Supporting Information

Multicomponent Reactions of Phosphines, Diynedioates and Aryl Aldehydes Generated Furans Appending Reactive Phosphorus Ylides through Cumulated Trienoates as Key Intermediates: A Phosphine α-Addition-δ-Evolvement of an Anion Pathway

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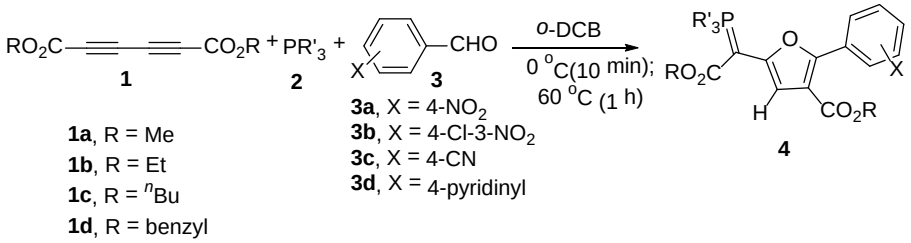
Table S1. Reaction scope of diynedioates **1**, phosphines **2**, and aldehydes **3** to generate furans **4** with [**3**] = 0.026 M.[a]



entry	**1**	**2**, PR′$_3$	**3**	**4**	yield (%)[b]
1	**1a**	**2a**, PPh_3	**3a**	**4a**	71 (75)
2	**1a**	**2b**, P(*p*-tolyl)$_3$	**3a**	**4b**	76(79)
3	**1a**	**2c**, PPh_2(*p*-tolyl)	**3a**	**4c**	68 (72)
4	**1a**	**2d**, P(4-OMe-Ph)$_3$	**3a**	**4d**	72 (76)
5	**1a**	**2e**, P(4-Cl-Ph)$_3$	**3a**	**4e**	40 (46)
6	**1a**	**2f**, P(4-F-Ph)$_3$	**3a**	**4f**	55 (60)
7	**1a**	**2g**, P(2-thienyl)$_3$	**3a**	**4g**	42 (46)
8[c]	**1a**	**2h**, HMPT	**3a**	**4h**	54
9	**1a**	**2a**, PPh_3	**3b**	**4i**	58 (62)
10	**1a**	**2d**, P(4-OMe-Ph)$_3$	**3b**	**4j**	57 (60)
11	**1a**	**2a**, PPh_3	**3c**	**4k**	59 (63)
12	**1a**	**2b**, P(*p*-tolyl)$_3$	**3c**	**4l**	71 (74)
13	**1a**	**2c**, PPh_2(*p*-tolyl)	**3c**	**4m**	68 (71)
14	**1a**	**2d**, P(4-OMe-Ph)$_3$	**3c**	**4n**	60 (65)
15	**1a**	**2i**, PCy_3	**3c**	**4o**	69
16	**1a**	**2b**, P(*p*-tolyl)$_3$	**3d**	**4p**	55 (60)
17	**1a**	**2d**, P(4-OMe-Ph)$_3$	**3d**	**4q**	47 (50)
18	**1b**	**2a**, PPh_3	**3a**	**4r**	67 (71)
19	**1c**	**2a**, PPh_3	**3a**	**4s**	77 (81)
20	**1d**	**2a**, PPh_3	**3a**	**4t**	50 (55)

[a]All reactions were performed with **1a**:**2a**:**3a** = 2:2:1 where [**3**] = 0.026 M (0.21 mmol in 8 mL of *o*-DCB after injection) in anhydrous condition unless otherwise noted. [b]Yields (%) in parentheses were determined based on converted aldehydes. [c]Injection at 0 °C for 10 min and reaction at rt for 1 h after injection.

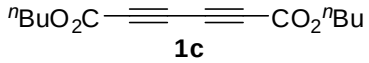
General Methods

All reactions were performed under argon. Anhydrous benzene and THF were distilled from sodium/benzophenone under argon. The chemical shift of ^{31}P NMR was taken with reference to 85% H_3PO_4 in D_2O and that of ^{1}H and ^{13}C with reference to TMS or $CHCl_3$.

General procedure for synthesis di-*n*-butyl hexa-2,4-diynedioates 1a-c:[1]

First, Hay catalyst is prepared by stirring 20 mol % of CuCl (1.26 mmol) and 3 mol % of TMEDA (tetramethylethylenediamine, 0.19 mmol) in anhydrous acetone (15 mL) with simultaneous bubbling of a stream of O_2 for 40 min. Another solution of methyl, ethyl, *n*-butyl or benzyl propiolate (12.6 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 oils or solid products. Spectral data of new compound follows:

Di-*n*-butyl hexa-2,4-diynedioate (1c):

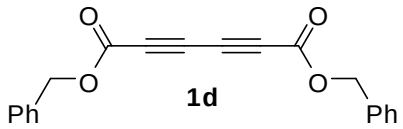


1c

Pale yellow oil. R_f = 0.31 (DCM/hexanes, 1:3). Isolated: yield 80% (1265 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 5.4 Hz, 6H), 1.39 (sext, *J* = 5.4 Hz, 4H), 1.65 (quint, *J* = 5.1 Hz, 4H), 4.21 (t, *J* = 5.1 Hz, 4H) ppm; ^{13}C NMR (100.0 MHz, $CDCl_3$) δ 13.5, 18.9, 30.2, 66.8, 67.8, 72.5, 151.8 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1720, 2157 cm^{-1}; HRMS (EI^{+}), calcd for $C_{10}H_9O_3$ (M-73) 177.0552, found 177.0547.

Dibenzyl hexa-2,4-diynedioate (1d):

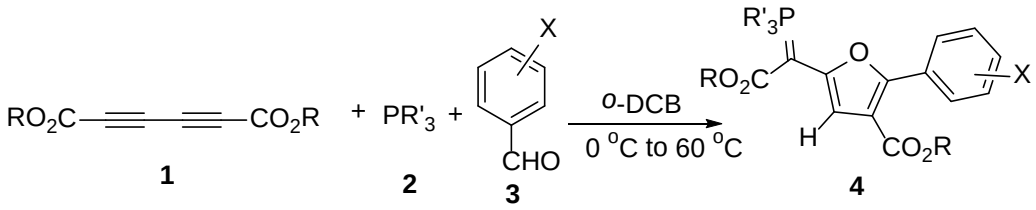
[1] Compounds **1a-b** were known: for **1a**, see: J. A. Varela, L. Castedo, M. Maestro, J. Mahía, C. Saá, *Chem. Eur. J.* **2001**, *7*, 5203-5213; for **1b**, see: H.-F. Jiang, J.-Y. Tang, A.-Z. Wang, G.-H. Deng, S.-R. Yang, *Synthesis*, **2006**, 1155–1161.



1d

Pale yellow oil. R_f = 0.30 (EA/hexanes, 1:20). Isolated: yield 60% (1202 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.25 (s, 4H), 7.40 (s, 10H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 68.3, 68.6, 72.6, 128.7, 128.8, 129.0, 134.1, 151.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1713, 2160 cm^{-1}; HRMS (EI^+), calcd for $C_{20}H_{14}O_4Na$ ($M+Na^+$) 341.0784, found 341.0784.

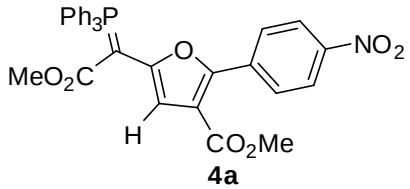
General procedure for the synthesis of furans 4a-t.



1 **2** **3** **4**

To 25 mL of anhydrous *o*-DCB solution containing phoshpines **2** (0.132 mmol) and aldehydes **3** (0.066 mmol) was added a solution of diynedioates **1** (0.132 mmol in 25 mL of *o*-DCB) *via* a digital syringe pump in 10 minutes at 0 °C. Upon completion of injection, the mixture was stirred for another 1 h at 60 °C. The mixture was then subjected to flash chromatography with EA/hexanes as eluents to give furans **4**.

Methyl 5-(2-methoxy-2-oxo-1-(triphenylphosphoranylidene)ethyl)-2-(4-nitrophenyl)furan-3-carboxylate (4a):

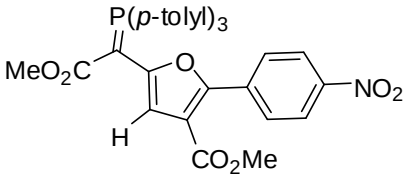


4a

Red oil. R_f = 0.26 (EA/hexanes = 1:1). Isolated yield: 90% (34 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.48 (s, 3H), 3.80 (s, 3H), 6.66 (d, *J* = 1.8 Hz, 1H), 7.44–7.52 (m,

11H), 7.54–7.72 (m, 6H), 8.03 (d, J = 9.0 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) δ 41.8 (d, $^1J_{PC}$ = 130.9 Hz), 50.1, 51.5, 112.5, 117.8, 122.9, 126.2 (d, $^1J_{PC}$ = 92.1 Hz), 127.3, 128.6 (d, $^3J_{PC}$ = 12.4 Hz), 132.1, 133.4 (d, $^2J_{PC}$ = 9.8 Hz), 136.0, 146.2, 150.0, 154.5 (d, $^2J_{PC}$ = 9.0 Hz), 164.1, 169.1 (d, $^2J_{PC}$ = 13.9 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 18.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1623, 1718 cm^{-1}; HRMS (ESI^+), calcd for $C_{33}H_{26}NO_7P$ (M^+) 579.1447 found 579.1450.

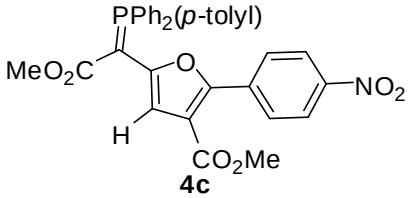
Methyl 5-(2-methoxy-2-oxo-1-(tri-*p*-tolylphosphoranylidene)ethyl)-2-(4-nitrophenyl)furan-3-carboxylate (4b):



4b

Red oil. R_f = 0.26 (EA/hexanes = 1:1.5). Isolated yield: 83% (34 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 9H), 3.47 (s, 3H), 3.81 (s, 3H), 6.66 (d, J = 1.8 Hz, 1H), 7.25 (dd, J = 2.4 Hz, J = 3.0 Hz, 6H), 7.51–7.58 (m, 8H), 8.02 (d, J = 9.1 Hz, 2H) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 21.4, 42.8 (d, $^1J_{PC}$ = 130.6 Hz), 50.1, 51.6, 111.9, 117.9, 122.9, 123.0 (d, $^1J_{PC}$ = 94.4 Hz), 127.2, 129.4 (d, $^3J_{PC}$ = 12.2 Hz), 133.4 (d, $^2J_{PC}$ = 10.0 Hz), 136.1, 142.7 (d, $^4J_{PC}$ = 2.3 Hz), 146.1, 149.6, 155.1 (d, $^2J_{PC}$ = 7.7 Hz), 164.2, 169.1 (d, $^2J_{PC}$ = 14.3 Hz) ppm; ^{31}P NMR (202.3 Hz, $CDCl_3$) 18.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1623, 1718 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{32}NO_7P$ (M^+) 621.1916 found 621.1916.

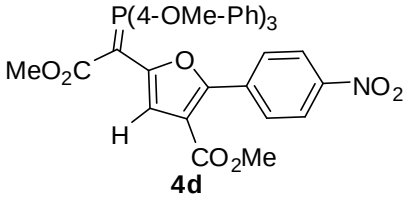
Methyl 5-(1-(diphenyl(*p*-tolyl)phosphoranylidene)-2-methoxy-2-oxoethyl)-2-(4-nitrophenyl)furan-3-carboxylate (4c)



4c

Red oil. R_f = 0.26 (EA/hexanes = 1:1.5). Isolated yield: 81% (32 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.47 (s, 3H), 3.81 (s, 3H), 6.66 (d, *J* = 1.7 Hz, 1H), 7.25–7.29 (m, 2H), 7.44–7.48 (m, 4H), 7.50–7.59 (m, 6H), 7.64–7.71 (m, 4H), 8.03 (d, *J* = 9.1 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) δ 21.4, 42.1 (d, $^1J_{PC}$ = 131.1 Hz), 50.0, 51.5, 112.3, 117.8, 122.5 (d, $^1J_{PC}$ = 94.3 Hz), 122.8, 126.5 (d, $^1J_{PC}$ = 92.4 Hz), 128.3, 128.6 (d, $^3J_{PC}$ = 12.4 Hz), 129.5 (d, $^3J_{PC}$ = 12.8 Hz), 132.0, 133.4 (d, $^2J_{PC}$ = 10.1 Hz), 133.5 (d, $^2J_{PC}$ = 12.5 Hz), 136.0, 142.9, 146.2, 149.8, 154.7 (d, $^2J_{PC}$ = 8.7 Hz), 164.1, 169.1 (d, $^2J_{PC}$ = 14.5 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 18.4; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1623, 1718 cm^{-1}; HRMS (ESI^+), calcd for $C_{34}H_{28}NO_7P$ (M^+) 593.1603 found 593.1606.

Methyl 5-(2-methoxy-2-oxo-1-(tris(4-methoxyphenyl)phosphoranylidene)ethyl)-2-(4-nitrophenyl)furan-3-carboxylate (4d):



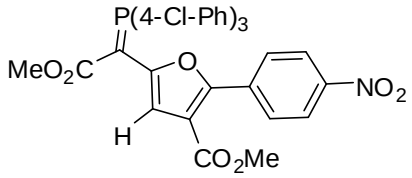
4d

Red oil. R_f = 0.31 (EA/hexanes = 2:1). Isolated yield: 85% (38 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.49 (s, 3H), 3.80 (s, 9H), 3.81 (s, 3H), 6.62 (d, *J* = 2.0 Hz, 1H), 6.94 (dd, *J* = 2.3, 8.9 Hz, 6H), 7.62–7.54 (m, 8H), 8.03 (d, *J* = 9.1 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) δ 43.4 (d, $^1J_{PC}$ = 131.5 Hz), 50.0, 51.5, 55.3, 111.9, 114.2 (d, $^3J_{PC}$ = 13.6 Hz), 117.5 (d, $^1J_{PC}$ = 99.1 Hz), 117.9, 122.9, 127.2, 135.2 (d, $^2J_{PC}$ =

11.3 Hz), 136.1, 146.1, 149.7, 155.3 (d, $^2J_{PC}$ = 8.6 Hz), 162.5, 164.2, 169.0 (d, $^2J_{PC}$ = 14.8 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 16.5 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1625, 1717 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{32}NO_{10}P$ (M^+) 669.1764 found 669.1759.

Methyl

5-(2-methoxy-2-oxo-1-(tris(4-chlorophenyl)phosphoranylidene)ethyl)-2-(4-nitrophenyl)furan-3-carboxylate (4e):

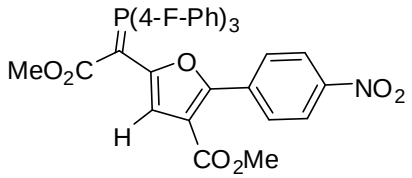


4e

Orange oil. R_f = 0.28 (EA/hexanes = 1:3). Isolated yield: 65% (29 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.53 (s, 3H), 3.82 (s, 3H), 6.58 (d, *J* = 2.0 Hz, 1H), 7.45 (dd, *J* = 2.3, 8.5 Hz, 6H), 7.52–7.64 (m, 8H), 8.11 (d, *J* = 9.0 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) δ 41.1 (d, $^1J_{PC}$ = 133.9 Hz), 50.5, 51.7, 113.6, 117.7, 123.2, 124.1 (d, $^1J_{PC}$ = 94.6 Hz), 127.6, 129.4 (d, $^3J_{PC}$ = 13.1 Hz), 134.6 (d, $^2J_{PC}$ = 10.8 Hz), 135.8, 139.6, 146.8, 150.8, 153.2 (d, $^2J_{PC}$ = 9.5 Hz), 163.9, 169.4 (d, $^2J_{PC}$ = 13.7 Hz) ppm; ^{31}P NMR (202.3 Hz, $CDCl_3$) 17.8 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1616, 1718 cm^{-1}; HRMS (ESI^+), calcd for $C_{33}H_{23}Cl_3NO_7P$ (M^+) 681.0278 found 681.0281.

Methyl

5-(2-methoxy-2-oxo-1-(tris(4-fluorophenyl)phosphoranylidene)ethyl)-2-(4-nitrophenyl)furan-3-carboxylate (4f):



4f

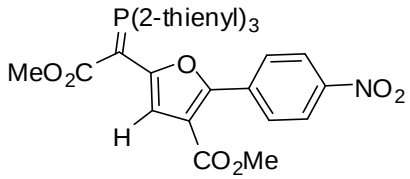
Red oil. R_f = 0.21 (EA/hexanes = 1:2.5). Isolated yield: 77% (32 mg). ^{1}H NMR (300

MHz, $CDCl_3$) δ 3.53 (s, 3H), 3.81 (s, 3H), 6.57 (d, *J* = 2.4 Hz, 1H), 7.15–7.21 (m, 6H), 7.61–7.72 (m, 8H), 8.10 (d, *J* = 9.1 Hz, 2H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) δ 41.5 (d, $^1J_{pc}$ = 134.2 Hz), 50.4, 51.6, 113.7, 116.4 (dd, $^3J_{PC}$ = 13.9 Hz, $^2J_{FC}$ = 21.5 Hz), 117.6, 121.7 (dd, $^4J_{FC}$ = 3.2 Hz, $^1J_{PC}$ = 96.1 Hz,), 123.1, 127.5, 135.9 (dd, $^3J_{FC}$ = 8.9 Hz, $^2J_{PC}$ = 11.6 Hz), 135.9, 146.7, 150.8, 153.5 (d, $^2J_{PC}$ = 9.8 Hz), 163.9, 165.2 (dd, $^4J_{PC}$ = 3.2 Hz, $^1J_{FC}$ = 256.0 Hz), 169.4 (d, $^2J_{PC}$ = 17.2 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 17.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1623, 1721 cm^{-1}; HRMS (ESI^+), calcd for $C_{33}H_{23}F_3NO_7P$ (M^+) 633.1164 found 633.1165.

Methyl

5-(2-methoxy-2-oxo-1-(tri(thiophen-2-yl)phosphoranylidene)ethyl)-2-(4-nitrophe

nyl)furan-3-carboxylate (4g):



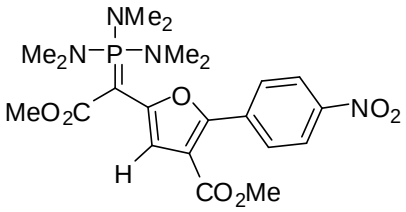
4g

Orange oil. R_f = 0.26 (EA/hexanes = 1:1). Isolated yield: 62% (24 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (s, 3H), 3.81 (s, 3H), 6.62 (d, *J* = 2.8 Hz, 1H), 7.16–7.18 (m, 3H), 7.52 (dd, *J* = 3.6, 8.4 Hz, 3H), 7.77 (t, *J* = 4.4 Hz, 3H), 7.85 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.4 (d, $^1J_{PC}$ = 143.5 Hz), 50.5, 51.6, 113.9 (d, $^3J_{PC}$ = 7.6 Hz), 117.7 (d, $^4J_{PC}$ = 1.2 Hz), 123.1, 127.7, 128.3 (d, $^3J_{PC}$ = 15.2 Hz), 128.4 (d, $^1J_{PC}$ = 113.4 Hz), 135.5 (d, $^2J_{PC}$ = 5.3 Hz), 136.0, 138.5 (d, $^2J_{PC}$ = 11.0 Hz), 146.6, 151.0, 152.7 (d, $^2J_{PC}$ = 11.4 Hz), 164.0, 169.1 (d, $^2J_{PC}$ = 17.1 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) -4.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1623, 1718 cm^{-1}; HRMS (ESI^+), calcd for $C_{27}H_{20}NO_7PS_3$ (M^+) 597.0140 found 597.0133.

Methyl

5-(2-methoxy-2-oxo-1-(tris(dimethylamino)phosphoranylidene)ethyl)-2-(4-nitrop

henyl)furan-3-carboxylate (4h):



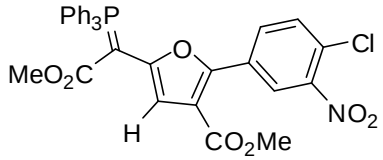
4h

Red oil. R_f = 0.31 (EA). Isolated: yield 66% (21 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.65 (d, *J* = 9.5 Hz, 18H), 3.62 (s, 3H), 3.85 (s, 3H), 6.61 (s, 1H), 8.24 (s, 4H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 37.4 (d, $^2J_{PC}$ = 4.9 Hz), 46.3 (d, $^1J_{PC}$ = 193.8 Hz), 50.1 (d, $^6J_{PC}$ = 1.3 Hz), 51.6, 111.7 (d, $^3J_{PC}$ = 6.6 Hz), 118.0, 123.4, 127.4, 136.3, 146.4, 150.4, 156.0 (d, $^2J_{PC}$ = 9.6 Hz), 164.3, 169.2 (d, $^2J_{PC}$ = 18.3 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 58.3 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1646, 1717 cm^{-1}; HRMS (ESI^+), calcd for $C_{21}H_{29}N_4O_7P$ (M^+) 480.1774 found 480.1778.

Methyl

2-(4-chloro-3-nitrophenyl)-5-(2-methoxy-2-oxo-1-(triphenylphosphoranylidene)et

hyl)furan-3-carboxylate (4i):

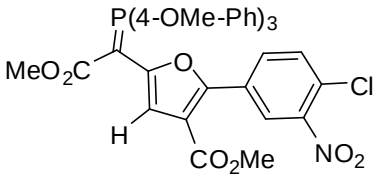


4i

Orange oil. R_f = 0.38 (EA/hexanes = 1:1). Isolated yield: 72% (29 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.47 (s, 3H), 3.80 (s, 3H), 6.63 (d, *J* = 1.2 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.43–7.48 (m, 6H), 7.51–7.54 (m, 2H), 7.64–7.70 (m, 8H), 7.85 (dd, *J* = 2.0, 8.60 Hz, 1H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) δ 41.5 (d, $^1J_{PC}$ = 131.4 Hz), 50.1, 51.5, 112.5, 116.9, 123.4, 125.1, 126.1 (d, $^1J_{PC}$ = 92.1 Hz), 128.7 (d, $^3J_{PC}$ = 12.4 Hz), 130.0, 130.9, 131.3, 132.1, 133.4 (d, $^2J_{PC}$ = 9.8 Hz), 147.5, 149.1, 153.9 (d, $^2J_{PC}$ = 8.7 Hz), 164.0, 169.2 (d, $^2J_{PC}$ = 15.4 Hz) ppm; ^{31}P NMR (202.3 Hz, $CDCl_3$) 18.7 ppm;

FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1622, 1717 cm^{-1}; HRMS (ESI^+), calcd for $C_{33}H_{25}ClNO_7P$ (M^+) 613.1057 found 613.1049.

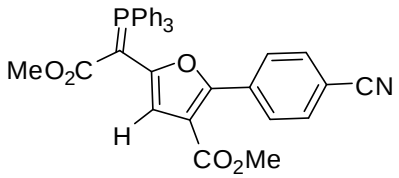
Methyl 2-(4-chloro-3-nitrophenyl)-5-(2-methoxy-2-oxo-1-(tris(4-methoxyphenyl)phosphoranylidene)ethyl)furan-3-carboxylate (4j):



4j

Orange oil. R_f = 0.23 (EA/hexanes = 1:1). Isolated yield: 70% (32 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 3.49 (s, 3H), 3.84 (s, 12H), 6.59 (d, *J* = 1.8 Hz, 1H), 6.94 (dd, *J* = 2.3, 8.9 Hz, 6H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.51–7.60 (m, 6H), 7.67 (d, *J* = 2.1 Hz, 1H), 7.94 (dd, *J* = 2.1, 8.6 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 43.0 (d, $^1J_{PC}$ = 131.6 Hz), 50.1, 51.6, 55.3, 111.9, 114.3 (d, $^3J_{PC}$ = 13.4 Hz), 116.9, 117.3 (d, $^1J_{PC}$ = 99.1 Hz), 123.4, 125.1, 130.2, 130.9, 131.4, 135.2 (d, $^2J_{PC}$ = 11.4 Hz), 147.5, 148.9, 154.7 (d, $^2J_{PC}$ = 8.8 Hz), 162.5 (d, $^4J_{PC}$ = 2.9 Hz), 164.2, 169.2 (d, $^2J_{PC}$ = 15.1 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 16.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1623, 1717 cm^{-1}; HRMS (ESI^+), calcd for $C_{36}H_{31}ClNO_{10}P$ (M^+) 703.1374 found 703.1367.

Methyl 2-(4-cyanophenyl)-5-(2-methoxy-2-oxo-1-(triphenylphosphoranylidene)ethyl)furan-3-carboxylate (4k):

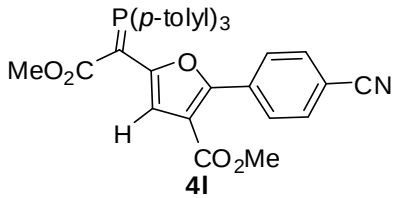


4k

Orange oil. R_f = 0.33 (EA/hexanes = 1:1). Isolated yield: 92% (34 mg). ^1H NMR (300

MHz, $CDCl_3$) δ 3.47 (s, 3H), 3.78 (s, 3H), 6.60 (d, *J* = 2.0 Hz, 1H), 7.44–7.48 (m, 8H), 7.50–7.56 (m, 5H), 7.63–7.70 (m, 6H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) δ 41.3 (d, $^1J_{PC}$ = 131.7 Hz), 50.1, 51.4, 110.5, 112.8, 117.0, 118.9, 126.2 (d, $^1J_{PC}$ = 92.1 Hz), 127.4, 128.6 (d, $^3J_{PC}$ = 12.4 Hz), 131.3, 132.1, 133.4 (d, $^2J_{PC}$ = 9.8 Hz), 134.2, 150.7, 153.8 (d, $^2J_{PC}$ = 9.3 Hz), 164.1, 169.2 (d, $^2J_{PC}$ = 15.2 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 18.9 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1624, 1718, 2226 cm^{-1}; HRMS (ESI^+), calcd for $C_{34}H_{26}NO_5P$ (M^+) 559.1549 found 559.1544.

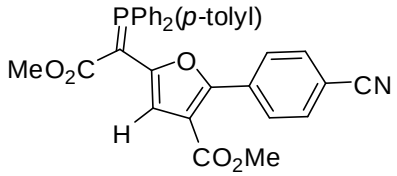
Methyl 2-(4-cyanophenyl)-5-(2-methoxy-2-oxo-1-(tri-*p*-tolylphosphoranylidene)ethyl)furan-3-carboxylate (4l):



4l

Orange oil. R_f = 0.18 (EA/hexanes = 1:2). Isolated yield: 85% (34 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 9H), 3.47 (s, 3H), 3.78 (s, 3H), 6.61 (s, 1H), 7.24 (dd, *J* = 2.5, 8.1, 6H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.50–7.57 (m, 8H) ppm; ^{13}C NMR (150.7 MHz, $CDCl_3$) δ 21.3, 42.1 (d, $^1J_{PC}$ = 131.4 Hz), 49.9, 51.3, 110.2, 112.1, 117.0, 118.9, 123.1 (d, $^1J_{PC}$ = 94.5 Hz), 127.2, 129.2 (d, $^3J_{PC}$ = 12.8 Hz), 1311, 133.3 (d, $^2J_{PC}$ = 10.1 Hz), 134.2, 142.5, 150.3, 154.3 (d, $^2J_{PC}$ = 8.8 Hz), 164.1, 169.1 (d, $^2J_{PC}$ = 15.1 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 17.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1627, 1717, 2225 cm^{-1}; HRMS (ESI^+), calcd for $C_{37}H_{32}NO_5P$ (M^+) 601.2018 found 601.2012.

Methyl 2-(4-cyanophenyl)-5-(1-(diphenyl(*p*-tolyl)phosphoranylidene)-2-methoxy-2-oxoethyl)furan-3-carboxylate (4m):

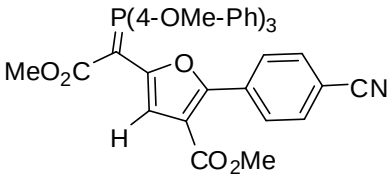


4m

Orange oil. R_f = 0.22 (EA/hexanes = 1:1.5). Isolated yield: 79% (30 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.47 (s, 3H), 3.79 (s, 3H), 6.60 (d, *J* = 1.3 Hz, 1H), 7.23–7.27 (m, 2H), 7.43–7.57 (m, 12H), 7.63–7.69 (m, 4H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.4, 41.6 (d, $^1J_{PC}$ = 131.6 Hz), 50.1, 51.4, 110.3, 112.5, 116.9, 118.9, 122.4 (d, $^1J_{PC}$ = 94.4 Hz), 126.3 (d, $^1J_{PC}$ = 92.0 Hz), 127.3, 128.5 (d, $^3J_{PC}$ = 12.4 Hz), 129.4 (d, $^3J_{PC}$ = 12.8 Hz), 131.3, 132.0 (d, $^4J_{PC}$ = 2.6 Hz), 133.3 (d, $^2J_{PC}$ = 9.8 Hz), 133.4 (d, $^2J_{PC}$ = 10.2 Hz), 134.1, 142.8 (d, $^4J_{PC}$ = 2.7 Hz), 150.6, 153.9 (d, $^2J_{PC}$ = 9.4 Hz), 164.1, 169.2 (d, $^2J_{PC}$ = 15.2 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 18.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1626, 1717, 2226 cm^{-1}; HRMS (ESI^+), calcd for $C_{35}H_{28}NO_5P$ (M^+) 573.1705 found 573.1699.

Methyl

2-(4-cyanophenyl)-5-(2-methoxy-2-oxo-1-(tris(4-methoxyphenyl)phosphoranylide ne)ethyl)furan-3-carboxylate (4n):



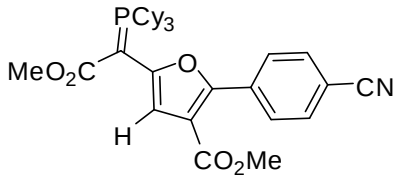
4n

Orange oil. R_f = 0.25 (EA/hexanes = 1:1). Isolated yield: 79% (34 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.48 (s, 3H), 3.83 (s, 12H), 6.56 (s, 1H), 6.92–6.94 (m, 6H), 7.46–7.59 (m, 10H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 42.9 (d, $^1J_{PC}$ = 131.9 Hz), 50.1, 51.5, 55.3, 110.2, 112.2, 114.2 (d, $^3J_{PC}$ = 13.4 Hz), 117.0, 117.4 (d, $^1J_{PC}$ = 99.1 Hz), 119.0, 127.3, 131.3, 134.3, 135.2 (d, $^3J_{PC}$ = 11.4 Hz), 150.5, 154.5 (d, $^2J_{PC}$ = 9.3 Hz),

162.4 (d, $^{4}J_{PC}$ = 2.9 Hz), 164.3, 169.2 (d, $^{2}J_{PC}$ = 15.1 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 16.9 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1623, 1718, 2226 cm^{-1}; HRMS (ESI^+), calcd for $C_{37}H_{32}NO_8P$ (M^+) 649.1866 found 649.1863.

Methyl

2-(4-cyanophenyl)-5-(2-methoxy-2-oxo-1-(tricyclohexylphosphoranylidene)ethyl) furan-3-carboxylate (4o):

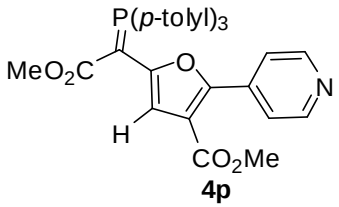


4o

Orange oil. R_f = 0.31 (EA/hexanes = 1:2). Isolated yield: 78% (30 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06–1.23 (m, 8H), 1.56–1.63 (m, 6H), 1.70–1.73 (m, 4H), 1.86–2.02 (m, 12H) , 2.51–2.62 (m, 3H), 3.55 (s, 3H), 3.84 (s, 3H), 6.57 (s. 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 8.14 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.8, 27.2 (d, $^{3}J_{PC}$ = 15.2 Hz), 27.3 (d, $^{2}J_{PC}$ = 5.7 Hz), 32.0 (d, $^{1}J_{PC}$ = 49.2 Hz), 35.0 (d, $^{1}J_{PC}$ = 115.1 Hz), 49.9, 51.5, 110.8, 113.5 (d, $^{3}J_{PC}$ = 5.3 Hz), 116.9, 118.8, 127.5, 131.7, 134.3, 151.2, 155.4 (d, $^{2}J_{PC}$ = 7.3 Hz), 164.1, 170.0 (d, $^{2}J_{PC}$ = 17.1 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 28.9 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1626, 1721, 2226 cm^{-1}; HRMS (ESI^+), calcd for $C_{34}H_{44}NO_5P$ (M^+) 577.2957 found 577.2951.

Methyl

5-(2-methoxy-2-oxo-1-(tri-*p*-tolylphosphoranylidene)ethyl)-2-(pyridin-4-yl)furan-3-carboxylate (4p):

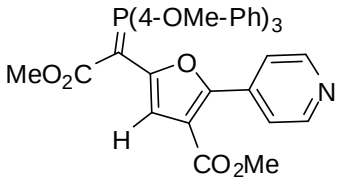


4p

Yellow oil. R_f = 0.28 (EA/hexanes = 2:1). Isolated yield: 69% (26 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 9H), 3.48 (s, 3H), 3.80 (s, 3H), 6.62 (d, *J* = 1.7 Hz, 1H), 7.22–7.25 (m, 6H), 7.31 (d, *J* = 6.3 Hz, 2H), 7.50–7.57 (m, 6H), 8.41 (d, *J* = 6.3 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.4 (d, $^5J_{PC}$ = 1.1 Hz), 42.3 (d, $^1J_{PC}$ = 131.2 Hz), 50.0, 51.5, 112.0, 117.9, 120.5, 123.0 (d, $^1J_{PC}$ = 94.5 Hz), 129.3 (d, $^3J_{PC}$ = 12.8 Hz), 133.4 (d, $^2J_{PC}$ = 10.3 Hz), 137.0, 142.6 (d, $^4J_{PC}$ = 2.9 Hz), 149.2, 149.3, 154.5 (d, $^2J_{PC}$ = 8.8 Hz), 164.2, 169.1 (d, $^2J_{PC}$ = 14.6 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 18.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1626, 1719 cm^{-1}; HRMS (ESI^+), calcd for $C_{35}H_{32}NO_5P$ (M^+) 577.2018 found 577.2013.

