Electronic Supplementary Information

Reactivities of allenic and olefinic Michael acceptors towards phosphines

Feng An,[a] Harish Jangra,[a] Yin Wei,[b] Min Shi,*[bc] Hendrik Zipse,*[a] and Armin R. Ofial*[a]

[a] Department Chemie, Ludwig-Maximilians-Universtität München, Butenandtstr. 5-13, 81377

München (Germany), E-Mail: zipse@cup.uni-muenchen.de (H.Z.), ofial@lmu.de (A.R.O.)

[b] State Key Laboratory of Organometallic Chemistry,

Shanghai Institute of Organic Chemistry, Chinese Academy of

Sciences, 354 Fenglin Road, Shanghai 200032 (P. R. China)

E-mail: mshi@mail.sioc.ac.cn

[a] Key Laboratory for Advanced Materials and Institute of Fine

Chemicals, East China University of Science and Technology,

130 MeiLong Road, Shanghai 200237 (P. R. China)

Table of Contents

1 Additional Figures and Tables

Figure S1. Linear relationship between **log k_2(Bu$_3$P)** for reactions of Bu$_3$P with alkyl allenoates **1** and calculated **methyl anion affinities (MAA)** of **1** (correlation drawn with data from Table 1, main text).
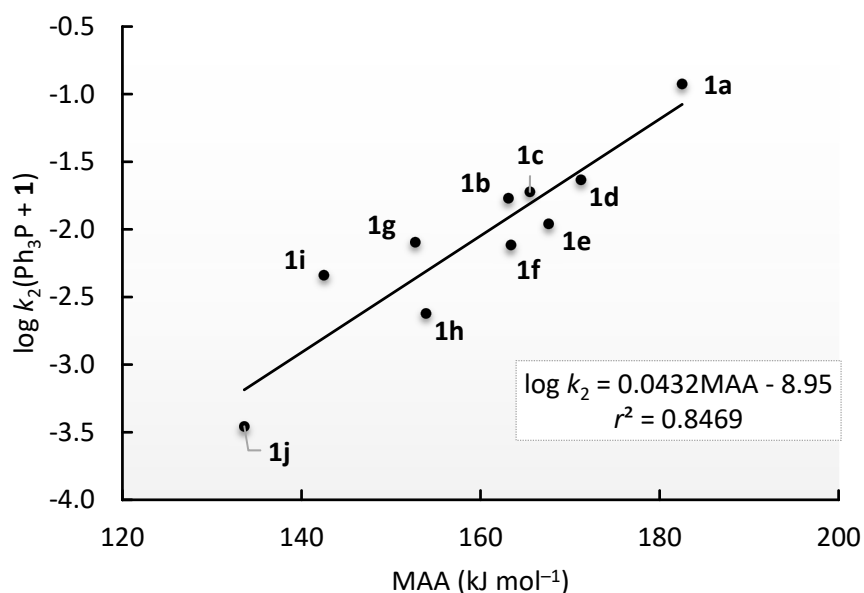
Figure S2. Linear relationship between **log k_2(Ph$_3$P)** for reactions of Ph$_3$P with alkyl allenoates **1** and calculated **methyl anion affinities MAA** of **1** (correlation drawn with data from Table 1, main text).
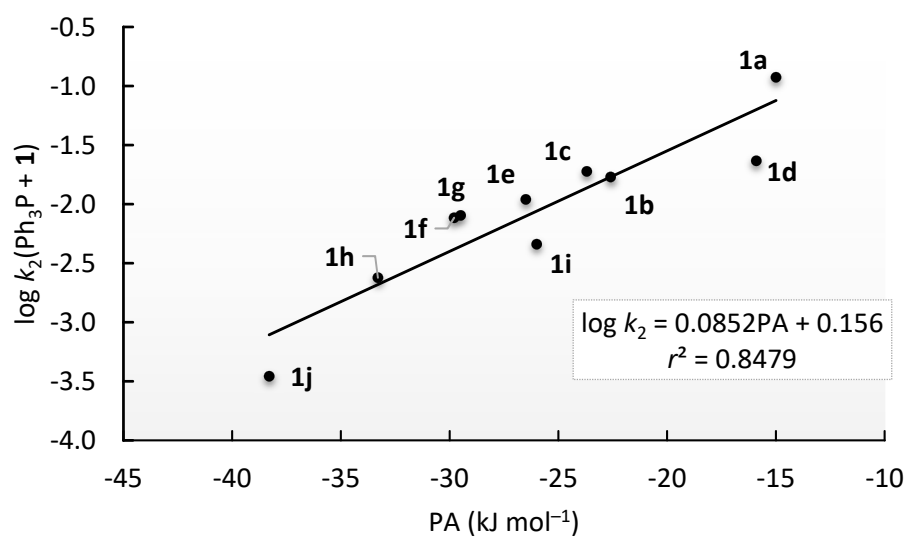
Figure S3. Linear relationship between **log k_2(Ph₃P)** for reactions of Ph₃P with alkyl allenoates **1** and calculated **phosphine affinities (PA)** of **1** (correlation drawn with data from Table S42).

Table S1 (data for Figure 6). Mayr electrophilicity parameters E for **4a-4r** and the second-order rate constants of their reactions of Bu$_3$P (CH$_2$Cl$_2$, 20 °C).
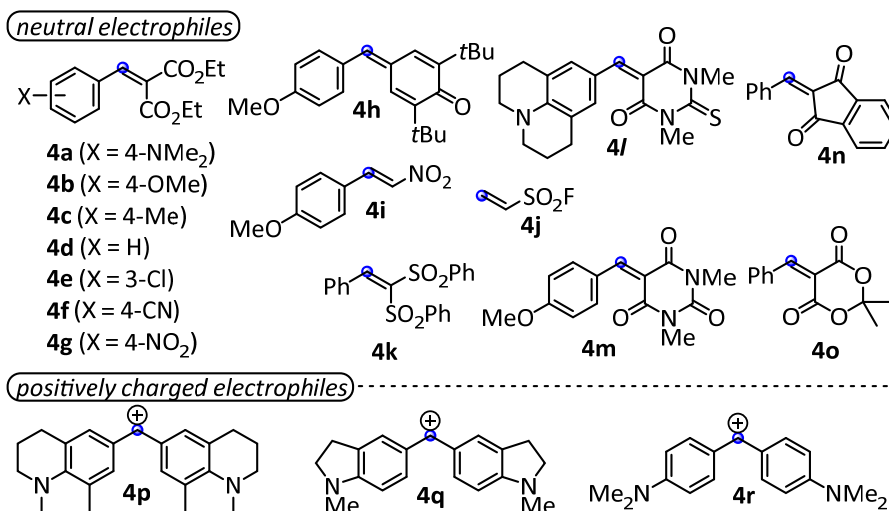
Michael acceptor	Electrophilicity E^a	$k_2(\text{Bu}_3\text{P})^b$ (M^{-1} s^{-1})	log $k_2(\text{Bu}_3\text{P})$
4a	-23.10	3.03×10^{-2}	-1.519
4b	-21.47	0.137	-0.863
4c	-21.11	0.208	-0.682
4d	-20.55	0.369	-0.433
4e	-18.98	0.979	-0.009
4f	-18.06	2.61	0.417
4g	-17.67	3.21	0.507
4h	-16.11	1.86	0.270
4i	-14.70	19.9	1.299
4j	-12.09	799	2.903
4k	-12.93	3.09×10^3	3.490
4l	-11.89	6.98×10^3	3.844
4m	-10.37	3.25×10^4	4.512
4n	-10.11	1.65×10^4	4.217
4o	-9.15	2.71×10^5	5.433
4p	-10.04	1.13×10^4	4.053
4q	-8.76	8.91×10^4	4.950
4r	-7.02	1.39×10^6	6.145

^{a} From ref S1. ^{b} This work.

Table S2 (data for Figure 7). Methyl anion affinities (MAAs) of Michael acceptors (with data from ref S2) and estimated Mayr E parameters for alkyl allenoates.

M1 CO_2Me

M2 CO_2Et

M3 CO_2tBu

M4 $C(O)NMe_2$

M5 SO_2Ph

M6 CN

M7 C(O)Me

M8 C(O)Ph

M9 CO_2Et

M10 SO_2F

M11 Me CO_2Et

M12 Ph CO_2Et

M13 Ph Ts

M14 Ph CN

M15 Ph C(O)Me

M16 Ph C(O)Ph

M17 Ph SO_2F

M18 Ph NO_2

M19 CO_2Et CO_2Et

M20 EtO_2C CO_2Et

M21 NC CN

M22 (N-Me maleimide)

M23 (maleic anhydride)

M24 SO_2Ph / SO_2Ph

M25 Ph CO_2Et / CO_2Et

M26 pnp C(O)Me

M27 pnp C(O)Ph

M28 dma CN / CN

M29 Ph SO_2Ph / SO_2Ph

M30 dma (Meldrum's acid derivative)

M31 ani (indanedione derivative)

M32 ani CN / CN

M33 ani (Meldrum's acid derivative)

M34 Ph (indanedione derivative)

M35 Ph CN / CN

M36 Ph (Meldrum's acid derivative)

M37 (tBu quinone methide, julolidine)

M38 tBu / tBu NMe_2

M39 Me / Me NMe_2

M40 tBu / tBu OMe

M41 tBu / tBu Me

M42 Ph / Ph NMe_2

M43 Ph / Ph OMe

M44 Ph / Ph (phenyl)

ani: *p*-methoxyphenyl
pnp: *p*-nitrophenyl
dma: *p*-(dimethylamino)phenyl

Michael acceptors	Mayr E^a	MAA^b (kJ mol^{-1})
M1	-18.84	80.7
M2	-19.07	75.1
M3	-20.22	71.6
M4	-23.54	59.6
M5	-18.36	96.8
M6	-19.05	109.4
M7	-16.76	104.2
M8	-15.25	116.7
M9	-22.77	51.9
M10 (= 4j)	-12.09	160.5
M11	-23.59	49.8
M12	-24.52	36.1
M13	-24.69	51.8
M14	-24.60	66.1
M15	-23.01	60.4
M16	-19.39	74.8

M17	-16.63	113.3
M18	-13.85	123.8
M19	-19.49	93.1
M20	-17.79	74.2
M21	-15.71	132.4
M22 (= 4s)	-14.07	113.9
M23	-11.31	149.8
M24	-7.50	174.8
M25	-20.55	104.8
M26	-19.36	75.2
M27	-17.33	86.8
M28	-13.30	141.3
M29 (= 4k)	-12.93	155.9
M30	-12.76	135.3
M31	-11.32	147.1
M32	-10.80	161.9
M33	-10.28	154.4
M34 (= 4n)	-10.11	160.7
M35 (= 4v)	-9.42	177.4
M36 (= 4o)	-9.15	169.6
M37	-17.90	120.4
M38	-17.29	123.2
M39	-16.36	130.7
M40 (= 4h)	-16.11	137.4
M41	-15.83	141.3
M42	-13.39	147.3
M43	-12.18	163.6
M44	-11.87	174.6
Alkyl allenoates	Estimated Mayr E^c	MAA^d (kJ mol^{-1})
1a	$(-17.57)^c$	182.5
1b	$(-18.97)^c$	163.1
1c	$(-19.02)^c$	165.5
1d	$(-19.15)^c$	171.2
1e	$(-19.26)^c$	167.6
1f	$(-19.51)^c$	163.4
1g	$(-19.73)^c$	152.7
1h	$(-20.37)^c$	153.9
1i	$(-20.55)^c$	142.5
1j	$(-22.65)^c$	133.6

^{a} Empirical Mayr electrophilicity parameter E (data taken from ref. S1). ^{b} Methyl anion affinities MAA = $-\Delta G_{sol\text{-}sp}$ (data taken from ref S2). ^{c} To construct Figure 7, electrophilicities E for the allenoates **1a-1j** were estimated by using the rearranged correlation equation from Figure 6, that is, $E = \{\log k_2(Bu_3P) - 9.208\}/0.482$. **Caveat:** These E parameters refer to single-point calibrations of the reactivities of **1a-1j** towards Bu$_3$P, which is not a member of the standard group of reference nucleophiles for the construction of Mayr reactivity scales. Furthermore, it remains to be shown that electrophilic reactivities of the allenoates **1a-1j** follow eqn (1) when calibrated with a wider range of reference nucleophiles. ^{d} Methyl anion affinities MAA from Table 1, main text.

2   Synthesis and Analytics

2.1   General

Analytics: ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were measured on 400 MHz, 600 MHz, or 800 MHz NMR spectrometers. Chemical shifts (δ) are given in ppm. ^{1}H and ^{13}C NMR spectra were calibrated to residual solvent peaks.[S3] Coupling constants are given in Hz. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, and br = broad. ^{13}C{^{1}H} NMR spectra were acquired with broad band proton decoupling. Numbers of C-attached hydrogen atoms were obtained from gHSQC experiments and reported as C, CH, CH_2, or CH_3. The assignments of individual NMR signals were based on additional 2D-NMR experiments (gHSQC, gHMBC, and COSY). HRMS spectra were determined on a Finnigan MAT 95 mass spectrometer. IR spectra were recorded on a FTIR Spectrometer SPECTRUM BX II (Perkin Elmer). Melting points were obtained on a BÜCHI M-560 melting point apparatus and are uncorrected.

Synthesis: Flash column chromatography was performed on Merck silica gel 60 (0.040–0.063 mm) using compressed air. Thin layer chromatography (TLC) was performed using Merck silica gel 60 F254 aluminum plates. Compounds on eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable stain followed by heating. Concentration under reduced pressure was performed on rotary evaporators with a water bath temperature of 40 °C. Starting materials and reagents were purchased from Sigma-Aldrich or ABCR and were used as supplied or, in the case of some liquids, distilled. Solvents were distilled or dried prior to use over appropriate drying agents: Dichloromethane (calcium hydride), diethyl ether (sodium/benzophenone), and acetonitrile (phosphorus pentoxide). Solvents for filtration, chromatography, and recrystallization were purchased from Fisher and used as received.

2.2 Synthesis and purification of alkyl allenoates

2.2.1 Phenyl buta-2,3-dienoate (1a)[S4]
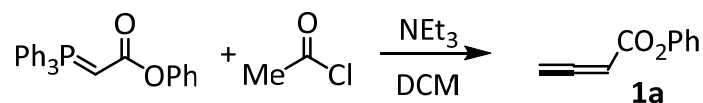
The ylide phenyl 2-(triphenyl-λ^5-phosphaneylidene)acetate[S5] (5.09 g, 12.8 mmol) and triethylamine (1.37 g, 13.5 mmol) were dissolved in dichloromethane (50 mL). Under ice bath cooling, acetyl chloride (1.04 g, 13.2 mmol) was added dropwise via a syringe. The reaction mixture was kept stirring at ambient temperature for 60 min. Then triethylamine (0.960 mL, 6.89 mmol) and acetyl chloride (0.200 mL, 2.80 mmol) were added dropwise into the reaction mixture by using a syringe. The mixture was kept stirring for 16 h. Then sat aq NaHCO$_3$ solution (50 mL) was added. After separating the phases, the volatiles of the organic phase were removed under reduced pressure. The residue was purified by column chromatography on silica gel (pentane/ethyl acetate 50:1 to 30:1 to provide **1a** (0.835 g, 41%) as a colorless oil, which was stored at −30 °C under Ar atmosphere. NMR spectroscopic data in CDCl$_3$ agree with those described in ref.[S4]

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40–7.36 (m, 2 H), 7.25–7.21 (m, 1 H), 7.14–7.11 (m, 2 H), 5.83 (t, J = 6.5 Hz, 1 H), 5.34 (d, J = 6.5 Hz, 2 H). **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$) δ 216.8, 164.3, 150.9, 129.6, 126.0, 121.7, 87.9, 80.0.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.43–7.36 (m, 2 H), 7.28–7.23 (m, 1 H), 7.13–7.09 (m, 2 H), 5.83 (t, J = 6.5 Hz, 1 H), 5.35 (d, J = 6.5 Hz, 1 H). **^{13}C{^{1}H} NMR** (101 MHz, CD$_2$Cl$_2$) δ 217.0, 164.5, 151.3, 129.8, 126.3, 122.0, 87.8, 79.9.

2.2.2 Benzyl buta-2,3-dienoate (1b)[S4]
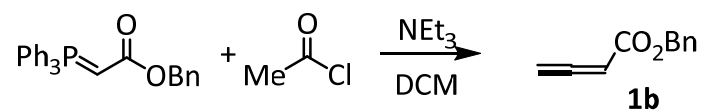
Benzyl 2-(triphenyl-λ^5-phosphaneylidene)acetate (6.56 g, 16.0 mmol) and triethylamine (2.70 mL, 19.4 mmol) were dissolved in dichloromethane (45 mL). Under ice bath cooling, acetyl chloride (1.25 mL, 17.6 mmol) was added dropwise via a syringe. The reaction mixture was kept stirring at ambient temperature for 60 min. The volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (pentane/ethyl acetate 30:1 to 20:1) followed by a quick distillation (9 × 10^{-3} mbar, 90 °C, distillate condensed under liquid nitrogen cooling bath) to furnish **1b** (1.66 g, 60%) as a colorless oil, which was stored at −30 °C under Ar atmosphere. NMR spectroscopic data in CDCl$_3$ agree with those described in ref.[S6]

¹H NMR (600 MHz, CDCl₃) δ 7.39–7.31 (m, 5 H), 5.69 (t, *J* = 6.6 Hz, 1 H), 5.24 (d, *J* = 6.5 Hz, 2 H), 5.20 (s, 3 H). **¹³C{¹H} NMR** (151 MHz, CDCl₃) δ 216.2, 165.7, 136.0, 128.7, 128.4, 128.3, 88.0, 79.6, 66.8.

¹H NMR (400 MHz, CD₂Cl₂) δ 7.42–7.27 (m, 5 H), 5.71–5.67 (m, 1 H), 5.24 (d, *J* = 6.5 Hz, 2 H), 5.17 (s, 2 H). **¹³C{¹H} NMR** (101 MHz, CD₂Cl₂) δ 216.3, 165.7, 136.5, 128.9, 128.6, 128.5, 88.0, 79.5, 66.9.

2.2.3   Ethyl 4-phenylbuta-2,3-dienoate (1c)
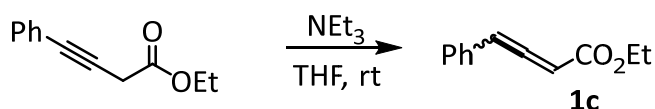
Ethyl 4-phenylbut-3-ynoate[S7] (5.39 g, 26.6 mmol) and triethylamine (2.93 g, 29.0 mmol) were dissolved in dry THF (65 mL). The reaction mixture was kept stirring at ambient temperature under nitrogen atmosphere for 15 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (pentane/ethyl acetate 100:1 to 50:1) to provide **1c** (0.871 g, 16%) as a slightly yellow oil, which was kept at −30 °C under Ar atmosphere. Starting materials were converted to a degree of around 85% after 15 h, and higher yields of **1c** can be achieved by repeated column chromatographic separations. NMR spectroscopic data agree with those reported in CDCl₃ solution.[S8]

¹H NMR (400 MHz, CD₂Cl₂) δ 7.41–7.22 (m, 5 H), 6.64 (d, *J* = 6.4 Hz, 1 H), 6.02 (dq, *J* = 6.4, 0.5 Hz, 1 H), 4.20 (qd, *J* = 7.1, 2.2 Hz, 2 H), 1.27 (t, *J* = 7.1 Hz, 3 H). **¹³C{¹H} NMR** (201 MHz, CD₂Cl₂) δ 214.8, 165.2, 131.7, 129.3, 128.5, 127.8, 98.8, 92.3, 61.5, 14.4.

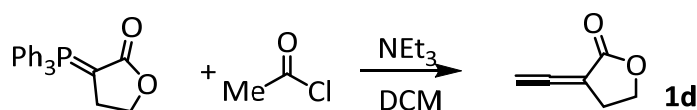### 2.2.4   3-Vinylidenedihydrofuran-2(3H)-one (1d)

3-(Triphenyl-λ⁵-phosphaneylidene)dihydrofuran-2(3*H*)-one[S9] (3.29 g, 9.50 mmol) and triethylamine (1.01 g, 9.98 mmol) were dissolved in dichloromethane (30 mL). Under ice bath cooling, acetyl chloride (0.798 g, 10.2 mmol) was added dropwise via a syringe. The reaction mixture was kept stirring at ambient temperature for 45 min. The volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (pentane/ethyl acetate 3:1 to 2:1) followed by a quick distillation (4 × 10⁻³ mbar, 80 °C, distillate condensed under liquid nitrogen cooling bath) to give **1d** (0.374 g, 36%) as a colorless oil, which was stored at −30 °C under Ar atmosphere. NMR spectroscopic data agree with those described in ref.[S9]

^{1}H NMR (600 MHz, CD$_2$Cl$_2$) δ. 5.28–5.27 (m, 2 H), 4.32 (t, J = 7.5 Hz, 2 H), 3.01 (tt, J = 7.5, 5.1 Hz, 2 H). **^{13}C{^{1}H} NMR** (151 MHz, CD$_2$Cl$_2$) δ 209.5, 170.4, 93.7, 82.1, 66.5, 26.8.

2.2.5 Methyl buta-2,3-dienoate (1e)[S10]
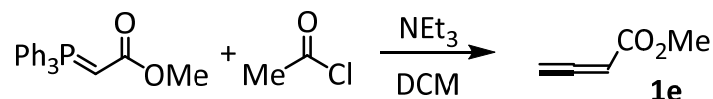
From methyl 2-(triphenyl-λ^5-phosphaneylidene)acetate (16.00 g, 47.85 mmol), trimethylamine (5.33 g, 52.64 mmol), and acetyl chloride (3.76 g, 47.85 mmol): **1e** (4.25 g, 91%). NMR spectroscopic data agree with those described in ref.[S11]

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 5.63 (t, J = 6.6 Hz, 1 H), 5.22 (d, J = 6.6 Hz, 2 H), 3.71 (s, 3 H). **^{13}C{^{1}H} NMR** (101 MHz, CD$_2$Cl$_2$) δ 216.2, 166.3, 87.9, 79.3, 52.3.

2.2.6 Ethyl buta-2,3-dienoate (1f)

Method 1: Commercially available **1f** (Aldrich) was purified by column chromatography on silica gel (pentane/diethyl ether 25:1 to 15:1).

Method 2: Ethyl 2,3-butadienoate **1f** was synthesized by a modified literature procedure reported by Hansen.[S10]

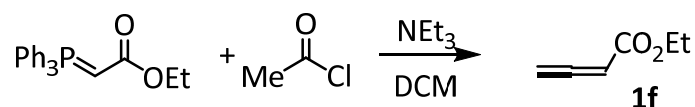Ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate (7.71 g, 22.1 mmol) and triethylamine (2.24 g, 22.1 mmol) were dissolved in dichloromethane (50 mL). Under ice bath cooling, acetyl chloride (1.74 g, 22.2 mmol) was added dropwise via a syringe. The mixture was kept stirring at ambient temperature for 60 min. Then sat aq NaHCO$_3$ solution (50 mL) was added. The organic phase was separated, and the aqueous phase was extracted by the dichloromethane (2 × 50 mL). After drying the unified organic phases (MgSO$_4$), the volatiles were removed under only slightly reduced pressure (500 mbar). After purification by column chromatography on silica gel (pentane/diethyl ether 25:1 to 15:1), the residue was kept in vacuum (5 mbar) at 0 °C for 30 min. A quick distillation (3 × 10^{-3} mbar, ambient temperature, distillate condensed under liquid nitrogen cooling bath) delivered **1f** (1.65 g, 67%) as a colorless oil. NMR spectroscopic data in CDCl$_3$ agree with those described in ref.[S12]

^{1}H NMR (600 MHz, CDCl$_3$) δ 5.64 (t, J = 6.5 Hz, 1 H), 5.22 (d, J = 6.5 Hz, 2 H), 4.21 (q, J = 7.1 Hz, 2 H), 1.29 (t, J = 7.1 Hz, 3 H). **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$) δ 215.9, 165.9, 88.2, 79.4, 61.2, 14.4.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 5.62 (t, J = 6.6 Hz, 1 H), 5.21 (d, J = 6.6 Hz, 2 H), 4.16 (q, J = 7.1 Hz, 2 H), 1.26 (t, J = 7.1 Hz, 3 H). **^{13}C{^{1}H} NMR** (101 MHz, CD$_2$Cl$_2$) δ 216.0, 165.8, 88.2, 79.3, 61.3, 14.4.

2.2.7 Ethyl penta-2,3-dienoate (1g)[S13]
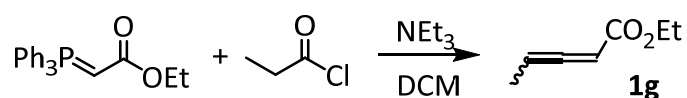
Ethyl 2-(triphenyl-λ^5-phosphaneylidene)acetate[S10] (4.50 g, 12.9 mmol) and triethylamine (2.00 mL, 14.4 mmol) was dissolved in dichloromethane (45 mL). Under ice bath cooling, acetyl chloride (1.25 mL, 17.6 mmol) added dropwise via a syringe. The reaction mixture was kept stirring at ambient temperature for 30 min. Then sat aq NaHCO$_3$ solution (50 mL) was added. The organic phase was separated, and the aqueous phase was extracted by the dichloromethane (3 × 50 mL). After drying (MgSO$_4$), the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (pentane/ethyl acetate 20:1) and provided **1g** (700 mg, 54%) as a colorless oil, which was stored at −30 °C under Ar atmosphere. NMR spectroscopic data in CDCl$_3$ agree with those described in ref.[S13]

¹H NMR (400 MHz, CDCl$_3$) δ 5.62–5.52 (m, 2 H), 4.18 (q, J = 7.1 Hz, 2 H), 1.77 (dd, J = 7.2, 3.3 Hz, 3 H), 1.27 (t, J = 7.1 Hz, 3 H). **¹³C{¹H} NMR** (101 MHz, CDCl$_3$) δ 213.0, 166.4, 90.4, 87.8, 60.9, 14.4, 13.0.

¹H NMR (400 MHz, CD$_2$Cl$_2$) δ 5.64–5.51 (m, 2 H), 4.15 (qd, J = 7.1, 0.9 Hz, 2 H), 1.77 (dd, J = 7.3, 3.3 Hz, 3 H), 1.25 (t, J = 7.1 Hz, 3 H). **¹³C{¹H} NMR** (101 MHz, CD$_2$Cl$_2$) δ 213.1, 166.3, 90.5, 87.9, 61.1, 14.4, 13.0.

2.2.8 *tert*-Butyl buta-2,3-dienoate (1h)
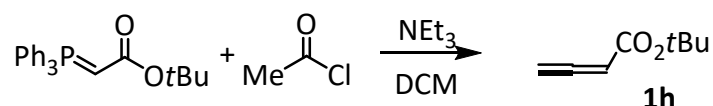
1h was prepared in a yield of 33% following the procedure reported by Hansen.[S10] NMR spectroscopic data agree with those reported in CDCl$_3$ solution.[S9]

¹H NMR (600 MHz, CD$_2$Cl$_2$) δ 5.53 (t, J = 6.6 Hz, 1 H), 5.16 (d, J = 6.6 Hz, 2 H), 1.45 (s, 9 H). **¹³C{¹H} NMR** (151 MHz, CD$_2$Cl$_2$) δ 215.6, 165.1, 89.7, 81.2, 78.9, 28.2.

2.2.9 Diethyl 2-vinylidenesuccinate (1i)

Commercially available **1i** (Aldrich) was purified by column chromatography on silica gel (pentane/diethyl ether 8:1 to 5:1). NMR spectroscopic data agree with those reported in CDCl$_3$ solution.[S14]

¹H NMR (400 MHz, CD$_2$Cl$_2$) δ 5.21 (t, J = 2.2 Hz, 2 H), 4.20–4.10 (m, 4 H), 3.22 (t, J = 2.2 Hz, 2 H), 1.25 (q, J = 7.1 Hz, 6 H). **¹³C{¹H} NMR** (101 MHz, CD$_2$Cl$_2$) δ 214.8, 170.7, 166.5, 95.1, 79.5, 61.7, 61.3, 35.2, 14.4.
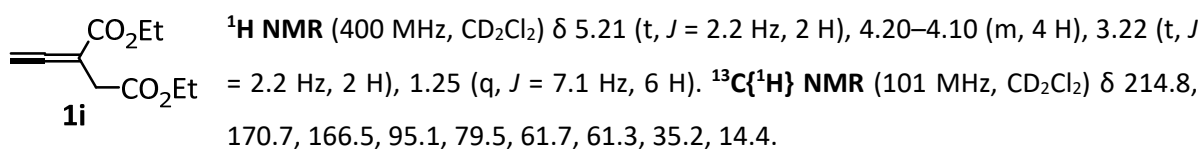
2.2.10 Ethyl 2-methylbuta-2,3-dienoate (1j)

Commercially available **1j** (Aldrich) was purified by column chromatography on silica gel (pentane/ diethyl ether 25:1 to 15:1). NMR spectroscopic data agree with those reported in CDCl$_3$ solution.[S13]

1j CO_2Et, Me

^{1}H NMR (800 MHz, CD$_2$Cl$_2$) δ 5.05 (q, J = 3.2 Hz, 2 H), 4.16 (q, J = 7.1 Hz, 2 H), 1.85 (t, J = 3.2 Hz, 3 H), 1.25 (t, J = 7.1 Hz, 3 H). **^{13}C{^{1}H} NMR** (201 MHz, CD$_2$Cl$_2$) δ 214.3, 167.7, 95.8, 77.8, 61.3, 15.0, 14.5.

2.3 Purification of phosphines

2.3.1 Tributylphosphine

Bu$_3$P was purified by vacuum distillation (83.5 °C, 0.75 mbar).

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 1.41–1.33 (m, 18 H), 0.93–0.87 (m, 9 H). **^{13}C{^{1}H} NMR** (101 MHz, CD$_2$Cl$_2$) δ 28.6 (d, $J_{C,P}$ = 12.8 Hz), 27.4 (d, $J_{C,P}$ = 12.6 Hz), 25.0 (d, $J_{C,P}$ = 10.9 Hz), 14.1. **^{31}P NMR** (162 MHz, CD$_2$Cl$_2$) δ −31.3.

2.3.2 Triphenylphosphine

Ph$_3$P was purified by a quick distillation (3 × 10^{-3} mbar, 140–165 °C, distillate condensed under liquid nitrogen cooling bath).

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.39–7.32 (m, 15 H). **^{13}C{^{1}H} NMR** (101 MHz, CD$_2$Cl$_2$) δ 137.8 (d, $J_{C,P}$ = 11.4 Hz), 134.1 (d, $J_{C,P}$ = 19.6 Hz), 129.1, 128.91 (d, $J_{C,P}$ = 6.9 Hz). **^{31}P NMR** (162 MHz, CD$_2$Cl$_2$) δ −5.5.
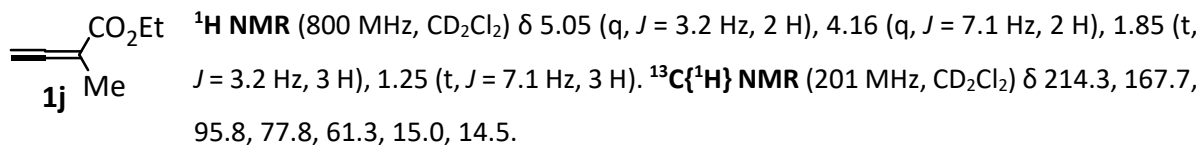
2.4 Synthesis and Purification of Phosphonium and 2,4,6-Collidinium Triflates

2.4.1 Tributylphosphonium Triflate (TBPT)

Under ice bath cooling and nitrogen atmosphere protection Bu$_3$P (1.30 g, 6.43 mmol) was added dropwise into a solution of triflic acid (964 mg, 6.42 mmol) in anhydrous diethyl ether (10 mL). The suspension was filtered, and the collected solid was washed with anhydrous diethyl ether under an inert gas atmosphere. Drying the solid under high vacuum provided Bu$_3$PH$^+$ TfO$^-$ (TBPT, 2.13 g, 94%) as a colorless solid. NMR spectroscopic data agree with those reported in CDCl$_3$ solution.[S15]

H, P$^{\oplus}$, $^{\ominus}$OTf, **TBPT**

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 6.13 (dhept, $^1J_{H,P}$ = 480.4 Hz, $J_{H,H}$ = 5.6 Hz, 1 H), 2.30–2.21 (m, 6 H), 1.67–1.55 (m, 6 H), 1.55–1.44 (m, 6 H), 0.96 (t, J = 7.3 Hz, 9 H). **^{13}C{^{1}H} NMR** (101 MHz, CD$_2$Cl$_2$) δ 121.2 (q, $J_{C,F}$ = 320.8 Hz), 25.0 (d, $J_{C,P}$ = 4.8 Hz), 24.0 (d, $J_{C,P}$ = 15.4 Hz), 16.8 (d, $J_{C,P}$ = 46.8 Hz), 13.4.
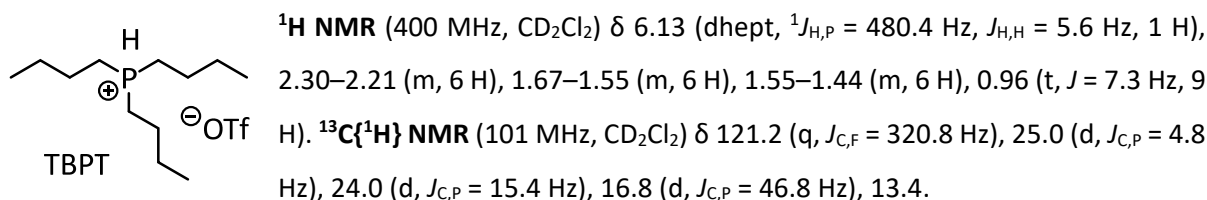
^{31}P NMR (162 MHz, CD$_2$Cl$_2$) δ 13.2 (dtt, $^1J_{P,H}$ = 480.9 Hz, $^2J_{P,H}$ = 25.2 Hz, $^3J_{P,H}$ =12.0 Hz).

2.4.2   Triphenylphosphonium Triflate (TPPT)

Under ice bath cooling and nitrogen atmosphere protection a solution of Ph$_3$P (3.49 g, 13.3 mmol) in anhydrous diethyl ether (15 mL) was added dropwise into a solution of triflic acid (2.03 g, 13.5 mmol) in anhydrous diethyl ether (5 mL). The suspension was filtered, and the collected solid was washed with anhydrous diethyl ether under inert gas atmosphere. Drying the solid under high vacuum furnished Ph$_3$PH$^+$ TfO$^-$ (TPPT, 4.55 g, 83%) as a colorless solid. NMR spectroscopic data agree with those reported in CDCl$_3$ solution.[S16]
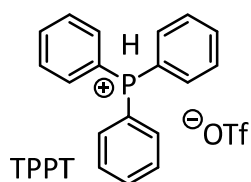
^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 9.47 (d, $^1J_{H,P}$ = 533.2 Hz, 1 H), 7.88–7.65 (m, 15 H). **^{13}C{^{1}H} NMR** (101 MHz, CD$_2$Cl$_2$) δ 135.9 (d, $J_{C,P}$ = 3.0 Hz), 134.5 (d, $J_{C,P}$ = 11.4 Hz), 130.9 (d, $J_{C,P}$ = 13.5 Hz), 121.2 (q, $J_{C,F}$ = 320.7 Hz), 116.0 (d, $J_{C,P}$ = 87.1 Hz). **^{31}P NMR** (162 MHz, CD$_2$Cl$_2$) δ 2.9 (d, $^1J_{P,H}$ = 533.4 Hz). **^{19}F NMR** (377 MHz, CD$_2$Cl$_2$) δ −79.0.

2.4.3   2,4,6-Collidinium Triflate (CT)

Under ice bath cooling and nitrogen atmosphere protection 2,4,6-trimethylpyridine (= 2,4,6-collidine, 1.12 g, 9.24 mmol) was added dropwise into an ethereal solution of triflic acid (1.38 g, 9.20 mmol in 15 mL). The suspension was filtered, and the collected solid was washed with anhydrous diethyl ether under inert gas atmosphere. Drying the solid under high vacuum furnished 2,4,6-collidinium triflate CT (2.32 g, 93%) as a colorless solid. NMR spectroscopic data agree with those reported in CDCl$_3$ solution.[S17]
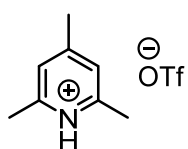
^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 14.38 (br t, $J_{H,N}$ = 53.3 Hz, 1 H), 7.28 (s, 2 H), 2.77 (s, 6 H), 2.53 (s, 3 H). **^{13}C{^{1}H} NMR** (101 MHz, CD$_2$Cl$_2$) δ 160.0, 153.3, 125.7, 120.8 (q, $J_{C,F}$ = 319.5 Hz), 22.3, 19.6.

3   Studies on the Interactions between Electrophiles, Nucleophiles and Proton Sources in CD$_2$Cl$_2$

3.1   Ph$_3$P with collidinium triflate (CT)

Figures S4 and S5 show that 2,4,6-collidine is a stronger Brønsted base than Ph$_3$P (in CD$_2$Cl$_2$).
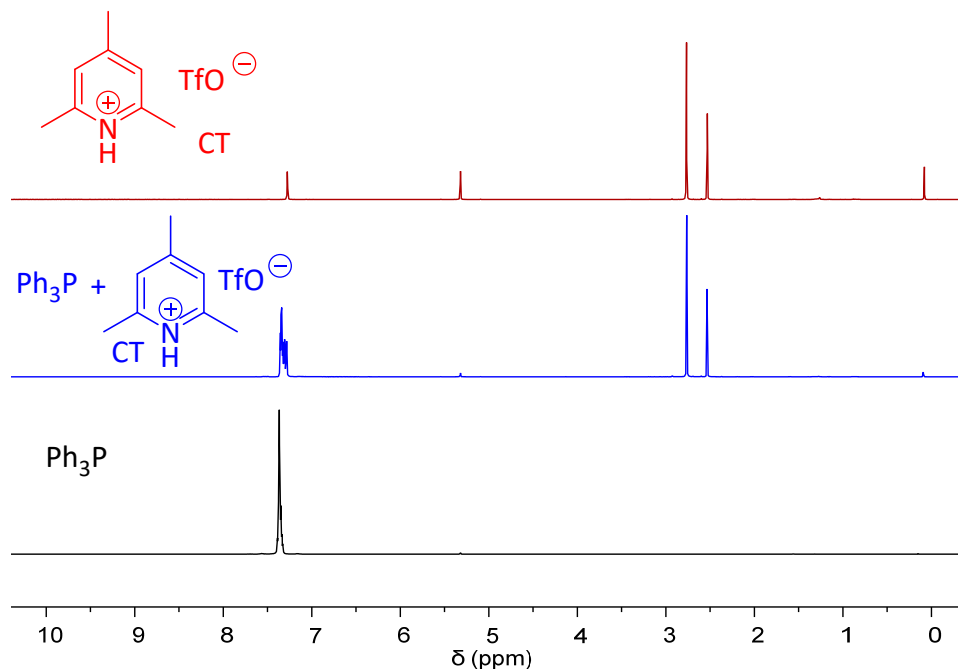
Figure S4. Comparison of the ^{1}H NMR spectra of CT (59.5 mM, top) and Ph$_3$P (58.3 mM, bottom) with that of the mixture of Ph$_3$P and CT in CD$_2$Cl$_2$ (central).
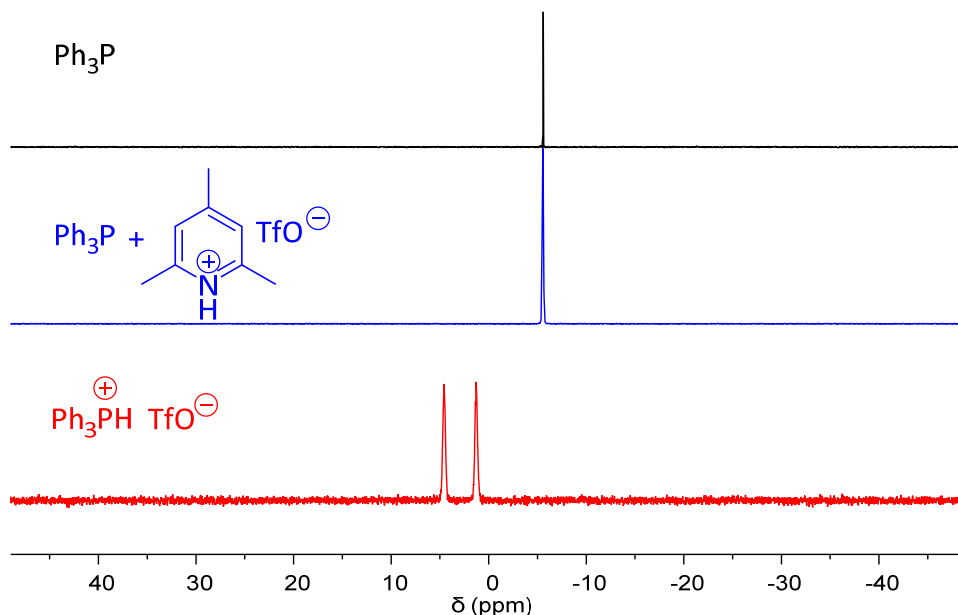
Figure S5. Comparison of the ^{31}P NMR spectra of Ph$_3$P (top), Ph$_3$PH$^+$ TfO$^-$ (bottom) with that of the mixture of Ph$_3$P (58.3 mM) and CT (59.5 mM) in CD$_2$Cl$_2$ (central).

