Supporting Information

Hydrodesulfurization of Dibenzothiophene using Pd promoted Co-Mo/Al$_2$O$_3$ and Ni-Mo/Al$_2$O$_3$ catalysts coupled with ionic liquid at ambient operating conditions

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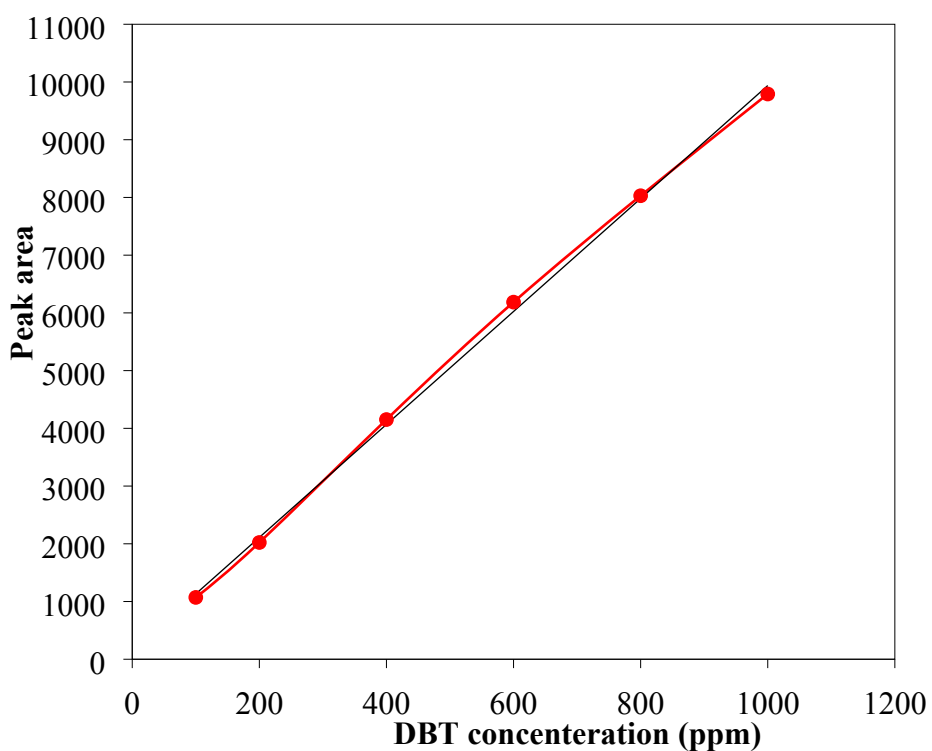
Corresponding author: Zhangfa Tong (zhftong@sina.com)

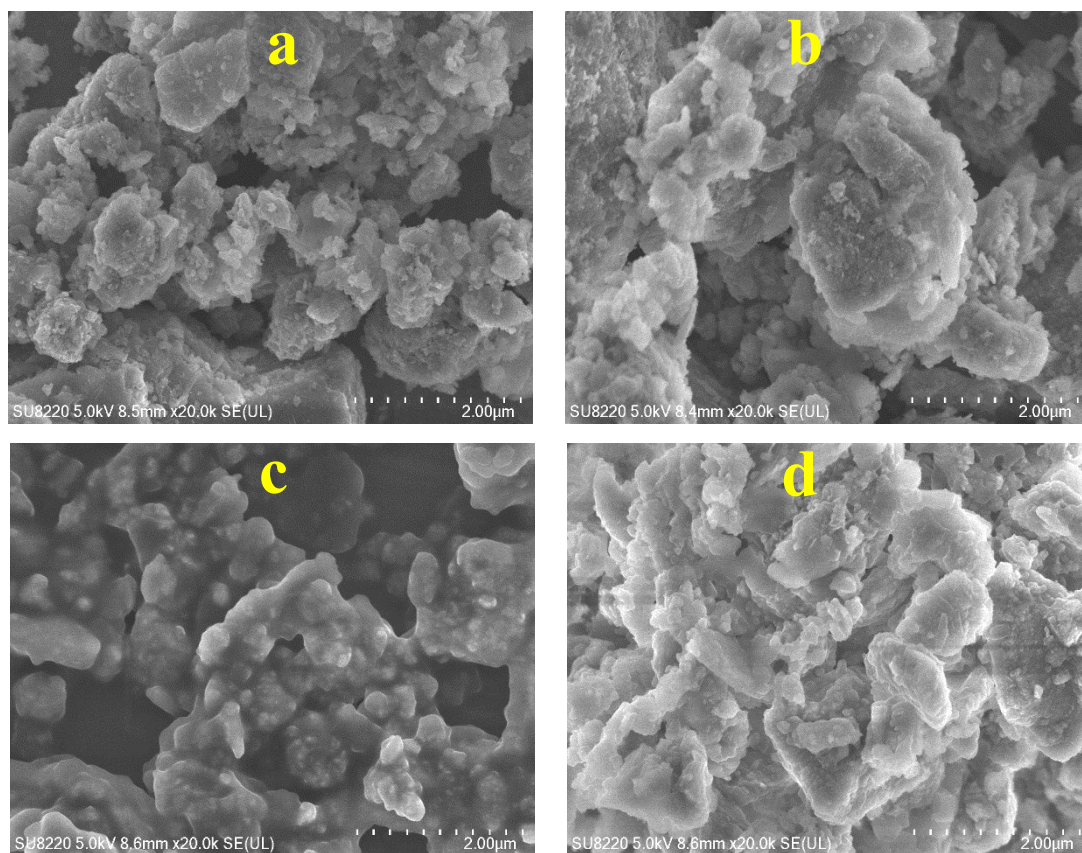**Figure S1.** Calibration curve of DBT in *n*-Octane

Figure S2. FESEM images of spent catalysts: (a) Co-M/Al$_2$O$_3$, (b) Ni-Mo/Al$_2$O$_3$, (c) Pd-Co-Mo/Al$_2$O$_3$ and (d) Pd-Ni-Mo/Al$_2$O$_3$ tested in HDS reaction at 1 MPa H$_2$ pressure, 4 h reaction time at 120 ^{o}C temperature using 3 g of [(n-C$_8$H$_{17}$)(C$_4$H$_9$)$_3$P]Br.

