Supporting Information

NaOH-Catalyzed Dimerization of Monofunctionalized Hydrofullerenes: Transition-metal-free, General and Efficient Synthesis of Single-bonded [60]Fullerene Dimers

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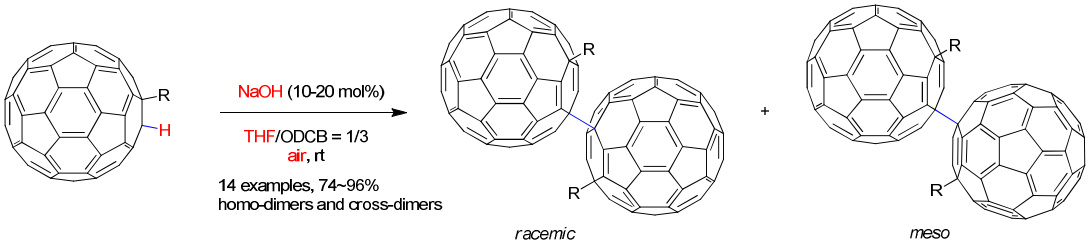

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General Information. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JMTC-270/54/SS (JASTEC, 400 MHz) spectrometers. ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer. Preparative recycling HPLC was used a LC-2000 Plus instrument equipped with a Buckyprep column (4.6 mm x 250 mm, nacalai tesque). HPLC analysis performed using toluene as an elution at 0.6 ml/min flow rate, detection at 320 nm in 12 ^{o}C. Column chromatography was carried out employing Silica gel 60 N (spherical, neutral, 40~100 μm, KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F_{254} (Merck).

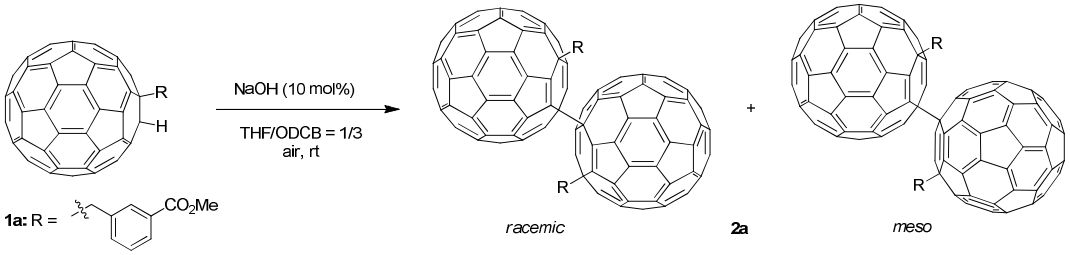
Materials. Anhydrous 1,2-dichlorobenzene (Aldrich), toluene, carbon disulfide, hexane, tetrahydrofuran, dimethylforamide, acetonitrile (WAKO), chloroform and base catalysts were purchased and used as received. Mono-functionalized hydrofullerenes **1** were prepared following the reported literatures.[1,2] The structures of new compounds **1d** and **2d** were determined by using ^{1}H NMR, ^{13}C NMR and high-resolution mass spectra (HMRS). The structures of reported products were determined by ^{1}H NMR which were consistent with our previously reported analytic data.[3]

(1) Lu, S.; Jin, T.; Bao, M.; Yamamoto, Y. *J. Am. Chem. Soc*. **2011**, *133*, 12842-12848.

(2) Matsuo, Y.; Iwashita, A.; Abe, Y.; Li, C.-Z.; Matsuo, K.; Hashiguchi, M.; Nakamura, E. *J. Am. Chem. Soc*. **2008**, *130*, 15429-15436.

(3) Lu, S.; Jin, T.; Kwon, E.; Bao, M.; Yamamoto, Y. *Angew. Chem. Int. Ed*. **2012**, *51*, 802-806.

Representative procedure for the synthesis of the homo-dimer 2a.



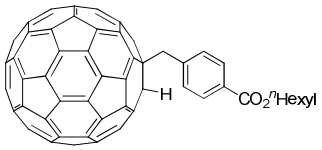
To a solution of hydrofullerene **1a** (26.2 mg, 0.03 mmol) in THF and 1,2-dichlorobenzene (1:3, 4 mL) was added an as-prepared NaOH (1.0 M in H_2O, 0.003mmol, 3μL) catalyst at room temperature under air atmosphere. The reaction mixture was stirred at room temperature for 12 hours. The reaction was monitored by HPLC analysis (elution with toluene at 0.6 mL/min flow rate, detection at 320 nm). The mixture was subjected directly with silica gel chromatography (toluene/hexane = 1/1). Toluene and hexane containing **2a** were evaporated at below 60 ^oC, and the residue was washed with acetone to afford **2a** in 91% yield (23.8 mg).

Representative procedure for the synthesis of the cross-dimer 3b.

To a solution of hydrofullerenes **1a** (26.2 mg, 0.03 mmol) and **1f** (26.2 mg, 0.03 mmol) in THF and 1,2-dichlorobenzene (1:3, 8 mL) solution of was added an as-prepared NaOH (1.0 M in H_2O, 0.009mmol, 9μL) catalyst at room temperature under air atmosphere. The reaction mixture was stirred at room temperature for 16 hours. The reaction was monitored by HPLC analysis (elution with toluene at 0.6 mL/min flow rate, detection at 320 nm). The mixture was subjected directly with silica gel chromatography using a mixed solvent (toluene/hexane = 1/2) as an eluent. **2f** was isolated as the first fragment, followed by **3b** and **2a** were isolated sequentially. Toluene solution containing **3b** was evaporated at below 50 ^oC, and the residue washed with acetone to remove the remaining toluene, affording **3b** in 34% yield (17.8 mg). Similarly, **2a** and **2f** were obtained in 26% (13.6 mg) and 28% (14.6 mg) yields after evaporation of toluene and washed with acetone. However, the HPLC yields of **2a**, **3b** and **2f** in the reaction mixture were 26%, 46% and 28%, respectively, which is different from the isolated yields of **2a**, **3b** and **2f** (26%, 34% and 28%). Some amounts of cross-dimer **3b** might convert into homo-dimer **2a** and **2f** during the silica gel column chromatography.

Analytical data of 1d and 2d

Hexyl 4-([60]fulleren-1(2*H*)-yl)methyl)benzoate (1d)

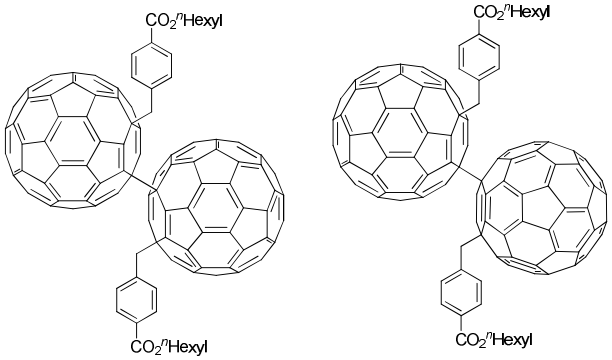


1d

Dark brown solid; ^1H NMR (400 MHz, $CDCl_3/CS_2$ = 1/4) δ 0.95 (t, *J* = 4.0 Hz, 3H), 1.38-1.52 (m, 6H), 1.77-1.84 (m, 2H), 4.33 (t, *J* = 4.0 Hz, 2H), 4.84 (s, 2H), 6.61 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 8.17 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ = 1/4) δ 14.25, 22.90, 25.93, 28.91, 31.66, 52.87, 59.10, 64.88, 65.24, 129.66, 129.80, 131.00, 135.77, 135.91, 139.63, 139.94, 140.33, 141.25, 141.33, 141.48, 141.69, 141.80, 142.23, 142.25, 142.89, 144.18, 144.35, 145.02, 145.12, 145.21, 145.37,

