Supporting Information

Metal-Catalyzed 1,2-Shift of Diverse Migrating Groups in Allenyl Systems as a New Paradigm Toward Densely Functionalized Heterocycles

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Content

GENERAL INFORMATION

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) and DPX-400 (400 MHz) instruments. GC/MS analyses were performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m × 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Merck silica gel (Kieselgel 60, 63-200 μm), ICN silica gel (ICN SiliTech, 63-200 μm), and SiliCycle silica gel (40-63 μm). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated Silica gel plates (60 F_{254}). Elemental analyses were performed at Midwest Microlabs, Indianapolis, Indiana. HRMS (EI) analysis was performed on a JEOL GCmate II instrument or CONCEPT/EXTREL mass spectrometer.

All manipulations with transition metal catalysts were conducted under inert atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous toluene, tetrahydrofuran, ether, and dichloromethane purchased from Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system. Hexanes and benzene were distilled over sodium prior to use. Triethylamine was stored over calcium hydride prior to use. Triethyl orthoformate was distilled prior to use. Anhydrous DMA, THF, and ether were purchased from Aldrich and additionally stored over calcium hydride prior to use. Bis(triphenylphosphine)dichloropalladium(II)[1] was prepared in our lab. All other chemicals and solvents were purchased from Aldrich, Strem Chemicals Inc., Lancaster Synthesis, Alfa Aesar, and Acros Organics and used without additional purification. Acetals,[2] (4-*t*-butyldimethylsiloxy)-1-pentyn-3-ol[3] and 5-hydroxy-3-hexyn-2-one[4] were prepared using published procedures.

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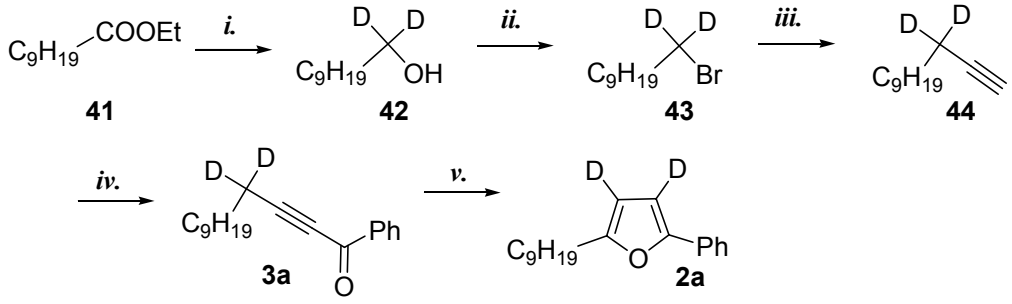
2 D. Bernard, A. Doutheau, J. Gore, *Tetrahedron*, **1987,** *43*, 2721.
3 G. Solladie, C. Hamdouchi, *Synlett*, special 1st issue **1989**, 66.
4 Li, P.; Fong, W. M.; Chao, L. C. F.; Fung, S. H. C.; Williams, I. D. *J. Org. Chem.* **2001**, *66,* 4087.

DEUTERIUM LABELING STUDIES FOR COPPER-CATALYZED SYNTHESIS OF 2,5-DISUBSTITUTED FURAN 2

Synthesis of 4-dideuterio-1-phenyl-2-trisdecyne-1-one:



i. $LiAlD_4$, ether, 78%; ***ii***. PBr_3, pyridine, ether, 86%; ***iii***. Li acetylide-ethylenediamine complex, 27%; ***iv***. $PdCl_2(PPh_3)_2$, CuI, PhCOCl, Et_3N, 80%; ***v***. CuI (5 mol %), Et_3N:DMA (1:7), 100 ^oC, 55% conversion

1-Bromo-1,1-dideuteriodecane **43** was prepared according to literature procedure.[5]

3,3-Dideuteriododec-1-yne (44): Lithium acetylide ethylenediamine complex (690 mg, 7.5 mmol) was added to a 25mL round-bottomed, two-necked flask equipped with a PTFE coated stir bar and rubber septum in a glovebox under nitrogen atmosphere. The flask was then fitted with a condenser and T-shaped stopcock with an argon balloon, and the apparatus was flushed with argon. To the flask were sequentially added: anhydrous DMSO (6 mL) and 1-bromo-1,1-dideuteriodecane **43** (980 mg, 4.39 mmol) in 2 mL of anhydrous THF. The reaction was stirred at 45^{o}C for 2 hours, then cooled, quenched by pouring into a separatory funnel containing cold unsaturated NaCl solution, and extracted two times with ether. The combined organic extracts were washed twice with water, once with brine, and dried over $MgSO_4$. After removal of solvents under reduced pressure, the crude residue was purified by column chromatography on 10 mL silica gel using pentane as eluent to afford 3,3-dideuteriododec-1-yne **44** in 27 % yield (210 mg, 1.18 mmol). NMR spectra are in accord with described data.[5]

1-Phenyl-4,4-dideuterio-trisdec-2-yn-1-one (3a): In a glovebox under nitrogen atmosphere to a 3 mL Wheaton microreactor equipped with a PTFE coated spin vane and an open-top phenolic cap with a PTFE faced silicone septum were sequentially added: $PdCl_2(PPh_3)_2$ (1.1 mg, 1.6 μmol) and CuI (1.1 mg, 5.8 μmol). To the microreactor while stirring were sequentially added: anhydrous Et_3N (2.0 mL), 3,3-dideuteriododec-1-yne **44** (220 mg, 1.24 mmol), and benzoyl chloride (197 μL, 239 mg, 1.7 mmol). The reaction was stirred for 26 hours at room temperature. Upon completion, the reaction mixture was poured into a separatory funnel containing saturated NH_4Cl solution (30 mL) and extracted twice with ether (20 mL). The combined organic extracts were dried over $MgSO_4$, concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel using 1:20 EtOAc:hexanes as eluent to afford 1-phenyl-4,4-dideuterio-trisdec-2-yn-1-one **3a** as a yellow oil in 80% yield (269 mg, 0.95 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ ppm 8.12 (2 H, d, J = 7.34 Hz), 7.57 (1 H, t, J = 7.43 Hz), 7.45 (2 H, t, J = 7.70 Hz), 1.63 (2 H, d, J = 7.89 Hz), 1.44 (2 H, d, J = 7.70 Hz), 1.35 -

[5] Kel'in, A. V.; Sromek, A. W.; Gevorgyan, V. *J. Am. Chem. Soc.* **2001**, *123*, 2074.

1.19 (12 H, m), 0.86 (3 H, t, J = 6.88 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 178.01, 136.79, 133.70, 129.38 (2 C), 128.32 (2 C), 96.67, 79.57, 31.76, 29.42, 29.35, 29.19, 28.94, 28.78, 27.50, 22.55, 18.51 (1 C, quint, J_{CD} = 20 Hz), 13.98. ^{2}H NMR (77 MHz, $CDCl_3$) δ ppm 2.20 (2 D). GC/MS *m/z*: 271 (M^+ - H; 4); 105 (PhCO, 100).

Determination of extent of deuterium scrambling of 1-Phenyl-4,4-dideuterio-trisdec-2-yn-1-one (3a) in cycloisomerization reaction:

In a glovebox, under nitrogen atmosphere, to a 1 mL Wheaton microreactor equipped with a PTFE coated spin vane and an open phenolic cap with a PTFE faced silicone septum was added CuI (1 mg, 0.01 mmol). To the microreactor were sequentially added: anhydrous DMA (440 μL), anhydrous Et_3N (60 μL), and 4,4-dideuterio-trisdec-2-yn-1-one **3a** (56 mg). The open-top cap with septum was replaced with a Mininert valve and the reaction was stirred at 100 ^{o}C until judged to be 50% complete by GC analysis. The cooled reaction mixture was poured into water (10 mL) and extracted three times with hexanes (5 mL each). The combined extracts were dried over Na_2SO_4, concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel using 1:20 to 1:5 EtOAc:hexanes eluent gradient to afford partially deuterated 2-nonyl-5-phenylfuran **2a** (12 mg, 21%) and 4,4-dideuterio-trisdec-2-yn-1-one **3a** (**3b)** (31 mg, 55%). ^{1}H and ^{2}H NMR analysis indicated no loss of the deuterium purity in alkynone **3b**.

2-nonyl-5-phenylfuran (2a):

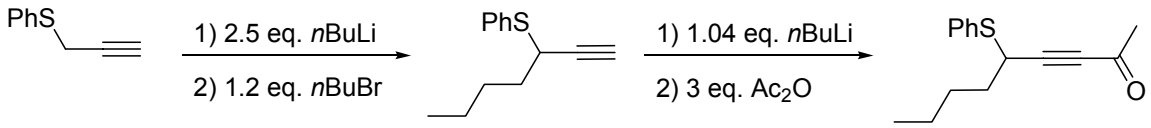
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.64 (2 H, d, J = 7.70 Hz), 7.36 (2 H, t, J = 7.70 Hz), 7.22 (1 H, t, J = 7.43 Hz) 6.55 (0.08 H, s) 6.06 (0.23 H, s) 2.68 (2 H, t, J = 7.52 Hz) 1.70 (2 H, quint, J = 7.24 Hz) 1.22 - 1.43 (12 H, m) 0.89 (3 H, t, J = 6.69 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 156.40, 151.96, 131.24, 128.55 (2 C), 126.64, 123.27 (2 C), 106.71, 31.89, 29.53, 29.39, 29.32, 29.21, 28.16, 28.10, 22.68, 14.12. GC/MS *m/z*: 272 (M^+, 19); 159 (M^+ - C_8H_{17}; 100).

4,4-dideuterio-trisdec-2-yn-1-one (3b):

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.14 (2 H, d, J = 7.34 Hz) 7.60 (1 H, t, J = 7.34 Hz) 7.48 (2 H, t, J = 7.70 Hz) 1.66 (2 H, s) 1.52 - 1.43 (2 H, m) 1.21 - 1.38 (12 H, m) 0.88 (3 H, t, J = 6.97 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 178.22, 136.89, 133.82, 129.51 (2 C), 128.43 (2 C), 96.87, 79.67, 31.86, 29.52, 29.44, 29.28, 29.03, 28.89, 27.60, 22.65, 18.64 (1 C, quint, J_{CD} = 20 Hz), 14.09. ^{2}H NMR (77 MHz, $CDCl_3$) δ ppm 2.20 (2 D). GC/MS *m/z*: 271 (M^+ - H; 4); 105 (PhCO, 100).

1,2-SULFUR MIGRATION

Preparation of Starting Materials

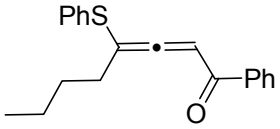


Representative procedure of propynyl ketone: *n*BuLi (52 mL, 130 mmol; 2.5 M in hexanes) was added dropwise to a solution of phenyl propargyl sulfide (7.78 g, 52.50 mmol) in anhydrous THF (100 mL) at -78 ^{o}C. The resulting mixture was warmed up to RT and stirred for 1h. After this period, the mixture was cooled to -78 ^{o}C and *n*BuBr (6.77 mL, 63.04 mmol) was added dropwise. The resulting mixture was stirred at -78 ^{o}C for 2h and warmed up to RT before quenching with saturated aqueous NH_4Cl (50 mL). The phases were separated and the aqueous phase was thoroughly extracted with EtOAc (2 x 50 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4 (10 g), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with hexanes to give (1-butyl-prop-2-ynylsulfanyl)-benzene **45** (10.17 g, 95 %).

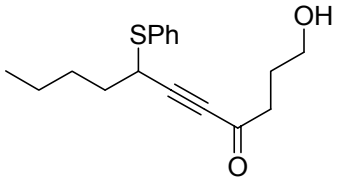
*n*BuLi (2.1 mL, 5.25 mmol; 2.5 M in hexanes) was added dropwise to a solution of (1-butyl-prop-2-ynylsulfanyl)-benzene **45** (1.0 g, 5.04 mmol) in anhydrous THF (10 mL) at -78 ^{o}C. The resulting mixture was warmed up to RT and stirred for 30 min. After this period, the mixture was cooled to -78 ^{o}C and transferred via cannula to acetic anhydride (1.42 mL, 15.12 mmol) in THF (10 mL) at -78 ^{o}C. The resulting mixture was stirred at -78 ^{o}C for 1h and warmed up to RT before quenching with saturated aqueous NH_4Cl (20 mL). The phases were separated and the aqueous phase was thoroughly extracted with EtOAc (2 x 20 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 (5 g), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with 1 % EtOAc/hexanes to give **12b** (1.09 g, 88 %).

Representative procedure of propynyl imine: *n*BuLi (1.6 mL, 4.0 mmol; 2.5 M in hexanes) dropwise was added to a solution of (1-Butyl-prop-2-ynylsulfanyl)-benzene **45** (690 mg, 3.38 mmol) in anhydrous Et_2O (15 mL) at -78 ^{o}C. The resulting mixture was stirred at -78 ^{o}C for 10 min and anhydrous DMF (390 μL, 5.0 mmol) was added. After stirring at -78 ^{o}C for 10 min, the mixture was transferred via cannula to the mixture of 85 % H_3PO_4 (1.0 g), H_2O (20 mL), and ice (2g). The resulting mixture was stirred at RT under argon atmosphere for 1h. After this period, the phases were separated and the aqueous phase was thoroughly extracted with hexanes (2 x 10 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 (2 g), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with 5% EtOAc/hexanes to give 1-phenylsulfanyl-oct-2-ynal **12d** (590 mg, 75 % yield).

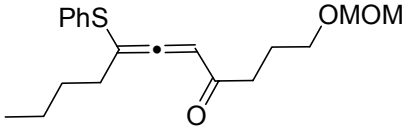
Powdered 4 A molecular sieves (500 mg), *t*-butyl amine (203 μL, 1.93 mmol), and SiO_2 (500 mg) were sequentially added to a solution of 1-phenylsulfanyl-oct-2-ynal (449 mg, 1.93 mmol) in anhydrous CCl_4. The resulting mixture was stirred at RT for 40 min and filtered quickly through a cotton plug. The filtrate was concentrated to give **12i** in quantitative yield with excellent purity.



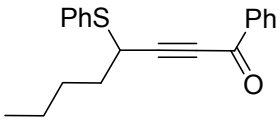
13a : 1-Phenyl-4-phenylthio-octa-2,3-dienone was made using a known procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.25 (m, 10H), 6.27 (t, 1H, J = 2.8 Hz), 2.26 (quint, 2H, J = 2.7 Hz), 1.50-1.49 (m, 2H), 1.29-1.24 (m, 2H), 0.84 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.5, 191.8, 137.7, 132.6, 132.0, 129.1, 128.7, 128.3, 127.8, 126.3, 106.3, 95.6, 32.3, 29.7, 21.9, 13.7.



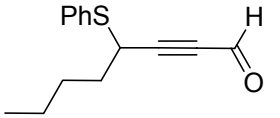
46 : To a 25 mL, round-bottomed, 2-necked flask, equipped with a PTFE coated stir bar, rubber septum, and three way stopcock with an argon balloon, were sequentially added: 3-phenylthio-1-heptyne **45** (870 mg, 4.26 mmol) and anhydrous ether (10 mL). The solution was allowed to cool to -78 ^{o}C, and *n*-butyllithium was added dropwise (1.9 mL, 4.75 mmol, 2.5 M solution in hexanes). The resulting mixture was allowed to stir at room temperature for one hour and then cooled to -78 ^{o}C, and butyrolactone was added dropwise (393 μL, 5.11 mmol). The mixture was allowed to return to room temperature, quenched with saturated ammonium chloride solution, extracted with ethyl actetate, dried over sodium sulfate, and concentrated under reduced pressure to afford 4-oxo-7-phenylthio-undec-5-yn-1-ol **46** in 68% yield (843 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.50 (2 H, dd, *J* = 7.43, 1.74 Hz) 7.27 - 7.36 (3 H, m) 3.87 (1 H, t, *J* = 7.15 Hz) 3.58 (2 H, t, *J* = 6.24 Hz) 2.57 (2 H, t, *J* = 7.15 Hz) 1.76 - 1.84 (4 H, m) 1.51 (2 H, s) 1.28 - 1.38 (2 H, m) 0.90 (3 H, t, *J* = 7.34 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 187.45, 133.36 (2 C), 132.79, 128.90 (2 C), 128.21, 92.51, 83.07, 61.54, 42.08, 38.53, 33.91, 29.18, 26.63, 22.02, 13.74.



13p: Under argon atmosphere, to a 50 mL round-bottomed, two neck flask, was sequentially added: 4-oxo-7-phenylthio-undec-5-yn-1-ol **46** (494 mg, 1.7 mmol), anhydrous dichloromethane (7 mL), Hunig's base (6.0 mL, 34.44 mmol), and methoxymethyl chloride (1.8 mL, 17.12 mmol). The mixture was allowed to stir at room temperature for 16 hours. The reaction was quenched with saturated ammonium chloride solution, the aqueous phase was extracted with dichloromethane, the combined organic extracts were dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified over silica gel using 5% ethyl acetate to hexanes as eluent to afford the phenylthioallenone **13p** in 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.26 (m, 5H), 5.68 (t, 1H, J = 2.9 Hz), 4.60 (s, 2H), 3.49 (t, 2H, J = 6.4 Hz), 3.35 (s, 3H), 2.56-2.46 (m, 2H), 2.30 (dt, 2H, J = 7.2 Hz, 2.9 Hz), 1.83-1.78 (m, 2H), 1.55 (quint, 2H, J = 7.3 Hz), 1.37 (sext, 2H, J = 7.4 Hz), 0.90 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 200.4, 133.5, 132.4, 129.5, 128.8, 108.3, 99.3, 96.7, 67.1, 55.5, 36.3, 32.8, 30.3, 24.6, 22.5, 14.1.

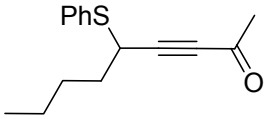


12a : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94-7.34 (m, 10H), 4.05 (t, 1H, J = 7.2 Hz), 1.92 (q, 2H, J = 7.8 Hz), 1.65-1.60 (m, 2H), 1.42-1.37 (m, 2H), 0.95 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 137.1, 134.4, 133.8, 130.0, 129.5, 129.2, 128.9, 128.7, 94.9, 82.5, 39.3, 34.5, 29.8, 22.6, 14.4; MS *m/z* (relative intensity) 308 (M^+, 59), 265 (100).

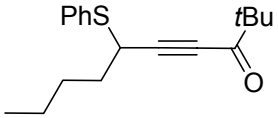


12d : ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.56-7.29 (m, 5H), 3.90 (t, 1H, J = 7.1 Hz), 1.86-1.83 (m, 2H), 1.58-1.55 (2H), 1.40-1.35 (m, 2H),

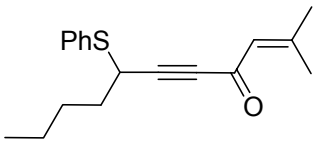
0.94 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1, 134.0, 133.0, 129.5, 128.9, 97.3, 84.1, 39.1, 34.4, 29.7, 22.5, 14.3; MS *m/z* (relative intensity) 232 (M^+, 27), 189 (55), 110 (100).



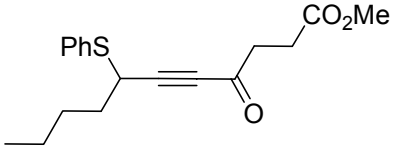
12b : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.33 (m, 5H), 3.86 (t, 1H, J = 7.2 Hz), 2.25 (s, 3H), 1.83-1.77 (m, 2H), 1.55-1.49 (m, 2H), 1.37-1.31 (m, 2H), 0.91 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4, 133.7, 132.8, 129.0. 128. 4, 91.9, 83.8, 38.7, 34.0, 32.8, 29.3, 22.1, 13.9; MS *m/z* (relative intensity) 246 (M^+, 35), 203 (70), 110 (100).



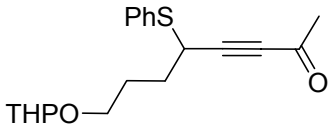
12c : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.26 (m, 5H), 3.93 (t, 1H, J = 6.7 Hz), 1.86-1.82 (m, 2H), 1.59-1.52 (m, 2H), 1.39-1.36 (m, 2H), 1.10 (s, 9H), 0.91 (t, 3H, J = 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.3, 135.4, 133.5, 129.4, 128.5, 93.8, 81.6, 45.1, 39.1, 34.5, 29.7, 26.3, 22.6, 14.3; MS *m/z* (relative intensity) 288 (M^+, 13), 231 (40)), 57 (100).



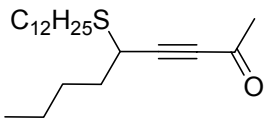
12e : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.24 (m, 5H), 5.96 (t, 1H, J = 1.1 Hz) 3.83 (t, 1H, J = 7.1 Hz), 2.1 (s, 3H), 1.82 (s, 3H), 1.75 (q, 2H, J = 7.8 Hz), 1.54-1.42 (m, 2H), 1.28 (sext, 2H, J = 7.4 Hz), 0.85 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 157.9, 133.4, 133.0, 128.9, 128.1, 125.9, 90.2, 85.7, 38.7, 34.1, 29.3, 27.8, 22.1, 21.0, 13.9; MS *m/z* (relative intensity) 286 (M^+, 7), 215 (21), 83 (100).



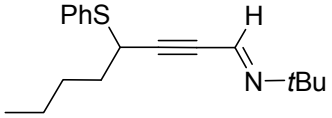
12f : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.32 (m, 5H), 3.96 (q, 1H, 7.0 Hz), 3.65 (s, 3H), 2.77 (t, 2H, J = 6.7 Hz), 2.55 (t, 2H, J = 6.7 Hz), 5.23 (d, 3H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 172.4, 133.8, 132.4, 129.0, 128.6, 93.4, 82.0, 51.9, 40.0, 33.1, 27.6, 20.6; MS *m/z* (relative intensity) 276 (M^+, 17), 161 (87), 115 (100).



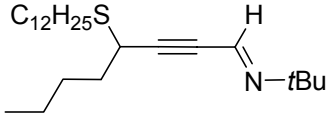
12g : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.26 (m, 5H), 4.55 (t, 1H, J = 4.0 Hz), 3.92 (t, 1H, J = 7.2 Hz), 3.78-3.74 (m, 2H), 3.49-3.39 (m, 2H), 2.24 (s, 3H), 1.90-1.50 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3, 133.8, 132.5, 129.0, 128.5, 98.8, 91.5, 83,9, 66.4, 62.3, 38.5, 32.8, 31.3, 30.6, 27.3, 25.4, 19.5; ; MS *m/z* (relative intensity) 248 (-THP, 43), 109 (25), 85 (100).



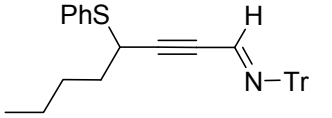
12h : ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.58 (t, 1H, J = 7.6 Hz), 2.75-2.62 (m, 2H), 1.78-1.75 (m, 2H), 1.61-1.47 (m, 5H), 1.38-1.25 (m, 22H), 0.91 (t, 3H, J = 7.3 Hz), 0.87 (t, 3H, J = 7.1 Hz);); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.8, 92.7, 83.4, 34.7, 34.6, 32.3, 31.8, 30.0 (x2), 29.9, 29.8 (x2), 29.6, 29.3, 23.1, 22.6, 14.5, 14.3; MS *m/z* (relative intensity) 338 (M^+, 5), 201 (90), 138 (100).



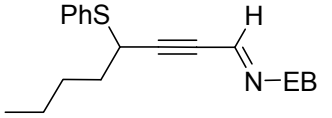
12i : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.28 (m, 6H), 3.91 (dt, 1H, J = 7.7 Hz, 1.4 Hz), 1.82-1.79 (m, 2H), 1.57-1.52 (m, 2H), 1.35-1.32 (m, 2H), 1.21 (s, 9H), 0.90 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 134.3, 133.0, 129.3, 128.1, 99.0, 92.5, 82.6, 59.2, 39.5, 35.0, 29.7, 22.6, 14.3; MS *m/z* (relative intensity) 287 (M^+, 6), 188 (60), 57 (100).



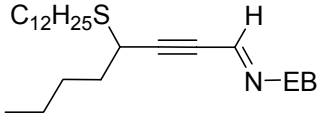
12j : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 3.60 (dt, 1H, J = 7.7 Hz, 1.3 Hz), 2.75-2.62 (m, 2H), 1.78-1.73 (m, 2H), 1.61-1.49 (m, 4H), 1.37-1.24 (m, 20H), 1.20 (s, 9H), 0.91-0.85 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 93.0, 81.7, 59.2, 35.4, 35.1, 32.3, 31.8, 30.0 (x2), 29.8 (x2), 29.7 (x2), 29.4, 23.1, 22.7, 14.5, 14.3; MS *m/z* (relative intensity) 379 (M^+, 4), 179 (100).



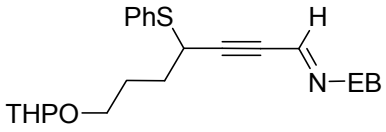
12k : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.12 (m, 21H), 3.96 (dt, 1H, J = 7.2 Hz, 1.3 Hz), 1.87-1.83 (m, 2H), 1.62- 1.54 (m, 2H), 1.39-1.35 (m, 2H), 0.94 (t, 3H, J = 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 145.6, 145.2, 133.9, 130.2, 129.3, 128.6, 128.3 (x2), 127.4, 127.0, 94.5, 83.1, 80.1, 39.9, 34.9, 29.8, 22.6, 14.4; MS *m/z* (relative intensity) 258 ().9), 182 (100).



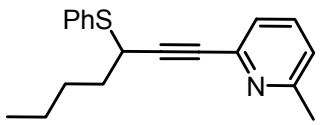
12l : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.51-7.28 (m, 5H), 4.13-4.08 (m, 2H), 2.57-2.50 (m, 2H), 1.82-1.79 (m, 2H), 1.62, 1.45 (m, 2H), 1.38-1.08 (m, 10H), 0,92-0.88 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 144.9, 142.3, 133.5, 129.3, 128.3, 92.9, 81.9, 63.6, 60.7, 57.4, 42.4, 39.5, 34.9, 29.7, 22.5, 21.4, 14.6, 14.3; MS *m/z* (relative intensity) 345 (M^+, 45), 302 (81), 148 (100).



12m : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 4.12-4.07 (m, 2H), 3.81-3.58 (m, 2H), 2.69-2.50 (m, 4H), 1.85-1.76 (m, 2H), 1.68-1.21 (m, 30H), 0.90-0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 144.6, 142.1, 92.9, 80.6, 63.2, 60.3, 57.0, 42.3, 41.9, 34,8, 34.5, 31.9, 31.3, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 22.6, 22.2, 22.0. 14.2, 14.1, 13.9; MS *m/z* (relative intensity) 437 (M^+, 5), 392 (10), 237 (100).



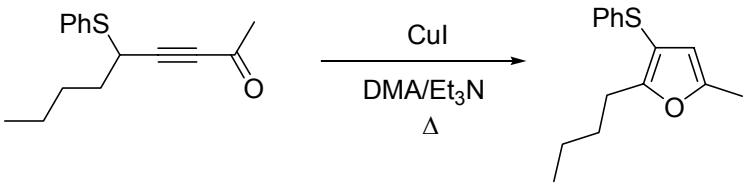
12n : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.26 (m, 6H), 4.55 (m, 1H), 4.12-4.07 (m, 2H), 3.82 (m, 2H), 3.50-3.31 (m, 2H), 2.56-2.51 (m, 2H), 2.56-2.50 (m, 2H), 1.89-1.87 (m, 5H), 1.53-1.51 (m, 4H), 1.24-1.20 (m, 5H), 1.20-1.06 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 144.9, 142.3, 133.5, 129.3, 128.4, 99.2, 92.5, 82.1, 67.0, 63.6, 62.6, 60.8, 57.4, 42.6, 42.4, 39.4, 32.1, 31.1, 27.8, 25.9, 22.4, 21.4, 19.9; MS *m/z* (relative intensity) 431 (M^+, 20), 347 (27), 85 (100).



12o : To a 100 mL round bottomed, two-necked flask, equipped with a Teflon-coated stir bar, condenser, and three way stopcock with an argon-filled balloon, was sequentially added: 5-bromopicoline (1.8 mL, 15.8 mmol), copper iodide (120 mg, 0.63 mmol), dichlorobis(triphenylphosphine)palladium (II) (222 mg, 0.32 mmol), anhydrous triethylamine (50 mL), and 3-(phenylthio)-1-heptyne **45** (2.8g, 18.9 mmol). The mixture was allowed to stir at

60 ^{o}C for two hours. After completion, the reaction mixture was filtered through silica gel, concentrated under reduced pressure, and purified by column chromatography using 5% ethyl acetate-hexanes as eluent to afford 2-(3'-phenylthio)-1-heptynyl-5-methyl-pyridine in 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.55 (2 H, d, *J* = 6.97 Hz) 7.45 (1 H, t, *J* = 7.79 Hz) 7.22 - 7.32 (3 H, m) 7.09 (1 H, d, *J* = 7.70 Hz) 7.02 (1 H, d, *J* = 7.89 Hz) 3.99 (1 H, t, *J* = 7.06 Hz) 2.50 (3 H, s) 1.79 - 1.91 (2 H, m) 1.49 - 1.66 (2 H, m) 1.27 - 1.37 (2 H, m) 0.89 (3 H, t, *J* = 7.34 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 158.56, 142.36, 136.05, 133.80, 132.92 (2 C), 128.64 (2 C), 127.54, 124.22, 122.31, 89.05, 83.90, 39.20, 34.59, 29.24, 24.41, 22.11,13.79. MS *m/z* (relative intensity) 294 (M^+ - 1, 27), 186 (100), 131 (80).

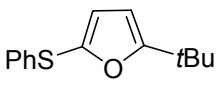
Synthesis of Furans and Pyrroles 14a-14p



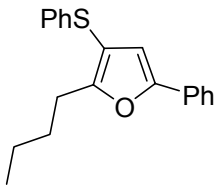
Representative procedure of furans and pyrroles (14b): A mixture of propynyl ketone **12b** (246 mg, 1.0 mmol), CuI (12 mg, 0.05 mmol), and anhydrous DMA (2.0 mL) was stirred in a Wheaton microreactor (3 mL) under argon atmosphere at 130 ^{o}C. The reaction was monitored by TLC and GC-MS until completion. After 12 h, the mixture was cooled to room temperature and poured into sat. NH_4Cl solution (20 mL). The phases were separated and the aqueous phase was thoroughly extracted with hexanes (2 x 10 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 (2 g), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with hexanes to give furan **14b** (187 mg, 76 % yield).

Table 1. Experimental details for the synthesis of compound 14a-p

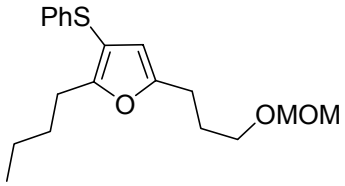
Entry	Compound	CuI	Et_3N	T (^{o}C)	Time (h)	Yield (%)
1	**14a**	5 %	None	130	12	91
2	**14b**	5 %	None	130	12	76
3	**14c**	5 %	20 %	130	12	89
4	**14d**	5 %	20 %	100	0.4	71
5	**14e**	5 %	20 %	130	14	95
6	**14f**	5 %	none	130	48	71
7	**14g**	5 %	20 %	130	12	93
8	**14h**	5 %	20 %	130	12	72
9	**14i**	5 %	20 %	100	0.4	78
10	**14j**	5 %	20 %	100	1.5	86
11	**14k**	30 %	5 eq	150	6	85
12	**14l**	30 %	5 eq	150	1	74
13	**14m**	30 %	5 eq	150	1	67
14	**14n**	30 %	5 eq	150	1	78
15	**14o**	50 %	11 eq	150	12	53



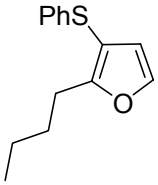
10 : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.13 (m, 5H), 6.67 (d, 1H, J = 3.1 Hz), 6.09 (d, 1H, J = 3.1 Hz), 1.33 (s, 9H);); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 139.7, 137.6, 128.9, 126.6, 125.8, 120.7, 104.4, 33.1, 28.9; MS *m/z* (relative intensity) 232 (M^+, 49), 217 (100).



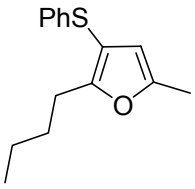
14a : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.15 (m, 10H), 6.66 (s, 1H), 2.84 (t, 2H, J = 7.4 Hz), 1.71 (quint, 2H, J = 7.5 Hz), 1.40 (sext, 2H, J = 7.6 Hz), 0.95 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 153.0, 138.6, 130.9, 129.3, 129.2, 127.9, 126.8, 125.6, 123.9, 110.8, 110.1, 31.0, 26.4, 22.7, 14.2; MS *m/z* (relative intensity) 308 (M^+, 57), 265 (100); Anal. Calcd. for $C_{20}H_{20}OS$: C, 77.88; H, 6.54. Found: C, 78.04; H, 6.62.



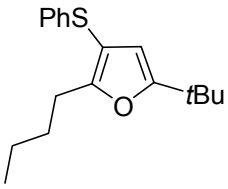
14p : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.10 (m, 5H), 6.00 (s, 1H), 4.64 (s, 2H), 3.59 (t, 2H, J = 7.8 Hz), 3.37 (s, 3H), 2.72 (m, 4H), 1.95 (quint, 2H, J = 6.5 Hz), 1.60 (quint, 2H, J = 7.4 Hz), 1.32 (sext, 2H, J = 7.6 Hz), 0.90 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 154.3, 138.6, 128.8, 126.1, 125.0, 110.4, 107.4, 96.4, 66.7, 55.1. 30.5, 28.0, 25.8, 24.8, 22.2, 13.8; MS *m/z* (relative intensity) 334 (M^+, 100), 289 (83); Anal. Calcd. for $C_{19}H_{26}OS$: C, 68.23; H, 7.84. Found: C, 68.46; H, 7.88.



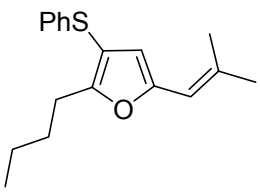
14d : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, 1H, J = 2.0 Hz), 7.26-7.11 (m, 5H), 6.39 (d, 1H, J = 1.9 Hz), 2.76 (t, 2H, J = 7.6 Hz), 1.63 (quint, 2H, J = 7.5 Hz), 1.33 (sext, 2H, J = 7,5 Hz), 0.91 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1, 141.7, 138.8, 129.3, 126.6, 125.5, 115.8, 107.9, 30.8, 26.2, 22.6, 14.2; MS *m/z* (relative intensity) 232 (M^+, 85), 189 (85), 171 (100); Anal. Calcd. for $C_{14}H_{16}OS$: C, 72.37; H, 6.94. Found: C, 72.50; H, 6.96.



14b : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.10 (m, 5H), 5.97 (s, 1H), 2.73 (t, 2H, J = 7.4 Hz), 2.31 (s, 3H), 1.63 (quint, 2H, J = 7.5 Hz), 1.35 (sext, 2H, J = 7.5 Hz), 0.92 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 150.8, 138.6, 128.8, 126.1, 125.0, 110.8, 107.5, 30.6, 25.8, 22.3, 13.8, 13.7; MS *m/z* (relative intensity) 246 (M^+, 69), 203 (100); Anal. Calcd. for $C_{15}H_{18}OS$: C, 72.13; H, 7.36. Found: C, 72.97; H, 7.22.

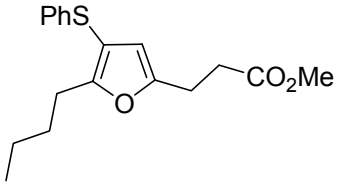


14c : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.12 (m, 5H), 5.95 (s, 1H), 2.73 (t, 2H, J = 7.6 Hz), 1.63 (quint, 2H, J = 7.5 Hz), 1.33 (sext, 2H, J = 7.5 Hz), 1.31 (s, 9H), 0.92 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 159.2, 139.2, 129.2, 126.5, 125.3, 107.6, 107.2, 33.1, 30.9, 29.3, 26.2, 22.7, 14.2; MS *m/z* (relative intensity) 288 (M^+, 69), 273 (100); Anal. Calcd. for $C_{18}H_{24}OS$: C, 74.95; H, 8.39. Found: C, 74.98; H, 8.45.

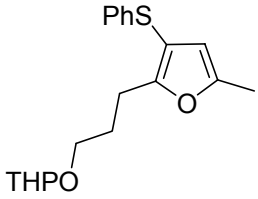


14e : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.10 (m, 5H), 6.17 (s, 1H), 6.06 (s, 1H), 2.75 (t, 2H, J = 7.4 Hz), 1.99 (s, 3H), 1.93 (s, 3H), 1.64 (quint, 2H, J = 7.5 Hz), 1.35 (sext, 2H, J = 7.5 Hz) 0.91 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 152.8, 136.0, 129.2, 126.5, 125.4, 114.5, 112.8, 108.9, 30.8, 27.5, 26.2, 22.7, 20.6, 14.2; MS *m/z* (relative intensity)

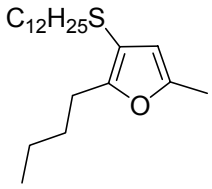
286 (M^+, 51), 243 (100); Anal. Calcd. for $C_{18}H_{22}OS$: C, 75.48; H, 7.74. Found: C, 75.56; H, 7.83.



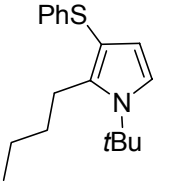
14f : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.08 (m, 5H), 6.00 (s, 1H), 3.69 (s, 3H), 2.95 (t, 2H, J = 7.4 Hz), 2.66 (t, 2H, J = 7.3 Hz), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 155.5, 152.8, 138.1, 128.8, 126.1, 125.1, 110.8, 107.9, 51.8, 32.3, 23.5, 11.8; MS *m/z* (relative intensity) 276 (M^+, 100), 216 (15), 203 (90); Anal. Calcd. for $C_{15}H_{16}OS$: C, 65.19; H, 5.84. Found: C, 65.47; H, 5.95.



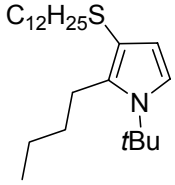
14g : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.09 (m, 5H), 5.95 (s, 1H), 4.51 (t, 1H, J = 2.9 Hz), 3.84 (dt, 1H, J = 10.7 Hz, 2.7 Hz), 3.74 (m, 1H), 3.45 (m, 1H), 3.35 (m, 1H), 2.84-2.76 (m, 2H), 2.28 (s, 3H), 1.92 (quint, 2H, J = 7.0 Hz), 1.75 (m, 1H), 1.67 (m, 1H), 1.57-1.49 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 151.4, 138.9, 129.2, 126.5, 125.4, 111.3, 108.3, 99.2, 67.0, 62.6, 31.1, 28.9, 25.9, 23.4, 20.0, 14.1; MS *m/z* (relative intensity) 332 (M^+, 5), 247 (100); Anal. Calcd. for $C_{19}H_{24}OS$: C, 68.64; H, 7.28. Found: C, 68.87; H, 7.35.



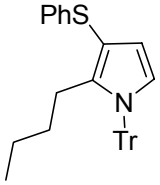
14h : ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (s, 1H), 2.66 (t, 2H, J = 7.6 Hz), 2.58 (t, 2H, J = 7.4 Hz), 2.23 (s, 3H), 1.61-1.49 (m, 4H), 1.38-1.21 (m, 20H), 0.92 (t, 3H, J = 7.4 Hz), 0.88 (t, 3H, J = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 150.0, 110.9, 110.7, 36.5, 32.3, 31.2, 30.1, 30.0, 29.8, 29.7, 29.0, 23.1, 22.7, 14.5, 14.3, 14.0; MS *m/z* (relative intensity) 338 (M^+, 36), 295 (50), 127 (100); Anal. Calcd. for $C_{21}H_{38}OS$: C, 74.49; H, 11.31. Found: C, 74.56; H, 11.42.



14i : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21-7.03 (m, 5H), 6.85 (d, 1H, J = 3.1 Hz), 6.19 (d, 1H, J = 3.1 Hz), 2.85 (t, 2H, J = 8.3 Hz), 1.65 (s, 9H), 1.55-1.50 (m, 2H), 1.41-1.34 (m, 2H), 0.89 (t, 3H, J = 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 139.6, 128.9, 125.7, 124.5, 118.5, 113.0, 107.6, 57.2, 34.0, 31.6, 27.6, 23.4, 14.2; MS *m/z* (relative intensity) 287 (M^+, 44), 231 (17), 188 (100). Anal. Calcd. for $C_{18}H_{25}NS$: C, 75.21; H, 8.77; N, 4.87. Found: C, 75.41; H, 8.92; N, 4.98.

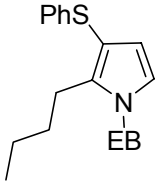


14j : ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.72 (d, 1H, J = 3.1 Hz), 6.11 (d, 1H, J = 3.1 Hz), 2.86 (t, 2H, J = 8.3 Hz), 2.64 (t, 2H, 7.5 Hz), 1.61-1.55 (m, 12H), 1.47-1.39 (m, 4H), 1.31-1.26 (m, 17H), 0.97 (t, 3H, J = 7.3 Hz), 0.89 (t, 3H, J = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.0, 117.6, 112.2, 111.3, 56.8, 37.7, 34.2, 32.4, 31.5, 30.2, 30.1, 30.0, 29.8, 29.7, 29.2, 27.6, 23.5, 23.1, 14.6, 14.3; MS *m/z* (relative intensity) 379 (M^+, 14), 323 (21), 112 (100). Anal. Calcd. for $C_{24}H_{45}NS$: C, 75.92; H, 11.95; N, 3.69. Found: C, 76.17; H, 12.07; N, 3.75.

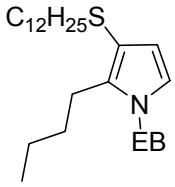


14k : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.11 (m, 20H), 6.56 (d, 1H, J = 3.2 Hz), 6.21 (d, 1H, J = 3.2 Hz), 2.14 (t, 2H, J = 8.4 Hz), 0.69 (sext, 2H, J = 7.5 Hz), 0.45 (t, 3H, J = 7.3 Hz), 0.42-0.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 141.5, 141.4, 130.7, 130.6, 128.9, 128.4, 128.2, 128.1, 127.9, 125.8, 124.6, 123.0, 113.0, 108.6, 76.5, 30.9, 29.6, 23.6, 13.9; MS *m/z* (relative intensity) 182 (100),

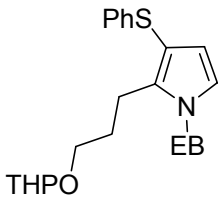
165 (19), 104 (31). Anal. Calcd. for $C_{33}H_{31}NS$: C, 83.68; H, 6.60; N, 2.96. Found: C, 83.33; H, 6.69; N, 2.81.



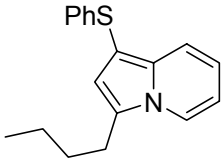
14l : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18-7.01 (m, 5H), 6.71 (d, 1H, J = 3.1Hz), 6.26 (d, 1H, J = 3.0 Hz), 4.67 (sext, 1H, J = 7.0 Hz), 4.10 (m, 2H), 2.79-2.70 (m, 4H), 1.50 (d, 3H, J = 6.7 Hz), 1.45-1.39 (m, 2H), 1.34-1.29 (m, 2H), 1.23 (t, 3H, J = 7.2 Hz), 0.86 (t, 3H, J = 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 141.6, 138.8, 128.9, 125.6, 116.3, 115.1, 104.7, 61.3, 49.2, 43.2, 32.9, 24.5, 22.9, 22.6, 14.5, 14.2; MS *m/z* (relative intensity) 345 (M^+, 100), 302 (65), 214 (30). Anal. Calcd. for $C_{20}H_{27}NO_2S$: C, 69.53; H, 7.88; N, 4.05. Found: C, 69.65; H, 7.92; N, 4.08.



14m : ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (d, 1H, J = 3.9 Hz), 6.17 (d, 1H, J = 3.8 Hz), 4.58 (m, 1H), 4.07 (q, 2H, J = 8.9 Hz), 2.82-2.63 (m, 4H), 2.55 (t, 2H, J = 9.4 Hz), 1.54-1.24 (m, 27H), 1.18 (t, 3H, J = 9.2 Hz), 0.94 (t, 3H, J = 9.1 Hz), 0.87 (t, 3H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 136.2, 115.0, 113.6, 108.5, 60.7, 48.5, 42.8, 37.5, 32.9, 31.9, 29.6, 29.4, 29.3, 28.7, 24.1, 22.7, 22.6, 22.1, 14.1, 14.0, 13.9; MS *m/z* (relative intensity) 437 (M^+, 100), 394 (38), 226 (89). Anal. Calcd. for $C_{26}H_{47}NO_2S$: C, 71.34; H, 10.82; N, 3.20. Found: C, 71.35; H, 10.89; N, 3.20.

