Supplementary Materials

Table S1. Key ^{1}H and ^{13}C NMR chemical shifts (δ, ppm) of amidines (1a-b) with and without methanol ($CDCl_3$, 500 MHz for ^{1}H, 125 MHz for ^{13}C).

Group / Assignment	Amidine (1a) (no MeOH)			Amidine (1b) (with MeOH)		
	^{1}H NMR δ (ppm)	**Multiplicity**	**^{13}C NMR δ (ppm)**	**^{1}H NMR δ (ppm)**	**Multiplicity**	**^{13}C NMR δ (ppm)**
–$N(CH_3)_2$ (2 × CH_3)	3.33 (6H)	s	38.62	2.85, 2.93 (each 3H)	s, s	38.62
–CH_2–OH (3 × CH_2)	3.52 (6H)	dd (J = 9.94, 11.47 Hz)	64.91	3.59 (6H)	dd (J = 11.51, 18.40 Hz)	64.91
–OH (hydroxyl)	4.11 (3H)	s	-	4.15 (2H)	s	-
=CH–N (amidine proton)	6.87 (1H)	s	156.88	6.91 (1H)	s	156.88
–OH (H-bonded to MeOH)	-	-	-	7.97 (1H)	s	-
– CH_3 (MeOH)	-	-	-	3.42 (3H)	s	70.73
Quaternary C	-	-	75.56	-	-	75.56