a

Element	Wt%	At%
O	46.00	58.96
Al	54.00	41.04
Matrix	Correction	ZAF

b

Element	Wt%	At%
Mo	91.34	86.63
Co	08.66	13.37
Matrix	Correction	ZAF

c

Element	Wt%	At%
Mo	88.09	81.91
Ni	11.91	18.09
Matrix	Correction	ZAF

d

Element	Wt%	At%
O	64.17	91.33
Mo	33.64	07.98
Pd	00.95	00.20
Co	01.25	00.48
Matrix	Correction	ZAF

e

Element	Wt%	At%
O	61.74	90.23
Mo	34.45	08.39
Pd	00.77	00.17
Ni	03.04	01.21
Matrix	Correction	ZAF
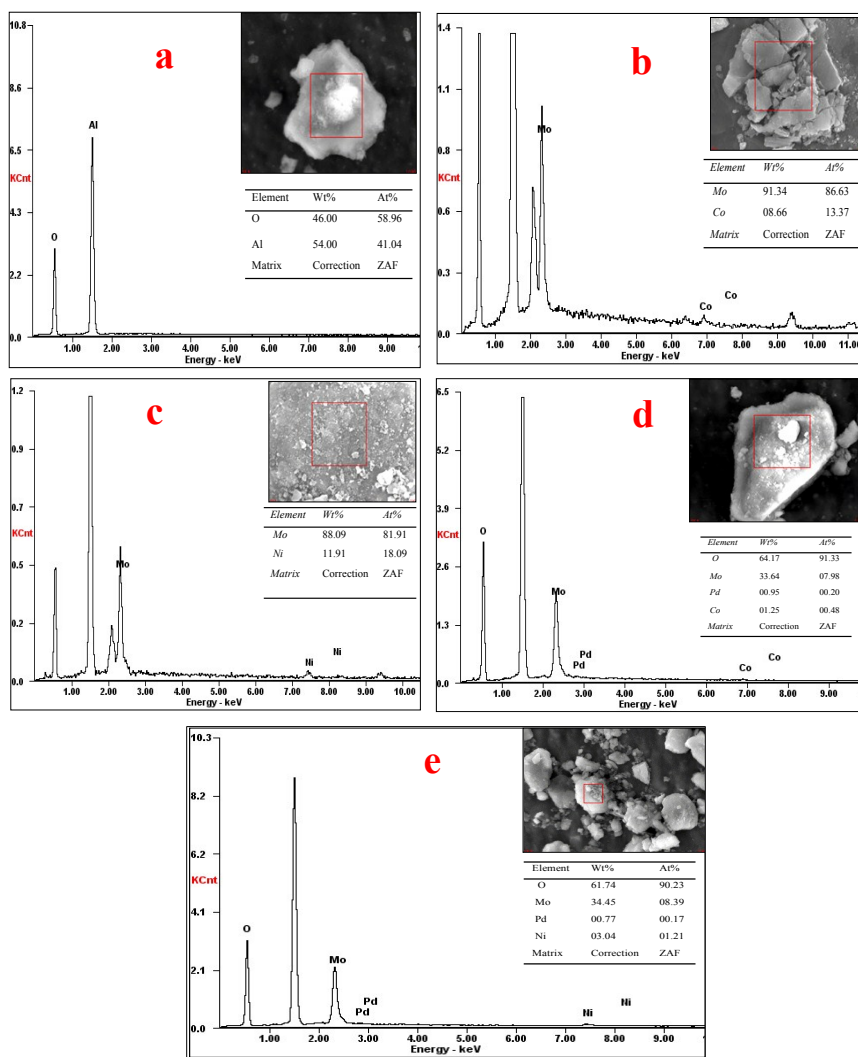
Figure S3.

EDX spectra of: (a) Al_2O_3, (b) Co-

M/Al$_2$O$_3$, (c) Ni-Mo/Al$_2$O$_3$, (d) Pd-Co-Mo/Al$_2$O$_3$ and (e) Pd-Ni-Mo/Al$_2$O$_3$
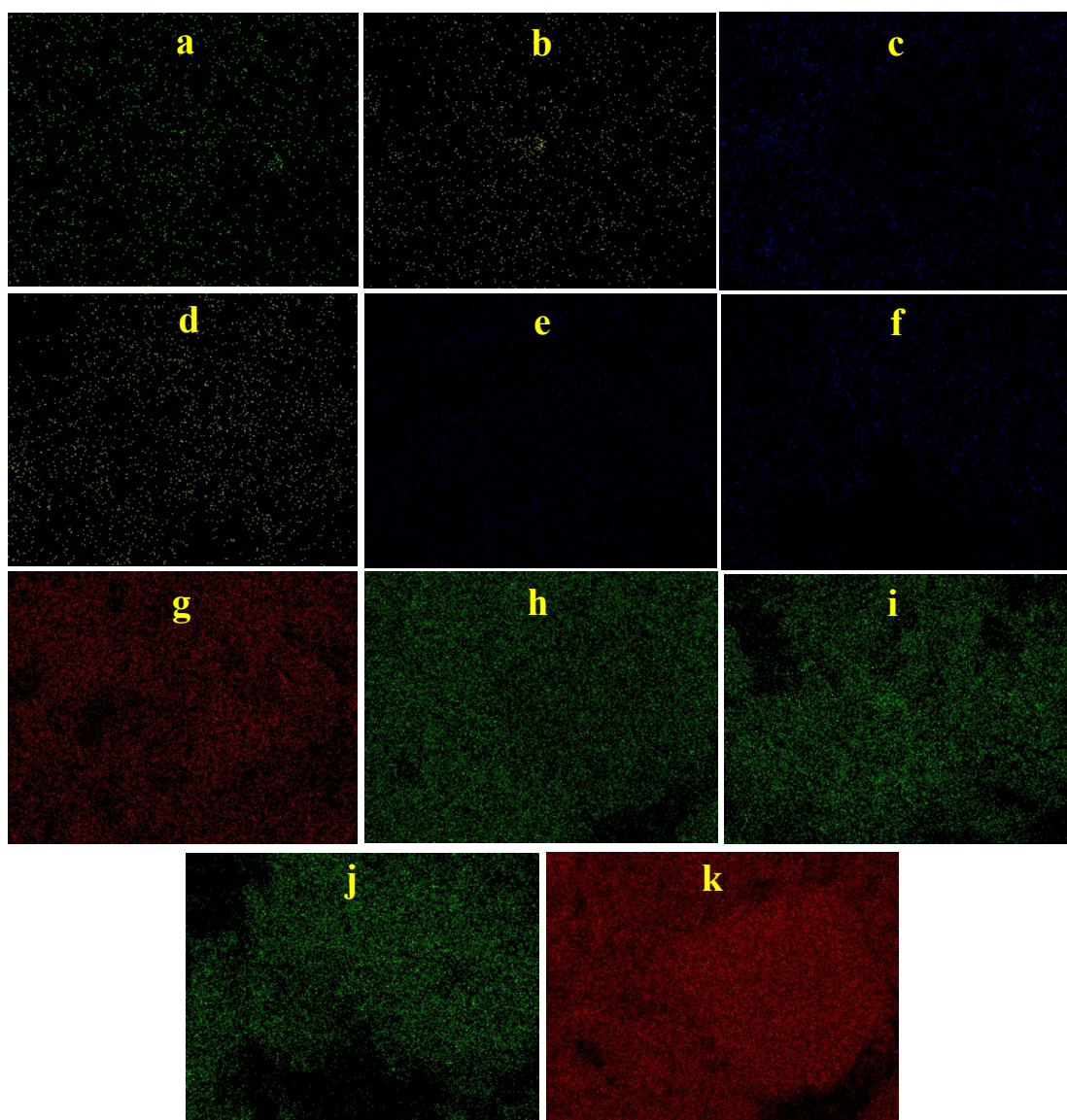
Figure S4A. EDX elemental mapping of various metals in fresh catalysts and in support.

