Supporting Information

Hydrodebromination of Allylic and Benzylic Bromides with Water Catalyzed by Rhodium Porphyrin Complex

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Experimental Section

Unless otherwise specified, all reagents were purchased from commercial suppliers and directly used without further purification. H_2(ttp),[1] Rh(ttp)Cl[2] and Rh(ttp)Me[3] were prepared according to the literature procedures. Benzene was distilled over sodium under nitrogen. All reactions were protected from light by wrapping with aluminum foil. For the reaction conducted in Rotaflos (Teflon screw capped pressure tubes), the reactions were heated in aluminum heating blocks on heaters and monitored by TLC and GC-MS until the complete consumption of the starting material of activated alkyl bromides. For the reaction conducted in a sealed NMR tube, the mixture was degassed by three freeze-pump-thaw cycles (77 K, 0.005 mmHg), and then flame-sealed under vacuum, heated in oven in dark. Hexane for chromatography was distilled from anhydrous calcium chloride. Thin-layer chromatography was performed on Merck pre-coated silica gel 60 F254 plates. Silica gel (Merck, 70–230 and 230–400 mesh) was used for column chromatography in air. NMR yields were determined with 1,1,2,2-tetrachloroethane or with benzene residue as the internal standard. GC yields were determined with naphthalene spiked as the internal standard.

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AV400 instrument at 400, 100 MHz, respectively. Chemical shifts for ^{1}H NMR were reported in ppm and referenced with the residual solvent protons in C_6D_6 (δ 7.15 ppm) or in $CDCl_3$ (δ 7.26 ppm) as the internal standards. Chemical shifts for ^{13}C NMR were referenced to $CDCl_3$ (δ 77.1 ppm) or C_6D_6 (δ 128.1 ppm). Coupling constants (*J*) were reported in hertz (Hz). High-resolution mass spectrometry (HRMS) was performed on a Bruker SolariX 9.4 Tesla FTICR MS / Thermofinnigan MAT 95 XL instrument in electrospray ionization (ESI) mode using MeOH/CH_2Cl_2 (1/1) as the solvent. GC-MS analysis was conducted on a GCMS-QP2010 Plus

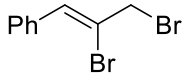
system using a Rtx-5MS column (30 m × 0.25 mm). The details of GC program are as follows: The column oven temperature and injection temperature were 100.0 and 250.0 °C. Helium was used as carrier gas. Flow control mode was chosen as linear velocity (36.3 cm s^{-1}) with pressure 68.8 kPa. The total flow, column flow and purge flow were 13.5, 0.95 and 3.0 mL min^{-1}, respectively. Split mode injection with split ratio 10.0 was applied. After injection, the column oven temperature was kept at 100 °C for 2 minutes and then temperature was elevated at a rate of 30 °C min^{-1} for 5 minutes until 250 °C. The temperature of 250 °C was kept for at least 1 minute.

Preparation of (2,2-Dibromocyclopropyl)benzene (1).[4] 1 was prepared according to the literature procedures.[5] A round-bottomed flask was charged with styrene (1150 μL, 10 mmol), tetrabutylammonium bromide (TBAB) (164.1 mg, 0.51 mmol, 5 mol %), a 17 M aqueous solution of NaOH (6 mL, 102 mmol). The mixture was stirred at rt and bromoform (5 mL, 57 mmol) was added in two portions. The reaction was carried out at rt until the complete consumption of styrene as judged by TLC analysis. After the reaction, the mixture was diluted with H_2O and extracted with CH_2Cl_2 (50 mL × 3), washed with brine, dried and concentrated. Purification of the residue by column chromatography with hexane as the eluent gave the title product (**1**) (1920.1 mg, 6.96 mmol, 70%) as a yellow oil. R_f = 0.42 (hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.02 (dd, *J* = 7.4, 8.4 Hz, 1H), 2.14 (dd, *J* = 7.4, 10.7 Hz, 1H), 2.96 (dd, *J* = 8.4, 10.7 Hz, 1H), 7.25-7.39 (m, 5H).

The Sealed NMR Tube Reaction of (2,2-Dibromocyclopropyl)benzene (1) Catalyzed by Rh(ttp)Me. (2,2-Dibromocyclopropyl)benzene (**1**; 16 μL, 0.10 mmol) stock solution with 2 mL C_6D_6 was prepared. Rh(ttp)Me (0.8 mg, 0.0010 mmol), H_2O (18 μL, 1.0 mmol) and **1** stock solution (400 μL, 0.020 mmol) were added into a Teflon screw head stoppered NMR tube,

degassed and flame-sealed under vacuum. The reaction was monitored by ^{1}H NMR spectroscopy. The reaction at 180 °C for 48 h gave (2-bromoprop-1-en-1-yl)benzene (**2a**)[6] in 45% yield.

The Sealed NMR Tube Reaction to Test the Thermal Stability of (2,2-Dibromocyclopropyl)benzene. 1 stock solution (400 μL, 0.020 mmol) and H_2O (18 μL, 1.0 mmol) were added into a Teflon screw head stoppered NMR tube, degassed and flame-sealed under vacuum. The reaction was monitored by ^{1}H NMR spectroscopy. The reaction at 180 °C for 48 h gave (2,3-dibromoprop-1-enyl)benzene (**1a**)[7] quantitatively. ^{1}H NMR ($CDCl_3$, 400 MHz): δ *E* isomer: 4.40 (s, 2H), 7.12 (s, 1H), 7.34-7.43 (m, 5H). Z-isomer: 4.44 (s, 2H), 7.13 (s, 1H), 7.34-7.40 (m, 3H), 7.64 (d, *J* = 7.1 Hz, 2H).



(*Z*)-**1a**

Preparation of (*Z*)-(2,3-Dibromoprop-1-enyl)benzene ((*Z*)-1a). (*Z*)-**1a** was prepared according to the literature procedures.[8] To a solution of (*Z)*-2-bromo-3-phenylacrylaldehyde (2.11 g, 10.0 mmol) in THF-H_2O (9:1, 20 mL) at 0 °C was added $NaBH_4$ (266 mg, 7.0 mmol). It was stirred at 0 °C for 0.5 h until the complete consumption of (*Z)*-2-bromo-3-phenylacrylaldehyde. Then water was added. The mixture was extracted with Et_2O, dried over Na_2SO_4. After that, it was concentrated to afford a pale-yellow liquid. It was directly involved into the next step without further purification.

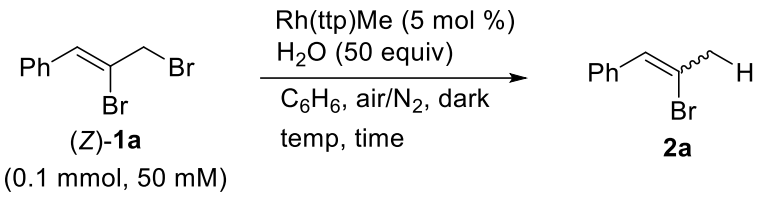
To a solution of the above alcohol in CH_2Cl_2 at 0 °C were added CBr_4 (3.97 g, 12.0 mmol), PPh_3 (3.15 g, 12.0 mmol). Then it was allowed to warm to rt for 4 h. After that, the reaction mixture was concentrated under a reduced pressure. The residue was directly purified by flash chromatography eluting with hexane to afford (*Z*)-**1a** (2.68 g, 9.8 mmol, 98%)[7b] as a colorless oil. R_f = 0.33 (hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.44 (s, 2H), 7.13 (s, 1H), 7.34-7.40 (m, 3H), 7.64 (d, *J* = 7.1 Hz, 2H).

General Procedures for the Reaction of (*Z*)-(2,3-Dibromoprop-1-enyl)benzene ((*Z*)-1a) with Water. Rh(ttp)Me (4.0 mg, 0.0051 mmol), (*Z*)-**1a** (15.5 μL, 0.10 mmol), H_2O (90 μL, 5.0 mmol) were added to benzene (2 mL). The mixture was heated at a specified temperature under air. Excess benzene was removed by rotary evaporation. The residue was purified by pipet column chromatography eluting with hexane to give (2-bromoprop-1-en-1-yl)benzene (**2a**)[6, 9] with an isolated yield. Alternatively, the crude product was taken for ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard to obtain the NMR yield. The product of **2a** contained *E* and *Z* isomer in 1.1:1.0 ratio. ^{1}H NMR ($CDCl_3$, 400 MHz): δ *E* isomer 2.49 (d, *J* = 0.9 Hz, 3H), 6.73 (s, 1H), 7.21-7.37 (m, 5H); *Z* isomer 2.47 (s, 3H), 6.97 (s, 1H), 7.21-7.37 (m, 5H). MS (EI, 70 eV) *m*/*z* (relative intensity) 198 (31%, M^+(^{81}Br)), 196 (32%, M^+(^{79}Br)), 117 (74%), 116 (33%) 115 (100%), 91 (35%).

Reaction Conditions Optimization. The optimization reactions followed the general procedures described above with the changes of atmosphere, temperature, catalyst loading, solvent, additive, and reaction time.

***Temperature and Atmosphere Effects*:** Rh(ttp)Me (4.0 mg, 0.0051 mmol), (*Z*)-**1a** (15.5 μL, 0.10 mmol), H_2O (90 μL, 5.0 mmol) were added to benzene (2 mL). For the reaction conducted under N_2, the mixture was degassed for three freeze-pump-thaw cycles, filled with N_2. The mixture was heated at 200 °C for 12 h. **2a** was obtained in 37% yield under N_2; 41% yield under air. Rh(ttp)Me (4.0 mg, 0.0051 mmol), (*Z*)-**1a** (15.5 μL, 0.10 mmol), H_2O (90 μL, 5.0 mmol) were added to benzene (2 mL). The mixture was heated under air. Yields of **2a** for the reaction at 180 °C for 37 h: 36%; at 200 °C for 12 h: 41%.

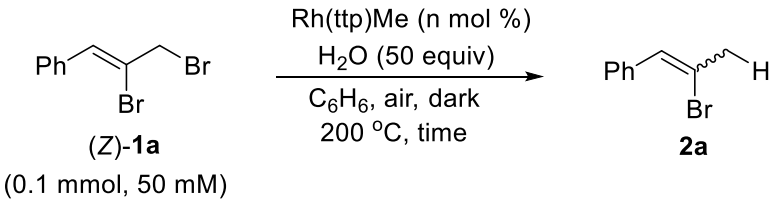
Table S1. Temperature and Atmosphere Effects of the Hydrodebromination Reaction



entry	air/N_2	temp/°C	time/h	**2a** yield[a]/%
1	air	180	37	36
2	air	200	12	41
3	N_2	200	12	37

[a]Isolated yield, *E*:*Z* = 1.1:1.0.

Table S2. Catalyst Loading Effect of the Hydrodebromination Reaction



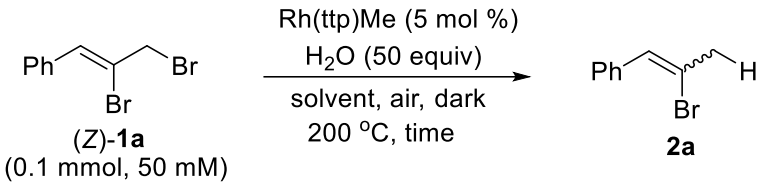
entry	n (Rh(ttp)Me)	time/h	**2a** yield[a]/%
1[b]	0	12	trace[d]
2[c]	2.5	12	24
3	5	12	41
4	10	6	36

[a]Isolated yield, *E*:*Z* = 1.1:1.0. [b]94% recovery of **1a** (including the *E* isomer). [c]17% recovery of **1a** (including the *E* isomer). [d]NMR yield.

Catalyst Loading Effect: Rh(ttp)Me (n mol %), (*Z*)-**1a** (15.5 μL, 0.10 mmol), H_2O (90 μL, 5.0 mmol) were added to benzene (2 mL). The mixture was heated at 200 °C under air. Yields of **2a**

for the reaction without Rh(ttp)Me for 12 h: trace amount, together with 94% recovery of **1a** (including the *E* isomer); with 2.5 mol % Rh(ttp)Me for 12 h: 24%;. with 5 mol % Rh(ttp)Me for 12 h: 41%;. with 10 mol % Rh(ttp)Me for 12 h: 36%.

Table S3. Solvent Effect of the Hydrodebromination Reaction



entry	solvent	time/h	**2a** yield[a]/%
1	C_6H_6	12	41
2[b]	$PhCH_3$	8	58
3	$PhCF_3$	12	36
4	DME	24	11
5	EtOAc	9	15[c]
6	$Cl_2C{=}CCl_2$	5	38[c]

[a]Isolated yield, *E*:*Z* = 1.1:1.0. [b]29% BnBr (w.r.t. (*Z*)-**1a**) was isolated. [c]NMR yield.

***Solvent Effect*:** Rh(ttp)Me (4.0 mg, 0.0051 mmol), (*Z*)-**1a** (15.5 μL, 0.10 mmol), H_2O (90 μL, 5.0 mmol) were added to a specified solvent (2 mL). The mixture was heated at 200 °C under air. Yields of **2a** for the reaction in C_6H_6 for 12 h: 41%; in $PhCH_3$ for 8 h: 58%, together with BnBr formed in 29% yield; in $PhCF_3$ for 12 h: 36%; in DME for 24 h: 11%; in EtOAc for 9 h: 15%; in $Cl_2C{=}CCl_2$ for 5 h: 38%.

Additive Effect: Rh(ttp)Me (4.0 mg, 0.0051 mmol), (*Z*)-**1a** (15.5 μL, 0.10 mmol), additive w/o H_2O (90 μL, 5.0 mmol) were added to benzene (2 mL). The mixture was heated at 200 °C under air. Yields of **2a** for the reaction without any additive for 12 h: 41%; with pH = 4.0 buffer (90 μL) for 9 h: 49%; with pH = 5.0 buffer (90 μL) for 12 h: 51%; with pH = 6.0 buffer (90 μL) for 12 h: 51%; with pH = 7.0 buffer (90 μL) for 12 h: 46%; with pH = 8.0 buffer (90 μL) for 8 h: 43%; with pH = 9.0 buffer (90 μL) for 8 h: 45%; with 5 equiv K_2CO_3 (69.1 mg, 0.50 mmol) for 12 h: 25%; with 1 equiv $CaCO_3$ (10.0 mg, 0.10 mmol) for 2 h: 10%, together with PhCH=C(Br)CH_2Ph (**2a'**) in 43% yield.

For (*Z*)-(2-bromoprop-1-ene-1,3-diyl)dibenzene ((*Z*)-**2a'**), R_f = 0.29 (hexane).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.96 (s, 2H), 6.83 (s, 1H), 7.29-7.39 (m, 8H), 7.60 (d, *J* = 7.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 49.5, 125.9, 127.1, 127.9, 128.2, 128.7, 129.0, 129.2, 129.2, 136.0, 127.8.

HRMS (ESIMS): calcd for $C_{15}H_{13}Br$ ($[M]^+$) *m*/*z* 272.0195, found 272.0194.

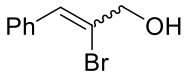
For (*E*)-(2-bromoprop-1-ene-1,3-diyl)dibenzene ((*E*)-**2a'**), R_f = 0.39 (hexane).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.04 (s, 2H), 7.22 (s, 1H), 7.27-7.37 (m, 10H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 42.4, 120.4, 126.9, 127.1, 127.8, 128.1, 128.6, 128.8, 128.8, 134.4, 137.6.

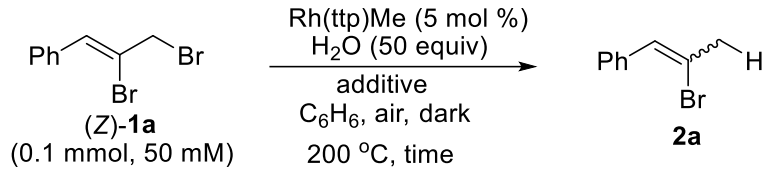
HRMS (ESIMS): calcd for $C_{15}H_{13}Br$ ($[M]^+$) *m*/*z* 272.0195, found 272.0195.

Yields of **2a** for the reaction with 1 equiv pyridine (8 μL, 0.10 mmol) for 24 h: 36%; with 1 equiv PhC≡CH (11 μL, 0.10 mmol) for 14 h: 64%, together with 29% yield of 1-bromostyrene and 26% yield of acetophenone formed; with 2,6-di-^{t}Bu-pyridine additive without Rh(ttp)Me for 12 h: trace amount, together with 92% recovery of **1a**; with DIPEA additive and without

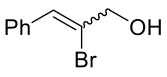
Rh(ttp)Me for 12 h: trace amount, together with 15% recovery of **1a**, 70% yield of 

,[10] 16% yield of $PhCH(OH)C(Br)=CH_2$;[10a] with 2,6-di-^{t}Bu-pyridine additive and 5 mol % Rh(ttp)Me for 6 h: 50% yield of **2a**, together with quantitative recovery of 2,6-di-^{t}Bu-pyridine; with DIPEA additive with 5 mol % Rh(ttp)Me for 3 h: 45%, together with $PhCH_2C(Br)=CH_2$ in 11% yield.[11]

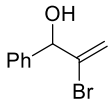
Table S4. Additive Effect of the Hydrodebromination Reaction

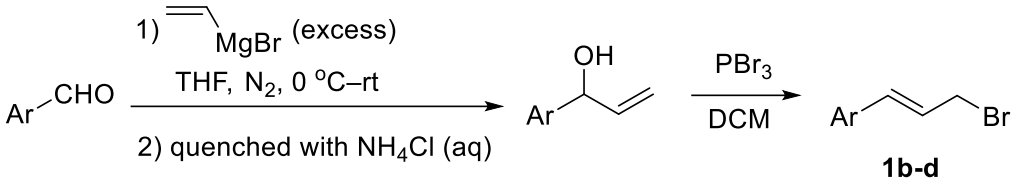


entry	additive	time/h	**2a** yield[a]/%
1	none	12	41[b]
2	pH = 4.0 buffer	9	49
3	pH = 5.0 buffer	12	51
4	pH = 6.0 buffer	12	51
5	pH = 7.0 buffer	12	46
6	pH = 8.0 buffer	8	43
7	pH = 9.0 buffer	8	45
8	5 equiv K_2CO_3	12	25
9[c]	1 equiv $CaCO_3$	2	10
10	1 equiv pyridine	24	36
11[d]	1 equiv DIPEA	3	45
12[e]	1 equiv DIPEA	12	trace
13[f]	1 equiv 2,6-di-(^{t}Bu)pyridine	6	50
14[g]	1 equiv 2,6-di-(^{t}Bu)pyridine	12	trace
15[h]	1 equiv PhC≡CH	14	64

[a]NMR yield, *E*:*Z* = 1.1:1.0. [b]Isolated yield. [c]43% yield of $PhCH=C(Br)CH_2Ph$. [d]11% formation of $PhCH_2C(Br)=CH_2$. [e]Without Rh(ttp)Me, 70% formation of 

and 16% formation

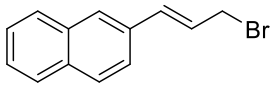
of  . [f]Quantitative recovery of 2,6-di-([t]Bu)pyridine, and trace amount of 2-bromo-3-phenylacrylaldehyde. [g]Without Rh(ttp)Me, 92% recovery of **1a** (including the *E* isomer). [h]29% yield of α-bromostyrene and 26% yield of acetophenone formed.



Scheme S1. The Synthetic Route for the Allylic Bromides **1b-d**

General Procedures for the Synthesis of Allylic Bromides 1b, 1c, and 1d.

Allylic bromides **1b**, **1c**, and **1d** were prepared by a two-step method.[12] First, vinylation of the corresponding aldehydes/ketones with the Grignard reagent of vinylmagnesium bromide gave the addition product of the allylic alcohols, then PBr_3-mediated bromination afforded the final desired products of the allylic bromides.



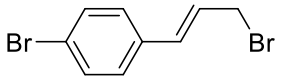
1c

Representative Synthesis of the Allylic Bromide of 1c.

To a stirred solution of 2-naphthaldehyde (1561.8 mg, 10 mmol) in anhydrous THF (10 mL) at 0 °C was added vinylmagnesium bromide (1 M in THF, 12 mL, 12 mmol) dropwise, it was allowed to react at 0 °C for 0.5 h, then warm to rt for 2.5 h. The reaction was quenched with NH_4Cl (aq). The mixture was extracted with Et_2O, then dried over Na_2SO_4. The allylic alcohol

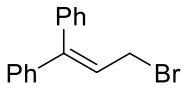
was obtained (1800.8 mg, 9.8 mmol, 98%) after rotary evaporation of the solvents.

To an ice-cold solution of the above prepared allylic alcohol (1800.8 mg, 9.8 mmol) in CH_2Cl_2 (20 mL) was added PBr_3 (0.95 mL, 10.0 mmol) dropwise. It was then allowed to warm to rt and reacted overnight. The reaction was quenched with sat. $NaHCO_3$ (aq), extracted with DCM, dried over Na_2SO_4, and concentrated by rotary evaporation. (*E*)-2-(3-bromoprop-1-en-1-yl)naphthalene[13] (**1c**; 2020.6 mg, 8.2 mmol, 84%) was obtained as a white solid after further recrystallization from DCM/MeOH. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.23 (d, *J* = 7.8 Hz, 2H), 6.52 (dt, *J* = 15.6, 7.8 Hz, 1H), 6.81 (d, *J* = 15.6 Hz, 1H), 7.46-7.50 (m, 2H), 7.59 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.75 (s, 1H), 7.79-7.81 (m, 3H).



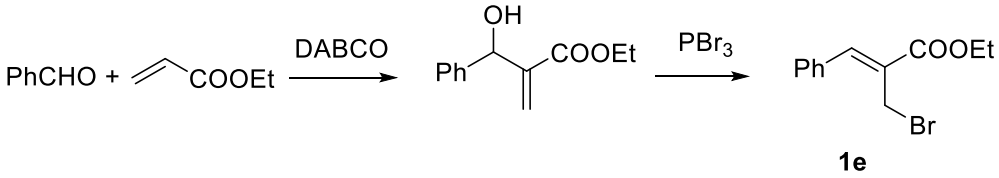
1b

Synthesis of the Allylic Bromide of 1b. (*E*)-1-(4-Bromophenyl)-l-propen-3-y1 bromide (**1b**) was prepared following the representative procedures for the synthesis of **1c**. Starting from *p*-bromobenzaldehyde (925 mg, 5.0 mmol) in THF (10 mL), with the addition of vinylmagnesium bromide solution (1 M in THF, 6.0 mL, 6.0 mmol), 1-(*p*-bromophenyl)prop-2-en-1-ol (989 mg, 4.64 mmol, 93%) was obtained.[14] Then 1-(*p*-bromophenyl)prop-2-en-1-ol (302 mg, 1.42 mmol) was utilized for further bromination reaction with PBr_3 (190 μL, 2.00 mmol) to give **1b** (316 mg, 1.14 mmol, 81%) as a brown solid.[15] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.14 (d, *J* = 7.8 Hz, 2H), 6.39 (dt, *J* = 15.6, 7.8 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 7.24-7.26 (m, 2H), 7.44-7.46(m, 2H).



