section

1. General: Reactions were carried out in oven-dried glassware under air atmosphere. All commercial reagents were used without purification, and all solvents were reaction grade. DMF was dried with CaH_2 . All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel precoated glass plates, which were visualized with UV light and then, developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using silica gel (230-400 mesh). ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on NMR spectrometer. Deuterated chloroform was used as the solvent and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.24 for ^1H (chloroform- d_3), δ 77.2 for ^{13}C (chloroform- d_3), δ 7.16 for ^1H (benzene- d_6), δ 128.06 for ^{13}C (benzene- d_6)]. Infrared spectra were recorded on FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. High resolution mass spectra (HRMS) were obtained by electron impact (EI) ionization technique (magnetic sector - electric sector double focusing mass analyzer) from the KBSI (Korea Basic Science Institute). Melting points were determined in open capillary tube.

2. Preparation of indium tri(organothiolate).

Scheme 1. Synthesis of Indium(III) Organothiolates



(ArS)₃In was prepared by slightly modified methods using standard Schlenk technique.^{1a,1b}

(PhS)₃In (1d) : To a suspension of indium (0.60 g, 5.23 mmol) in MeOH (15 mL) was added dropwise a solution of PhSSPh (1.75 g, 8.02 mmol) in CH₂Cl₂ (4 mL) and MeOH (5 mL) at room temperature. After being stirred at 80 °C for 5 h, the reaction mixture was cooled to room temperature and filtered through Celite under a nitrogen atmosphere to remove excess disulfide. The volatile materials were removed and the residue was dried under vacuum to give (PhS)₃In as a white powder (1.58 g, 89%).

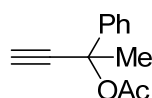
(4-R-C₆H₄S)₃In (R = Me, MeO, F) (1e, 1f, 1g): To a suspension of indium (0.50 g, 4.35 mmol) in MeOH (10 mL) was added dropwise a solution of (4-RC₆H₄S)₂ (7.00 mmol) in CH₂Cl₂ (5 mL) and MeOH (5 mL) at room temperature. After being stirred at 80 °C for 10 h, the reaction mixture was cooled to room temperature. Precipitates were filtered through glass filter and washed with Et₂O (2 × 10 mL) and CH₂Cl₂ (1 × 5 mL). The residue was dried under vacuum to give (4-R-C₆H₄S)₃In as a powder and used without further purification.

(RS)₃In (R = *tert*-Bu, *i*-Pr) (1b, 1c) was prepared by reported procedure.^{1c}

(*n*-PrS)₃In^{1d} (1a) : To a solution of InCl₃ (0.44 g, 2.0 mmol) in THF (25 mL) was added dropwise *n*-BuMgCl (3 mL, 6 mmol, 2.0 M solution in THF) at room temperature. After being stirred for 4 h, solvent was removed under reduced pressure and Et₂O (30 mL) was added. The ethereal solution of *n*-Bu₃In was collected by filtration through Celite and *n*-PrSH (586.4 mg, 7.7 mmol) was added at -78 °C. The mixture was allowed to room temperature and then, mixture was stirred for 10 h. Volatile materials were removed under vacuum and the residue was washed with Et₂O (2 × 5 mL) to give (*n*-PrS)₃In as a white powder (0.44 g, 65%).

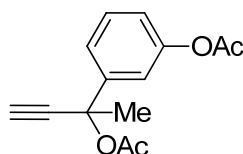
3. General procedure for the synthesis of propargyl acetates 2

: To a solution of 2-phenylbut-3-yn-2-ol (438.6 mg, 3.0 mmol) and DMAP (36.6 mg, 0.3 mmol) in 10 mL anhydrous CH_2Cl_2 was added pyridine (485 μL , 6.0 mmol) and the resulting solution was stirred at 0 °C for 5 min and slowly added acetyl chloride (427 μL , 6.0 mmol) and the reaction mixture was stirred at room temperature for 7 h. After completion of reaction, the resulting solution was quenched with aqueous NaHCO_3 solution (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL), and the combined organics were washed with sat. NaHCO_3 (10 mL) and sat. NaCl solution (20 mL), dried with anhydrous MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 1:10) to give 2-phenylbut-3-yn-2-yl acetate (**2a**) as a colorless oil (366.8 mg, 65%).



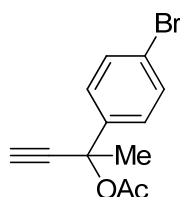
2a

2-Phenylbut-3-yn-2-yl acetate (2a) : 366.8 mg (65%), R_f = 0.4 (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.58 (d, J = 7.4 Hz, 4H), 7.36 (t, J = 7.3 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 2.81 (s, 1H), 2.08 (s, 3H), 1.89 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 168.7, 142.1, 128.4, 127.9, 124.8, 83.0, 75.6, 75.3, 32.1, 21.8; IR (film) 2992, 2359, 1750, 1367, 1234, 1063, 765, 699 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2$: 188.0837; found : 188.0833.



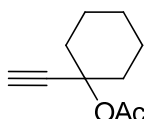
2b

3-(2-Aetoxybut-3-yn-2-yl)phenyl acetate (2b) : 494.6 mg (67%), R_f = 0.4 (EtOAc:Hexane = 1:5); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.44 (ddd, J = 7.9, 1.7, 1.2 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 7.31 (t, J = 2.0 Hz, 1H), 7.05 (ddd, J = 8.0, 2.3, 1.1 Hz, 1H), 2.82 (s, 1H), 2.3q (s, 3H), 2.09 (s, 3H), 1.89 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 169.3, 168.6, 150.6, 143.9, 129.4, 122.2, 121.2, 118.3, 82.5, 76.7, 75.8, 74.8, 31.9, 21.7, 21.2; IR (film) 2991, 2360, 1749, 1369, 1205, 1064, 1013, 943 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{14}\text{O}_4$: 246.0892; found : 246.0891.

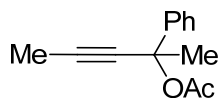


2c

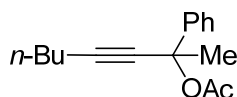
2-(4-Bomophenyl)but-3-yn-2-yl acetate (2c) : 558.6 mg (70%), $R_f = 0.6$ (EtOAc:Hexane = 1:10); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.47 (dd, $J = 13.0, 8.2$ Hz, 4H), 2.82 (s, 1H), 2.07 (s, 3H), 1.86 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 168.6, 141.3, 131.5, 126.7, 122.0, 82.4, 75.9, 74.8, 31.9, 21.7; IR (film) 3290, 2359, 1749, 1488, 1368, 1228, 1010, 824, 750, 549 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{12}\text{H}_{11}\text{BrO}_2$: 265.9942; found : 265.9942.

**2d**

1-Ethynylcyclohexyl acetate (2d) : 234.2 mg (47%), $R_f = 0.7$ (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 2.61 (s, 1H), 2.16-2.11 (m, 2H), 2.05 (s, 3H), 1.88-1.82 (m, 2H), 1.66-1.60 (m, 4H), 1.57-1.48 (m, 1H), 1.38-1.30 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 169.3, 83.7, 75.1, 74.2, 36.9, 25.1, 22.5, 22.0; IR (film) 2937, 2862, 2359, 1744, 1367, 1229, 1024, 750 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{10}\text{H}_{14}\text{O}_2$: 166.0994; found : 166.0997.

**2e**

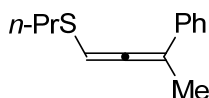
2-Phenylpent-3-yn-2-yl acetate (2e) : 364.1 mg (60%), $R_f = 0.6$ (EtOAc:Hexane = 1:20); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.57-7.55 (m, 2H), 7.36-7.32 (m, 2H), 7.29-7.25 (m, 1H), 2.06 (s, 3H), 1.96 (s, 3H), 1.84 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 168.8, 143.2, 128.3, 127.6, 124.9, 83.6, 78.7, 76.1, 32.4, 21.9, 3.9; IR (film) 2991, 2360, 1750, 1367, 1236, 1060, 1011, 765, 699 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2$: 202.0994; found : 202.0996.

**2f**

2-Phenyloct-3-yn-2-yl acetate (2f) : 424.8 mg (58%), $R_f = 0.4$ (EtOAc:Hexane = 1:20); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.56 (d, $J = 7.6$ Hz, 2H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.27 (t, $J = 7.3$ Hz, 1H), 2.32 (t, $J = 7.1$ Hz, 2H), 2.06 (s, 3H), 1.85 (s, 3H), 1.60-1.52 (m, 2H), 1.50-1.40 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 168.6, 143.3, 128.2, 127.6, 124.9, 88.1, 79.6, 76.1, 32.5, 30.7, 22.0, 21.9, 18.6, 13.6; IR (film) 2958, 2360, 1716, 1532, 1259, 750 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2$: 244.1463; found : 244.1462.

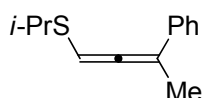
4. General procedure for the synthesis of allenyl sulfides 3aa–3cb

: To a suspension of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (6.2 mg, 0.006 mmol, 2.0 mol %) and DPEphos (12.9 mg, 0.024 mmol, 8.0 mol %) in DMF (0.6 mL) was added 2-phenylbut-3-yn-2-yl acetate (**2a**, 56.5 mg, 0.30 mmol) in DMF (0.2 mL) at room temperature under a nitrogen atmosphere. After being stirred for 1 min, $\text{In}(\text{S-}i\text{-Tol})_3$ (48.4 mg, 0.1 mmol) in DMF (0.7 mL) was transferred via double-ended needle and the mixture was stirred at room temperature for 5 h. The reaction mixture was quenched with sat. NH_4Cl solution (1.0 mL). The aqueous layer was extracted with ether (3 x 20 mL), and the combined organics were washed with sat. NH_4Cl (10 mL) and sat. NaCl solution (10 mL), dried with anhydrous MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give 3-phenyl-1,2-butadienyl 4-methylphenyl sulfide (**3ea**, 55.8 mg, 74%).



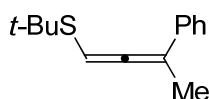
3aa

3-Phenyl-1,2-butadienyl *n*-propyl sulfide (3aa) : 55.1 mg (90%), R_f = 0.6 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.39 (d, J = 7.3 Hz, 2H), 7.13 (t, J = 7.9 Hz, 2H), 7.02 (t, J = 7.3 Hz, 1H), 5.96 (q, J = 2.7 Hz, 1H), 2.46-2.33 (m, 2H), 1.94 (d, J = 2.8 Hz, 3H), 1.50-1.40 (m, 2H), 0.74 (t, J = 7.4 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 201.1, 137.3, 128.7, 127.4, 126.4, 107.1, 91.0, 34.1, 23.1, 17.3, 13.5; IR (film) 3083, 3023, 2870, 1929, 1595, 777 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_{16}\text{S}$: 204.0973; found : 204.0972.



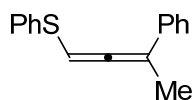
3ab

3-Phenyl-1,2-butadienyl *iso*-propyl sulfide (3ab) : 53.9 mg (88%), R_f = 0.5 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.41-7.39 (m, 2H), 7.14 (t, J = 7.6 Hz, 2H), 7.03 (t, J = 7.3 Hz, 1H), 5.99 (q, J = 2.7 Hz, 1H), 2.89 (septet, J = 6.7 Hz, 1H), 1.95 (d, J = 2.9 Hz, 3H), 1.16 (d, J = 6.7 Hz, 3H), 1.10 (d, J = 6.7 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 202.6, 137.1, 128.7, 127.4, 126.4, 105.8, 89.7, 36.6, 23.3, 23.2, 17.2; IR (film) 3082, 3023, 2863, 1929, 1598, 1578, 777 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_{16}\text{S}$: 204.0973; found : 204.0972.



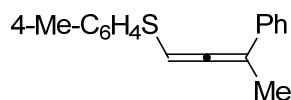
3ac

3-Phenyl-1,2-butadienyl *tert*-butyl sulfide (3ac) : 56.3 mg (86%), $R_f = 0.6$ (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.40 (d, $J = 7.4$ Hz, 2H), 7.16-7.12 (m, 2H), 7.03 (t, $J = 7.4$ Hz, 1H), 6.08 (q, $J = 2.7$ Hz, 1H), 1.92 (d, $J = 2.7$ Hz, 3H), 1.26 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 206.4, 136.9, 128.7, 127.3, 126.5, 103.2, 86.7, 44.2, 30.7, 17.0; IR (film) 3058, 2922, 2860, 1901, 1596, 1455, 753 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{18}\text{S}$: 218.1129; found : 218.1132.



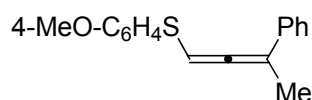
3ad

3-Phenyl-1,2-butadienyl phenyl sulfide (3ad) : 59.3 mg (83%), $R_f = 0.5$ (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.38-7.35 (m, 2H), 7.33-7.30 (m, 2H), 7.12-7.08 (m, 2H), 7.03-6.99 (m, 1H), 6.98-6.93 (m, 2H), 6.91-6.87 (m, 1H), 6.13 (q, $J = 2.7$ Hz, 1H), 1.82 (d, $J = 2.7$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 204.7, 136.3, 135.7, 130.4, 129.0, 128.5, 127.5, 126.8, 126.4, 106.2, 89.5, 16.7; IR (film) 3057, 2984, 2920, 1933, 1581, 1491, 1477, 737 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{14}\text{S}$: 238.0816; found : 238.0816.



3ae

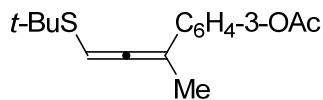
3-Phenyl-1,2-butadienyl 4-methylphenyl sulfide (3ae) : 55.8 mg (74%), $R_f = 0.6$ (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.34 (t, $J = 7.3$ Hz, 4H), 7.11 (t, $J = 7.6$ Hz, 2H), 7.01 (t, $J = 7.3$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 2H), 6.17 (q, $J = 2.6$ Hz, 1H), 1.96 (s, 3H), 1.84 (d, $J = 2.8$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 204.2, 137.1, 136.6, 132.0, 131.4, 130.0, 128.7, 127.6, 126.6, 106.5, 90.7, 20.9, 16.9; IR (film) 3057, 2947, 1932, 1892, 1596, 1442, 752 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{16}\text{S}$: 252.0973; found : 252.0973.



3af

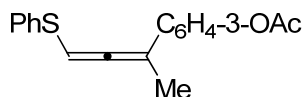
3-Phenyl-1,2-butadienyl 4-methoxyphenyl sulfide (3af) : 69.0 mg (86%), $R_f = 0.4$ (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.38 (d, $J = 8.9$ Hz, 2H), 7.34-7.32 (m, 2H), 7.13-7.09 (m, 2H), 7.03-6.99 (m, 1H), 6.56 (d, $J = 8.8$ Hz, 2H), 6.15 (q, $J = 2.6$ Hz, 1H), 3.13 (s, 3H), 1.82 (d, $J = 2.7$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 203.1, 160.0, 136.7, 134.4, 128.6, 127.5, 126.5, 125.2, 114.9,

107.0, 92.2, 54.8, 17.0; IR (film) 2924, 1938, 1591, 1492, 1245, 1028, 1028, 751 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{16}\text{OS}$: 268.0922; found : 268.0923.



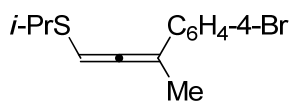
3bc

3-(4-(*tert*-Butylthio)buta-2,3-dien-2-yl)phenyl acetate (3bc) : 62.1 mg (75%), R_f = 0.4 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.34-7.33 (m, 1H), 7.20-7.18 (m, 1H), 7.04 (t, J = 7.9 Hz, 1H), 6.95-6.92 (m, 1H), 6.04 (q, J = 2.7 Hz, 1H), 1.86 (d, J = 2.8 Hz, 3H), 1.73 (s, 3H), 1.24 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 206.3, 168.4, 151.8, 138.7, 129.5, 123.7, 120.7, 119.8, 102.8, 87.2, 44.3, 30.7, 20.6, 16.9; IR (film) 3065, 2924, 1934, 1764, 1606, 1457, 1013, 763 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2\text{S}$: 276.1184; found : 276.1182.



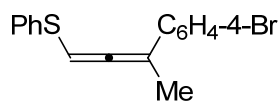
3bd

3-(4-(Phenylthio)buta-2,3-dien-2-yl)phenyl acetate (3bd) : 69.3 mg (78%), R_f = 0.4 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.38-7.35 (m, 2H), 7.27 (s, 1H), 7.10-7.08 (m, 1H), 7.03-6.87 (m, 5H), 6.09 (q, J = 2.5 Hz, 1H), 1.75 (d, J = 2.7 Hz, 3H), 1.72 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 204.6, 151.8, 138.2, 135.4, 130.9, 129.5, 129.2, 127.1, 123.7, 120.9, 119.8, 105.9, 90.4, 20.5, 16.7; IR (film) 3058, 2931, 1938, 1765, 1605, 1438, 1013, 740 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{S}$: 296.0871; found : 296.0875.



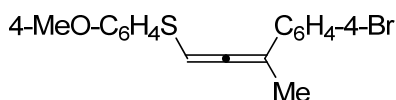
3cb

3-(4-Bromophenyl)-1,2-butadienyl *iso*-propyl sulfide (3cb) : 74.5 mg (88%), R_f = 0.7 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.24 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 8.6 Hz, 2H), 5.91 (q, J = 2.8 Hz, 1H), 2.83 (septet, J = 6.7 Hz, 1H), 1.79 (d, J = 2.8 Hz, 3H), 1.14 (d, J = 6.7 Hz, 3H), 1.08 (d, J = 6.8 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 202.4, 136.0, 131.8, 128.0, 121.4, 105.0, 90.3, 36.6, 23.24, 23.20, 17.0; IR (film) 3087, 3027, 2923, 2863, 1901, 1604, 1586, 1175, 754 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_{15}\text{BrS}$: 282.0078; found : 282.0076.



3cd

3-(4-Bromophenyl)buta-1,2-dienyl phenyl sulfide (3cd) : 76.8 mg (81%), R_f = 0.5 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.35-7.32 (m, 2 H), 7.21 (d, J = 8.5 Hz, 2H), 6.98-6.88 (m, 5 H), 6.07-6.06 (m, 1 H), 1.68-1.67 (m, 3 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 204.3, 135.35, 135.32, 131.8, 130.8, 129.2, 127.2, 121.7, 105.6, 90.4, 16.7; IR (film) 2922, 1582, 1479, 1438, 1076, 1024, 740, 688 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{13}\text{BrS}$: 315.9921; found : 315.9921.

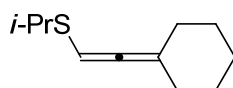


3cf

3-(4-Bromophenyl)-1,2-butadienyl 4-methoxyphenyl sulfide (3cf) : 85.1 mg (82%), R_f = 0.4 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.34 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 6.55 (d, J = 8.8 Hz, 2H), 6.07 (q, J = 2.6 Hz, 1H), 3.14 (s, 3H), 1.67 (d, J = 2.7 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 202.8, 160.2, 135.7, 134.7, 131.7, 128.0, 124.7, 121.5, 114.9, 106.3, 92.9, 54.8, 16.7; IR (film) 3064, 2938, 2834, 1887, 1590, 1571, 1172, 1007, 765 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{15}\text{BrOS}$: 346.0027; found : 346.0027.

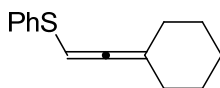
General procedure for the synthesis of allenyl sulfides 3dd-3ff

: To a suspension of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (6.2 mg, 0.006 mmol, 2.0 mol %) and DPEphos (12.9 mg, 0.024 mmol, 8.0 mol %) in DMF (6.0 mL) was added 1-ethynylcyclohexyl acetate (**2d**, 49.9 mg, 0.30 mmol) in DMF (0.2 mL) at room temperature under a nitrogen atmosphere. After being stirred for 1 min, $\text{In}(\text{SPh})_3$ (44.2 mg, 0.1 mmol) in DMF (0.4 mL) was transferred via double-ended needle and the mixture was stirred at 100 $^\circ\text{C}$ for 1 h. The reaction mixture was quenched with sat. NH_4Cl solution (1.0 mL). The aqueous layer was extracted with ether (3×20 mL), and the combined organics were washed with sat. NH_4Cl (10 mL) and sat. NaCl solution (10 mL), dried with anhydrous MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give 2-cyclohexylidenevinyl phenyl sulfide (**3dd**, 54.5 mg, 84%).



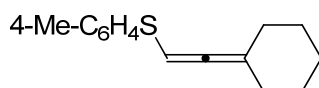
3db

2-Cyclohexylidenevinyl *iso*-propyl sulfide (3db) : 44.8 mg (82%), R_f = 0.6 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 5.71 (pentet, J = 2.0 Hz, 1H), 2.95 (septet, J = 6.7 Hz, 1H), 2.12-2.01 (m, 4H), 1.49-1.35 (m, 4H), 1.33-1.25 (m, 2H) 1.22 (d, J = 6.7 Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 197.1, 107.4, 85.0, 36.2, 31.8, 27.5, 26.1, 23.0; IR (film) 2927, 2854, 1948, 1446, 756 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{11}\text{H}_{18}\text{S}$: 182.1129; found : 182.1131.



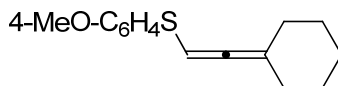
3dd

2-Cyclohexylidenevinyl phenyl sulfide (3dd) : 54.5 mg (84%), R_f = 0.5 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.40-7.38 (m, 2H), 7.03-6.98 (m, 2H), 6.94-6.90 (m, 1H), 5.85 (pentet, J = 1.9 Hz, 1H), 1.99 (td, J = 9.0, 1.9 Hz, 4H), 1.40-1.25 (m, 4H), 1.21-1.15 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 199.7, 136.7, 130.0, 129.0, 126.4, 107.7, 84.8, 31.3, 27.1, 25.9; IR (film) 3019, 2854, 1948, 1629, 1582, 1477, 1438, 712 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{16}\text{S}$: 216.0973; found : 216.0973.



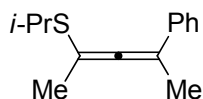
3de

2-Cyclohexylidenevinyl 4-methylphenyl sulfide (3de) : 66.7 mg (83%), R_f = 0.5 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.36 (d, J = 8.1 Hz, 2H), 6.86 (d, J = 7.9 Hz, 2H), 5.88 (pentet, J = 1.9 Hz, 1H), 2.02-1.98 (m, 7H), 1.41-1.25 (m, 4H), 1.24-1.17 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 199.1, 136.5, 133.0, 130.9, 130.0, 108.0, 86.0, 31.6, 27.3, 26.1, 21.0; IR (film) 3071, 2928, 1949, 1634, 1565, 1444, 765 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{18}\text{S}$: m/z 230.1129 [M^+], found: m/z 230.1131 HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{16}\text{OS}$: 268.0922; found : 268.0923.



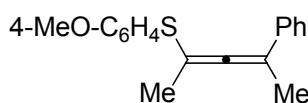
3df

2-Cyclohexylidenevinyl 4-methoxyphenyl sulfide (3df) : 59.1 mg (80%), R_f = 0.4 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.40 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 8.8 Hz, 2H), 5.86 (pentet, J = 1.9 Hz, 1H), 3.21 (s, 3H), 2.00-1.97 (m, 4H), 1.41-1.32 (m, 2H), 1.30-1.13 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 197.8, 159.8, 134.0, 126.2, 114.9, 108.7, 87.8, 54.9, 31.7, 27.3, 26.1; IR (film) 2999, 2929, 1947, 1591, 1492, 1441, 1172, 765 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{18}\text{OS}$: 246.1078; found : 246.1081.



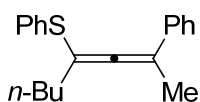
3eb

iso-Propyl 4-phenylpenta-2,3-dien-2-yl sulfide (3eb) : 55.0 mg (84%), R_f = 0.6 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.45-7.43 (m, 2H), 7.18-7.13 (m, 2H), 7.06-7.01 (m, 1H), 3.03-2.93 (m, 1H), 2.00 (s, 3H), 1.96 (s, 3H), 1.21 (d, J = 6.7 Hz, 3H), 1.11 (d, J = 6.7 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 199.4, 138.0, 128.7, 127.2, 126.4, 104.9, 100.2, 36.9, 23.4, 23.2, 20.2, 17.4; cm^{-1} ; IR (film) 3058, 3027, 2926, 1683, 1599, 1574, 1493, 794 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{18}\text{S}$: 218.1129; found : 218.1131.



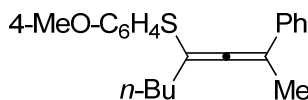
3ef

4-Methoxyphenyl 4-phenylpenta-2,3-dien-2-yl sulfide (3ef) : 70.2 mg (83%), R_f = 0.4 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.44-7.42 (m, 2H), 7.33-7.30 (m, 2H), 7.14-7.10 (m, 2H), 7.04-6.99 (m, 1H), 6.53 (d, J = 8.8 Hz, 2H), 3.12 (s, 3H), 2.00 (s, 3H), 1.81 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 201.1, 160.3, 137.7, 136.3, 128.6, 127.2, 126.4, 124.6, 114.7, 105.2, 101.9, 54.8, 19.7, 17.1; IR (film) 3058, 2938, 1940, 1591, 1492, 1140, 798 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{18}\text{OS}$: 282.1078; found : 282.1076.



3fd

2-Phenylocta-2,3-dien-4-yl phenyl sulfide (3fd) : 72.4 mg (82%), R_f = 0.5 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.50-7.48 (m, 2H), 7.35-7.33 (m, 2H), 7.15-7.11 (m, 2H), 7.02 (t, J = 7.3 Hz, 1H), 6.97-6.93 (m, 2H), 6.92-6.88 (m, 1H), 2.37-2.33 (m, 2H), 1.83 (s, 3H), 1.57 (pentet, J = 7.5 Hz, 2H), 1.25 (sextet, J = 7.4 Hz, 2H), 0.78 (t, J = 7.4 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 202.7, 137.4, 134.9, 132.9, 129.0, 128.6, 127.5, 127.3, 126.4, 105.1, 104.8, 34.1, 30.7, 22.5, 17.1, 14.0; IR (film) 3057, 3019, 2929, 2870, 1943, 1597, 1461, 758 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{22}\text{S}$: 294.1442; found : 294.1437.

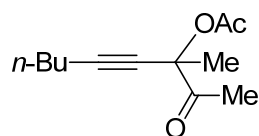


3ff

4-Methoxyphenyl 2-phenylocta-2,3-dien-4-yl sulfide (3ff) : 70.0 mg (72%), $R_f = 0.4$ (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.45 (d, $J = 8.8$ Hz, 2H), 7.35-7.33 (m, 2H), 7.15-7.11 (m, 2H), 7.01 (t, $J = 7.3$ Hz, 1H), 6.54 (d, $J = 8.8$ Hz, 2H), 3.13 (s, 3H), 2.39-2.35 (m, 2H), 1.83 (s, 3H), 1.67-1.58 (m, 2H), 1.29 (sextet, $J = 7.4$ Hz, 2H), 0.80 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 200.9, 160.3, 137.7, 136.3, 128.6, 127.2, 126.3, 124.7, 114.6, 107.2, 106.0, 54.8, 33.7, 30.8, 22.5, 17.2, 14.0; IR (film) 3082, 2956, 2939, 1940, 1571, 1066, 1007, 798 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{24}\text{OS}$: 324.1548; found : 324.1544.

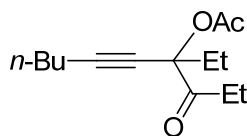
5. General procedure for the synthesis of acyl-substituted propargyl acetates 5

: To a solution of 3-hydroxy-3-methylnon-4-yn-2-one (336.5 mg, 2.0 mmol) in 5 mL anhydrous CH_2Cl_2 , was added pyridine (323 μL , 4.0 mmol) and the resulting solution was stirred at 0 $^\circ\text{C}$ for 5 min and slowly added acetyl chloride (284 μL , 4.0 mmol) and the reaction mixture was stirred at room temperature for 7 h. After completion of reaction, the resulting solution was quenched with aqueous NaHCO_3 solution (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL), and the combined organics were washed with sat. NaHCO_3 (10 mL) and sat. NaCl solution (20 mL), dried with anhydrous MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 1:20) to give 3-methyl-2-oxonon-4-yn-3-yl acetate (**5a**) as a yellow oil (374.0 mg, 89%).



5a

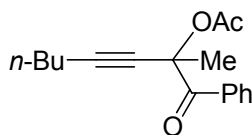
3-Methyl-2-oxonon-4-yn-3-yl acetate (5a) : 374.0 mg (89%), $R_f = 0.3$ (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 2.35 (s, 3H), 2.25 (t, $J = 7.0$ Hz, 2H), 2.10 (s, 3H), 1.63 (s, 3H), 1.55-1.48 (m, 2H), 1.45-1.36 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 202.3, 169.5, 88.7, 77.3, 30.5, 25.3, 24.9, 22.0, 21.0, 18.6, 13.7; IR (film) 2936, 2359, 1734, 1367, 1227, 1087, 1015 cm^{-1} ; HRMS (EI): m/z calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_3$: 210.1256; found: 210.1253.



5b

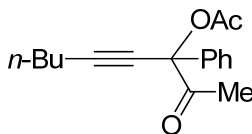
4-Ethyl-3-oxodec-5-yn-4-yl acetate (5b) : 424.2 mg (89%), $R_f = 0.4$ (EtOAc:Hexane = 1:15); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 3.03 (dq, $J = 18.7, 7.2$ Hz, 1H), 2.60 (dq, $J = 18.7, 7.2$ Hz, 1H), 2.27

(t, $J = 7.0$ Hz, 2H), 2.08 (s, 3H), 1.92-1.78 (m, 2H), 1.56-1.49 (m, 2H), 1.46-1.37 (m, 2H), 1.08 (t, $J = 7.2$ Hz, 3H), 1.03 (t, $J = 7.4$ Hz, 3H), 0.92 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 205.8, 169.4, 89.1, 80.4, 76.4, 32.1, 31.6, 30.5, 21.9, 20.8, 18.5, 13.6, 8.2, 7.7; IR (film) 2938, 1745, 1460, 1238, 1047, 1016 cm^{-1} ; HRMS (EI): m/z calcd. for $\text{C}_{14}\text{H}_{22}\text{O}_3$: 238.1569; found: 238.1570.



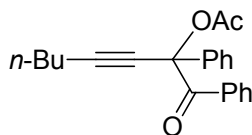
5c

2-Methyl-1-oxo-1-phenyloct-3-yn-2-yl acetate (5c) : 463.0 mg (85%), $R_f = 0.4$ (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.73-7.69 (m, 2H), 7.42-7.36 (m, 3H), 2.39 (t, $J = 7.1$ Hz, 2H), 2.27 (s, 3H), 2.19 (s, 3H), 1.65-1.57 (m, 2H), 1.52-1.42 (m, 2H), 0.95 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 199.2, 169.1, 135.2, 129.2, 128.6, 126.9, 91.3, 81.7, 86.0, 30.4, 25.2, 22.1, 21.2, 18.7, 13.6; IR (film) 2933, 1360, 1753, 1149, 1367, 1232, 1025, 968, 758, 698 cm^{-1} ; HRMS (EI): m/z calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_3$: 272.1412; found: 272.1414.



5d

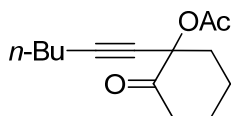
2-Oxo-3-phenylnon-4-yn-3-yl acetate (5d) : 490.2 mg (90%), $R_f = 0.5$ (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.16-8.14 (m, 2H), 7.55-7.50 (m, 1H), 7.44-7.40 (m, 2H), 2.24 (t, $J = 7.0$ Hz, 2H), 1.95 (s, 3H), 1.93 (s, 3H), 1.51-1.44 (m, 2H), 1.39-1.29 (m, 2H), 0.86 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 193.1, 169.3, 133.9, 132.7, 129.3, 128.1, 91.0, 78.2, 77.7, 30.1, 24.9, 21.9, 21.2, 18.6, 13.5; IR (film) 2934, 1742, 1701, 1369, 1217, 1087, 1015, 947, 713 cm^{-1} ; HRMS (EI): m/z calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_3$: 272.1412; found: 272.1411.



5e

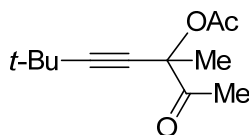
1-Oxo-1,2-diphenyloct-3-yn-2-yl acetate (5e) : 347.8 mg (52%), $R_f = 0.3$ (EtOAc:Hexane = 1:10); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.88-7.85 (m, 2H), 7.78-7.76 (m, 2H), 7.45-7.35 (m, 4H), 7.32-7.28 (m, 2H), 2.30 (t, $J = 7.0$ Hz, 2H), 2.14 (s, 3H), 1.52-1.45 (m, 2H), 1.38-1.28 (m, 2H), 0.85 (t, J

= 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 191.8, 168.8, 136.3, 134.3, 132.5, 129.8, 129.2, 128.8, 127.8, 127.1, 93.0, 81.3, 76.8, 30.2, 21.9, 21.4, 18.7, 13.6; IR (film) 3062, 2958, 1755, 1698, 1448, 1229, 697 cm^{-1} ; HRMS (EI): m/z calcd. for $\text{C}_{22}\text{H}_{22}\text{O}_3$: 334.1569; found: 334.1565.



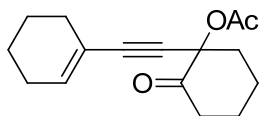
5f

1-(Hex-1-yn-1-yl)-2-oxocyclohexyl acetate (5f) : 273.9 mg (58%), R_f = 0.4 (EtOAc:Hexane = 1:10); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 2.89-2.81 (m, 1H), 2.47-2.42 (m, 1H), 2.32-2.23 (m, 3H), 2.19-2.15 (m, 1H), 2.13 (s, 3H), 2.03-1.94 (m, 2H), 1.89-1.83 (m, 1H), 1.78-1.71 (m, 1H), 1.56-1.49 (m, 2H), 1.45-1.36 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 202.1, 168.8, 91.0, 79.8, 76.2, 40.7, 38.5, 30.5, 27.9, 22.3, 22.1, 21.5, 18.8, 13.7; IR (film) 3061, 2936, 2866, 2245, 1736, 1367, 1224, 1050, 615 cm^{-1} ; HRMS (EI): m/z calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_3$: 236.1412; found: 236.1413.



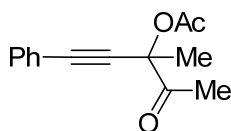
5g

3,6,6-Trimethyl-2-oxohept-4-yn-3-yl acetate (5g) : 277.6 mg (66%), R_f = 0.5 (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 2.36 (s, 3H), 2.09 (s, 3H), 1.61 (s, 3H), 1.23 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 202.3, 169.3, 96.4, 77.2, 76.1, 30.5, 27.5, 25.3, 24.7, 20.9; IR (film) 2968, 2359, 1735, 1367, 1242, 1082, 743 cm^{-1} ; HRMS (EI): m/z calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_3$: 210.1256; found: 210.1255.



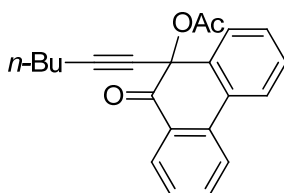
5h

1-(Cyclohex-1-en-1-ylethynyl)-2-oxocyclohexyl acetate (5h) : 218.5 mg (42%), R_f = 0.4 (EtOAc:Hexane = 1:50); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 6.20-6.18 (m, 1H), 2.89 (dt, J = 5.8, 12.7 Hz, 1H), 2.47-2.42 (m, 1H), 2.37-2.32 (m, 1H), 2.16-2.06 (m, 8H), 2.05-1.96 (m, 2H), 1.89-1.84 (m, 1H), 1.79-1.70 (m, 1H), 1.69-1.55 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 201.7, 168.6, 136.8, 119.7, 91.5, 82.1, 79.8, 40.5, 38.5, 28.9, 27.8, 25.6, 22.3, 22.1, 21.4, 21.3; IR (film) 2938, 2363, 1734, 1535, 1223, 1052 cm^{-1} ; HRMS (EI): m/z calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_3$: 260.1412; found: 260.1413.



5i

3-Methyl-4-oxo-1-phenylpent-1-yn-3-yl acetate (5i) : 358.9 mg (78%), R_f = 0.3 (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.48-7.45 (m, 2H), 7.38-7.30 (m, 3H), 2.45 (s, 3H), 2.14 (s, 3H), 1.75 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 201.6, 169.4, 131.9, 129.0, 128.3, 121.7, 87.2, 86.1, 77.1, 25.5, 24.7, 20.8; IR (film) 2997, 1737, 1369, 1239, 1085, 1016, 758, 692 cm^{-1} ; HRMS (EI): m/z calcd. for $\text{C}_{14}\text{H}_{14}\text{O}_3$: 230.0943; found: 230.0944.



5j

9-(Hex-1-yn-1-yl)-10-oxo-9,10-dihydrophenanthren-9-yl acetate (5j) : 637.8 mg (96%), R_f = 0.5 (EtOAc:Hexane = 1:10); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 8.19 (dd, J = 7.8, 1.4 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 8.00-7.97 (m, 1H), 7.70 (td, J = 11.3, 1.5 Hz, 1H), 7.59-7.57 (m, 1H), 7.47-7.37 (m, 3H), 2.18 (s, 3H), 2.11 (t, J = 7.2 Hz, 2H), 1.39-1.32 (m, 2H), 1.24-1.15 (m, 2H), 0.77 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 189.7, 169.2, 138.2, 136.6, 135.0, 129.5, 129.0, 128.7, 128.6, 128.4, 127.9, 125.5, 123.9, 123.4, 90.7, 75.4, 75.2, 30.0, 21.8, 20.9, 18.7, 13.4; IR (film) 2957, 2234, 1747, 1703, 1602, 1451, 1236, 1171, 900, 733 cm^{-1} ; HRMS (EI): m/z calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_3$: 332.1412; found: 332.1414.

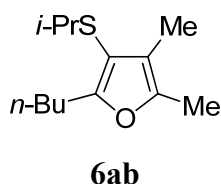
Table 1. Reaction Optimization for the Synthesis of Tetrasubstituted Furans *via* Tandem Pd-Catalyzed Propargyl Substitution and Cycloisomerization^a

entry	cat.	temp (°C)	time (h)	yield ^a (%)
1	2.0 mol % Pd ₂ dba ₃ CHCl ₃ 8.0 mol % DPEphos	100	21	34 (43) ^b
2	2.0 mol % Pd ₂ dba ₃ CHCl ₃ 8.0 mol % DPEphos	150	3	70
3	2.0 mol % Pd ₂ dba ₃ CHCl ₃ 8.0 mol % DPEphos 50 mol % CuI, Et ₃ N (1 equiv)	100	31	38
4	4.0 mol % Pd ₂ dba ₃ CHCl ₃ 16.0 mol % DPEphos	150	0.5	75

^aReactions were carried out with **5a** (0.3 mmol, 1 equiv) and **1d** (0.34 equiv). ^bIsolated yield of 5,6-dimethyl-3-(phenylthio)-2-propyl-2*H*-pyran (**11**).

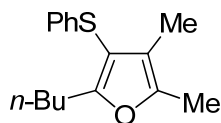
6. General procedure for the synthesis of furans 6

To a suspension of Pd₂(dba)₃·CHCl₃ (12.4 mg, 0.012 mmol, 4.0 mol %) and DPEphos (25.8 mg, 0.048 mmol, 16.0 mol %) in DMF (0.6 mL) was added 3-methyl-2-oxonon-4-yn-3-yl acetate (**5a**, 63.1 mg, 0.30 mmol) in DMF (0.2 mL) at room temperature under a nitrogen atmosphere. After being stirred for 1 min, In(SPh)₃ (44.2 mg, 0.1 mmol) in DMF (0.7 mL) was transferred via double-ended needle and the mixture was stirred at 150 °C for 0.5 h. The reaction mixture was quenched with sat. NH₄Cl solution (1.0 mL). The aqueous layer was extracted with ether (3 × 20 mL), and the combined organics were washed with sat. NH₄Cl (10 mL) and sat. NaCl solution (10 mL), dried with anhydrous MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give 2-*n*-butyl-4,5-dimethyl-3-(phenylthio)furan (**6aa**, 58.4 mg, 75%).



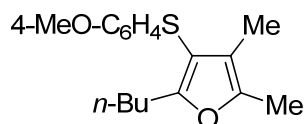
2-*n*-Butyl-3-(*iso*-propylthio)-4,5-dimethylfuran (6ab**)** : 55.6 mg (82%), *R_f* = 0.8 (EtOAc:Hexane = 1:10); colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 2.95-2.88 (m, 1H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.18 (s, 3H), 1.92 (s, 3H), 1.62-1.54(m, 2H), 1.38-1.32 (m, 2H), 1.19 (d, *J* = 6.7 Hz, 6H), 0.92 (t, *J* = 7.3 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 157.8, 145.1, 117.3, 110.9, 38.8, 30.8, 26.1, 23.1, 22.4, 13.9, 11.8,

8.9; IR (film) 2958, 2924, 1566, 1450, 1223, 1155, 698 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_{22}\text{OS}$: 226.1391; found : 226.1390.



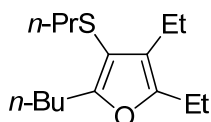
6ad

2-*n*-Butyl-4,5-dimethyl-3-(phenylthio)furan (6ad) : 58.4 mg (75%), R_f = 0.7 (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.22-7.18 (m, 2H), 7.09-7.05 (m, 3H), 2.68 (t, J = 7.5 Hz, 2H), 2.22 (s, 3H), 1.78 (s, 3H), 1.61-1.53 (m, 2H), 1.35-1.26 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 158.6, 146.0, 138.6, 128.7, 125.5, 124.7, 117.1, 108.5, 30.7, 26.1, 22.3, 13.8, 11.9, 8.5; IR (film) 3059, 2956, 2923, 2871, 2860, 1636, 1582, 1478, 1466, 1084, 738 cm^{-1} ; HRMS (EI): m/z calcd. for $\text{C}_{16}\text{H}_{20}\text{OS}$: 260.1235; found: 260.1237



6af

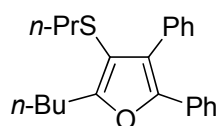
3-(4-Methoxyphenylthio)-2-*n*-butyl-4,5-dimethylfuran (6af) : 66.1 mg (76%), R_f = 0.8 (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.04 (d, J = 8.9 Hz, 2H), 6.78 (d, J = 8.9 Hz, 2H), 3.76 (s, 3H), 2.70 (t, J = 7.6 Hz, 2H), 2.20 (s, 3H), 1.77 (s, 3H), 1.61-1.54 (m, 2H), 1.36-1.26 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 158.0, 157.7, 145.8, 129.0, 128.0, 117.0, 114.5, 110.0, 55.3, 30.7, 26.1, 22.3, 13.8, 11.8, 8.5; IR (film) 2956, 2924, 1592, 1569, 1461, 1033, 822 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{22}\text{O}_2\text{S}$: 290.1341; found : 290.1345.



6ba

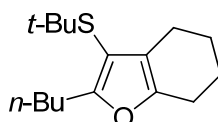
2-*n*-Butyl-4,5-diethyl-3-(propylthio)furan (6ba) : 54.1 mg (71%), R_f = 0.6 (EtOAc:Hexane = 1:20); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 2.69 (t, J = 7.6 Hz, 2H), 2.58-2.48 (m, 4H), 2.39 (q, J = 7.5 Hz, 2H), 1.63-1.48 (m, 4H), 1.36 (sextet, J = 7.4 Hz, 2H), 1.17 (t, J = 7.5 Hz, 3H), 1.11 (t, J = 7.5 Hz, 3H), 0.97 (t, J = 8.5 Hz, 3H), 0.93 (t, J = 8.5 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.4, 150.2, 122.5, 110.5, 38.6, 30.8, 26.1, 22.9, 22.5, 19.9, 17.0, 15.7, 13.9, 13.3; IR (film) 2961, 2931, 2873, 1566, 1459,

1377, 1250, 1081, 1061, 631 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{26}\text{OS}$: 254.1704; found : 254.1702.



