

Supporting Information for

Mechanism of Ni-catalyzed Oxidations of Unactivated C(sp³)-H Bonds

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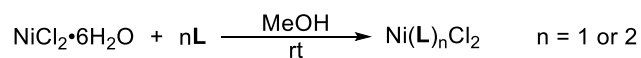
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1. General Procedures

Unless otherwise specified, all reactions were performed in oven-dried glassware under air. Reagents and solvents were used as received from commercial sources without further purification. Reaction temperatures refer to the temperatures of aluminum heating blocks or silicone oil baths. ^1H and ^2H NMR spectra were obtained on Bruker AV and NEO spectrometers operating at 300, 500, 600, or 700 MHz. Chemical shifts (δ) were reported relative to the residual solvent signal (δ 7.26 for CDCl_3 , δ 1.94 for CD_3CN). Infrared (IR) spectra were obtained on a Bruker Vertex 80 spectrometer and were reported in frequency of absorption (cm^{-1}). Electrospray ionization high-resolution mass spectra (ESI HRMS) were obtained on a PerkinElmer AxION 2 TOF mass spectrometer. Low-temperature X-band EPR spectra were recorded using a Varian E109 EPR spectrometer equipped with a Model 102 Microwave bridge. Sample temperature was maintained at 8K using an Air Products LTR liquid helium cryostat. The following spectrometer conditions were used: microwave frequency, 9.22 GHz; field modulation amplitude, 32 G at 100 kHz; microwave power, 2 mW. X-ray diffraction data were obtained at the Small Molecule X-ray Crystallography Facility (CheXray) at the University of California, Berkeley. Elemental analyses were performed by the Microanalytical Facility at University of California, Berkeley.

2. Synthesis and Characterization of Ni Complexes **1a-1h**



Complexes **1c-1e** were synthesized according to reported literature.¹⁻²

2.1 Synthesis of $\text{Ni}(\text{Me}_4\text{Phen})_2\text{Cl}_2$ (**1a**)

To a round bottom flask equipped with a stir bar was charged $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (118.8 mg, 0.5000 mmol), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4Phen , **L1**, 236.3 mg, 1.000 mmol), and methanol (10.0 mL). The resulting dark red solution was stirred at room temperature for 3 h. Acetonitrile (5.0 mL) was added, and the solvent was evaporated *in vacuo*. The remaining solid was washed twice with acetonitrile and

subsequently dried under high vacuum overnight. Product **1a** was collected as a blue-green powder (150.9 mg, 50.11% yield). Vapor diffusion of diethyl ether into a saturated solution of **1a** in methanol/acetonitrile afforded crystals suitable for X-ray analysis.

IR (neat, cm^{-1}): 3296, 1617, 1525, 1428, 1385, 1245, 1180, 1015, 946, 915, 888, 864, 824, 730, 620, 572, 554, 525, 467. ESI HRMS (m/z , amu): $[\text{Ni}(\text{Me}_4\text{Phen})_2]^{2+}$: calculated 265.0985, found 265.0933; $[\text{Ni}(\text{Me}_4\text{Phen})_2\text{Cl}]^+$: calculated 565.1663, found 565.1589.

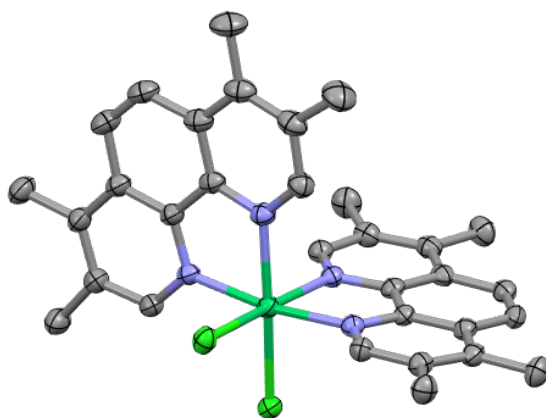


Figure S1. X-ray crystal structure of complex **1a**. Hydrogen atoms are omitted for clarity.

2.2 Synthesis of $\text{Ni}(\text{bpy})_2\text{Cl}_2$ (**1b**)

To a round-bottom flask equipped with a stir bar was charged $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (47.5 mg, 0.200 mmol), 2,2'-bipyridine (bpy, **L2**, 62.5 mg, 0.400 mmol), and methanol (2.0 mL). The reaction mixture was stirred at room temperature for 100 min. During the course of the reaction, the solution turned from pink to dark blue. Acetonitrile (3.0 mL) was added, and the solvent was evaporated *in vacuo*. The remaining solid was washed twice with acetonitrile and subsequently dried under high vacuum overnight. Product **1b** was collected as a blue-green powder.

IR (neat, cm^{-1}): 3429, 3026, 1599, 1565, 1493, 1473, 1440, 1314, 1249, 1172, 1153, 1104, 1057, 1041, 1020, 917, 770, 736, 652, 631, 530, 439, 420. ESI HRMS (m/z , amu): $[\text{Ni}(\text{bpy})_2]^{2+}$: calculated 185.0359,

found 185.0264; $[\text{Ni}(\text{bpy})_2\text{Cl}]^+$: calculated 405.0411, found 405.0228. Elemental analysis (%): calculated for $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{N}_4\text{NiO}_2$ (**1b**·2MeOH): C 52.22, H 4.78, N, 11.07; found: C 52.41, H 4.60, N 11.39.

2.3 Synthesis of $\text{Ni}(\text{Brbpy})_2\text{Cl}_2$ (**1f**)

To a round-bottom flask equipped with a stir bar was charged $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (23.8 mg, 0.100 mmol), 6-bromo-2,2'-bipyridine (Brbpy, **L6**, 47.0 mg, 0.200 mmol), and methanol (2.0 mL). The blue-green solution was stirred at room temperature for 80 min. The solvent was then evaporated *in vacuo*. The remaining solid was washed twice with acetonitrile and subsequently dried under high vacuum. Product **1f** was collected as a green powder (44 mg, 73% yield). Vapor diffusion of diethyl ether into a saturated solution of **1f** in methanol/acetonitrile afforded crystals suitable for X-ray analysis.

IR (neat, cm^{-1}): 3063, 1653, 1602, 1587, 1571, 1554, 1484, 1451, 1427, 1393, 1293, 1262, 1230, 1186, 1161, 1131, 1115, 1102, 1077, 1021, 995, 917, 817, 788, 770, 731, 685, 645, 634, 600. ESI HRMS (m/z , amu): $[\text{Ni}(\text{Brbpy})_2\text{Cl}]^+$: calculated 562.8601, found 562.8567. Elemental analysis (%): calculated for $\text{C}_{20}\text{H}_{14}\text{Br}_2\text{Cl}_2\text{N}_4\text{Ni}$: C 40.05, H 2.35, N 9.34; found: C 39.83, H 2.06, N 9.03.

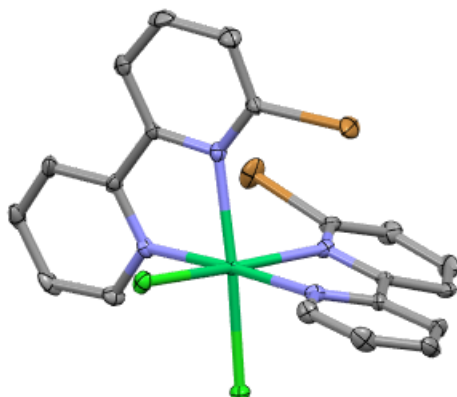


Figure S2. X-ray crystal structure of complex **1f**. Hydrogen atoms are omitted for clarity.

2.4 Synthesis of $\text{Ni}(\text{bpyPY2Me})\text{Cl}_2$ (**1g**)

The ligand bpyPY2Me (**L7**) was synthesized based on reported literature.³

To a round-bottom flask equipped with a stir bar was charged $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (118.8 mg, 0.5000 mmol), ligand **L7** (169.2 mg, 0.5000 mmol), and a mixture of acetonitrile and methanol (10.0 mL). The clear brown solution was stirred at room temperature for 1 h. The solution was then concentrated *in vacuo* until precipitate formed. The precipitate was collected by filtration, washed with acetonitrile, and subsequently dried under high vacuum. Product **1g** was obtained as a gray-green powder (84 mg, 36% yield). Vapor diffusion of diethyl ether into a saturated solution of **1g** in methanol/acetonitrile afforded crystals suitable for X-ray analysis.

IR (neat, cm^{-1}): 3066, 1593, 1566, 1471, 1452, 1408, 1389, 1329, 1303, 1287, 1257, 1160, 1117, 1104, 1076, 1051, 1024, 1014, 972, 905, 885, 870, 853, 811, 804, 780, 765, 756, 748, 707, 662, 639, 591, 570, 509, 494, 475, 436, 415. ESI HRMS (m/z , amu): $[\text{Ni}(\text{L7})\text{Cl}]^+$: calculated 431.0568, found 431.7147. Elemental analysis (%): calculated for $\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{N}_4\text{NiO}_2$ (**1g**·2MeOH): C 54.18, H 4.93, N 10.53; found: C 53.84, H 4.85, N 10.36.

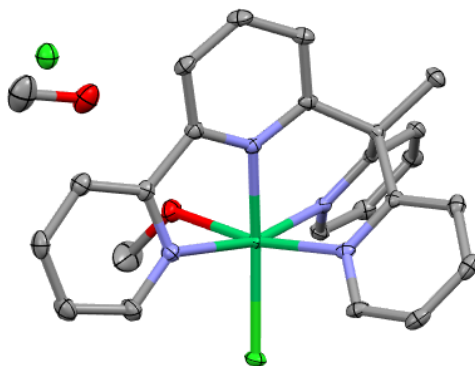


Figure S3. X-ray crystal structure of complex **1g**·2MeOH. Hydrogen atoms are omitted for clarity.

2.5 Synthesis of $\text{Ni}(\text{Me}_2\text{Phen})_2(\text{OAc})(\text{BPh}_4)$ (**1h**)

To a round bottom flask equipped with a stir bar was added $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (29.9 mg, 0.120 mmol) and methanol (3 mL). Then 2,9-dimethyl-1,10-phenanthroline (Me_2Phen , **L8**, 50.0 mg, 0.240 mmol), dissolved in 2 mL methanol, was added slowly and the reaction mixture was stirred at room temperature for 2 h. NaBPh_4 (41.1 mg, 0.120 mmol) was then added in one portion and the reaction mixture was stirred at room

temperature overnight. The resulting light blue precipitate was collected by filtration, washed with water, methanol and hexanes, then redissolved in DCM and filtered with a syringe filter. The filtrate was concentrated to ~ 2 mL and added dropwise to a 100 mL mixture of diethyl ether and hexanes (1:1 v/v). The resulting precipitate was collected by filtration and dried under high vacuum overnight. Product **1h** was obtained as a pale blue powder (47.5 mg, 46% yield). Vapor diffusion of diethyl ether into a concentrated solution of complex **1h** in DCM afforded crystals suitable for X-ray analysis.

IR (neat, cm^{-1}): 3054, 1594, 1543, 1499, 1453, 1425, 1380, 1293, 1154, 1032, 939, 855, 814, 775, 732, 704, 679, 656, 624, 612, 551, 468, 437, 408. ESI HRMS (m/z , amu): $[\text{Ni}(\text{L8})_2(\text{OAc})]^+$: calculated 533.1482, found 533.1277. Elemental analysis (%): calculated for $\text{C}_{55}\text{H}_{51}\text{BN}_4\text{NiO}_3$ (**1h**·MeOH): C 74.60, H 5.81, N 6.33; found: C 74.44, H 5.84, N 6.26.

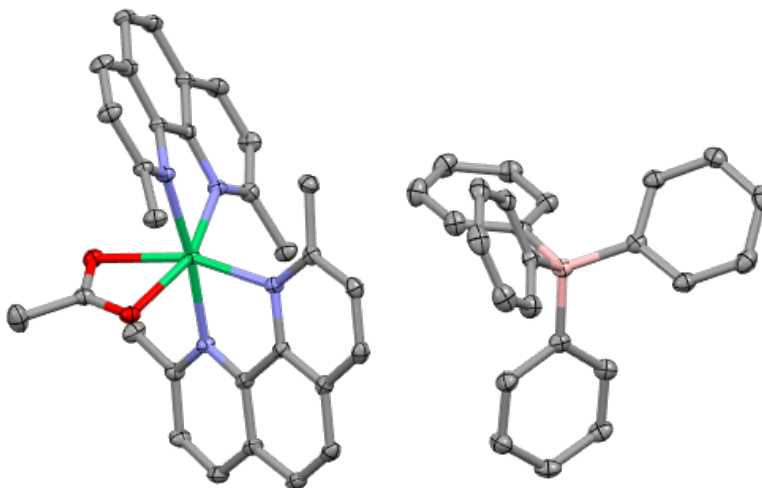


Figure S4. X-ray crystal structure of complex **1h**. Hydrogen atoms and DCM molecules are omitted for clarity.

3. Ni-catalyzed Oxidation of Cyclohexane (**2**)

3.1. General procedure for Ni-catalyzed oxidation of **2** by *m*CPBA

To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane **2** (7.50 equiv), and a mixture of dichloromethane and acetonitrile (3:1 v/v, 1.0 mL) as solvent. Ni complexes **1a-1h** were added as stock solutions or suspensions in DCM. NiCl₂ and CoCl₂ were added as stock solutions in a mixture of methanol-*d*₄ and acetonitrile (1:9 v/v). Methanol-*d*₄ was used to avoid overlapping of peaks with product **4a** in the ¹H NMR spectra. The vial was sealed, and the reaction mixture was stirred at 50 °C. The reaction was monitored by ¹H NMR spectroscopy until greater than 90% conversion of *m*CPBA was achieved. After cooling to room temperature, dibromomethane (4.4 μL, 0.50 equiv) was added as an internal standard. An aliquot (~ 30 μL) of the mixture was taken, diluted with chloroform-*d*₁, and subjected to analysis by ¹H NMR spectroscopy.

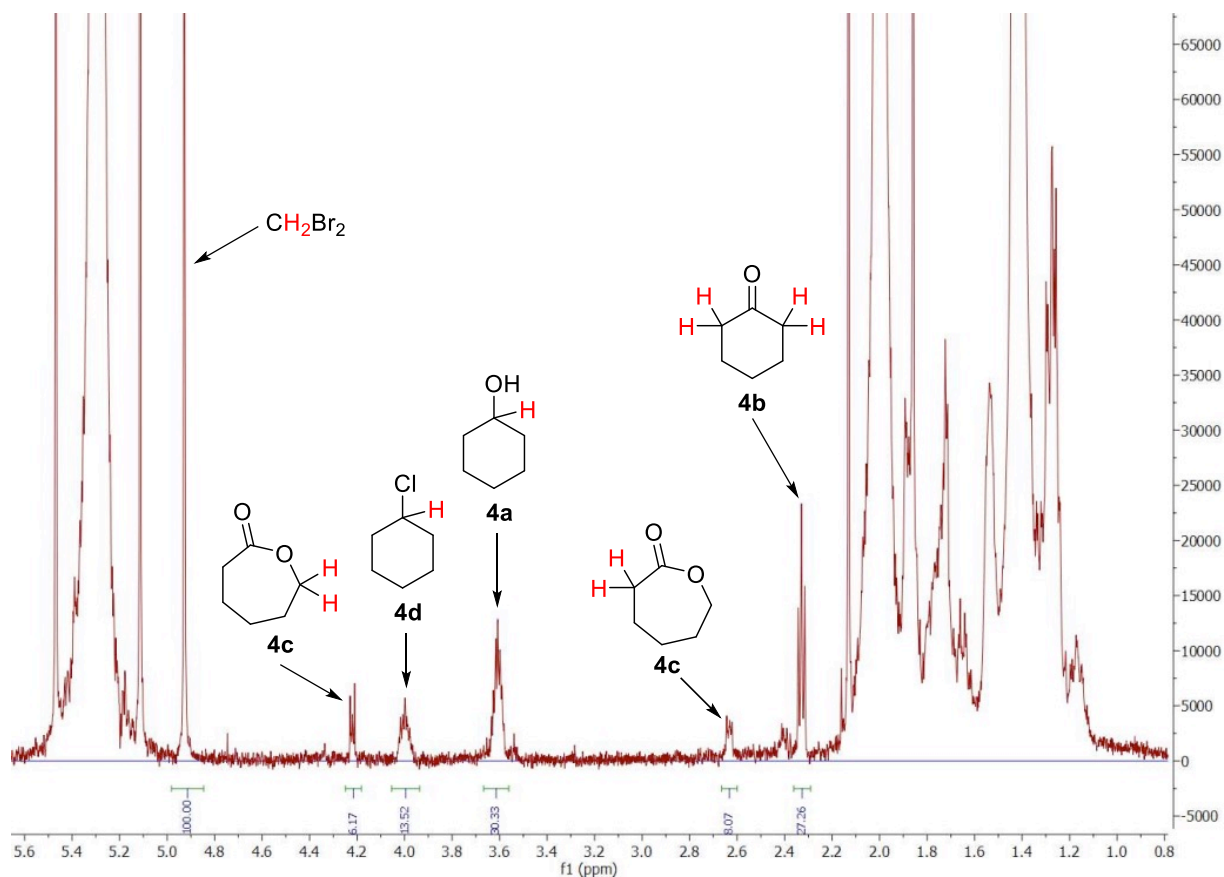
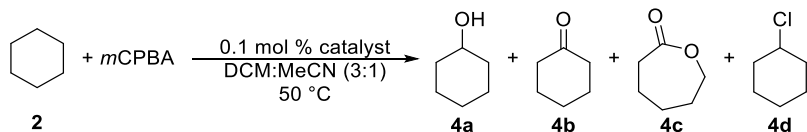


Figure S5. A typical ¹H NMR spectrum of the reaction mixture from the Ni-catalyzed oxidation of **2**.

3.2. Results of transition metal catalyzed oxidation of **2**

Table S1. Results of oxidation of cyclohexane in the presence of different catalysts



Entry	Catalyst	Time (h)	4a (%)	4b (%)	4c (%)	4d (%)	Conversion of <i>m</i> CPBA (%)
1	Ni(Me ₄ Phen) ₂ Cl ₂ (1a)	1	27.6	10.7	0	14.3	100
2			34.1	10.7	0	15.0	100
3			39.6	11.3	0	9.2	100
4	Ni(bpy) ₂ Cl ₂ (1b)	1	36.0	9.4	2.0	13.8	100
5			37.3	10.0	1.4	12.2	100
6			40.9	11.4	0	8.2	100
7	Ni(box) ₃ (BPh ₄) ₂ (1c)	1	37.9	9.9	1.1	15.0	100
8			38.0	10.2	0	13.1	100
9			41.5	11.1	2.0	9.2	100
10	Ni(tBubpy) ₃ (BPh ₄) ₂ (1d)	1.5	30.1	6.0	3.4	7.8	96
11			33.1	6.8	3.1	9.2	96
12			30.1	6.0	3.4	7.8	96
13	Ni(TPA)(H ₂ O)(OAc)(BPh ₄) (1e)	1.5	33.6	9.6	1.5	16.5	100
14			30.3	6.8	3.6	13.5	100
15			34.8	8.6	1.2	8.9	100
16	Ni(Brbpy) ₂ Cl ₂ (1f)	2	32.5	6.0	4.1	11.2	100
17			36.1	4.8	5.5	8.6	90
18			35.1	4.8	4.7	8.6	85
19	Ni(bpyPY2Me)Cl ₂ (1g)	3	32.0	5.7	5.0	10.4	96
20			33.1	3.1	6.3	10.2	94
21			36.1	5.4	4.9	11.2	96
22	Ni(Me ₂ Phen) ₂ (OAc)(BPh ₄) (1h)	4	8.7	2.7	5.0	5.7	31
23			8.6	2.0	4.9	4.8	36
24			12.6	2.3	5.5	7.0	45
25	NiCl ₂	4	31.8	6.6	6.5	10.5	100
26			30.2	8.5	3.5	8.9	100
27			30.0	9.8	3.2	9.7	100
28	CoCl ₂	1.5	21.7	11.0	0	9.6	100
29			30.6	10.2	0	8.0	100
30			21.9	10.9	0	9.7	100
31	none	4	0	0	0	0	0
32			0	0	0	0	0
33			3.8	2.6	1.9	0	< 10

3.3. Time courses of Ni-catalyzed oxidation of **2**

To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane **2** (7.50 equiv), dibromomethane (4.4 μ L, 0.50 equiv) as the internal standard and chloroform-*d*₁ (3:1 v/v, 1.0 mL) as solvent. Ni complexes **1a** and **1h** were added as stock solutions or suspensions in CDCl₃. The vial was capped, and the reaction mixture was stirred at 50 °C. Aliquots (~ 15 μ L) were periodically taken from the reaction mixture, diluted with chloroform-*d*₁, and subjected to analysis by ¹H NMR spectroscopy.

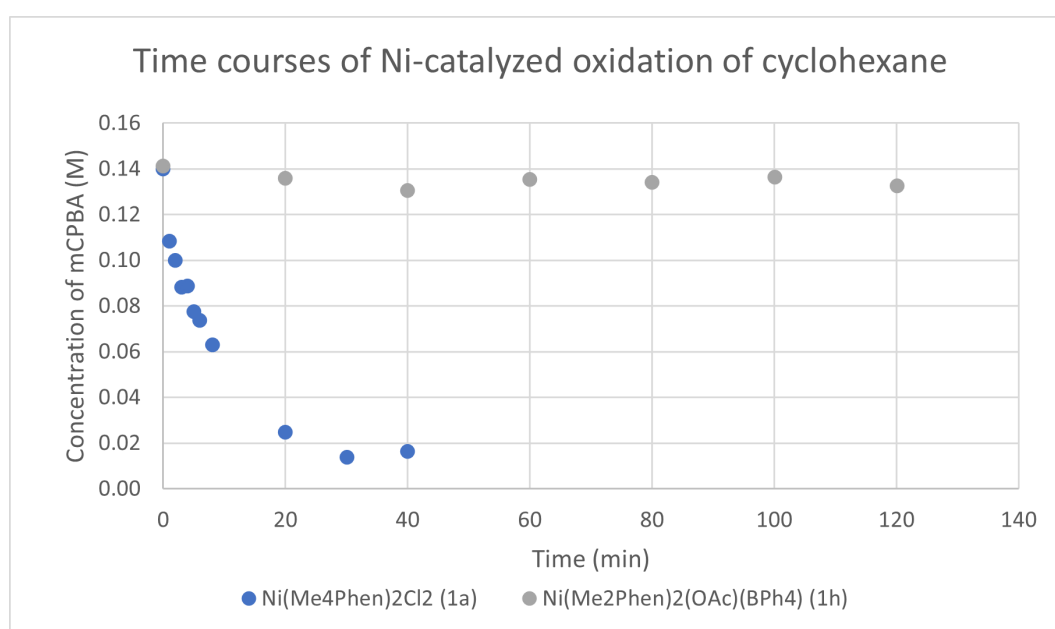


Figure S6. Time courses of the oxidation of cyclohexane catalyzed by Ni complexes **1a** and **1h**.

4. Ni-catalyzed Oxidation of Adamantane (**3**)

4.1. General procedure for Ni-catalyzed oxidation of **3** by *m*CPBA

To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane **3** (34.1 mg, 2.00 equiv), and a mixture of dichloromethane and acetonitrile (3:1 v/v, 1.0 mL) as solvent. Ni complexes **1a-1h** were added as stock solutions or suspensions in DCM. NiCl₂ and CoCl₂ were added as stock solutions in a mixture of methanol and acetonitrile (1:9 v/v). The vial was sealed, and the reaction

mixture was stirred at 50 °C for 1-4 h. After cooling to room temperature, n-dodecane (28.0 μL, 0.123 mmol) was added as an internal standard. An aliquot (~ 60 μL) of the mixture was taken, diluted with ethyl acetate, and subjected to analysis by GC.

