Supporting Information

Comparing extraction, synergism and separation of lanthanoids by use of acidic and neutral compounds in chloroform and one ionic liquid: Is the latter always "better"?

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Abbreviations

S	synergist
HL	3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one
S1	5,11,17,23-tetra-*tert*-butyl-25,26,27-tris(dimethylphosphinoylpropoxy)-28-hydroxy-calix[4]arene
S2	5,11,17,23-tetra-*tert*-butyl-25,27-bis(dimethylphosphinoylpropoxy)-26,28-dihydroxy-calix[4]arene
IL	1-butyl-3-methyl-imidazolium-bis(trifluoromethanesulfonyl)imide

1. EXPERIMENTAL SECTION

1.1. Synthesis and characterization of 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one (HL)

1.1.1. General: All reagents were purchased from Merck and Fluka and were used without any further purification. Fluka silica gel/TLC-cards 60778 with fluorescent indicator 254 nm were used for TLC chromatography. The melting point of pyrazolone was determined in a capillary tube on SRS MPA100 OptiMelt (Sunnyvale, CA, USA) automated melting point system. The NMR spectra were recorded on a Bruker Avance II+ 600 spectrometer (Rheinstetten, Germany) at 25^{o}C; the chemical shifts were quoted in ppm in δ-values against tetramethylsilane (TMS) as an internal standard or against H_3PO_4 as external standard in ^{31}P spectra; the coupling constants were calculated in Hz. For simplicity, the aromatic groups in the pyrazolones are designated as: Pyr – pyrozolone; Ph – phenyl, Ar – 4-trifluoromethylphenyl.

1.1.2. Synthesis: 3-Methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one (HL)[S1] was obtained according to an adapted literature procedure[S2] as follows: A mixture of 3-methyl-1-phenyl-1H-pyrazol-5-one (4.18 g, 24 mmol) and $Ca(OH)_2$ (3.5 g, 48 mmol) in dry dioxane (30 ml) was stirred at room temperature for 0.5 h. 4-Trifluorobenzoyl chloride (5 g, 24 mmol) was then added and the mixture was refluxed with stirring for 9 h. The reaction mixture was poured into 10 % aq. HCl. The solid phase formed was filtered off and washed with small portions of methanol to give the pure on TLC and NMR scale crude product: 85 % yield (7.1 g); R_f 0.42 (CH_2Cl_2:MeOH 95:5). A sample was recrystallized from methanol: colourless fine needles; m. p. 1^{o}/min – at 147.5-148^{o}C the sample became yellow, which melted at 149.7-150.1^{o}C; NMR ($CDCl_3$) ^{1}H 2.069 (s, 3H, C*H*$_3$), 7.334 (tt, 1H, J_{34} 7.5, J_{24} 1.1, C*H*-4 Ph), 7.486 (ddd, 2H, J_{23} 8.6, J_{34} 7.5, J_{35} 1.7, C*H*-3 and C*H*-5 Ph), 7.749 (d, 2H, J_{23} 8.2, C*H*-2 and C*H*-6 Ar), 7.793 (d, 2H, J_{23} 8.2, C*H*-3 and C*H*-5 Ar), 7.859 (ddd, 2H, J_{23} 8.7, J_{26} 1.8, J_{24} 1.1, C*H*-2 and C*H*-6 Ph), 8.578 (bs, 1H, O*H*); ^{13}C 15.79 (*C*H$_3$), 103.57 (C_{quat}-4 Pyr), 120.97 (*C*H-2 and *C*H-6 Ph), 123.62 (q, J_{CF} 272.1, *C*F$_3$), 125.58 (q, J_{CF} 3.5, *C*H-3 and *C*H-5 Ar), 127.07 (*C*H-4 Ph), 128.12 (*C*H-2 and *C*H-6 Ar), 129.24 (*C*H-3 and *C*H-5 Ph), 133.38 (q, J_{CF} 32.8, C_{quat}-4 Ar), 136.97 (C_{quat}-1 Ph), 141.22 (C_{quat}-1 Ar), 147.76 (C_{quat}-3 Pyr), 160. 08 (C_{quat}-5 Pyr), 191.39 (*C*=O); COSY cross peaks 7.334/7.486, 7.486/7.859, 7.749/7.793; NOESY cross peaks 2.069/7.749, 7.334/7.486, 7.486/7.859, 7.749/7.793; HSQC cross peaks 2.069/15.79, 7.334/127.07, 7.486/129.24, 7.749/128.12, 7.793/125.58, 7.859/120.97; HMBC cross peaks 2.069/103.57, 2.069/147.76, 7.334/120.97, 7.334/129.24, 7.334/136.97 (week), 7.486/120.97, 7.486/127.07

(week), 7.486/129.24, 7.486/141.22, 7.749/125.58 (week), 7.749/128.12, 7.749/133.38, 7.749/191.39, 7.793/120.91 (q of CF_3), 7.793/122.71 (q of CF_3), 7.793/124.52 (q of CF_3), 7.793/125.58, 7.793/126.32 (q of CF_3), 7.793/128.12 (week), 7.793/141.22, 7.859/120.97, 7.859/127.07, 7.859/136.97 (week).

[S1] H.-J. Chuang, H.-L. Chen, J.-L. Ye, Z.-Y. Chen, P.-L. Huang, T.-T. Liao, T.-E. Tsai, C.-C. Lin, *J. Polym. Sci. Pol. Chem.*, 2013, **51**, 696-707.

[S2] B. S. Jensen, *Acta Chim. Scand.*, 1959, **13**, 1668-1670.

1.1.3. NMR spectra of HL in $CDCl_3$:

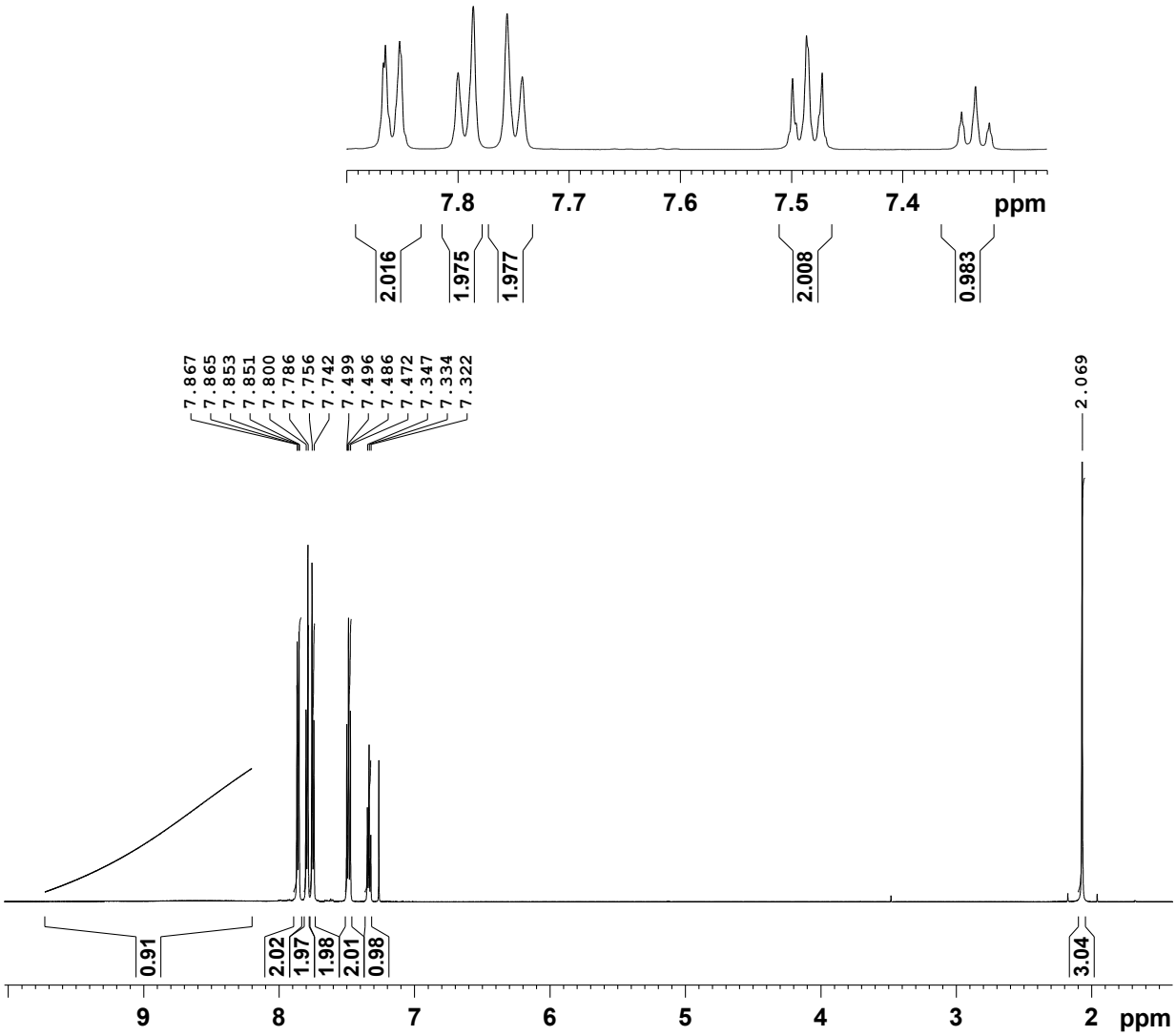


Figure S1. ^{1}H NMR spectrum of 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one, HL, in $CDCl_3$.

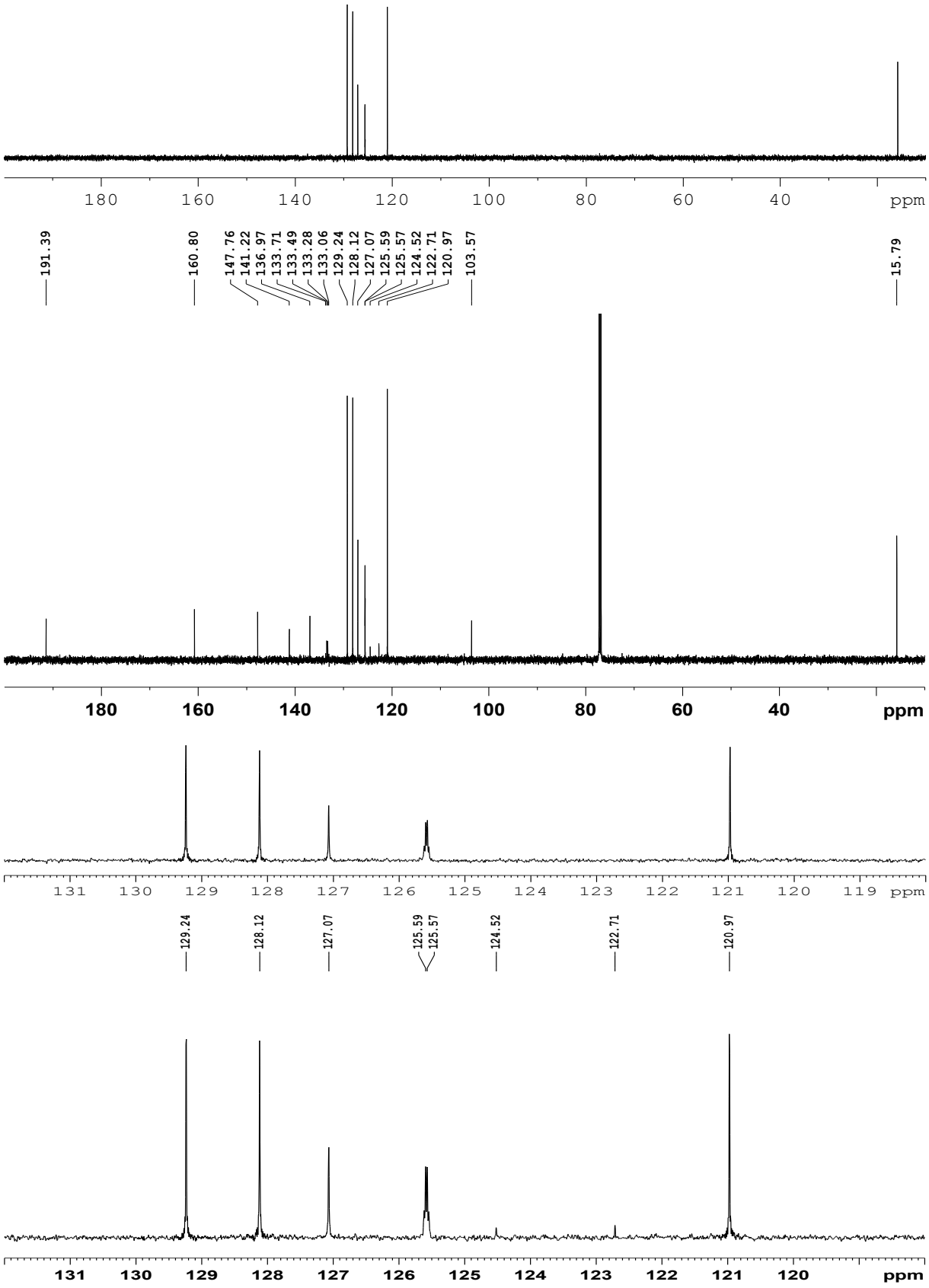


Figure S2. ^{13}C NMR spectrum of 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one, HL in $CDCl_3$: full spectrum (up) and a part of the aromatic area (down).

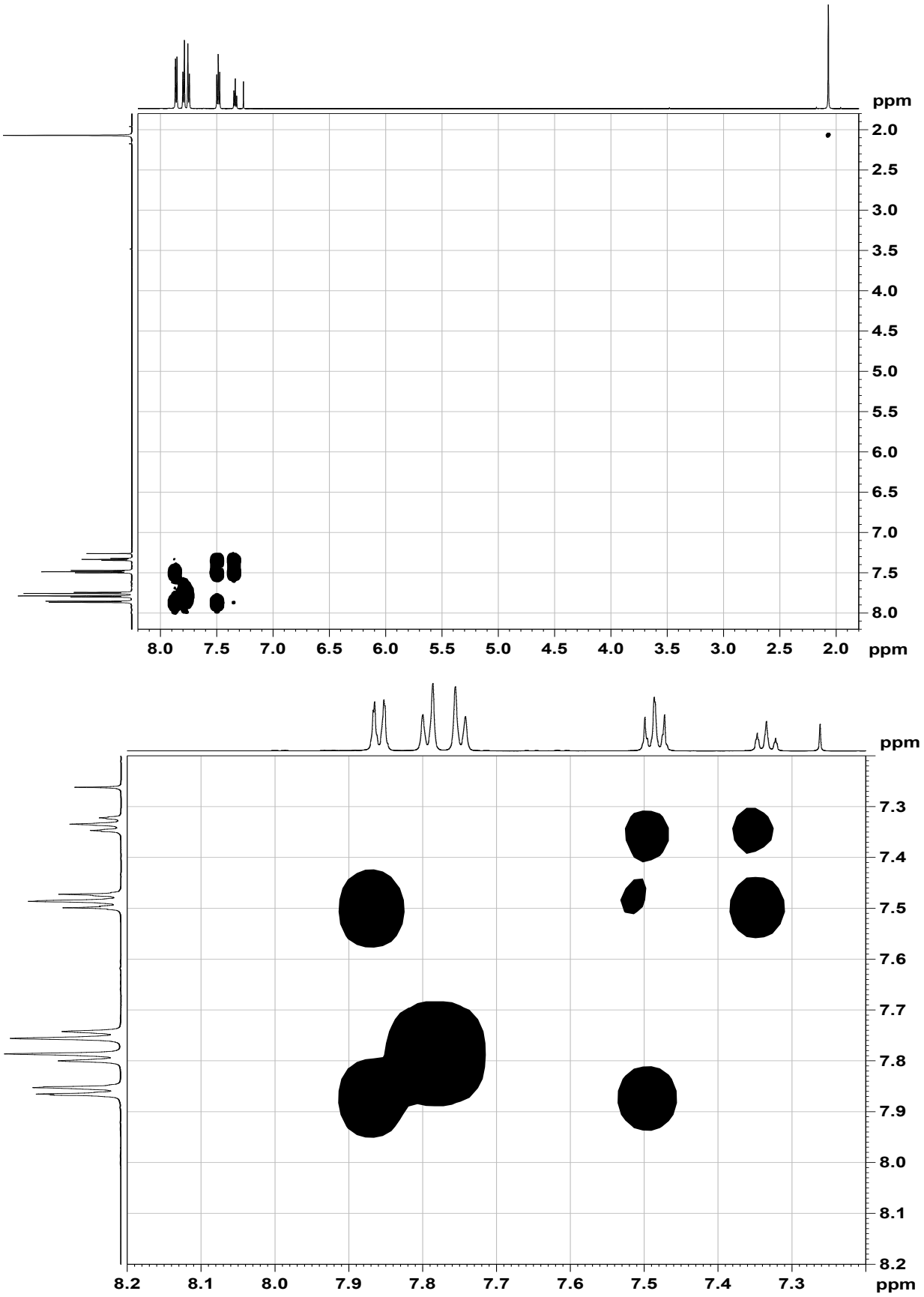


Figure S3. ^{1}H-^{1}H COSY spectrum of 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one, HL in $CDCl_3$: full spectrum (up) and a part of the aromatic area (down).