Methyl

5-(2-methoxy-2-oxo-1-(tris(4-methoxyphenyl)phosphoranylidene)ethyl)-2-(pyridin-4-yl)furan-3-carboxylate (4q):

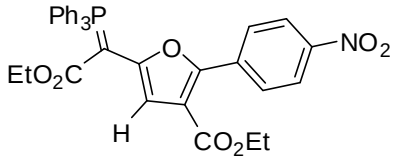


4q

Yellow oil. R_f = 0.43 (EA/DCM = 1:2). Isolated yield: 74% (31 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.49 (s, 3H), 3.79 (s, 3H), 3.81 (s, 9H), 6.58 (d, *J* = 1.8 Hz, 1H), 6.93 (dd, *J* = 2.2, 8.9 Hz, 6H), 7.4 (d, *J* = 6.2 Hz, 2H), 7.56 (dd, *J* = 8.8, 11.9 Hz, 6H), 8.43 (d, *J* = 5.9 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 43.5 (d, $^1J_{PC}$ = 132.1 Hz), 50.6, 52.0, 55.8, 112.6, 114.7 (d, $^3J_{PC}$ = 13.5 Hz), 117.9 (d, $^1J_{PC}$ = 99.1 Hz), 118.4, 121.0, 135.7 (d, $^2J_{PC}$ = 11.4 Hz), 137.6, 149.8, 149.7, 155.3 (d, $^2J_{PC}$ = 8.9 Hz), 162.9 (d, $^4J_{PC}$ = 2.8 Hz), 164.7, 169.6 (d, $^2J_{PC}$ = 14.9 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 16.9 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1623, 1722 cm^{-1}; HRMS (ESI^+), calcd for $C_{35}H_{32}NO_8P$ (M^+) 625.1866 found 625.1862.

Ethyl

5-(2-ethoxy-2-oxo-1-(triphenylphosphoranylidene)ethyl)-2-(4-nitrophenyl)furan-3-carboxylate (4r):

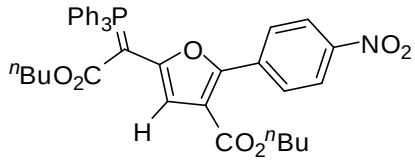


4r

Red oil. R_f = 0.30 (EA/hexanes = 1:2). Isolated yield: 70% (28 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (br, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 3.91 (q, *J* = 6.9 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 6.70 (s, 1H), 7.42–7.55 (m, 11H), 7.65–7.71 (m, 6H), 8.00 (d, *J* = 9.0 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.1, 14.3, 42.0 (d, $^1J_{PC}$ = 129.0 Hz), 58.4, 60.4, 112.0 (d, $^2J_{PC}$ = 6.4 Hz), 118.3, 122.9, 126.4 (d, $^1J_{PC}$ = 92.2 Hz), 127.2, 128.6 (d, $^3J_{PC}$ = 12.4 Hz), 132.1, 133.4 (d, $^2J_{PC}$ = 9.7 Hz), 136.1, 146.0, 149.5, 154.6 (d, $^2J_{PC}$ = 9.0 Hz), 163.7, 168.5 (d, $^2J_{PC}$ = 14.0 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 18.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1626, 1714 cm^{-1}; HRMS (ESI^+), calcd for $C_{35}H_{30}NO_7P$ (M^+) 607.1760 found 607.1761.

***n*-Butyl**

5-(2-butoxy-2-oxo-1-(triphenylphosphoranylidene)ethyl)-2-(4-nitrophenyl)furan-3-carboxylate (4s):

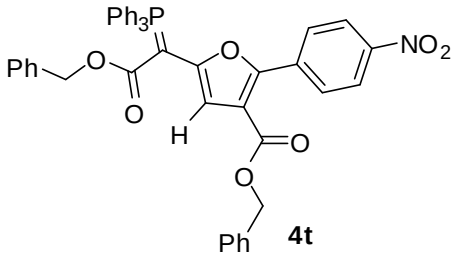


4s

Red oil. R_f = 0.31 (EA/hexanes = 1:3). Isolated yield: 82% (36 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.74 (t, *J* = 6.9 Hz, 3H), 0.96 (t, *J* = 7.5 Hz, 3H), 1.20–1.28 (m, 2H), 1.37–1.47 (m, 2H), 1.63–1.73 (m, 4H), 3.88 (t, *J* = 6.6 Hz, 2H), 4.21 (t, *J* = 6.6 Hz, 2H), 6.66 (s, 1H), 7.43–7.55 (m, 11H), 7.64–7.71 (m, 6H), 8.01 (d, *J* = 9.0 Hz, 2H)

ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.5, 13.6, 18.9, 19.1, 30.5, 30.8, 41.9 (d, $^1J_{PC}$ = 129.4 Hz), 62.3, 64.3, 111.9 (d, $^2J_{PC}$ = 6.6 Hz), 118.2, 122.9, 126.4 (d, $^1J_{PC}$ = 92.9 Hz), 127.1, 128.6 (d, $^3J_{PC}$ = 12.3 Hz), 132.0, 133.3 (d, $^2J_{PC}$ = 9.8 Hz), 136.0, 146.0, 149.5, 154.6 (d, $^2J_{PC}$ = 9.1 Hz), 163.8, 168.6 (d, $^2J_{PC}$ = 13.3 Hz) ppm; ^{31}P NMR (242.5 Hz, $CDCl_3$) 18.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1626, 1714 cm^{-1}; HRMS (ESI^+), calcd for $C_{39}H_{38}NO_7P$ (M^+) 663.2386 found 663.2388.

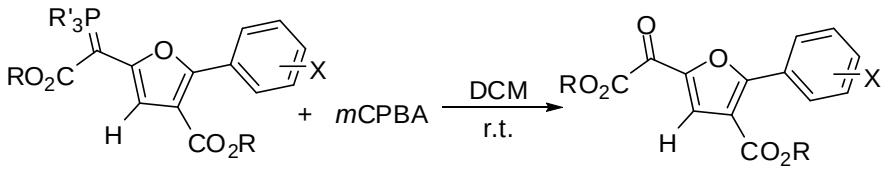
Benzyl 5-(2-(benzyloxy)-2-oxo-1-(triphenylphosphoranylidene)ethyl)-2-(4-nitrophenyl)furan-3-carboxylate (4t):



4t

Red oil. R_f = 0.37 (EA/hexanes = 1:2). Isolated yield: 64% (31 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.99 (s, 2H), 5.27 (s, 2H), 6.69 (s, 1H), 7.00–7.19 (m, 4H), 7.35–7.46 (m, 12H), 7.50–7.57 (m, 4H), 7.60–7.69 (m, 7H), 8.02 (d, J = 9.0 Hz, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 42.1 (d, $^1J_{PC}$ = 129.7 Hz), 64.5, 66.2, 112.4 (d, $^2J_{PC}$ = 6.0 Hz), 117.8, 123.0, 126.1 (d, $^1J_{PC}$ = 92.2 Hz), 127.1, 127.4, 127.7, 127.9, 128.1, 128.4, 128.5, 128.7 (d, $^3J_{PC}$ = 12.3 Hz), 132.1 (d, $^4J_{PC}$ = 1.9 Hz), 133.4 (d, $^2J_{PC}$ = 9.8 Hz), 135.8, 136.0, 137.6, 146.2, 150.3, 154.3 (d, $^2J_{PC}$ = 9.3 Hz), 163.4, 168.3 (d, $^2J_{PC}$ = 13.9 Hz) ppm; ^{31}P NMR (242.4 Hz, $CDCl_3$) 18.6 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1653, 1715 cm^{-1}; HRMS (ESI^+), calcd for $C_{45}H_{34}NO_7P$ (M^+) 731.2073 found 731.2074

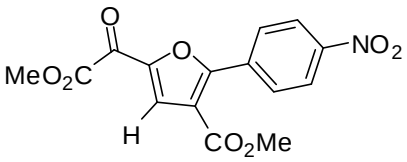
Representative procedure for the synthesis of furans 6.



4 **6**

To a 20 mL anhydrous DCM solution containing furan **4** (0.014 mmol) was added 10 mL of DCM containing *m*CPBA (0.034 mmol) through syringe slowly in 30 min at room temperature. The mixture was then stirred for another 30 min. Upon completion of the reaction, the solution was quenched with saturated sodium bicarbonate for 30 min and extracted with DCM. The extract was dried with sodium sulfate. After evaporation of DCM, the resulting solids were re-dissolved in chloroform (2 mL), precipitated with *n*-hexane (6 mL) and centrifuged for three times to give pure solids **6**.

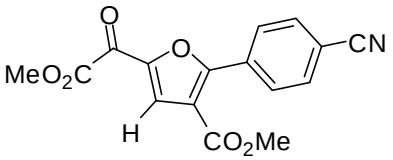
Methyl 5-(2-methoxy-2-oxoacetyl)-2-(4-nitrophenyl)furan-3-carboxylate (6a):



6a

Pale yellow solid (m.p. 199–202 ^{o}C). Quantitative isolated yield (4.7 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.93 (s, 3H), 4.00 (s, 3H), 8.17 (s, 1H), 8.33 (d, J = 9.0 Hz, 2H), 8.40 (d, J = 9.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.5, 53.5, 118.3, 123.6, 127.0, 130.2, 133.5, 148.0, 148.9, 159.4, 160.6, 162.1, 170.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1680, 1726 cm^{-1}; HRMS (ESI^{+}), calcd for $C_{15}H_{11}NO_8$ (M^{+}) 333.0485 found 333.0480.

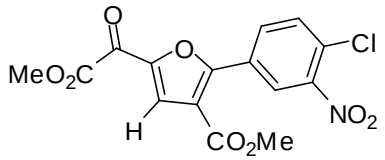
Methyl 2-(4-cyanophenyl)-5-(2-methoxy-2-oxoacetyl)furan-3-carboxylate (6b):



6b

Milky white solid (m.p. 180–183 ^{o}C). Quantitative isolated yield (4.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 3H), 4.00 (s, 3H), 7.77 (d, *J* = 8.0 Hz, 2H), 8.14 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 53.4, 114.5, 117.9, 118.1, 127.0, 129.6, 131.8, 132.1, 147.8, 159.7, 160.6, 162.1, 170.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1681, 1732, 2226 cm^{-1}; HRMS (ESI^{+}), calcd for $C_{16}H_{11}NO_6$ (M^{+}) 313.0586 found 313.0585.

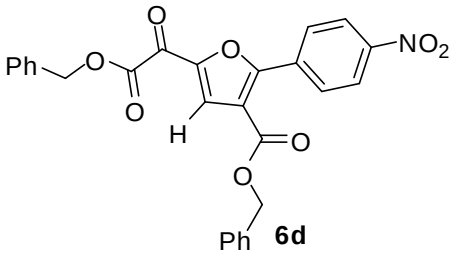
Methyl 2-(4-chloro-3-nitrophenyl)-5-(2-methoxy-2-oxoacetyl)furan-3-carboxylate (6c):



6c

Milky white solid (m.p. 125–128 ^{o}C). Quantitative isolated yield (5.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 4.00 (s, 3H), 7.67 (d, *J* = 8.4 Hz, 1H), 8.14 (s, 1H), 8.35 (dd, *J* = 2.0, 8.8 Hz, 1H), 8.88 (d, *J* = 2.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 53.5, 117.9, 126.2, 126.9, 127.6, 129.6, 132.1, 132.9, 147.7, 148.0, 158.1, 160.5, 162.0, 170.0 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1685, 1737 cm^{-1}; HRMS (ESI^{+}), calcd for $C_{15}H_{10}ClNO_8$ (M^{+}) 367.0095 found 367.0092.

Benzyl 5-(2-(benzyloxy)-2-oxoacetyl)-2-(4-nitrophenyl)furan-3-carboxylate (6d):



6d

Pale yellow oil. Quantitative yield (6.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (s, 2H), 5.40 (s, 2H), 7.37–7.40 (m, 8H), 7.44–7.47 (m, 2H), 8.10 (s, 1H), 8.25 (d, *J* = 9.2 Hz, 2H), 8.29 (d, *J* = 9.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.4, 68.5, 118.3, 123.5, 126.5, 128.6, 128.73, 128.73, 128.76, 128.77, 129.0, 130.2, 133.4, 134.1, 134.9, 148.1, 148.8, 159.3, 160.0, 161.4, 170.4 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1681, 1732 cm^{-1}; HRMS (ESI^+), calcd for $C_{27}H_{19}NO_8$ (M^+) 485.1111 found 485.1107.

Representative procedure for the synthesis of furans 7a and 7a'.

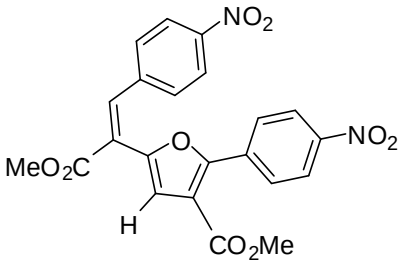
A pressure-affordable reaction tube containing ylide **4a** (0.1529 g, 0.2640 mmol), 4-nitrobenzaldehyde **3a** (0.0130 g, 0.0880 mmol), and a stirring bar in anhydrous toluene (15 mL) was bubbled argon and then stirred vigorously at 130 °C for 96 h. After completion of the reaction, the reaction mixture was subjected to column chromatography with hexanes/dichloromethane (DCM) (1:1) as eluents to obtain decarboxylated furan **7a'** (0.0151 g) in 49% yield (57% based on reacted **3a**) and with hexanes/DCM (1:3) as eluents to obtain a mixture of (*E*)- and (*Z*)-**7a** (0.0135 g) in 34% yield (39% based on reacted **3a**).

Methyl

5-(3-methoxy-1-(4-nitrophenyl)-3-oxoprop-1-en-2-yl)-2-(4-nitrophenyl)furan-3-carboxylate (7a):

Yellow solid mixtures of (*E*)-**7a** and (*Z*)-**7a**. R_f = 0.14 (DCM/hexanes = 3:1). Isolated yield: 34% (14 mg).

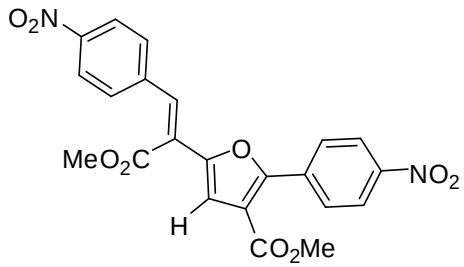
Spectral Data of Compound (*E*)-7a:



(*E*)-**7a**

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.90 (s, 3H), 7.02 (s, 1H), 7.43 (s, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 8.24 (d, *J* = 8.7 Hz, 2H), 8.31 (s, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 52.9, 117.9, 118.4, 123.6, 123.8, 126.1, 129.07, 129.14, 134.6, 139.7, 141.2, 147.5, 147.8, 148.0, 154.8, 162.9, 166.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1592, 1726 cm^{-1}; HRMS (ESI^+), calcd for $C_{22}H_{16}N_2O_9$ (M^+) 452.0856 found 452.0854.

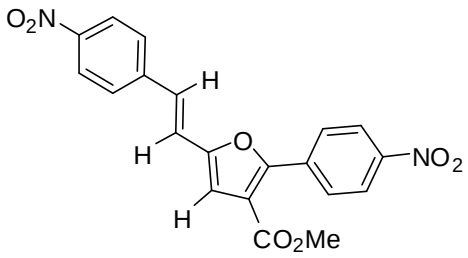
Spectral Data of Compound (*Z*)-7a:



(*Z*)-**7a**

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.89 (s, 3H), 3.94 (s, 3H), 7.12 (s, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.86 (d, *J* = 9.0 Hz, 2H), 7.94 (s, 1H), 8.13 (d, *J* = 8.7 Hz, 2H), 8.18 (d, *J* = 8.7 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 53.1, 114.2, 116.8, 123.4, 123.6, 123.9, 128.4, 130.1, 134.3, 139.7, 141.3, 147.3, 147.9, 149.5, 154.2, 163.0, 165.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1592, 1726 cm^{-1}; HRMS (ESI^+), calcd for $C_{22}H_{16}N_2O_9$ (M^+) 452.0856 found 452.0854.

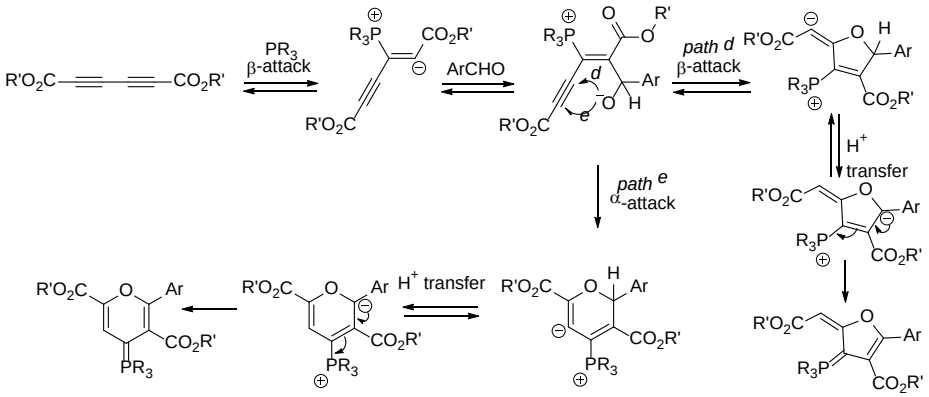
(*E*)-methyl 2-(4-nitrophenyl)-5-(4-nitrostyryl)furan-3-carboxylate (7a'):



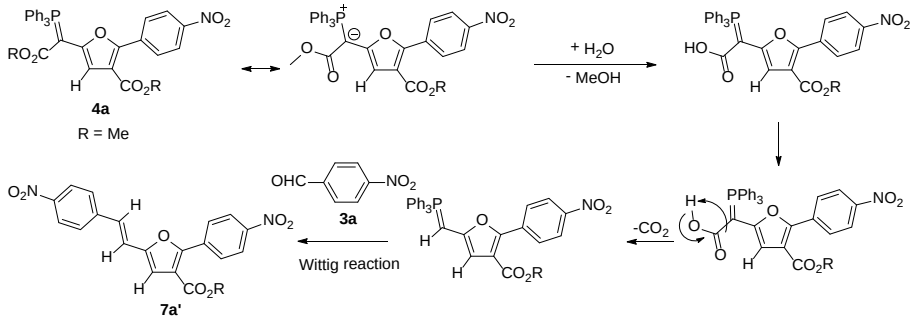
7a'

Orange Solid (m.p. 254–256 ^{o}C). R_f = 0.28 (DCM/hexanes = 1:1). Isolated yield: 49% (15 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 3H), 6.97 (s, 1H), 7.05 (d, *J* = 16.4 Hz, 1H), 7.23 (d, *J* = 16.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 8.25 (d, *J* = 8.4 Hz, 2H), 8.33 (s, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 113.9, 118.4, 118.9, 123.6, 124.3, 127.1, 127.5, 128.9, 134.9, 142.5, 147.2, 147.9, 152.0, 154.3, 163.1 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 1721 cm^{-1}; HRMS (ESI^+), calcd for $C_{20}H_{14}N_2O_7$ (M^+) 394.0801 found 394.0800.

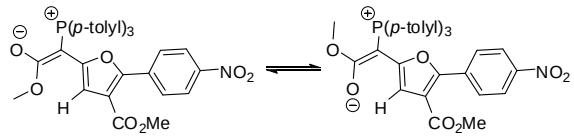
Scheme S1. Proposed mechanism through β-attack of phosphines on diynedioates **1** and formation of developed structures with arylaldehydes.



Scheme S2. Proposed mechanism for formation of furan **7a'** from reaction of **3a** and **4a** through decarboxylation.



Scheme S3. *E* and *Z* Isomerization of Furan **4b**.



***E*-4b** ***Z*-4b**

Note: We selected compound **4b** for ^{1}H and ^{31}P NMR study at variable temperature and found that the two ester groups displayed entirely different signals in the spectrum, one with sharp singlet at 3.81 ppm and the other with a broad peak at 3.47 ppm (Figures S57-58). This phenomenon could be rationalized on the basis of the existence of *E/Z* isomerism; *E*-**4b** and *Z*-**4b** underwent rapid interconversion at ambient temperature (Scheme S3). Further evidence by 2D-HMQC and 2D-HMBC correlation analyses (Fig. S59 and Fig. S60, respectively) indicated that the broad methyl signal in ^{1}H NMR spectrum corresponded to an α-phosphorus ylidic methyl ester moiety.

Fig. S1. ^{1}H NMR spectrum of compound **1c** (400 MHz, $CDCl_3$)

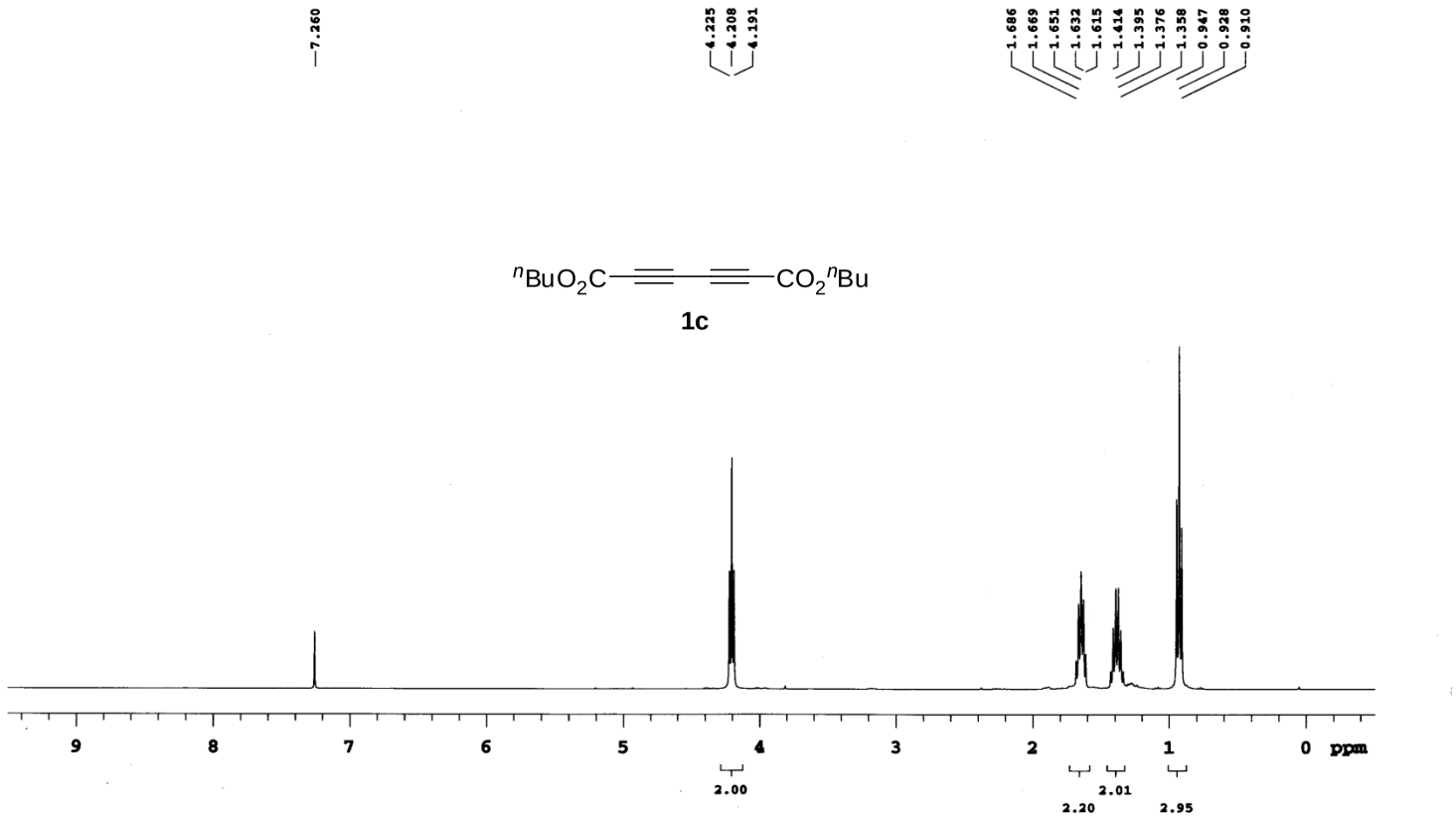


Fig. S2. ^{13}C NMR spectrum of compound **1c** (100 MHz, $CDCl_3$)

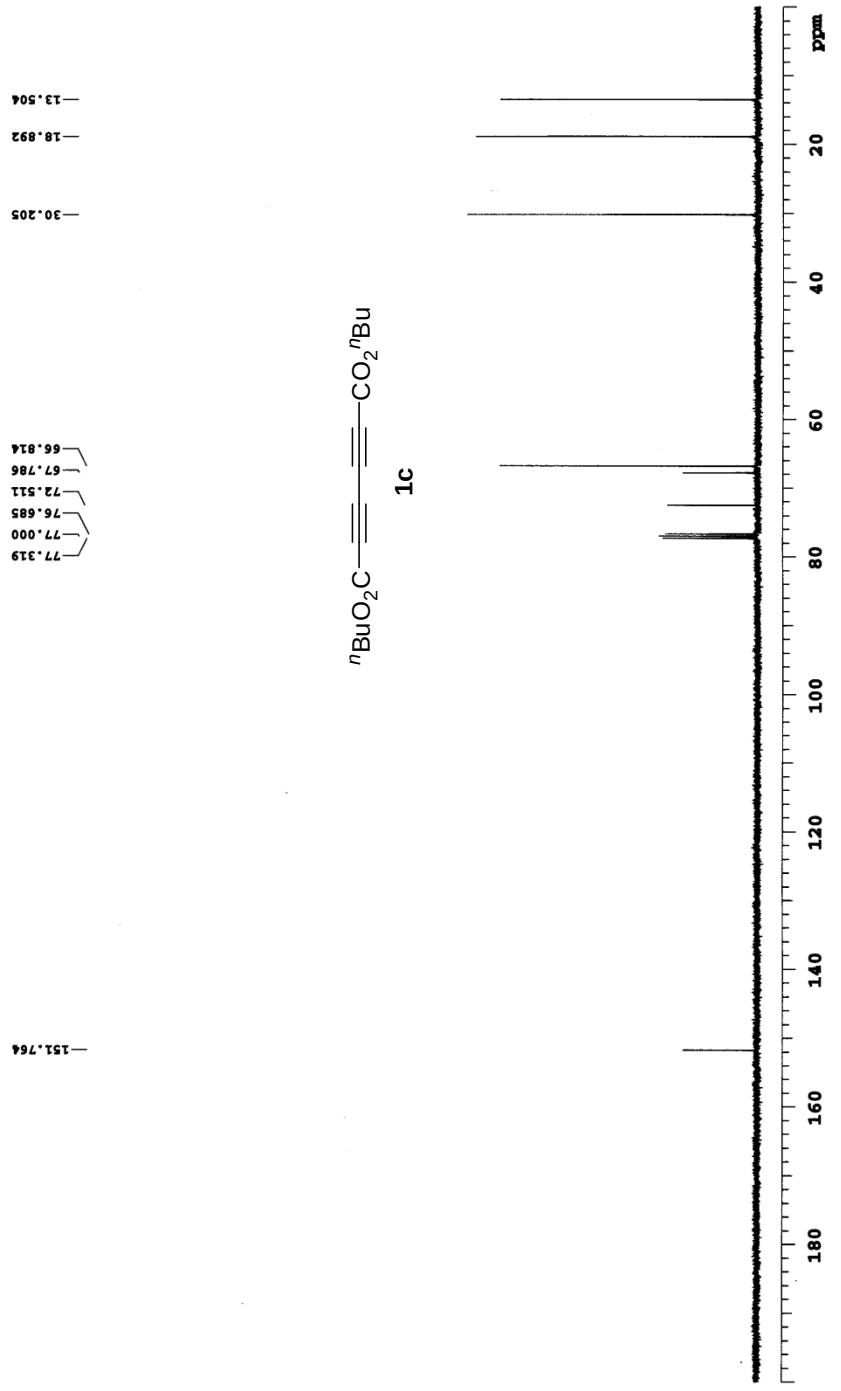


Fig. S3. ^{1}H NMR spectrum of compound **1d** (300 MHz, $CDCl_3$)

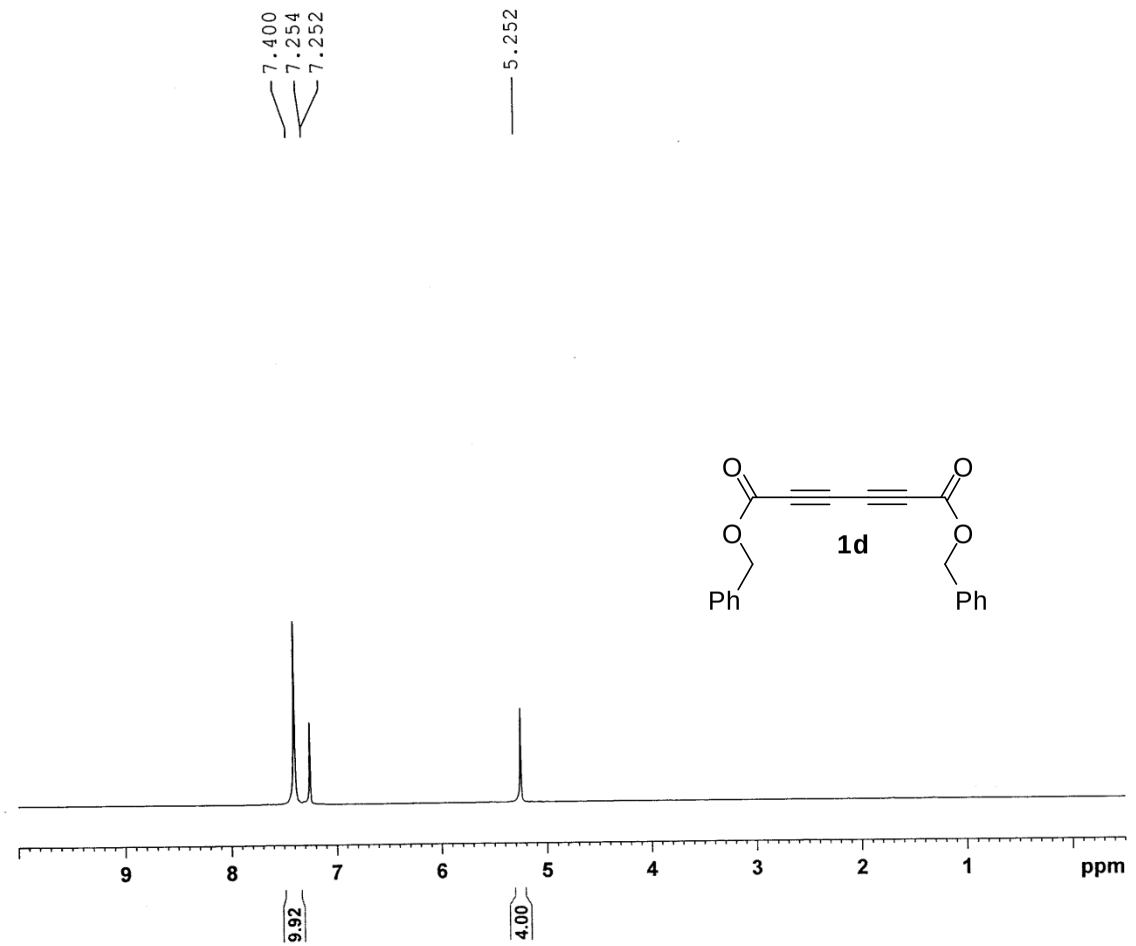


Fig. S4. ^{13}C NMR spectrum of compound **1d** (300 MHz, $CDCl_3$)

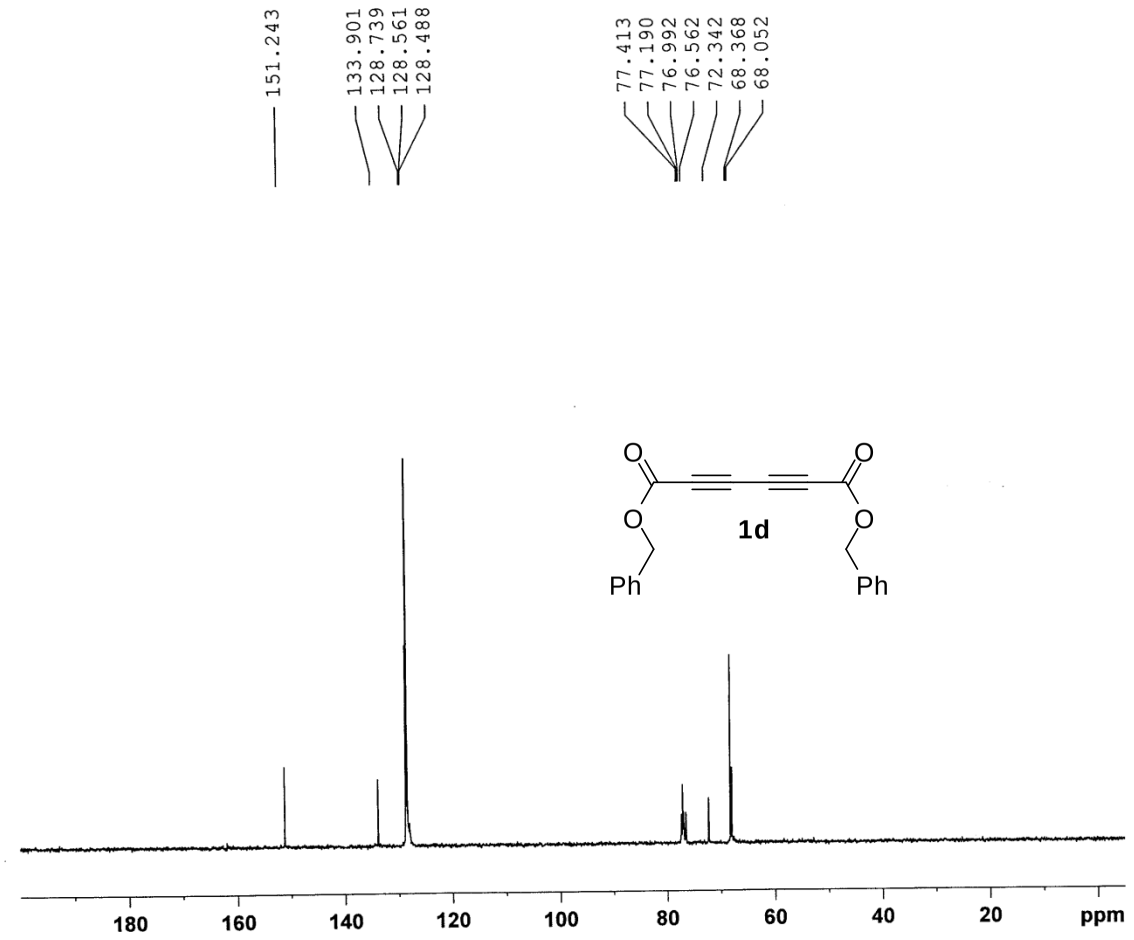


Fig. S5. ^{1}H NMR spectrum of compound **4a** (300 MHz, $CDCl_3$)

