Supporting Information

The influence of formation temperature on the morphology of MoS_2 and its catalytic properties in hydrogenation of isomeric bromoquinolines to bromo-1,2,3,4-tetrahydroquinolines

Anastasia V. Terebilenko[a,b], Maryna V. Olenchuk[c], Denys O. Mazur[a], Andrii S. Nikolenko[c,d], Vadym I. Popenko[d], Galyna I. Dovbeshko[c], Oleksii Bezkrovnyi[e], Tomash Sabov[d], Boris M. Romanyuk[d], Volodymir N. Poroshin[c], Serhiy V. Ryabukhin[b,f,g], Dmytro M. Volochnyuk[b,f,g], Sergey V. Kolotilov *[a]

[a] *L.V. Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, 31, pr. Nauky, 03028 Kyiv, Ukraine. E-mail: s.v.kolotilov@gmail.com.*
[b] *Enamine Ltd., 78 Winston Churchill St., 02094 Kyiv, Ukraine.*
[c] *Institute of Physics, National Academy of Sciences of Ukraine, 46, pr. Nauky, 03028 Kyiv, Ukraine.*
[d] *V.E.Lashkarev Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41, pr. Nauky, 03028 Kyiv, Ukraine.*
[e] *Institute of Low Temperature and Structure Research PAS, Okólna 2, 50-422 Wrocław, Poland*
[f] *Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Akademika Kukharya Street 5,02660 Kyiv, Ukraine.*
[g] *Institute of High Technologies, Taras Shevchenko National University of Kyiv, Volodymyrska Street 60, 01601 Kyiv, Ukraine.*

Contents

Fig. S8. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of quinoline at different pressures in the presence MoS140 (10 mol. % of MoS_2, 100 °C, 24 h).

Fig. S9. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of quinoline the presence MoS140 (10 mol. % of MoS_2, 100 °C, 100 atm, 24 h) in water or toluene.

Fig. S10. ^{1}H NMR spectra of the concentrated reaction mixture after hydrogenation of quinoline the presence MoS140 recycled after one run (10 mol. % of MoS_2, 100 °C, 100 atm, 24 h).

Fig. S11. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 5-bromoquinoline in presence of MoS130, MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).

Fig. S12. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 6-bromoquinoline in presence of MoS130, MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).

Fig. S13. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 7-bromoquinoline in presence of MoS130, MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).

Fig. S14. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 8-bromoquinoline in presence of MoS130, MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).

Fig. S15. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 5-chloroquinoline in presence MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).

Fig. S16. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 6-chloroquinoline in presence MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).

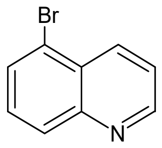
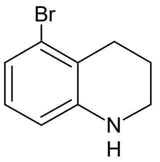
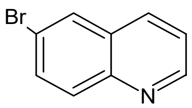
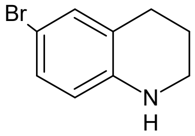
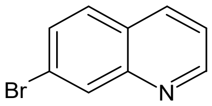
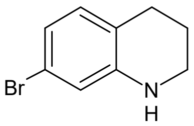
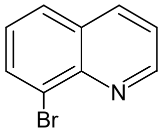
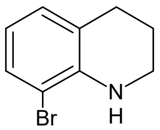
Fig. S17. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 7-chloroquinoline in presence MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).

Fig. S18. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 8-chloroquinoline in presence MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).

Table S1. Yields of MoS_2 samples for different entries (theoretically expected weight was 1000 mg in each case).

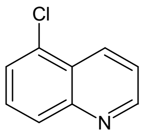
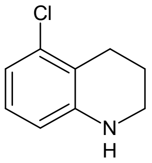
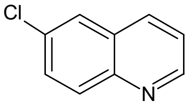
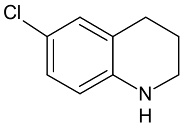
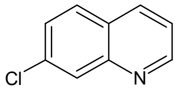
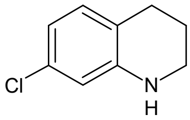
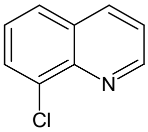
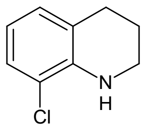
Sample No.	Temperature of synthesis, °C	Yield, g	Yield, %
MoS120	120	0.371	37
MoS130	130	0.498	50
MoS135	135	0.525	53
MoS140	140	0.566	57
MoS145	145	0.607	60
MoS150	150	0.639	64
MoS160	160	0.670	67
MoS180	180	0.750	75

Table S2. The products of bromoquinolines hydrogenation in the presence of MoS130, MoS135 and MoS140.

Substrate	Product	Catalyst	Yield, %	Conversion, %	Selectivity, %	Reaction by-products a)
		**MoS130**	99	100	99	1 % – N-Methyl-5-Bromo-THQ
		MoS135	60	64	96	3 % – 5- Bromo-N- Methyl-THQ 1% – THQ
		MoS140	62	66	96	4 % – N-Methyl-5-Bromo-THQ
		**MoS130**	23	99	24	15 % – N-Methyl -6-Bromo-THQ 44 % – THQ 7 % – N-Met-THQ
		MoS135	25	50	50	12 % – 6-Bromo-N- Methyl-THQ 11% – THQ 2 % – Quinoline
		MoS140	17	28	89	9 % – 6-Bromo-N-Methyl-THQ 2 % – Quinoline
		**MoS130**	97	97	100	–
		MoS135	86	86	100	–
		MoS140	26	34	92	8 % – N-Methyl-7-Bromo-THQ –
		**MoS130**	94	97	97	1 % – THQ 2 % – N-Methyl-8-Bromo-THQ
		MoS135	76	100	84	16 % – 8-Bromo-N-Methyl-THQ
		MoS140	28	29	99	1 % – N- Methyl-8-Bromo-THQ

[a] THQ = 1,2,3,4-tetrahydroquinoline

Table S3. The products of chloroquinolines hydrogenation in the presence of MoS135 and MoS140

Substrate	Product	Catalyst	Yield, %	Conversion, %	Selectivity, %	Reaction by-products
		**MoS135**	77	23	100	–
		MoS140	71	71	100	–
		**MoS135**	58	58	100	–
		MoS140	69	69	100	–
		**MoS135**	72	72	100	–
		MoS140	51	51	100	–
		**MoS135**	90	90	100	–
		MoS140	64	64	100	–

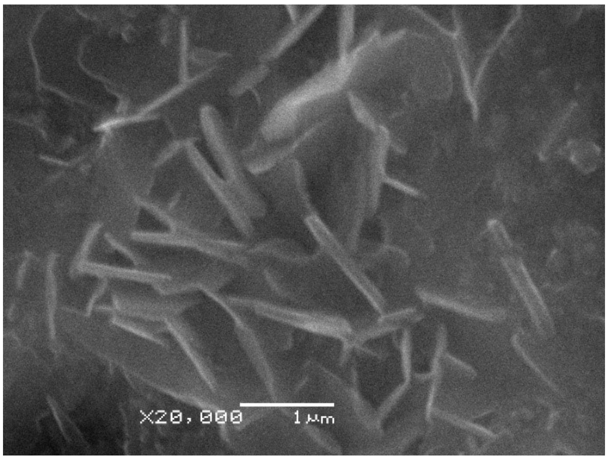


Fig. S1. SEM image of particles, suspended in the reaction mixture in the synthesis of MoS120.

