Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information for

Hydrophenylation of internal alkynes with boronic acids catalysed by a Ni-Zn hydroxy double salt-intercalated anionic rhodium(III) complex

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General

All chemical compounds were purified by standard procedures before use.[S1] Analytical gas chromatography (GC) was performed by a Shimadzu GC-2010 with a flame ionization detector equipped with a RESTEK Rtx®-5MS capillary column (30 m, 0.25 mmID, 0.25 μm) or a Shimadzu GC-8A with a flame ionization detector equipped a Silicon OV-17 packed column (2 m). Gas chromatograph-mass spectroscopy (GC-MS) was performed by Shimadzu GCMS-QP2010 Plus with a thermal conductivity detector equipped with a RESTEK Rtx®-5MS capillary column (30 m, 0.25 mmID, 0.25 μm), and ionizing by electron impact. Products were confirmed by use of GC-MS, FT-IR, and ^{1}H and ^{13}C NMR. ^{1}H and ^{13}C NMR spectroscopy were performed using a JNM-AL400 spectrometer at 400 MHz in $CDCl_3$ with TMS as an internal standard. Powder X-ray diffraction (XRD) was conducted using a RIGAKU MiniFlex600 with Cu Kα radiation. UV-Visible spectra were recorded on a Shimadzu UV-2101PC. Flame atomic absorption spectroscopy (AAS) was performed using a Thermo Elemental SOLARR AA series equipped with a Hamamatsu Photonics K. K. hollow cathode lamp (Rh: 343.49 nm), and atomizing by air-acetylene flame. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis HSi X-ray photoelectron spectrometer fitted with a charge neutraliser and magnetic focusing lens, using monochromated Al Kα radiation (1486.6 eV). Spectral fitting as performed with CasaXPS version 2.3.14. Binding energies were referenced to the adventitious C 1s peak at 284.6 eV. The peak of Rh 3d XP region was fitted adopting a common symmetrical Gaussian-Lorentzian function, and a spin-orbit doublet separation of 4.7 eV in agreement with literature values from the NIST surface database. Rh *K*-edge X-ray absorption fine structure spectra (XAFS) were recorded at room temperature in transmission and fluorescence modes using Lytle detector with a Si(311) double crystal monochromator at the beam line NW-10A station with 6.5 GeV storage ring of the Photon Factory, Advanced Ring for Pulse X-rays, Tsukuba, Japan (KEK-PF). The resulting EXAFS spectra were analysed with REX2000 (Rigaku Co.). Fourier transforms of k^3-weighted EXAFS spectra were performed the 35 nm^{-1} < k < 140 nm^{-1} range for analysis of catalysts and complex solution. Curve-fitting analysis was performed with the inverse FT of the 0.112 nm < R < 0.199 nm range in case of analysis of catalyst using R_2O_3 as a standard material.

Preparation of CH_3COO^-/NiZn

Acetate anion-intercalated Ni-Zn hydroxy double salt (CH_3COO^-/NiZn) was prepared according to the literature procedures.[S2] $Ni(OCOCH_3)_2 \cdot 4H_2O$ (134 mmol) and $Zn(OCOCH_3)_2 \cdot 2H_2O$ (66 mmol) were dissolved in deionised water (200 mL). The solution was hydrolysed by heating in a Teflon-linked pressure bottle at 200 ^oC for 24 h. The resulting precipitates were filtered, washed with deionised water, and dried under vacuum, yielding *ca*. 5 g of $Ni_{0.63}Zn_{0.37}(OH)_2(OCOCH_3)_{0.37} \cdot 1.93H_2O$ (i.e. Ni:Zn = 2.2, CH_3COO^-/NiZn) as a light green powder. The anion-exchange capacity of the parent NiZn was 2.44 mmol.g^{-1} on the basis of X-ray fluorescence (XRF) and thermogravimetric-differential thermal analysis (TG-DTA).

Preparation of $[Rh(OH)_6]^{3-}$/NiZn (Rh/NiZn)[S3]

$[Rh(OH)_6]^{3-}$/NiZn (Rh/NiZn) catalyst was prepared by a simple intercalation technique. $Na_3RhCl_6 \cdot nH_2O$ in 2M HCl *aq*. (Rh: 0.05 mmol, concentration of rhodium species was determined by AAS) was placed in a round bottom flask and the total volume was adjusted to 40 mL with deionised water. The red solution was heated with stirring at 50 ^oC for 30 minutes after addition of 10 M NaOH *aq*. (10 mL), turning the solution yellow. CH_3COO^-/NiZn (1 g) was added to the resulting solution and stirred at 50 ^oC for 8 h. The obtained slurry was filtered, washed with deionised water, and dried under vacuum, yielding Rh/NiZn as a light green powder. The resulting Rh/NiZn catalyst, a green powder, contained 0.034 mmol.g^{-1} of Rh conplex as determined by AAS.

Preparation of OH^-/NiZn[S3]

CH_3COO^-/NiZn (0.5 g) was stirred in 2 M NaOH (25 mL) at 50 °C for 8 h. The obtained slurry was filtered, washed with deionised water, and dried under vacuum, yielding OH^-/NiZn as a light green powder.

Synthesis of $Na_3RhCl_6\cdot nH_2O$

$Na_3RhCl_6\cdot nH_2O$ was prepared according to the literature procedures.[S4] $RhCl_3\cdot nH_2O$ (0.5 g) was dissolved in HCl*aq* (2 M, 5 mL) with stirring for 30 minutes. NaCl (0.375 g) dissolved in deionised water (5 mL) was added to the solution. The solution was heated with stirring at 95 °C for 1 h, and then evaporated to remove the solvent. The resulting solid was recrystallised from HCl *aq.* (2 M) and ethanol at 0 °C. The precipitates were filtered, washed with ethanol and diethyl ether, and dried under vacuum, yielding $Na_3RhCl_6\cdot nH_2O$ as a red powder.

Estimation of leached Rh amounts by AAS

After reaction, solid catalyst was separated by simple filtration. The reaction mixture was distillated under vacuum to remove all of liquid, followed by the addition of diluted HCl aqueous solution (0.5 mM, 5 mL). The obtained aqueous solution was measured by the AAS with acetylene/air flame.

General procedure for hydrophenylation of 1a with 2a

Into a Schlenk tube with a reflux condenser, 4-octyne (**1a**, 0.5 mmol), phenylboronic acid (**2a**, 1.5 mmol), Rh/NiZn catalyst (0.1 g, Rh: 0.68 mol%), 1,5-COD (4 eq. relative to Rh), toluene (4 mL), and H_2O (0.45 mL) were placed. The resulting mixture was heated at 100 °C for 5 h. The alkyne conversion and product yield were determined by GC analysis.

The procedure for the catalytic reaction with additional reactants

Into a Schlenk tube with a reflux condenser, Rh/NiZn catalyst (0.1 g, Rh: 0.68 mol%), **1a** (0.5 mmol), **2a** (1.5 mmol), 1,5-COD (4 eq. relative to Rh), toluene (4 mL), and H_2O (0.45 mL) were placed. The resulting mixture was heated at 100 ^oC for 150 min. After 150 minutes, additional quantities of **1a** (0.5 mmol) and **2a** (1.5 mmol) were added. The product yield and selectivity were periodically determined by GC analysis during the catalytic reaction.

