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Supporting Information

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Metal-Catalyzed [1,2]-Alkyl Shift in Allenyl Ketones: Synthesis of Multisubstituted Furans

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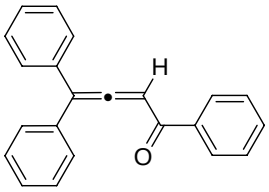
Content

General Information

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) or DPX-400 (400 MHz) instruments. (+) and (-) represent positive and negative intensities of signals in ^{13}C DEPT-135 experiments. GC/MS analysis was 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). Column chromatography was carried out employing Silicycle silica gel (Kieselgel 60, 63-200 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. Melting points were determined using a Thomas Hoover capillary melting point apparatus and are uncorrected. Anhydrous solvents were purchased from Aldrich and stored over calcium hydride. Alkynes, carboxylic acids, chloroanhydrides, α-bromo-ketones, phosphoranes and 2-bromo-2-methylpropanoyl bromide were commercially available and purchased from Aldrich, Strem Chemicals Inc., Lancaster Synthesis, Alfa Aesar or Acros Organics, or synthesized via known literature procedures. Reactions were typically run in oven-dried glassware under inert atmosphere.

Preparation of Starting Materials.

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

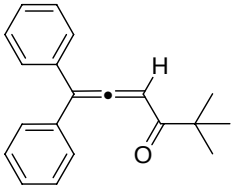


3a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.85 (m, 2 H), 7.49 – 7.53 (m, 1 H), 7.30 – 7.41 (m, 12 H), 6.82 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.14, 191.51, 137.48, 134.26 (2C), 132.79 (+), 128.77 (+, 4C) 128.73 (+, 2C) 128.61 (+, 4C) 128.34 (+, 4C) 113.75, 96.57 (+).

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

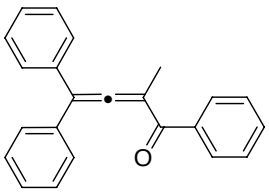
[1] Dupre, M.; Strzelecka, H. *C. R. Acad. Sci. Ser. C.* **1972**, *274*, 1091.
[2] Petasis, N. A.; Teets, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 10328.

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



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

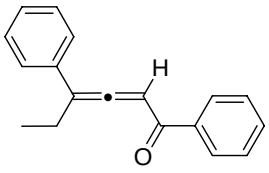
2-methyl-1,4,4-triphenylbuta-2,3-dien-1-one **(3d)** was prepared via Wittig olefination from 2-methyl-1-phenyl-2-(triphenylphosphoranylidene)ethanone[4] similar to the procedure reported by Bestmann and co-workers.[5] To a solution of 2-methyl-1-phenyl-2-(triphenylphosphoranylidene)ethanone (3.94 g, 10.0 mmol) in 12 ml of dry THF stirred under argon was added a solution of diphenylacetyl chloride (1.28 g, 5.0 mmol) in 4 ml of dry THF. The resulting solution was refluxed for 4 h. The reaction mixture was diluted with diethyl ether to precipitate triphenylphosphine oxide. After filtration, silica gel was added to adsorb the reaction products and the solvent was evaporated in vacuo. Flash Silica column chromatography (1:10 Et_2O/hexanes) gave the product as a colorless crystalline solid. Yield: 1.13 g (3.65 mmol, 73%).



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

1,4-diphenylpenta-2,3-dien-1-one[6] **(3e)** was prepared analogously to **3a** from commercially available 1-phenyl-2-(triphenylphosphoranylidene)ethanone and 2-phenylpropanoyl chloride (from 2-phenylpropanoic acid) in 81% yield.

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



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

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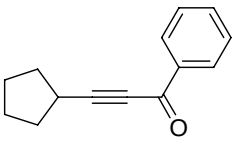
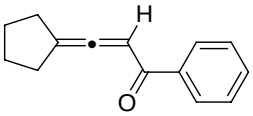
[3] Oare, D. A.; Henderson, M. A.; Sanner, M. A.; Heathcock, C. H. *J. Org. Chem.* **1990**, *55*, 132.
[4] Facchin, G.; Bertani, R.; Berton, A.; Gleria, M. *Inorg. Chim. Acta* **1988**, *147*, 165.
[5] Bestmann, H. J.; Hartung, H. *Chem. Ber.* **1966**, *99*, 1198.
[6] Trifonov, L.; Orakhovats, A.; Linden, A.; Heimgartner, H. *Helv. Chim. Acta* **1992**, *75*, 1872.

3-cyclopentyl-1-phenylprop-2-yn-1-one **(13).** To an oven dried flask were added anhydrous copper(I) iodide (40mg, 0.2 mmol, 2mol%) and $Pd(PPh_3)_2Cl_2$ (70mg, 0.1 mmol, 1mol%) under N_2 atmosphere. Sixteen ml of dry triethylamine and 1.21 ml (0.982g, 10 mmol) of cyclopentylacetylene were added sequentially to the same flask and the reaction mixture was stirred at room temperature for 10 minutes in the dark. Benzoyl chloride (1.27 ml, 11 mmol) was then added dropwise and the reaction mixture was stirred overnight. The reaction mixture was filtered through a layer of Silica (dichloromethane – eluent), all the solvents were removed in vacuo, and the residue was purified via flash Silica column chromatography (1:10 EtOAc/hexanes) to afford 1.91 g (9.63 mmol, 96%) of 3-cyclopentyl-1-phenylprop-2-yn-1-one **13** as yellow oil.



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

3-cyclopentylidene-1-phenylprop-2-en-1-one **(3h).** To an oven dried flask were added potassium *tert*-butoxide (1.081g, 9.63 mmol) under argon atmosphere and 96 ml of dry THF. The solution was cooled to -100°C and 3-cyclopentyl-1-phenylprop-2-yn-1-one **13** (1.91g, 9.63 mmol) in 96 ml of dry THF cooled to -100°C was added dropwise via cannula. The resulting bright red-orange solution was stirred at -100°C for 4 hours. Acetic acid (0.552 ml, 9.63 mmol) dissolved in 30 ml of anhydrous THF was then added at -100°C via cannula and reaction mixture was allowed to warm to room temperature. The reaction mixture was filtered through a layer of Silica (dichloromethane – eluent), the solvents were removed in vacuo, and the residue was purified via flash Silica column chromatography (1:10 EtOAc/hexanes) to afford 1.01 g (5.1 mmol, 53%) of 3-cyclopentylidene-1-phenylprop-2-en-1-one **3h** as yellow oil.