3.2   Ethyl allenoate 1f with CT

Figure S6 indicates that CT does not change the ^{1}H NMR spectrum of alkyl allenoate **1f** (in CD$_2$Cl$_2$).
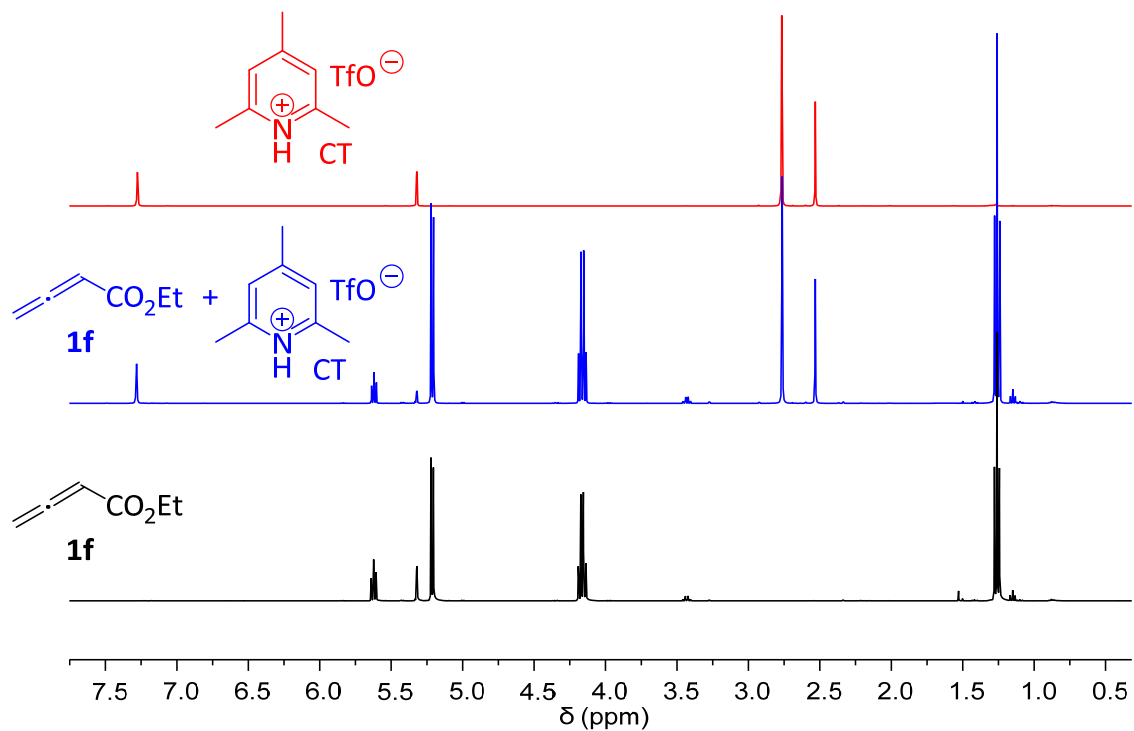
Figure S6. Comparison of the ^{1}H NMR spectra of CT (top) and **1f** (bottom) with that of the mixture of CT (60 mM) and **1f** (180 mM) in CD$_2$Cl$_2$ (central).

3.3 Ethyl allenoate 1f with TBPT

Figure S7 shows that TBPT does not change the ^{1}H NMR spectrum of alkyl allenoate **1f** (in CD$_2$Cl$_2$).
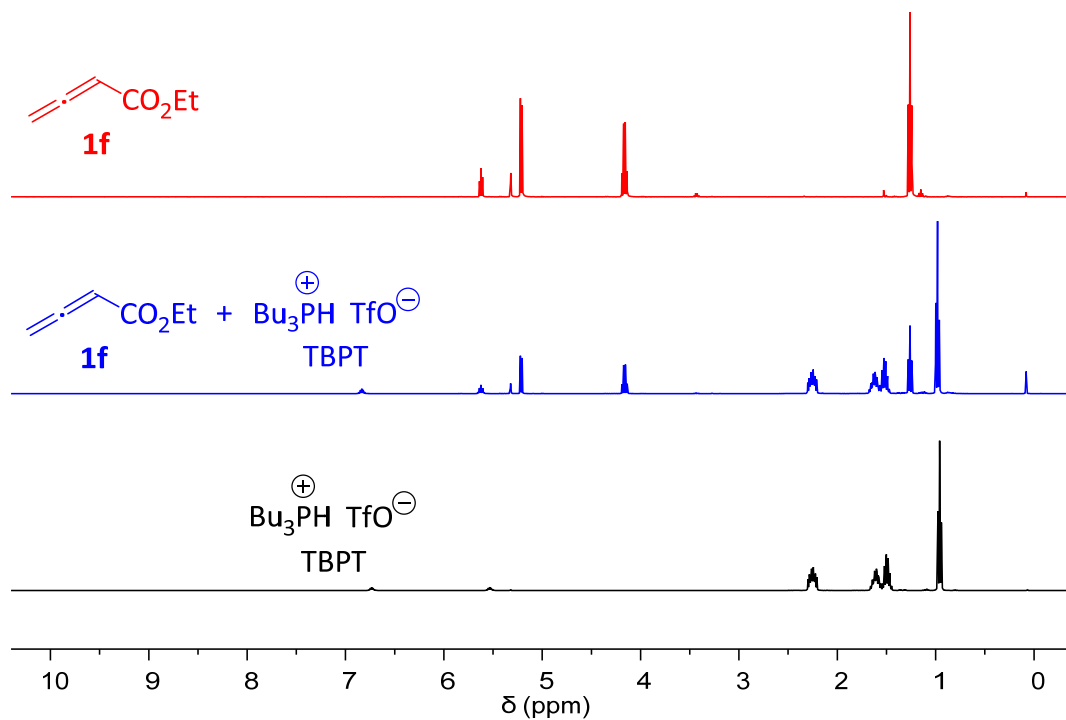
Figure S7. Comparison of the ^{1}H NMR spectra of **1f** (top) and TBPT (bottom) with that of the mixture of **1f** (28.5 mM) and TBPT (28.9 mM, central) in CD$_2$Cl$_2$ (central).

3.4 Stability of the R₃P adducts of alkyl allenoate 1f

3.4.1 Analysis of mixtures of Bu₃P with 1f

Figures S8 and S9 shows that Bu₃P reacts with alkyl allenoate **1f** (in CD₂Cl₂).
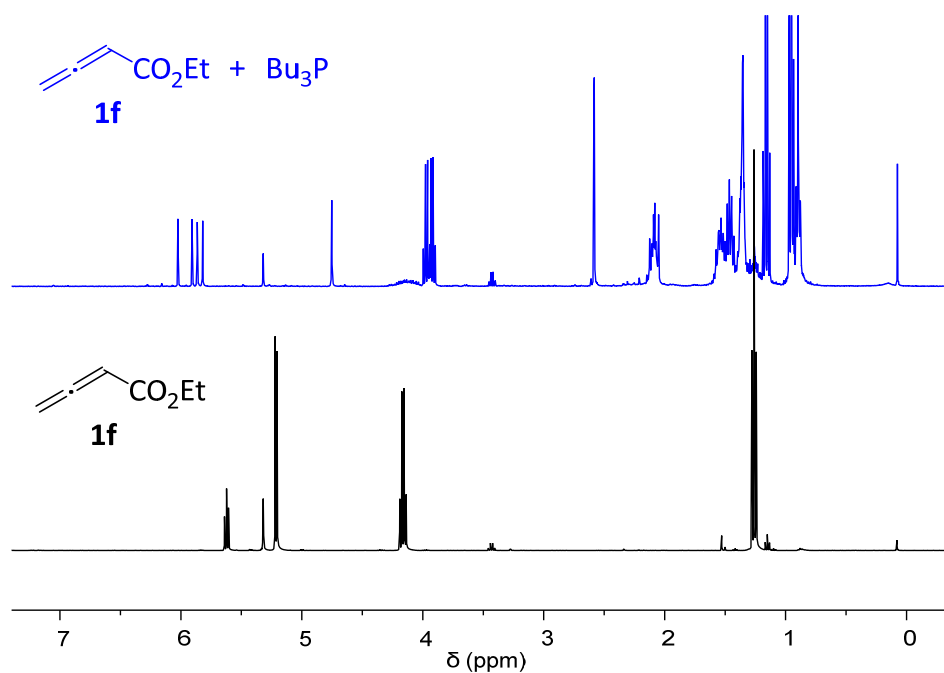
Figure S8. Comparison of the ^{1}H NMR spectra of **1f** (bottom) with that of a mixture of **1f** (69.0 mM) and Bu₃P (59.3 mM) in CD₂Cl₂ (top).
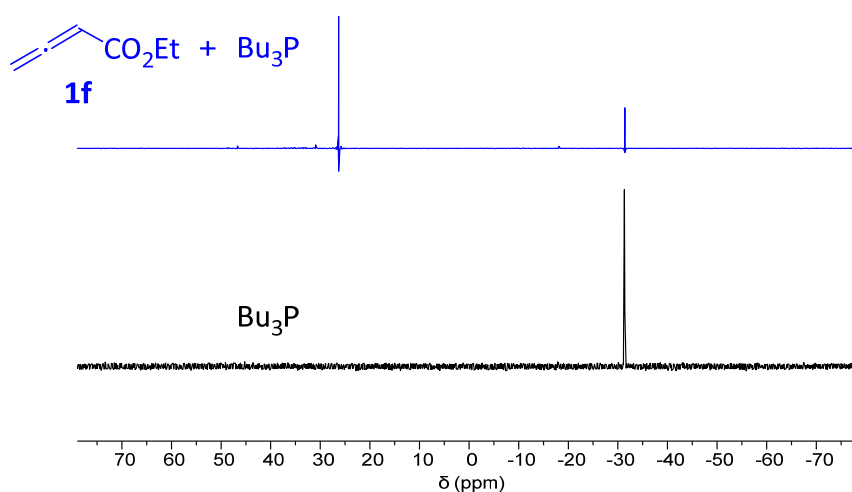
Figure S9. Comparison of the ^{31}P NMR spectra of Bu₃P (bottom) with that of a mixture of **1f** (69.0 mM) and Bu₃P (59.3 mM) in CD₂Cl₂ (top).

3.4.2 Analysis of mixtures of Ph₃P with 1f

Figure S10 shows that Ph₃P, without a proton source, forms only a minor equilibrium concentration of adduct with alkyl allenoate **1f** (in CD₂Cl₂).

Figure S10. Comparison of the ^{31}P NMR spectra of Ph₃P (bottom) with that of a mixture of **1f** (74.9 mM) and Ph₃P (88.8 mM) in CD₂Cl₂ at 20 °C (top).

3.4.3 Analysis of mixtures of Bu₃P with *N*-methylmaleimide (4s)
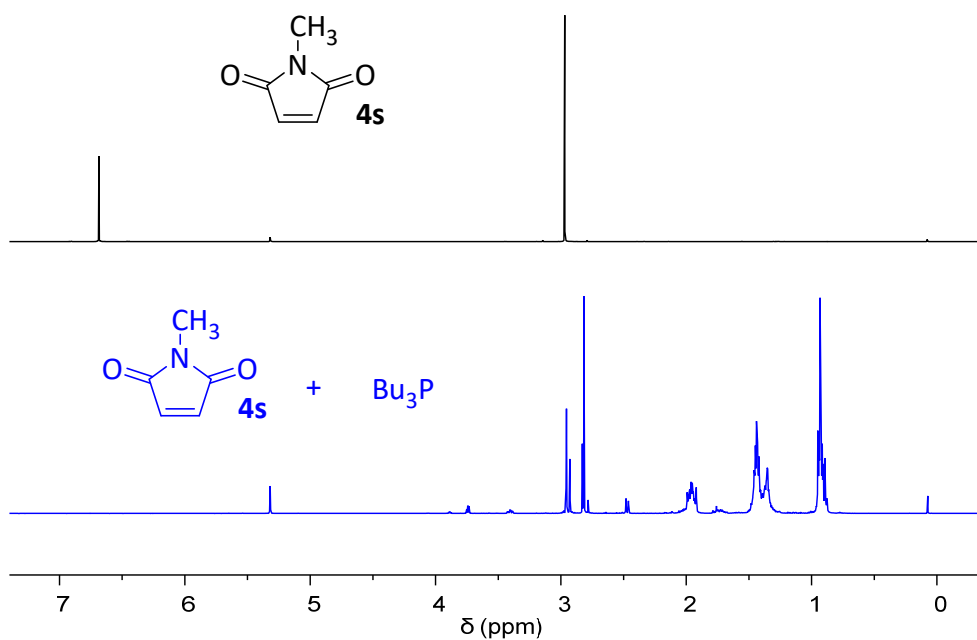
Figure S11. Comparison of the ^{1}H NMR spectra of **4s** (top) with that of the mixture of **4s** (54.3 mM) and Bu₃P (48.9 mM) in CD₂Cl₂ (bottom).
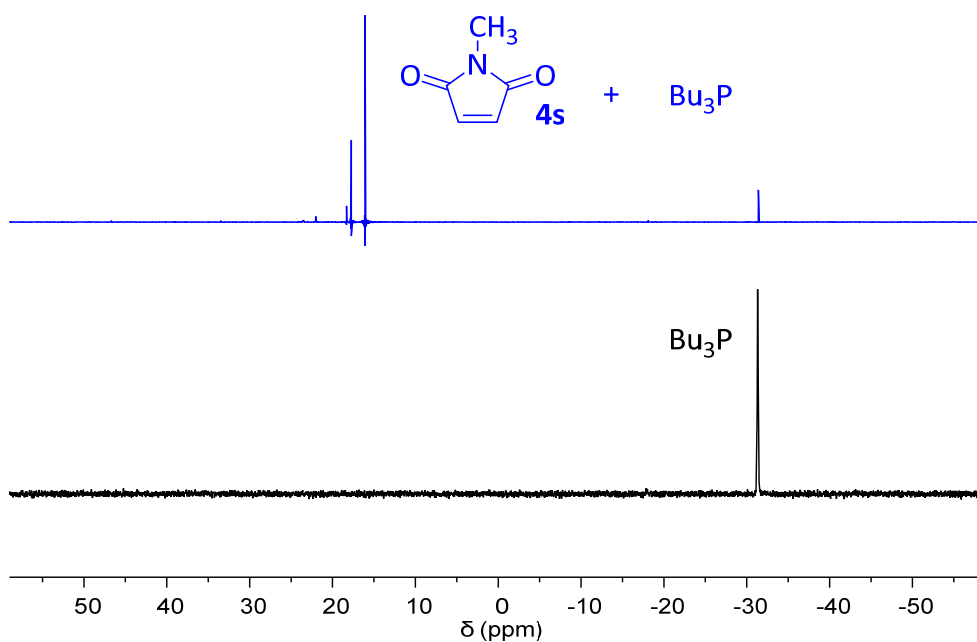
Figure S12. Comparison of the ^{31}P NMR spectra of Bu₃P (bottom) with that of a mixture of Bu₃P (48.9 mM) and **4s** (54.3 mM) in CD₂Cl₂ (top).

3.4.4   Analysis of mixtures of Ph₃P with *N*-methylmaleimide (4s)

Figures S13 and S14 indicate that Ph₃P does not form a detectable amount of adduct with **4s** (in CD₂Cl₂).
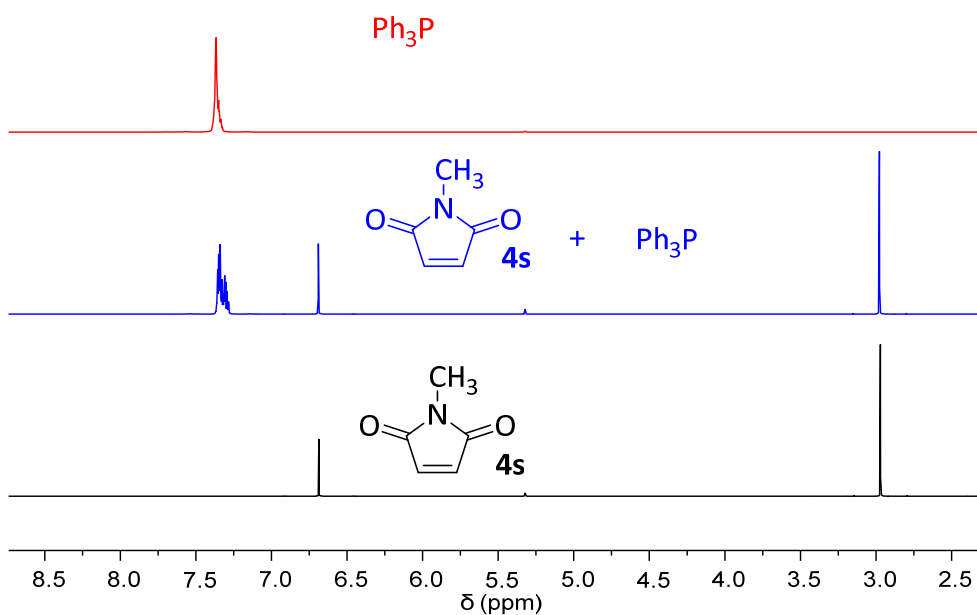
Figure S13. Comparison of the ^{1}H NMR spectra of Ph₃P (top) and **4s** (bottom) with that of a mixture of **4s** (79.9 mM) and Ph₃P (85.0 mM) in CD₂Cl₂ at 20 °C (central).
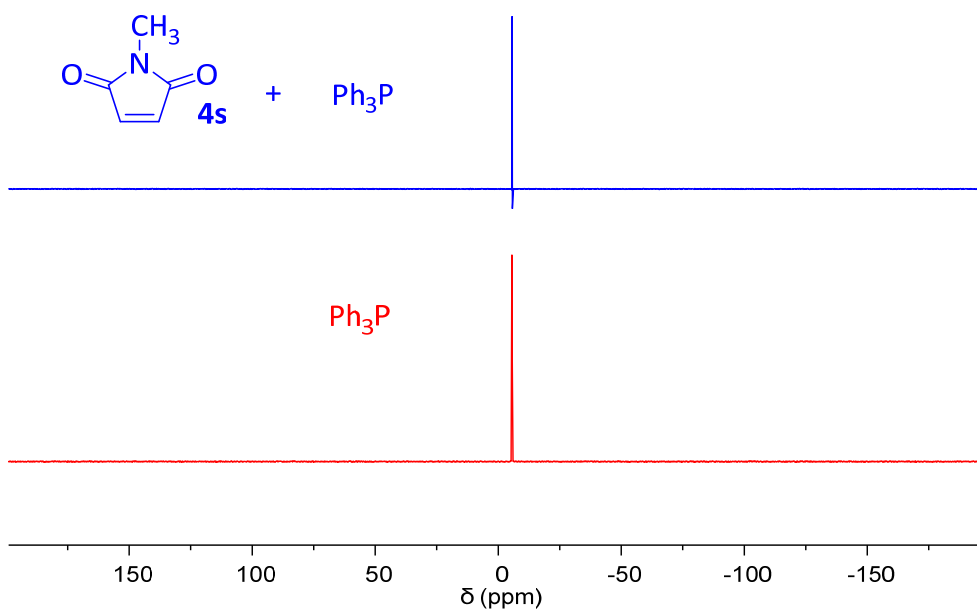
Figure S14. Comparison of the ^{31}P NMR spectra of Ph₃P (bottom) with that of a mixture of **4s** (79.9 mM) and Ph₃P (85.0 mM) in CD₂Cl₂ at 20 °C (top).

3.4.5 Analysis of mixtures of Bu₃P with phenyl N-tosyl imine (4t)

Figure S15 shows that Bu₃P slowly reacts with **4t** (in CD₂Cl₂). However, a major part of free Bu₃P remains in a 1:1 mixture of Bu₃P with **4t**.
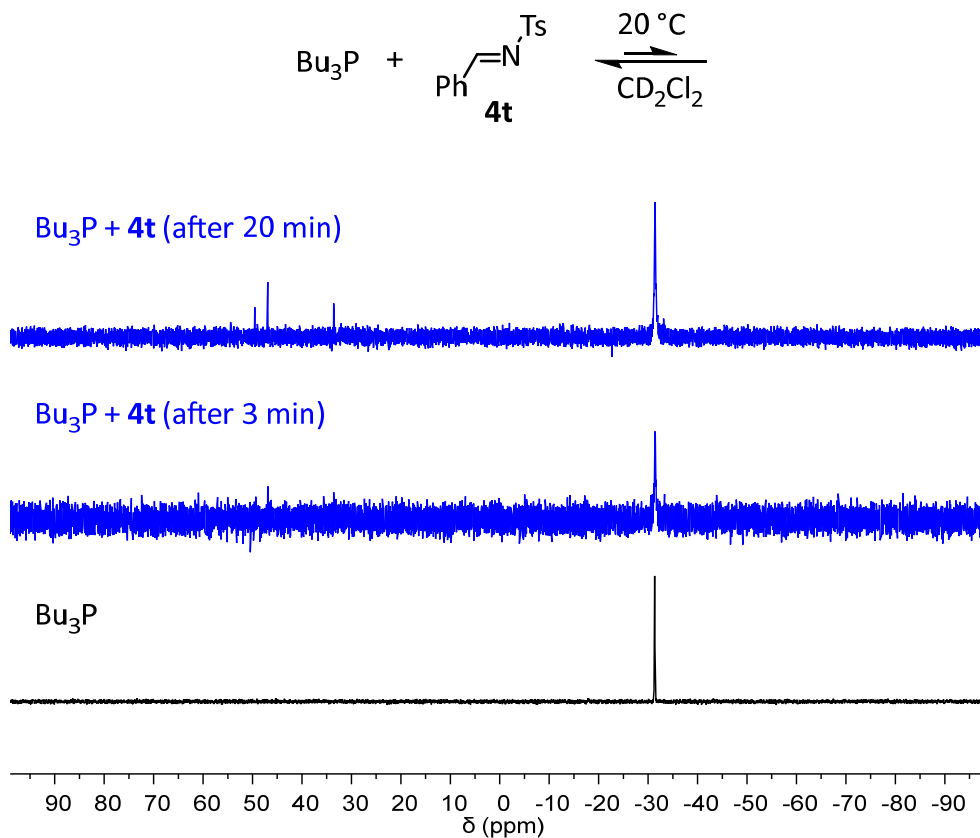
Figure S15. Comparison of the ^{31}P NMR spectra of Bu₃P (bottom) with those of the mixture of **4t** (21.2 mM) and Bu₃P (16.8 mM) in CD₂Cl₂ at different times (central: after 3 min, top: after 20 min).

3.4.6   Analysis of mixtures of Bu₃P with benzylidenemalononitrile (4v)

Figure S16 shows that Bu$_3$P reacts with **4v** (in CD$_2$Cl$_2$)**.** However, a part of free Bu$_3$P remains in an equilibrated 1:1 mixture of Bu$_3$P with **4v**.
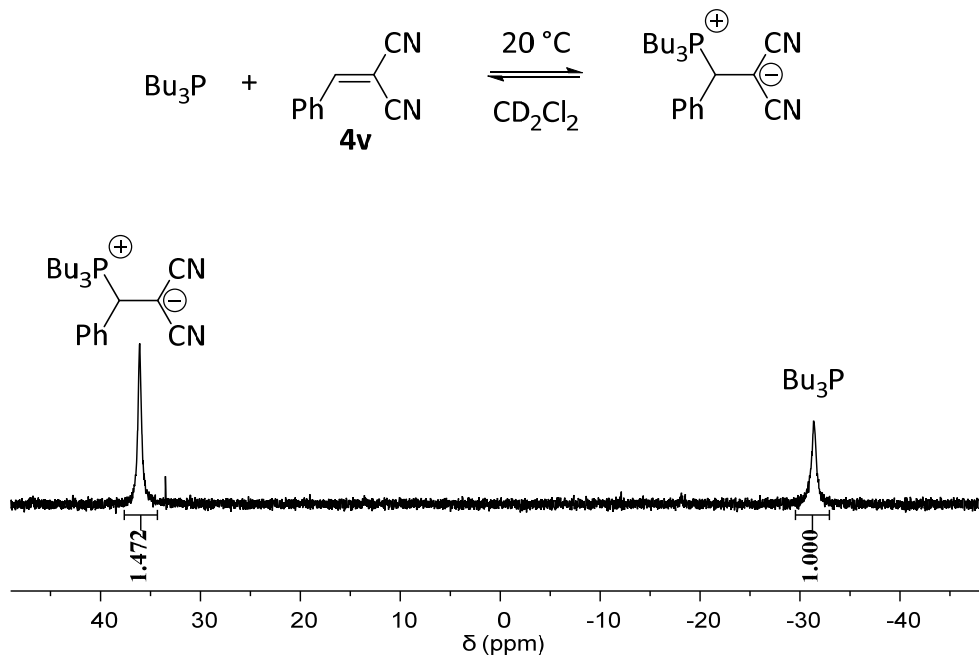
Figure S16. ^{31}P NMR spectrum of the mixture of **4v** (c_0 = 40.8 mM) and Bu$_3$P (c_0 = 37.6 mM) in CD$_2$Cl$_2$, which shows an equilibrium with the adduct zwitterion.

3.4.7 Analysis of mixtures of Ph₃P with benzylidenemalononitrile (4v)

Figures S17 and S18 indicate that Ph₃P does not form a detectable amount of adduct with **4v** (in CD₂Cl₂).
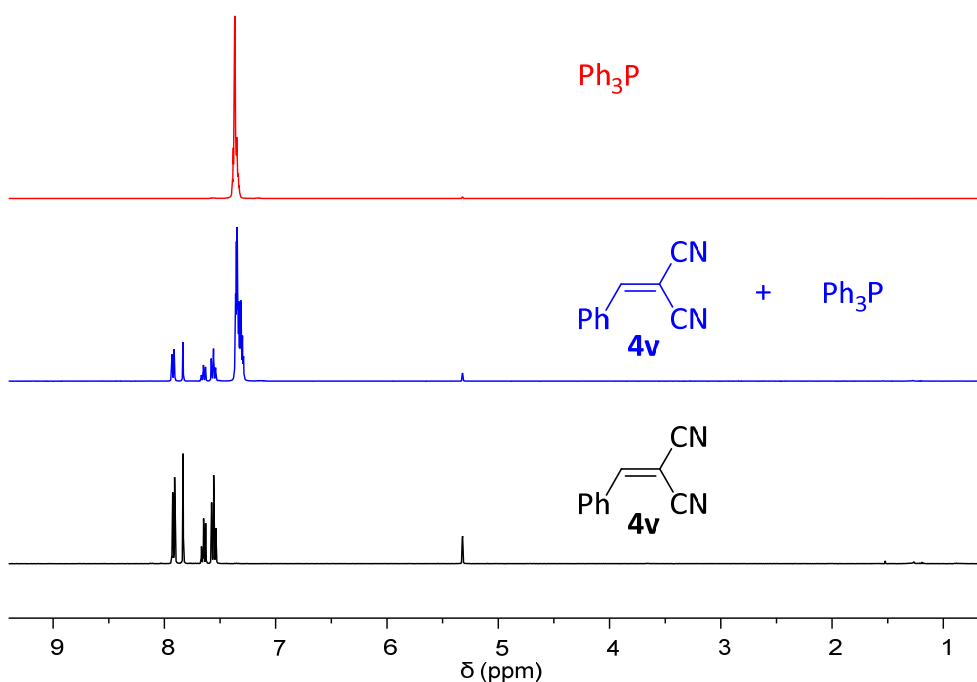
Figure S17. Comparison of the ^{1}H NMR spectra of Ph₃P (top) and **4v** (bottom) with that of the mixture of **4v** (69.4 mM) and Ph₃P (88.5 mM) in CD₂Cl₂ at 20 °C (central).
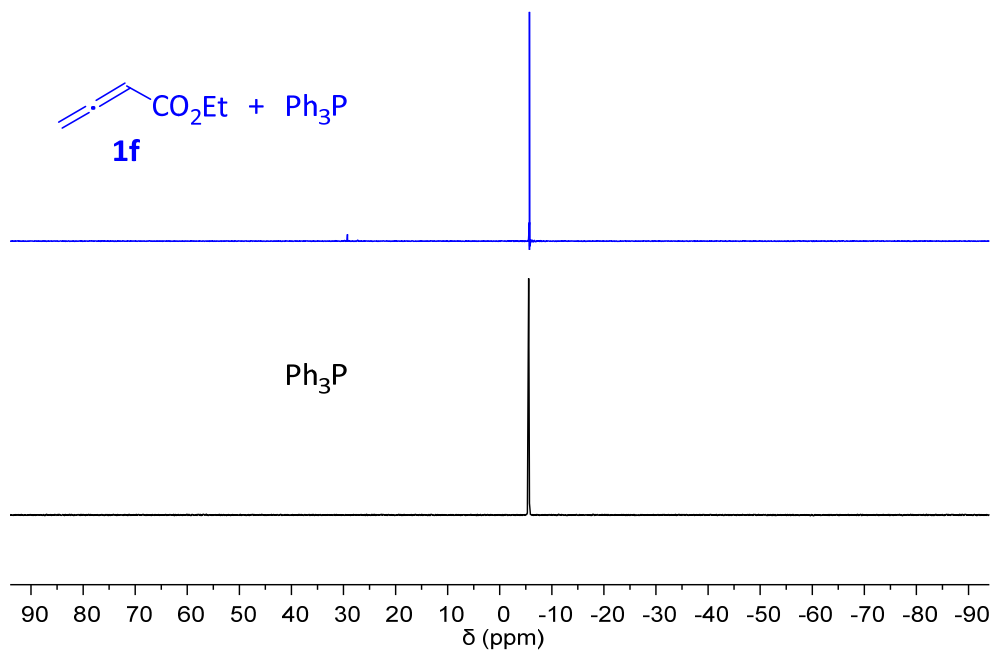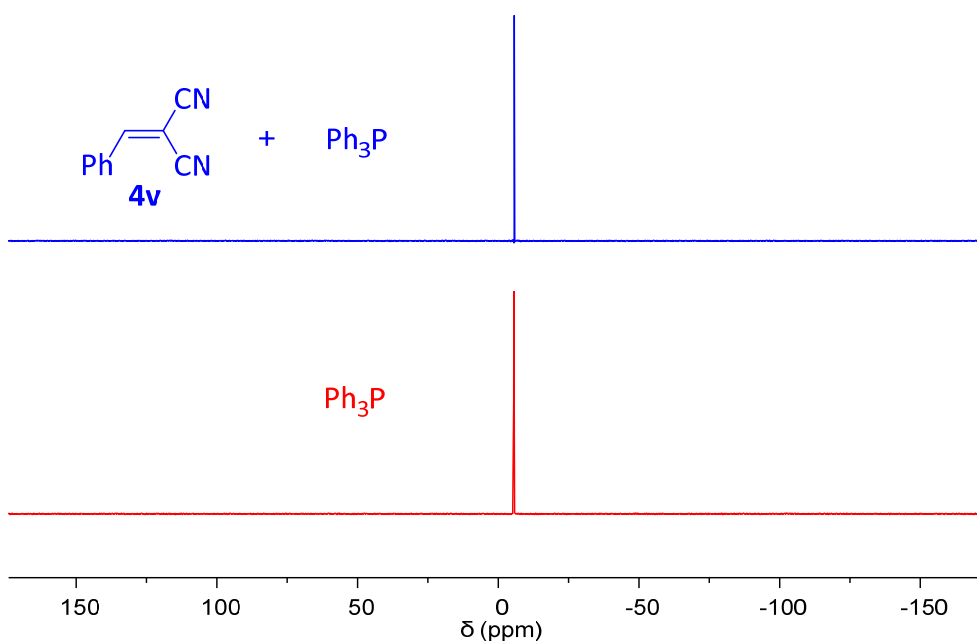

Figure S18. Comparison of the ^{31}P NMR spectra of Ph₃P (bottom) with that of the mixture of **4v** (69.4 mM) and Ph₃P (88.5 mM) in CD₂Cl₂ at 20 °C (top).

4 Product Studies

4.1 Reaction of triphenylphosphonium triflate with phenyl buta-2,3-dienoate (1a)
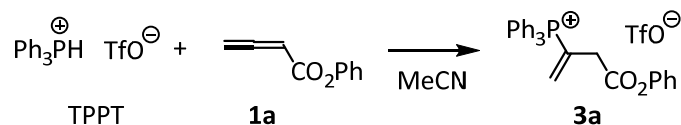
TPPT (48.9 mg, 119 mmol) and **1a** (30.7 mg, 192 mmol) were mixed in acetonitrile (1 mL). The mixture was kept under inert gas atmosphere at ambient temperature for 18 h. The volatiles were removed under reduced pressure. The residue was washed with diethyl ether and dried under high vacuum to provide **3a** (57.3 mg, 84%) as a white solid; mp 184.3–186.9 °C.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.99–7.86 (m, 3 H), 7.80–7.69 (m, 12 H), 7.35–7.32 (m, 2 H), 7.25–7.21 (m, 1 H), 7.09 (d, $J_{H,P}$ = 45.4 Hz, 1 H), 6.74 (d, $J_{H,P}$ = 7.9 Hz, 2 H), 6.37 (d, $J_{H,P}$ = 20.9 Hz, 1 H), 3.91 (d, $J_{H,P}$ = 15.3 Hz, 2 H). **^{13}C{^{1}H} NMR** (101 MHz, CD$_2$Cl$_2$) δ 168.6 (d, $^3J_{C,P}$ = 2.9 Hz, C$_q$), 150.4 (C$_q$), 146.5 (d, $^2J_{C,P}$ = 7.5 Hz, =CH$_2$), 136.2 (d, $J_{C,P}$ = 3.0 Hz, CH), 135.0 (d, $J_{C,P}$ = 10.4 Hz, CH), 131.0 (d, $J_{C,P}$ = 12.9 Hz, CH), 129.9 (CH), 126.8 (CH), 124.8 (d, $^1J_{C,P}$ = 78.7 Hz, C$_q$), 121.4 (CH), 117.1 (d, $^1J_{C,P}$ = 88.7 Hz, C$_q$), 39.2 (d $^2J_{C,P}$ = 11.4 Hz, CH$_2$); resonances of the CF$_3$ group superimpose with other signals and could not be assigned unequivocally. **^{31}P NMR** (162 MHz, CD$_2$Cl$_2$) δ 25.1. **^{19}F NMR** (377 MHz, CD$_2$Cl$_2$) δ −78.9. **IR** (neat, ATR): $\tilde{v}$ = 3065, 2925, 1752, 1589, 1485, 1439, 1340, 1261, 1224, 1192, 1147, 1108, 1030, 998, 754, 726, 712, 690 cm^{-1}. **HRMS** (ESI): m/z calcd for C$_{28}$H$_{24}$O$_2$P$^+$ (M − TfO$^-$): 423.15084, found: 423.15067.

4.2 Reaction of triphenylphosphonium triflate with 3-vinylidenedihydrofuran-2(3H)-one (1d)
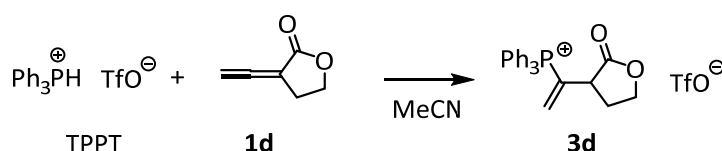
TPPT (50.8 mg, 123 mmol) and **1d** (22.8 mg, 207 mmol) were mixed in acetonitrile (1 mL). The mixture was kept under inert gas atmosphere at ambient temperature for 22 h. The volatiles were removed under reduced pressure. The residue was washed with diethyl ether and dried under high vacuum to provide **3d** (62.5 mg, 97%) as a white solid.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.92–7.77 (m, 15 H), 6.90 (d, $J_{H,P}$ = 46.1 Hz, 1 H), 6.35 (d, $J_{H,P}$ = 21.9 Hz, 1 H), 4.43–4.38 (m, 1 H), 4.21 (q, J = 8.7 Hz, 1 H), 3.63 (q, J = 10.7 Hz, 1 H), 2.44–2.38 (m, 2 H). **^{13}C{^{1}H} NMR** (101 MHz, CD$_2$Cl$_2$) δ 175.2 (d, $^3J_{C,P}$ = 6.9 Hz, C$_q$), 144.1 (d, $^2J_{C,P}$ = 7.8 Hz, =CH$_2$), 136.1 (d, $J_{C,P}$ = 3.1 Hz, CH), 135.0 (d, $J_{C,P}$ = 10.3 Hz, CH), 131.0 (d, $J_{C,P}$ = 12.9 Hz, CH), 129.3 (d, $^1J_{C,P}$ = 79.4 Hz, C$_q$), 121.4 (q, $^1J_{C,F}$ = 320.9 Hz, CF$_3$), 116.9 (d, $^1J_{C,P}$ = 88.8 Hz, C$_q$), 67.4 (CH$_2$), 43.7 (d, $^2J_{C,P}$ = 11.9 Hz, CH), 31.3 (d, $J_{C,P}$ = 3.8 Hz, CH$_2$). **^{31}P NMR** (162 MHz, CD$_2$Cl$_2$) δ 26.1. **^{19}F NMR** (377 MHz, CD$_2$Cl$_2$) δ −78.9. **IR** (neat, ATR): $\tilde{v}$

= 3065, 1762, 1588, 1485, 1439, 1379, 1263, 1224, 1153, 1108, 1030, 998, 754, 726, 692 cm⁻¹. **HRMS** (ESI): *m/z* calcd for $C_{24}H_{22}O_2P^+$ (M – TfO⁻): 373.13519, found: 373.13511.

4.3 Reaction of triphenylphosphonium triflate with ethyl buta-2,3-dienoate (1f)
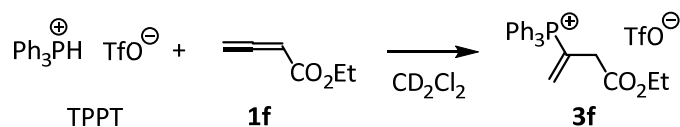
TPPT (186 mg, 451 mmol) and **1f** (54.5 mg, 486 mmol) were mixed in CD_2Cl_2 (1.5 mL). The mixture was kept under inert gas atmosphere at ambient temperature for 40 h. The volatiles were removed under reduced pressure. The residue was washed with pentane and dried under high vacuum to provide **3f** (230 mg, 97%) as a white solid; mp 97.3–98.3 °C.

¹H NMR (600 MHz, CD_2Cl_2) δ 7.92–7.89 (m, 3 H), 7.76–7.68 (m, 12 H), 6.94 (dd, $J_{H,P}$ = 45.6 Hz, $J_{H,H}$ = 1.2 Hz, 1 H), 6.29 (dd, $J_{H,P}$ = 21.0 Hz, $J_{H,H}$ = 1.2 Hz, 1 H), 3.86 (q, $J_{H,H}$ = 7.1 Hz, 2 H), 3.56 (dd, $J_{H,P}$ = 15.4 Hz, $J_{H,H}$ = 1.1 Hz, 2 H), 1.06 (t, $J_{H,H}$ = 7.1 Hz, 3 H). **¹³C{¹H} NMR** (151 MHz, CD_2Cl_2) δ 169.2 (d, $^3J_{C,P}$ = 3.1 Hz, C_q), 145.6–145.5 (m, =CH_2), 136.1 (d, $J_{C,P}$ = 3.1 Hz, CH), 134.9 (d, $J_{C,P}$ = 10.3 Hz, CH), 130.9 (d, $J_{C,P}$ = 12.9 Hz, CH), 125.3 (d, $^1J_{C,P}$ = 78.1 Hz, C_q), 121.4 (q, $^1J_{C,F}$ = 321.5 Hz, CF_3), 117.1 (d, $^1J_{C,P}$ = 88.6 Hz, C_q), 62.3 (CH_2), 39.2 (d, $^2J_{C,P}$ = 11.6 Hz, CH_2), 14.1 (CH_3). **³¹P NMR** (162 MHz, CD_2Cl_2) δ 25.3.[S18] **¹⁹F NMR** (377 MHz, CD_2Cl_2) δ −78.9. **IR** (neat, ATR): ṽ = 2983, 1732, 1586, 1484, 1441, 1334, 1258, 1223, 1204, 1154, 1107, 1027, 996, 970, 948, 861, 755, 724, 712, 690, 658 cm⁻¹. **HRMS** (ESI): *m/z* calcd for $C_{24}H_{24}O_2P^+$ (M – TfO⁻): 375.15084, found: 375.15072.

4.4 Reaction of triphenylphosphonium triflate with diethyl 2-vinylidenesuccinate (1i)
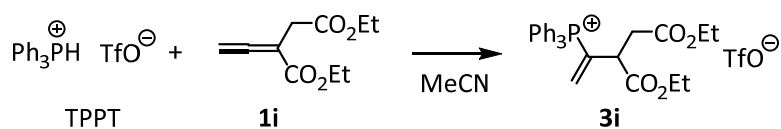
TPPT (50.0 mg, 121 mmol) and **1i** (30.5 mg, 154 mmol) were mixed in acetonitrile (1.0 mL). The mixture was kept under inert gas atmosphere at ambient temperature for one week. The volatiles were removed under reduced pressure. The residue was washed with pentane and dried under high vacuum to provide **3i** (55.5 mg, 75%) as a colorless liquid.

¹H NMR (400 MHz, CD_2Cl_2) δ 7.93–7.89 (m, 3 H), 7.77–7.68 (m, 12 H), 6.90 (ddd, $J_{H,P}$ = 46.3 Hz, $J_{H,H}$ = 2.4, 0.8 Hz, 1 H), 6.34 (dd, $J_{H,P}$ = 21.6 Hz, $J_{H,H}$ = 2.3 Hz, 1 H), 4.12–3.99 (m, 3 H), 3.89 (dq, J = 10.8, 7.1 Hz, 1 H), 3.77 (ddd, $^3J_{H,P}$ = 12.9 Hz, $^3J_{H,H}$ = 9.4 Hz, 5.8 Hz, 1 H), 3.06 (ddd, $^2J_{H,H}$ = 17.6 Hz, $^3J_{H,H}$ = 5.8 Hz, $^4J_{H,P}$ = 1.5 Hz, 1 H), 2.90 (dd, $^2J_{H,H}$ = 17.6 Hz, $^3J_{H,H}$ = 9.4 Hz, 1 H), 1.21 (t, $J_{H,H}$ = 7.1 Hz, 3 H), 1.03 (t, $J_{H,H}$ = 7.2 Hz, 3 H). **¹³C{¹H} NMR** (101 MHz, CD_2Cl_2) δ 170.7 (C_q), 170.1 (d, $^3J_{C,P}$ = 3.9 Hz, C_q), 142.0 (d, $^2J_{C,P}$ = 7.4

Hz, =CH$_2$), 136.2 (d, $J_{C,P}$ = 3.1 Hz, CH), 135.1 (d, $J_{C,P}$ = 10.3 Hz, CH), 130.8 (d, $J_{C,P}$ = 12.9 Hz, CH), 130.2 (d, $^1J_{C,P}$ = 77.8 Hz, C$_q$), 121.5 (q, $^1J_{C,F}$ = 321.3 Hz, CF$_3$), 117.2 (d, $^1J_{C,P}$ = 88.8 Hz, C^q), 62.9 (CH$_2$), 62.0 (CH$_2$), 42.9 (d, $^2J_{C,P}$ = 11.3 Hz, CH), 36.3 (d, $J_{C,P}$ = 5.4 Hz, CH$_2$), 14.3 (CH$_3$), 13.9 (CH$_3$). **^{31}P NMR** (162 MHz, CD$_2$Cl$_2$) δ 27.5. **^{19}F NMR** (377 MHz, CD$_2$Cl$_2$) δ −78.9. **IR** (neat, ATR): $\tilde{v}$ = 3066, 2985, 1730, 1587, 1485, 1440, 1263, 1224, 1150, 1107, 1030, 998, 857, 754, 725, 692 cm^{-1}. **HRMS** (ESI): m/z calcd for C$_{28}$H$_{30}$O$_4$P$^+$ (M − TfO$^-$): 461.18762, found: 461.18744.

