Supporting Information

Mechanistically Diverse Copper-, Silver-, and Gold-Catalyzed Acyloxy and Phosphatyloxy Migrations: Efficient Synthesis of Heterocycles via Cascade Migration/Cycloisomerization Approach

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General Information

NMR spectra were recorded on Bruker DPX-400 (400 MHz) and DRX-500 (500 MHz) instruments. ^{13}C and ^{31}P spectra are recorded with broadband ^{1}H decoupling. J_{CY} values are provided where applicable for ^{13}C coupling to other NMR active nuclei. ^{1}H signals are referenced either to residual $CHCl_3$ at 7.26 ppm or CHD_2CN at 1.94 ppm. ^{13}C signals are referenced to either $CDCl_3$ at 77.0 ppm or CD_3CN at 118.7 ppm. ^{31}P signals are referenced externally to 85% H_3PO_4 at 0.0 ppm. ^{17}O spectra were generally recorded in less viscous CD_3CN at either room temperature or 343 K, to afford narrower linewidths (provided), and are referenced externally to H_2O at 0.0 ppm. GC/MS analyses were performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). HR EI MS analysis was performed on a JEOL GCmate II mass spectrometer. Elemental analyses were performed at Midwest Microlabs, Indianapolis, Indiana. Column chromatography was carried out employing Merck (Kieselgel 60, 63-200 μm), ICN (ICN SiliTech, 63-200 μm), and SiliCycle (40-63 μm) silica gel. Precoated silica gel plates (0.2 mm, F-254) were used for thin-layer analytical chromatography.

All manipulations were conducted under an argon or nitrogen atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous dichloromethane, toluene, ether, and THF (BHT-free) was purchased from Aldrich, degassed with argon, and dried by passage through activated alumina on an Innovative Technology PureSolv system. Pentane, triethylamine, dichloroethane, and DMA were stored over calcium hydride and used without further purification. Water, 10 atom% ^{17}O, was purchased from ICON Services. Bis(triphenylphosphine)dichloropalladium(II)[1] was prepared in our lab according to a known procedure. Acetals,[2] (4-*t*-butyldimethylsiloxy)-1-pentyn-3-ol,[3] and 5-hydroxy-3-hexyn-2-one[4] were prepared using published procedures. All other reagents were purchased from various commercial sources and used without additional purification.

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Preparation and Characterization of Starting Materials

Preparation of ^{17}O-Labelled Materials

18: A 25 mL flask equipped with stirbar was charged with PCl_5 (416 mg, 2 mmol). Anhydrous pentane (2 mL) was added and the suspension cooled to -78ºC. $H_2{}^{17}O$ (36 μL, 2 mmol) was added dropwise as the suspension was stirred rapidly.[5] On complete addition, the reaction was warmed to room temperature and stirred for a further 2.5 hours. The resulting solution was then cooled to -78ºC, and a solution of ethanol (245 μL, 4.2 mmol) in anhydrous pentane (4 mL) cooled to -78ºC was added, dropwise, over 8 minutes. The reaction was kept at -78ºC a further 20 minutes before being warmed to 0ºC for 1 hour. The reaction was kept another 15.5 hours at room temperature before the volatiles were removed under reduced pressure (20 torr). Anhydrous ether (5 mL) was added to the residue and also removed under reduced pressure, to ensure removal of HCl. The residue was dissolved in 2 mL anhydrous ether. To a separate 25 mL flask containing a solution of 2-ethynylpyridine (202 μL, 2 mmol) in THF (5 mL) at -78ºC was added, dropwise, a solution of ^{n}BuLi (2.66 M, 789 μL, 2.1 mmol) in hexanes. The reaction was stirred for 20 minutes before 2-methylbutyraldehyde (236 μL, 2.2 mmol) was added. The reaction was kept for 5 minutes at -78ºC, then warmed to 0ºC for 30 minutes. The solution of diethylchlorophosphate in ether was added and the reaction warmed to room temperature. After an hour, TLC analysis showed the reaction to be complete. The reaction was diluted with ether (30 mL) and poured into sat. $NH_4Cl_{(aq)}$ (25 mL). The organic phase was washed (sat. $NH_4Cl_{(aq)}$, 25 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (silica gel, EtOAc) to afford **18** as a viscous oil (337 mg, 1.04 mmol, 52%). ^{1}H, ^{13}C, and ^{31}P NMR spectra matched those for unlabeled **15c**. ^{17}O NMR (54 MHz, CD_3CN, T=293 K) δ 82 ($W_{1/2}$=331 Hz, d, J_{OP}=149 Hz).

18': To a 30 mL pressure tube was added 2-methylbutyraldehyde (214μL, 2.0 mmol) and anhydrous toluene (5 mL). $H_2{}^{17}O$ (72μL, 2.0 mmol) and several beads of dry Amberlyst® 15 were added and the vessel was sealed and heated to 130ºC for 24 hours.

[5] Sammons, R. D.; Frey, P. A.; Bruzik, K.; Tsai, M.-D. *J. Am. Chem. Soc.* **1983**, *105*, 5455.

A small amount of $MgSO_4$ was added to the solution to removed water and the suspension was filtered. The solution was titrated by ^1H NMR using an internal standard for subsequent use. 2-Ethynyl pyridine (101μL, 1.0 mmol) was dissolved in THF (5 mL) and the solution was cooled to -78ºC. ^{n}BuLi (2.67M, 393μL, 1.05 mmol) was added and the reaction was stirred for 5 minutes before being brought to 0ºC and stirred for 20 minutes. The reaction was returned to -78ºC and a solution of ^{17}O-labeled 2-methylbutyraldehyde (0.3M, 3.5 mL, 1.05 mmol) in toluene was added. The reaction was brought to and stirred at 0ºC for 30 minutes and treated with chlorodiethylphosphate (173μL, 1.2 mmol). The reaction was diluted with ether (30 mL) and poured into sat. $NH_4Cl_{(aq)}$ (25 mL). The organic phase was washed (sat. $NH_4Cl_{(aq)}$, 25 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (silica gel, EtOAc) to afford **18'** as a viscous oil (97 mg, 0.3 mmol, 30%). ^1H, ^{13}C, and ^{31}P NMR spectra matched those for unlabeled **15c**. ^{17}O NMR (54 MHz, CD_3CN, T=293 K) δ 72 ($W_{1/2}$=854 Hz).

33: To a 5 mL Wheaton reactor was added, sequentially, dichloromethane (2 mL), acetyl chloride (142 μL, 2 mmol), and $H_2{}^{17}O$ (36 μL, 2 mmol). The reaction was vigorously stirred for 2 hours, when no beads of water could be seen. Solid DMAP (538 mg, 4.4 mmol) was added and allowed to dissolve, followed by solid dicyclohexylcarbodiimide (454 mg, 2.2 mmol). Once all solids had dissolved, 1-octyn-3-ol (291μL, 2 mmol) was added and the reaction was stirred for fourteen hours, when GC/MS analysis indicated the reaction had completed. The resulting suspension was filtered (silica gel, dichloromethane) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 10:1 hexanes/EtOAc) to afford a colorless oil, which was combined, under argon, with $PdCl_2(PPh_3)_2$ (28 mg, 0.04 mmol) and CuI (15 mg, 0.08 mmol) and dissolved in triethylamine (5mL). After brief stirring, about 3 minutes, benzoyl chloride (232 μL, 2 mmol) was added and the reaction stirred at room temperature for two hours. The reaction was diluted with diethyl ether (20 mL) and poured into 2M $HCl_{(aq)}$ (20 mL). The organic phase was washed (2M $HCl_{(aq)}$, 20 mL; sat. $NaHCO_{3(aq)}$, 20mL; brine, 30 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (silica gel, 2:1 hexanes/EtOAc) to afford

33 as a colorless oil (416 mg, 1.61 mmol, 81%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.09 (dd, *J*=8.3 Hz, *J*=1.2 Hz, 2H), 7.60 (tt, *J*=7.4 Hz, *J*=1.3 Hz, 1H), 7.45-7.49 (m, 2H), 5.57 (t, *J*=6.8 Hz, 1H), 2.12 (s, 3H), 1.86-1.92 (m, 2H), 1.46-1.54 (m, 2H), 1.30-1.35 (m, 4H), 0.87-0.91 (m, 3H); ^{1}3C NMR (125.76 MHz, $CDCl_3$) δ 177.3, 169.7, 136.4, 134.2, 129.5, 128.6, 90.9, 82.5, 63.5, 34.0, 31.1, 24.6, 22.3, 20.8, 13.8; ^{17}O NMR (54 MHz, CD_3CN, T=298 K) δ 366 ($W_{1/2}$=514 Hz).

52: To a 5 mL Wheaton reactor was added, sequentially, dichloromethane (2 mL), acetyl chloride (142 μL, 2 mmol), and $H_2{}^{17}O$ (36 μL, 2 mmol). The reaction was vigorously stirred for 2 hours, when no beads of water could be seen. Solid DMAP (538 mg, 4.4 mmol) was added and allowed to dissolve, followed by solid dicyclohexylcarbodiimide (454 mg, 2.2 mmol). Once all solids had dissolved, alcohol was added and the reaction was stirred for several hours, until TLC or GC/MS analysis indicated the reaction had completed. The resulting suspension was filtered (silica gel, dichloromethane) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 2:1 dichloromethane/hexanes) to afford **52** as a white solid (656 mg, 1.96 mmol, 98%). ^{1}H and ^{13}C NMR spectra matched those for unlabeled **39b**. ^{17}O NMR (54 MHz, CD_3CN, T=293 K) δ 385 ($W_{1/2}$=744 Hz).

59: A 25 mL flask equipped with stirbar was charged with PCl_5 (416 mg, 2 mmol). Anhydrous pentane (2 mL) was added and the suspension cooled to -78ºC. $H_2{}^{17}O$ (36 μL, 2 mmol) was added dropwise as the suspension was stirred rapidly. On complete addition, the reaction was warmed to room temperature and stirred for a further 2.5 hours. The resulting solution was then cooled to -78ºC, and a solution of ethanol (245 μL, 4.2 mmol) in anhydrous pentane (4 mL) cooled to -78ºC was added, dropwise, over 8 minutes. The reaction was kept at -78ºC a further 20 minutes before being warmed to 0ºC for 1 hour. The reaction was kept another 15.5 hours at room temperature before the volatiles were removed under reduced pressure (20 torr). Anhydrous ether (5 mL) was added to the residue and also removed under reduced pressure, to ensure removal of HCl. The residue was dissolved in 2 mL anhydrous ether. To a separate 10 mL flask containing a solution of alcohol (585 mg, 2 mmol) in THF (1 mL) at -78ºC was added,

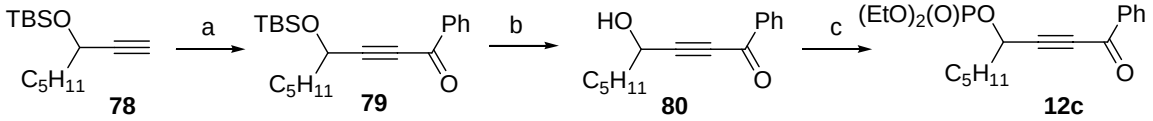
dropwise, KHMDS (0.5 M, 4.2 mL, 2.1 mmol). The solution was stirred for 10 minutes at -78ºC before the solution of diethylchlorophosphate in ether was added. The reaction was warmed to room temperature and stirred for 2 hours. The reaction was diluted with ether (30 mL) and poured into sat. $NH_4Cl_{(aq)}$ (20 mL). The organic phase was washed (sat. $NH_4Cl_{(aq)}$, 20 mL; brine, 30 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (silica gel, 2:1 hexanes/EtOAc) to afford **59** as a colorless, viscous oil (416 mg, 0.98 mmol, 49%). ^{1}H, ^{13}C, and ^{31}P NMR spectra matched those for unlabeled **41**. ^{17}O NMR (54 MHz, CD_3CN, T=343 K) δ 93 ($W_{1/2}$=391 Hz, d, *J*=116 Hz).

Preparation of Phosphatyloxy Conjugated Alkynyl Ketones 12

12a: (General procedure): To a Wheaton microreactor were sequentially added DMAP (11 mg, 0.09 mmol), anhydrous dichloromethane (1 mL), triethylamine (91 μL, 0.65 mmol), 5-hydroxy-3-decyne-2-one (93 μL, 0.50 mmol), and diethylchlorophosphate (94 μL, 0.65 mmol). The reaction was stirred at room temperature for 2.5 hours until judged complete by TLC and GC analysis. The reaction was washed with saturated sodium chloride solution (10 mL), the aqueous layer was extracted twice with dichloromethane (3 mL), and the organic extracts were dried over sodium sulfate and then concentrated. The residue was purified by chromatography (silica gel, 1:2 ethyl acetate/hexanes) to afford **12a** (111mg, 73%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 5.09 (q, *J*=6.85 Hz, 1H), 4.18–4.10 (m, 4H), 2.35 (s, 3H), 1.87 (dt, *J*=15.04 Hz, *J*=7.52 Hz, 2H), 1.51–1.43 (m, 2H), 1.37–1.29 (m, 10H), 0.93–0.85 (m, 3H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 184.1, 88.4, 85.5, 67.6, 64.6, 36.2, 36.1, 33.0, 31.5, 24.7, 22.8, 16.6, 16.5, 14.4; LRMS *m/z* (M^++H, 275), 155 (100), 99(100).

12b: Prepared using the general procedure for **12a** from known alcohol.[4] ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 5.40-5.30 (m, 1H), 4.16-4.10 (m, 4H), 2.35 (s, 3H), 1.62 (d, 3H, *J* = 6.6 Hz), 1.38-1.33 (m, 6H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 184.1, 88.7, 84.7, 64.6 (d, *J*=5.9 Hz), 64.5 (d, *J*=5.8 Hz), 63.8 (d, *J*=5.0 Hz), 60.8, 32.9, 22.9, 16.5 (d, *J*=6.9 Hz), 14.6. ^{31}P NMR (202.46 MHz, $CDCl_3$) δ -3.62; LRMS *m/z* 145 (60), 117 (100).

12c:



(a) $PhCOCl$, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 70%; (b) HF, MeCN, 94%; (c) DMAP, Et_3N, $P(O)(OEt)_2Cl$, 94%.

78 was made according to a known procedure, NMR data were in accordance with described data.[6]

79 was made according to a known procedure.[7] ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.15-8.12 (m, 2H), 7.61-7.60 (m, 1H), 7.50-7.46 (m, 2H), 4.61 (t, *J* = 7.1 Hz, 3H), 1.80 (q, *J*=7.1 Hz, 2H), 1.53-1.51 (m, 2H), 1.35-1.32 (m, 4H), 0.93 (s, 9H), 0.18 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 178.2, 137.1, 134.5, 130.0, 129.0, 96.5, 82.3, 63.4, 38.4, 31.8, 26.1, 25.2, 23.0, 18.6, 14.4, -4.2, -4.7; LRMS *m/z* 329 (M^+-15, 2), 287 (50), 105(70), 75 (100).

80 was made from the deprotection of **79** according to a known procedure.[8] ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.13-8.11 (m, 2H), 7.63-7.60 (m, 1H), 7.50-7.46 (m, 2H), 4.67 (t, *J* = 6.7 Hz, 1H), 2.39 (br s, 1H), 1.88-1.85 (m, 2H), 1.55-1.53 (m, 2H), 1.37-1.33 (m, 4H), 0.91-0.89 (m, 3H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 178.3, 136.8, 134.7, 130.1, 129.1, 95.3, 62.9, 37.5, 31.8, 25.2, 22.9, 14.4.

12c: Prepared using the general procedure for **12a** from alcohol **80**. ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.13-8.11 (d, *J*=8.0 Hz, 2H), 7.64-7.61 (m, 1H), 7.51-7.45 (m, 2H), 5.25-5.20 (m, 1H), 4.20-4.09 (m, 4H), 1.98-1.93 (m, 2H), 1.58-1.54 (m, 2H), 1.38-1.32 (m, 10H), 0.91 (t, *J*=6.9 Hz, 3H).

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Preparation of Phosphatyloxy Conjugated Alkynyl Pyridines 15

15a: (General Procedure): To a solution of 2-ethynyl pyridine (300 μL, 3 mmol) in THF (10 mL) at -78ºC was added, dropwise, ^{n}BuLi (2.67M, 1.2 mL, 3.3 mmol). The reaction was stirred for a further 5 minutes before being brought to 0ºC and stirred for 20 minutes. The reaction was returned to -78ºC and butyraldehyde (280 μL, 3.3 mmol) was added slowly. The reaction was brought to and stirred at 0ºC for 30 minutes and treated with chlorodiethylphosphate (564 μL, 3.9 mmol). The reaction was brought to room temperature and stirred for an hour, until TLC analysis indicated the reaction was complete. The reaction was diluted with ether (90 mL) and poured into sat. $NH_4Cl_{(aq)}$ (75 mL). The organic phase was washed (sat. $NH_4Cl_{(aq)}$, 75 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (silica gel, EtOAc) to afford **15a** as a viscous oil (880 mg, 2.8 mmol, 94%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.24 (d, *J*=4.0 Hz, 1H), 7.36 (tt, *J*=7.8 Hz, *J*=1.9 Hz, 1H), 7.11 (d, *J*=7.9 Hz, 1H), 6.92-6.97 (m, 1H), 4.87-4.93 (m, 1H), 3.78-3.90 (m, 4H), 1.52-1.67 (m, 2H), 1.21-1.30 (sext, *J*=7.3 Hz, 2H), 0.98-1.04 (m, 6H), 0.65 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 149.3, 141.6, 135.5, 126.5, 122.6, 85.4, 84.9, 67.2 (d, *J*=5.5 Hz), 63.2 (d, *J*=5.5 Hz), 63.1 (d, *J*=5.5 Hz), 37.7 (d, *J*=5.5 Hz), 17.4, 15.3 (d, *J*=5.5 Hz), 12.8.

15b: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.48 (dd, *J*=4.9 Hz, *J*=0.8 Hz, 1H), 7.57 (td, *J*=7.7 Hz, *J*=1.2 Hz, 1H), 7.34 (d, *J*=7.9 Hz, 1H), 7.16 (dd, *J*=7.6 Hz, *J*=4.9 Hz, 1H), 5.12 (q, *J*=6.8 Hz, 1H), 3.99-4.13 (m, 4H), 1.79-1.91 (m, 2H), 1.39-1.50 (m, 2H), 1.13-1.31 (m, 10H), 0.79 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 149.8, 142.2, 135.9, 127.1, 123.0, 86.1 (d, *J*=3.7 Hz), 85.3, 68.0 (d, *J*=5.5 Hz), 63.7 (dd, *J*=15.7, 5.5 Hz), 36.1 (d, *J*=5.5 Hz), 31.0, 24.2, 22.2, 15.9 (d, *J*=6.5 Hz), 13.7.

15c: ^{1}H NMR (500.13 MHz, CD_3CN) δ 8.56 (d, *J*=4.7 Hz, 1H), 7.75 (td, *J*=7.7 Hz, *J*=1.8 Hz, 1H), 7.47 (d, *J*=7.7 Hz, 1H), 7.33 (dd, *J*=7.2 Hz, *J*=5.3 Hz, 1H), 5.11 (ddd, *J*=7.5 Hz, *J*=4.7 Hz, *J*=3.2 Hz, 1H), 4.00-4.24 (m, 4H), 1.78-1.99 (m, 1H), 1.55-1.75 (m, 1H), 1.23-1.35 (m, 7H), 1.08 (dd, *J*=6.7 Hz, *J*=2.8 Hz, 3H), 0.96 (td, *J*=7.5 Hz, *J*=2.9 Hz, 3H); ^{13}C NMR (125.76 MHz, CD_3CN) δ 151.6, 143.5, 137.9, 128.7, 125.1, 73.0 (dd, *J*=24.7 Hz, *J*=5.5 Hz), 65.2 (dd, *J*=9.6 Hz, *J*=5.9 Hz), 41.9 (d, *J*=6.6 Hz), 41.7 (d, *J*=5.9 Hz), 26.3,

25.9, 16.9 (d, *J*=5.9 Hz), 15.4, 15.0, 12.3, 12.1; ^{31}P NMR (161.98 MHz, CD_3CN) δ -3.08.

15e: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.58 (d, *J*=4.4 Hz, 1H), 7.64 (td, *J*=7.7 Hz, *J*=1.8 Hz, 1H), 7.38 (d, *J*=7.7 Hz, 1H), 7.28-7.35 (m, 4H), 7.22-7.27 (m, 2H), 5.38 (q, *J*=7.1 Hz, 1H), 4.06-4.16 (m, 1H), 3.99-4.06 (m, 1H), 3.92-3.98 (m, 1H), 3.84-3.92 (m, 1H), 3.26 (d, *J*=7.0 Hz, 2H), 1.27 (td, *J*=7.1 Hz, *J*=0.9 Hz, 3H), 1.23 (td, *J*=7.1 Hz, *J*=1.1 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 150.0, 142.4, 136.1, 135.5, 129.8, 128.4, 127.3, 127.1, 123.3, 86.2, 85.9 (d, *J*=2.8 Hz), 68.5 (d, *J*=5.5 Hz), 63.9 (dd, *J*=22.2 Hz, *J*=5.5 Hz), 42.8 (d, *J*=6.5 Hz), 16.0 (d, *J*=6.5 Hz).

Preparation of Acyloxy Conjugated Alkynyl Ketones 22

Procedure A

To a 250 mL flash-dried round-bottomed, two-necked flask equipped an addition funnel were successively added 1-octyn-3-ol (7.3 mL, 50 mmol) and anhydrous THF (100 mL). The solution was cooled to -78^{o}C and ^{n}BuLi (2.5M, 44 mL, 0.11 mol) in hexanes was added dropwise *via* addition funnel (*ca*. 30 minutes). The resulting solution was allowed to warm to room temperature. Seperately, a 500 mL round bottomed, two-necked flask equipped with addition funnel was charged with acid anhydride (0.25 mol) and anhydrous ether (150 mL). The resulting solution was cooled to -78^{o}C, and the dianion solution from the first flask was slowly added via addition funnel. The solution was allowed to warm to room temperature overnight, and was quenched with a mixture of 1% NH_4OH and 200 mL saturated NH_4Cl, adjusted to reach pH 8. After thorough extraction with hexanes (50 mL) and 1:1 hexanes:diethyl ether (50 mL), the organic extracts were combined and dried with anhydrous Na_2SO_4 and concentrated. The resulting residue was purified either by high vacuum distillation or by column chromatography (silica gel).

Procedure B

Sonogashira coupling.[9] To a Wheaton microreactor was successively added copper iodide (2.5 mg, 1.3 μmol) and dichlorobis(triphenylphosphine)palladium (2.5 mg, 3.5 μmol) under argon atmosphere. Anhydrous triethylamine (2.5 mL) was added and the mixture was stirred. Propargylacyloxyalkyne (2.33 mmol) was added *via* syringe and the mixture was briefly stirred. Benzoyl chloride (2.90 μL, 2.5 mmol) was added dropwise. The reaction was stirred overnight at room temperature and monitored by TLC and GC/MS. The reaction was filtered (silica gel, EtOAc), concentrated under vacuum, and purified by column chromatography (silica gel).

22a: Procedure A (62%): ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 5.45 (t, *J*=6.7 Hz, 1H), 2.34 (s, 3H), 2.09 (s, 3H), 1.82-1.77 (m, 2H), 1.44-1.41 (m, 2H), 1.33-1.29 (m, 4H), 0.89 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 184.0, 170.0, 88.4, 84.1, 63.3, 3.9, 32.6, 31.1, 24.6, 22.4, 20.8, 13.9; LRMS *m/z* 195 (M^+-15, 1), 168 (44), 111 (100).

22c: Procedure B using 3-benzoyloxy-1-butyne[10] (74%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.13-8.09 (m, 4H), 7.62-7.59 (m, 2H), 5.93 (q, *J*=6.8 Hz, 1H), 1.78 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 177.9, 165.8, 136.7, 134.8, 133.9, 130.3, 130.1, 129.8, 129.1, 128.9, 91.9, 82.6, 60.8, 21.1; LRMS *m/z* 278 (M^+, 18), 105 (PhCO, 100).

22d: Procedure B using 3-acetoxy-1-butyne[11] (42%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.10 (d, *J*=7.7 Hz, 2H), 7.62 (t, *J*=7.4 Hz, 1H), 7.48 (t, *J*=7.7 Hz, 2H), 5.66 (q, *J*=6.8 Hz, 1H), 2.13 (s, 3H), 1.63 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 177.9, 170.2, 136.7, 134.8, 130.1, 129.1, 91.8, 82.3, 60.2, 21.3, 20.9; LRMS *m/z* 215 (M^+-1, 1), 174 (100), 128 (77), 105 (PhCO, 96), 77 (Ph, 75), 51 (47).

22e: Procedure B using 3-propionoxy-1-butyne[11] (43%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.10 (dd, *J*=8.3 Hz, *J*=1.3 Hz, 2H), 7.62 (t, *J*=7.4 Hz, 1H), 7.49 (t, *J*=7.8 Hz, 2H), 5.68

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[10] Nakamura, K.; Takenaka, K. *Tetrahedron: Asymm.* **2002**, *13*, 415.
[11] Nakamura, K.; Takenaka, K.; Ohno, A. *Tetrahedron: Asymm.* **1988**, *9*, 4429.

(q, *J*=6.8 Hz, 1H), 2.41 (q, *J*=7.6 Hz, 1H), 2.40 (q, *J*=7.6 Hz, 1H), 1.63 (d, *J*=6.8 Hz, 3H), 1.18 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 177.9, 173.6, 136.7, 134.8, 130.1, 129.1, 92.1, 82.3, 60.0, 27.9, 21.0, 9.4; LRMS *m/z* 229 (M^+-1, 0.1), 175 (87), 128 (100), 105 (PhCO, 94), 77 (Ph, 64), 57 (66).

22f: Procedure B using 3-isobutyroxy-1-butyne **81** (76%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.12 (dd, *J*=8.4 Hz, *J*=1.3 Hz, 2H), 7.64 (t, *J*=7.5 Hz, 1H), 7.51 (t, *J*=7.8 Hz, 2H), 5.70 (q, *J*=6.8 Hz, 1H), 2.65 (sept, *J*=7.0 Hz, 1H), 1.66 (d, *J*=6.9 Hz, 3H), 1.23 (d, *J*=7.0 Hz, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 177.9, 176.3, 136.8, 134.7, 130.0, 129.0, 92.2, 82.3, 60.0, 34.3, 20.9, 19.2; LRMS *m/z* 243 (M^+-1, 0.4), 175 (98), 128 (100), 105 (PhCO, 68), 77(Ph, 79).

22g: Procedure B using 3-pivaloxy-1-butyne (78%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.09 (dd, *J*=8.1 Hz, *J*=1.9 Hz, 2H), 7.61 (t, *J*=7.4 Hz, 1H), 7.48 (t, *J*=7.8 Hz, 2H), 5.65 (q, *J*=6.8 Hz, 1H), 1.62 (d, *J*=6.8 Hz, 3H), 1.25 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 177.9, 177.7, 136.8, 134.8, 130.0, 129.0, 92.3, 82.2, 60.1, 39.2, 27.4, 20.8; LRMS *m/z* 258 (M^+, 0.1), 57 (*t*Bu, 100).

22h: Procedure B using 3-benzoyloxy-1-octyne (69%) ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 8.11 (t, *J*=6.8 Hz, 4H), 7.61 (t, *J*=7.4 Hz, 2H), 7.48 (q, *J*=7.0 Hz, 4H), 5.85 (t, *J*=6.7 Hz, 1H), 2.10-2.03 (m, 2H), 1.62 (quint, *J*=7.4 Hz, 2H), 1.43-1.34 (m, 4H), 0.92 (t, *J*=6.9 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 177.9, 165.9, 136.8, 134.8, 133.9, 130.3, 130.1, 129.8, 129.1, 128.9, 91.4, 83.2, 64.6, 34.6, 31.7, 25.2, 22.9, 14.4; LRMS *m/z* 334 (M^+, 2), 105 (PhCO, 100).

22i: Procedure A (41%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 5.45 (t, *J*=6.7 Hz, 1H), 1.85-1.92 (m, 2H), 1.48-1.42 (m, 2H), 1.34-1.28 (m, 4H), 1.21 (s, 9H), 1.17 (s, 9H), 0.88 (t, *J*=6.9 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 194.0, 177.6, 91.1, 82.1, 63.7, 45.3, 39.2, 34.3, 31.5, 27.4, 26.3, 25.0, 22.8, 14.3; LRMS *m/z* 294 (M^+, 0.1), 57 (*t*Bu, 100).

22j: Procedure B using **82** (85%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.16 (d, *J*=8.4 Hz, 2H), 8.10 (dd, *J*=8.4 Hz, *J*=1.4 Hz), 7.61 (t, *J*=7.4 Hz, 2H), 7.50-7.45 (m, 4H), 5.83 (d, *J*=6.2 Hz, 0.2H), 5.78 (d, *J*=4.1 Hz, 0.8H), 4.29 (dquint, *J*=6.3 Hz, *J*=2.1 Hz, 0.8H), 4.24 (quint, *J*=6.2 Hz, 0.2H), 1.44 (d, *J*=6.2 Hz, 0.6H), 0.10 (s, 2.4H), 0.09 (s, 0.6H); ^{13}C NMR (125.76 MHz): δ 177.8, 165.8, 136.9, 134.7, 133.9, 130.3, 130.1, 129.7, 129.1, 128.9, 89.5, 89.4, 84.0, 83.8, 69.9, 69.3, 69.1, 68.7, 26.1, 20.4, 20.1, 18.4, -4.2, -4.4; LRMS *m/z* 407 (M^+ -15, 0.1), 179 (44), 105 (PhCO, 100).

81: Made using a known procedure[12] ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 5.46 (dd, *J*=6.6 Hz, *J*=2.2 Hz, 1H), 2.54-2.63 (m, 1H), 2.45 (d, *J*=2.2 Hz, 1H), 1.52 (d, *J*=6.6 Hz, 3H), 1.20 (dd, *J*=7.2 Hz, *J*=2.8 Hz, 6H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 175.9, 82.3, 59.7, 33.9, 21.1, 18.8, 18.7.

82: 1:4.3 mixture of diastereomers, made using a known procedure ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.08 (dd, *J*=8.3 Hz, *J*=1.3 Hz, 2H), 7.58 (t, *J*=7.4 Hz, 1H), 7.47-7.43 (m, 2H), 5.34-5.52 (m, 1H), 4.16-4.14 (m, 1H), 2.46 (d, *J*=2.2 Hz, 1H), 1.36 (d, *J*=6.2 Hz, 0.7H), 1.34 (d, *J*=6.2 Hz, 2.3H), 0.88 (s, 6.8 H), 0.83 (s, 2.2H), 0.084 (s, 5.3H), 0.022 (s, 0.7H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 165.9, 133.6, 130.2, 130.2, 128.8, 79.7, 75.0, 70.0, 69.0, 26.1, 19.8, 18.4, -4.2, -4.4.

Preparation of Skipped Acyloxy Propargyl Ketones 39

To a round bottomed two-necked flask were successively added anhydrous THF (10 mL) and 3,3-dimethyl-1-butyne (0.62 mL, 5.0 mmol). The solution was cooled to -78^{o}C and ^{n}BuLi (2.5M, 2.1 mL, 5.2 mmol) in hexanes was added dropwise. The resulting solution was allowed to warm to room temperature. To an additional 50 mL round bottomed two-necked flask the appropriate dione (4.8 mmol) was dissolved in anhydrous THF (10 mL). The dione solution was cooled to -78^{o}C and the acetylide solution from the first flask was added slowly via cannula to the dione solution at -78^{o}C. The resulting solution was allowed to warm to room temperature, then cooled down again to -78^{o}C and acetic anhydride (0.76 mL, 8.0 mmol) was added. The reaction was brought to room

[12] Höfle, G.; Steglich, W.; Vörbuggen, H. *Angew. Chem., Int. Ed.* **1978**, *17,* 569.

temperature and the solution was then poured into a separatory funnel containing saturated $NH_4Cl_{(aq)}$ (200 mL) and diethyl ether (50 mL). After extraction, the organic layer was separated, dried ($MgSO_4$), concentrated, and purified (silica gel) to afford pure acetoxy propargyl ketone **39**.

39a: (44%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.86 (d, *J*=7.7 Hz, 2H), 7.78 (d, *J*=7.0 Hz, 2H), 7.45-7.35 (m, 4H), 7.31-7.27 (m, 2H), 2.30 (t, *J*=7.0 Hz, 2H), 2.14 (s, 3H), 1.45 (quint, *J*=8.1 Hz, 2H), 1.36-1.30 (m, 2H), 0.87 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 191.8, 168.8, 136.3, 134.3, 132.5, 129.8, 129.2, 128.8, 127.8, 127.1, 93.0, 81.3, 30.1, 21.9, 21.3, 18.7, 13.5; LRMS *m/z* 334 (M^+, 6), 292 (M-42, 38), 249 (100).

39b: (83%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.88 (dd, *J*=8.3 Hz, *J*= 1.0 Hz, 2H), 7.77 (dd, *J*=8.0 Hz, *J*=1.1 Hz, 2H), 7.45-7.35 (m, 4H), 7.31 (t, *J*=7.7 Hz, 2H), 2.15 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 192.3, 169.0, 136.5, 134.9, 132.8, 130.3, 129.6, 129.2, 128.0, 127.8, 101.5, 81.3, 75.9, 30.7, 28.2, 21.8; LRMS *m/z* 334 (M^+, 10), 277 (M^+-*t*Bu, 100), 105 (PhCO, 63).

39c: (75%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.87-7.91 (m, 2H), 7.79-7.83 (m, 2H), 7.39-7.44 (m, 3H), 7.35-7.38 (m, 1H), 7.27-7.33 (m, 2H), 1.26 (s, 9H), 1.22 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 192.6, 175.6, 136.5, 135.0, 132.0, 129.5, 128.8, 128.5, 127.4, 126.9, 99.6, 80.6, 76.0, 38.7, 30.2, 27.6, 26.8.

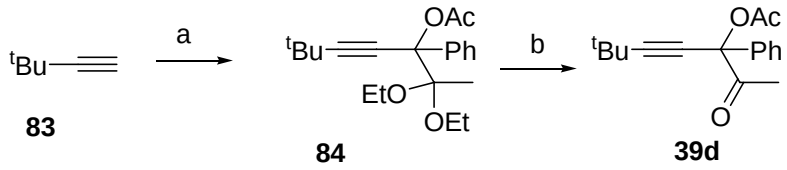
39e: (43%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.15 (dd, *J*=8.2 Hz, *J*=0.9 Hz, 2H), 7.51 (t, *J*=7.4 Hz, 3H), 7.41 (t, *J*=8.0 Hz, 2H), 1.93 (s, 3H), 1.90 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 193.7, 169.7, 134.4, 133.0, 129.8, 128.4, 99.1, 78.4, 76.8, 30.8, 28.0, 25.1, 21.6; LRMS *m/z* 272 (M^+, 12), 215 (M^+-*t*Bu, 100), 105 (PhCO, 73).

39f: (51%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.08 (s, 3H), 1.61 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 202.7, 169.7, 96.8, 77.4, 76.5, 30.9, 27.9, 25.6, 25.0, 21.3; LRMS *m/z* 210 (M^+, 7), 153 (M^+-*t*Bu, 100).

39h: (61%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.84 (dd, *J*=8.4 Hz, *J*=1.3 Hz, 2H), 7.76-7.80 (m, 2H), 7.38-7.43 (m, 3H), 7.33-7.37 (quint, *J*=7.3 Hz, 1H), 7.28 (t, *J*=7.8 Hz, 2H), 2.29 (td, *J*=7.0 Hz, *J*=1.7 Hz, 2H), 1.44-1.51 (m, 2H), 1.32-1.40 (m, 2H), 1.23 (s, 9H), 0.86 (t, *J*=7.3 Hz, 3H); 192.4, 175.6, 136.8, 134.6, 132.0, 129.4, 128.7, 128.6, 127.5, 126.5, 91.5, 81.0, 77.2, 38.7, 30.0, 26.7, 21.6, 18.5, 13.4.

39i: (55%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.89 (dd, *J*=8.34 Hz, *J*=1.19 Hz, 2H), 7.78 (d, *J*=7.15 Hz, 2H), 7.46-7.36 (m, 4H), 7.30 (t, *J*=7.89 Hz, 2H), 2.16 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 191.1, 168.5, 135.4, 134.1, 132.6, 129.9, 129.3, 128.8, 127.6, 127.2, 100.9, 97.8, 81.0, 21.2, -0.5; LRMS *m/z* 350 (M^+, 1), 308 (M^+ - 42, 40), 203 (53), 105 (PhCO; 100).

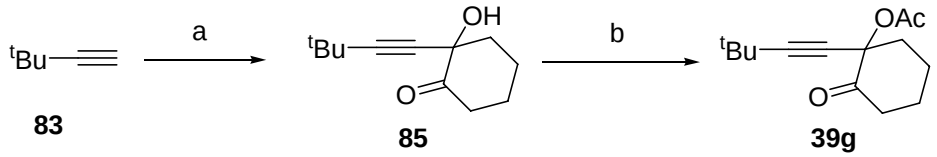
39j: (44%) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.94 (d, *J*=7.34 Hz, 2H), 7.86 (d, *J*=7.15 Hz, 2H), 7.50-7.38 (m, 6H), 7.36-7.27 (m, 4H) 2.20 (s, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 191.3, 168.8, 135.8, 134.2, 132.7, 131.8, 129.8, 129.4, 128.9, 128.2, 127.9, 127.1, 121.9, 91.3, 85.6, 81.4, 21.3; LRMS *m/z* 354 (M^+, 3), 312 (M^+-42, 44), 207 (90), 105 (100).



(a) *n*-BuLi, $PhCOC(OEt)_2CH_3$, Ac_2O, 48%; (b) HCOOH, dichloromethane, 86%.