3h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (m, 2 H), 7.49 – 7.54 (m, 1 H), 7.39 – 7.45 (m, 2 H), 6.21 – 6.25 (quintet, *J*=4.13 Hz, 1 H), 2.44 – 2.60 (m, 4 H), 1.66 – 1.78 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.94, 193.45, 138.11, 132.24 (+), 128.63 (+, 2C), 128.12 (+, 2C), 107.25, 94.67 (+), 31.47 (–, 2C), 27.27 (–, 2C).

4-methyl-1-phenylpenta-2,3-dien-1-one[7] **(3i).** To an oven dried flask were added 1-phenyl-2-(triphenylphosphoranylidene)ethanone (4.0 g, 10.5 mmol) under argon atmosphere and 32 ml of dry dichloromethane. The solution was cooled to 0°C and 2-methylprop-1-en-1-one **14** (10.8 mmol, generated from 2-bromo-2-methylpropanoyl bromide and activated Zn dust by known literature procedure[8]) in 22 ml of dry THF was added dropwise via cannula. The resulting solution was stirred overnight, allowing the reaction mixture to warm to room temperature. After removal of half of the solvent, the residue was diluted with diethyl ether to precipitate triphenylphosphine oxide. After filtration, silica gel was added to adsorb the reaction products and the solvent was evaporated in vacuo. Flash Silica column chromatography (1:10 EtOAc/hexanes) gave the product as a pale yellow oil. Yield: 0.38 g (2.21 mmol, 21%).

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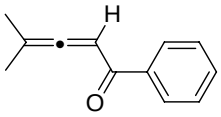
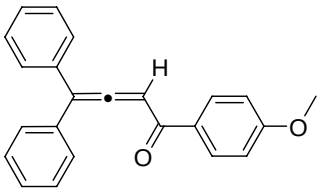
[7] Reuter, J. M.; Salomon, R. G. *Tetrahedron Lett.* **1978**, *19*, 3199.
[8] Wilson, J. E.; Fu, G. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 6358.



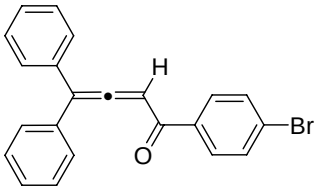
3i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.87 (m, 2 H), 7.49 – 7.55 (m, 1 H), 7.38 – 7.46 (m, 2 H), 6.14 – 6.20 (septet, *J*=2.92 Hz, 1 H), 1.80 (d, *J*=2.92 Hz, 6 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.29, 193.00, 137.98, 132.33 (+), 128.63 (+, 2C), 128.19 (+, 2C), 99.32, 92.43 (+), 19.42 (+, 2C).

1-(4-methoxyphenyl)-4,4-diphenylbuta-2,3-dien-1-one **(3j)** was prepared analogously to **3a** from 1-(4-methoxyphenyl)-2-(triphenylphosphoranylidene)ethanone[9] and diphenylacetyl chloride in 91% yield.



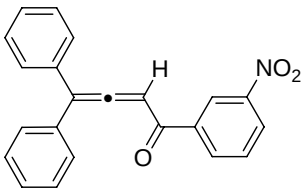
3j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.91 (m, 2 H), 7.31 – 7.42 (m, 10 H), 6.81 – 6.87 (m, 3 H), 3.83 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.38, 189.44, 163.45, 134.44 (2C), 131.12 (+, 2C), 130.32, 128.77 (+, 4C), 128.66 (+, 4C), 128.28 (+, 2C), 113.62 (+, 2C), 113.56, 96.22 (+), 55.47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

1-(4-bromophenyl)-4,4-diphenylbuta-2,3-dien-1-one **(3k)** was prepared analogously to **3a** from 1-(4-bromophenyl)-2-(triphenylphosphoranylidene)ethanone[9] and diphenylacetyl chloride in 76% yield.



3k: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J*=8.25 Hz, 2 H), 7.22 – 7.55 (m, 12 H), 6.75 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.17, 190.48, 136.13, 134.00 (2C), 131.62 (+, 2C), 130.28 (+, 2C), 128.85 (+, 4C), 128.57 (+, 4C), 128.49 (+, 2C), 127.87, 113.97, 96.50 (+); mp 100–102°C.

1-(3-nitrophenyl)-4,4-diphenylbuta-2,3-dien-1-one **(3l)** was prepared analogously to **3a** from 1-(3-nitrophenyl)-2-(triphenylphosphoranylidene)ethanone[10] and diphenylacetyl chloride in 61% yield.



3l: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (t, *J*=1.83 Hz, 1 H), 8.35 (ddd, *J*=8.21, 2.25, 1.10 Hz, 1 H), 8.10 (ddd, *J*=7.52, 1.47, 1.28 Hz, 1 H), 7.54 (t, *J*=7.98 Hz, 1 H), 7.35 – 7.44 (m, 6 H), 7.27 – 7.31 (m, 4 H), 6.81 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.76, 189.39, 148.06, 138.70, 134.30 (+), 133.52 (2C), 129.59 (+), 128.95 (+, 4C), 128.75 (+, 2C), 128.56 (+, 4C), 127.00 (+), 123.64 (+), 114.62, 96.64 (+).

4-(4,4-diphenylbuta-2,3-dienoyl)benzonitrile **(3m)** was prepared analogously to **3a** from 4-[(triphenylphosphoranylidene)acetyl]benzonitrile[10a,11] and diphenylacetyl chloride in 73% yield.

