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Selective alkylation and Suzuki coupling as an efficient strategy for introducing functional anchors to the ethylene-bis(indenyl) ligand

Anthony P. Panarello, Oleksiy Vassylyev and Johannes G. Khinast*

Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, 98, Brett Road, Piscataway, NJ 08854, USA

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Abstract—Chiral *ansa*-ethylene-bis(indenyl)-metal complexes, EBI–MX_2, are useful pre-catalysts for a wide variety of reactions, including hydrogenations, hydrosilylations, and polymerization reactions. In order to immobilize these complexes onto heterogeneous supports, a new methodology was developed to introduce functional anchors to the ethylene-bis(indenyl) ligand, EBI. This was accomplished by selective alkylation of indene to form toluene-4-sulfonic acid 2-(3*H*-inden-1-yl)-ethyl ester, which was then used to alkylate 6-bromoindene. The selective introduction of an aryl bromide then undergoes coupling reactions with aryl borates via the Suzuki coupling to efficiently introduce an alkenyl or alcohol, functional anchor in a simple four step synthesis.

Chiral *ansa*-ethylene-bis(tetrahydroindenyl)–metal complexes (EBTHI–MX_2), first introduced by Brintzinger and co-workers,[1] are highly active catalysts for enantioselective reactions, including reductions of olefins, ketones, and imines, as well as various polymerization reactions.[2] Since these organometallic complexes are homogeneous, they are less attractive for industrial use than heterogeneous catalysts. Thus, the focus of this work is to develop a strategy for immobilizing EBTHI–MX_2 catalysts onto heterogeneous supports.

We recently reported the preparation of an EBTHI ligand containing a carbon tether from the cyclohexane backbone[3] and now expand this concept to the more stable ethylene-bis(indenyl) ligand, EBI. The synthetic pathway presented herein describes the first successful approach for introducing functional anchors into the EBI ligand and offers a methodology for incorporating a diverse range of functional anchors.

As shown in Scheme 1, our initial approach was the coupling of 5-bromo-indanone, **1**, with 4-(hydroxymethyl)phenylboronic acid, **2**, to form 5-(4′-hydroxymethyl-phenyl)-indan-1-one, **3**, in 98% yield, using heterogeneous Pd/C as the catalyst and a isopropyl–water solvent mixture.[4] Reduction of indanone, **3**, to the indenyl derivative, **4**, was accomplished using standard reduction chemistry[5]. The terminal alcohol was then protected with either the TIPS, (triisopropylsilane) **5**, or MOM, (methoxymethyl ether) **6** protecting group.[6] Reversing the coupling and reduction sequences had little impact on the reaction yields as shown for the preparation of 6-(4′-vinylphenyl)-1*H*-indene and 6-[4′-(hydroxymethyl)phenyl]-1*H*-indene, **9** and **4**, respectively. However, indanone reduction of **1** to form bromoindene, yielded not only the desired 6-bromoindene, **7**, but also small amounts of its 5-isomers, **8**.[7] Interestingly, none of the indene derivatives, **4**, **5**, **6**, or **9** were successfully alkylated upon addition to toluene-4-sulfonic acid 2-(3*H*-inden-1′-yl)-ethyl ester, **11**, 3-(2′-bromoethyl)-1*H*-indene, **12**, or 3-(2′-chloroethyl)-1*H*-indene, **13**, even after numerous modifications of the alkylation procedure.[8] However, alkylation of **7** with either, **11**, **12**, or **13** did afford 6-bromo-3-[2′-(3*H*-inden-1″-yl)-ethyl]-1*H*-indene, **14**, in moderate yields (59%), with **11** offering the best results and easiest separation.[9] In addition, compared to the indenyllithium,

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* Corresponding author. Tel.: +1 732 455 2973; fax: +1 732 445 2581; e-mail: khinast@soemail.rutgers.edu