39d: To a 10 mL round-bottomed, two-necked flask, were sequentially added anhydrous THF (6 mL) and 3,3-dimethyl-1-butyne (406 μL, 3.3 mmol). The solution was cooled to -78^{o}C and ^{n}BuLi (2.5M, 1.4 mL, 0.56 mmol) in hexanes was added dropwise. The resulting solution was allowed to warm to room temperature. Another two-necked, round-bottomed, 25 mL flask was loaded with anhydrous THF (6 mL) and 1-phenyl-1-propanone-2,2-diethylacetal (650 mg, 3.0 mmol). The flask was cooled while stirring and the acetylide solution from the first flask was transferred dropwise *via* cannula. The

resulting solution was allowed to warm to room temperature and cooled again to -78 ^{o}C and quenched with acetic anhydride (410 μL, 5.0 mmol). The solution was allowed to warm to room temperature and was poured into a separatory funnel containing 120 mL saturated NH_4Cl and 30 mL ether. The mixture was extracted, and the organic layer was separated, dried ($MgSO_4$), concentrated, and purified by column chromatography (silica gel, 1:30 ethyl acetate/hexanes) to afford 502 mg (48%) of the acetal **84**. The acetal was hydrolyzed using a known procedure[13] to afford **39d** in 86% yield. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.71 (dd, *J*=8.1 Hz, *J*=1.6 Hz, 2H), 7.41-7.35 (m, 3H), 2.27 (s, 3H), 2.16 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 199.7, 169.2, 135.6, 129.6, 129.0, 127.3, 99.7, 77.7, 75.2, 30.9, 28.2, 25.7, 21.5; LRMS *m/z* 272 (M^+, 7), 215 (M^+-*t*Bu, 100).



83 **85** **39g**

(a) EtMgBr, b) 1,2-cyclohexanedione (0.5 eq), 51%; (b) Ac_2O, TMSOTf, DCM, 80-90%.

39g: To a round bottomed two-necked flask was added ethyl magnesium bromide (1.0M, 11 mL, 11 mmol) in THF and the flask was cooled to 0^{o}C. 3,3-Dimethyl-1-butyne (1.4 mL, 11 mmol) was added dropwise. The resulting mixture was allowed to warm to room temperature and monitored until evolution of ethane ceased (*ca.* 30 min.) and stirred for an additional 30 minutes. The flask was cooled to 0ºC and a solution of 1,2-cyclohexanedione (560 mg, 5.0 mmol) in anhydrous THF (3 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for another 30 minutes. After TLC and GC/MS analysis showed the reaction was complete, the contents of the flask were poured into saturated NH_4Cl solution (130 mL) and extracted with ether (30 mL). The organic layer was separated and the aqueous layer was acidified with 2N HCl and washed a second time with 2N HCl (30 mL). The organic extracts were combined, dried ($MgSO_4$), concentrated, and purified (silica gel, 1:10 ethyl

[13] Prakesch, M.; Gree, D.; Gree, R. *J. Org. Chem.* **2001**, *66*, 3146.

acetate/hexanes) to afford pure alcohol **85** (492 mg, 51%).[14] Alcohol **85** was acylated using a known procedure.[15] ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 2.86 (dt, *J*=13.2 Hz, *J*=5.9 Hz, 1H), 2.41 (td, *J*=13.2 Hz, *J*=3.3 Hz, 1H), 2.28 (qd, *J*=12.7 Hz, *J*=2.6 Hz, 1H); 2.12 (dt, *J*=12.0 Hz, *J*=3.8 Hz, 1H), 2.12 (s, 3H), 2.05-1.97 (m, 1H), 1.86-1.82 (m, 1H), 1.76-1.70 (m, 1H), 1.60-1.49 (m, 1H), 1.23 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 202.3, 168.9, 99.4, 79.9, 75.3, 40.7, 38.8, 31.4, 31.2, 31.0, 28.0, 27.9, 22.8, 21.8; LRMS *m/z* 236 (M^+, 6), 179 (M^+-*t*Bu, 100).

Preparation of Skipped Phosphatyloxy and Sulfonyloxy Propargyl Ketones 41, 45

41: To a round bottomed, two-necked flask were successively added anhydrous THF (10 mL) and 3,3-dimethyl-1-butyne (0.62 mL, 5.0 mmol). The solution was cooled to -78 ^{o}C while stirring and ^{n}BuLi (2.5 M, 2.2 mL, 5.5 mmol) was added dropwise. The flask was removed from the cooling bath and allowed to warm to room temperature. Benzil (1.05 g, 5.0 mmol) was dissolved in anhydrous THF (10 mL) in a 50 mL round bottomed, two-necked flask. The solution was cooled to -78^{o}C, and the acetylide solution from the first flask was transferred dropwise via cannula. The resulting purple-black solution was allowed to warm to room temperature while stirring and then cooled to -78 ^{o}C again. Diethylchlorophosphate (0.8 mL, 5.5 mmol) and anhydrous triethylamine[16] (0.8 mL, 5.5 mmol) were successively added. The solution was allowed to return to room temperature. The resulting amber solution was then poured into a separatory funnel containing 300 mL saturated NH_4Cl solution and 50 mL diethyl ether. After thorough extraction, the organic layer was separated, dried ($MgSO_4$), and concentrated. The resulting residue was purified by column chromatography (silica gel, 1:3 ethyl acetate/hexanes) to afford pure **41** (653 mg, 30%) and a second fraction of slightly contaminated **41** (878 mg, 41%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.89 (d, *J*=8.4 Hz, 2H), 7.70 (dd, *J*=7.8 Hz, *J*=0.9 Hz, 2H), 7.43-7.34 (m, 4H), 7.26 (t, *J*=7.7 Hz, 2H), 4.24-4.10 (m, 2H), 4.07-3.97 (m, 2H), 1.31 (t, *J*=7.1 Hz, 3H), 1.24 (t, *J*=8.1 Hz, 3H), 1.23 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 191.6, 137.8, 134.1, 133.0, 131.0, 129.7, 129.1, 128.0, 127.8, 103.8, 82.6, 75.3, 64.1 (d, *J*=38.9 Hz), 64.1 (d, *J*=39.0 Hz), 30.6, 28.3, 16.5

[14] Pilling, G. M.; Sondheimer, F. *J. Am. Chem. Soc.* **1971**, *93*, 1970.
[15] Procopiou, P. A.; Baugh, S. P. D.; Flack, S. S.; Inglis, G. G. A. *J. Org. Chem.* **1998**, *63*, 2342.
[16] Mikami, K.; Yoshida, A. *Tetrahedron*, **2001**, *57*, 889.

(d, *J*=12.7 Hz), 16.4 (d, *J*=12.8 Hz); ^{31}P NMR (202.46 MHz) δ -7.30; LRMS *m/z* 428 (M^+, 15), 155 (66), 105 (PhCO, 100).

45: To a 25 mL round-bottomed, two-necked flask were successively added anhydrous THF (10 mL) and 3,3-dimethyl-1-butyne (5.0 mmol, 0.62 mL). The solution was allowed to cool to -78^{o}C while stirring and ^{n}BuLi (2.5M, 2.2 mL, 5.5 mmol) in hexanes was added dropwiseThe reaction was allowed to warm to room temperature. Sepearately, a round bottomed, two-necked 50 mL flask was successively loaded with benzil (5.0 mmol, 1.05 g) and anhydrous THF (10 mL). The solution was stirred and cooled to -78^{o}C, and the acetylide solution was then transferred dropwise to the benzil solution via cannula. The resulting solution was allowed to reach room temperature before being returned to -78ºC and treated sequentially with *p*-toluenesulfonyl chloride (1.05 g, 5.5 mmol) in anhydrous THF (1 mL) and anhydrous triethylamine (0.77 mL, 5.5 mmol) were successively added. The flask was then removed from the cooling bath and allowed to warm to room temperature. The solution was then poured into a separatory funnel containing saturated $NH_4Cl_{(aq)}$ (300 mL) and diethyl ether (50 mL). After thorough extraction, the organic layer was separated, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography(silica gel, 1:10 ethyl acetate/hexanes) to afford pure **45** (1.32 g, 60%) as a yellow oil which solidifies upon refrigeration. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.81 (dd, *J*=8.3 Hz, *J*=1.2 Hz, 2H), 7.63 (d, *J*=8.4 Hz, 2H), 7.56 (t, *J*=7.4 Hz, 1H), 7.41 (t, *J*=7.8 Hz, 2H), 7.32-7.38 (m, 5H), 7.10 (d, *J*=7.9 Hz, 2H), 2.35 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 196.6, 192.2, 145.1, 137.0, 136.2, 133.3, 132.8, 132.7, 129.6, 129.5, 128.8, 128.6, 128.3, 128.1, 120.5, 36.0, 27.4, 21.6.

Cycloisomerization of Conjugated Phosphatyloxy Alkynyl Ketones and Pyridines 12 and 15

Procedure A

A Wheaton microreactor was charged with CuCl (2 mg, 0.02 mmol) under an inert atmosphere. Anhydrous DMA (0.4 mL) and phosphatyloxy alkynyl ketone or pyridine (0.4 mmol) were subsequently added and the reaction was stirred at 130 ºC until judged complete by TLC and GC/MS analysis, typically 5 hours. The mixture was then poured into water (3 mL), extracted (hexanes, 3 x 3 mL), dried (Na_2CO_3), filtered, and concentrated. The residue was purified by column chromatography (silica gel) to afford pure furan or indolizine.

Procedure B

A Wheaton microreactor was charged with $AgBF_4$ (1 mg, 0.05 mmol) under an inert atmosphere. Anhydrous DCE (0.5 mL) and phosphatyloxy alkynyl ketone (0.5 mmol) were subsequently added and the reaction was stirred at 80 ºC until judged complete by TLC and GC/MS analysis, typically 7 hours. The reaction mixture was then filtered (Al_2O_3, DCM) and concentrated. The residue was purified by column chromatography (silica gel) to afford pure furan.

Cycloisomerization of 18

A Wheaton microreactor was charged with CuCl (1 mg, 0.02 mmol) under an inert atmosphere. Anhydrous DMA (0.4 mL) and **18** (0.2 mmol) were subsequently added and the reaction was stirred at 130 ºC for 5 hours, when judged complete by TLC and GC/MS analysis. The mixture was then filtered (silica gel, EtOAc) and concentrated. The residue was purified by column chromatography (silica gel, EtOAc) to afford **20**. Residual signal of **21** was seen as determined by preparation of the inverse isotopomer via alternative route.

Cycloisomerization of Conjugated Acyloxy Alkynyl Ketones 22

A Wheaton microreactor was charged with CuCl (5 mg, 0.05 mmol). Anhydrous DMA (1 mL), anhydrous triethylamine (28 μL, 0.2 mmol), and acyloxy alkynyl ketone **22** (1 mmol) were added, successively. The microreactor was capped with a Mininert valve, protected from light, and stirred at 130°C until judged complete by TLC and GC/MS analysis, between 2 and 24 hours. The reaction was allowed to cool, then poured into water (10 mL), extracted (hexanes, 3 x 3 mL), dried (Na_2CO_3), filtered, and concentrated. The residue was purified by column chromatography (silica gel) to afford puran acyloxy furan.

Cycloisomerization of 22a

A Wheaton microreactor was charged with CuCl (51 mg, 0.5 mmol). Anhydrous DMA (2.5 mL) and **22a** (230 μL, 1.0 mmol) were added, sequentially. The microreactor was capped with a Mininert valve, protected from light, and stirred at 130°C until judged complete by TLC and GC/MS analysis, about 12 hours. The reaction was allowed to cool, then poured into water (15 mL), extracted (hexanes, 3 x 3 mL), dried (Na_2CO_3), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 20:1 hexanes/EtOAc) to afford a 6.7:1 mixture of **23a:23b** (29%).

A Wheaton microreactor was charged with CuCl (18 mg, 0.2 mmol). Anhydrous DMA (2.5 mL), anhydrous triethylamine (28 μL, 0.2 mmol), and **22a** (230 μL, 1.0 mmol) were added, sequentially. The microreactor was capped with a Mininert valve, protected from light, and stirred at 130°C until judged complete by TLC and GC/MS analysis, about 12 hours. The reaction was allowed to cool, then poured into water (15 mL), extracted (hexanes, 3 x 3 mL), dried (Na_2CO_3), and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 20:1 hexanes/EtOAc) to afford a 6.7:1 mixture of **23b:23a** (33%).

Cycloisomerization of Skipped Acyloxy Alkynyl Ketones 39

Procedure A

A Wheaton microreactor was charged with $AgBF_4$ (5 mg, 0.05 mmol). Alkynyl ketone (1 mmol) and anhydrous DCM (1 mL) were added, sequentially. The microreactor was capped with a Mininert valve, protected from light, and stirred at room temperature until judged complete by TLC and GC/MS analysis, about 2 to 15 minutes. The solution was then filtered (Al_2O_3, DCM) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel) to afford pure furan.

Procedure B

A Wheaton microreactor was charged with anhydrous CH_2Cl_2 (0.5 mL), alkynyl ketone (0.5 mmol), and TMSOTf (9μL, 0.05 mmol), sequentially. The microreactor was stirred at room temperature until judged complete by TLC and GC/MS analysis. The solution was then filtered (silica gel, DCM) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel) to afford pure furan.

Procedure C

A Wheaton microreactor was charged with $Cu(OTf)_2$ (18 mg, 0.05 mmol). Anhydrous PhMe (1 mL) and alkynyl ketone (1 mmol) were added, sequentially. The microreactor was capped with a Mininert valve, protected from light, and stirred at room temperature until judged complete by TLC and GC/MS analysis, about 15 minutes. The solution was then filtered (silica gel, DCM) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel) to afford pure furan.

Procedure D

A Wheaton microreactor was charged with $Cu(OTf)_2$ (18 mg, 0.05 mmol). Anhydrous CH_2Cl_2 (1 mL) and alkynyl ketone (1 mmol) were added, sequentially. The microreactor was capped with a Mininert valve, protected from light, and stirred at room temperature until judged complete by TLC and GC/MS analysis, about 15 minutes. The solution was then filtered (silica gel, DCM) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel) to afford pure furan.

Procedure E

A Wheaton microreactor was charged with $AuCl_3$ (7.4 mg, 0.024 mmol). Alkynyl ketone (0.48 mmol) and anhydrous PhMe (0.5 mL) were added, sequentially. The microreactor was stirred at room temperature until judged complete by TLC and GC/MS analysis. The solution was then filtered (silica gel, DCM) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel) to afford pure furan.

Isomerization/Cycloisomerization of Phosphatyloxy and Sulfonyloxy Alkynyl/Allenyl Ketones 41, 42, and 45

42: A Wheaton microreactor was charged with $AgBF_4$ (19 mg, 0.01 mmol). Anhydrous DCM (0.2 mL) and **41** (88 mg, 0.2 mmol) were added, sequentially. The microreactor was protected from light and stirred at room temperature until judged complete by TLC and GC/MS analysis, about 1 hour. The solution was then filtered (Al_2O_3, DCM) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 2:1 hexanes/EtOAc) to afford pure **42** (79 mg, 0.18 mmol, 90%).

43: A Wheaton microreactor was charged with $AgBF_4$ (8 mg, 0.04 mmol). Anhydrous DCE (1 mL) and **41** (403 mg, 0.94 mmol) were added, sequentially. The microreactor was capped with a Mininert valve, protected from light, and stirred at 60^{o}C until judged complete by TLC and GC/MS analysis, about 16 hours. The solution was then filtered (Al_2O_3, DCM) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 3:1 hexanes/EtOAc) to afford pure **43** (263 mg, 0.61 mmol, 65%). Alternatively, furan **43** could be prepared from the allene **42**. A Wheaton microreactor was charged with $AgBF_4$ (1 mg, 5 μmol). Anhydrous DCE (0.2 mL) and **42** (43 mg, 0.1 mmol) were added, sequentially. The microreactor was capped with a Mininert valve, protected from light, and stirred at 60^{o}C until judged complete by TLC and GC/MS analysis, about 20 hours. The solution was then filtered (Al_2O_3, DCM) and concentrated under reduced pressure. Analysis of the residue indicated a 77% NMR yield (CH_2Br_2 internal standard) of **43**.

46: A Wheaton microreactor was charged with $AgBF_4$ (1.8 mg, 0.01 mmol). **45** (461 mg, 1.03 mmol) and anhydrous DCE (1 mL) were added, sequentially. The microreactor was capped with a Mininert valve, protected from light, and stirred at 60°C until judged complete by TLC and GC/MS analysis, about 45 hours. The solution was then filtered (Al_2O_3, DCM) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 10:1 hexanes/EtOAc) to afford pure **46** (376 mg, 0.85 mmol, 82%).

Allylation of 39b

A Wheaton microreactor was charged with **39b** (90 mg, 0.27 mmol), anhydrous DCM (0.4 mL), methallyltrimethylsilane (138 μL, 0.81 mmol), and TMSOTf (5 μL, 0.027 mmol), sequentially. The microreactor was stirred at room temperature for several hours, until judged complete by TLC and GC/MS analysis. The solution was filtered (silica gel, DCM) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 2:1 hexanes/DCM) to give pure **57** (78 mg, 0.24 mmol, 88%) and **58** (12 mg, 0.036 mmol, 13%).

Kumada Cross-Coupling of Hetaryl Phosphates 14c and 17b

A Wheaton microreactor was charged with Pd_2dba_3 (2.8 mg, 5 μmol) and (R)-(-)-1-[(S)-2-(Dicyclohexylphosphino)ferrocenyl]ethyl-di-*t*-butylphosphine (3.1 mg, 5 μmol) under an inert atmosphere. Anhydrous toluene (0.20 mL), hetaryl phosphate (0.1 mmol), and a solution of organomagnesium halide (0.4 mmol). The reaction was stired at 110°C for 24 hours. The reaction mixture was then quenched (water, 10 mL), extracted (Et_2O, 30 mL), washed (sat. $NaHCO_{3(aq)}$, 3 x 30 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel) to afford pure furan or indolizine.

Characterization Data

Scheme 1

14a: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 5.97 (s, 1H), 4.11-4.24 (m, 4H), 2.47 (t, *J*=7.6 Hz, 2H), 2.19 (d, *J*=1.5 Hz, 3H), 1.52-1.61 (m, 2H), 1.34 (td, *J*=7.1 Hz, *J*=1.0 Hz, 6H), 1.23-1.32 (m, 4H), 0.87 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 152.7, 137.1 (d, *J*=8.8 Hz), 134.0 (d, *J*=7.2 Hz), 101.0, 64.5 (d, *J*=6.0 Hz), 31.3, 28.3, 27.4, 22.3, 16.1 (d, *J*=6.5 Hz), 13.9, 10.3; ^{31}P NMR (161.98 MHz, $CDCl_3$) δ -6.22; LRMS *m/z* 304 (M^+, 31), 247 (M^+-57; 100).

14b: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 5.95 (s, 1H), 4.09-4.21 (m, 4H), 2.16 (d, *J*=1.3 Hz, 3H), 2.14 (s, 3H), 1.31 (td, *J*=7.1 Hz, *J*=0.9 Hz, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 148.2, 137.2 (d, *J*=8.3 Hz), 133.9 (d, *J*=7.4 Hz), 101.8, 64.4 (d, *J*=6.5 Hz), 16.0 (d, *J*=6.5 Hz), 13.8, 10.2; ^{31}P NMR (202.46 MHz, $CDCl_3$) δ -6.18; Anal. calcd.: C, 48.39; H, 6.90. Found: C, 48.74; H, 6.94. LRMS *m/z* 248 (M^+, 48), 191 (M^+-57; 50), 111 (100).

14c: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.73 (d, *J*=7.7 Hz, 2H), 7.37 (t, *J*=7.6 Hz, 2H), 7.20 (t, *J*=7.4 Hz, 1H), 6.29 (s, 1H), 4.15-4.27 (m, 4H), 2.61 (t, *J*=7.7 Hz, 2H), 1.63-1.72 (m, 2H), 1.34-1.38 (m, 4H), 1.33 (t, *J*=7.2 Hz, 6H), 0.88-0.93 (m, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 154.2, 137.7 (d, *J*=10.2 Hz), 135.4 (d, *J*=6.5 Hz), 129.8, 128.4, 126.4, 123.5, 102.5, 64.7 (d, *J*=6.5 Hz), 31.3, 28.4, 27.3, 22.3, 16.0 (d, *J*=6.5 Hz), 13.9; ^{31}P NMR (202.46 MHz, $CDCl_3$) δ -6.89; Anal. calcd.: C, 62.28; H, 7.43. Found: C, 62.30; H, 7.47; LRMS *m/z* 366 (M^+, 87), 309 (M^+-57, 69), 105 (PhCO, 100).

Scheme 2

17a: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.58 (d, *J*=7.3 Hz, 1H), 7.40 (dt, *J*=9.1 Hz, *J*=1.2 Hz, 1H), 6.53-6.56 (dd, *J*=9.0 Hz, *J*=6.2 Hz, 1H), 6.52 (s, 1H), 6.42 (td, *J*=6.8 Hz, *J*=1.3 Hz, 1H), 4.17-4.27 (m, 4H), 2.72 (t, *J*=7.6 Hz, 2H), 1.74 (sext, *J*=7.5 Hz, 2H), 1.34 (td, *J*=7.1 Hz, *J*=1.1 Hz, 6H), 1.02 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 121.1 (d, *J*=7.4 Hz), 120.8, 116.3, 114.4, 110.1, 103.5, 64.5 (d, *J*=5.5 Hz), 27.8, 20.5,

16.1 (d, *J*=6.5 Hz), 14.0; ^{31}P NMR (202.46 MHz, $CDCl_3$) δ -5.88; HRMS (EI) calcd. for $C_{15}H_{22}NO_4P$ [M^+]: 311.12864 Found: 311.1280.

17b: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.56 (d, *J*=7.2 Hz, 1H), 7.38 (d, *J*=9.1Hz, 1H), 6.53-6.50 (m, 2H), 6.40 (t, *J*=6.7 Hz, 1H), 4.23-4.18 (m, 4H), 2.71 (t, *J*=7.7 Hz, 2H), 1.70 (quin, *J*=7.4 Hz, 2H), 1.38-1.34 (m, 4H), 1.32 (dt, *J*=7.0 Hz, *J*=0.6 Hz, 6H), 0.89 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 125.8 (d, *J*=7.0 Hz), 121.0 (d, *J*=7.0 Hz), 121.0, 120.8, 116.2, 114.5, 110.1, 103.4, 64.4 (d, *J*=7.2 Hz), 31.6, 26.8, 25.7, 22.5, 16.1 (d, *J*=6.4 Hz), 14.0; ^{31}P NMR (202.46 MHz, $CDCl_3$) δ -5.88; HRMS (EI) calcd. for $C_{17}H_{26}NO_4P$ [M^+]: 339.15994 Found: 339.1603; LRMS *m/z* 339 (M^+, 28), 282 (M^+-57, 100).

17c: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.61 (d, *J*=7.3 Hz, 1H), 7.38 (dt, *J*=8.9 Hz, *J*=1.2 Hz, 1H), 6.51 (dd, *J*=9.2 Hz, *J*=6.2 Hz, 1H), 6.50 (s, 1H), 6.40 (ddd, *J*=7.4 Hz, *J*=6.1 Hz, *J*=1.5 Hz, 1H), 4.15-4.25 (m, 4H), 2.93 (sext, *J*=6.7 Hz, 1H), 1.8 (dsext, *J*=7.2 Hz, *J*=6.2 Hz, 1H), 1.59 (dsext, *J*=7.3 Hz, *J*=6.6 Hz, 1H), 1.32 (tt, *J*=7.1 Hz, *J*=1.0 Hz, 6H), 1.27 (d, *J*=7.0 Hz, 3H), 0.90 (t, *J*=7.5 Hz, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 126.0 (d, *J*=7.4 Hz), 126.0, 121.0 (d, *J*=7.4 Hz), 120.8, 116.3, 114.3, 101.7, 64.4 (d, *J*=6.5 Hz), 31.7, 18.6, 16.0 (d, *J*=6.5 Hz), 11.6; ^{31}P NMR (202.46 MHz, $CDCl_3$) δ -6.01; HRMS (EI) calcd. for $C_{16}H_{24}NO_4P$ [M^+]: 325.14429 Found: 325.1458

17d: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.91 (d, *J*=7.3 Hz, 1H), 7.40 (dt, *J*=9.0 Hz, *J*=1.3 Hz, 1H), 6.51 (s, 1H), 6.50-6.54 (ddt, *J*=9.1 Hz, *J*=6.3 Hz, *J*=0.6 Hz, 1H), 6.38 (ddd, *J*=7.5 Hz, *J*=6.3 Hz, *J*=1.5 Hz, 1H), 4.15-4.28 (m, 4H), 1.43 (s, 9H), 1.34 (td, *J*=7.1, *J*=1.1 Hz, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 129.0, 125.7 (d, *J*=7.4 Hz), 123.5, 122.3 (d, *J*=7.4 Hz), 116.5, 114.0, 109.6, 102.5, 64.5 (d, *J*=6.5 Hz), 31.9, 28.4, 16.1 (d, *J*=5.5 Hz).

17e: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.47 (d, *J*=7.2 Hz, 1H), 7.44 (dt, *J*=9.0 Hz, *J*=1.2 Hz, 1H), 7.25-7.30 (m, 2H), 7.19-7.24 (m, 1H), 7.14 (d, *J*=7.3 Hz, 2H), 6.55-6.59 (m,

2H), 6.34-6.38 (m, 1H), 4.18-4.28 (m, 4H), 4.17 (s, 2H), 1.35 (td, *J*=7.1 Hz, *J*=0.9 Hz, 6H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 137.4, 128.6, 128.2, 126.5, 125.8 (d, *J*=6.5 Hz), 121.8 (d, *J*=6.5 Hz), 121.0, 118.6, 116.2, 115.0, 110.3, 105.5, 64.5 (d, *J*=5.5 Hz), 32.3, 16.1 (d, *J*=6.5 Hz); ^{31}P NMR (202.46 MHz, $CDCl_3$) δ -5.88; HRMS (EI) calcd. for $C_{19}H_{22}NO_4P$ [M^+]: 359.12864 Found: 359.1291.

Scheme 3

20: ^{17}O NMR (54 MHz, CD_3CN, T=293 K) δ 71 ($W_{1/2}$=843 Hz).

21: ^{17}O NMR (54 MHz, CD_3CN, T=293 K) δ 84 ($W_{1/2}$=288 Hz d, J_{OP}=159 Hz).

Scheme 4

23a: ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 5.95 (s, 1H), 2.51 (t, *J*=7.7 Hz, 2H), 2.23 (s, 3H), 2.15 (s, 3H), 1.62-1.58 (m, 2H), 1.34-1.29 (m, 4H), 0.89 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 168.7, 152.8, 137.7, 133.9, 101.7, 31.3, 28.3, 27.4, 22.3, 20.6, 13.9, 10.5; LRMS *m/z* 210 (M^+, 8), 168 (M^+-42, 49), 111 (M^+-99, 100).

23b: ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 5.94 (s, 1H), 2.48 (t, *J*=7.5 Hz, 2H), 2.23 (s, 3H), 2.21 (s, 3H), 1.64-1.52 (m, 2H), 1.31-1.26 (m, 4H), 0.88 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 168.9, 148.4, 142.1, 133.7, 102.6, 31.3, 27.4, 25.0, 22.3, 20.7, 14.0; LRMS *m/z* 210 (M^+, 6), 168 (M^+-42, 16), 111 (M^+-99, 100).

Table 1

23c: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.21 (d, *J*=8.4 Hz, 2H), 7.65 (d, *J*=8.5 Hz, 3H), 7.53 (t, *J*=9.8 Hz, 2H), 7.38 (t, *J*=7.8 Hz, 2H), 7.26 ("t", *J*=3.8 Hz, 1H), 6.78 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 164.6, 150.5, 140.5, 136.1, 134.1, 131.2, 130.6, 129.3, 129.0, 123.8, 102.4, 11.4; Anal. calcd.: C, 77.68; H, 5.07. Found: C, 77.29; H, 5.07; LRMS *m/z* 278 (M^+, 18), 105 (PhCO, 100).

23d: ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.60 (d, *J*=7.15 Hz, 2H), 7.35 (t, *J*=7.79 Hz, 2H), 7.23 (t, *J*=7.98 Hz, 1H), 6.64 (s, 1 H), 2.28 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 168.51, 149.93, 139.80, 135.43, 130.68, 128.55, 127.21, 123.28, 101.82, 20.82, 10.81; LRMS *m/z* 174 (100), 105 (PhCO, 82).

23e: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.61 (d, *J*=7.3 Hz, 2H), 7.36 (d, *J*=7.3 Hz, 2H), 7.23 (t, *J*=7.4 Hz, 1H), 6.65 (s, 1H), 2.58 (q, *J*=7.6 Hz, 2H), 2.28 (s, 3H), 1.27 (t, *J*=7.5 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 172.04, 149.87, 139.73, 135.47, 130.73, 128.55, 127.18, 123.27, 101.91, 27.39, 10.81, 9.09; LRMS *m/z* 230 (M^+, 14), 174 (100).

23f: ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.60 (dd, *J*=8.4 Hz, *J*=1.2 Hz, 2H), 7.36 (t, *J*=7.7 Hz, 2H), 7.23 (t, *J*=7.5 Hz, 1H), 6.65 (s, 1H), 2.80 (st, 1H, *J*=7.0 Hz), 2.27 (s, 3H), 1.32 (d, *J*=7.0 Hz, 6H); ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 174.7, 149.9, 139.7, 135.6, 130.8, 128.6, 127.2, 123.3, 102.0, 34.0, 19.0, 10.8; Anal. calcd.: C, 73.75; H, 6.60. Found: C, 74.09; H, 6.81; LRMS *m/z* 244 (M^+, 12), 174 (100).

23g: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.63 (d, *J*=7.2 Hz, 2H), 7.38 (t, *J*=7.8 Hz, 2H), 7.29 (t, *J*=7.4 Hz, 1H), 6.67 (s, 1H), 2.29 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 176.6, 150.3, 140.1, 136.1, 131.2, 129.0, 127.6, 124.0, 102.4, 39.5, 27.6, 11.2; Anal. calcd.: C, 74.39; H, 7.02. Found: C, 74.47; H, 7.07; LRMS *m/z* 258 (M^+, 21), 174 (M^+-84, 100), 57 (Me_3C^+, 81).

23h: ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 8.20 (dd, *J*=8.40 Hz, *J*=1.24 Hz, 2H), 7.65 (s, 3 H), 7.53 (t, *J*=7.67 Hz, 2H), 7.38 (t, *J*=7.75 Hz, 2H), 7.26 (d, *J*=3.22 Hz, 1H), 6.80 (s, 1 H), 2.71 (t, *J*=7.45 Hz, 2H), 1.68 - 1.78 (m, 2 H), 1.33 - 1.42 (m, 4 H), 0.89 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 164.25, 149.96, 144.01, 135.36, 133.63, 130.83, 130.12, 129.13, 128.60, 128.58, 127.20, 123.34, 101.93, 31.29, 27.36, 25.34, 22.33, 13.98; Anal. calcd.: C, 79.02; H, 6.63. Found: C, 78.76; H, 6.80; LRMS *m/z* 334 (M^+, 9), 105 ($PhCO^+$, 100).

23i: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 5.98 (s, 1H), 2.52 (t, *J*=7.4 Hz, 2H), 1.62 (quin, *J*=7.4 Hz, 2H), 1.37-1.29 (m, 4H), 1.33 (s, 9H), 1.26 (s, 9H), 0.91 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 176.8, 160.5, 141.8, 134.3, 99.4, 39.4, 33.1, 31.7, 29.2, 27.7, 27.6, 25.5, 22.7, 14.4; Anal. calcd.: C, 73.43; H, 10.27. Found: C, 73.42; H, 10.37; LRMS *m/z* 294 (M^+, 13), 153 (98), 57 (*t*Bu, 100).

23j: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.20 (dd, *J*=8.5 Hz, *J*=1.4 Hz, 2H), 7.68 (dd, *J*=8.2 Hz, *J*=0.9 Hz, 2H), 7.66 (d, *J*=7.5 Hz, 1H), 7.53 (t, *J*=7.8 Hz, 2H), 7.40 (t, *J*=7.8 Hz, 2H), 7.29 (t, *J*=7.4 Hz, 1H), 6.81 (s, 1H), 5.03 (q, *J*=6.6 Hz, 1H), 1.60 (d, *J*=6.6 Hz, 3H), 0.88 (s, 9H), 0.09 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 164.5, 151.1, 144.8, 135.5, 134.2, 131.0, 130.6, 129.4, 129.09, 129.06, 128.1, 124.1, 102.4, 62.6, 26.2, 22.6, 18.6, -4.4, -4.6; Anal. calcd.: C, 71.05; H, 7.16. Found: C, 71.03; H, 7.13; LRMS *m/z* 422 (M^+, 1), 105 ($PhCO^+$, 100).

Scheme 7

34: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.62 (dd, *J*=8.3 Hz, 1.0 Hz, 2H), 7.37 (t, *J*=7.8 Hz, 2H), 7.24 (tt, *J*=7.3 Hz, 1.1 Hz, 3H), 6.66 (s, 1H), 2.63 (t, *J*=7.5 Hz, 2H), 2.28 (s, 3H), 1.65-1.74 (m, 2H), 1.32-1.40 (m, 4H), 0.93 (s, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 168.5, 149.8, 143.8, 135.2, 130.8, 128.5, 127.1, 123.3, 101.8, 31.3, 27.3, 25.2, 22.3, 20.7, 13.9; ^{17}O NMR (54 MHz, CD_3CN, T=298 K) δ 170 ($W_{1/2}$=709 Hz).

35: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.62 (dd, *J*=8.3 Hz, 1.0 Hz, 2H), 7.37 (t, *J*=7.8 Hz, 2H), 7.24 (tt, *J*=7.3 Hz, 1.1 Hz, 3H), 6.66 (s, 1H), 2.63 (t, *J*=7.5 Hz, 2H), 2.28 (s, 3H), 1.65-1.74 (m, 2H), 1.32-1.40 (m, 4H), 0.93 (s, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 168.5, 149.8, 143.8, 135.2, 130.8, 128.5, 127.1, 123.3, 101.8, 31.3, 27.3, 25.2, 22.3, 20.7, 13.9; ^{17}O NMR (54 MHz, CD_3CN, T=298 K) δ 372.

Table 3

40a: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.44 (d, *J*=7.15 Hz, 2 H), 7.33-7.40 (m, 5 H), 7.24 (t, *J*=7.34 Hz, 2H), 7.17-7.22 (m, 1H), 2.64 (t, *J*=7.61 Hz, 2H), 2.13 (s, 3h), 1.71 (quin,

J=7.52 Hz, 2H), 1.45 (sext, *J*=7.52 Hz, 1H), 0.98 (t, *J*=7.43 Hz, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 168.90, 145.62, 144.32, 133.95, 131.46, 130.99, 129.43, 128.63, 128.23, 127.47, 127.18, 125.40, 117.95, 29.60, 25.15, 22.37, 20.34, 13.78; HRMS (EI) calcd. for $C_{22}H_{22}O_3$ [M^+]: 334.15689. Found 334.1557; LRMS *m/z* 334 (M^+, 14), 292 (M^+-42, 33), 249 (M^+-85, 100).

40b: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.42 (d, *J*=7.2 Hz, 2H), 7.37-7.33 (m, 6H), 7.23 (t, *J*=7.6 Hz, 2H), 7.19 (tt, *J*=7.2 Hz, *J*=1.3 Hz, 1H), 2.07 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 169.8, 149.9, 145.2, 132.0, 131.4, 130.0, 129.1, 128.7, 127.9, 127.6, 125.7, 118.9, 33.5, 29.0, 20.9; Anal. calcd.: C, 79.02; H, 6.63. Found: C, 78.95; H, 6.57; LRMS *m/z* 334 (M^+, 8), 277 (M^+-^{t}Bu, 100).

40c: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.41 (d, *J*=7.5 Hz, 2H), 7.28-7.38 (m, 5H), 7.22 (t, *J*=7.5 Hz, 2H), 7.13-7.19 (m, 1H), 1.38 (s, 9H), 1.07 (s, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 176.4, 149.3, 144.4, 132.7, 131.6, 131.1, 130.1, 128.4, 128.2, 127.5, 127.0, 125.0, 118.9, 38.7, 33.0, 28.7, 27.0; HRMS (EI) calcd. for $C_{25}H_{28}O_3$ [M^+]: 376.20384 Found: 376.2037.

40d: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.36 (t, *J*=7.6 Hz, 2H), 7.27 (t, *J*=7.1 Hz, 3H), 2.30 (s, 3H), 2.11 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 170.0, 148.5, 145.1, 132.2, 131.1, 128.9, 128.8, 127.1, 117.6, 33.2, 29.0, 21.0, 13.3; Anal. calcd.: C, 74.97; H, 7.40. Found: C, 75.02; H, 7.37; LRMS *m/z* 272 (M^+, 5), 215 (M^+-^{t}Bu, 100).

40e: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.59 (dd, *J*=8.5 Hz, *J*=0.9 Hz, 2H), 7.39 (t, *J*=7.8 Hz, 2H), 7.24 (t, *J*=7.4 Hz, 1H), 2.31 (s, 3H), 2.05 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$). δ169.8, 148.0, 145.1, 134.2, 132.3, 128.9, 127.0, 125.3, 112.9, 33.3, 21.0, 9.0; Anal. calcd.: C, 74.97; H, 7.40. Found: C, 74.60; H, 7.55; LRMS *m/z* 272 (M^+, 11), 215 (M^+-^{t}Bu, 100).

40f: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.25 (s, 3H), 2.14 (s, 3H), 1.73 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 170.0, 147.5, 144.0, 132.8, 110.7, 32.6, 29.1, 20.9; Anal. calcd.: C, 68.54; H, 8.63. Found: C, 68.45; H, 8.73; LRMS *m/z* 210 (M^+, 7), 153 (M^+-^{t}Bu, 100).