145.71, 145.83, 145.90, 146.04, 146.06, 146.45, 146.94, 147.10, 153.01, 154.12, 165.20; HRMS (ESI, positive) calcd. for $C_{74}H_{20}O_2Na$ $[M+Na]^+$: 963.1355, found 963.1349

Single bonded fullerene dimer (2d)

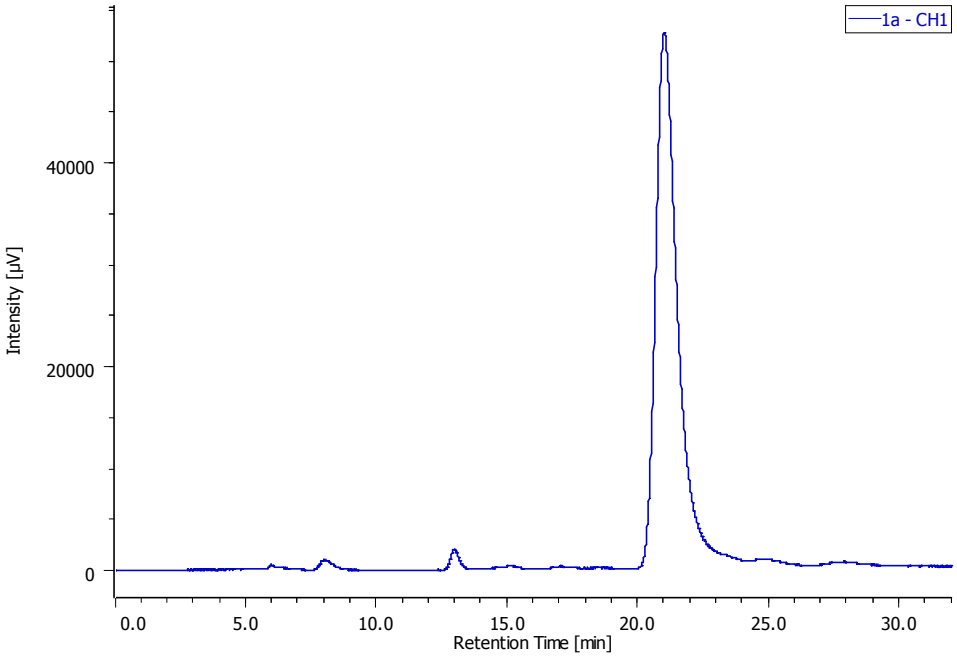


racemic **2d** *meso*

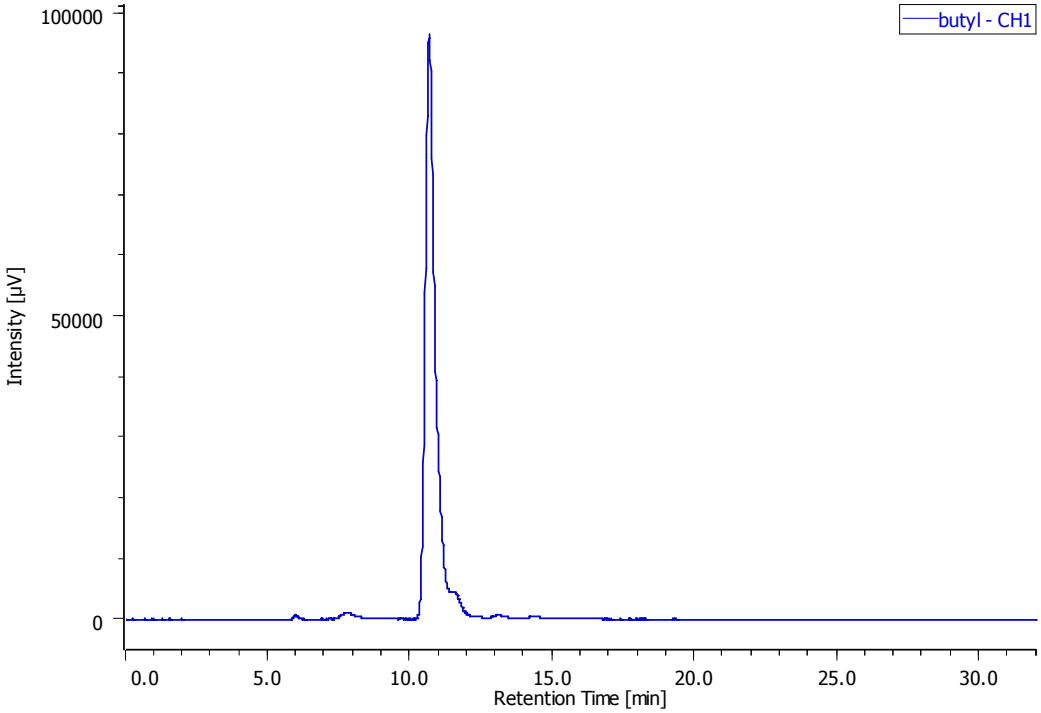
Dark brown solid; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ = 1/4) δ 0.93 (t, *J* = 4.0 Hz, 6H), 1.35-1.45 (m, 12H), 1.73-1.77 (m, 4H), 4.26 (t, *J* = 8.0 Hz, 4H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 4H), 7.99 (d, *J* = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ = 1/4) δ 14.26, 22.91, 25.92, 28.91, 31.65, 49.27, 49.56, 59.98, 64.68, 66.84, 129.31, 129.59, 130.41, 137.69, 137.79, 138.71, 138.75, 139.09, 139.20, 139.67, 139.71, 140.81, 140.88, 141.71, 141.78, 141.82, 141.93, 141.96, 142.19, 142.20, 142.43, 142.47, 142.69, 142.74, 142.85, 143.00, 143.12, 143.19, 143.45, 143.47, 143.57, 143.64, 143.79, 143.87, 143.91, 143.99, 144.04, 144.07, 144.09, 144.14, 144.18, 144.23, 144.32, 144.35, 144.50, 144.77, 145.40, 145.45, 146.24, 146.30, 146.62, 146.66, 146.75, 146.94, 147.05, 147.22, 147.97, 148.16, 148.26, 148.31, 148.39, 148.54, 148.67, 148.74, 148.93, 149.04, 152.24, 152.45, 153.41, 153.57, 155.79, 164.83; HRMS (ESI, positive) calcd. for $C_{148}H_{38}O_4Na$ $[M+Na]^+$: 1901.2662, found 1901.2677