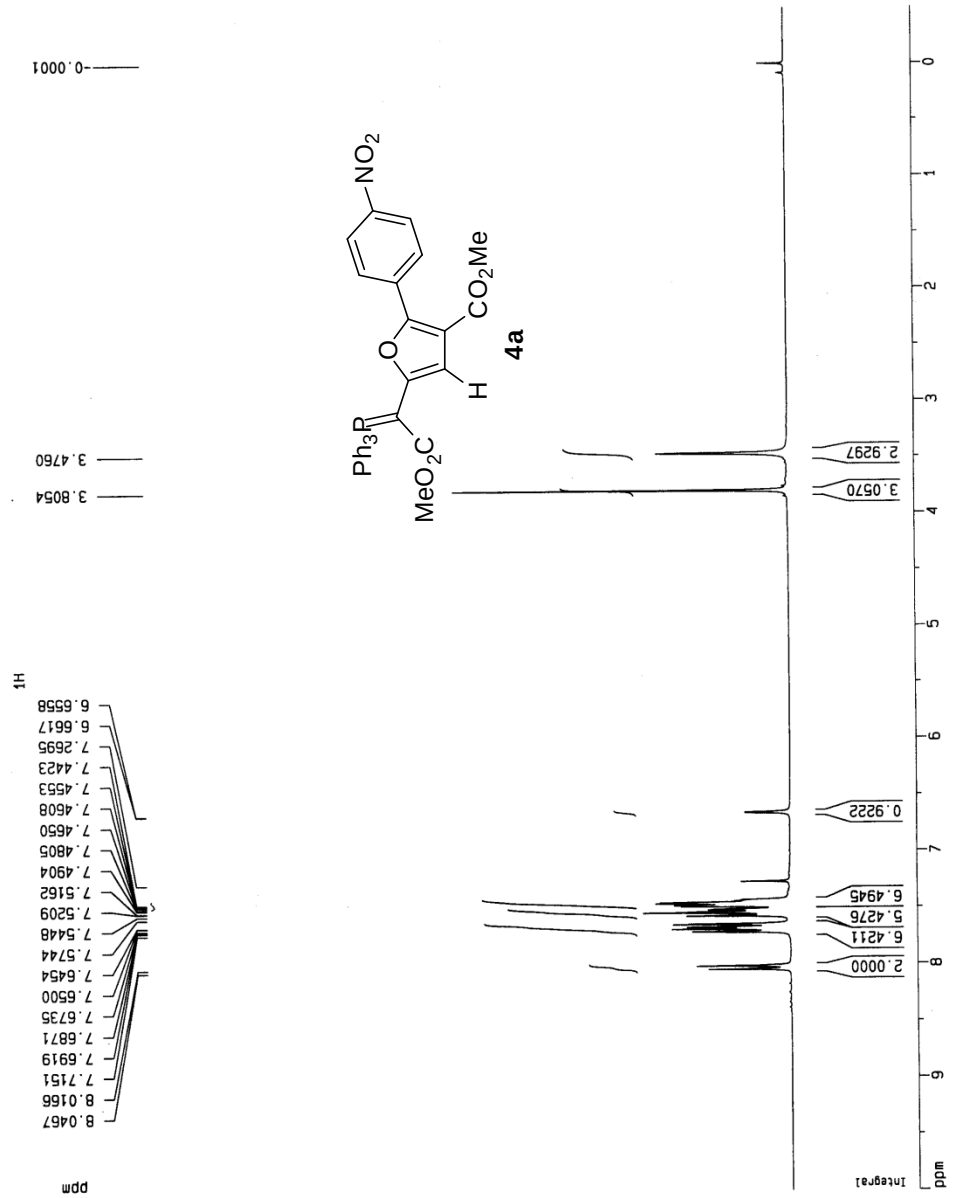


Fig. S6. ^{13}C NMR spectrum of compound **4a** (150.7 MHz, $CDCl_3$)

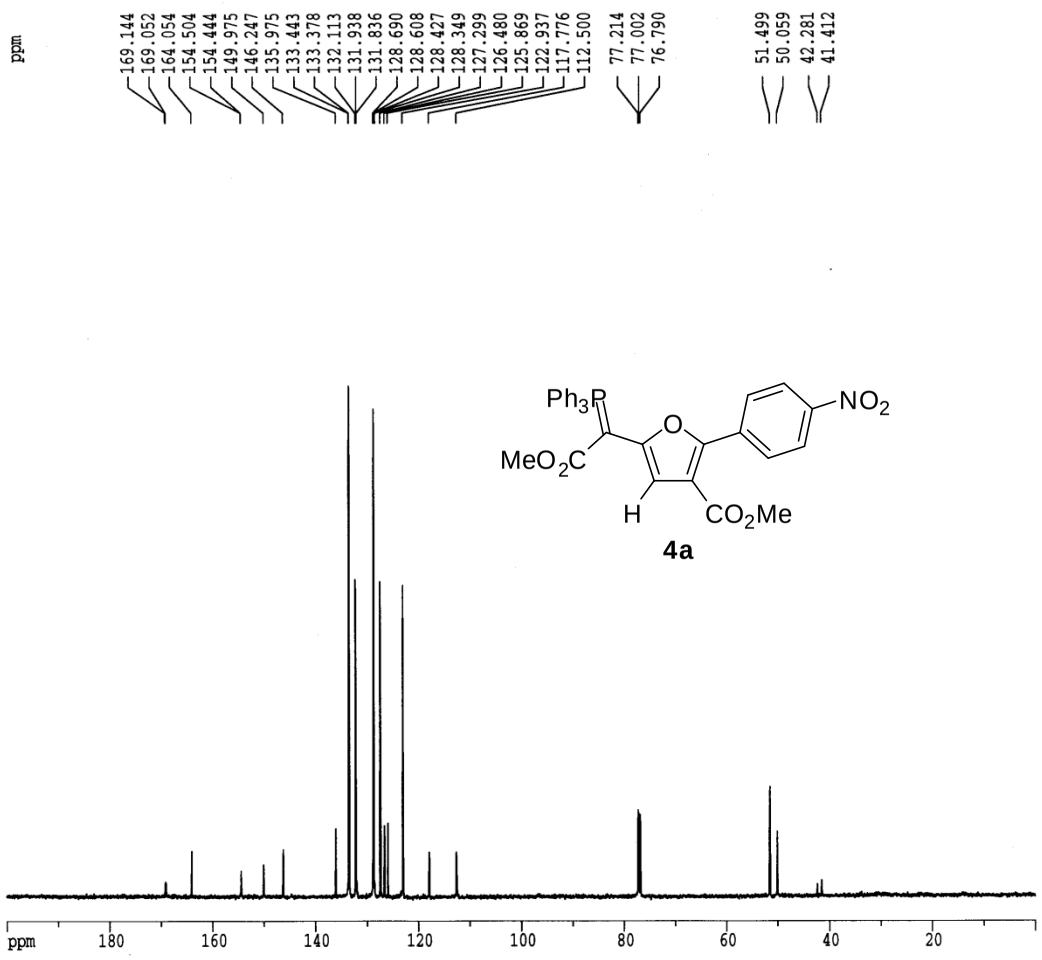


Fig. S7. ^{1}H NMR spectrum of compound **4b** (300 MHz, $CDCl_3$)

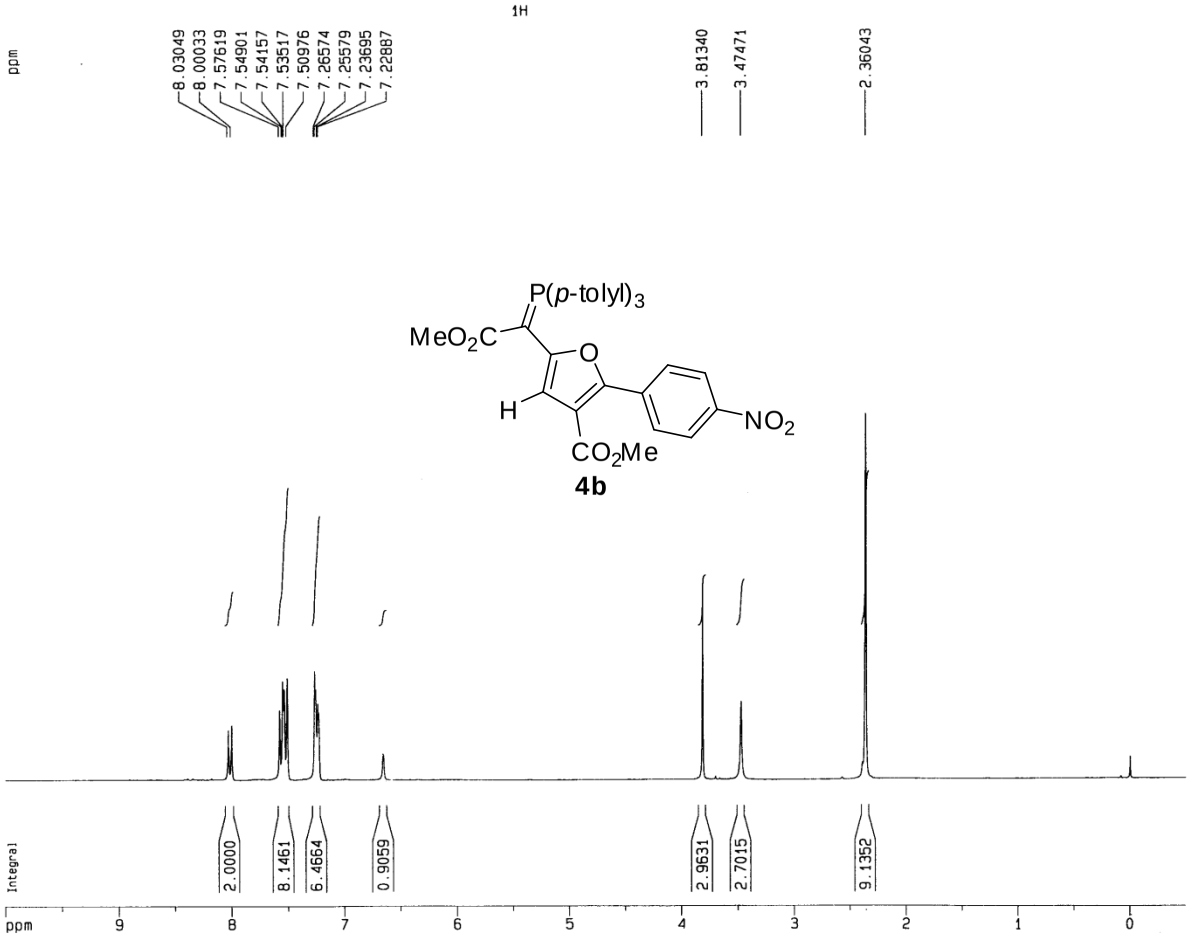


Fig. S8. ^{13}C NMR spectrum of compound **4b** (125.7 MHz, $CDCl_3$)

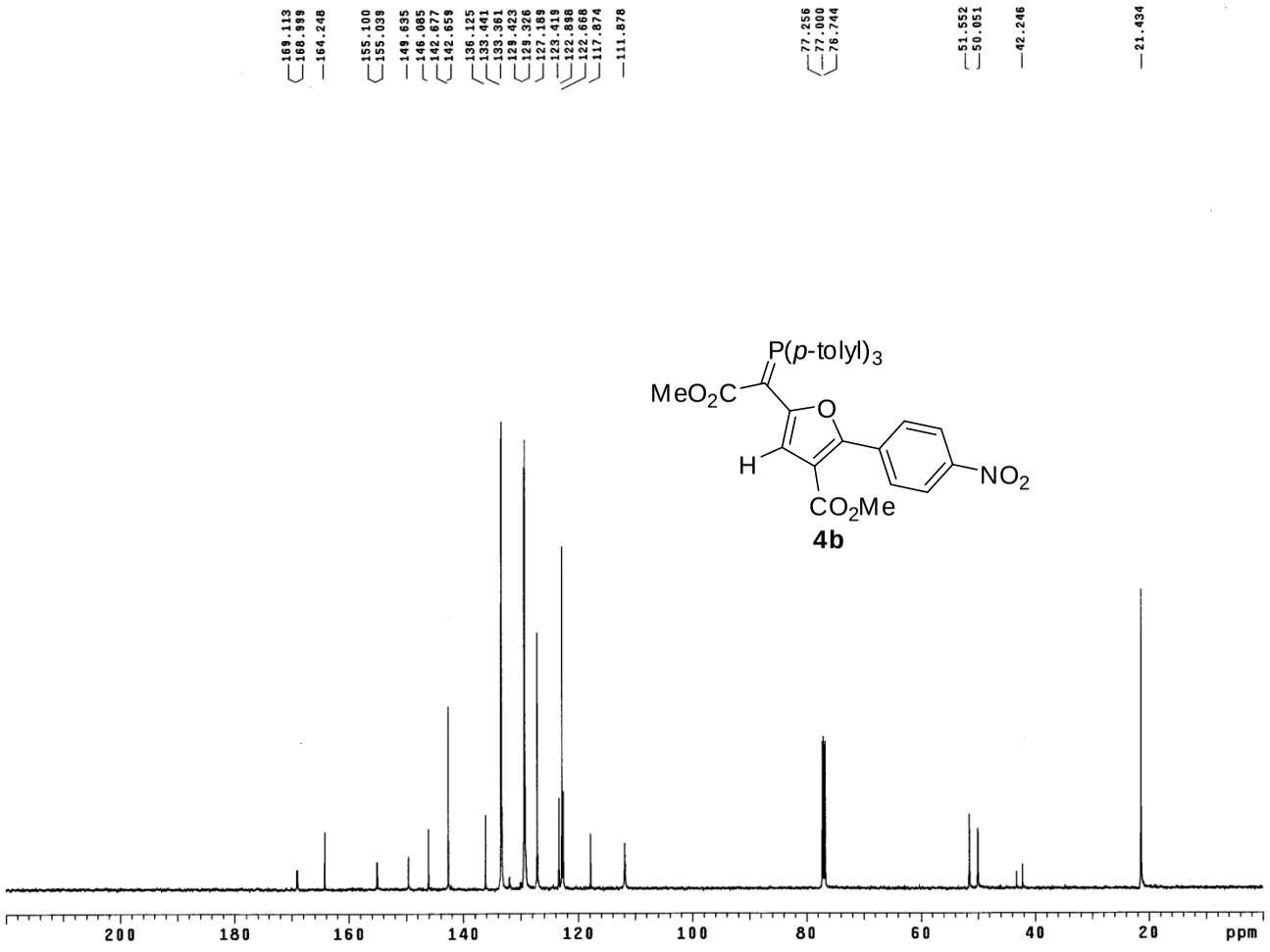


Fig. S9. ^{1}H NMR spectrum of compound **4c** (300 MHz, $CDCl_3$)

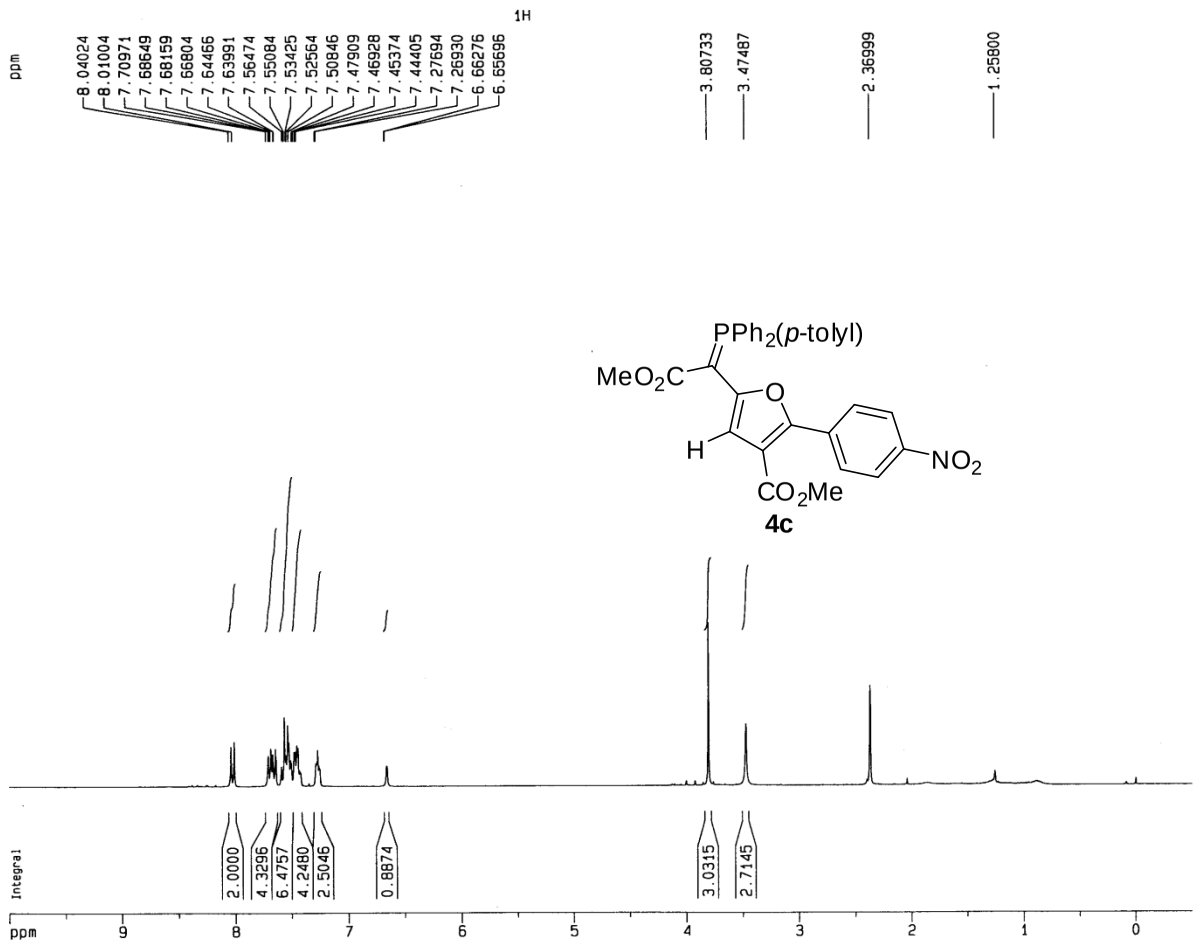


Fig. S10. ^{13}C NMR spectrum of compound **4c** (150.7 MHz, $CDCl_3$)

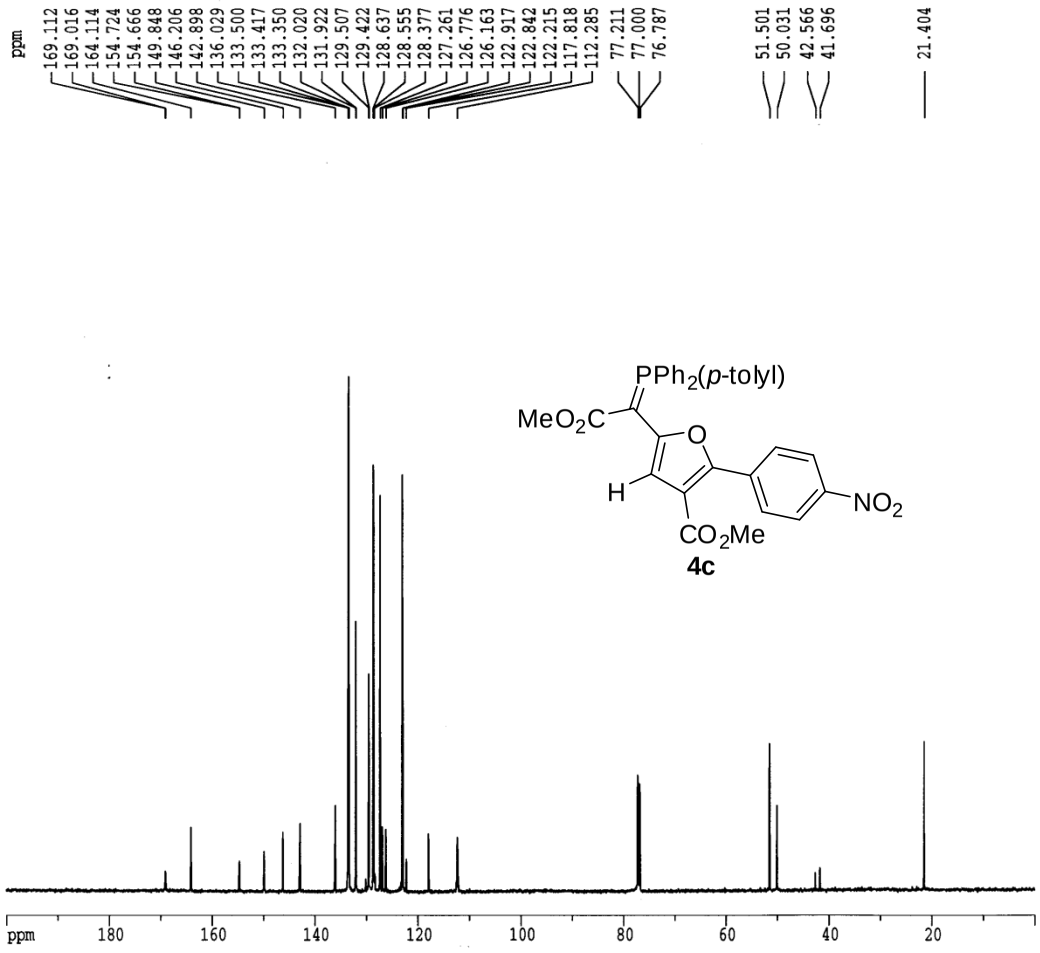


Fig. S11. ^{1}H NMR spectrum of compound **4d** (300 MHz, $CDCl_3$)

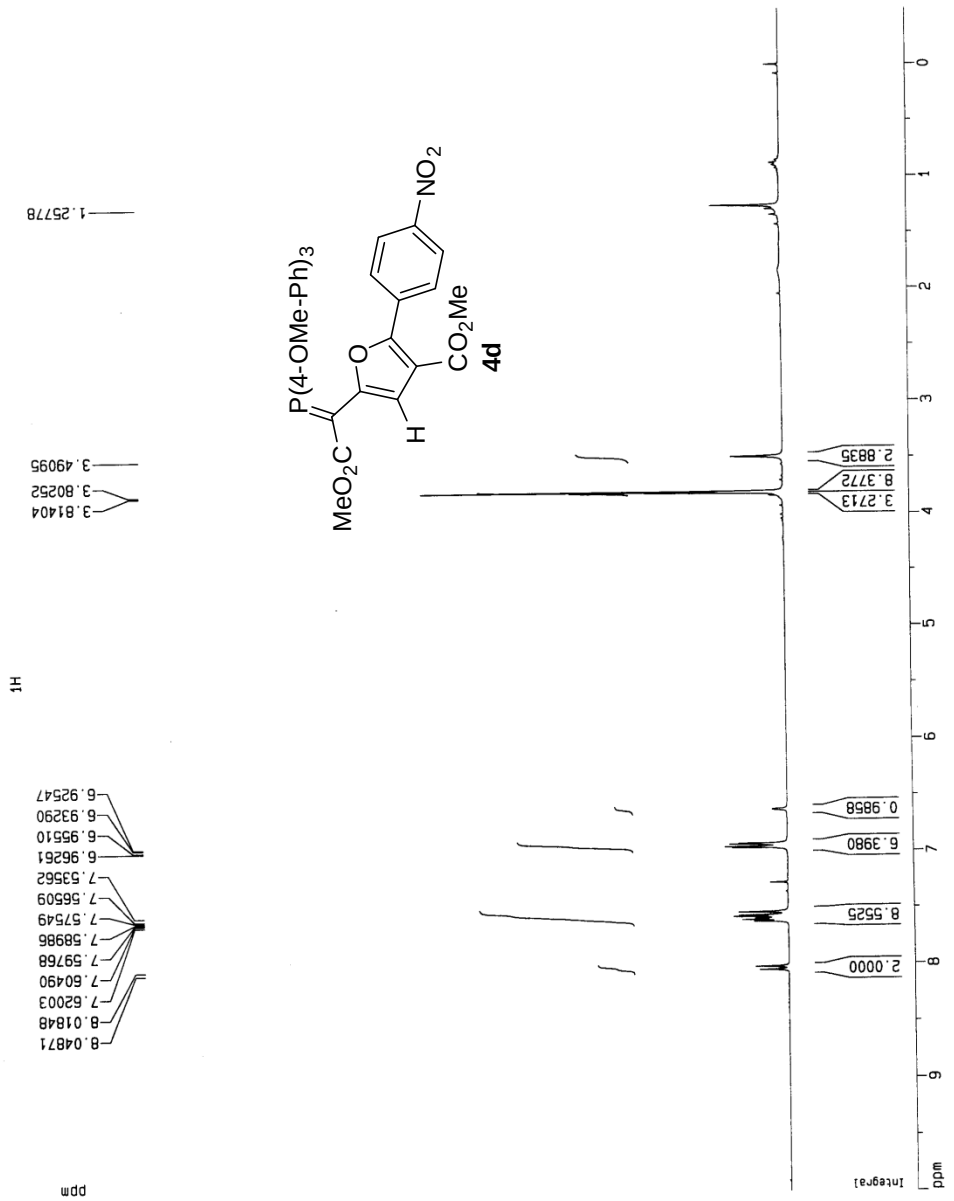


Fig. S12. ^{13}C NMR spectrum of compound **4d** (150.7 MHz, $CDCl_3$)

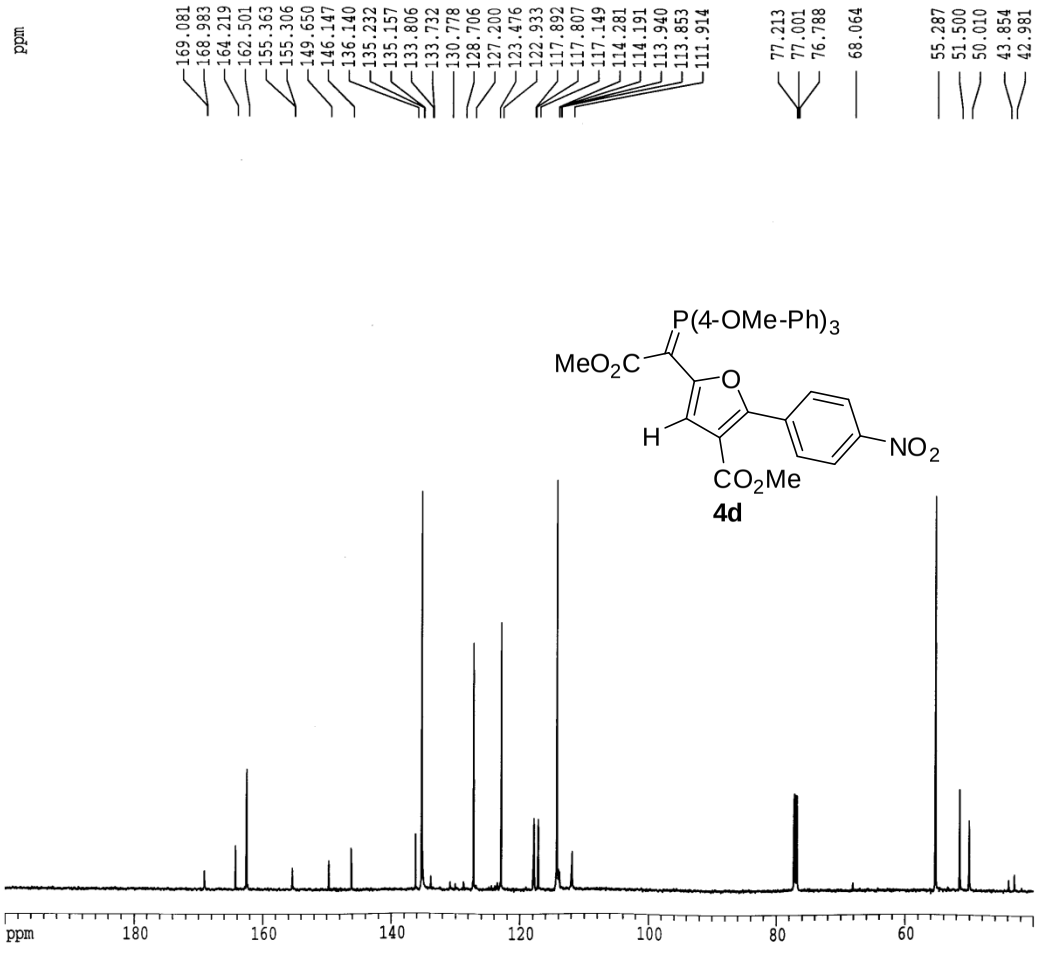


Fig. S13. ^{1}H NMR spectrum of compound **4e** (300 MHz, $CDCl_3$)

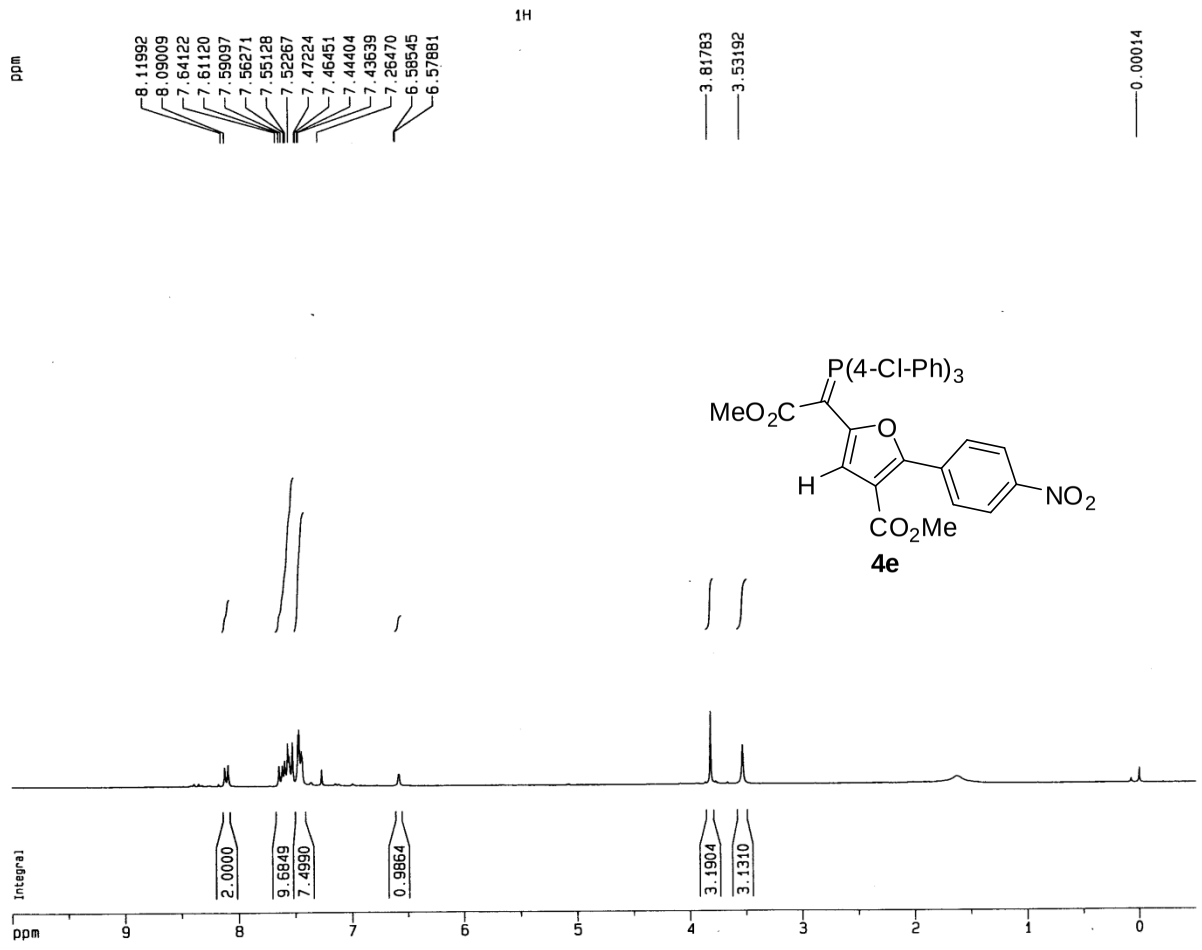


Fig. S14. ^{13}C NMR spectrum of compound **4e** (150.7 MHz, $CDCl_3$)

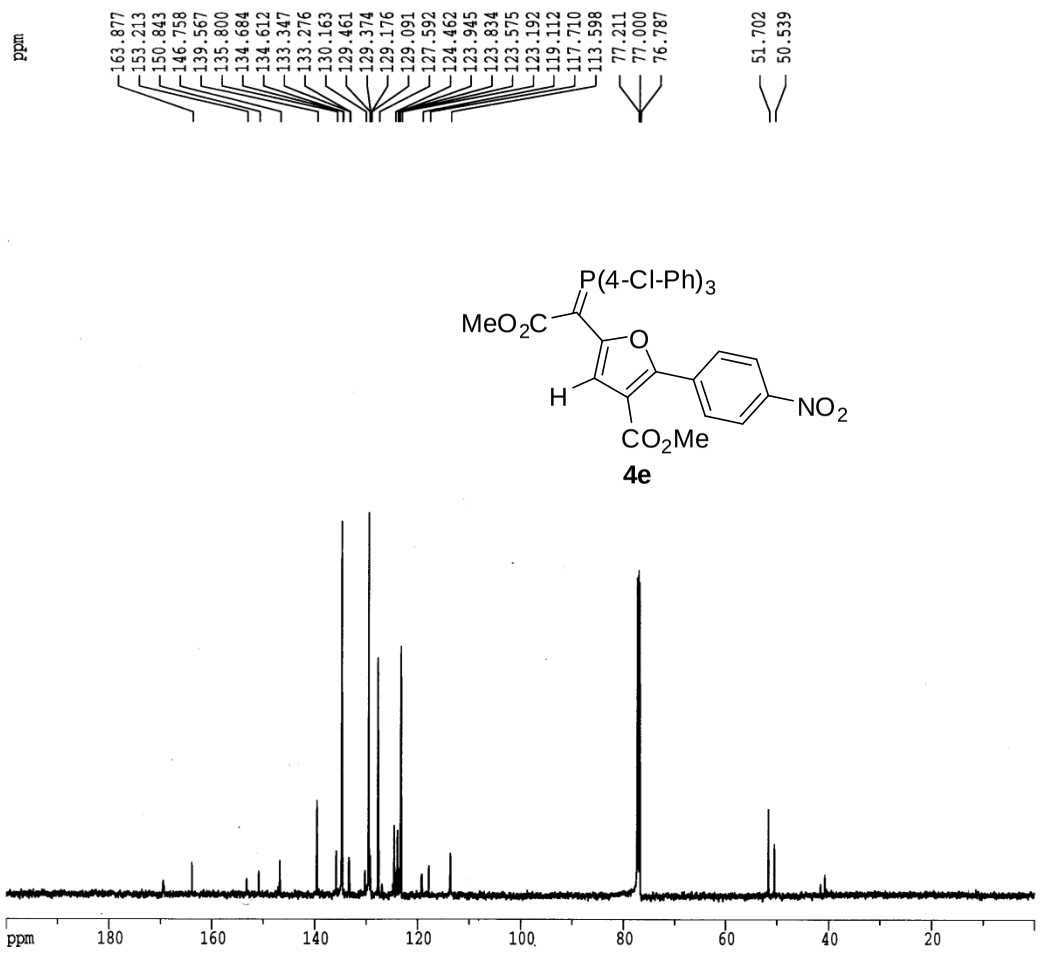


Fig. S15. ^{1}H NMR spectrum of compound **4f** (300 MHz, $CDCl_3$)