1d

Synthesis of the Allylic Bromide of 1d. (3-Bromoprop-1-ene-1,1-diyl)dibenzene (**1d**) was prepared following the representative procedures for the synthesis of **1c**. Starting from benzophenone (1826.5 mg, 10 mmol) in THF (10 mL), with the addition of vinylmagnesium bromide solution (1 M in THF, 12.0 mL, 12 mmol), 1,1-diphenyl-2-propen-1-ol[16] (2173.8 mg, 10 mmol, 100%) was obtained. Then, 1-diphenyl-2-propen-1-ol (105.1 mg, 0.5 mmol) was utilized for further bromination reaction with PBr_3 (50 μL, 0.53 mmol) to give **1d** (129.7 mg, 0.47 mmol, 94%).[13] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.06 (d, *J* = 8.5 Hz, 2H), 6.34 (t, *J* = 8.5 Hz, 1H), 7.23-7.44 (m, 10H).



1e

Scheme S2. Synthesis of the Allylic Bromide **1e**

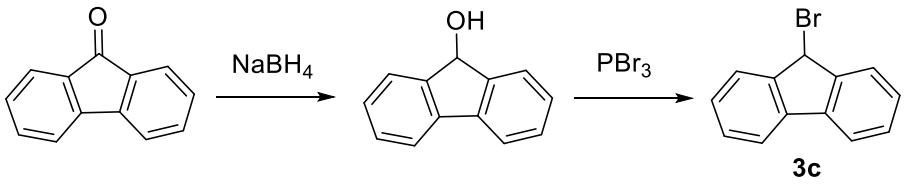
Synthesis of the Allylic Bromide of 1e. Synthesis of **1e** ((*Z*)-Ethyl 2-(bromomethyl)-3-phenylacrylate) involved the Baylis-Hillman reaction of benzaldehyde with ethyl acrylate to give the allylic alcohol, followed by the bromination mediated by PBr_3

Ethyl acrylate (4250 μL, 40.0 mmol) and 1,4-diazabicyclo[2,2,2]octane (DABCO) (1.12 g, 10.0 mmol) were added to the solution of benzaldehyde (2040 μL, 20.0 mmol) in 2 mL 1,4-dioxane/water (v:v = 1:1) at rt. The solution was stirred for 3 d at rt for another 5 d at 50 °C. Excess ethyl acrylate and solvent were removed by high vacuum. The crude product was purified

by column chromatography on silica gel eluting first with CH_2Cl_2/hexane then with CH_2Cl_2 to afford desired ethyl 2-[1-hydroxy(phenyl)methyl]acrylate (3.06 g, 14.8 mmol, 74%).[17] PBr_3 (340 μL, 3.6 mmol) was slowly injected into the solution of ethyl 2-[hydroxy(phenyl)methyl]acrylate (618 mg, 3.0 mmol) in Et_2O (15 mL) at 0 °C. The solution was stirred for 2 h at 0 °C. Saturated aqueous $NaHCO_3$ (10 mL) and water (10 mL) were added to the solution and stirred for 10 min. The reaction mixture was worked up by extraction with Et_2O (3 × 5 mL). The organic phase was washed with saturated aqueous $NaHCO_3$ and brine, dried by anhydrous $MgSO_4$ and concentrated to give **1e** (668 mg, 2.48 mmol, 83%).[18] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.38 (t, *J* = 7.1 Hz, 3H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.40 (s, 2H), 7.41-7.59 (m, 5H), 7.83 (s, 1H).

General Procedures for the Synthesis of Benzylic Bromides 3c, 3f

3a, **3b**, **3d**, and **3e** are commercially available and directly used without further purification. The benzylic bromides of **3c**, **3f** were prepared first by the reduction of corresponding ketones with $NaBH_4$, followed by the bromination mediated by PBr_3.

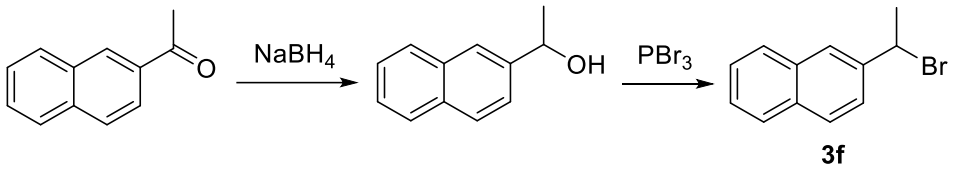


Scheme S3. Synthesis of the Allylic Bromide **3c**

Synthesis of 9-Bromofluorene (3c). To a stirred solution of 9-fluorenone (1840 mg, 10 mmol) in THF (4.5 mL)/H_2O (v:v = 9:1) was added $NaBH_4$ (263.0 mg, 7.0 mmol) in one portion. The mixture was stirred at rt for 20 h. The reaction was then quenched with water, extracted with Et_2O, dried over Na_2SO_4, and concentrated to give 9-hydroxyfluorene (1862 mg, 10 mmol, 100%) as a white solid.

To a stirred solution of 9-hydroxyfluorene (915.5 mg, 5.0 mmol) in DCM (10 mL) at rt was added PBr_3 (0.25 mL, 2.66 mmol). The mixture was stirred at rt for 1 h. The reaction was then

quenched with sat. $NaHCO_3$ (aq), extracted with DCM, dried over Na_2SO_4, and concentrated to give 9-bromofluorene (**3c**; 1171.2 mg, 4.8 mmol, 96%) as a pale yellow solid.[19] ^1H NMR ($CDCl_3$, 400 MHz): δ 6.00 (s, 1H), 7.34-7.42 (m, 4H), 7.67 (t, *J* = 8.1 Hz, 4H).



3f

Scheme S4. Synthesis of the Allylic Bromide **3f**

Synthesis of 2-(1-Bromoethyl)naphthalene (3f). To a stirred solution of 2-acetonaphthone (1702.3 mg, 10 mmol) in THF (9.0 mL)/H_2O (v:v = 9:1) was added $NaBH_4$ (259.2 mg, 6.8 mmol) in one portion. The mixture was stirred at rt for 16 h. The reaction was then quenched with water, extracted with Et_2O, dried over Na_2SO_4, and concentrated to give 1-(2-naphthyl)ethanol (1626.4 mg, 9.4 mmol, 94%) as a white solid.

To a stirred solution of 1-(2-naphthyl)ethanol (517.6 mg, 3.0 mmol) in DCM (5 mL) at 0 °C was added PBr_3 (0.14 mL, 1.5 mmol). The mixture was then allowed to warm to rt for 20 h. The reaction was then quenched with sat. $NaHCO_3$ (aq), extracted with DCM, dried over anhydrous Na_2SO_4, and concentrated to give 2-(1-bromoethyl)naphthalene (**3f**; 560.6 mg, 2.4 mmol, 80%) as a white solid.[20] ^1H NMR ($CDCl_3$, 400 MHz): δ 2.16 (d, *J* = 6.8 Hz, 3H), 5.41 (q, *J* = 6.8 Hz, 1H), 7.49-7.51 (m, 2H), 7.61 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.82-7.86 (m, 4H).

General Procedures for the Substrate Scope Examination of Allylic Bromides and Benzylic Bromides. Rh(ttp)Me (4.0 mg, 0.0051 mmol), an allylic/benzylic bromide (0.10 mmol), H_2O (90 μL, 5.0 mmol), and 2,6-di-^{t}Bu-pyridine (21 μL, 0.10 mmol) were added to benzene (2 mL). The mixture was heated at 200 °C under air until the complete consumption of the allylic/benzylic bromide monitored by GC-MS and TLC. Excess benzene was removed by rotary evaporation.

The crude reaction mixture was taken for ^{1}H NMR spectroscopy analysis with 1,1,2,2-tetrachloroethane (10 μL, 0.0945 mmol) as the internal standard to obtain the NMR yield.

Substrate Scope of Allylic Bromides

With (*Z*)-(2,3-Dibromoprop-1-enyl)benzene ((*Z*)-1a) Substrate. The reaction with (*Z*)-**1a** (15.5 μL, 0.10 mmol) was heated under air at 200 °C for 6 h to give (2-bromoprop-1-en-1-yl)benzene (**2a**)[6, 9] (*E*/*Z* = 1.1/1.0) in 50% NMR yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ *E* isomer 2.49 (d, *J* = 0.9 Hz, 3H), 6.73 (s, 1H), 7.21-7.37 (m, 5H); *Z* isomer 2.47 (s, 3H), 6.97 (s, 1H), 7.21-7.37 (m, 5H). MS (EI, 70 eV) *m*/*z* (relative intensity) 198 (31%, $M^+(^{81}Br)$), 196 (32%, $M^+(^{79}Br)$), 117 (74%), 116 (33%) 115 (100%), 91 (35%).

With (*E*)-1-(4-Bromophenyl)-l-propen-3-y1 bromide (1b) Substrate. The reaction with **1b** (27.5 mg, 0.10 mmol) was heated under air at 200 °C for 4 h to give 4-bromo-*β*-methylstyrene (**2b**)[21] (*E*/*Z* = 10/1) in 57% NMR yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ *E* isomer 1.88 (d, *J* = 6.3 Hz, 3H), 6.24 (dq, *J* = 15.8, 6.3 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H); *Z* isomer: characteristic 5.79-5.87 (m, 1H). MS (EI, 70 eV) *m*/*z* (relative intensity) 198 (31%, $M^+(^{81}Br)$), 196 (31%, $M^+(^{79}Br)$), 117 (100%), 115 (86%).

With (*E*)-2-(3-Bromoprop-1-en-1-yl)naphthalene (1c) Substrate. The reaction with **1c** (24.4 mg, 0.10 mmol) was heated under air at 200 °C for 4 h to give 1-(2-naphthyl)propene[22] (**2c**) (*E*/*Z* = 8/1) in 40% NMR yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ *E* isomer 1.92 (d, *J* = 6.4 Hz, 3H), 6.34 (dq, *J* = 15.8, 6.4 Hz, 1H), 6.54 (d, *J* = 15.8 Hz, 1H), 7.34-7.76 (m, 7H); *Z* isomer: characteristic 1.96 (dd, *J* = 7.2, 1.1 Hz, 3H). MS (EI, 70 eV) *m*/*z* (relative intensity) 168 (100%, M^+), 167 (85%), 153 (59%), 152 (43%).

With (3-Bromoprop-1-ene-1,1-diyl)dibenzene (1d) Substrate. The reaction with **1d** (24 μL, 28.2 mg, 0.10 mmol) was heated under air at 200 °C for 4 h to give 1,1-diphenylpropene (**2d**)[23]

in 76% NMR yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.75 (d, *J* = 7.0 Hz, 3H), 6.17 (q, *J* = 7.0 Hz, 1H), 7.17-7.50 (m, 10H). MS (EI, 70 eV) *m*/*z* (relative intensity) 194 (100%, M^+), 193 (60%), 179 (35%), 178 (44%), 165 (28%), 115 (78%).

With (*Z*)-Ethyl 2-(bromomethyl)-3-phenylacrylate (1e) Substrate. The reaction with **1e** (19 μL, 27.1 mg, 0.10 mmol) was heated under air at 200 °C for 12 h to give ethyl 2-methyl-3-phenylacrylate[24] (**2e**) (*E*/*Z* = 15/1) in 66% NMR yield with 10% recovery of **1e**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ *E* isomer 1.35 (t, *J* = 7.1 Hz, 3H), 2.12 (s, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 7.35-7.42 (m, 5H), 7.69 (s, 1H). *Z* isomer 1.10 (t, *J* = 7.1 Hz, 3H), 2.09 (s, 3H), 4.11 (q, *J* = 7.1 Hz, 2H), 6.70 (s, 1H), 7.22-7.40 (m, 5H). MS (EI, 70 eV) *m*/*z* (relative intensity) 190 (26%, M^+), 161 (15%), 145 (39%), 144 (30%), 117 (80%), 116 (86%), 115 (100%), 91 (33%).

Substrate Scope of Benzylic Bromides

With 2-(Bromomethyl)naphthalene (3a) Substrate. The reaction with **3a** (22.1 mg, 0.10 mmol) was heated under air at 200 °C for 18 h to give 2-methylnaphthalene[25] (**4a**) in 60% NMR yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.51 (s, 3H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.37-7.45 (m, 2H), 7.60 (s, 1H), 7.72-7.79 (m, 3H). MS (EI, 70 eV) *m*/*z* (relative intensity) 142 (100%, M^+), 141 (86%), 115 (30%).

With 4-^{t}Bu-Benzyl Bromide (3b) Substrate. The reaction with **3b** (18.5 μL, 22.9 mg, 0.10 mmol) was heated under air at 200 °C for 28 h to give 4-*tert*-butyltoluene[26] (**4b**) in 66% GC yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.32 (s, 9H), 2.33 (s, 3H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H). MS (EI, 70 eV) *m*/*z* (relative intensity) 148 (23%, M^+), 133 (100%), 105 (58%).

With 9-Bromofluorene (3c) Substrate. The reaction with **3c** (24.5 mg, 0.10 mmol) was heated under air at 200 °C for 12 h to give fluorene[27] (**4c**) in 43% NMR yield, together with 9,9'-bifluorene[27] (**4c'**) in 9% NMR yield. ^{1}H NMR ($CDCl_3$, **4c**, 400 MHz): δ 3.88 (s, 2H), 7.28 (t,

J = 7.6 Hz, 2H), 7.48 (t, *J* = 7.1 Hz, 2H),.7.53 (d, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 7.3 Hz, 2H). MS (EI, 70 eV) *m*/*z* (relative intensity) 166 (100%, M^+), 165 (94%); ^{1}H NMR ($CDCl_3$, **4c'**, 400 MHz): δ 4.83 (s, 2H), 6.95 (br, 4H), 7.09 (t, *J* = 7.4 Hz, 4H), 7.27 (t, *J* = 7.5 Hz, 4H), 7.65 (d, *J* = 7.6 Hz, 4H). (EI, 70 eV) *m*/*z* (relative intensity) 330 (9%, M^+), 165 (100%).

With 4-Phenyl-Benzyl Bromide (3d) Substrate. The reaction with **3d** (24.7 mg, 0.10 mmol) was heated under air at 200 °C for 48 h to give 4-methyl-1,1'-biphenyl[28] (**4d**) in 70% NMR yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.42 (s, 3H), 7.28-7.60 (m, 9H). (EI, 70 eV) *m*/*z* (relative intensity) 168 (100%, M^+), 167 (73%), 153 (26%), 152 (30%).

With Ethyl (4-Bromomethyl)benzoate (3e) Substrate. The reaction with **3e** (24.3 mg, 0.10 mmol) was heated under air at 200 °C for 48 h to give ethyl 4-methylbenzoate[29] (**4e**) in 38% NMR yield, together with 4-methylbenzoic acid[30] (**4e'**) in 25% NMR yield. ^{1}H NMR ($CDCl_3$, **4e**, 400 MHz): δ 1.39 (t, *J* = 7.3 Hz, 3H), 2.41 (s, 3H), 4.37 (q, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H). (EI, 70 eV) *m*/*z* (relative intensity) 164 (12%, M^+), 149 (5%), 136 (28%), 119 (100%), 91 (49%); ^{1}H NMR ($CDCl_3$, **4e'**, 400 MHz): δ 2.43 (s, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H).

With 2-(1-Bromoethyl)naphthalene (3f) Substrate. The reaction with **3f** (23.5 mg, 0.10 mmol) was heated under air at 200 °C for 14 h to give 2-ethylnaphthalene[31] (**4f**) in 57% NMR yield, together with 2-vinylnaphthalene[32] (**4f'**) in 7% NMR yield. ^{1}H NMR ($CDCl_3$, **4f**, 400 MHz): δ 1.35 (t, *J* = 7.5 Hz, 3H), 2.83 (q, *J* = 7.5 Hz, 3H), 7.35-7.47 (m, 3H), 7.64 (s, 1H), 7.77-7.82 (m, 3H). MS (EI, 70 eV) *m*/*z* (relative intensity) 156 (37%, M^+), 141 (100%), 115 (28%); ^{1}H NMR ($CDCl_3$, **4f'**, 400 MHz): δ characteristic 5.35 (d, *J* = 10.8 Hz, 1H), 5.89 (d, *J* = 17.6 Hz, 1H), 6.90 (dd, *J* = 17.6, 10.8 Hz, 1H). MS (EI, 70 eV) *m*/*z* (relative intensity) 154 (100%, M^+), 153 (61%), 152 (41%) 128 (17%).

Mechanistic Investigations

Deuterium Labeling Experiments

With (*Z*)-(2,3-Dibromoprop-1-enyl)benzene ((*Z*)-1a) Substrate. Rh(ttp)Me (4.0 mg, 0.0051 mmol), (*Z*)-**1a** (15.5 μL, 0.10 mmol), D_2O (90 μL, 5.0 mmol), and 2,6-di-^{t}Bu-pyridine (21 μL, 0.10 mmol) were added to benzene (2 mL). The mixture was heated at 200 °C under air for 6 h. Excess benzene was removed by rotary evaporation. The crude reaction mixture was passed through a plug of pipet column eluting with hexane/DCM (4/1), concentrated and then taken for ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane (10 μL, 0.0945 mmol) as the internal standard. **2a**-*d* was obtained in 42% NMR yield with 84% D incorporation into the allylic position. The olefinic position was trace deuterated.

The crude reaction mixture was also taken for GC-MS analysis. EI-MS analysis of **2a**-*d* at t = 4 h gave the relative intensity at *m*/*z* 196 (6.33%), 197 (35.20%), 198 (10.62%), 199 (34.52%) (Figure S1). Thus, **2a**-d_0 : **2a**-d_1 = 6.33 : (35.20 − 6.33 × 9 × 0.011) = 6.33 : 34.57 = 15.5 : 84.5. The deuterium incorporation of **2a**-*d* is (15.5% × 0 + 84.5 % × 1) = 84%. EI-MS analysis of **2a**-*d* at t = 6 h gave the relative intensity at *m*/*z* 196 (7.00%), 197 (34.18%), 198 (11.38%), 199 (34.26%) (Figure S1). Hence, **2a**-d_0 : **2a**-d_1 = 7.00 : (34.18 − 7.00 × 9 × 0.011) = 7.00 : 33.49 = 17.3 : 82.7. The deuterium incorporation of **2a**-*d* is (17.3% × 0 + 82.7 % × 1) = 83%. Therefore, the deuterium incorporations determined by MS analysis are in line with that obtained by ^{1}H NMR analysis. Furthermore, they did not change with time within the catalysis time scale.