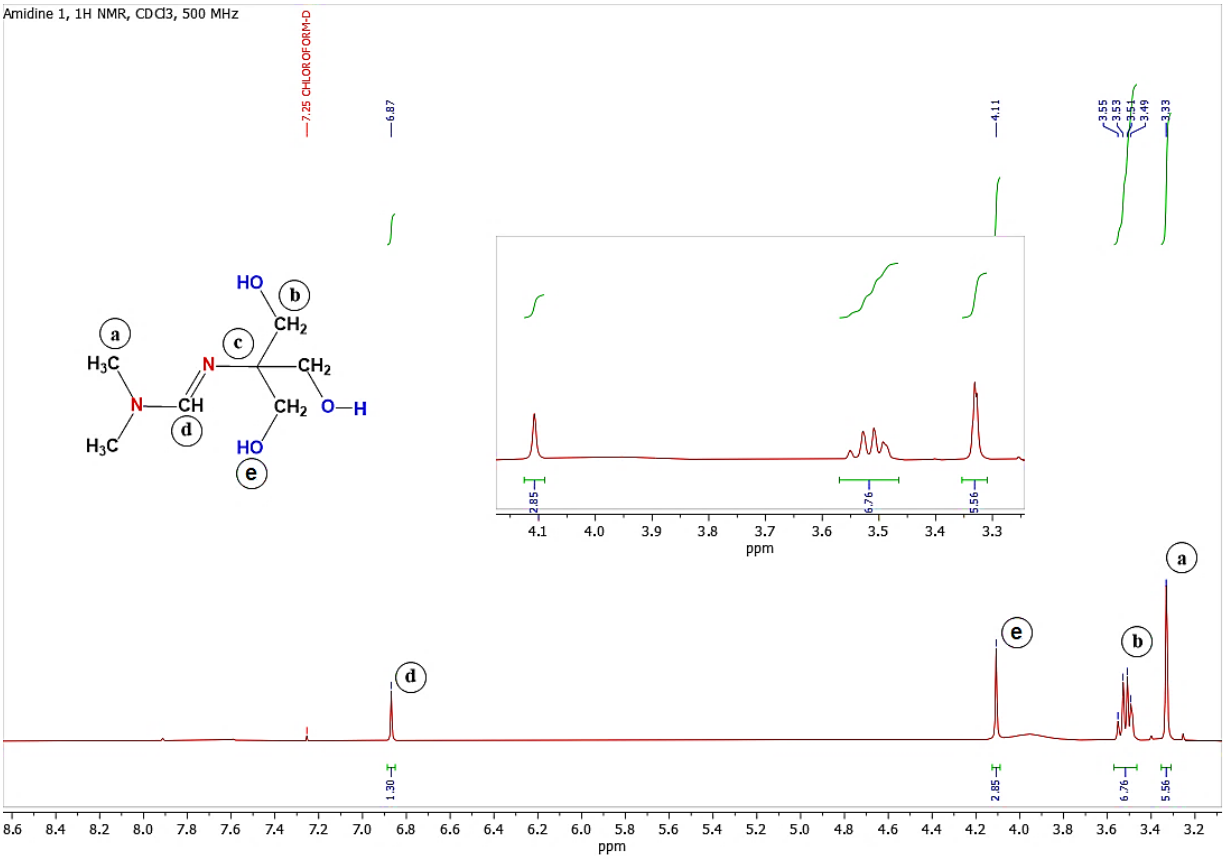


Figure S1.[1]H NMR spectrum of amidine (1a) in $CDCl_3$ (500 MHz, without methanol).

