Tris(2,4,6-trimethoxyphenyl)phosphine - A Lewis base able to compete with phosphazene bases in catalysing oxa-Michael reactions

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Electronic Supporting Information

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Experimental

General Information

All experiments were performed under ambient conditions. Chemicals were purchased from Sigma Aldrich, Carl Roth, Merck or TCI and were used as received. The catalyst TTMPP was purchased via Sigma Aldrich and re-crystallized from ethanol before use. Stabilizers present in the Michael acceptors were not removed. ^{1}H- and ^{13}C- NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 25 °C (^{1}H: 300.36 MHz; ^{13}C: 75.53 MHz). Chemical shifts δ are given in ppm relative to the residual protons and carbons of the deuterated solvent. ($CHCl_3$: 7.26 ppm and 77.16 ppm, DMSO: 2.50 and 39.52 for ^{1}H and ^{13}C, respectively). ^{31}P measurements were performed on a Varian Inova 500 MHz instrument operating at 202.547 MHz. Chemical shifts are reported in ppm relative to an external standard (85 % H_3PO_4). Spectra are ^{1}H-decoupled and as delay time (d1) 25 s was set. Deuterated solvents were obtained from Cambridge Isotope Laboratories Inc. Size exclusion chromatography (SEC) was performed on a system provided by Shimadzu (equipped with two separating columns from MZ-Gel SD plus, 500 A and 100 A, linear 5µ; UV detector (SPD-20A) and RI detector (RID-20A)) using THF as eluent. Poly(styrene) standards in the range of 350 to 17800 g/mol purchased from Polymer Standard Service were used for calibration. Temperature profiles were recorded with a FLIR ETS320 thermal imaging system. Low resolution mass spectra were acquired on an Expression CMS L compact mass spectrometer from Advion. The spectrometer was equipped with an APCI (atmospheric-pressure chemical ionization) ionization source and quadrupole mass analyzer (range 10-2000 m/z).

General procedure for oxa-Michael additions

Alcohol (2.0 equiv. for mono-functionalized Michael acceptors, 3.0 equiv. for **1**) and catalyst (0.01 equiv.) were added to a 4 mL sealed glass tube. Then, the Michael acceptor was added, and the reaction mixture was stirred at room temperature. The reaction progress was monitored by ^{1}H-NMR spectroscopy after 1 and 24 h. All experiments were performed at least three times.

General procedure for oxa-Michael polymerisations

Michael acceptor and alcohol were employed in a molar ratio of 1:1. First, alcohol and catalyst (5 mol % in respect to the Michael acceptor) were mixed in a 4 ml sealed glass tube. Then, Michael acceptor was added and the reaction mixture was stirred either at room temperature for 24 hours. Aliquots were sampled after 1 h and 24 h and subjected to NMR analysis. Molar mass distributions of the polymers were determined by SEC after 24 h reaction time.

Oxa-Michael reactions

NMR shifts of oxa-Michael products of acrylonitrile, divinyl sulfone and acrylamide correspond to the values published in literature.[1,2,3,4]

For work-up, excess alcohol was evaporated while catalyst was left in the product in all cases.

<u>Divinyl sulfone as acceptor:</u>

2-(2-((2-Isopropoxyethyl)sulfonyl)ethoxy)propane (1a):

^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.84 (t, 4H) 3.63 (m, 2H), 3.31 (t, 4H), 1.16 (d, 12H).

1-(2-((2-Propoxyethyl)sulfonyl)ethoxy)propane (1b):

^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.85 (dd, 4H), 3.42 (t, 4H), 3.32 (t, 4H), 1.70-1.43 (m, 4H), 0.91 (t, 6H).

3-(2-((2-(Allyloxy)ethyl)sulfonyl)ethoxy)prop-1-ene (1c):

^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.91 – 5.82 (m, 2H), 5.22 (m, 4H), 4.03 (d, 4H), 3.88 (t, 4H), 3.36 (t, 4H).

3-(2-((2-(Prop-2-yn-1-yloxy)ethyl)sulfonyl)ethoxy)prop-1-yne (1d):

^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.27 (d, 4H), 3.98 (t, 4H), 3.36 (t, 4H), 2.48 (d, 2H)

Acrylonitrile as acceptor:

3-Isopropoxypropanenitrile (2a):

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ 3.66 – 3.61 (m, 3H), 2.57 (t, 2H), 1.20 (d, 6H)

3-Propoxypropanenitrile (2b):

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ 3.66 – 3.60 (m, 2H), 3.44 (t, 2H), 2.59 (t, 2H), 1.60 (m, 2H), 0.93 (t, 3H)

3-(Allyloxy)propanenitrile (2c):

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ 5.86-5.78 (m, 1H), 5.27-5.13 (dd, 2H), 3.98 (d, 2H), 3.60 (t, 2H), 2.55 (t, 2H)

3-(Prop-2-yn-1-yloxy)propanenitrile (2d):

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ 4.22 (d, 2H), 3.76 (t, 2H), 2.65 (t, 2H), 2.48 (dt, 1H)

Acrylamide as acceptor:

3-Isopropoxypropanamide (3a):

^{1}H-NMR (300 MHz, DMSO-d_6) δ 7.26 (bs, 1H), 6.76 (bs, 1H), 3.55 (m, 3H), 2.23 (t, 2H), 1.05 (d, 6H)

3-Propoxypropanamide (3b):

^{1}H-NMR (300 MHz, DMSO-d_6) δ 7.27 (bs, 1H), 6.78 (bs, 1H), 3.54 (t, 2H), 3.31 (t, 2H), 1.47 (m, 2H), 0.84 (t, 3H)

3-(Allyloxy)propenamide (3c):

^{1}H-NMR (300 MHz, DMSO-d_6) δ 7.29 (bs, 1H), 6.79 (bs, 1H), 5.92-5.79 (m, 1H), 5.27-5.11 (dd, 2H), 3.91 (d, 2H), 3.56 (t, 2H), 2.29 (t, 2H)

3-(Prop-2-yn-1-yloxy)propenamide (3d):

^{1}H-NMR (300 MHz, DMSO-d_6) δ 7.31 (bs, 1H), 6.82 (bs, 1H), 4.09 (d, 2H), 3.62 (t, 2H), 3.39 (t, 1H), 2.29 (t, 2H)

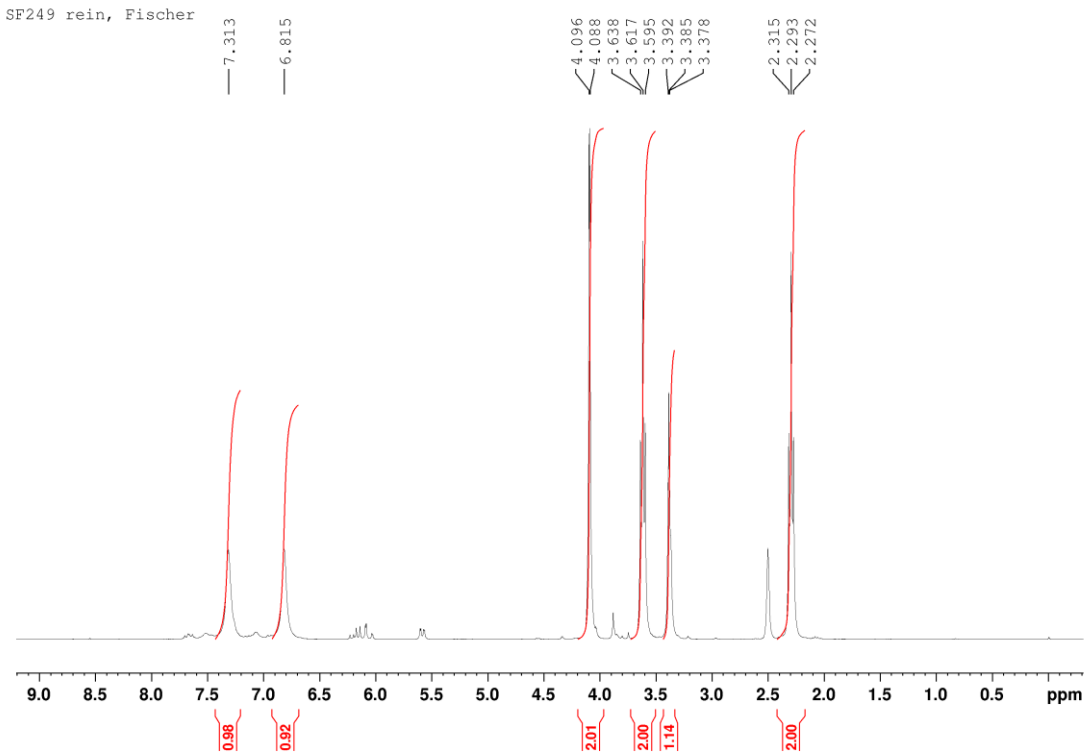
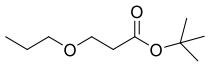


*Figure S1 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **3d** prepared with 5 mol % TTMPP after 24 h (containing still acrylamide)*

<u>t-Butyl acrylate as acceptor:</u>

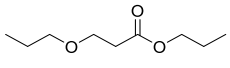
tert-butyl 3-propoxypropanoate (4b)



^{1}H-NMR (300.36 MHz, $CDCl_3$): δ 3.63 (t, 2H), 3.35 (t, 2H), 2.46 (t, 2H), 1.56 (m, 2H), 1.43 (s, 9H), 0.88 (t, 3H)

^{13}C-APT NMR (75.53 MHz, $CDCl_3$): δ 171.0, 80.4, 72.7, 66.3, 36.4, 28.1, 22.8, 10.5

*side product: propyl 3-propoxypropanoate (**4b-s**)*



After 24 hours, 10.4 % of **4b-s** could be observed. This number further increased to 15.7 % after 7 days.

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ 4.0 (t, 2H), 3.63 (t, 2H), 3.35 (t, 2H), 2.55 (t, 2H), 1.62 (m, 2H), 1.43 (s, 9H), 0.88 (t, 6H)

^{13}C-APT NMR (75.53 MHz, $CDCl_3$): δ 171.0, 72.7, 66.3, 66.1, 35.2, 22.8, 22.0, 10.5

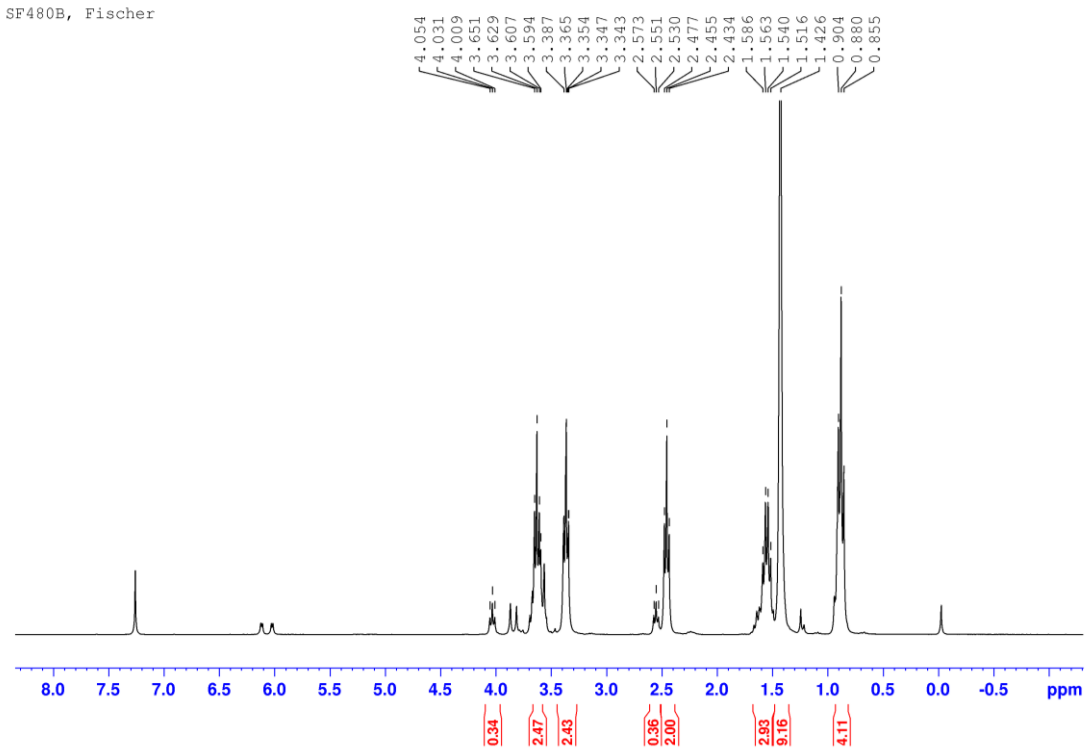


*Figure S2 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **4b** and **4b-s** prepared with 5 mol % TTMPP after 24 h*

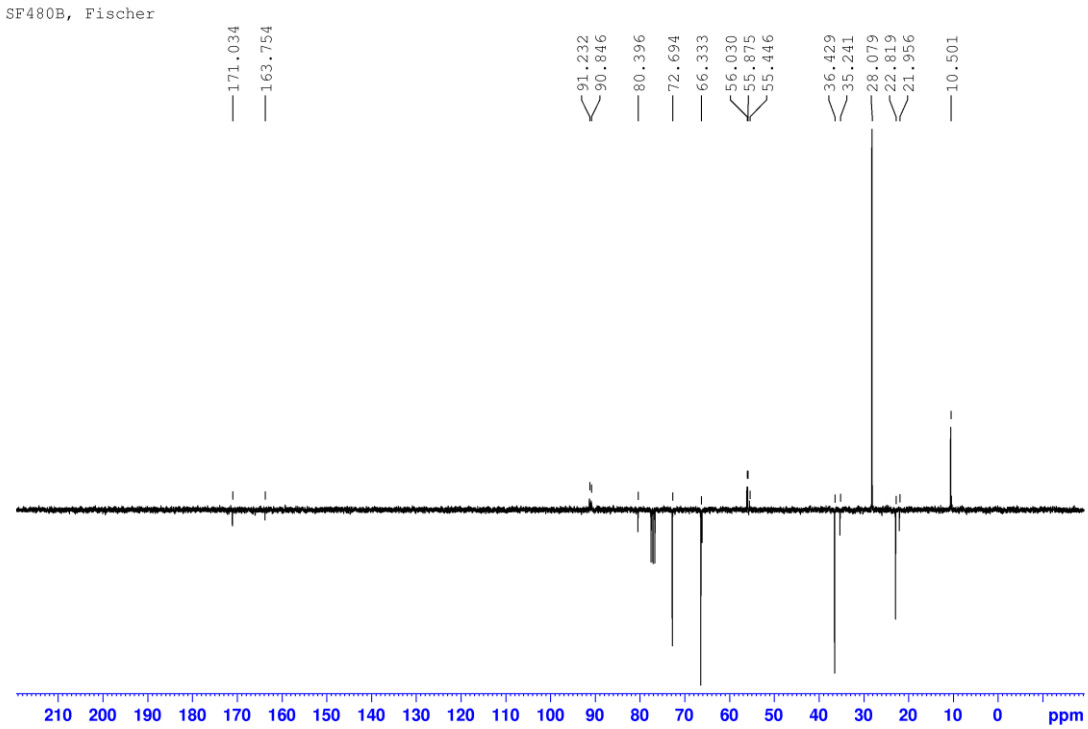


*Figure S3 ^{13}C-APT spectrum (75.53 MHz, $CDCl_3$) of of **4b** and **4b-s** prepared with 5 mol % TTMPP after 24 h*

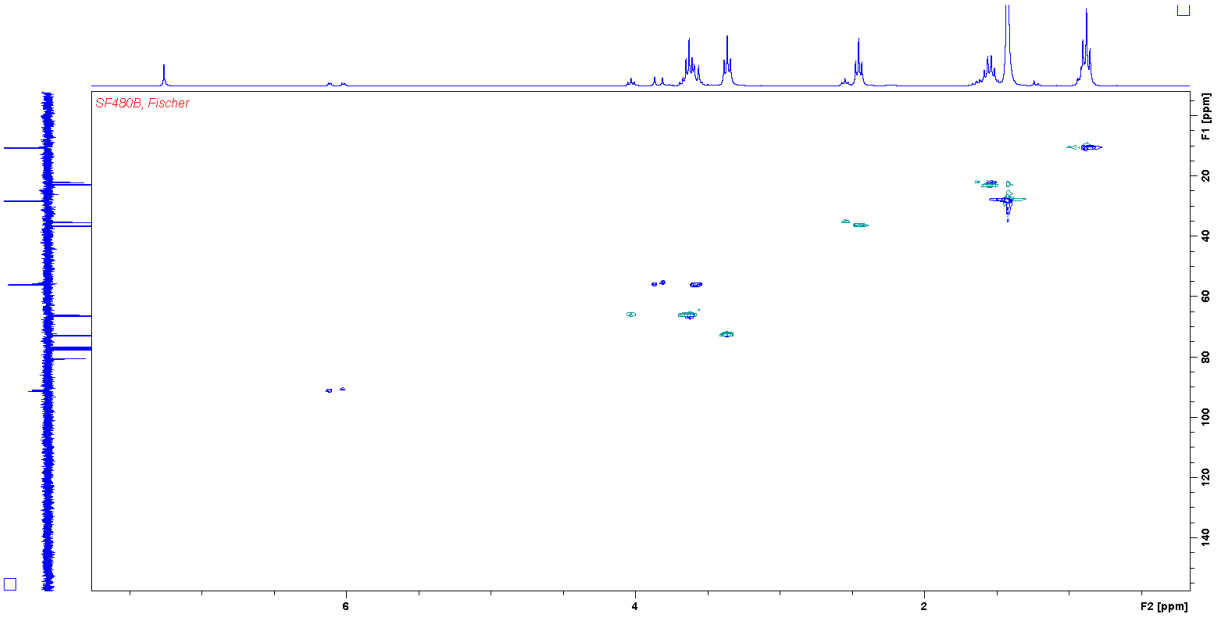
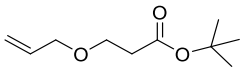


*Figure S4 HSQC of **4b** and **4b-s** prepared with 5 mol % TTMPP after 24 h*

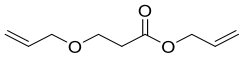
tert-butyl 3-(allyloxy)propanoate (4c)



^{1}H-NMR (300.36 MHz, $CDCl_3$): δ 5.87 (m, 1H), 5.33-5.14 (m, 2H), 3.97 (d, 2H), 3.65 (t, 2H), 2.48 (t, 2H), 1.43 (s, 9H)

^{13}C-APT NMR (75.53 MHz, $CDCl_3$): δ 171.0, 134.1, 117.2, 116.9, 80.6, 72.0, 65.9, 36.4, 28.2

*side product: allyl 3-(allyloxy)propanoate (**4c-s**)*



After 24 hours, 15.4 % of **4c-s** could be observed. This number further increased to 46.9 % after 7 days.