The procedure for large scale hydrophenylation of 1a with 2a

Into a 100 mL round-bottomed flask with a reflux condenser, 4-octyne (**1a**: 0.66 g, 6 mmol), phenylboronic acid (**2a**: 1.83 g, 15 mmol), Rh/NiZn catalyst (0.2 g, Rh: 6.8 μmol), 1,5-COD (4 eq. relative to Rh), toluene (20 mL), and H_2O (2.25 mL) were placed. The resulting mixture was heated at 100 ^oC. The **1a** conversion and product yield were determined by GC analysis. After 16 h, Rh/NiZn catalyst was separated by filtration. The reaction mixture was extracted with diethyl ether, washed with brine, and then dried over $MgSO_4$. Diethyl ether was removed under the reduced pressure, followed by silica gel column chromatography with *n*-hexane to give 0.95 g (84 % isolated yield) of analytically pure (*E*)-4-phenyl-4-octene (**3aa**) and 0.13 g of (4*Z*, 6*E*)-4-phenyl-5,6-dipropyl-4,6-undecadiene (**4aa**) as colorless oils.

Pre-treatment of Rh/NiZn catalyst with 1,5-COD

The Rh/NiZn catalyst (0.1 g, Rh: 3.4 μmol) was treated with 1,5-COD (13.8 μmol, 4 eq. relative to Rh) in toluene (4 mL) and H_2O (0.45 mL) solvent at 100 ^oC. After 1 h, the solid catalyst was filtered, washing with toluene, and dried under vacuum. The resultant catalyst was employed for the hydrophenylation of **1a** and **2a** under identical reaction conditions to those in Table 4, entry 1 without the addition of 1,5-COD.

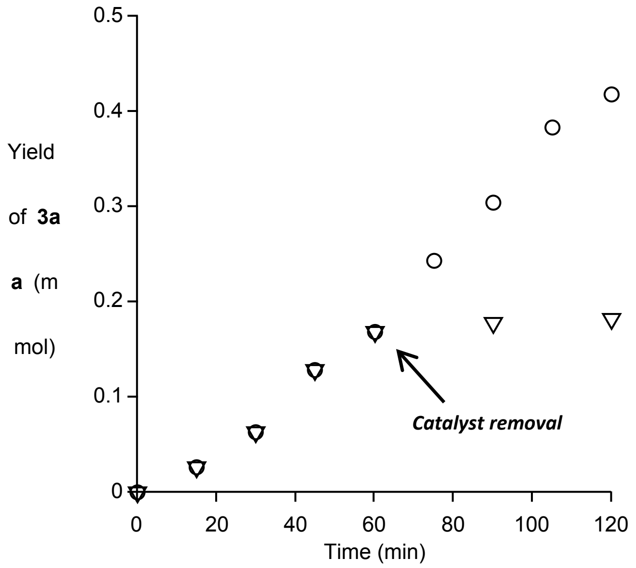


Fig. S1 Hot filtration experiment. Reaction conditions were as follows: Rh/NiZn catalyst (0.1 g, Rh: 0.68 mol%), **1a** (0.5 mmol), **2a** (1.5 mmol), 1,5-COD (4 eq. relative to Rh), toluene (4 mL), H_2O (0.45 mL), 100 °C.

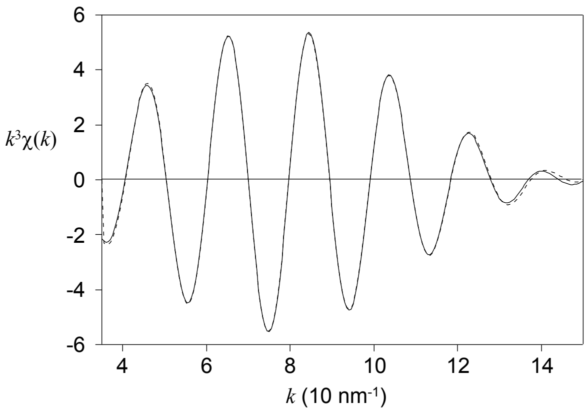


Fig. S2 Curve-fitting of Fourier-filtered k^3-weighted Rh *K*-edge EXAFS of recovered Rh/NiZn catalyst. The solid curve is obtained experimentally and the dashed curve is the calculated fit.

Table S1. XRD parameters based on (001) plane shown in **Fig. 3**

catalyst	2 theta (degree)	d_{001} (nm)	C.S.[a] (nm)	peak height (cps)	FWHM (degree)	crystalline size[b] (nm)
CH_3COO^-/NiZn	6.762	1.31	0.84	100333	0.218	38.1
fresh Rh/NiZn	10.847	0.82	0.36	42395	0.463	17.9
recovered Rh/NiZn	(7.900)	(1.12)	(0.66)	(4085)	(0.707)	11.8
	10.032	0.88	0.42	23414	0.342	24.3

[a] Clearance space = basal spacing (d_{001}) - thickness of the brucite layer (0.46 nm).

[b] Calculated from Sherrer equation.

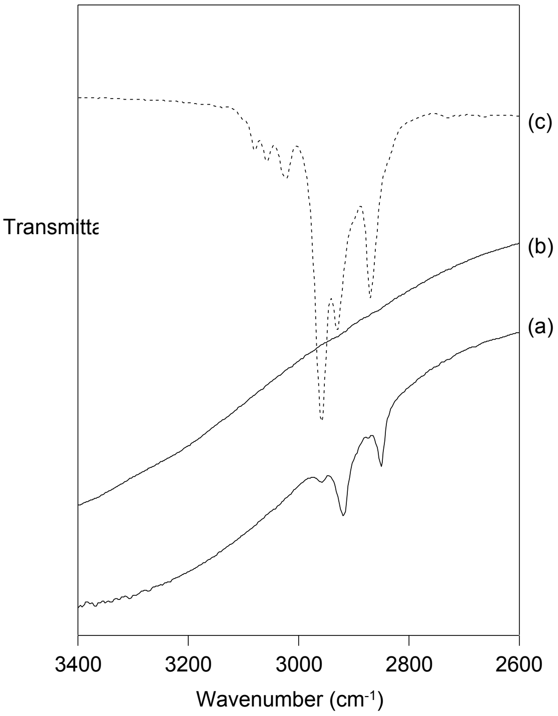


Fig. S3 FT-IR spectra for (a) recovered Rh/NiZn catalyst (KBr pellet), (b) fresh Rh/NiZn catalyst (KBr pellet), and (c) **3aa** (neat).

Scheme S1 Speculated reaction mechanism

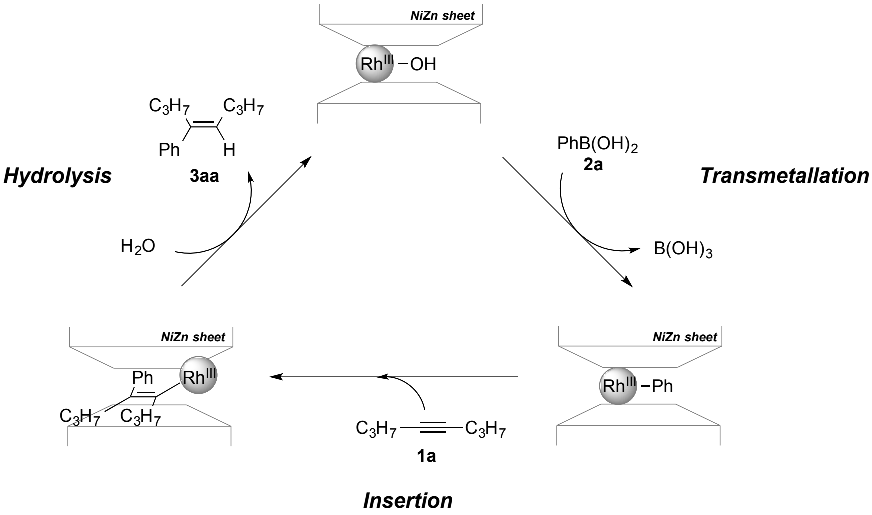
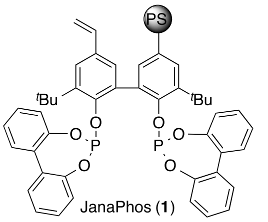