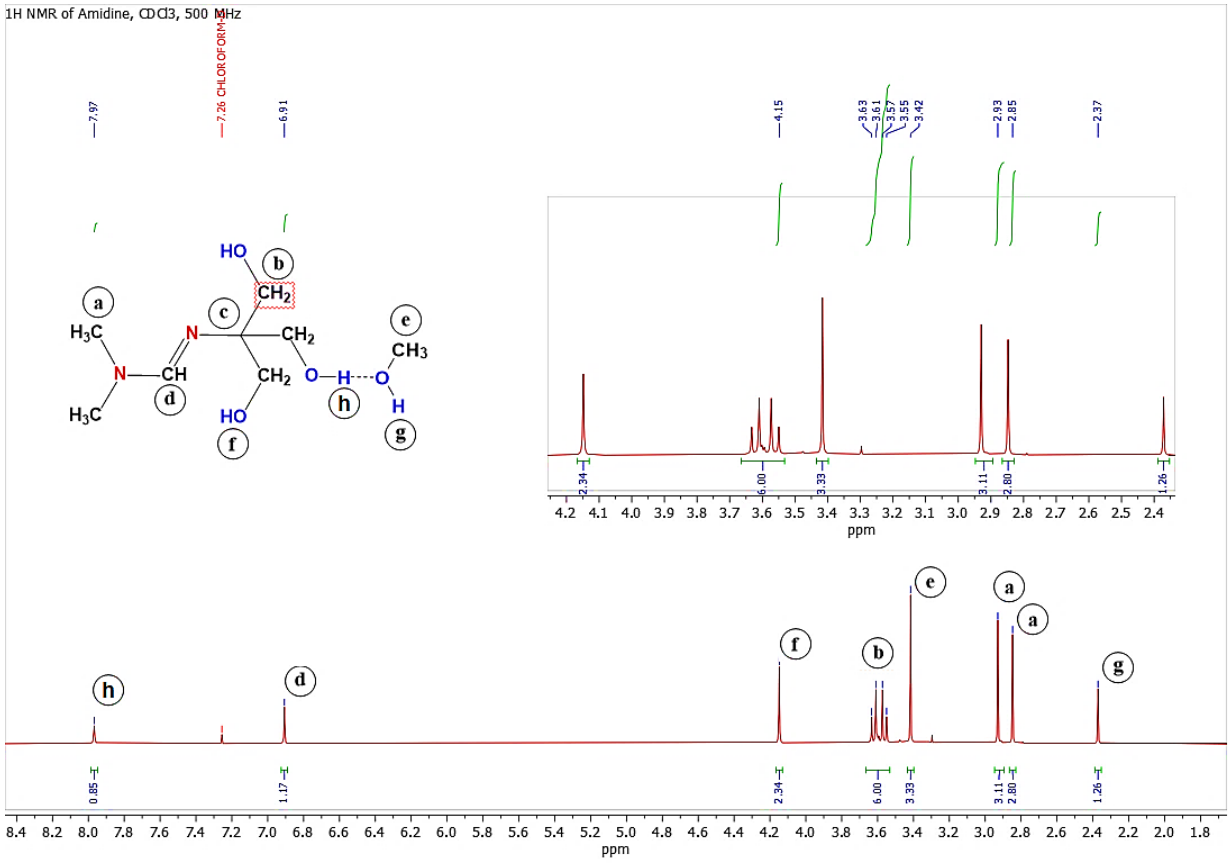


Figure S2.[1]H NMR spectrum of amidine (1b) in $CDCl_3$ (500 MHz, with methanol).