40g: 1H NMR (500.13 MHz, $CDCl_3$) δ 2.50 (tt, *J*= 6.4 Hz, *J*=1.7 Hz, 2H), 2.23 (s, 3H), 2.21 (tt, *J*=6.0 Hz, *J*=1.8 Hz, 2H), 1.79 (dquin, *J*=6.1 Hz, *J*=2.5 Hz, 2H), 1.68 (dquin, *J*=5.9 Hz, *J*=2.4 Hz, 2H), 1.26 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 169.7, 147.8, 147.4, 132.0, 113.8, 33.1, 29.2, 23.6, 23.2, 22.9, 21.0, 20.4; Anal. calcd.: C, 71.16; H, 8.53. Found: C, 70.86; H, 8.79; LRMS *m/z* 236 (M^+, 7), 179 (M^+-*t*Bu, 100).

40h: ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.41-7.47 (m, 2H), 7.27-7.39 (m, 5H), 7.14-7.27 (m, 3H), 2.60 (t, *J*=7.5 Hz, 2H), 1.63-1.75 (m, 2H), 1.37-1.48 (sext, *J*=7.4 Hz, 2H), 1.16 (s, 9H), 0.96 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 176.3, 145.4, 144.0, 134.3, 131.5, 131.2, 129.8, 128.5, 128.3, 127.5, 127.1, 125.3, 118.3, 38.8, 29.6, 27.1, 25.2, 22.4, 13.8; HRMS (EI) calcd. for $C_{25}H_{28}O_3$ [M^+]: 376.20384 Found: 376.2046.

40i: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.43-7.39 (m, 3H), 7.36 (t, *J*=1.6 Hz, 1H), 7.29 (dd, *J*=8.4 Hz, *J*=1.3 Hz, 2H), 7.18 (t, *J*=7.3 Hz, 1H), 7.14 (d, *J*=7.2 Hz, 1H), 2.36 (s, 3H), 0.01 (s, 9H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 168.5, 153.4, 143.4, 135.4, 130.4, 130.3, 128.5, 128.1, 127.7, 127.6, 126.7, 125.2, 104.9, 20.5, -0.6; HRMS (EI) calcd. for $C_{24}H_{18}O_3$ [M^+]: 350.13382. Found: 350.1348; LRMS *m/z* 350 (M^+, 5), 308 (M^+-42, 53), 292 (M^+-58, 100).

40j: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.76 (d, *J*=8.4 Hz, 2H), 7.54 (d, *J*=8.1 Hz, 2H), 7.47-7.37 (m, 6 H), 7.33-7.22 (m, 5H), 2.19 (s, 3H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 168.5, 146.6, 140.8, 135.1, 131.0, 130.6, 129.5, 129.3, 128.8, 128.7, 128.4, 127.9, 127.7, 127.5, 125.7, 124.1, 119.8, 20.6; HRMS (EI) calcd. for $C_{24}H_{18}O_3$ [M^+]: 354.1256. Found: 354.1260; LRMS *m/z* 354 (M^+, 5), 312 (M^+-42, 100), 105 ($PhCO^+$, 55).

Scheme 8

42: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.05 (d, *J*=7.2 Hz, 2H), 7.54 (t, *J*=7.3 Hz, 1H), 7.50 (d, *J*=7.5 Hz, 2H), 7.43 (t, *J*=7.7 Hz, 2H), 7.34 (t, *J*=7.5 Hz, 2H), 7.25-7.30 (m, 1H), 3.98-4.13 (m, 4H), 1.21 (td, *J*=7.1 Hz, *J*=0.9 Hz, 3H), 1.17 (td, *J*=7.1 Hz, *J*=0.9 Hz, 3H), 1.11 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 195.8 (d, *J*=2.8 Hz), 192.7, 137.1, 136.6, 136.5, 133.4, 133.2, 129.9, 128.6, 128.4, 128.2, 127.7, 119.8, 64.3 (t, *J*=6.5 Hz), 35.9 (d, *J*=6.2 Hz), 27.4, 15.9 (d, *J*=6.7 Hz), 15.8 (d, *J*=6.7 Hz); ^{31}P NMR (202.46 MHz, $CDCl_3$) δ -7.01.

43: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.30-7.45 (m, 7H), 7.21 (t, *J*=7.3 Hz, 2H), 7.16 (tt, *J*=7.2 Hz, *J*=1.3 Hz, 1H), 3.79-3.88 (m, 2H), 3.64-3.74 (m, 2H), 1.47 (s, 9H), 1.13 (td, *J*=7.1 Hz, *J*=0.9 Hz, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 149.0 (d, *J*=6.5 Hz), 144.1, 132.6 (d, *J*=8.3 Hz), 131.6, 131.0, 130.6, 128.4, 128.2, 127.5, 127.1, 125.2, 118.2, 64.0 (d, *J*=6.5 Hz), 33.2, 28.8, 15.9 (d, *J*=6.5 Hz); ^{31}P NMR (202.46 MHz, $CDCl_3$) δ -6.87.

46: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.33 (dd, *J*=8.2 Hz, *J*=1.6 Hz, 2H), 7.29 (d, *J*=8.3 Hz, 2H), 7.14-7.24 (m, 4H), 7.10 (t, *J*=7.5 Hz, 2H), 7.04-7.08 (m, 2H), 6.94 (d, *J*=7.9 Hz, 2H), 2.33 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 152.9, 144.6, 144.5, 132.9, 131.4, 130.9, 130.7, 129.9, 129.3, 128.2, 127.9, 127.4, 126.9, 125.5, 117.9, 109.6, 33.5, 28.8, 21.6.

Table 4

53: ^{17}O NMR (54 MHz, CD_3CN, T=343 K) δ 377 ($W_{1/2}$=851 Hz).

54: ^{17}O NMR (54 MHz, CD_3CN, T=343 K) δ 171 ($W_{1/2}$=965 Hz).

Scheme 12

57: ^{1}H NMR (500.64 MHz, $CDCl_3$) δ 7.89 (dd, *J*=8.34 Hz, *J*=1.01 Hz, 2H), 7.53 (d, *J*=7.34 Hz, 2H), 7.30 - 7.38 (m, 3H), 7.22 - 7.26 (m, 3H), 4.74 - 4.76 (m, 1H), 4.52 (br s, 1H), 3.01 (d, *J*=13.39 Hz, 1H), 2.77 (d, *J*=13.39 Hz, 1H), 1.53 (s, 3H), 1.17 (s, 9H); ^{13}C

NMR (125.90 MHz, $CDCl_3$) δ 196.7, 141.4, 140.2, 135.4, 131.8, 130.3, 128.6, 127.3, 127.1, 126.8, 115.1, 99.6, 79.0, 55.4, 48.2, 30.6, 27.7, 24.2.

58: ^{1}H NMR (500.64 MHz, $CDCl_3$) δ 7.81 - 7.86 (m, 2H), 7.48 - 7.53 (m, 1H), 7.38 - 7.45 (m, 4H), 7.31 - 7.37 (m, 2H), 7.23 - 7.29 (m, 1H), 4.82 (s, 2H), 2.83 (s, 2H), 1.55 (s, 3H), 1.03 (s, 9H); ^{13}C NMR (125.90 MHz, $CDCl_3$) δ 208.9, 194.8, 142.9, 139.4, 134.0, 131.9, 128.9, 128.3, 127.9, 127.8, 127.2, 116.9, 113.3, 111.8, 37.7, 35.5, 28.9, 21.9.

Scheme 13

60: ^{17}O NMR (54 MHz, CD_3CN, T=343 K) δ 86 ($W_{1/2}$=326 Hz, d, *J*=156 Hz).

61: ^{17}O NMR (54 MHz, CD_3CN, T=343 K) δ 87 ($W_{1/2}$=265 Hz, d, *J*=159 Hz).

62: ^{17}O NMR (54 MHz, CD_3CN, T=343 K) δ 70 ($W_{1/2}$=708 Hz).

Table 5

76a: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.60 (d, *J*=8.1 Hz, 2H), 7.40 (t, *J*=7.7 Hz, 2H), 7.24 (t, *J*=7.1 Hz, 1H), 5.94 (s, 1H), 2.64 (t, *J*=7.6 Hz, 2H), 2.25 (s, 3H), 1.69 (quin, *J*=7.1 Hz, 2H), 1.39-0.36 (m, 4H), 0.92 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 154.9, 146.7, 132.2, 128.4, 126.0, 124.8, 117.0, 110.5, 31.4, 28.0, 27.8, 22.5, 14.0, 12.0; Anal. calcd.: C, 60.17; H, 7.72. Found: C, 60.29; H, 7.74; LRMS *m/z* 228 (M^+, 30), 171 (M^+-57, 100).

76b: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.55-7.60 (m, 2H), 7.34-7.42 (m, 2H), 7.19-7.24 (m, 1H), 6.00 (s, 1H), 2.58-2.72 (m, 4H), 1.62-1.75 (m, 2H), 1.31-1.43 (m, 4H), 1.24 (t, *J*=7.7 Hz, 3H), 0.91 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 155.2, 132.2, 128.4, 126.2, 125.2, 123.8, 123.3, 108.3, 31.5, 28.1, 27.8, 22.4, 19.3, 14.4, 14.0; HRMS (EI) calcd. for $C_{17}H_{22}O$ [M^+]: 242.16707 Found: 242.1672.

76c: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.58-7.61 (m, 2H), 7.36-7.40 (m, 2H), 7.30-7.35 (m, 2H), 7.22-7.28 (m, 4H), 5.88 (s, 1H), 4.02 (s, 2H), 2.64 (t, *J*=7.7 Hz, 2H), 1.64-1.74 (m, 2H), 1.31-1.43 (m, 4H), 0.89-0.96 (m, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 155.5, 147.4, 140.3, 131.7, 128.5, 126.5, 126.1, 125.3, 120.0, 109.5, 32.0, 31.4, 28.1, 27.7, 22.4, 14.0; HRMS (EI) calcd. for $C_{22}H_{24}O$ [M^+]: 304.18272 Found: 304.1828.

76d: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.51-7.55 (m, 2H), 7.41-7.45 (m, 2H), 7.33-7.39 (m, 2H), 7.25-7.33 (m, 3H), 7.19-7.24 (m, 1H), 6.18 (s, 1H), 2.72 (t, *J*=7.5 Hz, 2H), 1.71-1.79 (m, 2H), 1.37-1.46 (m, 4H), 0.95 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 155.8, 146.5, 134.8, 131.6, 128.6, 128.5, 128.3, 126.9, 126.9, 125.9, 122.9, 109.2, 31.5, 28.0, 27.7, 22.4, 14.0; HRMS (EI) calcd. for $C_{21}H_{22}O$ [M^+]: 290.16707 Found: 290.1668.

77a: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.70 (d, *J*=7.2 Hz, 1H), 7.17-7.38 (m, 6H), 6.59 (dd, *J*=8.8 Hz, *J*=6.4 Hz, 1H), 6.49 (dt, *J*=7.0 Hz, *J*=1.1 Hz, 1H), 6.47 (s, 1H), 4.17 (s, 2H), 2.78 (t, *J*=7.7 Hz, 2H), 1.72-1.82 (m, 2H), 1.39-1.48 (m, 4H), 0.97 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 142.4, 129.3, 128.4, 128.2, 125.6, 123.8, 121.5, 117.4, 114.2, 112.4, 110.8, 109.6, 32.0, 31.8, 26.9, 25.9, 22.5, 14.0.

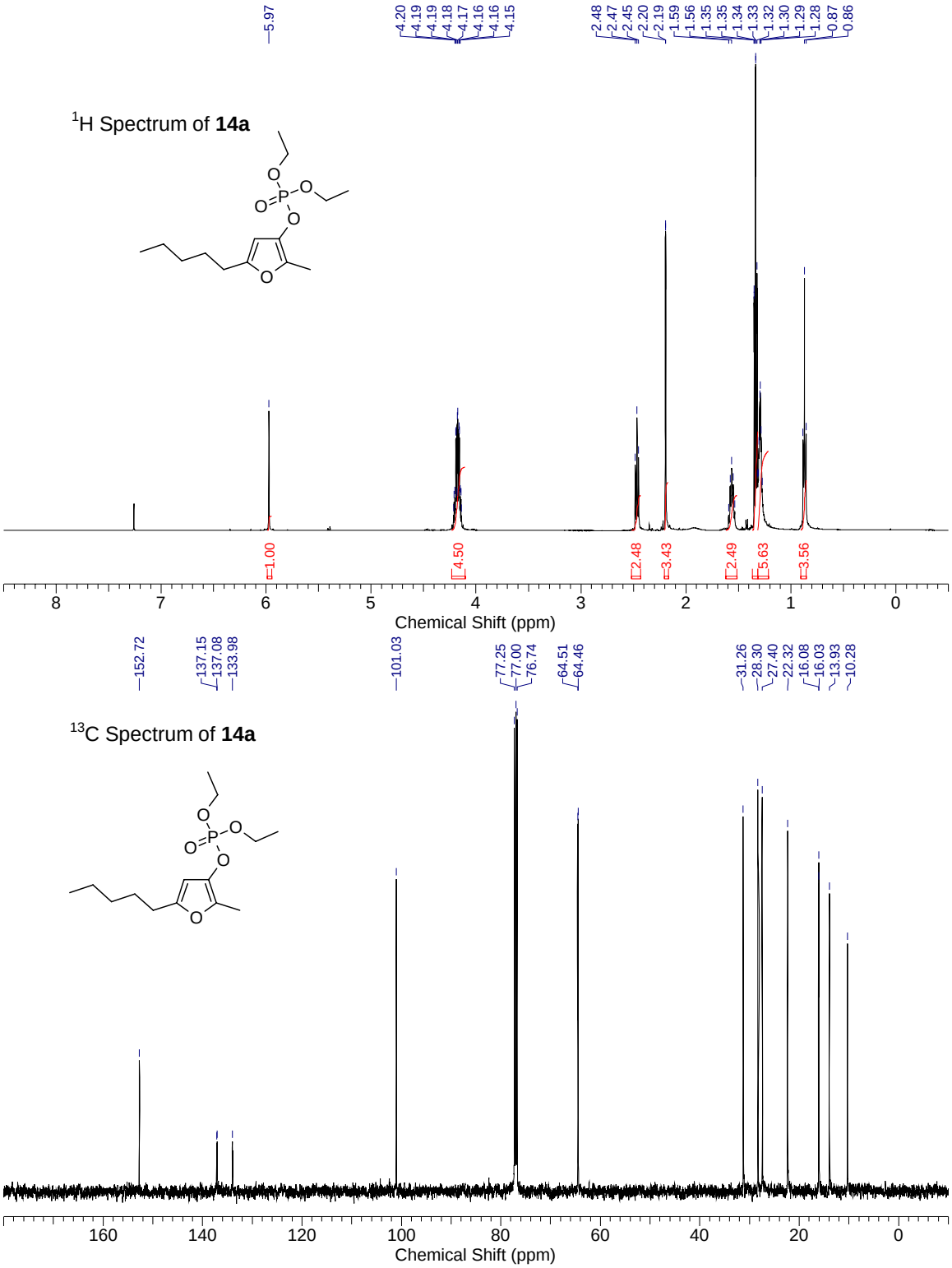
77b: 1H NMR (500.13 MHz, $CDCl_3$) δ 7.64 (dt, *J*=7.2 Hz, *J*=0.9 Hz, 1H), 7.29 (dt, *J*=9.0 Hz, *J*=1.2 Hz, 1H), 6.53 (ddd, *J*=9.1 Hz, *J*=6.4 Hz, *J*=0.8 Hz, 1H), 6.43 (s, 1H), 6.42 (td, *J*=6.7 Hz, *J*=1.3 Hz, 1H), 2.77 (t, *J*=7.7 Hz, 2H), 2.35 (s, 3H), 1.70-1.78 (m, 2H), 1.36-1.45 (m, 4H), 0.92 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 129.3, 123.4, 121.4, 117.5, 113.5, 112.7, 109.4, 107.0, 31.8, 27.1, 25.8, 22.5, 14.0, 10.5.

77c: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.81 (t, *J*=7.6 Hz, 2H), 7.67 (d, *J*=5.2 Hz, 2H), 7.48-7.46 (m, 2H), 7.28-7.26 (m, 1H), 6.86 (d, *J*=2.6 Hz, 1H), 6.74 (t, *J*=7.5 Hz, 1H), 6.59 (t, *J*=6.5 Hz, 1H), 2.86 (t, *J*=7.5 Hz, 2H), 1.86 (quin, *J*=6.9 Hz, 2H), 1.55-1.43 (m, 4H), 1.01-0.98 (m, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 136.8, 128.8, 128.7, 127.4, 127.2, 125.0, 122.1, 118.4, 116.6, 113.6, 111.5, 110.5, 31.8, 26.9, 25.9, 22.6, 14.1; Anal.

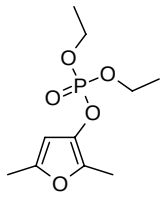
calcd.: C, 86.65; H, 8.04. Found: C, 85.70; H, 8.17; LRMS *m/z* 263 (M^+, 28), 206 (M^+-57, 100).

77d: ^{1}H NMR (500.13 MHz) δ 7.61 (d, *J*=7.0 Hz, 1H), 7.21 (d, *J*=9.0 Hz, 1H), 6.46 (dd, *J*=8.8 Hz, *J*=6.1 Hz, 1H), 6.38 (t, *J*=6.1 Hz, 1H), 6.31 (s, 1H), 2.77 (t, *J*=7.6 Hz, 2H), 2.12 (s, 2H), 1.70-1.79 (m, 2H), 1.35-1.43 (m, 4H), 0.90-0.95 (m, 3H), 0.01 (s, 9H); ^{13}C NMR (125.76 MHz) δ 128.4, 123.2, 121.3, 117.9, 112.6, 112.2, 109.2, 109.1, 31.8, 26.9, 25.8, 22.5, 15.1, 14.1, -1.5; LRMS 273 (M^+, 31), 216 (M^+-57, 72), 200 (M^+-TMS, 100).

Spectral Charts



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



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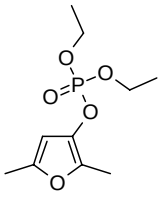

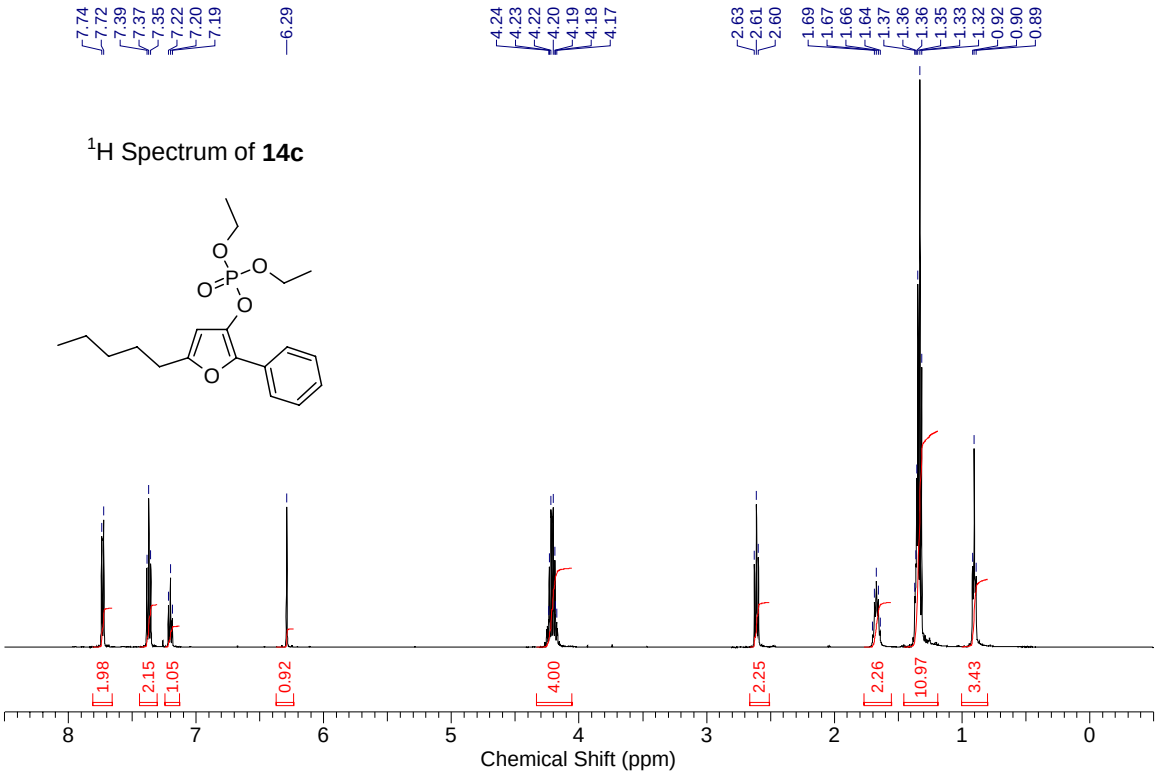
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0.90
0.89
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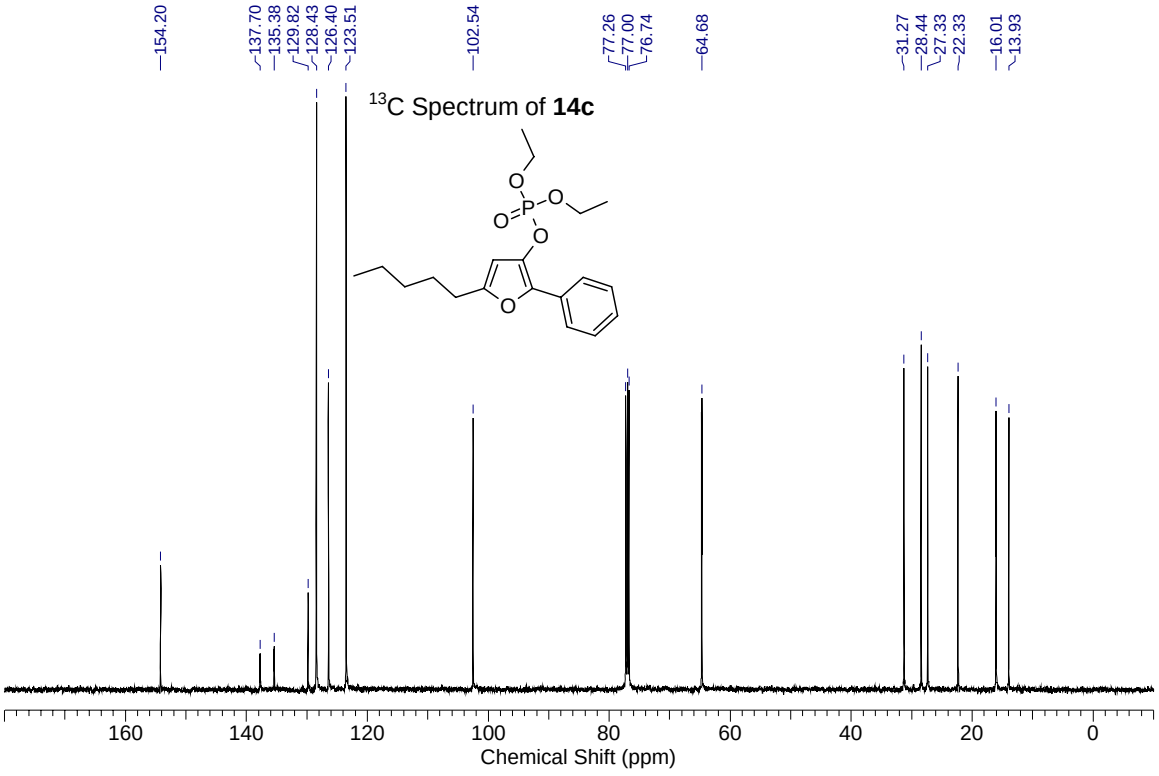
Chemical Shift (ppm)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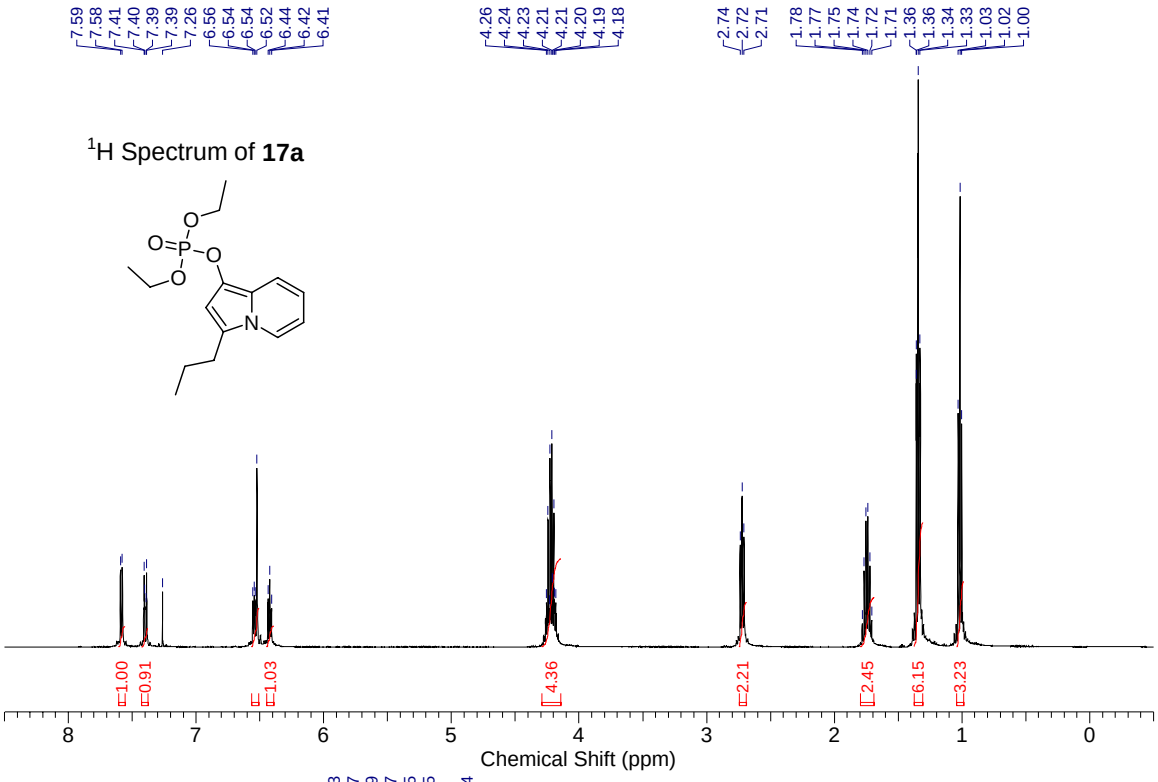
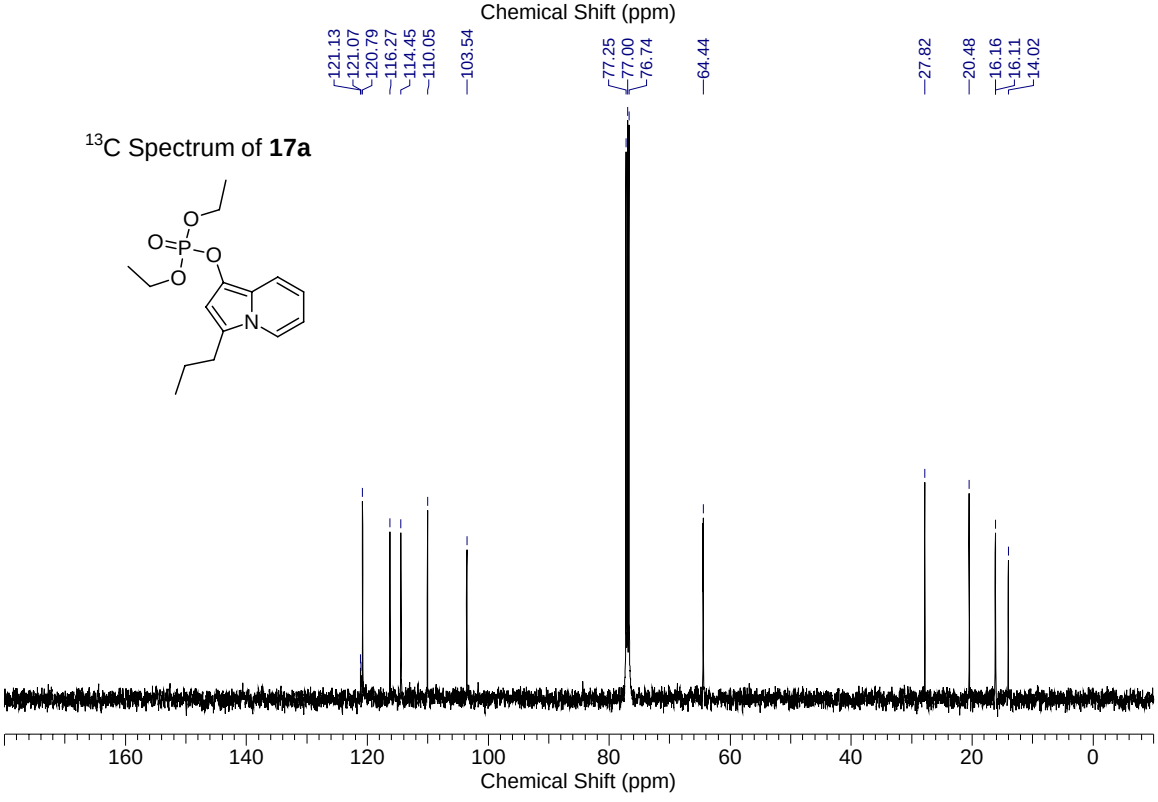
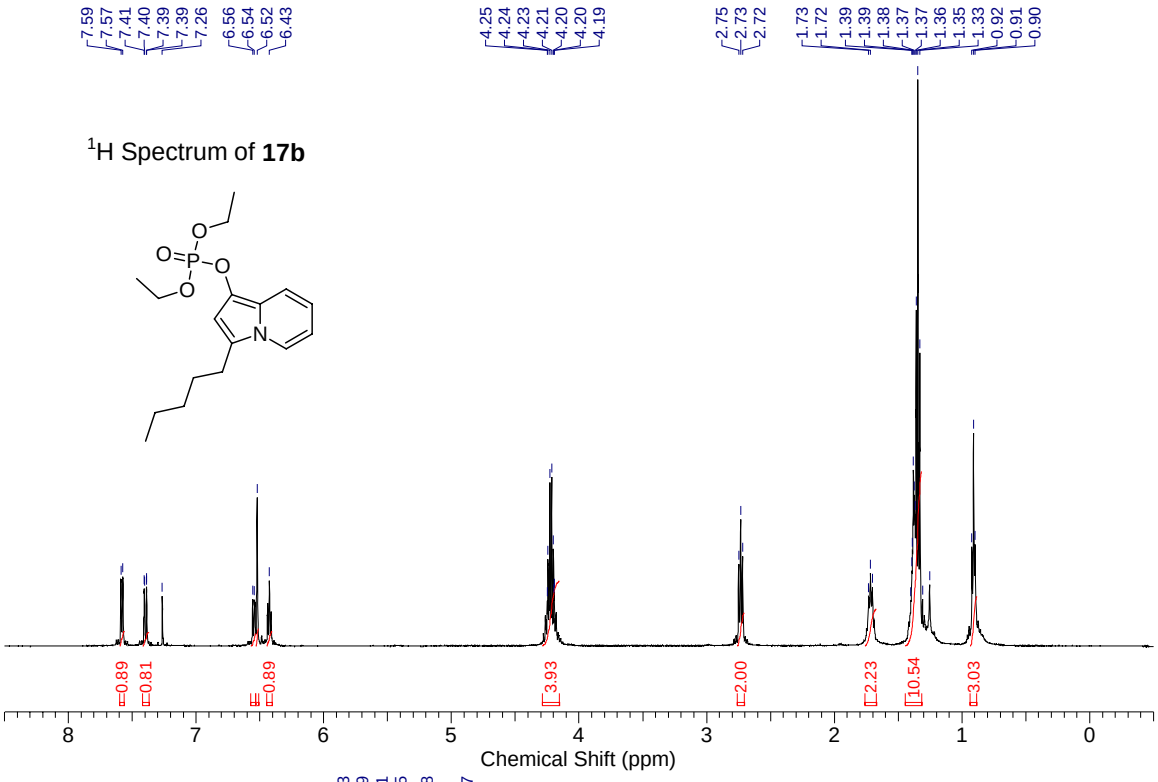
13C Spectrum of 14c
Chemical Shift (ppm)