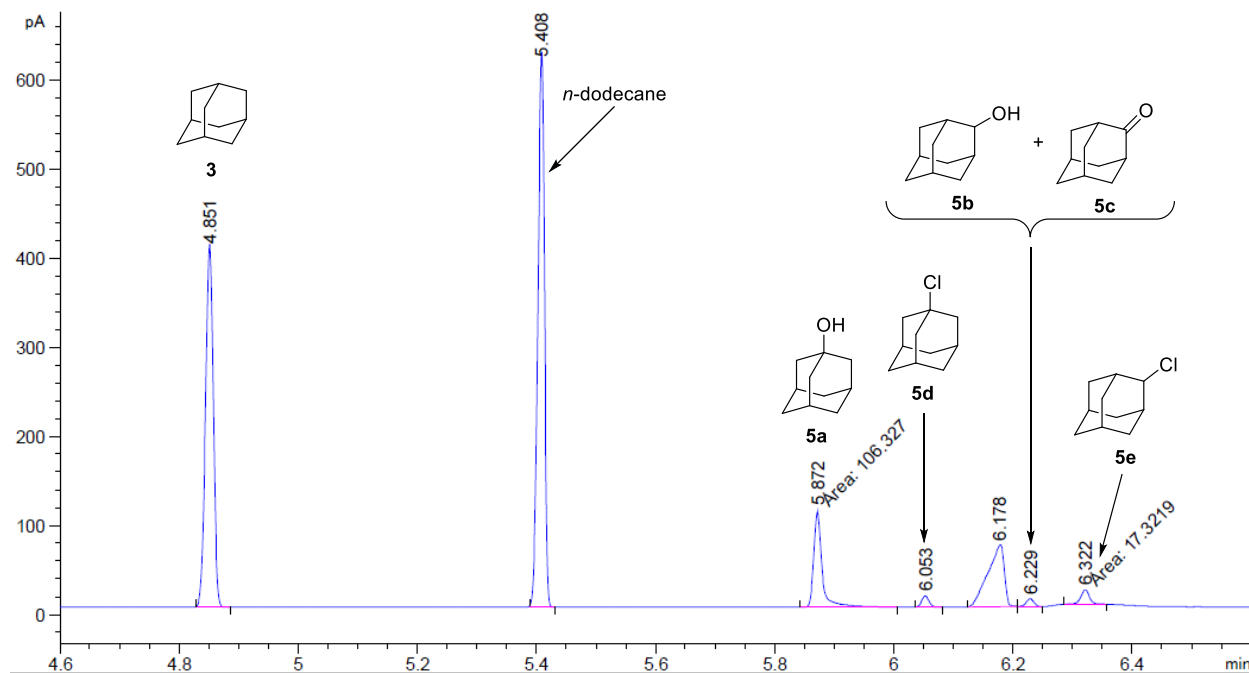


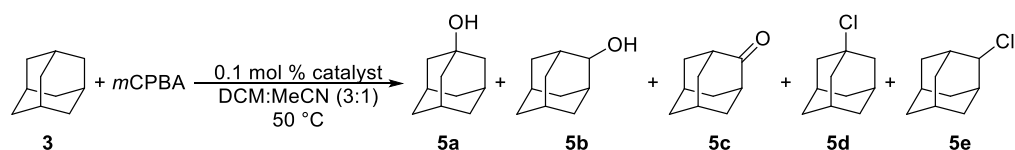
Figure S7. A typical GC trace of the reaction mixture from the Ni-catalyzed oxidation of **3**.

4.2. Results of transition metal catalyzed oxidation of **3**

$$\frac{A_{pdt}}{A_{I.S.}} = R_f \frac{m_{pdt}}{m_{I.S.}} \quad (\text{S1})$$

The response factor (R_f) for the products of oxidation with respect to the internal standard (n-dodecane) is defined in eq S1. A_{pdt} and $A_{I.S.}$ represent the area under the peak of the product and the internal standard in the GC trace, respectively. m_{pdt} and $m_{I.S.}$ represent the mass (measured in milligrams) of the product and the internal standard, respectively. The response factors for 1-adamantanol (**5a**), 2-adamantanol (**5b**), 2-adamantanone (**5c**), 1-chloroadamantane (**5d**) and 2-chloroadamantane (**5e**) were measured to be 0.9255 ($R^2 = 0.9907$), 0.9515 ($R^2 = 0.9942$), 0.8936 ($R^2 = 0.9961$), 0.8259 ($R^2 = 0.9962$) and 0.8425 ($R^2 = 0.9966$), respectively.

Table S2. Results of oxidation of adamantane in the presence of different catalysts



Entry	Catalyst	Time (h) ^a	5a (%)	5b+5c (%)	5d (%)	5e (%)
1	Ni(Me ₄ Phen) ₂ Cl ₂ (1a)	1	32.7	2.6	3.0	7.1
2			44.1	2.9	2.2	0
3			33.3	3.9	2.8	4.5
4	Ni(bpy) ₂ Cl ₂ (1b)	1	28.1	2.4	2.9	4.4
5			35.0	2.7	2.3	0
6			28.7	2.7	3.2	3.6
7	Ni(box) ₃ (BPh ₄) ₂ (1c)	1	27.3	2.1	2.5	4.1
8			37.2	2.7	2.2	0
9			27.2	2.4	2.5	3.1
10	Ni(tBubpy) ₃ (BPh ₄) ₂ (1d)	1.5	27.3	3.2	4.6	3.9
11			23.4	2.4	4.2	3.4
12			24.1	1.9	3.2	4.6
13	Ni(TPA)(H ₂ O)(OAc)(BPh ₄) (1e)	1.5	31.2	2.5	4.9	5.5
14			28.8	2.4	4.8	5.0
15			30.0	2.6	4.7	4.3
16	Ni(Brbpy) ₂ Cl ₂ (1f)	2	34.2	2.8	4.3	4.1
17			45.3	3.0	3.7	4.5
18			35.9	3.3	2.5	3.8
19	Ni(bpyPY2Me)Cl ₂ (1g)	3	29.2	3.1	5.2	5.1
20			30.1	2.5	5.8	5.6
21			27.8	2.1	4.6	4.2
22	Ni(Me ₂ Phen) ₂ (OAc)(BPh ₄) (1h)	4	22.8	1.6	4.4	2.9
23			20.6	1.3	3.9	2.6
24			18.7	1.3	3.6	2.3
25	NiCl ₂	4	27.6	2.5	4.1	3.6
26			26.7	2.3	4.5	3.5
27			30.2	2.5	4.6	3.5
28	CoCl ₂	1.5	27.6	2.9	2.3	3.2
29			27.4	2.8	2.3	3.2
30			28.7	2.8	1.4	0
31	none	4	5.9	0	0	0
32			14.6	1.9	1.2	0.6

33			6.0	0	0	0
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5. Ni-catalyzed Oxidation of Adamantane in the Presence of CCl₄

To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane **3** (34.1 mg, 2.00 equiv), CCl₄ (1.0 equiv, 12 μL) and a mixture of dichloromethane and acetonitrile (3:1 v/v, 1.0 mL) as solvent. Ni complex **1a** (0.1 mol %) was added as a suspension in DCM. The vial was sealed, and the reaction mixture was stirred at 50 °C for 1 h. After cooling to room temperature, *n*-dodecane (28.0 μL, 0.123 mmol) was added as an internal standard. An aliquot (~ 60 μL) of the mixture was taken, diluted with ethyl acetate, and subjected to analysis by GC.

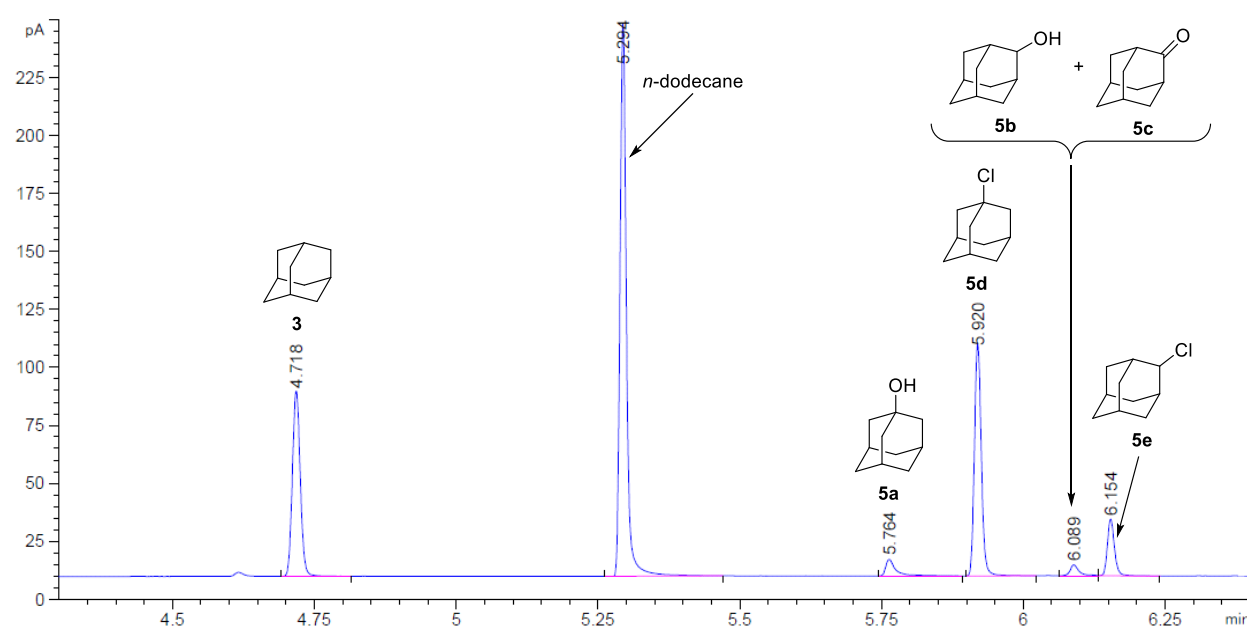


Figure S8. The GC trace of the reaction mixture from Ni-catalyzed oxidation of **3** in the presence of CCl₄.

6. Ni-catalyzed Oxidation of *cis*- and *trans*-1,2-Dimethylcyclohexane (*cis*- and *trans*-**6**)

6.1. General procedure for Ni-catalyzed oxidation of *cis*- or *trans*-**6** by *m*CPBA

To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane *cis*- or *trans*-**6** (7.50 equiv), and a mixture of dichloromethane and acetonitrile (3:1 v/v, 1.0 mL) as solvent.

Ni complexes **1a-1g** were added as stock solutions or suspensions in DCM. NiCl₂ was added as a stock solution in a mixture of methanol and acetonitrile (1:9 v/v). The vial was sealed, and the reaction mixture was stirred at 50 °C for 1-4 h. After cooling to room temperature, n-dodecane (28.0 μL, 0.123 mmol) was added as an internal standard. An aliquot (~ 60 μL) of the mixture was taken, diluted with ethyl acetate, and subjected to analysis by GC.

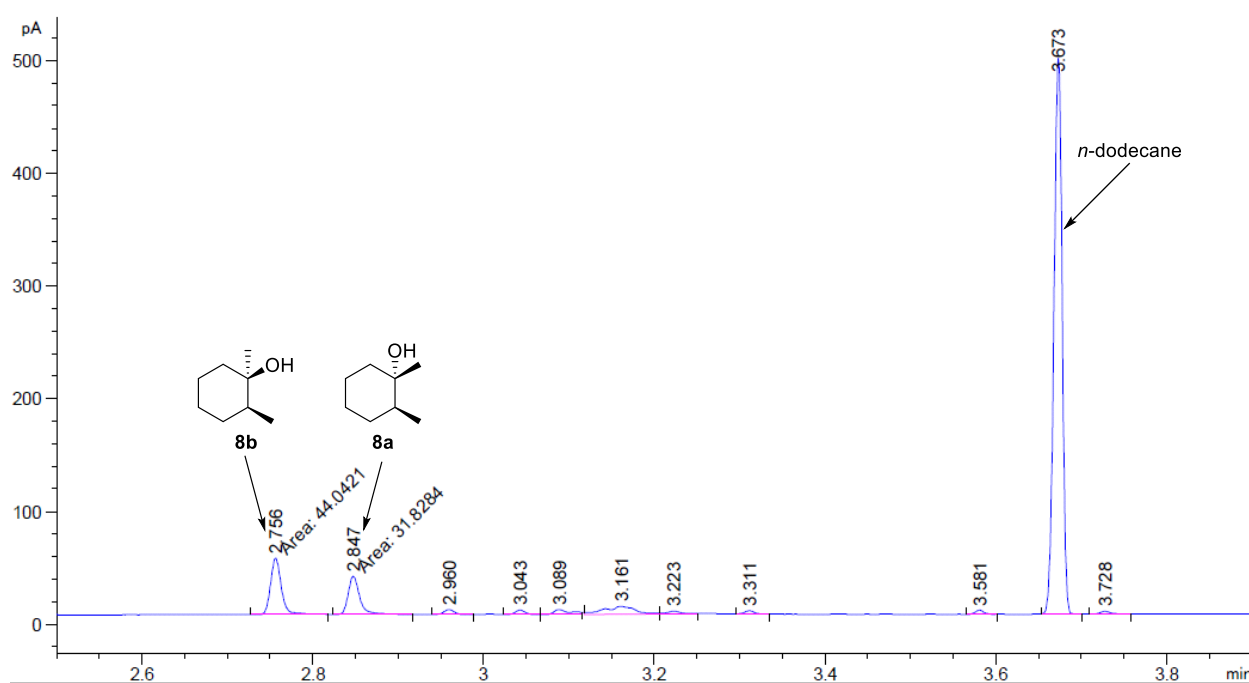
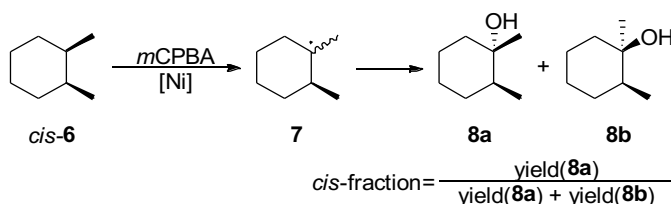


Figure S9. A typical GC trace of the reaction mixture from Ni-catalyzed oxidation of *cis*- or *trans*-**6**.

6.2. Results of Ni-catalyzed oxidation of *cis*-**6**

The GC response factor (R_f), defined in eq S1, of alcohol **8a** with respect to n-dodecane was determined to be 0.7457 ($R^2 = 0.9936$). The response factor of alcohol **8b**, which is a diastereomer of **8a**, was assumed to be identical to that of **8a**.

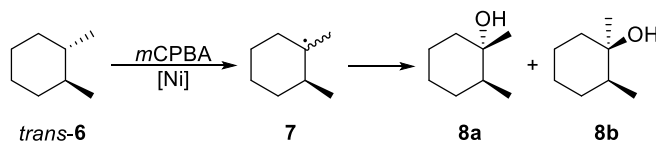
Table S3. Results of Ni-catalyzed oxidation of *cis*-6****



Entry	[Ni]	8a (%)	8b (%)	<i>cis</i> -fraction (%)
1	1a	28.0	37.4	42.7
2		23.4	30.9	43.1
3		17.3	23.9	42.0
4	1b	17.3	22.2	43.8
5		22.4	28.5	44.1
6		21.1	27.8	43.1
7	1c	18.2	23.9	43.3
8		15.7	20.8	43.0
9		19.5	25.8	43.0
10	1e	15.7	15.3	50.6
11		19.8	20.6	49.0
12		18.2	20.5	47.0
13	1f	26.0	28.6	47.6
14		26.4	27.8	48.7
15		19.1	24.1	44.2
16	1g	13.7	13.8	49.8
17		17.1	19.2	47.2
18		21.8	26.7	44.9
19	NiCl ₂	23.2	26.2	46.9
20		24.9	23.3	51.6
21		20.0	24.4	45.1

6.3. Results of Ni-catalyzed oxidation of *trans*-6

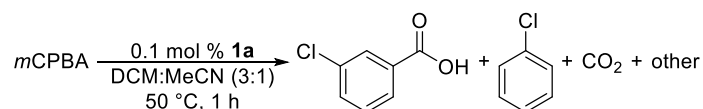
Table S4. Results of Ni-catalyzed oxidation of *trans*-6



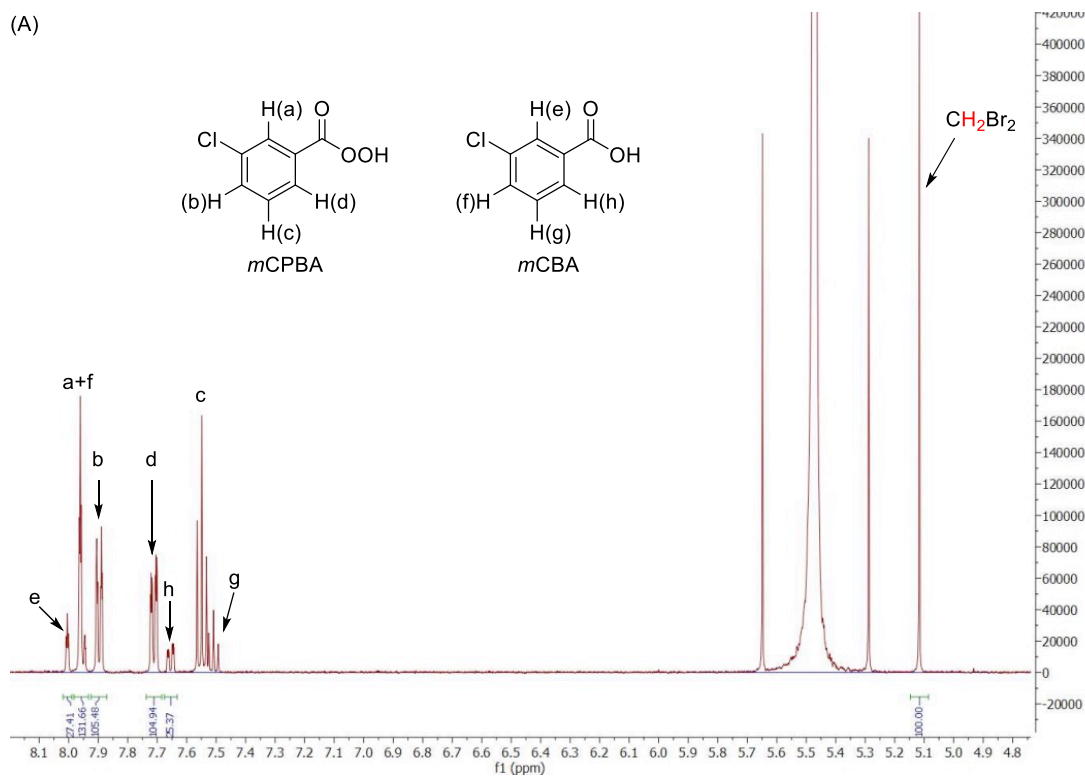
Entry	[Ni]	8a (%)	8b (%)	<i>cis</i> -fraction (%)
1	1a	10.8	15.0	41.8
2		11.1	15.6	41.7
3		12.4	17.3	41.6
4	1b	11.1	15.5	41.8
5		10.8	15.0	41.8
6		13.3	19.0	41.3
7	1c	9.6	13.3	41.8
8		11.1	15.8	41.3
9		12.8	18.4	41.1
10	1e	7.5	12.7	37.1
11		7.7	13.3	36.7
12		9.3	16.0	36.9
13	1f	10.7	16.5	39.3
14		9.7	15.1	39.2
15	1g	3.7	6.2	37.5
16		5.1	8.7	37.1

17		8.9	15.2	36.9
18	NiCl ₂	10.4	17.0	38.1
19		4.4	6.6	40.1
20		9.6	14.9	39.1

7. Ni-catalyzed Decomposition of *m*CPBA



To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), dibromomethane (4.4 μ L, 0.50 equiv) as the internal standard, and a mixture of dichloromethane and acetonitrile (3:1 v/v, 1.0 mL) as solvent. Ni complex **1a** (0.1 mol %) was added as a suspension in DCM. The vial was sparged with N₂ for 5 min, sealed, and the reaction mixture was stirred at 50 °C for 1 h. An aliquot (~ 30 μ L) of the mixture was taken, diluted with acetonitrile-*d*₃, and subjected to analysis by ¹H NMR spectroscopy.



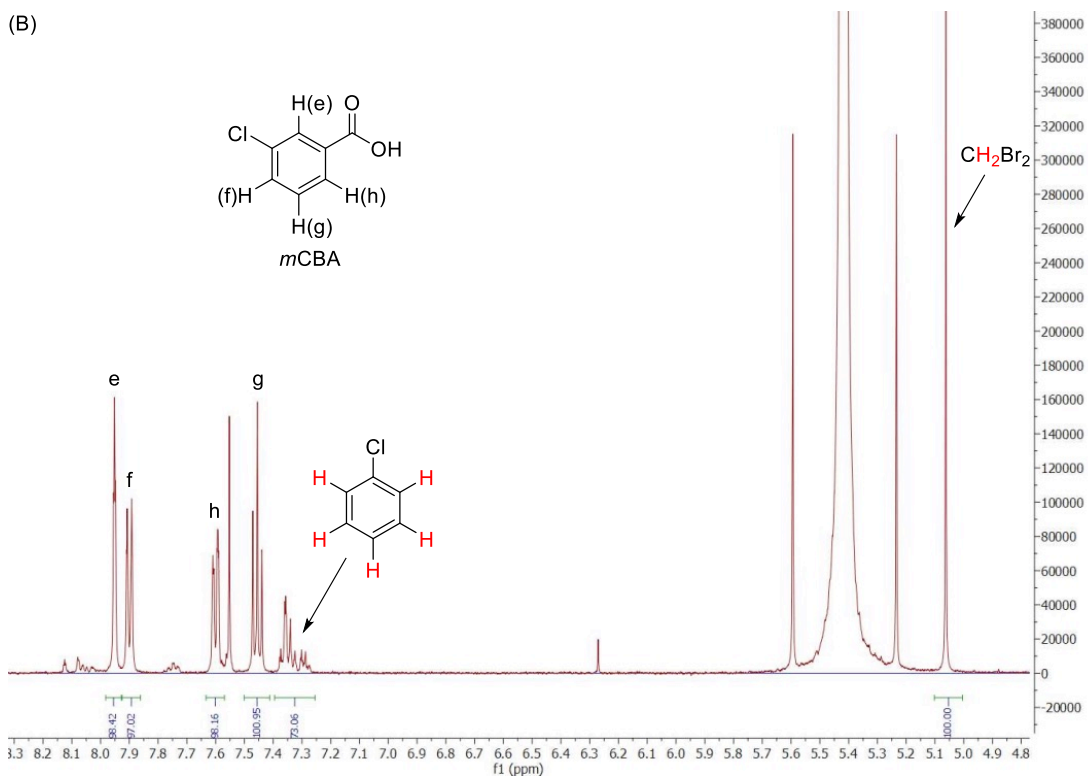


Figure S10. ^1H NMR spectra of the reaction mixture from Ni-catalyzed decomposition of *m*CPBA in the absence of alkane (A) at $t = 0$ and (B) at $t = 1$ h.

7.1. Time courses of Ni-catalyzed decomposition of *m*CPBA.

To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), dibromomethane (4.4 μL , 0.50 equiv) as the internal standard and chloroform- d_1 (3:1 v/v, 1.0 mL) as solvent. Ni complexes **1a** and **1h** were added as stock solutions or suspensions in CDCl_3 . The vial was capped, and the reaction mixture was stirred at 50 $^\circ\text{C}$. Aliquots (~ 15 μL) were periodically taken from the reaction mixture, diluted with chloroform- d_1 , and subjected to analysis by ^1H NMR spectroscopy.