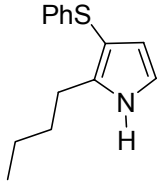


14n : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.00 (m, 5H), 6.72 (d, 1H, J = 3.1 Hz), 6.26 (d, 1H, J = 3.1 Hz), 4.72 (m, 1H), 4.49 (m, 1H), 4.10 (m, 1H), 3.81 (m, 1H), 3.70 (m, 1H), 3.45 (m, 1H), 3.34 (m, 1H), 2.82-2.73 (m, 4H), 1.85-1.47 (m, 12H), 1.20 (dt, 3H, J = 7.2 Hz, 1.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 141.6, 138.1, 128.9 125.5, 124.6, 116.6, 115.2, 104.8, 99.3, 99.1, 77.8, 77.3, 67.0, 62.9, 62.7, 61.2, 49.2, 43.2, 43.1, 31.1, 30.7, 25.9, 22.6, 21.5, 20.2, 20.0, 14.5; MS *m/z* (relative intensity) 431 (M^+, 43), 302 (64), 55 (100). Anal. Calcd. for $C_{24}H_{33}NO_4S$: C, 66.79; H, 7.71; N, 3.25. Found: C, 66.71; H, 7.74; N, 3.26.

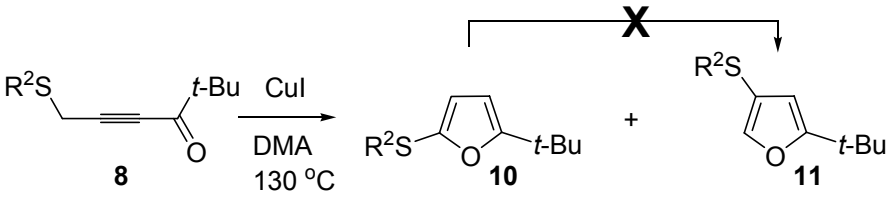


14o: To a 100 mL, round-bottomed, two-necked flask, equipped with a Teflon-coated stir bar, condenser, and three-way stopcock with an argon balloon, was sequentially added: 2-(3-phenylthio-1-heptynyl)-5-methylpyridine 1.15g, 3.89 mmol), copper (I) bromide (287 mg, 2.0 mmol), anhydrous DMA (42 mL), and anhydrous triethylamine (6 mL). The reaction mixture was stirred for 12 hours at 150 ^{o}C. Upon completion, the reaction mixture was quenched with saturated ammonium chloride solution, thoroughly extracted with hexanes, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel treated with 1% triethylamine, using hexanes as eluent, to afford 3-*n*-butyl-8-methyl-2-phenylthioindolizine **14o** in 53% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.27 (3 H, t, *J* = 7.70 Hz) 7.24 (2 H, s) 7.15 (1 H, t, *J* = 7.15 Hz) 6.67 (1 H, s) 6.61 (1 H, dd, *J* = 8.80, 6.60 Hz) 6.31 (1 H, d, *J* = 6.42 Hz) 3.32 (2 H, s) 2.86 (3 H, s) 1.54 - 1.63 (2 H, m) 1.46 (2 H, s) 0.98 (3 H, t, *J* = 7.34 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 139.48, 134.18 133.91, 128.54 (2 C), 126.41 (2 C), 124.73, 117.51, 116.51, 115.01, 112.70, 105.29, 35.15, 26.60, 22.21, 21.25, 13.77. MS *m/z* (relative intensity) 295 (M^+, 23), 252 (100).

Deprotection of EB-protecting group in pyrrole 14l



14q: KO*t*Bu (175 mg, 1.56 mmol) was added to 3-(2-butyl-3-phenylsulfanyl-pyrrol-1-yl)-butyric acid ethyl ester **14l** (180 mg, 0.52 mmol) in THF (10 mL). The reaction was stirred at r.t. and monitored by TLC and GC-MS until completion. After 10 min, the mixture was poured into sat. NH_4Cl solution. The phases were separated, and the aqueous phase was thoroughly extracted with EtOAc. The combined organic extracts were washed (brine), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with 20 % EtOAc/hexanes to give 2-butyl-3-phenylsulfanyl-1H-pyrrole **14q** (121 mg, >99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (bs, 1H), 7.23-7.03 (m, 5H), 6.76 (t, 1H, J = 2.8 Hz), 6.28 (t, 1H, J = 2.8 Hz), 2.69 (t, 2H, J = 7.7 Hz), 1.54 (quint, 2H, J = 7.2 Hz), 1.35-1.31 (m, 2H), 0.89 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 138.4, 129.0, 125.7, 124.7, 117.2, 115.2, 104.9, 32.3, 26.0, 22.8, 14.3; MS *m/z* (relative intensity) 231 (M^+, 45), 188 (100). Anal. Calcd. for $C_{14}H_{17}NS$: C, 72.68; H, 7.41; N, 6.05. Found: C, 72.31; H, 7.68; N, 5.93.



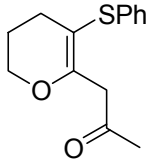
entry	time	standard: **10**:**11**:**8**[a]
1	1h	1 : 0.21: 0.018 : 0.10
2	18h	1 : 0.71 : 0.11 : 0.02
3	24h	1 : 0.70 : 0.082 : 0
4	3d	1 : 0.78 : 0.089 : 0

[a] GC ratios, pentadecane used as standard

In a glovebox, under nitrogen atmosphere, to a 3 mL Wheaton microreactor equipped with a PTFE coated spin vane and open cap with PTFE faced silicone septum was added CuI (0.09 mmol, 18 mg). To the reactor were sequentially added: anhydrous DMA (1 mL), 2,2-dimethyl-6-phenylthio-4-hexyn-3-one (0.5 mmol, 116 mg), and pentadecane (50 μL) as the internal standard for GC analysis. The reaction was stirred at 130 °C for 3 days and monitored by GC-MS analysis. After the starting material was consumed, the ratio of products to the internal standard remained relatively unchanged upon prolonged subjection to reaction conditions.

Competitive 6-*exo*-dig cyclization of 12g

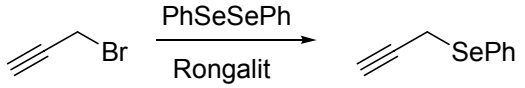
15 : Following the procedure for the synthesis of furan **14g** with no addition of triethylamine: 1.15 mmol scale, 150°C, 72h. Upon completion, the reaction mixture was quenched with saturated ammonium chloride solution, thoroughly extracted with hexanes, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford 1-[5-(phenylthio)-3,4-dihydro-2*H*-pyran-6-yl]acetone **15**.Yield: 266mg (93%).



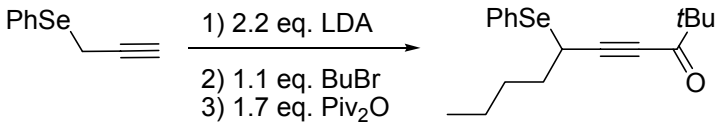
15 : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (2 H, d, *J*=7.52 Hz), 7.15 - 7.21 (2 H, m), 7.11 (1 H, t, *J*=7.24 Hz), 4.07 (2 H, s), 3.61 (2 H, s), 2.23 (2 H, t, *J*=6.33 Hz), 2.14 (3 H, s), 1.89 - 1.99 (2 H, m). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.16, 155.68, 136.49, 128.99 (+, 2C), 126.86 (+, 2C), 125.39 (+), 102.38, 66.64 (-), 47.34 (-), 29.44 (+), 26.72 (-), 23.60 (-). MS *m/z* (relative intensity) 248 (M^+, 100), 172 (25), 205 (7), 135 (40), 91 (30), 71 (20).

1,2-SELENIUM MIGRATION

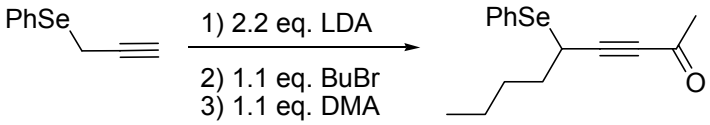
Preparation of Starting Materials



(51.2 mmol scale; 93% yield) Phenyl propargyl selenide **47** was prepared according to a literature procedure; NMR was in accordance with described data.[6]



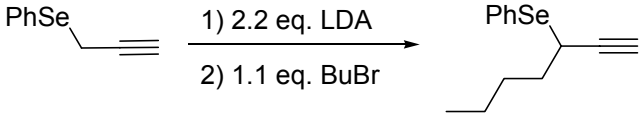
2,2-dimethyl-6-phenylselenodec-4-yn-3-one (16a): To a flash-dried 25 mL round-bottomed, 2-necked flask, equipped with a PTFE coated stir bar, rubber septum, and 3-way stopcock with argon balloon, were sequentially added anhydrous THF (10 mL) and phenyl propargyl selenide **47** (425 μL, 585 mg, 3.0 mmol). The solution was cooled to -78 °C while stirring and LDA solution (4.4 mL, 6.6 mmol, 1.5M in cyclohexane) was added dropwise. After 30 minutes, the flask was allowed to warm to room temperature, cooled again to -78 °C, and *n*BuBr (360 μL, 452 mg, 3.3 mmol) was added dropwise. After 1 hour, the acetylide solution was transferred dropwise via cannula to a similarly prepared 100 mL round-bottomed 2-necked flask containing anhydrous THF (10 mL) and pivalic anhydride (1.0 mL, 930 mg, 5.0 mmol) at -78 °C. The reaction was allowed to stir while slowly warming overnight, then poured into saturated NH_4Cl solution (100 mL) and extracted with ether (30 mL). The organic phase was washed twice with saturated $NaHCO_3$, once with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (100 mL) using 1:20 EtOAc:hexanes as eluent to afford 2,2-dimethyl-6-phenylselenodec-4-yn-3-one as a yellow oil (553 mg, 1.65 mmol, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.67 - 7.63 (2 H, m), 7.36 - 7.28 (3 H, m), 3.91 (1 H, dd, *J* = 7.89, 6.42 Hz), 1.89 - 1.82 (2 H, m), 1.60 - 1.47 (2 H, m), 1.40 - 1.31 (2 H, m), 1.12 (9 H, s), 0.91 (3 H, t, *J* = 7.34 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 193.87, 135.56 (2 C), 129.07 (2 C), 128.28, 127.93, 94.47, 81.76, 44.67, 34.59, 30.14, 30.07, 25.90 (3 C), 22.03, 13.84. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 465.93. GC/MS *m/z*: 336 (M^+, 17); 57 (*t*Bu, 100).



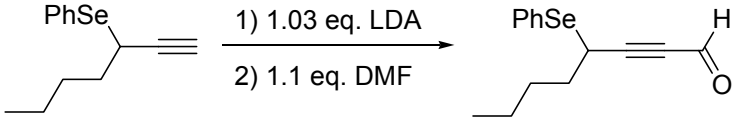
5-phenylselenonon-3-yne-2-one (16c): To a flash-dried, 10 mL round-bottomed, 2-necked flask, equipped with a PTFE coated stir bar, rubber septum, and 3-way stopcock with an argon balloon, were sequentially added: anhydrous THF (3 mL) and phenyl propargyl selenide **47** (140 μL, 1.0 mmol). The solution was cooled to -78 °C and LDA solution (2.2 mL, 3.3 mmol, 1.5M solution in cyclohexane) was added dropwise. The flask was allowed to stir for 2 hours and then *n*BuBr (240 μL, 2.2 mmol) was added dropwise. After stirring for 30 minutes, the acetylide

[6] Reich, H. J.; Shah, S. K.; Gold, P. M.; Olson, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 3112.

mixture was transferred via cannula at -78 °C to a similarly prepared flask containing anhydrous THF (3 mL) and acetic anhydride (2.2 mmol, 170 μL). After warming to room temperature, the mixture was poured into a separatory funnel containing saturated NH_4Cl solution (70 mL), then extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using 1:20 EtOAC:hexanes as eluent to afford 5-phenylselenonon-3-yne-2-one (133 mg, 0.45 mmol, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.65 (2 H, dd, *J* = 8.07, 1.47 Hz), 7.38 - 7.28 (3 H, m), 3.84 (1H, t, *J* = 7.3 Hz), 2.21 (3 H, s), 1.85 - 1.77 (2 H, m), 1.54 - 1.42 (2 H, m), 1.37 - 1.28 (2 H, m), 0.89 (3 H, t, *J* = 7.34 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 184.18, 135.87 (2 C), 128.95 (2 C), 128.64, 127.67, 92.80, 84.24, 34.43, 32.61, 30.04, 29.80, 21.95, 13.76. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 467.42. GC/MS *m/z*: 294 (M^+, 88); 251 (M^+ - COMe, 97); 171 (94); 157 (PhSe, 76); 77 (100).

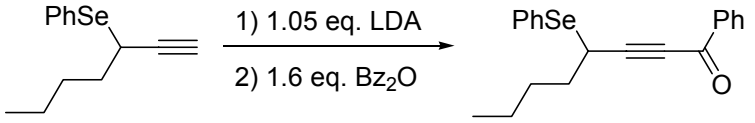


3-phenylseleno-1-heptyne (48): To a flash-dried, 10 mL round-bottomed, 2-necked flask, equipped with a PTFE coated stir bar, rubber septum, and 3-way stopcock with an argon balloon, were sequentially added: anhydrous THF (6 mL) and phenyl propargyl selenide (425 μL, 585 mg, 3.0 mmol). The solution was cooled to -78 °C, and LDA solution (4.4 mL, 6.6 mmol, 1.5M in cyclohexane) was added dropwise. The solution was stirred for 30 minutes, allowed to warm to room temperature, and cooled again to -78 °C. Next, *n*BuBr (356 μL, 452 mg, 3.3 mmol) was added dropwise. The flask was allowed to warm to room temperature again, cooled again to -78 °C, and then poured into a separatory funnel containing saturated NH_4Cl solution (70 mL), and extracted with hexanes (30 mL). The organic phase was washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography on flash silica gel (30 mL) using hexanes as eluent to afford 3-phenylseleno-1-heptyne **48** as a yellow oil (524 mg, 2.1 mmol, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.66 (2 H, dd, *J* = 7.70, 1.65 Hz), 7.36 - 7.28 (3 H, m), 3.78 (1 H, ddd, *J* = 7.43, 3.58, 3.30 Hz), 2.38 (1 H, d, *J* = 2.57 Hz), 1.83 - 1.76 (2 H, m), 1.59 - 1.45 (2 H, m), 1.38 - 1.27 (2 H, m), 0.90 (3 H, t, *J* = 7.34 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 135.20 (2 C), 128.92 (2 C), 128.73, 128.14, 84.58, 72.66, 35.24, 30.49, 30.00, 22.09, 13.90. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 458.39. GC/MS *m/z*: 252 (M^+, 29); 158 (PhSeH, 84); 129 (100); 77 (97).

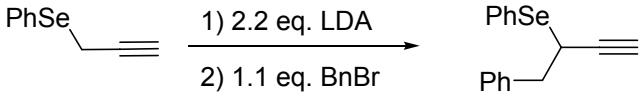


4-phenylseleno-2-octynal (16b): To a flash-dried, 25 mL round bottomed, 2-necked flask, equipped with a PTFE coated stir bar, rubber septum, and 3-way stopcock with argon balloon, were sequentially added: anhydrous THF (5 mL) and 3-phenylseleno-1-heptyne **48** (804 mg, 3.2 mmol). The flask was cooled to -78 °C, and LDA solution (2.2 mL, 3.3 mmol, 1.5M in cyclohexane) was added dropwise. The reaction was allowed to warm to room temperature, cooled again to -78 °C, and anhydrous DMF (270 μL, 256 mg, 3.5 mmol) was added dropwise. The reaction was allowed to warm to room temperature, cooled again to -78 °C, and transferred via cannula to a flask containing H_3PO_4 (85%, 738 mg) and ice (12.8 g) under argon atmosphere.

The mixture was allowed to stir until the ice melted, was poured into water, and extracted with ether, and washed with brine. The organic phase was dried over $MgSO_4$, concentrated under reduced pressure, and purified by column chromatography on silica gel (70 mL) using 1:20 EtOAc:hexanes as eluent to afford 4-phenylseleno-2-heptynal as an oil (542 mg, 1.94 mmol, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.16 (1 H, d, *J* = 0.88 Hz), 7.65 (2 H, dd, *J* = 8.04, 1.46 Hz), 7.39 - 7.29 (3 H, m), 3.85 (1 H, t, *J* = 7.23 Hz), 1.88 - 1.79 (2 H, m), 1.55 - 1.45 (2 H, m), 1.34 (1 H, s), 0.90 (3 H, t, *J* = 7.31 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 176.67, 135.90 (2 C), 129.13, 128.87 (2 C), 127.50, 98.03, 84.38, 34.38, 30.10, 29.85, 22.02, 13.81. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 471.64. GC/MS *m/z*: 280 (M^+, 43); 157 (100); 77 (70).

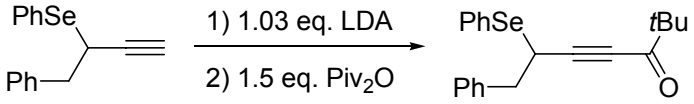


1-phenyl-4-phenylseleno-2-octyn-1-one (16d): To a flash-dried, 25 mL round bottomed, 2-necked flask, equipped with a PTFE coated stir bar, rubber septum, and 3-way stopcock with argon balloon, were sequentially added: 3-phenylseleno-1-heptyne **48** (341 mg, 1.24 mmol) and anhydrous THF (5 mL). The flask was cooled to -78 ^{o}C, and LDA solution (0.87 mL, 1.3 mmol, 1.5M in cyclohexane) was added dropwise. The reaction was allowed to warm to 0 ^{o}C, and cooled again to -78 ^{o}C. The acetylide solution was then transferred dropwise via cannula to a similarly prepared 25 mL round-bottomed 2-necked flask containing anhydrous THF (5 mL) and benzoic anhydride (452 mg, 2.0 mmol) at -78 ^{o}C. The reaction was allowed to stir while slowly warming overnight, then poured into saturated NH_4Cl solution (100 mL) and extracted with hexanes (40 mL). The organic phase was washed successively with saturated $NaHCO_3$ (100 mL), saturated NH_4Cl (100 mL), saturated $NaHCO_3$ (100 mL), brine (50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using 1:20 EtOAc:hexanes as eluent to afford 1-phenyl-4-phenylseleno-2-octyn-1-one **16d** as a viscous yellow oil (276 mg, 0.76 mmol, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.94 (2 H, dd, *J* = 8.26, 1.10 Hz), 7.70 (2 H, dd, *J* = 8.11, 1.39 Hz), 7.58 (1 H, t, *J* = 7.38 Hz), 7.41 (2 H, t, *J* = 7.82 Hz), 7.28 - 7.37 (3 H, m), 4.01 (1 H, t, *J* = 7.16 Hz), 1.93 (2 H, q, *J* = 7.55 Hz), 1.58 (2 H, td, *J* = 7.42, 5.19 Hz), 1.38 (2 H, s), 0.93 (3 H, t, *J* = 7.38 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.70, 136.71, 135.82 (2 C), 133.87, 129.46 (2 C), 129.13 (2 C), 128.68 (2 C), 128.41 (2 C), 127.81, 95.58, 82.64, 34.53, 30.21, 22.06, 13.85. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 467.53. GC/MS *m/z*: 356 (M^+, 9); 105 (100); 77 (54).

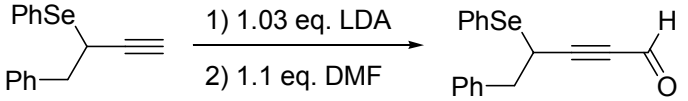


4-phenyl-3-phenylseleno-1-butyne (49): To a flash-dried, 50 mL round-bottomed, 2-necked flask, equipped with a PTFE coated stir bar, rubber septum, and 3-way stopcock with an argon balloon, were sequentially added: anhydrous THF (25 mL) and phenyl propargyl selenide (1.4 mL, 1.95 g, 10.0 mmol). The solution was cooled to -78 ^{o}C, and LDA solution (11 mL, 22 mmol, 1.5M in cyclohexane) was added dropwise. The solution was stirred for 30 minutes, allowed to warm to room temperature, and cooled again to -78 ^{o}C. Next, *n*BnBr (1.3 mL, 1.88 g, 11 mmol) was added dropwise. The flask was stirred for 30 minutes, checked for completion, and then poured into a separatory funnel containing saturated NH_4Cl solution (300 mL), and extracted with hexanes (100 mL). The organic phase was washed with brine, dried over Na_2SO_4,

concentrated under reduced pressure, and purified by column chromatography on flash silica gel using hexanes to 1:50 to 1:20 EtOAc:hexanes gradient as eluent to afford 4-phenyl-3-phenylseleno-1-butyne **49** as a yellow oil (2.34 g, 8.2 mmol, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.69 (1 H, d, *J* = 7.02 Hz), 7.39 - 7.23 (8 H, m), 4.02 (1 H, ddd, *J* = 8.37, 6.18, 2.12 Hz), 3.19 - 3.07 (2 H, m), 2.42 (1 H, d, *J* = 2.48 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 138.30, 135.31 (2 C), 129.12, 129.00 (2 C), 128.55 (2 C), 128.27, 126.85 (2 C), 83.78, 73.82, 41.87, 31.40. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 466.85. GC/MS *m/z*: 286 (M^+, 8); 128 (100).



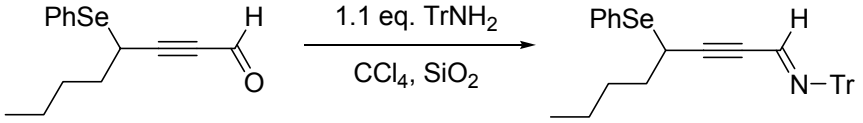
2,2-dimethyl-7-phenyl-6-phenylseleno-4-heptyn-3-one (16e): To a flash-dried, 25 mL round-bottomed, 2-necked flask, equipped with a PTFE coated stir bar, rubber septum, and 3-way stopcock with an argon balloon, were sequentially added: anhydrous THF (10 mL) and 4-phenyl-3-phenylseleno-1-butyne **49** (855 mg, 3.0 mmol). The solution was cooled to -78 ^{o}C, and LDA solution (2.1 mL, 3.1 mmol, 1.5M in cyclohexane) was added dropwise. The solution was stirred for 30 minutes, allowed to warm to room temperature, and cooled again to -78 ^{o}C. The acetylide solution was transferred dropwise via cannula to a similarly prepared 50 mL round-bottomed 2-necked flask containing anhydrous THF (10 mL) and pivaloic anhydride (0.9 mL, 830 mg, 4.5 mmol) at -78 ^{o}C. The reaction was allowed to stir while slowly warming overnight, then poured into saturated NH_4Cl solution (250 mL) and extracted with 2:1 hexanes:EtOAc. The organic phase was washed successively with saturated $NaHCO_3$, brine, and 2% Na_2CO_3 solution, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (100 mL) using 1:3 DCM:hexanes as eluent to afford 2,2-dimethyl-7-phenyl-6-phenylseleno-4-heptyn-3-one **16e** as a yellow oil (693 mg, 1.86 mmol, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.66 (2 H, dd, *J* = 7.82, 1.53 Hz), 7.38 - 7.21 (8 H, m), 4.13 (1 H, dd, *J* = 8.99, 6.07 Hz), 3.18 (1 H, d, *J* = 5.99 Hz), 3.13 (1 H, d, *J* = 8.92 Hz), 1.04 (9 H, s). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 193.72, 137.78, 135.76 (2 C), 129.17, 129.05 (2 C), 128.74 (2 C), 128.46 (2 C), 127.77, 127.11, 93.51, 82.65, 41.26, 31.10, 26.98, 25.79 (3 C). ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 475.07. GC/MS *m/z*: 370 (M^+, 23); 355 (M^+ - CH_3, 29); 91 (80); 57 (*t*Bu; 100).



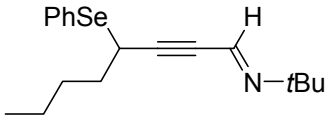
5-phenyl-4-phenylseleno-2-pentynal (16f): To a flash-dried, 25 mL round-bottomed, 2-necked flask, equipped with a PTFE coated stir bar, rubber septum, and 3-way stopcock with an argon balloon, were sequentially added: anhydrous THF (10 mL) and 4-phenyl-3-phenylseleno-1-butyne (855 mg, 3.0 mmol). The solution was cooled to -78 ^{o}C, and LDA solution (2.1 mL, 3.1 mmol, 1.5M in cyclohexane) was added dropwise. The solution was stirred for 30 minutes, allowed to warm to room temperature, and cooled again to -78 ^{o}C. The reaction was allowed to warm to room temperature, cooled again to -78 ^{o}C, and anhydrous DMF (260 μL, 241 mg, 3.3 mmol) was added dropwise. The reaction was allowed to warm to room temperature, cooled again to -78 ^{o}C, and transferred via cannula to a flask containing H_3PO_4 (85%, 6.0 mmol, 692 mg) and ice (12 g) under argon atmosphere. The mixture was allowed to stir until the ice melted,

was poured into water, and extracted with 1:1 hexanes:EtOAc, and washed with brine. The organic phase was dried over $MgSO_4$, concentrated under reduced pressure, and purified by column chromatography on silica gel using 1:20 EtOAc:hexanes as eluent to afford 5-phenyl-4-phenylseleno-2-pentynal **16f** as an oil (415 mg, 1.32 mmol, 44% yield). (Mixture of alkynal and allenal 0.2:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.28 (0.2 H, d, *J* = 7.16 Hz), 9.12 (1 H, d, *J* = 0.73 Hz), 7.68 (2 H, dd, *J* = 8.11, 1.39 Hz), 7.56 (1 H, dd, *J* = 7.60, 1.75 Hz), 7.44 - 7.27 (8 H, m), 7.25 (2 H, d, *J* = 1.61 Hz), 5.56 (0.2 H, dt, *J* = 7.16, 2.63 Hz), 4.10 (1 H, dd, *J* = 8.92, 5.99 Hz), 3.71 (1 H, d, *J* = 2.48 Hz), 3.24 - 3.08 (2 H, m). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 191.13, 176.42, 137.43, 135.96 (2 C), 134.91, 129.42, 129.16, 128.96 (2 C), 128.82 (2 C), 128.48, 127.33, 127.16 (2 C), 98.32, 97.04, 85.09, 40.95, 39.68, 30.84. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 480.67. GC/MS *m/z*: 314 (M^+, 48); 128 (100).

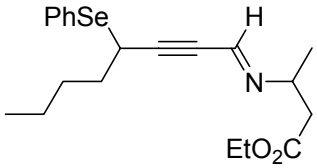
Alkynyl Imines: Alkynyl imines were prepared using previously published procedure A or B[7].



16i : N-Trityl-4-(phenylseleno)-2-octynimine: (A; 100%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.70 (2 H, dd, *J* = 6.79, 1.47 Hz) 7.23 - 7.36 (14 H, m) 7.21 (4 H, s) 7.10 (1 H, d, *J* = 1.65 Hz) 3.96 (1 H, t, *J* = 7.15 Hz) 1.87 (2 H, q, *J* = 7.34 Hz) 1.45 - 1.62 (2 H, m) 1.30 - 1.40 (2 H, m) 0.92 (3 H, t, *J* = 7.34 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 145.26, 144.73, 135.91 (2 C), 129.74 (6 C), 128.90 (2 C), 128.41, 128.09, 127.88, 127.79 (6 C), 126.93 (3 C), 126.56, 95.02, 83.25, 79.60, 35.05, 31.25, 30.16, 22.10. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 465.40 (1 Se, s).



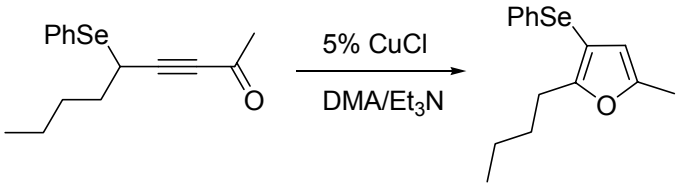
16g : N-*t*Butyl-4-(phenylseleno)-2-octynimine: (A; 100%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.64 (2 H, dd, *J* = 7.89, 1.65 Hz) 7.47 (1 H, d, *J* = 1.47 Hz) 7.32 – 7.28 (m, 3H) 3.90 (1 H, s) 1.77 - 1.89 (2 H, m) 1.42 - 1.58 (2 H, m) 1.26 - 1.36 (2 H, m) 1.20 (9 H, s) 0.88 (3 H, t, *J* = 7.34 Hz) ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 140.22, 135.28 (2 C), 134.42, 128.84 (2 C), 128.12, 92.89, 82.75, 58.63, 35.08, 31.12, 30.01, 29.18 (3 C), 22.03, 13.79. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 463.38. GC/MS *m/z*: 335 (M^+, 47); 236 (73); 156 (100); 57 (97).



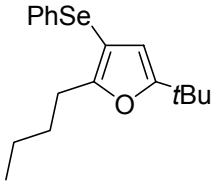
16h : N-(EB)-4-(phenylseleno)-2-octynimine: (B; 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 - 7.65 (2 H, m) 7.55 (0.57 H, d, *J* = 1.32 Hz) 7.39 (0.42 H, s) 7.24 - 7.35 (3 H, m) 4.19 (0.42 H, d, *J* = 6.28 Hz) 4.10 (2 H, q, *J* = 7.16 Hz) 3.90 - 3.97 (0.48 H, m) 3.84 - 3.90 (0.59 H, m) 3.65 - 3.74 (1 H, m) 2.41 - 2.64 (2 H, m) 1.75 - 1.89 (2 H, m) 1.41 - 1.56 (2 H, m) 1.25 - 1.39 (2 H, m) 1.20 - 1.26 (6 H, m) 1.10 (1 H, dd, *J* = 6.43, 4.53 Hz) 0.88 (1.26 H, t, *J* = 7.31 Hz), 0.87 (1.74 H, t, *J* = 7.31 Hz) ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.34, 144.55, 142.04, 135.47 (2 C), 135.39 (2 C), 128.99 (2 C), 128.91 (2 C), 128.40, 128.36, 128.29, 99.50, 93.37, 82.05, 63.13, 60.32, 60.21, 56.88, 42.21, 41.93, 34.99, 34.90, 34.79, 30.91, 30.69, 30.61, 30.13, 30.06, 22.03, 20.91, 18.39, 14.19, 13.82. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 464.57. GC/MS *m/z*: 393 (M^+, 25); 148 (100); 77 (100).

[7] Kim, J. T.; Kel'in, A. V.; Gevorgyan, V. *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 98

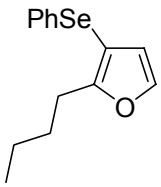
Synthesis of Furans and Pyrroles 17a-17i



2-*n*-butyl-5-methyl-3-phenylselenofuran (17c): In a glovebox under nitrogen atmosphere, to a 1 mL Wheaton microreactor was added CuCl (23 μmol, 2.2 mg). To the microreactor were then sequentially added: anhydrous DMA (250 μL), anhydrous Et_3N (50 μL), and 5-phenylselenonon-3-yne-2-one (133 mg, 0.45 mmol) in anhydrous DMA (250 μL) and was allowed to stir for one day at room temperature. After completion, the reaction mixture was poured into water (10 mL) and extracted three times with hexanes (3 mL). The combined extracts were dried over Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography on 20 mL flash silica gel using hexanes as the eluent to afford 2-n-butyl-5-methyl-3-phenylselenofuran (94 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.28 (2 H, d, J = 1.32 Hz), 7.22 (2 H, t, J = 7.16 Hz), 7.18 (1 H, t, J = 1.39 Hz), 6.00 (1 H, d, J = 0.88 Hz), 2.75 (2 H, t, J = 7.60 Hz), 2.31 (3 H, s), 1.61 (2 H, quint, J = 7.60 Hz), 1.37 – 1.31 (2 H, m), 0.91 (3 H, t, J = 7.38 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 158.73, 150.86, 133.16, 128.96 (2 C), 128.92 (2 C), 125.73, 111.93, 102.33, 30.79, 26.43, 22.19, 13.76, 13.53. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 232.78. HRMS (EI) calcd. for $C_{15}H_{18}OSe$ [M^+]: 294.0523. Found: 294.0515. GC/MS *m/z*: 294 (M^+, 95); 251 (M^+ - Pr, 95); 171 (100).

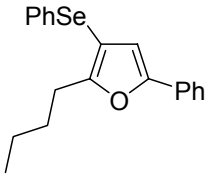


2-*n*-butyl-5-*t*-butyl-3-phenylselenofuran (17a) (General Procedure: Conditions A): In a glovebox, under nitrogen atmosphere, to a 1 mL Wheaton microreactor was added CuCl (25 μmol, 2.5 mg). To the microreactor were then sequentially added: anhydrous DMA (500 μL), anhydrous Et_3N (50 μL), and 2,2-dimethyl-6-phenylselenodec-4-yn-3-one (165 mg, 0.5 mmol) and was allowed to stir for one day at room temperature. After completion, the reaction mixture was poured into water (10 mL) and extracted three times with hexanes (3 mL). The combined extracts were dried over Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography on 25 mL flash silica gel using hexanes as the eluent to afford 2-n-butyl-5-t-butyl-3-phenylselenofuran (158 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.25 (2 H, d, J = 1.17 Hz), 7.21 (2 H, t, J = 7.38 Hz), 7.17 (1 H, t, J = 1.53 Hz), 5.95 (1 H, s), 2.73 (2 H, t, J = 7.53 Hz), 1.57 (2 H, quint, J = 7.75 Hz), 1.32 – 1.28 (2 H, m), 1.27 (9 H, s), 0.89 (3 H, t, J = 7.31 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 162.96, 158.52, 133.30, 128.98 (2 C), 128.86 (2 C), 125.68, 108.30, 101.60, 32.60, 30.72, 28.88 (3 C), 26.45, 22.18, 13.79. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 232.21. HRMS (EI) calcd. for $C_{18}H_{24}OSe$ [M^+]: 336.0992. Found: 336.0997. GC/MS *m/z*: 336 (M^+, 67); 321 (M^+ - Me, 100); 293 (50).

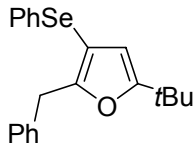


2-*n*-butyl-3-phenylselenofuran (17b) (General Procedure: Conditions B): In a glovebox, under nitrogen atmosphere, to a 3 mL Wheaton microreactor was added CuCl (15 mol %, 75 μmol, 7.5 mg). To the microreactor were then sequentially added: anhydrous DMA (1 mL), anhydrous Et_3N (14 μL), and 4-phenylseleno-2-heptynal (142 mg, 0.5 mmol), and was allowed to stir for one day at room temperature. After completion, the reaction mixture was poured into water (10

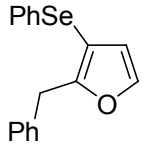
mL) and extracted three times with hexanes (3 mL). The combined extracts were dried over Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography on 50 mL flash silica gel using hexanes as the eluent to afford 2-*n*-butyl-3-phenylselenofuran (105 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.39 (1 H, d, *J* = 1.90 Hz), 7.27 - 7.22 (3 H, m), 7.22 - 7.13 (2 H, m), 6.41 (1 H, d, *J* = 1.90 Hz), 2.77 (2 H, t, *J* = 7.53 Hz), 1.64 - 1.55 (2 H, m), 1.33 – 1.29 (2 H, m), 0.88 (3 H, t, *J* = 7.31 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 160.48, 141.37, 132.91, 129.04 (2 C), 128.99 (2 C), 125.88, 116.45, 102.06, 30.53, 26.40, 22.17, 13.73. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 231.29. HRMS (EI) calcd. for $C_{14}H_{16}OSe$ [M^+]: 280.0366. Found: 280.0366. GC/MS *m/z*: 280 (M^+, 73); 157 (100); 128 (80).



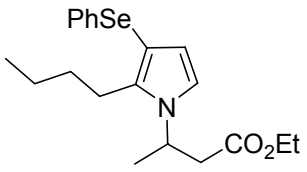
2-*n*-butyl-5-phenyl-3-phenylselenofuran (17d): Using Conditions B, extracted with 1:1 ether:hexanes, hexanes to 1:20 EtOAc:hexanes as eluent; 152 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.66 (2 H, dd, *J* = 8.40, 1.10 Hz), 7.39 (2 H, t, *J* = 7.75 Hz), 7.31 (2 H, d, *J* = 1.02 Hz), 7.30 - 7.14 (4 H, m), 6.69 (1 H, s), 2.85 (2 H, t, *J* = 7.53 Hz), 1.69 (2 H, quint, *J* = 7.60 Hz), 1.38 (2 H, sext, *J* = 7.45 Hz), 0.93 (3 H, t, *J* = 7.31 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 160.10, 152.65, 132.78, 130.42, 129.09 (4 C), 128.66 (2 C), 127.30, 125.96, 123.42 (2 C), 111.60, 104.30, 30.70, 26.59, 22.22, 13.78. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 236.66. HRMS (EI) calcd. for $C_{20}H_{20}OSe$ [M^+]: 356.0679. Found: 356.0687. GC/MS *m/z*: 356 (M^+, 28); 313 (33); 105 (PhCO, 100).



2-benzyl-5-*t*-butyl-3-phenylselenofuran (17e): Using Conditions B, extracted using 1:1 ether:hexanes, hexanes as eluent; 134 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.31 - 7.25 (4 H, m), 7.24 - 7.14 (6 H, m), 6.03 (1 H, s), 4.13 (2 H, s), 1.29 (9 H, s). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 163.73, 155.96, 138.40, 132.79, 129.18 (2 C), 129.00 (2 C), 128.45 (2 C), 128.32 (2 C), 126.16, 125.86, 108.53, 103.13, 32.95, 32.64, 28.86 (3 C). ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 234.95. HRMS (EI) calcd. for $C_{21}H_{22}OSe$ [M^+]: 370.0836. Found: 370.0827. GC/MS *m/z*: 370 (M^+, 70); 355 (M^+ - Me, 100); 91 (96).

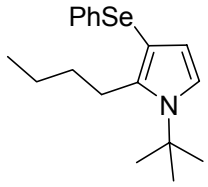


2-benzyl-3-phenylselenofuran (17f): Using Conditions B, hexanes to 1:50 to 1:20 EtOAc:hexanes gradient as eluent; 88 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41 (2 H, d, *J* = 1.90 Hz), 7.28 (4 H, s), 7.22 (4 H, d, *J* = 6.58 Hz), 6.47 (1 H, d, *J* = 1.02 Hz), 4.16 (2 H, s). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 158.16, 142.13, 137.78, 132.50, 129.29 (2 C), 129.10 (2 C), 128.61 (2 C), 128.45(2 C), 126.45, 126.08, 116.54, 103.33, 32.95. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 233.92. HRMS (EI) calcd. for $C_{17}H_{14}OSe$ [M^+]: 314.0210. Found: 314.0221. GC/MS *m/z*: 314 (M^+, 50); 128 (100).

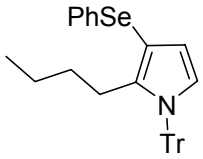


N-EB-2-*n*Bu-3-phenylselenopyrrole (17h): Procedure C: In a glovebox, under nitrogen atmosphere, to a 3 mL Wheaton microreactor was added CuCl (30 mol %, 0.15 mmol, 15 mg). To the microreactor were then sequentially added: *N*-EB-4-phenylseleno-2-octyn-1-imine (142 mg, 0.5 mmol) in anhydrous DMA (1.0 mL) and anhydrous Et_3N (350 μL). The mixture was allowed to stir for one hour at room temperature. After judged complete, the reaction mixture was poured into water (10 mL) and extracted three times with hexanes (3 mL). The combined extracts were dried over Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography on 20 mL flash silica gel treated with 3% Et_3N using 1:10 EtOAc:hexanes as the eluent to afford N-EB-2-*n*-butyl-3-phenylselenopyrrole (115

mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.12 - 7.20 (4 H, m) 7.05 - 7.12 (1 H, m) 6.73 (1 H, d, *J* = 3.07 Hz) 6.32 (1 H, d, *J* = 2.92 Hz) 4.69 (1 H, sext, *J* = 6.92 Hz) 4.11 (2 H, q, *J* = 7.11 Hz) 2.68 - 2.86 (4 H, m) 1.51 (3 H, d, *J* = 6.72 Hz) 1.37 - 1.47 (2 H, m) 1.32 (2 H, s) 1.21 (3 H, t, *J* = 7.16 Hz) 0.88 (3 H, t, *J* = 7.23 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.35, 138.03, 135.50, 128.67 (2 C), 128.04 (2 C), 124.99, 116.10, 115.67, 100.33, 60.76, 48.79, 42.83, 32.68, 24.97, 22.45, 22.23, 14.06, 13.80. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 235.51. GC/MS *m/z*: 393 (M^+, 77); 156 (100); 80 (67).

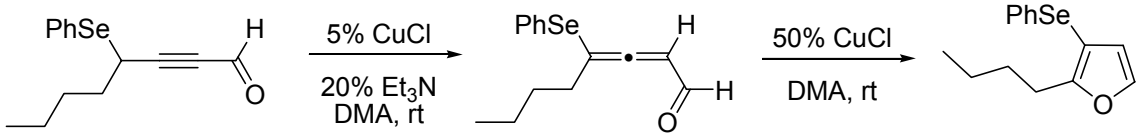


N-*t*Bu-2-*n*Bu-3-phenylselenopyrrole (17g): Procedure C: overnight; 1:20 EtOAc:hexanes eluent, 3% Et_3N treated silica gel column; 74% isolated yield (135 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.25 (2 H, d, *J* = 1.02 Hz) 7.21 (2 H, t, *J* = 7.45 Hz) 7.11 - 7.17 (1 H, m) 6.89 (1 H, d, *J* = 3.07 Hz) 6.28 (1 H, d, *J* = 3.07 Hz) 2.93 (2 H, s) 1.68 (9 H, s) 1.51 - 1.62 (2 H, m) 1.37 - 1.48 (2 H, m) 0.94 (3 H, t, *J* = 7.31 Hz) ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 138.55, 135.51, 128.68 (2 C), 128.04 (2 C), 124.93, 118.24, 113.60, 103.46, 56.62, 33.90, 31.04 (3 C), 27.98, 22.92, 13.69. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 238.48. GC/MS *m/z*: 335 (M^+, 47); 236 (73); 156 (100); 57 (97).



N-EB-2-*n*Bu-3-phenylselenopyrrole (17i): Procedure C with the following modifications: run at 110°C overnight; extracted with 1:1 ether:hexanes; 1:20 EtOAc:hexanes eluent, 3% Et_3N treated silica gel column; 54% isolated yield (164 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.21 - 7.39 (19 H, m) 7.16 (1 H, t, *J* = 6.42 Hz) 6.60 (1 H, d, *J* = 3.30 Hz) 6.29 (1 H, d, *J* = 3.12 Hz) 2.20 (2 H, s) 0.68 - 0.78 (2 H, m) 0.49 (3 H, t, *J* = 7.34 Hz) 0.36 - 0.45 (2 H, m) ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 143.25 (3 C), 140.49, 135.45, 130.20 (6 C), 128.73 (2 C), 128.14 (2 C), 127.73 (6 C), 127.34 (3 C), 125.03 (1 C), 122.67, 113.55, 104.02, 75.96, 31.04, 29.77, 23.13, 13.47. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 246.16.

Direct Observation of Selenoallenic Intermediate 19b



4-phenylseleno-octa-2,3-dienal 19b: In a glovebox, under nitrogen atmosphere, to a 3 mL Wheaton microreactor was added CuCl (5 mol %, 25 μmol, 2.5 mg). To the microreactor were then sequentially added: anhydrous DMA (1 mL), anhydrous Et_3N (14 μL), and 4-phenylseleno-2-heptynal (159 mg, 0.5 mmol), and was allowed to stir for one day at room temperature. The reaction mixture was poured into water (10 mL) and extracted three times with hexanes (3 mL). The combined extracts were dried over Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography on 50 mL flash silica gel using 1:20 EtOAc:hexanes as the eluent to afford 2-*n*-butyl-3-phenylselenofuran (37 mg, 23% yield) and 4-phenylseleno-octa-2,3-dienal (44 mg, 28% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.31 (1 H, d, *J* = 7.34 Hz) 7.54 - 7.58 (2 H, m) 7.28 - 7.34 (3 H, m) 5.57 (1 H, dt, *J* = 7.24, 2.89 Hz) 2.38 (2 H, td, *J* = 7.43, 2.75 Hz) 1.55 (2 H, s) 1.32 - 1.41 (2 H, m) 0.90 (3 H, t, *J* = 7.43 Hz) ^{13}C NMR (126 MHz, $CDCl_3$) δ

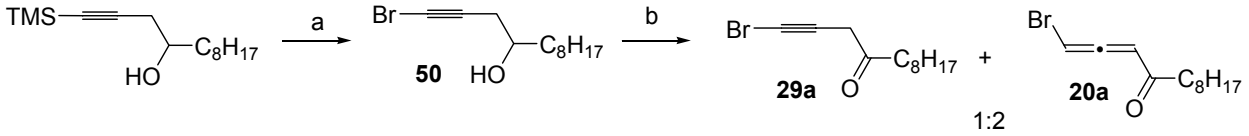
ppm 211.47, 191.57, 134.93, 129.43 (2 C), 128.80, 128.19, 101.82, 98.26, 33.07, 30.35, 21.88, 13.68. ^{77}Se NMR (76 MHz, $CDCl_3$) δ ppm 430.59.