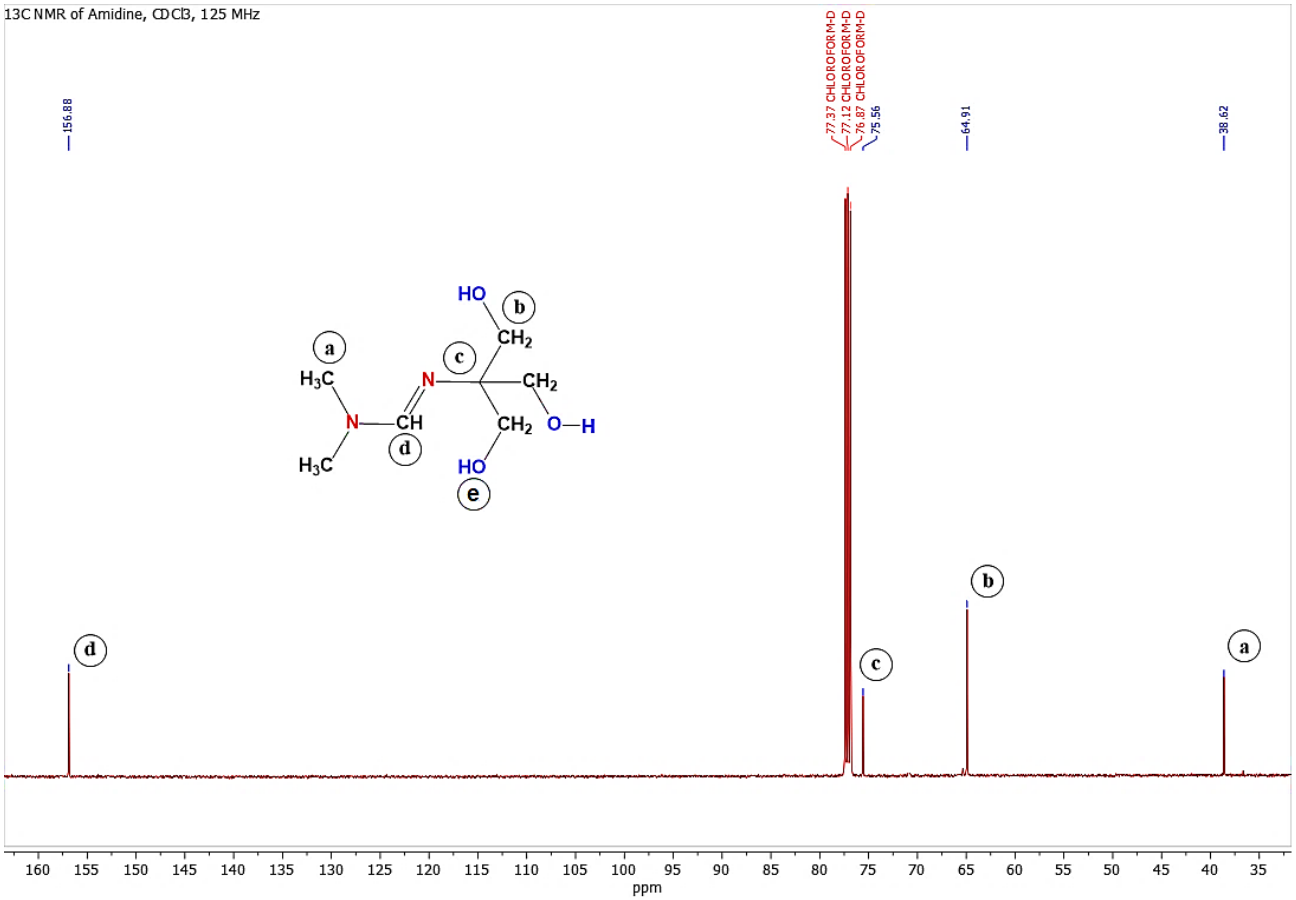


Figure S3. ^{13}C NMR spectrum of amidine (1a) in $CDCl_3$ (125 MHz, without methanol).

