Supplementary Materials: Polystyrene-Supported Acyclic Diaminocarbene Palladium Complexes in Sonogashira Cross-Coupling: Stability vs. Catalytic Activity

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I. Crystallographic data

7

Table 1 Crystal data and structure refinement for 7.

Identification code	7
Empirical formula	$C_{18}H_{29}Cl_4N_3Pd$
Formula weight	535.64
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.0475(5)
b/Å	18.5954(8)
c/Å	12.1466(5)
α/°	90
β/°	109.119(5)
γ/°	90
Volume/Å^3	2357.67(18)
Z	4
ρ_{calc}g/cm^3	1.509
μ/mm^{-1}	1.248
F(000)	1088.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.638 to 54.998
Index ranges	$-14 \le h \le 14$, $-24 \le k \le 23$, $-15 \le l \le 14$
Reflections collected	12524
Independent reflections	5422 [R_{int} = 0.0267, R_{sigma} = 0.0354]
Data/restraints/parameters	5422/0/260
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0278, wR_2 = 0.0618
Final R indexes [all data]	R_1 = 0.0358, wR_2 = 0.0660
Largest diff. peak/hole / e Å^{-3}	0.76/-0.64

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 7. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	1315.2(2)	3459.0(2)	4576.8(2)	13.05(6)
Cl1	1808.3(5)	4011.5(3)	3011.3(5)	19.92(12)
Cl1S	8447.8(6)	3397.9(4)	10018.7(6)	32.27(15)
Cl2	-493.3(5)	2904.7(3)	3309.7(4)	17.98(12)
Cl2S	7981.7(12)	4920.5(5)	10261.1(8)	73.5(4)
C11	2087(2)	1898.3(13)	5525(2)	20.0(5)
N5	315.0(17)	3250.4(11)	6545.2(16)	16.0(4)
N2	1433.3(17)	2320.0(11)	6181.8(16)	16.7(4)
N1	3678.9(18)	4162.9(12)	6336.8(17)	21.4(4)
C10	-729(2)	4000.7(13)	7561(2)	21.6(5)
C13	4325(2)	1996.3(16)	6963(2)	27.2(6)
C1	2818(2)	3888.2(13)	5678.9(19)	17.8(5)
C7	-338(2)	3957.1(12)	6463.6(19)	15.6(4)
C14	5632(3)	2122.1(17)	7231(2)	34.1(6)
C1S	8418(3)	4099.1(16)	10982(2)	36.6(7)
C15	6118(3)	2315.7(18)	6374(3)	37.0(7)
C12	3499(2)	2062.6(13)	5830(2)	20.3(5)
C17	4005(3)	2277(2)	4986(2)	41.9(8)
C3	4740(2)	4521.0(18)	7216(3)	39.5(8)
C2	974(2)	2973.7(12)	5904.5(18)	14.3(4)
C16	5310(3)	2405(2)	5254(3)	53.8(10)
C8	562(2)	4580.0(13)	6477(2)	21.2(5)
C9	-1528(2)	3983.2(14)	5375(2)	21.9(5)
C4A	5967(4)	4374(4)	7035(5)	50.1(15)
C6A	4398(5)	5259(3)	7336(5)	48.9(15)
C5A	4767(5)	4085(3)	8407(4)	51.5(15)
C6	5102(10)	5144(7)	6246(10)	53(2)
C5	4371(11)	4969(8)	7997(11)	53(2)
C4	5807(12)	4092(8)	7514(11)	53(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 7. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	13.64(8)	13.13(9)	12.93(8)	-0.48(7)	5.10(6)	-0.61(7)
Cl1	27.5(3)	16.3(3)	20.1(3)	0.3(2)	13.4(2)	-1.7(2)
Cl1S	35.0(3)	40.3(4)	24.5(3)	5.4(3)	13.8(3)	10.5(3)
Cl2	18.0(2)	19.2(3)	15.2(2)	-2.9(2)	3.29(19)	-2.2(2)
Cl2S	108.6(8)	25.9(4)	44.2(5)	5.0(4)	-32.1(5)	-8.5(5)
C11	22.4(11)	17.6(12)	20.4(11)	-3.1(10)	7.7(9)	4.4(10)
N5	19.3(9)	13.7(9)	15.8(9)	3.1(8)	7.1(7)	1.7(8)
N2	18.0(9)	16.7(10)	16.9(9)	2.1(8)	7.8(7)	2.5(8)
N1	16.5(9)	23.8(11)	23.7(10)	-1.3(9)	6.3(8)	-0.4(9)
C10	28.4(12)	19.3(12)	21.8(11)	1.1(10)	14.7(10)	3.0(11)
C13	25.8(12)	32.5(15)	24.1(12)	-0.1(12)	9.4(10)	4.6(12)
C1	17.1(11)	18.7(12)	18.8(10)	2.1(10)	7.6(9)	1(1)
C7	18.4(10)	12.5(10)	17.4(10)	1.4(9)	7.8(8)	2.8(9)
C14	23.8(13)	43.6(17)	30.3(13)	-4.9(14)	2.8(11)	5.6(13)
C1S	46.7(17)	32.1(16)	30.1(14)	6.0(13)	11.3(13)	13.2(14)
C15	19.5(12)	45.6(18)	45.9(16)	1.4(15)	10.6(12)	5.1(13)
C12	22.2(11)	16.4(11)	24.0(11)	3.1(10)	9.8(9)	7(1)
C17	25.5(14)	72(2)	28.1(13)	15.0(16)	9.1(11)	6.7(15)
C3	16.4(12)	42.6(18)	48.7(17)	-23.8(16)	-4.0(12)	0.1(13)
C2	12.0(9)	15.9(11)	13.0(9)	-0.3(9)	1.4(8)	-1.7(9)
C16	28.2(15)	96(3)	43.4(17)	20(2)	19.7(14)	5.5(18)
C8	22.9(11)	15.4(11)	28.0(12)	0.4(10)	12(1)	0.7(10)
C9	18.2(11)	23.6(13)	21.8(11)	-0.1(11)	3.5(9)	2.8(10)
C4A	18(2)	64(4)	71(4)	-27(3)	19(2)	-16(2)
C6A	34(2)	32(3)	64(3)	-15(3)	-6(2)	0(2)
C5A	52(3)	61(4)	28(2)	6(2)	-6(2)	-4(3)
C6	38(4)	63(5)	50(4)	-15(4)	4(3)	-19(4)
C5	38(4)	63(5)	50(4)	-15(4)	4(3)	-19(4)
C4	38(4)	63(5)	50(4)	-15(4)	4(3)	-19(4)

Table 4 Bond Lengths for 7.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	Cl1	2.3764(5)	C13	C14	1.393(4)
Pd1	Cl2	2.3256(6)	C13	C12	1.386(3)
Pd1	C1	1.932(2)	C7	C8	1.523(3)
Pd1	C2	1.989(2)	C7	C9	1.529(3)
Cl1S	C1S	1.760(3)	C14	C15	1.367(4)
Cl2S	C1S	1.748(3)	C15	C16	1.370(4)
C11	N2	1.466(3)	C12	C17	1.378(3)
C11	C12	1.512(3)	C17	C16	1.391(4)
N5	C7	1.487(3)	C3	C4A	1.469(5)
N5	C2	1.331(3)	C3	C6A	1.444(6)

N2	C2	1.318(3)	C3	C5A	1.650(6)
N1	C1	1.143(3)	C3	C6	1.788(12)
N1	C3	1.462(3)	C3	C5	1.420(12)
C10	C7	1.532(3)	C3	C4	1.370(14)

Table 5 Bond Angles for 7.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	Pd1	Cl1	91.97(2)	C13	C12	C11	121.1(2)
C1	Pd1	Cl1	90.32(7)	C17	C12	C11	120.9(2)
C1	Pd1	Cl2	177.53(7)	C17	C12	C13	118.0(2)
C1	Pd1	C2	88.49(9)	C12	C17	C16	121.2(3)
C2	Pd1	Cl1	177.52(6)	N1	C3	C4A	111.4(3)
C2	Pd1	Cl2	89.18(6)	N1	C3	C5A	101.4(3)
N2	C11	C12	114.27(19)	N1	C3	C6	96.5(4)
C2	N5	C7	130.48(19)	C4A	C3	C5A	106.7(4)
C2	N2	C11	124.82(19)	C6A	C3	N1	109.5(3)
C1	N1	C3	177.1(2)	C6A	C3	C4A	118.5(4)
C12	C13	C14	120.8(2)	C6A	C3	C5A	108.0(4)
N1	C1	Pd1	177.4(2)	C5	C3	N1	114.7(5)
N5	C7	C10	104.94(17)	C5	C3	C6	103.6(8)
N5	C7	C8	111.76(18)	C4	C3	N1	110.0(6)
N5	C7	C9	110.27(19)	C4	C3	C6	101.1(8)
C8	C7	C10	108.64(19)	C4	C3	C5	125.2(8)
C8	C7	C9	110.97(19)	N5	C2	Pd1	125.73(17)
C9	C7	C10	110.07(18)	N2	C2	Pd1	117.80(15)
C15	C14	C13	120.1(3)	N2	C2	N5	116.47(19)
Cl2S	C1S	Cl1S	112.11(16)	C15	C16	C17	120.0(3)
C14	C15	C16	119.8(3)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 7.