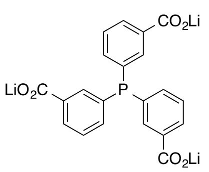
Table S2. Hydrophenylation of internal alkynes with various catalysts

Catalyst	Additive ligand	TON (-) based on metal amount	Reference
Heterogeneous catalysis			
Rh/NiZn	1,5-COD	740	This work
Rh-*m*-TPPTC/Hydrotalcite	-	1	(a)
Homogeneous catalysis			
Rh catalysts			
Rh(acac)(CO)$_2$	JanaPhos (**1**)	46	(b)
Rh(acac)(CO)$_2$	-	18	(c)
[Rh(1,5-COD)OH]$_2$	*m*-TPPTC (**2**)	59	(d)
[Rh(1,5-COD)Cl]$_2$	Ligand (**3**)	43	(e)
Rh(acac)(C$_2$H$_4$)$_2$	dppb (**4**)	32	(f)
Pd catalytsts			
PdCl$_2$	^{i}Pr$_2$NPPh$_2$	~20	(g)
PdCl$_2$(PPh$_3$)$_2$	AcOH	~34	(h)
Pd(OAc)$_2$	Ligand (**5**)	~34	(i)
Pd(PPh$_3$)$_4$	AcOH	~34	(j)
Other transition metal catalysts			
CuOAc	-	~100	(k)
Co(acac)$_2$	dppe (**6**)	~ 20	(l)
Ni(1,5-COD)$_2$	-	~192	(m)

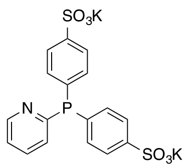
(a) F. Neaţu, M. Ciobanu, L. E. Ştoflea, L. Frunză, V. I. Pârvulescu and V. Michelet, *Catal. Today*, 2015, **247**, 155.
(b) R. Jana and J. A. Tunge, *J. Org. Chem.*, 2011, **76**, 8376.
(c) W. Zhang, M. Liu, H. Wu, J. Ding and J. Cheng, *Tetrahedron Lett.*, 2008, **49**, 5214
(d) E. Genin, V. Michelet and J.-P. Genêt, *J. Organometal. Chem.*, 2004, **689**, 3820
(e) M. Lautens and M. Yoshida, *J. Org. Chem.*, 2003, **68**, 762
(f) T. Hayashi, K. Inoue, N. Taniguchi and M. Ogasawara, *J. Am. Chem. Soc.*, 2001, **123**, 9918.
(g) X.-L. Xu, J.-X. Chen, W.-X. Gao, H.-Y. Wu, J.-C. Ding and W.-K. Su, *Tetrahedron*, 2010, **66**, 2433.
(h) H.-X. Zeng and R.-M. Hua, *J. Org. Chem.*, 2008, **73**, 558.
(i) A. K. Gupta, K. S. Kim and C. H. Oh, *Synlett*, 2005, 457.
(j) C. H. Oh, H. H. Jung, K. S. Kim and N. Kim, *Angew. Chem. Int. Ed.*, 2003, **42**, 805.
(k) Y. Yamamoto, N. Kirai and Y. Harada, *Chem. Commun.*, 2008, 2010.
(l) P.-S. Lin, M. Jeganmohan and C.-H. Cheng, *Chem. Eur. J.*, 2008, **14**, 11296.
(m) E. Shirakawa, G. Takahashi, T. Tsuchimoto and Y. Kawakami, *Chem. Commun.*, 2001, 2688.



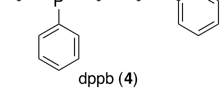
JanaPhos (**1**)



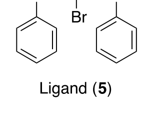
m-TPPTC (**2**)



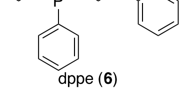
TPPDS (**3**)



dppb (**4**)

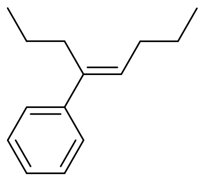


Ligand (**5**)

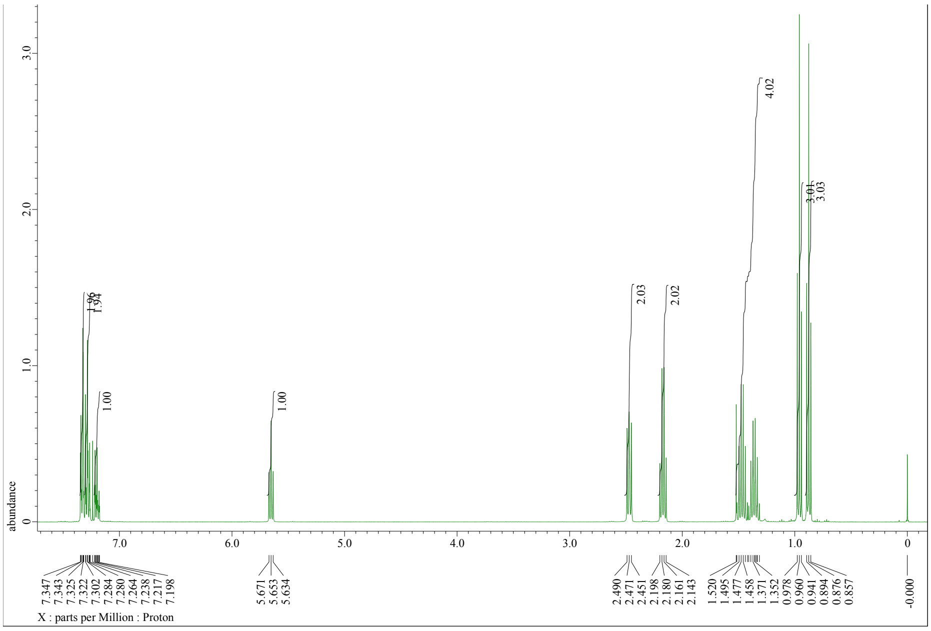


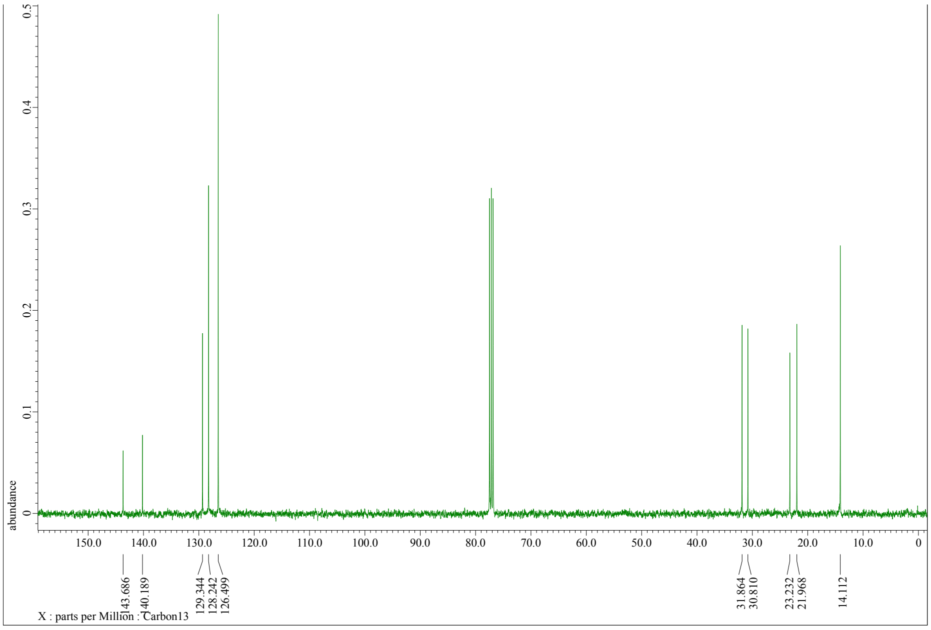
dppe (**6**)

(*E*)-4-phenyl-4-octene (**3aa**; CAS: 42353-94-6)[S5]

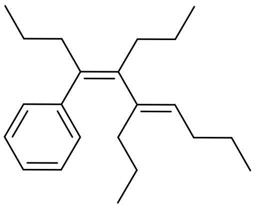


A colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm:□0.88 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H), 1.36 (sext, *J* = 7.6 Hz, 2H), 1.47 (sext, *J* = 7.6 Hz, 2H), 2.17 (q, *J* = 7.2 Hz, 2H), 2.47 (t, *J* = 7.6 Hz, 2H), 5.65 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm:□14.1, 22.0, 23.2, 30.8, 31.9, 126.5, 128.2, 129.3, 140.2, 143.7.