Co in (a) Co-Mo/Al$_2$O$_3$, (b) Pd-Co-Mo/Al$_2$O$_3$

Ni in: (c) Ni-Mo/Al$_2$O$_3$ and (d) Pd-Ni-Mo/Al$_2$O$_3$

Pd in: (e) Pd-Co-Mo/Al$_2$O$_3$, and (f) Pd-Ni-Mo/Al$_2$O$_3$

Mo in: (g) Co-Mo/Al$_2$O$_3$, (h) Ni-Mo/Al$_2$O$_3$, (i) Pd-Co-Mo/Al$_2$O$_3$ and (j) Pd-Ni-Mo/Al$_2$O$_3$

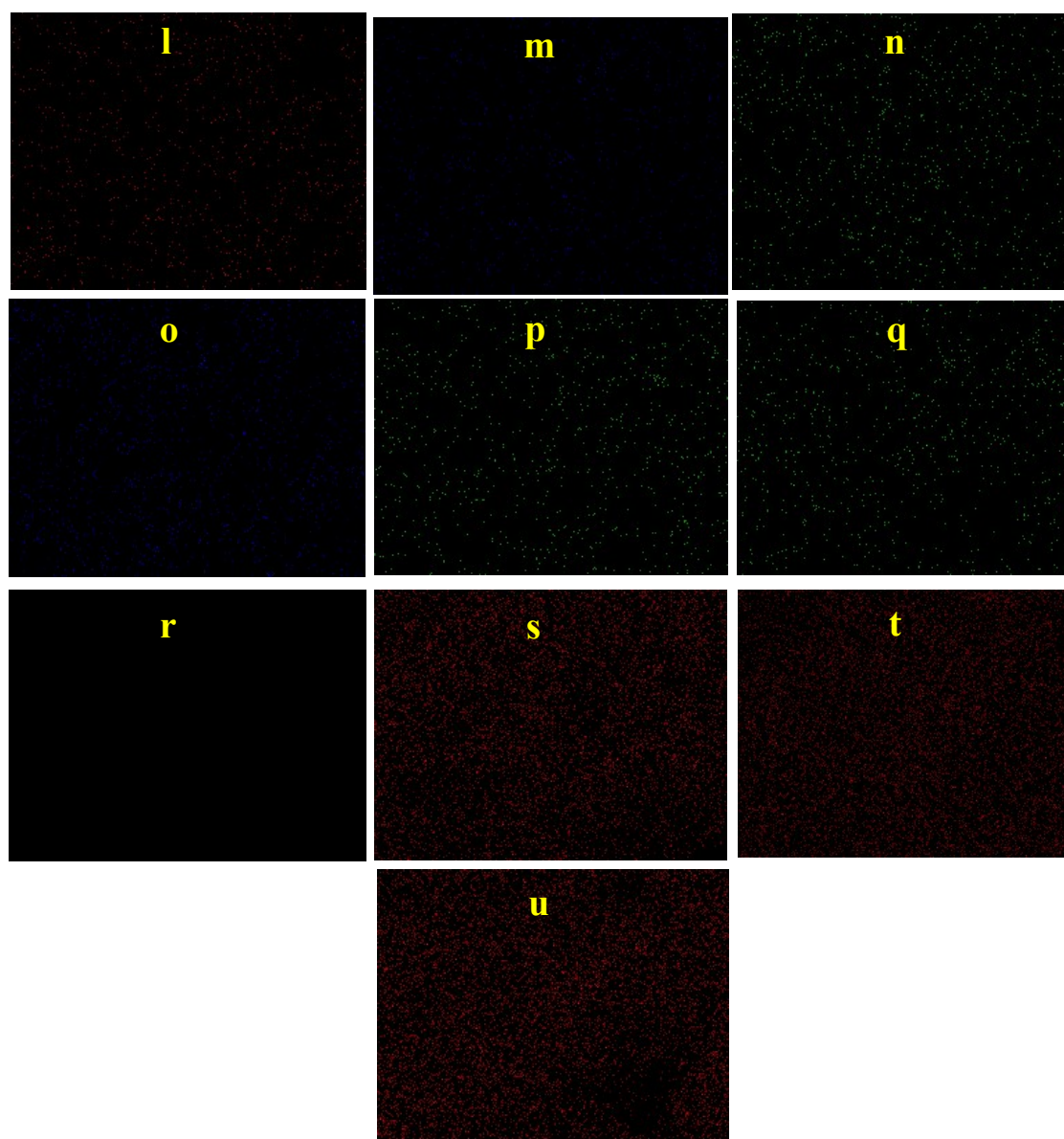and Al in: (k) Pd-Co-Mo/Al$_2$O$_3$

Figure S4B. EDX elemental mapping of Co, Ni, Mo and Pd in spent catalysts.