Atom	*x*	*y*	*z*	U(eq)
H11A	1671	1987	4700	24
H11B	1987	1392	5664	24
H5	258	2976	7096	19
H2	1343	2126	6793	20
H10A	-1301	3612	7561	32
H10B	-1152	4451	7570	32
H10C	20	3967	8239	32
H13	4002	1866	7552	33
H14	6176	2074	7995	41
H1SA	7814	3980	11381	44
H1SB	9259	4145	11565	44

H15	6995	2386	6549	44
H17	3465	2336	4223	50
H16	5635	2552	4674	65
H8A	1342	4522	7118	32
H8B	160	5025	6561	32
H8C	750	4585	5760	32
H9A	-1276	3936	4693	33
H9B	-1960	4434	5350	33
H9C	-2093	3596	5399	33
H4AA	6105	3864	7042	75
H4AB	6649	4595	7646	75
H4AC	5950	4567	6297	75
H6AA	4342	5520	6639	73
H6AB	5039	5475	7988	73
H6AC	3584	5274	7462	73
H5AA	3972	4159	8550	77
H5AB	5460	4262	9057	77
H5AC	4886	3581	8308	77
H6A	5330	4884	5659	79
H6B	5805	5444	6676	79
H6C	4365	5438	5882	79
H5A	3765	5321	7563	79
H5B	5112	5209	8508	79
H5C	3985	4682	8449	79
H4A	5684	3691	7962	79
H4B	6538	4365	7968	79
H4C	5947	3921	6820	79

Table 7 Atomic Occupancy for 7.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C4A	0.690(6)	H4AA	0.690(6)	H4AB	0.690(6)
H4AC	0.690(6)	C6A	0.690(6)	H6AA	0.690(6)
H6AB	0.690(6)	H6AC	0.690(6)	C5A	0.690(6)
H5AA	0.690(6)	H5AB	0.690(6)	H5AC	0.690(6)
C6	0.310(6)	H6A	0.310(6)	H6B	0.310(6)
H6C	0.310(6)	C5	0.310(6)	H5A	0.310(6)
H5B	0.310(6)	H5C	0.310(6)	C4	0.310(6)
H4A	0.310(6)	H4B	0.310(6)	H4C	0.310(6)

Experimental

Single crystals of $C_{18}H_{29}Cl_4N_3Pd$ [**7**] were growth from dichloromethane/ hexane mixture. A suitable crystal was selected and placed on a SuperNova, Dual, Cu at zero, Xcalibur, Eos diffractometer. The crystal was kept at 100.01(10) K during data collection. Using Olex2[1], the

structure was solved with the Superflip[2] structure solution program using Charge Flipping and refined with the ShelXL[3] refinement package using Least Squares minimization.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.
2. J. Appl. Cryst. (2007) 40, 786-790
3. SHELXL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122

Crystal structure determination of [7]

Crystal Data. $C_{18}H_{29}Cl_4N_3Pd$ (*M* =535.64 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 11.0475(5) Å, *b* = 18.5954(8) Å, *c* = 12.1466(5) Å, *β* = 109.119(5)°, *V* = 2357.67(18) $Å^3$, *Z* = 4, *T* = 100.00(10) K, μ(MoKα) = 1.248 mm^{-1}, *Dcalc* = 1.509 g/cm^3, 12524 reflections measured (5.638° ≤ 2Θ ≤ 54.998°), 5422 unique (R_{int} = 0.0267, R_{sigma} = 0.0354) which were used in all calculations.

II. NMR Spectra

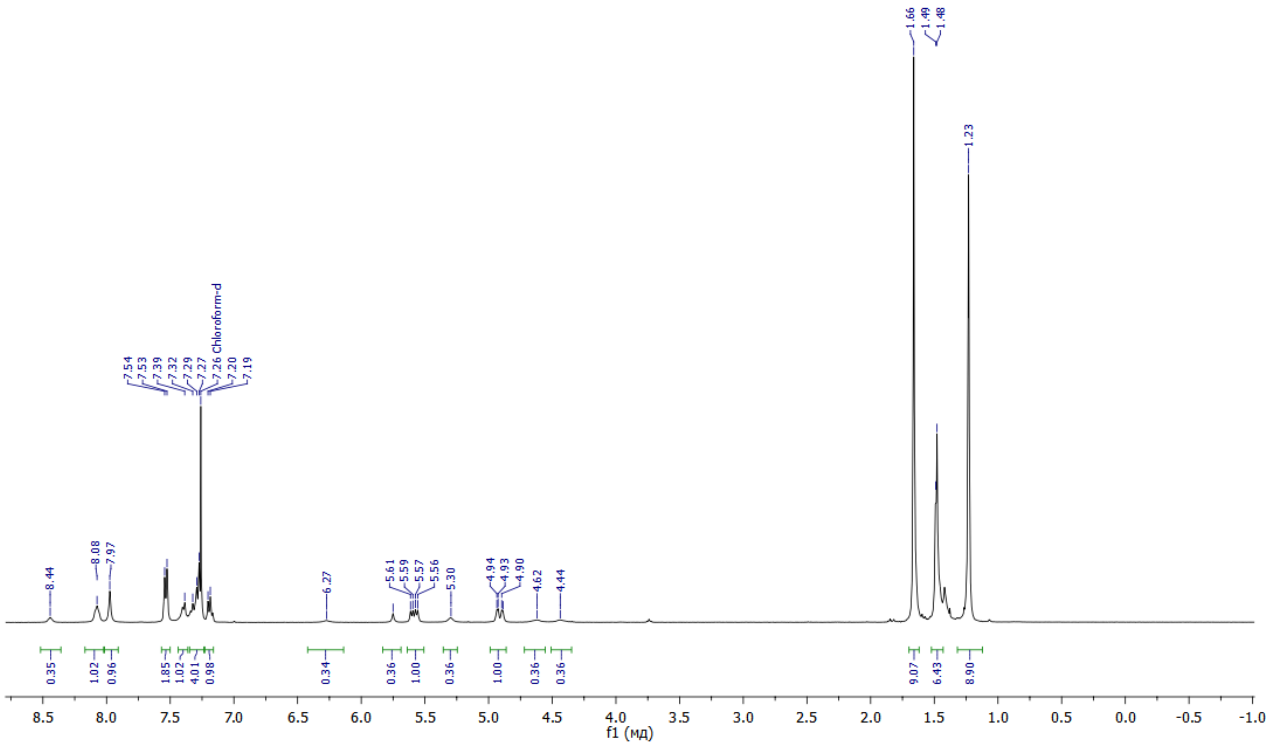

Figure S1. ^{1}H NMR spectrum of 7.