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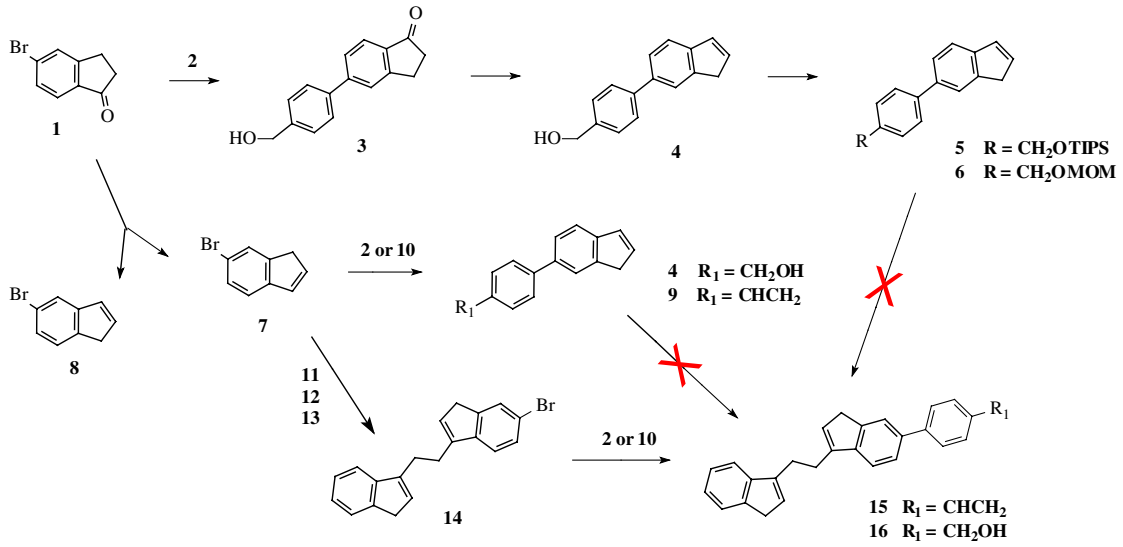


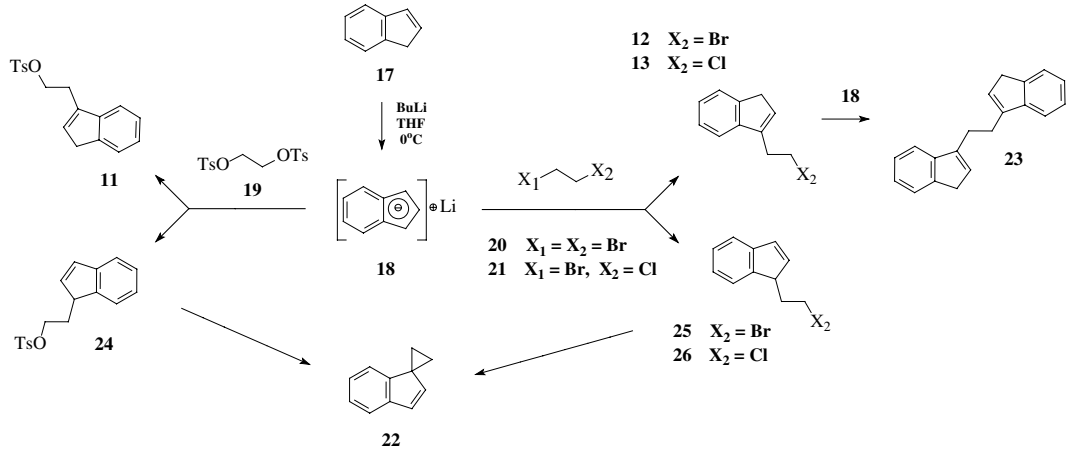
Scheme 1. Synthetic pathway of functionalized ethylene-bis(indenyl) ligands.

lithiated **7** was found to be extremely sensitive to moisture contamination.

Next, coupling **14** with different aryl borates, **2** and **10**, was found to be highly dependent on the reaction conditions and the catalyst. Poor solubility of **14** in an aqueous solvent system limited the applicability of the heterogeneous Pd/C catalyst and did not afford the desired coupling product. Use of palladium acetate, the ligandless Suzuki coupling catalyst, was also unsuccessful.[10] However, the tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] catalyst afforded favorable yields (40–70%) for the preparation of the 1-[2′-(3*H*-inden-1″-yl)ethyl]-5-(4‴-vinylphenyl)-3*H*-indene (**15**) and 1-[2′-(3*H*-inden-1″-yl)ethyl]-5-[4‴-(hydroxymethyl) phenyl]-3*H*-indene (**16**), EBI-derivatives.[11] While a THF/MeOH solvent mixture led to a successful coupling, when the solvent was replaced with toluene, a common coupling solvent, the reaction did not afford the desired product. Both EBI-derivatives, **15** and **16**, represent different functional anchors suitable for immobilizing organic molecules onto heterogeneous supports.