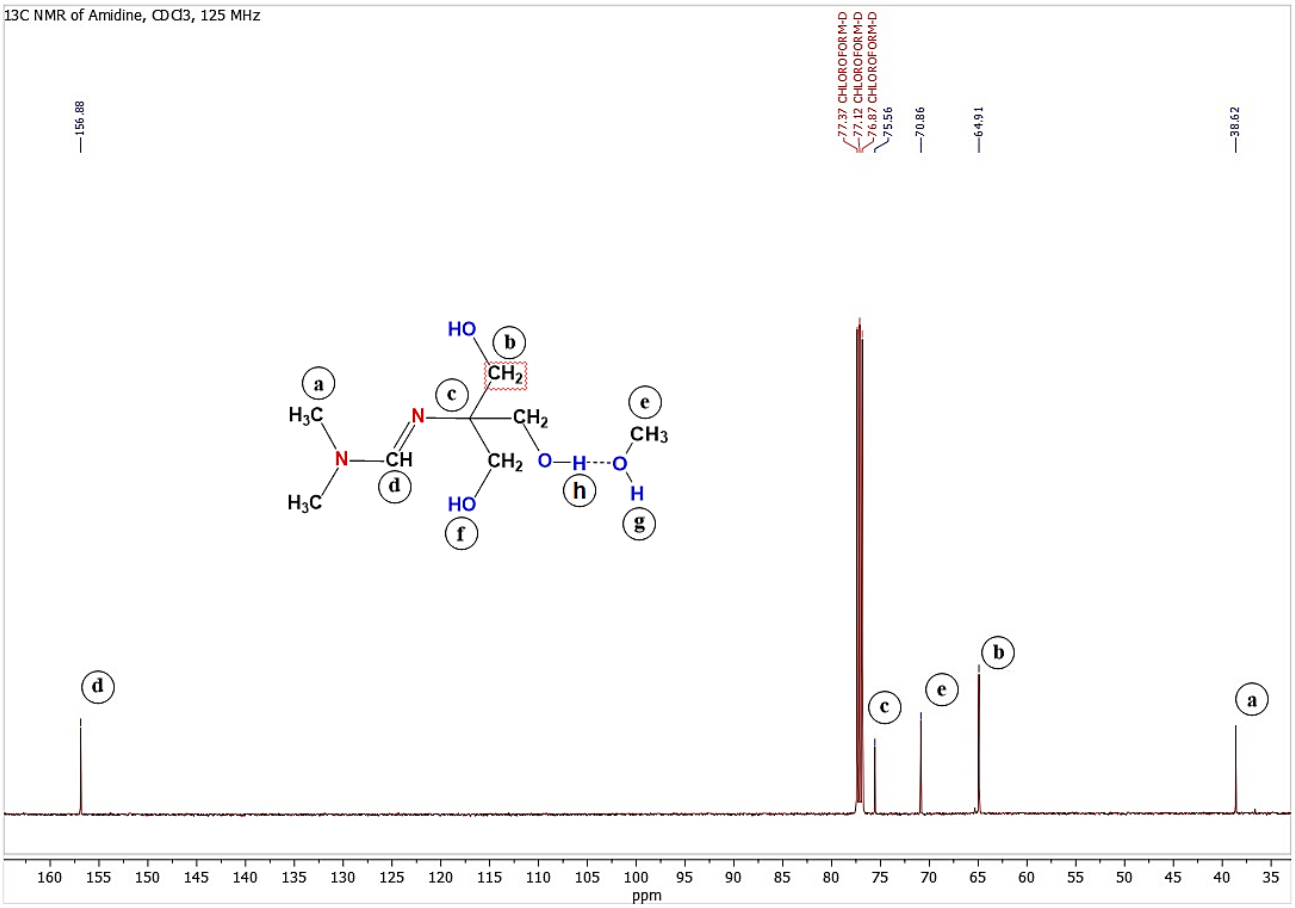


Figure S4. ^{13}C NMR spectrum of amidine (1b) in $CDCl_3$ (125 MHz, with methanol).

Table S2. Results of efflux time measurements for amidine (1b) and PIL samples.

Sample	ET-1, s	ET-2, s	ET-3, s	AET ± SD, s
i-Pr-OH (ref.)	234	234	234	234.0 ± 0.00
Amidine (1b)	247	246	246	246.3 ± 0.58
PIL-10	244	243	243	243.3 ± 0.58
PIL-20	248	250	250	249.3± 1.15
PIL-40	256	254	253	254.3 ± 1.53
PIL-60	256	256	257	256.3 ± 0.58
PIL-80	257	256	257	256.7 ± 0.58

*ET - Efflux Time; AET – Average Efflux Time; SD – Standard Deviation; i-Pr-OH – Isopropanol.

Table S3. Relative viscosity (η_{Rel}) of amidine (1b) and PILs at different CO_2 bubbling times.

Sample	Relative viscosity η_{rel}	η_{rel} ± SD
Amidine (1b)	1.050	1.050 ± 0.003
PIL-10	1.040	1.040 ± 0.002
PIL-20	1.065	1.065 ± 0.005
PIL-40	1.087	1.087 ± 0.007
PIL-60	1.095	1.095 ± 0.002
PIL-80	1.097	1.097 ± 0.002

*SD – Standard Deviation.