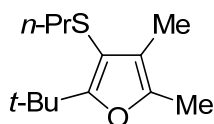
6ea

2-*n*-Butyl-4,5-diphenyl-3-(propylthio)furan (6ea) : 44.1 mg (42%), R_f = 0.5 (Hexane); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.41-7.34 (m, 7H), 7.24-7.19 (m, 2H), 7.18-7.14 (m, 1H), 2.86 (t, J = 7.6 Hz, 2H), 2.20 (t, J = 7.2 Hz, 2H), 1.73 (quintet, J = 7.6 Hz, 2H), 1.45 (sextet, J = 7.4 Hz, 2H), 1.34 (sextet, J = 7.3 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H), 0.78 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 158.8, 147.0, 133.6, 131.0, 130.2, 128.5, 128.3, 127.4, 127.0, 125.35, 125.26, 113.0, 37.4, 30.7, 26.3, 22.5, 22.4, 13.9, 13.1; IR (film) 2960, 2929, 2871, 2050, 1602, 1445, 1259, 1067, 1049, 793, 698, 632 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{23}\text{H}_{26}\text{OS}$: 350.1704; found : 350.1706.



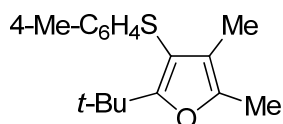
6fc

3-(*tert*-Butylthio)-2-*n*-butyl-4,5,6,7-tetrahydrobenzofuran (6fc) : 62.3 mg (78%), R_f = 0.6 (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 2.73 (t, J = 7.8 Hz, 2H), 2.56-2.53 (m, 2H), 2.40-2.36 (m, 2H), 1.85-1.79 (m, 2H), 1.72-1.66 (m, 2H), 1.64-1.57 (m, 2H), 1.41-1.32 (m, 2H), 1.25 (s, 9H), 0.92 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 159.7, 148.7, 121.0, 108.5, 46.7, 31.0, 30.7, 26.2, 23.22, 23.21, 23.1, 22.6, 21.8, 13.9; IR (film) 2930, 1556, 1455, 1361, 1219, 1169, 1125, 757 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{26}\text{OS}$: 266.1704; found : 266.1704.



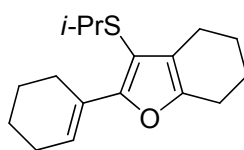
6ga

2-*tert*-Butyl-4,5-dimethyl-3-(*n*-propylthio)furan (6ga) : 47.5 mg (70%), R_f = 0.7 (EtOAc:Hexane = 1:20); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 2.54 (t, J = 7.4 Hz, 2H), 2.16 (s, 3H), 1.92 (s, 3H), 1.64-1.55 (m, 2H), 1.39 (s, 9H), 0.98 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 161.8, 143.9, 118.4, 109.9, 38.8, 34.2, 29.8, 22.8, 13.6, 11.7, 8.7; IR (film) 2963, 2923, 1536, 1456, 1172, 1130, 757 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_{22}\text{OS}$: 226.1391; found : 226.1391.



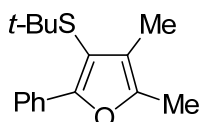
6ge

3-(*p*-Tolylthio)-2-*tert*-butyl-4,5-dimethylfuran (6ge) : 55.9 mg (68%), R_f = 0.7 (EtOAc:Hexane = 1:20); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.02 (d, J = 8.1 Hz, 2H), 6.93 (d, J = 8.3 Hz, 2H), 2.27 (s, 3H), 2.21 (d, J = 0.6 Hz, 3H), 1.72 (d, J = 0.6 Hz, 3H), 1.37 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 163.6, 144.6, 135.4, 134.1, 129.5, 125.2, 118.4, 106.6, 34.2, 29.5, 20.9, 11.8, 8.3; IR (film) 2967, 2921, 1282, 1173, 1130, 1058, 757 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{22}\text{OS}$: 274.1391; found : 274.1393.



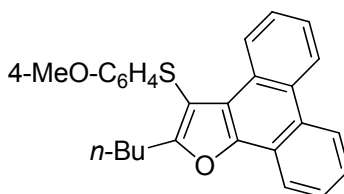
6hb

2-Cyclohexenyl-4,5,6,7-tetrahydro-3-(*iso*-propylthio)benzofuran (6hb) : 60.5 mg (73%), R_f = 0.6 (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 6.51-6.48 (m, 1H), 3.09-2.99 (m, 1H), 2.56-2.51 (m, 4H), 2.41-2.37 (m, 2H), 2.24-2.18 (m, 2H), 1.84-1.78 (m, 2H), 1.75-1.68 (m, 4H), 1.67-1.60 (m, 2H), 1.21 (d, J = 6.7 Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 154.7, 148.4, 128.6, 126.3, 122.4, 109.5, 39.1, 26.3, 25.6, 23.2, 23.1, 23.0, 22.7, 22.1, 21.3; IR (film) 2929, 1634, 1445, 1272, 1153, 1070, 801 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{24}\text{OS}$: 276.1548; found : 276.1552.



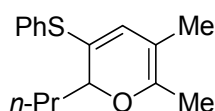
6ic

3-(*tert*-Butylthio)-4,5-dimethyl-2-phenylfuran (6ic) : 42.9 mg (55%), R_f = 0.7 (EtOAc:Hexane = 1:20); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.21-8.19 (m, 2H), 7.37-7.33 (m, 3H), 7.26-7.22 (m, 1H), 2.30 (s, 3H), 1.99 (s, 3H), 1.18 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 153.8, 146.5, 131.6, 128.0, 127.3, 126.2, 120.8, 112.0, 49.0, 31.0, 12.1, 9.2; IR (film) 3058, 2938, 2861, 1741, 1666, 1553, 1536, 1315, 1294, 806 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{20}\text{OS}$: 260.1235; found : 260.1238.



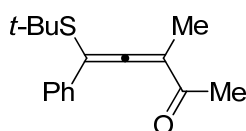
6jf

2-*n*-Butyl-3-((4-methoxyphenyl)thio)phenanthro[9,10-*b*]furan (6jf) : 80.3 mg (65%), R_f = 0.5 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 9.06-9.04 (m, 1H), 8.66 (d, J = 8.3 Hz, 2H), 8.34 (dd, J = 7.9, 1.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.62-7.58 (m, 1H), 7.57-7.49 (m, 2H), 7.12 (d, J = 9.0 Hz, 2H), 6.71 (d, J = 9.0 Hz, 2H), 3.66 (s, 3H), 3.07 (t, J = 7.6 Hz, 2H), 1.78 (quintet, J = 7.5 Hz, 2H), 1.42 (sextet, J = 7.4 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 163.7, 157.9, 148.5, 129.0, 128.5, 128.4, 128.0, 127.8, 127.10, 127.07, 126.0, 125.3, 123.9, 123.5, 123.3, 122.1, 120.4, 119.6, 114.9, 106.8, 55.3, 30.8, 26.3, 22.5, 14.0; IR (film) 3063, 3025, 3000, 2833, 2534, 2042, 1872, 1804, 1377, 908, 859 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{27}\text{H}_{24}\text{O}_2\text{S}$: 412.1497; found : 412.1497.



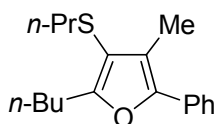
11

5,6-Dimethyl-3-(phenylthio)-2-propyl-2H-pyran (11) : 33.6 mg (43%), R_f = 0.5 (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.31-7.29 (m, 2H), 7.27-7.21 (m, 3H), 5.78 (s, 1H), 4.10 (dd, J = 6.4, 8.5 Hz, 1H), 2.17 (s, 3H), 1.97-1.77 (m, 5H), 1.47-1.36 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 151.3, 146.5, 134.7, 132.8, 128.6, 127.1, 114.3, 110.3, 46.4, 35.9, 20.7, 13.7, 11.4, 9.9; IR (film) 3398, 3058, 2870, 1638, 1563, 1222, 1090, 807 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{20}\text{OS}$: 260.1235; found : 260.1237.



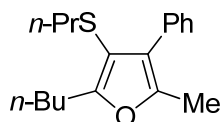
7ic

5-(*tert*-Butylthio)-3-methyl-5-phenylpenta-3,4-dien-2-one (7ic) : 40.6 mg (52%), R_f = 0.5 (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, C_6D_6): δ 7.69-7.67 (m, 2H), 7.13-7.11 (m, 2H), 7.05-7.01 (m, 1H), 2.04 (s, 3H), 1.91 (s, 3H), 1.17 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 217.6, 196.1, 135.5, 128.8, 127.4, 103.5, 102.8, 47.2, 31.2, 27.0, 13.4; IR (film) 3058, 2962, 1919, 1682, 1446, 1363, 1246, 984 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{20}\text{OS}$: 260.1235; found : 260.1237.



6ca

2-*n*-Butyl-4-methyl-5-phenyl-3-(propylthio)furan (6ca) : 69.1 mg (80%), $R_f = 0.7$ (EtOAc:Hexane = 1:20); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, $J = 7.4$ Hz, 2H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.24 (t, $J = 7.4$ Hz, 1H), 2.81 (t, $J = 7.6$ Hz, 2H), 2.52 (t, $J = 7.3$ Hz, 2H), 2.30 (s, 3H), 1.71-1.63 (m, 2H), 1.59-1.50 (m, 2H), 1.45-1.35 (m, 2H), 0.99 (t, $J = 7.3$ Hz, 3H), 0.95 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 158.7, 146.8, 131.9, 128.5, 126.5, 125.1, 124.9, 119.6, 113.9, 38.1, 30.7, 30.3, 26.3, 22.8, 22.4, 13.9, 13.3, 10.5; IR (film) 3054, 2958, 2928, 1596, 1492, 1292, 1236, 1056, 761 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{24}\text{OS}$: 288.1548; found : 288.1548.

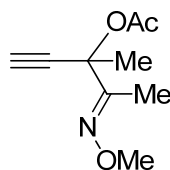


6da

2-*n*-Butyl-5-methyl-4-phenyl-3-(propylthio)furan (6da) : 70.8 mg (82%), $R_f = 0.7$ (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.45-7.37 (m, 4H), 7.29 (t, $J = 7.2$ Hz, 1H), 2.76 (t, $J = 7.6$ Hz, 2H), 2.29 (s, 3H), 2.20 (t, $J = 7.2$ Hz, 2H), 1.68-1.61 (m, 2H), 1.45-1.36 (m, 2H), 1.36-1.27 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H), 0.77 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.5, 146.6, 133.4, 129.5, 128.1, 126.6, 123.3, 110.3, 37.5, 30.8, 26.1, 22.44, 22.39, 13.9, 13.0, 12.6; IR (film) 3054, 2958, 2928, 1598, 1496, 1293, 1168, 1011, 761 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{24}\text{OS}$: 288.1548; found : 288.1548.

7. General procedure for the synthesis of imido-yl-substituted propargyl acetates 8

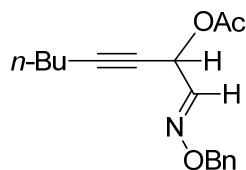
: To a solution of pyridine (323 μL , 4.0 mmol) was added dropwise 3-hydroxy-3-methylpent-4-yn-2-one *O*-methyl oxime (282.3 mg, 2.0 mmol) in CH_2Cl_2 (6 ml) at 0°C . After being stirred for 10 min, and acetyl chloride (284 μL , 4.0 mmol) added dropwise this solution. The mixture was allowed to room temperature and then, mixture was stirred for 12 h. The reaction mixture was quenched with H_2O (5 mL). The aqueous layer was extracted with CH_2Cl_2 ($3 \times 20\text{ mL}$), dried with anhydrous MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 1:10) to give 4-(methoxyimino)-3-methylpent-1-yn-3-yl acetate (**8a**, 285.7 mg, 78%).



8a

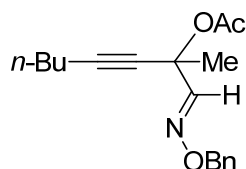
4-(Methoxyimino)-3-methylpent-1-yn-3-yl acetate (8a) : 285.7 mg (78%), $R_f = 0.4$ (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 3.90 (s, 3H), 2.66 (s, 1H), 2.08 (s, 3H), 1.92 (s, 3H),

1.81 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 168.9, 155.2, 81.6, 74.83, 74.78, 62.0, 25.9, 21.5, 10.8; IR (film) 3270, 1746, 1369, 1230, 1044, 1014, 919, 656 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_9\text{H}_{13}\text{NO}_3$: 183.0895; found : 183.0899.



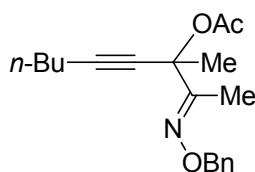
8b

1-(Benzyloxyimino)oct-3-yn-2-yl acetate (8b) : 408.0 mg (71%), R_f = 0.5 (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.41 (d, J = 6.8 Hz, 1H), 7.37-7.32 (m, 5H), 5.92 (dt, J = 6.8, 2.1 Hz, 1H), 5.11 (s, 2H), 2.23 (dt, J = 10.6, 2.0 Hz, 2H), 2.10 (s, 3H), 1.53-1.46 (m, 2H), 1.43-1.34 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 169.2, 145.5, 136.8, 128.51, 128.46, 128.1, 89.3, 73.9, 61.7, 30.3, 21.9, 20.9, 18.5, 13.6; IR (film) 2934, 1747, 1370, 1221, 1013, 938, 793, 754, 699 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_3$: 287.1521; found : 287.1518.



8c

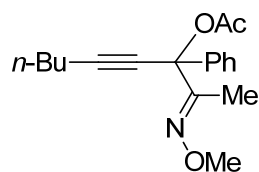
1-(Benzyloxyimino)-2-methyloct-3-yn-2-yl acetate (8c) : 373.5 mg (62%), R_f = 0.5 (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.74 (s, 1H), 7.37-7.35 (m, 4H), 7.34-7.29 (m, 1H), 5.10 (s, 2H), 2.23 (t, J = 7.0 Hz, 2H), 2.03 (s, 3H), 1.76 (s, 3H), 1.52-1.45 (m, 2H), 1.43-1.36 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 169.0, 150.2, 137.1, 128.42, 128.38, 128.0, 87.8, 78.0, 76.4, 72.0, 30.4, 26.0, 21.9, 21.6, 18.5, 13.6; IR (film) 2934, 1745, 1368, 1236, 1014, 909, 731, 698, 648 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_3$: 301.1678; found : 301.1679.



8d

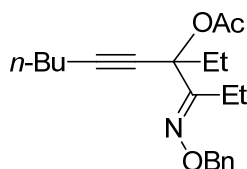
2-((Benzyloxy)imino)-3-methylnon-4-yn-3-yl acetate (8d) : 441.3 mg (70%), R_f = 0.4 (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.37-7.27 (m, 5H), 5.12 (s, 2H), 2.23 (t, J = 7.0 Hz, 2H), 2.02 (s, 3H), 1.97 (s, 3H), 1.78 (s, 3H), 1.53-1.46 (m, 2H), 1.43-1.35 (m, 2H), 0.90 (t, J = 7.2, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 168.9, 156.5, 138.0, 128.2, 128.1, 127.6, 87.4, 78.4, 76.0, 75.8, 30.5, 25.9, 21.9, 21.7, 18.5, 13.6, 11.4; IR (film) 3280, 2934, 1747, 1366, 1234, 1012, 939, 856, 698

cm⁻¹; HRMS (EI): *m/z* calcd for C₁₉H₂₅NO₃: 315.1834; found : 315.1830.



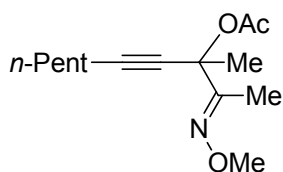
8e

2-(Methoxyimino)-3-phenylnon-4-yn-3-yl acetate (8e) : 325.4 mg (54%), *R_f* = 0.3 (EtOAc:Hexane = 1:10); white solid; Melting Point : 152-154 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.64-7.60 (m, 2H), 7.38-7.29 (m, 3H), 3.90 (s, 3H), 2.34 (t, *J* = 7.0 Hz, 2H), 2.14 (s, 3H), 1.77 (s, 3H), 1.61-1.51 (m, 2H), 1.49-1.39 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ¹³C{¹H} NMR(100 MHz, CDCl₃): δ 168.3, 155.0, 139.0, 128.3, 128.2, 126.6, 90.8, 78.9, 76.6, 62.0, 30.4, 22.0, 21.7, 18.7, 13.6, 11.6; IR (film) 3323, 2930, 1656, 1411, 1388, 1153, 1094, 1025, 946, 864 cm⁻¹; HRMS (EI): *m/z* calcd for C₁₈H₂₃NO₃: 301.1678; found : 301.1680.



8f

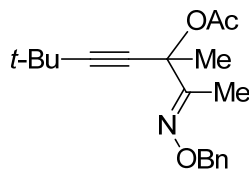
3-(Benzyloxyimino)-4-ethyldec-5-yn-4-yl acetate (8f) : 398.1 mg (58%), *R_f* = 0.4 (Acetone:Pentane = 1:15); colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.27 (m, 5H), 5.09 (s, 2H), 2.57-2.37 (m, 2H), 2.24 (t, *J* = 7.0 Hz, 2H), 2.10-2.01 (m, 1H), 1.98 (s, 3H), 1.97-1.86 (m, 1H), 1.54-1.47 (m, 2H), 1.45-1.36 (m, 2H), 1.13 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); ¹³C{¹H} NMR(100 MHz, CDCl₃): δ 168.8, 160.5, 138.3, 128.2, 127.9, 127.5, 88.2, 78.7, 75.9, 33.3, 30.6, 21.9, 21.5, 20.9, 18.5, 13.6, 10.8, 8.5; IR (film) 3343, 2935, 1673, 1387, 1233, 1087, 1017, 948, 845, 699 cm⁻¹; HRMS (EI): *m/z* calcd for C₂₁H₂₉NO₃: 343.2147; found : 343.2149.



8g

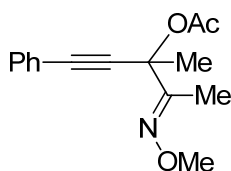
2-(Methoxyimino)-3-methyldec-4-yn-3-yl acetate (8g) : 379.8 mg (75%), *R_f* = 0.3 (EtOAc:Hexane = 1:20); colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 3.88 (s, 3H), 2.22 (t, *J* = 7.2 Hz, 2H), 2.05 (s, 3H), 1.92 (s, 3H), 1.79 (s, 3H), 1.55-1.48 (m, 2H), 1.39-1.28 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H); ¹³C{¹H} NMR(100 MHz, CDCl₃): δ 168.9, 156.0, 87.4, 78.4, 75.8, 61.9, 31.0, 28.0, 25.8, 22.1, 21.7, 18.8, 14.0,

11.0; IR (film) 3281, 2938, 2255, 1742, 1368, 1243, 1048, 906, 728 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_3$: 253.1678; found : 253.1676.



8h

2-(Benzyloxyimino)-3,6,6-trimethylhept-4-yn-3-yl acetate (8h) : 327.8 mg (52%), R_f = 0.4 (EtOAc:Hexane = 1:10); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.35-7.27 (m, 5H), 5.12 (s, 2H), 2.01 (s, 3H), 1.97 (s, 3H), 1.77 (s, 3H), 1.20 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 168.8, 156.6, 138.1, 128.2, 128.1, 127.6, 95.2, 76.0, 75.7, 30.7, 27.4, 25.8, 21.7, 11.5; IR (film) 3380, 2970, 1747, 1365, 1230, 1203, 1013, 937, 856, 698 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_3$: 315.1834; found : 315.1837.



8i

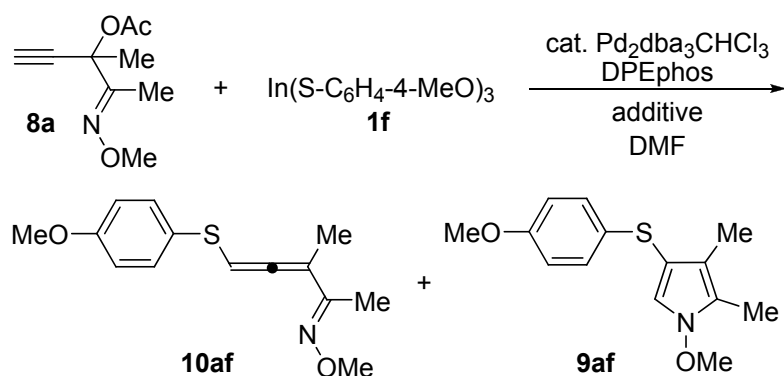
4-(Methoxyimino)-3-methyl-1-phenylpent-1-yn-3-yl acetate (8i) : 310.9 mg (60%), R_f = 0.3 (EtOAc:Hexane = 1:20); colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.46-7.44 (m, 2H), 7.32-7.28 (m, 3H), 3.90 (s, 3H), 2.09 (s, 3H), 2.00 (s, 3H), 1.91 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 168.9, 155.5, 131.9, 128.7, 128.2, 122.2, 87.2, 86.2, 75.8, 62.0, 25.6, 21.7, 11.2; IR (film) 3322, 1742, 1369, 1235, 1048, 904, 726 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_3$: 259.1208; found : 259.1204.

Table 2. Reactions of Imidoyl Propargyl Acetates with Indium(III) Organothiولات^a

R^1 $\equiv$ C $\begin{matrix} OAc \\ \\ R^3 \end{matrix}$ $\begin{matrix} R^2 \\ \\ N \\ \\ OR^5 \end{matrix}$ $+$ $In(SR^4)_3$ 1 $cat. Pd_2dba_3CHCl_3$ $DPEphos$ $\xrightarrow{DMF}$ R^4S $\begin{matrix} \\ \\ \\ \end{matrix}$ $\begin{matrix} R^3 \\ \\ C \\ \\ N \\ \\ OR^5 \end{matrix}$ R^1 10 $+$ R^4S $\begin{matrix} R^3 \\ \\ C \\ \\ N \\ \\ OR^5 \end{matrix}$ R^1 9					
entry	R^4	14	time (min)	product	yield (%) (10:9)
1	4-MeO-C ₆ H ₄	$\equiv$ $\begin{matrix} OAc \\ \\ Me \end{matrix}$ $\begin{matrix} R^2 \\ \\ N \\ \\ OMe \end{matrix}$ 8a	1	$4-MeO-C_6H_4S$ $\begin{matrix} \\ \\ \\ \end{matrix}$ $\begin{matrix} Me \\ \\ C \\ \\ N \\ \\ OMe \end{matrix}$ Me 10af $4-MeO-C_6H_4S$ $\begin{matrix} Me \\ \\ C \\ \\ N \\ \\ OMe \end{matrix}$ Me 9af	55 (27:73)
2	4-Me-C ₆ H ₄	$n-Bu \equiv$ $\begin{matrix} OAc \\ \\ Et \end{matrix}$ $\begin{matrix} Et \\ \\ N \\ \\ OBn \end{matrix}$ 8f	5	$4-Me-C_6H_4S$ $\begin{matrix} \\ \\ \\ \end{matrix}$ $\begin{matrix} Et \\ \\ C \\ \\ N \\ \\ OBn \end{matrix}$ Et 10fe $4-Me-C_6H_4S$ $\begin{matrix} Et \\ \\ C \\ \\ N \\ \\ OBn \end{matrix}$ Et 9fe	77 (19:81)
3	<i>i</i> -Pr	$t-Bu \equiv$ $\begin{matrix} OAc \\ \\ Me \end{matrix}$ $\begin{matrix} Me \\ \\ N \\ \\ OBn \end{matrix}$ 8h	0.5	$i-PrS$ $\begin{matrix} \\ \\ \\ \end{matrix}$ $\begin{matrix} Me \\ \\ C \\ \\ N \\ \\ OBn \end{matrix}$ Me 10hb $t-Bu$ $\begin{matrix} \\ \\ \\ \end{matrix}$ $\begin{matrix} Me \\ \\ C \\ \\ N \\ \\ OBn \end{matrix}$ Me —	84
4	<i>n</i> -Pr	$Ph \equiv$ $\begin{matrix} OAc \\ \\ Me \end{matrix}$ $\begin{matrix} Me \\ \\ N \\ \\ OMe \end{matrix}$ 8i	0.5	$n-PrS$ $\begin{matrix} \\ \\ \\ \end{matrix}$ $\begin{matrix} Me \\ \\ C \\ \\ N \\ \\ OMe \end{matrix}$ Ph 10ia Ph $\begin{matrix} \\ \\ \\ \end{matrix}$ $\begin{matrix} Me \\ \\ C \\ \\ N \\ \\ OMe \end{matrix}$ Me —	84

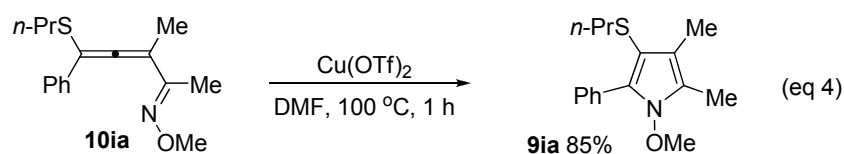
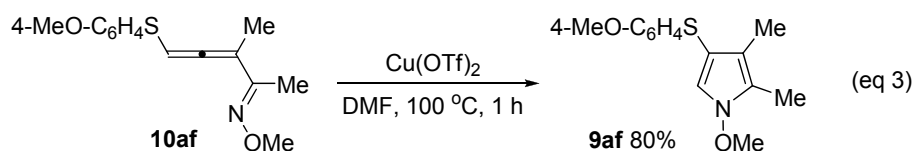
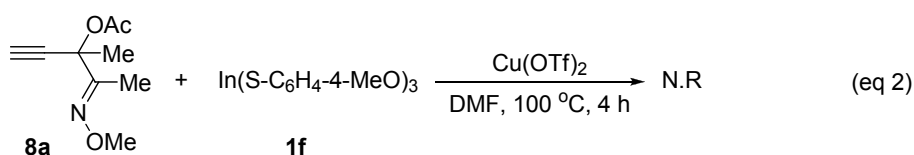
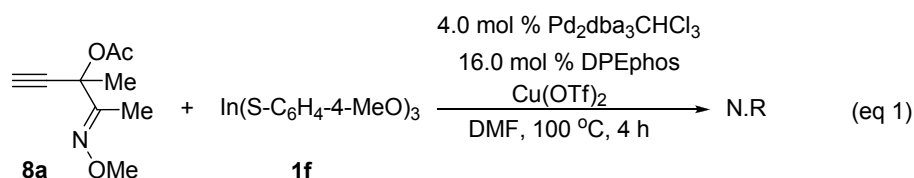
^aReactions were carried out with **8** (0.3 mmol, 1 equiv) and **1** (0.34 equiv) in the presence of 4.0 mol % Pd₂dba₃CHCl₃ and 16.0 mol % DPEphos in DMF at 150 °C.

Table 3. Reaction Optimization for the Synthesis of Tetrasubstituted Pyrroles *via* Pd-Catalyzed Propargyl Substitution and Cycloisomerization^a



entry	additive (equiv)	temp (°C)	time (h)	yield (%)
1	TfOH (0.5)	100	4	20 (15)
2	AgOTf (0.5)	100	2	15 (55)
3	In(OTf) ₃ (0.5)	100	2	23 (50)
4	Cu(OTf) ₂ (0.5)	100	1	68
5	Cu(OTf) ₂ (0.3)	100	1	60 (10)
6	Cu(OTf) ₂ (0.1)	100	1	54 (20)
7	CuI (0.5)	100	2	18 (51)

^aReactions were carried out with **8a** (0.3 mmol, 1 equiv) and **1f** (0.34 equiv) in the presence of 4.0 mol % $\text{Pd}_2\text{dba}_3\text{CHCl}_3$, 16.0 mol % DPEphos, and additive (0.1 ~ 0.5 equiv) in DMF. ^bNumbers in parentheses indicate the isolated yields of **10af**.

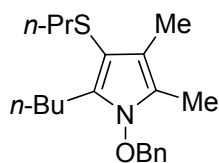


8. General procedure for the synthesis of pyrroles 9d, 9g

: To a suspension of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (12.4 mg, 0.012 mmol, 4.0 mol %) and DPEphos (25.8 mg, 0.048 mmol, 16.0 mol %) in DMF (0.6 mL) was added 2-(benzyloxyimino)-3-methylnon-4-yn-3-yl acetate (**8d**, 94.6 mg, 0.30 mmol) in DMF (0.2 mL) at room temperature under a nitrogen atmosphere. After being stirred for 1 min, $\text{In}(\text{SPh})_3$ (44.2 mg, 0.1 mmol) in DMF (0.7 mL) was transferred via double-ended needle and the mixture was stirred at 150 °C for 1 h. The reaction mixture was quenched with sat. NH_4Cl solution (1.0 mL). The aqueous layer was extracted with ether (3×20 mL), and the combined organics were washed with sat. NH_4Cl (10 mL) and sat. NaCl solution (10 mL), dried with anhydrous MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 1:10) to give 1-(benzyloxy)-2-*n*-butyl-4,5-dimethyl-3-(phenylthio)-1*H*-pyrrole (**9dd**, 81.2 mg, 74%).

General procedure for the synthesis of pyrroles 9a, 9b, 9c, 9e, 9f, 9h, 9i

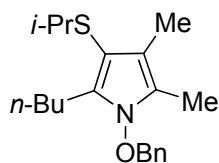
: To a suspension of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (12.4 mg, 0.012 mmol, 4.0 mol %) and DPEphos (25.8 mg, 0.048 mmol, 16.0 mol %) in DMF (0.6 mL) was added 4-(methoxyimino)-3-methylpent-1-yn-3-yl acetate (**8a**, 55.0 mg, 0.3 mmol) in DMF (0.2 mL) at room temperature under a nitrogen atmosphere. After being stirred for 1 min, $\text{In}(\text{SPh})_3$ (44.2 mg, 0.1 mmol) in DMF (0.7 mL) was transferred via double-ended needle and the mixture was stirred at 100 °C for 1 h. And 50 mol % $\text{Cu}(\text{OTf})_2$ (54.3 mg, 0.15 mmol) in DMF (0.2 mL) was transferred via double-ended needle and the mixture was stirred at 100 °C for 30 min. The reaction mixture was quenched with H_2O (1.0 mL). The aqueous layer was extracted with ether (3×20 mL), and the combined organics were washed with sat. NH_4Cl (10 mL) and sat. NaCl solution (10 mL), dried with anhydrous MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 1:10) to give 1-methoxy-2,3-dimethyl-4-(phenylthio)-1*H*-pyrrole (**9ad**, 47.7 mg, 68%).



9da

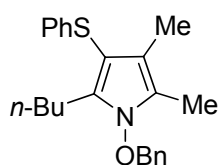
1-(Benzyloxy)-2-*n*-butyl-4,5-dimethyl-3-(propylthio)-1*H*-pyrrole (9da) : 70.5 mg (71%), R_f = 0.6 (EtOAc:Hexane = 1:10); brown oil; ^1H NMR (400 MHz, CDCl_3): δ 7.40 (s, 5H), 4.97 (s, 2H), 2.65 (t, J = 7.9 Hz, 2H), 2.46 (t, J = 7.3 Hz, 2H), 2.17 (s, 3H), 2.03 (s, 3H), 1.62-1.57 (m, 2H), 1.55-1.47 (m, 2H), 1.36 (sext, J = 7.4 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 134.3, 131.7, 129.3, 129.1, 128.7, 119.8, 113.8, 103.7, 80.5, 39.2, 32.4, 24.2, 22.8, 22.7, 13.9,

13.5, 9.6, 9.0; IR (film) 3280, 2959, 1700, 1456, 998, 907, 729, 697 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{29}\text{NOS}$: 331.1970; found : 331.1968.



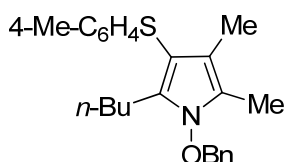
9db

1-(Benzyloxy)-2-*n*-butyl-3-(*iso*-propylthio)-4,5-dimethyl-1*H*-pyrrole (9db) : 72.7 mg (73%), R_f = 0.5 (EtOAc:Hexane = 1:10); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.39 (s, 5H), 4.97 (s, 2H), 2.90-2.83 (m, 1H), 2.64 (t, J = 7.9 Hz, 2H), 2.17 (s, 3H), 2.02 (s, 3H), 1.62-1.54 (m, 2H), 1.39-1.30 (m, 2H), 1.18 (d, J = 6.7 Hz, 6H), 0.91 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 134.3, 132.2, 129.3, 129.1, 128.7, 119.8, 114.2, 103.2, 80.5, 39.5, 32.3, 24.3, 23.1, 22.8, 14.0, 9.9, 9.0; IR (film) 2956, 2925, 2859, 2107, 1498, 1404, 1236, 1080, 907 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{29}\text{NOS}$: 331.1970; found : 331.1969.



9dd

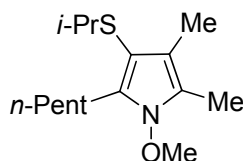
1-(Benzyloxy)-2-*n*-butyl-4,5-dimethyl-3-(phenylthio)-1*H*-pyrrole (9dd) : 81.2 mg (74%), R_f = 0.5 (EtOAc:Hexane = 1:10); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.41 (s, 5H), 7.18 (t, J = 7.7 Hz, 2H), 7.04-6.99 (m, 3H), 5.03 (s, 2H), 2.59 (t, J = 7.7 Hz, 2H), 2.21 (s, 3H), 1.90 (s, 3H), 1.51 (quintet, J = 7.7 Hz, 2H), 1.26 (sext, J = 7.4 Hz, 2H), 0.82 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 140.8, 134.1, 132.8, 129.4, 129.2, 128.8, 128.5, 124.9, 124.0, 120.5, 114.4, 99.9, 80.7, 32.0, 24.0, 22.5, 13.8, 9.4, 9.1; IR (film) 2930, 1653, 1583, 1477, 1024, 905, 727 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{23}\text{H}_{27}\text{NOS}$: 365.1813; found : 365.1812.



9de

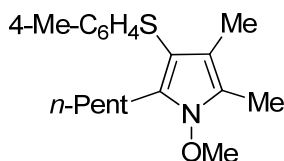
1-(Benzyloxy)-2-*n*-butyl-4,5-dimethyl-3-(*p*-tolylthio)-1*H*-pyrrole (9de) : 107.1 mg (94%), R_f = 0.7 (EtOAc:Hexane = 1:10); pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.41 (s, 5H), 7.00 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.1 Hz, 2H), 5.02 (s, 2H), 2.60 (t, J = 7.7 Hz, 2H), 2.26 (s, 3H), 2.21 (s, 3H), 1.90 (s,

3H), 1.51 (quintet, $J = 7.6$ Hz, 2H), 1.32-1.22 (m, 2H), 0.83 (t, $J = 7.3$, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 137.2, 134.2, 133.7, 132.7, 129.4, 129.3, 129.2, 128.8, 125.1, 120.5, 114.3, 100.3, 80.7, 32.1, 24.0, 22.6, 20.9, 13.8, 9.4, 9.1; IR (film) 3287, 1653, 1491, 1457, 1017, 904, 725 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{24}\text{H}_{29}\text{NOS}$: 379.1970; found : 379.1967.



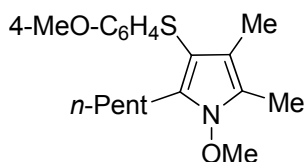
9gb

3-(*iso*-Propylthio)-1-methoxy-4,5-dimethyl-2-pentyl-1H-pyrrole (9gb) : 62.1 mg (78%), $R_f = 0.5$ (EtOAc:Hexane = 1:10); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 3.88 (s, 3H), 2.85 (septet, $J = 6.7$ Hz, 1H), 2.68 (t, $J = 8.0$ Hz, 2H), 2.16 (s, 3H), 2.00 (s, 3H), 1.63-1.57 (m, 2H), 1.37-1.31 (m, 4H), 1.17 (d, $J = 6.7$ Hz, 6H), 0.90 (t, $J = 6.9$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 131.7, 119.4, 114.1, 103.2, 65.7, 39.5, 31.9, 30.0, 24.3, 23.1, 22.5, 14.0, 9.7, 8.7; IR (film) 3311, 1653, 1420, 1265, 1153, 1021, 896, 733, 704 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{27}\text{NOS}$: 269.1813; found : 269.1812.



9ge

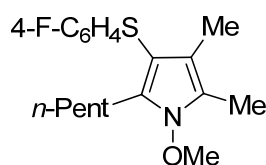
1-Methoxy-2,3-dimethyl-5-pentyl-4-(*p*-tolylthio)-1H-pyrrole (9ge) : 78.3 mg (82%), $R_f = 0.5$ (EtOAc:Hexane = 1:10); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 6.98 (d, $J = 8.0$ Hz, 2H), 6.89 (d, $J = 8.2$ Hz, 2H), 3.93 (s, 3H), 2.65 (t, $J = 7.8$ Hz, 2H), 2.26 (s, 3H), 2.21 (s, 3H), 1.88 (s, 3H), 1.55-1.51 (m, 2H), 1.26-1.23 (m, 4H), 0.81 (t, $J = 6.9$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 137.1, 133.7, 132.2, 129.3, 125.1, 120.0, 114.2, 100.2, 66.0, 31.6, 29.8, 24.0, 22.4, 20.8, 13.9, 9.3, 8.8; IR (film) 3281, 2925, 1700, 1265, 1017, 994, 736, 705 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{27}\text{NOS}$: 317.1813; found : 317.1815.



9gf

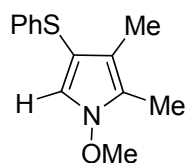
1-Methoxy-3-(4-methoxyphenylthio)-4,5-dimethyl-2-pentyl-1H-pyrrole (9gf) : 56.1 mg (84%), $R_f = 0.4$ (EtOAc:Hexane = 1:10); brown oil; ^1H NMR (400 MHz, CDCl_3): δ 6.96 (d, $J = 8.9$ Hz, 2H), 6.75 (d, $J = 8.9$ Hz, 2H), 3.92 (s, 3H), 3.74 (s, 3H), 2.66 (t, $J = 7.8$ Hz, 2H), 2.20 (s, 3H), 1.89 (s, 3H), 1.56-1.49

(m, 2H), 1.29-1.24 (m, 4H), 0.82 (t, $J = 7.0$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 157.1, 132.1, 131.4, 126.9, 120.0, 114.3, 114.1, 101.1, 66.0, 55.3, 31.6, 29.8, 24.1, 22.4, 14.0, 9.3, 8.7; IR (film) 3293, 2928, 1492, 1241, 1032, 904, 824, 726 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_2\text{S}$: 333.1762; found : 333.1765.



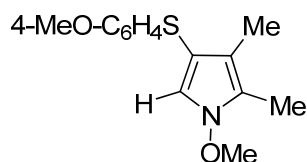
9gg

3-(4-Fluorophenylthio)-1-methoxy-4,5-dimethyl-2-pentyl-1H-pyrrole (9gg) : 77.2 mg (80%), $R_f = 0.6$ (EtOAc:Hexane = 1:10); brown oil; ^1H NMR (400 MHz, CDCl_3): δ 6.97-6.92 (m, 2H), 6.90-6.85 (m, 2H), 3.93 (s, 3H), 2.65 (t, $J = 7.8$ Hz, 2H), 2.21 (s, 3H), 1.88 (s, 3H), 1.55-1.47 (m, 2H), 1.28-1.22 (m, 4H), 0.81 (t, $J = 6.9$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 160.5 ($J_{\text{CF}} = 242.6$ Hz), 135.7 ($J_{\text{CF}} = 2.9$ Hz), 132.3, 126.5 ($J_{\text{CF}} = 7.6$ Hz), 120.2, 115.5 ($J_{\text{CF}} = 21.9$ Hz), 114.1, 100.2, 66.0, 31.6, 29.7, 24.0, 22.3, 13.9, 9.3, 8.7; IR (film) 3302, 2928, 1653, 1489, 1227, 1155, 992, 904, 726 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{24}\text{FNOS}$: 321.1563; found : 321.1566.



9ad

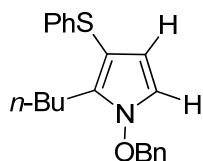
1-Methoxy-2,3-dimethyl-4-(phenylthio)-1H-pyrrole (9ad) : 36.4 mg (52%), $R_f = 0.6$ (EtOAc:Hexane = 1:10); red oil; ^1H NMR (400 MHz, CDCl_3): δ 7.19 (t, $J = 7.6$ Hz, 2H), 7.06-7.03 (m, 3H), 6.95 (s, 1H), 3.97 (s, 3H), 2.20 (s, 3H), 1.89 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 140.3, 128.6, 125.3, 124.4, 122.4, 118.3, 115.2, 103.0, 66.9, 9.2, 8.6; IR (film) 3033, 2956, 1722, 1477, 1024, 904, 725, 650 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_{15}\text{NOS}$: 233.0874; found : 233.0874.



9af

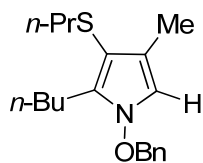
1-Methoxy-4-(4-methoxyphenylthio)-2,3-dimethyl-1H-pyrrole (9af) : 53.7 mg (68%), $R_f = 0.6$ (EtOAc:Hexane = 1:10); brown oil; ^1H NMR (400 MHz, CDCl_3): δ 7.05 (d, $J = 8.9$ Hz, 2H), 6.93 (s, 1H), 6.77 (d, $J = 8.9$ Hz, 2H), 3.95 (s, 3H), 3.75 (s, 3H), 2.17 (s, 3H), 1.89 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz,

CDCl₃): δ 157.5, 130.6, 127.8, 122.3, 117.9, 114.8, 114.4, 104.7, 66.8, 55.3, 9.2, 8.6; IR (film) 3295, 1653, 1494, 1246, 904, 725, 650 cm⁻¹; HRMS (EI): m/z calcd for C₁₄H₁₇NO₂S: 263.0980; found : 263.0981.



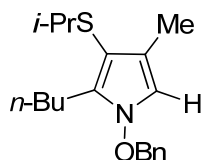
9bd

1-(Benzyloxy)-2-n-butyl-4-methyl-3-(phenylthio)-1H-pyrrole (9bd) : 31.4 mg (31%), R_f = 0.4 (EtOAc:Hexane = 1:10); colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.41-7.38 (m, 3H), 7.37-7.33 (m, 2H), 7.18 (t, J = 7.7 Hz, 2H), 7.06-6.99 (m, 3H), 6.72 (d, J = 3.2 Hz, 1H), 6.09 (d, J = 3.2 Hz, 1H), 5.11 (s, 2H), 2.48 (t, J = 7.7 Hz, 2H), 1.46 (quintet, J = 7.6 Hz, 2H), 1.24 (sextet, J = 7.4 Hz, 2H), 0.81 (t, J = 7.3 Hz, 3H); ¹³C{¹H} NMR(100 MHz, CDCl₃): δ 140.9, 134.8, 134.1, 129.6, 129.4, 128.8, 128.5, 125.2, 124.3, 115.1, 110.5, 100.4, 81.5, 31.4, 23.5, 22.5, 13.8; IR (film) 3033, 2956, 1722, 1477, 1024, 908, 738, 697, 632 cm⁻¹; HRMS (EI): m/z calcd for C₂₁H₂₃NOS: 337.1500; found : 337.1500.



9ca

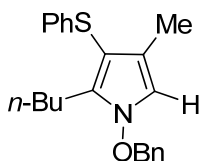
1-(Benzyloxy)-2-n-butyl-4-methyl-3-(n-propylthio)-1H-pyrrole (9ca) : 57.2 mg (60%), R_f = 0.6 (EtOAc:Hexane = 1:10); red oil; ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.36 (m, 3H), 7.34-7.31 (m, 2H), 6.49 (s, 1H), 5.02 (s, 2H), 2.54 (t, J = 7.8 Hz, 2H), 2.45 (t, J = 7.3 Hz, 2H), 2.08 (s, 3H), 1.57-1.47 (m, 4H), 1.33 (sextet, J = 7.4 Hz, 2H), 0.96 (t, J = 7.3 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H); ¹³C{¹H} NMR(100 MHz, CDCl₃): δ 134.5, 133.7, 129.4, 129.1, 128.7, 118.2, 112.0, 104.3, 81.3, 39.1, 32.0, 24.0, 22.8, 22.7, 13.9, 13.5, 10.7; IR (film) 2961, 1704, 905, 728, 699, 649 cm⁻¹; HRMS (EI): m/z calcd for C₁₉H₂₇NO₂S: 317.1813; found : 317.1811.



