Electronic Supplementary Information

Nucleophilic Conjugate 1,3-Addition of Phosphines to Oligoynoates

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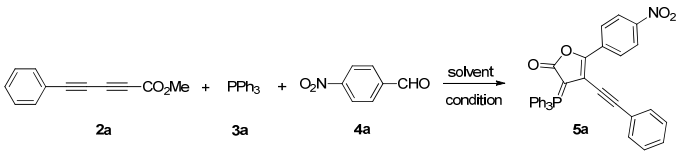
Content

Table S1. Conditions optimization.[a]



entry	molar ratio **2a**:**3a**:**4a**	solvent	t (h)	Temp (^{o}C)	Yield[a]
1	1:1:1	THF	24	20	38(55)
2	1:1:1	DCM	24	20	42(66)
3	1:1:1	*o*-DCB	24	20	47(64)
4	1:1:1	*o*-DCB	2	60	43(61)
5	1:1:1	*o*-DCB	1	80	47(78)
6	1:1:1	*o*-DCB	2	80	53(61)
7	1:1:1	*o*-DCB	3	80	48(66)
8	1.5:1.5:1	*o*-DCB	2	80	65
9	2:2:1	*o*-DCB	2	80	67
10[c]	1.5:1.5:1	*o*-DCB	2	80	65

[a] Reaction was carried out by initial slow addition of **2a** in anhydrous solvents to a solution of **3a** and **4a** in anhydrous solvents at specified reaction temperature unless otherwise noted. [b] Yields (%) were determined by ^{1}H NMR using mesitylene as an internal standard after isolation of products by column chromatography. Yields in parentheses are based on recovered aldehydes. [c] All reactants are mixed and heated simultaneously.

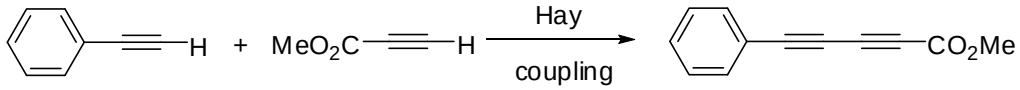
General methods. All reactions were performed under argon. Anhydrous benzene and THF were distilled from sodium/benzophenone under argon. Anhydrous 1,2-dichlorobenzene (*o*-DCB) and dichloromethane (DCM) were distilled from CaH_2 under argon. The chemical shifts of ^{31}P NMR were taken with reference to 85% of H_3PO_4 in D_2O and those of ^{1}H and ^{13}C with reference to TMS or $CHCl_3$.

General procedure for synthesis of diynoates 2a-j and 2n

First, Hay catalyst is prepared by stirring 20 mol % of CuCl (1.26 mmol) and 3 mol % of TMEDA (tetramethylethylenediamine, 0.19 mmol) in acetone (15 mL) with simultaneous bubbling of a stream of O_2 for 40 min. Another solution of aryl acetylene **A1-7** or **C** (6.32 mmol) and methyl or ethyl propiolate (**B1** and **B2** respectively, 6.32 mmol) in anhydrous acetone (20 mL) was then introduced into the flask containing heterogeneous Hay catalysts in acetone and then stirred for overnight. The resulting mixtures were chromatographed through a silica gel column to yield corresponding pale yellow oil or solid hetero-coupling products. The obtained hetero-coupling product yields are 13–48% in one step and the major product is that from homo-coupling of alkyl propiolates (23–40%). The diynoates can also be prepared from a multi-step process starting with substituted aryl halides for preparation of arylpropargyl aldehydes.[1] Subsequent Corey-Fuchs reaction provided dibromoalkenes.[2] Further treatment of dibromoalkenes with *n*-butyl lithium and quenched with methyl or ethyl chloro formates generated desired diynoates. However, some of the halo-substituted diynoates cannot be prepared with the second approach due to side-reactions with *n*-butyl lithium upon generating alkynilides. The direct Hay coupling method is relatively more step-efficient than multi-step process. Physical data of new diynoates are of followings.

Methyl 5-phenylpenta-2,4-diynoate (2a):

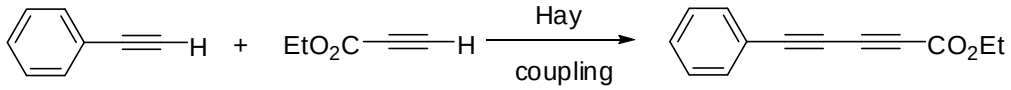
(1) Nowak-Król, A.; Koszarna, B.; Yoo, S. Y.; Chromiński, J.; Węcławski, M. K.; Lee, C.-H.; Gryko, D. T. *J. Org. Chem.* **2011**, *76*, 2627-2634.
(2) Gibtner, T.; Hampel, F.; Gisselbrecht, J.-P.; Hirsch, A. *Chem. Eur. J.*, **2002**, *68*, 408-432.



A1 **B1** **2a**

Pale yellow oil. R_f = 0.35 (DCM/hexanes, 1:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 3H), 7.40–7.54 (m, 5H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) 52.9, 71.3, 71.4, 72.0, 83.6, 119.9, 128.6, 130.5, 133.1, 153.4; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1715, 2224 cm^{-1}; HRMS (EI^+), calcd for $C_{16}H_{16}O_2$ (M^+) 184.0524, found 184.0524.

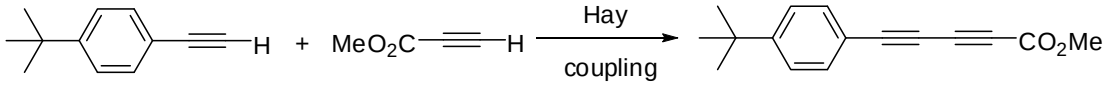
Ethyl 5-phenylpenta-2,4-diynoate (2b):



A1 **B2** **2b**

Pale yellow oil. R_f = 0.34 (DCM/hexanes, 1:3). Spectral data are identical to those of reported.[3]

Methyl 5-(4-*tert*-butylphenyl)penta-2,4-diynoate (2c):

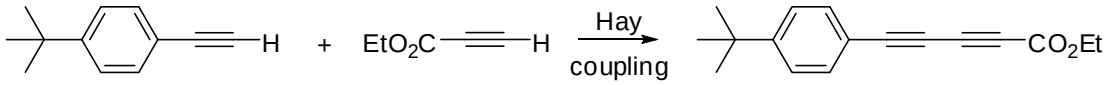


A2 **B1** **2c**

Pale yellow oil. R_f = 0.55 (DCM/hexanes, 1:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29 (s, 9H), 3.79 (s, 3H), 7.36 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) 29.7, 35.1, 53.0, 71.3, 71.5, 71.7, 84.2, 116.8, 125.7, 133.0, 153.4, 154.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1716, 2224 cm^{-1}; HRMS (EI^+), calcd for $C_{16}H_{16}O_2$ (M^+) 240.1159, found 240.1143.

Ethyl 5-(4-*tert*-butylphenyl)penta-2,4-diynoate (2d):

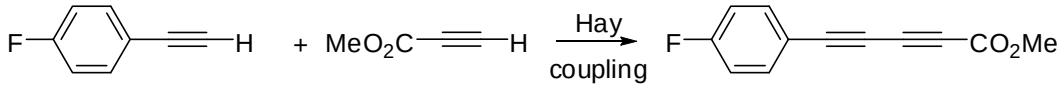
(3) (a) Liang, Y.; Tao, L.-M.; Zhang, Y.-H.; Li, J.-H. *Synthesis*, **2008**, *24*, 3988. (b) Hirsh, A.; Vostrowsky, O. *Science of Synthesis*, **2008**, *43*, 37. (c) Aitken, R. A.; Seth, S. *J. Chem. Soc., Perkin Trans.* 1, **1994**, *17*, 2461. (d) Aitken, R. A.; Seth, S. *Synlett*, **1990**, *4*, 213.



A2 **B2** **2d**

Pale yellow oil. R_f = 0.31 (DCM/hexanes, 1:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 9H), 1.33 (t, J = 7.1 Hz, 3H), 4.27 (q, J = 7.1 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 14.0, 31.0, 35.0, 62.4, 71.2, 71.6, 77.2, 83.9, 116.8, 125.6, 132.9, 153.0, 154.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1714, 2226 cm^{-1}; HRMS (ESI^+), calcd for $C_{17}H_{18}O_2$ (M^+) 254.1307 found 254.1308.

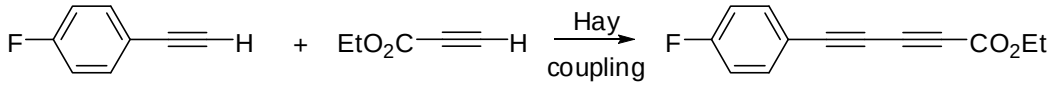
Methyl 5-(4-fluorophenyl)penta-2,4-diynoate (2e):



A3 **B1** **2e**

Pale yellow oil. R_f = 0.35 (DCM/hexanes, 1:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3H), 7.03–7.09 (m, 2H), 7.52–7.56 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 53.0, 71.0, 71.4, 71.8, 82.5, 116.0 (d, $^4J_{FC}$ = 3.4 Hz), 116.1 (d, $^2J_{FC}$ = 22.4 Hz), 135.3 (d, $^3J_{FC}$ = 8.8 Hz), 153.2, 163.7 (d, $^1J_{FC}$ = 253.8 Hz) ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1711, 2230 cm^{-1}; HRMS (ESI^+), calcd for $C_{12}H_7FO_2$ (M^+) 202.0430 found 202.0427.

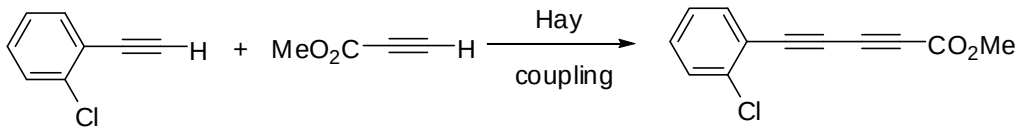
Ethyl 5-(4-fluorophenyl)penta-2,4-diynoate (2f):



A3 **B2** **2f**

Pale yellow oil. R_f = 0.23 (DCM/hexanes, 1:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (t, J = 7.2 Hz , 3H), 4.27 (q, J = 7.2 Hz, 2H), 7.02–7.10 (m, 2H), 7.51–7.57 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 13.8, 62.4, 70.5, 71.8, 77.2, 82.3, 116.0 (d, $^4J_{FC}$ = 3.6 Hz), 116.1 (d, $^2J_{FC}$ = 22.4 Hz), 135.2 (d, $^3J_{FC}$ = 8.8 Hz), 152.7, 163.6 (d, $^1J_{FC}$ = 253.8 Hz) ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1703, 2231 cm^{-1}; HRMS (ESI^+), calcd for $C_{13}H_9FO_2$ (M^+) 216.0587 found 216.0586.

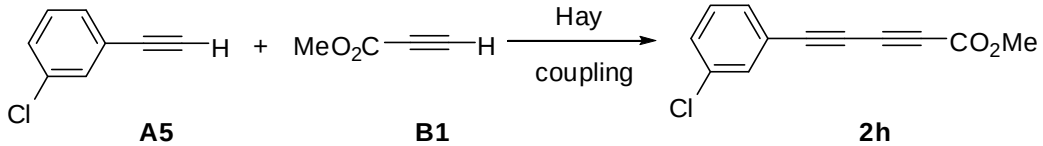
Methyl 5-(2-chlorophenyl)penta-2,4-diynoate (2g):



A4 **B1** **2g**

Pale yellow solid (m.p. 98–100 °C). R_f = 0.33 (DCM/hexanes, 1:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 3H), 7.23–7.27 (m, 1H), 7.33–7.43 (m, 2H), 7.54–7.57 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 53.1, 70.7, 72.6, 76.4, 79.8, 120.2, 126.7, 129.6, 131.4, 134.8, 137.6, 153.1 ppm; FT-IR (KBr) $\tilde{v}$ (cm^{-1}) 1703, 2228 cm^{-1}; HRMS (EI^+), calcd for $C_{12}H_7ClO_2$ (M^+) 218.0135 found 218.0134.

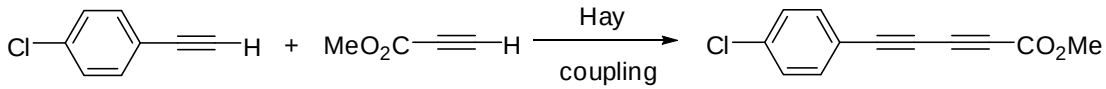
Methyl 5-(3-chlorophenyl)penta-2,4-diynoate (2h):



A5 **B1** **2h**

Pale yellow solid (m.p. 88–90 °C). R_f = 0.36 (DCM/hexanes, 1:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82 (s, 3H), 7.28–7.32 (m, 1H), 7.39–7.43 (m, 2H), 7.50 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 53.0, 70.6, 71.9, 72.9, 81.7, 121.6, 129.8, 130.7, 131.1, 132.6, 134.4, 153.0 ppm; FT-IR (KBr) $\tilde{v}$ (cm^{-1}) 1706, 2231 cm^{-1}; HRMS (EI^+), calcd for $C_{12}H_7ClO_2$ (M^+) 218.0135 found 218.0138.

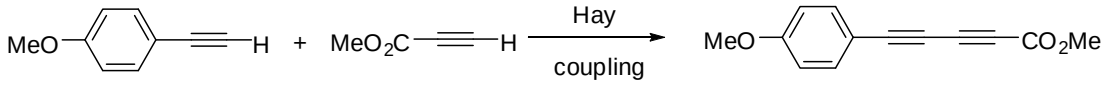
Methyl 5-(4-chlorophenyl)penta-2,4-diynoate (2i):



A6 **B1** **2i**

Pale yellow solid (m.p. 116–118 °C). R_f = 0.50 (DCM/hexanes, 1:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 3H), 7.34 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 7.8 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 53.1, 70.9, 71.9, 72.9, 82.3, 118.4, 129.0, 134.2, 136.8, 153.2 ppm; FT-IR (KBr) $\tilde{v}$ (cm^{-1}) 1712, 2231 cm^{-1}; HRMS (EI^+), calcd for $C_{12}H_7ClO_2$ (M^+) 218.0135 found 218.0131.

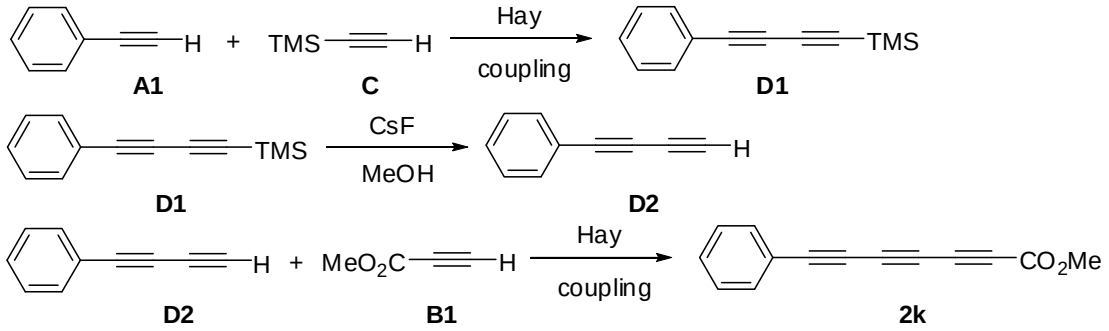
Methyl 5-(4-methoxyphenyl)penta-2,4-diynoate (2j):



A7 **B1** **2j**

Pale yellow solid (m.p. 79–81 °C). R_f = 0.18 (DCM/hexanes, 1:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.83 (s, 3H), 6.86 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 52.9, 55.3, 71.1, 71.2, 71.8, 84.2, 111.5, 114.3, 134.9, 153.4, 161.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1710, 2224 cm^{-1}; HRMS (EI^+), calcd for $C_{13}H_{10}O_3$ (M^+) 214.0630 found 214.0621.

Procedure and spectral data of methyl 7-phenylhepta-2,4,6-triynoate (2k):



A1 **C** **D1**

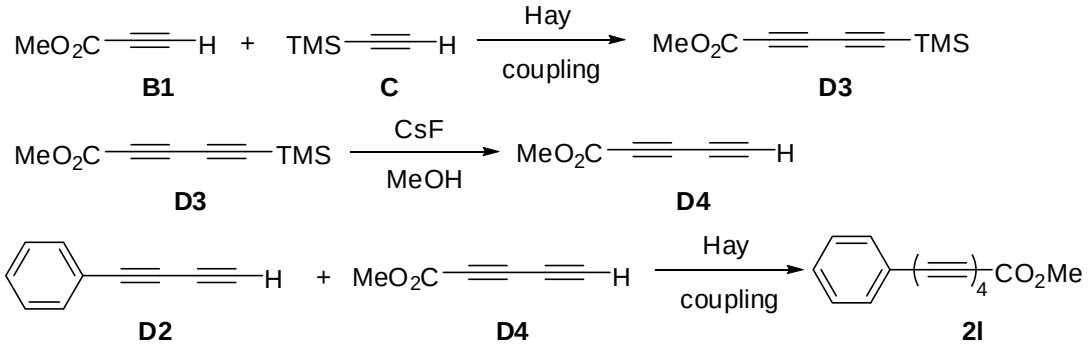
D1 **D2**

D2 **B1** **2k**

First, Hay catalyst was prepared by stirring CuCl (117 mg, 1.19 mmol) and TMEDA (tetramethylethylenediamine, 60 μL, 0.400 mmol) in anhydrous acetone (15 mL) for 40 min at room temperature. A solution of phenyl acetylene **A1** (600 mg, 5.88 mmol) and (trimethylsilyl)acetylene **C** (570 mg, 5.81 mmol) in anhydrous acetone (10 mL) was introduced into the flask containing the prepared Hay catalysts. After bubbling a stream of O_2 for five minutes through a stainless needle, the mixture was stirred for 12 h, and then the solution was concentrated and passed through a short SiO_2 column for filtering off copper powder. Hexanes were then used as an eluent to get compound **D1** (TLC, R_f= 0.5, hexanes). Compound **D2** was obtained by adding a 5 mL methanol solution of CsF (383 mg, 2.52 mmol) to **D1** in methanol (5 mL) and stirred for 2 h before subjected to SiO_2 chromatography. Next, a solution of methyl propiolate **B1** (435 mg, 5.18 mmol) and compound **D2** (654 mg, 5.19 mmol) in 5 mL of anhydrous acetone was added to prepared Hay catalyst again [(CuCl, 15.8 mg, 0.161 mmol) and

TMEDA (4 μL, 0.027 mmol)] for further hetero-coupling reaction. The reaction mixture was subjected to SiO_2 chromatography to give compound **2k** (226 mg, 21 %) as an yellow oil with dichloromethane:hexanes = 1:3 as eluents. (TLC, R_f = 0.38). After characterization, compound **2k** was stored in *o*-DCB solution at –18 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 3.76 (s, 3H), 7.29–7.52 (m, 5H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 52.9, 64.1, 68.0, 68.2, 71.0, 73.3, 79.9, 119.5, 128.4, 130.4, 133.1, 152.5 ppm; FTIR (KBr) $\tilde{\nu}$ (cm^{-1}) 1714, 2106, 2183 cm^{-1}; HRMS (EI^+), calcd for $C_{14}H_9O_2$ (M^+) 208.0524 found 208.0521.

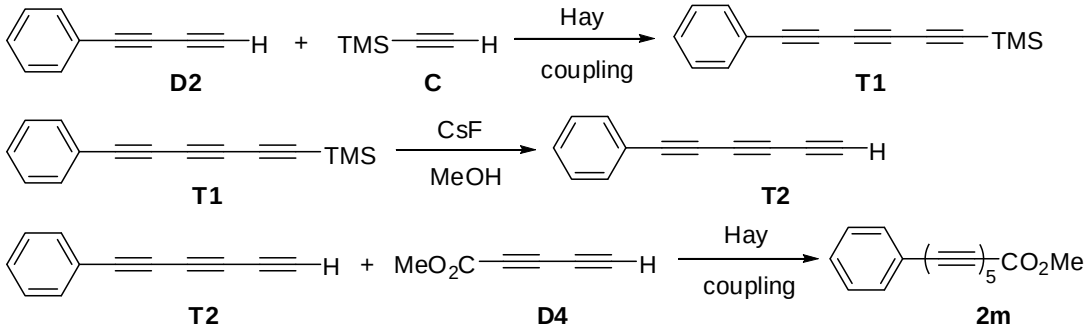
Procedure and spectral data of methyl 9-phenylnona-2,4,6,8-tetraynoate (2l):



A solution of methyl propiolate **B1** (500 mg, 6.01 mmol) and (trimethylsilyl)acetylene **C** (590 mg, 6.02 mmol) in anhydrous acetone (5 mL) was added to the prepared Hay catalyst [CuCl (114 mg, 1.16 mmol) and TMEDA (tetramethylethylenediamine, 30 μL, 0.200 mmol) in acetone (15 mL)]. After bubbling a stream of O_2 for five minutes, the mixture was stirred for 12 h, and then concentrated at reduced pressure. Copper powder was removed by passing the mixture through a short SiO_2 column and the filtrate was collected. The filtrate was subjected to chromatography with hexanes and dichloromethane (1:1) as eluents to obtain compound **D3** (TLC, R_f = 0.45) in 20 % yield (216 mg). Next, compound **D4** was obtained by adding a 5 mL methanol solution of CsF (378 mg, 2.52 mmol) to **D3** in methanol (5 mL), and then partitioned with water and CH_2Cl_2. Last, compound **D4** (67 mg, 0.60 mmol) and compound **D2**

(79 mg, 0.60 mmol) in 5 mL of anhydrous acetone was added to the prepared Hay catalyst [CuCl (12.2 mg, 0.124 mmol) and TMEDA (1.25 μL, 8.00 μmol) in 15 mL acetone] for last coupling reaction. The mixture was concentrated at reduced pressure and subjected to SiO_2 chromatography using dichloromethane: hexanes = 1:3 as eluents (TLC, R_f= 0.36), giving compound **2l** (22 mg, 16 %) as an yellow oil. After characterization, compound **2l** was stored in *o*-DCB solution at –18 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3H), 7.33–7.44 (m, 3H), 7.54–7.57 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 53.2, 61.4, 64.9, 66.1, 67.0, 68.9, 71.1, 73.8, 78.8, 119.7, 128.6, 130.5, 133.4, 152.5 ppm; FTIR (KBr) $\tilde{\nu}$ (cm^{-1}) 1714, 2139, 2173 cm^{-1}; HRMS (EI^+), calcd for $C_{16}H_8O_2$ (M^+) 232.0524 found 232.0517.

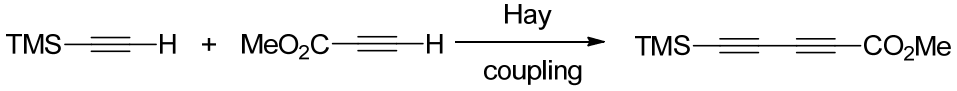
Procedure and spectral data of methyl 11-phenylundeca-2,4,6,8,10-pentaynoate (2m):



Compound **D2** (1.20 g, 9.52 mmol) and (trimethylsilyl)acetylene **C** (0.940 g, 9.59 mmol) was added to a prepared Hay catalyst, [CuCl (471 mg, 4.76 mmol) and TMEDA (110 μL, 0.72 mmol)], in a round-bottom flask and bubbled O_2 for 40 minutes. After stirred for 12 h, the solution was concentrated and passed through a short SiO_2 column to filter off copper powder. The filtrate was subjected to SiO_2 chromatography using hexanes as eluents to give compound **T1** (R_f = 0.45, hexanes). Compound **T2** was obtained by adding a 5 mL of methanol solution of CsF (1.40 g, 9.20 mmol) to **T1** in methanol (10 mL). The mixture was stirred for 2 h and then

concentrated prior to SiO_2 chromatography using hexanes as eluents. Last, pentayne **2m** was obtained by coupling of **T2** and **D4**. Compound **T2** (255 mg, 1.70 mmol) and compound **D4** (130 mg, 1.20 mmol) was added to a prepared Hay catalyst, CuCl (24 mg, 0.3 mmol) and TMEDA (5 μL, 0.04 mmol) in oxygen atmosphere. The mixture was stirred for 12 h and passed through a short SiO_2 column for filtering off copper powder. After chromatography with CH_2Cl_2:hexanes = 1:2 as eluents, product **2m** was isolated in 17% yield (52 mg; R_f = 0.43 in CH_2Cl_2:hexanes = 1 ∶ 2) as an yellow oil. After characterization, compound **2m** was stored in *o*-DCB solution at –18 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 3.79 (s, 3H), 7.33 (t, J = 7.5 Hz, 2H), 7.40–7.44 (m, 1H), 7.52–7.54 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) 53.4, 60.5, 63.3, 63.7, 65.6, 66.5, 66.6, 68.8, 71.0, 74.0, 78.2, 119.8, 128.7, 130.6, 133.5, 152.5 ppm; FTIR (KBr) $\tilde{\nu}$ (cm^{-1}) 1699, 2100, 2139, 2191 cm^{-1}; HRMS (EI^+) calcd for $C_{18}H_8O_2$ (M^+) 256.0524 found 256.0523.

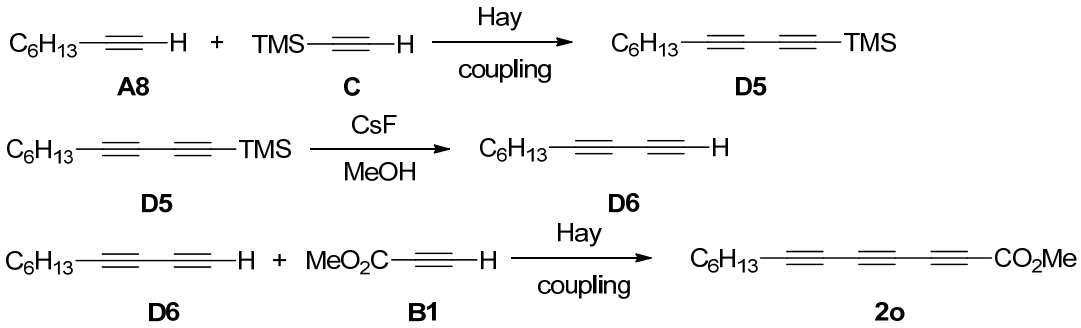
Procedure and spectral data of methyl 5-(trimethylsilyl)penta-2,4-diynoate (2n)



C **B1** **2n**

Pale yellow oil. R_f = 0.48 (DCM/hexanes, 1:2). ^1H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 9H), 3.76 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ -0.89, 53.0 66.3, 71.0, 85.5, 94.6, 153.0; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1721, 2111, 2232 cm^{-1}; HRMS (ESI^+), calcd for $C_9H_{13}O_2Si$ (M^+) 181.0679 found 181.0685.

Procedure and spectral data of methyl trideca-2,4,6-triynoate (2o):



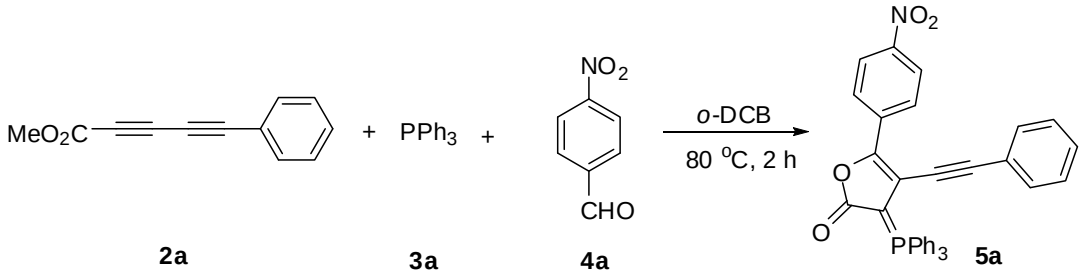
First, Hay catalyst was prepared by stirring CuCl (117 mg, 1.19 mmol) and TMEDA (tetramethylethylenediamine, 60 μL, 0.400 mmol) in anhydrous acetone (15 mL) for 40 min at room temperature. A solution of oct-1-yne **A8** (647 mg, 5.88 mmol) and (trimethylsilyl)acetylene **C** (570 mg, 5.81 mmol) in anhydrous acetone (10 mL) was introduced into the flask containing the prepared Hay catalysts. After bubbling a stream of O_2 for five minutes through a stainless needle, the mixture was stirred for 12 h, and then the solution was concentrated and passed through a short SiO_2 column for filtering out copper powder. Hexanes were then used as an eluent to get compound **D5** (TLC, R_f = 0.5, hexanes). Compound **D6** was obtained by adding a 5 mL methanol solution of CsF (383 mg, 2.52 mmol) to **D5** in methanol (5 mL) and stirred for 2 h before subjected to SiO_2 chromatography. Next, a solution of methyl propiolate **B1** (435 mg, 5.18 mmol) and compound **D6** (654 mg, 5.19 mmol) in 5 mL of anhydrous acetone was added to prepared Hay catalyst again [(CuCl 15.8 mg, 0.161 mmol) and TMEDA (4 μL, 0.027 mmol)] for further hetero-coupling reaction. The reaction mixture was subjected to SiO_2 chromatography to give compound **2o** (430 mg, 38 %) as an yellow oil with dichloromethane:hexanes = 1:3 as eluents. (TLC, R_f = 0.36). After characterization, compound **2o** was stored in *o*-DCB solution at –18 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.24–1.40 (m, 6H), 1.55 (quint, J = 7.3 Hz, 2H), 2.33 (t, J = 6.8 Hz, 2H), 3.76 (s, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 13.8, 19.4, 22.4, 27.6, 28.4, 31.1, 52.9, 57.3, 64.8, 65.0, 69.2, 71.5, 84.6, 152.7 ppm; FTIR (KBr) $\tilde{\nu}$ (cm^{-1}) 1716, 2113, 2200 cm^{-1}; HRMS (ESI^{+}), calcd for

$C_{14}H_{17}O_2$ (M^++1) 217.1223 found 217.1222.

General procedure for synthesis 5a to 5ae, 5ay and 5aab

To 3.5 mL of anhydrous *o*-DCB solution containing phoshpine **3** (0.21 mmol) and aldehyde **4** (0.14 mmol) at 80 °C was added **2** (0.21 mmol in 1.5 mL of *o*-DCB) *via* a digital syringe pump in 1 h (for syntheses of **5g** and **5u**; these two reactions were carried out at r.t.). Upon completion of injection, the mixture was stirred for another 1 h. The mixture was then subjected to flash SiO_2 chromatography with hexanes/EA as eluents to give products **5**.

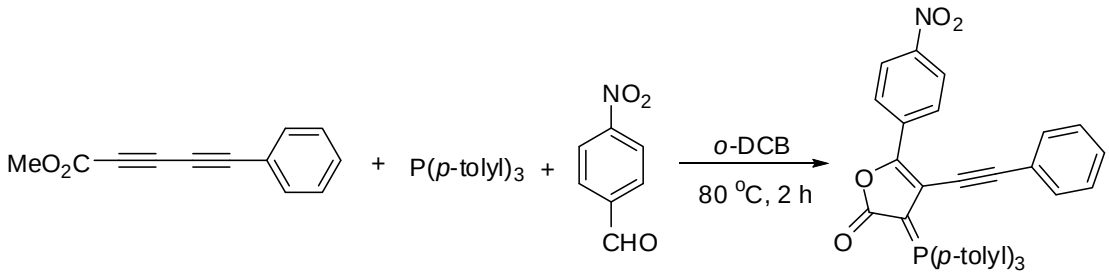
5-(4-nitrophenyl)-4-(phenylethynyl)-3-(triphenylphosphoranylidene)furan-2(3H)-one (5a):



2a **3a** **4a** **5a**

Red solid (m.p. 252–255 °C). R_f = 0.25 (EA/hexanes = 2:1). Isolated yield 65% (51 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78–6.81 (m, 2H), 7.15–7.24 (m, 4H), 7.51–7.57 (m, 6H), 7.61–7.68 (m, 2H), 7.72–7.80 (m, 6H), 8.09–8.18 (m, 4H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 57.3 (d, $^1J_{PC}$ = 134.2 Hz), 83.4, 99.3, 108.4 (d, $^2J_{PC}$ = 11.5 Hz), 122.3, 122.6 (d, $^1J_{PC}$ = 93.8 Hz), 123.4, 124.0, 128.1, 128.4, 129.1 (d, $^3J_{PC}$ = 13.0 Hz), 130.9, 133.4 (d, $^4J_{PC}$ = 3.0 Hz), 134.2 (d, $^2J_{PC}$ = 10.6 Hz), 136.3, 141.6 (d, $^3J_{PC}$ = 10.9 Hz), 144.4, 169.1 (d, $^2J_{PC}$ = 18.1 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{24}NO_4P$ (M^+) 565.1443 found 565.1449.

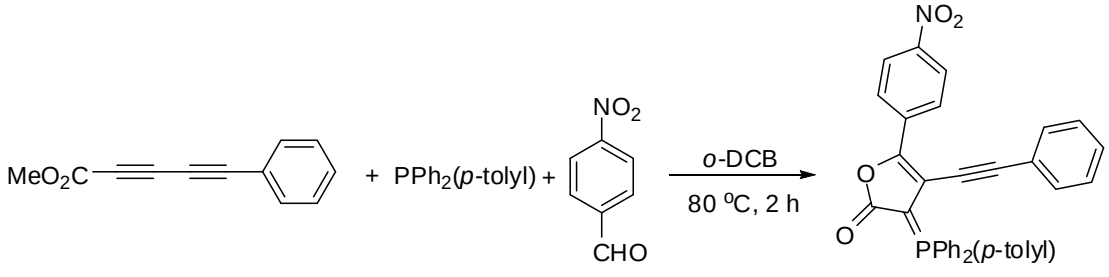
5-(4-nitrophenyl)-4-(phenylethynyl)-3-(tri-*p*-tolylphosphoranylidene)furan-2(3H)-one (5b):



2a **3b** **4a** **5b**

Red solid (m.p. 233–235 °C). R_f = 0.28 (EA/hexanes = 1.5:1). Isolated yield 66% (56 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 9H), 6.52 (dd, *J* = 1.7, 8.1 Hz, 2H), 7.20–7.26 (m, 3H), 7.30 (dd, *J* = 2.8, 8.1 Hz, 6H), 7.61 (d, *J* = 13.1 Hz, 3H), 7.63 (d, *J* = 13.1 Hz, 3H), 8.09 (d, *J* = 9.3 Hz, 2H), 8.15 (d, *J* = 9.3 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) 21.6, 58.6 (d, $^1J_{PC}$ = 134.3 Hz), 83.5, 98.9, 108.9 (d, $^2J_{PC}$ = 11.5 Hz), 119.6 (d, $^1J_{PC}$ = 96.4 Hz), 122.7, 123.3, 124.0, 128.1, 128.3, 129.8 (d, $^3J_{PC}$ = 13.3 Hz), 131.0, 134.1 (d, $^2J_{PC}$ = 11.0 Hz), 136.5, 141.4 (d, $^3J_{PC}$ = 13.0 Hz), 144.2, 144.3, 169.2 (d, $^2J_{PC}$ = 17.5 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{39}H_{30}NO_4P$ (M^+) 607.1913 found 607.1911.

3-(diphenyl(*p*-tolyl)phosphoranylidene)-5-(4-nitrophenyl)-4-(phenylethynyl) furan-2(3H)-one (5c):

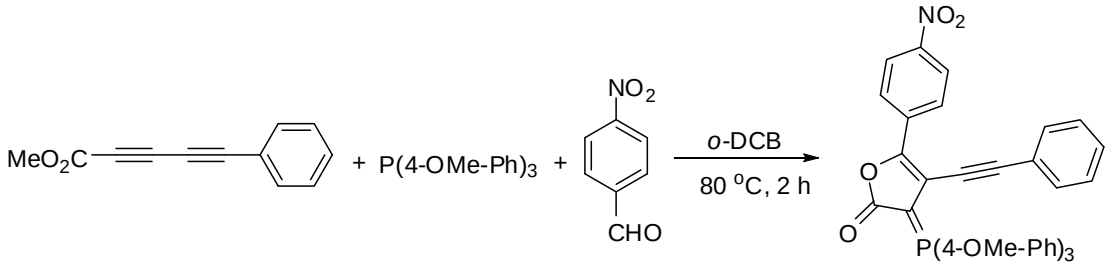


2a **3c** **4a** **5c**

Red solid (m.p. 217–220 °C). R_f = 0.31 (EA/hexanes, 2:1). Isolated yield 73% (59 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 6.82 (d, *J* = 6.9 Hz, 2H), 7.16–7.24 (m, 3H), 7.31–7.33 (m, 2H), 7.53–7.65 (m, 8H), 7.77 (d, *J* = 7.5, 13.0 Hz, 4H), 8.10 (d, *J* = 9.1 Hz, 2H), 8.15 (d, *J* = 9.1 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 21.5,

57.9 (d, $^{1}J_{PC}$ = 133.3 Hz), 83.2, 99.1, 108.6 (d, $^{2}J_{PC}$ = 11.6 Hz), 118.6 (d, $^{1}J_{PC}$ = 96.3 Hz), 122.3, 122.8 (d, $^{1}J_{PC}$ = 94.0 Hz), 123.2, 123.9, 128.0, 128.2, 129.0 (d, $^{3}J_{PC}$ = 13.0 Hz), 129.8 (d, $^{3}J_{PC}$ = 13.4 Hz), 130.8, 133.2 (d, $^{4}J_{PC}$ = 2.9 Hz), 134.0 (d, $^{2}J_{PC}$ = 10.7 Hz), 134.2, 136.3, 141.3 (d, $^{3}J_{PC}$ = 13.0 Hz), 144.2, 144.4 (d, $^{4}J_{PC}$ = 3.2 Hz), 169.1 (d, $^{2}J_{PC}$ = 17.8 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{37}H_{26}NO_4P$ (M^+) 579.1600 found 579.1604.

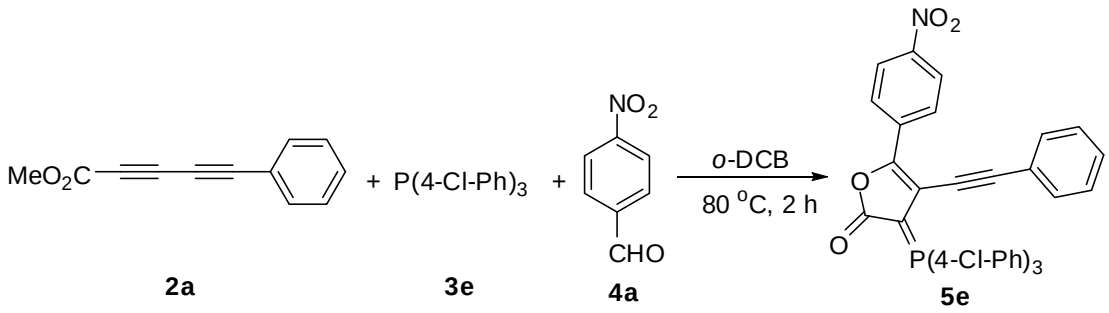
5-(4-nitrophenyl)-4-(phenylethynyl)-3-(tris(4-methoxyphenyl)phosphoranylidene) furan-2(3H)-one (5d):



2a **3d** **4a** **5d**

Red solid (m.p. 208–211 °C). R_f = 0.28 (EA/hexanes, 3:1). Isolated yield 62% (57 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 9H), 6.90 (dd, *J* = 1.5, 8.1 Hz, 2H), 7.00 (dd, *J* = 2.3, 8.9 Hz, 6H), 7.19–7.25 (m, 3H), 7.65 (dd, *J* = 8.8, 12.6 Hz, 6H), 8.09 (d, *J* = 9.2 Hz, 2H), 8.15 (d, *J* = 9.3 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) 55.4, 59.9 (d, $^{1}J_{PC}$ = 134.3 Hz), 83.6, 98.8, 108.9 (d, $^{2}J_{PC}$ = 11.0 Hz), 114.0 (d, $^{1}J_{PC}$ = 101.2 Hz), 114.8 (d, $^{3}J_{PC}$ = 14.0 Hz), 122.8, 123.3, 124.0, 128.1, 128.3, 131.1, 136.0 (d, $^{2}J_{PC}$ = 12.2 Hz), 136.5, 141.4 (d, $^{3}J_{PC}$ = 13.1 Hz), 144.3, 163.4, 169.3 (d, $^{2}J_{PC}$ = 18.6 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1677 cm^{-1}; HRMS (ESI^+), calcd for $C_{39}H_{30}NO_7P$ (M^+) 655.1760 found 655.1756.

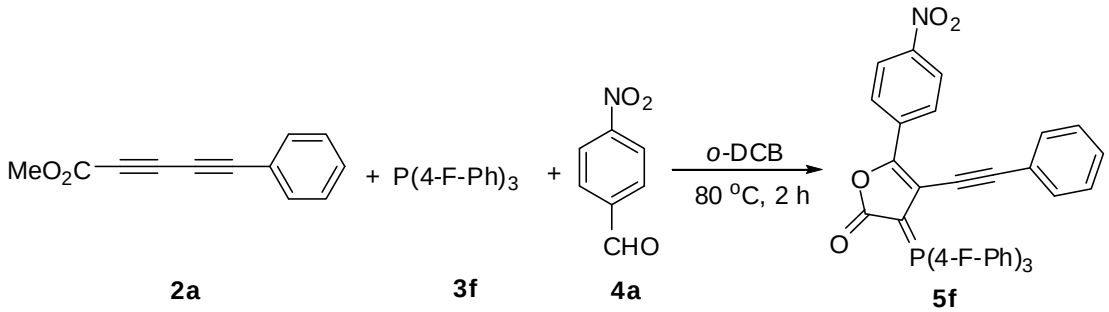
5-(4-nitrophenyl)-4-(phenylethynyl)-3-(tris(4-chlorophenyl)phosphoranylidene) furan-2(3H)-one (5e):



2a **3e** **4a** **5e**

Red solid (m.p. 215–217 °C). R_f = 0.35 (EA/hexanes, 1:1.5). Isolated yield 58% (54 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (d, J = 6.6 Hz, 2H), 7.26–7.30 (m, 4H), 7.52–7.58 (m, 5H), 7.67 (dd, J = 8.5, 12.7 Hz, 6H), 8.08 (d, J = 8.9 Hz, 2H), 8.16 (d, J = 8.9 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 56.0 (d, $^1J_{PC}$ = 136.4 Hz), 82.8, 99.4, 107.1 (d, $^2J_{PC}$ = 11.7 Hz), 120.4 (d, $^1J_{PC}$ = 96.7 Hz), 121.9, 123.3, 124.0, 128.4, 128.8, 129.8 (d, $^3J_{PC}$ = 13.8 Hz), 130.8, 135.2 (d, $^2J_{PC}$ = 11.9 Hz), 136.0, 141.0 (d, $^4J_{PC}$ = 3.6 Hz), 142.2 (d, $^3J_{PC}$ = 13.2 Hz), 144.8, 169.0 (d, $^2J_{PC}$ = 18.0 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1688 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{21}Cl_3NO_4P$ (M^+) 667.0274 found 667.0279.

5-(4-nitrophenyl)-4-(phenylethynyl)-3-(tris(4-fluorophenyl)phosphoranylidene) furan-2(3H)-one (5f):

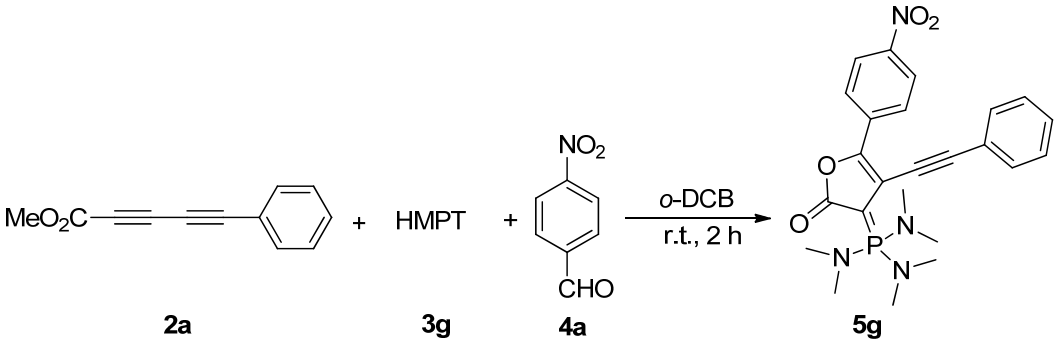


2a **3f** **4a** **5f**

Red solid (m.p. 182–185 °C). R_f = 0.21 (EA/hexanes, 1:1.5). Isolated yield 47% (41 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (dd, J = 1.4, 6.6 Hz, 2H), 7.21–7.29 (m, 9H), 7.71–7.80 (m, 6H), 8.08 (d, J = 9.2 Hz, 2H), 8.15 (d, J = 9.2 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 56.8 (d, $^1J_{PC}$ = 136.6 Hz), 82.9, 99.3, 107.4 (d, $^2J_{PC}$ = 12.4 Hz), 117.0 (dd, $^3J_{PC}$ = 14.3 Hz, $^2J_{FC}$ = 29.4 Hz), 118.1 (dd, $^4J_{FC}$ = 3.4 Hz, $^1J_{PC}$ = 96.7 Hz),

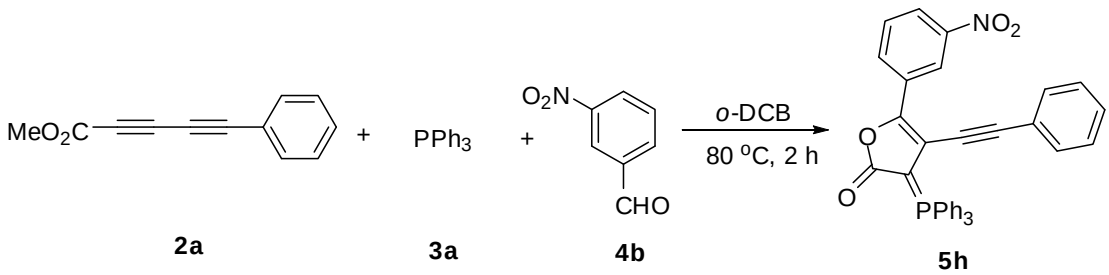
122.0, 123.5, 124.0, 128.3, 130.7, 136.0, 136.7 (dd, $^{3}J_{FC}$ = 9.3 Hz, $^{2}J_{PC}$ = 12.5 Hz), 141.9 (d, $^{3}J_{PC}$ = 13.3 Hz), 144.6, 166.0 (dd, $^{1}J_{FC}$ = 258.1 Hz, $^{4}J_{PC}$ = 3.3 Hz), 169.0 (d, $^{2}J_{PC}$ = 18.4 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1688 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{21}F_3NO_4P$ (M^+) 619.1160 found 619.1166.

5-(4-nitrophenyl)-4-(phenylethynyl)-3-(tris(dimethylamino)phosphoranylidene) furan-2(3H)-one (5g):



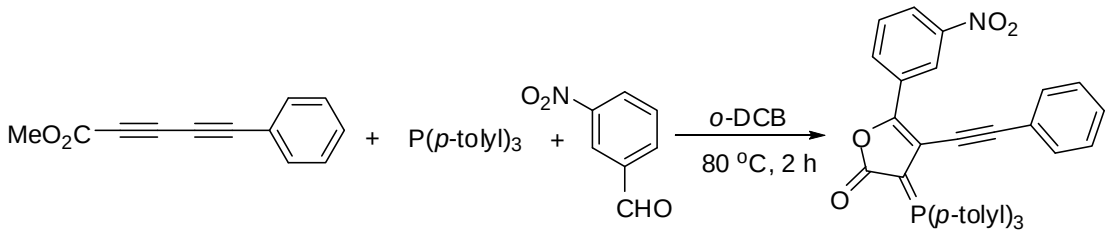
Red solid (decomposed easily). R_f = 0.24 (DCM/MeOH, 20:1). Isolated yield 41% (27 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.83 (d, J = 9.9 Hz, 18H), 7.40–7.47 (m, 5H), 8.12 (d, J = 9.1 Hz, 2H), 8.18 (d, J = 9.0 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 37.4 (d, $^{2}J_{PC}$ = 5.2 Hz), 65.4 (d, $^{1}J_{PC}$ = 200.0 Hz), 84.2, 96.7, 108.5 (d, $^{2}J_{PC}$ = 11.3 Hz), 123.0, 123.2, 124.0, 128.7, 128.8, 130.9, 136.5, 140.6 (d, $^{3}J_{PC}$ = 14.3 Hz), 144.3, 168.9 (d, $^{2}J_{PC}$ = 20.6 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 49.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1689 cm^{-1}; HRMS (ESI^+), calcd for $C_{24}H_{27}N_4O_4P$ (M^+) 466.1770 found 466.1767.

5-(3-nitrophenyl)-4-(phenylethynyl)-3-(triphenylphosphoranylidene)furan-2(3H) -one (5h):



Orange solid (m.p. 185–188 °C). R_f = 0.25 (EA/hexanes, 1.5:1). Isolated yield 58% (46 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (dd, *J* = 1.4, 7.9 Hz, 2H), 7.13–7.21 (m, 3H), 7.44–7.50 (m, 1H), 7.56 (dd, *J* = 3.2, 7.7 Hz, 6H), 7.61–7.64 (m, 3H), 7.74–7.81 (m, 6H), 7.96 (dd, *J* = 1.4, 8.2 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 9.15 (t, *J* = 1.9 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 54.9 (d, $^1J_{PC}$ = 135.0 Hz), 83.4, 99.0, 105.3 (d, $^2J_{PC}$ = 11.5 Hz), 118.4, 120.0, 122.6, 123.1 (d, $^1J_{PC}$ = 93.8 Hz), 128.0, 128.4, 128.6, 129.1 (d, $^3J_{PC}$ = 12.9 Hz), 130.9, 132.0, 132.2, 133.4 (d, $^4J_{PC}$ = 2.9 Hz), 134.2 (d, $^2J_{PC}$ = 10.6 Hz), 141.4 (d, $^3J_{PC}$ = 13.1 Hz), 148.4, 169.2 (d, $^2J_{PC}$ = 18.4 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{24}NO_4P$ (M^+) 565.1443 found 565.1442.

5-(3-nitrophenyl)-4-(phenylethynyl)-3-(tri-*p*-tolylphosphoranylidene)furan-2(3H)-one (5i):

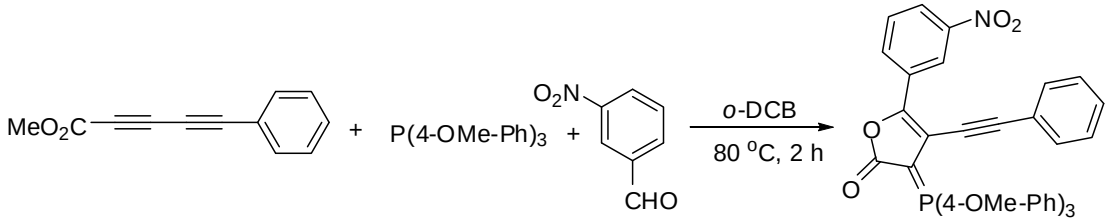


2a **3b** **4b** **5i**

Orange solid (m.p. 188–191 °C). R_f = 0.20 (EA/hexanes, 1.5:1). Isolated yield 64% (54 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 9H), 2.16 (m, 2H), 7.17–7.20 (m, 3H), 7.32 (dd, *J* = 2.7, 8.1 Hz, 6H), 7.45 (t, *J* = 8.1 Hz, 1H), 7.60–7.67 (m, 6H), 7.91–7.95 (m, 1H), 8.1 (d, *J* = 6.6 Hz, 1H), 9.13 (t, *J* = 1.9 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 22.1 (d, $^5J_{PC}$ = 1.1 Hz) 56.4 (d, $^1J_{PC}$ = 135.0 Hz), 83.9, 99.0, 106.0 (d, $^2J_{PC}$ = 11.5 Hz), 118.8, 120.2, 120.4 (d, $^1J_{PC}$ = 96.3 Hz), 123.2, 128.4, 129.6 (d, $^4J_{PC}$ = 4.5 Hz), 130.2 (d, $^3J_{PC}$ = 13.3 Hz), 131.4, 132.9, 134.6 (d, $^2J_{PC}$ = 11.0 Hz), 141.6 (d, $^3J_{PC}$ = 12.9 Hz), 144.5 (d, $^4J_{PC}$ = 2.9 Hz), 148.8, 169.7 (d, $^2J_{PC}$ = 18.1 Hz) ppm (two fewer carbons are observed due to coincidental overlap); ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{39}H_{30}NO_4P$ (M^+)

607.1913 found 607.1912.

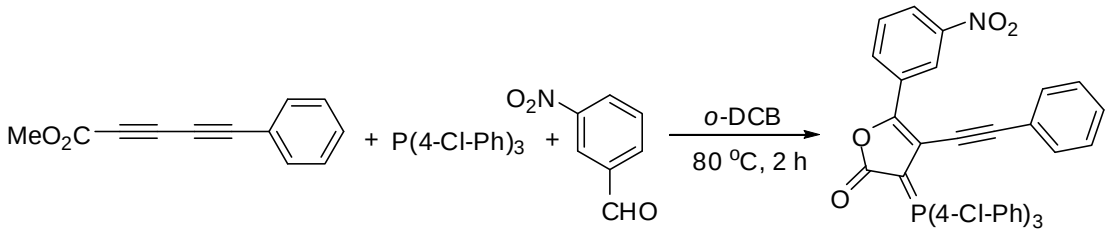
5-(3-nitrophenyl)-4-(phenylethynyl)-3-(tris(4-methoxyphenyl)phosphoranylidene) furan-2(3H)-one (5j):



2a **3d** **4b** **5j**

Orange solid (m.p. 172–175 °C). R_f = 0.35 (EA/hexanes, 3:1). Isolated yield 56% (51 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 9H), 6.95 (dd, *J* = 1.6, 7.4 Hz, 2H), 7.00 (dd, *J* = 2.4, 9.0 Hz, 6H), 7.19–7.21 (m, 3H), 7.46 (t, *J* = 6.0 Hz, 1H), 7.62–7.71 (m, 6H), 7.93 (d, *J* = 5.9 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 9.13 (t, *J* = 1.8 Hz, 1H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) 55.4, 57.0 (d, $^1J_{PC}$ = 135.7 Hz), 83.5, 98.4, 105.7 (d, $^2J_{PC}$ = 11.6 Hz), 114.3 (d, $^1J_{PC}$ = 99.1 Hz), 114.7 (d, $^3J_{PC}$ = 13.9 Hz), 118.3, 119.7, 122.8, 128.0, 129.1, 129.2, 131.0, 132.5, 135.9 (d, $^2J_{PC}$ = 12.2 Hz), 141.1 (d, $^3J_{PC}$ = 12.8 Hz), 148.4, 163.3, 169.3 (d, $^2J_{PC}$ = 18.2 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{39}H_{30}NO_7P$ (M^+) 655.1760 found 655.1756.

5-(3-nitrophenyl)-4-(phenylethynyl)-3-(tris(4-chlorophenyl)phosphoranylidene) furan-2(3H)-one (5k):

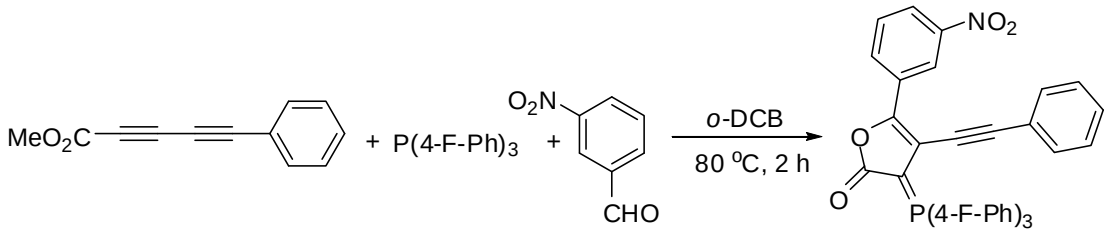


2a **3e** **4b** **5k**

Orange solid (m.p. 183–185 °C). R_f = 0.36 (EA/hexanes, 1:2). Isolated yield 49% (46 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.83 (dd, *J* = 1.7, 7.6 Hz, 2H), 7.16–7.21 (m, 3H), 7.47 (dd, *J* = 2.6, 8.6 Hz, 7H), 7.57–7.64 (m, 6H), 7.92 (dd, *J* = 1.4, 8.1 Hz, 1H), 8.08

(d, J = 8.0 Hz, 1H), 9.04 (t, J = 2.0 Hz, 1H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) 53.7 (d, $^1J_{PC}$ = 137.5 Hz), 82.9, 99.2, 104.2 (d, $^2J_{PC}$ = 12.2 Hz), 118.6, 120.4, 120.9 (d, $^1J_{PC}$ = 96.6 Hz), 122.1, 128.3, 128.5, 129.3, 129.4, 129.8 (d, $^3J_{PC}$ = 13.7 Hz), 130.9, 132.0, 135.3 (d, $^2J_{PC}$ = 11.8 Hz), 140.9 (d, $^4J_{PC}$ = 2.6 Hz), 142.1 (d, $^3J_{PC}$ = 13.4 Hz), 148.4, 169.1 (d, $^2J_{PC}$ = 18.8 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.9 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{21}Cl_3NO_4P$ (M^+) 667.0274 found 667.0274.

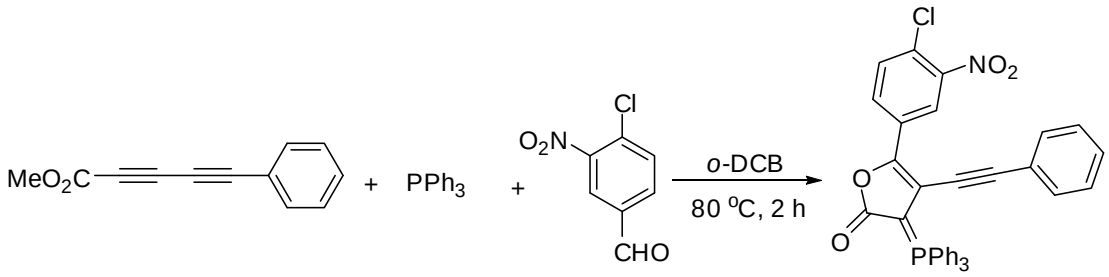
5-(3-nitrophenyl)-4-(phenylethynyl)-3-(tris(4-fluorophenyl)phosphoranylidene) furan-2(3H)-one (5l):



2a **3f** **4b** **5l**

Orange solid (m.p. 186–189 °C). R_f = 0.38 (EA/hexanes, 1:1). Isolated yield 51% (44 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (dd, J = 1.7, 6.2 Hz, 2H), 7.18–7.29 (m, 9H), 7.48 (t, J = 8.1 Hz, 1H), 7.72–7.81 (m, 6H), 7.98 (dd, J = 1.7, 7.9 Hz, 1H), 8.15 (d, J = 7.9 Hz, 1H), 9.11 (s, 1H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) 54.5 (d, $^1J_{PC}$ = 137.3 Hz), 83.0, 99.1, 104.4 (d, $^2J_{PC}$ = 11.9 Hz), 116.9 (dd, $^3J_{PC}$ = 14.6 Hz, $^2J_{FC}$ = 21.8 Hz), 118.6 (dd, $^4J_{FC}$ = 2.9 Hz, $^1J_{PC}$ = 98.4 Hz), 118.5, 120.3, 122.2, 128.3, 128.5, 129.2, 129.3, 130.8, 132.0, 136.8 (dd, $^2J_{PC}$ = 10.5 Hz, $^3J_{FC}$ = 29.2 Hz), 141.9 (d, $^3J_{PC}$ = 13.1 Hz), 148.4, 166.0 (dd, $^4J_{PC}$ = 2.1 Hz, $^1J_{FC}$ = 257.4 Hz), 169.0 (d, $^2J_{PC}$ = 18.8 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{21}F_3NO_4P$ (M^+) 619.1160 found 619.1159.

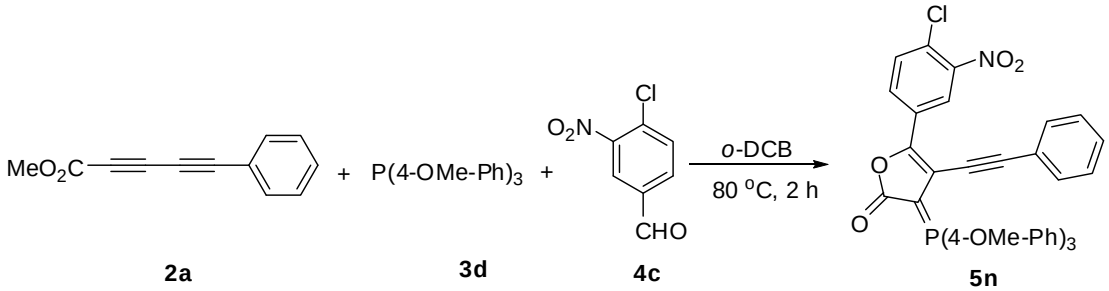
5-(4-chloro-3-nitrophenyl)-4-(phenylethynyl)-3-(triphenylphosphoranylidene) furan-2(3H)-one (5m):



2a **3a** **4c** **5m**

Red solid (m.p. 236–239 °C). R_f = 0.22 (EA/hexanes, 3:1). Isolated yield 55% (46 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.80 (d, *J* = 6.7 Hz, 2H), 7.13–7.21 (m, 3H), 7.24–7.66 (m, 8H), 7.61–7.66 (m, 4H), 7.73–7.80 (m, 4H), 7.99 (dd, *J* = 1.9, 8.6 Hz, 1H), 8.74 (d, *J* = 1.9 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 55.4 (d, $^1J_{PC}$ = 134.7 Hz), 83.0, 99.2, 106.0 (d, $^2J_{PC}$ = 11.5 Hz), 120.3, 122.2, 122.5, 122.7 (d, $^1J_{PC}$ = 93.9 Hz), 127.6, 128.0, 128.3, 129.1 (d, $^3J_{PC}$ = 13.0 Hz), 130.6, 130.8, 131.6, 133.3 (d, $^4J_{PC}$ = 3.0 Hz), 134.1 (d, $^2J_{PC}$ = 10.7 Hz), 140.2 (d, $^3J_{PC}$ = 13.1 Hz), 147.7, 168.9 (d, $^2J_{PC}$ = 18.3 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1696 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{23}ClNO_4P$ (M^+) 599.1053 found 565.1052.

5-(4-chloro-3-nitrophenyl)-4-(phenylethynyl)-3-(tris(4-methoxyphenyl)phosphor anylidene)furan-2(3H)-one (5n):

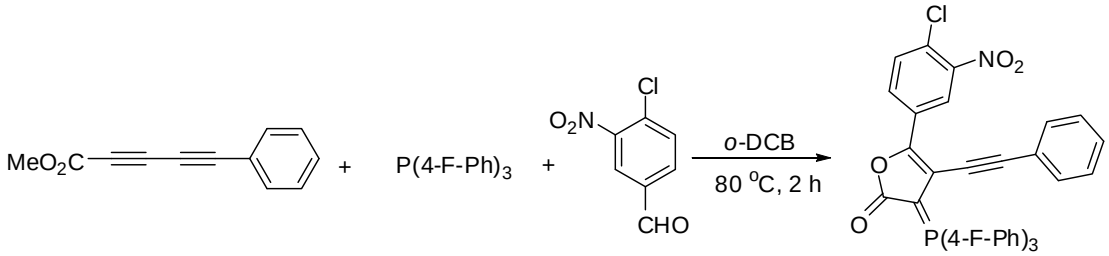


2a **3d** **4c** **5n**

Red solid (m.p. 98–101 °C). R_f = 0.31 (EA/hexanes, 3:1). Isolated yield 52% (50 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 9H), 6.89 (d, *J* = 6.3 Hz, 2H), 7.00 (dd, *J* = 1.8, 8.6 Hz, 6H), 7.17–7.23 (m, 3H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.65 (dd, *J* = 8.7, 12.5 Hz, 6H), 7.98 (dd, *J* = 1.6, 8.7 Hz, 1H), 8.71 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 55.3, 57.8 (d, $^1J_{PC}$ = 135.1 Hz), 83.0, 98.7, 106.4 (d, $^2J_{PC}$ = 11.8 Hz), 113.8 (d, $^1J_{PC}$ =

102.4 Hz), 114.6 (d, $^{3}J_{PC}$ = 14.2 Hz), 120.1, 122.0, 122.4, 127.4, 128.0, 128.1, 130.7, 130.9, 131.5, 135.8 (d, $^{2}J_{PC}$ = 12.4 Hz), 139.8 (d, $^{3}J_{PC}$ = 12.9 Hz), 147.6, 163.3 (d, $^{4}J_{PC}$ = 2.9 Hz), 169.0 (d, $^{2}J_{PC}$ = 17.9 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1689 cm^{-1}; HRMS (ESI^+), calcd for $C_{39}H_{29}ClNO_7P$ (M^+) 689.1370 found 689.1372.

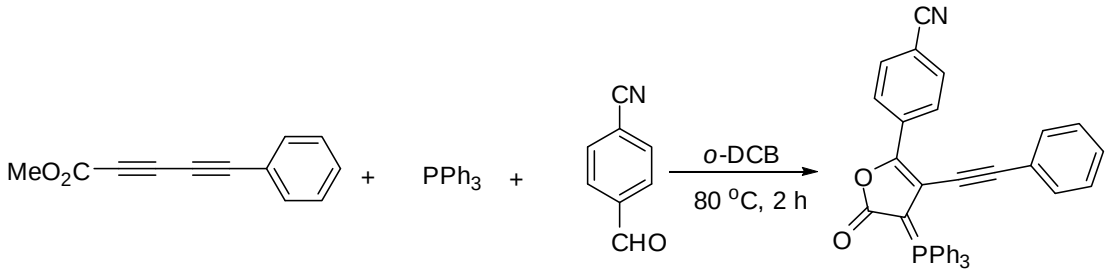
5-(4-chloro-3-nitrophenyl)-4-(phenylethynyl)-3-(tris(4-fluorophenyl)phosphoran ylidene)furan-2(3H)-one (5o):



2a **3f** **4c** **5o**

Red solid m.p. (100–103 °C). R_f = 0.31 (EA/hexanes, 1:1). Isolated yield 46% (42 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (d, *J* = 6.3 Hz, 2H), 7.24–7.26 (m, 8H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.71–7.80 (m, 7H), 7.98 (d, *J* = 8.0 Hz, 1H), 8.69 (s, 1H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) 55.0 (d, $^{1}J_{PC}$ = 137.1 Hz), 82.7, 99.3, 105.1 (d, $^{2}J_{PC}$ = 11.9 Hz), 116.9 (dd, $^{3}J_{PC}$ = 14.5 Hz, $^{2}J_{FC}$ = 21.8 Hz), 118.4 (dd, $^{4}J_{FC}$ = 3.3 Hz, $^{1}J_{PC}$ = 98.5 Hz), 120.4, 121.9, 122.9, 127.7, 128.3, 128.6, 130.4, 130.7, 131.7, 136.7 (dd, $^{3}J_{FC}$ = 9.6 Hz, $^{2}J_{PC}$ = 12.0 Hz), 140.7 (d, $^{3}J_{PC}$ = 13.4 Hz), 147.8, 165.9 (dd, $^{1}J_{FC}$ = 257.9 Hz, $^{4}J_{PC}$ = 3.3 Hz), 168.8 (d, $^{2}J_{PC}$ = 18.4 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.8 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1673 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{20}ClF_3NO_4P$ (M^+) 653.0771 found 653.0766.

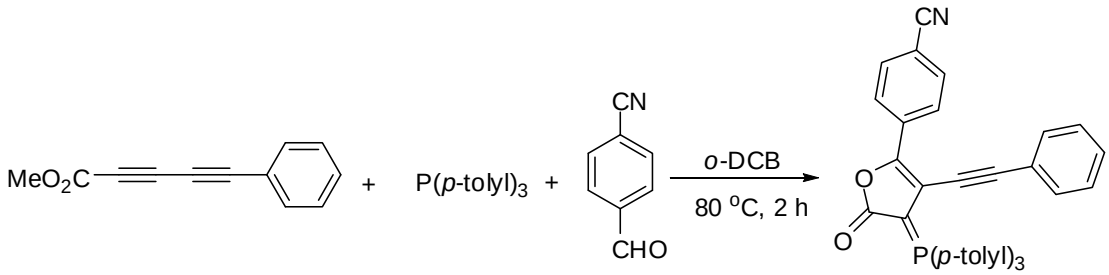
4-(5-oxo-3-(phenylethynyl)-4-(triphenylphosphoranylidene)-4,5-dihydrofuran-2-yl)benzonitrile (5p):



2a **3a** **4d** **5p**

Orange solid (m.p. 218–221 °C). R_f = 0.28 (EA/hexanes, 3:1). Isolated yield 43% (33 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 (d, J = 6.9 Hz, 2H), 7.14–7.23 (m, 3H), 7.44–7.56 (m, 10H), 7.60–7.68 (m, 3H), 7.72–7.79 (m, 4H), 8.07 (d, J = 8.5 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 56.1 (d, $^1J_{PC}$ = 135.0 Hz), 83.4, 98.8, 106.7 (d, $^2J_{PC}$ = 11.6 Hz), 107.7, 119.5, 122.3, 122.7 (d, $^1J_{PC}$ = 93.9 Hz), 123.6, 128.0, 128.2, 129.0 (d, $^3J_{PC}$ = 12.9 Hz), 130.8, 131.9, 133.3 (d, $^4J_{PC}$ = 2.9 Hz), 134.1 (d, $^2J_{PC}$ = 10.7 Hz), 134.4, 141.5 (d, $^3J_{PC}$ = 13.0 Hz), 169.1 (d, $^2J_{PC}$ = 18.0 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684, 2220 cm^{-1}; HRMS (ESI^+), calcd for $C_{37}H_{24}NO_2P$ (M^+) 545.1548 found 545.1551.

4-(5-oxo-3-(phenylethynyl)-4-(tri-*p*-tolylphosphoranylidene)-4,5-dihydrofuran-2-yl)benzonitrile (5q):

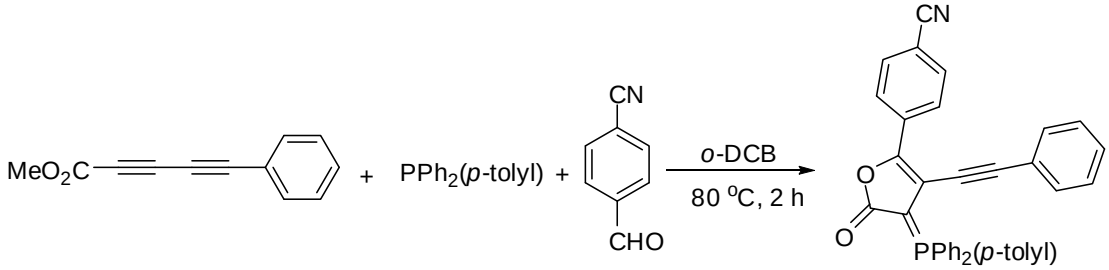


2a **3b** **4d** **5q**

Orange solid (m.p. 244–247 °C). R_f = 0.32 (EA/hexanes, 2:1). Isolated yield 58% (48 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.38 (s, 9H), 6.80 (d, J = 7.0 Hz, 2H), 7.15–7.23 (m, 3H), 7.26–7.28 (m, 6H), 7.52 (d, J = 8.3 Hz, 2H), 7.60 (dd, J = 8.1, 13.1 Hz, 6H), 8.03 (d, J = 8.5 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) 21.4, 57.3 (d, $^1J_{PC}$ = 134.2 Hz), 83.4, 98.4, 107.2 (d, $^2J_{PC}$ = 11.6 Hz), 107.4, 119.5, 119.6 (d, $^1J_{PC}$ = 96.3

Hz), 122.7, 123.5, 127.9, 128.0, 129.7 (d, $^3J_{PC}$ = 13.3 Hz), 131.8, 132.0, 134.0 (d, $^2J_{PC}$ = 11.0 Hz), 134.6, 141.4 (d, $^3J_{PC}$ = 12.8 Hz), 144.0, 169.2 (d, $^2J_{PC}$ = 17.6 Hz) ppm; ^{31}P NMR (202.3 Hz, $CDCl_3$) 11.9 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1679 cm^{-1}; HRMS (ESI^+), calcd for $C_{40}H_{30}NO_2P$ (M^+) 587.2014 found 587.2000.

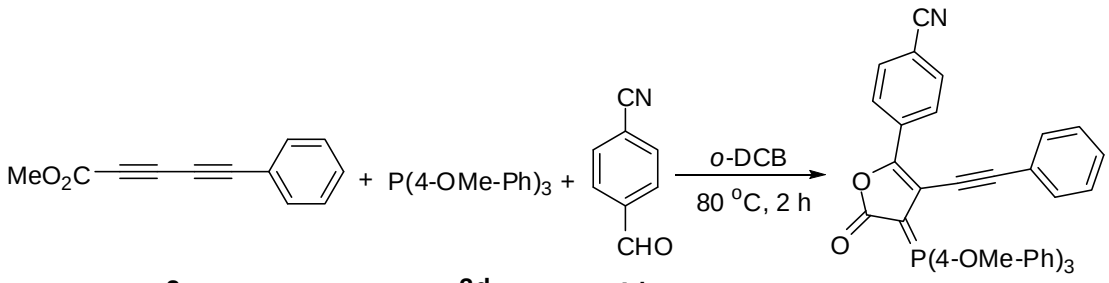
4-(4-(diphenyl(*p*-tolyl)phosphoranylidene)-5-oxo-3-(phenylethynyl)-4,5-dihydro furan-2-yl)benzonitrile (5r):



2a **3c** **4d** **5r**

Orange solid (m.p. 225–228 °C). R_f = 0.28 (EA/hexanes, 1.5:1). Isolated yield 61% (48 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 6.80 (d, *J* = 7.0 Hz, 2H), 7.15–7.23 (m, 3H), 7.26–7.32 (m, 2H), 7.52–7.64 (m, 10H), 7.73–7.80 (m, 4H), 8.07 (d, *J* = 8.3 Hz, 2H), 8.15 (d, *J* = 9.1 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 21.5, 56.6 (d, $^1J_{PC}$ = 134.3 Hz), 83.3, 98.6, 106.9 (d, $^2J_{PC}$ = 11.6 Hz), 107.5, 118.8 (d, $^1J_{PC}$ = 96.2 Hz), 119.6, 122.4, 123.0 (d, $^1J_{PC}$ = 93.9 Hz), 123.5, 127.9, 128.2, 128.9 (d, $^3J_{PC}$ = 13.0 Hz), 129.8 (d, $^3J_{PC}$ = 13.4 Hz), 130.8, 131.9, 133.1 (d, $^4J_{PC}$ = 2.9 Hz), 134.0 (d, $^2J_{PC}$ = 10.7 Hz), 134.1 (d, $^2J_{PC}$ = 9.3 Hz), 134.5, 141.5 (d, $^3J_{PC}$ = 13.0 Hz), 144.3 (d, $^4J_{PC}$ = 3.1 Hz), 169.1 (d, $^2J_{PC}$ = 17.9 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683 cm^{-1}; HRMS (ESI^+), calcd for $C_{38}H_{26}NO_2P$ (M^+) 559.1701 found 559.1701.

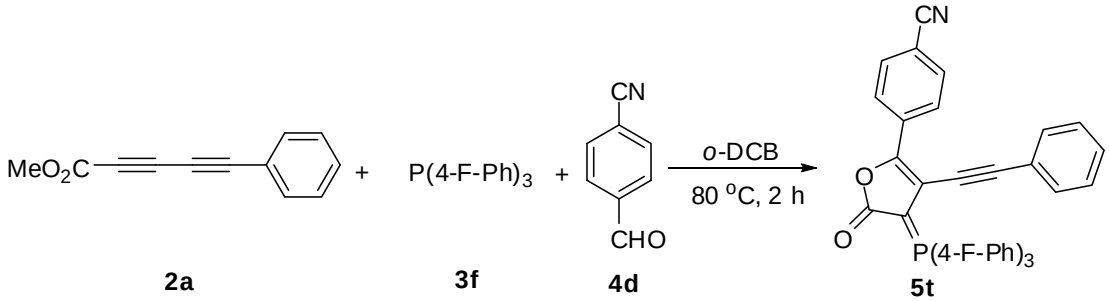
4-(5-oxo-3-(phenylethynyl)-4-(tris(4-methoxyphenyl)phosphoranylidene)-4,5-dihydrofuran-2-yl)benzonitrile (5s):



2a **3d** **4d** **5s**

Orange solid (m.p. 98–101 °C). R_f = 0.31 (EA/hexanes, 4:1). Isolated yield 59% (57 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 9H), 6.89 (d, J = 6.3 Hz, 2H), 7.00 (dd, J = 1.8, 8.6 Hz, 6H), 7.17–7.23 (m, 4H), 7.41 (d, J = 8.6 Hz, 1H), 7.65 (dd, J = 8.7, 12.5 Hz, 6H), 7.98 (dd, J = 1.6, 8.7 Hz, 1H), 8.71 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 55.2, 58.6 (d, $^1J_{PC}$ = 134.8 Hz), 83.3, 98.2, 107.20 (d, $^2J_{PC}$ = 11.7 Hz), 107.22, 113.8 (d, $^1J_{PC}$ = 103.3 Hz), 114.5 (d, $^3J_{PC}$ = 14.1 Hz), 119.6, 122.6, 123.3, 127.9, 128.1, 130.8, 131.8, 134.5, 135.8 (d, $^2J_{PC}$ = 12.3 Hz), 141.1 (d, $^3J_{PC}$ = 12.8 Hz), 163.3 (d, $^4J_{PC}$ = 2.9 Hz), 169.0 (d, $^2J_{PC}$ = 17.9 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1689 cm^{-1}; HRMS (ESI^+), calcd for $C_{39}H_{29}ClNO_7P$ (M^+) 689.1370 found 689.1372.

4-(5-oxo-3-(phenylethynyl)-4-(tris(4-fluorophenyl)phosphoranylidene)-4,5-dihydrofuran-2-yl)benzonitrile (5t):

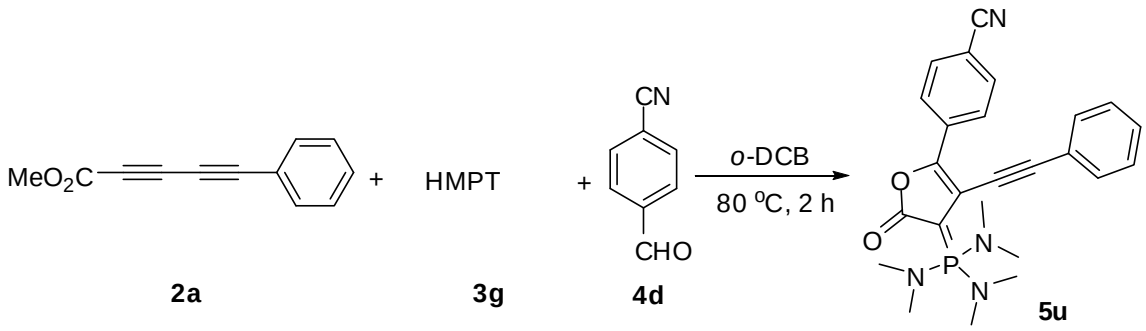


2a **3f** **4d** **5t**

Orange solid (m.p. 106–108 °C). R_f = 0.29 (EA/hexanes, 1:1). Isolated yield 54% (49 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (d, J = 6.3 Hz, 2H), 7.24–7.26 (m, 8H), 7.45 (d, J = 8.5 Hz, 1H), 7.71–7.80 (m, 8H), 7.98 (d, J = 8.0 Hz, 1H), 8.69 (s, 1H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) 55.0 (d, $^1J_{PC}$ = 137.1 Hz), 82.7, 99.3, 105.1 (d, $^2J_{PC}$ =

11.9 Hz), 116.9 (dd, $^{3}J_{PC}$ = 14.5 Hz, $^{2}J_{FC}$ = 21.8 Hz), 118.4 (dd, $^{4}J_{FC}$ = 3.3 Hz, $^{1}J_{PC}$ = 98.5 Hz), 120.4, 121.9, 122.9, 127.7, 128.3, 128.6, 130.4, 130.7, 131.7, 136.7 (dd, $^{3}J_{FC}$ = 9.6 Hz, $^{2}J_{PC}$ = 12.0 Hz), 140.7 (d, $^{3}J_{PC}$ = 13.4 Hz), 147.8, 165.9 (dd, $^{1}J_{FC}$ = 257.9 Hz, $^{4}J_{PC}$ = 3.3 Hz), 168.8 (d, $^{2}J_{PC}$ = 18.4 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.8 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1673 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{20}ClF_3NO_4P$ (M^+) 653.0771 found 653.0766.

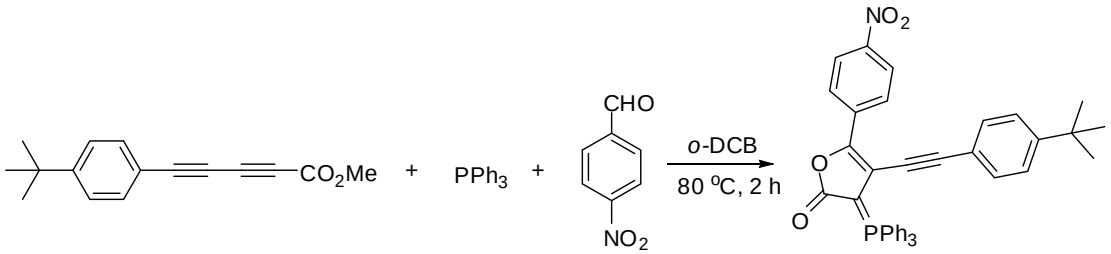
4-(5-oxo-3-(phenylethynyl)-4-(tris(dimethylamino)phosphoranylidene)-4,5-dihydrofuran-2-yl)benzonitrile (5u):



2a **3g** **4d** **5u**

Orange solid (decomposed easily). R_f = 0.16 (EA/MeOH, 50:1). Isolated yield 32% (20 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.82 (d, *J* = 9.9 Hz, 18H), 7.38–7.46 (m, 5H), 7.58 (d, *J* = 8.6 Hz, 2H), 8.09 (d, *J* = 8.6 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) 37.5 (d, $^{2}J_{PC}$ = 5.0 Hz), 64.2 (d, $^{1}J_{PC}$ = 200.2 Hz), 84.4, 96.1, 106.7 (d, $^{2}J_{PC}$ = 11.3 Hz), 107.8, 119.6, 123.3, 123.6, 128.5, 128.7, 130.9, 132.1, 134.8, 140.9 (d, $^{3}J_{PC}$ = 14.3 Hz), 169.0 (d, $^{2}J_{PC}$ = 23.1 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 50.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683 cm^{-1}; HRMS (ESI^+), calcd for $C_{25}H_{27}N_4O_2P$ (M^+) 446.1872 found 446.1871

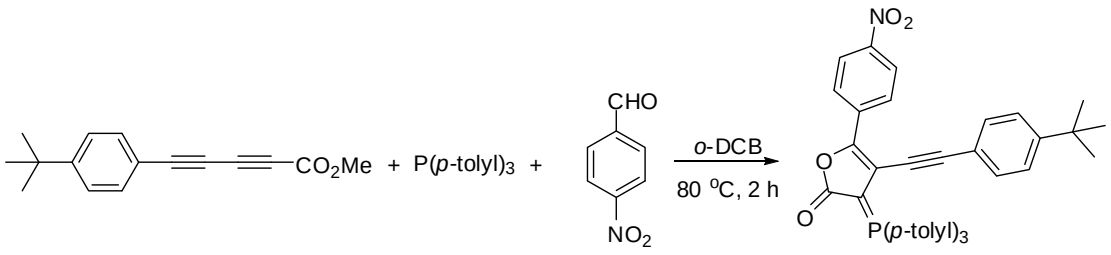
4-((4-(*tert*-butyl)phenyl)ethynyl)-5-(4-nitrophenyl)-3-(triphenylphosphoranylidene)furan-2(3H)-one (5v):



2c **3a** **4a** **5v**

Red solid (m.p. 238–241 °C). R_f = 0.36 (EA/hexanes, 2:1). Isolated yield 72% (63 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (s, 9H), 6.76 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.51–7.57 (m, 6H), 7.61–7.66 (m, 3H), 7.73–7.80 (m, 6H), 8.10 (d, J = 9.4 Hz, 2H), 8.15 (d, J = 9.4 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 30.9, 34.6, 57.4 (d, $^1J_{PC}$ = 133.9 Hz), 82.6, 99.6, 108.8 (d, $^2J_{PC}$ = 11.5 Hz), 119.1, 122.4 (d, $^1J_{PC}$ = 93.7 Hz), 123.1, 123.9, 125.0, 129.0 (d, $^3J_{PC}$ = 12.8 Hz), 130.6, 133.3 (d, $^4J_{PC}$ = 2.9 Hz), 134.0 (d, $^2J_{PC}$ = 10.7 Hz), 136.2, 141.2 (d, $^3J_{PC}$ = 13.1 Hz), 144.1, 151.8, 169.0 (d, $^2J_{PC}$ = 18.0 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684, 2240 cm^{-1}; HRMS (ESI^+), calcd for $C_{40}H_{32}NO_4P$ (M^+) 621.2069 found 621.2062.