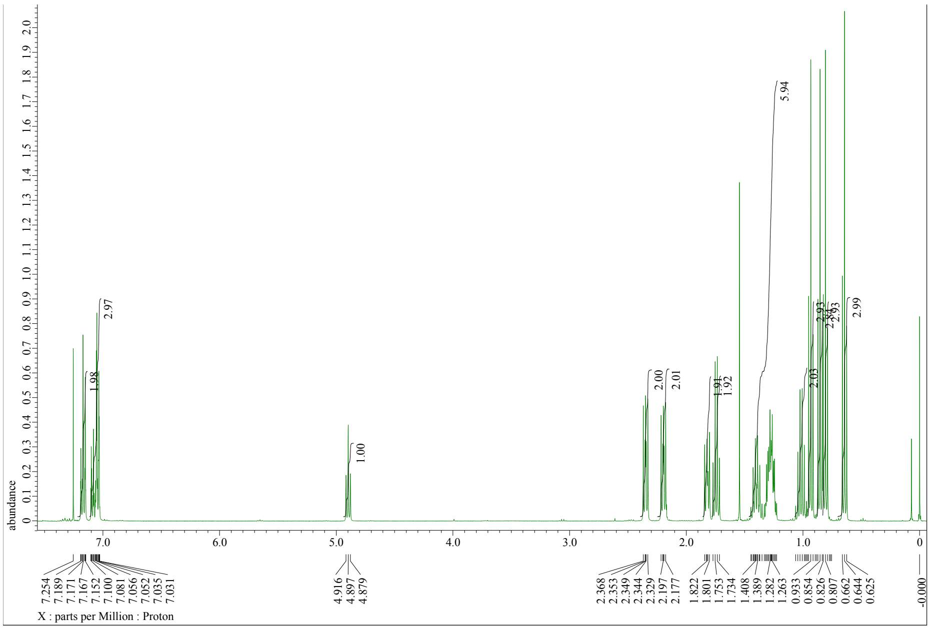


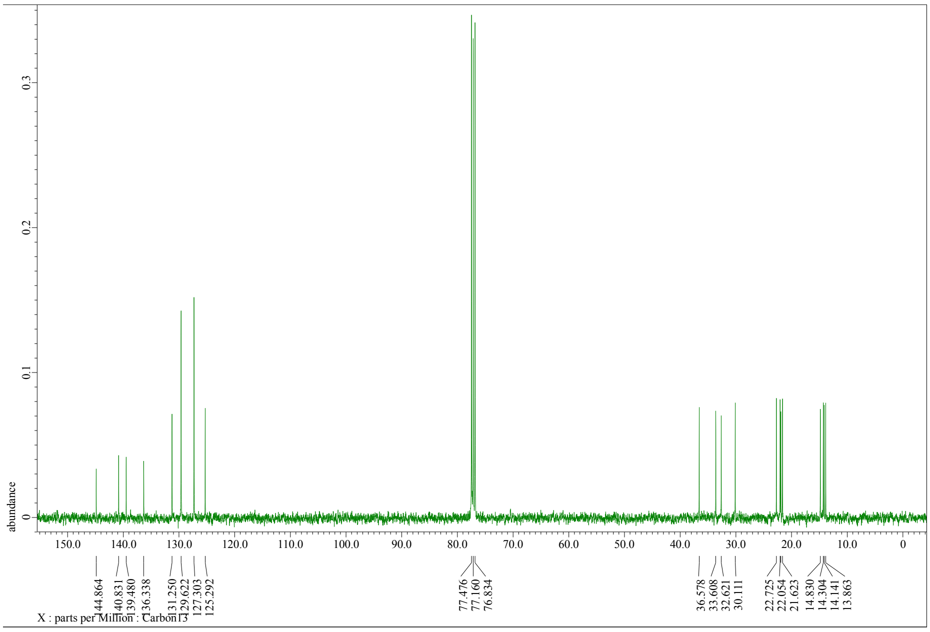
(4*Z*, 6*E*)-4-phenyl-5,6-dipropyl-deca-4,6-diene (4aa; CAS: 201864-12-2)[S6]



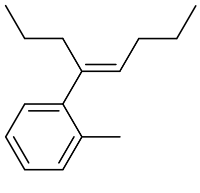
A colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm:□ 0.64 (t, *J* = 7.2 Hz, 3H), 0.81 (t, *J* = 7.6 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H), 1.02 (sext, *J* = 7.6 Hz, 2H), 1.22-1.33 (m, 4H), 1.40 (sext, *J* = 7.6 Hz, 2H), 1.74 (q, *J* = 7.2 Hz, 2H), 1.82 (t, *J* = 8.0 Hz, 2H), 2. 20 (t, *J* = 7.6 Hz, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 4.90 (t, *J* = 7.6 Hz, 1H), 7.04-7.10 (m, 3H), 7.17 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, CDCl$_3$) δ ppm:□ 13.9, 14.1, 14.3, 14.8, 21.6, 21.9, 22.1, 22.7, 30.1, 32.6, 33.6, 36.6, 125.3, 127.3, 129.6, 131.3, 136.3, 139.5, 140.8, 144.9.