9cb

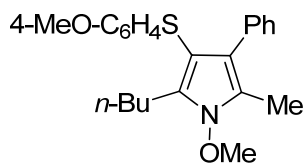
1-(Benzyloxy)-2-n-butyl-3-(iso-propylthio)-4-methyl-1H-pyrrole (9cb) : 72.1 mg (76%), R_f = 0.7 (EtOAc:Hexane = 1:10); red oil; ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.35 (m, 3H), 7.34-7.31 (m, 2H), 6.50 (s, 1H), 5.02 (s, 2H), 2.86 (septet, J = 6.7 Hz, 1H), 2.51 (t, J = 7.9 Hz, 2H), 2.07 (s, 3H), 1.57-1.49

(m, 2H), 1.36-1.27 (m, 2H), 1.16 (d, $J = 6.7$ Hz, 6H), 0.89 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 134.4, 134.2, 129.5, 129.1, 128.7, 118.6, 112.0, 103.8, 81.2, 39.4, 31.8, 24.1, 23.0, 22.7, 13.9, 10.9; IR (film) 903, 725, 650 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{27}\text{NOS}$: 317.1813; found : 317.1816.



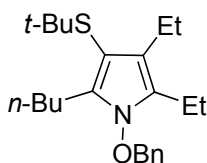
9cd

1-(Benzyloxy)-2-n-butyl-4-methyl-3-(phenylthio)-1H-pyrrole (9cd) : 88.6 mg (84%), $R_f = 0.7$ (EtOAc:Hexane = 1:10); red oil; ^1H NMR (400 MHz, CDCl_3): δ 7.42-7.34 (m, 5H), 7.18 (t, $J = 7.7$ Hz, 2H), 7.03 (t, $J = 7.3$ Hz, 1H), 6.97-6.95 (m, 2H), 6.60 (d, $J = 1.0$ Hz, 1H), 5.08 (s, 2H), 2.47 (t, $J = 7.7$ Hz, 2H), 1.95 (d, $J = 0.9$ Hz, 3H), 1.45 (quintet, $J = 7.6$ Hz, 2H), 1.23 (sextet, $J = 7.4$ Hz, 2H), 0.81 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 140.6, 134.9, 134.2, 129.5, 129.2, 128.7, 128.5, 124.8, 124.1, 118.9, 112.7, 100.4, 81.4, 31.6, 23.8, 22.5, 13.8, 10.4; IR (film) 3033, 2956, 1722, 1477, 1024, 908, 738, 697, 632 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{22}\text{H}_{25}\text{NOS}$: 351.1657; found : 351.1661.



9ef

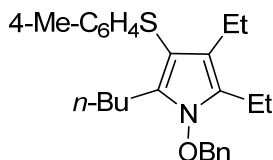
2-n-Butyl-1-methoxy-3-(4-methoxyphenylthio)-5-methyl-4-phenyl-1H-pyrrole (9ef) : 92.8 mg (81%), $R_f = 0.5$ (EtOAc:Hexane = 1:10); red oil; ^1H NMR (400 MHz, CDCl_3): δ 7.29-7.23 (m, 4H), 7.20-7.16 (m, 1H), 6.93 (d, $J = 8.9$ Hz, 2H), 6.71 (d, $J = 8.9$ Hz, 2H), 4.00 (s, 3H), 3.72 (s, 3H), 2.73 (t, $J = 7.8$ Hz, 2H), 2.31 (s, 3H), 1.59-1.51 (m, 2H), 1.34 (sextet, $J = 7.4$ Hz, 2H), 0.87 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 157.2, 134.9, 133.3, 131.9, 130.0, 127.8, 127.2, 125.9, 121.3, 120.9, 114.3, 100.5, 66.1, 55.3, 32.0, 24.0, 22.7, 13.9, 9.6; IR (film) 3295, 1653, 1492, 1242, 1153, 1027, 904, 724 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{23}\text{H}_{27}\text{NO}_2\text{S}$: 381.1762; found : 381.1759.



9fc

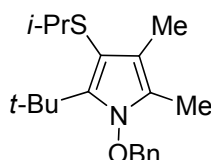
1-(Benzyloxy)-2-n-butyl-3-(tert-butylthio)-4,5-diethyl-1H-pyrrole (9fc) : 92.1 mg (82%), $R_f = 0.7$ (EtOAc:Hexane = 1:10); green oil; ^1H NMR (400 MHz, CDCl_3): δ 7.39 (s, 5H), 5.01 (s, 2H), 2.68-2.58

(m, 4H), 2.53 (q, $J = 7.5$ Hz, 2H), 1.62 (quintet, $J = 7.7$ Hz, 2H), 1.37-1.29 (m, 2H), 1.22 (s, 9H), 1.20 (t, $J = 7.6$ Hz, 3H), 1.09 (t, $J = 7.5$ Hz, 3H), 0.90 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 134.4, 132.9, 129.2, 129.0, 128.7, 125.5, 121.4, 101.7, 80.6, 46.3, 31.5, 31.0, 25.1, 22.9, 18.2, 17.6, 16.3, 14.8, 13.9; IR (film) 2926, 1653, 1457, 994, 904, 727 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{23}\text{H}_{35}\text{NOS}$: 373.2439; found : 373.2442.



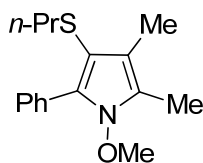
9fe

1-(Benzyloxy)-2-*n*-butyl-4,5-diethyl-3-(*p*-tolylthio)-1*H*-pyrrole (9fe) : 114.6 mg (94%), $R_f = 0.5$ (EtOAc:Hexane = 1:20); green oil; ^1H NMR (400 MHz, CDCl_3): δ 7.42 (s, 5H), 6.99 (d, $J = 8.2$ Hz, 2H), 6.89 (d, $J = 8.2$ Hz, 2H), 5.06 (s, 2H), 2.67-2.59 (m, 4H), 2.38 (q, $J = 7.5$ Hz, 2H), 2.26 (s, 3H), 1.57-1.49 (m, 2H), 1.32-1.22 (m, 5H), 0.99 (t, $J = 7.5$ Hz, 3H), 0.82 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 137.7, 134.2, 133.5, 132.8, 129.2, 129.1, 128.8, 126.2, 125.0, 120.6, 99.5, 81.0, 31.9, 24.1, 22.7, 20.9, 18.0, 17.4, 16.5, 15.0, 13.8; IR (film) 2930, 1653, 1491, 1457, 1017, 904, 806, 726 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{26}\text{H}_{33}\text{NOS}$: 407.2283; found : 407.2281.



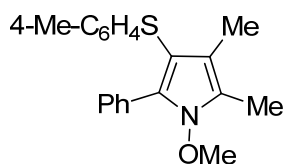
9hb

1-(Benzyloxy)-2-*tert*-butyl-3-(*iso*-propylthio)-4,5-dimethyl-1*H*-pyrrole (9hb) : 72.2 mg (63%), $R_f = 0.7$ (EtOAc:Hexane = 1:10); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.46-7.38 (m, 5H), 5.01 (s, 2H), 2.95 (septet, $J = 6.7$ Hz, 1H), 2.24 (s, 3H), 2.04 (s, 3H), 1.57 (s, 9H), 1.22 (d, $J = 6.7$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 136.5, 134.2, 128.9, 128.8, 128.5, 120.9, 116.1, 104.3, 79.8, 40.2, 34.6, 32.0, 22.9, 10.2, 9.6; IR (film) 3302, 1653, 1457, 995, 904, 726 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{29}\text{NOS}$: 331.1970; found : 331.1970.



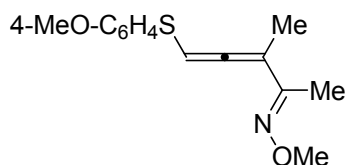
9ia

1-Methoxy-2,3-dimethyl-5-phenyl-4-(*iso*-propylthio)-1-pyrrole (9ia) : 68.7 mg (83%), R_f = 0.5 (EtOAc:Hexane = 1:10); red oil; ^1H NMR (400 MHz, CDCl_3): δ 7.68-7.65 (m, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 3.54 (s, 3H), 2.38 (t, J = 7.2 Hz, 2H), 2.24 (s, 3H), 2.11 (s, 3H), 1.33 (sextet, J = 7.3 Hz, 2H), 0.76 (t, J = 7.3 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 130.2, 129.7, 129.5, 127.9, 126.9, 121.5, 115.1, 106.3, 65.3, 38.8, 22.4, 13.1, 9.6, 8.8; IR (film) 3323, 1653, 1457, 1021, 904, 725 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{21}\text{NOS}$: 275.1344; found : 275.1346.



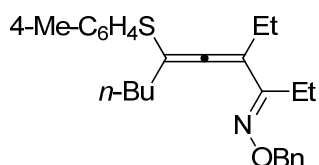
9ie

1-Methoxy-2,3-dimethyl-5-phenyl-4-(*p*-tolylthio)-1H-pyrrole (9ie) : 89.3 mg (92%), R_f = 0.5 (Acetone:Pentane = 1:40); red oil; ^1H NMR (400 MHz, CDCl_3): δ 7.58-7.55 (m, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 3.60 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 1.95 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, CDCl_3): δ 136.8, 133.9, 130.5, 129.6, 129.5, 129.3, 128.0, 127.2, 125.2, 122.2, 115.8, 102.7, 65.4, 20.9, 9.4, 8.9; IR (film) 2921, 1602, 1521, 1491, 1445, 1323, 1084, 1017, 976, 906, 805, 757, 728, 696 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{21}\text{NOS}$: 323.1344; found : 323.1341.



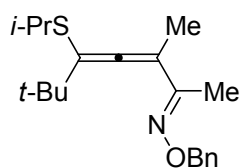
10af

(*E*)-5-((4-methoxyphenyl)thio)-3-methylpenta-3,4-dien-2-one O-methyl oxime (10af) : 21.3 mg (27%), R_f = 0.6 (EtOAc:Hexane = 1:20); colorless oil; ^1H NMR (400 MHz, C_6D_6): δ 7.31 (dt, J = 9.7, 2.6 Hz, 2H), 6.57 (dt, J = 9.7, 2.6 Hz, 2H), 5.97 (q, J = 2.4 Hz, 1H), 3.74 (s, 3H), 3.14 (s, 3H), 1.94 (d, J = 2.5 Hz, 3H), 1.92 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, C_6D_6): δ 205.1, 160.1, 152.3, 134.7, 124.1, 114.8, 107.8, 93.4, 61.7, 54.6, 15.0, 12.5; IR (film) 3248, 2907, 1945, 1615, 1517, 920, 730 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{S}$: 263.0980; found : 263.0983.



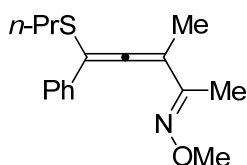
10fe

(E)-4-Ethyl-6-(p-tolylthio)deca-4,5-dien-3-one O-benzyl oxime (10fe) : 23.2 mg (19%), $R_f = 0.6$ (EtOAc:Hexane = 1:20); colorless oil; ^1H NMR (400 MHz, C_6D_6): δ 7.43-7.39 (m, 4H), 7.09-7.05 (m, 1H), 6.82 (d, $J=7.8$ Hz, 2H), 6.75 (d, $J=7.9$ Hz, 2H), 5.11 (s, 2H), 2.63-2.53 (m, 2H), 2.51-2.35 (m, 2H), 2.29-2.24 (m, 2H), 1.95 (s, 3H), 1.59-1.51 (m, 2H), 1.26-1.20 (m, 2H), 1.15 (t, $J = 7.5$ Hz, 3H), 1.06 (t, $J = 7.4$ Hz, 3H), 0.78 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR(100 MHz, C_6D_6): δ 203.6, 157.8, 138.7, 137.9, 137.3, 133.5, 129.9, 129.8, 128.9, 128.4, 111.3, 108.1, 76.3, 33.5, 30.7, 30.3, 30.1, 22.4, 22.1, 21.3, 20.8, 20.7, 13.8, 12.8, 11.6; IR (film) 3308, 3078, 1680, 1422, 1036, 899, 711 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{26}\text{H}_{33}\text{NOS}$: 407.2283; found : 407.2281.



10hb

(E)-5-(Isopropylthio)-3,6,6-trimethylhepta-3,4-dien-2-one O-benzyl oxime (10hb) : 83.5 mg (84%), $R_f = 0.6$ (EtOAc:Hexane = 1:20); yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.41-7.29 (m, 5H), 5.15 (s, 2H), 2.86 (sept, $J=6.7$ Hz, 1H), 1.93 (d, $J=2.5$ Hz, 6H), 1.27 (d, $J=6.7$ Hz, 3H), 1.26 (d, $J=6.7$ Hz, 3H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 200.6, 154.9, 138.5, 128.73, 128.72, 128.2, 116.4, 107.0, 76.6, 37.2, 36.7, 30.1, 23.9, 23.4, 15.7, 13.4; IR (film) 3258, 2819, 1929, 1614, 1513, 938, 760, 700 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{29}\text{NOS}$: 331.1970; found : 331.1969.



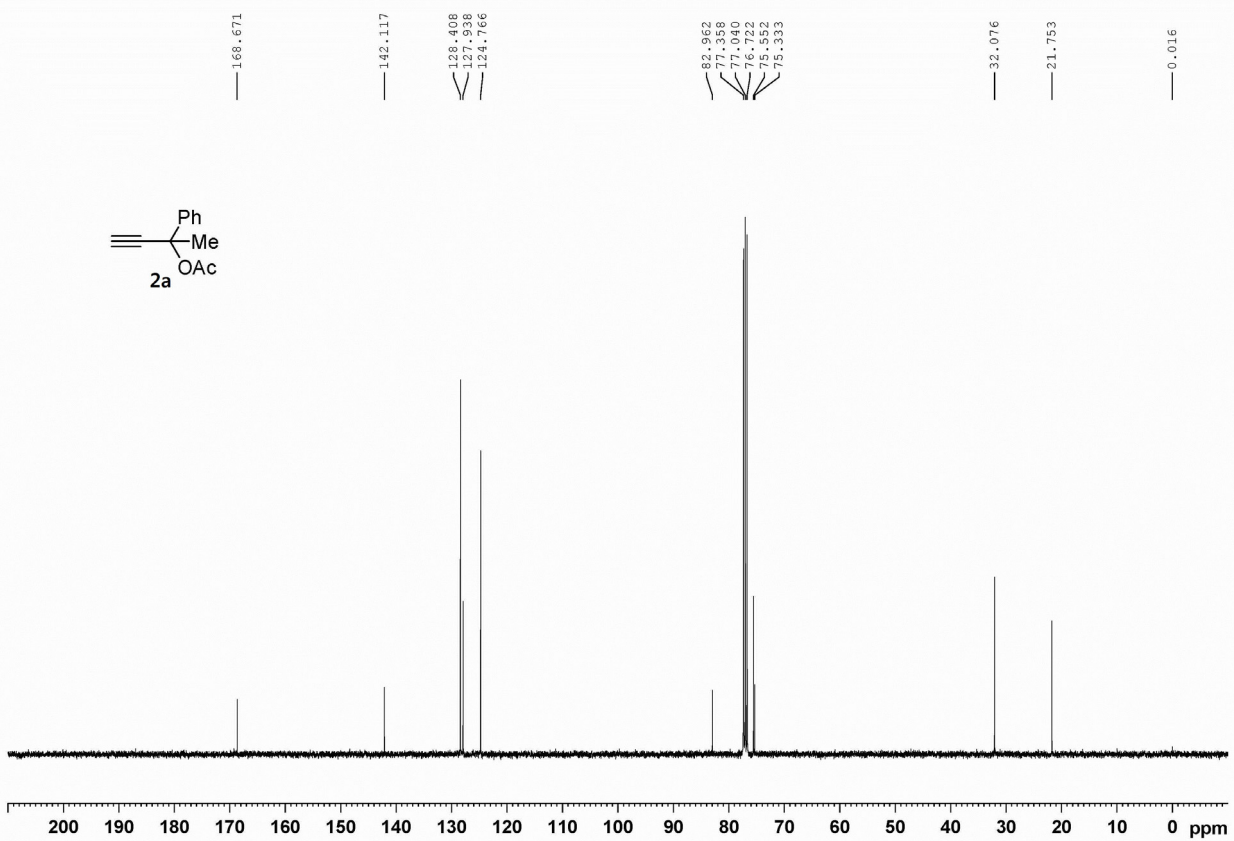
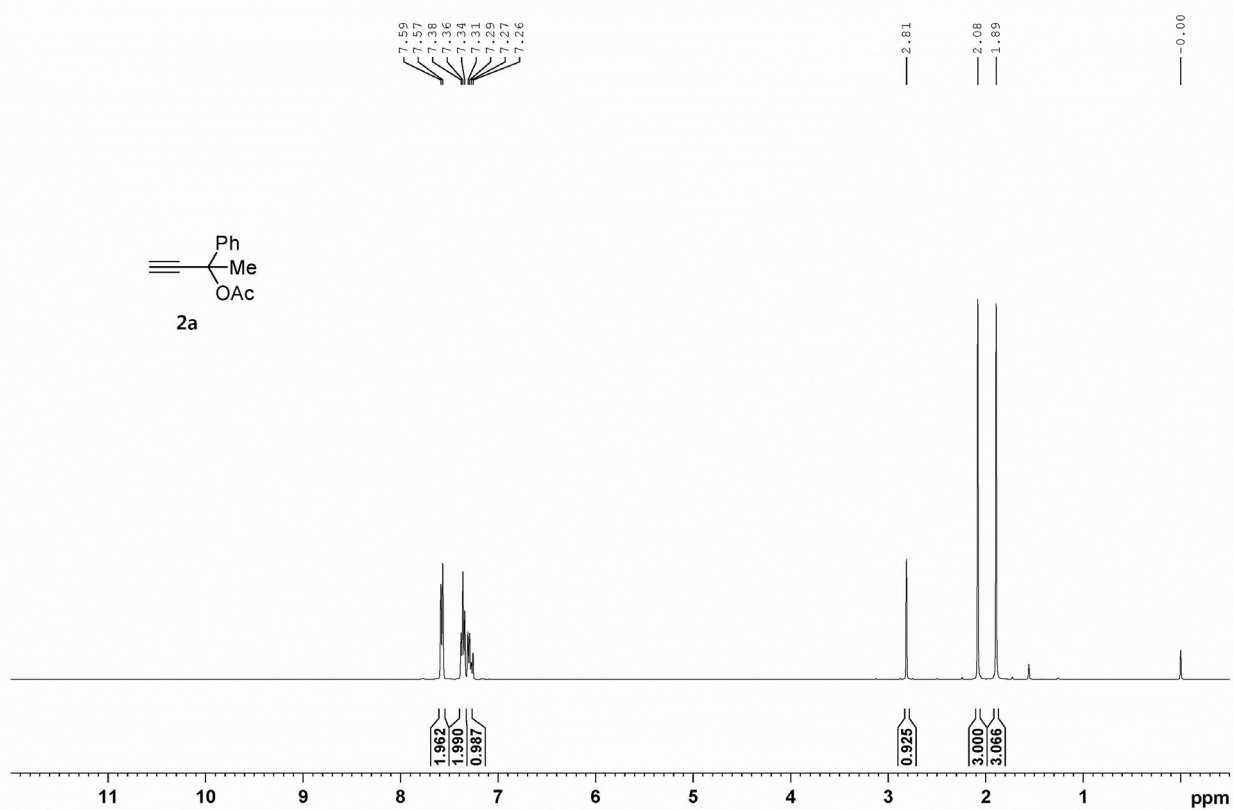
10ia

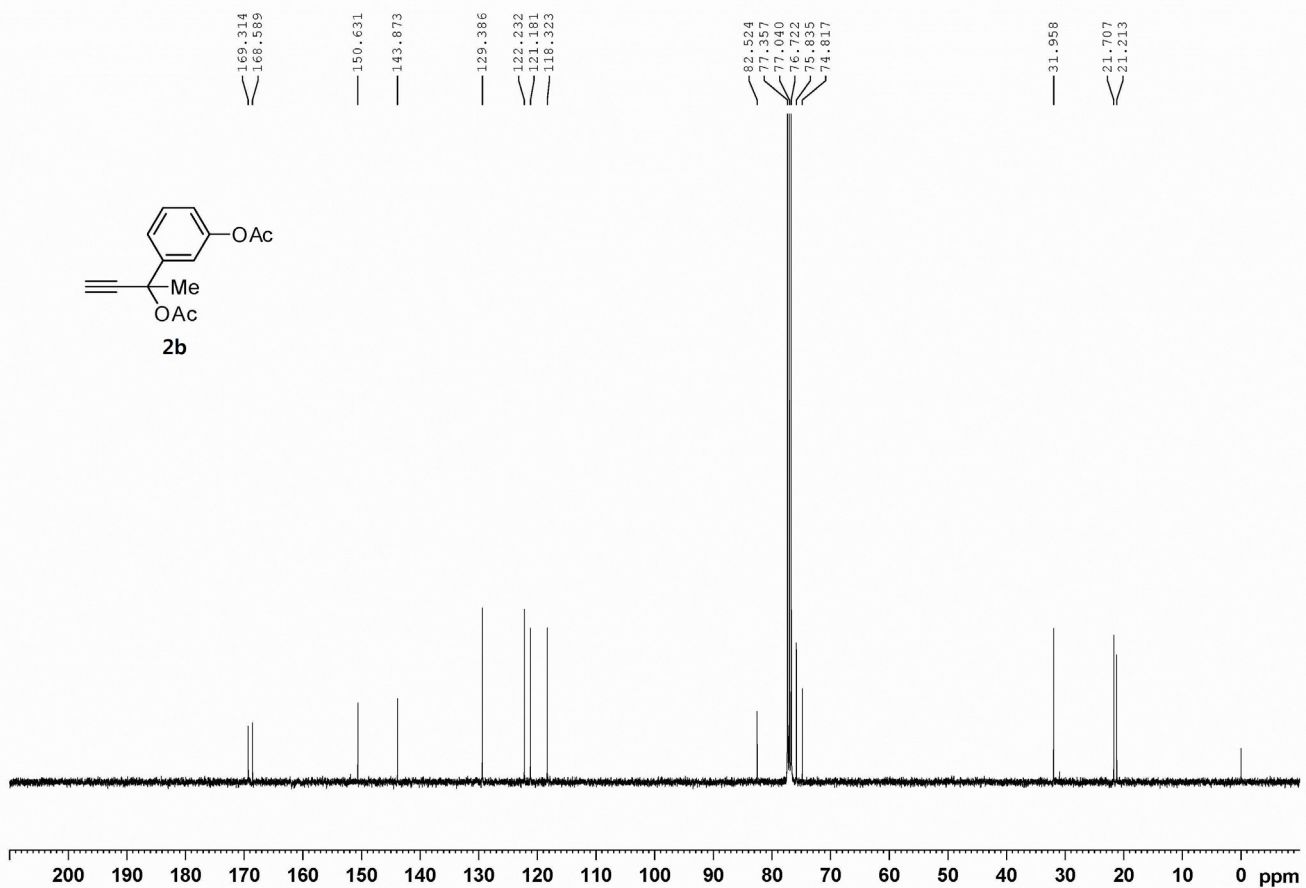
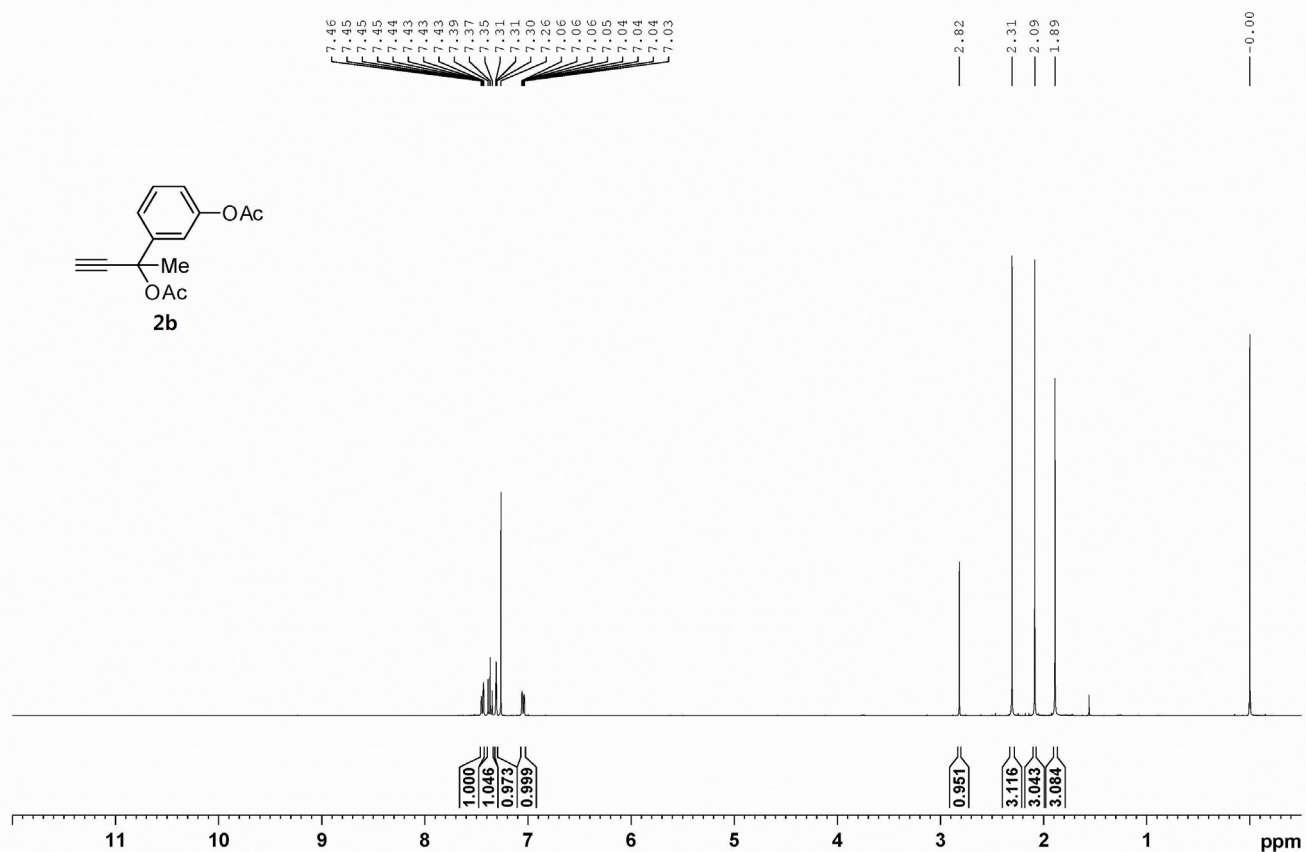
(E)-3-Methyl-5-phenyl-5-(propylthio)penta-3,4-dien-2-one O-methyl oxime (10ia) : 69.4 mg (84%), $R_f = 0.6$ (EtOAc:Hexane = 1:20); pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.50 (d, $J=7.3$ Hz, 2H), 7.34 (t, $J=7.8$ Hz, 2H), 7.28-7.25 (m, 1H), 3.95 (s, 3H), 2.64-2.60 (m, 2H), 2.04 (s, 3H), 1.94 (s, 3H), 1.71-1.58 (m, 2H), 1.00 (t, $J=7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 205.0, 153.6, 135.1, 128.9, 128.4, 127.0, 108.9, 108.0, 62.4, 35.2, 23.0, 15.7, 14.0, 13.3; IR (film) 3260, 2700, 1909, 1603, 1452, 901, 763, 695 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{21}\text{NOS}$: 275.1344; found : 275.1347.

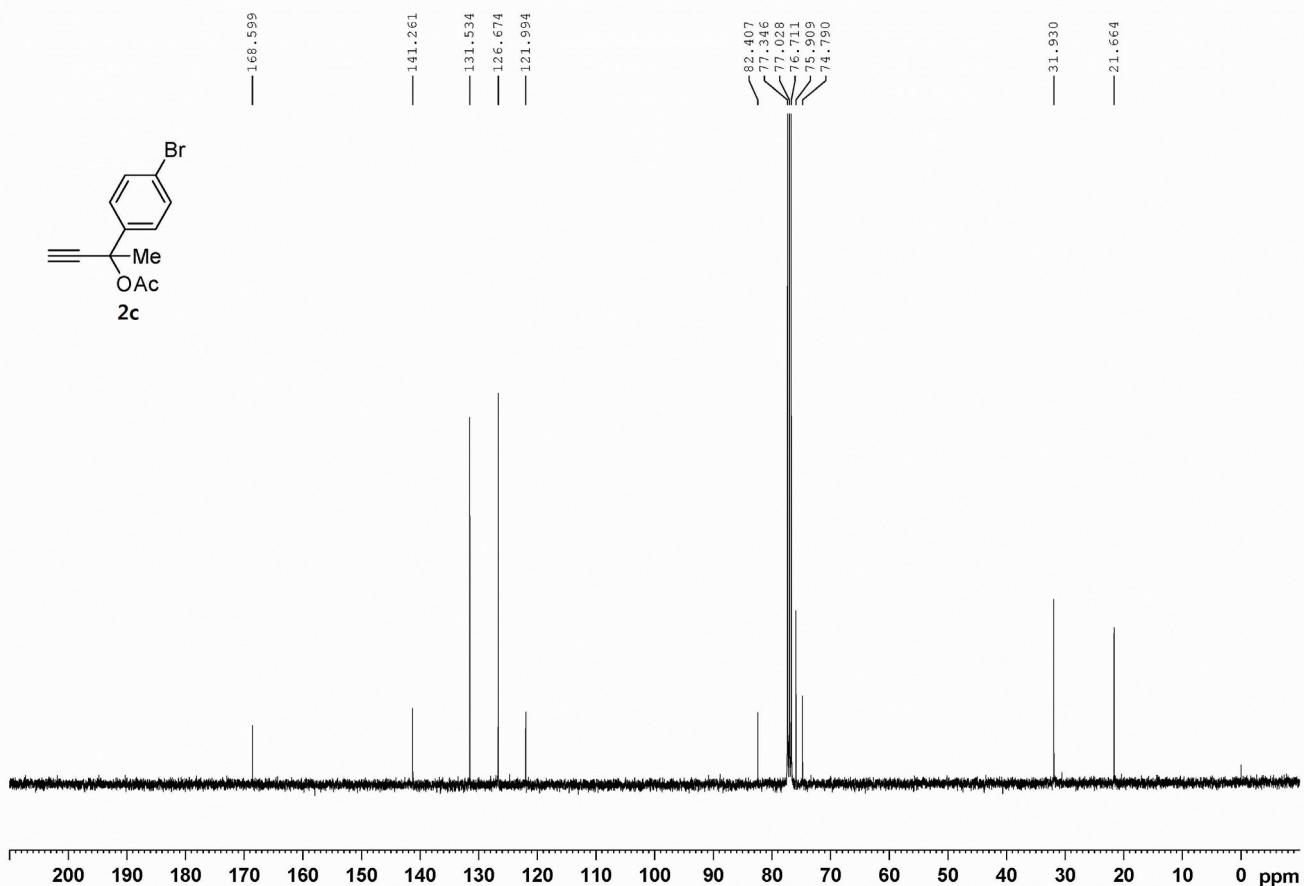
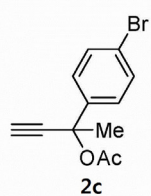
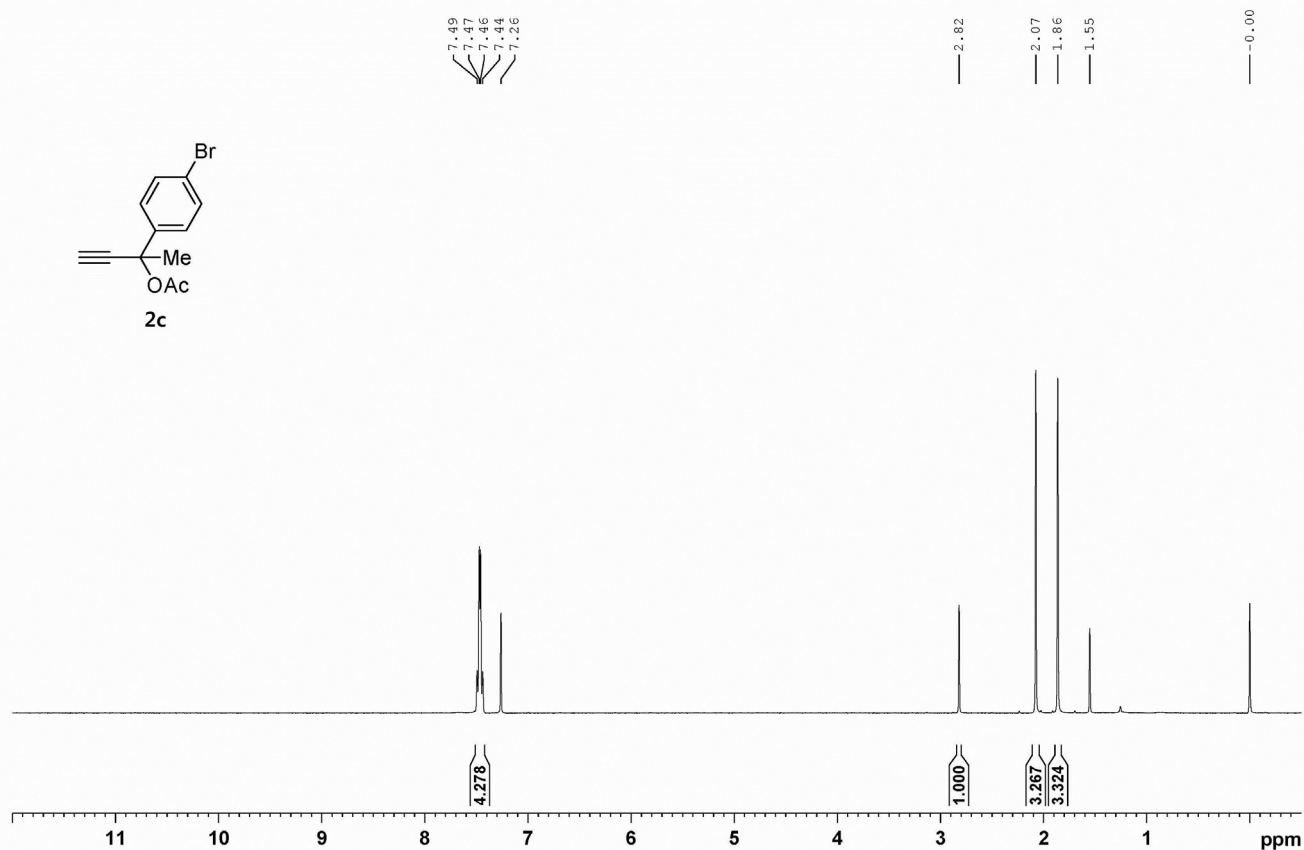
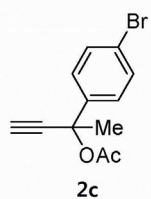
9. References

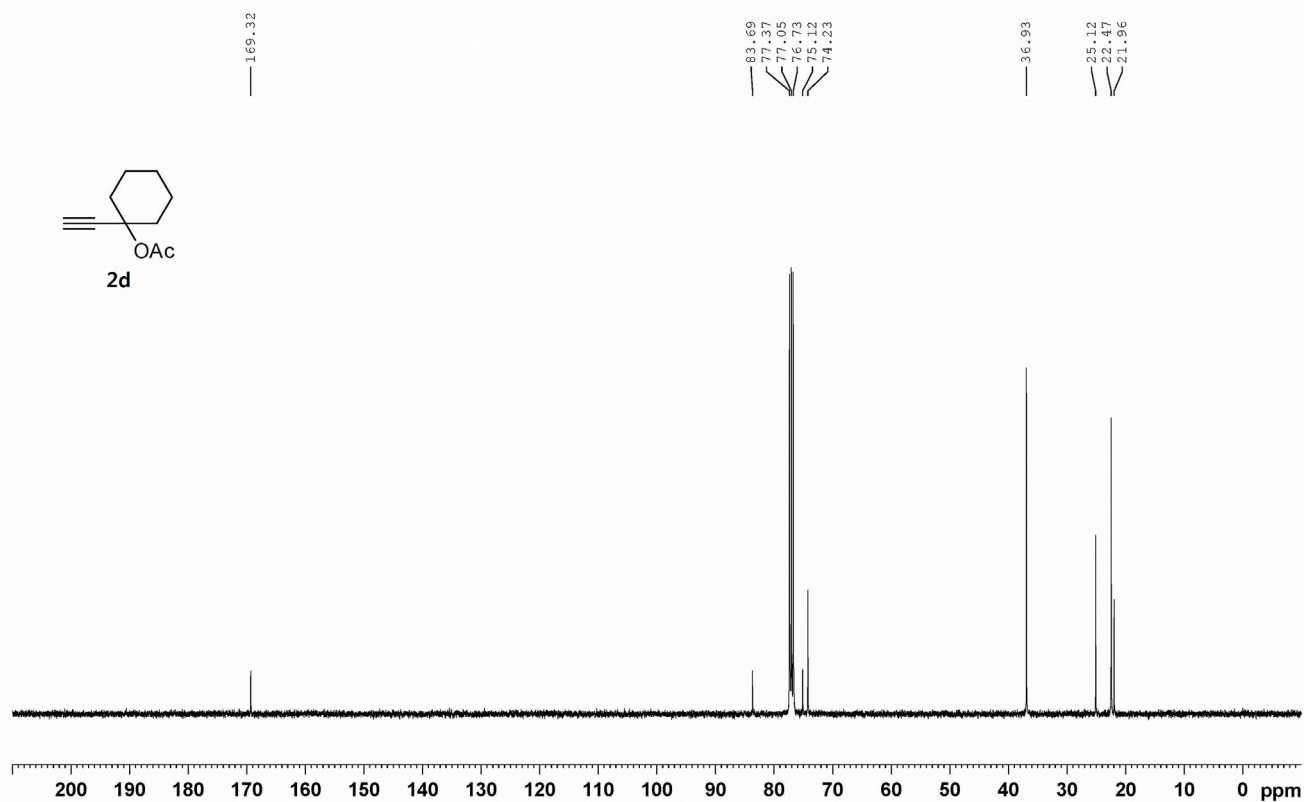
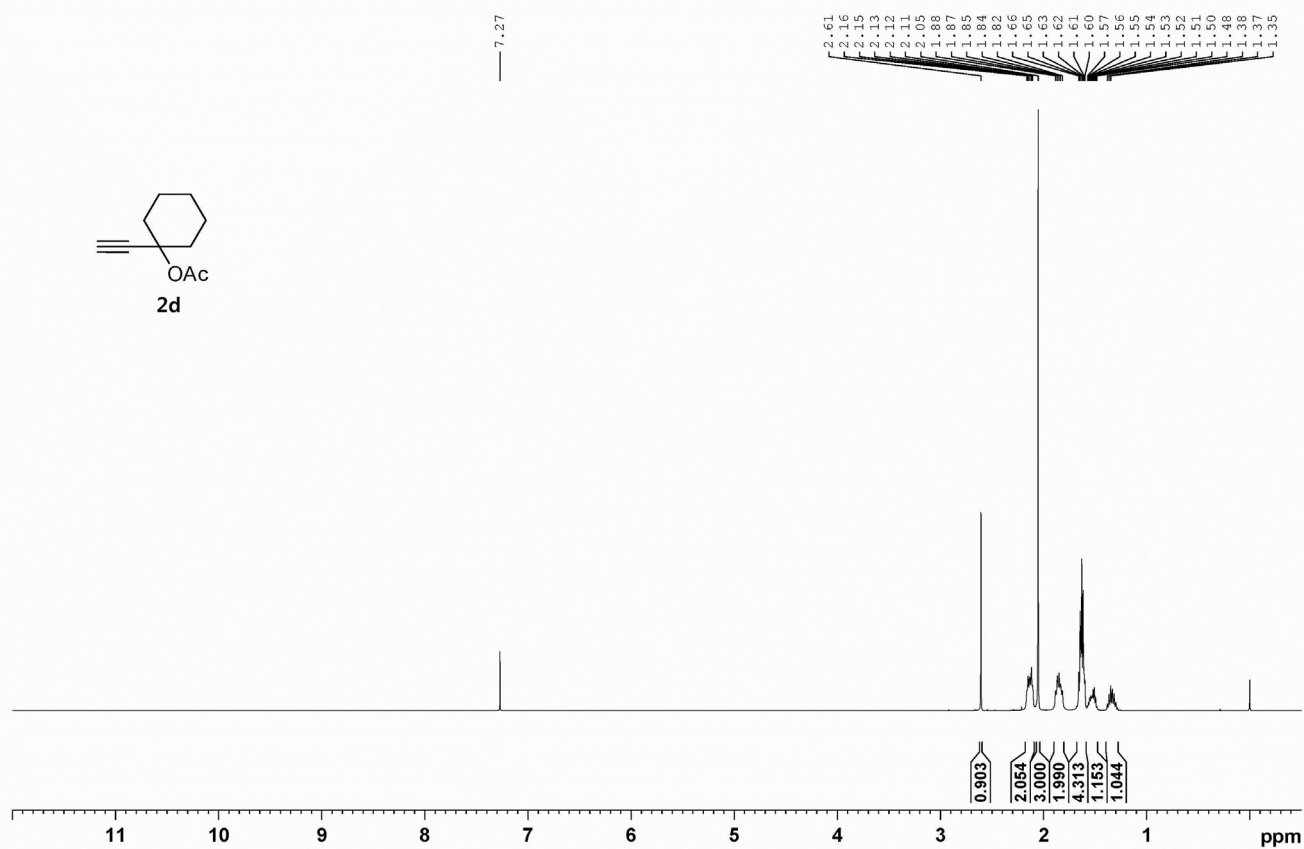
(1) (a) J. H. Green, R. Kumar, N. Seudeal, D. G. Tuck, *Inorg. Chem.* **1989**, 28, 123. (b) Nomura, R.; Inazawa, S.; Kanaya, K.; Matsuda, H. *Polyhedron* **1989**, 37, 5823. (c) G. G. Briand, R. J. Davidson, A. Decken, *Inorg. Chem.* **2005**, 44, 9914. (d) S. Suh, D. A. Hoffman, *Inorg. Chem.* **1998**, 37, 5823.