Cycloisomerization of allenal 19b into furan 17b: In a glovebox, under nitrogen atmosphere, to a 1 mL Wheaton microreactor was added CuCl (50 mol %, 30 μmol, 4 mg). A solution of 4-phenylseleno-octa-2,3-dienal (20 mg, 0.071 mmol) in anhydrous DMA (300 μL) was added. The mixture was allowed to stir for 45 minutes at room temperature. After judged complete, the reaction mixture was quenched with water (0.5 mL) and extracted three times with hexanes (250 μL). The combined extracts were filtered through Na_2SO_4 and concentrated under reduced pressure, affording 2-*n*-butyl-3-phenylselenofuran in 58% NMR yield, using dibromomethane as the standard.

1,2-HALOGEN MIGRATION

Preparation of Starting Materials

Synthesis of 20a.

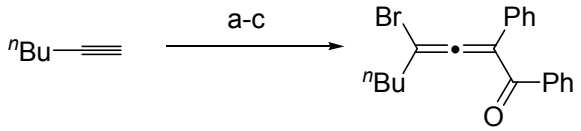


(a) NBS, $AgNO_3$, acetone, 82%; (b) DMP, DCM, 81%.

50 : A solution of 1-trimethylsilyldodec-1-yn-4-ol (see below for preparation) (0.50 g, 1.96 mmol) in acetone (2 mL) was added to a stirred mixture of NBS (0.42 g, 2.34 mmol) and $AgNO_3$ (0.022 g, 0.13 mmol) in acetone (10 mL). The reaction flask was covered with aluminum foil and the mixture was stirred for 3 hrs at room temperature. The reaction was quenched with water, extracted with ether, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated. Purification by column chromatography (eluent hexane/EtOAc 20:1 to 10:1) afforded **50** (0.42 g, 1.6 mmol, 82%).

Typical procedure for Dess-Martin oxidation of homopropargylic alcohols.

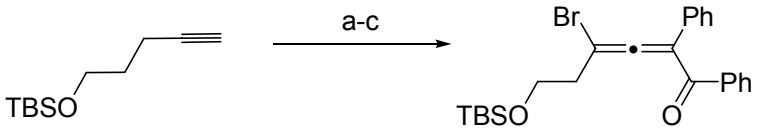
20a : Dess-Martin periodinane (15 wt% solution in DCM, 2.6 mL, 1.2 equiv.) was added to the neat alcohol **50** (0.26 g, 1 mmol) and the mixture was stirred at room temperature for 1 h (monitored by TLC). Water was added and the organic layer was separated. The aqueous layer was extracted with DCM; the combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated. Purification by column chromatography on silica gel (eluent hexane/DCM 7:3) afforded allene **20a** in a 2:1 mixture with alkyne **29a** (0.21 g, 0.81 mmol, 81%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ6.34 (d, J = 5.9 Hz, 1H, allene CH), 5.72 (d, J = 5.9 Hz, 1H, allene CH), 3.24 (s, 2H, propargyl CH_2), 2.56 (m, 2H), 1.57 (br.m, 2H), 1.25 (br.m, 10H), 0.84 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 210.1, 203.7, 199.0, 101.4, 74.3, 72.7, 43.2, 41.5, 39.9, 34.7, 31.8, 29.3, 29.1, 24.3, 23.5, 22.6, 14.1.



(a) n-BuLi, $(PhCO)_2$ THF; (b) TsCl, THF; (c) $LiCuBr_2$ (1.5 equiv), 41%.

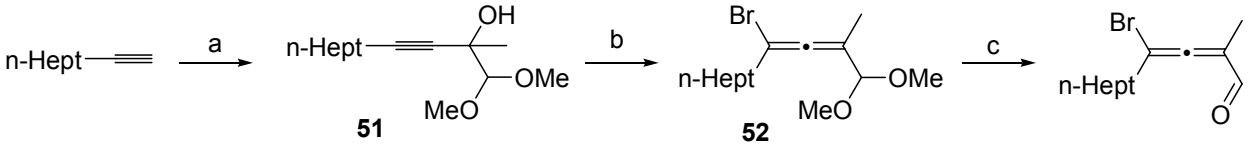
20b : To a 25 ml flash-dried round-bottomed two-necked flask equipped with a stir bar, rubber septum, and T-shaped stopcock with an argon filled balloon were added anhydrous THF (20 mL) and 1-hexyne (1.1 mL, 9.8 mmol). The solution was cooled to -78 ^{o}C while stirring in a dry ice/acetone bath and n-butyllithium (11.0 mmol, 4.4 mL, 2.5M solution in hexanes) was added slowly dropwise. The solution was allowed to warm to room temperature and was transferred dropwise via cannula to an identically prepared 100 ml round-bottomed two-necked flask containing benzil (2.1 g, 10 mmol) in anhydrous THF (20 mL) at 78 ^{o}C under argon atmosphere. The resulting purple-brown solution was allowed to warm to room temperature and then cooled again to -78 ^{o}C. To this flask was added a solution of tosyl chloride (2.1 g, 11 mmol) in anhydrous THF (4 mL), and after ten minutes of stirring at -78 ^{o}C was then added a well-stirred

solution of lithium bromide (1.74 g, 20 mmol) and copper bromide (2.87 g, 20 mmol) in anhydrous THF (20 mL).[8] The solution was left in the dry ice/acetone bath to warm slowly overnight. The reaction mixture was poured into saturated ammonium chloride solution (600 mL) and was thoroughly extracted with ether (150 mL). The organic phase was then washed with brine (300 mL), dried with anhydrous magnesium sulfate, concentrated, and purified over silica gel (200 mL) using 1:40 ethyl acetate:hexanes as eluent to afford **20b** (1.40 g, 41%) as a red oil. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.53-7.48 (m, 4H), 7. 41 (t, *J* = 7.2 Hz, 2H), 7.37-7.35 (m, 1H), 2.56-2.47 (m, 2H), 1.48 (quint, *J* = 7.4 Hz, 2H), 1.19 (dsext, *J* = 7.4 Hz, 3.1 Hz, 2H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 202.5, 192.0, 137.5, 133.4, 131.9, 129.6 (2C), 128.7 (2C), 128.6 (2C), 128.4 (3C), 111.7, 98.3, 37.2, 29.7, 21.4, 13.6.



(a) *n*-BuLi, THF; (b) $(PhCO)_2$; (c) TsCl, LiBr, 37%.

20c : To a 10 ml flash-dried round-bottomed two-necked flask equipped with a stir bar, rubber septum, and T-shaped stopcock with an argon filled balloon were added anhydrous THF (6 mL) and 3-butynyl (*t*-butyldimethyl)silyl ether (0.66 mL, 3.0 mmol). The solution was cooled to -78 ^{o}C while stirring in a dry ice/acetone bath and *n*-butyllithium (1.32 mL of a 2.5M solution in hexanes, 3.3 mmol) was added slowly dropwise. The solution was allowed to warm to room temperature and was transferred dropwise via cannula to an identically prepared 50 ml round-bottomed two-necked flask containing benzyl (660 mg, 3.14 mmol) in anhydrous THF (6 mL) at 78 ^{o}C under argon atmosphere. The resulting purple-brown solution was allowed to warm to room temperature and then cooled again to -78 ^{o}C. To this flask were added: anhydrous lithium bromide (287 mg, 3.3 mmol) in THF (3 mL) and tosyl chloride (2 mL of a 1.65M THF solution, 3.3 mmol). The solution was left in the dry ice/acetone bath to warm slowly overnight. The reaction mixture was poured into brine (300 mL) and was thoroughly extracted with ether (50 mL). The organic phase was then dried with anhydrous magnesium sulfate, concentrated, and purified over silica gel (150 mL) using 1:20 ethyl acetate:hexanes as eluent to afford **20c** (501 mg, 37%) as an orange oil. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.52-7.48 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 3.80 (ddd, *J* = 10.1 Hz, 7.3 Hz, 5.9 Hz, 1H), 3.73 (dt, *J* = 10.1 Hz, 5.9 Hz, 1H), 2.73 (dt, *J* = 15.0 Hz, 6.4 Hz, 1H), 2.66 (dt, *J* = 15.0 Hz, 5.9 Hz, 1H), 0.84 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 202.6, 191.8, 137.3, 133.6, 131.8, 129.7 (2C), 128.70 (2C), 128.66, 128.5 (2C), 128.4 (2C), 111.6, 95.1, 60.6, 40.8, 25.9 (3C), 18.3, -5.41 (2C).



(a) *n*-BuLi, pyruvaldehyde dimethyl acetal, 66%; (b) *n*-BuLi, TsCl, $LiCuBr_2{\cdot}SMe_2$, 55%; (c) H_2SO_4, SiO_2, DCM, 86%.

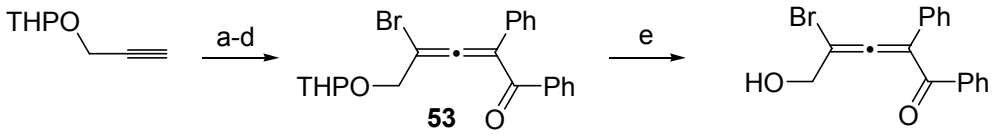
[8]. Montmury, M.; Goré, J. *Synth. Comm*. **1980**, *10*, 873.

51 : To a flash dried, argon-filled, round-bottomed two-necked 25 ml flask equipped with a rubber septum, stir bar, and T-shaped stopcock with argon balloon, were sequentially added anhydrous THF (10 mL) and 1-nonyne (0.83 mL, 621 mg, 5.0 mmol). The flask was placed in a dry ice/acetone bath and cooled to -78 ^{o}C. To the flask was added dropwise *n*-butyllithium (2.2 mL, 2.5 M solution in hexanes, 5.5 mmol). The resulting solution was allowed to warm to room temperature, stirred for 30 minutes, and cooled again to -78 ^{o}C. To the flask was then added pyruvaldehyde dimethyl acetal (0.59 mL, 590 mg, 5.0 mmol). The resulting solution was allowed to warm to room temperature, then poured into saturated ammonium chloride solution (120 mL), and thoroughly extracted with ether (30 mL). The organic phase was then dried with magnesium sulfate, concentrated, and purified over silica gel (100 mL) treated with 3% triethylamine using 1:20 ethyl acetate:hexanes as eluent to afford **51** (758 mg, 66%). ^{1}H NMR (500.13 MHz, $CDCl_3$) ẟ4.12 (s, 1H), 3.57 (s, 6H), 3.54 (d, J = 5.9 Hz, 2H), 2.20 (t, J = 7.2 Hz, 2H), 1.53-1.45 (m, 2H), 1.43 (s, 3H), 1.34-1.24 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H). NMR (125.76 MHz, $CDCl_3$) δ 111.1, 109.2, 85.1, 81.1, 74.6, 70.0, 57.8, 31.7, 28.8, 25.2, 24.6, 22.6, 18.8, 14.1.

52 : To a flash dried, argon-filled, round-bottomed two-necked 50 ml flask equipped with a rubber septum, stir bar, and T-shaped stopcock with argon balloon were sequentially added anhydrous THF (10 mL) and acetal **51** (353 μL, 342.5 mg, 1.41 mmol). The flask was stirred while cooling in a dry ice/acetone bath to -78 ^{o}C, and *n*-butyllithium (0.6 mL, 2.5 M solution in hexanes, 1.5 mmol) was added dropwise. The resulting solution was allowed to stir for 30 minutes, and then allowed to warm to room temperature. The flask was then cooled again to -78 ^{o}C and to the flask was added a solution of tosyl chloride (343 mg, 1.8 mmol) in anhydrous THF (1 mL). The resulting solution was allowed to stir for 30 minutes at -78 ^{o}C and then allowed to warm to room temperature. After the alcohol was judged to be consumed by TLC, the flask was again cooled to -78 ^{o}C and treated with a solution of $CuBr{\cdot}SMe_2$ (514 mg, 2.5 mmol) and lithium bromide (217 mg, 2.5 mmol) in anhydrous THF (1 mL).[8] The reaction mixture was then left in the cooling bath and allowed to warm slowly to room temperature overnight. The reaction was then poured into saturated ammonium chloride solution (100 mL) and extracted with ether (50 mL). The ethereal phase was then washed once each with saturated sodium bicarbonate solution (60 mL) and brine (50 mL), dried over magnesium sulfate, and concentrated. The residue was purified over silica gel (50 mL) treated with 3% triethylamine using 1:1 dichloromethane:hexanes as eluent to afford acetal **52** and a trace amount of aldehyde (194 mg, 55%). ^{1}H NMR (400.13 MHz, $CDCl_3$) ẟ4.67 (s, 1H), 3.34 (s, 3H), 3.33 (s, 3H),2.45-2.38 (m, 2H), 1.74 (s, 3H), 1.50 (dq, J = 7.3, 7.1 Hz, 2H), 1.35-1.24 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H). NMR (100.62 MHz, $CDCl_3$) δ 197.7, 104.7, 103.5, 94.2, 53.8, 53.5, 38.1, 31.8, 29.0, 28.4, 27.9, 22.7, 14.1, 13.7.

20d : Acetal **52** was hydrolyzed to give aldehyde **20d (**86%) using a known procedure.[9] ^{1}H NMR (500.13 MHz, $CDCl_3$) ẟ9.60 (s, 1H), 2.57-2.48 (m, 2H), 1.86 (s, 3H), 1.60-1.51 (m, 2H), 1.35-1.25 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H). NMR (125.76 MHz, $CDCl_3$) δ 211.9, 190.7, 109.3, 95.4, 37.1, 31.7, 28.9, 28.4, 27.7, 22. 6, 14.1, 11.0.

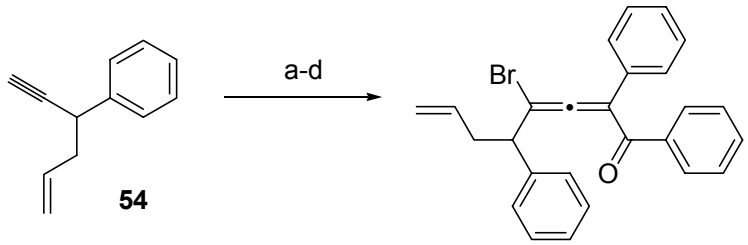
[9] Huet, F.; Lechevalier, A.; Pellet, M.; Conia, J. M. *Synthesis*, **1978**, 63.



(a) *n*-BuLi; (b) $(PhCO)_2$; (c) TsCl; (d) $LiCuBr_2$ (1.5 equiv), 32%; (e) PPTS, EtOH, 64%.

53 : To a 25 ml flash-dried round-bottomed two-necked flask equipped with a stir bar, rubber septum, and T-shaped stopcock with an argon filled balloon were added anhydrous THF (20 mL) and THP ether (1.4 mL, 10 mmol).[10] The solution was cooled to -78 ^oC while stirring in a dry ice/acetone bath and *n*-butyllithium (4.4 mL of a 2.5M solution in hexanes, 11.0 mmol) was added slowly dropwise. The solution was allowed to warm to room temperature and was transferred dropwise via cannula to an identically prepared 100 mL round-bottomed two-necked flask containing benzil (2.1 g, 10 mmol) in anhydrous THF (20 mL) at -78 ^oC under argon atmosphere. The resulting purple-brown solution was allowed to warm to room temperature and then cooled again to -78 ^oC. To this flask was added a solution of tosyl chloride (2.48 g, 13 mmol) in anhydrous THF (4 mL), and after ten minutes of stirring at -78 ^oC was then added a well-stirred solution of lithium bromide (1.3 g, 15 mmol) and copper bromide dimethylsulfide complex (3.1 g, 15 mmol) in anhydrous THF (20 mL).[11] The solution was left in the dry ice/acetone bath to warm slowly overnight. The reaction mixture was poured into saturated ammonium chloride solution (450 mL) and was thoroughly extracted with ether (100 mL). The organic phase was then washed once each with of saturated sodium bicarbonate and brine (300 mL each), dried with anhydrous magnesium sulfate, concentrated, and purified over silica gel (200 mL) using 1:20 ethyl acetate:hexanes as eluent to afford **53 (**826 mg, 32% yield). ^1H NMR (400.13 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 2H), 7.61 (t, J = 7.6 Hz, 2H), 7.52-7.47 (m, 4H), 7.42-7.32 (m, 3H), 4.61 (t, J = 3.5 Hz, 0.5H), 4.42-4.32 (m, 3H), 3.80-3.72 (m, 4H), 3.42-3.32 (m, 1H), 1.80-1.71 (m, 2H), 1.57-1.45 (m, 4H); ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 203.7, 202.8, 191.3, 137.3, 133.7 (2C), 133.5 (2C), 131.4, 129.6 (2C), 128.7 (4C), 128.5 (4C), 128.4 (2C), 113.6, 113.3, 97.2 (2C), 94.0, 93.9, 67.8, 67.6, 62.3, 62.1, 60.3, 30.1, 25.2, 21.0, 19.0, 14.1.

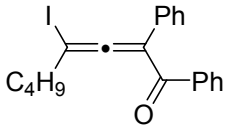
20e : 53 (426 mg, 1.03 mmol) was hydrolyzed to give **20e (**64%) using 1:1 ether:hexanes as eluent. ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.04 (d, J = 7.3 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.52-7.46 (m, 4H), 7.41-7.35 (m, 3H), 4.35 (d, J = 2.2 Hz, 2H), 2.26 (s, 1H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 201.0, 191.3, 137.0, 133.9, 131.4, 129.8 (2C), 129.1, 128.9 (2C), 128.6 (2C), 128.3 (2C), 114.5, 97.0, 64.9.



(a) *n*-BuLi, THF, -78 ºC; (b) $(PhCO)_2$; (c) TsCl; (d) $LiCuBr_2 \cdot SMe_2$, 31%.

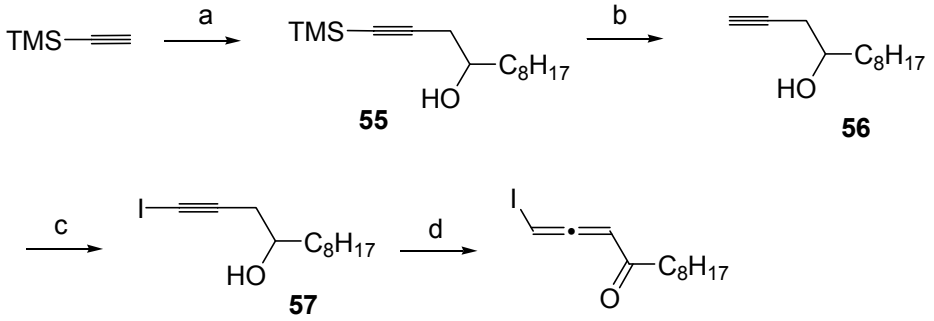
[10].Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem*. **1977**, *42*, 3772.
[11].Montmury, M.; Goré, J. *Synth. Comm*. **1980**, *10*, 873.

20f : To a stirred solution of enyne **54**[12] (0.59 g, 3.8 mmol) in THF (15 mL) at -78 ^{o}C was added dropwise *n*-BuLi (2.5 M solution in hexanes, 1.6 mL, 3.8 mmol) followed by stirring for 30 min. The resultant mixture was then added *via* cannula to a solution of benzil (0.80 g, 3.8 mmol) in THF (10 mL) at -78 ^{o}C. The mixture was allowed to warm to room temperature and after 10 minutes, was cooled down again to -78 ^{o}C. To this mixture, a solution of TsCl (0.87 g, 4.6 mmol) in THF was added dropwise followed by stirring for 1 h at -78 ^{o}C. In a separate flask, a solution of $LiCuBr_2$ was prepared by mixing $CuBr{\cdot}Me_2S$ (1.20 g, 5.7 mmol) and LiBr (0.50 g, 5.7 mmol) in THF (6 mL). This solution was added to the reaction mixture at -78 ^{o}C, which was then allowed to warm up to room temperature. After 1 h, the reaction mixture was poured into a 5% aqueous solution of $Na_2S_2O_3$, and extracted with ether. The combined organic phases were washed with sodium bicarbonate solution, water, and brine, dried over Na_2SO_4, filtered, and concentrated. Crude residue was purified by column chromatography eluted with hexane/DCM/Et_2O (20/2/1) to give ca. 90% pure material, which was additionally purified in the same manner to obtain **20f** (0.51 g, 1.2 mmol, 31%) as a mixture of two diastereomers ca.1:1. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.06 (ps.dd, *J* = 8.4 Hz, 1.2 Hz, 2H), 8.00 (ps.dd, *J* = 8.4 Hz, 1.2 Hz, 2H), 7.65-7.13 (group of multiplets, 24 H), 6.88 (dd, *J* = 8.8 Hz, 1.8 Hz, 2H), 5.63-5.44 (m, 2H), 5.03-4.81 (m, 4H), 3.70 (q, *J* = 7.7 Hz, 2H), 2.65 (ps.sextet, *J* = 7.3 Hz, 2H), 2.51 (quintet, *J* = 6.6 Hz, 1H), 2.43 (quintet, *J* = 6.6 Hz, 1H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 203.8, 203.0, 192.0, 191.6, 140.0, 137.8, 137.5, 134.8, 134.6, 133.4, 133.3, 131.7, 131.5, 130.2, 129.6(2C), 129.4(2C), 128.8(2C), 128.7(3C), 128.52(2C), 128.47(2C), 128.43(2C), 128.40(2C), 128.36(2C), 128.2(2C), 127.9(2C), 127.8(2C), 127.3, 127.2, 127.0, 117.3(2C), 113.2, 113.0, 101.4, 101.2, 53.1, 52.6, 39.1, 38.2. ^{1}H and ^{13}C NMR charts are provided; see Appendix Y.



20g : To a 25 ml flash-dried round-bottomed two-necked flask equipped with a stir bar, rubber septum, and T-shaped stopcock with an argon filled balloon were added anhydrous THF (10 mL) and 1-hexyne (0.6 mL, 5.5 mmol). The solution was cooled to -78 ^{o}C while stirring in a dry ice/acetone bath and *n*-butyllithium (2.2 mL of a 2.5M solution in hexanes, 5.5 mmol) was added slowly dropwise. The solution was allowed to warm to room temperature and was transferred dropwise via cannula to an identically prepared 100 mL round-bottomed two-necked flask containing benzil (1.05 g, 5.0 mmol) and anhydrous lithium iodide (1.0 g, 7.5 mmol) in anhydrous THF (10 mL) at -78 ^{o}C under argon atmosphere. The resulting solution was allowed to warm to room temperature and then cooled again to -78 ^{o}C. To this flask was added a solution of tosyl chloride (1.05 g, 5.5 mmol) in anhydrous THF (5 mL). The solution was allowed to warm to room temperature and stirred for 40 minutes. The reaction mixture was then poured into saturated ammonium chloride solution (500 mL) and was thoroughly extracted with ether (150 mL). The organic phase was then washed twice with saturated sodium thiosulfite (150 mL), twice with brine (200 mL), dried with anhydrous magnesium sulfate, concentrated, and purified over silica gel (100 mL) using 1:3 dichloromethane:hexanes as eluent to afford **20g** (182 mg, 9%) as an orange oil. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.99-7.97(m, 2H), 7.63-7.59 (m, 1H), 7.53-7.49 (m, 4H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.36-7.32 (m, 1H), 2.48-2.38 (m, 2H), 1.43 (quint, *J* = 7.4 Hz, 2H), 1.15 (dsext, 14.7, 7.3 Hz, 2H), 0.80 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 203.9, 192.2, 138.0, 133.2, 131.8, 129.3 (2C), 128.7, 128.5 (2C), 128.5 (2C), 128.2 (2C), 108.0, 68.8, 39.7, 31.0, 21.3, 13.6.

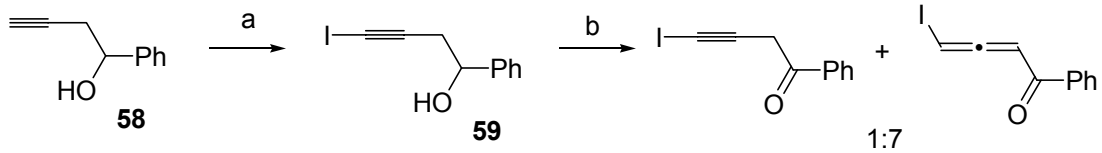
[12].Schwier, T.; Rubin, M.; Gevorgyan, V. *Org. Lett.* **2004**, *6*, 1999.



(a) *n*-BuLi, $BF_3{\cdot}OEt_2$ -78 ºC, 1,2-epoxydecane, 77%; (b) K_2CO_3, MeOH, quant.; (c) *n*-BuLi, NIS, 80%; (d)DMP, DCM, 81%.

55: To a stirred solution of trimethylsilylacetylene (2.2 mL, 15.4 mmol) at -78 ^oC was added dropwise *n*-BuLi (2.5 M in hexanes, 6.2 mL, 15.5 mmol). After stirring for 30 min, $BF_3{\cdot}Et_2O$ (2.8 mL, 23.1 mmol) was added followed by 1,2-epoxydecane (3.6 mL, 20.0 mmol), and the mixture was stirred for 1 h at -78 ^oC. The reaction mixture was quenched with aqueous NH_4Cl and extracted with ethyl acetate. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (5-10% EtOAc in hexane) to give homopropargyl alcohol **55** (3.03 g, 11.9 mmol, 77%). Treatment of **55** with 1.1 equiv of K_2CO_3 in methanol followed by purification of a concentrated reaction mixture on silica gel (10% EtOAc in hexane as eluent) afforded **56** in quantitative yield.

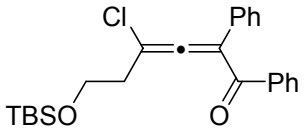
20h : To a stirred solution of alcohol **56** (0.57 g, 3.1 mmol) in THF at -78 ^oC was added dropwise *n*-BuLi (2.5 M in hexanes, 2.5 mL, 6.2 mmol) followed by stirring for 30 min at -78 ^oC. A solution of NIS (1.40 g, 6.2 mmol) in THF was added to the mixture and the reaction was allowed to warm up to room temperature and then was quenched with H_2O, and extracted with ether. The combined organic phases were washed with aqueous $Na_2S_2O_3$ (5%), water, and brine, dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (5-10% EtOAc in hexane as eluent) to give **57** (0.77 g, 2.5 mmol, 80%). Dess-Martin oxidation following the typical procedure afforded **20h** (0.62 g, 2.0 mmol, 81%). ^1H NMR (500.13 MHz, $CDCl_3$) δ 6.22 (d, J = 5.9 Hz, 1H), 5.45 (d, J = 5.9 Hz, 1H), 2.60-2.49 (m, 2H), 1.60-1.52 (m, 2H), 1.28-1.20 (m, 10H), 0.83 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 210.8, 199.3, 97.1, 39.9, 36.7, 29.2, 29.1, 29.0, 24.3, 22.5, 14.0.



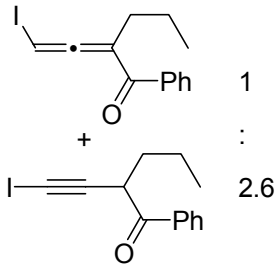
(a) NIS, $AgNO_3$, 65%; (b) DMP, DCM, 89%.

20i: A solution of **58** (0.27 g, 1.86 mmol) in acetone (2 mL) was added to a stirred mixture of NIS (0.50 g, 2.23 mmol, 1.2 equiv.) and $AgNO_3$ (0.32 g, 1.86 mmol) in acetone (15 mL). The reaction flask was covered with aluminum foil and the mixture was stirred for 20 hrs at room temperature. The reaction was quenched with water, extracted with ether, washed with water and brine; dried over Na_2SO_4, filtered, and concentrated. Purification by column chromatography (eluent hexane/EtOAc/DCM/benzene 6:1:1:1) afforded **59** (0.33 g, 1.2 mmol, 65%). Dess-Martin oxidation following the typical procedure afforded allene **20i** as a 7:1 mixture with alkyne

29i (0.29 g, 1.1 mmol, 89%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.97 (ps.d, *J* = 8.4 Hz, 2H, minor), 7.89 (ps.d, *J* = 7.7 Hz, 2H, major), 7.59 (ps.t, *J* = 7.3 Hz, 1H), 7.48 (ps.t, *J* = 7.7 Hz, 3H), 6.25 (d, *J* = 5.9 Hz, 1H, allene CH), 6.08 (d, *J* = 5.9 Hz, 1H, allene CH), 4.03 (s, 2H, propargyl CH_2); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ210.9, 189.9, 137.1, 133.2, 128.7, 128.5, 94.8, 38.3.

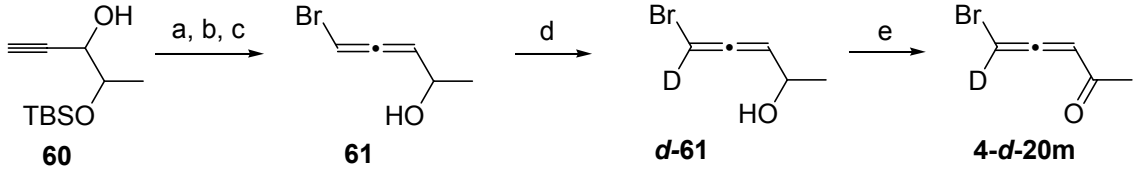


20j : To a 25 ml flash-dried round-bottomed two-necked flask equipped with a stir bar, rubber septum, and T-shaped stopcock with an argon filled balloon were added: anhydrous THF (10 mL) and 3-butynyl (*t*-butyldimethyl)silyl ether (1.1 mL, 5.1 mmol). The solution was cooled to -78 ^{o}C while stirring in a dry ice/acetone bath and *n*-butyllithium (2.2 mL, 2.5M solution in hexanes, 5.5 mmol) was added slowly dropwise. The solution was allowed to warm to room temperature and was transferred dropwise via cannula to an identically prepared 50 ml round-bottomed two-necked flask containing benzil (1.18 mg, 5.6 mmol) in anhydrous THF (10 mL) at -78 ^{o}C under argon atmosphere. The resulting purple-brown solution was allowed to warm to room temperature and then cooled again to -78 ^{o}C. To this flask was added a solution of tosyl chloride (1.4 g, 7.3 mmol, 1.4 equiv.) in anhydrous THF (2 mL). The solution was allowed to stir at -78 ^{o}C for 15 minutes, and was then treated with a solution of LiCl (379 mg, 7.5 mmol) and CuCl (742 mg, 7.5 mmol) in anhydrous THF (10 mL).[8] The resulting mixture was left in the dry ice/acetone bath to warm slowly overnight. The reaction mixture was poured into saturated ammonium chloride solution (500 mL) and extracted with ether (200 mL). The organic extract was washed once each with saturated $NaHCO_3$ (300 mL) and brine (200 mL). The organic phase was then dried with anhydrous magnesium sulfate and concentrated. Purification over silica (220 mL) using 1:3 dichloromethane:hexanes as eluent afforded **20j** (403 mg, 20%) contaminated with unreacted benzil. Additional purification over silica (100 mL) using 1:20 ethyl acetate:hexanes as eluent gave analytically pure chloroallenone **20j**. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ8.05 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.63-7.60 (m, 1H), 7.53-7.48 (m, 4H), 7.41-7.37 (m, 2H), 7.36-7.32 (m, 1H), 3.86-3.80 (m, 1H), 3.76 (dt, *J* = 10.3, 5.9 Hz, 1H), 2.71-2.63 (m, 1H), 2.60 (ddd, *J* = 14.9, 5.9, 5.7 Hz, 1H), 0.85 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 203.7, 192.0, 137.2, 133.6, 132.2, 129.7 (2C), 128.7 (4C), 128.3 (2C), 112.9, 108.0, 59.8, 39.6, 25.9 (3C), 18.3, -5.5 (2C).



20k : (analagously to **20a**: 0.292g, 0.94 mmol, 18% yield from 1-iodohexa-1,2-diene[13]). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 - 8.06 (m, 2 H), 7.79 - 7.84 (m, 2 H), 7.52 - 7.60 (m, 3 H), 7.41 - 7.51 (m, 3 H), 6.07 (s, 1 H), 4.29 (dd, *J*=7.52, 6.79 Hz, 1 H), 2.48 (td, *J*=7.43, 2.38 Hz, 2 H), 1.81 - 1.91 (m, 2 H), 1.51 - 1.64 (m, 2 H), 1.39 - 1.50 (m, 2 H), 1.02 (t, *J*=7.34 Hz, 3 H), 0.96 (t, *J*=7.34 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.4, 195.2, 193.1, 138.0, 135.4, 133.5, 132.6, 128.9, 128.8, 128.7, 128.3, 109.4, 91.4, 41.9, 39.7, 33.6, 29.7, 20.8, 20.6, 13.9, 13.8, 0.0.

Synthesis of 4-*d*-20m:



[13] Baker, C. S. L.; Landor, P. D.; Landor, S. R.; Patel, A. N. *J. Chem. Soc.* **1965**, 4348.

(a) MsCl, Et_3N, DCM, 100%; (b) $LiCuBr_2 \cdot SMe_2$; (c) TBAF, THF, 70%; (d) NaOD, DMF, D_2O, (e) DMP, DCM, 34%.

61 : Mesyl chloride (3.5 mL, 45.5 mmol, 1.3 equiv.) was added dropwise to a stirred solution of diol **60**[3] (7.56 g, 35 mmol) and triethylamine (10 mL, 70 mmol, 2 equiv.) in DCM at 0 ^oC. The reaction mixture was stirred for 30 min, and then quenched by addition of ice cold saturated ammonium chloride solution. The aqueous phase was extracted with DCM, washed with cold water, brine, dried over Na_2SO_4, filtered, and concentrated to give crude mesylate (10.24 g, 35 mmol, 100%). The resulting mesylate (4.48 g, 15.3 mmol) was dissolved in THF (10 mL) and added to a stirred solution of $CuBr \cdot Me_2S$ (4.72 g, 23.0 mmol) and LiBr (2.0 g, 23.0 mmol) in THF (25 mL). The reaction mixture was stirred for 13 hrs, quenched by addition of saturated ammonium chloride solution, extracted with pentane/ether (2:1), washed with water, brine, dried over $MgSO_4$, filtered, and concentrated. To the crude residue dissolved in THF (5 mL) was added a solution of TBAF (1 M in THF, 18 mL), and the mixture was stirred at room temperature for 30 min. Brine was added and the product was extracted with ether. The combined organic extracts were washed with ammonium chloride, water, brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure using an ice bath. Column chromatography on silica gel (eluent pentane/ether 2:1 to 2:3) afforded allenol **61** (1.75 g, 10.7 mmol, 70%) as a 1:3 mixture of two diastereomers. ^1H NMR (500.13 MHz, $CDCl_3$) δ6.10 (dd, J = 5.6 Hz, 1.9 Hz, 1H, minor), 6.08 (dd, J = 5.6 Hz, 1.9 Hz, 1H, major), 5.489 (t, J = 5.4 Hz, 1H, minor), 5.494 (t, J = 5.6 Hz, 1H, major), 4.48 (br.m, 1H), 2.14 (br.s, 1H), 1.35 (dd, J = 6.5 Hz, 3H, minor), 1.34 (dd, J = 6.3 Hz, 3H, major); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ200.4, 105.4 (minor), 105.3 (major), 74.4 (minor), 74.2 (major), 65.1, 22.9.

***d*-61 :** Deuterated allenol ***d*-61** was obtained by hydrogen-deuterium exchange under conditions described in the literature.[14] To freshly distilled DMF (4 mL) was added Na (10 mg, 0.44 mmol) followed by D_2O (1 mL). After sodium was completely dissolved, allenol **61** (0.71 g, 4.36 mmol) was added and the mixture was stirred for 15 hrs. The reaction was quenched by addition of D_2O and ether. The ethereal fraction was washed 4 times with D_2O, dried over $MgSO_4$, filtered, and concentrated. Crude ^1H NMR analysis showed deuterium incorporation of 90%. The entire procedure was repeated one more time; after 7 hr stirring and analogous workup crude 5-bromopenta-3,4-dien-2-ol-d_1 ***d*-61** was obtained with >98% deuterium incorporation.

4-*d*-20m: Crude alcohol ***d*-61** was subjected to standard conditions for Dess-Martin oxidation (see above). The reaction mixture was stirred for 30 min; then quenched by addition of D_2O, and extracted with DCM. Combined DCM extracts were dried over Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography on silica gel (eluent pentane/ether 10:1) afforded 5-bromopenta-3,4-dien-2-one-d_1 **4-*d*-20m:** (0.242 g, 1.5 mmol, 34%; 98% deuterium purity). ^1H NMR (400.13 MHz, $CDCl_3$) δ 6.36 (d, J = 5.9 Hz, 0.02H), 5.73 (s, 1H), 2.26 (s, 1H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ210.7, 196.2, 102.1, 74.3 (t, $J_{C\text{-}D}$ = 32.1 Hz), 27.1.

General procedure for catalyst optimization for cycloisomerization of 20 to 21

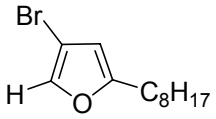
In a glovebox under nitrogen atmosphere, to a 0.5 ml Wheaton microreactor equipped with a spin vane and screw cap with a PTFE-faced silicone septum under nitrogen atmosphere was added catalyst. The microreactor was removed from the glovebox and anhydrous solvent

[14].Mavrov, M. V.; Rodionov, A. P.; Kucherov, V. F. *Izvestiya Akad. Nauk SSSR, Ser. Khim.* **1971**, 885.

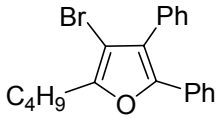
(100 μL) was added followed by allenyl ketone **20a** or **20c** (0.1 mmol). For **20a, y**ields were determined by GC/MS using tetradecane as the internal standard. For **20c**, the reactions were monitored by GC/MS using pentadecane as the internal standard. For reported NMR yields the reaction mixtures were filtered through aluminum oxide followed by dichloromethane, concentrated, and analyzed by ^{1}H NMR using dibromomethane as an internal standard.

Typical procedure for cycloisomerization:

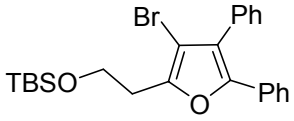
20b: In a glovebox under nitrogen atmosphere, to a 3.0 mL Wheaton microreactor equipped with a spin vane and screw cap with a PTFE faced silicone septum under nitrogen atmosphere was added $AuCl_3$ (6.2 mg, 0.02 mmol, 2 mol%). The microreactor was removed from the glovebox and 1 mL of anhydrous toluene and **20b** (360 mg, 1.02 mmol) were sequentially added and stirred for 24 hours. After the reaction was judged compete by TLC, it was quenched by filtration through a pad of alumina with dichloromethane, concentrated, and purified over silica gel (30 mL) using hexanes as eluent to afford **21b** (270 mg, 0.75 mmol, 75%) as a colorless oil which solidifies upon storage.



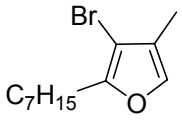
21a: (hexanes as eluent; yield 87 mg, 0.34 mmol, 86%, contains ca. 5% of regioisomer **22a**) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.28 (s, 1H), 6.04 (s, 1H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.60 (quintet, *J* = 7.6 Hz, 2H), 1.34-1.21 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 157.7, 138.9, 108.4, 99.7, 31.8, 29.3, 29.2, 29.1, 28.0, 27.7, 22.7, 14.1; HRMS (EI) calcd. for $C_{12}H_{19}BrO$ [M^+]: 258.0619. Found: 258.0632.



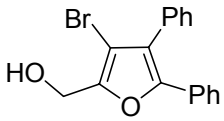
21b: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.45-7.37 (m, 7H), 7.25 (t, *J* = 7.3 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 2.79 (t, *J* = 7.4 Hz, 2H), 1.79-1.72 (quintet, 2H), 1.51-1.43 (sextet, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 152.3, 147.1, 132.5, 130.5, 130.2 (2C), 128.6 (2C), 128.3 (2C), 127.8, 127.3, 125.4 (2C), 122.7, 100.7, 29.9, 26.3, 22.3, 13.8. HRMS (EI) calcd. for $C_{20}H_{19}BrO$ [M^+]: 354.0619. Found: 354.0639.



21c: (1:2 dichloromethane:hexanes as eluent; yield 175 mg, 0.38 mmol, 73%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.45-7.35 (m, 7H), 7.26-7.18 (m, 3H), 3.98 (t, *J* = 6.8 Hz, 2H), 3.02 (t, *J* = 6.8 Hz, 2H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 149.3, 147.6, 132.4, 130.4, 130.1 (2C), 128.6 (2C), 128.3 (2C), 127.8, 127.4, 125.4 (2C), 122.9, 102.2, 61.0, 30.7, 25.9 (3C), 18.3, -5.4 (2C). HRMS (EI) calcd. for $C_{24}H_{29}BrO_2Si$ [M^+]: 456.1120. Found: 456.1118.

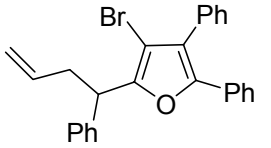


21d: (hexanes as eluent; yield 78.4 mg, 0.3 mmol, 73%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.10 (d, *J* = 1.5 Hz, 1H), 2.65-2.56 Hz (m, 2H), 1.96 (d, *J* = 1.1 Hz, 3H), 1.62-1.59 (m, 2H), 1.34-1.25 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 153.0, 137.0, 120.9, 99.8, 31.8, 29.0, 27.7, 26.5 (2C), 22.6, 14.1, 9.1. MS *m/z* (relative intensity): 260 [M^+] (10), 258 [M^+] (11), 175 [M^+ - Hexyl] (94), 175 [M^+ - Hexyl] (100).

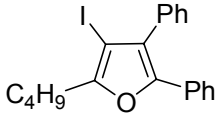


21e: (1:3 dichloromethane:hexanes as eluent; yield 94 mg, 0.29 mmol, 61%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ7.46-7.38 (m, 7H), 7.27-7.19 (m, 3H), 4.31

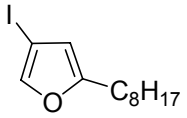
(s, 2H), 1.27 (s, 1H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 148.3, 146.2, 132.1, 130.2 (2C), 128.6 (2C), 128.3 (2C), 128.0, 127.7, 125.6 (2C), 123.0, 109.5, 102.4, 24.9.



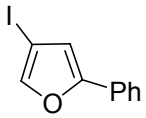
21f: (5:1:1 hexanes:DCM:benzene as eluent; yield 256 mg, 0.6 mmol, 88%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.46-7.42 (m, 5H), 7.41-7.38 (m, 4H), 7.31-7.22 (m, 4H), 5.84 (ddt, *J* = 16.9 Hz, 10.3 Hz, 6.6 Hz, 1H), 5.17 (ddt, *J* = 16.9 Hz, 1.5 Hz, 1.5 Hz, 1H), 5.06 (ddt, *J* = 10.3 Hz, 1.5 Hz, 1.5 Hz, 1H), 4.36 (dd, *J* = 8.8 Hz, 7.3 Hz, 1H), 3.10-3.04 (m, 1H), 2.93-2.87 (m, 1H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 151.9, 147.7, 141.2, 135.7, 132.2, 130.5, 130.2 (2C), 128.61 (2C), 128.55 (2C), 128.4 (2C), 127.9 (3C), 127.5, 126.8, 125.5 (2C), 122.7, 116.9, 101.4, 43.7, 36.5. HRMS (EI) calcd. for $C_{26}H_{21}BrO$ [M^+]: 428.0776. Found: 428.0759.



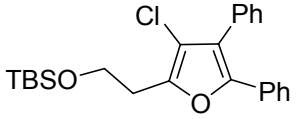
21g: (1:40 ethyl acetate:hexanes as eluent; yield 121 mg 0.30 mmol, 73%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.45-7.40 (m, 4H), 7.37-7.32 (m, 3H), 2.81 (t, *J* = 7.4 Hz, 2H), 1.77-1.71 (quintet, 2H), 1.50-1.42 (sextet, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 155.8, 147.7, 134.0, 130.5, 130.3 (2C), 128.6 (2C), 128.3 (2C), 127.8, 127.2, 125.3 (2C), 71.6, 30.3, 27.8, 22.3, 13.9. HRMS (EI) calcd. for $C_{20}H_{19}IO$ [M^+]: 402.0481. Found: 402.0479.



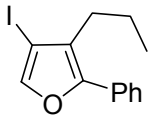
21h: (hexanes as eluent; yield 148 mg, 0.49 mmol, 97%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.30 (d, *J* = 0.7 Hz, 1H), 6.09 (d, *J* = 0.7 Hz, 1H), 2.61 (t, *J* = 7.5 Hz, 2H), 1.62 (quintet, *J* = 7.3 Hz, 2H), 1.37-1.25 (m, 10H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 158.3, 143.7, 111.8, 64.1, 31.8, 29.3, 29.2, 29.1, 27.82, 27.75, 22.6, 14.1. HRMS (EI) calcd. for $C_{12}H_{19}IO$ [M^+]: 306.0481. Found: 306.0476.