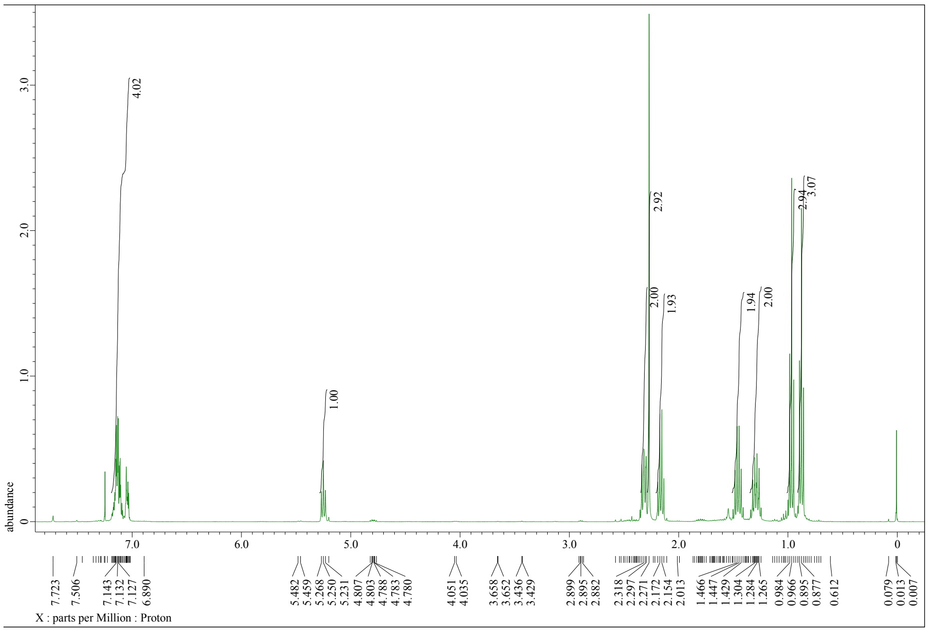


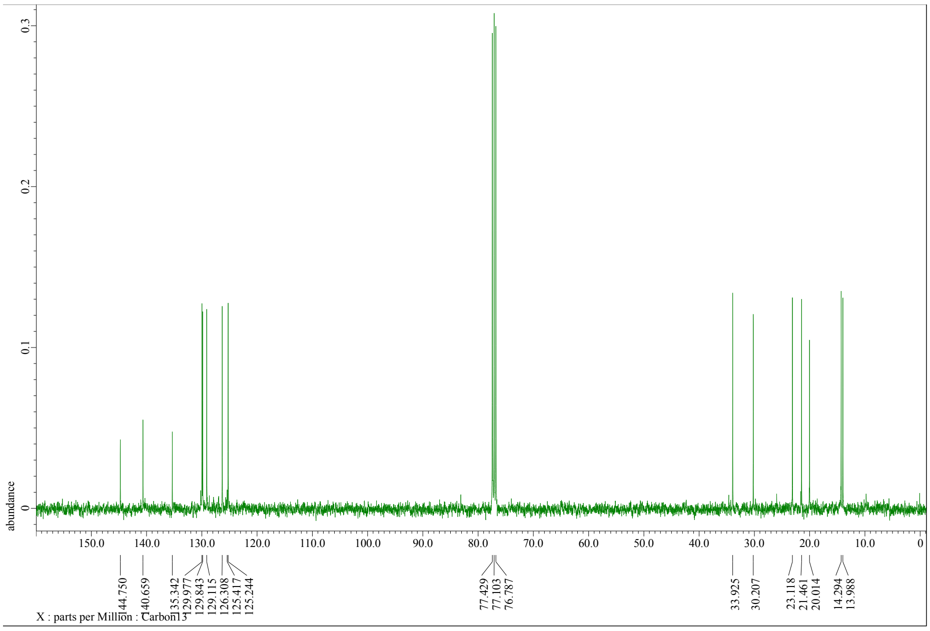


(*E*)-4-(2-methylphenyl)-4-octene (3ab; CAS: 819047-58-0)[S7]



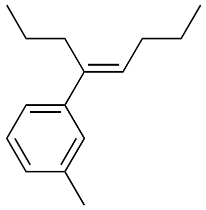
A colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 0.88 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H), 1.29 (sext, *J* = 7.6 Hz, 2H), 1.46 (sext, *J* = 7.6 Hz, 2H), 2.16 (q, *J* = 7.2 Hz, 2H), 2.27 (s, 3H), 2.32 (t, *J* = 7.6 Hz, 2H), 5.25 (t, *J* = 7.2 Hz, 1H), 7.02-7.19 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm: 14.0, 14.3, 20.0, 21.5, 23.1, 30.2, 33.9, 125.2, 126.3, 129.1, 129.8, 130.0, 135.3, 140.7, 144.8.





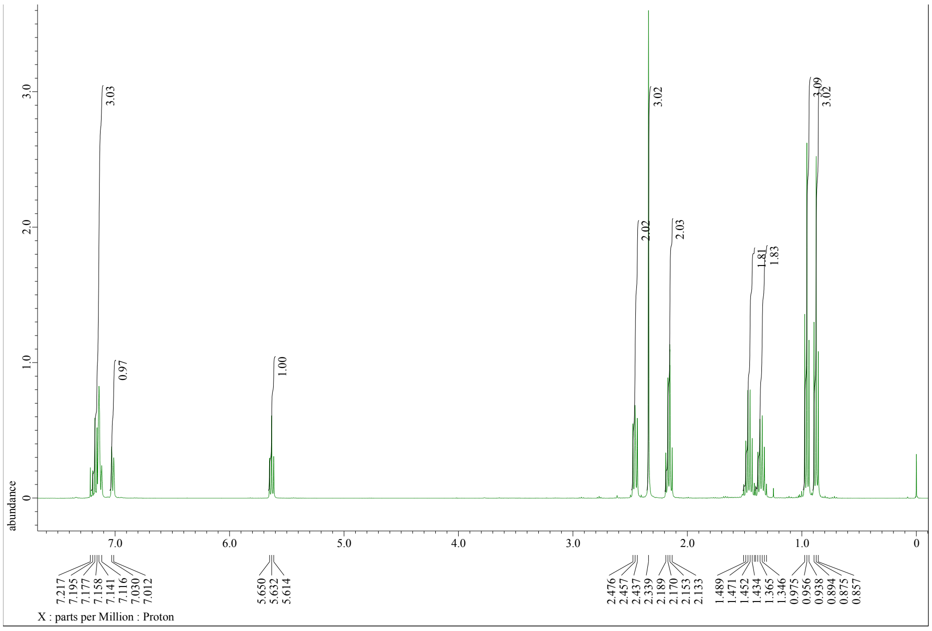
(*E*)-4-(3-methylphenyl)-4-octene (**3ac**; CAS: 873297-54-2)^{S7}

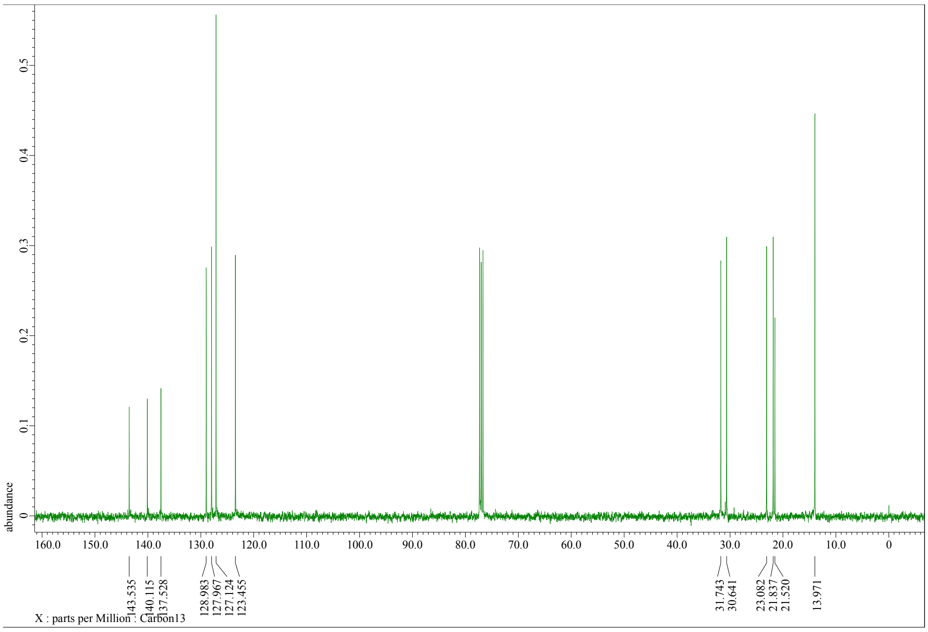
A colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 0.88 (t, *J* = 7.6 Hz,



3H), 0.96 (t, *J* = 7.6 Hz, 3H), 1.36 (sext, *J* = 7.2 Hz, 2H), 1.46 (sext, *J* = 7.6 Hz, 2H), 2.16 (q, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 2.46 (t, *J* = 7.6 Hz, 2H), 5.63 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 7.12-7.21 (m, 2H).