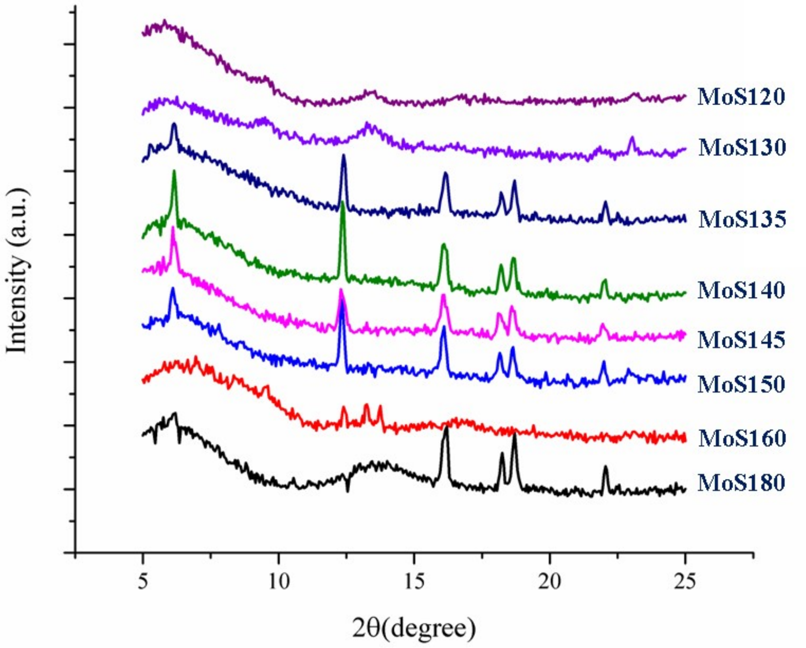


Fig. S2. XRD patterns of MoS120-MoS180 samples aged for 8 months.

The reflexes from the crystallographic planes in the stored specimens' XRD patterns had sharpened, however the positions did not correspond to those in the diffractograms of the fresh samples. The apparent phase changes observed in the XRD patterns may well be due to the oxidation of molybdenum disulphide. However, their position does not correspond to the most expected phases for these systems: MoO_2, MoO_3, and Mo_2O_5 [1]. In addition, variations were noted in a series of powder XRD patterns of aged MoS120-MoS180 samples. Presumably, mixtures of oxides and intercalation products formed upon the aging process.

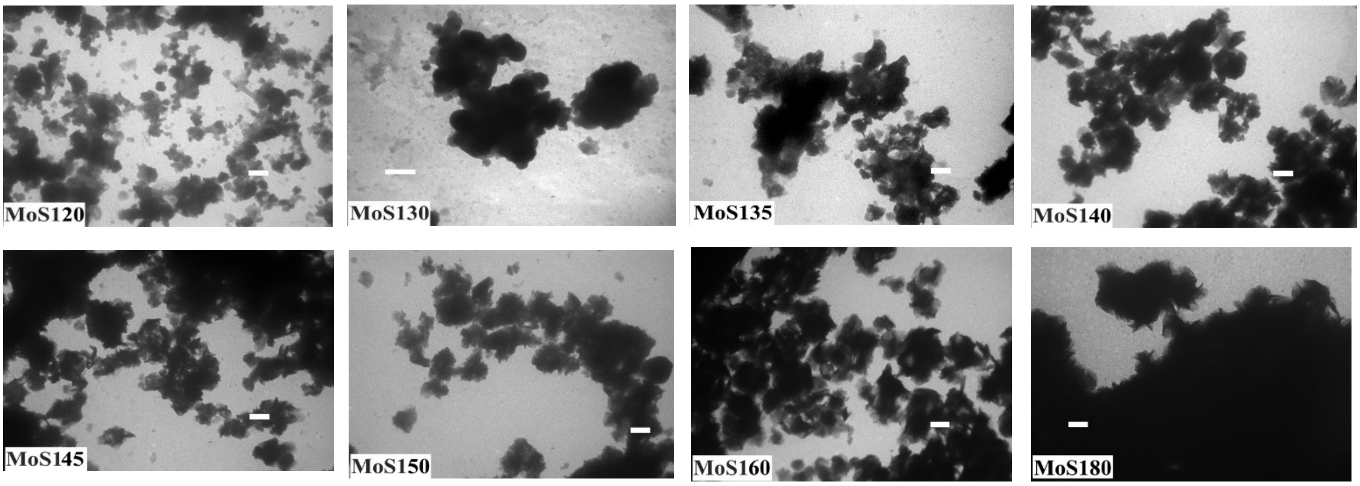


Fig. S3. TEM images of the MoS120 – MoS180 samples, the scale bar is 200 nm.