4-((4-(*tert*-butyl)phenyl)ethynyl)-5-(4-nitrophenyl)-3-(tri-*p*-tolylphosphoranylide ne)furan-2(3H)-one (5w):

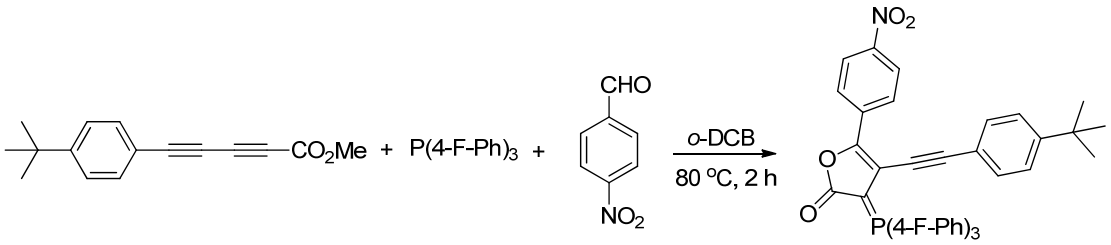


2c **3b** **4a** **5w**

Red solid (m.p. 253–256 °C). R_f = 0.32 (EA/hexanes, 1:1). Isolated yield 73% (68 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 9H), 2.36 (s, 9H), 6.82 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.31 (dd, J = 2.6, 8.0 Hz, 6H), 7.63 (dd, J = 8.1, 13.0 Hz, 6H), 8.08 (d, J = 9.5 Hz, 2H) , 8.13 (d, J = 9.4 Hz, 2H) ppm; ^{13}C NMR (75.5

MHz, $CDCl_3$) 21.5 (d, $^5J_{PC}$ = 1.4 Hz), 30.9, 34.6, 58.9 (d, $^1J_{PC}$ = 133.7 Hz), 82.5, 99.2, 109.3 (d, $^2J_{PC}$ = 11.5 Hz), 119.2 (d, $^1J_{PC}$ = 96.4 Hz), 119.4, 123.0, 123.8, 124.9, 129.7 (d, $^3J_{PC}$ = 13.4 Hz), 130.7, 133.9 (d, $^2J_{PC}$ = 11.1 Hz), 136.4, 141.0 (d, $^3J_{PC}$ = 12.9 Hz), 143.9, 144.0 (d, $^4J_{PC}$ = 3.0 Hz), 151.5, 169.2 (d, $^2J_{PC}$ = 17.3 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1688, 2239 cm^{-1}; HRMS (ESI^+), calcd for $C_{43}H_{38}NO_4P$ (M^+) 663.2539 found 663.2531.

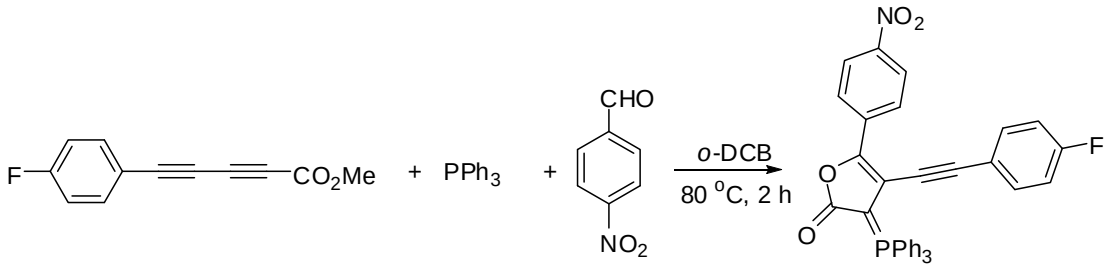
4-((4-(*tert*-butyl)phenyl)ethynyl)-5-(4-nitrophenyl)-3-(tris(4-fluorophenyl)phosphoranylidene)furan-2(3H)-one (5x):



2c **3f** **4a** **5x**

Red solid (m.p. 271–273 °C). R_f = 0.24 (EA/hexanes, 1:1.5). Isolated yield 63% (60 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 9H), 6.83 (d, *J* = 8.4 Hz, 2H), 7.23–7.29 (m, 8H), 7.72–7.80 (m, 6H), 8.07 (d, *J* = 9.3 Hz, 2H), 8.14 (d, *J* = 9.3 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 30.9, 34.7, 56.9 (d, $^1J_{PC}$ = 136.3 Hz), 82.2, 99.7, 107.8 (d, $^2J_{PC}$ = 11.8 Hz), 116.9 (dd, $^3J_{PC}$ = 14.3 Hz, $^2J_{FC}$ = 21.9 Hz), 118.1 (dd, $^4J_{FC}$ = 3.4 Hz, $^1J_{PC}$ = 98.5 Hz), 118.9, 123.4, 123.9, 125.3, 130.5, 136.0, 136.6 (dd, $^3J_{FC}$ = 9.3 Hz, $^2J_{PC}$ = 12.6 Hz), 141.6 (d, $^3J_{PC}$ = 13.3 Hz), 144.4, 152.2, 165.9 (dd, $^4J_{PC}$ = 3.3 Hz, $^1J_{FC}$ = 257.9 Hz), 168.9 (d, $^2J_{PC}$ = 18.4 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1686, 2240 cm^{-1}; HRMS (ESI^+), calcd for $C_{40}H_{29}F_3NO_4P$ (M^+) 675.1786 found 675.1788.

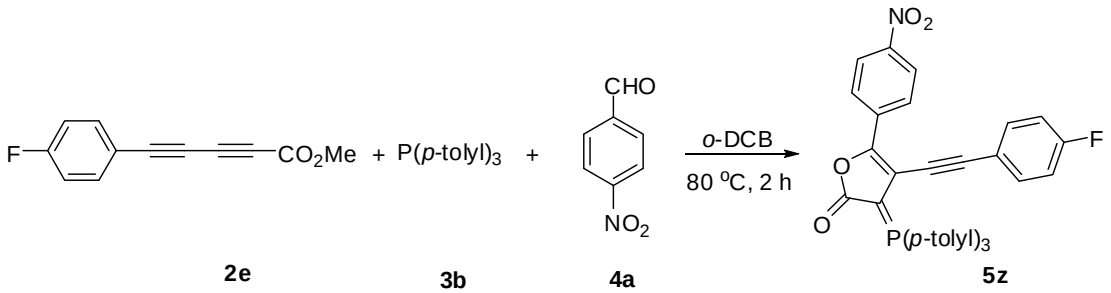
4-((4-fluorophenyl)ethynyl)-5-(4-nitrophenyl)-3-(triphenylphosphoranylidene) furan-2(3H)-one (5y):



2e **3a** **4a** **5y**

Red solid (m.p. 229–231 °C). R_f = 0.37 (EA/hexanes, 2:1). Isolated yield 43% (35 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76–6.80 (m, 2H), 6.86–6.91 (m, 2H), 7.52–7.58 (m, 6H), 7.61–7.67 (m, 3H), 7.72–7.79 (m, 6H), 8.08 (d, J = 9.3 Hz, 2H), 8.15 (d, J = 9.3 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 57.3 (d, $^1J_{PC}$ = 133.9 Hz), 83.0, 98.1, 108.2 (d, $^2J_{PC}$ = 11.5 Hz), 115.4 (d, $^2J_{FC}$ = 22.0 Hz), 118.3 (d, $^4J_{FC}$ = 3.6 Hz), 122.4 (d, $^1J_{PC}$ = 93.8 Hz), 123.3, 123.9, 129.1 (d, $^3J_{PC}$ = 12.9 Hz), 132.8 (d, $^3J_{FC}$ = 8.5 Hz), 133.4 (d, $^4J_{PC}$ = 2.9 Hz), 134.1 (d, $^2J_{PC}$ = 10.6 Hz), 136.2, 141.4 (d, $^3J_{PC}$ = 12.9 Hz), 144.3, 162.4 (d, $^1J_{FC}$ = 250.7 Hz), 169.0 (d, $^2J_{PC}$ = 17.9 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684, 2238 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{23}FNO_4P$ (M^+) 583.1349 found 583.1342.

4-((4-fluorophenyl)ethynyl)-5-(4-nitrophenyl)-3-(tri-*p*-tolylphosphoranylidene) furan-2(3H)-one (5z):

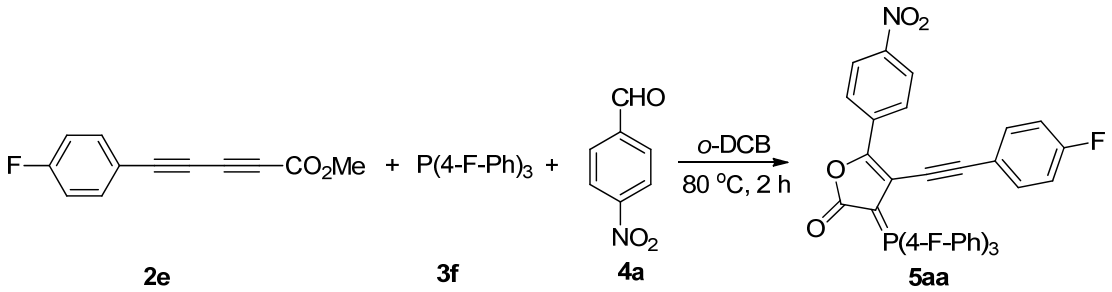


2e **3b** **4a** **5z**

Red solid (m.p. 235–238 °C). R_f = 0.33 (EA/hexanes, 2:1). Isolated yield 48% (42 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 9H), 6.79–6.84 (m, 2H), 6.88–6.97 (m, 2H), 7.32 (dd, J = 2.5, 8.0 Hz, 6H), 7.62 (dd, J = 8.1, 13.0 Hz, 6H), 8.06 (d, J = 9.2 Hz, 2H), 8.14 (d, J = 9.2 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.5 (d, $^5J_{PC}$ =

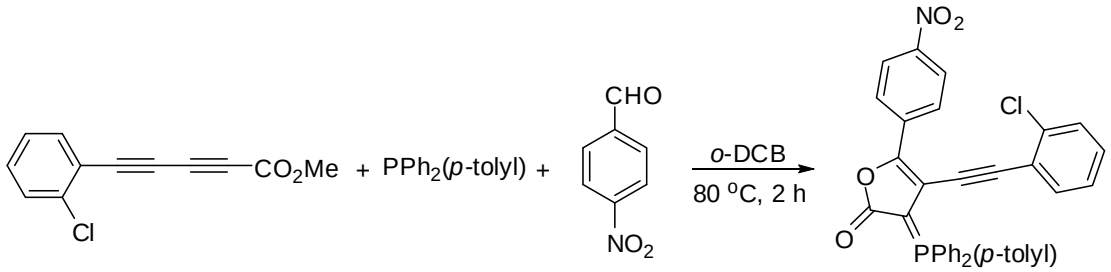
1.1 Hz), 58.6 (d, $^{1}J_{PC}$ = 133.7 Hz), 83.0, 97.7, 108.6 (d, $^{2}J_{PC}$ = 11.5 Hz), 115.3 (d, $^{2}J_{FC}$ = 22.0 Hz), 118.6 (d, $^{4}J_{FC}$ = 3.5 Hz), 119.3 (d, $^{1}J_{PC}$ = 96.5 Hz), 123.1, 123.9, 129.8 (d, $^{3}J_{PC}$ = 13.3 Hz), 132.8 (d, $^{3}J_{FC}$ = 8.4 Hz), 133.0 (d, $^{2}J_{PC}$ = 11.2 Hz), 136.3, 141.2 (d, $^{3}J_{PC}$ = 13.0 Hz), 144.0, 144.1 (d, $^{4}J_{PC}$ = 2.6 Hz), 162.2 (d, $^{1}J_{FC}$ = 250.6 Hz), 169.1 (d, $^{2}J_{PC}$ = 17.5 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684, 2238 cm^{-1}; HRMS (ESI^+), calcd for $C_{39}H_{29}FNO_4P$ (M^+) 625.1818 found 625.1820.

4-((4-fluorophenyl)ethynyl)-5-(4-nitrophenyl)-3-(tris(4-fluorophenyl)phosphoranylidene)furan-2(3H)-one (5aa):



Red solid (m.p. 118–120 °C). R_f = 0.33 (EA/hexanes, 1:1). Isolated yield 32% (29 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.83–6.88 (m, 2H), 6.92–6.98 (m, 2H), 7.23–7.29 (m, 6H), 7.71–7.80 (m, 6H), 8.05 (d, J = 9.1 Hz, 2H), 8.16 (d, J = 9.2 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 59.44 (d, $^{1}J_{PC}$ = 135.8 Hz), 82.6, 98.0, 107.1 (d, $^{2}J_{PC}$ = 11.8 Hz), 115.7 (d, $^{2}J_{FC}$ = 22.3 Hz), 117.0 (dd, $^{3}J_{PC}$ = 14.3 Hz, $^{2}J_{FC}$ = 21.9 Hz), 118.0 (d, $^{4}J_{FC}$ = 3.5 Hz), 118.1 (dd, $^{4}J_{FC}$ = 3.3 Hz, $^{1}J_{PC}$ = 98.5 Hz), 123.5, 124.0, 132.7 (d, $^{3}J_{FC}$ = 8.5 Hz), 136.0, 136.7 (dd, $^{3}J_{FC}$ = 9.3 Hz, $^{2}J_{PC}$ = 12.6 Hz), 142.0 (d, $^{3}J_{PC}$ = 13.1 Hz), 144.7, 162.6 (d, $^{1}J_{FC}$ = 251.4 Hz), 166.0 (dd, $^{4}J_{PC}$ = 3.3 Hz, $^{1}J_{FC}$ = 258.1 Hz), 169.0 (d, $^{2}J_{PC}$ = 19.2 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1686 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{20}F_4NO_4P$ (M^+) 637.1066 found 637.1071.

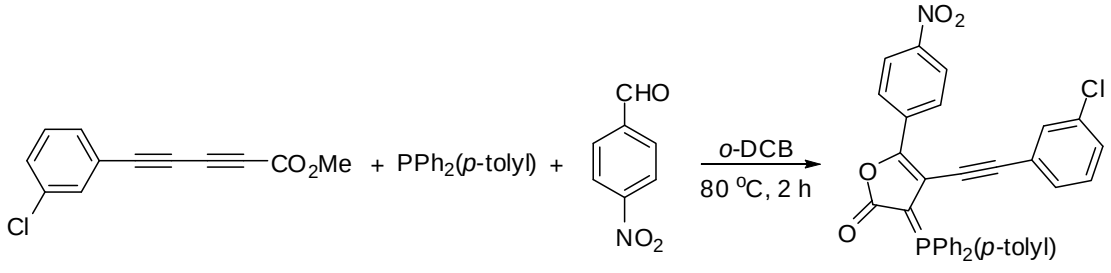
4-((2-chlorophenyl)ethynyl)-3-(diphenyl(*p*-tolyl)phosphoranylidene)-5-(4-nitrophenyl)furan-2(3H)-one (5ab):



2g **3c** **4a** **5ab**

Red solid (m.p. 221–224 °C). R_f = 0.31 (EA/hexanes, 2:1). Isolated yield 60% (52 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H), 6.46 (d, J = 7.7 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.26–7.33 (m, 3H), 7.50–7.55 (m, 4H), 7.59–7.66 (m, 4H), 7.74–7.81 (m, 4H), 8.13 (d, J = 9.1 Hz, 2H), 8.21 (d, J = 9.1 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.5, 57.4 (d, $^1J_{PC}$ = 133.6 Hz), 88.1, 96.0, 107.9 (d, $^2J_{PC}$ = 11.3 Hz), 118.6 (d, $^1J_{PC}$ = 95.9 Hz), 122.3, 122.8 (d, $^1J_{PC}$ = 94.1 Hz), 123.5, 123.9, 126.0, 129.0 (d, $^3J_{PC}$ = 13.1 Hz), 129.3, 129.8 (d, $^3J_{PC}$ = 13.4 Hz), 132.7, 133.2 (d, $^4J_{PC}$ = 2.9 Hz), 134.0 (d, $^2J_{PC}$ = 10.6 Hz), 134.1 (d, $^2J_{PC}$ = 11.0 Hz), 134.8, 136.0, 141.7 (d, $^3J_{PC}$ = 12.8 Hz), 144.4, 168.9 (d, $^2J_{PC}$ = 18.0 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.9 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683 cm^{-1}; HRMS (ESI^+), calcd for $C_{37}H_{26}ClNO_4P$ (M+1) 614.1282 found 614.1279.

4-((3-chlorophenyl)ethynyl)-3-(diphenyl(*p*-tolyl)phosphoranylidene)-5-(4-nitrophenyl)furan-2(3H)-one (5ac):

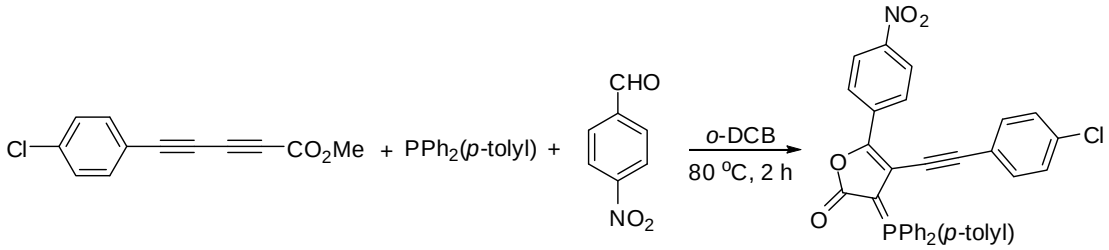


2h **3c** **4a** **5ac**

Red solid (m.p. 212–215 °C). R_f = 0.38 (EA/hexanes, 2:1). Isolated yield 66% (57 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 6.60 (s, 1H), 6.81 (d, J = 7.5 Hz, 1H) 7.11–7.20 (m, 2H), 7.35 (dd, J = 2.8, 8.1 Hz, 2H), 7.52–7.59 (m, 5H), 7.62–7.66 (m,

3H), 7.73–7.80 (m, 4H), 8.07 (d, J = 9.2 Hz, 2H), 8.15 (d, J = 9.2 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.5, 57.6 (d, $^1J_{PC}$ = 134.4 Hz), 84.5, 97.5, 107.9 (d, $^2J_{PC}$ = 11.5 Hz), 118.5 (d, $^1J_{PC}$ = 96.3 Hz), 122.7 (d, $^1J_{PC}$ = 94.2 Hz), 123.3, 123.5, 123.9, 128.5, 128.8, 129.0 (d, $^3J_{PC}$ = 13.0 Hz), 129.3, 129.9 (d, $^3J_{PC}$ = 13.4 Hz), 130.7, 133.3 (d, $^4J_{PC}$ = 2.9 Hz), 133.7, 134.0 (d, $^2J_{PC}$ = 10.6 Hz), 134.1 (d, $^2J_{PC}$ = 10.8 Hz), 136.1, 141.7 (d, $^3J_{PC}$ = 12.8 Hz), 144.3, 144.5 (d, $^4J_{PC}$ = 2.9 Hz), 169.0 (d, $^2J_{PC}$ = 17.8 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683 cm^{-1}; HRMS (ESI^+), calcd for $C_{37}H_{26}ClNO_4P$ (M+1) 614.1282 found 614.1268.

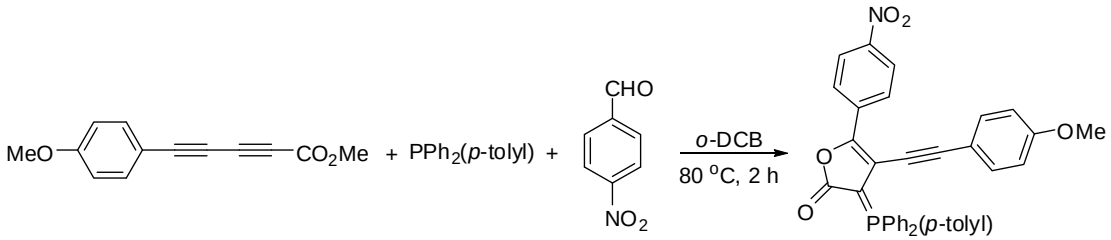
4-((4-chlorophenyl)ethynyl)-3-(diphenyl(*p*-tolyl)phosphoranylidene)-5-(4-nitrophenyl)furan-2(3H)-one (5ad):



2i **3c** **4a** **5ad**

Red solid (m.p. 206–209 °C). R_f = 0.33 (EA/hexanes, 2:1). Isolated yield 47% (40 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H), 6.72 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 7.32–7.34 (m, 2H) 7.45–7.64 (m, 8H), 7.72–7.79 (m, 4H), 8.07 (d, J = 8.9 Hz, 2H), 8.16 (d, J = 8.9 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) δ 21.6, 57.5 (d, $^1J_{PC}$ = 135.0 Hz), 84.5, 97.8, 108.0 (d, $^2J_{PC}$ = 11.6 Hz), 118.9 (d, $^1J_{PC}$ = 96.0 Hz), 120.9, 123.0 (d, $^1J_{PC}$ = 94.0 Hz), 123.4, 124.0, 128.5, 129.1 (d, $^3J_{PC}$ = 12.8 Hz), 130.0 (d, $^3J_{PC}$ = 13.3 Hz), 132.1, 133.3 (d, $^4J_{PC}$ = 2.6 Hz), 134.1 (d, $^2J_{PC}$ = 10.8 Hz), 134.2 (d, $^2J_{PC}$ = 11.1 Hz), 134.5, 136.3, 141.8 (d, $^3J_{PC}$ = 12.7 Hz), 144.47, 144.54, 169.1 (d, $^2J_{PC}$ = 18.1 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683 cm^{-1}; HRMS (ESI^+), calcd for $C_{37}H_{26}ClNO_4P$ (M+1) 614.1282 found 614.1280.

3-(diphenyl(*p*-tolyl)phosphoranylidene)-4-((4-methoxyphenyl)ethynyl)-5-(4-nitro phenyl)furan-2(3H)-one (5ae):



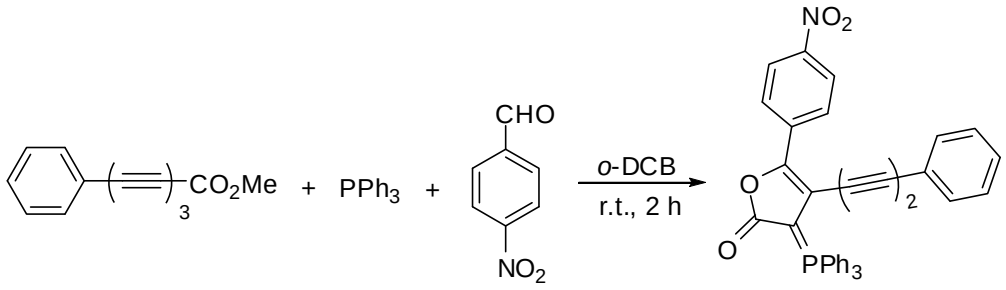
2j **3c** **4a** **5ae**

Red solid (m.p. 206–209 °C). R_f = 0.33 (EA/hexanes, 2:1). Isolated yield 33% (28 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.78 (s, 3H), 6.69–6.78 (m, 4H) 7.31–7.34 (m, 2H) 7.53–7.65 (m, 8H), 7.72–7.79 (m, 4H), 8.08 (d, J = 9.1 Hz, 2H), 8.15 (d, J = 9.1 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.6, 55.2, 58.0 (d, $^1J_{PC}$ = 135.4 Hz), 82.0, 99.4, 109.1 (d, $^2J_{PC}$ = 10.7 Hz), 113.7, 114.4, 118.7 (d, $^1J_{PC}$ = 96.3 Hz), 122.9 (d, $^1J_{PC}$ = 94.0 Hz), 123.1, 123.9, 129.0 (d, $^3J_{PC}$ = 12.9 Hz), 129.8 (d, $^3J_{PC}$ = 13.3 Hz), 132.4, 133.2 (d, $^4J_{PC}$ = 2.9 Hz), 134.1 (d, $^2J_{PC}$ = 10.7 Hz), 134.2 (d, $^2J_{PC}$ = 10.9 Hz), 136.4, 141.0 (d, $^3J_{PC}$ = 13.2 Hz), 144.1, 144.3 (d, $^4J_{PC}$ = 2.9 Hz), 159.6, 169.2 (d, $^2J_{PC}$ = 17.8 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683 cm^{-1}; HRMS (ESI^+), calcd for $C_{38}H_{29}NO_5P$ (M+1) 610.1778 found 610.1773.

General procedure for synthesis 5af to 5aq, 5az to 5aaa

To 2.0 mL of anhydrous *o*-DCB solution containing phoshpine **3** (0.15 mmol) and aldehyde **4** (0.10 mmol) was added **2** (0.15 mmol in 5.0 mL of *o*-DCB) *via* a syringe pump in 1 h at room temperature. Upon completion of injection, the mixture was stirred for another 1 h. The mixture was then subjected to flash silica gel chromatography. Elution with hexanes/EA gave products **5af** to **5aq**, and **5az** to **5aaa**.

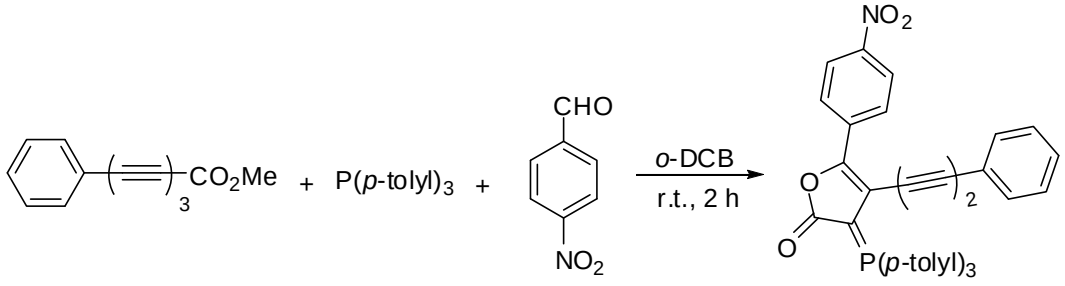
5-(4-nitrophenyl)-4-(phenylbuta-1,3-diyn-1-yl)-3-(triphenylphosphoranylidene) furan-2(3H)-one (5af):



2k **3a** **4a** **5af**

Red solid (m.p. 257–260 °C). R_f = 0.20 (EA/hexanes, 1:1). Isolated yield 68% (40 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.42 (m, 5H), 7.57–7.63 (m, 6H), 7.68–7.81 (m, 9H), 8.04 (d, J = 9.1 Hz, 2H), 8.17 (d, J = 9.1 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 57.5 (d, $^1J_{PC}$ = 134.1 Hz), 73.6, 74.2, 83.2, 85.0, 106.9 (d, $^2J_{PC}$ = 12.0 Hz), 122.0 (d, $^1J_{PC}$ = 93.8 Hz), 123.4, 124.0, 128.5, 129.2 (d, $^3J_{PC}$ = 13.1 Hz), 132.0, 133.6 (d, $^4J_{PC}$ = 2.9 Hz), 134.1 (d, $^2J_{PC}$ = 10.7 Hz), 135.7, 144.79, 144.80 (d, $^3J_{PC}$ = 12.7 Hz), 168.9 (d, $^2J_{PC}$ = 17.1 Hz) ppm (two fewer carbons are observed due to coincidental overlap); ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683 cm^{-1}; HRMS (ESI^+), calcd for $C_{38}H_{24}NO_4P$ (M^+) 589.1443 found 589.1438.

5-(4-nitrophenyl)-4-(phenylbuta-1,3-diyn-1-yl)-3-(tri-*p*-tolylphosphoranylidene) furan-2(3H)-one (5ag):

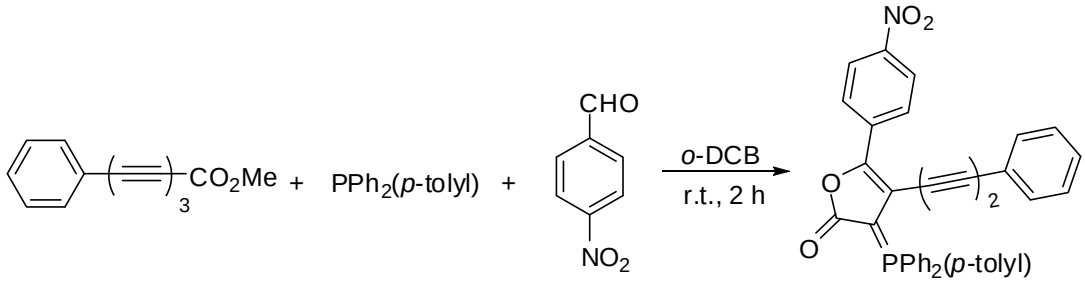


2k **3b** **4a** **5ag**

Red solid (m.p. 130–132 °C). R_f = 0.08 (EA/hexanes, 1:2). Isolated yield 67% (42 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 9H), 7.26–7.44 (m, 11H), 7.60–7.67 (m, 6H), 8.02 (d, J = 9.2 Hz, 2H), 8.14 (d, J = 9.2 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7 (d, $^5J_{PC}$ = 1.1 Hz), 59.1 (d, $^1J_{PC}$ = 133.7 Hz), 73.6, 74.3, 82.8, 84.7,

107.4 (d, $^{2}J_{PC}$ = 11.9 Hz), 118.9 (d, $^{1}J_{PC}$ = 96.5 Hz), 121.4, 123.3, 124.0, 128.4, 129.3, 129.9 (d, $^{3}J_{PC}$ = 13.4 Hz), 132.1, 134.0 (d, $^{2}J_{PC}$ = 11.2 Hz), 135.8, 144.4 (d, $^{4}J_{PC}$ = 3.0 Hz), 144.59, 144.61 (d, $^{3}J_{PC}$ = 12.8 Hz), 168.8 (d, $^{2}J_{PC}$ = 16.7 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683 cm^{-1}; HRMS (ESI^+), calcd for $C_{41}H_{30}NO_4P$ (M^+) 631.1912 found 631.1908.

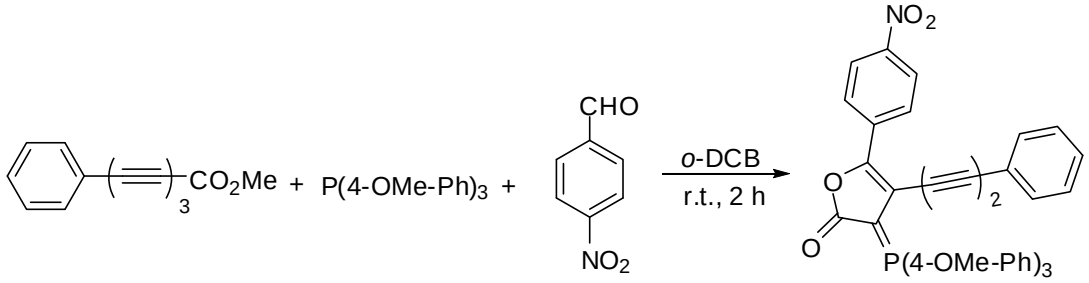
3-(diphenyl(*p*-tolyl)phosphoranylidene)-5-(4-nitrophenyl)-4-(phenylbuta-1,3-diyn-1-yl)furan-2(3H)-one (5ah):



2k **3c** **4a** **5ah**

Red solid (m.p. 207–210 °C). R_f = 0.17 (EA/hexanes, 1:2). Isolated yield 69% (42 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H) 7.30–7.36 (m, 2H), 7.37–7.43 (m, 4H), 7.56–7.63 (m, 6H), 7.66–7.71 (m, 3H), 7.74–7.81 (m, 4H), 8.03 (d, *J* = 9.0 Hz, 2H), 8.16 (d, *J* = 9.0 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7 (d, $^{5}J_{PC}$ = 1.5 Hz), 58.1 (d, $^{1}J_{PC}$ = 133.6 Hz), 73.6, 74.3, 83.1, 84.9, 107.1 (d, $^{2}J_{PC}$ = 12.1 Hz), 118.2 (d, $^{1}J_{PC}$ = 96.2 Hz), 121.4, 122.8, 122.9 (d, $^{1}J_{PC}$ = 94.0 Hz), 123.4, 124.0, 128.4, 129.2 (d, $^{3}J_{PC}$ = 12.8 Hz), 129.3, 130.0 (d, $^{3}J_{PC}$ = 13.6 Hz), 132.0, 133.5 (d, $^{4}J_{PC}$ = 3.0 Hz), 134.0 (d, $^{2}J_{PC}$ = 10.6 Hz), 134.1 (d, $^{2}J_{PC}$ = 10.6 Hz), 135.8, 144.7, 144.7 (d, $^{3}J_{PC}$ = 12.8 Hz), 168.9 (d, $^{2}J_{PC}$ = 17.4 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{39}H_{26}NO_4P$ (M^+) 603.1599 found 603.1603.

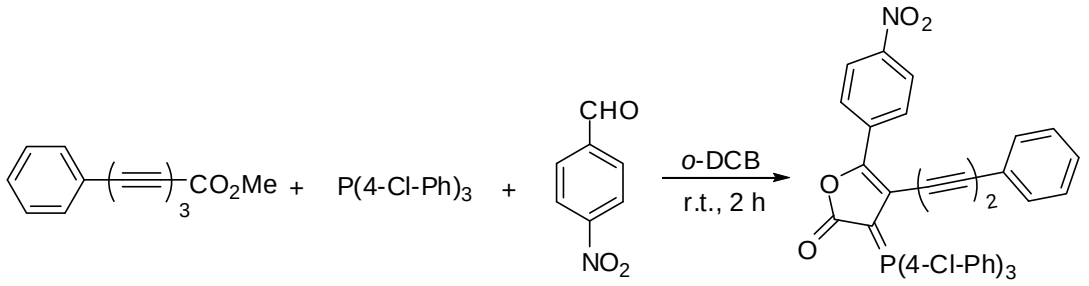
5-(4-nitrophenyl)-4-(phenylbuta-1,3-diyn-1-yl)-3-(tris(4-methoxyphenyl)phosphoranylidene)furan-2(3H)-one (5ai):



2k **3d** **4a** **5ai**

Red solid (m.p. 120–122 °C). R_f = 0.26 (EA/hexanes, 2:1). Isolated yield 68% (46 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82 (s, 9H) 7.04–7.10 (m, 6H), 7.31–7.38 (m, 3H), 7.45–7.48 (m, 2H), 7.62–7.71 (m, 6H), 8.02 (d, J = 9.2 Hz, 2H), 8.25 (d, J = 9.2 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.4, 60.5 (d, $^1J_{PC}$ = 134.2 Hz), 73.6, 74.3, 82.7, 85.1, 107.6 (d, $^2J_{PC}$ = 12.0 Hz), 113.2 (d, $^1J_{PC}$ = 101.4 Hz), 114.8 (d, $^3J_{PC}$ = 14.1 Hz), 121.4, 123.2, 124.0, 128.4, 129.3, 132.2, 135.8 (d, $^2J_{PC}$ = 12.3 Hz), 135.9, 144.5 (d, $^3J_{PC}$ = 12.5 Hz), 144.5, 163.5 (d, $^4J_{PC}$ = 2.9 Hz), 168.9 (d, $^2J_{PC}$ = 16.7 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1680 cm^{-1}; HRMS (ESI^+), calcd for $C_{41}H_{30}NO_7P$ (M^+) 679.1760 found 679.1769.

5-(4-nitrophenyl)-4-(phenylbuta-1,3-diyn-1-yl)-3-(tris(4-chlorophenyl)phosphoranylidene)furan-2(3H)-one (5aj):

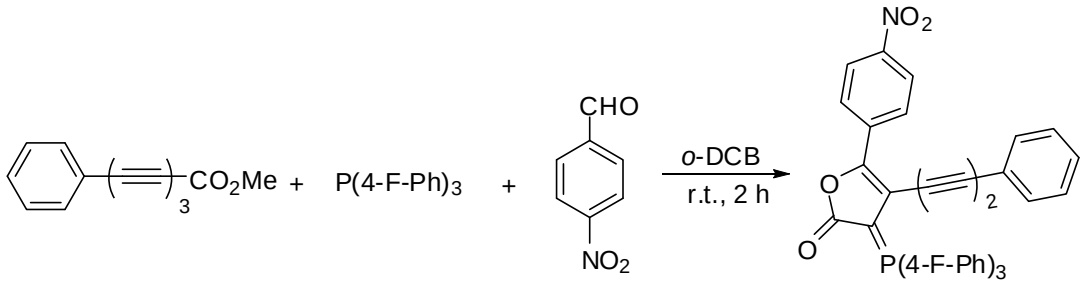


2k **3e** **4a** **5aj**

Red solid (m.p. 185–188 °C). R_f = 0.13 (EA/hexanes, 1:2). Isolated yield 62% (43 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.41 (m, 3H), 7.48–7.54 (m, 2H), 7.58–7.72 (m, 12H), 8.00 (d, J = 9.1 Hz, 2H), 8.16 (d, J = 9.1 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 56.5 (d, $^1J_{PC}$ = 136.4 Hz), 72.8, 73.6, 83.4, 85.8, 106.0 (d, $^2J_{PC}$ = 12.5

Hz), 119.8 (d, $^{1}J_{PC}$ = 96.7 Hz), 121.0, 123.5, 123.9, 128.3, 129.4, 129.8 (d, $^{3}J_{PC}$ = 13.8 Hz), 132.4, 135.2 (d, $^{2}J_{PC}$ = 11.9 Hz), 135.4, 141.1 (d, $^{4}J_{PC}$ = 3.6 Hz), 144.9, 145.2 (d, $^{3}J_{PC}$ = 13.3 Hz), 168.6 (d, $^{2}J_{PC}$ = 17.3 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{38}H_{21}Cl_3NO_4P$ (M^+) 691.0274 found 691.0272.

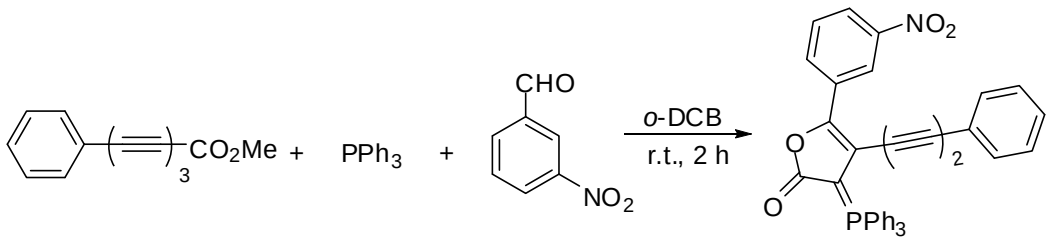
5-(4-nitrophenyl)-4-(phenylbuta-1,3-diyn-1-yl)-3-(tris(4-fluorophenyl)phosphoranylidene)furan-2(3H)-one (5ak):



2k **3f** **4a** **5ak**

Red solid (m.p. 230–233 ^{o}C). R_f = 0.18 (EA/hexanes, 1:2). Isolated yield 73% (47 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.42 (m, 9H), 7.45–7.48 (m, 2H), 7.72–7.81 (m, 6H), 8.02 (d, *J* = 9.1 Hz, 2H), 8.18 (d, *J* = 9.1 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) δ 57.3 (d, $^{1}J_{PC}$ = 137.1 Hz), 73.1, 73.8, 83.2, 85.8, 106.1 (d, $^{2}J_{PC}$ = 12.3 Hz), 117.2 (dd, $^{3}J_{PC}$ = 14.6 Hz, $^{2}J_{FC}$ = 21.8 Hz), 117.8 (d, $^{1}J_{PC}$ = 98.6 Hz), 121.2, 123.7, 124.1, 128.5, 129.6, 132.3, 135.6, 136.7 (dd, $^{3}J_{FC}$ = 9.5 Hz, $^{2}J_{PC}$ = 12.5 Hz), 145.2, 145.4 (d, $^{3}J_{PC}$ = 12.8 Hz), 166.2 (dd, $^{4}J_{PC}$ = 3.0 Hz, $^{1}J_{FC}$ = 258.1 Hz), 168.9 (d, $^{2}J_{PC}$ = 17.6 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{38}H_{21}F_3NO_4P$ (M^+) 643.1160 found 643.1162.

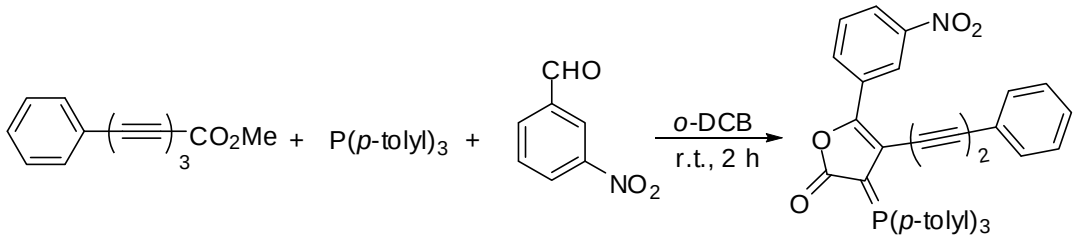
5-(3-nitrophenyl)-4-(phenylbuta-1,3-diyn-1-yl)-3-(triphenylphosphoranylidene) furan-2(3H)-one (5al):



2k **3a** **4b** **5al**

Orange solid (m.p. 178–181 °C). R_f = 0.10 (EA/hexanes, 1:1). Isolated yield 60% (35 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.35 (m, 3H), 7.37–7.48 (m, 3H), 7.56–7.62 (m, 6H), 7.66–7.71 (m, 3H), 7.74–7.81 (m, 6H), 7.96 (dd, *J* = 6.3, 9.6 Hz, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 8.85 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) 55.3 (d, $^1J_{PC}$ = 134.4 Hz), 73.6, 74.3, 82.5, 84.5, 104.1 (d, $^2J_{PC}$ = 12.1 Hz), 118.5, 120.5, 121.6, 122.2 (d, $^1J_{PC}$ = 94.3 Hz), 128.4, 129.0, 129.1, 129.2 (d, $^3J_{PC}$ = 12.8 Hz), 129.2, 131.8, 132.0, 133.5 (d, $^4J_{PC}$ = 3.0 Hz), 134.1 (d, $^2J_{PC}$ = 10.6 Hz), 144.9 (d, $^3J_{PC}$ = 12.8 Hz), 148.4, 168.9 (d, $^2J_{PC}$ = 17.4 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683 cm^{-1}; HRMS (ESI^+), calcd for $C_{38}H_{24}NO_4P$ (M^+) 589.1443 found 589.1445.

5-(3-nitrophenyl)-4-(phenylbuta-1,3-diyn-1-yl)-3-(tri-*p*-tolylphosphoranylidene) furan-2(3H)-one (5am):

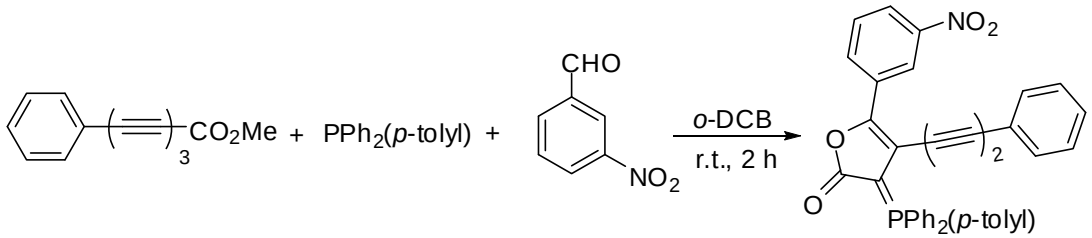


2k **3b** **4b** **5am**

Orange solid (m.p. 218–221 °C). R_f = 0.15 (EA/hexanes, 1:2). Isolated yield 55% (35 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 9H), 7.30–7.46 (m, 12H), 7.61–7.68 (m, 6H), 7.93 (d, *J* = 7.9 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.85 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.6 (d, $^5J_{PC}$ = 1.5 Hz), 56.8 (d, $^1J_{PC}$ = 134.4 Hz), 73.6, 74.3,

82.0, 84.2, 104.4 (d, $^{2}J_{PC}$ = 12.1 Hz), 118.3, 119.1 (d, $^{1}J_{PC}$ = 96.6 Hz), 120.2, 121.6, 128.3, 128.8, 129.08, 129.12, 129.8 (d, $^{3}J_{PC}$ = 13.6 Hz), 131.9, 132.0, 133.9 (d, $^{2}J_{PC}$ = 11.3 Hz), 144.2 (d, $^{4}J_{PC}$ = 3.0 Hz), 144.7 (d, $^{3}J_{PC}$ = 12.8 Hz), 148.3, 168.9 (d, $^{2}J_{PC}$ = 17.4 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683 cm^{-1}; HRMS (ESI^+), calcd for $C_{41}H_{30}NO_4P$ (M^+) 631.1912 found 631.1914.

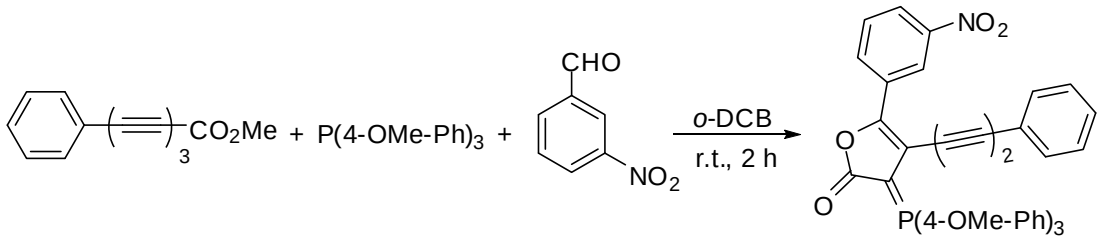
3-(diphenyl(*p*-tolyl)phosphoranylidene)-5-(3-nitrophenyl)-4-(phenylbuta-1,3-diyn-1-yl)furan-2(3H)-one (5an):



2k **3c** **4b** **5an**

Orange solid (m.p. 175–178 °C). R_f = 0.13 (EA/hexanes, 1.5:1). Isolated yield 60% (36 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H), 7.30–7.33 (m, 3H), 7.38–7.44 (m, 5H), 7.57–7.68 (m, 8H), 7.75–7.82 (m, 4H), 7.94 (dd, *J* = 2.0, 8.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.85 (t, *J* = 1.7 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7, 55.8 (d, $^{1}J_{PC}$ = 135.1 Hz), 73.6, 74.3, 82.3, 84.4, 104.2 (d, $^{2}J_{PC}$ = 12.8 Hz), 118.4, 118.4 (d, $^{1}J_{PC}$ = 96.6 Hz), 120.4, 121.5, 122.8 (d, $^{1}J_{PC}$ = 94.0 Hz), 123.2, 128.3, 128.9, 129.1 (d, $^{2}J_{PC}$ = 12.8 Hz), 129.1, 129.9 (d, $^{3}J_{PC}$ = 13.6 Hz), 131.8, 132.0, 133.4 (d, $^{4}J_{PC}$ = 3.0 Hz), 134.0 (d, $^{2}J_{PC}$ = 10.6 Hz), 134.2, 144.6 (d, $^{4}J_{PC}$ = 3.0 Hz), 144.8 (d, $^{3}J_{PC}$ = 12.8 Hz), 148.4, 168.9 (d, $^{2}J_{PC}$ = 17.4 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.8 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{39}H_{26}NO_4P$ (M^+) 603.1599 found 603.1605.

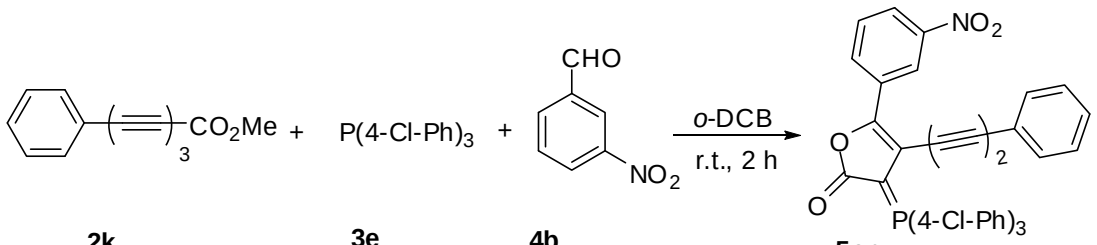
5-(3-nitrophenyl)-4-(phenylbuta-1,3-diyn-1-yl)-3-(tris(4-methoxyphenyl)phospho ranylidene)furan-2(3H)-one (5ao):



2k **3d** **4b** **5ao**

Orange solid (m.p. 105–108 °C). R_f = 0.20 (EA/hexanes, 2.5:1). Isolated yield 54% (37 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 9H), 7.06 (dd, *J* = 6.6, 11.1 Hz, 6H), 7.27–7.34 (m, 3H), 7.44–7.47 (m, 3H), 7.64–7.71 (m, 6H), 7.92 (dd, *J* = 6.6, 9.6 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.84 (t, *J* = 1.8 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.3, 58.0 (d, $^1J_{PC}$ = 135.1 Hz), 73.6, 74.3, 81.9, 84.5, 104.6 (d, $^2J_{PC}$ = 12.1 Hz), 113.5 (d, $^1J_{PC}$ = 101.2 Hz), 114.7 (d, $^3J_{PC}$ = 13.6 Hz), 118.2, 120.1, 121.6, 128.3, 128.7, 129.08, 129.12, 132.1, 132.5, 135.8 (d, $^2J_{PC}$ = 12.1 Hz), 144.5 (d, $^3J_{PC}$ = 12.8 Hz), 148.4, 163.4 (d, $^4J_{PC}$ = 3.0 Hz), 168.9 (d, $^2J_{PC}$ = 16.6 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1682 cm^{-1}; HRMS (ESI^+), calcd for $C_{41}H_{30}NO_7P$ (M^+) 679.1760 found 679.1761.

5-(3-nitrophenyl)-4-(phenylbuta-1,3-diyn-1-yl)-3-(tris(4-chlorophenyl)phosphoranylidene)furan-2(3H)-one (5ap):

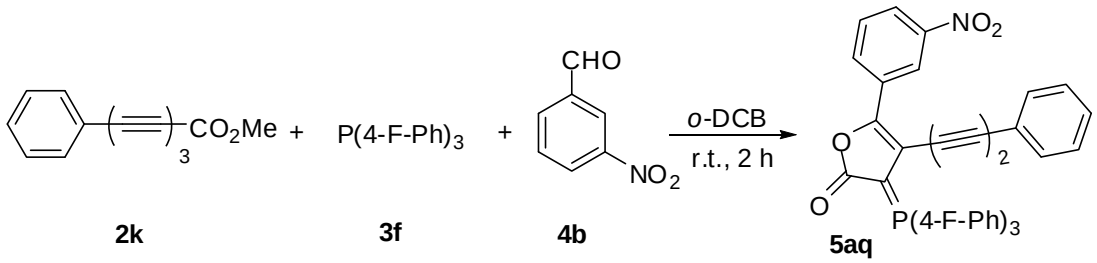


2k **3e** **4b** **5ap**

Orange solid (m.p. 118–121 °C). R_f = 0.18 (EA/hexanes, 1:2). Isolated yield 46% (32 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.35 (m, 3H), 7.47–7.51 (m, 3H), 7.57–7.61 (m, 6H), 7.65–7.73 (m, 6H), 7.96–7.99 (m, 1H), 8.17–8.19 (m, 1H), 8.81 (t, *J* = 1.9 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 54.5 (d, $^1J_{PC}$ = 137.3 Hz), 72.9, 73.7,

82.8, 85.3, 103.3 (d, $^{2}J_{PC}$ = 12.4 Hz), 118.5, 120.2 (d, $^{1}J_{PC}$ = 96.8 Hz), 120.8, 121.3, 128.3, 129.0, 129.3, 129.9 (d, $^{3}J_{PC}$ = 13.7 Hz), 131.5, 132.4, 135.2 (d, $^{2}J_{PC}$ = 11.9 Hz), 141.0 (d, $^{4}J_{PC}$ = 3.5 Hz), 145.5 (d, $^{3}J_{PC}$ = 13.2 Hz), 148.4, 168.7 (d, $^{2}J_{PC}$ = 17.6 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.4 ppm (one fewer carbons are observed due to coincidental overlap); FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1685 cm^{-1}; HRMS (ESI^+), calcd for $C_{38}H_{21}Cl_3NO_4P$ (M^+) 691.0274 found 691.0267.

5-(3-nitrophenyl)-4-(phenylbuta-1,3-diyn-1-yl)-3-(tris(4-fluorophenyl)phosphoranylidene)furan-2(3H)-one (5aq):



2k **3f** **4b** **5aq**

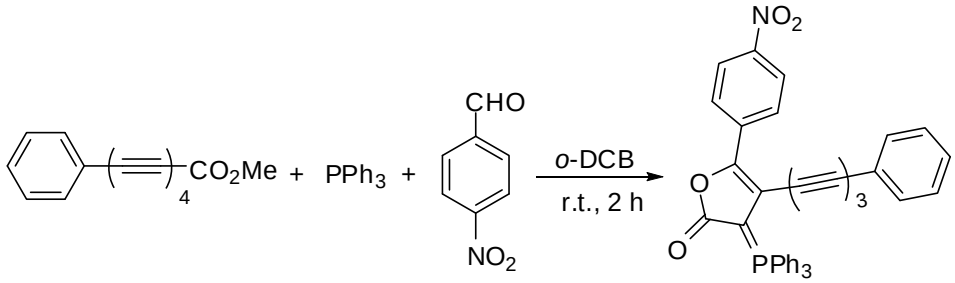
Orange solid (m.p. 115–118 °C). R_f = 0.23 (EA/hexanes, 1:1). Isolated yield 62% (40 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.36 (m, 9H), 7.44–7.50 (m, 3H), 7.74–7.82 (m, 6H), 7.95–7.99 (m, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.80 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.4 (d, $^{1}J_{PC}$ = 137.4 Hz), 73.0, 73.7, 82.6, 85.3, 103.5 (d, $^{2}J_{PC}$ = 12.8 Hz), 117.1 (dd, $^{3}J_{PC}$ = 14.3 Hz, $^{2}J_{FC}$ = 21.9 Hz), 117.9 (dd, $^{4}J_{FC}$ = 3.8 Hz, $^{1}J_{PC}$ = 97.4 Hz), 118.5, 120.8, 121.3, 128.4, 129.0, 129.3, 131.6, 132.2, 136.7 (dd, $^{3}J_{FC}$ = 9.8 Hz, $^{2}J_{PC}$ = 12.8 Hz), 145.3 (d, $^{3}J_{PC}$ = 13.6 Hz), 148.4, 166.1 (dd, $^{4}J_{PC}$ = 3.0 Hz, $^{1}J_{FC}$ = 261.2 Hz), 168.8 (d, $^{2}J_{PC}$ = 17.4 Hz) ppm (one fewer carbons are observed due to coincidental overlap); ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684 cm^{-1}; HRMS (ESI^+), calcd for $C_{38}H_{21}F_3NO_4P$ (M^+) 643.1160 found 643.1159.

General procedure for synthesis 5ar to 5aw

To 2.0 mL of anhydrous *o*-DCB solution containing phoshpine **3** (0.12 mmol) and aldehyde **4** (0.08 mmol) was added **2l** (0.12 mmol in 5.0 mL of *o*-DCB) *via* a syringe pump in 1 h at room temperature. Upon completion of injection, the mixture was

stirred for another 1 h. The mixture was then subjected to flash silica gel chromatography. Elution with hexanes/EA gave products **5ar** to **5aw**.

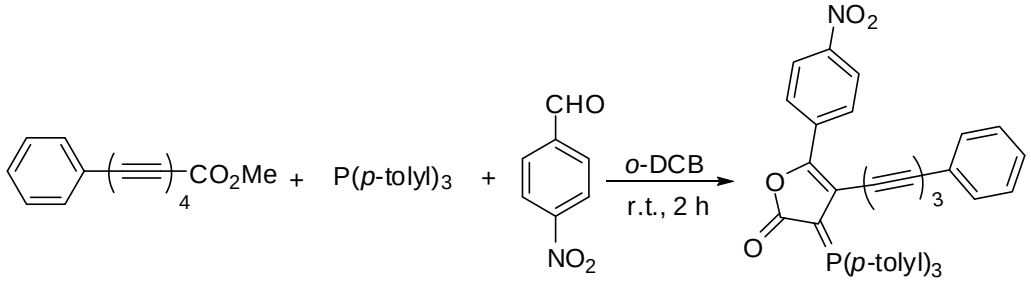
5-(4-nitrophenyl)-4-(phenylhexa-1,3,5-triyn-1-yl)-3-(triphenylphosphoranylidene) furan-2(3H)-one (5ar):



2l **3a** **4a** **5ar**

Red solid (m.p. 225–228 ^{o}C). R_f = 0.28 (EA/hexanes, 1:1). Isolated yield 38% (19 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.42 (m, 3H), 7.51 (d, J = 7.2 Hz, 2H), 7.61–7.63 (m, 6H), 7.70–7.79 (m, 9H), 8.00 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 57.2 (d, $^{1}J_{PC}$ = 134.2 Hz), 65.8, 70.5, 71.3, 74.1, 80.8, 83.5, 106.0 (d, $^{2}J_{PC}$ = 12.1 Hz), 120.7, 121.9 (d, $^{1}J_{PC}$ = 94.0 Hz), 123.6, 124.1, 128.5, 129.3 (d, $^{3}J_{PC}$ = 13.0 Hz), 129.8, 132.8, 133.8 (d, $^{4}J_{PC}$ = 3.0 Hz), 134.1 (d, $^{2}J_{PC}$ = 10.7 Hz), 135.5, 145.1, 146.8 (d, $^{3}J_{PC}$ = 12.7 Hz), 168.6 (d, $^{2}J_{PC}$ = 16.9 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684, 2158, 2191 cm^{-1}; HRMS (ESI^{+}), calcd for $C_{40}H_{24}NO_4P$ (M^{+}) 613.1443 found 613.1442.

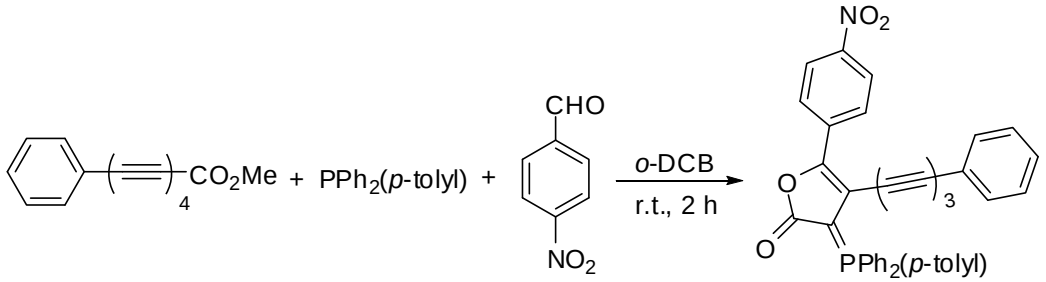
5-(4-nitrophenyl)-4-(phenylhexa-1,3,5-triyn-1-yl)-3-(tri-*p*-tolylphosphoranylidene)furan-2(3H)-one (5as):



2l **3b** **4a** **5as**

Red solid (m.p. 104–107 °C; decomposed). R_f = 0.25 (EA/hexanes, 1:1). Isolated yield 30% (16 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 9H), 7.31–7.40 (m, 9H), 7.49–7.54 (m, 2H), 7.59–7.66 (m, 6H), 7.99 (d, J = 9.1 Hz, 2H), 8.15 (d, J = 9.1 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7, 58.9 (d, $^1J_{PC}$ = 134.7 Hz), 65.9, 70.0, 71.3, 74.1, 80.8, 83.1, 106.5 (d, $^2J_{PC}$ = 12.2 Hz), 118.7 (d, $^1J_{PC}$ = 96.4 Hz), 120.7, 123.4, 124.0, 128.5, 129.8, 130.0 (d, $^3J_{PC}$ = 13.4 Hz), 132.7, 134.0 (d, $^2J_{PC}$ = 11.1 Hz), 135.6, 144.7 (d, $^4J_{PC}$ = 2.9 Hz), 144.9, 146.5 (d, $^3J_{PC}$ = 13.1), 168.7 (d, $^2J_{PC}$ = 16.5 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684, 2157, 2193 cm^{-1}; HRMS (ESI^+), calcd for $C_{43}H_{30}NO_4P$ (M^+) 655.1912 found 655.1918.

3-(diphenyl(*p*-tolyl)phosphoranylidene)-5-(4-nitrophenyl)-4-(phenylhexa-1,3,5-triyn-1-yl)furan-2(3H)-one (5at):

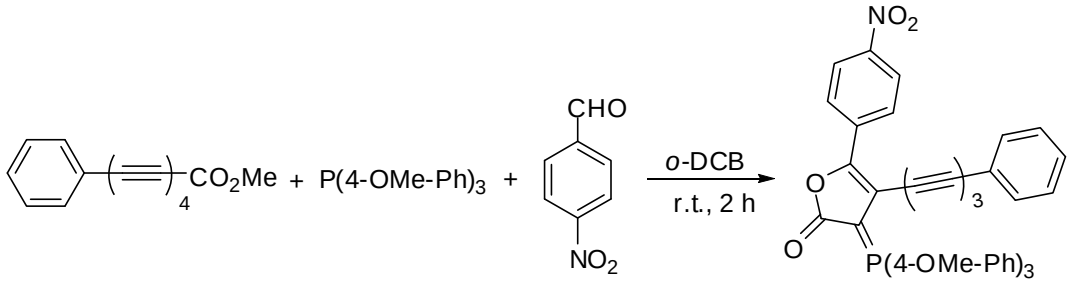


2l **3c** **4a** **5at**

Red solid (m.p. 107–110 °C; decomposed). R_f = 0.20 (EA/hexanes, 1:1). Isolated yield 43% (22 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.49 (s, 3H) 7.32–7.42 (m, 5H), 7.49–7.52 (m, 2H), 7.55–7.63 (m, 6H), 7.69–7.81 (m, 6H), 8.00 (d, J = 9.1 Hz, 2H), 8.17 (d, J = 9.1 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.8, 57.8 (d, $^1J_{PC}$ = 134.3 Hz), 65.8, 70.3, 71.3, 74.1, 80.8, 83.4, 106.2 (d, $^2J_{PC}$ = 11.9 Hz), 118.0 (d, $^1J_{PC}$ = 96.1 Hz), 120.7, 122.3 (d, $^1J_{PC}$ = 94.1 Hz), 122.9, 123.6, 124.1, 128.5, 129.3 (d, $^3J_{PC}$ = 13.1 Hz), 129.8, 130.2 (d, $^3J_{PC}$ = 13.4 Hz), 132.8, 133.7 (d, $^4J_{PC}$ = 3.1 Hz), 134.1 (d, $^2J_{PC}$ = 10.9 Hz), 134.3, 135.6, 145.1, 146.8 (d, $^3J_{PC}$ = 12.3 Hz), 168.7 (d, $^2J_{PC}$ = 16.9 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683, 2159,

2193 cm^{-1}; HRMS (ESI^+), calcd for $C_{41}H_{26}NO_4P$ (M^+) 627.1599 found 627.1605.

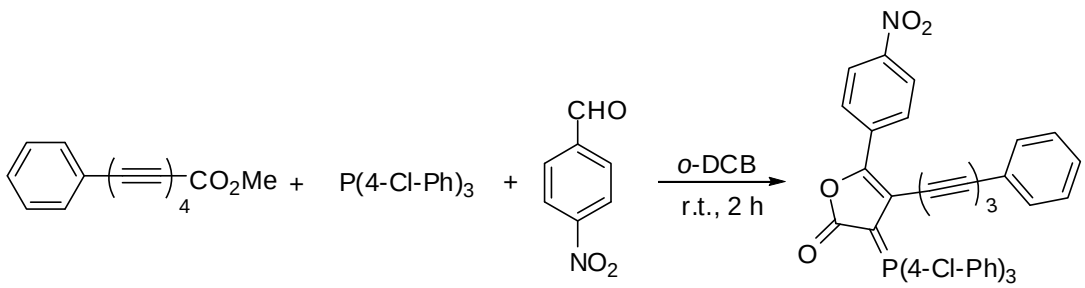
5-(4-nitrophenyl)-4-(phenylhexa-1,3,5-triyn-1-yl)-3-(tris(4-methoxyphenyl)phosphoranylidene)furan-2(3H)-one (5au):



2l **3d** **4a** **5au**

Red solid (m.p. 107–110 °C). R_f = 0.35 (EA/hexanes, 2:1). Isolated yield 27% (15 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (s, 9H) 7.07 (dd, *J* = 2.4, 9.0 Hz, 6H), 7.34–7.38 (m, 3H), 7.49–7.52 (m, 2H), 7.62–7.69 (m, 6H), 7.99 (d, *J* = 9.2 Hz, 2H), 8.15 (d, *J* = 9.2 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.5, 60.3 (d, $^1J_{PC}$ = 134.2 Hz), 65.8, 70.4, 71.4, 74.1, 80.8, 83.0, 106.6 (d, $^2J_{PC}$ = 12.1 Hz), 113.1 (d, $^1J_{PC}$ = 101.5 Hz), 114.9 (d, $^3J_{PC}$ = 14.1 Hz), 120.7, 123.3, 124.0, 128.5, 129.8, 132.7, 135.6, 135.8 (d, $^2J_{PC}$ = 12.4 Hz), 144.8, 146.3 (d, $^3J_{PC}$ = 12.2 Hz), 163.6 (d, $^4J_{PC}$ = 2.9 Hz), 168.7 (d, $^2J_{PC}$ = 16.8 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1681, 2158, 2193 cm^{-1}; HRMS (ESI^+), calcd for $C_{41}H_{30}NO_7P$ (M^+) 703.1760 found 703.1761.

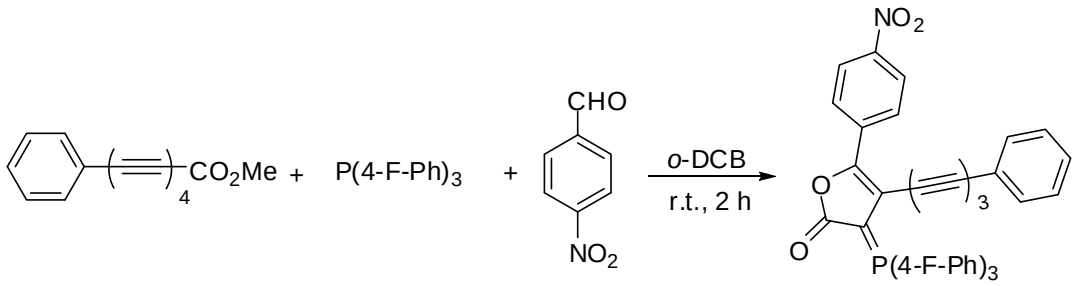
5-(4-nitrophenyl)-4-(phenylhexa-1,3,5-triyn-1-yl)-3-(tris(4-chlorophenyl)phosphoranylidene)furan-2(3H)-one (5av):



2l **3e** **4a** **5av**

Red solid (m.p. 139–142 °C). R_f = 0.25 (EA/DCM, 1:50). Isolated yield 35% (20 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.41 (m, 3H), 7.48–7.53 (m, 2H), 7.59–7.71 (m, 12H), 7.98 (d, J = 9.1 Hz, 2H), 8.17 (d, J = 9.1 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 56.2 (d, $^1J_{PC}$ = 136.7 Hz), 65.1, 70.8, 71.1, 74.0, 81.3, 83.8, 105.1 (d, $^2J_{PC}$ = 12.1 Hz), 119.8 (d, $^1J_{PC}$ = 96.6 Hz), 120.7, 123.8, 124.1, 128.5, 129.9, 130.0 (d, $^3J_{PC}$ = 13.6 Hz), 132.9, 135.2 (d, $^2J_{PC}$ = 12.1 Hz), 135.4, 141.5 (d, $^4J_{PC}$ = 3.0 Hz), 145.4 , 147.1 (d, $^3J_{PC}$ = 12.8 Hz), 168.5 (d, $^2J_{PC}$ = 16.6 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683, 2159, 2193 cm^{-1}; HRMS (ESI^+), calcd for $C_{40}H_{21}Cl_3NO_4P$ (M^+) 715.0274 found 715.0278.

5-(4-nitrophenyl)-4-(phenylhexa-1,3,5-triyn-1-yl)-3-(tris(4-fluorophenyl)phosphoranylidene)furan-2(3H)-one (5aw):

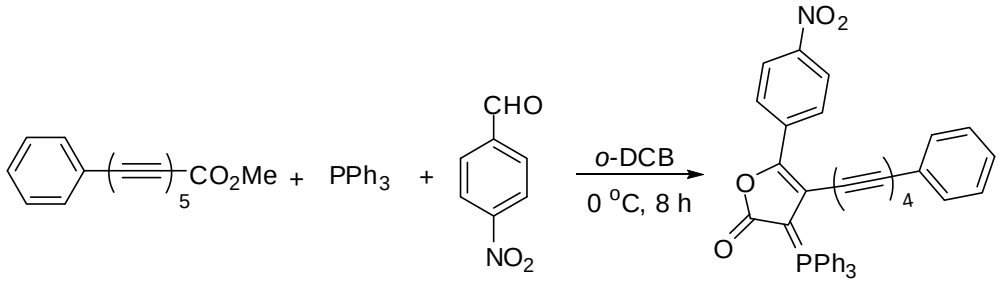


2l **3f** **4a** **5aw**

Red solid (m.p. 110–113 °C). R_f = 0.30 (EA/hexanes, 1:1.5). Isolated yield 43% (23 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.41 (m, 9H), 7.51–7.54 (m, 2H), 7.70–7.81 (m, 6H), 7.99 (d, J = 9.1 Hz, 2H), 8.18 (d, J = 9.1 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) δ 57.0 (d, $^1J_{PC}$ = 136.7 Hz), 65.1, 70.9, 71.0, 73.8, 81.2, 83.6, 105.2 (d, $^2J_{PC}$ = 12.1 Hz), 117.2 (dd, $^3J_{PC}$ = 14.3 Hz, $^2J_{FC}$ = 21.9 Hz), 117.5 (d, $^4J_{FC}$ = 3.0 Hz, $^1J_{PC}$ = 98.9 Hz), 120.6, 123.7, 124.1, 128.5, 129.9, 132.9, 135.3, 136.7 (dd, $^3J_{FC}$ = 9.1 Hz, $^2J_{PC}$ = 12.1 Hz), 145.4, 147.0 (d, $^3J_{PC}$ = 12.8 Hz), 166.2 (dd, $^4J_{PC}$ = 3.0 Hz, $^1J_{FC}$ = 255.2 Hz), 168.5 (d, $^2J_{PC}$ = 17.4 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 10.9 ppm;

FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1683, 2159, 2193 cm^{-1}; HRMS (ESI^+), calcd for $C_{40}H_{21}F_3NO_4P$ (M^+) 667.1160 found 667.1168.

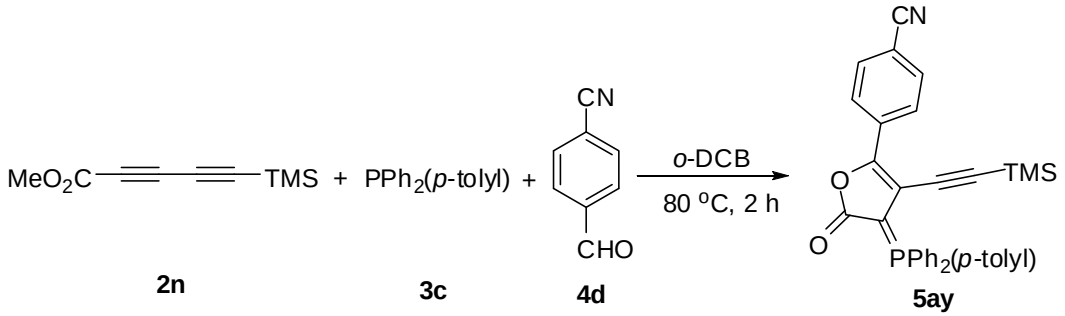
5-(4-nitrophenyl)-4-(phenylocta-1,3,5,7-tetrayn-1-yl)-3-(triphenylphosphoranylidene)furan-2(3H)-one (5ax):



2m **3a** **4a** **5ax**

To 20 mL of anhydrous *o*-DCB solution containing **3a** (0.094 g, 0.34 mmol) and aldehyde **4a** (0.199 g, 1.32 mmol) was added **2m** (0.083 g, 0.32 mmol in 80.0 mL of *o*-DCB) *via* a syringe pump in 8 h at 0 ºC. The mixture was then subjected to flash silica gel chromatography. Elution first with hexanes/EA (1/1.5, R_f = 0.18) gave red products **5ax** in 32% (65 mg) yield after removal of solvent. Spectral data for compound **5ax** are as followings. Red solid (m.p. 297–300 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.42 (m, 3H), 7.53 (d, J = 7.2 Hz, 2H), 7.61–7.62 (m, 6H), 7.71–7.78 (m, 9H), 7.99 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) δ 56.9 (d, $^1J_{PC}$ = 134.1 Hz), 62.9, 66.1, 66.8, 70.7, 71.6, 74.2, 79.1, 83.5, 105.5 (d, $^2J_{PC}$ = 12.1 Hz), 120.4, 121.9 (d, $^1J_{PC}$ = 93.6 Hz), 123.8, 124.1, 128.6, 129.4 (d, $^3J_{PC}$ = 12.7 Hz), 130.1, 133.2, 133.8, 134.1 (d, $^2J_{PC}$ = 10.9 Hz), 135.4, 145.4, 147.9 (d, $^3J_{PC}$ = 12.8 Hz), 168.5 (d, $^2J_{PC}$ = 16.7 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1685, 2145, 2336, 2360; HRMS (ESI^+), calcd for $C_{42}H_{24}NO_4P$ (M+1) 638.1516 found 638.1521.

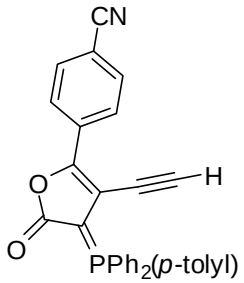
4-(4-(diphenyl(*p*-tolyl)phosphoranylidene)-5-oxo-3-((trimethylsilyl)ethynyl)-4,5-dihydrofuran-2-yl)benzonitrile (5ay):



2n **3c** **4d** **5ay**

Yellow solid (m.p. 228–230 °C). R_f = 0.38 (EA/hexanes, 2:1). Isolated yield 48 % (37 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ -0.15 (s, 9H), 2.42 (s, 3H), 7.33 (dd, *J* = 3.0, 8.1 Hz, 2H), 7.48–7.57 (m, 7H), 7.60–7.73 (m, 7H), 8.04 (dd, *J* = 2.0, 7.4 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ -0.85, 21.5, 56.3 (d, $^1J_{PC}$ = 133.4 Hz), 98.6, 105.2, 106.8 (d, $^2J_{PC}$ = 11.3 Hz), 107.6, 118.3, 118.9 (d, $^1J_{PC}$ = 96.5 Hz), 123.4 (d, $^1J_{PC}$ = 93.2 Hz), 123.5, 128.8 (d, $^3J_{PC}$ = 12.6 Hz), 129.60 (d, $^3{}_{PC}$ = 13.2 Hz), 131.64, 133.0 (d, $^4{}_{PC}$ = 2.0 Hz), 134.0 (d, $^2{}_{PC}$ = 10.4 Hz), 134.0 (d, $^2{}_{PC}$ = 10.9 Hz), 134.3, 142.2 (d, $^3J_{PC}$ = 12.8 Hz), 144.1 (d, $^4J_{PC}$ = 2.6 Hz), 168.7 (d, $^2J_{PC}$ = 18.3 Hz) ppm; ^{31}P NMR (242.4 Hz, $CDCl_3$) 11.9 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1684, 2147, 2220 cm^{-1}; HRMS (ESI^+), calcd for $C_{35}H_{31}NO_2PSi$ (M^+) 556.1856 found 556.1859.

4-(4-(diphenyl(*p*-tolyl)phosphoranylidene)-3-ethynyl-5-oxo-4,5-dihydrofuran-2-yl)benzonitrile (5ay'):

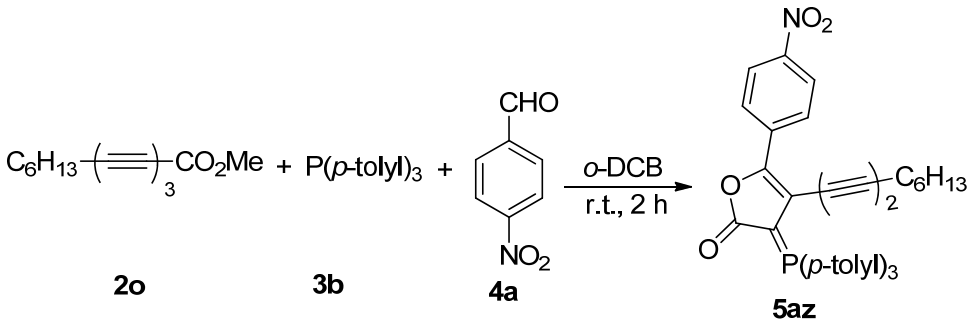


5ay'

Yellow solid (m.p. 148–151 °C). R_f = 0.38 (EA/hexanes = 1:2). Isolated yield: 10 % (7 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.85 (s, 1H), 7.31–7.34 (m, 2H), 7.45–7.53 (m, 6H), 7.56–7.63 (m, 4H), 7.67–7.74 (m, 4H), 7.99 (d, *J* = 8.7 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.4, 57.3 (d, $^1J_{PC}$ = 134.0 Hz), 76.5, 86.7,

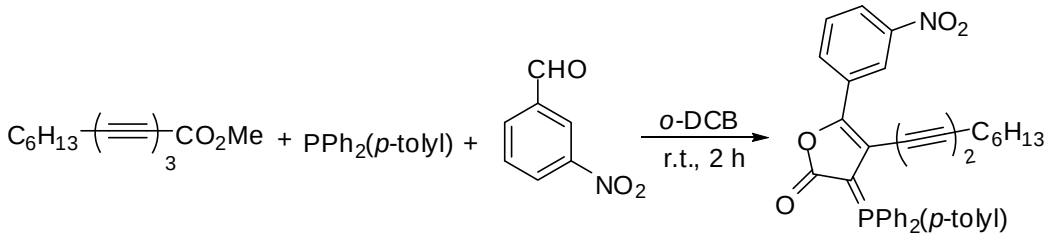
105.6 (d, $^{2}J_{PC}$ = 11.7 Hz), 107.5, 118.0, 119.3, 121.9, 123.1, 123.2, 128.7 (d, $^{3}J_{PC}$ = 12.8 Hz), 129.6 (d, $^{3}J_{PC}$ = 13.3 Hz), 131.7, 133.0 (d, $^{4}J_{PC}$ = 1.7 Hz), 134.0 (d, $^{2}J_{PC}$ = 10.6 Hz), 134.1, 142.2 (d, $^{3}J_{PC}$ = 13.0 Hz), 144.1 (d, $^{4}J_{PC}$ = 2.3 Hz), 168.7 (d, $^{2}J_{PC}$ = 17.4 Hz) ppm; ^{31}P NMR (242.4 Hz, $CDCl_3$) 11.8 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1677, 2101, 2220 cm^{-1}; HRMS (ESI^+), calcd for $C_{32}H_{23}NO_2P$ (M^+) 484.1461 found 484.1469.

4-(deca-1,3-diyn-1-yl)-5-(4-nitrophenyl)-3-(tri-p-tolylphosphoranylidene)furan-2(3H)-one (5az):



Red oil. R_f = 0.19 (EA/hexanes, 1:2). Isolated yield 66% (42 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.28–1.37 (m, 6H), 1.50 (quint, *J* = 7.5 Hz, 2H), 2.28 (t, *J* = 7.1 Hz, 2H), 2.44 (s, 9H), 7.35 (dd, *J* = 2.9, 8.0 Hz, 6H), 7.59 (dd, *J* = 8.2, 13.1 Hz, 6H), 7.99 (d, *J* = 9.2 Hz, 2H), 8.13 (d, *J* = 9.2 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.0, 19.7, 21.7 (d, $^{5}J_{PC}$ = 1.1 Hz), 22.4, 28.2, 28.5, 31.2, 59.2 (d, $^{1}J_{PC}$ = 133.9 Hz), 64.9, 67.4, 83.7, 88.0, 107.8 (d, $^{2}J_{PC}$ = 11.9 Hz), 119.0 (d, $^{1}J_{PC}$ = 96.3 Hz), 123.1, 124.0, 129.9 (d, $^{3}J_{PC}$ = 13.4 Hz), 134.0 (d, $^{2}J_{PC}$ = 11.2 Hz), 136.0, 144.2 (d, $^{4}J_{PC}$ = 3.1 Hz), 144.3, 144.5, 169.0 (d, $^{2}J_{PC}$ = 16.9 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 11.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1690, 2146, 2228 cm^{-1}; HRMS (ESI^+), calcd for $C_{41}H_{39}NO_4P$ (M^++1) 640.2611 found 640.2625.

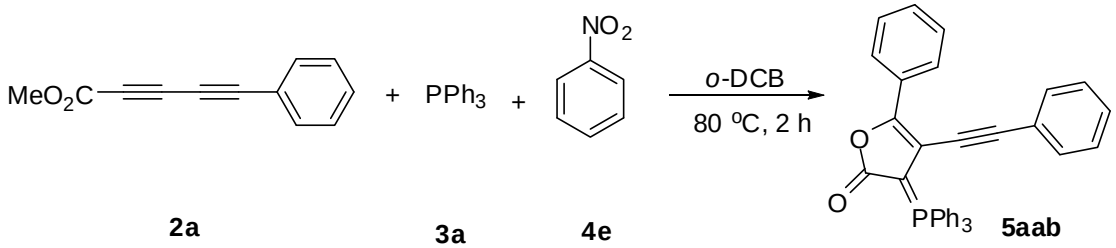
4-(deca-1,3-diyn-1-yl)-3-(diphenyl(p-tolyl)phosphoranylidene)-5-(3-nitrophenyl)furan-2(3H)-one (5aaa):



2o **3c** **4b** **5aaa**

Orange oil. R_f = 0.25 (EA/hexanes, 1:1). Isolated yield 72% (44 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.24–1.35 (m, 6H), 1.49 (quint, *J* = 7.3 Hz, 2H), 2.25 (t, *J* = 6.8 Hz, 2H), 2.45 (s, 3H), 7.34–7.45 (m, 3H), 7.55–7.60 (m, 6H), 7.63–7.68 (m, 2H), 7.71–7.78 (m, 4H), 7.93 (dd, *J* = 2.0, 8.0 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.81 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.9, 19.5, 21.6, 22.4, 28.0, 28.3, 31.1, 55.9 (d, $^1J_{PC}$ = 134.9 Hz), 64.8, 67.2, 83.1, 87.6, 104.5 (d, $^2J_{PC}$ = 12.1 Hz), 118.2, 118.5 (d, $^1J_{PC}$ = 96.3 Hz), 120.1, 122.6 (d, $^1J_{PC}$ = 93.8 Hz), 128.9, 129.0 (d, $^3J_{PC}$ = 12.8 Hz), 129.3, 129.8 (d, $^3J_{PC}$ = 13.4 Hz), 131.8, 133.3 (d, $^4J_{PC}$ = 3.0 Hz), 133.96 (d, $^2J_{PC}$ = 10.7 Hz), 134.02 (d, $^2J_{PC}$ = 12.8 Hz), 144.3 (d, $^4J_{PC}$ = 2.9 Hz), 144.4 (d, $^3J_{PC}$ = 12.8 Hz), 148.3, 168.9 (d, $^2J_{PC}$ = 17.2 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1690, 2147, 2231 cm^{-1}; HRMS (ESI^+), calcd for $C_{39}H_{25}NO_4P$ (M^++1) 612.2298 found 612.2310.