The investigation of a selectively mono-alkylated indene intermediate was a critical prerequisite for our synthetic efforts toward introducing a functional anchor to the EBI ligand. An overview of the alkylation reactions are shown in Scheme 2.[12] Indene, **17**, was first lithiated using published procedures[13], followed by addition to 1,2-di-nucleophilic-ethane, (ethylene glycol di-tosylate, **19**, 1,2-dibromoethane, **20**, or 1-chloro-2-bromoethane, **21**). Small variations in the reaction conditions lead to significant variations in product distributions. Regardless of the starting material, in addition to the desired mono-alkylated product, observed by-products included the spiro-product, **22**, as well as double alkylation product, EBI, **23**.

Alkylation results were most favorable when the indenyllithium, **18**, was slowly added to the nucleophile. Reversing the addition sequence resulted in significantly lower yields of the mono-alkylated products and higher yields of undesired side products **22** and **23**. Addition of **18** to **19** afforded two isolated products: **11**, (45%) and **22** (30%). This sequence of addition eliminated the for-



Scheme 2. Selective mono-alkylation of indene.

mation of **23** as well as the less stable isomer, **24** which is believed to rapidly convert into the spiro-alkylation product, **22**.

Addition of indenyllithium, **18**, to either **20** or **21** afforded predominately two mono-alkylation isomers, **12** and **13** (70/80%) and **25** and **26** (30/20%) and less than 1% of **23**. Mono-alkylation isomers were easily identified by ^{1}H NMR. Although **13** and **26** were readily separated using flash chromatography, **12** and **25** were unable to be separated. At this time, the mechanism that results in the formation of isomers remains unclear, however, when a catalytic (Cp_2ZrCl_2 as the catalyst) pathway was employed a single isomer, **26**, was observed (20%).[14] When greater than 10 M equiv of the alkylating agent was used, **23** was no longer observed, and decreasing the addition rate minimized the formation of **22**. Lastly, **12** and **13**, were found to be much less stable then **11**, even when stored at low temperature.

Yields and properties of all obtained compounds are presented in Table 1.

In conclusion, the four-step synthetic methodology described above offers a favorable and convenient strategy for introducing functional anchors into the EBI ligand. The use of Suzuki coupling further expands the scope of this pathway, due to the broad reactivity of aryl bromides with alkenylborates. Ligand development represents the first step in the engineering of heterogeneous catalysts. The next step is the introduction of an active metal species (Ti or Zr) to the functionalized EBI ligand, followed by immobilization of the active catalytic complex onto a heterogeneous support. Using terminal alkenes, immobilization can be accomplished by hydrosilylation reactions with silica or silica-containing materials having surface Si–H groups. Furthermore, hydroxyl-terminated complexes can be anchored using an esterification reaction procedure. In both cases, it is necessary to pre-treat the various heterogeneous surfaces (i.e., silica or alumina) before immobilizing the complexes.

Table 1. Indene derivatives[15]

#	Product	Eluent (R_f)	Yield, %
3	Yellow crystals[16]	—	98
4	Yellowish solid	Hexane/EE, 1:2 (0.25)	90 (from **3**) 95 (from **7**)
5	Light yellow oil	Hexane (0.3)	93
6	Yellow oil	Hexane/EE, 5:2 (0.5)	82
7	Yellowish oil[7]	Hexane/EE, 100:1 (0.6)	90
9	White solid	Hexane/EE, 50:1 (0.35)	80
11	Dark reddish oil	Hexane/EE, 5:2 (0.35)	45
12	Colorless oil	Hexane (0.65)	75
13	Light yellow oil	Hexane (0.6)	80
14	Light yellow oil	Hexane/EE, 100:1 (0.25)	59
15	Yellow crystals	Hexane/EE, 50:1 (0.35)	71
16	Orange-yellow oil	Hexane/EE, 5:2 (0.55)	78
22	Yellowish oil[17]	Hexane/EE, 100:1 (0.4)	Variable
23	Yellowish oil[13]	Hexane/EE, 50:1 (0.3)	Variable
25	Yellowish oil	Hexane/EE, 50:1 (0.35)	Variable
26	Colorless oil	Hexane/EE, 50:1 (0.35)	Variable