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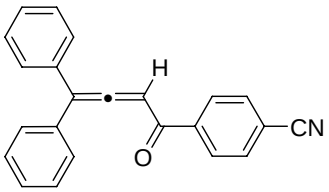
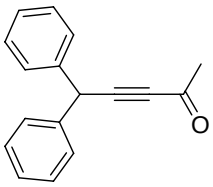
[9] Denney, D. B.; Smith, L. C.; Song, J.; Rossi, C. J.; Hall, C. D. *J. Org. Chem.* **1963**, *28*, 778.
[10] (a) Froeyen, P.; Morris, D. G. *Acta. Chem. Scand., Ser. B.* **1976**, *B30*, 790. (b) Yoshida, H.; Shimizu, J.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Japan*. **1985**, *58*, 2445.
[11] Dragovich, P. S.; Webber, S. E.; Babine, R. E.; Fuhrman, S. A.; et al. *J. Med. Chem*. **1998**, *41*, 2806.



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

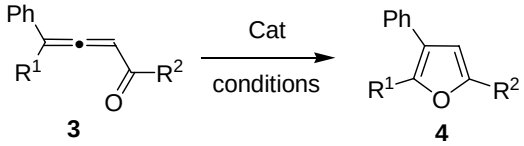
5,5-diphenylpent-3-yn-2-one **(5b).** To an oven dried flask charged with a solution of 3,3-diphenylprop-1-yne[12] **15** (0.385 g, 2.0 mmol) in 6 ml of dry THF and cooled to -78°C was added dropwise a 2.64M solution of n-BuLi in hexanes (0.760 ml, 2.0 mmol) and the reaction mixture was stirred at -78°C for 3 hours. The resulting solution was then transferred via cannula to the analogously prepared flask containing a solution of acetic anhydride (1.021 g, 10 mmol) in 6 ml of diethyl ether at -78°C and the reaction mixture was stirred overnight. The reaction mixture was quenched with 50 ml of water and extracted with hexanes (1×100 ml) and diethyl ether – hexanes (1:1, 2×75 ml). Combined organic extracts were dried over anhydrous sodium sulfate. All the solvents were removed in vacuo, and the residue was purified via flash Silica column chromatography (1:10 EtOAc/hexanes) to afford 0.33 g (1.41 mmol, 70%) of 5,5-diphenylpent-3-yn-2-one **5b** as a colorless oil.



5b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.43 (m, 10 H), 5.17 (s, 1 H), 2.40 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.61, 139.58 (2C), 128.89 (+, 4C), 127.87 (+, 4C), 127.47 (+, 2C), 92.50, 84.56, 43.19 (+), 32.92 (+).

[12] Porter, N. A.; Hogenkamp, D. J.; Khouri, F. F. *J. Am. Chem. Soc.* **1990**, *112*, 2402.

Optimization of Reaction Conditions



3 **4**

Optimization Procedure. To an oven dried 1–5 ml Wheaton vial charged with catalyst and the appropriate amount of anhydrous solvent was added allenyl ketone **3 (**0.1 mmol)[13] under N_2 or argon atmosphere and the reaction mixture was stirred at temperature defined in Table 1 until judged complete by TLC and GC/MS analysis. The reaction mixture was filtered through a layer of flash Silica (EtOAc – eluent), the solvents were removed in vacuo, and the residue was analyzed by ^{1}H NMR using dibromomethane as an internal standard. Selected results are summarized in Table 1. For several examples isolated yield of the furan **4** is given in parentheses.

Table 1: Optimization of Reaction Conditions

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

[a] NMR yield, isolated yield in parentheses. [b] 2.2:1 mixture of **4f:4g** by ^{1}H NMR. [c] 7:1 mixture of **4f:4g** by ^{1}H NMR. [d] 2:1 mixture of **4f:4g**. [e] 2.3:1 mixture of **4f:4g**. [f] 2.8:1 mixture of **4f:4g**. [g] 3.15:1 mixture of **4f:4g**. [h] 4.2:1 mixture of **4f:4g**.

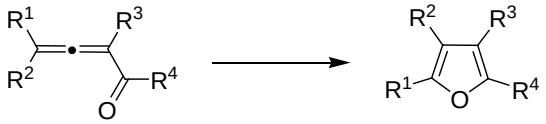
[13] Solid allenyl ketones were loaded into vial along with the catalyst followed by the addition of solvent. Liquid compounds were transferred via cannula from the separate vial as an approximately 1M solution in the anhydrous toluene to the reaction vial containing catalyst and solvent.

Synthesis of Furans

Typical Preparative Procedure. To an oven dried ChemGlass pressure tube (or 5 ml Wheaton vial) charged with $Sn(OTf)_2$ (8.3 mg, 0.02 mmol, 5mol%) as the catalyst and 3.6 ml of anhydrous toluene was added 1,4,4-triphenylbuta-2,3-dien-1-one **3a** (118.4 mg, 0.4 mmol) in 0.4 ml of anhydrous toluene under argon atmosphere and the reaction mixture was stirred at 100°C for 6 hours. The reaction mixture was allowed to cool to room temperature and triethylamine (0.017 ml, 0.12 mmol) was added to quench the catalyst. The reaction mixture was filtered through a layer of Silica (EtOAc – eluent), the solvents were removed, and the residue was purified via flash Silica column chromatography (1:10:0.08 benzene/hexanes/Et_3N) to afford 96.3 mg (0.325 mmol, 81%) of 2,3,5-triphenylfuran **4a** as white crystalline solid (see page S9 for analytical data).

Note: Reaction conditions (Temperature, catalyst, time, etc.) for the cycloisomerization of allenyl ketones **3a-m** into furans **4a-m** are summarized in Table 2.