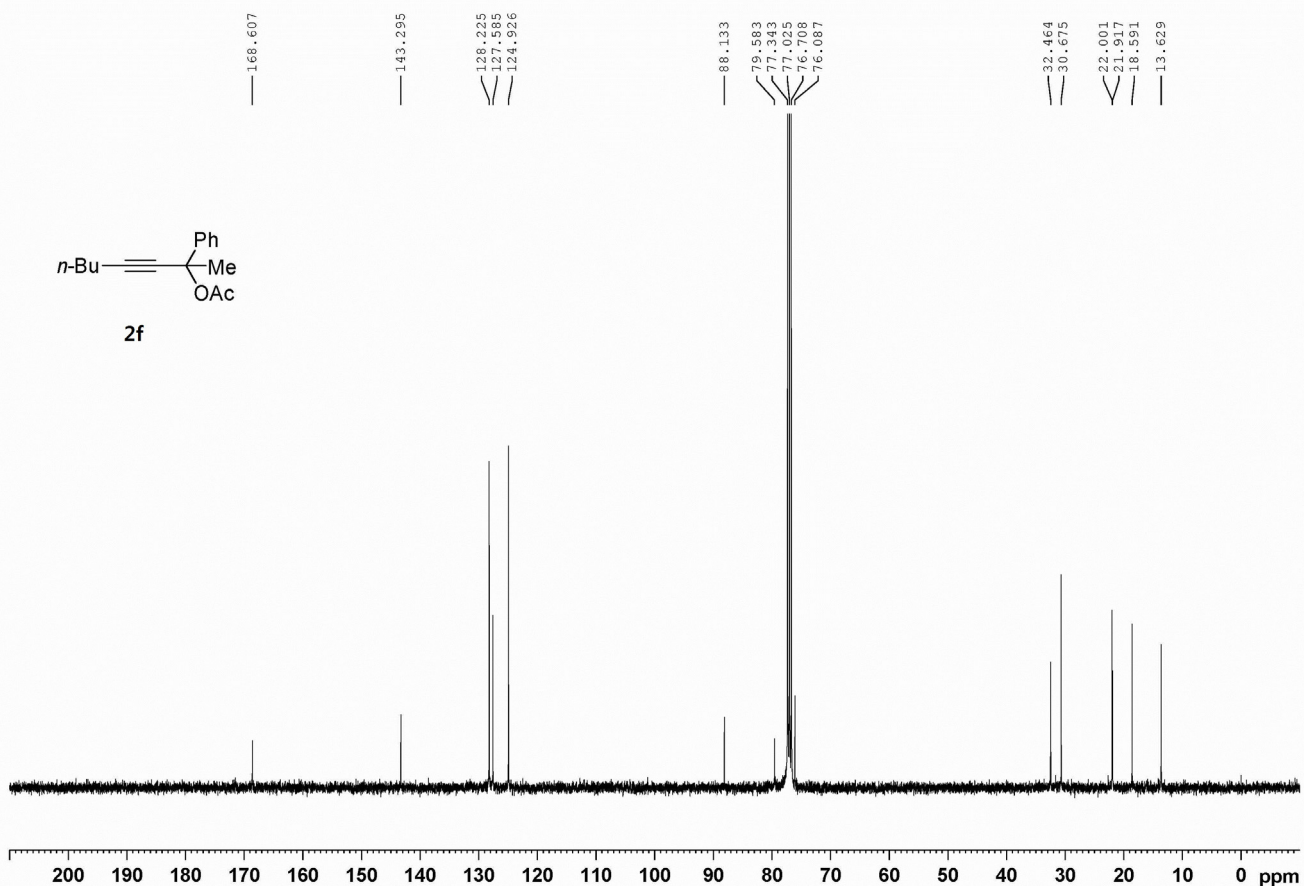
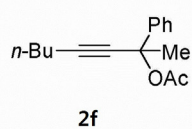
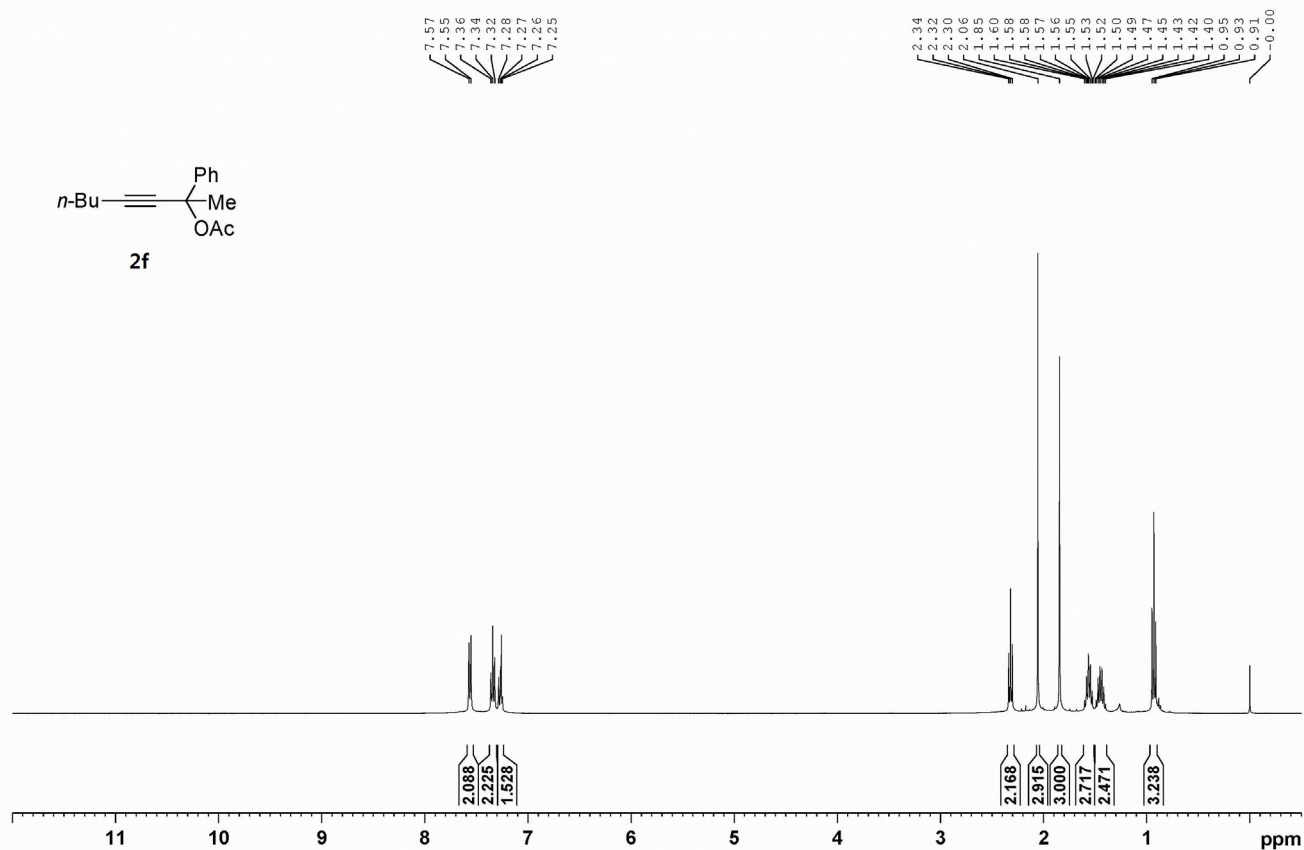
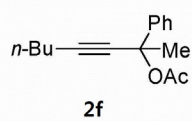
10. ^1H and ^{13}C NMR spectra

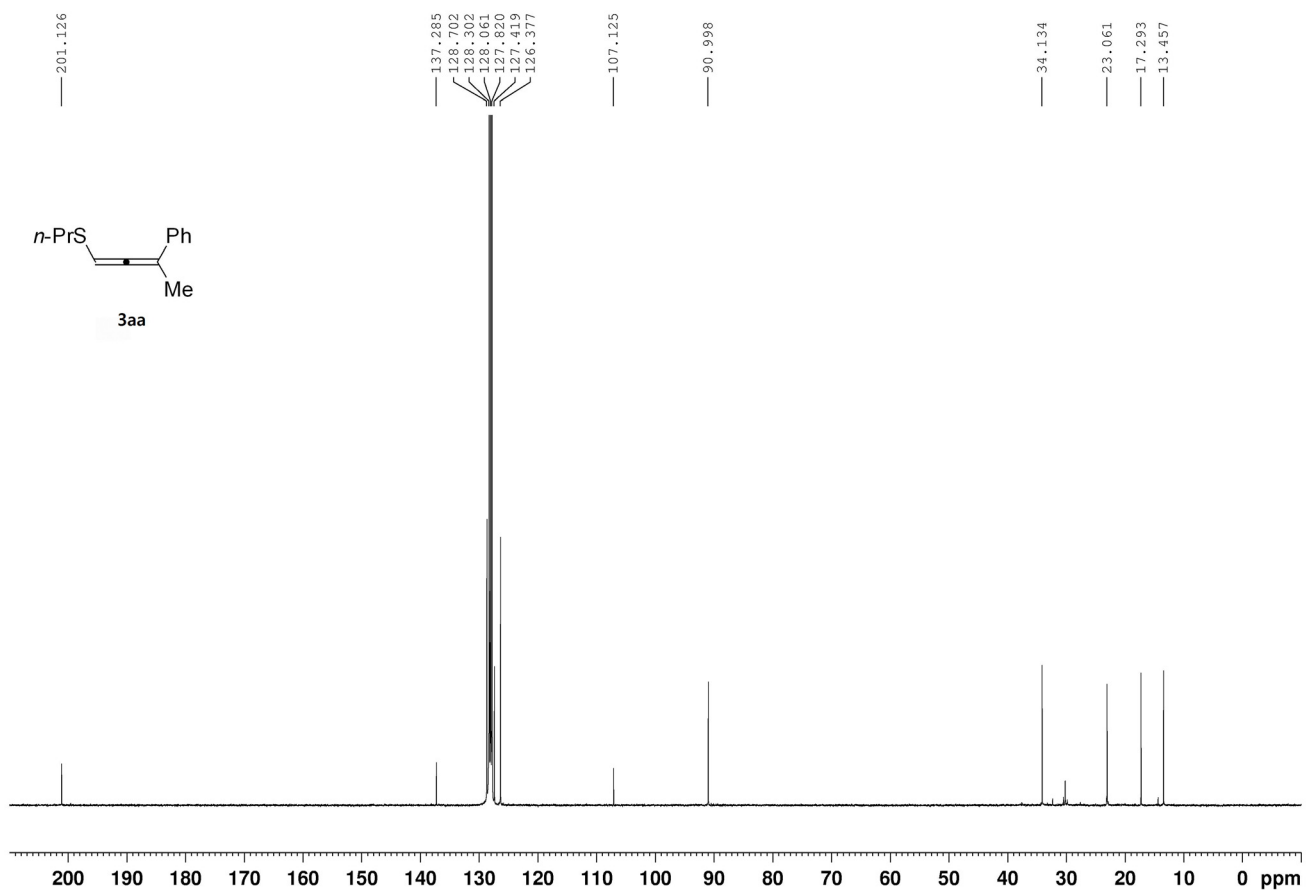
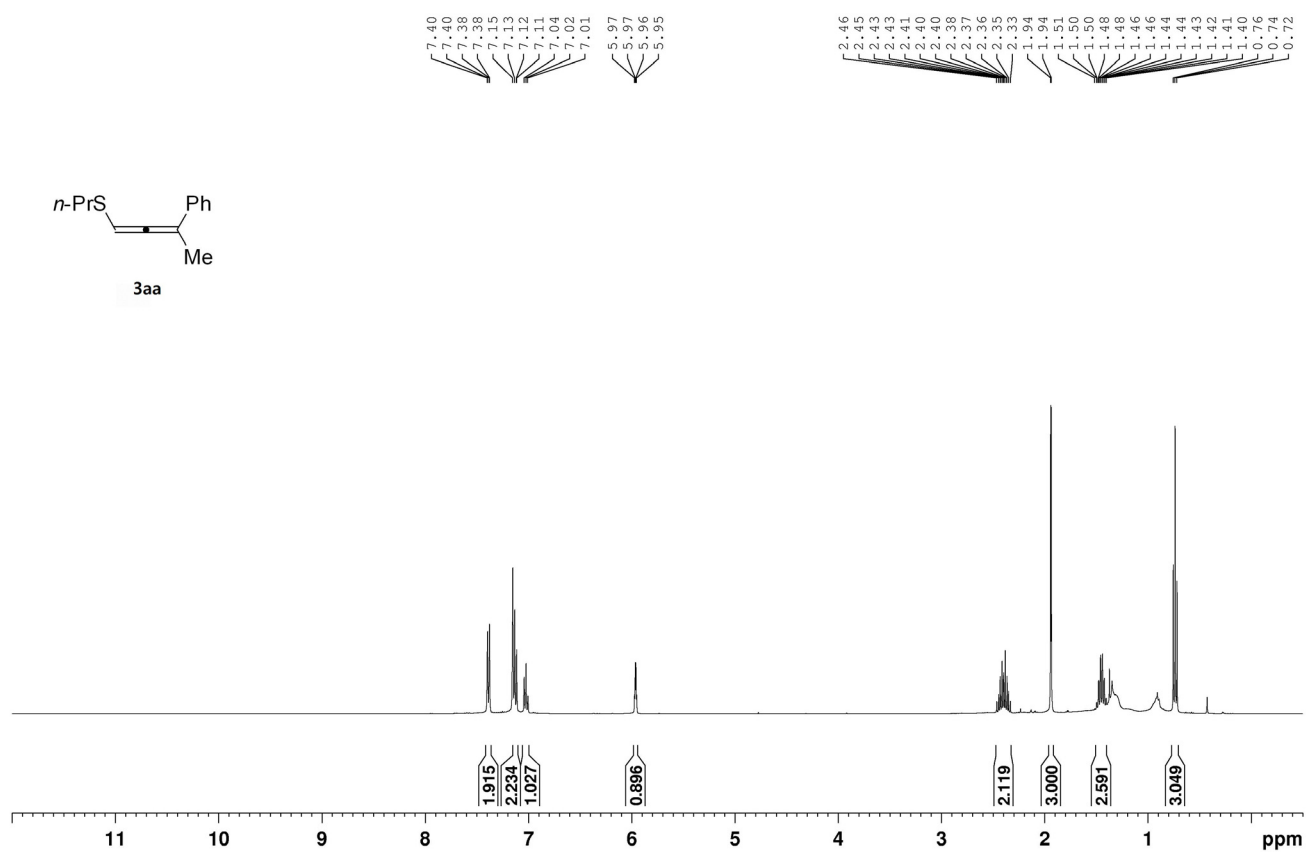


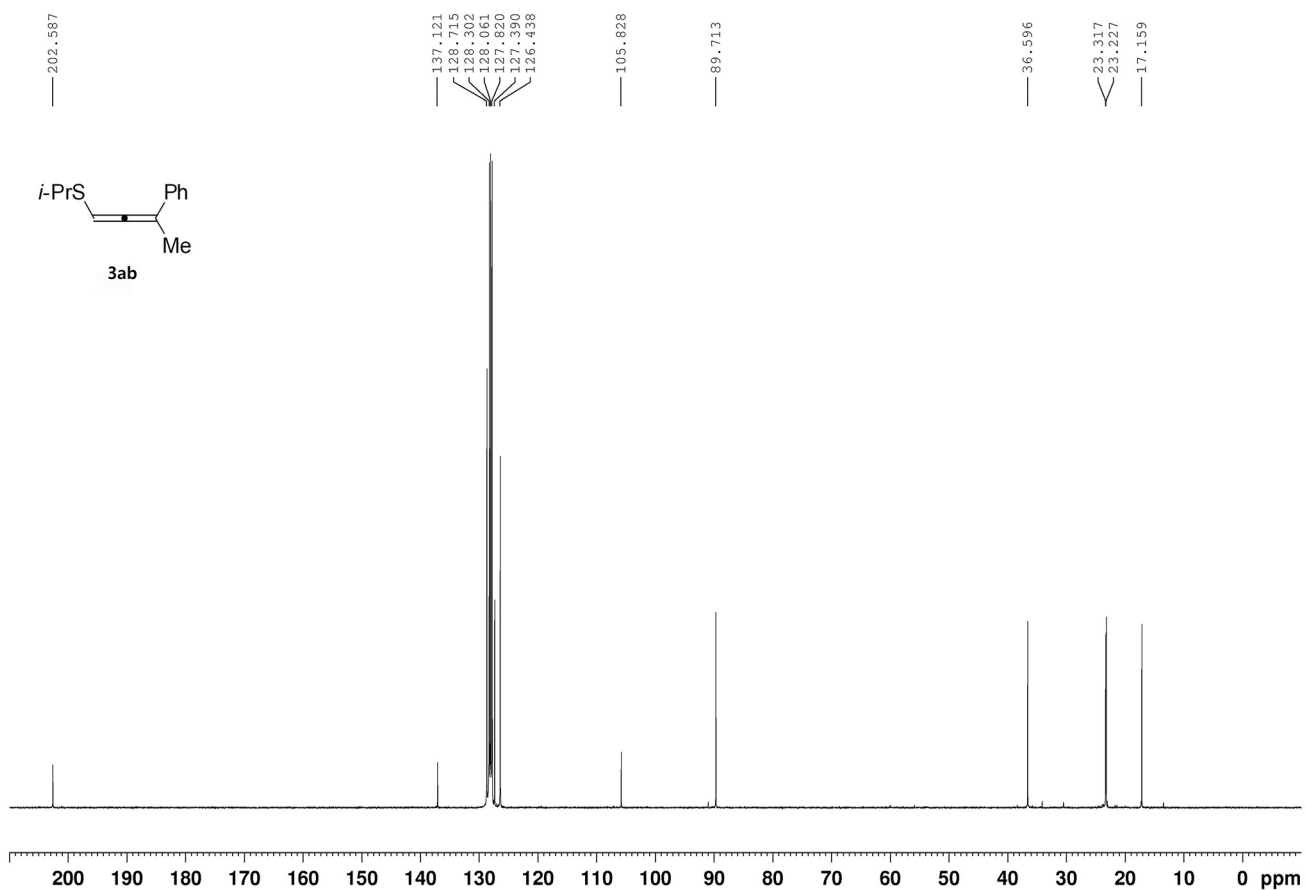
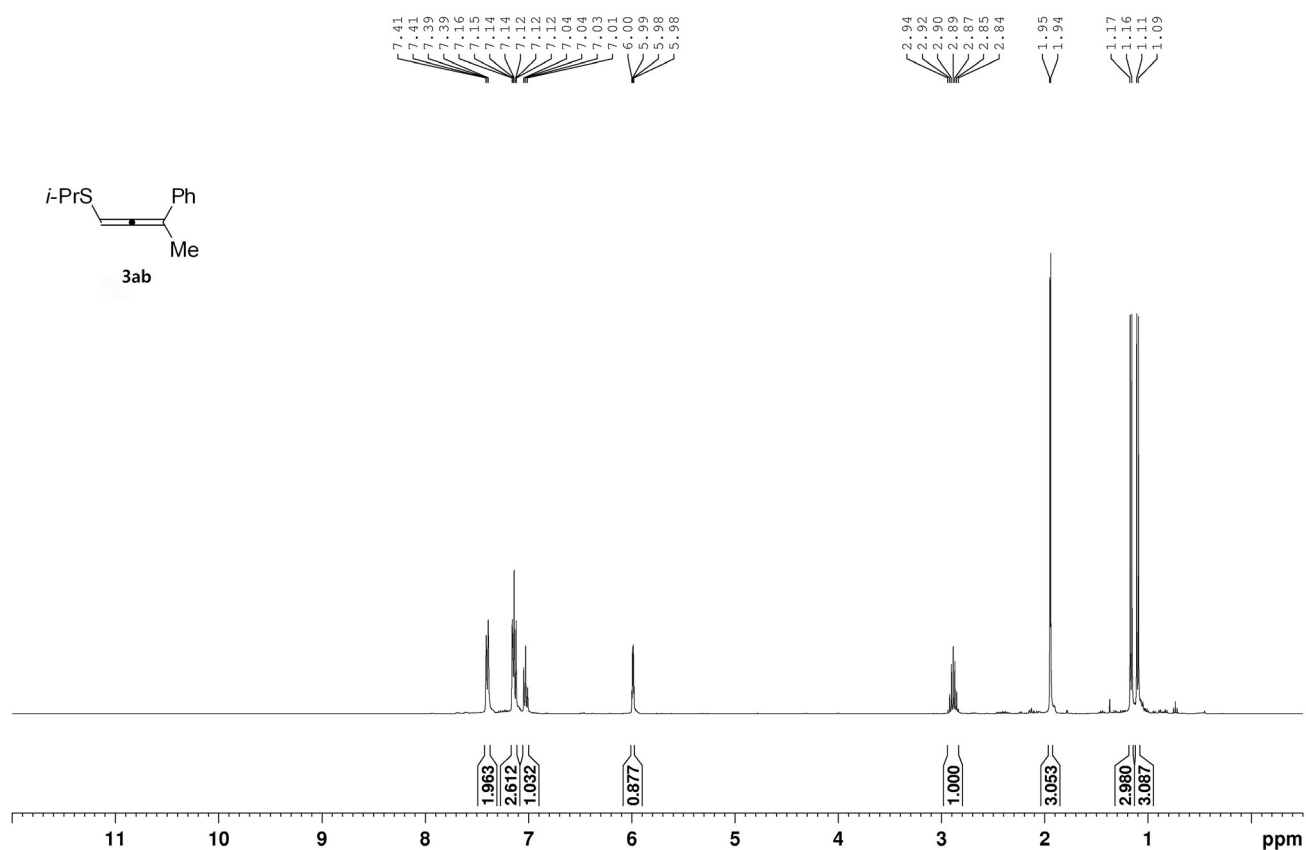


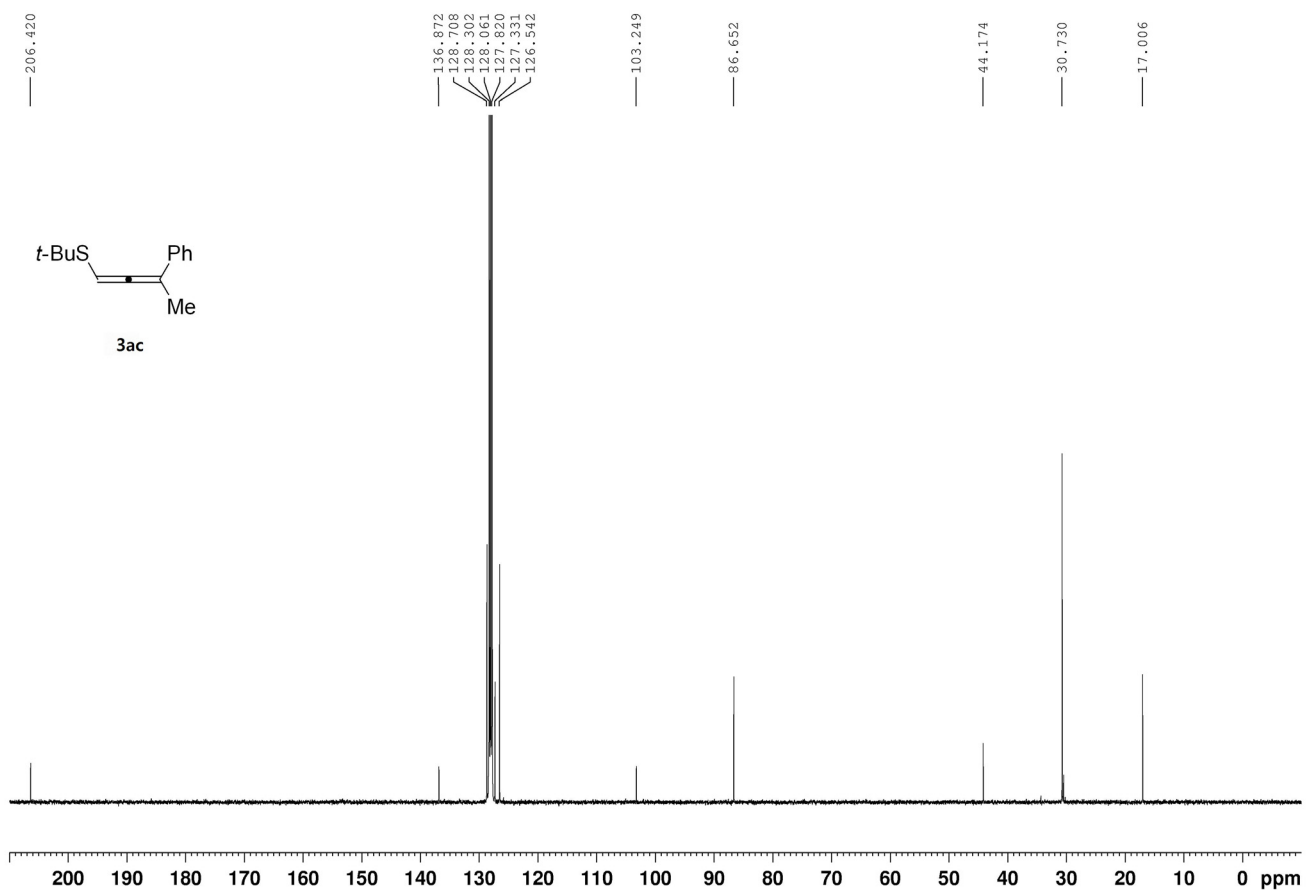
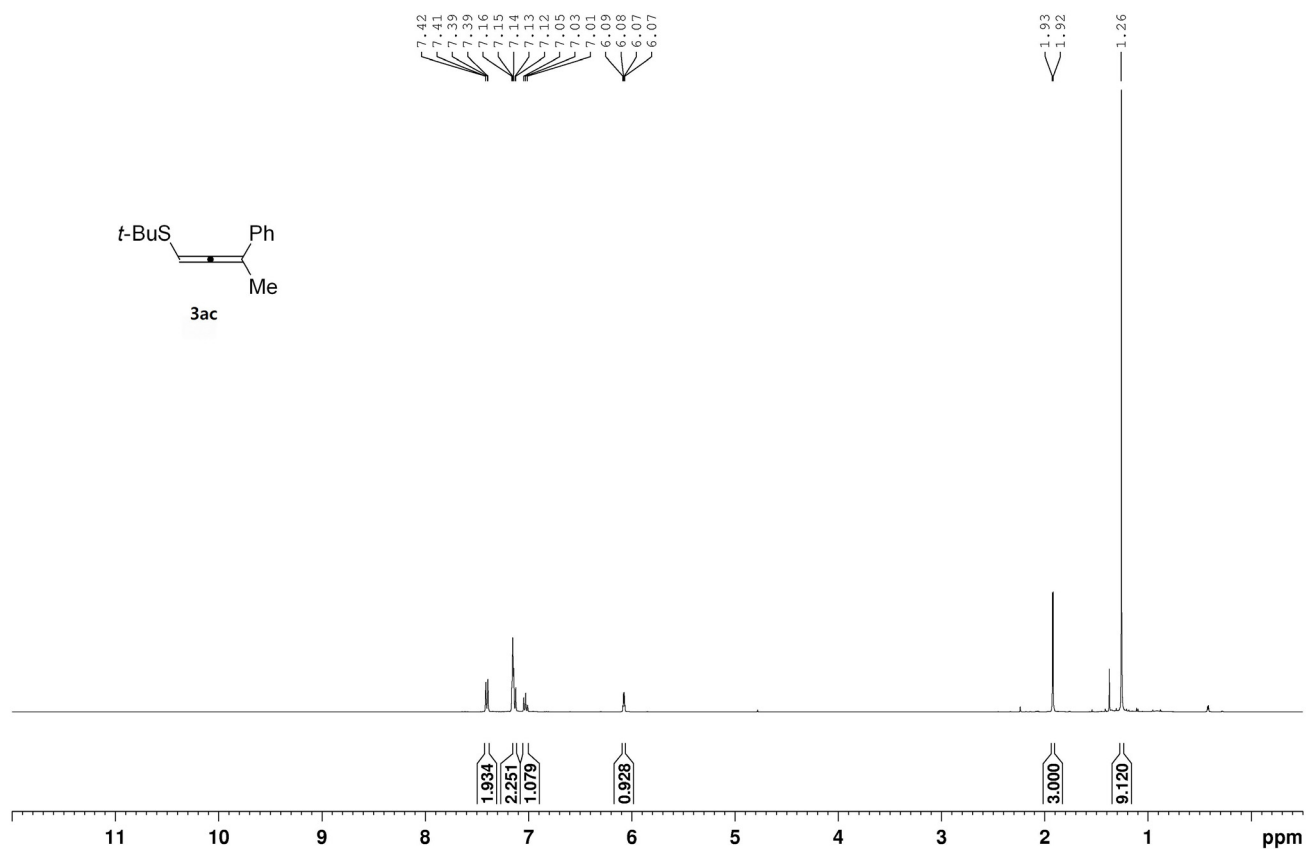


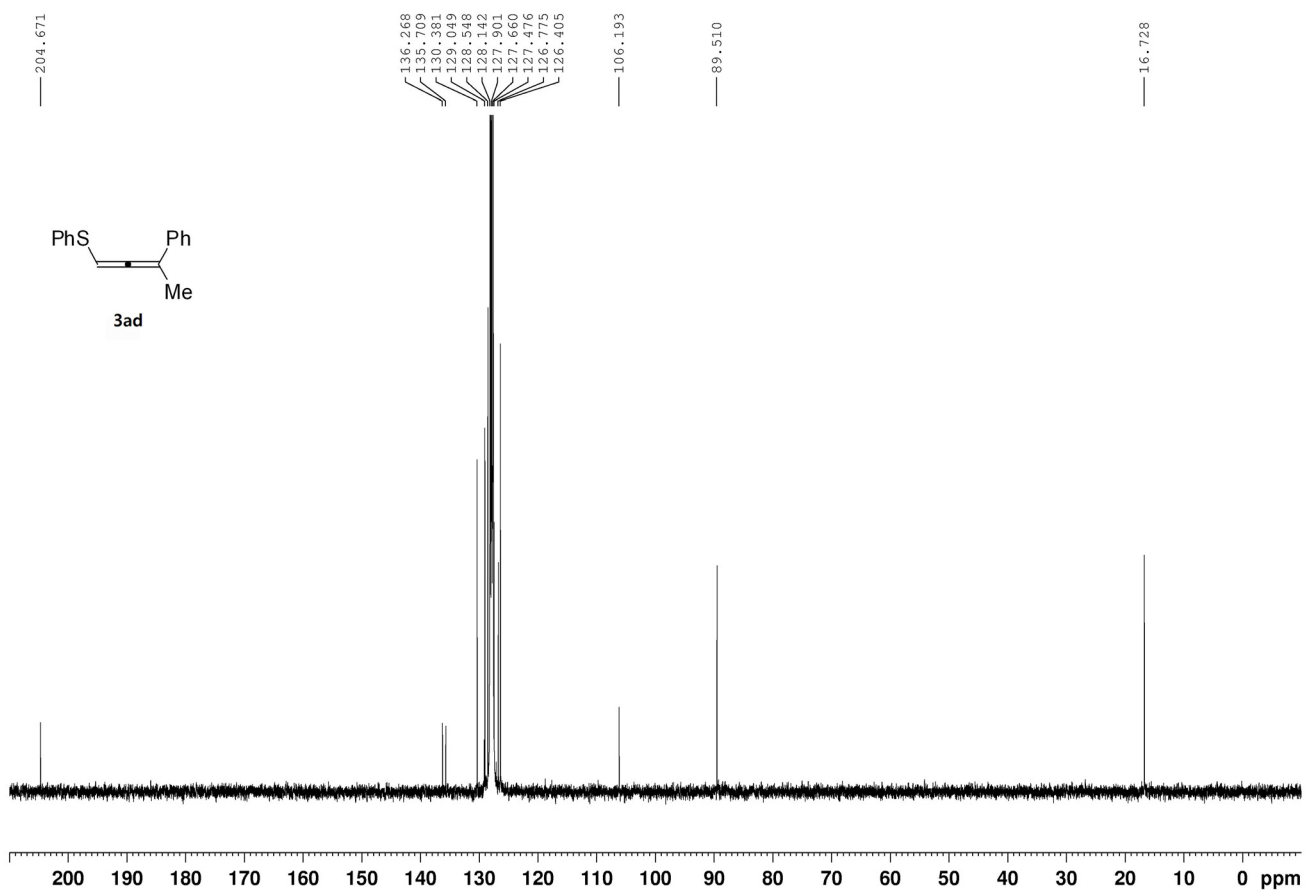
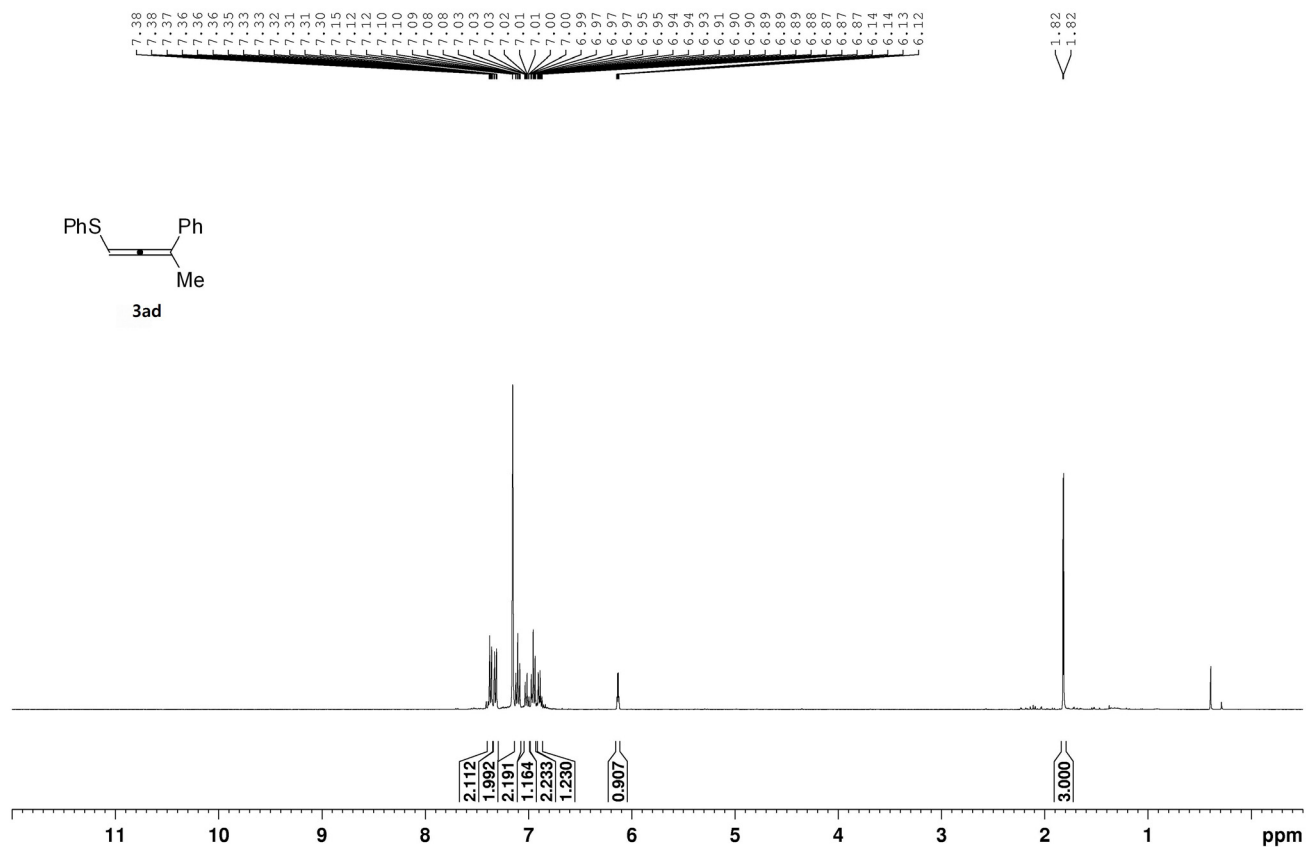


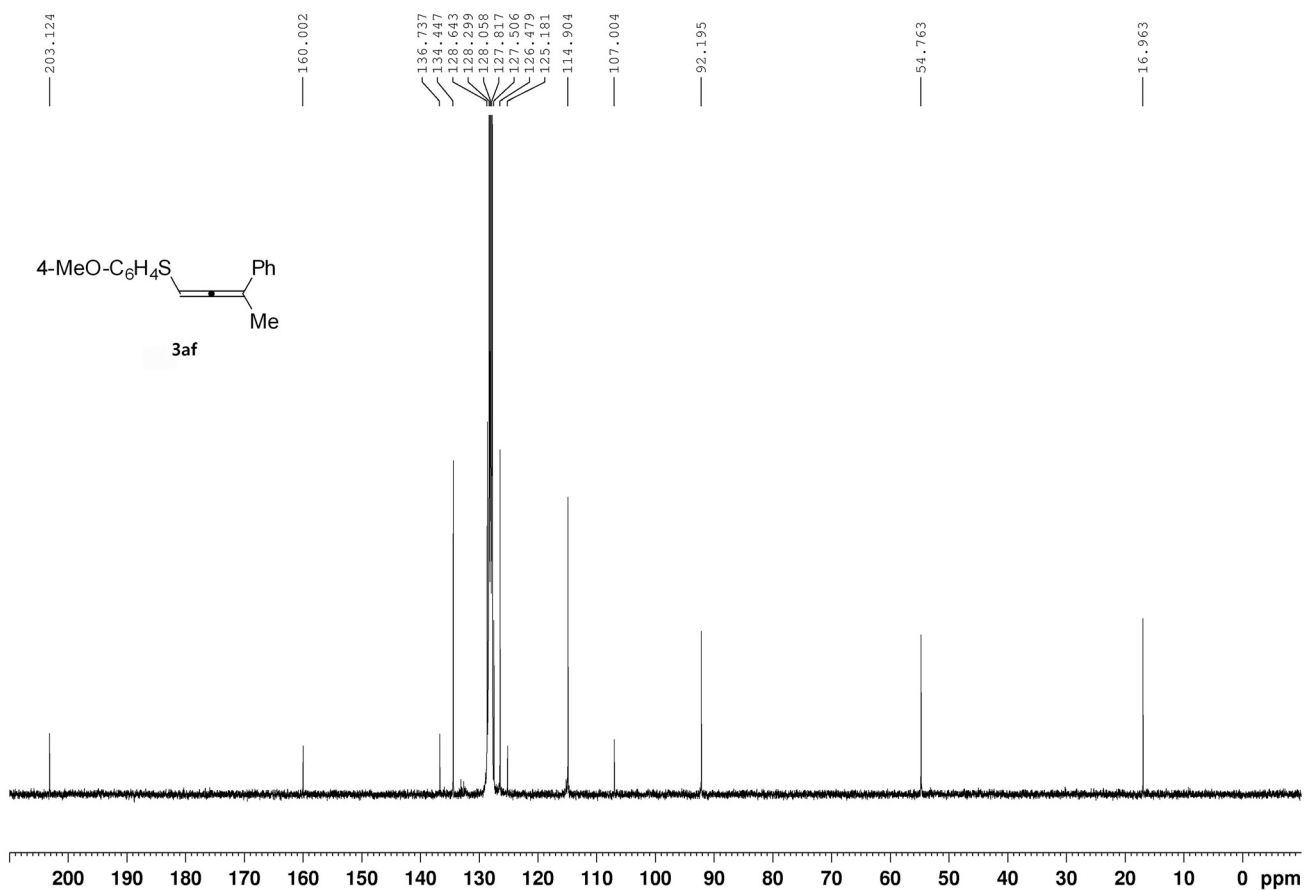
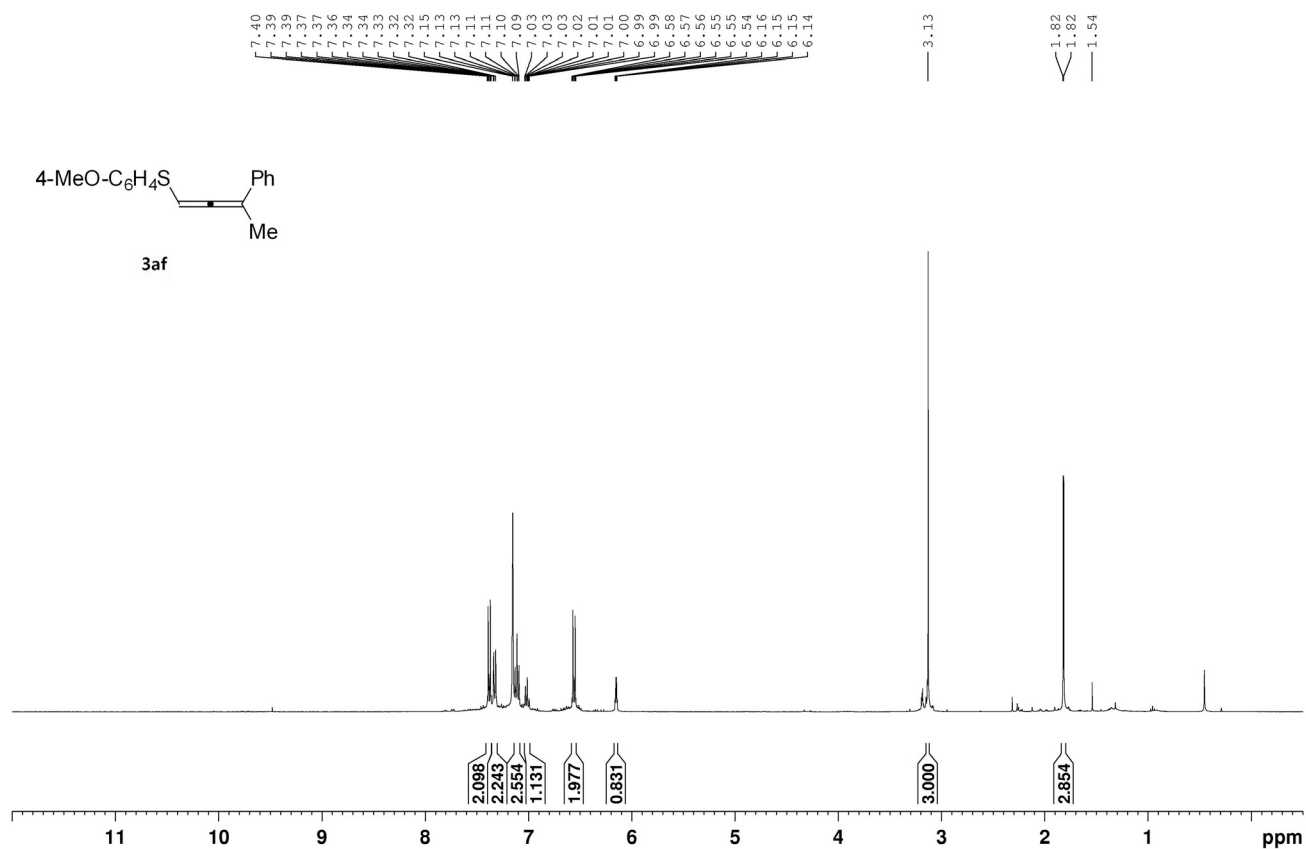


