

Supporting Information

Pd/Light Induced Alkyl-Alkenyl Coupling Reaction between Unactivated Alkyl Iodides and Alkenylboronic Acids

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General Information

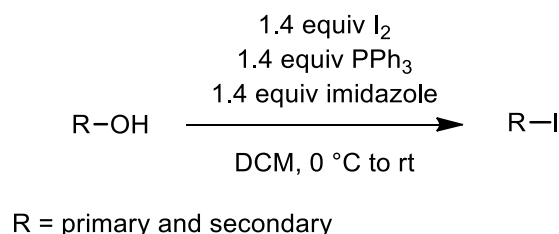
For photo-irradiation, we used 15 W black light (EFD15BLB-T, Toshiba). The reaction was carried out in a 15 mmφ Pyrex tube equipped with Teflon cap. Thin layer chromatography (TLC) was performed on Merck precoated plates (silica gel 60 F254, Art 5715, 0.25 mm), and were visualized by UV light or by staining with KMnO₄/KOH/NaOH/H₂O. The products were purified by flash chromatography on silica gel (KM3 Scientific Co. Silica Gel (45-75 μm)). Melting points were uncorrected. ¹H NMR spectra were

recorded with Agilent 400-MR DD2 (400 MHz) and referenced to the solvent peak for chloroform at 7.26 ppm, for benzene at 7.16 ppm, or for d_4 -MeOH at 3.31 ppm (quint). ^{13}C NMR spectra were recorded with Agilent 400-MR DD2 (100 MHz) and referenced to the solvent peak for chloroform at 77.00 ppm or for d_4 -MeOH at 49.0 ppm (sept.). ^{19}F NMR spectra were recorded with Agilent 400-MR DD2 (375 MHz) and trifluoroacetic acid is used as standard at -76.55 ppm. Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sept, septet; m, multiplet. Coupling constants (J) are reported in Hertz (Hz). Infrared (IR) spectra were measured on KBr salt plates. Infrared spectra were recorded on a Bruker, Tensor27 and are reported as wavenumber (cm^{-1}). High-resolution mass spectra were recorded with a JEOL AccuTOF GCX. 2-Arylalkenylboronic acids were commercially available and purchased from Sigma Aldrich (**2a**, **2b**, **2c**, **2d**), ACROS (**2e**), and Matrix (**2g**). (*E*)-(2-(Naphthalen-2-yl)vinyl)boronic acid **2f** was prepared by the known protocol.

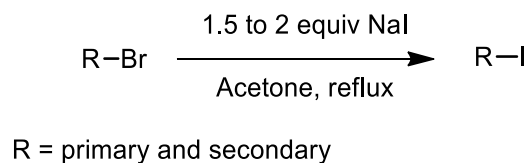
Preparation of Starting Materials

Primary and secondary alkyl iodides **1** were prepared from the corresponding alcohols by the known procedure depicted in Scheme S1. [ref 1] Precursor alcohols for compound **1b**, **1c**, and **1d**, were prepared from ethylene carbonate and the corresponding phenols according to our recent procedure. [ref 2] Compounds **1e**, **1l**, and **1m** were prepared from the corresponding alkyl bromides according to the method of Hoveyda. [ref 3]

Scheme S1. Conversion of primary and secondary alcohols to alkyl iodides

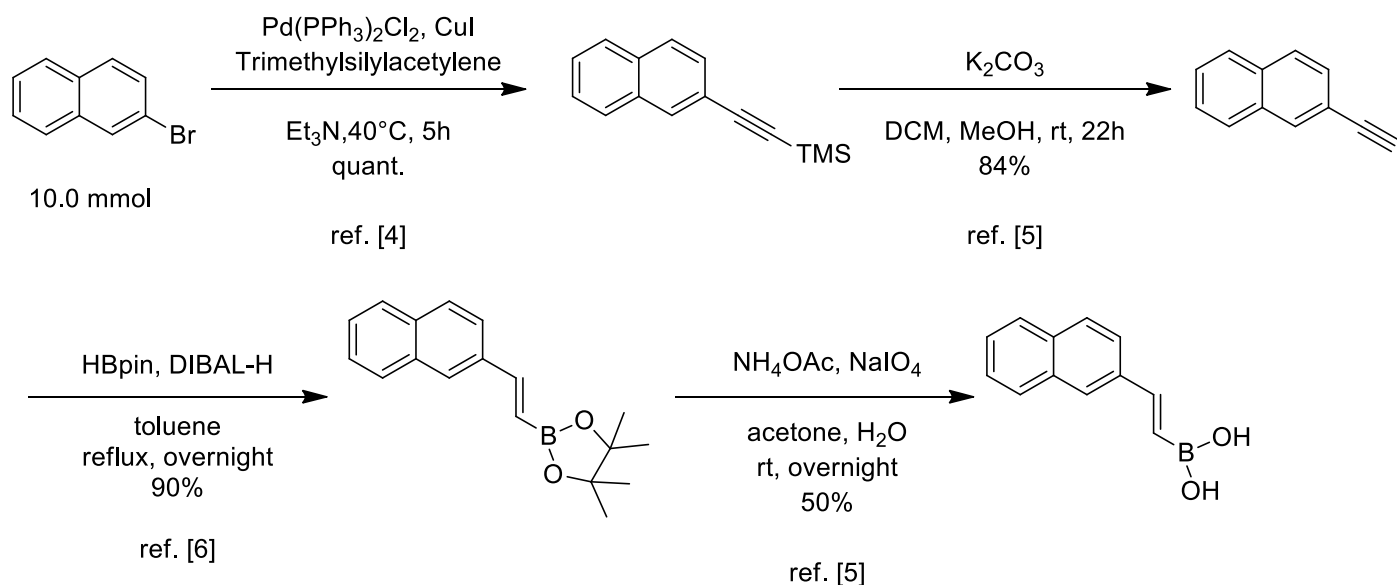


Scheme S2. Conversion of alkyl bromides to alkyl iodides



(*E*)-(2-(Naphthalen-2-yl)vinyl)boronic acid (**2f**) was prepared via four steps starting from 2-naphthylbromide (Scheme S3). [ref 4,5,6]

Scheme S3. Synthesis of 2f



(*E*)-(2-(Naphthalen-2-yl)vinyl)boronic acid (2f**):** According to the method from the references, the boronic acid was obtained from the corresponding bromide (2.06 g, 10 mmol) for four steps. Purified by column chromatography (eluent: hexane) for the first three steps and by recrystallization for the last step to obtained **2f** as yellow solid (0.75 g, 38% yield overall). mp: 196-197 °C; IR (cast): 3270, 1614, 1590, 812

cm-1; ¹H NMR (400 MHz, MeOD): δ 7.87-7.80 (m, 4H), 7.75 (dd, J = 14.0, 8.7 Hz, 1H), 7.50 (d, J = 18.1 Hz, 1H), 7.47-7.43 (m, 2H), 6.49 (d, J = 18.1 Hz, 1H); ¹³C NMR (100MHz, MeOD): δ 149.41, 136.65, 135.11, 134.99, 129.32, 129.22, 128.78, 128.63, 127.37, 127.33, 124.39.