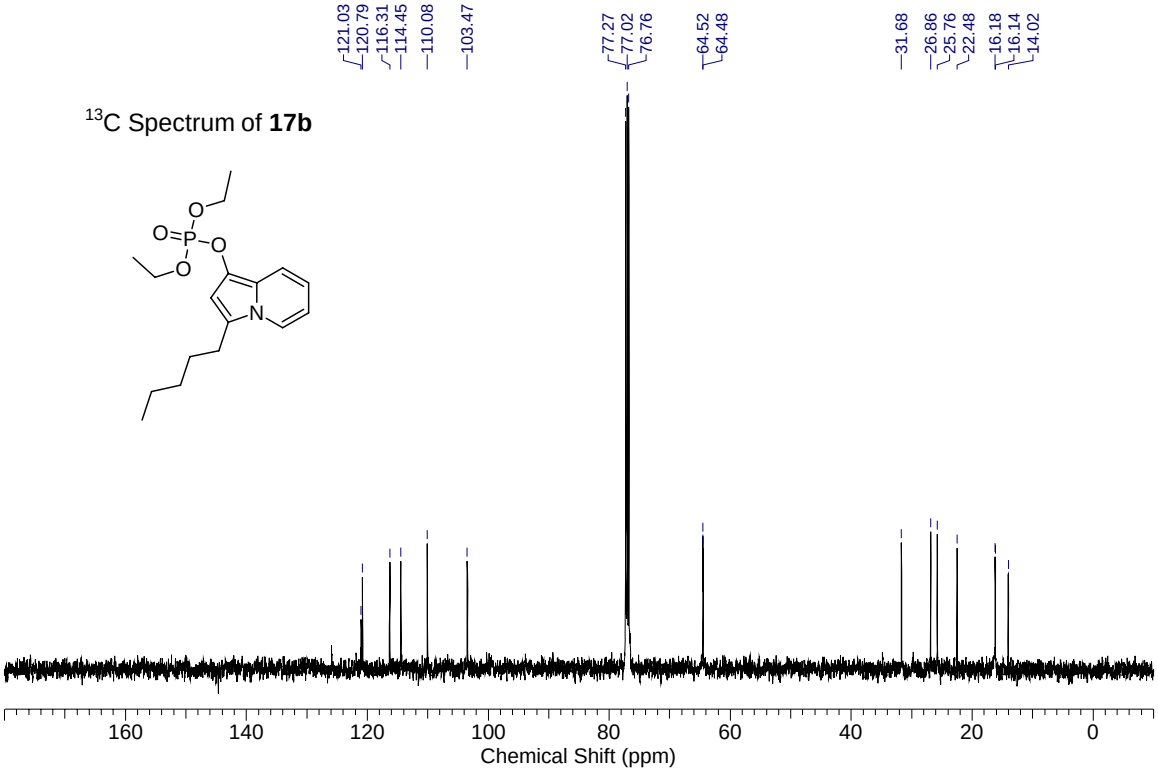
^{1}H Spectrum of **17a**



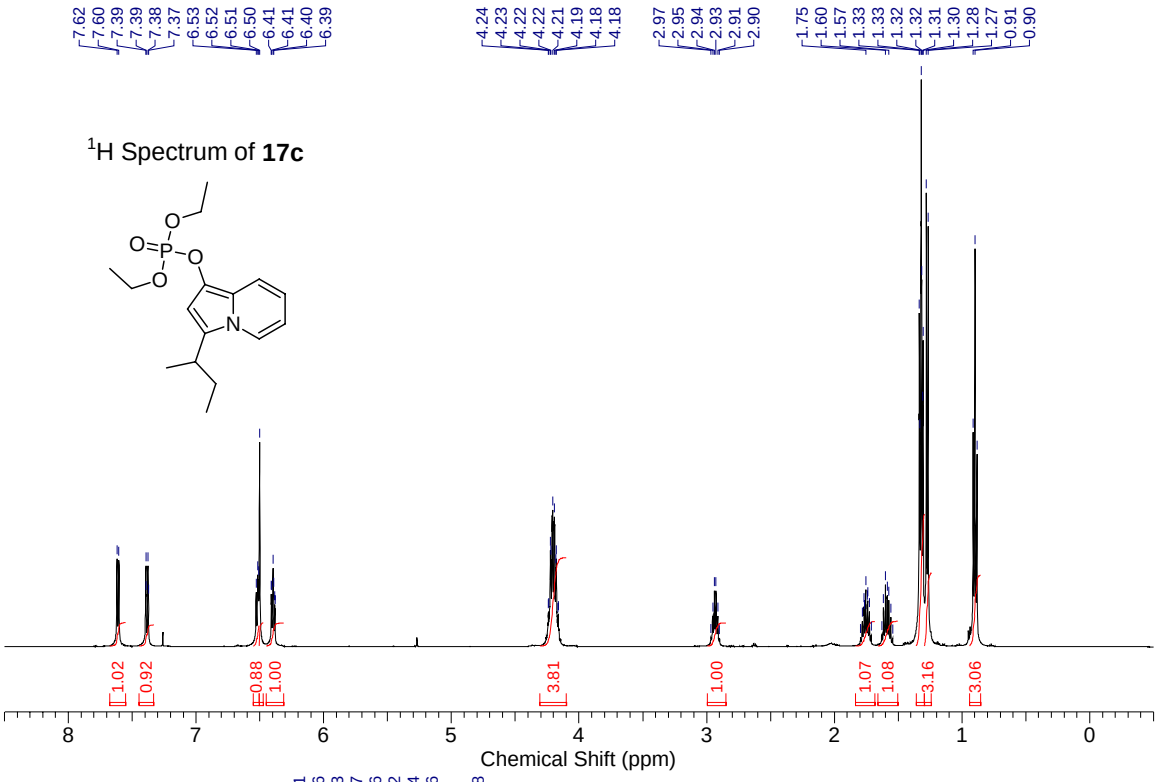
^{13}C Spectrum of **17a**



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



^{13}C Spectrum of **17b**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1.27
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0.90
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O
O
N
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1.08
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3.06
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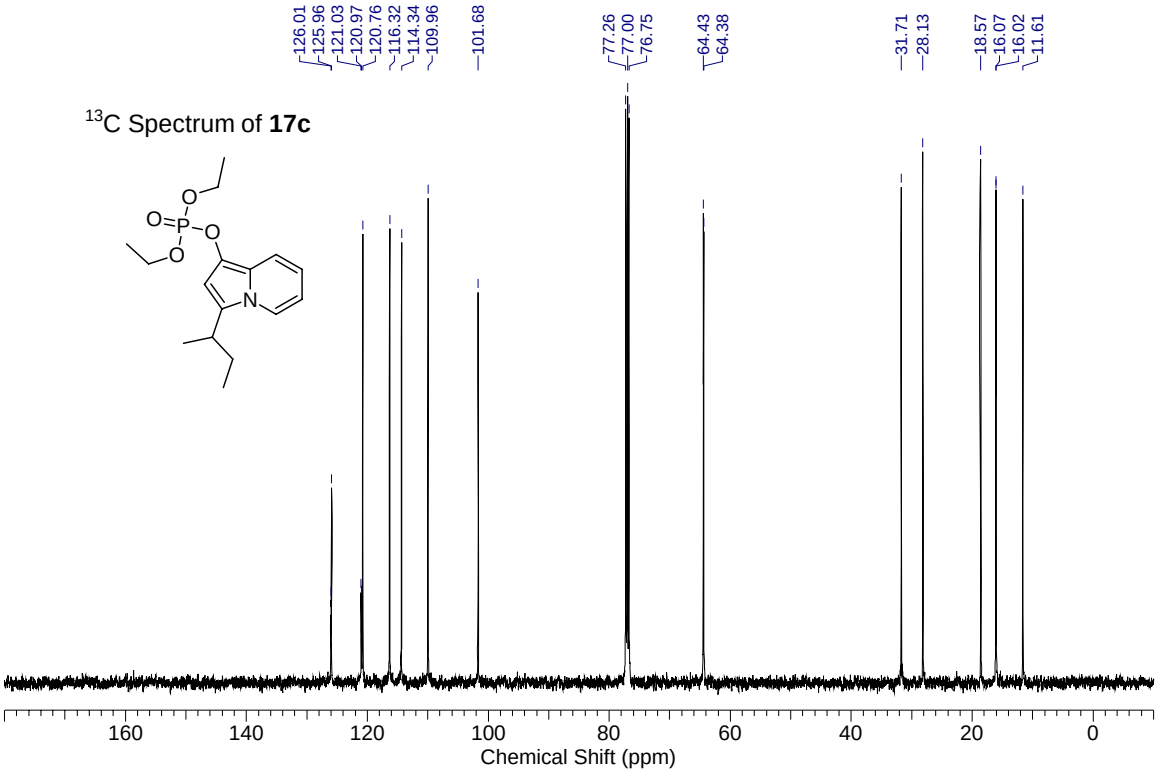
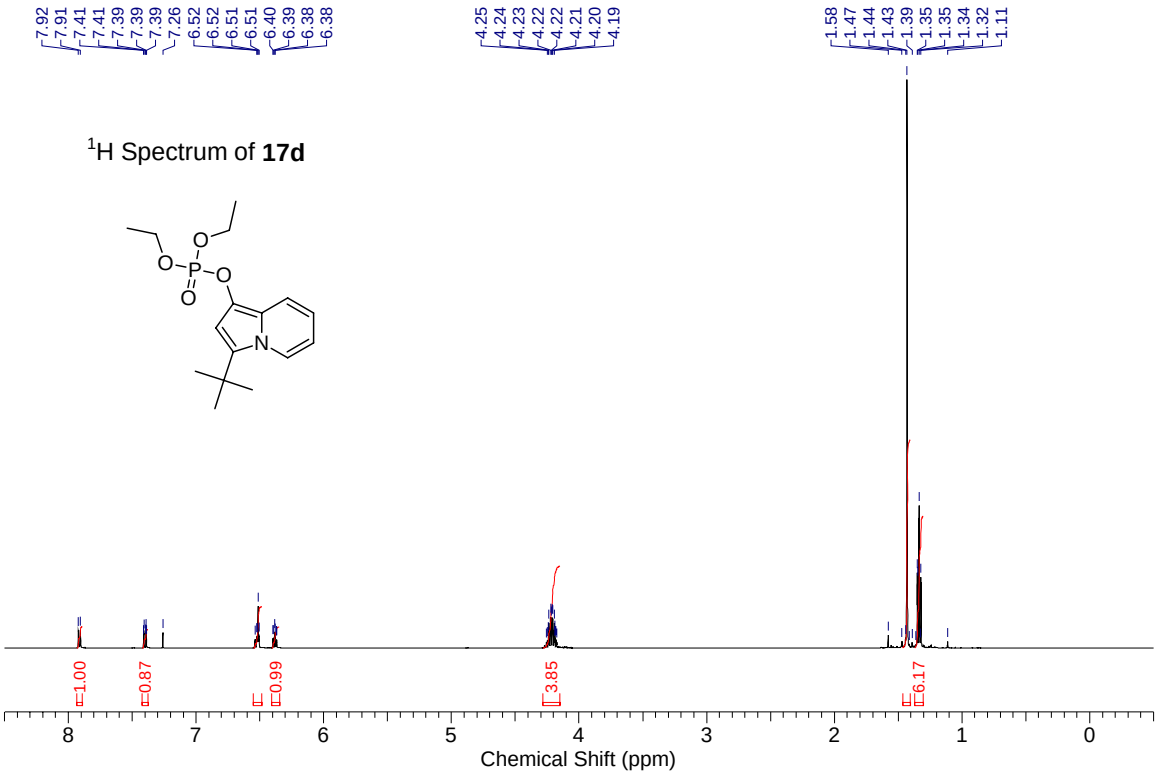
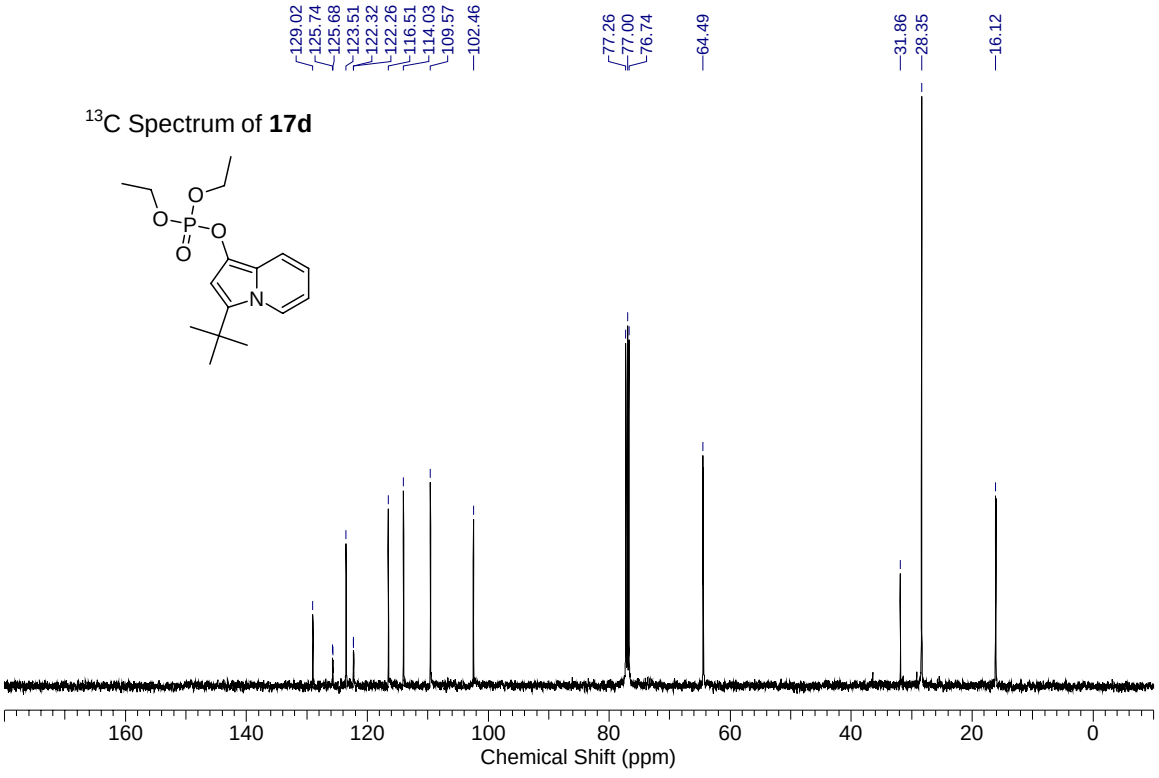
6
5
4
3
2
1
0
Chemical Shift (ppm)

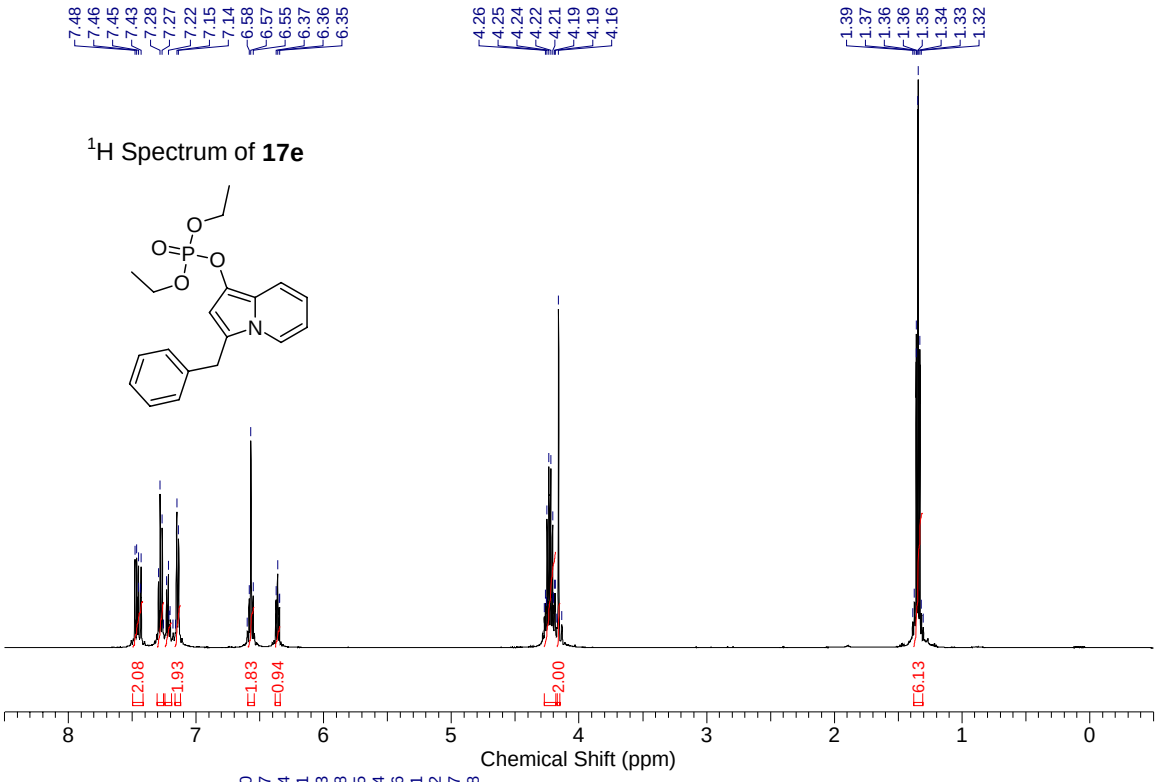

126.01
125.96
121.03
120.97
120.76
116.32
114.34
109.96
101.68
77.26
77.00
76.75
64.43
64.38
31.71
28.13
18.57
16.07
16.02
11.61
13C Spectrum of 17c
O
O=P
O
O
N
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



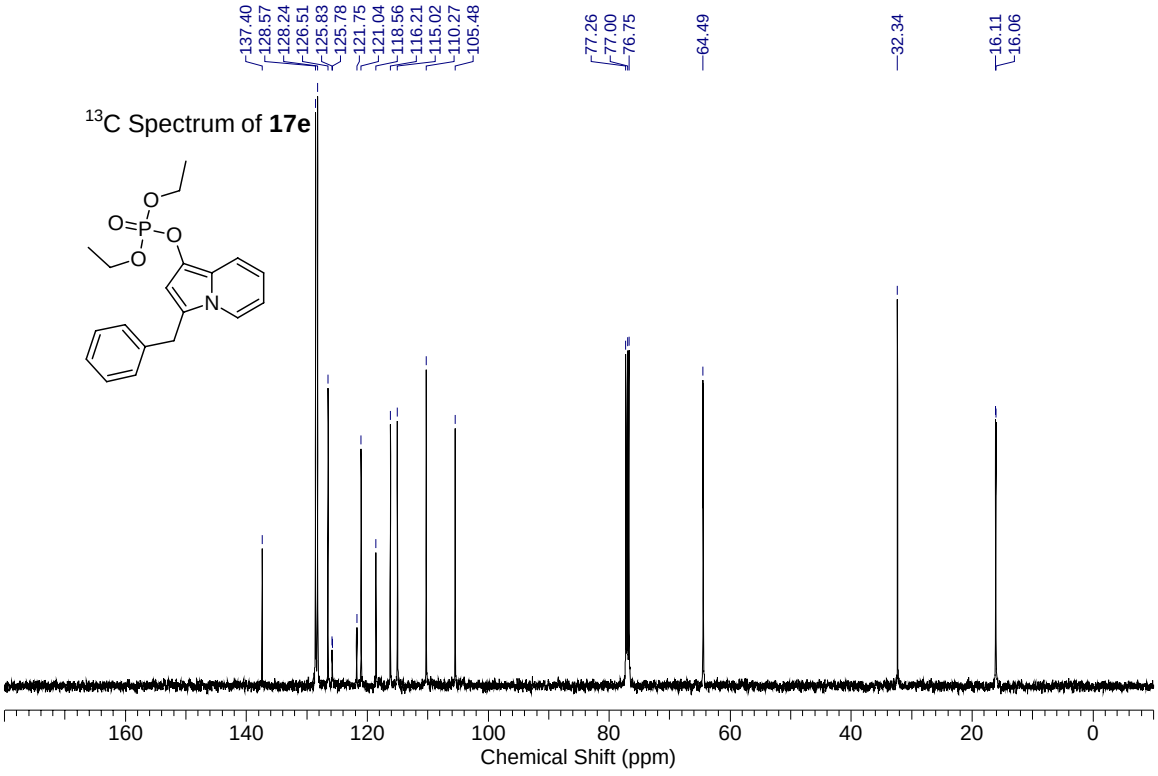
^{1}H Spectrum of **17d**



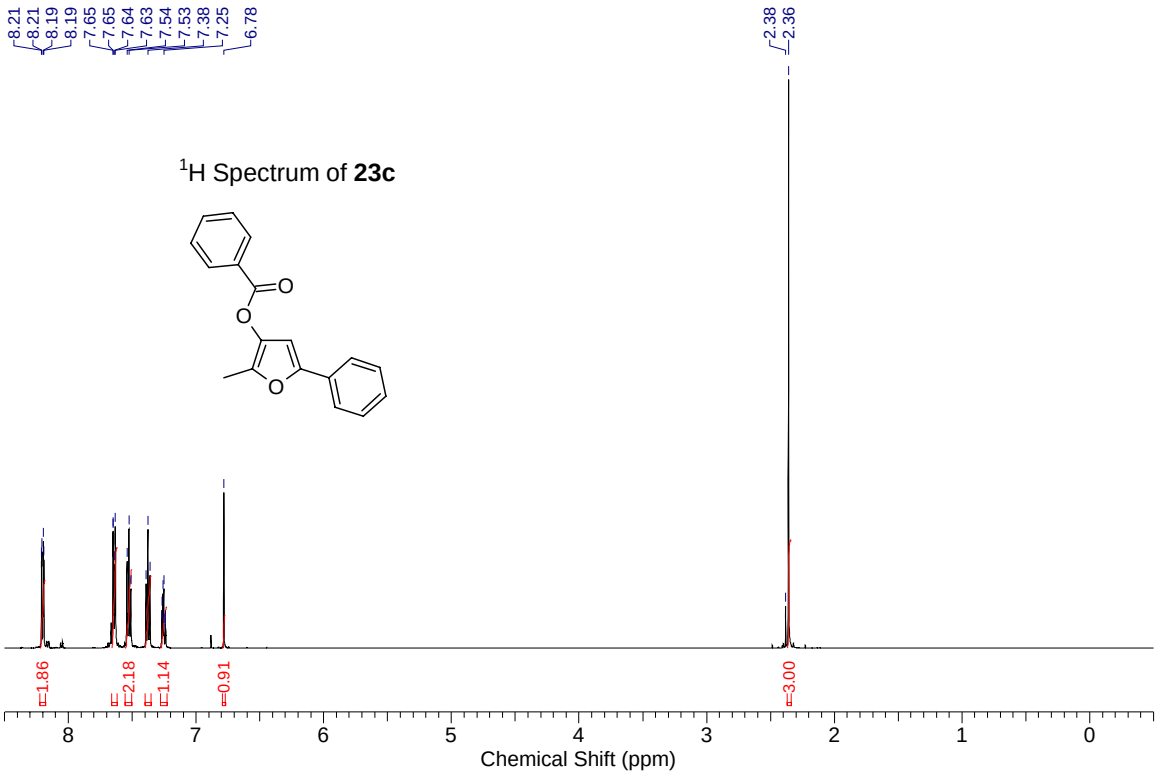
^{13}C Spectrum of **17d**

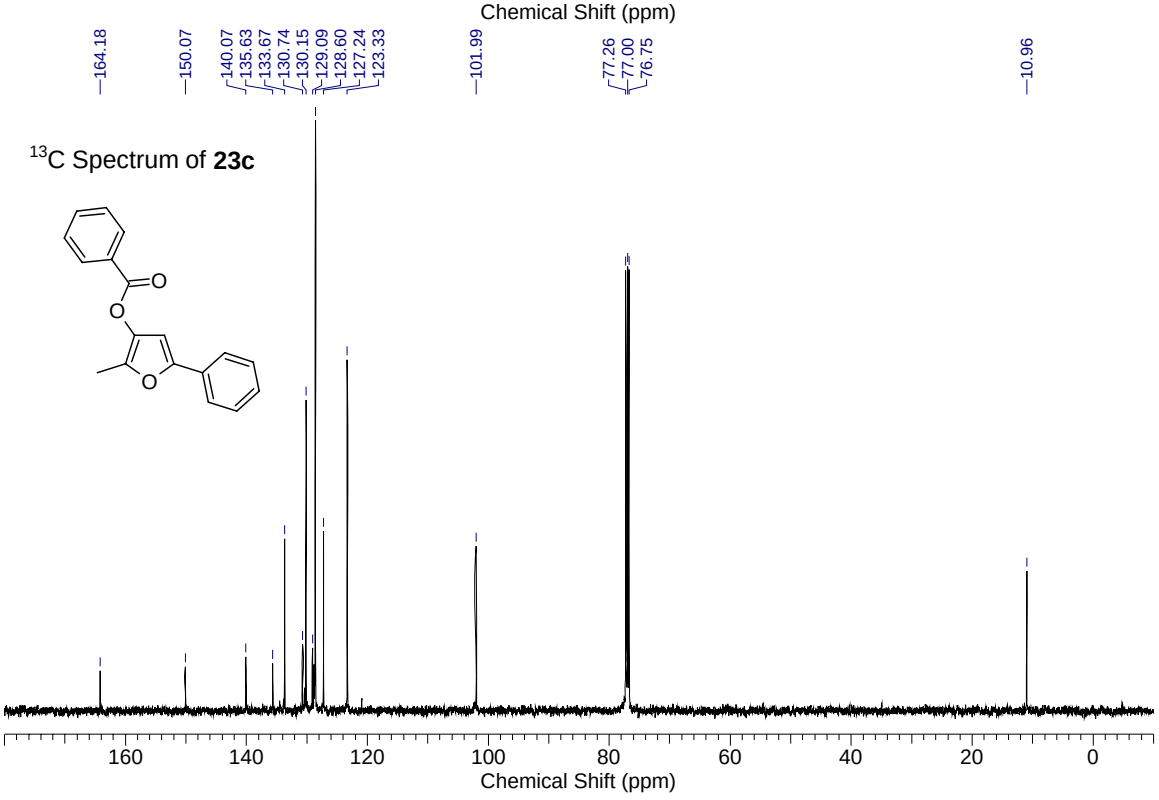


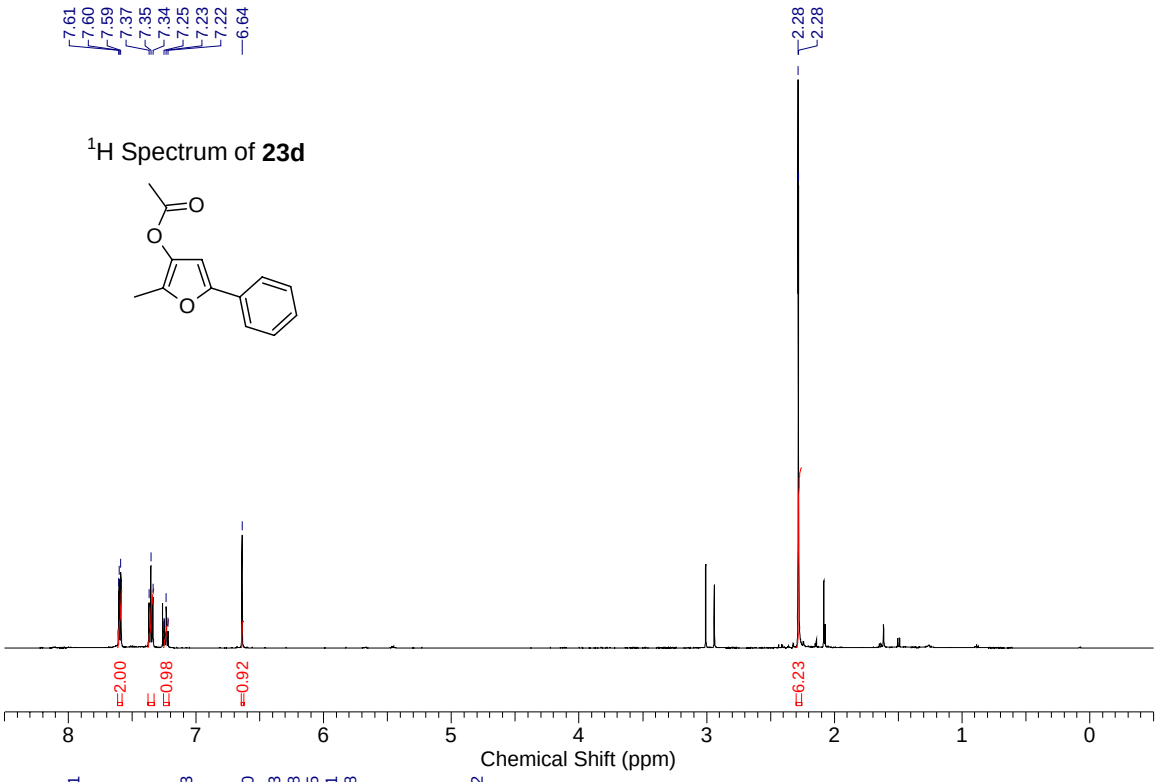
^{1}H Spectrum of **17e**



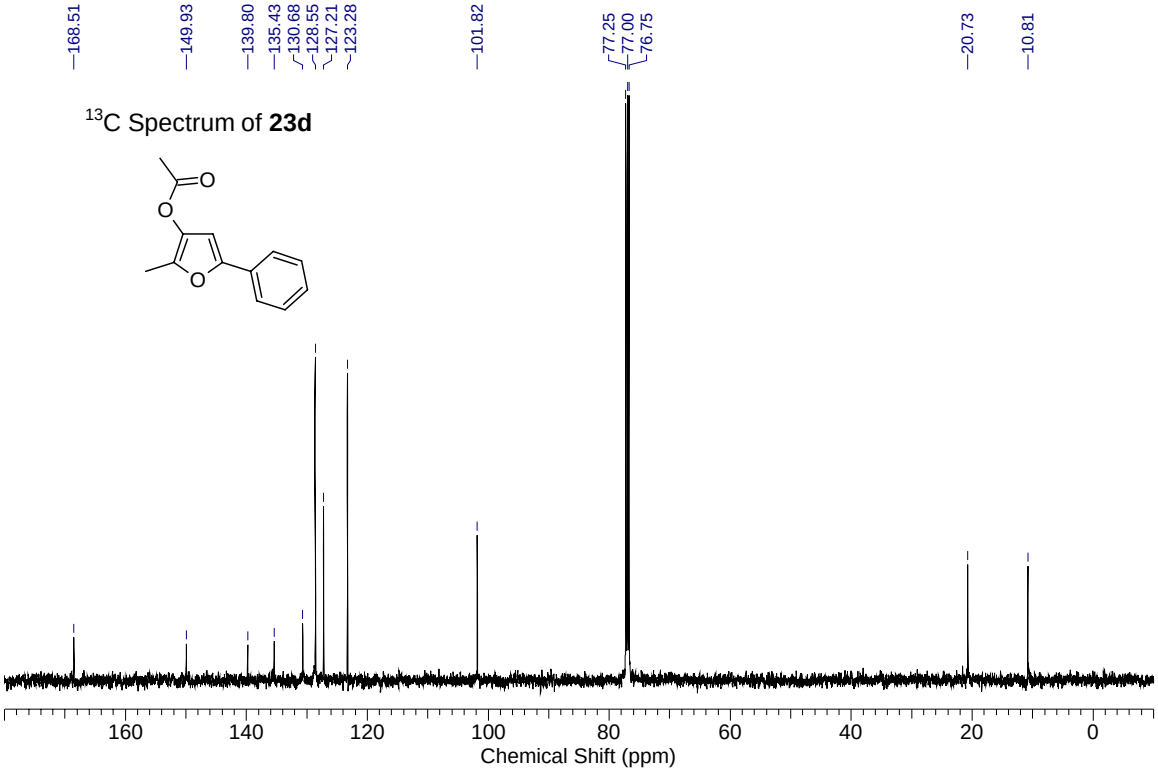
^{13}C Spectrum of **17e**


8.21
8.21
8.19
8.19
7.65
7.65
7.64
7.63
7.54
7.53
7.38
7.25
6.78
2.38
2.36
1H Spectrum of 23c
O
O
O
1.86
2.18
1.14
0.91
3.00
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

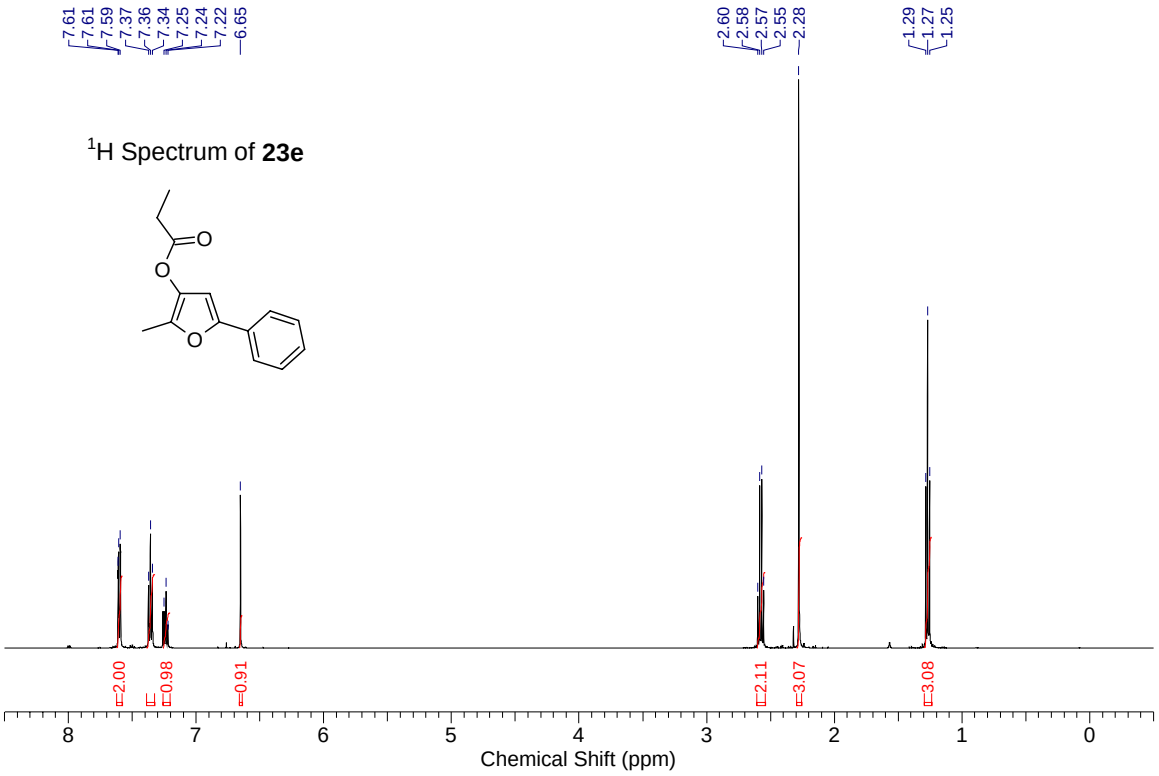

164.18
150.07
140.07
135.63
133.67
130.74
130.15
129.09
128.60
127.24
123.33
101.99
77.26
77.00
76.75
10.96
13C Spectrum of 23c
O
O
O
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