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ 5.87 (m, 2H), 5.33-5.14 (m, 4H), 4.58 (d, 2H), 3.97 (d, 2H), 3.65 (t, 2H), 2.61 (t, 2H)

^{13}C-APT NMR (75.53 MHz, $CDCl_3$): δ 171.0, 134.1, 132.1, 118.25, 117.2, 116.9, 72.0, 65.9, 65.6, 65.3, 35.2,

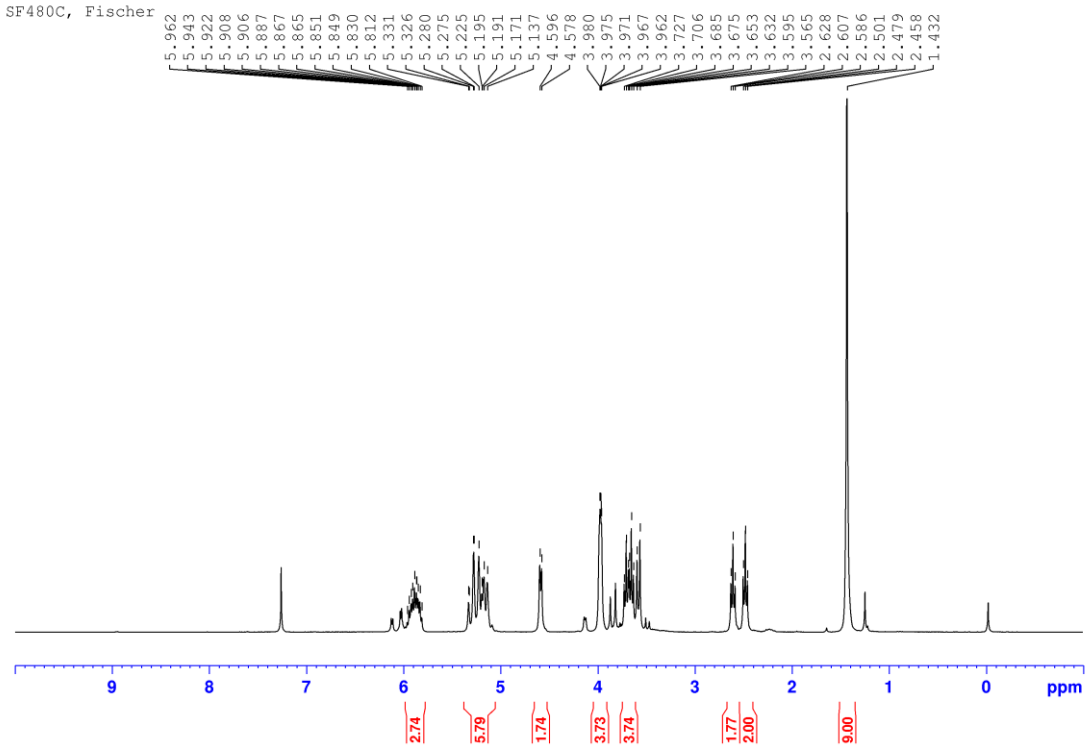


*Figure S5 [1]H-NMR spectrum (300 MHz, $CDCl_3$) of **4c** and **4c-s** prepared with 5 mol % TTMPP after 24 h*

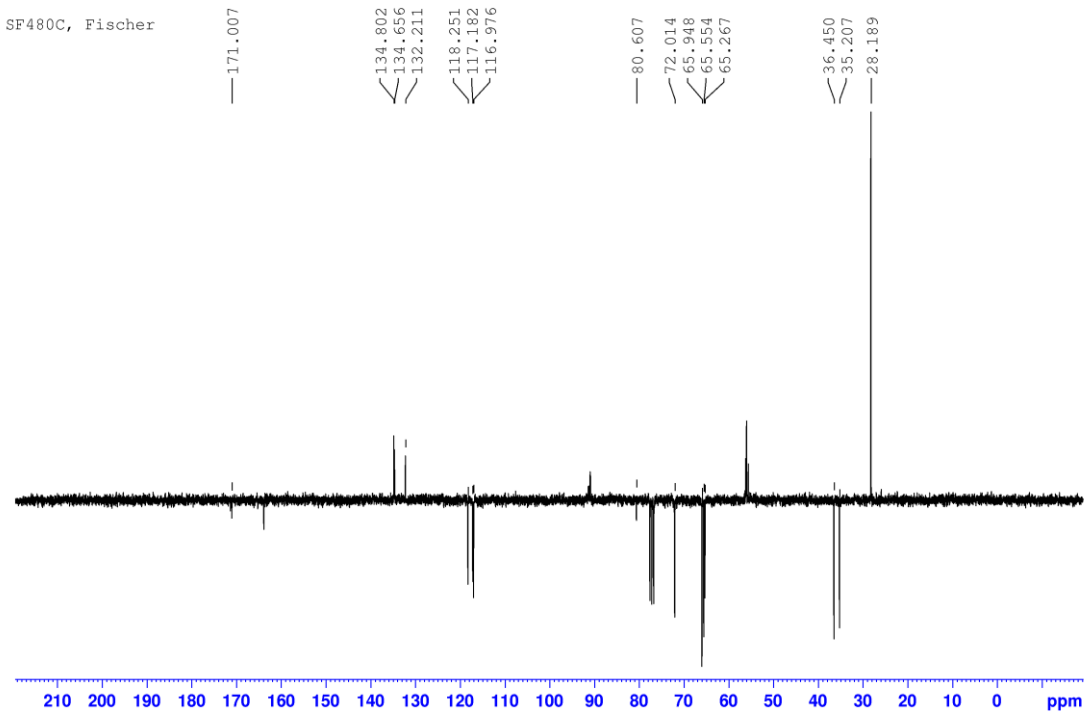


*Figure S6 [13]C-APT spectrum (75.53 MHz, $CDCl_3$) of **4c** and **4c-s** prepared with 5 mol % TTMPP after 24 h*

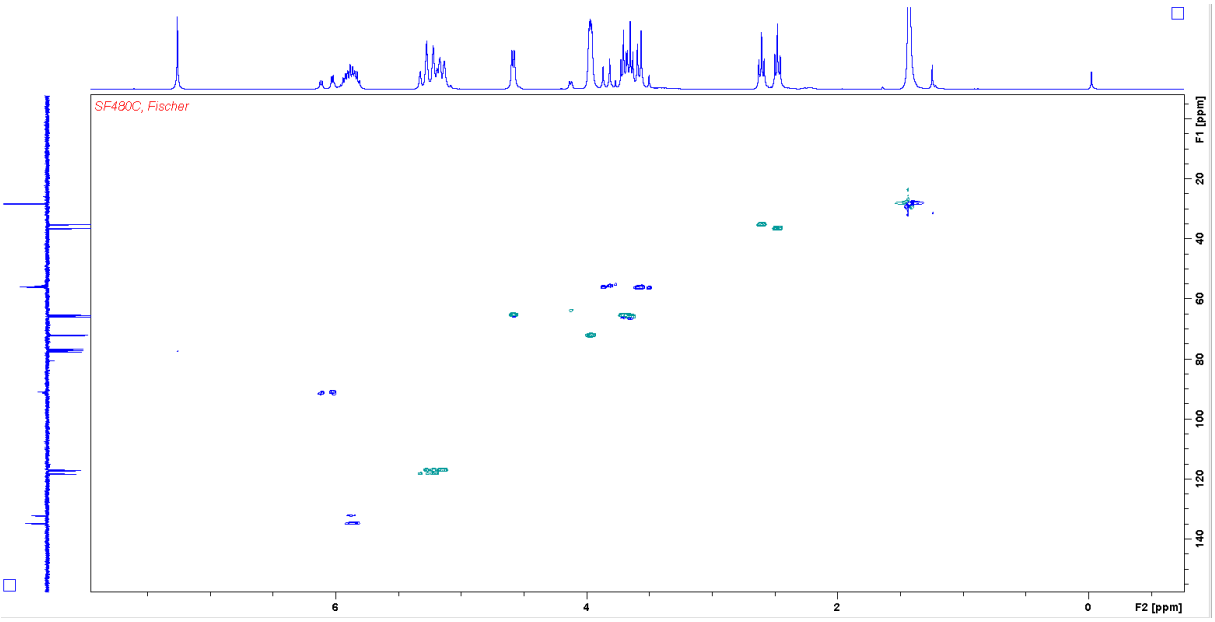
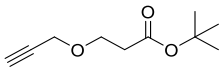


*Figure S7 HSQC of **4c** and **4c-s** prepared with 5 mol % TTMPP after 24 h*

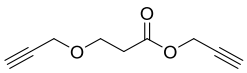
tert-butyl 3-(prop-2-yn-1-yloxy)propanoate (4d)



^{1}H-NMR (300.36 MHz, $CDCl_3$): δ 4.13 (d, 2H, C-*CH2*-O), 3.74 (t, 2H, O-*CH2*-CH2-), 2.49 (t, 2H, O-CH2-*CH2*), 1.43 (s, 9H, CH3), 2.41 (1H)

^{13}C-APT NMR (75.53 MHz, $CDCl_3$): δ 170.7, 80.8, 79.7, 74.5, 65.7, 58.3, 36.2, 28.2

*side product: prop-2-yn-1-yl 3-(prop-2-yn-1-yloxy)propanoate (**4d-s**)*



After 24 hours, no side product could be observed. After 7 days, 7.1 % of **4d-s** could be detected.

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ 4.68 (d, 2H), 4.13 (d, 2H), 3.74 (t, 2H), 2.64 (t, 2H)

^{13}C-APT NMR (75.53 MHz, $CDCl_3$): δ 170.7, 79.7, 74.5, 65.1, 52.2, 34.7, 28.2

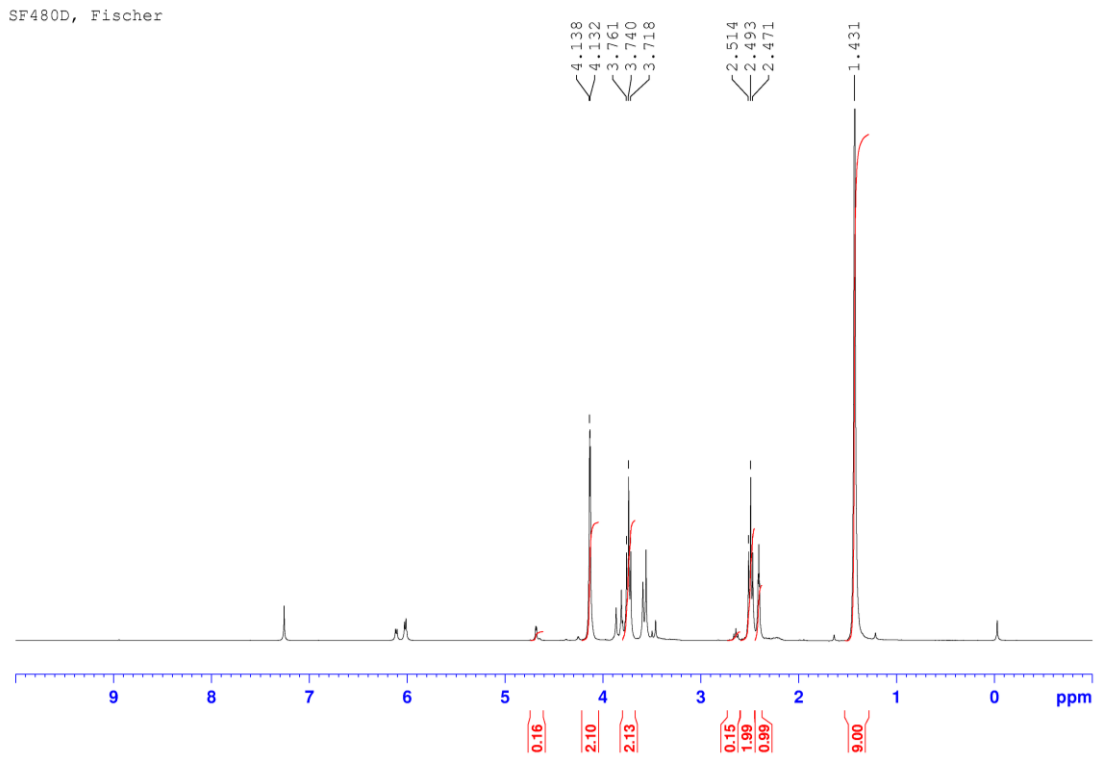


*Figure S8 ^{13}C-APT spectrum (75.53 MHz, $CDCl_3$) of **4d** and **4d-s** prepared with 5 mol % TTMPP after 24 h*

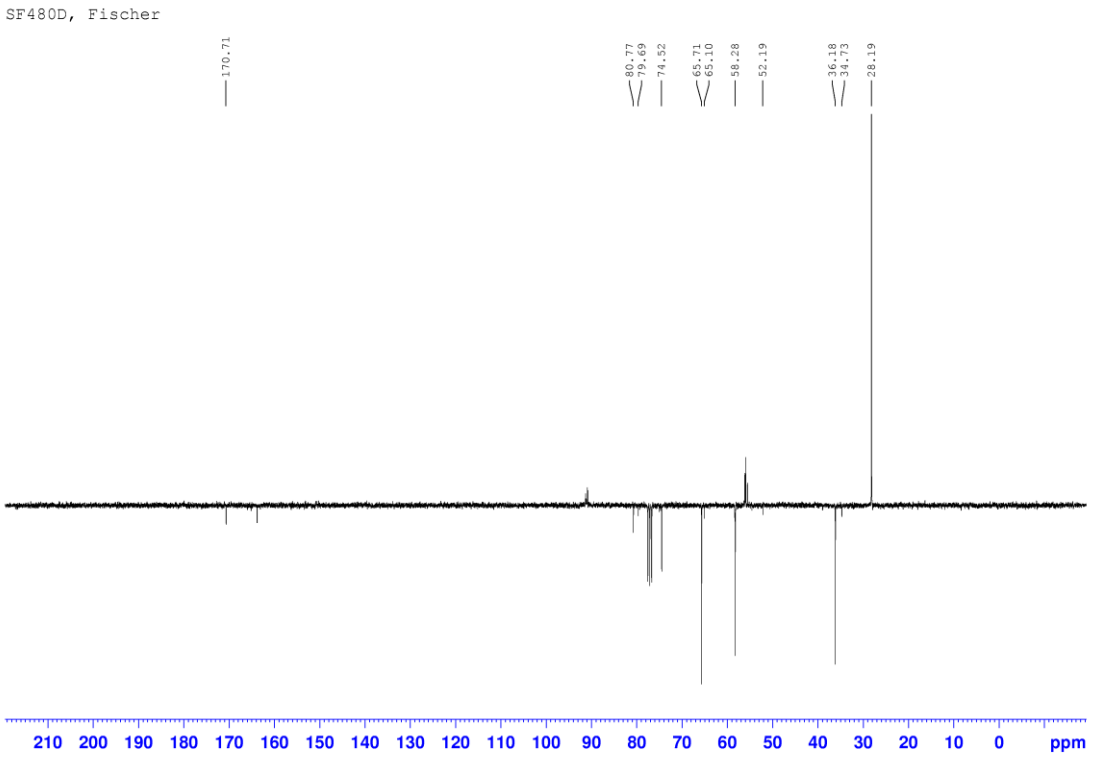


*Figure S9 ^{13}C-APT spectrum (75.53 MHz, $CDCl_3$) of **4d** prepared with 5 mol % TTMPP after 24 h*

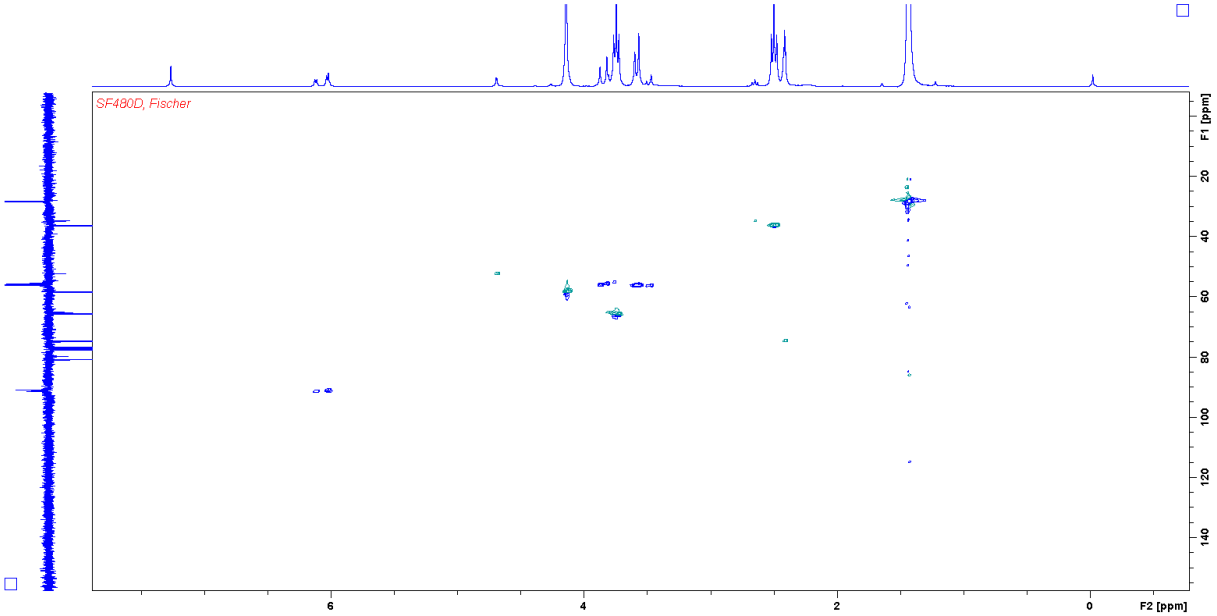
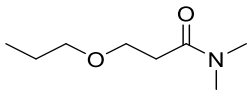


*Figure S10 HSQC of **4d** and **4d-s** prepared with 5 mol % TTMPP after 24 h*

N,N-Dimethylacrylamide as acceptor :



N,N-dimethyl-3-propoxypropanamide (5b)

^{1}H-NMR (300.36 MHz, $CDCl_3$): δ 3.73 (t, 2H, -O-*CH2*-CH2), 3.39 (t, 2H, CH3-CH2-*CH2*-), 3.00 (s, 3H, CH3), 2.93 (s, 3H, CH3), 2.60 (t, 2H, -O-CH2-*CH2*), 1.57 (m, 2H, CH3-*CH2*-CH2), 0.89 (t, 3H, CH3)

^{13}C-APT NMR (75.53 MHz, $CDCl_3$): δ 171.0, 72.9, 66.9, 37.3, 35.2, 33.8, 22.8, 10.5

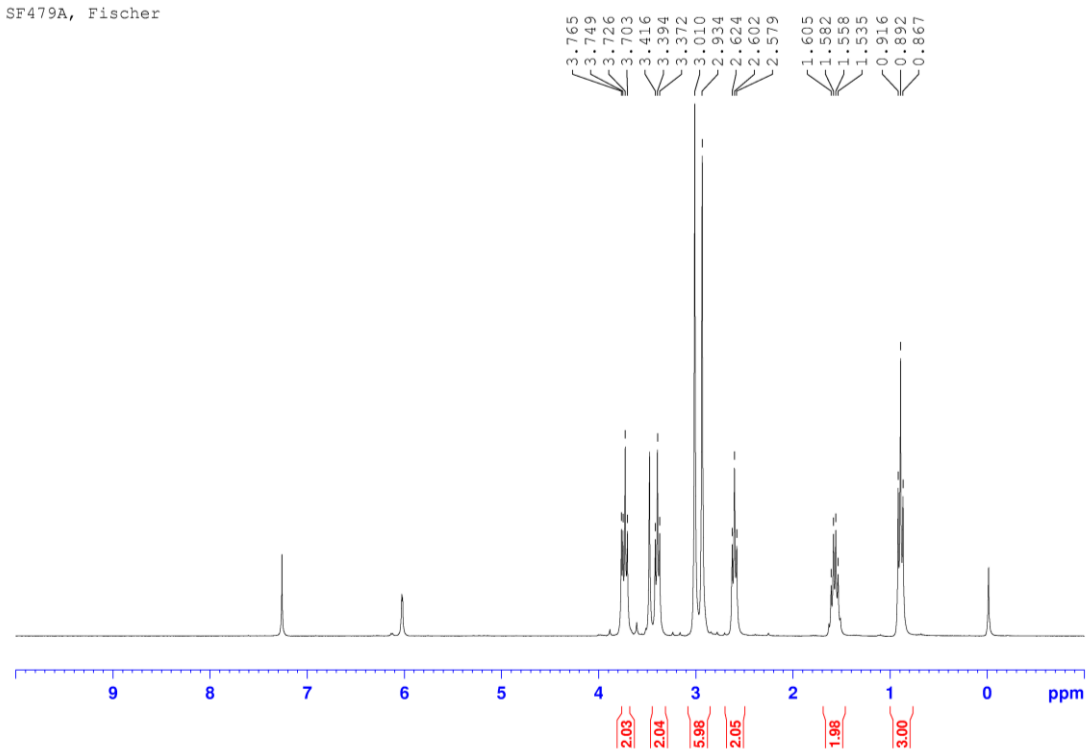


*Figure S11 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **5b** prepared with 5 mol % TTMPP after 24 h*