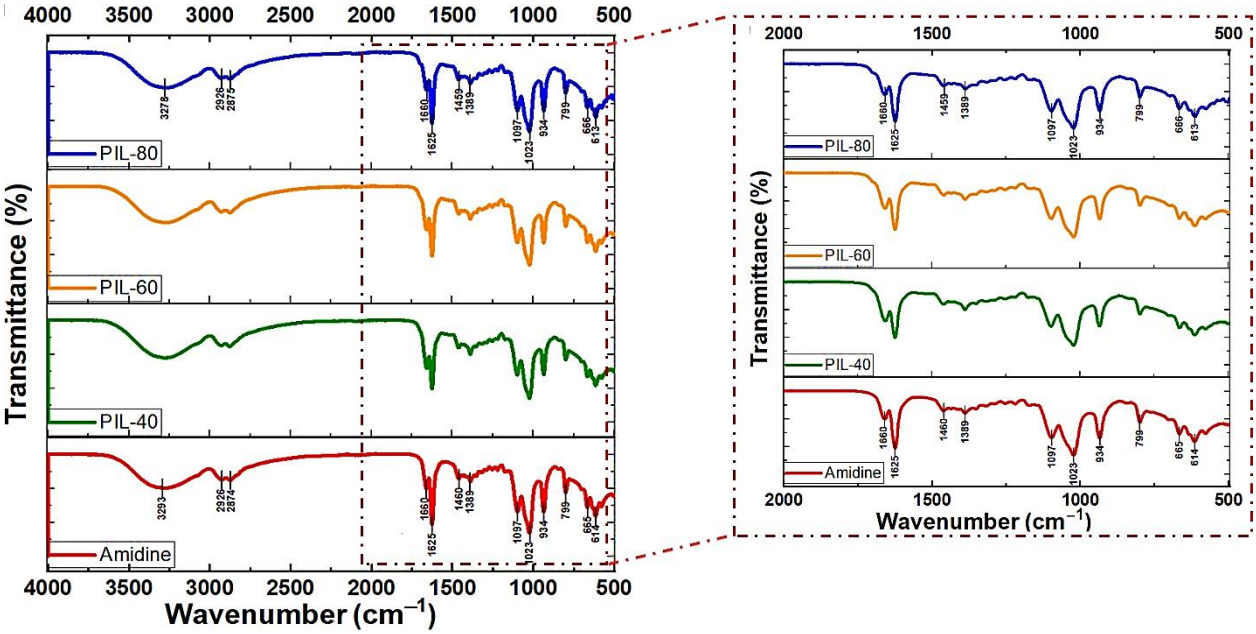


Figure S5. FT-IR spectra of amidine (1a) before and after CO_2 bubbling, showing no significant changes.

Table S4. Key IR bands (cm^{-1}) and assignments for amidine (1b) vs. PIL (2).

Assignment (main contribution)	Amidine (1b) ν (cm^{-1})	PIL (2) ν (cm^{-1})	Comment
ν(O–H) stretch (H-bonded)	3308	3257	Red-shift on CO_2 uptake (stronger H-bonding)
ν(N…H)$^+$ (H-bonded/ion pair)	-	3257	Due to protonated N-center
ν_{as}, ν_s(CH_3, CH_2)	2934, 2829	2927, 2834	Small intensity/position changes
ν(C=O) (CO_2-derived)	—	1698 (s)	New diagnostic for PIL formation
ν(–CH=N$^+$H–) (protonated amidinium)	—	1662 (sh)	Shoulder near 1698 cm^{-1}
ν(C=N)	1628	1627	Persists with slight shift
δ(CH_3), w(CH_2), τ(CH_2), δ(C-OH)	1460	1536, 1505, 1440	Intensity growth in PIL
mixed (ν(C–N), ϱ(CH), δ(OH))	1387	1371	Amidine zone (partly shifts/splits)
ν(C(O_2)–O), w(CH_2)	—	1258	CO_2-related skeletal/C–O
ν_{as}, ν_s(C–O) / ν(C–N)	1096, 1023 (s)	1096, 1026 (s)	Strengthening/splitting in PIL
ν((CH_2)–O)), δ(C-OH), ϱ(CH_2)	936	934	Moving into neighboring mixed region
ϱ(OH), ν_S(C–C), δ(NCN)	800	799	Small shift upon PIL formation
δ(OCO), ϱ(CH_2), δ(HCH), δ(NCN)	—	799	Bending of OCO fragment

*ν – stretching; ν_{as} – asymmetric stretching; ν_s – symmetric stretching; δ – bending; γ – rocking; ϱ – wagging; τ – twisting.