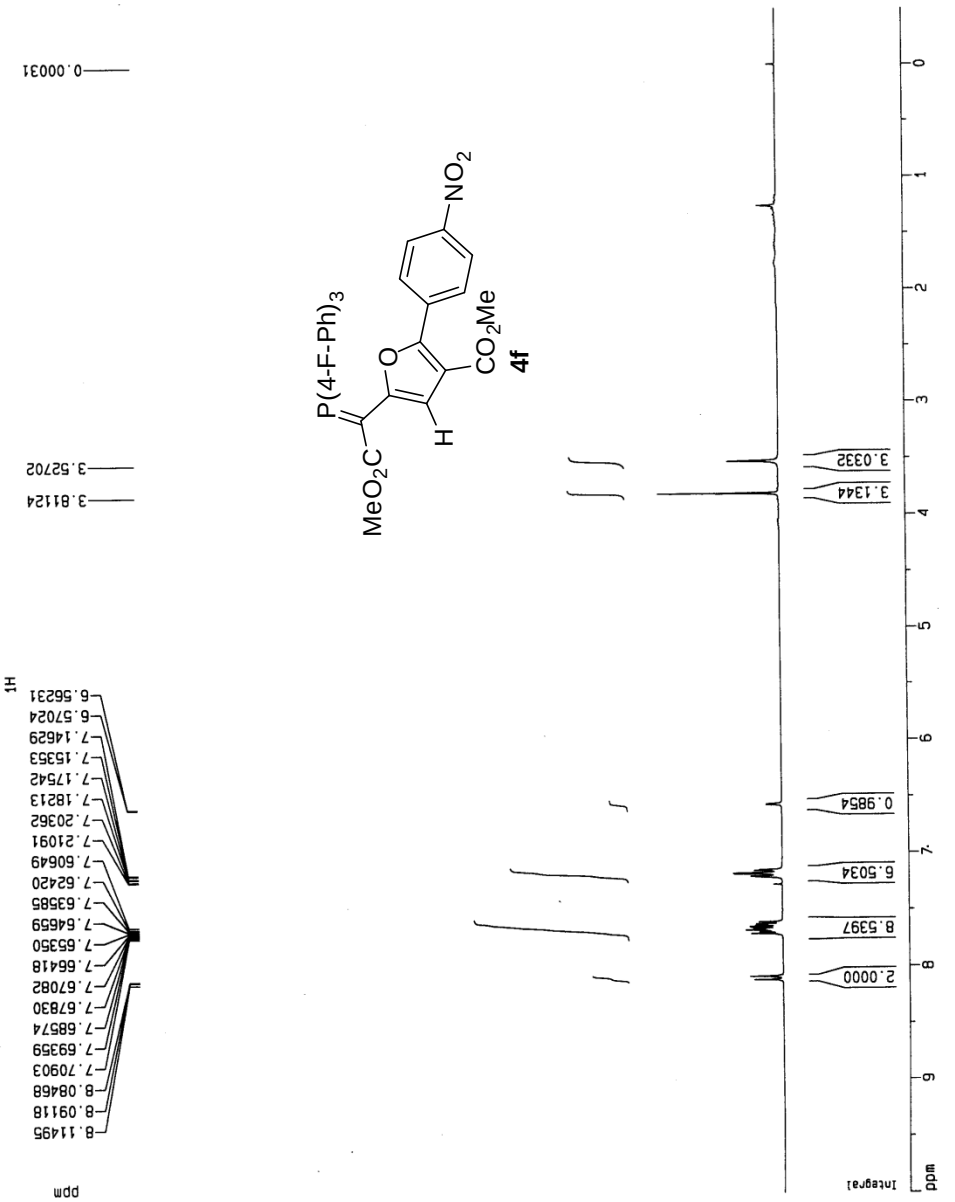


Fig. S16. ^{13}C NMR spectrum of compound **4f** (150.7 MHz, $CDCl_3$)

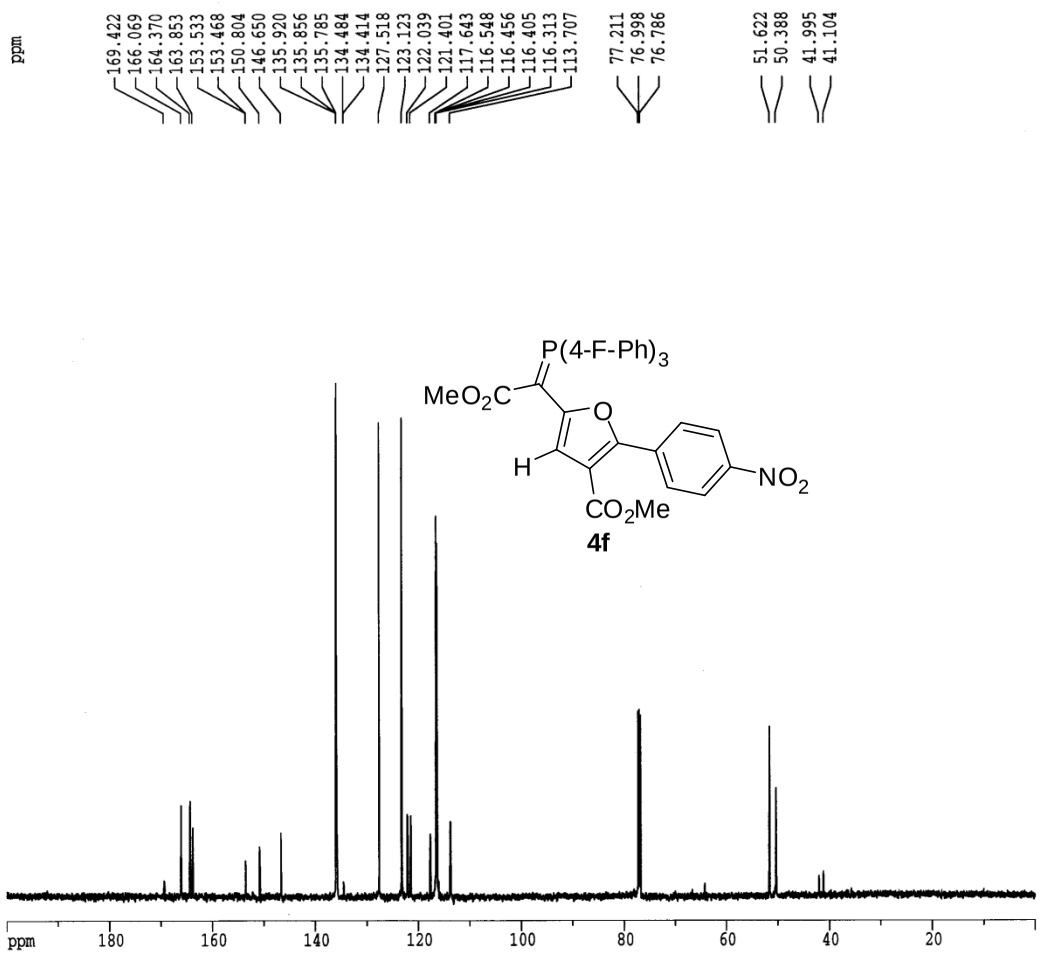


Fig. S17. ^{1}H NMR spectrum of compound **4g** (400 MHz, $CDCl_3$)

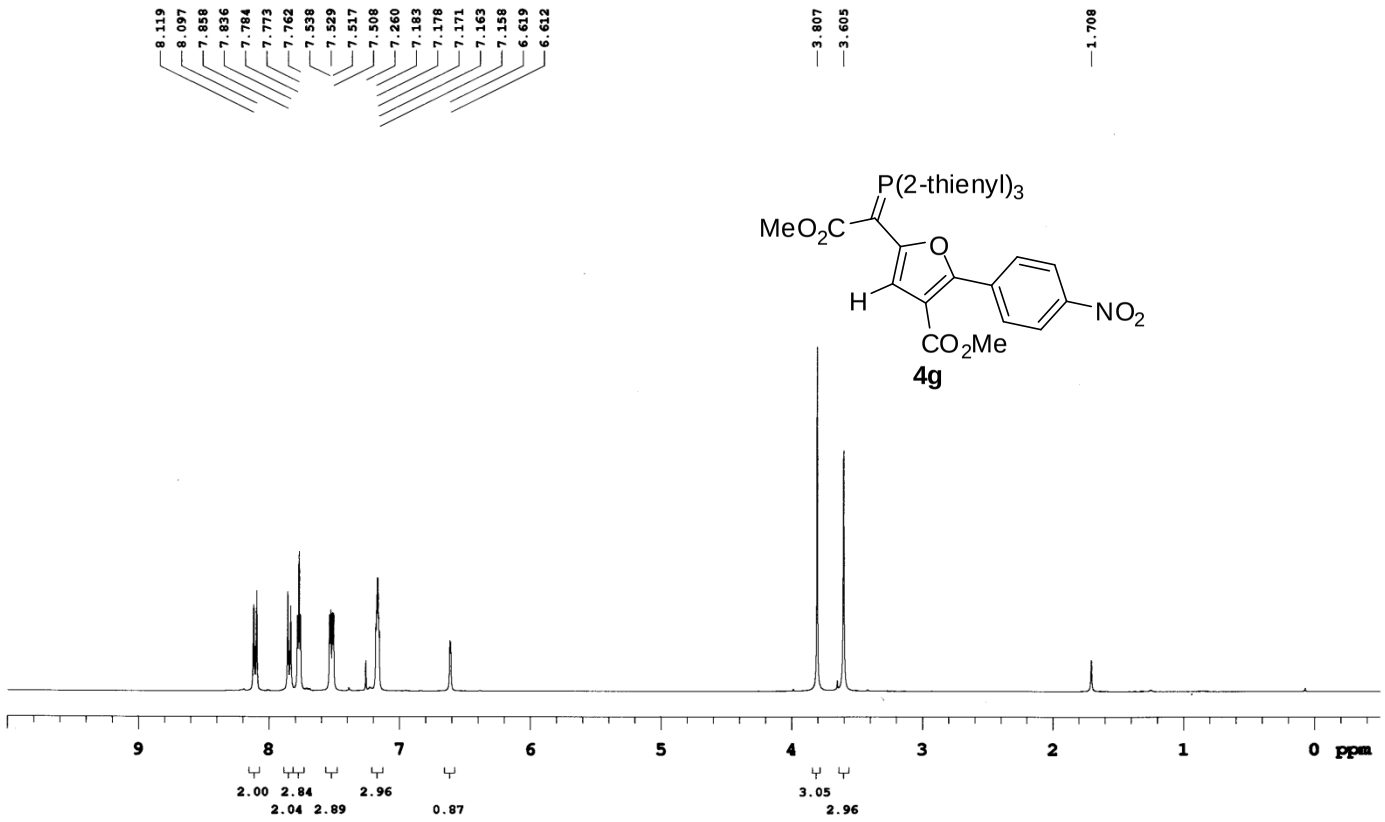


Fig. S18. ^{13}C NMR spectrum of compound **4g** (100 MHz, $CDCl_3$)

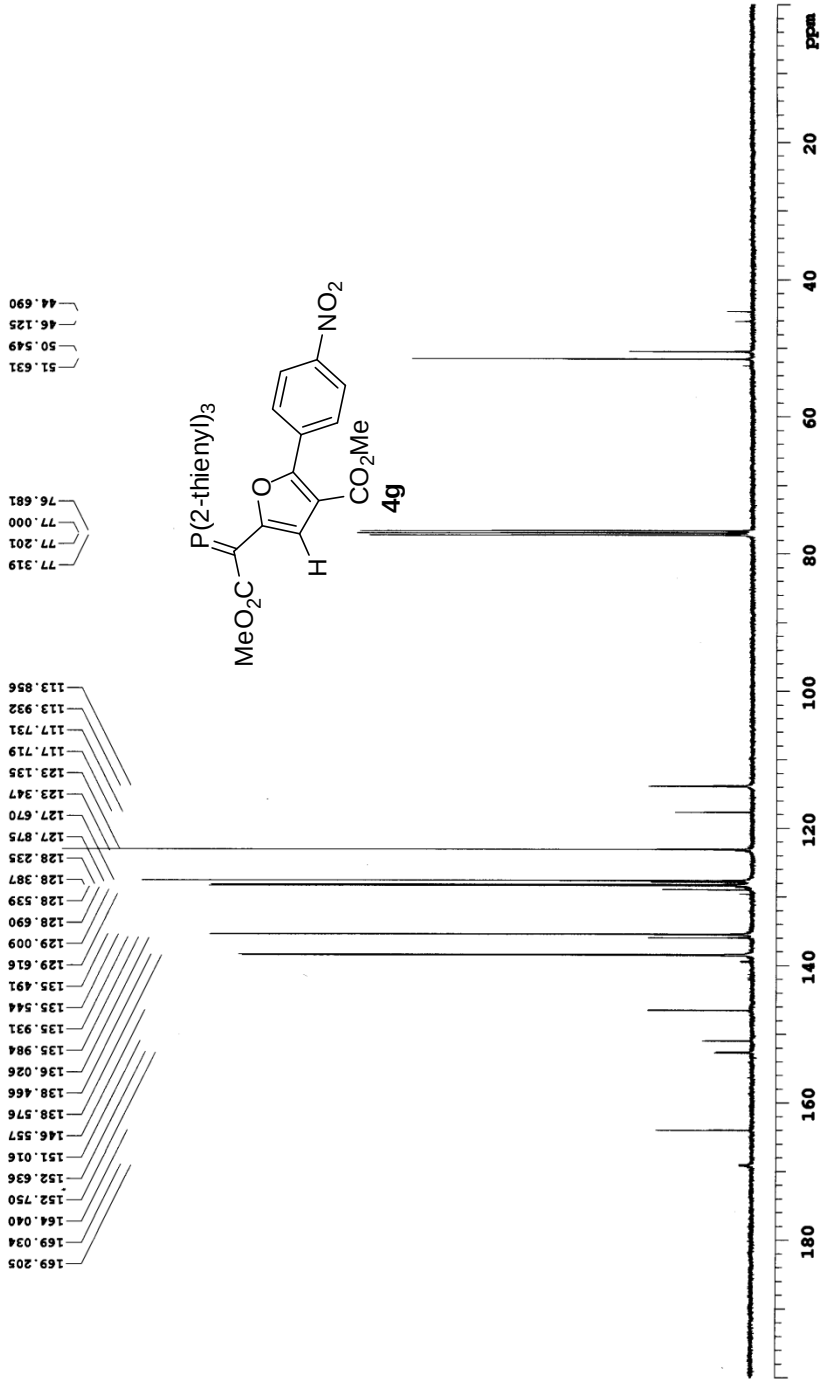


Fig. S19. ^{1}H NMR spectrum of compound **4h** (300 MHz, $CDCl_3$)

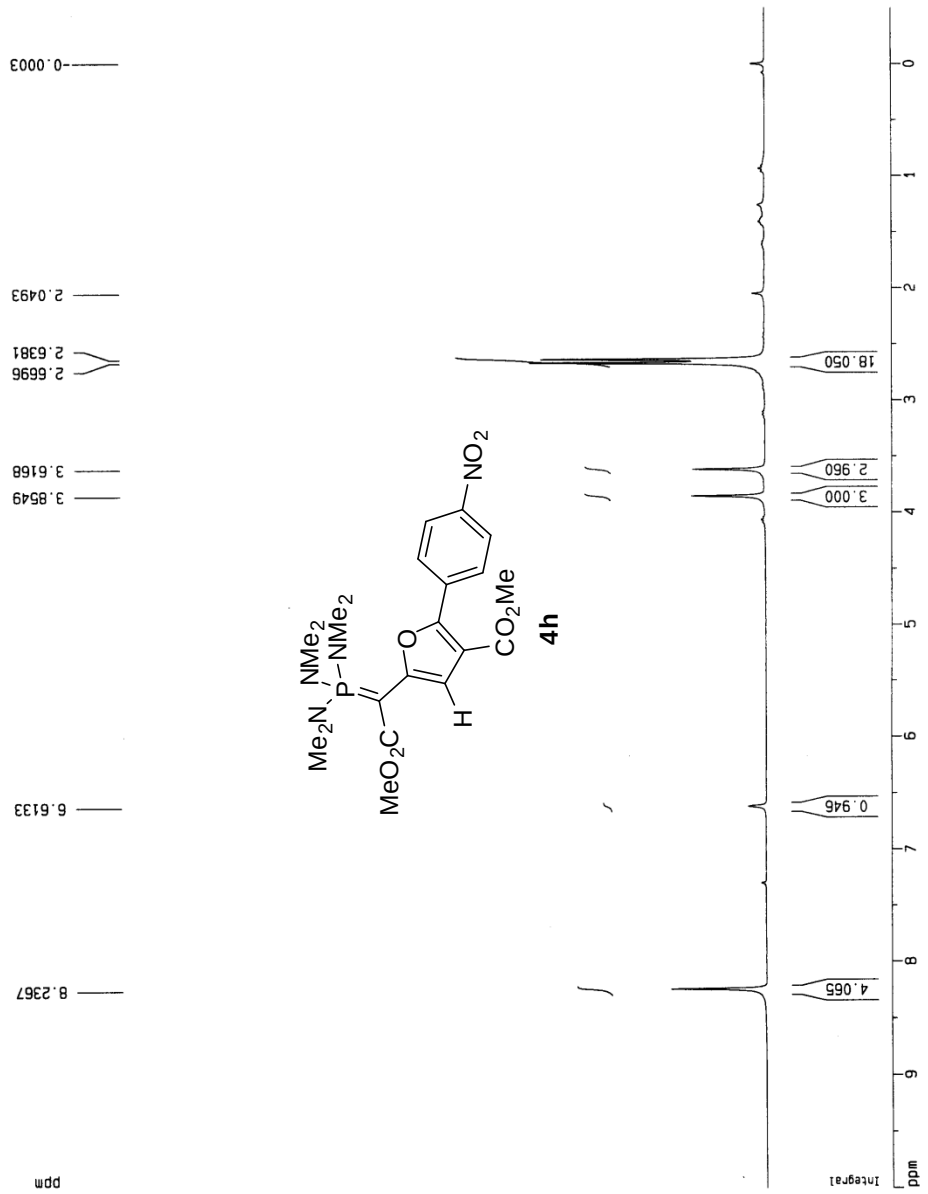


Fig. S20. ^{13}C NMR spectrum of compound **4h** (75.5 MHz, $CDCl_3$)

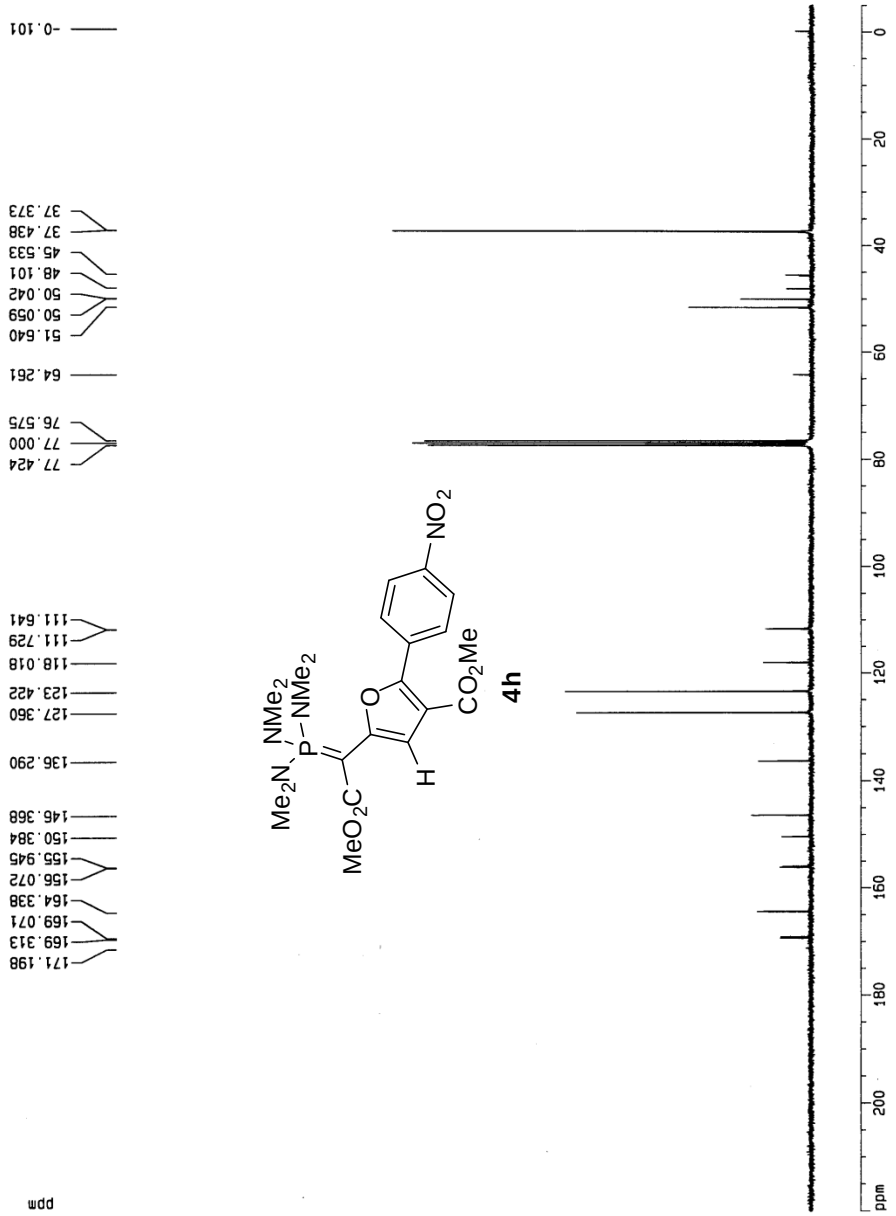


Fig. S21. ^{1}H NMR spectrum of compound **4i** (300 MHz, $CDCl_3$)

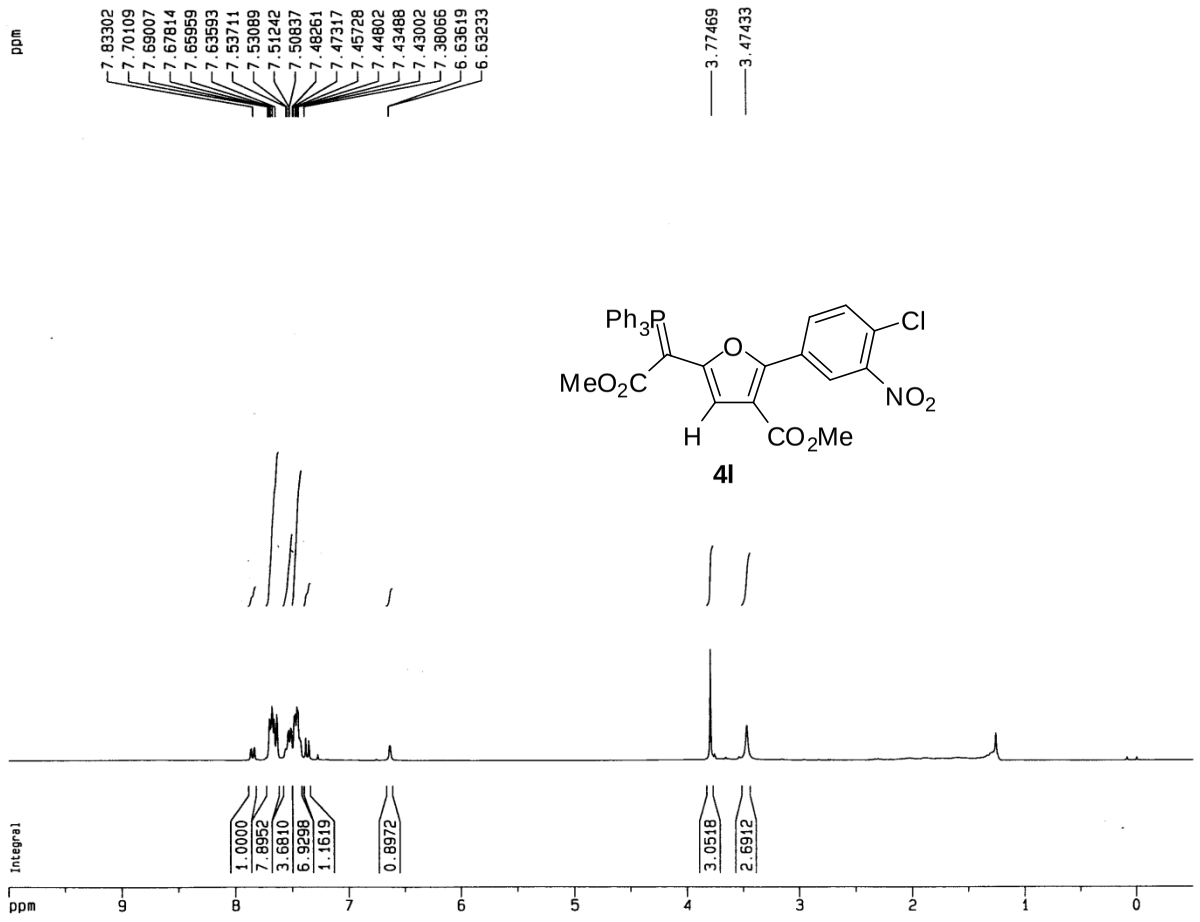


Fig. S22. ^{13}C NMR spectrum of compound **4i** (150.7 MHz, $CDCl_3$)

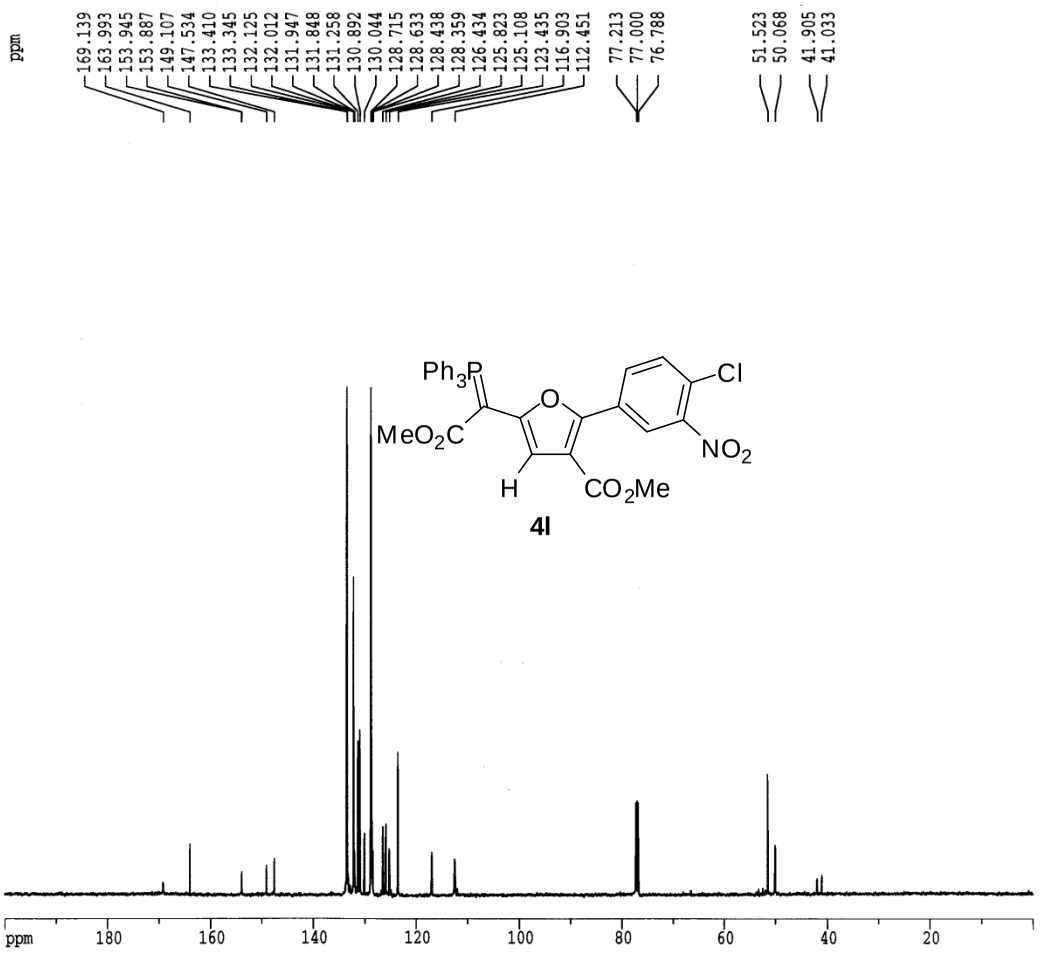


Fig. S23. ^{1}H NMR spectrum of compound **4j** (300 MHz, $CDCl_3$)

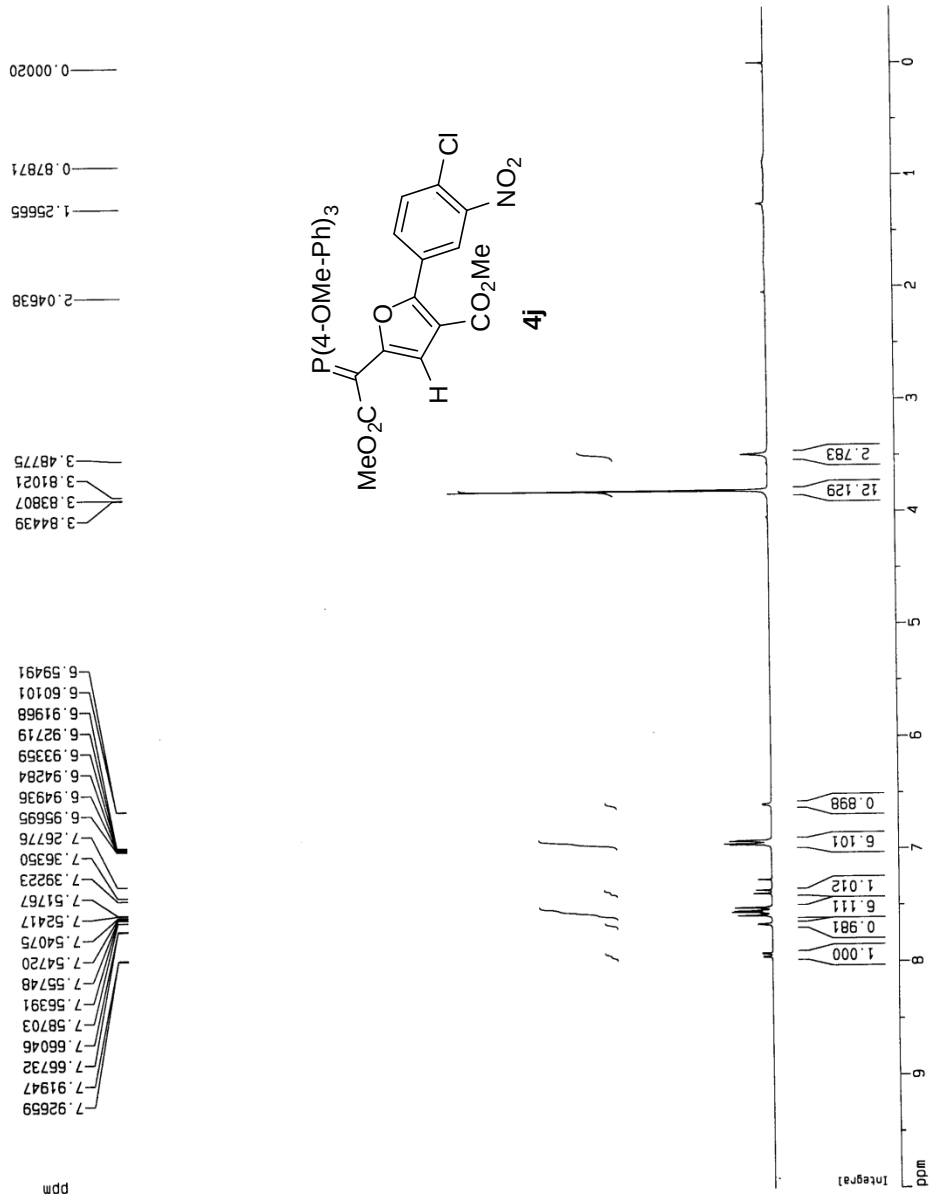


Fig. S24. ^{13}C NMR spectrum of compound **4j** (75.5 MHz, $CDCl_3$)