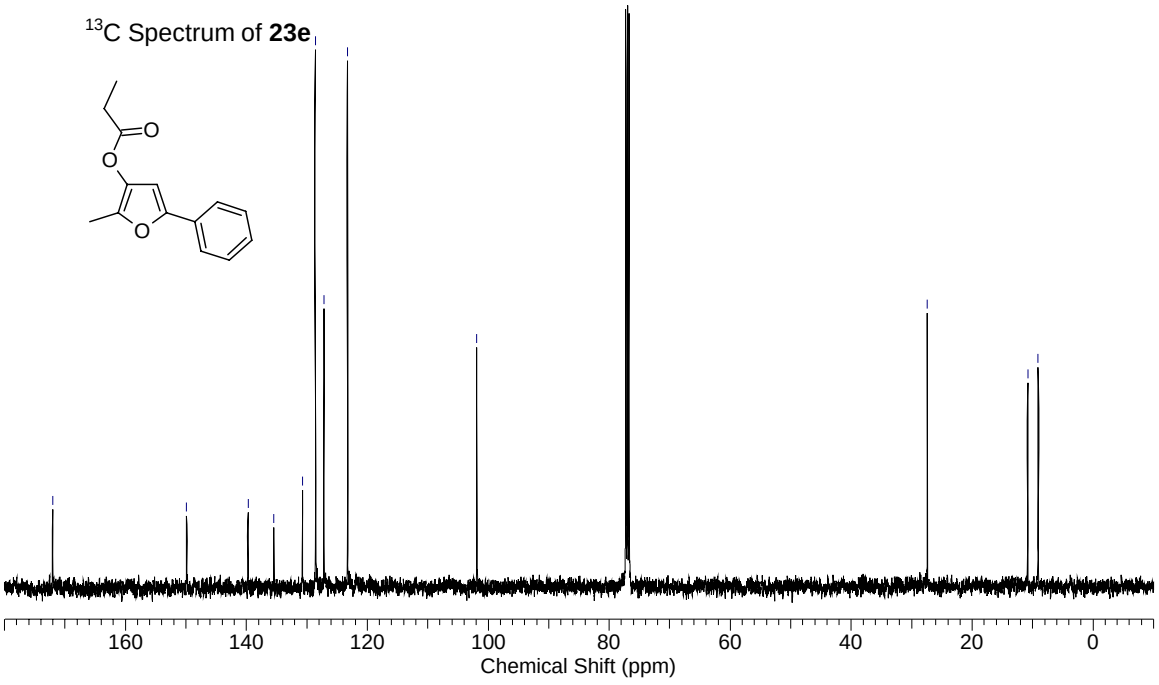
^{1}H Spectrum of **23d**



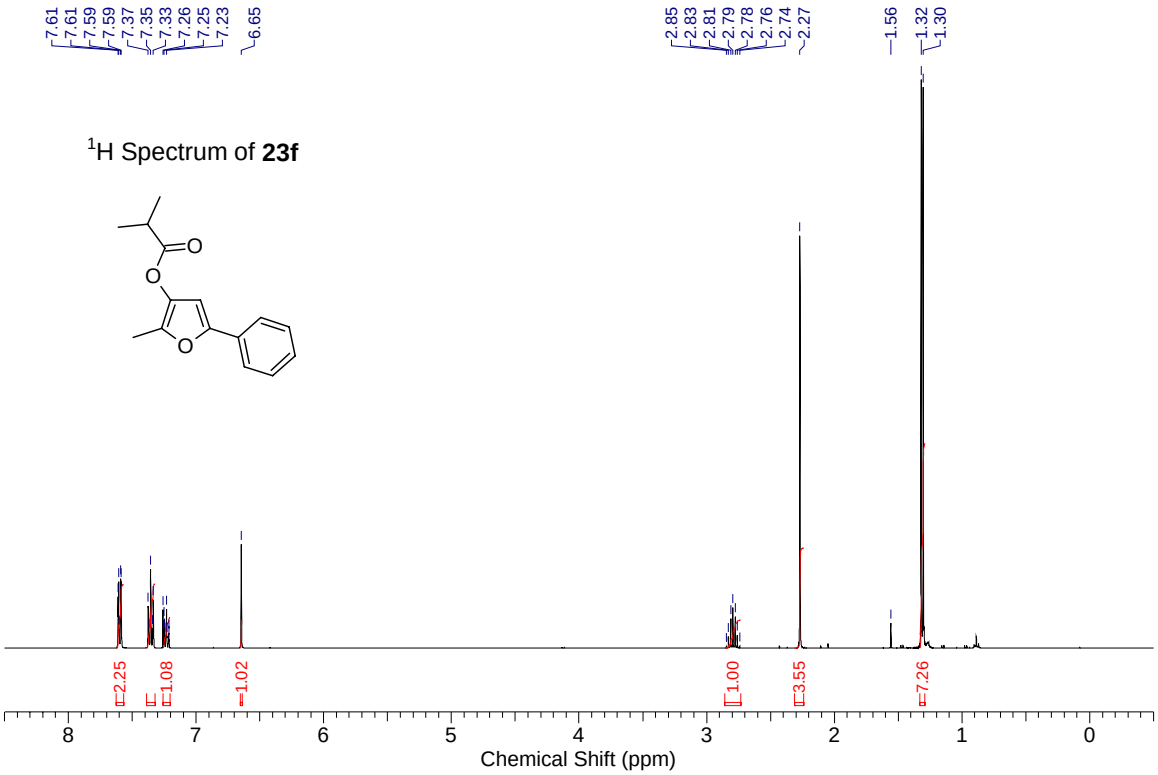
^{13}C Spectrum of **23d**



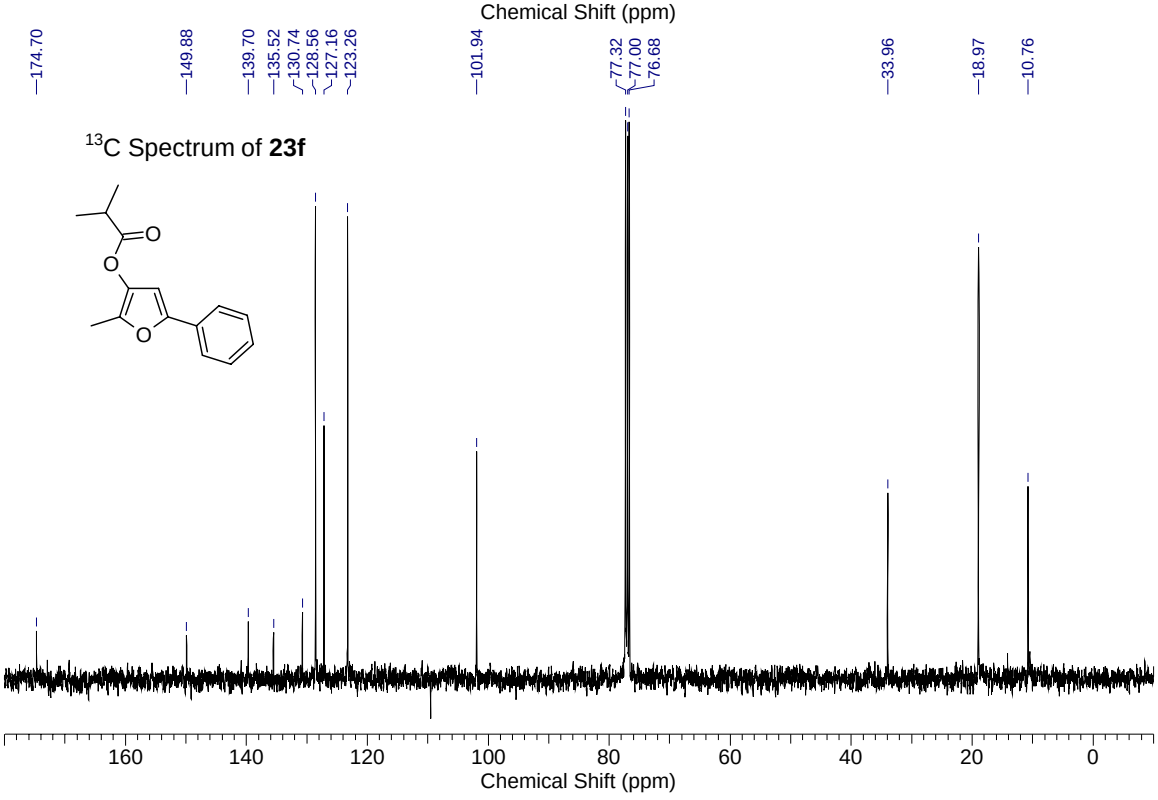
^{1}H Spectrum of **23e**



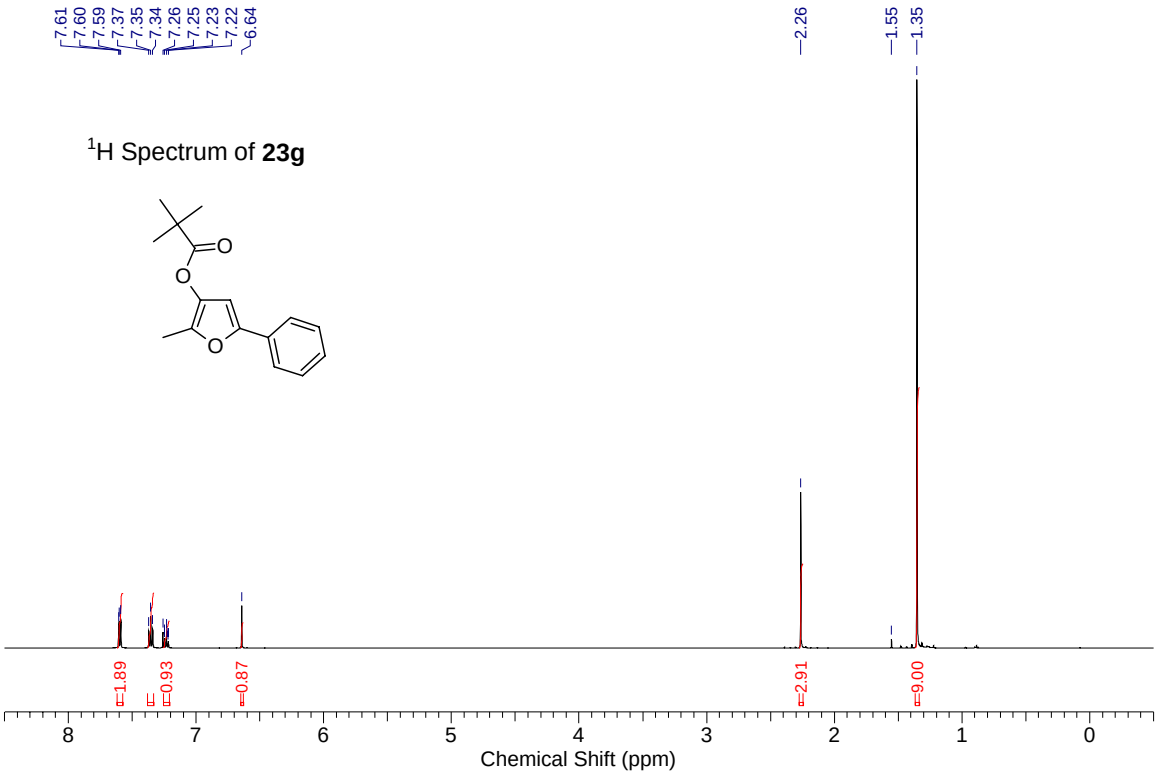
^{13}C Spectrum of **23e**



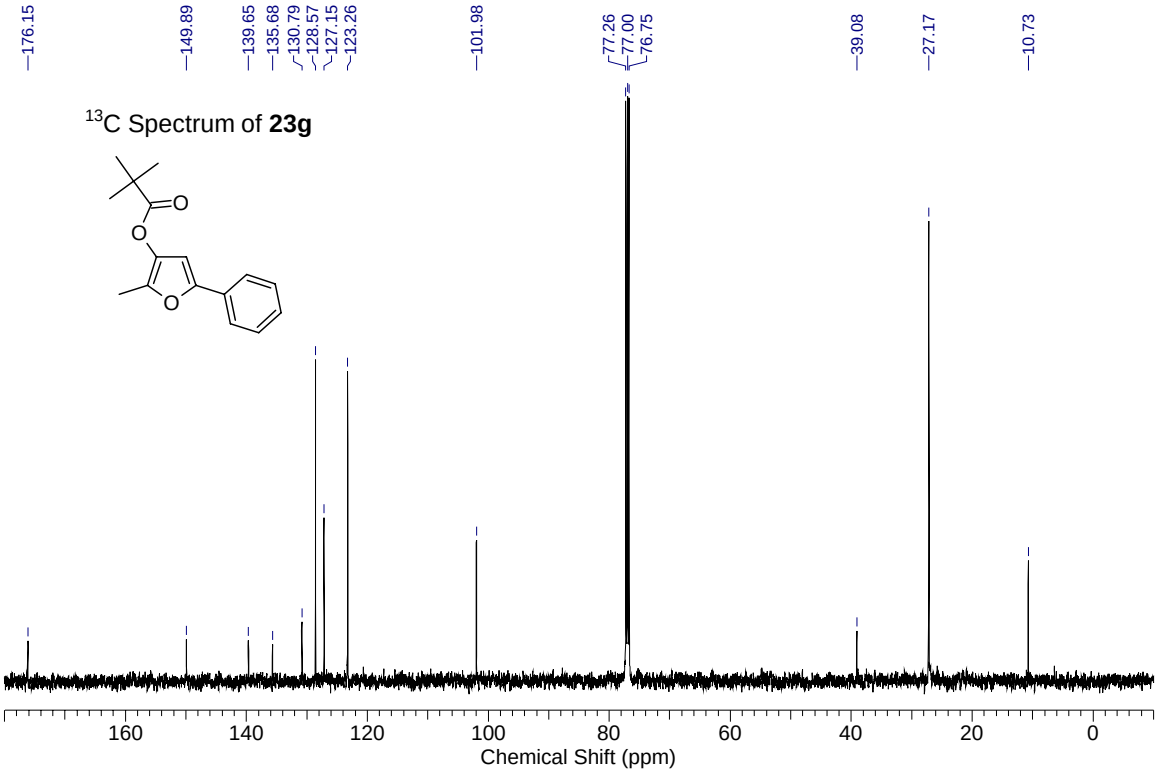
^{1}H Spectrum of **23f**



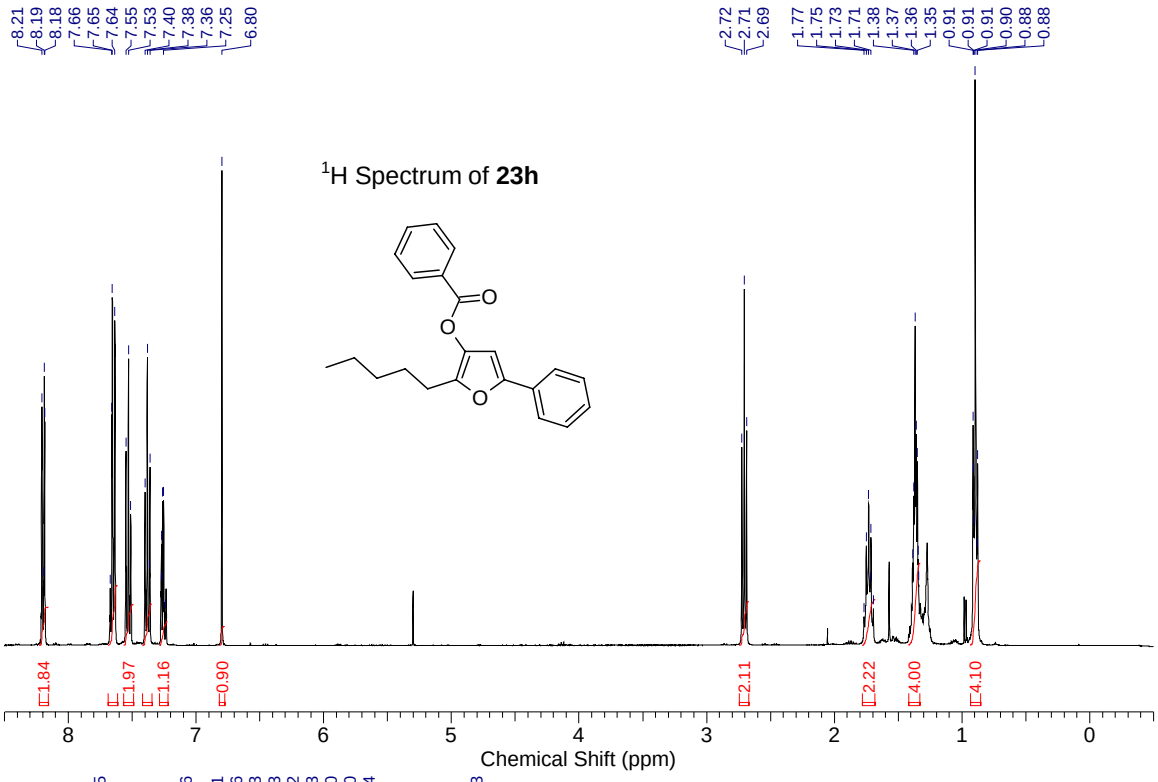
^{13}C Spectrum of **23f**

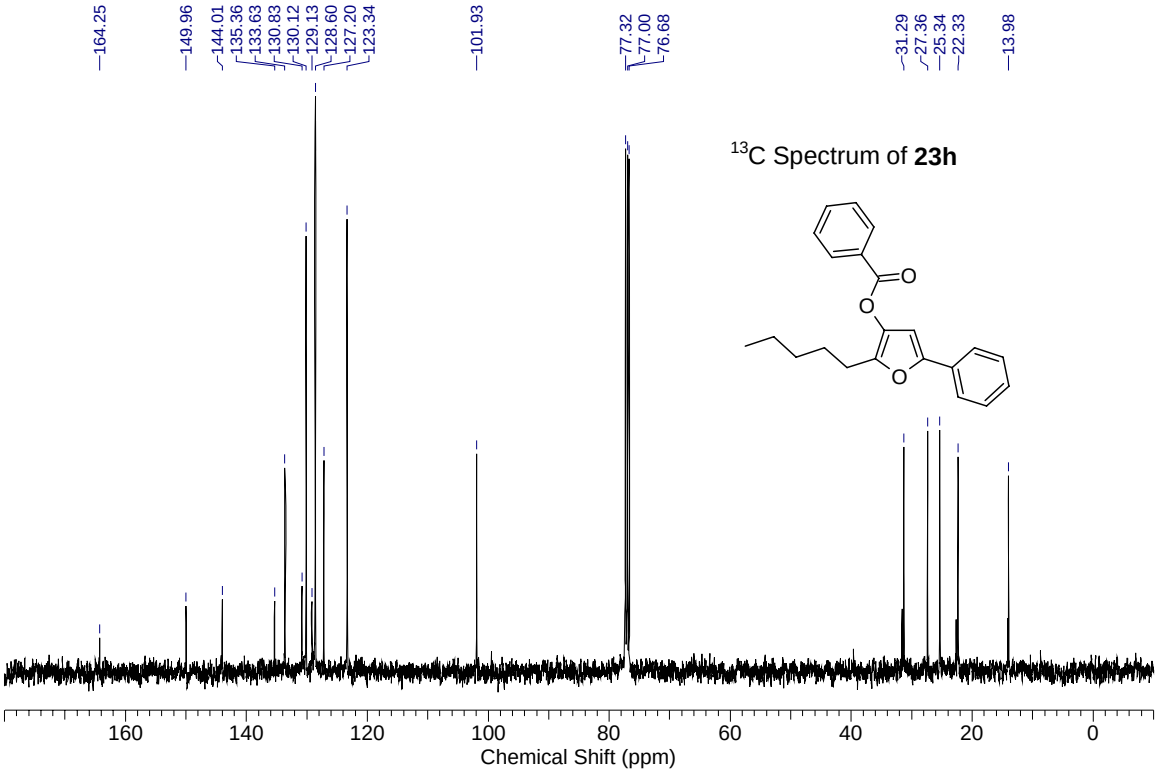


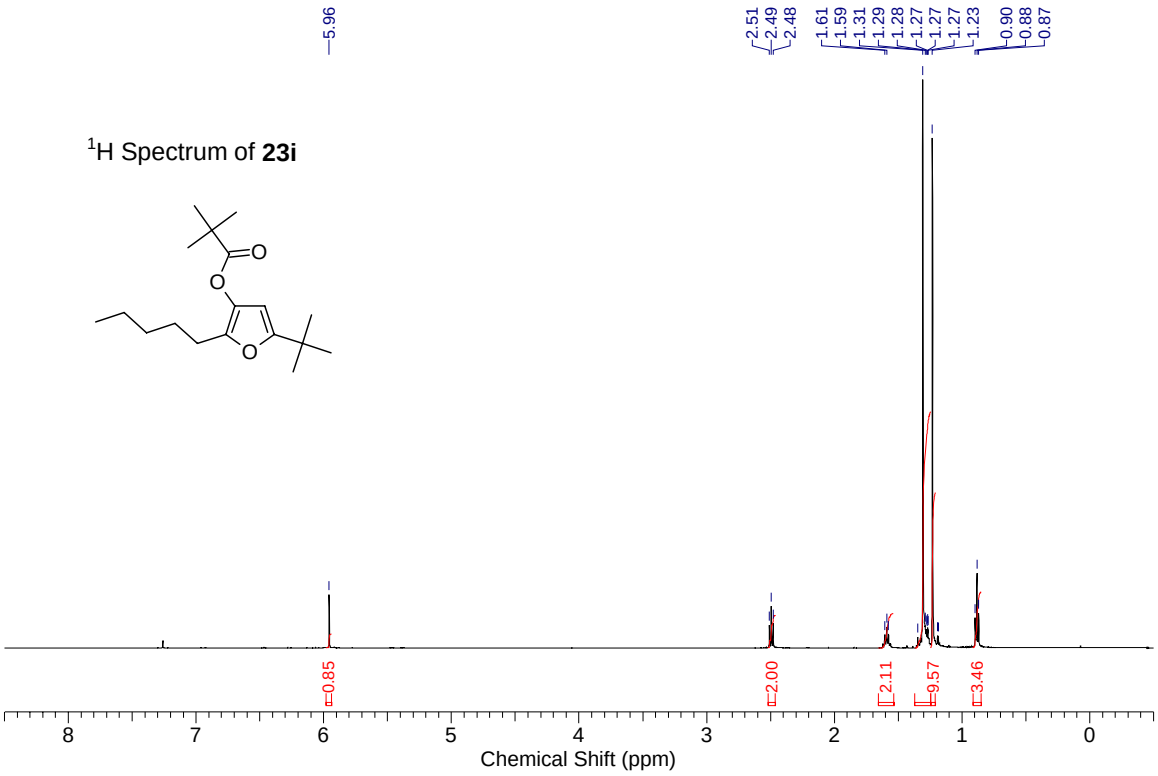
^{1}H Spectrum of **23g**



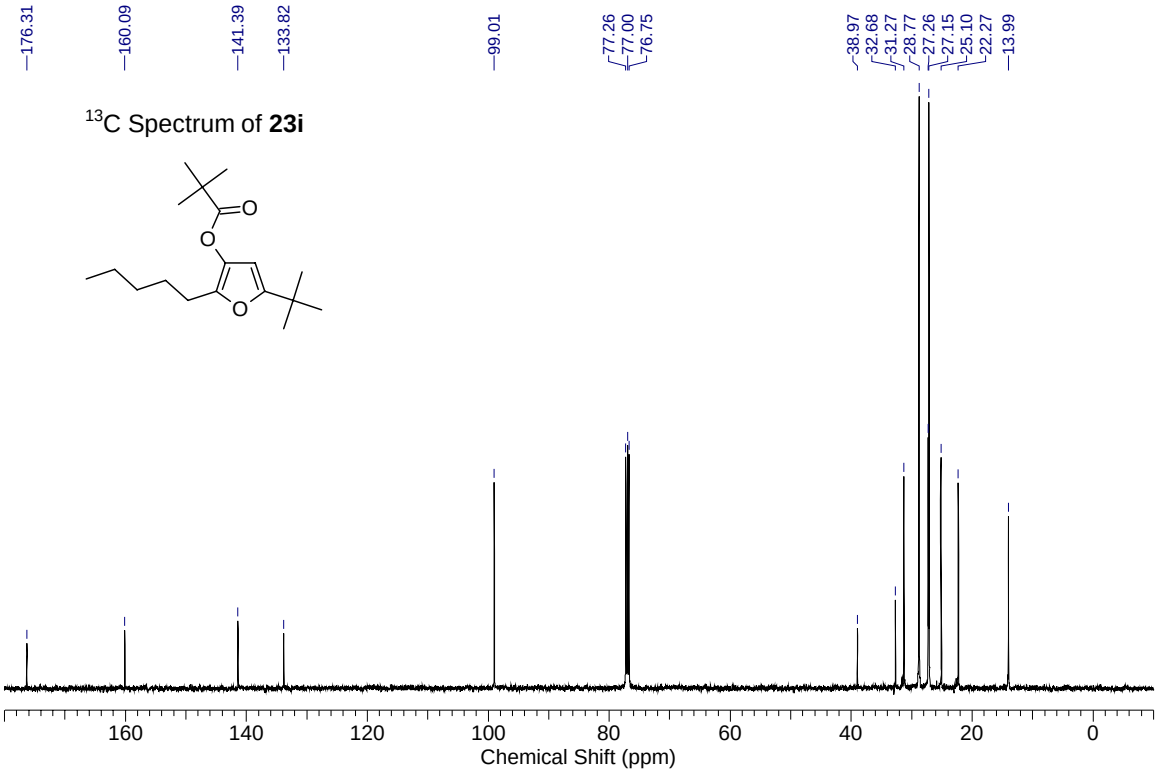
^{13}C Spectrum of **23g**


8.21
8.19
8.18
7.66
7.65
7.64
7.55
7.53
7.40
7.38
7.36
7.25
6.80
2.72
2.71
2.69
1.77
1.75
1.73
1.71
1.38
1.37
1.36
1.35
0.91
0.91
0.90
0.88
0.88
1H Spectrum of 23h
O
O
O
1.84
1.97
1.16
0.90
2.11
2.22
4.00
4.10
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

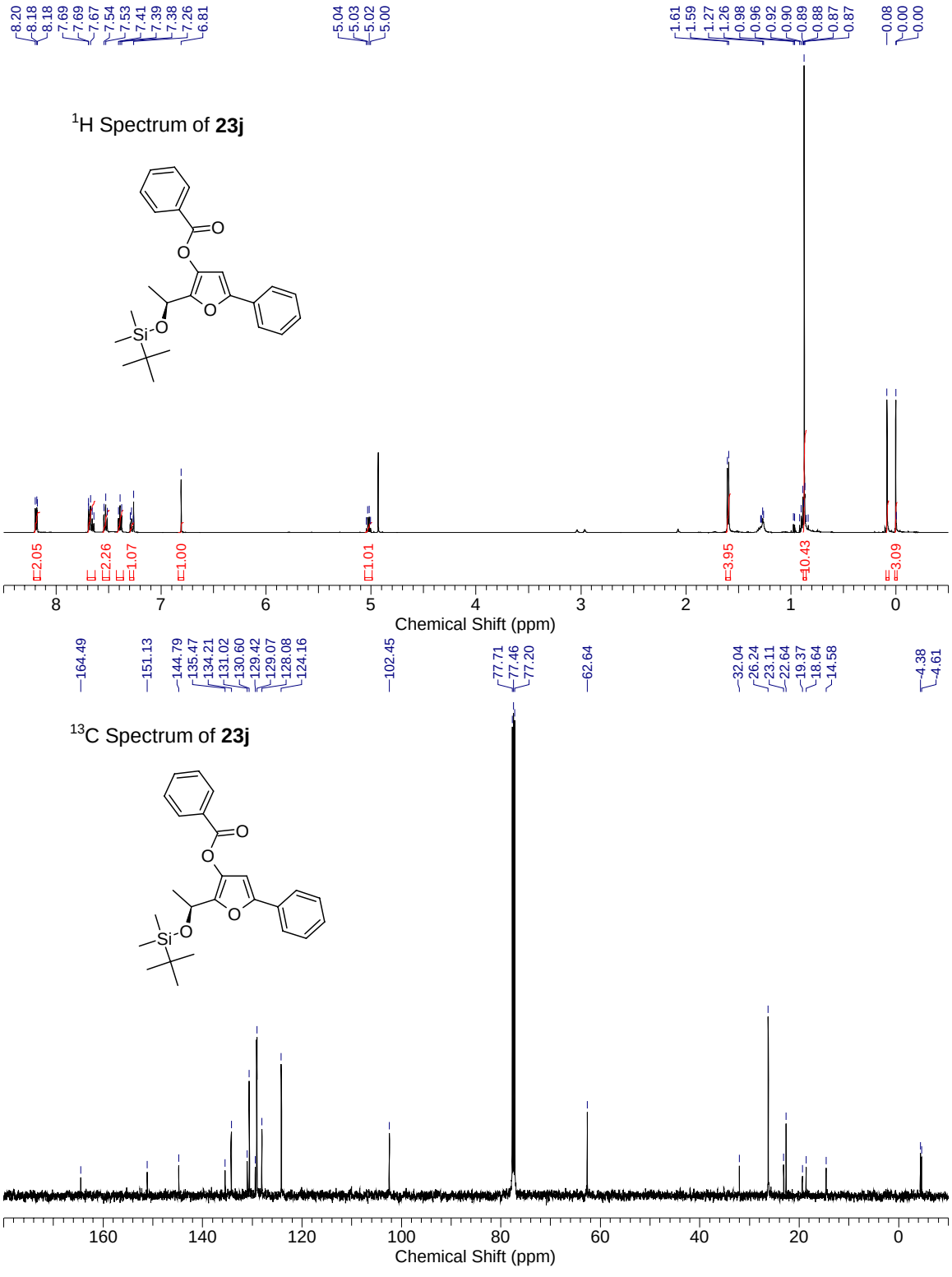

164.25
149.96
144.01
135.36
133.63
130.83
130.12
129.13
128.60
127.20
123.34
101.93
77.32
77.00
76.68
31.29
27.36
25.34
22.33
13.98
13C Spectrum of 23h
O
O
O
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

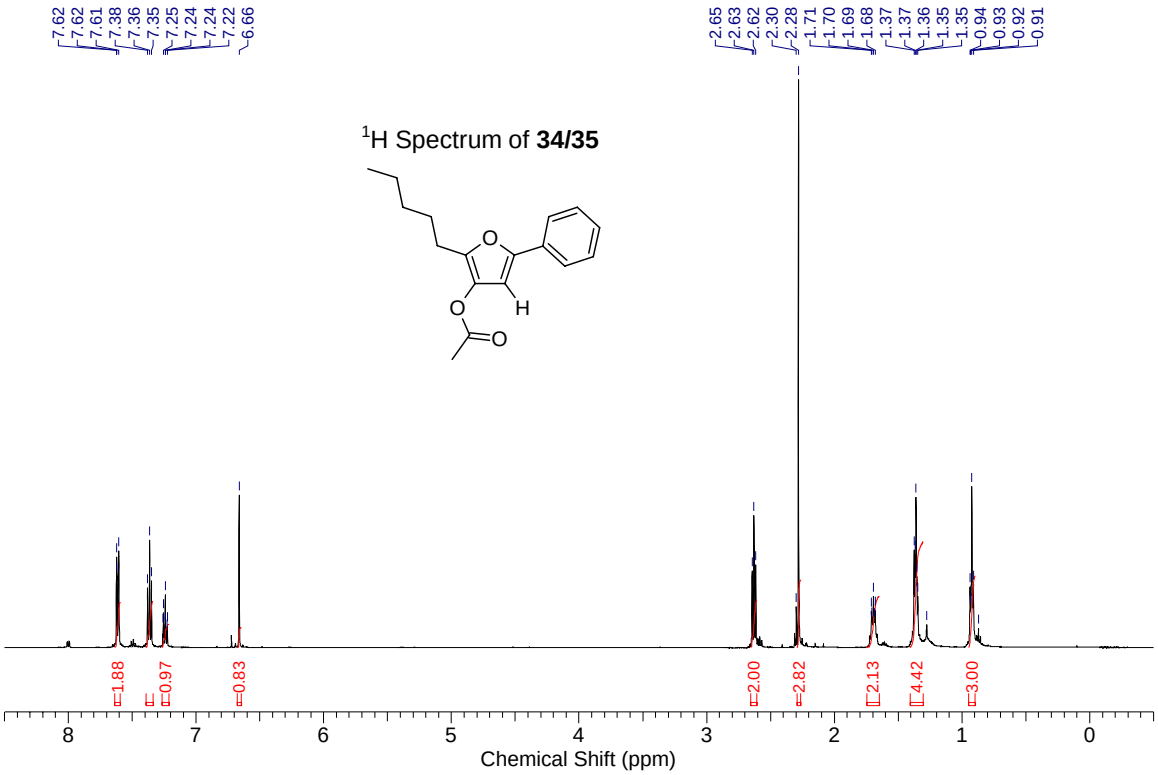


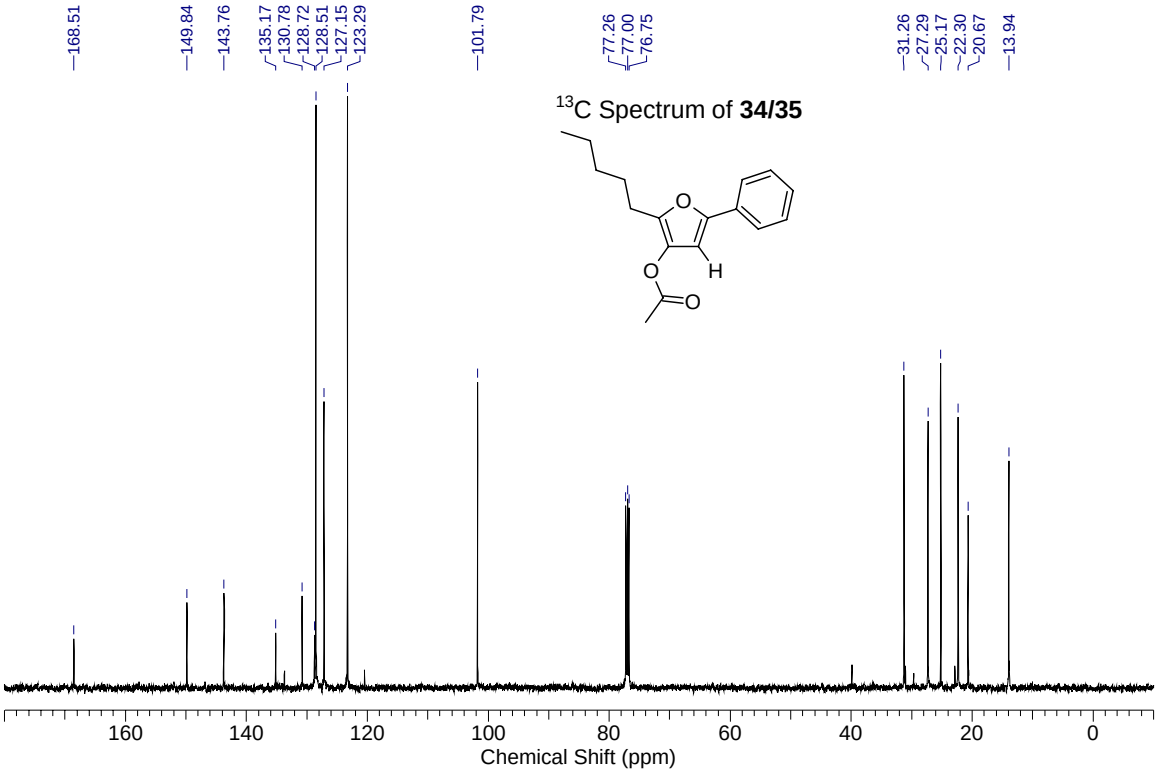
^{1}H Spectrum of **23i**

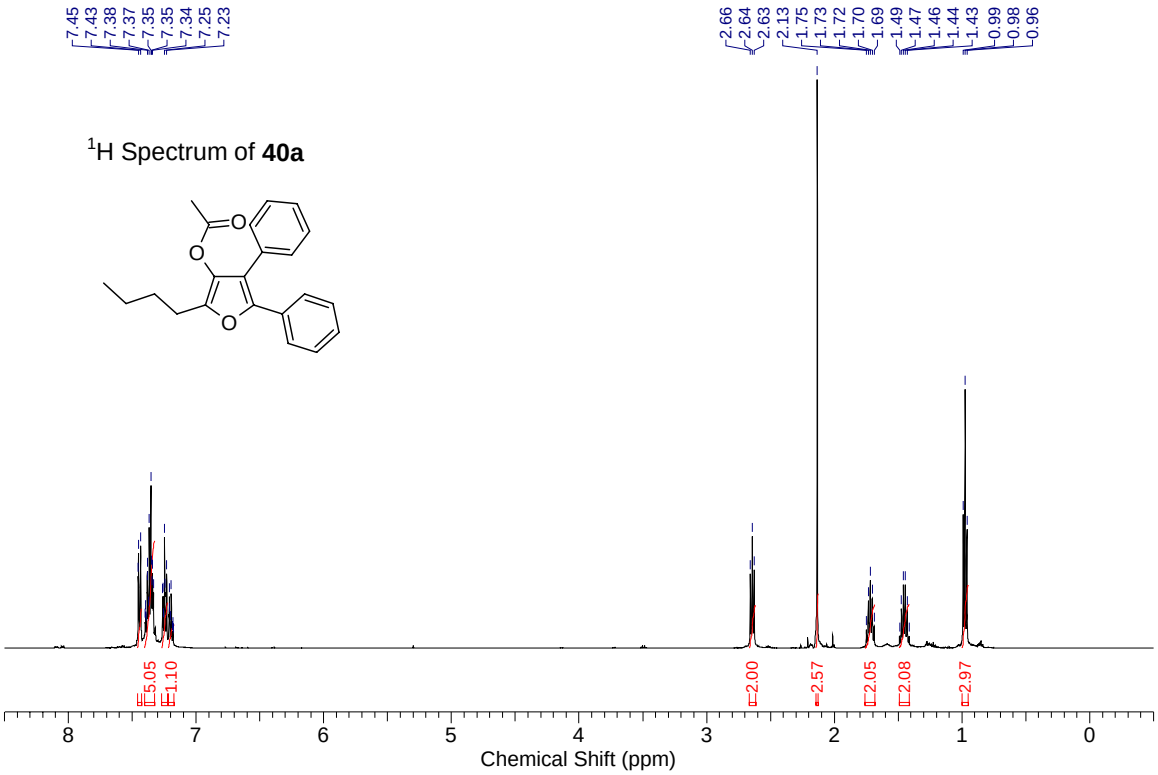


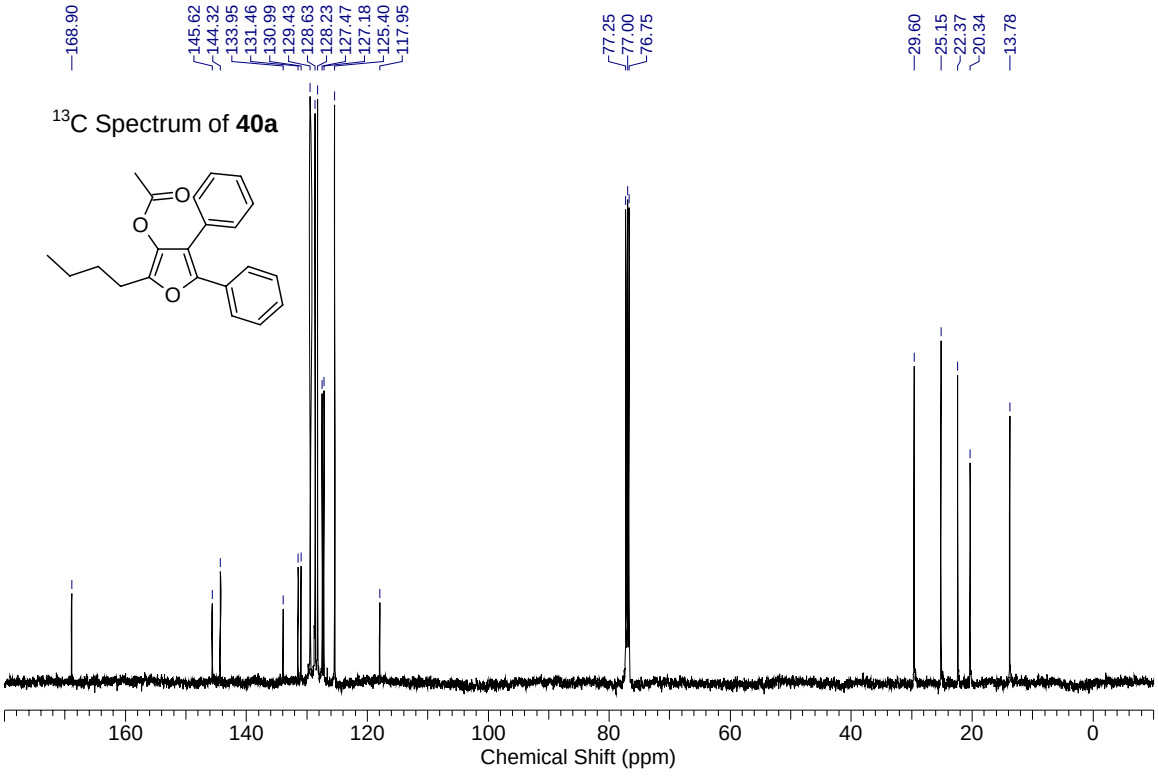
^{13}C Spectrum of **23i**

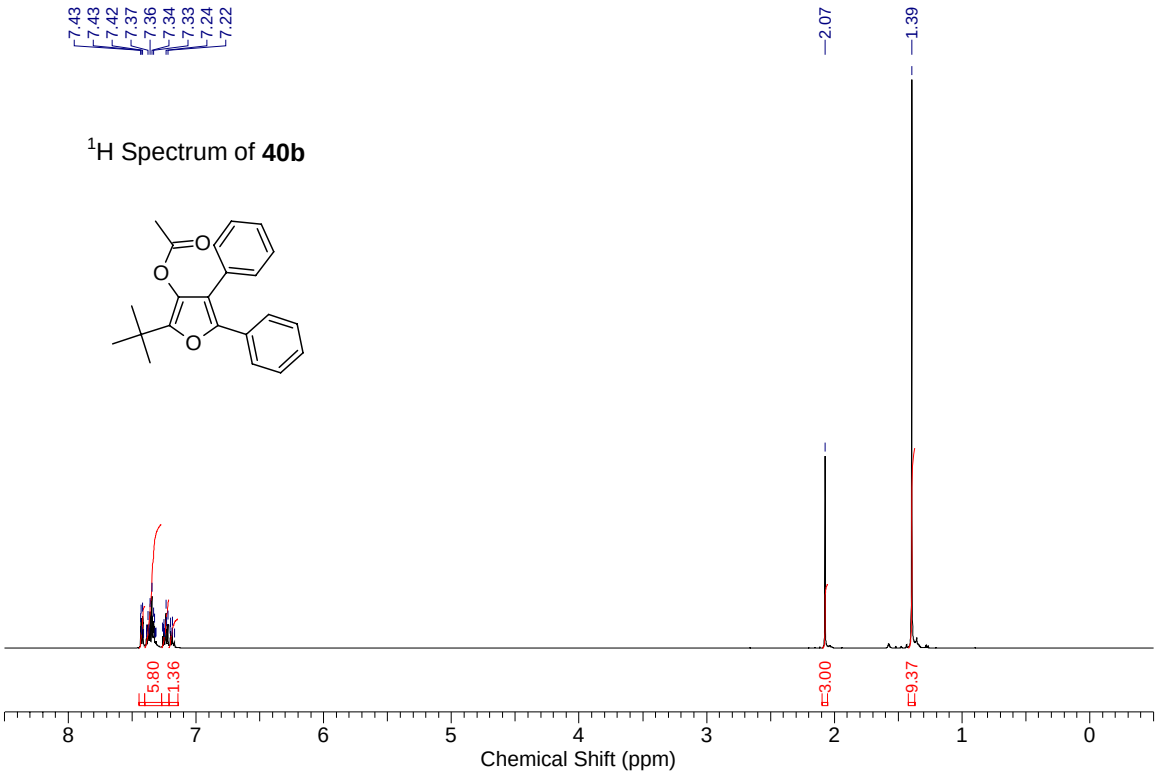

8.20
8.18
8.18
7.69
7.69
7.67
7.54
7.53
7.41
7.39
7.38
7.26
6.81
5.04
5.03
5.02
5.00
1.61
1.59
1.27
1.26
0.98
0.96
0.92
0.90
0.89
0.88
0.87
0.87
0.08
0.00
0.00
1H Spectrum of 23j
2.05
2.26
1.07
1.00
1.01
3.95
10.43
3.09
Chemical Shift (ppm)
164.49
151.13
144.79
135.47
134.21
131.02
130.60
129.42
129.07
128.08
124.16
102.45
77.71
77.46
77.20
62.64
32.04
26.24
23.11
22.64
19.37
18.64
14.58
4.38
4.61
13C Spectrum of 23j
Chemical Shift (ppm)


7.62
7.62
7.61
7.38
7.36
7.35
7.25
7.24
7.24
7.22
6.66
2.65
2.63
2.62
2.30
2.28
1.71
1.70
1.69
1.68
1.37
1.37
1.36
1.35
1.35
0.94
0.93
0.92
0.91
1H Spectrum of 34/35
O
O
H
O
1.88
0.97
0.83
2.00
2.82
2.13
4.42
3.00
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