Ref 1: Cheung, C. W.; Ren, P.; Hu, X. L. *Org. Lett.* **2014**, *16*, 2566–2569.

Ref 2: Kao, S. C.; Lin, Y. C.; Ryu, I.; Wu, Y. K. *Adv. Synth. Catal.* **2019**, *361*, 3639–3644

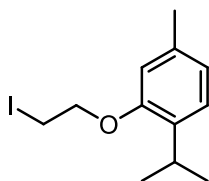
Ref 3: McGrath, K. P. and Hoveyda, A. H. *Angew. Chem., Int. Ed.*, **2014**, *53*, 1910–1914.

Ref 4: Blanco, B., Sedes, A.; Peón, A.; Lamb, H.; Hawkins, A. R.; Castedo, L. and González-Bello, C. *Org. Biomol. Chem.* **2012**, *10*, 3662

Ref 5: Boelke, A.; Caspers, L. D.; Nachtsheim, B. J. *Org. Lett.* **2017**, *19*, 5344–5347.

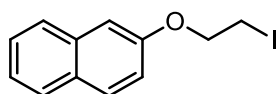
Ref 6: Bismuto, A.; Thomas, S. P.; Cowley, M. J. *Angew. Chem. Int. Ed.* **2016**, *55*, 15356 – 15359.

Spectral Data for Alkyl Iodides

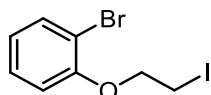


2-(2-Bromophenoxy)ethan-1-ol (1b): According to the method from the reference, the iodide was obtained from the corresponding alcohol (0.37 g, 1.9 mmol) and was purified by column chromatography (eluent: hexane) to obtain **1b** as white solid (1.38 g, 72% yield). mp: 35-36 °C; IR (cast): 3058, 2956, 2919, 2866, 1607, 1576, 1504, 1451 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.12 (d, J = 7.7 Hz, 1H), 6.78 (d, J = 7.7 Hz, 1H), 6.62 (s, 1H), 4.27-4.24 (t, J = 6.6 Hz, 2H), 3.48-3.45 (t, J = 6.6 Hz, 2H), 3.40-3.29 (m, 1H), 2.33 (s,

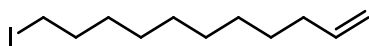
3H), 1.23 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (100MHz, CDCl_3): δ 154.98, 136.34, 134.37, 126.15, 121.85, 112.53, 68.59, 26.54, 22.88, 21.28, 1.75; HRMS: (EI, $[\text{M}]^+$) for $\text{C}_{12}\text{H}_{17}\text{IO}$ calcd. 304.0319, found: 304.0324



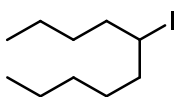
2-(2-Iodoethoxy)naphthalene (1c): This compound is previously known (Brinkø, A.; Larsen, M. T.; Koldsø, H.; Besenbacher, L.; Kolind, A.; Schiøtt, B.; Sinning, S.; Jensen, H. H. *Biorg. Med. Chem.* **2016**, *24*, 2725–2738). According to the method from the reference, the iodide was obtained from the corresponding alcohol (1.54 g, 8.2 mmol) and was purified by column chromatography (eluent: hexane) to obtained **1c** as white solid (1.22 g, 50% yield). mp: 99-100 °C; IR (cast): 3055, 3021, 2942, 1626, 1599, 1508, 1470, 1456 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.79-7.72 (m, 3H), 7.47-7.74 (m, 1H), 7.38-7.34 (m, 1H), 7.19-7.16 (m, 1H), 7.13-7.12 (m, 1H), 4.38 (t, $J = 6.9$ Hz, 2H), 3.49 (t, $J = 6.9$ Hz, 2H); ^{13}C NMR (100MHz, CDCl_3): δ 155.83, 134.36, 129.64, 129.21, 127.65, 126.75, 126.49, 123.91, 118.72, 107.16, 68.60, 1.02; HRMS: (EI, $[\text{M}]^+$) for $\text{C}_{12}\text{H}_{11}\text{IO}$ calcd. 297.9849, found: 297.9846



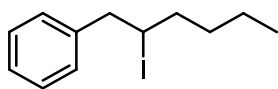
1-Bromo-2-(2-iodoethoxy)benzene (1d): According to the method from the reference, the iodide was obtained from the corresponding alcohol (0.35 g, 1.6 mmol) and was purified by column chromatography (eluent: hexane) to obtained **1d** as white solid (0.36 g, 69% yield). mp: 41-42 °C; IR (cast): 2925, 2886, 2354, 1567, 1478, 1459 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.56-7.54 (m, 1H), 7.28-7.24 (m, 1H), 6.90-6.86 (m, 2H), 4.30 (t, $J = 7.0$ Hz, 2H), 3.47 (t, $J = 7.0$ Hz, 2H); ^{13}C NMR (100MHz, CDCl_3): δ 154.39, 133.61, 128.49, 122.74, 114.10, 112.65, 69.95, 0.38; HRMS: (EI, $[\text{M}]^+$) for $\text{C}_8\text{H}_8\text{BrIO}$ calcd. 325.8798, found: 325.8805