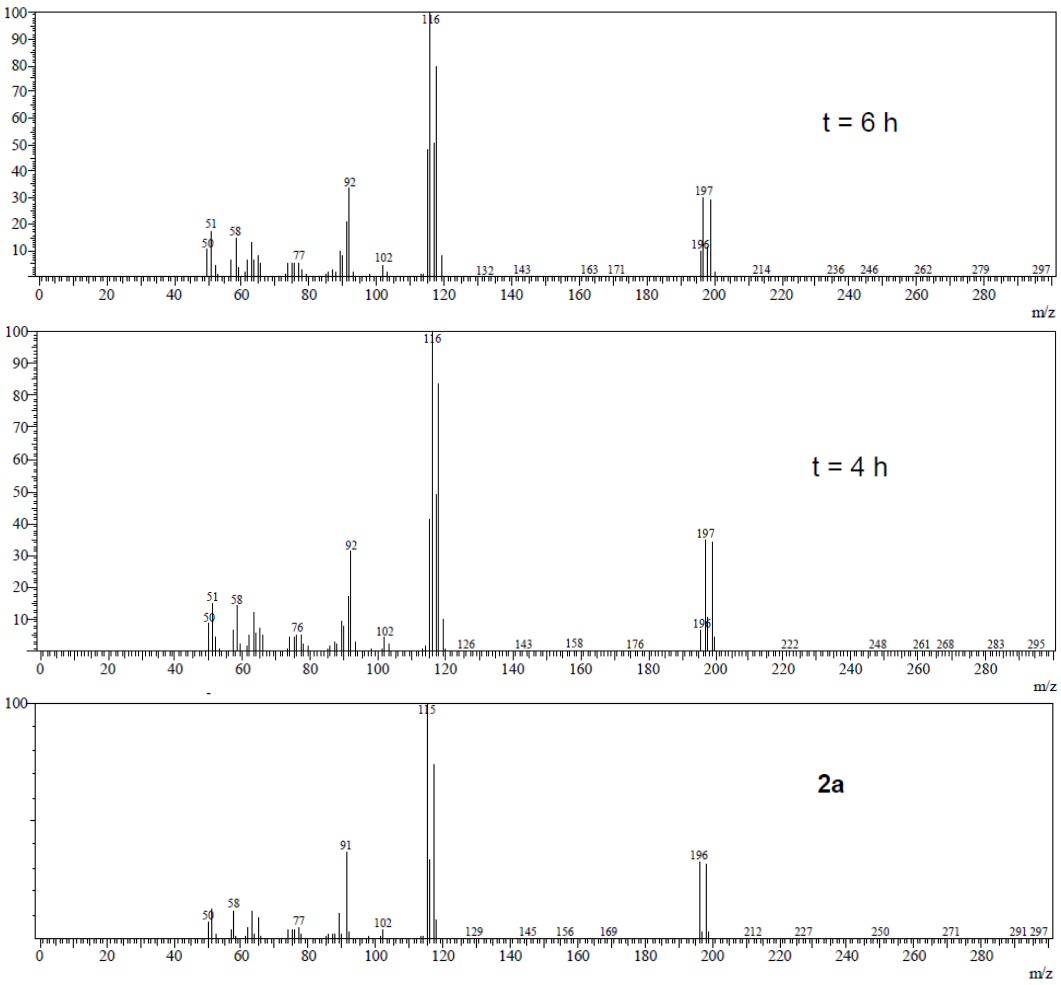
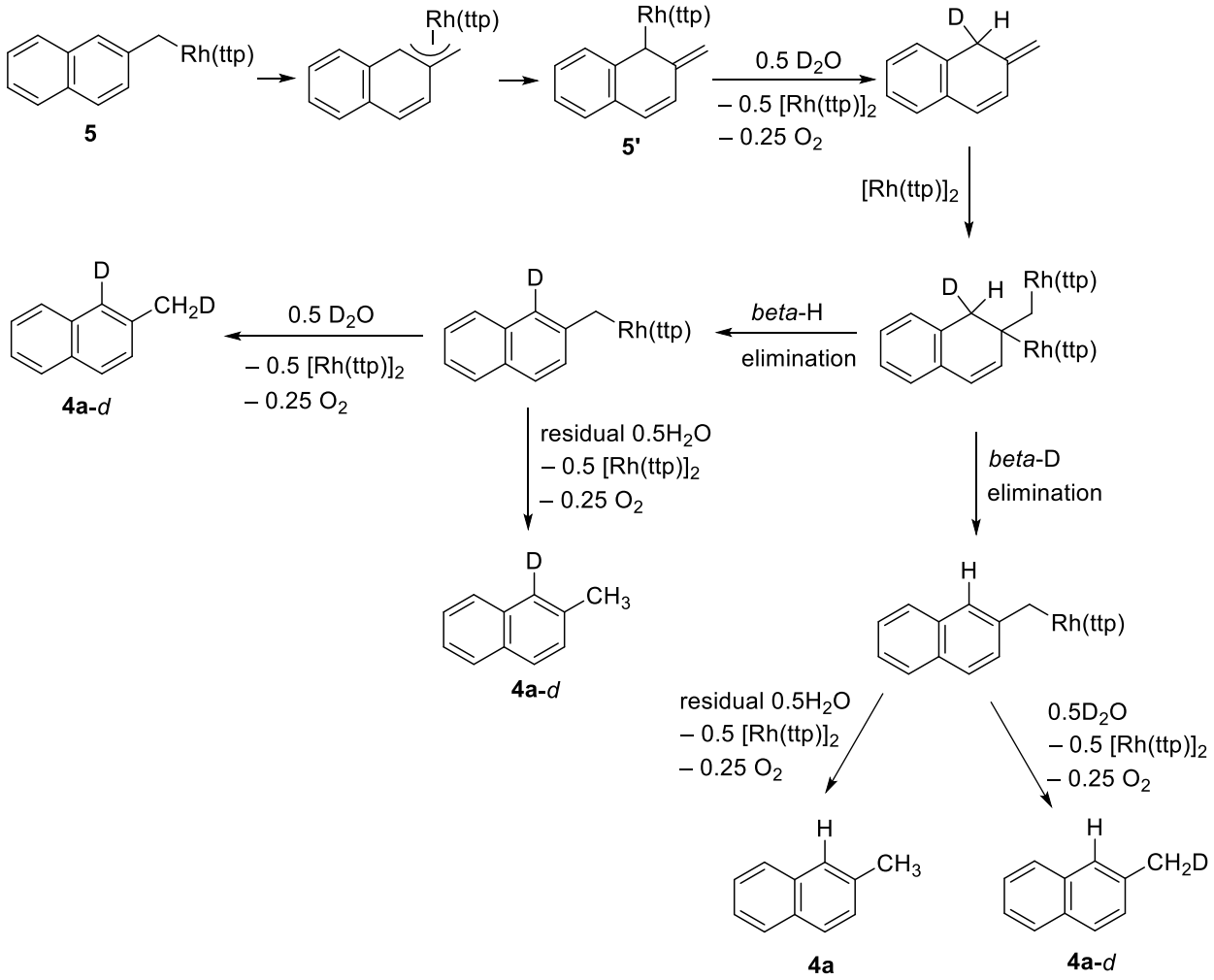


Figure S1. EI-MS spectra of **2a** (reference), and **2a**-*d* at t = 4 h, 6 h.

With 2-(Bromomethyl)naphthalene (3a) Substrate. Rh(ttp)Me (4.0 mg, 0.0051 mmol), **3a** (22.1 mg, 0.10 mmol), D_2O (90 μL, 5.0 mmol), and 2,6-di-^{t}Bu-pyridine (21 μL, 0.10 mmol) were added to benzene (2 mL). The mixture was heated at 200 °C under air for 48 h. Excess benzene was removed by rotary evaporation. The crude reaction mixture was taken for ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane (10 μL, 0.0945 mmol) as the internal standard. After that, the mixture was passed through a plug of pipet column eluting with hexane/DCM (4/1), concentrated and taken for further ^{1}H NMR analysis. **4a**-*d* was obtained in 56% NMR yield with 95% D incorporation into the benzylic position, together with 73% D incorporation into the naphthalene C-1 position. The 73% deuterium incorporation at the naphthalene C-1 position is likely resulted

from the Rh(ttp)-catalyzed H/D exchange with D_2O via the intermediate of Rh(ttp)(2-naphthylmethyl) (**5**), which might isomerize to **5'** for the deuterium incorporation at the naphthalene C-1 position (Scheme S5).[33]



Scheme S5. Proposed Pathway for the Deuterium Incorporation into **4a**-*d*

Determination of Isotopic Product Composition of 4a-*d*. The hydrodebromination of **3a** with D_2O catalyzed by Rh(ttp)Me was repeated following the standard experimental procedures for 8 times. The reactions mixtures were mixed and the benzene solvent was removed with rotary evaporator. The resulted black oil was dissolved in 15 mL of DCM and 15 mL 3 M HCl was

added. The mixture was stirred at room temperature for overnight to remove residual 2,6-*di*-*tert*-butylpyridine. The crude mixture was further purified with column chromatography on silica gel using hexane as eluent and the first fraction was collected as white solid (**4a**-*d*, 36 mg, 35%). ^{1}H NMR, ^{13}C{1H} NMR and quantitative ^{13}C{1H} NMR spectra with inverse-gated decoupling were recorded for **4a**-*d*. ^{1}H NMR, ^{13}C NMR of **4a** was also recorded as a reference. The longitudinal relaxation time (T_1) of ^{13}C NMR signal by inversion recovery experiment were done and calculated using **4a** and directly applied to **4a**-*d*. All T_1 values of ^{13}C signal were no more than 10 s. Long relaxation delay of 60 s (d1 = 5 × T_1) was applied to the quantitative ^{13}C NMR.

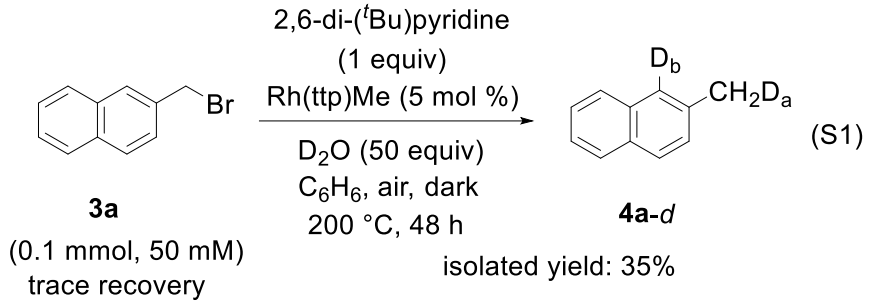
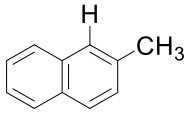
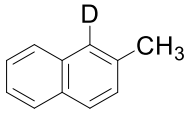
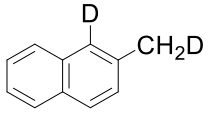
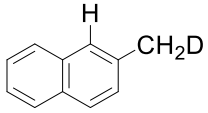


Table S5. Deuterium Incorporation Determined by NMR Analysis

Determining D% via NMR	D_a incorporation%	D_b incorporation%
^{1}H NMR (d1 = 10 s)	83%	70%
Quantitative ^{13}C NMR (d1 = 60 s)	80%	70%

Table S6. Isotopic Product Composition Determined by Quantitative $^{13}C\{^{1}H\}$ NMR Analysis

Label	Structure	Percentage
●		5%
●		14%
●		55%
●		26%

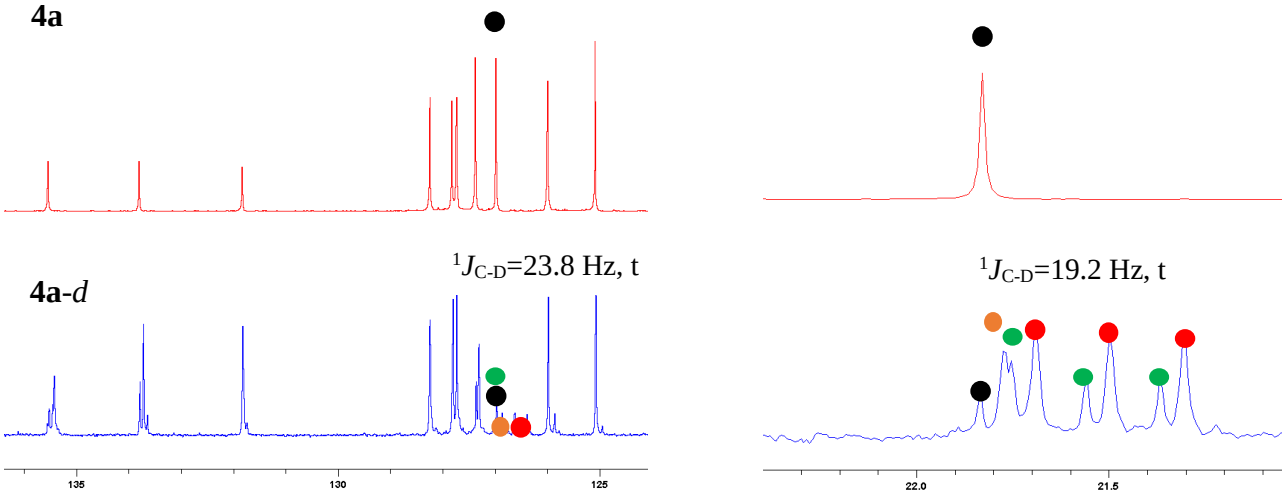


Figure S2. Expanded ^{13}C NMR spectrum of **4a** and quantitative ^{13}C NMR spectrum of **4a**-*d*.

The Control Experiment for the Post-H/D Exchange of 2-Methylnaphthalene (4a) with D_2O. Rh(ttp)Me (4.0 mg, 0.0051 mmol), **4a** (14.2 mg, 0.10 mmol), D_2O (90 μL, 5.0 mmol), and 2,6-di-^{t}Bu-pyridine (21 μL, 0.10 mmol) were added to benzene (2 mL). The mixture was heated at 200 °C under air for 48 h. After the reaction, 25 μL of the reaction mixture was taken for GC-MS analysis with naphthalene spiked as the internal standard. Excess benzene was removed by rotary evaporation. The crude reaction mixture was taken for ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane (10 μL, 0.0945 mmol) as the internal standard. **4a**-*d* was quantitatively recovered with trace D incorporation into both the naphthalene C-1 position and benzylic position. 2,6-Di-^{t}Bu-pyridine was also quantitatively recovered with no D incorporation.

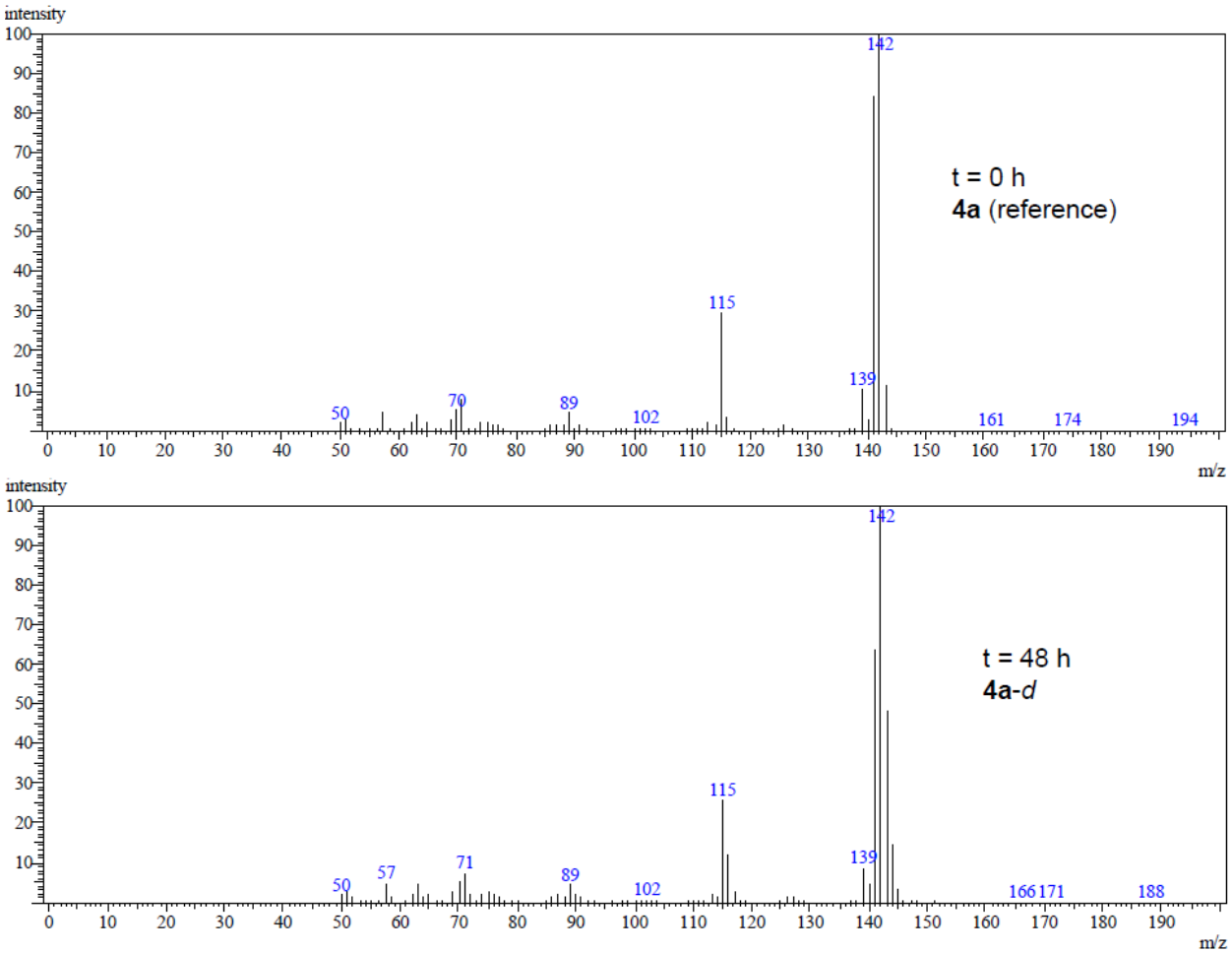
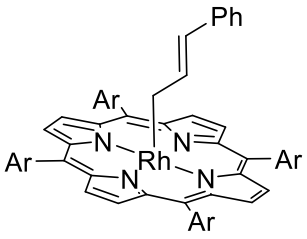


Figure S3. EI-MS spectra of **4a** (reference), and **4a**-*d* at t = 0 h and 48 h, respectively.

Hydrolysis of Rh(ttp)(*trans*-cinnamyl)



Ar = 4-tolyl, Rh(ttp)(*trans*-cinnamyl)

Preparation of Rh(ttp)(*trans*-cinnamyl) (6). Rh(ttp)Cl (20.0 mg, 0.025 mmol) in EtOH (2 mL) and a solution of $NaBH_4$ (55.6 mg, 1.47 mmol) in aqueous NaOH (0.1 M, 1 mL) were purged with nitrogen separately for about 15 minutes. The solution of $NaBH_4$ was added slowly to the suspension of Rh(ttp)Cl via a cannula in a period of 30 s under N_2. The reaction mixture was heated at 70 °C for 3 h and the color changed to deep brown. The reaction mixture was then cooled down to 0 °C and *trans*-cinnamyl bromide (15 μL, 0.10 mmol) was added under nitrogen. An orange suspension formed immediately and it was stirred for 10 minutes. After the reaction, the mixture was diluted with H_2O (10 mL), extracted with DCM (5 mL × 3). The combined organic extracts were washed with H_2O (10 mL × 2). Then recrystallization from DCM/MeOH afforded the purified product **6** as an orange solid (16.1 mg, 0.018 mmol, 72%). R_f = 0.81 (hexane:DCM = 1:1).

^{1}H NMR ($CDCl_3$, 400 MHz): δ −4.03 (dd, $^2J_{Rh\text{-}H}$ = 3.6 Hz, $^3J_{H\text{-}H}$ = 8.6 Hz, 2H), −0.90 (dt, *J* = 15.4, 8.6 Hz, 1H), 2.69 (s, 12H), 2.84 (d, *J* = 15.3 Hz, 1H), 6.01 (d, *J* = 7.6 Hz, 2H), 6.91 (t, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 4H), 7.52 (d, *J* = 7.8 Hz, 4H), 7.77 (d, *J* = 7.0 Hz, 4H), 8.06 (d, *J* = 7.0 Hz, 4H), 8.70 (s, 8H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.2 ($^1J_{Rh\text{-}C}$ = 26.2 Hz), 21.7, 122.7, 124.0, 125.0, 126.1, 127.4, 127.5, 128.3, 131.6, 133.9, 137.2, 137.6, 139.4, 143.7.

HRMS (ESIMS): calcd for $C_{57}H_{45}N_4Rh$ ($[M]^+$) *m*/*z* 888.2694, found 888.2697.

The Sealed NMR Tube Reaction of the Hydrolysis of Rh(ttp)(*trans*-cinnamyl) (6) with H_2O. **6** (1.4 mg, 0.0016 mmol), H_2O (29 μL, 1.6 mmol) and C_6D_6 (400 μL) were added into a Teflon screw head stoppered NMR tube. The mixture was degassed by three freeze-pump-thaw cycles (77 K, 0.005 mmHg), and then flame-sealed under vacuum, heated in oven in dark. The reaction was monitored by ^{1}H NMR spectroscopy. Rh(ttp)(*trans*-cinnamyl) (**6**) underwent smooth hydrolysis at 180 °C for 4 h to give *trans-β*-methylstyrene in 22% NMR yield with 62% recovery of **6**. The NMR yields carry 16% error, which is responsible for the unaccounted mass balance.

The Sealed NMR Tube Reaction of the Hydrolysis of Rh(ttp)(*trans*-cinnamyl) (6) with D_2O. Rh(ttp)(*trans*-cinnamyl) (**6**; 1.5 mg, 0.0017 mmol), D_2O (30 μL, 33.2 mg, 1.6 mmol) and C_6D_6 (400 μL) were added into a Teflon screw head stoppered NMR tube. The mixture was degassed by three freeze-pump-thaw cycles (77 K, 0.005 mmHg), and then flame-sealed under vacuum, heated in oven in dark. The reaction was monitored by ^{1}H NMR spectroscopy. The reaction at 180 ˚C for 4 h gave deuterated *trans β*-methyl styrene in 30% yield with 55% recovery of **6**. The NMR yields carry 15% error, which is responsible for the unaccounted mass balance. There are 77% D, 23% D and 90% D incorporation at the C1, C2 and C3 positions, respectively, as determined by ^{1}H NMR analysis (eq S2). EI-MS results also support the formation of the deuterated *trans-β*-methylstyrene (Figure S4). The allylic C3 position is almost all deuterated, which means the formation of $–CD_3$. The D incorporation at the C1, C2 positions might due to the Rh(por)-catalyzed H/D exchange with D_2O, which also accounts for the over-deuteration at the allylic C3 position.

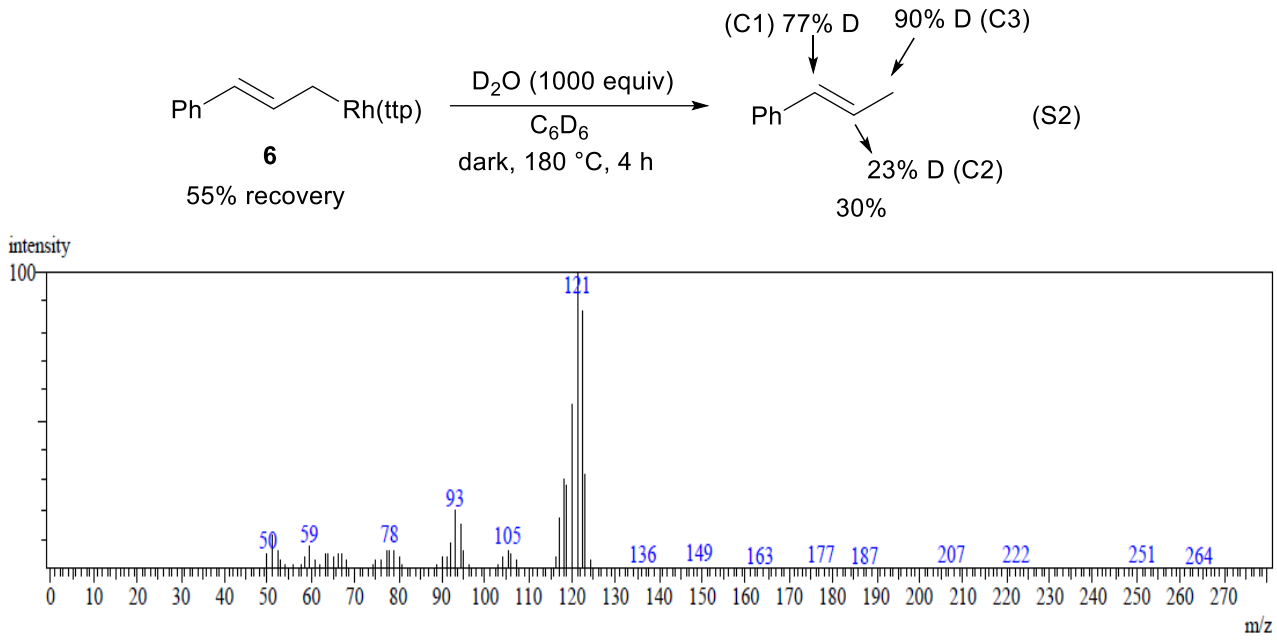


Figure S4. EI-MS spectrum of deuterated *trans-β*-methylstyrene.