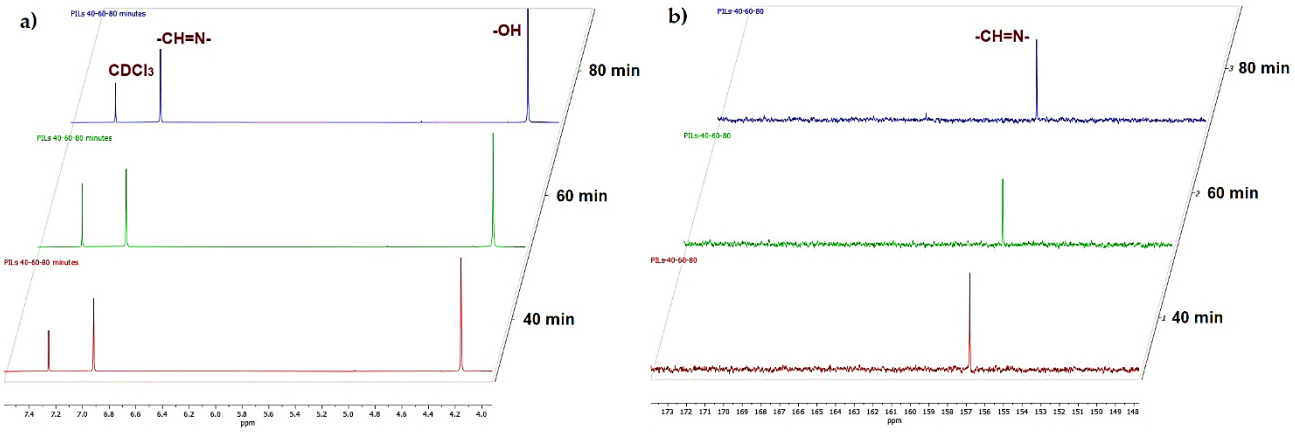


Figure S6.(**a**) ^{1}H NMR spectra of amidine (without MeOH) after CO_2 bubbling for 40, 60, and 80 min (recorded in $CDCl_3$). (**b**) ^{13}C NMR spectra of amidine (without MeOH) after CO_2 bubbling for 40, 60, and 80 min (recorded in $CDCl_3$).