Acknowledgements

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4. The Suzuki coupling was carried using slightly modified procedure from Marck, G.; Villiger, A.; Buchecker, R. *Tetrahedron Lett.* **1994**, *35*, 3277–3280, **1** or **7** (5.62 mmol, 1 M equiv), aryl boronic acid (6.58 mmol, 1.3 M equiv) were charged to a 100 mL reaction flask containing 50 mL of an isopropyl alcohol (10% v/v) and water reaction solvent. Na_2CO_3 (2.25 M equiv) and Pd/C catalyst (5 mol %, Degussa E1002 XU/W, 5 wt%, dry basis, on 50% wet activated carbon) were then added to the reaction flask. The reaction was then placed in a 75 °C oil bath and monitored by either HPLC or TLC, where the aryl bromide was completely consumed in less than 1 h. After allowing the reaction to cool to room temperature, the reaction was diluted by adding additional (50 mL) reaction solvent followed by filtering off the Pd/C catalyst.
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12. General procedure of indene alkylation. Under argon, indene and dry THF (20 M equiv) were charged to an oven dried reaction flask and placed in an ice bath. BuLi (1.6 M, 1 M equiv) was dropwise added yielding a deep red solution. The reaction mixture was then allowed to slowly warm up to room temperature over 1 h. A second flask was purged with argon and charged with the appropriate alkylating agent (1.05 M equiv) and THF (40 M equiv). The indenyllithium solution was then dropwise added to the alkylating agent at room temperature using a syringe pump (15 mL/h). A syringe pump allowed for better control of the addition rate, which proved critical for the selective alkylation reactions. The reaction was then allowed to stand over night at room temperature and quenched the following morning using an saturated aqueous NH_4Cl solution. CH_2Cl_2 was added and a liquid–liquid extraction was performed. The organic phase was then collected and dried with $MgSO_4$. The solvent was removed under reduced pressure, and obtained oil was purified by Flash Column Chromatography with elution by hexane or its mixture with ethyl ether (EE).
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15. Analytical data. 5-(4′-Hydroxymethyl-phenyl)-indan-1-one (**3**). Mp (°C): 156 (THF). ^{1}H NMR (δ, $CDCl_3$): 7.9 (d, H), 7.7–7.55 (m, 4H), 7.45 (d, 2H), 4.75 (s, 2H), 3.2 (t, 2H), 2.78 (t, 2H), 1.75 (br s, 1H). ^{13}C NMR (δ, $CDCl_3$): 155.9, 147.3, 141.1, 139.5, 136, 127.7, 127.5, 126.7, 125.1, 124.1, 64.9, 36.5, 25.9. MS (APPI, *m*/*z*): 261 (M^++Na^+). IR (ν_{max}, cm^{-1}, NaBr): 3380 (OH), 2925–2825, 1682 (C=O), 1608, 1440, 1405, 1300, 1199, 1111, 1058, 799, 636. 