21i: (hexanes as eluent; yield 57 mg, 0.21 mmol, 71%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.2 Hz, 1.4 Hz, 2H), 7.47 (s, 1H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.30 (tt, *J* = 7.3 Hz, 1.4 Hz, 1H), 6.73 (s, 1H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 155.3, 144.9, 129.6, 128.8(2C), 128.1, 123.9(2C), 111.8, 65.7. HRMS (EI) calcd. for $C_{10}H_7IO$ [M^+]: 269.9542. Found: 269.9558.



21j: (1:20 ethyl acetate:hexanes as eluent; yield 25.4 mg, 0.06 mmol, 48%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.45-7.37 (m, 7H), 7.26-7.19 (m, 3H), 3.97 (t, *J* = 6.8 Hz, 2H), 3.01 (t, *J* = 6.8 Hz, 2H), 0.90 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 147.6, 147.2, 131.7, 130.5, 130.0 (2C), 128.6 (2C), 128.3 (2C), 127.8, 127.4, 125.5 (2C), 121.6, 114.8, 60.9, 29.9, 25.8 (3C), 18.3, -5.4 (2C). HRMS (EI) calcd. for $C_{24}H_{29}ClO_2Si$ [M^+]: 412.1625. Found: 412.1633.

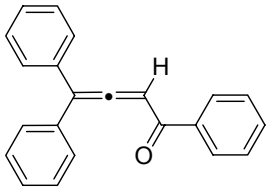


21k : (hexanes as eluent; yield 194 mg, 67%, contains ca. 33% of regioisomer **21l**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 - 7.64 (m, 4 H), 7.47 (s, 1 H), 7.40 - 7.46 (m, 4 H), 7.27 - 7.35 (m, 2 H), 6.54 (s, 1 H), 2.57 - 2.65 (m, 4 H), 1.61 - 1.72 (m, 4 H), 1.05 (t, *J*=7.43 Hz, 3 H), 1.01 (t, *J*=7.34 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 149.0, 143.9, 130.9, 130.8, 128.7, 128.5, 127.6, 127.4, 125.6, 125.6, 124.5, 123.9, 123.1, 86.5, 73.6, 28.3, 27.7, 23.1, 14.2, 14.1.

1,2-ALKYL/ARYL MIGRATION

Preparation of Starting Materials

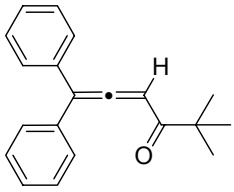
1,4,4-triphenylbuta-2,3-dien-1-one[15] **(25a)** was prepared via Wittig olefination similar to the procedure reported by Petasis and co-workers.[16] To an ice-cooled (0°C) solution of 1-phenyl-2-(triphenylphosphoranylidene)ethanone (3.0 g, 7.89 mmol) and triethylamine (1.1 ml, 7.89 mmol) in 23 ml of dry dichloromethane stirred under argon was added dropwise a solution of diphenylacetyl chloride (2.02 g, 7.89 mmol) in 8 ml of dry dichloromethane. The resulting bright yellow solution was stirred for 2 h. After removal of half of the solvent, the residue was diluted with diethyl ether to precipitate triphenylphosphine oxide. After filtration, silica gel was added to adsorb the reaction products and the solvent was evaporated in vacuo. Flash Silica column chromatography (1:10 EtOAc/hexanes) gave the product as a light yellow oil. Yield: 2.3 g (7.65 mmol, 97%).



25a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.85 (m, 2 H), 7.49 – 7.53 (m, 1 H), 7.30 – 7.41 (m, 12 H), 6.82 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.14, 191.51, 137.48, 134.26 (2C), 132.79 (+), 128.77 (+, 4C) 128.73 (+, 2C) 128.61 (+, 4C) 128.34 (+, 4C) 113.75, 96.57 (+).

5,5-diphenylpenta-3,4-dien-2-one[16] **(25b)** was prepared analogously to **25a** from commercially available 1-(triphenylphosphoranylidene)propan-2-one and diphenylacetyl chloride in 83% yield.

2,2-dimethyl-6,6-diphenylhexa-4,5-dien-3-one (25c) was prepared analogously to **25a** from 3,3-dimethyl-1-(triphenylphosphoranylidene)butan-2-one[17] in 92% yield according to the reported literature procedure.[16]

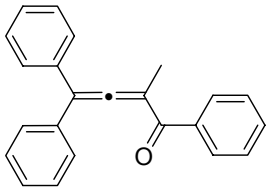


25c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 - 7.43 (m, 10 H), 6.60 (s, 1 H), 1.25 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.79, 204.00, 134.50 (2C) 128.69 (+, 4C) 128.62 (+, 4C) 128.12 (+, 2C) 113.49, 93.88 (+), 44.38, 26.65 (+, 3C).

2-methyl-1,4,4-triphenylbuta-2,3-dien-1-one (25d) was prepared via Wittig olefination from 2-methyl-1-phenyl-2-(triphenylphosphoranylidene)ethanone[18] similar to the procedure reported by Bestmann and co-workers.[19] To a solution of 2-methyl-1-phenyl-2-(triphenylphosphoranylidene)ethanone (3.94 g, 10.0 mmol) in 12 ml of dry THF stirred under argon was added a solution of diphenylacetyl chloride (1.28 g, 5.0 mmol) in 4 ml of dry THF. The resulting solution was refluxed for 4 h. The reaction mixture was diluted with diethyl ether to precipitate triphenylphosphine oxide. After filtration, silica gel was added to adsorb the

[15] Dupre, M.; Strzelecka, H. *C. R. Acad. Sci. Ser. C.* **1972**, *274*, 1091.
[16] Petasis, N. A.; Teets, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 10328.
[17] Oare, D. A.; Henderson, M. A.; Sanner, M. A.; Heathcock, C. H. *J. Org. Chem.* **1990**, *55*, 132.
[18] Facchin, G.; Bertani, R.; Berton, A.; Gleria, M. *Inorg. Chim. Acta* **1988**, *147*, 165.
[19] Bestmann, H. J.; Hartung, H. *Chem. Ber.* **1966**, *99*, 1198.

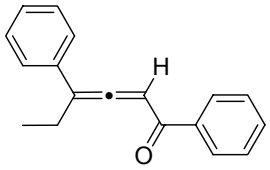
reaction products and the solvent was evaporated in vacuo. Flash Silica column chromatography (1:10 Et_2O/hexanes) gave the product as a colorless crystalline solid. Yield: 1.13 g (3.65 mmol, 73%).



25d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, J = 8.44, 1.28 Hz, 2 H), 7.38 – 7.43 (m, 1 H), 7.30 – 7.38 (m, 7 H), 7.15 – 7.23 (m, 5 H), 2.20 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.75, 195.11, 138.25, 135.25 (2C), 131.98 (+), 128.69 (+, 4C), 128.59 (+, 2C), 128.48 (+, 4C), 128.02 (+, 2C), 127.84 (+, 2C), 112.31, 104.92, 14.96 (+); mp 95–97°C.

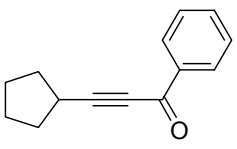
1,4-diphenylpenta-2,3-dien-1-one[20] **(25e)** was prepared analogously to **25a** from commercially available 1-phenyl-2-(triphenylphosphoranylidene)ethanone and 2-phenylpropanoyl chloride (from 2-phenylpropanoic acid) in 81% yield.

1,4-diphenylhexa-2,3-dien-1-one (25f) was prepared analogously to **25a** from commercially available 1-phenyl-2-(triphenylphosphoranylidene)ethanone and 2-phenylbutanoyl chloride in 42% yield.



3f: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.91 (m, 2 H), 7.49 – 7.54 (m, 1 H), 7.34 – 7.42 (m, 6 H), 7.27 – 7.31 (m, 1 H), 6.72 (t, J = 3.30 Hz, 1 H), 2.52 – 2.64 (m, 2 H), 1.16 (t, J = 7.34 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.11, 191.61, 137.70, 134.04, 132.59 (+), 128.75 (+, 2C), 128.59 (+, 2C), 128.31 (+, 2C), 127.84 (+), 126.43 (+, 2C), 111.69, 97.48 (+), 23.16 (–), 12.35 (+).

3-cyclopentyl-1-phenylprop-2-yn-1-one (27h). To an oven dried flask were added anhydrous copper(I) iodide (40mg, 0.2 mmol, 2mol%) and $Pd(PPh_3)_2Cl_2$ (70mg, 0.1 mmol, 1mol%) under N_2 atmosphere. Sixteen ml of dry triethylamine and 1.21 ml (0.982g, 10 mmol) of cyclopentylacetylene were added sequentially to the same flask and the reaction mixture was stirred at room temperature for 10 minutes in the dark. Benzoyl chloride (1.27 ml, 11 mmol) was then added dropwise and the reaction mixture was stirred overnight. The reaction mixture was filtered through a layer of Silica (dichloromethane – eluent), all the solvents were removed in vacuo, and the residue was purified via flash Silica column chromatography (1:10 EtOAc/hexanes) to afford 1.91 g (9.63 mmol, 96%) of 3-cyclopentyl-1-phenylprop-2-yn-1-one **27h** as yellow oil.

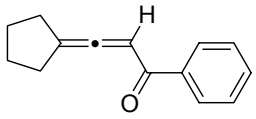


27h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.16 (m, 2 H), 7.55 – 7.61 (m, 1 H), 7.47 (s, 2 H), 2.85 – 2.97 (m, 1 H), 1.97 – 2.12 (m, 2 H), 1.73 – 1.88 (m, 4 H), 1.57 – 1.71 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.38, 137.01, 133.83 (+), 129.53 (+, 2C), 128.48 (+, 2C), 101.01, 79.19, 33.36 (–, 2C), 30.30 (+), 25.28 (–, 2C).

3-cyclopentylidene-1-phenylprop-2-en-1-one (25h). To an oven dried flask were added potassium *tert*-butoxide (1.081g, 9.63 mmol) under argon atmosphere and 96 ml of dry THF. The solution was cooled to -100°C and 3-cyclopentyl-1-phenylprop-2-yn-1-one **27h** (1.91g, 9.63

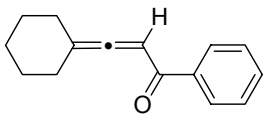
[20] Trifonov, L.; Orakhovats, A.; Linden, A.; Heimgartner, H. *Helv. Chim. Acta* **1992**, *75*, 1872.

mmol) in 96 ml of dry THF cooled to -100°C was added dropwise via cannula. The resulting bright red-orange solution was stirred at -100°C for 4 hours. Acetic acid (0.552 ml, 9.63 mmol) dissolved in 30 ml of anhydrous THF was then added at -100°C via cannula and reaction mixture was allowed to warm to room temperature. The reaction mixture was filtered through a layer of Silica (dichloromethane – eluent), the solvents were removed in vacuo, and the residue was purified via flash Silica column chromatography (1:10 EtOAc/hexanes) to afford 1.01 g (5.1 mmol, 53%) of 3-cyclopentylidene-1-phenylprop-2-en-1-one **25h** as yellow oil.



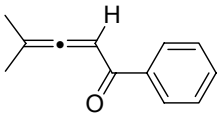
25h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (m, 2 H), 7.49 – 7.54 (m, 1 H), 7.39 – 7.45 (m, 2 H), 6.21 – 6.25 (quintet, *J* = 4.13 Hz, 1 H), 2.44 – 2.60 (m, 4 H), 1.66 – 1.78 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.94, 193.45, 138.11, 132.24 (+), 128.63 (+, 2C), 128.12 (+, 2C), 107.25, 94.67 (+), 31.47 (–, 2C), 27.27 (–, 2C).

1,4-diphenylhexa-2,3-dien-1-one (25i) was prepared analogously to **25a** from commercially available 1-phenyl-2-(triphenylphosphoranylidene)ethanone and cyclohexanecarbonyl chloride in 16% yield.



25i: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 2 H), 7.48 - 7.53 (m, 1 H), 7.38 - 7.44 (m, 2 H), 6.12 (quint, *J*=2.15 Hz, 1 H), 2.16 - 2.29 (m, 4 H), 1.57 - 1.67 (m, 2 H), 1.47 - 1.57 (m, 4 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.6, 193.4, 138.1, 132.1 (+), 128.7 (+, 2C), 128.0 (+, 2C), 105.5, 92.7 (+), 30.1 (-, 2C), 26.5 (-, 2C), 25.6 (-).

4-methyl-1-phenylpenta-2,3-dien-1-one[21] **(25j).** To an oven dried flask were added 1-phenyl-2-(triphenylphosphoranylidene)ethanone (4.0 g, 10.5 mmol) under argon atmosphere and 32 ml of dry dichloromethane. The solution was cooled to 0°C and 2-methylprop-1-en-1-one (10.8 mmol, generated from 2-bromo-2-methylpropanoyl bromide and activated Zn dust by known literature procedure[22]) in 22 ml of dry THF was added dropwise via cannula. The resulting solution was stirred overnight, allowing the reaction mixture to warm to room temperature. After removal of half of the solvent, the residue was diluted with diethyl ether to precipitate triphenylphosphine oxide. After filtration, silica gel was added to adsorb the reaction products and the solvent was evaporated in vacuo. Flash Silica column chromatography (1:10 EtOAc/hexanes) gave the product as a pale yellow oil. Yield: 0.38 g (2.21 mmol, 21%).



25j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.87 (m, 2 H), 7.49 – 7.55 (m, 1 H), 7.38 – 7.46 (m, 2 H), 6.14 – 6.20 (septet, *J* = 2.92 Hz, 1 H), 1.80 (d, *J* = 2.92 Hz, 6 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.29, 193.00, 137.98, 132.33 (+), 128.63 (+, 2C), 128.19 (+, 2C), 99.32, 92.43 (+), 19.42 (+, 2C).

1-(4-methoxyphenyl)-4,4-diphenylbuta-2,3-dien-1-one (25k) was prepared analogously to **3a** from 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone[23] and diphenylacetyl chloride in 91% yield.

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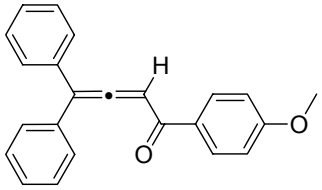
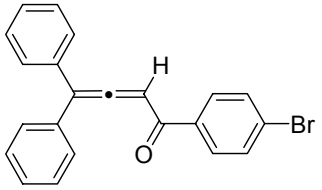
[21] Reuter, J. M.; Salomon, R. G. *Tetrahedron Lett.* **1978**, *19*, 3199.
[22] Wilson, J. E.; Fu, G. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 6358.
[23] Denney, D. B.; Smith, L. C.; Song, J.; Rossi, C. J.; Hall, C. D. *J. Org. Chem.* **1963**, *28*, 778.



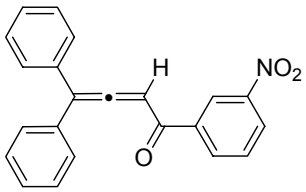
25k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.91 (m, 2 H), 7.31 – 7.42 (m, 10 H), 6.81 – 6.87 (m, 3 H), 3.83 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.38, 189.44, 163.45, 134.44 (2C), 131.12 (+, 2C), 130.32, 128.77 (+, 4C), 128.66 (+, 4C), 128.28 (+, 2C), 113.62 (+, 2C), 113.56, 96.22 (+), 55.47 (+); mp 95–96°C.

1-(4-bromophenyl)-4,4-diphenylbuta-2,3-dien-1-one (25l) was prepared analogously to **3a** from 1-(4-bromophenyl)-2-(triphenylphosphoranylidene)ethanone[23] and diphenylacetyl chloride in 76% yield.



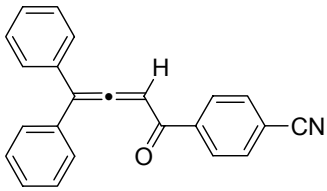
25l: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.25 Hz, 2 H), 7.22 – 7.55 (m, 12 H), 6.75 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.17, 190.48, 136.13, 134.00 (2C), 131.62 (+, 2C), 130.28 (+, 2C), 128.85 (+, 4C), 128.57 (+, 4C), 128.49 (+, 2C), 127.87, 113.97, 96.50 (+); mp 100–102°C.

1-(3-nitrophenyl)-4,4-diphenylbuta-2,3-dien-1-one (25m) was prepared analogously to **3a** from 1-(3-nitrophenyl)-2-(triphenylphosphoranylidene)ethanone[24] and diphenylacetyl chloride in 61% yield.



25m: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (t, *J* = 1.83 Hz, 1 H), 8.35 (ddd, *J* = 8.21, 2.25, 1.10 Hz, 1 H), 8.10 (ddd, *J* = 7.52, 1.47, 1.28 Hz, 1 H), 7.54 (t, *J* = 7.98 Hz, 1 H), 7.35 – 7.44 (m, 6 H), 7.27 – 7.31 (m, 4 H), 6.81 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.76, 189.39, 148.06, 138.70, 134.30 (+), 133.52 (2C), 129.59 (+), 128.95 (+, 4C), 128.75 (+, 2C), 128.56 (+, 4C), 127.00 (+), 123.64 (+), 114.62, 96.64 (+).

4-(4,4-diphenylbuta-2,3-dienoyl)benzonitrile (25n) was prepared analogously to **3a** from 4-[(triphenylphosphoranylidene)acetyl]benzonitrile[24a,25] and diphenylacetyl chloride in 73% yield.

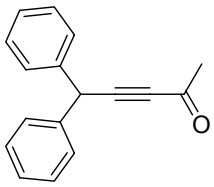


3m: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.84 (m, 2 H), 7.60 – 7.64 (m, 2 H), 7.34 – 7.43 (m, 6 H), 7.23 – 7.28 (m, 4 H), 6.75 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.93, 190.60, 140.78, 133.62 (2C), 132.13 (+, 2C), 129.07 (+, 2C), 128.95 (+, 4C), 128.73 (+, 2C), 128.50 (+, 4C), 117.95, 115.88, 114.45, 96.79 (+); mp 104–105°C.

5,5-diphenylpent-3-yn-2-one (27b). To an oven dried flask charged with a solution of 3,3-diphenylprop-1-yne[26] (0.385 g, 2.0 mmol) in 6 ml of dry THF and cooled to -78°C was added dropwise a 2.64M solution of n-BuLi in hexanes (0.760 ml, 2.0 mmol) and the reaction mixture was stirred at -78°C for 3 hours. The resulting solution was then transferred via cannula to the analogously prepared flask containing a solution of acetic anhydride (1.021 g, 10 mmol) in 6 ml

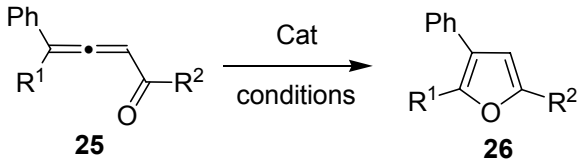
[24] (a) Froeyen, P.; Morris, D. G. *Acta. Chem. Scand., Ser. B*. **1976**, *B30*, 790. (b) Yoshida, H.; Shimizu, J.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Japan*. **1985**, *58*, 2445.
[25] Dragovich, P. S.; Webber, S. E.; Babine, R. E.; Fuhrman, S. A.; et al. *J. Med. Chem*. **1998**, *41*, 2806.
[26] Porter, N. A.; Hogenkamp, D. J.; Khouri, F. F. *J. Am. Chem. Soc.* **1990**, *112*, 2402.

of diethyl ether at -78°C and the reaction mixture was stirred overnight. The reaction mixture was quenched with 50 ml of water and extracted with hexanes (1×100 ml) and diethyl ether – hexanes (1:1, 2×75 ml). Combined organic extracts were dried over anhydrous sodium sulfate. All the solvents were removed in vacuo, and the residue was purified via flash Silica column chromatography (1:10 EtOAc/hexanes) to afford 0.33 g (1.41 mmol, 70%) of 5,5-diphenylpent-3-yn-2-one **27b** as a colorless oil.



27b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.43 (m, 10 H), 5.17 (s, 1 H), 2.40 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.61, 139.58 (2C), 128.89 (+, 4C), 127.87 (+, 4C), 127.47 (+, 2C), 92.50, 84.56, 43.19 (+), 32.92 (+).

Optimization of Reaction Conditions



25 **26**

Optimization Procedure. To an oven dried 1–5 ml Wheaton vial charged with catalyst and the appropriate amount of anhydrous solvent was added allenyl ketone **25 (**0.1 mmol) under N_2 or argon atmosphere and the reaction mixture was stirred at temperature defined in Table 1 until judged complete by TLC and GC/MS analysis. The reaction mixture was filtered through a layer of flash Silica (EtOAc – eluent), the solvents were removed in vacuo, and the residue was analyzed by ^{1}H NMR using dibromomethane as an internal standard. Selected results are summarized in Table 1. For several examples isolated yield of the furan **26** is given in parentheses.

Table 1: Optimization of Reaction Conditions

#	R^1 / R^2	Cat	mol%	Solvent	T, °C	Concentration, M	Yield, %[a]
1	Ph / 4-Br-C_6H_4	$AuBr_3$	5	Toluene	100	0.05	23
2	″	AuI	″	″	″	″	traces
3	″	$Au(PPh_3)OTf$	1	″	″	″	100 (89)
4	″	″	5	DCM	rt	0.02	99
5	″	$In(OTf)_3$	″	Toluene	100	″	100 (93)
6	Ph / Ph	$PtCl_2$	″	″	″	1	21
7	″	$PtCl_4$	″	″	″	″	21
8	″	$PdCl_2(PhCN)_2$	″	″	″	″	35
9	″	CuX (X = Cl, Br, I)	″	″	″	″	0
10	″	CuOTf·PhH	″	″	″	″	42
11	″	$Cu(OTf)_2$	″	″	″	0.1	95
12	″	$AgPF_6$	″	″	″	″	47
13	″	AgOTf	″	″	″	″	(80)
14	″	″	20	DCM	rt	0.02	70 (62)
15	″	$Al(OTf)_3$	5	Toluene	100	0.1	64
16	″	$Zn(OTf)_2$	″	″	″	″	39
17	″	TMSOTf	20	DCM	rt	0.02	82 (62)
18	″	″	5	″	″	″	76
19	″	$In(OTf)_3$	5	Toluene	100	0.1	91 (81)
20	″	″	2	″	″	″	89
21	″	″	1	″	″	″	87
22	″	$Sn(OTf)_2$	5	″	″	″	97 (81)
23	″	″	″	″	80	″	90
24	″	″	″	″	60	″	82
25	″	″	2	″	100	″	94
26	″	TIPSOTf	5	″	″	″	100 (81)
27	″	″	″	″	80	″	96
28	″	″	″	″	60	″	85
29	″	″	2	″	100	″	98
30	″	″	1	″	″	″	96
31	″	$TMSNTf_2$	5	″	″	″	72
32	Et / Ph	$Au(PPh_3)OTf$	1	″	″	0.02	76[b]
33	″	TMSOTf	20	DCM	rt	″	32[c]
34	″	TIPSOTf	5	Toluene	100	0.1	43[d]
35	″	$Sn(OTf)_2$	″	″	″	″	50[d]
36	″	$In(OTf)_3$	″	″	″	0.02	100 (88)[e]
37	″	″	″	″	85	″	98[f]
38	″	″	″	″	65	″	96[g]
39	″	″	″	″	45	″	64[h]
40	Me / Ph	$Au(PPh_3)OTf$	2	″	100	″	52
41	″	$In(OTf)_3$	5	″	″	″	77 (72)
42	″	″	″	″	″	0.1	53
43	″	TIPSOTf	″	″	″	″	0
44	Ph / Me	$Sn(OTf)_2$	″	″	″	″	20
45	″	$In(OTf)_3$	″	″	″	″	44
46	″	$In(OTf)_3$	10	″	115	0.05	75(64)

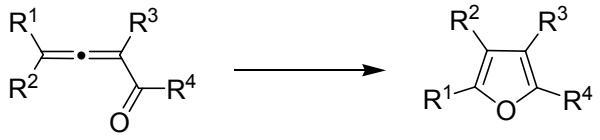
[a] NMR yield, isolated yield in parentheses. [b] 2.2:1 mixture of **26f:26g** by ^{1}H NMR. [c] 7:1 mixture of **26f:26g** by ^{1}H NMR. [d] 2:1 mixture of **26f:26g**. [e] 2.3:1 mixture of **26f:26g**. [f] 2.8:1 mixture of **26f:26g**. [g] 3.15:1 mixture of **26f:26g**. [h] 4.2:1 mixture of **26f:26g**.

Synthesis of Furans 26a-26n

Typical Preparative Procedure. To an oven dried ChemGlass pressure tube (or 5 ml Wheaton vial) charged with $Sn(OTf)_2$ (8.3 mg, 0.02 mmol, 5mol%) as the catalyst and 3.6 ml of anhydrous toluene was added 1,4,4-triphenylbuta-2,3-dien-1-one **25a** (118.4 mg, 0.4 mmol) in 0.4 ml of anhydrous toluene under argon atmosphere and the reaction mixture was stirred at 100°C for 6 hours. The reaction mixture was allowed to cool to room temperature and triethylamine (0.017 ml, 0.12 mmol) was added to quench the catalyst. The reaction mixture was filtered through a layer of Silica (EtOAc – eluent), the solvents were removed, and the residue was purified via flash Silica column chromatography (1:10:0.08 benzene/hexanes/Et_3N) to afford 96.3 mg (0.325 mmol, 81%) of 2,3,5-triphenylfuran **26a** as white crystalline solid (see page S41 for analytical data).

Note: Reaction conditions (Temperature, catalyst, time, etc.) for the cycloisomerization of allenyl ketones **25a-n** into furans **26a-n** are summarized in Table 2.

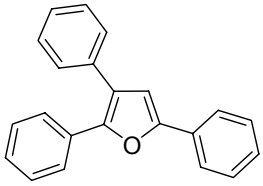
Table 2: Reaction Conditions



25a-n **26a-n**

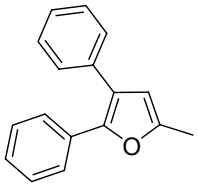
#	R^1	R^2	R^3	R^4	Catalyst	T, °C	Solvent	Concentration, M	Cat. %	Time, h	Product	Yield %
1	Ph	Ph	H	Ph	$Sn(OTf)_2$	100	toluene	0.1	5	6	**26a**	81
2	Ph	Ph	H	Me	$In(OTf)_3$	115	″	0.05	10	12	**26b**	64
3	Ph	Ph	H	*t*-Bu	″	100	″	″	5	1	**26c**	90
4	Ph	Ph	Me	Ph	AgOTf	140	p-xylene	″	20	1	**26d**	79
5	Ph	Me	H	Ph	$In(OTf)_3$	100	toluene	0.02	5	12	**26e**	72
6	Ph	Et	H	Ph	″	″	″	″	″	6	**26f/26g**	88
7	-$(CH_2)_4$-		H	Ph	″	″	″	″	″	3	**26h**	75
8	Ph	Ph	H	4-MeO-C_6H_4	″	″	″	0.05	″	2	**26k**	62
9	Ph	Ph	H	4-Br-C_6H_4	″	″	″	″	″	1	**26l**	93
10	Ph	Ph	H	4-Br-C_6H_4	$Au(PPh)_3OTf$	″	″	″	1	2	**26l**	89
11	Ph	Ph	H	3-O_2N-C_6H_4	$Sn(OTf)_2$	″	″	″	5	1	**26m**	85
12	Ph	Ph	H	4-NC-C_6H_4	″	″	″	″	″	1.5	**26n**	94

2,3,5-triphenylfuran[27] (26a)



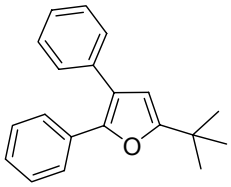
26a (81%, 0.4 mmol): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.86 (m, 2 H), 7.60 – 7.65 (m, 2 H), 7.46 – 7.52 (m, 2 H), 7.37 – 7.46 (m, 4 H), 7.24 – 7.37 (m, 5 H), 6.83 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.55, 147.89, 134.33, 131.12, 130.53, 128.75 (+, 2C), 128.70 (+, 4C), 128.41 (+, 2C), 127.53 (+), 127.50 (+), 127.31 (+), 126.14 (+, 2C) 124.53, 123.82 (+, 2C), 109.48 (+); mp 91–92°C.

5-methyl-2,3-diphenylfuran[28] (26b)



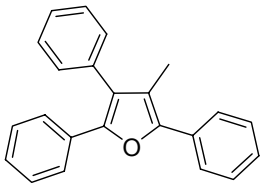
4a (64%, 0.8 mmol): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.55 (m, 2 H), 7.18 – 7.44 (m, 8 H), 6.17 (nonresolved q, J = 0.90 Hz, 1 H), 2.40 (d, J = 0.90 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.31, 146.78, 134.72, 131.48, 128.59 (+, 2C), 128.57 (+, 2C), 128.33 (+, 2C), 127.04 (+), 126.95 (+), 125.93 (+, 2C), 123.17, 110.15 (+), 13.62 (+); mp 54–56°C.

5-tert-butyl-2,3-diphenylfuran[29] (26c)



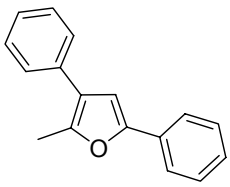
4c (90%, 0.4 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.57, (m, 2 H), 7.42 – 7.47 (m, 2 H), 7.33 – 7.39 (m, 2 H), 7.26 – 7.32 (m, 3 H), 7.19 – 7.25 (m, 1 H), 6.16 (s, 1 H), 1.39 (s, 9 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.27, 146.26, 134.91, 131.69, 128.63 (+, 2C), 128.55 (+, 2C), 128.30 (+, 2C), 126.99 (+), 126.90 (+), 125.92 (+, 2C), 122.66, 106.63 (+), 32.74, 29.13 (+, 3C); mp 68–69°C.

3-methyl-2,4,5-triphenylfuran[30] (26d)



4d (79%, 0.25 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 2 H), 7.44 – 7.54 (m, 6 H), 7.36 – 7.44 (m, 3 H), 7.29 – 7.35 (m, 1 H), 7.23 – 7.29 (m, 2 H), 7.16 – 7.23 (m, 1 H), 2.17 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.73, 147.19, 133.92, 131.73, 131.09, 130.25 (+, 2C), 128.83 (+, 2C), 128.62 (+, 2C), 128.33 (+, 2C), 127.48 (+), 127.02 (+), 126.90 (+), 126.06, 125.56 (+, 2C), 125.47 (+, 2C), 118.88, 10.51 (+); mp 120–122°C.

2-methyl-3,5-diphenylfuran[31] (26e)



26e (72%, 0.5 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.75 (m, 2 H), 7.37 – 7.50 (m, 6 H), 7.23 – 7.34 (m, 2 H), 6.81 (s, 1 H), 2.55 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.63, 147.62, 134.08, 130.86, 128.69 (+, 2C), 128.65 (+, 2C), 127.52 (+, 2C), 127.05 (+), 126.48 (+), 123.44 (+, 2C), 123.04, 106.47 (+), 13.25 (+).

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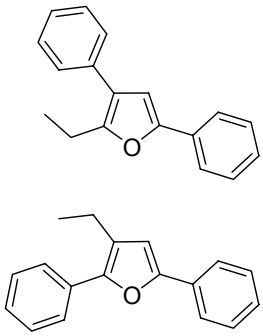
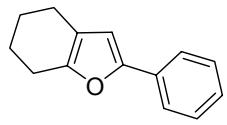
2-ethyl-3,5-diphenylfuran[31] (26f) and 3-ethyl-2,5-diphenylfuran[32] (26g)



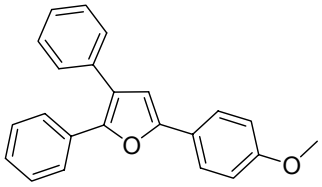
26f:26g (88%, 0.8 mmol, 2.3:1 mixture): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.78 (m, 2 H, **26g**), 7.69 – 7.73 (m, 2 H, **26f**), 7.38 – 7.48 (m, 12 H, **26f**+**26g**), 7.24 – 7.34 (m, 4 H, **26f**+**26g**), 6.79 (s, 1 H, **26f**), 6.71 (s, 1 H, **26g**), 2.90 (q, *J* = 7.58 Hz, 2 H, **26f**), 2.77 (q, *J* = 7.64 Hz, 2 H, **26g**), 1.38 (t, *J* = 7.52 Hz, 3 H, **26f**), 1.33 (t, *J* = 7.52 Hz, 3 H, **26g**); ^{13}C NMR (**26f**+**26g**) (126 MHz, $CDCl_3$) δ 152.72 (**26f**), 151.99, 151.59 (**26f**), 147.64, 134.18 (**26f**), 131.76, 130.96 (**26f**), 130.86, 128.67 (**26f**), 128.62 (**26f**), 127.71 (**26f**), 127.20, 127.03 (**26f**), 126.81, 126.53 (**26f**), 125.50, 125.43, 123.68, 123.47 (**26f**), 122.45 (**26f**), 108.68, 106.57 (**26f**), 20.57 (–, **26f**), 19.37 (–, **26g**), 14.46(+, **26g**), 13.12 (+, **26f**).

2-phenyl-4,5,6,7-tetrahydro-1-benzofuran[33] (26h)



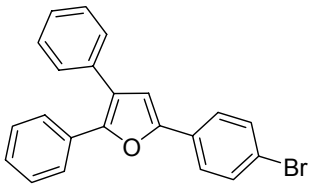
26h (75%, 0.5 mmol): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.68 (m, 2 H), 7.32 – 7.41 (m, 2 H), 7.18 – 7.25 (m, 1 H), 6.49 (s, 1 H), 2.64 – 2.74 (m, 2 H), 2.44 – 2.52 (m, 2 H), 1.84 – 1.94 (m, 2 H), 1.73 – 1.82 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.61, 150.81, 131.46, 128.57 (+, 2C), 126.56 (+), 123.27 (+, 2C), 119.00, 106.03 (+), 23.34 (–), 23.18 (–), 23.13 (–), 22.19 (–).

5-(4-methoxyphenyl)-2,3-diphenylfuran[34] (26k)



4j (62%, 0.5 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.75 (m, 2 H), 7.58 – 7.65 (m, 2 H), 7.47 – 7.51 (m, 2 H), 7.37 – 7.44 (m, 2 H), 7.29 – 7.37 (m, 3 H), 7.23 – 7.28 (m, 1 H), 6.95 – 7.00 (m, 2 H), 6.70 (s, 1 H), 3.86 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.24, 152.68, 147.22, 134.49, 131.26, 128.71 (+, 2C), 128.68 (+, 2C), 128.41 (+, 2C), 127.31 (+), 127.26 (+), 126.03 (+, 2C), 125.32 (+, 2C), 124.52, 123.62, 114.24 (+, 2C), 107.99 (+), 55.37 (+); mp 96–98°C.

5-(4-bromophenyl)-2,3-diphenylfuran[34] (26l)



26l (93%, 0.5 mmol): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.67 (m, 4 H), 7.53 – 7.58 (m, 2 H), 7.46 – 7.50 (m, 2 H), 7.27 – 7.44 (m, 6 H), 6.83 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.50, 148.29, 134.07, 131.92 (+, 2C), 130.91, 129.45, 128.76 (+, 2C), 128.70 (+, 2C), 128.49 (+, 2C), 127.74 (+), 127.46 (+), 126.21 (+, 2C), 125.28 (+, 2C), 124.67, 121.30, 110.03 (+); mp 106–108°C.

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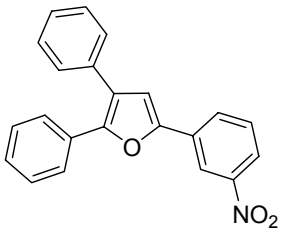
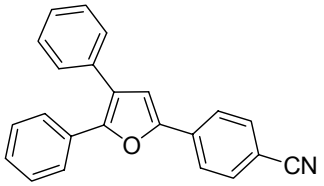
[32] Schoening, A.; Debaerdemaeker, T.; Zander, M.; Friedrichsen, W. *Chem. Ber.* **1989**, *122*, 1119.
[33] Crotti, P.; Badalassi, F.; Di Bussolo, V.; Favero, L.; Pineschi, M. *Tetrahedron.* **2001**, *57*, 8559.
[34] (a) Demirdji, S. H.; *J. Het. Chem.* **1985**, *22*, 495. (b) Horspool, W. M.; Khalaf, A. I.; *J. Chem. Soc. Perkin Trans. 1*. **1989**, 1147.

5-(3-nitrophenyl)-2,3-diphenylfuran (26m)



26m (85%, 0.5 mmol): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (t, *J* = 1.83 Hz, 1 H), 8.12 (ddd, *J* = 8.16, 2.11, 0.73 Hz, 1 H), 8.04 (dt, *J* = 7.84, 1.22 Hz, 1 H), 7.61 – 7.65 (m, 2 H), 7.58 (t, *J* = 7.98 Hz, 1 H), 7.44 – 7.49 (m, 2 H), 7.28 – 7.44 (m, 6 H), 6.97 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.00, 149.28, 148.82, 133.62, 132.08, 130.49, 129.80 (+), 129.14 (+), 128.81 (+, 2C), 128.64 (+, 2C), 128.55 (+, 2C), 128.12 (+), 127.64 (+), 126.37 (+, 2C), 124.78, 121.79 (+), 118.43 (+) 111.61 (+); mp 128–129°C; HRMS (EI) calcd. for $C_{22}H_{15}NO_3$ [M^+]: 341.10519. Found: 341.10357.

4-(4,5-diphenyl-2-furyl)benzonitrile[34b] **(26n)**



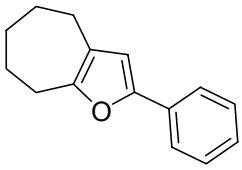
26n (94%, 0.5 mmol): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.62 Hz, 2 H), 7.69 (d, *J* = 8.62 Hz, 2 H), 7.61 (dd, *J* = 8.16, 1.38 Hz, 2 H), 7.28 – 7.49 (m, 8 H), 6.97 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.42, 149.64, 134.30, 133.59, 132.66 (+, 2C), 130.46, 128.83 (+, 2C), 128.65 (+, 2C), 128.56 (+, 2C), 128.20 (+), 127.69 (+), 126.36 (+, 2C), 125.00, 123.87 (+, 2C) 119.02, 112.51 (+), 110.31; mp 160–161°C.

5-methyl-2,3-diphenylfuran[28] **(26b) from 5,5-diphenylpent-3-yn-2-one (27b):**

Cycloisomerization of **27b** into furan **26b** was performed similar to that reported above for allenyl ketone **25b**. 5mol% of $In(OTf)_3$ (14 mg, 0.025 mmol) was used as the catalyst. The reaction was performed on 0.5 mmol scale by heating a 0.1M solution of **27b** in toluene at 100°C for 5 hours. The reaction mixture was treated as described in typical procedure to afford 62.2 mg (0.266 mmol, 53%) of 5-methyl-2,3-diphenylfuran **26b** (*vide supra*).

2,3-dimethyl-5-phenylfuran[35] **(26j):**

Prepared according to the typical procedure. 5mol% of $In(OTf)_3$ (5.6 mg, 0.01 mmol) was used as the catalyst. The reaction was performed on 0.2 mmol scale by heating a 0.05M solution of 4-methyl-1-phenylpenta-2,3-dien-1-one **25j** in toluene at 120°C for 24 hours. The reaction mixture was treated as described in typical procedure to give approximately 10% yield of **26j** as it was determined by ^{1}H NMR.

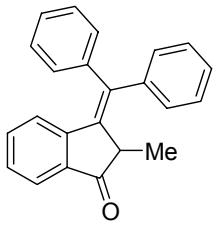


2,3-dimethyl-5-phenylfuran[36] **(26i):** As described above for **26j** to give 18% yield of **26i** as it was determined by ^{1}H NMR.

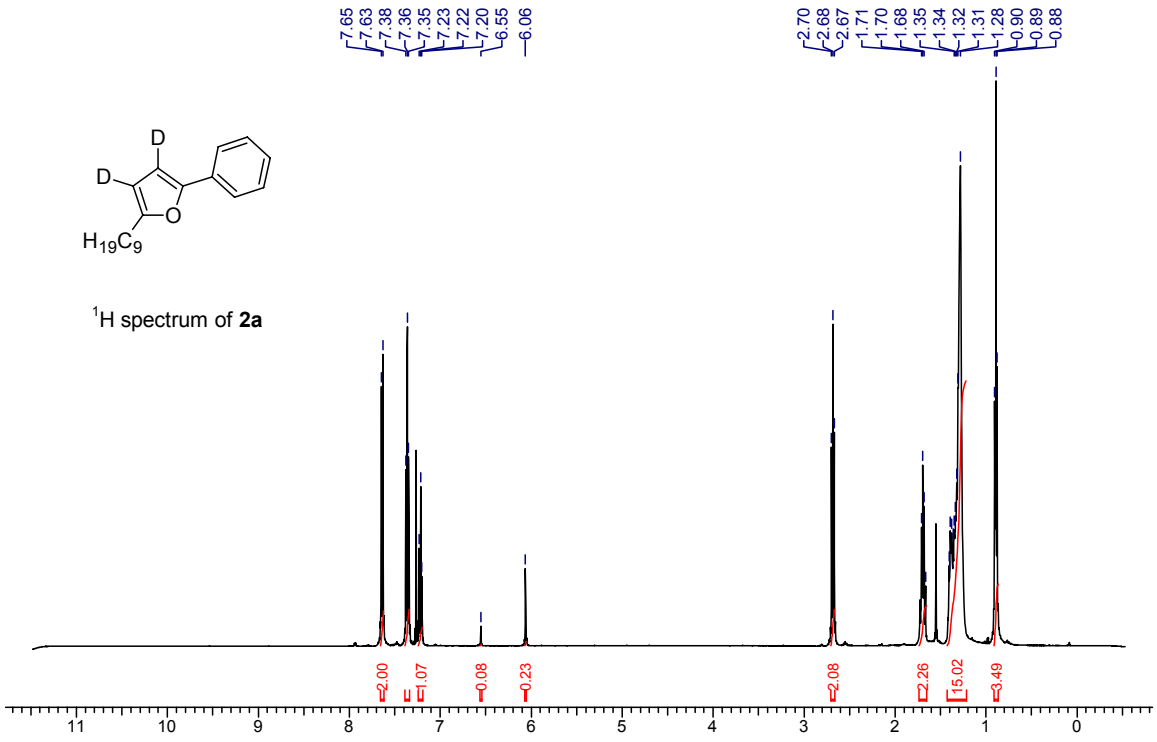
[35] Seiller, B.; Bruneau, C.; Dixneuf, P. H. *Tetrahedron* **1995**, *51*, 13089.
[36] Chowdhury, M. A.; Senboku, H.; Tokuda, M. *Synlett* **2004**, 1933.

Synthesis of 28d via Nazarov Cyclization

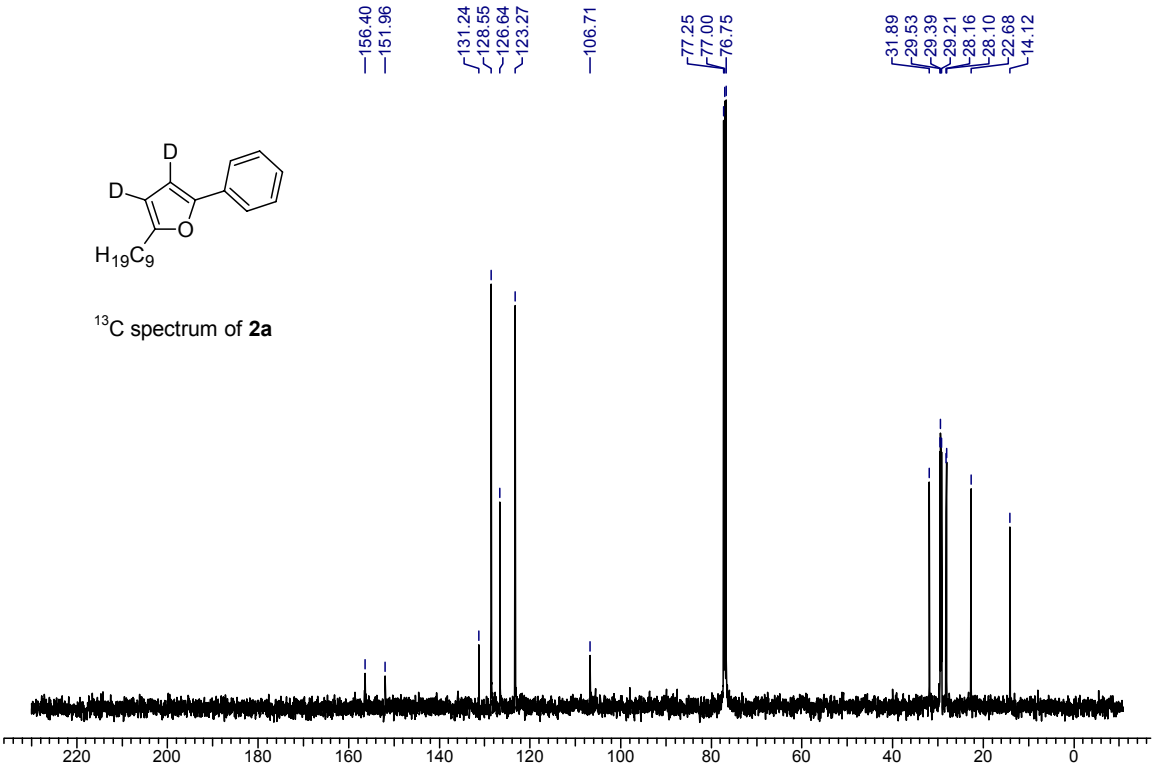
3-(diphenylmethylene)-2-methylindan-1-one 28d: To an oven dried 50 ml flask with septa charged with TMSOTf (22.2 mg, 18.1 μl, 0.1 mmol, 20mol%) as the catalyst and 20 ml of anhydrous DCM was added 2-methyl-1,4,4-triphenylbuta-2,3-dien-1-one **25d** (155.2 mg, 0.5 mmol) in 5 ml of anhydrous DCM under argon atmosphere and the reaction mixture was stirred at room temperature for 2 hours. Triethylamine (0.34 ml, 2.4 mmol) was added to quench the catalyst. The reaction mixture was filtered through a layer of Silica (EtOAc – eluent), the solvents were removed, and the residue was purified via flash Silica column chromatography (1:10 EtOAc/hexanes) to afford 147.6 mg (0.476 mmol, 95%) of **28d** as white crystalline solid.