1-Iodoundec-1-ene (1e): This compound is previously known (Bauer, K. N.; Tee, H. T.; Lieberwirth, I.; Wurm, F. R. *Macromolecules* **2016**, *49*, 3761–3768). According to the method from the reference, the iodide was obtained from the corresponding bromide (1.94 g, 8.32 mmol) and was purified by column chromatography (eluent: hexane) to obtained **1e** as colorless oil (2.3 g, 99% yield); IR (film): 3075, 2926, 2854, 1640, 1464 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 5.81 (ddt, $J = 17.2, 10, 7.2$ Hz, 1H), 4.99 (d, $J = 17.2$ Hz, 1H), 4.93 (d, $J = 10$ Hz, 1H), 3.18 (t, $J = 7.1$, 2H), 2.04 (dt, $J = 7.2, 7.2$ Hz, 2H), 1.82 (tt, $J = 7.1, 7.1$, 2H), 1.45-1.23 (m, 12H); ^{13}C NMR (100MHz, CDCl_3): δ 139.17, 114.13, 33.77, 33.55, 30.48, 29.34, 29.05, 28.88, 28.50, 7.30; HRMS: (FI, $[\text{M}]^+$) for $\text{C}_{11}\text{H}_{21}\text{I}$ calcd. 280.0683, found: 280.0682

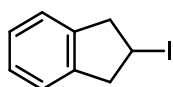


5-Iododecane (1f): This compound is previously known (Tanemura, K. *Tetrahedron. Lett.* **2018**, *59*, 4293–4298). According to the method from the reference, the iodide was obtained from the corresponding alcohol (6.46g, 40.8 mmol) and was purified by column chromatography (eluent: hexane) to obtained **1f** as colorless oil (10.9 g, 98% yield); IR (film): 2954, 2926, 2870, 2856, 1456 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 4.16-4.08 (m, 1H), 1.91-1.80 (m, 2H), 1.75-1.63 (m, 2H), 1.56-1.46 (m, 2H), 1.43-1.22 (m, 8H), 0.94-0.83 (m, 6H); ^{13}C NMR (100MHz, CDCl_3): δ 40.63, 40.60, 40.39, 31.68, 31.04, 29.19, 22.51, 21.97, 14.01, 13.96; HRMS: (FI, $[\text{M}]^+$) for $\text{C}_{10}\text{H}_{21}\text{I}$ calcd. 268.0683, found: 268.0678

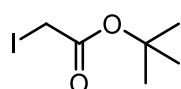


(2-Iodoethyl)benzene (1g): This compound is previously known (Shibli, A; Varghese, J. P.; Knochel, P.; Marek, I. *synlett*, **2001**, *06*, 0818–0820). According to the method from the reference, the iodide was

obtained from the corresponding alcohol (1.30g, 7.25 mmol) and was purified by column chromatography (eluent: hexane) to obtained **1g** as colorless oil; IR (film): 3064, 3026, 2954, 2924, 2874, 2856, 1600, 1494, 1453 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.33-7.24 (m, 3H), 7.20-7.18 (m, 2H), 4.32-4.25 (m, 1H), 3.28 (dd, $J = 14.3, 7.7$ Hz, 2H), 3.17 (dd, $J = 14.3, 7.6$ Hz, 2H), 1.83-1.79 (m, 1H), 1.74-1.66 (m, 1H), 1.61-1.55 (m, 1H), 1.44-1.30 (m, 1H), 0.90 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 139.87, 128.96, 128.41, 126.73, 47.48, 39.24, 38.86, 31.78, 21.86, 13.93; HRMS: (EI, $[\text{M}]^+$) for $\text{C}_{12}\text{H}_{17}\text{I}$ calcd. 288.0369, found: 288.0362

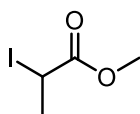


2-Iodo-2,3-dihydro-1H-indene (1i): This compound is previously known (Cheung, C. W.; Ren, P.; Hu, X. L. *Org. Lett.* **2014**, *16*, 2566–2569). According to the method from the reference, the iodide was obtained from the corresponding alcohol (2.01 g, 15 mmol) and was purified by column chromatography (eluent: hexane) to obtained **1i** as white solid (3.26 g, 89% yield). mp: 60-61 $^\circ\text{C}$; IR (cast): 3067, 3037, 2956, 2908, 2839, 1460, 1428 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.33-7.16 (m, 4H), 4.70 (quint, $J = 5.7$ Hz, 1H), 3.55-3.35 (m, 4H); ^{13}C NMR (100MHz, CDCl_3): δ 141.44, 126.92, 124.29, 46.55, 23.82, 23.79; HRMS: (FI, $[\text{M}]^+$) for $\text{C}_9\text{H}_9\text{I}$ calcd. 243.9743, found: 243.9741



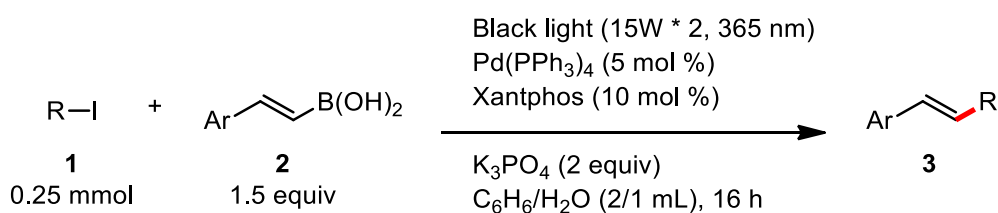
tert-Butyl 2-iodoacetate (11): This compound is previously known (Jiang, S; Li, P.; Lai, C. C.; Kelley, J. A.; Roller, P. P. *J. Org. Chem.*, **2006**, *71*, 7307–7314). According to the method from the reference, the iodide was prepared from the corresponding bromide (3.2 g, 16.4 mmol) and was purified by column chromatography (eluent: hexane/ethyl acetate = 5/1) to obtained **11** as colorless oil (3.58 g, 90% yield), IR (film): 3430, 2980, 2933, 1729, 1369 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 3.60 (s, 2H), 1.46 (s, 9H); ^{13}C

NMR (100MHz, CDCl₃): δ 167.85, 82.31, 27.63, -2.60; HRMS: (FI, [M]⁺) for C₆H₁₁O₂I calcd. 241.9798, found: 241.9791