6-[4′-(Hydroxymethyl)phenyl]-1*H*-indene (**4**). ^{1}H NMR (δ, $CDCl_3$): 7.73 (s, 1H), 7.65 (d, 2H), 7.55–7.45 (m, 4H), 6.95 (d, 1H), 6.6 (d, 1H), 4.75 (d, 2H), 3.49 (s, 2H), 1.65 (t, 1H). ^{13}C NMR (δ, $CDCl_3$): 144.5, 144.2, 141.2, 139.4, 137.4, 134.7, 131.8, 127.5, 127.3, 125.5, 122.6, 121.1, 65.2, 39.2. MS (*m*/*z*): 108 ($BzOH^+$), 116 (Ind^+). IR (ν_{max}, cm^{-1}, NaBr): 3335–3240 (OH), 2920–2860, 1613, 1465, 1405, 1120, 1050 (–OH), 1010, 806 (C=C), 682. 6-{4′-[(Triisopropylsiloxy)methyl]phenyl}-1*H*-indene (**5**). ^{1}H NMR (δ, $CDCl_3$): 7.75 (s, 1H), 7.63 (d, 2H), 7.57 (d, 1H), 7.5–7.4 (d(s), 3H), 6.95 (d, 1H), 6.6 (d, 1H), 4.95 (s, 2H), 3.49 (s, 2H), 1.15 (d, 3H), 1.05 (br s, 18H). ^{13}C NMR (δ, $CDCl_3$): 144.5, 144.2, 140.6, 140.5, 138, 134.7, 132, 127.2, 125.6, 122.8, 121.3, 65.1, 39.4, 18.3, 17.9, 12.3. MS (APPI, *m*/*z*): 237, 379 (M^+). 6-{4′-[(Methoxymethoxy)methyl]phenyl}-1*H*-indene (**6**). ^{1}H NMR (δ, $CDCl_3$): 7.7 (s, 1H), 7.6 (d, 2H), 7.55–7.42 (m, 4H), 6.95 (dt, 1H), 6.6 (dt, 1H), 4.75 (s, 2H), 4.65 (s, 2H), 3.55 (s, 3H), 3.45 (s 2H). ^{13}C NMR (δ, $CDCl_3$): 144.4, 144.2, 141.3, 137.5, 136.4, 134.7, 131.7, 128.4, 127.2, 125.5, 122.6, 121.1, 95.7, 69, 55.4, 39.2. IR (ν_{max}, cm^{-1}, NaBr): 2960–30, 2865, 1761, 1644, 1598, 1467, 1368, 1291, 1181, 1089 (MOMO), 1046, 958, 813 (C=C), 767, 661. 6-(4′-Vinylphenyl)-1*H*-indene (**9**). ^{1}H NMR (δ, $CDCl_3$): 7.73–7.65 (d, 1H), 7.6 (d, 2H), 7.6–7.55 (m, 1H), 7.5 (d, 2H), 7.48–7.45 (m, 2H), 6.95 (t, 1H), 6.83–6.73 (q, 1H), 6.62 (t, 1H), 5.85–5.75 (d, 1H), 5.3–5.28 (d, 1H), 4.0–3.95 (d, 2H). ^{13}C NMR (δ, $CDCl_3$): 145.6, 144.4, 144.2, 142.9, 141.3, 141.2, 139.2, 137.3, 136.5, 136.4, 136.3, 136.2, 134.9, 134.7, 132.1, 131.8, 127.4, 127.3, 127, 126.9, 126.7, 126.6, 125.3, 123.9, 123.7, 122.4, 121.1, 119.6, 113.9, 113.7, 113.6, 39.2, 38.8. IR (ν_{max}, cm^{-1}, NaBr): 3430, 2924, 1699, 1605, 1398, 1073, 908, 818 (C=C), 733, 698, 623–510 (*ter*-C=C). Toluene-4-sulfonic acid 2-(3*H*-inden-1′-yl)-ethyl ester (**11**).^{1}H NMR (δ, $CDCl_3$): 7.83 (d, 1H), 7.73 (d, 2H), 7.45–7.35 (dd, 2H), 7.28 (d, 2H), 7.23 (d, 1H), 6.25 (s, 1H), 4.33 (t, 2H), 3.29 (s, 2H), 2.95 (t, 2H), 2.45 (s, 3H). ^{13}C NMR (δ, $CDCl_3$): 144.7, 144.3, 144.1, 138.7, 130.5, 129.8, 127.8, 126.2, 124.9, 123.9, 118.6, 68.7, 37.9, 37.9, 27.5, 21.7. MS (*m*/*z*): 337 (M^++Na^+). IR (ν_{max}, cm^{-1}, NaBr): 3065–20 (m), 2959–2856 (m), 1709, 1598, 1461, 1359 (S=O), 1176 (S–Ph), 1096, 980–960, 904, 771, 662. 3-(2′-Bromoethyl)-1*H*-indene (**12**). ^{1}H NMR (δ, $CDCl_3$): 7.5–7.2 (m, 4H), 6.38 (s, 1H), 3.72 (t, 2H), 3.39 (s, 2H), 3.18 (t, 2H). ^{13}C NMR (δ, $CDCl_3$): 144.3, 144.2, 137.5, 129.9, 124.9, 124, 122.9, 118, 34.7, 31.5, 30.6. 3-(2′-Chloroethyl)-1*H*-indene (**13**). ^{1}H NMR (δ, $CDCl_3$): 7.45 (d, 1H), 7.4–7.3 (m, 2H), 7.2–7.25 (t, 1H), 6.35 (s, 1H), 3.73 (t, 2H), 3.39 (s, 2H), 3.05 (t, 2H). ^{13}C NMR (δ, $CDCl_3$): 144.6, 140.4, 130, 126.2, 124.9, 123.9, 118.6, 42.7, 37.9, 31.3. 