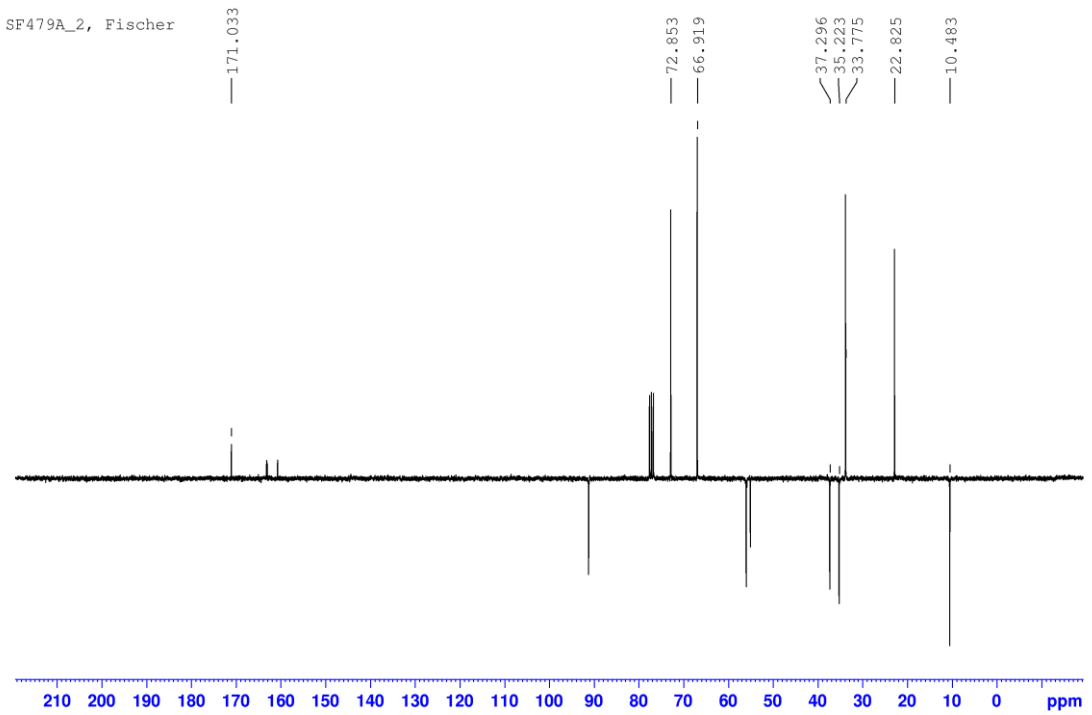
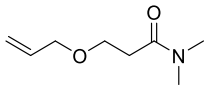


*Figure S12 ^{13}C-APT spectrum (75.53 MHz, $CDCl_3$) of **5b** prepared with 5 mol % TTMPP after 24 h*

3-(allyloxy)-N,N-dimethylpropanamide (5c)



^{1}H-NMR (300.36 MHz, $CDCl_3$): δ 5.95-5.82 (m, 1H, CH2=C*H*-CH2), 5.28-5.14 (dd, 2H, *CH2*=CH-CH2), 3.98 (d, 2H, - CH2=CH-*CH2*-), 3.75 (t, 2H, -O-*CH2*-CH2), 3.00 (s, 3H, CH3), 2.93 (s, 3H, CH3), 2.60 (t, 2H, -O-CH2-*CH2*)

^{13}C-APT NMR (75.53 MHz, $CDCl_3$): δ 170.9 (C=O), 134.7 (CH2=*CH*-CH2), 117.0 (*CH2*=CH-CH2), 72.1 (CH2=CH-*CH2*), 66.5 (-O-*CH2*-CH2), 37.3 (CH3), 35.3 (CH3), 33.7 (-O-CH2-*CH2*)

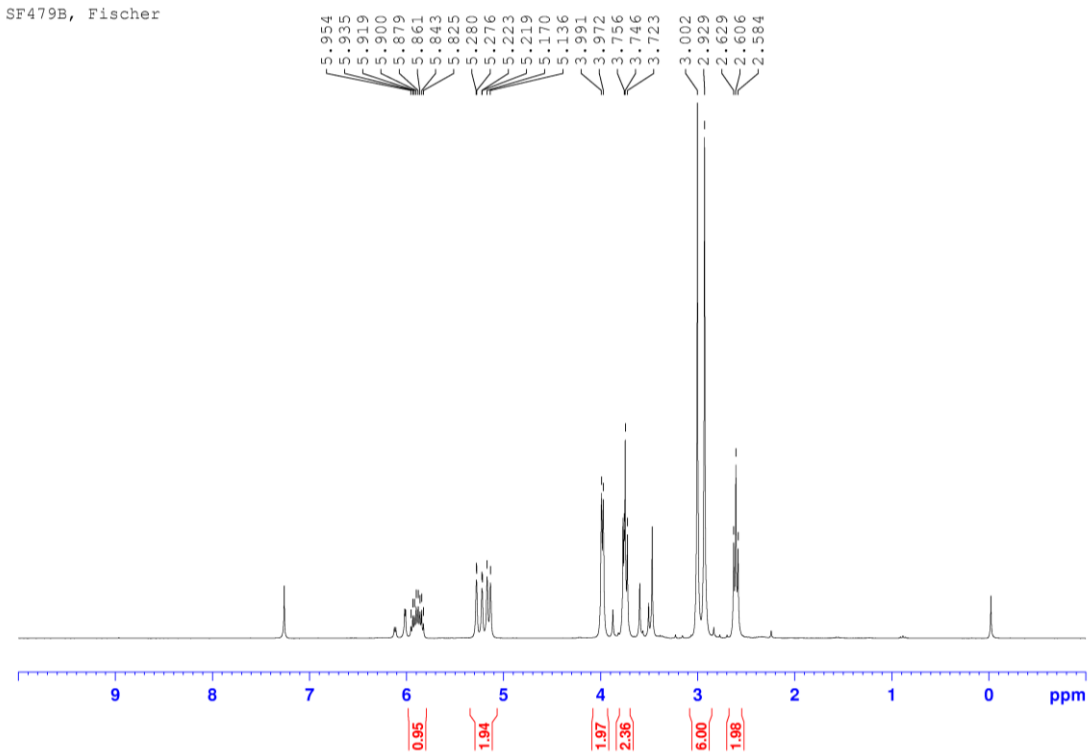


*Figure S13 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **5c** prepared with 5 mol % TTMPP after 24 h*

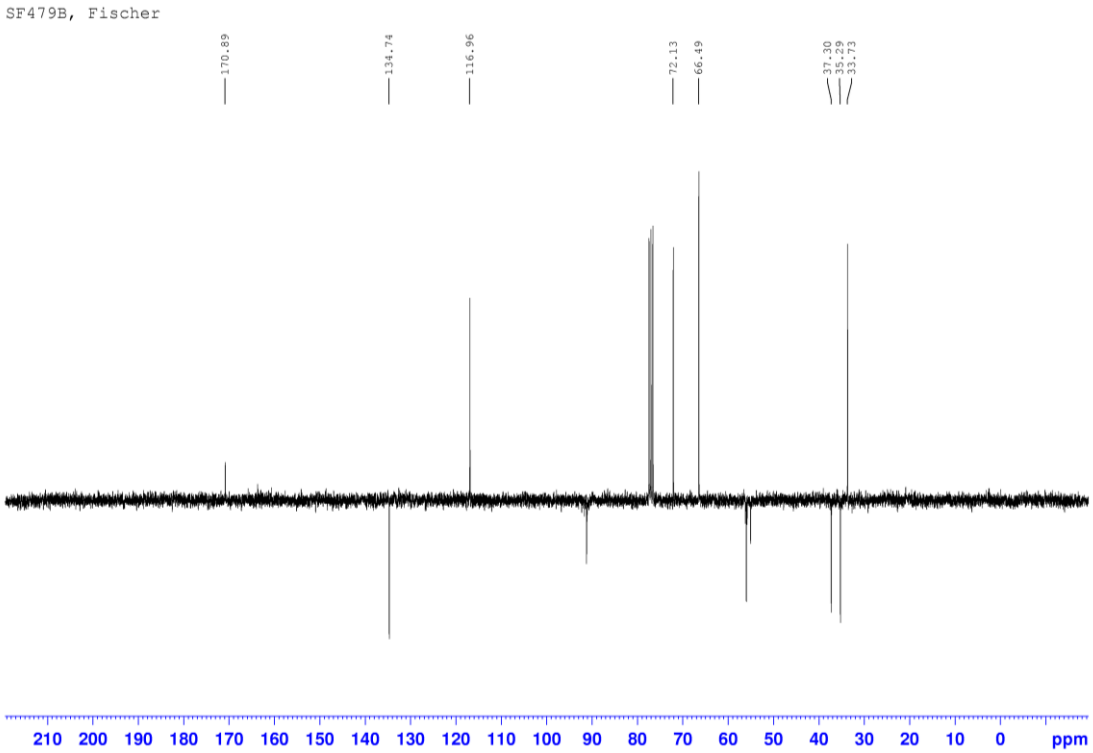


*Figure S14 ^{13}C-APT spectrum (75.53 MHz, $CDCl_3$) of **5c** prepared with 5 mol % TTMPP after 24 h*

Computational Details

All calculations were run with the TURBOMOLE program (version 7.4.1).[5] Conformational searches of all structures were performed with the COSMO-conf programme with geometries optimized at the PBE[6]/def2-SVPD[7,8] level using D3[9]-dispersion correction. Furthermore, single point energies were calculated using PBE+D3/def2-TZVPPD. All structures were then re-optimized using the hybrid functional B3LYP[10,11,12,13]-D3 with the def2-TZVPPD basis set using the conductor like screening model (COSMO) [14,15] to consider solvent effects of *t*-butanol (ε=12.4, r=3.35). Analytical normal modes were determined using the TURBOMOLE's aoforce program for confirmation of the stationary points and calculation of the frequencies. Temperature effects (298 K) and zero-point energies have been approximated by the rigid-rotor-harmonic oscillator (RRHO) approximation. The zero-point energies have been scaled by a factor of 1.0030 (B3LYP/def2-TZVPPD) to account for anharmonic effects.[16]

The Gibbs' free energies of products **3a-d** and **4a-d** were calculated using the abovementioned method to clarify the experimentally observed reactivity trends. Products containing i-propanol and propargyl alcohol are thermodynamically unfavored compared to products containing n-propanol and allyl alcohol.

Table S1 Energies of reaction products 3a-d [kJ/mol], calculated at B3LYP-D3/def2-TZVPPD level

	Electronic energy [kJ/mol]	Δ E el [kJ/mol]	Chem. Pot. [kJ/mol]	Gibbs free energy [kJ/mol]	Δ G [kJ/mol]
Acrylamide (**3**)	-649250.9		132.2	-649118.7	
iso-propanol (**a**)	-510232.7		210.4	-510022.2	
n-propanol (**b**)	-510199.7		212.6	-509987.1	
allyl alcohol (**c**)	-506968.1		152.2	-506815.9	
propargyl alcohol (**d**)	-503705.5		89.4	-503616.1	
3a	-1159531.2	-47.7	404.1	-1159127.2	13.8
3b	-1159521.1	-70.5	407.4	-1159113.7	-7.9
3c	-1156287.8	-68.9	346.6	-1155941.3	-6.7
3d	-1153005.7	-49.3	284.0	-1152721.8	13.0

Table S2 Energies of reaction products 4a-d [kJ/mol], calculated at B3LYP-D3/def2-TZVPPD level

	Electronic energy [kJ/mol]	Δ E el [kJ/mol]	Chem. Pot. [kJ/mol]	Gibbs free energy [kJ/mol]	Δ G [kJ/mol]
t-butyl acrylate (**4**)	-916603.9		367.5	-916236.5	
iso-propanol (**a**)	-510232.7		210.4	-510022.2	
n-propanol (**b**)	-510199.7		212.6	-509987.1	
allyl alcohol (**c**)	-506968.1		152.2	-506815.9	
propargyl alcohol (**d**)	-503705.5		89.4	-503616.1	
4a	-1426879.7	-43.1	636.5	-1426243.2	15.5
4b	-1426870.5	-67.0	639.7	-1426230.8	-7.3
4c	-1423638.9	-66.9	580.5	-1423058.4	-6.1
4d	-1420354.7	45.3	513.4	-1419841.3	11.3

Solvents and dilution

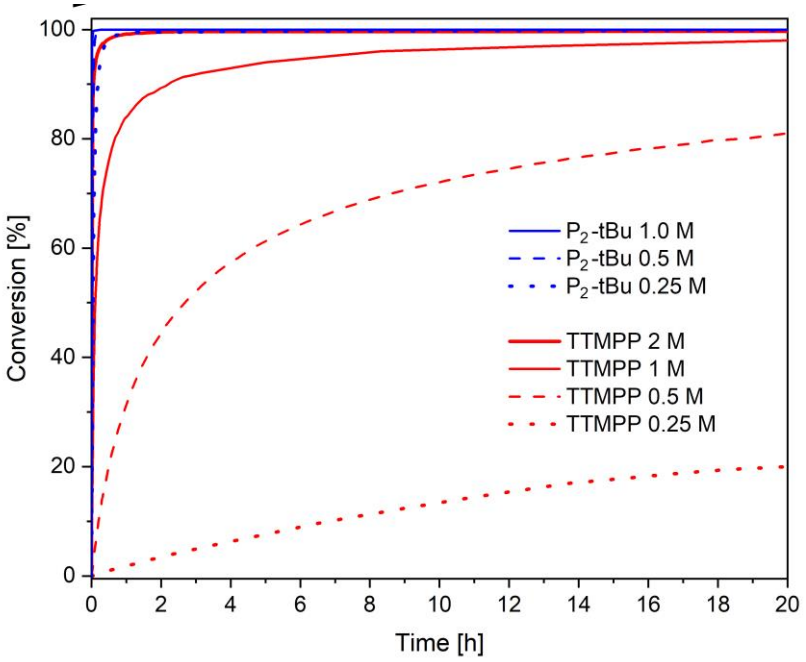


Figure S15 Double bond conversion of acrylonitrile [%] in the reaction with 1.5 equiv. n-propanol and 1 mol % TTMPP in various concentrations in benzene-d6.

Nucleophile or base?

^{31}P-NMR reaction monitoring

Experimental

TTMPP (23.4 mg, 0.084 equiv.) was dissolved in DMSO-d6 and an excess of allyl alcohol (50 µl, 1.4 equiv.) was added. Then, ^{1}H- and ^{31}P-NMR spectra were recorded and no change of signals could be observed (Figure S17). This indicates that no acid-base reaction has occurred between the alcohol and TTMPP. Protonation or nucleophilic addition of TTMPP would be indicated by an upfield shift of the phosphorous signal (Figure S19, Figure S22).

Then, acrylonitrile (34.2 µl, 1.0 equiv.) was added, and the reaction mixture was again subjected to NMR analysis. After 5 minutes, 77.2 % of acrylonitrile were converted, which increased to 90.1 % after 15 minutes and to 93.6 % after 24 hours. ^{31}P-NMR spectra were recorded after 5 minutes and after 24 hours (Figure S18). After 5 minutes, a new peak at 5.08 ppm arose which increased in intensity after 24 hours. The structure of the postulated phosphonium species is displayed in Figure S16.

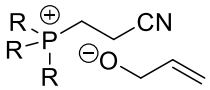


Figure S16 Postulated β-phosphonium species (ion pair) forming after addition of allyl alcohol and acrylonitrile to TTMPP

Table S3 Relative share of species detected in ^{31}P NMR in the reaction of acrylonitrile with allyl alcohol in DMSO-d6 [%]

Time	Phosphine [%]	Ion pair[%]	Phosphine oxide [%]
5 min	96.2	3.8	0
24 hours	70.8	19.6	9.6

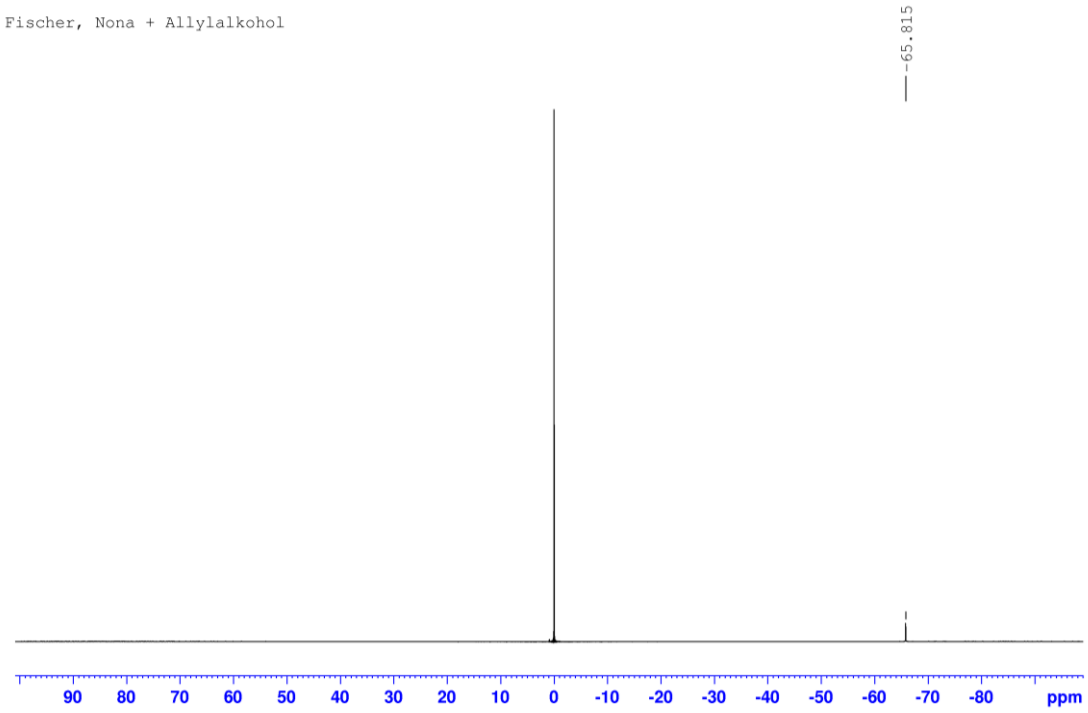


Figure S17 ^{31}P-NMR (202.55 MHz, DMSO-d_6) spectrum of TTMPP with an excess of allyl alcohol (relative to 85% H_3PO_4)

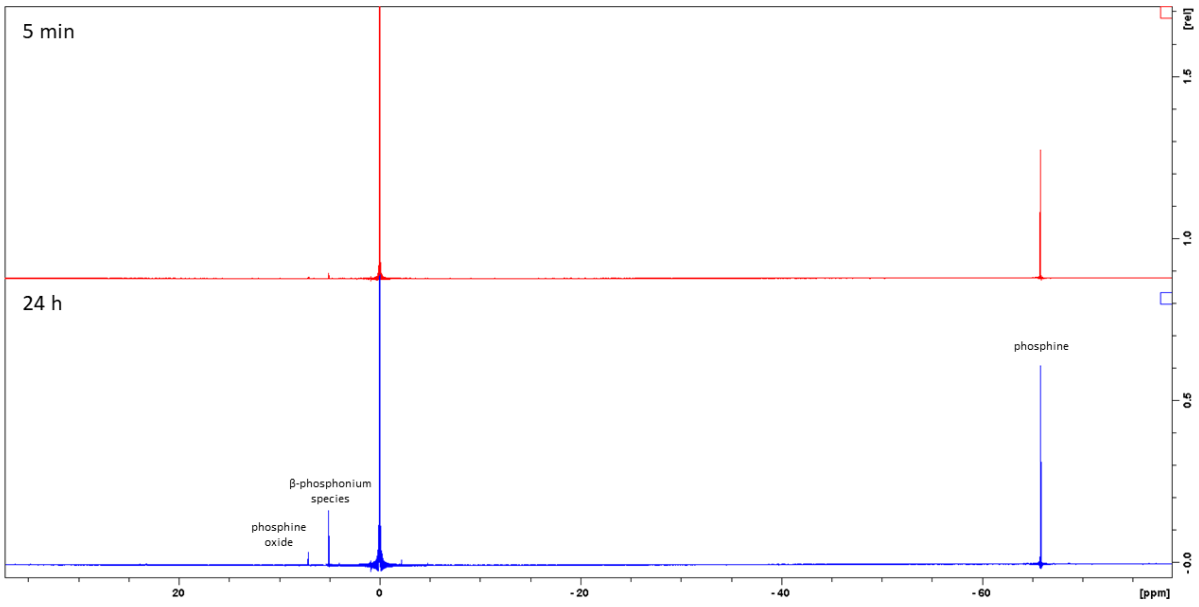


Figure S18 ^{31}P NMR spectra (relative to 85% H_3PO_4) of the reaction of acrylonitrile with allyl alcohol in DMSO-d6. Top: after 5 min; Bottom: after 24 h

Protonation of TTMPP

Experimental

TTMPP was dissolved in DMSO-d_6 and an excess of concentrated HCl was added. The NMR tube was shaked and subjected to ^{31}P- and ^{1}H-NMR measurements.