5-phenyl-4-(phenylethynyl)-3-(triphenylphosphoranylidene)furan-2(3H)-one (5aab):



2a **3a** **4e** **5aab**

Yellow solid (m.p. 138–141 °C). R_f = 0.15 (EA/hexanes = 2:1). Isolated yield 10% (7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, *J* = 7.2 Hz, 2H), 7.13–7.18 (m, 4H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.51–7.53 (m, 6H), 7.59–7.61 (m, 3H), 7.77 (dd, *J* = 7.6, 12.8 Hz, 6H), 8.04 (d, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 53.1 (d, $^1J_{PC}$ = 135.4

Hz), 84.7, 96.9, 102.0 (d, $^{2}J_{PC}$ = 11.8 Hz), 123.3, 123.6 (d, $^{1}J_{PC}$ = 93.4 Hz), 124.2, 126.2, 127.6, 127.9, 128.2, 128.9 (d, $^{3}J_{PC}$ = 12.9 Hz), 130.8, 131.0, 133.1 (d, $^{4}J_{PC}$ = 3.0 Hz), 134.3 (d, $^{2}J_{PC}$ = 10.6 Hz), 144.2 (d, $^{3}J_{PC}$ = 12.9 Hz), 169.7 (d, $^{2}J_{PC}$ = 18.2 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 12.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1678 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{25}O_2P$ (M^+) 520.1592 found 520.1592.

Fig S1. ^{1}H NMR spectrum of compound **2a** (300 MHz, $CDCl_3$)

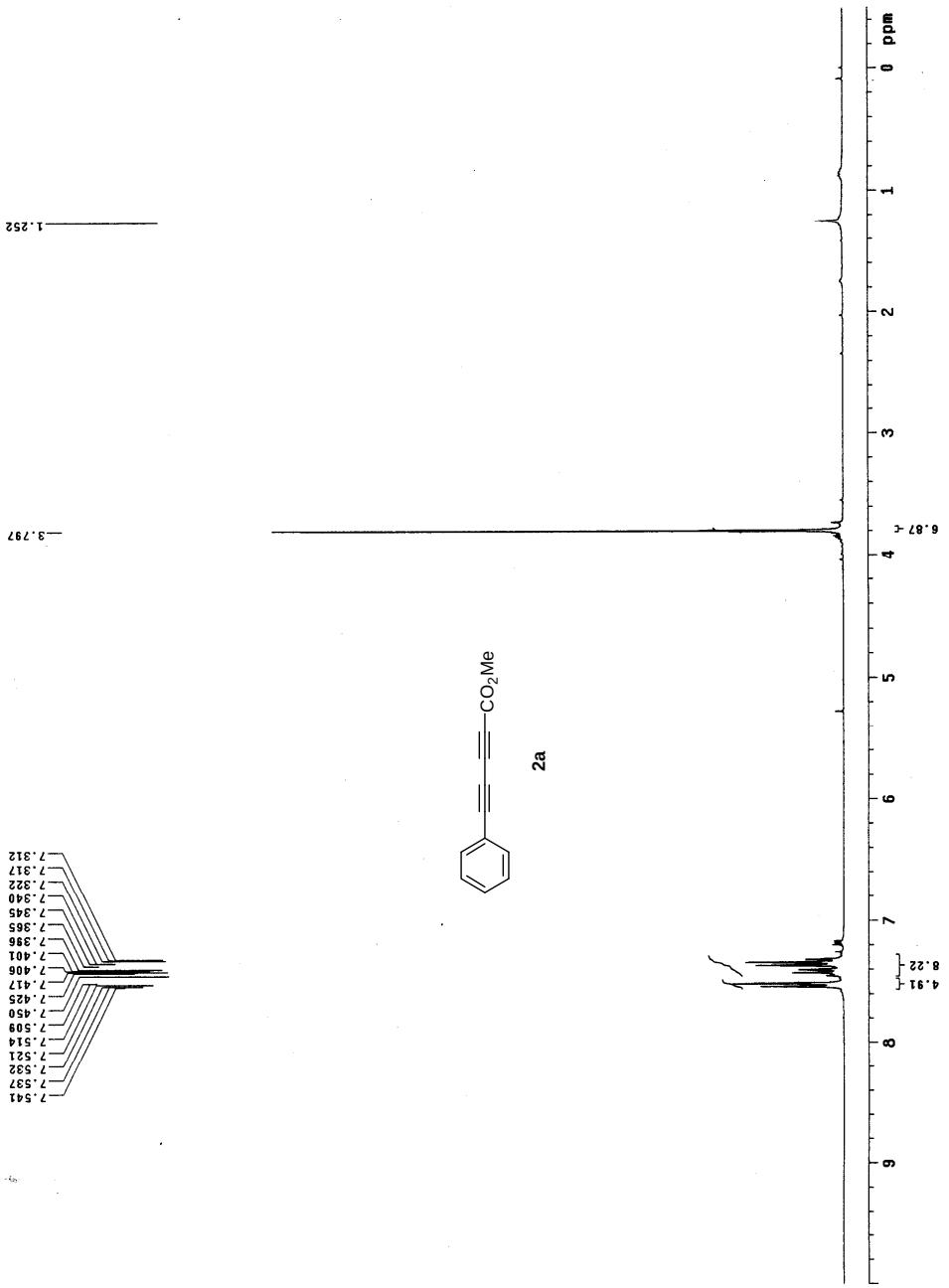


Fig S2. ^{13}C NMR spectrum of compound **2a** (150.7 MHz, $CDCl_3$)

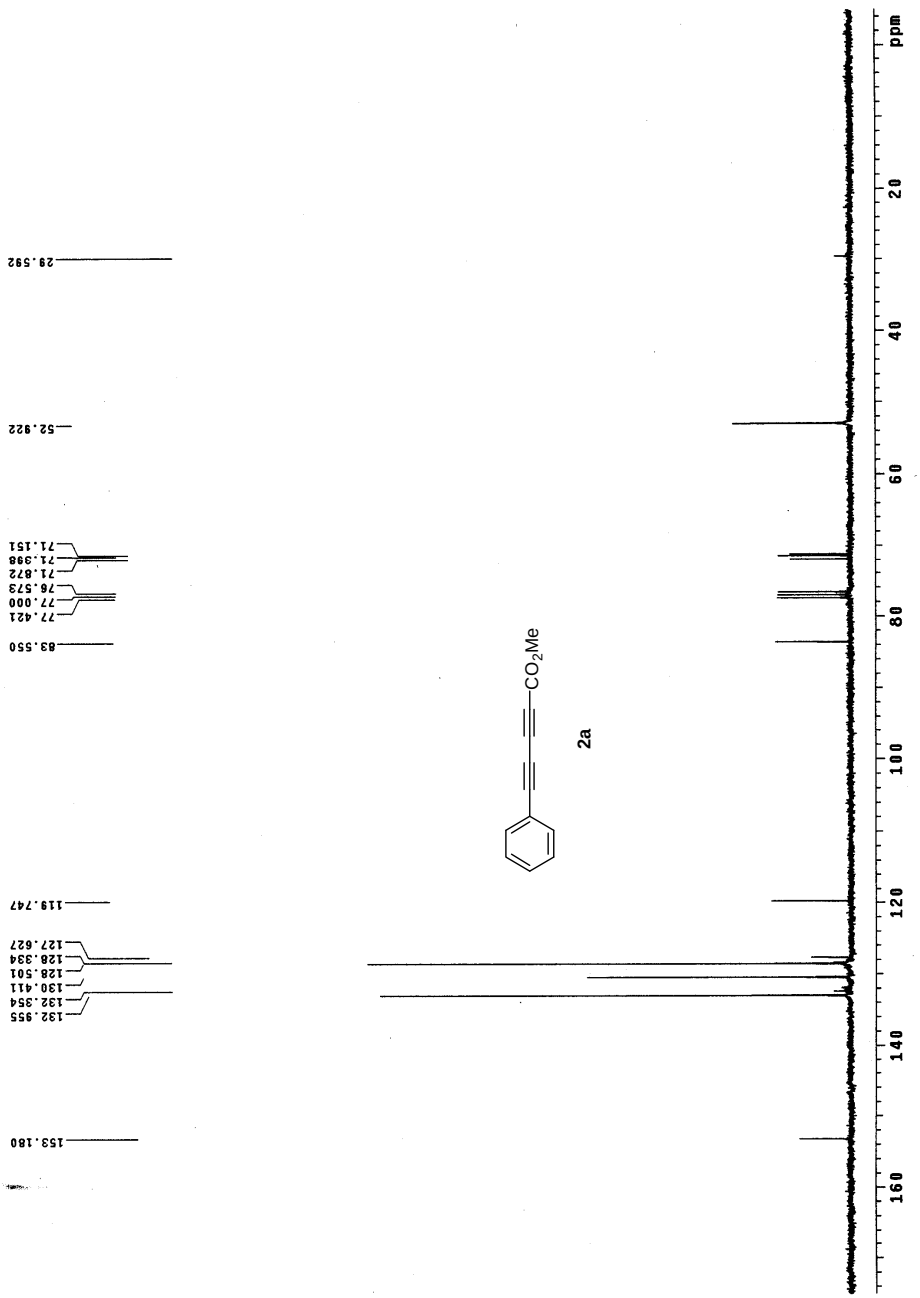


Fig S3. ^{1}H NMR spectrum of compound **2c** (500 MHz, $CDCl_3$)

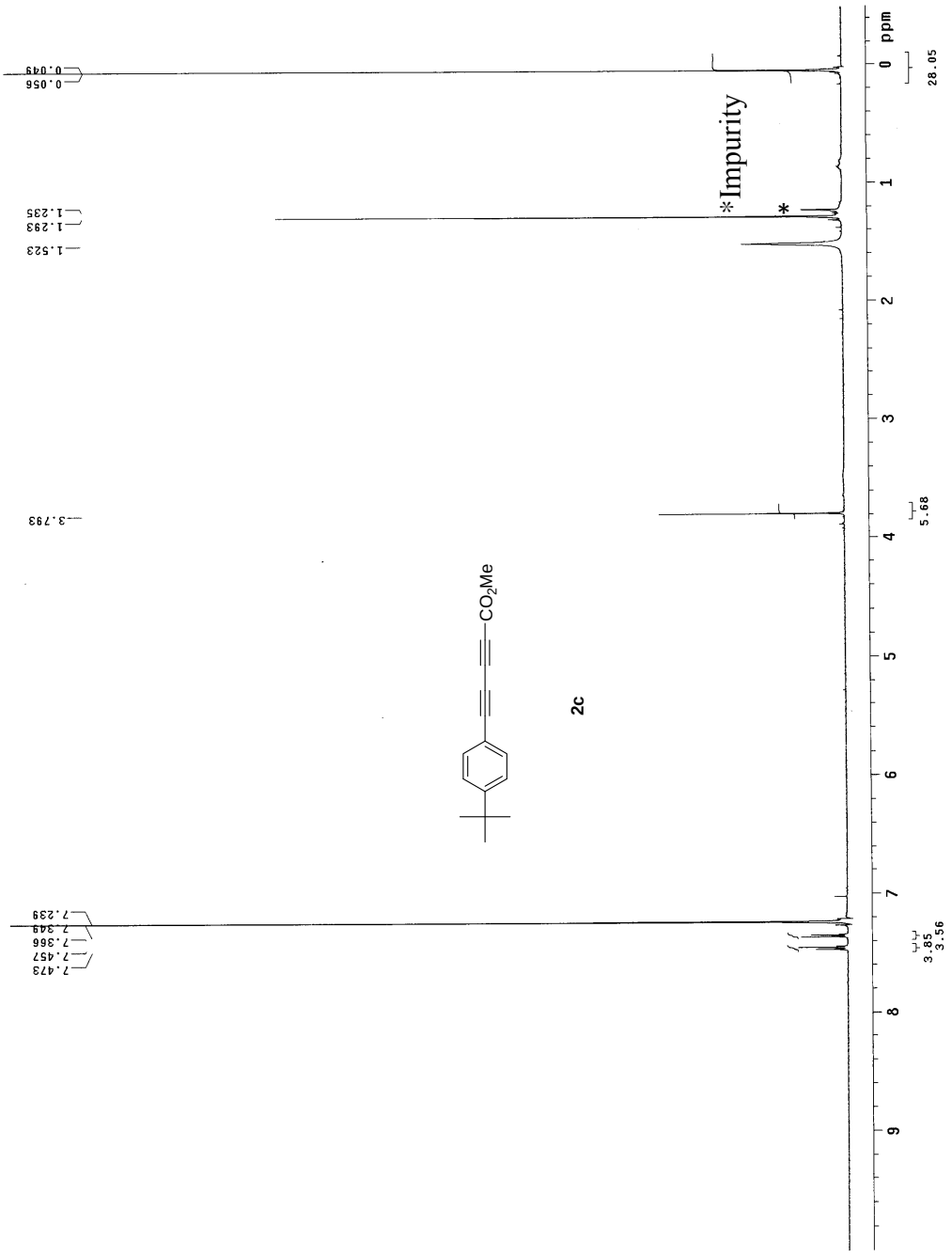


Fig S4. ^{13}C NMR spectrum of compound **2c** (125 MHz, $CDCl_3$)

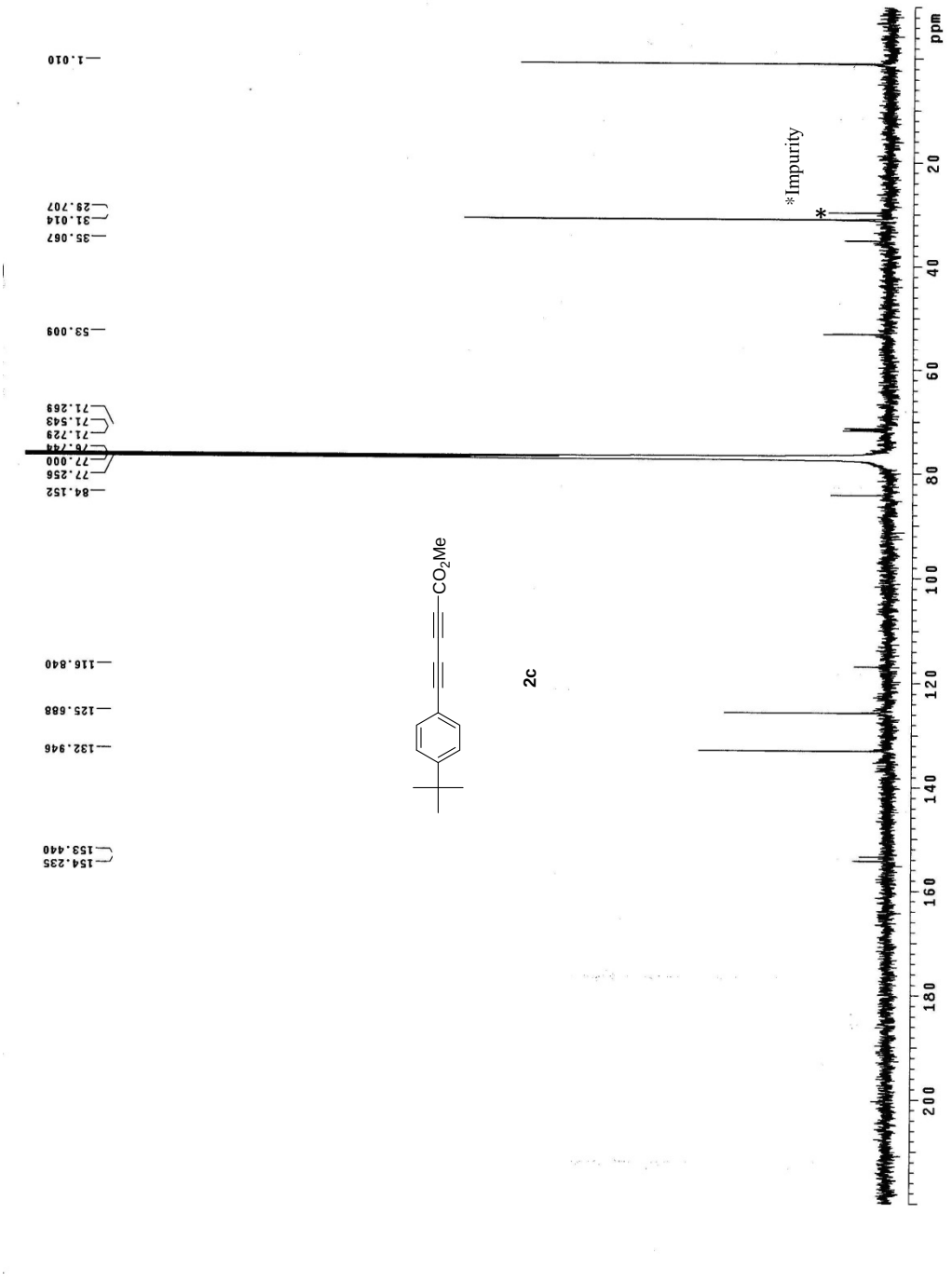


Fig S5. ^{1}H NMR spectrum of compound **2d** (300 MHz, $CDCl_3$)

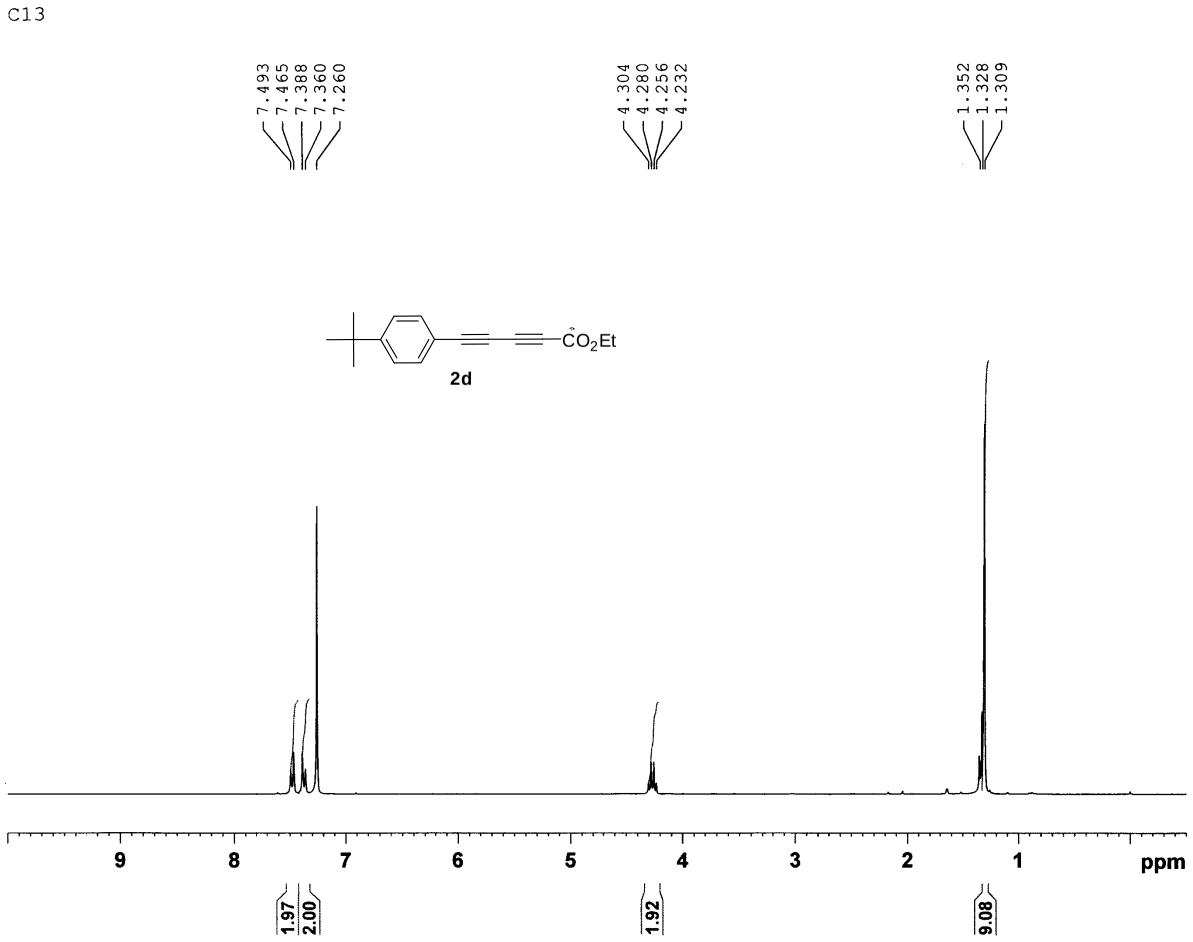


Fig S6. ^{13}C NMR spectrum of compound **2d** (75.5 MHz, $CDCl_3$)

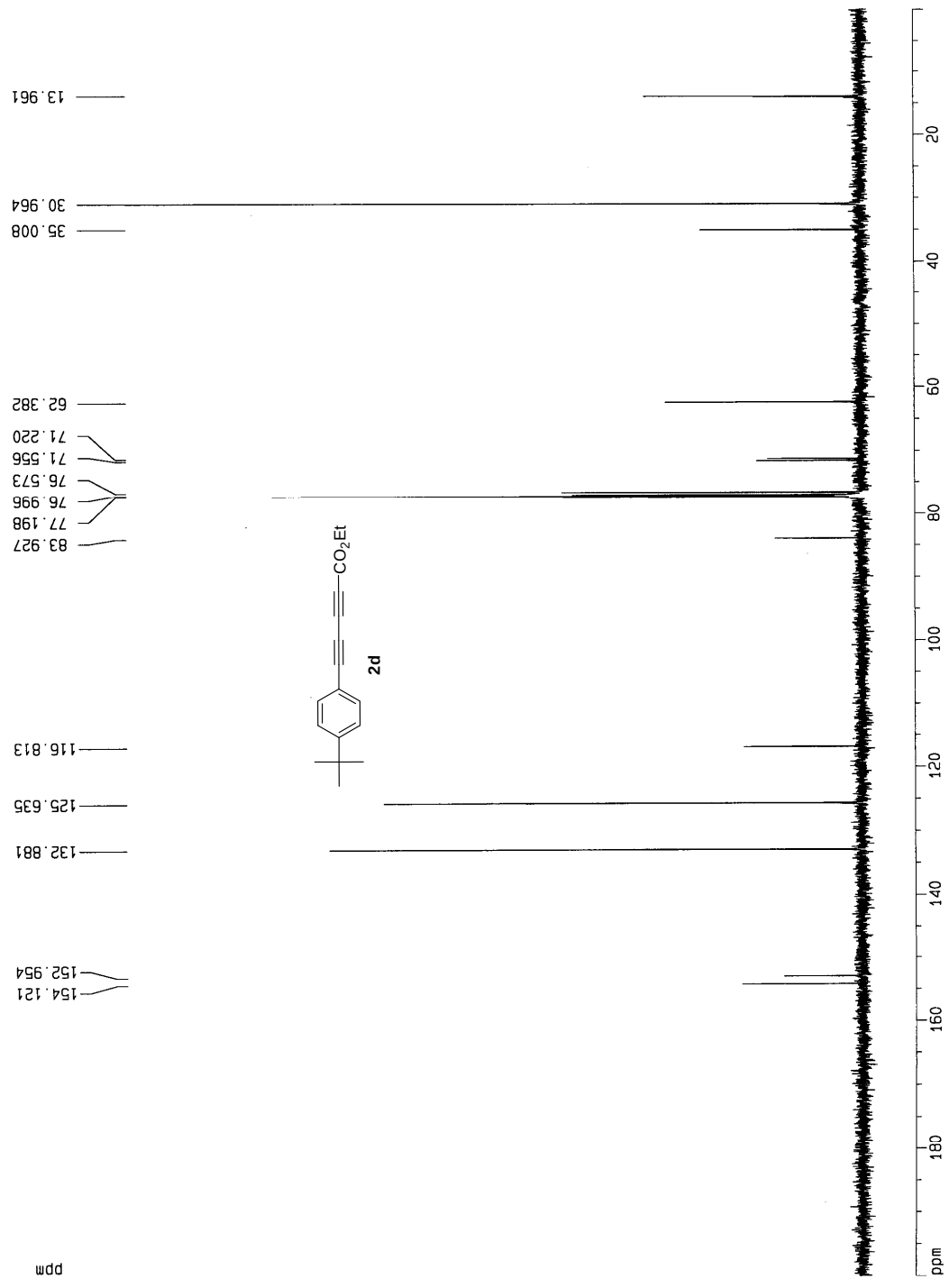


Fig S7. ^{1}H NMR spectrum of compound **2e** (300 MHz, $CDCl_3$)

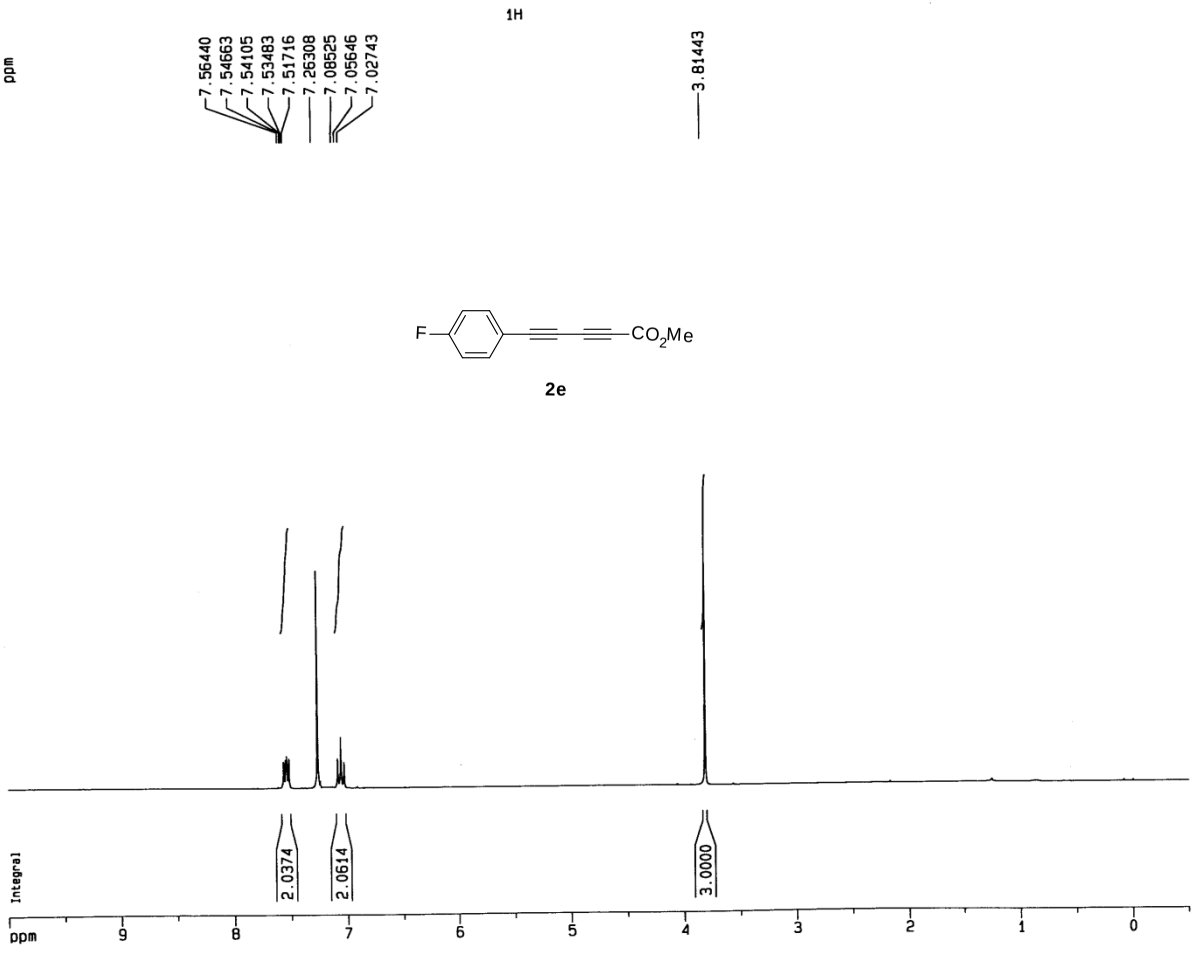


Fig S8. ^{13}C NMR spectrum of compound **2e** (75.5 MHz, $CDCl_3$)

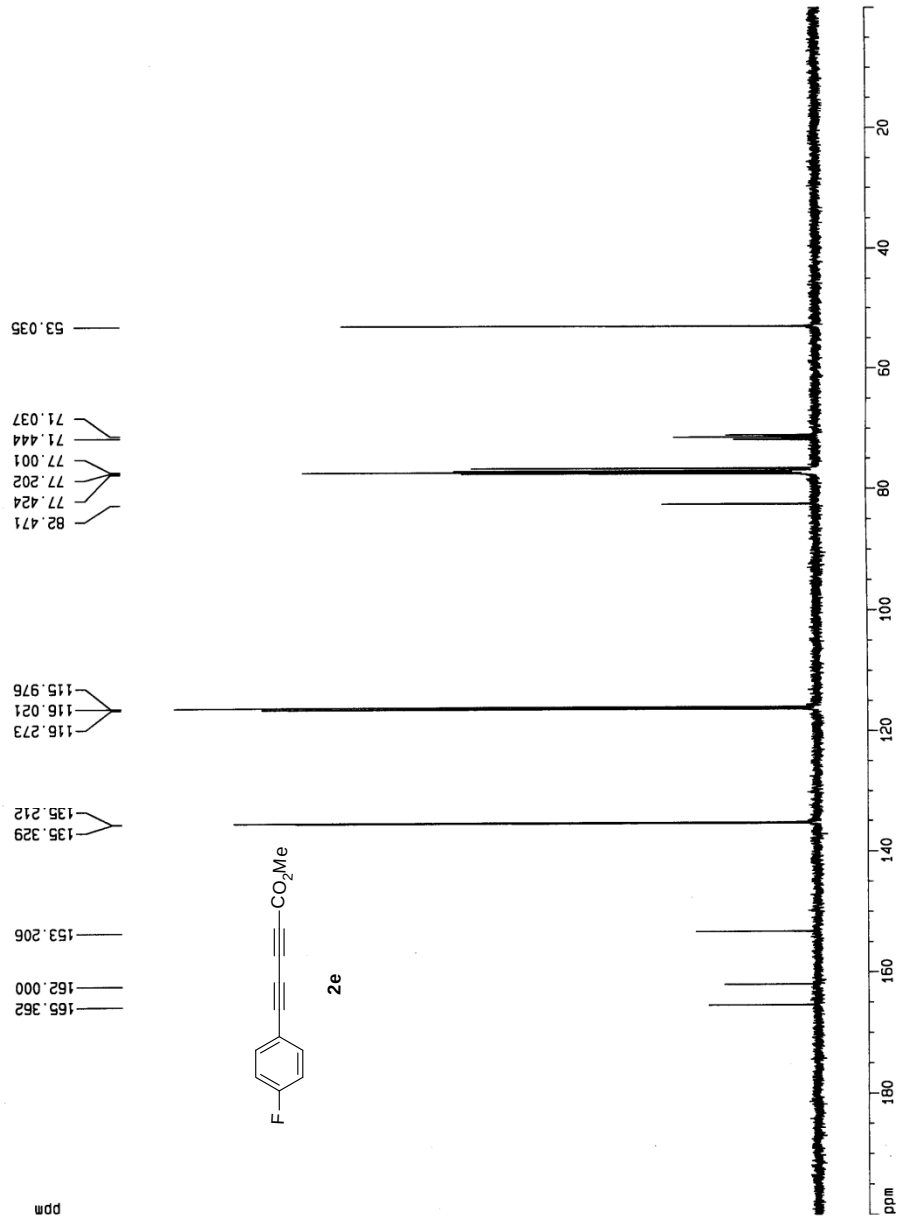


Fig S9. ^{1}H NMR spectrum of compound **2f** (300 MHz, $CDCl_3$)

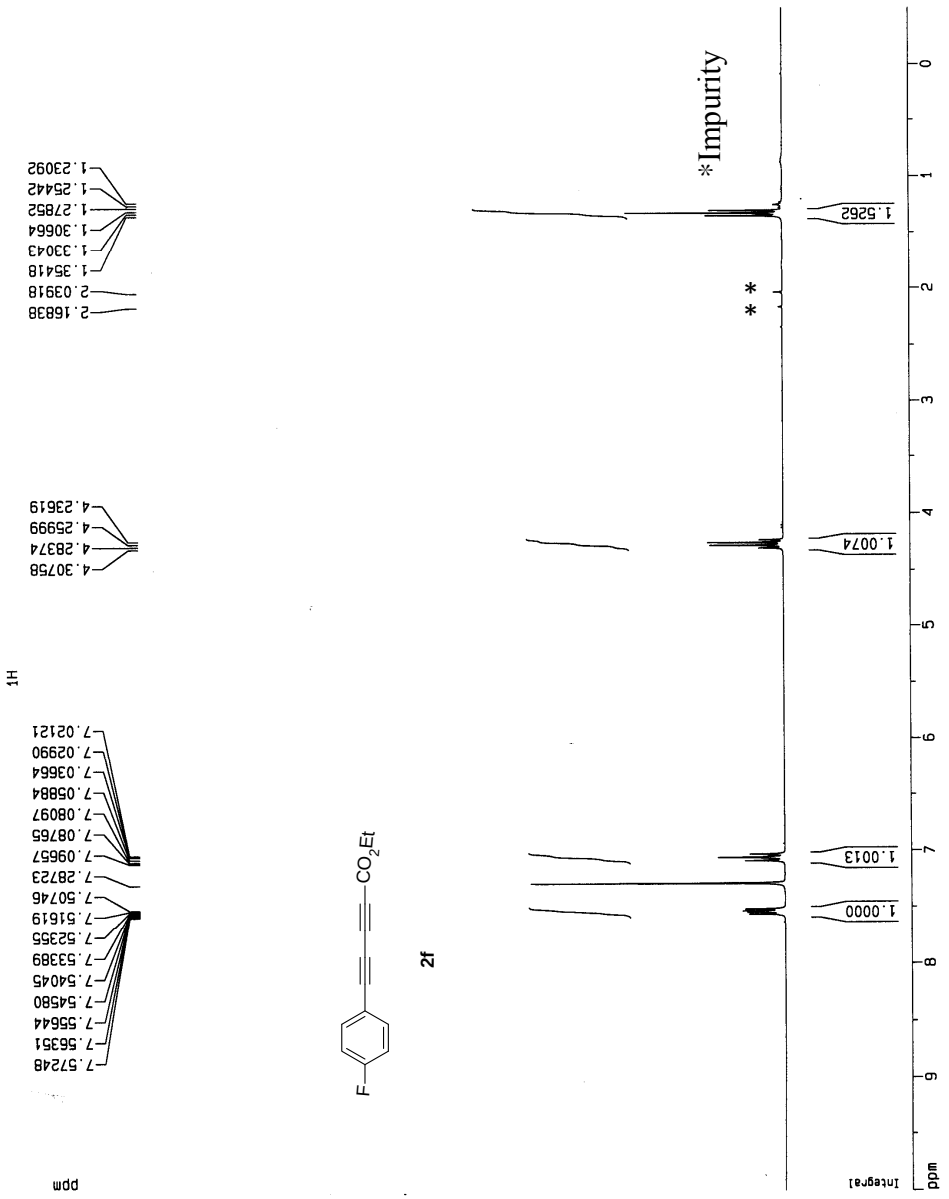


Fig S10. ^{13}C NMR spectrum of compound **2f** (75.5 MHz, $CDCl_3$)

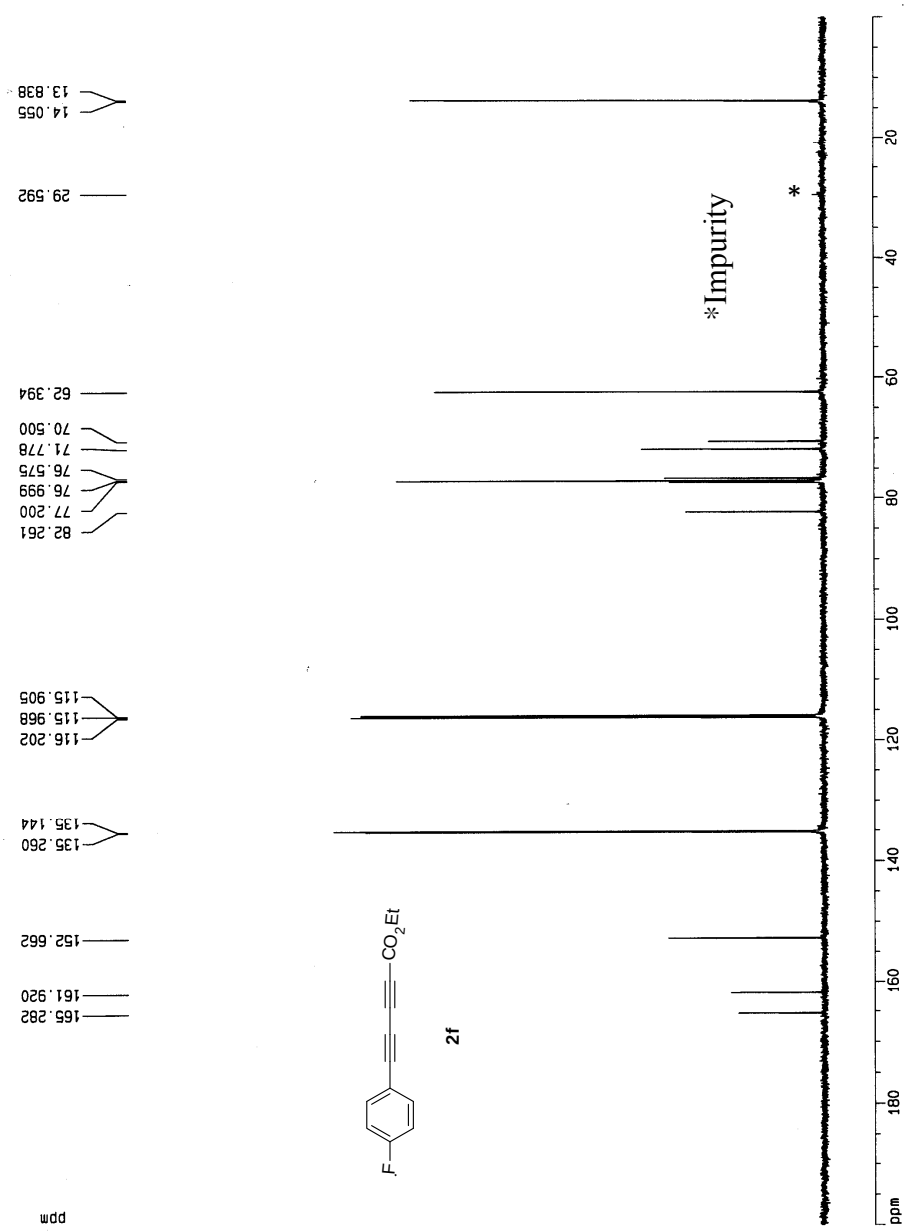


Fig S11. ^{1}H NMR spectrum of compound **2g** (300 MHz, $CDCl_3$)

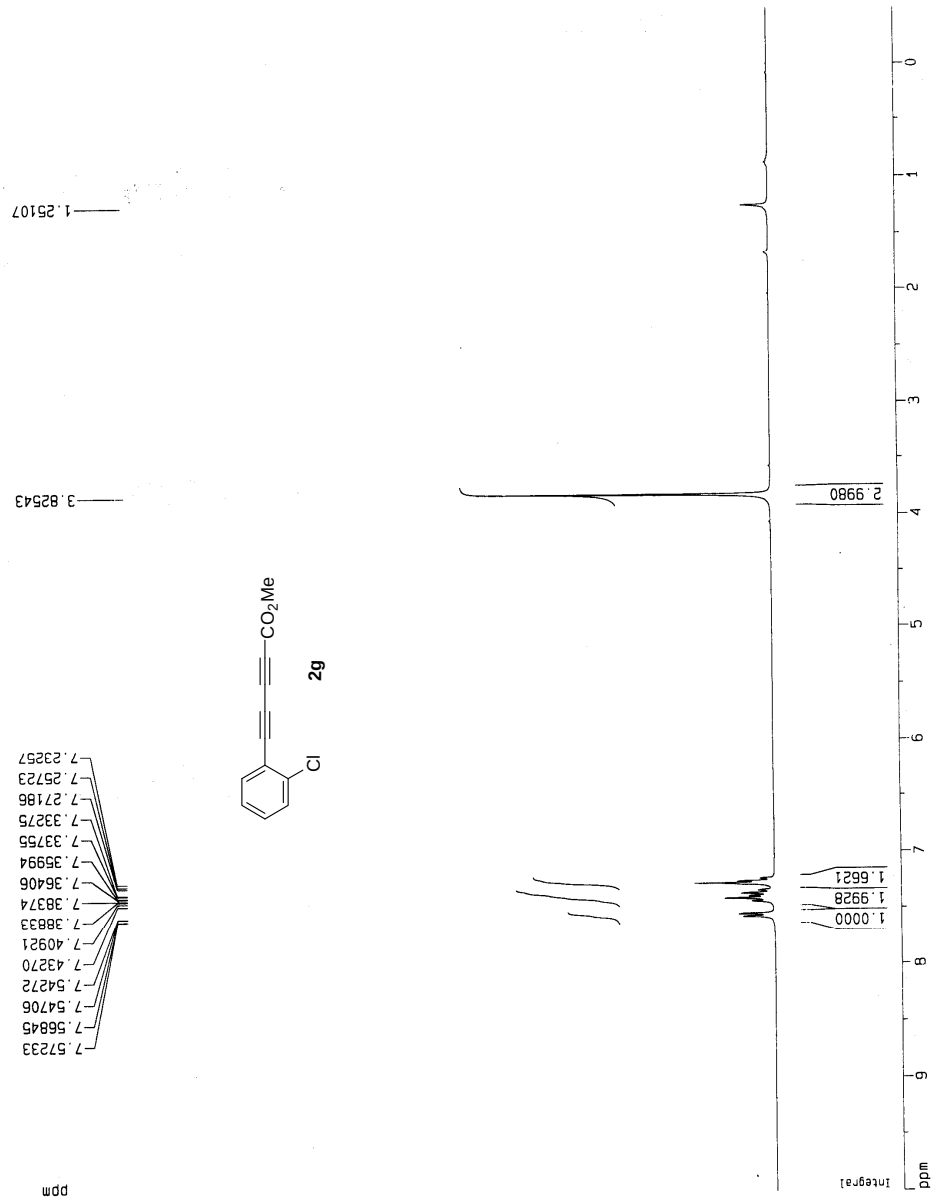


Fig S12. ^{13}C NMR spectrum of compound **2g** (75.5 MHz, $CDCl_3$)

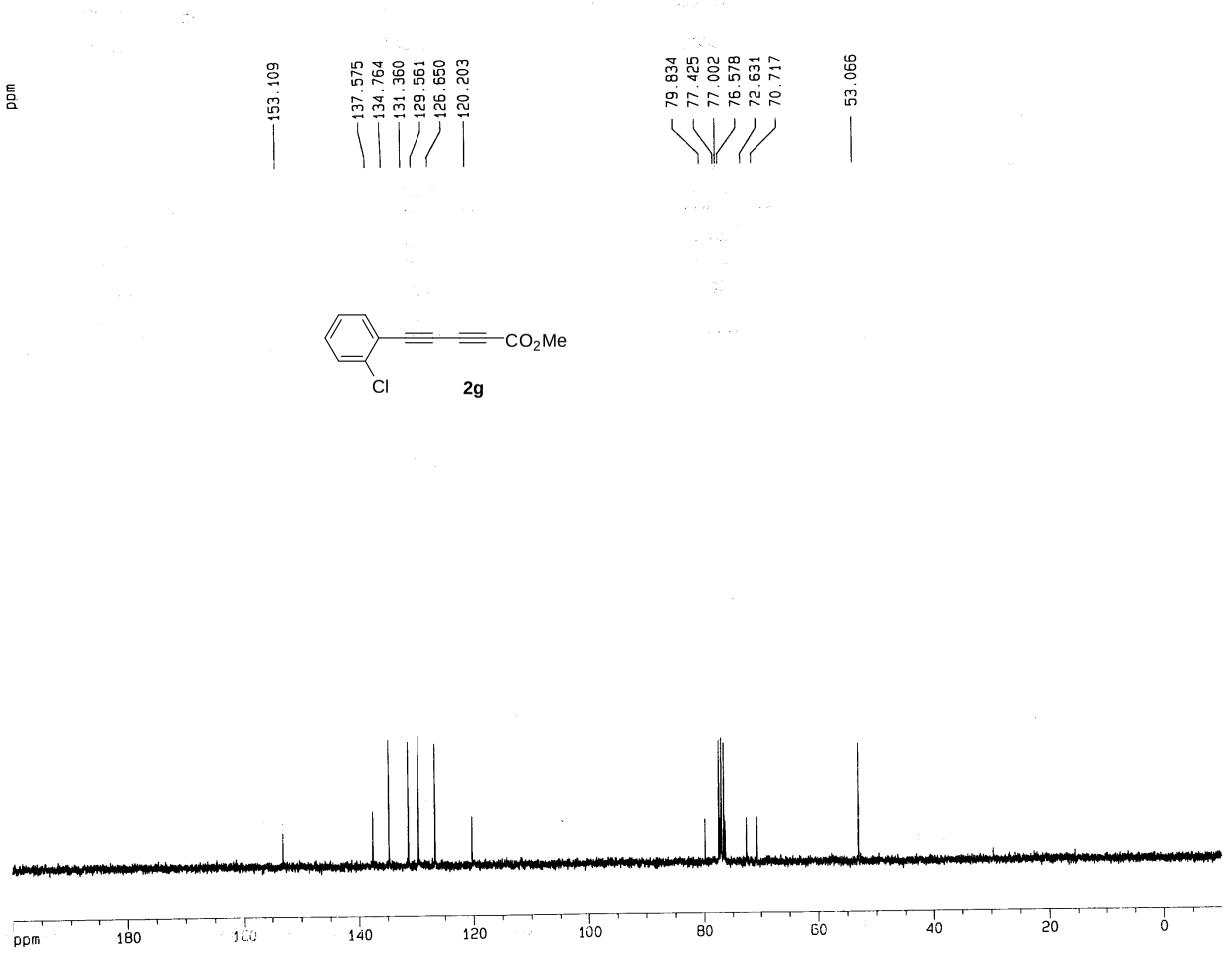


Fig S13. ^{1}H NMR spectrum of compound **2h** (300 MHz, $CDCl_3$)

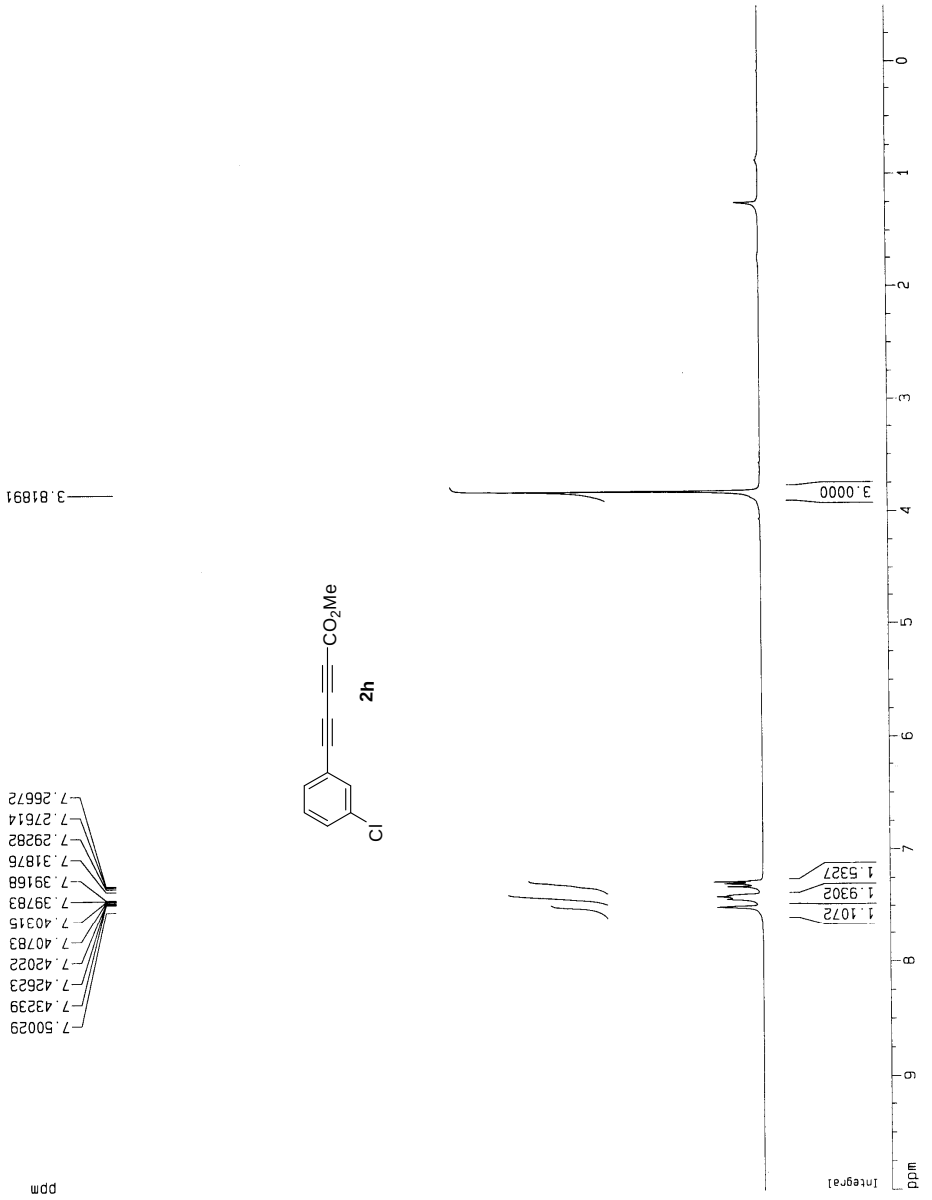


Fig S14. ^{13}C NMR spectrum of compound **2h** (75.5 MHz, $CDCl_3$)

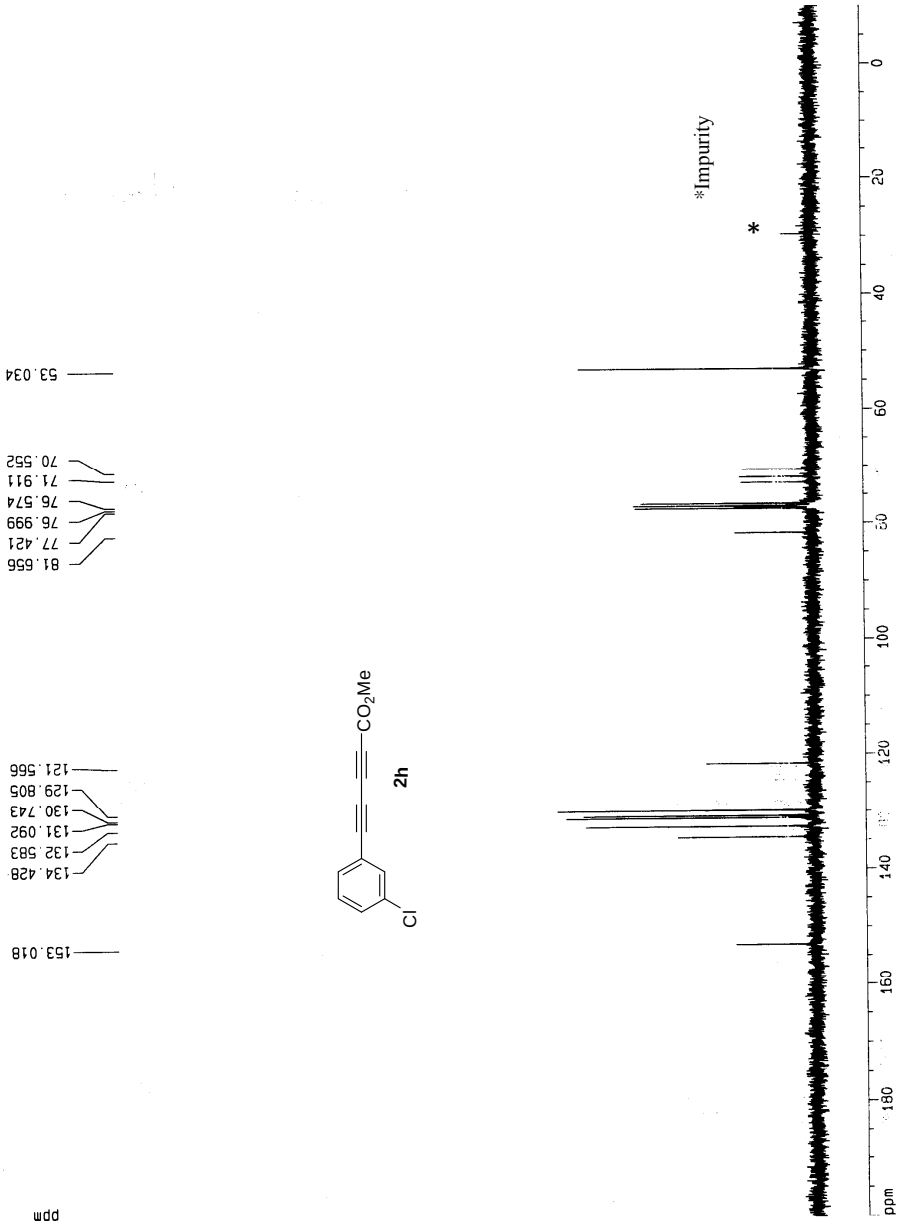


Fig S15. ^{1}H NMR spectrum of compound **2i** (300 MHz, $CDCl_3$)

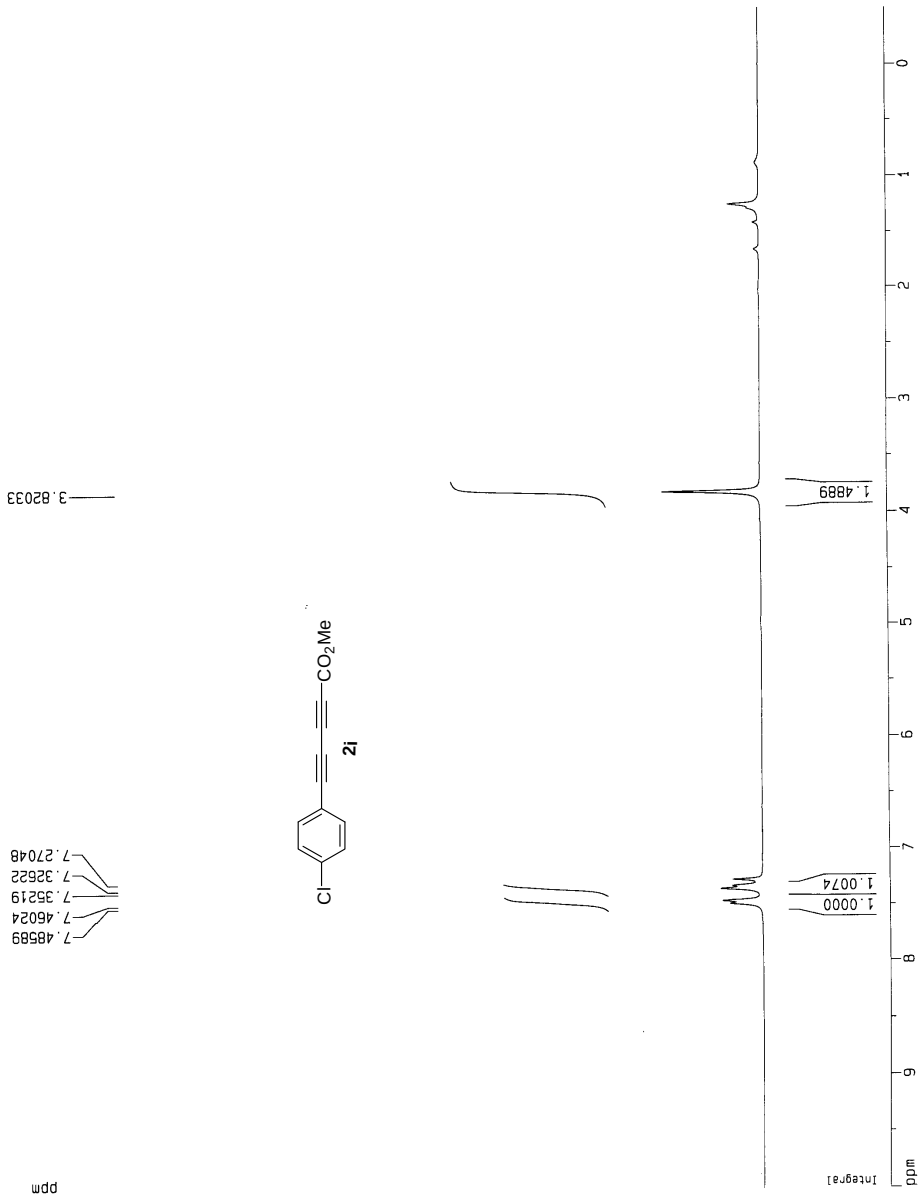


Fig S16. ^{13}C NMR spectrum of compound **2i** (75.5 MHz, $CDCl_3$)

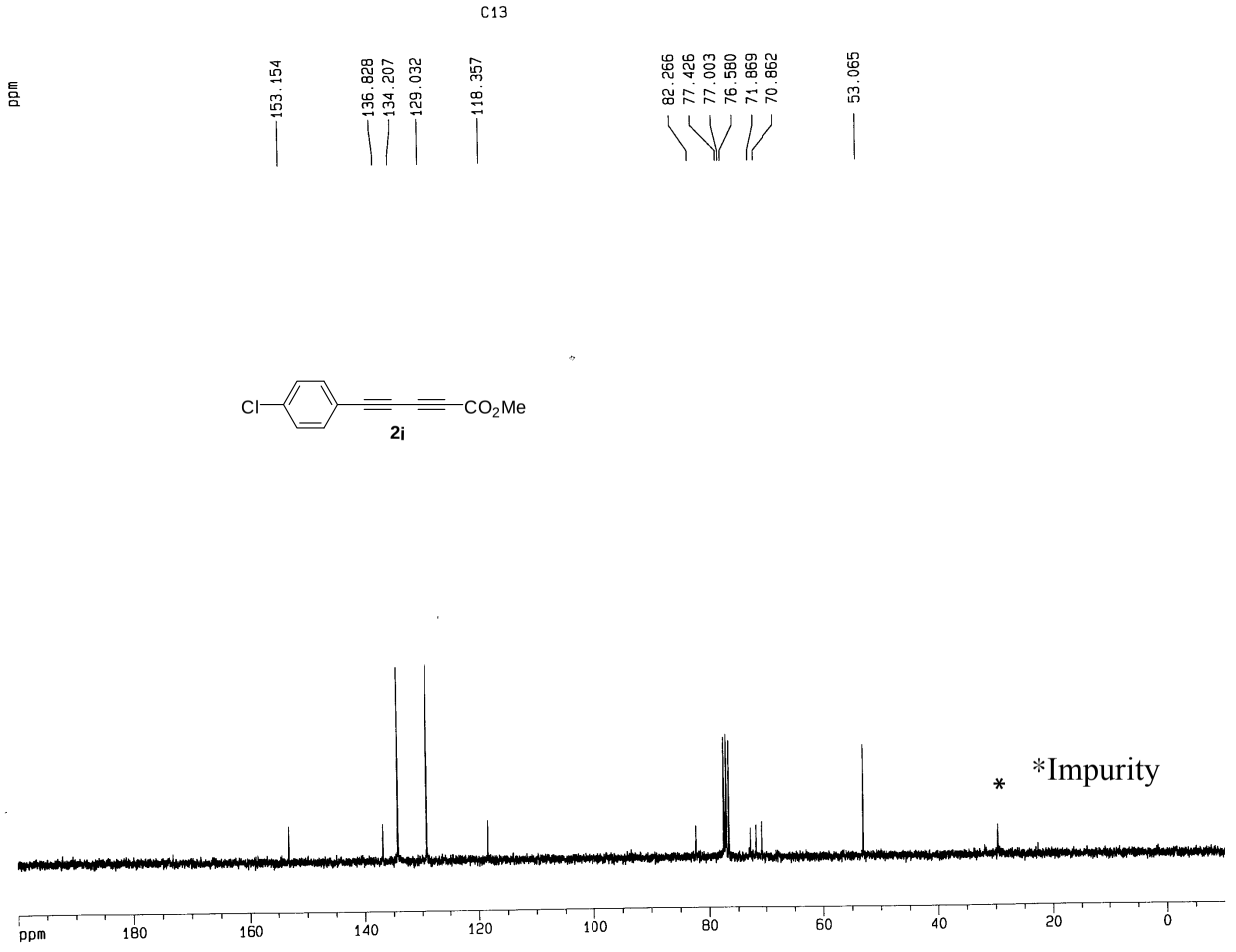


Fig S17. ^{1}H NMR spectrum of compound **2j** (300 MHz, $CDCl_3$)

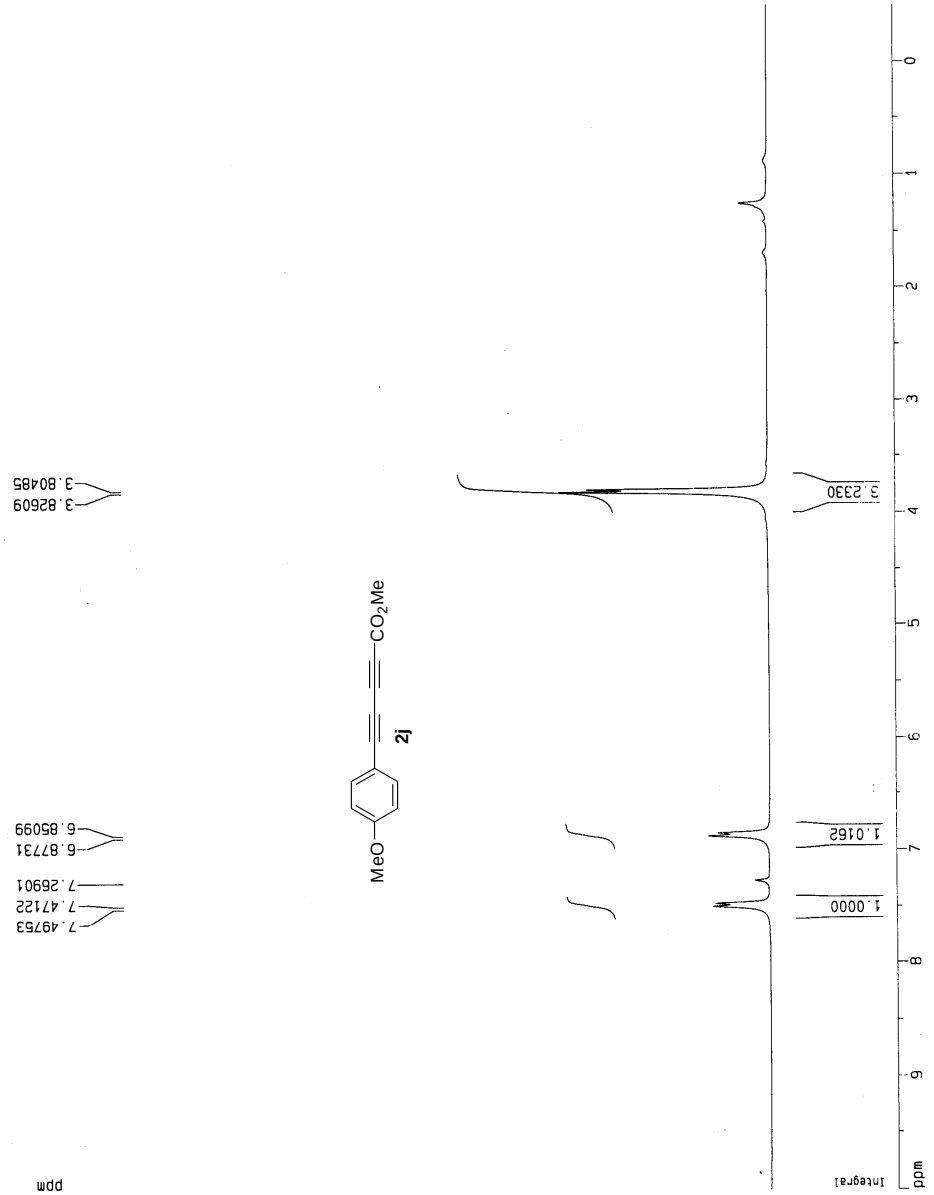


Fig S18. ^{13}C NMR spectrum of compound **2j** (75.5 MHz, $CDCl_3$)

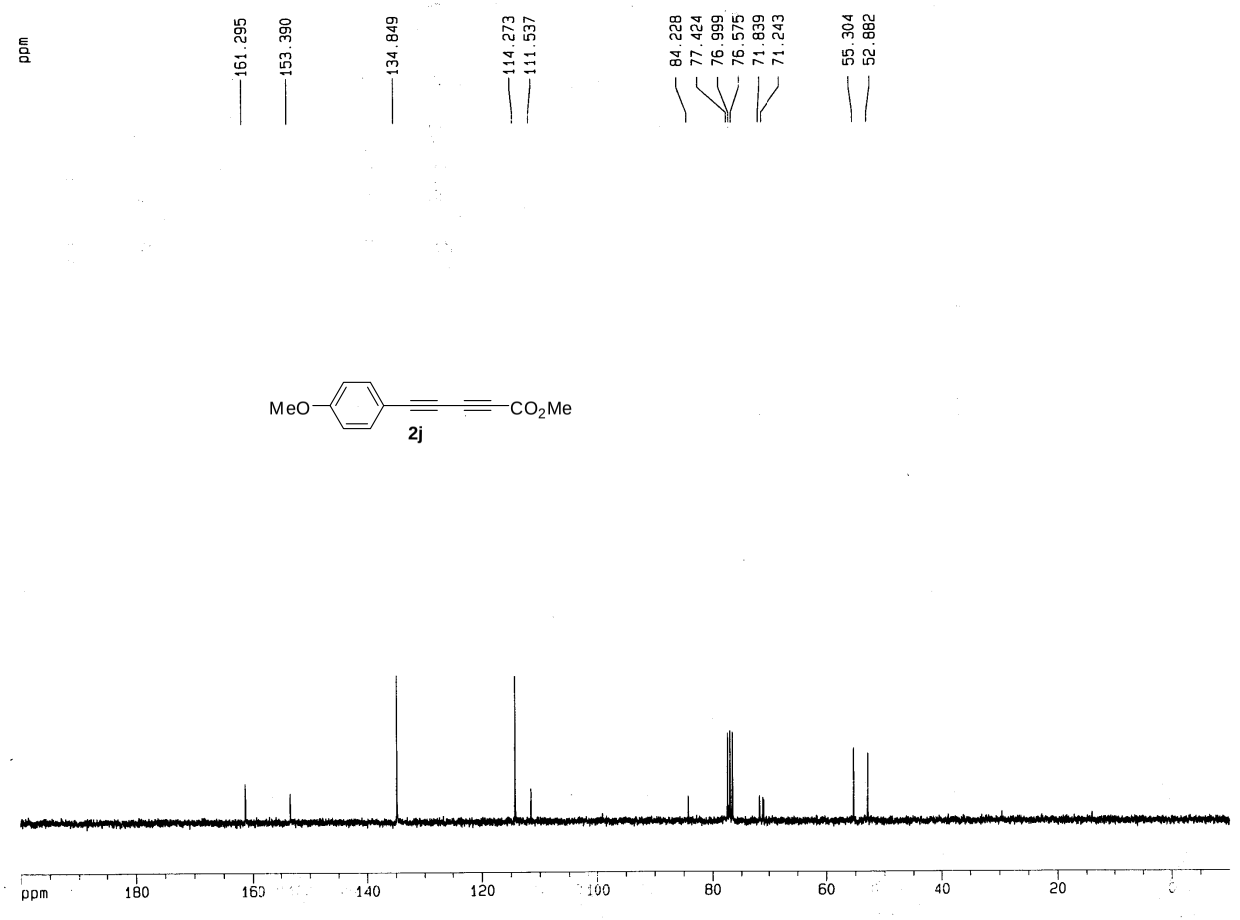


Fig S19. ^{1}H NMR spectrum of compound **2k** (300 MHz, $CDCl_3$)

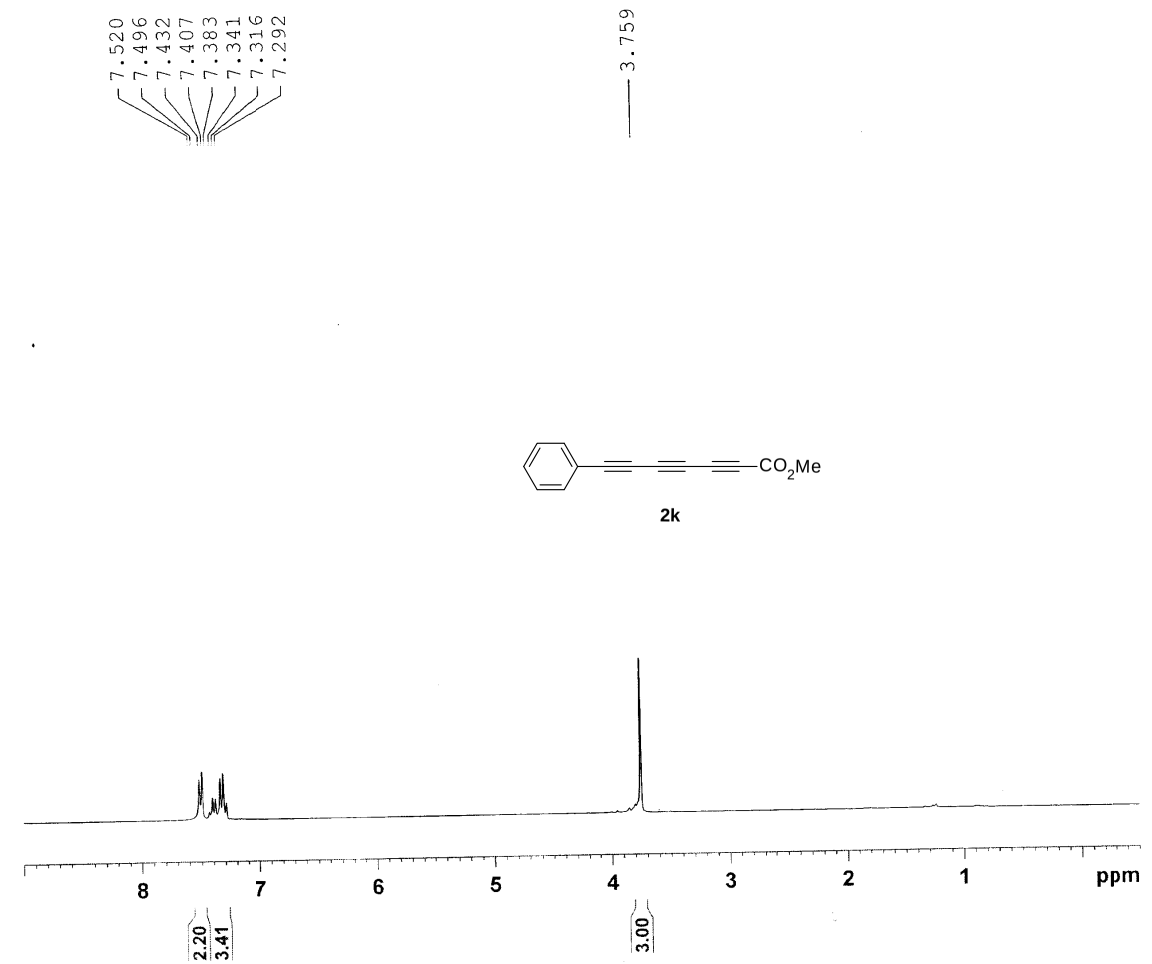


Fig S20. ^{13}C NMR spectrum of compound **2k** (75.5 MHz, $CDCl_3$)

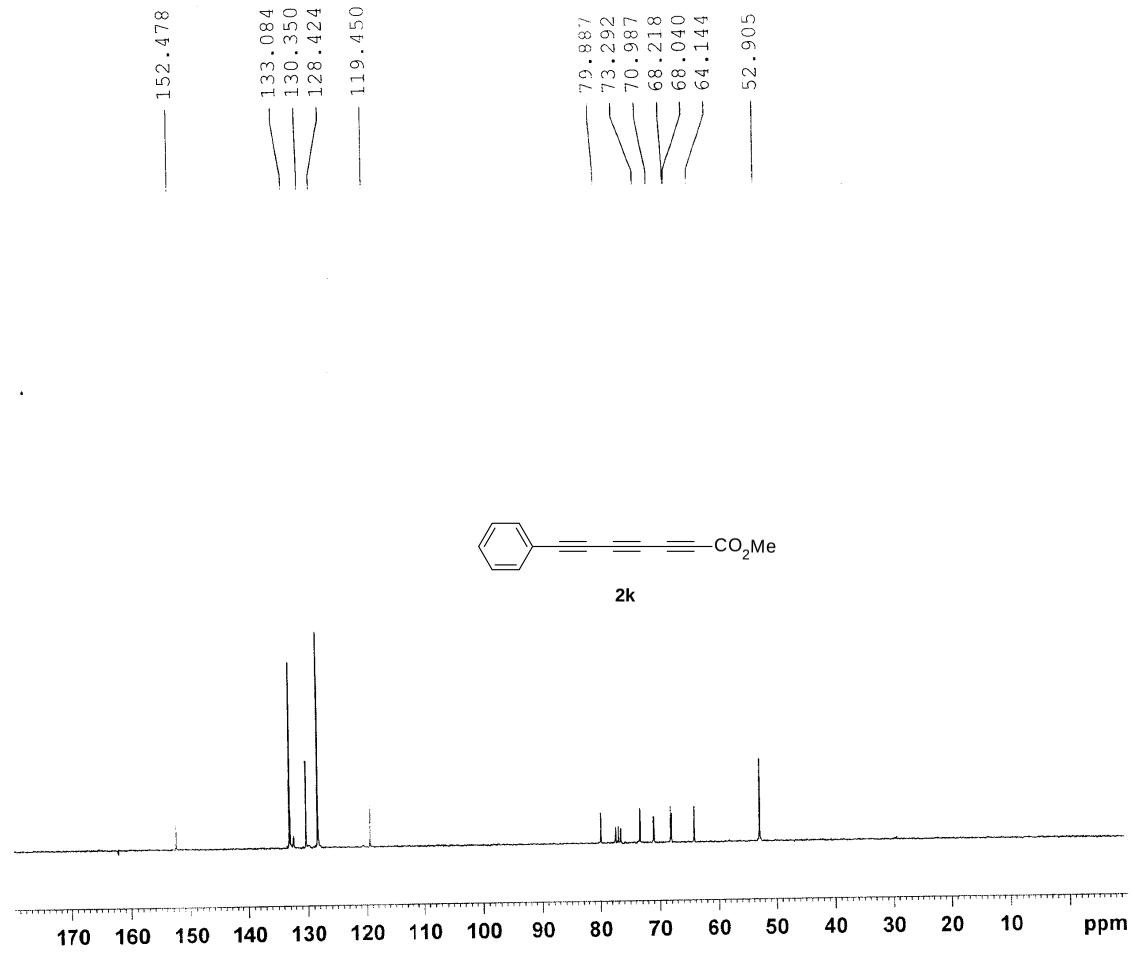


Fig S21. ^{1}H NMR spectrum of compound **2l** (300 MHz, $CDCl_3$)

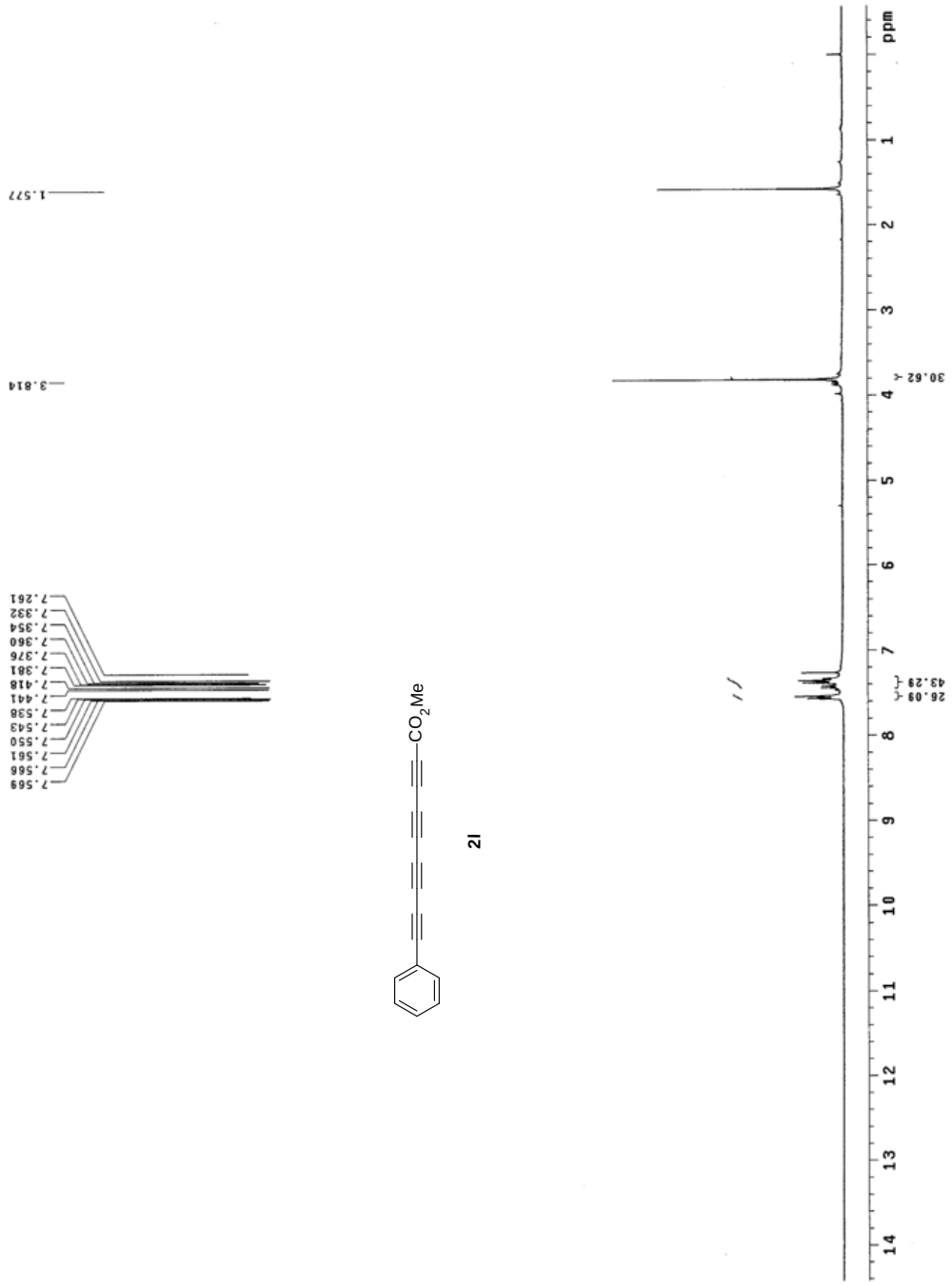


Fig S22. ^{13}C NMR spectrum of compound **2l** (100 MHz, $CDCl_3$)

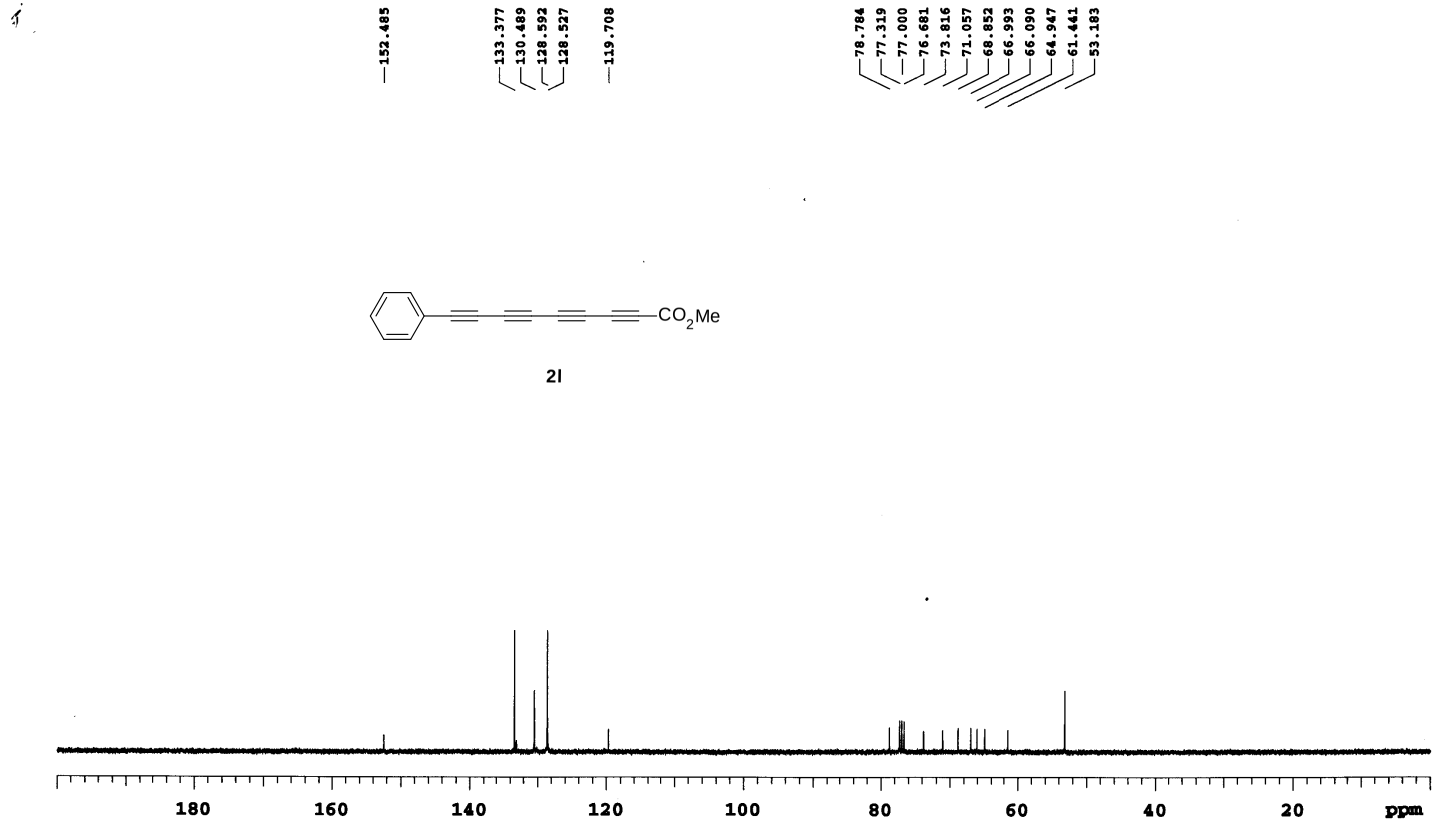


Fig S23. ^{1}H NMR spectrum of compound **2m** (500 MHz, $CDCl_3$)