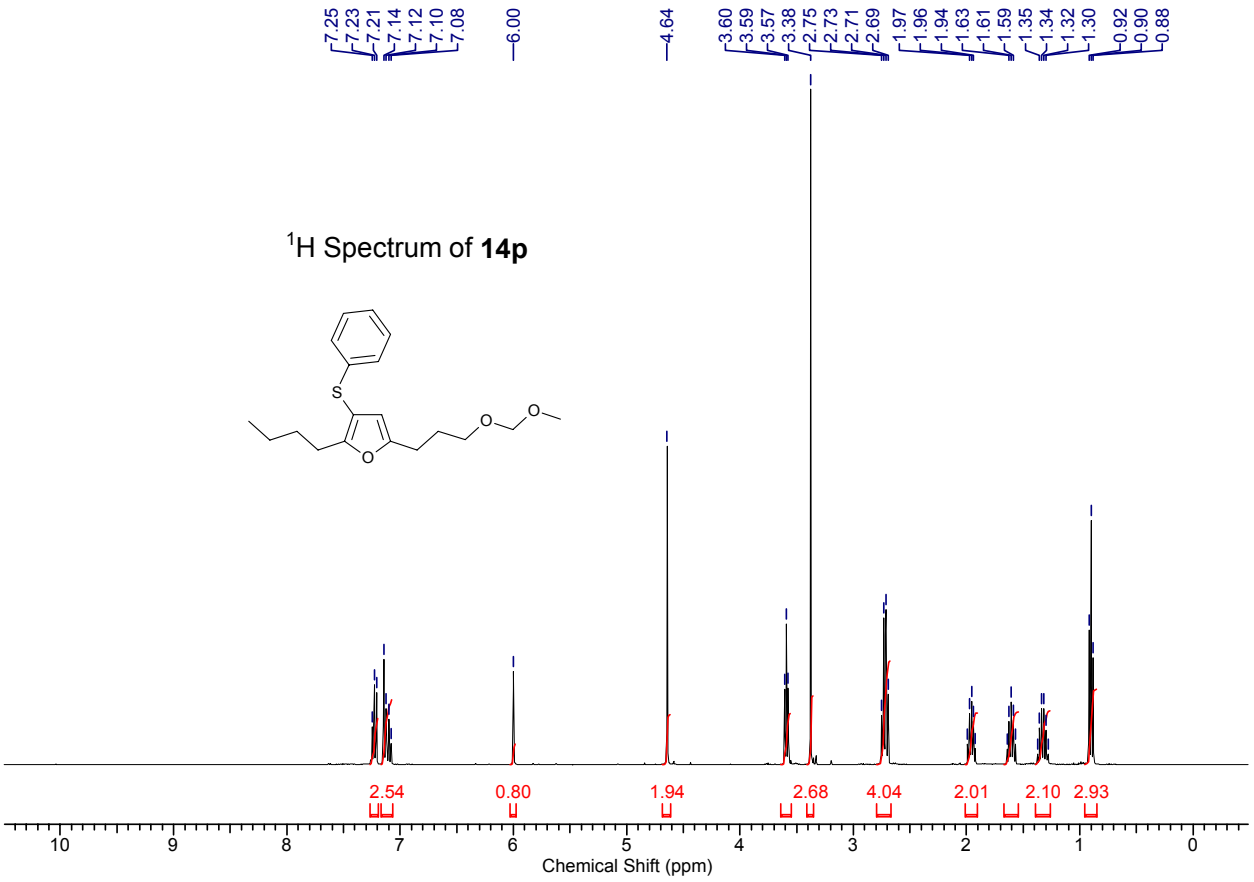
28d : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J*=6.97 Hz, 1 H), 7.23 - 7.48 (m, 12 H), 6.64 (d, *J*=8.07 Hz, 1 H), 3.57 (q, *J*=7.52 Hz, 1 H), 1.01 (d, *J*=7.52 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.9, 149.0, 142.6, 142.5, 140.9, 136.7, 136.6, 134.3 (+), 129.2 (+, 2C), 128.9 (+, 3C), 128.5 (+, 4C), 127.9 (+), 127.5 (+), 125.5 (+), 123.6 (+), 46.3 (+), 15.5 (+); mp 151–152°C; HRMS (EI) calcd. for $C_{23}H_{18}O$ [M^+]: 310.135765. Found: 310.1358.



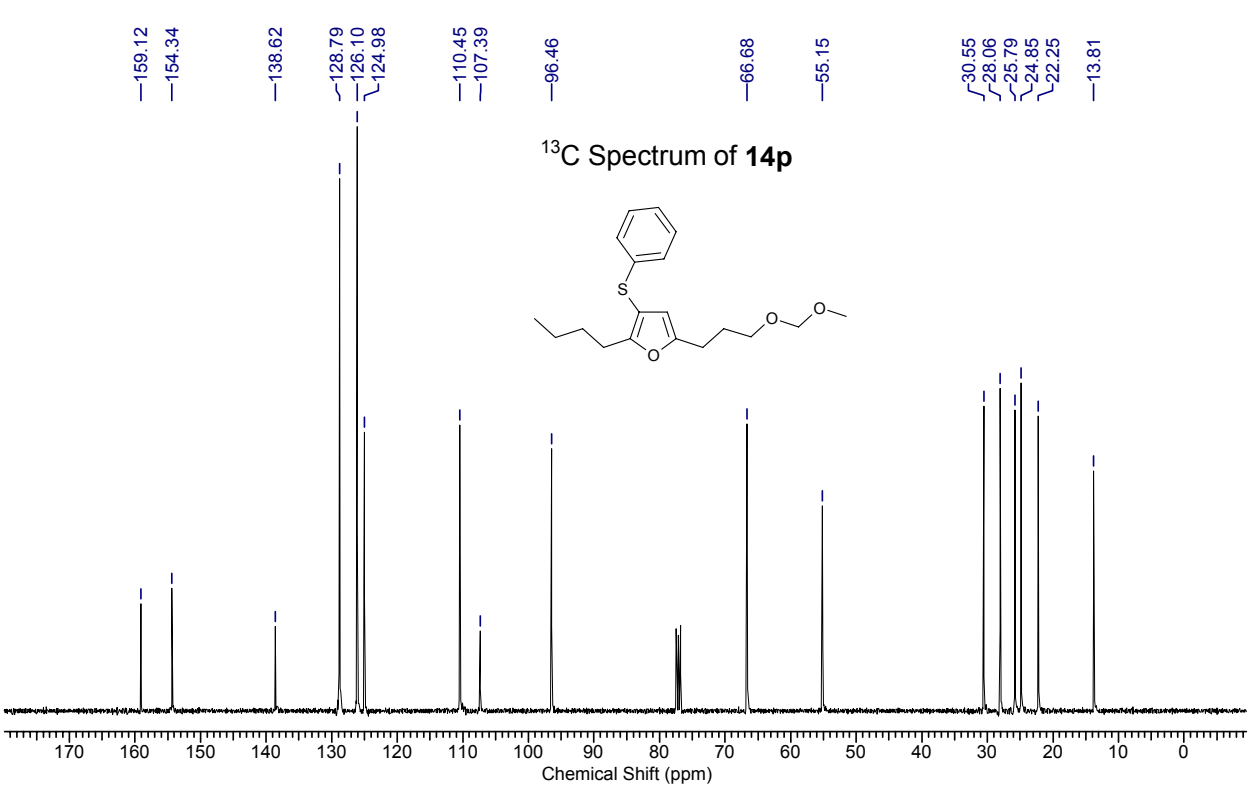
^{1}H spectrum of **2a**



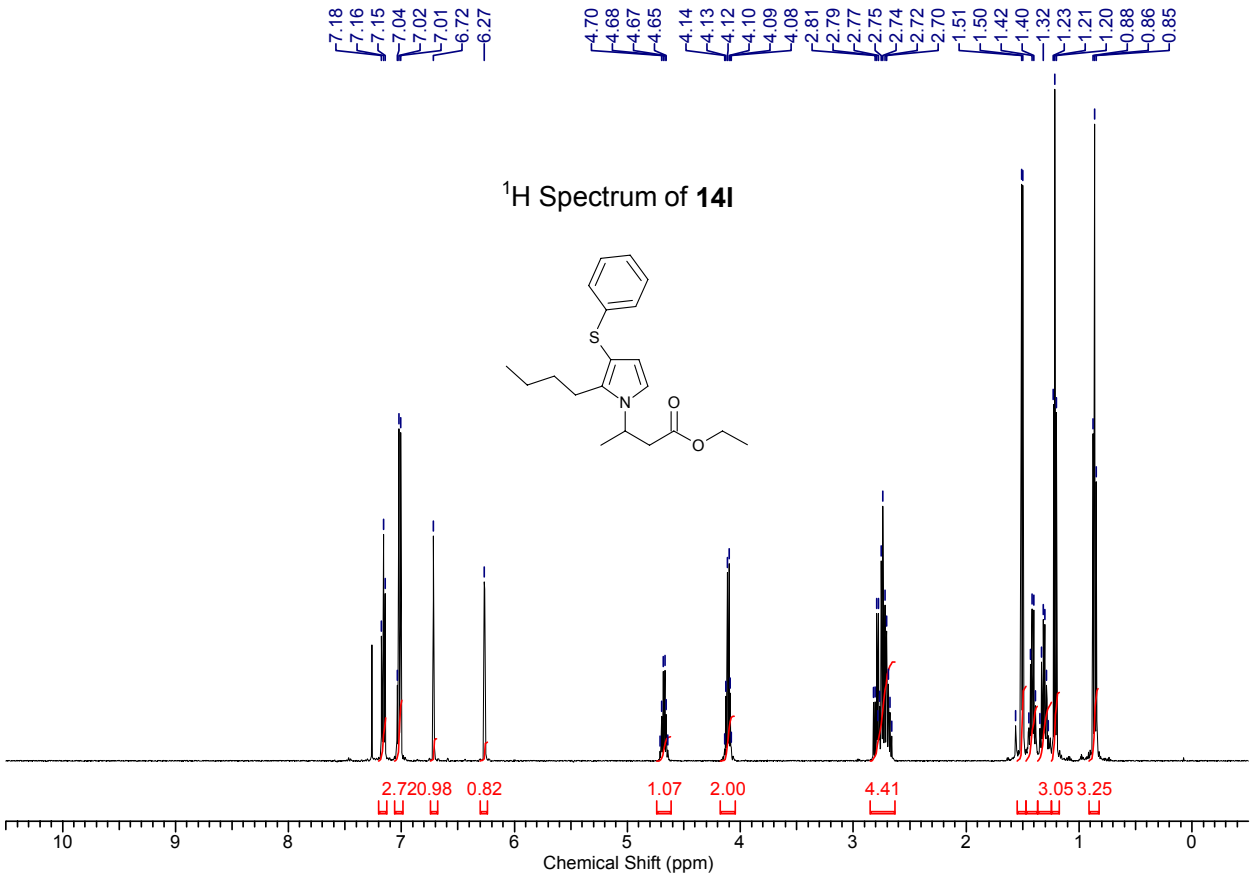
^{13}C spectrum of **2a**



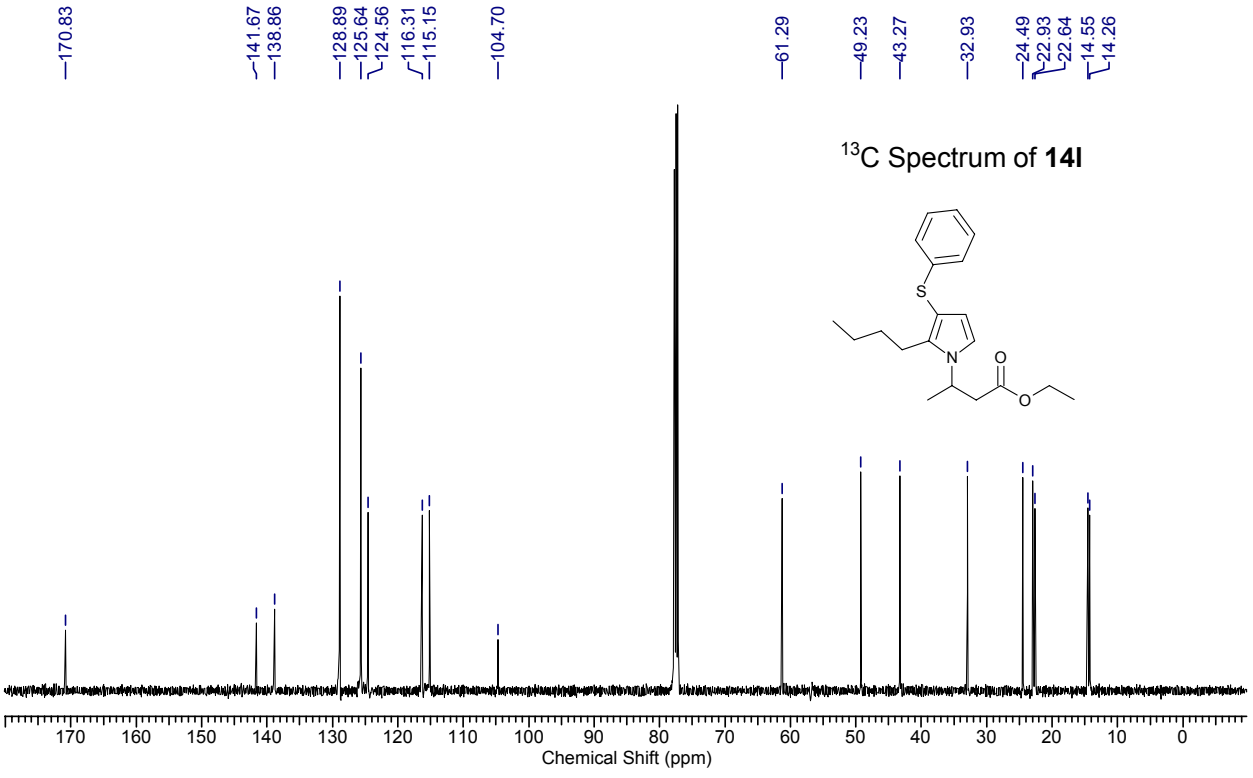
^{1}H Spectrum of **14p**



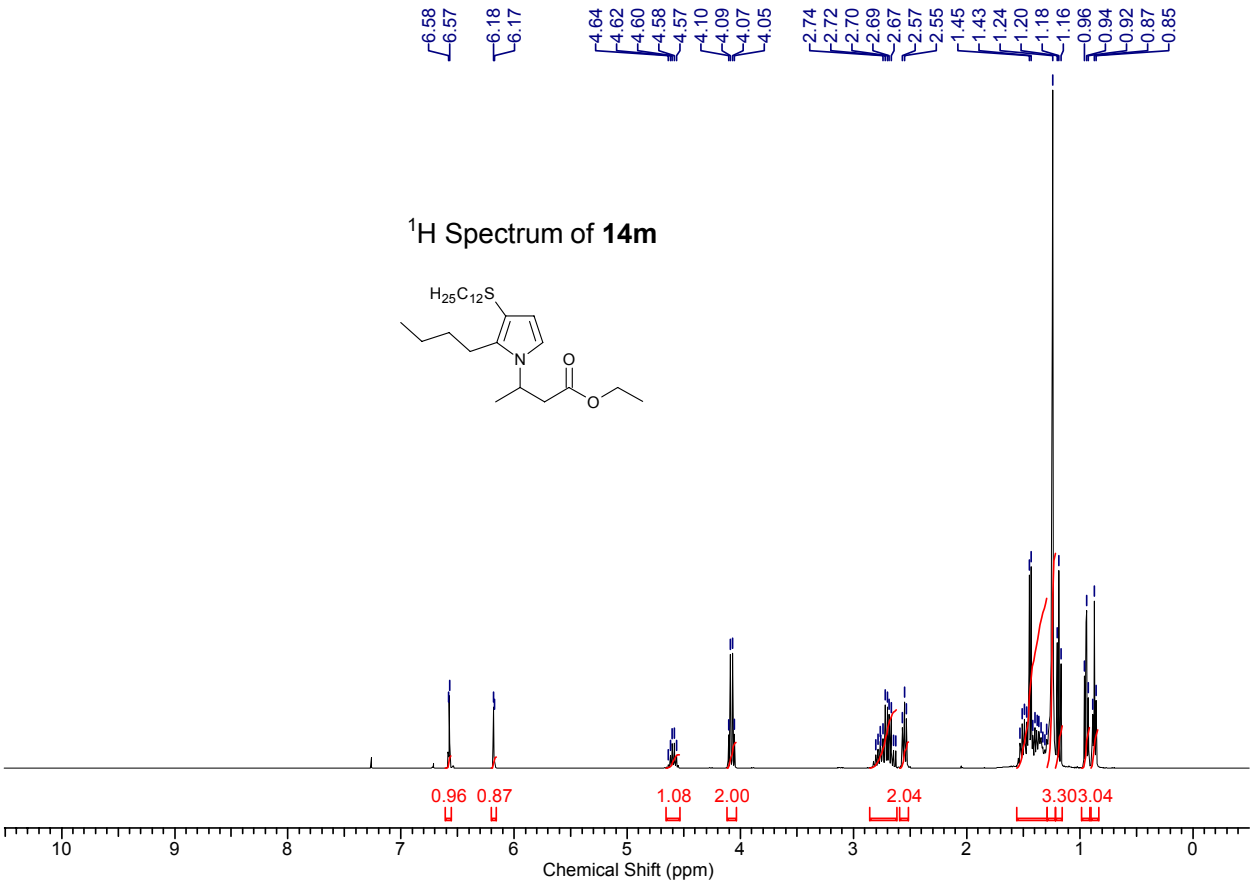
^{13}C Spectrum of **14p**



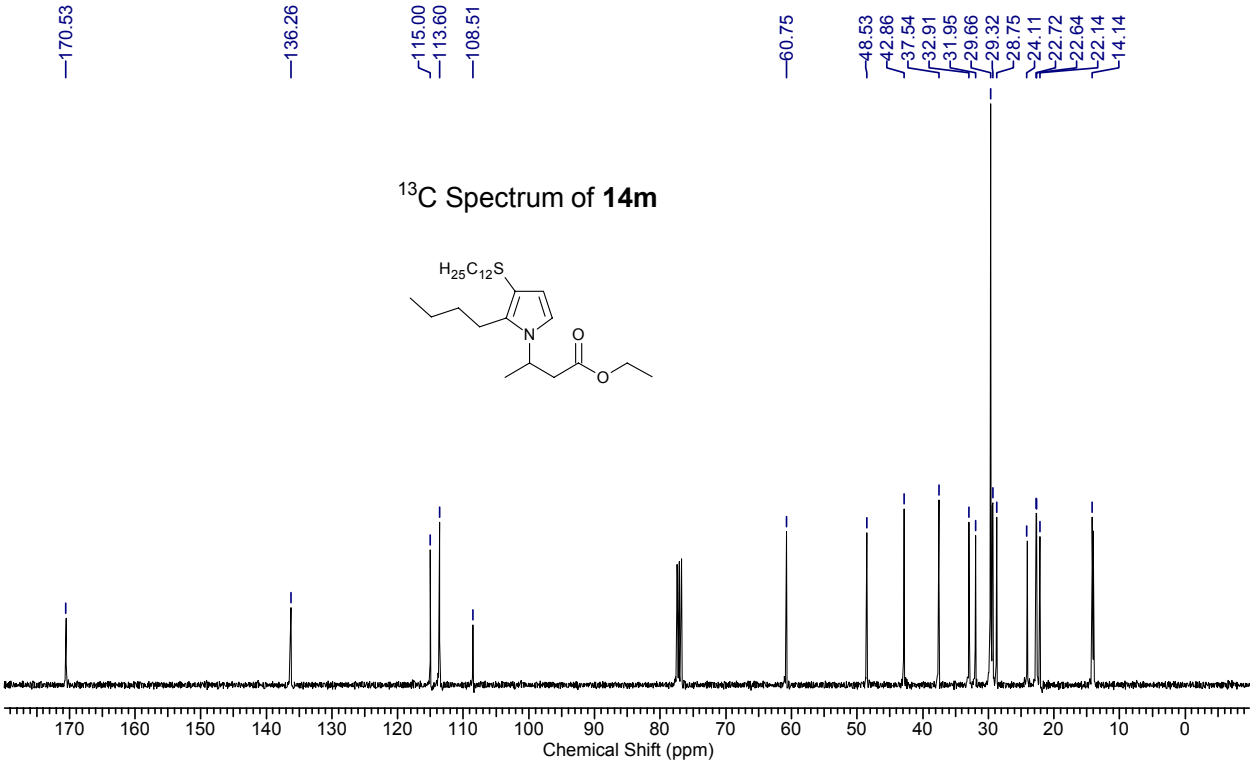
^{1}H Spectrum of **14l**



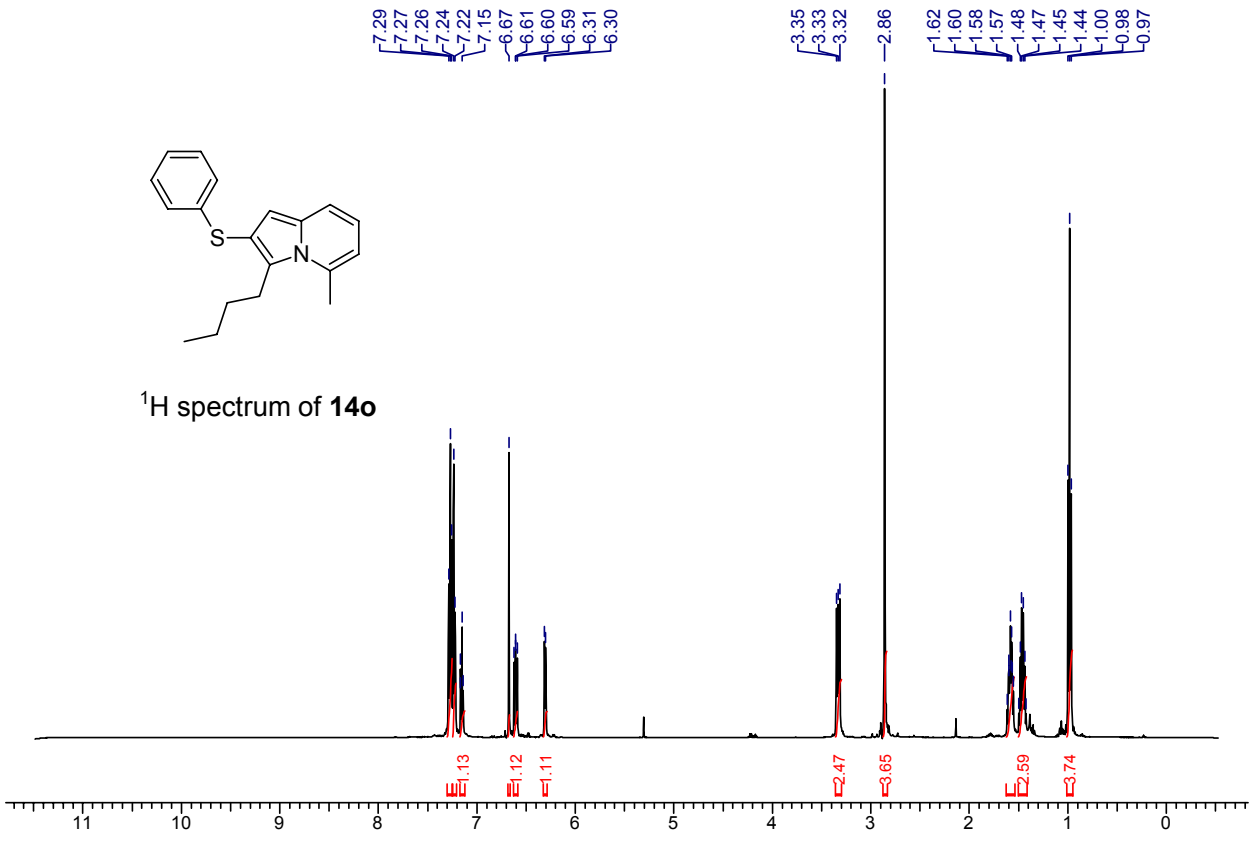
^{13}C Spectrum of **14l**



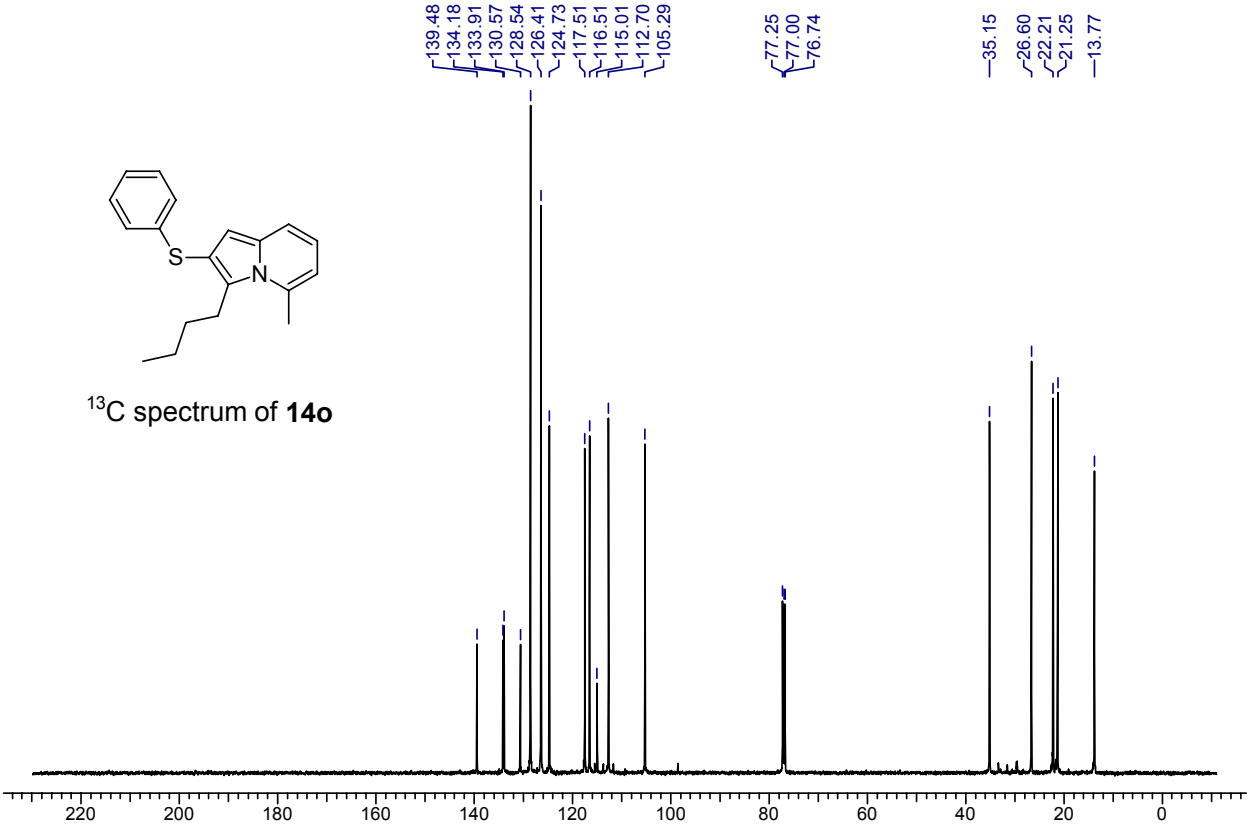
^{1}H Spectrum of **14m**



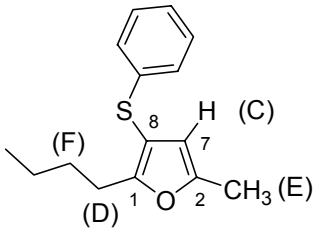
^{13}C Spectrum of **14m**



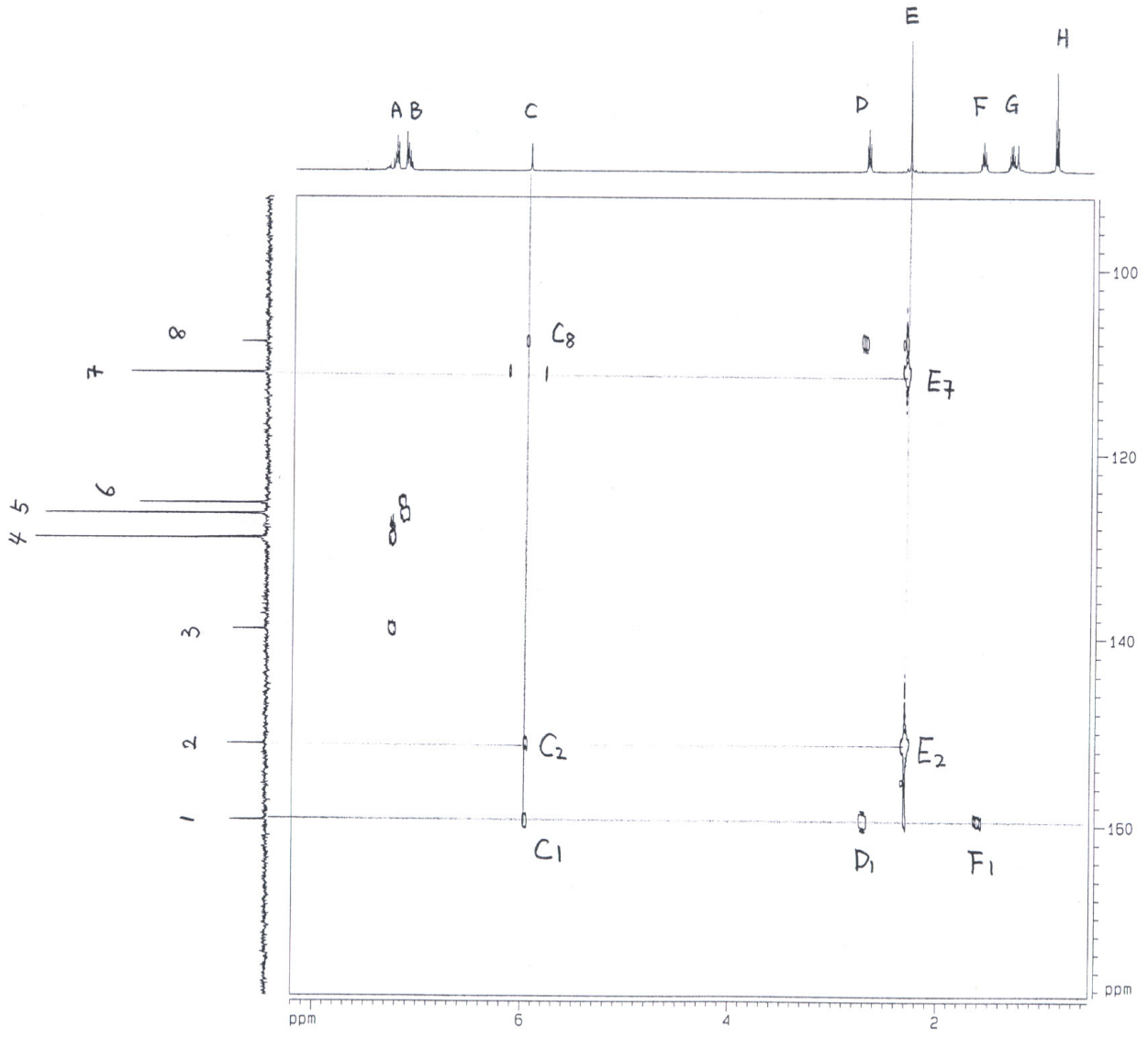
^{1}H spectrum of **14o**

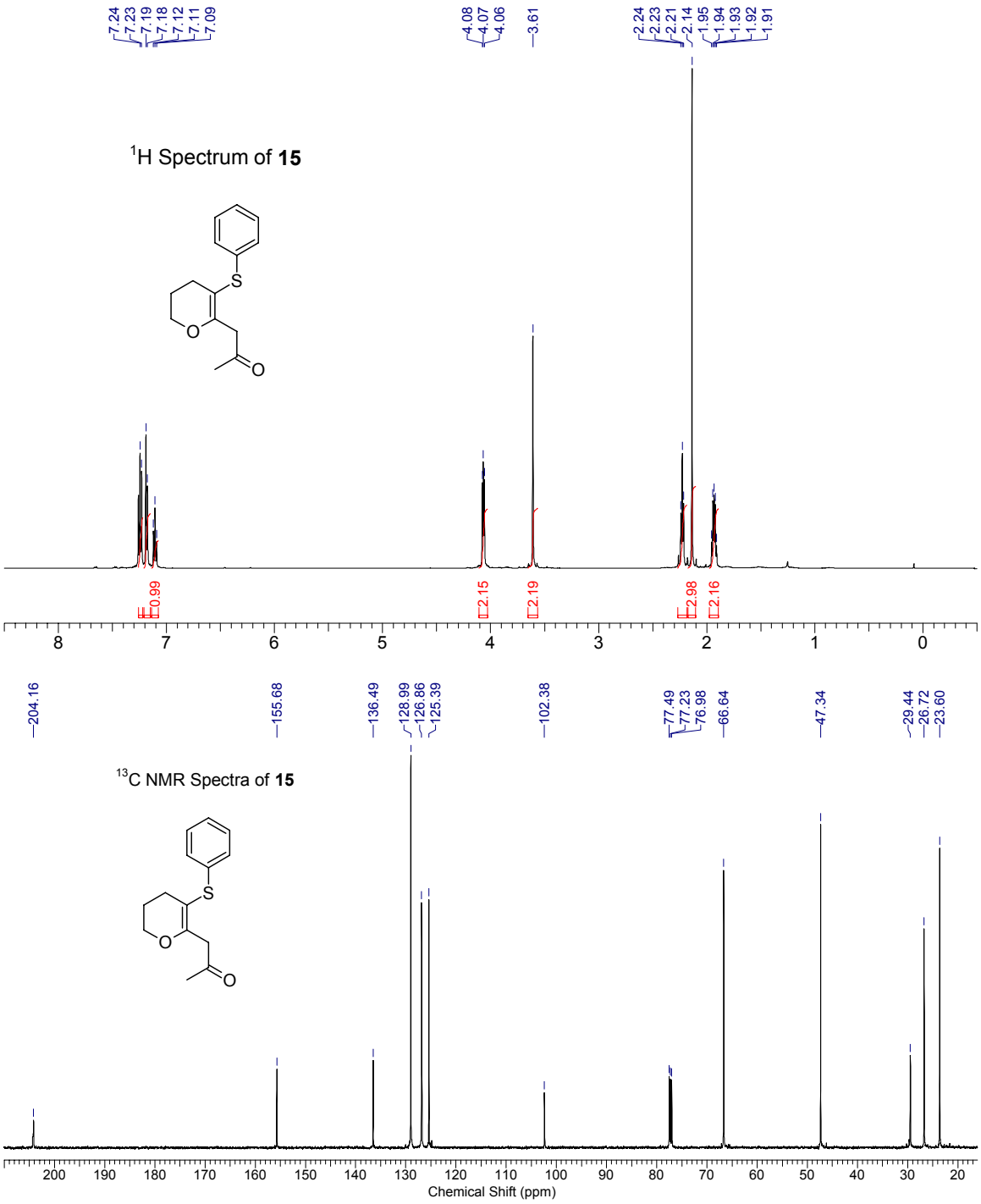


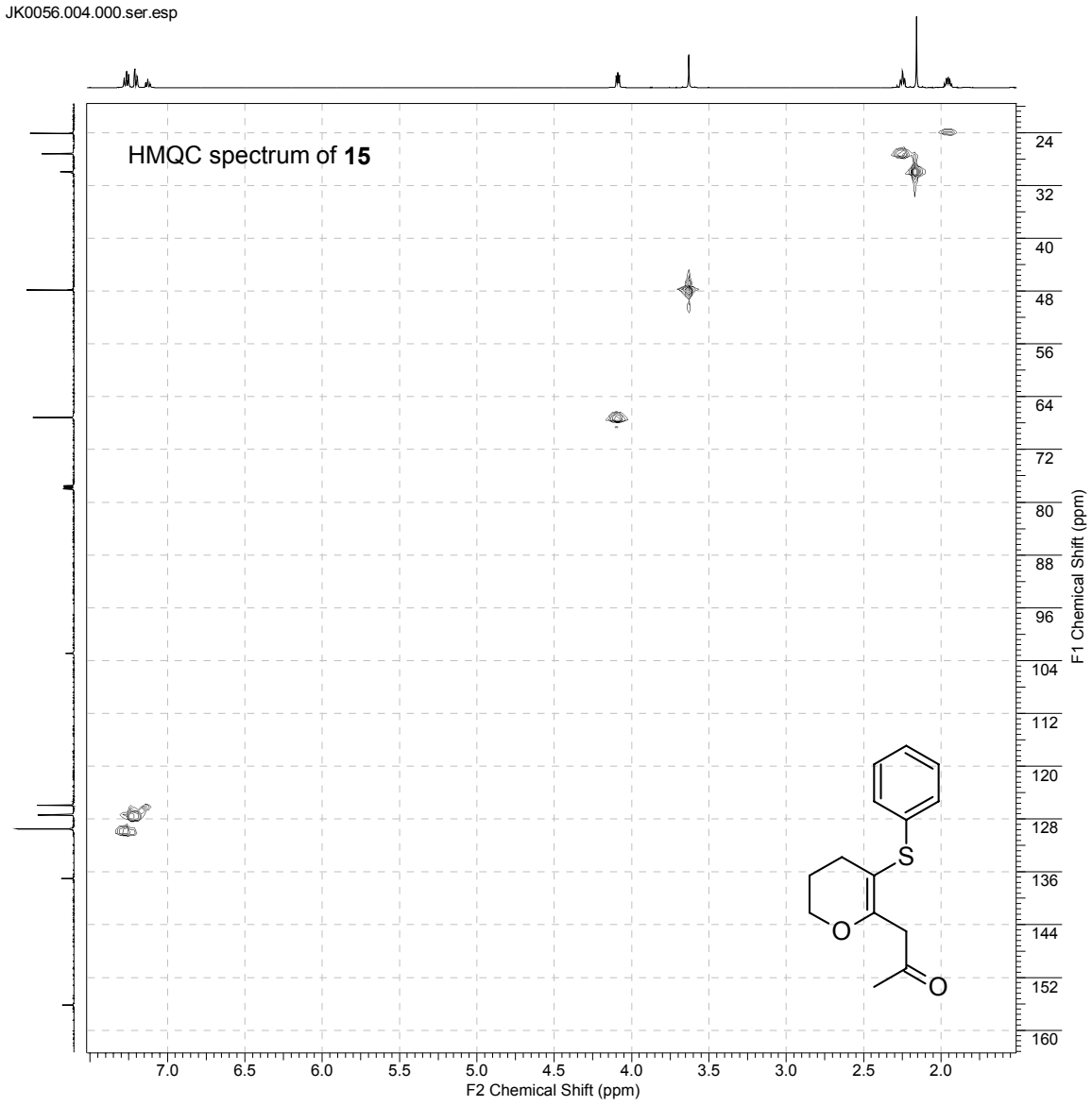
^{13}C spectrum of **14o**

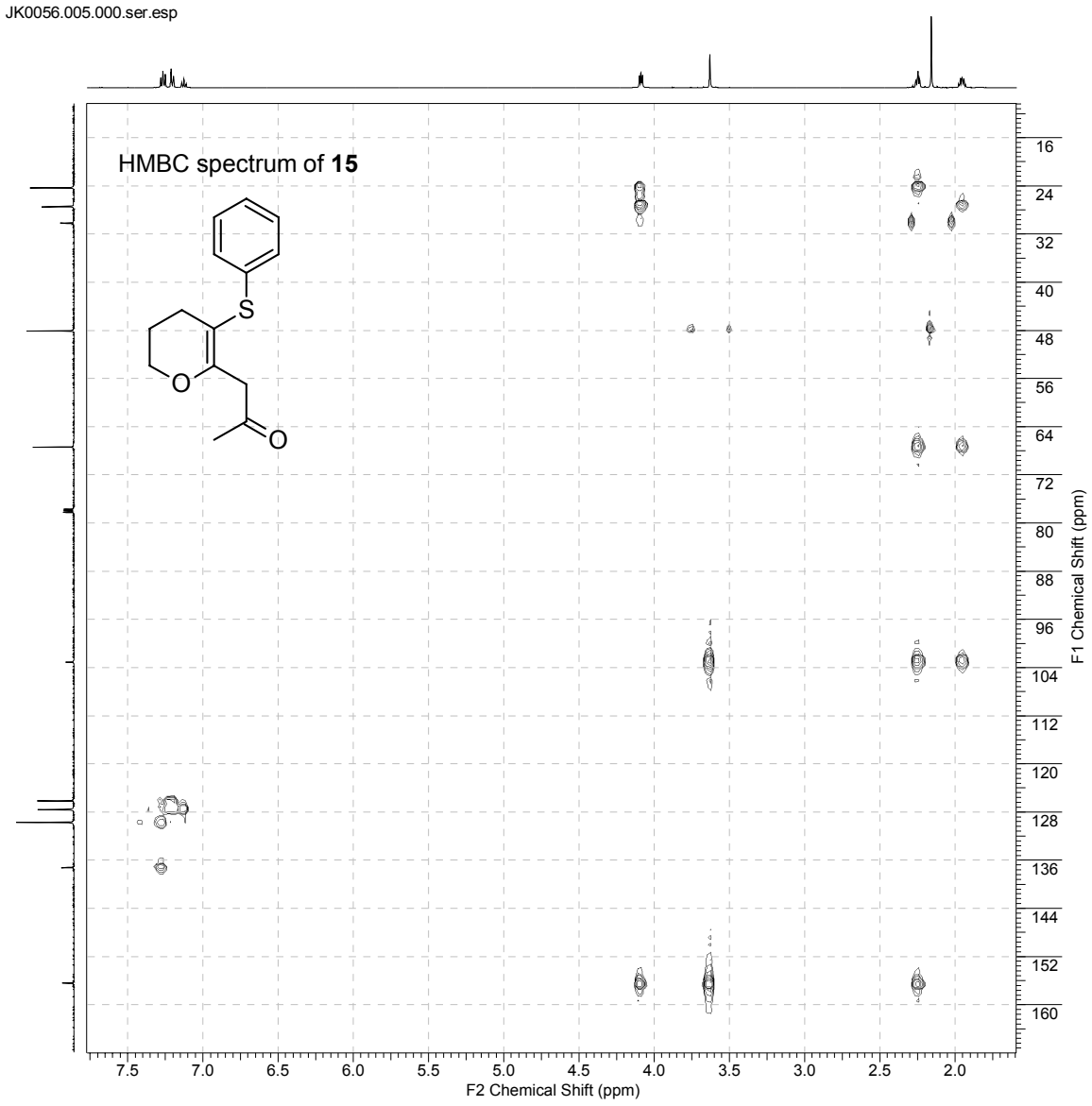


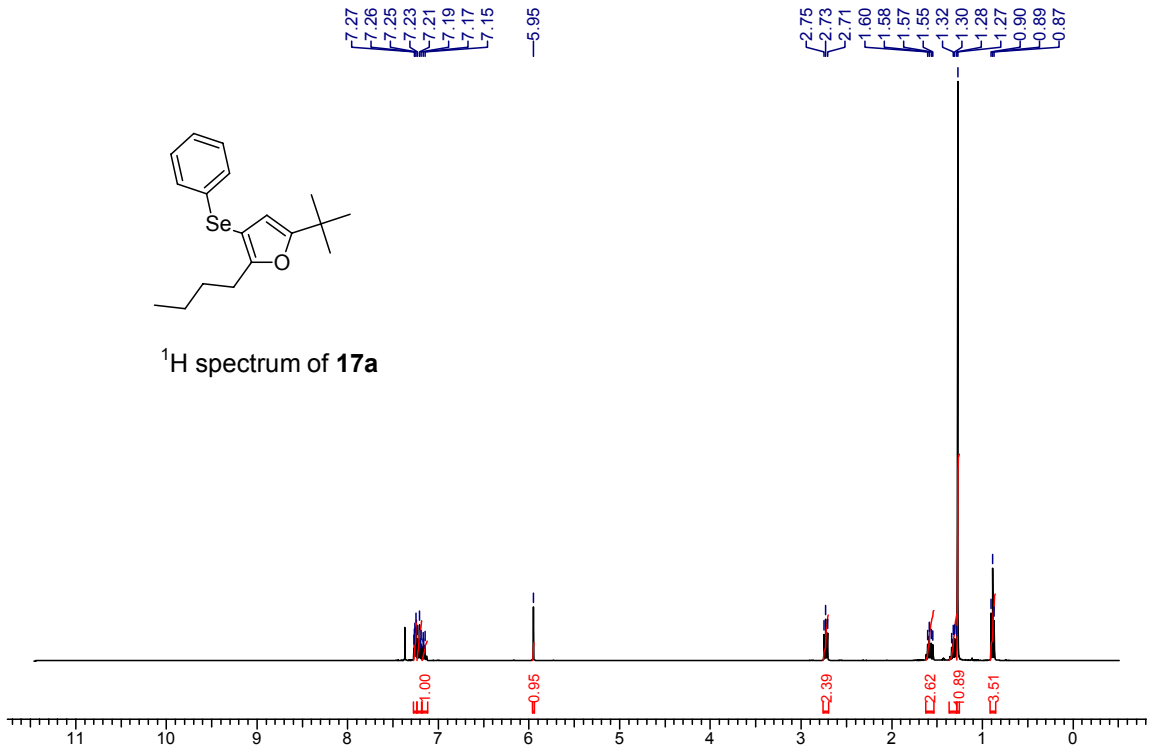
HMBC spectrum of 14b



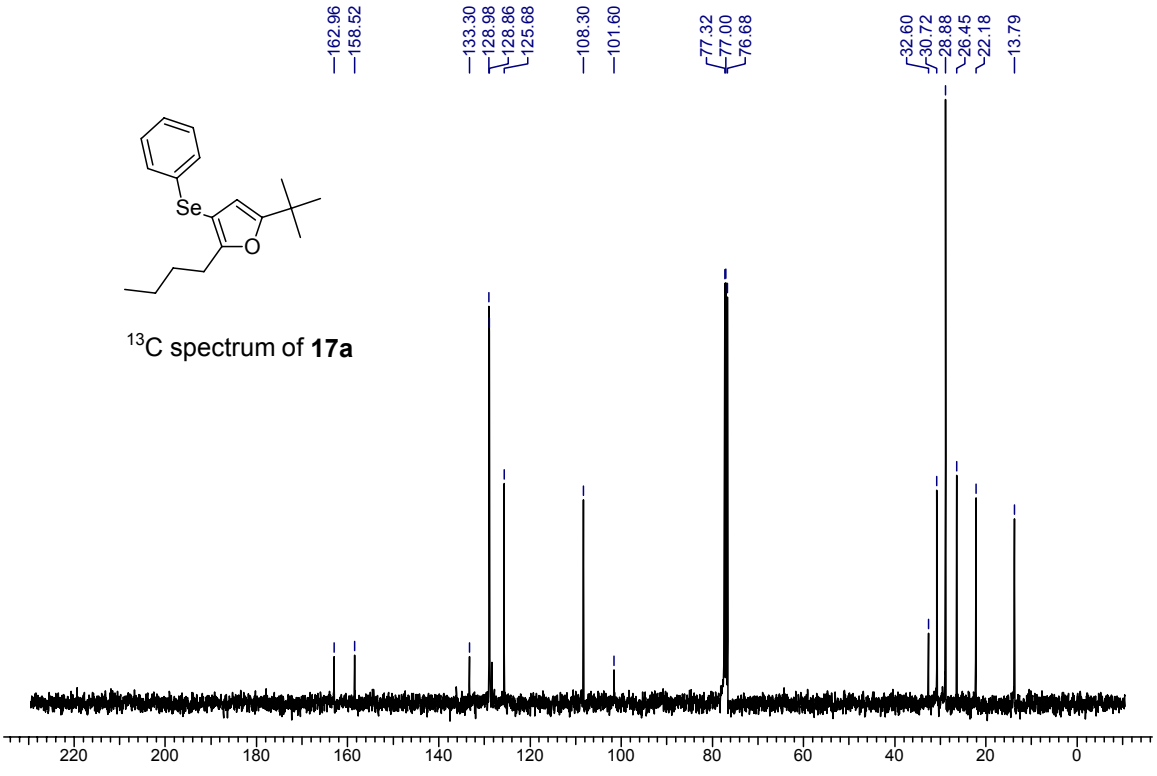

7.24
7.23
7.19
7.18
7.12
7.11
7.09
4.08
4.07
4.06
3.61
2.24
2.23
2.21
2.14
1.95
1.94
1.93
1.92
1.91
1H Spectrum of 15
S
O
O
0.99
2.15
2.19
2.98
2.16
8
7
6
5
4
3
2
1
0
204.16
155.68
136.49
128.99
126.86
125.39
102.38
77.49
77.23
76.98
66.64
47.34
29.44
26.72
23.60
13C NMR Spectra of 15
S
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
Chemical Shift (ppm)