5   Kinetics

5.1   General

Kinetic Measurements with the stopped-flow UV-Vis spectrometer

The kinetics of the faster reactions ($t_{1/2} < 20$ s) were followed by UV/vis spectroscopy by using a stopped-flow spectrophotometer system (Applied Photophysics SX20 Stopped Flow Spectrometers; 5 or 10 mm light path). The kinetic runs were initiated by mixing equal volumes of dichloromethane solutions of the nucleophiles and the electrophiles. The temperature of the solutions during the kinetic studies was maintained to 20 ± 0.2 °C by using circulating bath cryostats. Stock solutions were prepared in anhydrous dichloromethane, which was freshly distilled from calcium hydride. The R_3P solutions were freshly prepared under argon atmosphere before each measurement.

Kinetic measurements with conventional UV-Vis spectroscopy

The rates of slow reactions ($t_{1/2} > 20$ s) were determined by using a J&M TIDAS diode array spectrophotometers controlled by Labcontrol Spectacle or TIDAS DAQ 3.8.1 software and connected to Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) via fiber optic cables and standard SMA connectors. The temperature of the solutions during the kinetic studies was maintained to 20 ± 0.1 °C by using circulating bath cryostats. Anhydrous dichloromethane was freshly distilled from calcium hydride under an atmosphere of dry nitrogen. The R_3P solutions were freshly prepared under argon atmosphere before each measurement.

Kinetic measurements with NMR spectroscopy

The kinetics for reactions with $k_2 < 2.0 \times 10^{-1}$ M^{-1} s^{-1} were followed by using a Bruker Avance III HD 400 MHz NMR spectrophotometer, which is equipped with a N_2 cooling temperature unit (20 ± 0.1 °C). ^1H NMR kinetics used mesitylene (internal integration standard) or CD_2Cl_2 residual peak as internal reference standard. Stock solutions were prepared in CD_2Cl_2, which was stored under Ar atmosphere protection. The exact 1.0 mL solutions in NMR tube were prepared freshly under Ar atmosphere protection and monitored immediately after complete mixing of the reactants.

5.2 Kinetics of the reactions of R₃P with alkyl allenoates 1

5.2.1 Kinetics of the reactions of 1 with Bu₃P in dichloromethane

5.2.1.1 Kinetics of the reaction of Bu₃P with phenyl buta-2,3-dienoate (1a)

$$Bu_3P \ + \ \overset{}{=\!=}\!\!\diagdown_{CO_2Ph} \ \xrightarrow[CH_2Cl_2]{TBPT} \ Bu_3\overset{\oplus}{P}\diagdown \ TfO^{\ominus} \ \diagdown_{CO_2Ph}$$

1a

Table S3. Kinetics of the reactions of Bu₃P and **1a** (proton source: TBPT, conventional UV-Vis method, detection at 242 nm, in CH₂Cl₂)

[Bu₃P] (M)	[**1a**] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
1.10×10^{-3}	1.13×10^{-4}	2.39×10^{-4}	5.86×10^{-3}
1.95×10^{-3}	1.90×10^{-4}	3.95×10^{-4}	1.07×10^{-2}
3.18×10^{-3}	2.94×10^{-4}	6.52×10^{-4}	1.75×10^{-2}
3.99×10^{-3}	3.91×10^{-4}	8.53×10^{-4}	2.18×10^{-2}
$k_2 = 5.52 \ M^{-1} \ s^{-1}$			

y = 5.5182x - 0.0001
R² = 0.9998

5.2.1.2 Kinetics of the reaction of Bu₃P with benzyl buta-2,3-dienoate (1b)

$$Bu_3P \ + \ \overset{}{=\!=}\!\!\diagdown_{CO_2Bn} \ \xrightarrow[CH_2Cl_2]{TBPT} \ Bu_3\overset{\oplus}{P}\diagdown \ TfO^{\ominus} \ \diagdown_{CO_2Bn}$$

1b

Table S4. Kinetics of the reactions of Bu₃P and **1b** (proton source: TBPT, conventional UV-Vis method, detection at 250 nm, in CH₂Cl₂)

[Bu₃P] (M)	[**1b**] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
2.94×10^{-3}	3.01×10^{-4}	7.72×10^{-4}	3.53×10^{-3}
4.85×10^{-3}	4.97×10^{-4}	1.28×10^{-3}	5.75×10^{-3}
9.47×10^{-3}	6.06×10^{-4}	1.56×10^{-3}	1.11×10^{-2}
1.89×10^{-2}	6.07×10^{-4}	1.56×10^{-3}	2.23×10^{-2}
3.78×10^{-2}	6.04×10^{-4}	1.55×10^{-3}	4.40×10^{-2}
$k_2 = 1.16 \ M^{-1} \ s^{-1}$			

y = 1.1622x + 0.0001
R² = 1

5.2.1.3 Kinetics of the reaction of Bu₃P with ethyl 4-phenylbuta-2,3-dienoate (1c)

$$\text{Bu}_3\text{P} \;+\; \underset{\textbf{1c}}{\overset{\text{Ph}}{\underset{\text{CO}_2\text{Ph}}{\parallel}}} \quad \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{TBPT}} \quad \text{Bu}_3\overset{\oplus}{\text{P}} \;\; \text{TfO}^{\ominus}\;\; \underset{\text{Ph}}{\overset{}{}}\text{CO}_2\text{Ph}$$

Table S5. Kinetics of the reactions of Bu₃P and **1c** (proton source: TBPT, conventional UV-Vis method, detection at 248 nm, in CH₂Cl₂)

[Bu₃P] (M)	[1c] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
3.06×10^{-3}	7.70×10^{-5}	2.41×10^{-4}	3.48×10^{-3}
5.26×10^{-3}	7.56×10^{-5}	2.37×10^{-4}	6.10×10^{-3}
7.70×10^{-3}	7.73×10^{-5}	2.79×10^{-4}	8.55×10^{-3}
1.00×10^{-2}	7.65×10^{-5}	2.76×10^{-4}	1.12×10^{-2}
$k_2 = 1.10\ \text{M}^{-1}\ \text{s}^{-1}$			

Plot: k_{obs} (s⁻¹) vs [Bu₃P] (M); $y = 1.1004x + 0.0002$, $R^2 = 0.9990$

5.2.1.4 Kinetics of the reaction of Bu₃P with 3-vinylidenedihydrofuran-2(3*H*)-one (1d)

$$\text{Bu}_3\text{P} \;+\; \underset{\textbf{1d}}{\text{(lactone)}} \quad \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{TBPT}} \quad \text{Bu}_3\overset{\oplus}{\text{P}} \;\; \text{TfO}^{\ominus}$$

Table S6 Kinetics of the reactions of Bu₃P and **1d** (proton source: TBPT, conventional UV-Vis method, detection at 259 nm, in CH₂Cl₂)

[Bu₃P] (M)	[1d] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
3.48×10^{-3}	2.04×10^{-4}	6.55×10^{-4}	3.09×10^{-3}
4.09×10^{-3}	4.07×10^{-4}	1.07×10^{-3}	3.77×10^{-3}
5.09×10^{-3}	5.10×10^{-4}	1.34×10^{-3}	4.76×10^{-3}
6.16×10^{-3}	6.13×10^{-4}	1.62×10^{-3}	5.76×10^{-3}
7.29×10^{-3}	7.30×10^{-4}	1.92×10^{-3}	6.74×10^{-3}
$k_2 = 9.55 \times 10^{-1}\ \text{M}^{-1}\ \text{s}^{-1}$			

Plot: k_{obs} (s⁻¹) vs [Bu₃P] (M); $y = 0.955x - 0.0002$, $R^2 = 0.9983$

5.2.1.5 Kinetics of the reaction of Bu₃P with methyl buta-2,3-dienoate (1e)

$$\text{Bu}_3\text{P} \quad + \quad \overset{\displaystyle =}{\underset{\text{CO}_2\text{Me}}{}} \quad \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{TBPT}} \quad \text{Bu}_3\overset{\oplus}{\text{P}} \quad \text{TfO}^{\ominus}$$

1e

Table S7. Kinetics of the reactions of Bu₃P and **1e** (proton source: TBPT, conventional UV-Vis method, detection at 250 nm, in CH₂Cl₂)

[Bu₃P] (M)	[1e] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
3.20×10^{-3}	3.17×10^{-4}	6.43×10^{-4}	2.49×10^{-3}
6.16×10^{-3}	6.43×10^{-4}	1.26×10^{-3}	4.68×10^{-3}
9.05×10^{-3}	9.04×10^{-4}	1.82×10^{-3}	7.48×10^{-3}
1.20×10^{-2}	1.21×10^{-3}	2.42×10^{-3}	9.76×10^{-3}
$k_2 = 8.40 \times 10^{-1}$ M⁻¹ s⁻¹			

y = 0.8400x - 0.0003
R² = 0.9974

5.2.1.6 Kinetics of the reaction of Bu₃P with ethyl buta-2,3-dienoate (1f)

$$\text{Bu}_3\text{P} \quad + \quad \overset{\displaystyle =}{\underset{\text{CO}_2\text{Et}}{}} \quad \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{TBPT}} \quad \text{Bu}_3\overset{\oplus}{\text{P}} \quad \text{TfO}^{\ominus}$$
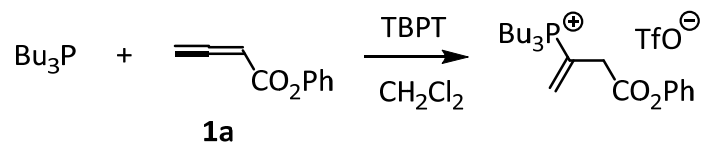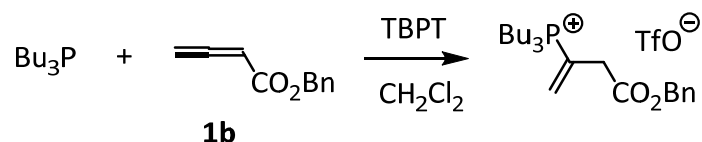
1f

Table S8. Kinetics of the reactions of Bu₃P and **1f** (proton source: TBPT, conventional UV-Vis method, detection at 250 nm, in CH₂Cl₂)

[Bu₃P] (M)	[1f] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
1.23×10^{-2}	1.21×10^{-3}	2.73×10^{-3}	7.49×10^{-3}
1.09×10^{-2}	8.83×10^{-4}	2.72×10^{-3}	6.59×10^{-3}
8.59×10^{-3}	8.98×10^{-4}	2.77×10^{-3}	5.03×10^{-3}
5.74×10^{-3}	5.95×10^{-4}	1.84×10^{-3}	3.34×10^{-3}
3.26×10^{-3}	3.38×10^{-4}	9.94×10^{-4}	1.73×10^{-3}
$k_2 = 6.35 \times 10^{-1}$ M⁻¹ s⁻¹			

y = 0.6347x - 0.0003
R² = 0.9996

5.2.1.7 Kinetics of the reaction of Bu₃P with ethyl penta-2,3-dienoate (1g)

$$Bu_3P \quad + \quad \overset{\text{\raisebox{2pt}{$\smallsetminus$}}}{\underset{CO_2Et}{\diagup\diagdown}} \quad \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{TBPT}} \quad Bu_3P^{\oplus} \quad TfO^{\ominus}$$
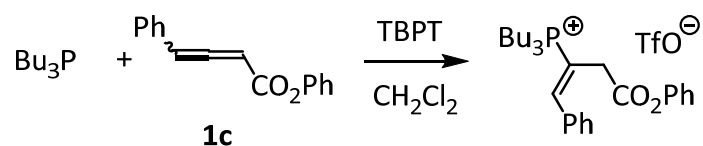
1g

Table S9. Kinetics of the reactions of Bu₃P and **1g** (proton source: TBPT, conventional UV-Vis method, detection at 258 nm, in CH₂Cl₂)

[Bu₃P] (M)	[1g] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
4.39×10^{-3}	4.37×10^{-4}	1.10×10^{-3}	2.50×10^{-3}
7.07×10^{-3}	7.13×10^{-4}	1.80×10^{-3}	3.80×10^{-3}
9.37×10^{-3}	9.24×10^{-4}	2.25×10^{-3}	4.94×10^{-3}
1.21×10^{-2}	1.20×10^{-3}	2.90×10^{-3}	6.36×10^{-3}
$k_2 = 5.00 \times 10^{-1}$ M⁻¹ s⁻¹			

y = 0.5003x + 0.0003
R² = 0.9997

5.2.1.8 Kinetics of the reaction of Bu₃P with *tert*-butyl buta-2,3-dienoate (1h)

$$Bu_3P \quad + \quad \overset{}{\underset{CO_2tBu}{=\!=\!=}} \quad \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{TBPT}} \quad Bu_3P^{\oplus} \quad TfO^{\ominus}$$
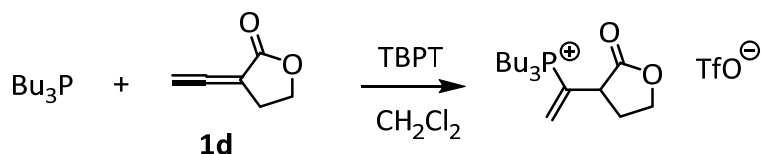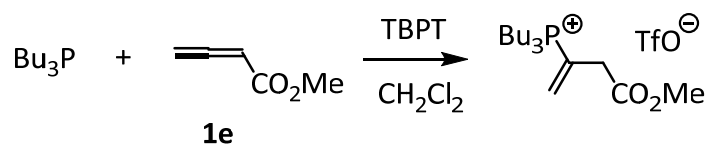
1h

Table S10. Kinetics of the reactions of Bu₃P and **1h** (proton source: TBPT, conventional UV-Vis method, detection at 256 nm, in CH₂Cl₂)

[Bu₃P] (M)	[1h] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
7.08×10^{-3}	6.98×10^{-4}	1.71×10^{-3}	1.68×10^{-3}
9.06×10^{-3}	8.90×10^{-4}	2.19×10^{-3}	2.09×10^{-3}
1.31×10^{-2}	1.03×10^{-3}	2.34×10^{-3}	3.13×10^{-3}
1.73×10^{-2}	1.36×10^{-3}	3.09×10^{-3}	4.18×10^{-3}
$k_2 = 2.47 \times 10^{-1}$ M⁻¹ s⁻¹			

y = 0.2472x - 0.0001
R² = 0.9991

5.2.1.9 Kinetics of the reaction of Bu₃P with diethyl 2-vinylidenesuccinate (1i)

1i

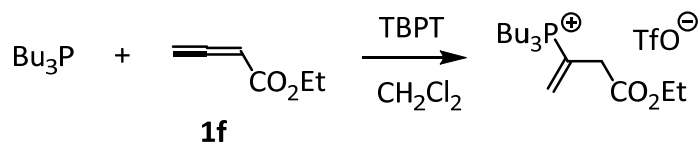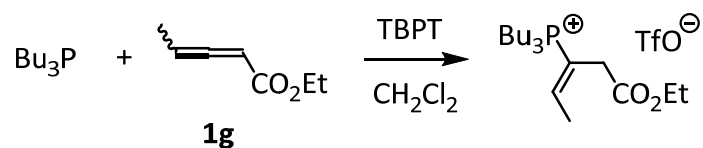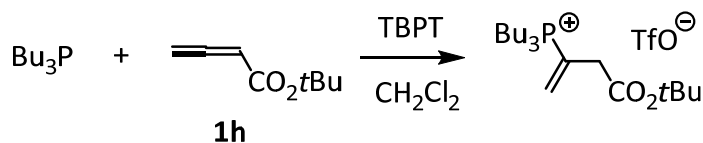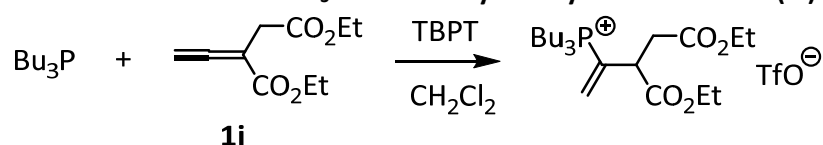**Table S11.** Kinetics of the reactions of Bu₃P and **1i** (proton source: TBPT, conventional UV-Vis method, detection at 250 nm, in CH_2Cl_2)

[Bu₃P] (M)	[1i] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
6.33×10^{-3}	6.24×10^{-4}	1.34×10^{-3}	1.17×10^{-3}
9.12×10^{-3}	8.80×10^{-4}	1.61×10^{-3}	1.72×10^{-3}
1.31×10^{-2}	1.21×10^{-3}	2.67×10^{-3}	2.59×10^{-3}
1.59×10^{-2}	8.52×10^{-4}	1.98×10^{-3}	3.03×10^{-3}
2.04×10^{-2}	1.11×10^{-3}	2.56×10^{-3}	4.01×10^{-3}
	$k_2 = 2.01 \times 10^{-1}$ M⁻¹ s⁻¹		

Graph: y = 0.2006x - 1E-04, R² = 0.9984; axes k_{obs} (s⁻¹) vs [Bu₃P] (M)

5.2.1.10 Kinetics of the reaction of Bu₃P with ethyl 2-methylbuta-2,3-dienoate (1j)

1j

$k_{obs} = 2.25 \times 10^{-3}$ s⁻¹

Graph: [1j]/[IS] vs time (s)

Table S12. Kinetics of the reactions of Bu₃P and **1j** (proton source: TBPT, ¹H NMR method, monitoring of the decreasing signal for the =CH₂ group in **1j** at 5.05 ppm, in CD_2Cl_2, residual solvent signal as internal integration standard IS)

[Bu₃P] (M)	[1j] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
4.50×10^{-2}	4.14×10^{-3}	8.62×10^{-3}	9.17×10^{-4}
6.52×10^{-2}	6.02×10^{-3}	1.23×10^{-2}	1.36×10^{-3}
1.11×10^{-1}	7.91×10^{-3}	1.60×10^{-2}	2.25×10^{-3}
1.40×10^{-1}	7.91×10^{-3}	1.60×10^{-2}	2.79×10^{-3}
	$k_2 = 1.96 \times 10^{-2}$ M⁻¹ s⁻¹		

Graph: y = 0.0196x + 6E-05, R² = 0.9993; axes k_{obs} (s⁻¹) vs [Bu₃P] (M)

5.2.2 Kinetics of the reactions of 1 with Ph₃P in dichloromethane

5.2.2.1 Kinetics of the reaction of Ph₃P with phenyl buta-2,3-dienoate (1a)

Table S13. Kinetics of the reactions of Ph$_3$P and **1a** (proton source: CT, ^{1}H NMR method, monitoring of the decreasing signal for the =CH$_2$ group in **1a** at 5.34 ppm, in CD$_2$Cl$_2$, mesitylene as internal integration standard IS)

[Ph$_3$P] (M)	[1a] (M)	[CT] (M)	k_{obs} (s^{-1})
3.09×10^{-2}	3.03×10^{-3}	6.13×10^{-3}	3.35×10^{-3}
5.07×10^{-2}	4.78×10^{-3}	1.02×10^{-2}	5.79×10^{-3}
6.79×10^{-2}	6.69×10^{-3}	1.43×10^{-2}	7.60×10^{-3}
8.60×10^{-2}	8.28×10^{-3}	1.76×10^{-2}	9.98×10^{-3}

$$k_2 = 1.19 \times 10^{-1}\,\text{M}^{-1}\,\text{s}^{-1}$$

^{31}P NMR spectroscopic analysis of selected samples indicated selective conversion of **1a** to **3a** under the conditions of the kinetic experiments (Figure S19).

Figure S19. ^{31}P NMR (162 MHz) spectrum of the sample with [Ph$_3$P]$_0$ = 76.6 mM, [1a]$_0$ = 7.59 mM and [CT]$_0$ = 15.4 mM in CD$_2$Cl$_2$ after completion of their reaction.

5.2.2.2 Kinetics of the reaction of Ph₃P with benzyl buta-2,3-dienoate (1b)

$$Ph_3P \ + \ \overset{}{=\!\!=}\!\!\diagup_{CO_2Bn} \quad \xrightarrow[CD_2Cl_2]{CT} \quad Ph_3\overset{\oplus}{P}\diagup \quad TfO^{\ominus}$$

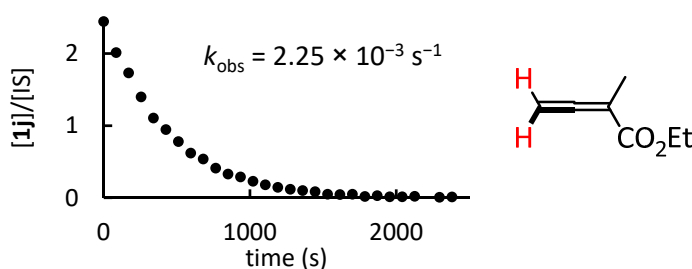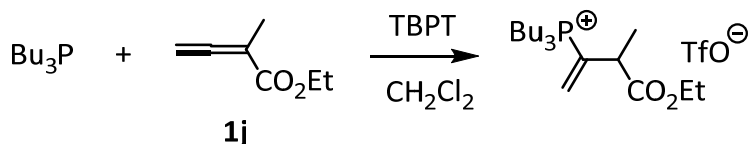**1b** **3b**

$k_{obs} = 1.51 \times 10^{-3}\ s^{-1}$

Table S14. Kinetics of the reactions of Ph₃P and **1b** (proton source: CT, ¹H NMR method, monitoring of the decreasing signal for the =CH₂ group in **1b** at 5.24 ppm, in CD₂Cl₂, mesitylene as internal integration standard)

[Ph₃P] (M)	[1b] (M)	[CT] (M)	k_{obs} (s⁻¹)
3.24×10^{-2}	3.28×10^{-3}	6.66×10^{-3}	5.76×10^{-4}
4.84×10^{-2}	4.68×10^{-3}	9.43×10^{-3}	8.22×10^{-4}
6.79×10^{-2}	6.55×10^{-3}	1.33×10^{-2}	1.17×10^{-3}
8.77×10^{-2}	8.42×10^{-3}	1.72×10^{-2}	1.51×10^{-3}

$k_2 = 1.70 \times 10^{-2}\ M^{-1}\ s^{-1}$

$y = 0.0170x + 1E-05$
$R^2 = 0.9993$

5.2.2.3 Kinetics of the reaction of Ph₃P with ethyl 4-phenylbuta-2,3-dienoate (1c)

$k_{obs} = 4.70 \times 10^{-4} \text{ s}^{-1}$

Time scale does not consider the time needed between the sample preparation and the first measured NMR spectrum (ca. 300 s).
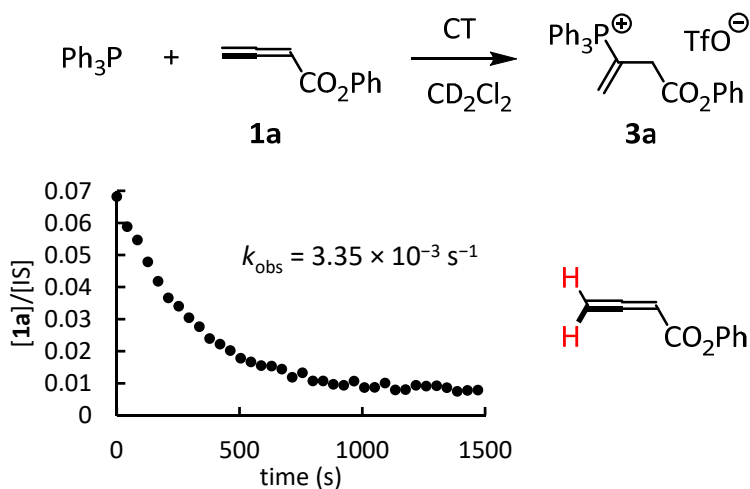
Table S15. Kinetics of the reactions of Ph₃P and **1c** (proton source: CT, ¹H NMR method, monitoring of the increasing signal for the CH₂ group in **3c** at 3.67 ppm, in CD₂Cl₂, mesitylene as internal integration standard)

$[Ph_3P]$ (M)	$[1c]$ (M)	$[CT]$ (M)	k_{obs} (s^{-1})
2.29×10^{-2}	2.36×10^{-3}	1.13×10^{-2}	4.70×10^{-4}
3.81×10^{-2}	3.15×10^{-3}	6.45×10^{-3}	8.09×10^{-4}
5.64×10^{-2}	5.12×10^{-3}	1.05×10^{-2}	1.10×10^{-3}
6.90×10^{-2}	6.69×10^{-3}	1.37×10^{-2}	1.37×10^{-3}

$$k_2 = 1.90 \times 10^{-2} \text{ M}^{-1}\text{ s}^{-1}$$

y = 0.0190x + 5E-05
R² = 0.9956

³¹P NMR spectroscopic analysis indicated selective conversion of **1c** to **3c** under the conditions of the kinetic experiments (Figure S20).

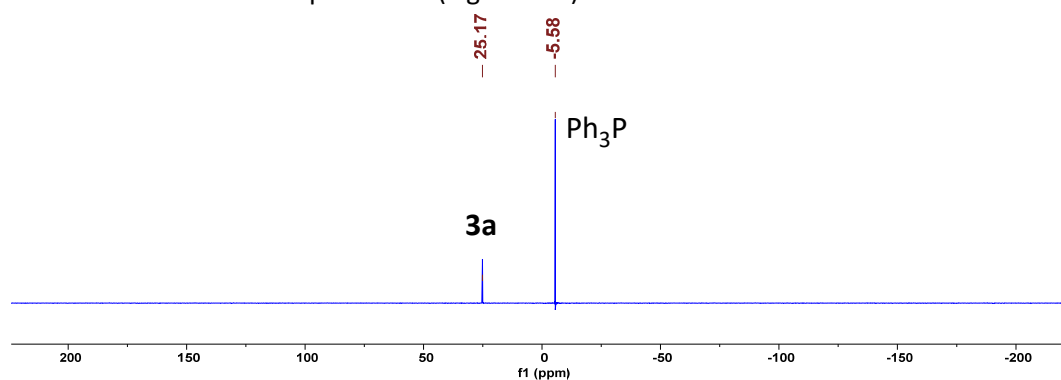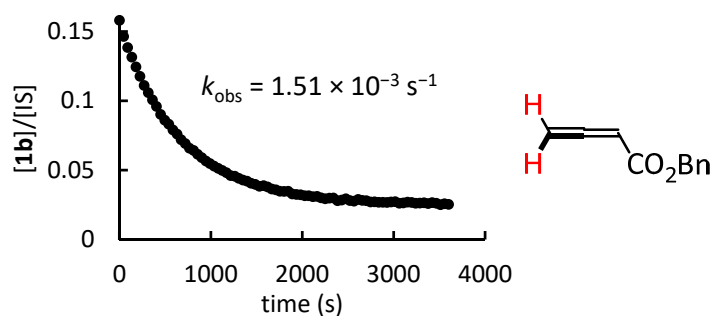**Figure S20.** ³¹P NMR (162 MHz) spectrum of the sample with $[Ph_3P]_0 = 38.1$ mM, $[1c]_0 = 3.15$ mM and $[CT]_0 = 6.45$ mM in CD₂Cl₂ after completion of their reaction.

5.2.2.4 Kinetics of the reaction of Ph_3P with 3-vinylidenedihydrofuran-2(3H)-one (1d)

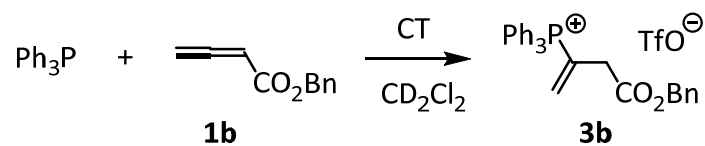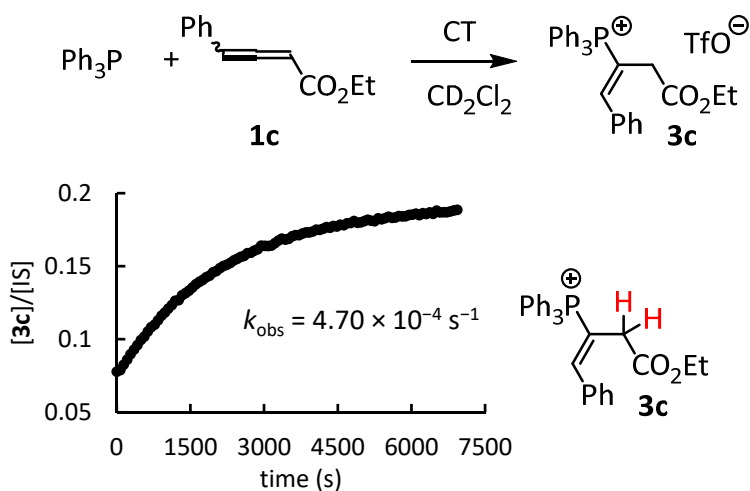**Table S16.** Kinetics of the reactions of Ph_3P and **1d** (proton source: CT, ^{1}H NMR method, monitoring of the decreasing signal for the $=CH_2$ group in **1d** at 5.28–5.27 ppm, in CD_2Cl_2, mesitylene as internal integration standard)

$[Ph_3P]$ (M)	$[1d]$ (M)	$[CT]$ (M)	k_{obs} (s^{-1})
2.34×10^{-2}	2.26×10^{-3}	9.34×10^{-3}	5.59×10^{-4}
3.62×10^{-2}	3.01×10^{-3}	1.04×10^{-2}	8.01×10^{-4}
4.69×10^{-2}	4.52×10^{-3}	1.37×10^{-2}	1.09×10^{-3}
6.02×10^{-2}	5.65×10^{-3}	1.81×10^{-2}	1.40×10^{-3}
7.05×10^{-2}	6.78×10^{-3}	2.09×10^{-2}	1.64×10^{-3}
	$k_2 = 2.33 \times 10^{-2}\,M^{-1}\,s^{-1}$		

^{31}P NMR spectroscopic analysis indicated selective conversion of **1d** to **3d** under the conditions of the kinetic experiments (Figure S21).
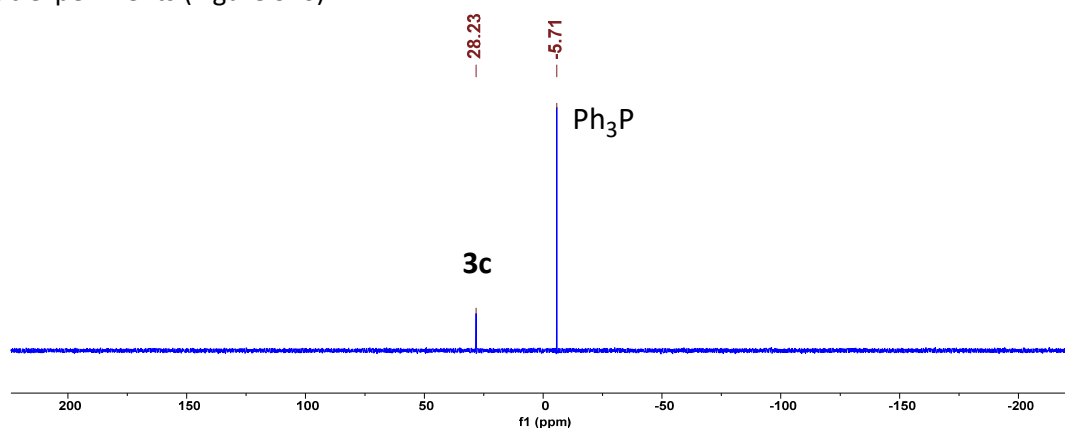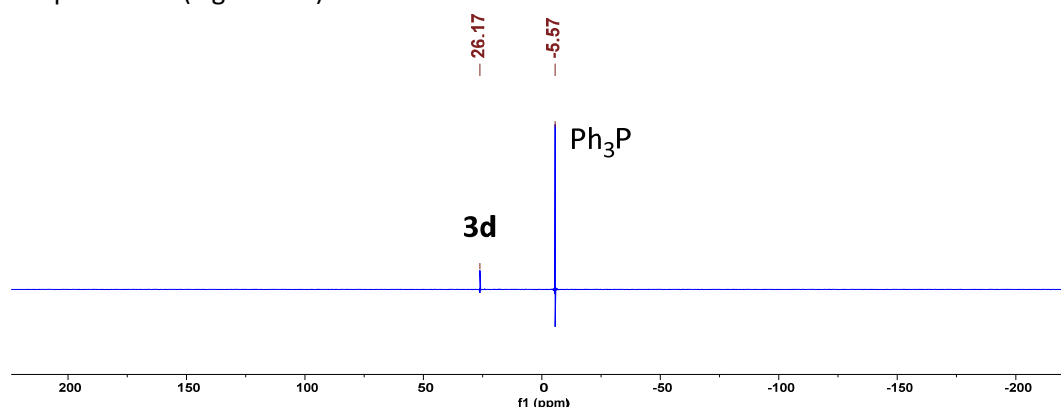

Figure S21. ^{31}P NMR (162 MHz) spectrum of a sample with $[Ph_3P]_0$ = 141 mM, $[1d]_0$ = 12.7 mM and $[CT]_0$ = 25.9 mM in CD_2Cl_2 after completion of their reaction.

5.2.2.5   Kinetics of the reaction of Ph₃P with methyl buta-2,3-dienoate (1e)

Table S17. Kinetics of the reactions of Ph₃P and **1e** (proton source: CT, ^{1}H NMR method, monitoring of the decreasing signal for the =CH₂ group in **1e** at 5.22 ppm, in CD₂Cl₂, mesitylene as internal integration standard)

[Ph₃P] (M)	[1e] (M)	[CT] (M)	k_{obs} (s^{-1})
1.15×10^{-1}	1.03×10^{-2}	2.09×10^{-2}	1.13×10^{-3}
1.95×10^{-1}	1.29×10^{-2}	2.68×10^{-2}	1.98×10^{-3}
2.71×10^{-1}	1.54×10^{-2}	3.13×10^{-2}	2.87×10^{-3}
3.43×10^{-1}	1.80×10^{-2}	3.57×10^{-2}	3.63×10^{-3}

$$k_2 = 1.10 \times 10^{-2} \, M^{-1} \, s^{-1}$$

5.2.2.6 Kinetics of the reaction of Ph₃P with ethyl buta-2,3-dienoate (1f)

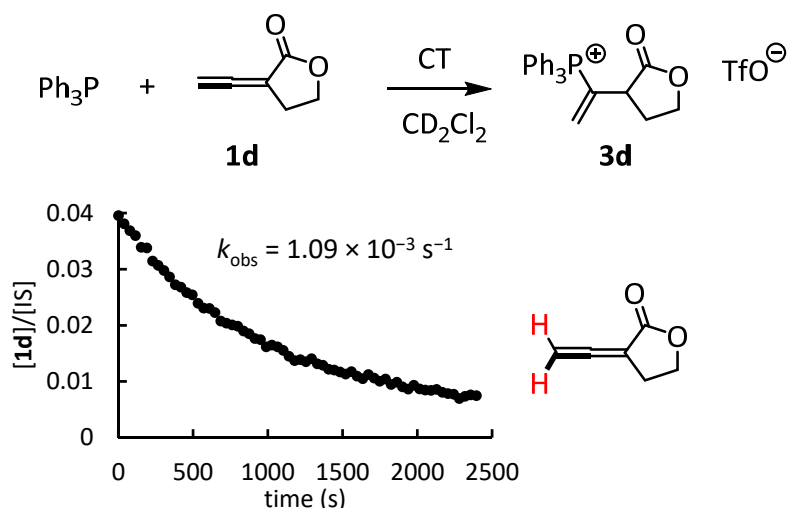

$k_{obs} = 1.56 \times 10^{-3} \ s^{-1}$

Table S18. Kinetics of the reactions of Ph₃P and **1f** (proton source: CT, ^{1}H NMR method, monitoring of the decreasing signal for the =CH₂ group in **1f** at 5.21 ppm, in CD₂Cl₂, mesitylene as internal integration standard)

[Ph₃P] (M)	[**1f**] (M)	[CT] (M)	k_{obs} (s⁻¹)
1.75×10^{-1}	1.82×10^{-2}	3.71×10^{-2}	1.56×10^{-3}
2.34×10^{-1}	1.82×10^{-2}	3.71×10^{-2}	1.99×10^{-3}
2.90×10^{-1}	2.90×10^{-2}	5.93×10^{-2}	2.44×10^{-3}
3.48×10^{-1}	2.90×10^{-2}	5.93×10^{-2}	2.88×10^{-3}
$k_2 = 7.67 \times 10^{-3} \ M^{-1} \ s^{-1}$			

y = 7.67E-03x + 2.10E-04
R² = 0.9992

Our attempts to generate zwitterion **2f** in order to determine the rate constant of the Ph₃P-retroaddition did not allow us to measure the kinetics of the C-P bond cleavage reaction. Already the first ^{1}H NMR spectrum recorded after mixing the vinylphosphonium triflate **3f** with 4 equiv of potassium *tert*-butoxide in DMSO showed quantitative conversion to free Ph₃P and polymerised **1f** (Figure S22). Subsequent ^{13}C and ^{31}P NMR spectroscopic analysis of this sample confirmed this interpretation (Figure S23 and S24).
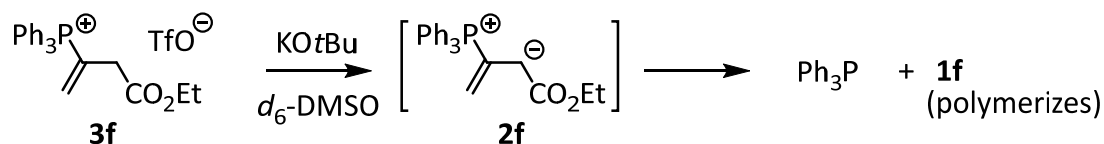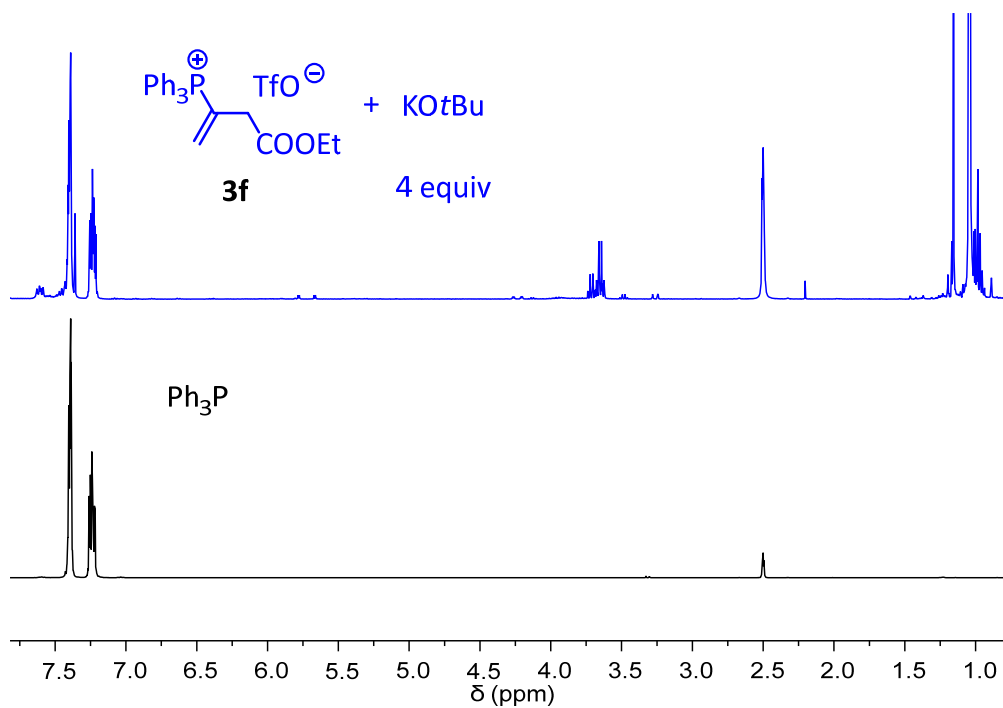
Figure S22. Comparison of the 400 MHz ^{1}H NMR spectrum of the **3f**/KO*t*Bu mixture with that of Ph$_3$P (*d$_6$*-DMSO).
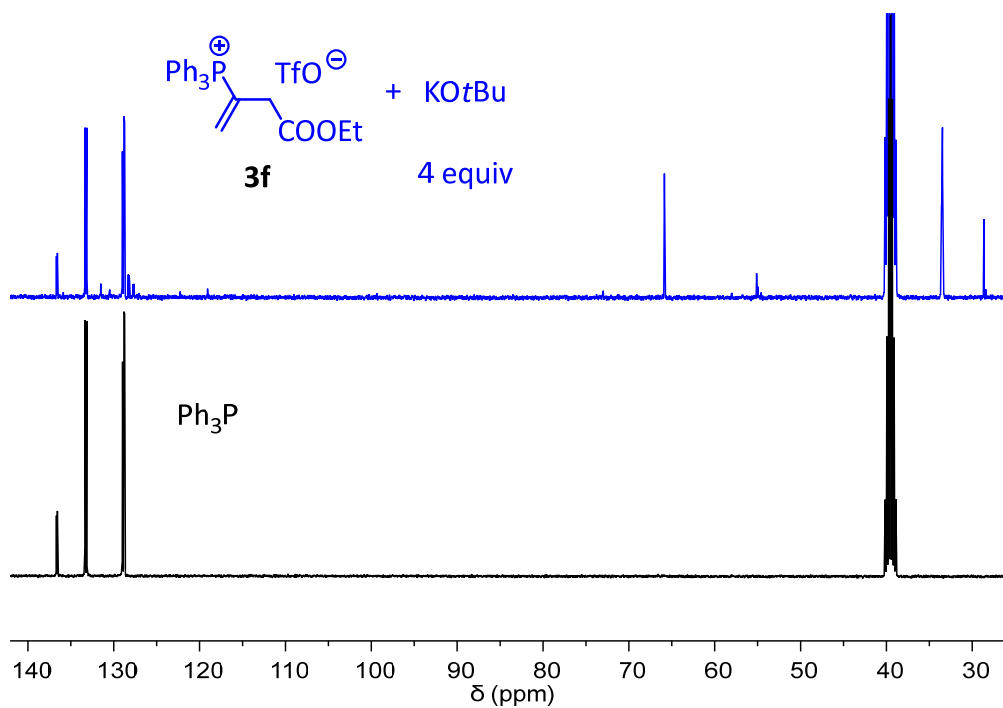
Figure S23. Comparison of the 101 MHz ^{13}C NMR spectrum of the **3f**/KO*t*Bu mixture with that of Ph$_3$P (*d$_6$*-DMSO).
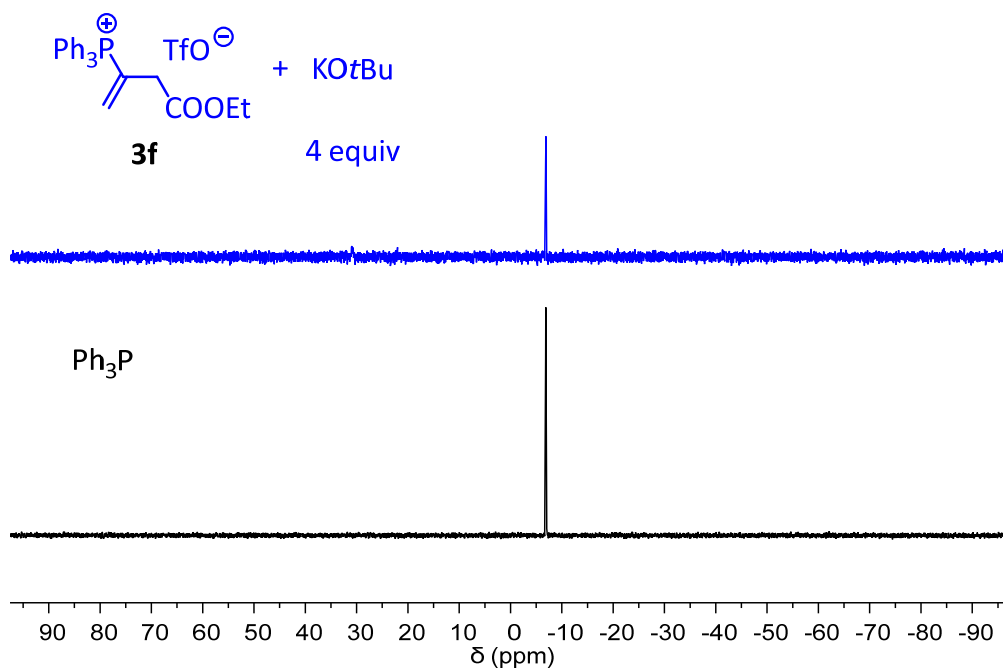
Figure S24. Comparison of the 162 MHz ^{31}P NMR spectrum of the **3f**/KO*t*Bu mixture with that of Ph$_3$P (*d*$_6$-DMSO).

