Supporting Information

to

Polymerization of Methyl Methacrylate by Latent Pre-Catalysts Based on CO_2-Protected N-Heterocyclic Carbenes

Stefan Naumann[1], Friedrich Georg Schmidt[2], Roman Schowner[1], Wolfgang Frey[3], and Michael R. Buchmeiser[1,4]*

Table S1. Polymerization results for MMA obtained with different imidazolinium- and imidazolium-2-carboxylates in the presence of DMSO. All polymerizations [NHC]:[MMA]=1:280. $M_{n(theor.)}$ for PMMA= 28,000 g/mol.

#	initiator	T [°C]	t [h]	MMA:DMSO [vol:vol]	Yield [%]	M_n (PDI)[a] [g/mol]
1	**5-iPr-CO_2**	50	18	1:1	0	-
2	**5-tBu-CO_2**	85	19	1:1	40	12 000 (1.66)
3	**5-tBu-CO_2**	85	20	1:0	61	>2000 000
4	**5s-tBu-CO_2**	85	25	1:0.5	22	12 000 (2.1)
5	**5s-tBu-CO_2**	85	24	1:0	4	-
6[b]	**5-Cy-CO_2**	85	24	1:0.3	6	10 000 (1.78)
7	**5-Ad-CO_2**	50	6	1:0.6	0	-
8[c]	**5-Mes-CO_2**	50	21	1:0.9	18	-
9[c]	**5-Mes-CO_2**	75	2	1:0.8	7	-

a) UV detector; b) oligomeric peaks detected; c) ill defined GPC results.

Table S2. Polymerization results for **5-tBu-CO_2**/MMA/DMSO. All polymerizations [NHC]:[MMA]=1:280. $M_{n(theor.)}$ for PMMA= 28,000 g/mol.

#	T [°C]	t [h]	MMA:DMSO [vol:vol]	Yield [%]	M_n (PDI)[a] [g/mol]
1[b]	60	18	1:0.3	32	23 000 (1.64)
2[b]	85	18	1:0.3	39	13 000 (1.66)
3[b]	85	18	1:0.2	35	18 000 (1.70)
4	85	19	1:1	40	12 000 (1.66)
5	85	68	1:1	44	14 000 (1.61)
6[c]	85	18	1:1	45	12 000 (1.67)

a) UV detector; b) oligomeric peaks/bimodal molecular weight distribution; c) [NHC]:[MMA] = 1:140.

Table S3. Polymerization results for **5-tBu-CO_2**/MMA/solvent. All polymerizations [NHC]:[MMA]=1:280. $M_{n(theor.)}$ for PMMA= 28,000 g/mol. T=85°C.

#	t [h]	MMA:solvent [vol:vol]	Yield [%]	M_n (PDI)[a] [g/mol]
1	20	bulk	61	ca. 2 000 000
2	21	toluene, 1:1	56	420 000 (1.33)
3	68	toluene, 1:2	64	350 000 (1.46)
4	69	toluene, 1:3	68	240 000 (1.60)
5[b]	71	toluene, 1:4	91	150 000 (1.85)
6	22	DME, 1:1	32	490 000 (1.25)
7	24	DME, 1:4	29	200 000 (1.84)
8	22	THF	5	n.a.

a) RI detector; b) [NHC]:[MMA] = 1:200.

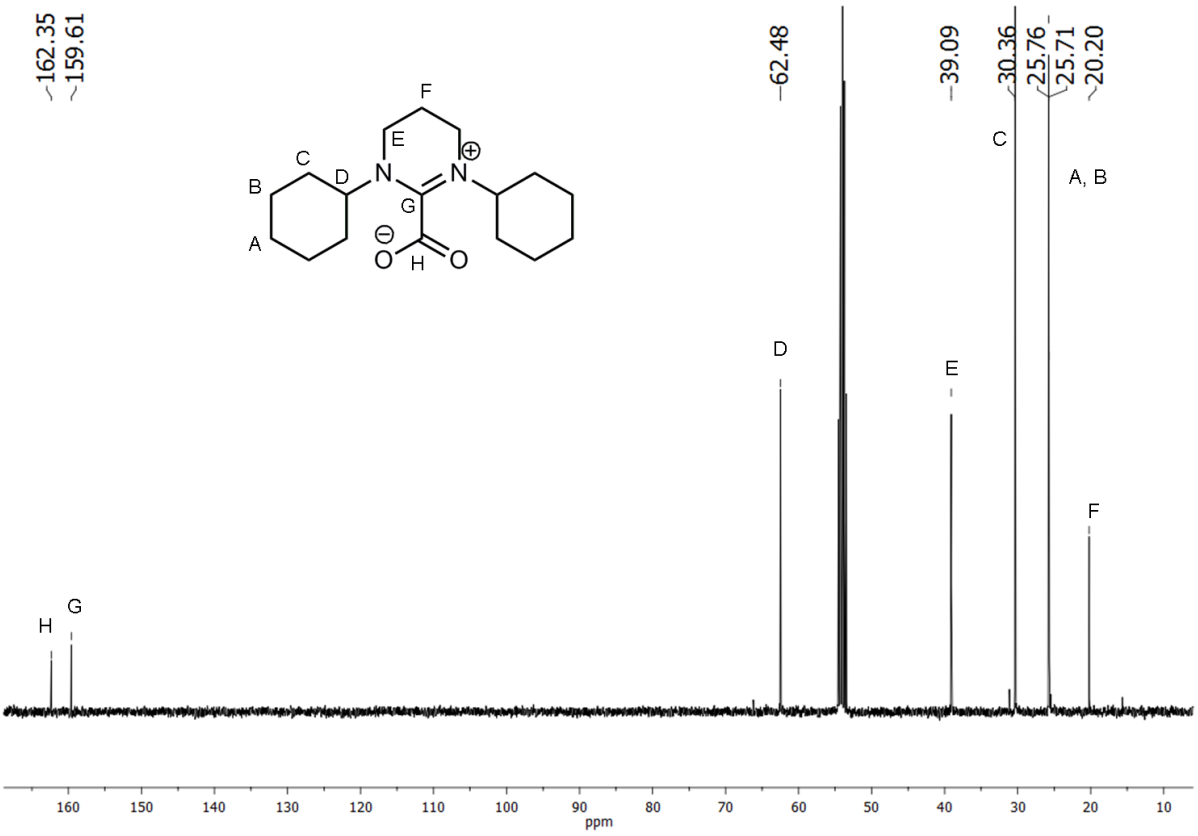


Figure S1. ^{13}C-NMR spectrum of **6-Cy-CO$_2$** (CD_2Cl_2).