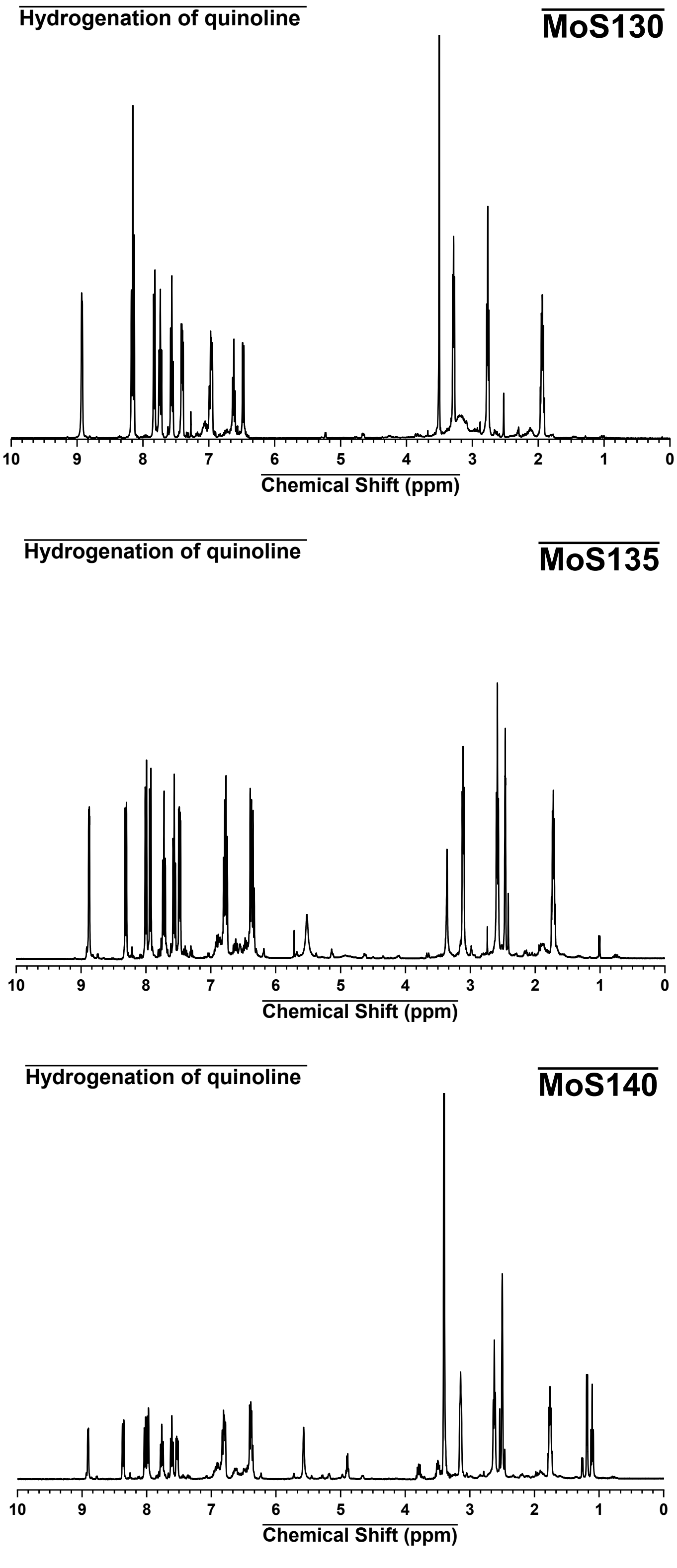


Fig. S4. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of quinoline in the presence MoS130, MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS$_2$, 24 h).

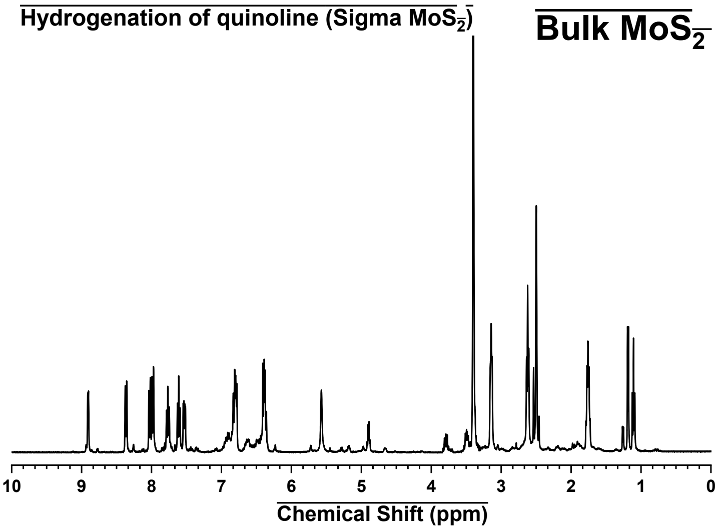


Fig. S5. ^{1}H NMR spectra of the concentrated reaction mixture after hydrogenation of quinoline the presence bulk MoS_2 (10 mol. % of MoS_2, 100 °C, 100 atm, 24 h).

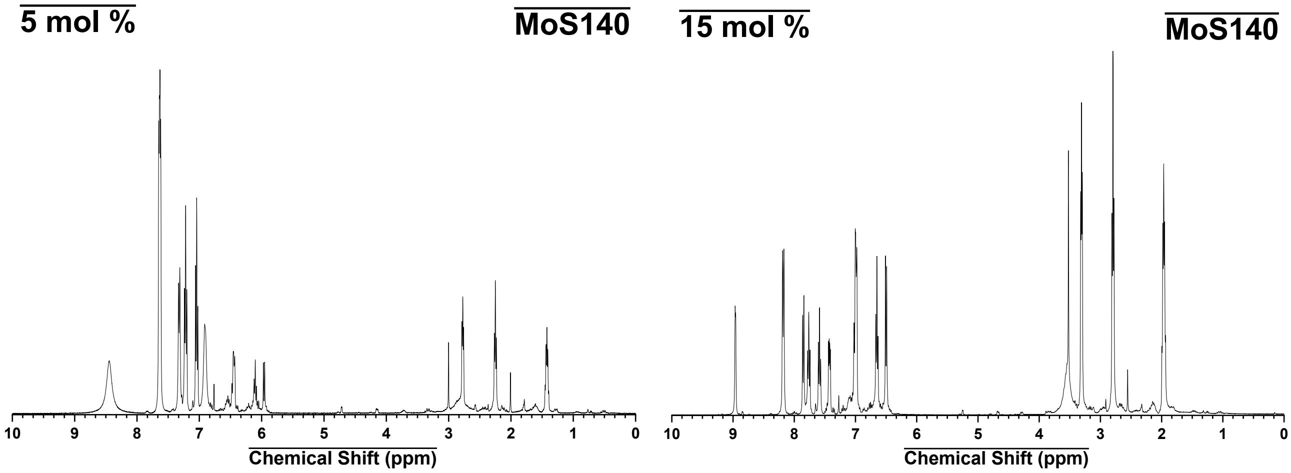


Fig. S6. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of quinoline in the presence MoS140 (100 °C, 100 atm, 24 h) at different catalyst loading. Catalyst loading is shown as the spectrum legend.

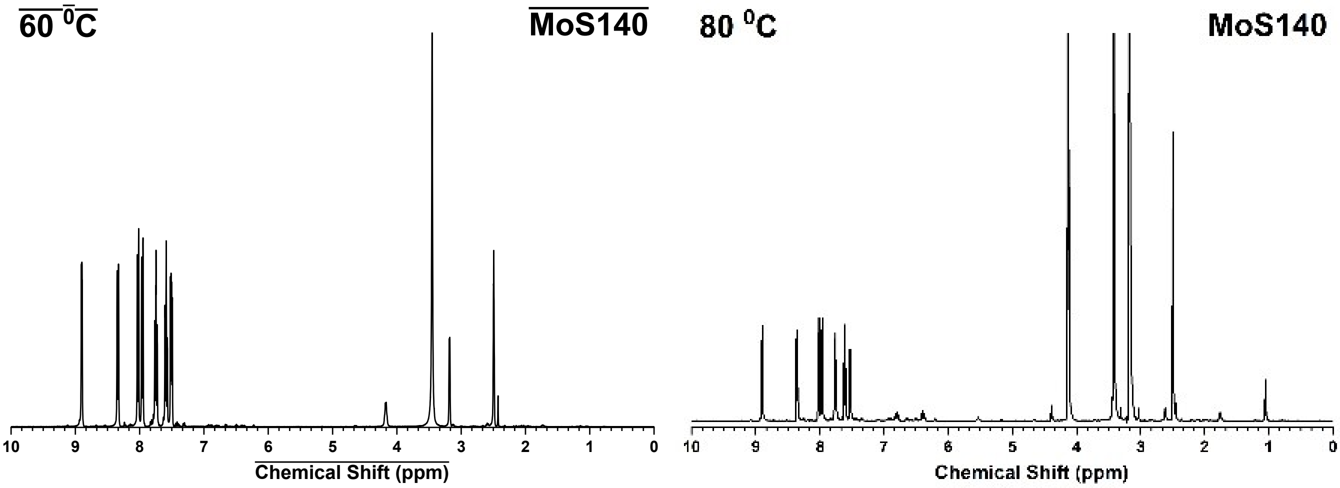


Fig. S7. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of quinoline at different temperatures in the presence MoS140 (10 mol. % of MoS_2, 100 atm, 24 h). Temperature is shown as the spectrum legend.