Attempted Determination of Isotopic Product Composition of the Hydrolysis Product of Deuterated *trans-beta*-Methylstyrene. Rh(ttp)(*trans*-cinnamyl) (**6**; 35.6 mg, 0.04 mmol), D_2O (725 μL, 802.6 mg, 40 mmol) and benzene (2.0 mL) were added into a Teflon screw head stoppered glass tube, degassed with three freeze-pump-thaw cycles, filled with N_2 and heated at 200 ˚C for 8 h. After the reaction, 25 μL of the reaction mixture was taken for GC-MS analysis with naphthalene spiked as the internal standard. The reaction was repeated for 8 times and the reaction mixtures were combined, extracted with DCM, and dried with rotary evaporation. The residue was purified with column chromatography on silica gel using hexane as eluent to give the products with a single fraction as a colorless oil. (13.0 mg, 33%). The products contain deuterated *trans-beta*-methylstyrene (29%) and deuterated *n*-propylbenzene (4%) in 8:1 molar ratio, as determined by ^{1}H NMR and quantitative $^{13}C\{^1H\}$ NMR analysis. The product of *trans-beta*-methylstyrene is easy to evaporate with the b.p. of 175 °C, and should be handled with care. ^{1}H NMR and quantitative $^{13}C\{^1H\}$ NMR spectra were recorded.

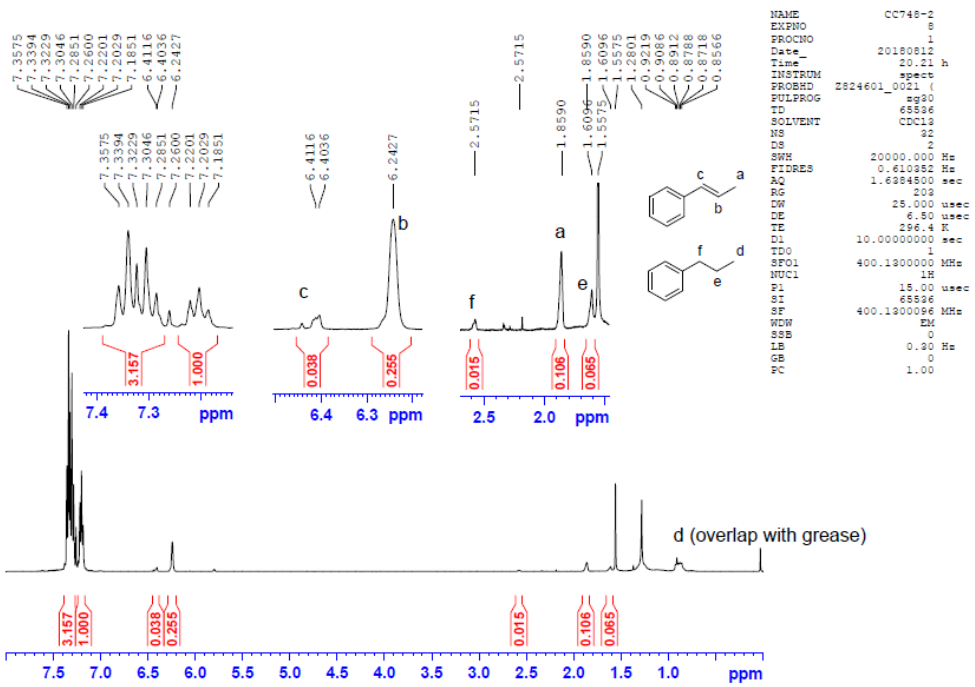


Figure S5. ^{1}H NMR spectrum of the hydrolysis products of Rh(ttp)(*trans*-cinnamyl) with D_2O.

Calculating of the molar ratio between the deuterated *trans-beta*-methylstyrene and deuterated *n*-propylbenzene: Regarding the aromatic proton signals' integrations, setting the molar of deuterated *n*-propylbenzene: x; deuterated *trans-beta*-methylstyrene: y. Then 3x + y = 1; 2x + 4y = 3.1. Thus, x = 0.09, y = 0.73 can be obtained. The molar ratio between the deuterated *trans-beta*-methylstyrene and deuterated *n*-propylbenzene is 0.73:0.09 = 8:1. For the quantitative $^{13}C\{^{1}H\}$ NMR analysis, the calculated molar ratio is 1:(0.25/2) = 8:1, which is in agreement with the result of the ^{1}H NMR analysis. The C1 position is (0.73 – 0.038)/0.73 = 95% deuterated. The C2 position is (0.73 – 0.255)/0.73 = 65% deuterated. The C3 position is (0.73 × 3 – 0.106)/(0.73 × 3) = 95% deuterated (eq S3). The allylic C3 position is almost all deuterated, which means the formation of $–CD_3$, which also accounts for the over-deuteration at the allylic C3 position.

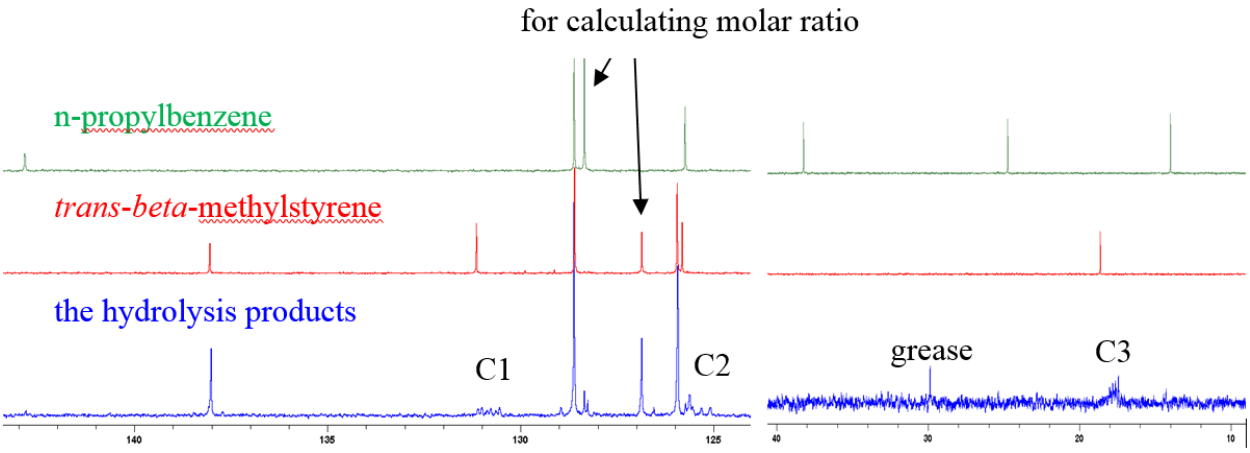
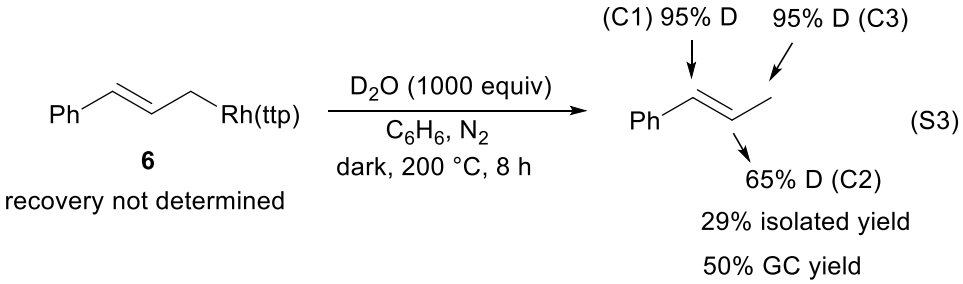
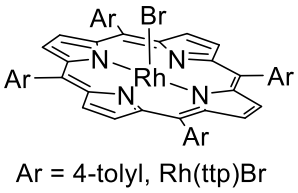


Figure S6. Expanded quantitative $^{13}C\{^{1}H\}$ NMR spectra of the hydrolysis products with D_2O (blue), *trans-beta*-methylstyrene (red), and *n*-propylbenzene (green).



Conversion of Rh(ttp)Br



Preparation of Bromo[5,10,15,20-tetratolylporphyrinato]rhodium [Rh(ttp)Br]. Rh(ttp)Cl (52.1 mg, 0.0645 mmol) and KBr (375.0 mg, 3.15 mmol, 50 equiv) were added to the anhydrous DCM (20 mL) under N_2. The resulting reddish solution with white precipitates was allowed to react at rt for 40 h in dark by wrapping with aluminum foil until the complete consumption of Rh(ttp)Cl monitored by TLC. After the reaction, H_2O was added and the mixture was extracted with DCM. The organic layer was combined and evaporated to dryness. The product was further

purified by filtering through a plug of silica eluting with DCM. Recrystallization from CH_2Cl_2/MeOH afforded the reddish product of Rh(ttp)Br[34] (45.0 mg, 0.0528 mmol, 82%). R_f = 0.69 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.71 (s, 12H), 7.55 (d, *J* = 7.8 Hz, 8H), 8.10 (t, *J* = 6.8 Hz, 8H), 8.93 (s, 8H).

The Sealed NMR Tube Reaction of the Conversion of Rh(ttp)Br. Rh(ttp)Br (0.9 mg, 0.001 mmol), H_2O (18 μL, 1.0 mmol) and C_6D_6 (400 μL) were added into a Teflon screw head stoppered NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy. Rh(ttp)H[3a] was obtained in 27% NMR yield at 180 °C for 52 h together with 62% recovery of Rh(ttp)Br. The NMR yields carry 11% error, which accounts for the unaccounted mass balance.

X-ray Crystallographic Data

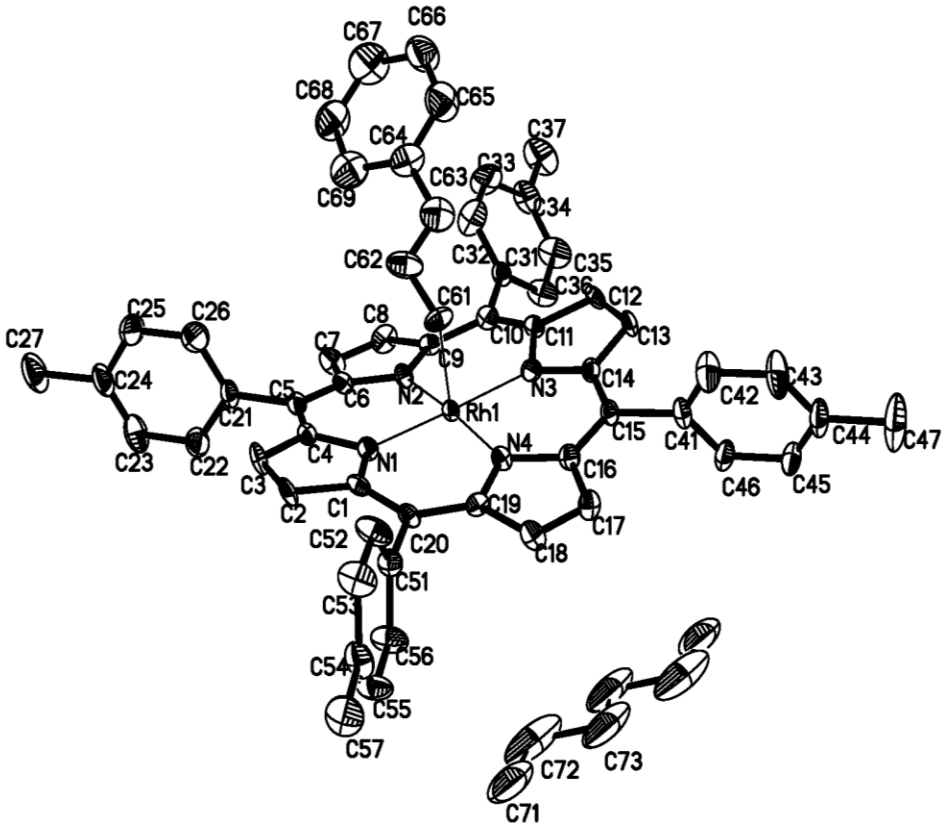


Figure S7. ORTEP presentation of the molecular structure with the numbering scheme for Rh(ttp)(*trans*-cinnamyl) (**6**; CCDC 1813321). with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). Rh(ttp)(*trans*-cinnamyl) (**6**) selected bond lengths (Å): Rh(1)–C(61): 2.100(9); C(61)–C(62): 1.482(8); C(62)–C(63): 1.292(17); C(63)–C(64): 1.514(18). Bond angles (°): N(1)-Rh(1)-C(61): 89.2(4); N(2)-Rh(1)-C(61): 96.0(3); N(3)-Rh(1)-C(61): 89.0(4); N(4)-Rh(1)-C(61): 91.0(3); C(62)-C(61)-Rh(1): 111.6(6); C(63)-C(62)-C(61): 118.9(13); C(62)-C(63)-C(64): 122.3(14).

Table S7. Crystallographic Data and Structure Refinement for Rh(ttp)(*trans*-cinnamyl) (**6**)

Compound	Rh(ttp)(*trans*-cinnamyl) (**6**)
CCDC deposition No.	1813321
Empirical formula	$C_{58.50}\ H_{48.50}\ N_4\ Rh$
Formula weight	910.42
Temperature	222(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 12.498(2) Å alpha = 112.876(4)° b = 14.419(2) Å beta = 91.885(4)°
Volume	2356.3(6) $Å^3$
Z, Calculated density	2, 1.283 mg/m^3
Absorption coefficient	0.405 mm^{-1}
F(000)	945
Crystal size	0.500 × 0.400 × 0.300 mm^3
Theta range for data collection	2.056 to 25.302 deg.
Index ranges	$-14 \le h \le 14$, $-17 \le k \le 17$, $-11 \le l \le 18$
Reflections collected / Independent reflections	8476 / 8476
Completeness to theta = 25.242 deg	99.7%
Absorption correction	multi-scan
Max. and min. transmission	0.7441 and 0.5655
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8476 / 10 / 587
Goodness-of-fit on F2	0.995
Final R indices [I>2sigma(I)]	R1 = 0.0960, wR2 = 0.2507
R indices (all data)	R1 = 0.1330, wR2 = 0.2743
Largest diff. peak and hole	3.817 and −2.051 $e.Å^{-3}$

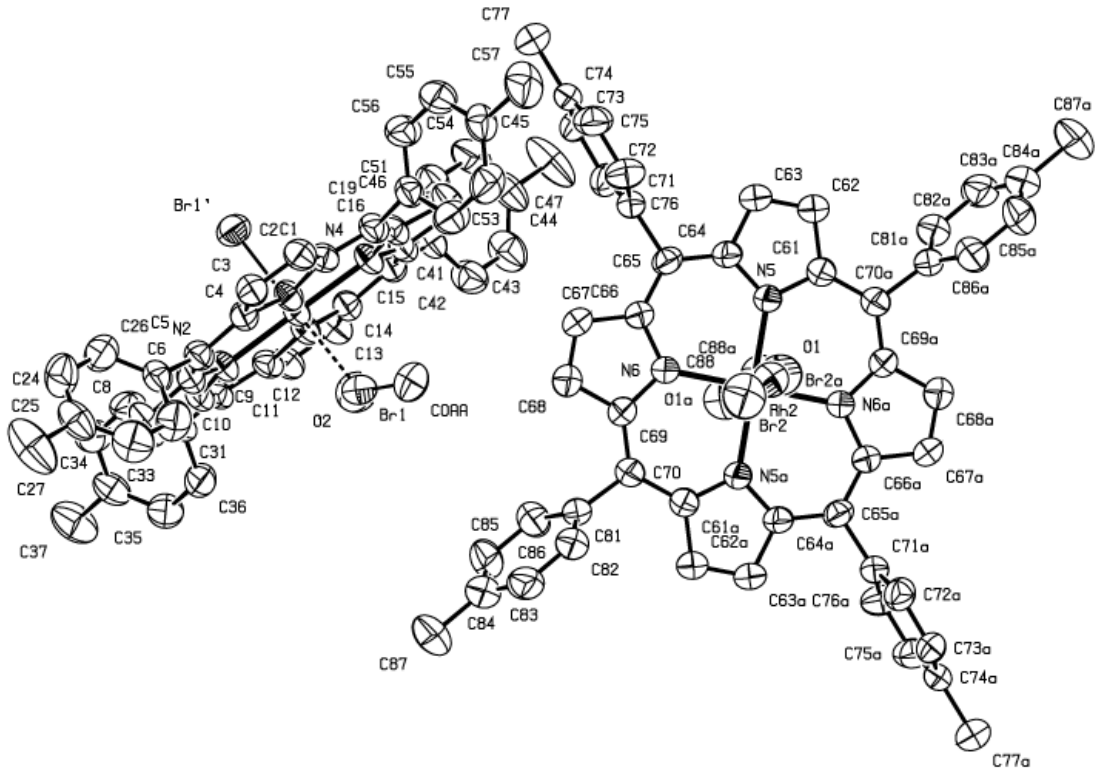


Figure S8. ORTEP presentation of the molecular structure with the numbering scheme for Rh(ttp)Br (CCDC 1813320) with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). Rh(ttp)Br selected bond lengths (Å): Rh(1)–Br(1'): 2.3619(9); Rh(1)–Br(1): 2.300(7). Bond angles (^{o}): N(4)-Rh(1)-N(1): 90.07(17); N(4)-Rh(1)-N(2): 179.14(19); N(4)-Rh(1)-Br(1): 87.7(2).

Table S8. Crystallographic Data and Structure Refinement for Rh(ttp)Br

Compound	Rh(ttp)Br
CCDC deposition No.	1813320
Empirical formula	$C_{146.44}H_{115.31}Br_3N_{12}O_{2.44}Rh_3$
Formula weight	2630.59
Temperature	302(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 11.4853(8) Å alpha = 97.727(2)° b = 12.4928(9) Å beta = 102.976(2)° c = 23.5322(17) Å gamma = 97.590(2)°
Volume	3214.0(4) $Å^3$
Z, Calculated density	1, 1.359 mg/m^3
Absorption coefficient	1.370 mm^{-1}
F(000)	1337.0
Crystal size	0.500 × 0.400 × 0.300 mm^3
Theta range for data collection	2.657 to 25.248 deg.
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-28 \le l \le 28$
Reflections collected / Independent reflections	117626 / 11583 [R(int) = 0.0379]
Completeness to theta = 25.242 deg	99.8 %
Absorption correction	multi-scan
Max. and min. transmission	0.7456 and 0.5843
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11583 / 0 / 784
Goodness-of-fit on F^2	1.216
Final R indices [I>2sigma(I)]	R1 = 0.0577, wR2 = 0.1373
R indices (all data)	R1 = 0.0645, wR2 = 0.1404
Largest diff. peak and hole	0.52 and −1.10 e.$Å^{-3}$

NMR Spectra

Figure S9. ^{1}H NMR Spectrum of (2,2-Dibromocyclopropyl)benzene

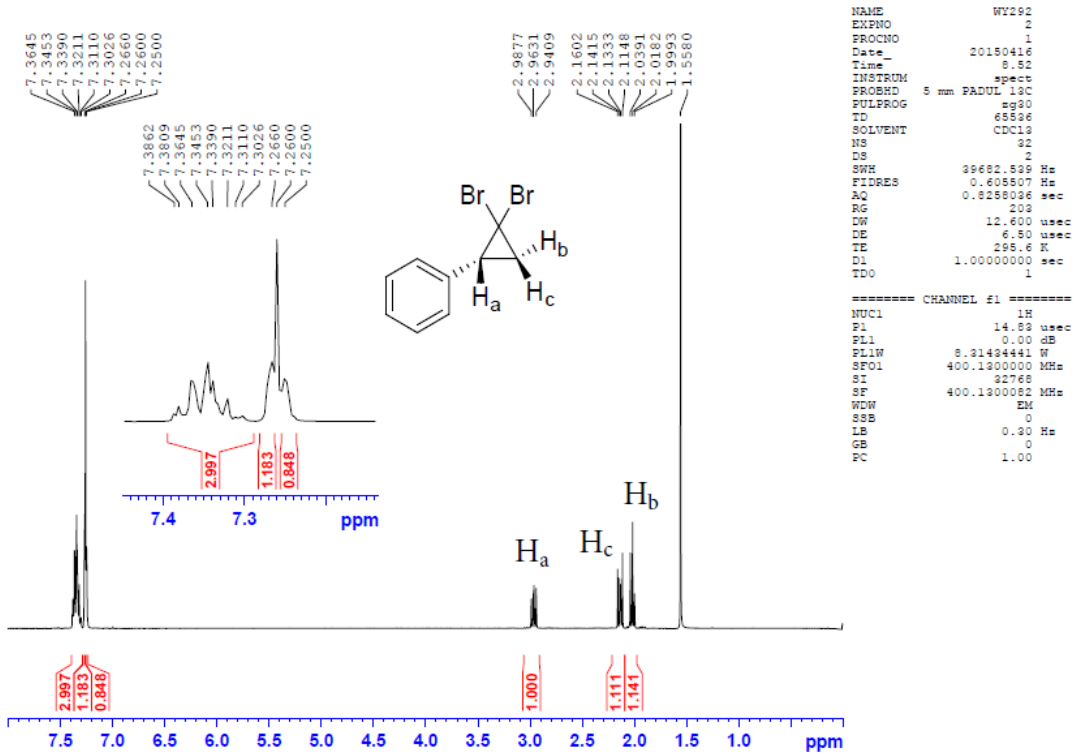


Figure S10. ^{1}H NMR Spectrum of (*Z*)-(2,3-dibromoprop-1-enyl)benzene ((*Z*)-**1a**)