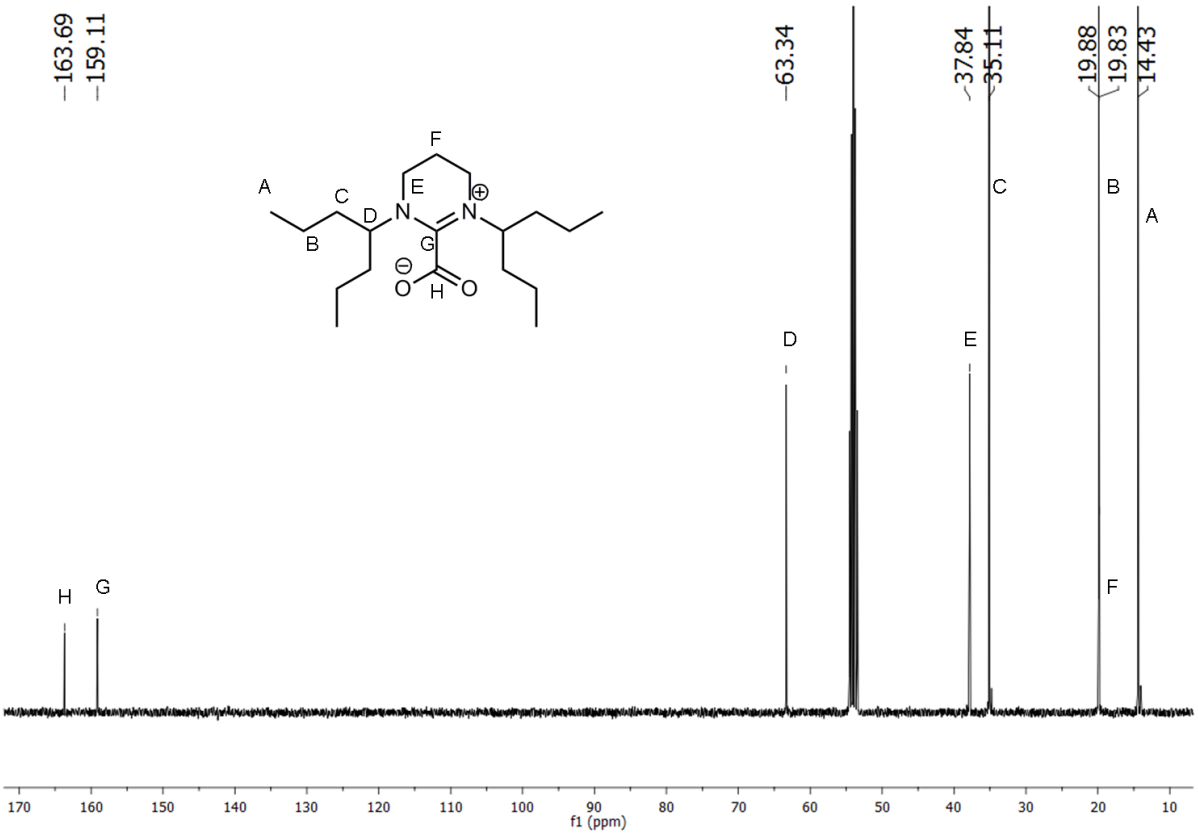


Figure S2. ^{13}C-NMR spectrum of **6-Hep-CO$_2$** (CD_2Cl_2).