Results

Protonation of TTMPP with HCl results in a downfield shift of the ^{31}P signal from -69.54 to -53.17 ppm.

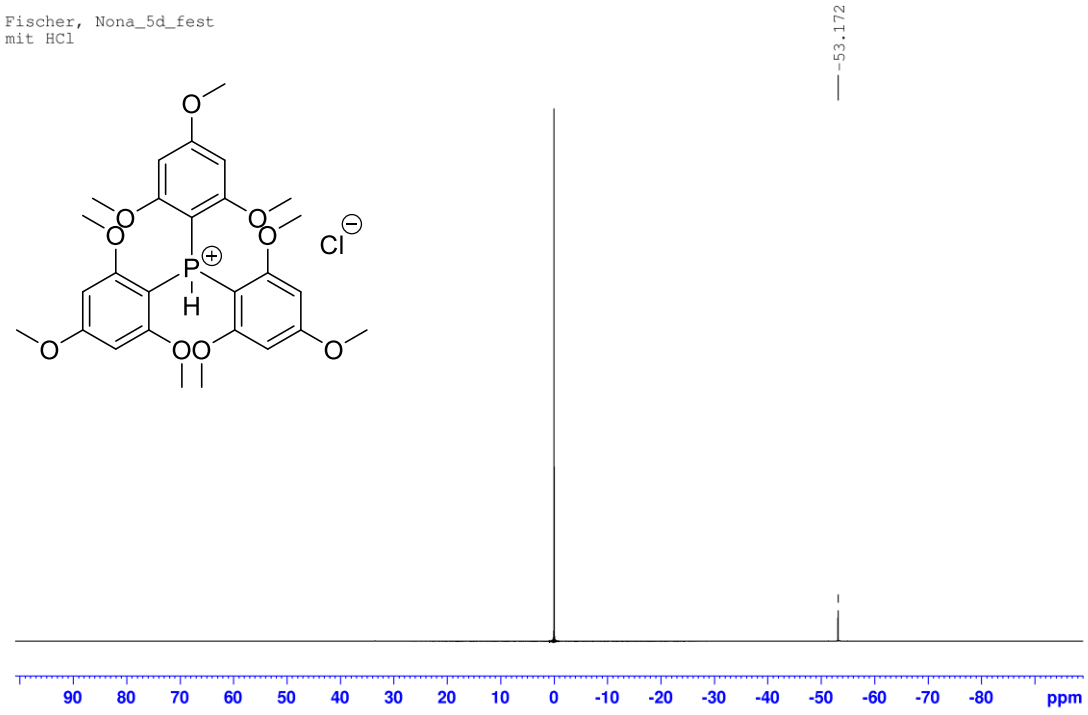


Figure S19 ^{31}P-NMR (202.55 MHz, DMSO-d_6) spectrum of protonated TTMPP (relative to 85% H_3PO_4)

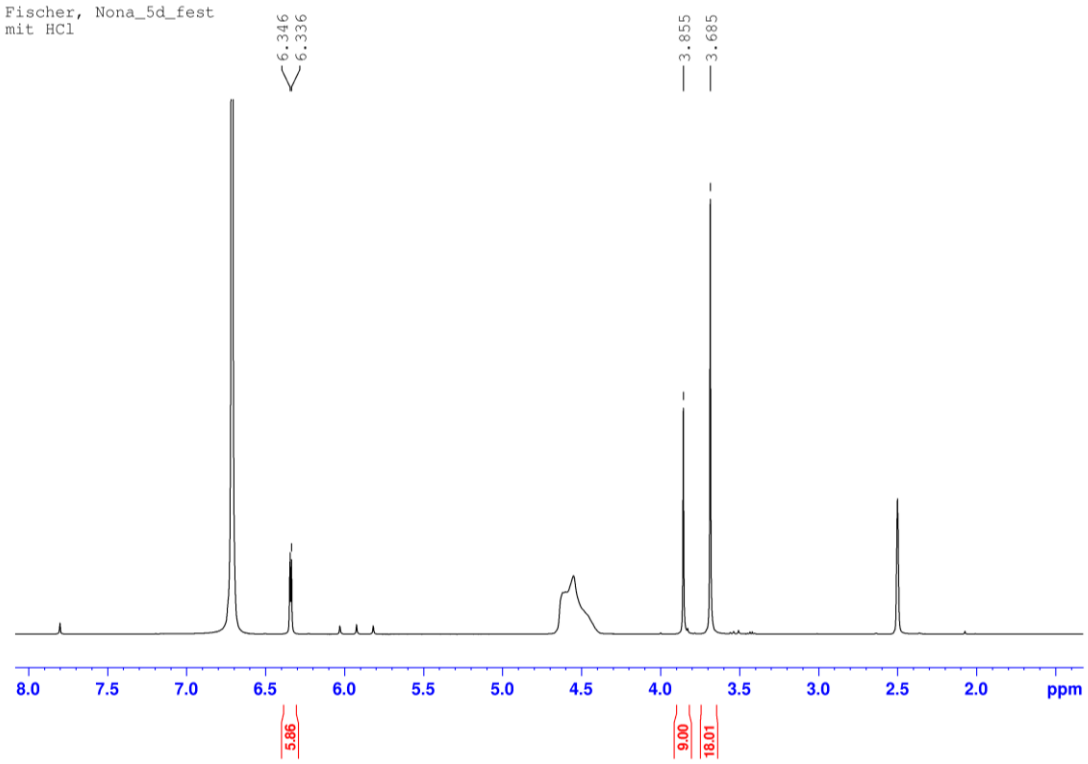


Figure S20 ^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of protonated TTMPP

Reaction with dichloromethane

Experimental

TTMPP (32.7 mg, 0.061 mmol) was dissolved in 2 mL of dichloromethane. The solution was stirred for 20 minutes before the solvent was evaporated. The product was dried under reduced pressure and was obtained as white solid in quantitative yield.

Characterization

^{1}H, ^{13}C-APT, HSQC and ^{31}P NMR spectra were recorded in DMSO-d6. The methylene protons are characterized by a doublet at 4.92 ppm in the ^{1}H spectrum. Since the signal in the ^{13}C NMR spectrum is superimposed by the solvent's residual signal, the spectrum was also recorded in $CDCl_3$ (Figure S25) where a doublet at 4.71 ppm in the ^{1}H NMR spectrum and a doublet at 40.8 ppm in the ^{13}C-APT spectrum could be attributed to the methylene protons.

^{1}H-NMR (500 MHz, DMSO-d_6): δ 6.31 (d, 6H, aryl-CH), 4.92 (d, 2H, CH_2), 3.86 (s, 9H, CH_3), 3.59 (s, 18H, CH_3)

^{13}C-APT spectrum (75.53 MHz, DMSO-d_6): δ 165.8, 163.8, 91.55, 91.45, 56.2, 55.8

^{13}C-APT spectrum (75.53 MHz, $CDCl_3$): δ 166.4, 164.1, 91.44, 91.35, 41.16, 40.27

^{31}P-NMR (202.55 MHz, DMSO-d_6): δ 8.5

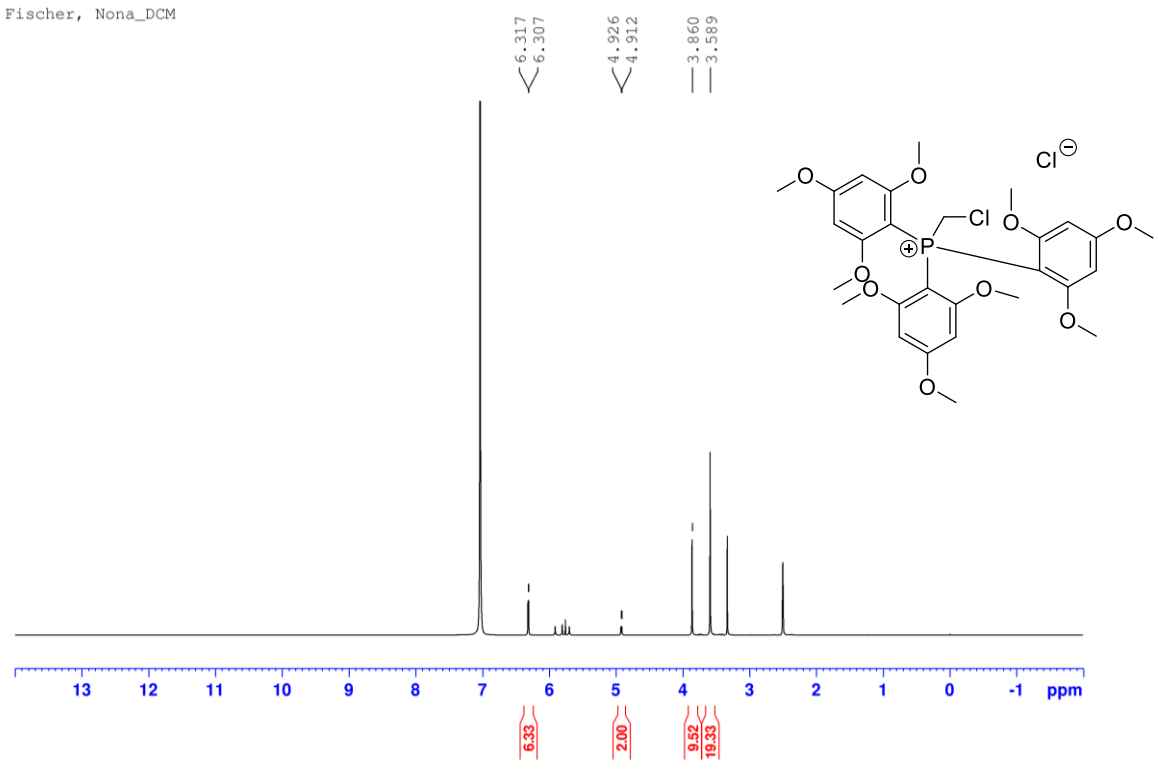


Figure S21 ^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of TTMPP-DCM

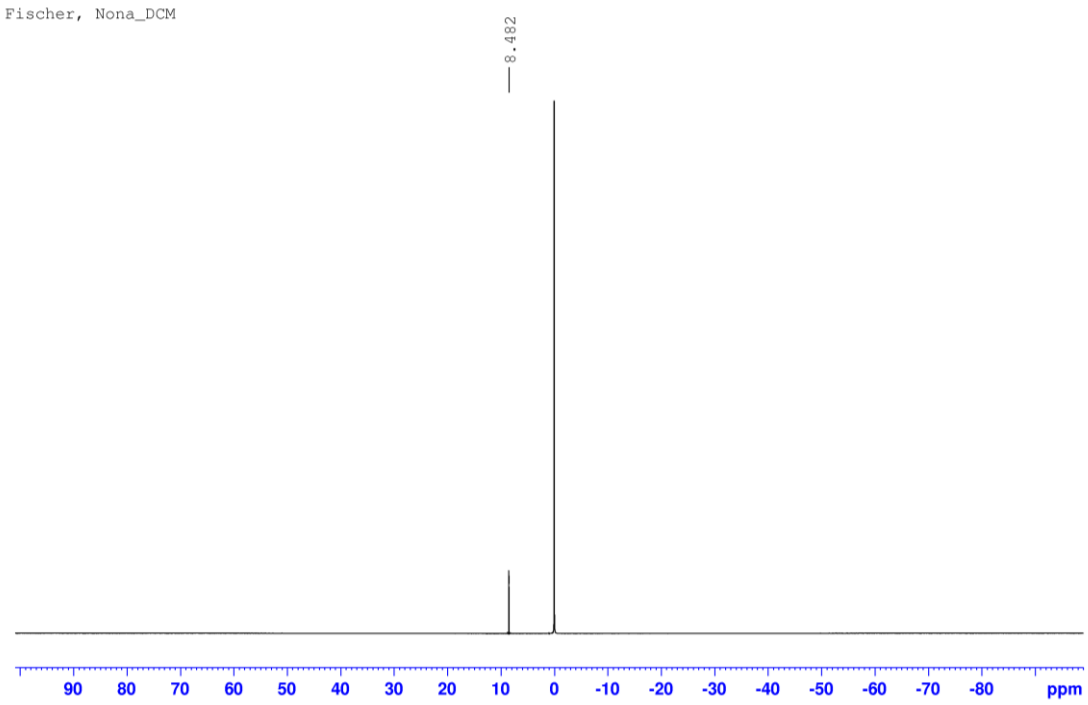


Figure S22 ^{31}P-NMR (202.55 MHz, DMSO-d_6) spectrum of TTMPP-DCM (relative to 85% H_3PO_4)

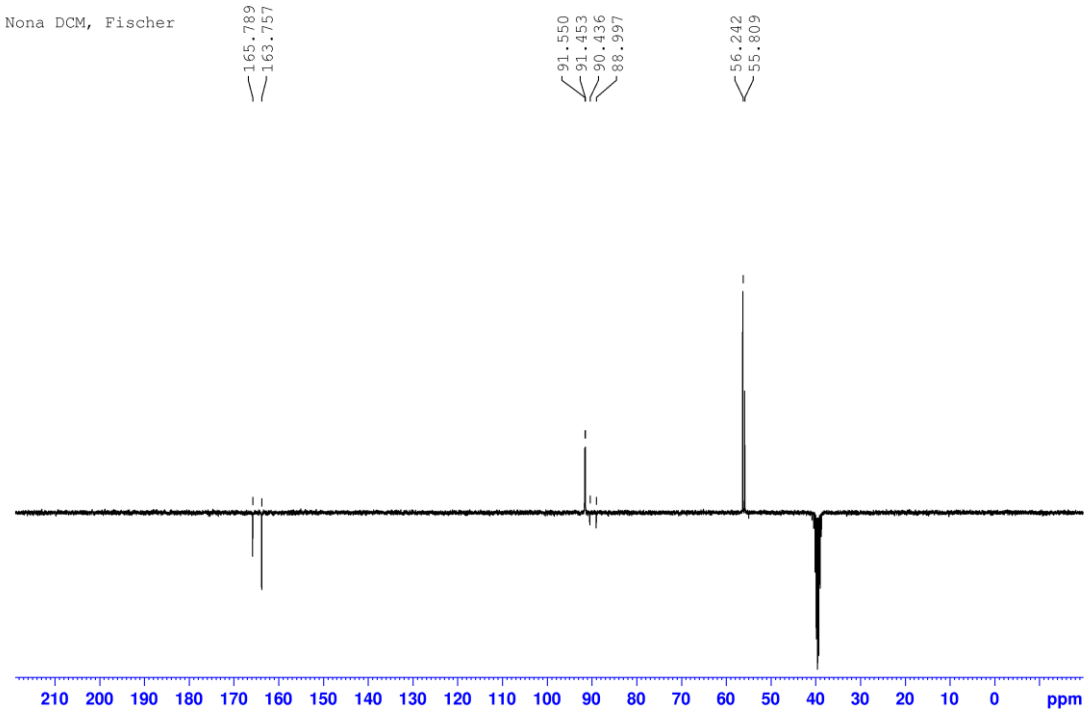


Figure S23 ^{13}C-APT spectrum (75.53 MHz, DMSO-d_6) of TTMPP-DCM

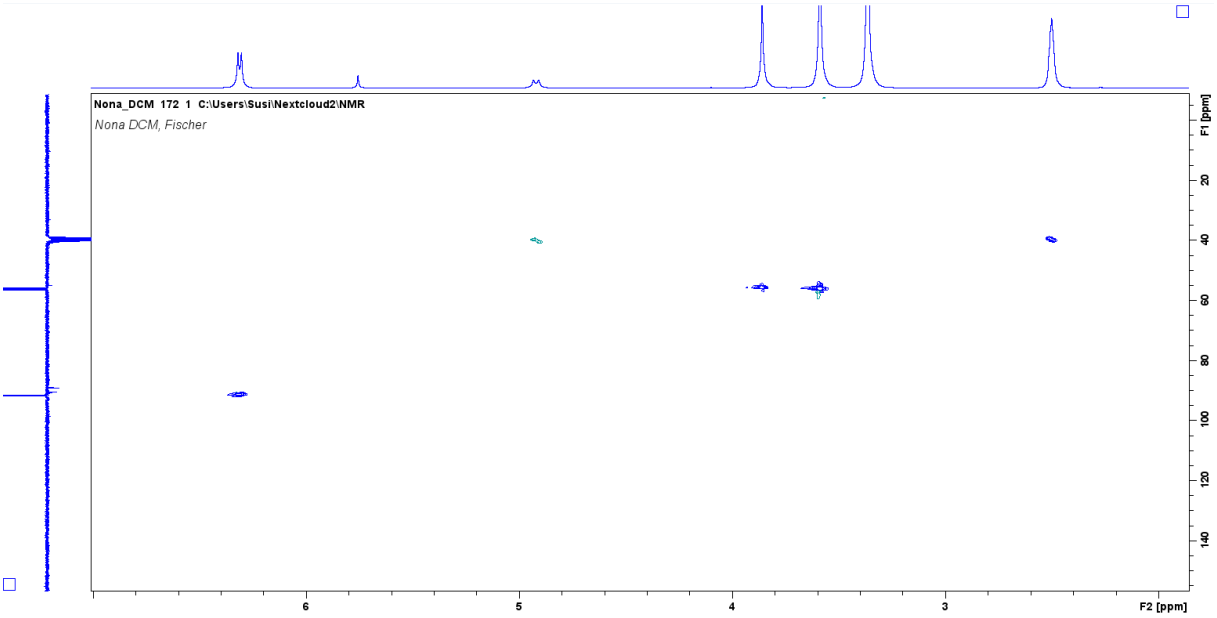


Figure S24 HSQC of TTMPP-DCM in DMSO-d_6

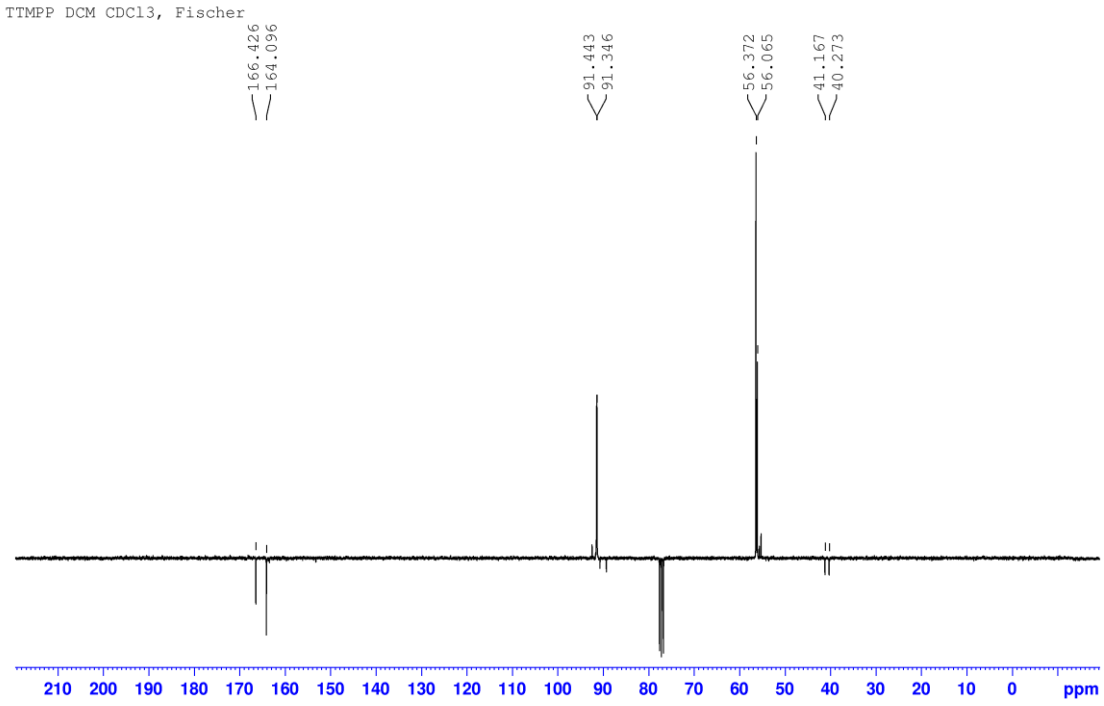


Figure S25 ^{13}C-APT spectrum (75.53 MHz, $CDCl_3$) of TTMPP-DCM

Oxa-Michael polymerisation

Oxa-Michael addition polymerisation of 2-hydroxyethyl acrylate (HEA)