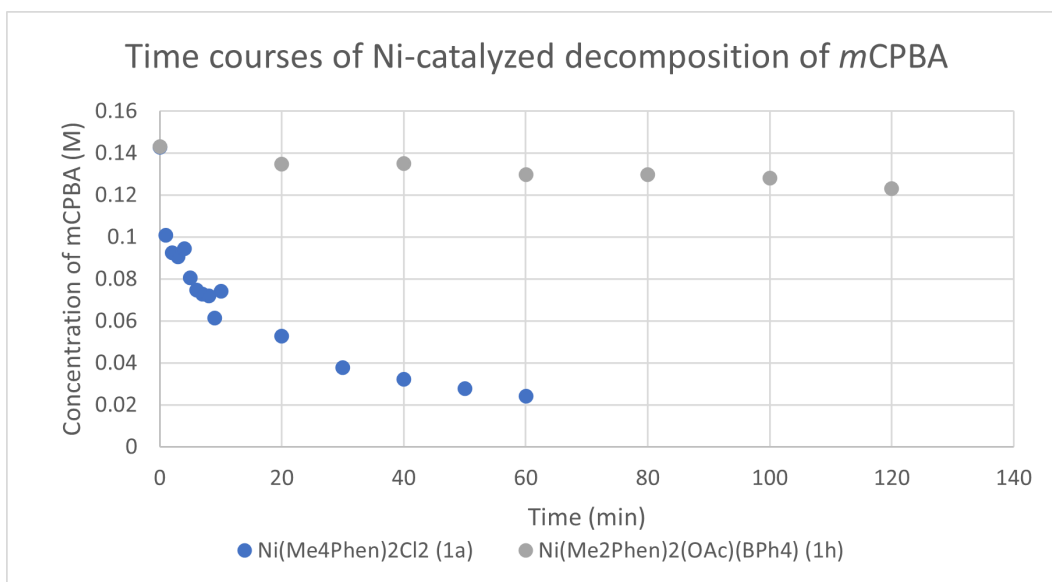


Figure S11. Time courses of the decomposition of *m*CPBA catalyzed by Ni complexes **1a** and **1h**.

8. EPR Spectra of Stoichiometric Reactions of Ni Complex **1a**

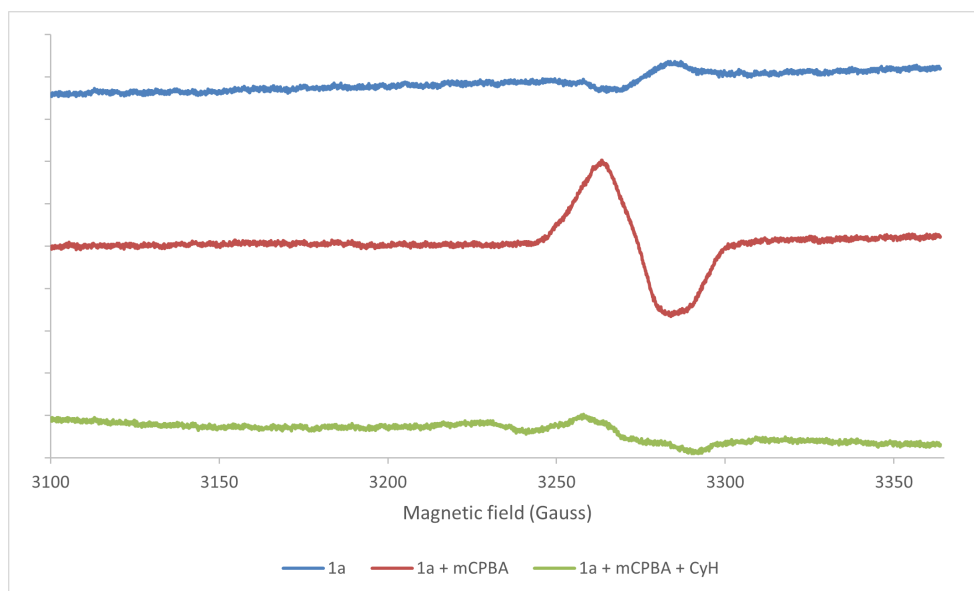
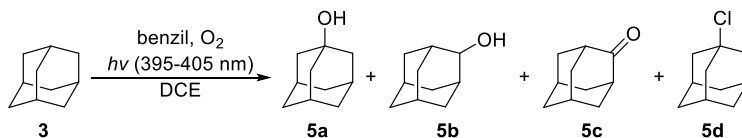


Figure S12. Overlaid EPR spectra of (a) 10 mM methanol solution of complex **1a** (**1a**, blue); (b) 10 mM methanol solution of complex **1a** with 5 equiv of *m*CPBA after heating at 50 °C for 30 s (**1a** + *m*CPBA, red); (c) 10 mM methanol solution of complex **1a** with 5 equiv of *m*CPBA and 10 equiv of cyclohexane after heating at 50 °C for 30 s (**1a** + *m*CPBA + CyH, green).

Complex **1a**, which is a Ni(II) compound with d^8 electron configuration, is EPR-silent (Figure S12, blue curve). Reaction of **1a** with 5 equivalents of *m*CPBA resulted in an isotropic signal ($g = 2.007$) at 3282 Gauss (Figure S12, red curve), which likely corresponds to an oxygen-centered organic free radical rather than a species containing a Ni-O bond because the signals of reported Ni-OH and Ni-O• or Ni=O species are generally centered around 3100 Gauss and have more complex peak shapes.⁴⁻⁶ Reaction of **1a** with 5 equivalents of *m*CPBA in methanol and 10 equivalents (with respect to Ni) of cyclohexane did not lead to a pronounced EPR signal, likely due to quenching of the oxygen-centered free radical by the cyclohexane (Figure S12, green curve).

9. Photo-mediated Oxidation of Adamantane (**3**) by Benzil and Oxygen



To a 4 mL vial equipped with a stir bar was added benzil (26.3 mg, 0.125 mmol), adamantane (34.1 mg, 0.250 mmol) and 1,2-dichloroethane (DCE, 1.5 mL) as the solvent. The solution was sparged with O₂ for 10 min. Then a UV lamp (395-405 nm) was turned on and the solution was sparged with O₂ for another 10 min. Sparging was then stopped to prevent extensive evaporation of solvent and the solution was stirred under an atmosphere of O₂ and UV irradiation for the required time. After the UV lamp was turned off, *n*-dodecane (28.0 μ L, 0.123 mmol) was added to the reaction mixture as an internal standard. An aliquot (40-50 μ L) of this mixture was transferred to a GC vial, diluted with ethyl acetate, and subjected to analysis by GC.

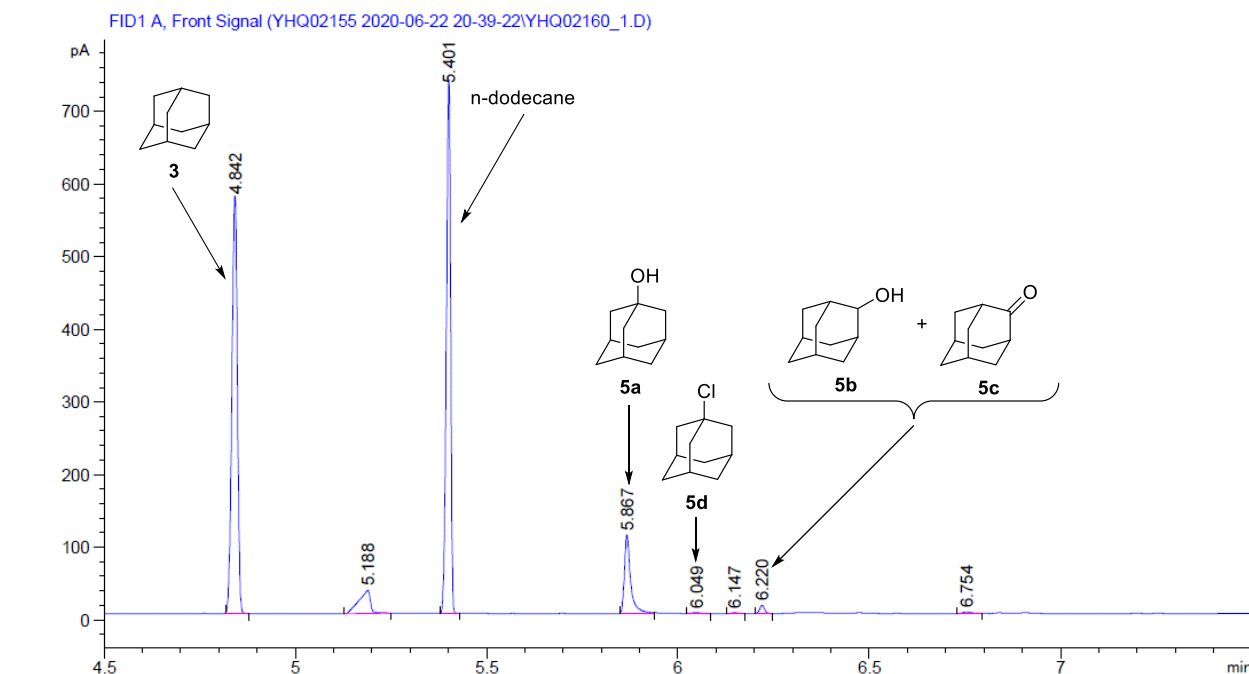


Figure S13. A typical GC trace of the reaction mixture from the photo-mediated oxidation of **3** by benzil and O₂.

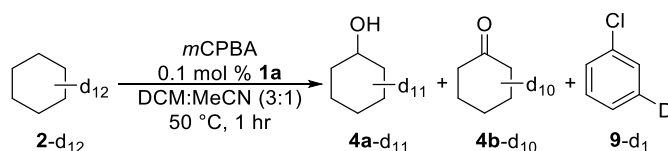
1-Adamantanol (**5a**) was formed as the major product and byproducts **3b**, **3c** and **3d** were formed in less than 3% yield. 2-Chloroadamantane (**5e**) was not observed. The results of this experiment were summarized in Table S5.

Table S5. Results of the photo-mediated oxidation of adamantane by benzil and O₂

Entry	Time (min)	Temperature	5a (%) ^a	5b + 5c (%) ^a	5d (%) ^a	3°/2° ^b
1	75	rt	20.9	1.9	0.3	11.3
2	133	rt	25.8	2.3	0.3	11.5
3	133	rt	28.4	2.4	0.4	12.1
4	128	50 °C	31.8	2.9	0.5	11.2
5	128	50 °C	31.3	2.8	0.5	11.4

^aAll yields were calculated based on benzil. ^bDefined as the ratio of the combined yield of **5a+5d** to the combined yield of **5b+5c**.

10. Ni-catalyzed Oxidation of Cyclohexane-*d*₁₂ (**2-d**₁₂)



To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), deuterated alkane **2-d₁₂** (5.00 equiv) and acetonitrile (1.0 mL) as solvent. Ni complex **1a** was added as a suspension in DCM. The vial was sealed, and the reaction mixture was stirred at 50 °C for 75 min. After cooling to room temperature, saturated aqueous solution of Na₂CO₃ (2.0 mL) was added, and the mixture was extracted three times with DCM. The organic layer was separated, concentrated *in vacuo* to remove unreacted **2-d₁₂**, then diluted to ~0.6 mL with DCM. CD₂Cl₂ (2.4 μL, 0.30 equiv) was added as an internal standard, and the mixture was subjected to analysis by ²H NMR spectroscopy.

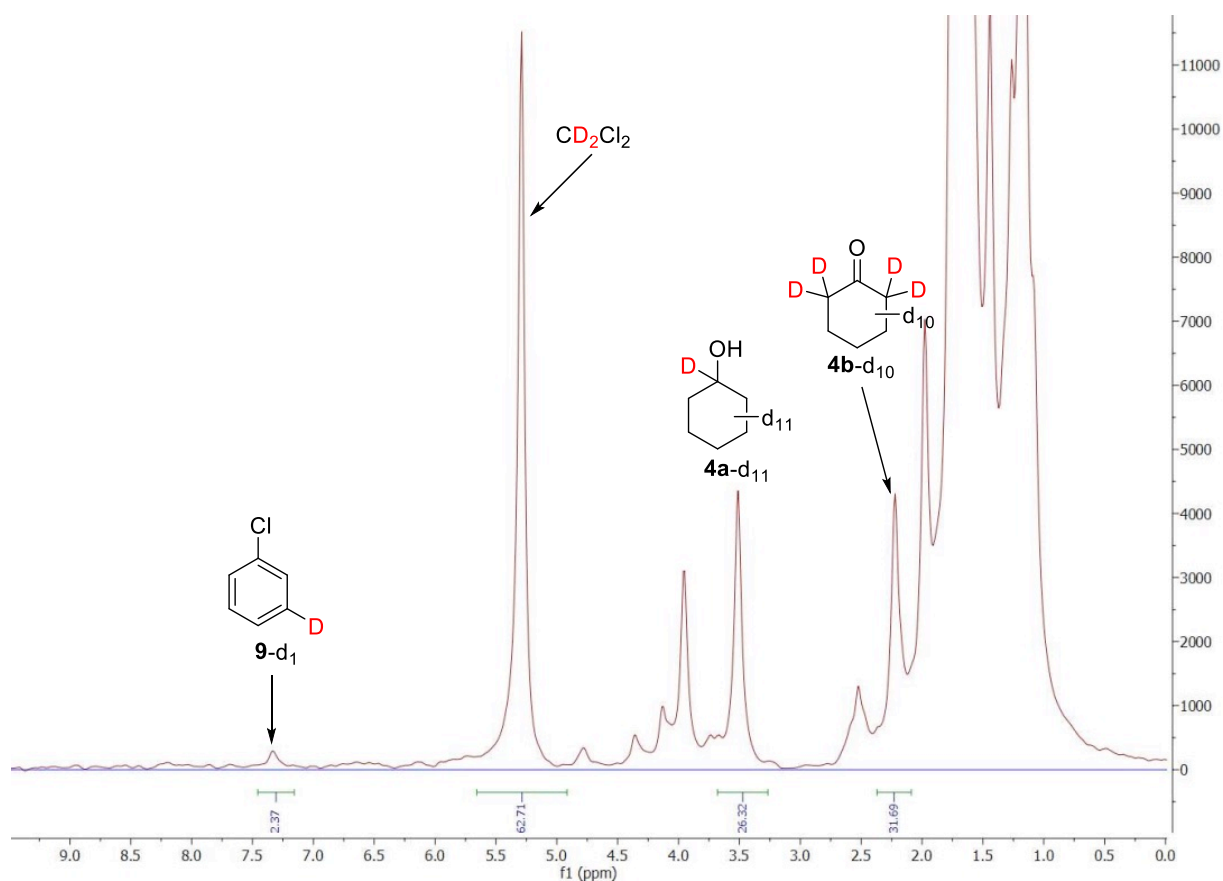
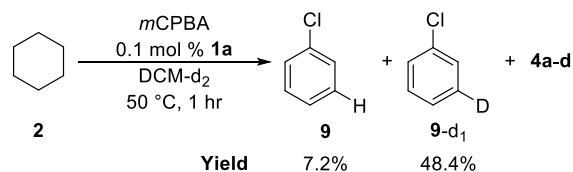


Figure S14. ²H NMR spectrum of Ni-catalyzed oxidation of **2-d₁₂** by *m*CPBA.

9.1. Hydrogen atom transfer (HAT) from solvent molecules to 3-chlorophenyl radical (**12**)



To a 4 mL vial equipped with a stir bar was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), cyclohexane (68.0 μ L, 0.625 mmol), catalyst **1a** (0.1 mol %), and DCM-*d*₂ (1 mL). The vial was sealed, and the reaction mixture was stirred at 50 °C for 1 h. After cooling to room temperature, dibromomethane (4.4 μ L, 0.5 equiv) was added to the reaction mixture as an internal standard. Half of this solution (0.5 mL) was then transferred to an NMR tube and subjected to analysis by ¹H NMR spectroscopy. The remaining half of the solution was evaporated under reduced pressure (340 mbar) until it was almost dry, then diluted with CH₂Cl₂ (0.6 mL) and CD₃CN (1.1 μ L, 0.17 equiv) was added as the internal standard. This mixture was transferred to another NMR tube and subjected to analysis by ²H NMR spectroscopy.

The yields (based on *m*CPBA) of chlorobenzene (**9**) and deuterated chlorobenzene (**9-d**₁) were determined, from ¹H and ²H NMR spectra, to be 7.2% and 48.4%, respectively. This result shows that 87% of product **9** is labelled by deuterium for the reaction conducted in DCM-*d*₂ and strongly supports our hypothesis that most of the chlorobenzene byproduct is formed by hydrogen atom transfer from solvent molecules to radical **12** in Ni-catalyzed oxidation of alkanes.

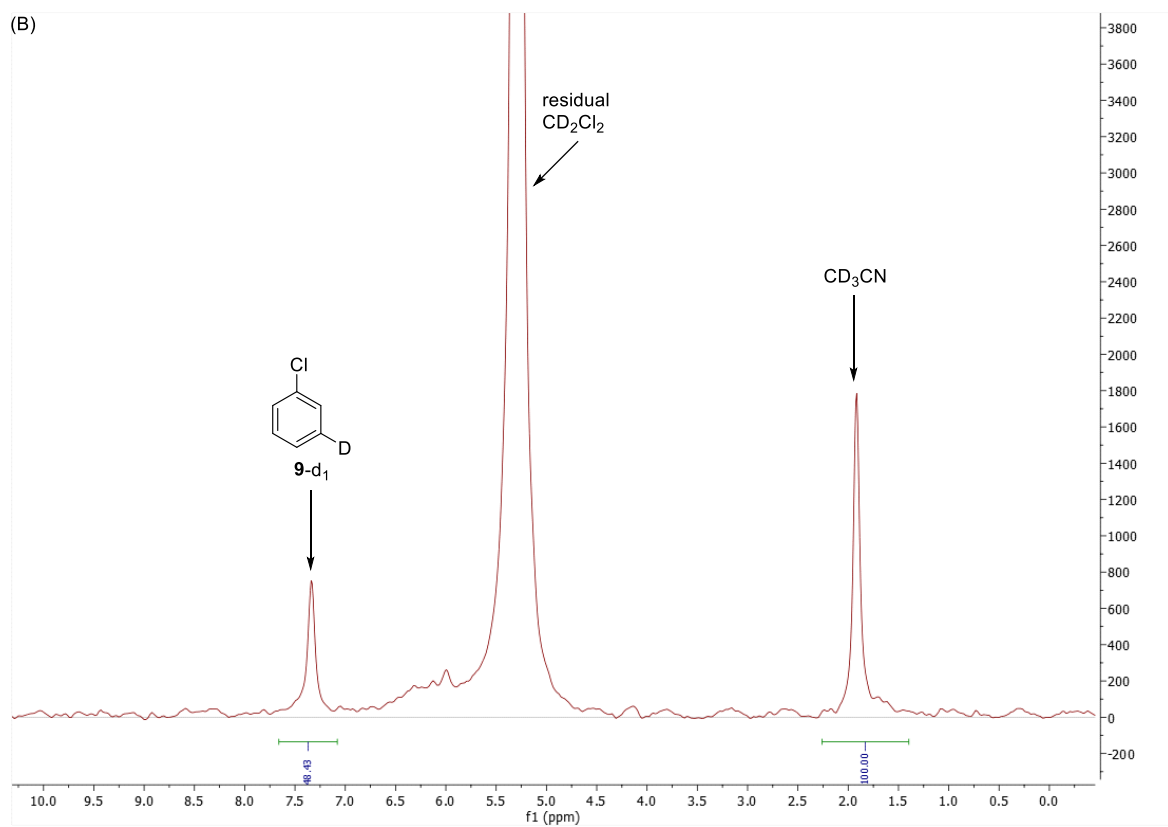
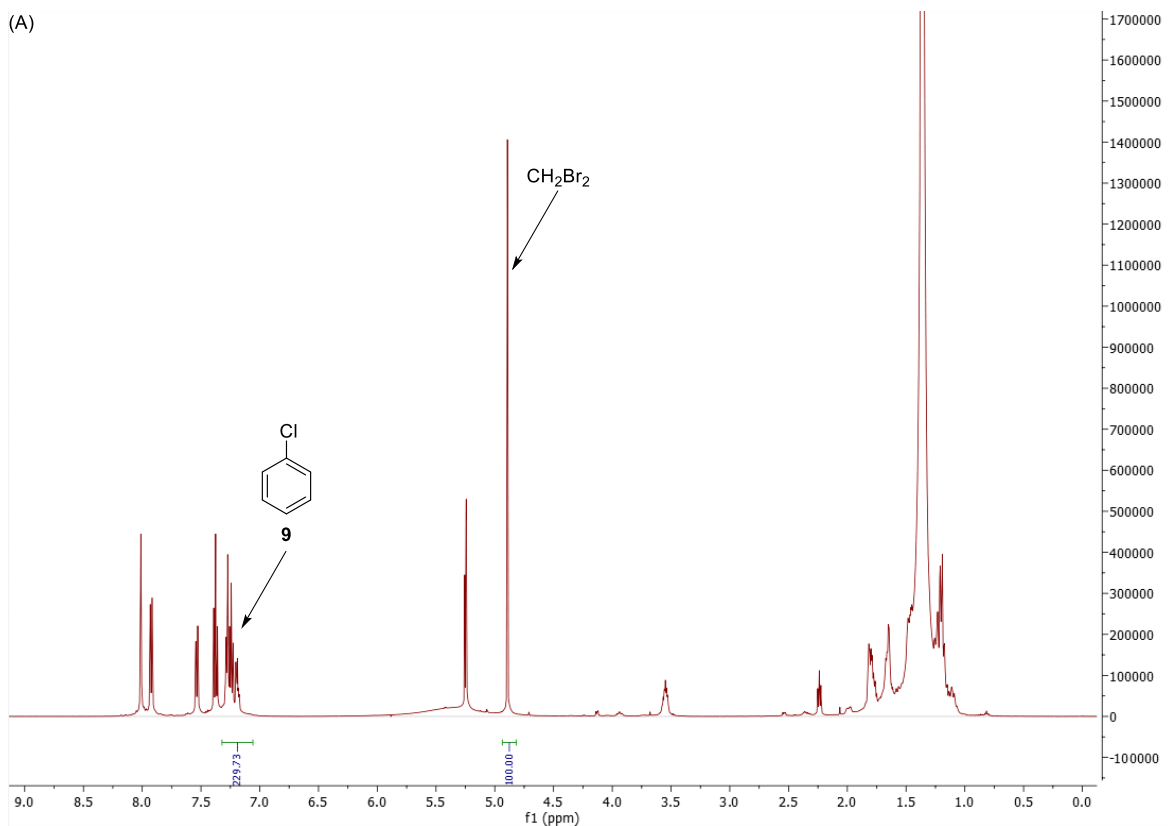
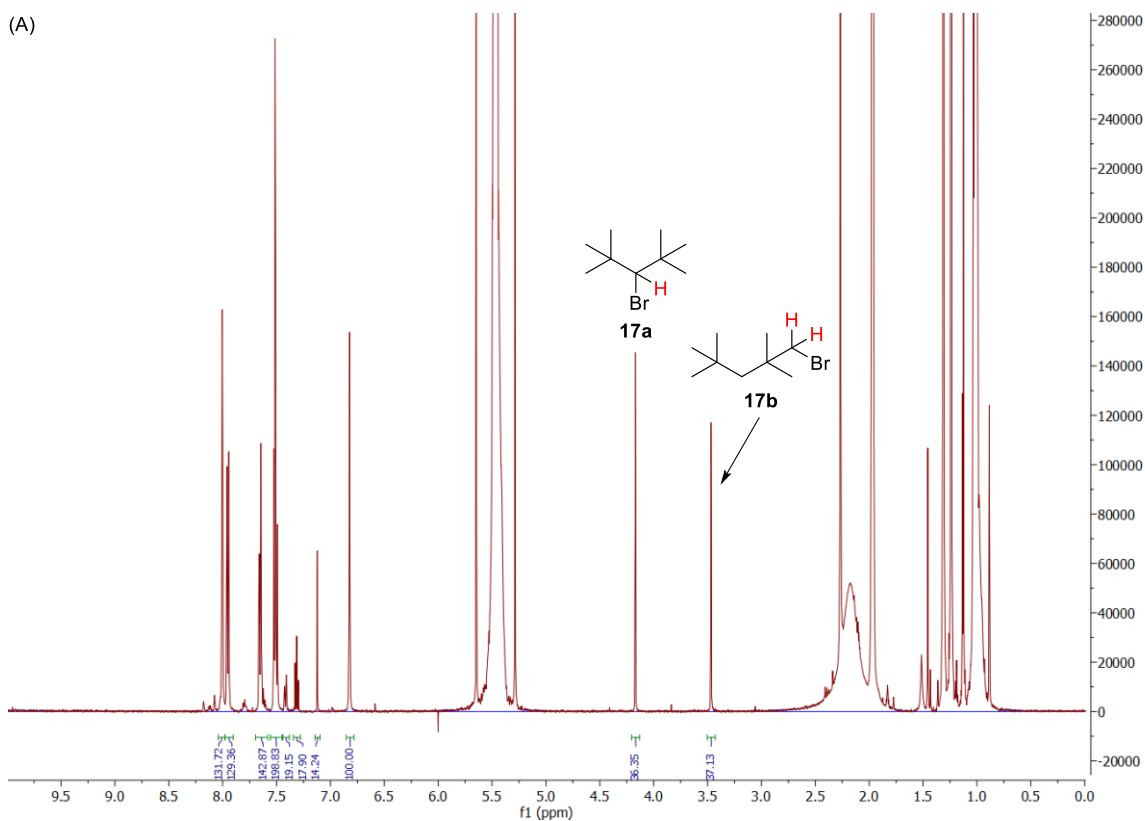


Figure S15. (A) ^1H NMR spectrum and (B) ^2H NMR spectrum from Ni-catalyzed oxidation of cyclohexane by *m*CPBA in $\text{DCM-}d_2$.