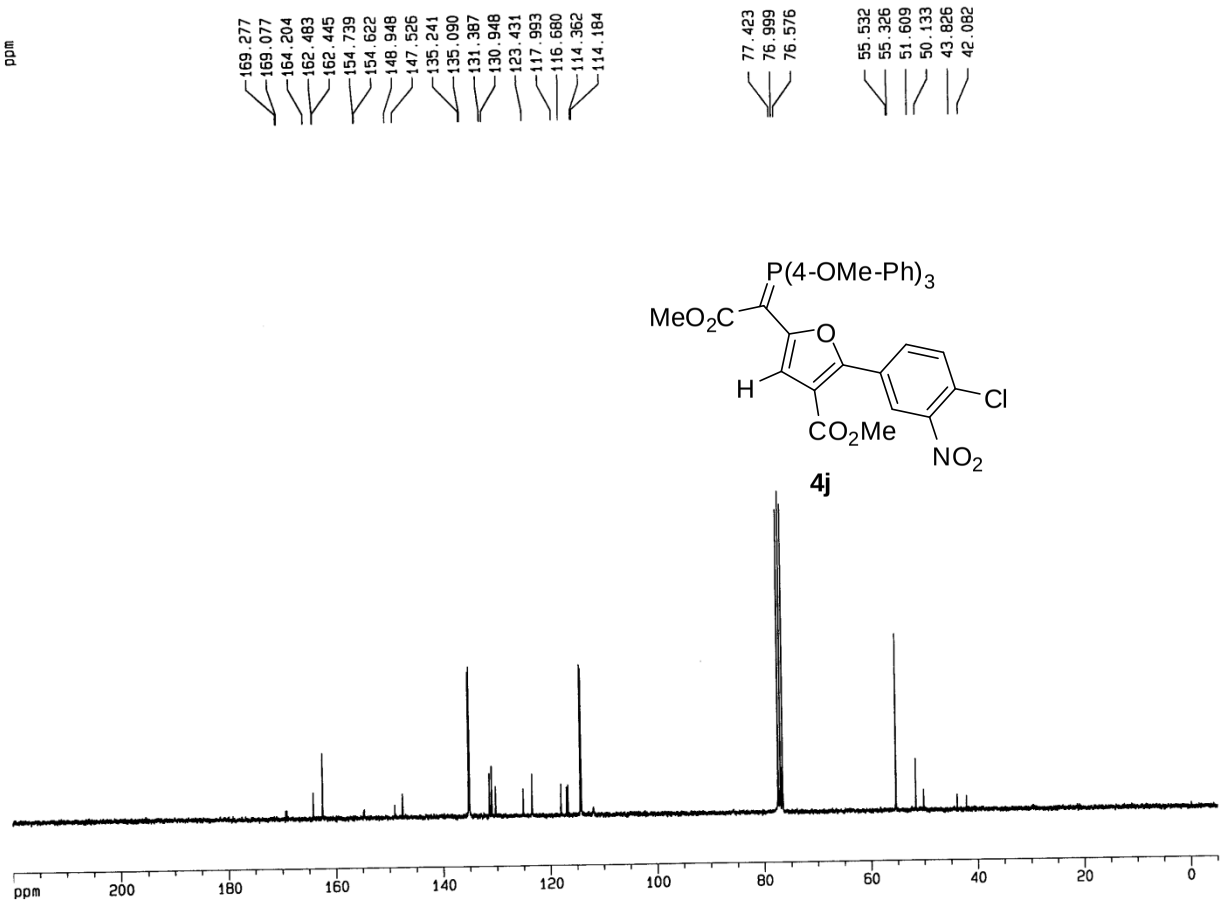


Fig. S25. ^{1}H NMR spectrum of compound **4k** (300 MHz, $CDCl_3$)

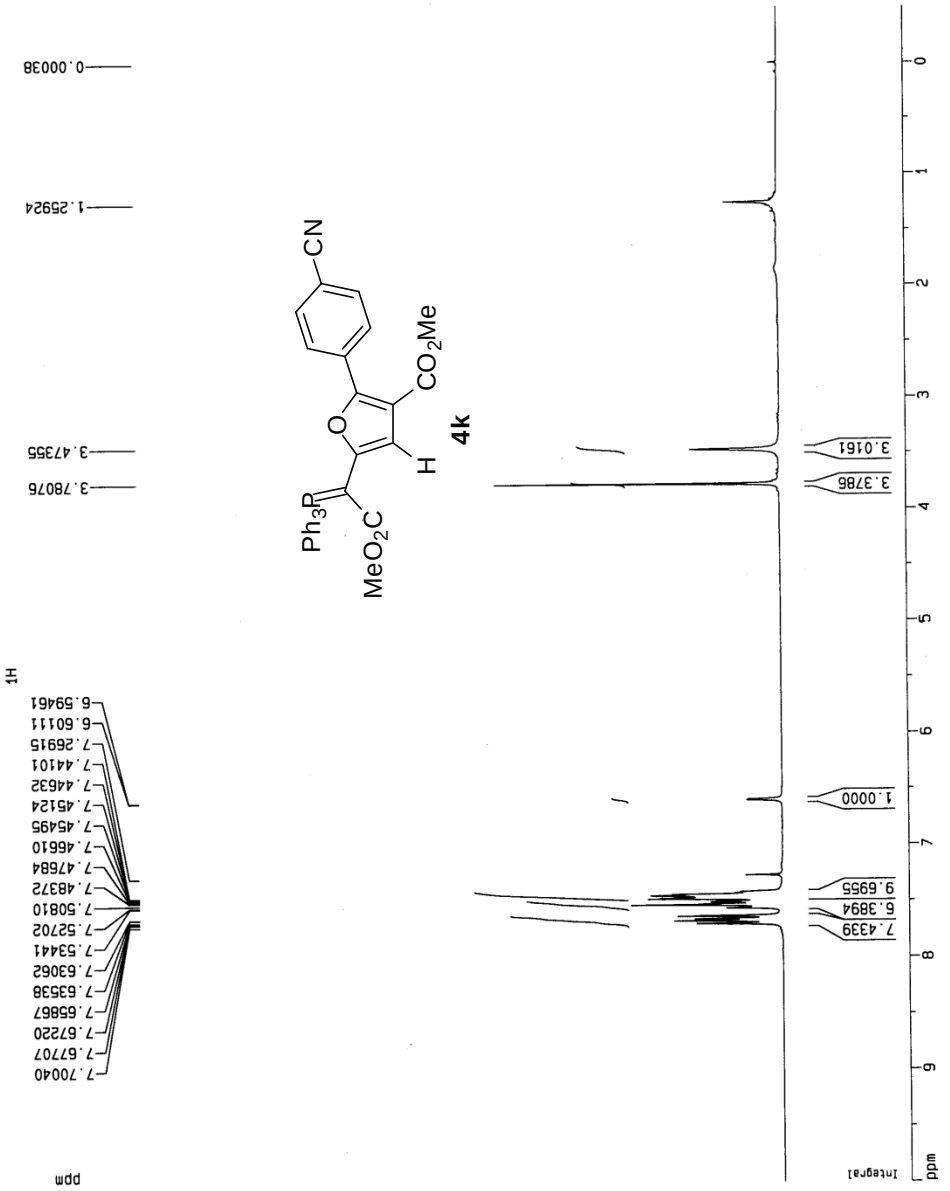


Fig. S26. ^{13}C NMR spectrum of compound **4k** (150.7 MHz, $CDCl_3$)

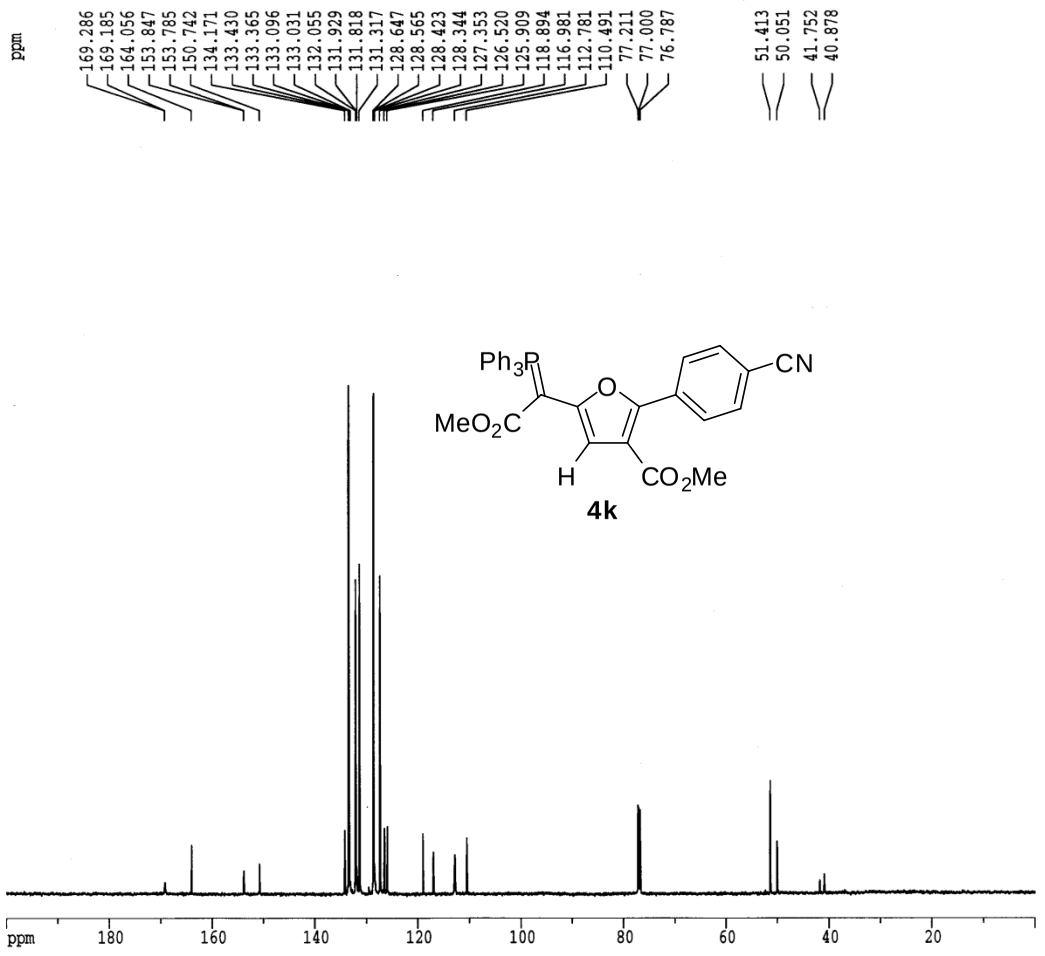


Fig. S27. ^{1}H NMR spectrum of compound **4l** (300 MHz, $CDCl_3$)

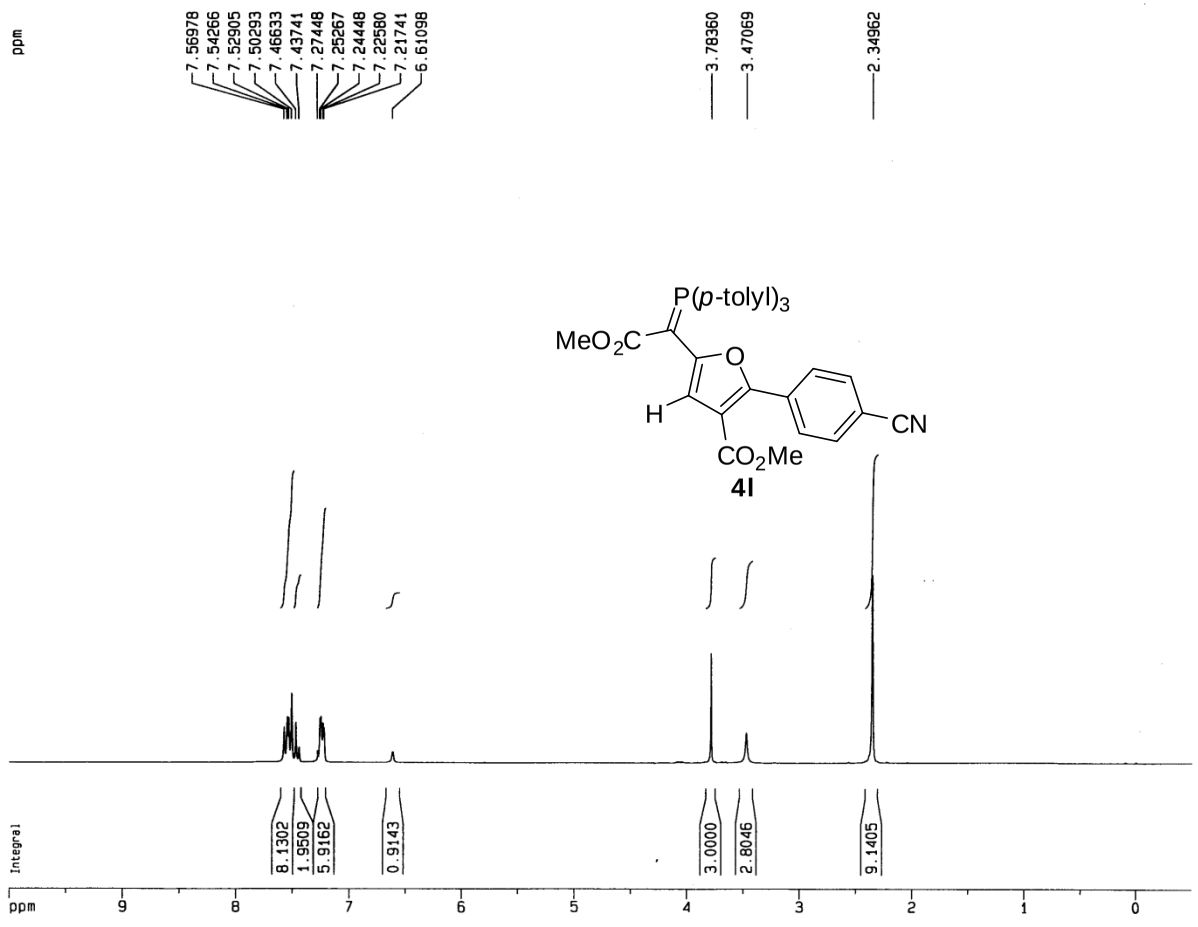


Fig. S28. ^{13}C NMR spectrum of compound **4l** (150.7 MHz, $CDCl_3$)

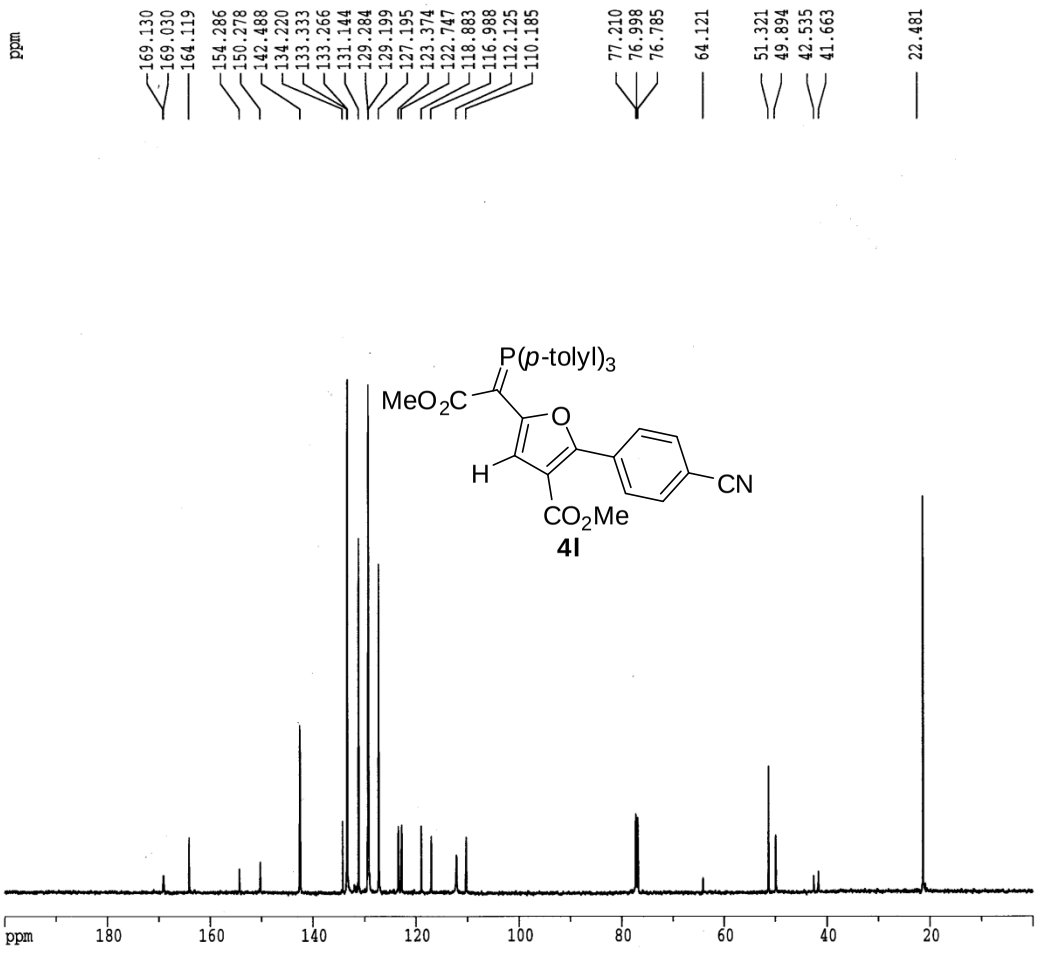


Fig. S29. ^{1}H NMR spectrum of compound **4m** (300 MHz, $CDCl_3$)

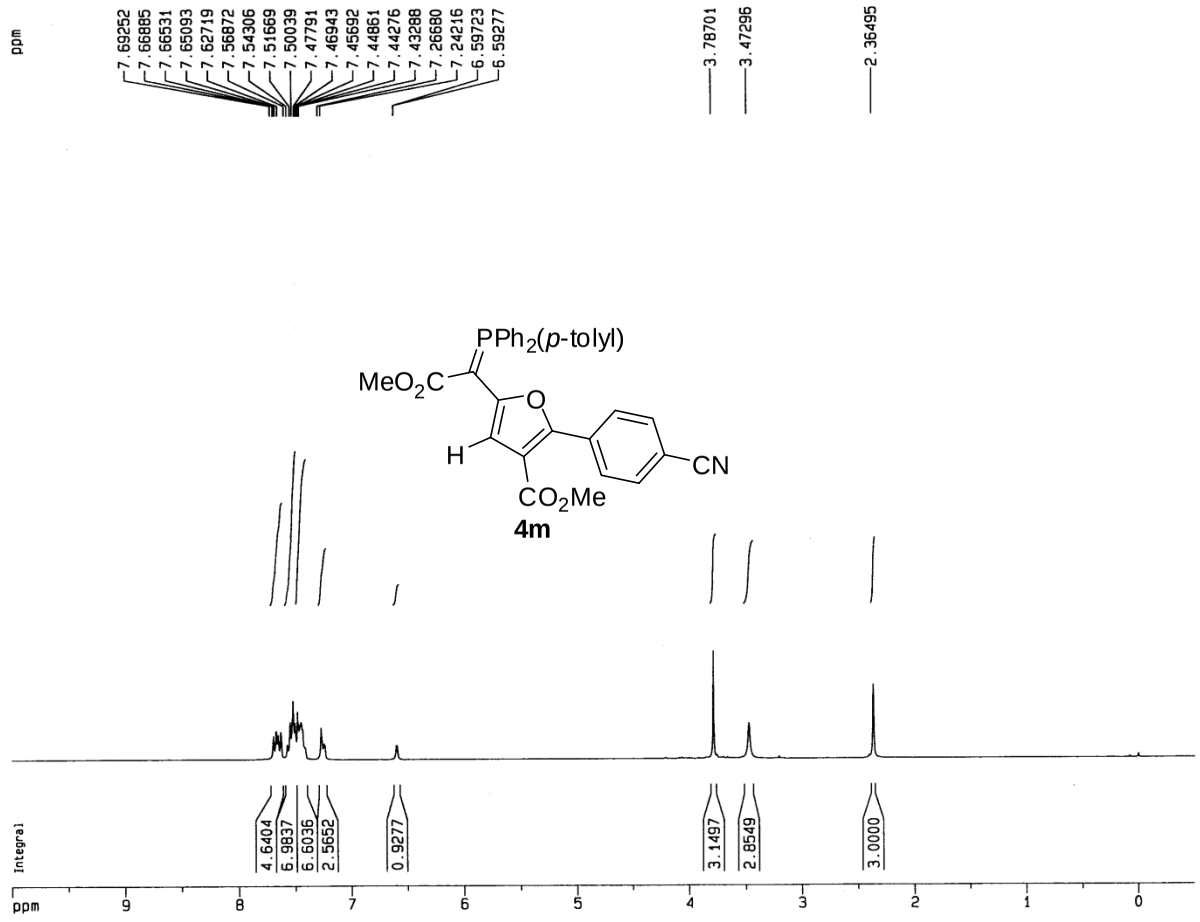


Fig. S30. ^{13}C NMR spectrum of compound **4m** (75.5 MHz, $CDCl_3$)

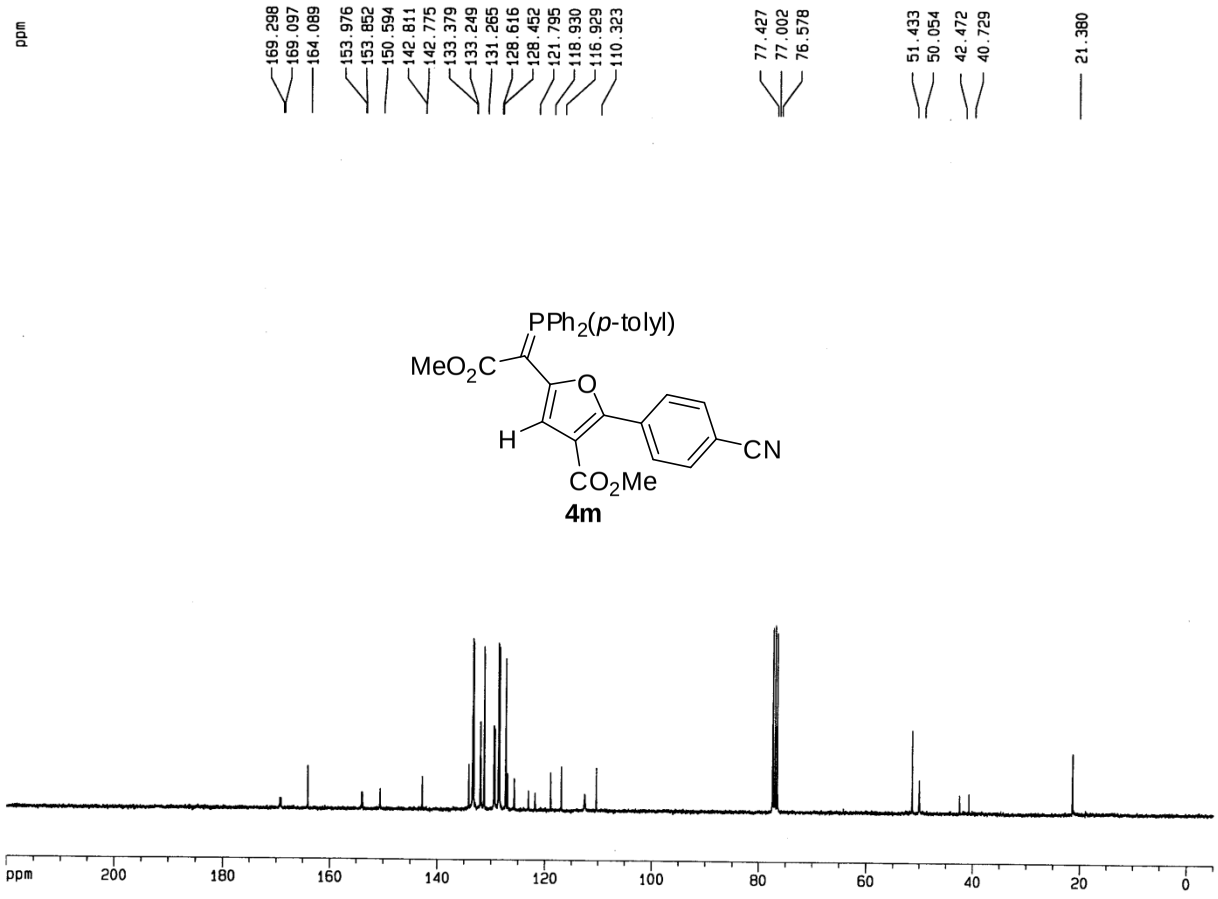


Fig. S31. ^{1}H NMR spectrum of compound **4n** (300 MHz, $CDCl_3$)

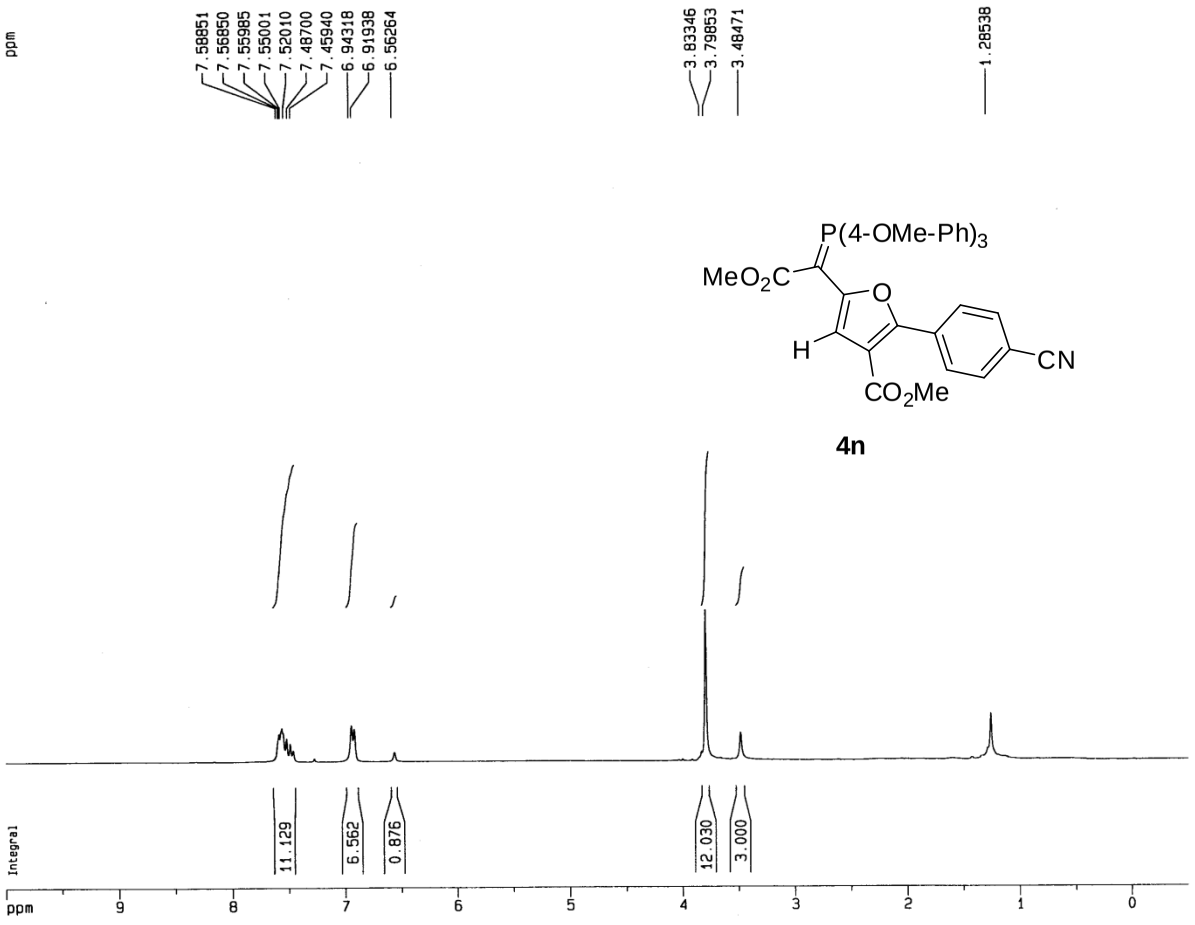


Fig. S32. ^{13}C NMR spectrum of compound **4n** (75.5 MHz, $CDCl_3$)

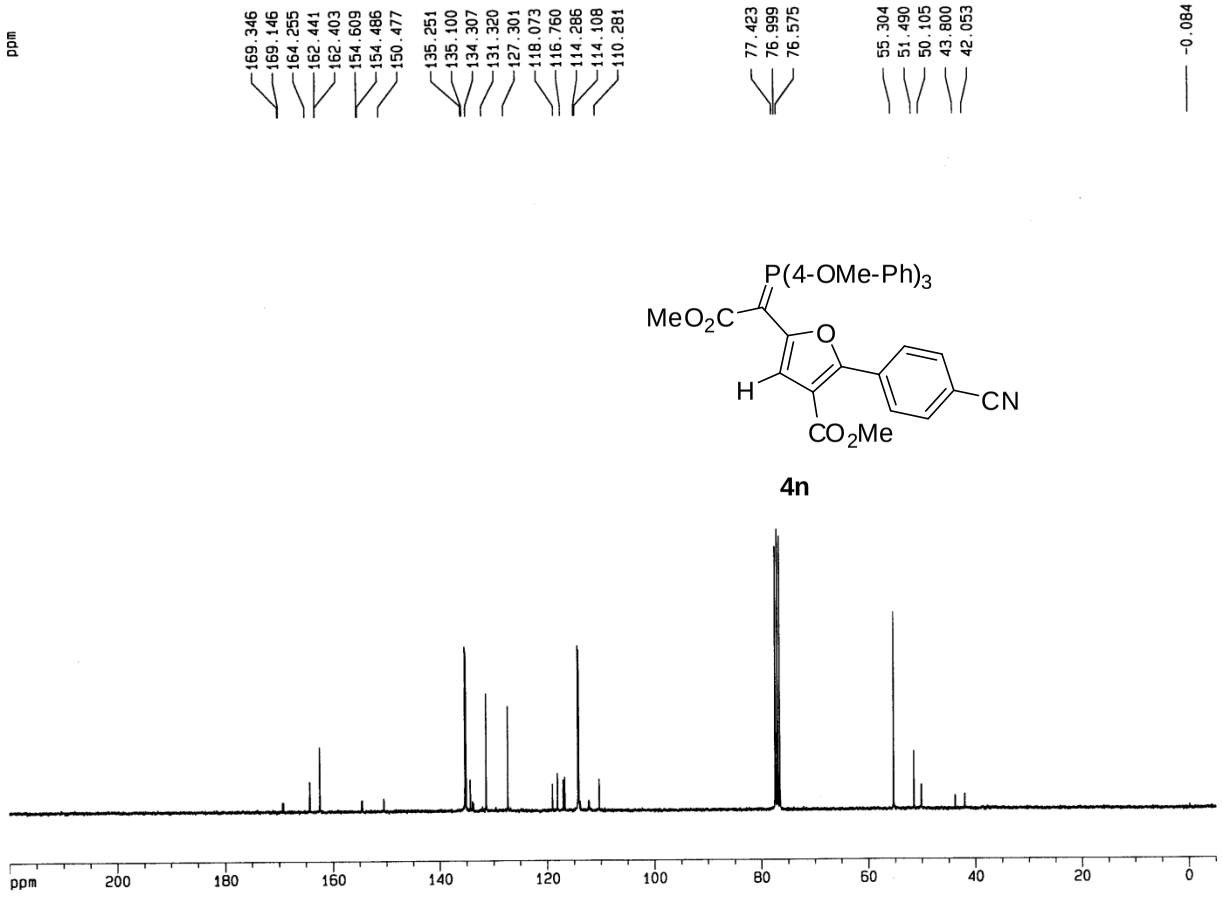


Fig. S33. ^{1}H NMR spectrum of compound **4o** (300 MHz, $CDCl_3$)

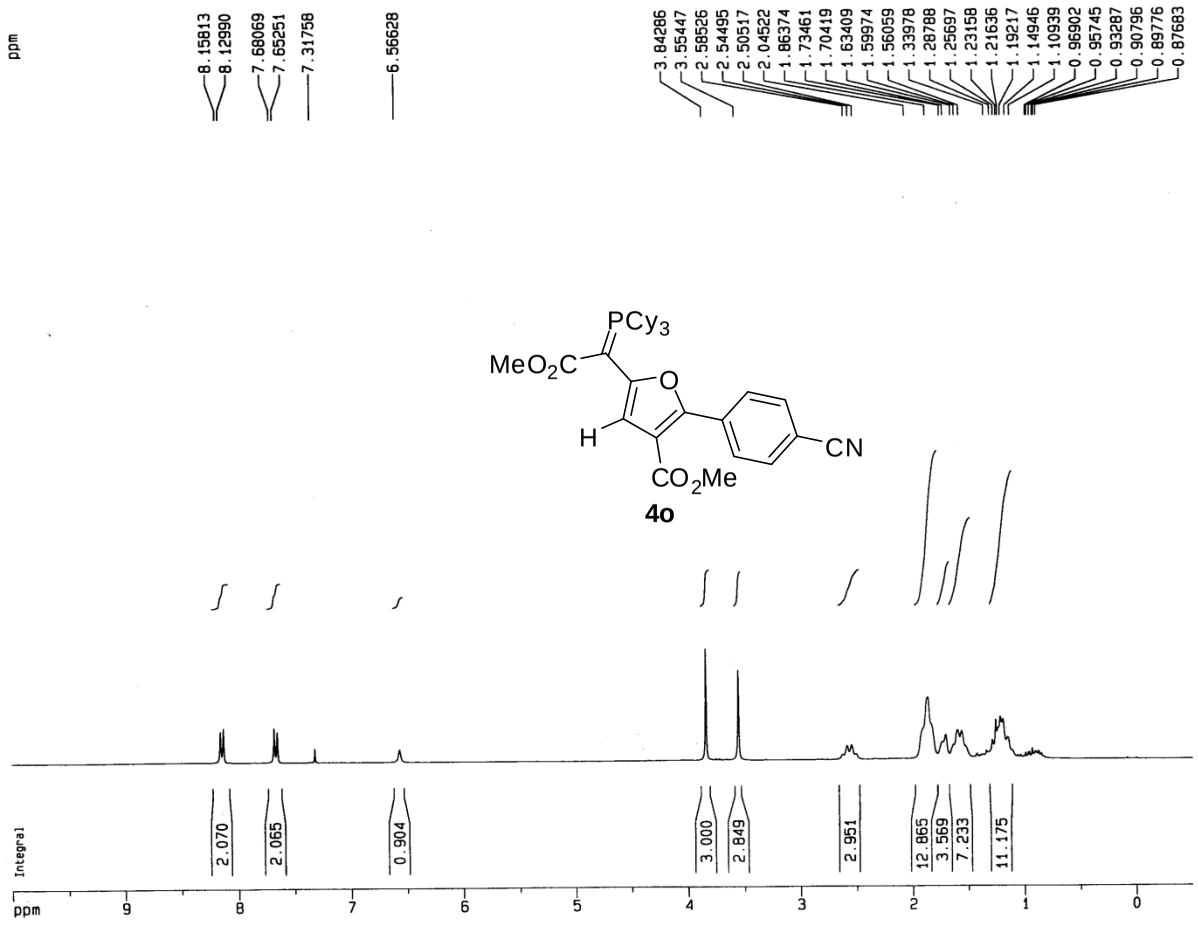


Fig. S34. ^{13}C NMR spectrum of compound **4o** (75.5 MHz, $CDCl_3$)