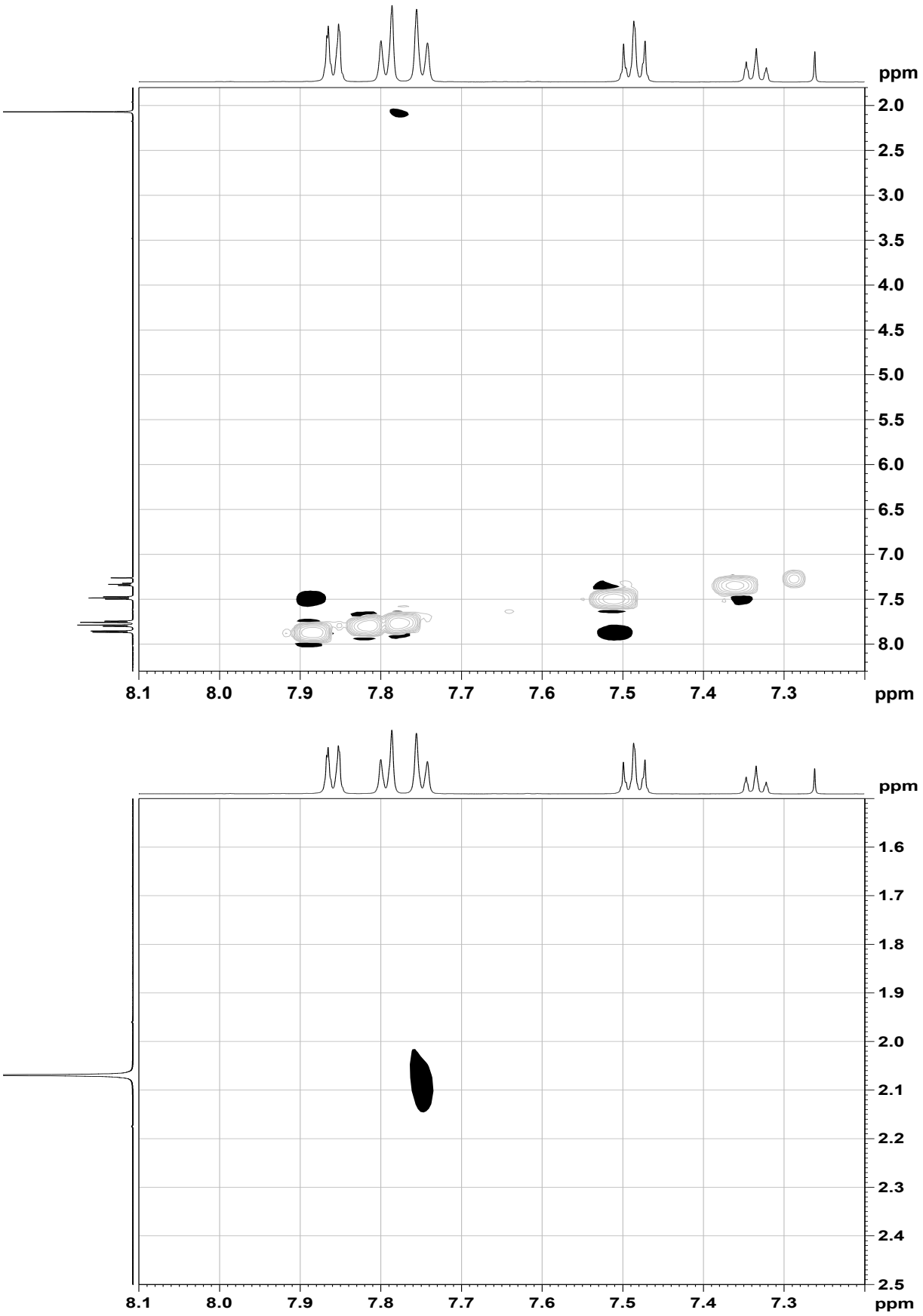


Figure S4. ^{1}H-^{1}H NOESY spectrum of 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one, HL in $CDCl_3$: full spectrum (up) and methyl group interaction (down).

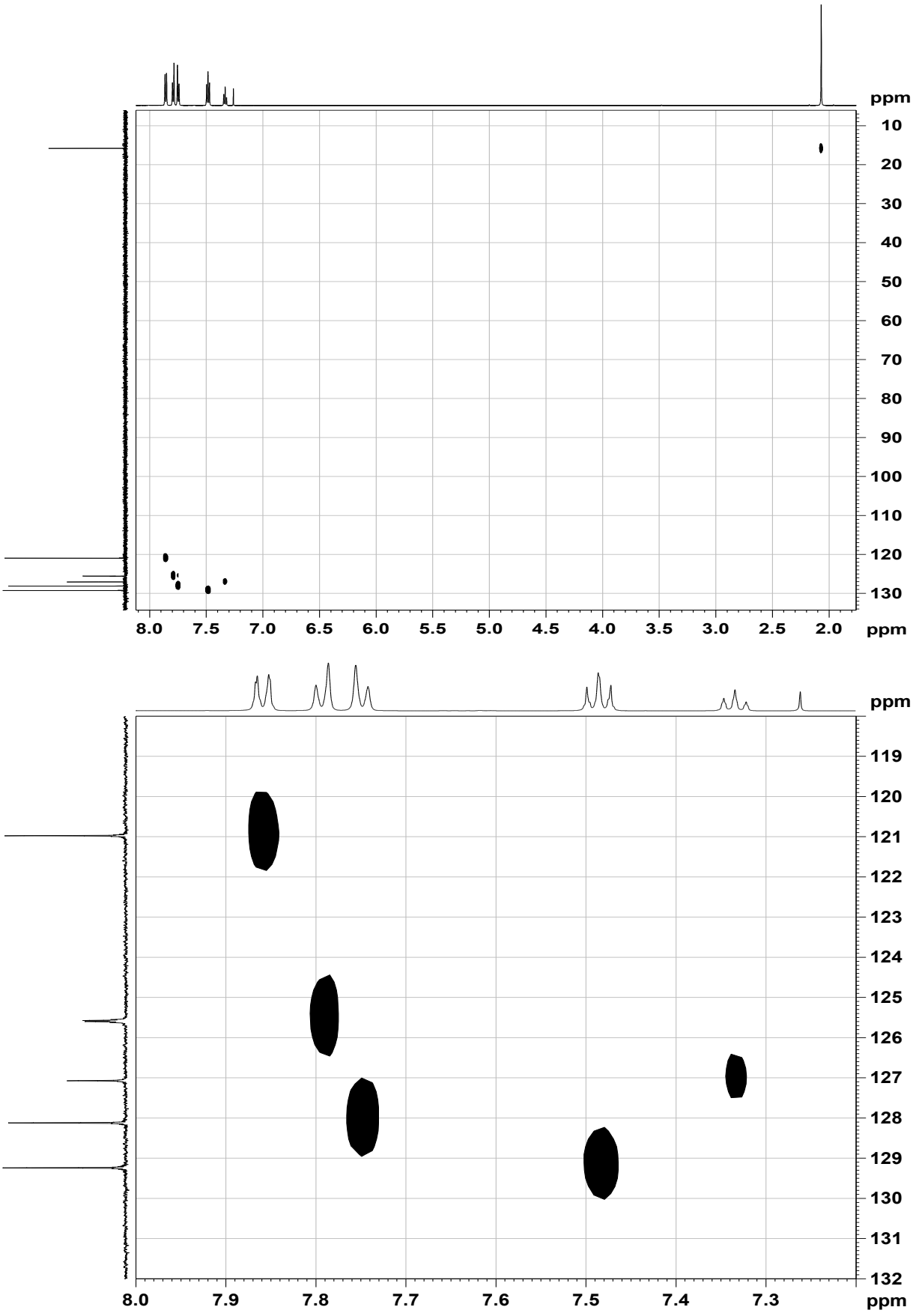


Figure S5. ^{1}H-^{13}C HSQC spectrum of 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one, HL in $CDCl_3$: full spectrum (up) and a part of the aromatic area (down).

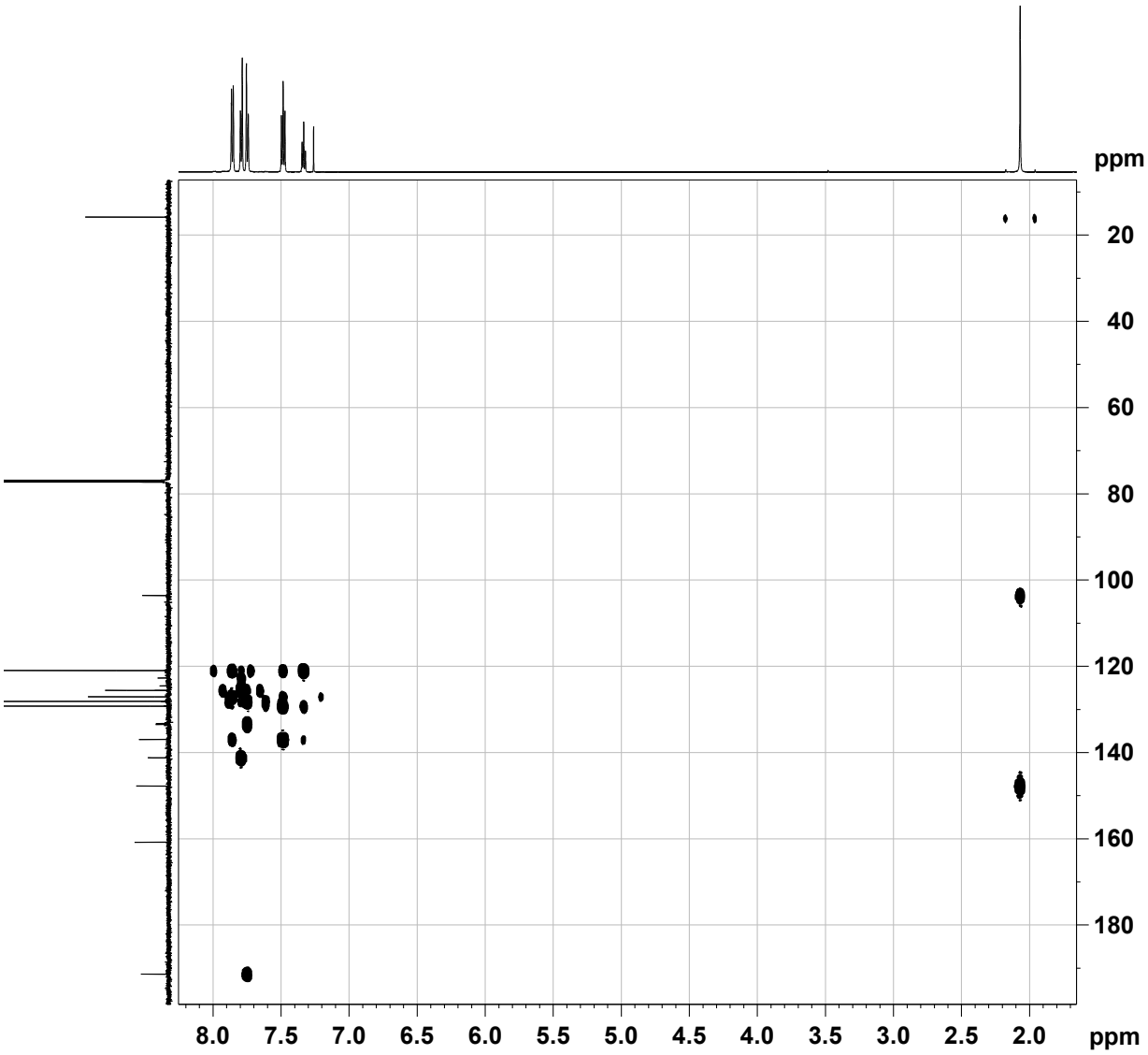


Figure S6. ^{1}H-^{13}C HMBC spectrum of 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one, HL in $CDCl_3$.

2. RESULTS AND DISCUSSION

2.1. Solvent extraction of Ln(III) ions with 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one in $CHCl_3$.

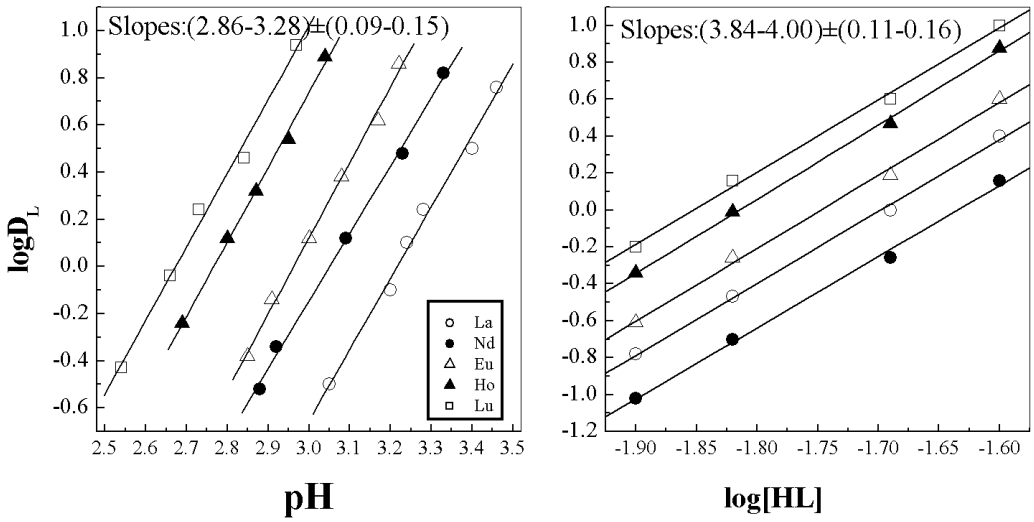


Figure S7. LogD_L vs. pH for the extraction of lanthanoid(III) ions with HL at [HL]=2.5×10^{-2} mol/dm^3.

LogD_L vs. log[HL] for the extraction of lanthanoid(III) ions with HL: La, pH=3.35; Nd, pH=3.10; Eu, pH=3.15; Ho, pH=3.05; Lu, pH=3.00.

2.2. Interaction between 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one (HL) and 5,11,17,23-tetra-tert-butyl-25,26,27-tris(dimethylphosphinoylpropoxy)-28-hydroxy-calix[4]arene (S1) or 5,11,17,23-tetra-tert-butyl-25,27-bis(dimethylphosphinoylpropoxy)-26,28-dihydroxy-calix[4]arene (S2).

The interactions between acidic (HL) and neutral (S) extractant applied in the present study were studied at different molar ratios in chloroform by NMR experiments. The NMR spectra were recorded on a Bruker Avance II+ 600 spectrometer (Rheinstetten, Germany) at 25^{o}C; the chemical shifts were quoted in ppm in δ-values against tetramethylsilane (TMS) as an internal standard or against H_3PO_4 as external standard in ^{31}P spectra. All samples were prepared separately by using pure dry compounds dissolved in deuterochloroform (Deutero GmbH). The spectra of the individual ligand (HL) and synergist (S) were recorded in 0.05 M concentrations. The spectra of the 3:1, 3:2, 1:1, 1:2, and 1:3 S–HL mixtures were recorded as 0.05 M calixarene and 0.017 M, 0.033 M, 0.05 M, 0.1 M, and 0.15 M pyrazolone, respectively.