11. Bromination of 2,2,4,4-Tetramethylpentane (**16**)

10.1. General procedure for Ni-catalyzed bromination of **16** by *m*CPBA

In a N_2 -filled dry box, *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane **16** (111 μL , 0.625 mmol), CBr_4 (83.0 mg, 2.00 equiv) and dichloromethane (1.0 mL) were added to a 4 mL vial equipped with a stir bar. Ni complex **1a** (0.1 mol %) was added as a suspension in DCM. The vial was capped, sealed with electrical tape, and the reaction mixture was stirred at 50 $^\circ\text{C}$ for 1 h. After cooling to room temperature, mesitylene (5.8 μL , 0.33 equiv) was added as an internal standard. An aliquot (~30 μL) of the mixture was taken, diluted with acetonitrile- d_3 , and subjected to analysis by ^1H NMR spectroscopy.



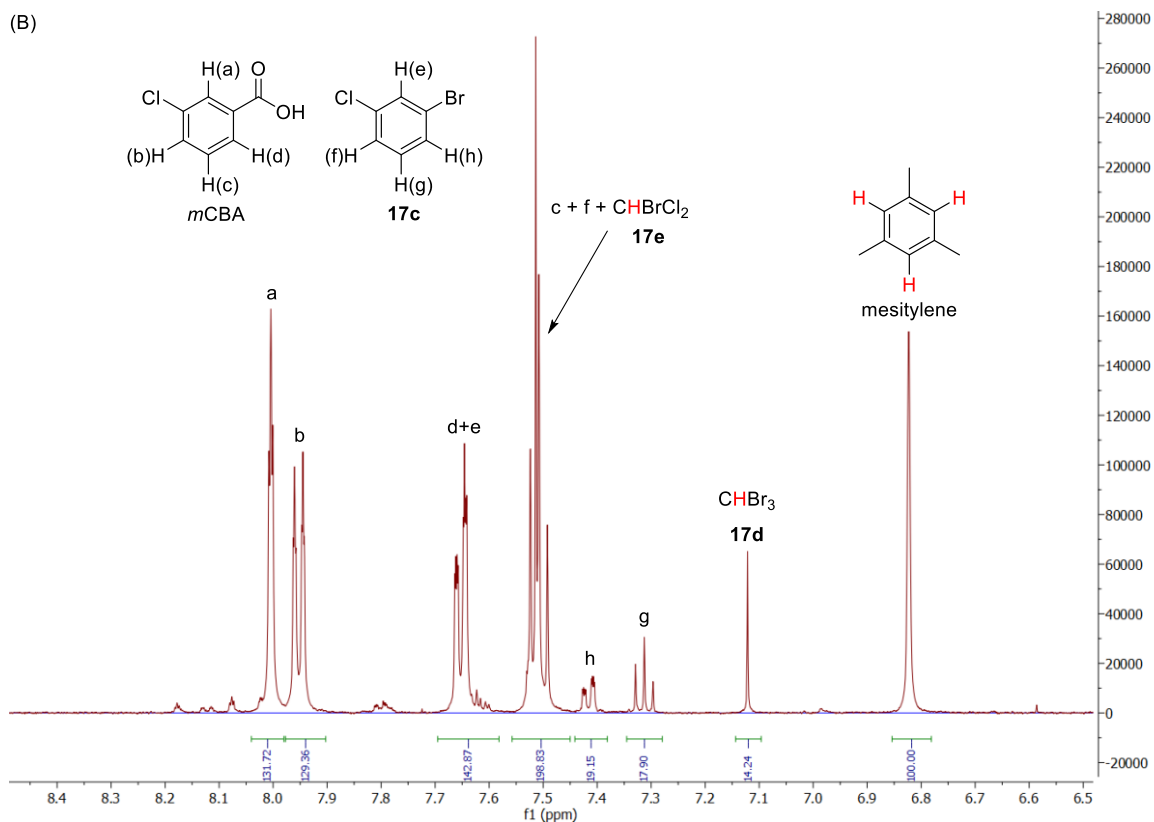
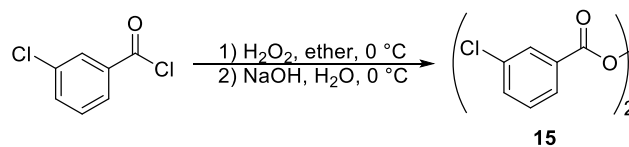


Figure S16. (A) A typical ^1H NMR spectrum of the reaction mixture from Ni-catalyzed bromination of **16** by *m*CPBA; (B) the aromatic region of the spectrum in (A).

10.2. Synthesis of Bis(3-chlorobenzoyl)peroxide (**15**)



The following procedure was adapted from reported literature.⁷

In a 50 mL round bottom flask equipped with a stir bar, 3-chlorobenzoyl chloride (5.0 mmol, 0.88 g, 0.64 mL) was dissolved in ethyl ether (2.5 mL) and cooled to 0 °C. Hydrogen peroxide (2.90 mmol, 162 μL , 50% w/w aqueous solution) was added to the stirring solution by slow addition over 10 min. Sodium hydroxide (6.300 mmol, 252.8 mg, dissolved in 2 mL H_2O) was then added to the stirring solution by slow addition over 20 min. The resulting white precipitate was collected by filtration, washed with H_2O (5.0 mL \times 2 times)

and ethyl ether (5.0 mL \times 2 times), and dried under high vacuum for 4 h. Product **15** was obtained as a white powder (339.2 mg, 43.61% yield) and stored at -20 °C.

^1H NMR (500 MHz, CDCl_3): δ 8.06 (t, $J = 1.9$ Hz, 1H), 7.96 (ddd, $J = 7.8, 1.6, 1.1$ Hz, 1H), 7.65 (ddd, $J = 8.1, 2.2, 1.1$ Hz, 1H), 7.48 (t, $J = 7.9$ Hz, 1H).

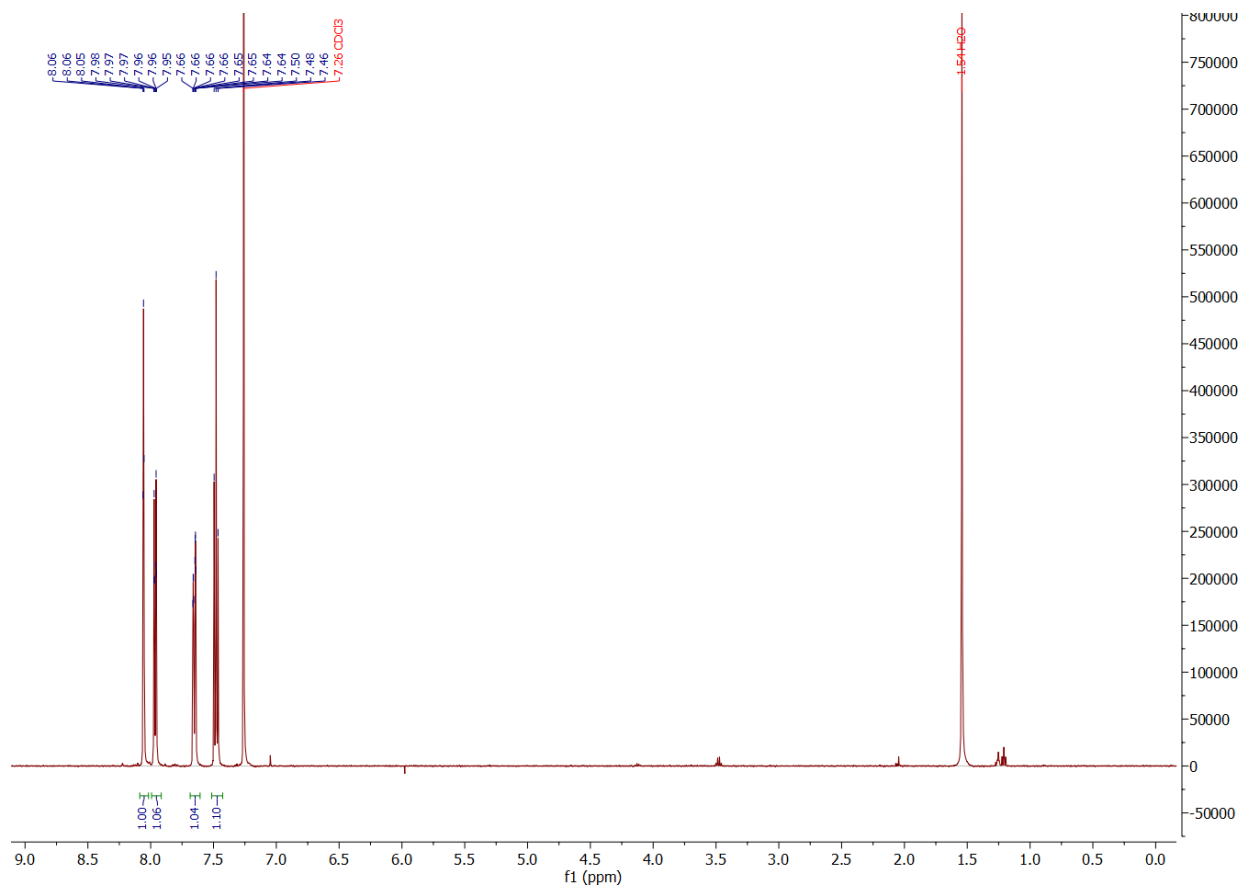
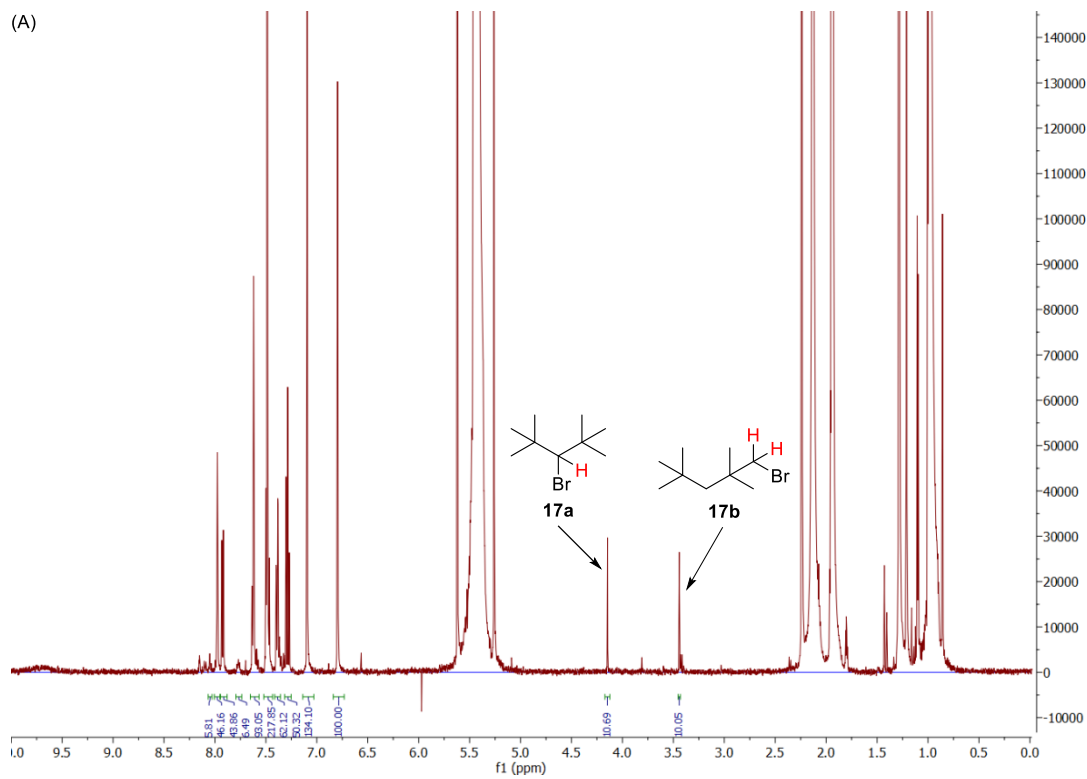


Figure S17. ^1H NMR spectrum of compound **15**.

10.3. General procedure for bromination of **16** by peroxide **15**

In a N_2 -filled dry box, peroxide **15** (19.4 mg, 0.0625 mmol), alkane **16** (111 μL , 0.625 mmol), CBr_4 (83.0 mg, 2.00 equiv) and dichloromethane (1.0 mL) were added to a 4 mL vial equipped with a stir bar. Ni complex **1a** (0.1 mol %) was added as a suspension in DCM. The vial was capped, sealed with electrical tape, and the reaction mixture was stirred at 80 °C for 13 h. After cooling to room temperature, mesitylene

(5.8 μL , 0.33 equiv) was added as an internal standard. An aliquot ($\sim 30 \mu\text{L}$) of the mixture was taken, diluted with acetonitrile- d_3 , and subjected to analysis by ^1H NMR spectroscopy.



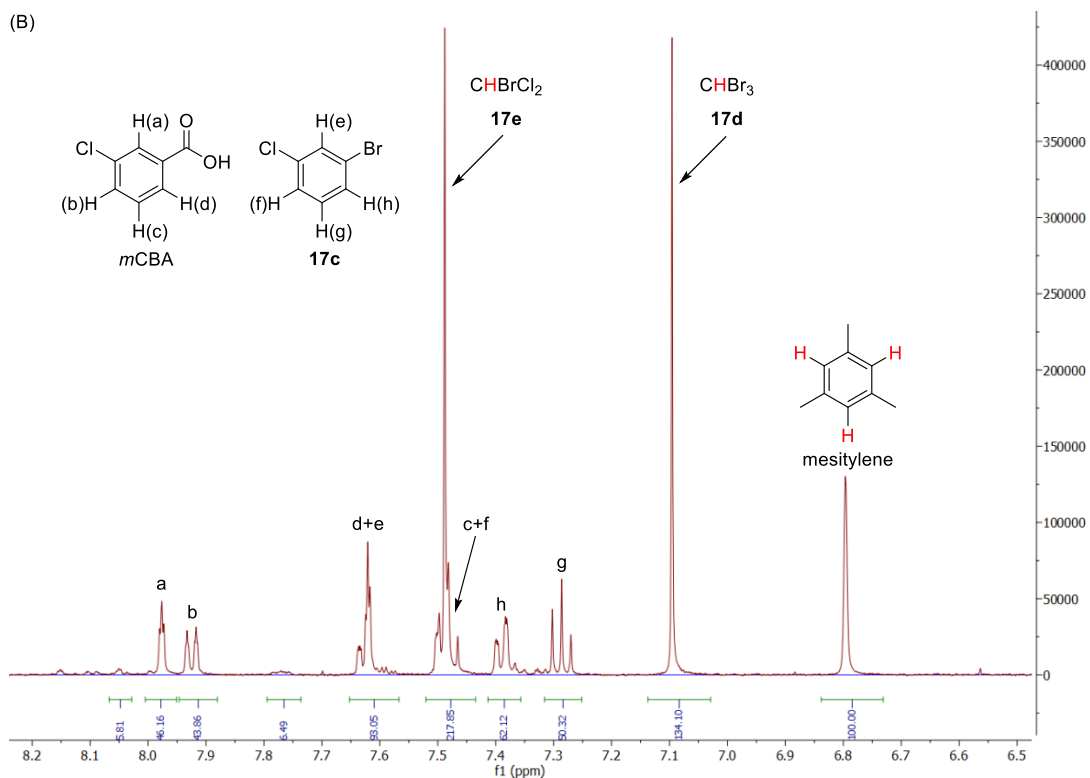
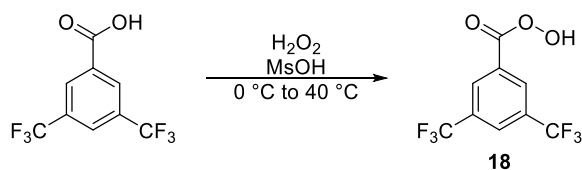


Figure S18. (A) A typical ^1H NMR spectrum of the reaction mixture from the bromination of **16** by peroxide **15**; (B) the aromatic region of the spectrum in (A).

10.4. Synthesis of 3,5-bis(trifluoromethyl)perbenzoic acid (**18**)



The following procedure was adapted from reported literature.⁸

Concentrated H_2O_2 (approx. 90% w/w in H_2O) was prepared by subjecting commercial H_2O_2 solution (50 % w/w in H_2O) to high vacuum for 8 h. **CAUTION:** Concentrated hydrogen peroxide should be stored in the freezer and handled with care due to potential hazard of explosion.

To a 25 mL pear-shaped flask equipped with a stir bar was added 3,5-bis(trifluoromethyl)benzoic acid (774.4 mg, 3.000 mmol, 1.000 equiv) and methanesulfonic acid (1.0 mL). The resulting slurry was stirred at 0 °C for 30 min, then H_2O_2 (0.24 mL, 3 equiv, approx. 90% w/w in H_2O) was added dropwise. The

reaction mixture was stirred at 40 °C for 1.5 h and subsequently quenched with 5 mL ice water. The white precipitate was collected by filtration and washed with 25 mL ice water. The crude product was obtained as a white solid (736.3 mg, approx. 85% purity by NMR) and used for Ni-catalyzed bromination of **16** without further purification. The major impurities in the crude product are water and the unreacted 3,5-bis(trifluoromethyl)benzoic acid.

^1H NMR (300 MHz, CDCl_3): δ 8.46 (s, 2H), 8.16 (s, 1H).

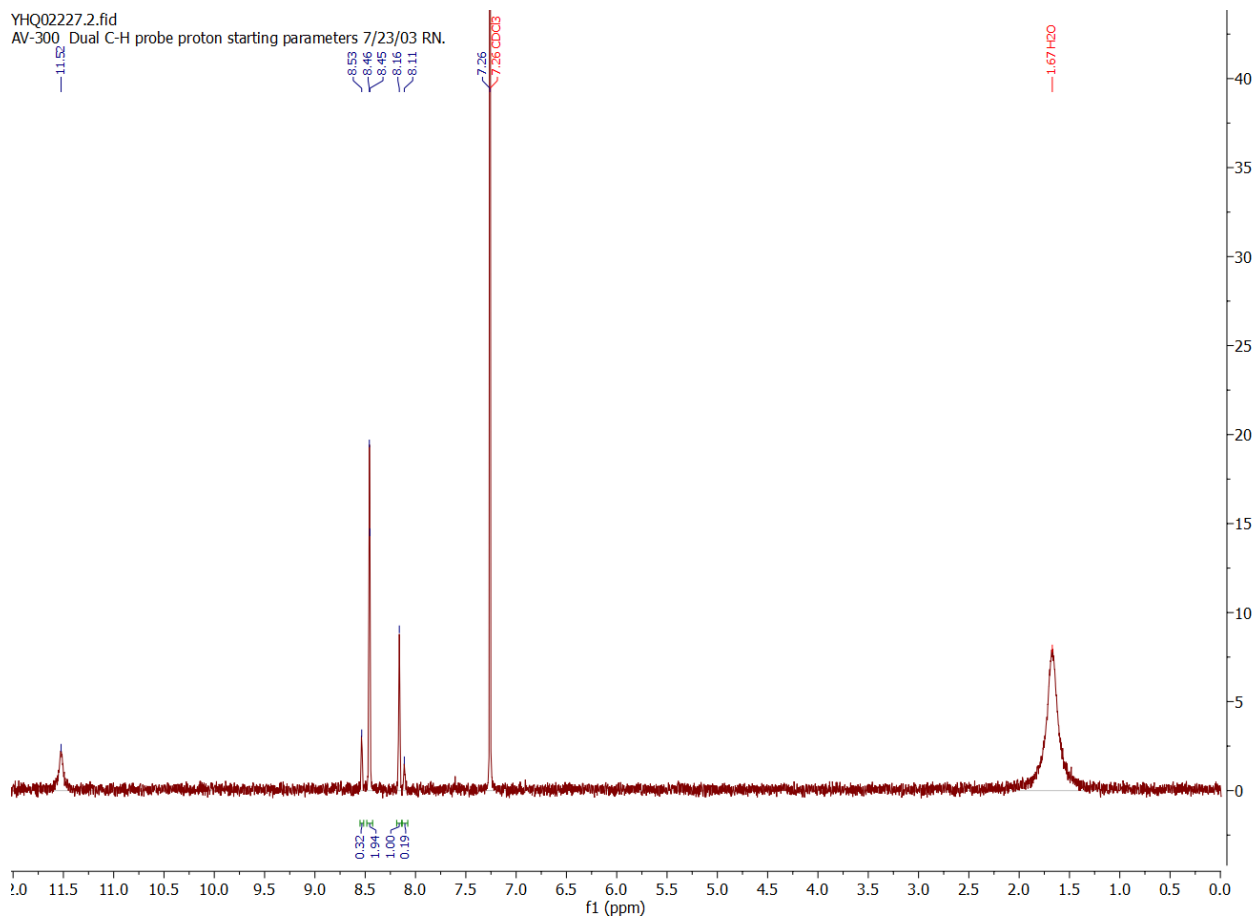


Figure S19. ^1H NMR spectrum of the crude product of peracid **18**.