Co in (l) Co-Mo/Al$_2$O$_3$, (m) Pd-Co-Mo/Al$_2$O$_3$

Ni in: (n) Ni-Mo/Al$_2$O$_3$ and (o) Pd-Ni-Mo/Al$_2$O$_3$

Pd in: (p) Pd-Co-Mo/Al$_2$O$_3$, and (q) Pd-Ni-Mo/Al$_2$O$_3$

and Mo in: (r) Co-Mo/Al$_2$O$_3$, (s) Ni-Mo/Al$_2$O$_3$, (t) Pd-Co-Mo/Al$_2$O$_3$ and (u) Pd-Ni-Mo/Al$_2$O$_3$
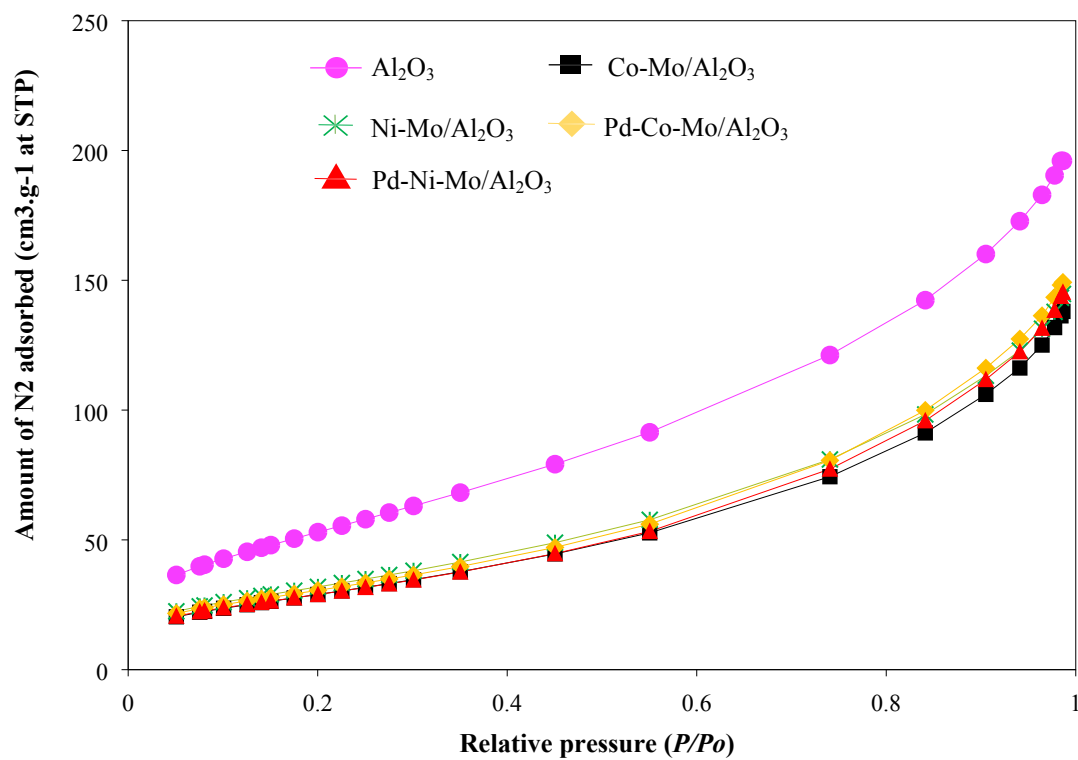

Figure S5. Nitrogen adsorption isotherms of Al$_2$O$_3$ support and different types of catalysts