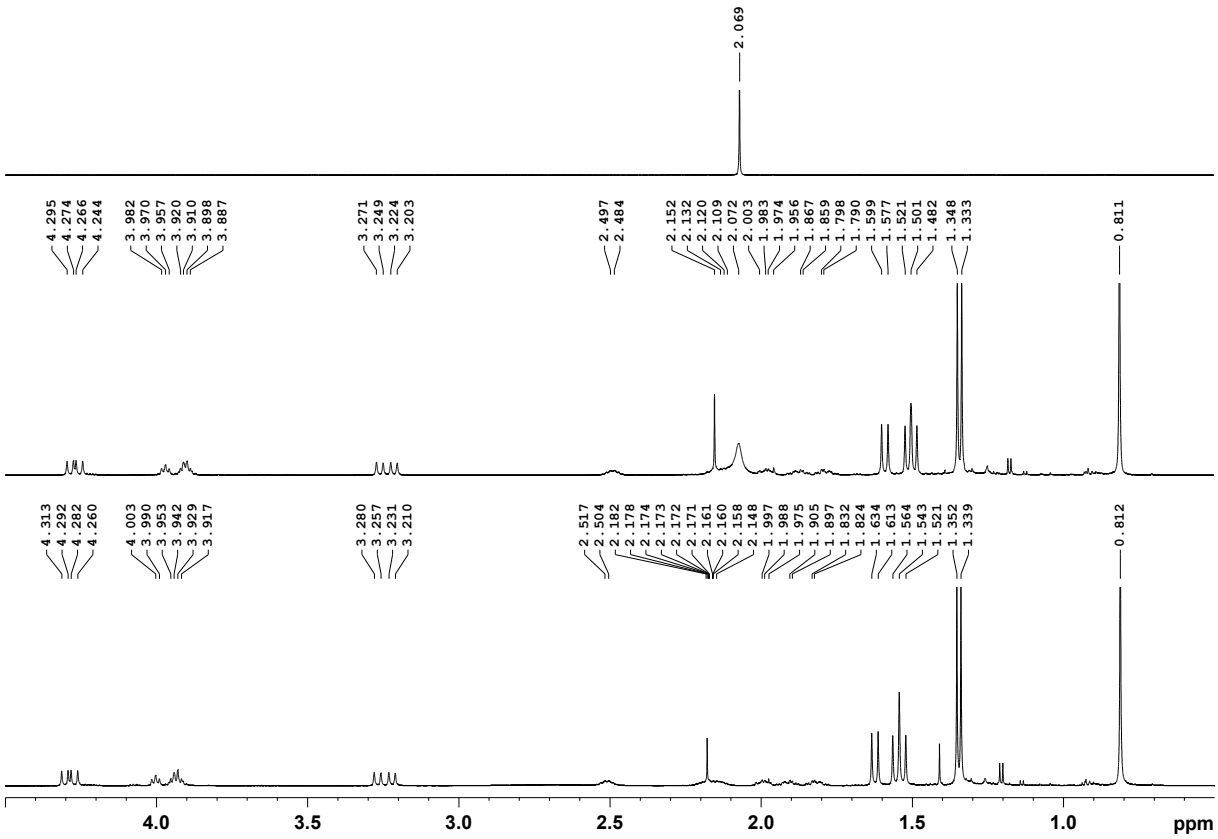


Figure S8. Strong field area of ^{1}H NMR spectra of HL (up), S1 (middle) and S1:HL 1:3 (down).

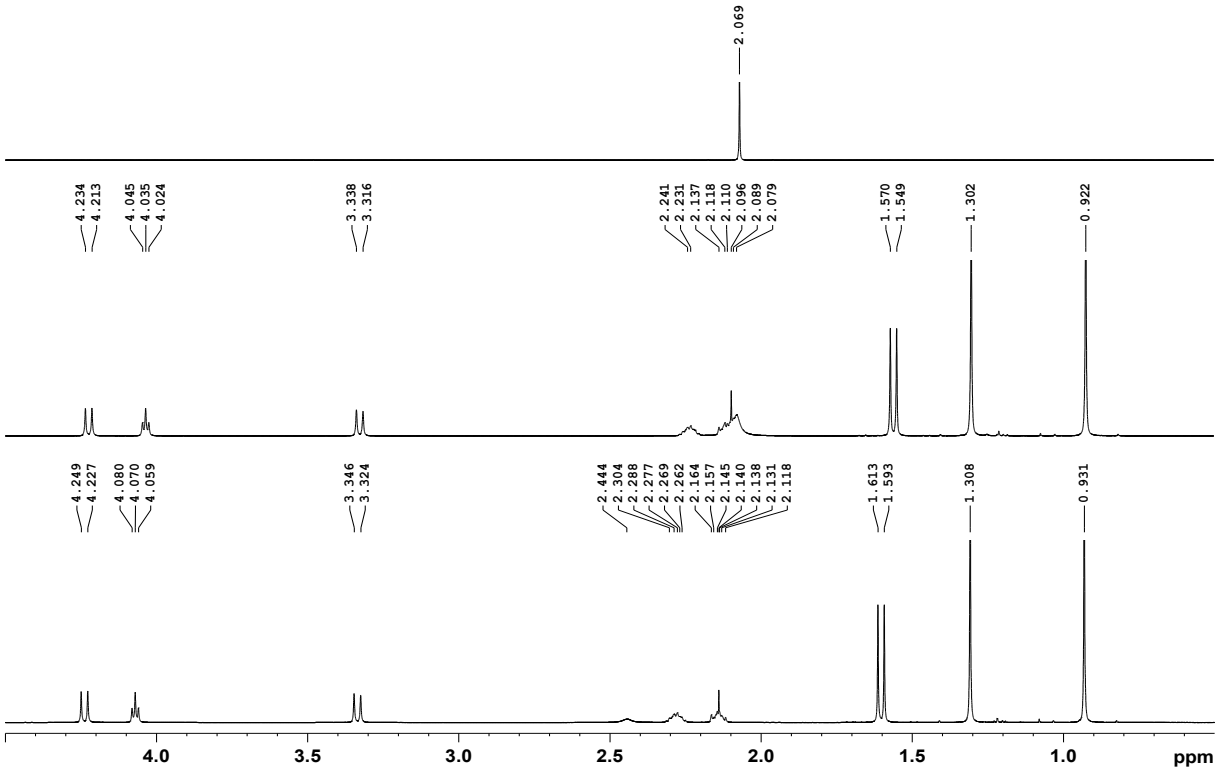
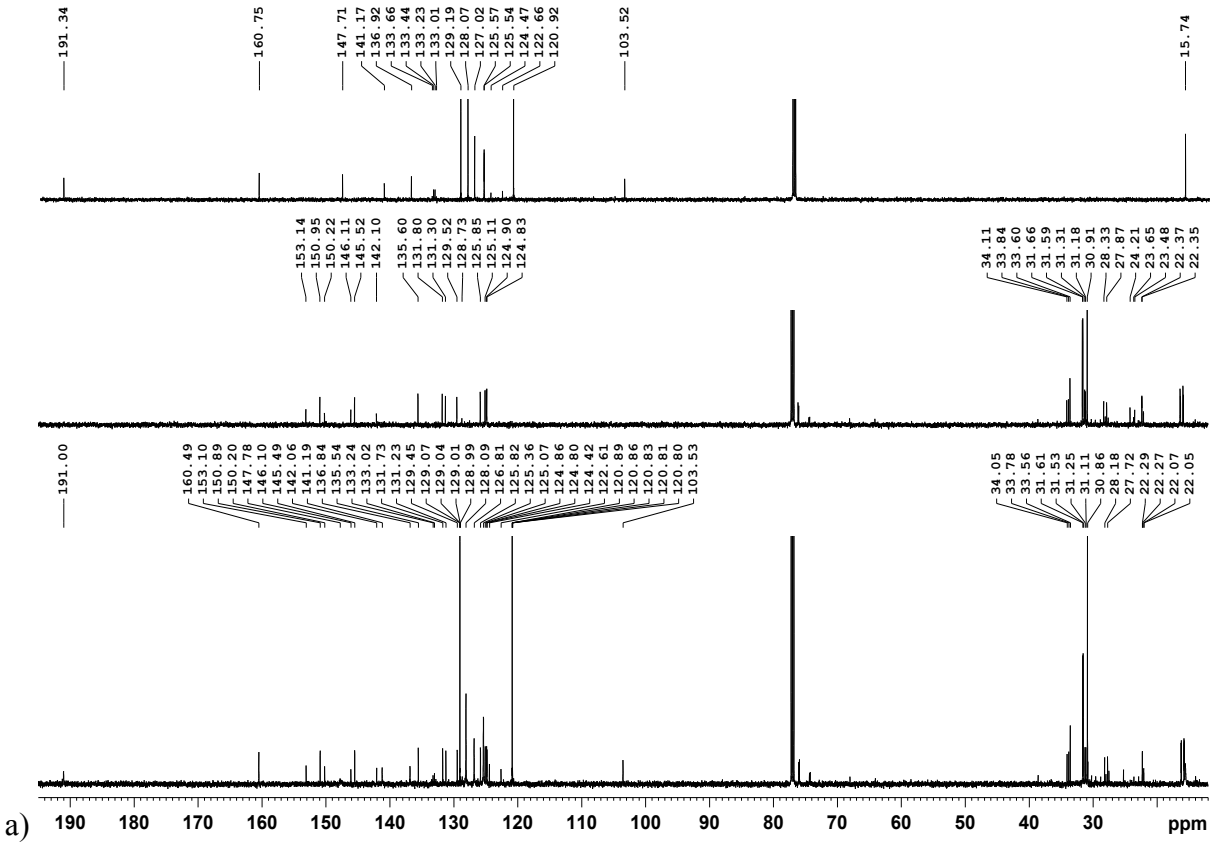
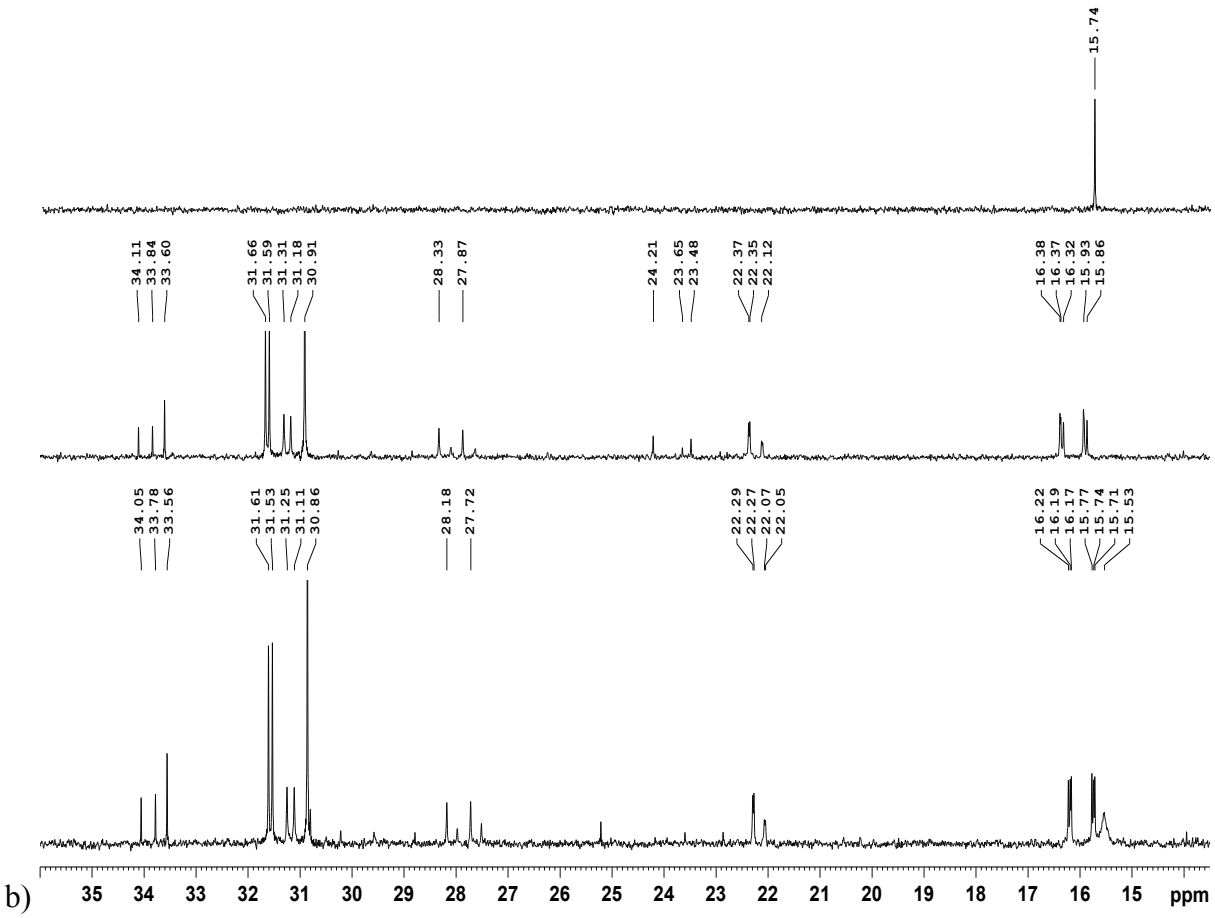


Figure S9. Strong field area of ^{1}H NMR spectra of HL (up), S2 (middle) and S2:HL 1:3 (down).


191.34
160.75
147.71
141.17
136.92
133.66
133.44
133.23
133.01
129.19
128.07
127.02
125.57
125.54
124.47
122.66
120.92
103.52
15.74
153.14
150.95
150.22
146.11
145.52
142.10
135.60
131.80
131.30
129.52
128.73
125.85
125.11
124.90
124.83
34.11
33.84
33.60
31.66
31.59
31.31
31.18
30.91
28.33
27.87
24.21
23.65
23.48
22.37
22.35
191.00
160.49
153.10
150.89
150.20
147.78
146.10
145.49
142.06
141.19
136.84
135.54
133.24
133.02
131.73
131.23
129.45
129.07
129.04
129.01
128.99
128.09
126.81
125.82
125.36
125.07
124.86
124.80
124.42
122.61
120.89
120.86
120.83
120.81
120.80
103.53
34.05
33.78
33.56
31.61
31.53
31.25
31.11
30.86
28.18
27.72
22.29
22.27
22.07
22.05
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

a)


15.74
34.11
33.84
33.60
31.66
31.59
31.31
31.18
30.91
28.33
27.87
24.21
23.65
23.48
22.37
22.35
22.12
16.38
16.37
16.32
15.93
15.86
34.05
33.78
33.56
31.61
31.53
31.25
31.11
30.86
28.18
27.72
22.29
22.27
22.07
22.05
16.22
16.19
16.17
15.77
15.74
15.71
15.53
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
ppm

b)