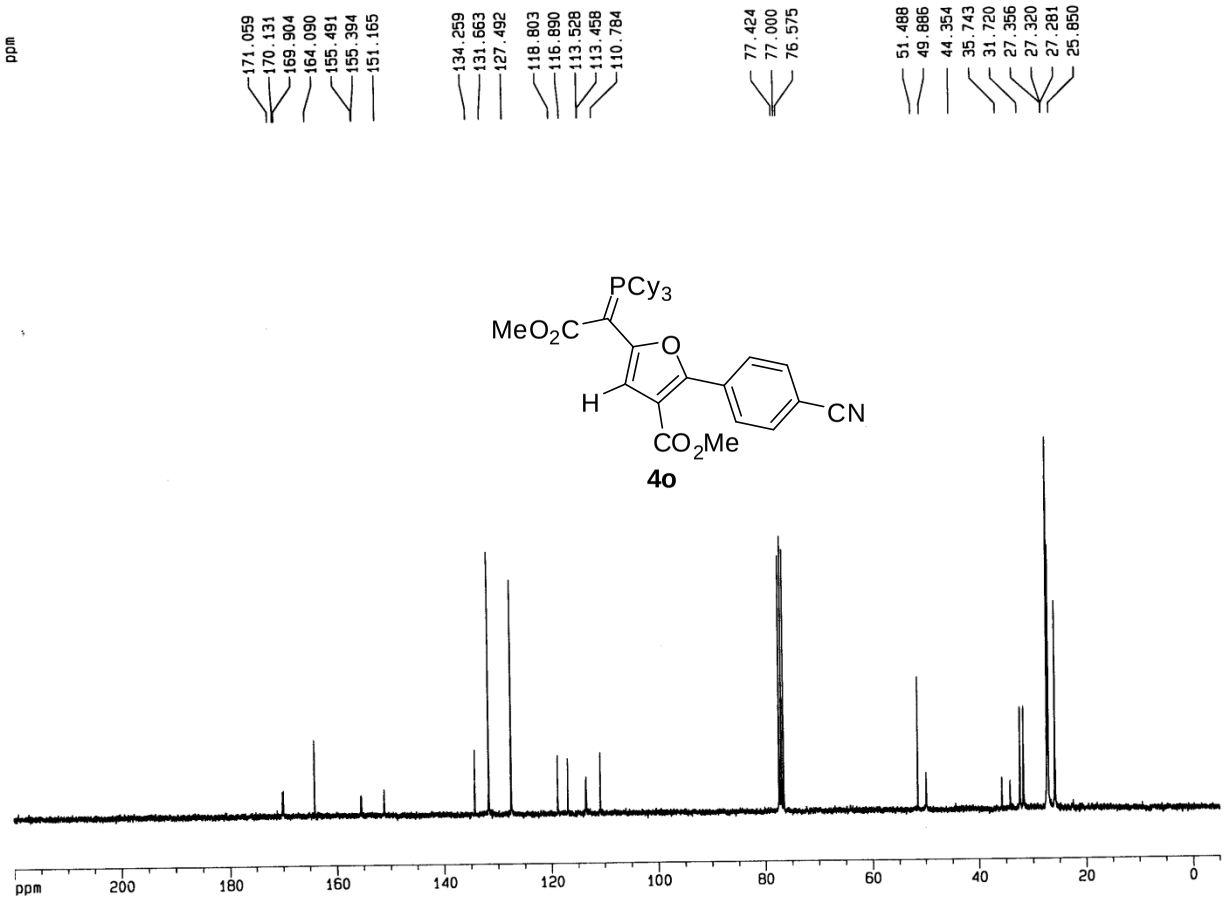


Fig. S35. ^{1}H NMR spectrum of compound **4p** (300 MHz, $CDCl_3$)

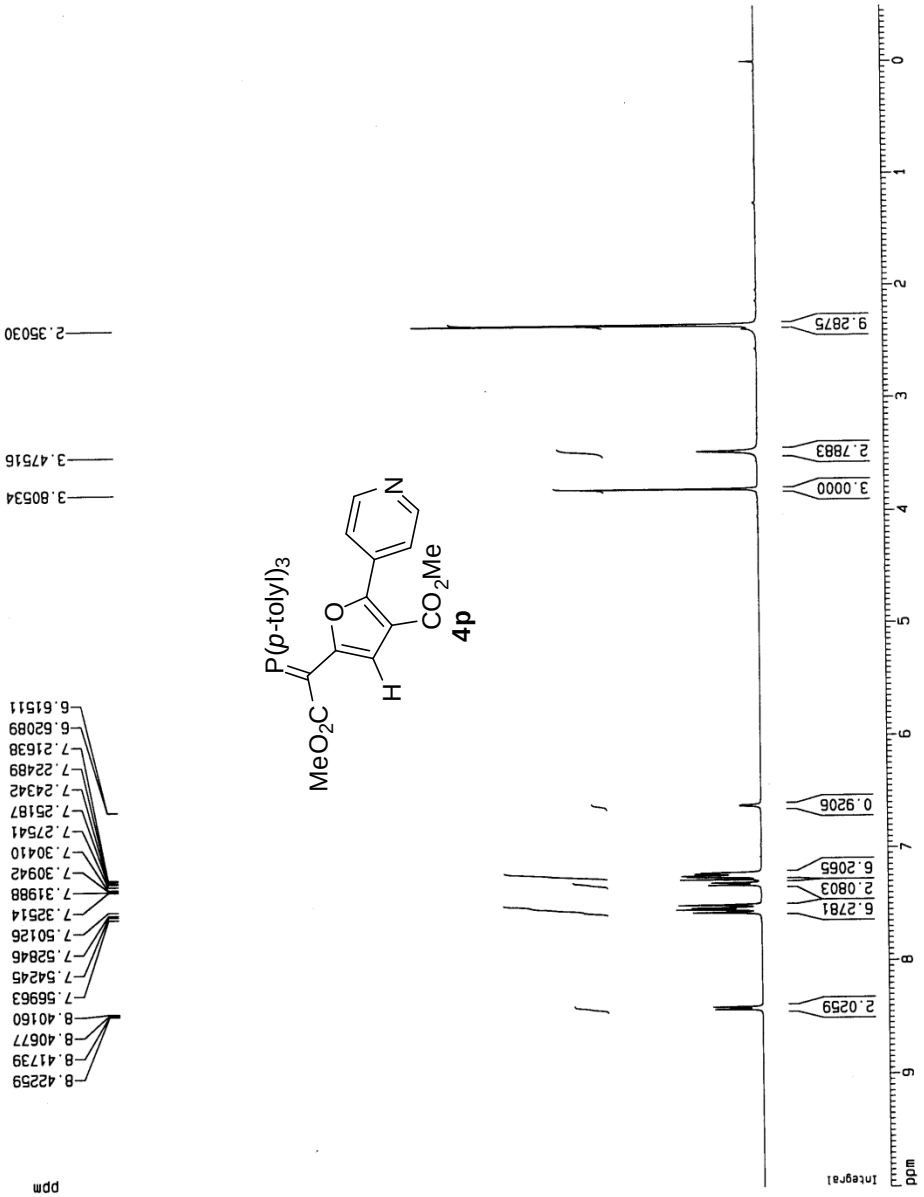


Fig. S36. ^{13}C NMR spectrum of compound **4p** (75.5 MHz, $CDCl_3$)

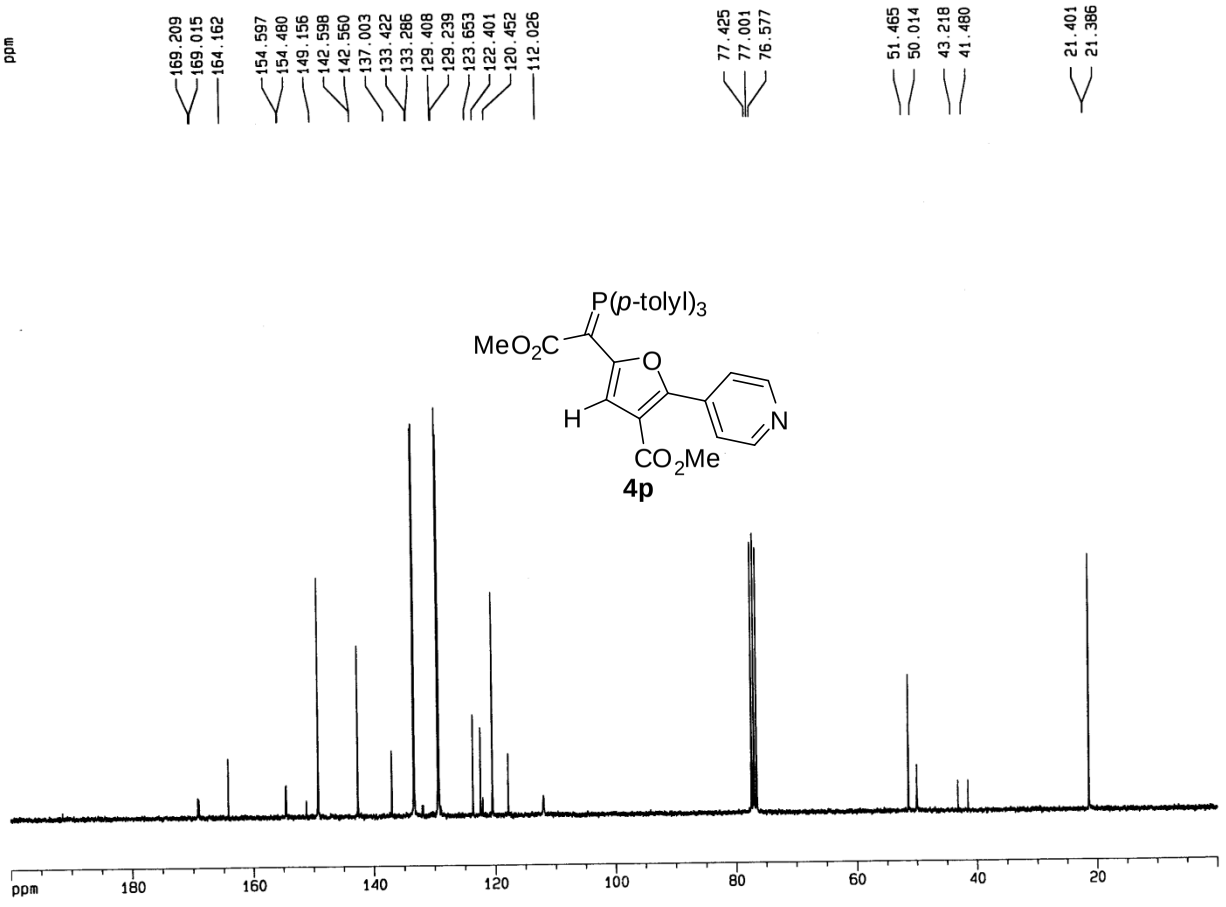


Fig. S37. ^{1}H NMR spectrum of compound **4q** (300 MHz, $CDCl_3$)

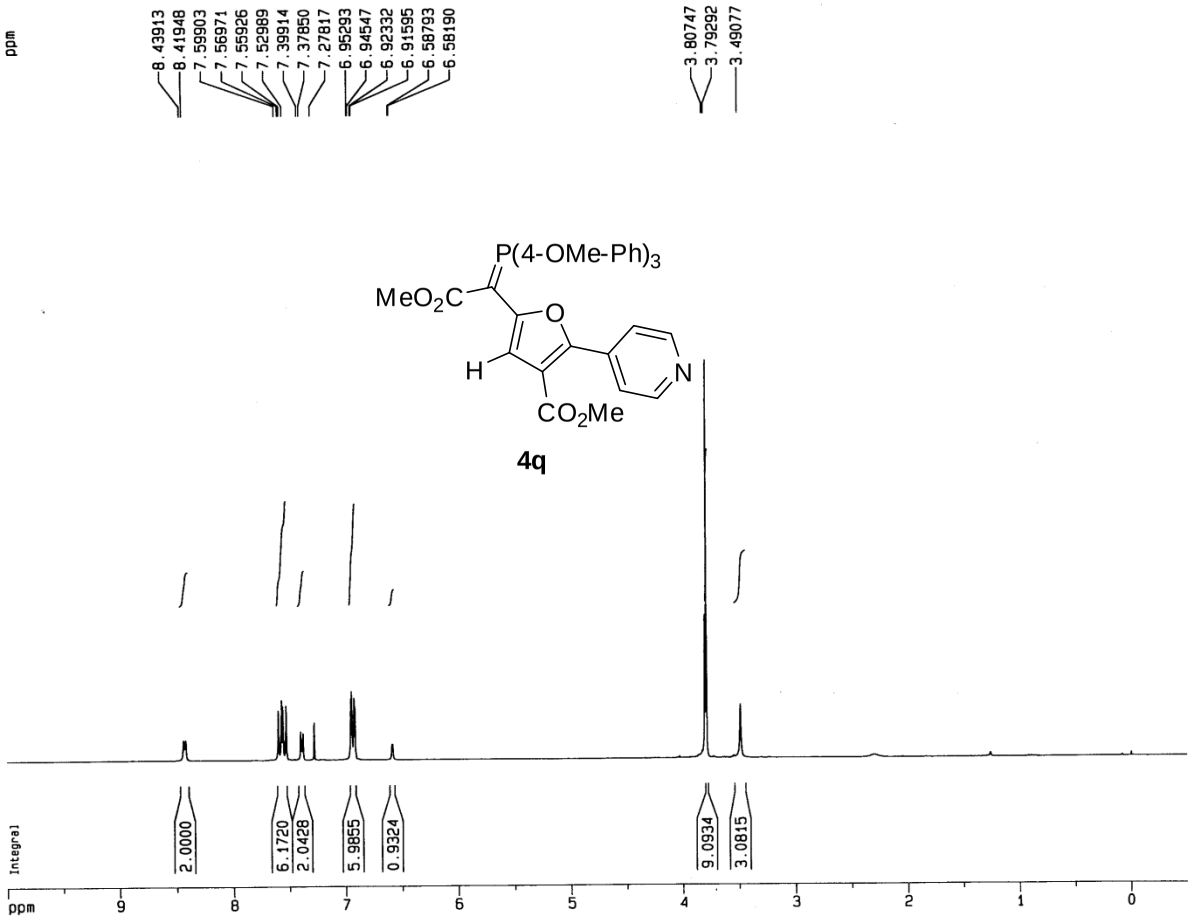


Fig. S38. ^{13}C NMR spectrum of compound **4q** (75.5 MHz, $CDCl_3$)

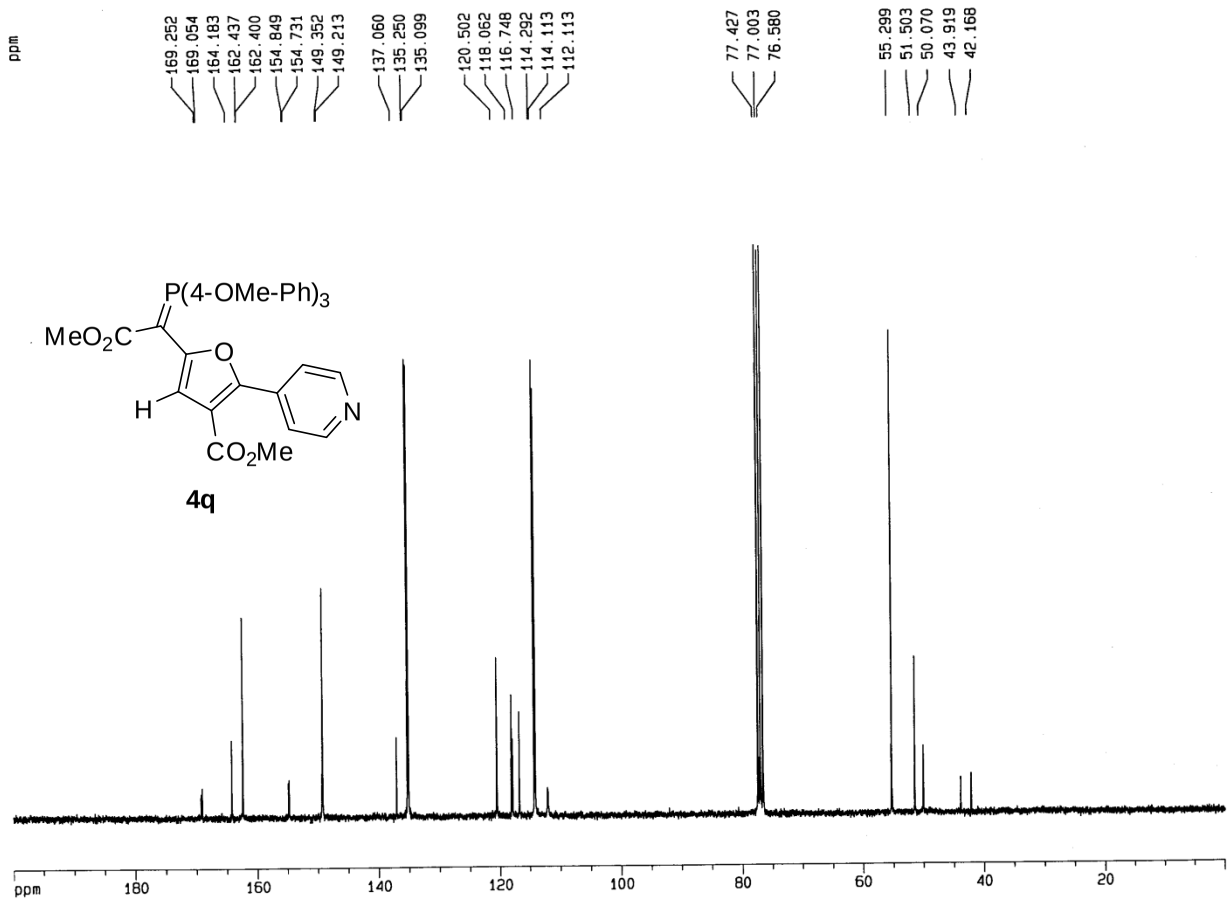


Fig. S39. ^{1}H NMR spectrum of compound **4r** (300 MHz, $CDCl_3$)

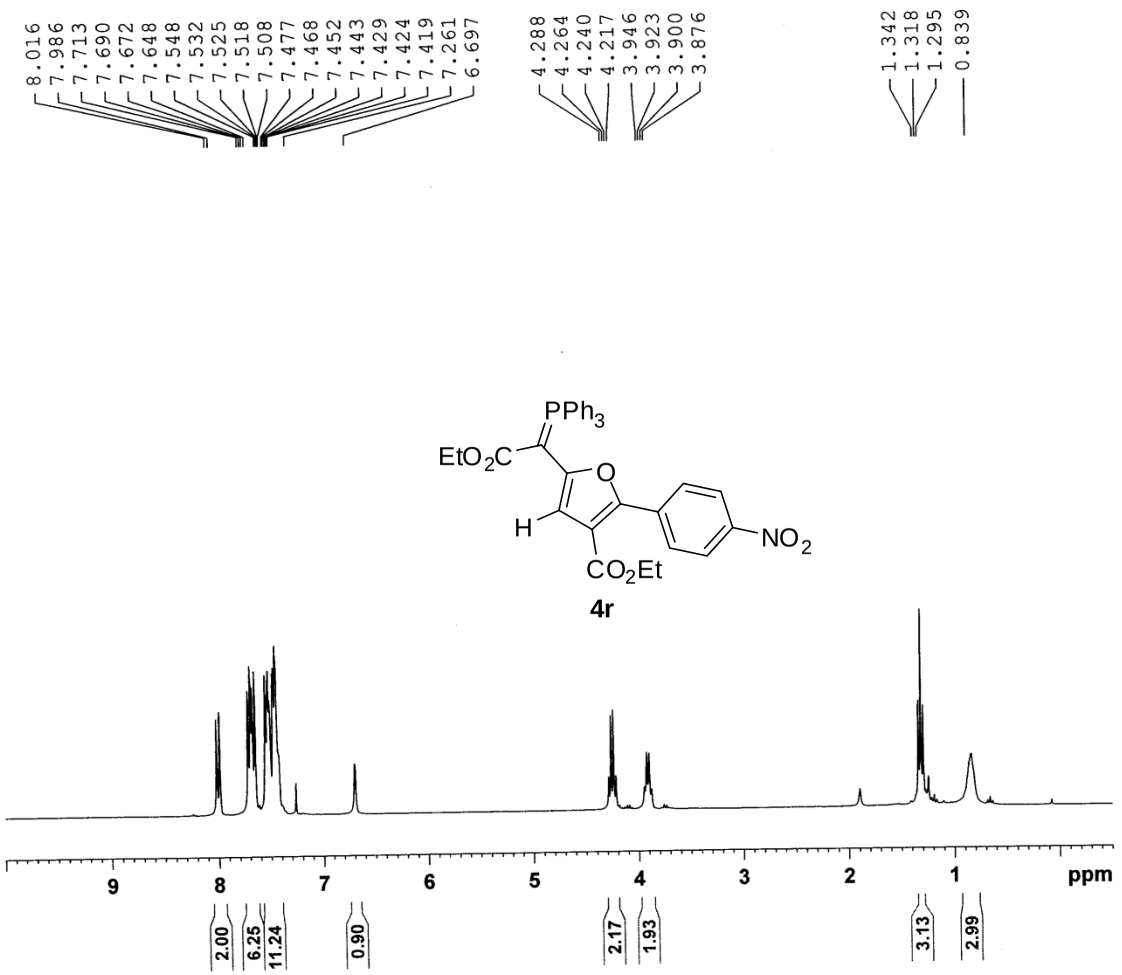


Fig. S40. ^{13}C NMR spectrum of compound **4r** (75.5 MHz, $CDCl_3$)

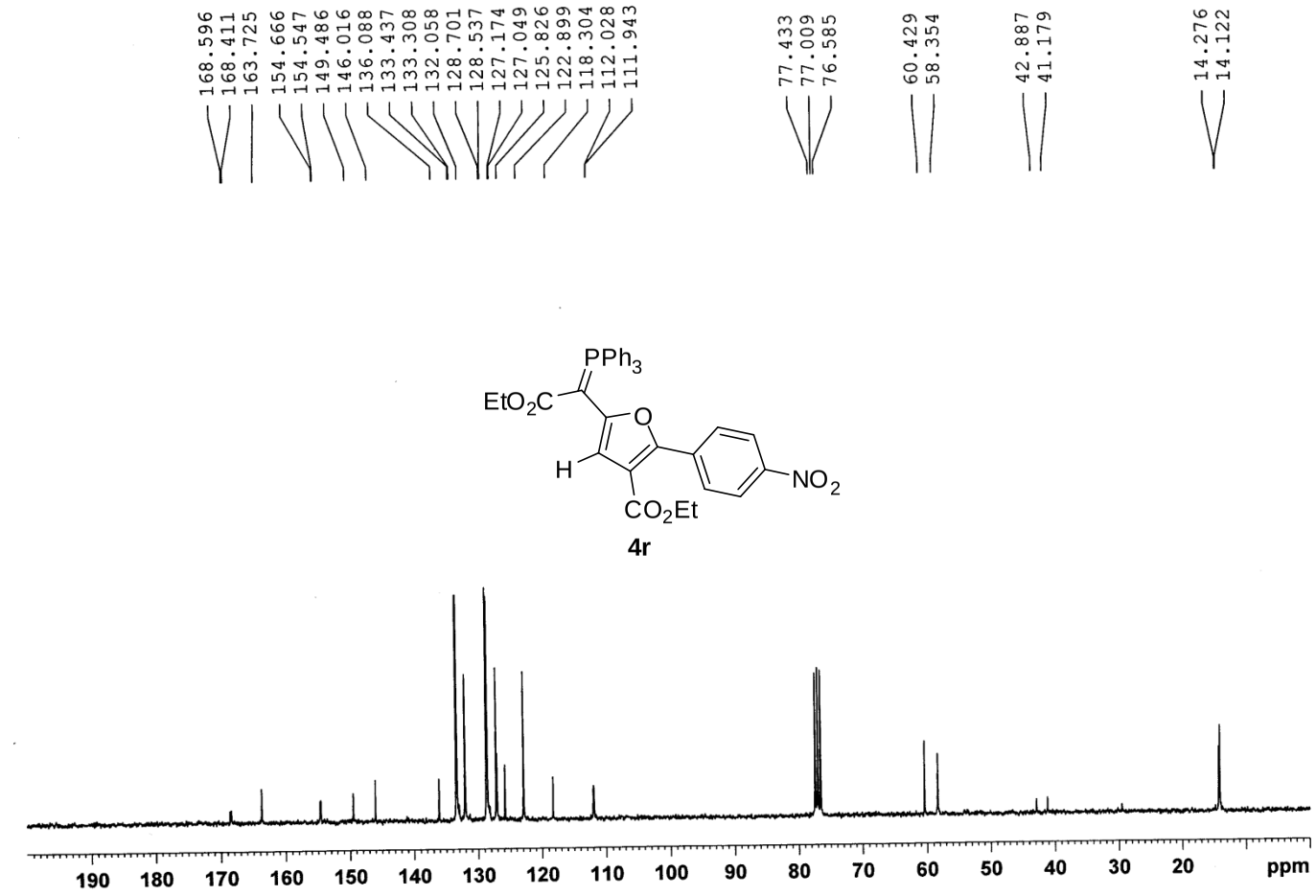


Fig. S41. ^{1}H NMR spectrum of compound **4s** (300 MHz, $CDCl_3$)

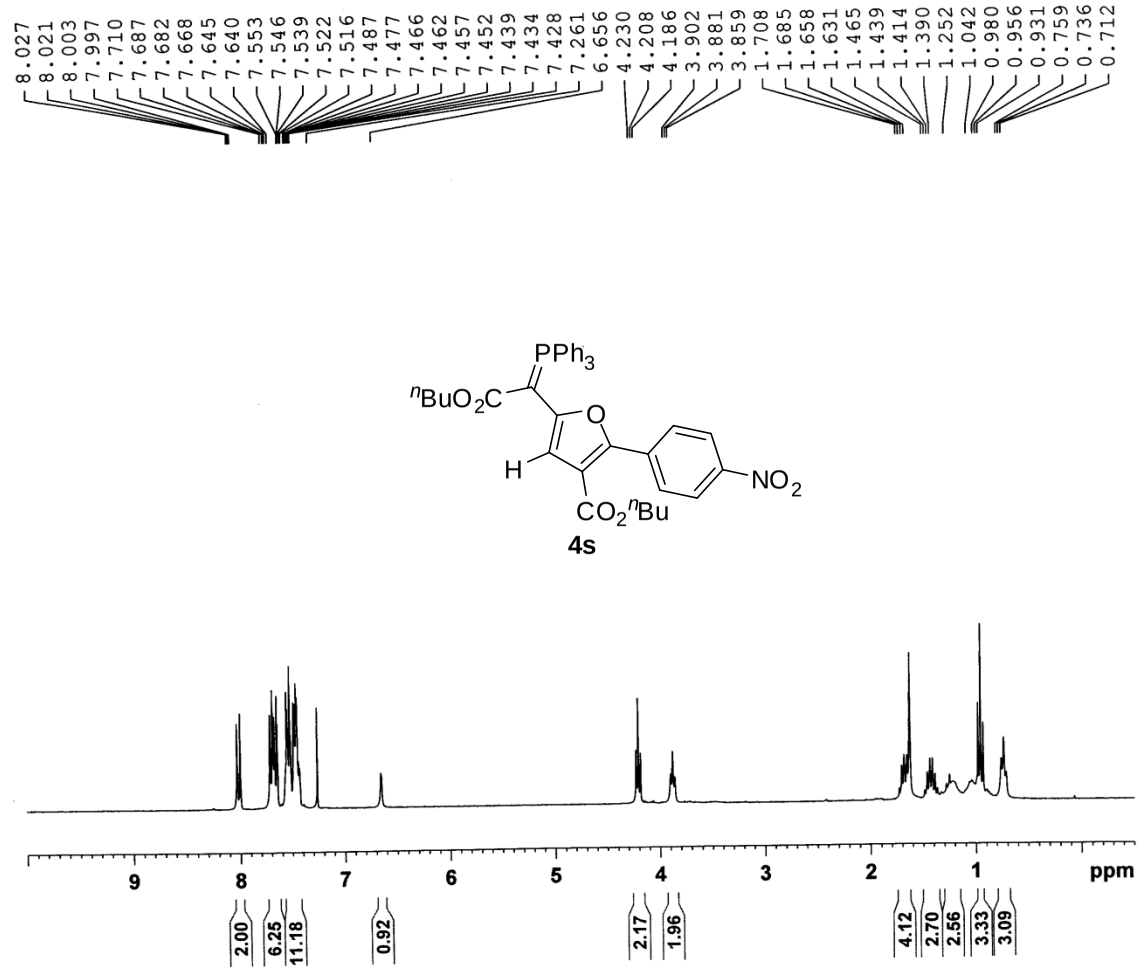


Fig. S42. ^{13}C NMR spectrum of compound **4s** (75.5 MHz, $CDCl_3$)

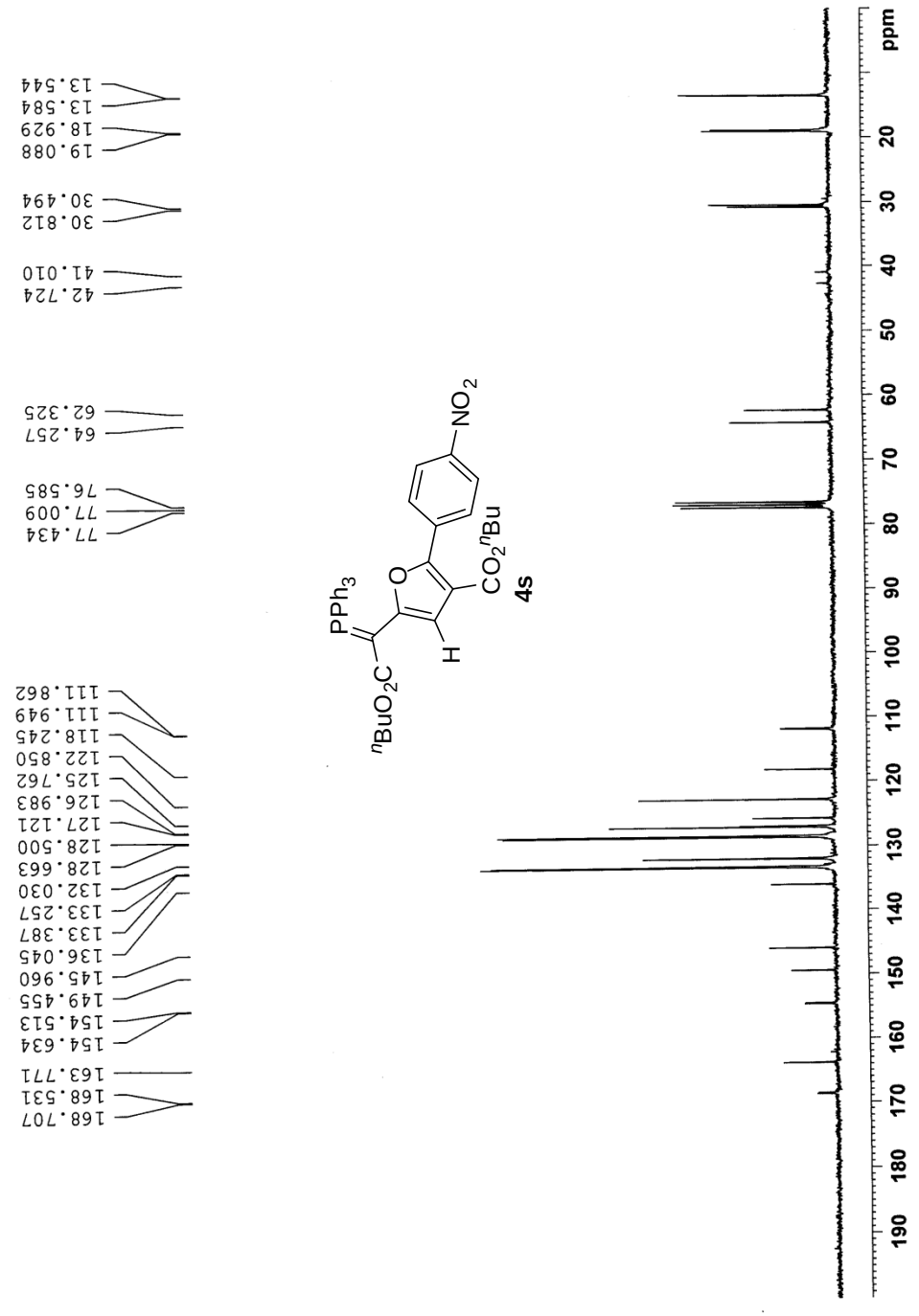


Fig. S43. ^{1}H NMR spectrum of compound **4t** (300 MHz, $CDCl_3$)

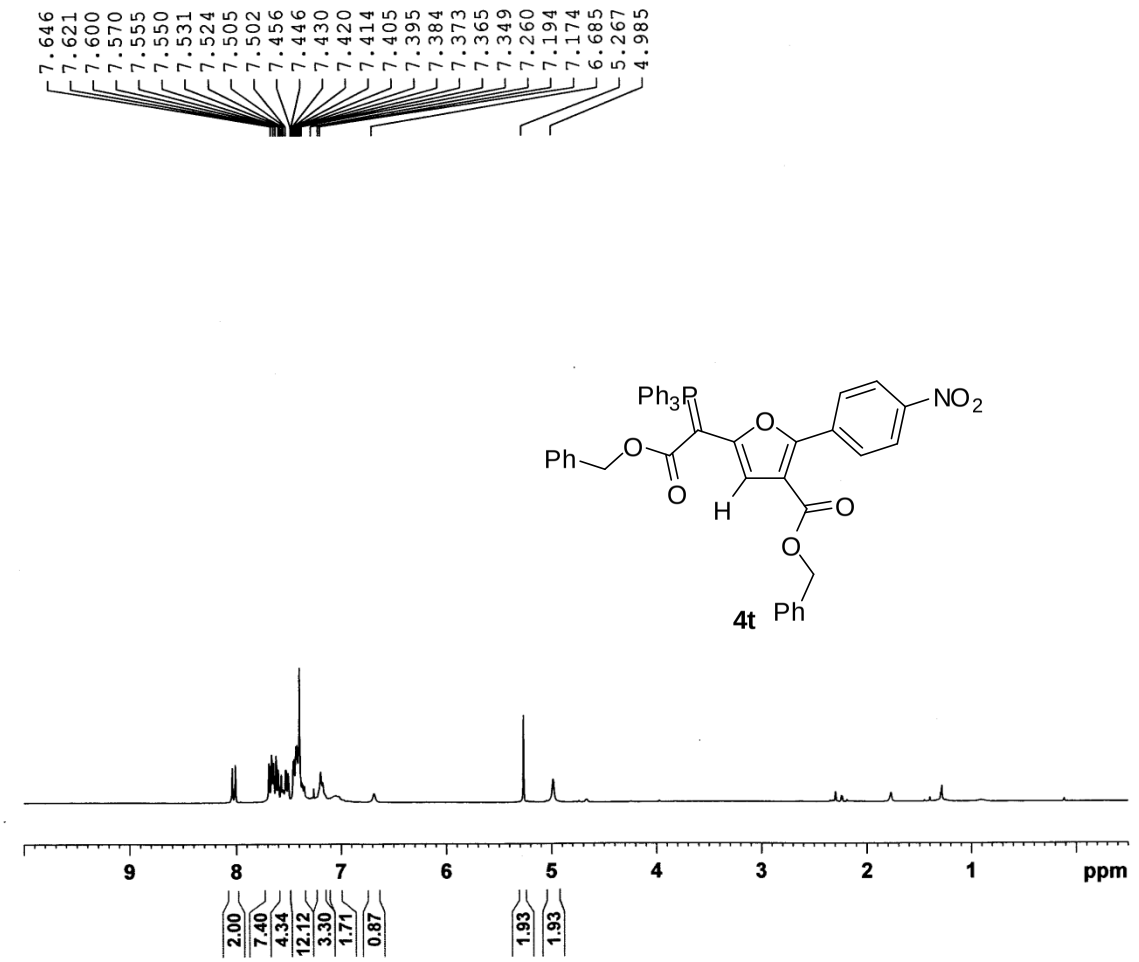


Fig. S44. ^{13}C NMR spectrum of compound **4t** (75.5 MHz, $CDCl_3$)