(I)
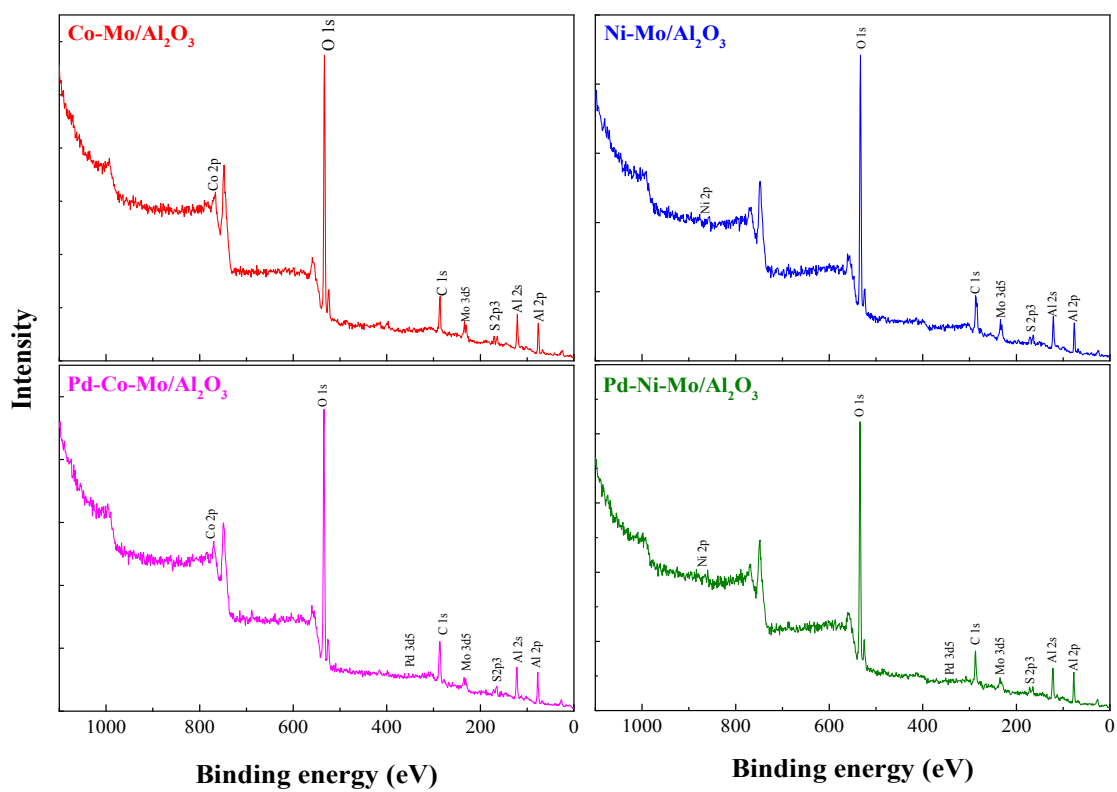
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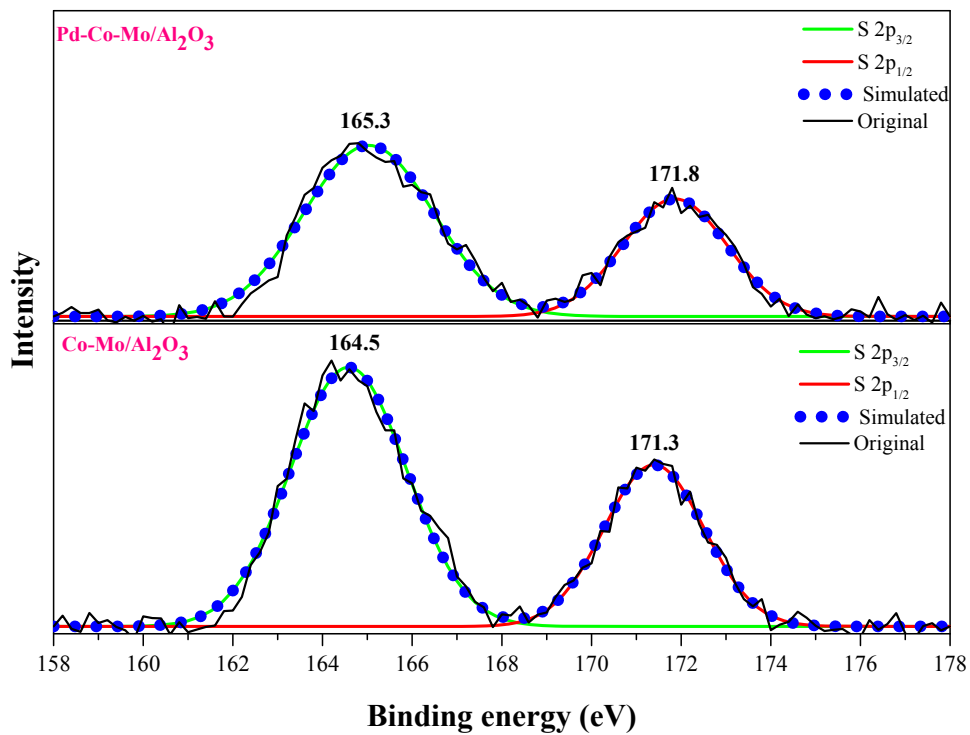
(III)
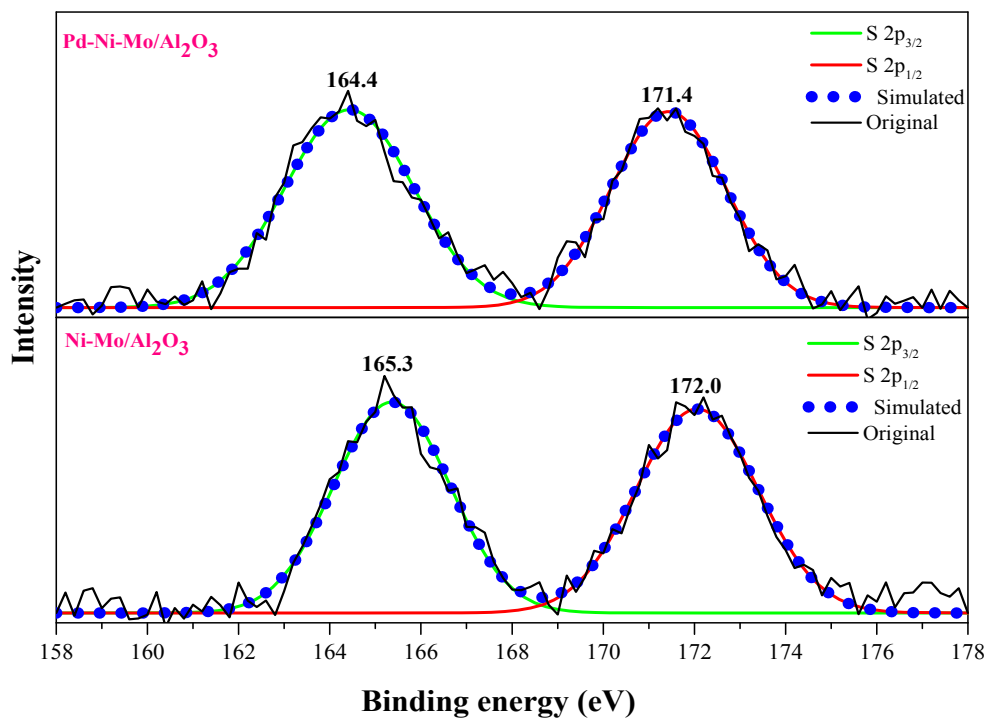
Figure S6. (I) Full survey XPS spectra of various catalysts, and **(II)** and **(III)** high resolution XPS spectra of S 2p in various catalysts.