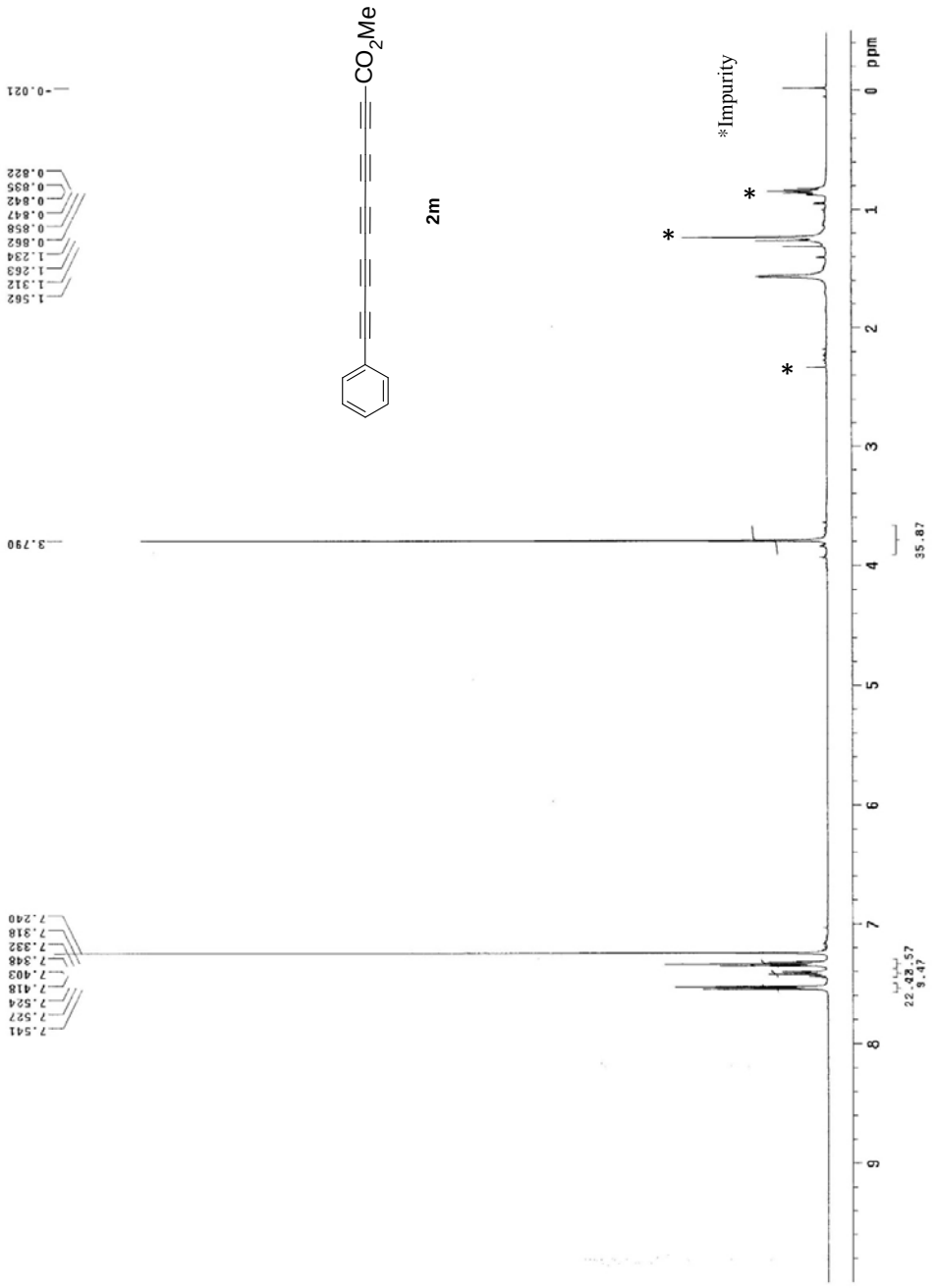


Fig S24. ^{13}C NMR spectrum of compound **2m** (125 MHz, $CDCl_3$)

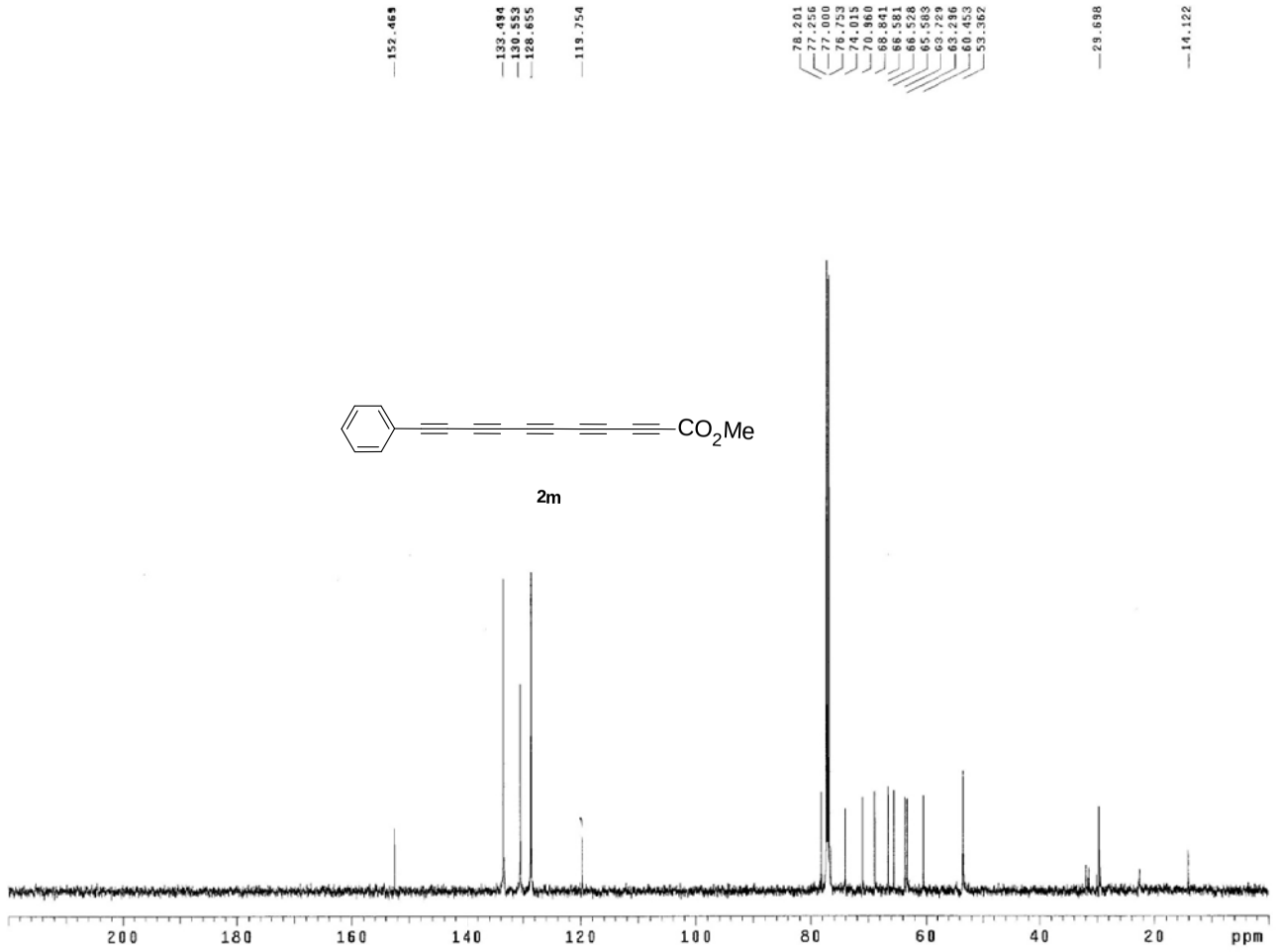


Fig. S25. ^{1}H NMR spectra of compound **2n** (300 MHz, $CDCl_3$)

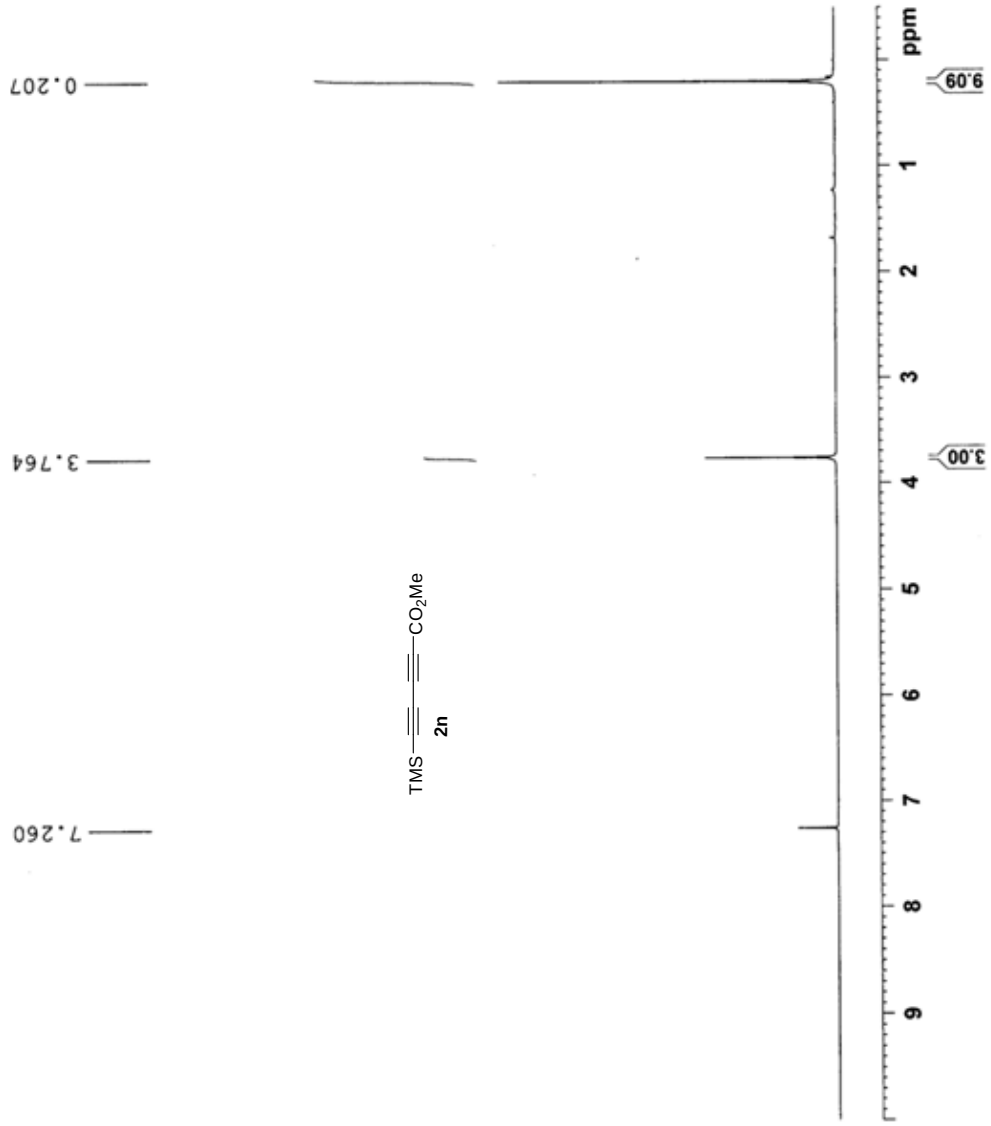


Fig. S26. ^{13}C NMR spectra of compound **2n** (75.5 MHz, $CDCl_3$)

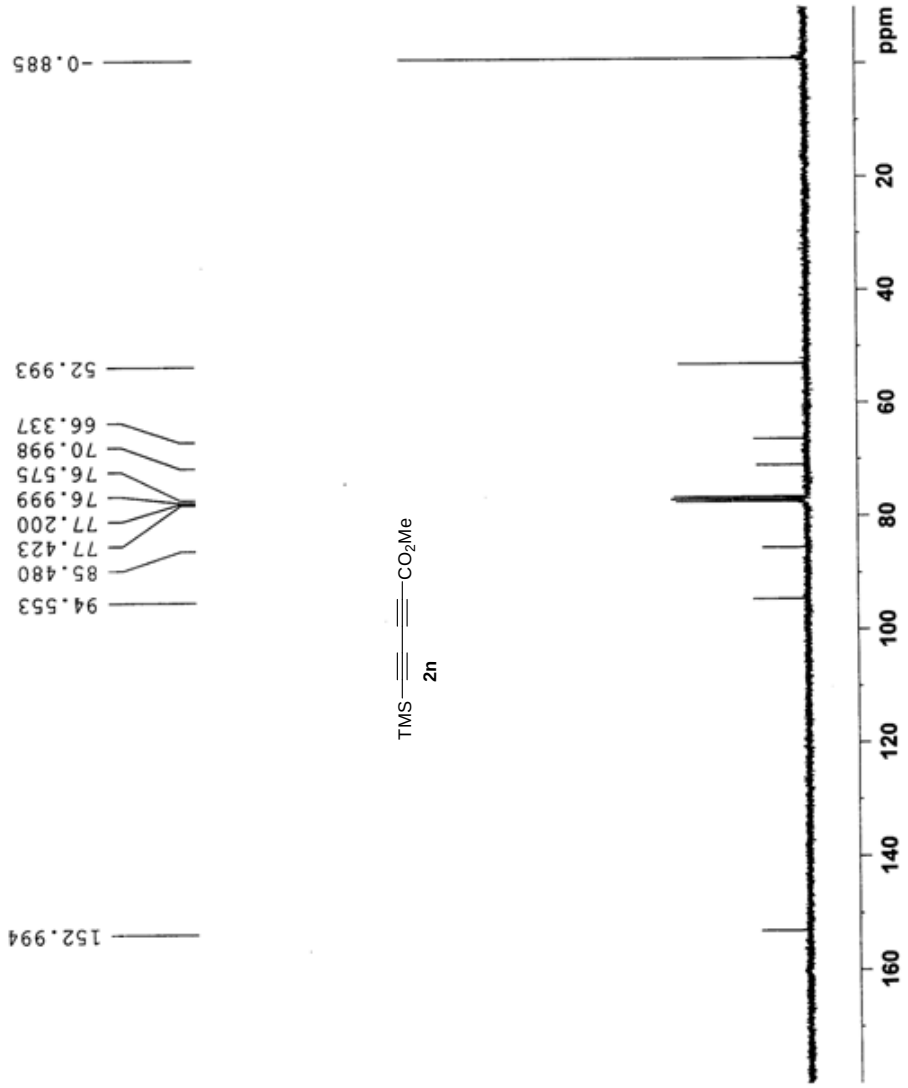


Fig. S27. ^{1}H NMR spectra of compound **2o** (300 MHz, $CDCl_3$)

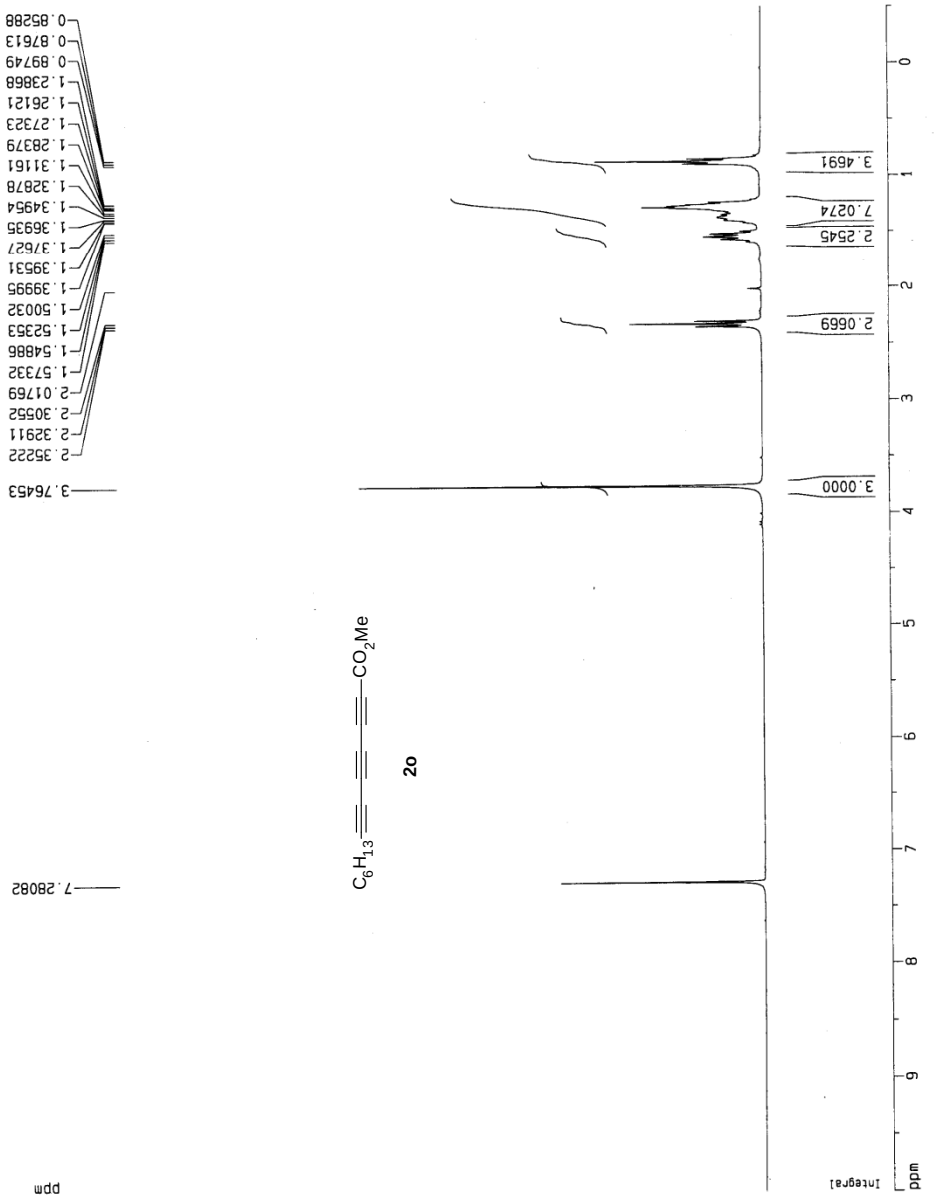


Fig. S28. ^{13}C NMR spectra of compound **2o** (75.5 MHz, $CDCl_3$)

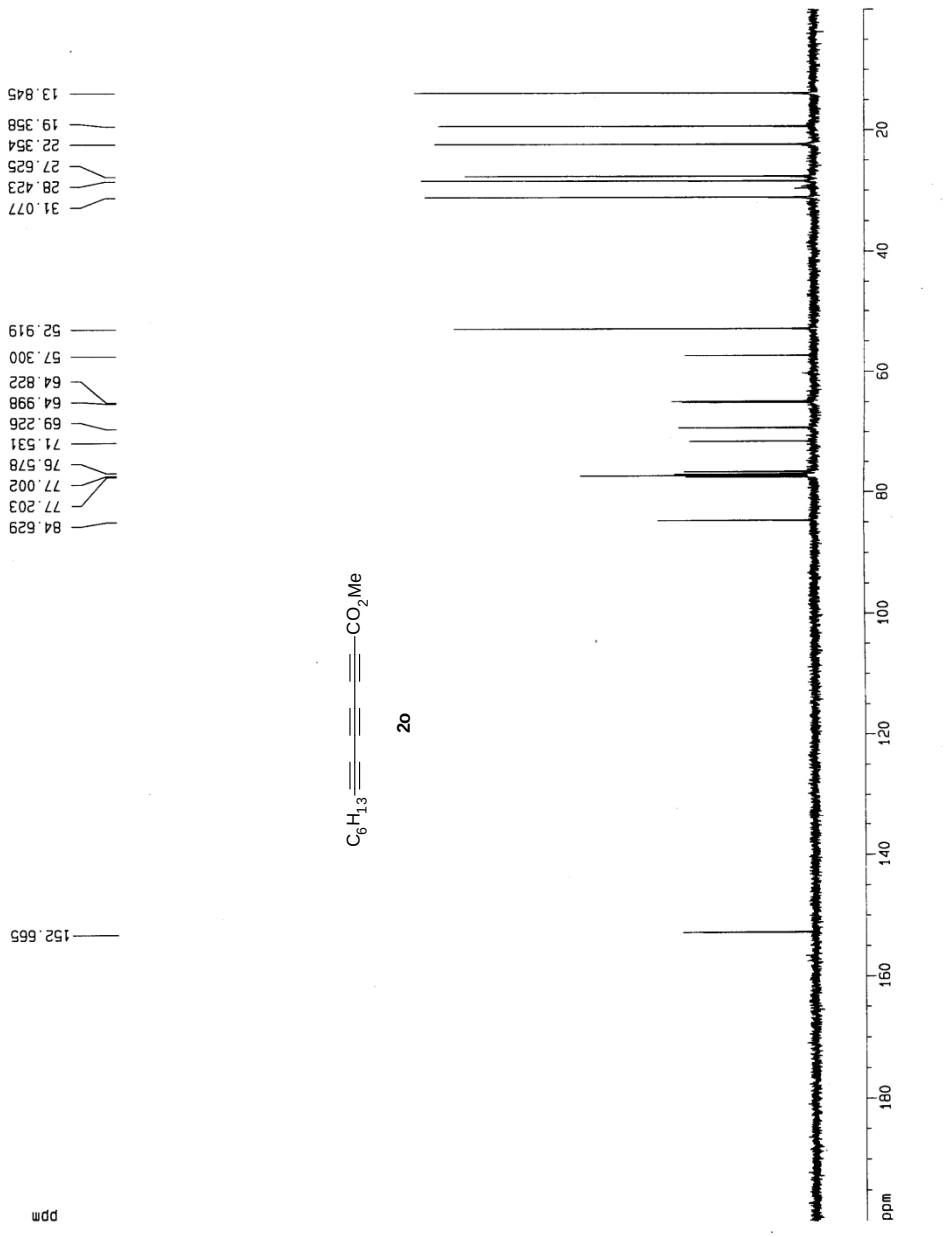


Fig S29. ^{1}H NMR spectrum of compound **5a** (300 MHz, $CDCl_3$)

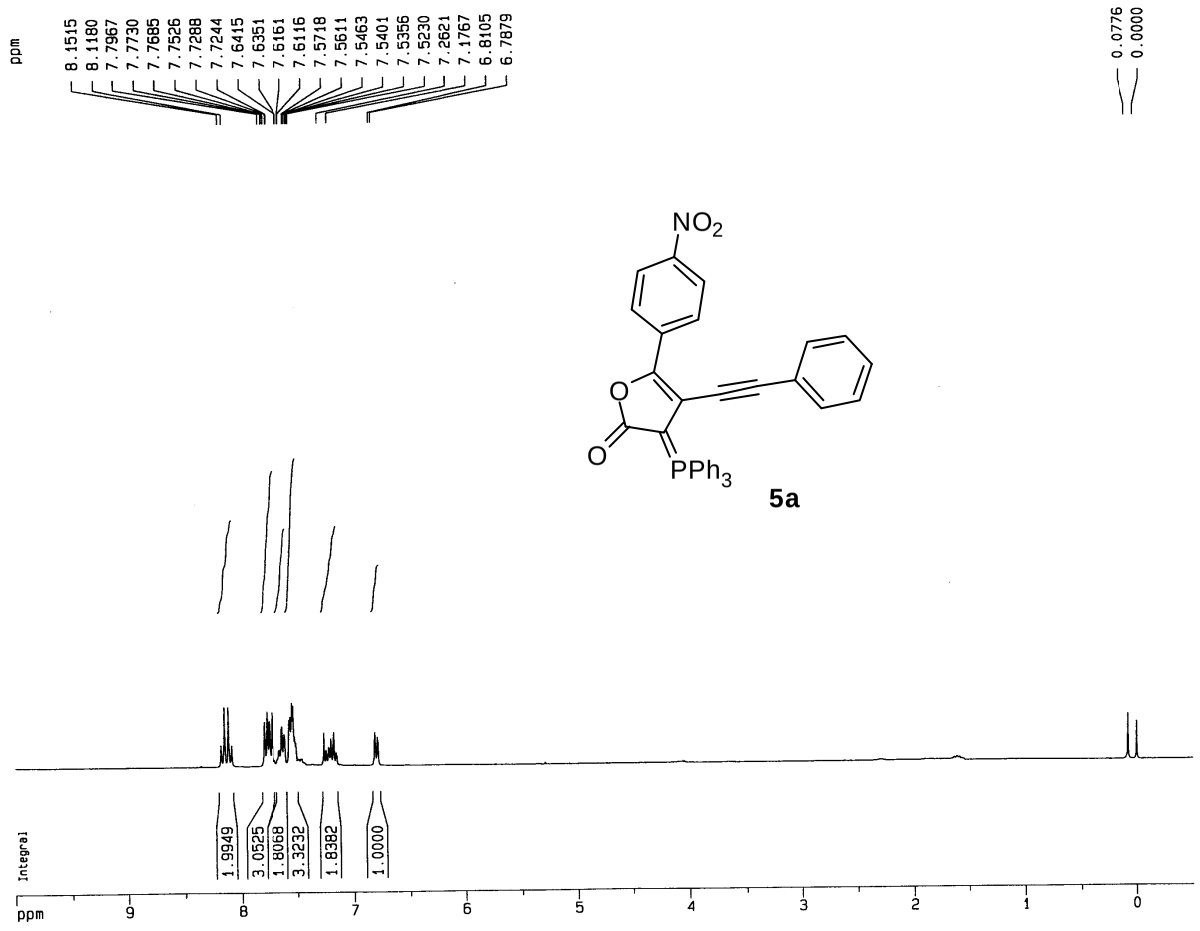


Fig S30. ^{13}C NMR spectrum of compound **5a** (75.5 MHz, $CDCl_3$)

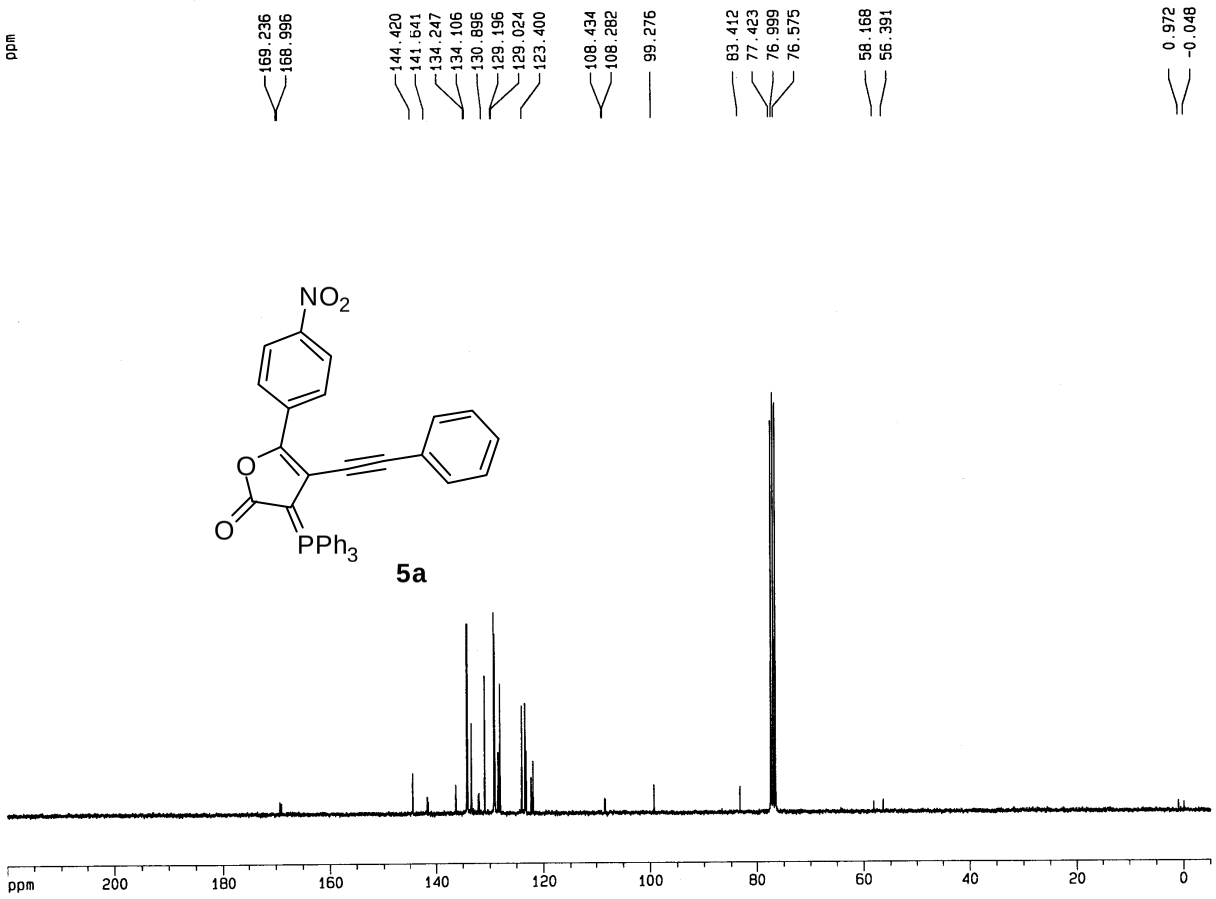


Fig S31. ^{1}H NMR spectrum of compound **5b** (300 MHz, $CDCl_3$)

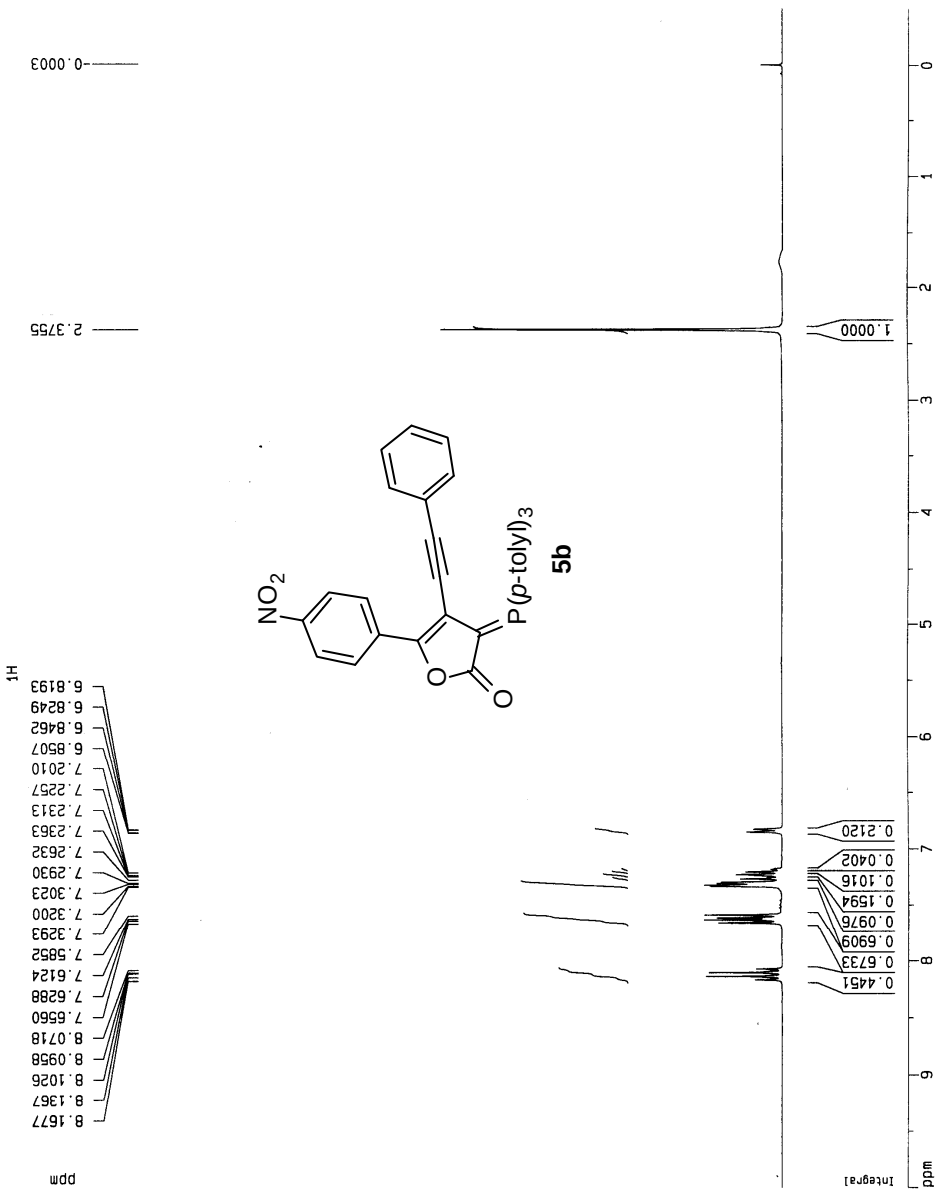


Fig S32. ^{13}C NMR spectrum of compound **5b** (150.7 MHz, $CDCl_3$)

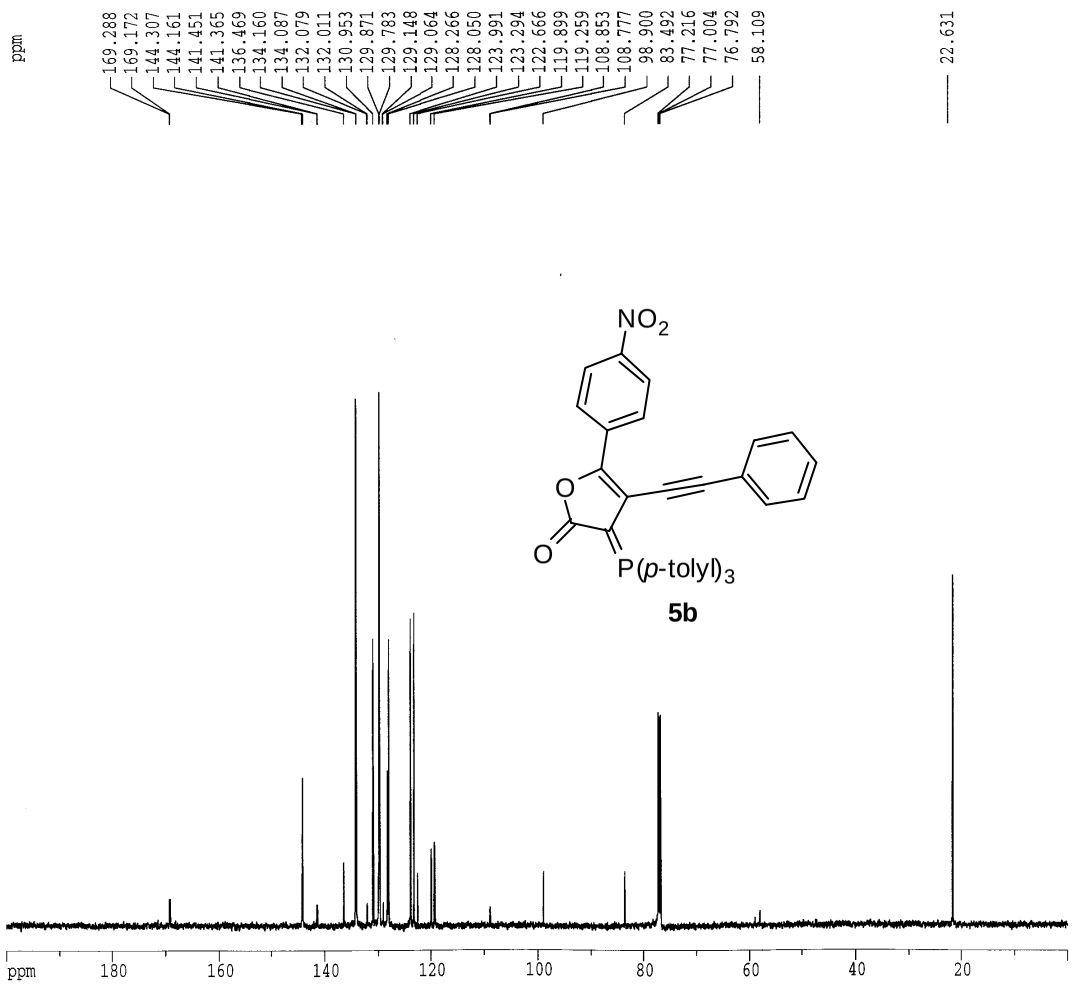


Fig S33. ^{1}H NMR spectrum of compound **5c** (300 MHz, $CDCl_3$)

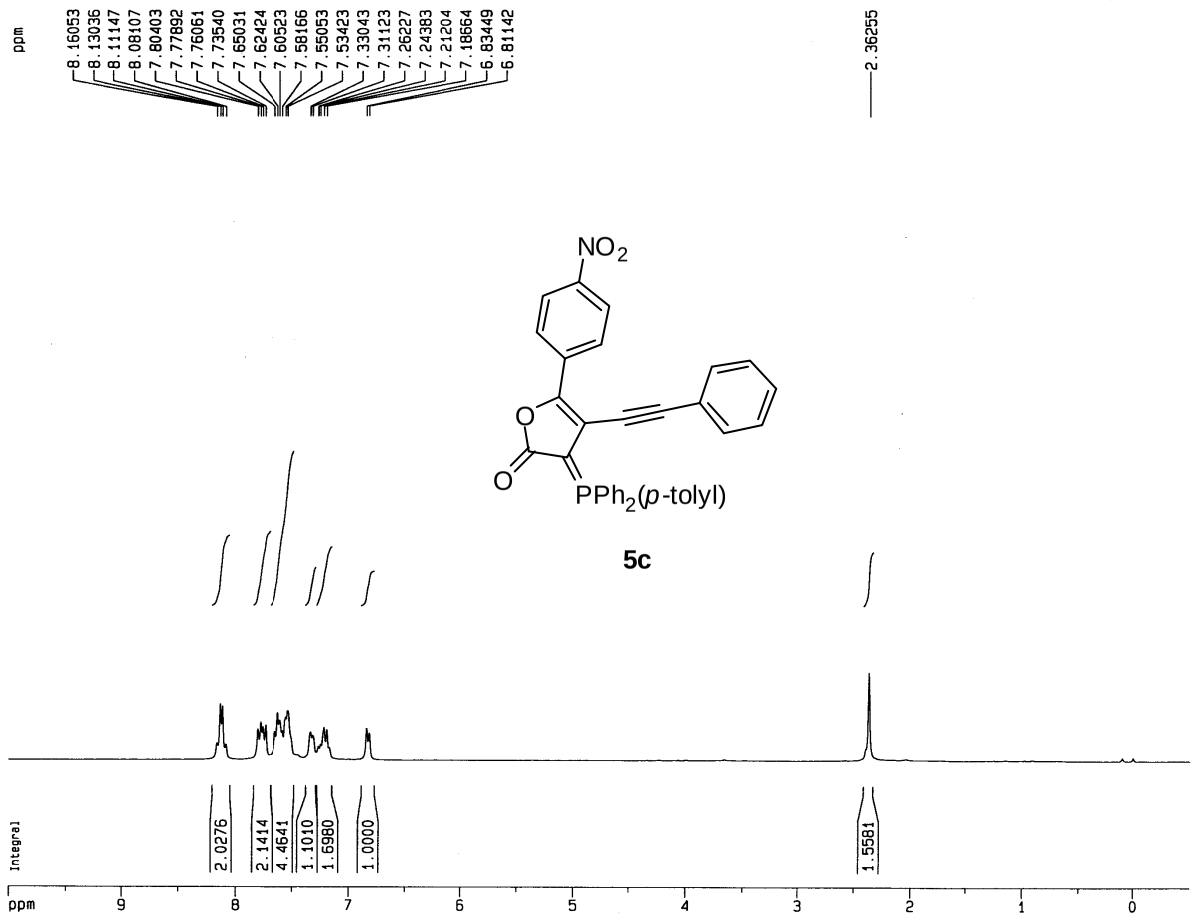


Fig S34. ^{13}C NMR spectrum of compound **5c** (75.5 MHz, $CDCl_3$)

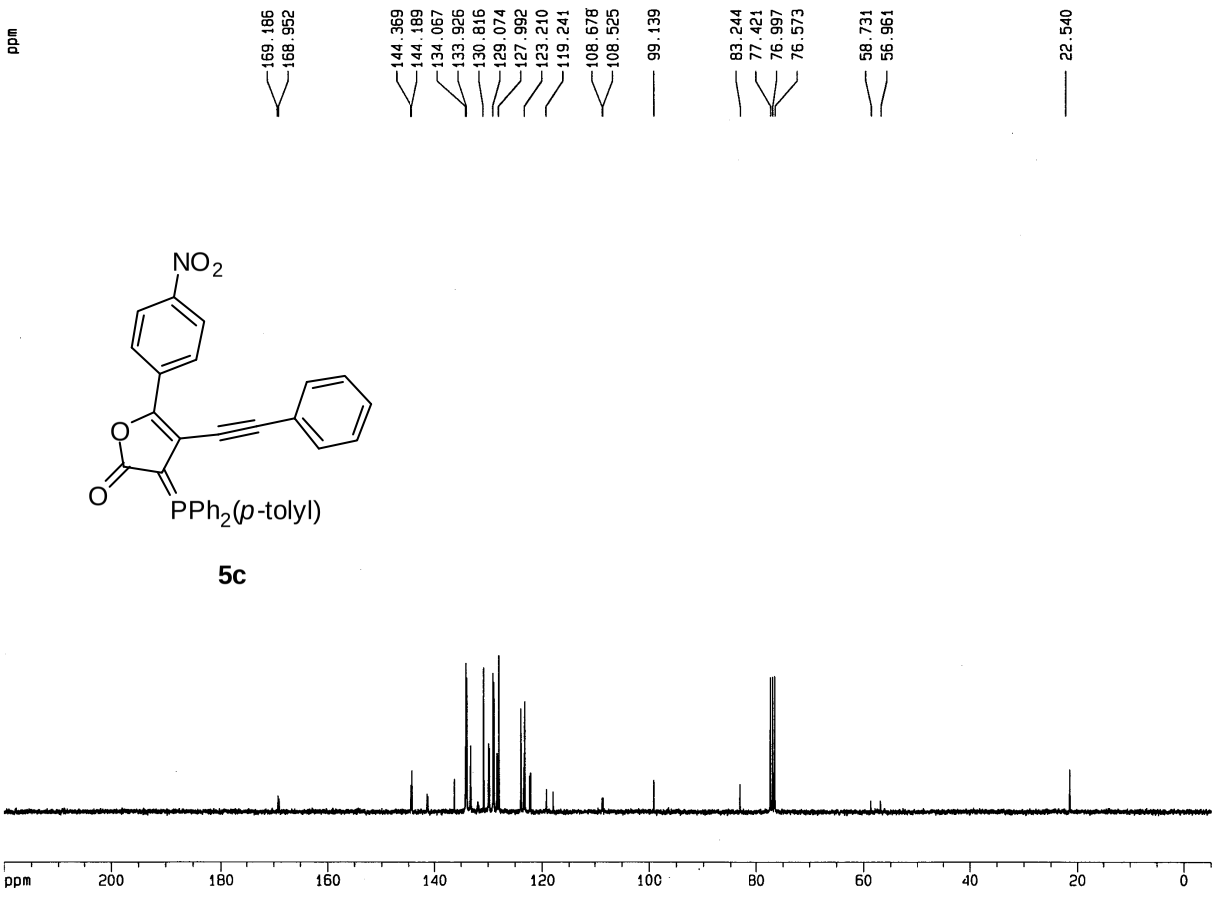


Fig S35. ^{1}H NMR spectrum of compound **5d** (300 MHz, $CDCl_3$)

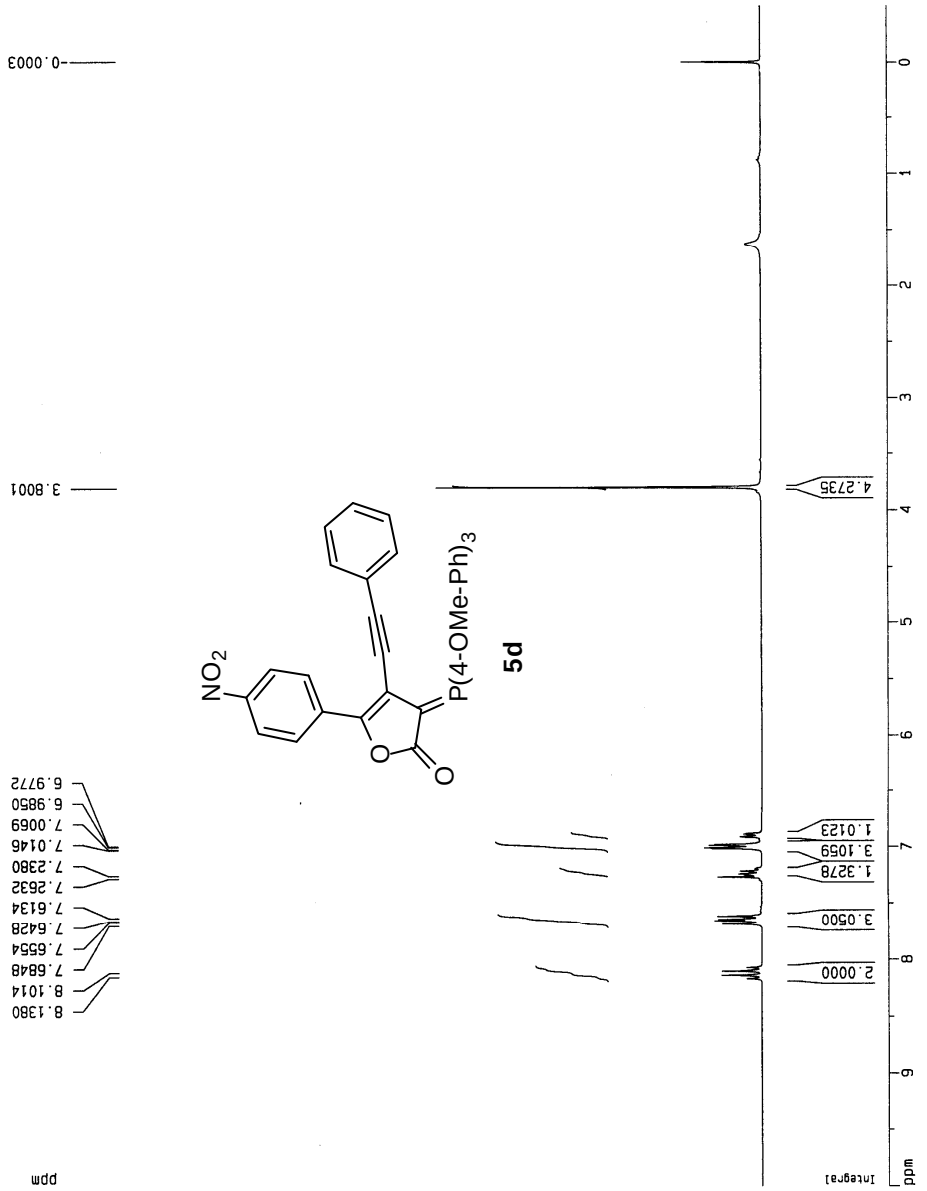


Fig S36. ^{13}C NMR spectrum of compound **5d** (150.7 MHz, $CDCl_3$)

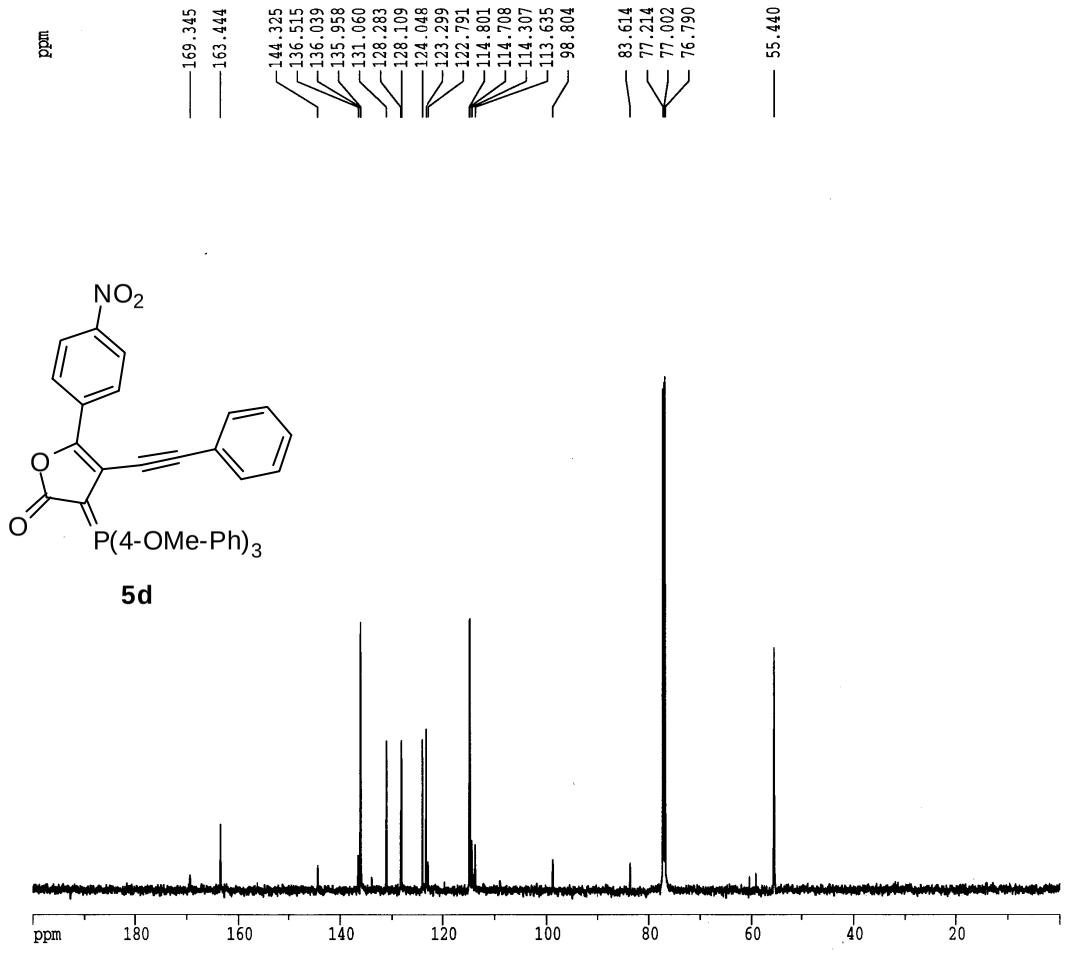


Fig S37. ^{1}H NMR spectrum of compound **5e** (300 MHz, $CDCl_3$)

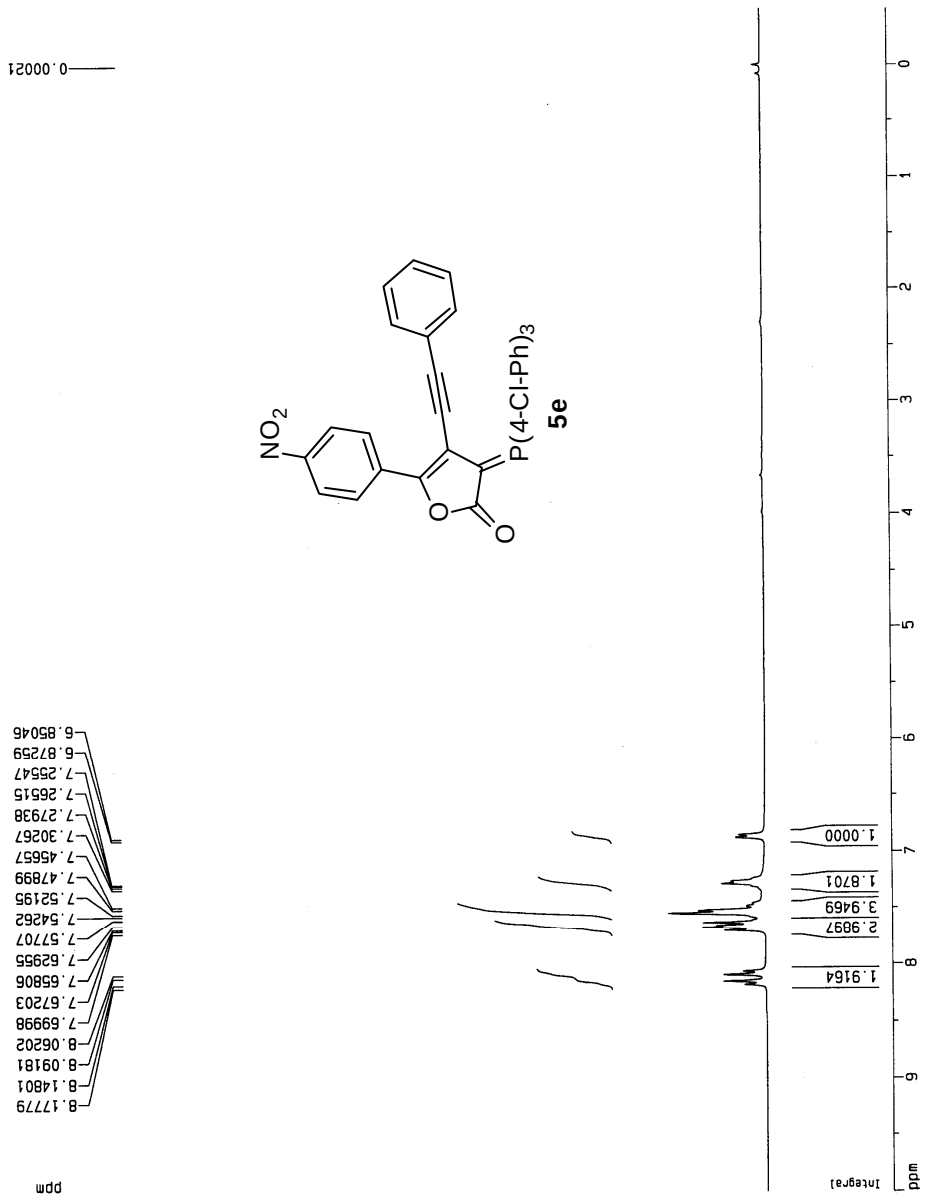


Fig S38. ^{13}C NMR spectrum of compound **5e** (75.5 MHz, $CDCl_3$)

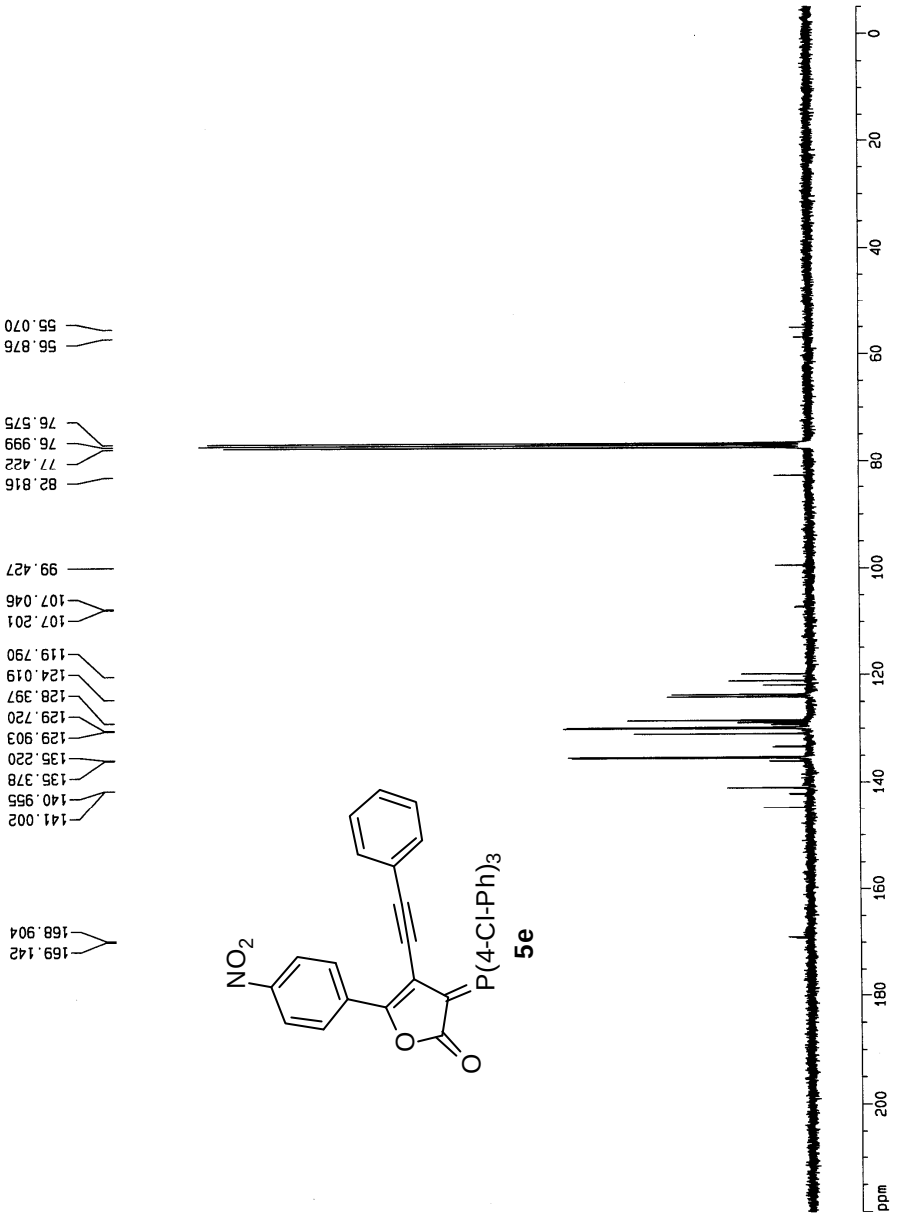


Fig S39. ^{1}H NMR spectrum of compound **5f** (300 MHz, $CDCl_3$)

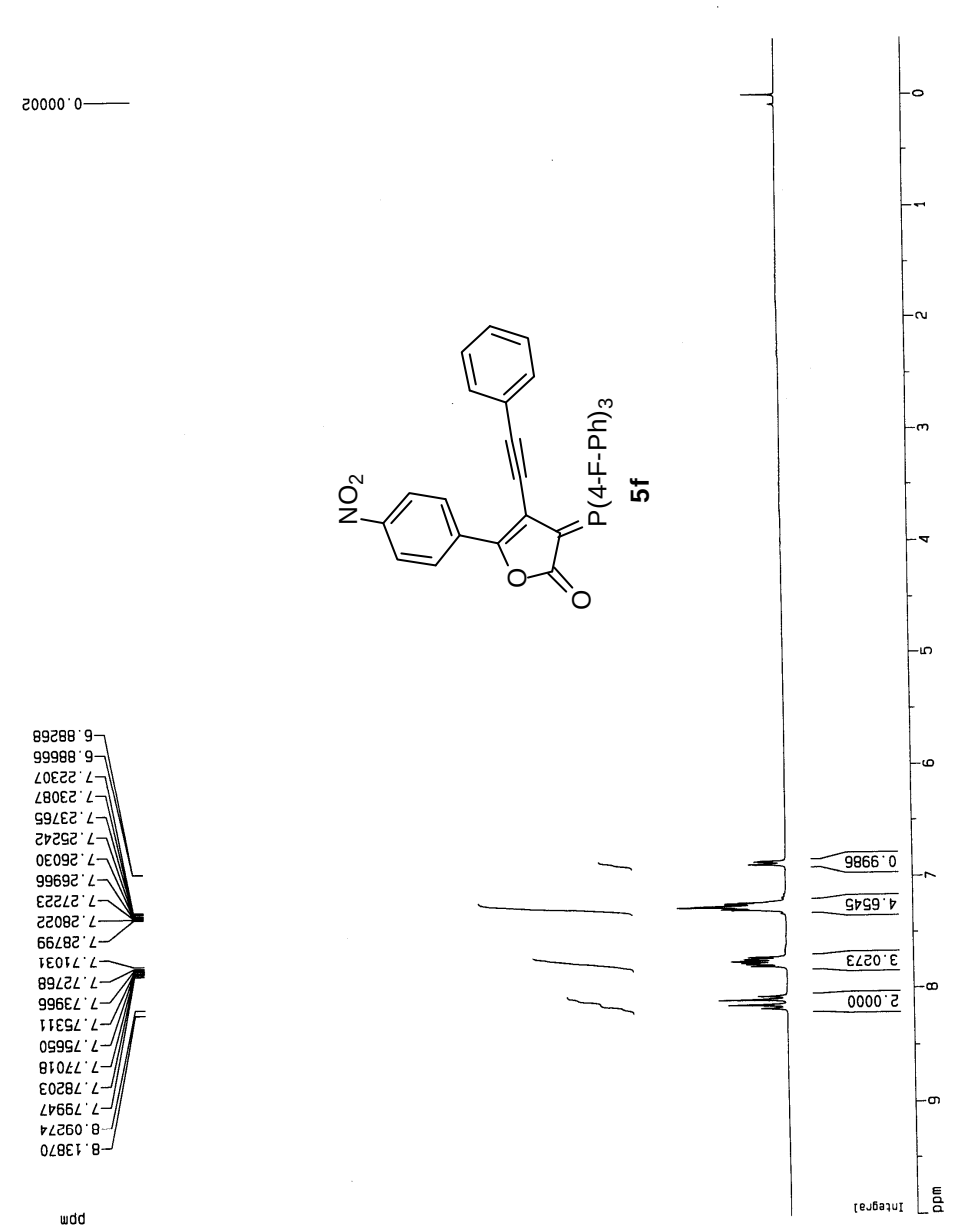


Fig S40. ^{13}C NMR spectrum of compound **5f** (75.5 MHz, $CDCl_3$)

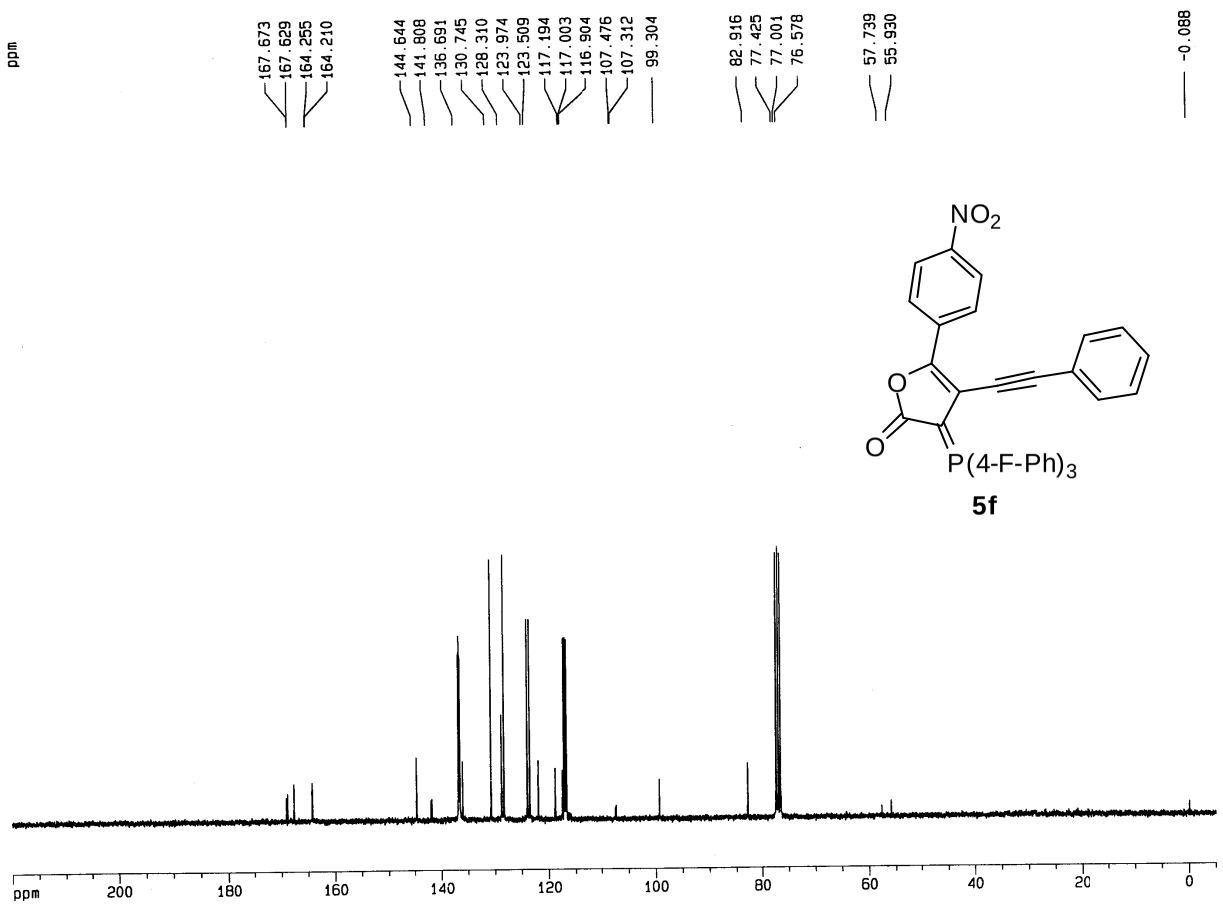


Fig S41. ^{1}H NMR spectrum of compound **5g** (300 MHz, $CDCl_3$)

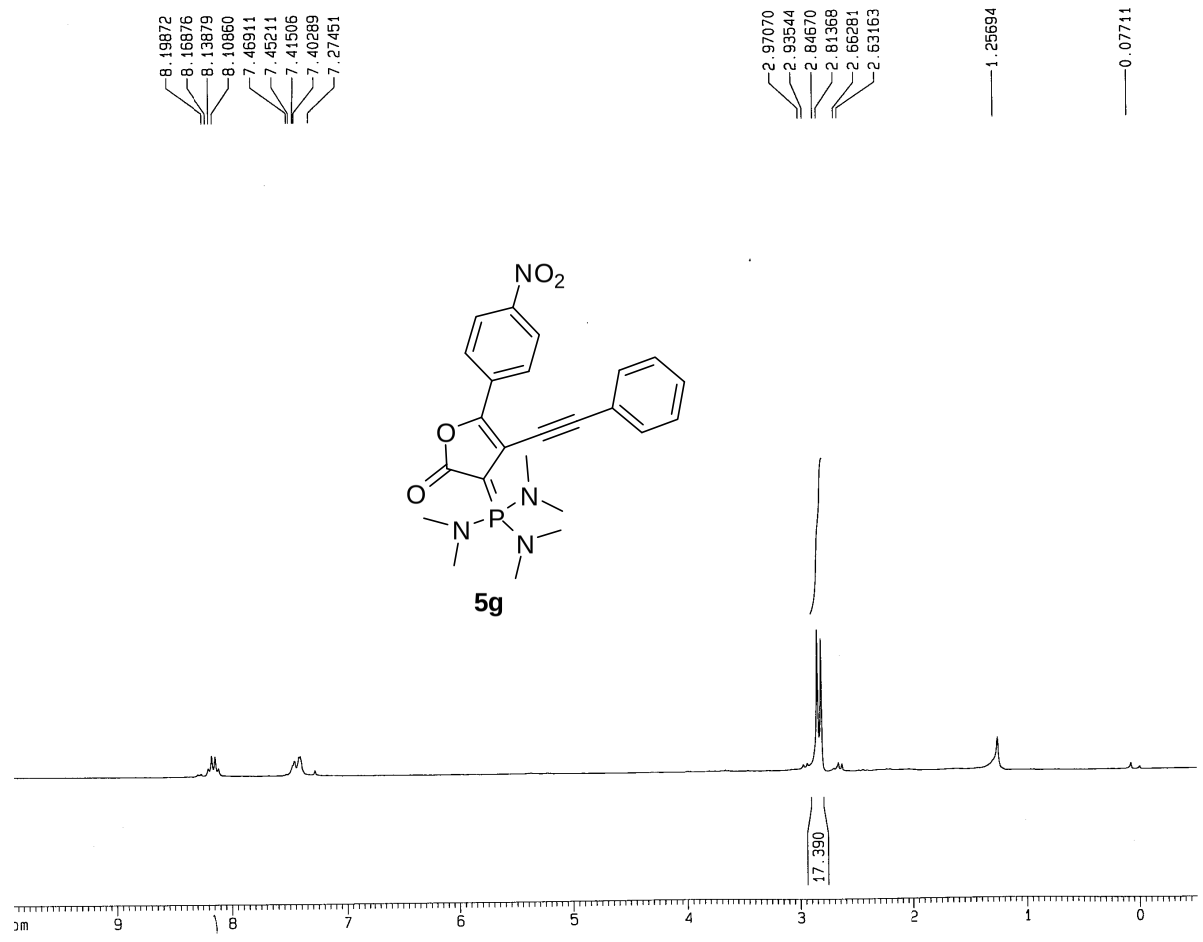


Fig S42. ^{13}C NMR spectrum of compound **5g** (75.5 MHz, $CDCl_3$)

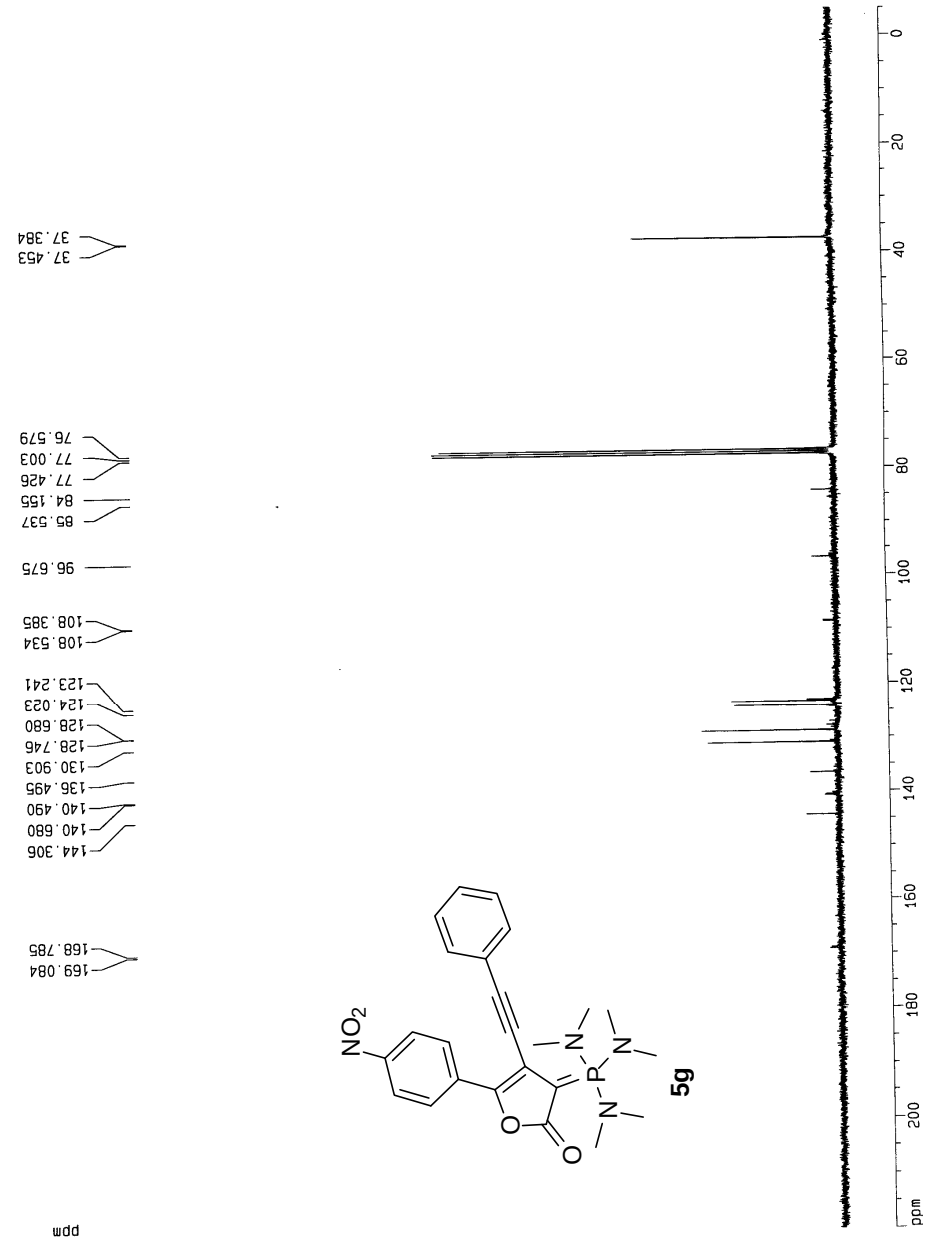


Fig S43. ^{1}H NMR spectrum of compound **5h** (300 MHz, $CDCl_3$)

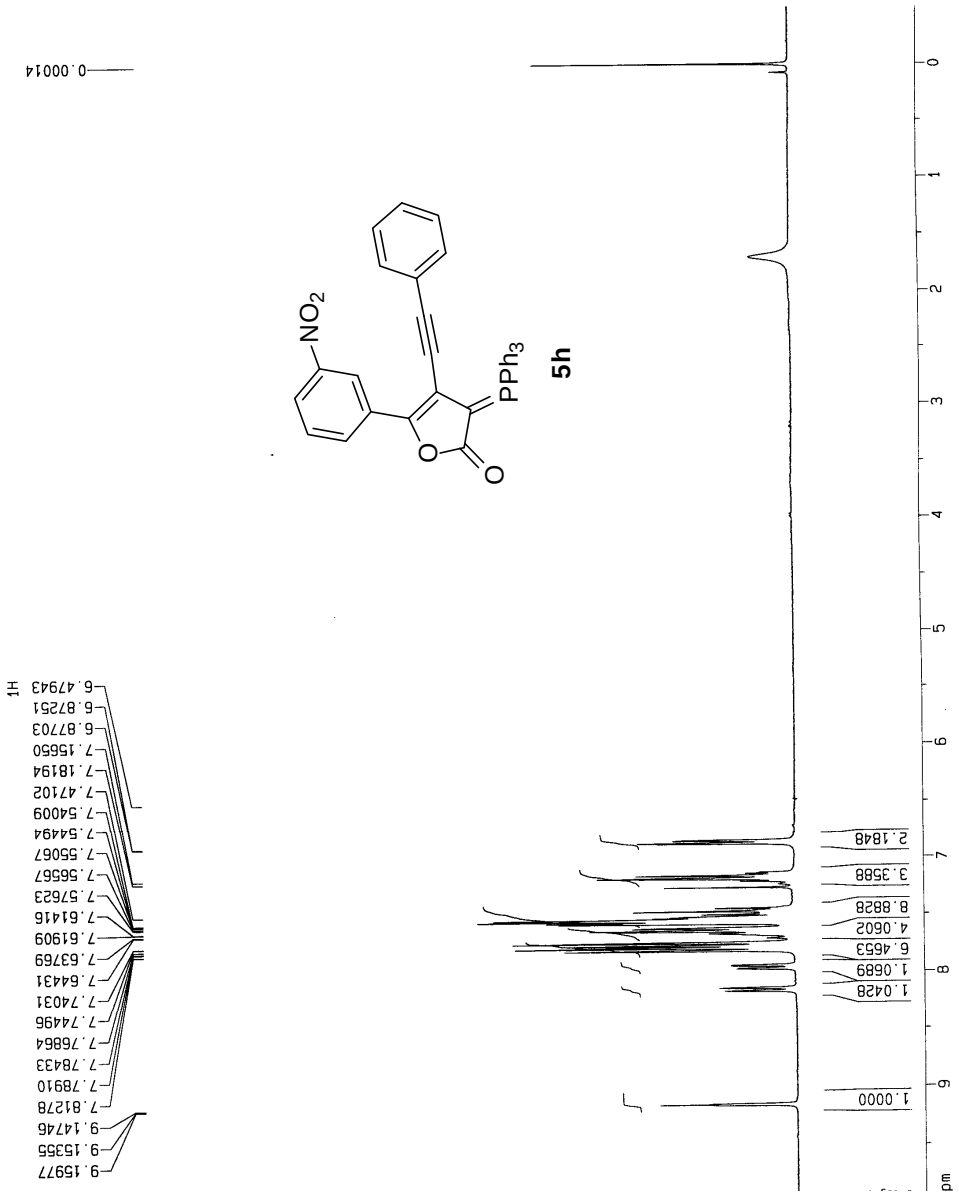


Fig S44. ^{13}C NMR spectrum of compound **5h** (75.5 MHz, $CDCl_3$)

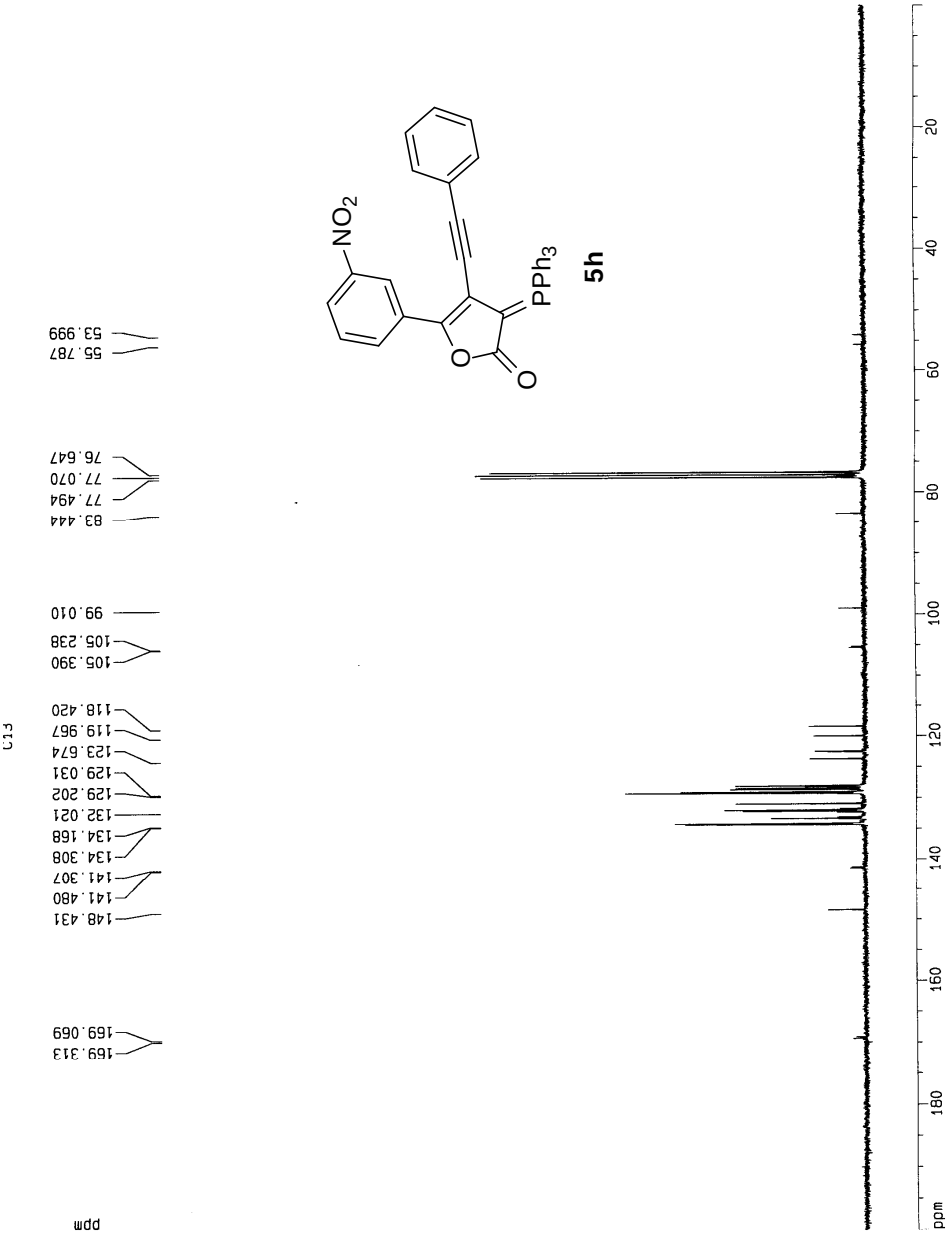


Fig S45. ^{1}H NMR spectrum of compound **5i** (300 MHz, $CDCl_3$)

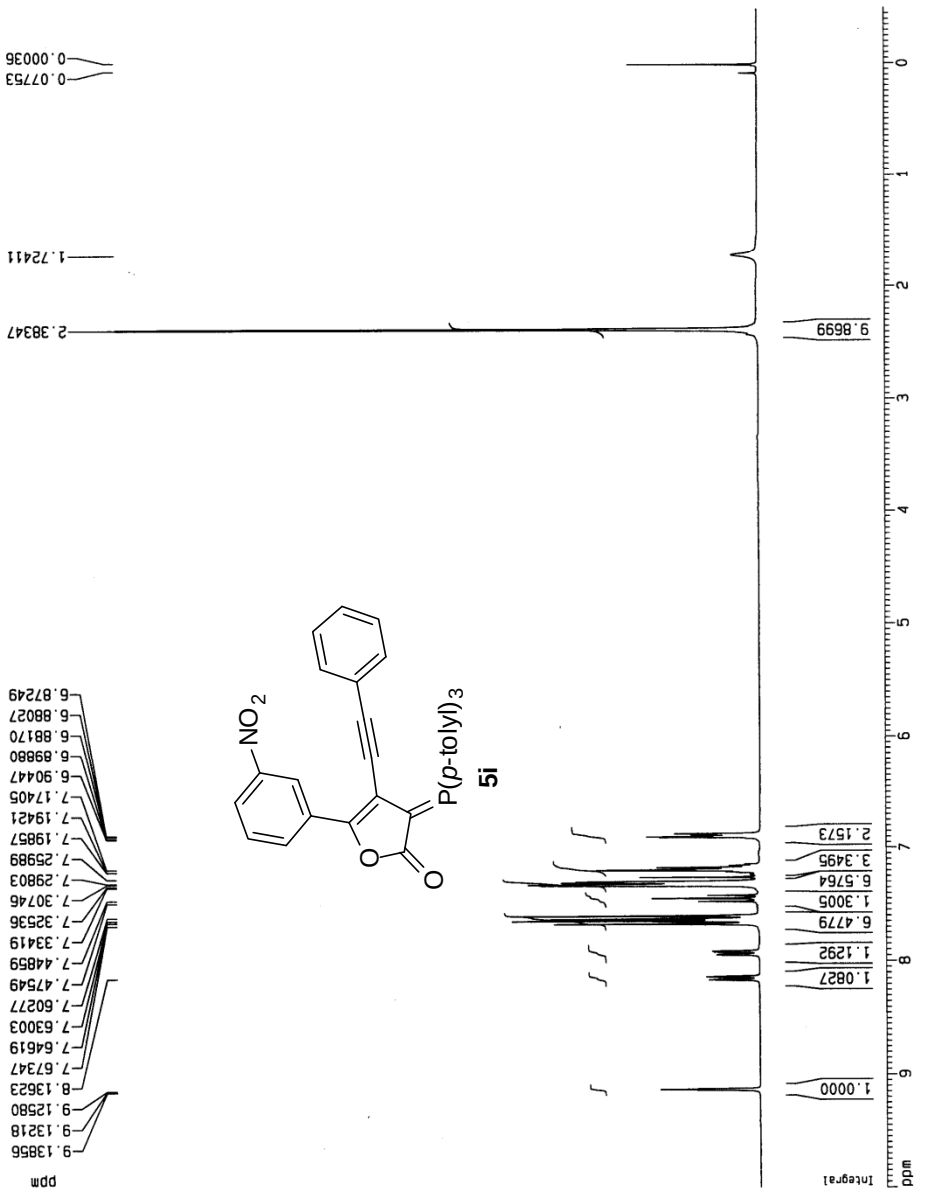


Fig S46. ^{13}C NMR spectrum of compound **5i** (75.5 MHz, $CDCl_3$)