Methyl 2-iodopropanoate (1m): This compound is previously known (McGrath, K. P. and Hoveyda, A. H. *Angew. Chem., Int. Ed.*, **2014**, *53*, 1910–1914). According to the method from the reference, the iodide was prepared from the corresponding bromide (2.93 g, 17.5 mmol) and was purified by column chromatography (eluent: hexane/ethyl acetate = 10/1) to obtain **1m** as colorless oil (2.58 g, 69% yield). IR (film): 2953, 2923, 1736, 1445, 1345 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 4.48 (q, *J* = 7 Hz, 1H), 3.74 (s, 3H), 1.96 (d, *J* = 7.1, 3H); ¹³C NMR (100MHz, CDCl₃): δ 172.39, 52.88, 23.36, 12.39; HRMS: (FI, [M]⁺) for C₄H₇O₂I calcd. 213.9485, found: 213.9480

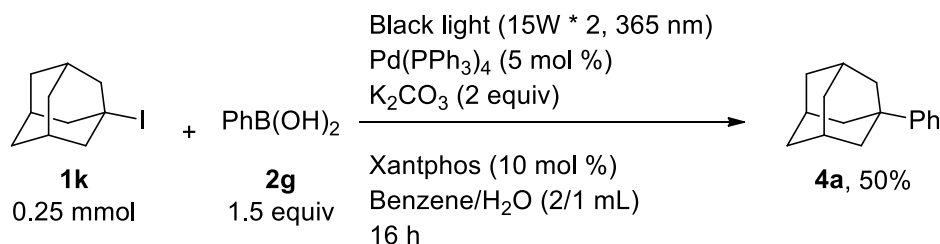
General Procedure for Alkyl-Alkenyl Coupling Reaction



K₃PO₄ (2 equiv, 106.1 mg), (*E*)-2-arylalkenylboronic acid (1.5 equiv, 0.375 mmol), alkyl iodide (1 equiv, 0.25 mmol), Xantphos (10 mol %, 14.5 mg) and Pd(PPh₃)₄ (5 mol %, 14.4 mg) were placed in a pyrex tube equipped with a stir bar. After benzene (2 ml) and water (1 ml) were added, the tube sealed with a septum was purged N₂ for ca 5 min. Quickly changed the septum to the Teflon cap and sealed with PTFE tape. The reaction mixture was stirred vigorously under irradiation of two 15 W black lights at room temperature

(with fan cooling) for 16 h. The reaction mixture was extracted with diethyl ether (3 x 10 ml). The combined organic layer was washed with brine, dried over MgSO₄ and concentrated by rotary evaporation. The product was purified by column chromatography on silica gel.

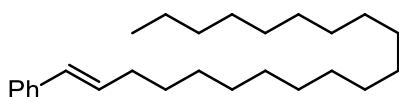
Reaction of 1-Iodoadamantane (1k) with Phenylboronic Acid (2g)



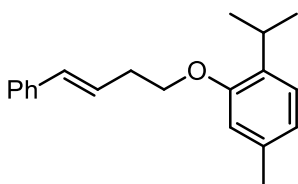
K₂CO₃ (2 equiv, 69.1 mg) phenylboronic acid (1.5 equiv, 45.7mg), 1-iodoadamantane (1 equiv, 0.25 mmol, 65.5mg), Xantphos (10 mol %, 14.5 mg) and Pd(PPh₃)₄ (5 mol %, 14.4 mg) were placed in a pyrex tube equipped with a stir bar. After benzene (2 ml) and water (1 ml) were added, the tube sealed with a septum was purged N₂ for ca 5 min. Quickly changed the septum to the Teflon cap and sealed with PTFE tape. The reaction mixture was stirred vigorously under irradiation of two 15 W black lights at room temperature (with fan cooling) for 16 h. The reaction extracted with diethyl ether (3 x 10 ml). The combined organic layer was washed with brine, dried over MgSO₄ and concentrated by rotary evaporation. The product was purified by column chromatography (eluent: hexane) to obtain **4a** as colorless solid (26.4 mg, 50% yield).

(3r, 5r, 7r)-1-Phenyladamantane (4a): This compound is previously known (Mosset, P.; Gree, R. *Synlett.*, **2013**, *24*, 1142–1146). ¹H NMR (400 MHz, CDCl₃): δ 7.38-7.37 (m, 2H), 7.34-7.30 (m, 2H), 7.19-7.16 (m, 1H), 2.10 (m, 3H), 1.93 (m, 6H), 1.81-1.74 (m, 6H); ¹³C NMR (100MHz, CDCl₃): δ 151.31, 128.07, 125.48, 124.82, 43.16, 36.81, 36.16, 28.96

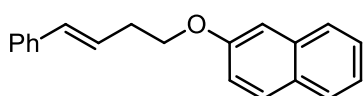
Spectral Data for Products



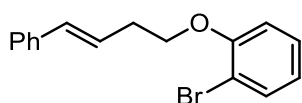
(E)-Icos-1-en-1-ylbenzene (3a): Purified by column chromatography (eluent: hexane) to obtain **3a** as white solid (66.4 mg, 72% yield). mp: 41-42 °C; IR (cast): 3080, 3024, 2917, 2848, 1463, cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.41-7.35 (m, 2H), 7.35-7.28 (m, 2H), 7.25-7.18 (m, 1H), 6.41 (d, $J = 15.8$ Hz, 1H), 6.26 (dt, $J = 15.8, 6.8$ Hz, 1H), 2.24 (dt, $J = 7.2, 7.2$ Hz, 2H), 1.56-1.45 (m, 2H), 1.40-1.20 (m, 30H), 0.99-0.87 (m, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 137.96, 131.19, 129.69, 128.43, 126.70, 125.89, 33.07, 31.95, 29.73, 29.66, 29.57, 29.42, 29.40, 29.27, 22.71, 14.13; HRMS: (CI, $[\text{M}]^+$) for $\text{C}_{26}\text{H}_{44}$ calcd. 356.3438, found: 356.3432