HPLC analysis reaction mixture for synthesis of single-bonded fullerene dimers

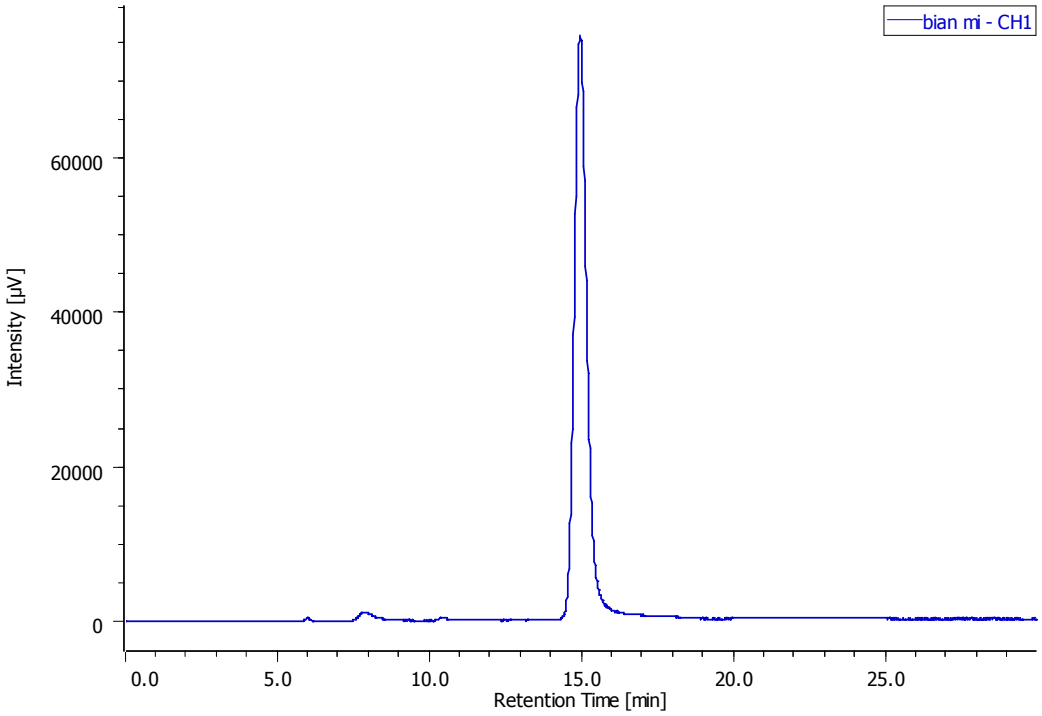
Note: It should be mentioned that HPLC monitors were performed at 12 °C, while in the previous $Cu(OAc)_2$-catalyzed dimerization, the HPLC were carried out at different temperatures (4 °C or 18 °C). Thus, HPLC chromatograms showed the slightly different retention times compared to the previously reported HPLC chromatograms for the same product, but they showed same NMR spectra.



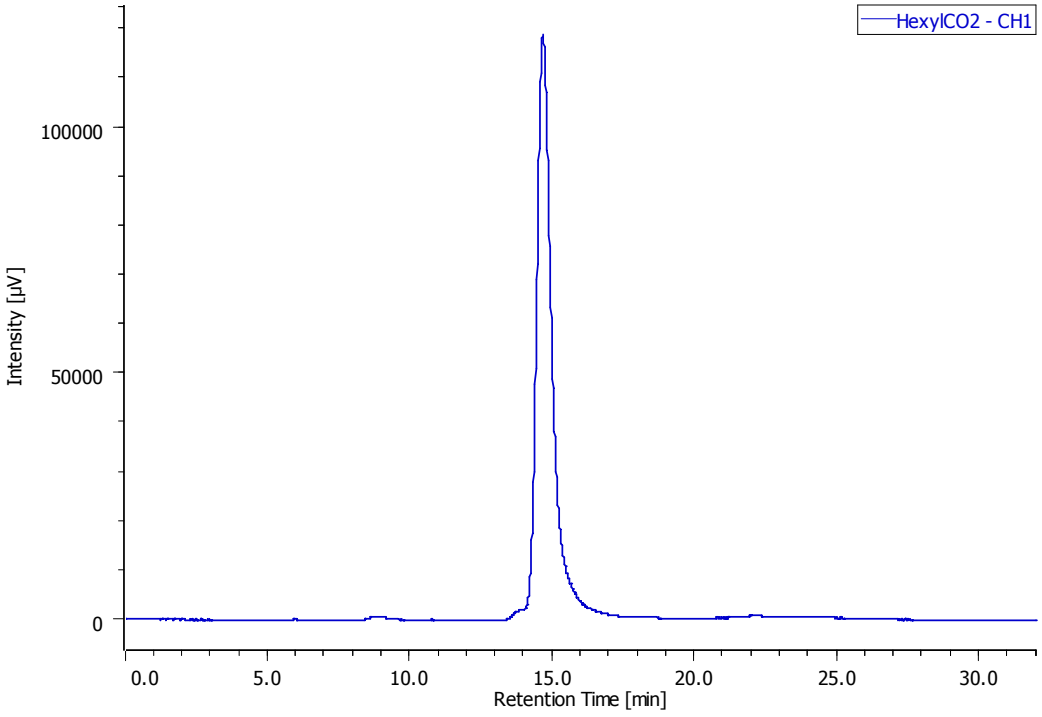
HPLC analysis of reaction mixture of **1a**



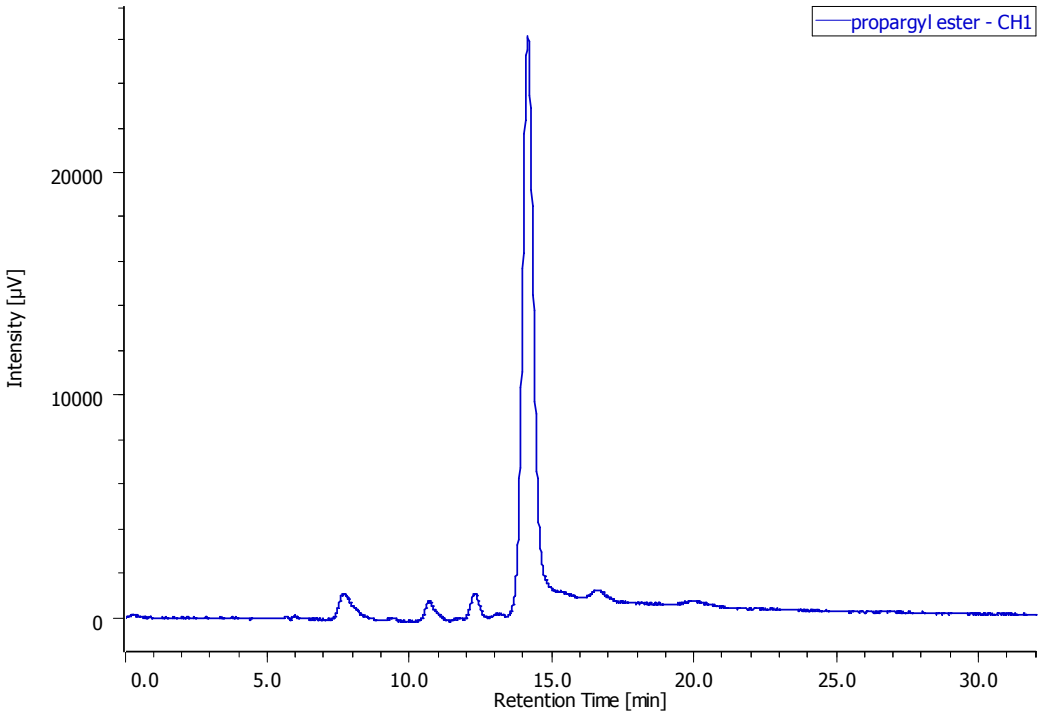
HPLC analysis of reaction mixture of **1b**