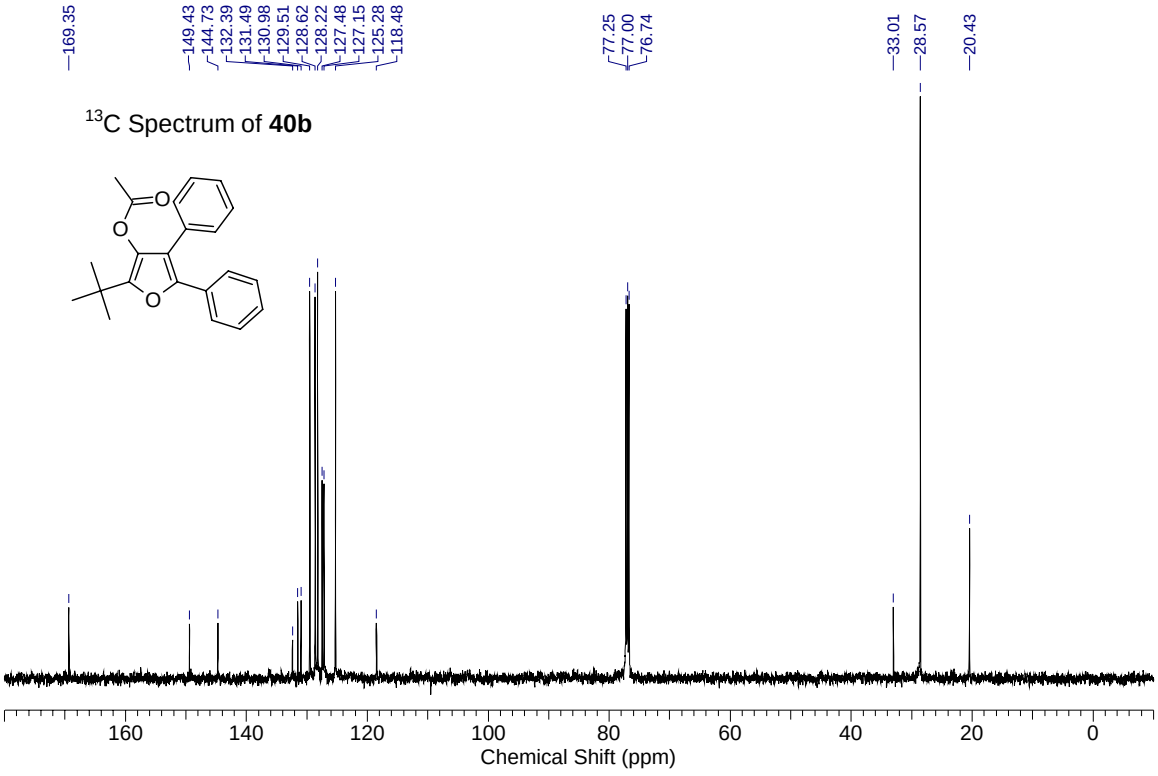

168.51
149.84
143.76
135.17
130.78
128.72
128.51
127.15
123.29
101.79
77.26
77.00
76.75
31.26
27.29
25.17
22.30
20.67
13.94
13C Spectrum of 34/35
O
O
H
O
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.45
7.43
7.38
7.37
7.35
7.35
7.34
7.25
7.23
2.66
2.64
2.63
2.13
1.75
1.73
1.72
1.70
1.69
1.49
1.47
1.46
1.44
1.43
0.99
0.98
0.96
1H Spectrum of 40a
O
O
O
5.05
1.10
2.00
2.57
2.05
2.08
2.97
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

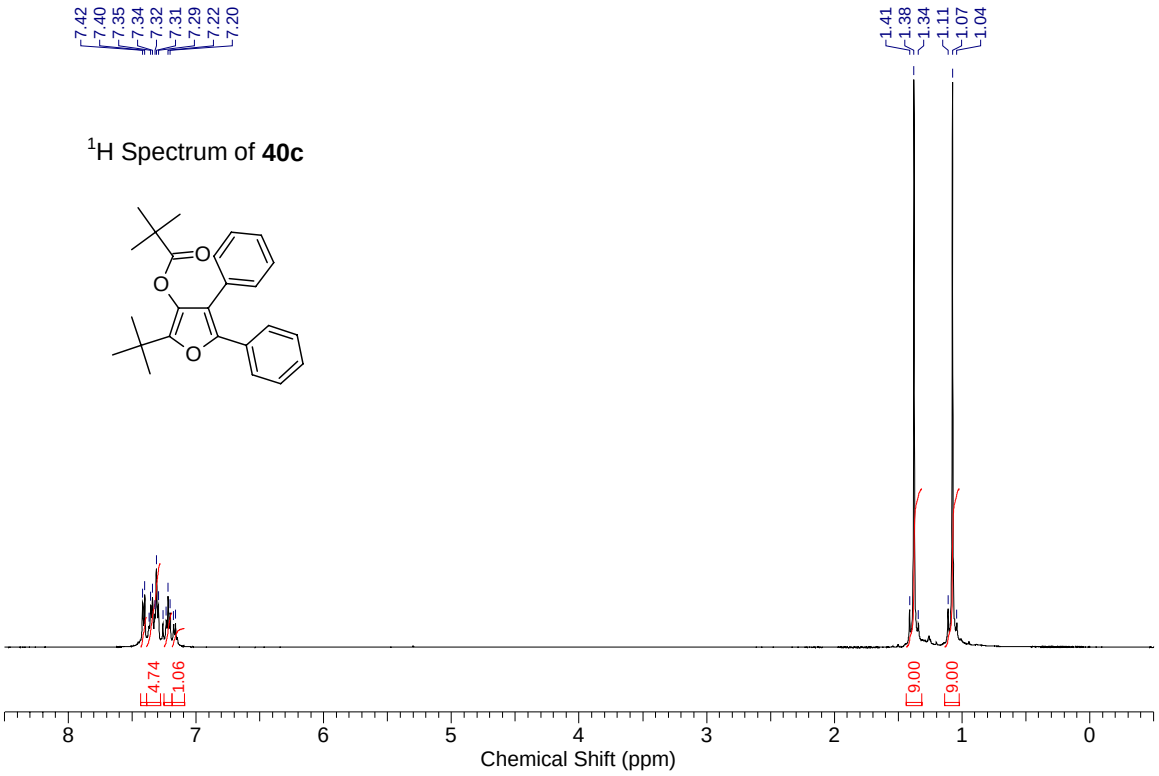

168.90
145.62
144.32
133.95
131.46
130.99
129.43
128.63
128.23
127.47
127.18
125.40
117.95
77.25
77.00
76.75
29.60
25.15
22.37
20.34
13.78
13C Spectrum of 40a
O
O
O
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

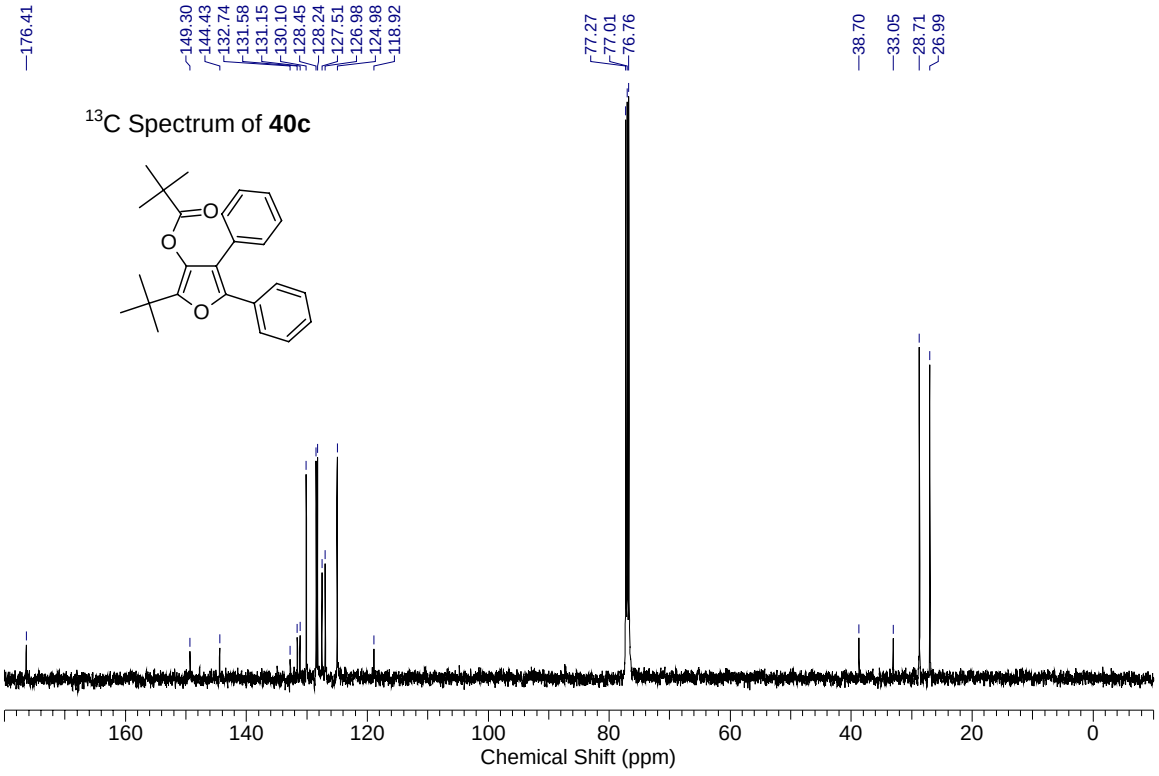


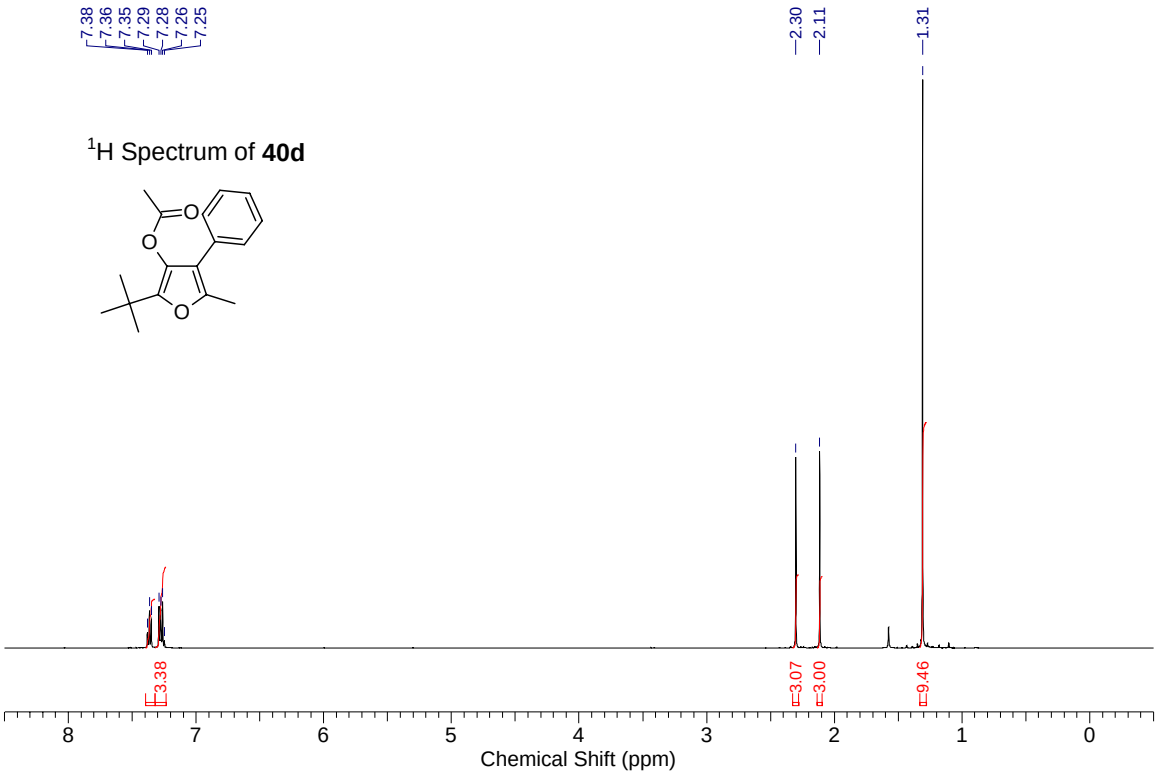
^{1}H Spectrum of **40b**



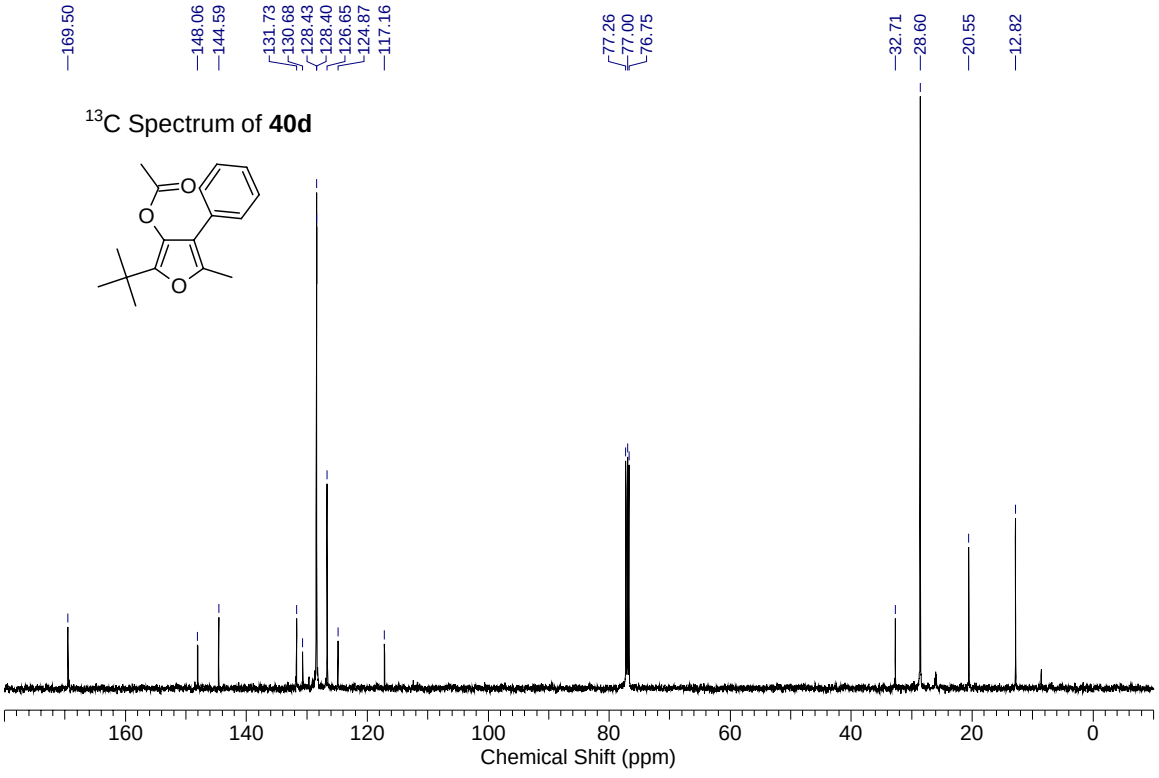
^{13}C Spectrum of **40b**


7.42
7.40
7.35
7.34
7.32
7.31
7.29
7.22
7.20
1.41
1.38
1.34
1.11
1.07
1.04
^{1}H Spectrum of **40c**
4.74
1.06
9.00
9.00
Chemical Shift (ppm)


176.41
149.30
144.43
132.74
131.58
131.15
130.10
128.45
128.24
127.51
126.98
124.98
118.92
77.27
77.01
76.76
38.70
33.05
28.71
26.99
^{13}C Spectrum of **40c**
Chemical Shift (ppm)

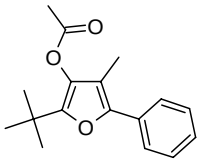


^{1}H Spectrum of **40d**

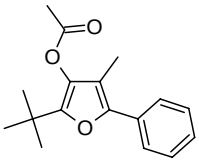


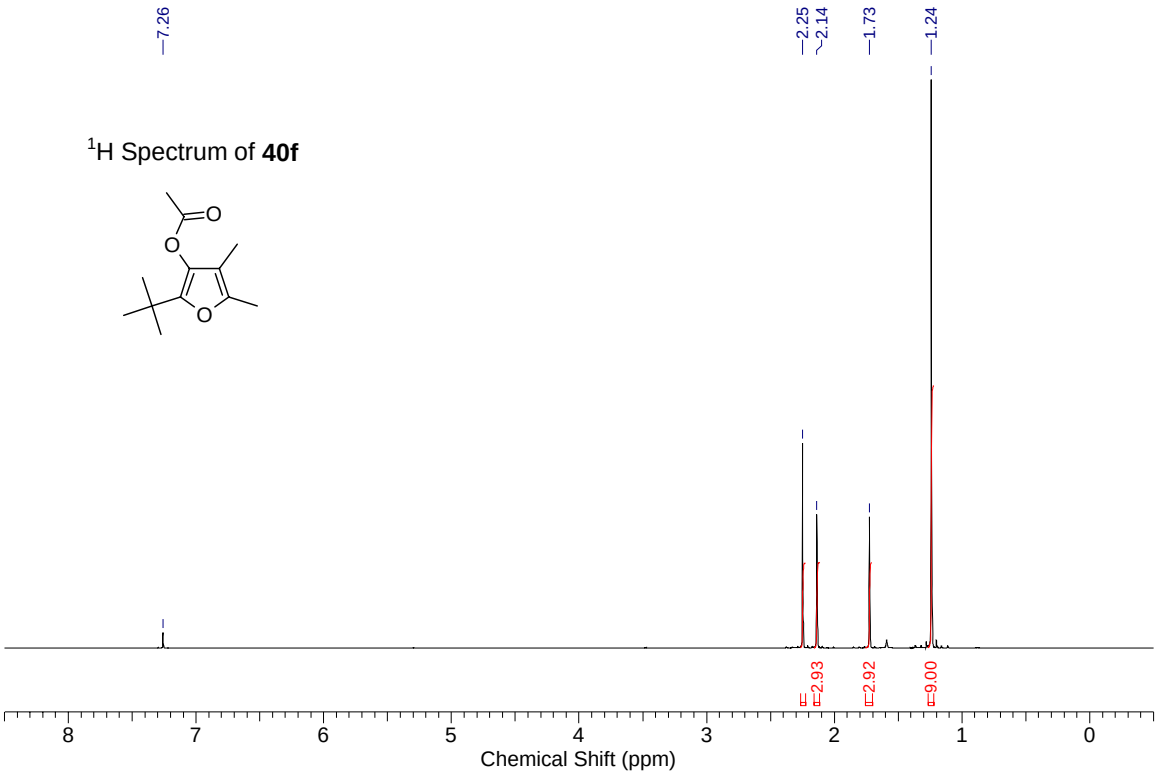
^{13}C Spectrum of **40d**

^{1}H Spectrum of **40e**

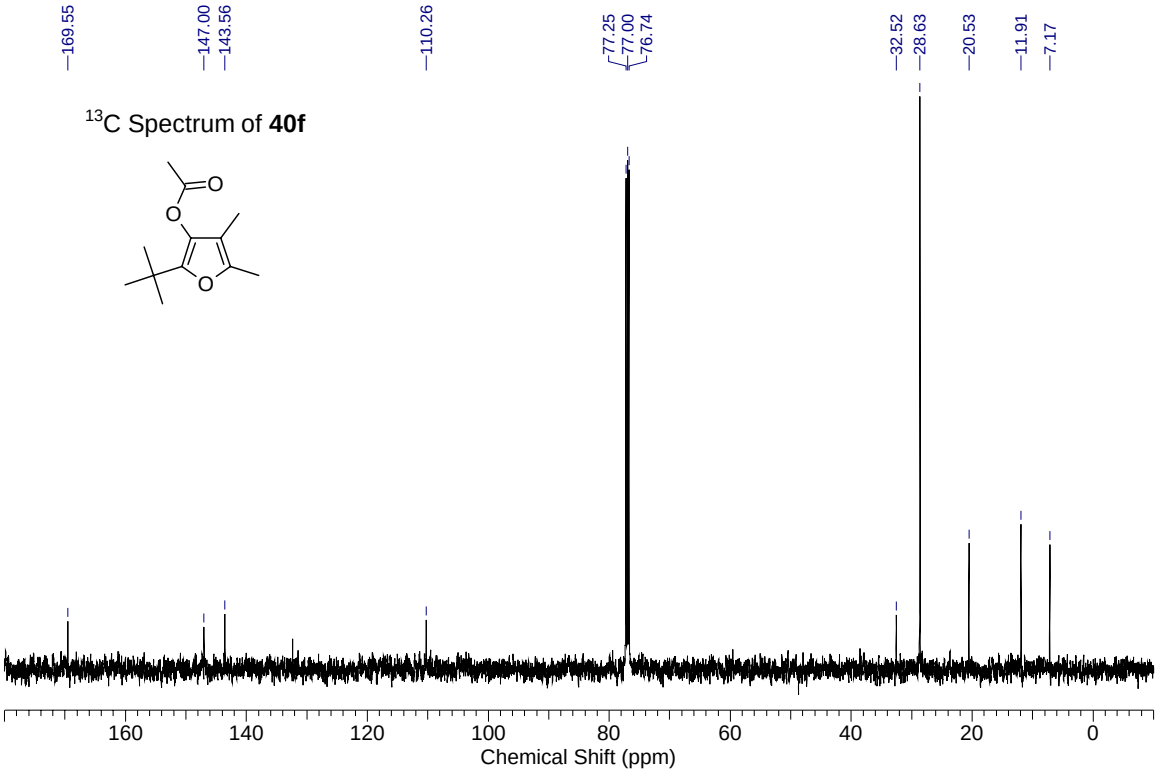


^{13}C Spectrum of **40e**



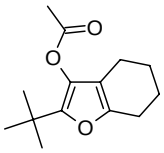


^{1}H Spectrum of **40f**

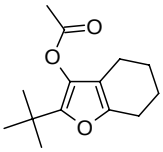


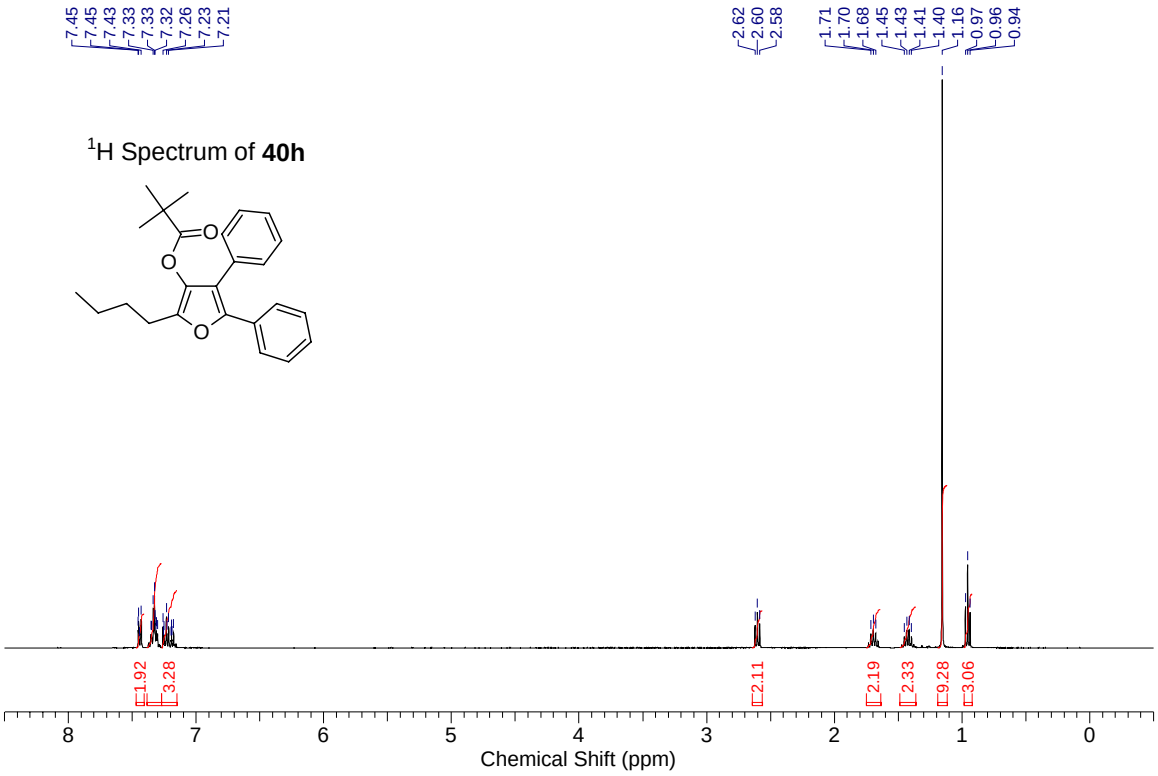
^{13}C Spectrum of **40f**

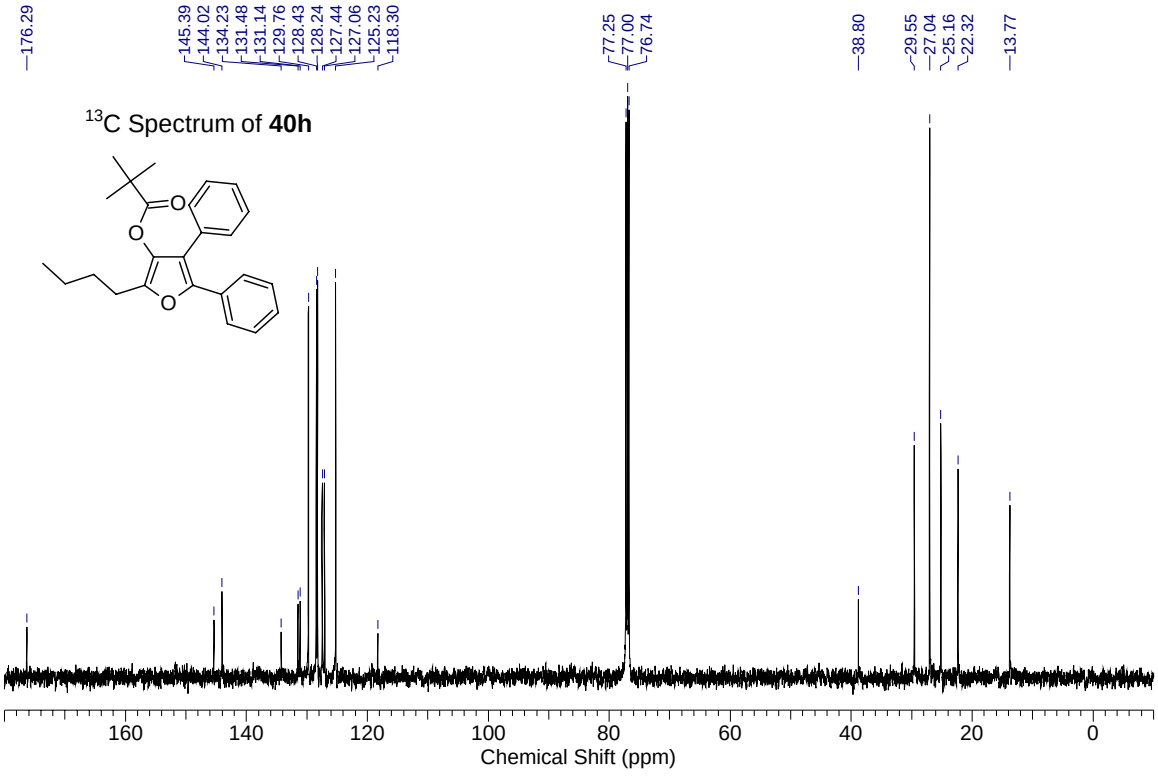
^{1}H Spectrum of **40g**

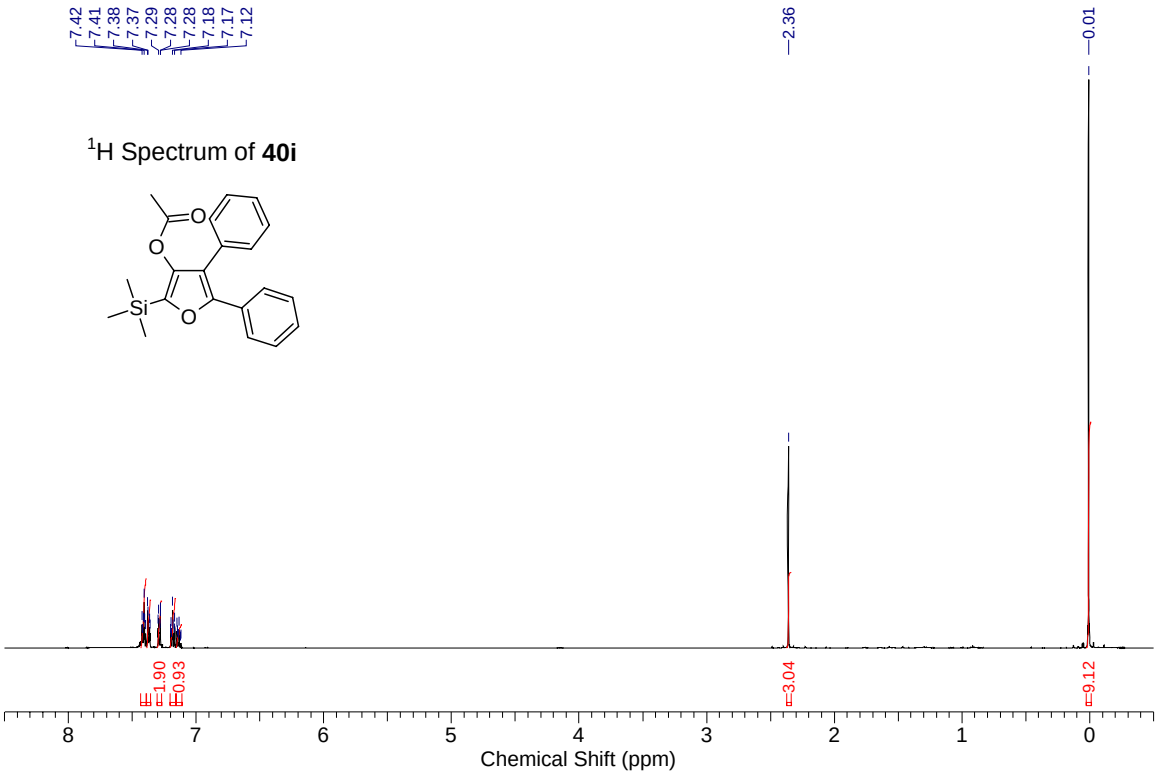


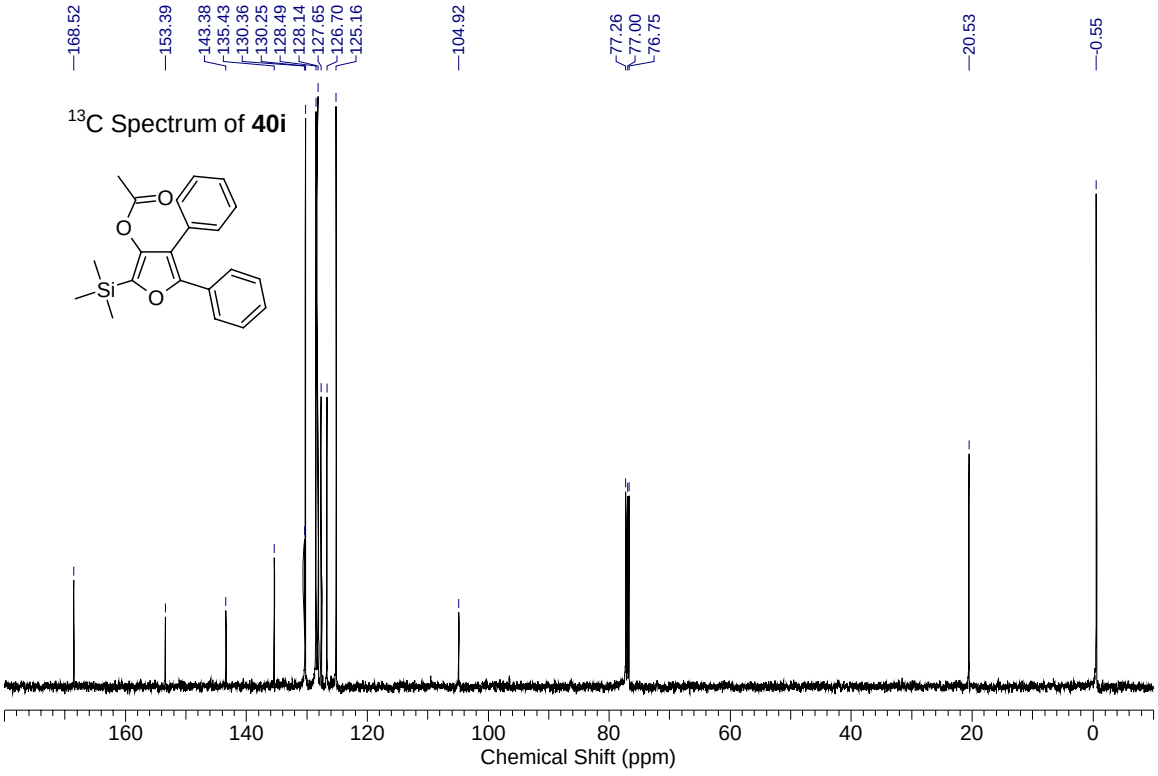
^{13}C Spectrum of **40g**

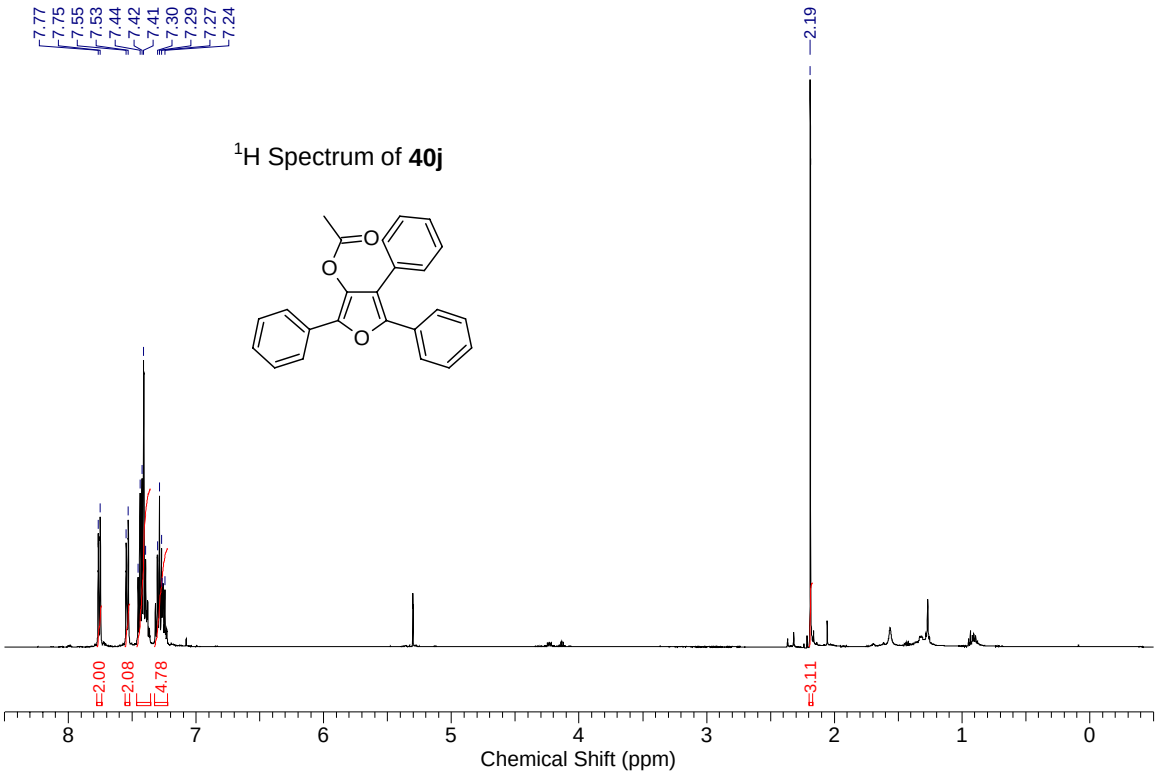


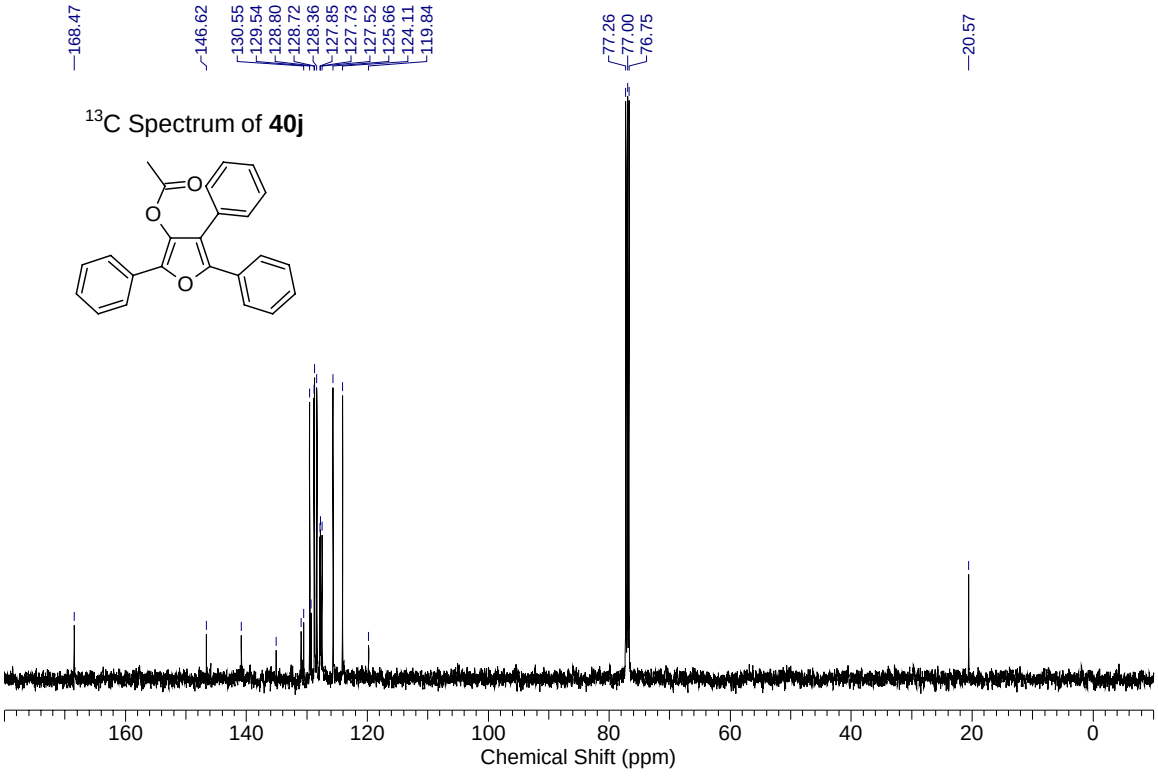

7.45
7.45
7.43
7.33
7.33
7.32
7.26
7.23
7.21
2.62
2.60
2.58
1.71
1.70
1.68
1.45
1.43
1.41
1.40
1.16
0.97
0.96
0.94
1H Spectrum of 40h
O
O
O
1.92
3.28
2.11
2.19
2.33
9.28
3.06
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