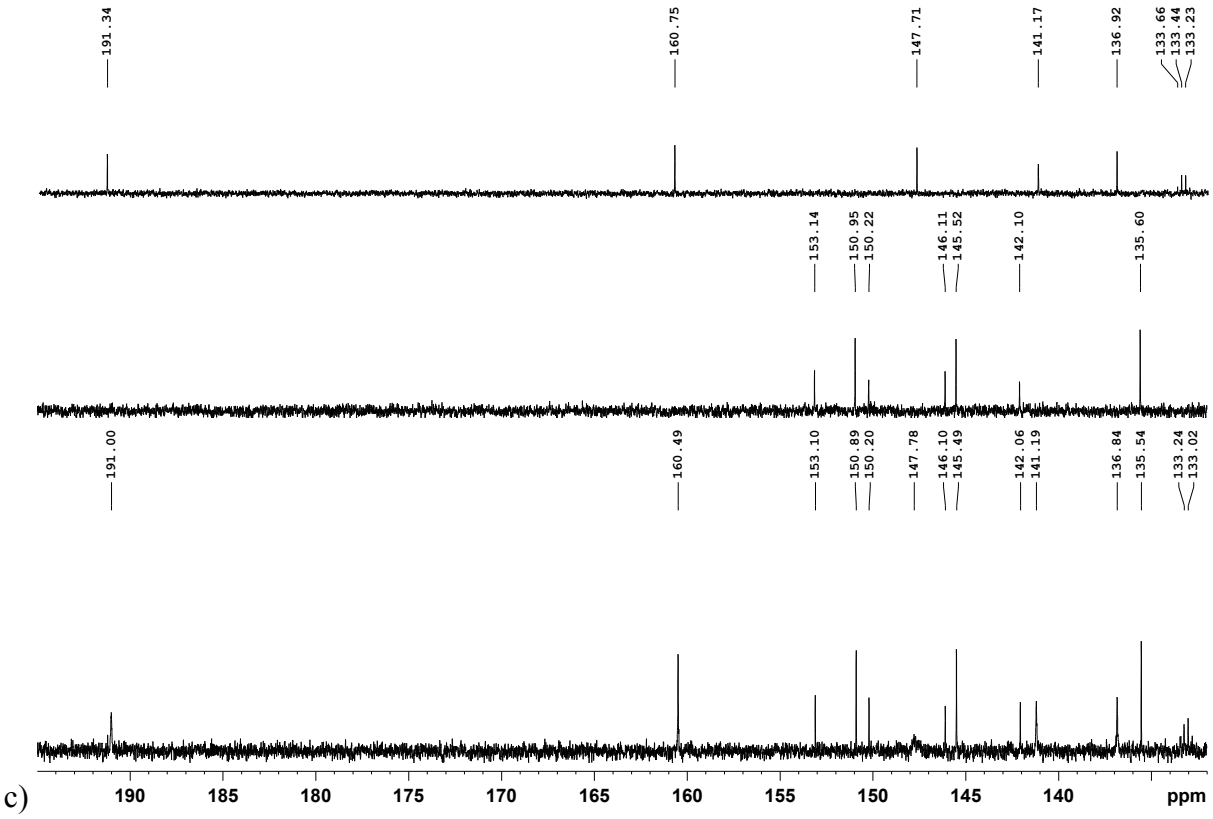
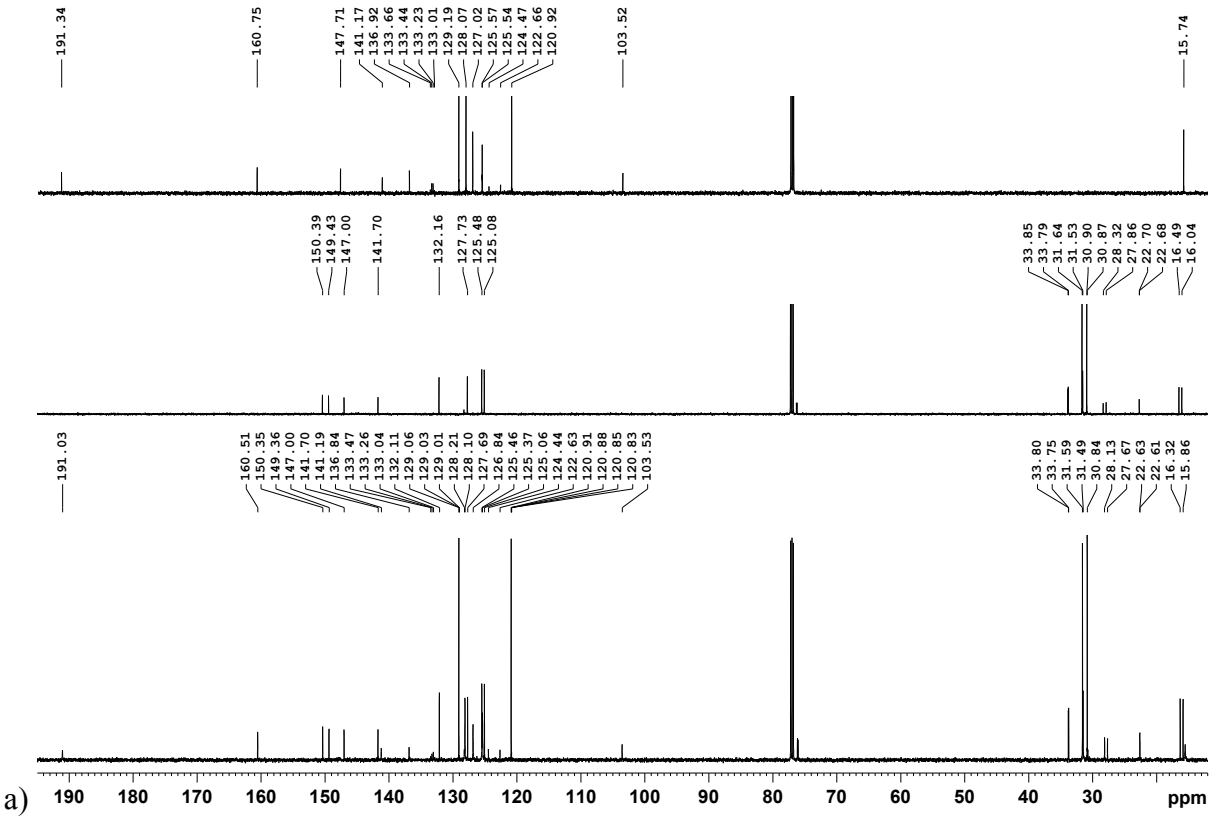


Figure S10. ^{13}C NMR spectra of HL (up), S1 (middle) and S1:HL 1:3 (down): a) full spectra; b) strong field area; c) low field region.



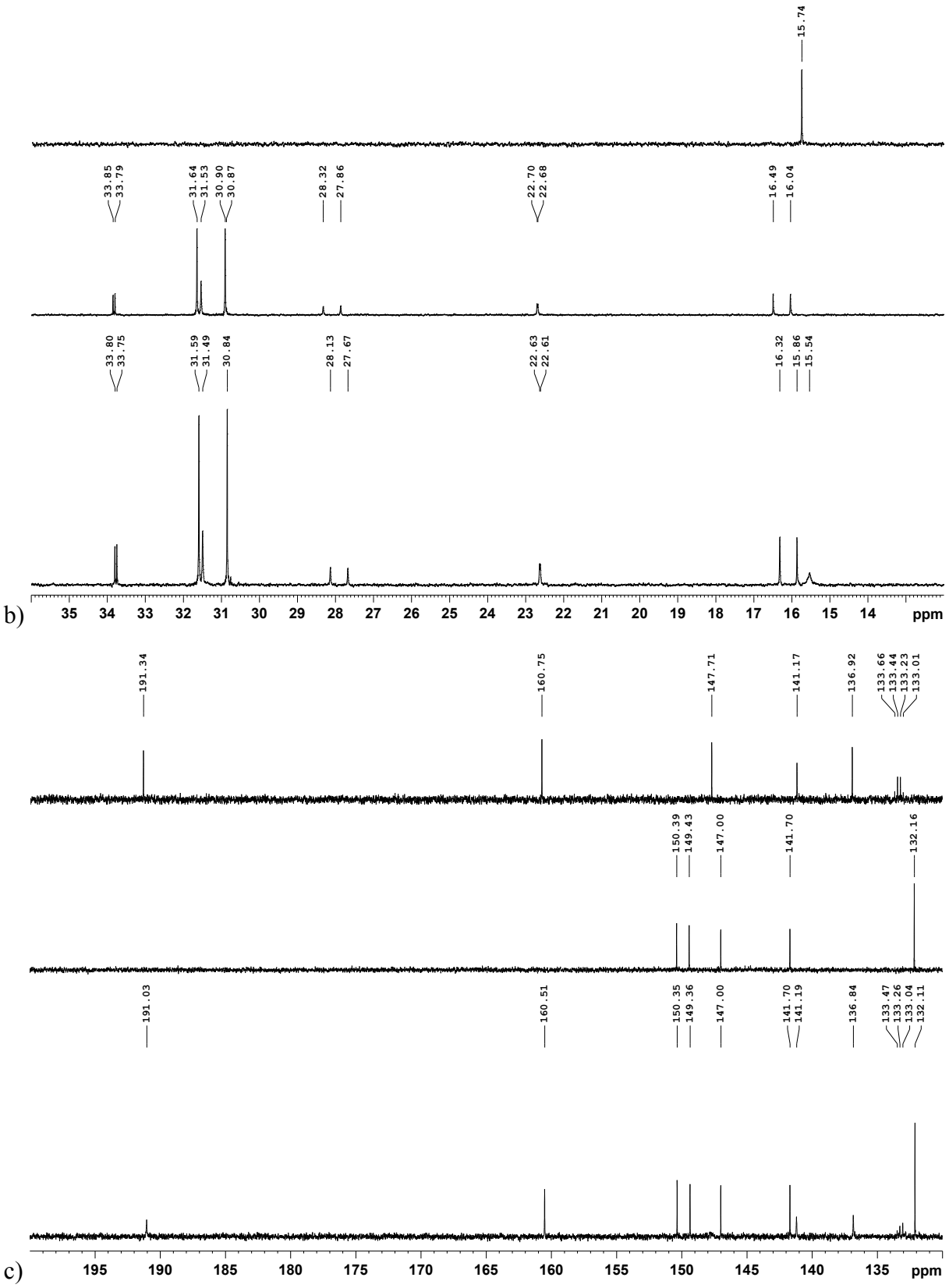


Figure S11. ^{13}C NMR spectra of HL (up), S2 (middle) and S2:HL 1:3 (down): a) full spectra; b) strong field area; c) low field region.

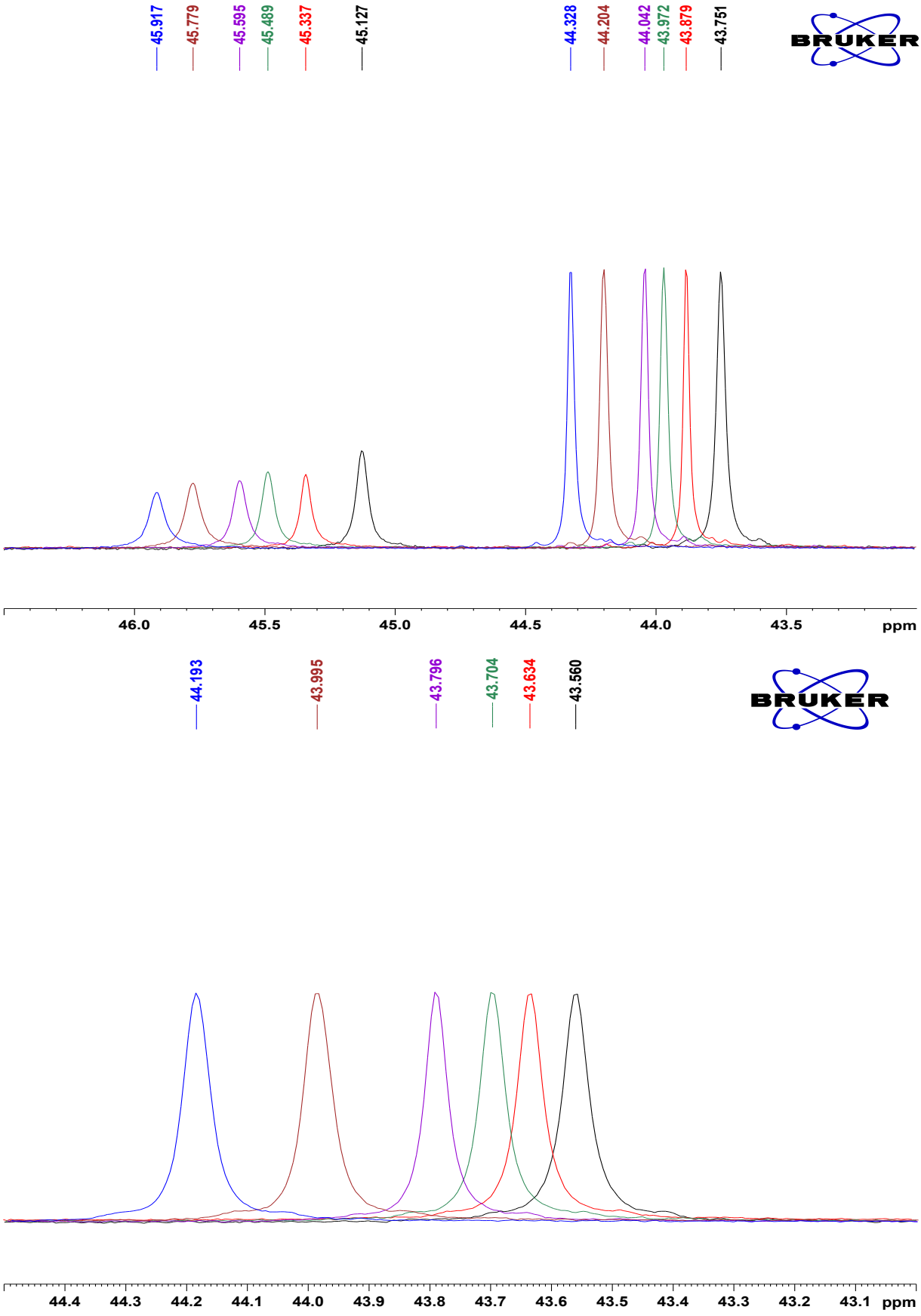


Figure S12. ^{31}P NMR spectra of S1 (up) or S2 (down) and S:HL mixtures in $CDCl_3$: S (black), S:HL 3:1 (red), S:HL 3:2 (green), S:HL 1:1 (violet), S:HL 1:2 (brown), S:HL 1:3 (blue).

2.3. Interactions between 1-butyl-3-methyl-imidazolium-bis(trifluoromethanesulfonyl)imide (IL) and **3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one** *(HL).*

The NMR spectra were recorded on a Bruker Avance II+ 600 spectrometer (Rheinstetten, Germany) at 25°C; the chemical shifts were quoted in ppm in δ-values. All samples were prepared separately by using pure dry compounds dissolved in deuterated solvents (Deutero GmbH).

2.3.1. NMR spectra in benzene-d_6

The spectra of IL and IL:HL 1:1 mixture were corroded in $2x10^{-3}$ M concentration due to very low solubility of IL in benzene. The spectra of HL were recorded in 0.05 M concentration.

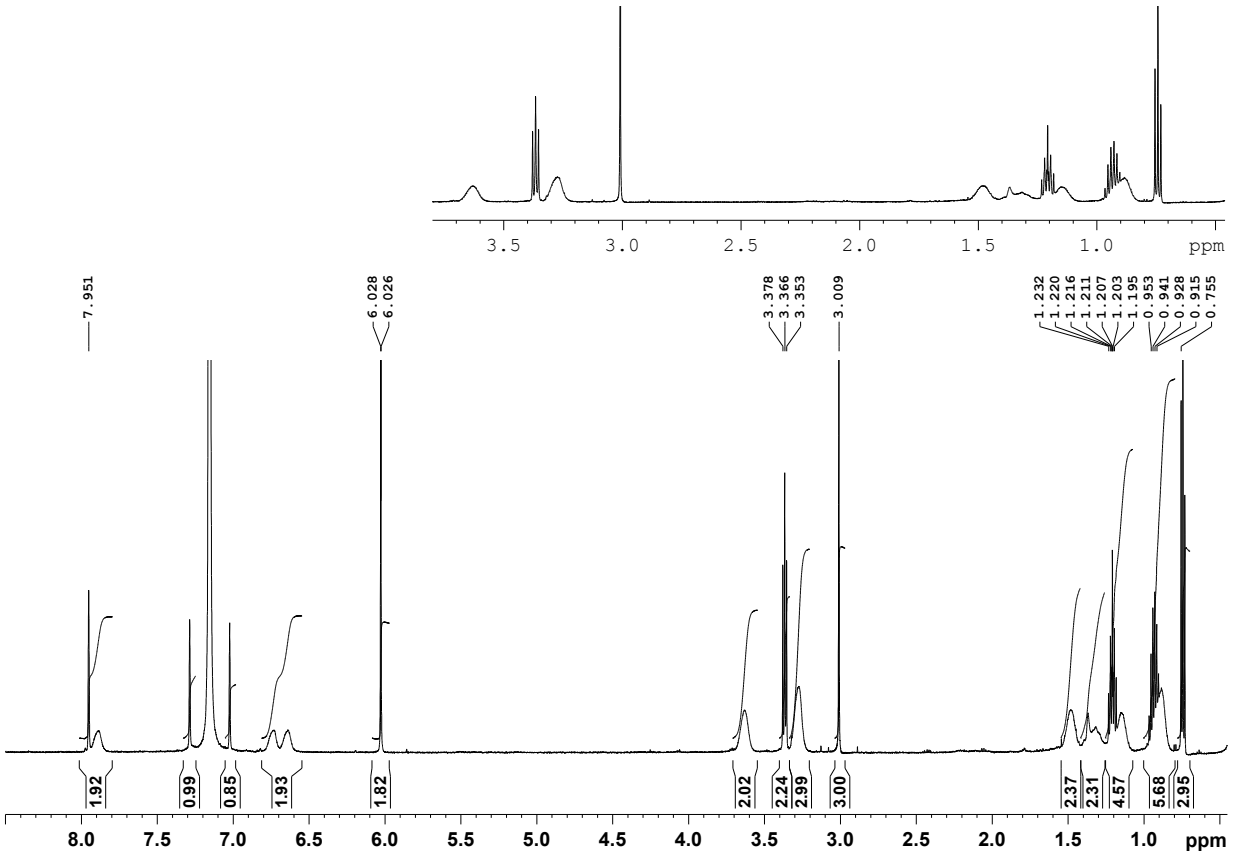


Figure S13. ^{1}H NMR spectrum of 1IL.