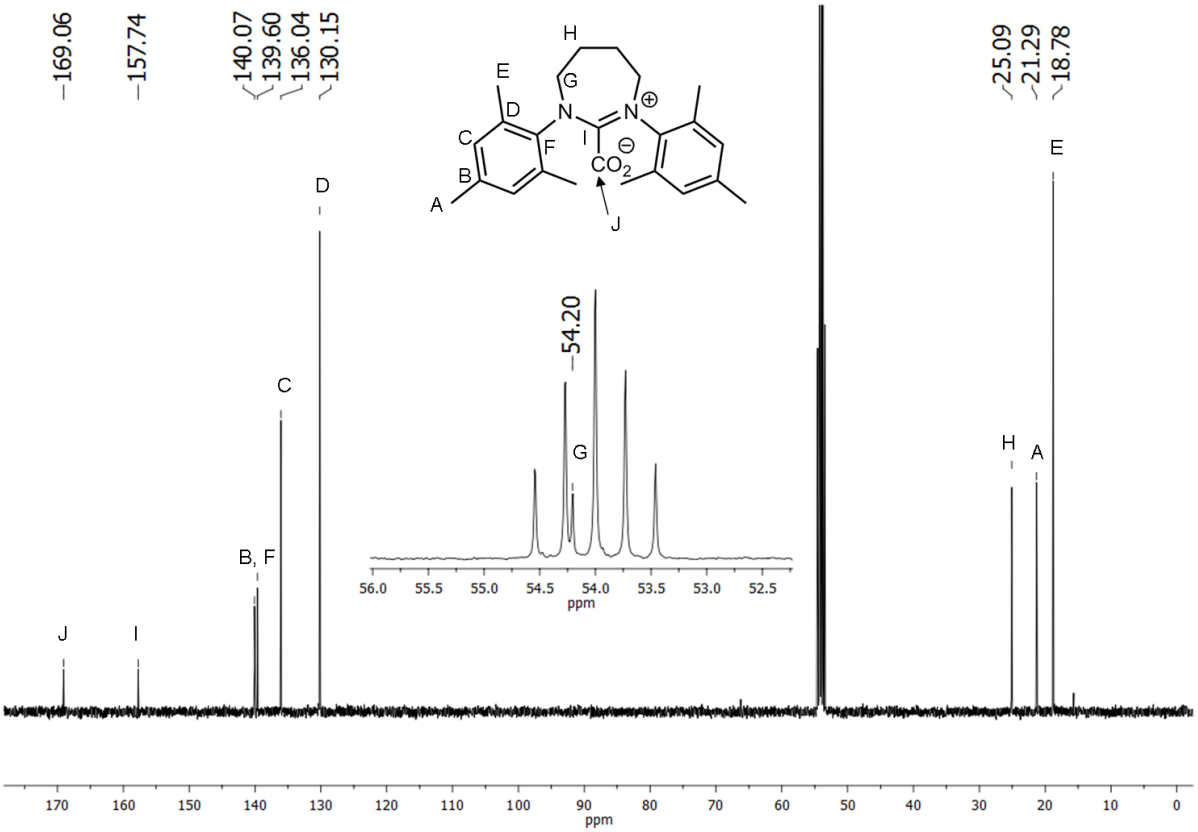


Figure S2. ^{13}C-NMR spectrum of **7-Mes-CO$_2$** (CD_2Cl_2).

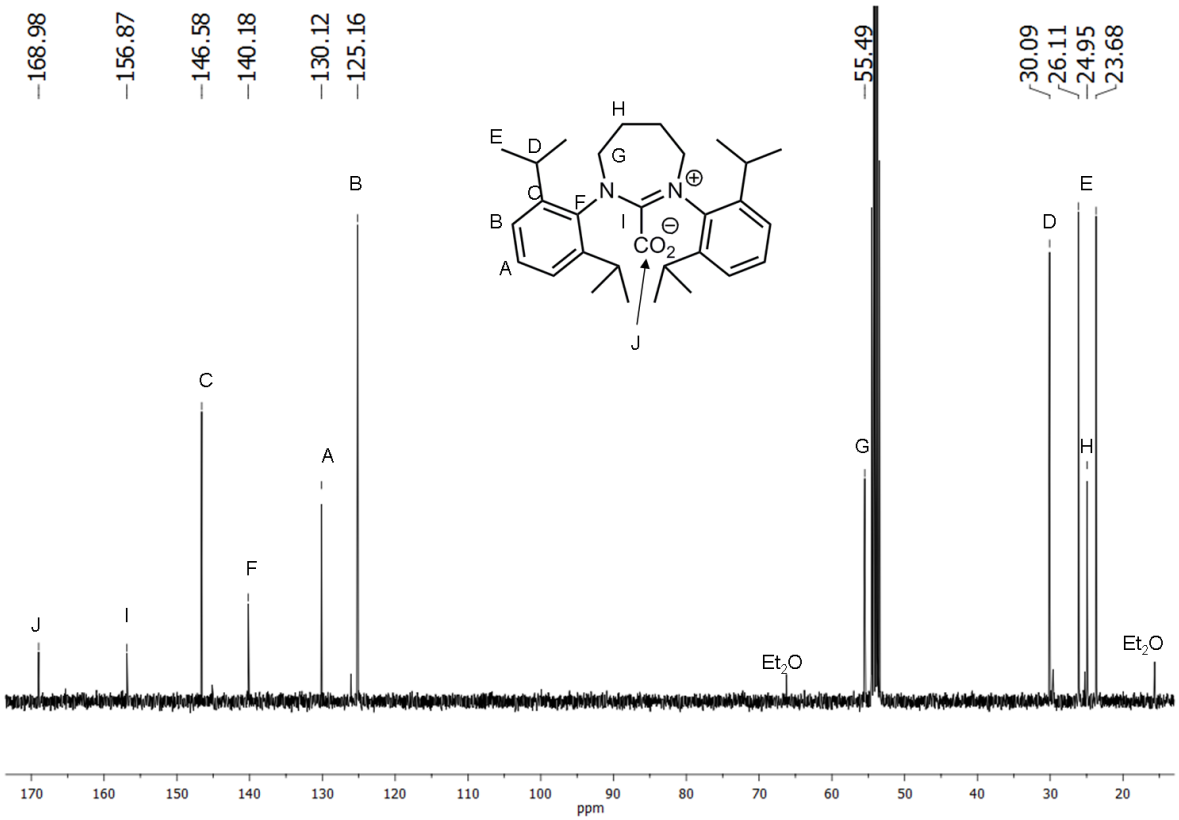


Figure S4. ^{13}C-NMR spectrum of **7-Dipp-CO_2** (CD_2Cl_2).