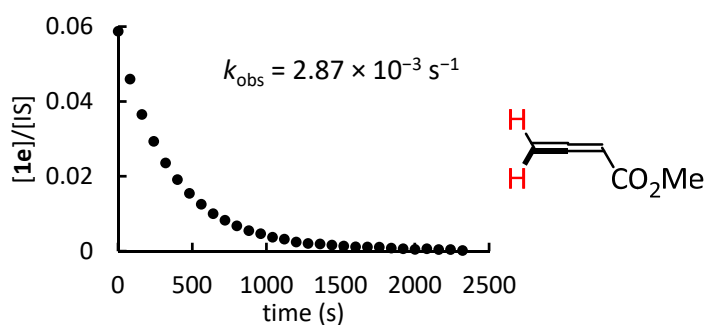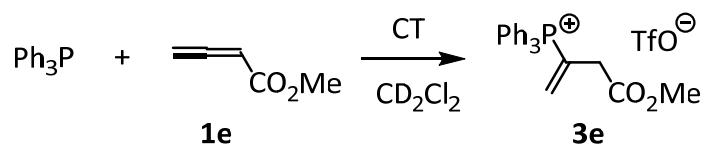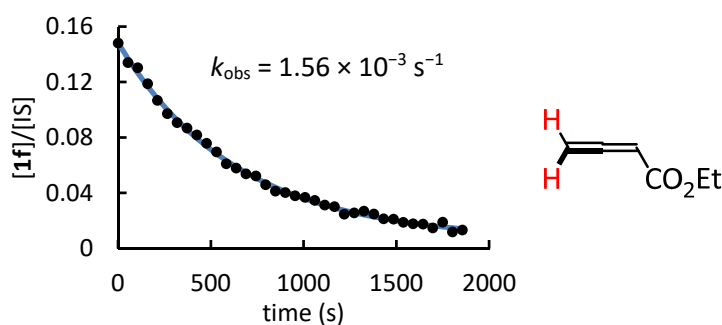### 5.2.2.7 Kinetics of the reaction of Ph₃P with ethyl penta-2,3-dienoate (1g)

Table S19. Kinetics of the reactions of Ph$_3$P and **1g** (proton source: CT, ^{1}H NMR method, monitoring of the increasing signal for the OCH$_2$C$\underline{\text{H}}_3$ group in **3g** at 1.07 ppm, in CD$_2$Cl$_2$, mesitylene as internal integration standard)

[Ph$_3$P] (M)	[1g] (M)	[CT] (M)	k_{obs} (s^{-1})
2.97×10^{-2}	2.66×10^{-3}	6.14×10^{-3}	2.58×10^{-4}
4.00×10^{-2}	3.96×10^{-3}	8.32×10^{-3}	3.48×10^{-4}
6.44×10^{-2}	6.34×10^{-3}	1.43×10^{-2}	5.44×10^{-4}
8.96×10^{-2}	8.72×10^{-3}	1.78×10^{-2}	7.49×10^{-4}
1.14×10^{-1}	1.11×10^{-2}	2.24×10^{-2}	9.37×10^{-4}

$$k_2 = 8.05 \times 10^{-3} \text{ M}^{-1}\text{ s}^{-1}$$

5.2.2.8 Kinetics of the reaction of Ph₃P with *tert*-butyl buta-2,3-dienoate (1h)

$$Ph_3P \ + \ \overset{}{=\!=\!=}\!CO_2t\text{Bu} \ \xrightarrow[\text{CD}_2\text{Cl}_2]{\text{CT}} \ Ph_3\overset{\oplus}{P} \ \ TfO^{\ominus}$$

1h   **3h**
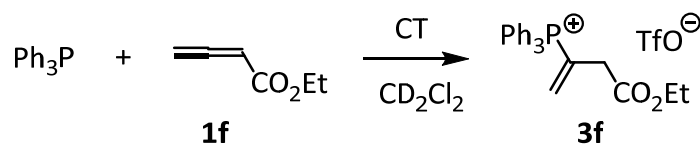
$k_{obs} = 4.08 \times 10^{-4} \ s^{-1}$

Table S20. Kinetics of the reactions of Ph₃P and **1h** (proton source: CT, ^{1}H NMR method, monitoring of the decreasing signal for the =CH₂ group in **1h** at 5.16 ppm, in CD₂Cl₂, mesitylene as internal integration standard)

[Ph₃P] (M)	[1h] (M)	[CT] (M)	k_{obs} (s⁻¹)
8.77×10^{-2}	8.56×10^{-3}	1.78×10^{-2}	2.01×10^{-4}
1.31×10^{-1}	1.29×10^{-2}	2.66×10^{-2}	3.06×10^{-4}
1.73×10^{-1}	1.43×10^{-2}	2.87×10^{-2}	4.08×10^{-4}
2.12×10^{-1}	2.00×10^{-2}	4.09×10^{-2}	4.98×10^{-4}

$k_2 = 2.39 \times 10^{-3} \ M^{-1} \ s^{-1}$

y = 2.39E-03x - 8.06E-06
R² = 0.9999

5.2.2.9 Kinetics of the reaction of Ph₃P with diethyl 2-vinylidenesuccinate (1i)

$k_{obs} = 1.16 \times 10^{-3}\ s^{-1}$
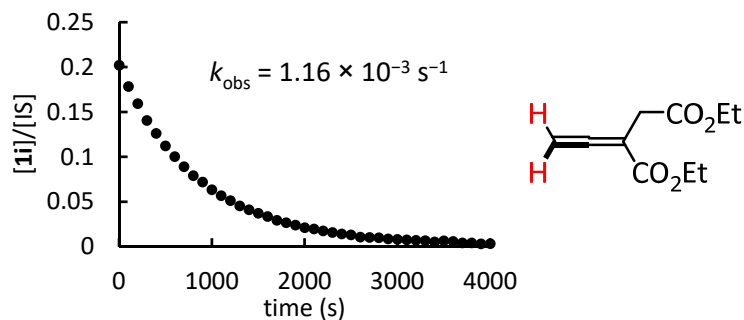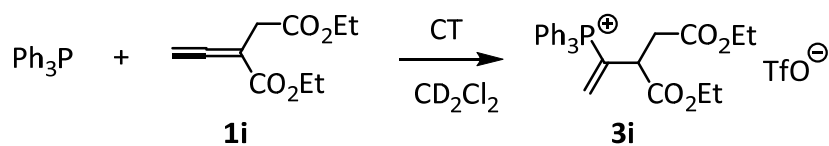
Table S21. Kinetics of the reactions of Ph₃P and **1i** (proton source: CT, ^{1}H NMR method, monitoring of the decreasing signal for the =CH₂ group in **1i** at 5.21 ppm, in CD₂Cl₂, mesitylene as internal integration standard)

[Ph₃P] (M)	[1i] (M)	[CT] (M)	k_{obs} (s⁻¹)
8.62×10^{-2}	8.40×10^{-3}	1.80×10^{-2}	3.80×10^{-4}
1.49×10^{-1}	1.42×10^{-2}	2.98×10^{-2}	6.66×10^{-4}
2.06×10^{-1}	$1,57 \times 10^{-2}$	3.14×10^{-2}	9.41×10^{-4}
2.57×10^{-1}	1.57×10^{-2}	3.13×10^{-2}	1.16×10^{-3}
	$k_2 = 4.59 \times 10^{-3}\ M^{-1}\ s^{-1}$		

y = 4.59E-03x - 1.53E-05
R² = 0.9996

[1]P NMR spectroscopic analysis indicated selective conversion of **1i** to **3i** under the conditions of the kinetic experiments (Figure S25).
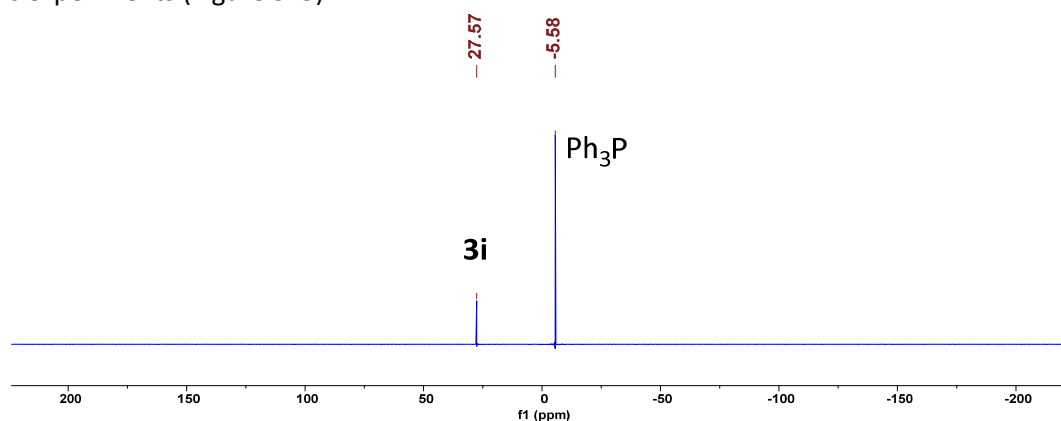
Figure S25. ^{31}P NMR (162 MHz) spectrum of a sample with [Ph₃P]₀ = 118 mM, [1i]₀ = 11.2 mM and [CT]₀ = 22.8 mM in CD₂Cl₂ after completion of their reaction.

5.2.2.10 Kinetics of the reaction of Ph₃P with ethyl 2-methylbuta-2,3-dienoate (1j)

Ph_3P + [structure 1j, CO₂Et] $\xrightarrow[CD_2Cl_2]{CT}$ [structure 3j: $Ph_3P^\oplus$, CO_2Et] $TfO^\ominus$

1j   **3j**

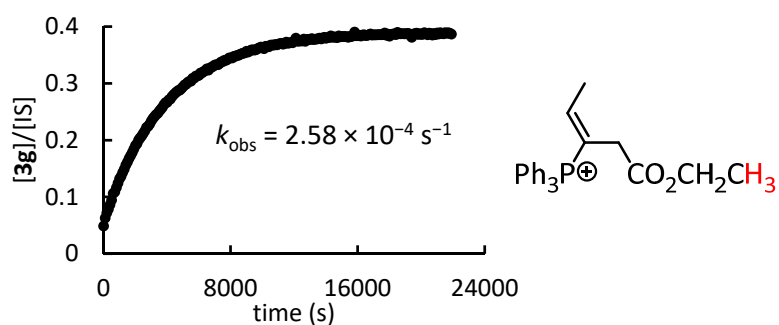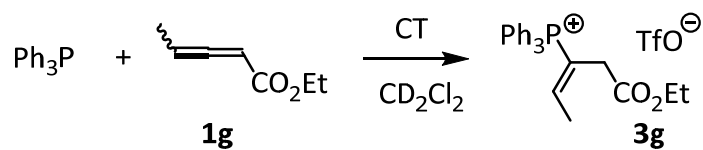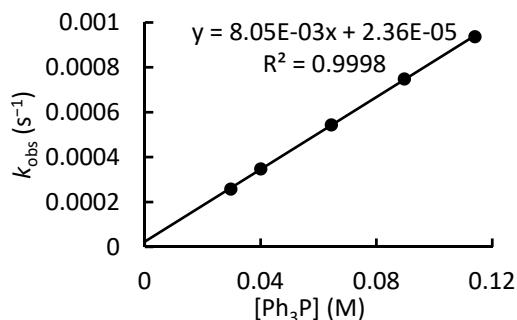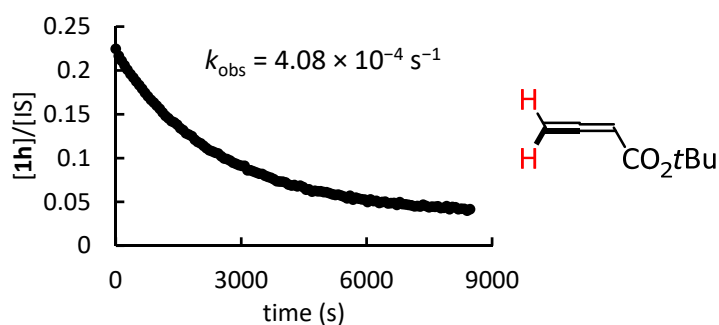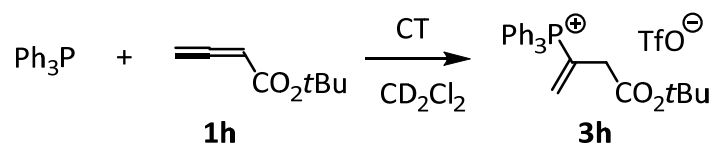$k_{obs} = 7.28 \times 10^{-5}\ s^{-1}$

[structure: H, H, CO₂Et]
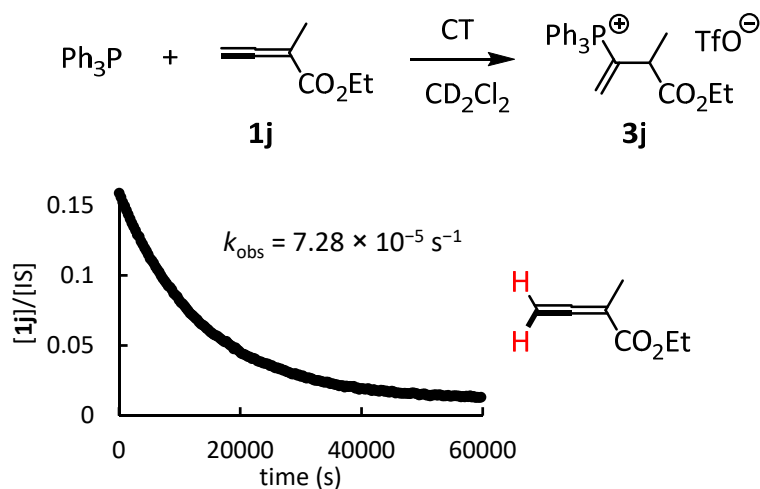
Table S22. Kinetics of the reactions of Ph₃P and **1j** (proton source: CT, ¹H NMR method, monitoring of the decreasing signal for the =CH₂ group in **1j** at 5.05 ppm, in CD₂Cl₂, mesitylene as internal integration standard)

$[Ph_3P]$ (M)	$[1j]$ (M)	$[CT]$ (M)	k_{obs} (s⁻¹)
1.16×10^{-1}	1.13×10^{-2}	2.38×10^{-2}	4.14×10^{-5}
1.96×10^{-1}	1.51×10^{-2}	3.13×10^{-2}	7.28×10^{-5}
3.06×10^{-1}	1.51×10^{-2}	3.13×10^{-2}	1.07×10^{-4}
3.82×10^{-1}	1.78×10^{-2}	3.75×10^{-2}	1.36×10^{-4}

$k_2 = 3.49 \times 10^{-4}\ M^{-1}\ s^{-1}$

$y = 3.49E\text{-}04x + 2.02E\text{-}06$
$R^2 = 0.9979$

³¹P NMR spectroscopic analysis indicated selective conversion of **1j** to **3j** under the conditions of the kinetic experiments (Figure S26).
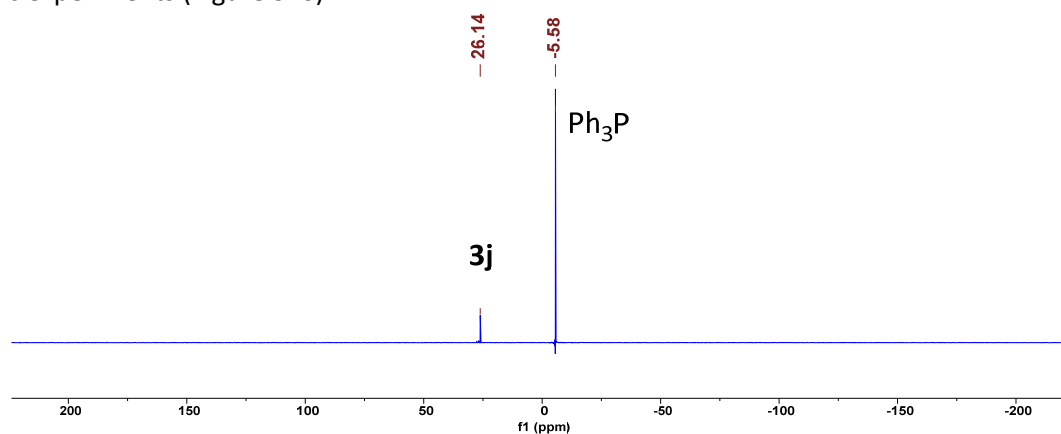
Figure S26. ³¹P NMR (162 MHz) spectrum of a sample with $[Ph_3P]_0 = 118$ mM, $[1j]_0 = 10.8$ mM and $[CT]_0 = 19.8$ mM in CD₂Cl₂ after completion of their reaction.

5.3 Kinetics of the reactions of tributylphosphine with Michael acceptors 4

5.3.1 Kinetics of the reaction of Bu₃P with 4a

$$Bu_3P \quad + \quad Me_2N-\underset{\text{4a}}{\underset{\|}{\overset{EtO_2C}{\diagdown}}}=\overset{CO_2Et}{\diagup} \quad \xrightarrow[\quad CH_2Cl_2 \quad]{TBPT}$$

$k_{obs} = 2.98 \times 10^{-4}\ s^{-1}$

Table S23. Kinetics of the reactions of Bu₃P and **4a** (proton source: TBPT, conventional UV-Vis method, detection at 376 nm, in CH₂Cl₂)

[Bu₃P] (M)	[4a] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
5.13×10^{-3}	3.13×10^{-5}	1.59×10^{-4}	1.51×10^{-4}
1.01×10^{-2}	3.09×10^{-5}	1.57×10^{-4}	2.98×10^{-4}
1.54×10^{-2}	3.14×10^{-5}	1.59×10^{-4}	4.60×10^{-4}
2.05×10^{-2}	3.14×10^{-5}	1.59×10^{-4}	6.17×10^{-4}
	$k_2 = 3.03 \times 10^{-2}$ M⁻¹ s⁻¹		

y = 0.0303x - 6E-06
R² = 0.9999

5.3.2 Kinetics of the reaction of Bu₃P with 4b

Table S24. Kinetics of the reactions of Bu₃P and **4b** (proton source: TBPT, conventional UV-Vis method, detection at 312 nm, in CH_2Cl_2)

[Bu₃P] (M)	[**4b**] (M)	[TBPT] (M)	k_{obs} (s^{-1})
1.69×10^{-3}	6.34×10^{-5}	0	2.78×10^{-4}
1.85×10^{-3}	6.27×10^{-5}	3.10×10^{-4}	3.05×10^{-4}
3.50×10^{-3}	6.22×10^{-5}	0	5.71×10^{-4}
5.07×10^{-3}	6.02×10^{-5}	2.98×10^{-4}	7.53×10^{-4}
6.76×10^{-3}	6.01×10^{-5}	2.98×10^{-4}	9.77×10^{-4}
	$k_2 = 1.37 \times 10^{-1}$ M^{-1} s^{-1}		

5.3.3 Kinetics of the reaction of Bu3P with 4c

Table S25. Kinetics of the reactions of Bu_3P and **4c** (proton source: TBPT, conventional UV-Vis method, detection at 291 nm, in CH_2Cl_2)

$[Bu_3P]$ (M)	**[4c]** (M)	[TBPT] (M)	k_{obs} (s^{-1})
1.25×10^{-3}	4.61×10^{-5}	2.30×10^{-4}	3.29×10^{-4}
1.78×10^{-3}	4.20×10^{-5}	0	4.13×10^{-4}
2.48×10^{-3}	4.57×10^{-5}	2.29×10^{-4}	5.69×10^{-4}
3.67×10^{-3}	4.50×10^{-5}	2.25×10^{-4}	8.11×10^{-4}
4.51×10^{-3}	4.43×10^{-5}	2.22×10^{-4}	1.00×10^{-3}
	$k_2 = 2.08 \times 10^{-1}$ M^{-1} s^{-1}		

5.3.4 Kinetics of the reaction of Bu₃P with 4d

$$k_{obs} = 4.33 \times 10^{-4} \text{ s}^{-1}$$

Table S26. Kinetics of the reactions of Bu₃P and **4d** (proton source: TBPT, conventional UV-Vis method, detection at 280 nm, in CH₂Cl₂)

[Bu₃P] (M)	[4d] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
1.13×10^{-3}	1.08×10^{-4}	5.35×10^{-4}	4.33×10^{-4}
2.24×10^{-3}	1.07×10^{-4}	5.28×10^{-4}	8.31×10^{-4}
3.24×10^{-3}	1.01×10^{-4}	5.18×10^{-4}	1.18×10^{-3}
4.25×10^{-3}	1.02×10^{-4}	5.02×10^{-4}	1.59×10^{-3}

$$k_2 = 3.69 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$$

y = 0.3686x + 8E-06
R² = 0.9989

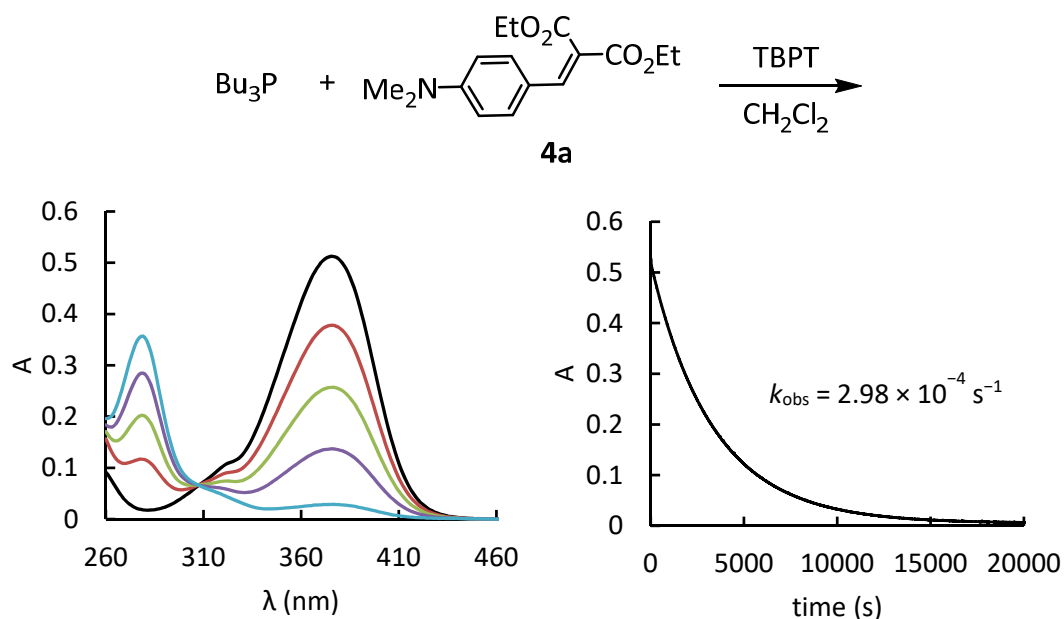### 5.3.5 Kinetics of the reaction of Bu₃P with 4e

Table S27. Kinetics of the reactions of Bu₃P and **4e** (proton source: TBPT, conventional UV-Vis method, detection at 274 nm, in CH₂Cl₂)

[Bu₃P] (M)	[4e] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
1.24×10^{-3}	5.60×10^{-5}	0	1.27×10^{-3}
1.90×10^{-3}	5.54×10^{-5}	2.75×10^{-4}	1.84×10^{-3}
3.63×10^{-3}	5.45×10^{-5}	2.70×10^{-4}	3.50×10^{-3}
4.77×10^{-3}	5.37×10^{-5}	2.67×10^{-4}	4.73×10^{-3}

$k_2 = 9.79 \times 10^{-1}\ \text{M}^{-1}\ \text{s}^{-1}$

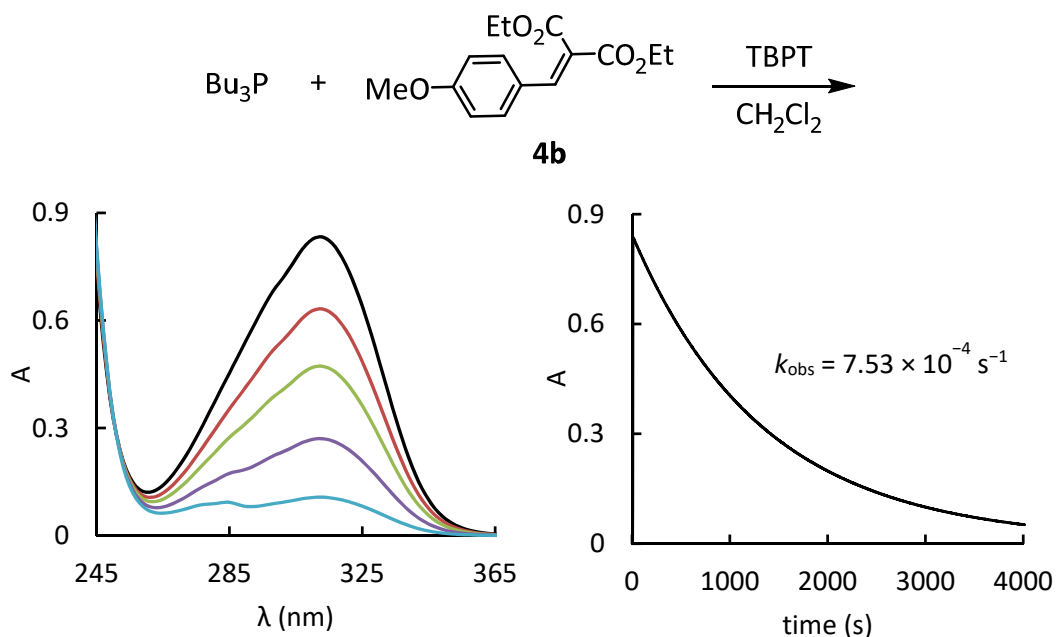## 5.3.6   Kinetics of the reaction of Bu₃P with 4f
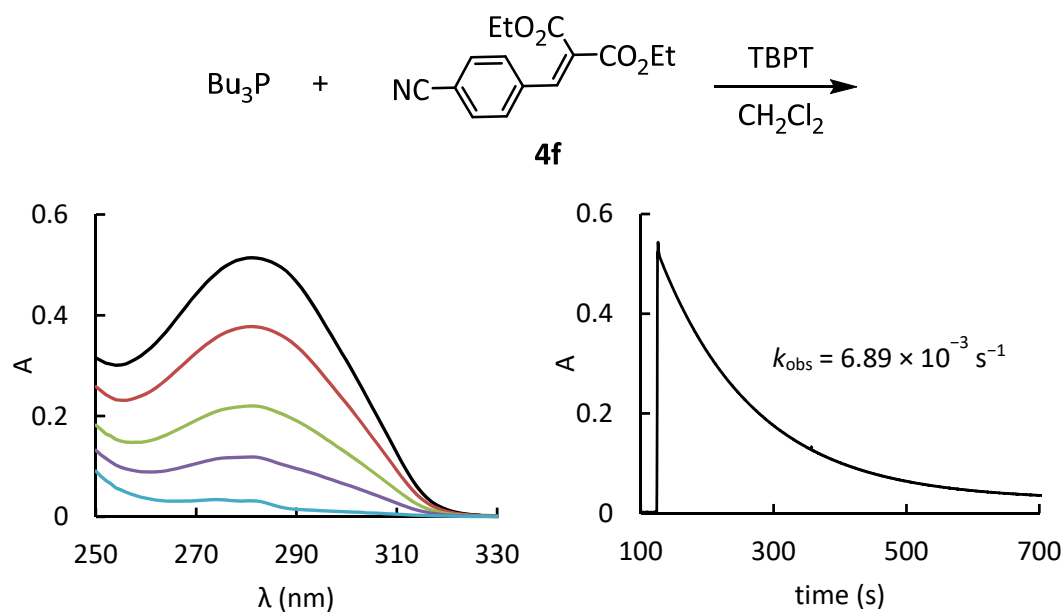
Table S28. Kinetics of the reactions of Bu₃P and **4f** (proton source: TBPT, conventional UV-Vis method, detection at 282 nm, in CH₂Cl₂)

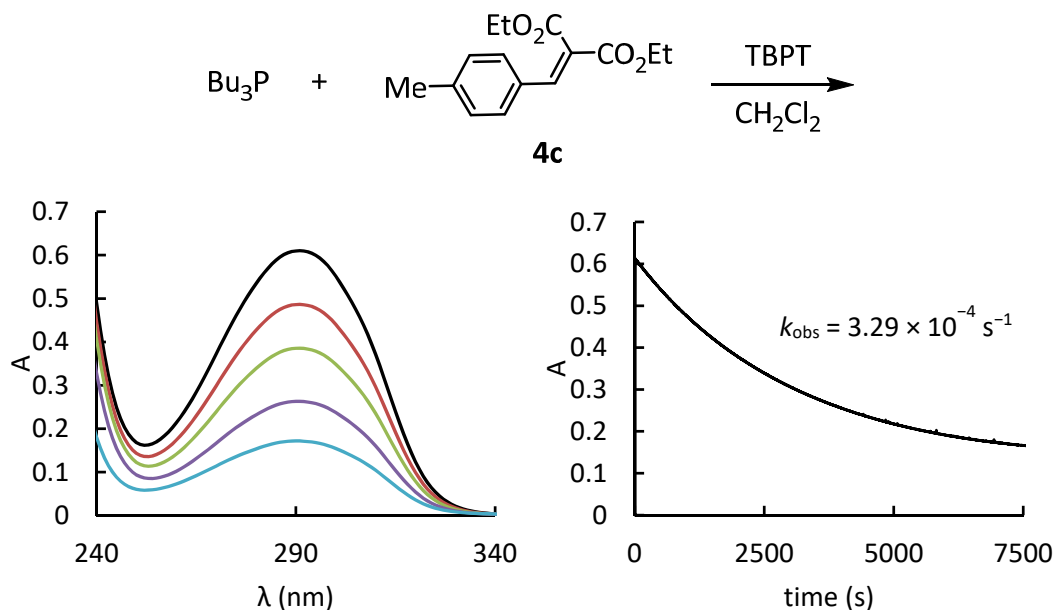| [Bu₃P] (M)	[4f] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
9.26×10^{-4}	3.92×10^{-5}	1.97×10^{-4}	2.24×10^{-3}
1.82×10^{-3}	3.86×10^{-5}	1.94×10^{-4}	4.69×10^{-3}
2.71×10^{-3}	3.83×10^{-5}	1.92×10^{-4}	6.89×10^{-3}
3.62×10^{-3}	3.83×10^{-5}	1.93×10^{-4}	9.31×10^{-3}
$k_2 = 2.61$ M⁻¹ s⁻¹			

5.3.7   Kinetics of the reaction of Bu$_3$P with 4g
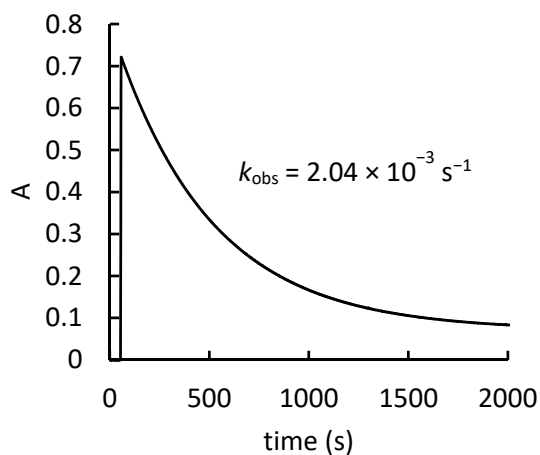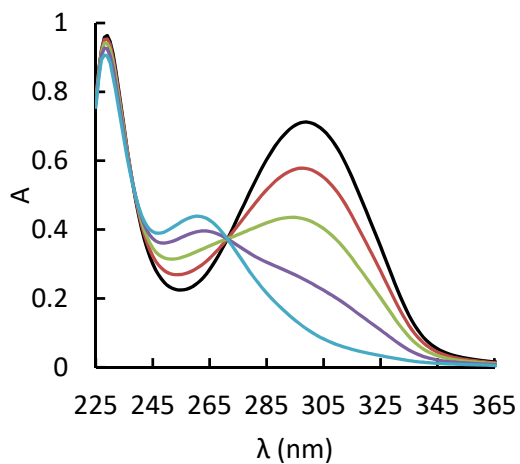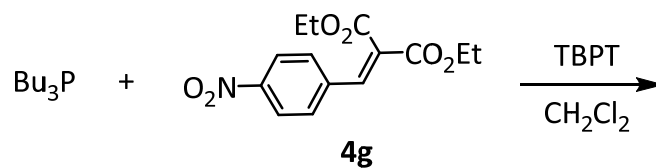
Table S29. Kinetics of the reactions of Bu$_3$P and **4g** (proton source: TBPT, conventional UV-Vis method, detection at 300 nm, in CH$_2$Cl$_2$)

[Bu$_3$P] (M)	[4g] (M)	[TBPT] (M)	k_{obs} (s^{-1})
4.17×10^{-4}	4.00×10^{-5}	2.12×10^{-4}	1.33×10^{-3}
6.29×10^{-4}	4.01×10^{-5}	2.13×10^{-4}	2.04×10^{-3}
8.30×10^{-4}	3.98×10^{-5}	2.11×10^{-4}	2.62×10^{-3}
1.04×10^{-3}	3.97×10^{-5}	2.11×10^{-4}	3.35×10^{-3}
	$k_2 = 3.21$ M^{-1} s^{-1}		
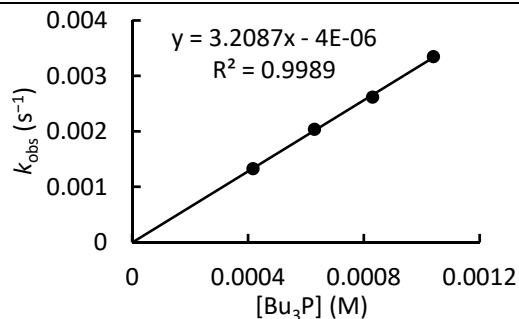
5.3.8 Kinetics of the reaction of Bu₃P with 4h
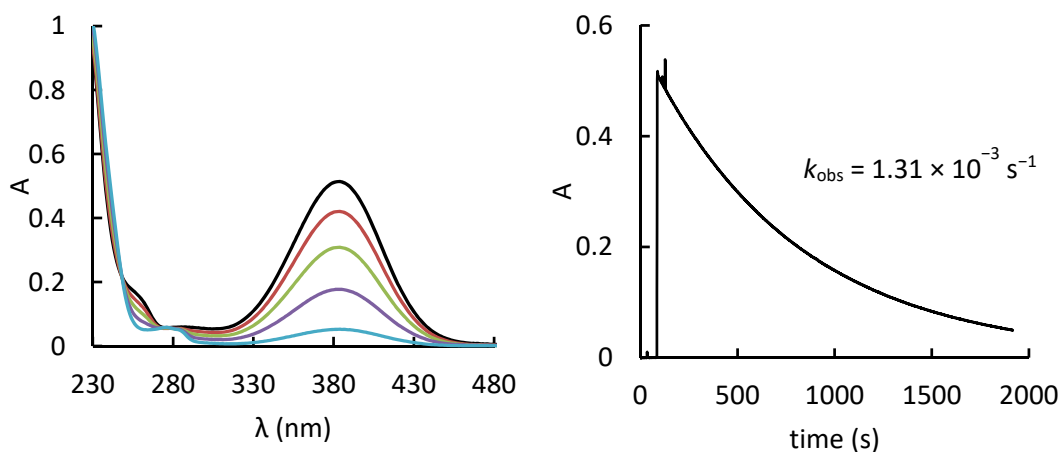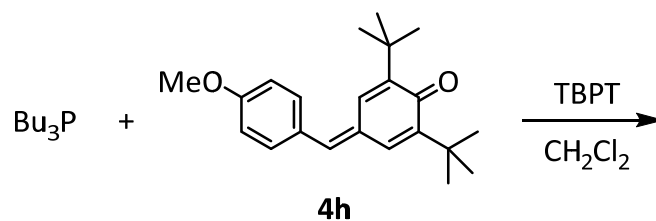
Table S30. Kinetics of the reactions of Bu$_3$P and **4h** (proton source: TBPT, conventional UV-Vis method, detection at 383 nm, in CH$_2$Cl$_2$)

[Bu$_3$P] (M)	[4h] (M)	[TBPT] (M)	k_{obs} (s^{-1})
3.21×10^{-4}	2.45×10^{-5}	1.28×10^{-4}	4.44×10^{-4}
4.75×10^{-4}	2.42×10^{-5}	1.27×10^{-4}	7.37×10^{-4}
6.34×10^{-4}	2.43×10^{-5}	1.27×10^{-4}	1.03×10^{-3}
7.86×10^{-4}	2.41×10^{-5}	1.26×10^{-4}	1.31×10^{-3}
$k_2 = 1.86$ M^{-1} s^{-1}			

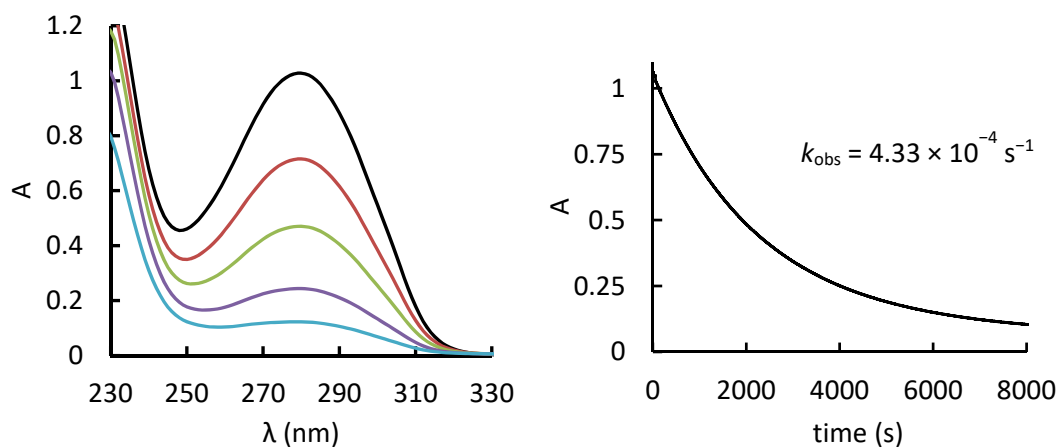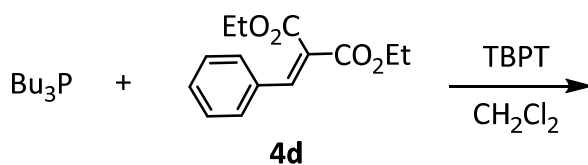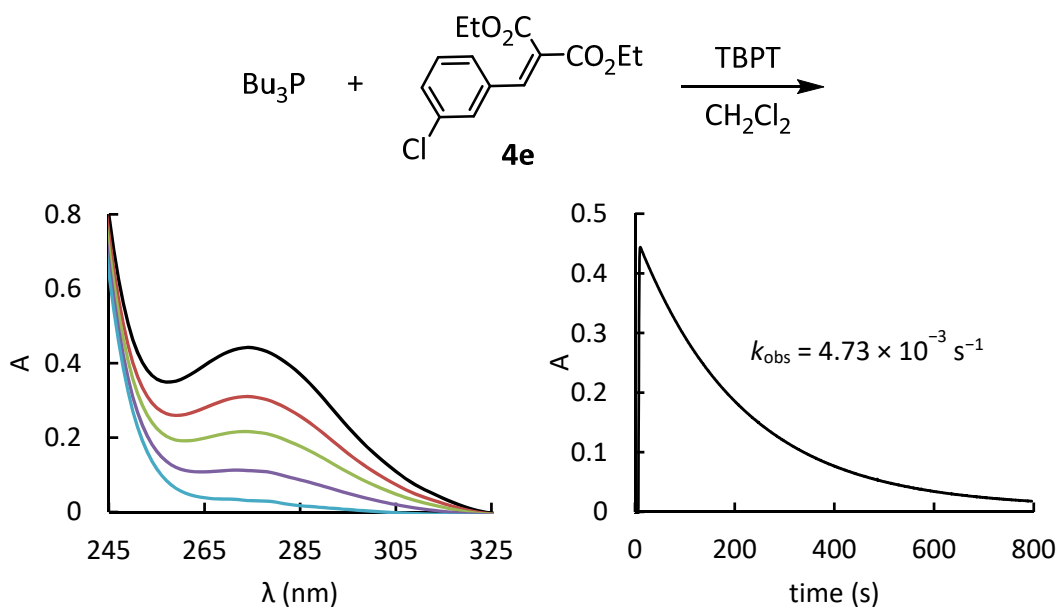### 5.3.9 Kinetics of the reaction of Bu₃P with 4i
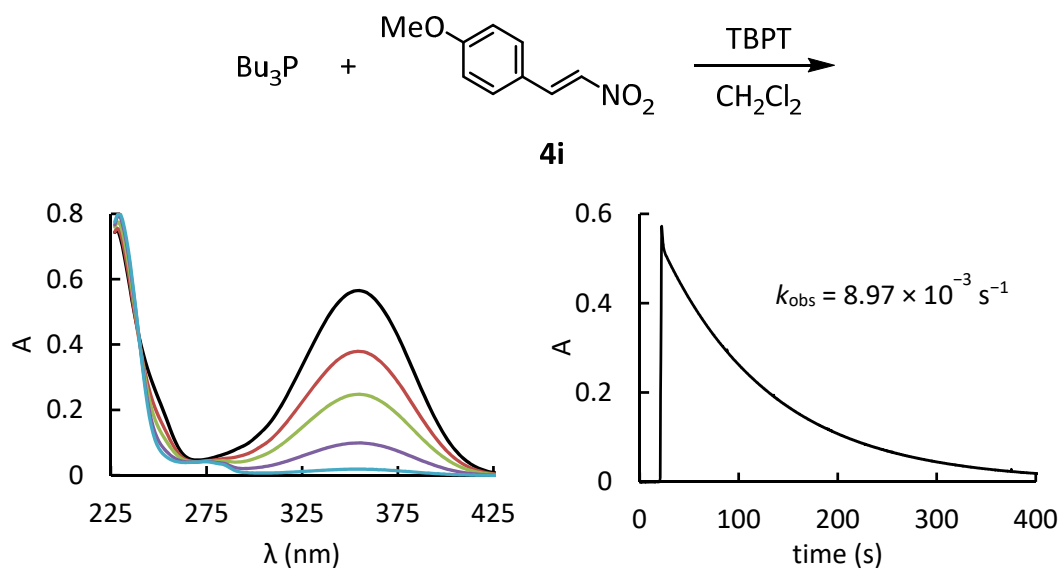
Table S31. Kinetics of the reactions of Bu₃P and **4i** (proton source: TBPT, conventional UV-Vis method, detection at 353 nm, in CH₂Cl₂)