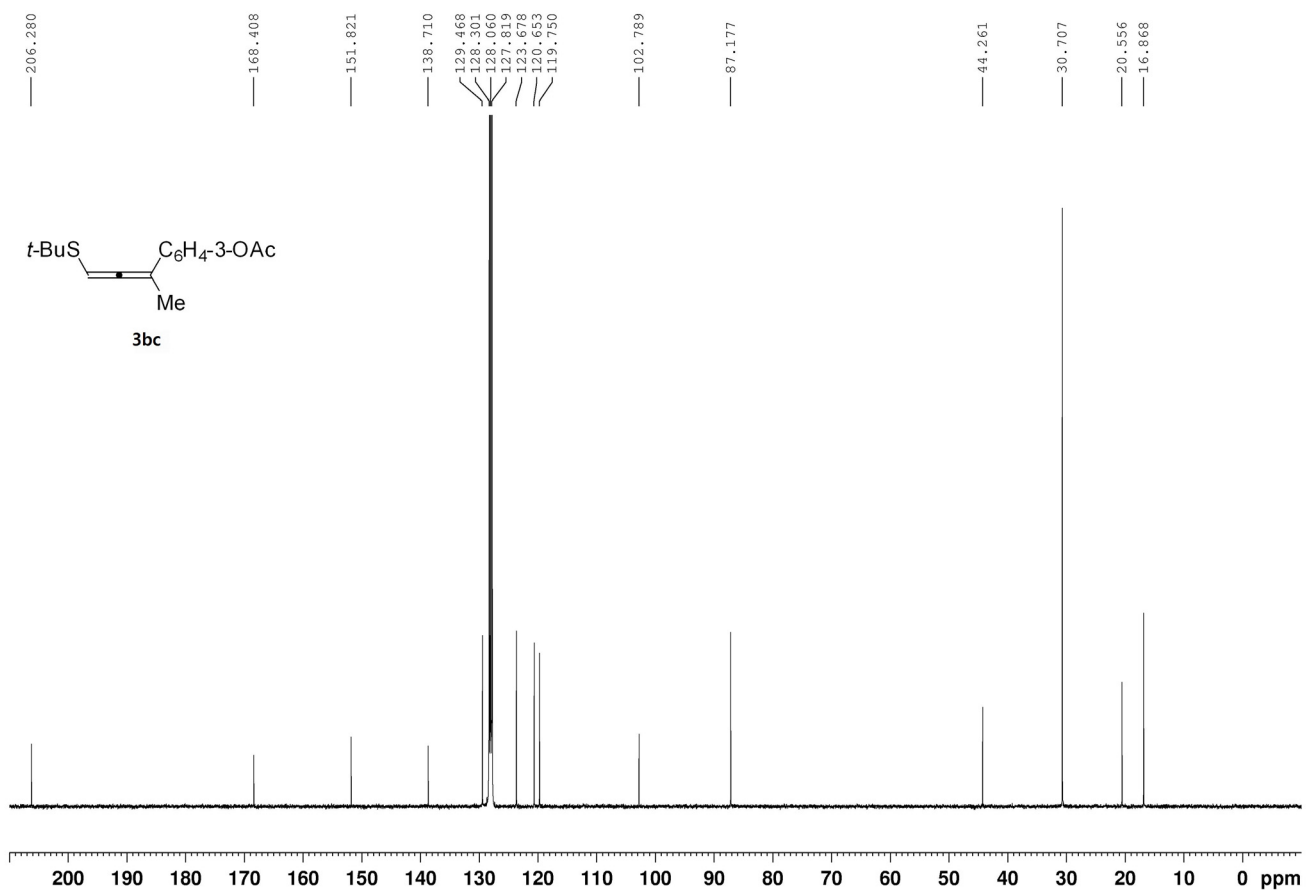
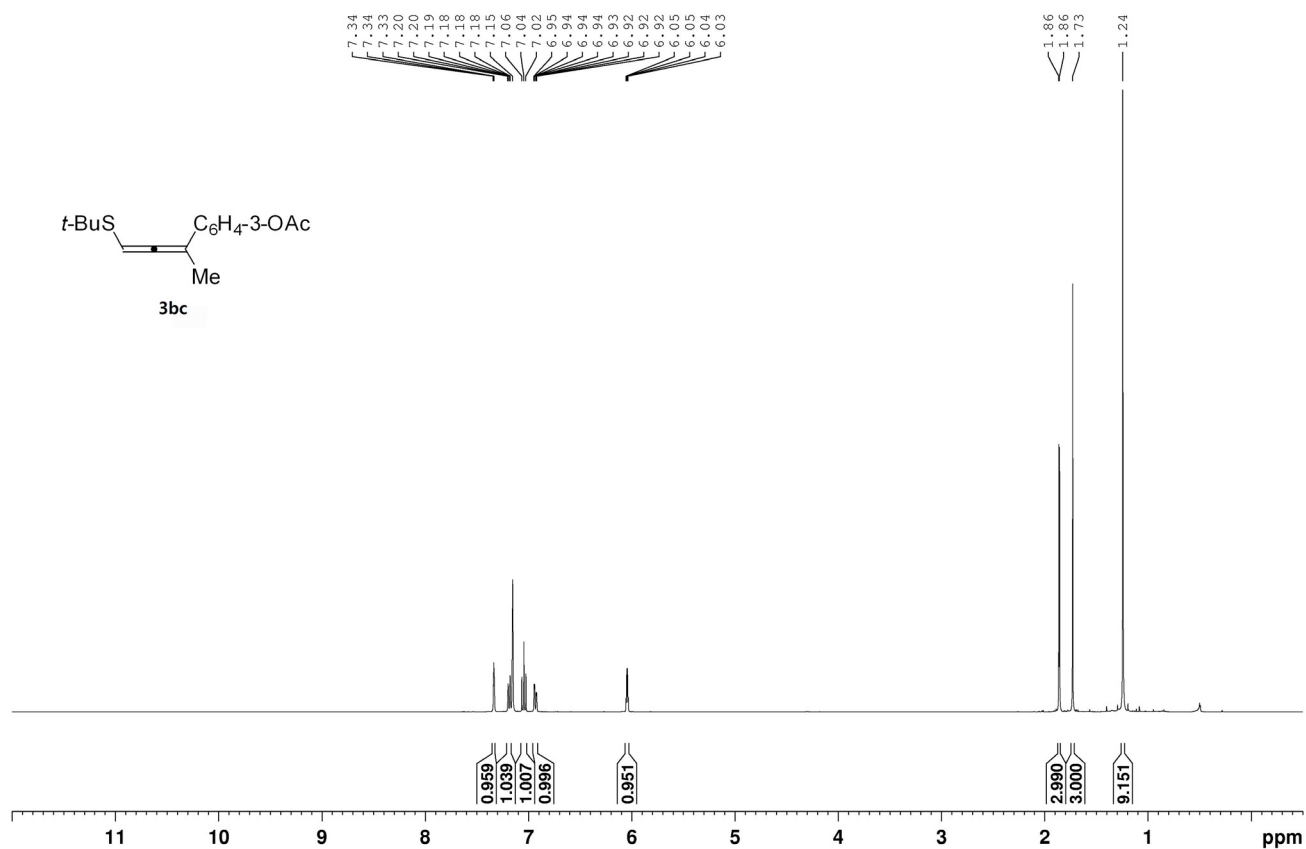


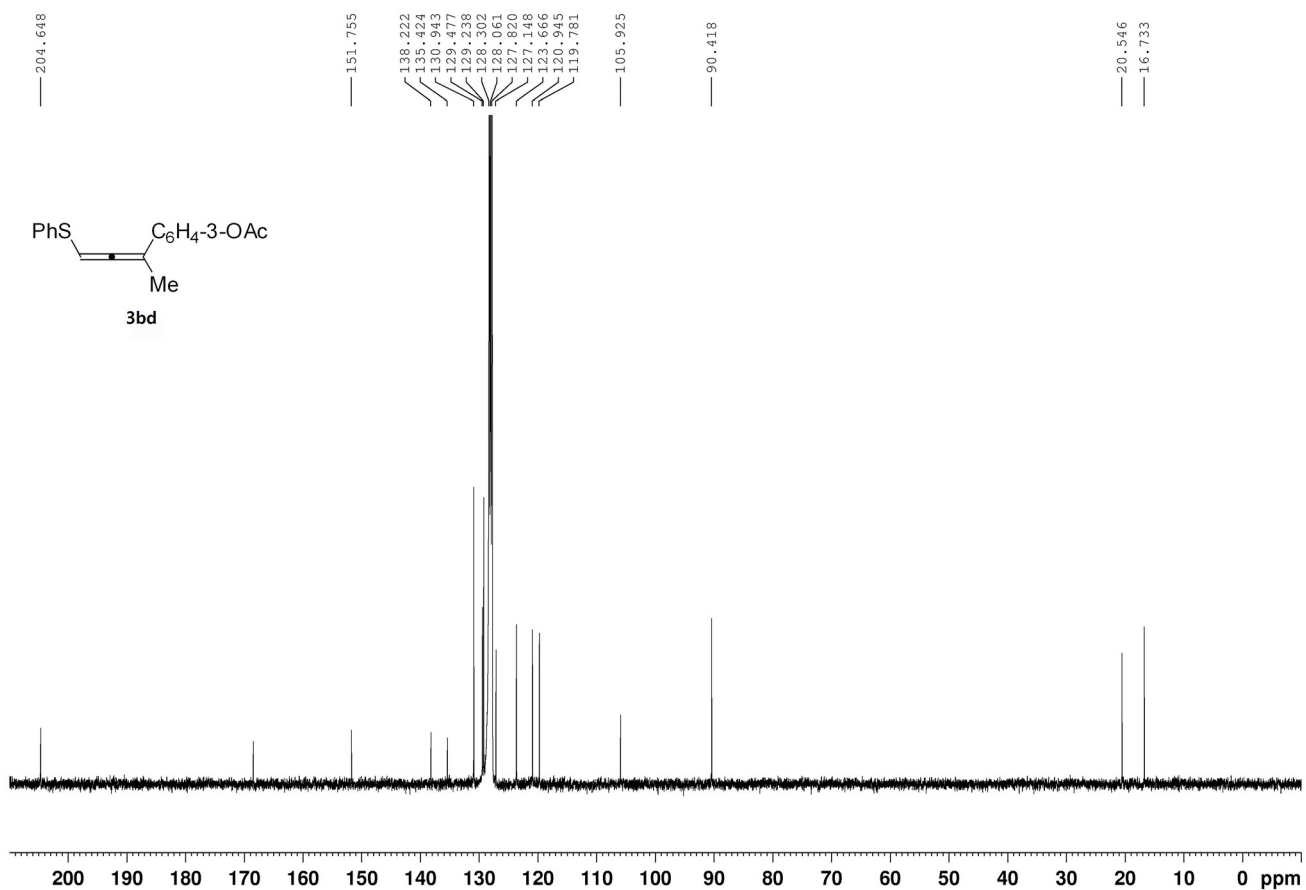
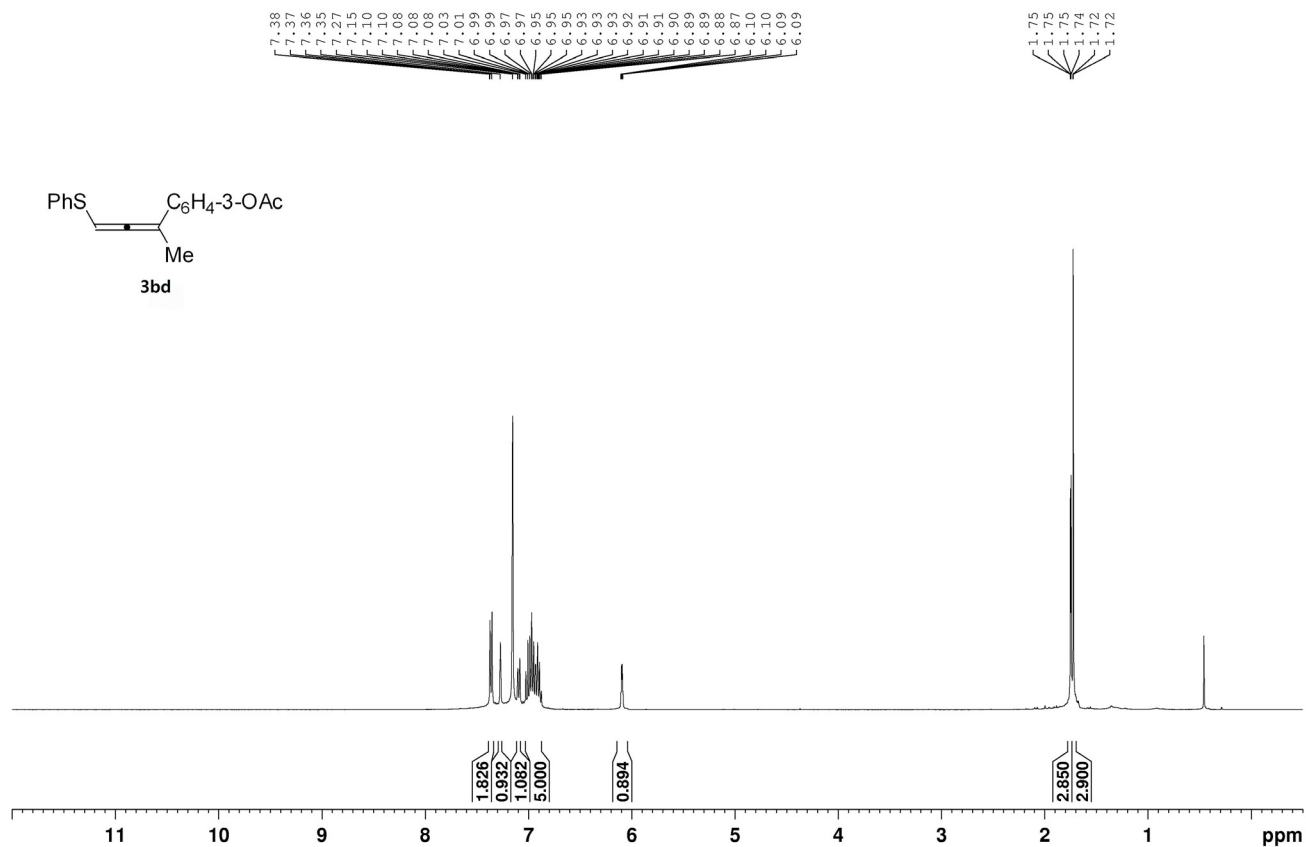


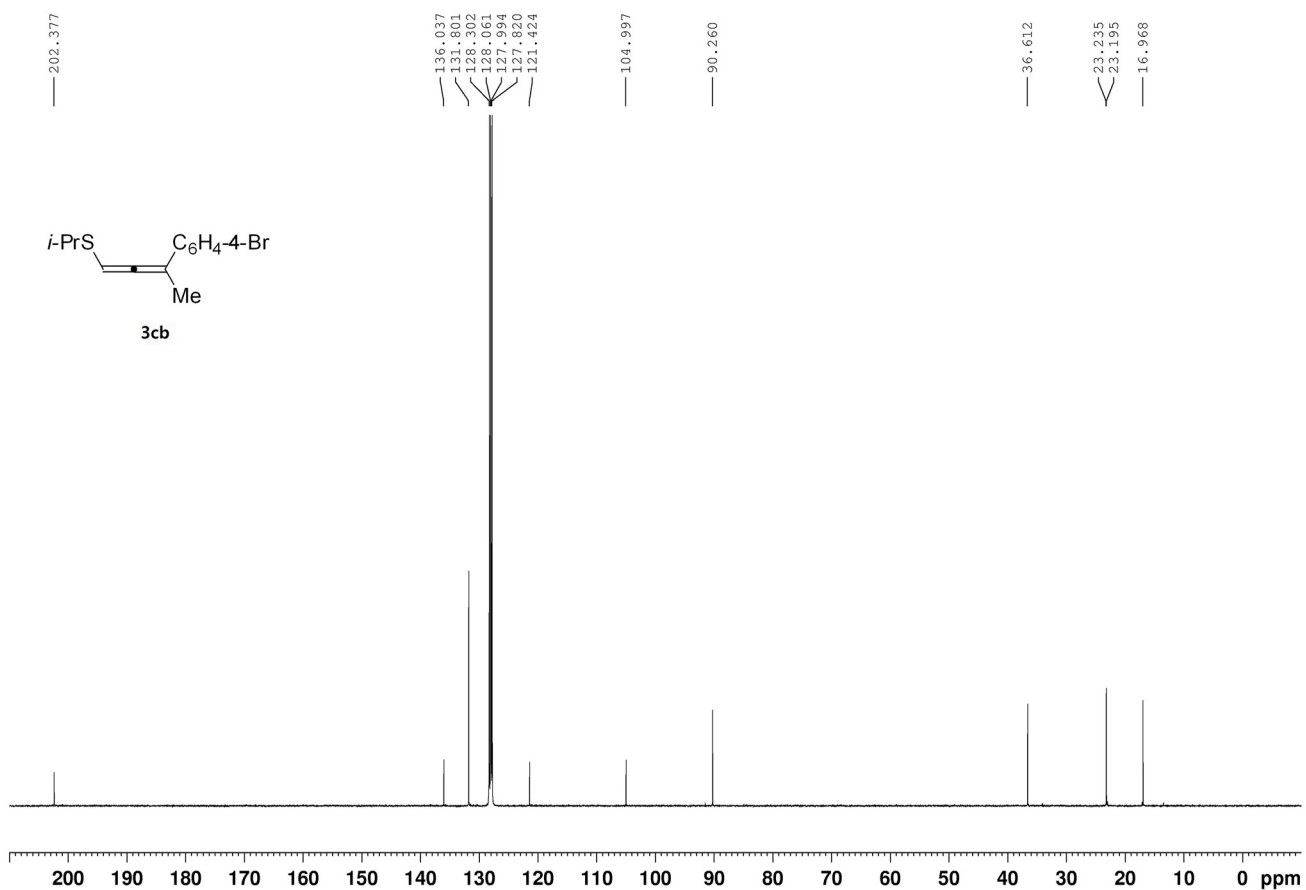
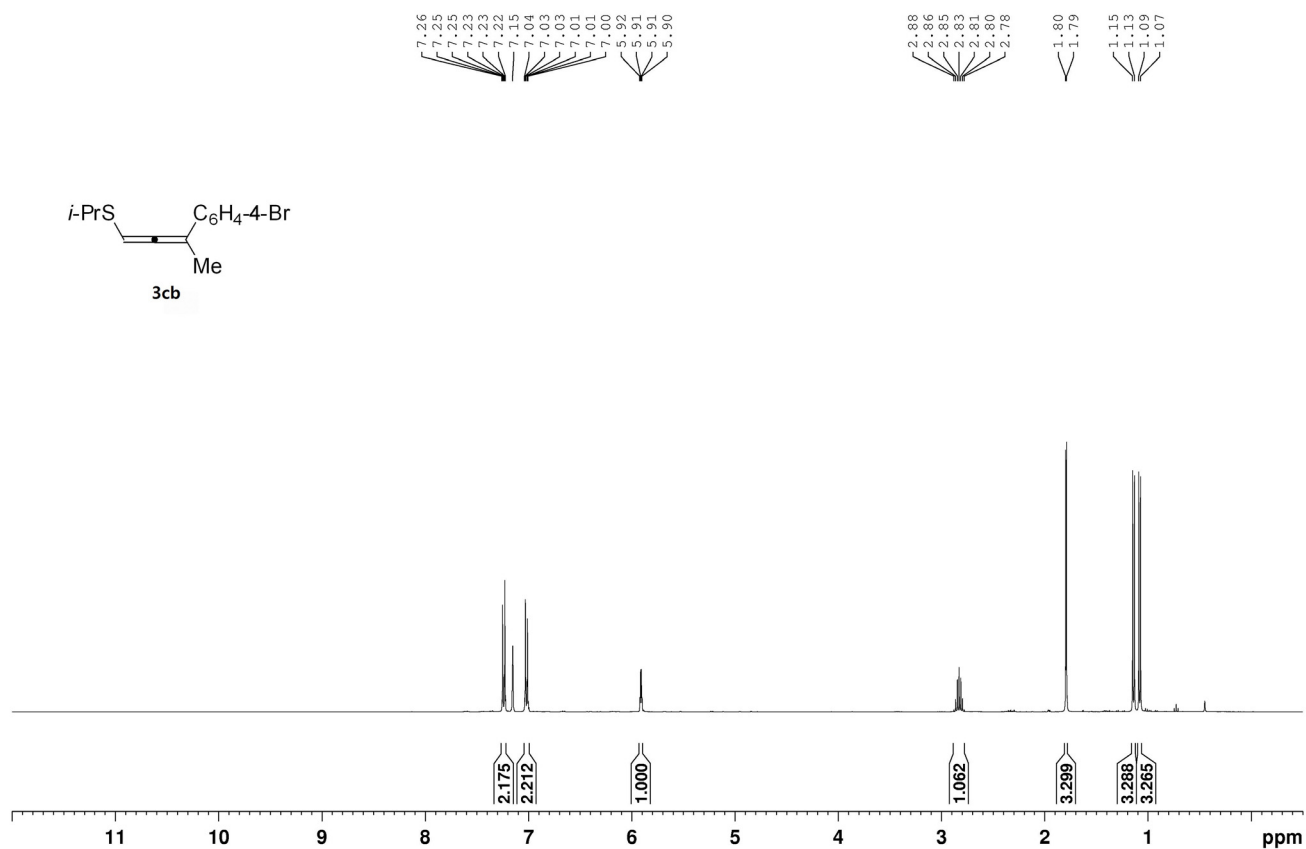


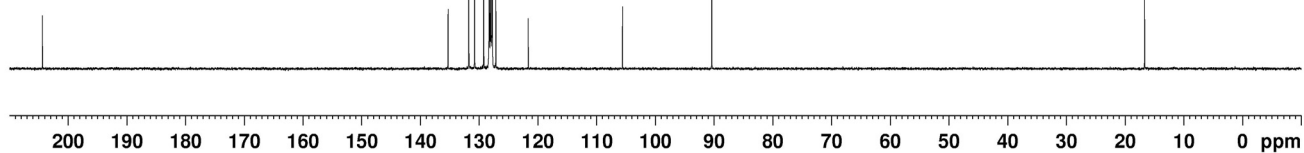
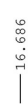
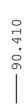
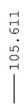
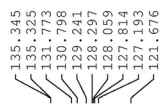
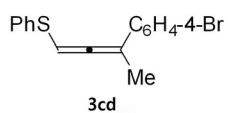
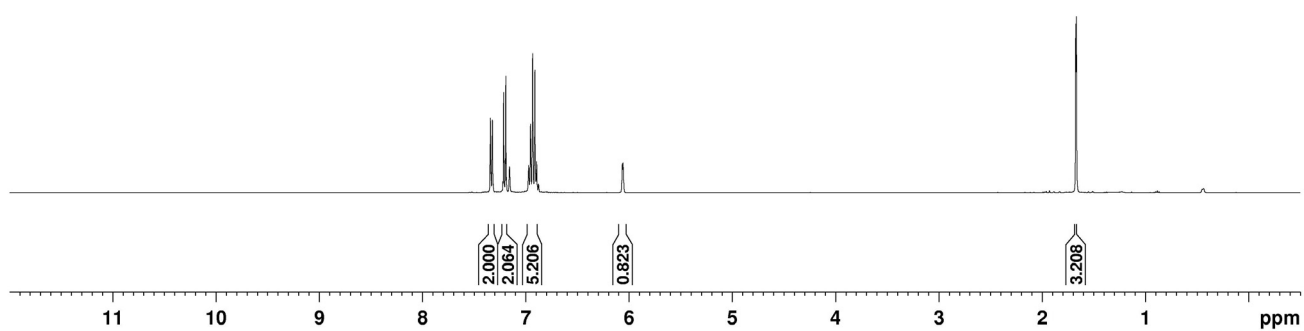
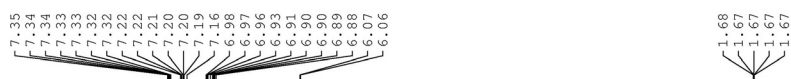
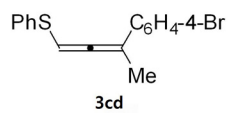


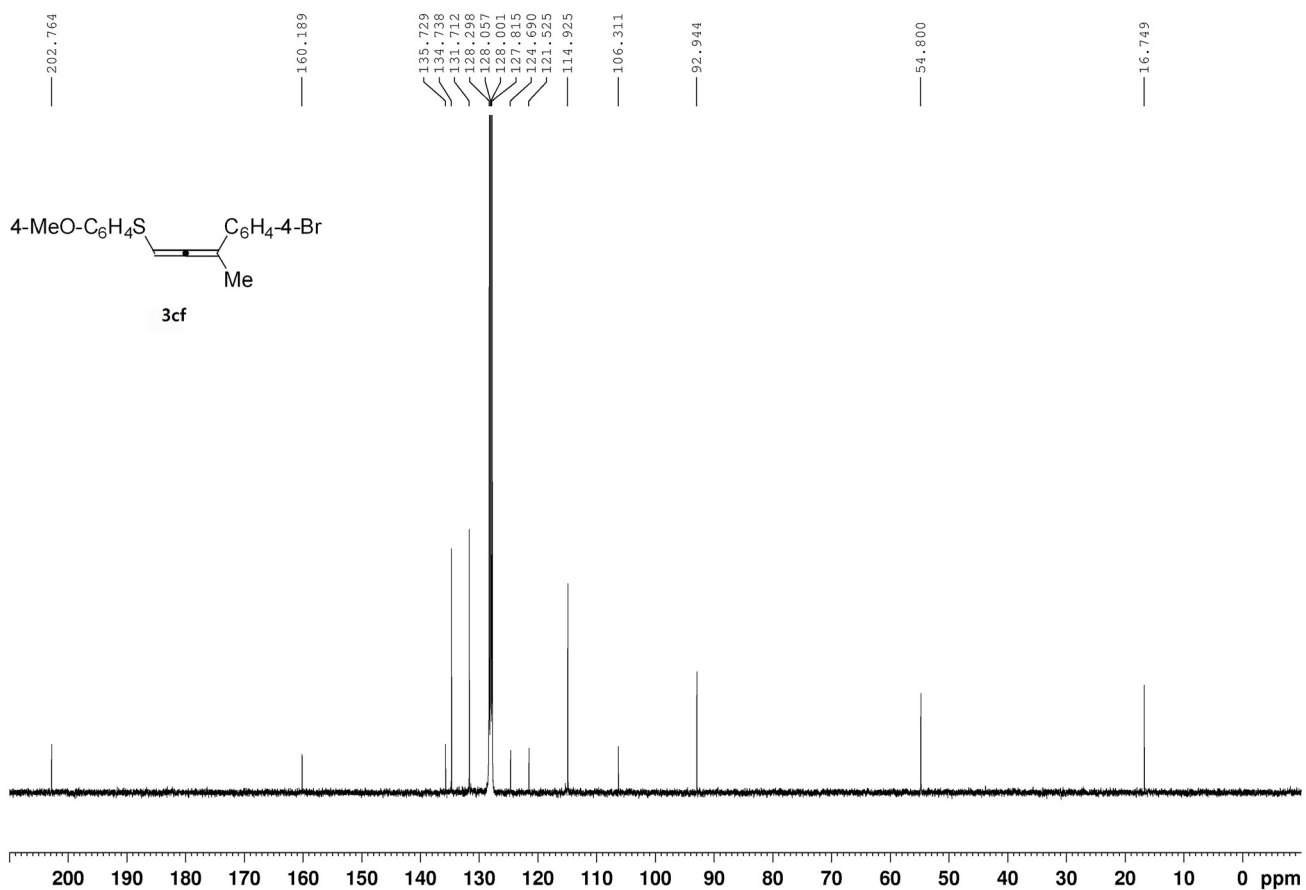
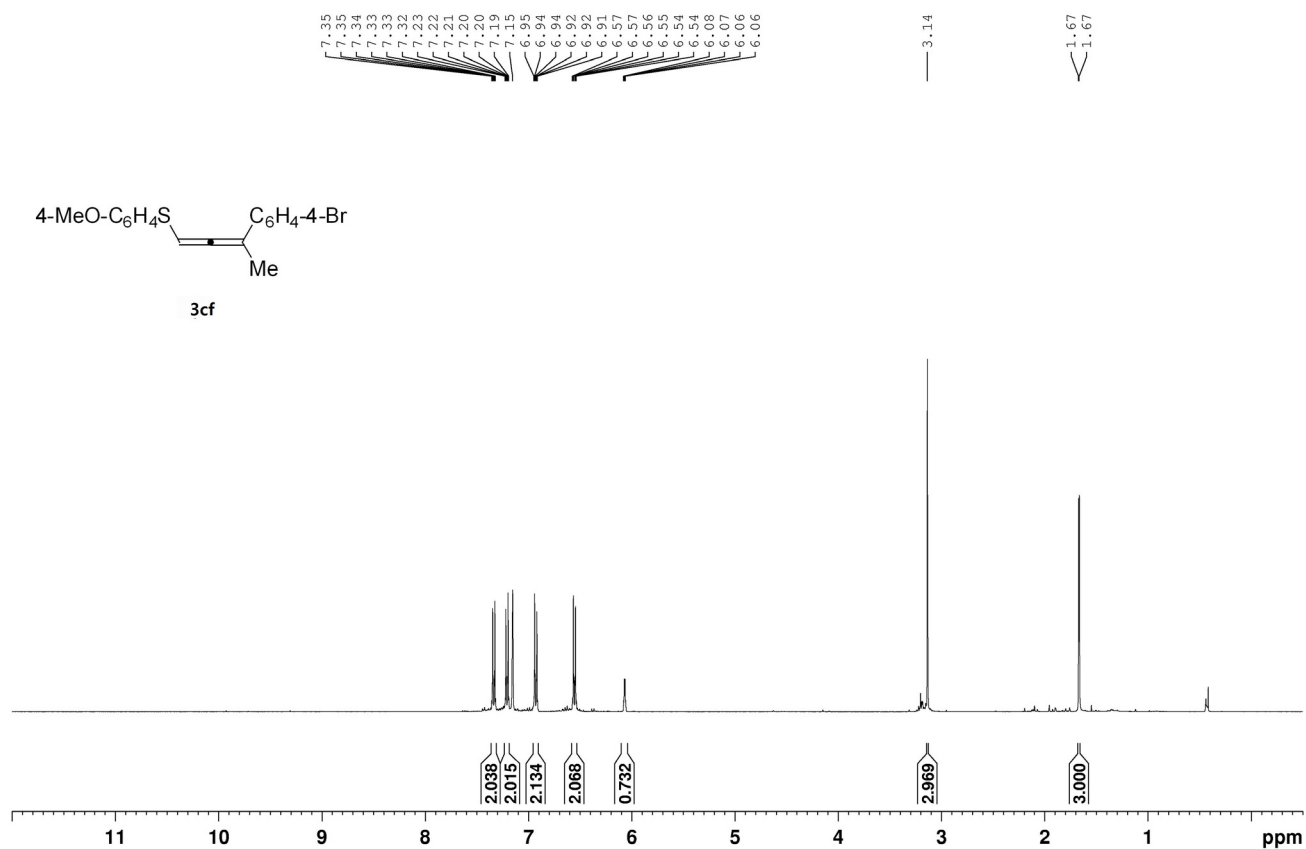


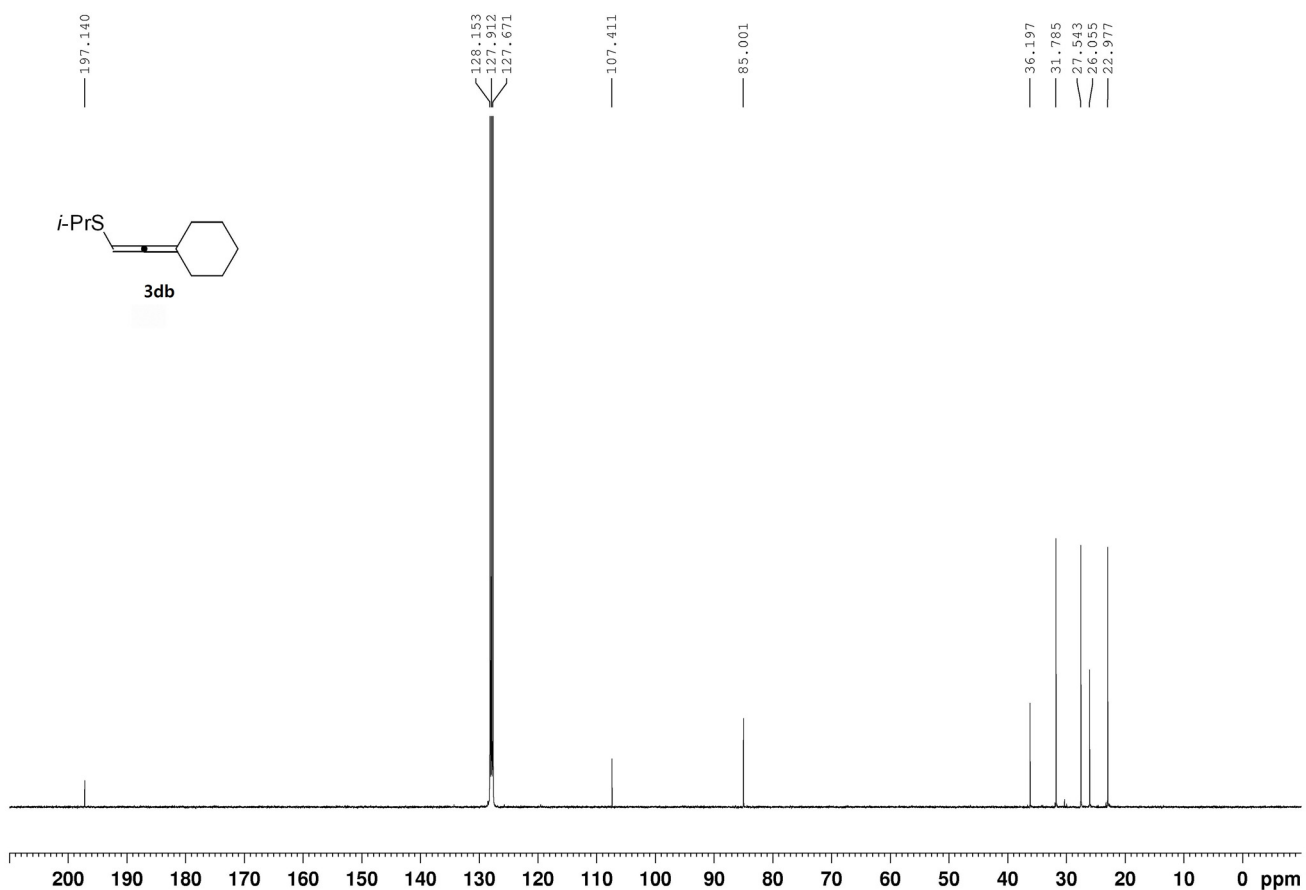
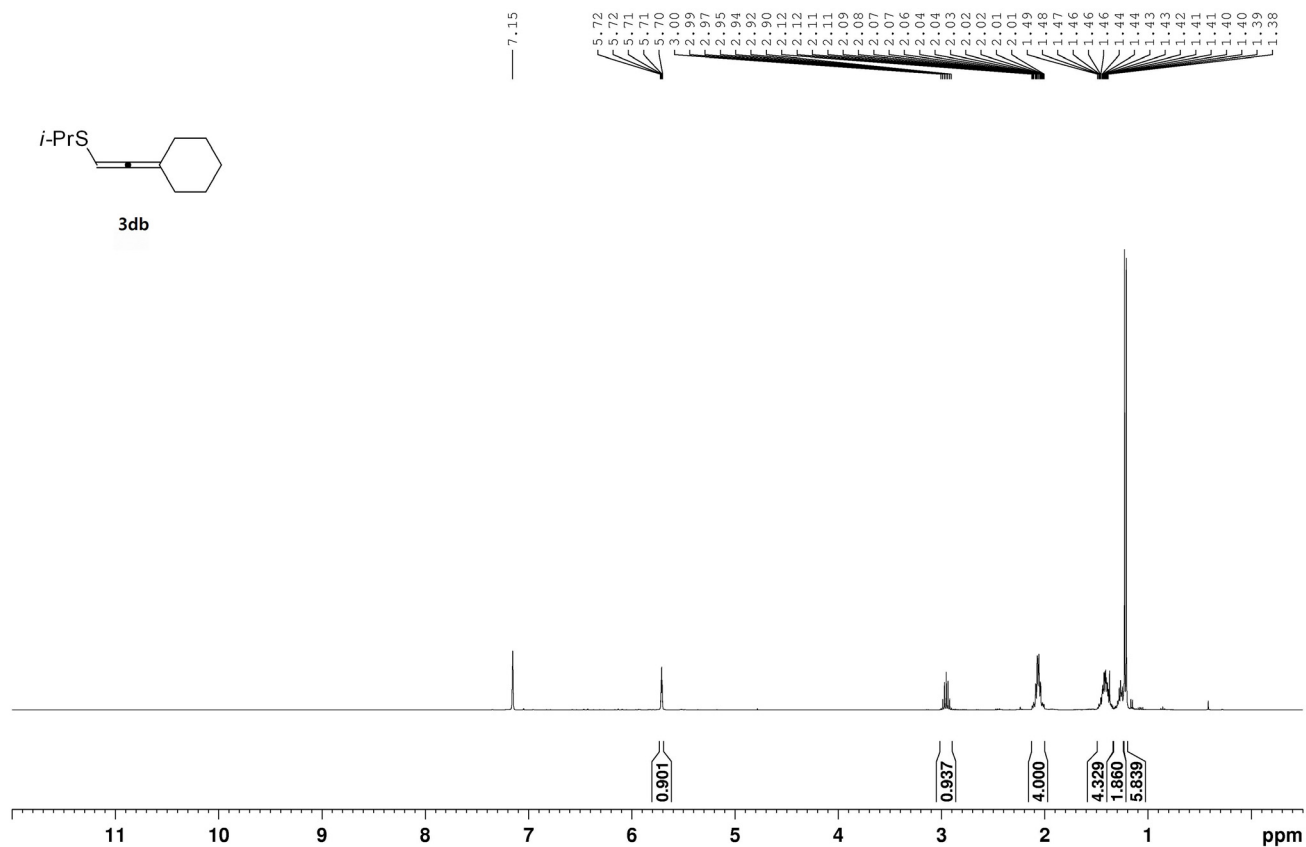


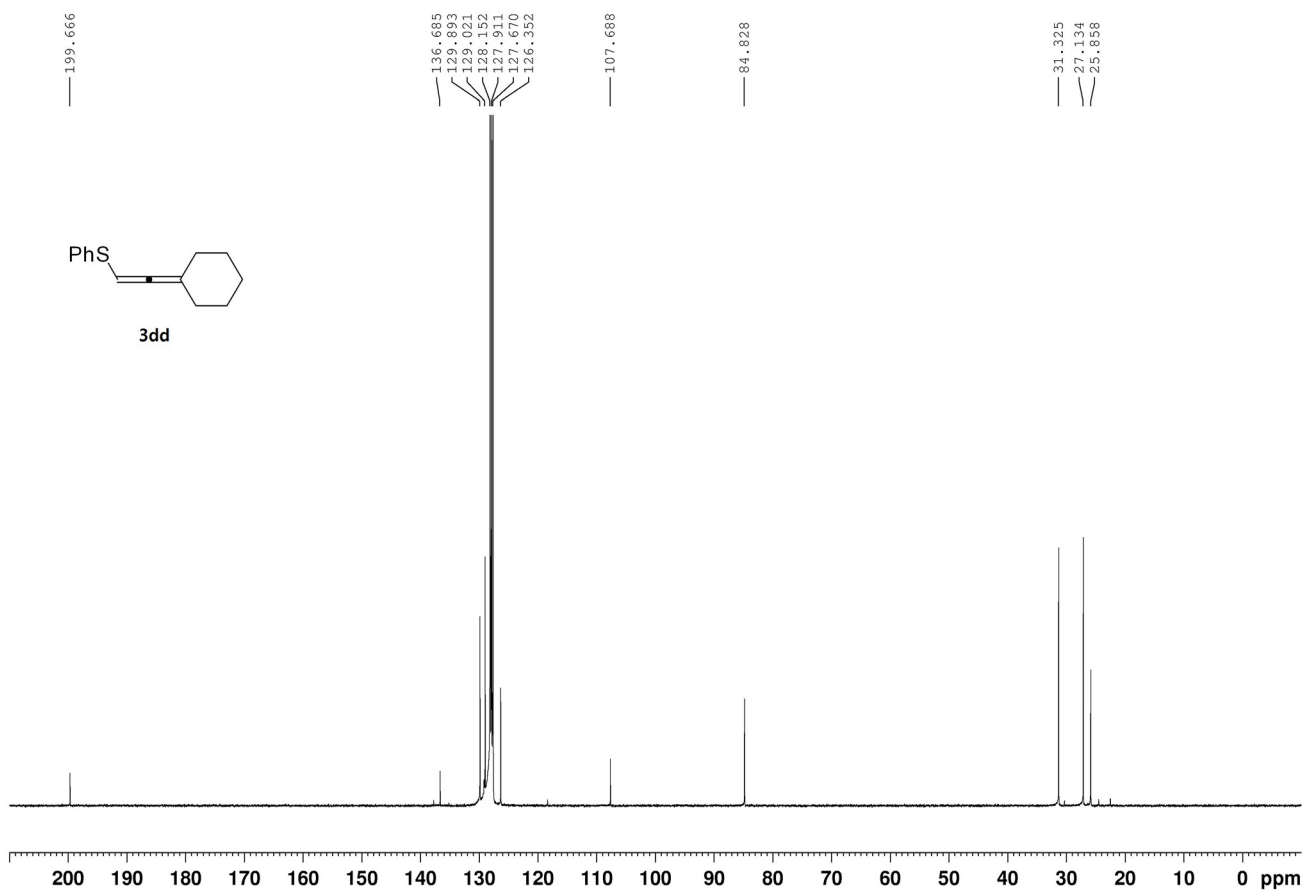
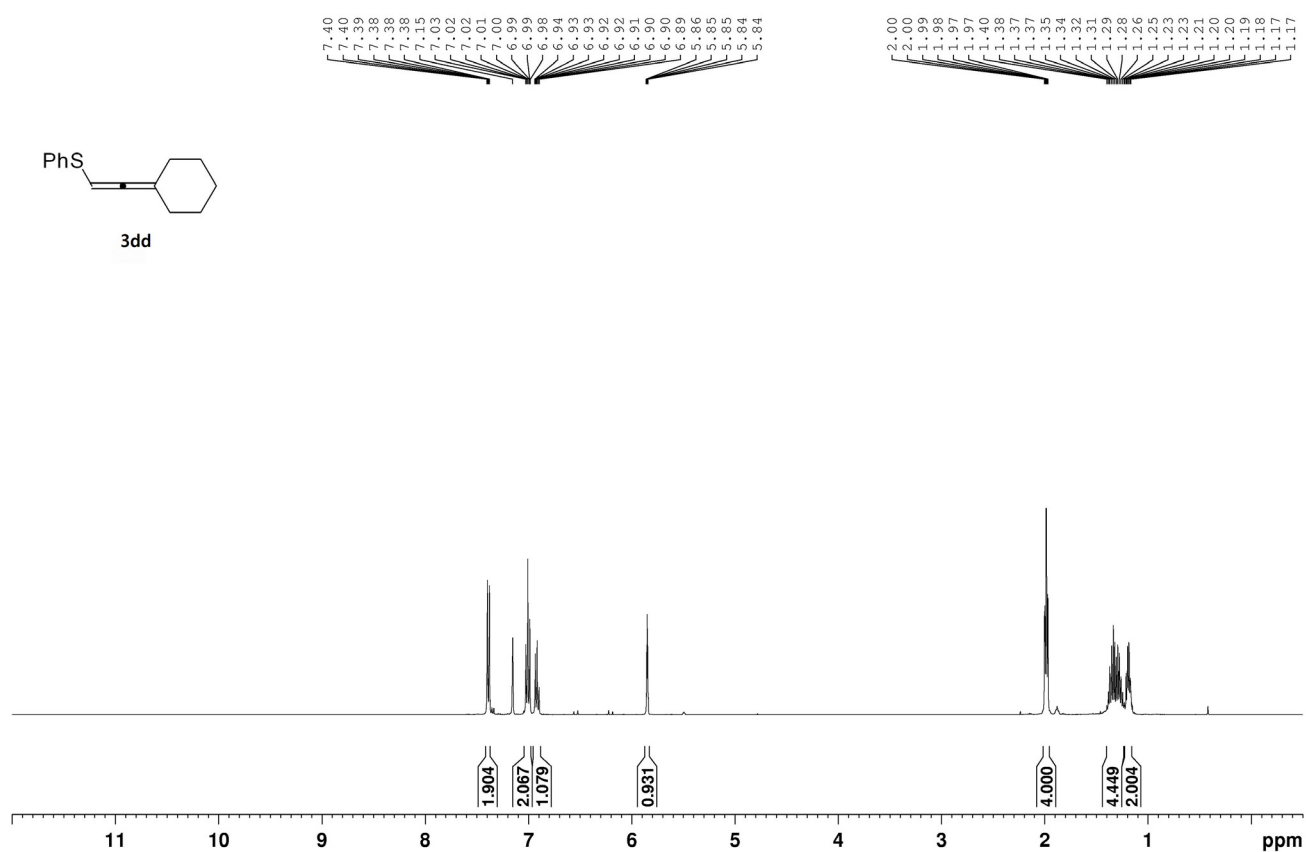