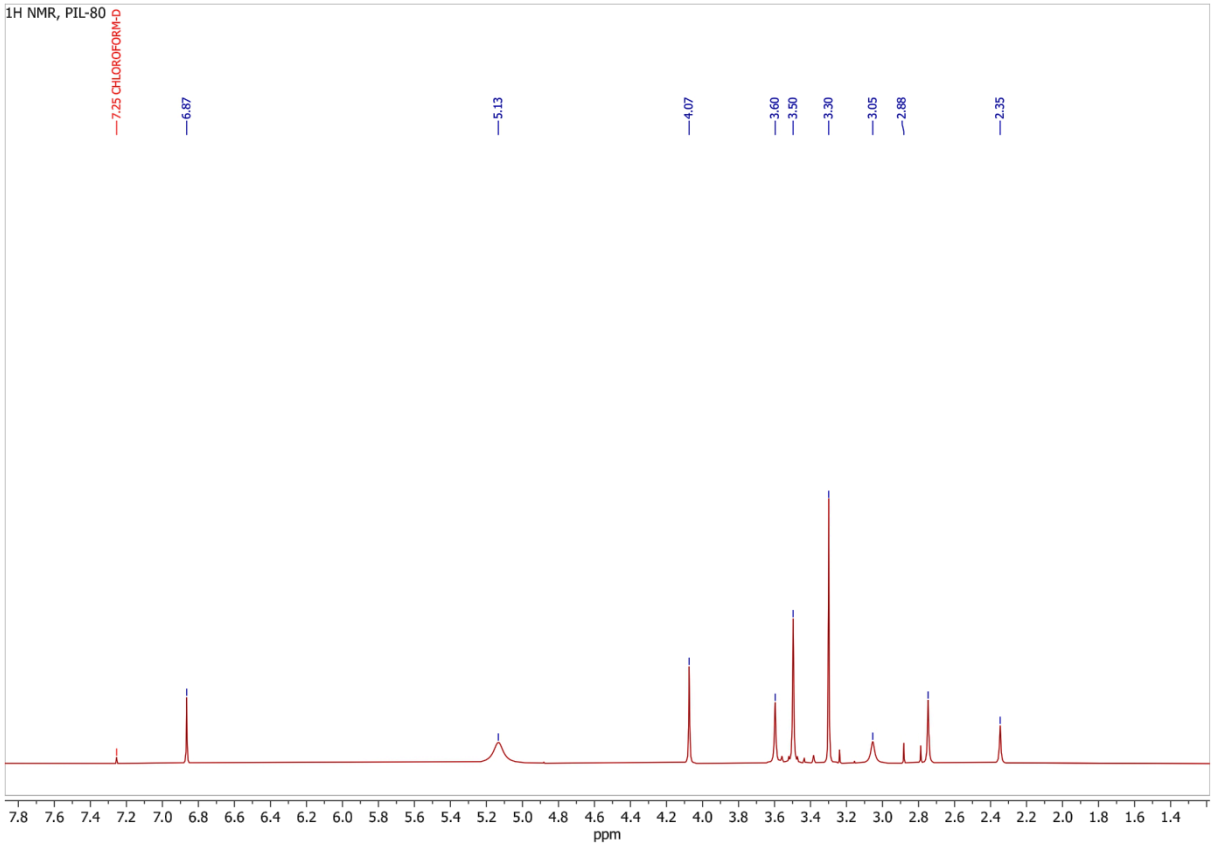


Figure S7.[1]H NMR spectrum of PIL-80 (2) recorded in $CDCl_3$.

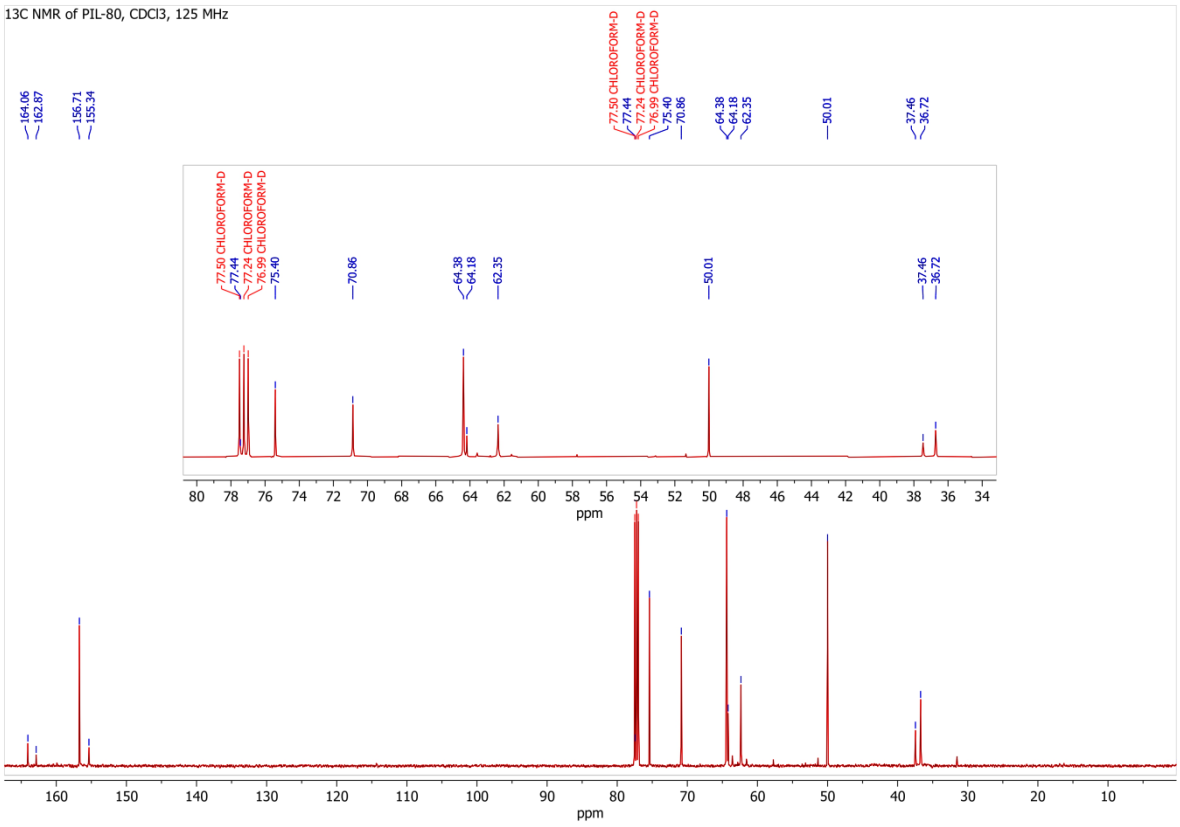


Figure S8.[13]C NMR spectrum of PIL-80 (2) recorded in $CDCl_3$.