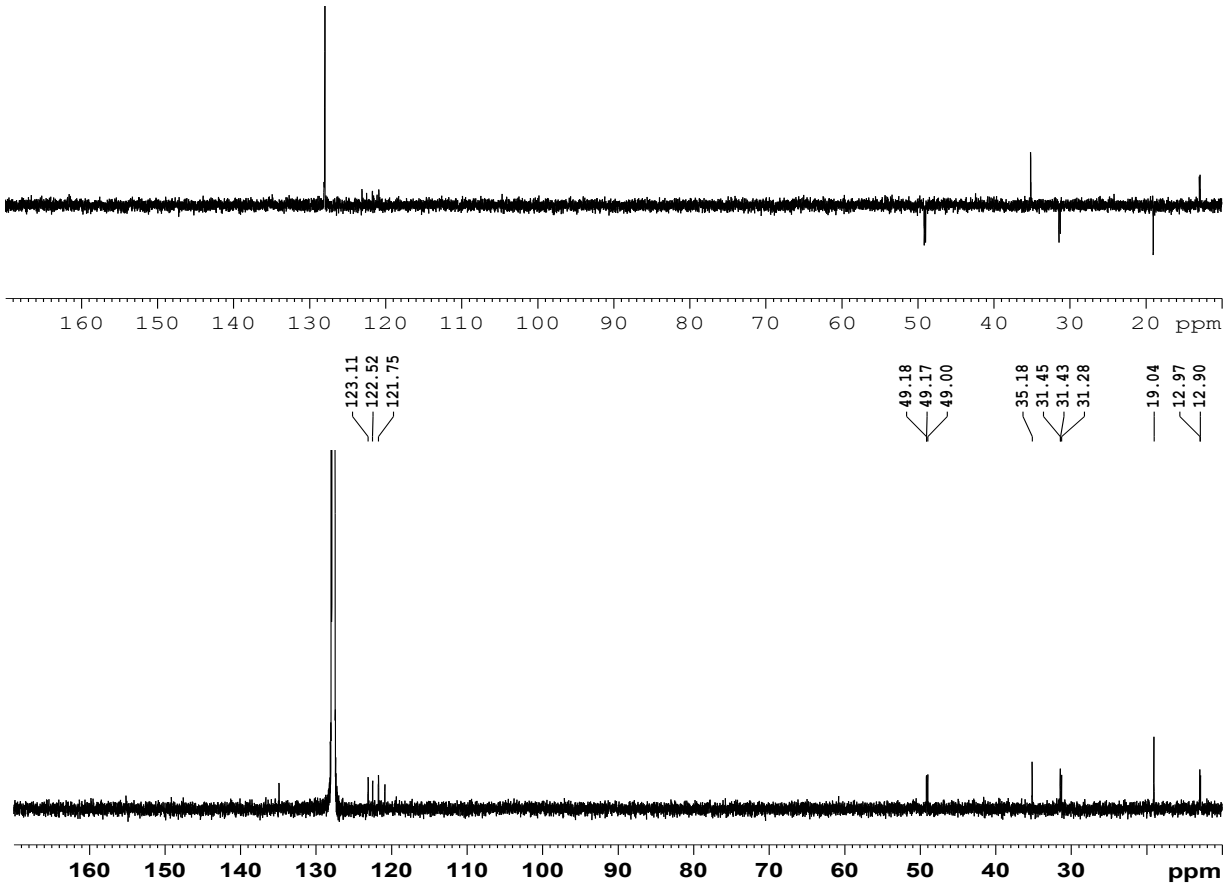
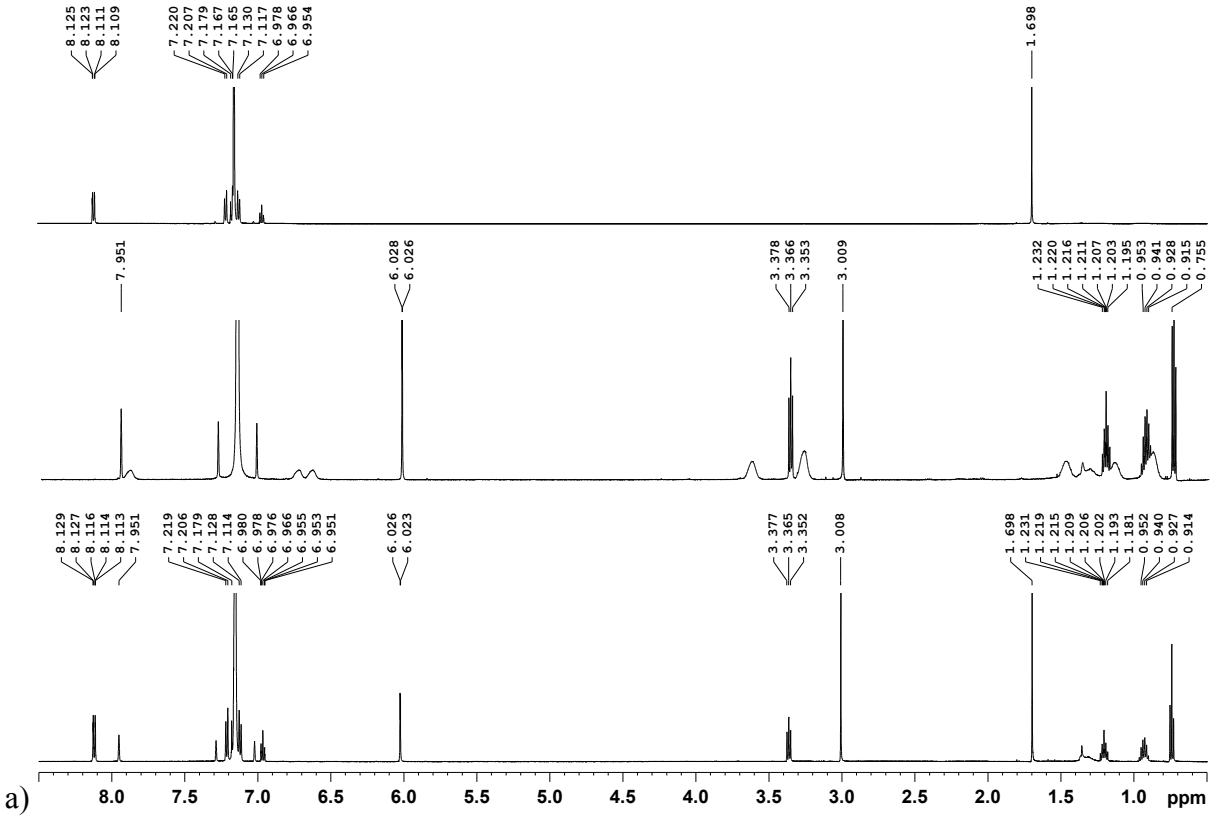


Figure 14. ^{13}C NMR (down) and DEPT (up) spectra of IL.



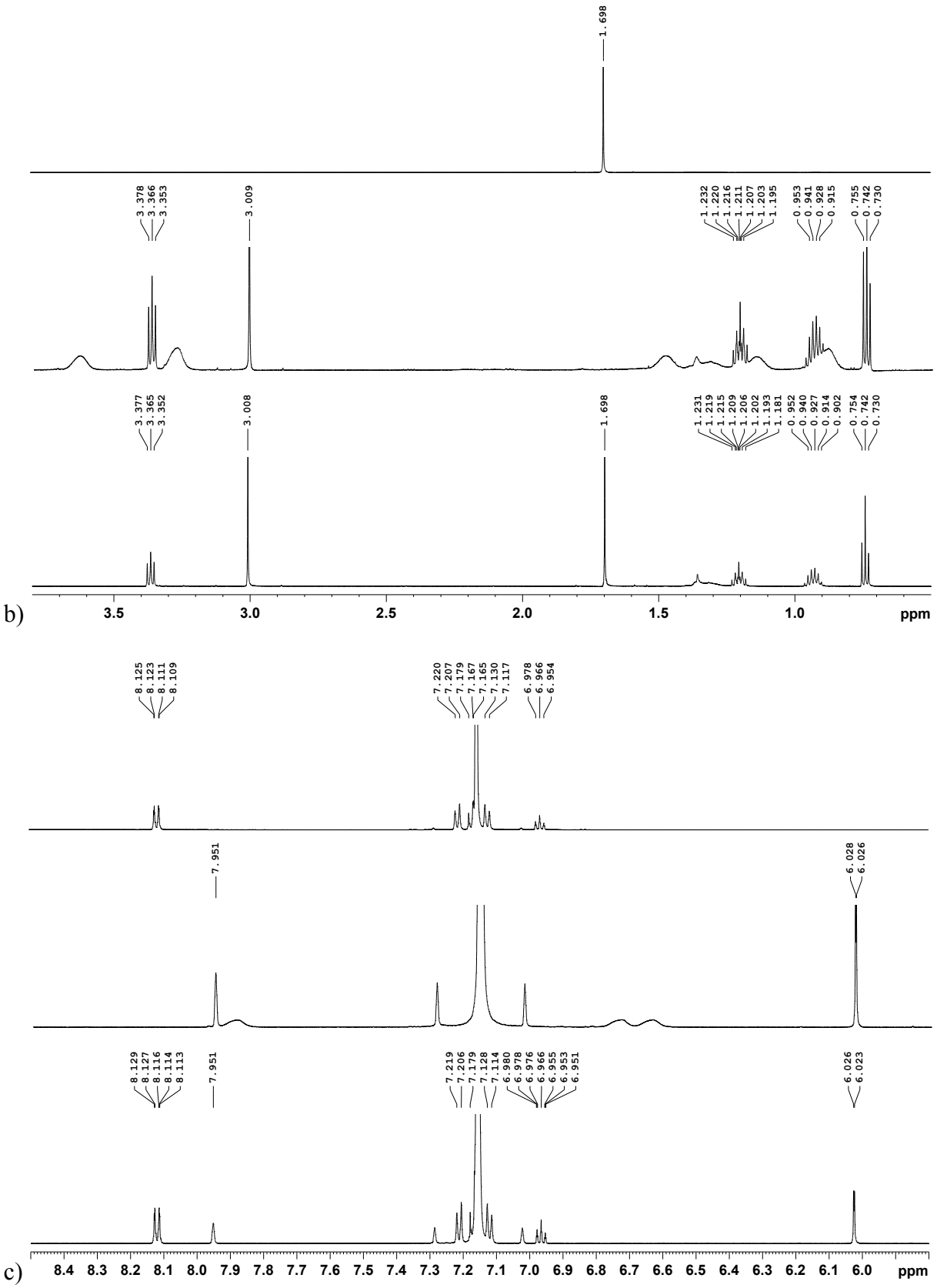
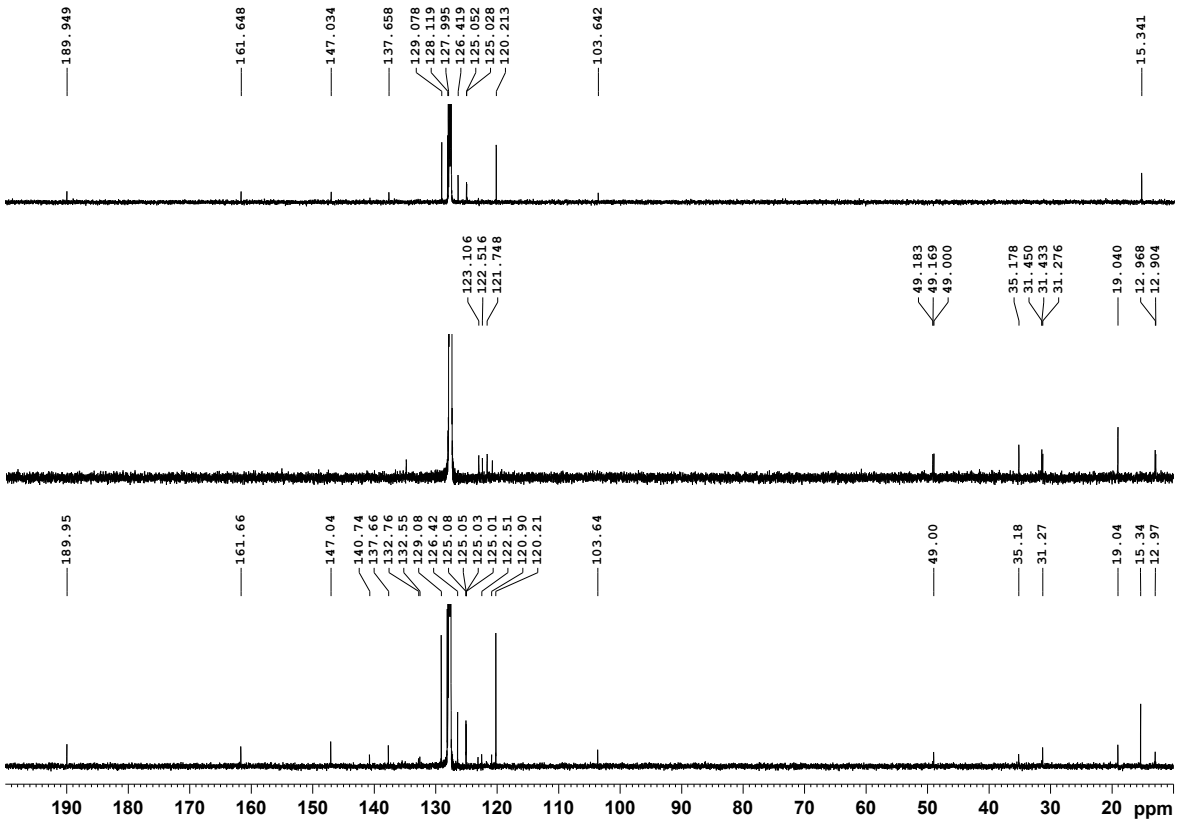
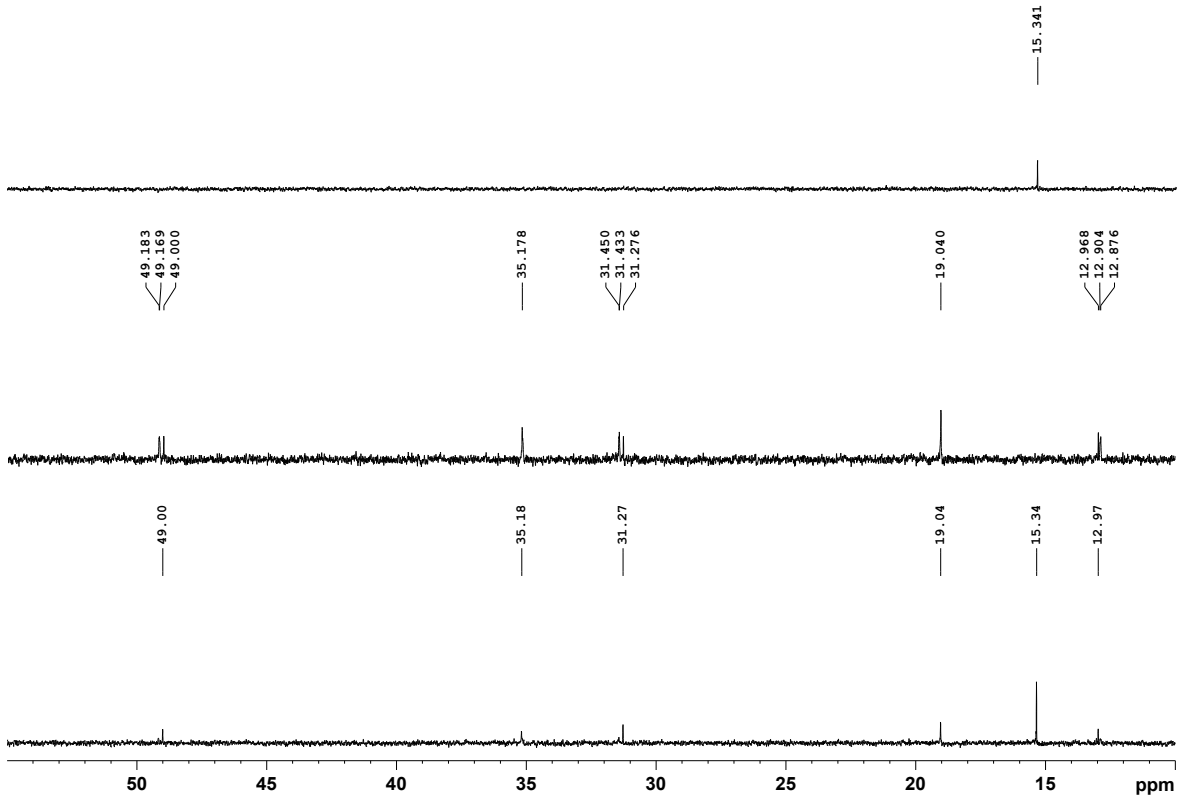