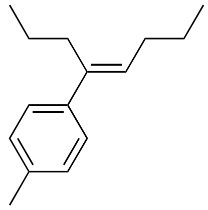
^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.0, 21.5, 21.8, 23.1, 30.6, 31.7, 123.5, 127.1, 128.0, 129.0, 137.5, 140.1, 143.5.





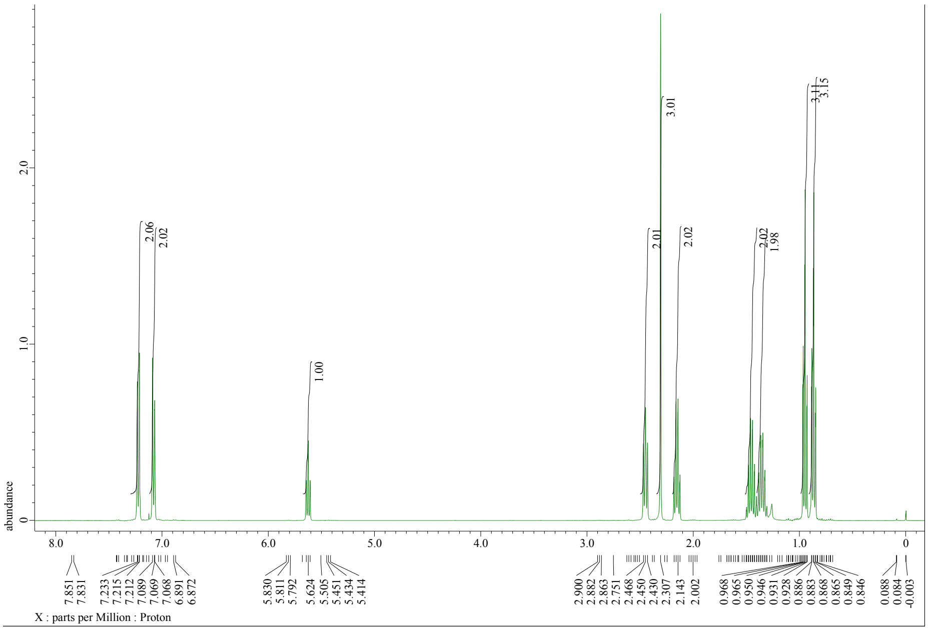
(*E*)-4-(4-methylphenyl)-4-octene (**3ad**; CAS: 42353-96-8)^{S5}

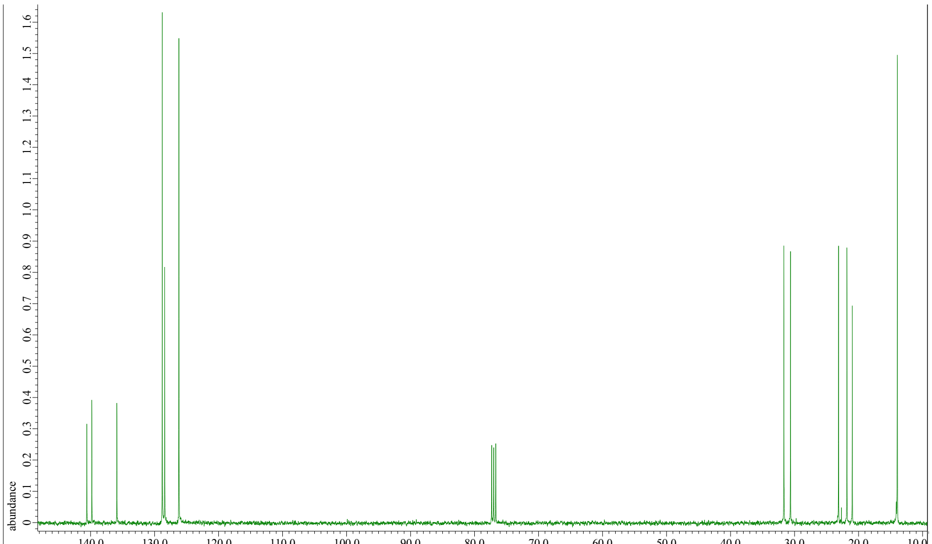
A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 0.86 (t, *J* = 7.2



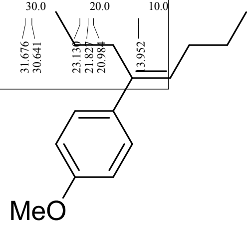
Hz, 3H), 0.95 (t, *J* = 7.6 Hz, 3H), 1.35 (sext, *J* = 7.6 Hz, 2H), 1.46 (sext, *J* = 7.6 Hz, 2H), 2.16 (q, *J* = 7.6 Hz, 2H), 2.30 (s, 3H), 2.45 (t, *J* = 7.2 Hz, 2H), 5.62 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.0, 21.0, 21.8, 23.1, 30.6, 31.7, 126.2, 128.4, 128.8, 135.9, 139.8, 140.6.





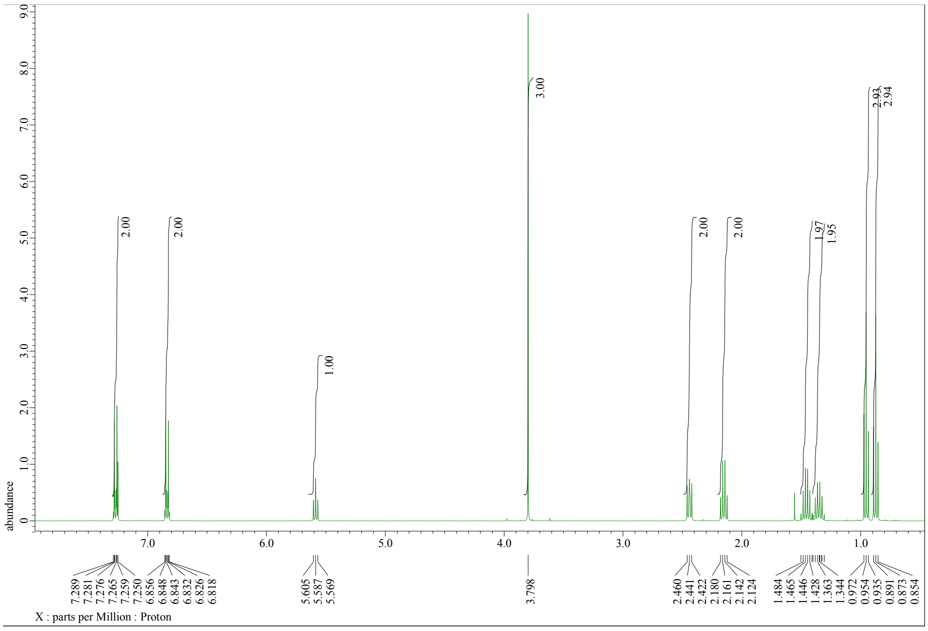
(*E*)-4-(4-methoxyphenyl)-4-octene (3ae; CAS: 374106-95-3)[S5]