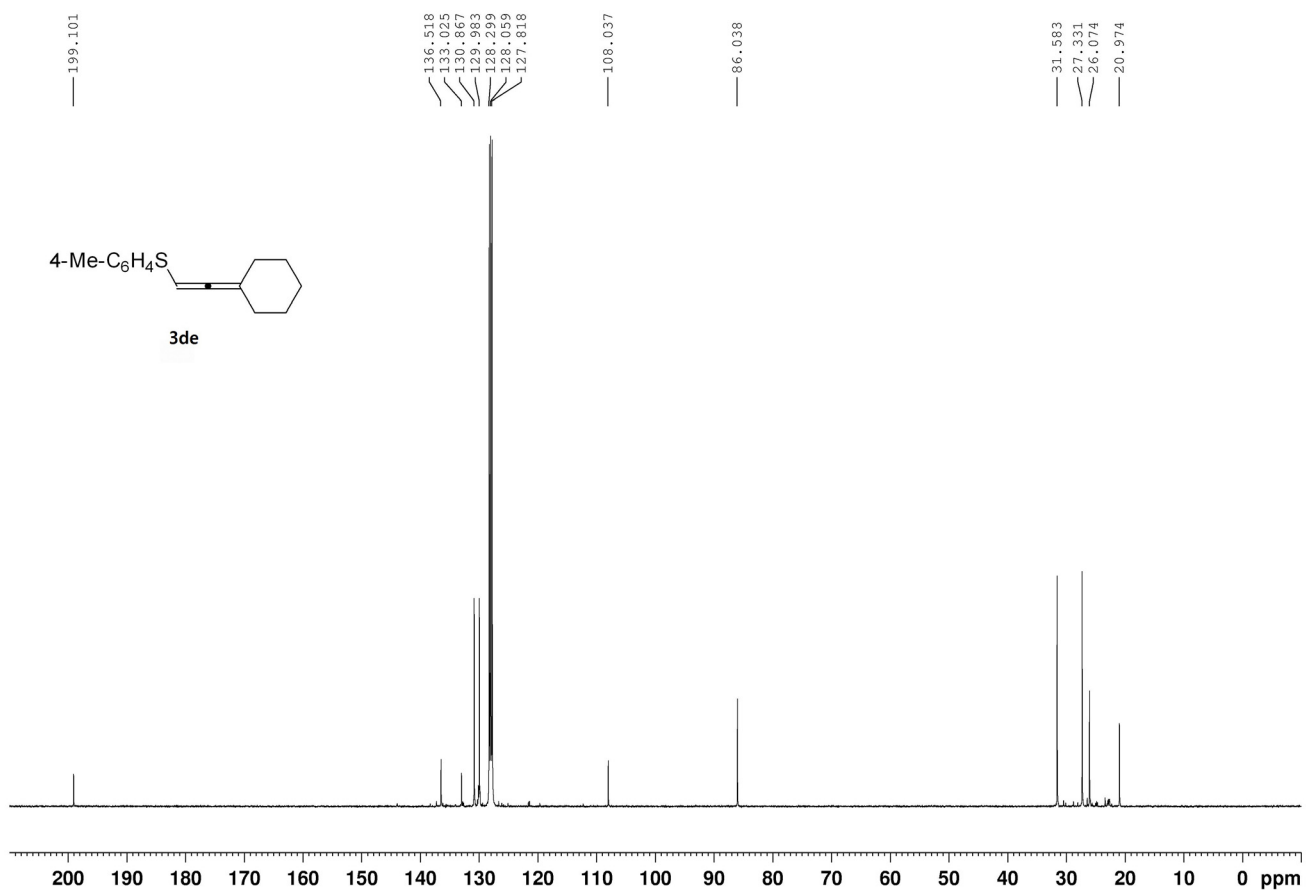
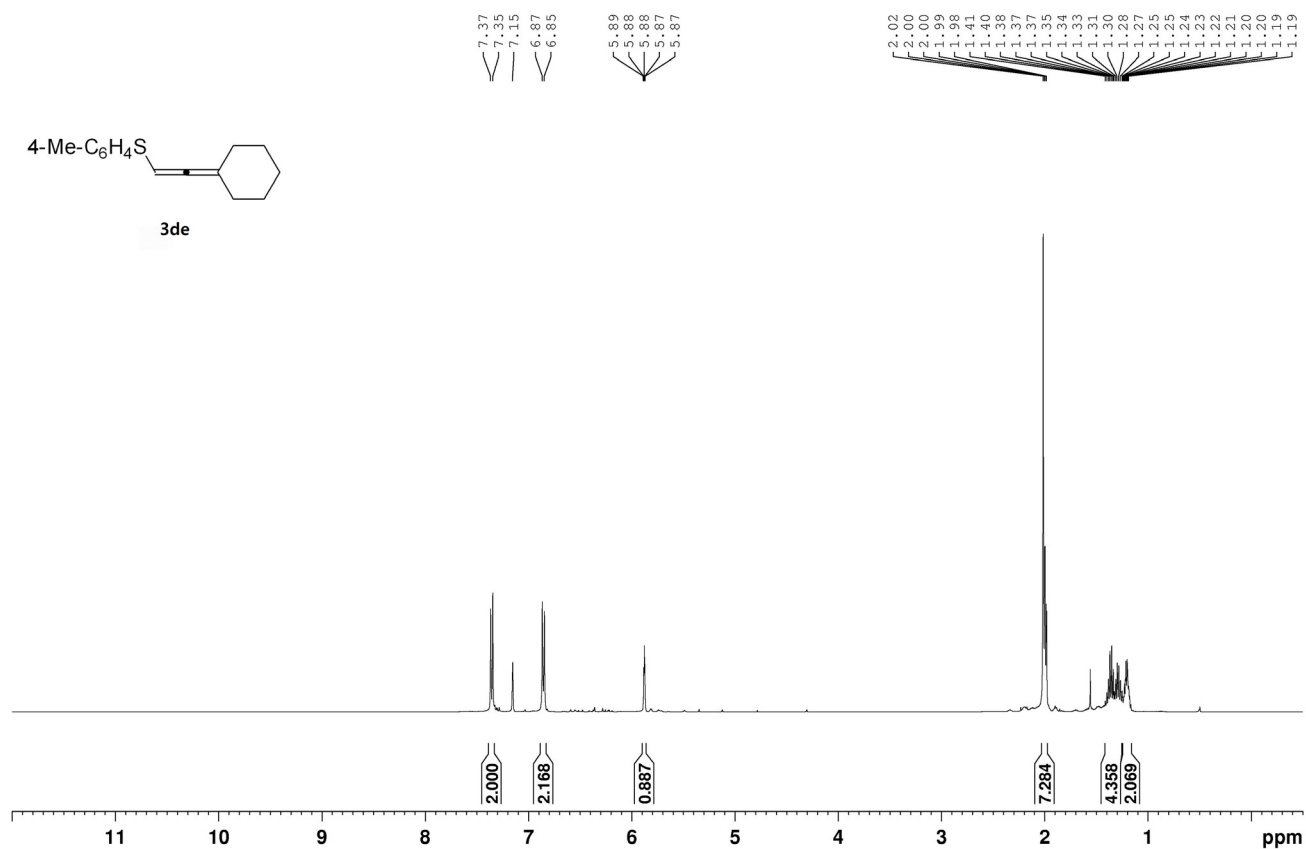


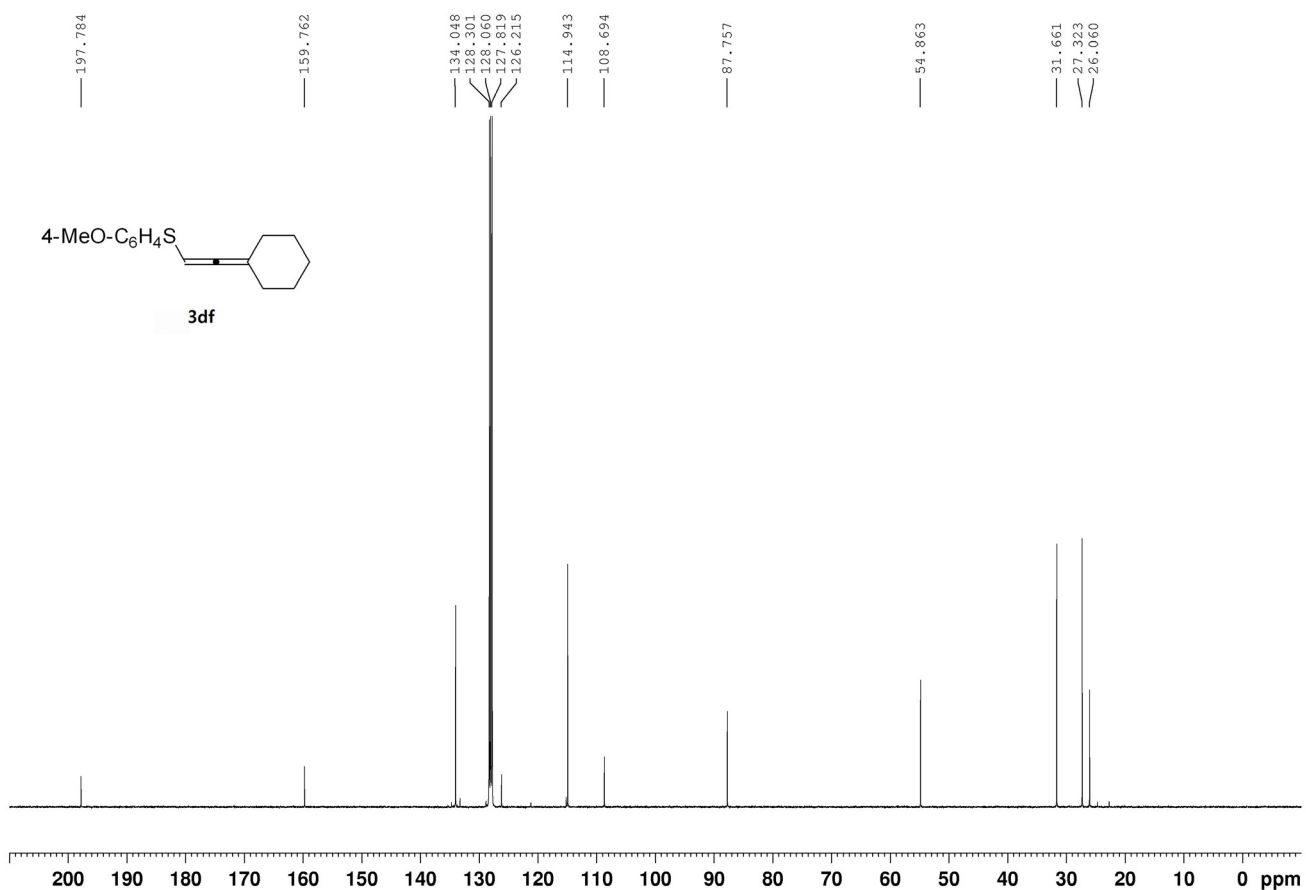
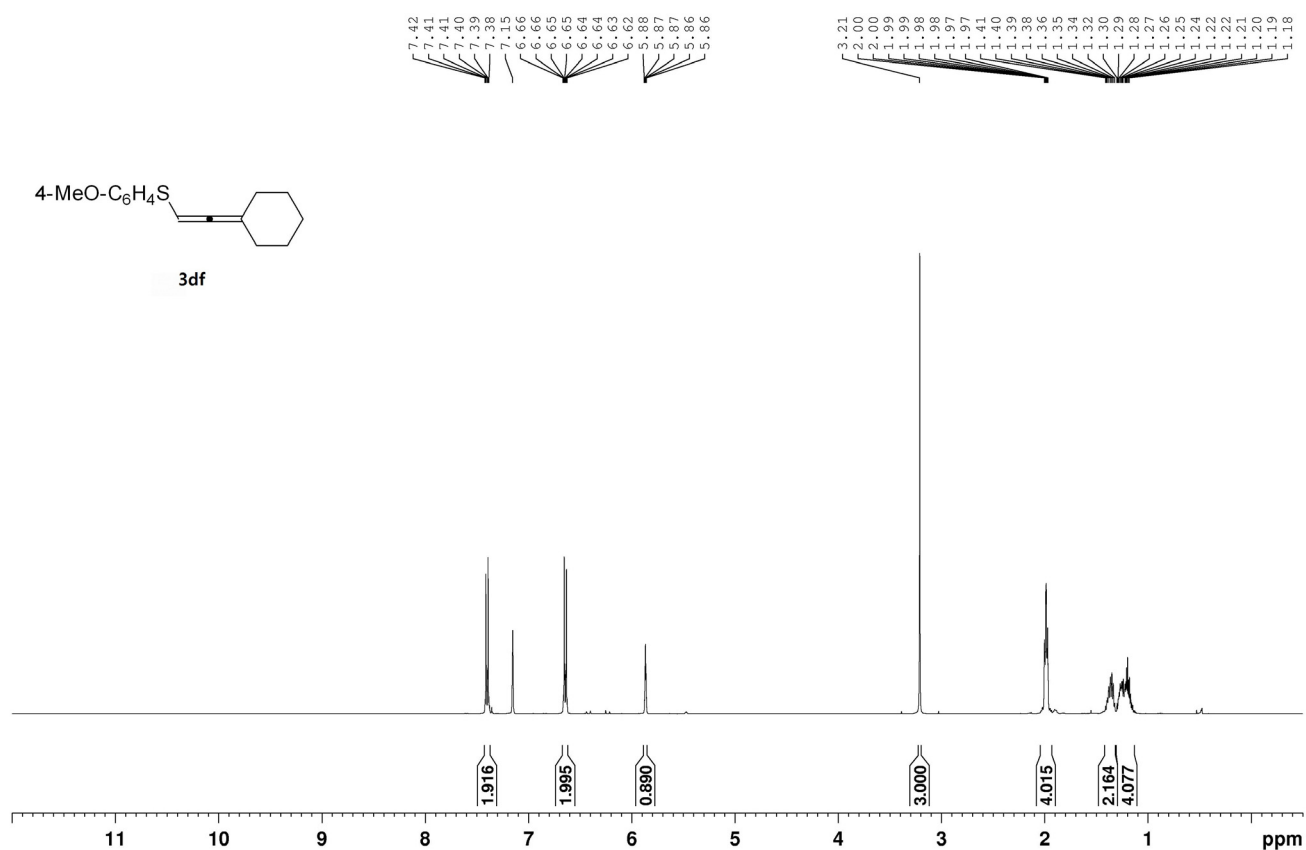


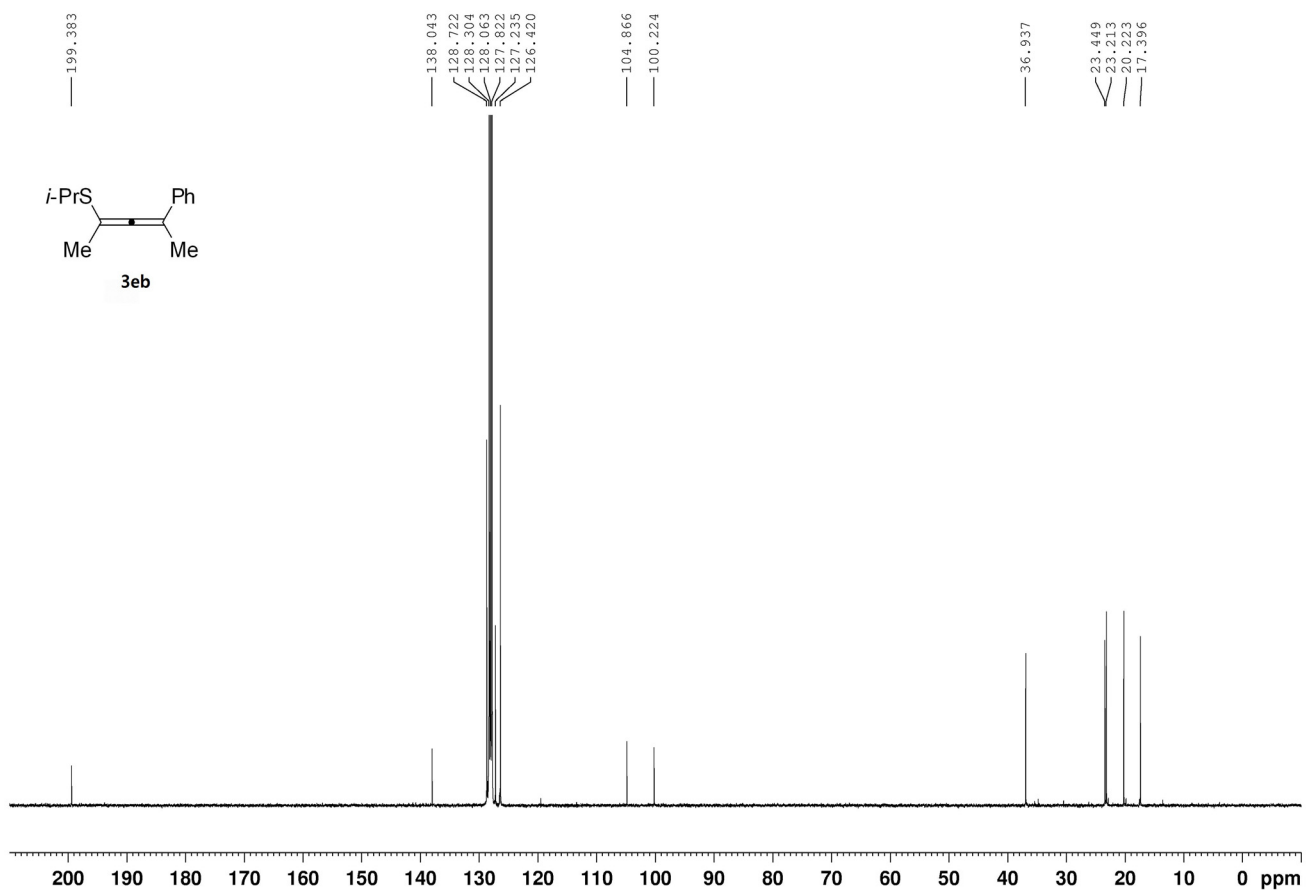
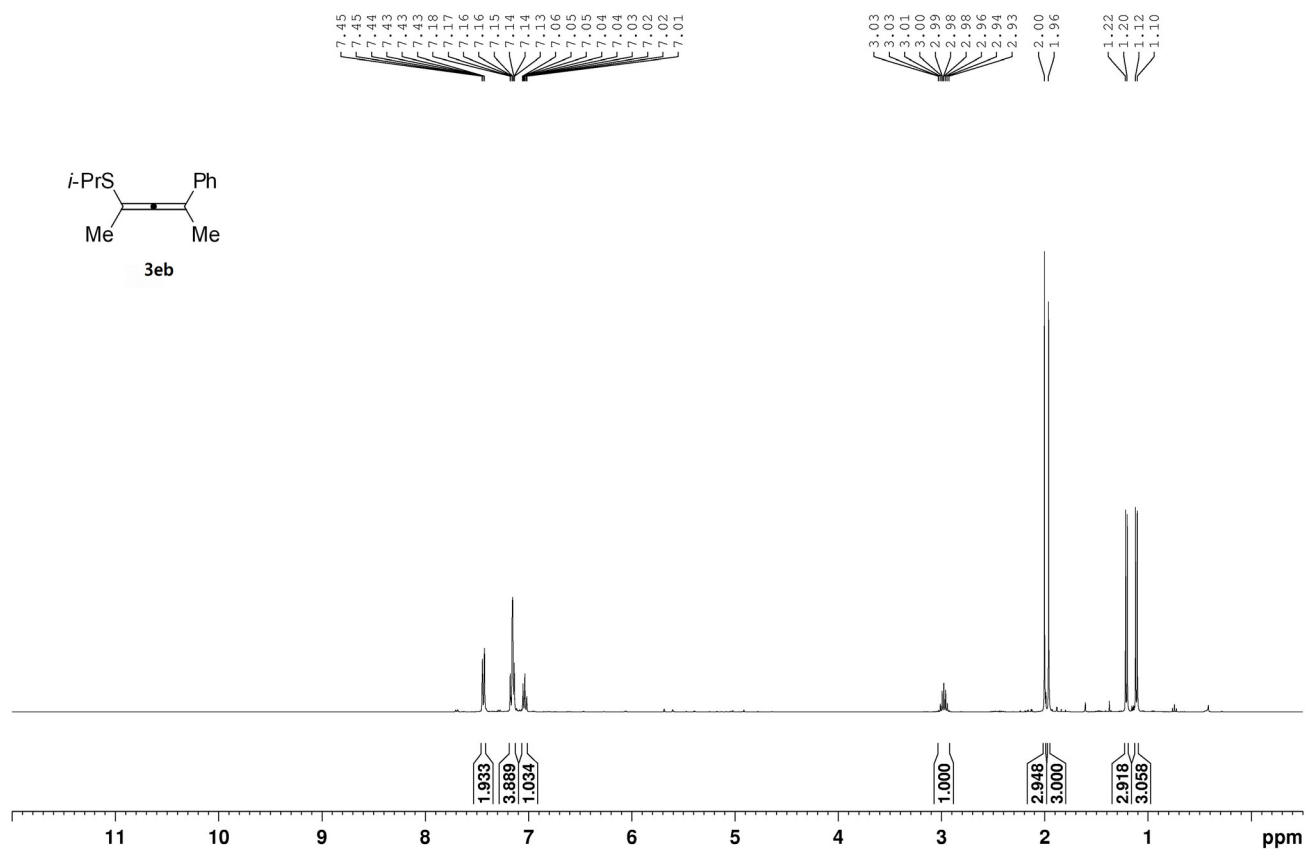


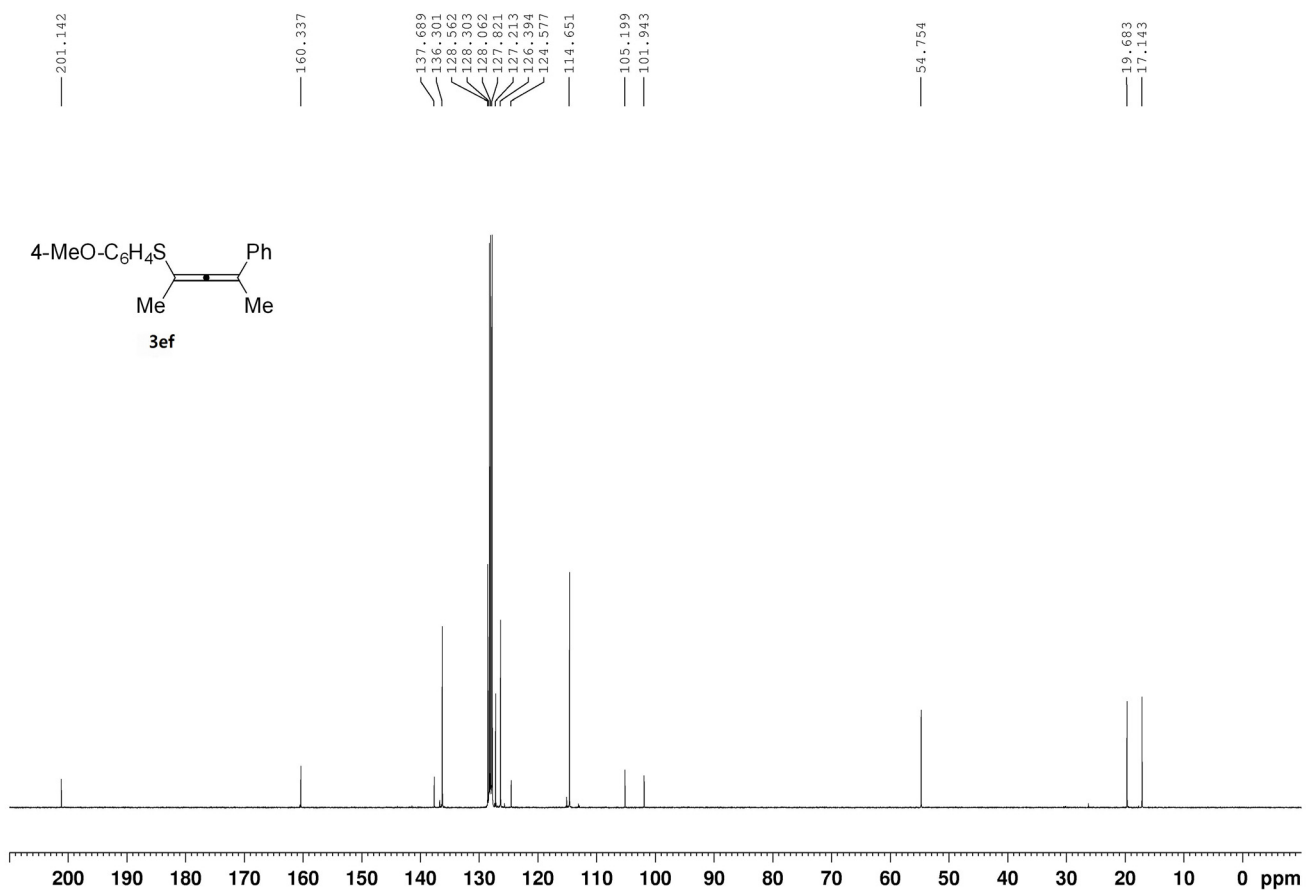
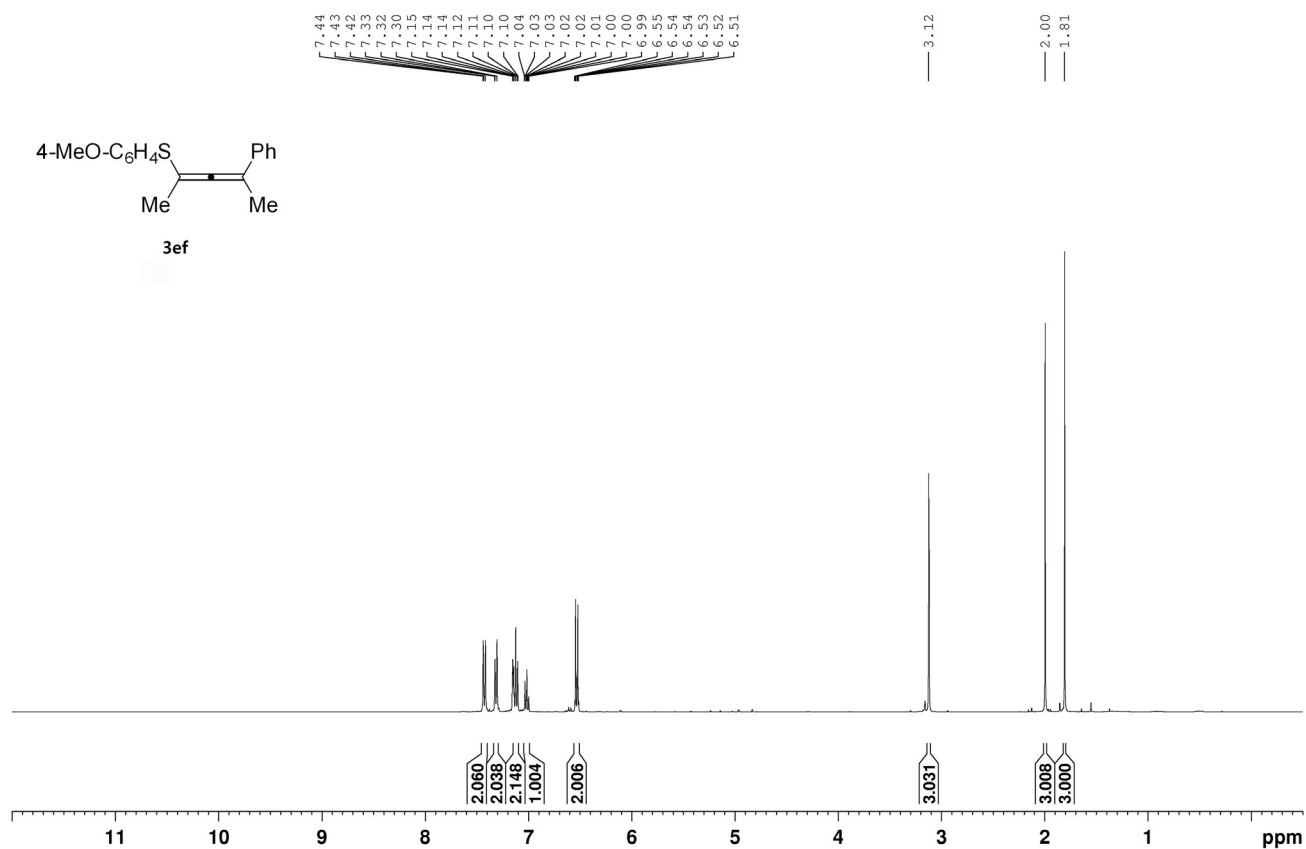


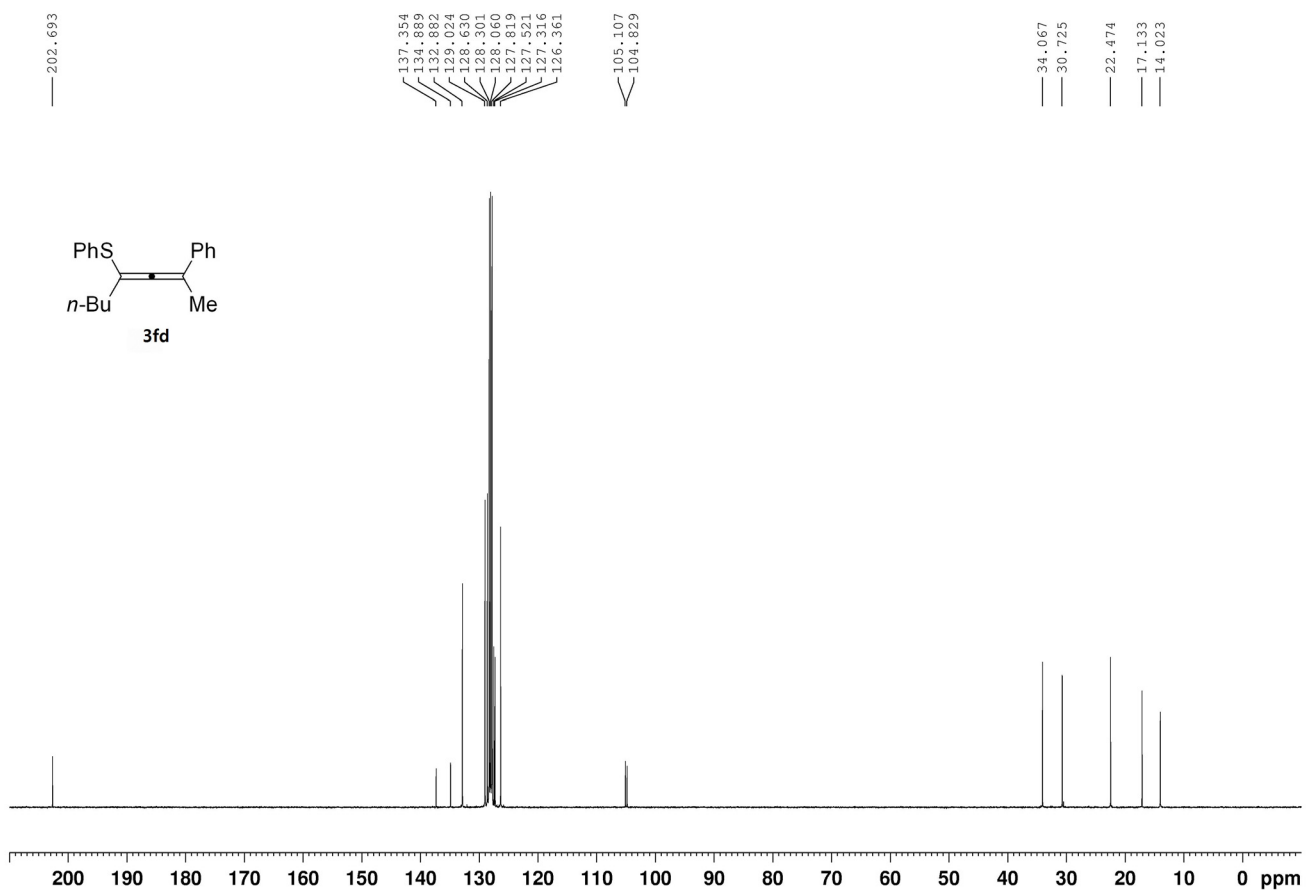
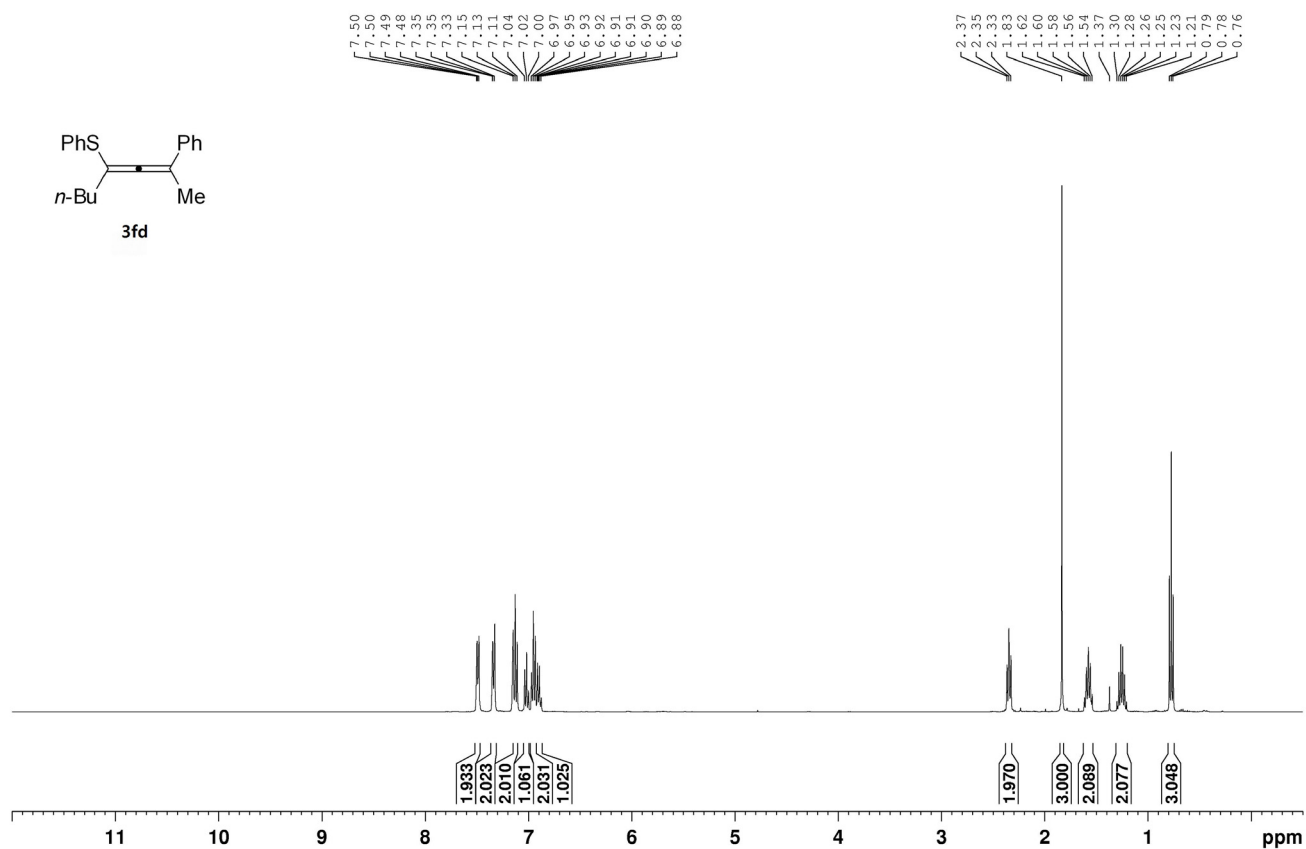


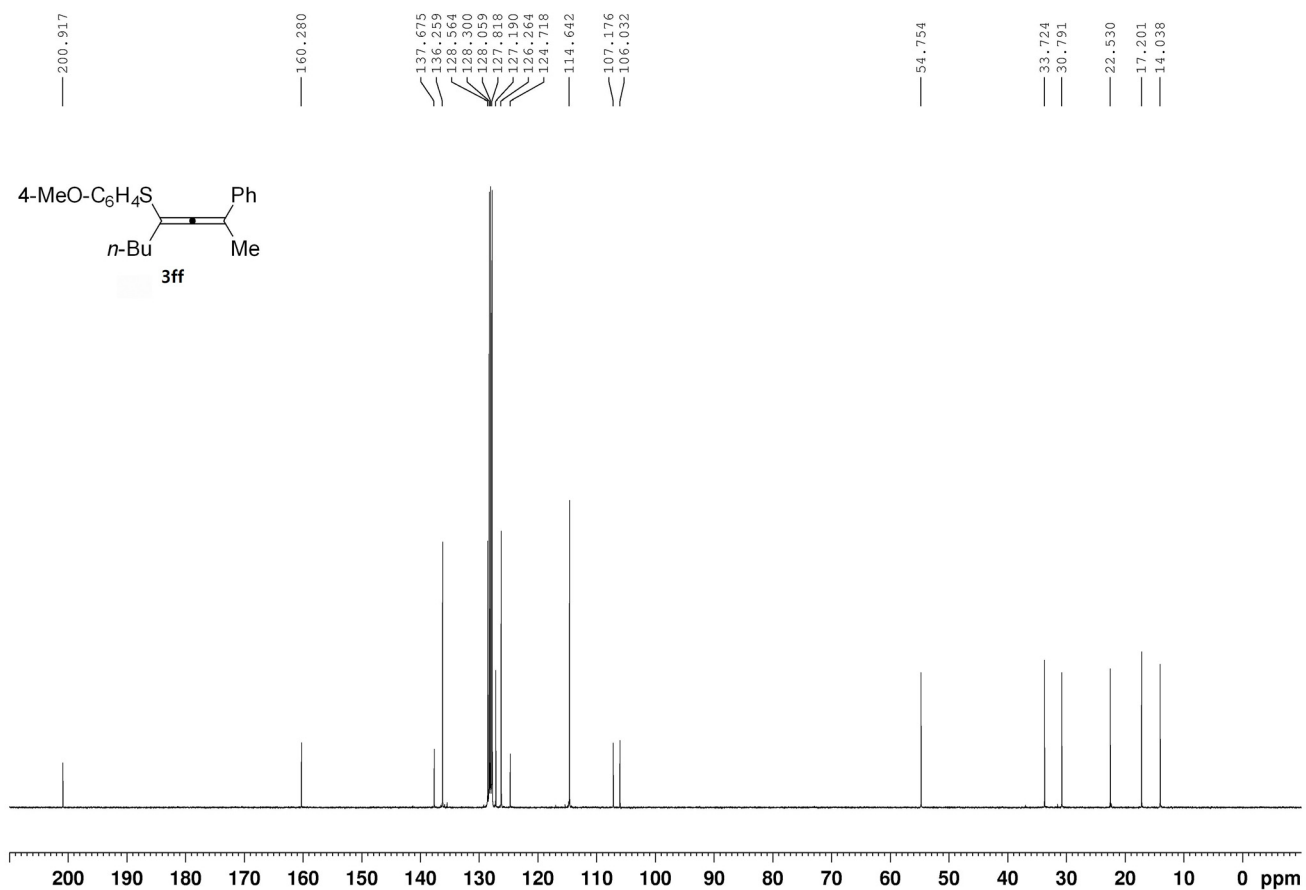
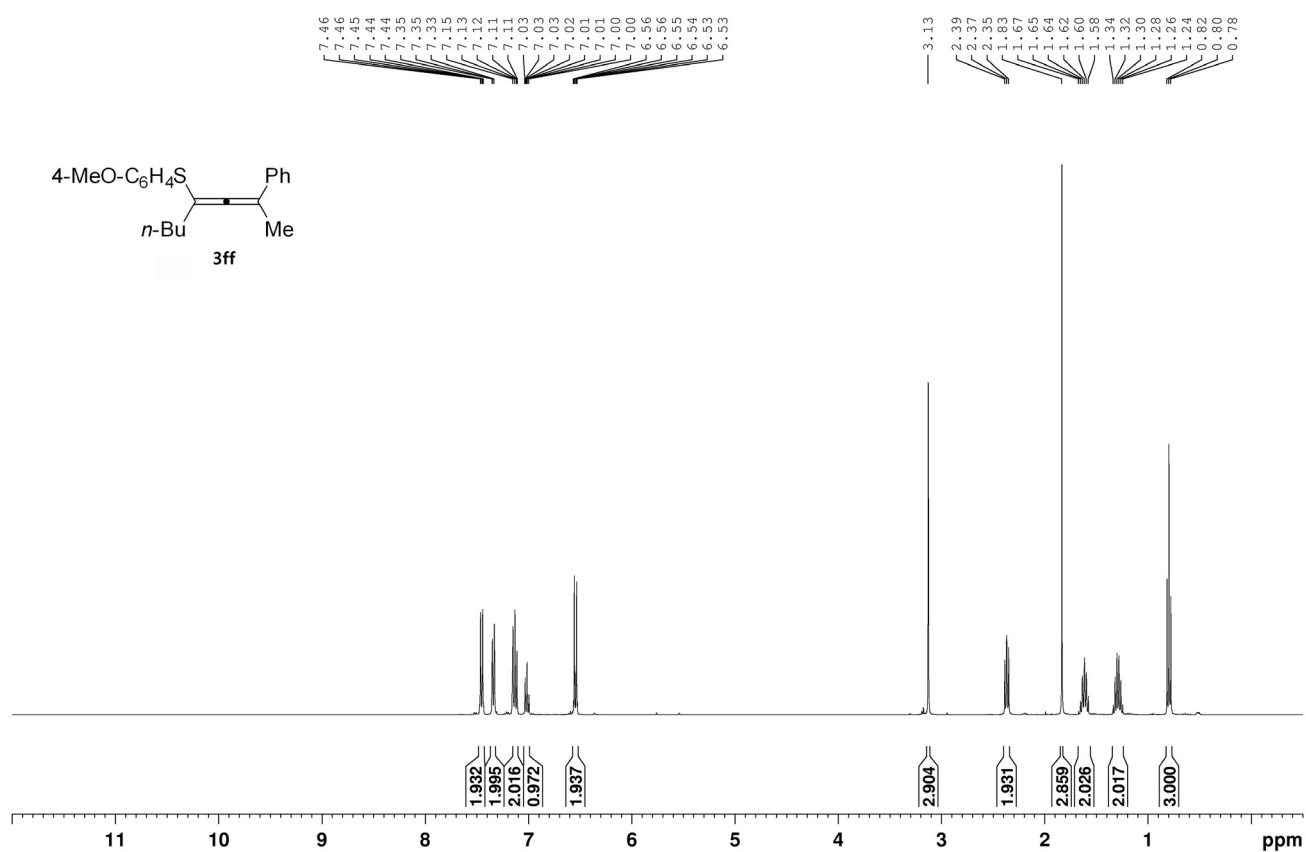