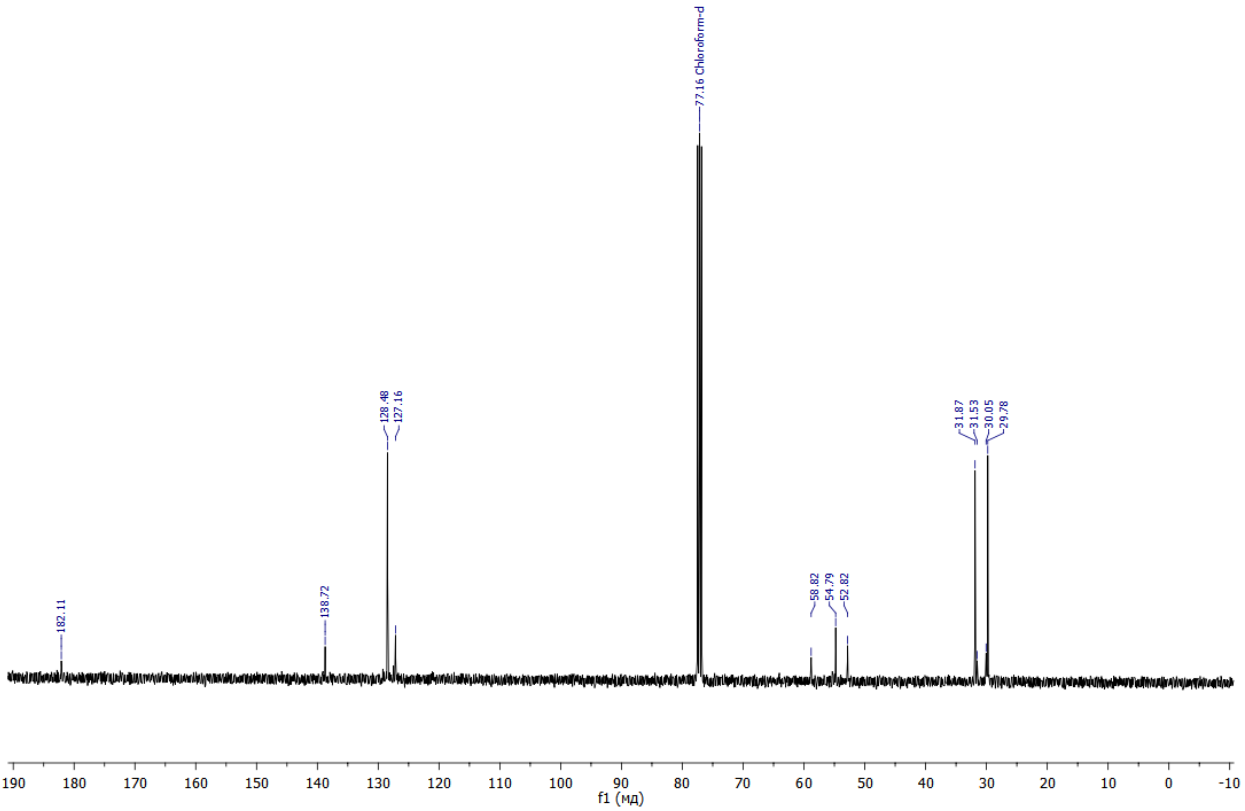

Figure S2. ^{13}C NMR spectrum of 7.

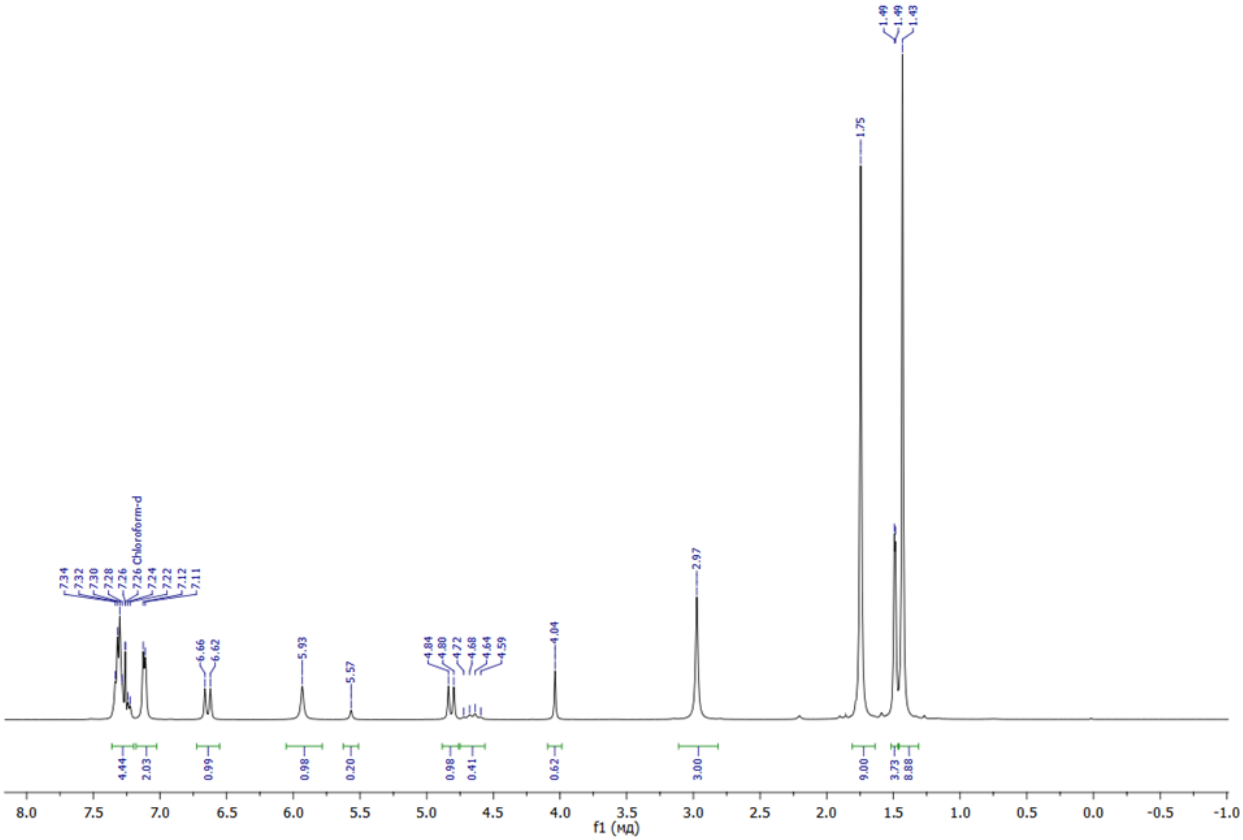

Figure S3. ^{1}H NMR spectrum of 8.

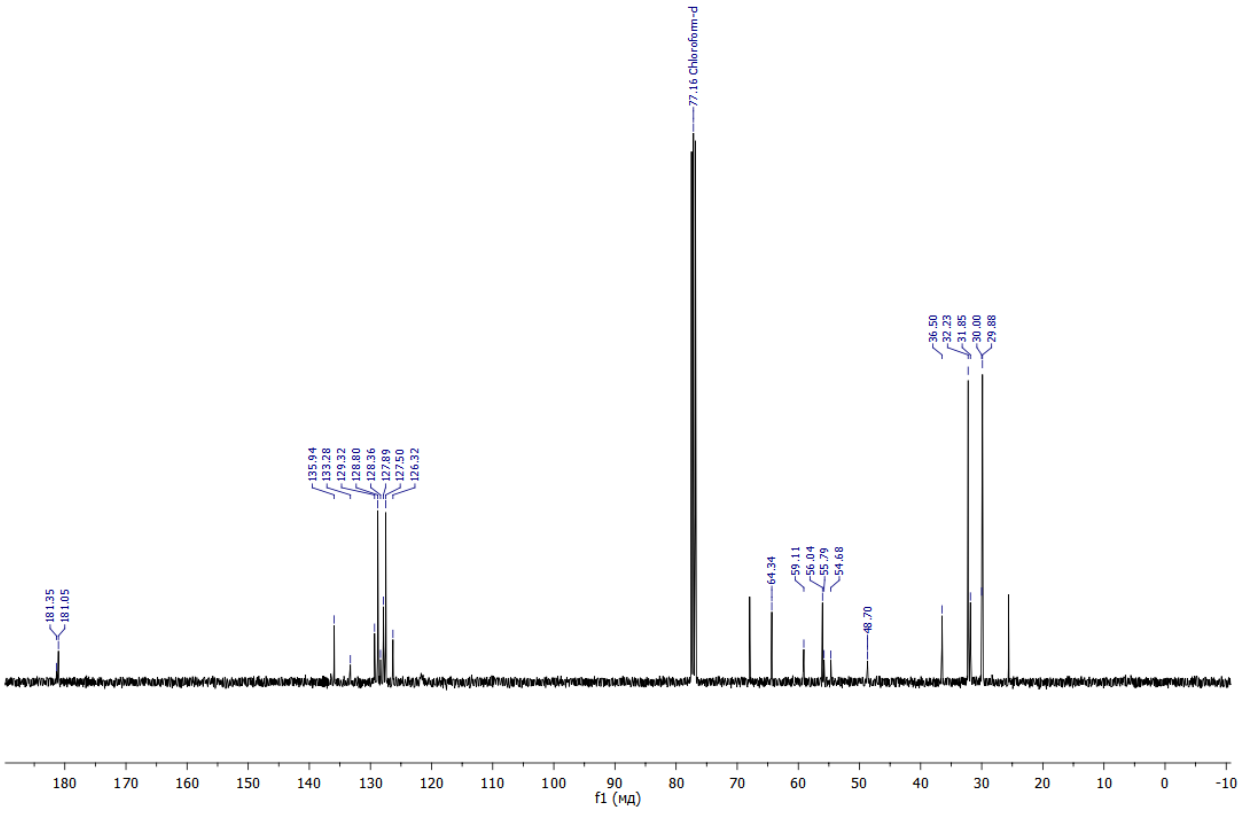

Figure S4. ^{13}C NMR spectrum of 8.