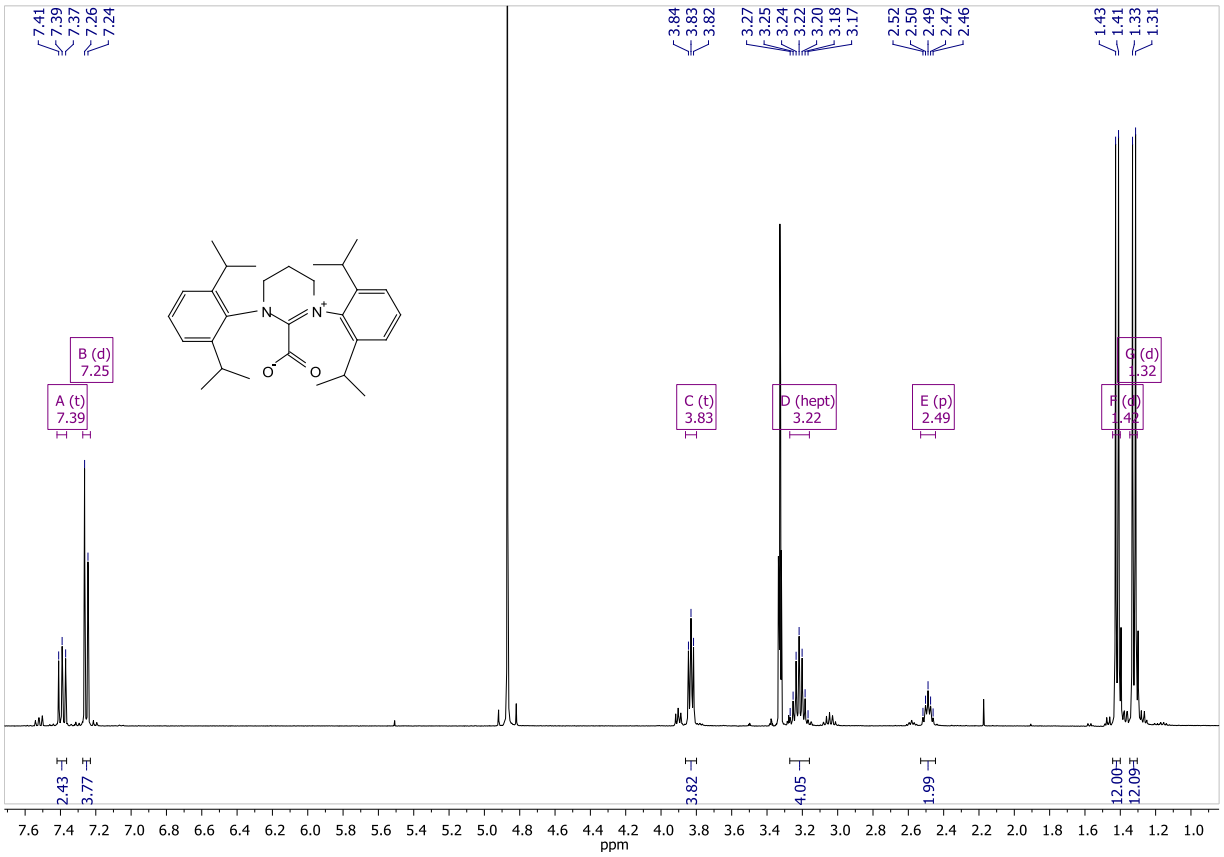


Figure S5. ^{1}H NMR spectrum (CD_3OD) of **6-Dipp-CO_2**.

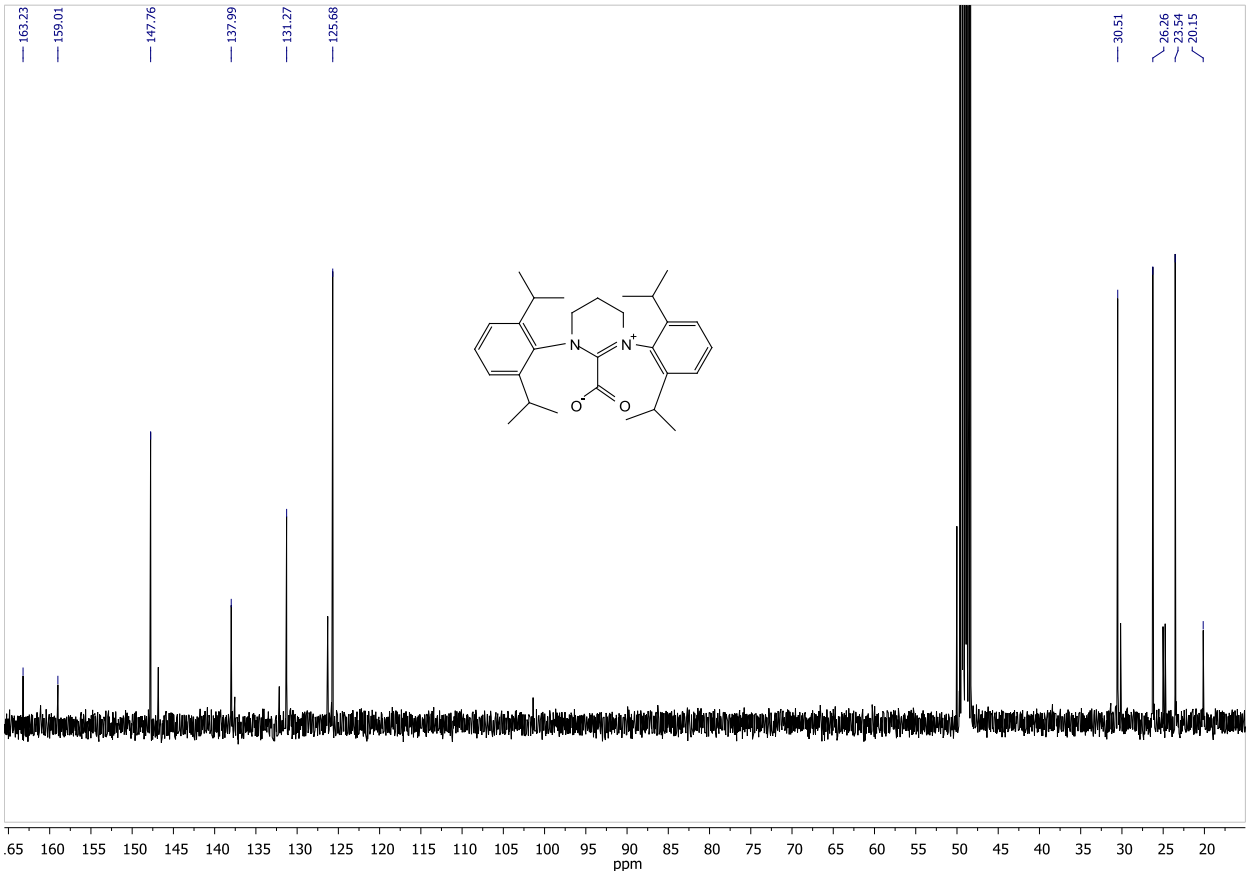


Figure S6. ^{13}C NMR spectrum (CD_3OD) of **6-Dipp-CO_2**.