JK0056.004.000.ser.esp
HMQC spectrum of **15**
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)
S
O
O

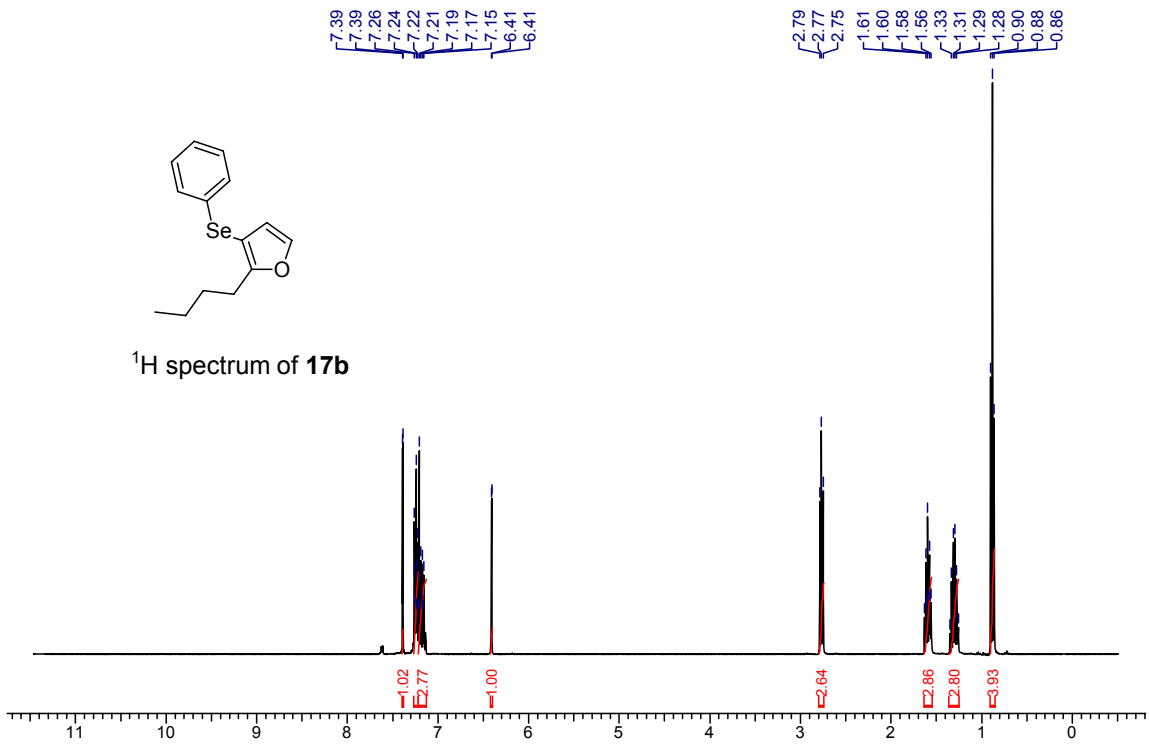

JK0056.005.000.ser.esp
HMBC spectrum of **15**
S
O
O
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)



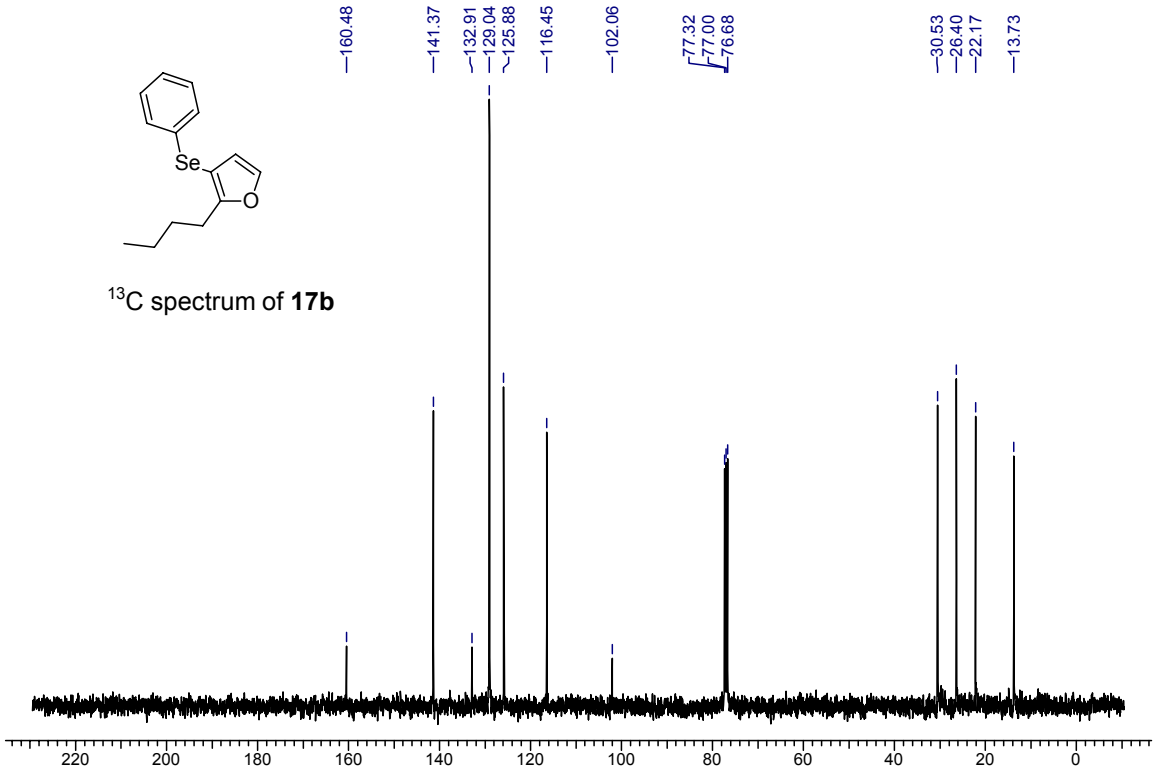
^{1}H spectrum of **17a**



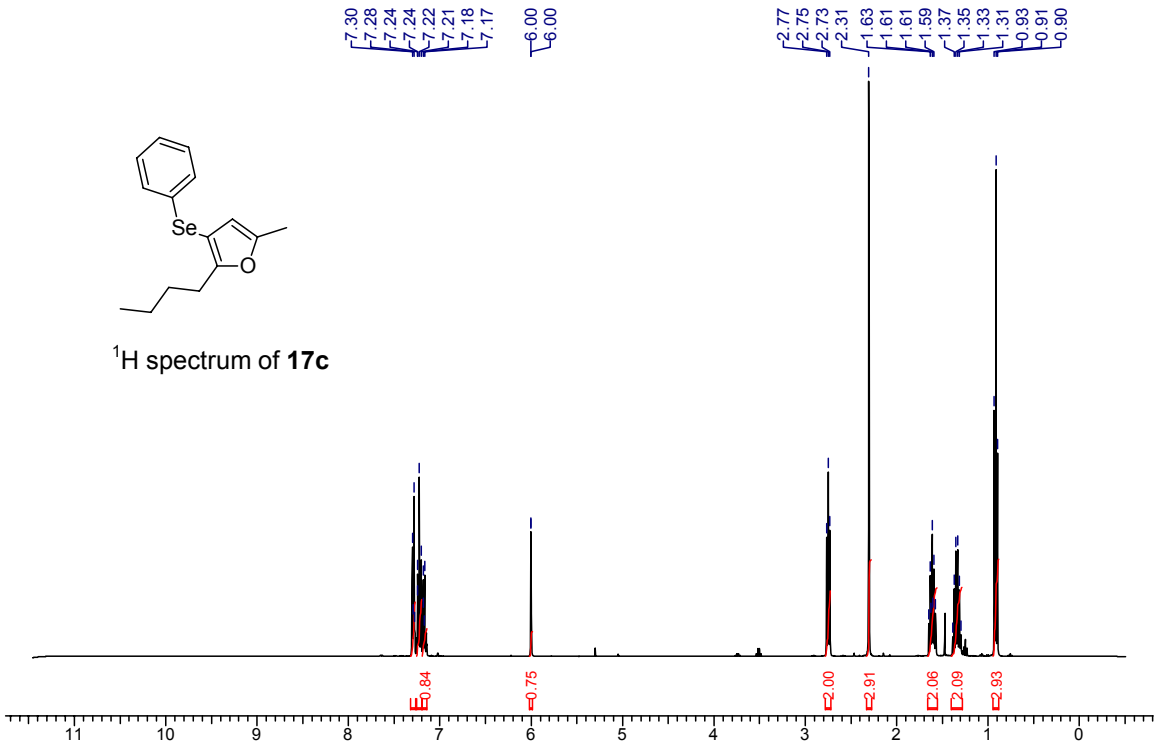
^{13}C spectrum of **17a**



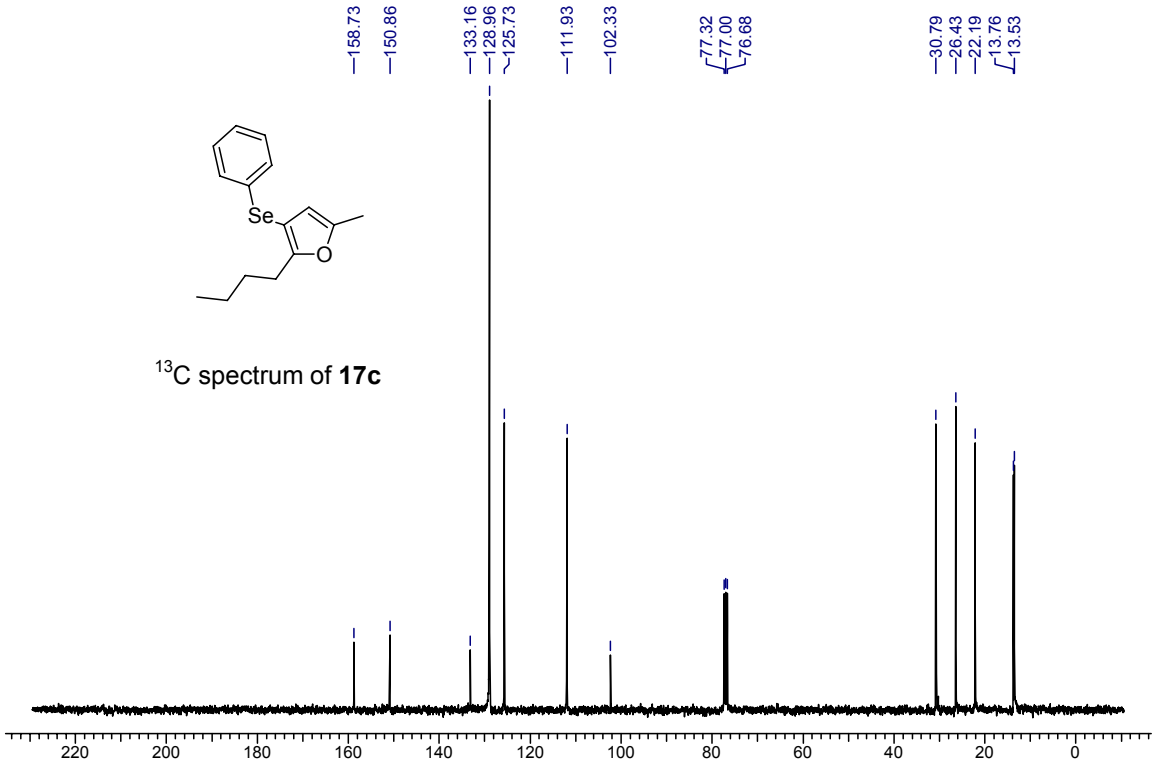
^{1}H spectrum of **17b**



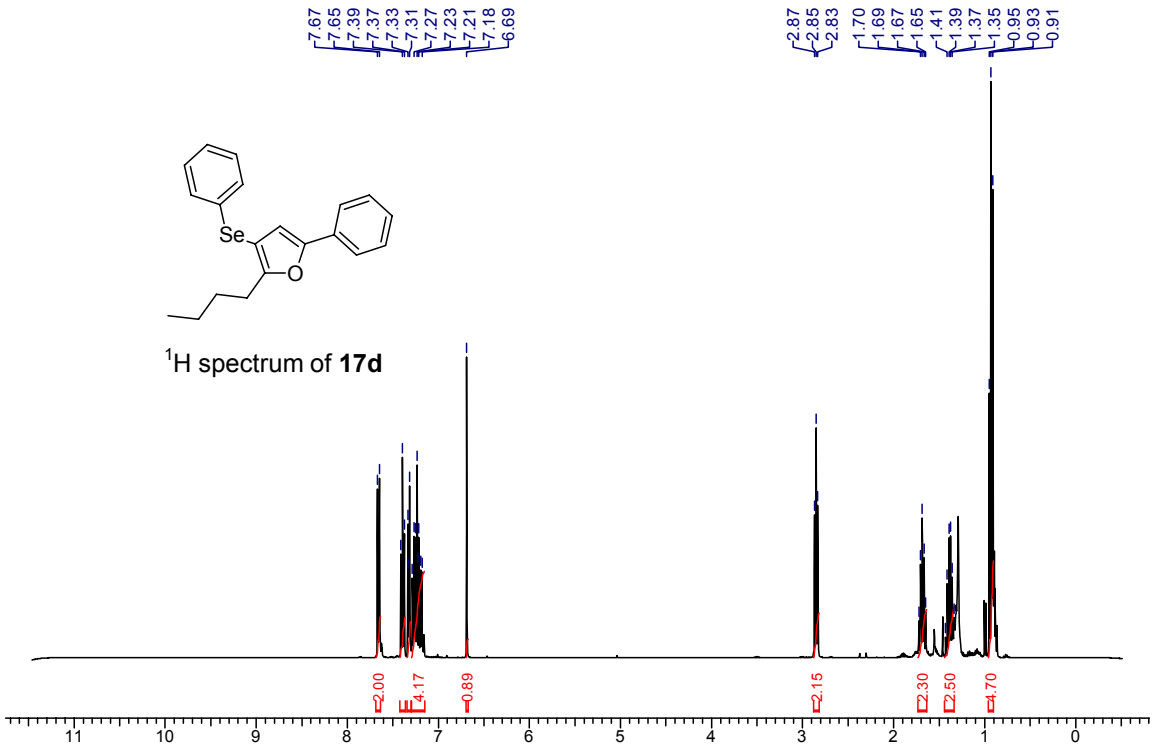
^{13}C spectrum of **17b**



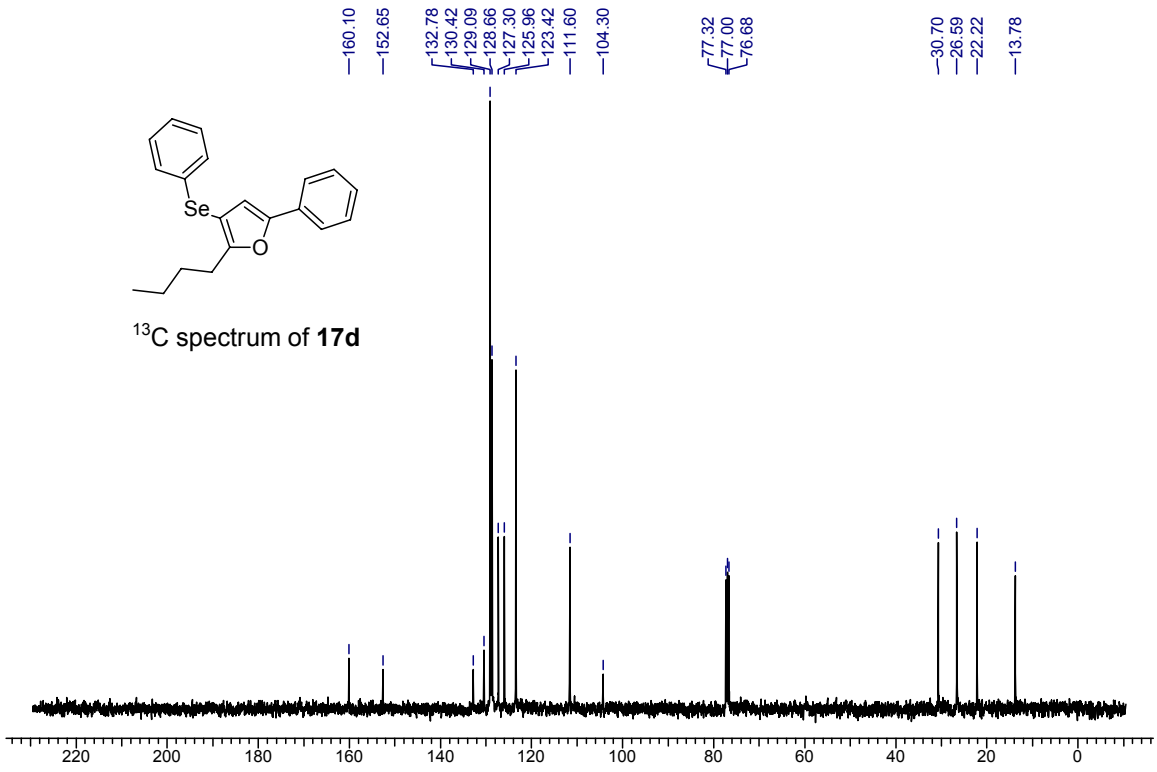
^{1}H spectrum of **17c**



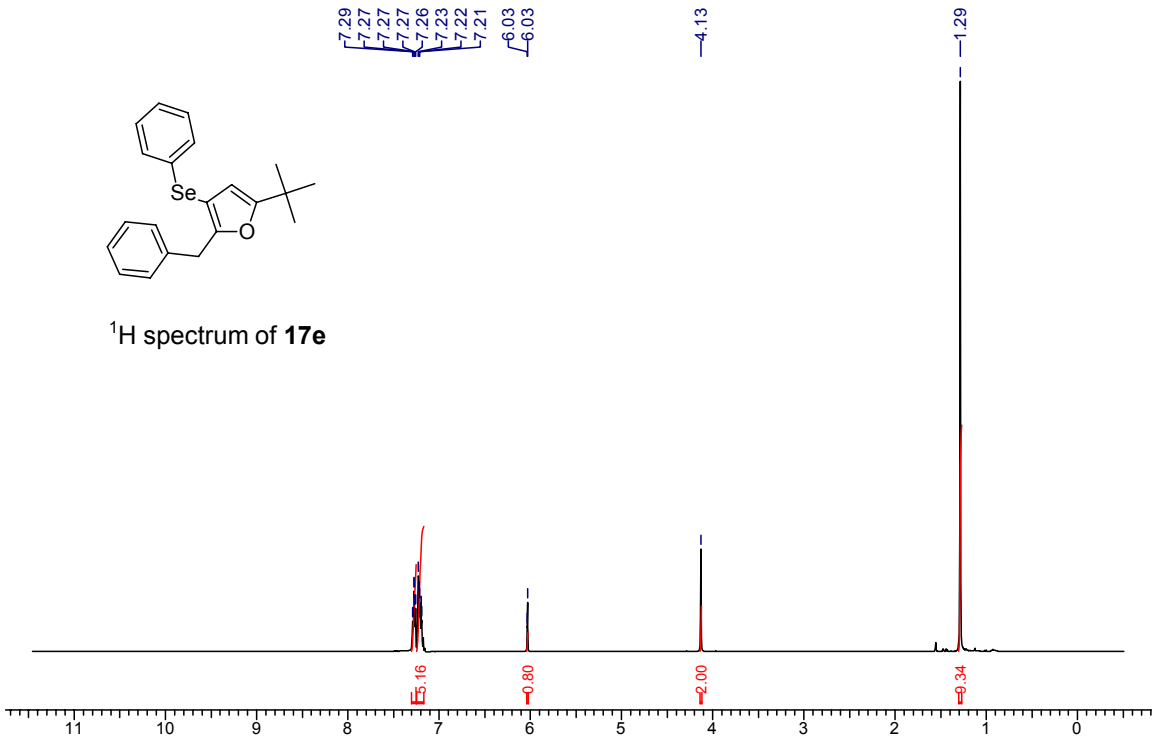
^{13}C spectrum of **17c**



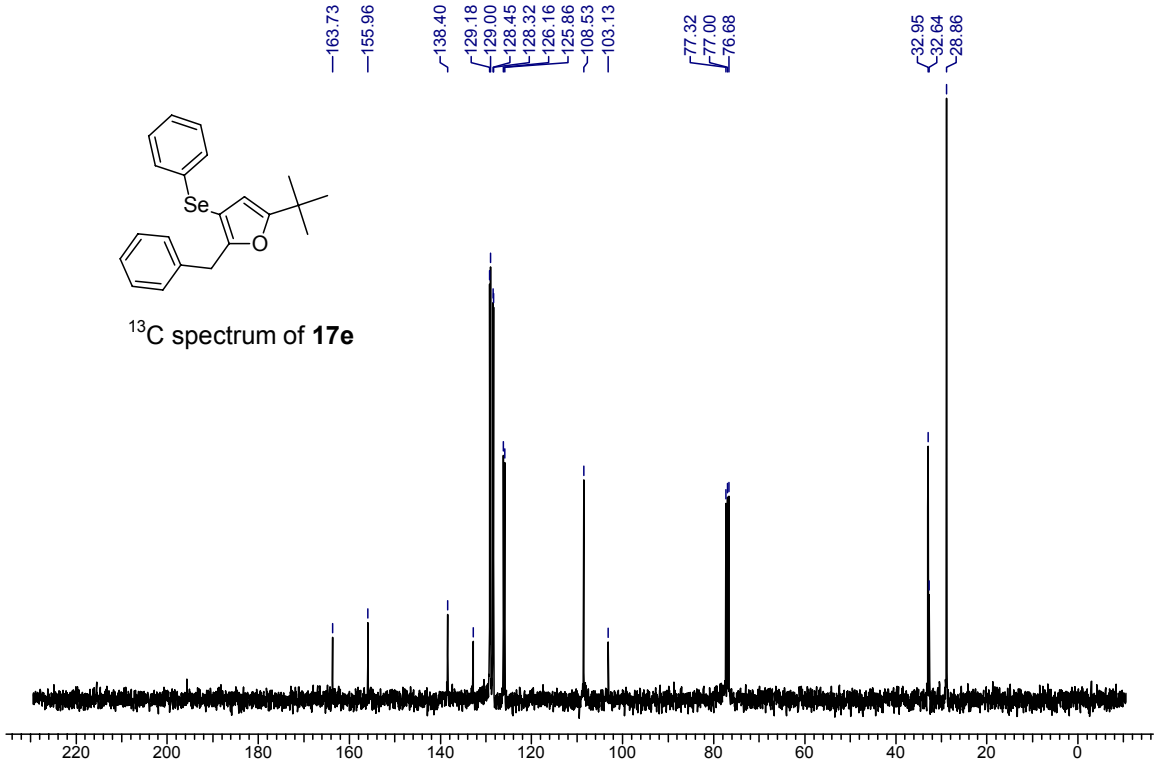
^{1}H spectrum of **17d**



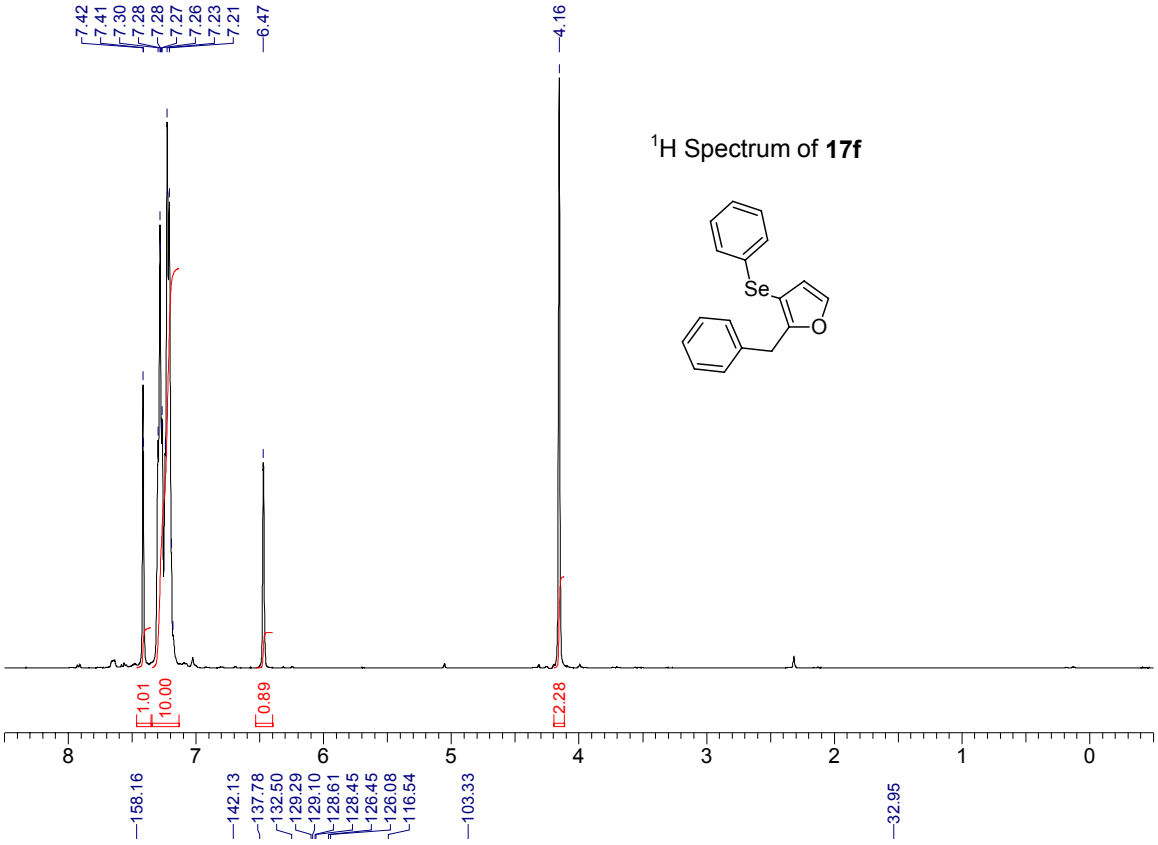
^{13}C spectrum of **17d**



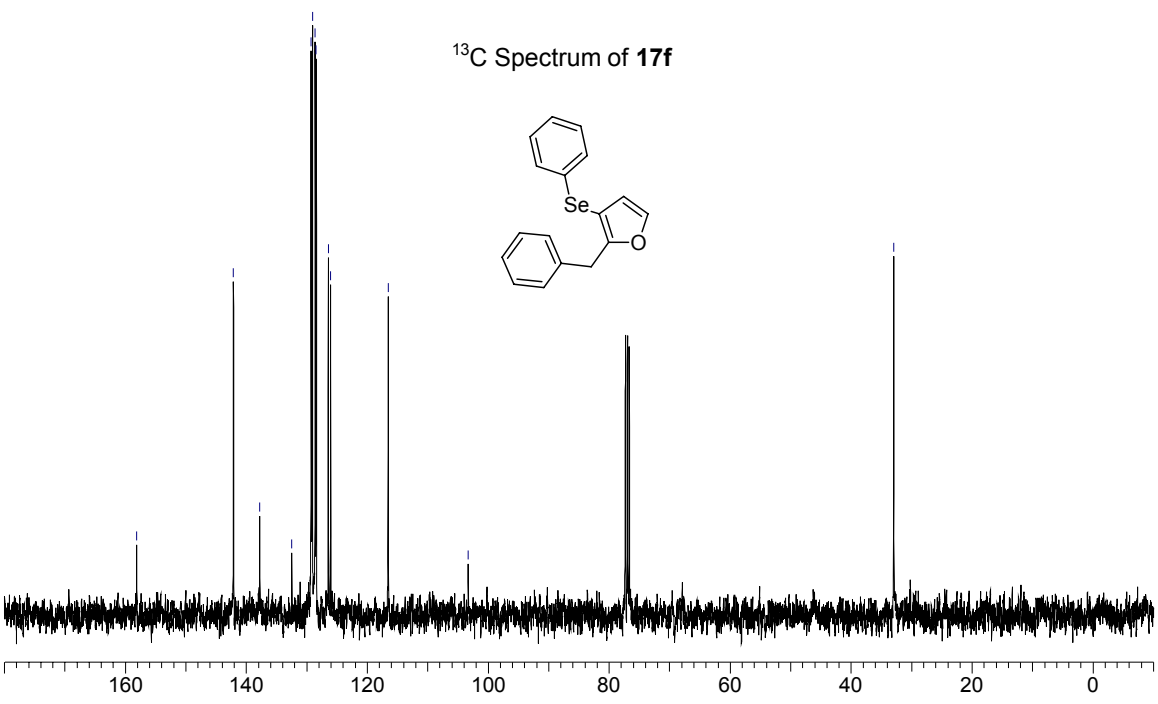
^{1}H spectrum of **17e**



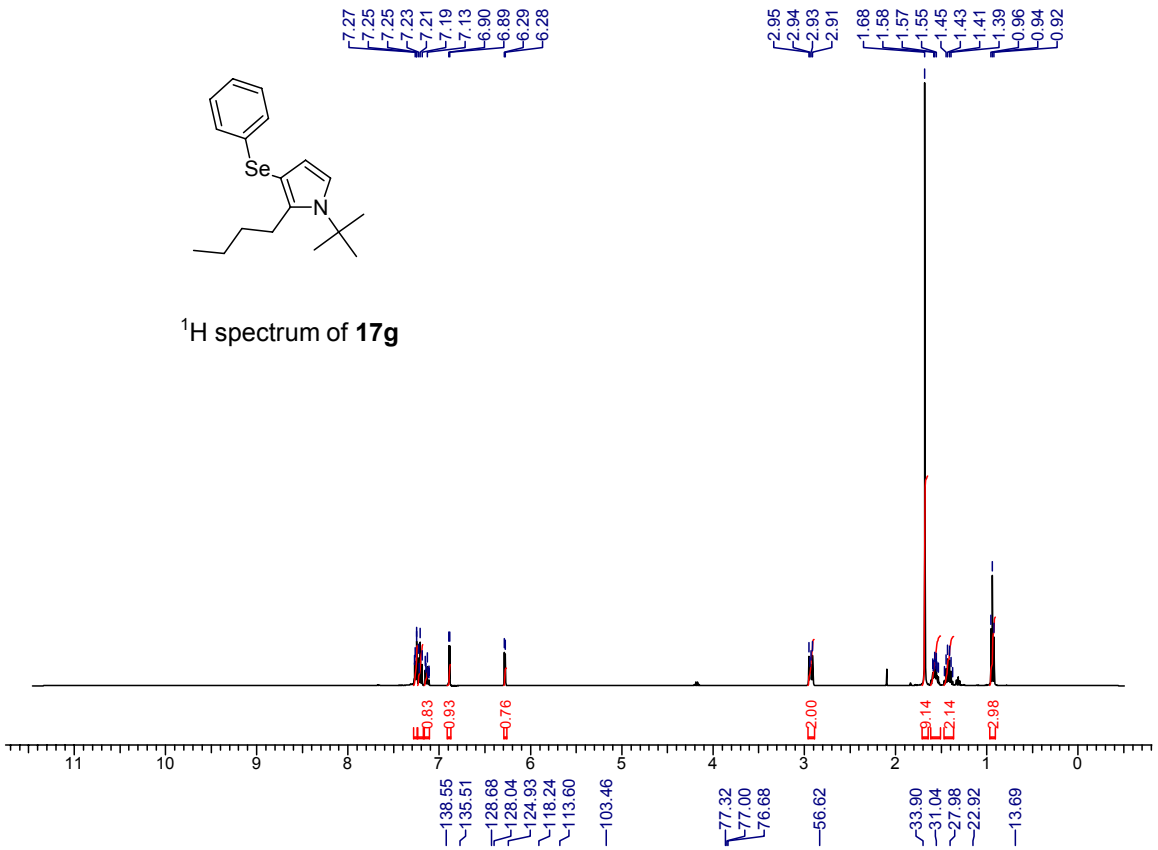
^{13}C spectrum of **17e**



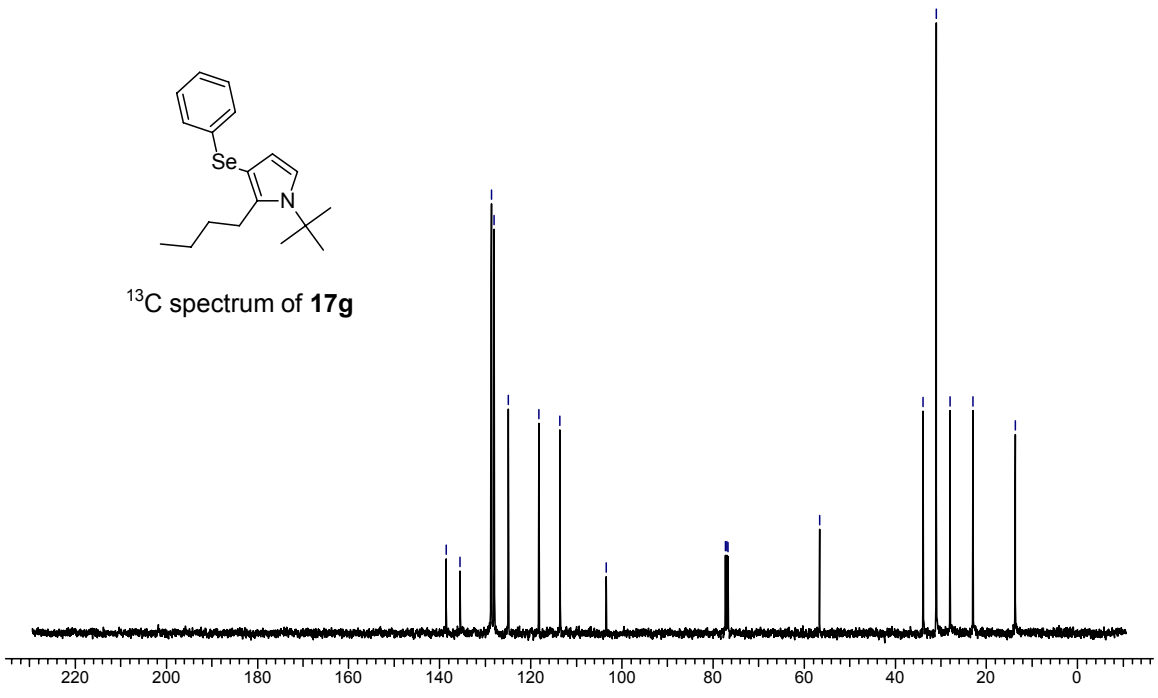
^{1}H Spectrum of **17f**



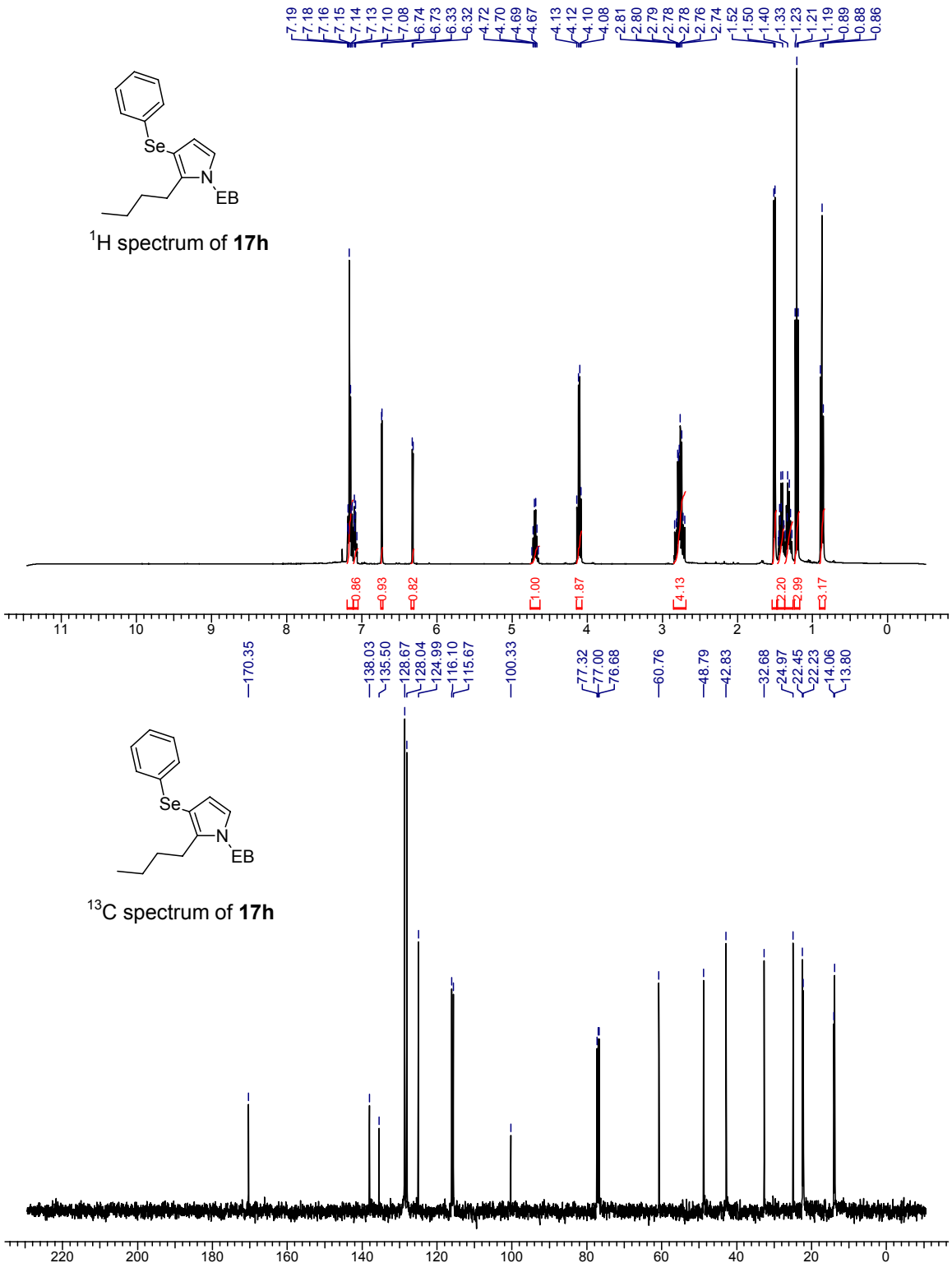
^{13}C Spectrum of **17f**

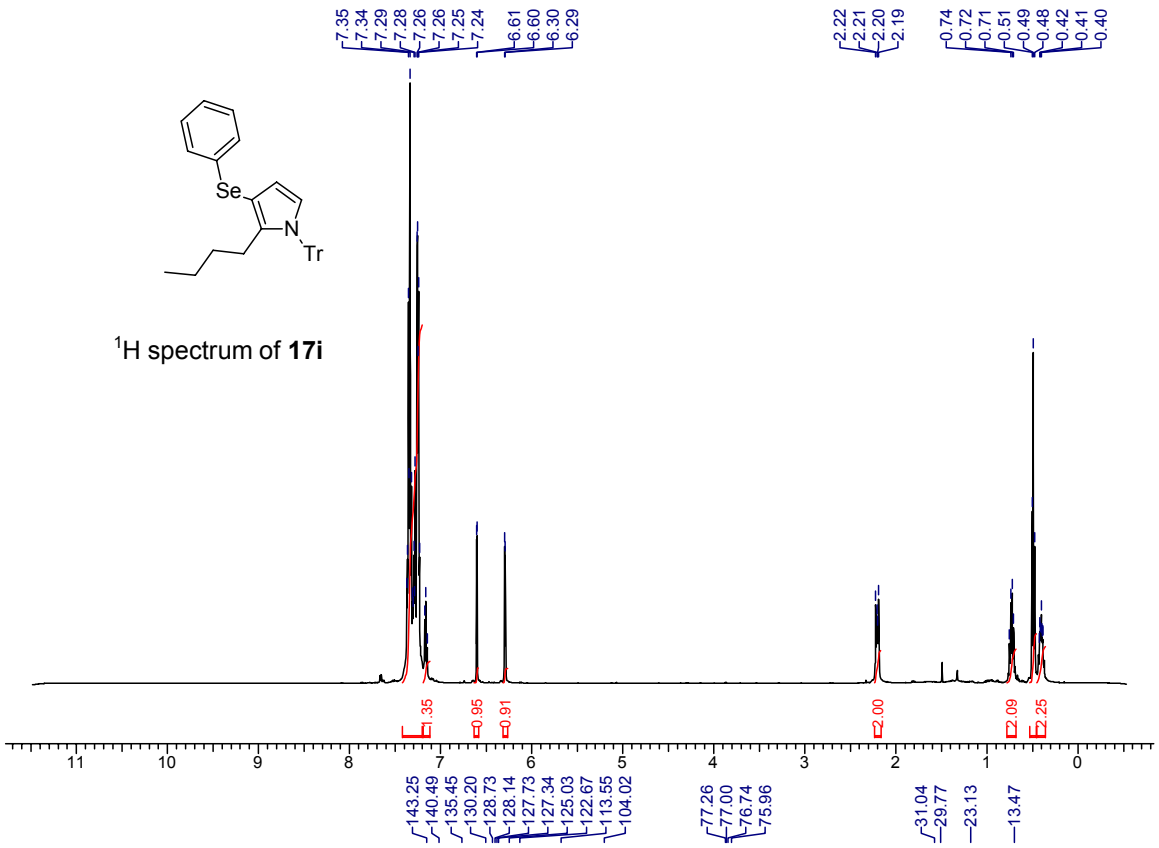


^{1}H spectrum of **17g**

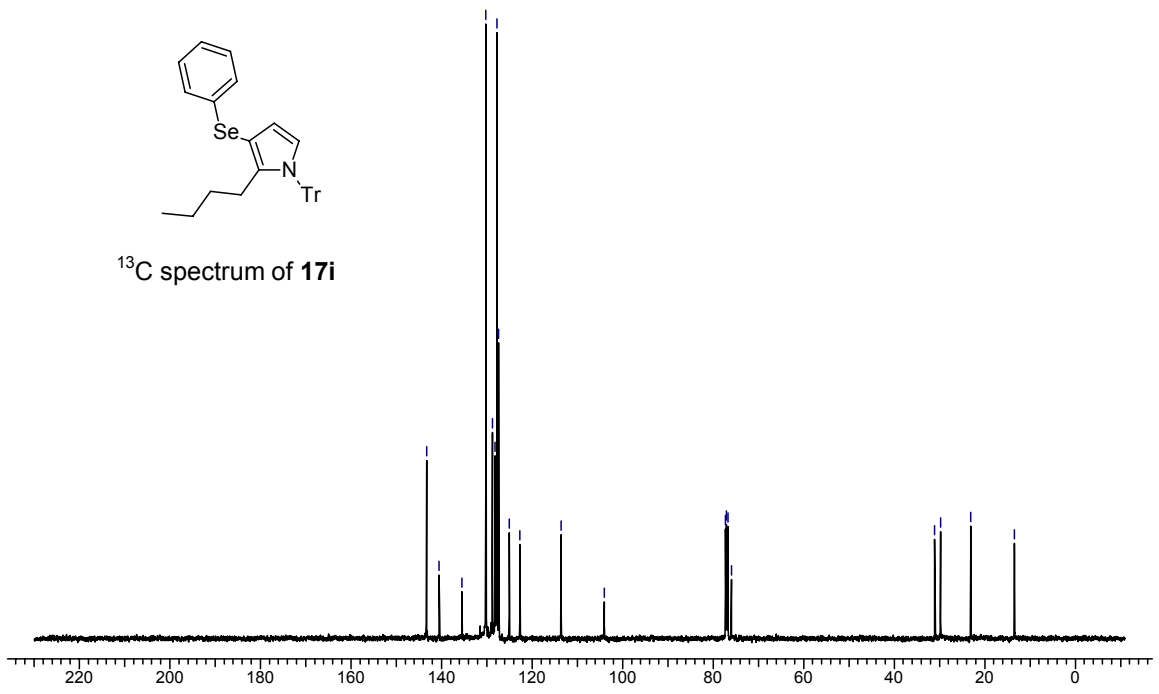


^{13}C spectrum of **17g**


Se
N
EB
1H spectrum of 17h
7.19
7.18
7.16
7.15
7.14
7.13
7.10
7.08
6.74
6.73
6.33
6.32
4.72
4.70
4.69
4.67
4.13
4.12
4.10
4.08
2.81
2.80
2.79
2.78
2.78
2.76
2.74
1.52
1.50
1.40
1.33
1.23
1.21
1.19
0.89
0.88
0.86
0.86
0.93
0.82
1.00
1.87
4.13
2.20
2.99
3.17
11
10
9
8
7
6
5
4
3
2
1
0
170.35
138.03
135.50
128.67
128.04
124.99
116.10
115.67
100.33
77.32
77.00
76.68
60.76
48.79
42.83
32.68
24.97
22.45
22.23
14.06
13.80
Se
N
EB
13C spectrum of 17h
220
200
180
160
140
120
100
80
60
40
20
0