6-Bromo-3-[2′-(3*H*-inden-1″-yl)-ethyl]-1*H*-indene (**14**). ^{1}H NMR (δ, $CDCl_3$): 7.45 (d, 1H), 7.4 (d, 2H), 7.35 (s, 2H), 7.25 (d, 2H), 6.29 (s, 2H), 3.35 (s, 4H), 2.95 (s, 4H). ^{13}C NMR (δ, $CDCl_3$) 147.7, 146.6, 145.3, 144.5, 143.9, 143.7, 143.6, 143.2, 129.7, 129.1, 128.4, 128.1, 127.3, 127.1, 126.1, 125.1, 124.7, 123.9, 122.2, 120.3, 120.1, 118.9, 118.8, 37.8, 37.7, 37.5, 26.2, 26.1. IR (ν_{max}, cm^{-1}, NaBr): 3063, 2902, 1599, 1563, 1459, 1396, 1273, 1245, 1230, 1202, 1168, 1121, 1059, 1014, 967, 917, 863 (C=C), 809 (C=C), 773 (C=C), 719 (C=C). Elemental analysis (%): $C_{20}H_{17}Br$, C: 71.2 (calcd), 69.32 (found), H: 5.08 (calcd), 5.07 (found). 1-[2′-(3*H*-Inden-1″-yl)ethyl]-5-(4‴-vinylphenyl)-3*H*-indene (**15**). Mp (°C): 104 (hexane). ^{1}H NMR (δ, $CDCl_3$): 7.75 (s, 1H), 7.6 (d, 2H), 7.59 (d, 1H), 7.5 (dd, 4H), 7.45 (t, 1H), 7.35 (t, 1H), 7.25 (t, 1H), 6.85–6.75 (q, 1H), 6.35 (d, 2H), 5.85–5.78 (d, 1H), 5.32–5.25 (d, 1H), 3.45–3.39 (d, 4H), 2.9 (s, 4H). ^{13}C NMR (δ, $CDCl_3$): 197.9, 145.3, 144.8, 144.5, 144.1, 144, 137.3, 136.5, 136.2, 128.5, 128, 127.4, 127.2, 126.6, 126, 125.1, 124.6, 123.8, 122.5, 119.1, 118.9, 113.6, 37.9, 37.8, 26.3 IR (ν_{max}, cm^{-1}, NaBr): 3049, 2920, 1715, 1603 (C=C), 1460, 1396, 1265, 1167, 1060, 914, 821, 770, 736. 1-[2′-(3*H*-Inden-1″-yl)ethyl]-5-[4‴-(hydroxymethyl) phenyl]-3*H*-indene (**16**). ^{1}H NMR (δ, $CDCl_3$): 7.79–7.72 (m, 1H), 7.7–7.65 (m-t, 3H), 7.55–7.45 (m, 5H), 7.35 (d, 1H), 7.25 (d, 1H), 6.3 (br s, 2H), 4.75 (s, 2H), 3.45–3.75 (dd, 4H), 3.0 (d, 4H), 2.2(br s, 1H). ^{13}C NMR (δ, $CDCl_3$): 146.2, 145.2, 144.5, 144.1, 144, 143.7, 141.3, 139.5, 139.1, 129.9, 128.7, 128.5, 128.1, 128, 127.5, 127.4, 127.3, 126, 125.2, 124.6, 124, 123.8, 123.8, 122.6, 119.1, 118.9, 117.6, 66.7, 37.9, 37.8, 26.3, 26.2. IR (ν_{max}, cm^{-1}, NaBr): 3427 (OH), 2924, 2854, 1699, 1604, 1580, 1541, 1470, 1362, 1176, 1045 (OH), 1013 (OH), 919, 816 (C=C), 769 (C=C), 664, 554. 1-(2′-Bromoethyl)-1*H*-indene (**25**). ^{1}H NMR (δ, $CDCl_3$): 7.55–7.25 (m, 4H), 6.93 (d, 1H), 6.6 (d, 1H), 3.78 (t, 1H), 3.45 (t, 2H), 2.52–2.4 (m, 1H), 2.25–2.1 (m, 1H). ^{13}C NMR (δ, $CDCl_3$): 146.3, 141.3, 131.9, 129.9, 126.9, 126.2, 125.1, 121.3, 49.6, 37.9, 31.6. 1-(2′-Chloroethyl)-1*H*-indene (**26**). ^{1}H NMR (δ, $CDCl_3$): δ 7.45 (d, 1H), 7.4 (d, 1H), 7.35–7.2 (m, 2H), 6.85 (d, 1H), 6.55 (d, 1H), 3.7 (t, 1H), 3.6 (t, 2H), 2.4–2.27 (m, 1H), 2.15–2.0 (m, 1H).
16. Compound **3** was purified by the addition of THF to the reaction mixture followed by a liquid–liquid extraction where the organic phase was collected, dried with $MgSO_4$, and concentrated.
17. The isolated product confirms to previously published results: Kauffman, T.; Berghus, K.; Rensing, A. *Chem. Ber.* **1985**, *118*, 3737–3747.