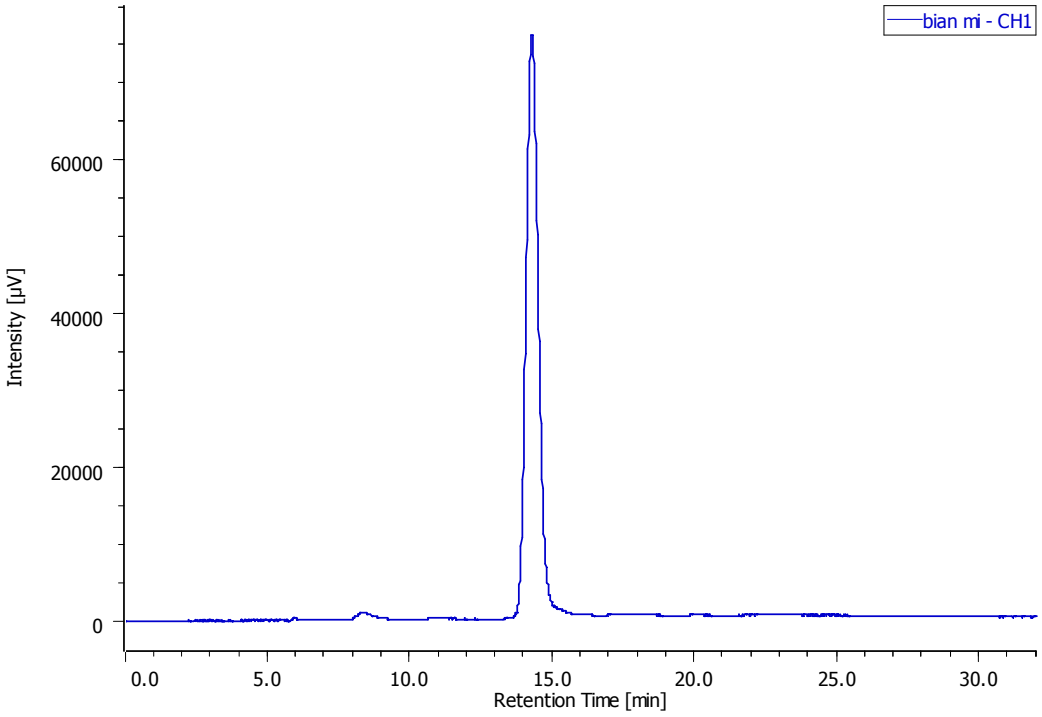
HPLC analysis of reaction mixture of **1c**



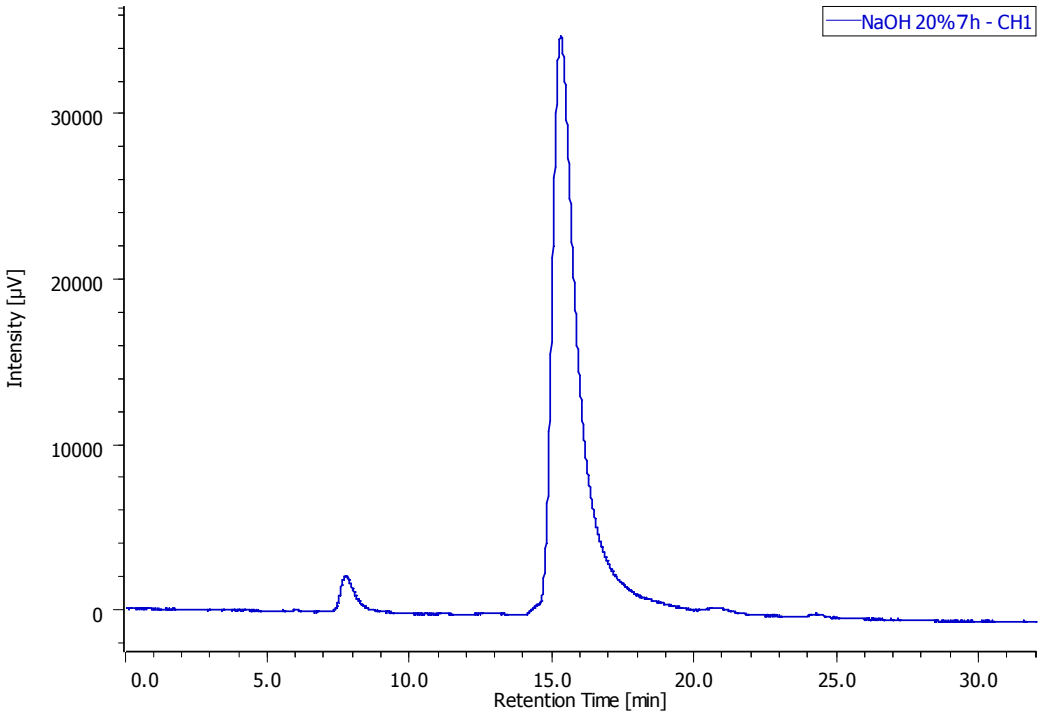
HPLC analysis of reaction mixture of **1d**



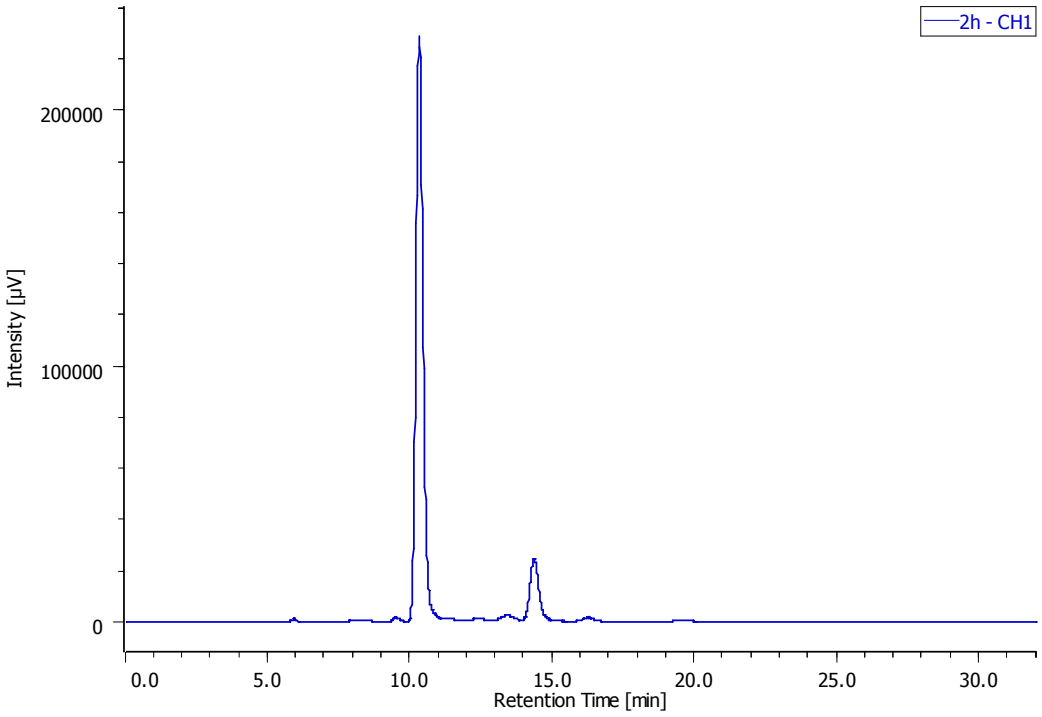
HPLC analysis of reaction mixture of **1e**