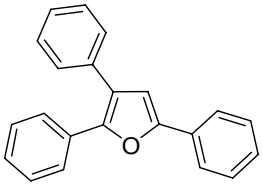
Table 2: Reaction Conditions



3a-m **4a-m**

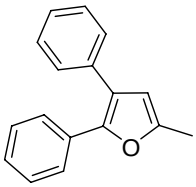
#	R^1	R^2	R^3	R^4	Catalyst	T, °C	Solvent	Concentration, M	Cat. %	Time, h	Product	Yield %
1	Ph	Ph	H	Ph	$Sn(OTf)_2$	100	toluene	0.1	5	6	**4a**	81
2	Ph	Ph	H	Me	$In(OTf)_3$	115	″	0.05	10	12	**4b**	64
3	Ph	Ph	H	*t*-Bu	″	100	″	″	5	1	**4c**	90
4	Ph	Ph	Me	Ph	AgOTf	140	p-xylene	″	20	1	**4d**	79
5	Ph	Me	H	Ph	$In(OTf)_3$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

2,3,5-triphenylfuran[14] **(4a)**



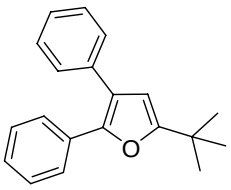
4a (81%, 0.4 mmol): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.86 (m, 2 H), 7.60 – 7.65 (m, 2 H), 7.46 – 7.52 (m, 2 H), 7.37 – 7.46 (m, 4 H), 7.24 – 7.37 (m, 5 H), 6.83 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.55, 147.89, 134.33, 131.12, 130.53, 128.75 (+, 2C), 128.70 (+, 4C), 128.41 (+, 2C), 127.53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

5-methyl-2,3-diphenylfuran[15] **(4b)**



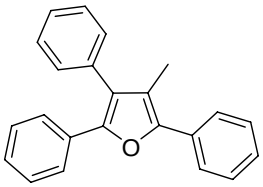
4a (64%, 0.8 mmol): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.55 (m, 2 H), 7.18 – 7.44 (m, 8 H), 6.17 (nonresolved q, *J*=0.90 Hz, 1 H), 2.40 (d, *J*=0.90 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.31, 146.78, 134.72, 131.48, 128.59 (+, 2C), 128.57 (+, 2C), 128.33 (+, 2C), 127.04 (+), 126.95 (+),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

5-tert-butyl-2,3-diphenylfuran[16] **(4c)**



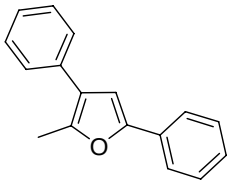
4c (90%, 0.4 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.57, (m, 2 H), 7.42 – 7.47 (m, 2 H), 7.33 – 7.39 (m, 2 H), 7.26 – 7.32 (m, 3 H), 7.19 – 7.25 (m, 1 H), 6.16 (s, 1 H), 1.39 (s, 9 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.27, 146.26, 134.91, 131.69, 128.63 (+, 2C), 128.55 (+, 2C), 128.30 (+,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

3-methyl-2,4,5-triphenylfuran[17] **(4d)**



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

2-methyl-3,5-diphenylfuran[18] **(4e)**



4e (72%, 0.5 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.75 (m, 2 H), 7.37 – 7.50 (m, 6 H), 7.23 – 7.34 (m, 2 H), 6.81 (s, 1 H), 2.55 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.63, 147.62, 134.08, 130.86, 128.69 (+, 2C), 128.65 (+, 2C), 127.52 (+, 2C), 127.05 (+), 126.48 (+), 123.44 (+, 2C), 123.04, 106.47 (+), 13.25 (+).

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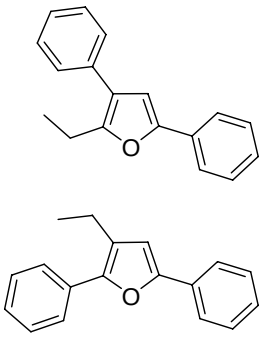
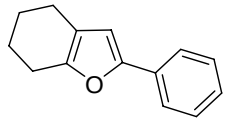
[15] Komendantov, M. I.; Smirnova, T. S.; Domnin, I. N.; Krakhmal'naya, L. A. *Zhurnal Organicheskoi Khimii* **1971**, *7*, 2455.
[16] Couture, A.; Lablache-Combier, A.; Ofenberg, H. *Tetrahedron* **1975**, *31*, 2023.
[17] Bailey, P. S.; Pomerantz, S. H. *J. Am. Chem. Soc.* **1953**, *75*, 281.
[18] Mattson, A. E.; Bharadwaj, A. R.; Zuhl, A. M.; Scheidt, K. A. *J. Org. Chem.* **2006**, *71*, 5715.

2-ethyl-3,5-diphenylfuran[18] **(4f)** ***and 3-ethyl-2,5-diphenylfuran***[19] **(4g)**



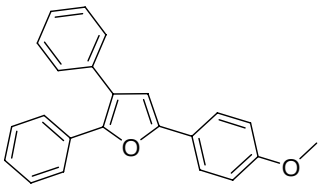
4f:4g (88%, 0.8 mmol, 2.3:1 mixture): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.78 (m, 2 H, **4g**), 7.69 – 7.73 (m, 2 H, **4f**), 7.38 – 7.48 (m, 12 H, **4f**+**4g**), 7.24 – 7.34 (m, 4 H, **4f**+**4g**), 6.79 (s, 1 H, **4f**), 6.71 (s, 1 H, **4g**), 2.90 (q, *J*=7.58 Hz, 2 H, **4f**), 2.77 (q, *J*=7.64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

2-phenyl-4,5,6,7-tetrahydro-1-benzofuran[20] **(4h)**



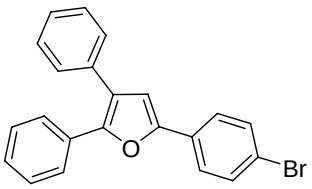
4h (75%, 0.5 mmol): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.68 (m, 2 H), 7.32 – 7.41 (m, 2 H), 7.18 – 7.25 (m, 1 H), 6.49 (s, 1 H), 2.64 – 2.74 (m, 2 H), 2.44 – 2.52 (m, 2 H), 1.84 – 1.94 (m, 2 H), 1.73 – 1.82 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.61, 150.81, 131.46, 128.57 (+, 2C), 126.56 (+), 123.27 (+, 2C), 119.00, 106.03 (+), 23.34 (–), 23.18 (–), 23.13 (–), 22.19 (–).