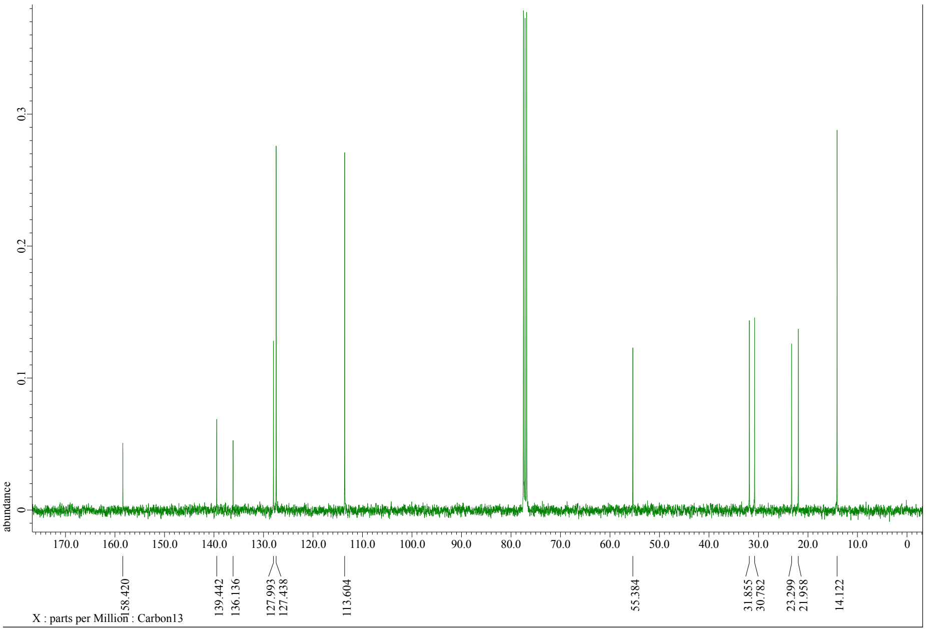


A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 0.87 (t, *J* = 7.6 Hz, 3H), 0.95 (t, *J* = 7.6 Hz, 3H), 1.35 (sext, *J* = 7.6 Hz, 2H), 1.46

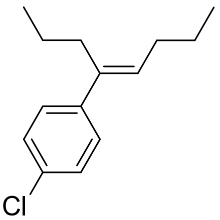
(sext, J = 7.6 Hz, 2H), 2.15 (q, J = 7.6 Hz, 2H), 2.44 (t, J = 7.6 Hz, 2H), 3.80 (s, 3H), 5.59 (t, J = 7.2 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.1, 21.9, 23.3, 30.8, 31.9, 55.4, 113.6, 127.4, 128.00, 136.1, 139.4, 158.4.





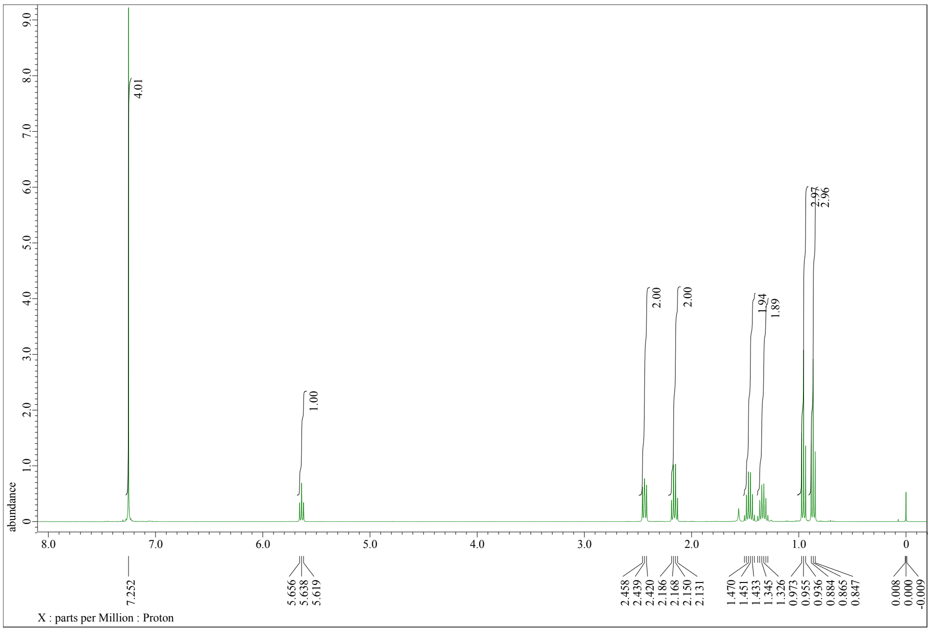
(E)-4-(p-chlorophenyl)-4-octene (3af; CAS: 107558-67-8)

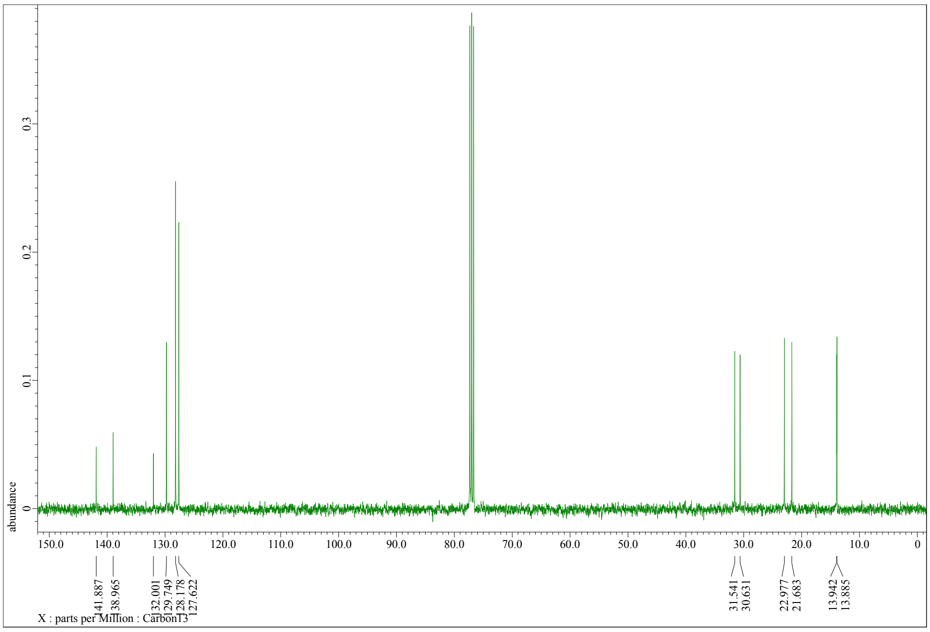


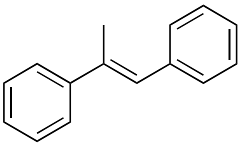
A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 0.87 (t, J = 7.6 Hz, 3H), 0.96 (t, J = 7.6 Hz, 3H), 1.34 (sext, J = 7.6 Hz, 2H), 1.46

(sext, J = 7.6 Hz, 2H), 2.16 (q, J = 7.2 Hz, 2H), 2.44 (t, J = 7.6 Hz, 2H), 5.64 (t, J = 7.6 Hz, 1H), 7.25 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 13.9, 13.9, 21.7, 23.0, 30.6, 31.5, 127.6, 128.2, 129.7, 132.0, 139.0, 141.9.