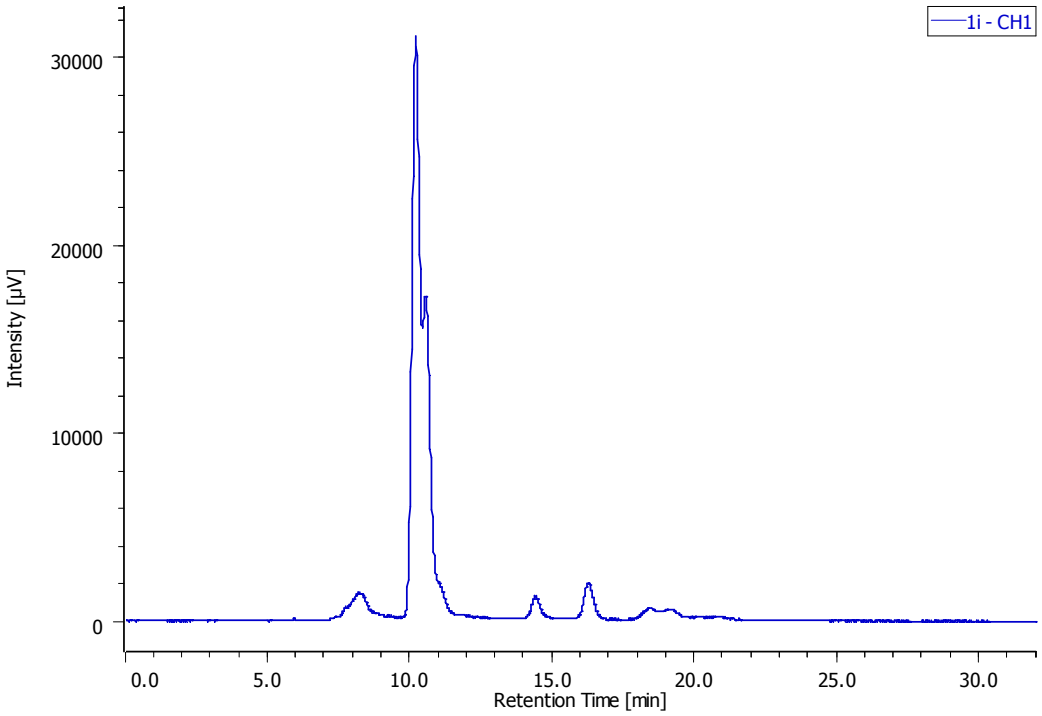
HPLC analysis of reaction mixture of **1f**



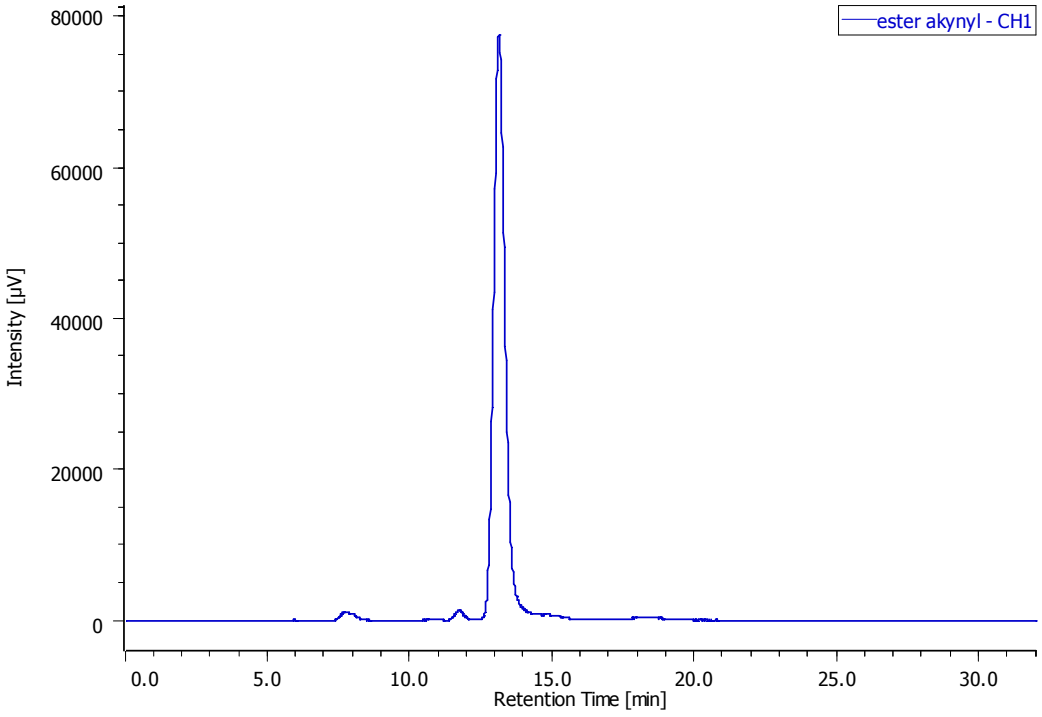
HPLC analysis of reaction mixture of **1g**



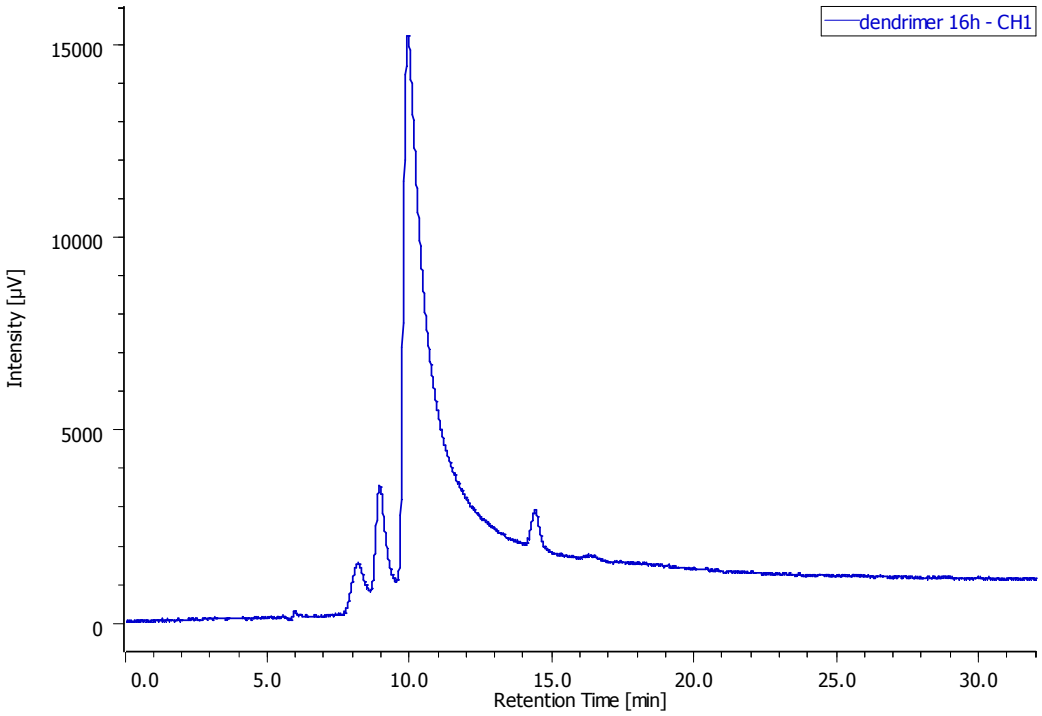
HPLC analysis of reaction mixture of **1h**