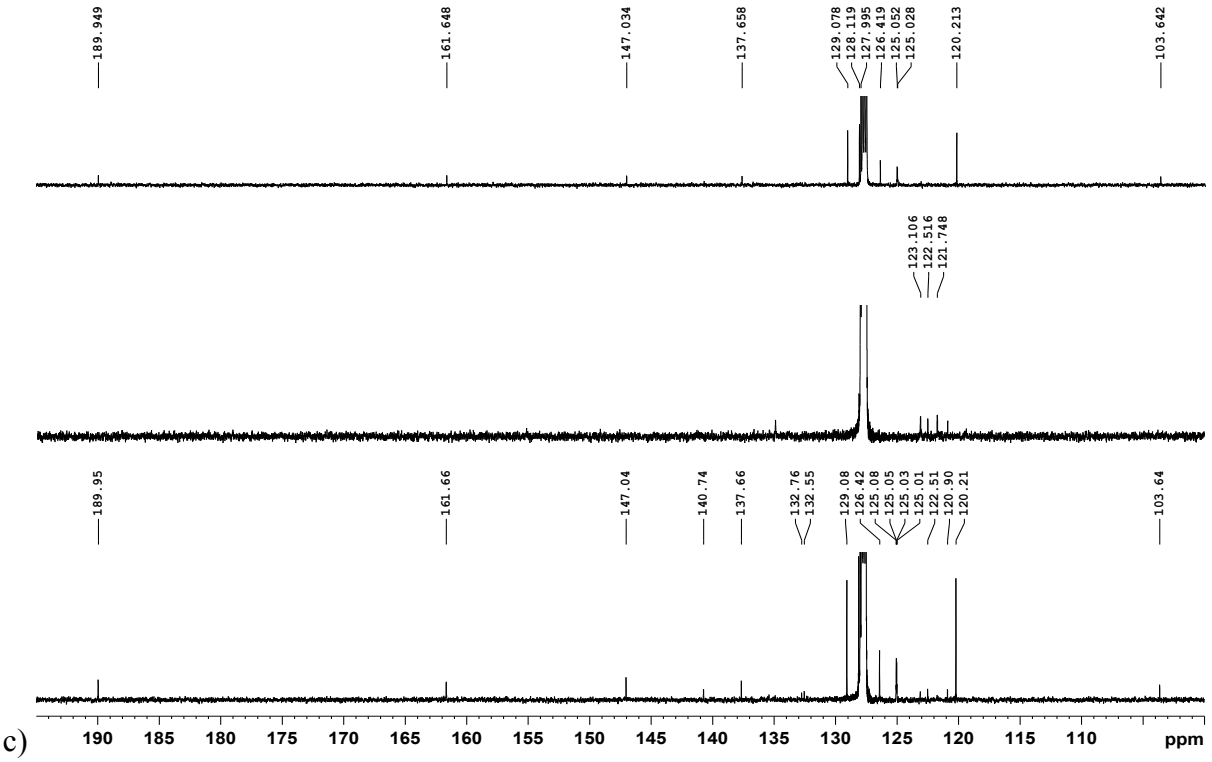
Figure S15. [1]H NMR spectra of IL:HL 1:1 (down), IL (middle), HL (up); a) full spectra, b) strong field area, c) aromatic area.


189.949
161.648
147.034
137.658
129.078
128.119
127.995
126.419
125.052
125.028
120.213
103.642
15.341
123.106
122.516
121.748
49.183
49.169
49.000
35.178
31.450
31.433
31.276
19.040
12.968
12.904
189.95
161.66
147.04
140.74
137.66
132.76
132.55
129.08
126.42
125.08
125.05
125.03
125.01
122.51
120.90
120.21
103.64
49.00
35.18
31.27
19.04
15.34
12.97
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

a)


15.341
49.183
49.169
49.000
35.178
31.450
31.433
31.276
19.040
12.968
12.904
12.876
49.00
35.18
31.27
19.04
15.34
12.97
50 45 40 35 30 25 20 15 ppm

b)

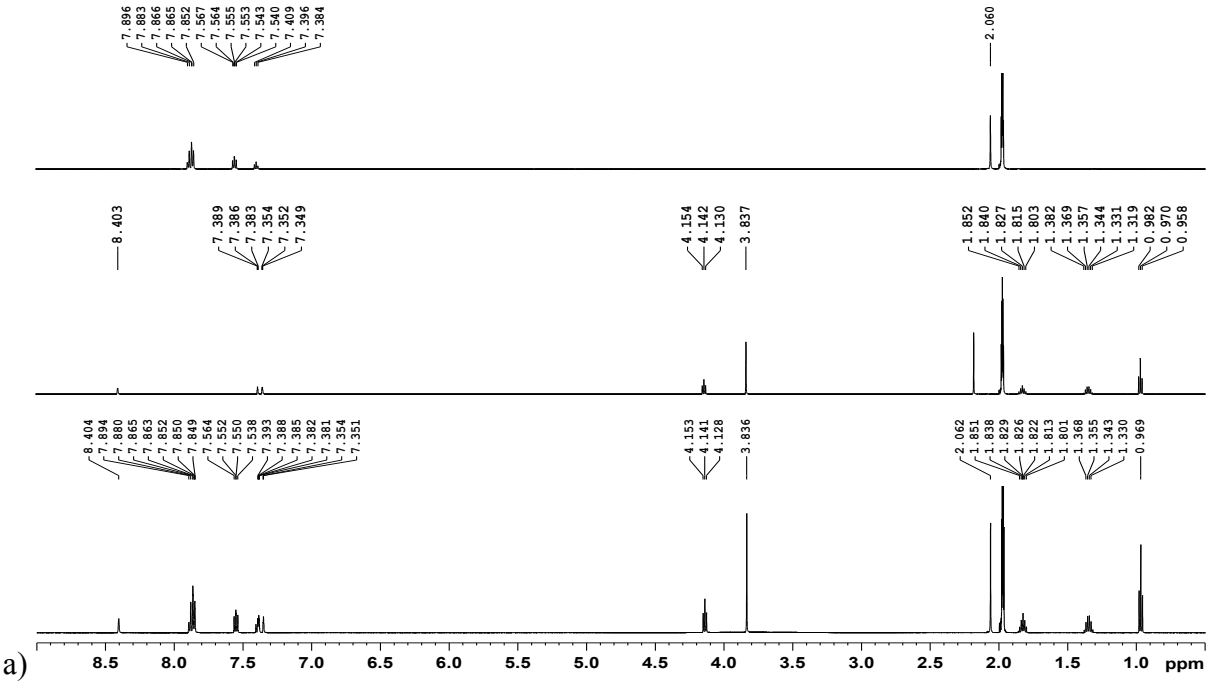


c)

Figure S16. ^{13}C NMR spectra of IL:HL 1:1 (down), IL (middle), HL (up); a) full spectra, b) strong field area, c) aromatic area.

2.3.2. NMR spectra in acetonitrile-d_3

The spectra of the ionic liquid (IL), the ligand (HL) and their 1:1 mixture were recorded in $2x10^{-2}$ M concentration.



a)

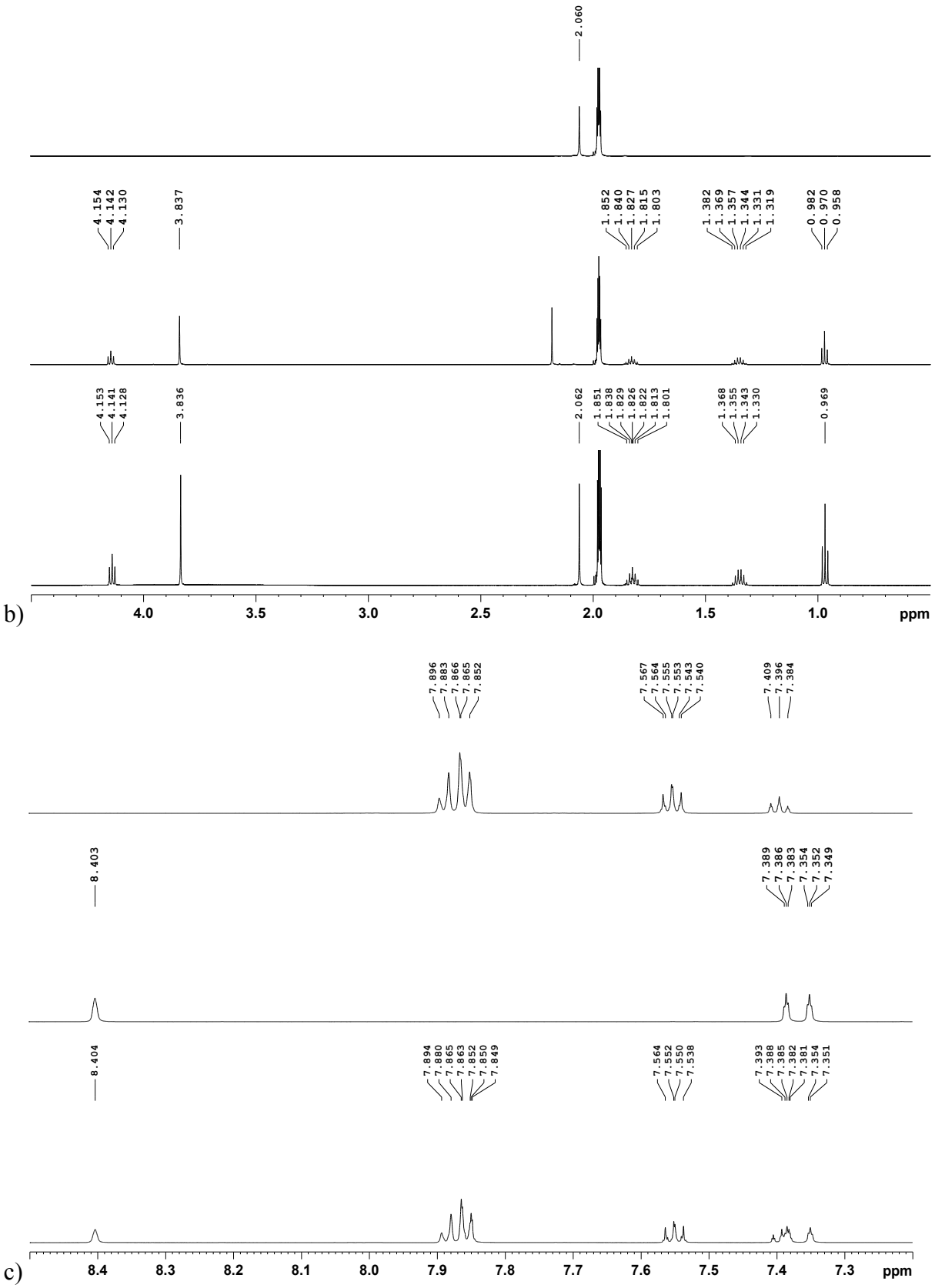
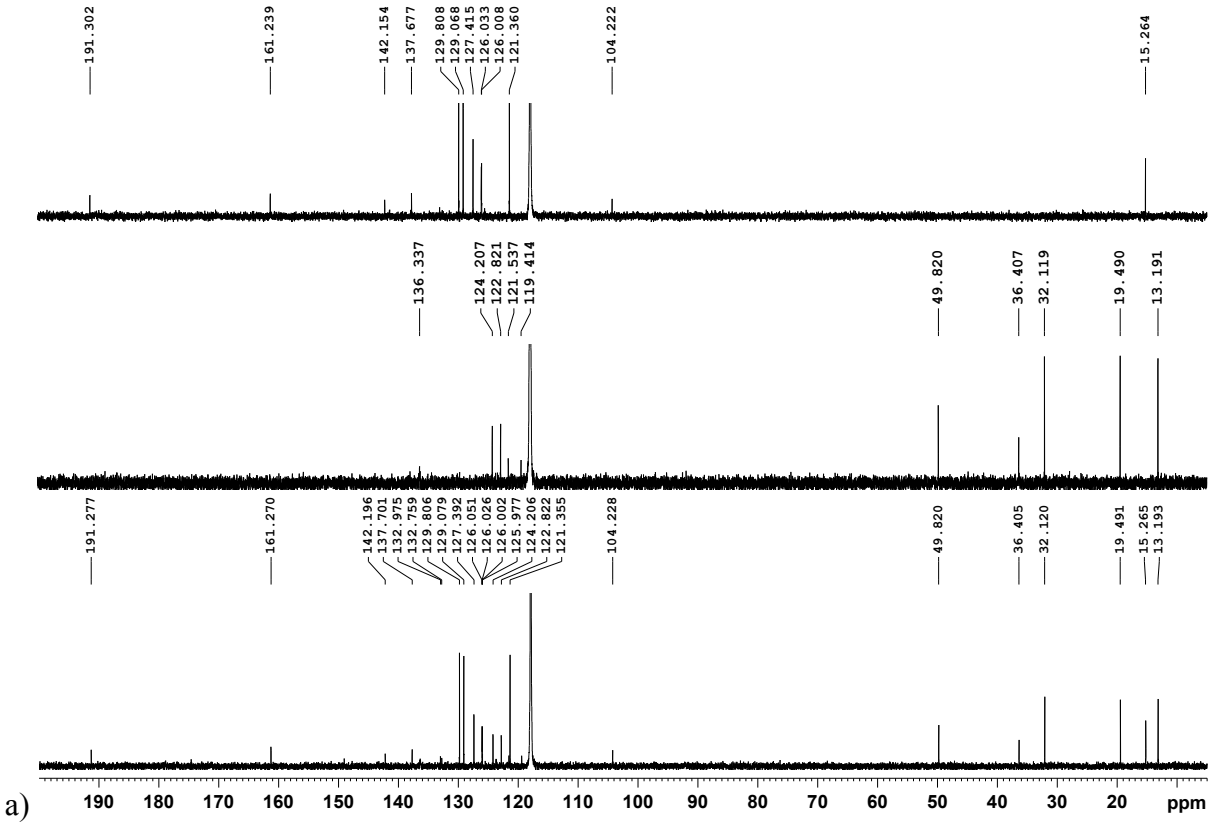
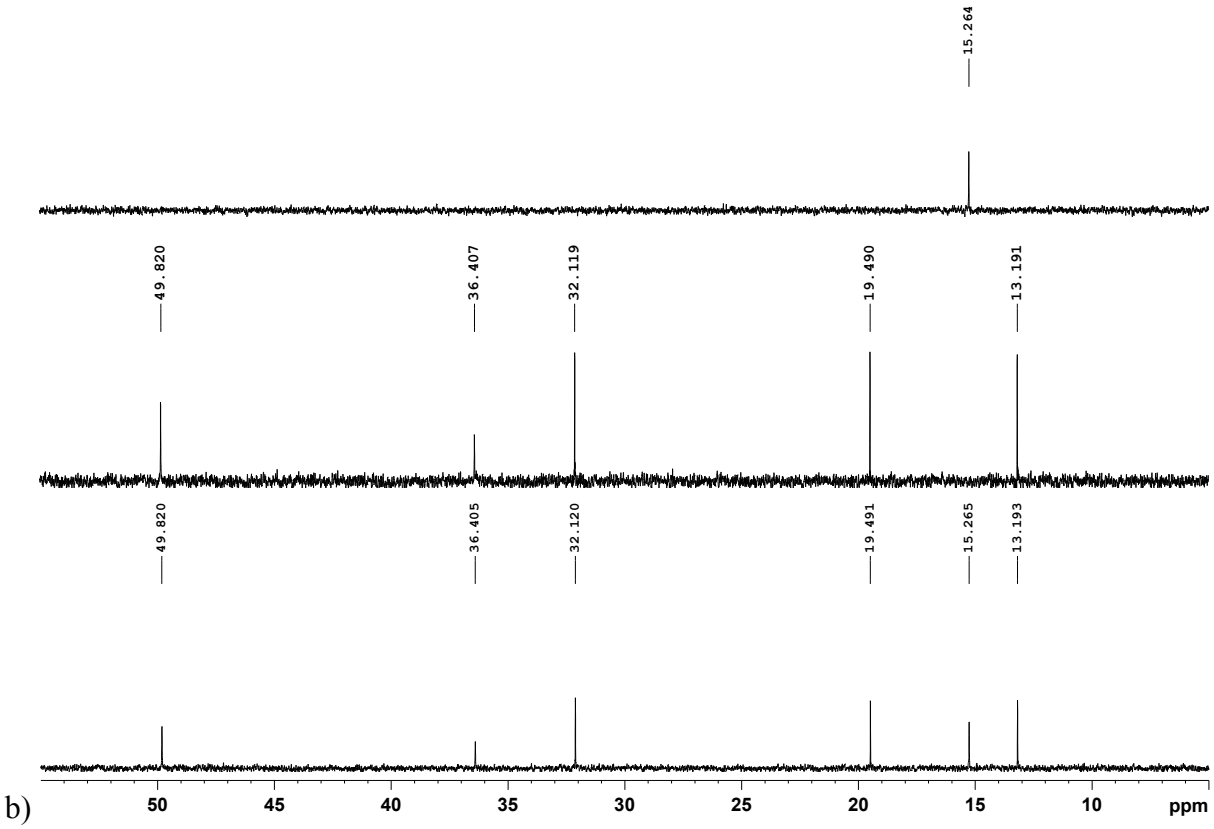