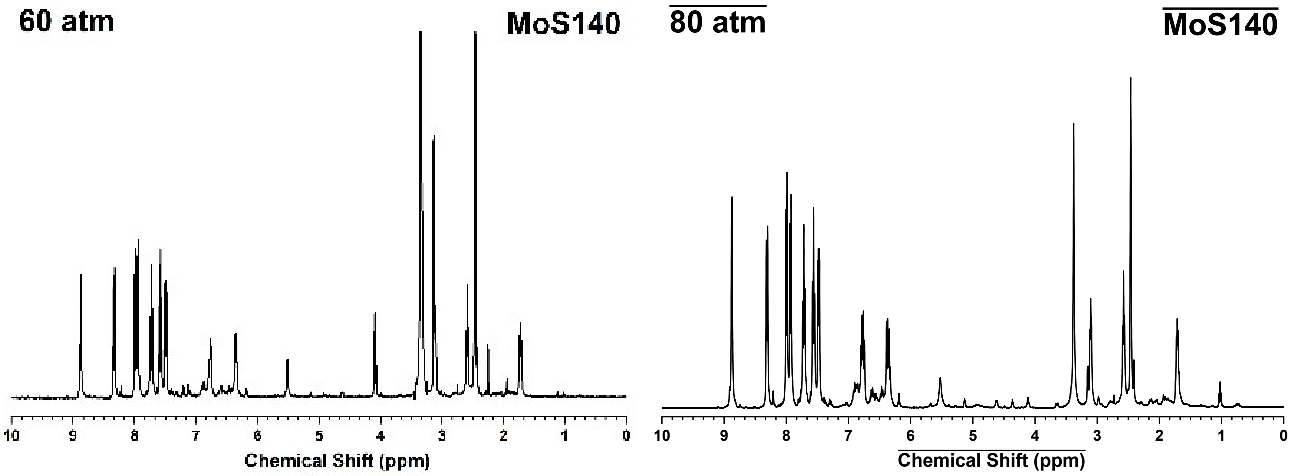


Fig. S8. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of quinoline at different pressures in the presence MoS140 (10 mol. % of MoS_2, 100 °C, 24 h). Hydrogen pressure is shown as the spectrum legend.

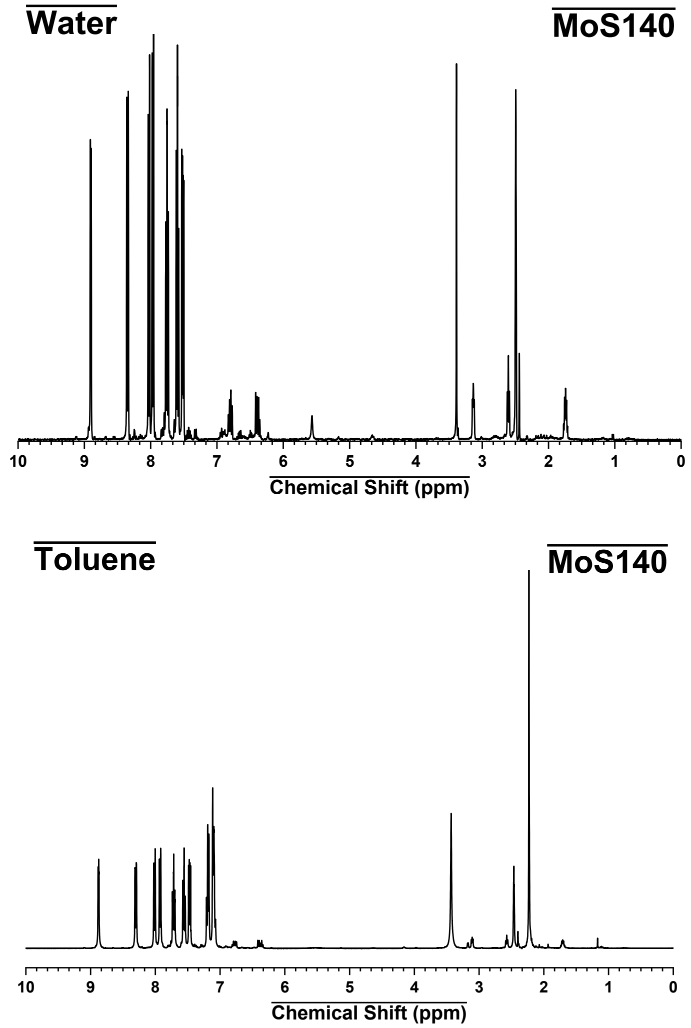


Fig. S9. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of quinoline the presence MoS140 (10 mol. % of MoS_2, 100 °C, 100 atm, 24 h) in water or toluene.

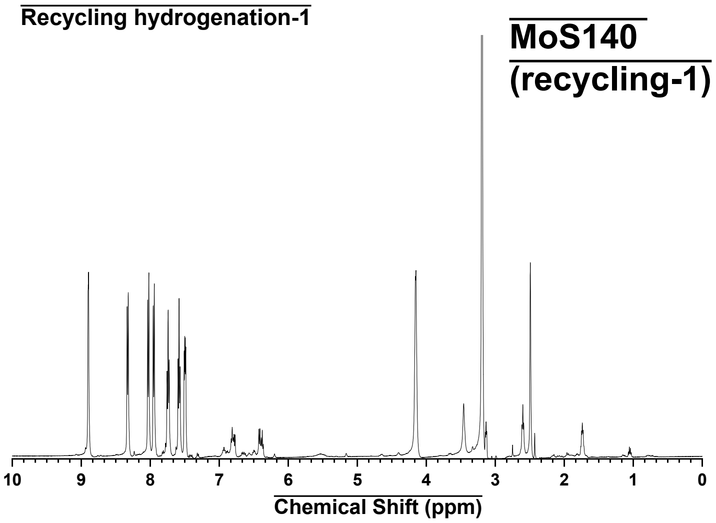


Fig. S10. ^{1}H NMR spectra of the concentrated reaction mixture after hydrogenation of quinoline the presence MoS140 recycled after one run (10 mol. % of MoS_2, 100 °C, 100 atm, 24 h).