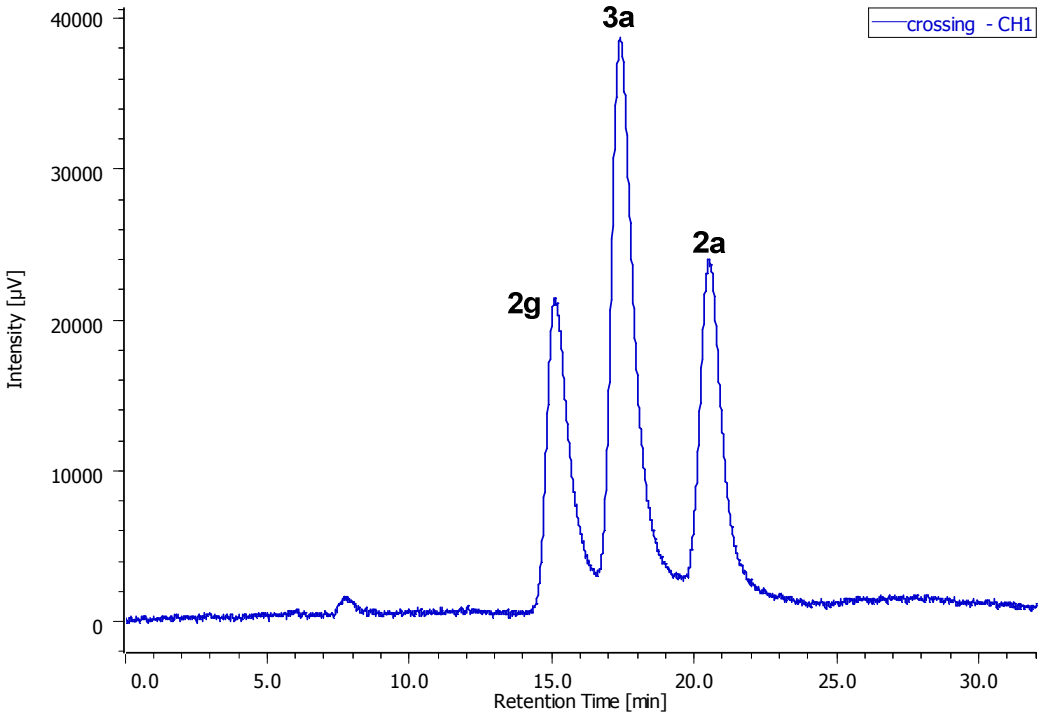
HPLC analysis of reaction mixture of **1i**



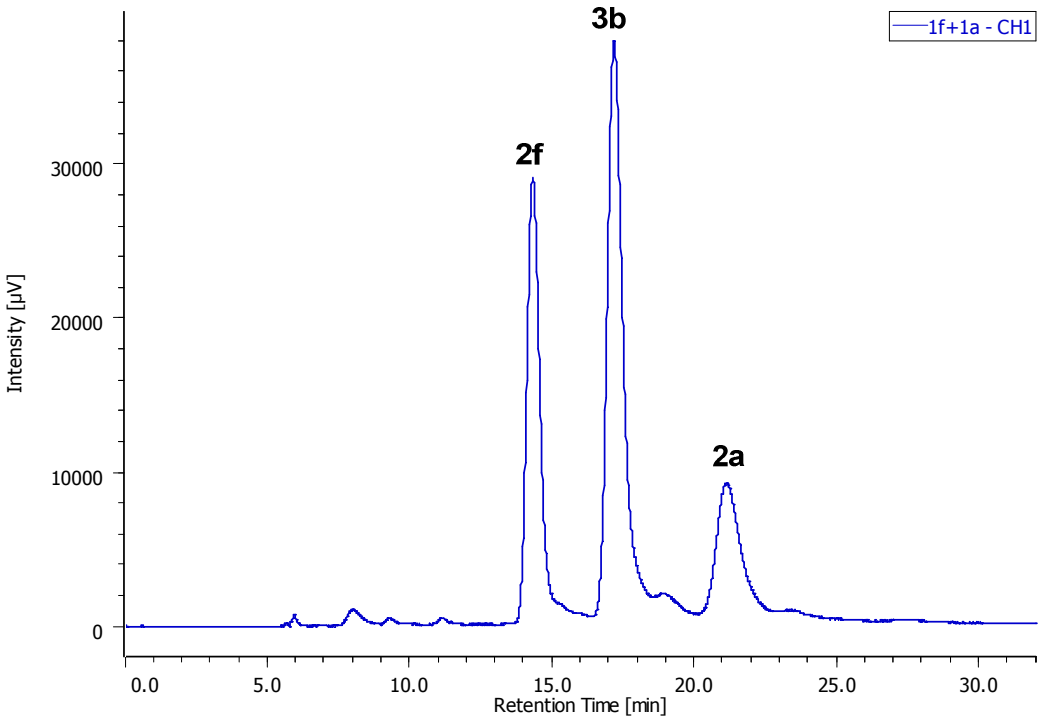
HPLC analysis of reaction mixture of **1j**



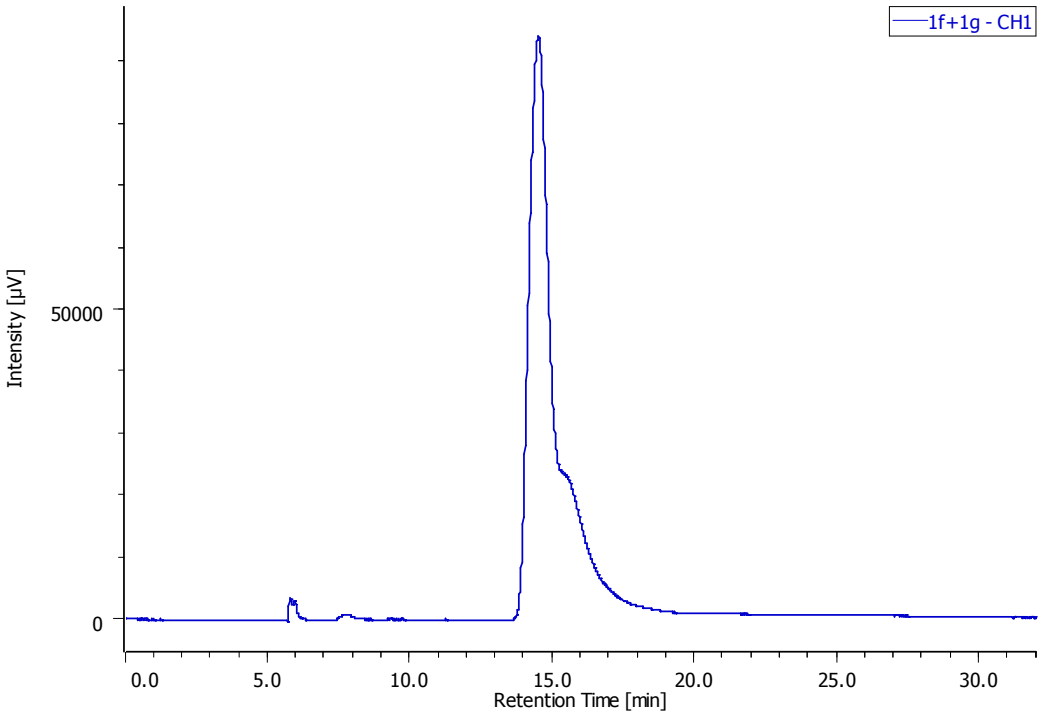
HPLC analysis of reaction mixture of **1k**