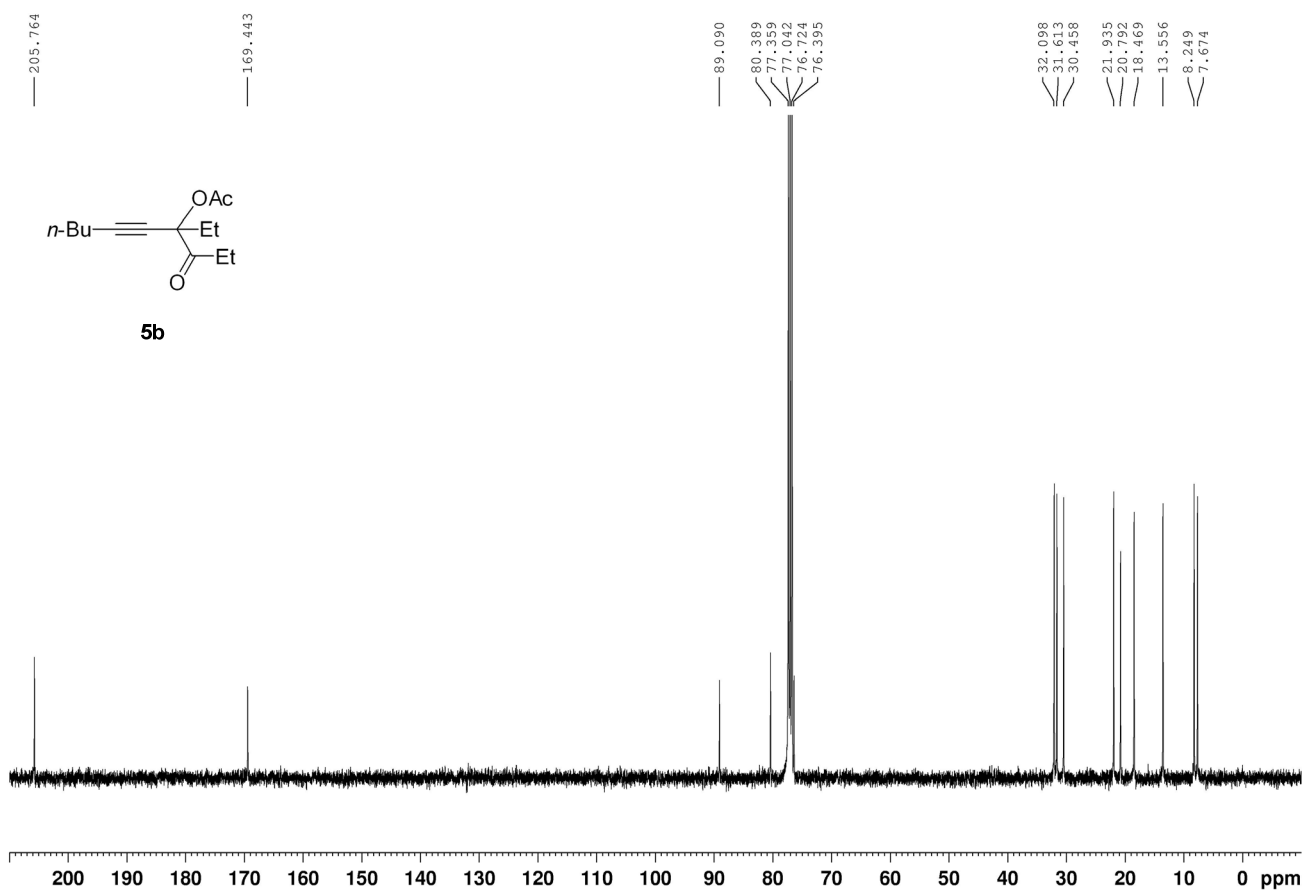
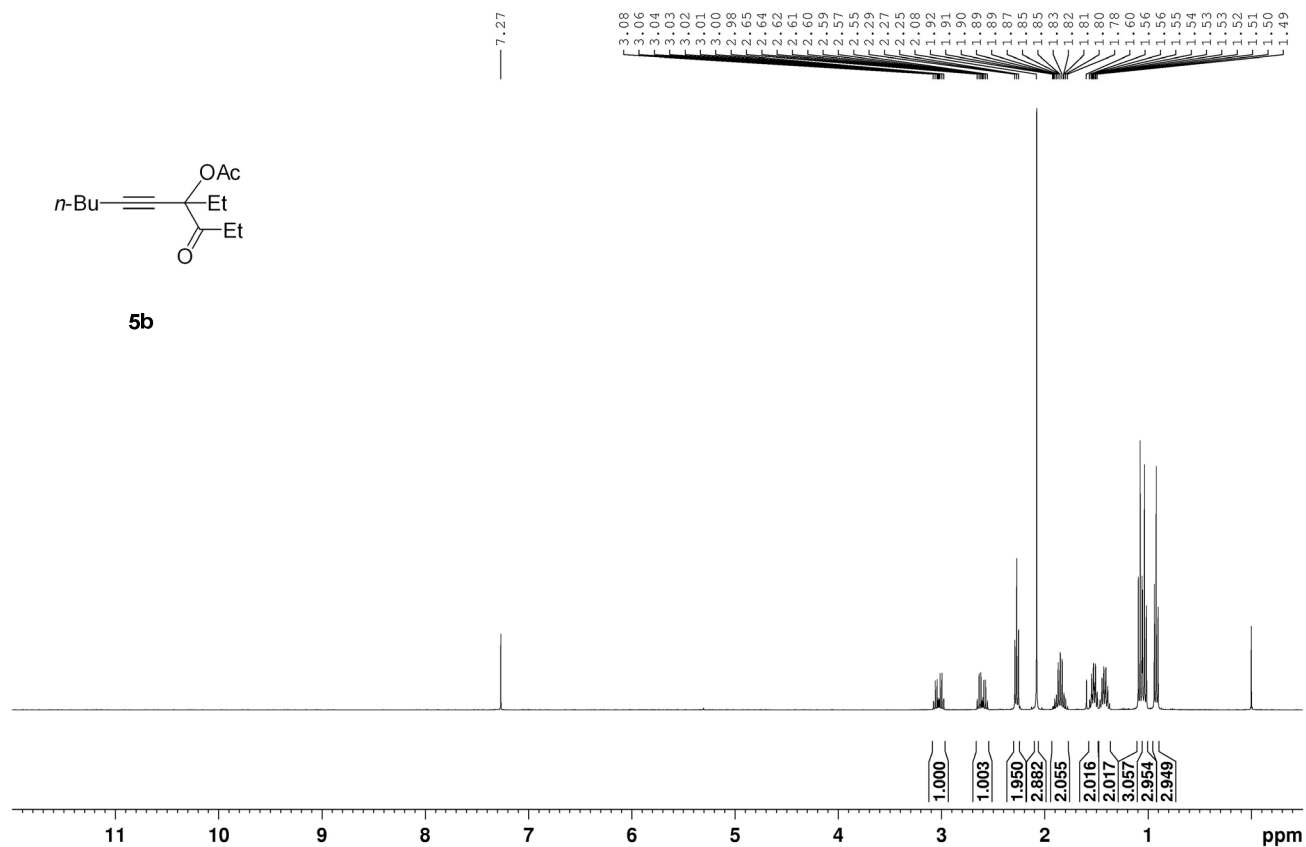


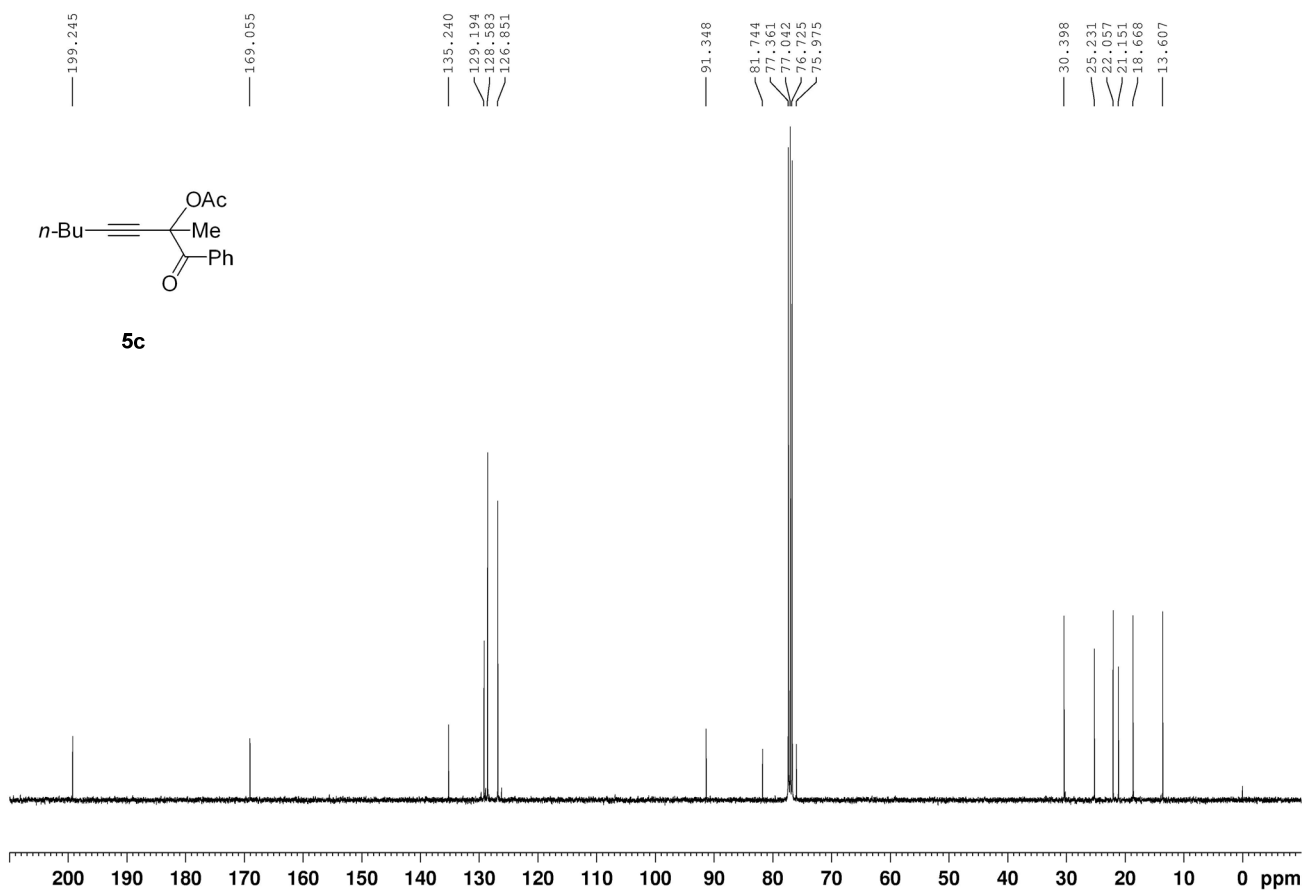
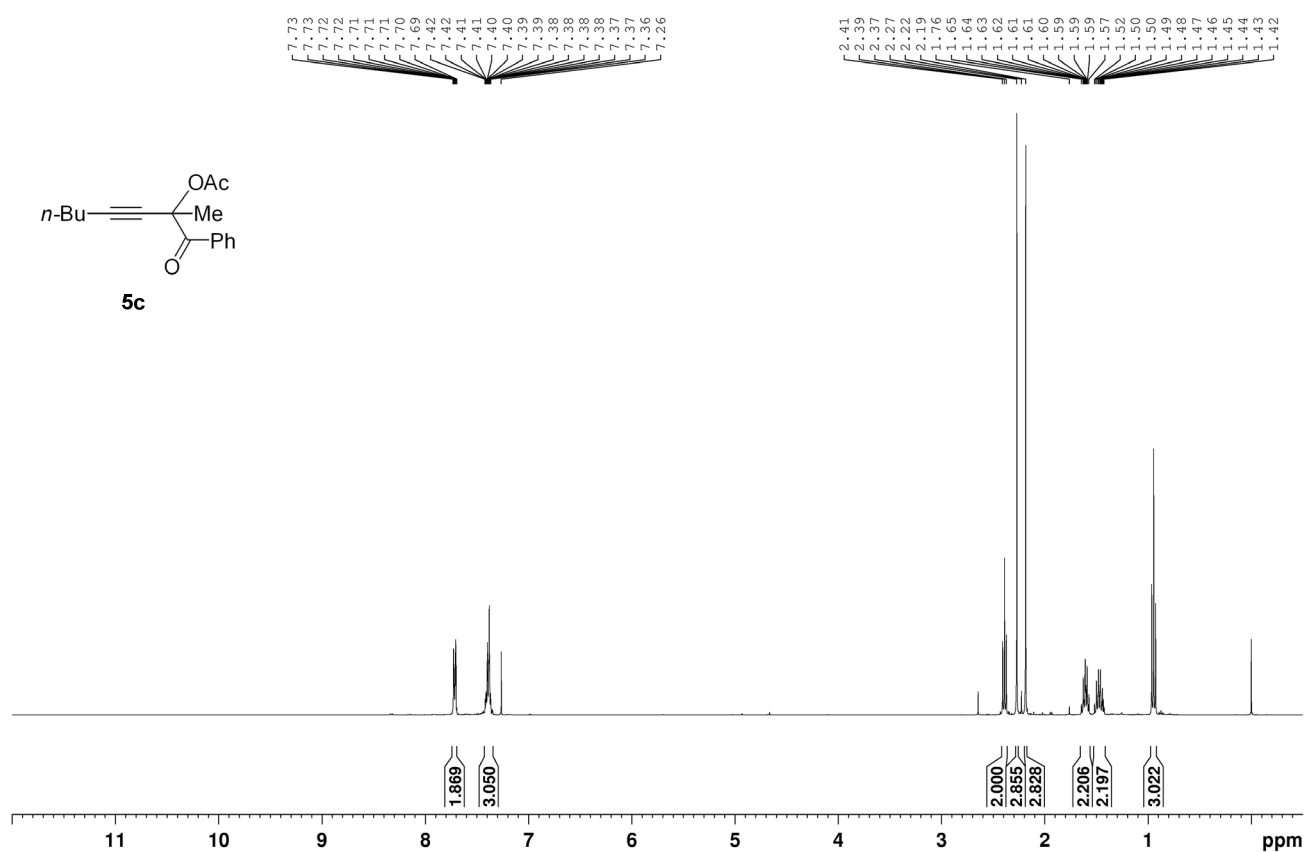


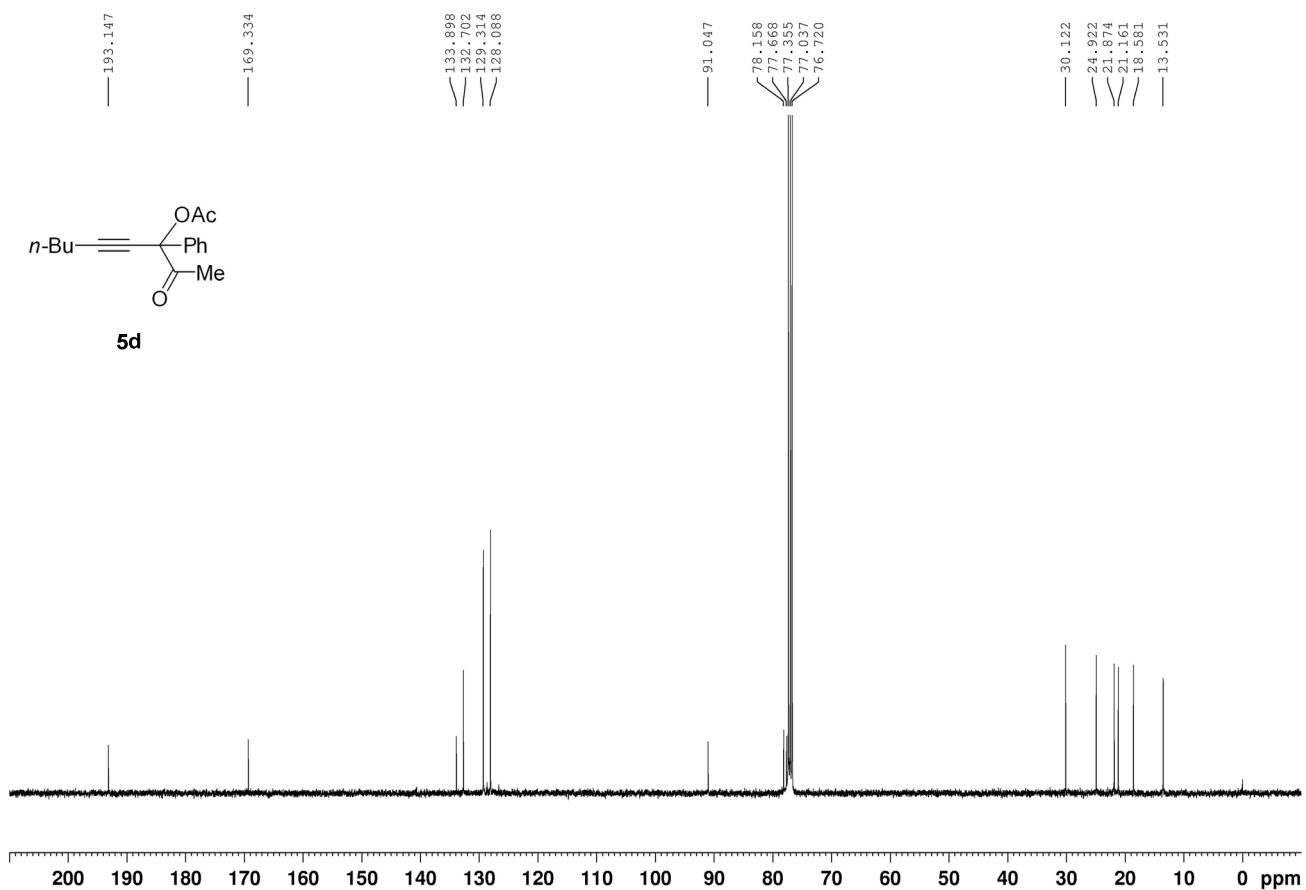
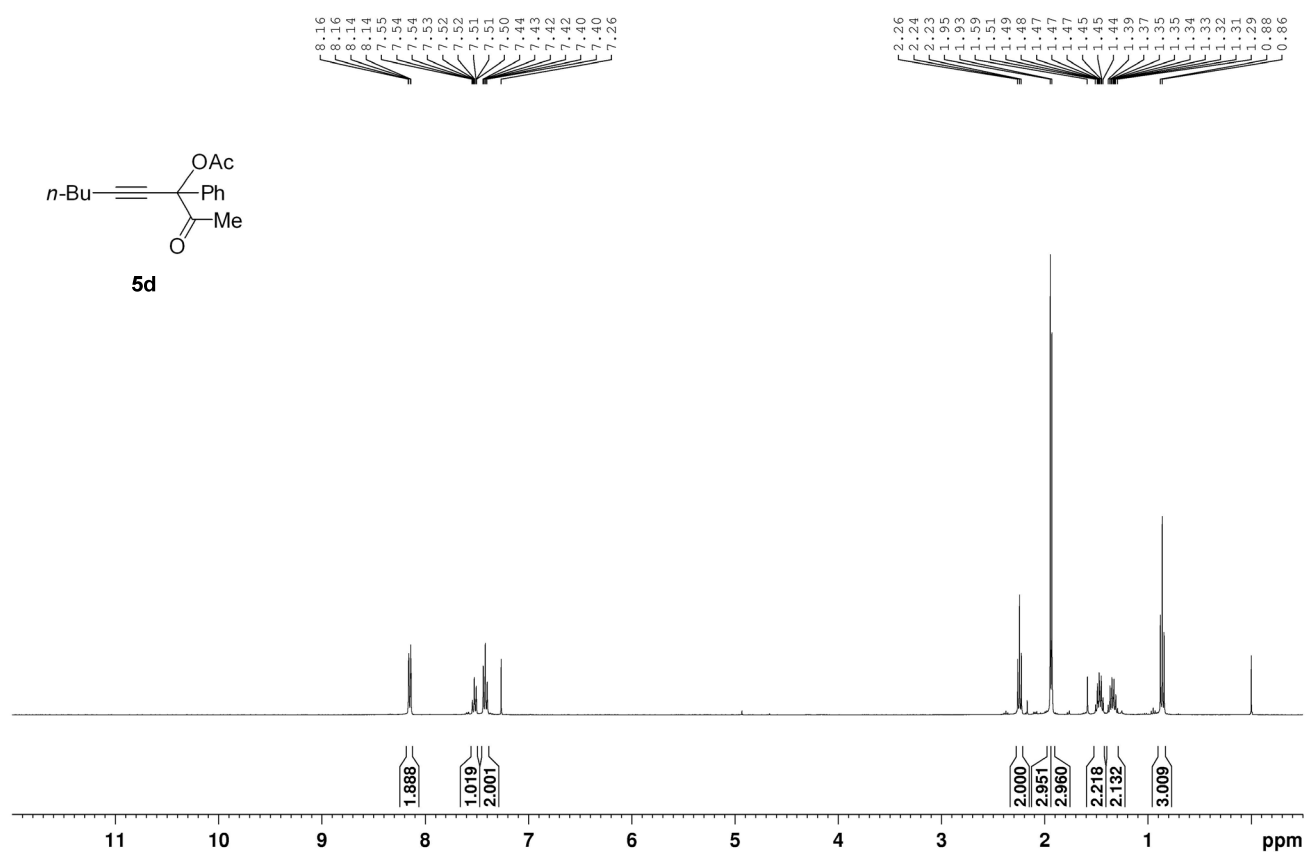


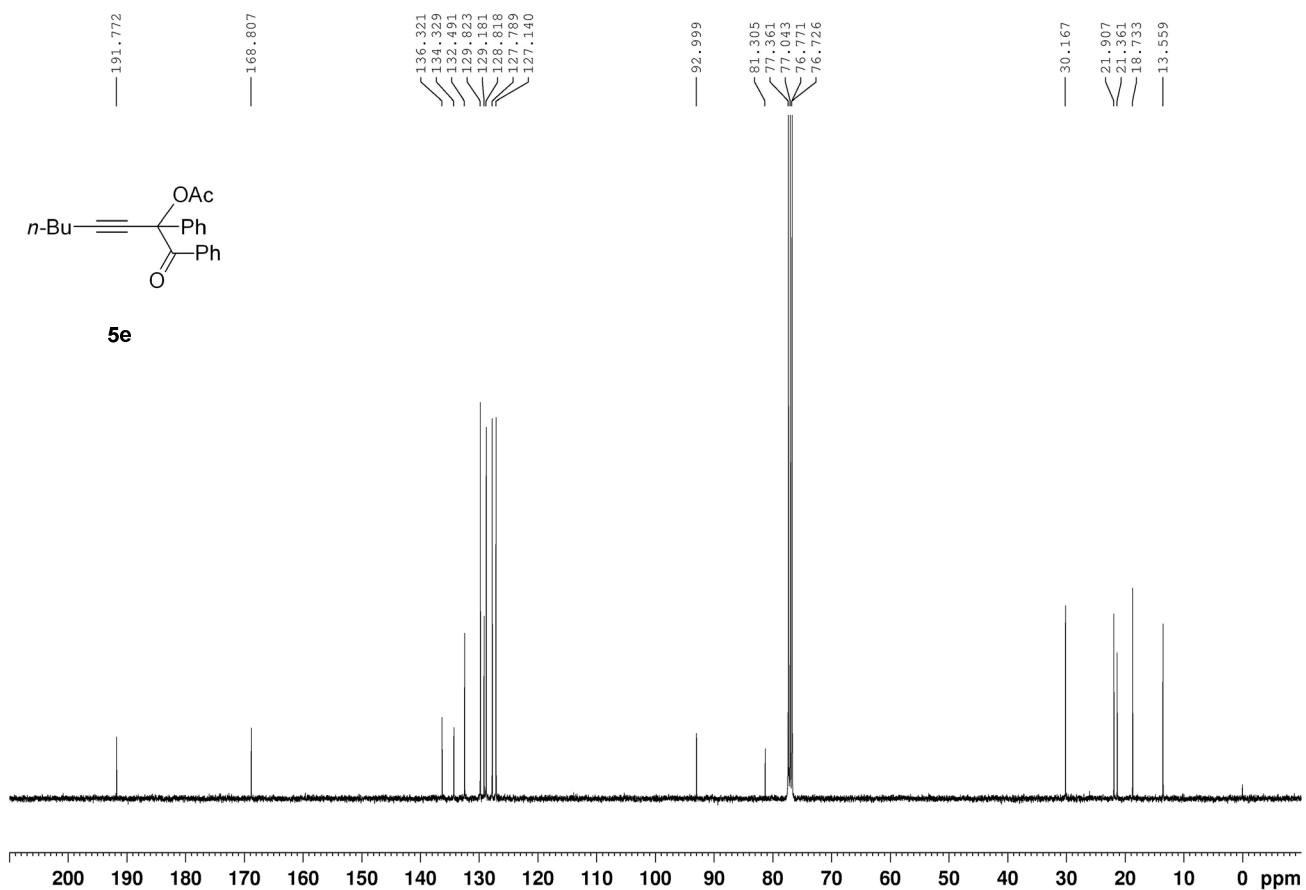
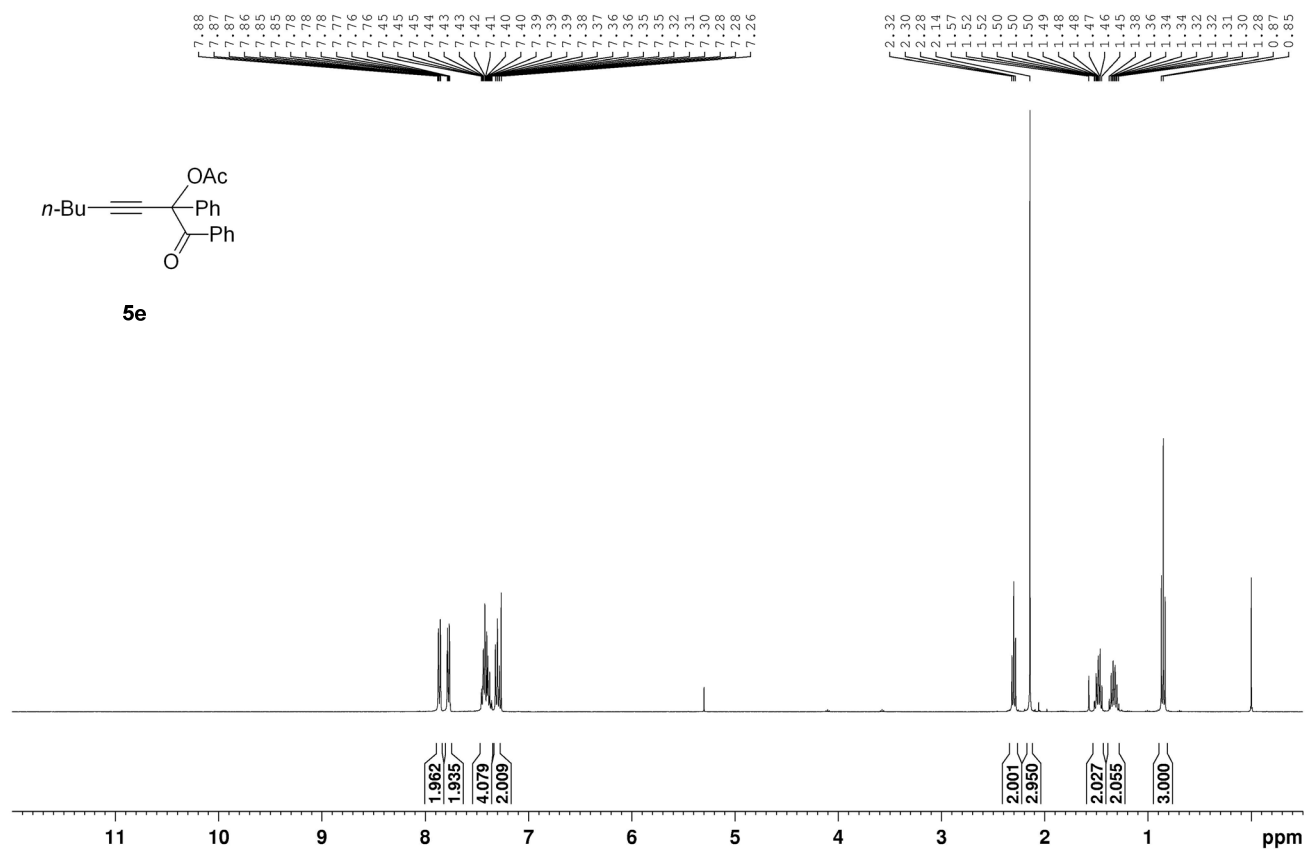


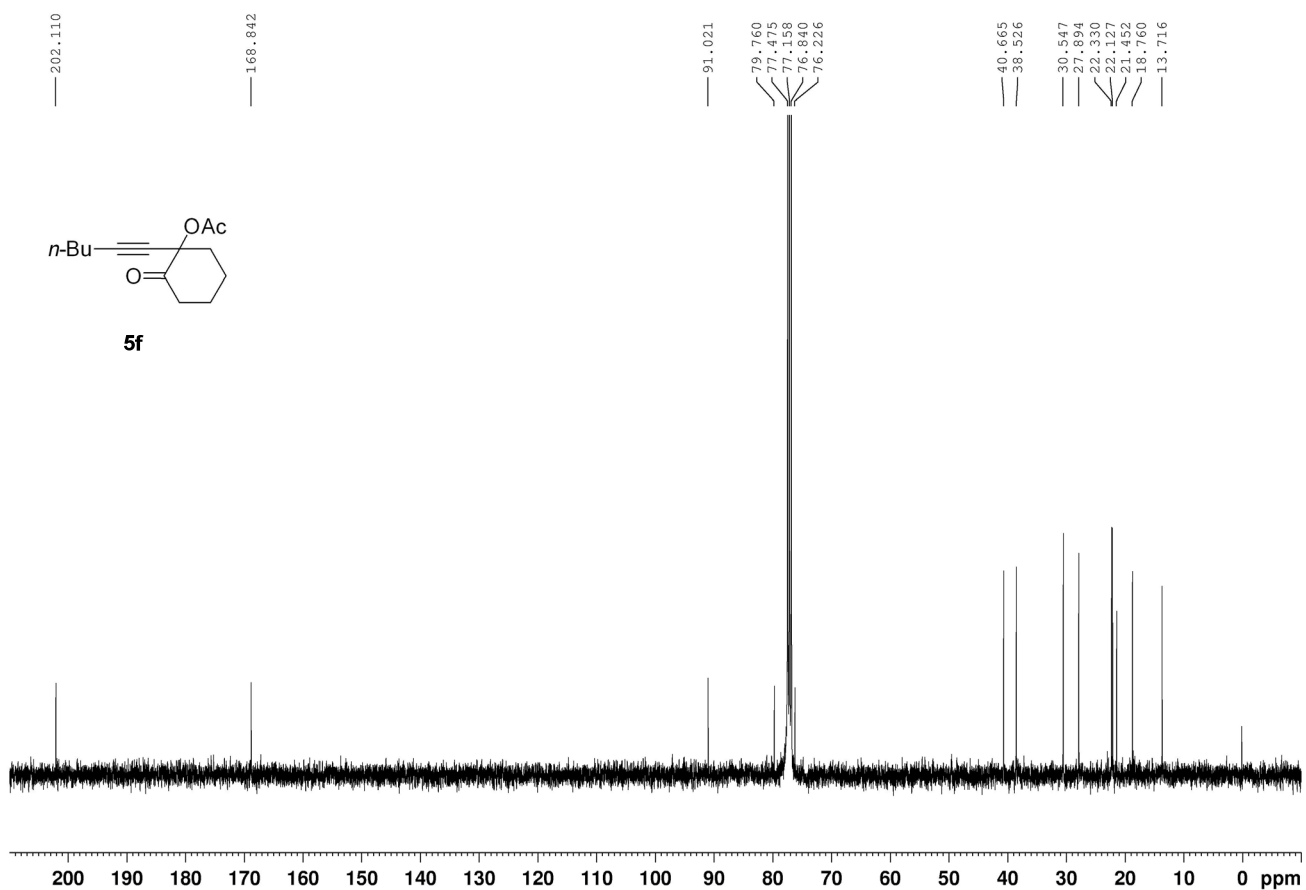
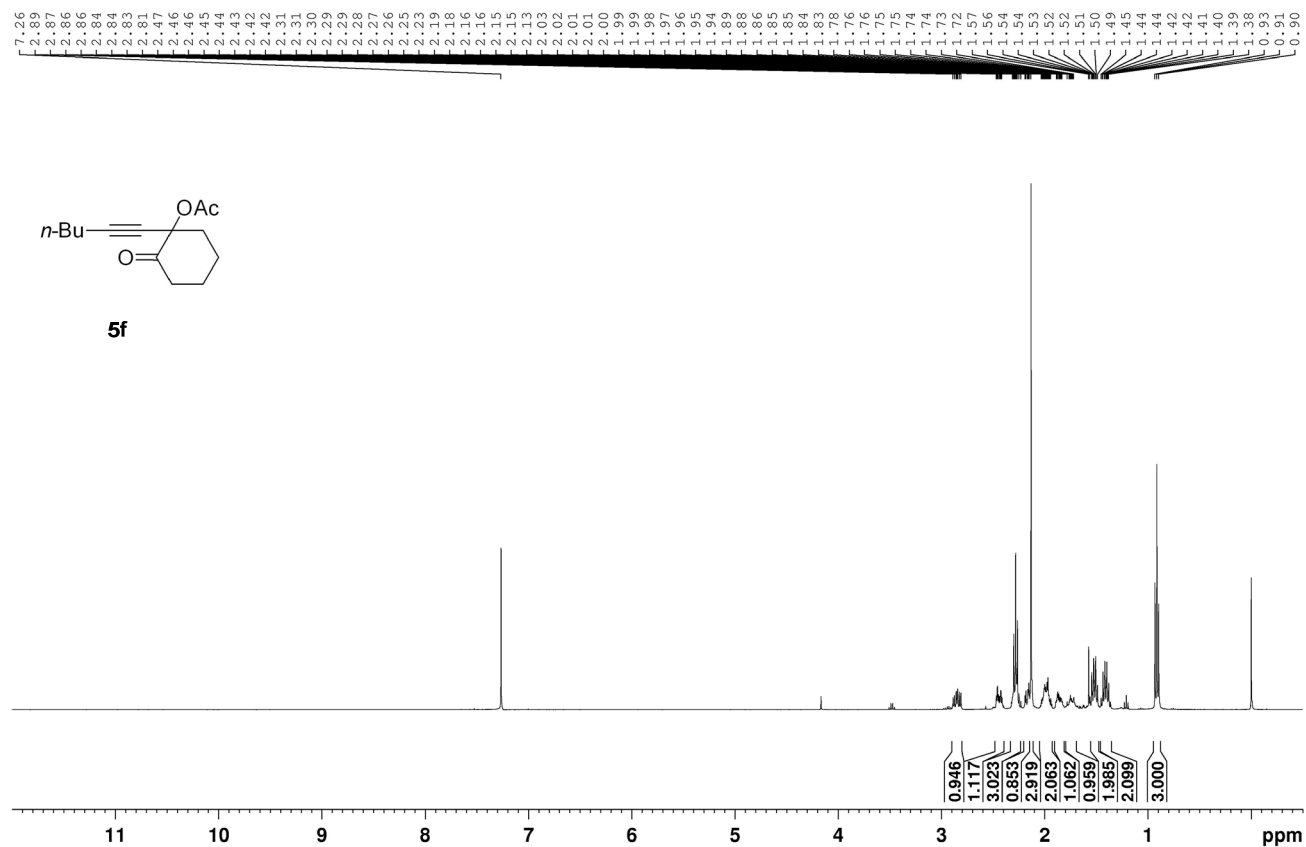


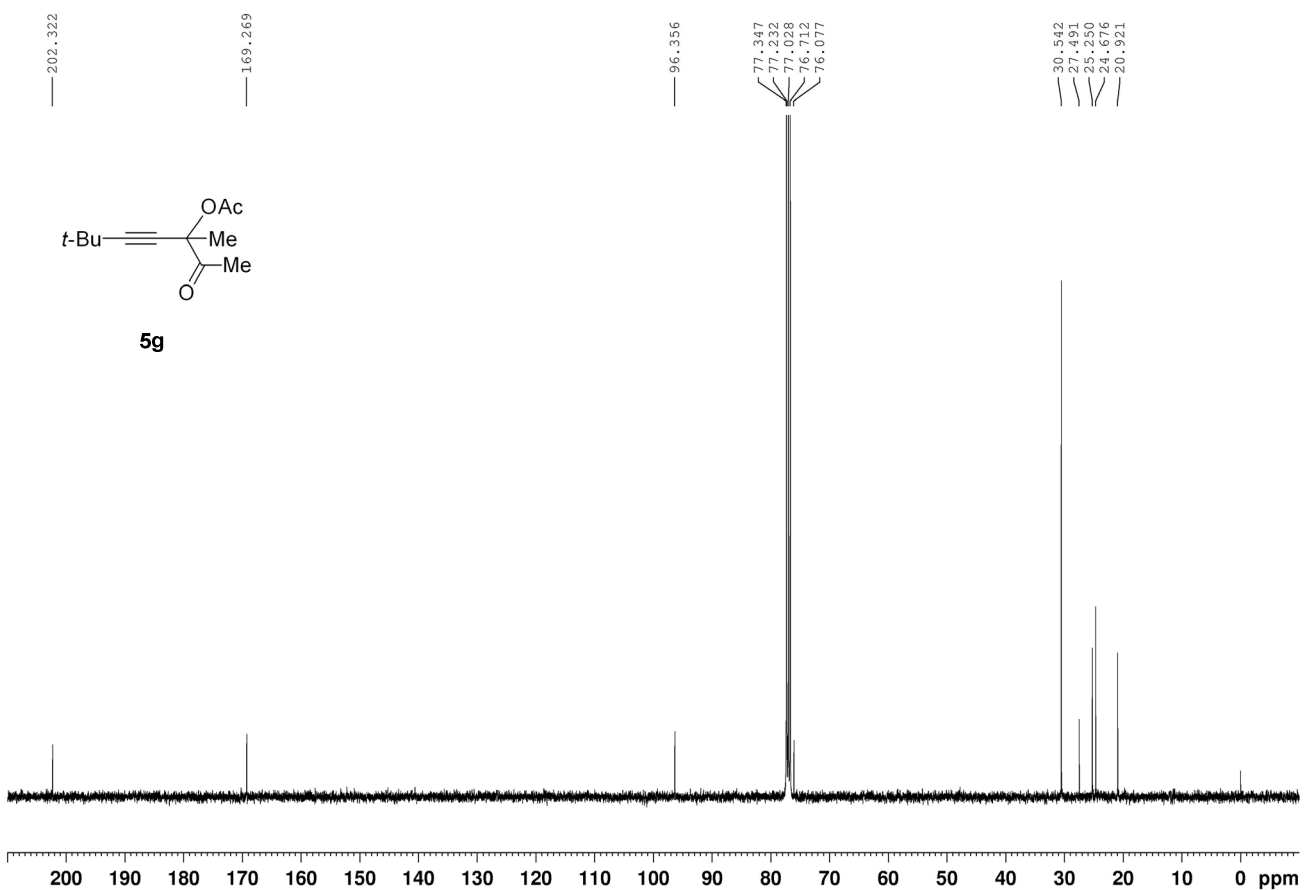
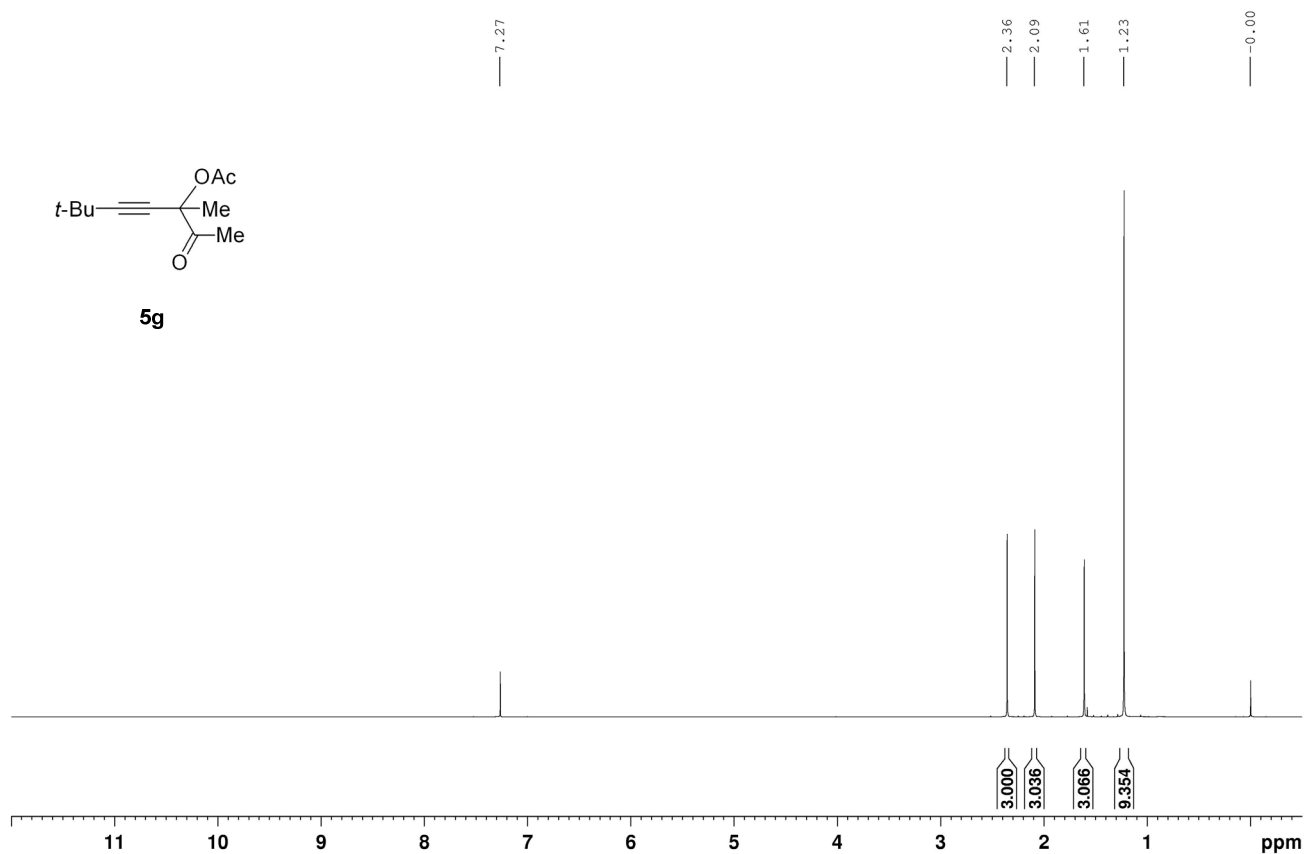