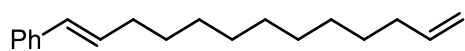
(E)-1-isopropyl-4-methyl-2-((4-phenylbut-3-en-1-yl)oxy)benzene (3b): Purified by column chromatography (eluent: hexane/ ethyl acetate = 30/1) to obtain **3b** as yellow oil (53.5 mg, 69% yield). IR (film): 3083, 3060, 3025, 2957, 2917, 2867, 1610, 1578, 1504, 1447 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.42-7.39 (m, 2H), 7.37-7.33 (m, 2H), 7.28-7.24 (m, 1H), 7.15 (d, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 7.6$ Hz, 1H), 6.74 (s, 1H), 6.59 (d, $J = 15.9$ Hz, 1H), 6.38 (dt, $J = 15.9, 6.9$ Hz, 1H), 4.13 (t, $J = 6.5$ Hz, 2H), 3.38 (m, 1H), 2.76 (dt, $J = 6.7, 6.7$ Hz, 2H), 2.38 (s, 3H), 1.26 (d, $J = 6.9$ Hz, 2H); ^{13}C NMR (100MHz, CDCl_3): δ 155.92, 137.49, 136.25, 134.14, 132.07, 128.49, 127.10, 126.58, 126.01, 125.89, 121.10, 112.30, 67.37, 33.17, 26.68, 22.72, 21.33; HRMS: (EI, $[\text{M}]^+$) for $\text{C}_{20}\text{H}_{24}\text{O}$ calcd. 280.1822, found: 280.1827



(E)-2-((4-Phenylbut-3-en-1-yl)oxy)naphthalene (3c): Purified by column chromatography (eluent: hexane/ethyl acetate = 30/1) to obtain **3c** as white solid (44.1 mg, 64% yield). mp: 99-100 °C; IR (cast): 3080, 3058, 3021, 2964, 2922, 2864, 1627, 1599, 1509, 1492, 1463 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.80-7.74 (m, 3H), 7.48-7.32 (m, 6H), 7.27-7.19 (m, 3H), 6.58 (d, $J = 15.9$ Hz, 1H), 6.37 (dt, $J = 15.9, 6.9$ Hz, 1H), 4.23 (t, $J = 6.7$ Hz, 2H), 2.79 (dt, $J = 6.7, 6.7$ Hz, 2H); ^{13}C NMR (100MHz, CDCl_3): δ 156.82, 137.35, 134.54, 132.24, 129.36, 128.95, 128.51, 127.62, 127.20, 126.70, 126.31, 126.08, 126.07, 123.56, 118.96, 106.71, 67.39, 32.91; HRMS: (EI, $[\text{M}]^+$) for $\text{C}_{20}\text{H}_{18}\text{O}$ calcd. 274.1352, found: 274.1349

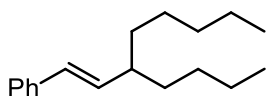


(E)-1-Bromo-2-((4-phenylbut-3-en-1-yl)oxy)benzene (3d): Purified by column chromatography (eluent: hexane/ethyl acetate = 30/1) to obtain **3d** as yellow oil (54.1 mg, 71% yield). IR (film): 3061, 3024, 2954, 2874, 2854, 1585, 1571, 1481, 1465 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.58-7.55 (m, 1H), 7.41-7.39 (m, 2H), 7.36-7.31 (m, 2H), 7.29-7.22 (m, 2H), 6.94-6.92 (m, 1H), 6.87-6.83 (m, 1H), 6.58 (d, $J = 15.9$ Hz, 1H), 6.42-6.34 (dt, $J = 15.9, 6.9$ Hz, 1H), 4.15 (t, $J = 6.6$ Hz, 2H), 2.77 (dt, $J = 6.7, 6.7$ Hz, 2H), ^{13}C NMR (100MHz, CDCl_3): δ 155.23, 137.35, 133.34, 132.45, 128.48, 128.38, 127.19, 126.08, 125.76, 121.89, 113.42, 112.37, 68.06, 32.78; HRMS: (EI, $[\text{M}]^+$) for $\text{C}_{16}\text{H}_{15}\text{BrO}$ calcd. 302.0302, found: 302.0301

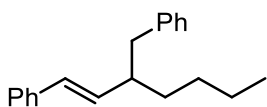


(E)-Trideca-1,12-dien-1-ylbenzene (3e): Purified by column chromatography (eluent: hexane) to obtain **3e** as colorless oil (29.1 mg, 43% yield). IR (film): 3077, 3024, 2923, 2852, 1639, 1458 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.36-7.34 (m, 2H), 7.31-7.26 (m, 2H), 7.20-7.17 (m, 1H), 6.39 (d, $J = 15.8$ Hz, 1H), 6.23 (dt, $J = 15.8, 6.9$ Hz, 1H), 5.82 (ddt, $J = 17.2, 10.1, 7.2$ Hz, 1H), 5.00 (d, $J = 17.2$ Hz, 1H), 4.94 (d, $J = 10.1$ Hz, 1H), 2.24-2.19 (m, 2H), 2.08-2.02 (m, 2H), 1.49-1.30 (m, 14H); ^{13}C NMR (100MHz, CDCl_3): δ 139.25,

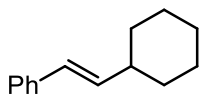
137.95, 131.24, 129.66, 128.44, 126.72, 125.88, 114.08, 33.81, 33.04, 29.54, 29.50, 29.48, 29.37, 29.21, 29.13, 28.93; HRMS: (CI, [M]⁺) for C₁₉H₂₈ calcd. 256.2191, found: 256.2183



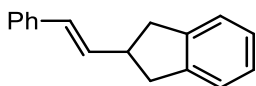
(E)-(3-Butyloct-1-en-1-yl)benzene (3f): Purified by column chromatography (eluent: hexane) to obtain **3f** as colorless oil (54.2 mg, 85% yield). IR (film): 3082, 3026, 2957, 2926, 2857, 1598, 1494 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.40-7.38 (m, 2H), 7.34-7.31 (m, 2H), 7.24-7.20 (m, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 5.99 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.16-2.11 (m, 1H), 1.48-1.45 (m, 2H), 1.39-1.26 (m, 12H), 0.95-0.87 (m, 6H); ¹³C NMR (100MHz, CDCl₃): δ 138.00, 135.92, 129.34, 128.43, 126.67, 125.94, 43.44, 35.51, 35.25, 32.06, 29.62, 27.05, 22.87, 22.65, 14.12, 14.10; HRMS: (CI, [M]⁺) for C₁₈H₂₈ calcd. 244.2191, found: 244.2180