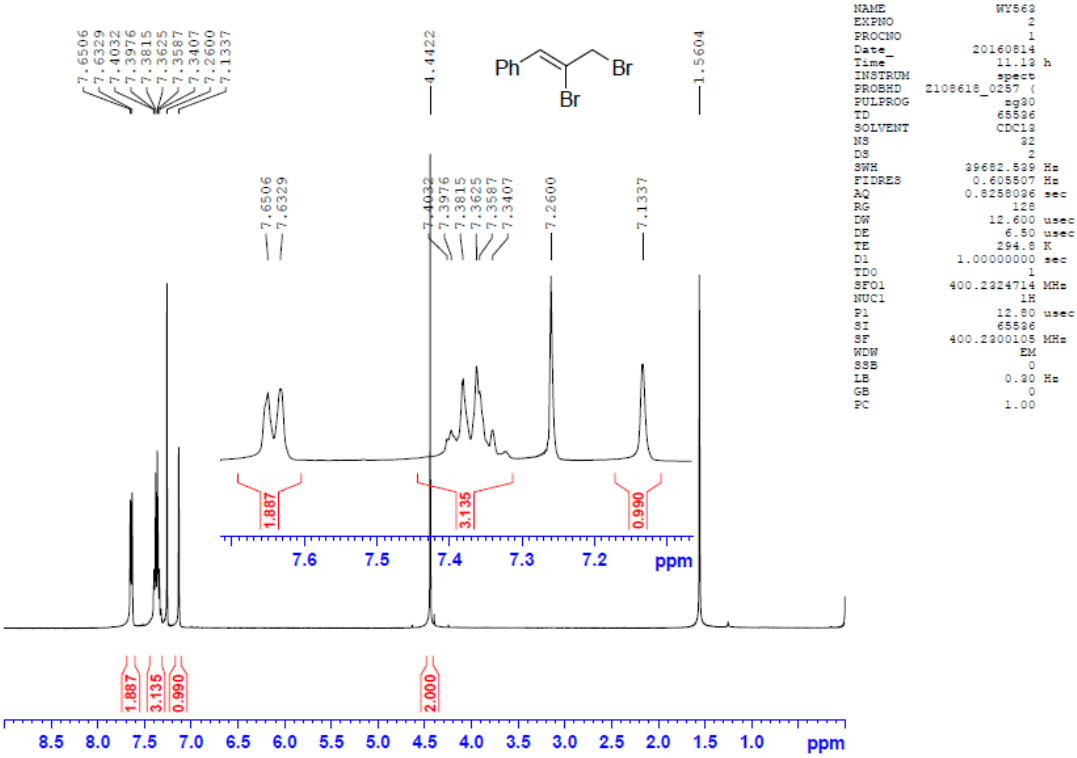


Figure S11. ^{1}H NMR Spectrum of **2a**

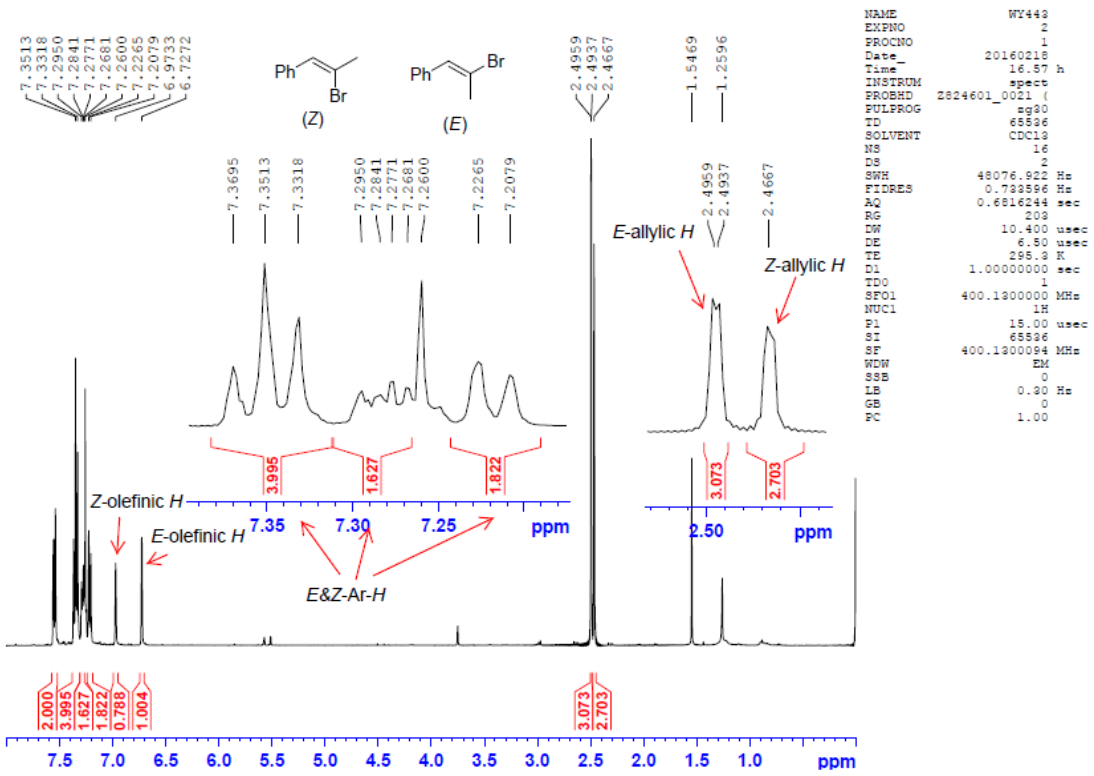


Figure S12. ^{1}H NMR Spectrum of (*Z*)-**2a'**

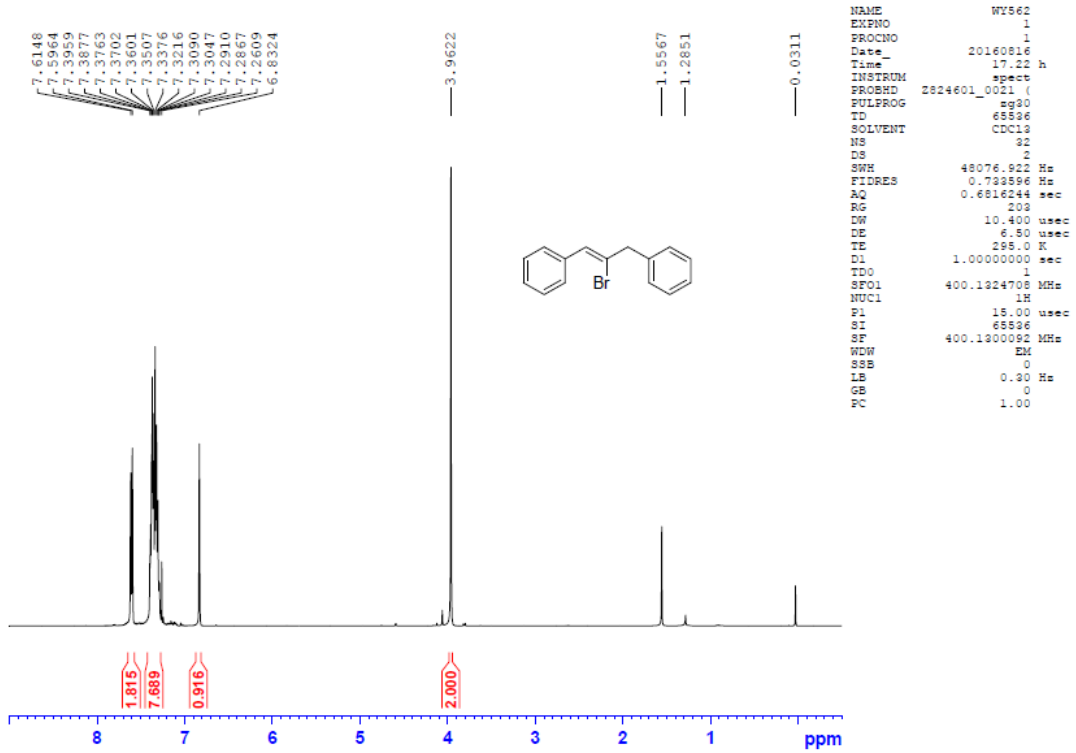


Figure S13. ^{13}C NMR Spectrum of (*Z*)-**2a'**

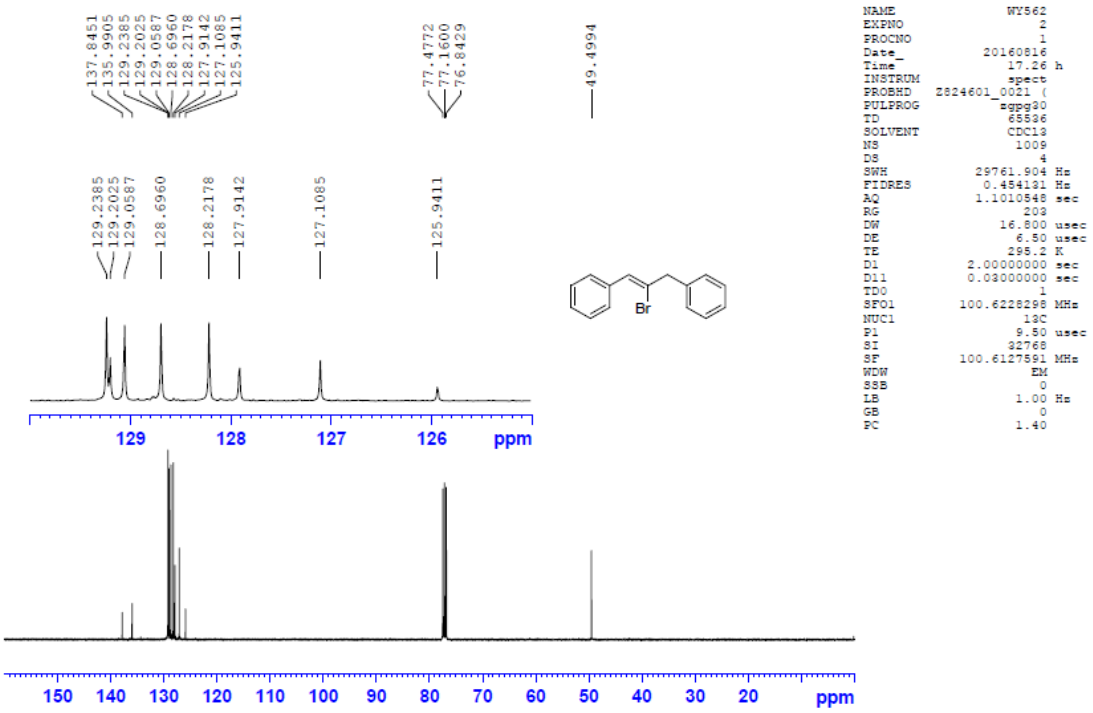


Figure S14. ^{1}H NMR Spectrum of (*E*)-**2a'**

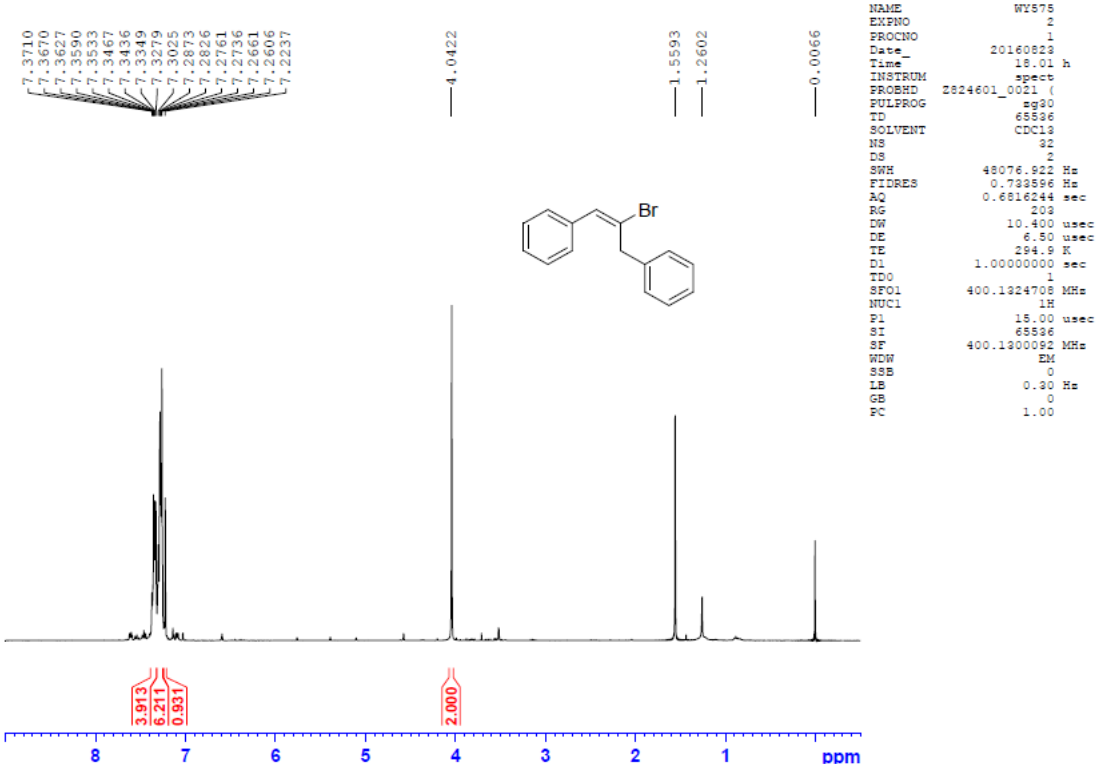


Figure S15. ^{13}C NMR Spectrum of (*E*)-**2a'**

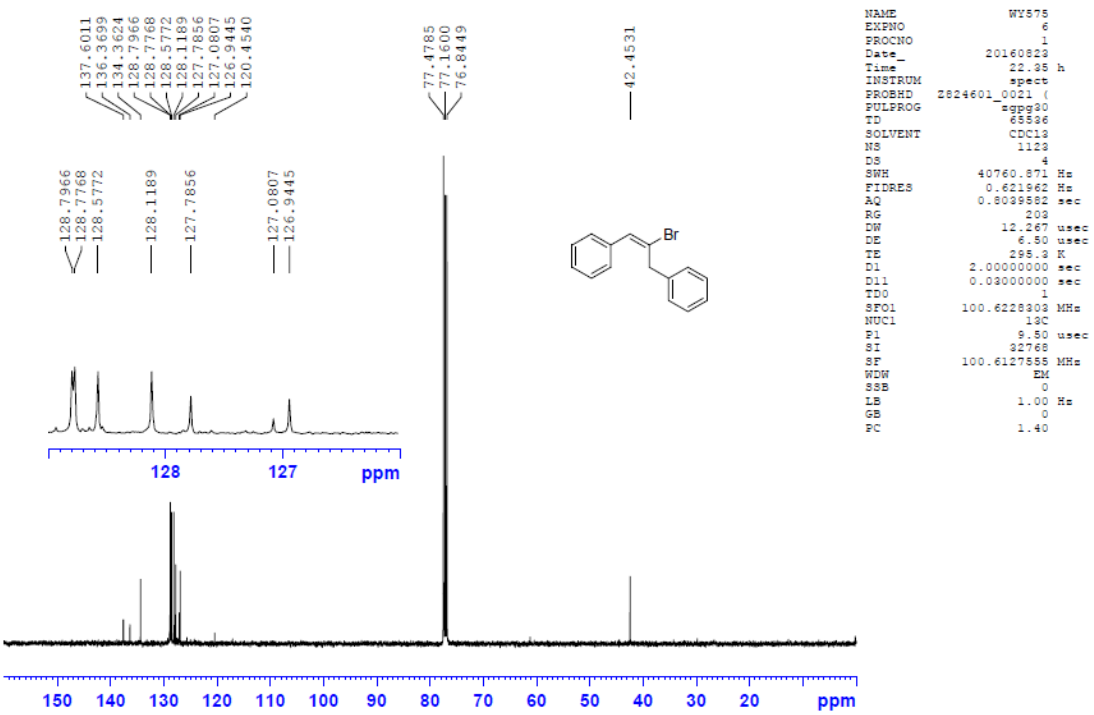


Figure S16. ^{1}H NMR Spectrum of **1b**

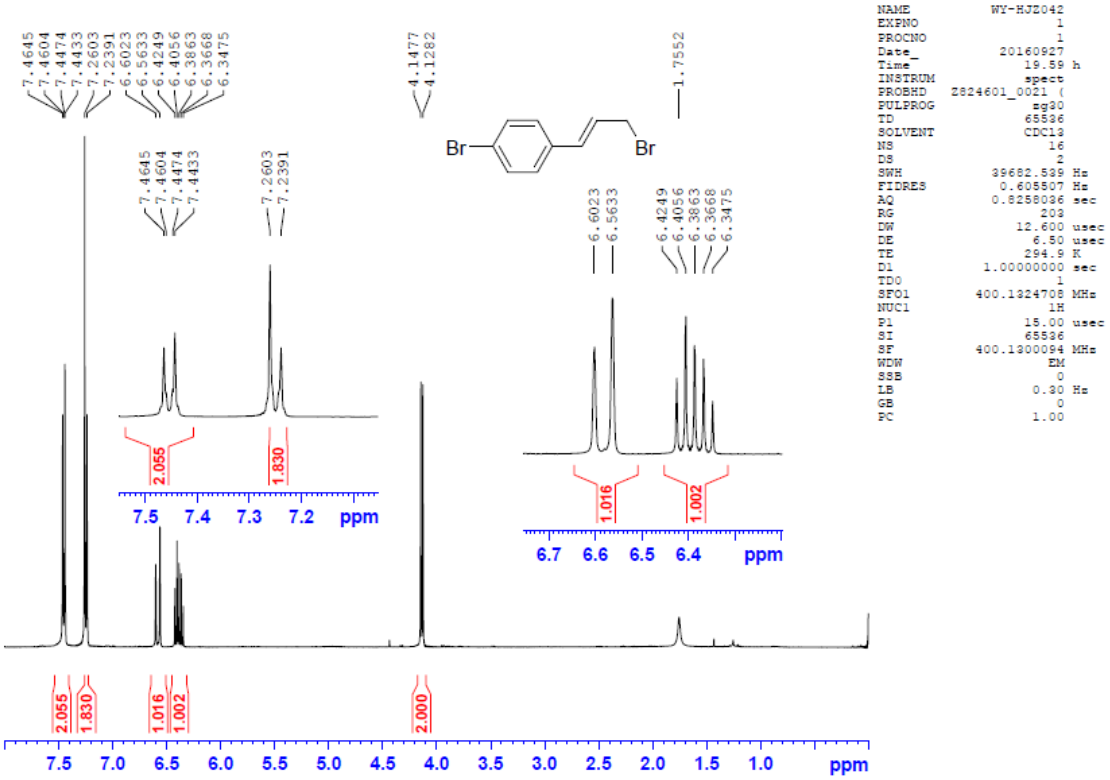


Figure S17. ^{1}H NMR Spectrum of **1c**

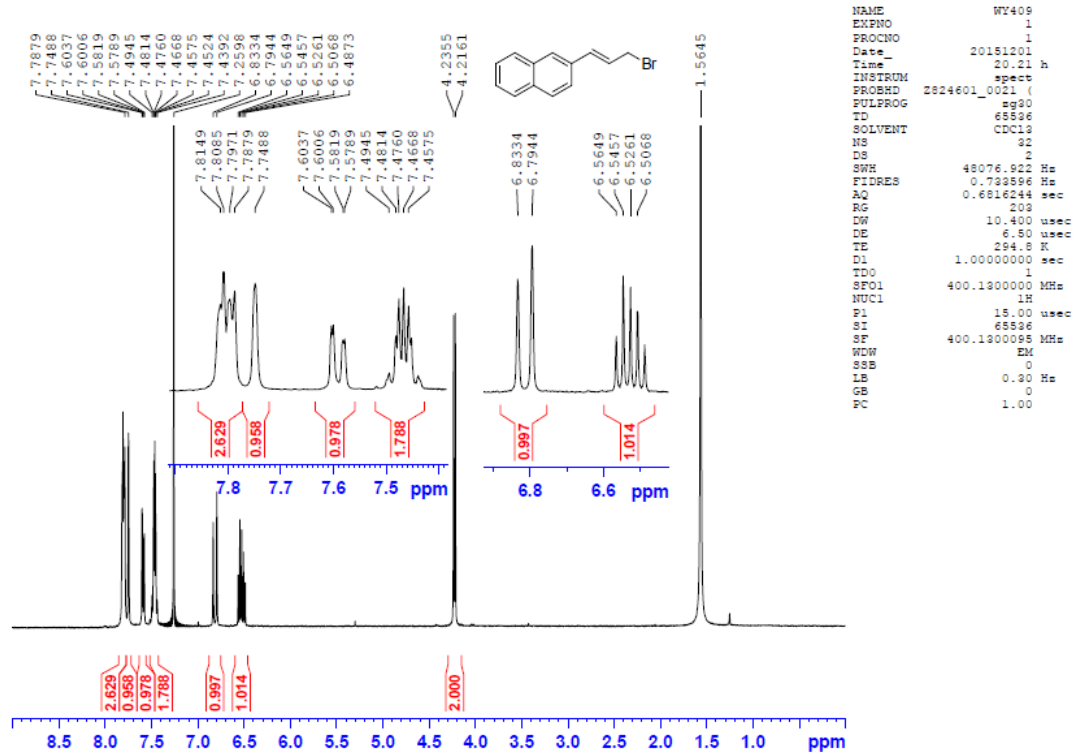