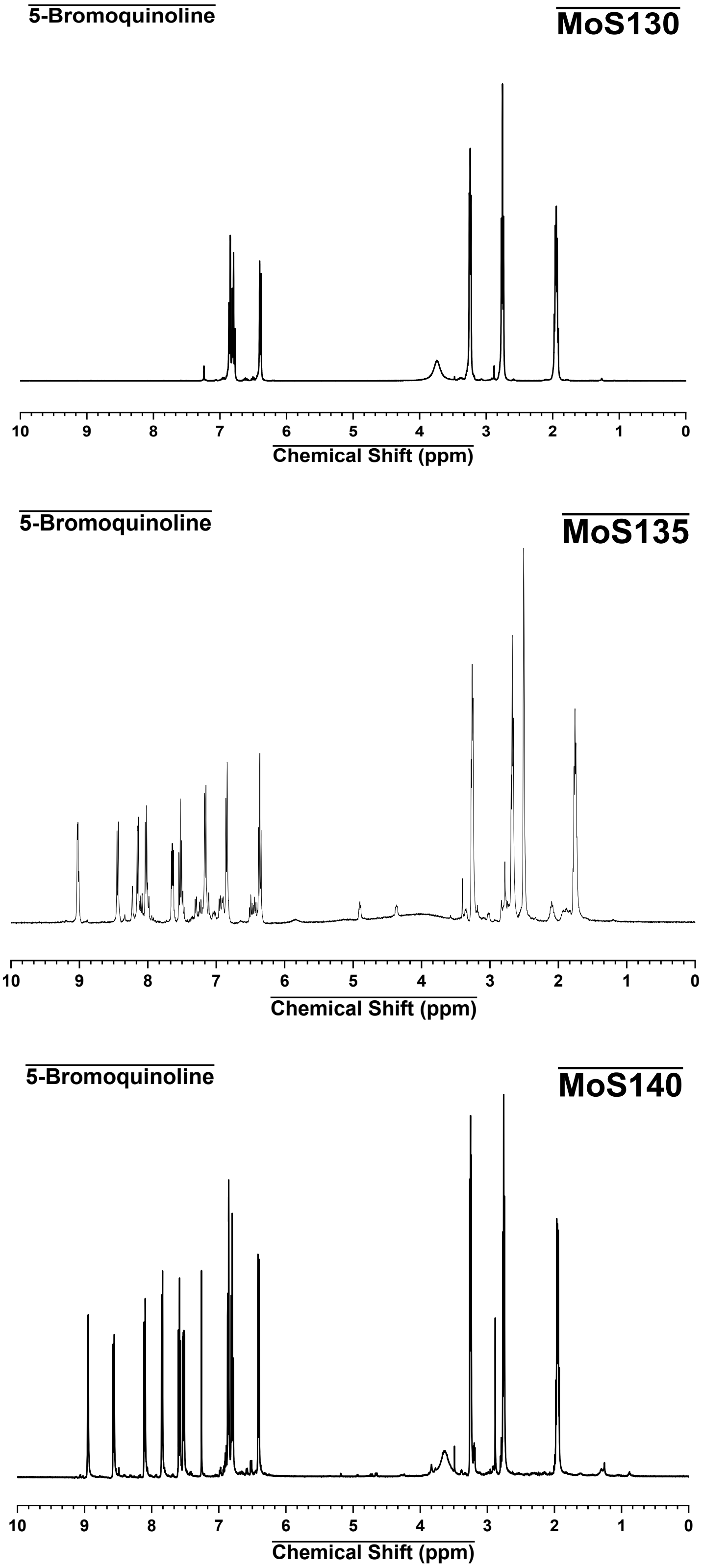


Fig. S11. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 5-bromoquinoline in presence of MoS130, MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).

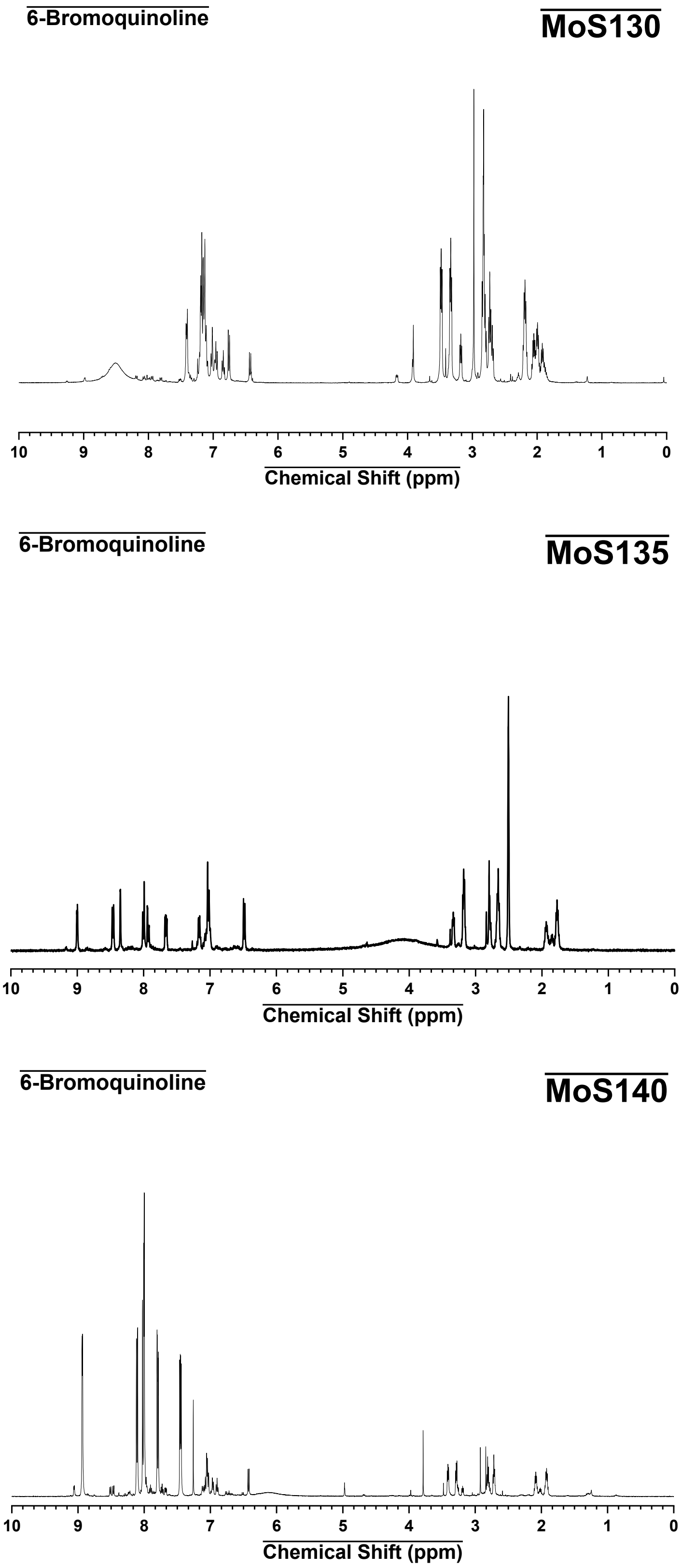


Fig. S12. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 6-bromoquinoline in presence of MoS130, MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).