5-(4-methoxyphenyl)-2,3-diphenylfuran[21] **(4j)**



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

5-(4-bromophenyl)-2,3-diphenylfuran[21] **(4k)**



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

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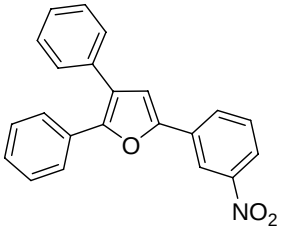
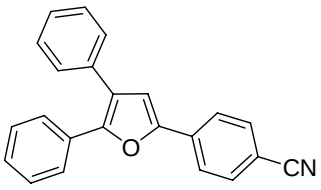
[20] Crotti, P.; Badalassi, F.; Di Bussolo, V.; Favero, L.; Pineschi, M. *Tetrahedron.* **2001**, *57*, 8559.
[21] (a) Demirdji, S. H.; *J. Het. Chem.* **1985**, *22*, 495. (b) Horspool, W. M.; Khalaf, A. I.; *J. Chem. Soc. Perkin Trans. 1.* **1989**, 1147.

***5-(3-nitrophenyl)-2,3-diphenylfuran* (4l)**



4l (85%, 0.5 mmol): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (t, *J*=1.83 Hz, 1 H), 8.12 (ddd, *J*=8.16, 2.11, 0.73 Hz, 1 H), 8.04 (dt, *J*=7.84, 1.22 Hz, 1 H), 7.61 – 7.65 (m, 2 H), 7.58 (t, *J*=7.98 Hz, 1 H), 7.44 – 7.49 (m, 2 H), 7.28 – 7.44 (m, 6 H), 6.97 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.00, 149.28, 148.82, 133.62, 132.08, 130.49, 129.80 (+), 129.14 (+), 128.81 (+, 2C), 128.64 (+, 2C), 128.55 (+, 2C), 128.12 (+), 127.64 (+), 126.37 (+, 2C), 124.78, 121.79 (+), 118.43 (+) 111.61 (+); mp 128–129°C; HRMS (EI) calcd. for $C_{22}H_{15}NO_3$ [M^+]: 341.10519. Found: 341.10357.

***4-(4,5-diphenyl-2-furyl)benzonitrile*[21b] (4m)**



4m (94%, 0.5 mmol): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J*=8.62 Hz, 2 H), 7.69 (d, *J*=8.62 Hz, 2 H), 7.61 (dd, *J*=8.16, 1.38 Hz, 2 H), 7.28 – 7.49 (m, 8 H), 6.97 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.42, 149.64, 134.30, 133.59, 132.66 (+, 2C), 130.46, 128.83 (+, 2C), 128.65 (+, 2C), 128.56 (+, 2C), 128.20 (+), 127.69 (+), 126.36 (+, 2C), 125.00, 123.87 (+, 2C) 119.02, 112.51 (+), 110.31; mp 160–161°C.

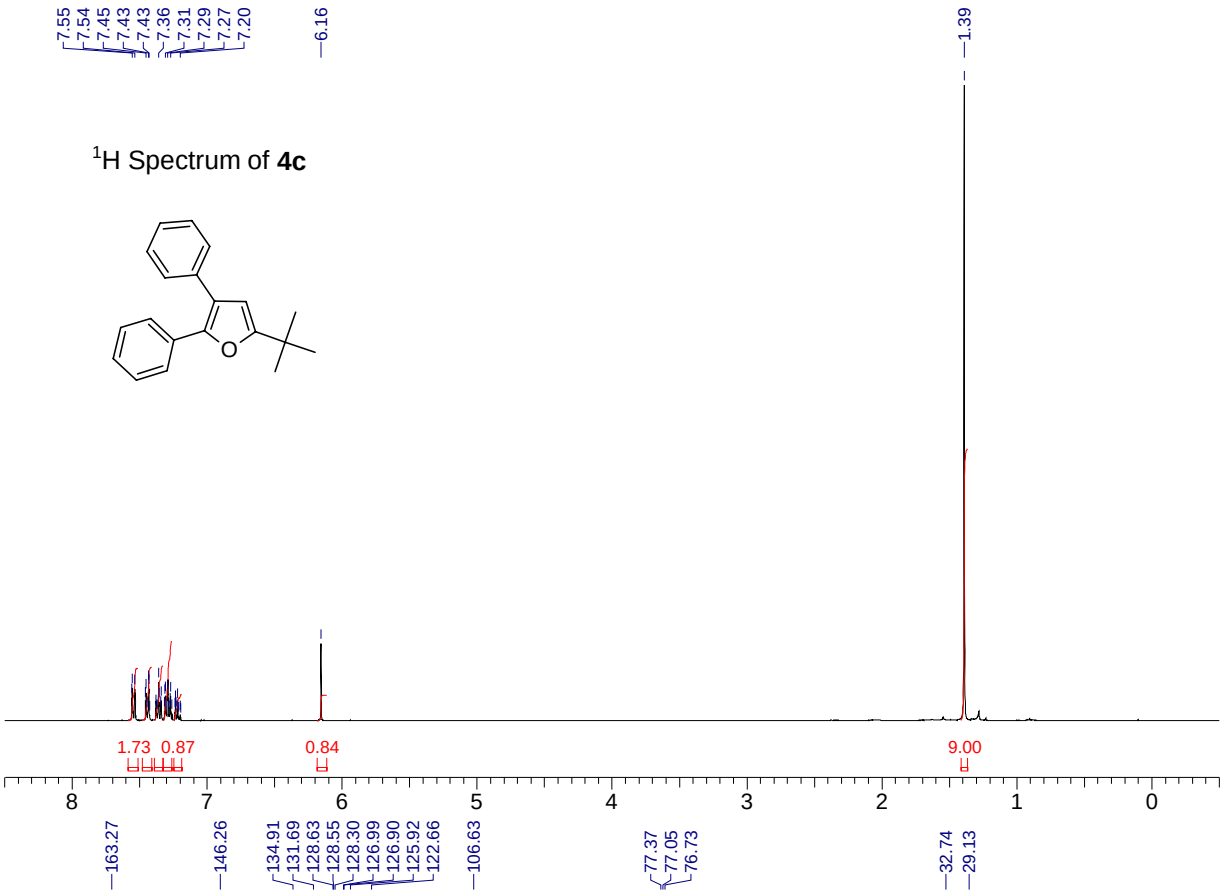
***5-methyl-2,3-diphenylfuran*[15] (4b) *from 5,5-diphenylpent-3-yn-2-one* (5b):**

Cycloisomerization of **5b** into furan **4b** was performed similar to that reported above for allenyl ketone **3b**. 5mol% of $In(OTf)_3$ (14 mg, 0.025 mmol) was used as the catalyst. The reaction was performed on 0.5 mmol scale by heating a 0.1M solution of **5b** in toluene at 100°C for 5 hours. The reaction mixture was treated as described in typical procedure to afford 62.2 mg (0.266 mmol, 53%) of 5-methyl-2,3-diphenylfuran **4b** (see page S9 for analytical data).