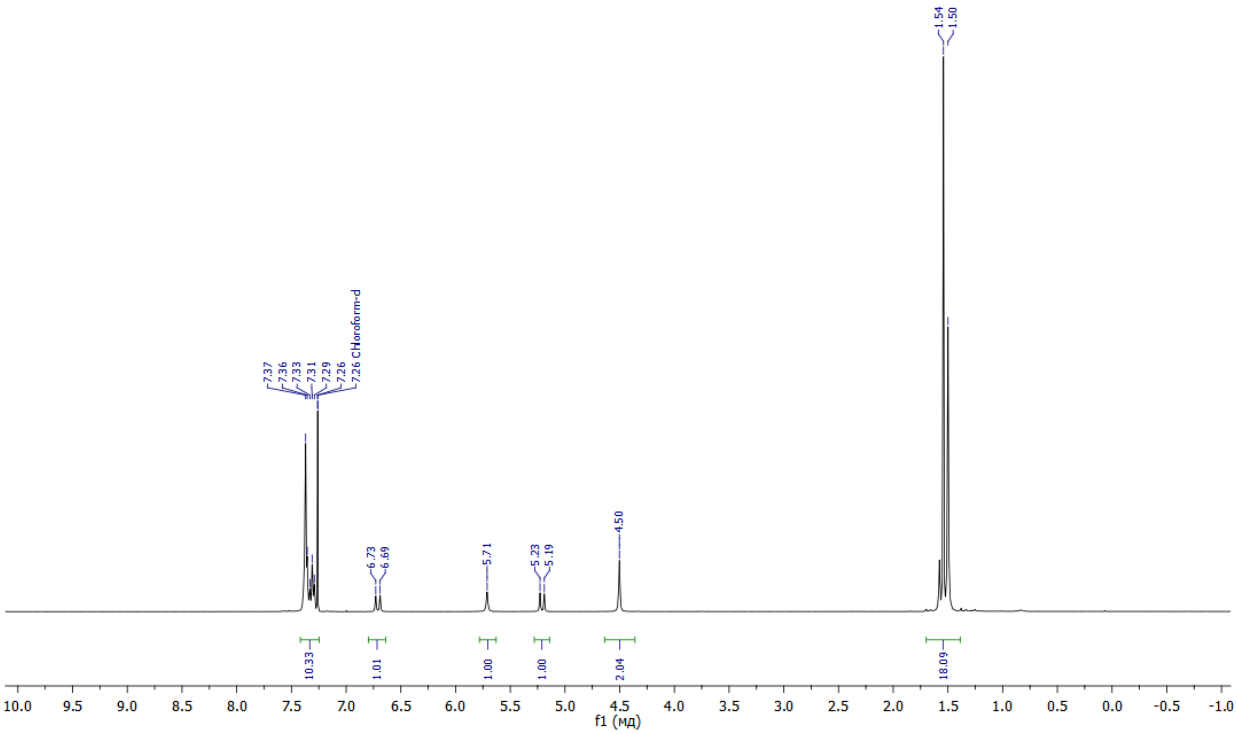

Figure S5. ^{1}H NMR spectrum of 9.

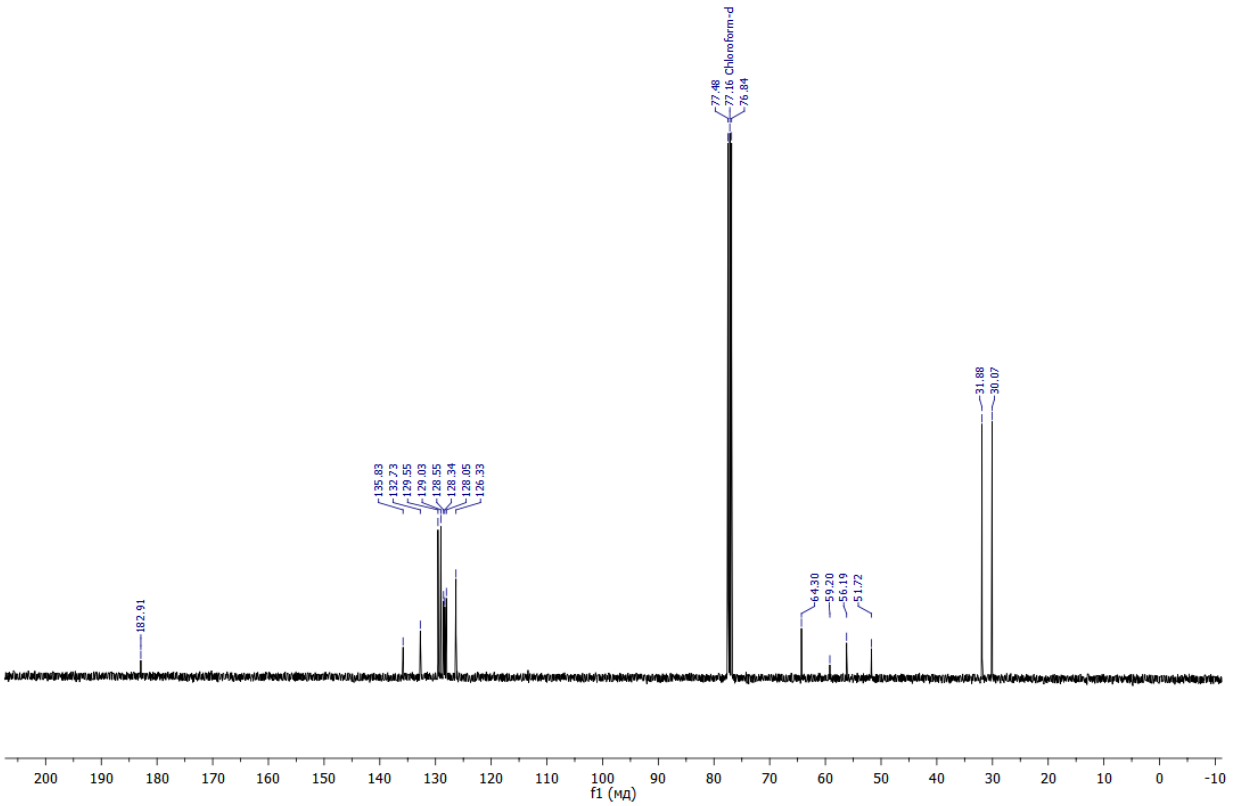

Figure S6. ^{13}C NMR spectrum of 9.