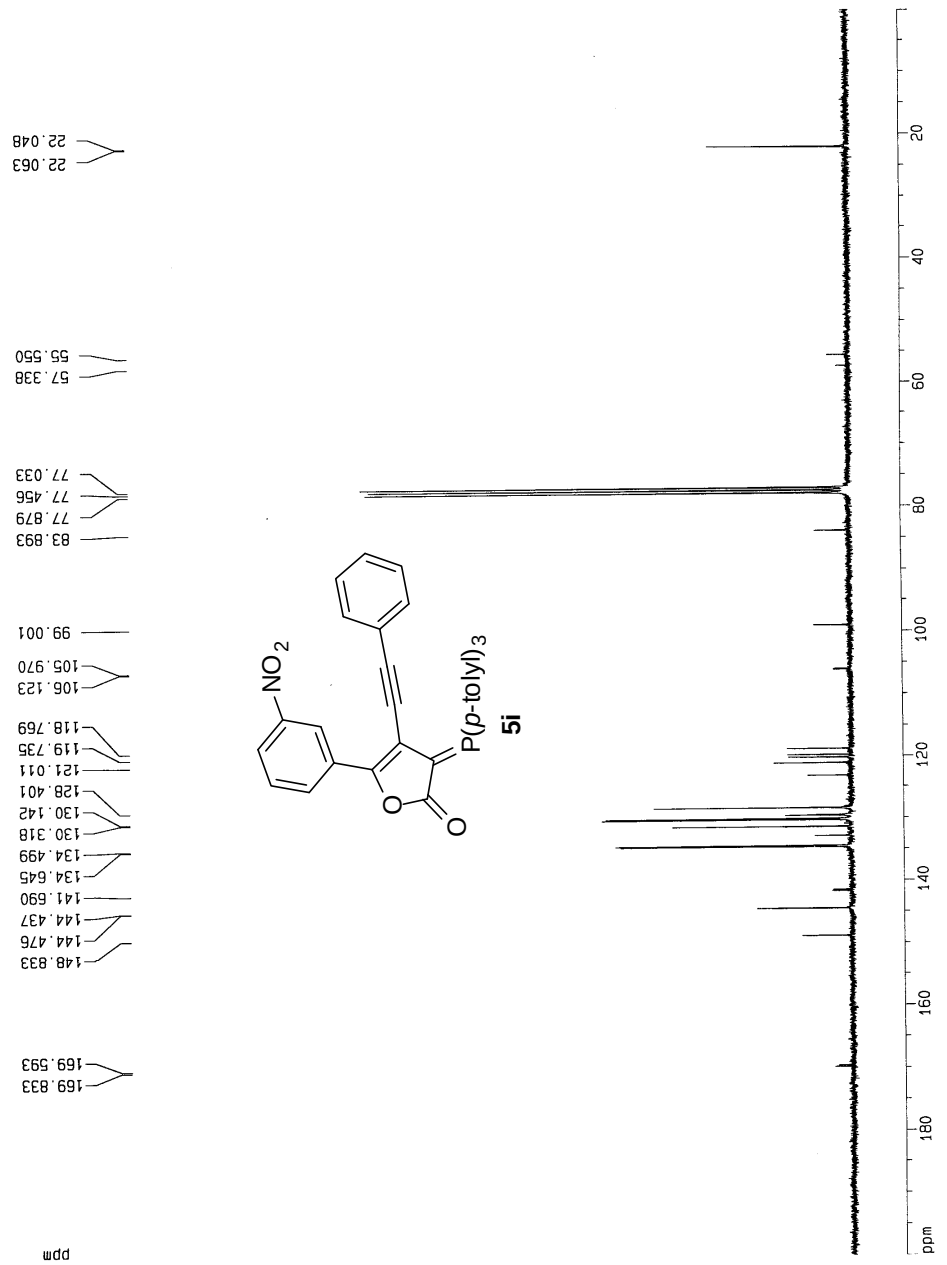


Fig S47. ^{1}H NMR spectrum of compound **5j** (300 MHz, $CDCl_3$)

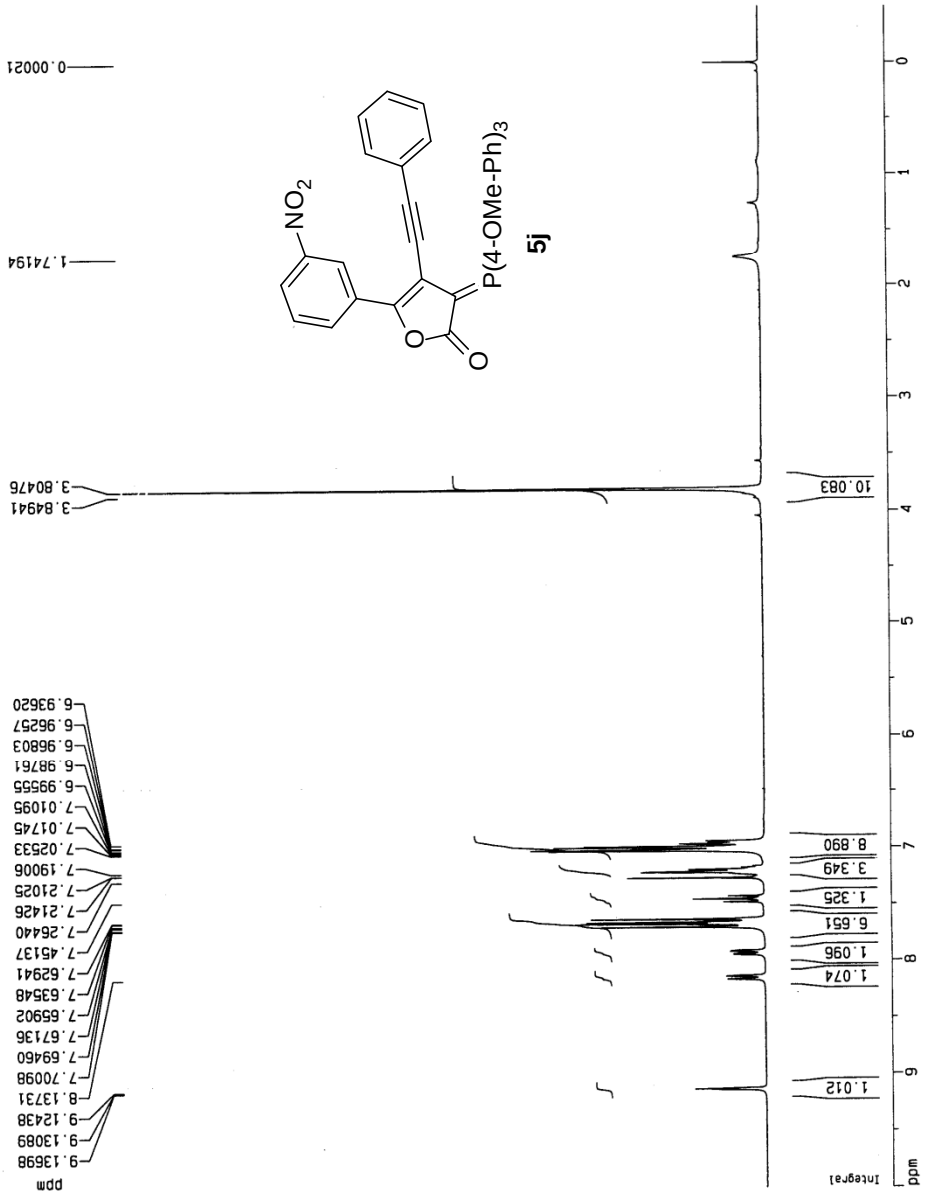


Fig S48. ^{13}C NMR spectrum of compound **5j** (150.7 MHz, $CDCl_3$)

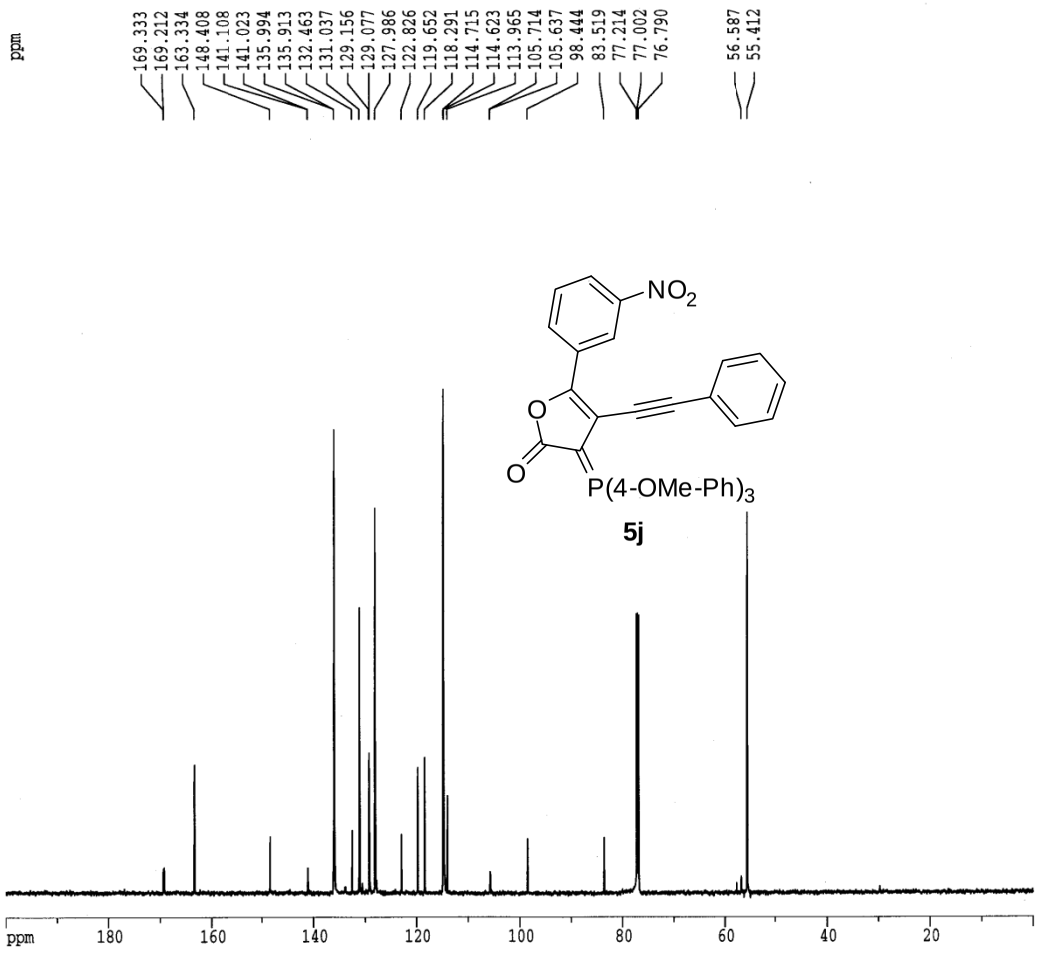


Fig S49. ^{1}H NMR spectra of compound **5k** (300 MHz, $CDCl_3$)

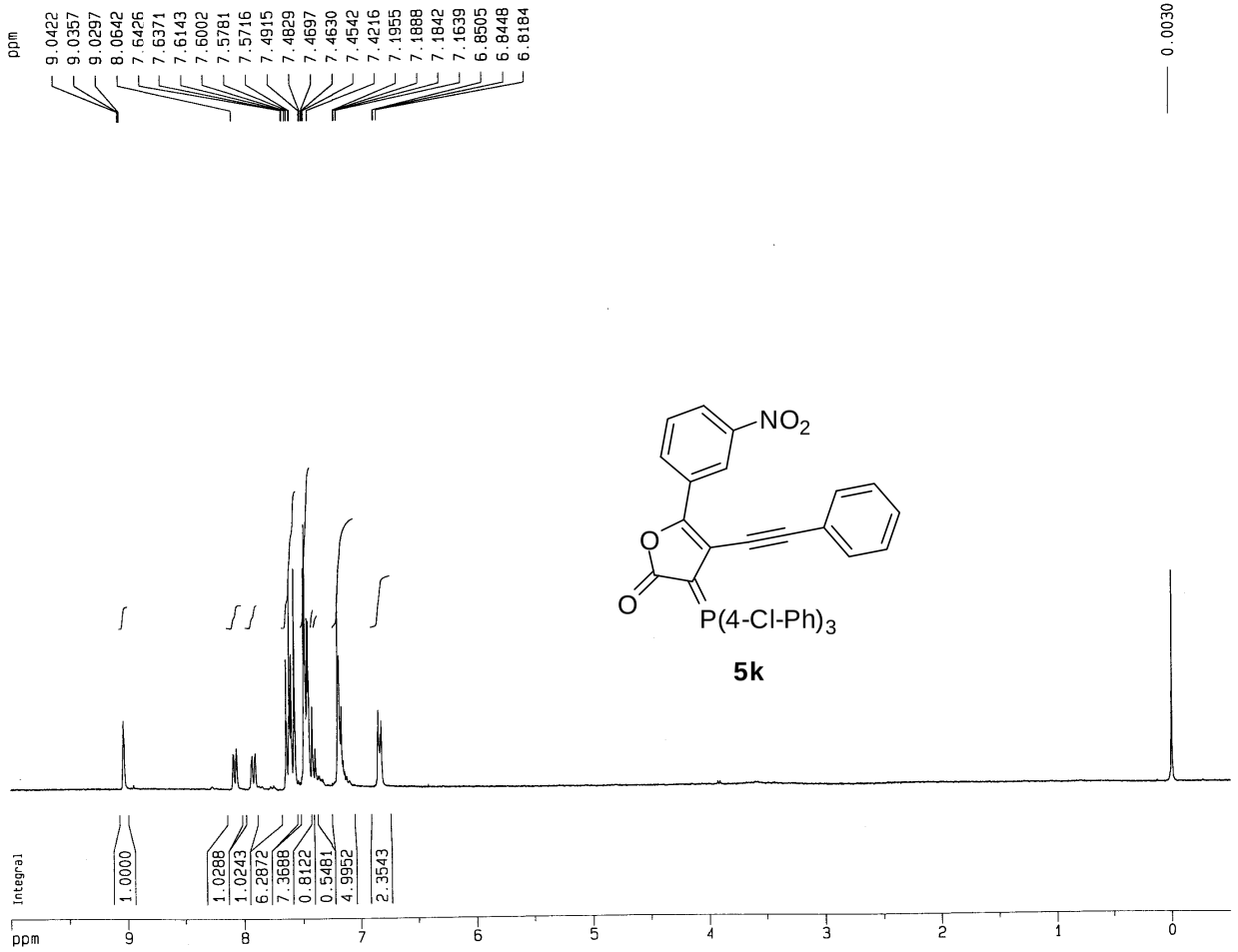


Fig S50. ^{13}C NMR spectra of compound **5k** (150.7 MHz, $CDCl_3$)

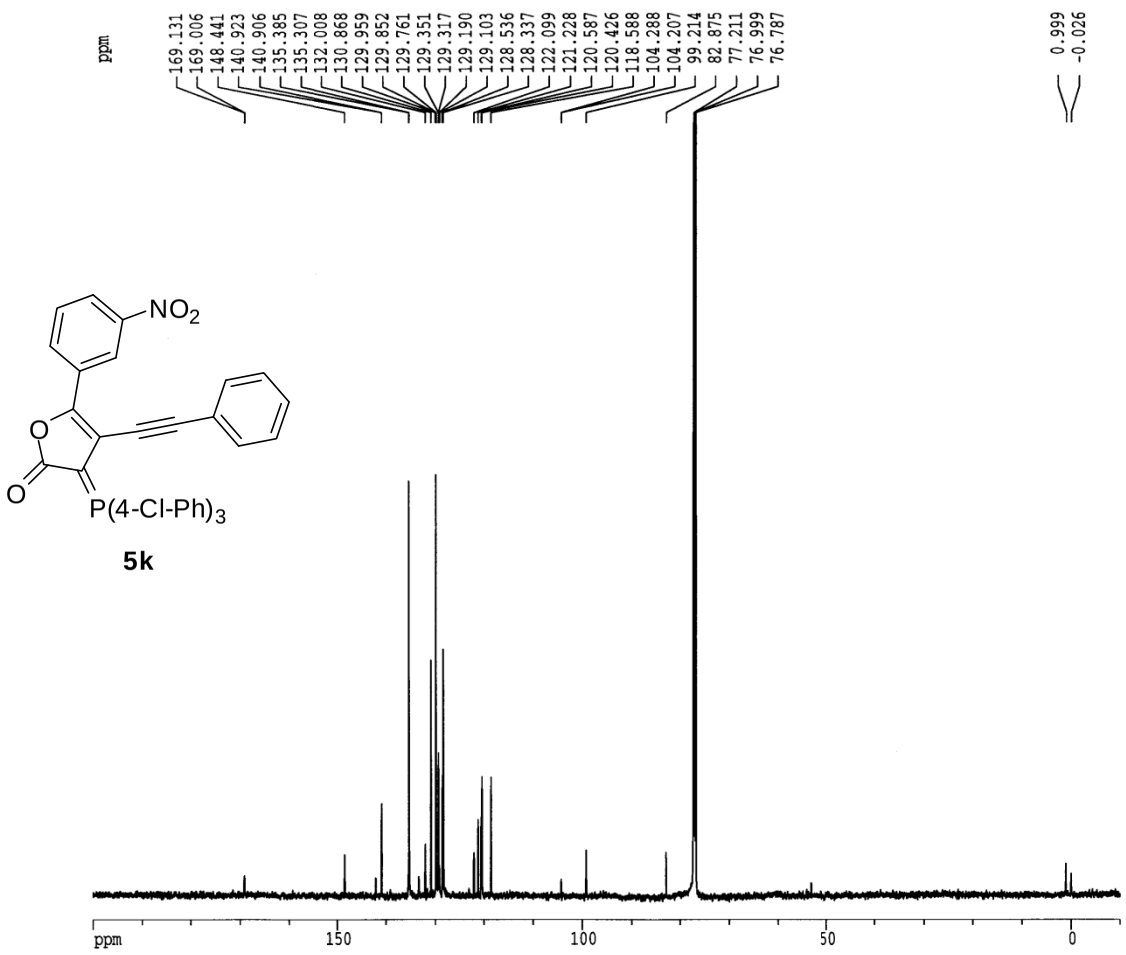


Fig S51. ^{1}H NMR spectra of compound **5l** (300 MHz, $CDCl_3$)

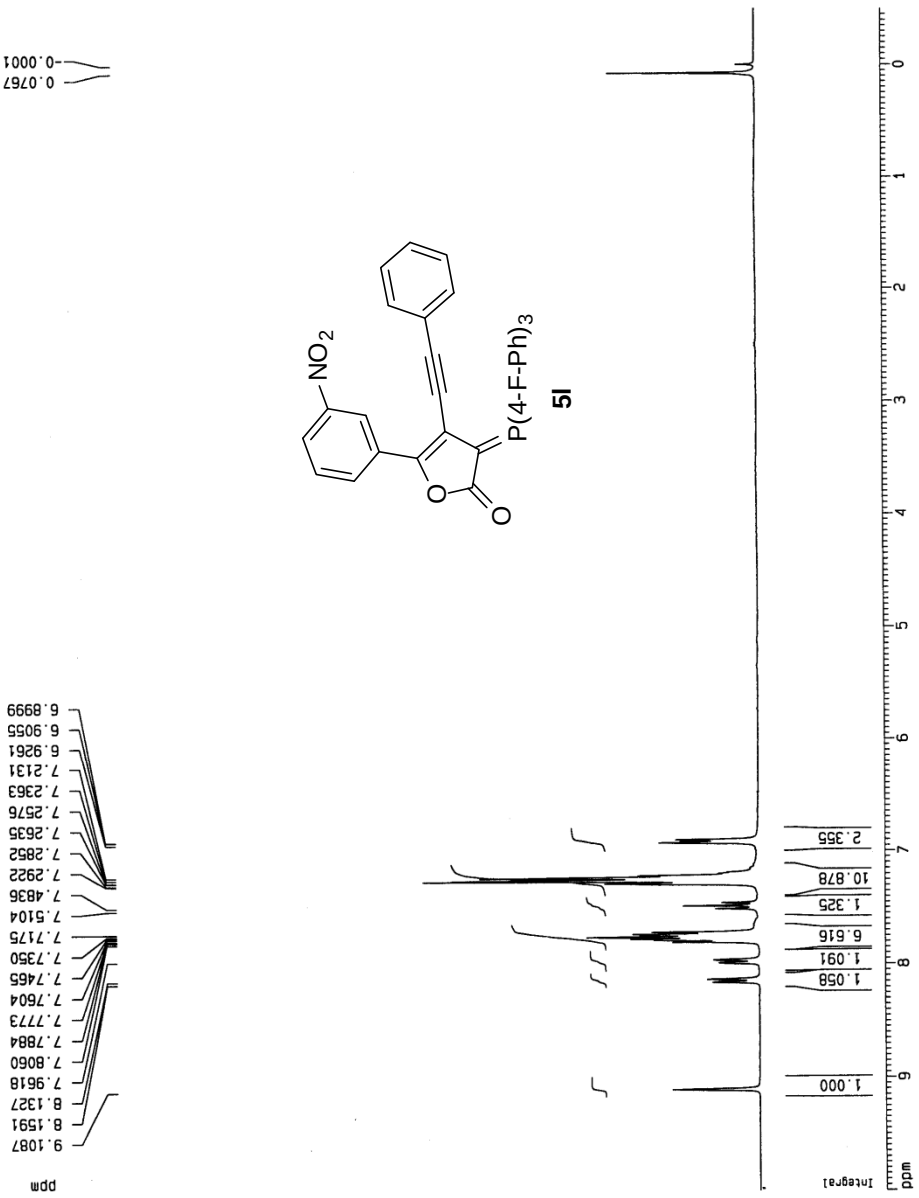


Fig S52. ^{13}C NMR spectra of compound **5l** (150.7 MHz, $CDCl_3$)

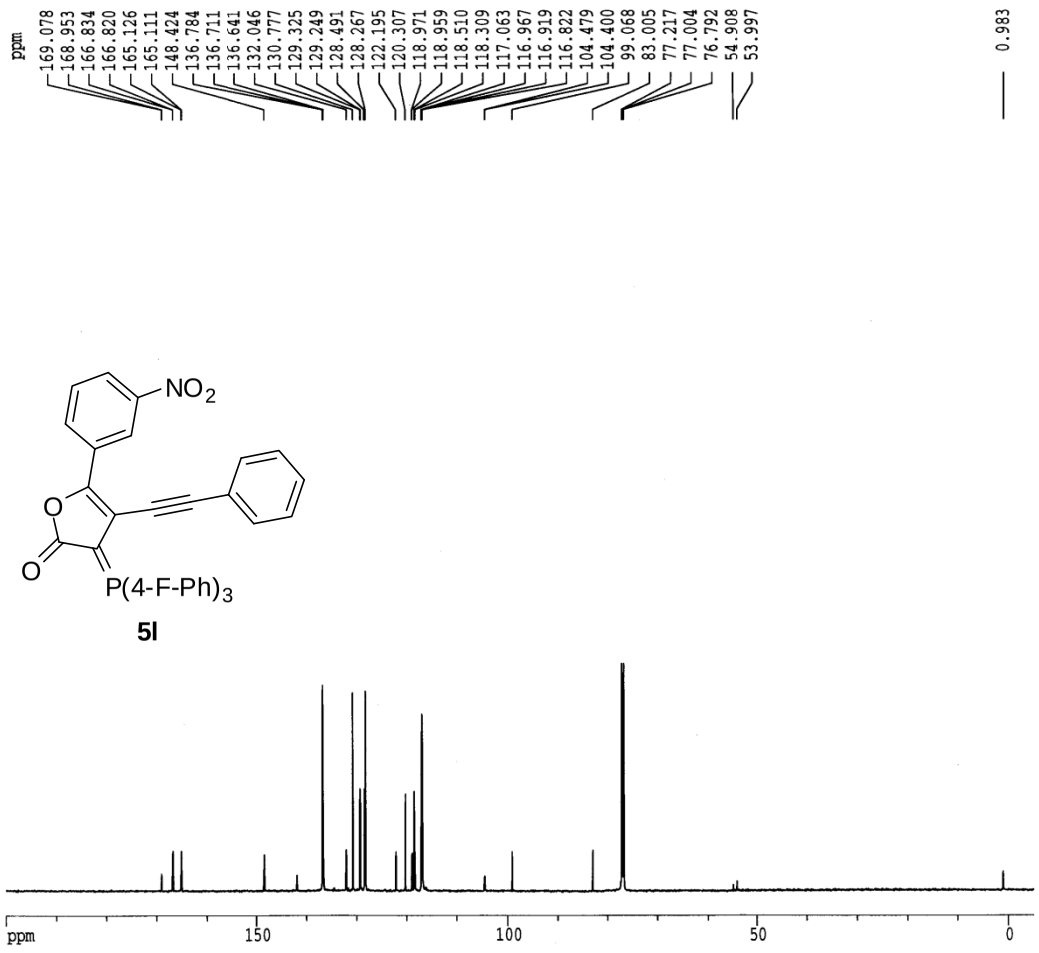


Fig S53. ^{1}H NMR spectra of compound **5m** (300 MHz, $CDCl_3$)

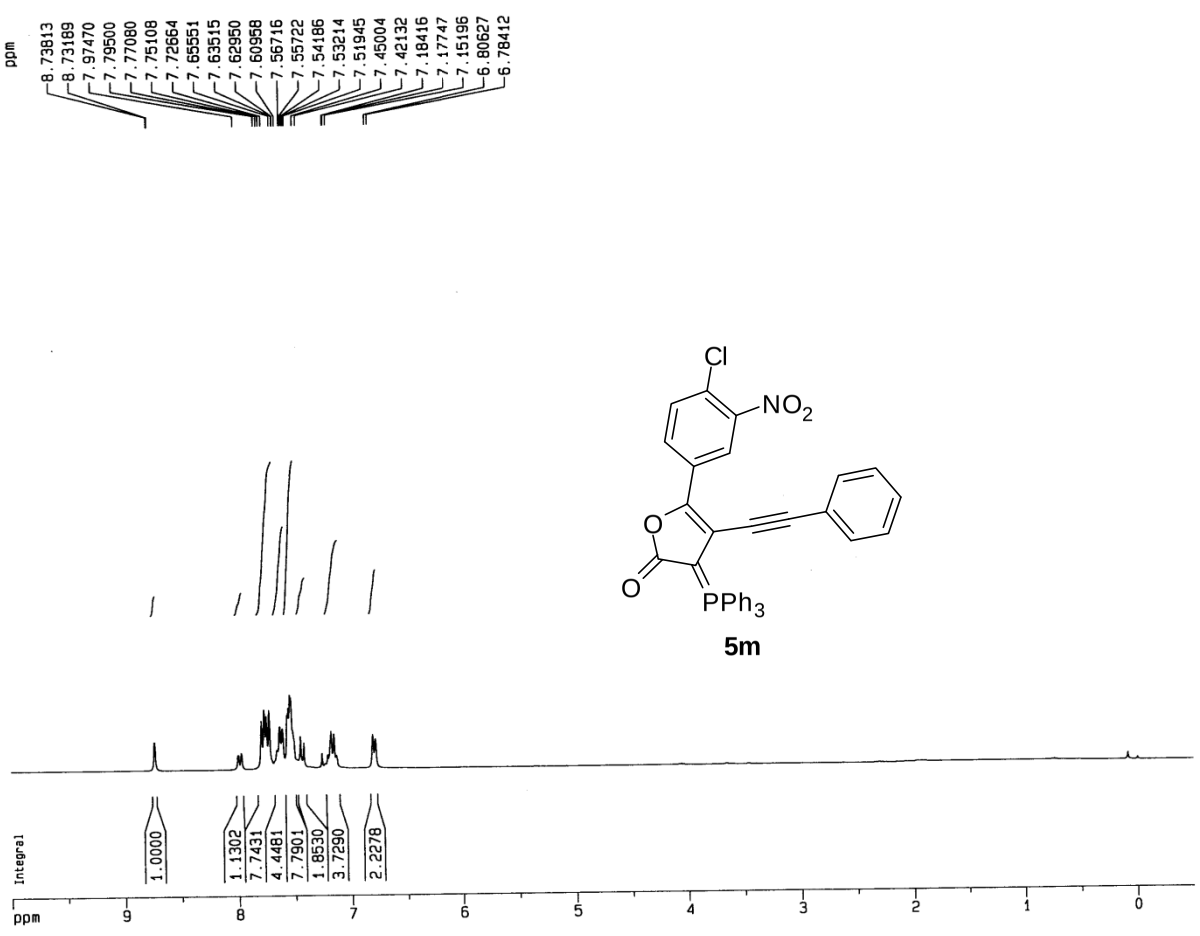


Fig S54. ^{13}C NMR spectra of compound **5m** (75.5 MHz, $CDCl_3$)

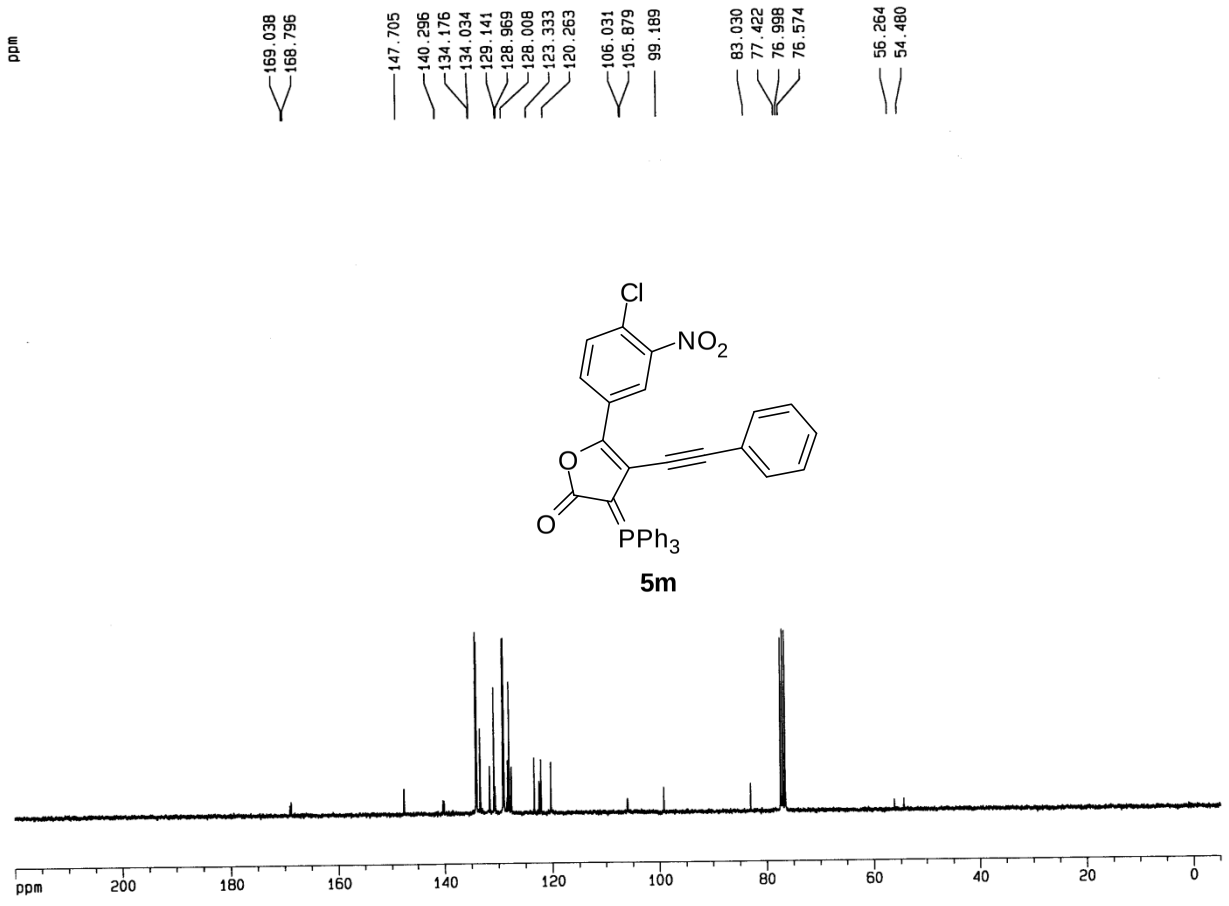


Fig S55. ^{1}H NMR spectra of compound **5n** (300 MHz, $CDCl_3$)

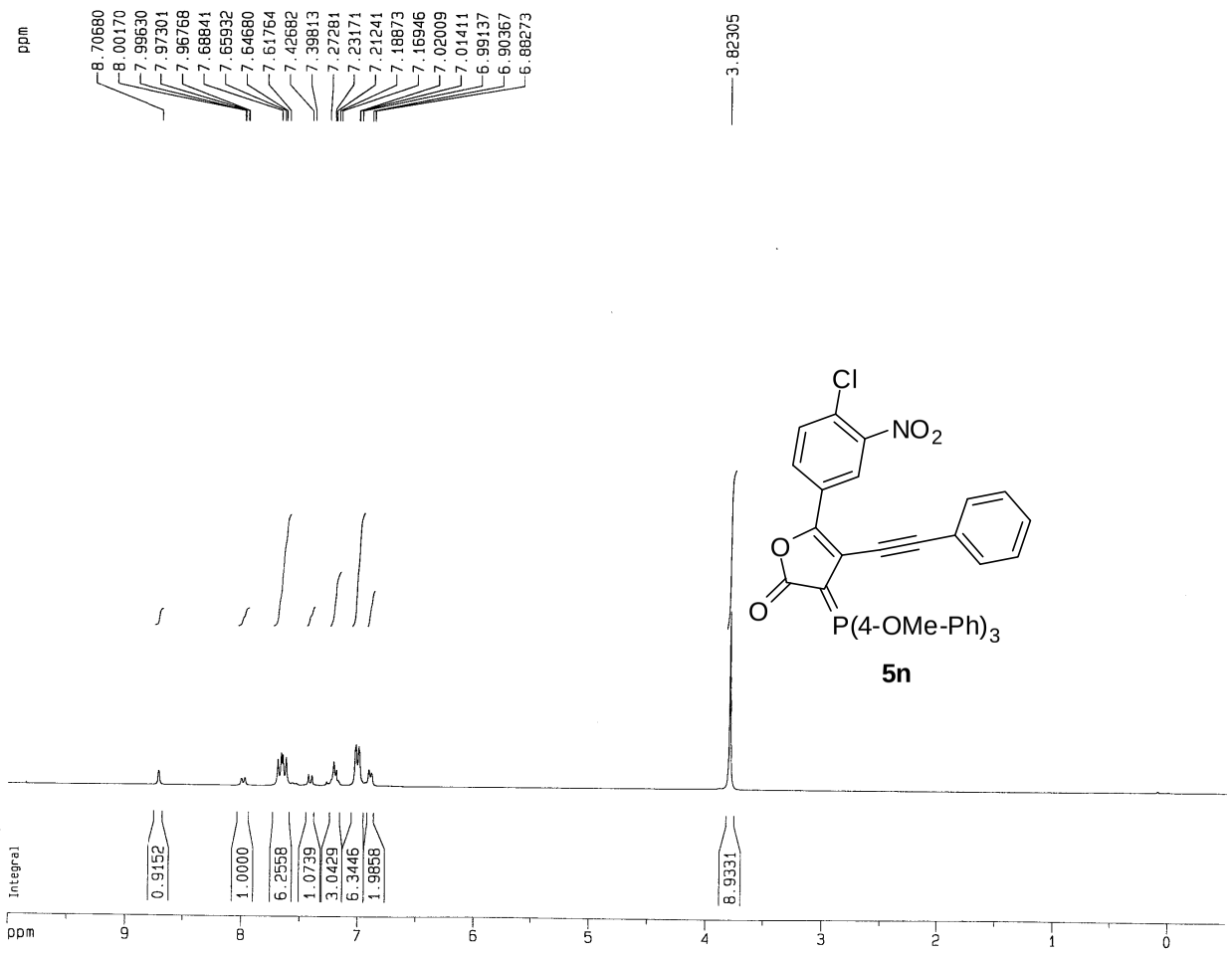


Fig S56. ^{13}C NMR spectra of compound **5n** (75.5 MHz, $CDCl_3$)

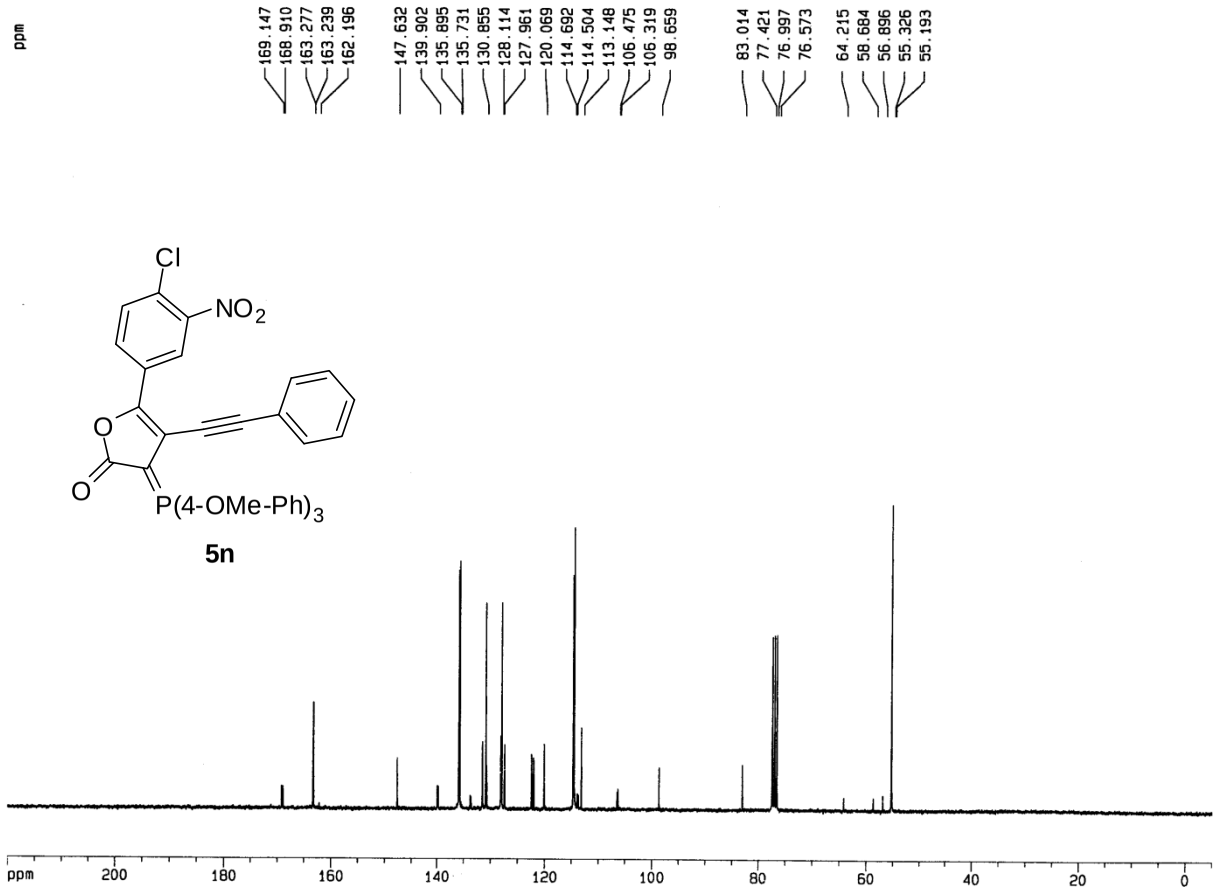


Fig S57. ^{1}H NMR spectra of compound **5o** (300 MHz, $CDCl_3$)

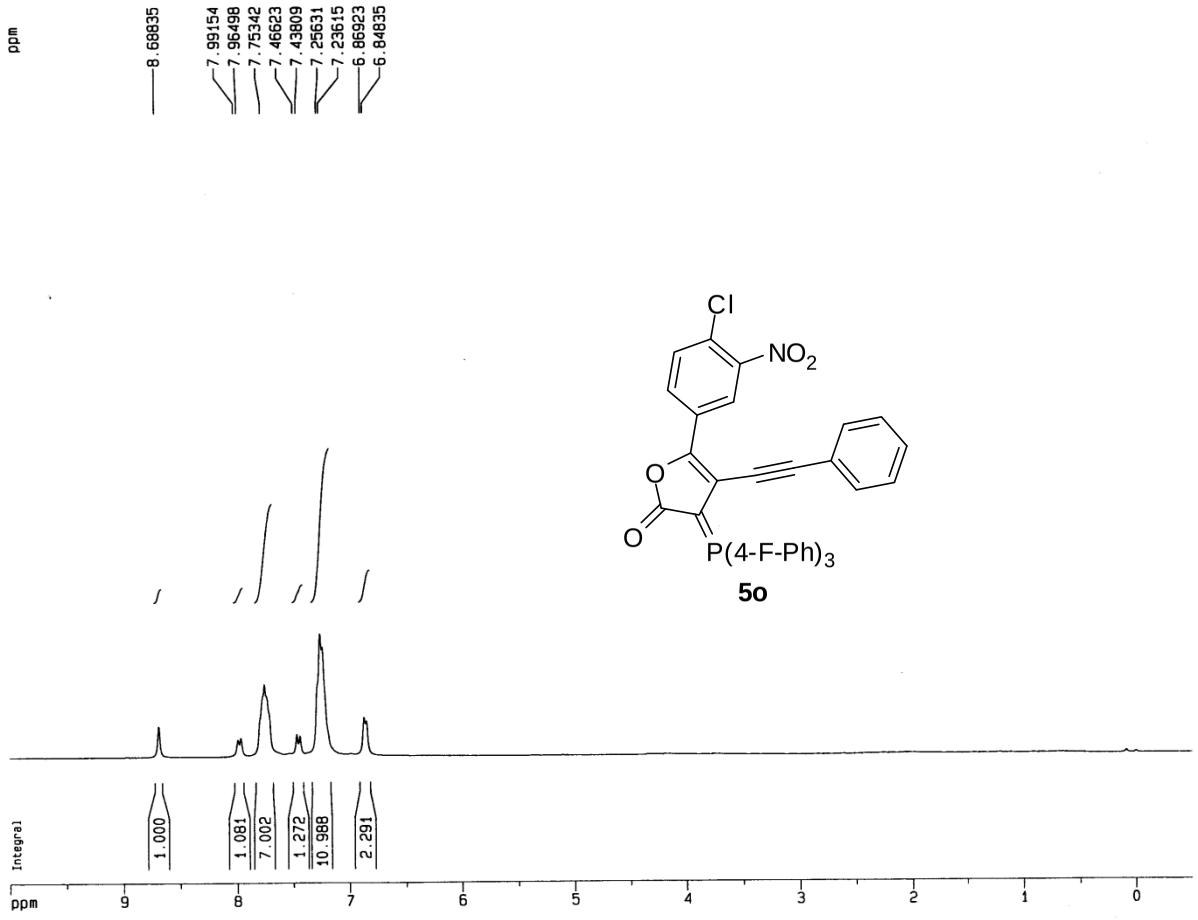


Fig S58. ^{13}C NMR spectra of compound **5o** (150.7 MHz, $CDCl_3$)

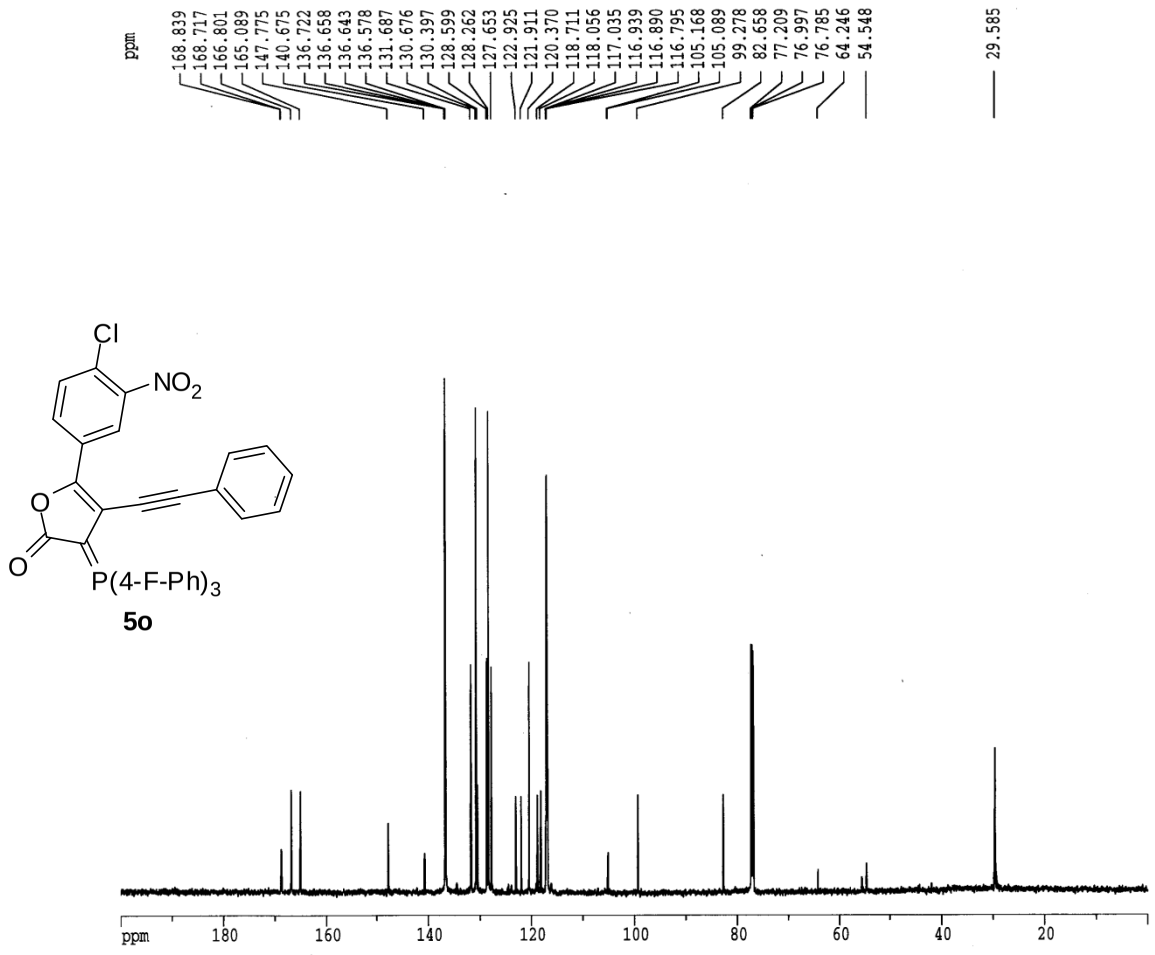


Fig S59. ^{1}H NMR spectra of compound **5p** (300 MHz, $CDCl_3$)

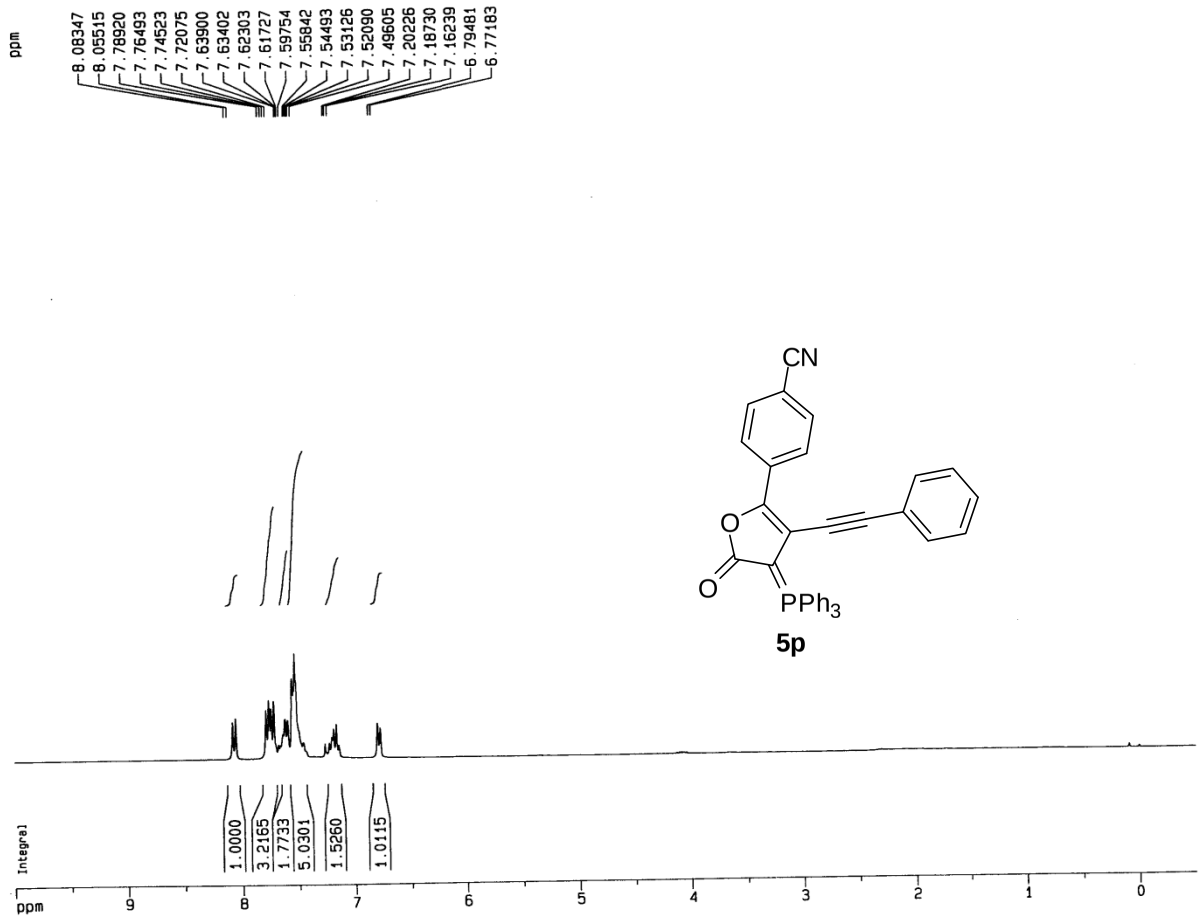


Fig S60. ^{13}C NMR spectra of compound **5p** (75.5 MHz, $CDCl_3$)

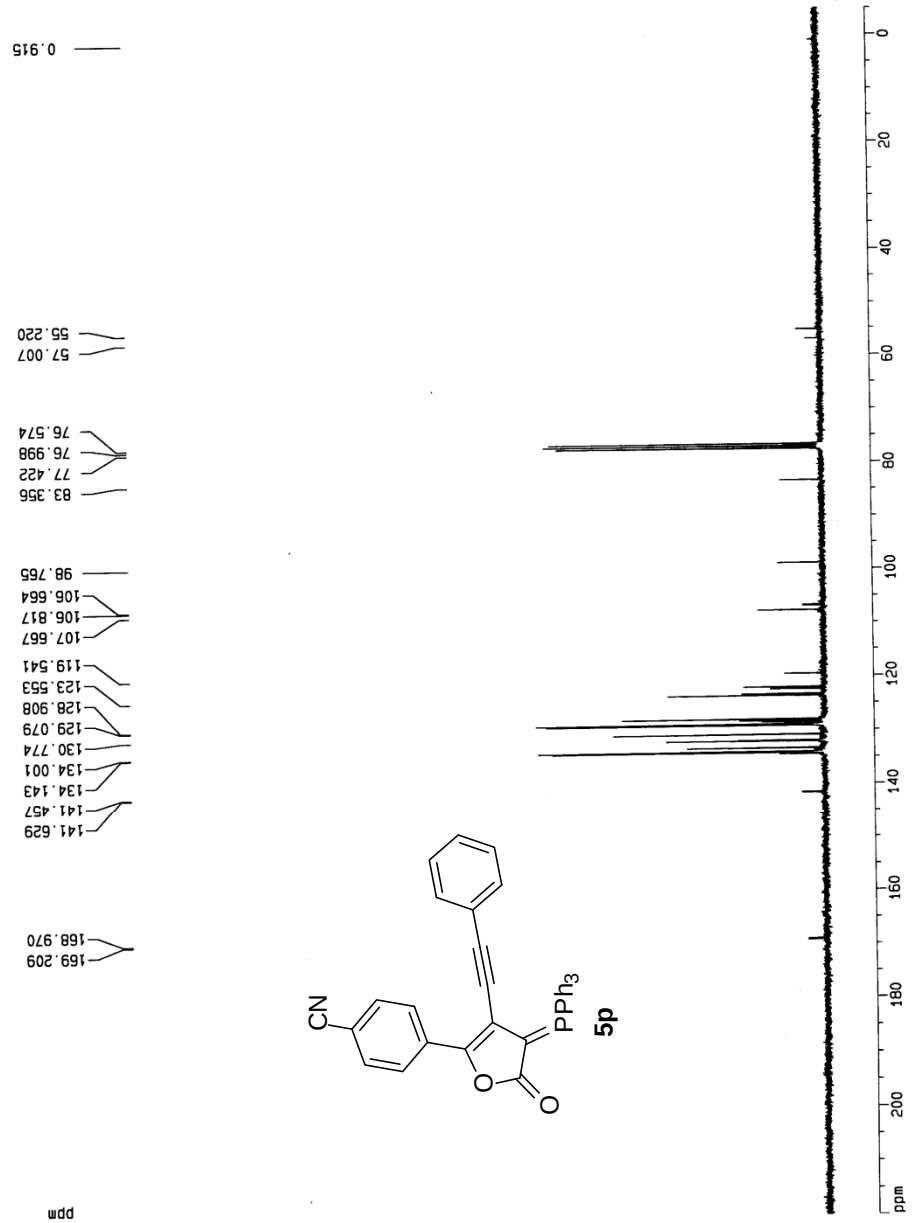


Fig S61. ^{1}H NMR spectra of compound **5q** (600 MHz, $CDCl_3$)

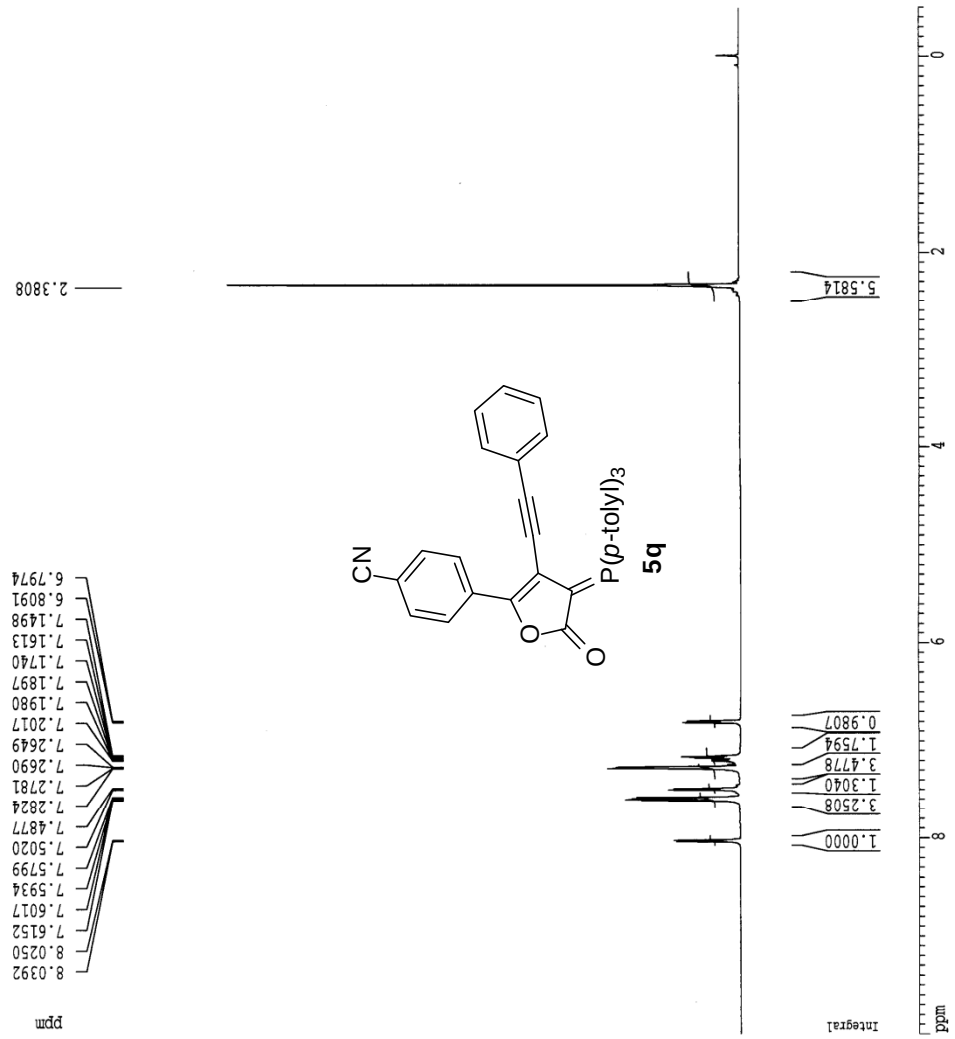


Fig S62. ^{13}C NMR spectra of compound **5q** (150.7 MHz, $CDCl_3$)

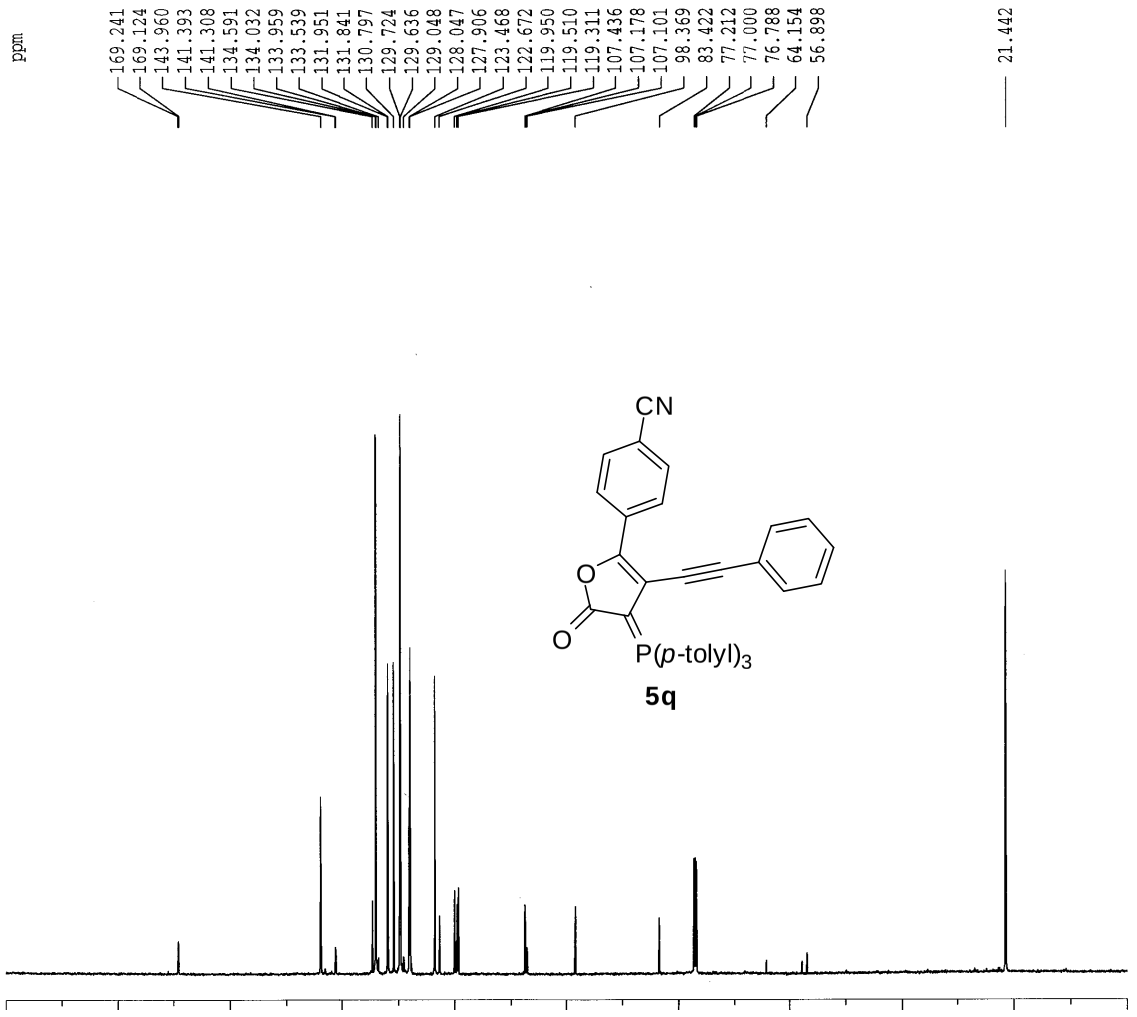


Fig S63. ^{1}H NMR spectra of compound **5r** (300 MHz, $CDCl_3$)

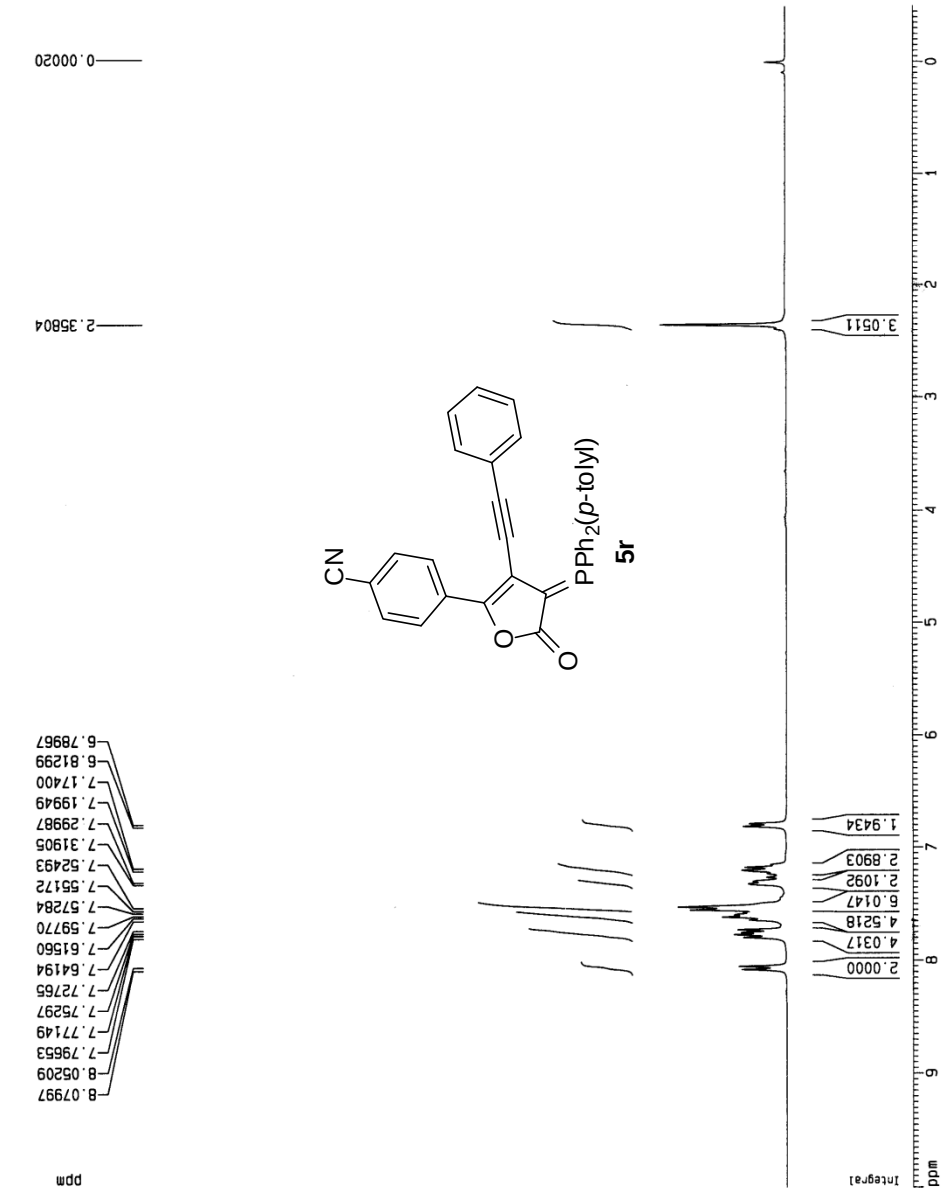


Fig S64. ^{13}C NMR spectra of compound **5r** (75.5 MHz, $CDCl_3$)

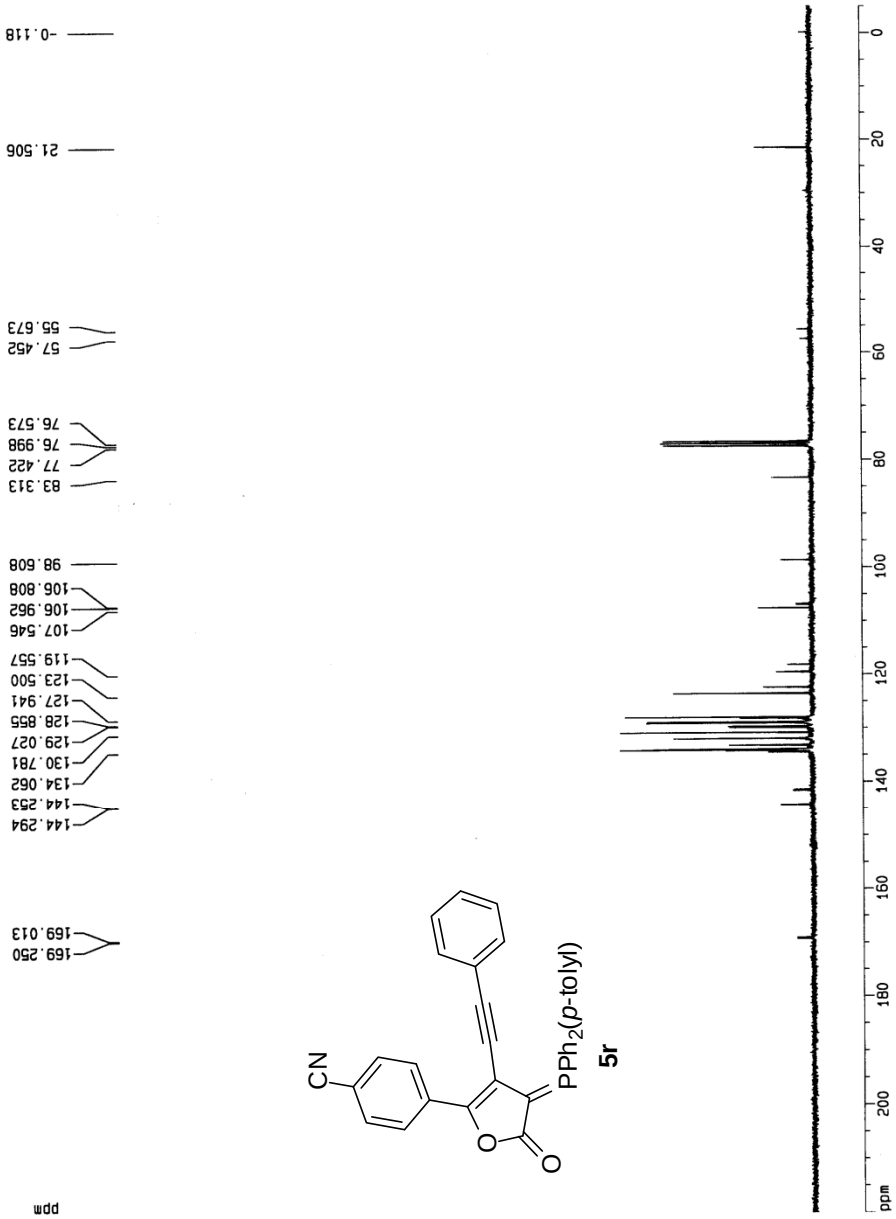


Fig S65. ^{1}H NMR spectra of compound **5s** (300 MHz, $CDCl_3$)

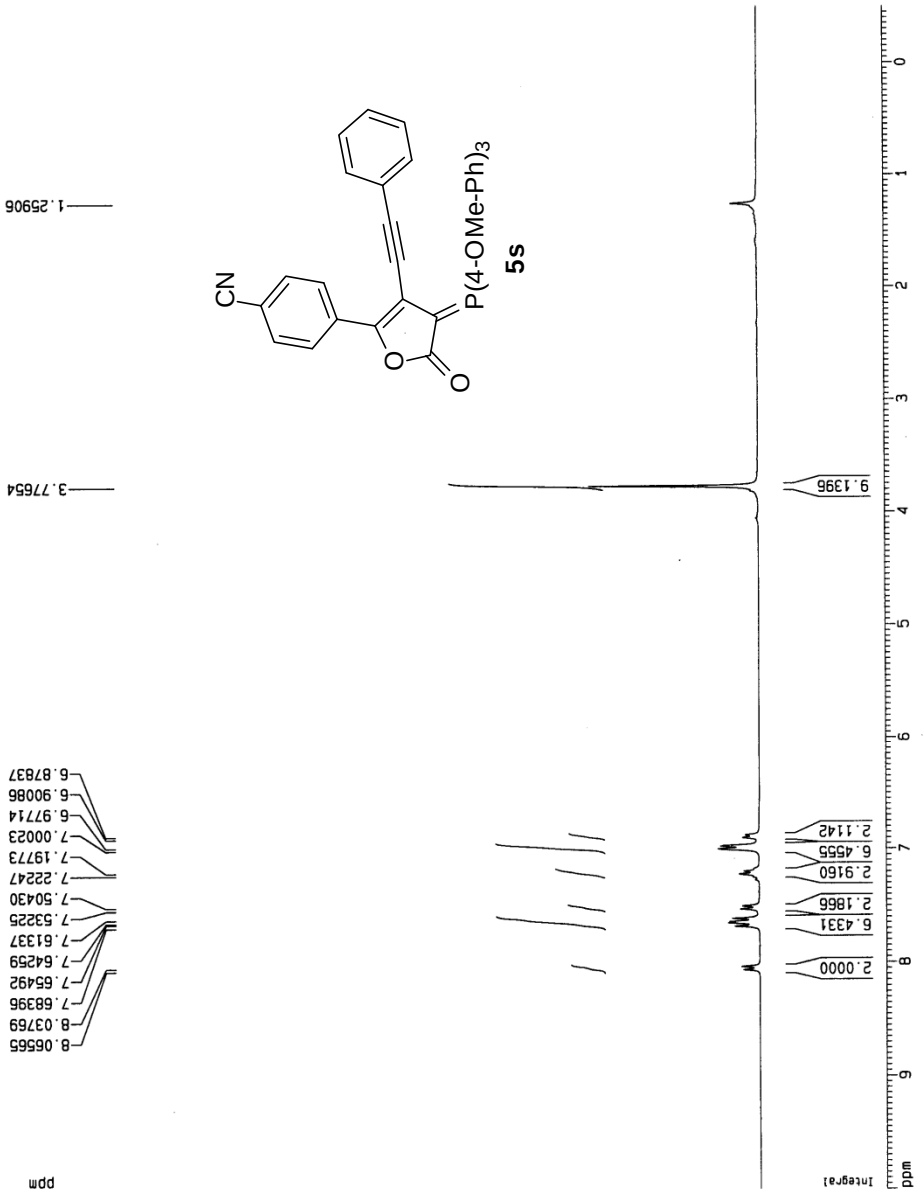


Fig S66. ^{13}C NMR spectra of compound **5s** (75.5 MHz, $CDCl_3$)

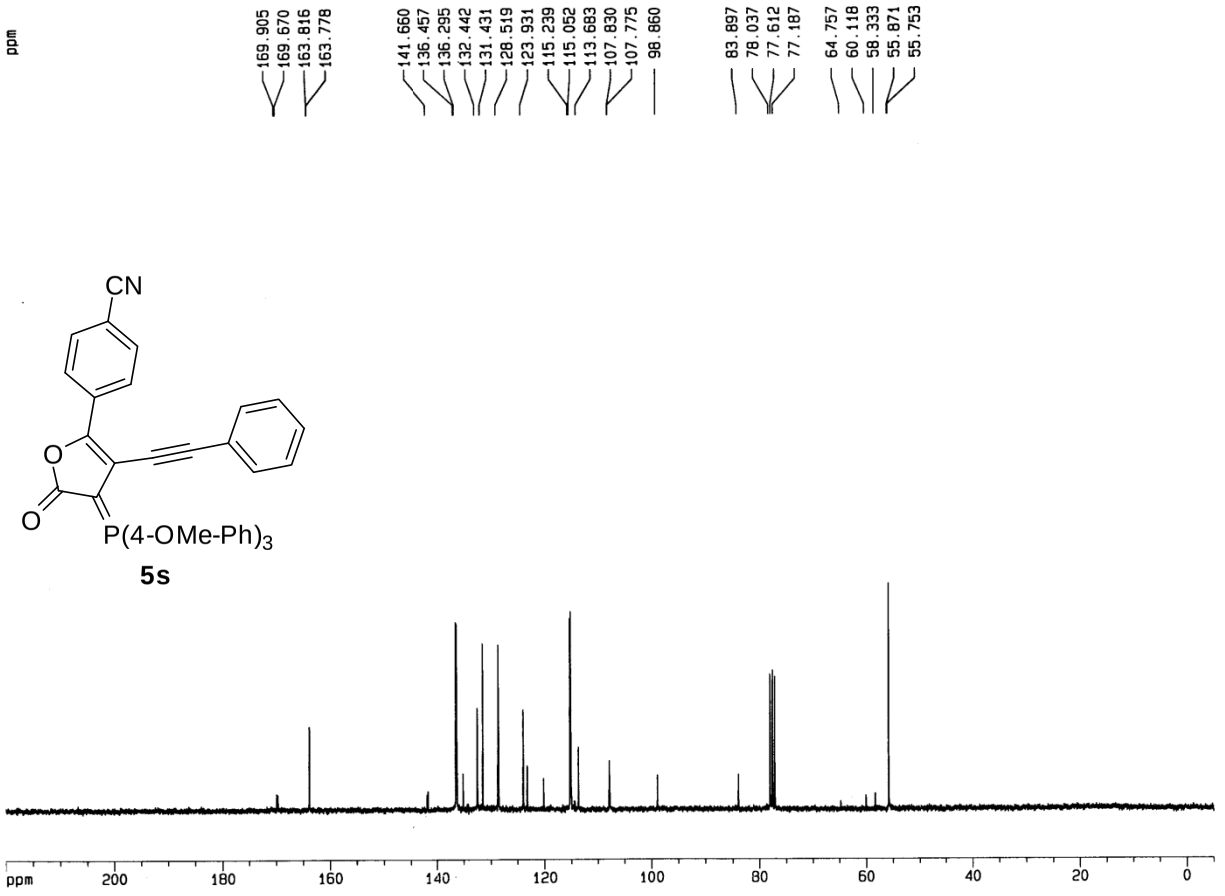


Fig S67. ^{1}H NMR spectra of compound **5t** (300 MHz, $CDCl_3$)

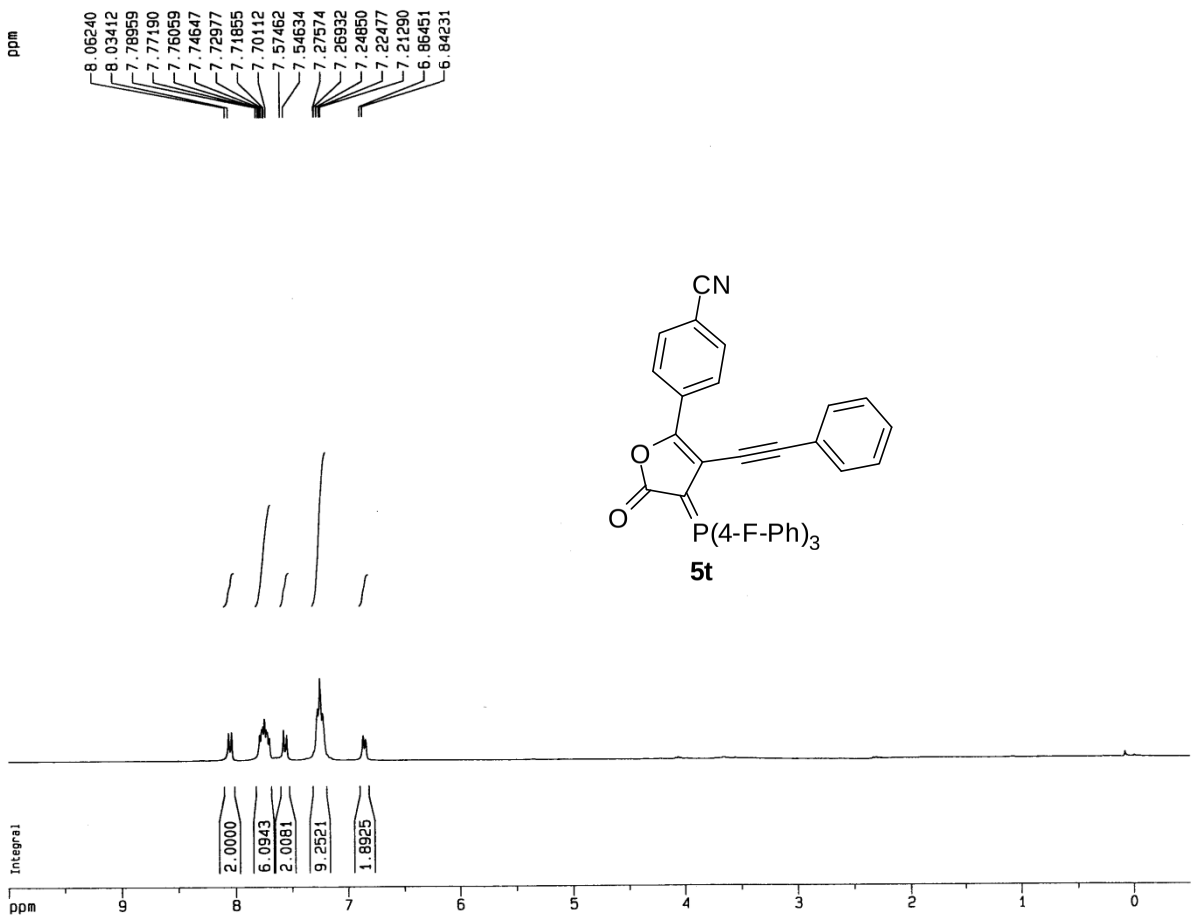


Fig S68. ^{13}C NMR spectra of compound **5t** (150.7 MHz, $CDCl_3$)

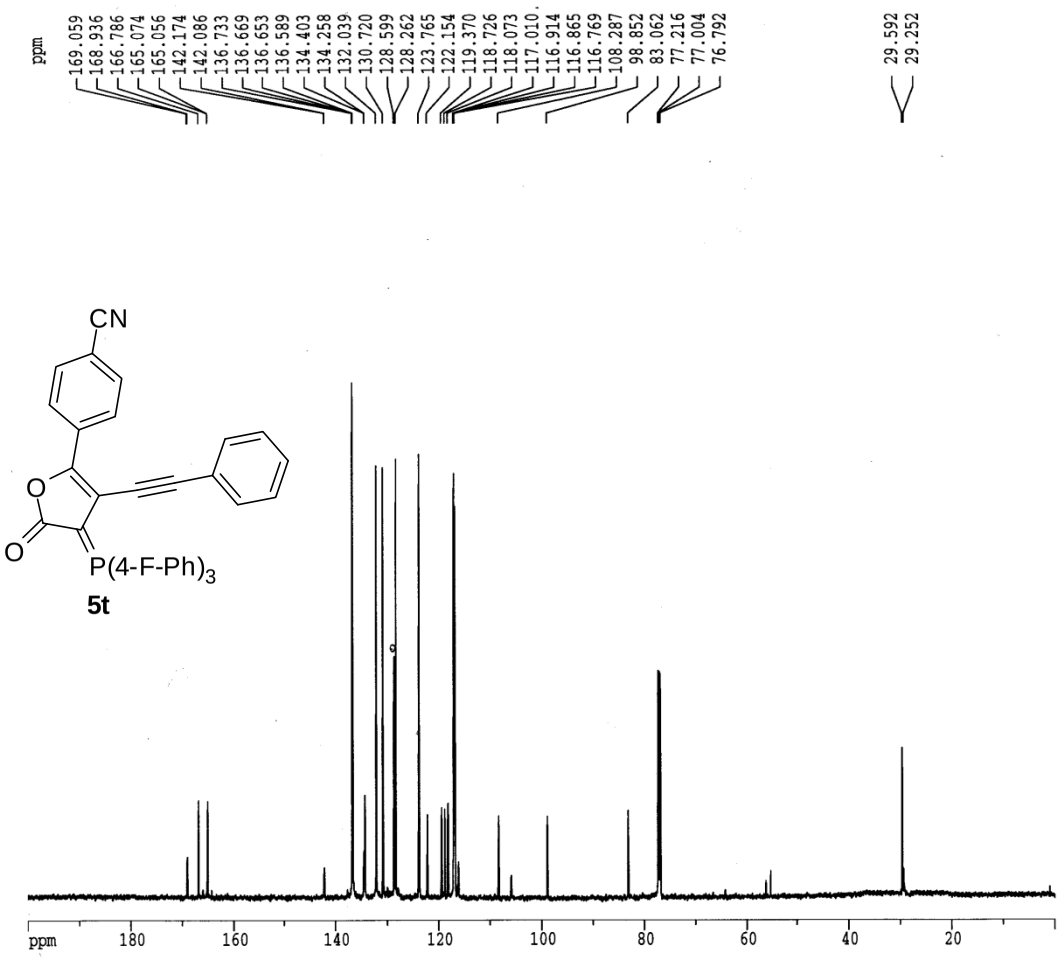


Fig S69. ^{1}H NMR spectra of compound **5u** (300 MHz, $CDCl_3$)