[Bu₃P] (M)	[4i] (M)	[TBPT] (M)	k_{obs} (s⁻¹)
2.81×10^{-4}	2.64×10^{-5}	1.47×10^{-4}	4.65×10^{-3}
4.78×10^{-4}	4.19×10^{-5}	2.18×10^{-4}	8.97×10^{-3}
6.75×10^{-4}	4.18×10^{-5}	2.17×10^{-4}	1.26×10^{-2}
8.67×10^{-4}	4.15×10^{-5}	2.16×10^{-4}	1.64×10^{-2}

$$k_2 = 1.99 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$$

5.3.10 Kinetics of the reaction of Bu$_3$P with 4j

$$Bu_3P \quad + \quad \diagup\!\!\!\!\diagup\!\!\!\diagdown SO_2F \quad \xrightarrow{\quad CH_2Cl_2 \quad}$$

4j

$k_{obs} = 2.06 \text{ s}^{-1}$

Table S32. Kinetics of the reactions of Bu$_3$P and **4j** (without added proton source, stopped-flow method, detection at 249 nm, in CH$_2$Cl$_2$)

[Bu$_3$P] (M)	[**4j**] (M)	k_{obs} (s^{-1})
	3.11×10^{-3}	2.06
	4.14×10^{-3}	2.88
	5.18×10^{-3}	3.61
3.21×10^{-4}	6.21×10^{-3}	4.45
	8.28×10^{-3}	6.20
	9.32×10^{-3}	6.99
$k_2 = 7.99 \times 10^2 \text{ M}^{-1}\cdot\text{s}^{-1}$		

y = 798.88x - 0.4602
R^2 = 0.9994

5.3.11 Kinetics of the reaction of Bu₃P with 4k

4k

$k_{obs} = 3.14 \text{ s}^{-1}$
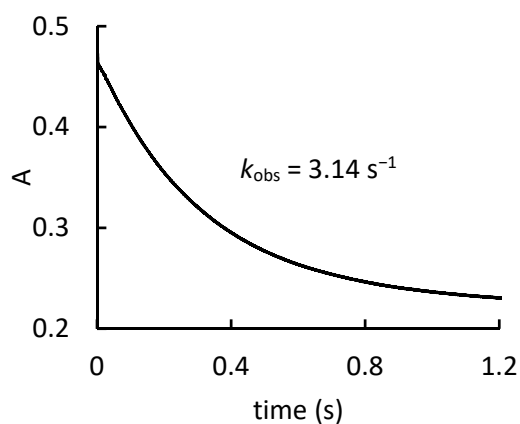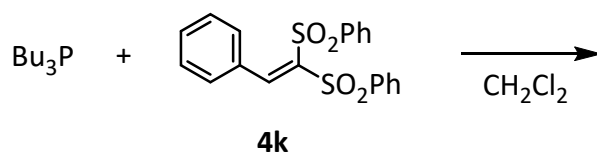
Table S33. Kinetics of the reactions of Bu₃P and **4k** (without added proton source, stopped-flow method, detection at 294 nm, in CH₂Cl₂)

[Bu₃P] (M)	[4k] (M)	k_{obs} (s⁻¹)
3.13×10^{-4}		8.88×10^{-1}
4.92×10^{-4}		1.44
6.71×10^{-4}	3.12×10^{-5}	1.99
8.50×10^{-4}		2.47
1.03×10^{-3}		3.14
$k_2 = 3.09 \times 10^3 \text{ M}^{-1}\text{ s}^{-1}$		

y = 3088.3x - 0.0873
R² = 0.9978
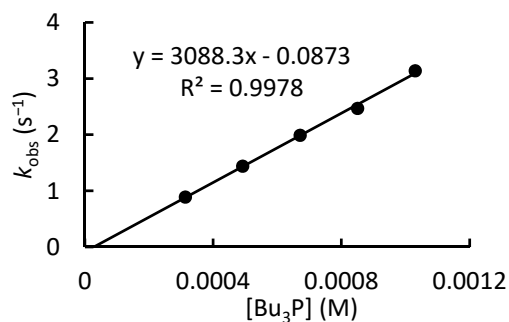
5.3.12 Kinetics of the reaction of Bu₃P with 4l

4l

$k_{obs} = 3.30\ s^{-1}$
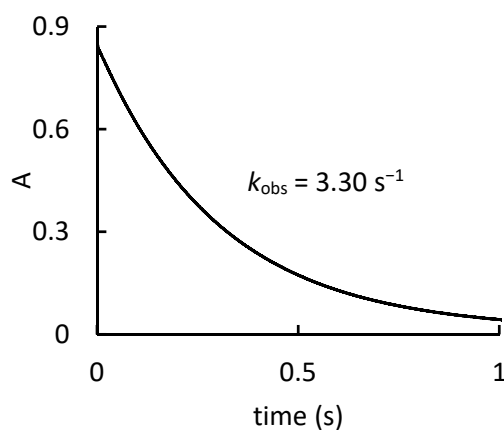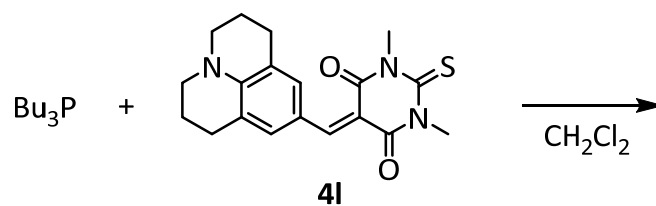
Table S34. Kinetics of the reactions of Bu_3P and **4l** (without added proton source, stopped-flow method, detection at 522 nm, in CH_2Cl_2)

[Bu₃P] (M)	[4l] (M)	k_{obs} (s^{-1})
1.34×10^{-4}		8.08×10^{-1}
2.24×10^{-4}		1.42
3.13×10^{-4}	6.19×10^{-6}	2.08
4.03×10^{-4}		2.68
4.92×10^{-4}		3.30
$k_2 = 6.98 \times 10^3\ M^{-1}\ s^{-1}$		

y = 6976.4x - 0.1274
R² = 0.9998

5.3.13   Kinetics of the reaction of Bu_3P with 4m

$$Bu_3P \quad + \quad \text{[structure of 4m]} \quad \xrightarrow{CH_2Cl_2}$$

4m

$k_{obs} = 1.49 \times 10^1 \text{ s}^{-1}$
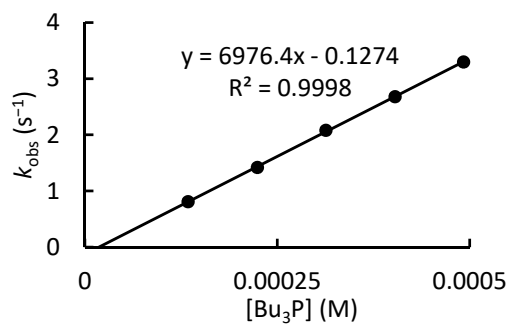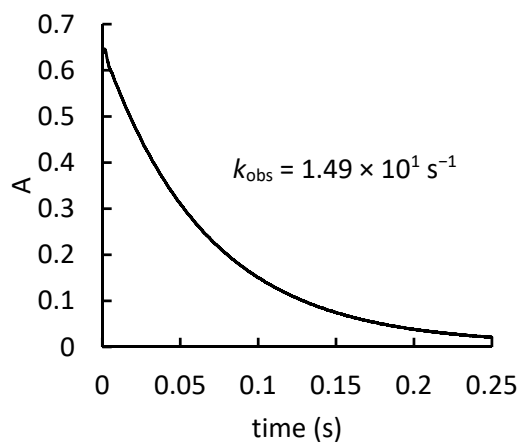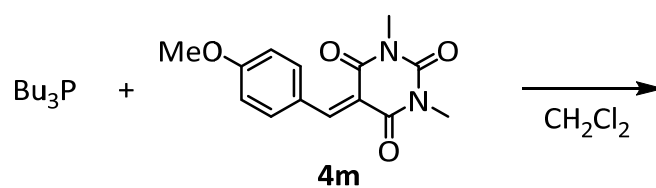
Table S35. Kinetics of the reactions of Bu_3P and **4m** (without added proton source, stopped-flow method, detection at 378 nm, in CH_2Cl_2)

$[Bu_3P]$ (M)	[4m] (M)	k_{obs} (s^{-1})
1.58×10^{-4}		4.33
2.37×10^{-4}		7.10
3.15×10^{-4}	1.64×10^{-5}	9.28
3.94×10^{-4}		1.15×10^1
4.73×10^{-4}		1.49×10^1
$k_2 = 3.25 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$		

y = 32456x - 0.8147
R^2 = 0.9936

5.3.14 Kinetics of the reaction of Bu₃P with 4n

$$Bu_3P \quad + \quad \text{[structure of 4n]} \quad \xrightarrow{CH_2Cl_2}$$

4n

$k_{obs} = 7.86 \text{ s}^{-1}$
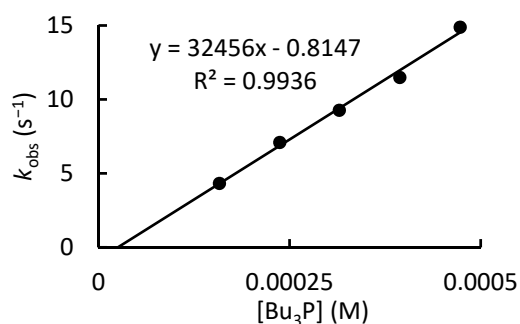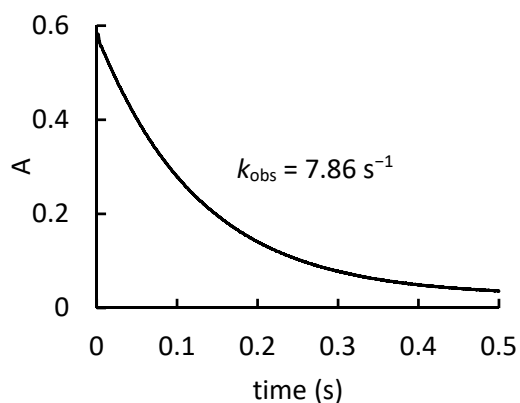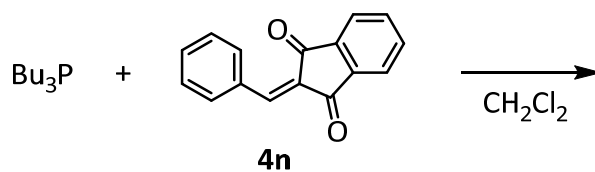
Table S36. Kinetics of the reactions of Bu₃P and **4n** (without added proton source, stopped-flow method, detection at 344 nm, in CH_2Cl_2)

[Bu₃P] (M)	[**4n**] (M)	k_{obs} (s^{-1})
1.34×10^{-4}		1.94
2.24×10^{-4}		3.29
3.13×10^{-4}	1.15×10^{-5}	4.83
4.03×10^{-4}		6.20
4.92×10^{-4}		7.86
	$k_2 = 1.65 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	

y = 16479x - 0.3373
R² = 0.9987

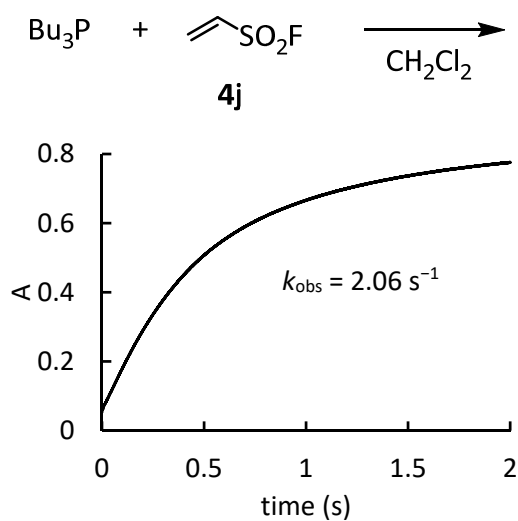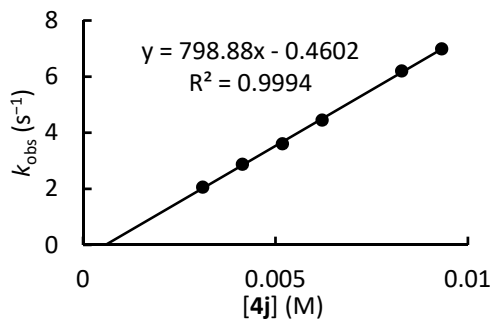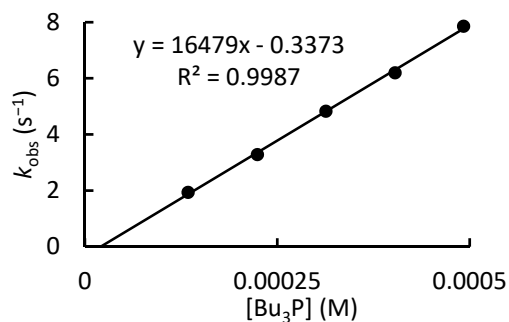### 5.3.15 Kinetics of the reaction of Bu_3P with 4o
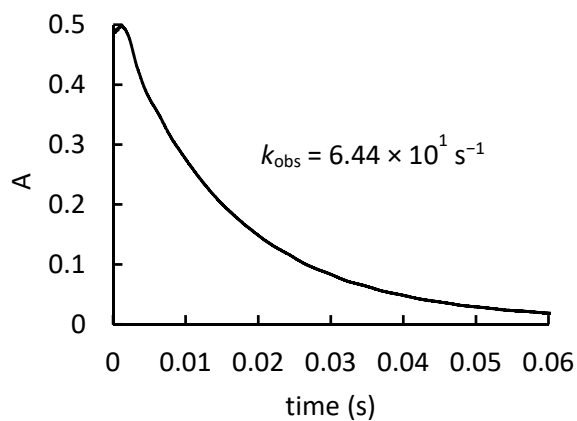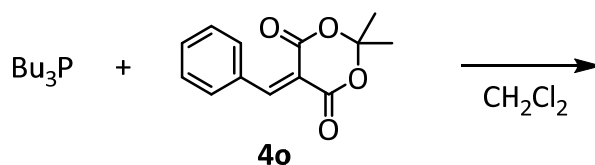
Table S37. Kinetics of the reactions of Bu_3P and **4o** (without added proton source, stopped-flow method, detection at 321 nm, in CH_2Cl_2)

$[Bu_3P]$ (M)	$[4o]$ (M)	k_{obs} (s^{-1})	
2.68×10^{-4}		6.44×10^1	
4.03×10^{-4}		9.92×10^1	
5.37×10^{-4}	2.71×10^{-5}	1.37×10^2	
6.71×10^{-4}		1.74×10^2	
8.05×10^{-4}		2.09×10^2	
	$k_2 = 2.71 \times 10^5$ M^{-1} s^{-1}		
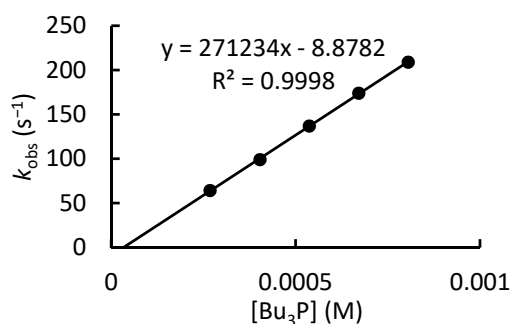
5.3.16 Kinetics of the reaction of Bu$_3$P with 4p

first mixer: generation of a known concentration of Bu$_3$P

$$\text{TBPT (excess)} + \text{Et}_3\text{N} \xrightarrow{\text{CH}_2\text{Cl}_2} \text{Bu}_3\text{P} + \text{TBPT} + \text{Et}_3\text{NH}^+ \text{TfO}^-$$

second mixer: reaction of Bu$_3$P with **4p**

$k_{obs} = 8.40 \times 10^{-1}$ s^{-1}
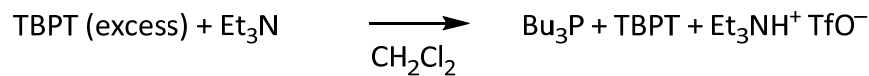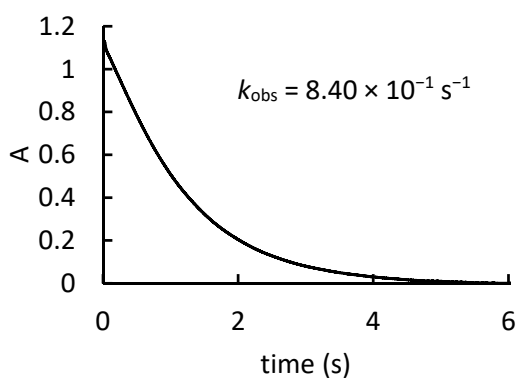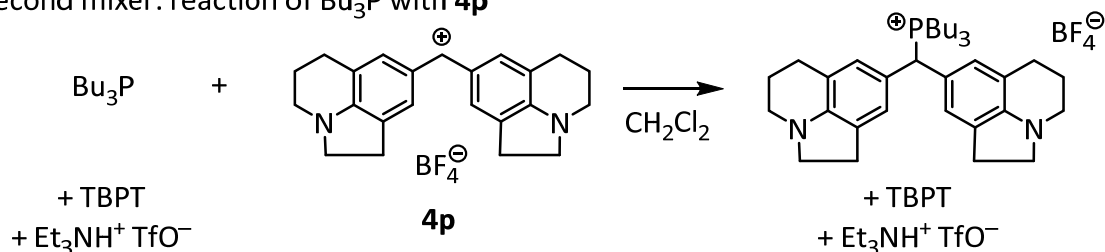
Table S38. Kinetics of the reactions of Bu$_3$P and **4p** (Bu$_3$P was generated by the deprotonation of TBPT with NEt$_3$ in the first step of the sequential mixing stopped-flow method, detection at 640 nm, in CH$_2$Cl$_2$)

[Bu$_3$P] (M)	[**4p**] (M)	k_{obs} (s^{-1})
7.51×10^{-5}		8.40×10^{-1}
1.50×10^{-4}		1.74
1.88×10^{-4}	7.19×10^{-6}	2.20
2.25×10^{-4}		2.53
2.63×10^{-4}		2.97
$k_2 = 1.13 \times 10^4$ M$^{-1}\cdot$s^{-1}		

y = 11272x + 0.0245
R^2 = 0.9977
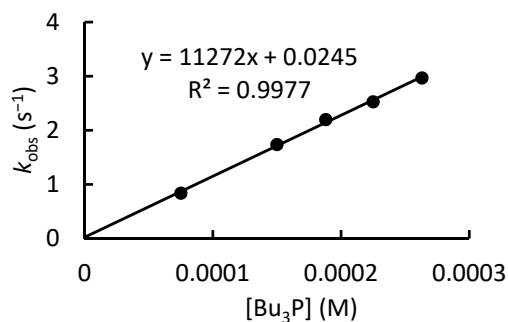
5.3.17 Kinetics of the reaction of Bu_3P with 4q

first mixer: generation of a known concentration of Bu_3P

$$TBPT \text{ (excess) } + Et_3N \xrightarrow{CH_2Cl_2} Bu_3P + TBPT + Et_3NH^+ TfO^-$$

second mixer: reaction of Bu_3P with **4q**

Bu_3P + [**4q** structure with $BF_4^\ominus$] $\xrightarrow{CH_2Cl_2}$ [product with $^\oplus PBu_3$ and $BF_4^\ominus$]

+ TBPT
+ $Et_3NH^+ TfO^-$

4q

+ TBPT
+ $Et_3NH^+ TfO^-$

$k_{obs} = 4.00 \times 10^1 \text{ s}^{-1}$
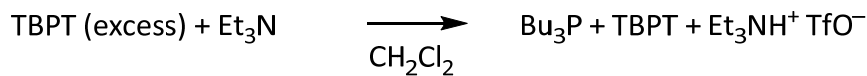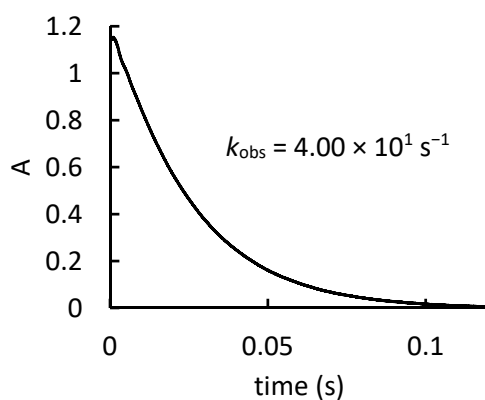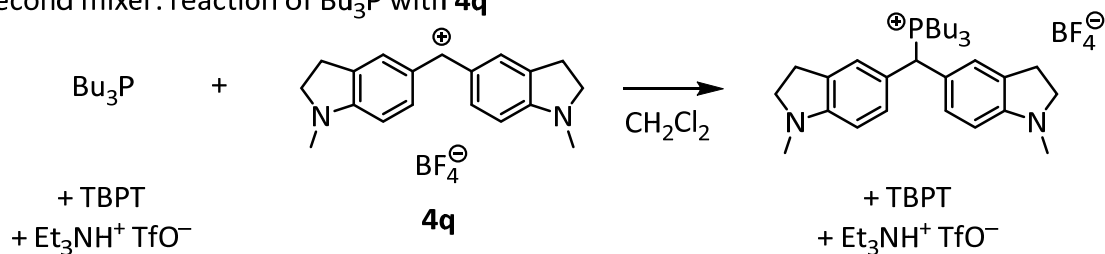
Table S39 Kinetics of the reactions of Bu_3P and **4q** (Bu_3P was generated by the deprotonation of TBPT with NEt_3 in the first step of the sequential mixing stopped-flow method, detection at 626 nm, in CH_2Cl_2)

$[Bu_3P]$ (M)	[**4q**] (M)	k_{obs} (s^{-1})
1.33×10^{-4}		1.01×10^1
2.00×10^{-4}		1.60×10^1
2.67×10^{-4}	7.35×10^{-6}	2.20×10^1
3.34×10^{-4}		2.80×10^1
4.00×10^{-4}		3.36×10^1
4.67×10^{-4}		4.00×10^1
$k_2 = 8.91 \times 10^4 \text{ M}^{-1}\cdot\text{s}^{-1}$		

y = 89132x - 1.8045
R² = 0.9998
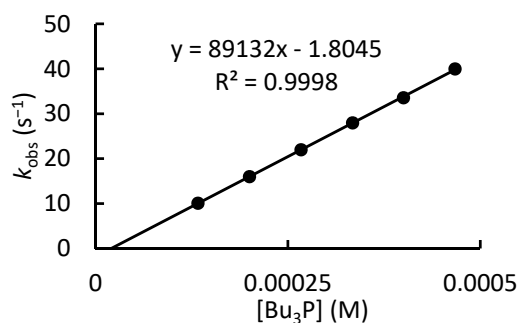
5.3.18 Kinetics of the reaction of Bu_3P with 4r

first mixer: generation of a known concentration of Bu_3P

$$TBPT \text{ (excess)} + Et_3N \xrightarrow{CH_2Cl_2} Bu_3P + TBPT + Et_3NH^+ \ TfO^-$$

second mixer: reaction of Bu_3P with **4r**

Bu_3P +

+ TBPT
+ $Et_3NH^+ \ TfO^-$

4r

$\xrightarrow{CH_2Cl_2}$

+ TBPT
+ $Et_3NH^+ \ TfO^-$

$k_{obs} = 7.53 \times 10^1 \ s^{-1}$
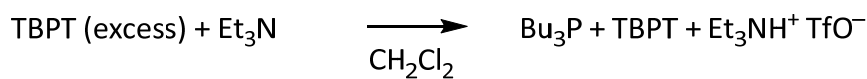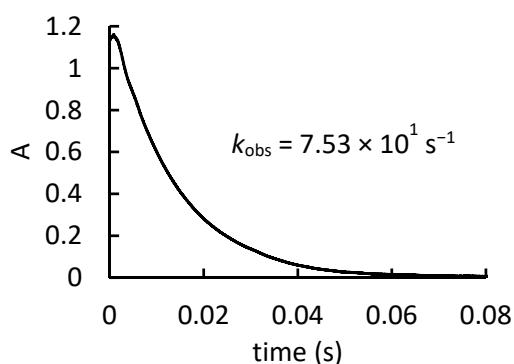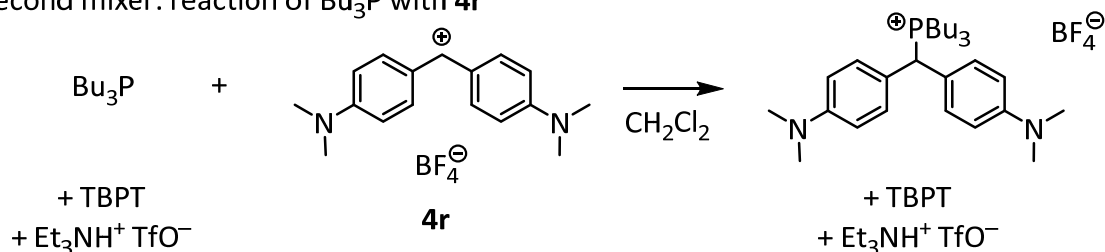
Table S40. Kinetics of the reactions of Bu_3P and **4r** (Bu_3P was generated by the deprotonation of TBPT with NEt_3 in the first step of the sequential mixing stopped-flow method, detection at 613 nm, in CH_2Cl_2)

$[Bu_3P]$ (M)	$[\mathbf{4r}]$ (M)	k_{obs} (s^{-1})
6.42×10^{-5}		7.53×10^1
9.64×10^{-5}		1.20×10^2
1.28×10^{-4}	6.47×10^{-6}	1.56×10^2
1.61×10^{-4}		2.10×10^2
1.93×10^{-4}		2.56×10^2
2.25×10^{-4}		2.96×10^2
$k_2 = 1.39 \times 10^6 \ M^{-1} \cdot s^{-1}$		

y = 1.390E+06x - 1.538E+01
$R^2 = 0.9983$
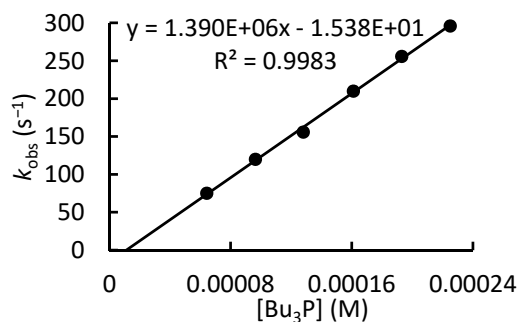
6   Methyl Anion Affinities (MAA) and Phosphine Affinities (PA)

Methyl Anion Affinities (MAA). Using the same methodology employed successfully in earlier studies,[S2] methyl anion affinities (MAAs) were calculated as the free energy at 298.15 K (ΔG_{sol}) for the reaction shown in equation S1. [MAA = (ΔG_{sol} of eqn S1)].
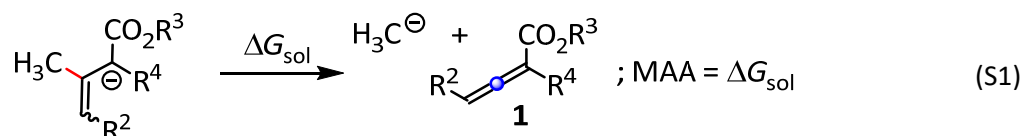
Geometry optimizations were performed at the B3LYP/6-31G(d,p) levels of theory.[S19],[S20] Thermochemical corrections to Gibbs energies (corr. ΔG) and enthalpy (corr. ΔH) at 298.15 K were calculated using the rigid rotor/harmonic oscillator model without any scaling. Thermal corrections to Gibbs energies were alternatively evaluated using the quasi-harmonic approximation with a cutoff value of 100 cm^{-1} (corr. qh-ΔG) using Goodvibes.[S21]

Single point total electronic energies (ΔE_{tot}) were subsequently calculated using a combination of the B3LYP hybrid functional and the larger 6-311++G(3df,2pd) basis set.[S20,S22] Solvent effects on MAA values were estimated by adding single point solvation corrections (ΔG_{Solv}). ΔG_{Solv} was calculated for gas phase optimized geometries using the SMD continuum solvation model.[S23] Thermal corrections to Gibbs energies are identical to those calculated before.[S21] The final free energy in solution (ΔG_{Sol}) is then obtained as:

ΔG_{sol} [B3LYP/6-311++G(3df,2pd)] = ΔE_{tot} [B3LYP/6-311++G(3df,2pd)] + corr. qh-ΔG [B3LYP/6-31G(d,p)] + ΔG_{Solv} [SMD(DMSO)/B3LYP/6-31G(d,p)]

Phosphine Affinities (PA) were calculated as the free energy at 298.15 K (ΔG_{sol}) for reaction shown in equation S2. [PA = (ΔG_{sol} of eqn S2)].
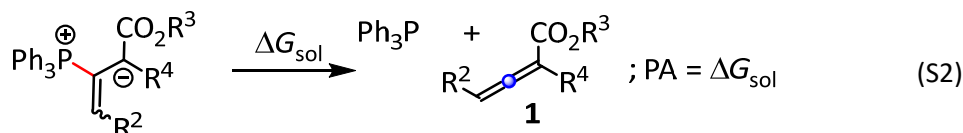
Geometry optimizations were performed with a combination of the B3LYP hybrid functional[S19] complemented by the D3 dispersion correction[S24] and the 6-31+G(d,p)[S20] basis set under implicit solvation that is implemented using polarizable continuum model[S25] (solvent=dichloromethane, radii=ua0). In the text and the tables, we refer to these settings as the PCM(DCM,ua0)/B3LYP-D3/6-31+G(d,p) level of theory. Thermochemical corrections to Gibbs energies (corr. ΔG) and enthalpies (corr. ΔH) at 298.15 K were calculated using the rigid rotor/harmonic oscillator model without any scaling. Thermal correction to Gibbs energies (corr. ΔG) are future treated for quasi-harmonic

approximation with cutoff value of 100 cm^{-1} using Goodvibes (corr. qh-ΔG).[S21] Free energies in solution have been corrected to a reference state of 1 mol/l at 298.15 K through addition of RTln(24.46) = +7.925 kJ mol^{-1} (= 0.0030185 Hartree) to the gas phase (1 atm) free energies. The value for R = 8.31451 J K^{-1} mol^{-1}.

All calculations have been performed with Gaussian 09, Rev. D.[S26]

Table S41. Methyl anion affinities (kJ mol^{-1}, MAA) calculated at the SMD(DMSO)/B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) level of theory for electrophiles **1a**-**1j** and **4t**-**4u**.

Electrophile	Internal Reference	Based on Best Conformer					Based on Boltzmann Avg.			
		ΔE_{tot}	ΔH_{sol}	$\Delta G_{sol}{}^a$	$\Delta G_{sol}{}^b$		ΔE_{tot}	ΔH_{sol}	$\Delta G_{sol}{}^a$	$\Delta G_{sol}{}^b$
1a	b3	254.9	234.6	182.4	183.1		254.7	234.5	**182.5**	183.3
1b	b5	235.1	215.5	162.8	155.9		235.3	215.7	**163.1**	156.2
1c	b14	237.3	217.2	165.6	162.9		237.1	217.0	**165.5**	162.8
1d	d1	241.6	222.2	171.4	171.5		241.4	222.0	**171.2**	171.4
1e	b2	237.9	218.1	168.3	169.2		237.0	217.4	**167.6**	168.7
1f	b9	234.8	215.0	163.9	165.8		233.9	214.2	**163.4**	165.3
1g	b13	220.2	202.0	152.4	152.7		220.4	202.3	**152.7**	153.4
1h	b15	226.1	206.4	153.9	155.1		225.9	206.2	**153.9**	155.1
1i	b16	216.2	196.3	142.9	144.0		215.8	195.9	**142.5**	143.7
1j	b11	207.4	187.6	133.1	133.5		207.9	188.1	**133.6**	134.0
4t	e2	192.1	171.4	119.6	123.1		192.5	171.7	**120.1**	122.9
4u	e5	216.1	194.1	144.4	141.1		215.7	194.4	**144.6**	141.0

^{a} With Truhlar's quasi-harmonic approximation based (corr. qh-ΔG) thermal correction. ^{b} With standard (corr. ΔG) thermal correction.

Table S42. Phosphine affinities (kJ mol^{-1}, PA) calculated at the PCM(DCM,ua0)/B3LYP-D3/6-31+G(d,p) level of theory for electrophiles **1a**-**1j**.

Electrophile	Internal Reference	Based on Best Conformer					Based on Boltzmann Avg.			
		ΔE_{tot}	ΔH_{sol}	ΔG_{sol}^{a}	ΔG_{sol}^{b}		ΔE_{tot}	ΔH_{sol}	ΔG_{sol}^{a}	ΔG_{sol}^{b}
1a	b3	65.6	56.1	-13.8	-15.7		64.6	54.9	**-15.0**	-15.9
1b	b5	57.5	48.4	-21.4	-24.4		56.0	47.1	**-22.6**	-24.8
1c	b14	54.7	46.1	-23.7	-23.4		54.1	45.5	**-23.7**	-23.1
1d	d1	55.8	48.0	-15.8	-14.8		55.7	48.0	**-15.9**	-14.8
1e	b2	45.8	37.6	-26.2	-26.7		45.3	37.1	**-26.5**	-27.2
1f	b9	45.4	39.5	-29.4	-27.5		45.0	38.2	**-29.8**	-28.2
1g	b13	45.5	37.9	-29.5	-27.9		45.9	38.1	**-29.5**	-27.7
1h	b15	43.0	35.0	-33.1	-30.9		43.1	34.8	**-33.3**	-31.4
1i	b16	55.6	46.2	-26.1	-25.9		55.1	45.9	**-26.0**	-26.3
1j	b11	38.2	29.9	-38.8	-39.3		38.7	30.4	**-38.3**	-38.4

[a] With Truhlar's quasi-harmonic approximation based (corr. qh-ΔG) thermal correction. [b] With standard (corr. ΔG) thermal correction.
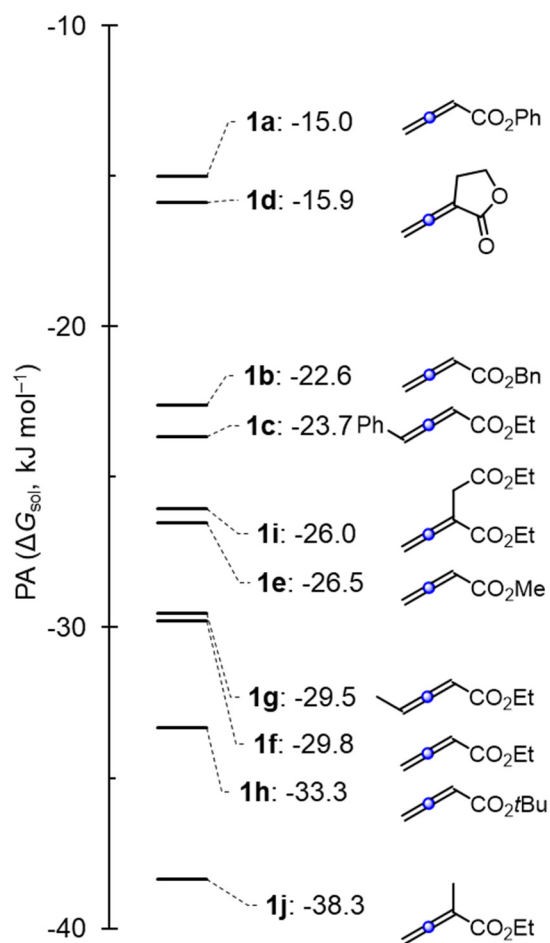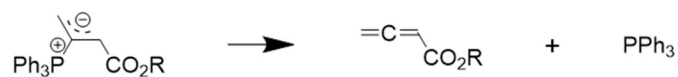
Figure S27. Phosphine affinities PA (= ΔG_{sol}, kJ mol^{-1}) calculated at the PCM(DCM,ua0)/B3LYP-D3/6-31+G(d,p) level of theory. PA values used here are Boltzmann averaged with Truhlar's quasi-harmonic approximation based (corr. qh-ΔG) thermal corrections (from Table S42).