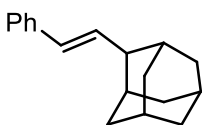
(E)-(3-Butylbut-1-ene-1,4-diyl)dibenzene (3g): This compound is previously known (Lv, L.; Zhu, D.; Qiu, Z.; Li, J.; Li, C. J. *ACS catal.* **2019**, *9*, 9199–9205). Purified by column chromatography (eluent: hexane) to obtain **3g** as yellow oil (46.1 mg, 66% yield). IR (film): 3059, 3024, 2954, 2924, 2854, 1600, 1493, 1453 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.24 (m, 6H), 7.20-7.15 (m, 4H), 6.24 (d, *J* = 15.8 Hz, 1H), 6.02 (dd, *J* = 15.8, 8.7 Hz, 1H), 2.75-2.69 (m, 2H), 2.49-2.40 (m, 1H), 1.53-1.50 (m, 1H), 1.37-1.25 (m, 5H), 0.86 (t, *J* = 6.0 Hz, 3H); ¹³C NMR (100MHz, CDCl₃): δ 140.56, 137.83, 134.75, 129.78, 129.32, 128.42, 128.06, 126.79, 125.99, 125.73, 45.00, 42.26, 34.26, 29.56, 22.76, 14.06; HRMS: (EI, [M]⁺) for C₂₀H₂₄ calcd. 264.1873, found: 264.1868



(E)-2-Cyclohexylvinylbenzene (3h): This compound is previously known (Hu, J.; Cheng, B.; Yang, X.; Loh, T. P. *Adv. Synth. Catal.* **2019**, *361*, 4902–4908). Purified by column chromatography (eluent: hexane) to obtain **3h** as colorless oil (31.5 mg, 68% yield). IR (film): 3082, 3026, 2924, 2851, 1600, 1495, 1448 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.40–7.38 (m, 2H), 7.34–7.30 (m, 2H), 7.24–7.20 (m, 1H), 6.39 (d, $J = 16.0$ Hz, 1H), 6.22 (dd, $J = 16.0, 6.9$ Hz, 1H), 2.21–2.14 (m, 1H), 1.87–1.71 (m, 4H), 1.41–1.21 (m, 6H); ^{13}C NMR (100MHz, CDCl_3): δ 138.03, 136.79, 128.41, 127.21, 126.69, 125.91, 41.14, 32.94, 26.16, 26.03; HRMS: (CI, $[\text{M}]^+$) for $\text{C}_{14}\text{H}_{18}$ calcd. 186.1409, found: 186.1401

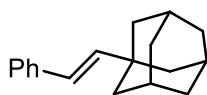


(E)-2-Styryl-2,3-dihydro-1H-indene (3i): This compound is previously known (Hu, J.; Cheng, B.; Yang, X.; Loh, T. P. *Adv. Synth. Catal.* **2019**, *361*, 4902–4908). Purified by column chromatography (eluent: hexane) to obtain **3i** as white solid (39.2 mg, 69% yield). mp: 46–47 $^{\circ}\text{C}$; IR (cast): 3078, 3064, 2931, 2899, 2834, 1431 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.44–7.41 (m, 2H), 7.37–7.33 (m, 2H), 7.30–7.26 (m, 3H), 7.24–7.20 (m, 2H), 6.54 (d, $J = 15.8$ Hz, 1H), 6.42 (dd, $J = 15.8, 7.7$ Hz, 1H), 3.38–3.28 (m, 1H), 3.20 (dd, $J = 15.4, 7.9$ Hz, 1H), 2.93 (dd, $J = 15.3, 8.2$ Hz, 2H); ^{13}C NMR (100MHz, CDCl_3): δ 142.96, 137.50, 134.04, 129.13, 128.49, 127.01, 126.26, 126.03, 124.35, 43.82, 39.59; HRMS: (CI, $[\text{M}]^+$) for $\text{C}_{17}\text{H}_{16}$ calcd. 220.1247, found: 220.1243

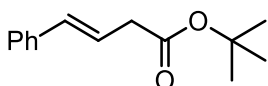


(1r,3r,5r,7r)-2-((E)-Styryl)adamantane (3j): Purified by column chromatography (eluent: hexane) to obtain **3j** as colorless oil (34.9 mg, 61% yield). IR (cast): 3083, 3023, 2900, 2847, 1647, 1599, 1495, 1448 cm^{-1} ; ^1H

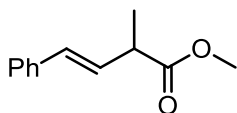
NMR (400 MHz, CDCl₃): δ 7.40-7.37 (m, 2H), 7.32-7.28 (m, 2H), 7.21-7.17 (m, 1H), 6.54 (dd, $J = 16.1, 6.4$ Hz, 1H), 6.43 (d, $J = 16.2$ Hz, 1H), 2.59 (d, $J = 5.5$ Hz, 1H), 2.04-1.77 (m, 12H), 1.61-1.57 (m, 2H); ¹³C NMR (100MHz, CDCl₃): δ 138.20, 135.07, 128.86, 128.46, 126.72, 125.92, 47.37, 38.73, 38.04, 33.06, 32.20, 28.07, 27.83; HRMS: (EI, [M]⁺) for C₁₈H₂₂ calcd. 238.1716, found: 238.1709



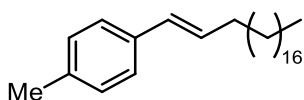
(3r,5r,7r)-1-((E)-Styryl)adamantane (3k): This compound is previously known (Sumino, S.; Uno, M.; Huang, H. J.; Wu, Y. K.; Ryu, I. *Org. Lett.* **2018**, *20*, 1078–1081). Purified by column chromatography (eluent: hexane) to obtain **3k** as white solid (45.3 mg, 75% yield). mp: 65-66 °C; IR (cast): 3021, 2953, 2914, 2848, 1490, 1464 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.41-7.39 (m, 2H), 7.34-7.30 (m, 2H), 7.23-7.19 (m, 1H), 6.29 (d, $J = 16.3$ Hz, 1H), 6.15 (d, $J = 16.2$ Hz, 1H), 2.10-2.04 (m, 3H), 1.85-1.71 (m, 12H); ¹³C NMR (100MHz, CDCl₃): δ 142.03, 138.17, 128.41, 126.65, 125.94, 124.49, 42.21, 36.87, 35.12, 28.46; HRMS: (CI, [M]⁺) for C₁₈H₂₂ calcd. 238.1716, found: 238.1710