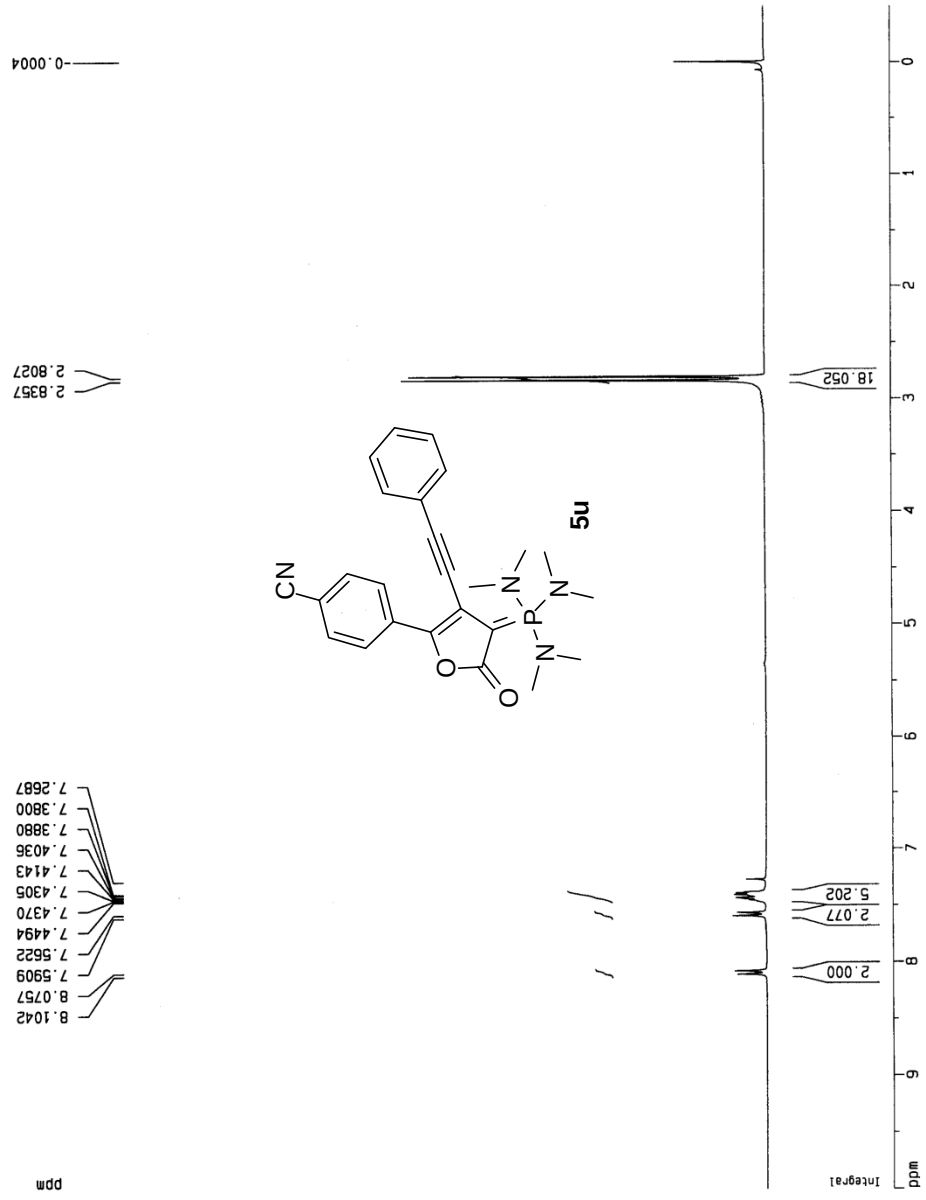


Fig S70. ^{13}C NMR spectra of compound **5u** (150.7 MHz, $CDCl_3$)

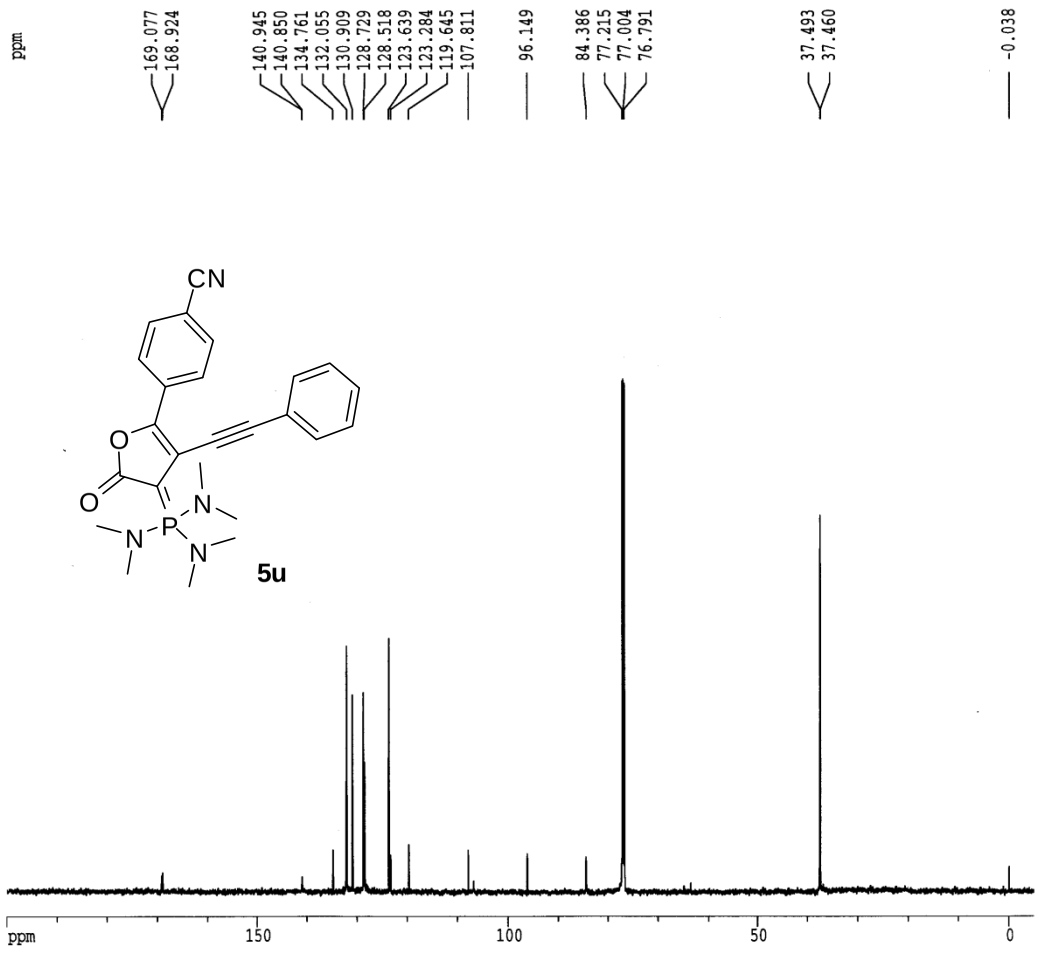


Fig S71. ^{1}H NMR spectra of compound **5v** (300 MHz, $CDCl_3$)

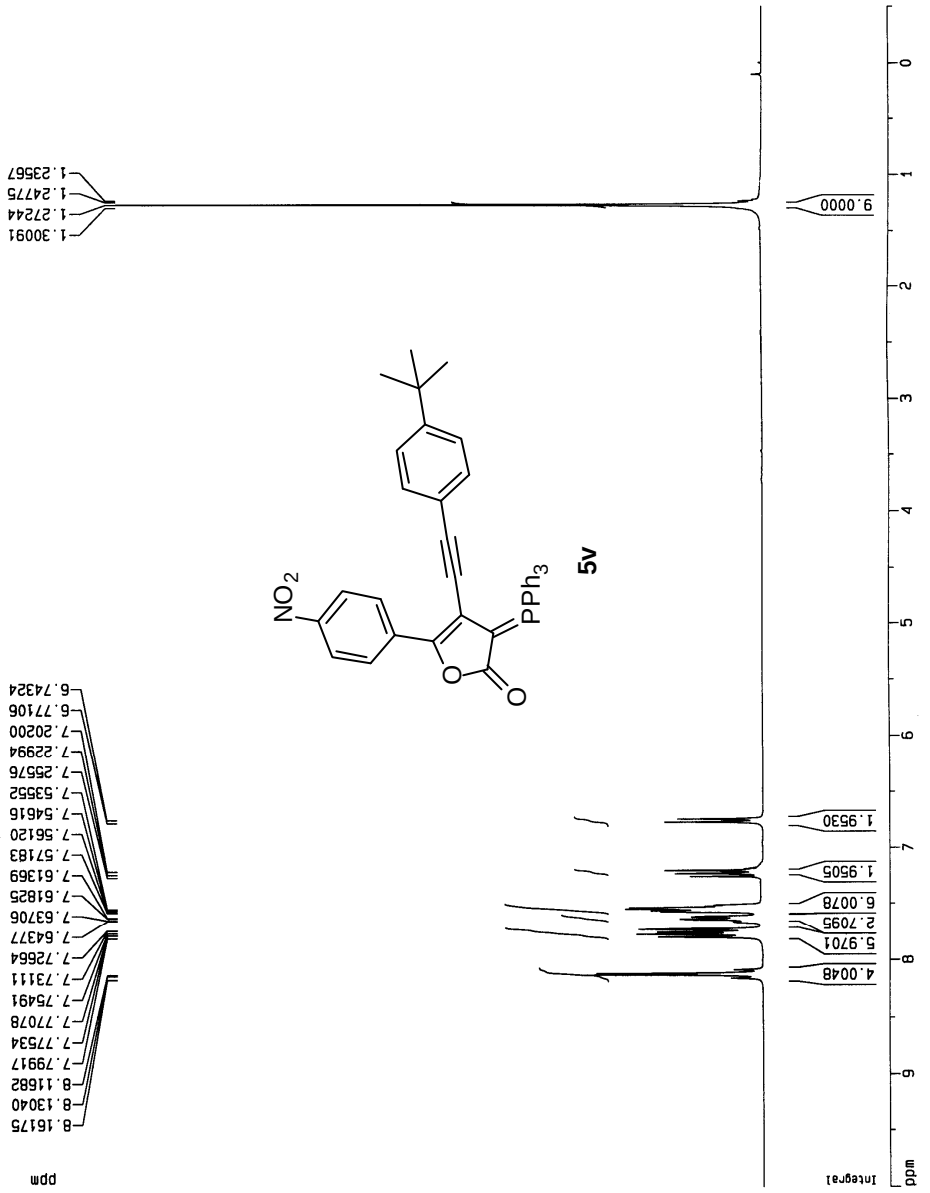


Fig S72. ^{13}C NMR spectra of compound **5v** (75.5 MHz, $CDCl_3$)

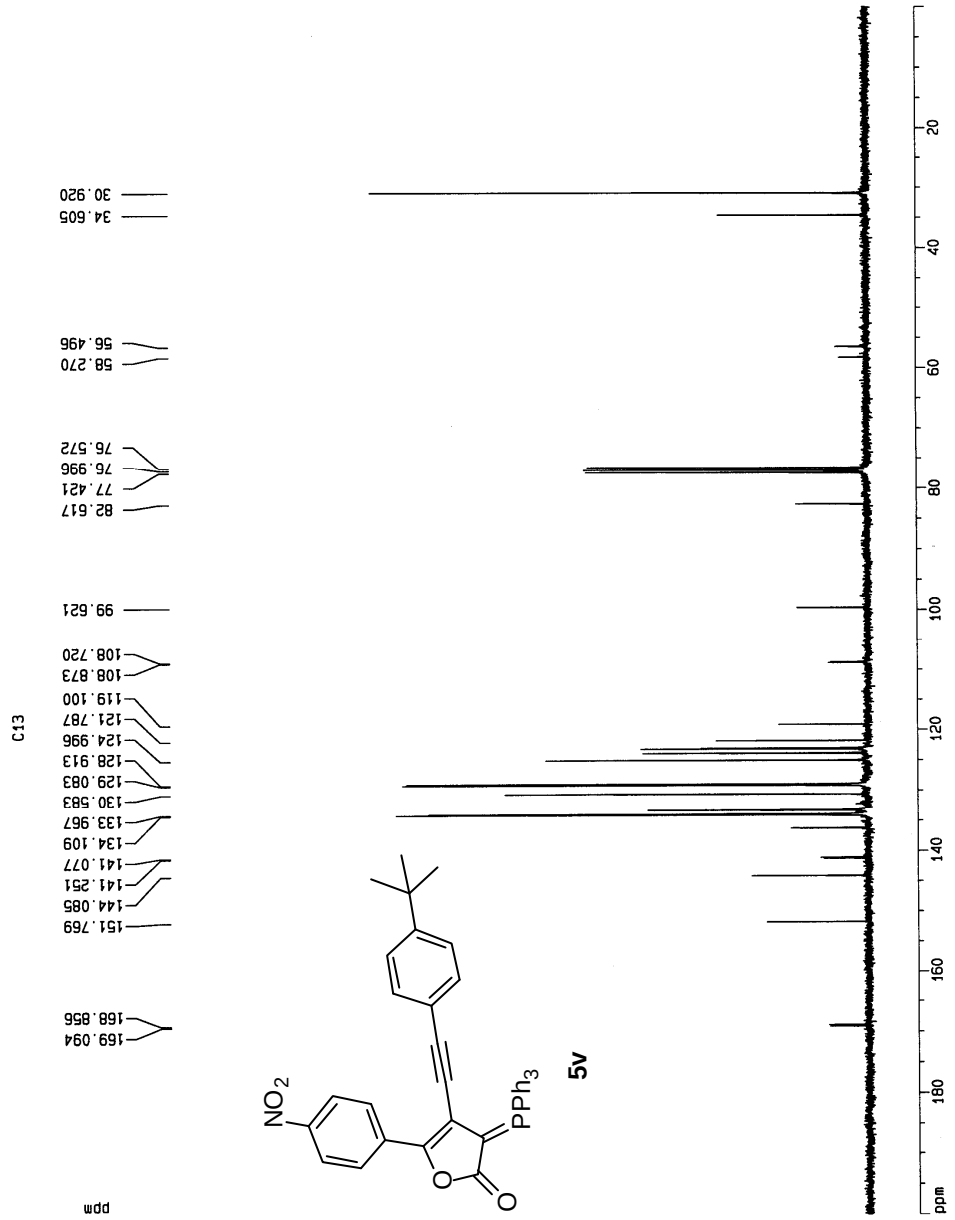


Fig S73. ^{1}H NMR spectra of compound **5w** (300 MHz, $CDCl_3$)

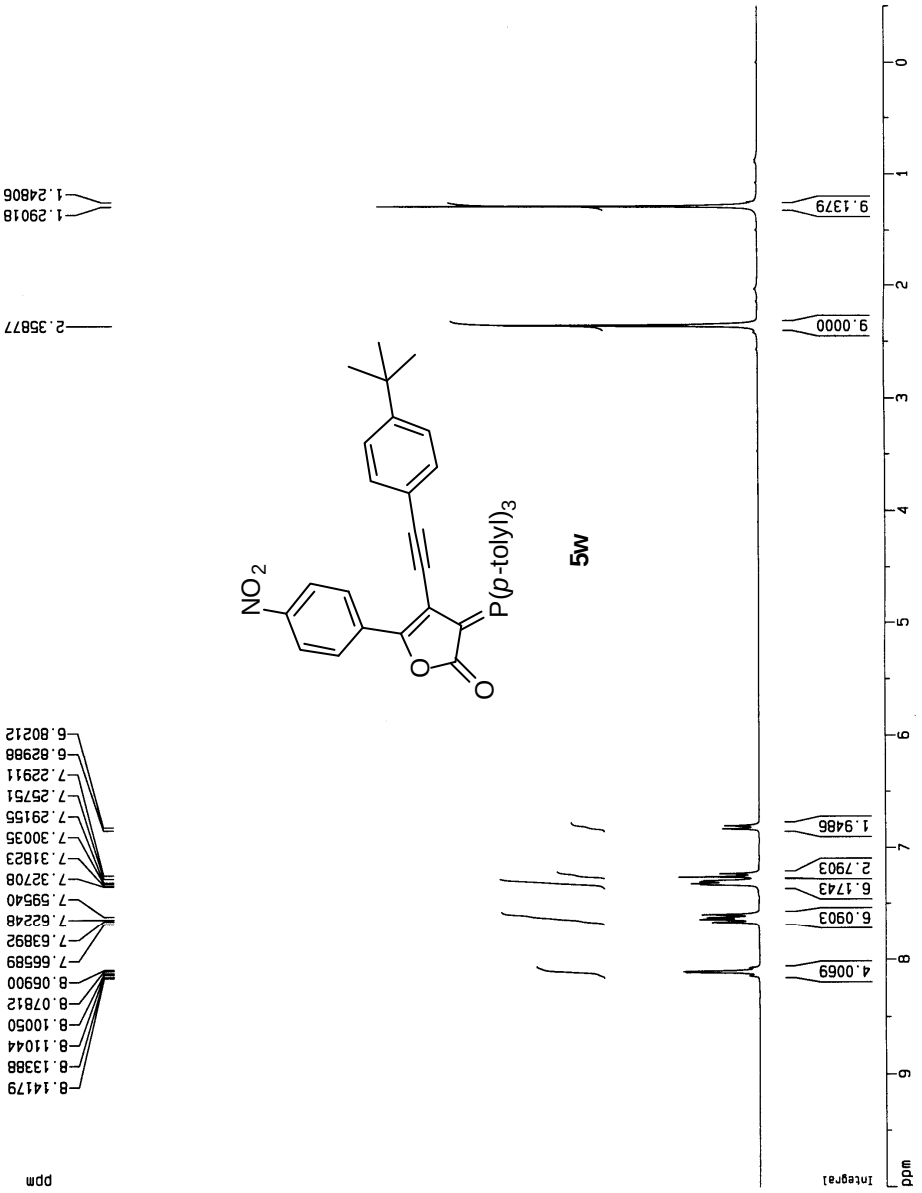


Fig S74. ^{13}C NMR spectra of compound **5w** (75.5 MHz, $CDCl_3$)

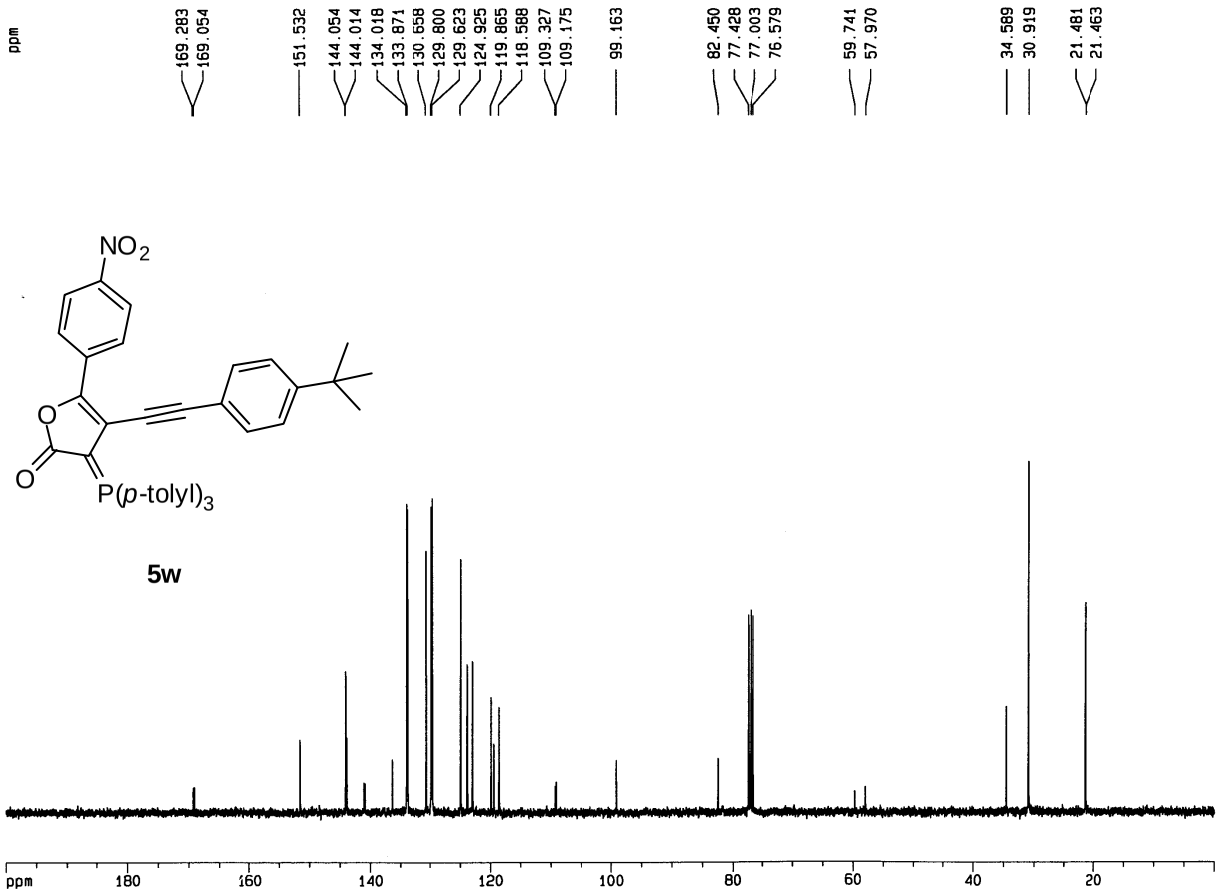


Fig S75. ^{1}H NMR spectra of compound **5x** (300 MHz, $CDCl_3$)

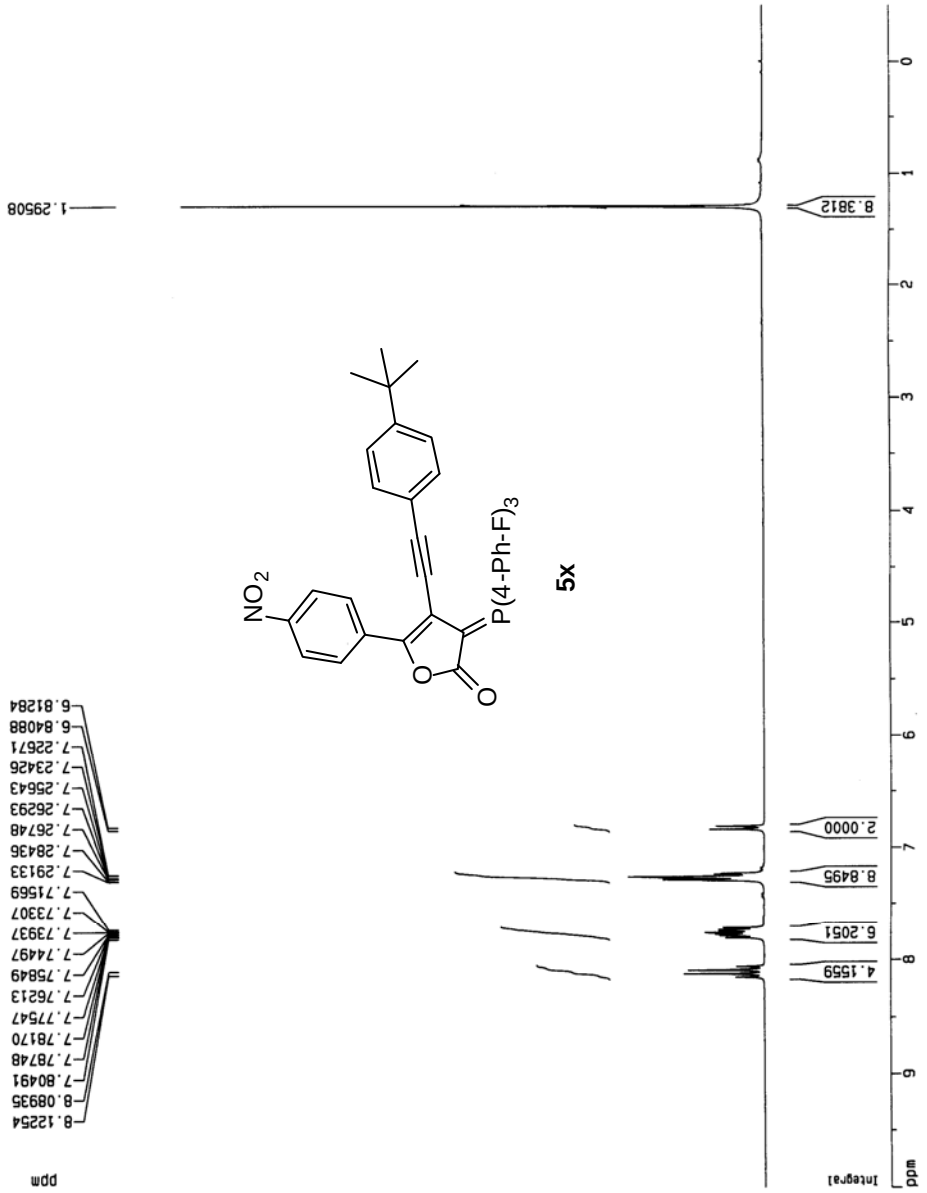


Fig S76. ^{13}C NMR spectra of compound **5x** (75.5 MHz, $CDCl_3$)

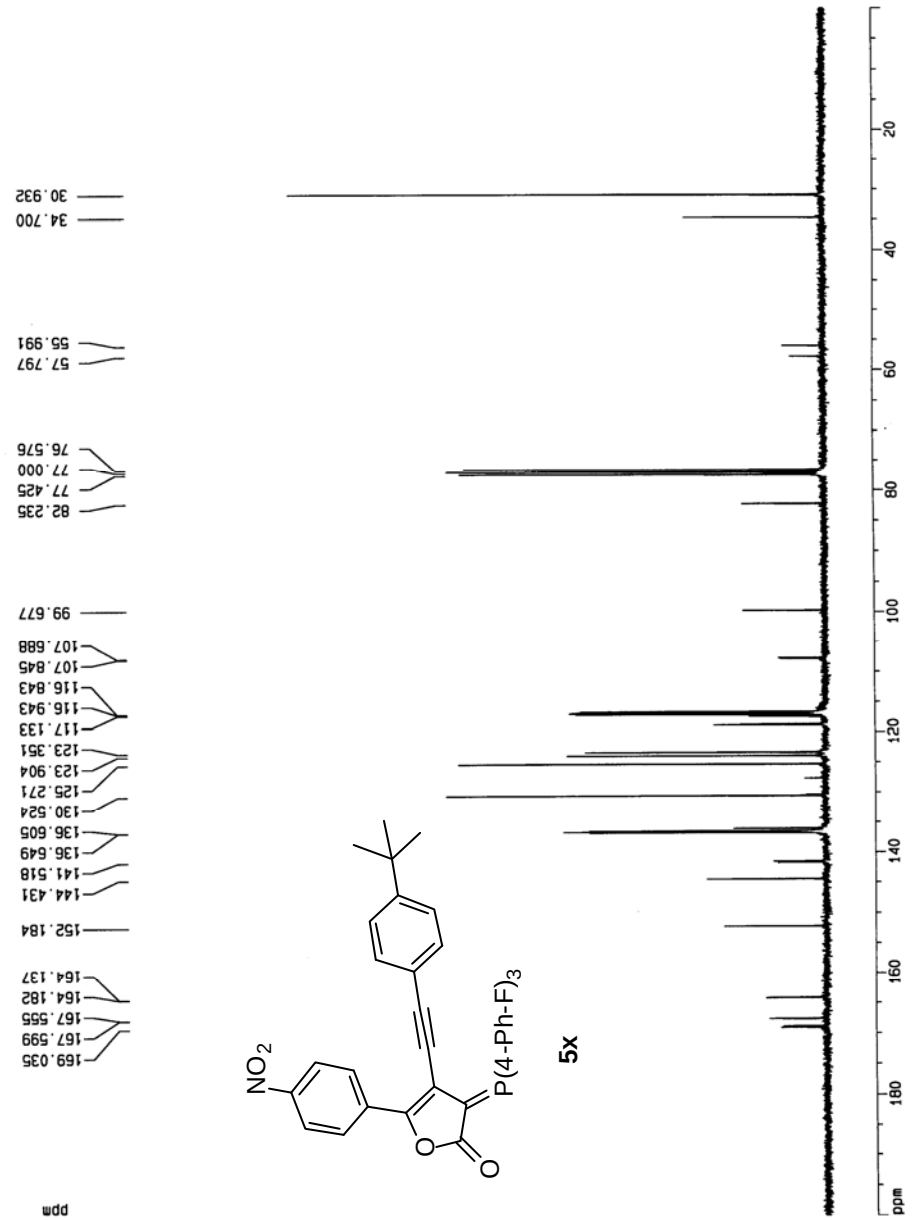


Fig S77. ^{1}H NMR spectra of compound **5y** (300 MHz, $CDCl_3$)

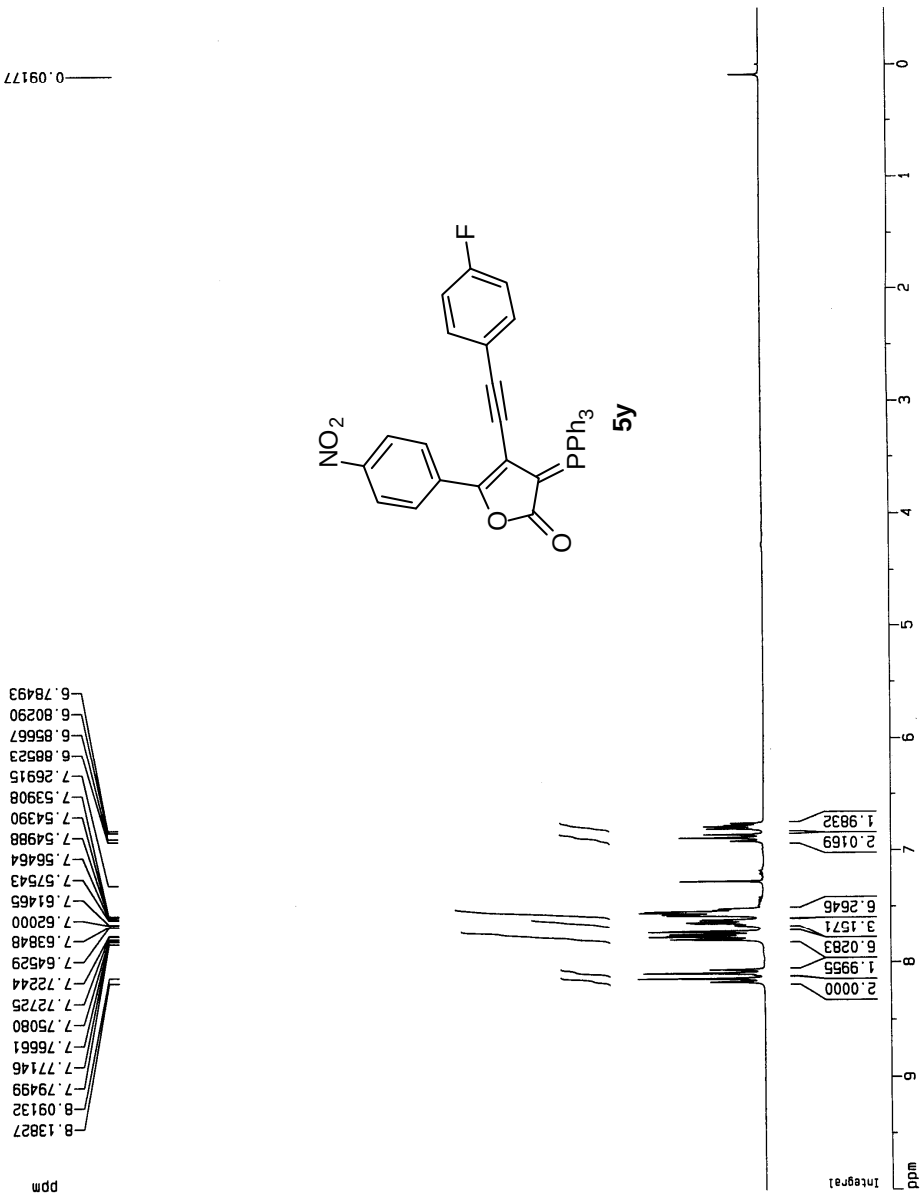


Fig S78. ^{13}C NMR spectra of compound **5y** (75.5 MHz, $CDCl_3$)

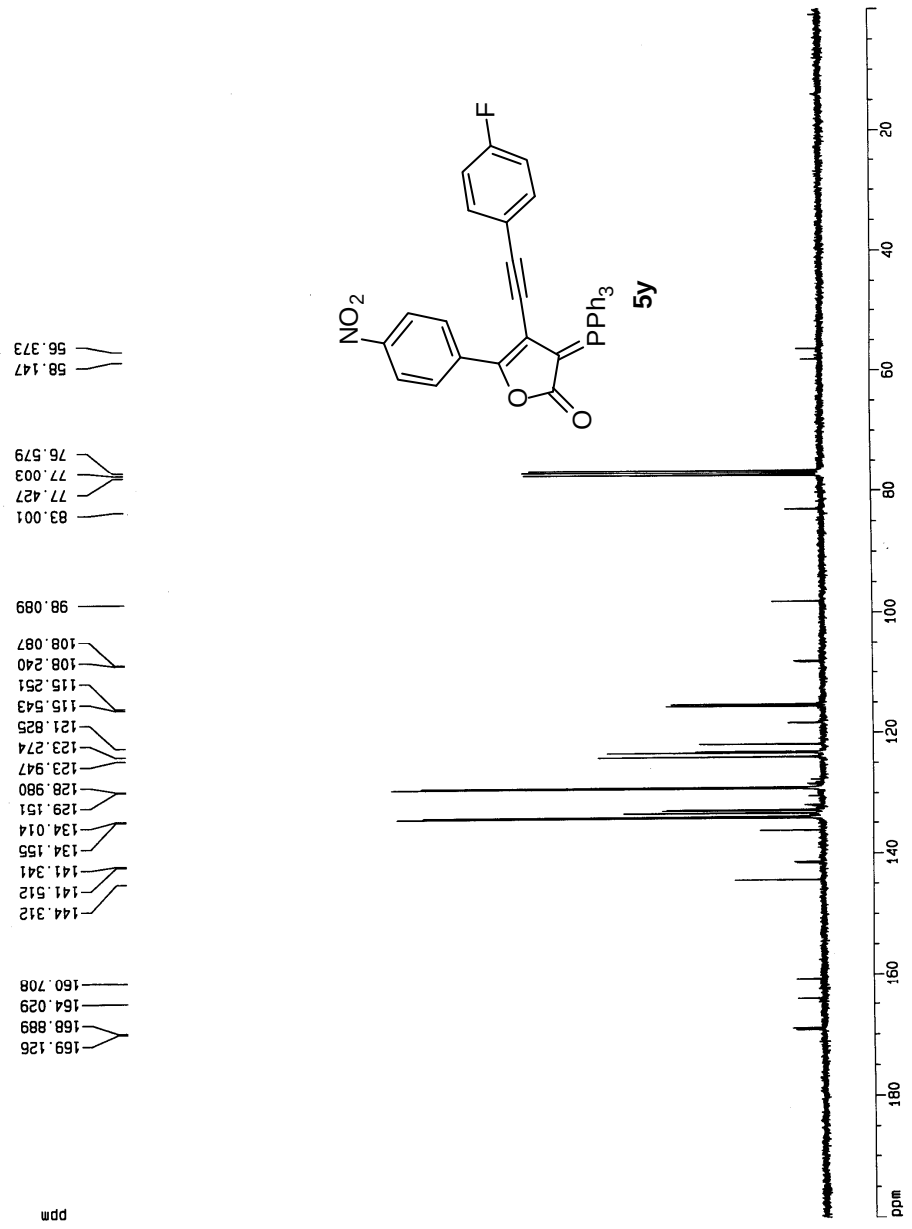


Fig S79. ^{1}H NMR spectra of compound **5z** (300 MHz, $CDCl_3$)

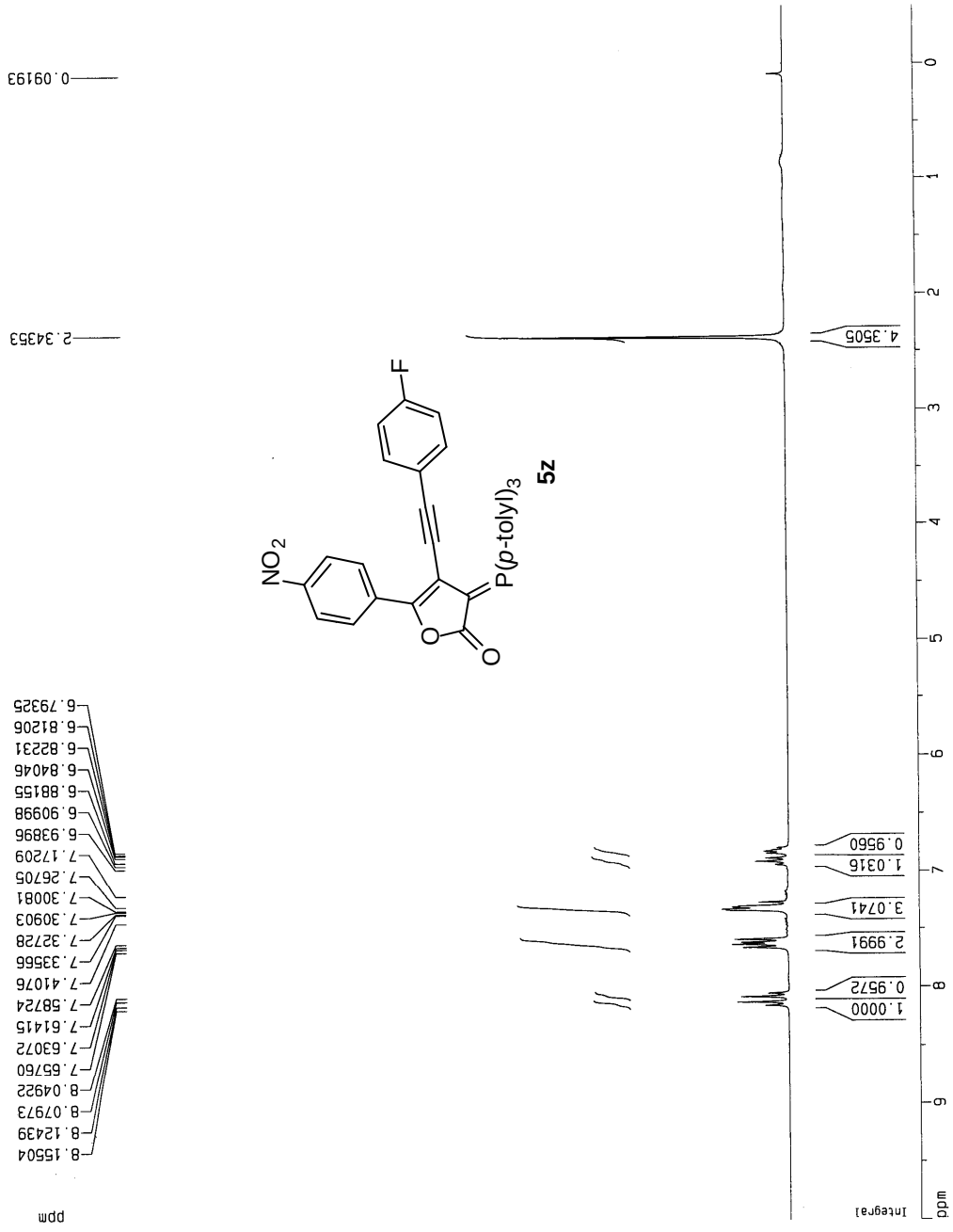


Fig S80. ^{13}C NMR spectra of compound **5z** (75.5 MHz, $CDCl_3$)

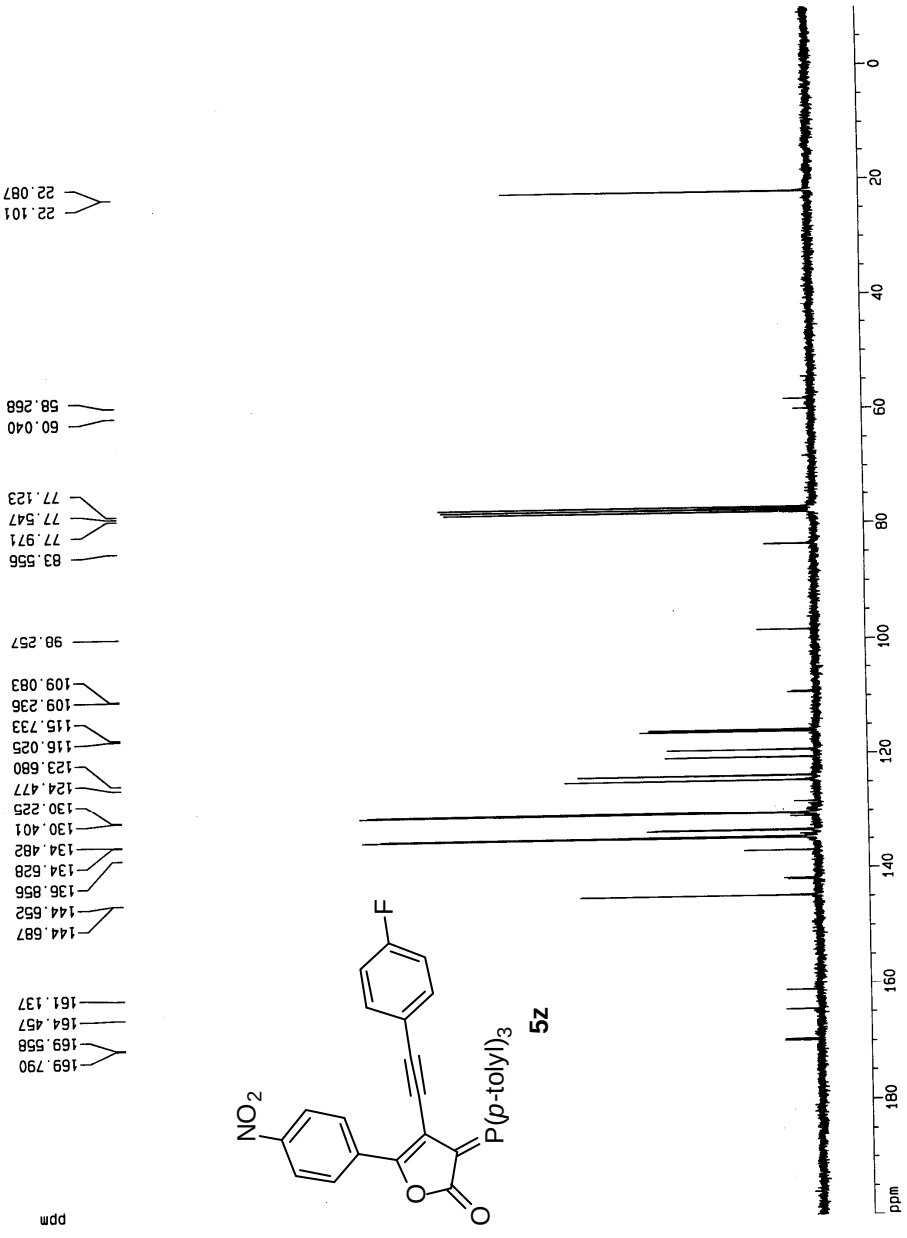


Fig S81. ^{1}H NMR spectra of compound **5aa** (300 MHz, $CDCl_3$)

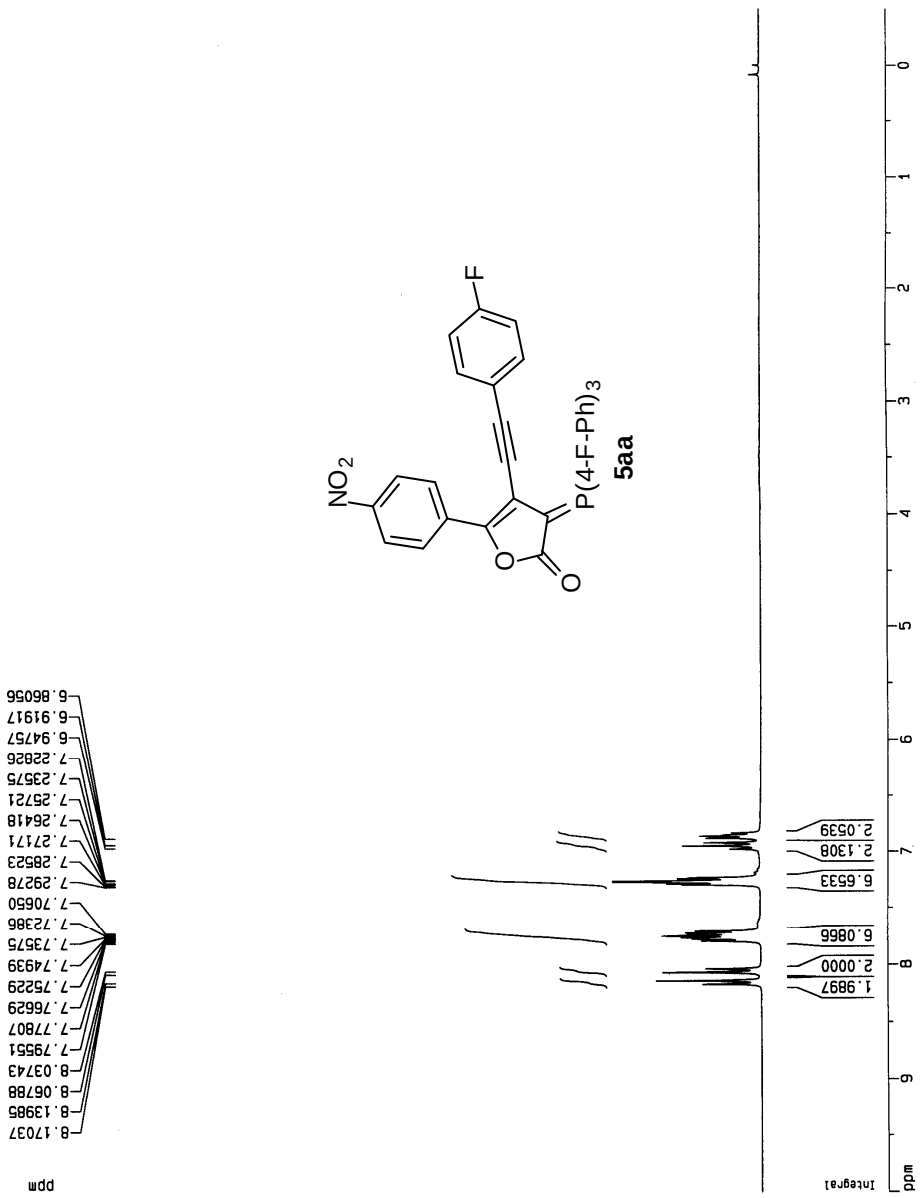


Fig S82. ^{13}C NMR spectra of compound **5aa** (75.5 MHz, $CDCl_3$)

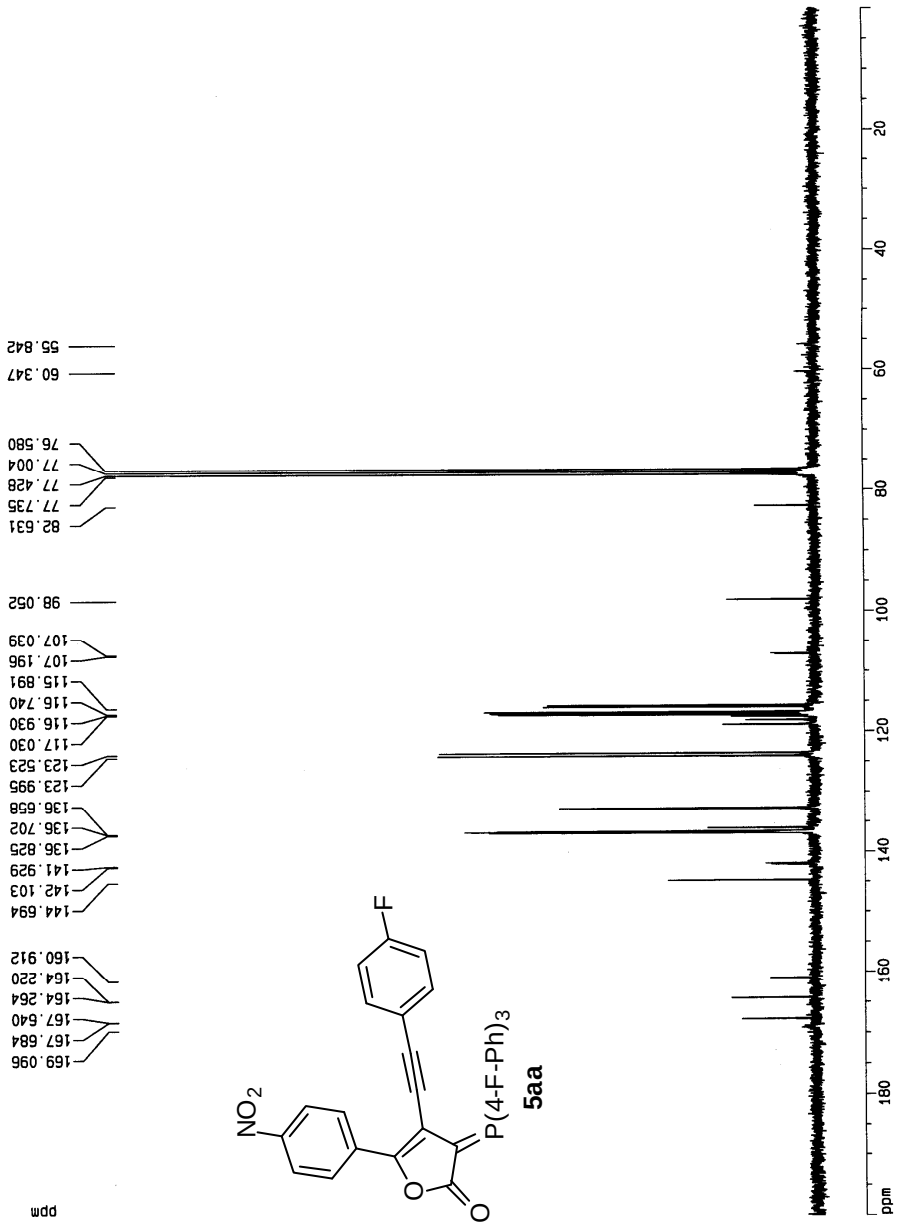


Fig S83. ^{1}H NMR spectra of compound **5ab** (300 MHz, $CDCl_3$)

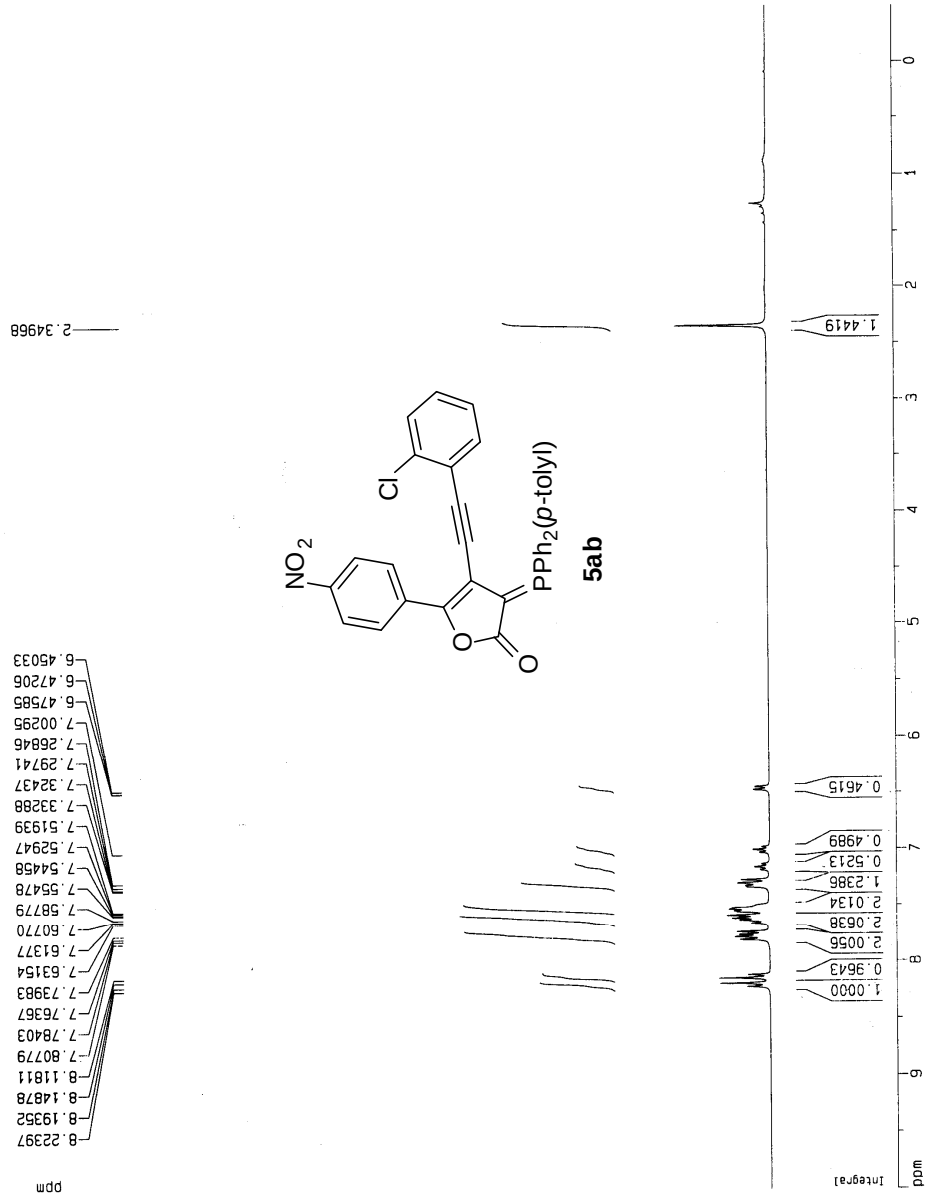


Fig S84. ^{13}C NMR spectra of compound **5ab** (75.5 MHz, $CDCl_3$)

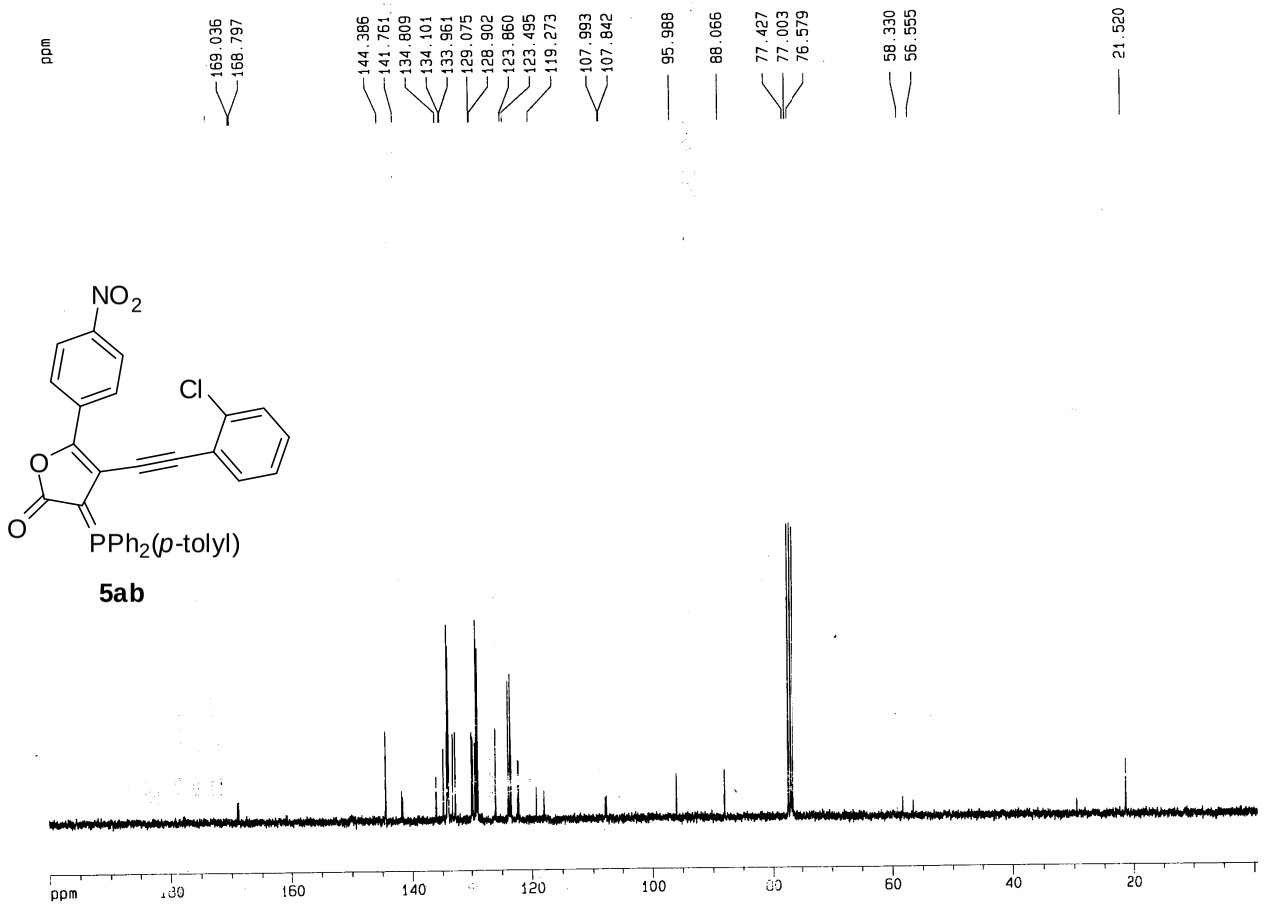


Fig S85. ^{1}H NMR spectra of compound **5ac** (300 MHz, $CDCl_3$)

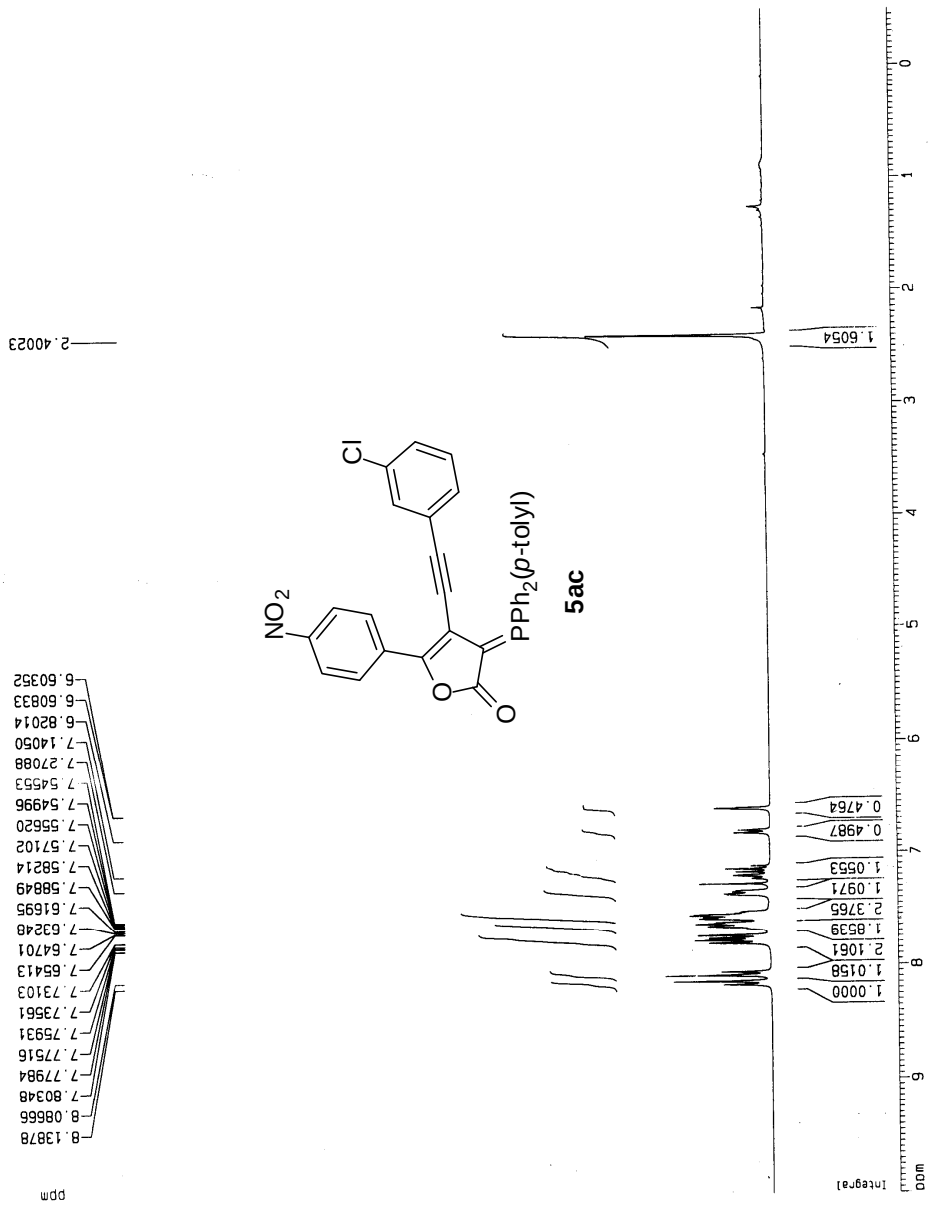


Fig S86. ^{13}C NMR spectra of compound **5ac** (75.5 MHz, $CDCl_3$)

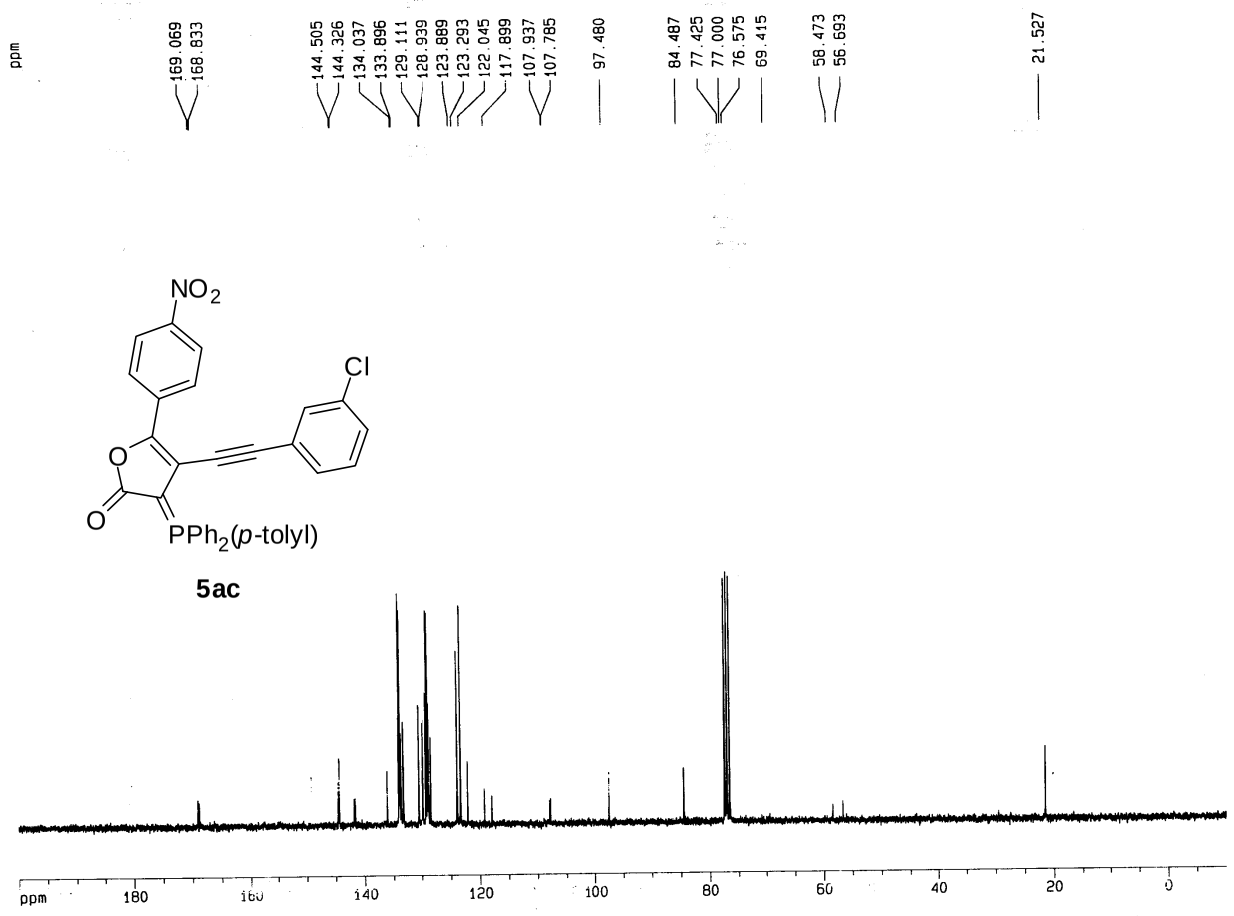


Fig S87. ^{1}H NMR spectra of compound **5ad** (300 MHz, $CDCl_3$)

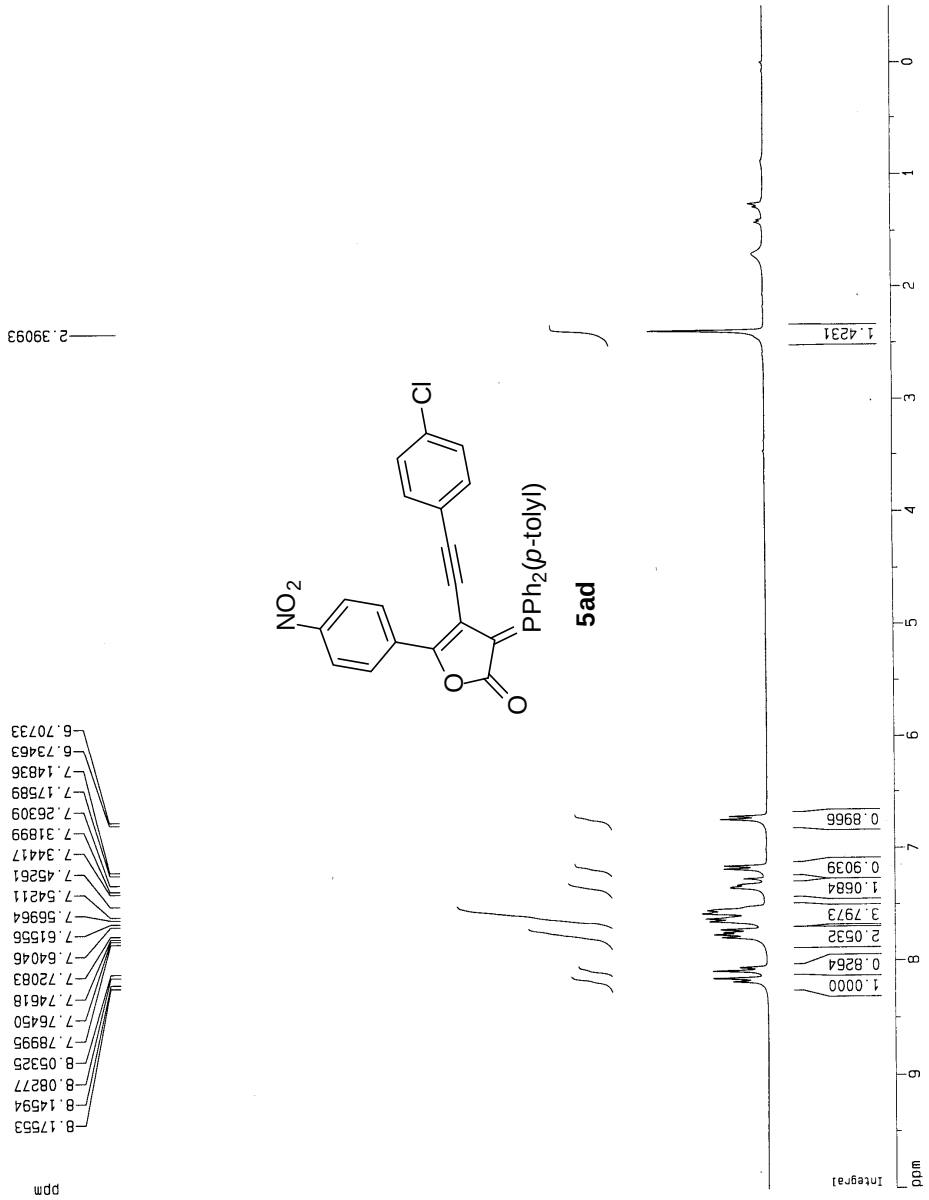


Fig S88. ^{13}C NMR spectra of compound **5ad** (150.7 MHz, $CDCl_3$)

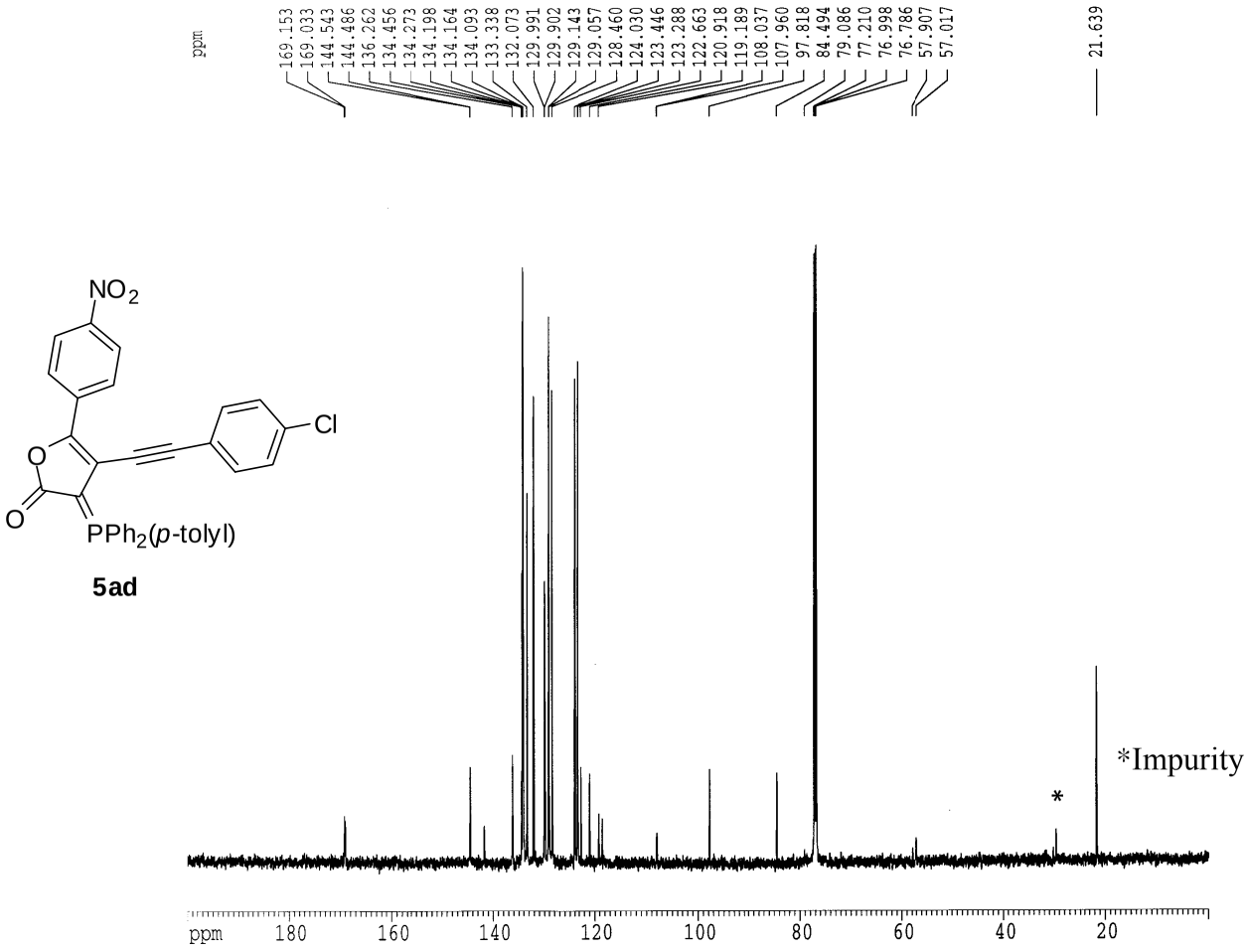


Fig S89. ^{1}H NMR spectra of compound **5ae** (300 MHz, $CDCl_3$)

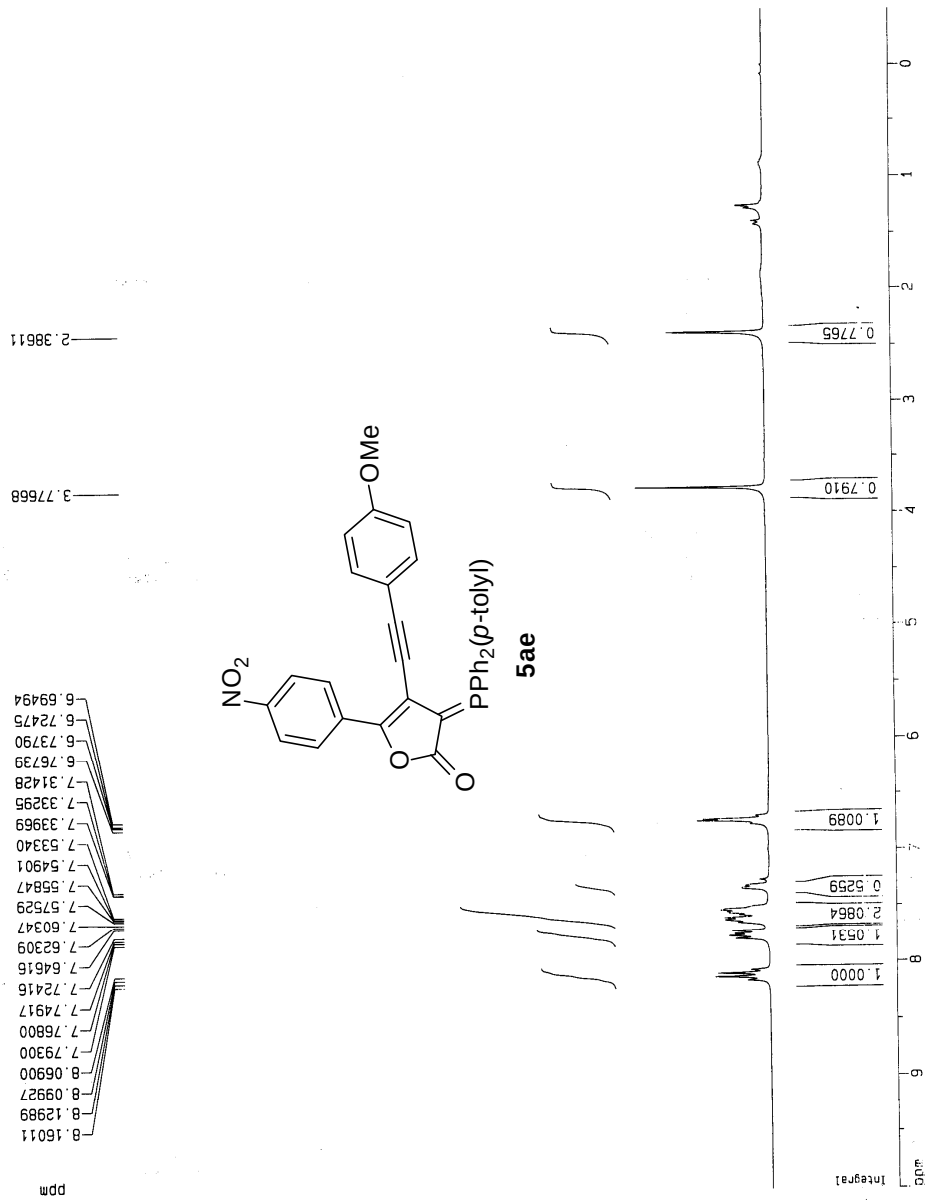


Fig S90. ^{13}C NMR spectra of compound **5ae** (75.5 MHz, $CDCl_3$)

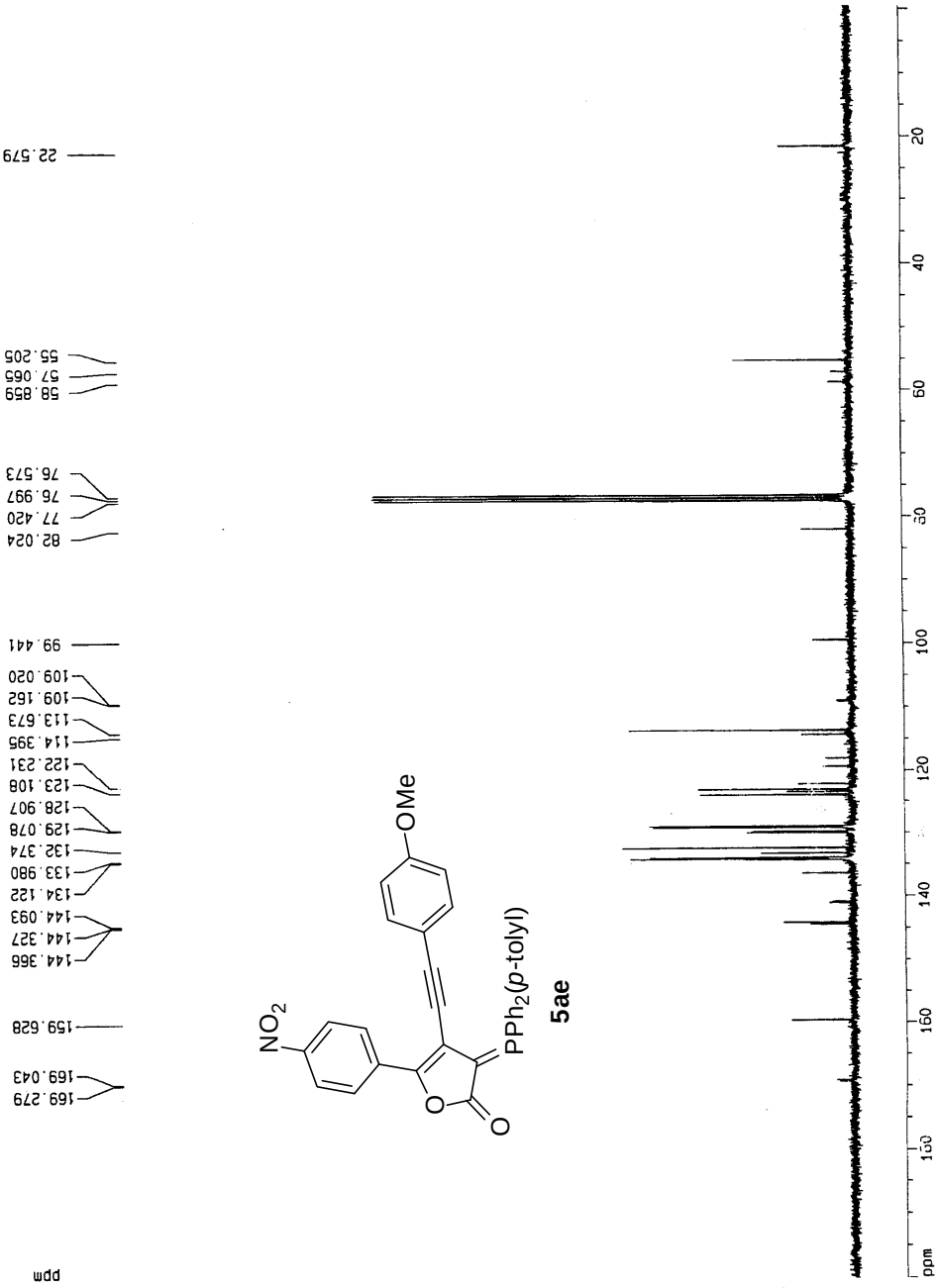


Fig S91. ^{1}H NMR spectra of compound **5af** (300 MHz, $CDCl_3$)

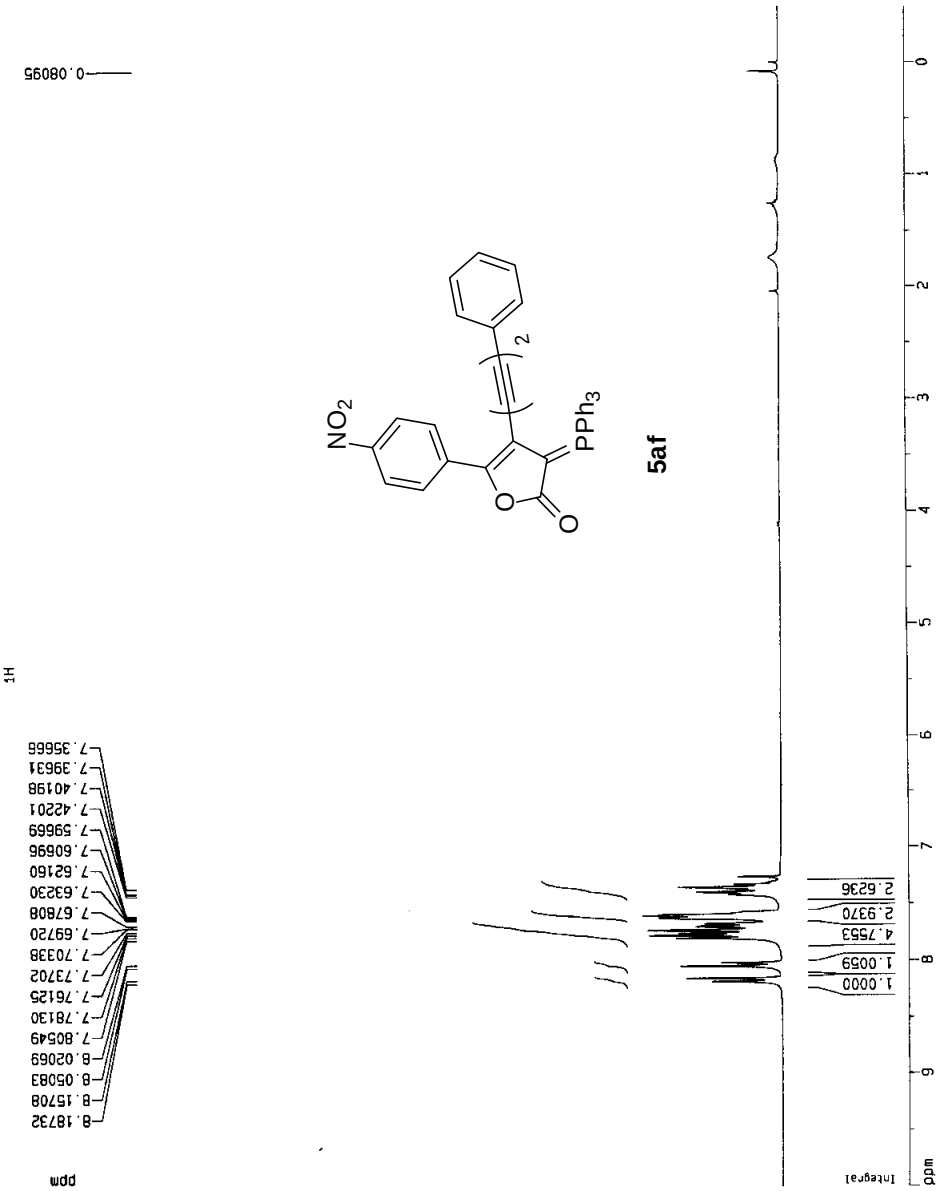


Fig S92. ^{13}C NMR spectra of compound **5af** (75.5 MHz, $CDCl_3$)

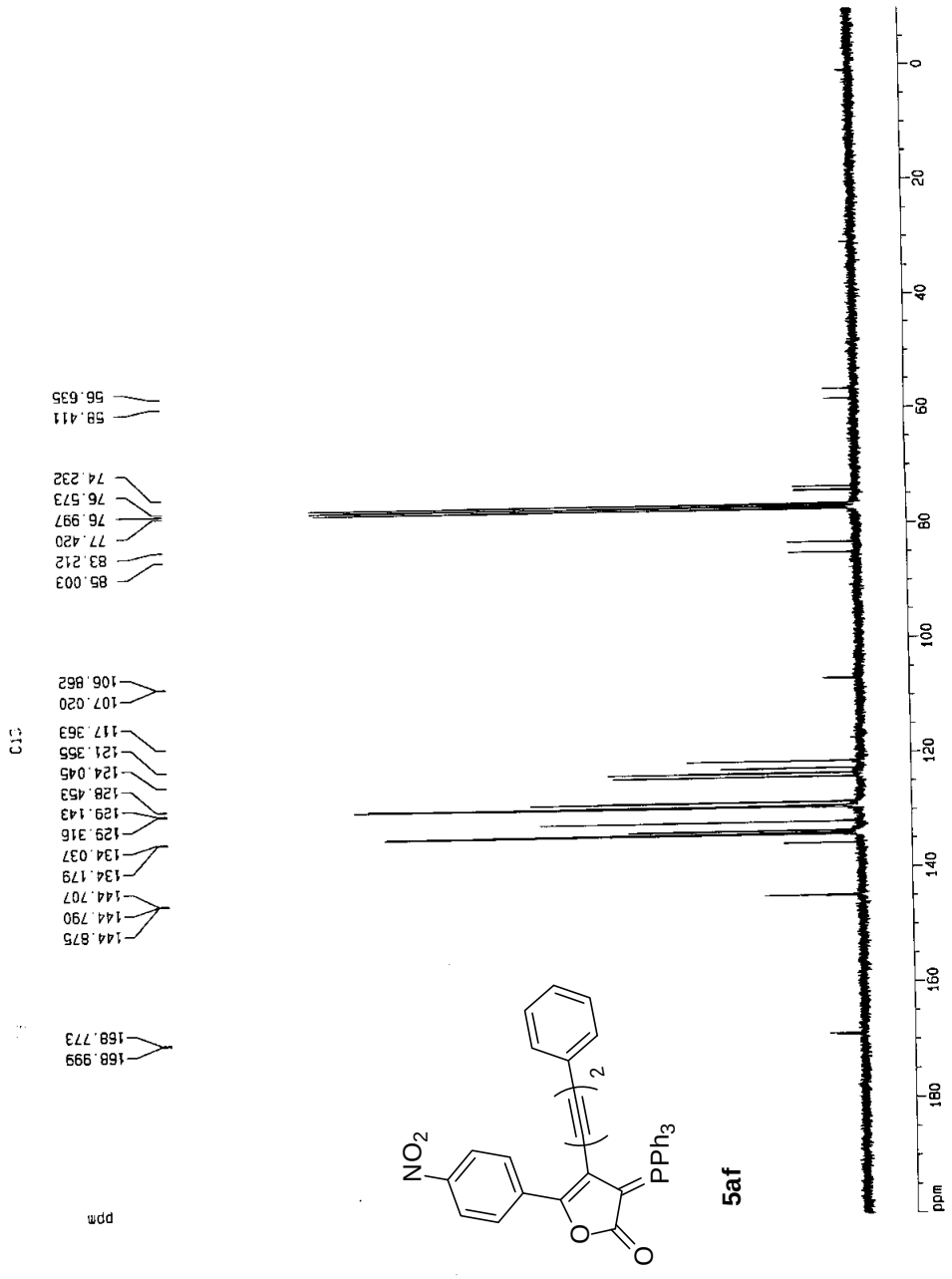


Fig S93. ^{1}H NMR spectra of compound **5ag** (300 MHz, $CDCl_3$)