Figure S17. ^{1}H NMR spectra of IL:HL 1:1 (down), IL (middle), HL (up); a) full spectra, b) strong field area, c) aromatic area.


191.302
161.239
142.154
137.677
129.808
129.068
127.415
126.033
126.008
121.360
104.222
15.264
136.337
124.207
122.821
121.537
119.414
49.820
36.407
32.119
19.490
13.191
191.277
161.270
142.196
137.701
132.975
132.759
129.806
129.079
127.392
126.051
126.026
126.002
125.977
124.206
122.822
121.355
104.228
49.820
36.405
32.120
19.491
15.265
13.193
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

a)


15.264
49.820
36.407
32.119
19.490
13.191
49.820
36.405
32.120
19.491
15.265
13.193
50 45 40 35 30 25 20 15 10 ppm

b)

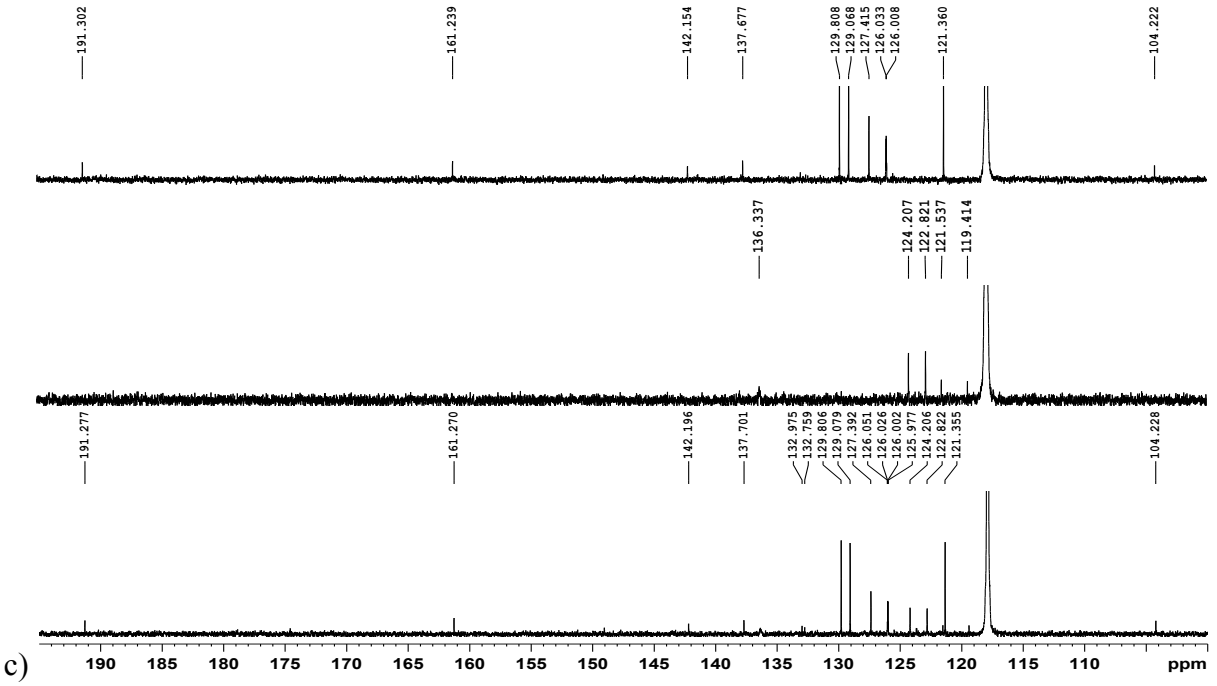


Figure S18. ^{13}C NMR spectra of IL:HL 1:1 (down), IL (middle), HL (up); a) full spectra, b) strong field area, c) aromatic area.

2.3.3. NMR spectra in chloroform-d

The spectra of IL and HL were recorded in 0.05 M concentrations; the 4:1, 2:1, and 1:1 IL–HL mixtures were recorded as 0.1 M IL and 0.025 M, 0.05 M, and 0.1 M HL, respectively.

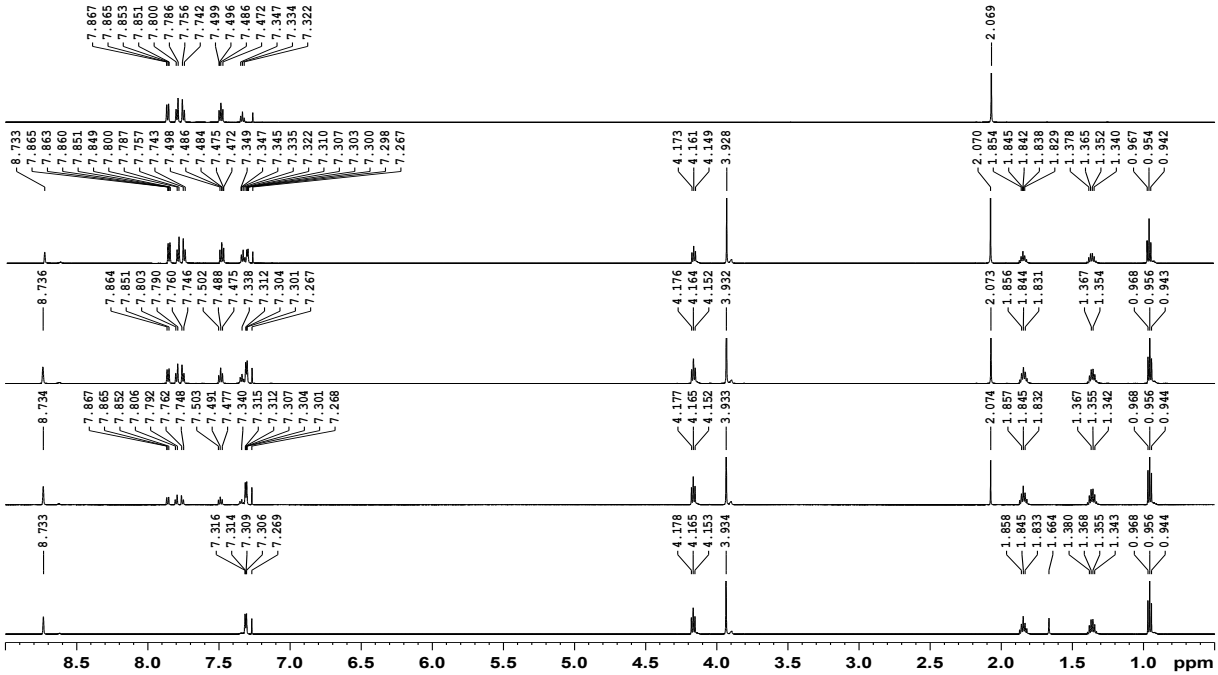


Figure S19. ^{1}H NMR spectra of IL (down), IL:HL 4:1, IL:HL 2:1, IL:HL 1:1, HL (up).

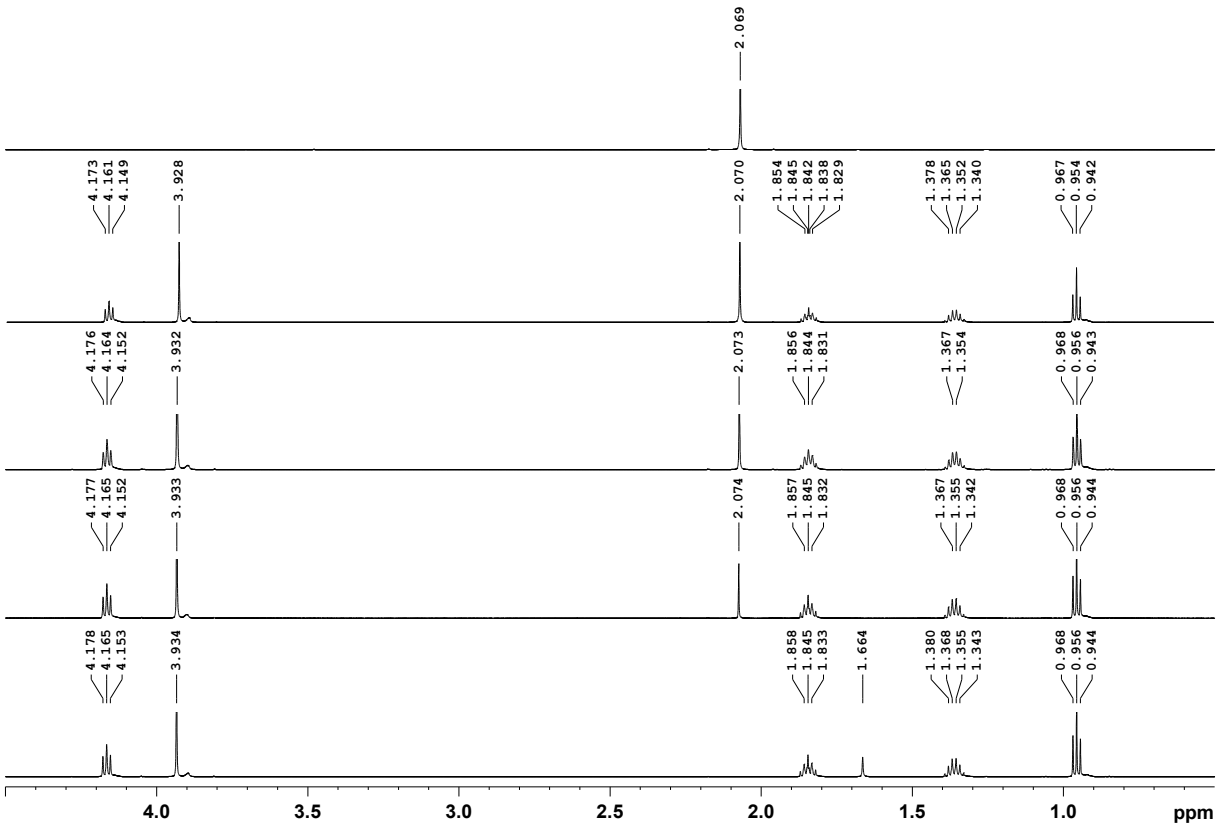


Figure S20. Strong field area of ^{1}H NMR spectra of IL (down), IL:HL 4:1, IL:HL 2:1, IL:HL 1:1, HL (up).

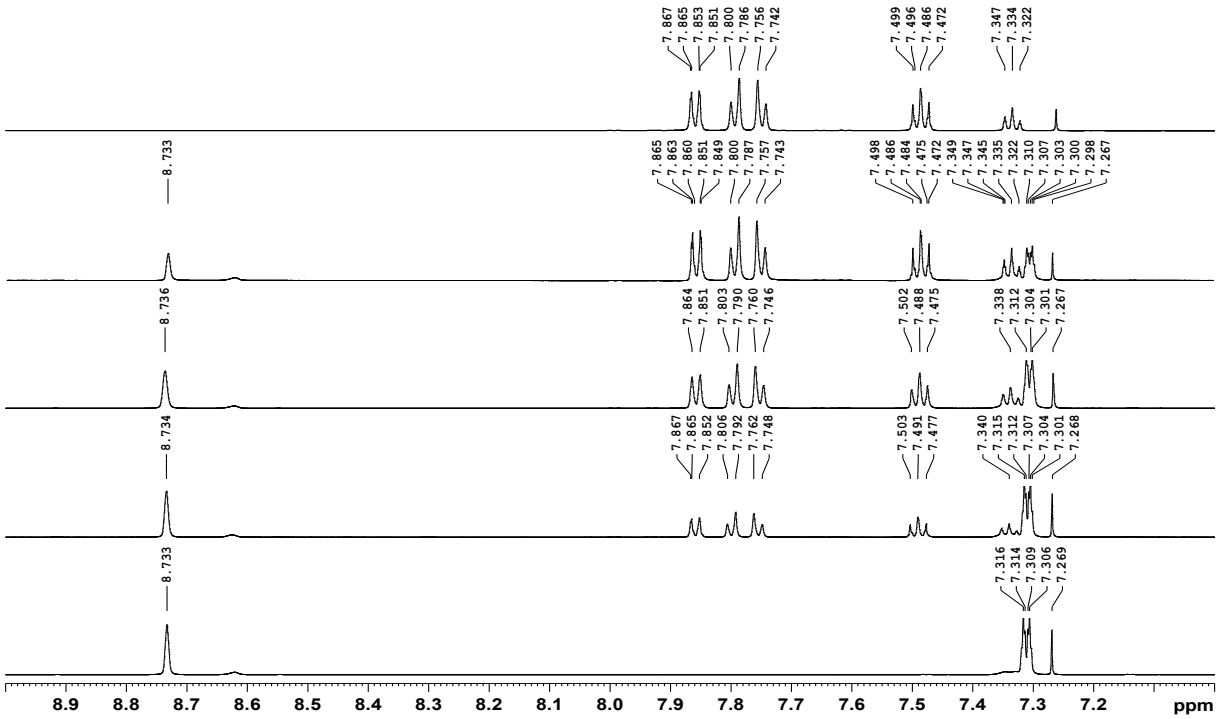


Figure S21. Low field area of ^{1}H NMR spectra of IL (down), IL:HL 4:1, IL:HL 2:1, IL:HL 1:1, HL (up).