Table S43. QM properties for gas phase optimised conformers of selected allenoates (**1a-j**, a) and their corresponding methyl anion adducts (ma). [a] Methyl anion adducts=ma, Allenoate=a. [b] Truhlar quasi-harmonic treatment was used for thermal corrections. [c] Single point solvation corrections (in kcal mol^{-1}) calculated at SMD(DMSO)/B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory. [d] Single point total electronic energies (ΔE_{tot}) calculated at B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p). [e] Relative Gibbs energies (Rel. ΔG_{sol}) = ΔE_{tot} [B3LYP/6-311++G(3df,2pd)] + corr. qh-ΔG [B3LYP/6-31G(d,p)] + ΔG_{Solv} [SMD(DCM)/B3LYP/6-31G(d,p)].

| SI	Mol.	Type[a]	File Name Internal Reference	B3LYP\6-31G(d,p) ΔE_{tot} (hartree)	HOMO$_E$ (hartree)	LUMO$_E$ (hartree)	Low Frequency			corr. ZPE (hartree)	corr. ΔH (hartree)	corr. ΔG (hartree)	corr. qh-ΔG[b] (hartree)	ΔG_{Solv}[c]	ΔE_{tot}[d] (hartree)	Rel. ΔG_{sol}[e]
1	CH$_3^-$	Ref.	ch3anion	-39.7960280	0.13514	0.37353	-29	0	0	0.027840	0.031650	0.008651	0.008651	-78.86	-39.8566373	0.0
2	**1a**	a	b3_2	-536.2852306	-0.23821	-0.04796	-7	-5	-3	0.151706	0.163245	0.113531	0.115692	-6.51	-536.4625979	0.0
3		a	b3_1	-536.2850363	-0.23821	-0.04769	-4	0	0	0.151697	0.163246	0.113691	0.115854	-6.60	-536.4623199	0.8
4		a	b3_3	-536.2774258	-0.24699	-0.04823	-4	0	0	0.151426	0.163026	0.112892	0.115429	-8.43	-536.4553970	10.2
5		a	b3_4	-536.2746318	-0.23990	-0.04880	-5	0	0	0.151322	0.162888	0.113686	0.115376	-8.29	-536.4527299	17.6
6		ma	ma_b3_3	-576.2722893	0.00062	0.12682	-10	-2	0	0.189411	0.202626	0.149500	0.151944	-48.10	-576.4757030	0.0
7		ma	ma_b3_6	-576.2653644	0.00453	0.12814	-5	0	0	0.189621	0.202750	0.149888	0.152214	-49.86	-576.4696981	9.1
8		ma	ma_b3_1	-576.2669971	0.00318	0.12594	0	0	0	0.189773	0.202793	0.150231	0.152689	-48.63	-576.4708625	12.4
9	**1b**	a	b5_3	-575.6025457	-0.24944	-0.03704	-9	-6	-2	0.180668	0.193687	0.137059	0.143322	-8.11	-575.7921399	0.0
10		a	b5_2	-575.6025513	-0.24860	-0.03739	-10	-4	0	0.180669	0.193673	0.138840	0.143305	-8.02	-575.7920488	0.6
11		a	b5_5	-575.6028220	-0.24577	-0.04012	-6	0	0	0.180694	0.193671	0.138773	0.143240	-7.62	-575.7918664	2.6
12		a	b5_4	-575.6037632	-0.24727	-0.03919	-5	0	0	0.181227	0.193953	0.141116	0.143884	-7.02	-575.7921996	5.9
13		a	b5_1	-575.6035430	-0.24701	-0.03854	-4	0	0	0.181201	0.193941	0.141147	0.143915	-7.13	-575.7919823	6.1
14		a	b5_7	-575.5886826	-0.24709	-0.04689	-5	-4	0	0.180359	0.193420	0.138954	0.142766	-10.42	-575.7783665	25.0
15		a	b5_6	-575.5899441	-0.25240	-0.04233	-7	0	0	0.180759	0.193545	0.140618	0.143570	-9.68	-575.7788268	29.0
16		ma	ma_b5_10	-615.5820501	0.01134	0.10428	-4	0	0	0.218343	0.232780	0.175863	0.179478	-50.12	-615.7970296	0.0
17		ma	ma_b5_8	-615.5820983	0.01177	0.10767	-4	-2	0	0.218810	0.233115	0.177360	0.179907	-50.02	-615.7962934	3.5
18		ma	ma_b5_1	-615.5771846	0.01349	0.10423	-4	0	0	0.218647	0.232947	0.176380	0.180226	-50.69	-615.7925760	11.3
19		ma	ma_b5_5	-615.5780057	0.01334	0.10755	-12	-4	0	0.219050	0.233230	0.177707	0.180487	-50.42	-615.7924501	13.4
20	**1c**	a	b14_5	-614.9321547	-0.22790	-0.03889	-6	-2	0	0.209769	0.224125	0.166913	0.170541	-8.25	-615.1308316	0.0
21		a	b14_1	-614.9316059	-0.22776	-0.03775	-3	-3	0	0.209719	0.224084	0.167029	0.170519	-8.51	-615.1303272	0.2
22		a	b14_7	-614.9319277	-0.22791	-0.03946	-6	-1	0	0.210034	0.224252	0.167689	0.170962	-7.95	-615.1301857	4.1
23		a	b14_6	-614.9319120	-0.22804	-0.03947	-9	-4	0	0.210024	0.224248	0.167531	0.170955	-7.95	-615.1301572	4.1
24		a	b14_3	-614.9314564	-0.22803	-0.03840	0	0	0	0.210030	0.224246	0.167794	0.171011	-8.18	-615.1297173	4.5
25		ma	ma_b14_7	-654.9174389	-0.00138	0.12458	-2	0	0	0.247510	0.263444	0.203919	0.206500	-47.78	-655.1405304	0.0
26		ma	ma_b14_10	-654.9180858	-0.00262	0.12351	-8	0	0	0.247757	0.263551	0.204461	0.206998	-47.12	-655.1402590	4.8
27		ma	ma_b14_9	-654.9180551	-0.00263	0.12351	-11	-7	0	0.247713	0.263519	0.204261	0.206923	-47.12	-655.1401746	4.8

28		ma	ma_b14_1	-654.9093864	-0.00566	0.12082	-9	-5	-5	0.247561	0.263428	0.203914	0.206769	-48.59	-655.1337883	15.0
29		ma	ma_b14_8	-654.9055867	0.00004	0.13255	-5	0	0	0.246841	0.262852	0.203089	0.205853	-50.58	-655.1296561	15.1
30		ma	ma_b14_11	-654.9063862	-0.00117	0.13158	-6	-2	0	0.247172	0.262972	0.204258	0.206445	-49.90	-655.1294304	20.1
31		ma	ma_b14_3	-654.9076026	-0.00617	0.12088	-7	-3	0	0.247724	0.263436	0.204597	0.207253	-48.33	-655.1312501	24.0
32		ma	ma_b14_4	-654.9077258	-0.00581	0.12058	0	0	0	0.247859	0.263523	0.204819	0.207366	-48.36	-655.1313123	24.0
33		ma	ma_b14_2	-654.8970912	-0.00430	0.13026	-6	-4	0	0.246868	0.262776	0.203722	0.205922	-51.97	-655.1226048	28.0
34		ma	ma_b14_6	-654.8955455	-0.00445	0.12991	-6	-2	0	0.246967	0.262796	0.203792	0.206278	-51.75	-655.1204626	35.5
35		ma	ma_b14_5	-654.8953944	-0.00483	0.13016	-6	0	0	0.246988	0.262758	0.204109	0.206433	-51.69	-655.1198853	37.7
36	**1d**	a	d1_1	-382.6511448	-0.26101	-0.04077	-7	0	0	0.107421	0.115538	0.075548	0.075767	-8.08	-382.7831211	0.0
37		ma	ma_d1_2	-422.6292500	0.02045	0.20083	-7	0	0	0.144768	0.154586	0.110891	0.111172	-50.78	-422.7894073	0.0
38		ma	ma_d1_1	-422.6229489	0.02595	0.20202	-13	-8	0	0.144846	0.154486	0.111420	0.111541	-52.83	-422.7826006	10.3
39	**1e**	a	b2_1	-344.5438333	-0.26749	-0.03802	-10	-4	-3	0.099406	0.108053	0.067112	0.067542	-4.50	-344.6669600	0.0
40		a	b2_2	-344.5441270	-0.26480	-0.03898	-7	-6	0	0.099484	0.108095	0.067212	0.067493	-4.29	-344.6671856	0.2
41		a	b2_3	-344.5299781	-0.26444	-0.04472	-9	0	0	0.099201	0.107814	0.066623	0.067471	-7.45	-344.6537030	22.3
42		ma	ma_b2_2	-384.5146697	0.02715	0.20713	-4	-3	0	0.136814	0.147217	0.101911	0.102692	-50.82	-384.6660460	0.0
43		ma	ma_b2_5	-384.5094172	0.02934	0.20724	-9	0	0	0.137115	0.147391	0.102557	0.103152	-52.47	-384.6620716	4.7
44		ma	ma_b2_1	-384.5107363	0.02849	0.20501	-9	0	0	0.137156	0.147382	0.102660	0.103448	-51.18	-384.6624460	9.9
45		ma	ma_b2_4	-384.5073991	0.02222	0.20420	-15	-4	0	0.137117	0.147217	0.102685	0.103663	-51.66	-384.6600719	14.7
46	**1f**	a	b9_3	-383.8659710	-0.26273	-0.03757	-11	-8	0	0.127844	0.137752	0.093202	0.094110	-4.78	-383.9992046	0.0
47		a	b9_1	-383.8656605	-0.26502	-0.03649	-6	0	0	0.127816	0.137737	0.093307	0.094346	-4.95	-383.9989643	0.5
48		a	b9_4	-383.8657690	-0.26358	-0.03816	-9	0	0	0.128117	0.137886	0.093854	0.094594	-4.51	-383.9985832	4.0
49		a	b9_2	-383.8655085	-0.26617	-0.03722	0	0	0	0.128127	0.137895	0.093993	0.094797	-4.66	-383.9983477	4.6
50		a	b9_5	-383.8522707	-0.26221	-0.04301	-7	-6	0	0.127553	0.137534	0.092545	0.093872	-7.69	-383.9861814	21.4
51		a	b9_6	-383.8509049	-0.26215	-0.04213	0	0	0	0.127832	0.137635	0.093328	0.094436	-7.81	-383.9845082	26.8
52		a	b9_7	-383.8508840	-0.26186	-0.03990	-9	-3	0	0.127589	0.137538	0.093060	0.093823	-6.71	-383.9844083	30.0
53		ma	ma_b9_4	-423.8366995	0.02535	0.20546	-9	-7	0	0.165292	0.176929	0.128194	0.129827	-50.78	-423.9976867	0.0
54		ma	ma_b9_10	-423.8314089	0.02758	0.20556	-10	-4	-1	0.165503	0.177047	0.128606	0.130016	-52.47	-423.9935981	4.2
55		ma	ma_b9_5	-423.8378318	0.02324	0.20347	0	0	0	0.165761	0.177116	0.129617	0.130641	-49.99	-423.9976439	5.6
56		ma	ma_b9_1	-423.8326363	0.02685	0.20334	-9	-3	0	0.165542	0.177043	0.128507	0.130322	-51.18	-423.9938176	9.8
57		ma	ma_b9_12	-423.8324293	0.02570	0.20378	-1	0	0	0.165970	0.177255	0.129970	0.130907	-51.71	-423.9935107	9.9
58		ma	ma_b9_7	-423.8295742	0.02079	0.20281	-9	-3	0	0.165466	0.176945	0.128864	0.130143	-51.66	-423.9919704	12.2
59		ma	ma_b9_2	-423.8338096	0.02475	0.20153	-11	-2	0	0.165979	0.177211	0.130106	0.131136	-50.33	-423.9938747	15.3
60		ma	ma_b9_9	-423.8281844	0.01990	0.20267	0	0	0	0.165738	0.177011	0.129754	0.130660	-51.24	-423.9895380	21.7

61	1g	a	b13_4	-423.1873427	-0.25287	-0.03345	-4	-3	0	0.156478	0.167929	0.119438	0.120828	-5.67	-423.3308445	0.0
62		a	b13_1	-423.1871602	-0.25640	-0.03219	-17	-5	-3	0.156363	0.167878	0.119086	0.120926	-5.79	-423.3307496	0.0
63		a	b13_3	-423.1870134	-0.25725	-0.03291	-12	-5	0	0.156660	0.168020	0.119874	0.121237	-5.48	-423.3301464	3.7
64		a	b13_6	-423.1871496	-0.25341	-0.03402	-6	0	0	0.156730	0.168062	0.119961	0.121159	-5.38	-423.3302159	3.7
65		a	b13_5	-423.1871460	-0.25343	-0.03405	-4	-1	0	0.156732	0.168055	0.120109	0.121111	-5.35	-423.3302040	3.8
66		ma	ma_b13_7	-463.1553748	0.02449	0.19933	-5	0	0	0.193108	0.206447	0.153452	0.155396	-50.43	-463.3257890	0.0
67		ma	ma_b13_10	-463.1564463	0.02263	0.19758	-12	-5	0	0.193429	0.206573	0.154283	0.156093	-49.63	-463.3257528	5.3
68		ma	ma_b13_1	-463.1483542	0.01973	0.19734	-8	-7	0	0.193296	0.206479	0.154059	0.155919	-51.30	-463.3202681	12.2
69		ma	ma_b13_12	-463.1493140	0.02096	0.20103	-3	0	0	0.193545	0.206481	0.155285	0.156487	-50.58	-463.3187082	20.8
70		ma	ma_b13_11	-463.1493565	0.02086	0.20076	-3	0	0	0.193500	0.206456	0.155140	0.156480	-50.45	-463.3186099	21.6
71		ma	ma_b13_3	-463.1469913	0.01882	0.19692	-12	-6	0	0.193496	0.206486	0.154867	0.156434	-50.81	-463.3175915	22.7
72		ma	ma_b13_2	-463.1413587	0.01784	0.20123	-6	0	0	0.193266	0.206257	0.154992	0.156069	-52.30	-463.3131548	27.1
73		ma	ma_b13_6	-463.1398811	0.01748	0.19978	-12	-10	-5	0.193308	0.206235	0.154975	0.156294	-51.96	-463.3109995	34.8
74		ma	ma_b13_5	-463.1397914	0.01667	0.20089	-10	-9	0	0.193380	0.206235	0.155334	0.156578	-51.87	-463.3103814	37.5
75	1h	a	b15_2	-462.5035176	-0.25679	-0.03576	-11	-7	0	0.183449	0.195942	0.146320	0.147271	-4.35	-462.6559840	0.0
76		a	b15_1	-462.5032082	-0.25877	-0.03459	-5	0	0	0.183440	0.195930	0.146414	0.147320	-4.51	-462.6556887	0.2
77		ma	ma_b15_2	-502.4757427	0.01959	0.19900	-4	0	0	0.221053	0.235116	0.182030	0.183413	-48.58	-502.6539346	0.0
78		ma	ma_b15_1	-502.4715450	0.02118	0.19670	-16	-11	-7	0.221248	0.235186	0.182429	0.183988	-48.99	-502.6499318	10.3
79	1i	a	b16_7	-690.3824887	-0.26006	-0.03324	-5	-2	0	0.227746	0.244796	0.181394	0.185690	-9.02	-690.6189587	0.0
80		a	b16_8	-690.3815225	-0.25338	-0.03690	-3	0	0	0.227709	0.244789	0.181050	0.185853	-9.24	-690.6176437	3.0
81		a	b16_1	-690.3797924	-0.25602	-0.03523	-4	0	0	0.227742	0.244775	0.181516	0.186026	-9.44	-690.6157071	7.7
82		a	b16_6	-690.3799728	-0.26211	-0.03252	-1	0	0	0.228018	0.244898	0.182252	0.186213	-9.21	-690.6157431	9.0
83		a	b16_4	-690.3800104	-0.26240	-0.03213	-5	-2	0	0.227943	0.244846	0.182044	0.186146	-9.14	-690.6155928	9.5
84		a	b16_5	-690.3802253	-0.26199	-0.03195	-7	-5	0	0.227846	0.244811	0.181346	0.186110	-8.99	-690.6157012	9.8
85		a	b16_11	-690.3811994	-0.25466	-0.03777	-7	-2	0	0.228212	0.245023	0.182648	0.186599	-8.59	-690.6161774	11.5
86		a	b16_9	-690.3793030	-0.25668	-0.03622	-6	0	0	0.228164	0.244998	0.182180	0.186629	-8.89	-690.6143398	15.1
87		a	b16_2	-690.3790237	-0.25629	-0.03659	-5	-5	0	0.228317	0.245050	0.183188	0.186741	-8.83	-690.6140158	16.5
88		ma	ma_b16_12	-730.3576450	0.00917	0.15527	-10	-4	0	0.265518	0.284032	0.217542	0.222268	-49.36	-730.6193365	0.0
89		ma	ma_b16_2	-730.3563036	0.00966	0.15889	-12	-1	0	0.265731	0.284115	0.218284	0.222577	-49.45	-730.6180759	3.7
90		ma	ma_b16_8	-730.3546796	0.01030	0.15834	-4	-1	0	0.265706	0.284072	0.218485	0.222514	-50.66	-730.6160808	3.8
91		ma	ma_b16_10	-730.3585729	0.00738	0.15486	-8	-4	0	0.265925	0.284216	0.218627	0.223042	-48.48	-730.6191722	6.1
92		ma	ma_b16_6	-730.3563530	0.00904	0.15758	-8	0	0	0.266085	0.284318	0.219031	0.223089	-49.04	-730.6170496	9.5
93		ma	ma_b16_15	-730.3582709	0.00735	0.15287	-5	0	0	0.266226	0.284363	0.219483	0.223304	-48.39	-730.6182591	9.6

94		ma	ma_b16_11	-730.3586622	0.00677	0.15379	-6	0	0	0.266205	0.284373	0.219179	0.223426	-48.18	-730.6183127	10.7
95		ma	ma_b16_5	-730.3569348	0.00799	0.15615	-10	0	0	0.266462	0.284484	0.219961	0.223736	-48.50	-730.6170611	13.4
96		ma	ma_b16_7	-730.3569361	0.00793	0.15619	-4	0	0	0.266506	0.284485	0.220282	0.223829	-48.50	-730.6170333	13.7
97		ma	ma_b16_1	-730.3540099	0.00601	0.17316	-7	-5	0	0.265602	0.283957	0.218615	0.222618	-48.83	-730.6149116	14.8
98		ma	ma_b16_4	-730.3542372	0.00501	0.16945	0	0	0	0.266279	0.284263	0.220511	0.223685	-48.10	-730.6136965	23.8
99	1j	a	b11_3	-423.1875852	-0.25754	-0.03100	-9	0	0	0.155912	0.167440	0.119000	0.120363	-4.44	-423.3304022	0.0
100		a	b11_4	-423.1873664	-0.25819	-0.03162	-7	0	0	0.156203	0.167570	0.119892	0.120853	-4.21	-423.3297139	4.1
101		a	b11_1	-423.1856083	-0.25816	-0.02967	-5	0	0	0.155999	0.167442	0.119483	0.120720	-4.93	-423.3281430	4.8
102		a	b11_2	-423.1854317	-0.25856	-0.03039	-10	0	0	0.156242	0.167560	0.119931	0.121129	-4.59	-423.3275275	8.9
103		ma	ma_b11_10	-463.1505478	0.02436	0.20083	-11	-5	0	0.193874	0.206647	0.155819	0.157310	-49.39	-463.3200794	0.0
104		ma	ma_b11_5	-463.1516378	0.02241	0.19912	-17	0	0	0.194261	0.206806	0.156872	0.158107	-48.57	-463.3200936	5.5
105		ma	ma_b11_1	-463.1450568	0.02922	0.20247	0	0	0	0.193714	0.206541	0.155665	0.156862	-50.65	-463.3142054	9.0
106		ma	ma_b11_3	-463.1460068	0.02746	0.20078	-13	0	0	0.194031	0.206670	0.156356	0.157673	-49.84	-463.3140734	14.8
107	4t	a	e2_1	-1144.6604725	-0.25325	-0.07526	-4	-3	0	0.241158	0.258291	0.194102	0.199002	-12.79	-1144.9686985	0.0
108		a	e2_2	-1144.6547663	-0.25776	-0.07343	-31	-11	-5	0.240884	0.257228	0.195835	0.199360	-14.71	-1144.9650800	2.4
109		ma	ma_e2_2	-1184.6230863	-0.05639	0.10814	-7	-4	0	0.278568	0.297370	0.229421	0.235239	-53.72	-1184.9589197	0.0
110		ma	ma_e2_1	-1184.6229082	-0.05364	0.10930	-4	0	0	0.278565	0.297331	0.229693	0.235282	-53.62	-1184.9591214	0.0
111		ma	ma_e2_4	-1184.6223730	-0.05529	0.10927	-12	-4	-1	0.278505	0.297352	0.228913	0.235296	-53.73	-1184.9588237	0.4
112		ma	ma_e2_8	-1184.6163866	-0.05721	0.10918	-5	0	0	0.278739	0.297480	0.230630	0.235526	-54.26	-1184.9513732	18.3
113		ma	ma_e2_10	-1184.6149012	-0.05507	0.11151	-8	0	0	0.278770	0.297557	0.229575	0.235759	-54.63	-1184.9497771	21.6
114		ma	ma_e2_12	-1184.6164873	-0.03978	0.10929	-3	0	0	0.278797	0.297517	0.230615	0.235375	-53.37	-1184.9499128	25.5
115		ma	ma_e2_11	-1184.6159449	-0.03960	0.10976	-7	0	0	0.278693	0.297479	0.229779	0.235273	-53.49	-1184.9495971	25.5
116	4u	a	e5_1	-1387.2683067	-0.23897	-0.08281	-5	-3	0	0.250831	0.270489	0.200762	0.206356	-13.05	-1387.6662036	0.0
117		a	e5_3	-1387.2683063	-0.23897	-0.08282	-9	-5	0	0.250782	0.269546	0.202878	0.207054	-13.05	-1387.6662033	1.8
118		ma	ma_e5_2	-1427.2481016	-0.02865	0.06069	-9	0	0	0.288280	0.309565	0.237986	0.242296	-49.76	-1427.6723115	0.0
119		ma	ma_e5_1	-1427.2458821	-0.03243	0.06313	-4	0	0	0.288307	0.309691	0.237576	0.242198	-49.17	-1427.6698618	8.6
120		ma	ma_e5_3	-1427.2410800	-0.02518	0.05234	0	0	0	0.288067	0.309486	0.236984	0.241913	-51.61	-1427.6648273	10.9
121		ma	ma_e5_4	-1427.2418801	-0.02634	0.05595	-11	-4	-1	0.288287	0.309685	0.237139	0.242283	-50.34	-1427.6658762	14.4

Table S44. QM properties for gas phase optimized conformers of selected allenoates (**1a-j**, a) and their corresponding PPh$_3$ adducts (pa). [a] PPh$_3$ adducts=pa, Allenoate=a. [b] Truhlar quasi-harmonic treatment was used for thermal corrections. [c] Relative Gibbs energies (Rel. ΔG_{sol}) = ΔE_{tot} + corr. qh-ΔG calculated at PCM(DCM,ua0)/B3LYP-D3/6-31+G(d,p) level of theory.

SI	Mol.	Type[a]	File Name Internal Reference	ΔE_{tot} (hartree)	HOMO$_E$ (hartree)	LUMO$_E$ (hartree)	Low Frequency			corr. ZPE (hartree)	corr. ΔH (hartree)	corr. ΔG (hartree)	corr. qh-ΔG[b] (hartree)	Rel. ΔG_{Sol}[c]
1	PPh3	Ref.	p1_3	-1036.3867840	-0.22445	-0.03450	0	0	0	0.272896	0.289760	0.226637	0.231592	0.0
2	**1a**	a	b3_2	-536.3288171	-0.25968	-0.06174	-16	-6	0	0.150655	0.162288	0.111760	0.114650	0.0
3		a	b3_1	-536.3285250	-0.25914	-0.06290	-16	-5	0	0.150628	0.162259	0.112103	0.114697	0.9
4		a	b3_3	-536.3240374	-0.26048	-0.06779	-13	0	0	0.150539	0.162147	0.111890	0.114551	12.3
5		a	b3_4	-536.3224907	-0.25503	-0.06410	-11	0	0	0.150490	0.162045	0.112790	0.114695	16.7
6		pa	pa_b3_200	-1572.7375669	-0.17432	-0.05627	-3	0	0	0.428062	0.455675	0.369964	0.376470	0.0
7		pa	pa_b3_8	-1572.7358786	-0.17675	-0.05364	-10	-6	0	0.427586	0.455418	0.367655	0.375833	2.8
8		pa	pa_b3_7	-1572.7349136	-0.17545	-0.05307	-7	-4	0	0.427545	0.455409	0.367212	0.375774	5.1
9		pa	pa_b3_13	-1572.7349749	-0.17681	-0.06118	-12	0	0	0.427655	0.455639	0.366778	0.375988	5.5
10		pa	pa_b3_12	-1572.7336307	-0.17508	-0.06149	-7	0	0	0.427521	0.455531	0.366376	0.375470	7.7
11		pa	pa_b3_4	-1572.7332041	-0.17651	-0.05374	-5	0	0	0.427587	0.455427	0.367411	0.375719	9.5
12		pa	pa_b3_10	-1572.7252180	-0.17813	-0.05821	-12	-11	0	0.427035	0.455034	0.366263	0.375054	28.7
13	**1b**	a	b5_5	-575.6519010	-0.26129	-0.05682	-13	-3	0	0.179916	0.192871	0.138806	0.142401	0.0
14		a	b5_2	-575.6517700	-0.26159	-0.05731	-2	0	0	0.179927	0.192852	0.139278	0.142512	0.6
15		a	b5_4	-575.6518587	-0.26032	-0.05669	-11	0	0	0.180240	0.193029	0.139677	0.142899	1.4
16		a	b5_1	-575.6517246	-0.26033	-0.05705	-8	0	0	0.180196	0.192997	0.139633	0.142926	1.8
17		a	b5_6	-575.6427432	-0.26010	-0.06457	-25	-10	0	0.179808	0.192659	0.139093	0.142646	24.7
18		a	b5_7	-575.6419924	-0.26341	-0.06465	-9	0	0	0.179760	0.192752	0.138870	0.142249	25.6
19		pa	pa_b5_154	-1612.0575812	-0.16728	-0.05621	-8	-4	0	0.457165	0.486125	0.397330	0.404066	0.0
20		pa	pa_b5_111	-1612.0569534	-0.16994	-0.05473	-8	0	0	0.457070	0.485981	0.397164	0.404144	1.9
21		pa	pa_b5_1	-1612.0569154	-0.16686	-0.05776	-1	0	0	0.457239	0.486185	0.397345	0.404146	2.0
22		pa	pa_b5_143	-1612.0568299	-0.16777	-0.05419	-10	-1	0	0.456981	0.485988	0.396192	0.404175	2.3
23		pa	pa_b5_158	-1612.0565335	-0.17006	-0.05107	-12	-4	0	0.457059	0.485922	0.396696	0.404298	3.4
24		pa	pa_b5_151	-1612.0563183	-0.16874	-0.05074	-8	0	0	0.456940	0.485788	0.397188	0.404086	3.4
25		pa	pa_b5_4	-1612.0560393	-0.16833	-0.05416	0	0	0	0.456871	0.485890	0.396201	0.403978	3.8
26		pa	pa_b5_116	-1612.0562405	-0.16959	-0.05120	-9	-4	0	0.457095	0.486088	0.395302	0.404250	4.0

27		pa	pa_b5_115	-1612.0535517	-0.16812	-0.05142	-10	-8	0	0.456517	0.485837	0.393104	0.403109	8.1
28		pa	pa_b5_137	-1612.0522463	-0.17345	-0.05091	-13	-7	0	0.457170	0.486032	0.396413	0.404395	14.9
29		pa	pa_b5_120	-1612.0519109	-0.17256	-0.05072	-14	-7	0	0.457133	0.486094	0.395643	0.404327	15.6
30		pa	pa_b5_110	-1612.0508626	-0.17316	-0.05713	-9	-8	-4	0.456254	0.485411	0.395397	0.403291	15.6
31		pa	pa_b5_123	-1612.0513717	-0.17344	-0.05105	-10	-7	0	0.456919	0.485893	0.395239	0.404181	16.6
32		pa	pa_b5_126	-1612.0496272	-0.17473	-0.05098	-8	-3	0	0.456779	0.485984	0.393971	0.403381	19.1
33		pa	pa_b5_139	-1612.0420121	-0.17689	-0.05687	-5	0	0	0.456165	0.485425	0.393798	0.402946	37.9
34	1c	a	b14_5	-614.9829014	-0.23902	-0.05716	-10	-5	0	0.208749	0.223123	0.165864	0.169482	0.0
35		a	b14_1	-614.9824898	-0.24002	-0.05729	-8	-3	0	0.208724	0.223101	0.165987	0.169493	1.1
36		a	b14_6	-614.9823329	-0.23904	-0.05730	-8	-4	0	0.208958	0.223215	0.166442	0.169872	2.5
37		a	b14_7	-614.9822752	-0.23899	-0.05732	-11	0	0	0.208969	0.223220	0.166592	0.169870	2.7
38		a	b14_2	-614.9820129	-0.24002	-0.05752	0	0	0	0.209016	0.223237	0.166785	0.169927	3.5
39		a	b14_3	-614.9819694	-0.23996	-0.05746	-10	0	0	0.208962	0.223208	0.166709	0.169914	3.6
40		pa	pa_b14_18	-1651.3874877	-0.16535	-0.05439	-4	-2	0	0.485521	0.516139	0.422650	0.430930	0.0
41		pa	pa_b14_9	-1651.3867843	-0.16530	-0.05391	-4	0	0	0.485264	0.516118	0.421514	0.430338	0.3
42		pa	pa_b14_201	-1651.3870125	-0.16549	-0.05750	-7	-6	0	0.485710	0.516244	0.423728	0.430972	1.4
43		pa	pa_b14_19	-1651.3865537	-0.16554	-0.05359	-6	0	0	0.485501	0.516223	0.421521	0.431013	2.7
44		pa	pa_b14_16	-1651.3853467	-0.16588	-0.05321	-10	-5	0	0.485258	0.516187	0.420814	0.430454	4.4
45		pa	pa_b14_200	-1651.3856223	-0.16496	-0.05702	-4	0	0	0.485565	0.516195	0.422846	0.430889	4.8
46		pa	pa_b14_27	-1651.3855217	-0.16627	-0.05291	-7	0	0	0.485487	0.516217	0.421629	0.430955	5.2
47		pa	pa_b14_23	-1651.3854150	-0.16624	-0.05328	-2	0	0	0.485517	0.516207	0.422304	0.430931	5.4
48		pa	pa_b14_1	-1651.3829721	-0.17108	-0.05438	-6	-4	0	0.485572	0.516285	0.422106	0.430753	11.4
49		pa	pa_b14_6	-1651.3820645	-0.17010	-0.05464	-8	-1	0	0.485646	0.516247	0.422601	0.431098	14.7
50		pa	pa_b14_14	-1651.3820110	-0.17045	-0.05422	-7	0	0	0.485639	0.516244	0.422356	0.431127	14.9
51		pa	pa_b14_2	-1651.3817294	-0.17171	-0.05348	-5	0	0	0.485704	0.516436	0.422187	0.430967	15.2
52		pa	pa_b14_12	-1651.3807027	-0.17086	-0.05338	-11	-6	-3	0.485625	0.516305	0.422052	0.431052	18.1
53		pa	pa_b14_11	-1651.3804385	-0.17093	-0.05329	-5	-1	0	0.485717	0.516394	0.422159	0.431079	18.9
54		pa	pa_b14_26	-1651.3745597	-0.17199	-0.05831	-10	-5	0	0.485083	0.515859	0.421060	0.430477	32.8
55	1d	a	d1_1	-382.6858145	-0.28036	-0.05999	-9	0	0	0.106955	0.115068	0.075123	0.075314	0.0
56		pa	pa_d1_2	-1419.0908257	-0.16798	-0.05371	-11	-7	0	0.383226	0.407779	0.328629	0.334185	0.0
57		pa	pa_d1_1	-1419.0862075	-0.16577	-0.06328	0	0	0	0.383937	0.408208	0.330132	0.335220	14.8
58	1e	a	b2_2	-344.5732599	-0.28378	-0.05735	-14	-13	0	0.098890	0.107487	0.066683	0.066966	0.0
59		a	b2_1	-344.5732682	-0.28896	-0.05762	-15	-10	0	0.098854	0.107463	0.066699	0.067114	0.4

60		a	b2_3	-344.5635137	-0.29020	-0.06556	-19	0	0	0.098791	0.107371	0.066234	0.067165	26.1
61		pa	pa_b2_11	-1380.9744888	-0.16735	-0.05123	-12	0	0	0.375521	0.400361	0.320956	0.326005	0.0
62		pa	pa_b2_12	-1380.9744271	-0.16734	-0.05125	-12	0	0	0.375517	0.400360	0.320922	0.326004	0.2
63		pa	pa_b2_1	-1380.9729478	-0.16783	-0.05496	0	0	0	0.375525	0.400352	0.321199	0.326065	4.2
64		pa	pa_b2_14	-1380.9709872	-0.17429	-0.05084	-12	-9	0	0.375809	0.400495	0.321093	0.326696	11.0
65		pa	pa_b2_3	-1380.9661837	-0.17190	-0.05780	-7	0	0	0.375111	0.399872	0.321144	0.325904	21.5
66		pa	pa_b2_110	-1380.9621797	-0.17595	-0.05630	-9	0	0	0.375316	0.400073	0.320616	0.326151	32.7
67		pa	pa_b2_114	-1380.9528496	-0.17734	-0.06030	-14	-7	0	0.374785	0.399705	0.319833	0.325441	55.3
68	1f	a	b9_3	-383.8985206	-0.28214	-0.05598	-27	-12	0	0.127113	0.137031	0.092515	0.093335	0.0
69		a	b9_1	-383.8984764	-0.28720	-0.05639	0	0	0	0.127174	0.137044	0.092935	0.093726	1.1
70		a	b9_4	-383.8979756	-0.28224	-0.05621	-15	0	0	0.127320	0.137118	0.093027	0.093752	2.5
71		a	b9_2	-383.8979223	-0.28719	-0.05650	0	0	0	0.127365	0.137142	0.093265	0.094016	3.4
72		a	b9_5	-383.8891899	-0.28815	-0.06370	-18	-14	-9	0.126983	0.136937	0.092055	0.093394	24.7
73		a	b9_6	-383.8882269	-0.28848	-0.06271	-25	-15	0	0.127139	0.136969	0.092198	0.093817	28.3
74		a	b9_7	-383.8875722	-0.28277	-0.05826	-7	-4	0	0.127035	0.136943	0.092658	0.093319	28.7
75		pa	pa_b9_16	-1420.2992854	-0.16693	-0.05107	-4	0	0	0.403745	0.429947	0.346620	0.353120	0.0
76		pa	pa_b9_111	-1420.2993378	-0.16789	-0.05530	-8	-5	0	0.404159	0.430108	0.348789	0.353662	1.3
77		pa	pa_b9_17	-1420.2992889	-0.16739	-0.05080	-5	0	0	0.404126	0.430060	0.348126	0.353853	1.9
78		a	ts_p1a_9_ircr_o	-1420.2995844	-0.16720	-0.05063	-24	-10	0	0.403906	0.429053	0.349559	0.354261	2.2
79		pa	pa_b9_118	-1420.2985171	-0.16600	-0.05501	-8	0	0	0.404147	0.430094	0.348550	0.353710	3.6
80		pa	pa_b9_121	-1420.2981638	-0.16628	-0.05477	-3	0	0	0.404032	0.430029	0.348103	0.353690	4.4
81		pa	pa_b9_1	-1420.2958438	-0.17354	-0.05062	-5	0	0	0.404021	0.430068	0.347454	0.353414	9.8
82		pa	pa_b9_2	-1420.2946083	-0.17287	-0.05050	0	0	0	0.404174	0.430127	0.347576	0.353841	14.2
83		pa	pa_b9_113	-1420.2922301	-0.17183	-0.05794	-12	-9	0	0.403647	0.429615	0.348162	0.353373	19.2
84		pa	pa_b9_119	-1420.2905995	-0.17101	-0.05741	0	0	0	0.403484	0.429527	0.347666	0.353021	22.5
85		pa	pa_b9_120	-1420.2886045	-0.17031	-0.05833	-13	-8	0	0.403538	0.429574	0.347730	0.353147	28.1
86	1g	a	b13_4	-423.2228539	-0.26924	-0.05380	-14	-8	0	0.155661	0.167111	0.118716	0.119958	0.0
87		a	b13_1	-423.2227431	-0.27355	-0.05407	-20	-9	-5	0.155563	0.167064	0.118472	0.120075	0.6
88		a	b13_5	-423.2222889	-0.26927	-0.05405	-6	0	0	0.155840	0.167194	0.119166	0.120172	2.0
89		a	b13_6	-423.2222677	-0.26926	-0.05401	-13	-1	0	0.155843	0.167201	0.119083	0.120217	2.2
90		a	b13_2	-423.2222370	-0.27360	-0.05432	-8	0	0	0.155801	0.167175	0.119048	0.120326	2.6
91		pa	pa_b13_7	-1459.6237884	-0.16372	-0.05015	-7	-3	0	0.431924	0.459735	0.373004	0.379960	0.0
92		pa	pa_b13_19	-1459.6239639	-0.16391	-0.04975	-11	0	0	0.432143	0.459791	0.373387	0.380440	0.8

93		pa	pa_b13_12	-1459.6236044	-0.16411	-0.04984	-9	0	0	0.432172	0.459782	0.374016	0.380479	1.8
94		pa	pa_b13_200	-1459.6239297	-0.16469	-0.05422	0	0	0	0.432673	0.460033	0.376040	0.381043	2.5
95		pa	pa_b13_1	-1459.6205267	-0.17042	-0.04975	-12	0	0	0.432058	0.459795	0.373248	0.380015	8.7
96		pa	pa_b13_8	-1459.6191079	-0.16959	-0.04962	-4	0	0	0.432421	0.459972	0.374297	0.380620	14.0
97		pa	pa_b13_3	-1459.6191575	-0.16950	-0.04967	0	0	0	0.432415	0.459930	0.374398	0.380706	14.1
98		pa	pa_b13_4	-1459.6190305	-0.16972	-0.04981	-5	0	0	0.432462	0.460011	0.374156	0.380680	14.4
99		pa	pa_b13_17	-1459.6153200	-0.16520	-0.05486	0	0	0	0.431217	0.459151	0.372474	0.378624	18.7
100		pa	pa_b13_11	-1459.6127515	-0.17207	-0.05511	-12	-10	0	0.431263	0.459278	0.371319	0.378806	25.9
101		pa	pa_b13_16	-1459.6112788	-0.17123	-0.05507	-6	0	0	0.431518	0.459353	0.372543	0.379212	30.9
102	1h	a	b15_2	-462.5446932	-0.27554	-0.05305	-15	-8	0	0.182821	0.195267	0.145646	0.146670	0.0
103		a	b15_1	-462.5444808	-0.28005	-0.05339	-7	-6	0	0.182788	0.195241	0.145749	0.146671	0.6
104		pa	pa_b15_3	-1498.9448304	-0.16467	-0.04962	-10	-1	0	0.459444	0.488059	0.401006	0.407223	0.0
105		pa	pa_b15_2	-1498.9447072	-0.16497	-0.04938	-11	-6	0	0.459383	0.488049	0.400294	0.407220	0.3
106		pa	pa_b15_4	-1498.9448089	-0.16368	-0.06036	-19	-5	0	0.460405	0.488689	0.402704	0.408565	3.6
107		pa	pa_b15_5	-1498.9353007	-0.16802	-0.05728	-15	-6	0	0.459343	0.487885	0.401452	0.407152	24.8
108	1i	a	b16_7	-690.4414700	-0.28046	-0.05476	-21	-4	0	0.226676	0.243714	0.180279	0.184563	0.0
109		a	b16_8	-690.4413506	-0.27411	-0.05531	-11	-6	0	0.226694	0.243701	0.180820	0.184769	0.9
110		a	b16_1	-690.4409317	-0.27512	-0.05479	-7	0	0	0.226738	0.243699	0.181232	0.184971	2.5
111		a	b16_4	-690.4409664	-0.28074	-0.05460	-16	-12	0	0.227145	0.243915	0.182206	0.185404	3.5
112		a	b16_11	-690.4407141	-0.27440	-0.05510	-13	-10	0	0.227180	0.243934	0.181965	0.185631	4.8
113		a	b16_5	-690.4401999	-0.28057	-0.05464	-7	0	0	0.226964	0.243825	0.181340	0.185247	5.1
114		a	b16_6	-690.4399280	-0.28085	-0.05480	-3	0	0	0.226883	0.243782	0.180956	0.185076	5.4
115		a	b16_9	-690.4401894	-0.27561	-0.05532	-10	0	0	0.227203	0.243925	0.182280	0.185673	6.3
116		a	b16_2	-690.4400728	-0.27491	-0.05597	-11	0	0	0.227436	0.244060	0.182918	0.185961	7.3
117		pa	pa_b16_4	-1726.8462372	-0.17011	-0.05478	-8	-5	0	0.504159	0.537043	0.438567	0.447113	0.0
118		pa	pa_b16_18	-1726.8464033	-0.17052	-0.05005	-14	-10	-7	0.504131	0.537039	0.438355	0.447399	0.3
119		pa	pa_b16_2	-1726.8459853	-0.17023	-0.04889	-4	0	0	0.504043	0.536944	0.438399	0.447093	0.6
120		pa	pa_b16_21	-1726.8458553	-0.16917	-0.05498	-4	0	0	0.504111	0.536993	0.439144	0.447195	1.2
121		pa	pa_b16_16	-1726.8460370	-0.17043	-0.04940	-9	-4	0	0.504242	0.537077	0.438980	0.447406	1.3
122		pa	pa_b16_8	-1726.8445277	-0.17031	-0.04979	0	0	0	0.503534	0.536779	0.436061	0.446274	2.3
123		pa	pa_b16_3	-1726.8455869	-0.17002	-0.05475	-11	-10	-6	0.504208	0.537014	0.438890	0.447387	2.4
124		pa	pa_b16_12	-1726.8450198	-0.16921	-0.05372	-8	0	0	0.503877	0.536911	0.437576	0.446847	2.5
125		pa	pa_b16_1	-1726.8454387	-0.16999	-0.04885	-7	0	0	0.504186	0.537009	0.438298	0.447415	2.9

126		pa	pa_b16_24	-1726.8451486	-0.17065	-0.04941	-10	0	0	0.504136	0.537058	0.438007	0.447407	3.6
127		pa	pa_b16_26	-1726.8450996	-0.16916	-0.05516	-7	-6	0	0.504281	0.537111	0.439218	0.447487	4.0
128		pa	pa_b16_23	-1726.8446667	-0.17062	-0.04954	-5	0	0	0.504015	0.536974	0.437448	0.447064	4.0
129		pa	pa_b16_22	-1726.8446602	-0.17057	-0.04968	-4	0	0	0.504097	0.537039	0.437376	0.447288	4.6
130		pa	pa_b16_9	-1726.8443666	-0.16927	-0.05379	-11	-7	0	0.503998	0.536970	0.437845	0.447070	4.8
131		pa	pa_b16_29	-1726.8444587	-0.16884	-0.05414	-9	0	0	0.504248	0.537062	0.439189	0.447306	5.2
132		pa	pa_b16_20	-1726.8434891	-0.16878	-0.05400	-9	-1	0	0.504057	0.536920	0.438566	0.447068	7.1
133		pa	pa_b16_17	-1726.8438750	-0.17059	-0.05013	-13	-7	0	0.504398	0.537204	0.438768	0.447752	7.9
134		pa	pa_b16_13	-1726.8414265	-0.16973	-0.05796	-11	-9	-6	0.503889	0.536835	0.439742	0.446858	12.0
135		pa	pa_b16_6	-1726.8404896	-0.16891	-0.05633	-10	0	0	0.504187	0.536914	0.440495	0.447314	15.6
136		pa	pa_b16_19	-1726.8396092	-0.17005	-0.05789	-15	-10	0	0.503824	0.536824	0.438635	0.446867	16.8
137		pa	pa_b16_27	-1726.8370619	-0.16996	-0.05801	-7	-1	0	0.503256	0.536387	0.436611	0.446106	21.4
138		pa	pa_b16_11	-1726.8382404	-0.16808	-0.05614	-10	0	0	0.504251	0.537020	0.440231	0.447516	22.1
139		pa	pa_b16_15	-1726.8378338	-0.16893	-0.05650	-10	0	0	0.504161	0.537087	0.438162	0.447330	22.6
140		pa	pa_b16_14	-1726.8373065	-0.16839	-0.05853	0	0	0	0.503855	0.536779	0.439045	0.446875	22.8
141		pa	pa_b16_28	-1726.8363574	-0.17042	-0.05958	-9	0	0	0.503289	0.536555	0.437189	0.445927	22.8
142		pa	pa_b16_30	-1726.8345277	-0.16989	-0.05928	-11	0	0	0.503245	0.536494	0.437481	0.445834	27.4
143		pa	pa_b16_31	-1726.8268128	-0.16796	-0.06388	-9	0	0	0.503776	0.536738	0.439906	0.446533	49.5
144	1j	a	b11_3	-423.2218997	-0.27338	-0.05034	-16	-7	0	0.155220	0.166692	0.118658	0.119738	0.0
145		a	b11_4	-423.2213195	-0.27351	-0.05061	-7	0	0	0.155369	0.166747	0.119095	0.120026	2.3
146		a	b11_1	-423.2207766	-0.27265	-0.05024	-15	-4	0	0.155258	0.166697	0.118842	0.119935	3.5
147		a	b11_2	-423.2201887	-0.27272	-0.05056	-11	0	0	0.155462	0.166777	0.119224	0.120362	6.1
148		pa	pa_b11_201	-1459.6199522	-0.16288	-0.04800	0	0	0	0.432141	0.459626	0.374543	0.380378	0.0
149		pa	pa_b11_16	-1459.6202236	-0.16312	-0.04763	-2	0	0	0.432278	0.459618	0.375021	0.380863	0.6
150		pa	pa_b11_202	-1459.6202235	-0.16312	-0.04763	-2	0	0	0.432278	0.459618	0.375025	0.380863	0.6
151		pa	pa_b11_200	-1459.6198476	-0.16352	-0.04752	-9	-1	0	0.432236	0.459618	0.374471	0.380858	1.5
152		pa	pa_b11_2	-1459.6189621	-0.16184	-0.05329	-6	0	0	0.432577	0.459789	0.376246	0.381111	4.5
153		pa	pa_b11_6	-1459.6185601	-0.16203	-0.05307	-7	0	0	0.432386	0.459703	0.375436	0.380886	5.0
154		pa	pa_b11_4	-1459.6121839	-0.16255	-0.05693	-4	0	0	0.431934	0.459314	0.375734	0.380233	20.0
155		pa	pa_b11_5	-1459.6103835	-0.16163	-0.05622	-11	-1	0	0.431201	0.458953	0.372987	0.379256	22.2