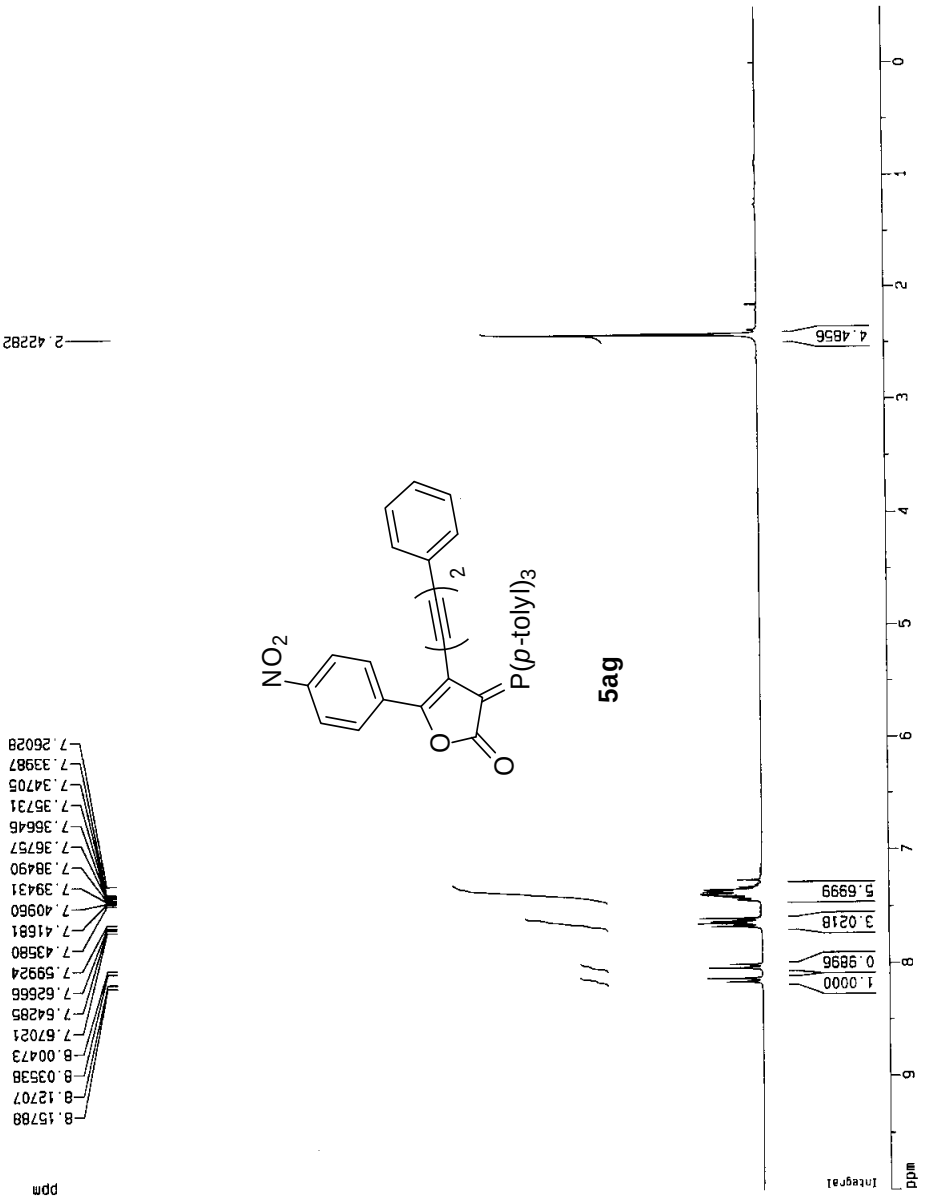


Fig S94. ^{13}C NMR spectra of compound **5ag** (75.5 MHz, $CDCl_3$)

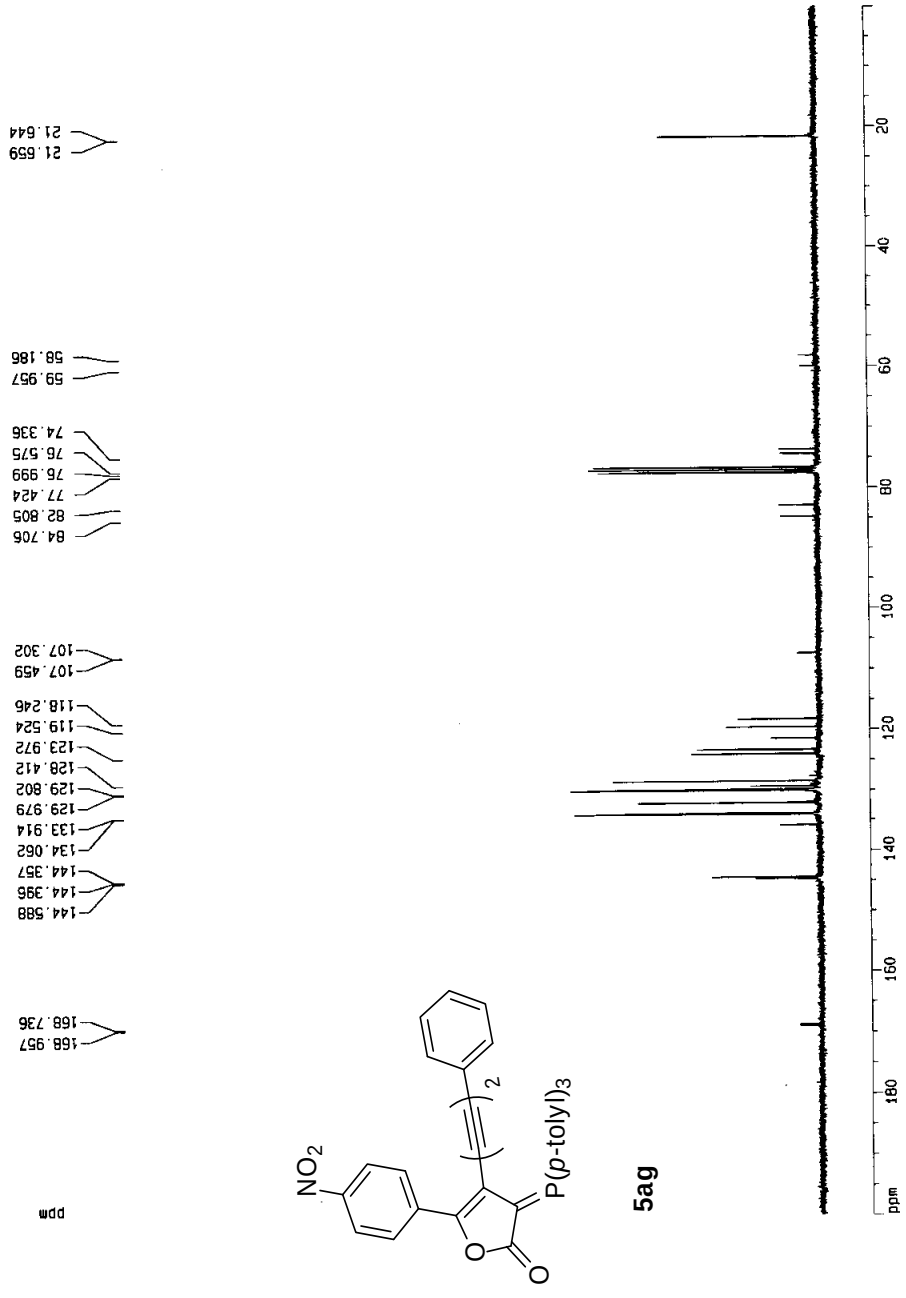


Fig S95. ^{1}H NMR spectra of compound **5ah** (300 MHz, $CDCl_3$)

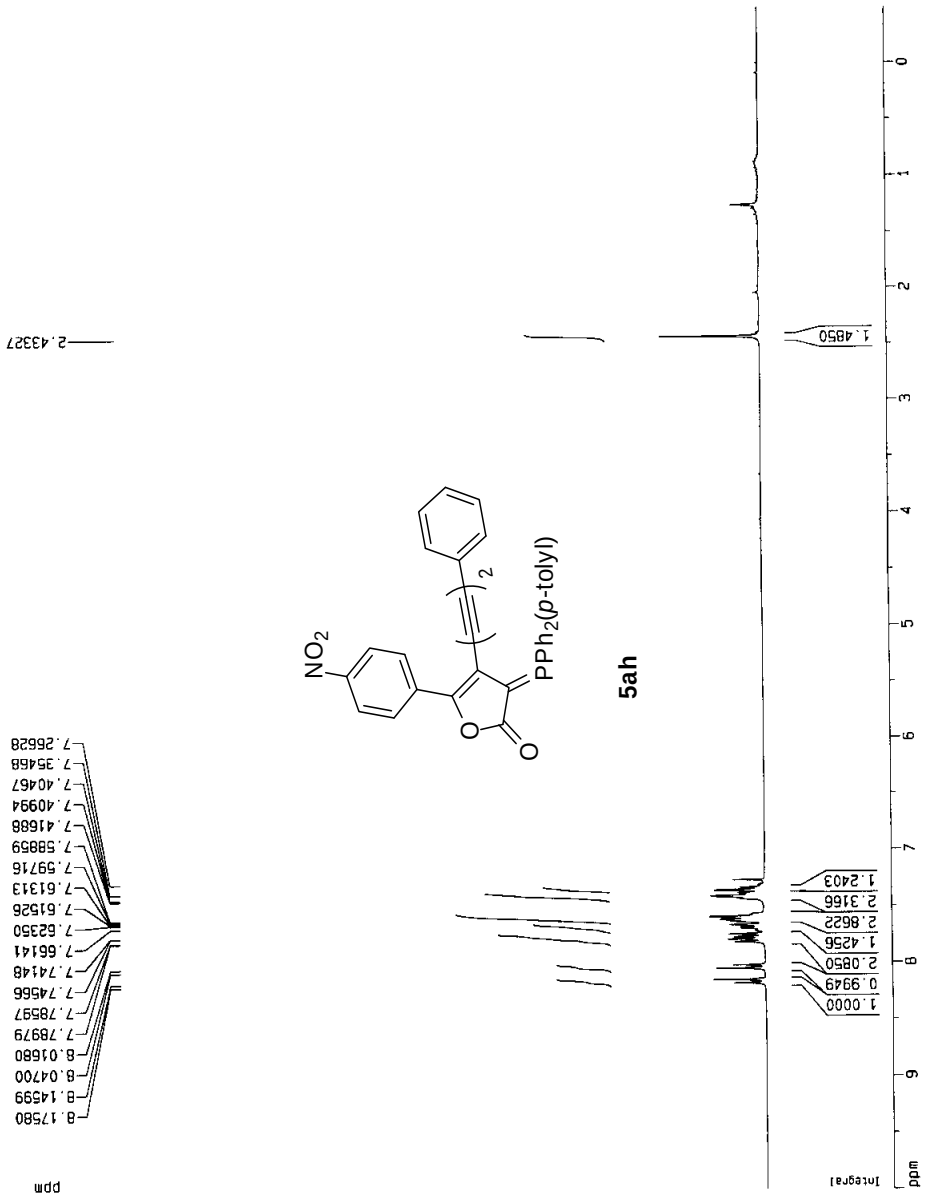
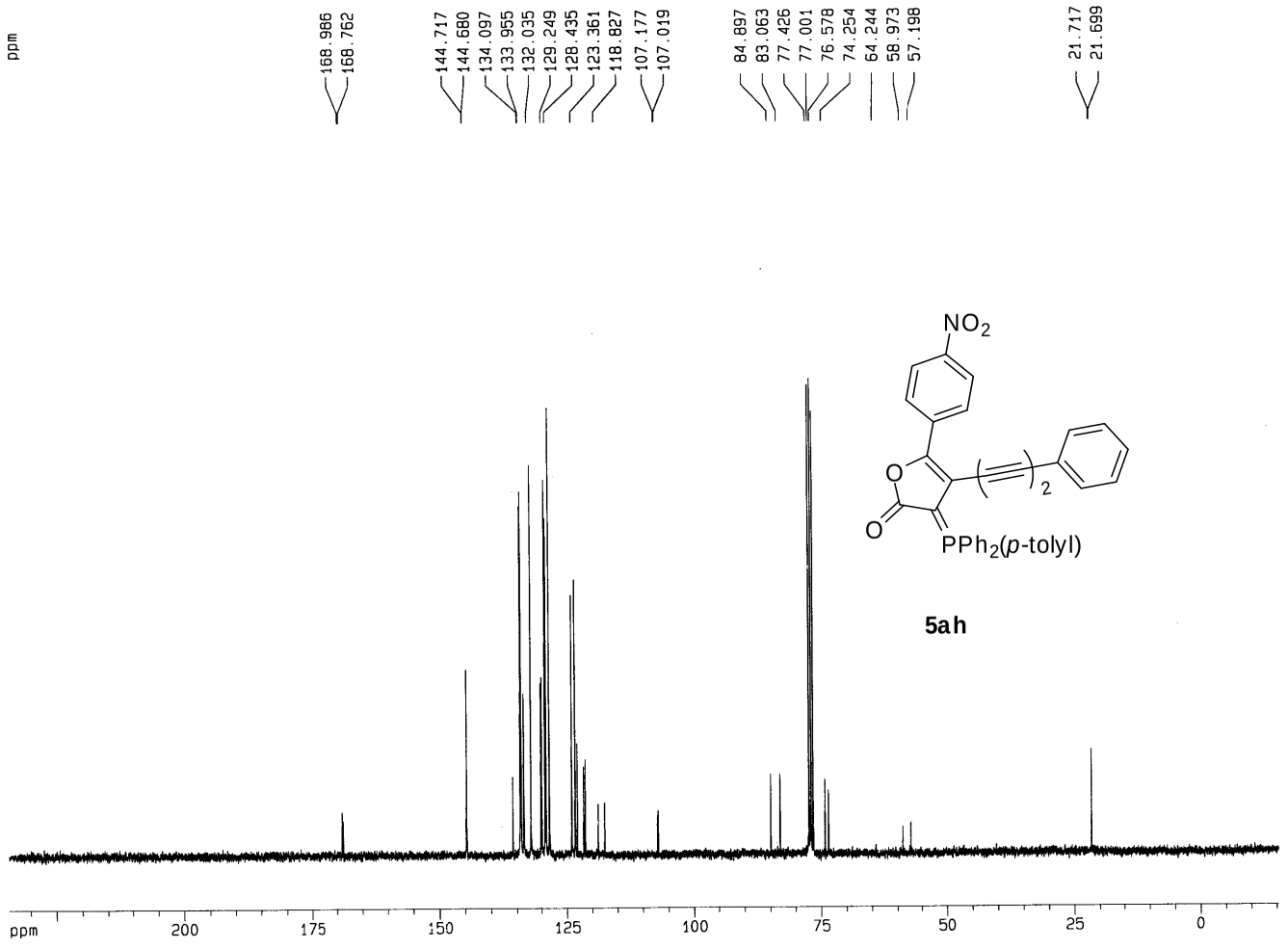


Fig S96. ^{13}C NMR spectra of compound **5ah** (75.5 MHz, $CDCl_3$)



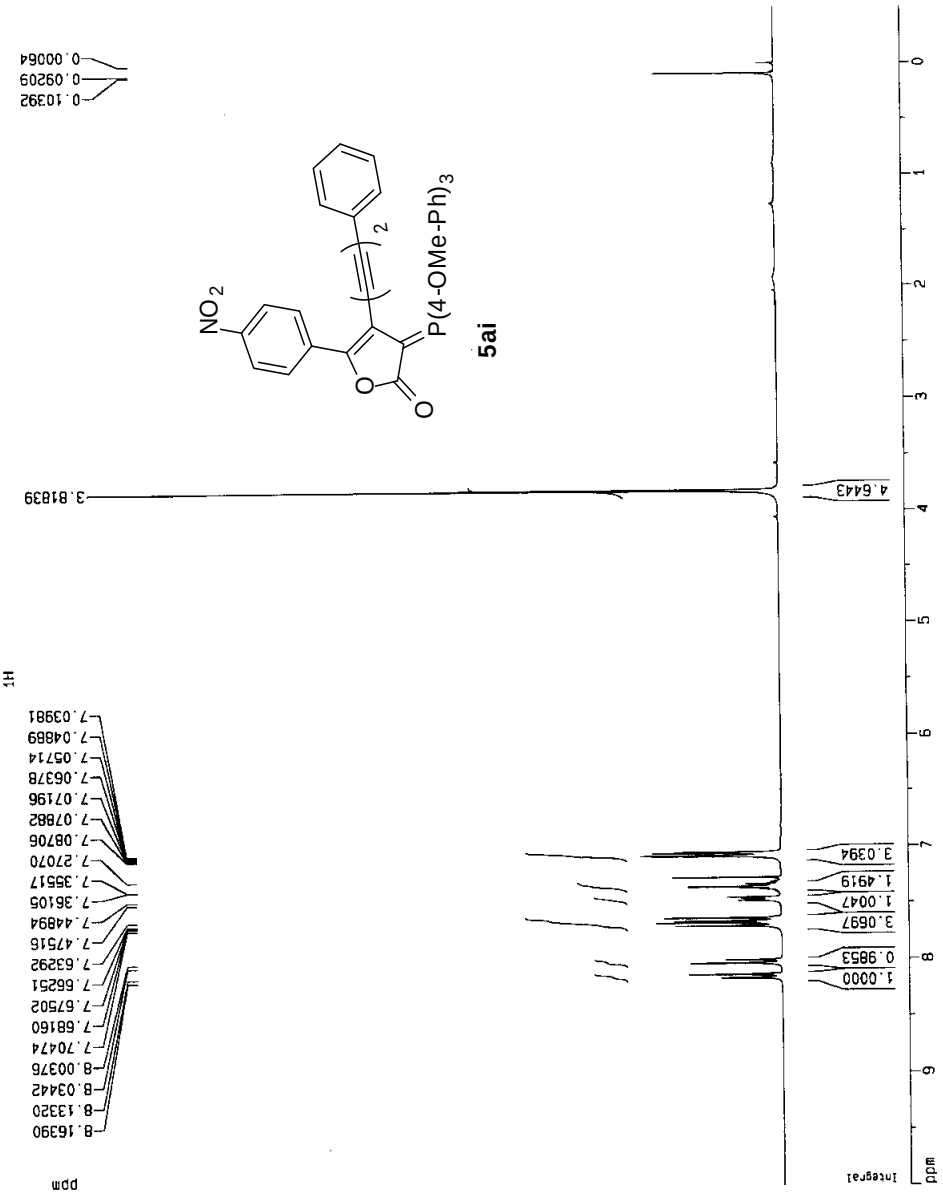


Fig S97. ^{1}H NMR spectra of compound **5ai** (300 MHz, $CDCl_3$)

Fig S98. ^{13}C NMR spectra of compound **5ai** (75.5 MHz, $CDCl_3$)

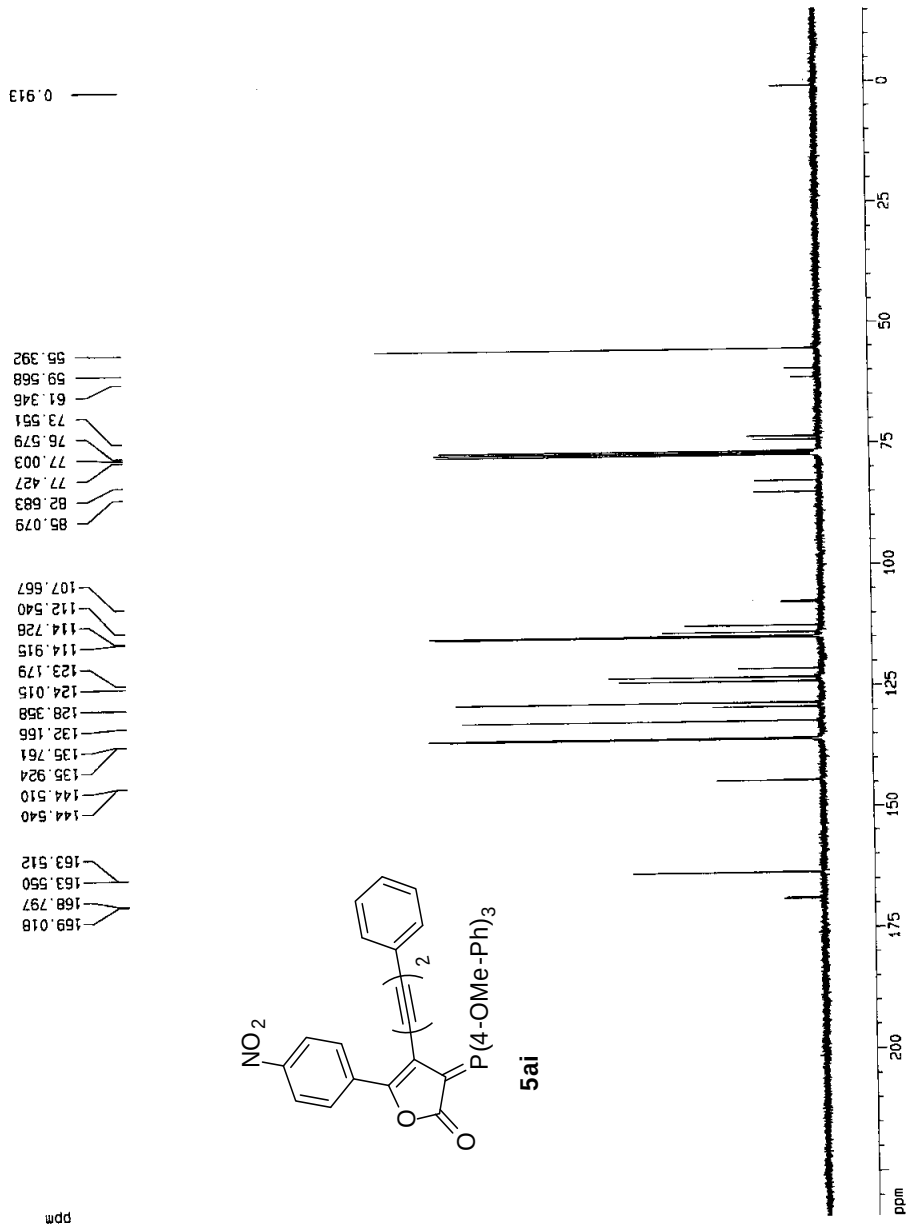


Fig S99. ^{1}H NMR spectra of compound **5aj** (300 MHz, $CDCl_3$)

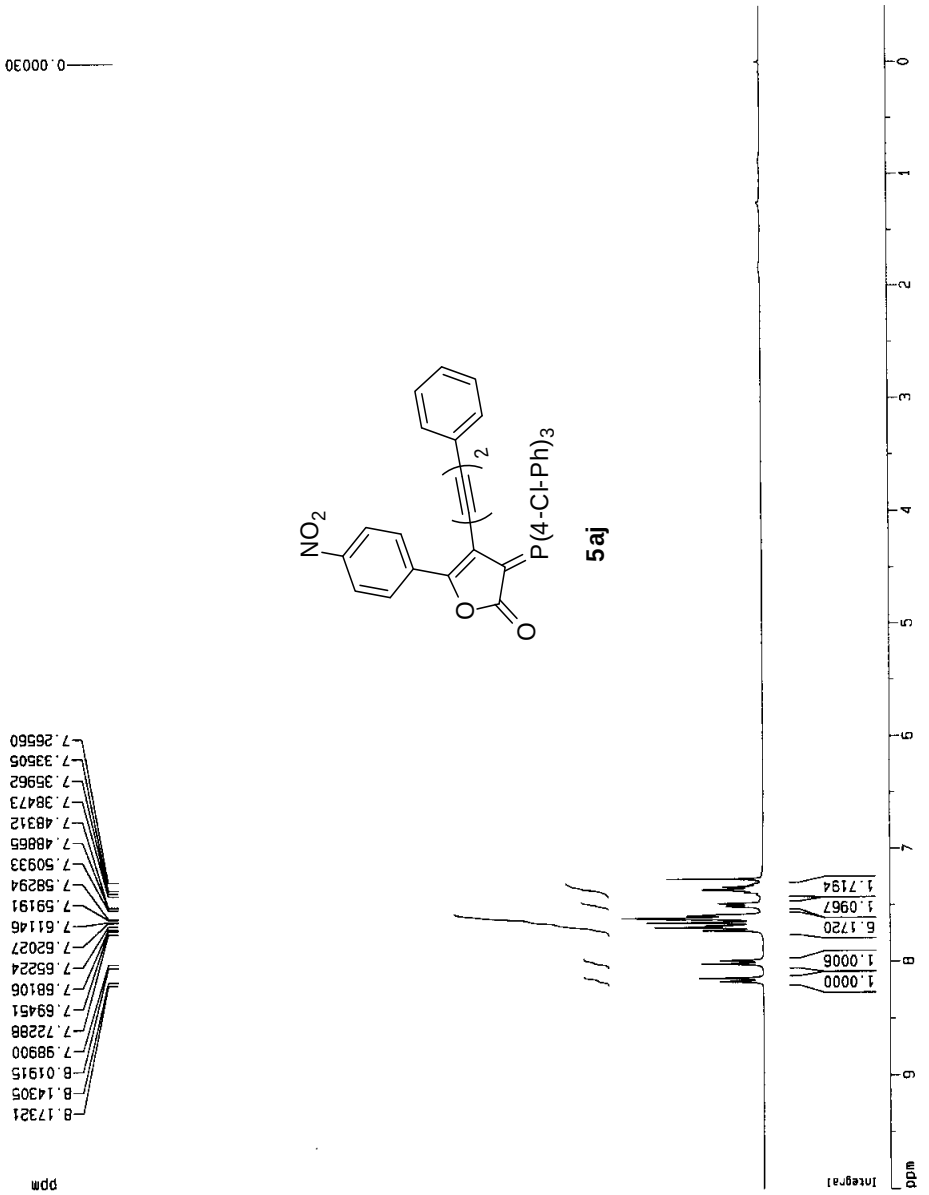


Fig S100. ^{13}C NMR spectra of compound **5aj** (75.5 MHz, $CDCl_3$)

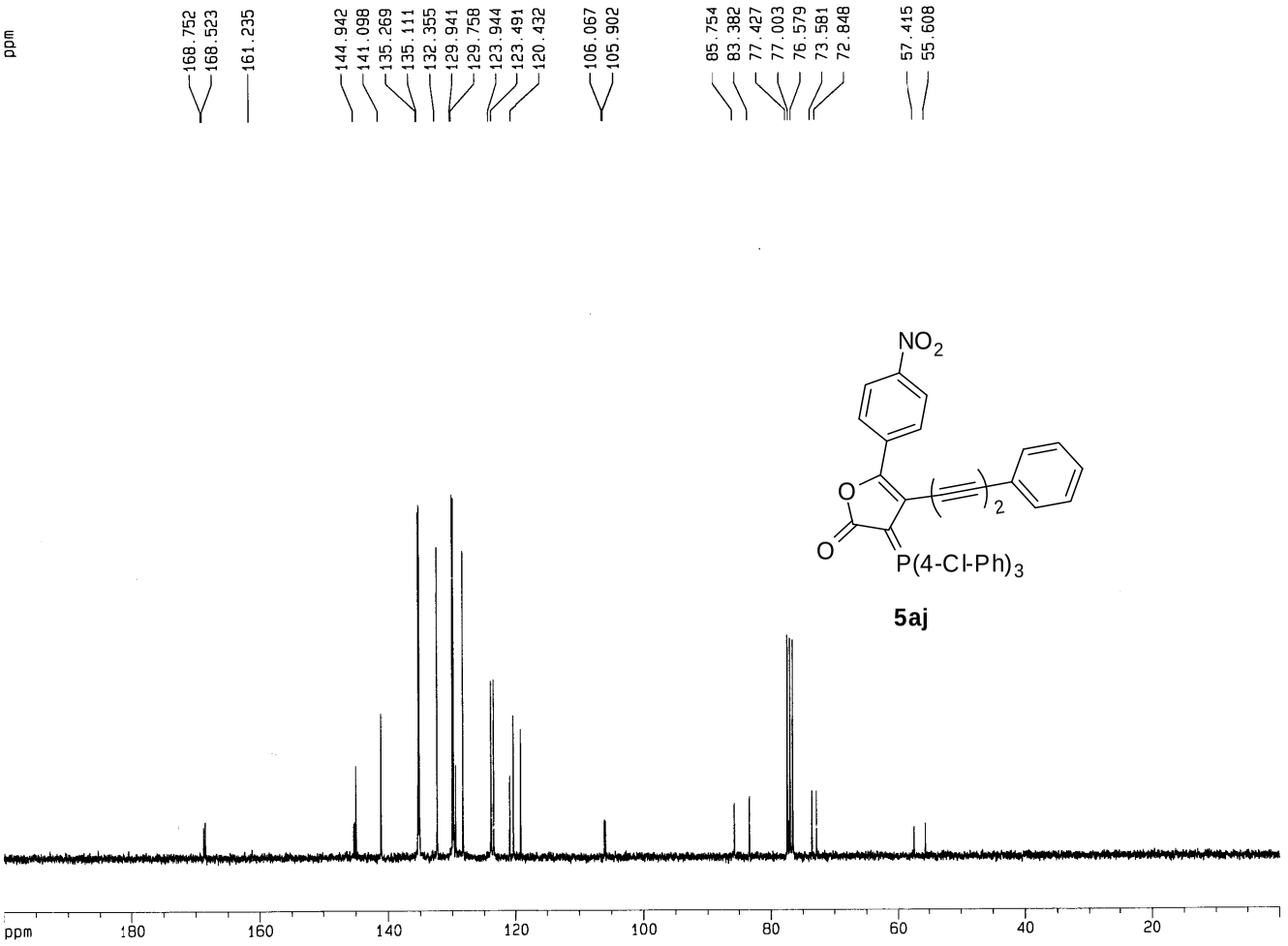


Fig S101. ^{1}H NMR spectra of compound **5ak** (300 MHz, $CDCl_3$)

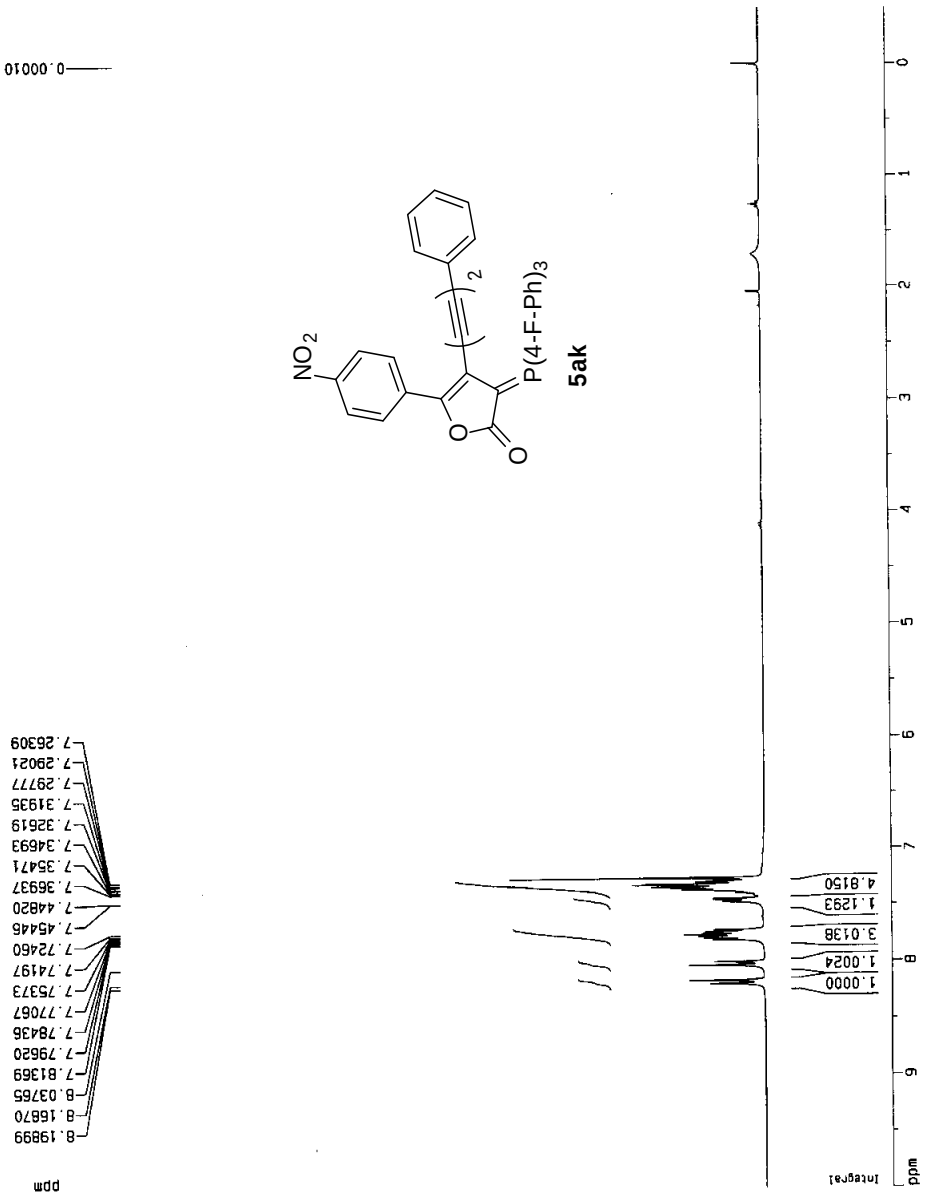


Fig S102. ^{13}C NMR spectra of compound **5ak** (150.7 MHz, $CDCl_3$)

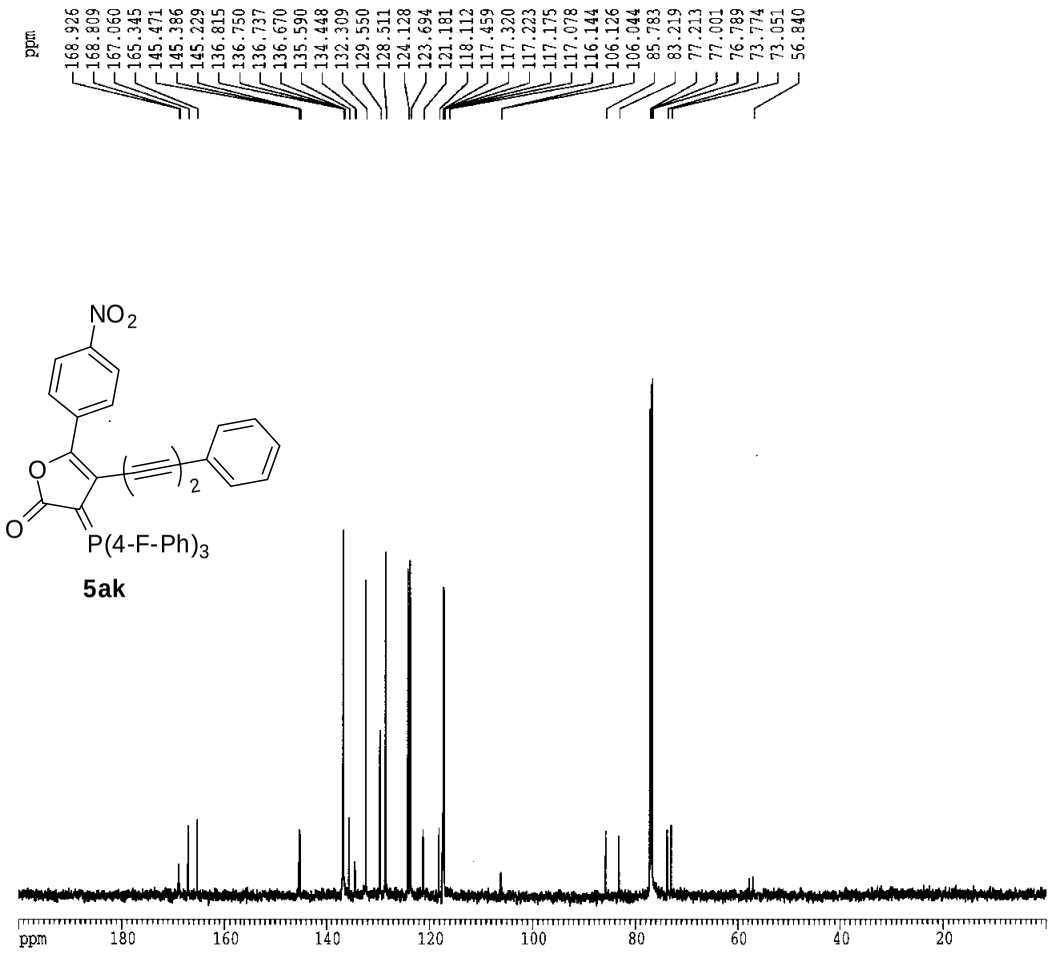


Fig S103. ^{1}H NMR spectra of compound **5al** (300 MHz, $CDCl_3$)

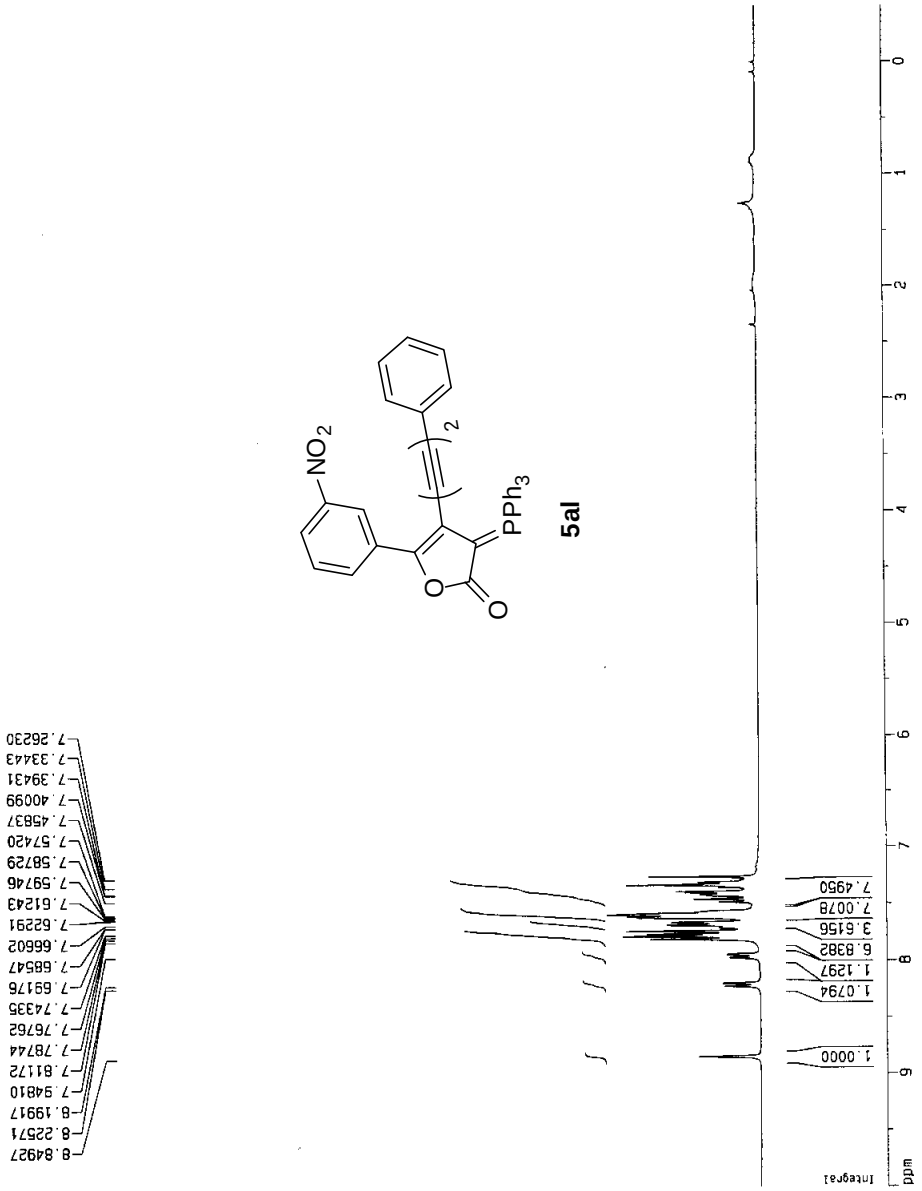


Fig S104. ^{13}C NMR spectra of compound **5al** (75.5 MHz, $CDCl_3$)

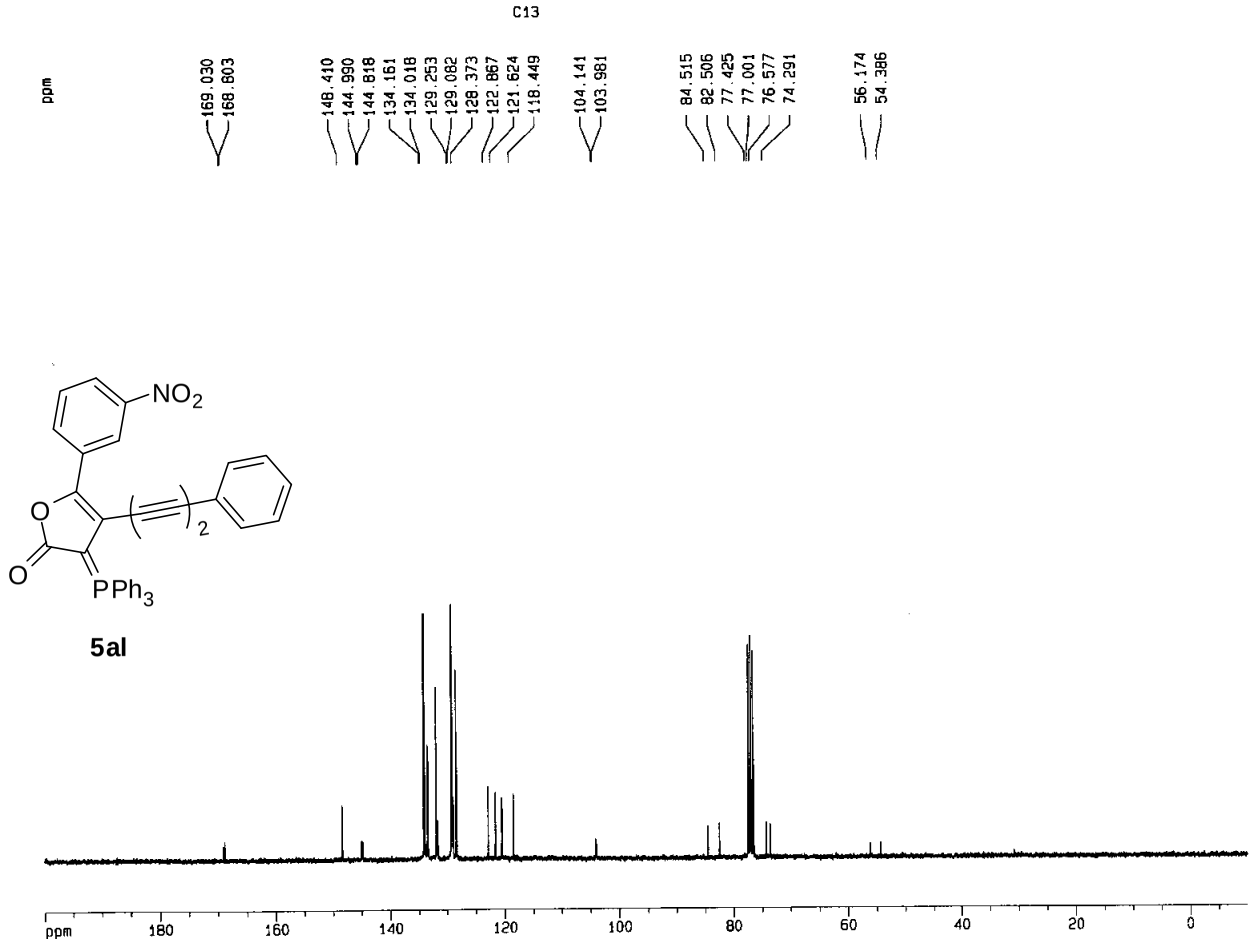


Fig S105. ^{1}H NMR spectra of compound **5am** (300 MHz, $CDCl_3$)

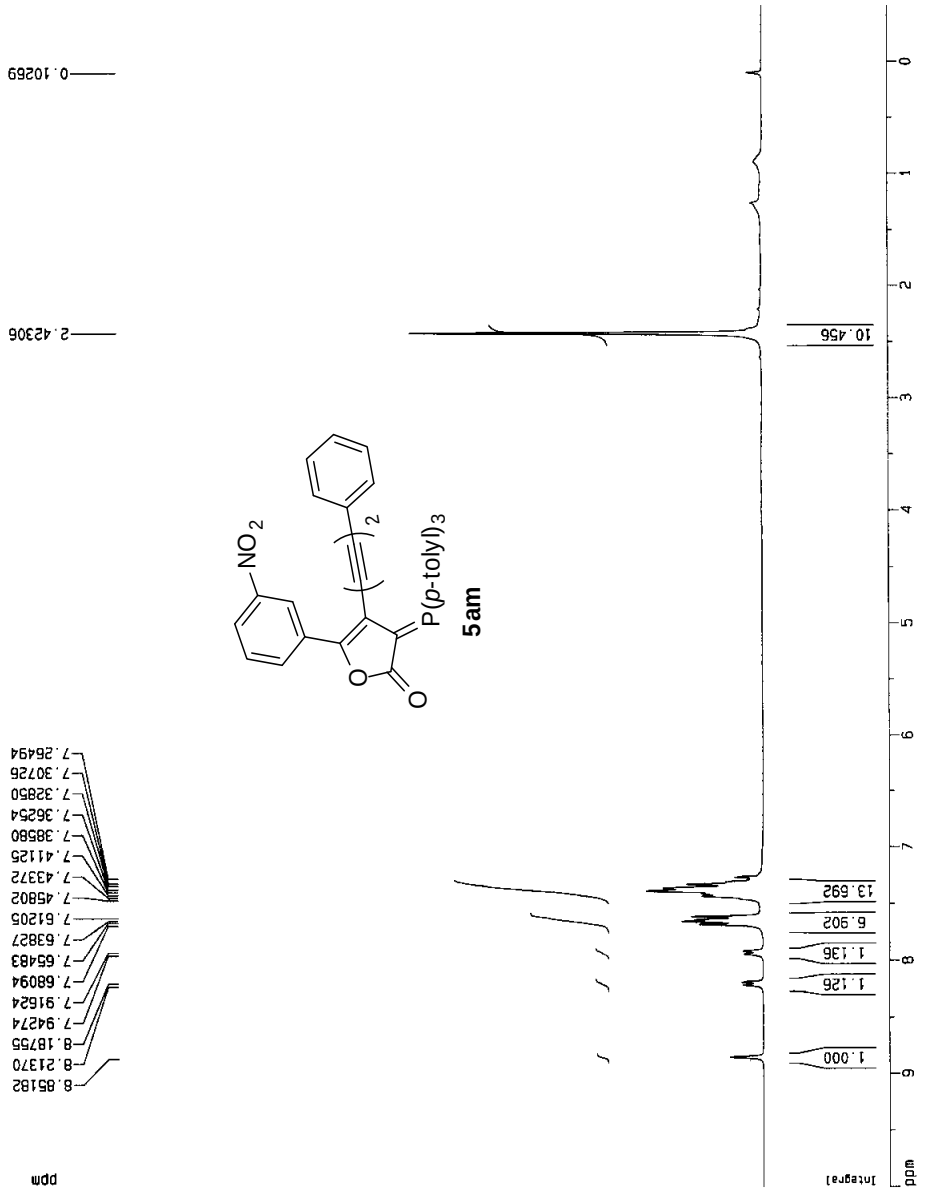


Fig S106. ^{13}C NMR spectra of compound **5am** (75.5 MHz, $CDCl_3$)

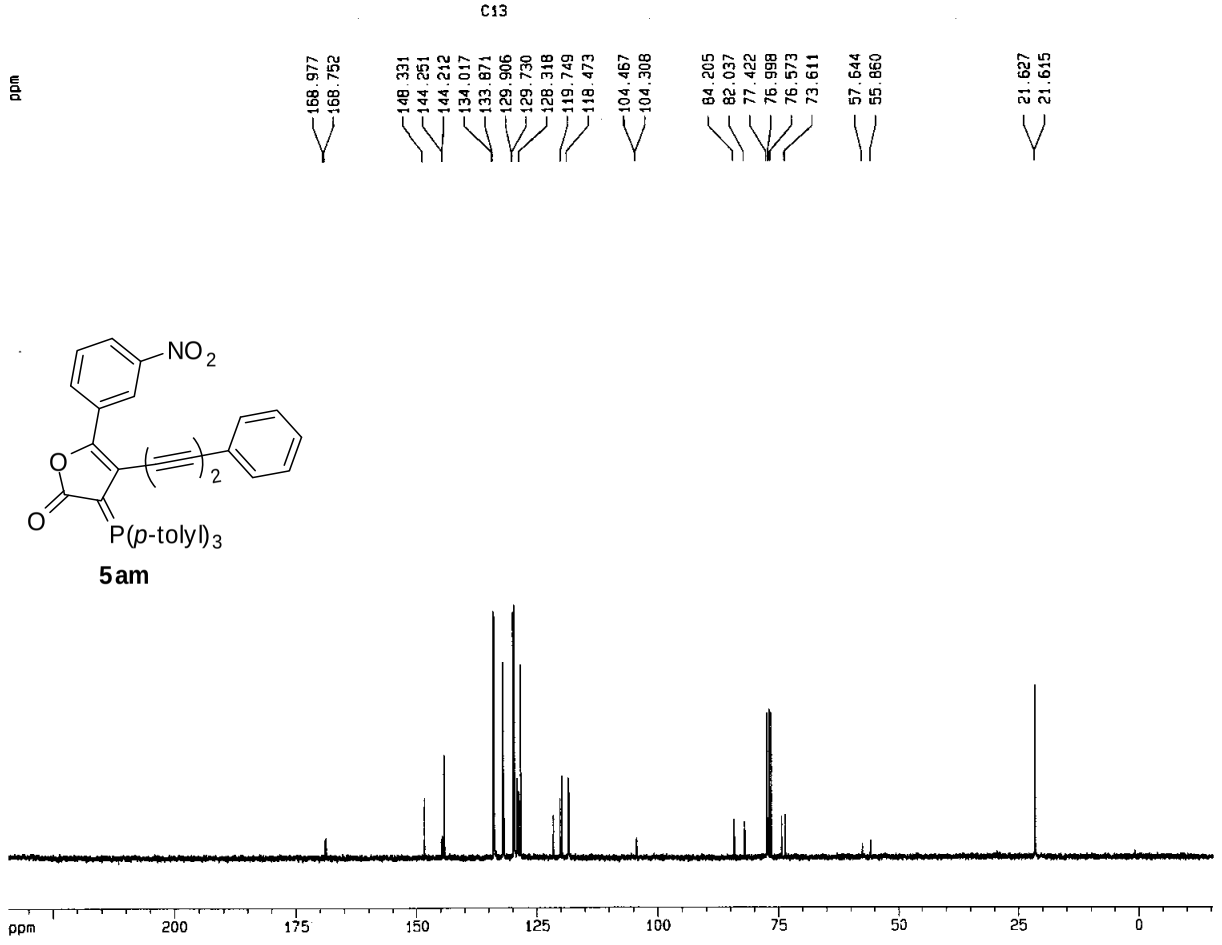


Fig S107. ^{1}H NMR spectra of compound **5an** (300 MHz, $CDCl_3$)

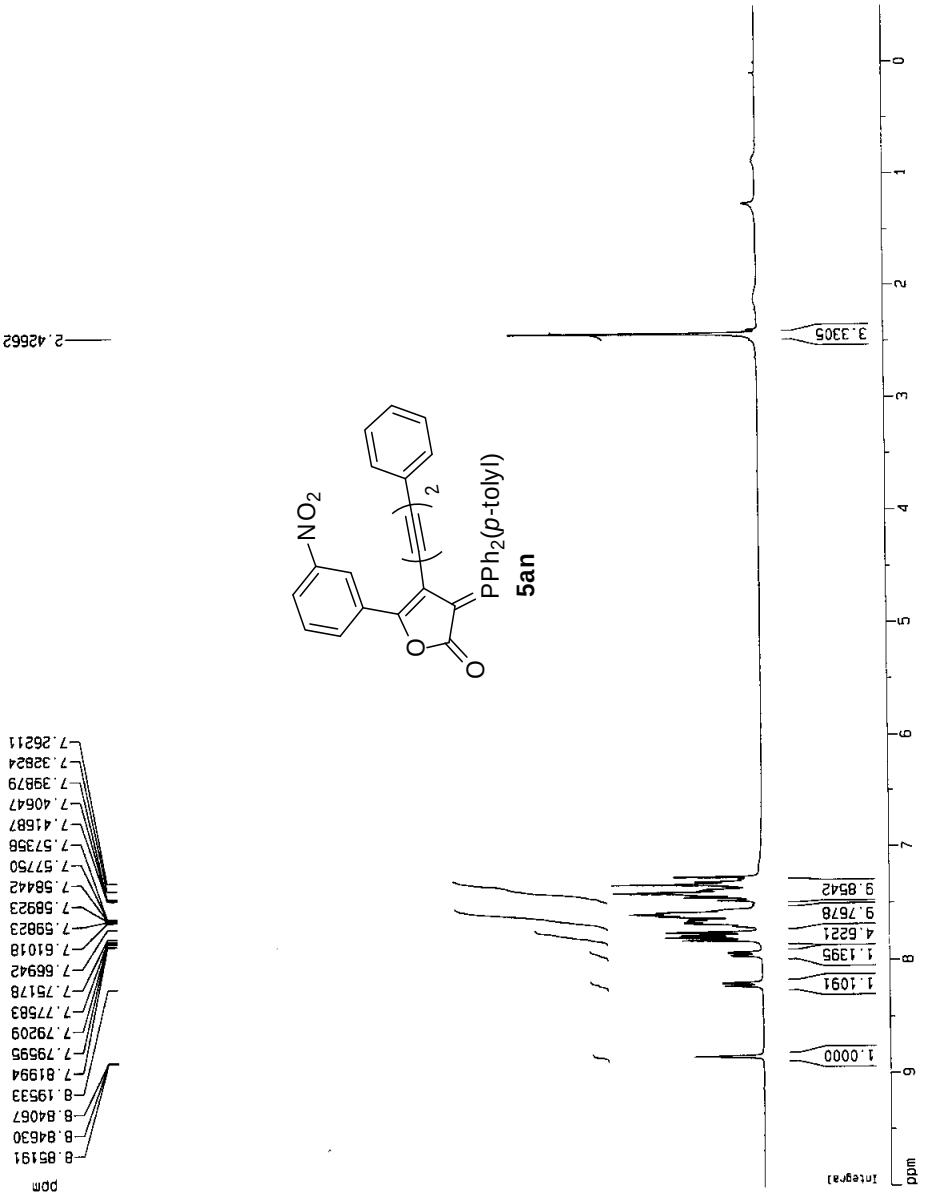


Fig S108. ^{13}C NMR spectra of compound **5an** (75.5 MHz, $CDCl_3$)

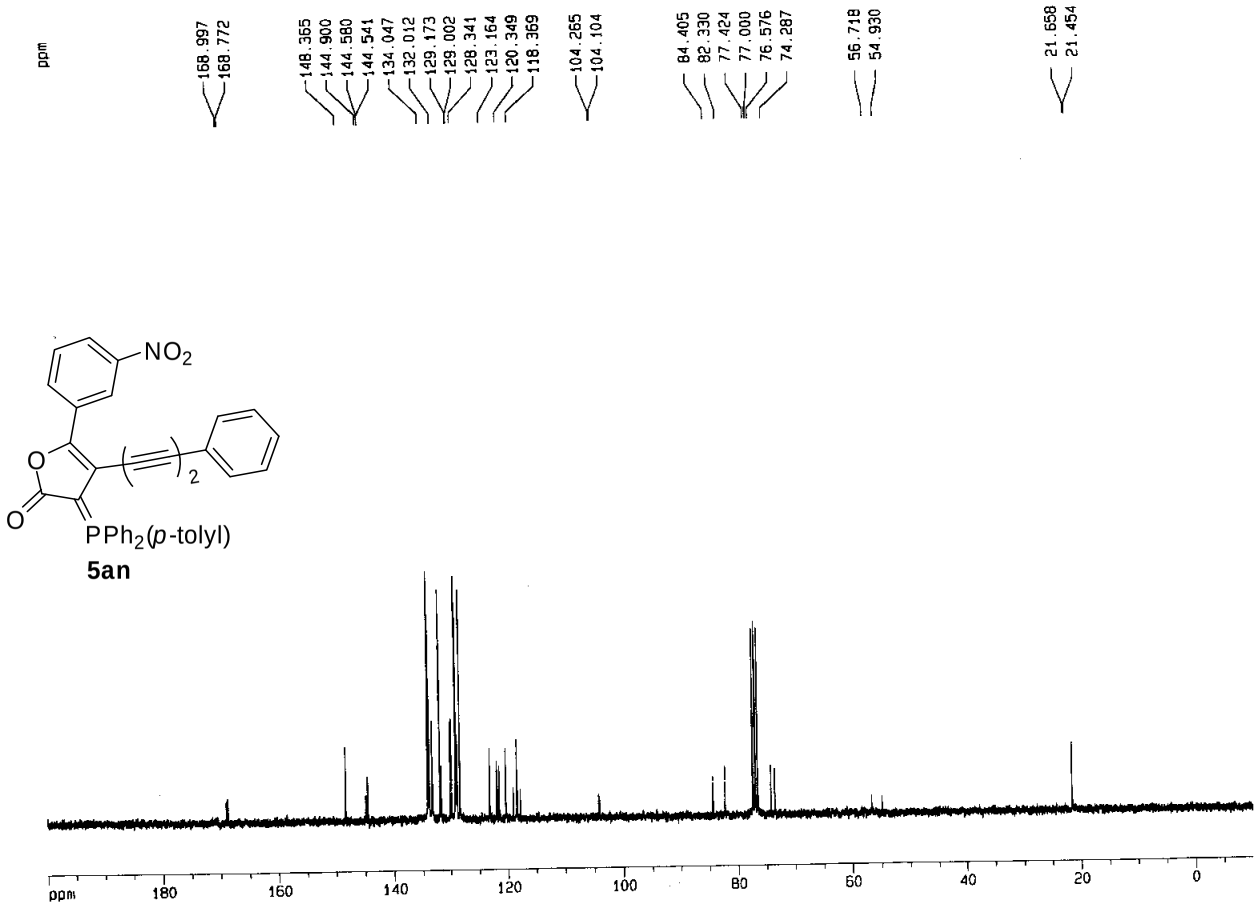


Fig S109. ^{1}H NMR spectra of compound **5ao** (300 MHz, $CDCl_3$)

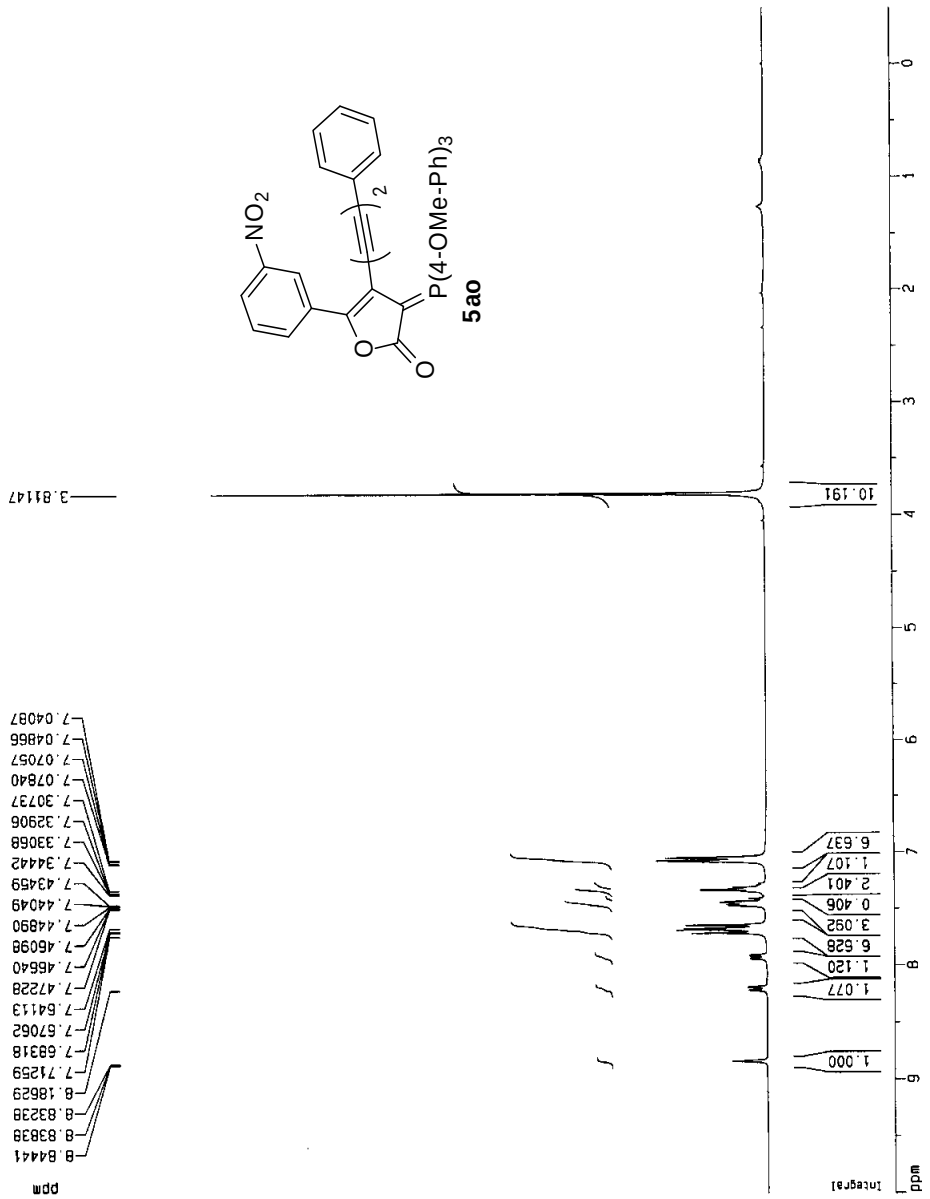


Fig S110. ^{13}C NMR spectra of compound **5ao** (75.5 MHz, $CDCl_3$)

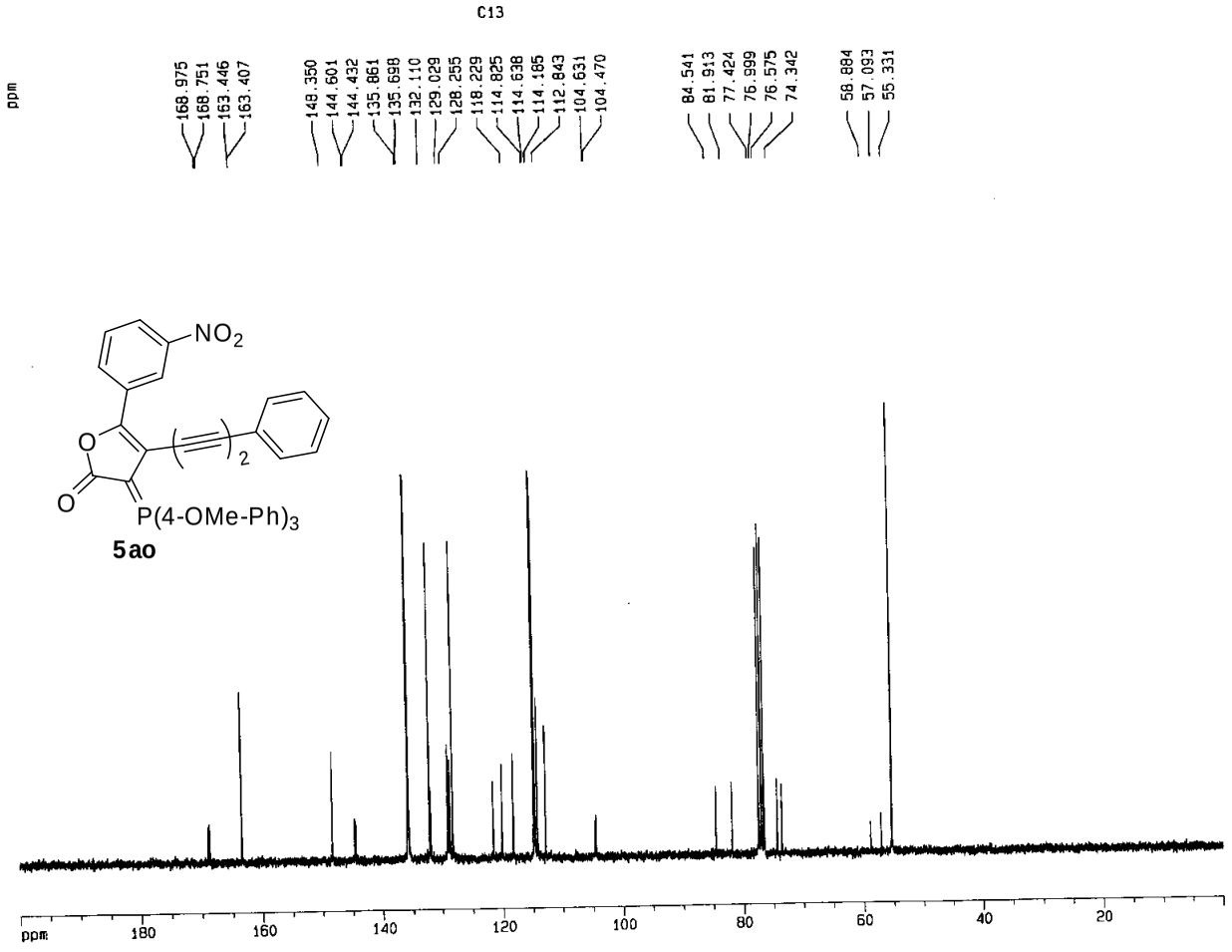


Fig S111. ^{1}H NMR spectra of compound **5ap** (300 MHz, $CDCl_3$)

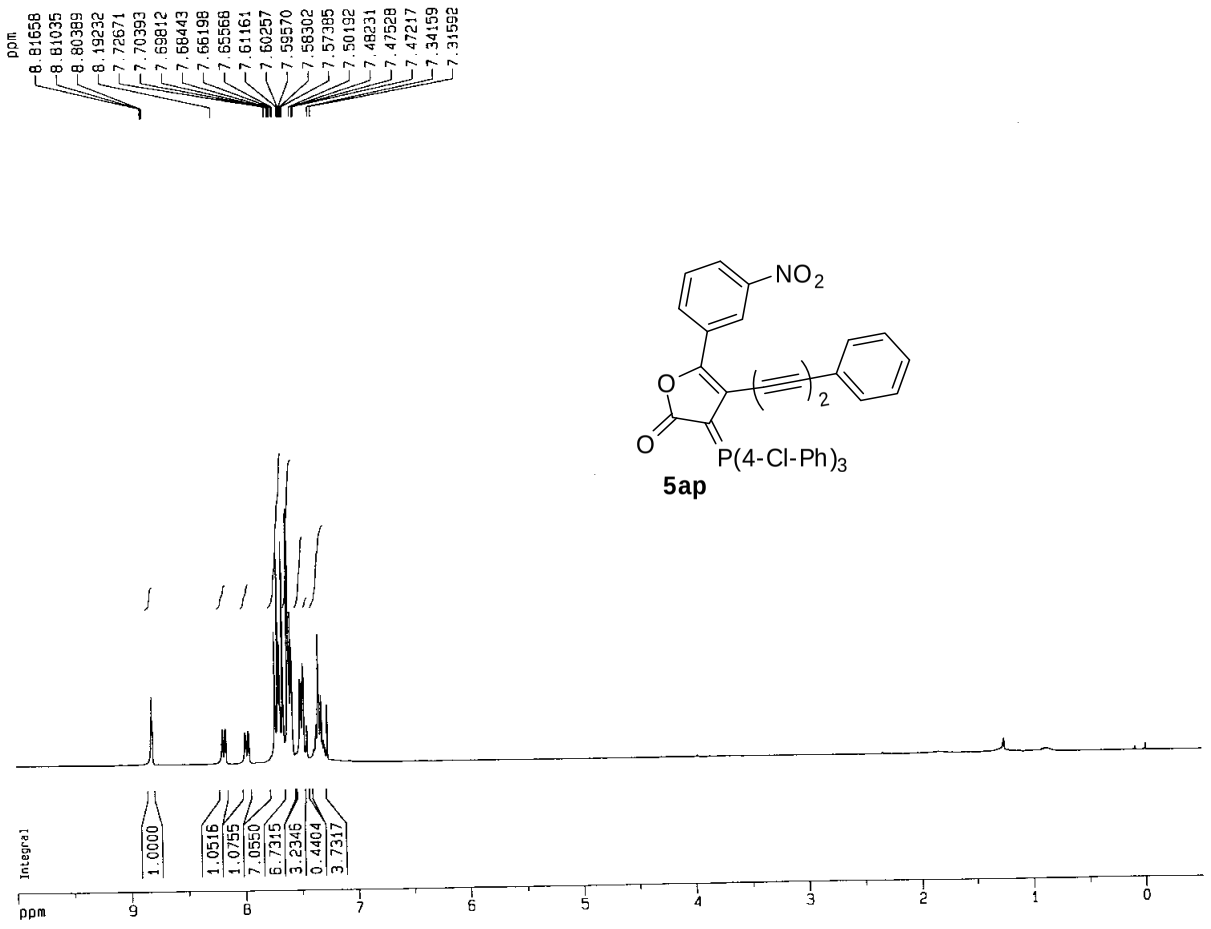


Fig S112. ^{13}C NMR spectra of compound **5ap** (75.5 MHz, $CDCl_3$)

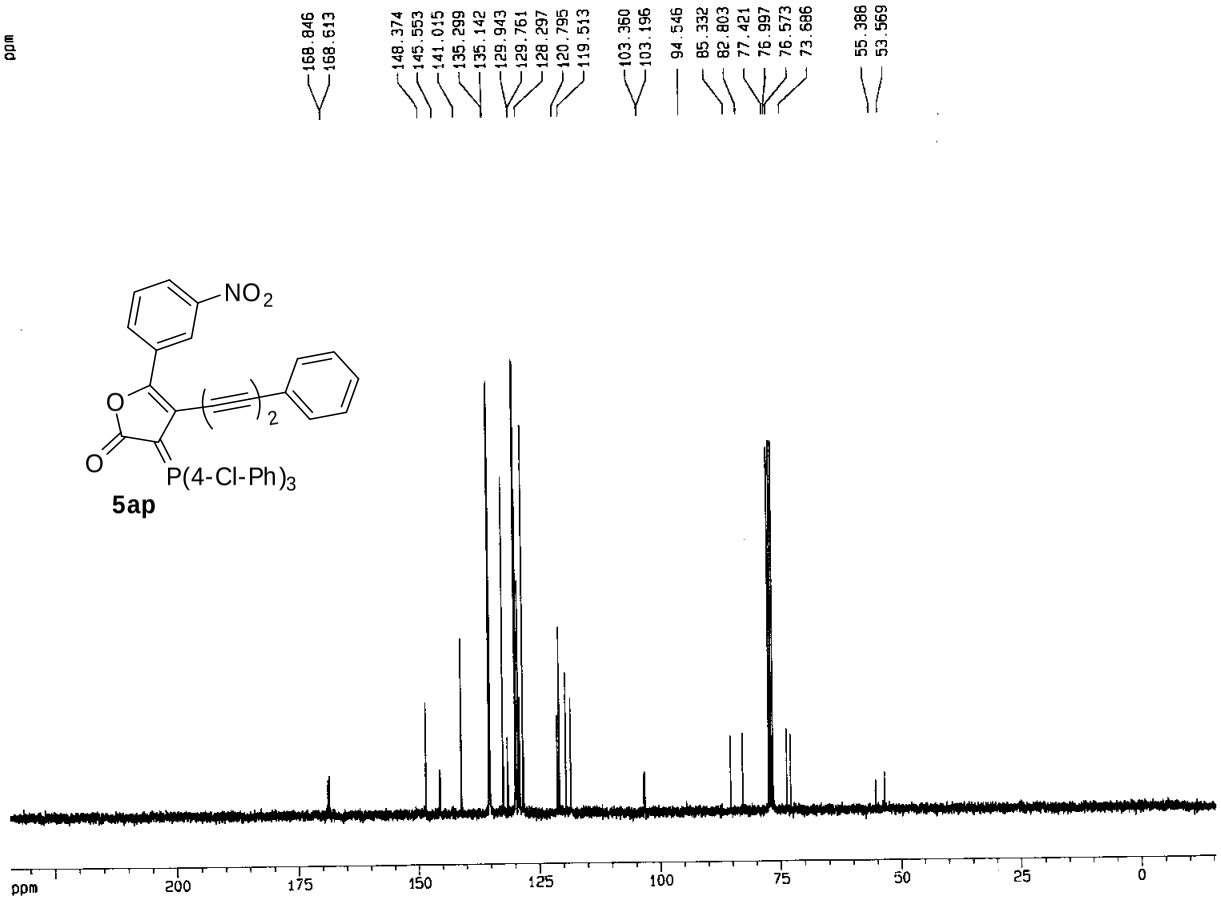


Fig S113. ^{1}H NMR spectra of compound **5aq** (300 MHz, $CDCl_3$)

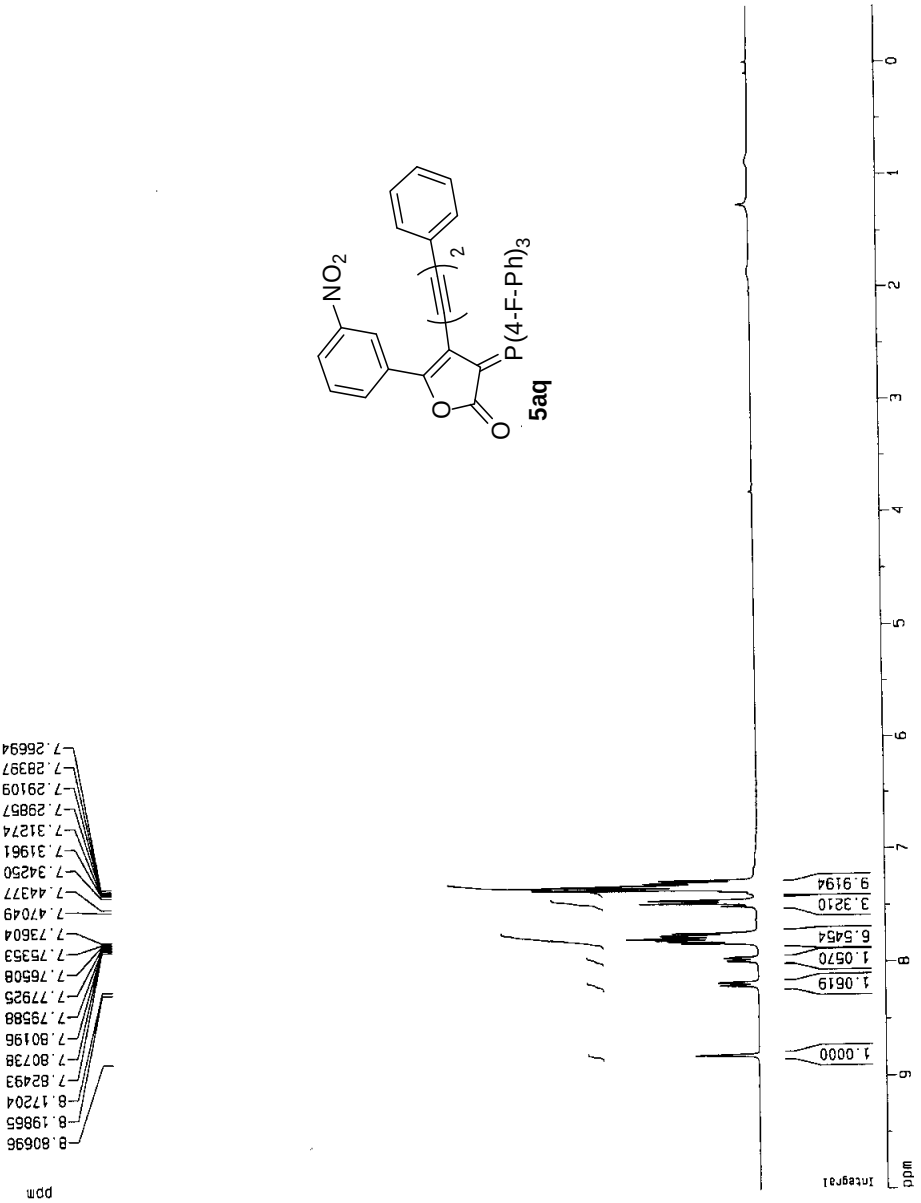


Fig S114. ^{13}C NMR spectra of compound **5aq** (75.5 MHz, $CDCl_3$)

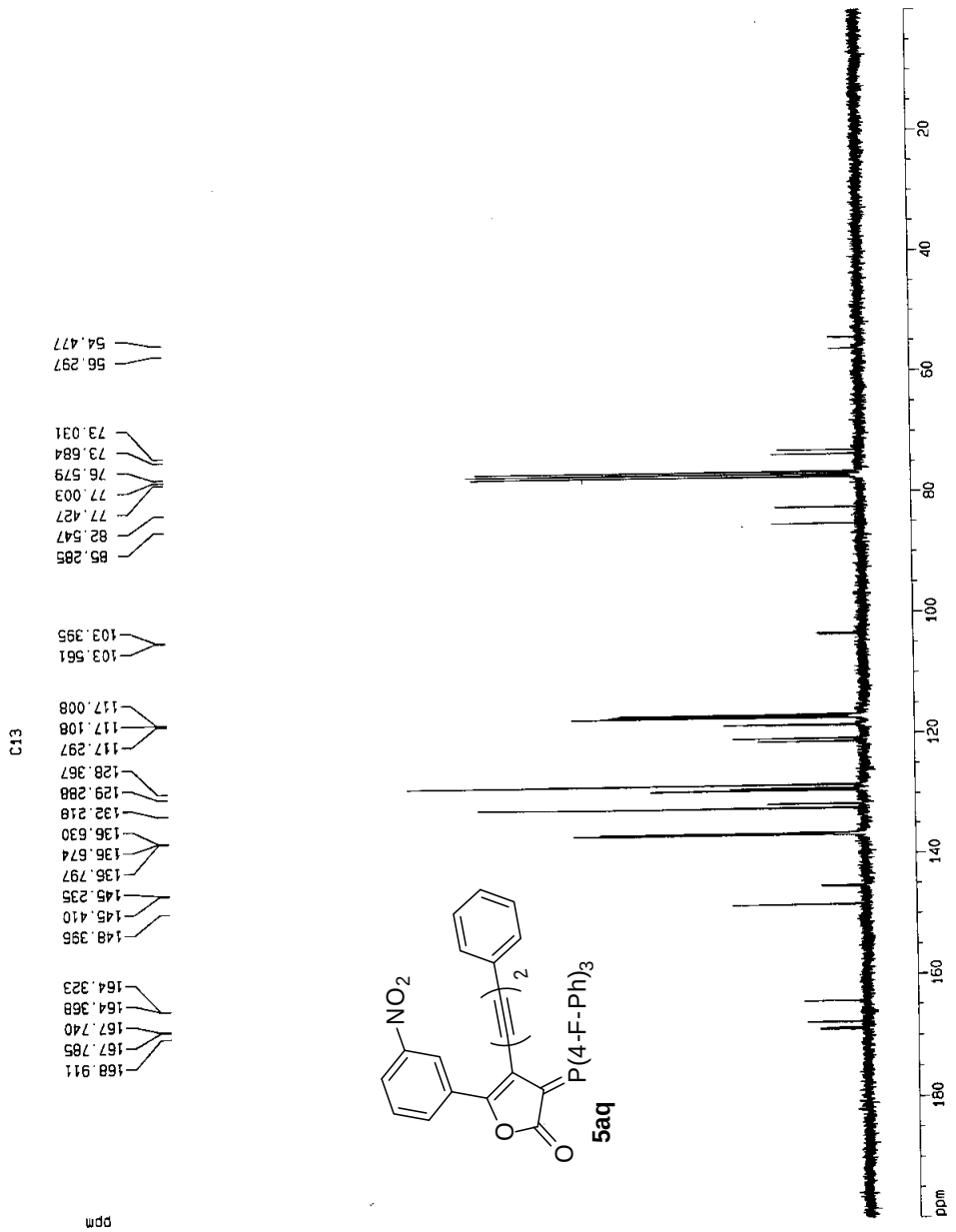


Fig S115. ^{1}H NMR spectra of compound **5ar** ($CDCl_3$)