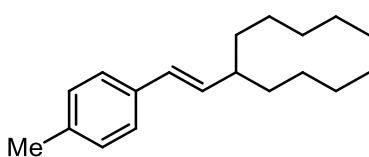
(E)-tert-Butyl 4-phenylbut-3-enoate (3l): This compound is previously known (Molander, G. A.; Barcellos, T.; Traister, K. M. *Org. Lett.* **2013**, *15*, 3342–3345). Purified by column chromatography (eluent: hexane/dichloromethane = 10/1 to 3/1) to obtain **3l** as colorless oil (32.2 mg, 57% yield). IR (film): 3083, 2978, 2927, 1732, 1600, 1449 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.37 (m, 2H), 7.33-7.26 (m, 2H), 7.24-7.21 (m, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 6.30 (dd, $J = 15.9, 7.1$ Hz, 1H), 3.16 (dd, $J = 7.1, 1.3$ Hz, 2H), 1.48 (s, 9H); ¹³C NMR (100MHz, CDCl₃): δ 170.91, 137.03, 132.93, 128.46, 127.36, 126.22, 122.46, 80.79, 39.64, 28.07; HRMS: (CI, [M]⁺) for C₁₄H₁₈O₂ calcd. 218.1301, found: 218.1292



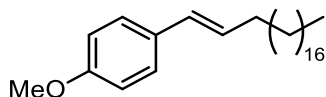
(E)-Methyl 2-methyl-4-phenylbut-3-enoate (3m): This compound is previously known (Cannes, C.; Condon, S.; Durandetti, M.; Perichon, J.; Nédélec, J. Y. *J.Org. Chem.* **2000**, *65*, 4575–4583). Purified by column chromatography (eluent: hexane/ dichloromethane = 10/1 to 3/1) to obtain **3m** as colorless oil (27.8 mg, 57% yield). IR (film): 3083, 3027, 2953, 2927, 1738, 1450 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 6.28 (dd, $J = 15.9, 8.0$ Hz, 1H), 3.71 (s, 3H), 3.37-3.29 (m, 1H), 1.37 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 174.94, 136.80, 131.13, 128.65, 128.50, 127.50, 126.27, 51.93, 43.11, 17.38; HRMS: (CI, $[\text{M}]^+$) for $\text{C}_{12}\text{H}_{14}\text{O}_2$ calcd. 190.0988, found: 190.0986



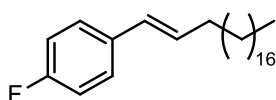
(E)-1-(Icos-1-en-1-yl)-4-methylbenzene (3n): Purified by column chromatography (eluent: hexane/ ethyl acetate = 30/1) to obtain **3n** as white solid (60.6mg, 66% yield; 231.9mg, 62% for 1 mmol scale). mp: 45-46 $^{\circ}\text{C}$; IR (cast): 3024, 2953, 2915, 2847, 1511, 1470 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.25 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 7.7$ Hz, 2H), 6.35 (d, $J = 15.8$ Hz, 1H), 6.18 (dt, $J = 15.8, 6.8$ Hz, 1H), 2.33 (s, 3H), 2.20 (dt, $J = 7.2, 7.2$ Hz, 2H), 1.48-1.44 (m, 2H), 1.36-1.23 (m, 30H), 0.90 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 136.38, 135.18, 130.22, 129.46, 129.13, 125.77, 33.03, 31.93, 29.70, 29.67, 29.62, 29.54, 29.45, 29.36, 29.23, 22.69, 21.11, 14.11; HRMS: (CI, $[\text{M}]^+$) for $\text{C}_{27}\text{H}_{46}$ calcd. 370.3594, found: 370.3592



(E)-1-(3-Butyloct-1-en-1-yl)-4-methylbenzene (3o): Purified by column chromatography (eluent: hexane) to obtain **3o** as colorless oil (30.6mg, 48% yield). IR (cast): 3049, 3018, 2954, 2922, 2855, 1890, 1611, 1513, 1456 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.29 (d, $J = 7.8$ Hz, 2H), 7.13 (d, $J = 7.8$ Hz, 2H), 6.32 (d, $J = 15.8$ Hz, 1H), 5.93 (dd, $J = 15.8, 8.9$ Hz, 1H), 2.36 (s, 3H), 2.11 (m, 1H), 1.50-1.26 (m, 14H), 0.92 (m, 6H); ^{13}C NMR (100MHz, CDCl_3): δ 136.34, 135.23, 134.91, 129.14, 129.12, 125.83, 43.42, 35.56, 35.30, 32.07, 29.62, 27.05, 22.87, 22.66, 21.09, 14.12; HRMS: (EI, $[\text{M}]^+$) for $\text{C}_{19}\text{H}_{30}$ calcd. 258.2342, found: 258.2345

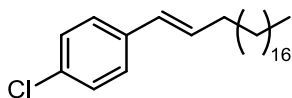


(E)-1-(Icos-1-en-1-yl)-4-methoxybenzene (3p): Purified by column chromatography (eluent: hexane) to obtain **3p** as white solid (50.3mg, 52% yield). mp: 61-62 $^{\circ}\text{C}$; IR (cast): 3007, 2953, 2914, 2847, 1723, 1607, 1577, 1512, 1466 cm^{-1} ; ^1H NMR (400 MHz, C_6D_6): δ 7.25 (d, $J = 8.5$ Hz, 2H), 6.78 (d, $J = 8.6$ Hz, 2H), 6.39 (d, $J = 15.8$ Hz, 1H), 6.08 (dt, $J = 15.8, 6.9$ Hz, 1H), 3.28 (s, 3H), 2.13 (dt, $J = 7.0, 7.0$ Hz, 2H), 1.49-1.26 (m, 32H), 0.92 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 158.58, 130.82, 129.08, 128.98, 126.93, 113.87, 55.23, 33.03, 31.93, 29.71, 29.70, 29.66, 29.55, 29.37, 29.25, 22.69, 14.11; HRMS: (CI, $[\text{M}]^+$) for $\text{C}_{27}\text{H}_{46}\text{O}$ calcd. 386.3543, found: 386.3542