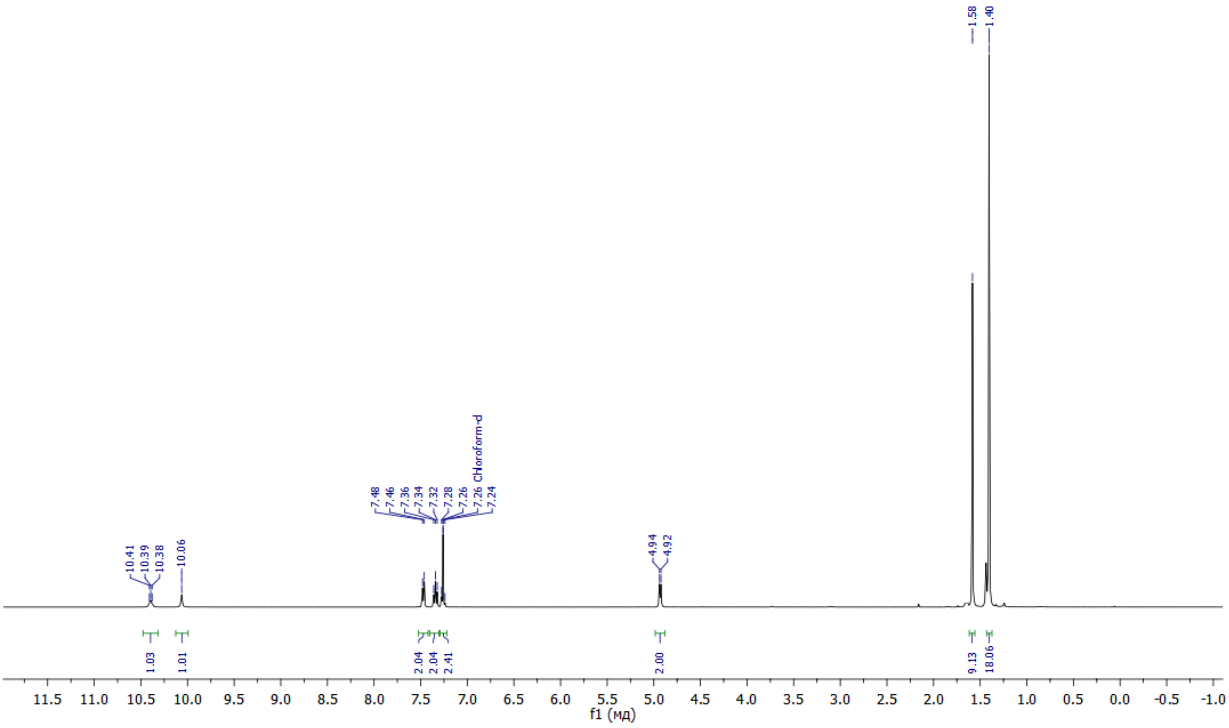

Figure S7. ^{1}H NMR spectrum of 10.

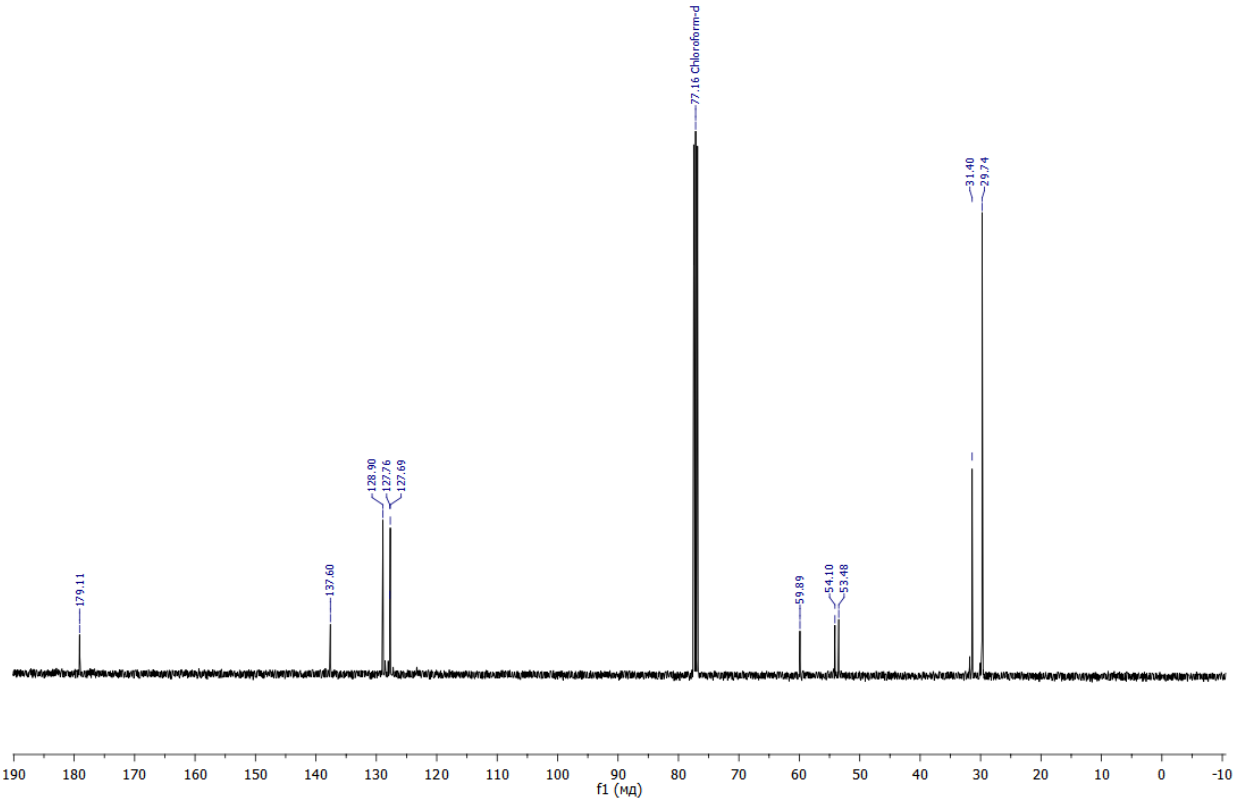

Figure S8. ^{13}C NMR spectrum of 10.

III. IR Spectra

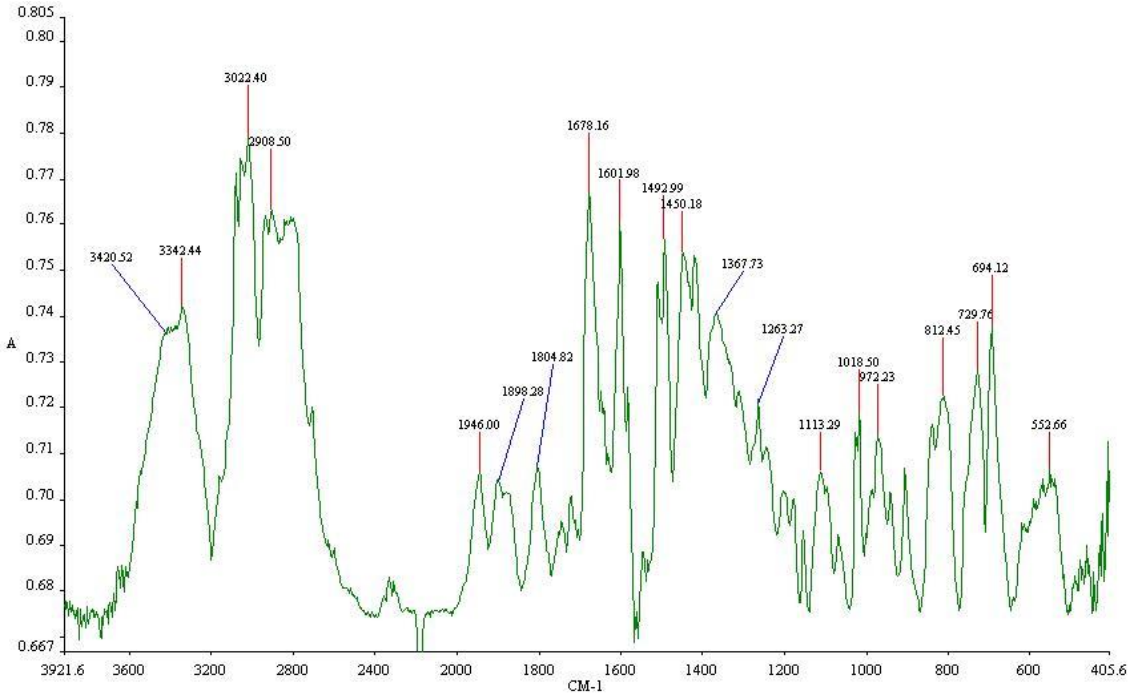

Figure S9. IR spectrum of DBA@PS.