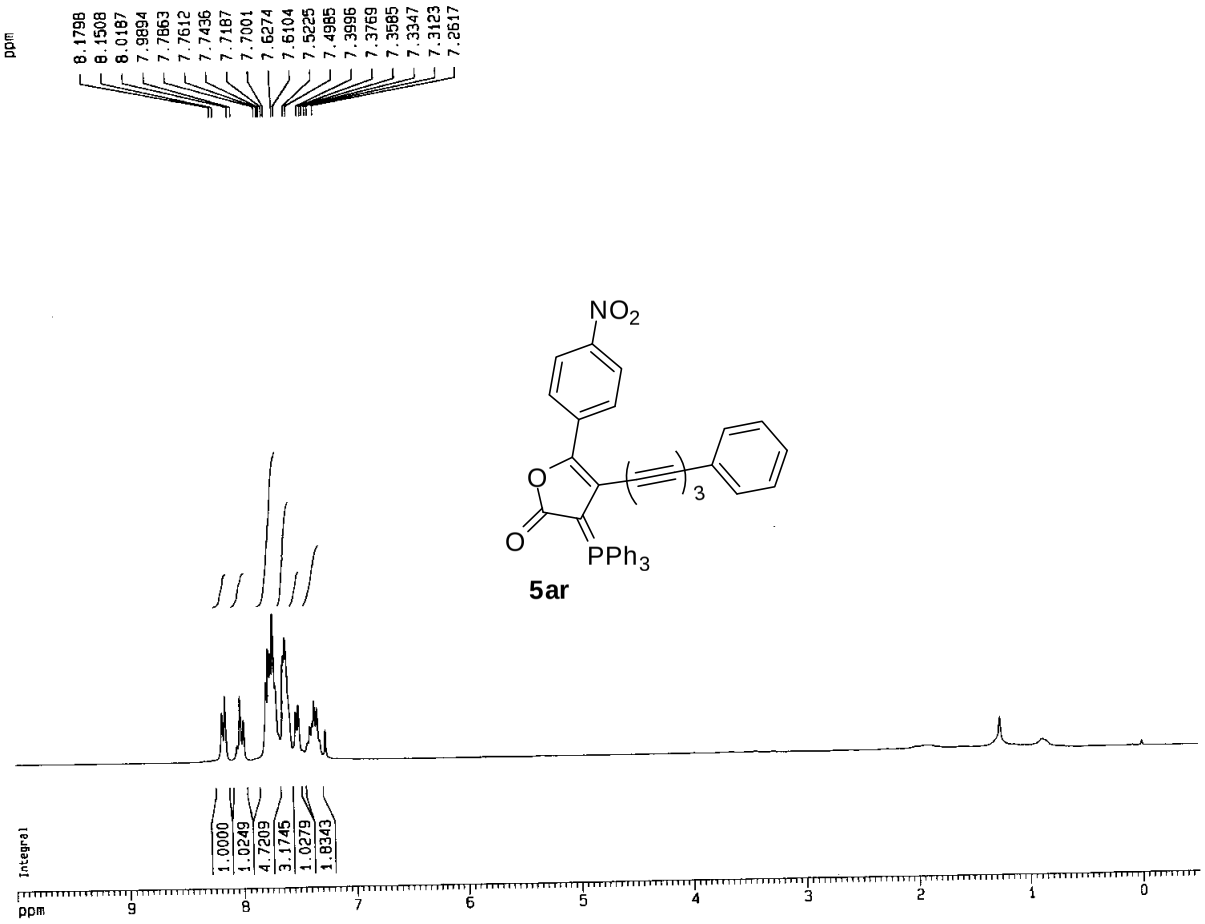


Fig S116. ^{13}C NMR spectra of compound **5ar** (75.5 MHz, $CDCl_3$)

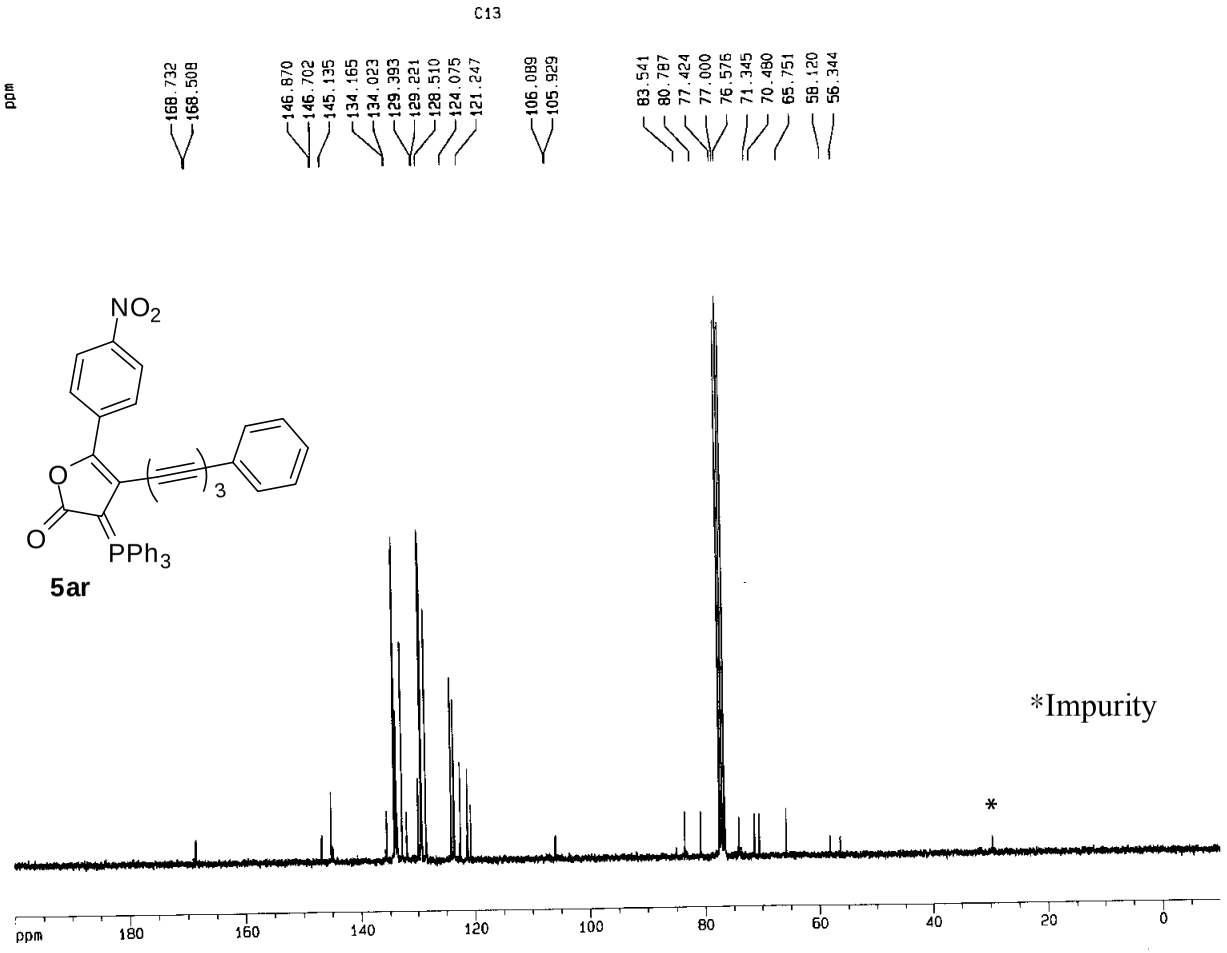


Fig S117. ^{1}H NMR spectra of compound **5as** (300 MHz, $CDCl_3$)

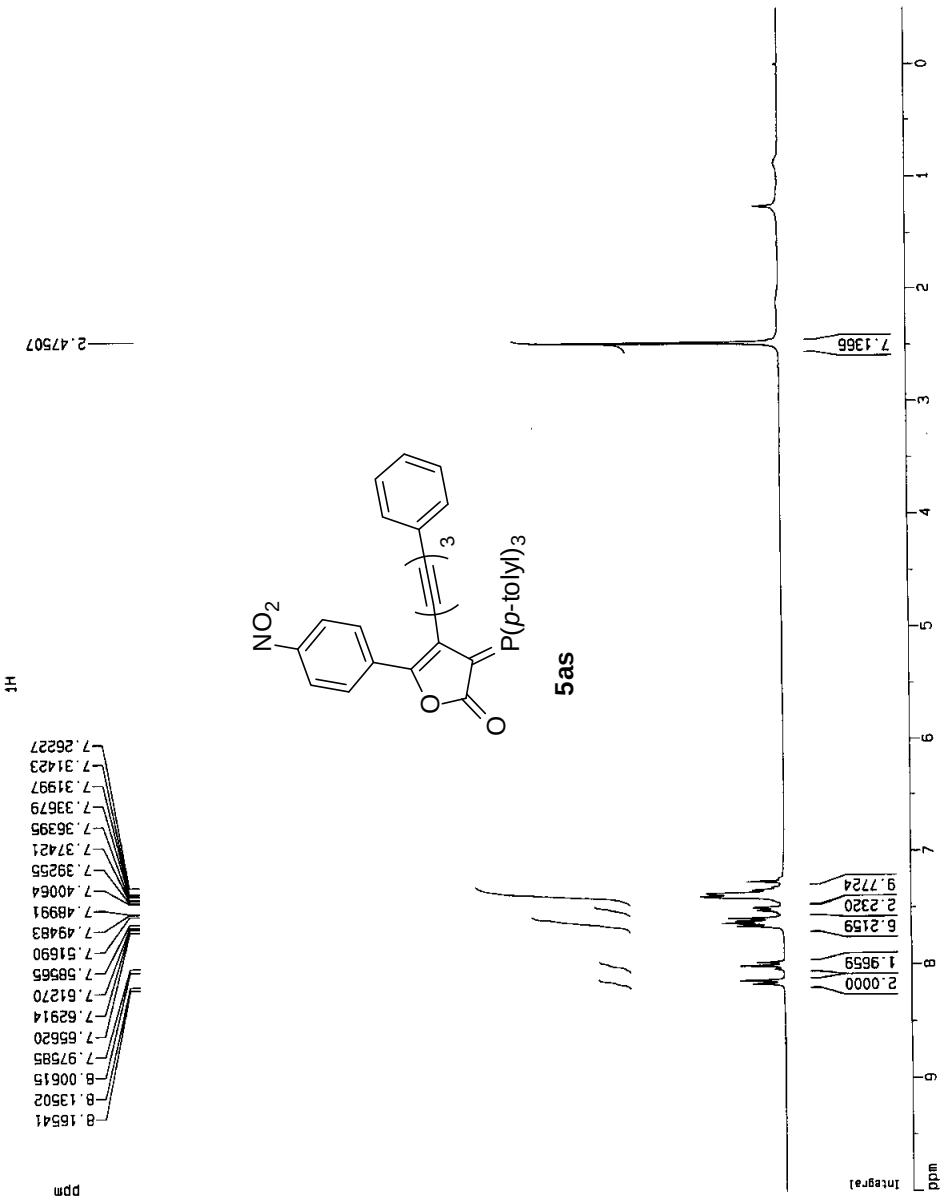


Fig S118. ^{13}C NMR spectra of compound **5as** (75.5 MHz, $CDCl_3$)

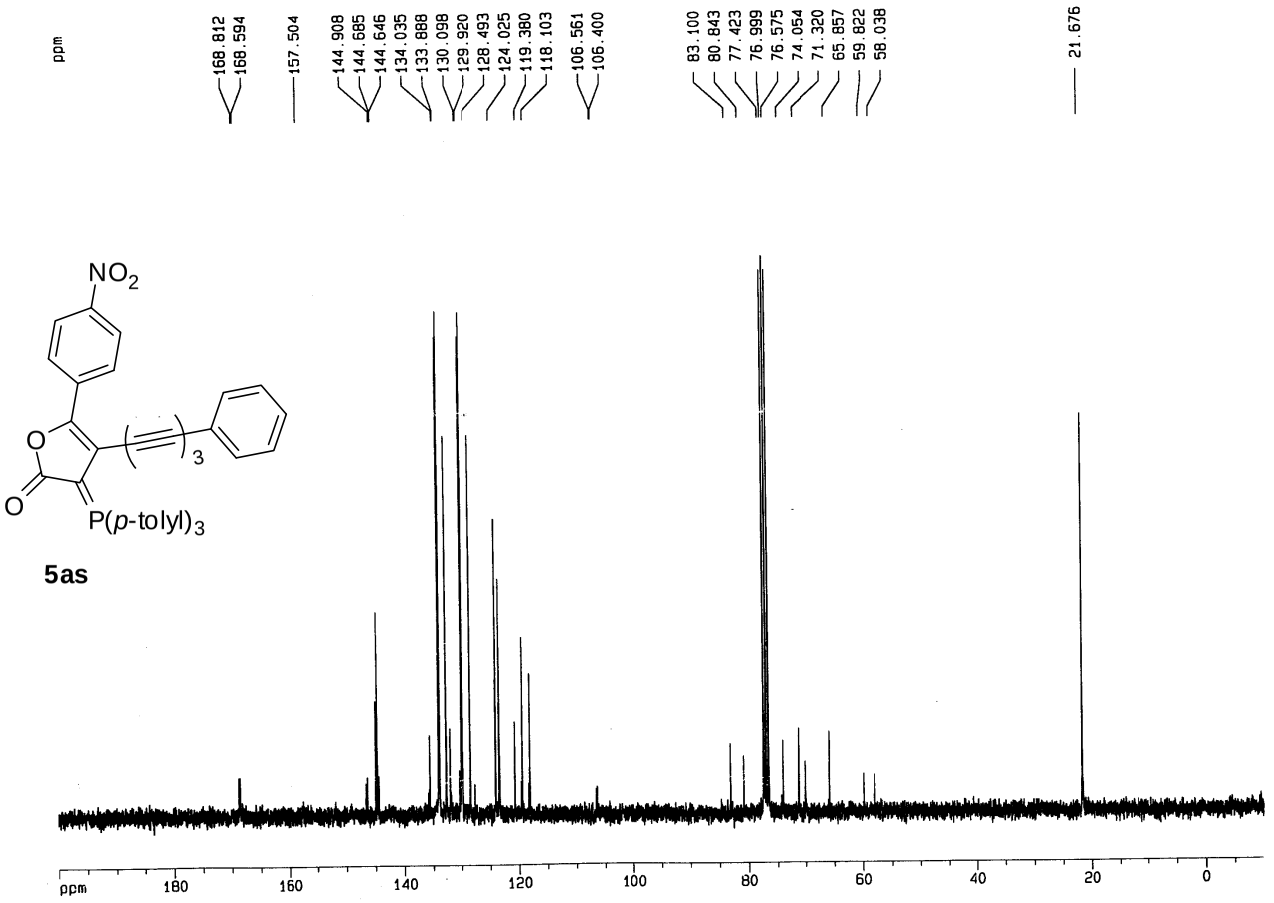


Fig S119. ^{1}H NMR spectra of compound **5at** (300 MHz, $CDCl_3$)

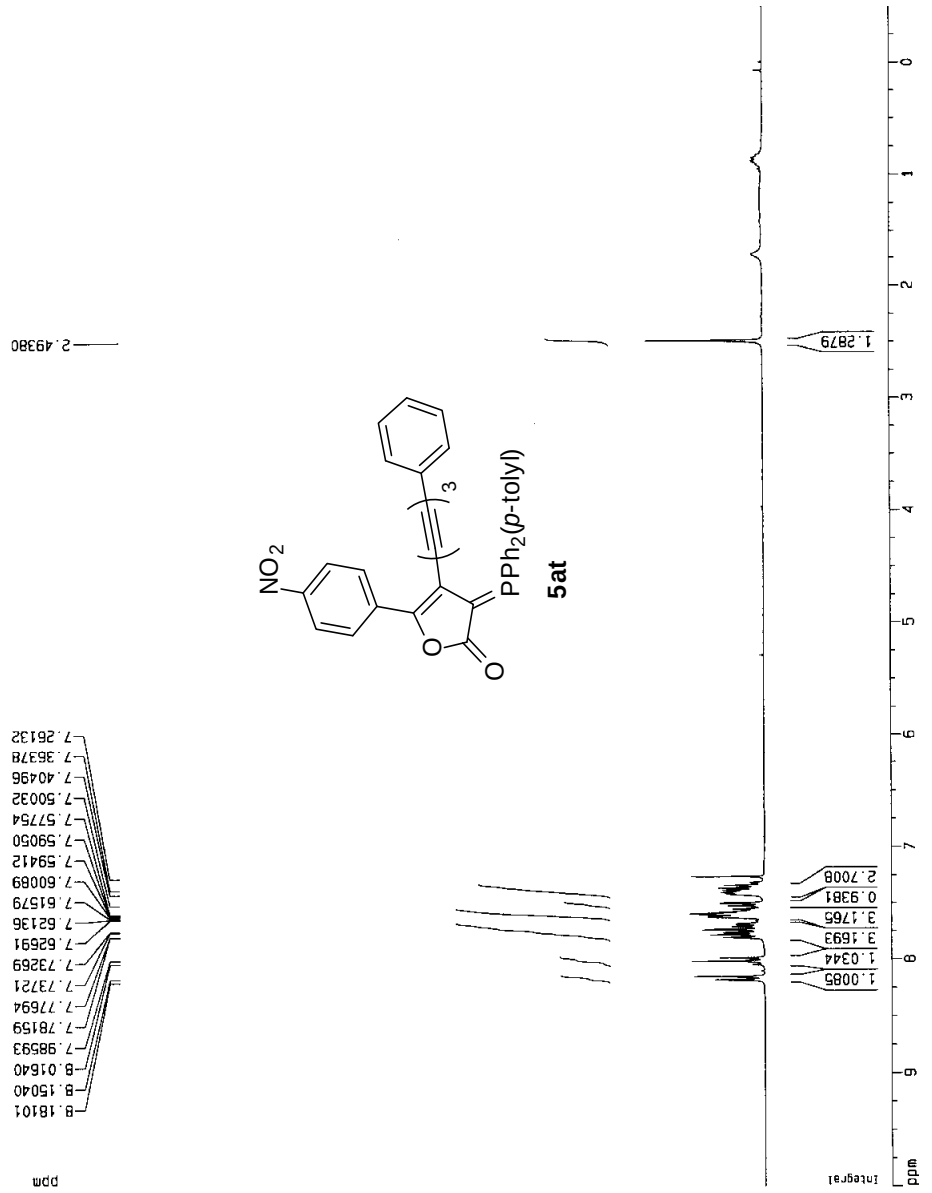


Fig S120. ^{13}C NMR spectra of compound **5at** (75.5 MHz, $CDCl_3$)

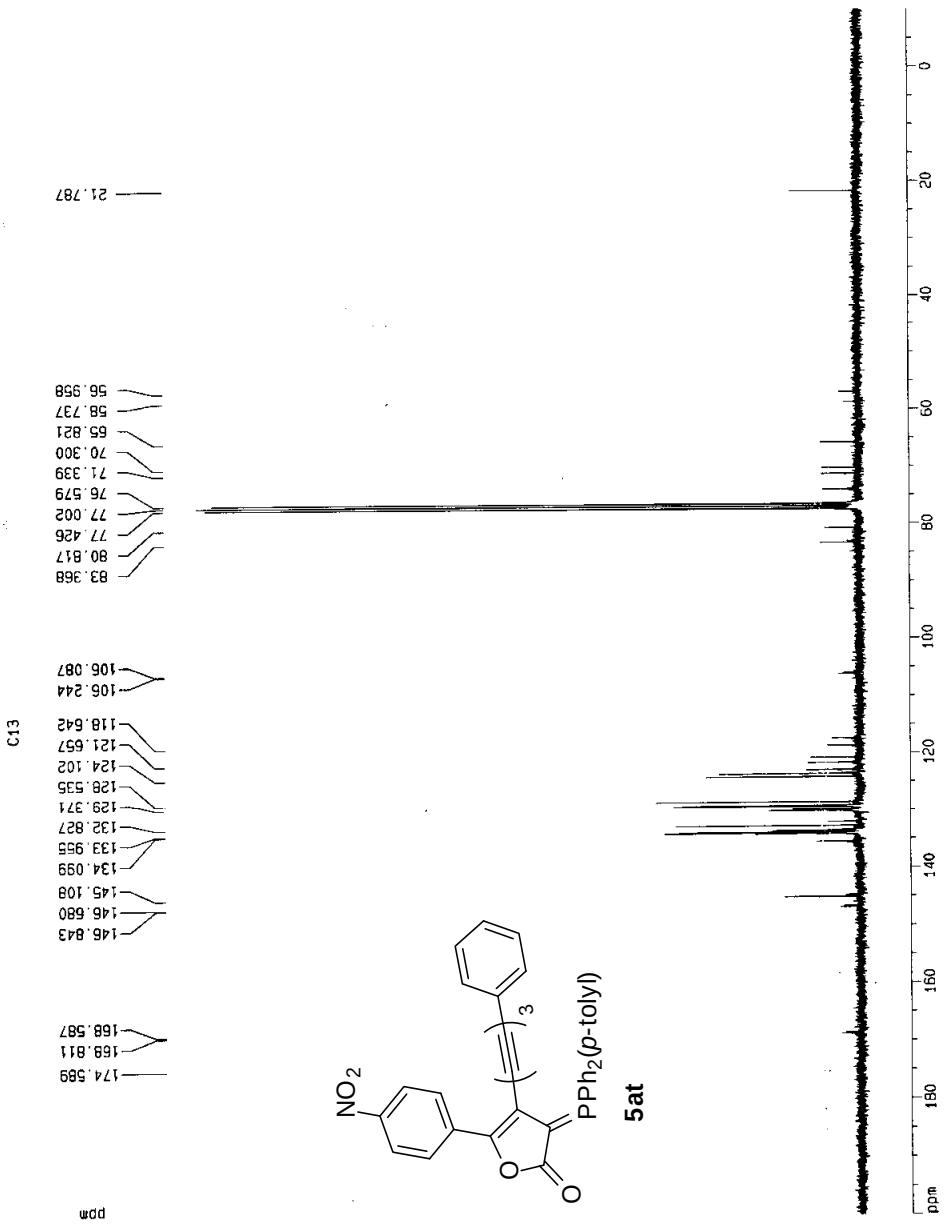


Fig S121. ^{1}H NMR spectra of compound **5au** (300 MHz, $CDCl_3$)

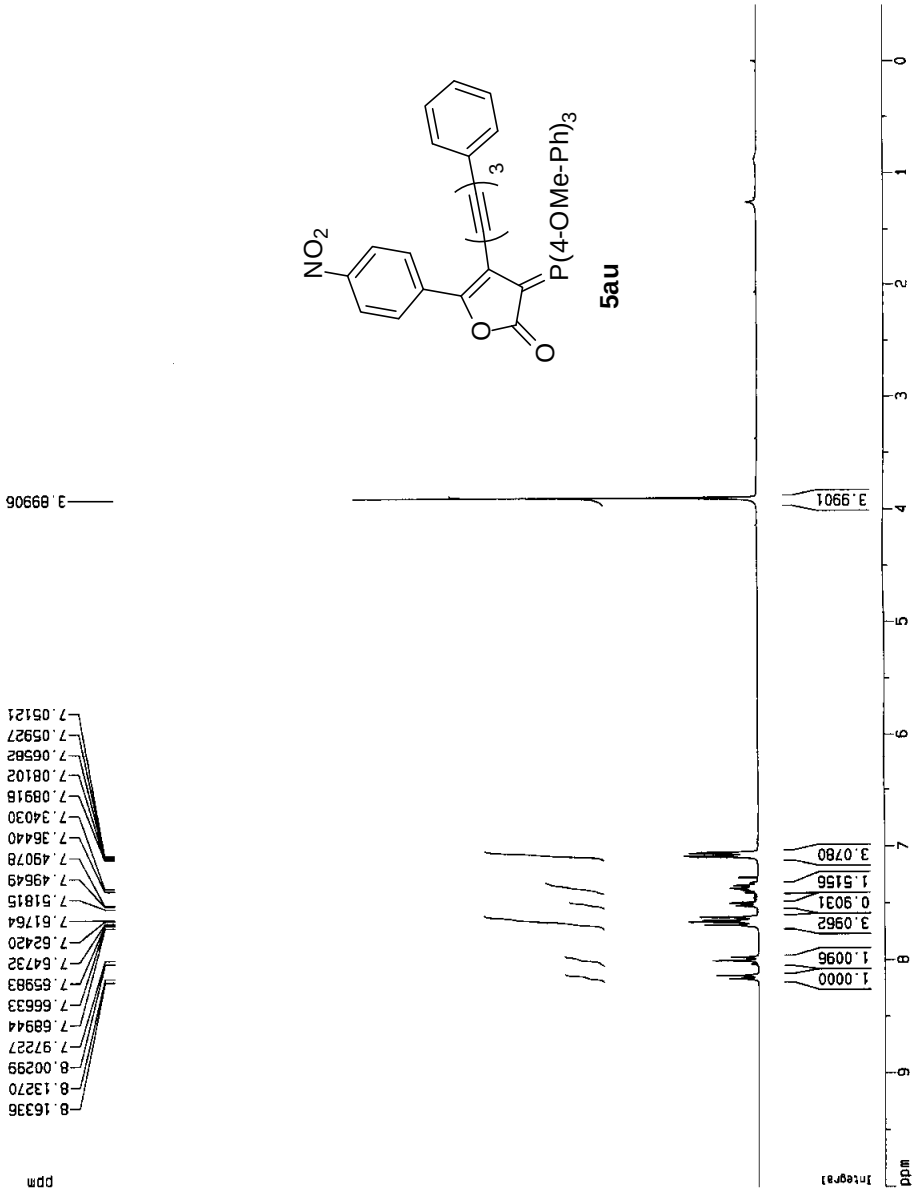


Fig S122. ^{13}C NMR spectra of compound **5au** (75.5 MHz, $CDCl_3$)

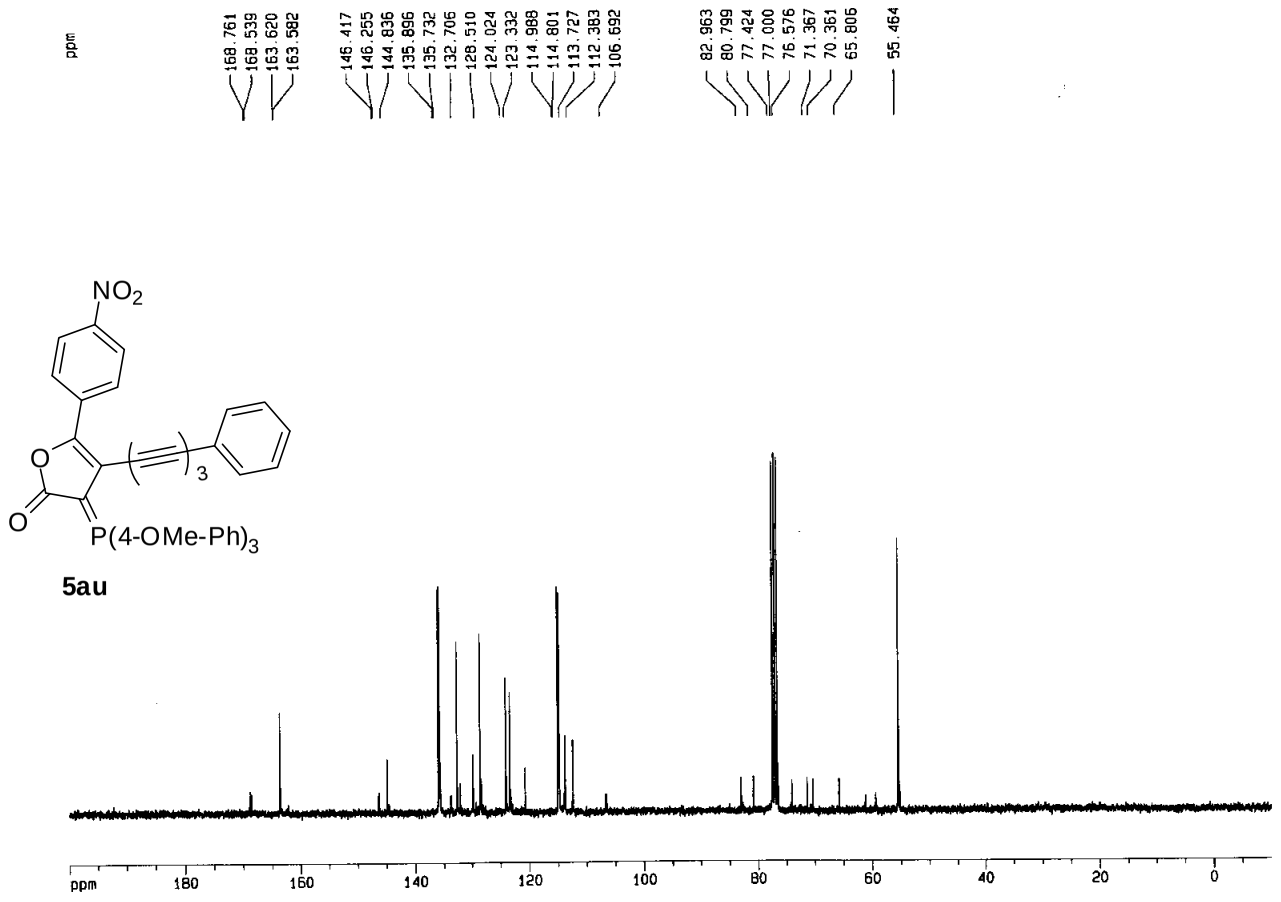


Fig S123. ^{1}H NMR spectra of compound **5av** (300 MHz, $CDCl_3$)

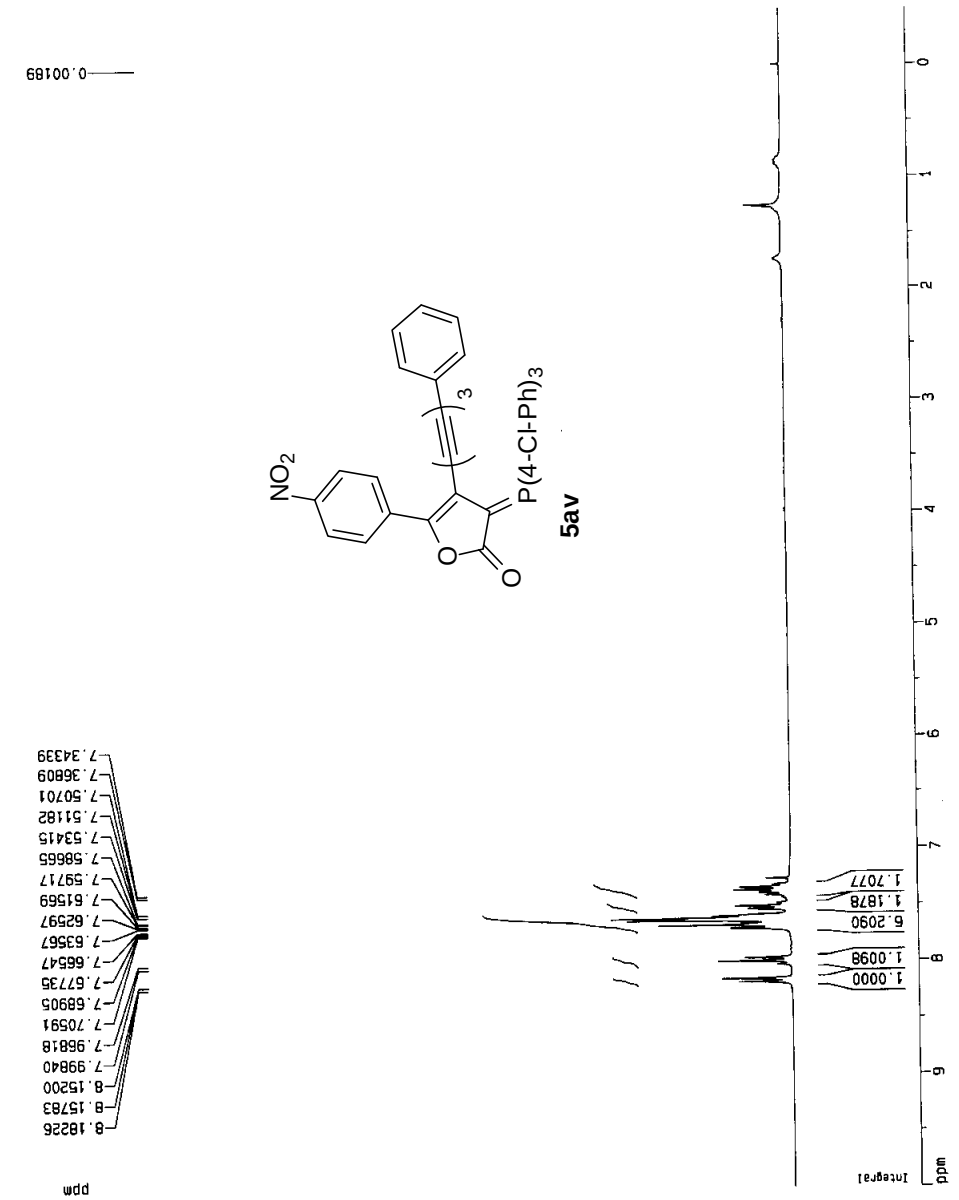


Fig S124. ^{13}C NMR spectra of compound **5av** (75.5 MHz, $CDCl_3$)

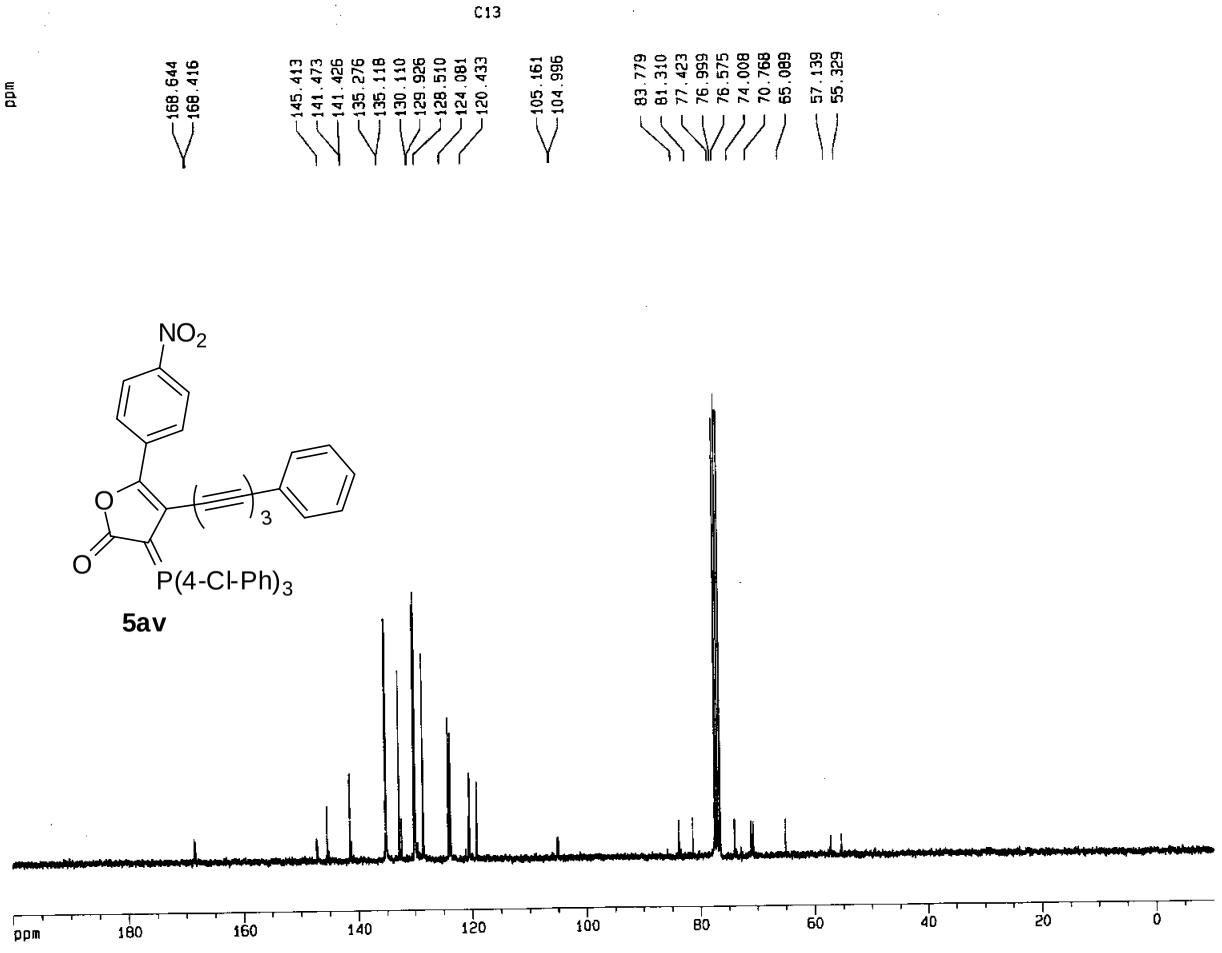


Fig S125. ^{1}H NMR spectra of compound **5aw** (300 MHz, $CDCl_3$)

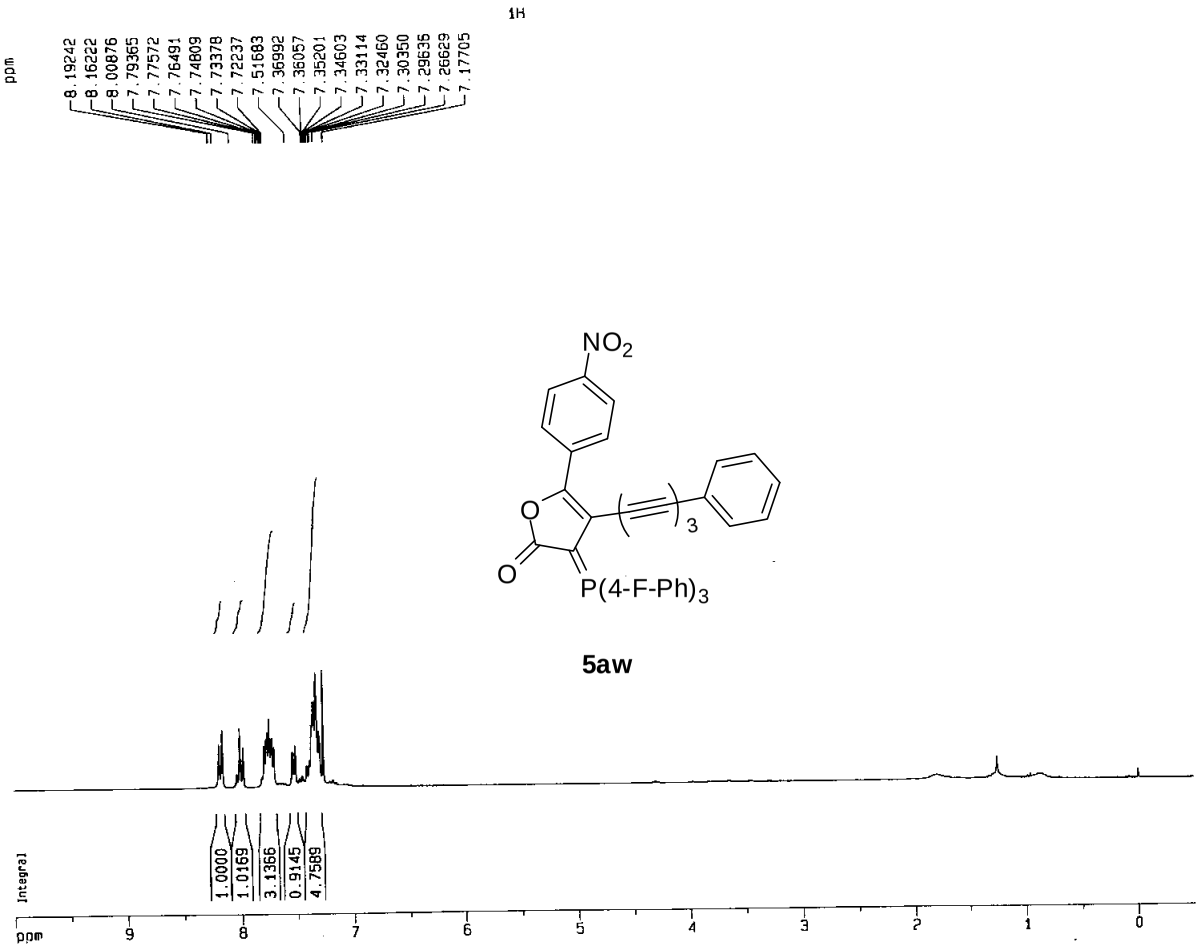


Fig S126. ^{13}C NMR spectra of compound **5aw** (150.7 MHz, $CDCl_3$)

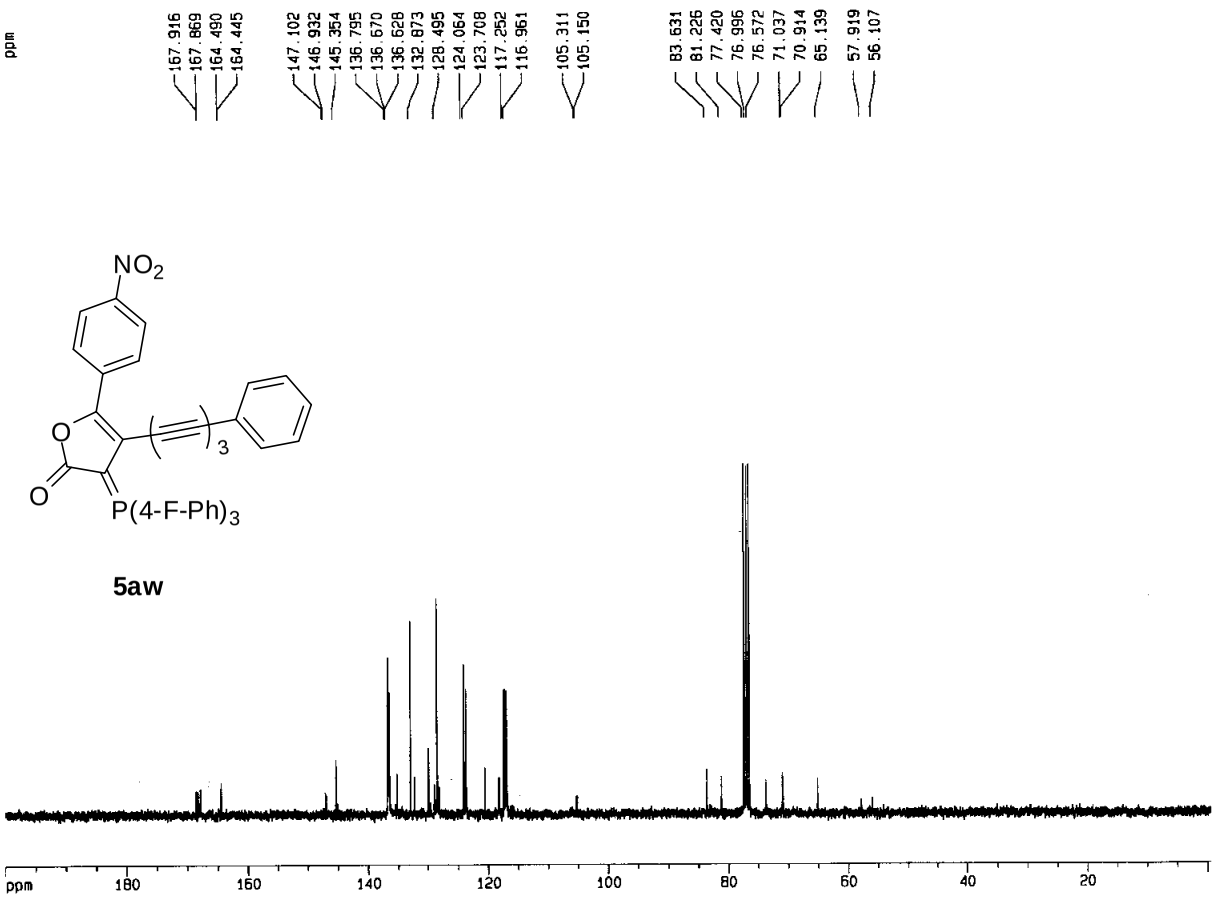


Fig S127. ^{1}H NMR spectra of compound **5ax** (300 MHz, $CDCl_3$)

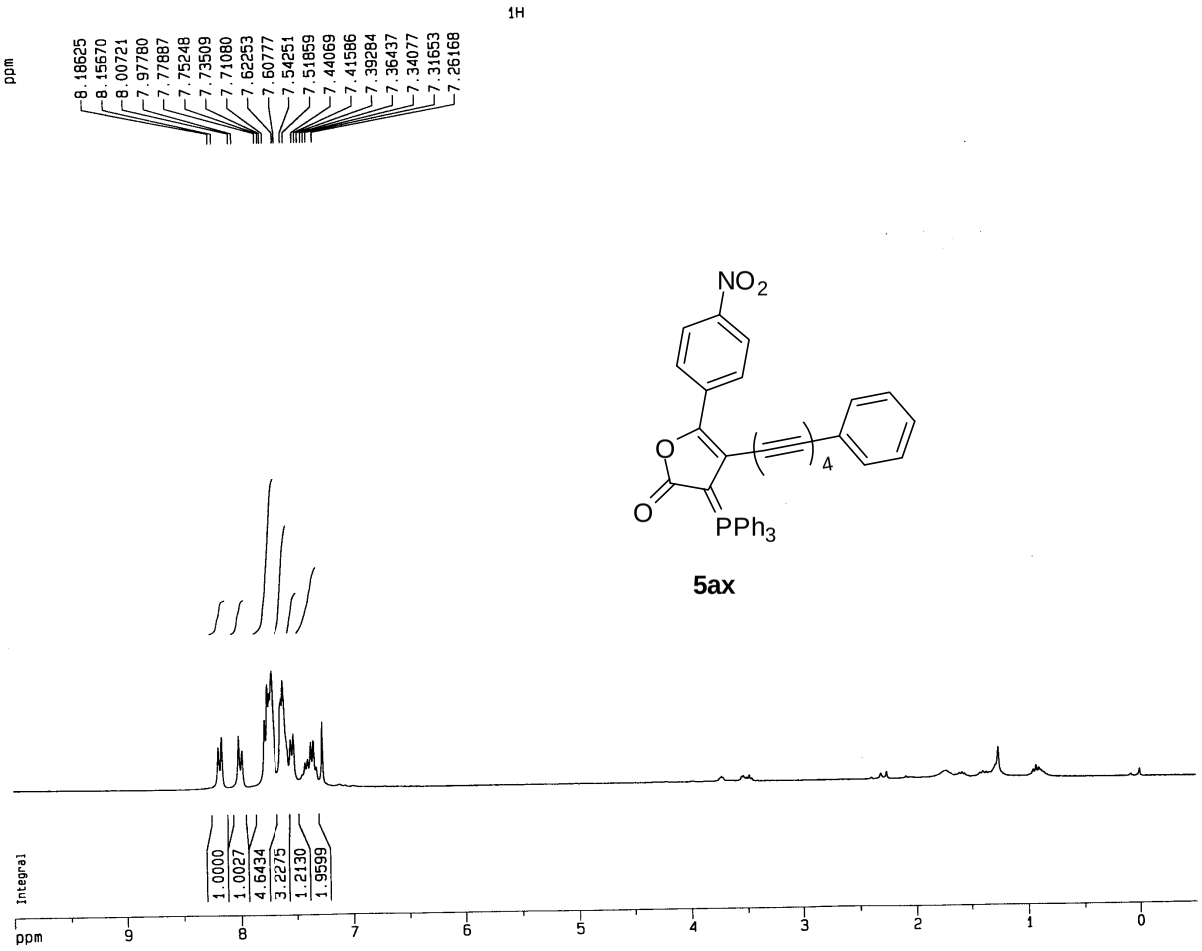
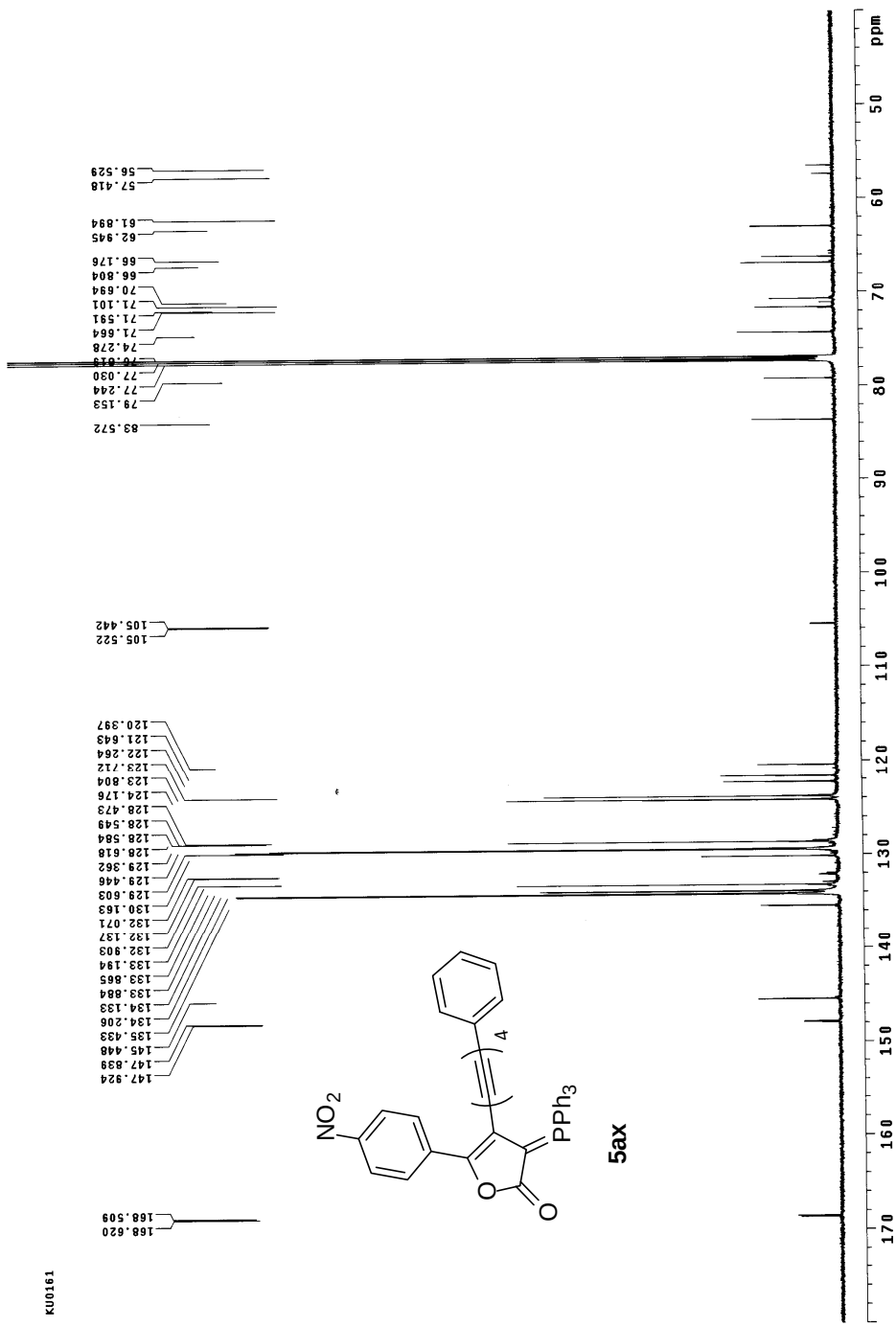


Fig S128. ^{13}C NMR spectra of compound **5ax** (150.7 MHz, $CDCl_3$)



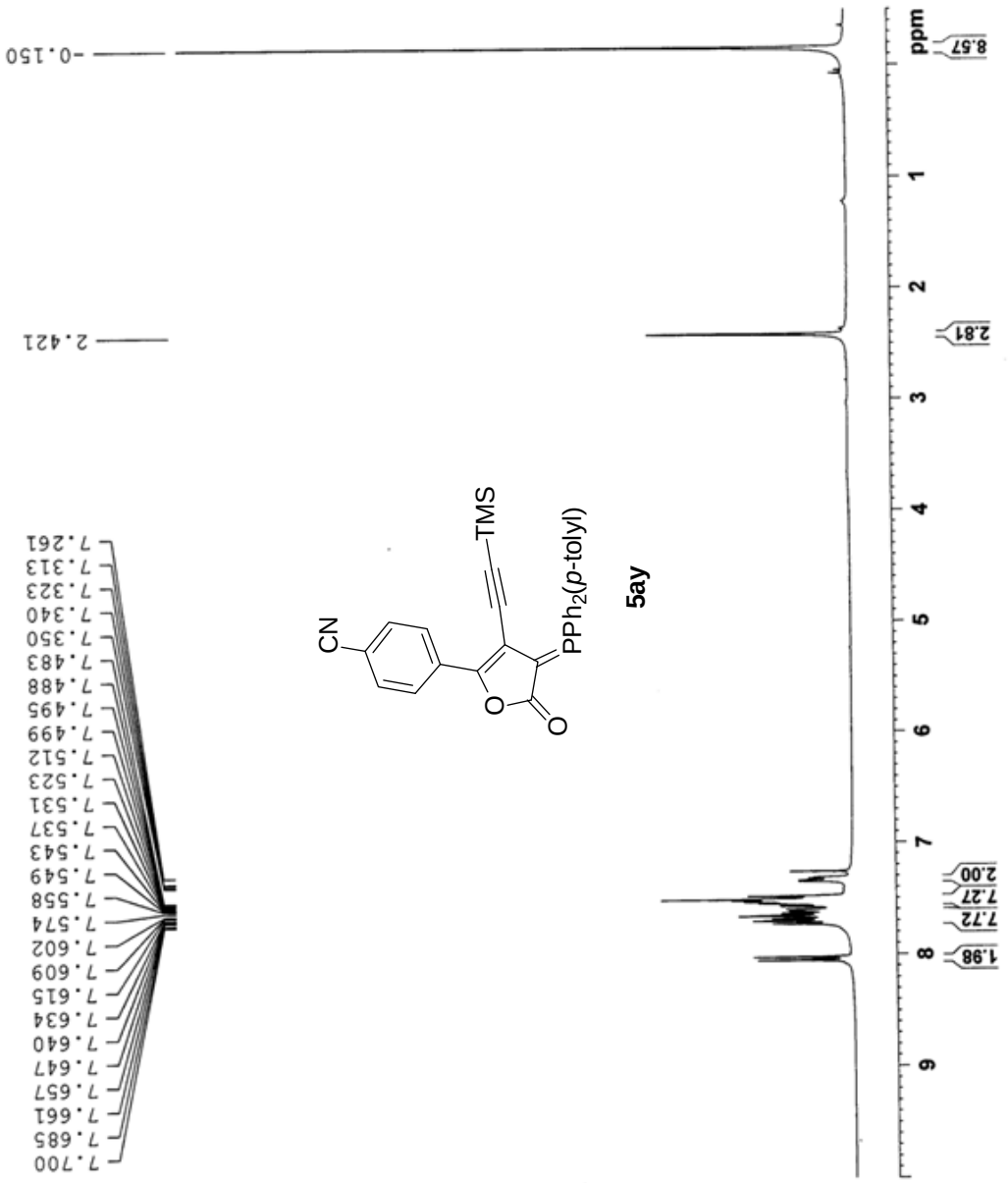


Fig S129. ^{1}H NMR spectra of compound **5ay** (300 MHz, $CDCl_3$)

Fig S130. ^{13}C NMR spectra of compound **5ay** (75.5 MHz, $CDCl_3$)

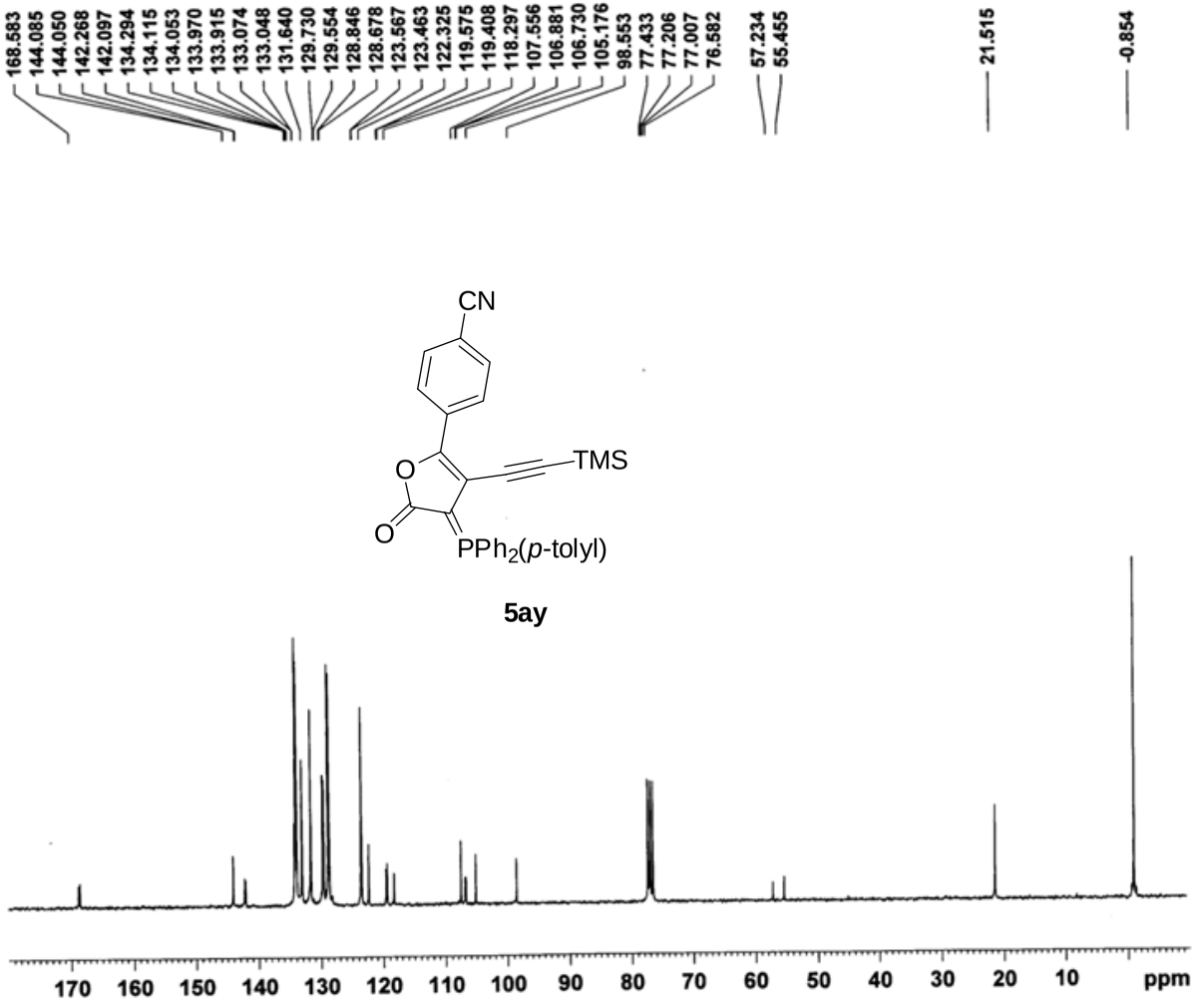


Fig S131. ^{1}H NMR spectra of compound **5ay'** (300 MHz, $CDCl_3$)

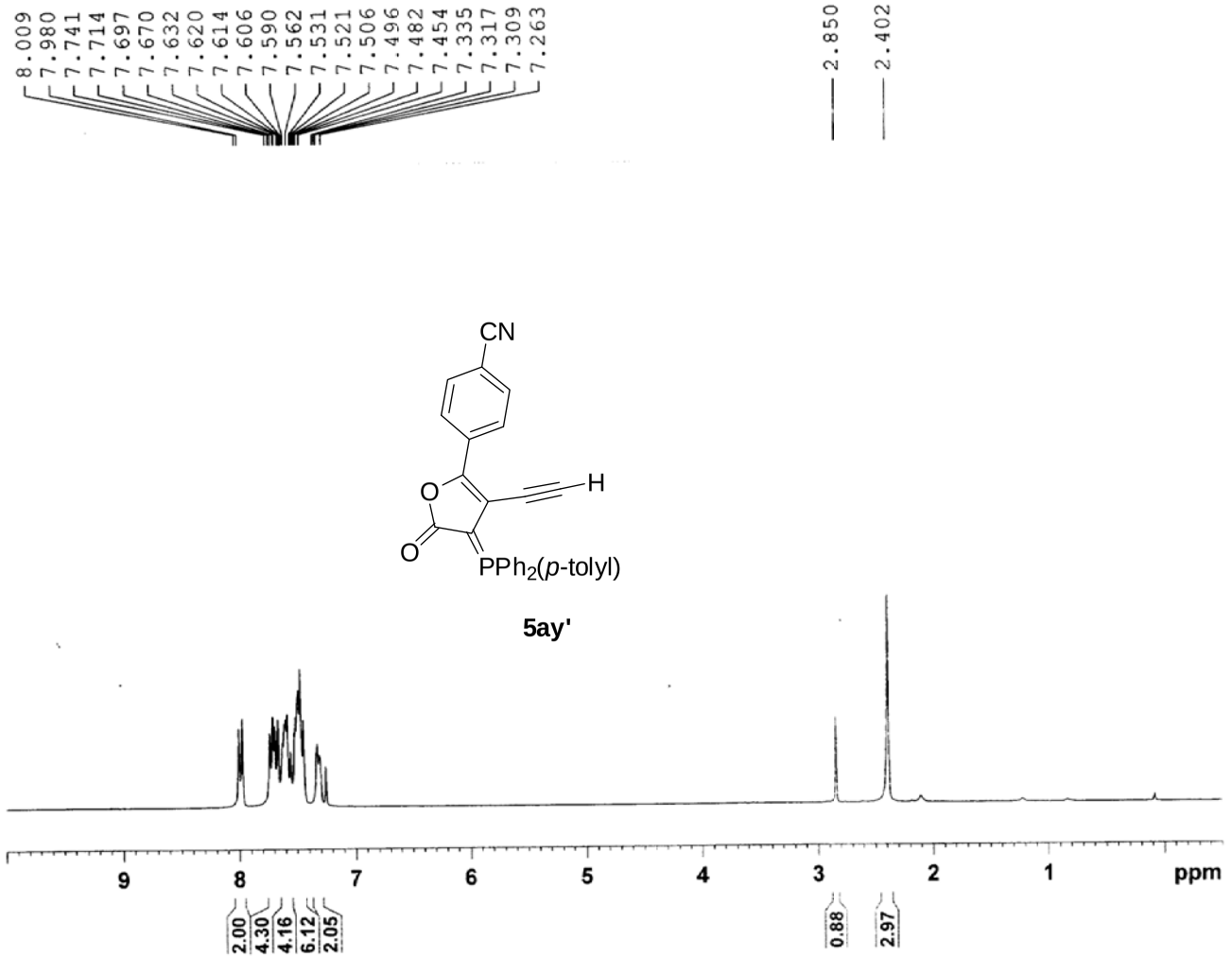


Fig S132. ^{13}C NMR spectra of compound **5ay'** (75.5 MHz, $CDCl_3$)

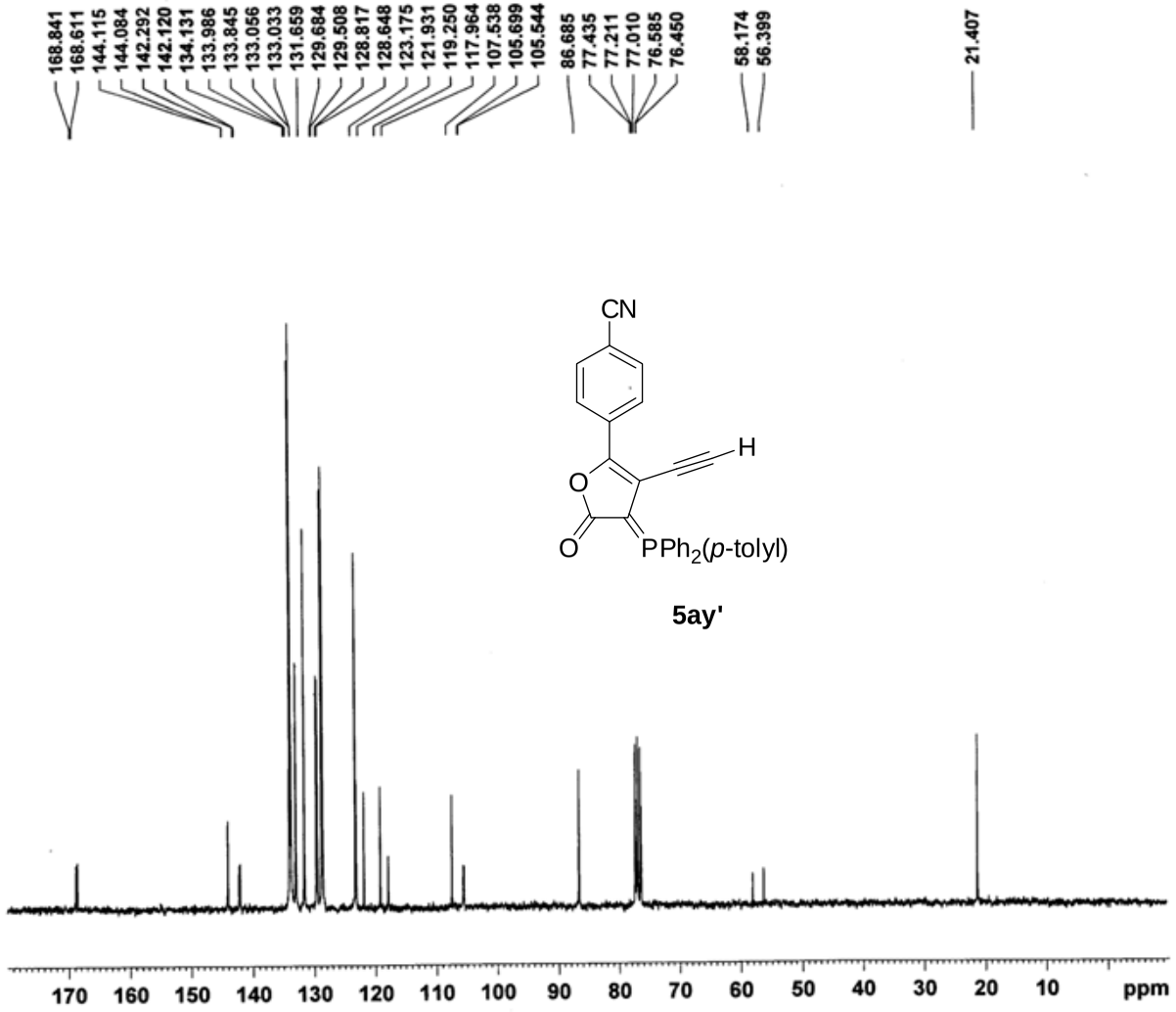


Fig. S133. ^{1}H NMR spectra of compound **5az** (300 MHz, $CDCl_3$)

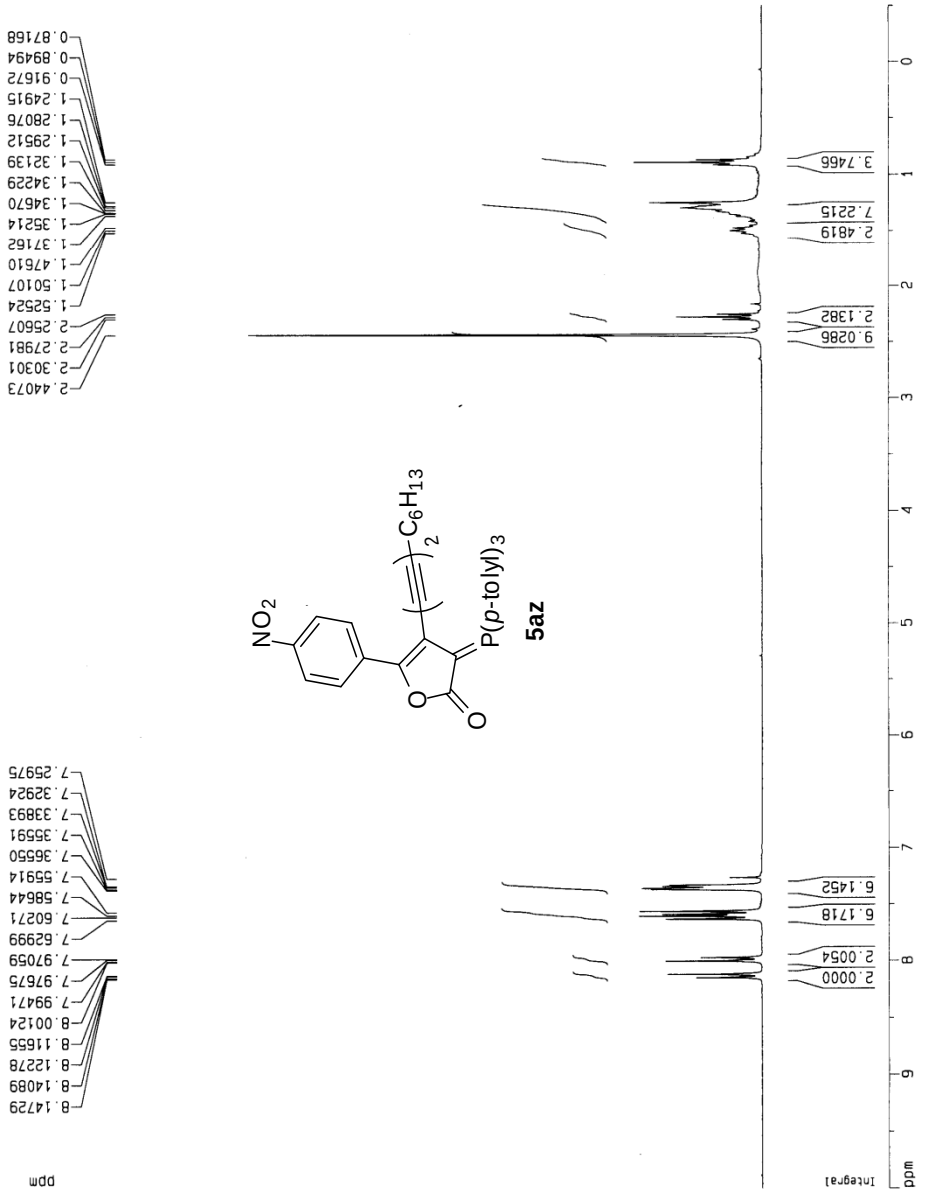


Fig. S134. ^{13}C NMR spectra of compound **5az** (75.5 MHz, $CDCl_3$)

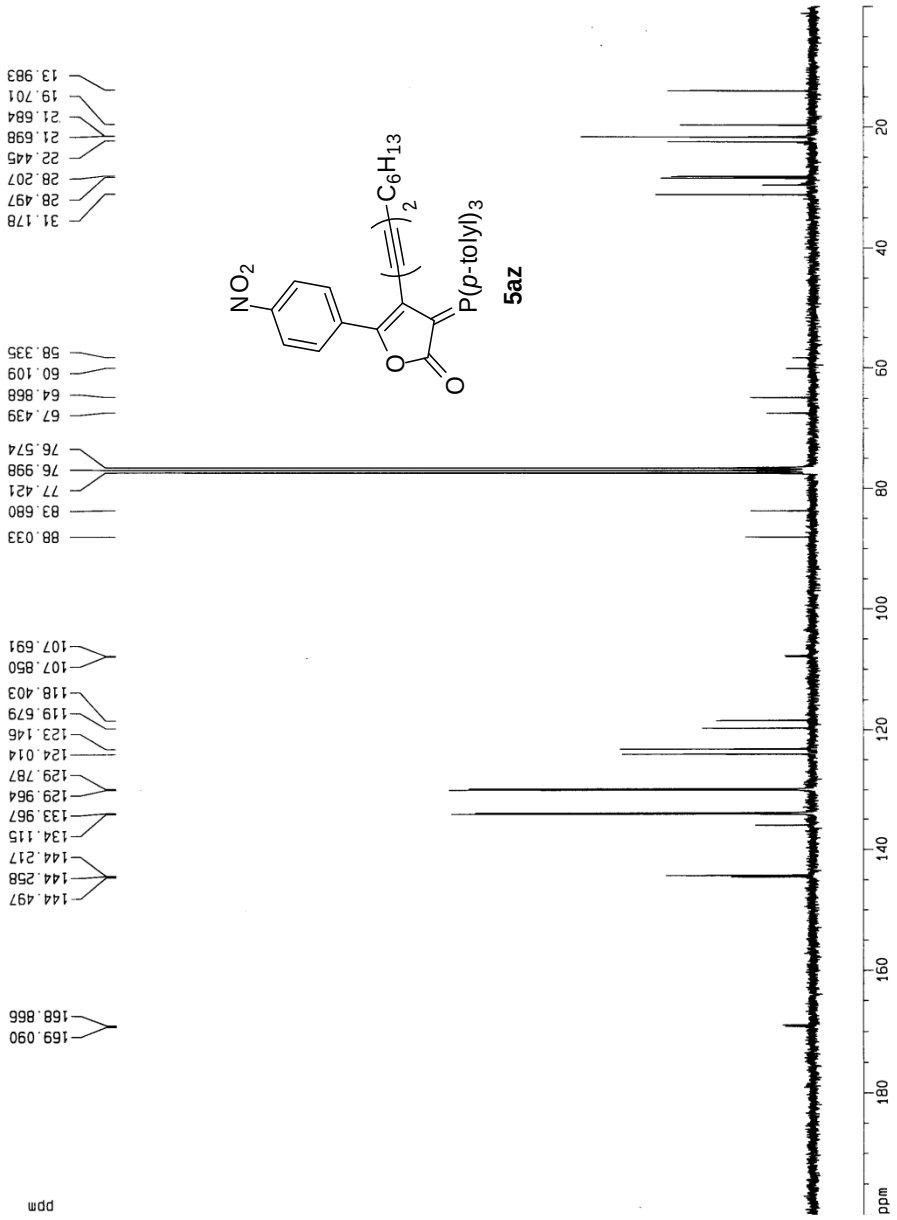


Fig. S135. ^{1}H NMR spectra of compound **5aaa** (300 MHz, $CDCl_3$)

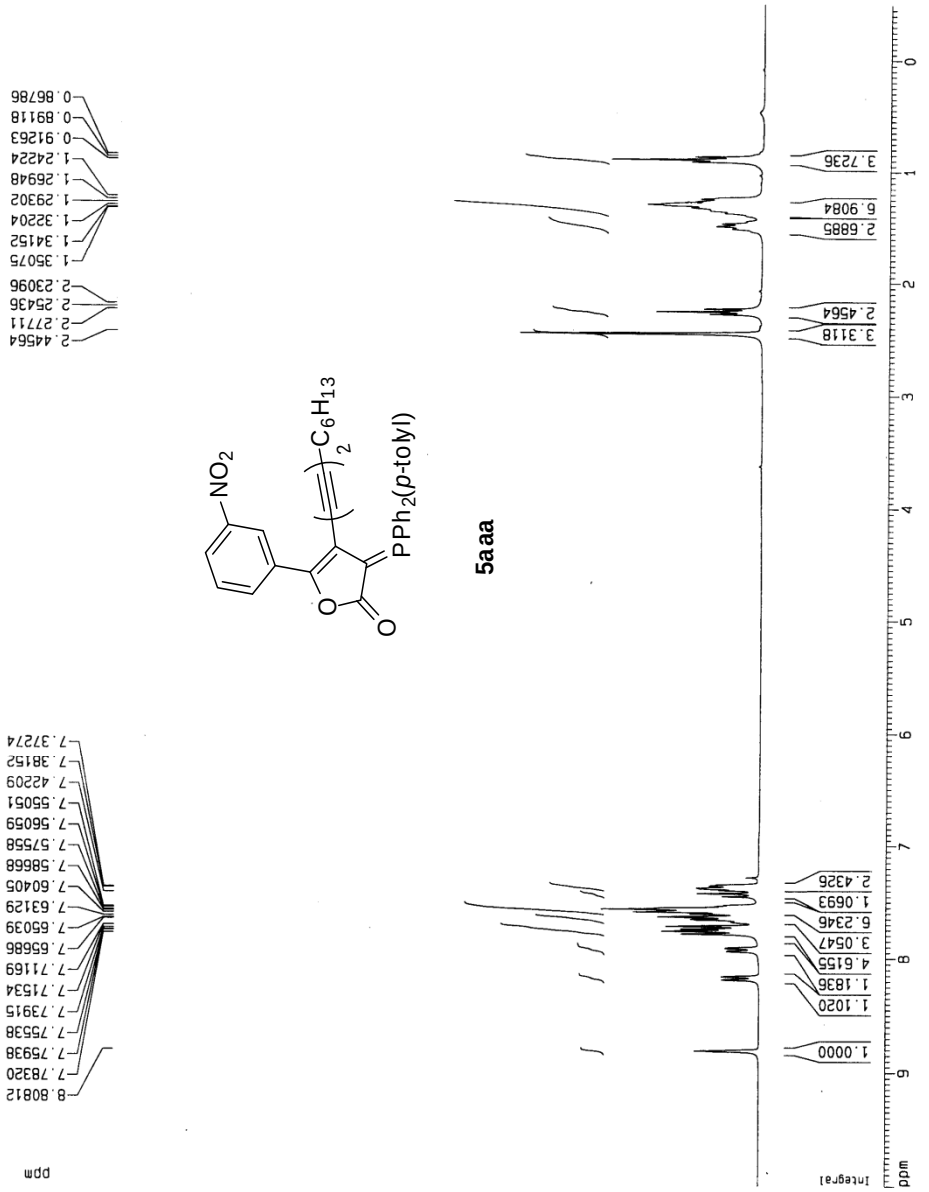


Fig. S136. ^{13}C NMR spectra of compound **5aaa** (75.5 MHz, $CDCl_3$)

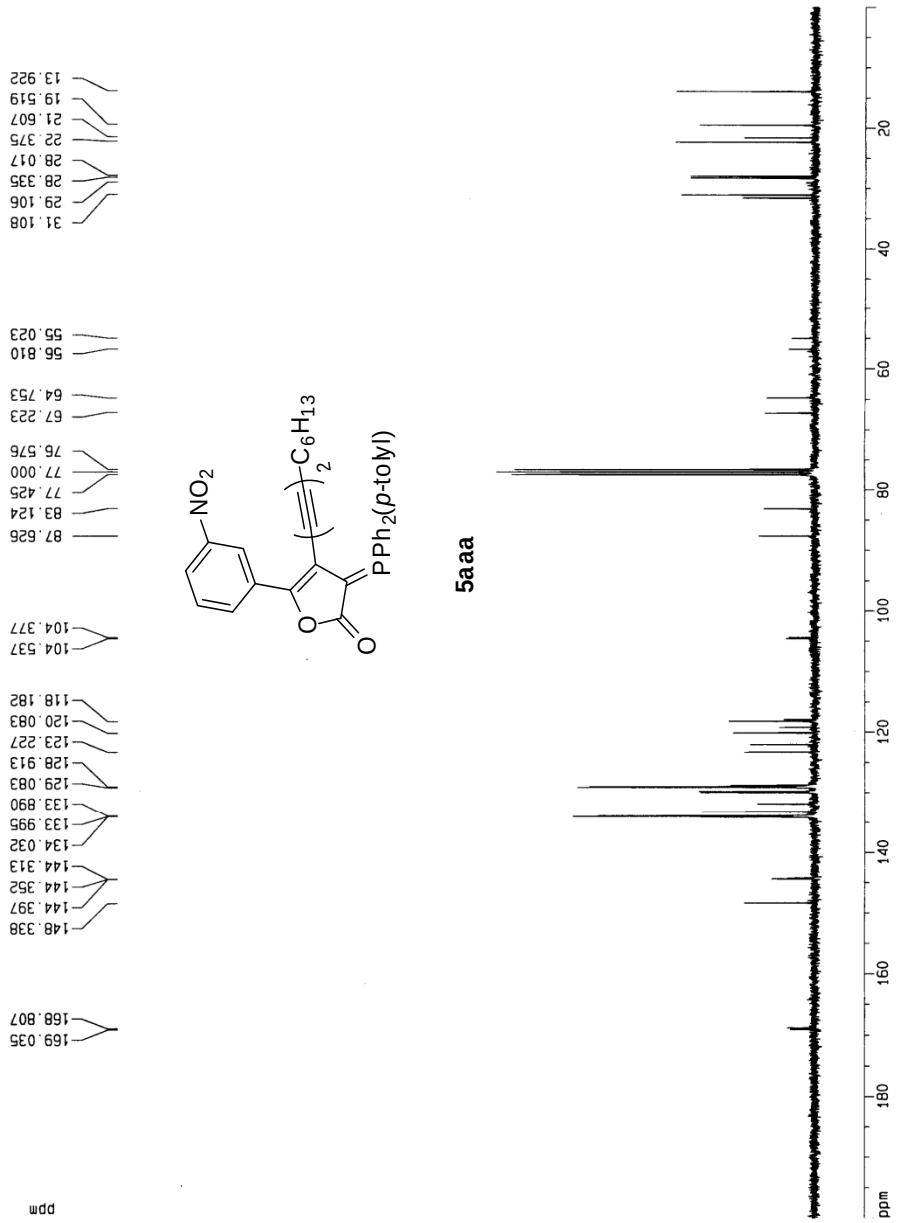


Fig. S137. ^{1}H NMR spectra of compound **5aab** (400 MHz, $CDCl_3$)

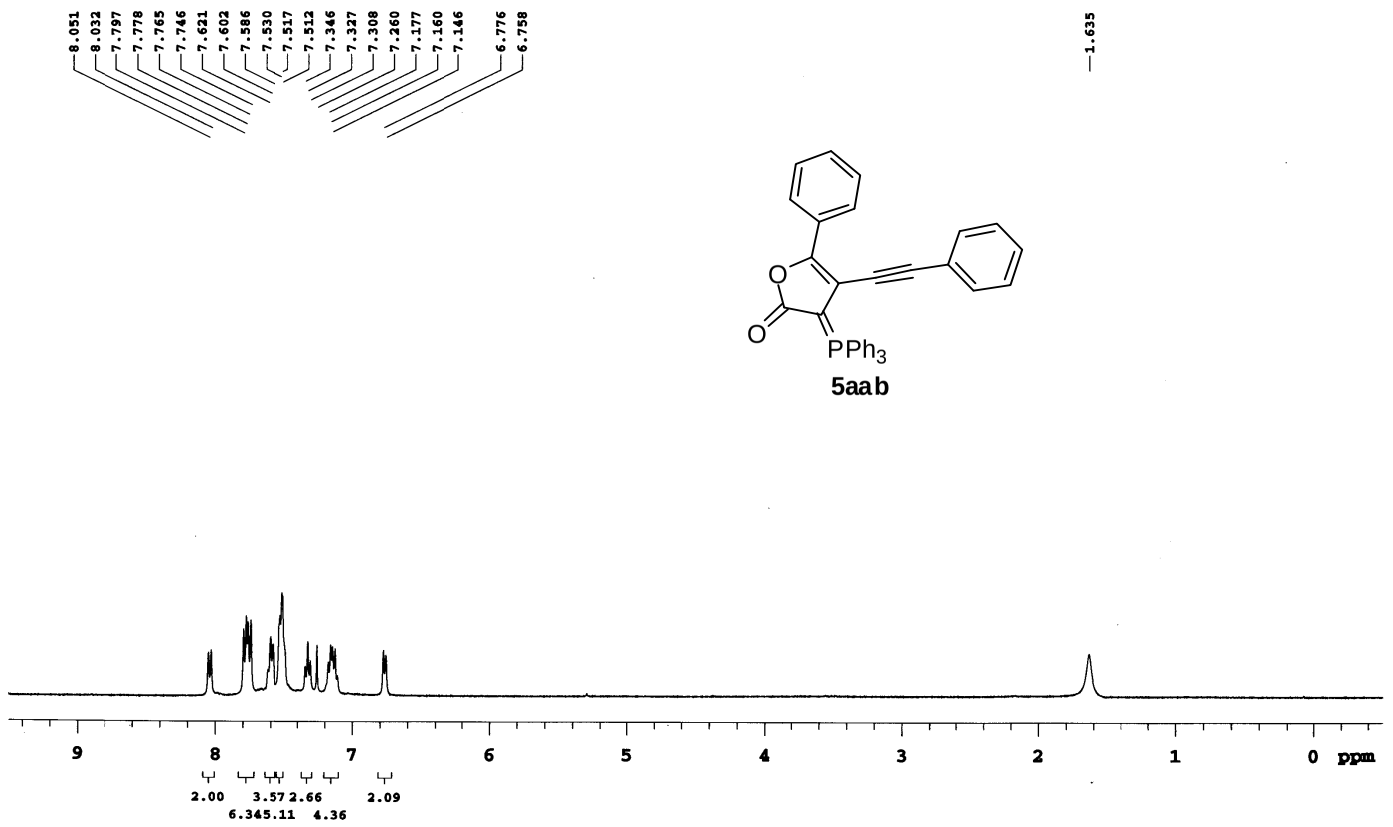


Fig. S138. ^{13}C NMR spectra of compound **5aab** (100 MHz, $CDCl_3$)