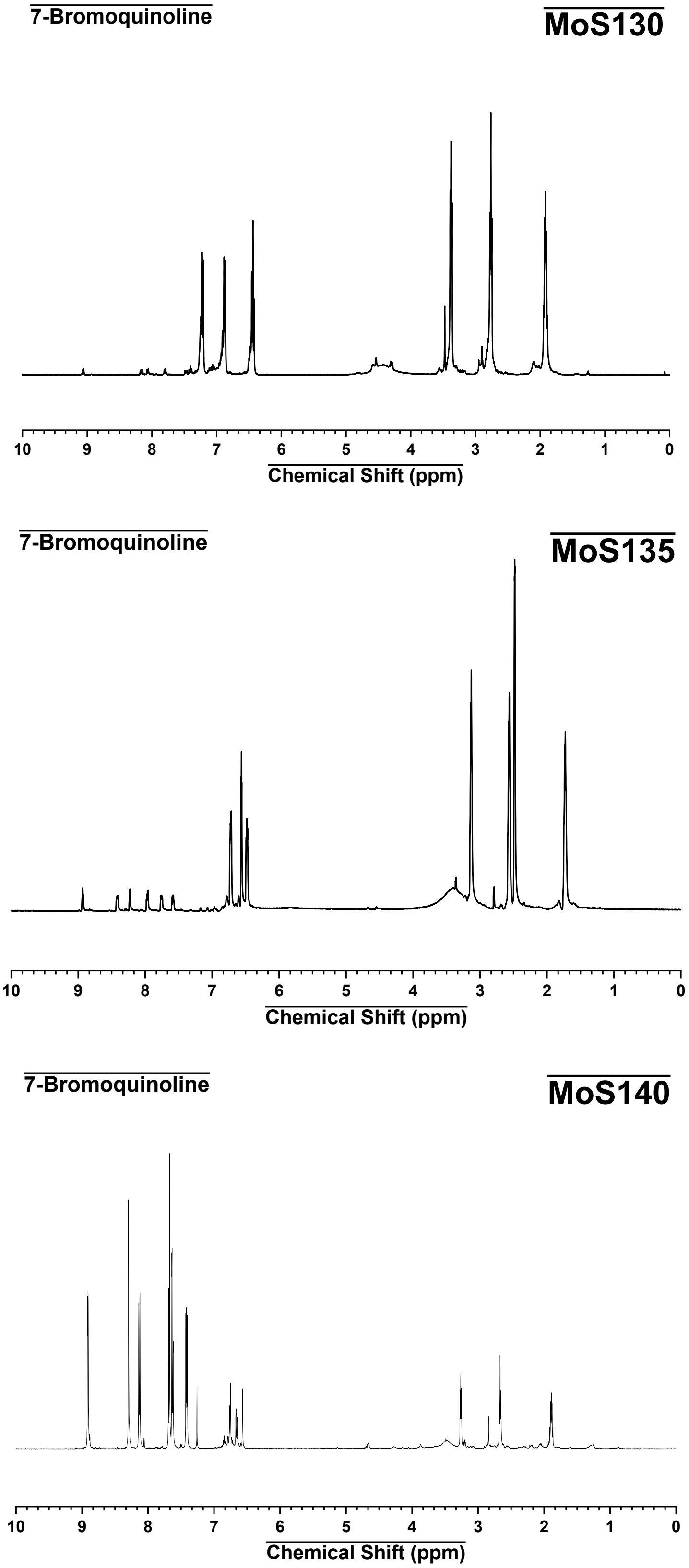


Fig. S13. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 7-bromoquinoline in presence of MoS130, MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).

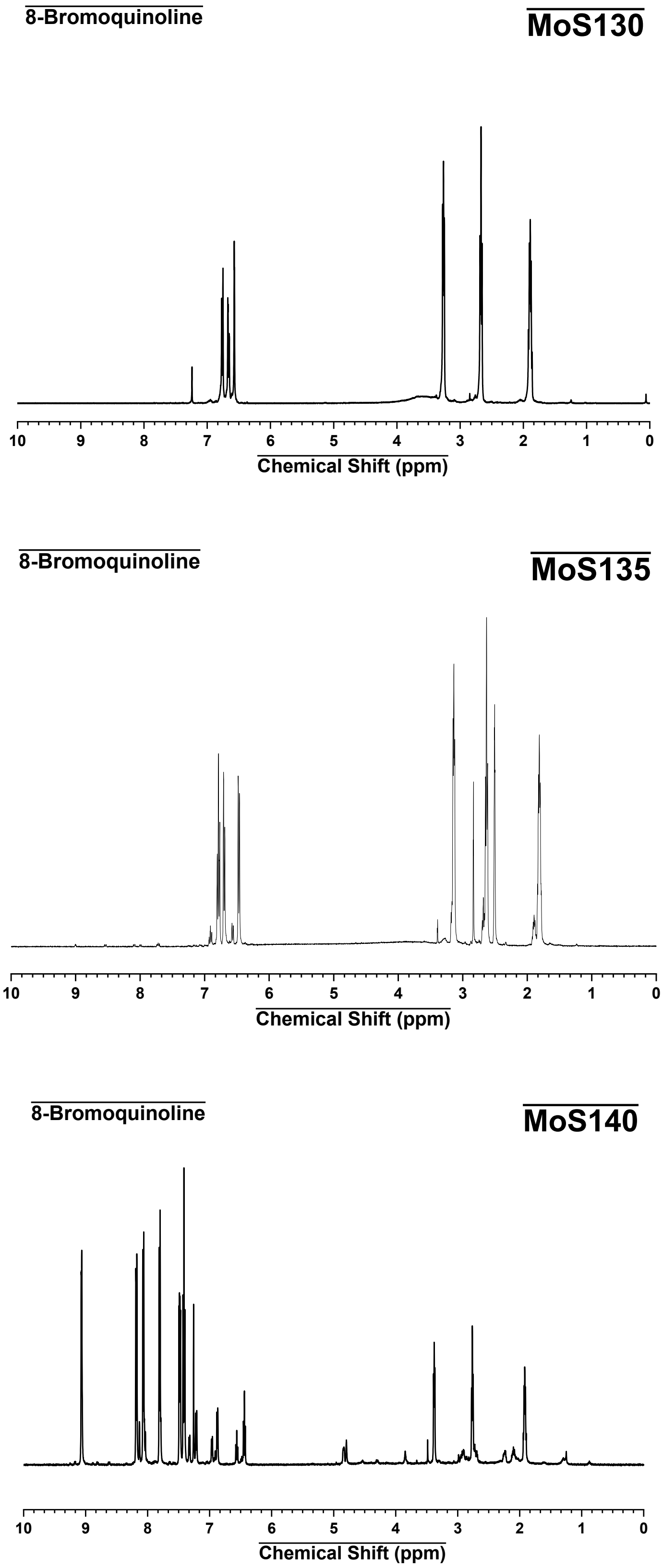
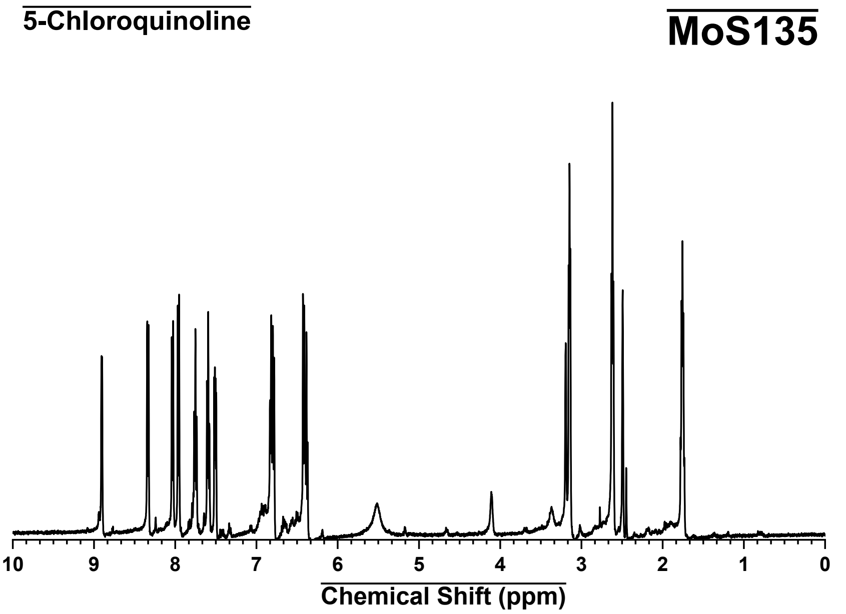


Fig. S14. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 8-bromoquinoline in presence of MoS130, MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).