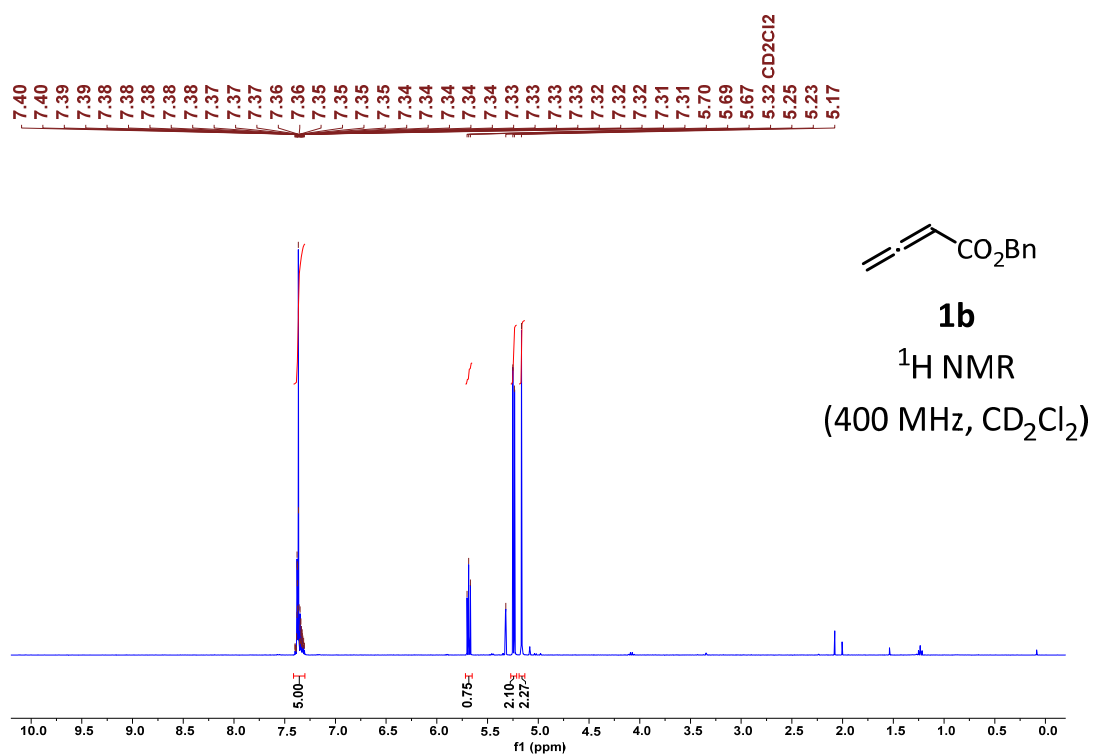# 7   Copies of NMR Spectra

7.1   NMR spectra of alkyl allenoates 1

7.1.1   Phenyl buta-2,3-dienoate (1a)
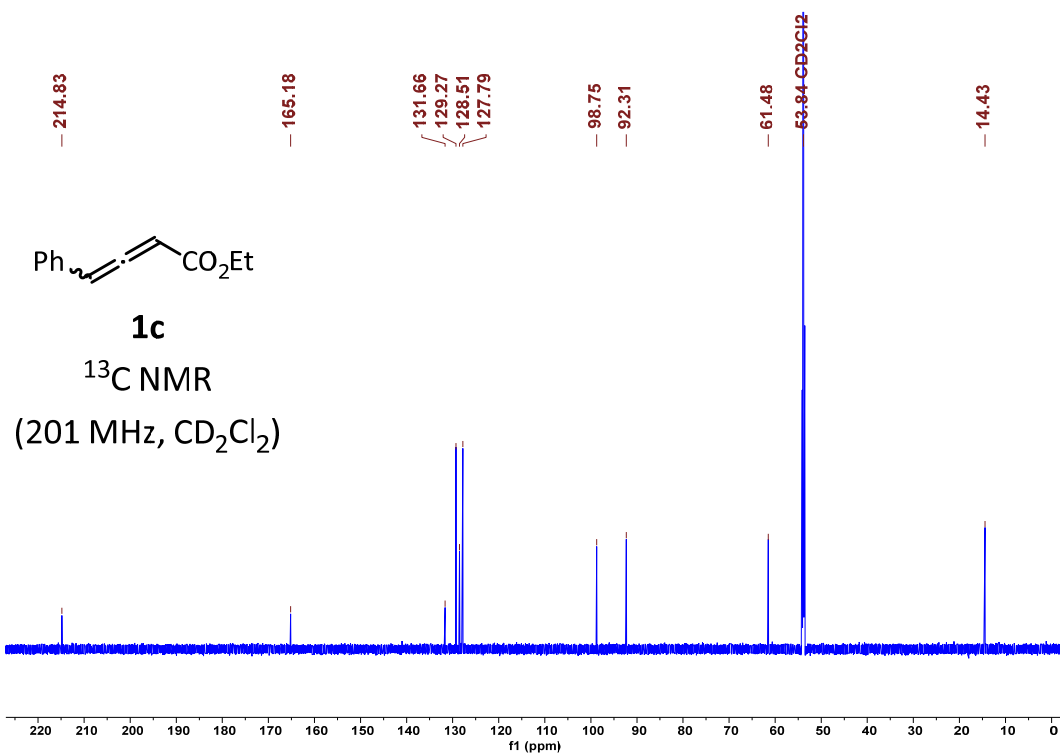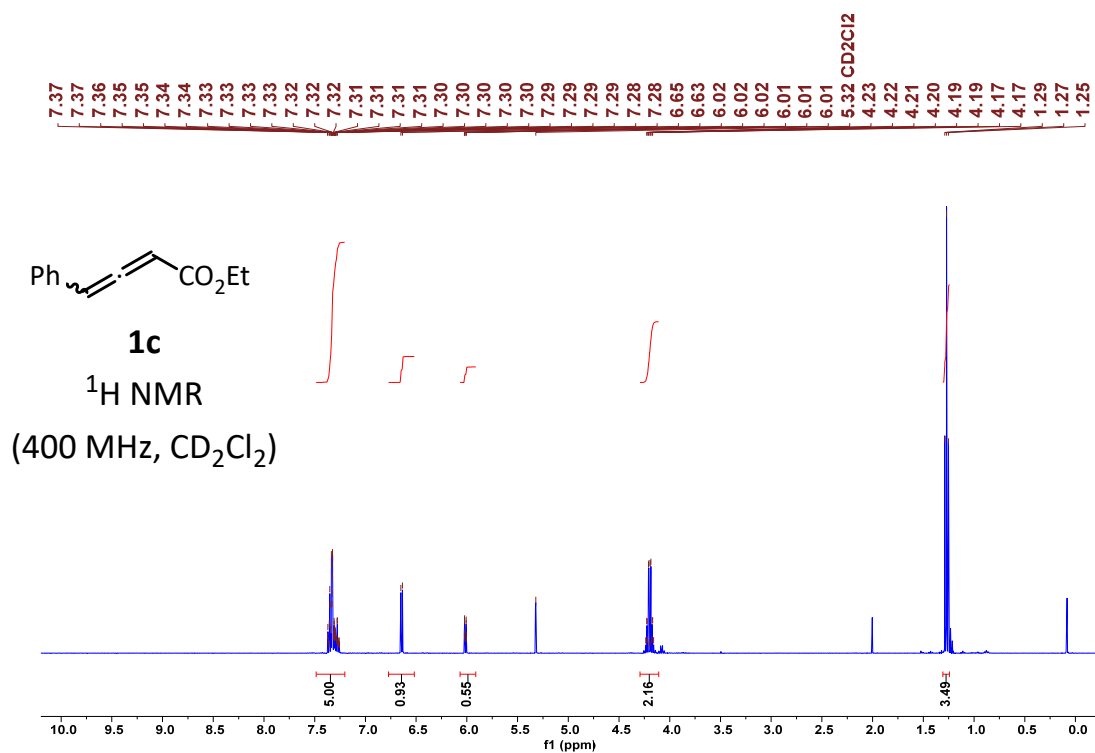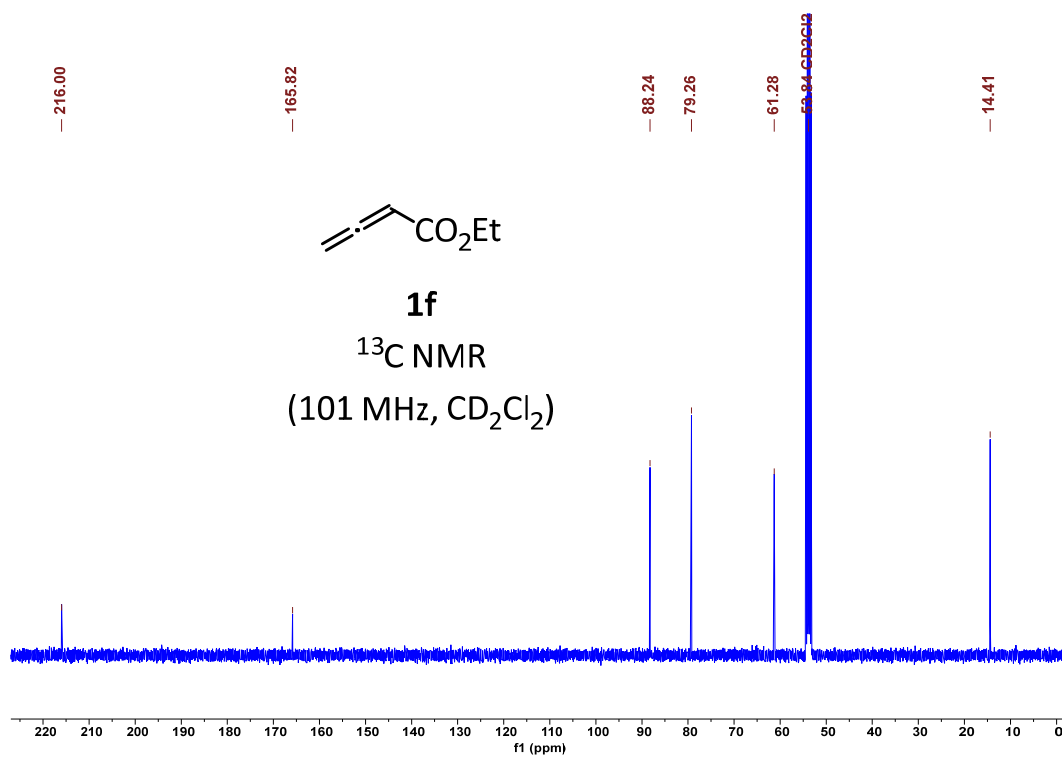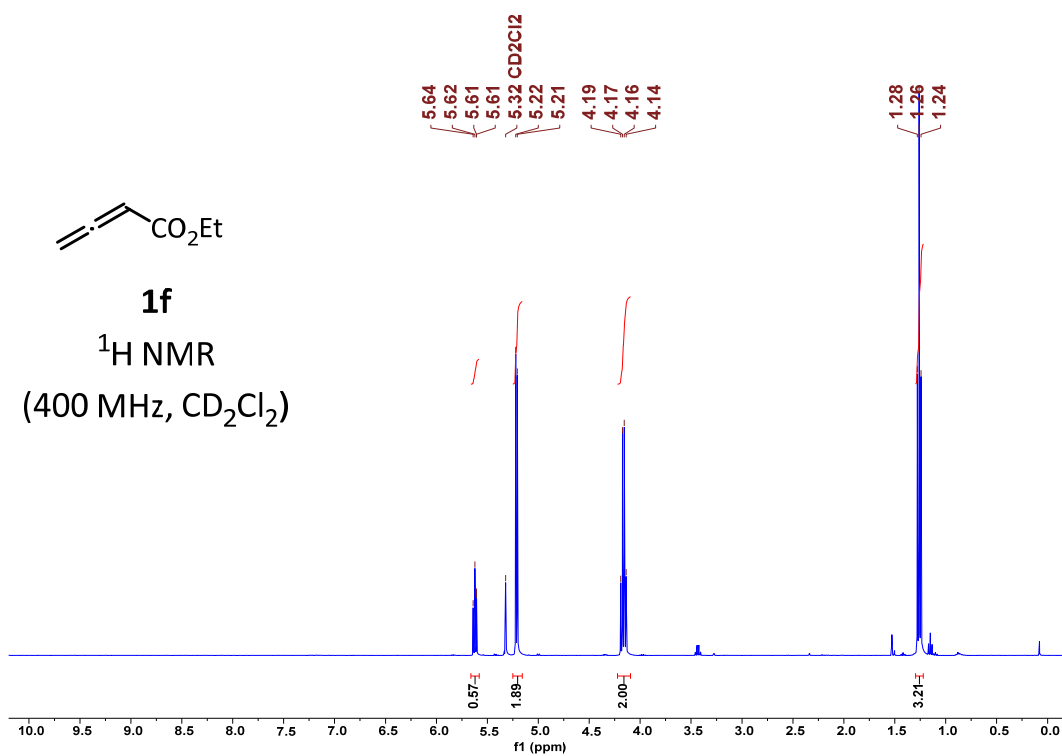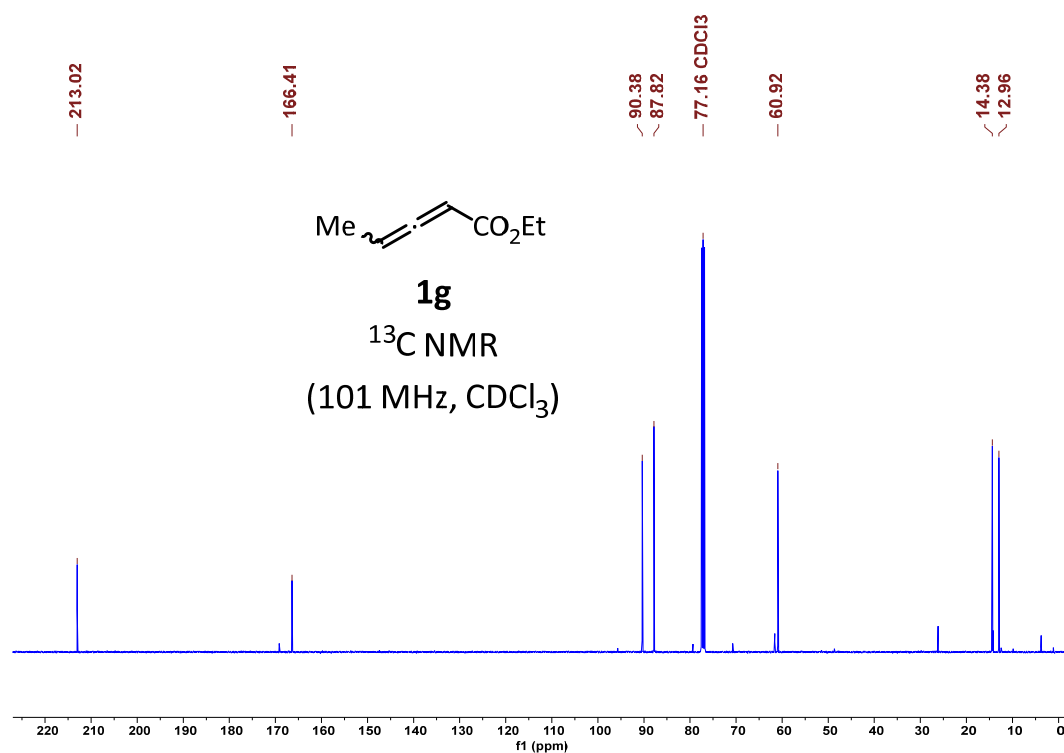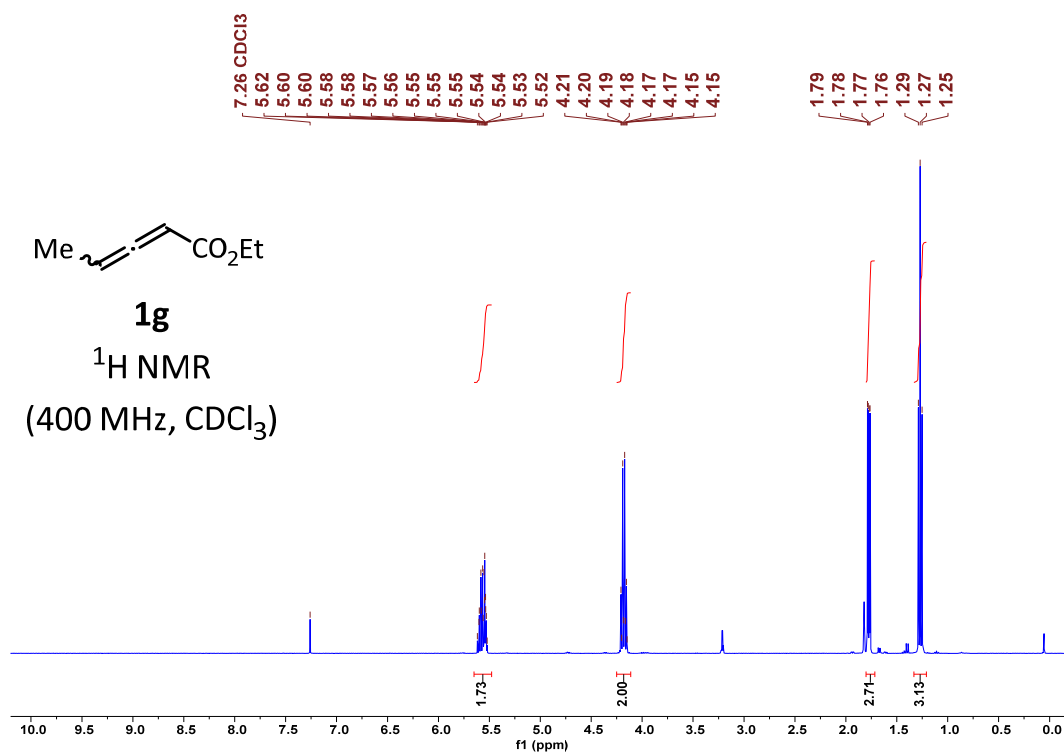
1a
^{1}H NMR
(600 MHz, CDCl$_3$)

1a
^{13}C NMR
(151 MHz, CDCl$_3$)

7.42, 7.42, 7.42, 7.42, 7.41, 7.40, 7.40, 7.40, 7.40, 7.40, 7.39, 7.38, 7.38, 7.38, 7.38, 7.37, 7.27, 7.27, 7.27, 7.26, 7.26, 7.25, 7.25, 7.25, 7.24, 7.23, 7.23, 7.13, 7.13, 7.12, 7.12, 7.11, 7.11, 7.10, 7.10, 7.10, 7.09, 5.85, 5.83, 5.82, 5.37, 5.36, 5.35, 5.32 CD2Cl2

1a

^{1}H NMR

(400 MHz, CD$_2$Cl$_2$)

2.12, 1.00, 2.02, 0.86, 2.12

f1 (ppm): 10.0, 9.5, 9.0, 8.5, 8.0, 7.5, 7.0, 6.5, 6.0, 5.5, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, 0.0

216.95, 164.51, 151.27, 129.80, 126.26, 122.01, 87.82, 79.91, 53.84 CD2Cl2

1a

^{13}C NMR

(101 MHz, CD$_2$Cl$_2$)

f1 (ppm): 220, 210, 200, 190, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0

7.1.2   Benzyl buta-2,3-dienoate (1b)

1b

^{1}H NMR

(600 MHz, CDCl$_3$)

1b

^{13}C NMR

(151 MHz, CDCl$_3$)

7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.34
7.34
7.33
7.33
7.33
7.32
7.32
7.32
7.31
7.31
5.70
5.69
5.67
5.32 CD2Cl2
5.25
5.23
5.17

CO₂Bn

1b

¹H NMR

(400 MHz, CD₂Cl₂)

5.00

0.75

2.10
2.27

f1 (ppm)

216.28
165.67
136.53
128.90
128.57
128.46
88.02
79.46
66.91
53.84 CD2Cl2

CO₂Bn

1b

¹³C NMR

(101 MHz, CD₂Cl₂)

f1 (ppm)

7.1.3 Ethyl 4-phenylbuta-2,3-dienoate (1c)

Ph~=•=^CO₂Et

1c

¹H NMR

(400 MHz, CD₂Cl₂)

Ph~=•=^CO₂Et

1c

¹³C NMR

(201 MHz, CD₂Cl₂)

7.1.4   3-Vinylidenedihydrofuran-2(3H)-one (1d)

1d

^{1}H NMR

(600 MHz, CD$_2$Cl$_2$)

1d

^{13}C NMR

(151 MHz, CD$_2$Cl$_2$)

7.1.5   Methyl buta-2,3-dienoate (1e)

1e
^{1}H NMR
(400 MHz, CD$_2$Cl$_2$)

5.65
5.64
5.62
5.32 CD2Cl2
5.23
5.21
3.71

0.61
2.00
3.27

f1 (ppm)

1e
^{13}C NMR
(101 MHz, CD$_2$Cl$_2$)

216.15
166.26
87.90
79.32
53.84 CD2Cl2
52.31

f1 (ppm)

7.1.6　Ethyl buta-2,3-dienoate (1f)

1f
^{1}H NMR
(600 MHz, CDCl$_3$)

1f
^{13}C NMR
(151 MHz, CDCl$_3$)

1f

^{1}H NMR

(400 MHz, CD$_2$Cl$_2$)

1f

^{13}C NMR

(101 MHz, CD$_2$Cl$_2$)

7.1.7 Ethyl penta-2,3-dienoate (1g)

Me ~=•=CO₂Et

1g
¹H NMR
(400 MHz, CDCl₃)

Me ~=•=CO₂Et

1g
¹³C NMR
(101 MHz, CDCl₃)

Me~CO2Et

1g

^{1}H NMR

(400 MHz, CD$_2$Cl$_2$)

5.63, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.55, 5.54, 5.53, 5.52, 5.51, 5.32 CD2Cl2, 4.18, 4.17, 4.16, 4.16, 4.14, 4.14, 4.12, 4.12, 1.78, 1.77, 1.76, 1.76, 1.27, 1.25, 1.24

1.30 2.00 2.79 3.12

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

Me~CO2Et

1g

^{13}C NMR

(101 MHz, CD$_2$Cl$_2$)

213.14, 166.28, 90.46, 87.93, 61.07, 53.84 CD2Cl2, 14.45, 13.00

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7.1.8 *tert*-Butyl buta-2,3-dienoate (1h)

1h

^{1}H NMR

(600 MHz, CD$_2$Cl$_2$)

1h

^{13}C NMR

(151 MHz, CD$_2$Cl$_2$)

7.1.9 Diethyl 2-vinylidenesuccinate (1i)

1i

^{1}H NMR

(400 MHz, CD$_2$Cl$_2$)

1i

^{13}C NMR

(101 MHz, CD$_2$Cl$_2$)

1j

^{1}H NMR

(800 MHz, CD$_2$Cl$_2$)

1j

^{13}C NMR

(201 MHz, CD$_2$Cl$_2$)

7.2 NMR spectra of phosphines

7.2.1 Tributylphosphine (Bu₃P)

Bu$_3$P
^{1}H NMR
(400 MHz, CD$_2$Cl$_2$)

Bu$_3$P
^{13}C NMR
(101 MHz, CD$_2$Cl$_2$)

Bu₃P
^{31}P NMR
(162 MHz, CD₂Cl₂)

−31.31

7.2.2 Triphenylphosphine (Ph₃P)

7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32

5.32 CD2Cl2

Ph₃P
^{1}H NMR
(400 MHz, CD₂Cl₂)

15.00

Ph$_3$P
^{13}C NMR
(101 MHz, CD$_2$Cl$_2$)

137.85
137.74
134.20
134.00
129.14
128.95
128.88

53.84 CD2Cl2

Ph$_3$P
^{31}P NMR
(162 MHz, CD$_2$Cl$_2$)

-5.54
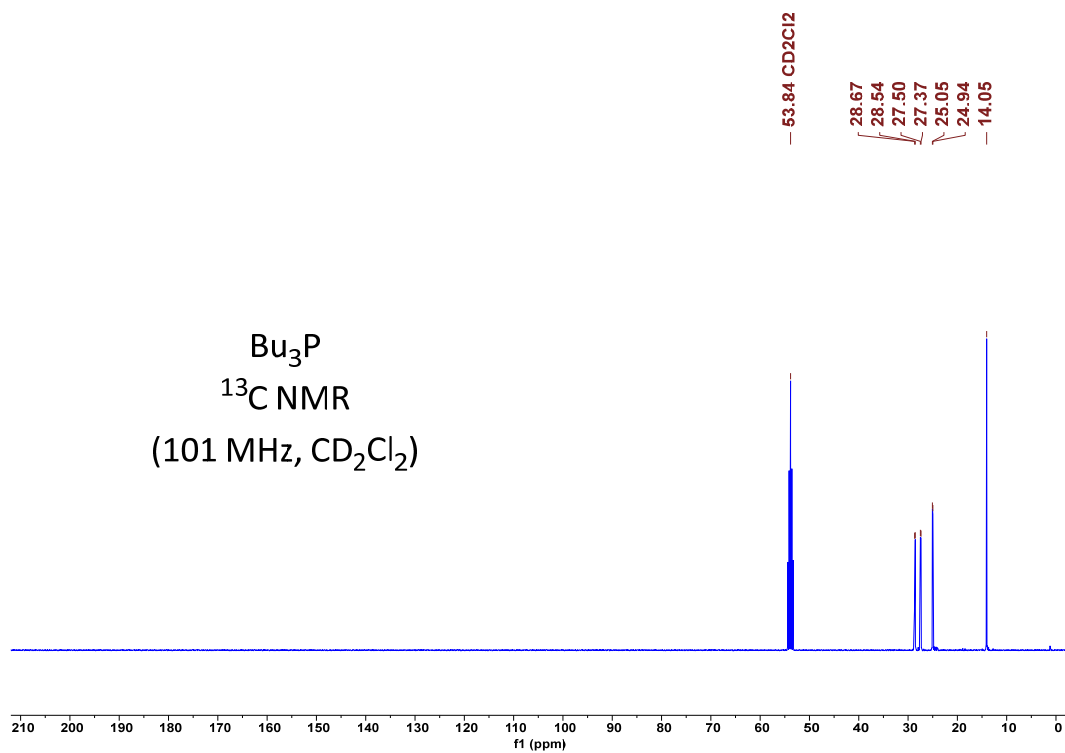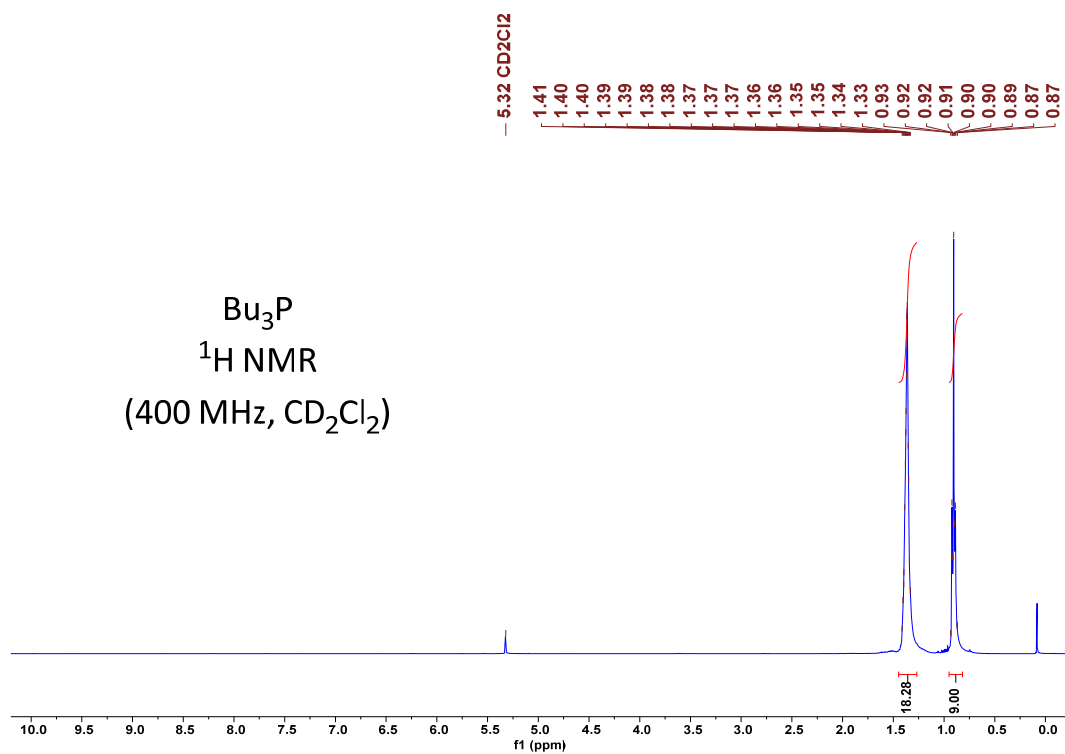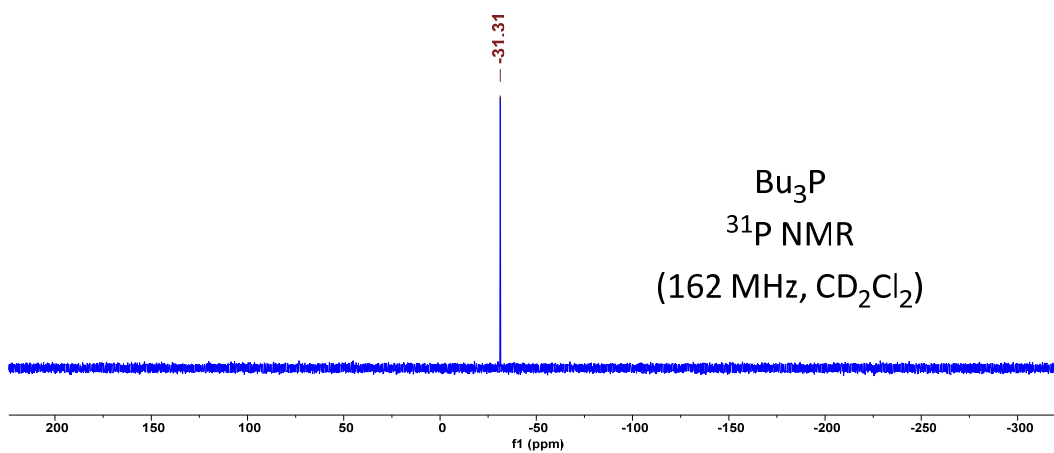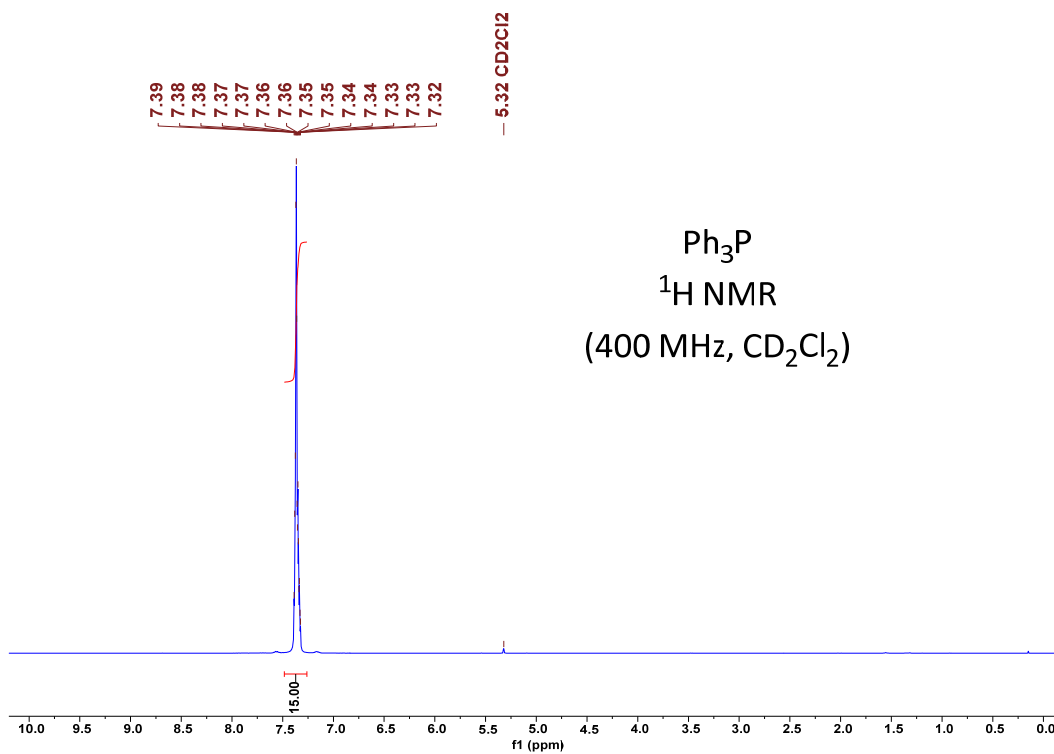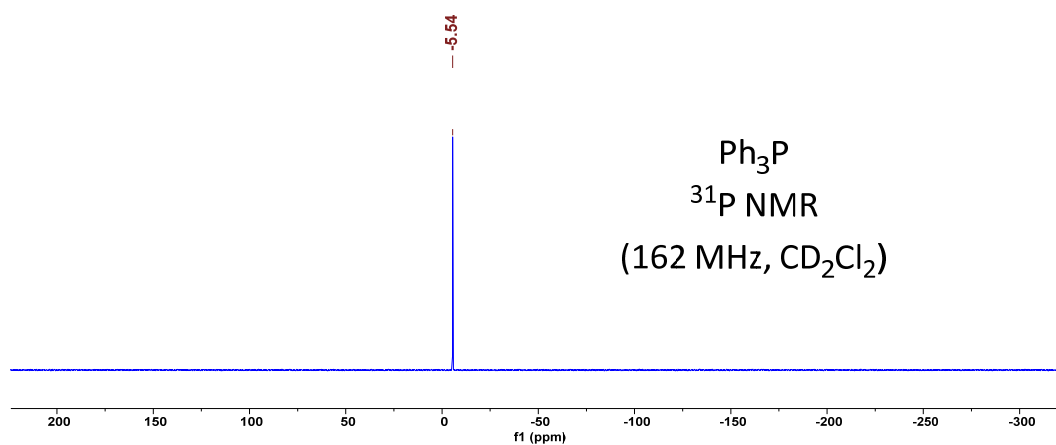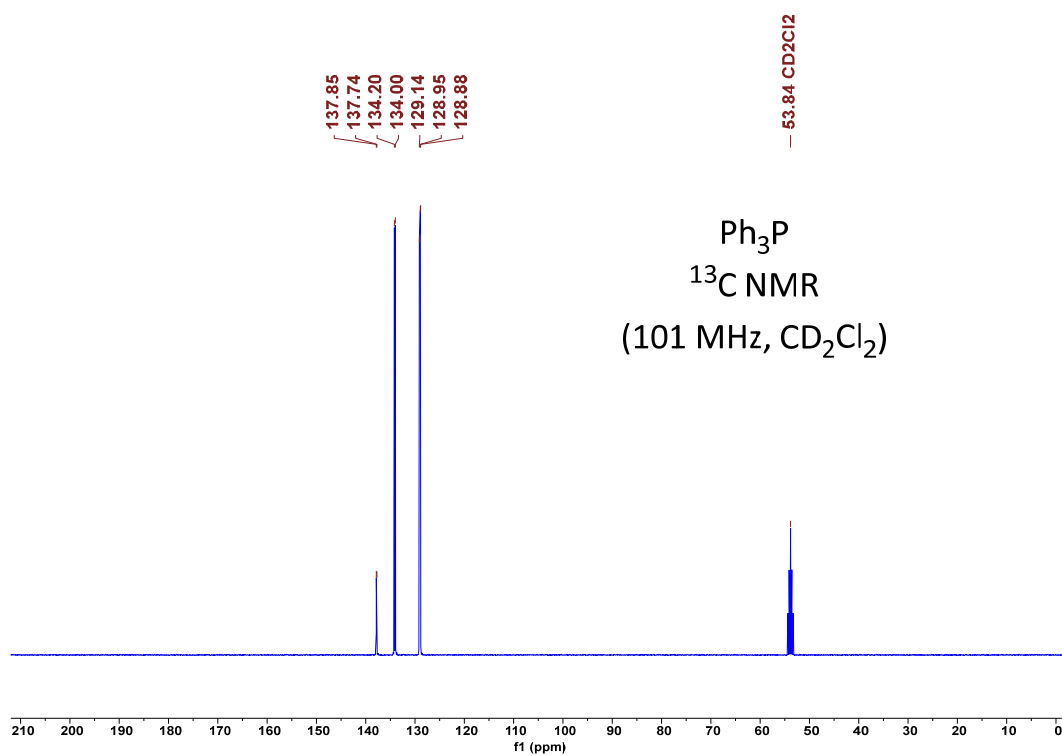
7.3 NMR spectra of phosphonium triflates and 2,4,6-collidinium triflate

7.3.1 Tributylphosphonium triflate (TBPT)

$Bu_3PH^{\oplus}$ $TfO^{\ominus}$

^1H NMR

(400 MHz, CD_2Cl_2)

$Bu_3PH^{\oplus}$ $TfO^{\ominus}$

^{13}C NMR

(101 MHz, CD_2Cl_2)
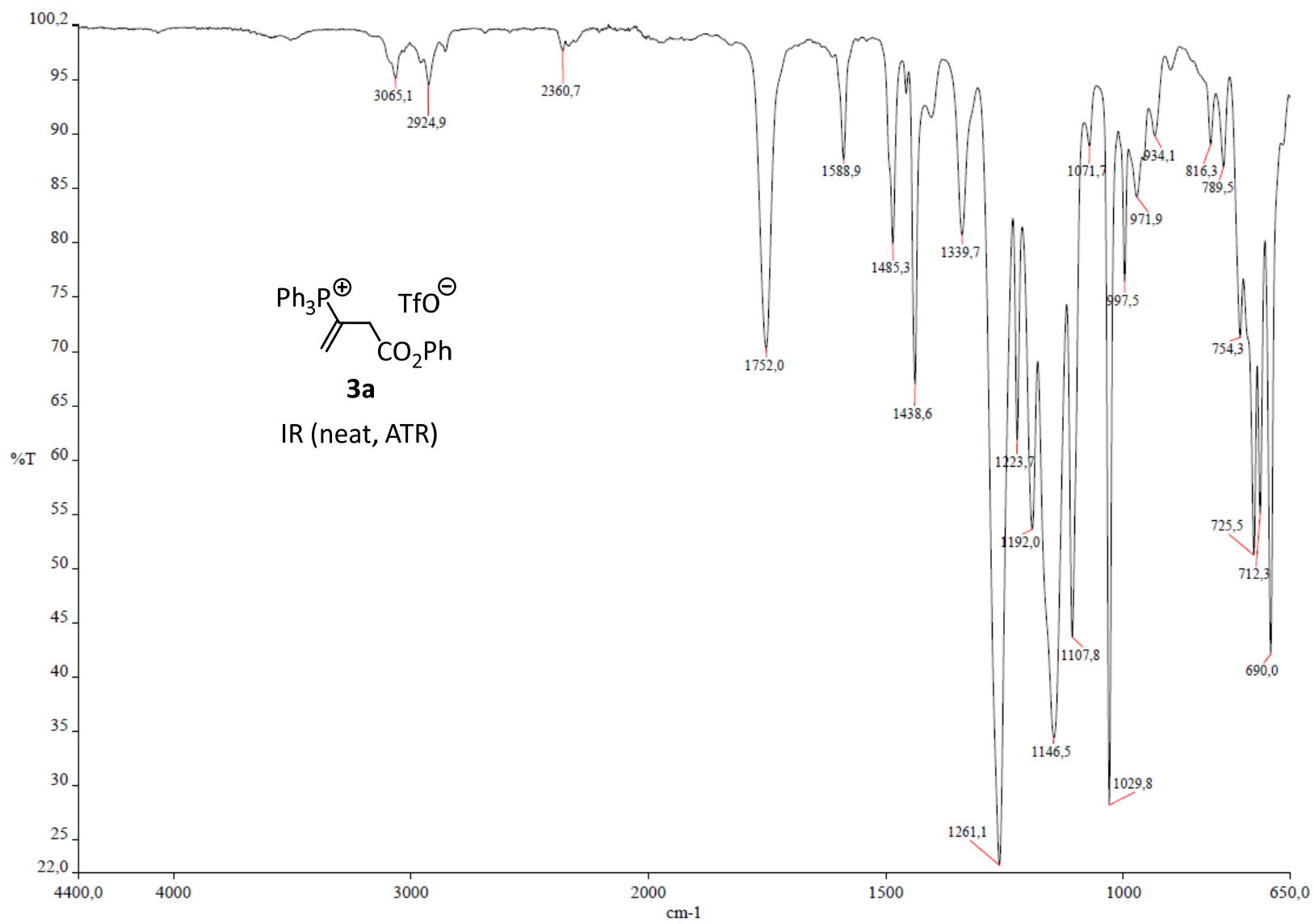
Bu₃PH⁺ TfO⁻
³¹P NMR
(162 MHz, CD₂Cl₂)

15.02
14.94
14.87
14.80
14.72
14.64
14.57
14.50
14.42
11.98
11.91
11.83
11.76
11.68
11.60
11.53
11.45

7.3.2 Triphenylphosphonium triflate (TPPT)

Ph₃PH⁺ TfO⁻
¹H NMR
(400 MHz, CD₂Cl₂)

10.13

8.80
7.87
7.86
7.85
7.84
7.83
7.82
7.81
7.80
7.79
7.78
7.78
7.77
7.77
7.72
7.72
7.70
7.70
7.69
7.69
7.68
5.32 CD2Cl2

0.48   0.49   15.00

Ph$_3$PH$^{\oplus}$ TfO$^{\ominus}$

^{13}C NMR

(101 MHz, CD$_2$Cl$_2$)

135.95
135.92
134.54
134.43
130.96
130.83
125.99
122.80
119.61
116.50
116.43
115.63

Ph$_3$PH$^{\oplus}$ TfO$^{\ominus}$

^{31}P NMR

(162 MHz, CD$_2$Cl$_2$)

4.57
1.28

Ph$_3$PH$^{\oplus}$ TfO$^{\ominus}$

^{19}F NMR

(377 MHz, CD$_2$Cl$_2$)

−78.98

7.3.3   2,4,6-Collidinium triflate (CT)

^{1}H NMR

(400 MHz, CD$_2$Cl$_2$)

^{13}C NMR

(101 MHz, CD$_2$Cl$_2$)

7.4 NMR and IR spectra of the product studies

7.4.1 (4-Oxo-4-phenoxybut-1-en-2-yl)triphenylphosphonium triflate (3a) from TPPT and phenyl buta-2,3-dienoate (1a)