Calculation of double bond conversion of 2-hydroxyethyl acrylate:

$$Double\ bond\ conversion\ [\%] = \frac{integral\ 2.62\ ppm\ /2}{integral\ 5.85 + integral\ 2.62/2} * 100$$

Calculation of Rauhut-Currier share:

$$Rauhut - Currier\ share\ [\%] = \frac{integral\ 5.61}{\frac{integral\ 2.62 - 4 * integral\ 5.61}{2}} * 100$$

Table S4 Double bond conversion of 2-hydroxyethyl acrylate [%] after 1 and 24 hours and Rauhut-Currier share [%] in parentheses

	TMTPP		TTMPP		P2-tBu	
Time	1h	24h	1h	24h	1h	24h
Double bond conversion [%] (Rauhut-Currier share)	75 (4)	94 (8)	95 (0)	98 (4)	95 (3)	97 (5)*

* Partly insoluble polymer, double bond conversion calculated from soluble fraction

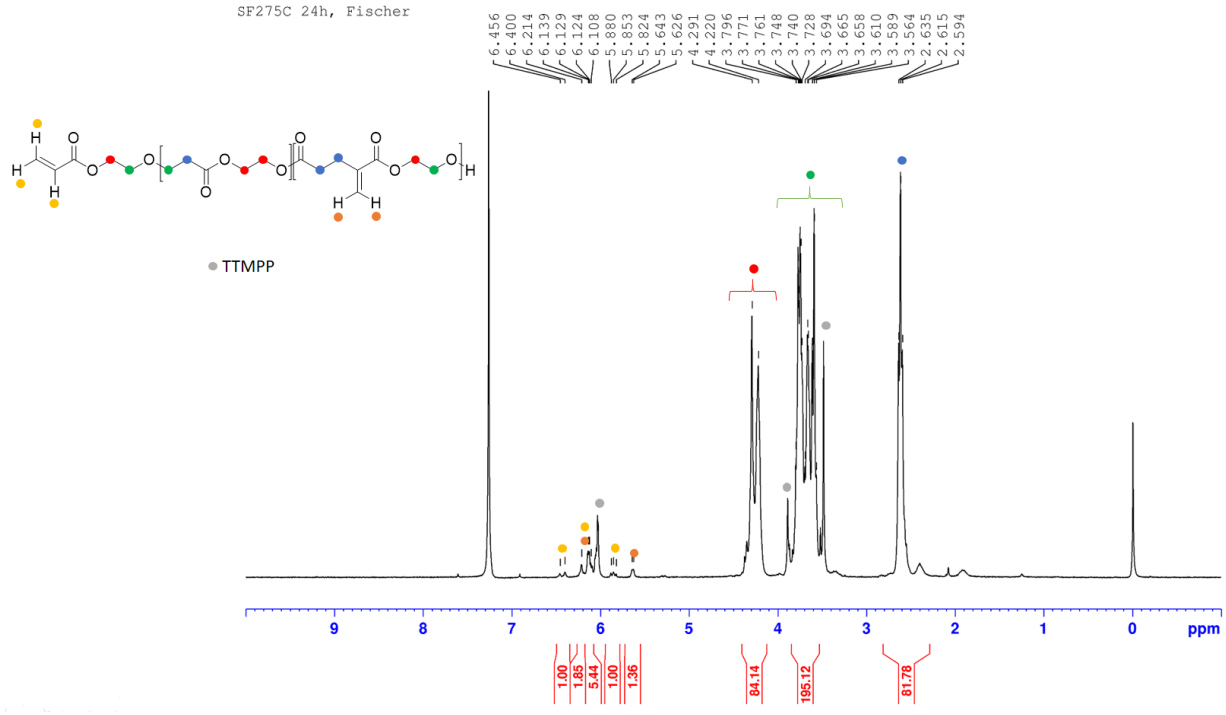


Figure S26 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of poly(HEA) after 24h at 23°C with TTMPP (5 mol %) as catalyst

^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.47 (d, 1H), 6.20 (s, 6H), 5.84 (d, 1H), 4.33-4.21 (m, 76 H), 3.82-3.56 (m, 141 H), 2.61 (t, 70H).

^{13}C-APT NMR (75.53 MHz, $CDCl_3$) δ 171.4, 126.6, 72.27, 70.39, 68.96, 66.80-66.15, 64.07, 63.88, 63.62, 62.33, 61.66, 60.98, 34.99.

Table S5 Molecular weight (M_n) [g/mol] and dispersities (~~Đ~~) of poly(HEA) obtained with 5 mol % TTMPP or P2-tBu at 23°C

Catalyst	Mn (~~Đ~~)
TTMPP	1190 g/mol (2.2) 1370 g/mol (2.3)
P_2-tBu	720 g/mol (2.6) 820 g/mol (2.8)

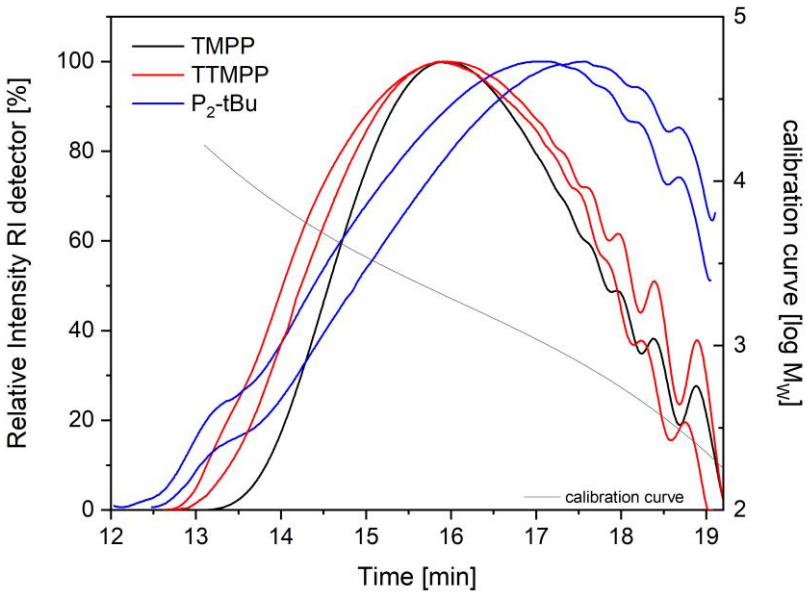
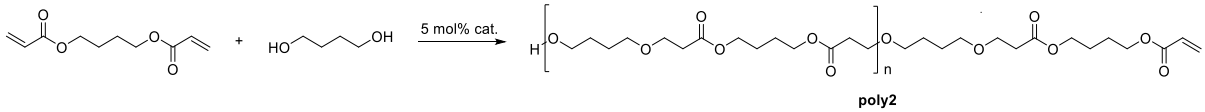


Figure S27 Size exclusion chromatograms (in THF, relative to poly(styrene) standards) of poly(HEA), prepared with 5 mol % TTMPP P_2-tBu using a reaction time of 24 h and a reaction temperature of 23°C

Oxa-Michael addition polymerisation with butane-1,4-diacrylate as Michael acceptor



poly2

Table S6 Double bond conversion of butane-1,4-diacrylate [%] after 1 and 24 hours reaction time at 23°C

Catalyst	Double bond conversion 1h [%]	Double bond conversion 24h [%]
TTMPP	86	88
TMG	25	66
P_2-tBu	93	94
TMTPP	24	33
MMTPP	10	27
DBU	11	22
TPP	4	17
DMAP	5	10
ABCO	0	9
K54	0	7

Table S7 Conversion of butane-1,4-diol [%] after 1 and 24 hours, molecular weight M_n of the formed polymers and polydispersity index (~~Đ~~)

Polymer	Alcohol	Catalyst	Conversion after 1h [%]	Conversion after 24h [%]	M_n [g/mol]	~~Đ~~
poly2	Butane-1,4-diol	TTMPP	88	88	1590	1.7
		TTMPP	86	87	1180	1.6
		TTMPP	85	86	1450	1.7
		P_2-tBu	94	94	2650	2.0
poly3	(Z)-butene-1,4-diol	TTMPP	84	83	1110	1.6
		TTMPP	83	84.	1200	1.6
		P_2-tBu	95	94.	1500	1.8
		P_2-tBu	87	87	1330	1.7
poly4	Butyne-1,4,-diol	TTMPP	72	90	1330	1.7
		P_2-tBu	63	90	1350	1.9
		P_2-tBu	63	92	1900	2.0

Calculation of degree of transesterification (DT) [%] for poly3 and poly4:

$$DT\ [\%\} = \frac{int\ (TE)}{int(TE) + int(OM)} * 100$$

poly2

^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.37 (d, 1H), 6.04 (m, 1H), 5.79 (dd, 1H), 4.07 (t, 17H), 3.65 (t, 22H), 3.42 (t, 16H), 2.53 (t, 16H), 1.59 (m, 37H)

^{13}C-APT NMR (75.53 MHz, $CDCl_3$) δ 171.7, 163.8, 130.7, 128.6, 70.7, 66.1, 64.2, 62.2, 35.2, 29.6, 26.2, 25.4

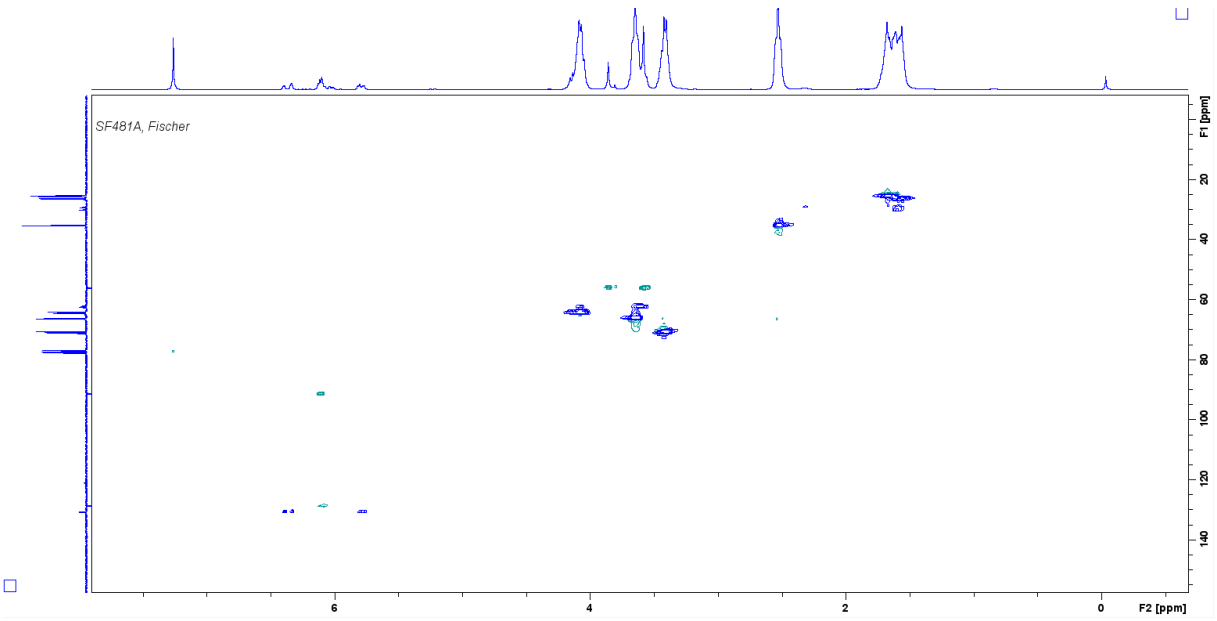


*Figure S28 HSQC of **poly2** prepared with 5 mol % TTMPP*

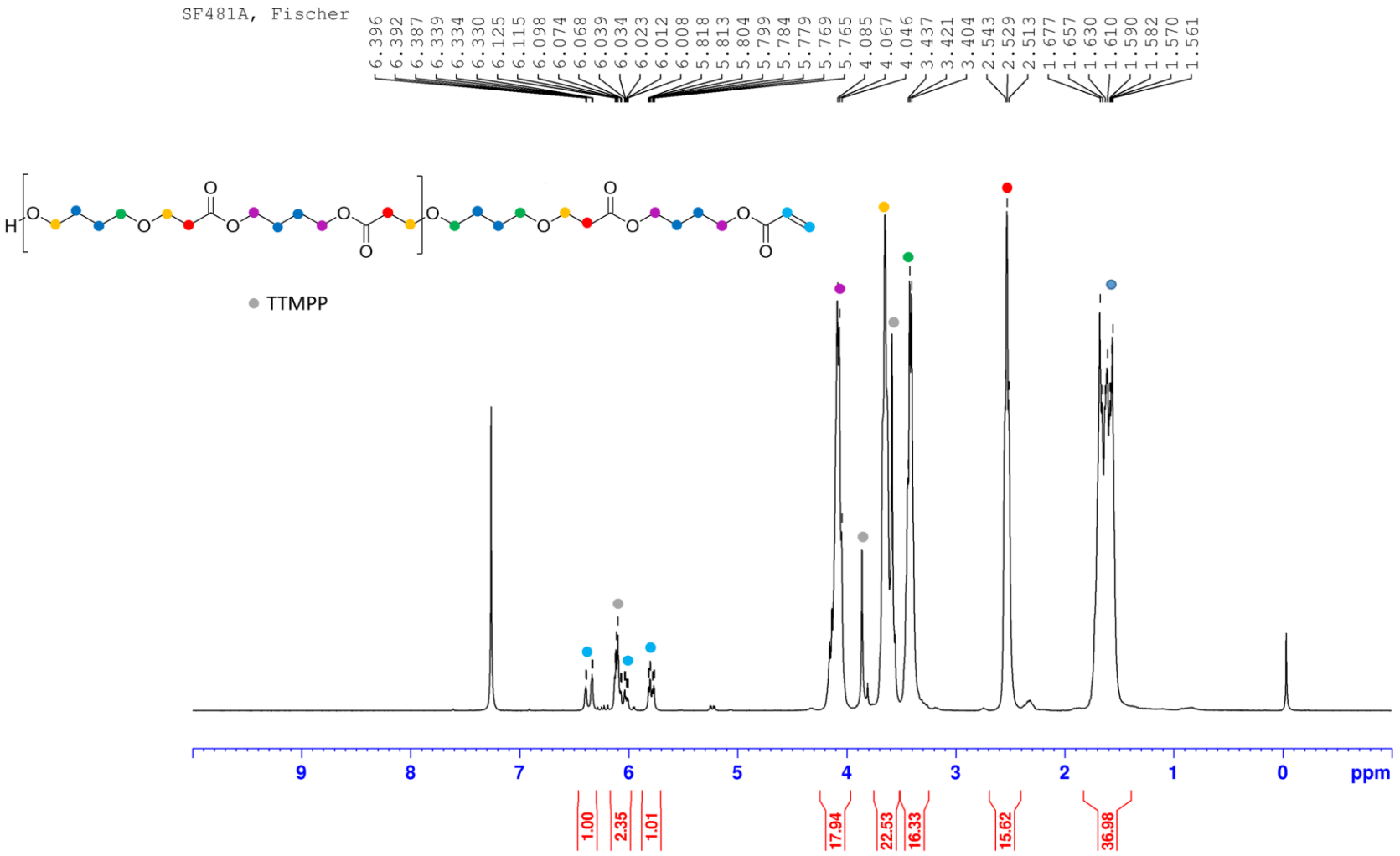


*Figure S29 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **poly2** prepared with 5 mol % TTMPP*