10.5. General procedure for Ni-catalyzed bromination of **16** by peracid **18**

To a 4 mL vial equipped with a stir bar, peracid **18** (40.3 mg, 0.125 mmol, ~85% purity), alkane **16** (111 μL , 0.625 mmol), CBr_4 (83.0 mg, 2.00 equiv) and dichloromethane (1.0 mL) were added. Ni complex **1a**

(1 mol %) was added as a suspension in DCM. The vial was sparged with N₂ for 1 min, capped, sealed with electrical tape, and the reaction mixture was stirred at 50 °C for 1 h. After cooling to room temperature, mesitylene (5.8 μL, 0.33 equiv) was added as an internal standard. An aliquot (~ 25 μL) of the mixture was taken, diluted with acetonitrile-*d*₃, and subjected to analysis by ¹H NMR spectroscopy.

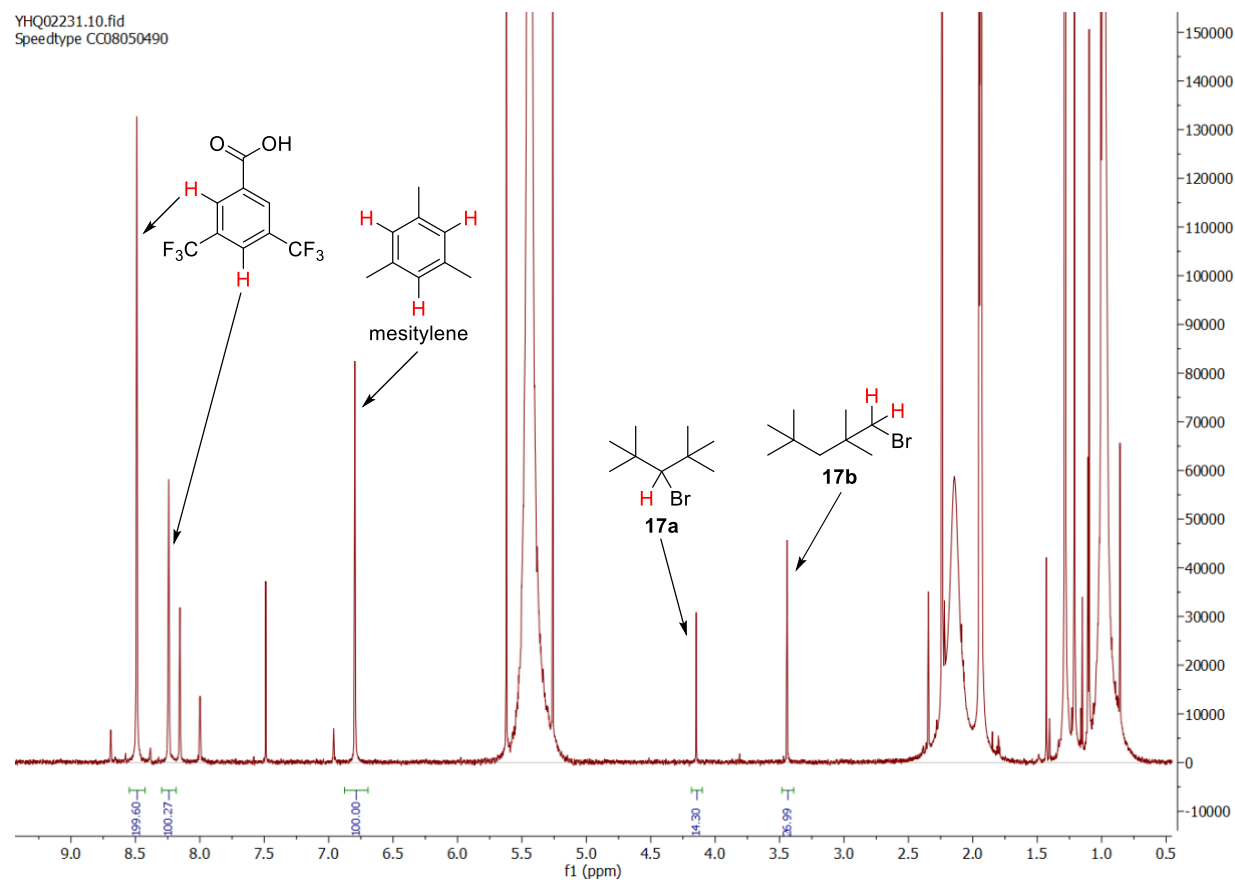


Figure S20. A typical ¹H NMR spectrum of the reaction mixture from the Ni-catalyzed bromination of **16** by peracid **18**.

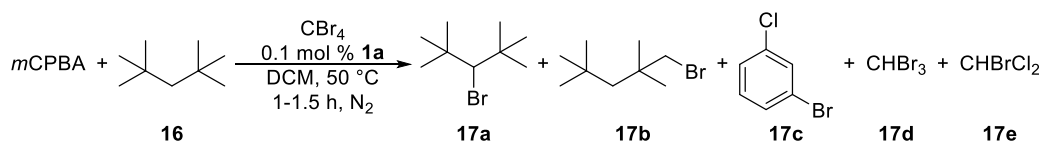
10.6. Results and discussions

Results of three repeated experiments of Ni-catalyzed bromination of **16** by *m*CPBA and those of eight repeated experiments of bromination of **16** by peroxide **15** are summarized in Table S6 and S7, respectively.

In both reactions, byproducts *meta*-bromochlorobenzene (**17c**), bromoform (**17d**) and bromodichloromethane (**17e**) were formed together with brominated alkanes **17a** and **17b**. Compound **17c**

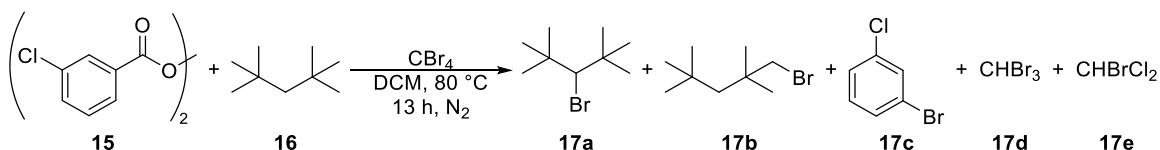
was likely formed by decarboxylation of radical **10**, followed by trapping with CBr₄. Byproduct **17e** can be formed by the reaction of CHCl₂· radical and CBr₄. The formation of **17a** and **17b** in low yields in the nickel-free reaction can be attributed to acceleration of decarboxylation of the 3-chlorobenzoyloxy radical **10** at elevated temperature (80 °C), which is supported by the formation of **17c** in higher yield in the nickel-free reaction (~50%, Table S7) than in the Ni-catalyzed reaction (~20%, Table S6).

Table S6. Results of Ni-catalyzed Bromination of 16 by *m*CPBA



Entry	17a (%)	17b (%)	2°/1°	17c (%)	17d (%)	17e (%)
1	35.0	18.9	1.9	17	13.7	55
2	36.4	18.6	2.0	19	14.2	56
3	34.3	16.3	2.1	19	11.5	54

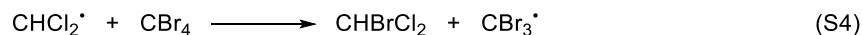
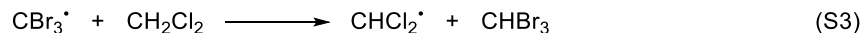
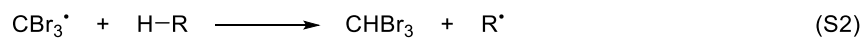
Table S7. Results of Bromination of 16 by Peroxide 15



Entry	17a (%)	17b (%)	2°/1°	<i>m</i> CBA (%)	17c (%)	17d (%)	17e (%)
1	7.0	5.5	1.3	47	50	130	120
2	13.5	6.5	2.1	43	50	131	123
3	10.7	5.0	2.1	44	50	134	118
4	11.5	5.6	2.1	38	52	132	110
5	10.5	5.3	2.0	41	50	125	100
6	11.6	4.7	2.5	39	48	131	115
7	6.7	5.7	1.2	44	49	123	110
8	11.9	5.5	2.2	41	49	128	109

In the Ni-catalyzed reactions, tribromomethyl radical (CBr₃·) cannot be the major species that cleaves C–H bonds in alkane **16** (eq S2) because byproduct **17d** was formed in only 11%-15% yield, which is much lower than the yield of products **17a** and **17b** (Table S6). The large amount of **17d** and **17e** formed in the

nickel-free reaction (Table S7) can be explained by a radical chain pathway that would occur at elevated temperature (eq S3-S4).



Bromine radical (Br^\cdot) cannot be the major species that cleaves C–H bonds, because the solutions of both Ni-catalyzed and Ni-free reactions were either colorless or very slightly orange, indicating that Br_2 was either not formed or formed in only trace amount. In addition, the selectivity of Br^\cdot for the secondary C–H bonds in the photo-mediated reaction of **16** and Br_2 was high ($2^\circ/1^\circ$ ratio = 31, Figure S21). This ratio, which is much larger than those presented in Tables S6 and S7, suggests that Br^\cdot does not cleave the C–H bonds in **16** in these reactions. Thus, we have demonstrated that radicals such as Br^\cdot and CBr_3^\cdot do not interfere with abstraction of hydrogen atoms from substrate **16**.

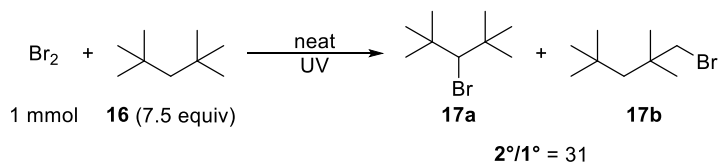
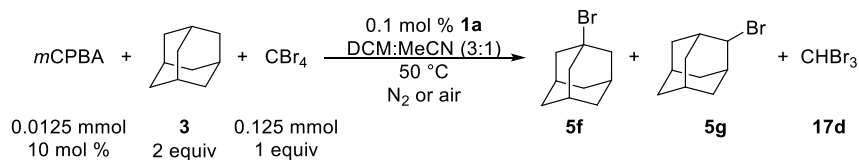


Figure S21. Photoinduced bromination of **16** by Br_2 .

Bromination of adamantane (**3**) with substoichiometric amounts (10 mol % with respect to CBr_4) of *m*CPBA and catalytic amounts of Ni complex **1a** was conducted under an atmosphere of N_2 or air (Table S8) to assess whether CBr_3^\cdot or Br^\cdot cleaves the C–H bonds in adamantane. 1- and 2-bromoadamantane (**5f** and **5g**) were formed as the major products. The formation of the combination of **5f** and **5g** in higher than 10% yield in the reactions under air, along with the orange color of the reaction mixture (Table S8, Entries 1-2) suggests that Br^\cdot abstracts hydrogen atoms from adamantane in reactions conducted under air. The formation of the combination of **5f** and **5g** in approximately 30% yield in the reactions under nitrogen, the formation of bromoform (**17d**), and the colorlessness of the reaction mixture (Table S8, Entries 3-4) indicate that CBr_3^\cdot abstracts hydrogen atoms from adamantane in reactions conducted under nitrogen. Due to such

interference from $\text{CBr}_3\cdot$ and $\text{Br}\cdot$ in hydrogen-atom abstraction, adamantane is not a suitable substrate for the measurement of the selectivity of aryloxy radical **10**.

Table S8. Results of Bromination of Adamantane

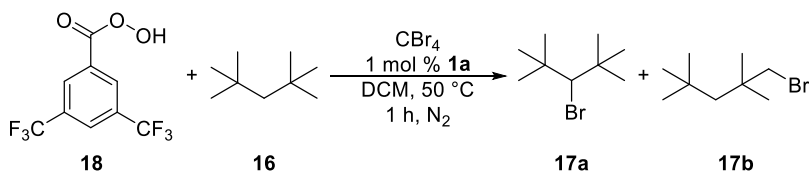


Entry	N ₂ or air	5f (%)	5g (%)	17d (%)	Color of reaction mixture
1	Air	12.0	2.0	0	Orange
2	Air	9.8	1.6	0	Orange
3	N ₂	24.6	2.1	14	Colorless
4	N ₂	27.2	2.3	18	Colorless

All yields were determined based on CBr_4 .

Results of three repeated experiments of Ni-catalyzed bromination of **16** by aromatic peracid **18**, along with those of a control experiment conducted in the absence of Ni, are summarized in Table S9.

Table S9. Results of Ni-catalyzed Bromination of 16 by peracid 18



Entry	17a (%)	17b (%)	2°/1°
1	14.3	13.5	1.1
2	15.6	13.5	1.2
3	14.2	13.1	1.1
4 ^a	0	0	-

^aIn the absence of Ni.

12. Assay for the Alkylperoxy Intermediate by GC

11.1. General procedure for the assay for alkylperoxy intermediates by GC

To a set of two 4 mL vials, each equipped with a stir bar, was added *m*CPBA (28.8 mg, 0.125 mmol, ~75% purity), alkane **2** (7.50 equiv) and a mixture of dichloromethane and acetonitrile (3:1 v/v, 1.0 mL) as solvent.

Ni complex **1a** was added as a suspension in DCM. One of these two vials was sparged with N₂ for 30-60 s before both were sealed and heated at 50 °C for 5 min. After cooling to room temperature, half of the reaction mixture in each vial was transferred to a clean GC vial, diluted with ethyl acetate, and immediately subjected to analysis by GC. The remaining mixture in each vial was treated with PPh₃ (18.1 mg, 0.0700 mmol), diluted with ethyl acetate, and then subjected to analysis by GC.

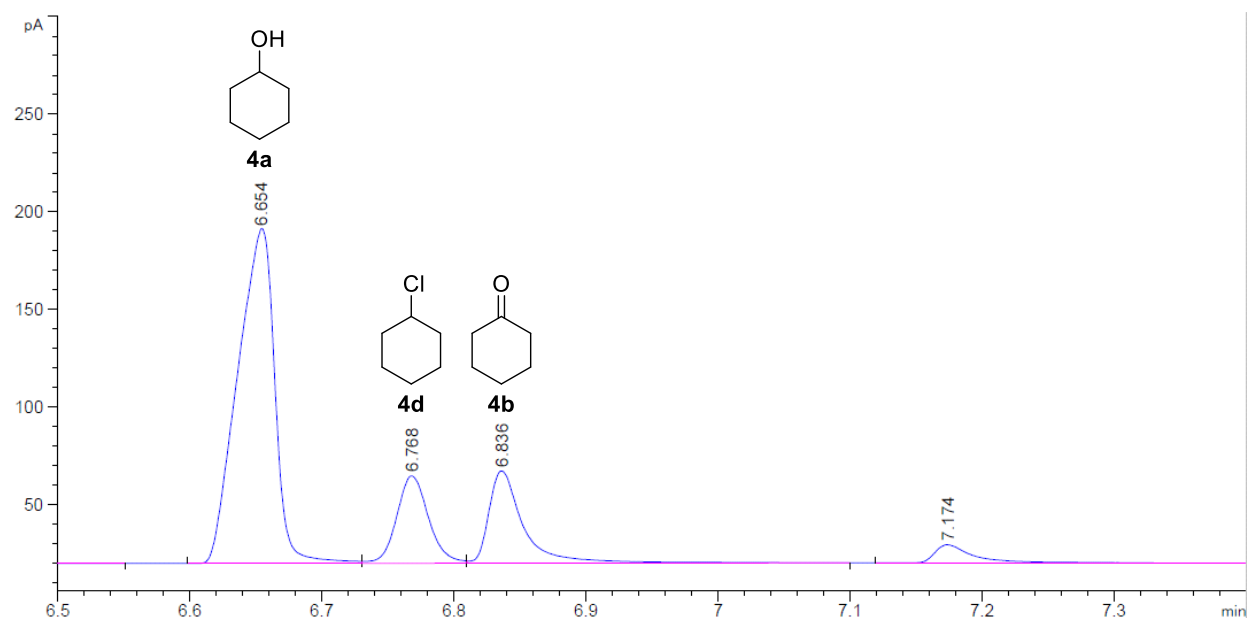
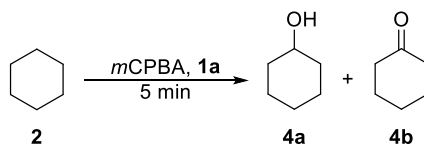


Figure S22. A typical GC trace of the reaction mixture from Ni-catalyzed oxidation of **2** after 5 min.

11.2. Results and derivation of the percentage of alkylperoxy intermediate **19**

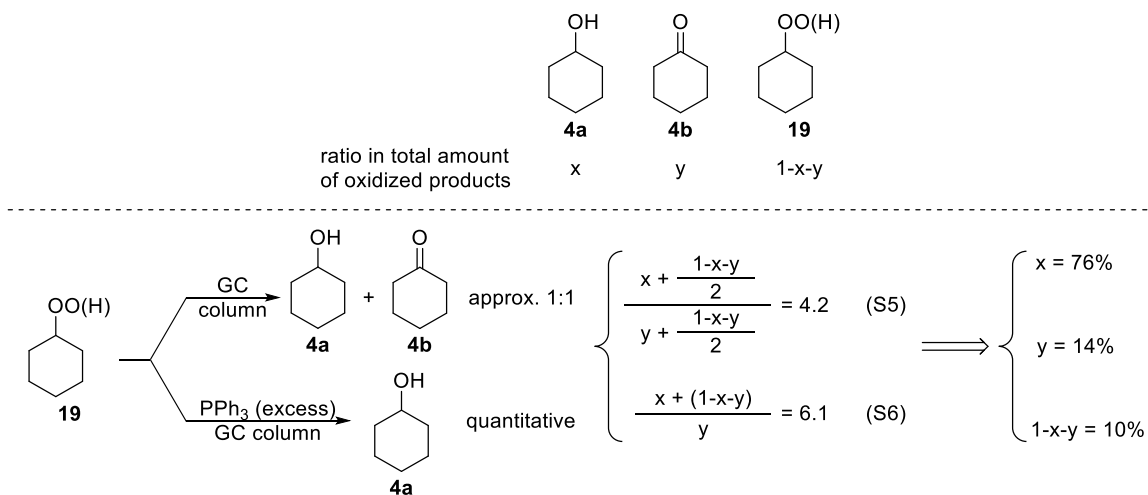
Table S10. Results of the Assay for Alkylperoxy Intermediate **19**



Entry	N ₂ /air	Treatment with PPh ₃	A/K ^a	Average A/K
1	N ₂	yes	4.5	4.6±0.1
2			4.6	
3			4.6	
4		no	4.5	
5			4.5	
6			4.5	
7	air	yes	6.8	6.1±0.8

8			5.2	
9			6.2	
10		no	4.5	4.2±0.7
11			3.4	
12			4.8	

Results of the assay for intermediate **19** in Ni-catalyzed oxidation of **2** by GC before and after addition of PPh₃ are summarized in Table S10. All reactions were repeated three times and the average A/K ratio was calculated as the arithmetic mean of the ratios from the three reactions. The derivation of the percentage of **19** in the total amount of oxidized products is presented in Scheme S1. The ratio of alcohol **4a** in the total amount of oxidized products is assumed to be x and that of ketone **4b** is assumed to be y ; in this case the ratio of intermediate **19** would be $1-x-y$. Because intermediate **19** decomposes in the GC to afford **4a** and **4b** in roughly 1:1 ratio, eq S5 can be established based on experimental data from Table S10, Entries 10-12. Because treatment of **19** with PPh₃ results in quantitative formation of **4a**, eq S6 can be established based on data from Table S10, Entries 7-9. Solving for equations S5, S6 gives $x = 76%$, $y = 14%$, and $1-x-y = 10%$, indicating that intermediate **19** only accounts for 10% of the total amount of oxidized products and that trapping of alkyl radicals by O₂ is not the major pathway for the formation of C–O bonds.



Scheme S1. Derivation of the percentage of **19** in the total amount of oxidized products.

13. References

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14. X-ray Crystallographic Data

13.1. Ni(Me₄Phen)₂Cl₂ (**1a**)

A light blue block 0.23 x 0.14 x 0.07 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 30.23 mm and exposure time was 0.50 seconds per frame at low angles and 1.50 seconds per frame at high angles, using a scan width of 0.5°. Data collection was 100% complete to 74.000° in θ . A total of 37258 reflections were collected covering the indices $-14 \leq h \leq 14$, $-20 \leq k \leq 32$, $-15 \leq l \leq 15$. 6886 reflections were found to be symmetry independent, with an R_{int} of 0.0585. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21/c (No. 14). The data were integrated using the CrysAlis^{Pro} 1.171.40.50a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the

proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Electron density most likely corresponding to one or (possibly) more highly disordered methanol molecules was masked using the SQUEEZE function.

Table 1. Crystal data and structure refinement for Yehao003_Hartwig.

Identification code	Yehao003_Hartwig	
Empirical formula	C ₃₄ H ₃₅ Cl ₂ N ₅ Ni	
Formula weight	643.28	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.4248(2) Å	α = 90°.
	b = 25.6713(3) Å	β = 115.298(2)°.
	c = 12.7082(2) Å	γ = 90°.
Volume	3369.73(10) Å ³	
Z	4	
Density (calculated)	1.268 Mg/m ³	
Absorption coefficient	2.515 mm ⁻¹	
F(000)	1344	
Crystal size	0.230 x 0.140 x 0.070 mm ³	
Theta range for data collection	3.443 to 74.502°.	
Index ranges	-14 ≤ h ≤ 14, -20 ≤ k ≤ 32, -15 ≤ l ≤ 15	
Reflections collected	37258	
Independent reflections	6886 [R(int) = 0.0585]	
Completeness to theta = 74.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.78221	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6886 / 0 / 388	
Goodness-of-fit on F ²	1.067	

Final R indices [$I > 2\sigma(I)$]	R1 = 0.0427, wR2 = 0.1227
R indices (all data)	R1 = 0.0461, wR2 = 0.1252
Extinction coefficient	n/a
Largest diff. peak and hole	0.415 and -0.493 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for yehao003_hartwig. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5031(2)	3761(1)	9766(2)	28(1)
C(2)	5628(2)	3474(1)	10803(2)	31(1)
C(3)	6313(2)	3761(1)	11933(2)	41(1)
C(4)	5569(2)	2934(1)	10745(2)	32(1)
C(5)	6226(2)	2609(1)	11828(2)	43(1)
C(6)	4879(2)	2699(1)	9641(2)	31(1)
C(7)	4715(2)	2145(1)	9461(2)	38(1)
C(8)	4024(2)	1938(1)	8395(2)	39(1)
C(9)	3429(2)	2258(1)	7376(2)	35(1)
C(10)	2711(2)	2060(1)	6236(2)	38(1)
C(11)	2513(3)	1483(1)	6011(3)	50(1)
C(12)	2198(2)	2412(1)	5326(2)	38(1)
C(13)	1423(3)	2246(1)	4092(2)	53(1)
C(14)	2396(2)	2948(1)	5579(2)	34(1)
C(15)	3576(2)	2801(1)	7525(2)	29(1)
C(16)	4308(2)	3021(1)	8660(2)	27(1)
C(17)	1220(2)	4341(1)	4879(2)	28(1)
C(18)	690(2)	4561(1)	3761(2)	30(1)
C(19)	-733(2)	4672(1)	3186(2)	36(1)
C(20)	1510(2)	4668(1)	3234(2)	29(1)
C(21)	989(2)	4917(1)	2052(2)	38(1)
C(22)	2841(2)	4534(1)	3842(2)	27(1)
C(23)	3801(2)	4619(1)	3408(2)	29(1)
C(24)	5054(2)	4476(1)	4015(2)	30(1)
C(25)	5498(2)	4232(1)	5134(2)	28(1)

C(26)	6794(2)	4066(1)	5793(2)	30(1)
C(27)	7782(2)	4132(1)	5311(2)	37(1)
C(28)	7108(2)	3841(1)	6878(2)	31(1)
C(29)	8424(2)	3628(1)	7644(2)	40(1)
C(30)	6125(2)	3797(1)	7267(2)	28(1)
C(31)	4592(2)	4156(1)	5595(2)	26(1)
C(32)	3262(2)	4307(1)	4946(2)	25(1)
C(33)	7637(3)	4640(1)	9978(2)	53(1)
C(34)	7239(3)	5159(1)	9999(2)	50(1)
Cl(1)	1448(1)	3914(1)	7469(1)	32(1)
Cl(2)	4022(1)	4795(1)	7903(1)	30(1)
N(1)	4394(2)	3550(1)	8729(1)	25(1)
N(2)	3054(2)	3143(1)	6632(2)	28(1)
N(3)	2455(2)	4216(1)	5465(1)	26(1)
N(4)	4916(2)	3943(1)	6662(1)	25(1)
N(5)	7996(3)	4215(1)	9981(2)	74(1)
Ni(1)	3374(1)	3930(1)	7150(1)	24(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for yehao003_hartwig.