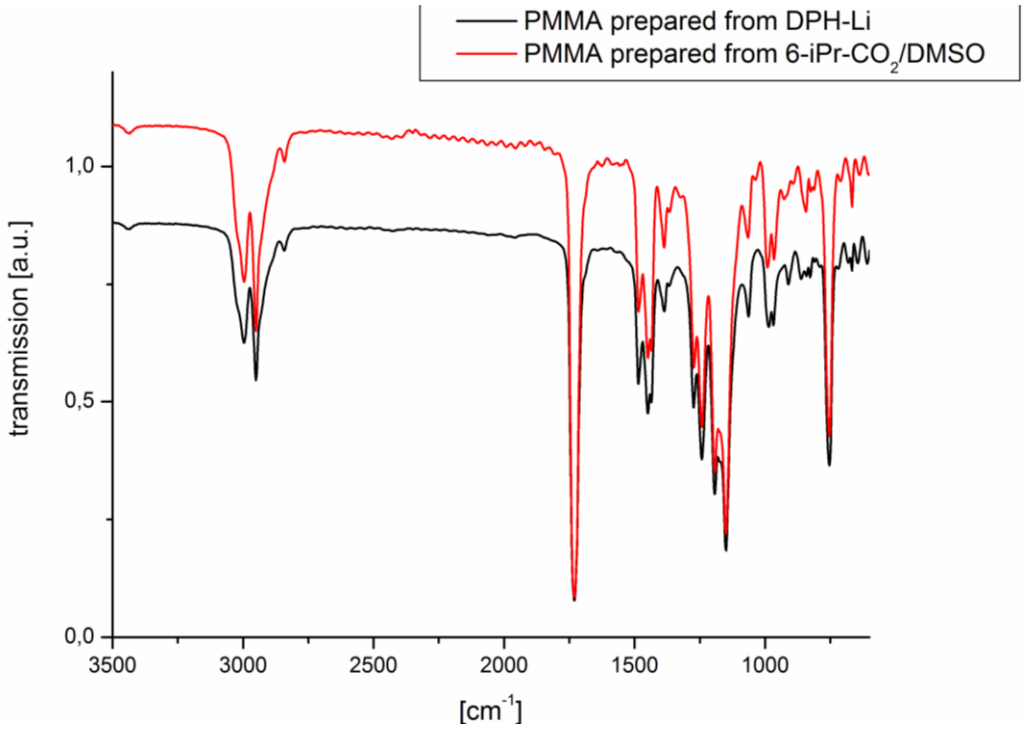


Figure S7. IR-spectra of PMMA obtained via **6-iPr-CO_2**/DMSO- (red) and DPH-Li (diphenylhexyllithium) triggered (black) anionic polymerization.

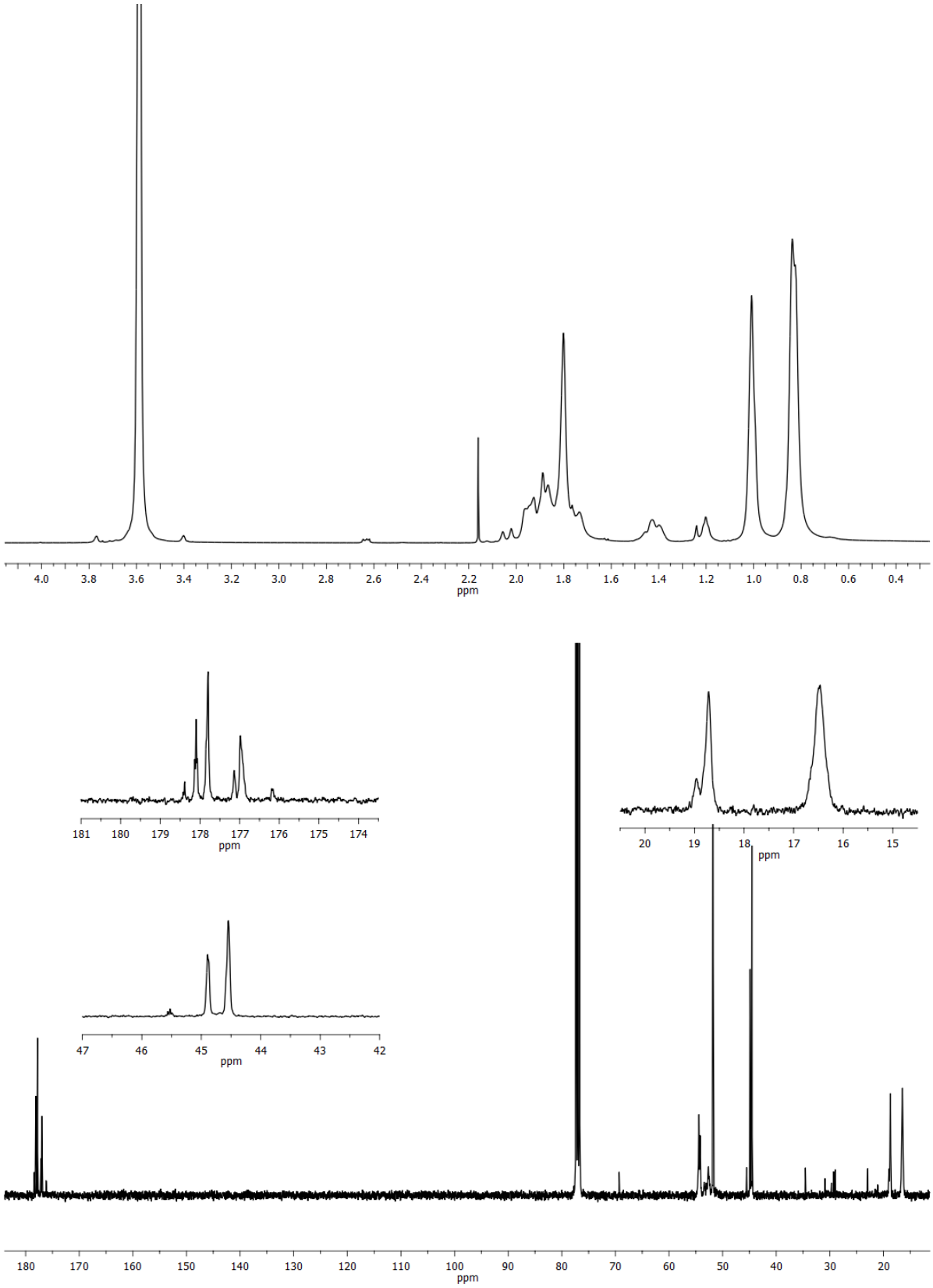
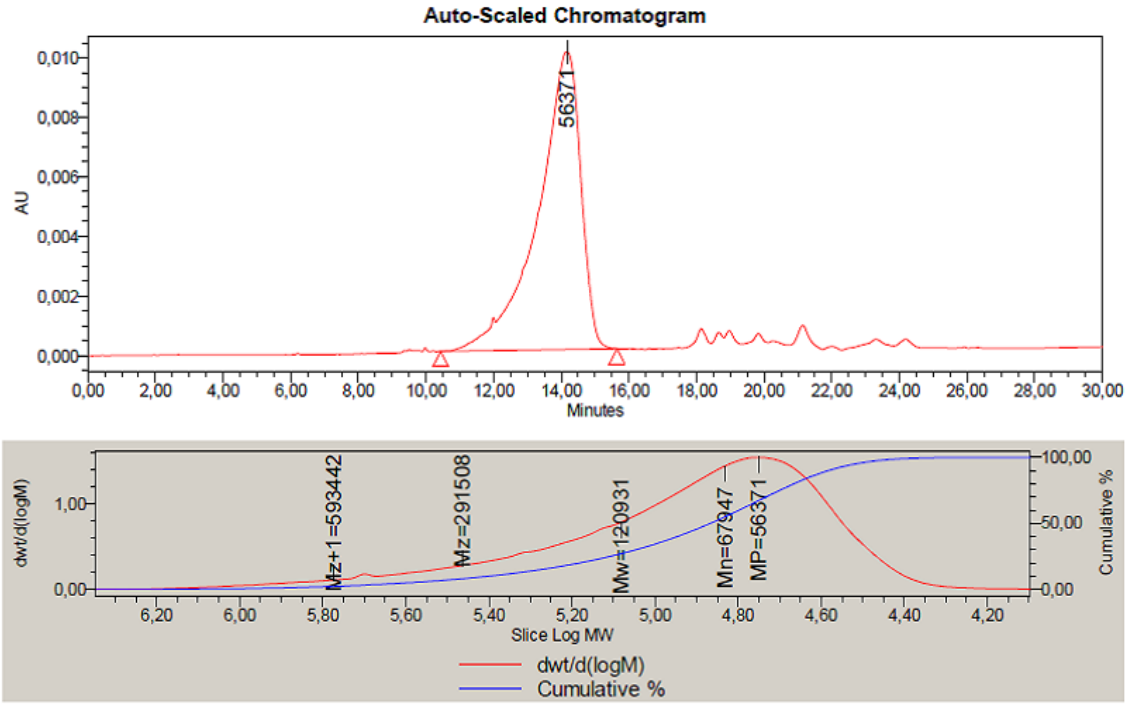