Figure S18. ^{1}H NMR Spectrum of **1d**

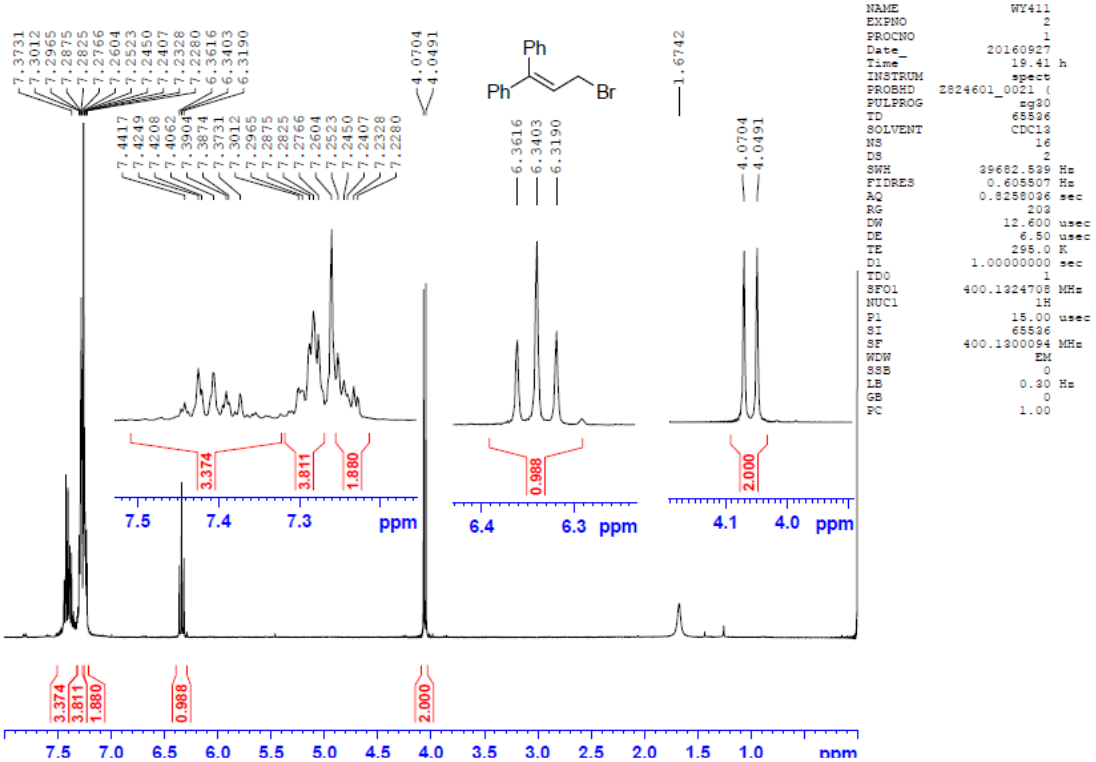


Figure S19. ^{1}H NMR Spectrum of **1e**

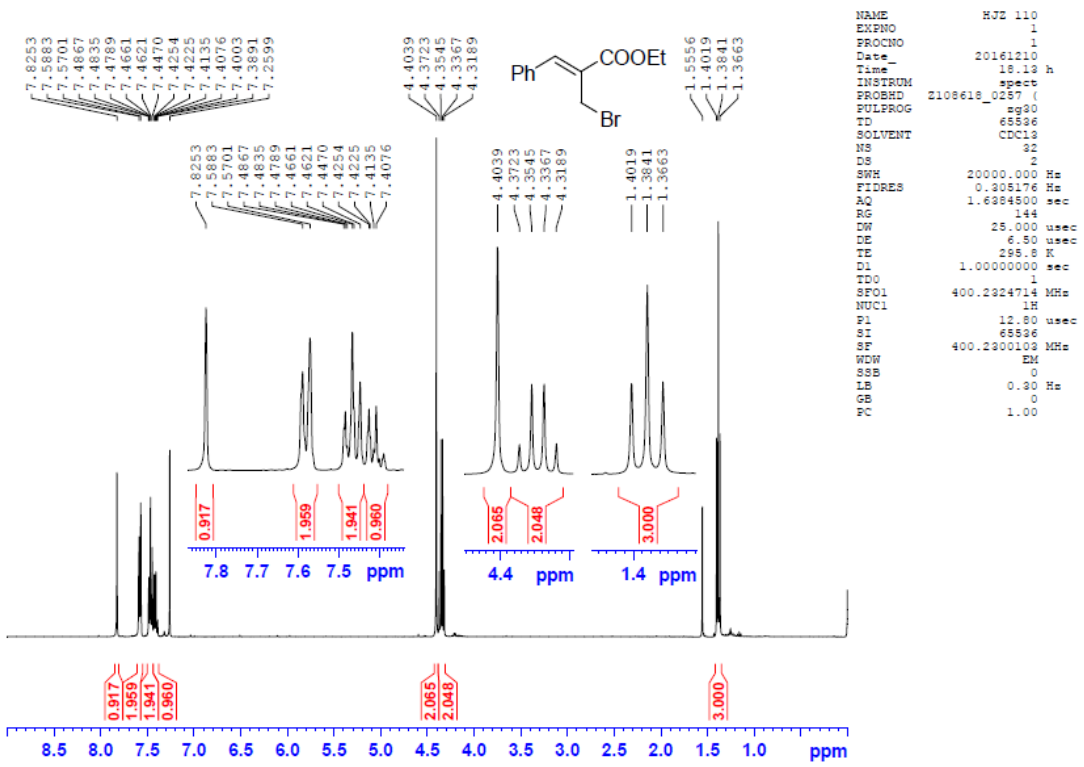


Figure S20. ^{1}H NMR Spectrum of **3c**

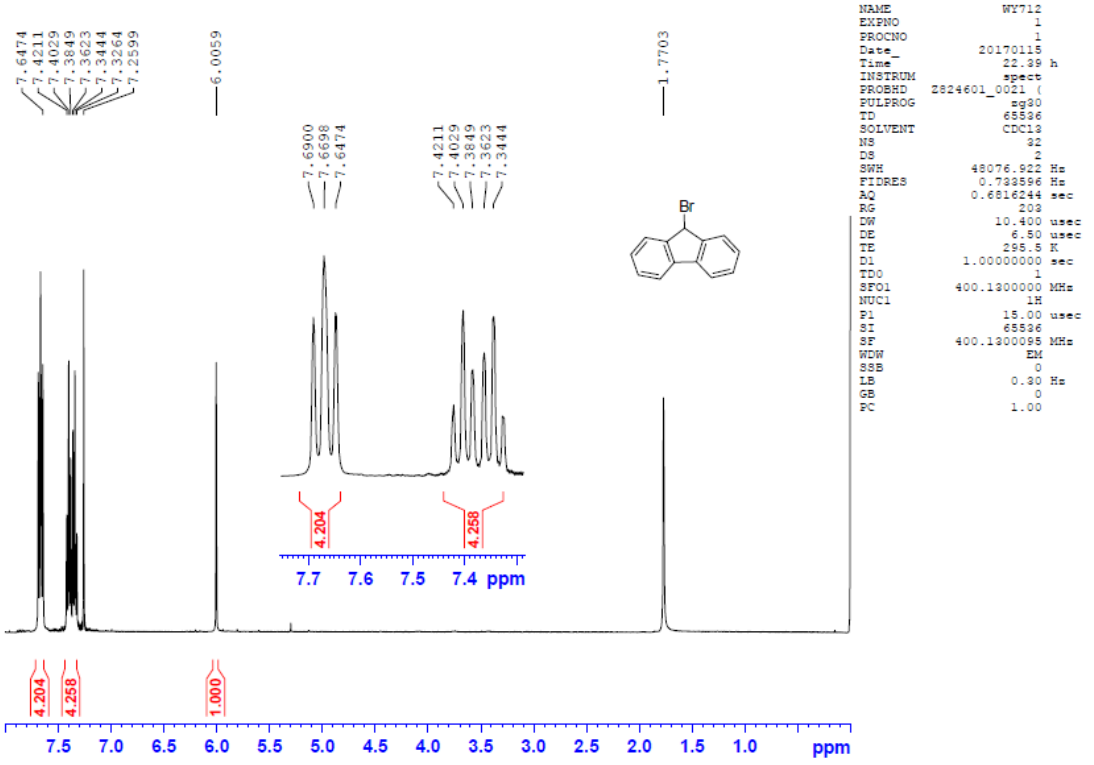


Figure S21. ^{1}H NMR Spectrum of **3f**

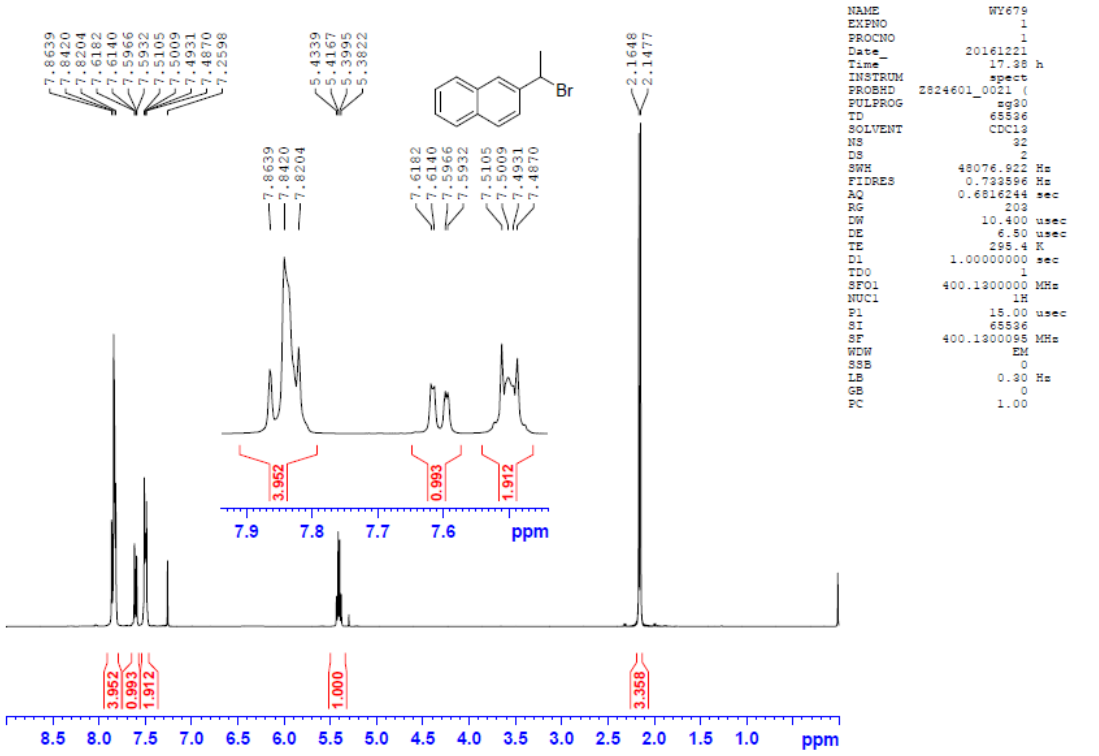


Figure S22. ^{1}H NMR Spectrum of Deuterium Labeling Experiment with (*Z*)-**1a**

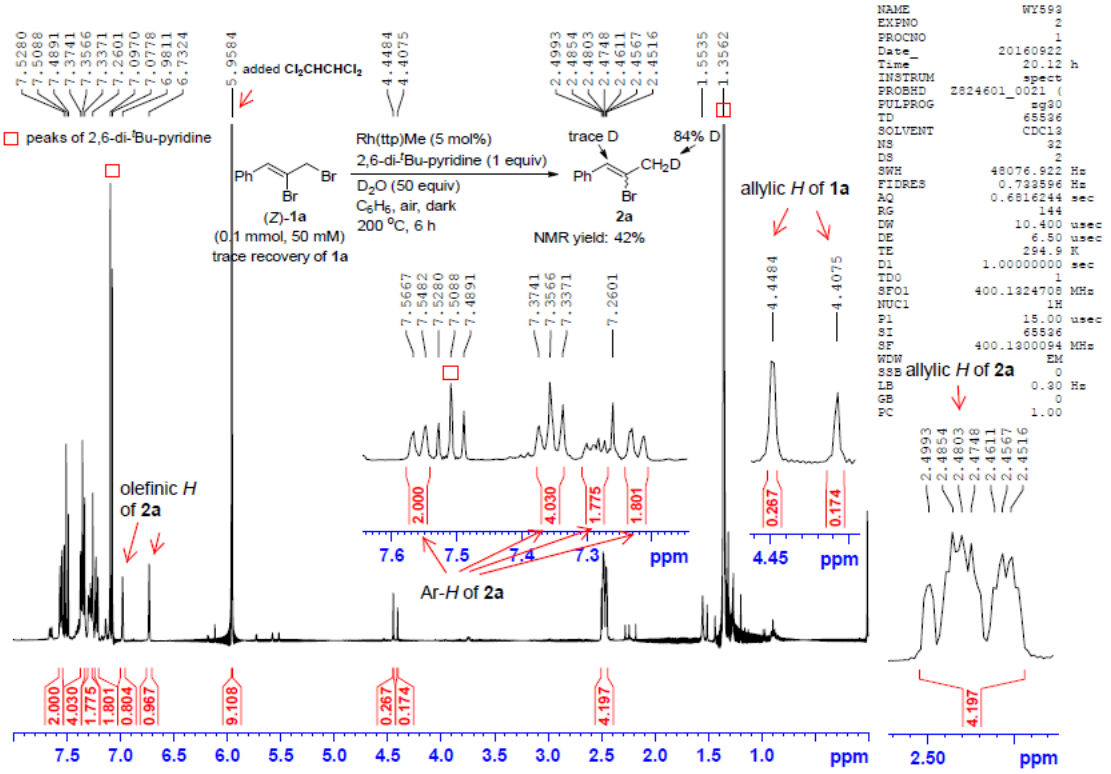


Figure S23. ^{1}H NMR Spectrum of Deuterium Labeling Experiment with **3a**

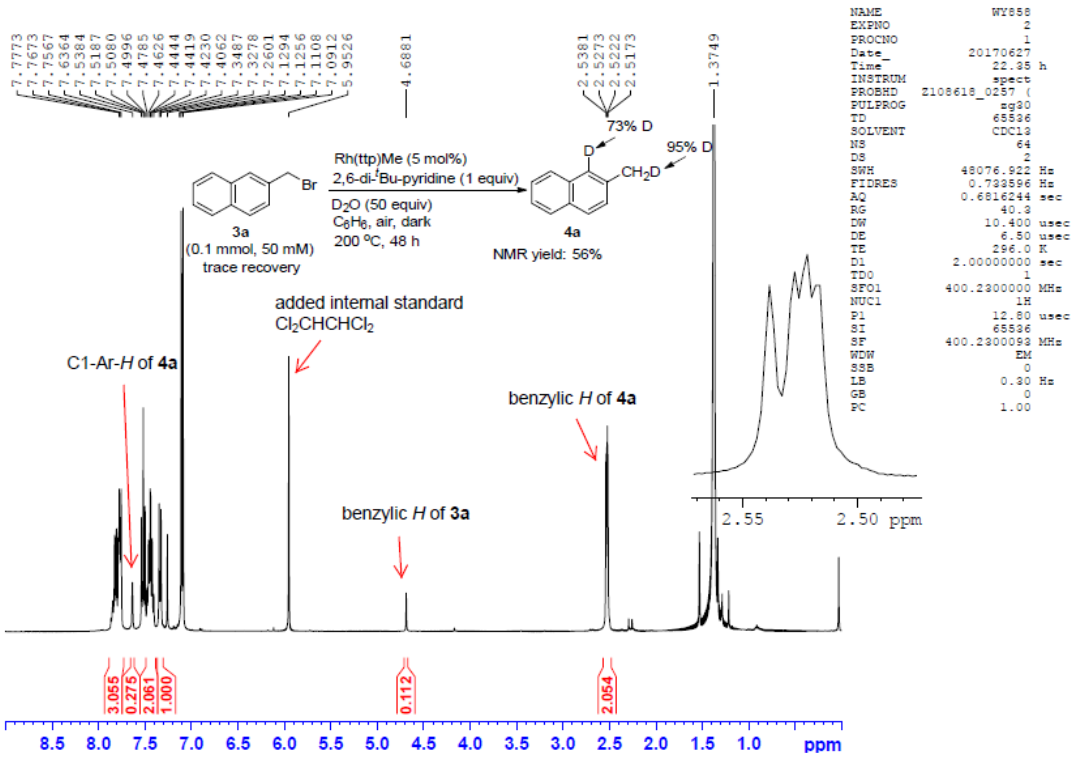


Figure S24. ^{1}H NMR Spectrum of Post-H/D Exchange of 2-Methylnaphthalene (**4a**) with D_2O