C(1)-N(1)	1.319(2)
C(1)-C(2)	1.406(3)
C(1)-H(1)	0.9500
C(2)-C(4)	1.387(3)
C(2)-C(3)	1.504(3)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-C(6)	1.418(3)
C(4)-C(5)	1.508(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(16)	1.404(3)
C(6)-C(7)	1.439(3)

C(7)-C(8)	1.351(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.436(3)
C(8)-H(8)	0.9500
C(9)-C(15)	1.407(3)
C(9)-C(10)	1.419(3)
C(10)-C(12)	1.385(3)
C(10)-C(11)	1.508(3)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(14)	1.408(3)
C(12)-C(13)	1.496(3)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-N(2)	1.322(3)
C(14)-H(14)	0.9500
C(15)-N(2)	1.355(3)
C(15)-C(16)	1.437(3)
C(16)-N(1)	1.362(2)
C(17)-N(3)	1.322(2)
C(17)-C(18)	1.404(3)
C(17)-H(17)	0.9500
C(18)-C(20)	1.391(3)
C(18)-C(19)	1.498(3)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(22)	1.423(3)
C(20)-C(21)	1.503(3)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(32)	1.400(3)
C(22)-C(23)	1.439(3)

C(23)-C(24)	1.354(3)
C(23)-H(23)	0.9500
C(24)-C(25)	1.433(3)
C(24)-H(24)	0.9500
C(25)-C(31)	1.405(3)
C(25)-C(26)	1.419(3)
C(26)-C(28)	1.392(3)
C(26)-C(27)	1.507(3)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-C(30)	1.411(3)
C(28)-C(29)	1.502(3)
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-N(4)	1.316(2)
C(30)-H(30)	0.9500
C(31)-N(4)	1.358(2)
C(31)-C(32)	1.438(3)
C(32)-N(3)	1.364(2)
C(33)-N(5)	1.164(4)
C(33)-C(34)	1.414(4)
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
Cl(1)-Ni(1)	2.4026(5)
Cl(2)-Ni(1)	2.4056(5)
N(1)-Ni(1)	2.0822(16)
N(2)-Ni(1)	2.1073(16)
N(3)-Ni(1)	2.0757(16)
N(4)-Ni(1)	2.1030(16)
N(1)-C(1)-C(2)	124.14(17)
N(1)-C(1)-H(1)	117.9
C(2)-C(1)-H(1)	117.9

C(4)-C(2)-C(1)	118.76(19)
C(4)-C(2)-C(3)	122.33(18)
C(1)-C(2)-C(3)	118.92(17)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(2)-C(4)-C(6)	118.17(18)
C(2)-C(4)-C(5)	120.75(19)
C(6)-C(4)-C(5)	121.08(18)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(16)-C(6)-C(4)	118.61(17)
C(16)-C(6)-C(7)	117.46(19)
C(4)-C(6)-C(7)	123.93(18)
C(8)-C(7)-C(6)	121.8(2)
C(8)-C(7)-H(7)	119.1
C(6)-C(7)-H(7)	119.1
C(7)-C(8)-C(9)	121.95(19)
C(7)-C(8)-H(8)	119.0
C(9)-C(8)-H(8)	119.0
C(15)-C(9)-C(10)	118.5(2)
C(15)-C(9)-C(8)	117.5(2)
C(10)-C(9)-C(8)	124.08(19)
C(12)-C(10)-C(9)	118.14(19)
C(12)-C(10)-C(11)	120.5(2)
C(9)-C(10)-C(11)	121.4(2)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5

C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-C(14)	118.5(2)
C(10)-C(12)-C(13)	122.6(2)
C(14)-C(12)-C(13)	118.9(2)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
N(2)-C(14)-C(12)	124.6(2)
N(2)-C(14)-H(14)	117.7
C(12)-C(14)-H(14)	117.7
N(2)-C(15)-C(9)	122.94(19)
N(2)-C(15)-C(16)	116.45(16)
C(9)-C(15)-C(16)	120.61(18)
N(1)-C(16)-C(6)	122.48(18)
N(1)-C(16)-C(15)	116.83(17)
C(6)-C(16)-C(15)	120.68(17)
N(3)-C(17)-C(18)	124.19(18)
N(3)-C(17)-H(17)	117.9
C(18)-C(17)-H(17)	117.9
C(20)-C(18)-C(17)	118.58(18)
C(20)-C(18)-C(19)	122.76(18)
C(17)-C(18)-C(19)	118.65(18)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-C(22)	118.31(17)
C(18)-C(20)-C(21)	120.33(18)
C(22)-C(20)-C(21)	121.36(18)

C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(32)-C(22)-C(20)	118.32(17)
C(32)-C(22)-C(23)	117.06(17)
C(20)-C(22)-C(23)	124.62(17)
C(24)-C(23)-C(22)	122.25(18)
C(24)-C(23)-H(23)	118.9
C(22)-C(23)-H(23)	118.9
C(23)-C(24)-C(25)	121.58(17)
C(23)-C(24)-H(24)	119.2
C(25)-C(24)-H(24)	119.2
C(31)-C(25)-C(26)	118.66(17)
C(31)-C(25)-C(24)	117.57(17)
C(26)-C(25)-C(24)	123.77(17)
C(28)-C(26)-C(25)	118.18(17)
C(28)-C(26)-C(27)	121.86(18)
C(25)-C(26)-C(27)	119.96(18)
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(28)-C(30)	118.19(18)
C(26)-C(28)-C(29)	123.79(18)
C(30)-C(28)-C(29)	117.99(19)
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5

N(4)-C(30)-C(28)	124.52(18)
N(4)-C(30)-H(30)	117.7
C(28)-C(30)-H(30)	117.7
N(4)-C(31)-C(25)	122.53(17)
N(4)-C(31)-C(32)	116.87(16)
C(25)-C(31)-C(32)	120.60(17)
N(3)-C(32)-C(22)	122.77(17)
N(3)-C(32)-C(31)	116.33(16)
C(22)-C(32)-C(31)	120.90(17)
N(5)-C(33)-C(34)	178.3(3)
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(1)-N(1)-C(16)	117.83(16)
C(1)-N(1)-Ni(1)	127.88(12)
C(16)-N(1)-Ni(1)	114.16(13)
C(14)-N(2)-C(15)	117.30(17)
C(14)-N(2)-Ni(1)	128.89(14)
C(15)-N(2)-Ni(1)	113.78(13)
C(17)-N(3)-C(32)	117.79(16)
C(17)-N(3)-Ni(1)	127.88(13)
C(32)-N(3)-Ni(1)	114.24(12)
C(30)-N(4)-C(31)	117.88(16)
C(30)-N(4)-Ni(1)	128.75(13)
C(31)-N(4)-Ni(1)	113.29(12)
N(3)-Ni(1)-N(1)	171.22(6)
N(3)-Ni(1)-N(4)	78.96(6)
N(1)-Ni(1)-N(4)	95.60(6)
N(3)-Ni(1)-N(2)	94.22(6)
N(1)-Ni(1)-N(2)	78.67(6)
N(4)-Ni(1)-N(2)	88.77(6)
N(3)-Ni(1)-Cl(1)	94.81(5)
N(1)-Ni(1)-Cl(1)	90.29(4)

N(4)-Ni(1)-Cl(1)	173.32(5)
N(2)-Ni(1)-Cl(1)	89.28(5)
N(3)-Ni(1)-Cl(2)	90.98(4)
N(1)-Ni(1)-Cl(2)	95.63(4)
N(4)-Ni(1)-Cl(2)	87.03(4)
N(2)-Ni(1)-Cl(2)	172.57(5)
Cl(1)-Ni(1)-Cl(2)	95.563(19)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for yehao003_hartwig. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	32(1)	23(1)	30(1)	1(1)	14(1)	1(1)
C(2)	34(1)	28(1)	31(1)	2(1)	14(1)	2(1)
C(3)	56(1)	32(1)	30(1)	2(1)	13(1)	0(1)
C(4)	36(1)	28(1)	33(1)	6(1)	15(1)	2(1)
C(5)	54(1)	32(1)	39(1)	10(1)	15(1)	4(1)
C(6)	33(1)	24(1)	37(1)	3(1)	16(1)	1(1)
C(7)	42(1)	24(1)	45(1)	5(1)	16(1)	1(1)
C(8)	43(1)	22(1)	51(1)	1(1)	19(1)	0(1)
C(9)	34(1)	27(1)	45(1)	-4(1)	18(1)	-2(1)
C(10)	35(1)	30(1)	49(1)	-8(1)	17(1)	-4(1)
C(11)	53(1)	30(1)	61(2)	-12(1)	18(1)	-5(1)
C(12)	37(1)	36(1)	41(1)	-12(1)	17(1)	-7(1)
C(13)	61(2)	48(1)	47(2)	-16(1)	20(1)	-13(1)
C(14)	35(1)	34(1)	31(1)	-4(1)	13(1)	-3(1)
C(15)	27(1)	24(1)	35(1)	-1(1)	14(1)	-1(1)
C(16)	28(1)	23(1)	34(1)	2(1)	16(1)	1(1)
C(17)	28(1)	28(1)	27(1)	1(1)	11(1)	-1(1)
C(18)	30(1)	27(1)	30(1)	0(1)	11(1)	0(1)
C(19)	32(1)	41(1)	31(1)	5(1)	10(1)	3(1)
C(20)	35(1)	24(1)	26(1)	1(1)	10(1)	-2(1)

C(21)	39(1)	41(1)	31(1)	8(1)	11(1)	-1(1)
C(22)	32(1)	22(1)	28(1)	0(1)	13(1)	-4(1)
C(23)	40(1)	25(1)	28(1)	1(1)	19(1)	-4(1)
C(24)	35(1)	25(1)	34(1)	-3(1)	20(1)	-5(1)
C(25)	32(1)	23(1)	31(1)	-5(1)	17(1)	-5(1)
C(26)	30(1)	26(1)	35(1)	-5(1)	17(1)	-5(1)
C(27)	32(1)	44(1)	40(1)	-3(1)	20(1)	-5(1)
C(28)	28(1)	31(1)	35(1)	-5(1)	14(1)	-3(1)
C(29)	29(1)	49(1)	44(1)	2(1)	16(1)	2(1)
C(30)	30(1)	26(1)	29(1)	-1(1)	13(1)	-1(1)
C(31)	29(1)	20(1)	29(1)	-2(1)	13(1)	-4(1)
C(32)	30(1)	21(1)	26(1)	0(1)	15(1)	-3(1)
C(33)	55(2)	68(2)	37(1)	-12(1)	21(1)	-17(1)
C(34)	49(1)	68(2)	35(1)	-1(1)	19(1)	-1(1)
Cl(1)	29(1)	36(1)	36(1)	8(1)	17(1)	3(1)
Cl(2)	37(1)	24(1)	30(1)	2(1)	15(1)	0(1)
N(1)	26(1)	21(1)	30(1)	1(1)	14(1)	1(1)
N(2)	29(1)	25(1)	33(1)	-2(1)	14(1)	-2(1)
N(3)	28(1)	25(1)	26(1)	-1(1)	12(1)	-2(1)
N(4)	27(1)	23(1)	27(1)	-1(1)	12(1)	-2(1)
N(5)	77(2)	78(2)	63(2)	-19(1)	24(1)	-14(2)
Ni(1)	25(1)	23(1)	25(1)	2(1)	11(1)	0(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for yehao003_hartwig.

	x	y	z	U(eq)
H(1)	5090	4130	9816	34
H(3A)	6208	4137	11790	61
H(3B)	7236	3673	12276	61
H(3C)	5943	3661	12471	61
H(5A)	5678	2309	11793	64
H(5B)	6367	2820	12514	64

H(5C)	7061	2485	11882	64
H(7)	5104	1918	10110	46
H(8)	3928	1571	8318	47
H(11A)	1884	1355	6285	75
H(11B)	3339	1301	6426	75
H(11C)	2188	1416	5174	75
H(13A)	609	2088	4015	79
H(13B)	1918	1991	3873	79
H(13C)	1235	2550	3579	79
H(14)	2031	3185	4948	41
H(17)	656	4277	5238	33
H(19A)	-872	5046	3032	54
H(19B)	-1128	4562	3699	54
H(19C)	-1130	4480	2450	54
H(21A)	1680	5115	1971	57
H(21B)	278	5153	1962	57
H(21C)	671	4646	1451	57
H(23)	3547	4780	2671	35
H(24)	5652	4539	3691	36
H(27A)	7630	3871	4703	56
H(27B)	8653	4085	5938	56
H(27C)	7706	4481	4980	56
H(29A)	8451	3529	8399	61
H(29B)	9081	3895	7760	61
H(29C)	8599	3322	7274	61
H(30)	6353	3653	8017	34
H(34A)	6379	5213	9360	75
H(34B)	7858	5398	9907	75
H(34C)	7202	5227	10743	75

13.2. Ni(Brbpy)₂Cl₂ (**1f**)

A green block 0.29 x 0.23 x 0.17 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 33.00 mm and exposure time was 1.00 seconds per frame at low and high angles using a scan width of 0.5°. Data

collection was 100% complete to 26.359° in θ . A total of 24612 reflections were collected covering the indices $-19 \leq h \leq 20$, $-15 \leq k \leq 15$, $-15 \leq l \leq 15$. 2418 reflections were founded to be symmetry independent, with an R_{int} of 0.1056. Indexing and unit cell refinement indicated a centered, monoclinic lattice. The space group was found to be C 2/c (No. 15). The data were integrated using the CrysAlis^{Pro} 1.171.40.79a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Electron density attributable to outer sphere solvent (unidentifiable amongst the solvents used: methanol, acetonitrile and diethyl ether) was treated using the solvent mask option included within the OLEX2 software.

Table 1. Crystal data and structure refinement for Yehao005_Hartwig.

Identification code	Yehao005_Hartwig	
Empirical formula	C ₂₀ H ₁₄ Br ₂ Cl ₂ N ₄ Ni	
Formula weight	599.78	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 16.1864(6) Å	$\alpha = 90^\circ$.
	b = 12.0596(4) Å	$\beta = 106.161(4)^\circ$.
	c = 12.6122(4) Å	$\gamma = 90^\circ$.
Volume	2364.63(15) Å ³	
Z	4	
Density (calculated)	1.685 Mg/m ³	
Absorption coefficient	4.439 mm ⁻¹	
F(000)	1176	
Crystal size	0.29 x 0.23 x 0.17 mm ³	
Theta range for data collection	2.937 to 26.359°.	
Index ranges	$-19 \leq h \leq 20$, $-15 \leq k \leq 15$, $-15 \leq l \leq 15$	

Reflections collected	24612
Independent reflections	2418 [R(int) = 0.1056]
Completeness to theta = 26.359°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.64989
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2418 / 0 / 132
Goodness-of-fit on F ²	1.267
Final R indices [I>2sigma(I)]	R1 = 0.0474, wR2 = 0.1174
R indices (all data)	R1 = 0.0485, wR2 = 0.1179
Extinction coefficient	n/a
Largest diff. peak and hole	0.620 and -0.731 e.Å ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for yehao005_hartwig. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3634(3)	4069(4)	7438(4)	14(1)
C(2)	2872(3)	4634(5)	6967(4)	19(1)
C(3)	2502(3)	4489(5)	5854(5)	21(1)
C(4)	2907(3)	3825(4)	5250(4)	16(1)
C(5)	3663(3)	3309(4)	5802(4)	12(1)
C(6)	4141(3)	2597(4)	5207(4)	13(1)
C(7)	3894(4)	2504(4)	4055(4)	21(1)
C(8)	4364(4)	1851(4)	3549(4)	19(1)
C(9)	5074(4)	1296(4)	4195(4)	20(1)
C(10)	5289(3)	1431(4)	5327(4)	16(1)
Br(1)	4153(1)	4346(1)	8961(1)	24(1)
Cl(1)	3821(1)	800(1)	7113(1)	16(1)
N(1)	4020(3)	3396(3)	6911(3)	13(1)
N(2)	4835(3)	2068(3)	5823(3)	12(1)
Ni(1)	5000	2124(1)	7500	9(1)

Table 3. Bond lengths [Å] and angles [°] for yehao005_hartwig.

C(1)-N(1)	1.313(6)
C(1)-C(2)	1.389(7)
C(1)-Br(1)	1.900(5)
C(2)-C(3)	1.375(8)
C(2)-H(2)	0.9500
C(3)-C(4)	1.388(7)
C(3)-H(3)	0.9500
C(4)-C(5)	1.378(7)
C(4)-H(4)	0.9500
C(5)-N(1)	1.361(6)
C(5)-C(6)	1.490(7)
C(6)-N(2)	1.336(6)
C(6)-C(7)	1.401(7)
C(7)-C(8)	1.369(8)
C(7)-H(7)	0.9500
C(8)-C(9)	1.382(8)
C(8)-H(8)	0.9500
C(9)-C(10)	1.382(7)
C(9)-H(9)	0.9500
C(10)-N(2)	1.333(6)
C(10)-H(10)	0.9500
Cl(1)-Ni(1)	2.4318(13)
N(1)-Ni(1)	2.183(4)
N(2)-Ni(1)	2.058(4)
Ni(1)-N(2)#1	2.058(4)
Ni(1)-N(1)#1	2.183(4)
Ni(1)-Cl(1)#1	2.4318(13)
N(1)-C(1)-C(2)	125.3(5)
N(1)-C(1)-Br(1)	118.8(4)
C(2)-C(1)-Br(1)	115.9(4)
C(3)-C(2)-C(1)	117.2(5)
C(3)-C(2)-H(2)	121.4
C(1)-C(2)-H(2)	121.4

C(2)-C(3)-C(4)	119.7(5)
C(2)-C(3)-H(3)	120.1
C(4)-C(3)-H(3)	120.1
C(5)-C(4)-C(3)	118.2(5)
C(5)-C(4)-H(4)	120.9
C(3)-C(4)-H(4)	120.9
N(1)-C(5)-C(4)	123.2(4)
N(1)-C(5)-C(6)	115.5(4)
C(4)-C(5)-C(6)	121.3(4)
N(2)-C(6)-C(7)	121.0(5)
N(2)-C(6)-C(5)	116.9(4)
C(7)-C(6)-C(5)	122.0(5)
C(8)-C(7)-C(6)	119.6(5)
C(8)-C(7)-H(7)	120.2
C(6)-C(7)-H(7)	120.2
C(7)-C(8)-C(9)	118.8(5)
C(7)-C(8)-H(8)	120.6
C(9)-C(8)-H(8)	120.6
C(10)-C(9)-C(8)	118.8(5)
C(10)-C(9)-H(9)	120.6
C(8)-C(9)-H(9)	120.6
N(2)-C(10)-C(9)	122.6(5)
N(2)-C(10)-H(10)	118.7
C(9)-C(10)-H(10)	118.7
C(1)-N(1)-C(5)	116.3(4)
C(1)-N(1)-Ni(1)	131.7(3)
C(5)-N(1)-Ni(1)	110.8(3)
C(10)-N(2)-C(6)	119.1(4)
C(10)-N(2)-Ni(1)	124.7(3)
C(6)-N(2)-Ni(1)	115.4(3)
N(2)#1-Ni(1)-N(2)	176.2(2)
N(2)#1-Ni(1)-N(1)	104.31(15)
N(2)-Ni(1)-N(1)	78.40(16)
N(2)#1-Ni(1)-N(1)#1	78.40(16)
N(2)-Ni(1)-N(1)#1	104.31(15)
N(1)-Ni(1)-N(1)#1	90.7(2)

N(2)#1-Ni(1)-Cl(1)	93.15(12)
N(2)-Ni(1)-Cl(1)	84.37(11)
N(1)-Ni(1)-Cl(1)	86.45(11)
N(1)#1-Ni(1)-Cl(1)	170.14(11)
N(2)#1-Ni(1)-Cl(1)#1	84.37(11)
N(2)-Ni(1)-Cl(1)#1	93.15(12)
N(1)-Ni(1)-Cl(1)#1	170.14(11)
N(1)#1-Ni(1)-Cl(1)#1	86.45(11)
Cl(1)-Ni(1)-Cl(1)#1	97.89(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for yehao005_hartwig. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	12(2)	12(2)	16(2)	-4(2)	3(2)	-1(2)
C(2)	14(2)	20(3)	24(3)	-3(2)	6(2)	2(2)
C(3)	10(2)	19(3)	30(3)	4(2)	1(2)	5(2)
C(4)	13(2)	12(2)	19(2)	-2(2)	0(2)	-5(2)
C(5)	12(2)	9(2)	12(2)	-1(2)	0(2)	-2(2)
C(6)	15(2)	12(2)	11(2)	2(2)	0(2)	-2(2)
C(7)	30(3)	14(2)	12(2)	-1(2)	-5(2)	-2(2)
C(8)	35(3)	13(2)	10(2)	-1(2)	6(2)	-5(2)
C(9)	34(3)	16(3)	16(2)	-4(2)	16(2)	1(2)
C(10)	16(2)	16(2)	16(2)	0(2)	8(2)	2(2)
Br(1)	25(1)	28(1)	16(1)	-9(1)	3(1)	12(1)
Cl(1)	14(1)	16(1)	16(1)	2(1)	1(1)	-5(1)
N(1)	11(2)	14(2)	12(2)	-1(2)	3(2)	-2(2)
N(2)	14(2)	13(2)	12(2)	-2(2)	7(2)	-2(2)
Ni(1)	9(1)	9(1)	8(1)	0	2(1)	0

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for yehao005_hartwig.

	x	y	z	U(eq)
H(2)	2618	5101	7395	23
H(3)	1972	4841	5500	25
H(4)	2668	3730	4478	19
H(7)	3404	2893	3626	25
H(8)	4205	1781	2768	23
H(9)	5407	831	3867	24
H(10)	5780	1055	5770	19

Table 6. Torsion angles [$^\circ$] for yehao005_hartwig.