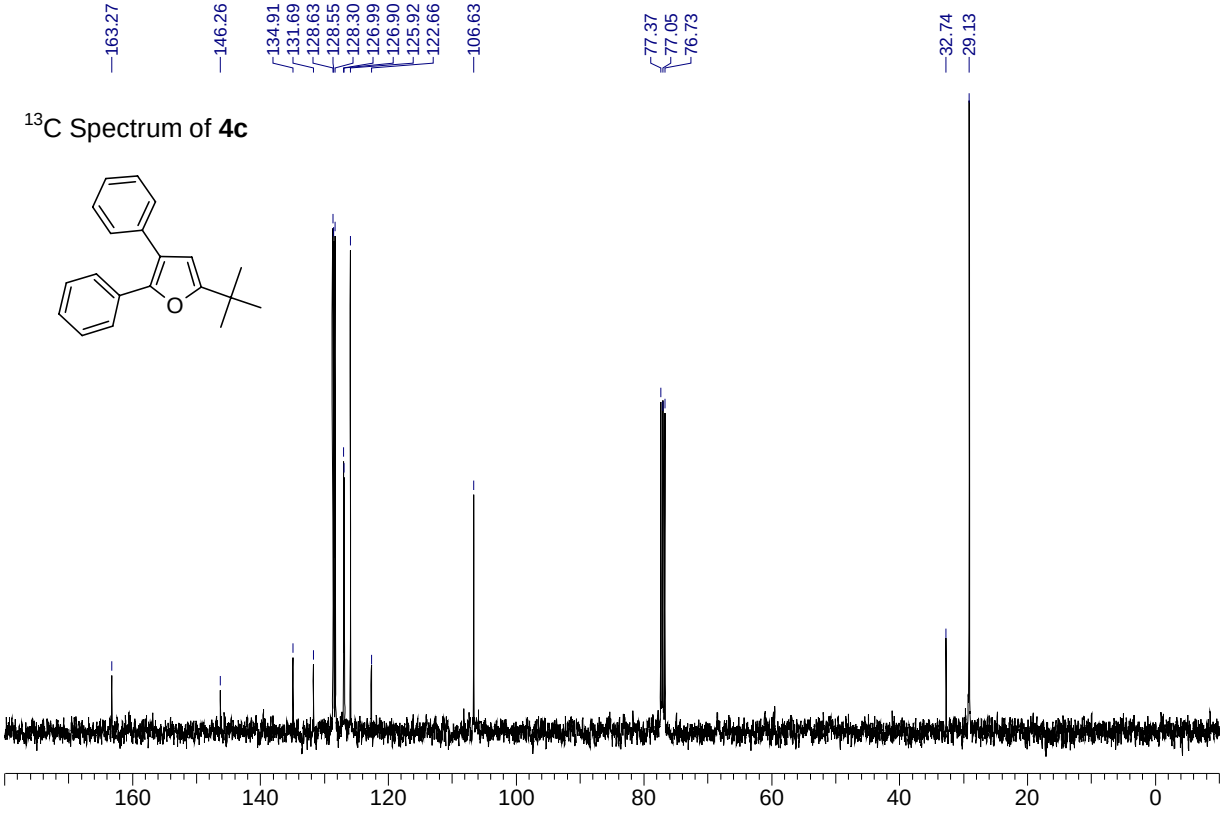
***2,3-dimethyl-5-phenylfuran*[22] (4i):**

Prepared according to the typical procedure. 5mol% of $In(OTf)_3$ (5.6 mg, 0.01 mmol) was used as the catalyst. The reaction was performed on 0.2 mmol scale by heating a 0.05M solution of 4-methyl-1-phenylpenta-2,3-dien-1-one **3i** in toluene at 120°C for 24 hours. The reaction mixture was treated as described in typical procedure to give approximately 10.4% yield of **4i** as it was determined by ^{1}H NMR.