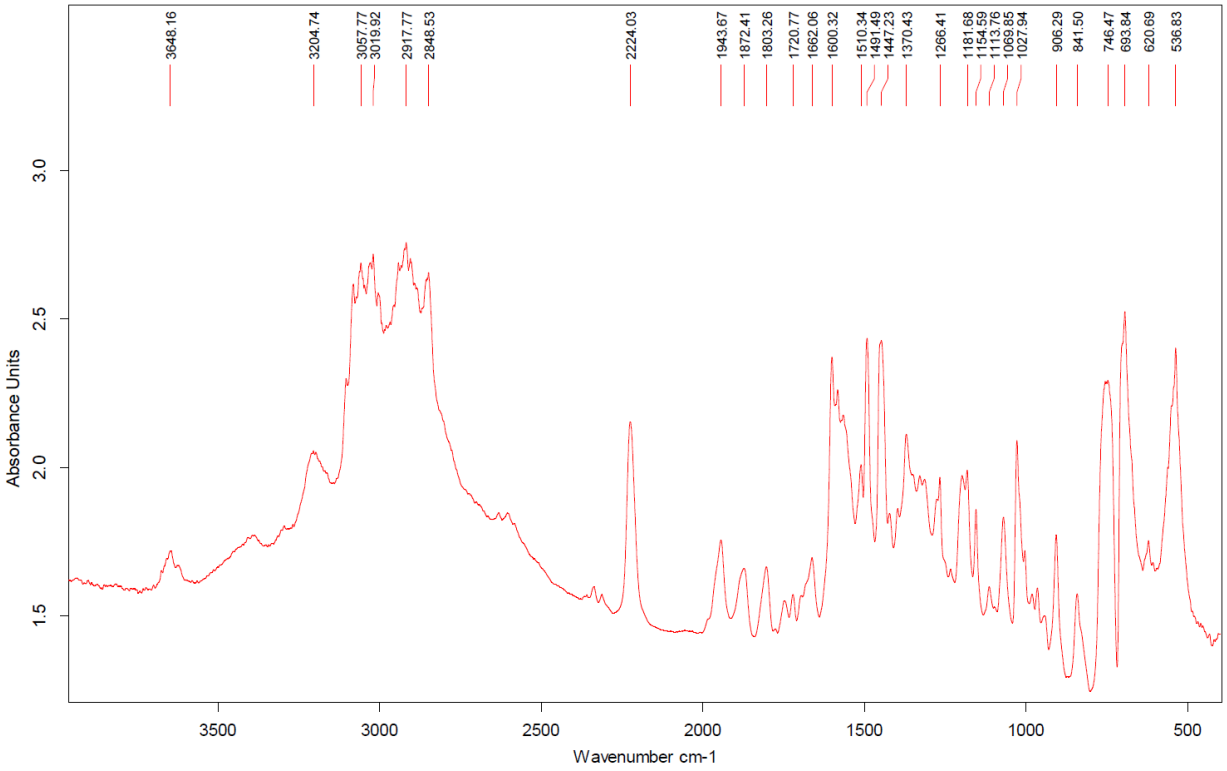

Figure S10. IR spectrum of 1a.

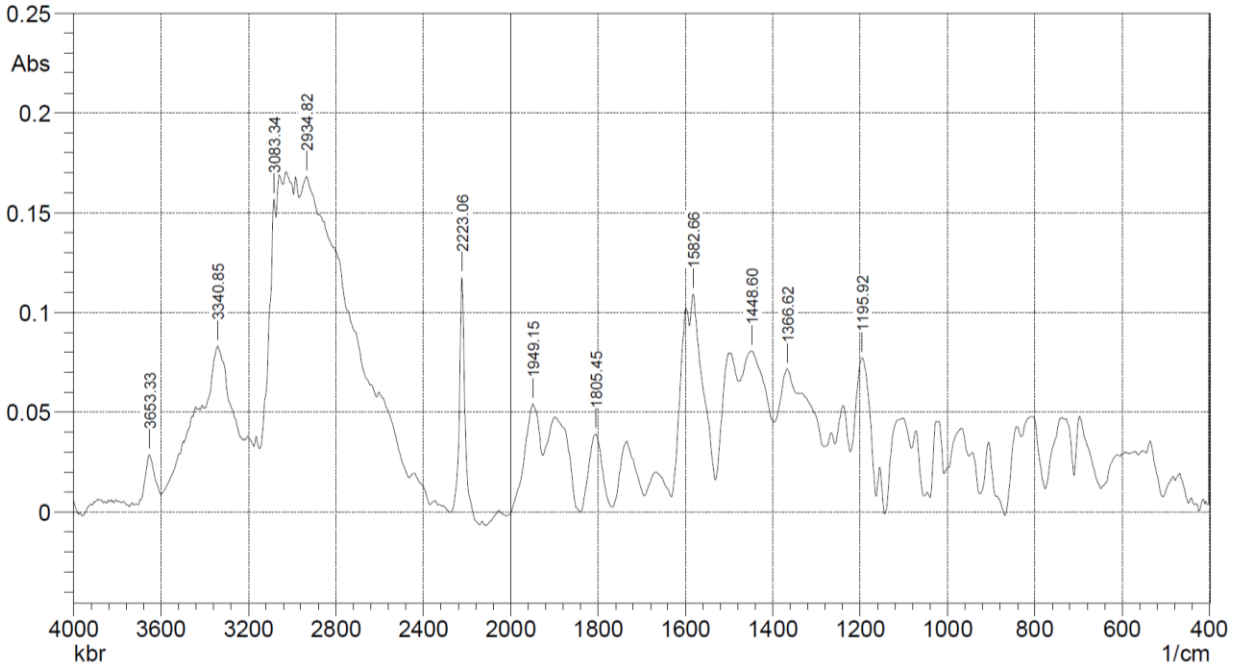

Figure S11. IR spectrum of 2a.

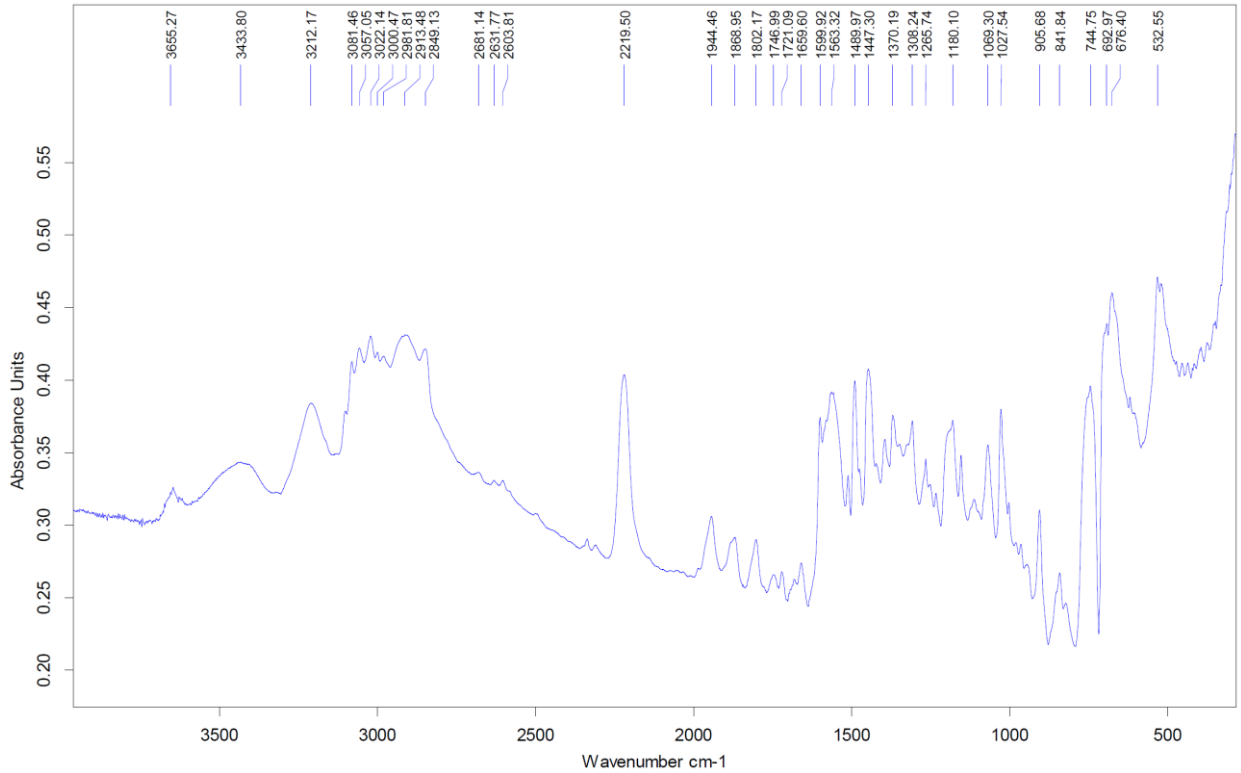

Figure S12. IR spectrum of 1b.