N(1)-C(1)-C(2)-C(3)	-1.1(8)
Br(1)-C(1)-C(2)-C(3)	177.1(4)
C(1)-C(2)-C(3)-C(4)	-1.9(8)
C(2)-C(3)-C(4)-C(5)	1.6(8)
C(3)-C(4)-C(5)-N(1)	1.7(7)
C(3)-C(4)-C(5)-C(6)	-179.1(5)
N(1)-C(5)-C(6)-N(2)	3.9(6)
C(4)-C(5)-C(6)-N(2)	-175.4(4)
N(1)-C(5)-C(6)-C(7)	-174.3(5)
C(4)-C(5)-C(6)-C(7)	6.4(7)
N(2)-C(6)-C(7)-C(8)	0.9(8)
C(5)-C(6)-C(7)-C(8)	179.0(5)
C(6)-C(7)-C(8)-C(9)	0.0(8)
C(7)-C(8)-C(9)-C(10)	-0.7(8)
C(8)-C(9)-C(10)-N(2)	0.6(8)
C(2)-C(1)-N(1)-C(5)	4.2(7)
Br(1)-C(1)-N(1)-C(5)	-174.0(3)

C(2)-C(1)-N(1)-Ni(1)	-162.2(4)
Br(1)-C(1)-N(1)-Ni(1)	19.6(6)
C(4)-C(5)-N(1)-C(1)	-4.4(7)
C(6)-C(5)-N(1)-C(1)	176.3(4)
C(4)-C(5)-N(1)-Ni(1)	164.7(4)
C(6)-C(5)-N(1)-Ni(1)	-14.5(5)
C(9)-C(10)-N(2)-C(6)	0.3(8)
C(9)-C(10)-N(2)-Ni(1)	170.2(4)
C(7)-C(6)-N(2)-C(10)	-1.0(7)
C(5)-C(6)-N(2)-C(10)	-179.2(4)
C(7)-C(6)-N(2)-Ni(1)	-171.8(4)
C(5)-C(6)-N(2)-Ni(1)	10.0(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

13.3. Ni(bpyPY2Me)Cl₂ (**1g**)

A red block 0.43 x 0.31 x 0.24 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 33.00 mm and exposure time was 0.50 seconds per frame at low and high angles using a scan width of 0.5°. Data collection was 100% complete to 26.372° in θ . A total of 23753 reflections were collected covering the indices $-12 \leq h \leq 11$, $-13 \leq k \leq 13$, $-15 \leq l \leq 15$. 4753 reflections were founded to be symmetry independent, with an R_{int} of 0.0873. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be P -1 (No. 2). The data were integrated using the CrysAlis^{Pro} 1.171.40.79a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Table 1. Crystal data and structure refinement for Yehao004_Hartwig.

Identification code	Yehao004_Hartwig	
Empirical formula	C ₂₄ H ₂₆ Cl ₂ N ₄ Ni O ₂	
Formula weight	532.10	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.6088(2) Å	α = 102.911(2)°.
	b = 10.9517(3) Å	β = 95.301(2)°.
	c = 12.2940(2) Å	γ = 109.822(2)°.
Volume	1166.19(5) Å ³	
Z	2	
Density (calculated)	1.515 Mg/m ³	
Absorption coefficient	1.091 mm ⁻¹	
F(000)	552	
Crystal size	0.43 x 0.31 x 0.24 mm ³	
Theta range for data collection	2.915 to 26.372°.	
Index ranges	-12 ≤ h ≤ 11, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15	
Reflections collected	23753	
Independent reflections	4753 [R(int) = 0.0873]	
Completeness to theta = 26.372°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.71519	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4753 / 0 / 309	
Goodness-of-fit on F ²	1.101	
Final R indices [I > 2σ(I)]	R1 = 0.0352, wR2 = 0.0960	
R indices (all data)	R1 = 0.0374, wR2 = 0.0974	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.437 and -0.420 e.Å ⁻³	

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for yehao004_hartwig. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2736(2)	5517(2)	4843(2)	14(1)
C(2)	1795(2)	4863(2)	3798(2)	16(1)
C(3)	665(2)	5300(2)	3500(2)	16(1)
C(4)	522(2)	6395(2)	4248(2)	14(1)
C(5)	1534(2)	7031(2)	5270(1)	11(1)
C(6)	1546(2)	8339(2)	6079(1)	12(1)
C(7)	281(2)	8735(2)	5598(2)	16(1)
C(8)	3107(2)	9458(2)	6181(1)	12(1)
C(9)	3259(2)	10596(2)	5814(2)	16(1)
C(10)	4688(2)	11571(2)	5940(2)	18(1)
C(11)	5924(2)	11386(2)	6431(2)	18(1)
C(12)	5701(2)	10210(2)	6751(2)	15(1)
C(13)	1381(2)	8213(2)	7288(1)	12(1)
C(14)	277(2)	8491(2)	7846(2)	16(1)
C(15)	350(2)	8507(2)	8981(2)	19(1)
C(16)	1537(2)	8333(2)	9570(2)	17(1)
C(17)	2609(2)	8084(2)	8969(2)	14(1)
C(18)	4058(2)	8077(2)	9500(2)	14(1)
C(19)	4382(2)	8124(2)	10633(2)	19(1)
C(20)	5795(2)	8177(2)	11062(2)	21(1)
C(21)	6837(2)	8182(2)	10357(2)	22(1)
C(22)	6411(2)	8124(2)	9229(2)	21(1)
C(23)	4128(3)	4620(3)	7370(3)	44(1)
C(24)	1820(3)	4814(2)	9979(2)	39(1)
Cl(1)	6199(1)	7257(1)	6403(1)	16(1)
Cl(2)	-217(1)	1665(1)	7801(1)	23(1)
N(1)	2617(2)	6584(1)	5563(1)	11(1)
N(2)	4329(2)	9269(1)	6637(1)	12(1)
N(3)	2467(2)	7948(1)	7844(1)	11(1)
N(4)	5059(2)	8073(2)	8802(1)	15(1)
Ni(1)	4073(1)	7492(1)	7079(1)	10(1)
O(1)	3299(2)	5477(1)	7376(1)	19(1)
O(2)	1443(2)	4666(2)	8806(1)	30(1)

Table 3. Bond lengths [Å] and angles [°] for yehao004_hartwig.

C(1)-N(1)	1.345(2)
C(1)-C(2)	1.385(3)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.378(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.394(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.391(2)
C(4)-H(4)	0.9500
C(5)-N(1)	1.345(2)
C(5)-C(6)	1.546(2)
C(6)-C(7)	1.535(2)
C(6)-C(13)	1.541(2)
C(6)-C(8)	1.555(2)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-N(2)	1.352(2)
C(8)-C(9)	1.385(3)
C(9)-C(10)	1.394(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.379(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.384(3)
C(11)-H(11)	0.9500
C(12)-N(2)	1.342(2)
C(12)-H(12)	0.9500
C(13)-N(3)	1.342(2)
C(13)-C(14)	1.396(2)
C(14)-C(15)	1.387(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.384(3)

C(15)-H(15)	0.9500
C(16)-C(17)	1.387(3)
C(16)-H(16)	0.9500
C(17)-N(3)	1.347(2)
C(17)-C(18)	1.485(2)
C(18)-N(4)	1.348(2)
C(18)-C(19)	1.384(3)
C(19)-C(20)	1.388(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.382(3)
C(20)-H(20)	0.9500
C(21)-C(22)	1.391(3)
C(21)-H(21)	0.9500
C(22)-N(4)	1.333(2)
C(22)-H(22)	0.9500
C(23)-O(1)	1.421(2)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-O(2)	1.413(3)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
Cl(1)-Ni(1)	2.3463(4)
N(1)-Ni(1)	2.0409(14)
N(2)-Ni(1)	2.0773(15)
N(3)-Ni(1)	2.0242(14)
N(4)-Ni(1)	2.0989(15)
Ni(1)-O(1)	2.2031(14)
O(1)-H(1)	0.87(3)
O(2)-H(2A)	0.83(4)
N(1)-C(1)-C(2)	122.57(16)
N(1)-C(1)-H(1A)	118.7
C(2)-C(1)-H(1A)	118.7
C(3)-C(2)-C(1)	118.56(16)

C(3)-C(2)-H(2)	120.7
C(1)-C(2)-H(2)	120.7
C(2)-C(3)-C(4)	119.23(16)
C(2)-C(3)-H(3)	120.4
C(4)-C(3)-H(3)	120.4
C(5)-C(4)-C(3)	119.23(16)
C(5)-C(4)-H(4)	120.4
C(3)-C(4)-H(4)	120.4
N(1)-C(5)-C(4)	121.19(15)
N(1)-C(5)-C(6)	116.75(14)
C(4)-C(5)-C(6)	121.92(15)
C(7)-C(6)-C(13)	109.36(14)
C(7)-C(6)-C(5)	110.04(14)
C(13)-C(6)-C(5)	112.86(14)
C(7)-C(6)-C(8)	110.49(14)
C(13)-C(6)-C(8)	106.77(13)
C(5)-C(6)-C(8)	107.27(13)
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
N(2)-C(8)-C(9)	120.87(16)
N(2)-C(8)-C(6)	117.05(15)
C(9)-C(8)-C(6)	122.08(15)
C(8)-C(9)-C(10)	119.37(17)
C(8)-C(9)-H(9)	120.3
C(10)-C(9)-H(9)	120.3
C(11)-C(10)-C(9)	119.39(17)
C(11)-C(10)-H(10)	120.3
C(9)-C(10)-H(10)	120.3
C(10)-C(11)-C(12)	118.42(17)
C(10)-C(11)-H(11)	120.8
C(12)-C(11)-H(11)	120.8
N(2)-C(12)-C(11)	122.56(17)

N(2)-C(12)-H(12)	118.7
C(11)-C(12)-H(12)	118.7
N(3)-C(13)-C(14)	120.12(16)
N(3)-C(13)-C(6)	116.02(14)
C(14)-C(13)-C(6)	123.52(15)
C(15)-C(14)-C(13)	118.43(16)
C(15)-C(14)-H(14)	120.8
C(13)-C(14)-H(14)	120.8
C(16)-C(15)-C(14)	121.02(17)
C(16)-C(15)-H(15)	119.5
C(14)-C(15)-H(15)	119.5
C(15)-C(16)-C(17)	117.47(16)
C(15)-C(16)-H(16)	121.3
C(17)-C(16)-H(16)	121.3
N(3)-C(17)-C(16)	121.47(16)
N(3)-C(17)-C(18)	114.06(15)
C(16)-C(17)-C(18)	124.20(16)
N(4)-C(18)-C(19)	122.44(17)
N(4)-C(18)-C(17)	114.68(15)
C(19)-C(18)-C(17)	122.84(17)
C(18)-C(19)-C(20)	118.48(18)
C(18)-C(19)-H(19)	120.8
C(20)-C(19)-H(19)	120.8
C(21)-C(20)-C(19)	119.72(17)
C(21)-C(20)-H(20)	120.1
C(19)-C(20)-H(20)	120.1
C(20)-C(21)-C(22)	117.87(18)
C(20)-C(21)-H(21)	121.1
C(22)-C(21)-H(21)	121.1
N(4)-C(22)-C(21)	123.26(19)
N(4)-C(22)-H(22)	118.4
C(21)-C(22)-H(22)	118.4
O(1)-C(23)-H(23A)	109.5
O(1)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
O(1)-C(23)-H(23C)	109.5

H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
O(2)-C(24)-H(24A)	109.5
O(2)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
O(2)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(1)-N(1)-C(5)	119.18(15)
C(1)-N(1)-Ni(1)	119.63(11)
C(5)-N(1)-Ni(1)	121.19(11)
C(12)-N(2)-C(8)	119.36(15)
C(12)-N(2)-Ni(1)	120.72(12)
C(8)-N(2)-Ni(1)	119.86(11)
C(13)-N(3)-C(17)	120.96(14)
C(13)-N(3)-Ni(1)	122.27(11)
C(17)-N(3)-Ni(1)	116.56(11)
C(22)-N(4)-C(18)	118.23(16)
C(22)-N(4)-Ni(1)	126.84(13)
C(18)-N(4)-Ni(1)	113.00(12)
N(3)-Ni(1)-N(1)	91.37(6)
N(3)-Ni(1)-N(2)	81.62(6)
N(1)-Ni(1)-N(2)	84.56(6)
N(3)-Ni(1)-N(4)	78.19(6)
N(1)-Ni(1)-N(4)	163.66(6)
N(2)-Ni(1)-N(4)	106.00(6)
N(3)-Ni(1)-O(1)	91.29(6)
N(1)-Ni(1)-O(1)	85.67(5)
N(2)-Ni(1)-O(1)	167.77(5)
N(4)-Ni(1)-O(1)	82.06(6)
N(3)-Ni(1)-Cl(1)	171.20(4)
N(1)-Ni(1)-Cl(1)	96.40(4)
N(2)-Ni(1)-Cl(1)	94.97(4)
N(4)-Ni(1)-Cl(1)	95.08(4)
O(1)-Ni(1)-Cl(1)	93.40(4)
C(23)-O(1)-Ni(1)	126.91(14)

C(23)-O(1)-H(1)	108.6(19)
Ni(1)-O(1)-H(1)	117.0(19)
C(24)-O(2)-H(2A)	106(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for yehao004_hartwig. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	12(1)	14(1)	17(1)	5(1)	4(1)	7(1)
C(2)	15(1)	13(1)	18(1)	2(1)	4(1)	4(1)
C(3)	13(1)	16(1)	15(1)	4(1)	1(1)	2(1)
C(4)	11(1)	16(1)	15(1)	6(1)	1(1)	5(1)
C(5)	10(1)	12(1)	13(1)	6(1)	5(1)	5(1)
C(6)	11(1)	12(1)	12(1)	4(1)	2(1)	6(1)
C(7)	15(1)	19(1)	18(1)	5(1)	2(1)	10(1)
C(8)	13(1)	14(1)	9(1)	2(1)	4(1)	5(1)
C(9)	22(1)	16(1)	12(1)	4(1)	4(1)	9(1)
C(10)	29(1)	12(1)	14(1)	4(1)	10(1)	6(1)
C(11)	20(1)	16(1)	16(1)	3(1)	9(1)	2(1)
C(12)	13(1)	18(1)	12(1)	1(1)	5(1)	4(1)
C(13)	11(1)	10(1)	15(1)	3(1)	3(1)	3(1)
C(14)	12(1)	16(1)	19(1)	3(1)	3(1)	7(1)
C(15)	15(1)	23(1)	20(1)	4(1)	9(1)	7(1)
C(16)	18(1)	18(1)	13(1)	5(1)	6(1)	5(1)
C(17)	14(1)	13(1)	14(1)	5(1)	4(1)	5(1)
C(18)	17(1)	12(1)	14(1)	4(1)	3(1)	5(1)
C(19)	22(1)	18(1)	16(1)	4(1)	4(1)	7(1)
C(20)	27(1)	22(1)	12(1)	4(1)	-2(1)	8(1)
C(21)	20(1)	26(1)	18(1)	4(1)	-3(1)	9(1)
C(22)	17(1)	30(1)	15(1)	5(1)	0(1)	10(1)
C(23)	54(2)	39(1)	69(2)	34(1)	35(1)	38(1)
C(24)	46(1)	28(1)	33(1)	10(1)	3(1)	1(1)

Cl(1)	12(1)	22(1)	17(1)	5(1)	4(1)	9(1)
Cl(2)	24(1)	24(1)	19(1)	6(1)	2(1)	9(1)
N(1)	9(1)	13(1)	14(1)	6(1)	3(1)	4(1)
N(2)	12(1)	13(1)	10(1)	1(1)	4(1)	4(1)
N(3)	11(1)	11(1)	12(1)	4(1)	3(1)	4(1)
N(4)	15(1)	19(1)	14(1)	5(1)	3(1)	7(1)
Ni(1)	9(1)	14(1)	10(1)	4(1)	2(1)	6(1)
O(1)	23(1)	18(1)	23(1)	10(1)	8(1)	11(1)
O(2)	33(1)	24(1)	30(1)	11(1)	9(1)	5(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for yehao004_hartwig.

	x	y	z	U(eq)
H(1A)	3496	5199	5061	16
H(2)	1925	4129	3297	19
H(3)	-8	4861	2793	19
H(4)	-259	6703	4061	17
H(7A)	414	8861	4845	25
H(7B)	316	9578	6105	25
H(7C)	-694	8020	5538	25
H(9)	2397	10711	5479	19
H(10)	4810	12355	5691	22
H(11)	6906	12050	6546	22
H(12)	6553	10063	7065	18
H(14)	-505	8666	7457	19
H(15)	-427	8638	9361	23
H(16)	1613	8383	10356	20
H(19)	3653	8120	11106	23
H(20)	6046	8210	11836	25
H(21)	7813	8224	10635	27
H(22)	7118	8120	8738	25

H(23A)	4590	4562	6692	65
H(23B)	3449	3718	7364	65
H(23C)	4915	4989	8050	65
H(24A)	2892	4977	10176	58
H(24B)	1219	3988	10161	58
H(24C)	1612	5578	10414	58
H(1)	2690(30)	5340(30)	7860(30)	44(8)
H(2A)	960(40)	3850(40)	8510(30)	54(9)

Table 6. Torsion angles [°] for yehao004_hartwig.

N(1)-C(1)-C(2)-C(3)	-1.9(3)
C(1)-C(2)-C(3)-C(4)	1.0(3)
C(2)-C(3)-C(4)-C(5)	0.8(3)
C(3)-C(4)-C(5)-N(1)	-2.0(3)
C(3)-C(4)-C(5)-C(6)	173.41(16)
N(1)-C(5)-C(6)-C(7)	177.82(15)
C(4)-C(5)-C(6)-C(7)	2.2(2)
N(1)-C(5)-C(6)-C(13)	-59.72(19)
C(4)-C(5)-C(6)-C(13)	124.66(17)
N(1)-C(5)-C(6)-C(8)	57.59(19)
C(4)-C(5)-C(6)-C(8)	-118.02(17)
C(7)-C(6)-C(8)-N(2)	177.45(14)
C(13)-C(6)-C(8)-N(2)	58.62(18)
C(5)-C(6)-C(8)-N(2)	-62.61(18)
C(7)-C(6)-C(8)-C(9)	-3.2(2)
C(13)-C(6)-C(8)-C(9)	-122.07(17)
C(5)-C(6)-C(8)-C(9)	116.70(17)
N(2)-C(8)-C(9)-C(10)	-1.4(3)
C(6)-C(8)-C(9)-C(10)	179.30(15)
C(8)-C(9)-C(10)-C(11)	-0.2(3)
C(9)-C(10)-C(11)-C(12)	1.9(3)
C(10)-C(11)-C(12)-N(2)	-2.2(3)
C(7)-C(6)-C(13)-N(3)	-176.15(14)

C(5)-C(6)-C(13)-N(3)	61.02(19)
C(8)-C(6)-C(13)-N(3)	-56.59(18)
C(7)-C(6)-C(13)-C(14)	-2.9(2)
C(5)-C(6)-C(13)-C(14)	-125.69(17)
C(8)-C(6)-C(13)-C(14)	116.70(17)
N(3)-C(13)-C(14)-C(15)	1.0(3)
C(6)-C(13)-C(14)-C(15)	-172.07(16)
C(13)-C(14)-C(15)-C(16)	3.9(3)
C(14)-C(15)-C(16)-C(17)	-2.8(3)
C(15)-C(16)-C(17)-N(3)	-3.2(3)
C(15)-C(16)-C(17)-C(18)	170.48(17)
N(3)-C(17)-C(18)-N(4)	6.3(2)
C(16)-C(17)-C(18)-N(4)	-167.80(17)
N(3)-C(17)-C(18)-C(19)	-176.07(17)
C(16)-C(17)-C(18)-C(19)	9.8(3)
N(4)-C(18)-C(19)-C(20)	0.4(3)
C(17)-C(18)-C(19)-C(20)	-177.02(16)
C(18)-C(19)-C(20)-C(21)	0.0(3)
C(19)-C(20)-C(21)-C(22)	-0.4(3)
C(20)-C(21)-C(22)-N(4)	0.5(3)
C(2)-C(1)-N(1)-C(5)	0.8(3)
C(2)-C(1)-N(1)-Ni(1)	-179.35(13)
C(4)-C(5)-N(1)-C(1)	1.2(2)
C(6)-C(5)-N(1)-C(1)	-174.46(15)
C(4)-C(5)-N(1)-Ni(1)	-178.64(13)
C(6)-C(5)-N(1)-Ni(1)	5.7(2)
C(11)-C(12)-N(2)-C(8)	0.7(2)
C(11)-C(12)-N(2)-Ni(1)	177.75(13)
C(9)-C(8)-N(2)-C(12)	1.2(2)
C(6)-C(8)-N(2)-C(12)	-179.50(15)
C(9)-C(8)-N(2)-Ni(1)	-175.91(12)
C(6)-C(8)-N(2)-Ni(1)	3.40(19)
C(14)-C(13)-N(3)-C(17)	-7.0(2)
C(6)-C(13)-N(3)-C(17)	166.53(15)
C(14)-C(13)-N(3)-Ni(1)	178.50(12)
C(6)-C(13)-N(3)-Ni(1)	-7.96(19)

C(16)-C(17)-N(3)-C(13)	8.3(3)
C(18)-C(17)-N(3)-C(13)	-166.05(15)
C(16)-C(17)-N(3)-Ni(1)	-176.95(13)
C(18)-C(17)-N(3)-Ni(1)	8.74(19)
C(21)-C(22)-N(4)-C(18)	-0.1(3)
C(21)-C(22)-N(4)-Ni(1)	-163.07(16)
C(19)-C(18)-N(4)-C(22)	-0.4(3)
C(17)-C(18)-N(4)-C(22)	177.25(16)
C(19)-C(18)-N(4)-Ni(1)	164.90(14)
C(17)-C(18)-N(4)-Ni(1)	-17.49(19)

Symmetry transformations used to generate equivalent atoms:

13.4. Ni(Me₂Phen)₂(OAc)(BPh₄) (**1h**)

A colorless rod 0.26 x 0.09 x 0.06 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 30.23 mm and exposure time was 1.00 seconds per frame at low angles and 2.50 seconds per frame at high angles, using a scan width of 0.5°. Data collection was 100% complete to 74.000° in θ . A total of 63840 reflections were collected covering the indices $-23 \leq h \leq 23$, $-22 \leq k \leq 18$, $-34 \leq l \leq 40$. 11084 reflections were found to be symmetry independent, with an R_{int} of 0.0438. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be Pbc_a (No. 61). The data were integrated using the CrysAlis^{Pro} 1.171.40.50a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Table 1. Crystal data and structure refinement for Yehao002_Hartwig.