Figure S8. ^{1}H- and ^{13}C-NMR of PMMA prepared by the action of **6-iPr-CO$_2$** at T=85°C in DMSO.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		67947	120931	56371	291508	593442		1,779784		

Figure S9. GPC-trace of PMMA obtained by the action of **6-iPr-CO_2** in DMSO at 50°C.

Table 1. Crystal data and structure refinement for **6-Dipp-CO_2**.

Empirical formula	$C_{31}H_{44}Cl_4N_2O_2$
Formula weight	618.48
Temperature	100(2) K
Wavelength	71.073 nm
Crystal system, space group	monoclinic, C 2/c
Unit cell dimensions	a = 16.2658(17) Å α = 90°.
	b = 9.9841(11) Å β = 108.293(5)°
	c = 21.212(2) Å γ = 90°.
Volume	3270.7(6) A^3
Z, Calculated density	4, 1.256 Mg/m^3
Absorption coefficient	0.391 mm^{-1}
F(000)	1312
Crystal size	0.32 x 0.16 x 0.14 mm
Theta range for data collection	2.02 to 26.4°.
Limiting indices	-19<=h<=20, -12<=k<=12, -26<=l<=26
Reflections collected / unique	21570 / 3320 [R(int) = 0.0400]
Completeness to theta = 26.42	98.8 %
Max. and min. transmission	0.9472 and 0.8850
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3320 / 6 / 186
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1162
R indices (all data)	R1 = 0.0614, wR2 = 0.1221
Largest diff. peak and hole	0.718 and -0.501 $e.A^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **6-Dipp-CO_2**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	732(1)	2495(2)	2672(1)	28(1)
N(1)	-50(1)	-210(2)	3032(1)	20(1)
C(1)	0	435(3)	2500	18(1)
C(2)	-78(2)	-1690(2)	3062(1)	30(1)
C(3)	318(3)	-2292(5)	2621(2)	24(1)
C(4)	0	1987(3)	2500	20(1)
C(5)	-34(2)	515(2)	3631(1)	18(1)
C(6)	-822(2)	913(2)	3713(1)	19(1)
C(7)	-780(2)	1560(2)	4306(1)	22(1)
C(8)	7(2)	1787(2)	4792(1)	23(1)
C(9)	772(2)	1376(2)	4696(1)	21(1)
C(10)	773(2)	729(2)	4110(1)	19(1)
C(11)	-1696(2)	627(3)	3197(1)	25(1)
C(12)	-2276(2)	1870(3)	3039(1)	34(1)
C(13)	-2155(2)	-528(3)	3426(1)	32(1)
C(14)	1623(2)	291(3)	4016(1)	23(1)
C(15)	2259(2)	1460(3)	4116(2)	38(1)
C(16)	2030(2)	-878(3)	4475(1)	32(1)
C(1X)	-106(2)	4404(3)	1362(1)	27(1)
Cl(1X)	892(1)	5226(1)	1519(1)	49(1)
Cl(2X)	-949(1)	5316(1)	801(1)	52(1)

Table 3. Bond lengths [Å] and angles [°] for **6-Dipp-CO_2**.