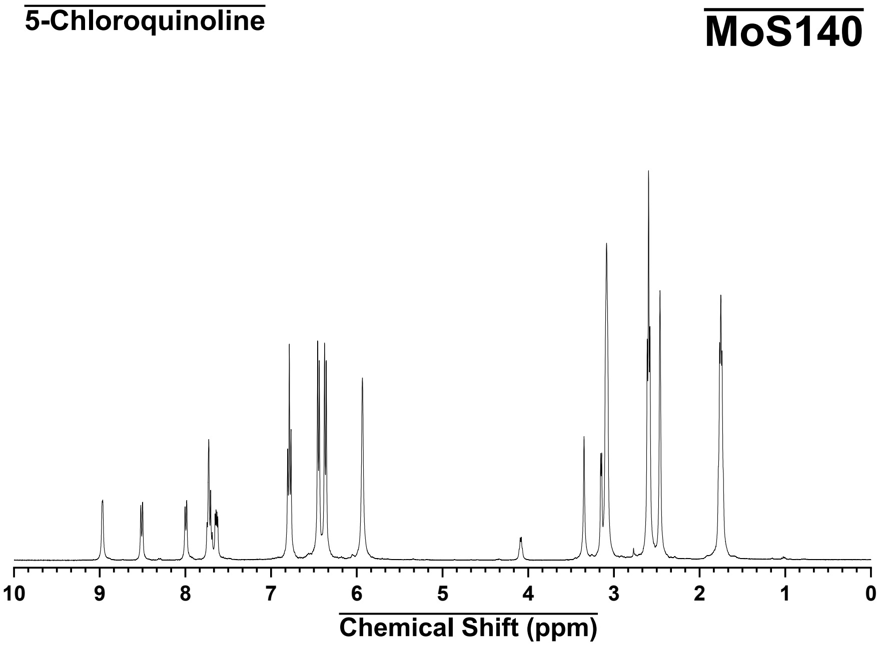
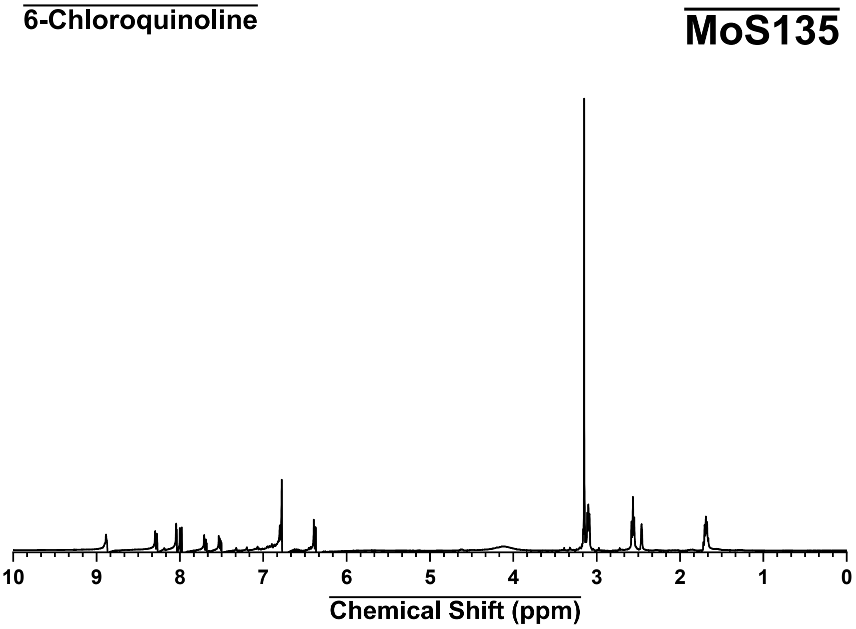


Fig. S15. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 5-chloroquinoline in presence MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).



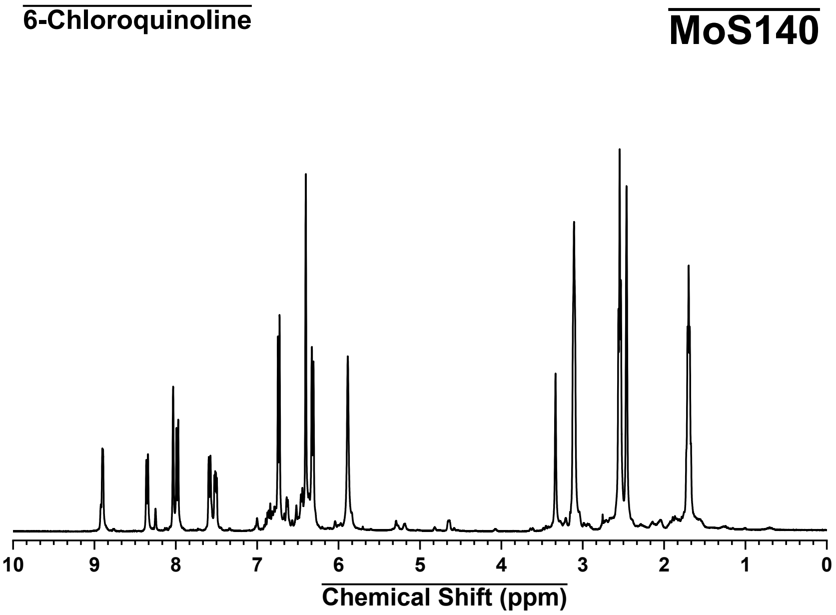
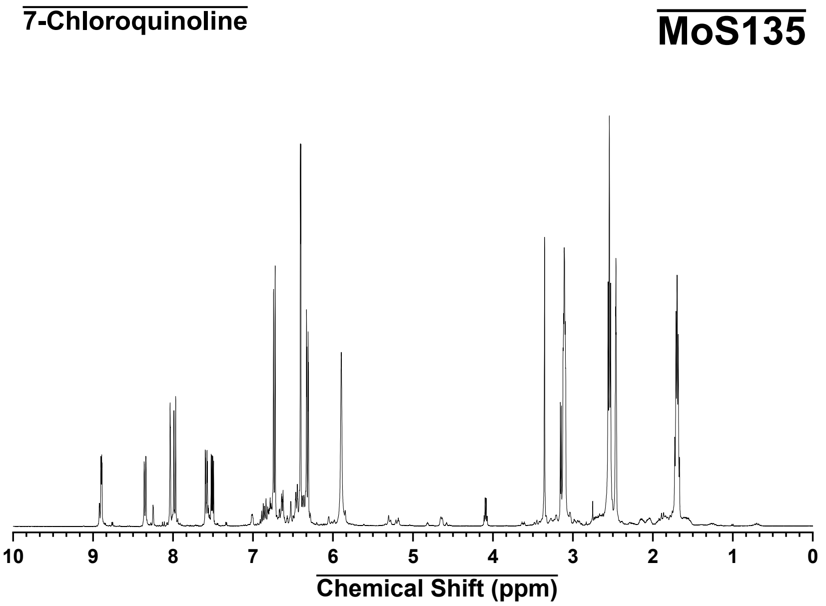


Fig. S16. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 6-chloroquinoline in presence MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).