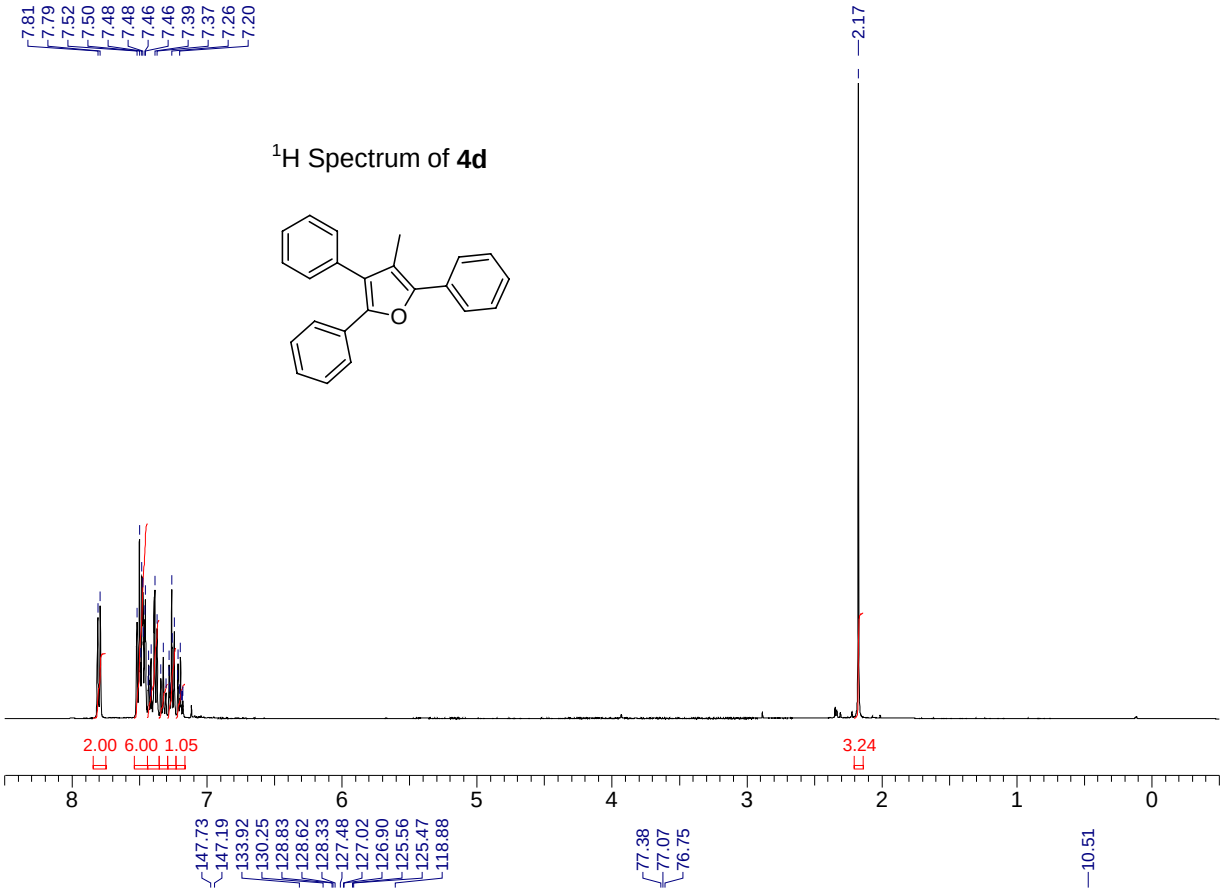
[22] Seiller, B.; Bruneau, C.; Dixneuf, P. H. *Tetrahedron* **1995**, *51*, 13089.