O(1)-C(4)	1.239(2)
N(1)-C(1)	1.325(2)
N(1)-C(5)	1.455(3)
N(1)-C(2)	1.480(3)
C(1)-N(1)#1	1.324(2)
C(1)-C(4)	1.549(5)
C(2)-C(3)	1.425(6)
C(2)-C(3)#1	1.503(5)
C(2)-H(2A)	0.9958
C(2)-H(2B)	1.0113
C(2)-H(2C)	0.9576
C(2)-H(2D)	0.9661
C(3)-C(3)#1	1.002(10)
C(3)-C(2)#1	1.503(5)
C(3)-H(2D)	1.4548
C(3)-H(3A)	1.0156
C(3)-H(3B)	1.0309
C(4)-O(1)#1	1.239(2)
C(5)-C(10)	1.401(3)
C(5)-C(6)	1.404(3)
C(6)-C(7)	1.396(3)
C(6)-C(11)	1.524(3)
C(7)-C(8)	1.387(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.385(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.401(3)
C(9)-H(9)	0.9500
C(10)-C(14)	1.523(3)
C(11)-C(12)	1.531(4)
C(11)-C(13)	1.532(4)
C(11)-H(11)	1.0000

C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(15)	1.529(4)
C(14)-C(16)	1.532(4)
C(14)-H(14)	1.0000
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(1X)-Cl(1X)	1.756(3)
C(1X)-Cl(2X)	1.761(3)
C(1X)-H(1X1)	0.9900
C(1X)-H(1X2)	0.9900

C(1)-N(1)-C(5)	120.9(2)
C(1)-N(1)-C(2)	122.2(2)
C(5)-N(1)-C(2)	116.84(18)
N(1)#1-C(1)-N(1)	121.8(3)
N(1)#1-C(1)-C(4)	119.10(15)
N(1)-C(1)-C(4)	119.10(15)
C(3)-C(2)-N(1)	111.5(3)
C(3)-C(2)-C(3)#1	39.9(4)
N(1)-C(2)-C(3)#1	111.1(2)
C(3)-C(2)-H(2A)	124.8
N(1)-C(2)-H(2A)	107.8
C(3)#1-C(2)-H(2A)	140.9
C(3)-C(2)-H(2B)	98.1
N(1)-C(2)-H(2B)	104.4

C(3)#1-C(2)-H(2B)	59.1
H(2A)-C(2)-H(2B)	108.0
C(3)-C(2)-H(2C)	136.1
N(1)-C(2)-H(2C)	109.7
C(3)#1-C(2)-H(2C)	109.8
H(2A)-C(2)-H(2C)	52.0
H(2B)-C(2)-H(2C)	56.9
C(3)-C(2)-H(2D)	72.1
N(1)-C(2)-H(2D)	109.2
C(3)#1-C(2)-H(2D)	109.3
H(2A)-C(2)-H(2D)	59.1
H(2B)-C(2)-H(2D)	146.3
H(2C)-C(2)-H(2D)	107.7
C(3)#1-C(3)-C(2)	74.3(5)
C(3)#1-C(3)-C(2)#1	65.8(5)
C(2)-C(3)-C(2)#1	115.4(4)
C(3)#1-C(3)-H(2D)	110.8
C(2)-C(3)-H(2D)	39.2
C(2)#1-C(3)-H(2D)	145.2
C(3)#1-C(3)-H(3A)	60.4
C(2)-C(3)-H(3A)	103.5
C(2)#1-C(3)-H(3A)	98.4
H(2D)-C(3)-H(3A)	109.8
C(3)#1-C(3)-H(3B)	167.5
C(2)-C(3)-H(3B)	101.1
C(2)#1-C(3)-H(3B)	107.2
H(2D)-C(3)-H(3B)	68.4
H(3A)-C(3)-H(3B)	132.0
O(1)-C(4)-O(1)#1	131.6(3)
O(1)-C(4)-C(1)	114.19(16)
O(1)#1-C(4)-C(1)	114.19(16)
C(10)-C(5)-C(6)	123.4(2)
C(10)-C(5)-N(1)	117.7(2)
C(6)-C(5)-N(1)	118.8(2)

C(7)-C(6)-C(5)	116.9(2)
C(7)-C(6)-C(11)	120.3(2)
C(5)-C(6)-C(11)	122.7(2)
C(8)-C(7)-C(6)	121.3(2)
C(8)-C(7)-H(7)	119.4
C(6)-C(7)-H(7)	119.4
C(9)-C(8)-C(7)	120.3(2)
C(9)-C(8)-H(8)	119.9
C(7)-C(8)-H(8)	119.9
C(8)-C(9)-C(10)	121.2(2)
C(8)-C(9)-H(9)	119.4
C(10)-C(9)-H(9)	119.4
C(5)-C(10)-C(9)	116.9(2)
C(5)-C(10)-C(14)	122.9(2)
C(9)-C(10)-C(14)	120.2(2)
C(6)-C(11)-C(12)	112.1(2)
C(6)-C(11)-C(13)	110.5(2)
C(12)-C(11)-C(13)	110.6(2)
C(6)-C(11)-H(11)	107.8
C(12)-C(11)-H(11)	107.8
C(13)-C(11)-H(11)	107.8
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(10)-C(14)-C(15)	111.4(2)

C(10)-C(14)-C(16)	111.3(2)
C(15)-C(14)-C(16)	110.8(2)
C(10)-C(14)-H(14)	107.7
C(15)-C(14)-H(14)	107.7
C(16)-C(14)-H(14)	107.7
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
Cl(1X)-C(1X)-Cl(2X)	111.34(14)
Cl(1X)-C(1X)-H(1X1)	109.4
Cl(2X)-C(1X)-H(1X1)	109.4
Cl(1X)-C(1X)-H(1X2)	109.4
Cl(2X)-C(1X)-H(1X2)	109.4
H(1X1)-C(1X)-H(1X2)	108.0