HPLC analysis of reaction mixture of **1a** and **1g**

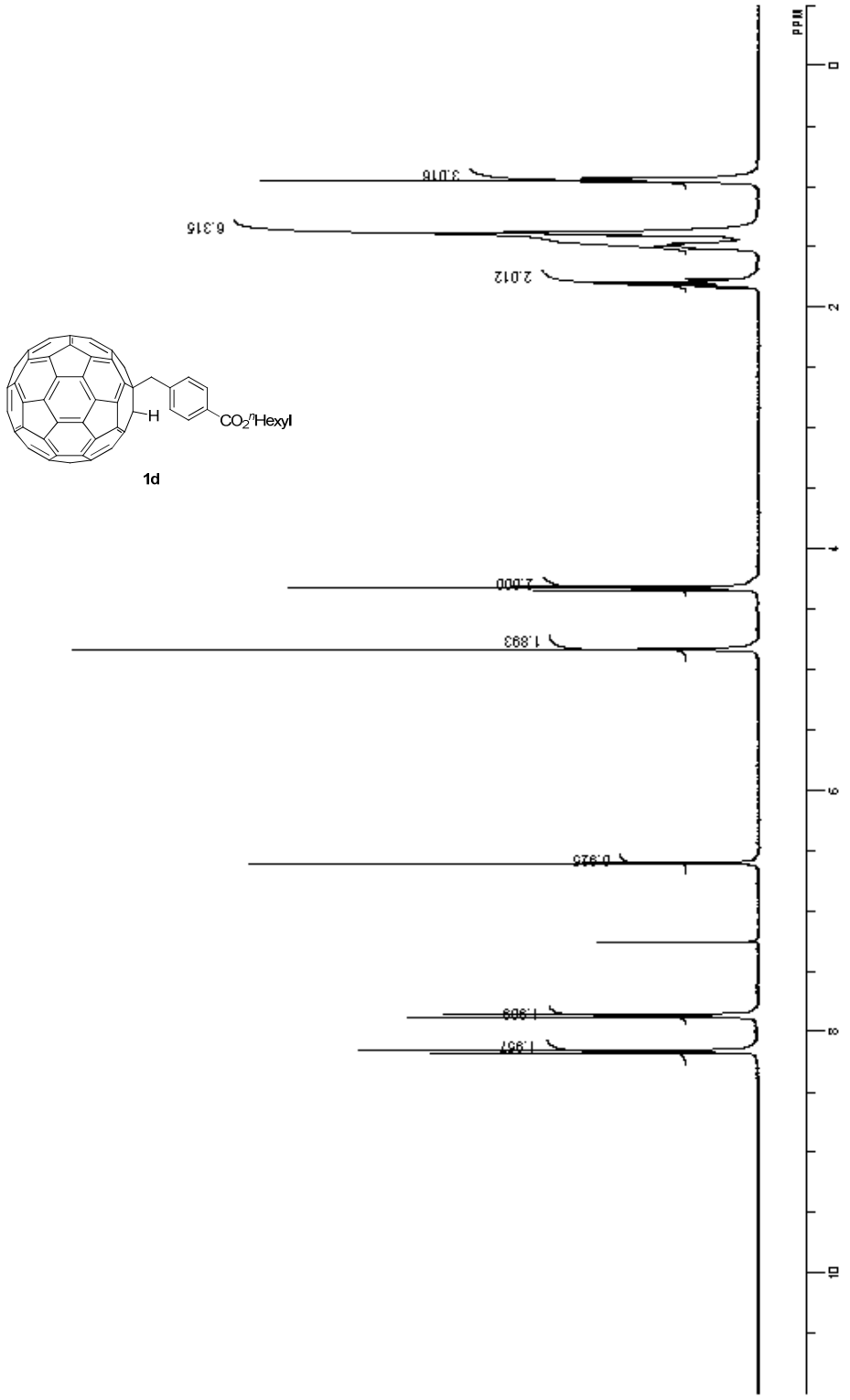


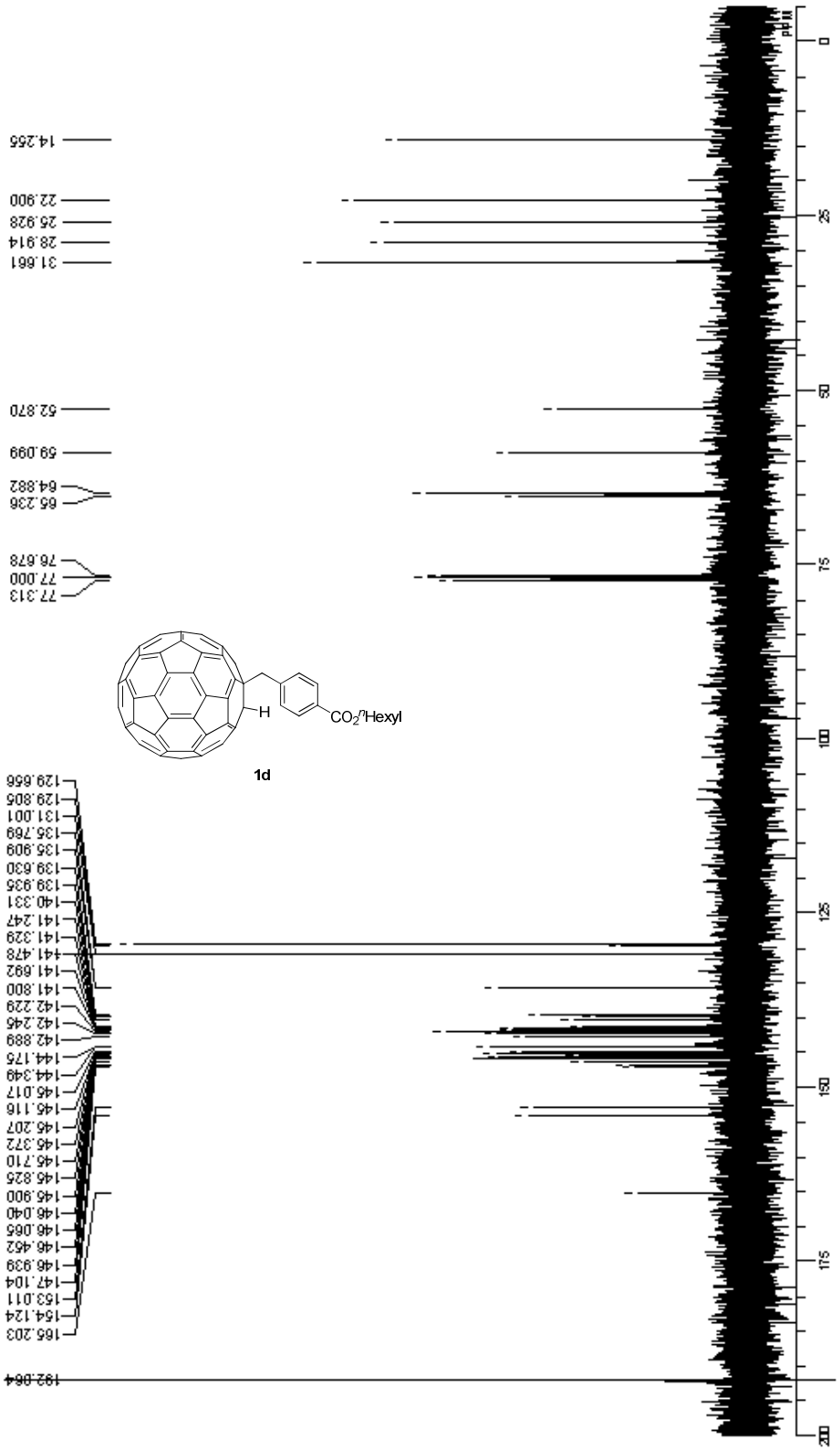
HPLC analysis of reaction mixture of **1a** and **1f**