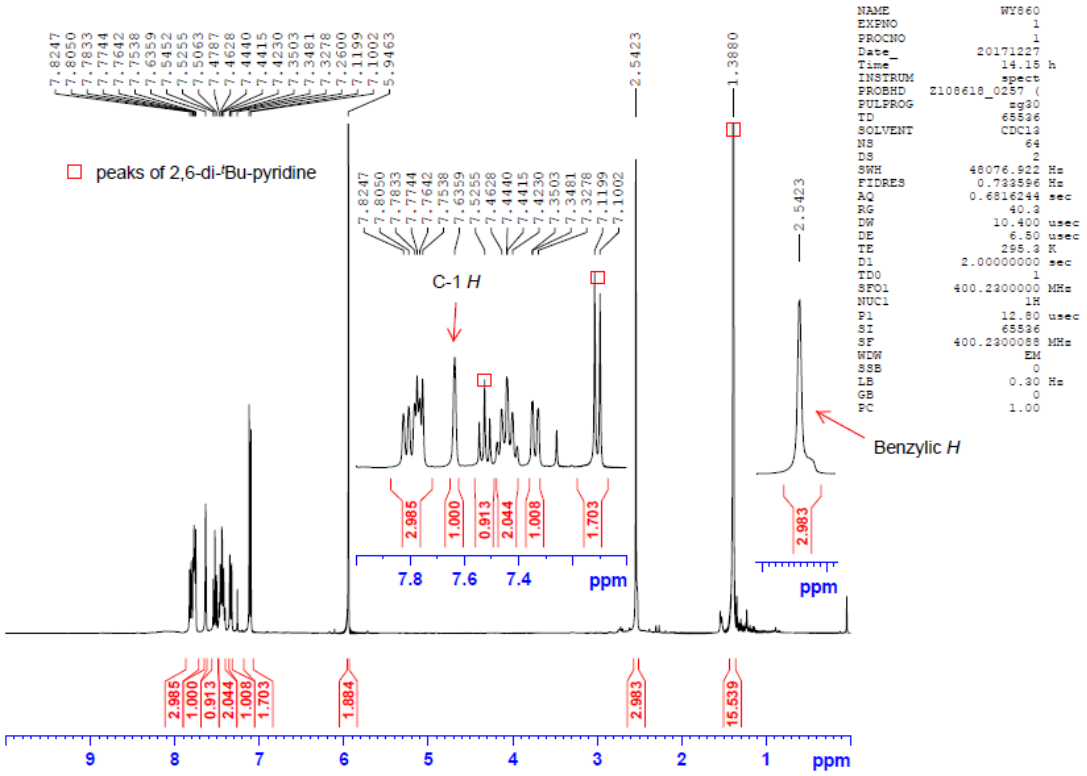


Figure S25. ^{1}H NMR Spectrum of **4a**-*d* with d1 = 10 s

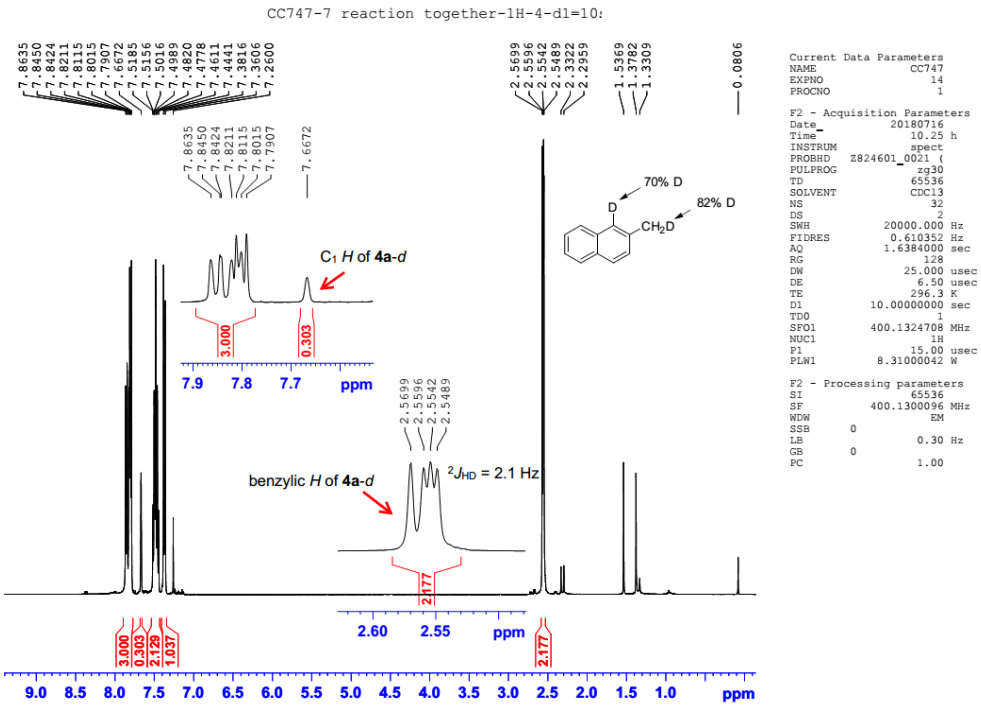


Figure S26. ^{13}C NMR Spectrum of **4a**-*d* with d1 = 10 s

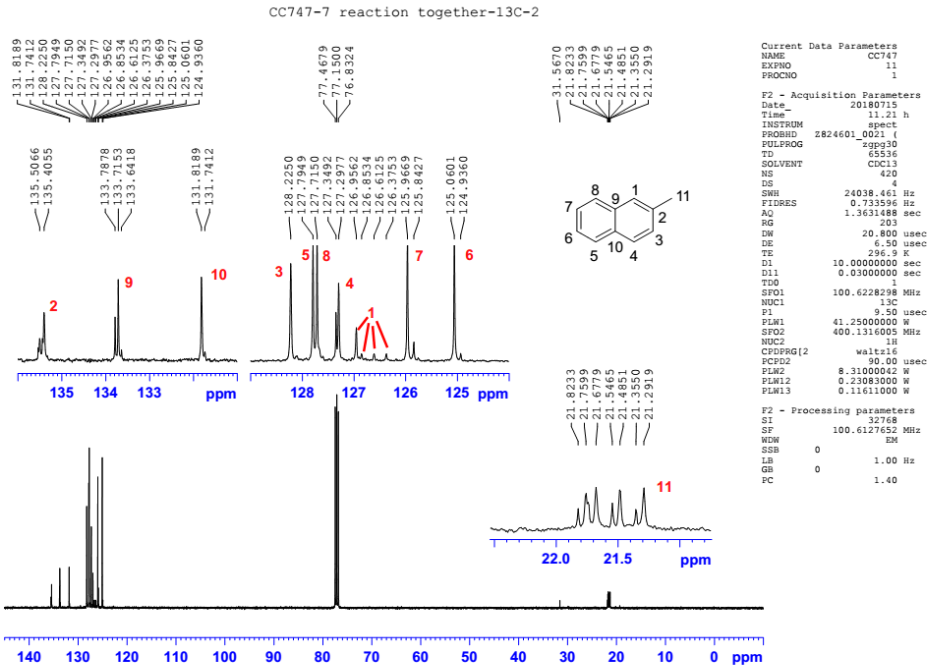


Figure S27. Inverse-Gated Decoupling ^{13}C NMR Spectrum of **4a**-*d*

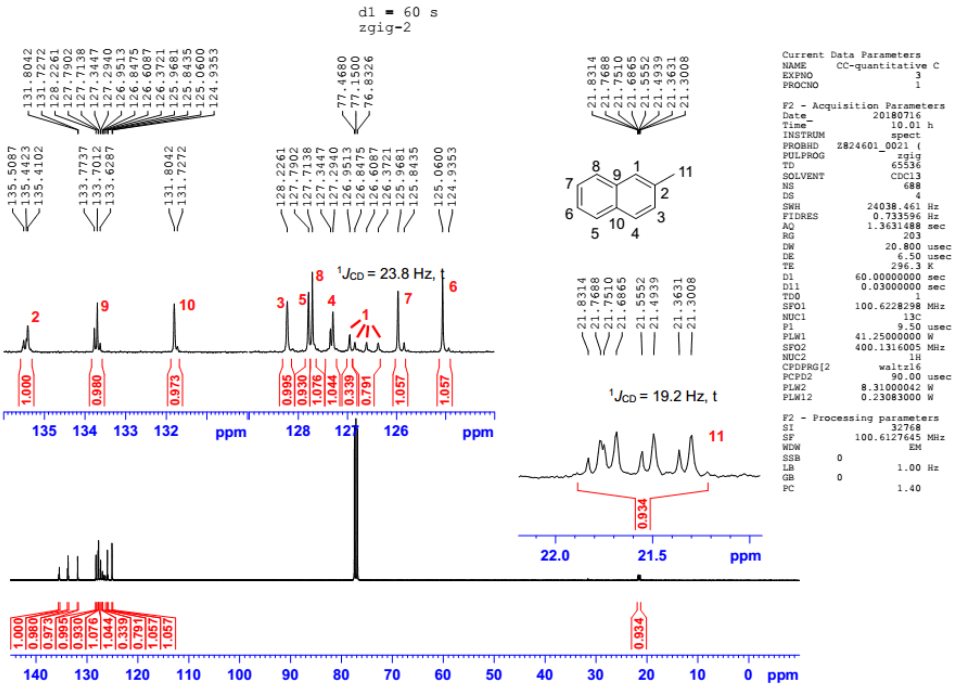


Figure S28. ^{1}H NMR Spectrum of **4a**

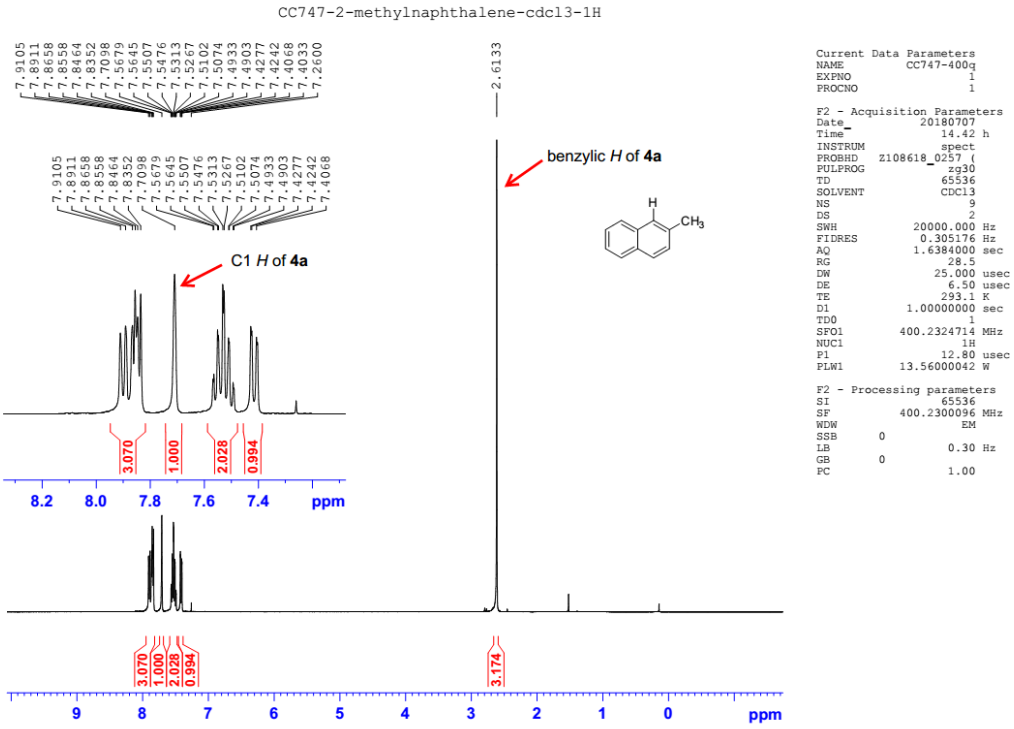


Figure S29. ^{13}C NMR Spectrum of **4a**

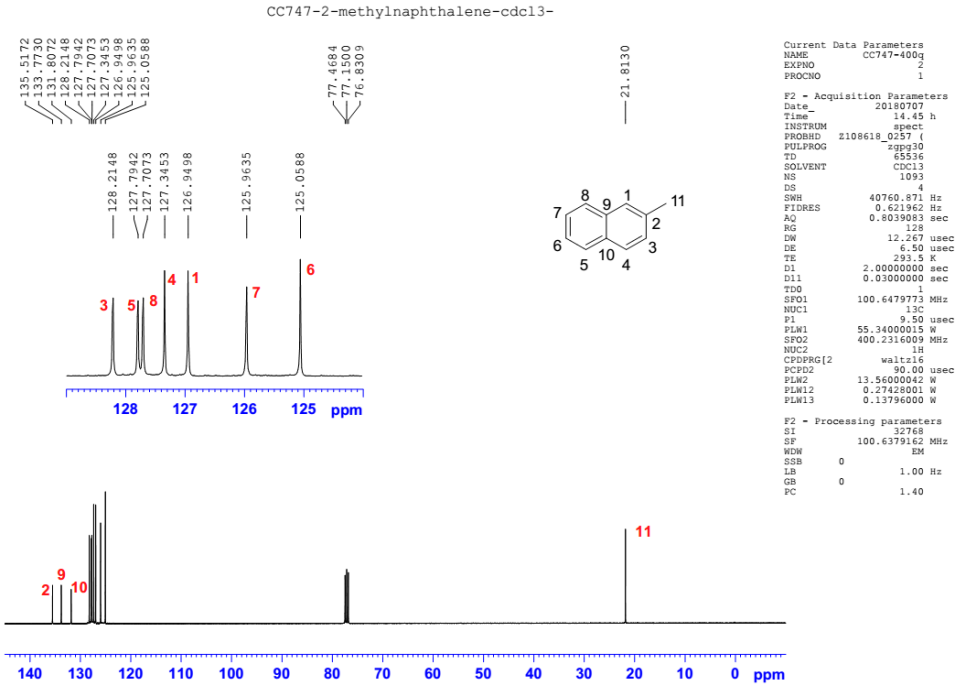


Figure S30. ^{1}H NMR Spectrum of Rh(ttp)(*trans*-cinnamyl)

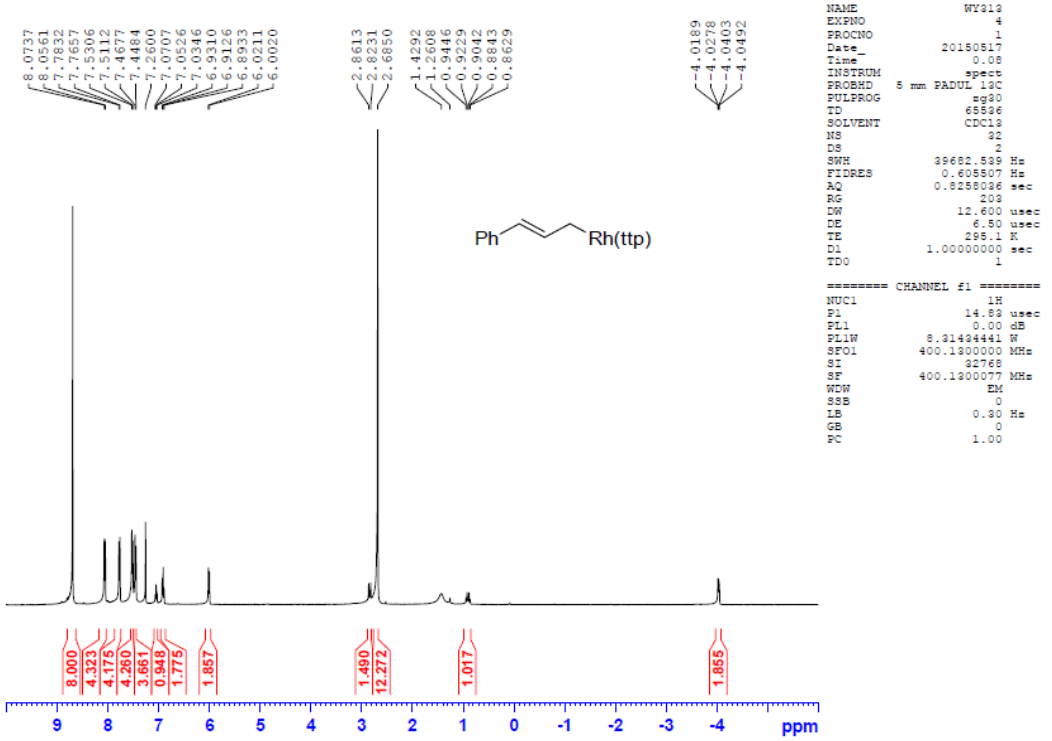
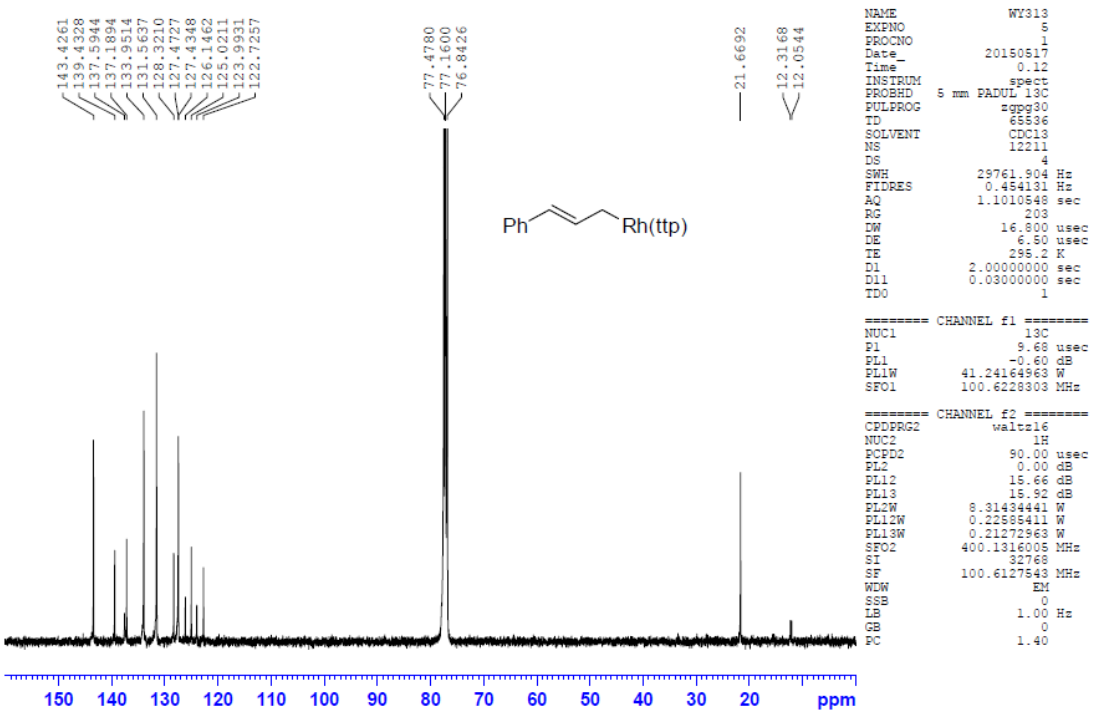


Figure S31. ^{13}C NMR Spectrum of Rh(ttp)(*trans*-cinnamyl)

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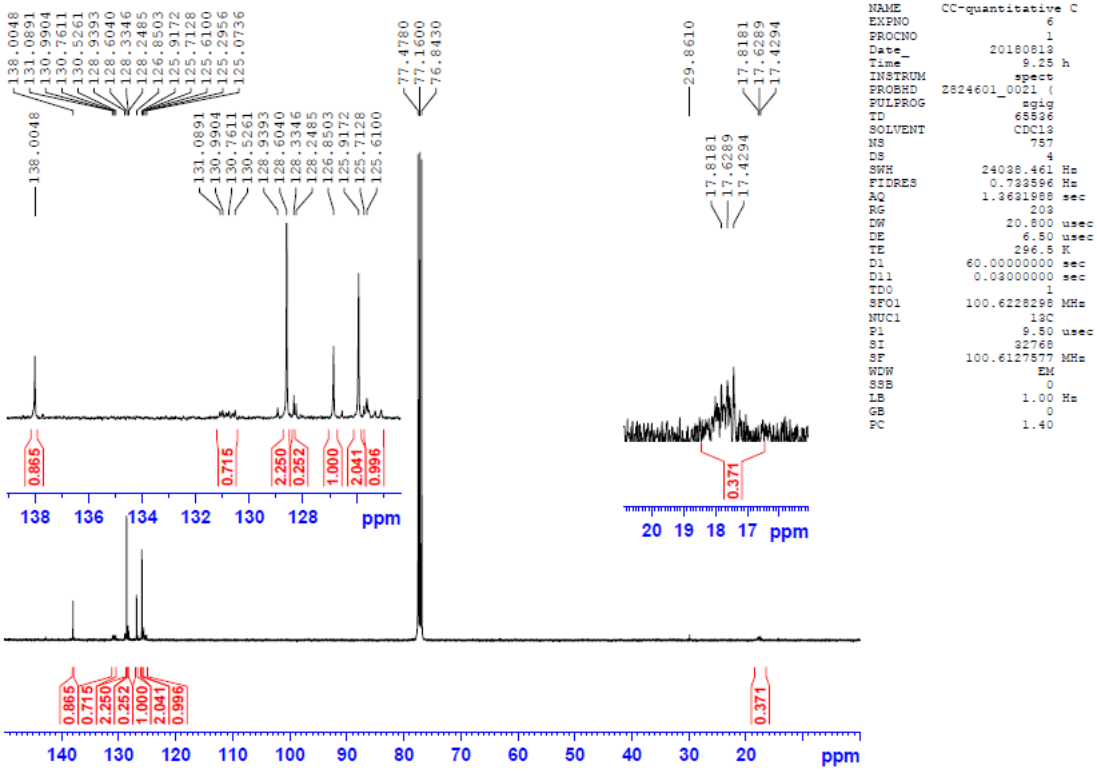
NAME                 WY313
EXPNO                    5
PROCNO                   1
Date_             20150517
Time                  0.12
INSTRUM              spect
PROBHD    5 mm PADUL 13C
PULPROG           zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    12211
DS                        4
SWH               29761.904 Hz
FIDRES            0.454131 Hz
AQ                1.1010548 sec
RG                      203
DW                   16.800 usec
DE                    6.50 usec
TE                  295.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     9.68 usec
PL1                   -0.60 dB
PL1W             41.24164963 W
SFO1            100.6228303 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                 90.00 usec
PL2                    0.00 dB
PL12                  15.66 dB
PL13                  15.92 dB
PL2W              8.31434441 W
PL12W             0.22585411 W
PL13W             0.21272963 W
SFO2            400.1316005 MHz
SI                    32768
SF              100.6127543 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

Figure S32. Quantitative $^{13}C\{^{1}H\}$ NMR spectra of the hydrolysis products with D_2O

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NAME          CC-quantitative C
EXPNO                        6
PROCNO                       1
Date_                 20180813
Time                      9.25 h
INSTRUM                  spect
PROBHD        Z824601_0021 (
PULPROG                  zgig
TD                      65536
SOLVENT                 CDCl3
NS                        757
DS                          4
SWH                 24038.461 Hz
FIDRES              0.733596 Hz
AQ                  1.3631988 sec
RG                        203
DW                     20.800 usec
DE                      6.50 usec
TE                    296.5 K
D1                  60.00000000 sec
D11                 0.03000000 sec
TD0                         1
SFO1              100.6228298 MHz
NUC1                      13C
P1                       9.50 usec
SI                      32768
SF                100.6127577 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