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+1/2

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **6-Dipp-CO_2**. The anisotropic displacement factor exponent takes the form: $-2\Pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	37(1)	20(1)	29(1)	-4(1)	15(1)	-7(1)
N(1)	31(1)	15(1)	14(1)	-1(1)	7(1)	-3(1)
C(1)	21(2)	17(2)	17(2)	0	6(1)	0
C(2)	53(2)	15(1)	20(1)	0(1)	10(1)	-5(1)
C(3)	34(3)	18(2)	20(3)	1(2)	8(2)	-3(2)
C(4)	36(2)	15(2)	14(2)	0	14(1)	0
C(5)	29(1)	13(1)	14(1)	1(1)	8(1)	-5(1)
C(6)	24(1)	17(1)	18(1)	4(1)	7(1)	-4(1)
C(7)	27(1)	20(1)	21(1)	1(1)	11(1)	-3(1)
C(8)	33(1)	20(1)	17(1)	-1(1)	10(1)	-3(1)
C(9)	25(1)	20(1)	17(1)	0(1)	5(1)	-5(1)
C(10)	26(1)	15(1)	17(1)	2(1)	9(1)	-3(1)
C(11)	25(1)	28(1)	19(1)	0(1)	4(1)	-6(1)
C(12)	28(1)	36(2)	34(2)	3(1)	1(1)	-2(1)
C(13)	32(2)	34(2)	29(1)	-1(1)	7(1)	-13(1)
C(14)	25(1)	26(1)	20(1)	-3(1)	9(1)	-2(1)
C(15)	32(2)	38(2)	53(2)	-5(1)	24(1)	-9(1)
C(16)	31(1)	33(2)	32(1)	4(1)	10(1)	6(1)
C(1X)	31(1)	18(1)	33(1)	1(1)	11(1)	-1(1)
Cl(1X)	29(1)	27(1)	85(1)	-3(1)	11(1)	-2(1)
Cl(2X)	35(1)	43(1)	67(1)	15(1)	-2(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **6-Dipp-CO_2**.

	x	y	z	U(eq)
H(2A)	36	-1951	3535	44
H(2B)	-700	-1925	2812	44
H(2C)	-488	-1959	3277	44
H(2D)	483	-2019	3324	44
H(3A)	0	-3177	2500	36
H(3B)	961	-2070	2856	36
H(7)	-1299	1849	4378	26
H(8)	21	2226	5193	27
H(9)	1306	1535	5034	25
H(11)	-1587	341	2778	29
H(12A)	-2430	2131	3433	51
H(12B)	-2804	1669	2674	51
H(12C)	-1965	2607	2909	51
H(13A)	-1798	-1337	3485	48
H(13B)	-2716	-695	3090	48
H(13C)	-2243	-290	3848	48
H(14)	1493	-27	3547	28
H(15A)	1984	2201	3823	57
H(15B)	2776	1169	4011	57
H(15C)	2425	1758	4580	57
H(16A)	2156	-598	4939	48
H(16B)	2568	-1151	4397	48
H(16C)	1625	-1634	4385	48
H(1X1)	-236	4286	1785	32
H(1X2)	-70	3504	1177	32

Table 6. Torsion angles [°] for **6-Dipp-CO_2**.

C(5)-N(1)-C(1)-N(1)#1	175.0(2)
C(2)-N(1)-C(1)-N(1)#1	-1.75(17)
C(5)-N(1)-C(1)-C(4)	-5.0(2)
C(2)-N(1)-C(1)-C(4)	178.25(17)
C(1)-N(1)-C(2)-C(3)	25.4(4)
C(5)-N(1)-C(2)-C(3)	-151.4(3)
C(1)-N(1)-C(2)-C(3)#1	-17.6(4)
C(5)-N(1)-C(2)-C(3)#1	165.6(3)
N(1)-C(2)-C(3)-C(3)#1	-97.6(3)
N(1)-C(2)-C(3)-C(2)#1	-44.8(4)
C(3)#1-C(2)-C(3)-C(2)#1	52.8(4)
N(1)#1-C(1)-C(4)-O(1)	-85.70(14)
N(1)-C(1)-C(4)-O(1)	94.31(14)
N(1)#1-C(1)-C(4)-O(1)#1	94.31(13)
N(1)-C(1)-C(4)-O(1)#1	-85.69(14)
C(1)-N(1)-C(5)-C(10)	-90.8(2)
C(2)-N(1)-C(5)-C(10)	86.1(3)
C(1)-N(1)-C(5)-C(6)	91.8(2)
C(2)-N(1)-C(5)-C(6)	-91.4(3)
C(10)-C(5)-C(6)-C(7)	0.3(3)
N(1)-C(5)-C(6)-C(7)	177.6(2)
C(10)-C(5)-C(6)-C(11)	-177.7(2)
N(1)-C(5)-C(6)-C(11)	-0.5(3)
C(5)-C(6)-C(7)-C(8)	-0.4(3)
C(11)-C(6)-C(7)-C(8)	177.7(2)
C(6)-C(7)-C(8)-C(9)	0.2(4)
C(7)-C(8)-C(9)-C(10)	0.2(4)
C(6)-C(5)-C(10)-C(9)	0.0(3)
N(1)-C(5)-C(10)-C(9)	-177.3(2)
C(6)-C(5)-C(10)-C(14)	180.0(2)
N(1)-C(5)-C(10)-C(14)	2.7(3)
C(8)-C(9)-C(10)-C(5)	-0.3(3)

C(8)-C(9)-C(10)-C(14)	179.8(2)
C(7)-C(6)-C(11)-C(12)	49.9(3)
C(5)-C(6)-C(11)-C(12)	-132.1(2)
C(7)-C(6)-C(11)-C(13)	-74.0(3)
C(5)-C(6)-C(11)-C(13)	104.0(3)
C(5)-C(10)-C(14)-C(15)	125.9(3)
C(9)-C(10)-C(14)-C(15)	-54.2(3)
C(5)-C(10)-C(14)-C(16)	-109.9(3)
C(9)-C(10)-C(14)-C(16)	70.0(3)

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+1/2.