3a

^{1}H NMR

(400 MHz, CD$_2$Cl$_2$)
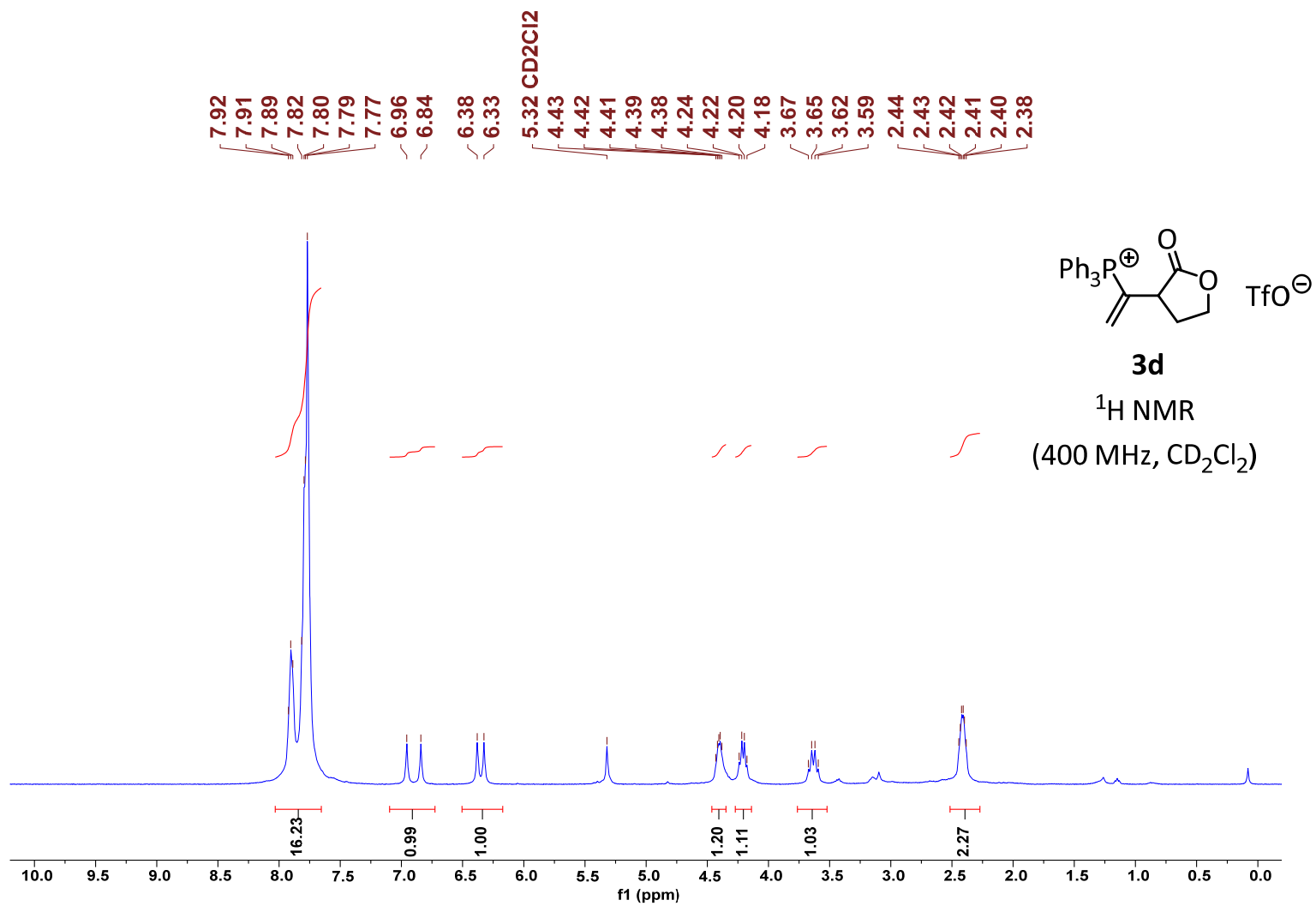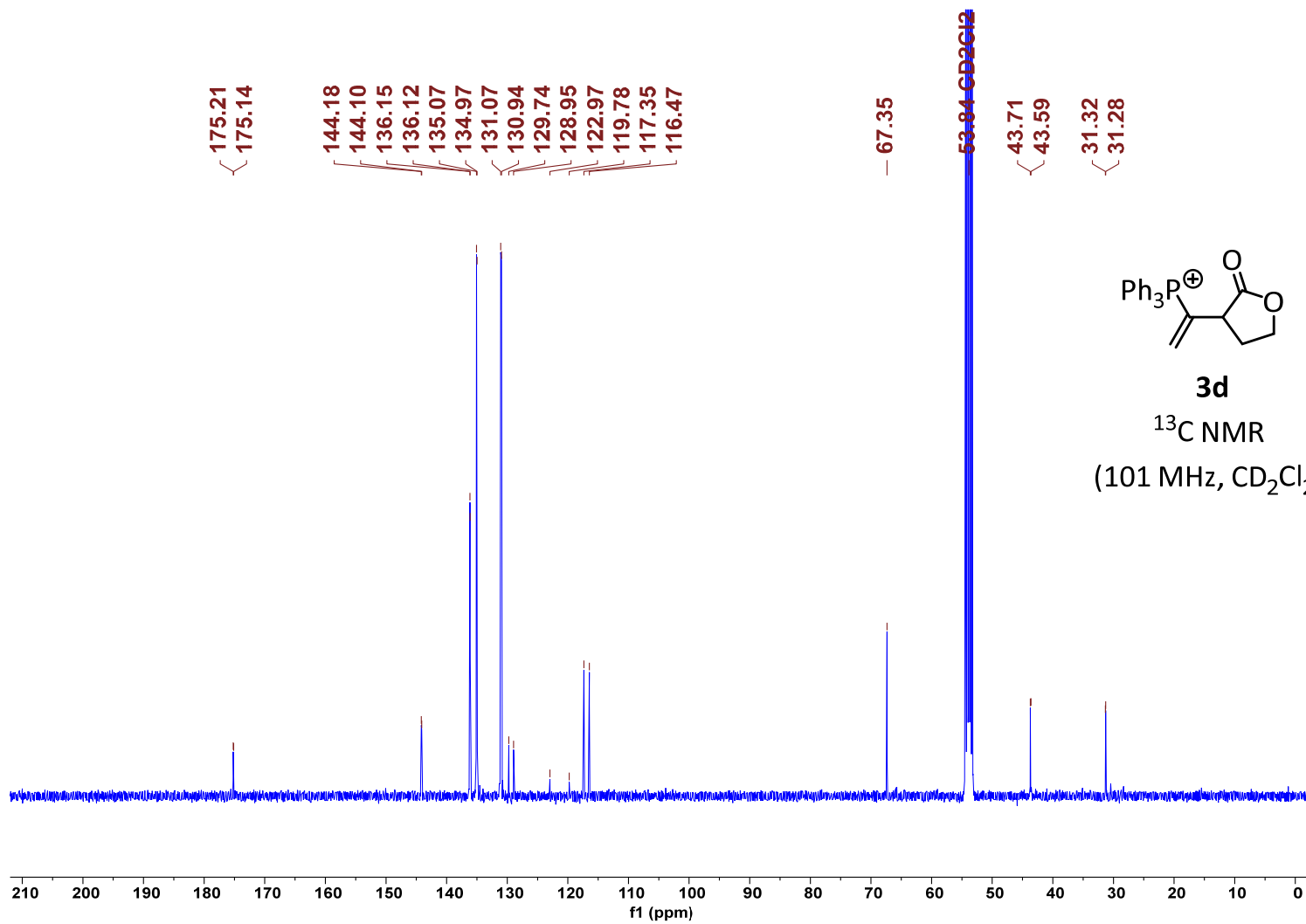
168.60
168.57
150.42
146.51
146.43
136.21
136.17
135.05
134.95
131.05
130.92
129.89
126.82
125.20
124.41
121.44
117.56
116.68
53.84 CD2Cl2
39.21
39.10

Ph$_3$P$^{\oplus}$ TfO$^{\ominus}$

CO$_2$Ph

3a

^{13}C NMR

(101 MHz, CD$_2$Cl$_2$)

—25.15

Ph$_3$P$^{\oplus}$ TfO$^{\ominus}$

CO$_2$Ph

3a

^{31}P NMR

(162 MHz, CD$_2$Cl$_2$)

200   150   100   50   0   -50   -100   -150   -200   -250   -300
f1 (ppm)

-78.87

Ph$_3$P$^{\oplus}$ TfO$^{\ominus}$

CO$_2$Ph

3a

^{19}F NMR

(377 MHz, CD$_2$Cl$_2$)

110   90   70   50   30   10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -27(
f1 (ppm)

3065,1
2924,9
2360,7
1752,0
1588,9
1485,3
1438,6
1339,7
1261,1
1223,7
1192,0
1146,5
1107,8
1071,7
1029,8
997,5
971,9
934,1
816,3
789,5
754,3
725,5
712,3
690,0

%T

cm-1

Ph₃P⊕   TfO⊖

CO₂Ph

3a

IR (neat, ATR)

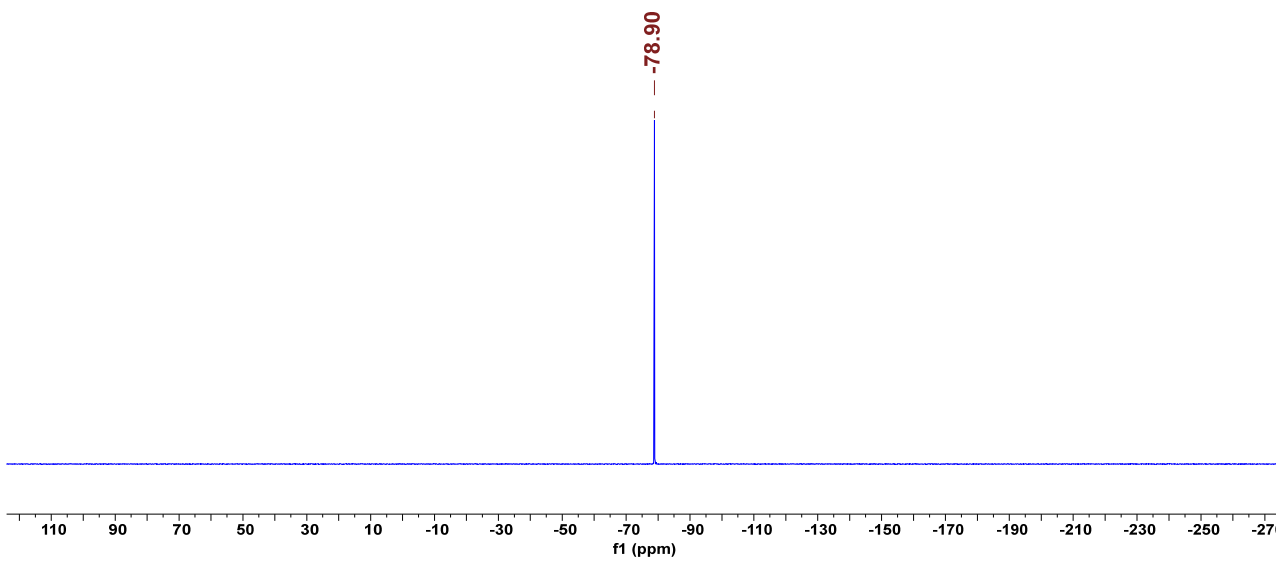**7.4.2** **(1-(2-Oxotetrahydrofuran-3-yl)vinyl)triphenylphosphonium triflate (3d)** from TPPT and 3-vinylidenedihydrofuran-2(3H)-one (**1d**)
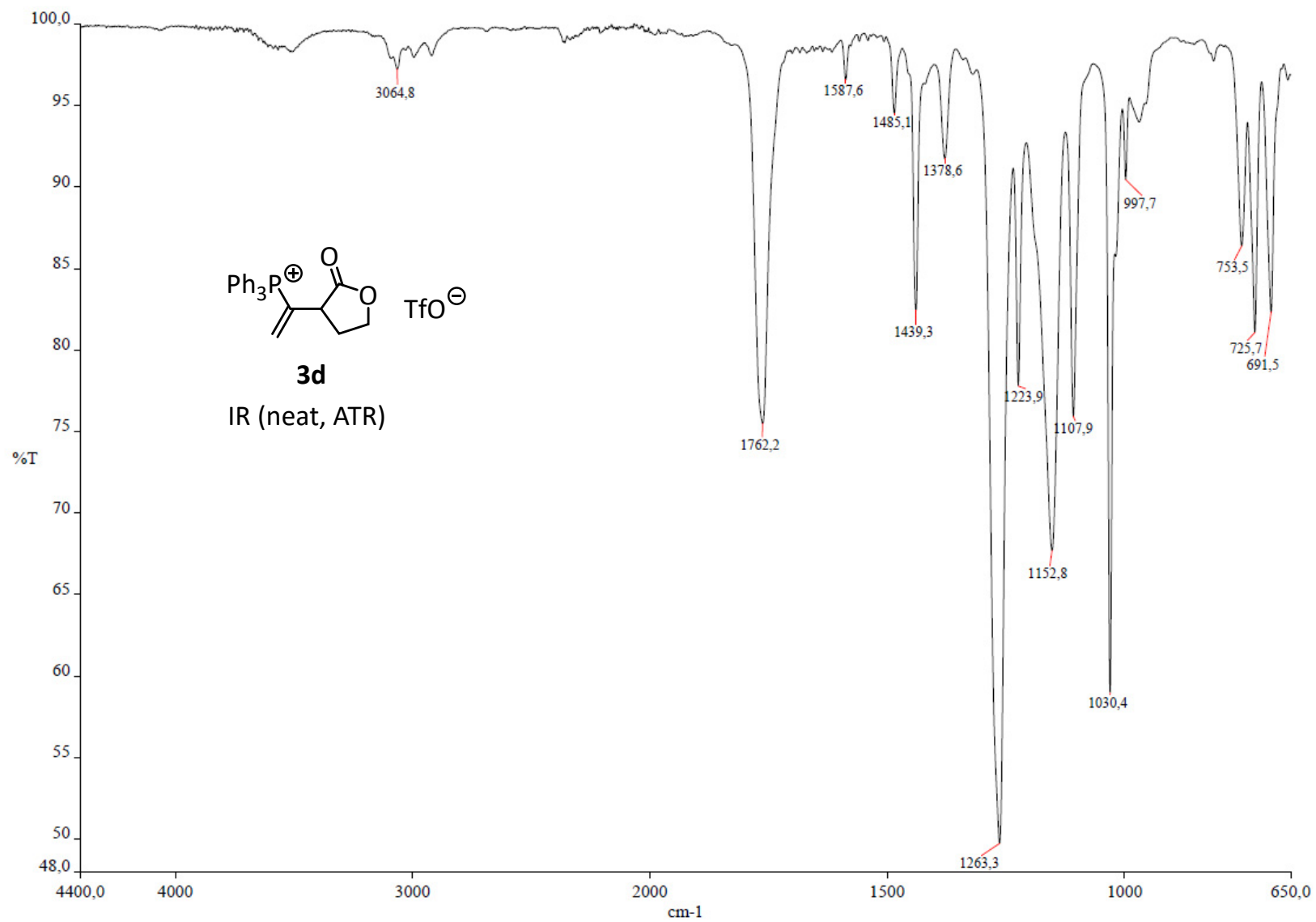

3d
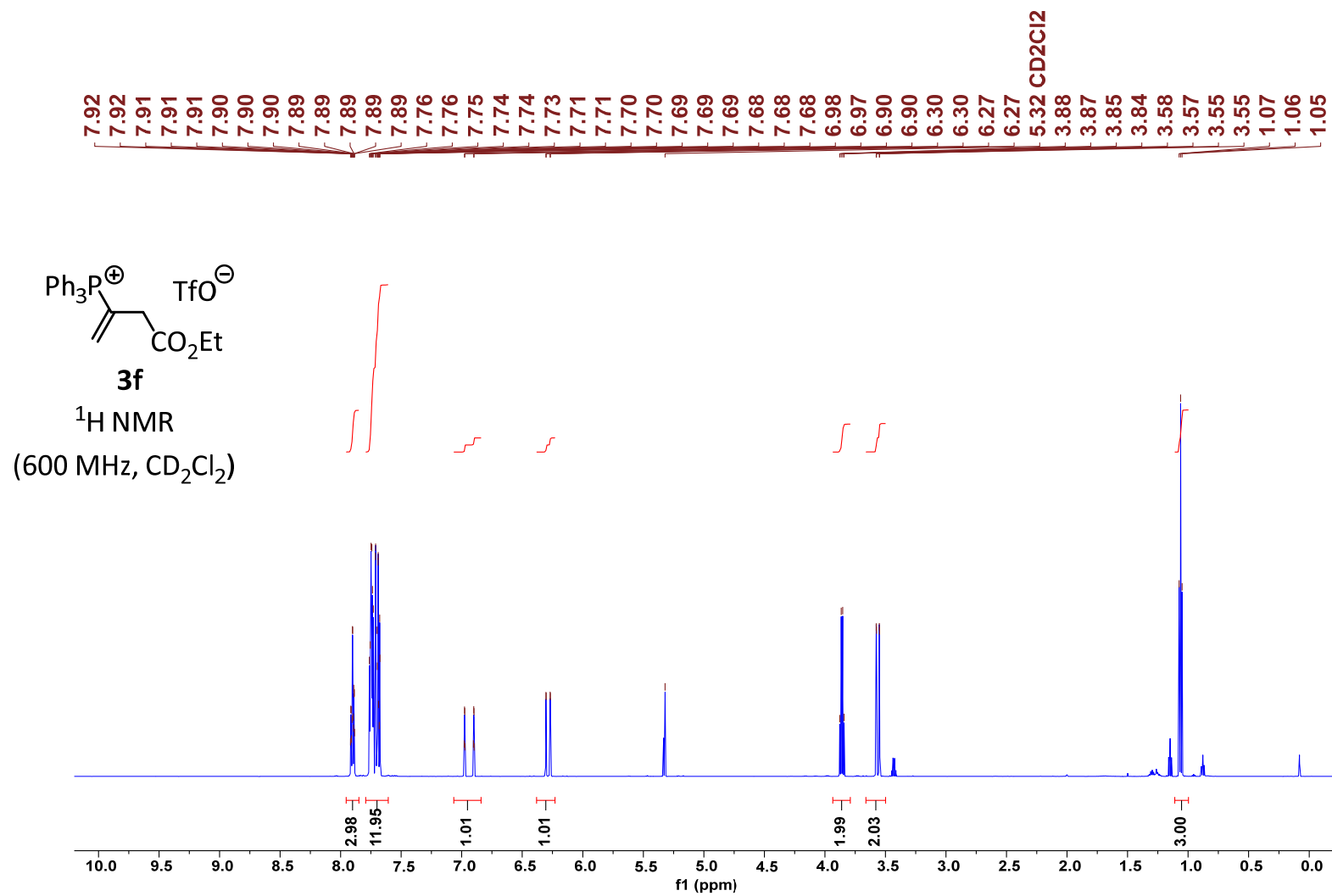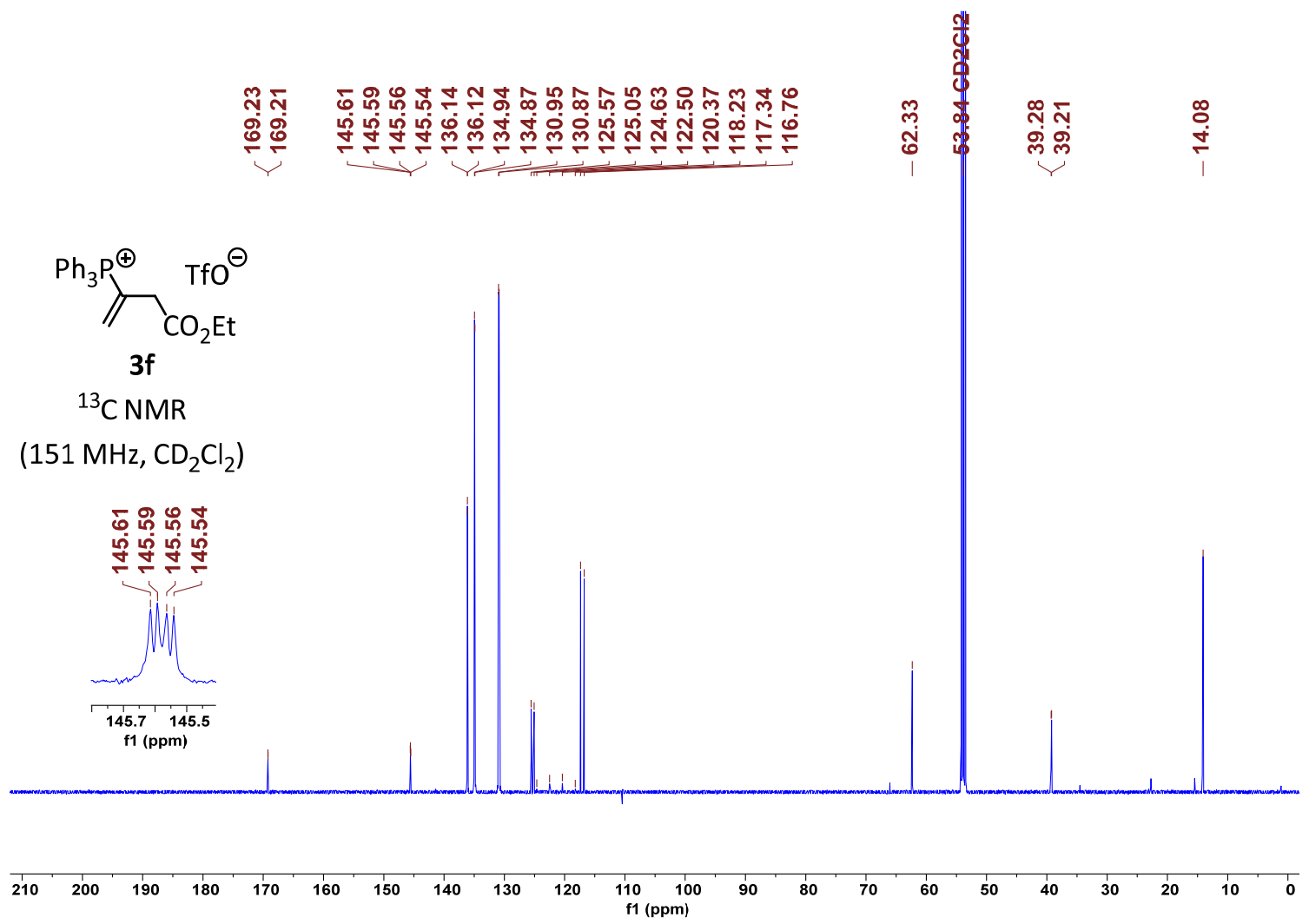
^{1}H NMR

(400 MHz, CD$_2$Cl$_2$)

175.21
175.14
144.18
144.10
136.15
136.12
135.07
134.97
131.07
130.94
129.74
128.95
122.97
119.78
117.35
116.47
67.35
53.84 CD2Cl2
43.71
43.59
31.32
31.28

3d

^{13}C NMR

(101 MHz, CD$_2$Cl$_2$)

— 26.13

Ph₃P⁺ ... O ... O ... TfO⁻

3d

^{31}P NMR

(162 MHz, CD$_2$Cl$_2$)

-78.90

Ph₃P⁺ ... O ... O ... TfO⁻

3d

^{19}F NMR

(377 MHz, CD$_2$Cl$_2$)

3d

IR (neat, ATR)

%T

3064,8
1587,6
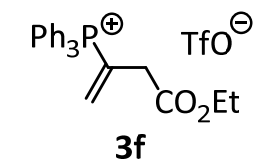1485,1
1378,6
1439,3
1223,9
1152,8
1107,9
997,7
753,5
725,7
691,5
1762,2
1263,3
1030,4

cm-1
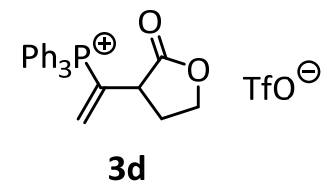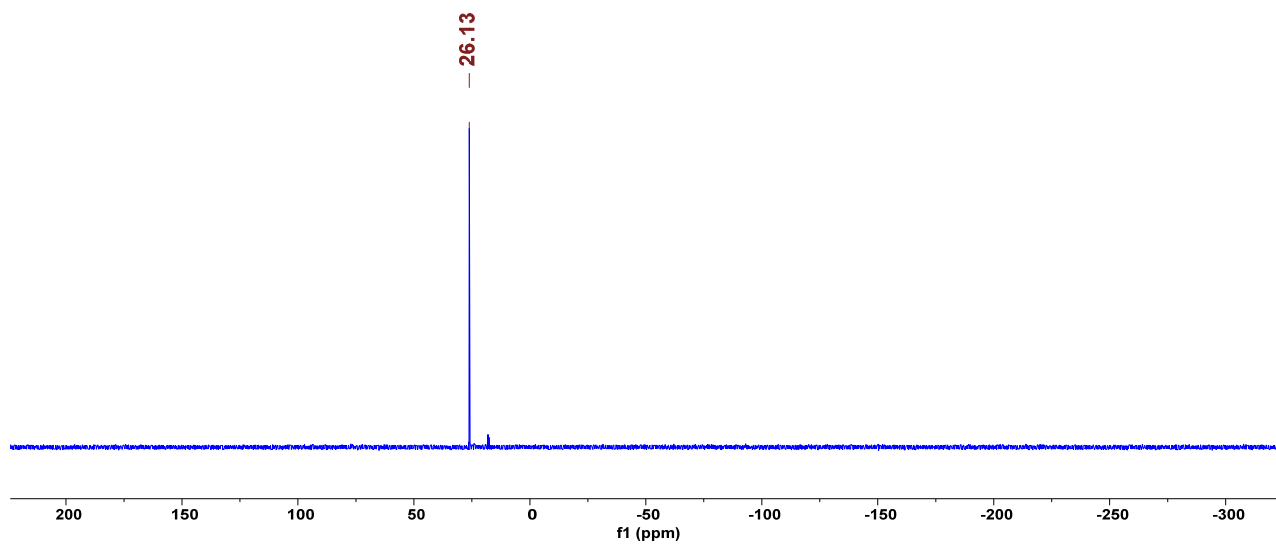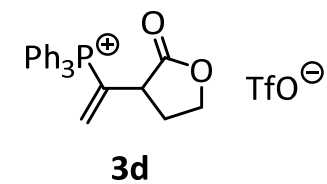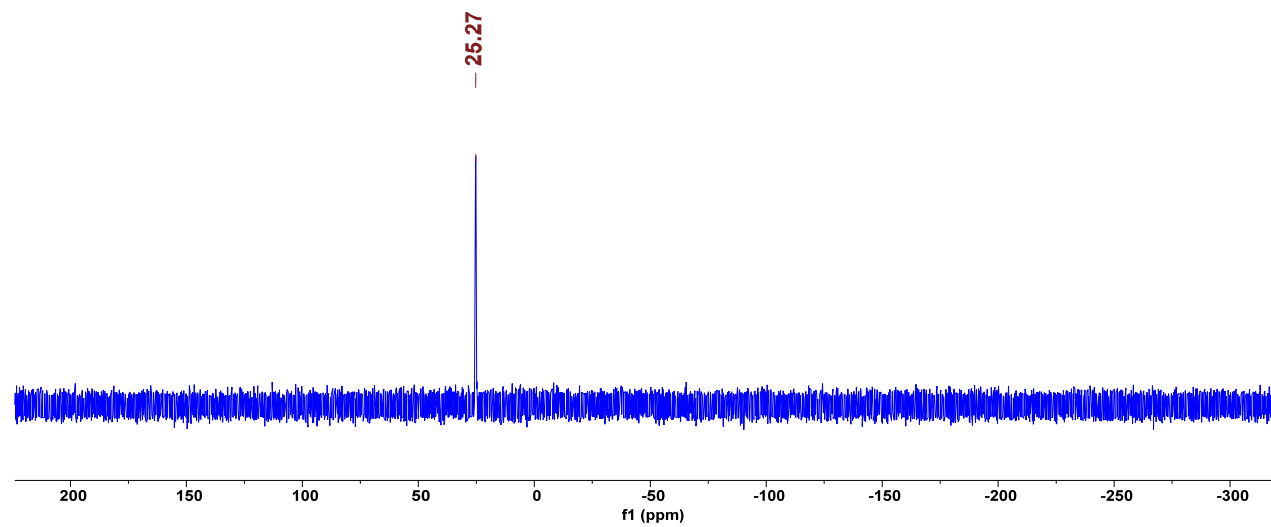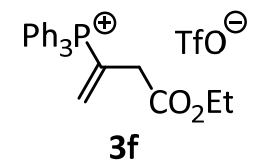
7.4.3 (4-Ethoxy-4-oxobut-1-en-2-yl)triphenylphosphonium triflate (3f) from TPPT and ethyl buta-2,3-dienoate (1f)

^{1}H NMR
(600 MHz, CD$_2$Cl$_2$)
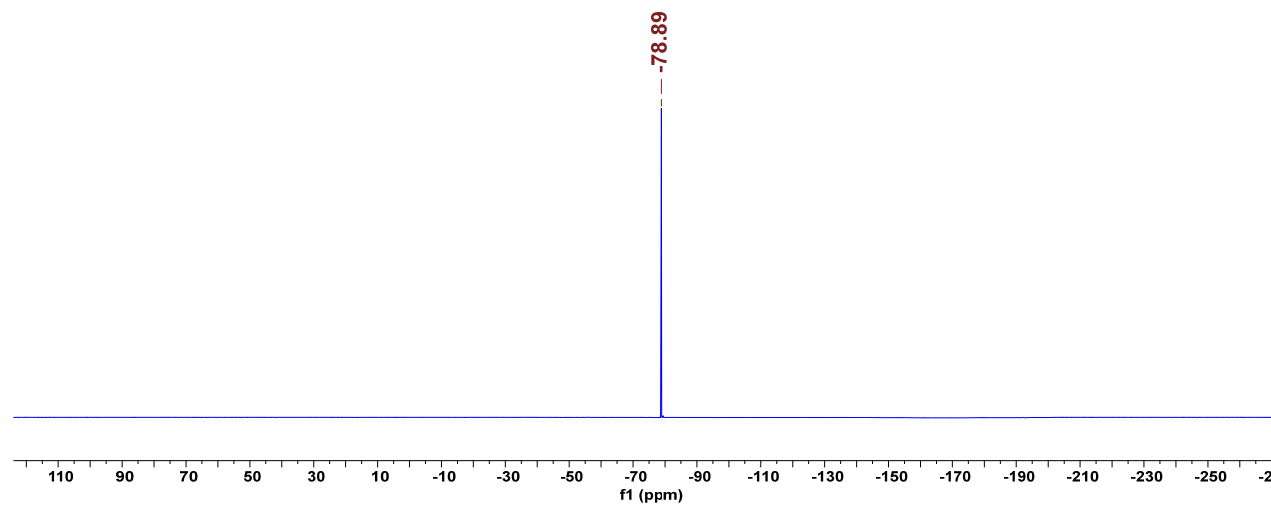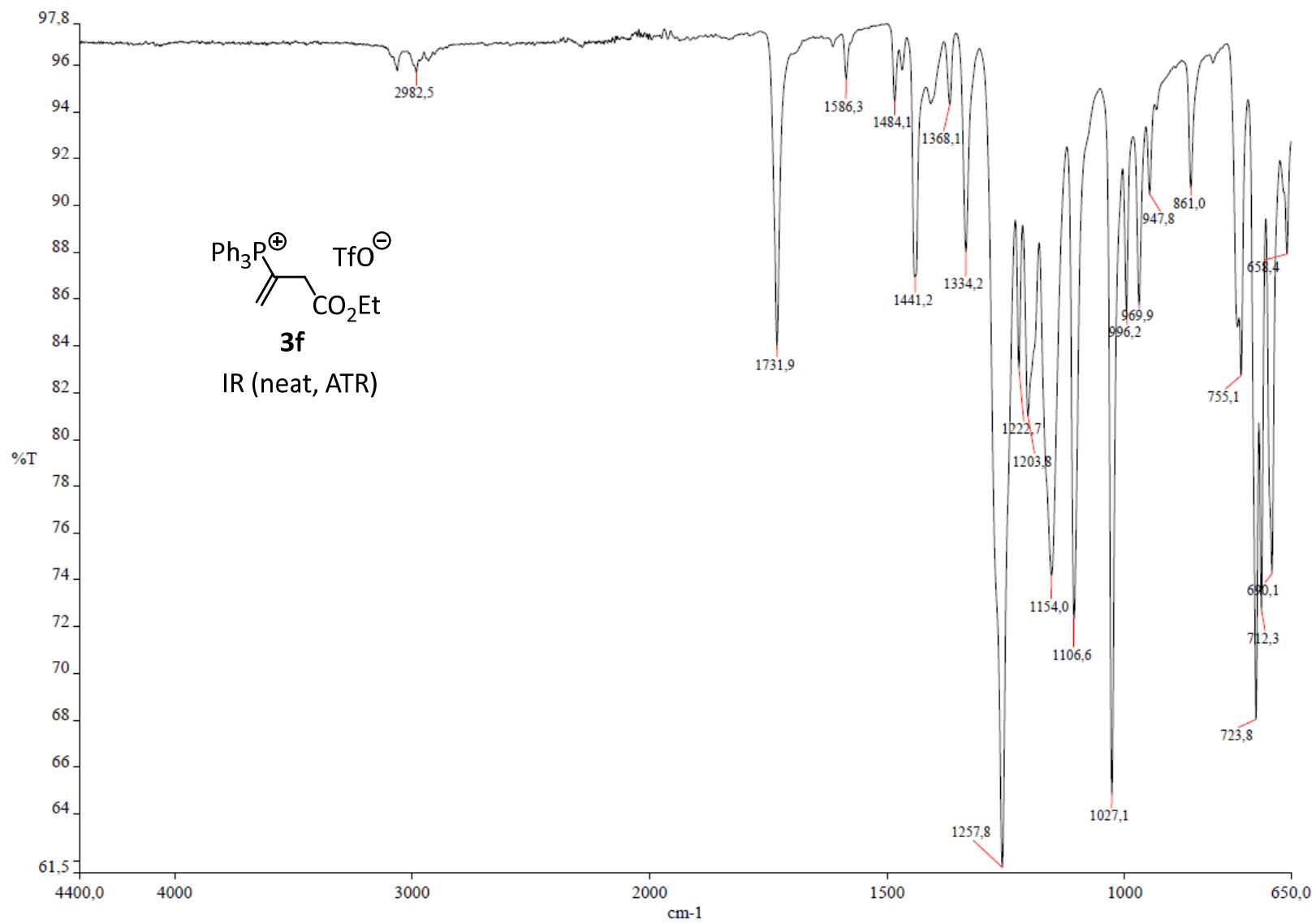
3f

169.23
169.21
145.61
145.59
145.56
145.54
136.14
136.12
134.94
134.87
130.95
130.87
125.57
125.05
124.63
122.50
120.37
118.23
117.34
116.76
62.33
53.84 CD2Cl2
39.28
39.21
14.08

Ph₃P⊕   TfO⊖

CO₂Et

3f

¹³C NMR

(151 MHz, CD₂Cl₂)

145.61
145.59
145.56
145.54

145.7   145.5
f1 (ppm)

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

— 25.27

Ph₃P⊕ TfO⊖

CO₂Et

3f

³¹P NMR

(162 MHz, CD₂Cl₂)

200 150 100 50 0 -50 -100 -150 -200 -250 -300
f1 (ppm)

-78.89

Ph₃P⊕ TfO⊖

CO₂Et

3f

¹⁹F NMR

(377 MHz, CD₂Cl₂)

110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -27
f1 (ppm)

Ph₃P⊕   TfO⊖

$Ph_3P^{\oplus}$ $TfO^{\ominus}$

CO_2Et

3f

IR (neat, ATR)

Peaks: 2982,5; 1586,3; 1484,1; 1368,1; 1441,2; 1334,2; 1731,9; 1257,8; 1222,7; 1203,8; 1154,0; 1106,6; 1027,1; 996,2; 969,9; 947,8; 861,0; 658,4; 755,1; 690,1; 712,3; 723,8
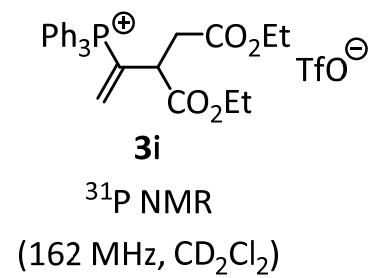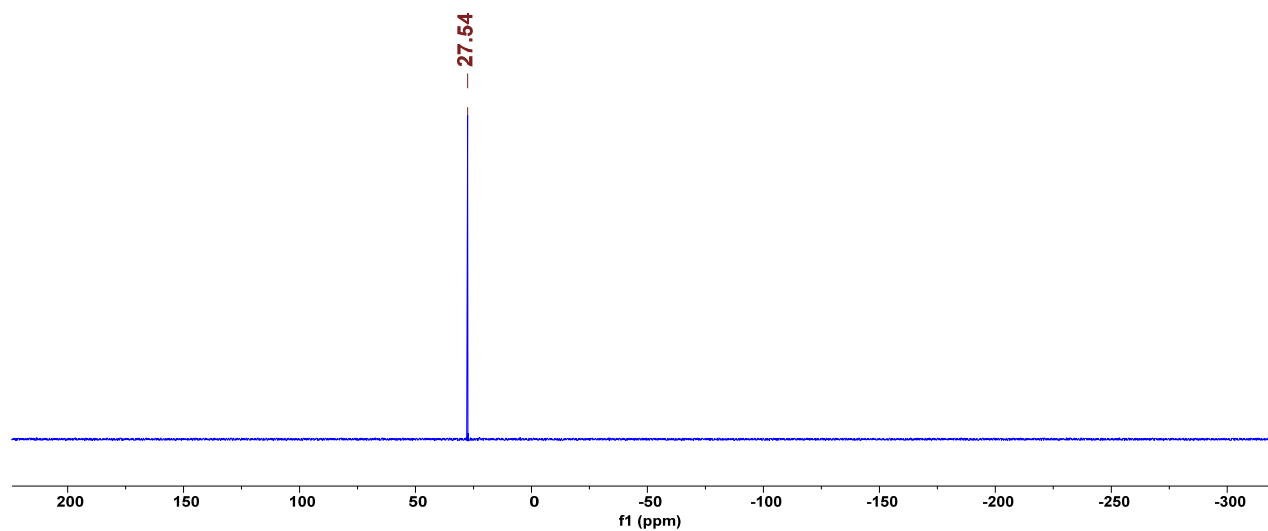
7.4.4 (5-Ethoxy-3-(ethoxycarbonyl)-5-oxopent-1-en-2-yl)triphenylphosphonium triflate (3i) from TPPT and diethyl 2-vinylidenesuccinate (1i)

Ph$_3$P$^{\oplus}$—CO$_2$Et
CO$_2$Et
TfO$^{\ominus}$

3i

^{1}H NMR

(400 MHz, CD$_2$Cl$_2$)

Ph$_3$P$^{\oplus}$—CO$_2$Et TfO$^{\ominus}$

CO$_2$Et

3i

^{13}C NMR

(101 MHz, CD$_2$Cl$_2$)

170.74
170.08
170.04
142.00
141.93
136.19
136.16
135.17
135.07
130.90
130.77
130.62
129.85
126.24
123.04
119.85
117.60
116.72
62.87
61.98
53.84 CD2Cl2
42.92
42.81
36.37
36.31
14.27
13.92

27.54

Ph₃P⊕ —CO₂Et TfO⊖

CO₂Et

3i

³¹P NMR

(162 MHz, CD₂Cl₂)

200 150 100 50 0 -50 -100 -150 -200 -250 -300
f1 (ppm)

-78.90

Ph₃P⊕ —CO₂Et TfO⊖

CO₂Et

3i

¹⁹F NMR

(377 MHz, CD₂Cl₂)

110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -27(
f1 (ppm)

Ph$_3$P$^{\oplus}$—CO$_2$Et TfO$^{\ominus}$

CO$_2$Et

3i

IR (neat, ATR)

8   References

(S1)   For a freely accessible database of *E*, *N*, and s_N parameters, see: https://www.cup.lmu.de/oc/mayr/DBintro.html.

(S2)   D. S. Allgäuer, H. Jangra, H. Asahara, Z. Li, Q. Chen, H. Zipse, A. R. Ofial and H. Mayr, *J. Am. Chem. Soc.*, 2017, **139**, 13318-13329.

(S3)   G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.

(S4)   B. J. Cowen, L. B. Saunders and S. J. Miller, *J. Am. Chem. Soc.*, 2009, **131**, 6105-6107.

(S5)   G. Himbert, D. Fink and K. Diehl, *Chem. Ber.*, 1988, **121**, 431-441.

(S6)   L. M. Conner, Y. Xu and K. M. Brown, *J. Am. Chem. Soc*., 2015, **137**, 3482-3485.

(S7)   Y. Gao, J. Zhang, W. Shan, W. Fei, J. Yao and W. Yao, *Org. Lett.*, 2021, **23**, 6377-6381.

(S8)   T. Liu, C. He, F. Wang, X. Shen, Y. Li, M. Lang, G. Li, C. Huang and F. Cheng, *Synthesis*, 2021, **53**, 518-526.

(S9)   H. Panchal, C. Clarke, C. Bell, S. N. Karad, W. Lewis and H. W. Lam, *Chem. Commun*., 2018, **54**, 12389-12392.

(S10) R. W. Lang and H. J. Hansen, *Org. Synth.,* 1984, **6**, 202.

(S11) E. Lee, J. Bang, J. Kwon and C.-M. Yu, *J. Org. Chem*., 2015, **80**, 10359-10363.

(S12) a) H. Clavier, K. Le Jeune, R. De Innocenzo, A. Tenaglia and G. Buono, *Org. Lett*., 2011, **13**, 308-311. b) D. Mal and S. Jana, *J. Org. Chem*., 2016, **81**, 11857-11865.

(S13) W. Chen, J. C. L. Walker and M. Oestreich, *J. Am. Chem. Soc.*, 2019, **141**, 1135-1140.

(S14) H. Guo, Q. Xu and O. Kwon, *J. Am. Chem. Soc*., 2009, **131**, 6318-6319.

(S15) Y.-R. Chen, G. M. Reddy, S.-H. Hong, Y.-Z. Wang, J.-K. Yu and W. Lin, *Angew. Chem. Int. Ed*., 2017, **56**, 5106-5110.

(S16) a) L. L. Tolstikova, A. V. Bel'skikh and B. A. Shainyan, *Russ. J. Gen. Chem*., 2011, **81**, 474-480., b) V. V. Levin and A. D. Dilman, *Chem. Commun*., 2021, **57**, 749-752.

(S17) C. Mao, Z. Wang, Z. Wang, P. Ji and J.-P. Cheng, *J. Am. Chem. Soc*., 2016, **138**, 5523-5526.

(S18) A ^{31}P NMR chemical shift of +25.5 ppm for **3f** with a phenyltetrazole counteranion was reported in: D. Virieux, A. F. Guillouzic and H.-J. Cristau, *Tetrahedron*, 2006, **62**, 3710-3720.

(S19) (a) A. D. Becke, *J. Chem. Phys*. 1993, **98**, 5648-5652. (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.

(S20) (a) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724-728. (b) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650-654.

(S21) G. Luchini, J. V. Alegre-Requena, I. Funes-Ardoiz and R. S. Paton. *GoodVibes*: automated thermochemistry for heterogeneous computational chemistry data [version 1; peer review: 2 approved with reservations]. *F1000Research* 2020, **9**: 291 (https://doi.org/10.12688/f1000research.22758.1).

(S22) T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. v. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294-301.

(S23) A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.

(S24) (a) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104. (b) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.

(S25) (a) E. Cances, B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3032-3041. (b) J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999-3094.

(S26) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09 Revision D.01*, Gaussian, Inc., Wallingford CT, **2013**.