Identification code	Yehao002_Hartwig
Empirical formula	C _{57.50} H ₅₄ B Cl ₇ N ₄ Ni O ₂

Formula weight	1150.71	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 18.9478(2) Å	$\alpha = 90^\circ$.
	b = 17.9054(2) Å	$\beta = 90^\circ$.
	c = 32.0064(2) Å	$\gamma = 90^\circ$.
Volume	10858.75(18) Å ³	
Z	8	
Density (calculated)	1.408 Mg/m ³	
Absorption coefficient	4.051 mm ⁻¹	
F(000)	4760	
Crystal size	0.260 x 0.090 x 0.060 mm ³	
Theta range for data collection	3.666 to 74.502°.	
Index ranges	-23<=h<=23, -22<=k<=18, -34<=l<=40	
Reflections collected	63840	
Independent reflections	11084 [R(int) = 0.0438]	
Completeness to theta = 74.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.58443	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11084 / 0 / 672	
Goodness-of-fit on F ²	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0860	
R indices (all data)	R1 = 0.0391, wR2 = 0.0893	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.664 and -0.481 e.Å ⁻³	

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for yehao002_hartwig. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(00M)	1265(1)	5683(1)	6150(1)	17(1)

C(1)	3866(1)	5270(1)	6868(1)	20(1)
C(2)	3698(1)	4672(1)	6555(1)	16(1)
C(01X)	477(1)	5642(1)	6140(1)	29(1)
C(3)	4006(1)	3957(1)	6599(1)	21(1)
C(4)	3863(1)	3406(1)	6315(1)	20(1)
C(5)	3429(1)	3564(1)	5971(1)	16(1)
C(6)	3281(1)	3028(1)	5651(1)	18(1)
C(7)	2890(1)	3220(1)	5313(1)	19(1)
C(8)	2614(1)	3959(1)	5269(1)	17(1)
C(9)	2222(1)	4194(1)	4918(1)	21(1)
C(10)	2009(1)	4920(1)	4888(1)	21(1)
C(11)	2172(1)	5434(1)	5211(1)	16(1)
C(12)	1980(1)	6237(1)	5156(1)	19(1)
C(13)	2735(1)	4491(1)	5583(1)	14(1)
C(14)	3146(1)	4291(1)	5944(1)	14(1)
C(15)	3830(1)	6249(1)	5424(1)	20(1)
C(16)	3586(1)	6843(1)	5721(1)	16(1)
C(17)	3796(1)	7590(1)	5652(1)	19(1)
C(18)	3612(1)	8138(1)	5929(1)	18(1)
C(19)	3225(1)	7944(1)	6289(1)	16(1)
C(20)	3049(1)	8477(1)	6605(1)	18(1)
C(21)	2694(1)	8266(1)	6952(1)	19(1)
C(22)	2484(1)	7506(1)	7012(1)	16(1)
C(23)	2139(1)	7253(1)	7374(1)	19(1)
C(24)	1988(1)	6514(1)	7418(1)	18(1)
C(25)	2168(1)	6004(1)	7096(1)	16(1)
C(26)	2017(1)	5190(1)	7157(1)	21(1)
C(27)	2640(1)	6969(1)	6703(1)	14(1)
C(28)	3017(1)	7193(1)	6333(1)	14(1)
C(29)	6047(1)	6997(1)	6207(1)	17(1)
C(30)	5388(1)	6664(1)	6136(1)	22(1)
C(31)	5236(1)	5928(1)	6243(1)	27(1)
C(32)	5751(1)	5487(1)	6432(1)	25(1)
C(33)	6403(1)	5799(1)	6517(1)	23(1)
C(34)	6546(1)	6541(1)	6408(1)	20(1)
C(35)	7010(1)	8070(1)	5970(1)	17(1)

C(36)	7470(1)	7548(1)	5788(1)	20(1)
C(37)	8151(1)	7729(1)	5660(1)	24(1)
C(38)	8406(1)	8451(1)	5712(1)	26(1)
C(39)	7965(1)	8988(1)	5885(1)	25(1)
C(40)	7286(1)	8796(1)	6009(1)	21(1)
C(41)	5916(1)	8345(1)	6502(1)	18(1)
C(42)	6367(1)	8541(1)	6831(1)	20(1)
C(43)	6126(1)	8885(1)	7197(1)	22(1)
C(44)	5414(1)	9046(1)	7246(1)	23(1)
C(45)	4949(1)	8853(1)	6929(1)	24(1)
C(46)	5198(1)	8506(1)	6568(1)	22(1)
C(47)	5732(1)	8105(1)	5664(1)	18(1)
C(48)	5426(1)	8812(1)	5603(1)	22(1)
C(49)	5052(1)	9000(1)	5243(1)	27(1)
C(50)	4980(1)	8485(1)	4921(1)	27(1)
C(51)	5295(1)	7786(1)	4963(1)	24(1)
C(52)	5660(1)	7608(1)	5326(1)	20(1)
C(53)	3846(1)	5555(1)	8380(1)	27(1)
C(54)	6420(1)	2884(1)	6779(1)	31(1)
C(55)	5107(1)	6903(1)	7280(1)	29(1)
C(56)	5539(3)	5158(2)	5264(1)	40(1)
B(1)	6184(1)	7880(1)	6087(1)	17(1)
Cl(1)	3580(1)	5817(1)	8888(1)	35(1)
Cl(2)	3217(1)	5820(1)	8003(1)	33(1)
Cl(3)	5557(1)	2617(1)	6635(1)	46(1)
Cl(4)	6432(1)	3756(1)	7035(1)	46(1)
Cl(5)	5212(1)	6105(1)	7606(1)	33(1)
Cl(6)	4205(1)	7125(1)	7216(1)	29(1)
Cl(7)	4881(1)	4498(1)	5393(1)	46(1)
Cl(8)	4614(1)	4412(1)	5220(1)	42(1)
N(1)	3263(1)	4828(1)	6240(1)	14(1)
N(2)	2510(1)	5216(1)	5555(1)	14(1)
N(3)	3186(1)	6653(1)	6047(1)	14(1)
N(4)	2475(1)	6231(1)	6744(1)	14(1)
Ni(1)	2558(1)	5719(1)	6149(1)	13(1)
O(1)	1579(1)	6284(1)	6056(1)	17(1)

O(2)	1621(1)	5106(1)	6249(1)	17(1)
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Table 3. Bond lengths [Å] and angles [°] for yehao002_hartwig.

C(00M)-O(1)	1.267(2)
C(00M)-O(2)	1.2720(19)
C(00M)-C(01X)	1.494(2)
C(00M)-Ni(1)	2.4513(17)
C(1)-C(2)	1.501(2)
C(2)-N(1)	1.333(2)
C(2)-C(3)	1.413(2)
C(3)-C(4)	1.368(2)
C(4)-C(5)	1.405(2)
C(5)-C(14)	1.410(2)
C(5)-C(6)	1.431(2)
C(6)-C(7)	1.355(2)
C(7)-C(8)	1.431(2)
C(8)-C(13)	1.403(2)
C(8)-C(9)	1.411(2)
C(9)-C(10)	1.365(2)
C(10)-C(11)	1.418(2)
C(11)-N(2)	1.331(2)
C(11)-C(12)	1.494(2)
C(13)-N(2)	1.3695(19)
C(13)-C(14)	1.436(2)
C(14)-N(1)	1.3702(19)
C(15)-C(16)	1.499(2)
C(16)-N(3)	1.334(2)
C(16)-C(17)	1.412(2)
C(17)-C(18)	1.368(2)
C(18)-C(19)	1.408(2)
C(19)-C(28)	1.408(2)
C(19)-C(20)	1.429(2)
C(20)-C(21)	1.352(2)

C(21)-C(22)	1.431(2)
C(22)-C(23)	1.405(2)
C(22)-C(27)	1.411(2)
C(23)-C(24)	1.361(2)
C(24)-C(25)	1.418(2)
C(25)-N(4)	1.330(2)
C(25)-C(26)	1.498(2)
C(27)-N(4)	1.366(2)
C(27)-C(28)	1.438(2)
C(28)-N(3)	1.370(2)
C(29)-C(30)	1.404(2)
C(29)-C(34)	1.404(2)
C(29)-B(1)	1.647(2)
C(30)-C(31)	1.392(2)
C(31)-C(32)	1.393(3)
C(32)-C(33)	1.383(3)
C(33)-C(34)	1.400(2)
C(35)-C(36)	1.405(2)
C(35)-C(40)	1.405(2)
C(35)-B(1)	1.645(2)
C(36)-C(37)	1.392(2)
C(37)-C(38)	1.391(3)
C(38)-C(39)	1.389(3)
C(39)-C(40)	1.392(3)
C(41)-C(42)	1.401(2)
C(41)-C(46)	1.407(2)
C(41)-B(1)	1.648(2)
C(42)-C(43)	1.402(2)
C(43)-C(44)	1.388(3)
C(44)-C(45)	1.388(3)
C(45)-C(46)	1.393(2)
C(47)-C(48)	1.406(2)
C(47)-C(52)	1.406(2)
C(47)-B(1)	1.651(2)
C(48)-C(49)	1.395(3)
C(49)-C(50)	1.389(3)

C(50)-C(51)	1.392(3)
C(51)-C(52)	1.390(2)
C(53)-Cl(2)	1.7625(19)
C(53)-Cl(1)	1.7644(18)
C(54)-Cl(4)	1.763(2)
C(54)-Cl(3)	1.766(2)
C(55)-Cl(6)	1.7669(19)
C(55)-Cl(5)	1.7795(19)
C(56)-Cl(8)#1	1.753(5)
C(56)-Cl(7)	1.766(5)
Cl(7)-Cl(8)	0.7680(16)
Cl(8)-C(56)#1	1.753(5)
N(1)-Ni(1)	2.0999(13)
N(2)-Ni(1)	2.1057(13)
N(3)-Ni(1)	2.0789(13)
N(4)-Ni(1)	2.1196(13)
Ni(1)-O(2)	2.1111(11)
Ni(1)-O(1)	2.1339(11)
O(1)-C(00M)-O(2)	119.92(15)
O(1)-C(00M)-C(01X)	120.41(14)
O(2)-C(00M)-C(01X)	119.67(15)
O(1)-C(00M)-Ni(1)	60.48(8)
O(2)-C(00M)-Ni(1)	59.45(8)
C(01X)-C(00M)-Ni(1)	178.17(13)
N(1)-C(2)-C(3)	121.39(14)
N(1)-C(2)-C(1)	119.07(14)
C(3)-C(2)-C(1)	119.53(14)
C(4)-C(3)-C(2)	120.38(15)
C(3)-C(4)-C(5)	119.45(15)
C(4)-C(5)-C(14)	117.21(14)
C(4)-C(5)-C(6)	122.73(14)
C(14)-C(5)-C(6)	120.06(14)
C(7)-C(6)-C(5)	120.51(14)
C(6)-C(7)-C(8)	120.81(14)
C(13)-C(8)-C(9)	117.02(14)

C(13)-C(8)-C(7)	119.89(14)
C(9)-C(8)-C(7)	123.09(14)
C(10)-C(9)-C(8)	119.72(15)
C(9)-C(10)-C(11)	120.11(15)
N(2)-C(11)-C(10)	121.21(14)
N(2)-C(11)-C(12)	119.82(14)
C(10)-C(11)-C(12)	118.94(14)
N(2)-C(13)-C(8)	123.03(14)
N(2)-C(13)-C(14)	117.31(13)
C(8)-C(13)-C(14)	119.58(14)
N(1)-C(14)-C(5)	122.95(14)
N(1)-C(14)-C(13)	117.92(13)
C(5)-C(14)-C(13)	119.10(14)
N(3)-C(16)-C(17)	121.61(14)
N(3)-C(16)-C(15)	119.36(14)
C(17)-C(16)-C(15)	119.01(14)
C(18)-C(17)-C(16)	120.37(15)
C(17)-C(18)-C(19)	119.12(14)
C(28)-C(19)-C(18)	117.54(14)
C(28)-C(19)-C(20)	120.06(14)
C(18)-C(19)-C(20)	122.40(14)
C(21)-C(20)-C(19)	120.74(14)
C(20)-C(21)-C(22)	120.96(14)
C(23)-C(22)-C(27)	117.16(14)
C(23)-C(22)-C(21)	123.19(14)
C(27)-C(22)-C(21)	119.63(14)
C(24)-C(23)-C(22)	119.73(14)
C(23)-C(24)-C(25)	120.05(14)
N(4)-C(25)-C(24)	121.56(14)
N(4)-C(25)-C(26)	119.37(14)
C(24)-C(25)-C(26)	119.06(14)
N(4)-C(27)-C(22)	122.86(14)
N(4)-C(27)-C(28)	117.65(13)
C(22)-C(27)-C(28)	119.43(14)
N(3)-C(28)-C(19)	122.83(14)
N(3)-C(28)-C(27)	117.94(13)

C(19)-C(28)-C(27)	119.17(14)
C(30)-C(29)-C(34)	115.21(15)
C(30)-C(29)-B(1)	120.69(14)
C(34)-C(29)-B(1)	123.96(15)
C(31)-C(30)-C(29)	123.11(16)
C(30)-C(31)-C(32)	119.97(17)
C(33)-C(32)-C(31)	118.74(16)
C(32)-C(33)-C(34)	120.54(16)
C(33)-C(34)-C(29)	122.39(16)
C(36)-C(35)-C(40)	114.97(15)
C(36)-C(35)-B(1)	123.10(14)
C(40)-C(35)-B(1)	121.66(14)
C(37)-C(36)-C(35)	122.85(16)
C(38)-C(37)-C(36)	120.21(16)
C(39)-C(38)-C(37)	118.82(16)
C(38)-C(39)-C(40)	120.00(16)
C(39)-C(40)-C(35)	123.14(16)
C(42)-C(41)-C(46)	115.13(15)
C(42)-C(41)-B(1)	122.96(14)
C(46)-C(41)-B(1)	121.62(14)
C(41)-C(42)-C(43)	122.71(16)
C(44)-C(43)-C(42)	120.15(16)
C(45)-C(44)-C(43)	118.85(15)
C(44)-C(45)-C(46)	120.16(16)
C(45)-C(46)-C(41)	122.97(16)
C(48)-C(47)-C(52)	115.06(15)
C(48)-C(47)-B(1)	123.13(14)
C(52)-C(47)-B(1)	121.72(14)
C(49)-C(48)-C(47)	122.72(16)
C(50)-C(49)-C(48)	120.21(17)
C(49)-C(50)-C(51)	118.88(16)
C(52)-C(51)-C(50)	119.98(16)
C(51)-C(52)-C(47)	123.09(16)
Cl(2)-C(53)-Cl(1)	111.49(10)
Cl(4)-C(54)-Cl(3)	111.88(11)
Cl(6)-C(55)-Cl(5)	110.91(10)

Cl(8)#1-C(56)-Cl(7)	112.6(3)
C(35)-B(1)-C(29)	113.68(13)
C(35)-B(1)-C(41)	111.81(13)
C(29)-B(1)-C(41)	104.35(12)
C(35)-B(1)-C(47)	104.91(12)
C(29)-B(1)-C(47)	110.10(13)
C(41)-B(1)-C(47)	112.18(13)
Cl(8)-Cl(7)-C(56)	115.6(3)
Cl(7)-Cl(8)-C(56)#1	131.2(3)
C(2)-N(1)-C(14)	118.48(13)
C(2)-N(1)-Ni(1)	131.15(10)
C(14)-N(1)-Ni(1)	109.52(10)
C(11)-N(2)-C(13)	118.79(13)
C(11)-N(2)-Ni(1)	129.98(11)
C(13)-N(2)-Ni(1)	109.37(10)
C(16)-N(3)-C(28)	118.36(13)
C(16)-N(3)-Ni(1)	130.82(11)
C(28)-N(3)-Ni(1)	109.26(10)
C(25)-N(4)-C(27)	118.59(13)
C(25)-N(4)-Ni(1)	131.34(11)
C(27)-N(4)-Ni(1)	108.32(9)
N(3)-Ni(1)-N(1)	105.57(5)
N(3)-Ni(1)-N(2)	103.08(5)
N(1)-Ni(1)-N(2)	80.12(5)
N(3)-Ni(1)-O(2)	157.37(5)
N(1)-Ni(1)-O(2)	96.92(5)
N(2)-Ni(1)-O(2)	83.02(5)
N(3)-Ni(1)-N(4)	80.54(5)
N(1)-Ni(1)-N(4)	104.56(5)
N(2)-Ni(1)-N(4)	173.25(5)
O(2)-Ni(1)-N(4)	91.51(5)
N(3)-Ni(1)-O(1)	95.39(5)
N(1)-Ni(1)-O(1)	158.80(5)
N(2)-Ni(1)-O(1)	92.21(5)
O(2)-Ni(1)-O(1)	62.35(4)
N(4)-Ni(1)-O(1)	81.71(5)

N(3)-Ni(1)-C(00M)	126.41(5)
N(1)-Ni(1)-C(00M)	128.02(5)
N(2)-Ni(1)-C(00M)	86.95(5)
O(2)-Ni(1)-C(00M)	31.26(5)
N(4)-Ni(1)-C(00M)	86.32(5)
O(1)-Ni(1)-C(00M)	31.10(5)
C(00M)-O(1)-Ni(1)	88.42(9)
C(00M)-O(2)-Ni(1)	89.30(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for yehao002_hartwig. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(00M)	21(1)	16(1)	14(1)	0(1)	0(1)	1(1)
C(1)	23(1)	19(1)	17(1)	-2(1)	-5(1)	2(1)
C(2)	17(1)	18(1)	15(1)	1(1)	0(1)	1(1)
C(01X)	19(1)	29(1)	38(1)	7(1)	0(1)	1(1)
C(3)	23(1)	21(1)	17(1)	1(1)	-4(1)	4(1)
C(4)	23(1)	16(1)	22(1)	3(1)	0(1)	5(1)
C(5)	18(1)	14(1)	16(1)	0(1)	2(1)	1(1)
C(6)	22(1)	13(1)	20(1)	0(1)	3(1)	2(1)
C(7)	26(1)	13(1)	18(1)	-4(1)	2(1)	-1(1)
C(8)	21(1)	14(1)	16(1)	-1(1)	2(1)	-1(1)
C(9)	30(1)	18(1)	16(1)	-5(1)	-3(1)	-1(1)
C(10)	28(1)	19(1)	15(1)	-1(1)	-5(1)	2(1)
C(11)	19(1)	16(1)	14(1)	0(1)	-1(1)	0(1)
C(12)	25(1)	16(1)	16(1)	1(1)	-1(1)	3(1)
C(13)	17(1)	12(1)	14(1)	-1(1)	2(1)	0(1)
C(14)	16(1)	13(1)	14(1)	0(1)	3(1)	-1(1)
C(15)	20(1)	21(1)	18(1)	-2(1)	4(1)	1(1)
C(16)	15(1)	19(1)	14(1)	1(1)	-2(1)	1(1)

C(17)	17(1)	20(1)	19(1)	4(1)	2(1)	-1(1)
C(18)	17(1)	15(1)	22(1)	4(1)	-1(1)	-2(1)
C(19)	16(1)	14(1)	17(1)	2(1)	-3(1)	0(1)
C(20)	21(1)	11(1)	23(1)	-1(1)	-3(1)	0(1)
C(21)	22(1)	14(1)	20(1)	-4(1)	-2(1)	2(1)
C(22)	19(1)	14(1)	17(1)	-2(1)	-1(1)	2(1)
C(23)	22(1)	19(1)	15(1)	-4(1)	1(1)	3(1)
C(24)	22(1)	19(1)	13(1)	0(1)	2(1)	0(1)
C(25)	18(1)	17(1)	14(1)	0(1)	0(1)	0(1)
C(26)	31(1)	16(1)	15(1)	1(1)	2(1)	-4(1)
C(27)	16(1)	13(1)	14(1)	-1(1)	-2(1)	1(1)
C(28)	15(1)	13(1)	15(1)	-1(1)	-2(1)	0(1)
C(29)	20(1)	18(1)	13(1)	-1(1)	2(1)	1(1)
C(30)	22(1)	24(1)	21(1)	5(1)	-1(1)	0(1)
C(31)	26(1)	28(1)	26(1)	6(1)	-3(1)	-7(1)
C(32)	34(1)	18(1)	24(1)	4(1)	0(1)	-3(1)
C(33)	28(1)	21(1)	21(1)	2(1)	-1(1)	4(1)
C(34)	22(1)	21(1)	17(1)	0(1)	-1(1)	0(1)
C(35)	21(1)	18(1)	13(1)	2(1)	-1(1)	0(1)
C(36)	24(1)	20(1)	17(1)	-1(1)	1(1)	0(1)
C(37)	25(1)	26(1)	21(1)	-1(1)	3(1)	2(1)
C(38)	22(1)	35(1)	20(1)	3(1)	2(1)	-6(1)
C(39)	32(1)	23(1)	20(1)	1(1)	-1(1)	-8(1)
C(40)	27(1)	19(1)	18(1)	-1(1)	1(1)	0(1)
C(41)	23(1)	15(1)	15(1)	3(1)	1(1)	0(1)
C(42)	23(1)	19(1)	17(1)	3(1)	0(1)	2(1)
C(43)	30(1)	21(1)	16(1)	0(1)	-5(1)	1(1)
C(44)	32(1)	22(1)	16(1)	-2(1)	2(1)	5(1)
C(45)	23(1)	27(1)	23(1)	-2(1)	2(1)	3(1)
C(46)	23(1)	24(1)	18(1)	-2(1)	-1(1)	-1(1)
C(47)	18(1)	19(1)	16(1)	3(1)	3(1)	-2(1)
C(48)	26(1)	19(1)	22(1)	3(1)	2(1)	-1(1)
C(49)	26(1)	26(1)	29(1)	12(1)	2(1)	1(1)
C(50)	23(1)	40(1)	19(1)	12(1)	0(1)	-4(1)
C(51)	22(1)	35(1)	16(1)	1(1)	3(1)	-7(1)
C(52)	20(1)	24(1)	17(1)	2(1)	4(1)	-1(1)

C(53)	28(1)	33(1)	21(1)	-3(1)	0(1)	6(1)
C(54)	30(1)	33(1)	29(1)	2(1)	-1(1)	4(1)
C(55)	26(1)	31(1)	30(1)	5(1)	1(1)	-3(1)
C(56)	48(3)	35(2)	37(2)	-4(2)	11(2)	6(2)
B(1)	20(1)	17(1)	16(1)	0(1)	0(1)	0(1)
Cl(1)	44(1)	40(1)	22(1)	-4(1)	7(1)	1(1)
Cl(2)	28(1)	44(1)	28(1)	0(1)	-5(1)	4(1)
Cl(3)	32(1)	57(1)	50(1)	-3(1)	-5(1)	1(1)
Cl(4)	69(1)	36(1)	33(1)	-1(1)	-2(1)	0(1)
Cl(5)	27(1)	39(1)	32(1)	10(1)	0(1)	2(1)
Cl(6)	27(1)	27(1)	32(1)	0(1)	-4(1)	0(1)
Cl(7)	44(1)	31(1)	62(1)	7(1)	21(1)	9(1)
Cl(8)	48(1)	32(1)	45(1)	5(1)	21(1)	10(1)
N(1)	17(1)	12(1)	13(1)	0(1)	1(1)	0(1)
N(2)	17(1)	12(1)	14(1)	0(1)	0(1)	1(1)
N(3)	16(1)	14(1)	14(1)	0(1)	-1(1)	1(1)
N(4)	17(1)	13(1)	12(1)	-1(1)	0(1)	0(1)
Ni(1)	17(1)	10(1)	12(1)	0(1)	0(1)	1(1)
O(1)	20(1)	13(1)	17(1)	1(1)	1(1)	1(1)
O(2)	20(1)	14(1)	17(1)	1(1)	0(1)	-1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for yehao002_hartwig.

	x	y	z	U(eq)
H(1A)	3768	5761	6746	30
H(1B)	4366	5240	6945	30
H(1C)	3574	5201	7118	30
H(01A)	321	5490	5861	43
H(01B)	279	6133	6208	43
H(01C)	314	5275	6346	43
H(3)	4315	3859	6827	25

H(4)	4056	2920	6351	24
H(6)	3459	2534	5676	22
H(7)	2798	2858	5103	23
H(9)	2106	3848	4704	25
H(10)	1751	5082	4650	25
H(12A)	1466	6292	5172	29
H(12B)	2146	6410	4882	29
H(12C)	2201	6535	5376	29
H(15A)	3815	5762	5564	30
H(15B)	4315	6356	5336	30
H(15C)	3521	6241	5179	30
H(17)	4068	7712	5412	22
H(18)	3742	8642	5879	21
H(20)	3183	8984	6571	22
H(21)	2583	8628	7158	22
H(23)	2013	7596	7588	22
H(24)	1762	6339	7664	22
H(26A)	1513	5097	7115	31
H(26B)	2151	5043	7441	31
H(26C)	2290	4898	6954	31
H(30)	5027	6955	6009	27
H(31)	4783	5726	6187	32
H(32)	5656	4981	6503	30
H(33)	6757	5508	6649	27
H(34)	6996	6744	6472	24
H(36)	7309	7050	5751	24
H(37)	8443	7357	5537	29
H(38)	8874	8576	5630	31
H(39)	8128	9487	5918	30
H(40)	6994	9173	6127	26
H(42)	6857	8437	6804	24
H(43)	6451	9007	7413	27
H(44)	5248	9285	7492	28
H(45)	4460	8956	6959	29
H(46)	4868	8373	6358	26
H(48)	5477	9177	5817	27

H(49)	4845	9481	5218	32
H(50)	4720	8607	4677	33
H(51)	5260	7431	4743	29
H(52)	5871	7128	5347	24
H(53A)	4304	5794	8315	33
H(53B)	3912	5007	8370	33
H(54A)	6622	2500	6967	37
H(54B)	6720	2911	6527	37
H(55A)	5356	7334	7407	35
H(55B)	5322	6804	7004	35
H(56A)	5557	5546	5484	48
H(56B)	6003	4905	5257	48