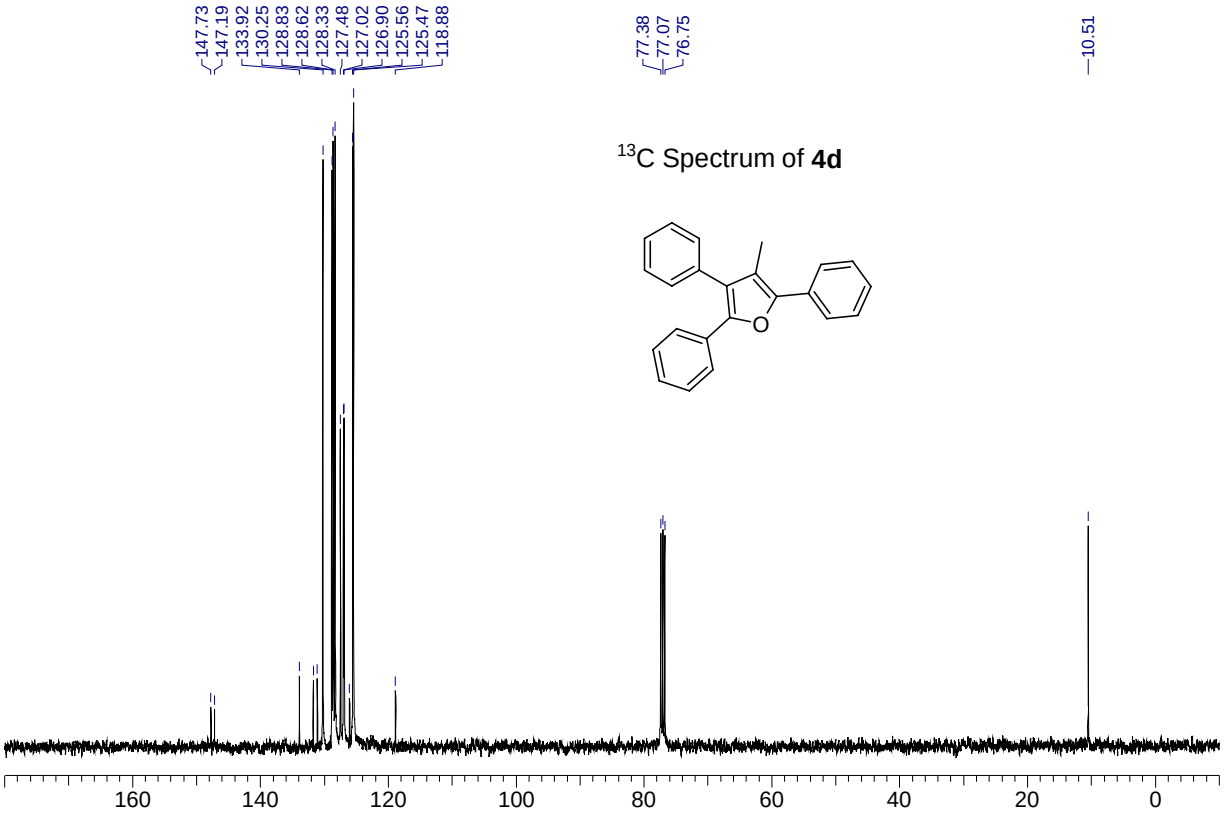
^{1}H Spectrum of **4c**



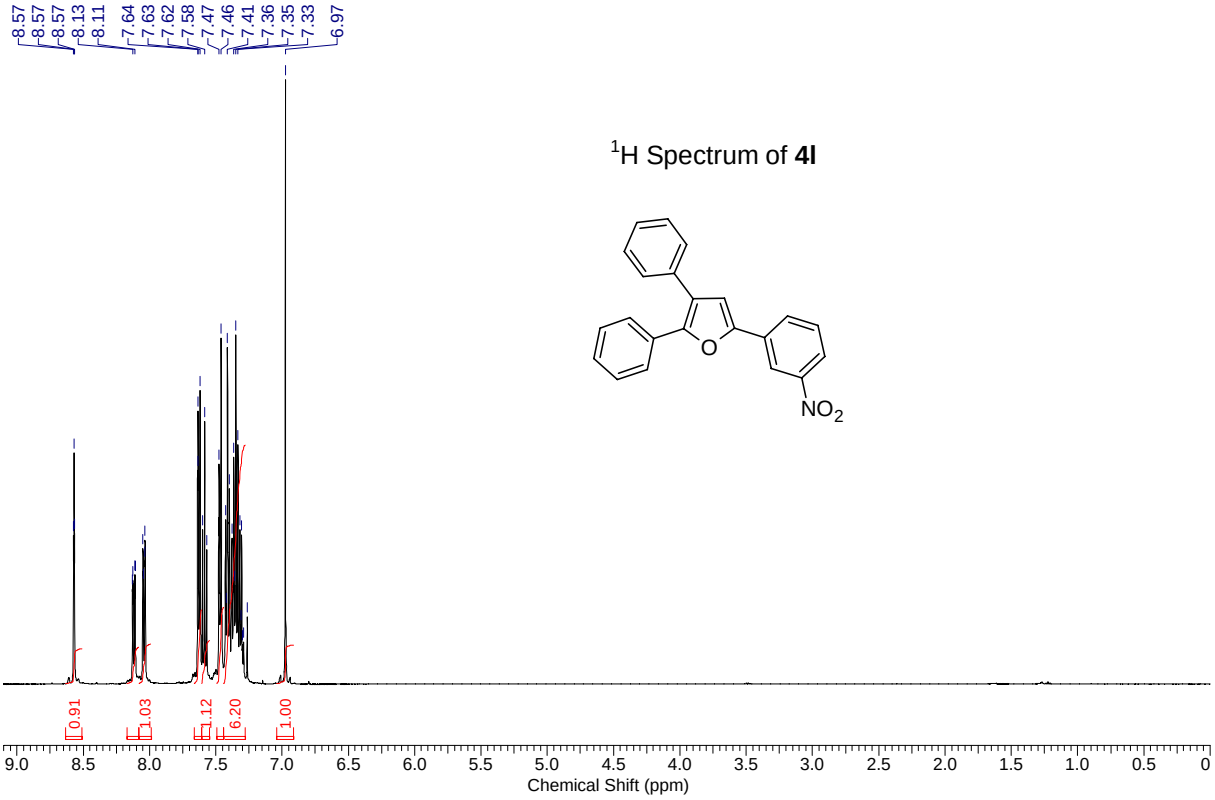
^{13}C Spectrum of **4c**



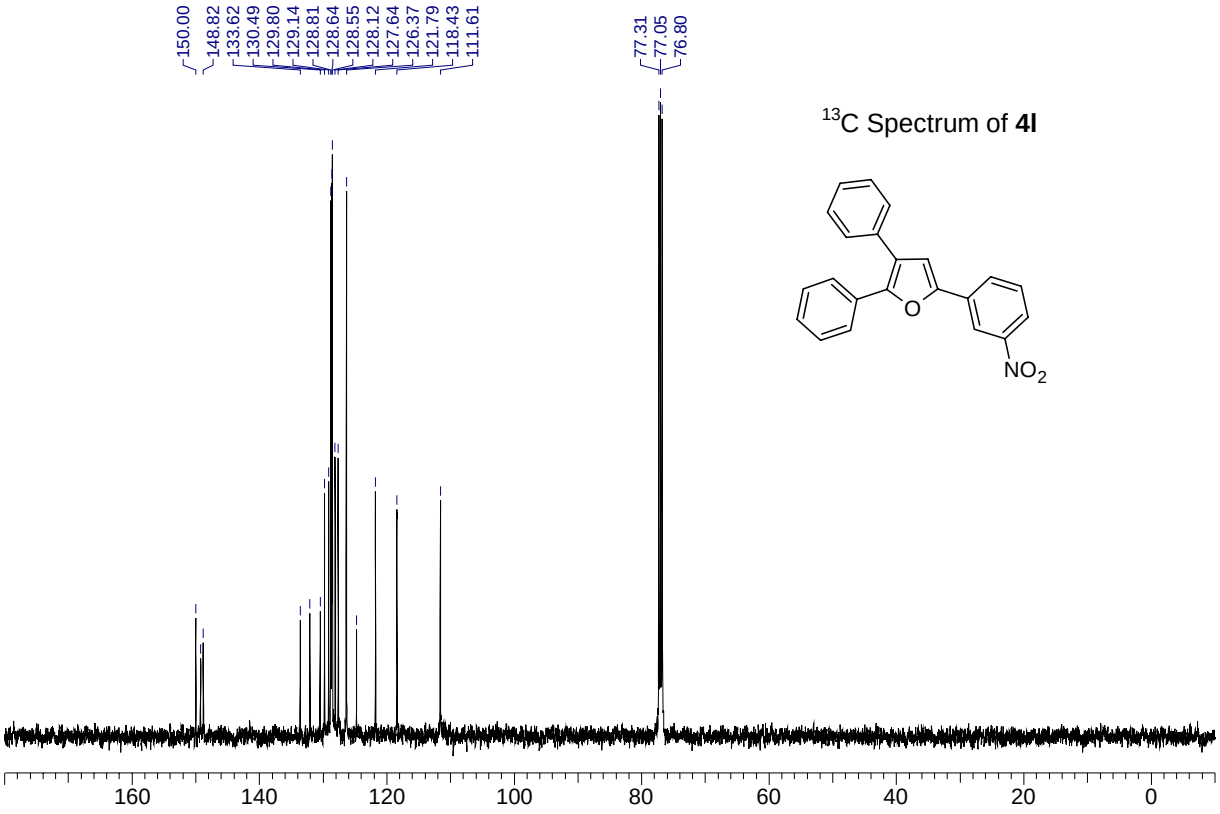
^{1}H Spectrum of **4d**



^{13}C Spectrum of **4d**



^{1}H Spectrum of **4l**



^{13}C Spectrum of **4l**