I

II
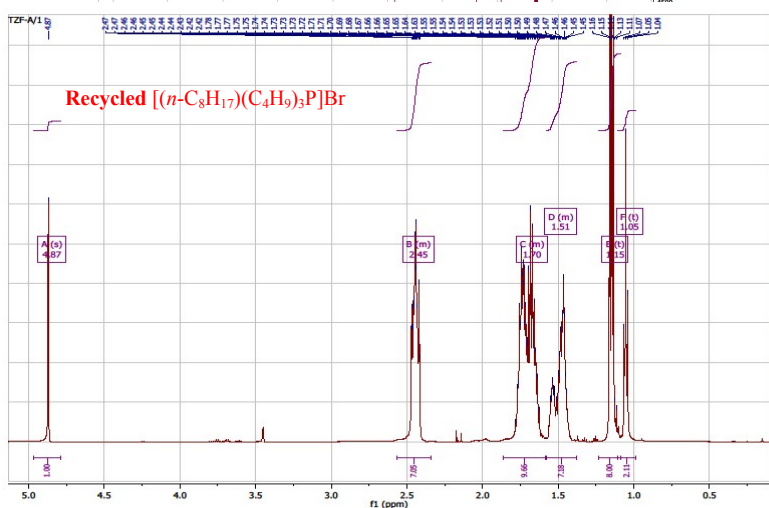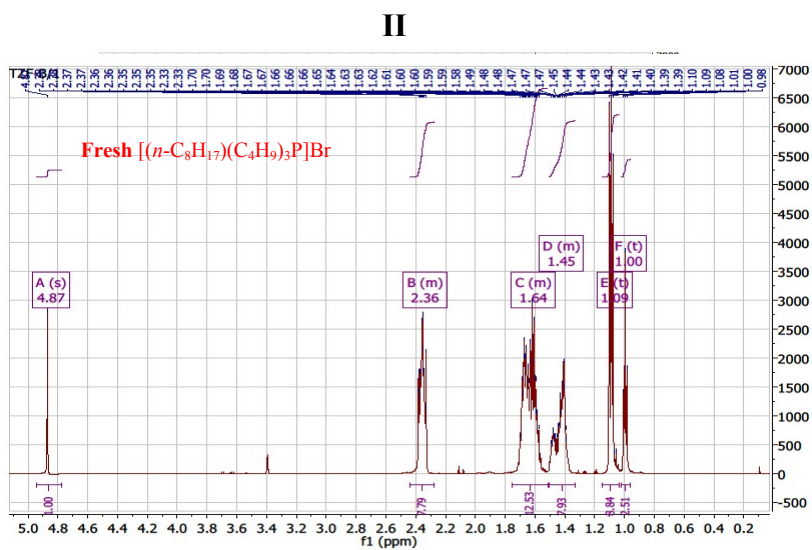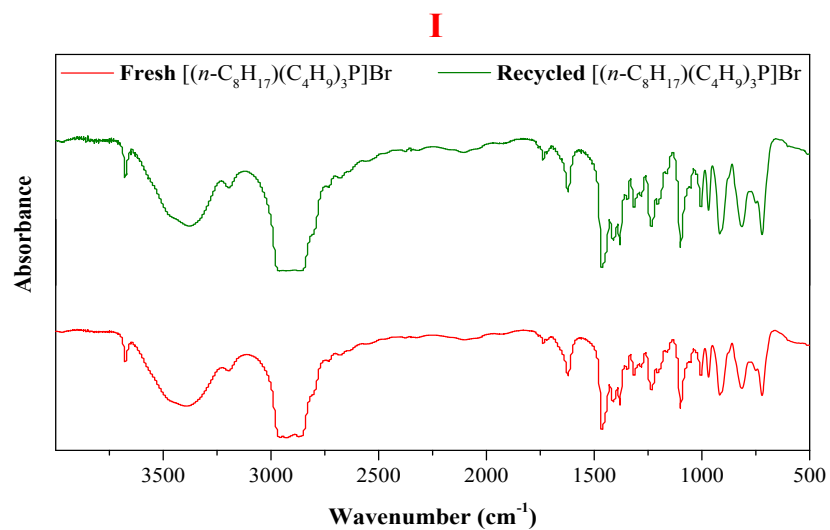
Figure S7. (I) FT-IR spectra and (II) ^{1}H NMR spectra of fresh and recycled [(n-C$_8$H$_{17}$)(C$_4$H$_9$)$_3$P]Br (after being used in HDS coupled with Pd-Ni-Mo/Al$_2$O$_3$ for four consecutive cycles at 1 MPa H$_2$ pressure, 120 °C temperature for 4 h).

(a)

(b)
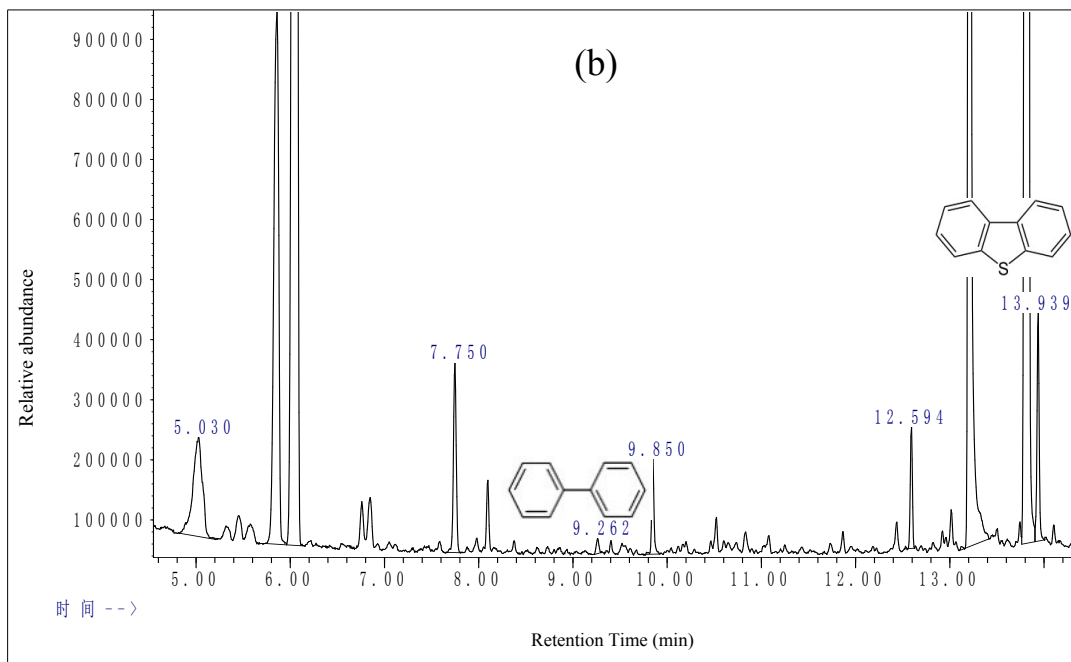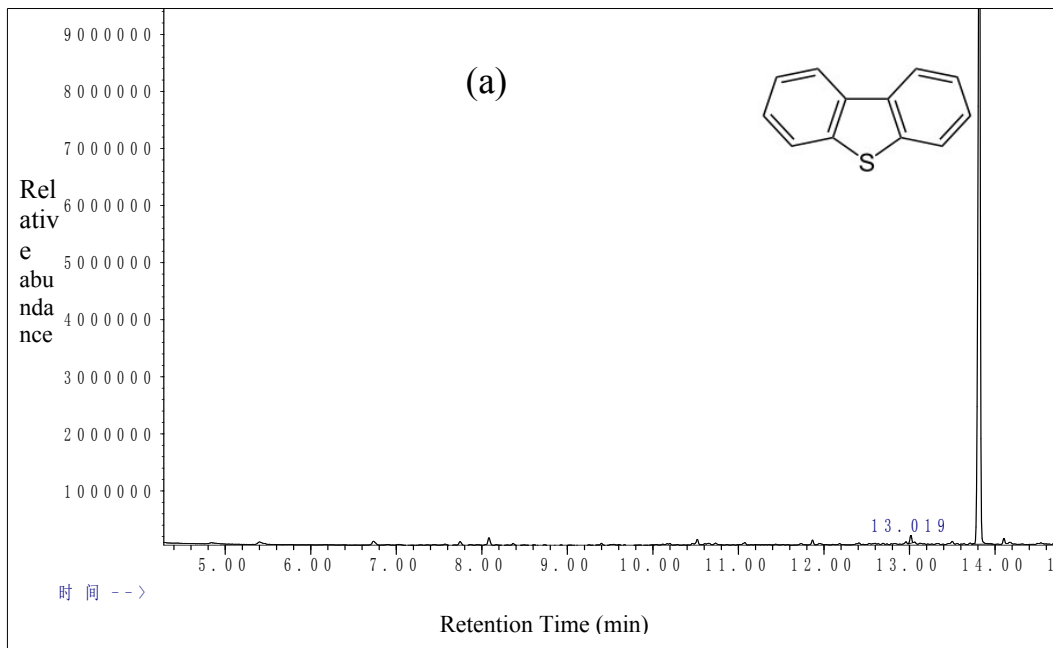
Figure S8. GC-MS chromatogram of: (a) Pre-reaction feed sample, (b) Post reaction HDS products sample