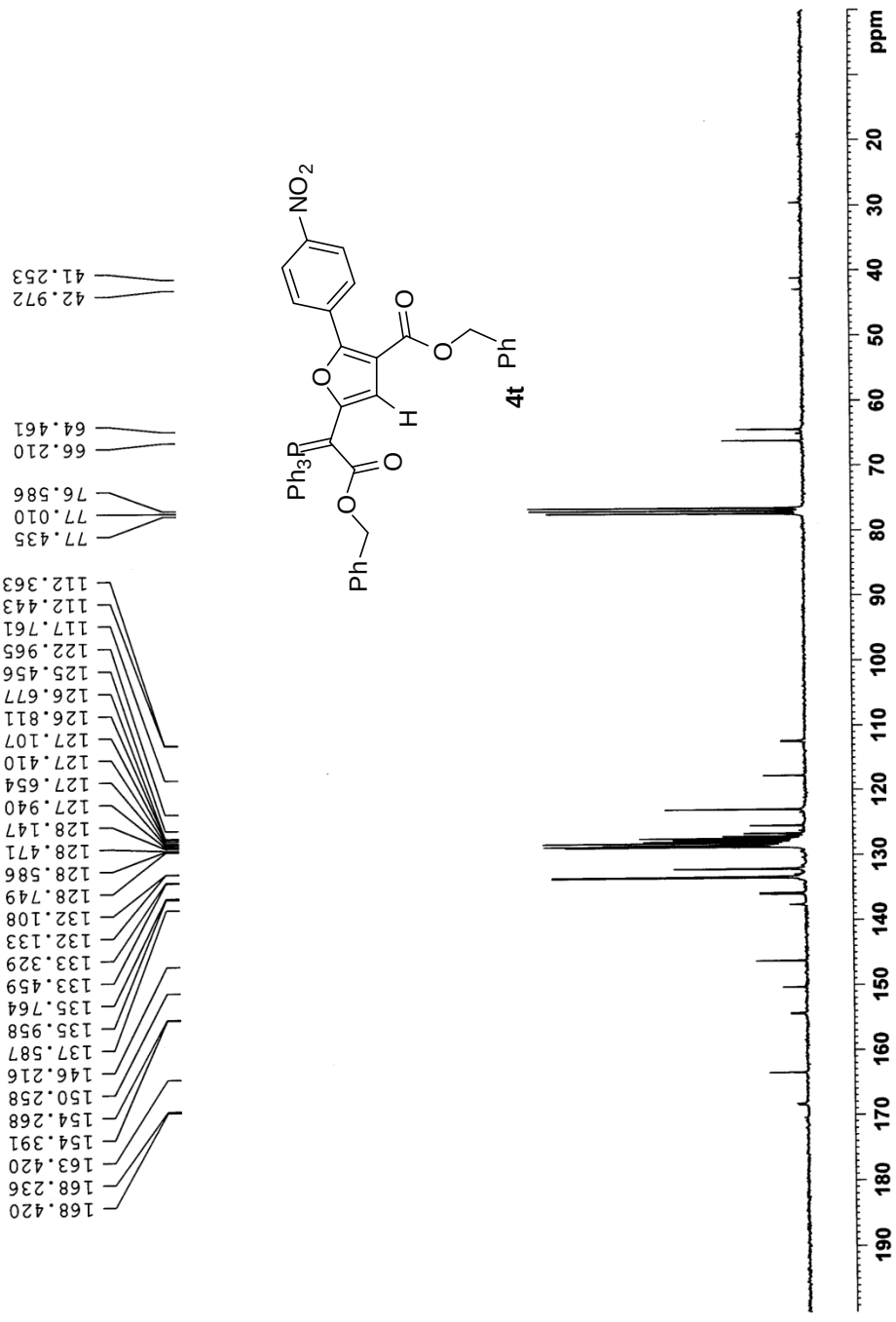


Fig. S45. ^{1}H NMR spectrum of compound **6a** (300 MHz, $CDCl_3$)

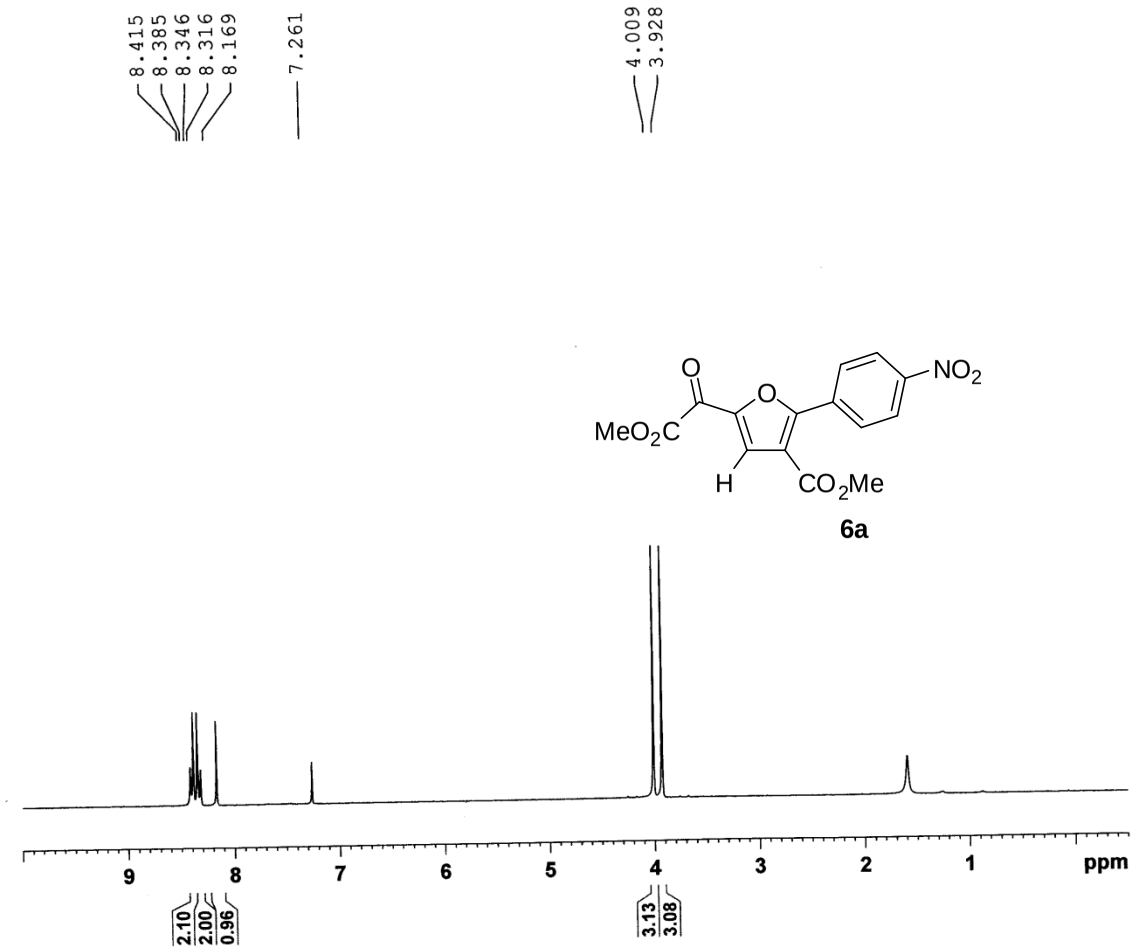


Fig. S46. ^{13}C NMR spectrum of compound **6a** (100 MHz, $CDCl_3$)

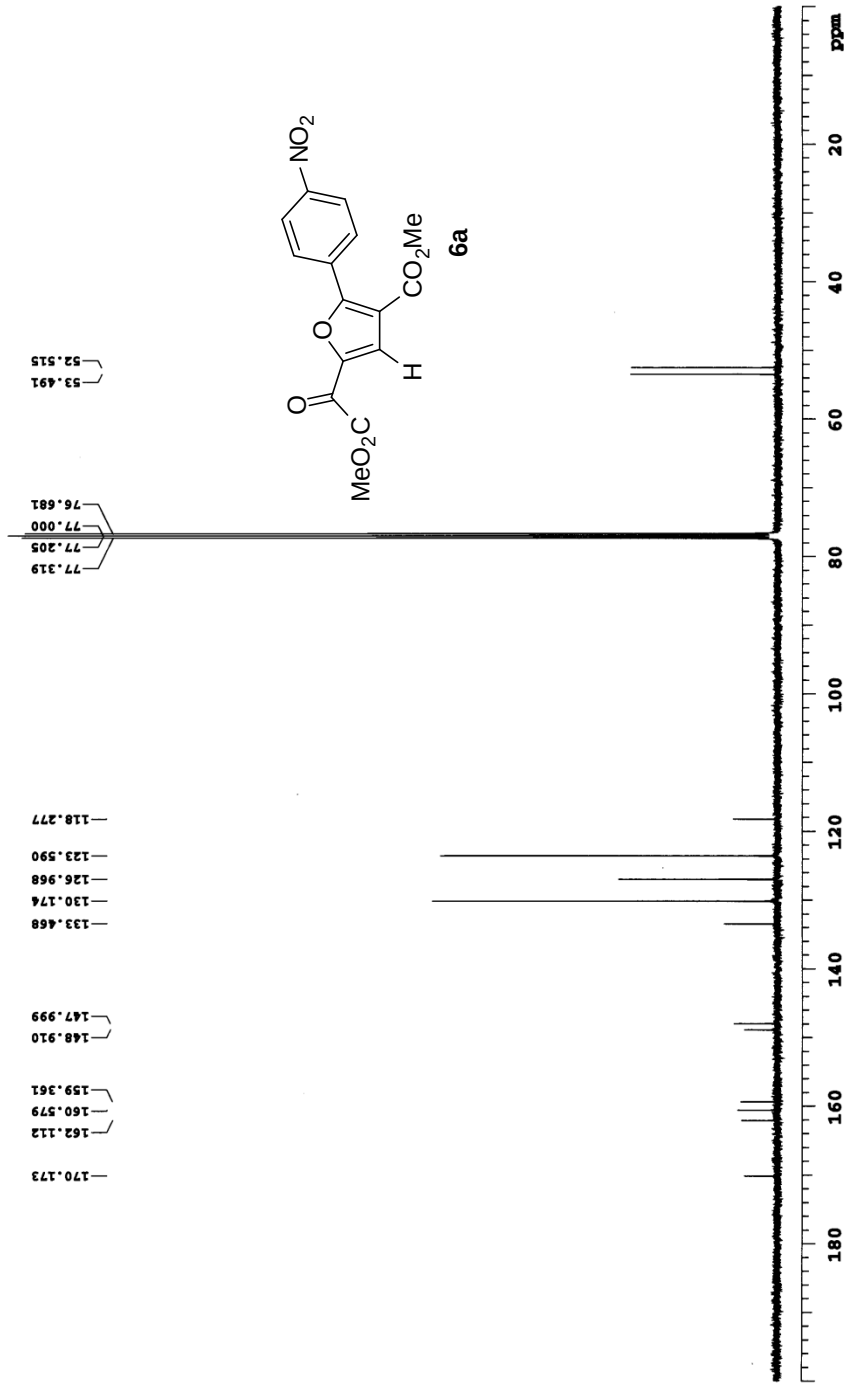


Fig. S47. ^{1}H NMR spectrum of compound **6b** (400 MHz, $CDCl_3$)

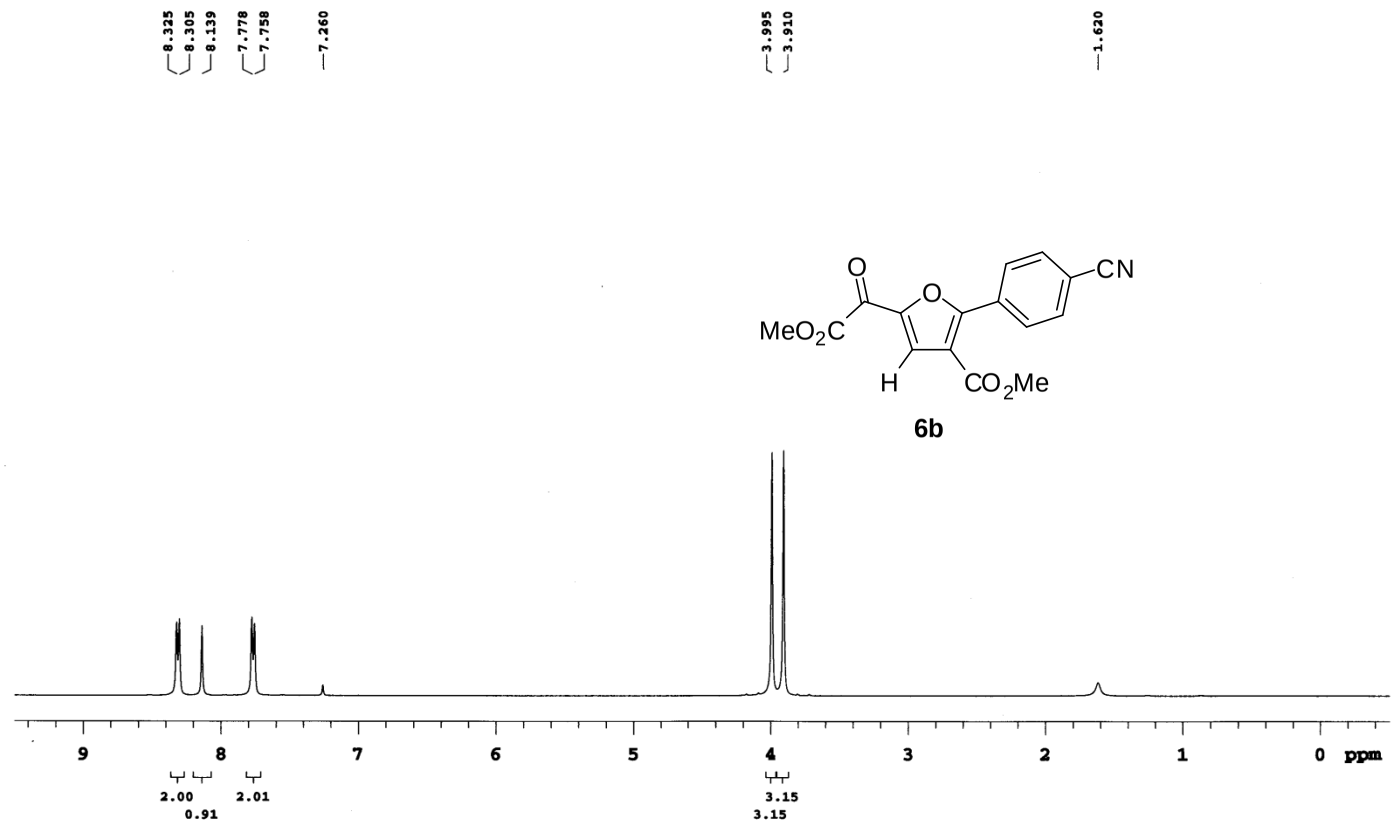


Fig. S48. ^{13}C NMR spectrum of compound **6b** (100 MHz, $CDCl_3$)

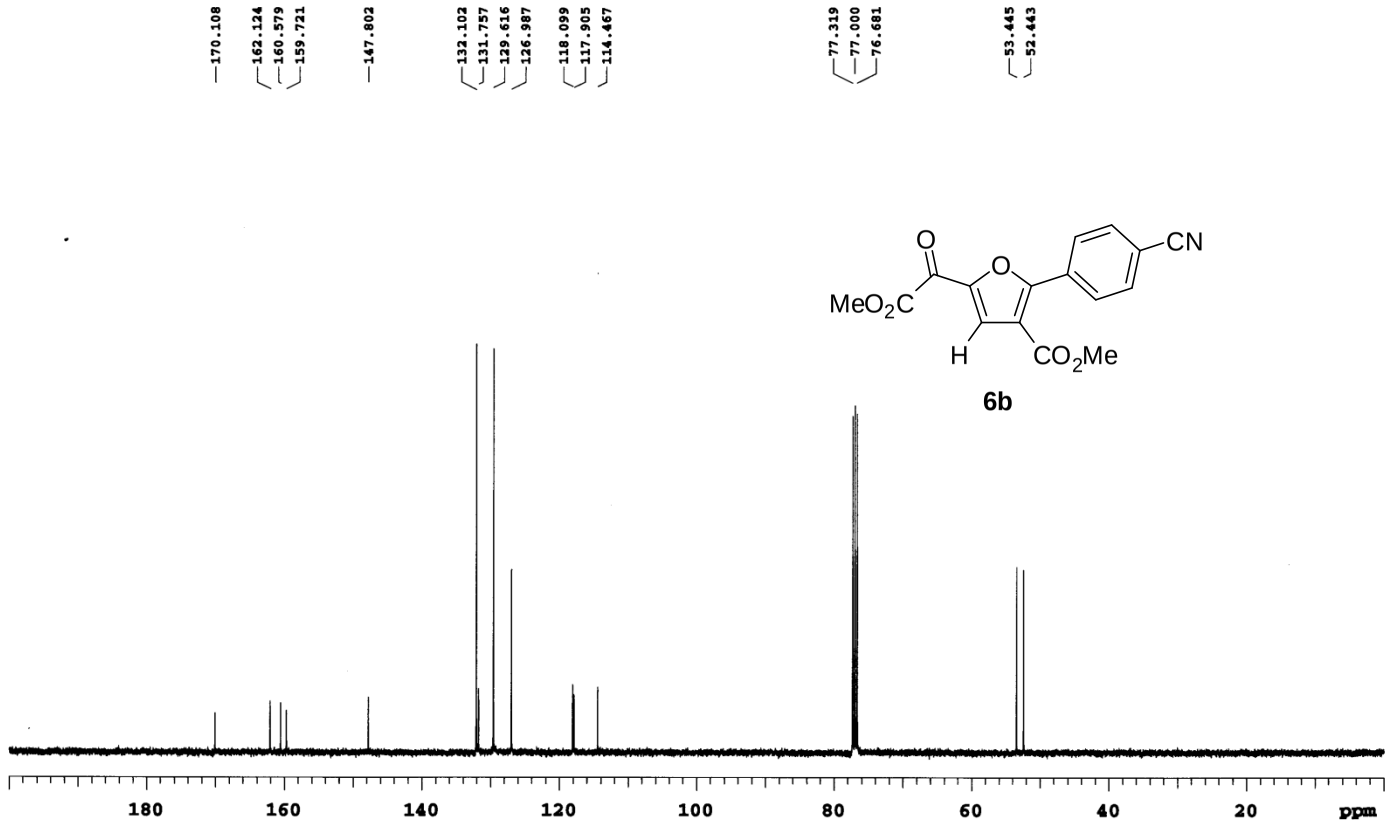


Fig. S49. ^{1}H NMR spectrum of compound **6c** (400 MHz, $CDCl_3$)

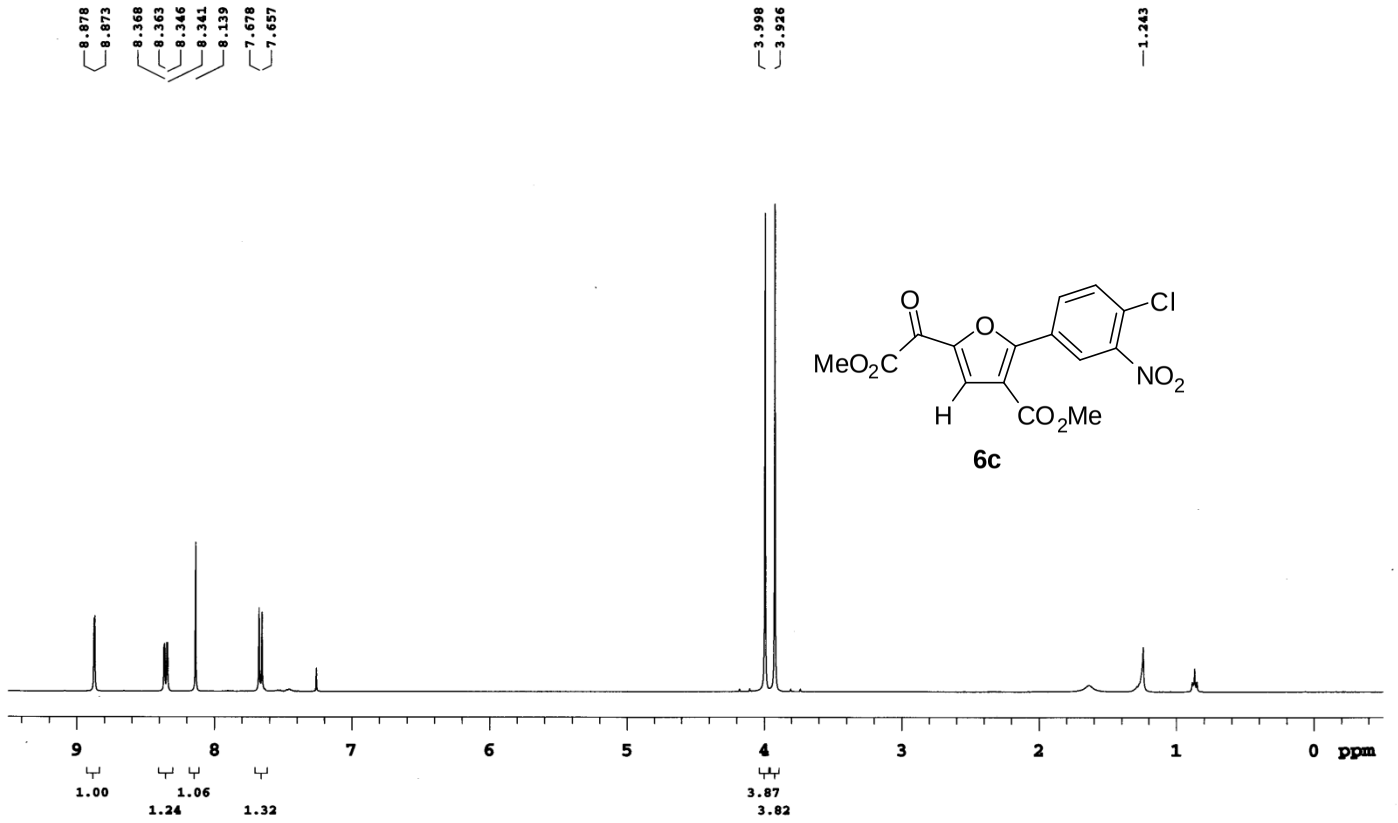


Fig. S50. ^{13}C NMR spectrum of compound **6c** (100 MHz, $CDCl_3$)

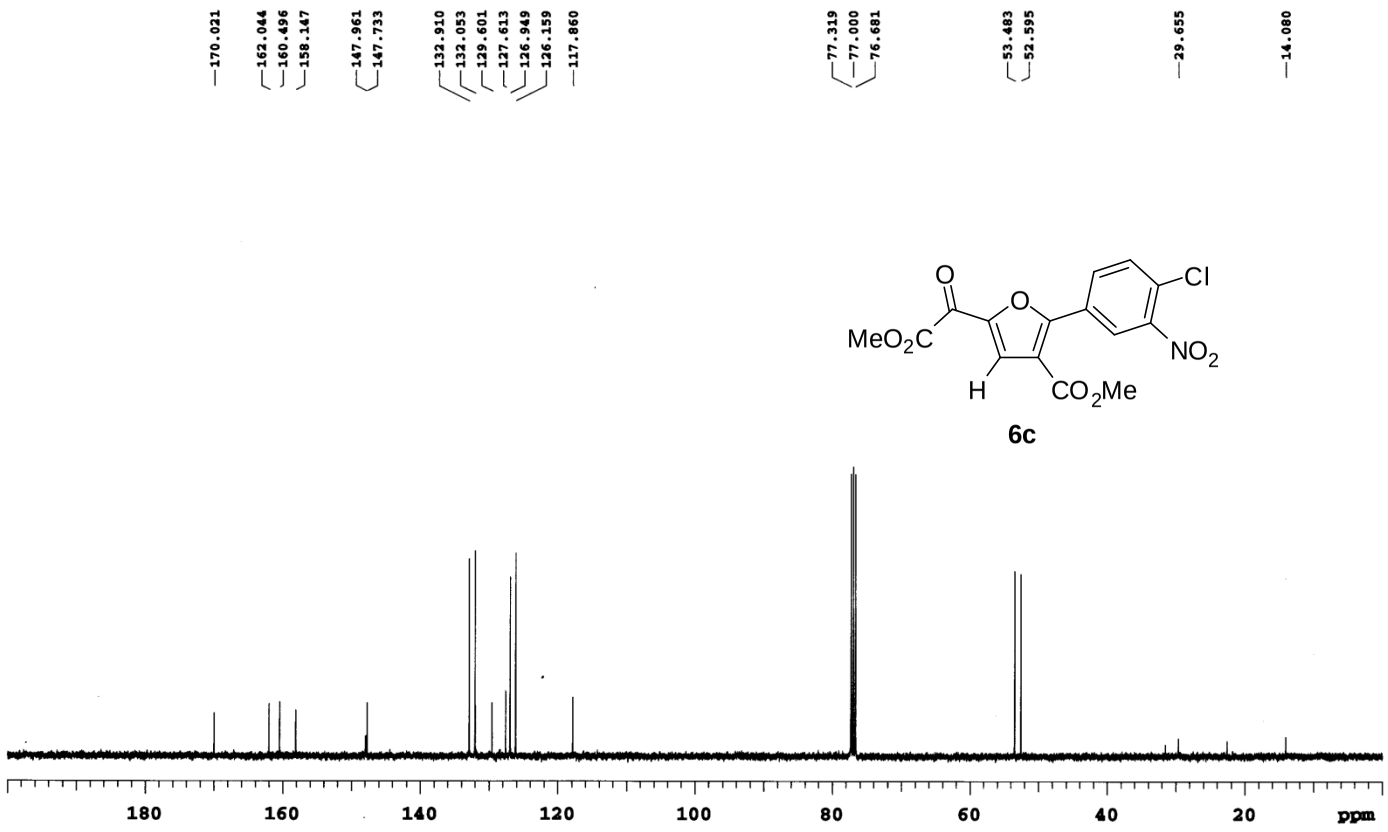


Fig. S51. ^{1}H NMR spectrum of compound **6d** (400 MHz, $CDCl_3$)

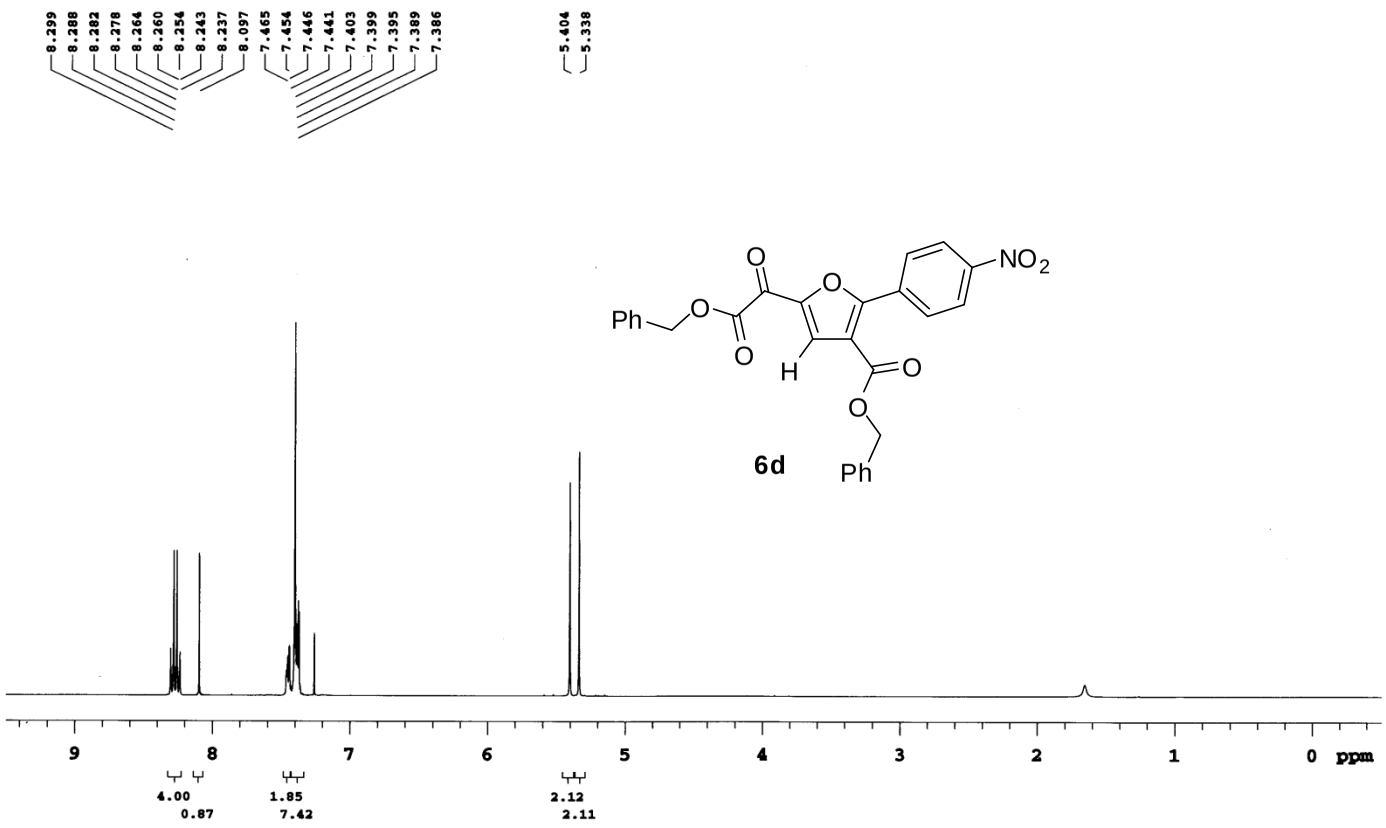


Fig. S52. ^{13}C NMR spectrum of compound **6d** (100 MHz, $CDCl_3$)

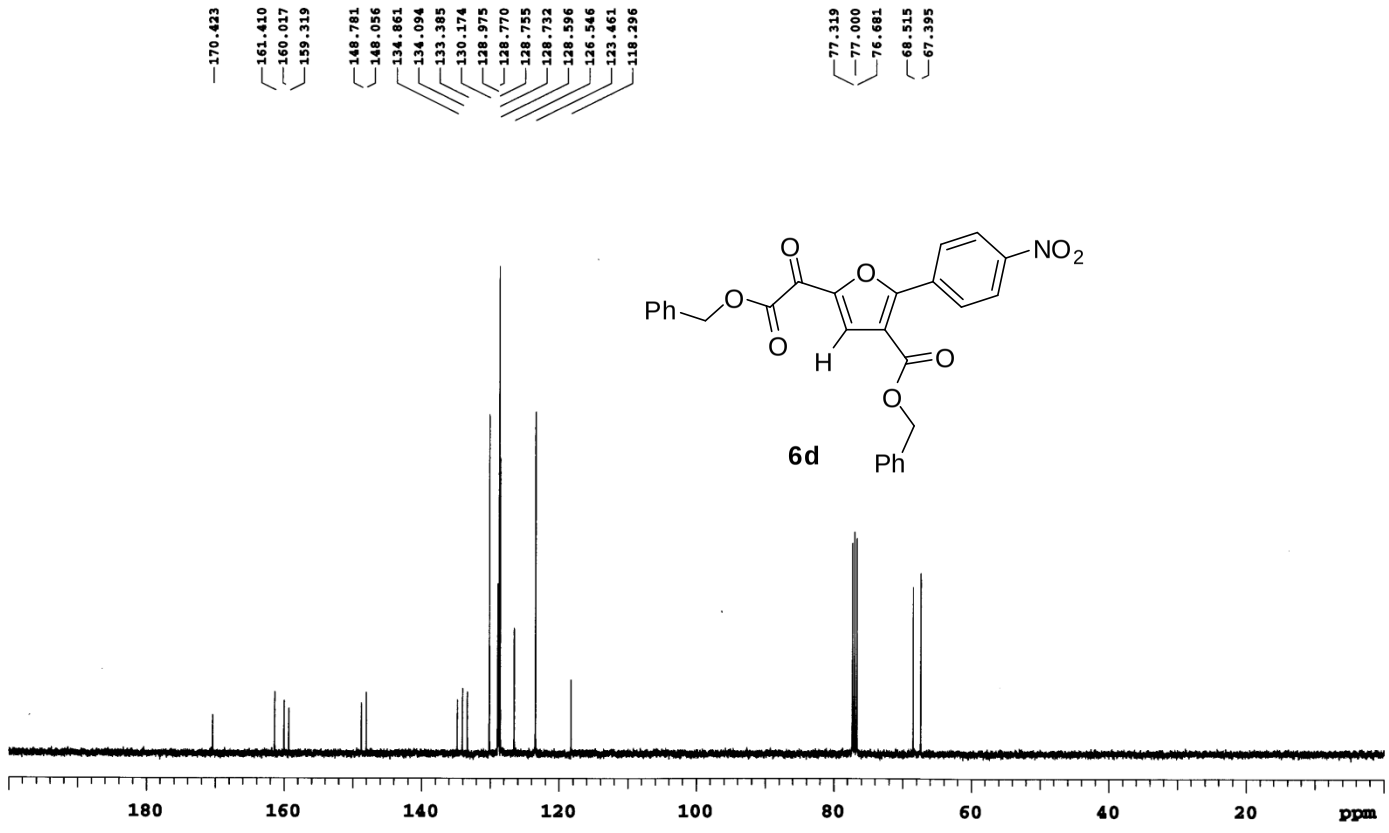


Fig. S53. ^{1}H NMR spectrum of a mixture of compounds (*E*)-**7a** and (*Z*)-**7a** (300 MHz, $CDCl_3$)