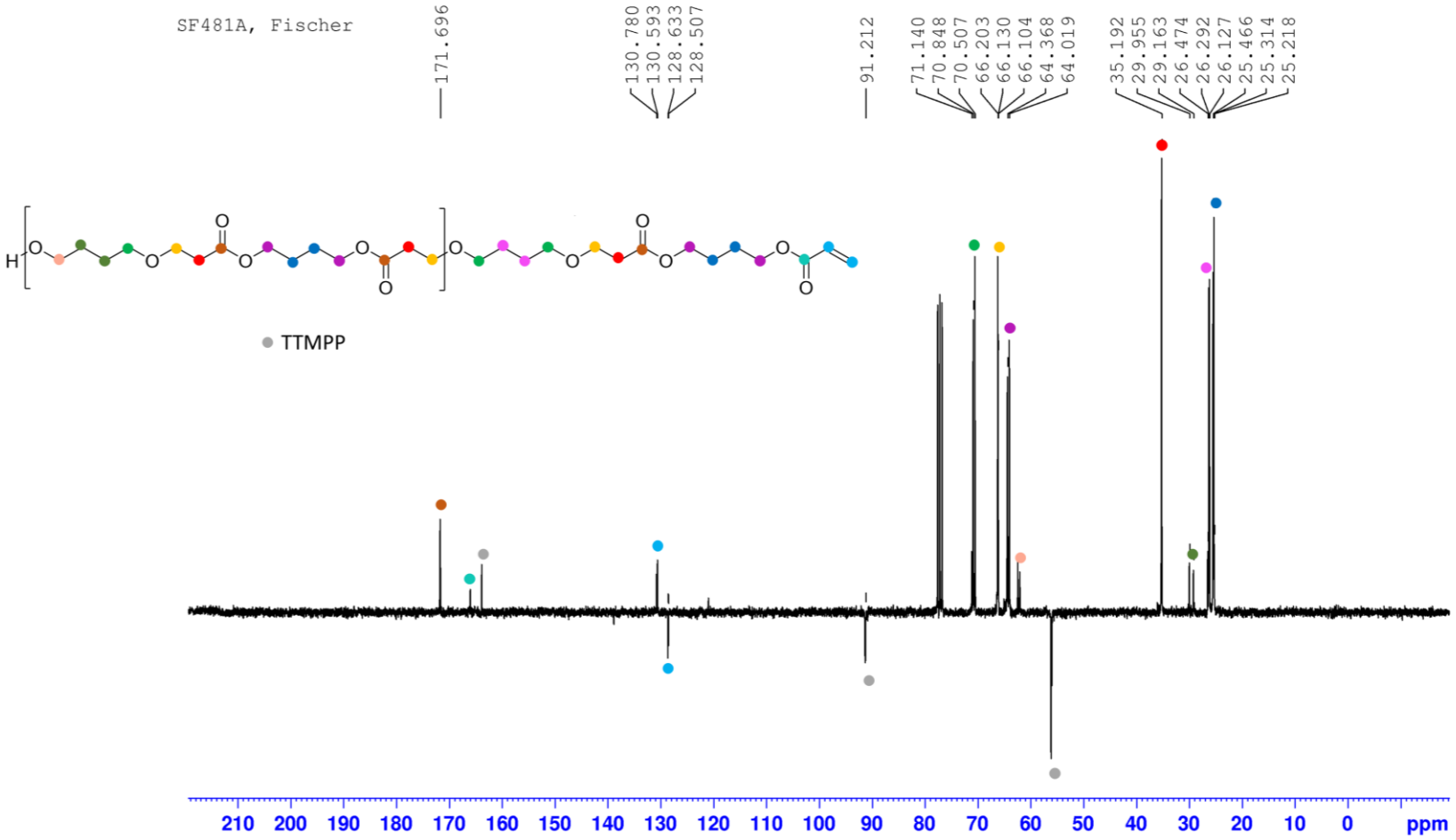
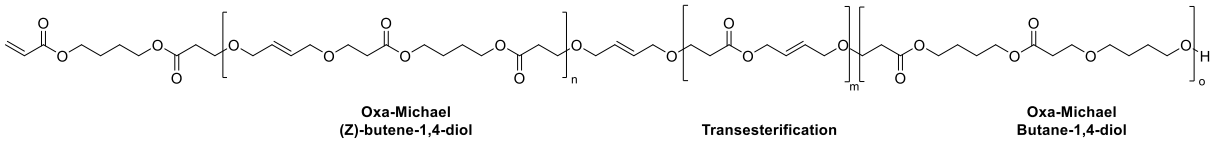


*Figure S30 ^{13}C-APT spectrum (75.53 MHz, CDCl3) of **poly2** prepared with 5 mol % TTMPP*

poly3



^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.36 (d, 1H), 6.09 (d, 1H), 5.79-5.63 (m, 8H), 4.67-4.61 (m, 4H), 4.14-4.00 (m, 21H), 3.64 (t, 17H), 3.41 (t, 2H), 2.53 (t, 12H), 1.67-1.59 (m, 14H)

^{13}C-APT NMR (75.53 MHz, $CDCl_3$) δ 171.5, 166.0, 130.7-126.6, 66.8-60.4, 35.1, 29.1, 25.2

Degree of transesterification was calculated from the integrals of the signal at 4.62 (TE) and 2.53 (OM) of the 1H NMR spectrum. Oxa-Michael BD product was calculated from the integral at 3.41 ppm.

Oxa-Michael ZBD: 48.5 %; Transester: 30.0%; Oxa-Michael BD: 21.5 %

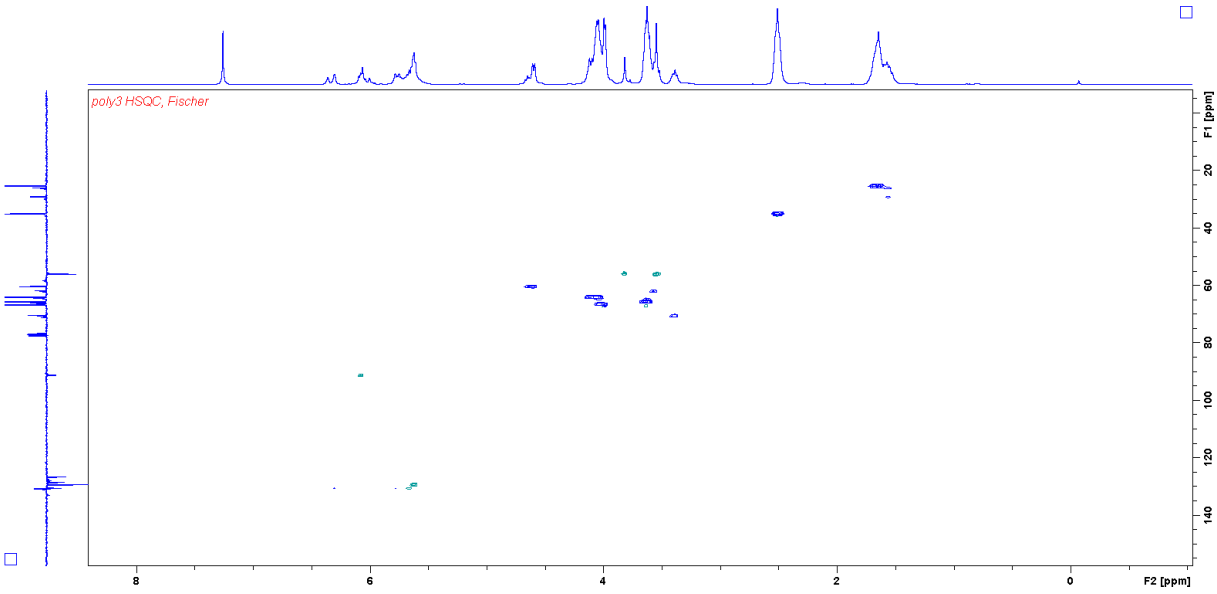


*Figure S31 HSQC of **poly3** prepared with 5 mol % TTMPP*

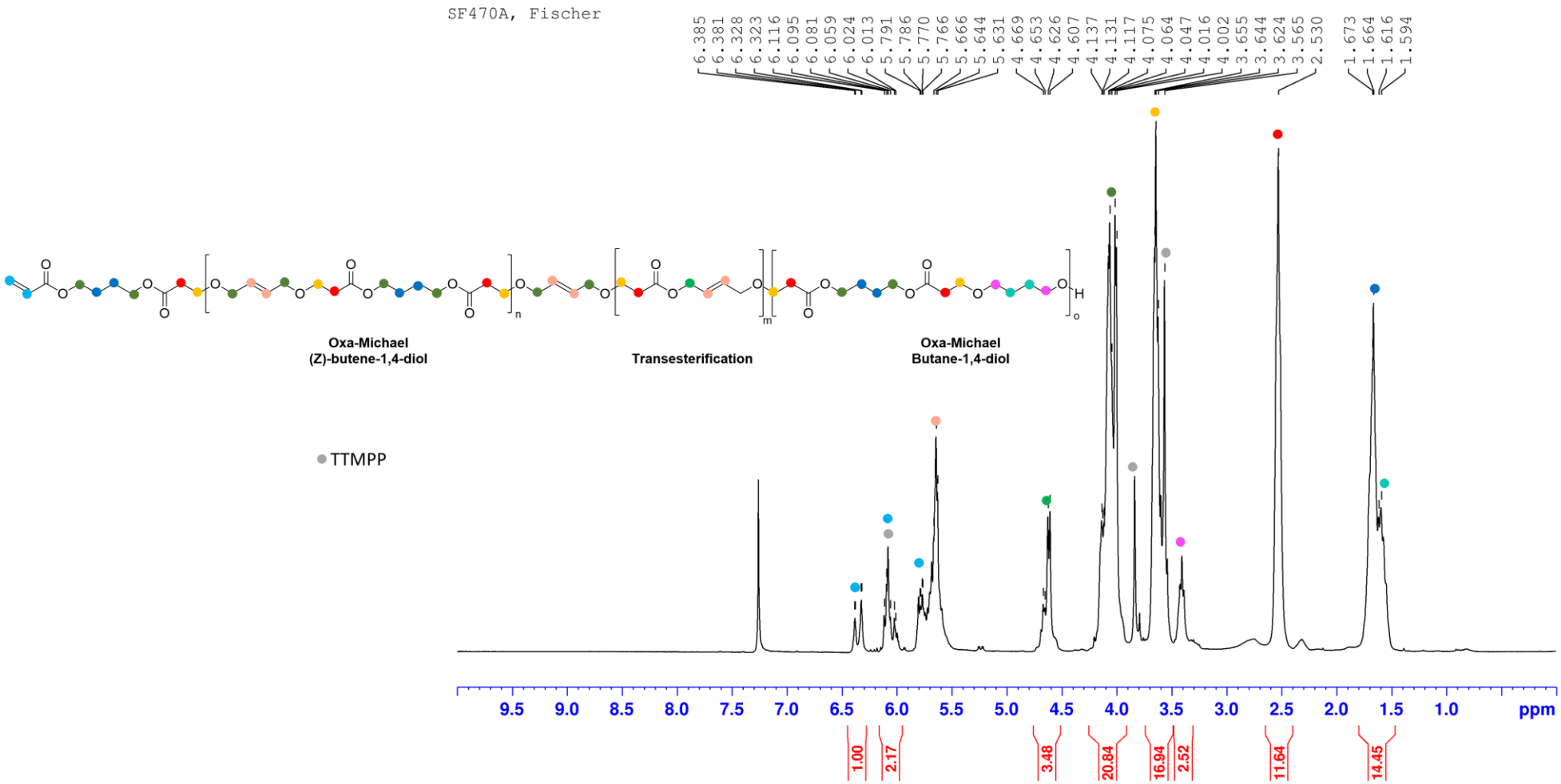


*Figure S32 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **poly3** prepared with 5 mol % TTMPP*

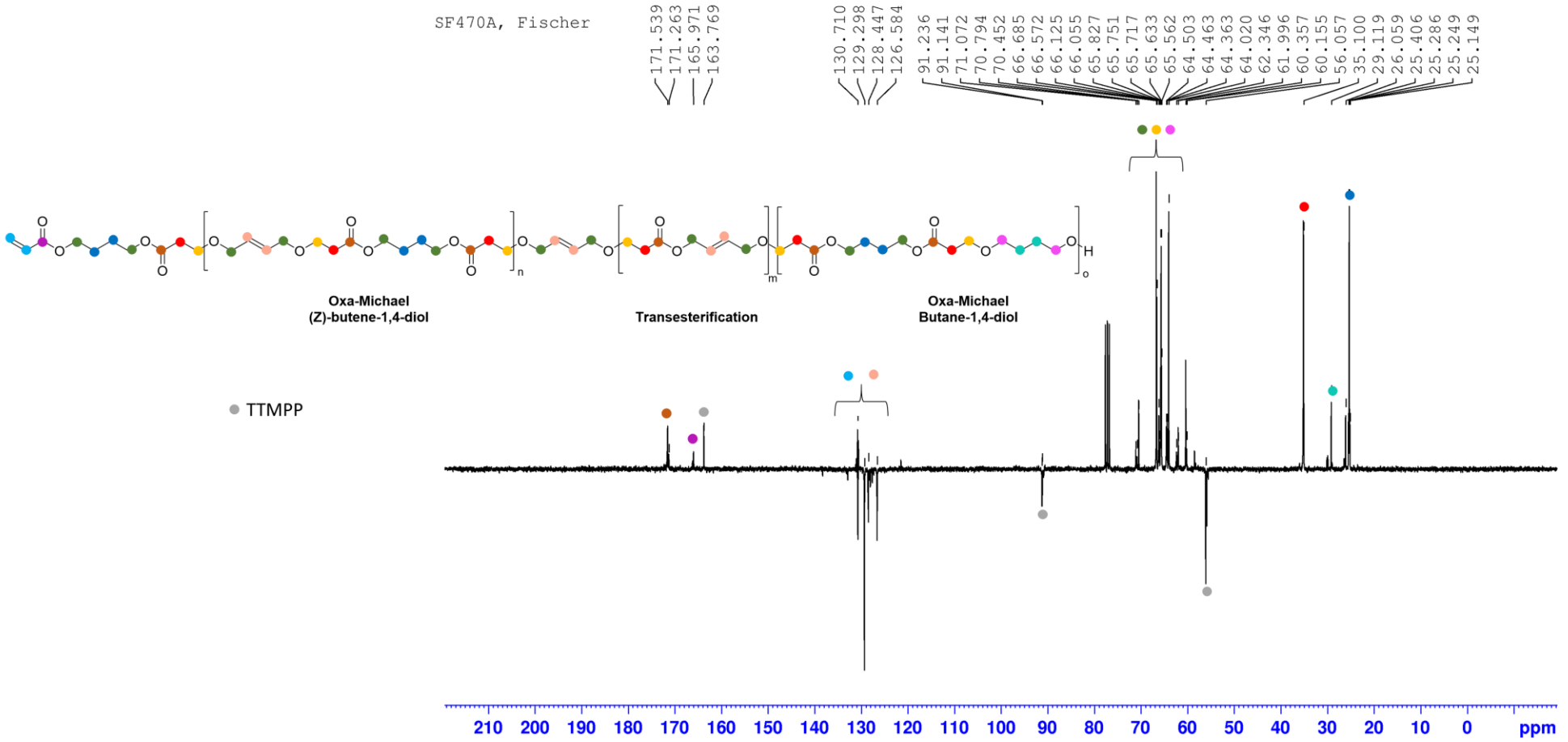
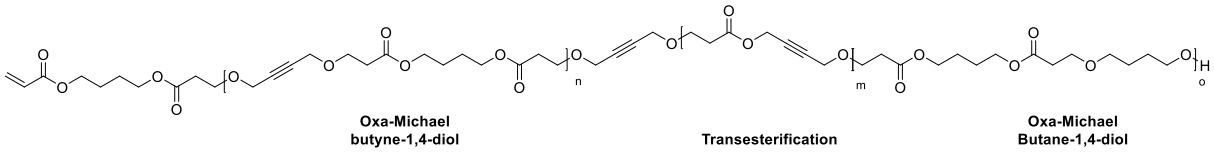


*Figure S33 ^{13}C-APT spectrum (75.53 MHz, CDCl3) of **poly3** prepared with 5 mol % TTMPP*

poly4:



^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.36 (d, 1H), 6.03 (d, 1H), 5.79 (d, 1H), 4.70 (s, 2H), 4.16-4.08 (bs, 38H), 3.73 (t, 18H), 3.41 (t,1H), 2.55 (t, 18H), 1.66 (bs, 22H)

^{13}C-APT NMR (75.53 MHz, $CDCl_3$) δ 171.4, 166.0, 130.8, 128.6, 82.2, 65.3-64.1, 58.5, 52.4, 34.9, 29.1, 25.4

Degree of transesterification was calculated from the integrals of the signals at 4.70 (TE) and 2.55 (OM). Oxa-Michael BD product was calculated from the integral at 3.41.

Oxa-Michael: 72.4%, TE: 16.0%, OM BD : 11.6%

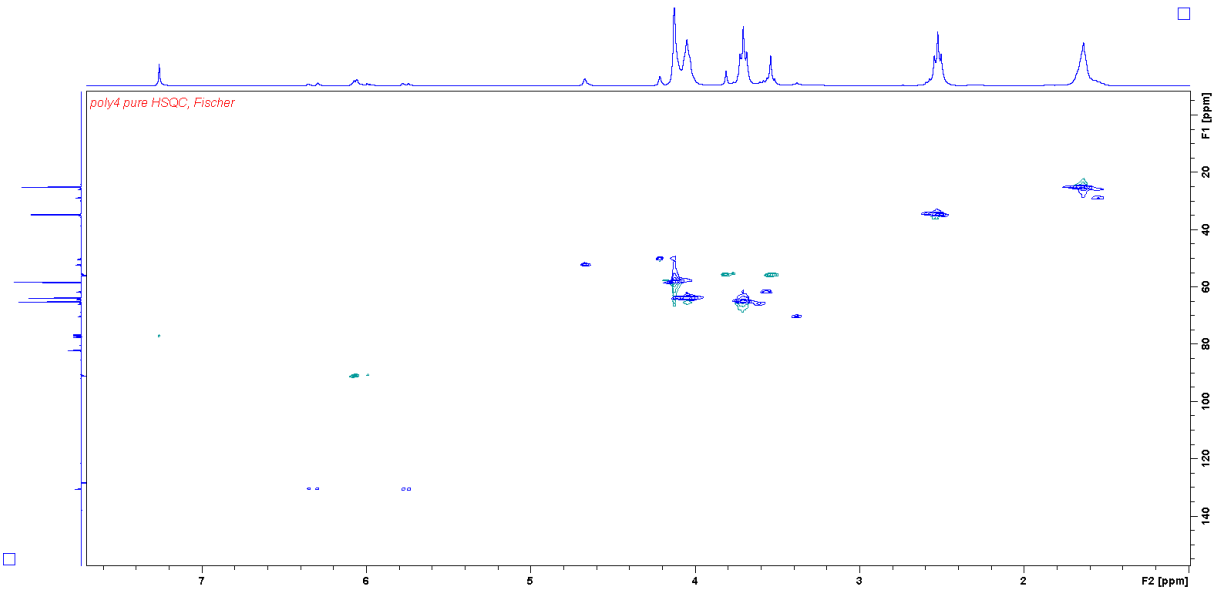


*Figure S34 HSQC of **poly4** prepared with 5 mol % TTMPP*

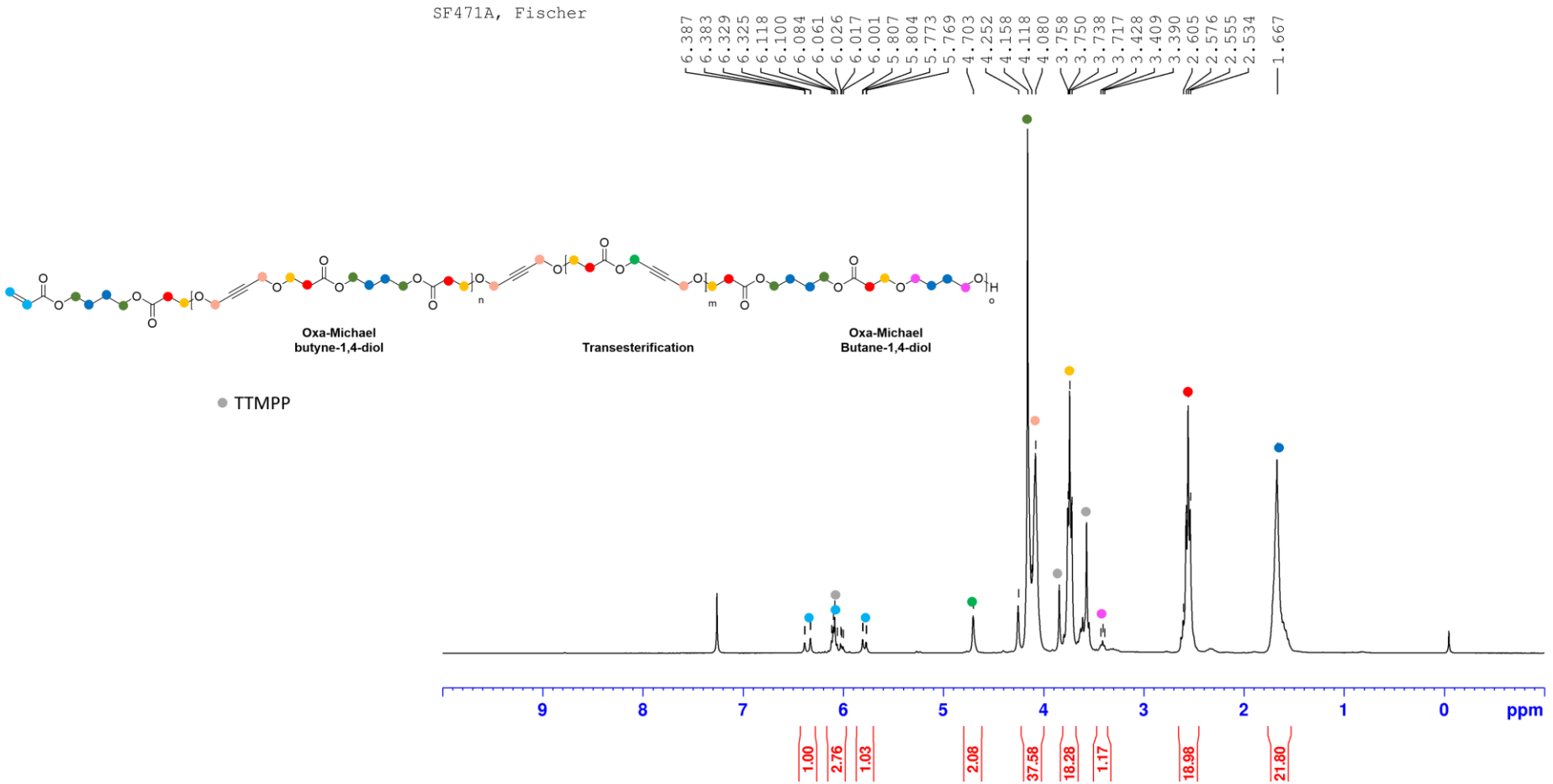


*Figure S35 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **poly4** prepared with 5 mol % TTMPP*