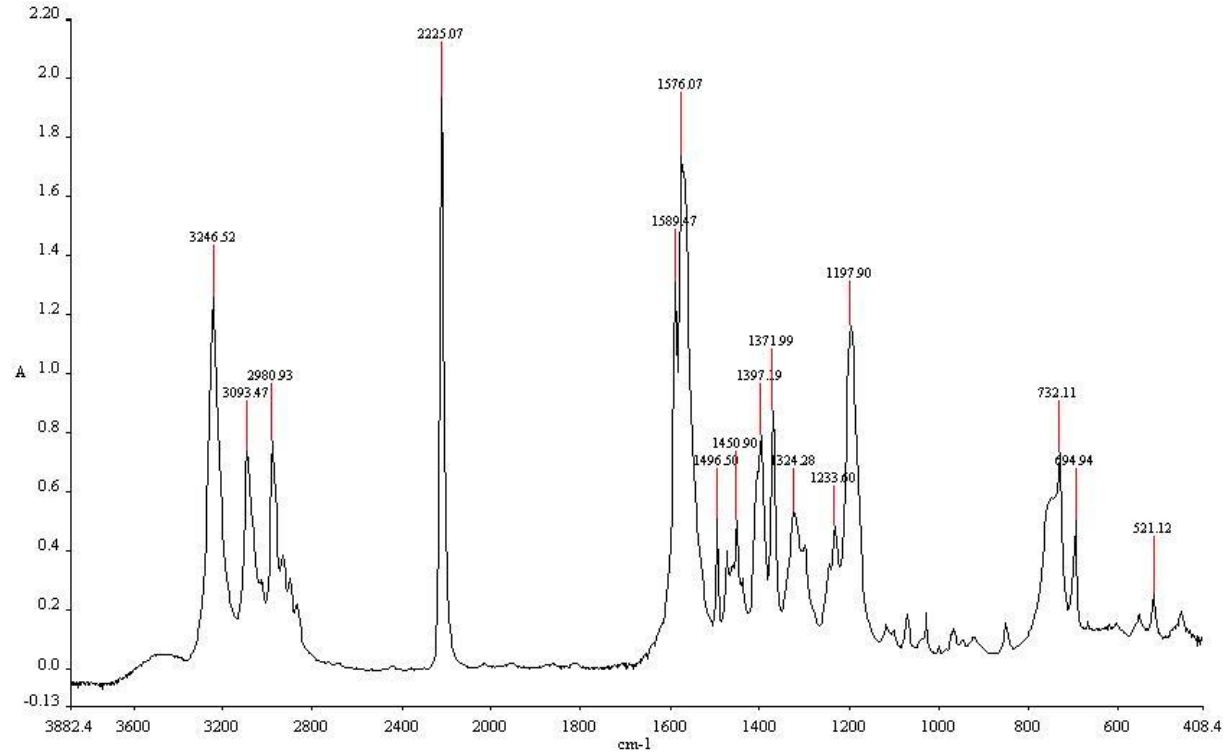

Figure S13. IR spectrum of 7.

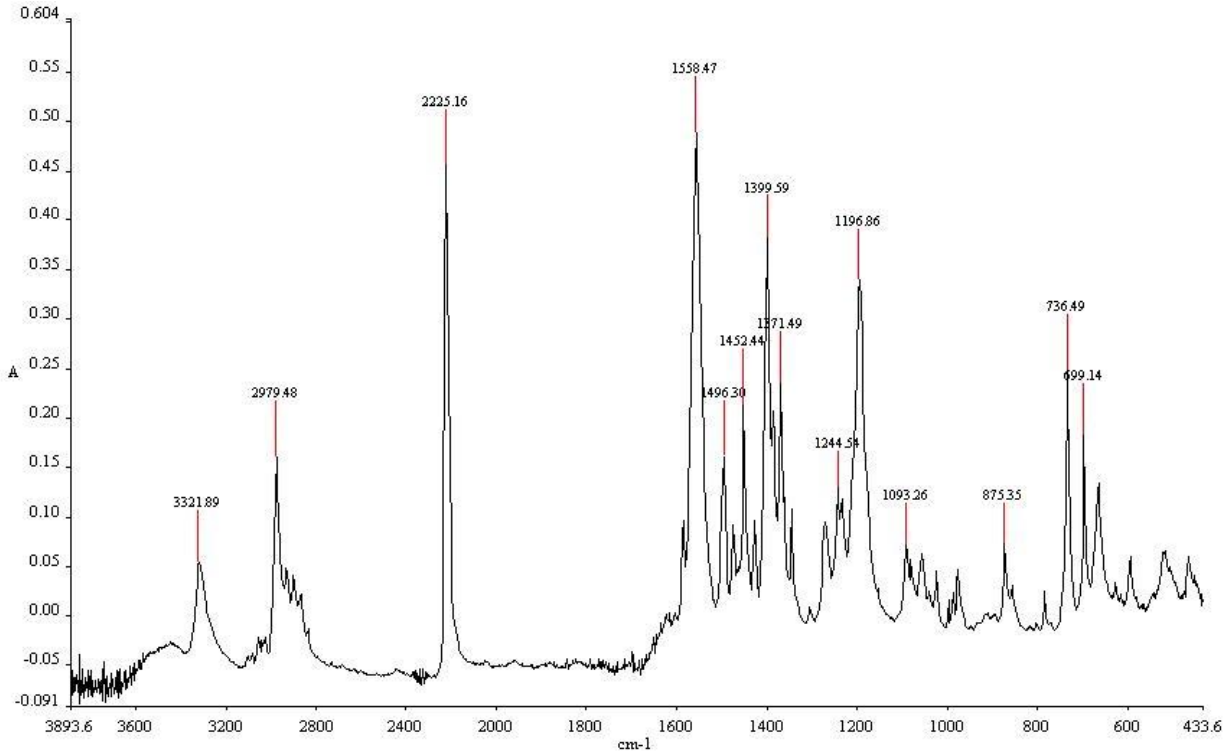

Figure S14. IR spectrum of 8.

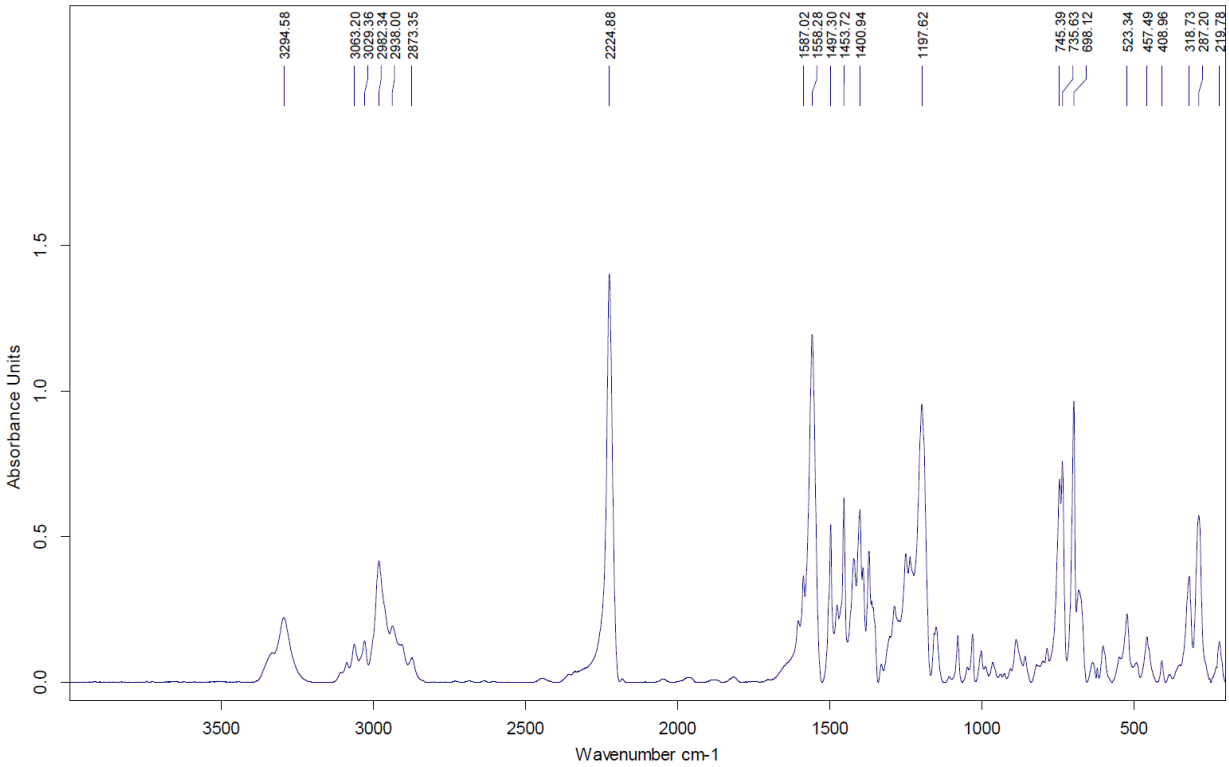

Figure S15. IR spectrum of 9.