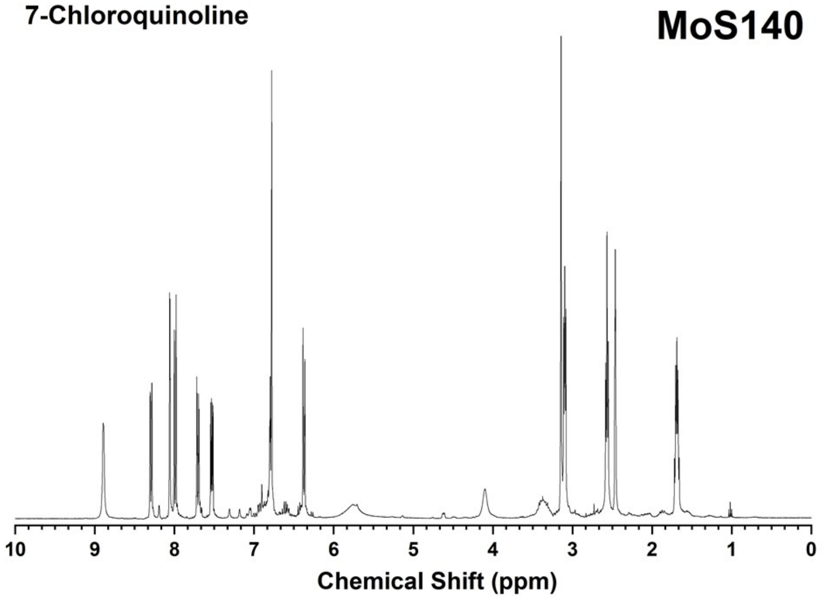
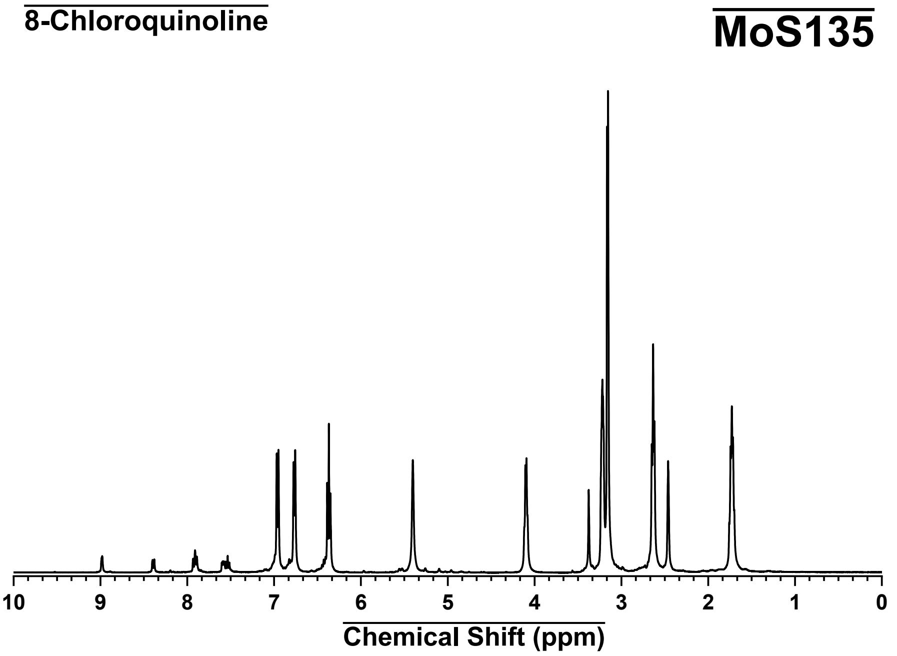


Fig. S17. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 7-chloroquinoline in presence MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).



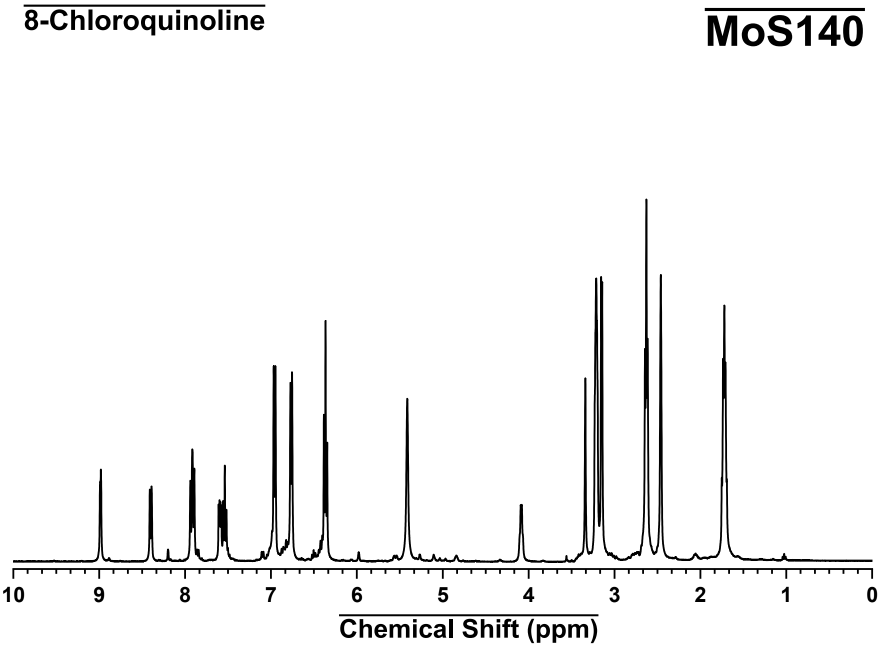


Fig. S18. ^{1}H NMR spectra of the concentrated reaction mixtures after hydrogenation of 8-chloroquinoline in presence MoS135, MoS140 (100 °C, 100 atm, 10 mol. % of MoS_2 48 h).

References for Supporting Information

1. J. Gao, B. Li, J. Tan, P. Chow, T.-M. Lu, N. Koratkar, Aging of Transition Metal Dichalcogenide Monolayers, *ACS Nano*, 2016, **10**, 2628–2635. https://doi.org/10.1021/acsnano.5b07677.