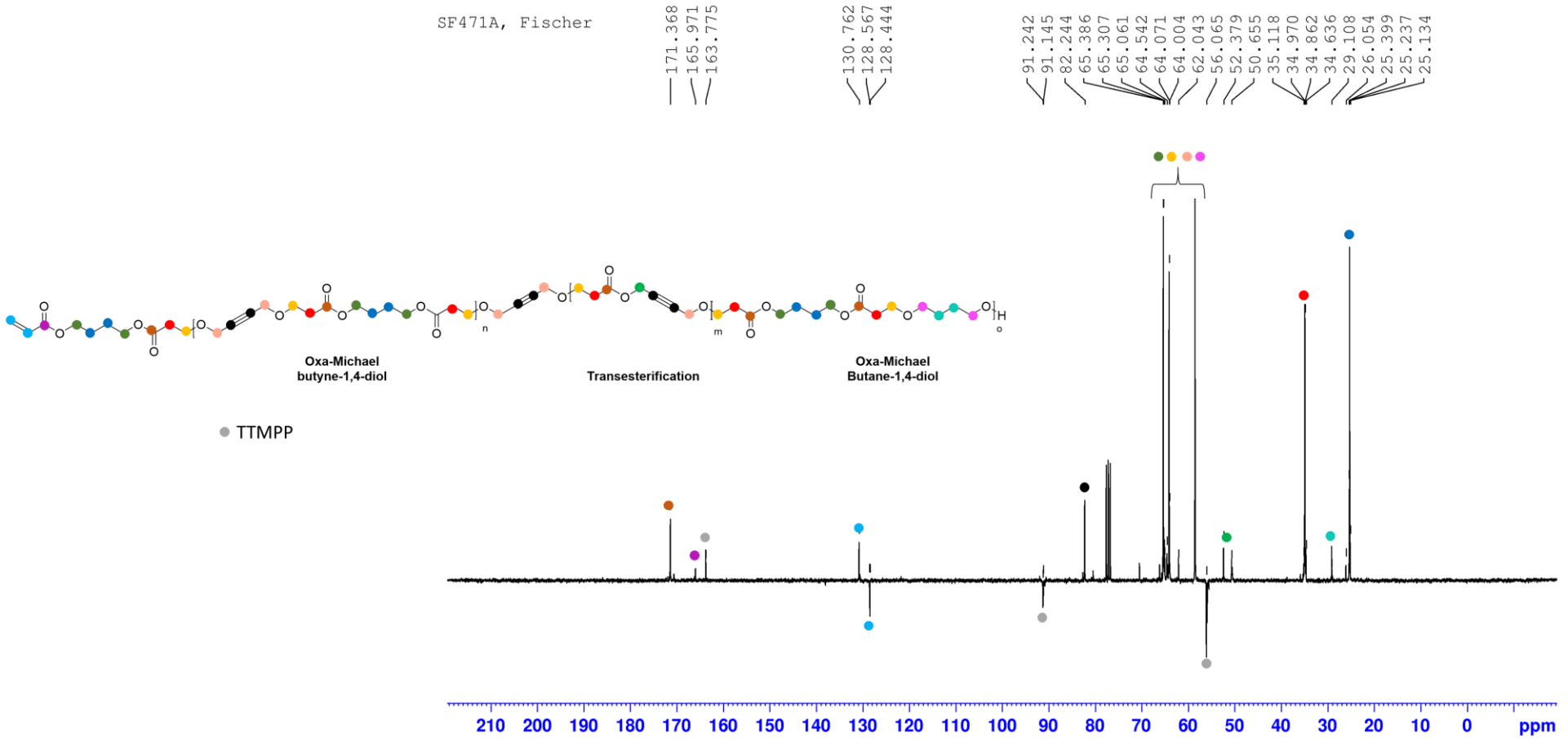


*Figure S36 ^{13}C-APT spectrum (75.53 MHz, CDCl3) of **poly4** prepared with 5 mol % TTMPP*

TTMPP Oxidation

Table S8 Relative share [%] of phosphine, phosphine oxide and other species as determined by ^{31}P NMR spectroscopy after storage of TTMPP under different conditions

Entry	Light source	Time	Solvent	Phosphine [%]	Phosphine oxide [%]	Other species [%]
1	Dark	5 d	None (solid)	100	0	0
2	Dark	5 d	Benzene-d6	100	0	0
3	Dark	5 d	Chloroform-d	71	16	13
4	Dark	5 d	Acetone-d6	89	11	0
5	Daylight	5 d	Acetone-d6	0	100	0
6	Daylight	5 d	DMSO-d6	30	70	0
7	250W tungsten-halogen lamp	1 h	Benzene-d6	85	14	0
8	Singlet oxygen sensitizer Pd4F + 250W tungsten-halogen lamp	20 min	Benzene-d6	0	95	5

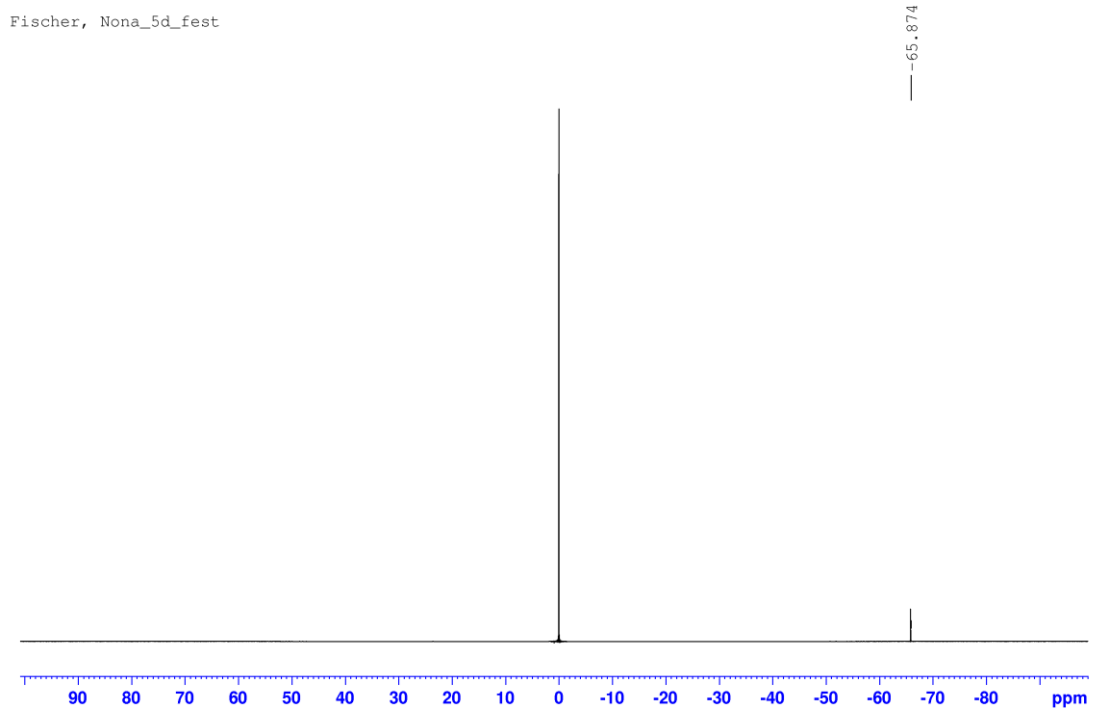


Figure S37 ^{31}P-NMR (202.55 MHz, DMSO-d_6) spectrum of TTMPP stored under conditions of entry 1 (relative to 85% H_3PO_4)

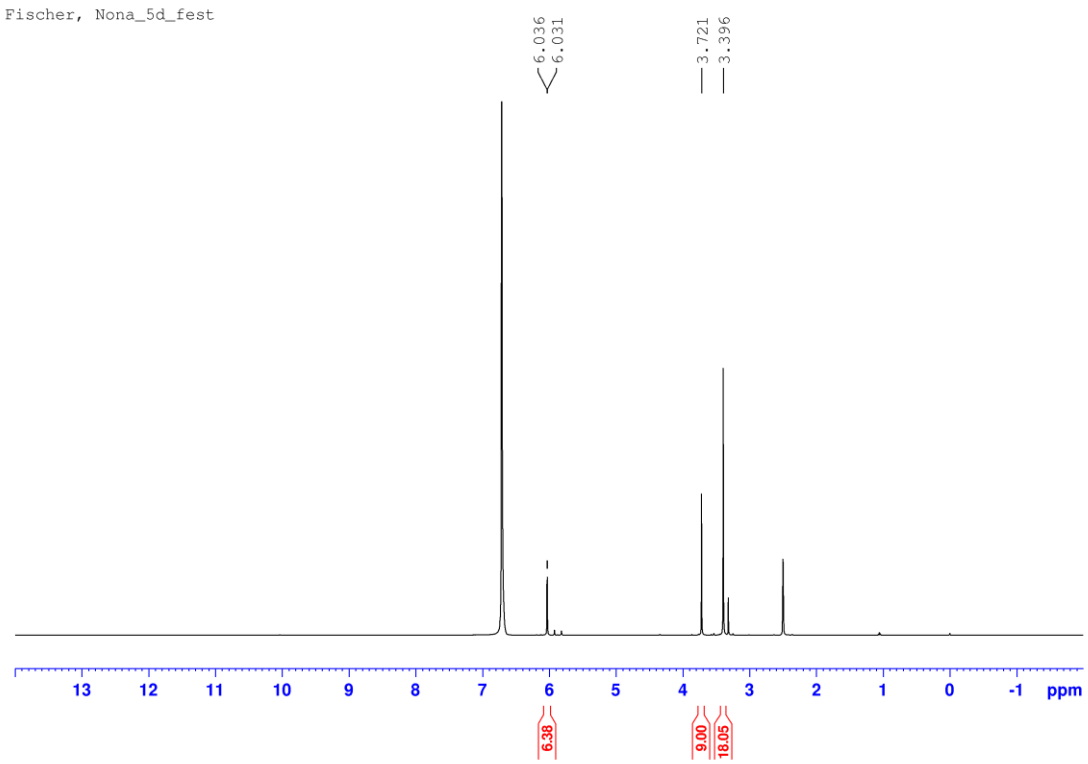


Figure S38 ^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of TTMPP stored under conditions of entry 1

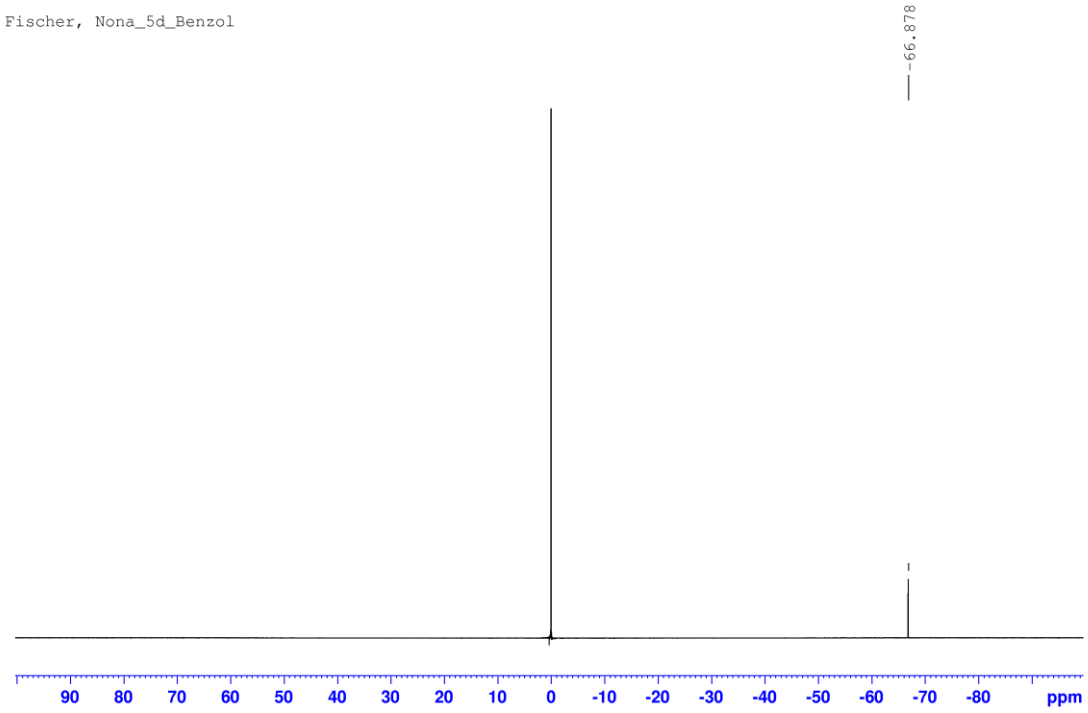


Figure S39 ^{31}P-NMR (202.55 MHz, benzene-d_6) spectrum of TTMPP stored under conditions of entry 2 (relative to 85% H_3PO_4)

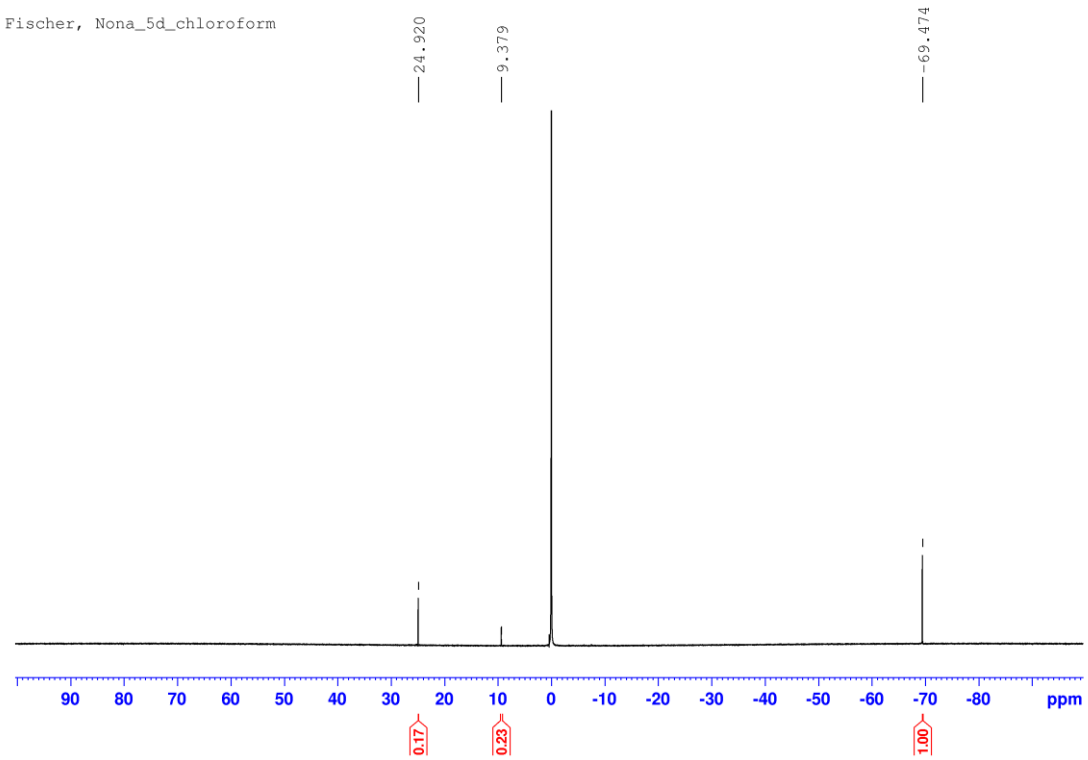


Figure S40 ^{31}P-NMR (202.55 MHz, $CDCl_3$) spectrum of TTMPP stored under conditions of entry 3 (relative to 85% H_3PO_4)

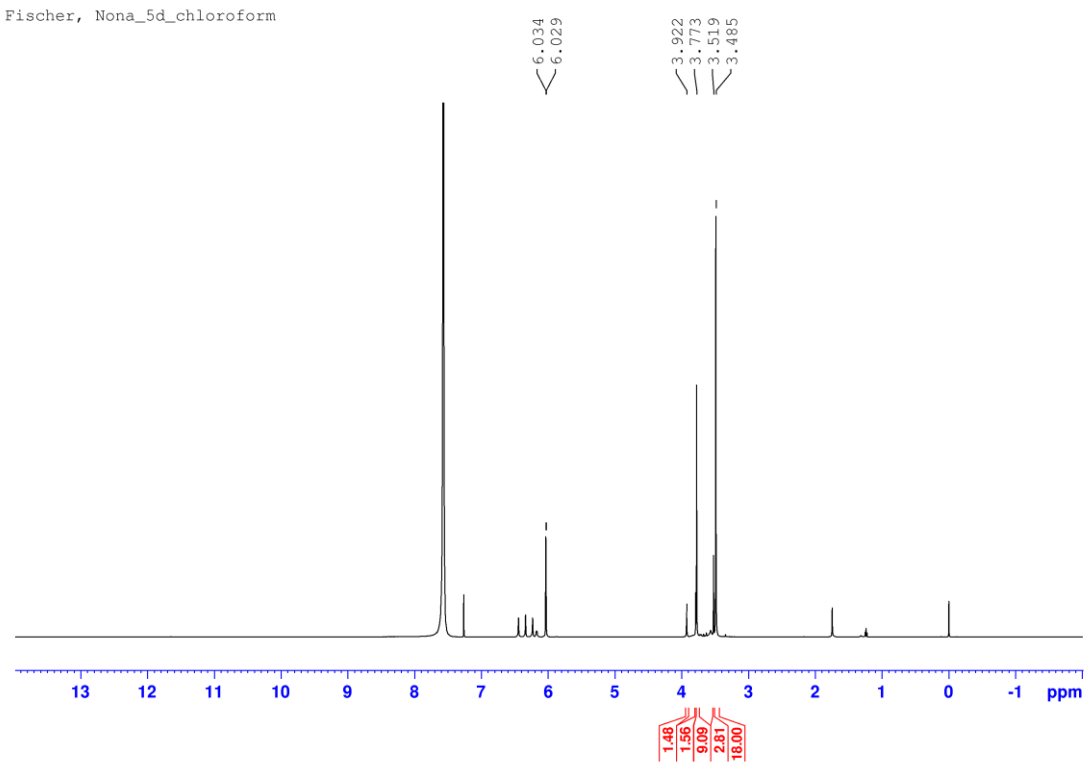


Figure S41 ^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of TTMPP stored under conditions of entry 3