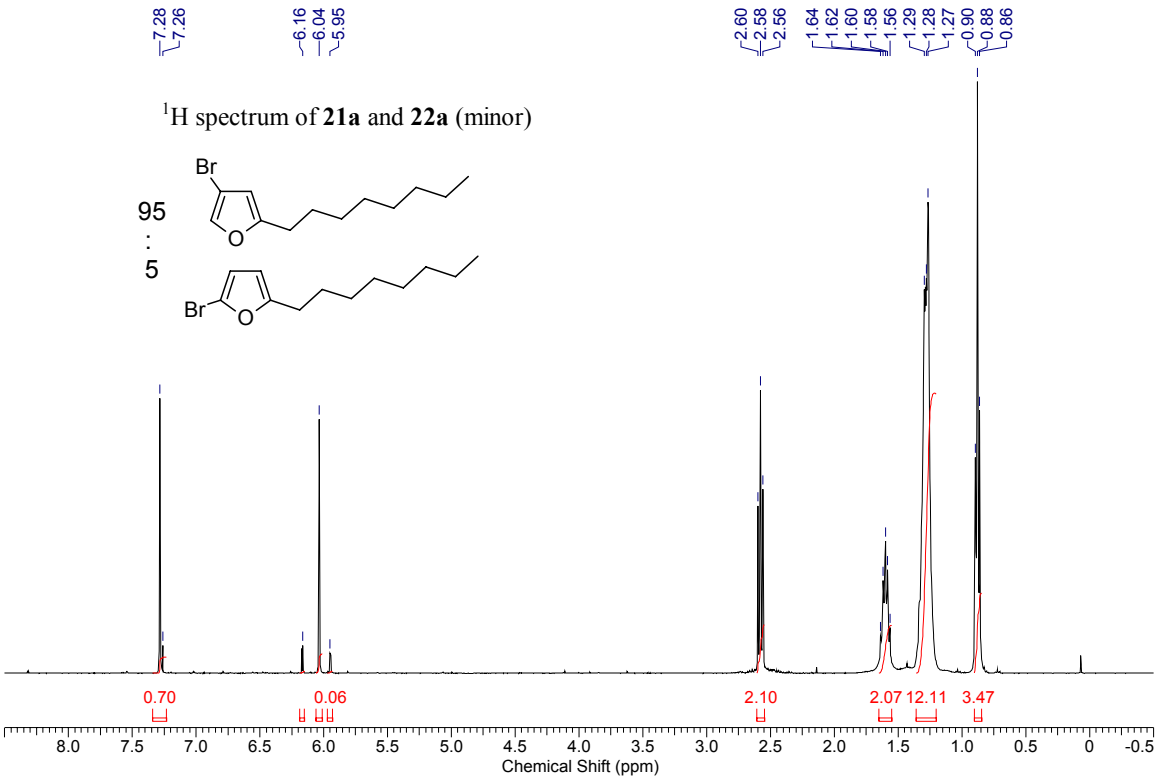


^{1}H spectrum of **17i**

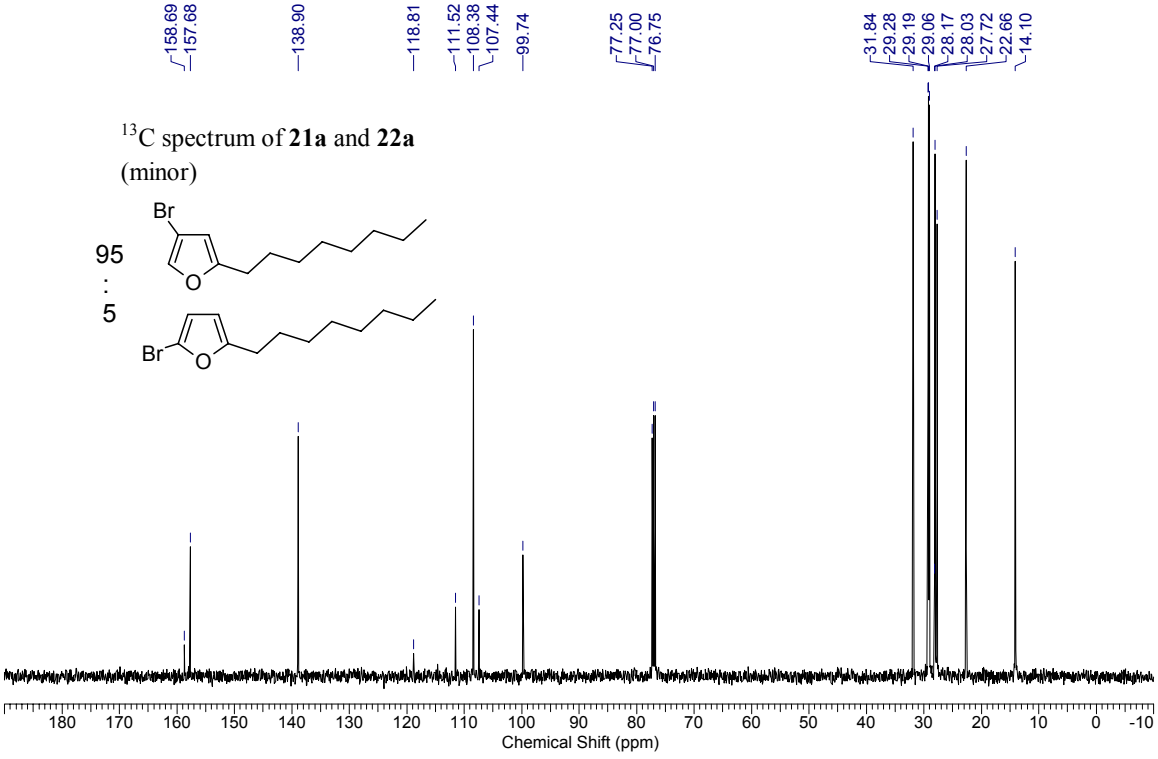


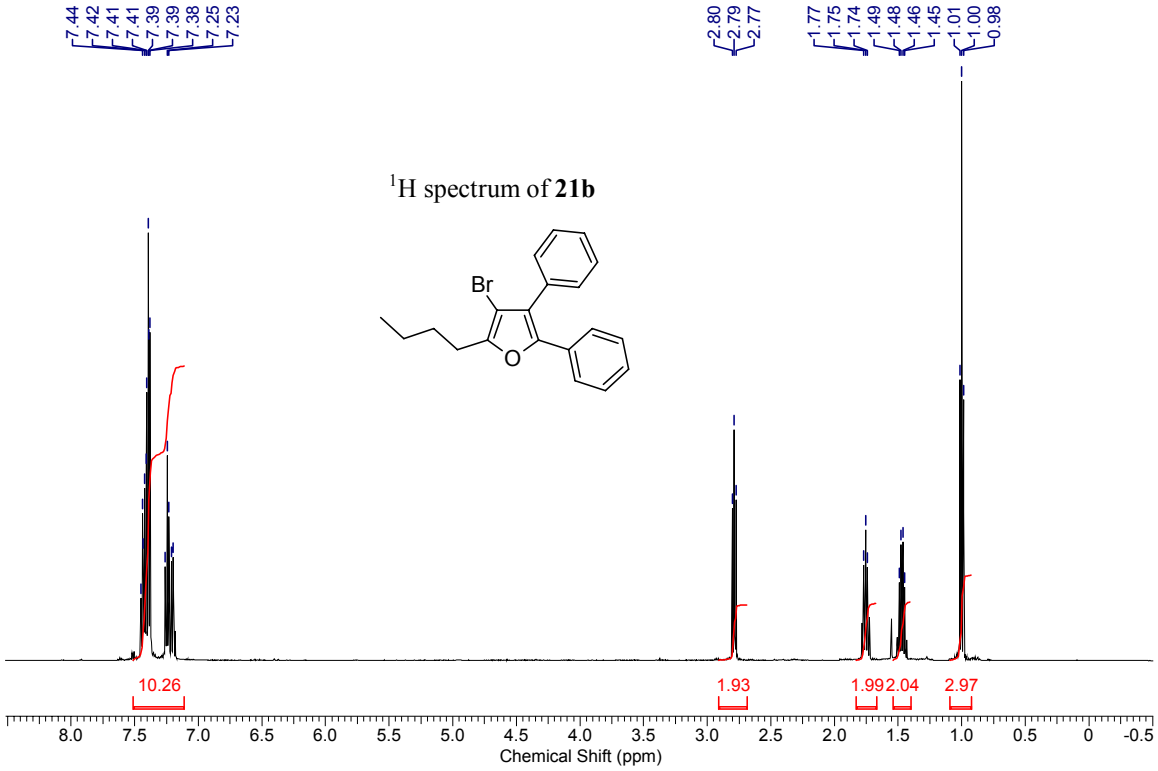
^{13}C spectrum of **17i**

^{1}H spectrum of **21a** and **22a** (minor)

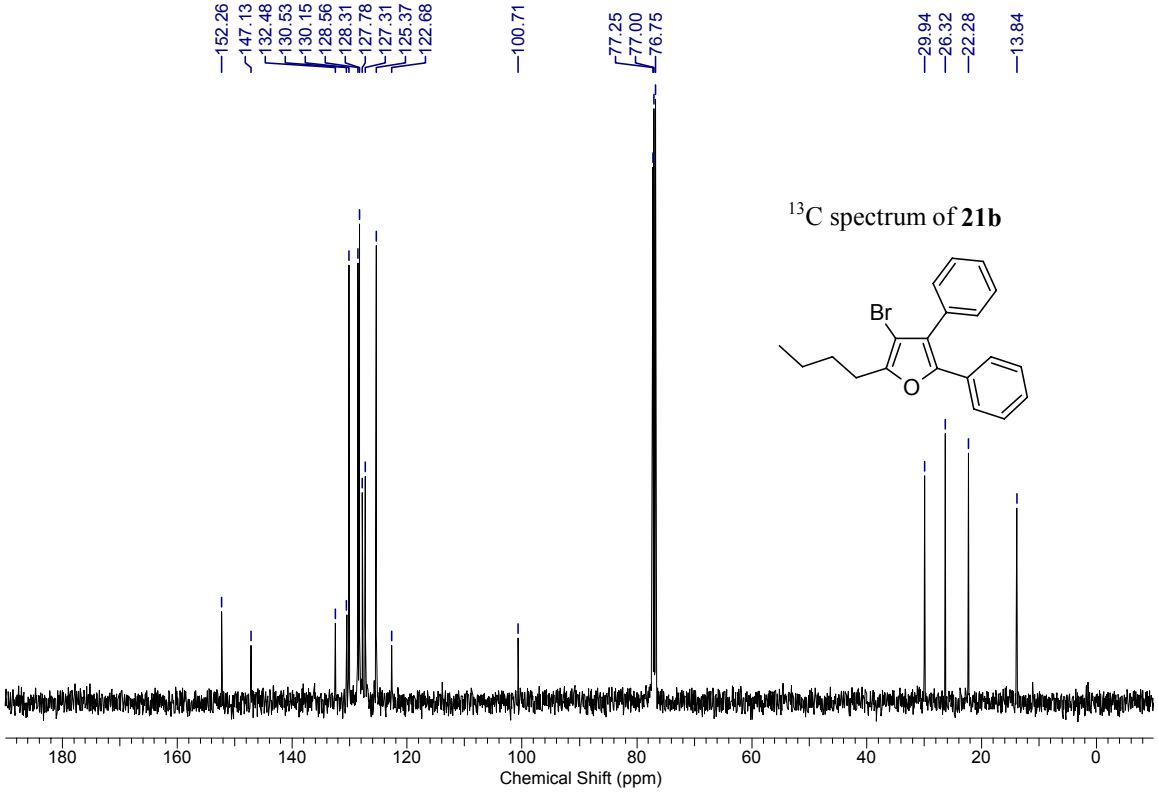


^{13}C spectrum of **21a** and **22a** (minor)