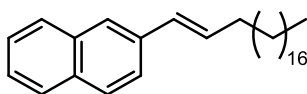


(E)-1-Fluoro-4-(icos-1-en-1-yl)benzene (3q): Purified by column chromatography (eluent: hexane) to obtain **3q** as white solid (44.0 mg, 47% yield). mp: 49-50 $^{\circ}\text{C}$; IR (cast): 3012, 2956, 2915, 1890, 1602, 1510 1462 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.31-7.28 (m, 2H). 7.00-6.95 (m, 2H), 6.33 (d, $J = 15.8$ Hz, 1H), 6.14 (dt, $J = 15.8, 6.8$ Hz, 1H), 2.22-2.17 (dt, $J = 6.8, 6.8$ Hz, 2H), 1.48-1.43 (m, 2H), 1.35-1.24 (m, 30H), 0.89 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 161.83 (d, $J = 244.2$ Hz), 134.09 (d, $J = 3.4$ Hz), 130.96 (d, $J = 2.3$ Hz), 128.49, 127.25 (d, $J = 7.8$ Hz), 115.25 (d, $J = 21.3$ Hz), 32.99, 31.94, 29.71, 29.68,

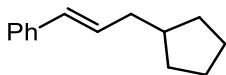
29.63, 29.53, 29.38, 29.25, 22.70; ^{13}F NMR (375MHz, CDCl_3): δ -116.98 (dd, $J = 8.0, 5.8$ Hz); HRMS: (EI, $[\text{M}]^+$) for $\text{C}_{26}\text{H}_{43}\text{F}$ calcd. 374.3343, found 374.3350



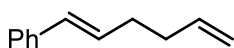
(E)-1-Chloro-4-(icos-1-en-1-yl)benzene (3r): Purified by column chromatography (eluent: hexane) to obtain **3r** as white solid (53.5 mg, 54% yield). mp: 50-51 °C; IR (cast): 3013, 2960, 2915, 2847, 1646, 1490, 1464 cm^{-1} ; ^1H NMR (400 MHz, C_6D_6): δ 7.10 (d, $J = 6.6, 1.8$ Hz, 1H), 6.50 (d, $J = 6.8, 1.7$ Hz, 1H), 6.18 (d, $J = 15.8$ Hz, 1H), 5.99 (dt, $J = 15.8, 6.8$ Hz, 1H), 2.07 (dt, $J = 6.8, 6.8$ Hz, 1H), 1.39-1.32 (m, 32H), 0.92 (t, $J = 6.8$ Hz, 1H); ^{13}C NMR (100MHz, CDCl_3): δ 136.42, 132.21, 132.00, 128.55, 128.47, 127.07, 33.02, 31.92, 29.70, 29.66, 29.60, 29.51, 29.36, 29.27, 29.23, 22.69, 14.13; HRMS: (EI, $[\text{M}]^+$) for $\text{C}_{26}\text{H}_{43}\text{Cl}$ calcd. 390.3048, found: 390.3052



(E)-2-(Icos-1-en-1-yl)naphthalene (3s): Purified by column chromatography (eluent: hexane) to obtain **3s** as white solid (37.4 mg, 37%). mp: 67-68 °C; IR (cast): 3052, 2955, 2915, 2847, 1602, 1509, 1470 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.79-7.75 (m, 3H), 7.67 (s, 1H), 7.59-7.57 (dd, $J = 8.6, 1.4$ Hz, 1H), 7.46-7.38 (m, 2H), 6.54 (d, $J = 15.8$ Hz, 1H), 6.36 (dt, $J = 15.8, 6.8$ Hz, 1H), 2.26 (dt, $J = 7.1, 7.0$ Hz, 2H), 1.53-1.47 (m, 2H), 1.39-1.24 (m, 30H), 0.89 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 135.42, 133.72, 132.62, 131.78, 129.79, 128.00, 127.79, 127.60, 126.07, 125.37, 125.25, 123.58, 33.19, 31.92, 29.70, 29.66, 29.63, 29.55, 29.42, 29.36, 29.28, 22.69, 14.12; HRMS: (EI, $[\text{M}]^+$) for $\text{C}_{30}\text{H}_{46}$ calcd. 406.3594, found: 406.3590



(E)-(3-Cyclopentylprop-1-en-1-yl)benzene (3t): This compound is previously known (Chen, L.; Hisaeda, Y.; Shimakoshi, H. *Adv. Synth. Catal.* **2019**, *361*, 2877–2884). Purified by column chromatography (eluent: hexane) to obtain **3t** as colorless oil (29.7 mg, 63% yield). IR (film): 3026, 2945, 2863, 1652, 1602, 1495, 1448 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.37-7.35 (m, 2H), 7.32-7.28 (m, 2H), 7.22-7.18 (m, 1H), 6.39 (d, $J = 15.9$ Hz, 1H), 6.25 (dt, $J = 15.8, 7.0$ Hz, 1H), 2.23 (t, $J = 7.0$ Hz, 2H), 2.00-1.91 (m, 1H), 1.83-1.75 (m, 2H), 1.66-1.52 (m, 4H), 1.26-1.19 (m, 2H); ^{13}C NMR (100MHz, CDCl_3): δ 137.98, 130.53, 130.11, 128.44, 126.71, 125.91, 40.00, 39.42, 32.31, 25.16; HRMS: (CI, $[\text{M}]^+$) for $\text{C}_{14}\text{H}_{18}$ calcd. 186.1403, found: 186.1404



(E)-Hexa-1,5-dien-1-ylbenzene (3u): This compound is previously known (Li, M. B.; Wang, Y.; Tian, S. K. *Angew. Chem., Int. Ed.*, **2012**, *51*, 2968–2971). Purified by column chromatography (eluent: hexane) to obtain **3u** as colorless oil (20.2 mg, 51% yield). IR (film): 3063, 2956, 2922, 2852, 1641, 1460, 1376 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.23-7.20 (m, 1H), 6.43 (d, $J = 15.8$ Hz, 1H), 6.25 (dt, $J = 15.8, 6.7$ Hz, 1H), 6.89 (ddt, $J = 16.9, 10.3, 6.4$ Hz, 1H), 5.11-5.01 (m, 2H), 2.37-2.32 (m, 2H), 2.30 (m, 2H); ^{13}C NMR (100MHz, CDCl_3): δ 138.08, 137.74, 130.18, 130.09, 128.45, 126.86, 125.94, 114.90, 33.53, 32.40; HRMS: (CI, $[\text{M}]^+$) for $\text{C}_{12}\text{H}_{14}$ calcd. 158.1090, found: 158.1087

NMR Charts (¹H, ¹³C, and ¹⁹F)