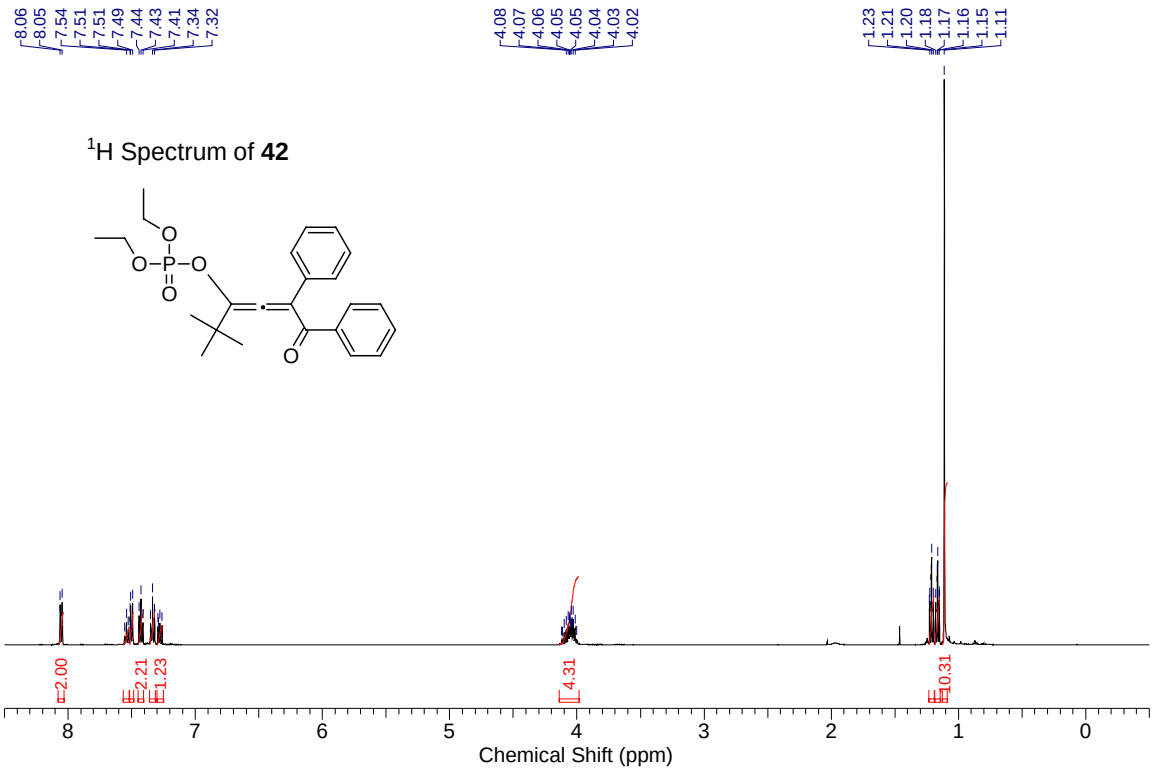

176.29
145.39
144.02
134.23
131.48
131.14
129.76
128.43
128.24
127.44
127.06
125.23
118.30
77.25
77.00
76.74
38.80
29.55
27.04
25.16
22.32
13.77
13C Spectrum of 40h
O
O
O
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

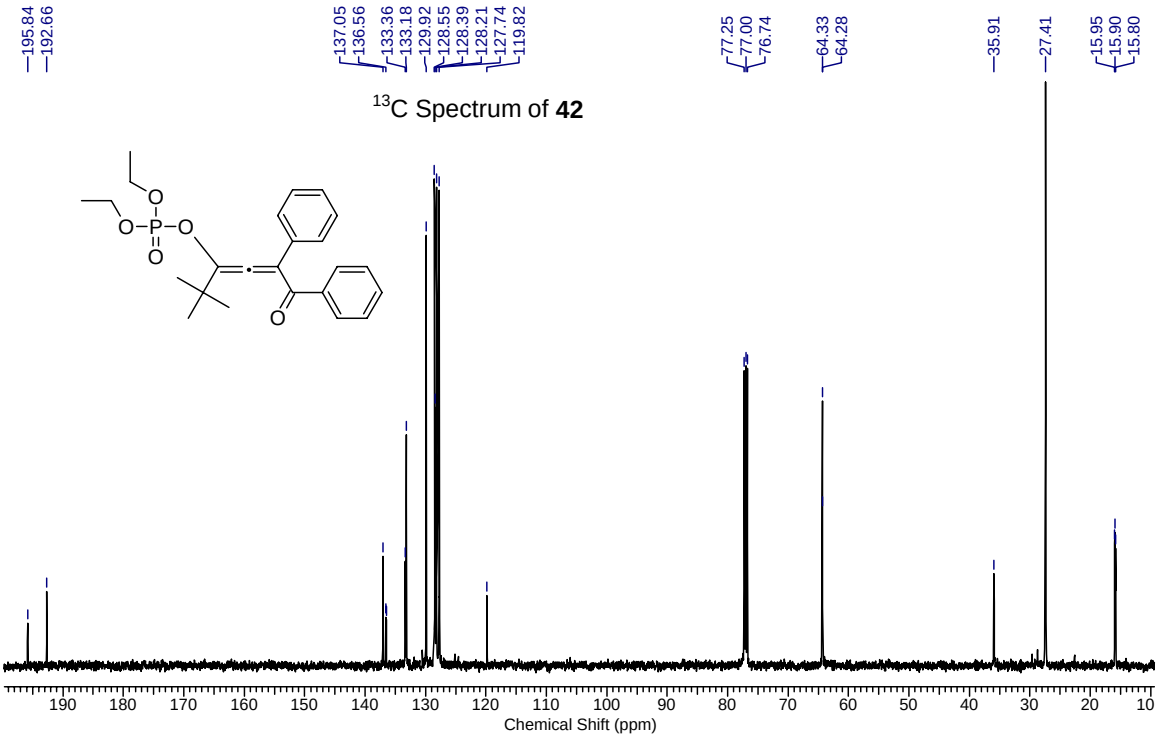

7.42
7.41
7.38
7.37
7.29
7.28
7.28
7.18
7.17
7.12
2.36
0.01
^{1}H Spectrum of **40i**
1.90
0.93
3.04
9.12
Chemical Shift (ppm)

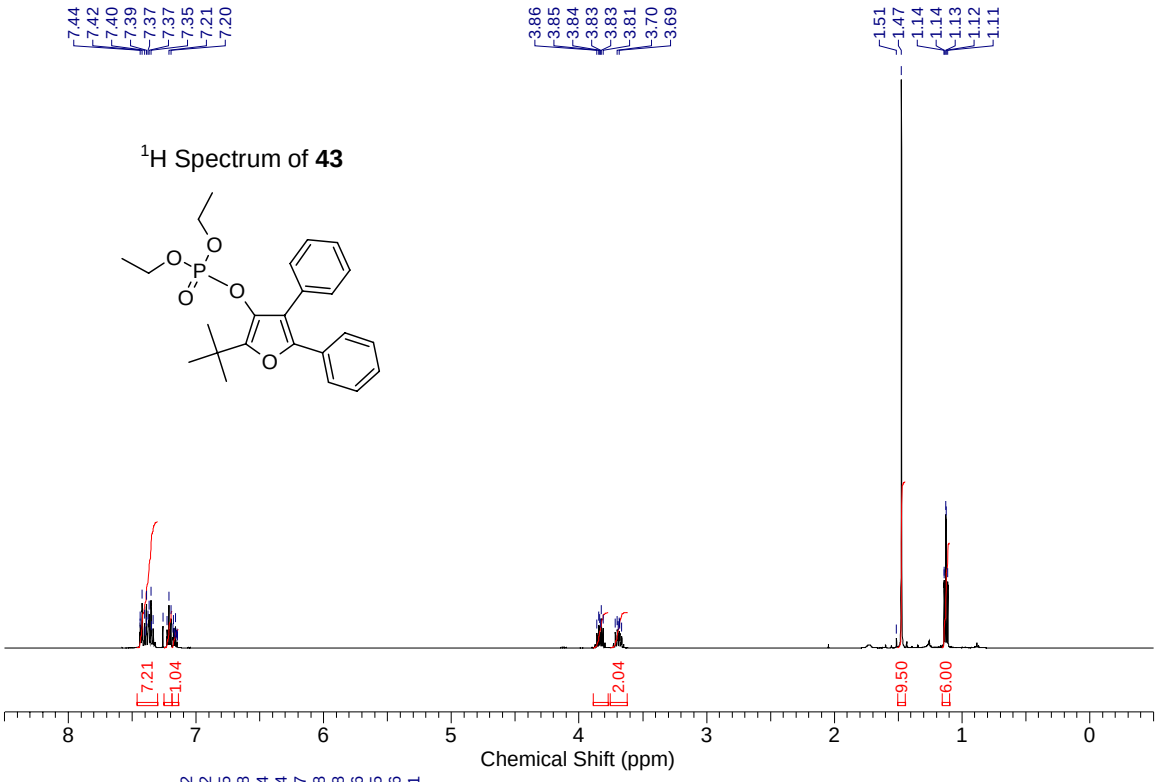

168.52
153.39
143.38
135.43
130.36
130.25
128.49
128.14
127.65
126.70
125.16
104.92
77.26
77.00
76.75
20.53
0.55
^{13}C Spectrum of **40i**
Chemical Shift (ppm)


7.77
7.75
7.55
7.53
7.44
7.42
7.41
7.30
7.29
7.27
7.24
2.19
^{1}H Spectrum of **40j**
2.00
2.08
4.78
3.11
Chemical Shift (ppm)

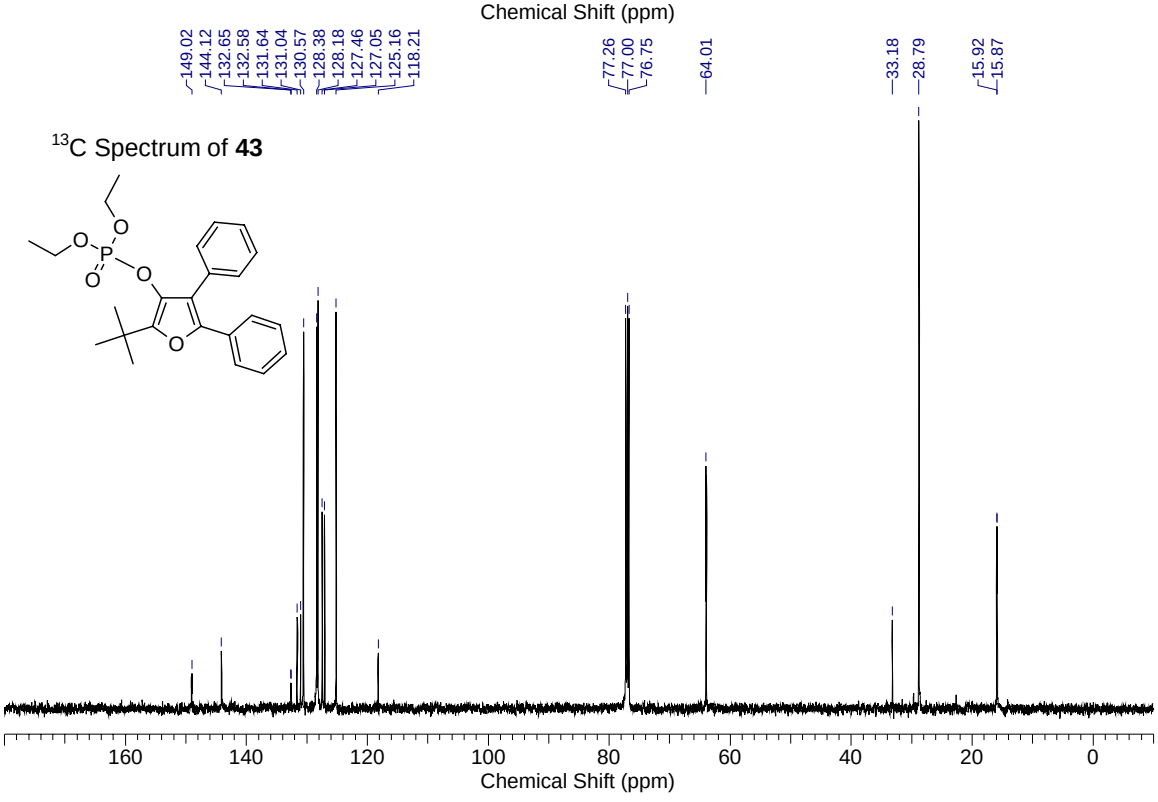

168.47
146.62
130.55
129.54
128.80
128.72
128.36
127.85
127.73
127.52
125.66
124.11
119.84
77.26
77.00
76.75
20.57
^{13}C Spectrum of **40j**
Chemical Shift (ppm)


8.06
8.05
7.54
7.51
7.51
7.49
7.44
7.43
7.41
7.34
7.32
4.08
4.07
4.06
4.05
4.05
4.04
4.03
4.02
1.23
1.21
1.20
1.18
1.17
1.16
1.15
1.11
1H Spectrum of 42
2.00
2.21
1.23
4.31
10.31
Chemical Shift (ppm)

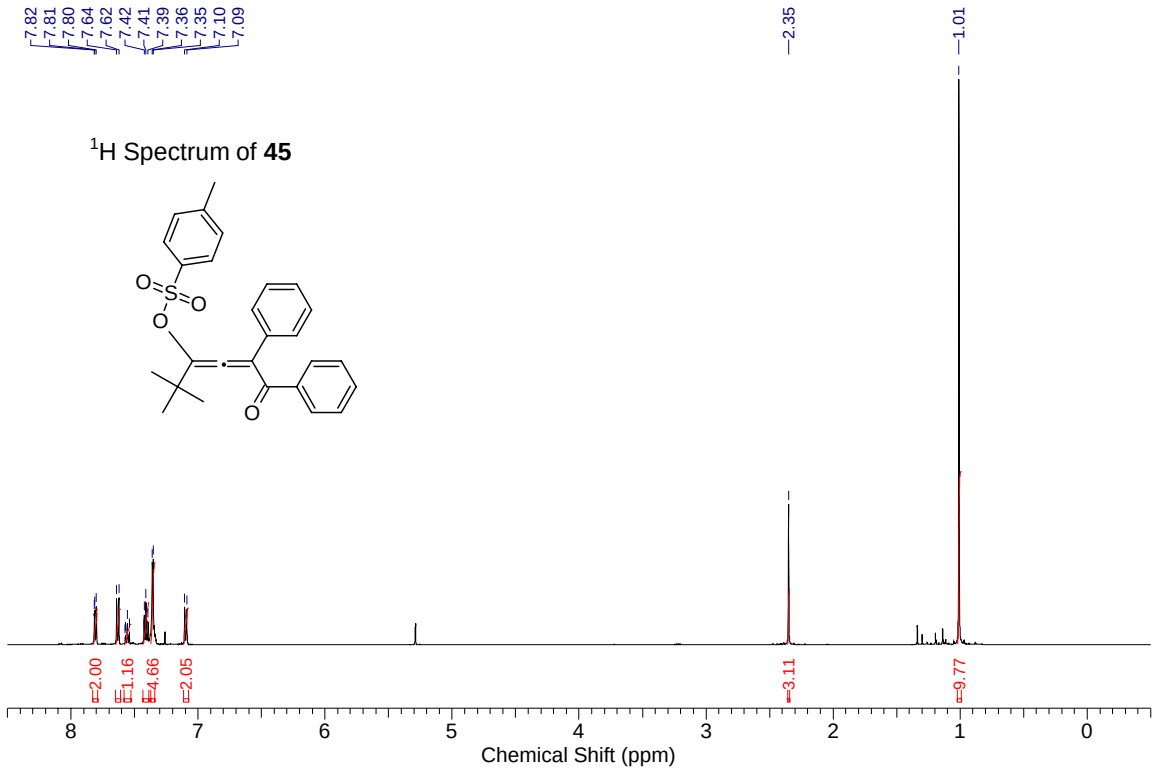

195.84
192.66
137.05
136.56
133.36
133.18
129.92
128.55
128.39
128.21
127.74
119.82
77.25
77.00
76.74
64.33
64.28
35.91
27.41
15.95
15.90
15.80
13C Spectrum of 42
Chemical Shift (ppm)

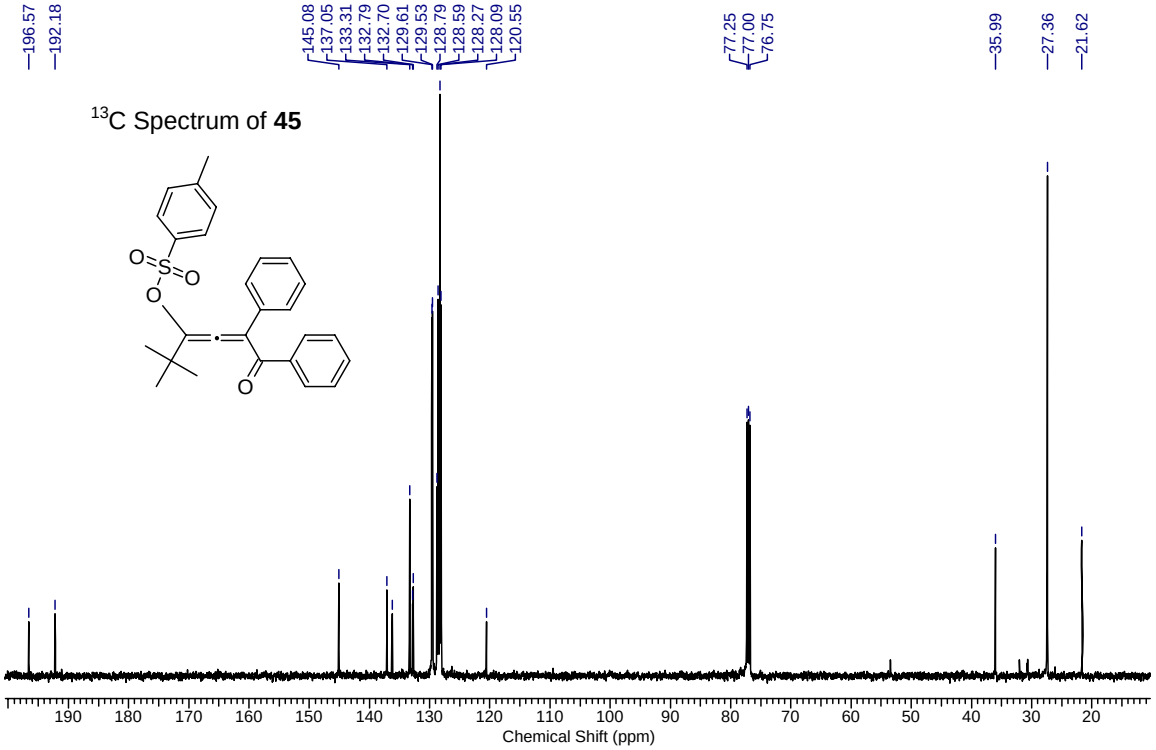


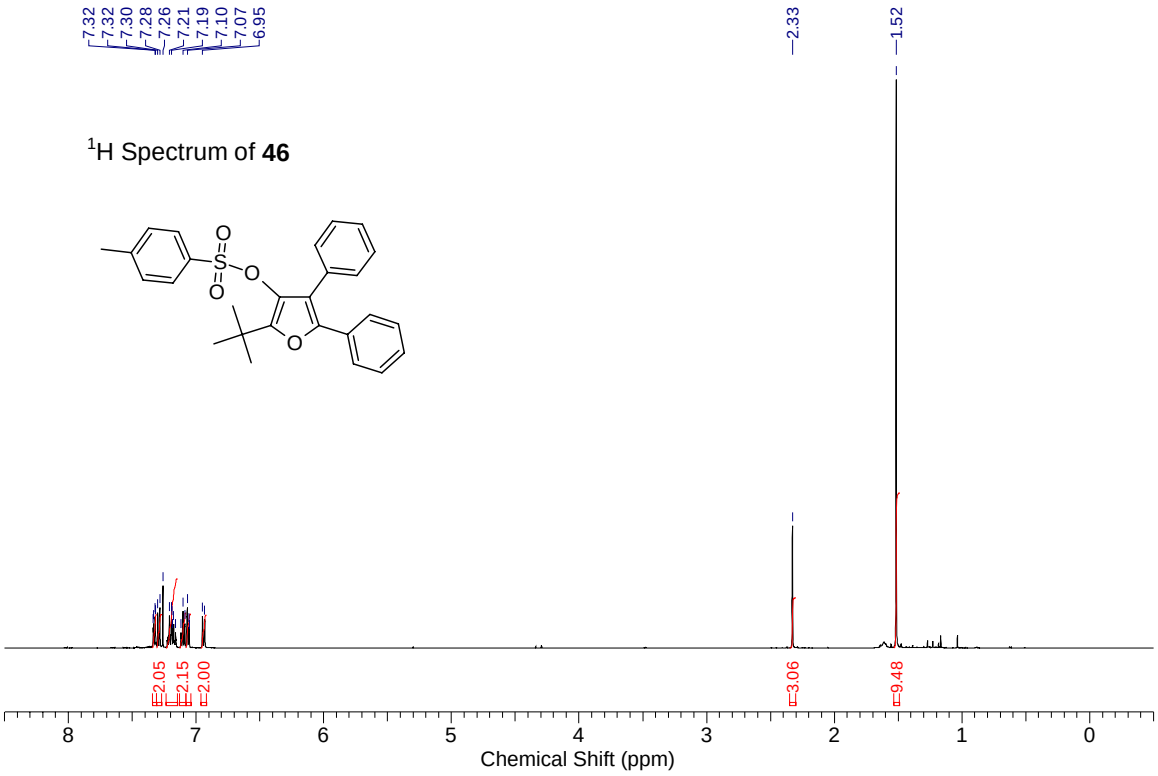
^{1}H Spectrum of **43**



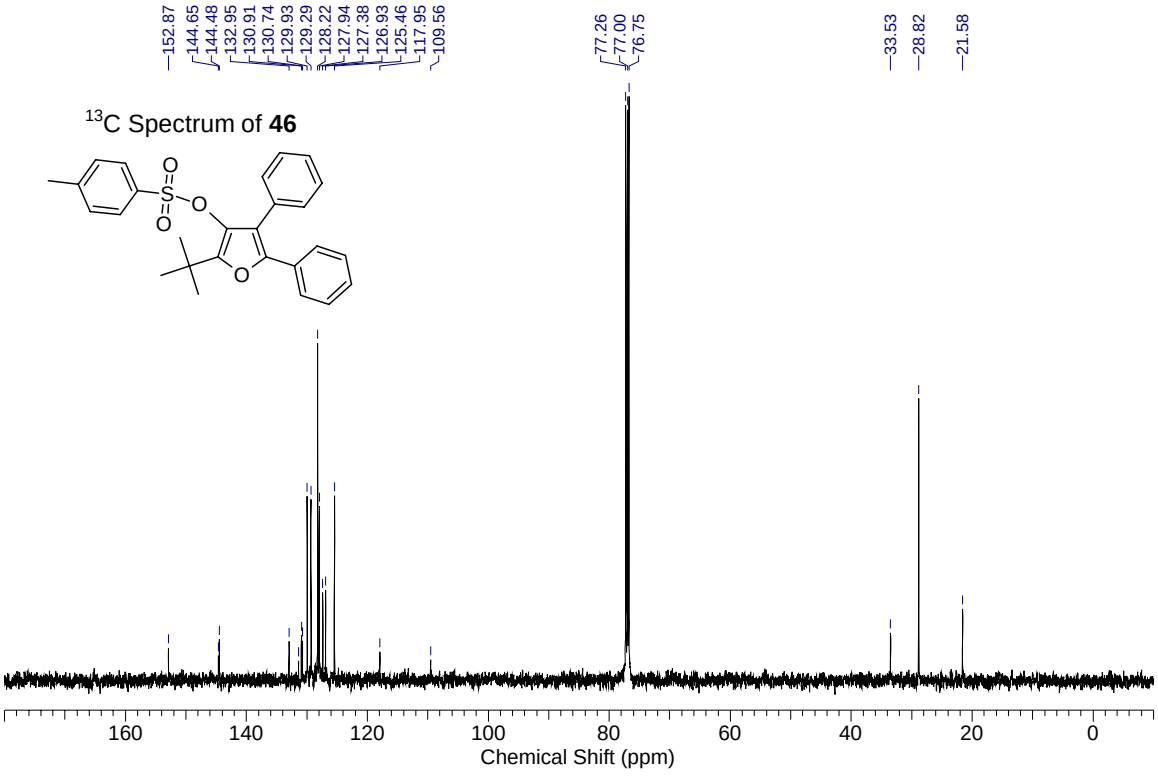
^{13}C Spectrum of **43**


7.82
7.81
7.80
7.64
7.62
7.42
7.41
7.39
7.36
7.35
7.10
7.09
2.35
1.01
^{1}H Spectrum of **45**
2.00
1.16
4.66
2.05
3.11
9.77
Chemical Shift (ppm)

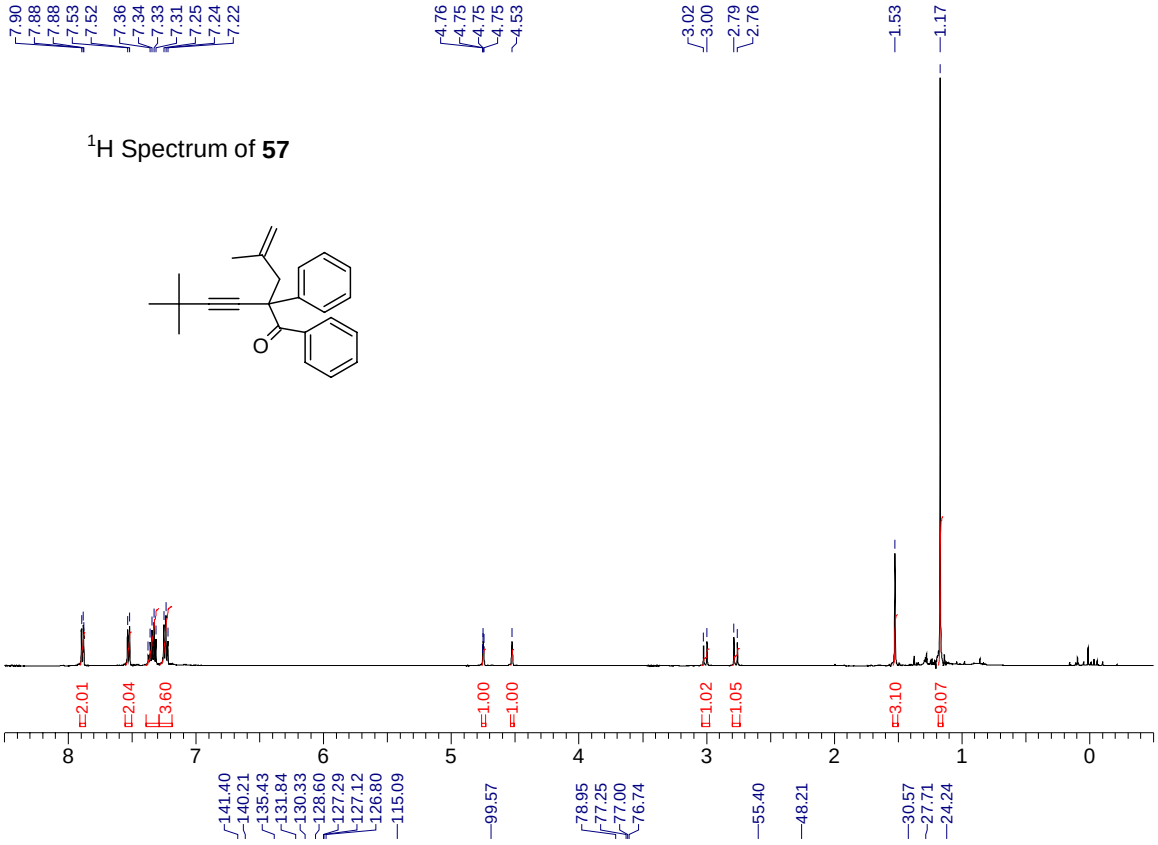

196.57
192.18
145.08
137.05
133.31
132.79
132.70
129.61
129.53
128.79
128.59
128.27
128.09
120.55
77.25
77.00
76.75
35.99
27.36
21.62
^{13}C Spectrum of **45**
Chemical Shift (ppm)