HPLC analysis of reaction mixture of **1f and 1g**

^{1}H and ^{13}C NMR spectra of 1d

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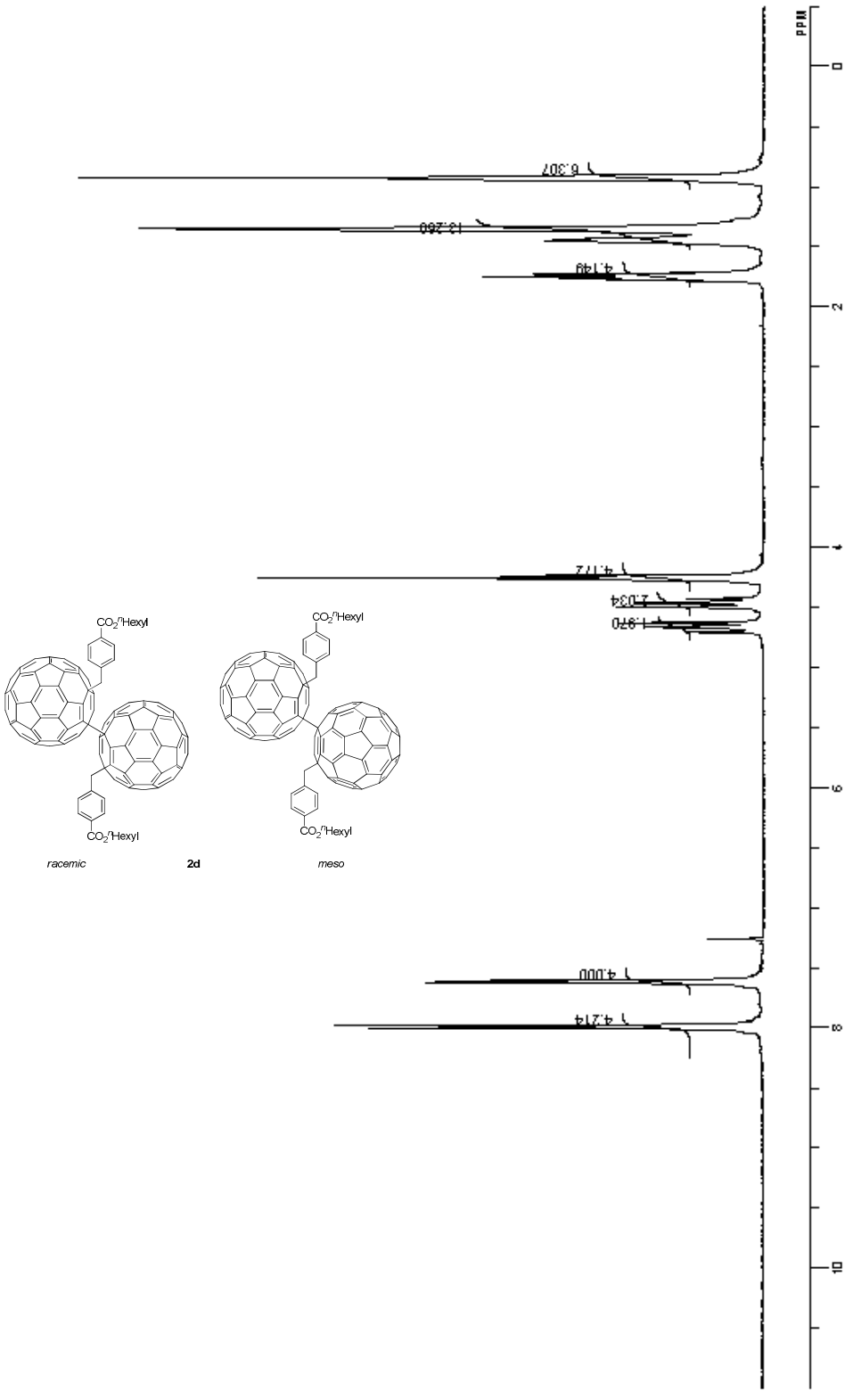
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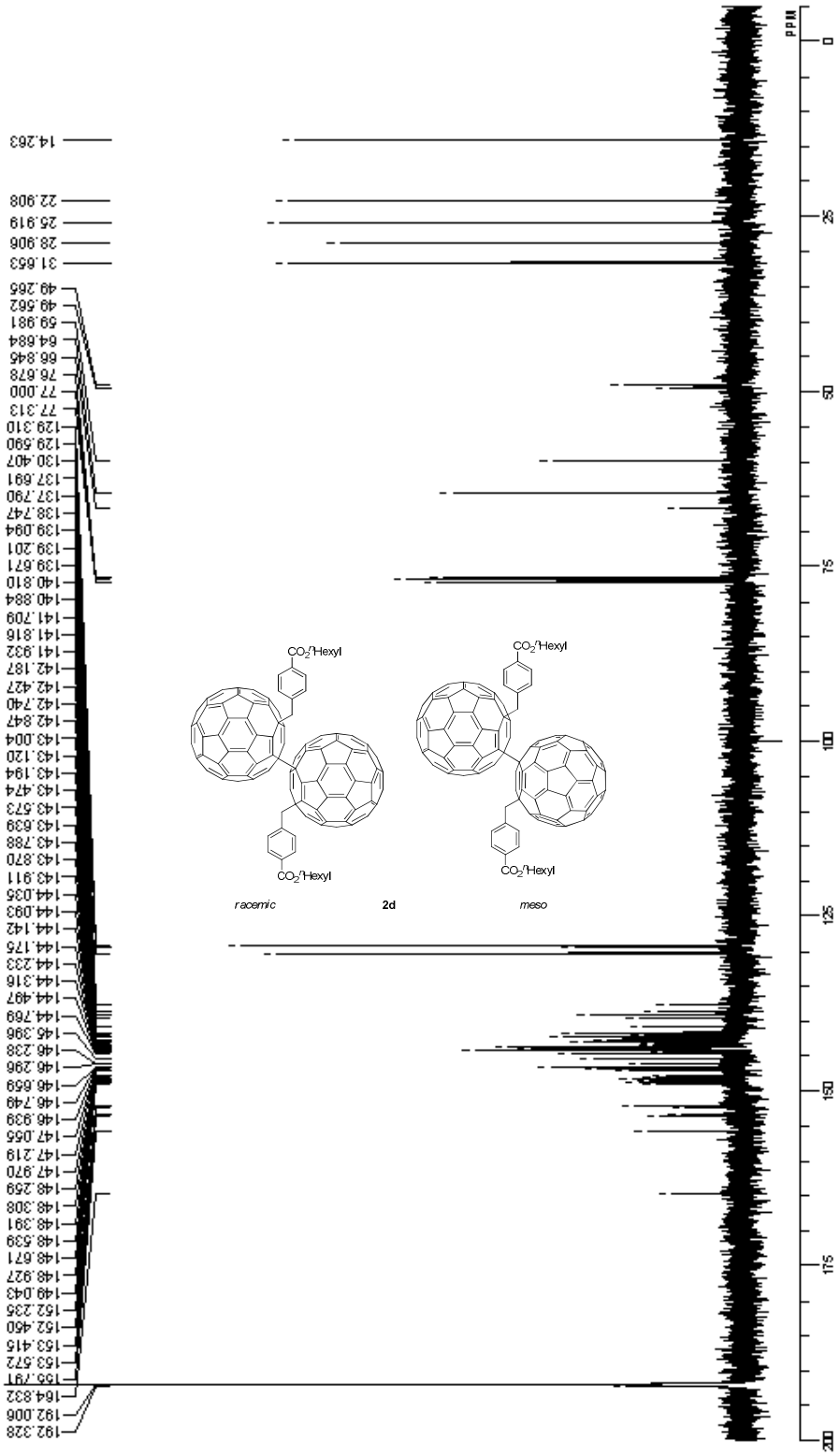
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