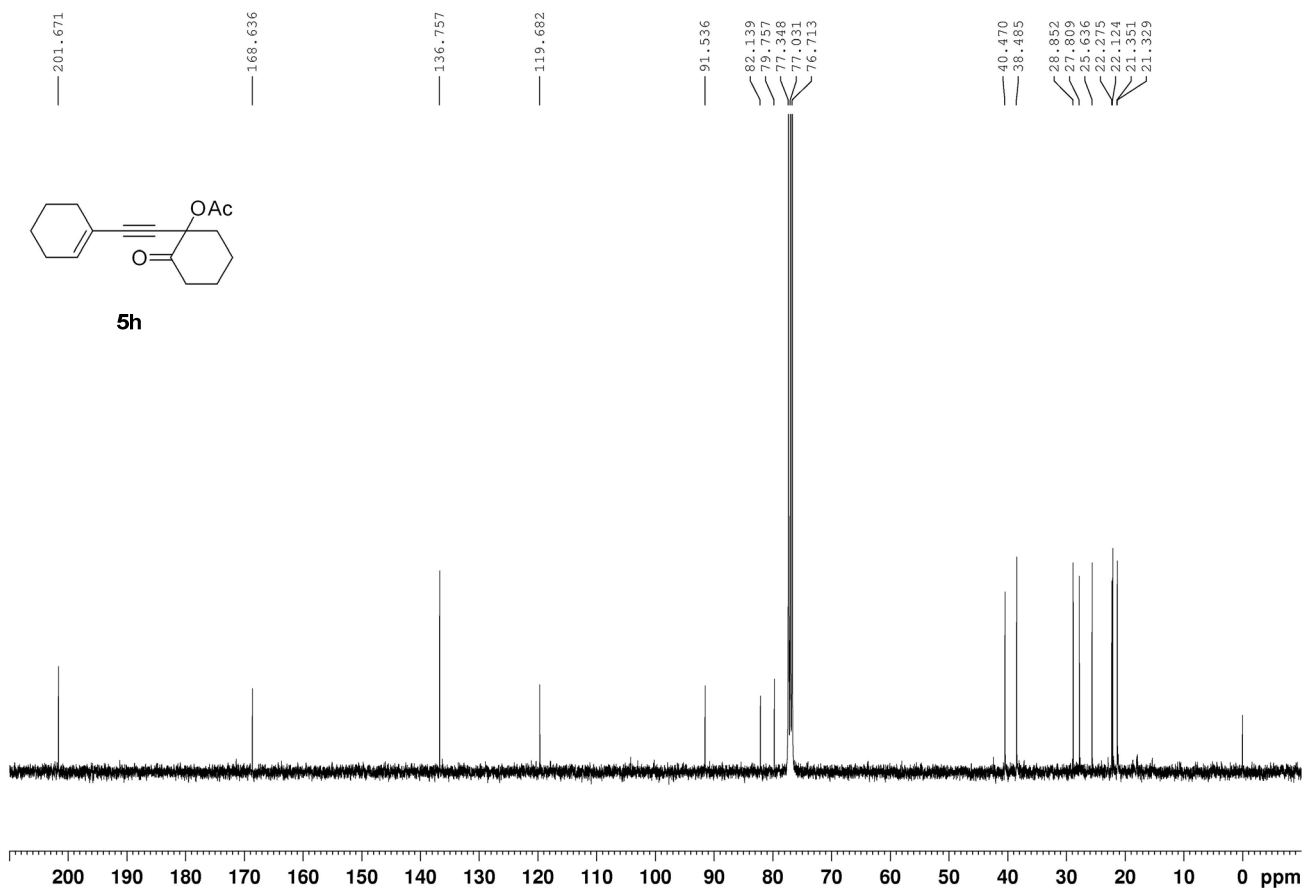
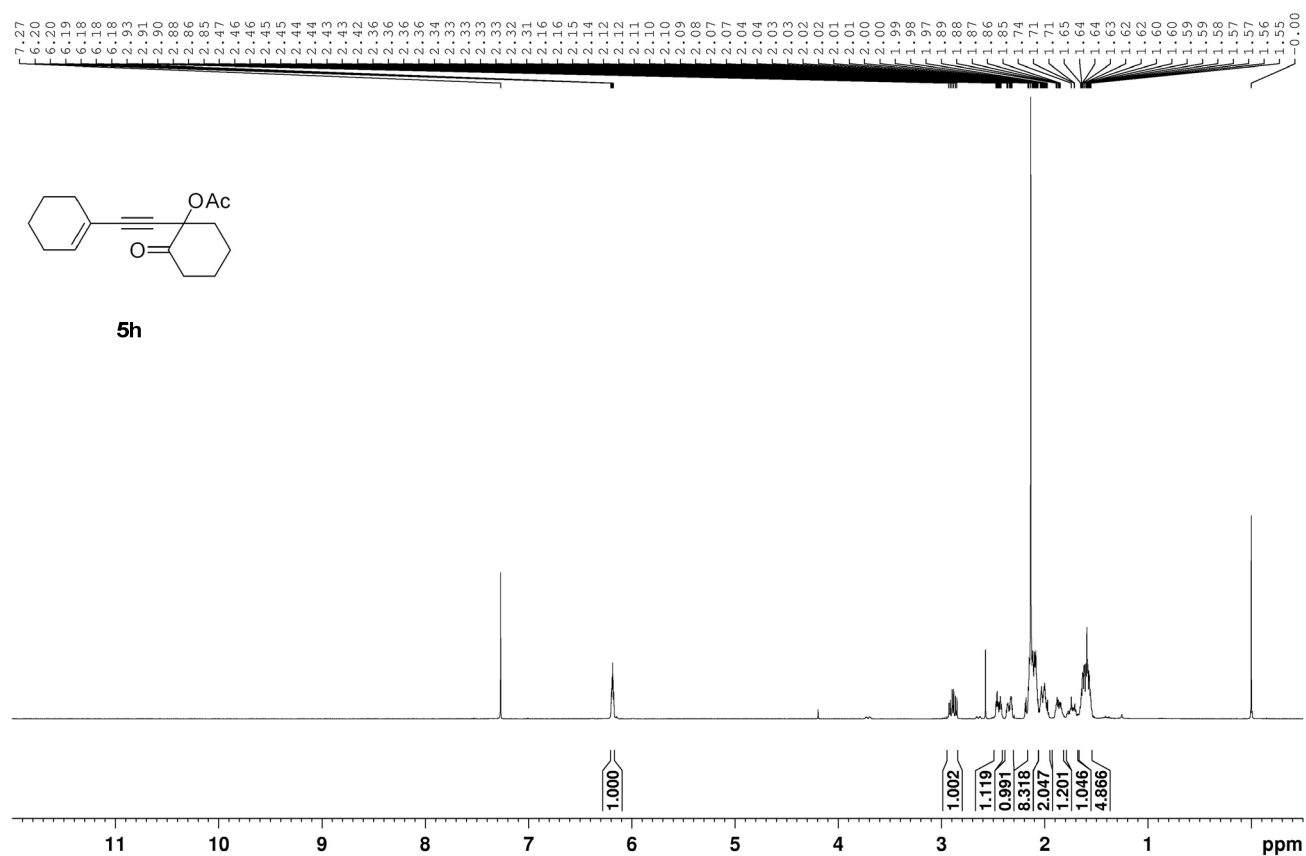


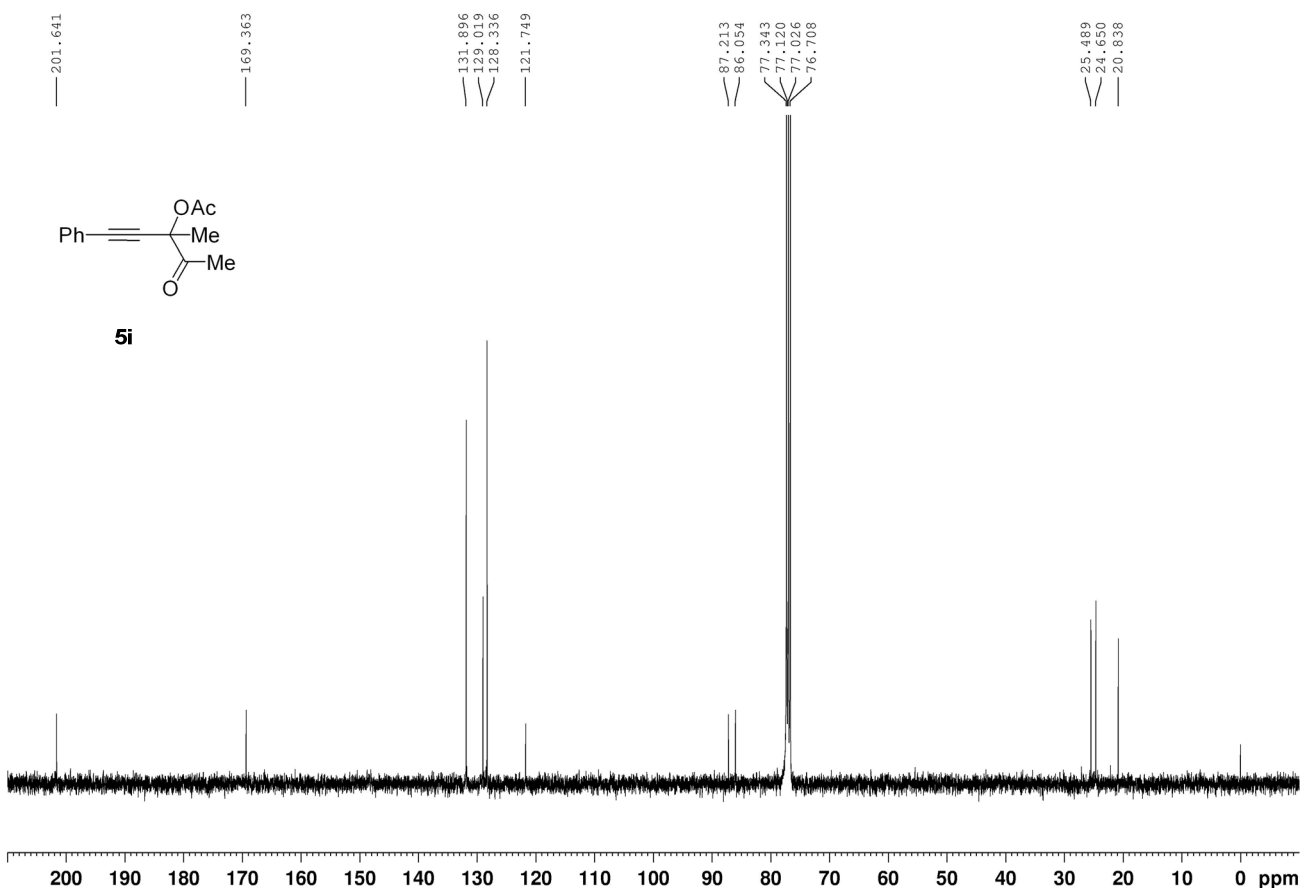
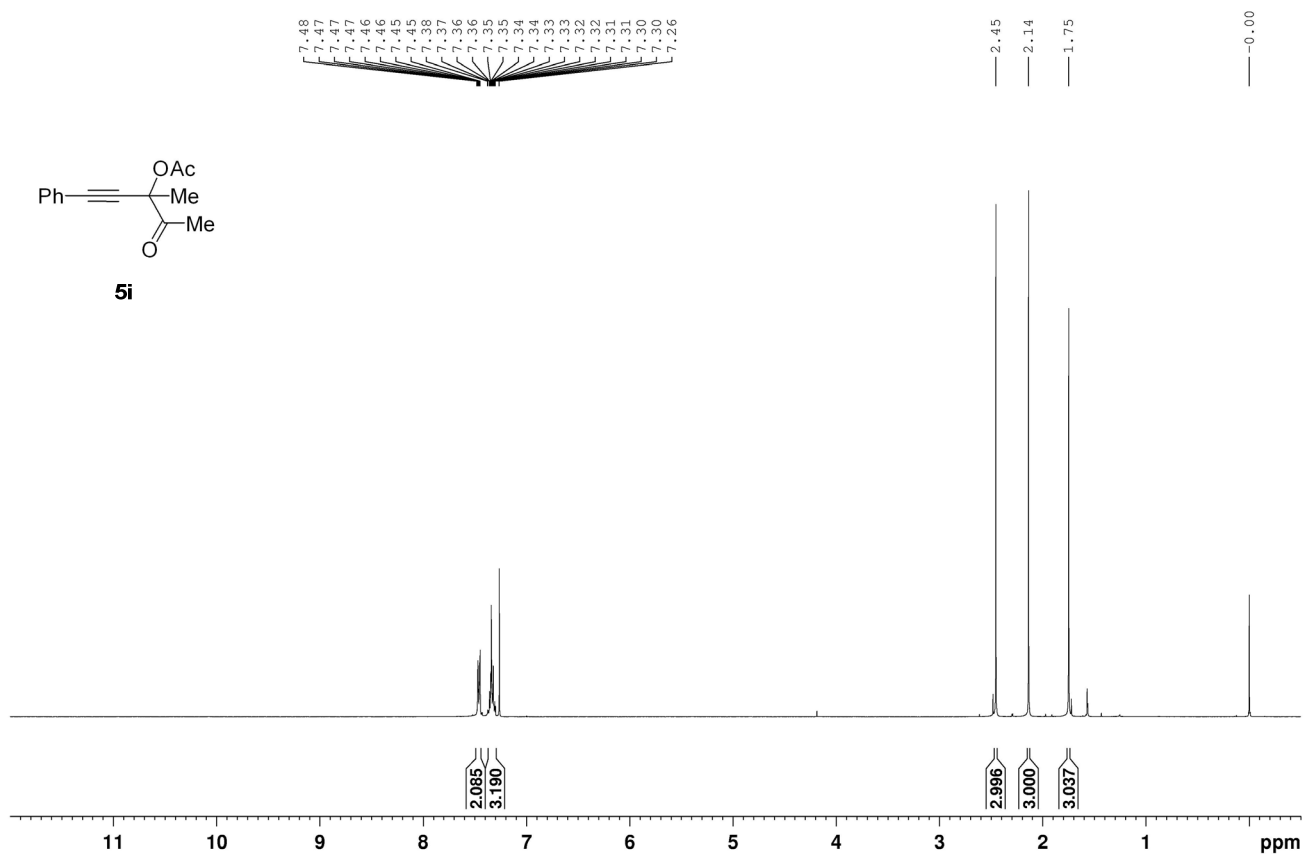


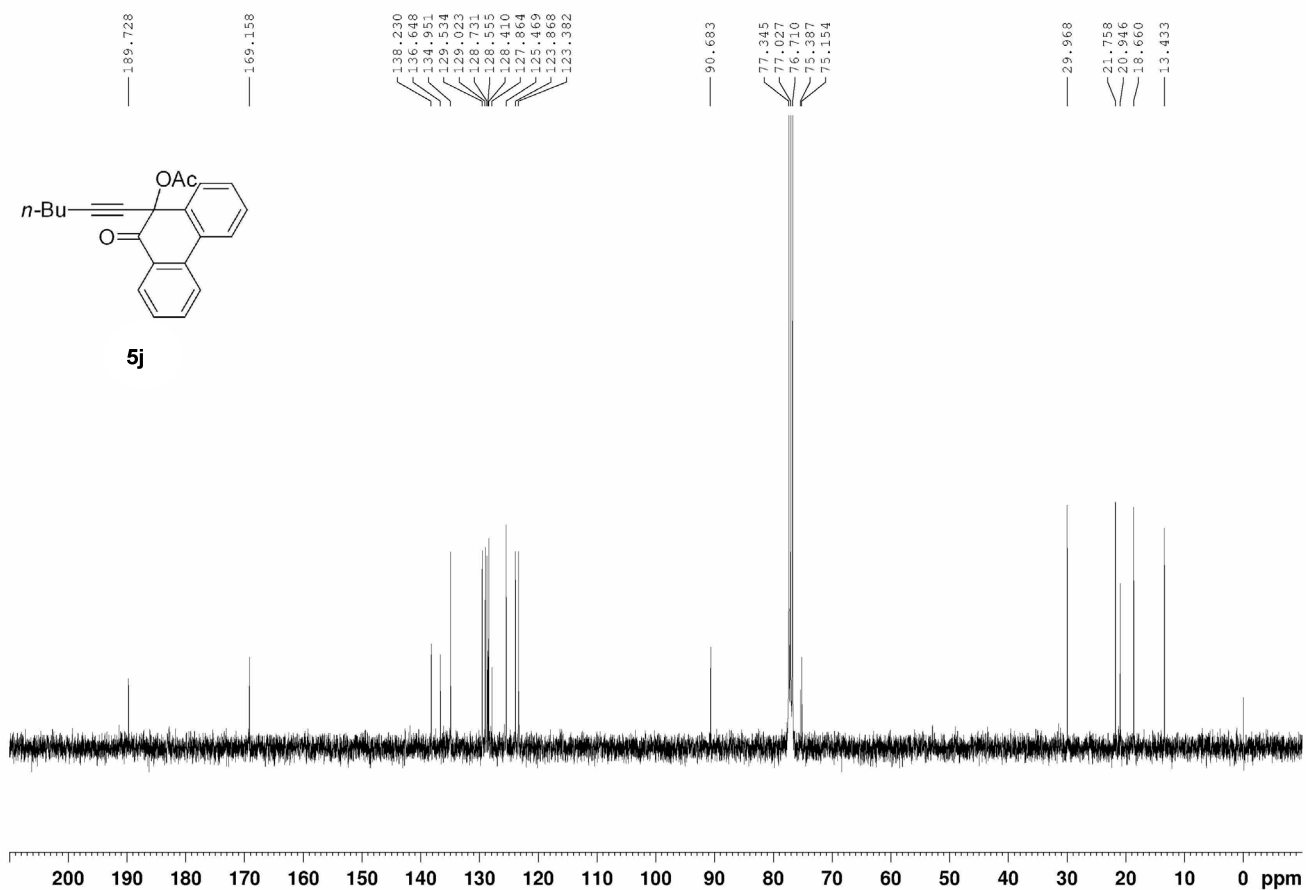
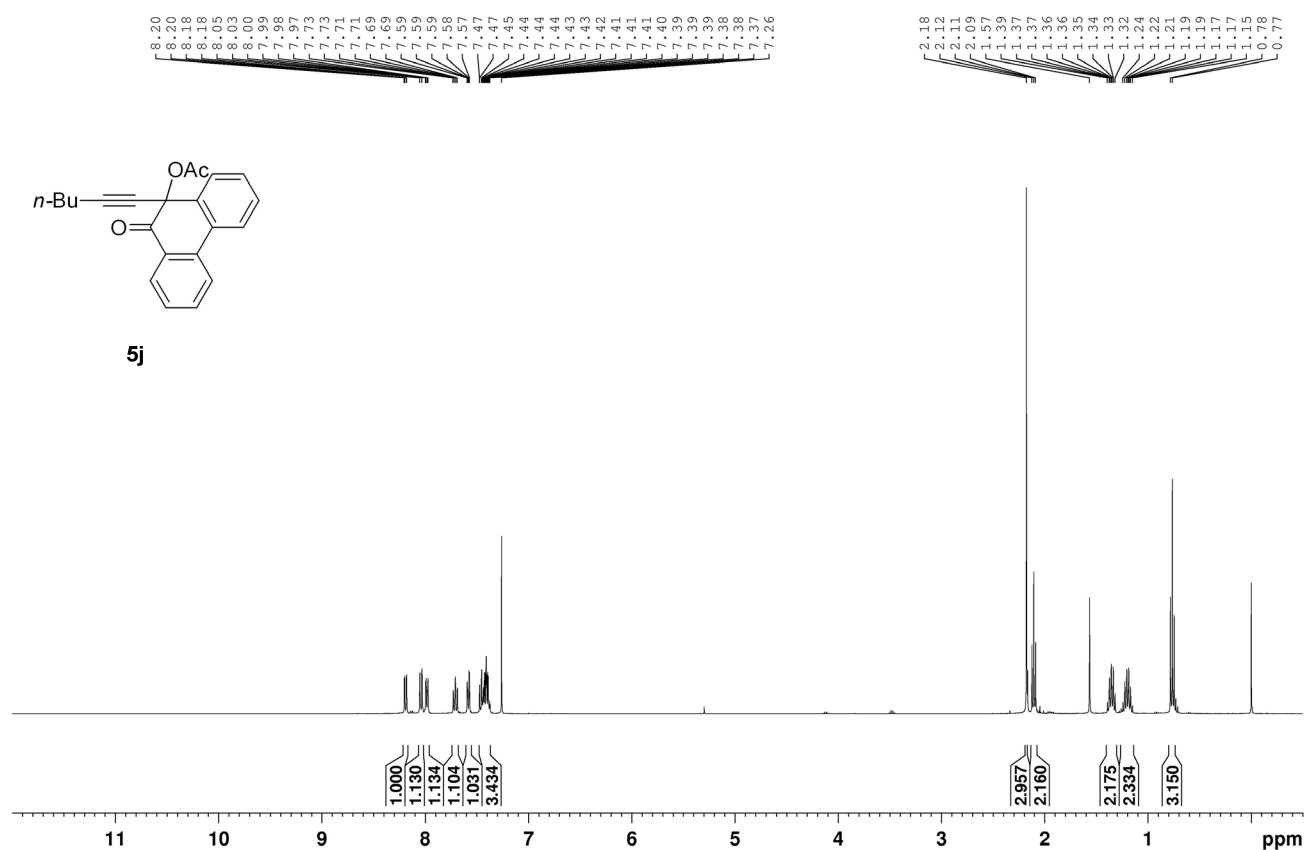


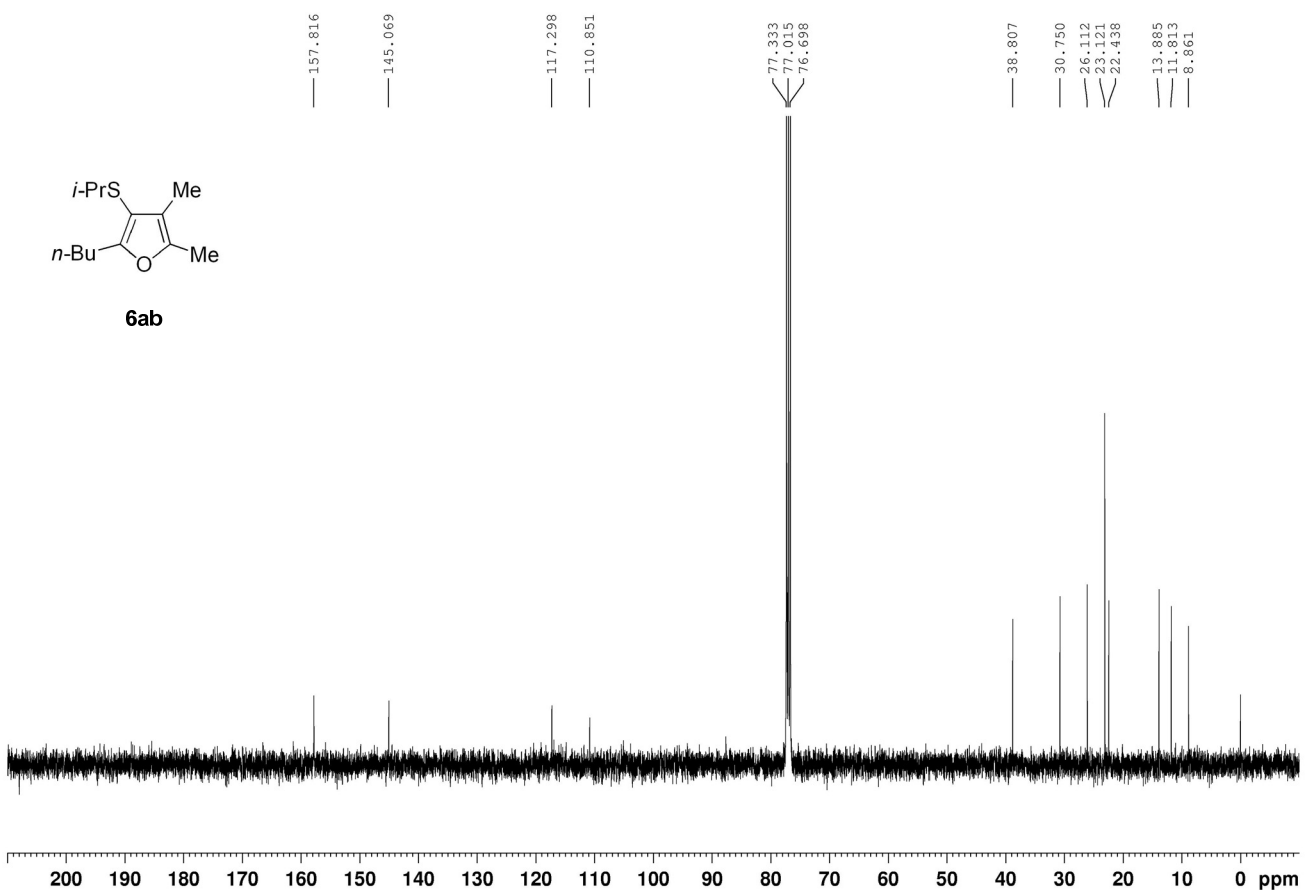
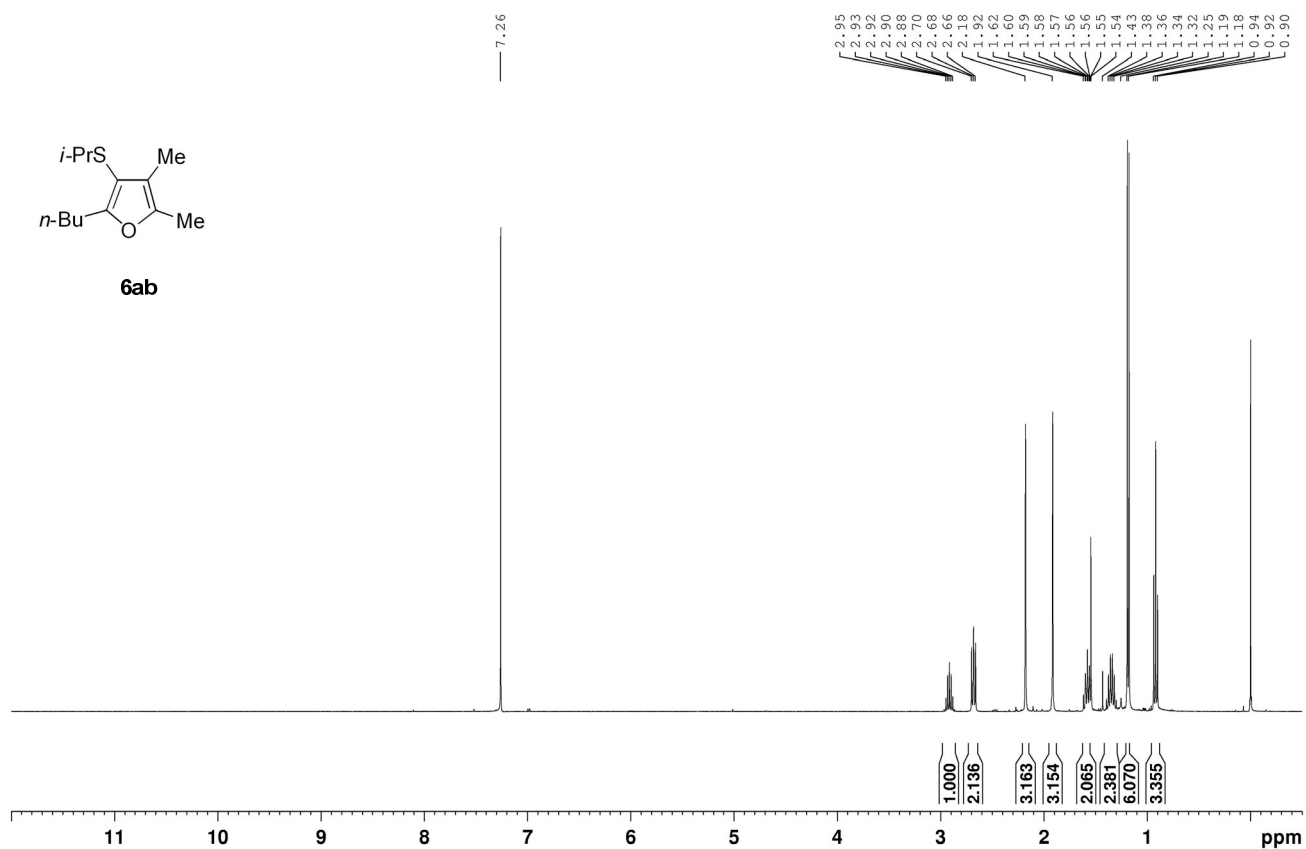


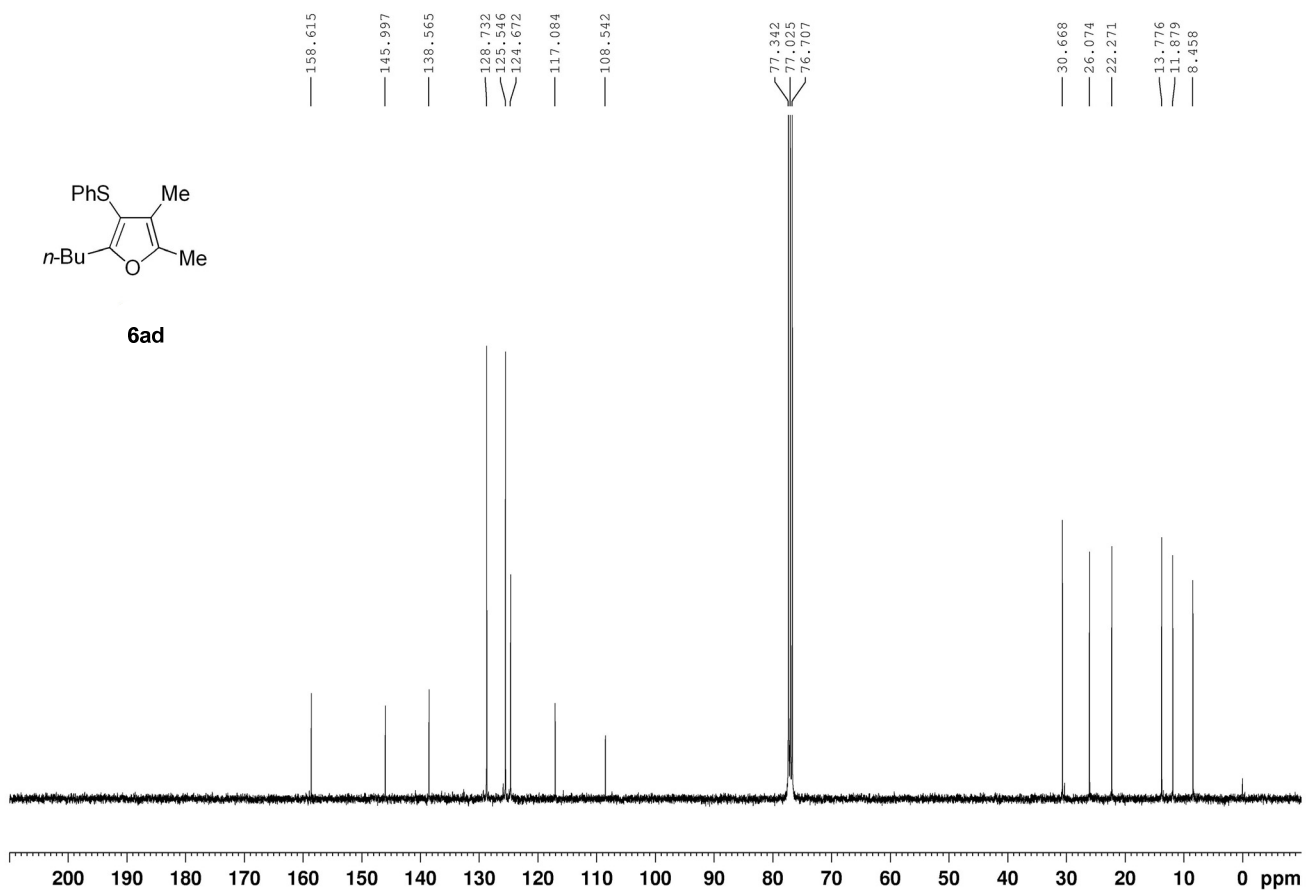
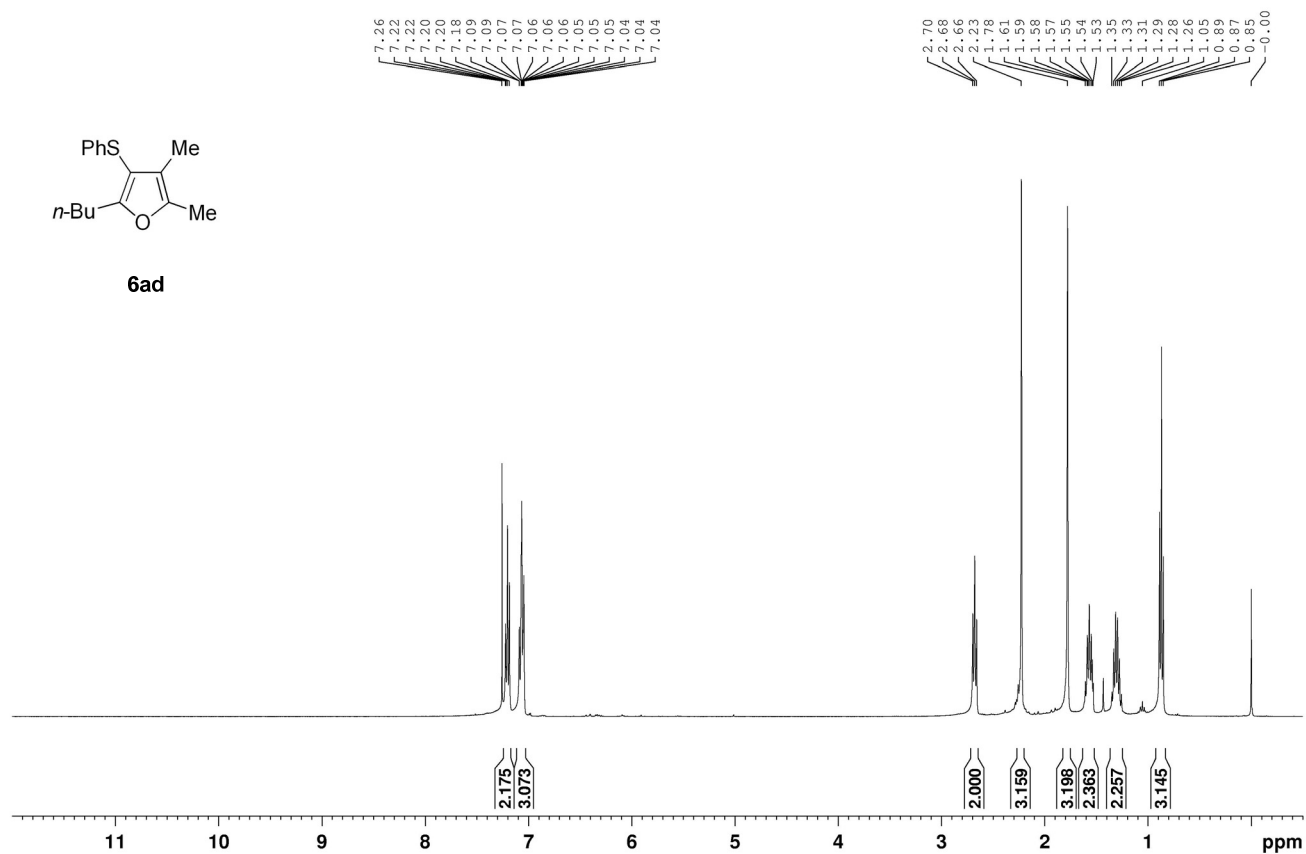


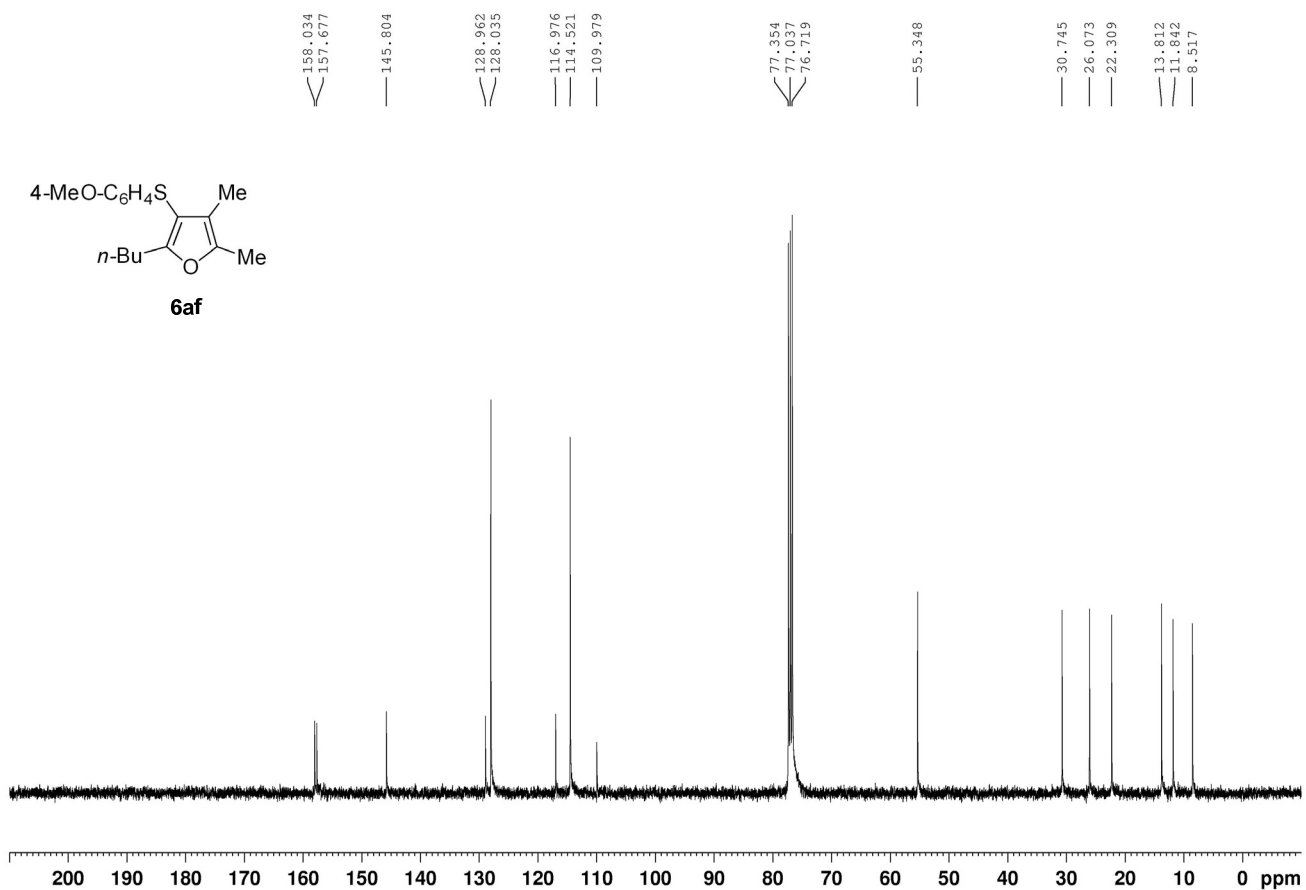
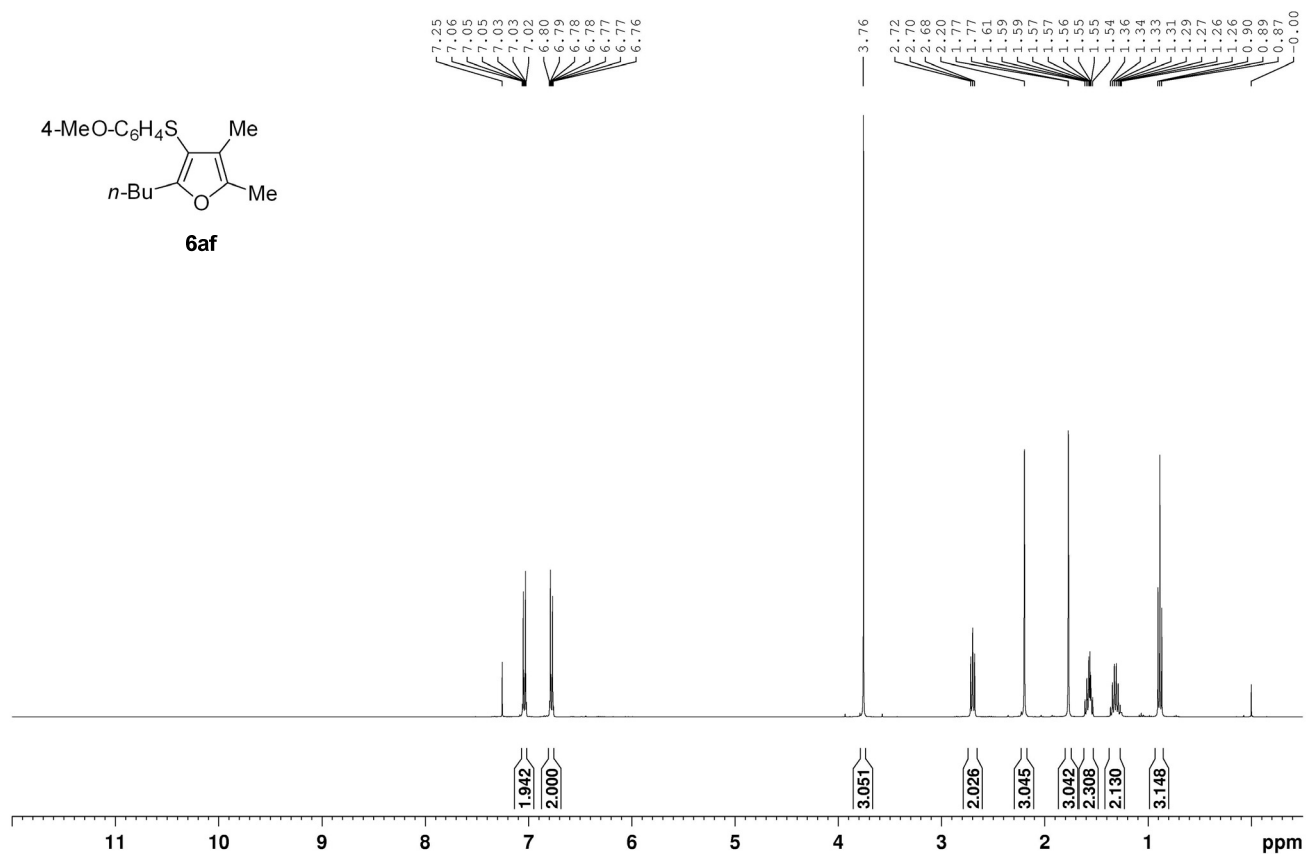


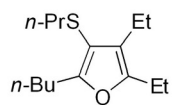




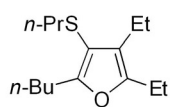
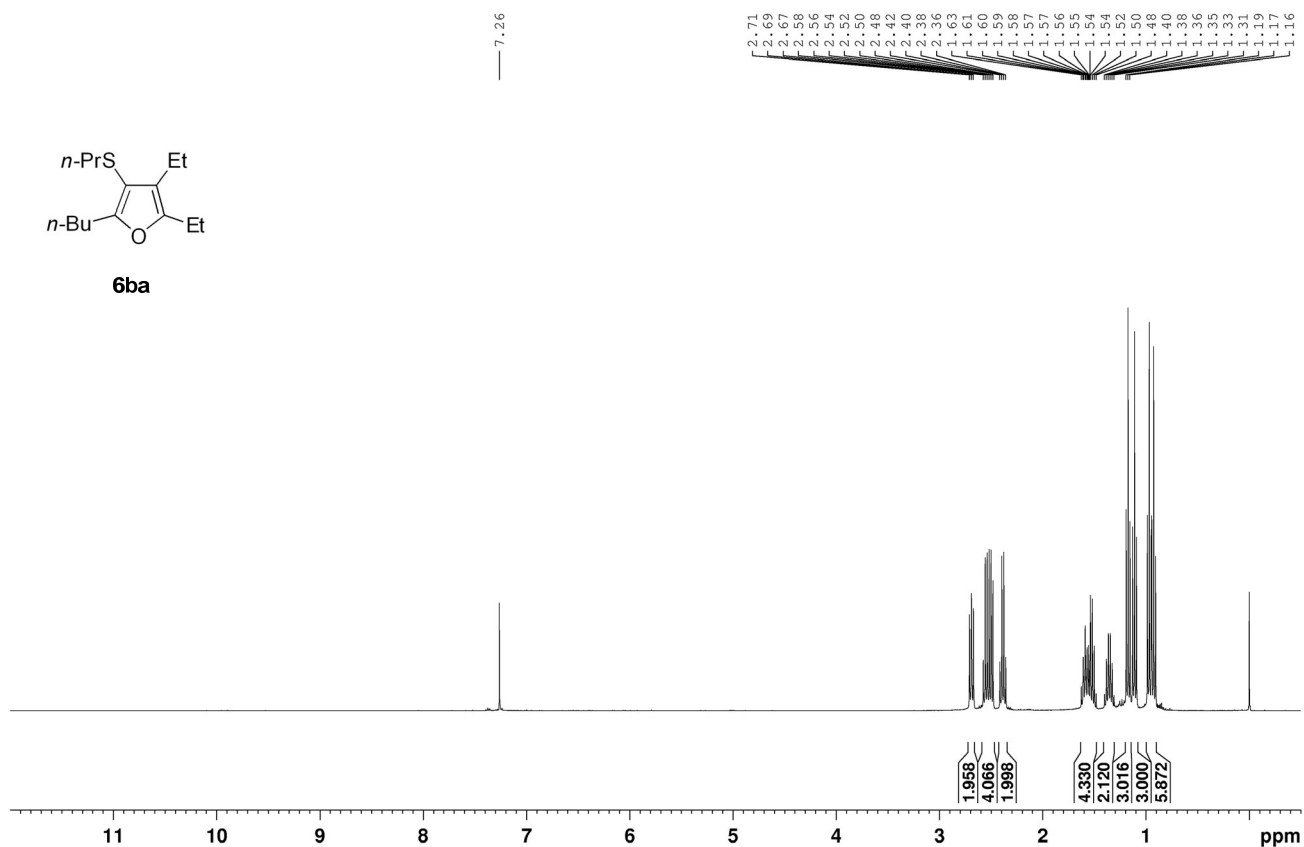








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