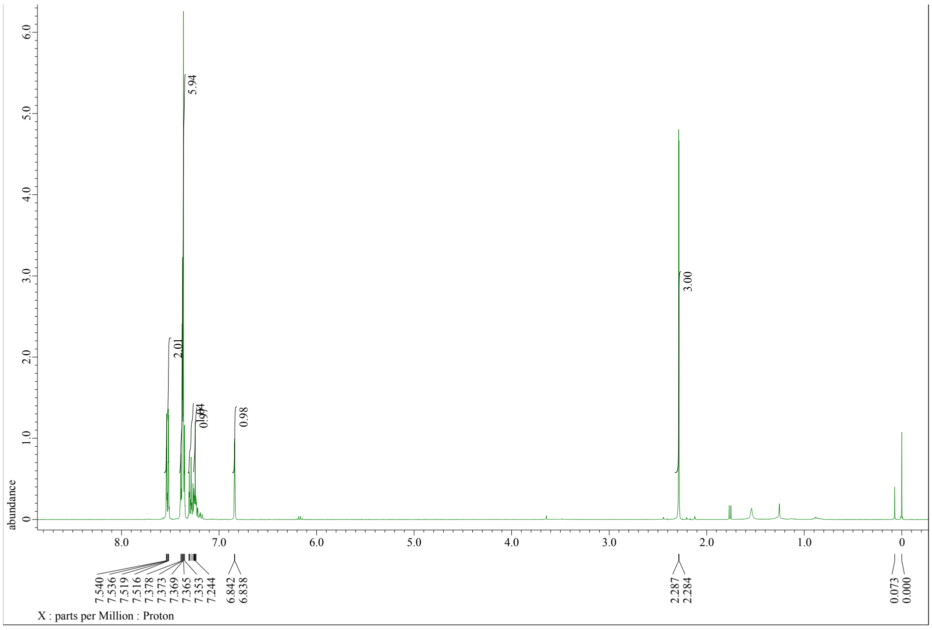


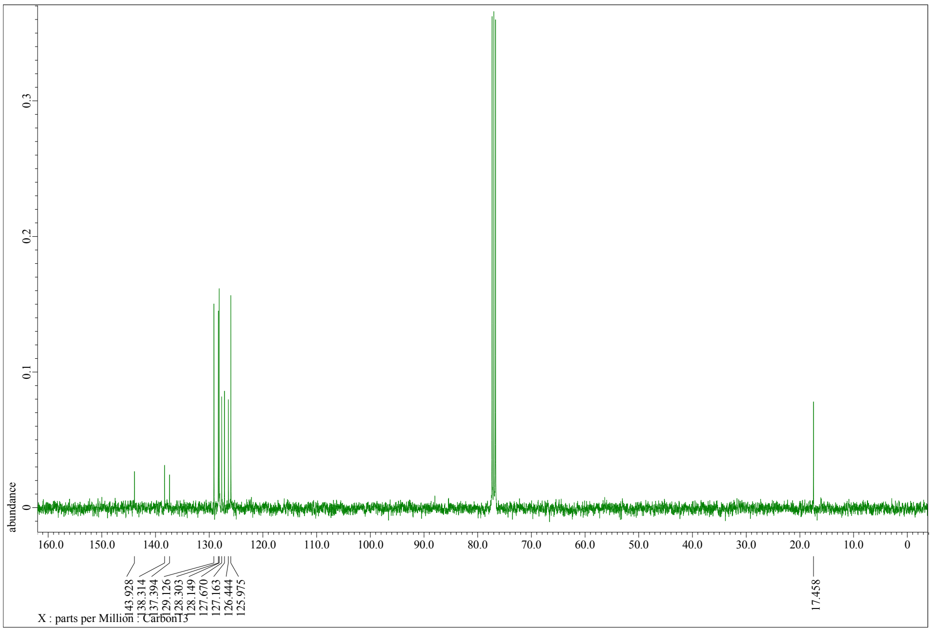
(*E*)-1,2-diphenylpropene (**3ba**; CAS: 833-81-8)[S5]

A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.29 (s, 3H), 6.84 (s, 1H), 7.22-7.27 (m, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.35-7.39

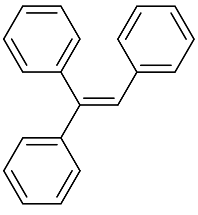
(m, 6H), 7.53 (d, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, CDCl$_3$) δ ppm: 17.5, 126.0, 126.4, 127.2, 127.7, 128.1, 128.3, 129.1, 137.4, 138.3, 143.9.



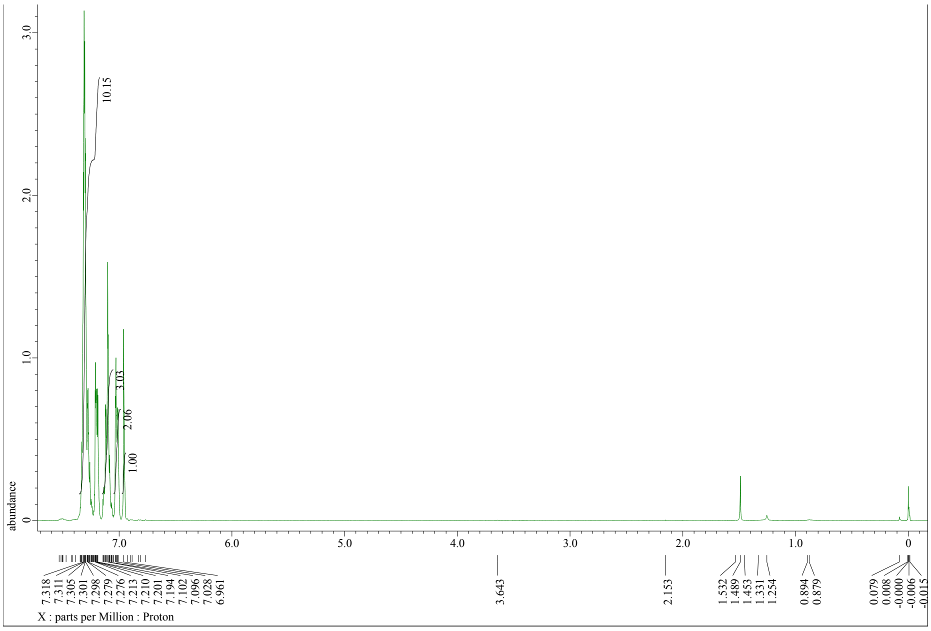


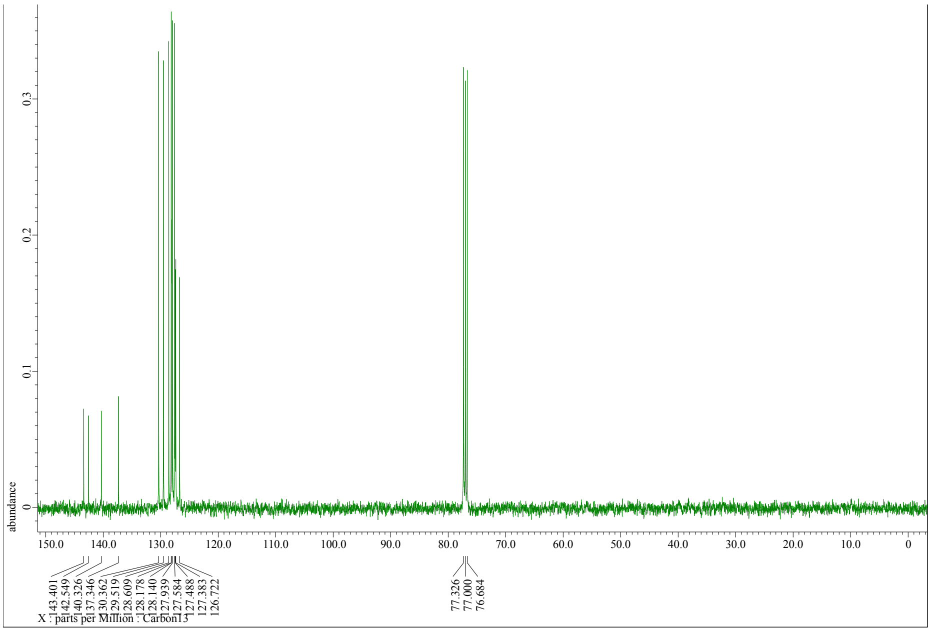
1,1,2-Triphenylethylene (**3da**; CAS: 58-72-0)[S8]



A colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 6.96 (s, 1H), 7.01-7.04 (m, 2H), 7.09-7.15 (m, 3H), 7.18-7.34 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 126.7, 127.4, 127.5, 127.6, 127.9, 128.1, 128.2, 128.6, 129.5, 130.4, 137.3, 140.3, 142.5, 143.4.





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