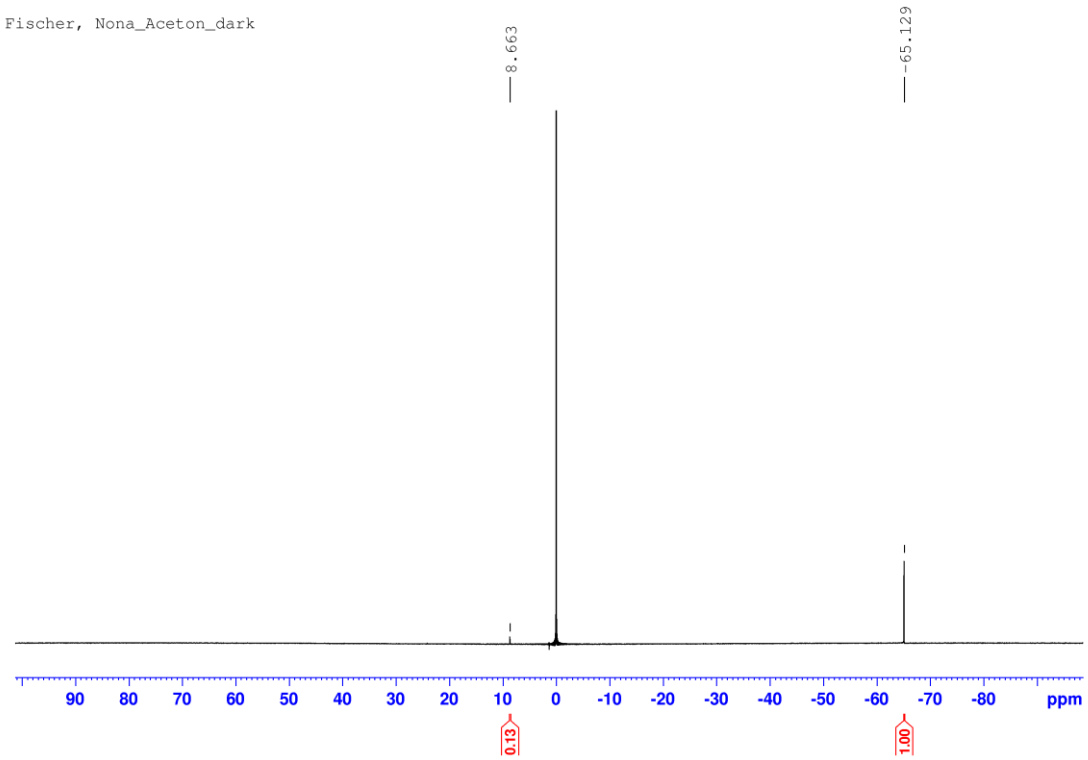


Figure S42 ^{31}P-NMR (202.55 MHz, acetone-d_6) spectrum of TTMPP stored under conditions of entry 4 (relative to 85% H_3PO_4)

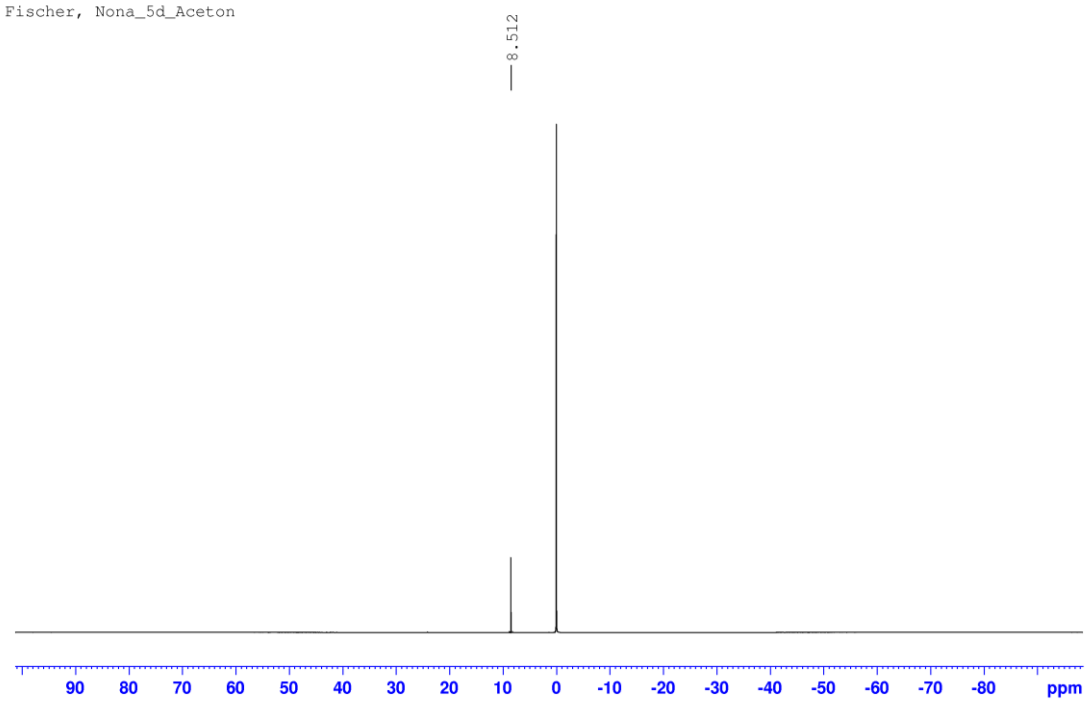


Figure S43 ^{31}P-NMR (202.55 MHz, acetone-d_6) spectrum of TTMPP stored under conditions of entry 5 (relative to 85% H_3PO_4)

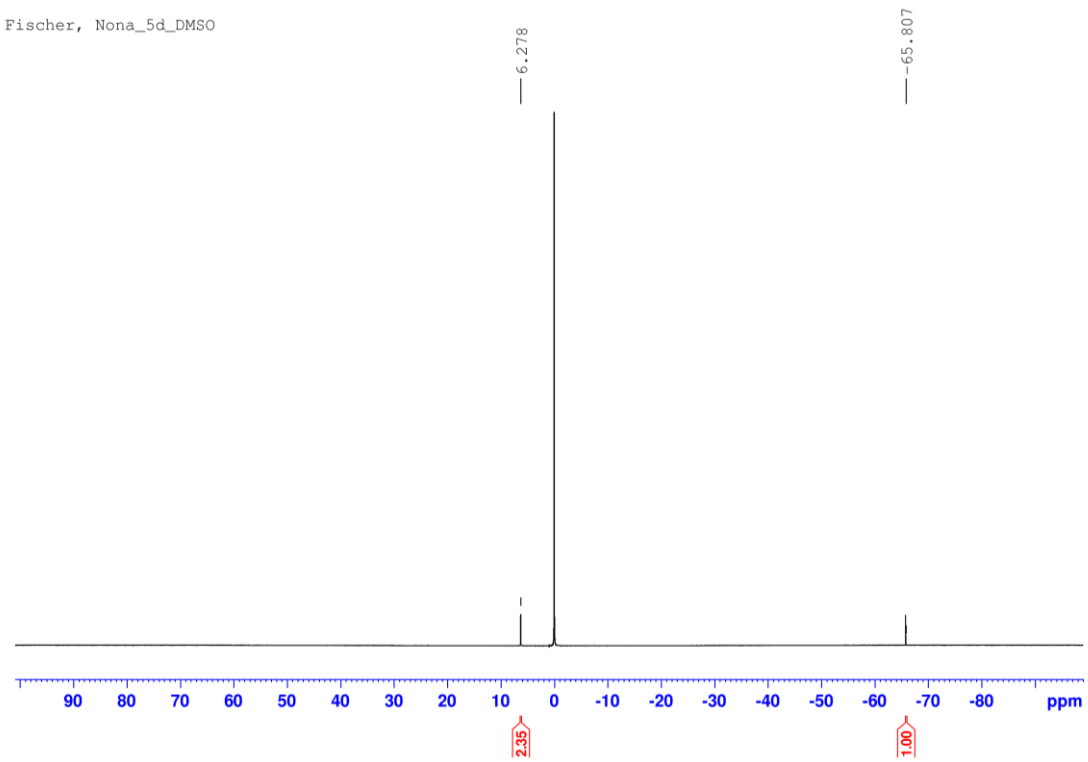
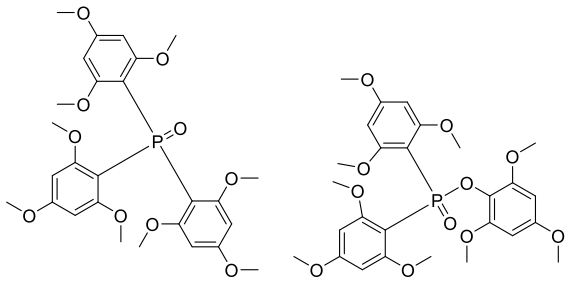


Figure S44 ^{31}P-NMR (202.55 MHz, acetone-d_6) spectrum of TTMPP stored under conditions of entry 6 (relative to 85% H_3PO_4)

Photooxidation experiments

Experimental

A solution of TTMPP (0.001 M) and singlet oxygen sensitizer Pd4F (0.00001 M) in benzene-d6 was irradiated with a metal-halogen lamp (Constant Color™ CMH Precise™, GE Lightening) with 14.000 nominal lumens. A heat protection filter (CALFLEX X; Qioptiq) and an UV blocking filter (UV-Blocking-Filters UV-B; Qioptiq) were used to narrow the spectrum of the lamp to 400 – 700 nm. The solution was stirred in a screw-capped quartz cuvette during the irradiation with the help of a magnetic stirrer.



phosphine oxide
^{31}P: 5.64 ppm
548.5 g/mol

phosphinate
^{31}P: 22.05 ppm
564.5 g/mol

Figure S45 Proposed structures of oxidation products of TTMPP for the reaction with singlet oxygen and their ^{31}P NMR shifts in benzene-d6. Left: phosphine oxide, right: phosphinate

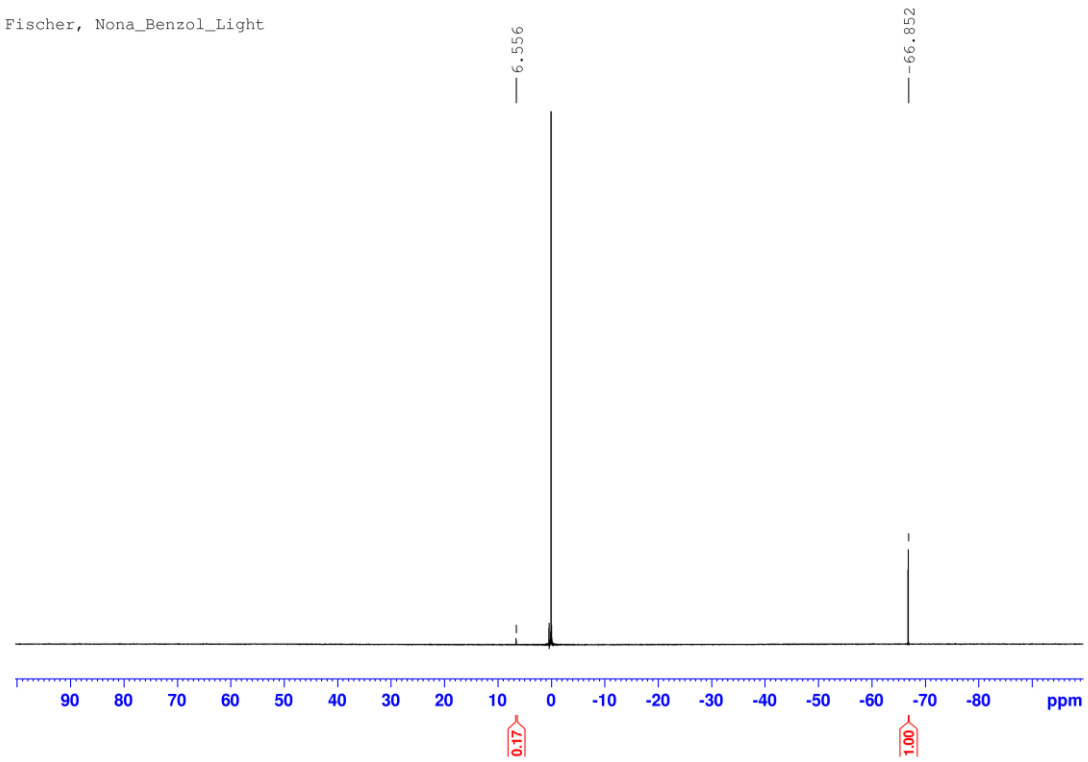


Figure S46 ^{31}P-NMR (202.55 MHz, benzene-d_6) spectrum of TTMPP stored under conditions of entry 7 (relative to 85% H_3PO_4)

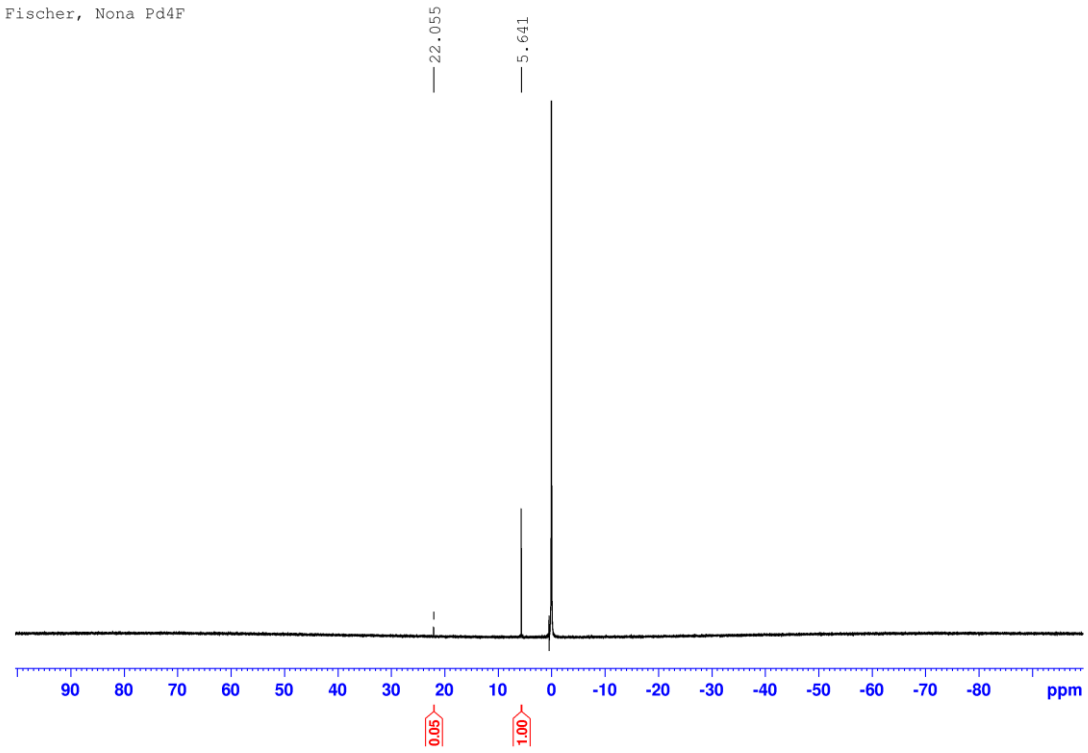


Figure S47 ^{31}P-NMR (202.55 MHz, benzene-d_6) spectrum of TTMPP stored under conditions of entry 8 (relative to 85% H_3PO_4)

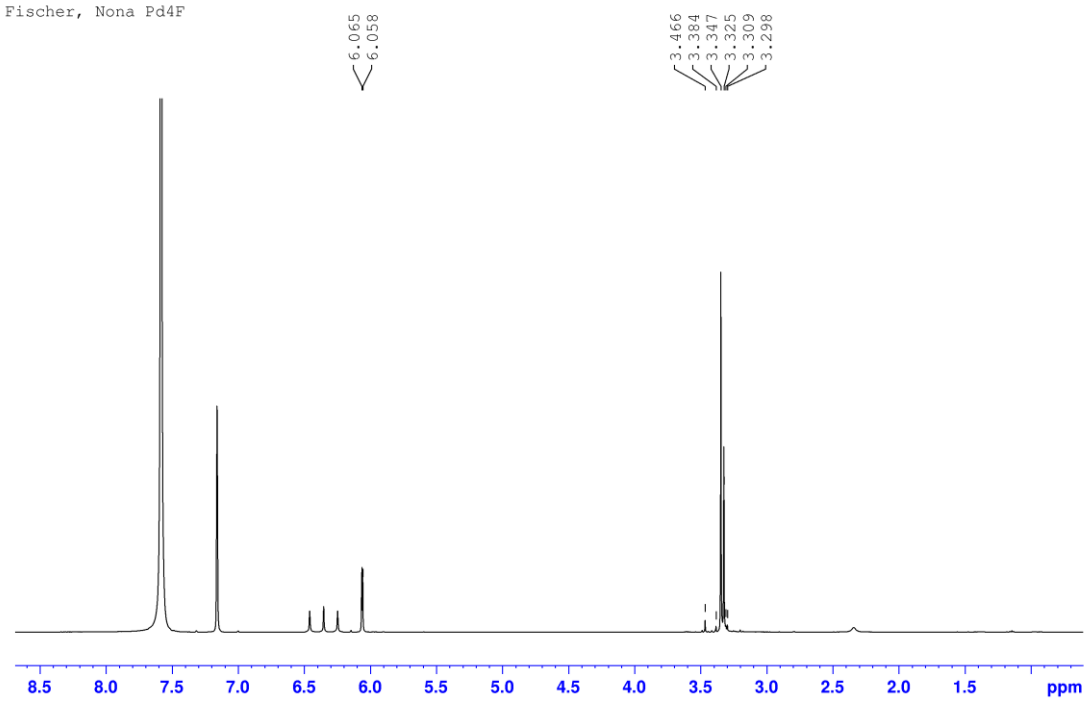


Figure S48 ^{1}H-NMR (500 MHz, benzene-d_6) spectrum of TTMPP stored under conditions of entry 8

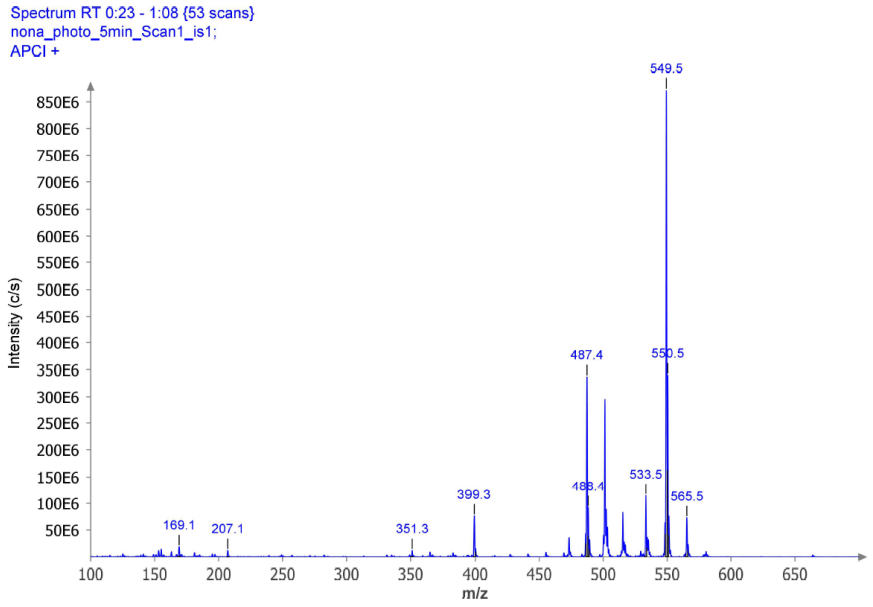


Figure S49 Low-resolution MS of TTMPP stored under conditions of entry 8; phosphine oxide: 549 m/z, phosphinate: 565 m/z

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