Figure S33. ^{1}H NMR Spectrum of *trans-beta*-Methylstyrene

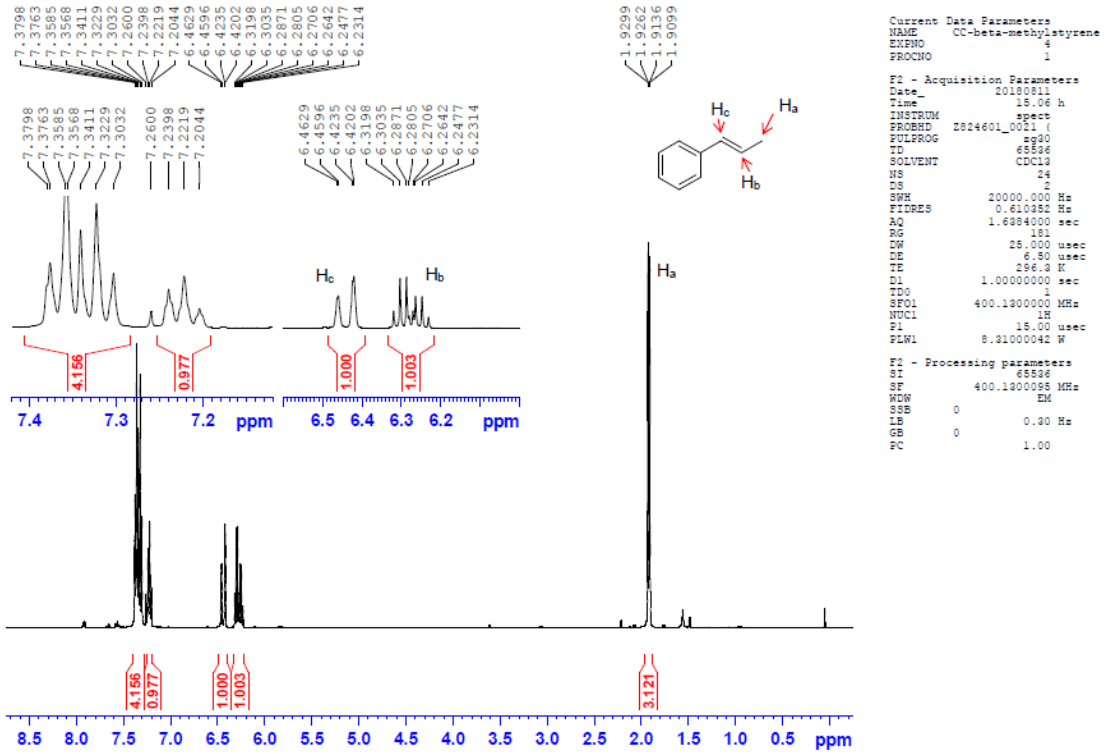


Figure S34. Quantitative ^{13}C NMR Spectrum of *trans-beta*-Methylstyrene

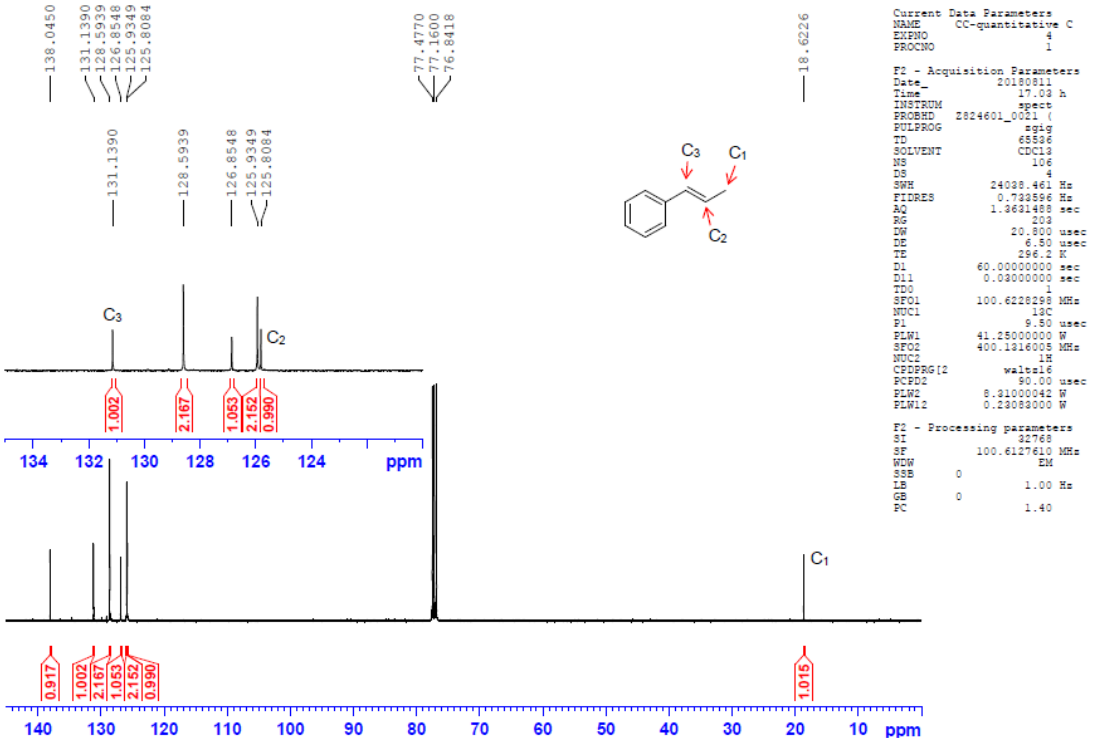


Figure S35. ^{1}H NMR Spectrum of *n*-Propylbenzene

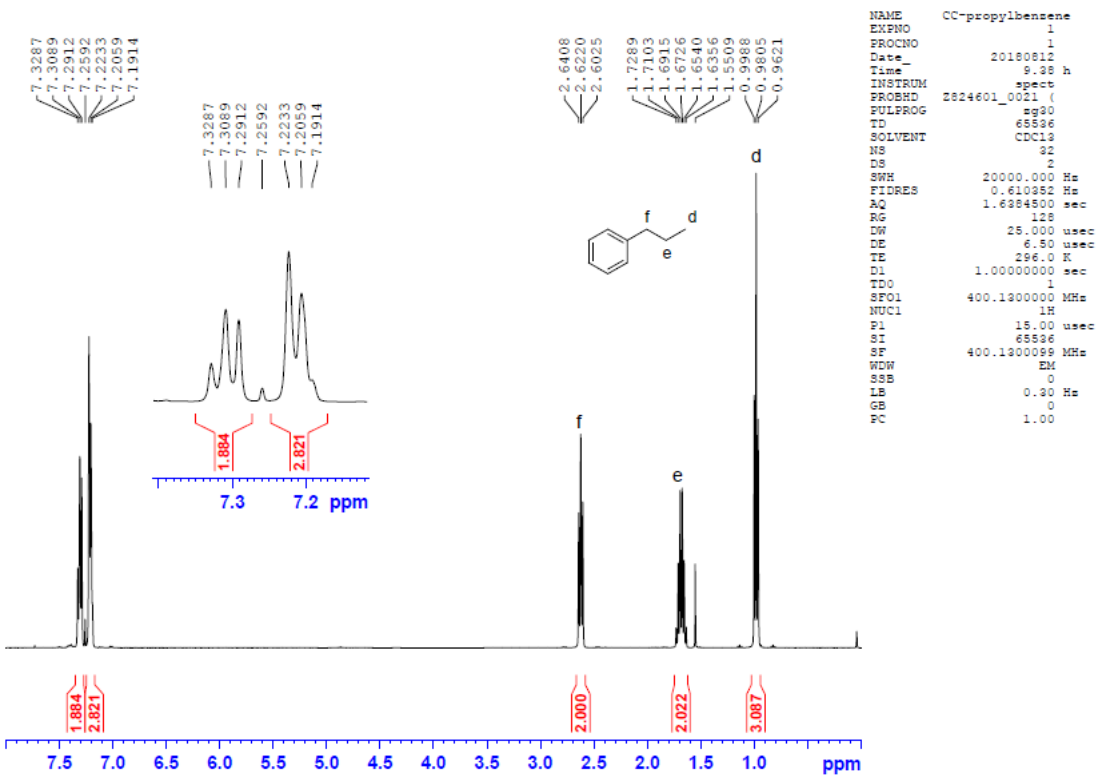


Figure S36. Quantitative ^{13}C NMR Spectrum of *n*-Propylbenzene

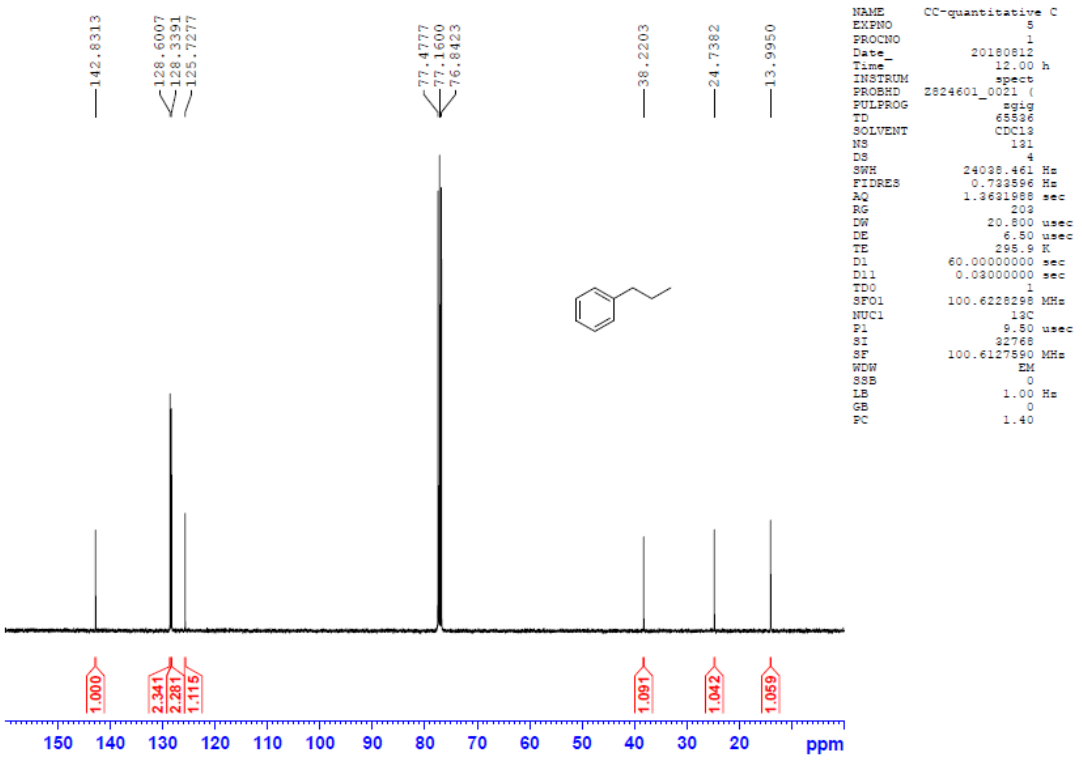
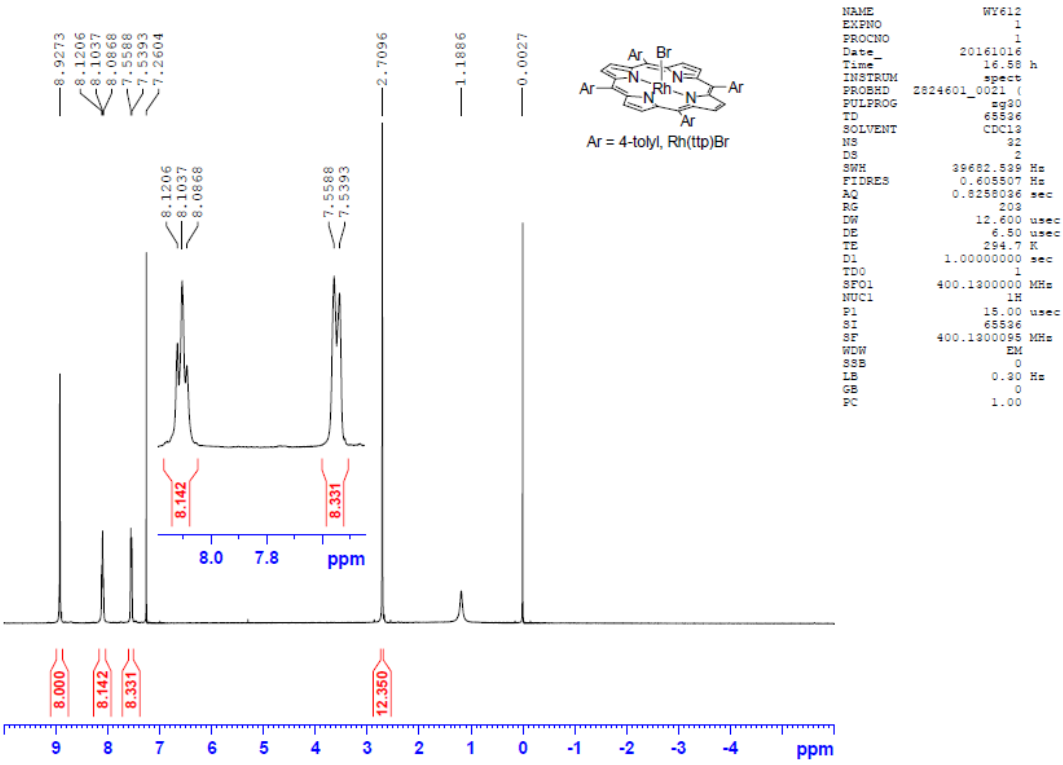


Figure S37. ^{1}H NMR Spectrum of Rh(ttp)Br

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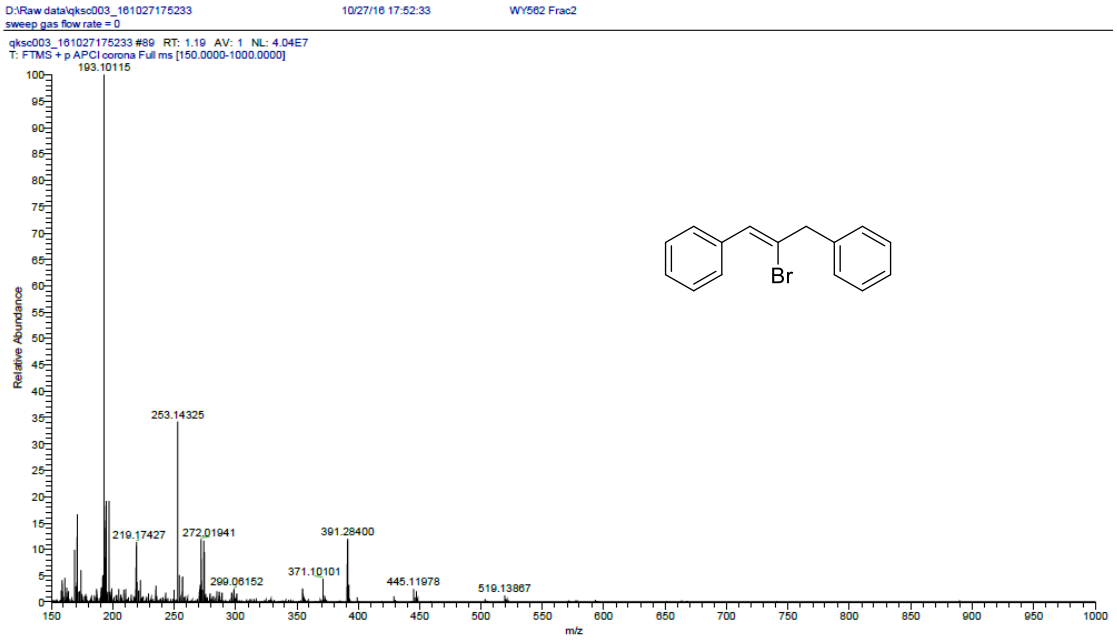
NAME                 WY612
EXPNO                    1
PROCNO                   1
Date_             20161016
Time                 16.58 h
INSTRUM              spect
PROBHD    Z824601_0021 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH              39682.539 Hz
FIDRES           0.605507 Hz
AQ               0.8258036 sec
RG                    203
DW                12.600 usec
DE                 6.50 usec
TE                294.7 K
D1             1.00000000 sec
TD0                      1
SFO1        400.1300000 MHz
NUC1                   1H
P1                15.00 usec
SI                  65536
SF          400.1300095 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```

HRMS Spectra

Figure S38. HRMS Spectrum of (*Z*)-(2-bromoprop-1-ene-1,3-diyl)dibenzene ((*Z*)-**2a'**)

Molecular formula :	C15H13Br
Experimental Mass $(M)^+$:	272.01941
Theoretical Mass $(M)^+$:	272.01951
Error (ppm) :	0.3



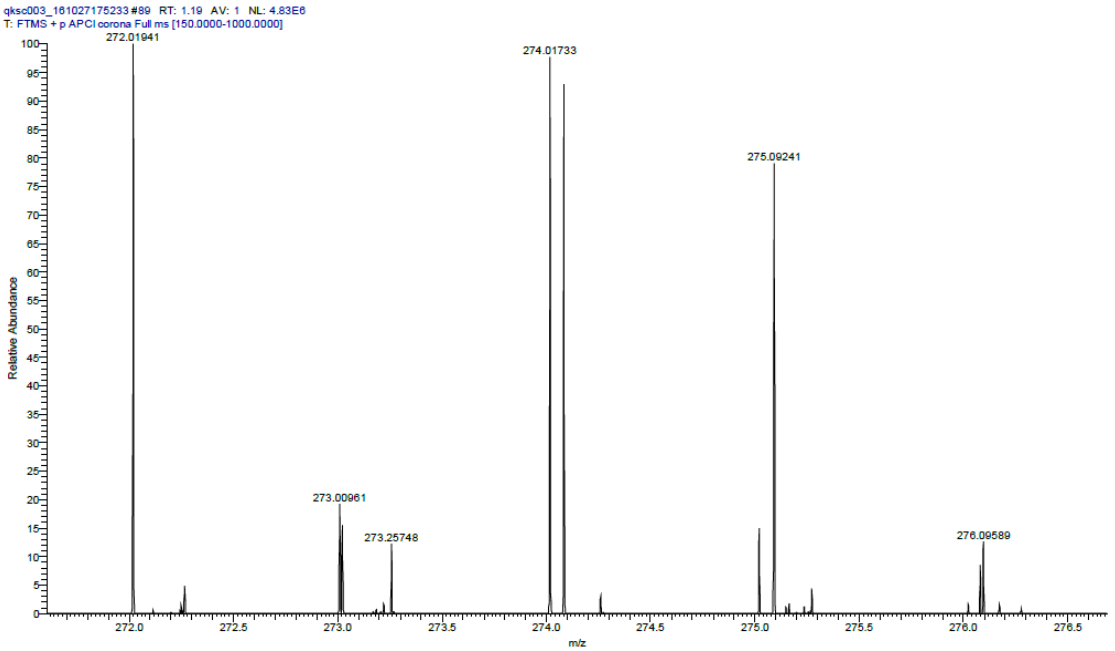
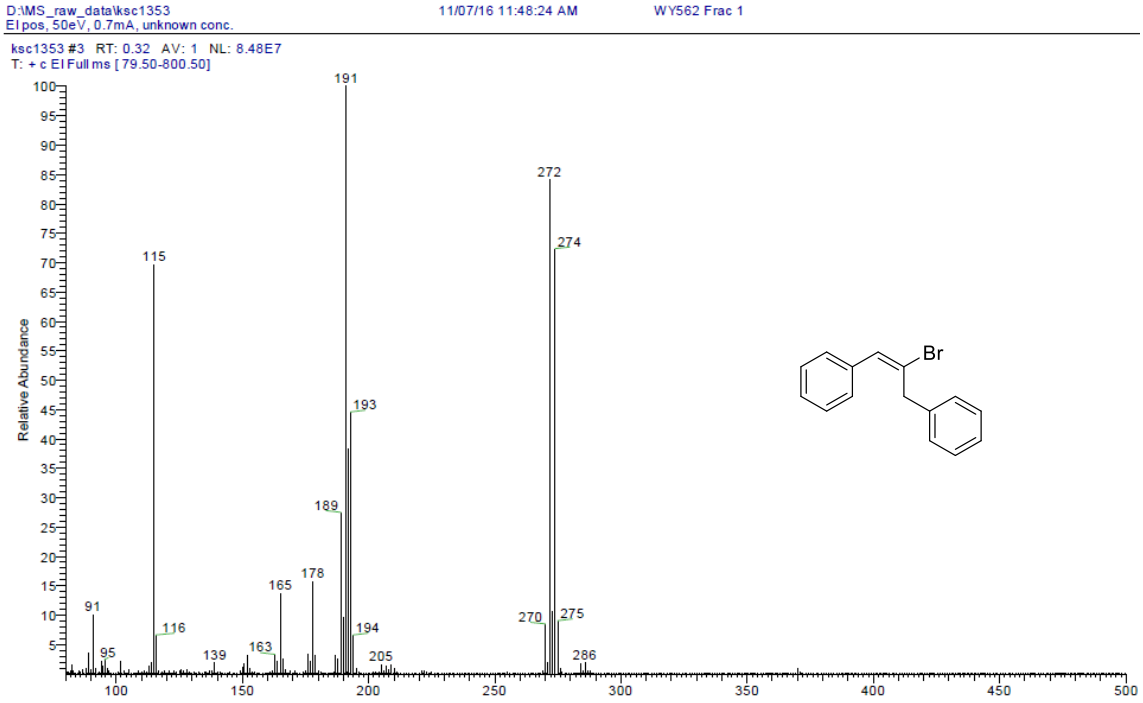
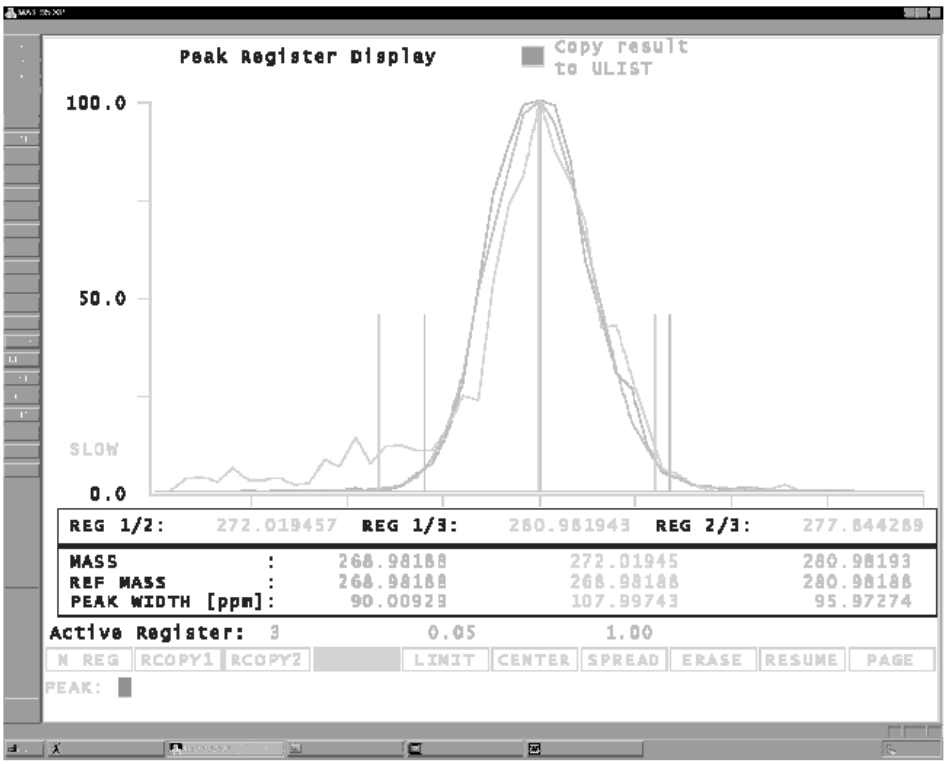


Figure S39. HRMS Spectrum of (*E*)-(2-bromoprop-1-ene-1,3-diyl)dibenzene ((*E*)-**2a'**)

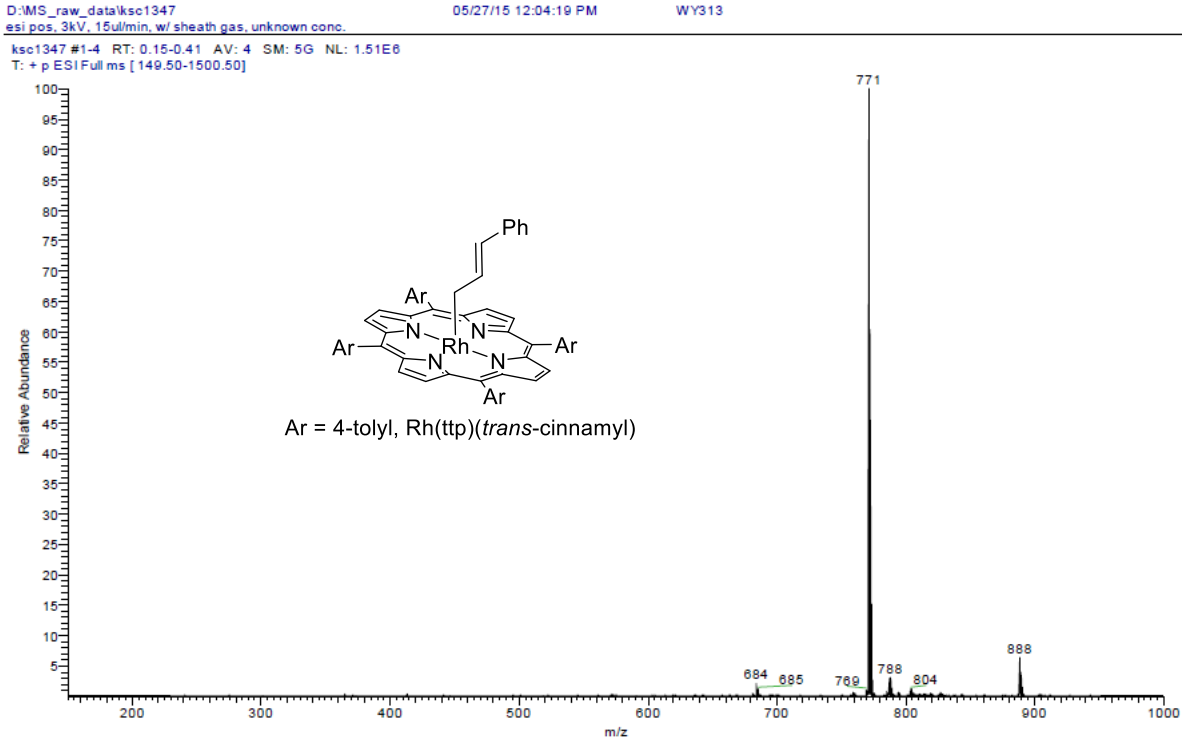


Accurate Mass Measurement

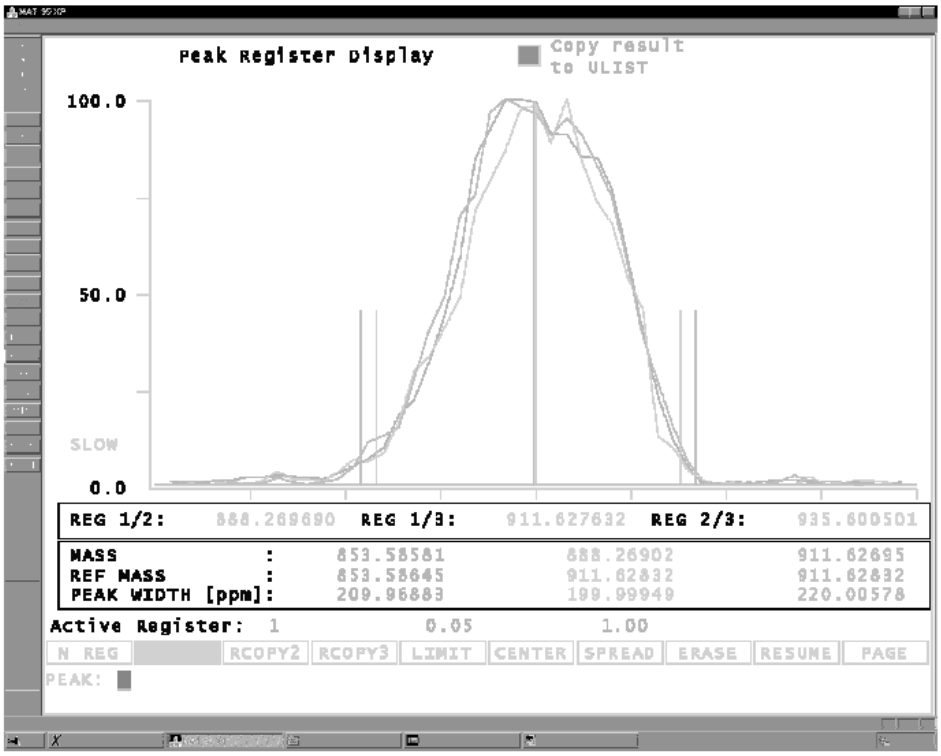


Molecular formula
$C_{15}H_{13}Br$
$[M]^+$ (theoretical)
= 272.0195

Figure S40. HRMS Spectrum of Rh(ttp)(*trans*-cinnamyl)



Accurate Mass Measurement



Molecular formula
$C_{57}H_{45}N_4Rh$
$[M]^+$ (theoretical)
= 888.2694

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