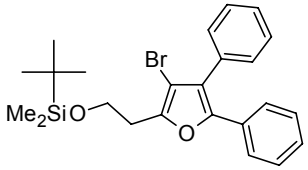


^{1}H spectrum of **21b**

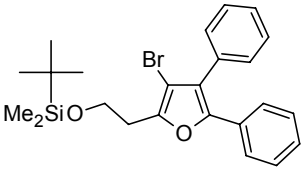


^{13}C spectrum of **21b**

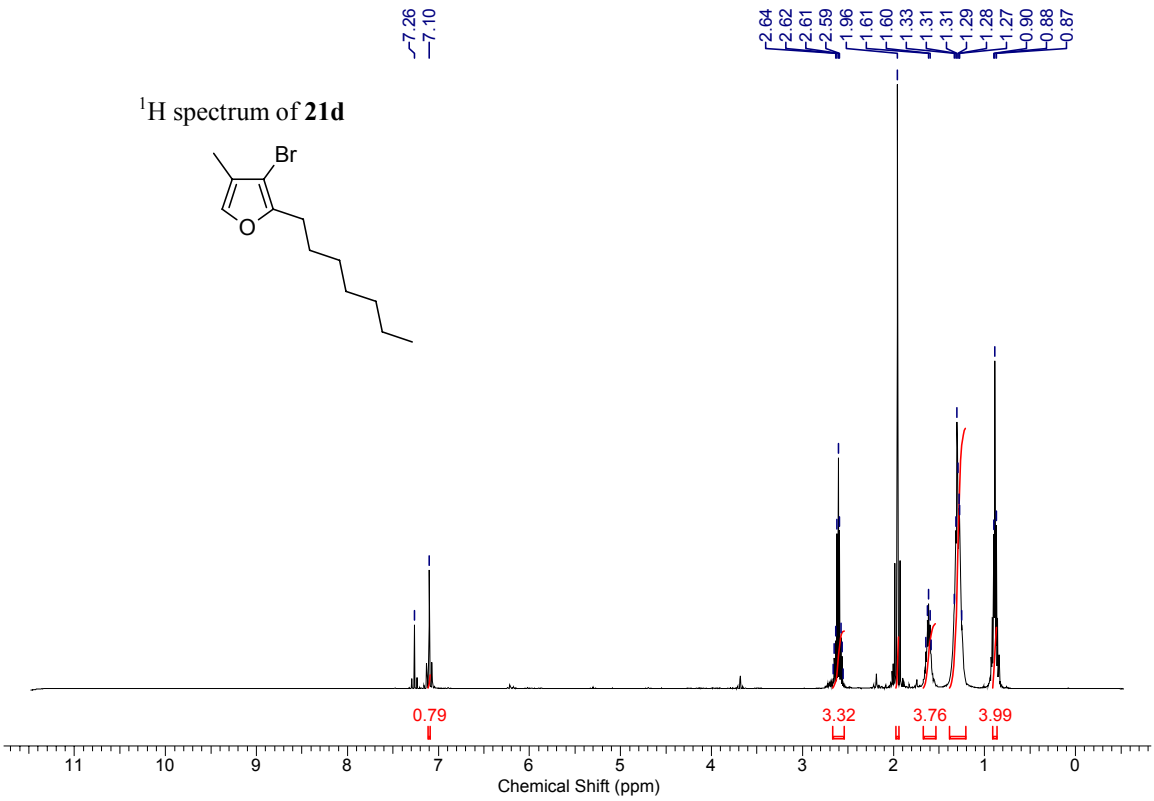
^{1}H spectrum of **21c**



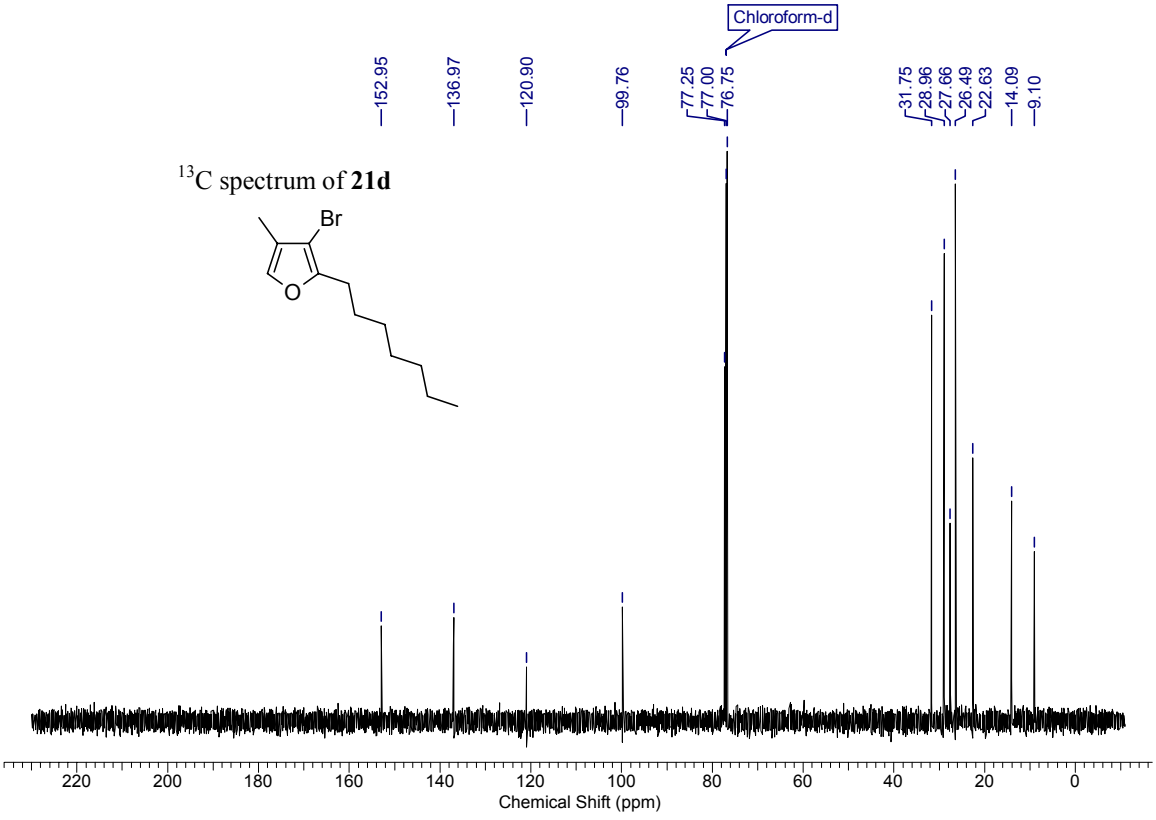
^{13}C spectrum of **21c**



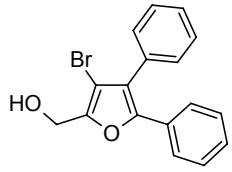
^{1}H spectrum of **21d**



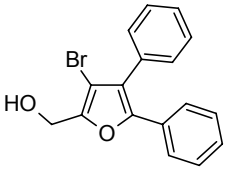
^{13}C spectrum of **21d**

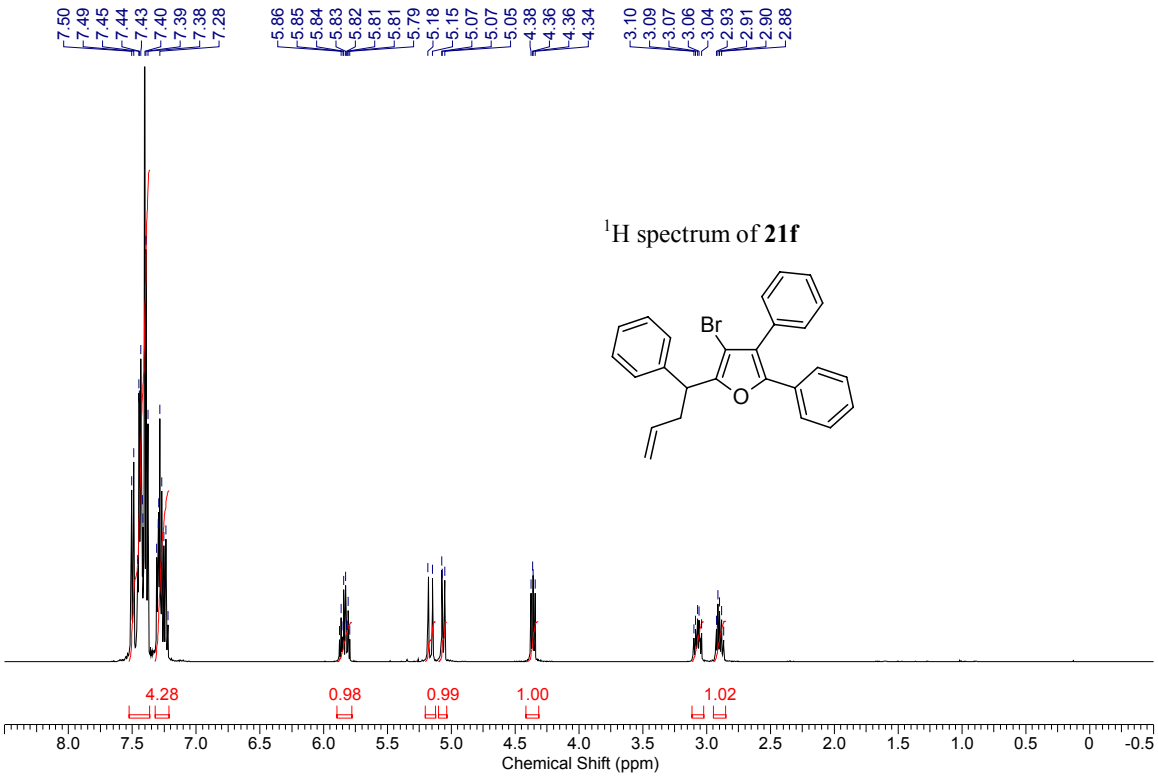


^{1}H spectrum of **21e**

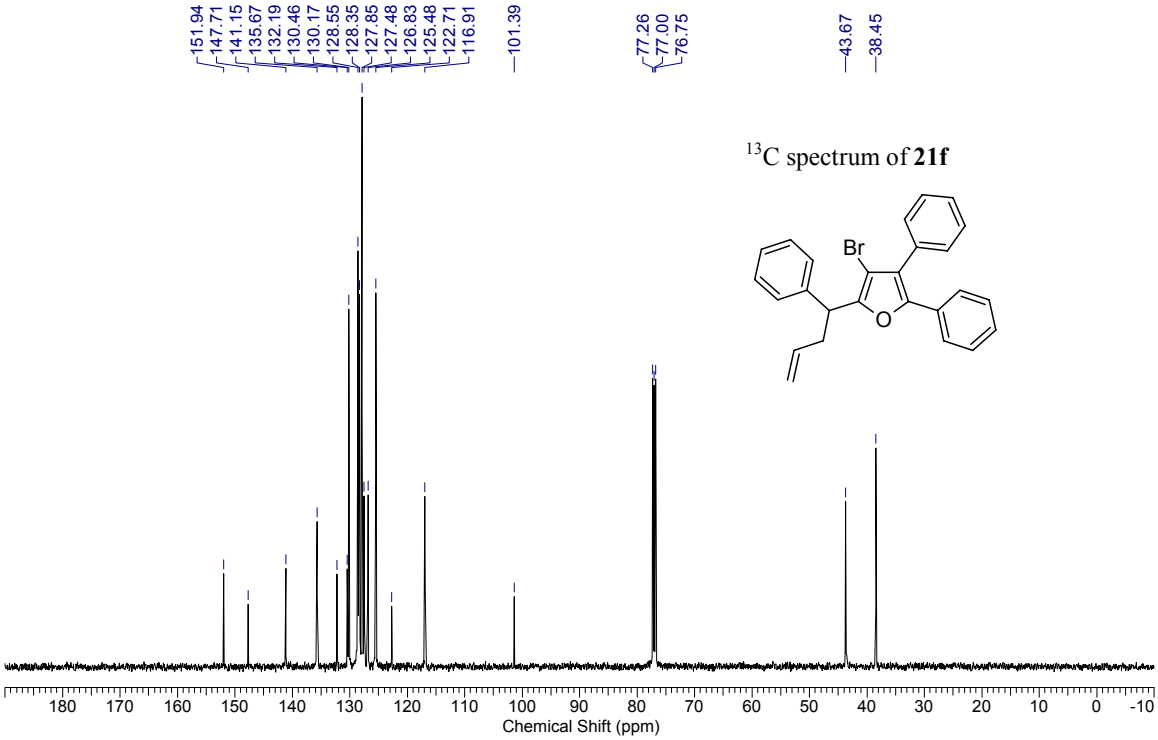


^{13}C spectrum of **21e**

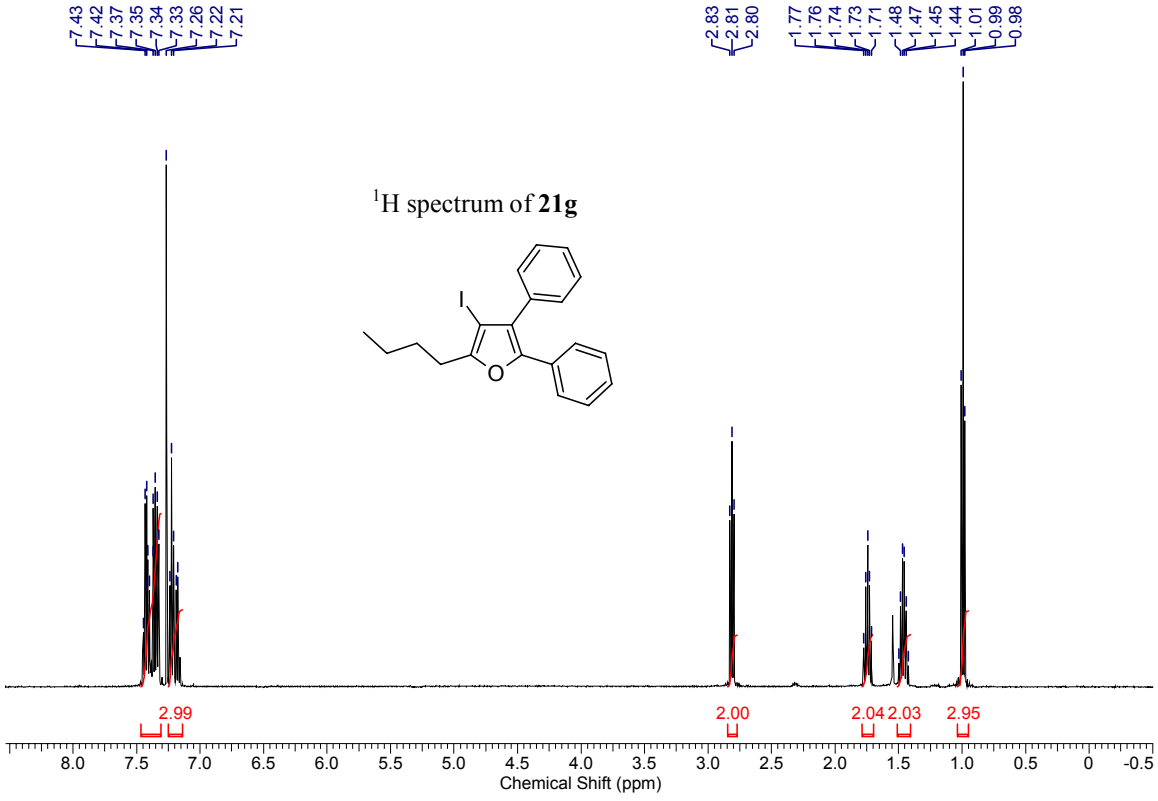




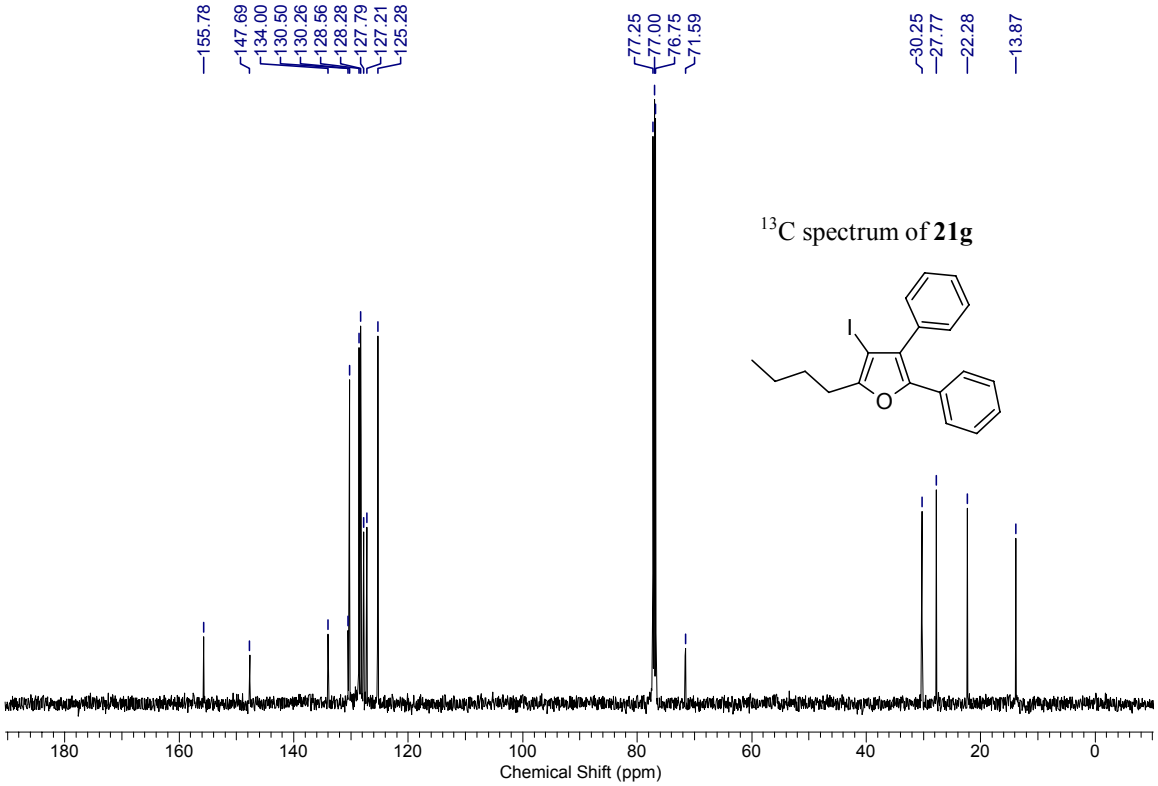
^{1}H spectrum of **21f**



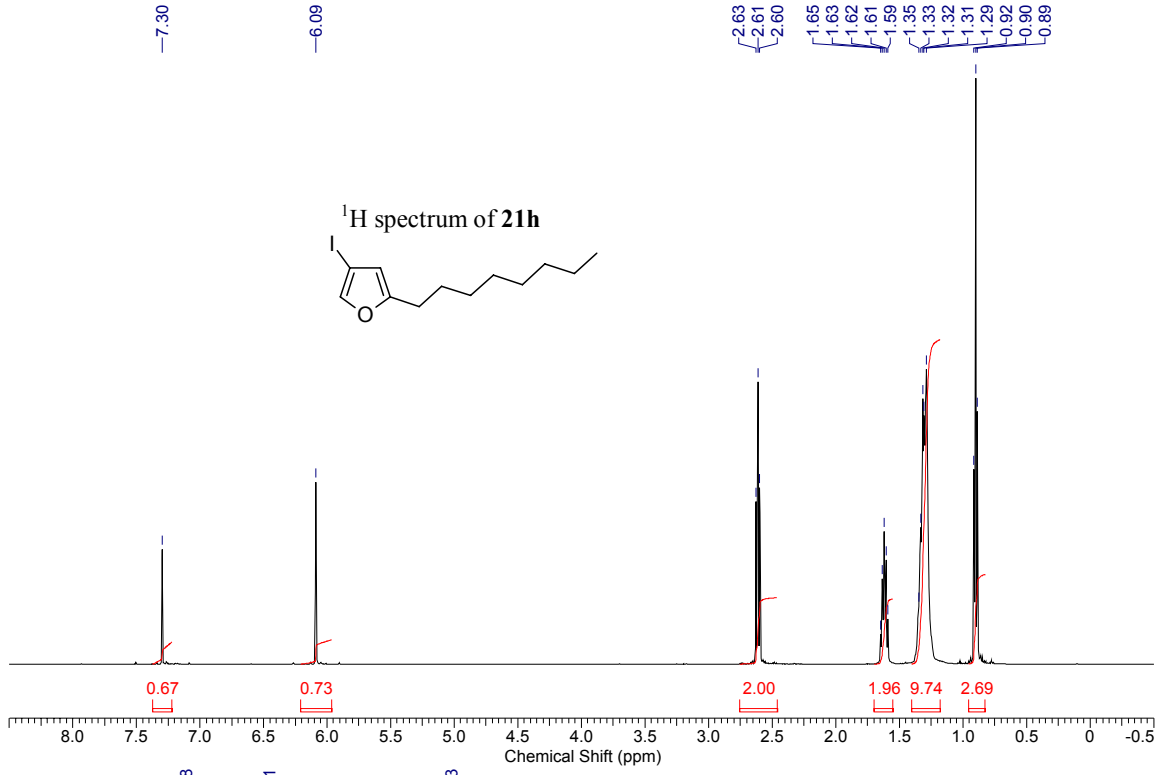
^{13}C spectrum of **21f**



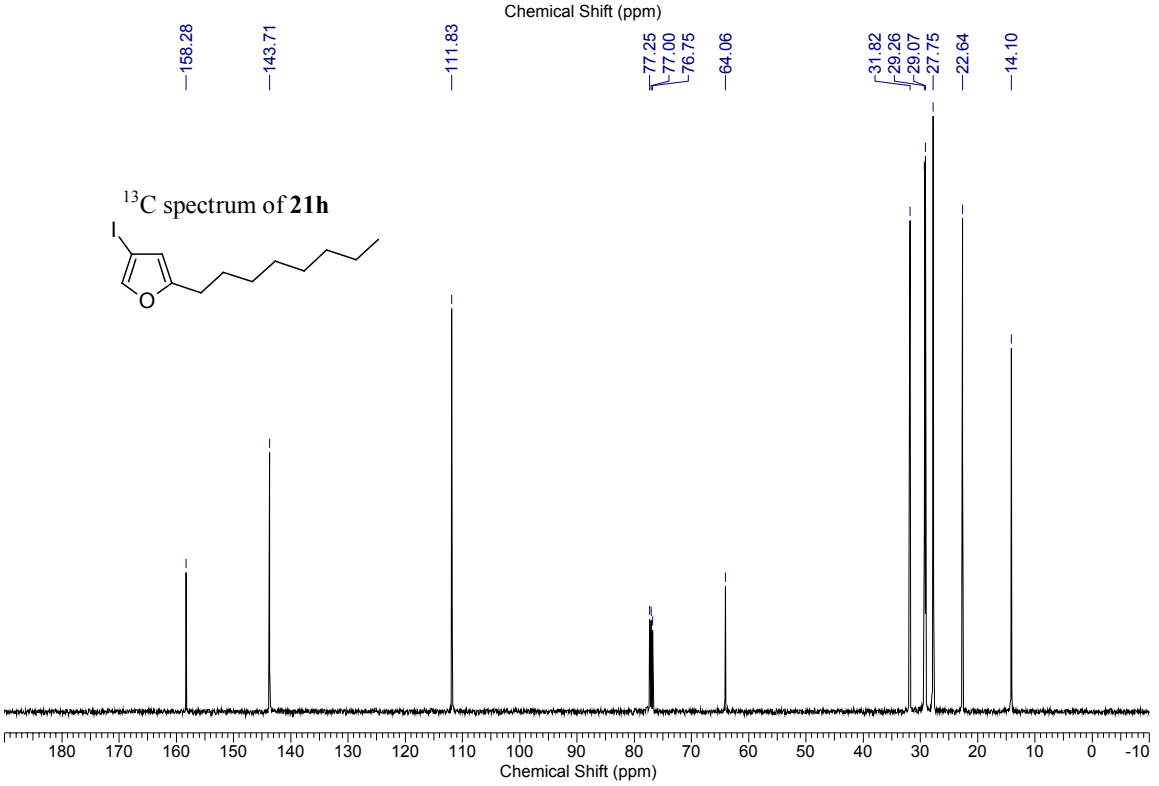
^{1}H spectrum of **21g**



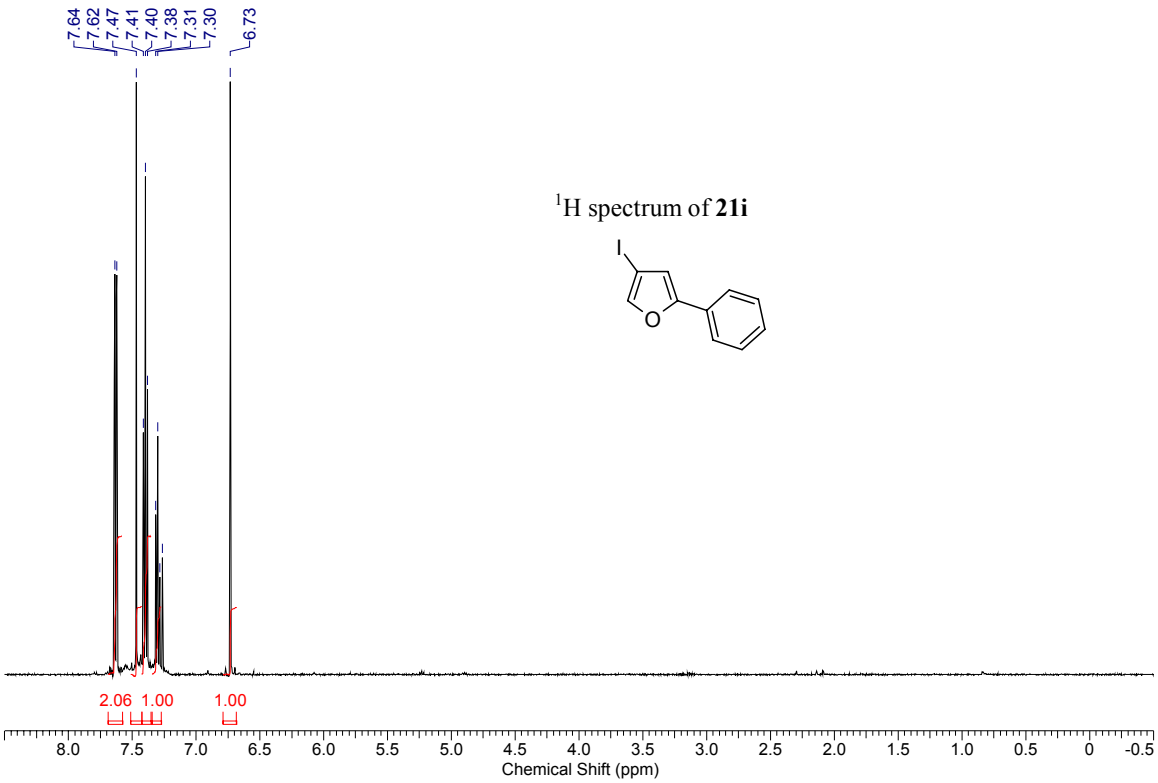
^{13}C spectrum of **21g**



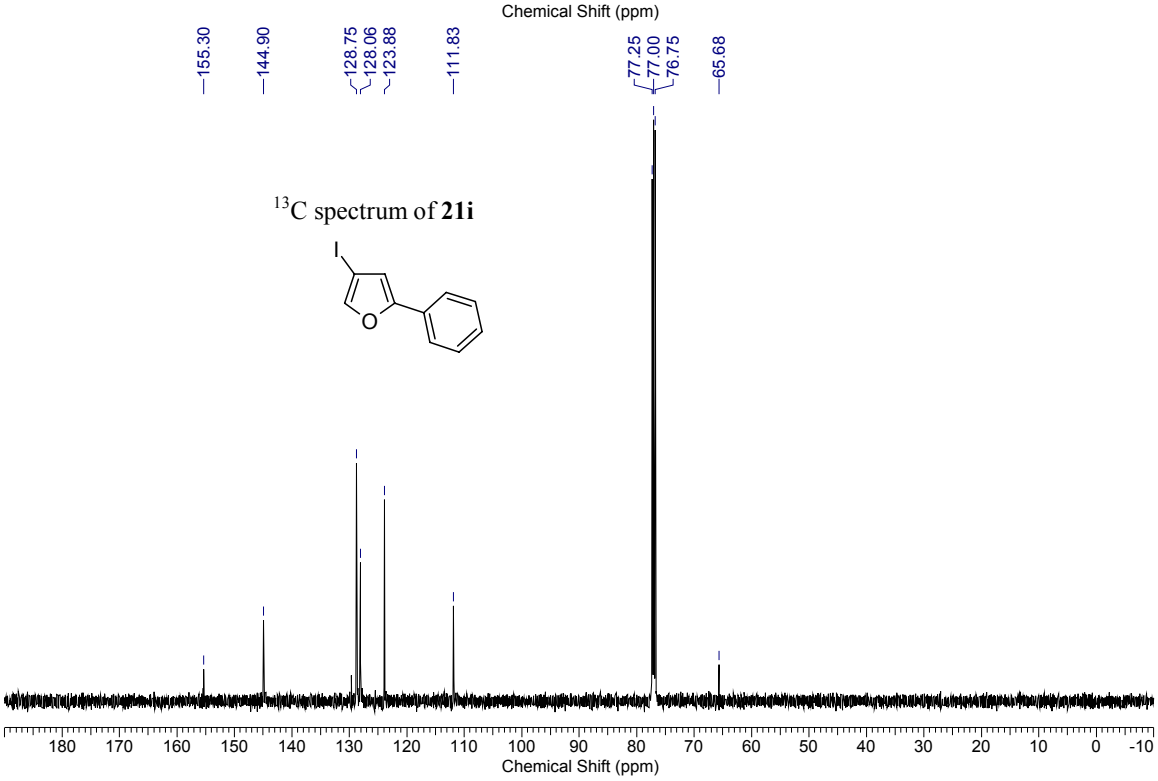
^{1}H spectrum of **21h**



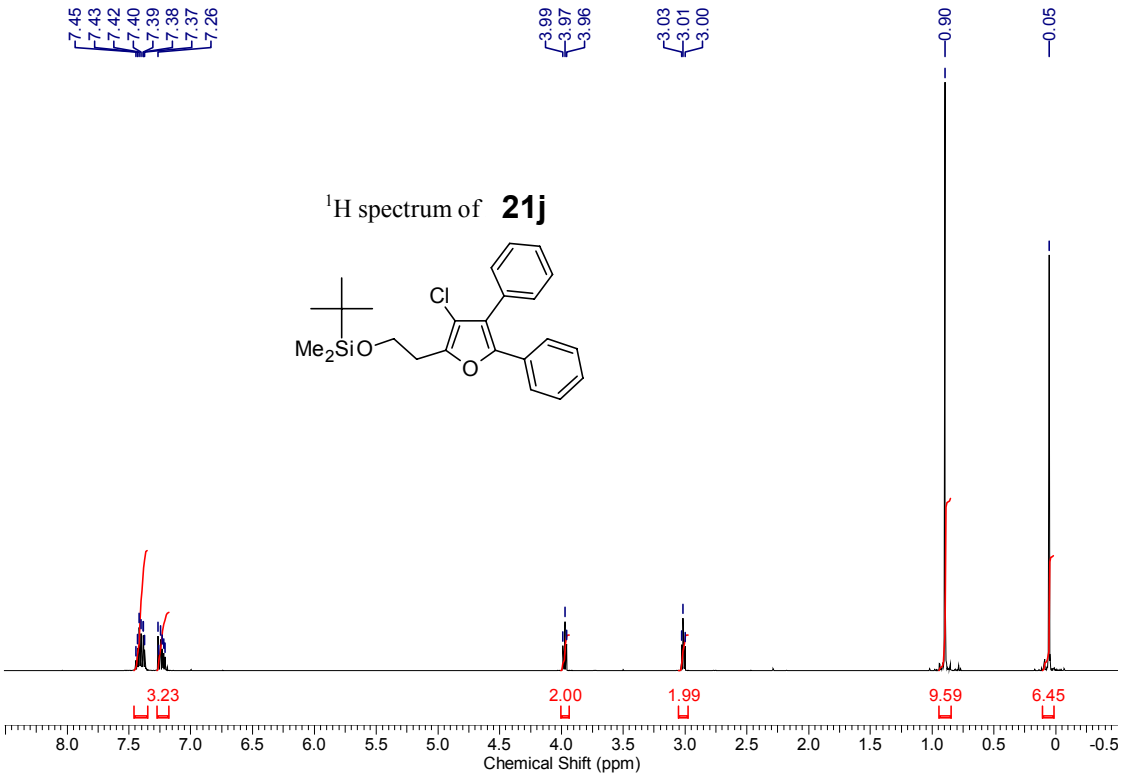
^{13}C spectrum of **21h**



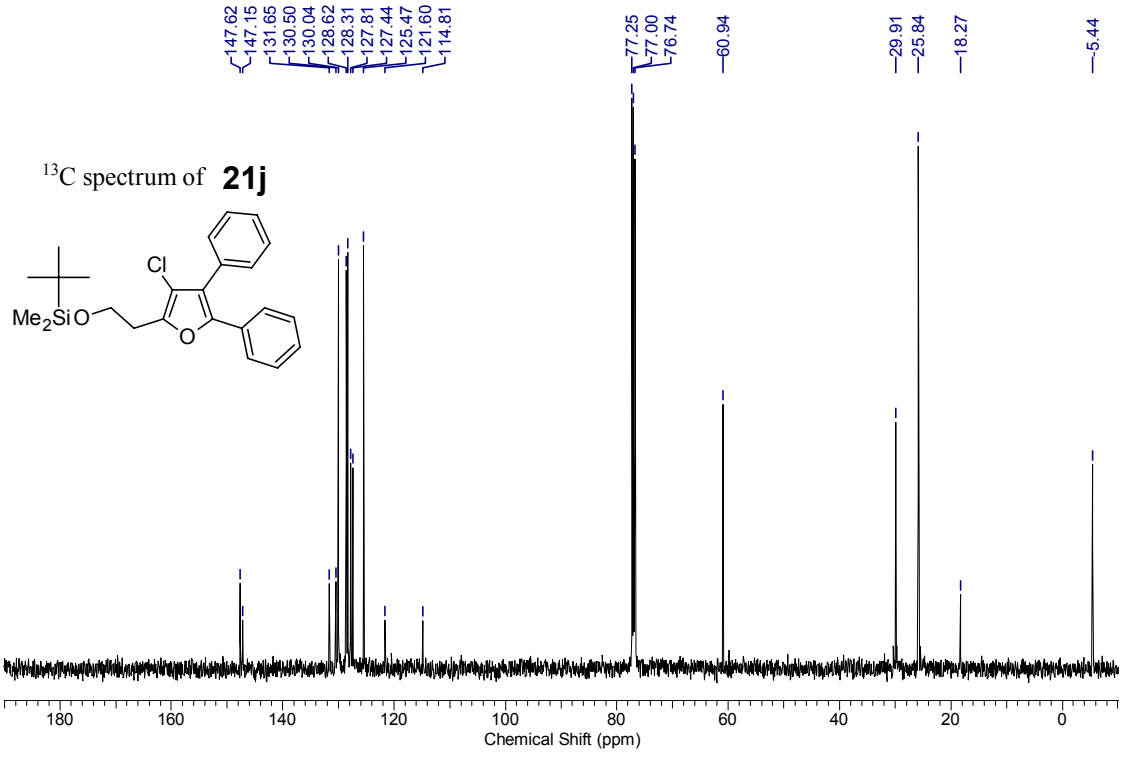
^{1}H spectrum of **21i**



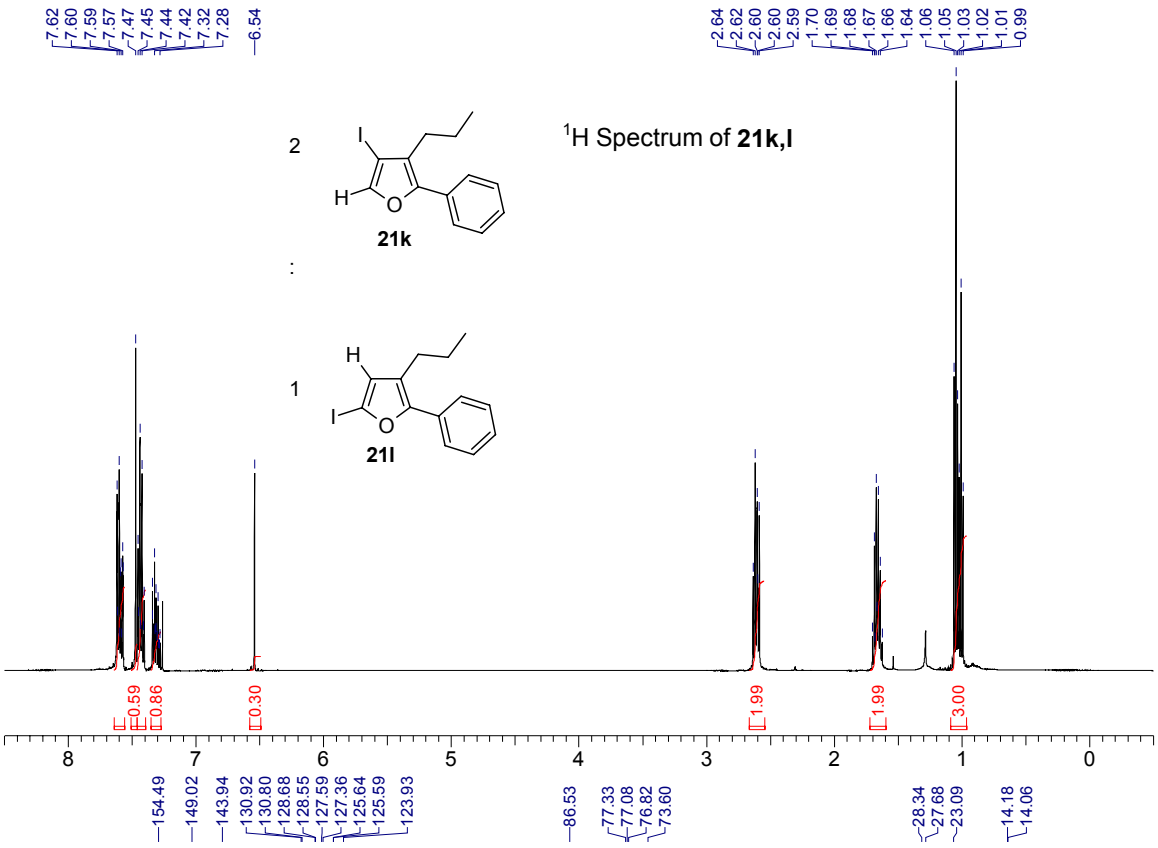
^{13}C spectrum of **21i**

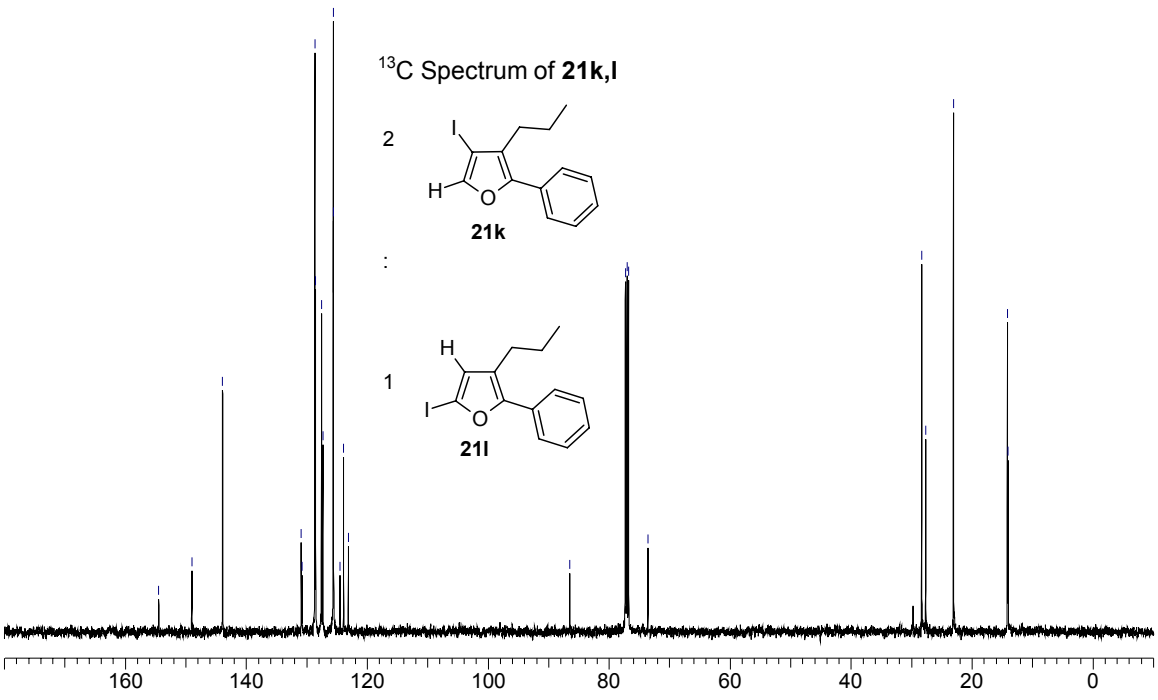


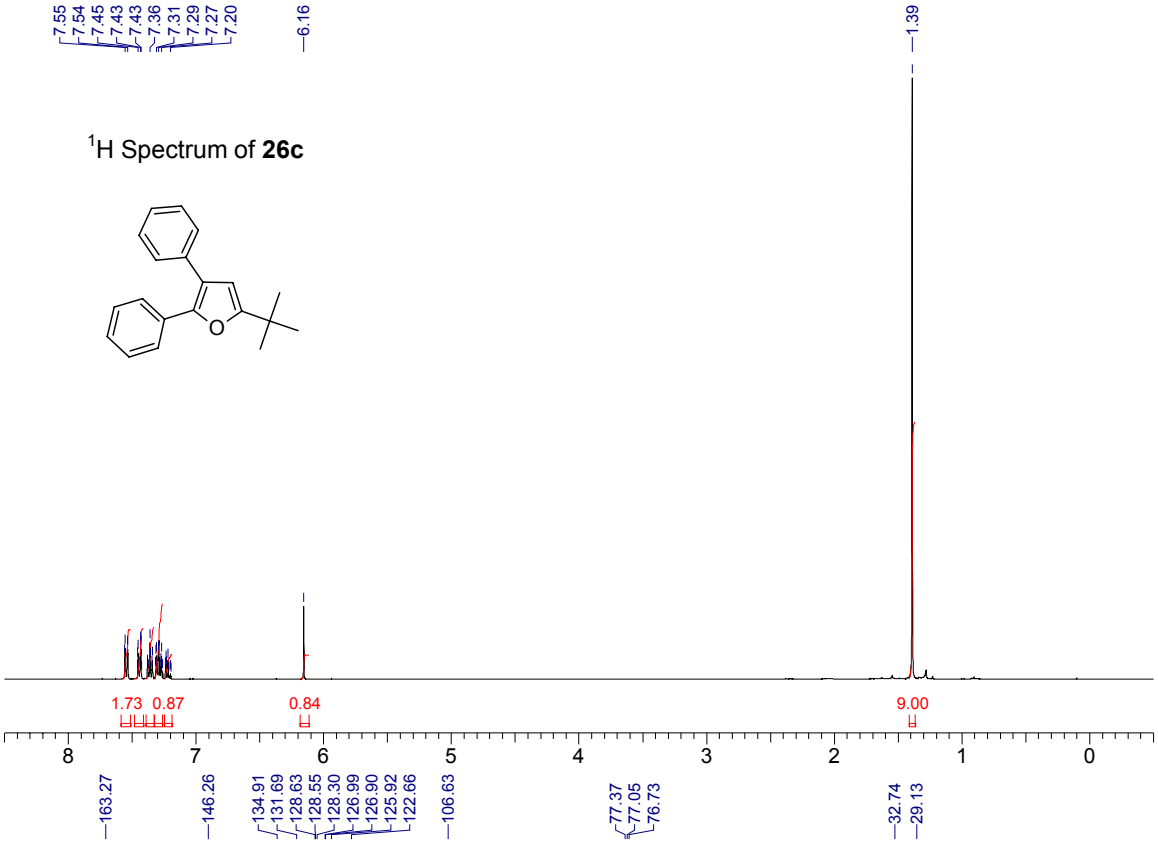
^{1}H spectrum of **21j**



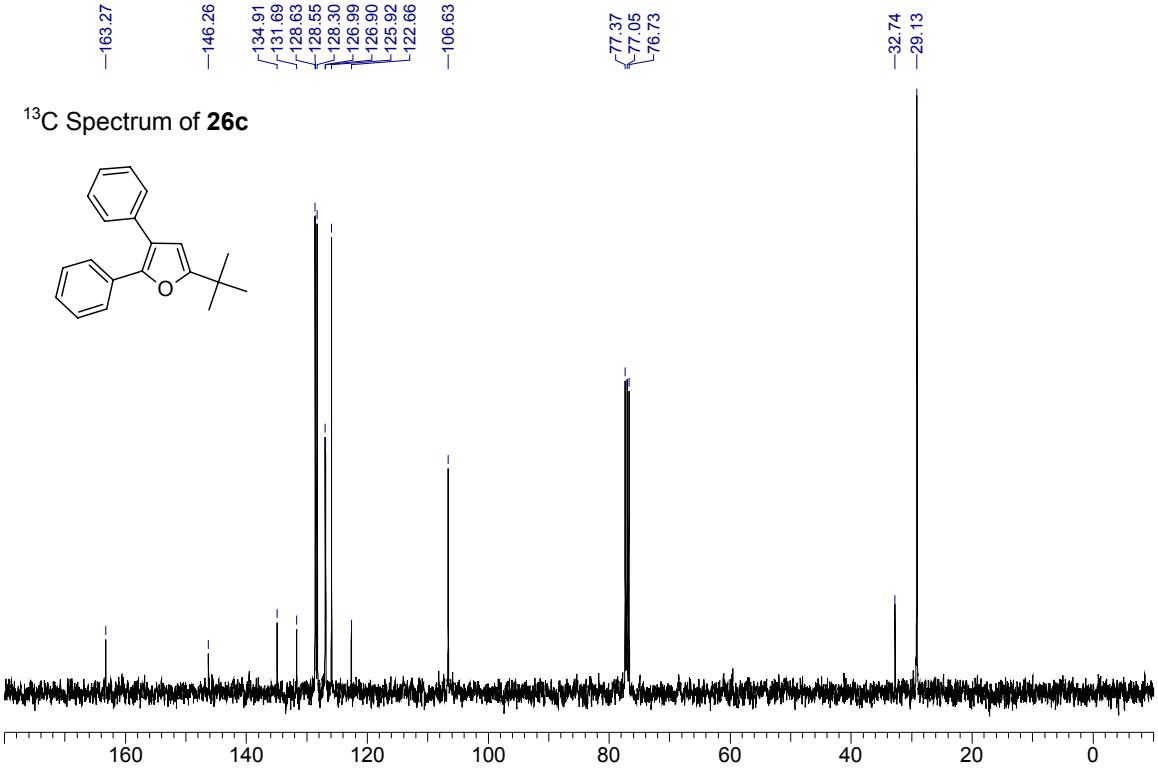
^{13}C spectrum of **21j**


7.62
7.60
7.59
7.57
7.47
7.45
7.44
7.42
7.32
7.28
6.54
2.64
2.62
2.60
2.60
2.59
1.70
1.69
1.68
1.67
1.66
1.64
1.06
1.05
1.03
1.02
1.01
0.99
2
1
21k
21l
1H Spectrum of 21k,l
0.59
0.86
0.30
1.99
1.99
3.00
8
7
6
5
4
3
2
1
0

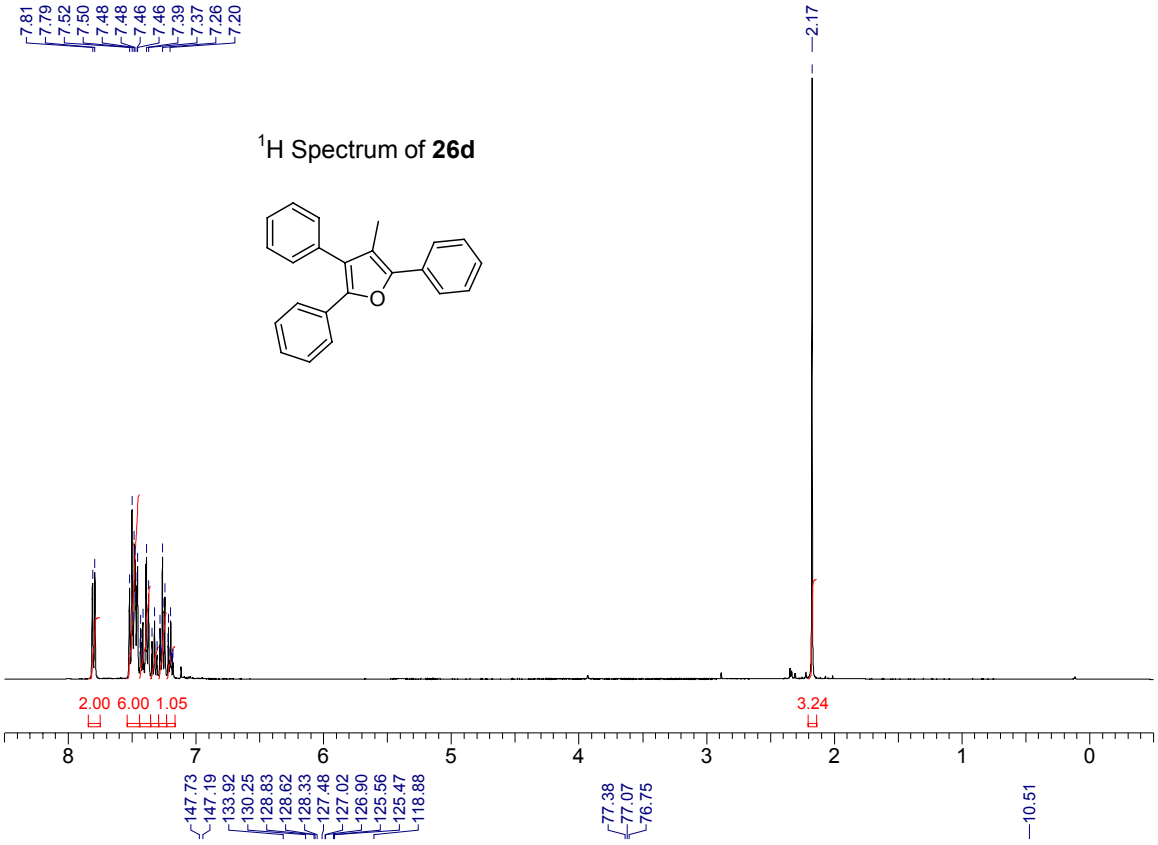

154.49
149.02
143.94
130.92
130.80
128.68
128.55
127.59
127.36
125.64
125.59
123.93
86.53
77.33
77.08
76.82
73.60
28.34
27.68
23.09
14.18
14.06
13C Spectrum of 21k,l
2
1
21k
21l
160
140
120
100
80
60
40
20
0



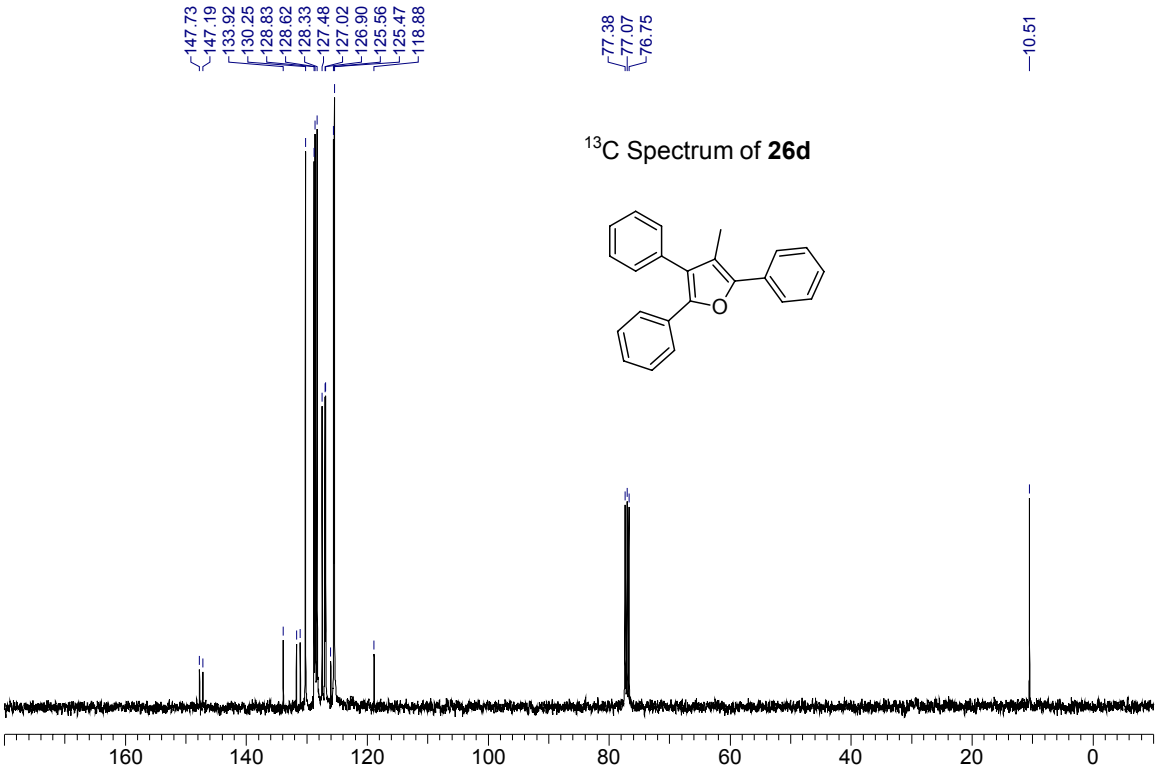
^{1}H Spectrum of **26c**



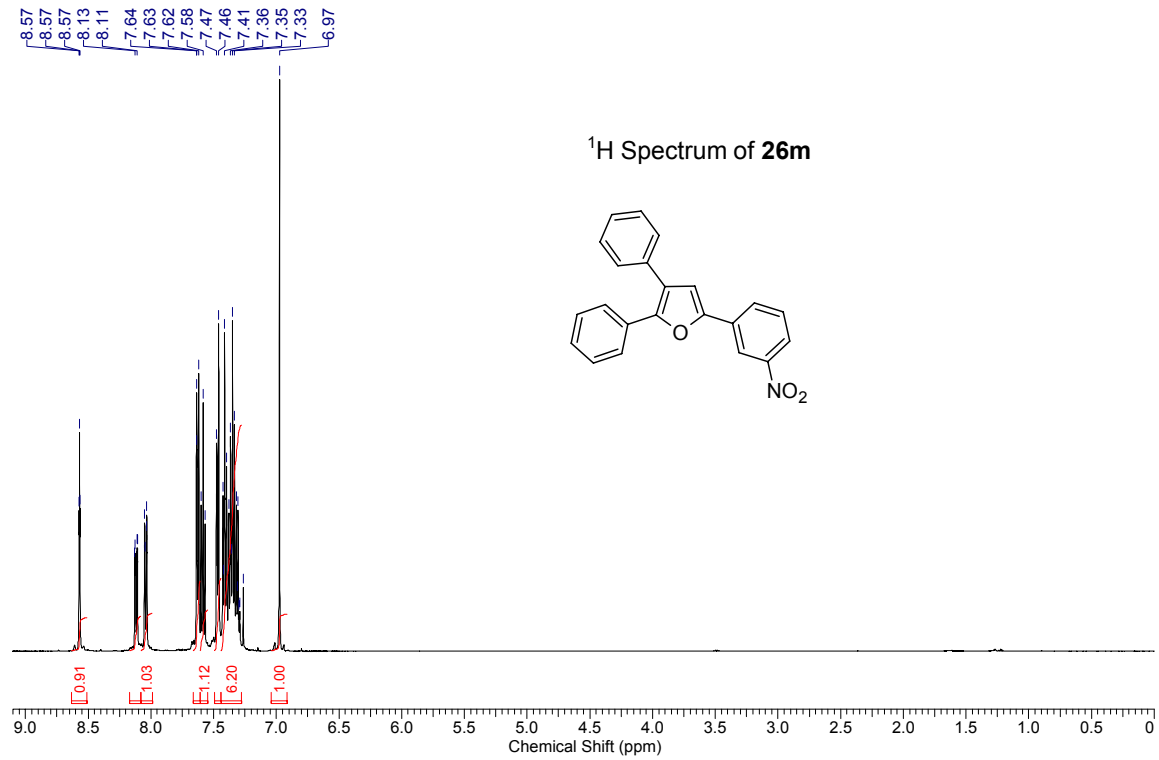
^{13}C Spectrum of **26c**



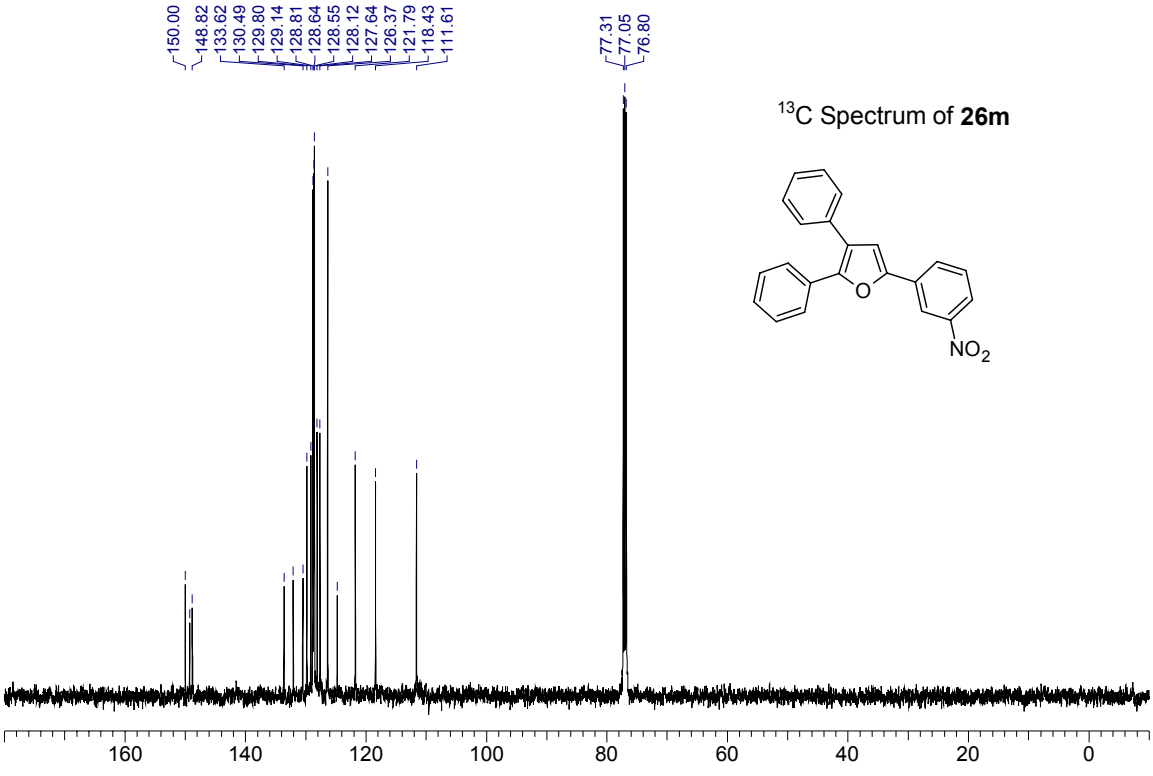
^{1}H Spectrum of **26d**



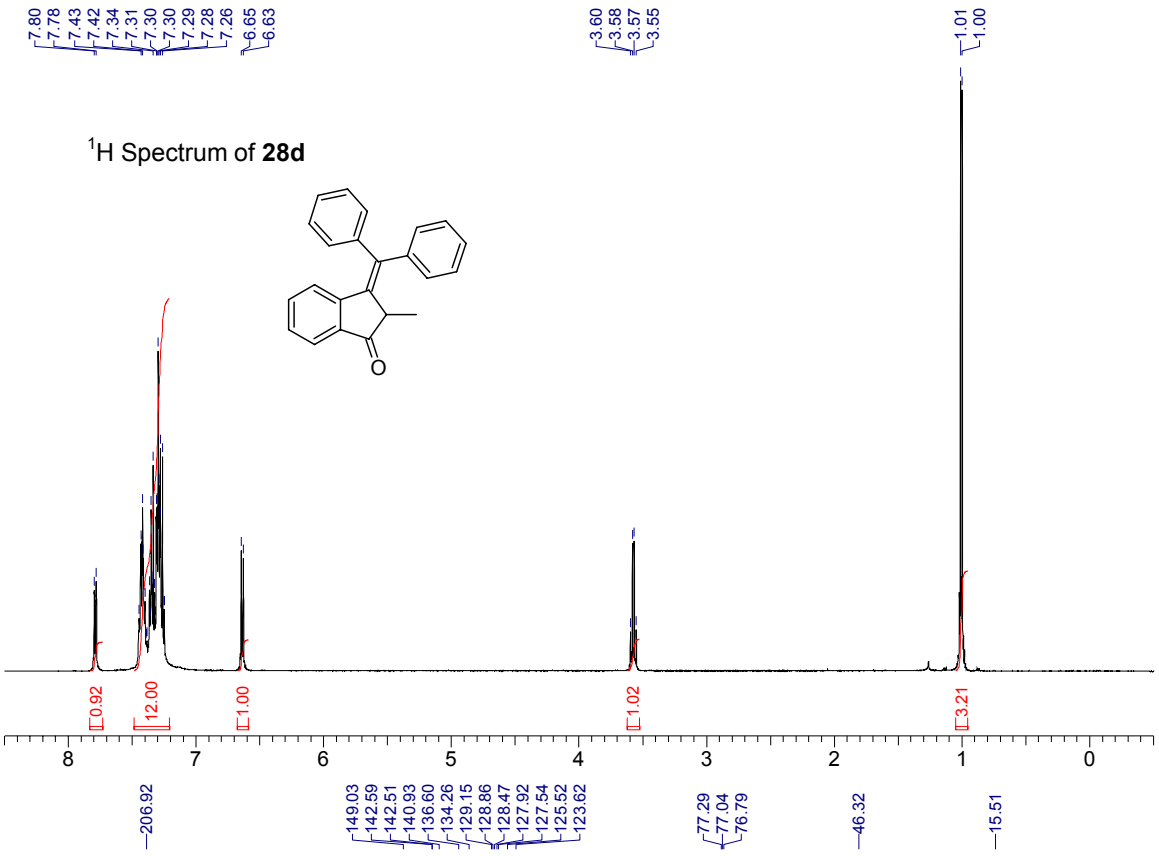
^{13}C Spectrum of **26d**



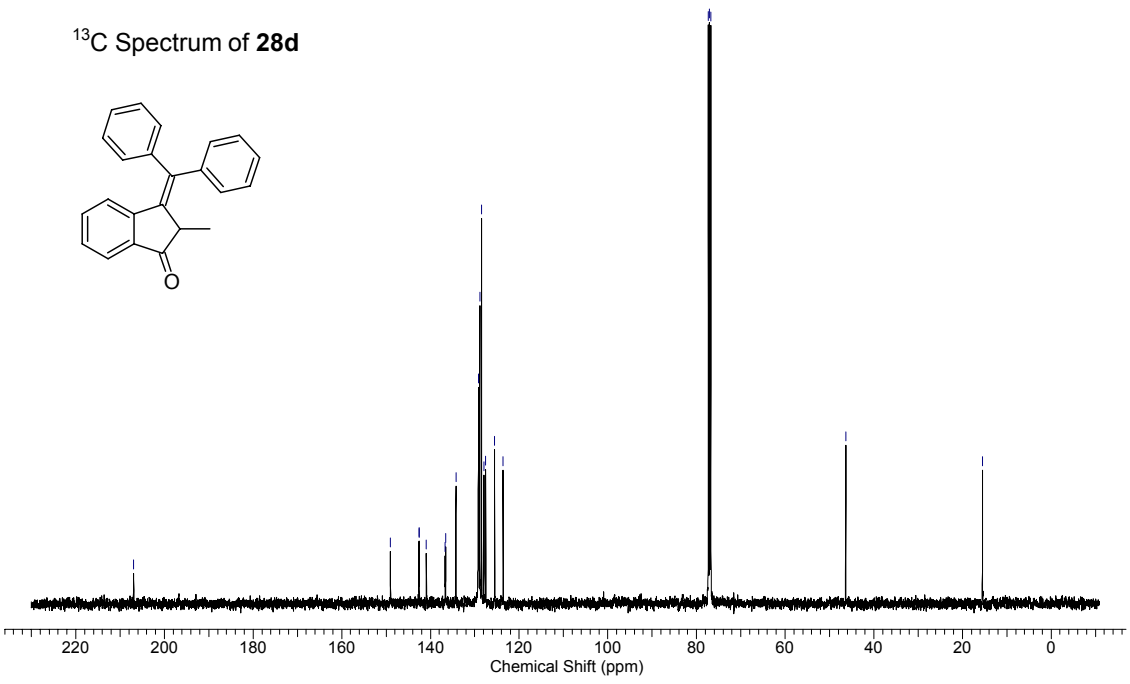
^{1}H Spectrum of **26m**



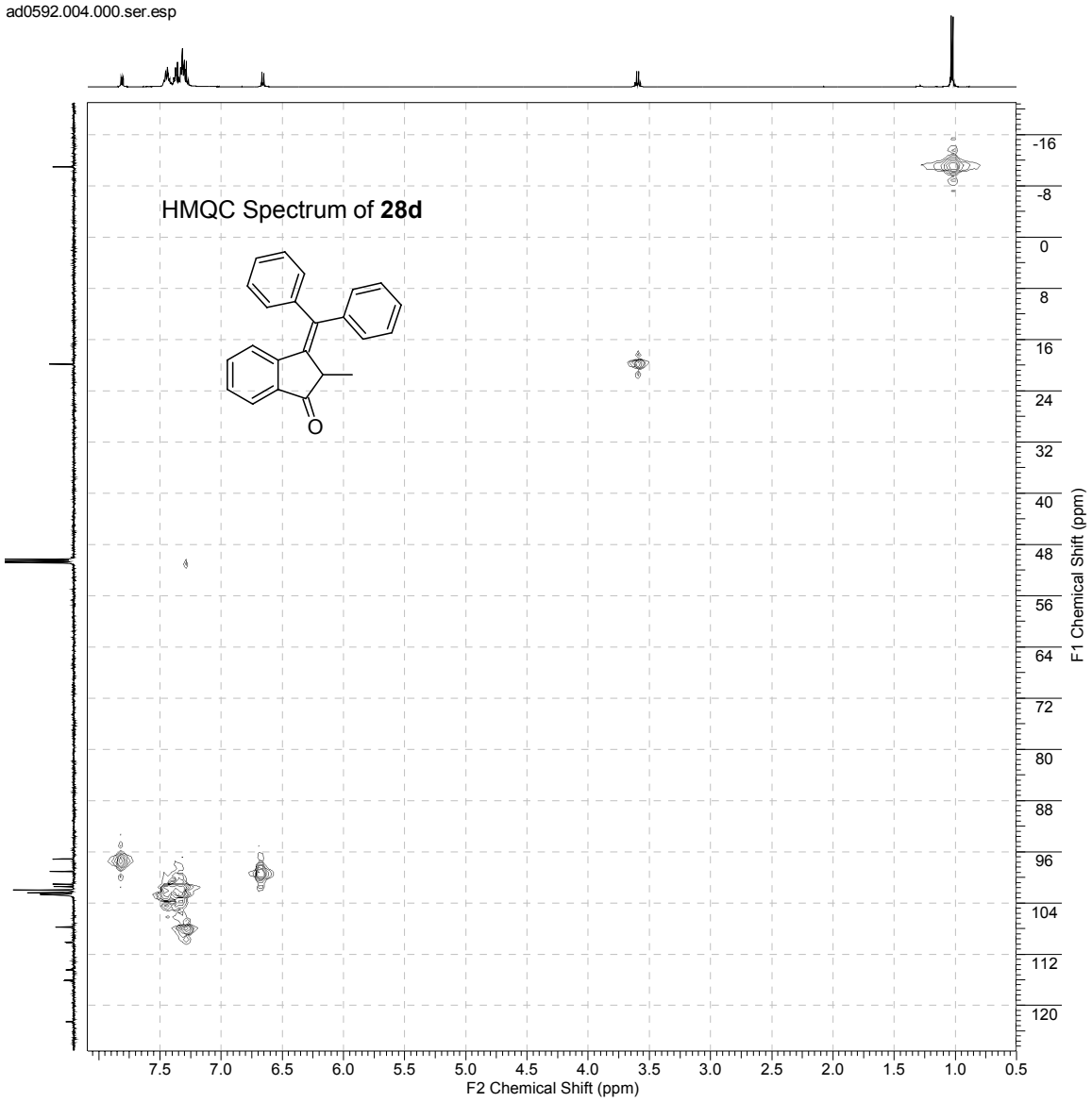
^{13}C Spectrum of **26m**

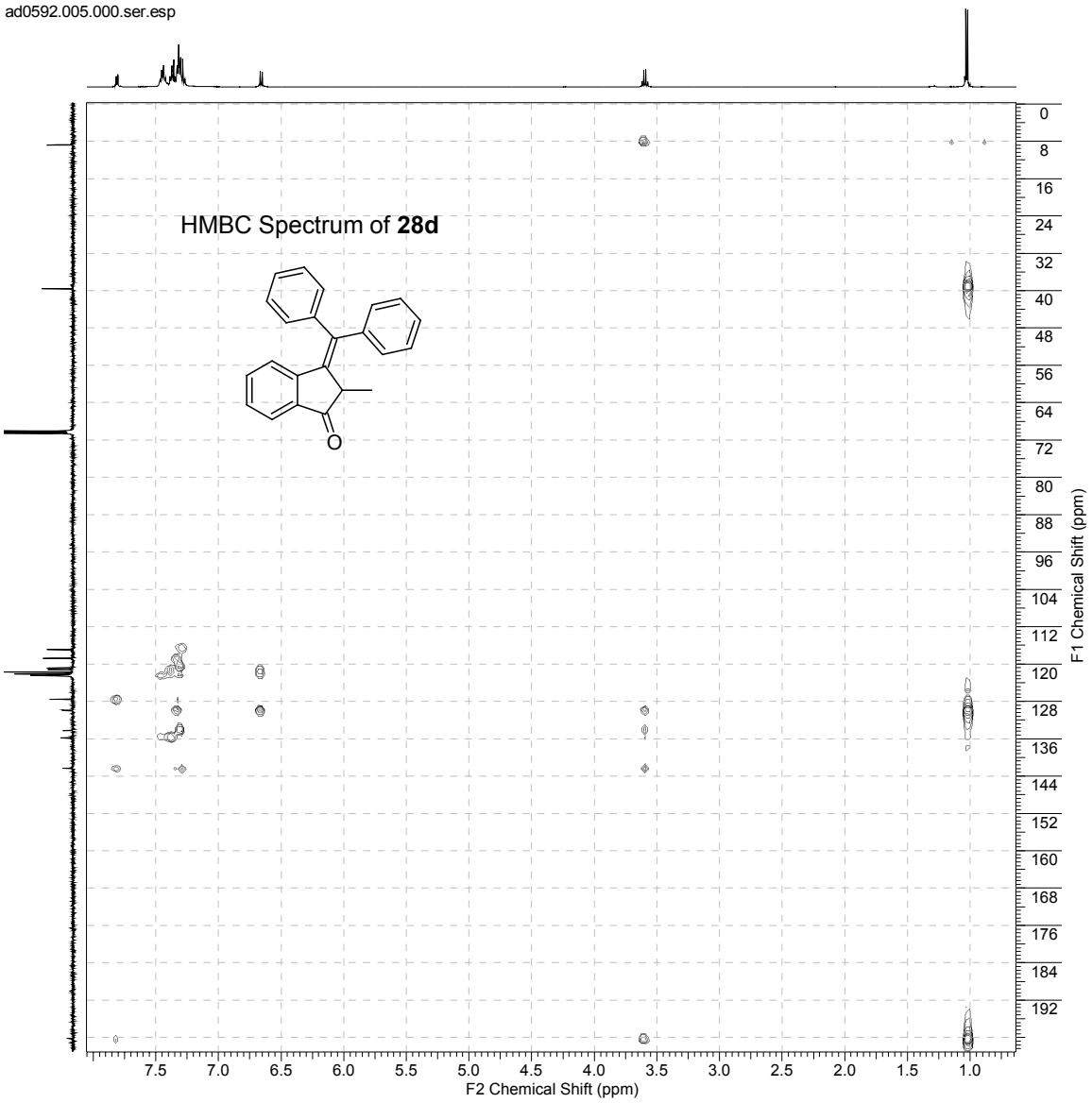


^{1}H Spectrum of **28d**



^{13}C Spectrum of **28d**


ad0592.004.000.ser.esp
HMQC Spectrum of **28d**
O
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)


ad0592.005.000.ser.esp
HMBC Spectrum of **28d**
O
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)