Catalyst type	Element concentration (ppm)				
	Al	Co	Ni	Mo	Pd
Co-Mo/Al$_2$O$_3$	69000	6000	–	24000	–
Ni-Mo/Al$_2$O$_3$	79000	–	18000	35000	–
Pd-Co-Mo/Al$_2$O$_3$	59000	5000	–	21000	3000
Pd-Ni-Mo/Al$_2$O$_3$	66000	–	9000	19000	3500
Pd-Co-Mo/Al$_2$O$_3$*	38000	4000	–	15000	2200
Pd-Ni-Mo/Al$_2$O$_3$*	43000	–	9000	17000	2500

(*represents spent catalysts)

Table S1. ICP-MS elemental distribution data in various catalysts.

1. *n*-Octane with H$_2$

C	-4.80532100	0.01914700	-0.05711500
C	-3.44233600	0.71098100	0.03805000
C	-2.26046600	-0.26198900	-0.04361000
C	-0.89186800	0.42178100	0.04902300
C	0.28952600	-0.55167600	-0.03361300
C	1.65809400	0.13220100	0.05870100
C	2.84003100	-0.84068200	-0.02292300
C	4.20294500	-0.14858000	0.07138600
H	-4.93870500	-0.70552700	0.75246200
H	-4.90957000	-0.52118800	-1.00344300
H	-5.62539300	0.74007100	0.00494600
H	-3.38289900	1.27211200	0.97870200
H	-3.35341900	1.45379100	-0.76416500
H	-2.32167900	-0.82446000	-0.98458400
H	-2.34951200	-1.00533900	0.75950100
H	-0.83159500	0.98383900	0.99013400
H	-0.80433100	1.16529900	-0.75390100
H	0.22916000	-1.11386300	-0.97463800
H	0.20211900	-1.29508600	0.76942600
H	1.71940100	0.69490000	0.99952700
H	1.74695800	0.87535900	-0.74460800
H	2.78035000	-1.40225100	-0.96329600
H	2.75153700	-1.58312600	0.77967200
H	4.30741600	0.39231000	1.01737400
H	4.33583600	0.57564900	-0.73867700
H	5.02306900	-0.86946500	0.00943600
H	10.24991500	2.34266500	-0.22287900
H	9.62770600	1.93720800	-0.27037700

2. [(CH$_3$)$_4$N]Cl with H$_2$

N	1.10188800	0.00500600	-0.00008500
C	0.52666500	0.56602300	1.27934100

C	2.58872700	0.15584700	-0.00032300
C	0.73066600	-1.45555200	-0.10510300
C	0.50736400	0.74731900	-1.17393200
H	-0.56020100	0.42729200	1.23400500
H	0.78864800	1.62202900	1.33823400
H	0.96154500	0.02114100	2.11700500
H	2.98865900	-0.25161800	-0.92824700
H	3.00223700	-0.38583000	0.84974400
H	2.84016500	1.21311300	0.07718100
H	-0.36471400	-1.51279800	-0.10066700
H	1.14411100	-1.84750200	-1.03412000
H	1.15873200	-1.97935200	0.74931800
H	-0.57885600	0.60160200	-1.13286300
H	0.92880500	0.33231800	-2.08924400
H	0.76914700	1.80096800	-1.08110700
Cl	-2.45739500	-0.35489600	-0.00000300
H	-2.52130800	3.30899500	-0.00177700
H	-2.61500900	2.56601200	0.00328500

3. [BMIM]BF$_4$ with H$_2$

C	0.27946500	-2.86007900	0.47311200
C	1.11227600	-2.05911000	1.19046300
N	0.92300900	-0.76548500	0.73626500
C	0.00291300	-0.78723600	-0.22980900
N	-0.40253400	-2.04485200	-0.41179100
C	-1.49348400	-2.44296500	-1.31016200
C	1.56279000	0.45809000	1.26409500
C	2.97143900	0.68953500	0.71186100
C	3.02867800	0.96081300	-0.79555500
C	4.44843400	1.25701000	-1.28700800
H	0.10435800	-3.92048700	0.52659500
H	1.80144100	-2.29276900	1.98308200
H	-0.39522800	0.07000500	-0.74873100
H	-1.93341800	-1.53912100	-1.72727200
H	-2.25354100	-2.96470500	-0.72988700