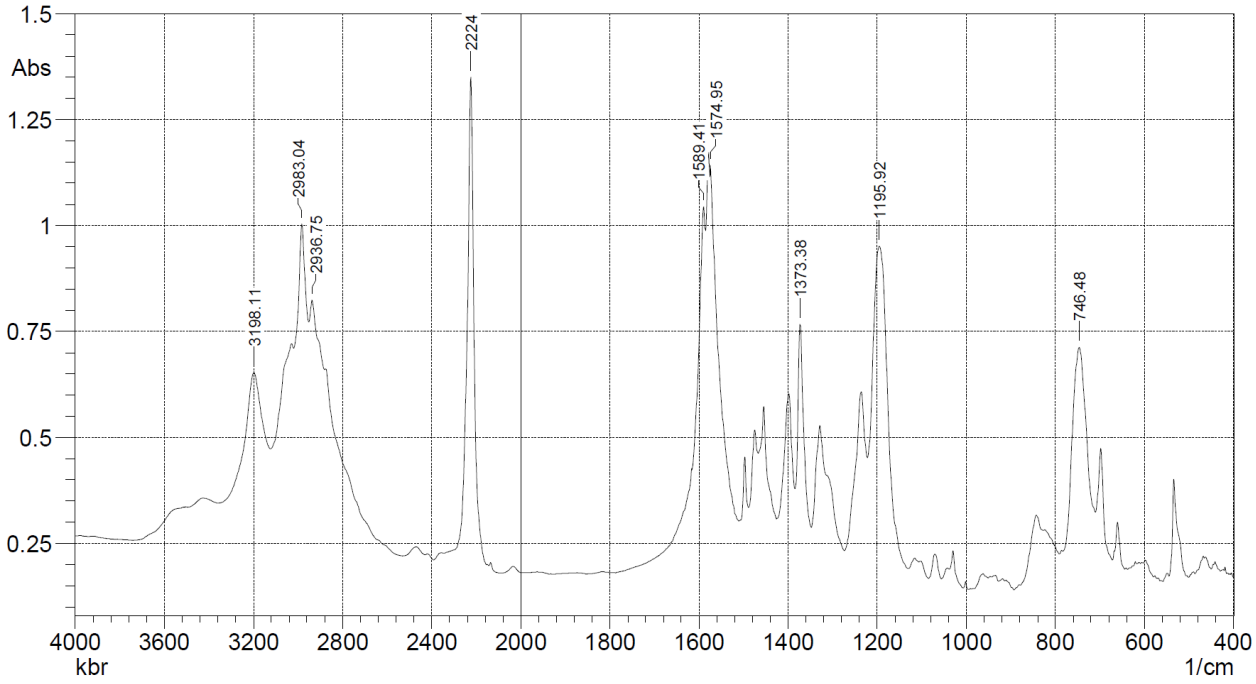

Figure S16. IR spectrum of 10.

IV. Kinetic data

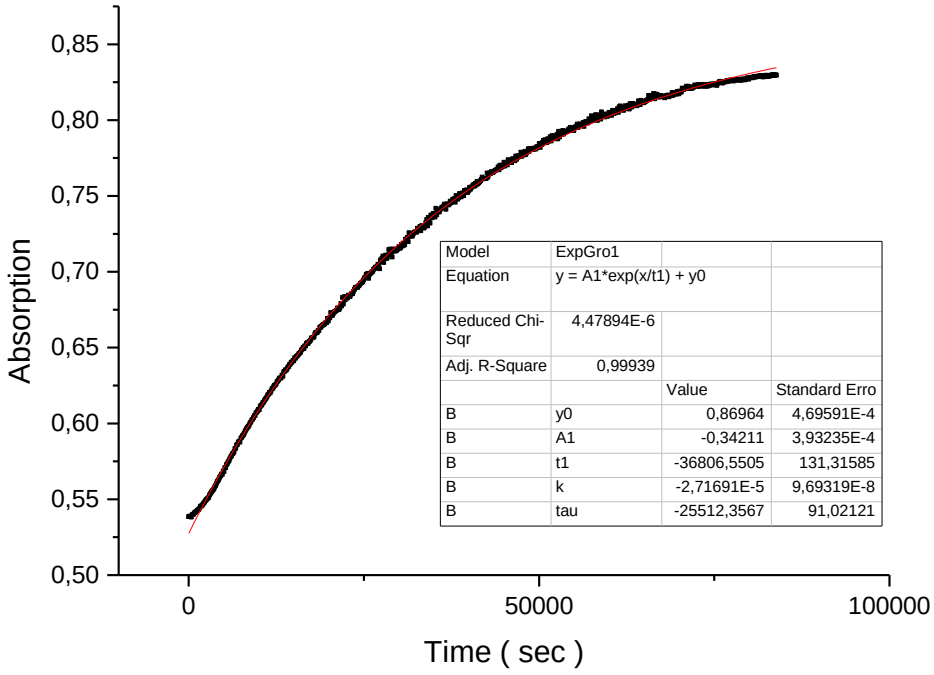

Figure S17. Fitting of decomposition of 6 in $CHCl_3$ solution with 10 equiv. of Et_3N.

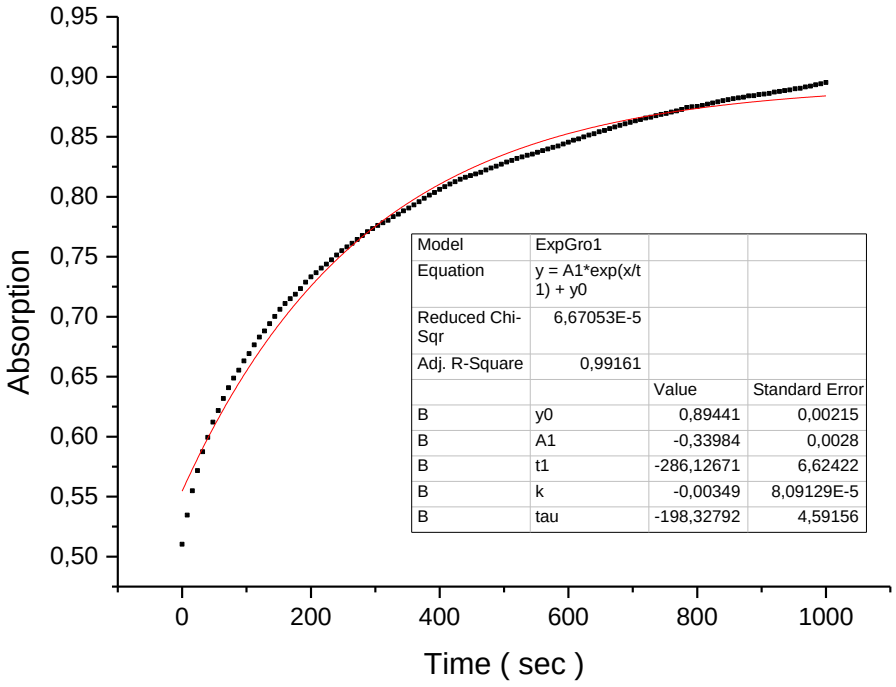

Figure S18. Fitting of decomposition of 6 with 10 equiv. of Et_3N in the presence of 10 equiv. $Et_3N{\cdot}HCl$