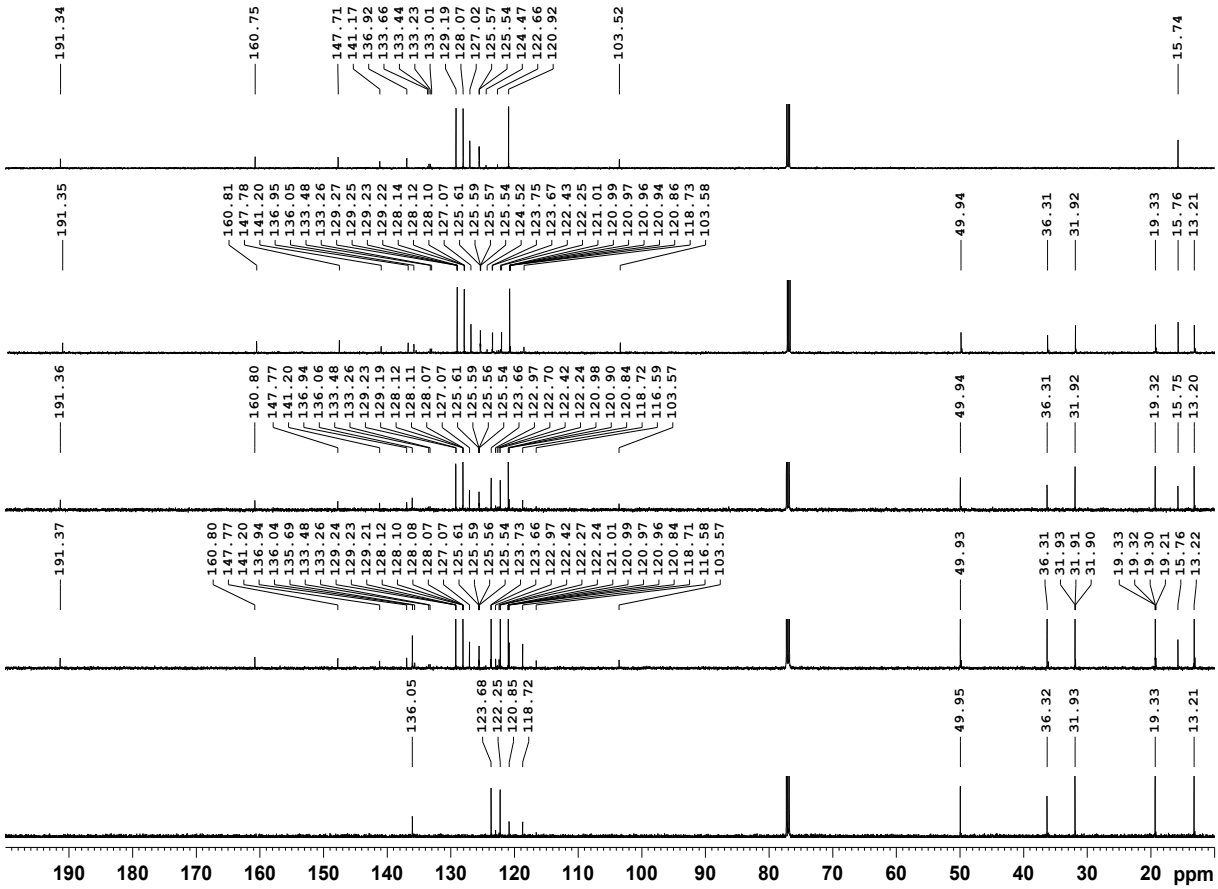


Figure S22. ^{13}C NMR spectra of IL (down), IL:HL 4:1, IL:HL 2:1, IL:HL 1:1, HL (up).

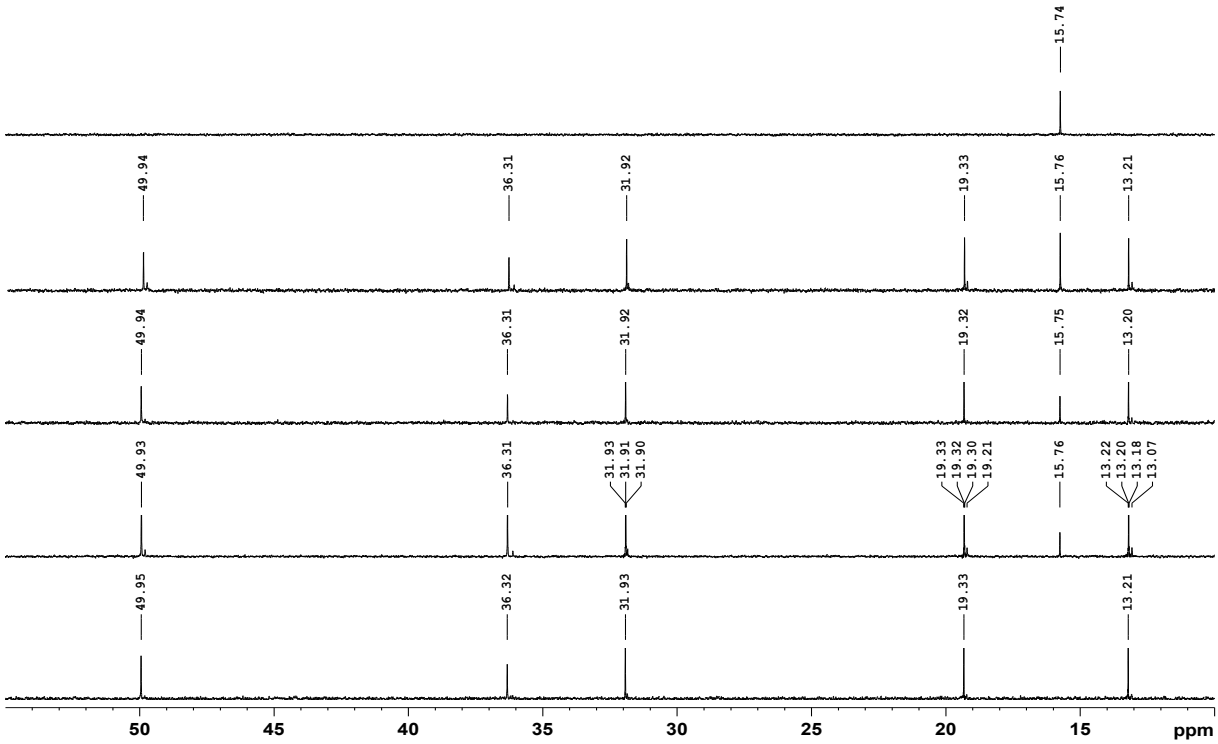


Figure S23. Strong field area of ^{13}C NMR spectra of IL (down), IL:HL 4:1, IL:HL 2:1, IL:HL 1:1, HL (up).

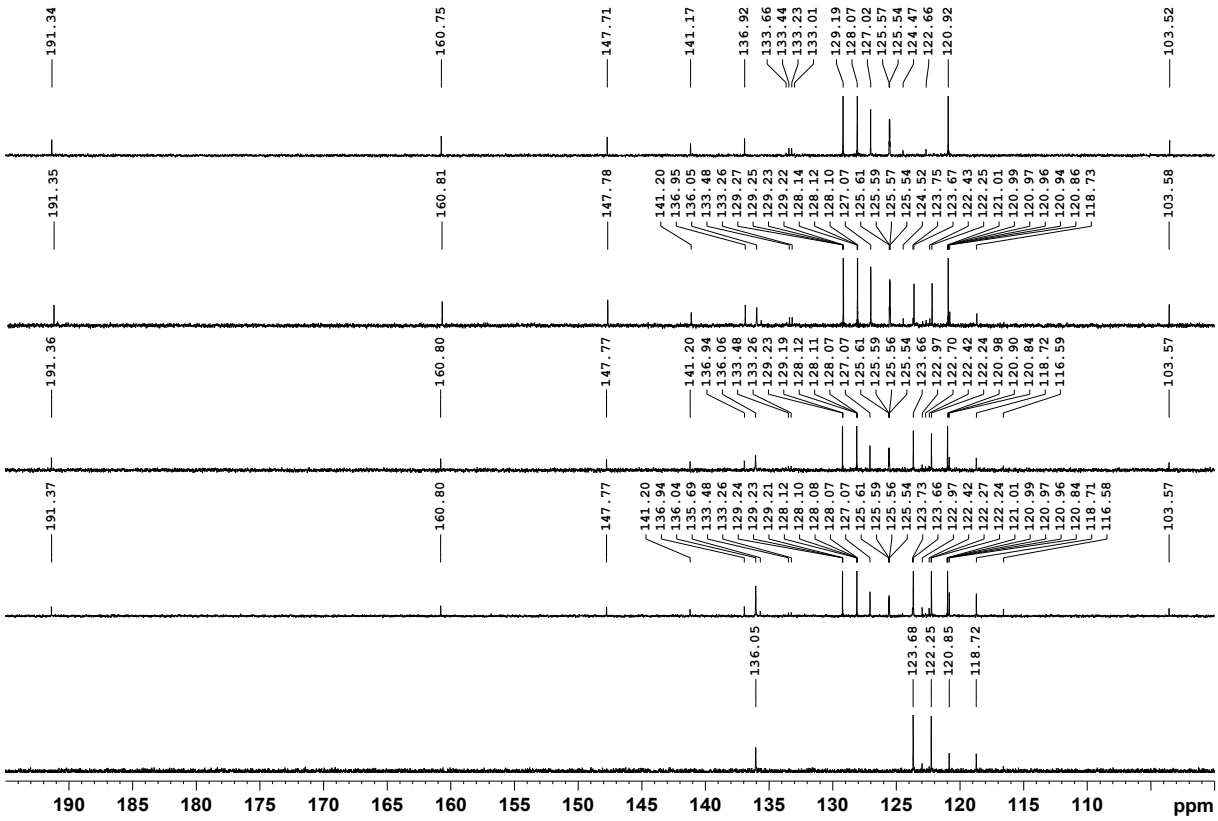


Figure S24. Low field area of ^{13}C NMR spectra of IL (down), IL:HL 4:1, IL:HL 2:1, IL:HL 1:1, HL (up).

2.4. Extraction by individual compounds HL, S1 and S2

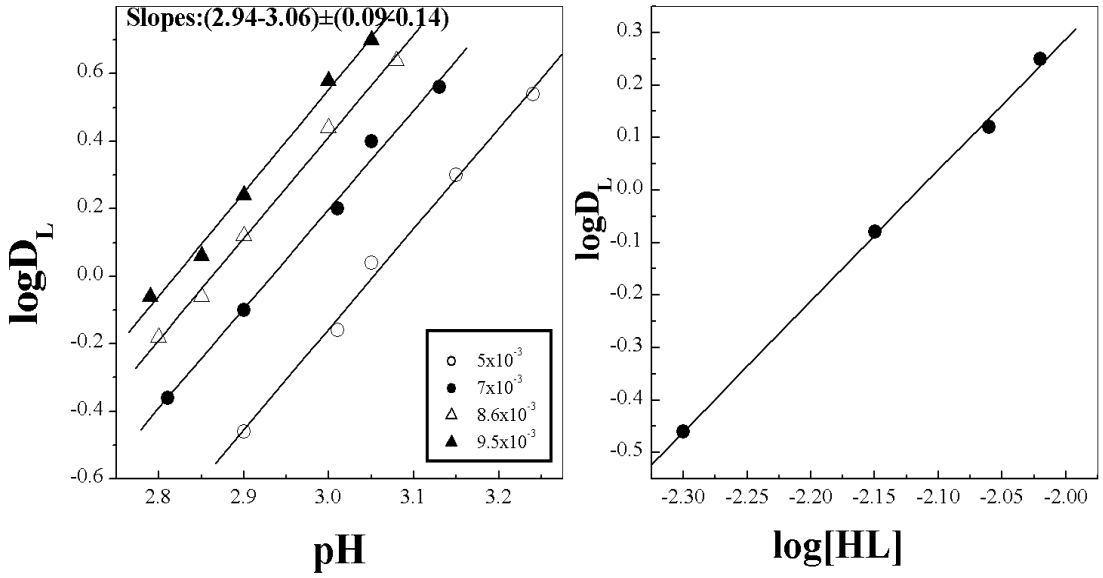


Figure S25. LogD_L vs. pH for La(III) ion extraction with HL and logD_L vs. log[HL] for La(III) ion extraction at pH=2.90 in IL.

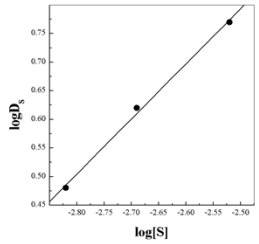


Figure S26. LogD_S vs. log[S] for La(III) ion extraction at pH=2.73.

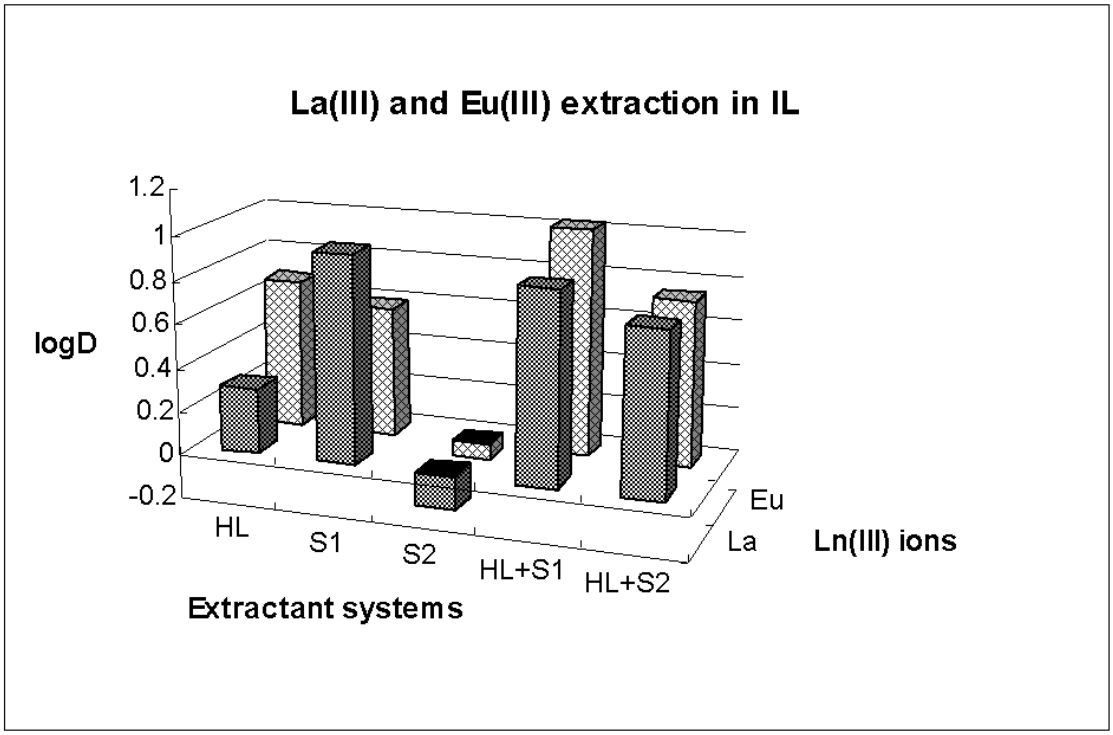


Figure S27. Log*D* of La (III) and Eu(III) ions with solution of extractants in IL:
La, [HL] = 8.6x10^{-3} mol/dm^3, pH$_{in.}$=2.86; [S]=2x10^{-3} mol/dm^3, pH$_{in.}$=2.86; [HL–S]=8.6x10^{-3}mol/dm^3 and 7x10^{-4} mol/dm^3, pH$_{in.}$=2.86.
Eu, [HL] = 8.6x10^{-3} mol/dm^3, pH$_{in.}$=2.67; [S]=2x10^{-3} mol/dm^3, pH$_{in.}$=2.60; [HL–S]=8.6x10^{-3}mol/dm^3 and 7x10^{-4} mol/dm^3, pH$_{in.}$=2.64.