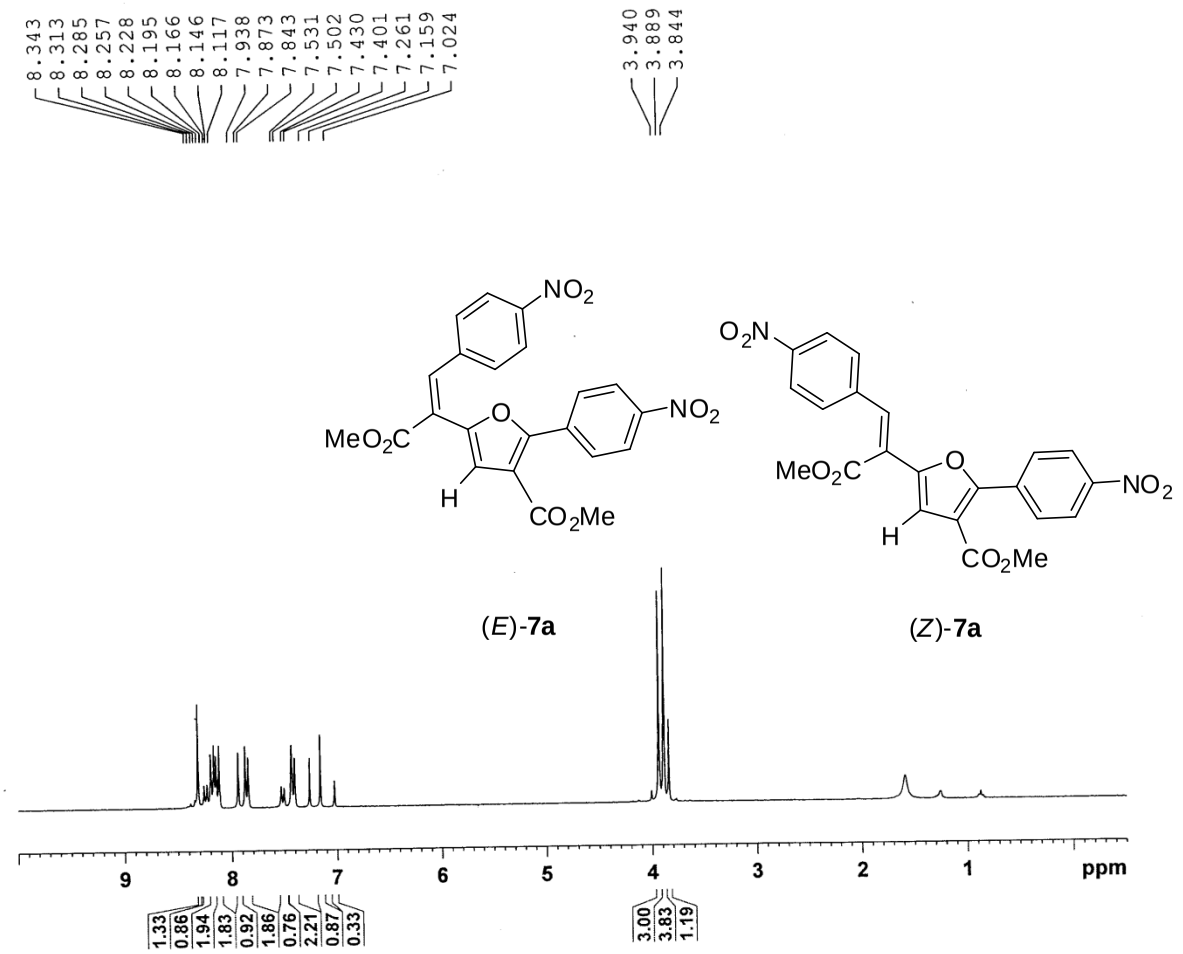


Fig. S54. ^{13}C NMR spectrum of a mixture of compounds (*E*)-**7a** and (*Z*)-**7a** (100 MHz, $CDCl_3$)

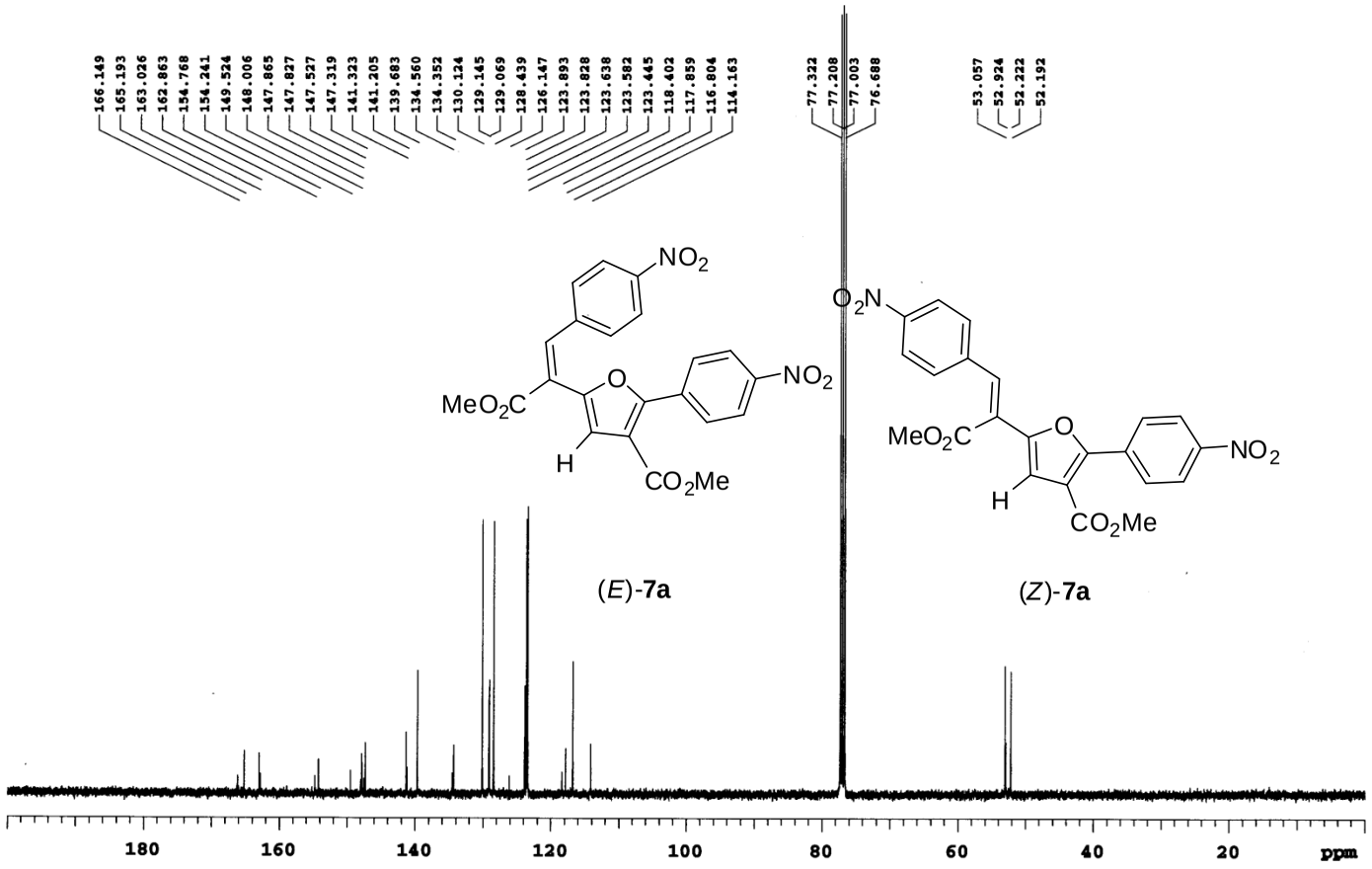


Fig. S55. ^{1}H NMR spectrum of compound **7a'** (400 MHz, $CDCl_3$)

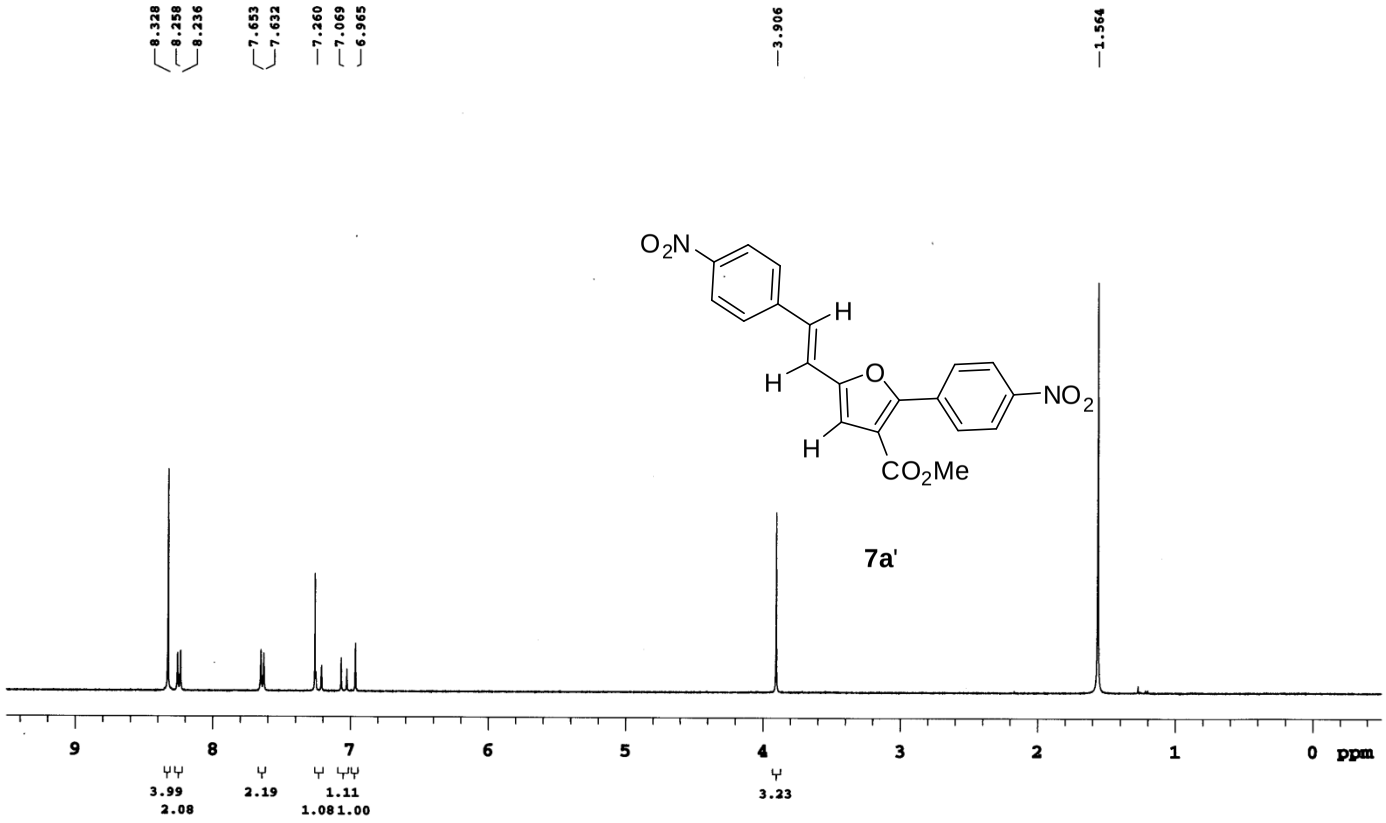


Fig. S56. ^{13}C NMR spectrum of compound **7a'** (100 MHz, $CDCl_3$)

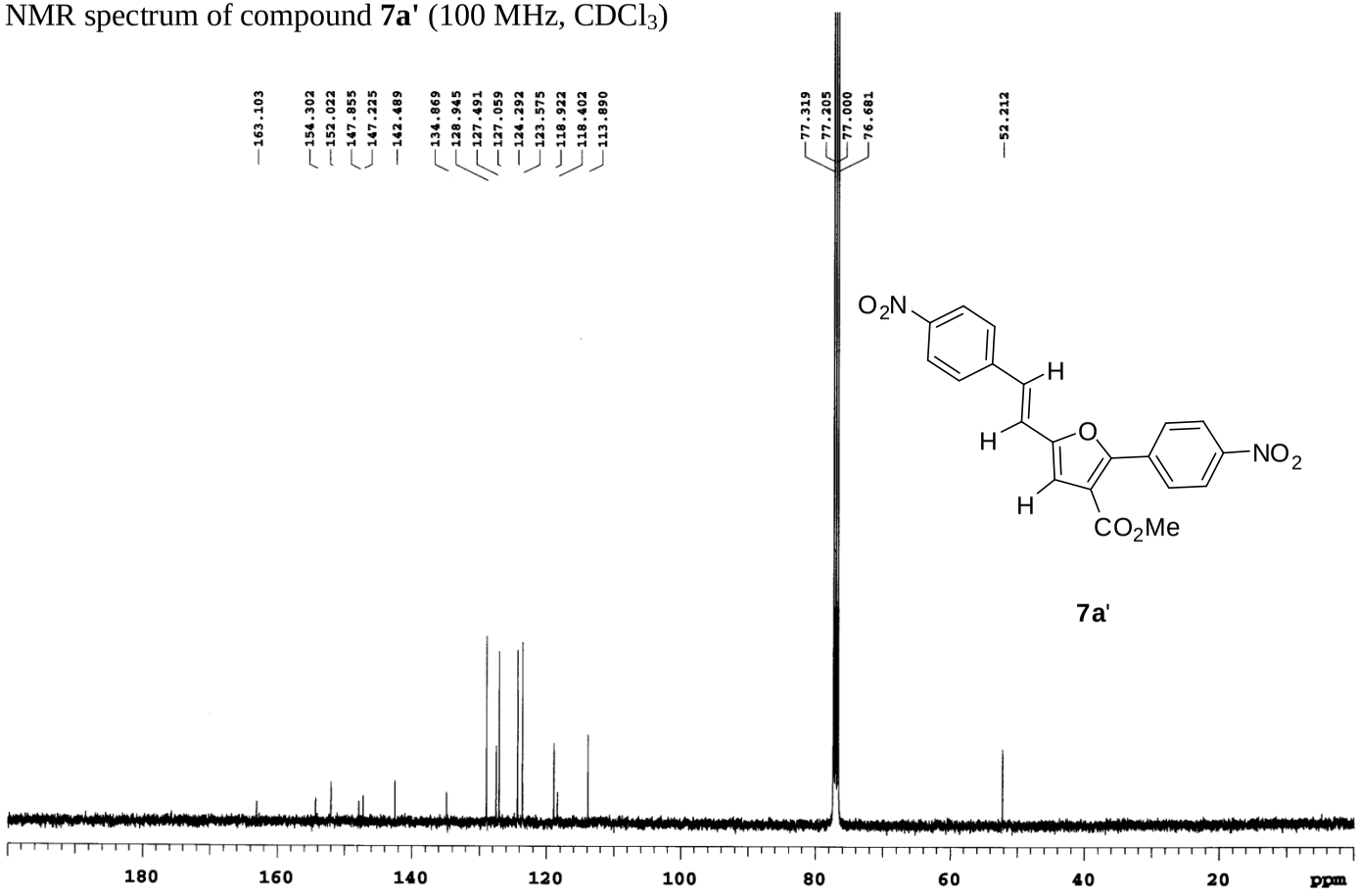


Fig. S57. ^{1}H NMR (left column) in 2.7-4.2 ppm and ^{31}P NMR (right column) spectra of **4b** at variable temperature.

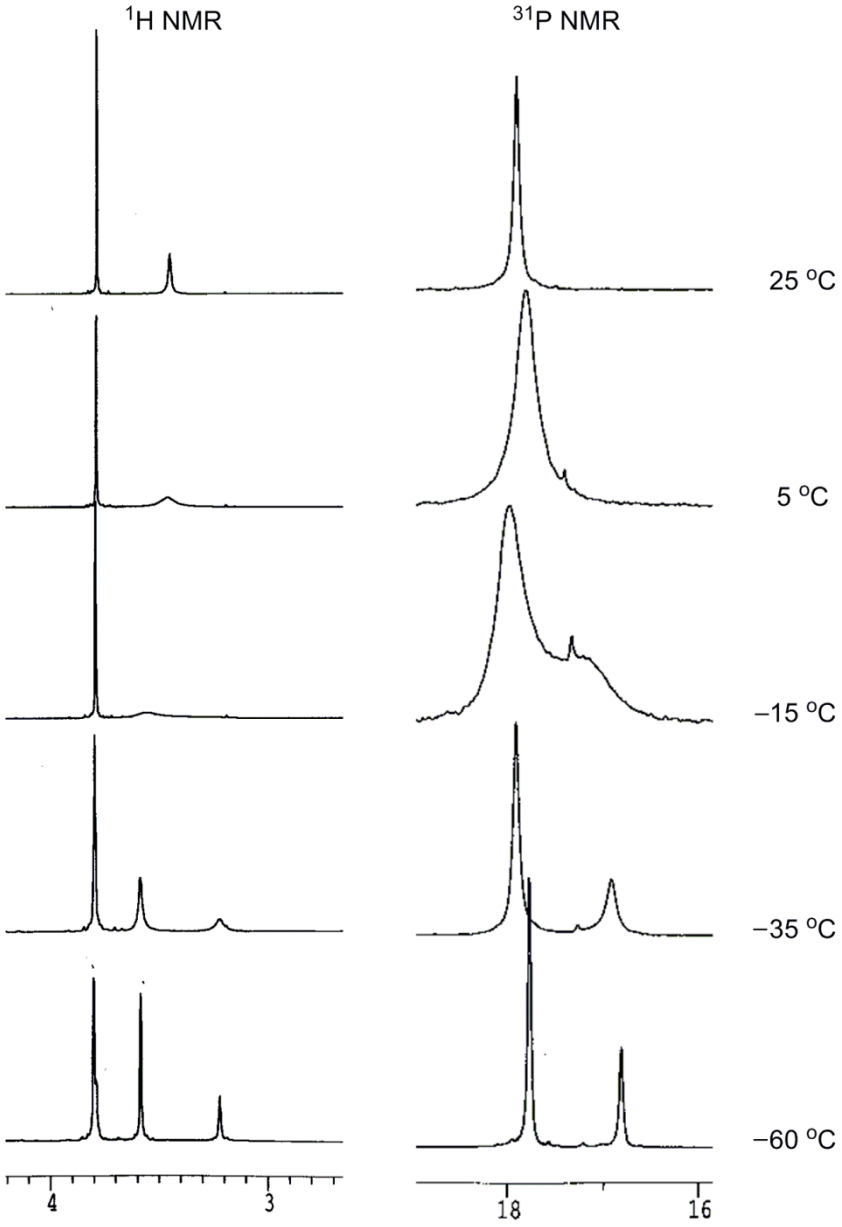


Fig. S58. Variable temperature full ^{1}H NMR of **4b** (600 MHz, $CDCl_3$)

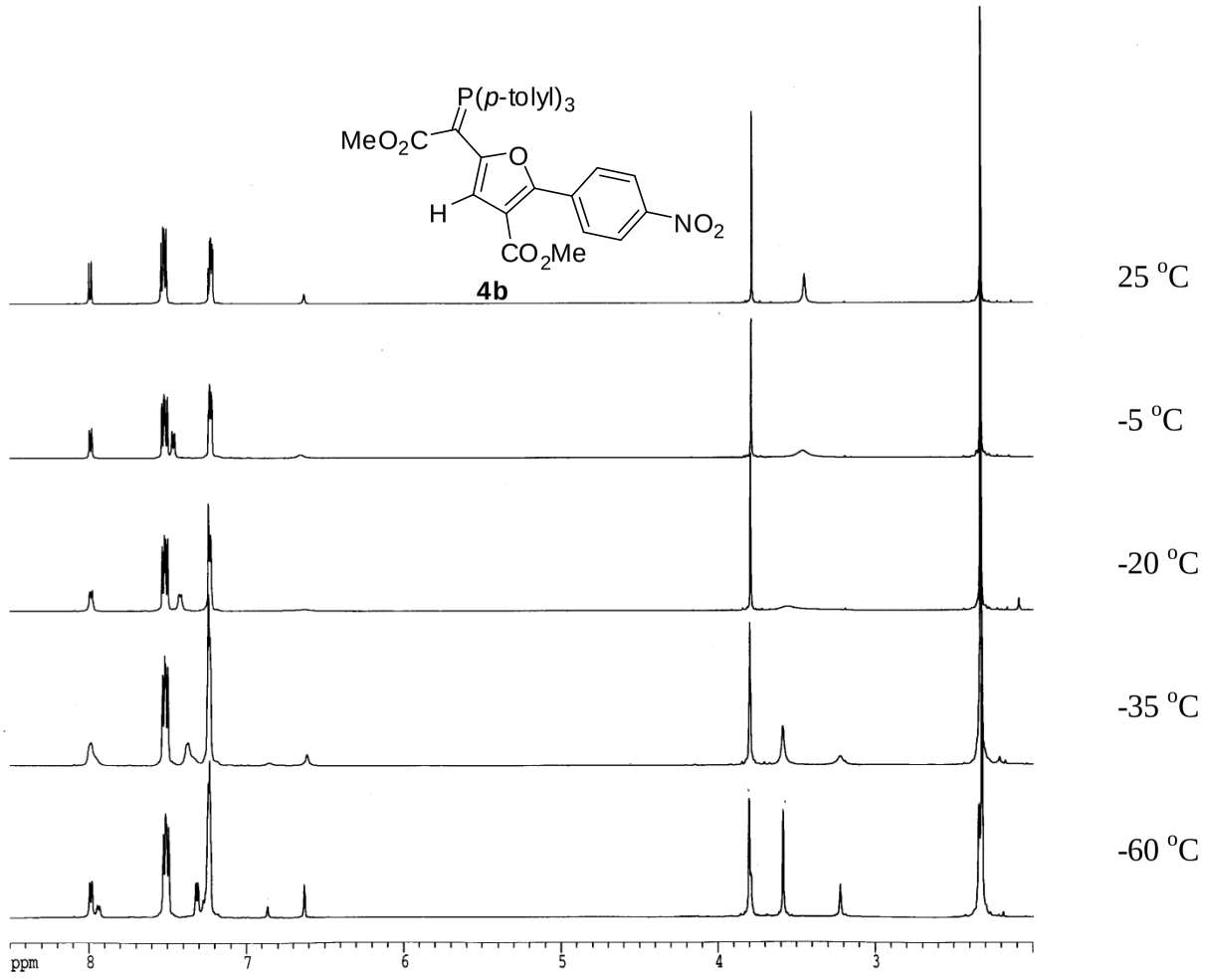


Fig. S59. 2D-HMQC spectrum of furan **4b**.

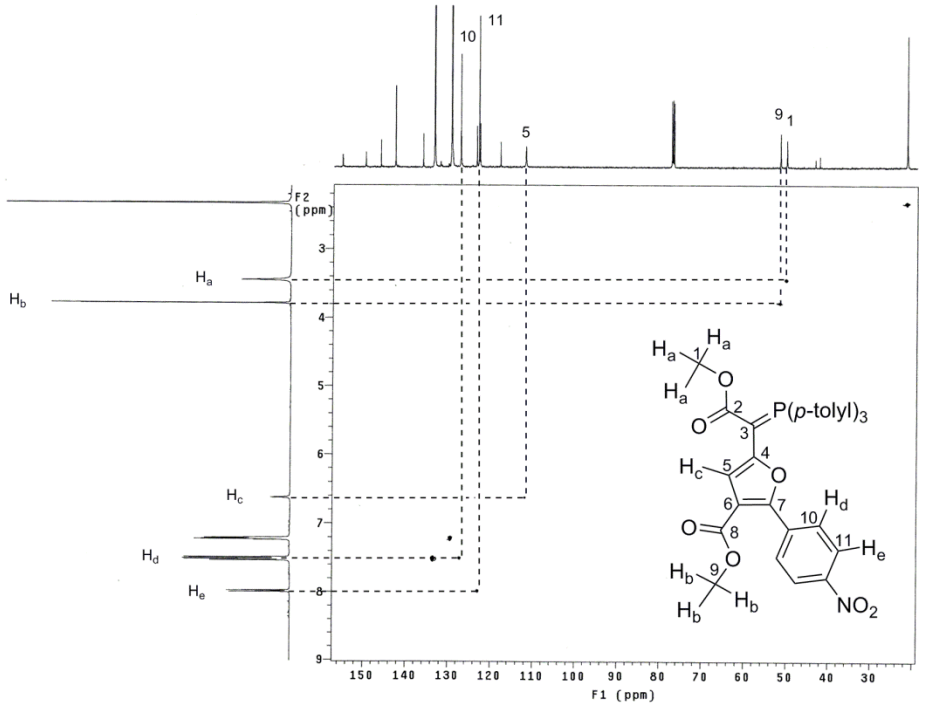
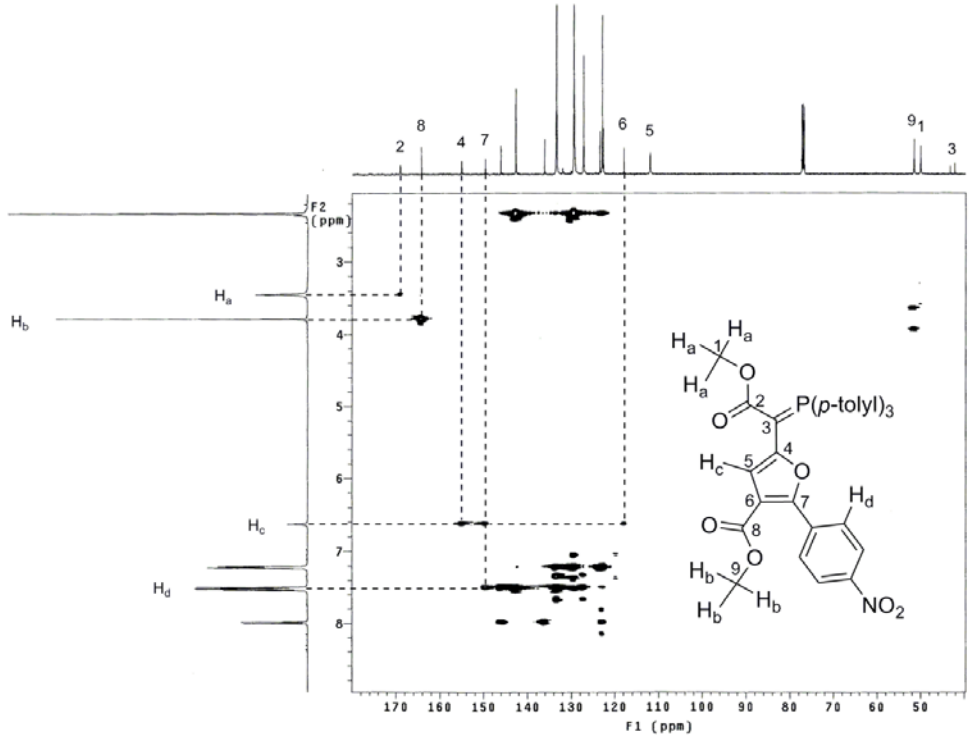


Fig. S60. 2D-HMBC spectrum of furan **4b**.



Notes:

All MS data corresponded to the expected formulas; for examples, the high-resolution mass spectrum (ESI, electron spray ionization method) (HRMS) of **4b** exhibited the combination of three starting reactants, showing *m*/*z* = 621.1916. Their IR spectra showed two carbonyl absorptions at *ca.* 1623 and 1718 cm^{-1}; further, the absorption at 1623 cm^{-1} indicated that these structures possessed phosphorus ylide ester group.[2] In the ^{1}H NMR spectrum, furan **4b** showed two methoxyl protons at 3.41 and 3.81 ppm and a singlet proton on furan appeared at 6.66 ppm. The ^{13}C NMR of **4b** displayed one singlet and one doublet at 164.2 and 169.1 ppm ($^{2}J_{PC}$ = 14.3 Hz), corresponding to ester carbon C8 and ester carbon adjacent to phosphorus ylide, C2 (Figure S60), respectively. Two singlets at δ = 50.1 and 51.6 ppm corresponded to two methoxyl groups C1 and C9 respectively. The signal of the phosphorus ylidic carbon C3, on the other hand, appeared at δ = 42.8 ppm with one bond coupling to P-atom ($^{1}J_{PC}$ = 130.6 Hz). Furthermore, we found a signal at δ = 18.5 ppm in the ^{31}P spectrum at room temperature. We also made partial peak assignments based on one- (2D-HMQC) and three-bond (2D-HMBC) ^{1}H-^{13}C correlation spetra (Figure S60). The one-bond coupling signals indicated that protons on C1, C5, and C9 were readily assignable (Fig. S59, see the Supporting Information). The carbonyl C2 and C8 showed clear correlations to H_a and H_b through three-bond couplings, respectively. H_c on the furan moiety possessed two-bond correlation signals with C4 and C6 (C4 bearing $^{2}J_{PC}$ = 7.7 Hz at 155.1 ppm) and that H_c exhibited three-bond correlations with C7 (C7 showing correlation with H_d three bonds away). The three-bond correlations of H_c with C3 and C8 were not observed due to disfavored dihedral angles.

[2] Seno, M.; Tsuchiya, S.; Kise, H.; Asahara, T. *Bull. Chem. Soc. Jpn* **1975**, *48*, 2001.

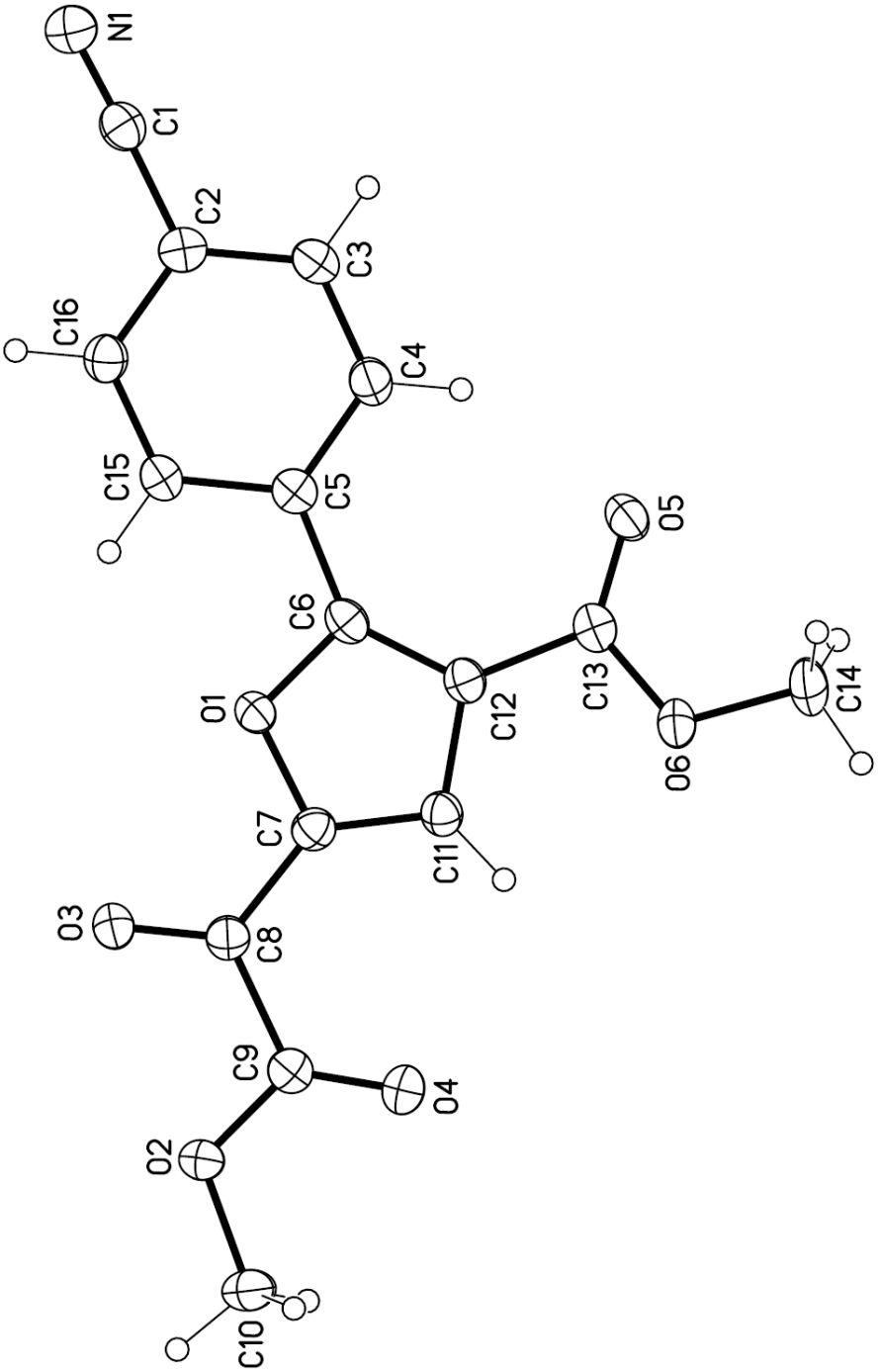


Fig. S61. X-ray crystal structure of **6c**

Table S2. Crystallographic data of furan **6c**.

Empirical formula	$C_{16}H_{11}NO_6$	
Formula weight	313.26	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 7.7210(9) Å	α= 90°.
	b = 6.8608(9) Å	β= 93.594(6)°.
	c = 26.644(3) Å	γ = 90°.
Volume	1408.6(3) $Å^3$	
Z	4	
Density (calculated)	1.477 Mg/m^3	
Absorption coefficient	0.978 mm^{-1}	
F(000)	648	
Crystal size	0.08 x 0.04 x 0.01 mm^3	
Theta range for data collection	3.324 to 67.198°.	
Index ranges	-9<=h<=9, -8<=k<=7, -31<=l<=31	
Reflections collected	10453	
Independent reflections	2502 [R(int) = 0.0296]	
Completeness to theta = 67.679°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9492 and 0.8295	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2502 / 0 / 210	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0913	
R indices (all data)	R1 = 0.0399, wR2 = 0.0946	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.176 and -0.244 $e.Å^{-3}$	