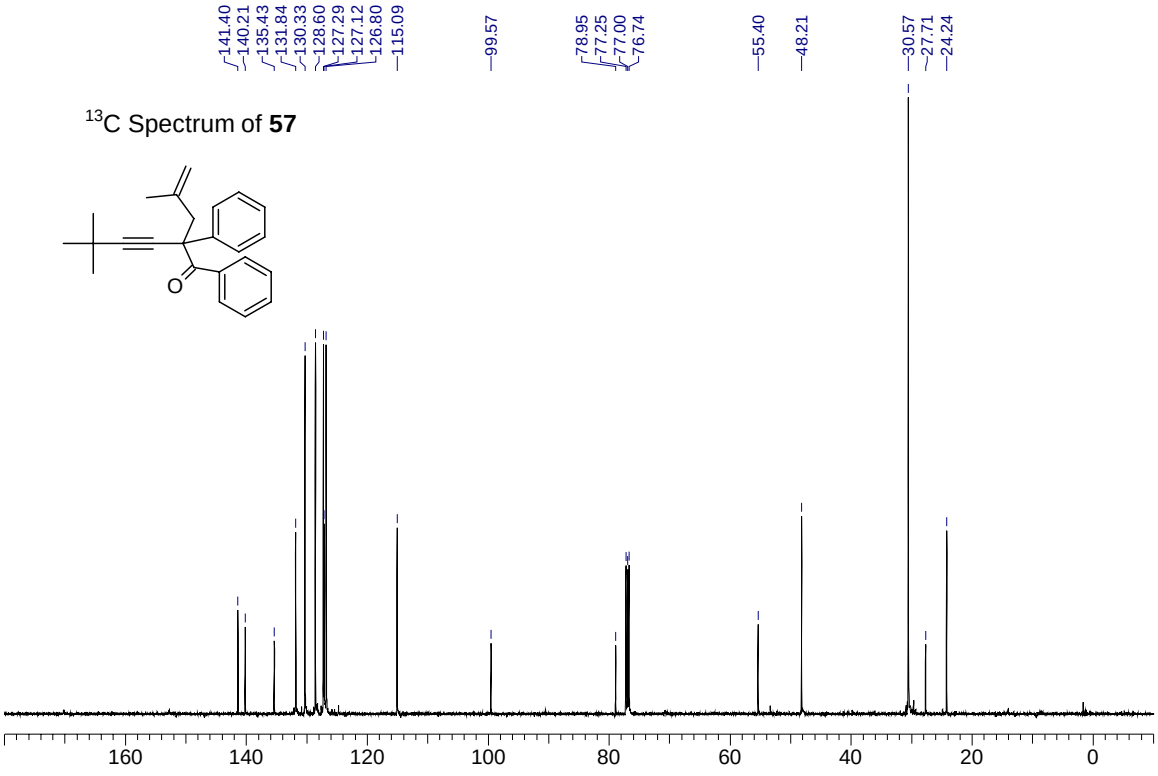
^{1}H Spectrum of **46**



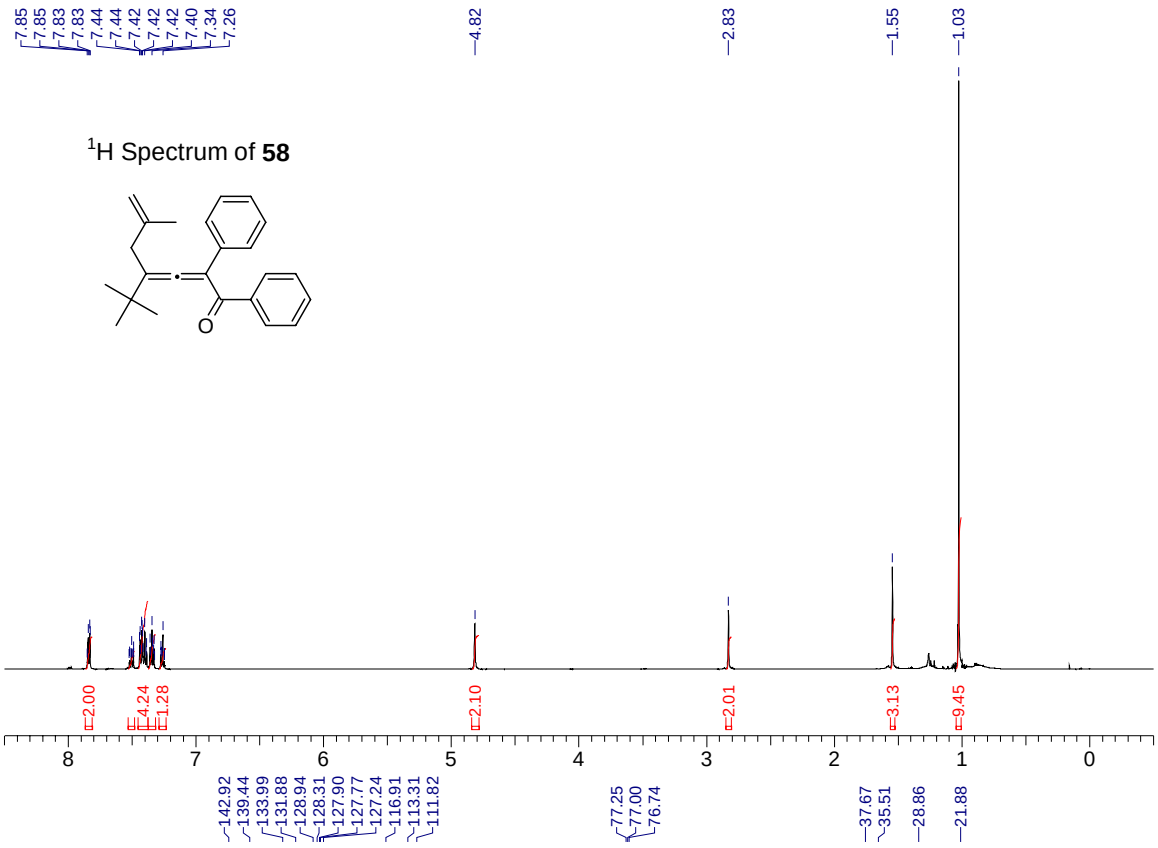
^{13}C Spectrum of **46**



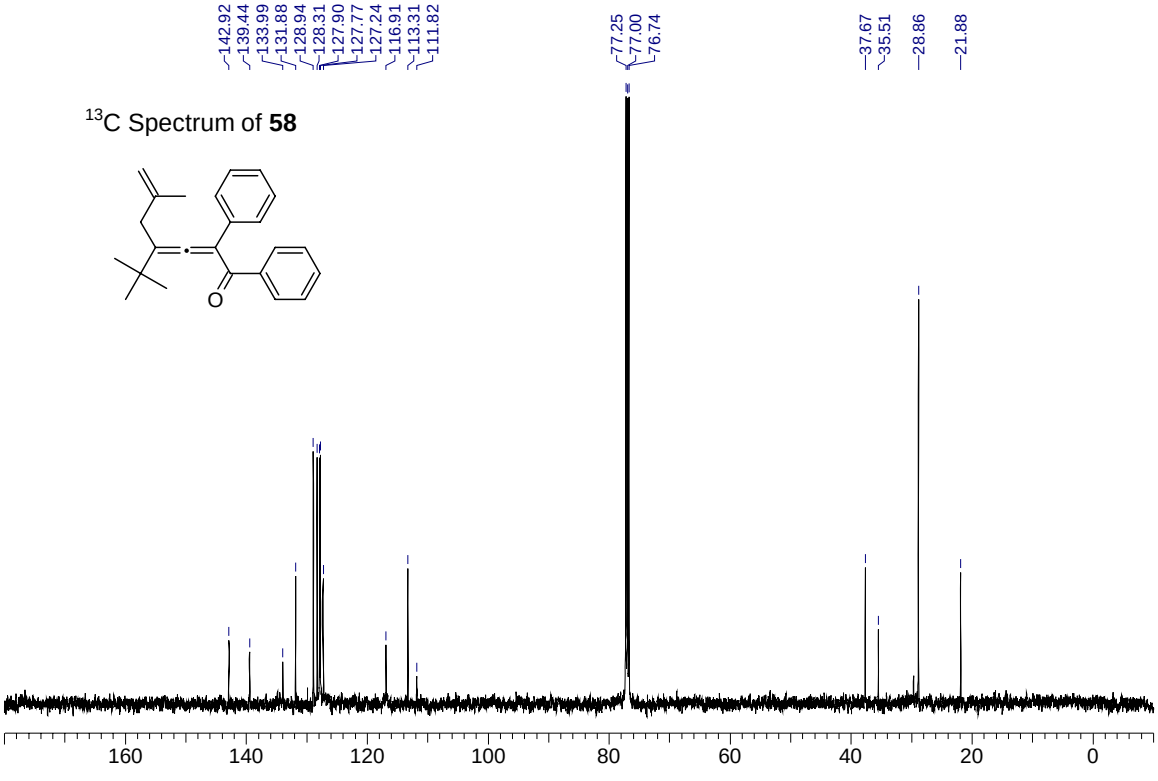
^{1}H Spectrum of **57**



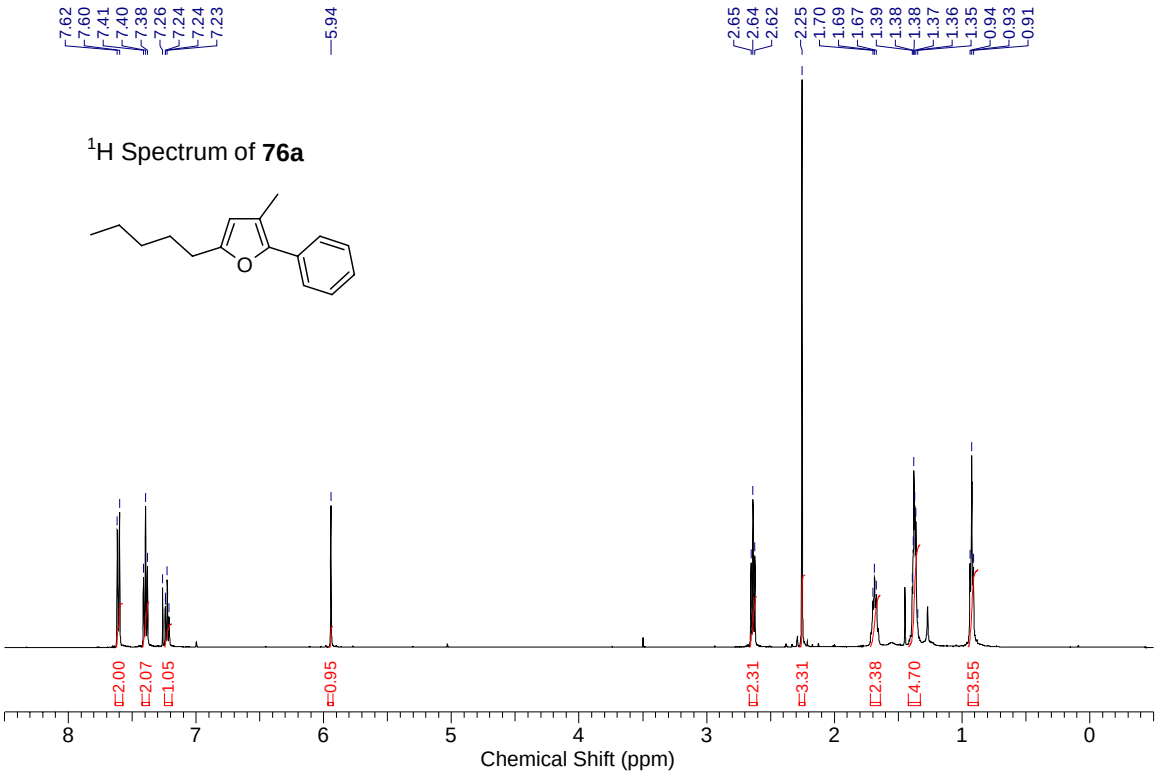
^{13}C Spectrum of **57**

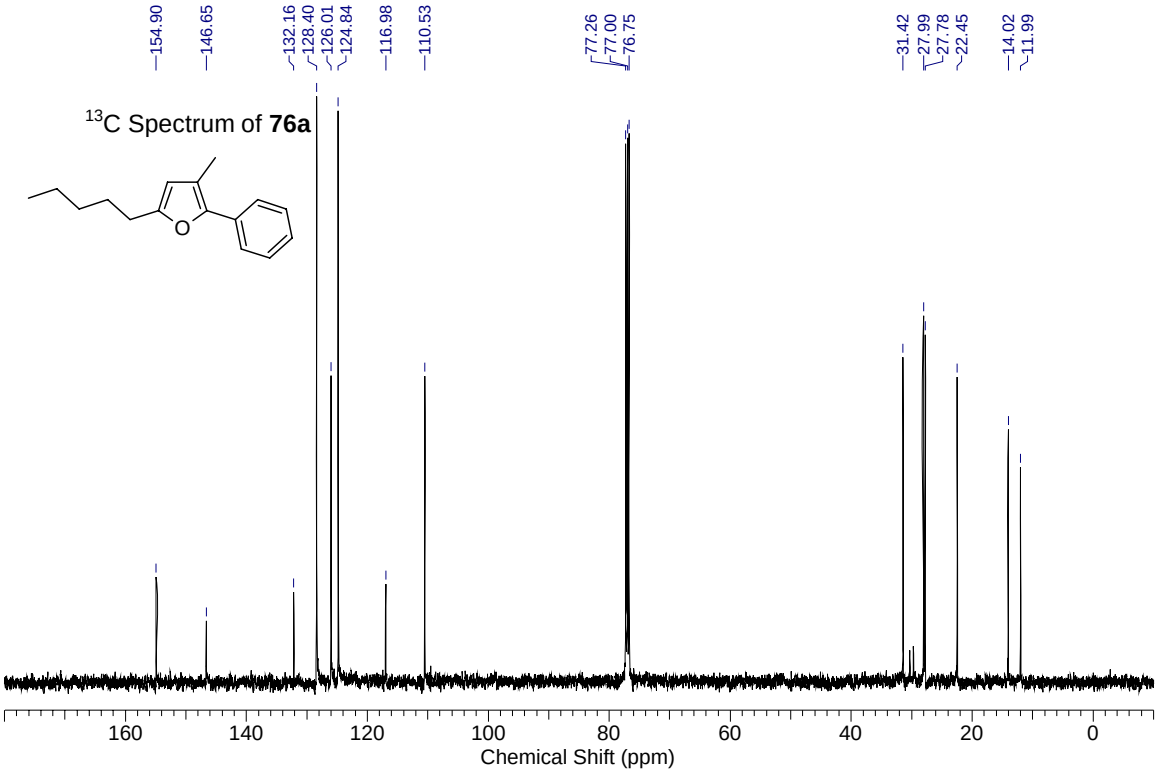


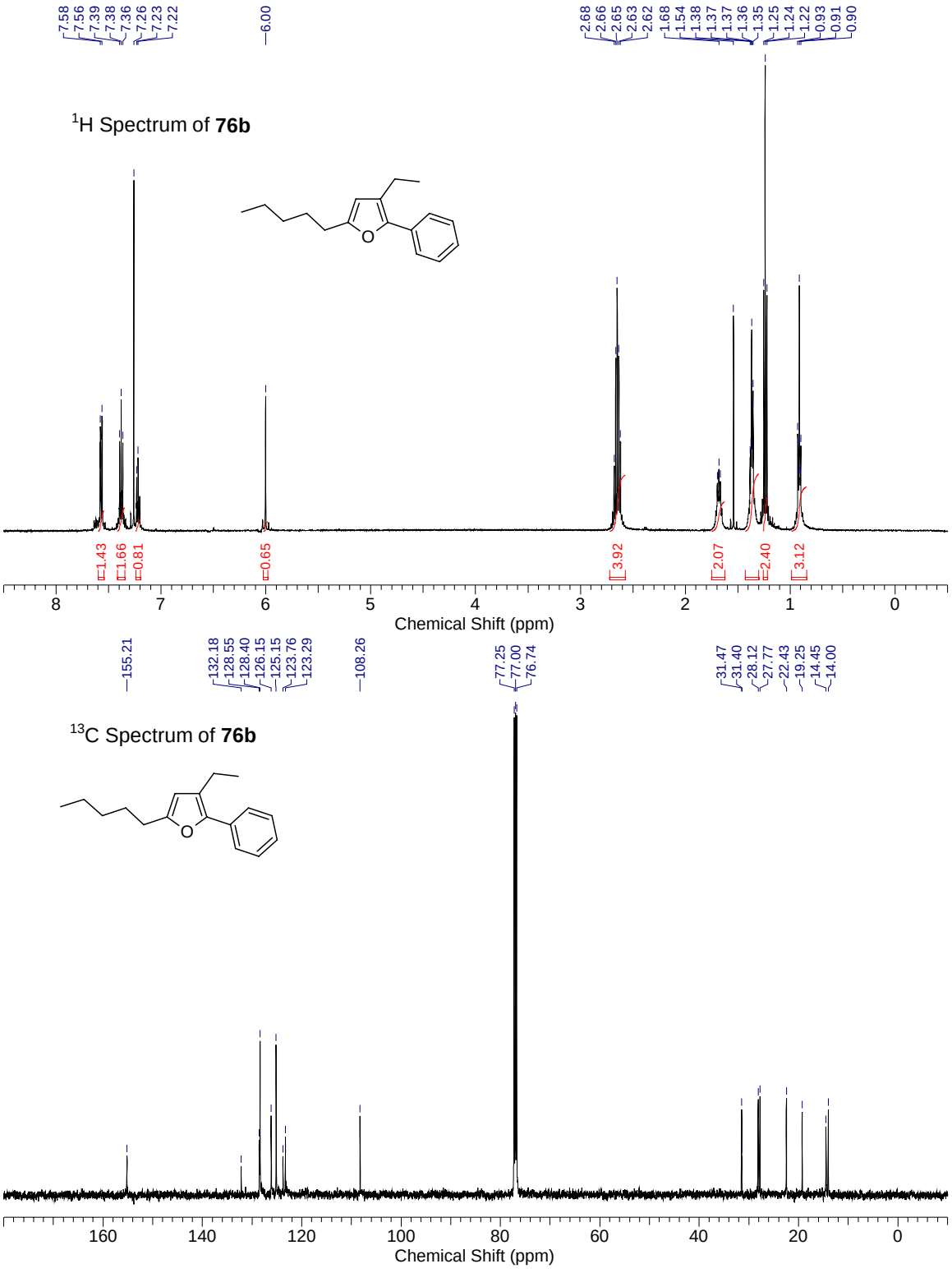
^{1}H Spectrum of **58**

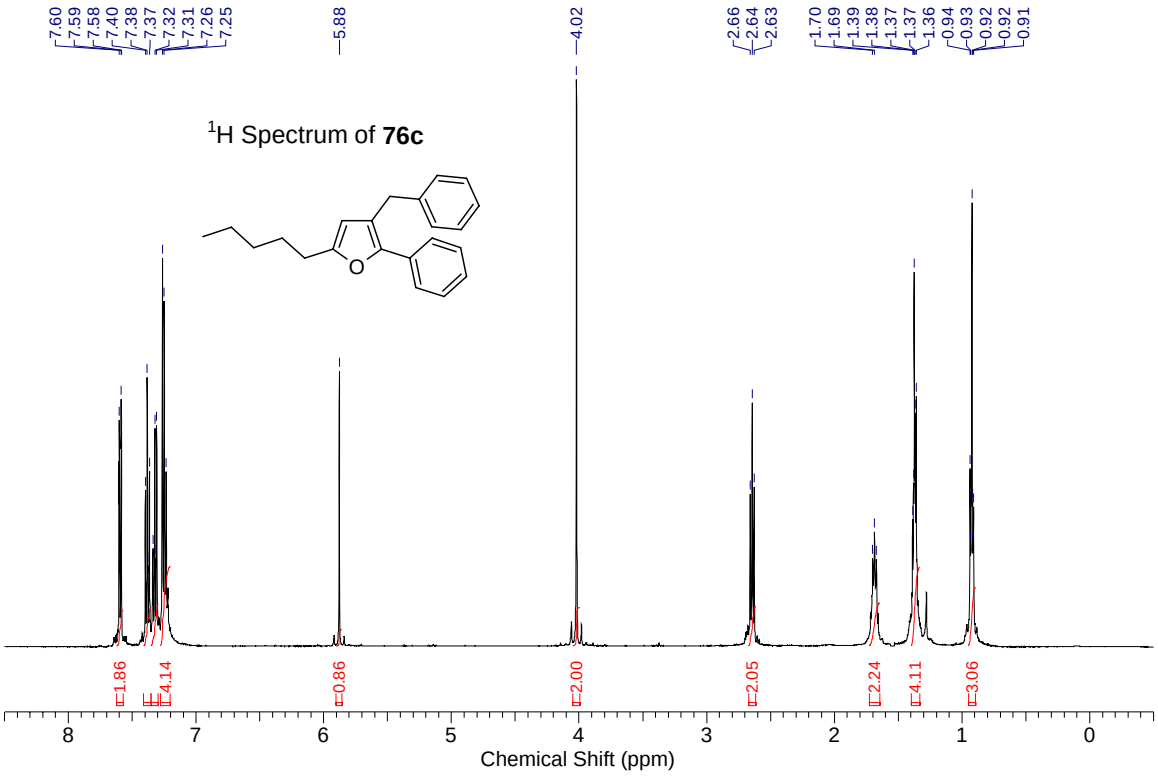


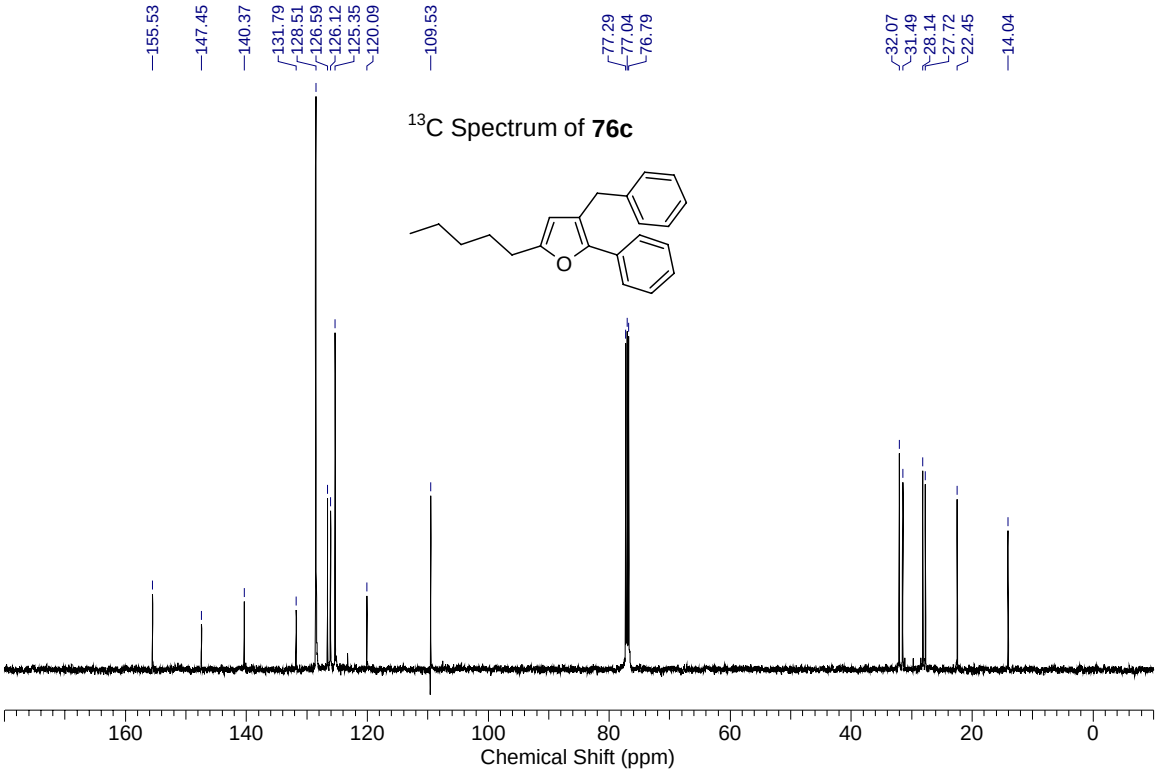
^{13}C Spectrum of **58**

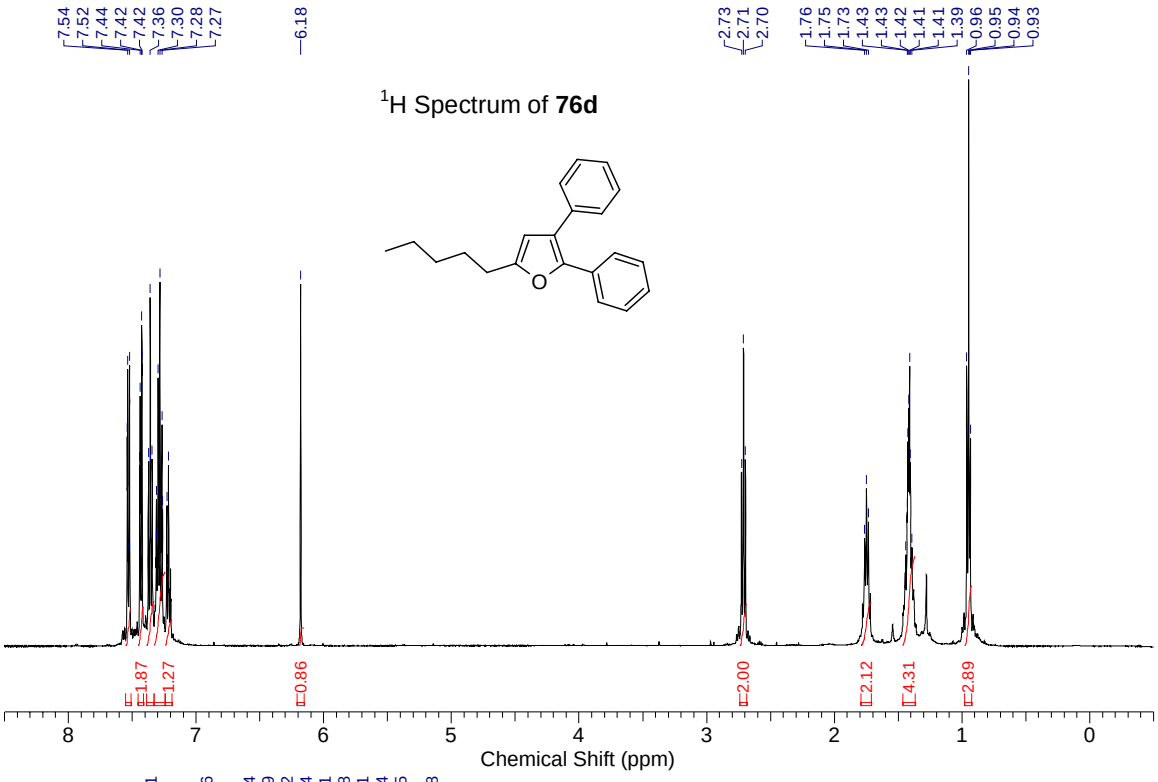

7.62
7.60
7.41
7.40
7.38
7.26
7.24
7.24
7.23
5.94
2.65
2.64
2.62
2.25
1.70
1.69
1.67
1.39
1.38
1.38
1.37
1.36
1.35
0.94
0.93
0.91
1H Spectrum of 76a
O
2.00
2.07
1.05
0.95
2.31
3.31
2.38
4.70
3.55
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

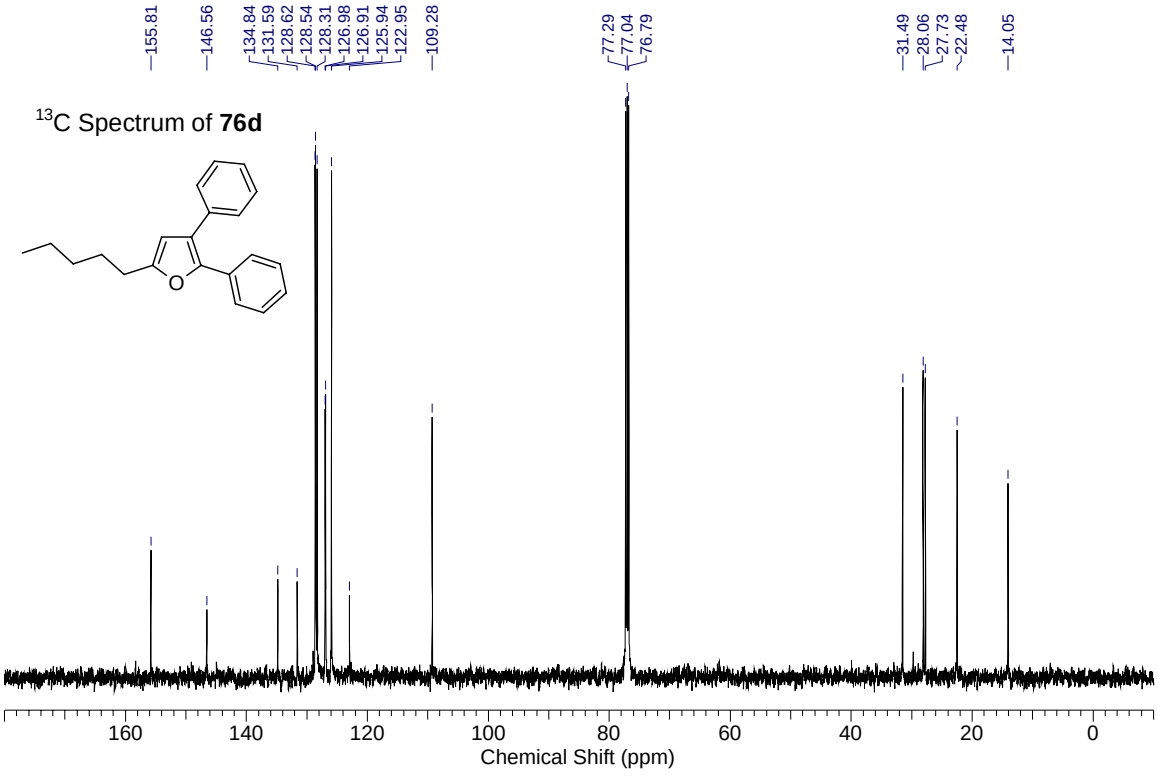

154.90
146.65
132.16
128.40
126.01
124.84
116.98
110.53
77.26
77.00
76.75
31.42
27.99
27.78
22.45
14.02
11.99
13C Spectrum of 76a
O
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

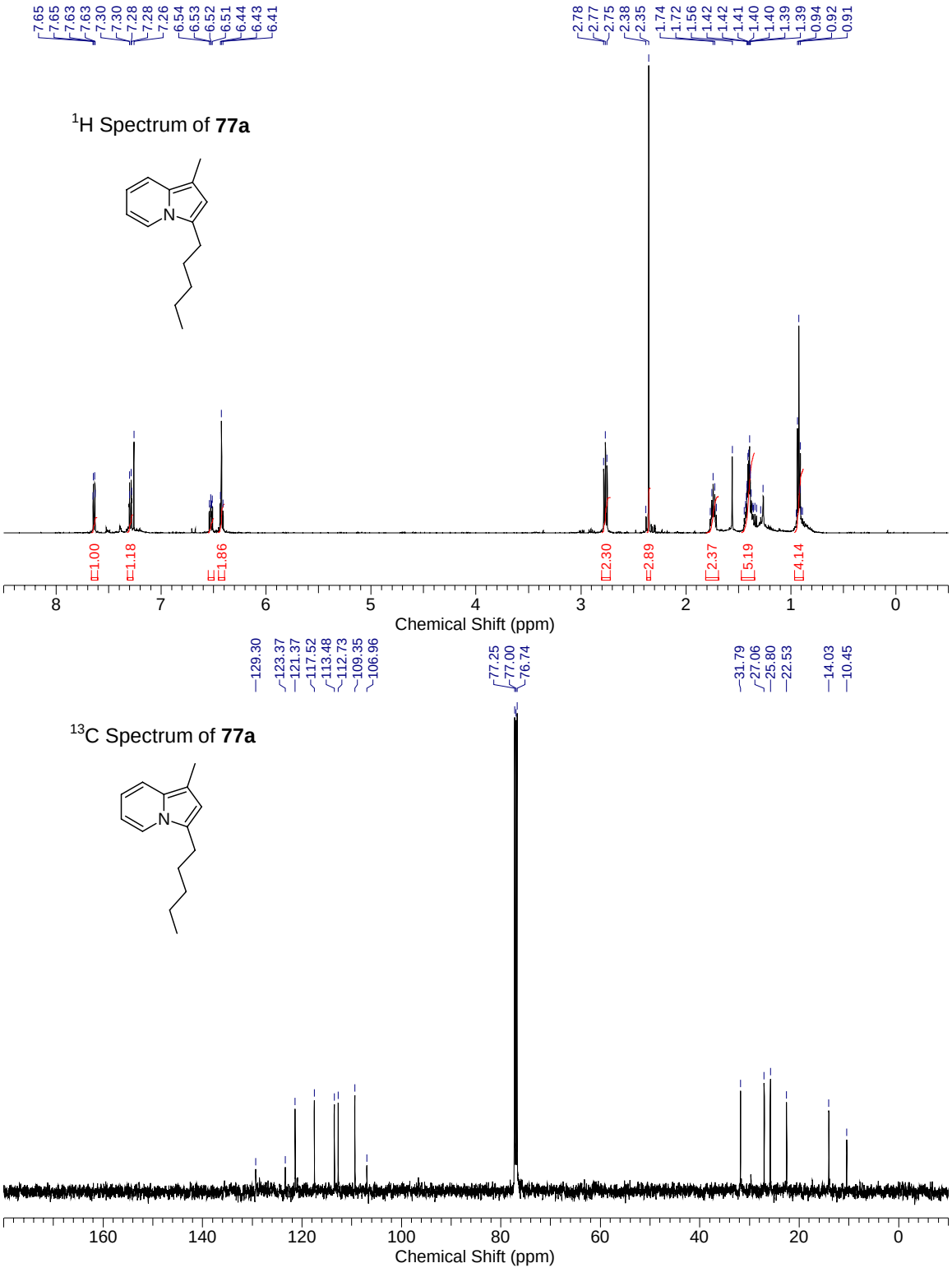

7.58
7.56
7.39
7.38
7.36
7.26
7.23
7.22
6.00
2.68
2.66
2.65
2.63
2.62
1.68
1.54
1.38
1.37
1.37
1.36
1.35
1.25
1.24
1.22
0.93
0.91
0.90
1H Spectrum of 76b
O
1.43
1.66
0.81
0.65
3.92
2.07
2.40
3.12
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
155.21
132.18
128.55
128.40
126.15
125.15
123.76
123.29
108.26
77.25
77.00
76.74
31.47
31.40
28.12
27.77
22.43
19.25
14.45
14.00
13C Spectrum of 76b
O
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

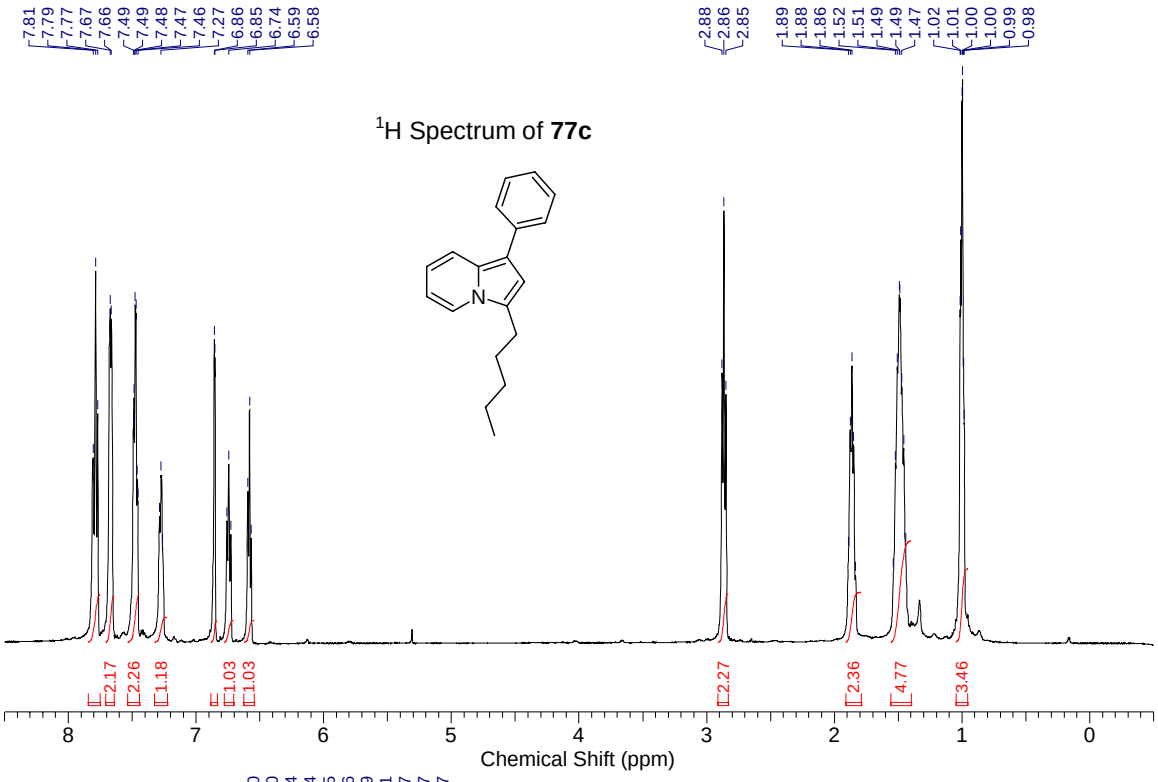

7.60
7.59
7.58
7.40
7.38
7.37
7.32
7.31
7.26
7.25
5.88
4.02
2.66
2.64
2.63
1.70
1.69
1.39
1.38
1.37
1.37
1.36
0.94
0.93
0.92
0.92
0.91
1H Spectrum of 76c
O
1.86
4.14
0.86
2.00
2.05
2.24
4.11
3.06
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


155.53
147.45
140.37
131.79
128.51
126.59
126.12
125.35
120.09
109.53
77.29
77.04
76.79
32.07
31.49
28.14
27.72
22.45
14.04
13C Spectrum of 76c
O
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

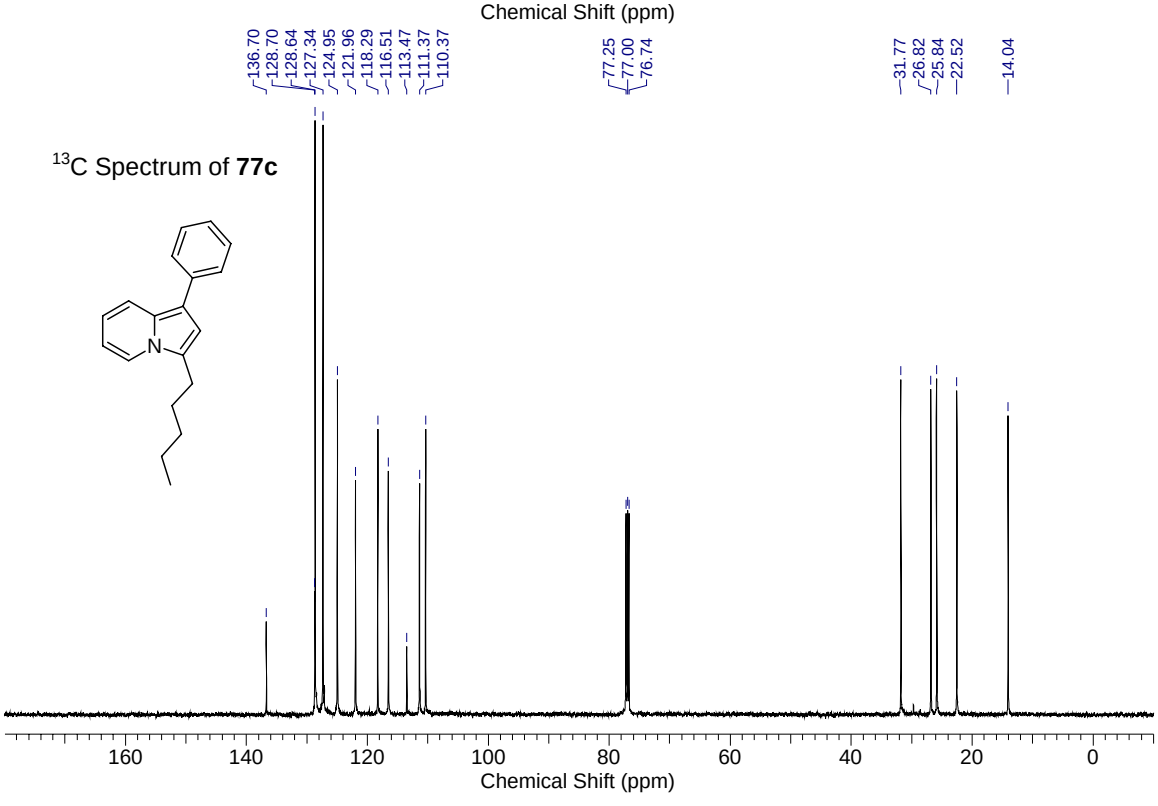

7.54
7.52
7.44
7.42
7.42
7.36
7.30
7.28
7.27
6.18
2.73
2.71
2.70
1.76
1.75
1.73
1.43
1.43
1.42
1.41
1.41
1.39
0.96
0.95
0.94
0.93
1H Spectrum of 76d
O
1.87
1.27
0.86
2.00
2.12
4.31
2.89
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


155.81
146.56
134.84
131.59
128.62
128.54
128.31
126.98
126.91
125.94
122.95
109.28
77.29
77.04
76.79
31.49
28.06
27.73
22.48
14.05
13C Spectrum of 76d
O
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.65
7.65
7.63
7.63
7.63
7.30
7.30
7.28
7.28
7.26
6.54
6.53
6.52
6.51
6.44
6.43
6.41
2.78
2.77
2.75
2.38
2.35
1.74
1.72
1.56
1.42
1.42
1.41
1.40
1.40
1.39
1.39
0.94
0.92
0.91
1H Spectrum of 77a
N
1.00
1.18
1.86
2.30
2.89
2.37
5.19
4.14
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
129.30
123.37
121.37
117.52
113.48
112.73
109.35
106.96
77.25
77.00
76.74
31.79
27.06
25.80
22.53
14.03
10.45
13C Spectrum of 77a
N
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

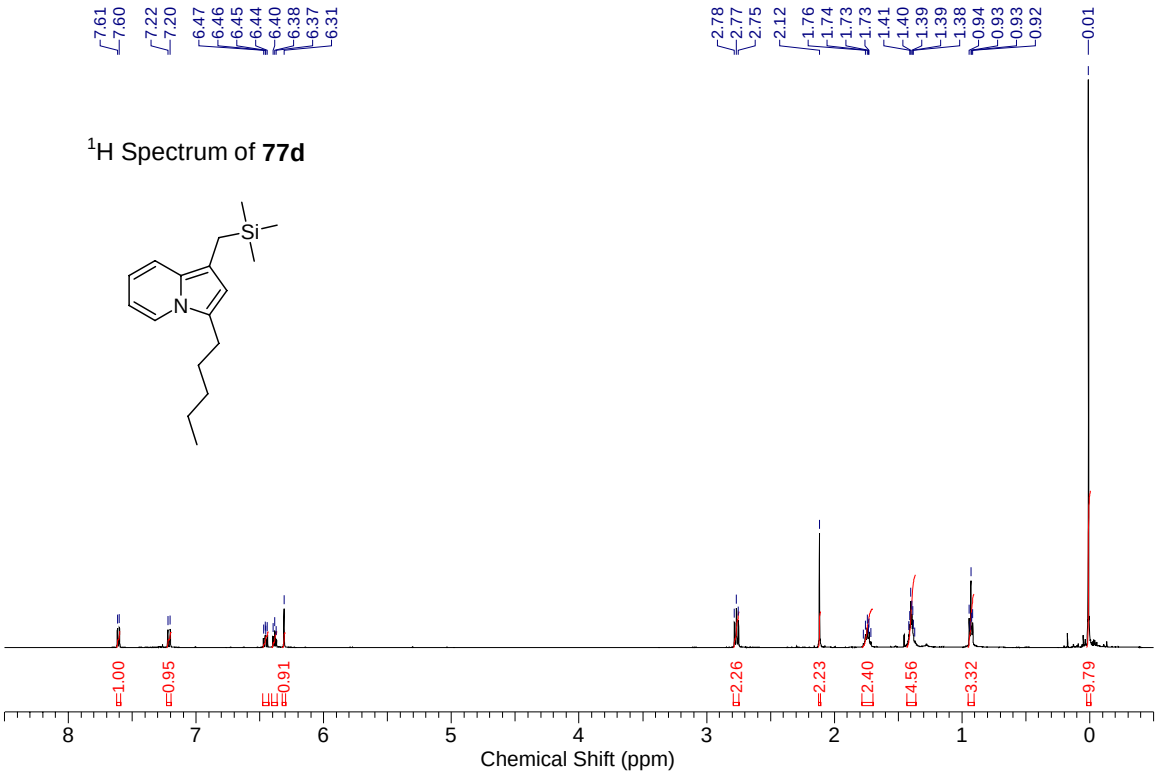


^{1}H Spectrum of **77c**



^{13}C Spectrum of **77c**

^{1}H Spectrum of **77d**



^{13}C Spectrum of **77d**