H	-1.10553800	-3.08882800	-2.09874800
H	1.58026500	0.35484700	2.35050600
H	0.88596300	1.27899000	1.02335900
H	3.61472400	-0.16230500	0.96495200
H	3.37976900	1.55082600	1.25245500
H	2.37211100	1.80503400	-1.03361900
H	2.63193500	0.09786400	-1.34263200
H	4.46133200	1.44492000	-2.36328100
H	5.12178500	0.41742100	-1.08757000
H	4.86244500	2.14000300	-0.79113700
H	0.00036900	4.68554000	0.93385500
H	-0.42693300	4.08698900	0.80664800
B	-2.47579700	1.10577600	0.00633100
F	-3.59301400	1.89640200	0.12683600
F	-2.58640000	-0.09823300	0.74931500
F	-1.29655700	1.78735600	0.45099800
F	-2.23972200	0.73479700	-1.36309600

4. [(C₈H₁₇)(C₄H₉)₃P]Br with H₂

P	-1.51354500	0.52283000	0.92858100
C	-1.44998600	-0.60455600	2.37755900
C	-1.02178600	-2.05752700	2.11184700
C	-1.22330200	-2.93877100	3.35095000
C	-0.75069800	-4.37765600	3.12381800
C	-1.52640800	2.20591200	1.67315400
C	-1.62645700	3.39881400	0.71021600
C	-1.52675000	4.74270200	1.44549200
C	-1.62162900	5.94397700	0.50105500
C	-3.06226300	0.21338500	0.00915400
C	-3.13452100	0.77091700	-1.42196700
C	-4.47334500	0.41532600	-2.08155300
C	-4.56748800	0.92100300	-3.52311600
C	-0.06080400	0.33104800	-0.15209900
C	1.30596500	0.49495100	0.52966300
C	2.45310300	0.28749600	-0.46992500

C	3.84036000	0.41804500	0.16786300
C	4.98659500	0.23096300	-0.83305400
C	6.37781100	0.35458600	-0.20209100
C	7.52405200	0.17391000	-1.20408400
C	8.91068700	0.30068200	-0.56668000
H	-2.46046200	-0.57550000	2.80331600
H	-0.79009100	-0.13323700	3.11431500
H	0.03245100	-2.07648800	1.81873100
H	-1.56411500	-2.47183400	1.25676400
H	-2.28705800	-2.94212600	3.61952700
H	-0.69131700	-2.50623200	4.20872000
H	-0.93255500	-4.99629900	4.00677300
H	0.32112700	-4.41127900	2.90697500
H	-1.27078400	-4.83155800	2.27646600
H	-0.60939300	2.27881800	2.26782100
H	-2.35851700	2.21992500	2.38599100
H	-2.57362700	3.35809000	0.16424200
H	-0.83178800	3.34203000	-0.04148700
H	-0.57991700	4.78304000	1.99695800
H	-2.32228800	4.80235700	2.19756700
H	-1.54760300	6.88491500	1.05176700
H	-2.57268100	5.94977800	-0.03981700
H	-0.81752800	5.92929100	-0.24078300
H	-3.87746400	0.59286000	0.63742800
H	-3.13163400	-0.87971600	-0.05399000
H	-2.33199500	0.31362200	-2.00691200
H	-2.99477900	1.85747500	-1.43595900
H	-5.29927900	0.82894400	-1.48855400
H	-4.58190900	-0.67362700	-2.06832900
H	-5.52763800	0.65269500	-3.97150600
H	-3.77910800	0.48199100	-4.14064700
H	-4.46955700	2.01081100	-3.57453900
H	-0.17993400	1.05875900	-0.96129400
H	-0.18866400	-0.66251600	-0.61280400

H	1.40872100	-0.23034600	1.34387200
H	1.40033300	1.49006800	0.98184200
H	2.35585600	1.01648900	-1.28412100
H	2.34839700	-0.70071700	-0.93057000
H	3.93993200	-0.32092700	0.97324100
H	3.93355600	1.40345000	0.64377700
H	4.88719900	0.97063700	-1.63785600
H	4.89060200	-0.75186000	-1.31078400
H	6.47991200	-0.38832300	0.59971500
H	6.47256800	1.33666800	0.28012700
H	7.42143700	0.91512500	-2.00600600
H	7.43092700	-0.80748600	-1.68436000
H	9.70452000	0.16568400	-1.30651400
H	9.05626700	-0.45010100	0.21649100
H	9.04757300	1.28575400	-0.10902700
Br	-1.62506600	-2.62958700	-1.52165000
H	1.11501200	-3.99474800	-2.31868200
H	1.78695200	-4.28251600	-2.47606600

5. [EMIM]AlCl$_4$ with H$_2$

C	3.15732800	1.68738000	-0.50216100
C	3.48804600	0.43051300	-0.90331300
N	2.61748100	-0.43961400	-0.27500000
C	1.78201600	0.27400100	0.48553300
N	2.09461100	1.56737800	0.37162000
C	1.34484000	2.67937100	0.97122300
C	2.60349400	-1.91256400	-0.41130700
C	3.52521800	-2.59874800	0.59204500
H	3.57193200	2.64366200	-0.76979700
H	4.25075400	0.08629100	-1.57988300
H	0.96716200	-0.11402700	1.07924000
H	0.61014700	2.27207800	1.66222900
H	0.82055500	3.21888300	0.18327500
H	2.03842400	3.33537800	1.49701000
H	2.89707800	-2.12910500	-1.43937000

H	1.56587700	-2.22743600	-0.29491900
H	3.47791500	-3.67912500	0.43938900
H	3.21493100	-2.39163800	1.61858400
H	4.56448100	-2.28320100	0.47079800
H	-1.36899700	4.35712400	-1.45260000
H	-1.22224000	5.08694600	-1.41566000
Al	-1.97789300	-0.24702300	-0.04692600
Cl	-1.40261500	0.34024100	1.98870500
Cl	-0.96130100	1.14928100	-1.38592200
Cl	-4.08807100	-0.23937300	-0.31356600
Cl	-1.08129000	-2.20418500	-0.37490600

Table S2. DFT simulation coordinates of optimized structures in Figure 8 using Gaussian 09 software package [1].

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian software, version 09 revision D01. Gaussian Inc.: Wallingford, CT, USA 2009.